

Base-mediated 1,6-conjugate addition of Seyferth-Gilbert reagent to *para*-quinone methides

Ashis Kumar Gupta, Shakir Ahamad, Narendra Kumar Vaishanv, Ruchir Kant and Kishor Mohanan

Medicinal and Process Chemistry Division,
CSIR-Central Drug Research Institute, Jankipuram Extension, Sitapur road,
Lucknow, India-226031
kishor.mohanan@cdri.res.in

SUPPORTING INFORMATION

Content:

1. General experimental information (p. S2)
2. General Procedure for the synthesis of diarylmethylated diazomethylphosphonate and alkenyl phosphonate (p. S3)
3. Characterization data for compounds **3a-3ai**, **4a-4k** (p. S5)
4. Copies of ^1H , ^{13}C and ^{31}P NMR spectra for all compounds (p. S28)

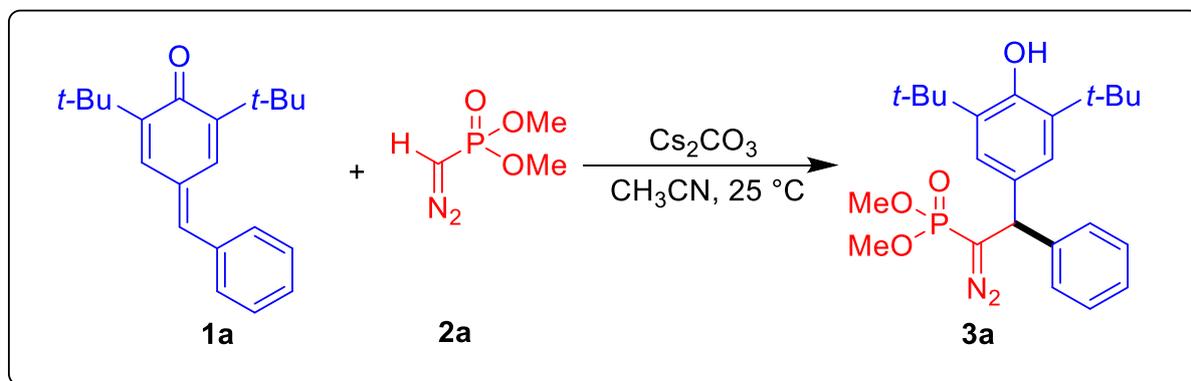
General experimental information:

Unless otherwise specified, all reactions were performed in oven-dried glassware under nitrogenous atmosphere using dry deoxygenated solvent. The reactions were monitored by TLC visualized by UV (254 nm) and/or with iodine. Column chromatography was performed on 100-200 mesh silica gel using the gradient system ethyl acetate-hexane (0-50%). NMR data were recorded at Bruker AV 400 MHz in CDCl₃ using as internal standards the residual CHCl₃ signal for ¹H NMR (δ = 7.26 ppm) and the deuterated solvent signal for ¹³C NMR (δ = 77.16 ppm). Coupling constants are given in Hertz (Hz) and the classical abbreviations are used to describe the signal multiplicities. Melting points were measured with a Büchi B-540 apparatus and are uncorrected. High resolution mass spectra were obtained using Q-TOF mass spectrometer. All commercially available reagents were used as received. All α -diazomethylphosphonate derivatives¹ and *p*-quinonemethides² were prepared according to the literature procedures.

-
1. (a) E. Quesada, S. A. Raw, M. Reid, E. Roman and R. J. K. Taylor, *Tetrahedron*, 2006, **62**, 6673; (b) J. Pietruszka and A. Witt, *Synthesis*, 2006, 4266; (c) S. Ohira, *Synth. Commun.*, 1989, **19**, 561; (d) P. Callant, L. Dhaenens and M. Vandewalle, *Synth. Commun.*, 1984, **14**, 155;
 2. V. Reddy and R. V. Anand, *Org. Lett.*, 2015, **17**, 3390.

Procedures

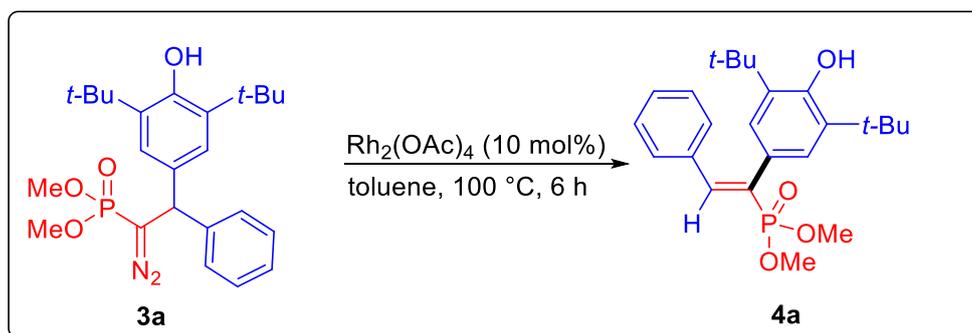
Synthesis of diarylmethylated diazomethylphosphonates 3a-3ai



General procedure for the synthesis of diarylmethylated diazomethylphosphonate 3a-3ah

To an oven-dried round bottom flask was added 4-benzylidene-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one **1a** (88 mg, 0.3 mmol) and dissolved in 2 mL of CH₃CN. Subsequently, solution of Seyferth-Gilbert reagent (68 mg, 0.45 mmol) in 1 mL of CH₃CN was added to the reaction mixture and kept stirring. After addition of cesium carbonate (196 mg, 0.6 mmol), the reaction mixture was further stirred at 25 °C for 45 min. After the completion of reaction, as indicated by TLC, solvent was evaporated off and extracted using ethyl acetate. The organic layer was dried over Na₂SO₄ and evaporated under reduced pressure. The residue was purified using column chromatography (100-200 mesh silica gel) using ethyl acetate/hexane as the eluent to afford the corresponding diarylmethylated diazomethylphosphonate **3a** as yellow solid (116 mg) in 95% yield.

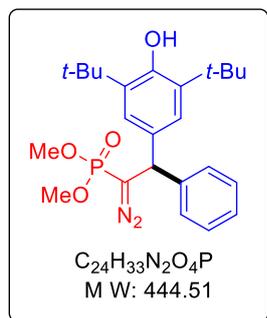
Synthesis of alkenyl phosphonate of 4a-4k



General procedure for the alkenylphosphonate of 4a–4k

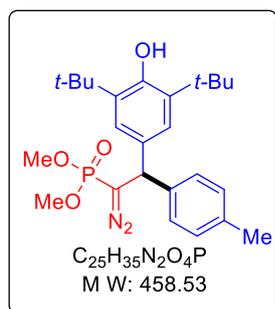
A 25 mL round-bottom flask charged with dimethyl (2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-diazo-2-phenylethyl)phosphonate (157 mg, 0.30 mmol) and $\text{Rh}_2(\text{OAc})_4$ (13 mg, 0.03 mmol) was sealed, evacuated, backfilled with nitrogen and dissolved in dry toluene (3 mL). This reaction mixture was stirred at 100 °C for 6 h. After the completion of reaction, as indicated by TLC, solvent was evaporated off. The residue was purified using column chromatography (100-200 mesh silica gel) using ethyl acetate/hexane as the eluent to afford the corresponding alkenyl phosphonate **4a** as a white solid (127 mg) in 93% yield.

Dimethyl (2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-diazo-2-phenylethyl)phosphonate (**3a**)



Following the general procedure, treatment of 4-benzylidene-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one (88 mg, 0.30 mmol) with SGR (68 mg, 0.45 mmol) in the presence of Cs_2CO_3 (196 mg, 0.60 mmol) in CH_3CN (3.0 mL) at 25 °C for 45 minute followed by column chromatography afforded the product **3a** as yellow solid (127 mg, 95%). R_f (Ethyl acetate/Hexane: 30/70) = 0.37. **Mp** 130-132 °C. ^{13}C NMR (100 MHz, ppm/ $CDCl_3$): 153.0 (C), 141.5 (d, J_{C-P} = 2.7 Hz, C), 136.2 (C), 136.2 (C), 131.1 (d, J_{C-P} = 3.2 Hz, C), 128.7 (CH), 128.7 (CH), 128.3 (CH), 128.3 (CH), 127.2 (CH), 124.9 (CH), 124.9 (CH), 53.0 (d, J_{C-P} = 4.1 Hz, CH_3), 53.0 (d, J_{C-P} = 4.1 Hz, CH_3), 46.7 (d, J_{C-P} = 184.3 Hz, C), 46.1 (d, J_{C-P} = 7.2 Hz, CH), 34.5 (C), 34.5 (C), 30.4 (CH_3), 30.4 (CH_3), 30.4 (CH_3), 30.4 (CH_3), 30.4 (CH_3). 1H NMR (400 MHz, ppm/ $CDCl_3$): 7.34 (t, J = 7.4 Hz, 2H), 7.27 (d, J = 7.4 Hz, 3H), 7.00 (s, 2H), 5.18 (s, 1H), 4.66 (d, J = 8.8 Hz, 1H), 3.65 (d, J = 9.6 Hz, 3H), 3.62 (d, J = 9.6 Hz, 3H), 1.40 (s, 18H). ^{31}P NMR (161.9 MHz, $CDCl_3$): 24.08. HRMS for $C_{24}H_{34}N_2O_4P^+$: calcd. $[M+H]^+$: 445.2251, found: 445.2251.

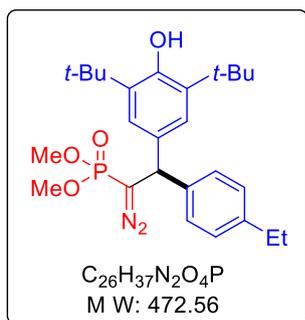
Dimethyl (2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-diazo-2-(*p*-tolyl)ethyl)phosphonate (**3b**)



Following the general procedure, treatment of 2,6-di-*tert*-butyl-4-(4-methylbenzylidene)cyclohexa-2,5-dien-1-one (92 mg, 0.30 mmol) with SGR (68 mg, 0.45 mmol) in the presence of Cs_2CO_3 (196 mg, 0.60 mmol) in CH_3CN (3.0 mL) at 25 °C for 45 minute followed by column chromatography afforded the product **3b** as yellow solid (128 mg, 93%). R_f (Ethyl acetate/Hexane: 30/70) = 0.33. **Mp** 142-144 °C. ^{13}C NMR (100 MHz, ppm/ $CDCl_3$): 152.9 (C), 138.4 (d, J_{C-P} = 3.3 Hz, C), 136.7 (C), 136.2 (C), 136.2 (C), 131.3 (d, J_{C-P} = 3.5 Hz, C), 129.4 (CH), 129.4 (CH), 128.2 (CH), 128.2 (CH), 124.8 (CH), 124.8 (CH), 53.0 (d, J_{C-P} = 3.5 Hz, CH_3), 52.9 (d, J_{C-P} = 3.5 Hz, CH_3), 46.7 (d, J_{C-P} = 230.4 Hz, C), 45.8 (d, J_{C-P} = 8.8 Hz, CH), 34.5 (C), 34.5 (C), 30.4 (CH_3), 21.1 (CH_3). 1H NMR (400 MHz, ppm/ $CDCl_3$): 7.13 (s, 4H), 6.99 (s, 2H), 5.15 (s, 1H), 4.60 (d, J = 9.2 Hz, 1H), 3.63 (d, J = 3.2 Hz, 3H), 3.60 (d, J = 3.2 Hz, 3H), 2.34 (s, 3H), 1.39 (s, 18H). ^{31}P NMR (161.9 MHz, $CDCl_3$): 24.21. HRMS for $C_{25}H_{36}N_2O_4P^+$: calcd. $[M+H]^+$: 459.2407, found: 459.2408.

Dimethyl (2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-diazo-2-(4-ethylphenyl)ethyl)phosphonate (**3c**)

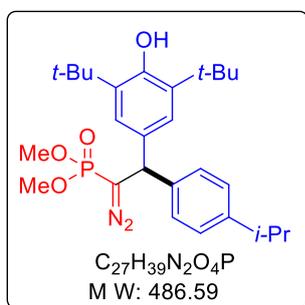
Following the general procedure, treatment of 2,6-di-*tert*-butyl-4-(4-ethylbenzylidene)cyclohexa-2,5-dien-1-one (97.0 mg, 0.30 mmol) with SGR (68 mg, 0.45 mmol) in the presence of Cs_2CO_3 (196 mg, 0.60 mmol) in CH_3CN (3.0 mL) at 25 °C for 45 minute followed by column chromatography afforded the product **3c** as yellow solid (135 mg, 95%). R_f (Ethyl acetate/Hexane: 30/70) = 0.42. **Mp** 150-152 °C. ^{13}C NMR (100 MHz, ppm/ $CDCl_3$): 152.9 (C), 143.1 (C), 138.6 (d, J_{C-P} = 3.7 Hz, C), 136.1 (C), 136.1 (C), 131.4 (d, J_{C-P} = 3.8 Hz, C),



128.2 (CH), 128.2 (CH), 128.1 (CH), 128.1 (CH), 124.9 (CH), 124.9 (CH), 53.0 (d, J_{C-P} = 2.0 Hz, CH₃), 52.9 (d, J_{C-P} = 2.0 Hz, CH₃), 46.8 (d, J_{C-P} = 230.2 Hz, C), 45.8 (d, J_{C-P} = 8.8 Hz, CH), 34.5 (C), 34.5 (C), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 28.6 (CH₂), 15.6 (CH₃). ¹H NMR (400 MHz, ppm/CDCl₃): 7.16 (s, 4H), 7.00 (s, 2H), 5.15 (s, 1H), 4.60 (d, J = 9.2 Hz, 1H), 3.61 (d, J = 11.6 Hz, 3H), 3.61 (d, J = 11.6 Hz, 3H), 2.64 (q, J = 7.6 Hz, 2H), 1.39 (s, 18H), 1.23 (t, J = 7.6 Hz, 3H). ³¹P NMR (161.9 MHz, CDCl₃): 24.26. HRMS for

C₂₆H₃₈N₂O₄P⁺: calcd. [M+H]⁺: 473.2564, found: 473.2574.

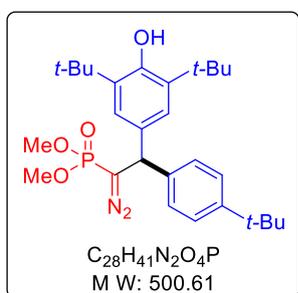
Dimethyl (2-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-diazo-2-(4-isopropylphenyl)ethyl)phosphonate (3d)



Following the general procedure, treatment of 2,6-di-tert-butyl-4-(4-isopropylbenzylidene)cyclohexa-2,5-dien-1-one (100 mg, 0.30 mmol) with SGR (68 mg, 0.45 mmol) in the presence of Cs₂CO₃ (196 mg, 0.60 mmol) in CH₃CN (3.0 mL) at 25 °C for 45 minute followed by column chromatography afforded the product **3d** as yellow solid (134 mg, 92%). R_f (Ethyl acetate/Hexane: 30/70) = 0.42. **Mp** 146-148 °C. ¹³C NMR (100 MHz, ppm/CDCl₃): 152.9 (C), 147.8 (C), 138.7

(d, J_{C-P} = 3.3 Hz, C), 136.2 (C), 136.2 (C), 131.5 (d, J_{C-P} = 3.1 Hz, C), 128.2 (CH), 128.2 (CH), 126.7 (CH), 126.7 (CH), 124.9 (CH), 124.9 (CH), 53.0 (d, J_{C-P} = 2.1 Hz, CH₃), 52.9 (d, J_{C-P} = 2.1 Hz, CH₃), 47.7 (C), 45.8 (d, J_{C-P} = 7.2 Hz, CH), 34.5 (C), 34.5 (C), 33.8 (CH), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 24.1 (CH₃), 24.1 (CH₃). ¹H NMR (400 MHz, ppm/CDCl₃): 7.20-7.15 (m, 4H), 7.00 (s, 2H), 5.15 (s, 1H), 4.59 (d, J = 8.8 Hz, 1H), 3.62 (d, J = 2.4 Hz, 3H), 3.60 (d, J = 2.8 Hz, 3H), 2.93-2.86 (m, 1H), 1.39 (s, 18H), 1.24 (d, J = 7.2 Hz, 6H). ³¹P NMR (161.9 MHz, CDCl₃): 24.28. HRMS for C₂₇H₄₀N₂O₄P⁺: calcd. [M+H]⁺: 487.2720, found: 487.2715

Dimethyl (2-(4-(tert-butyl)phenyl)-2-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-diazoethyl)phosphonate (3e)

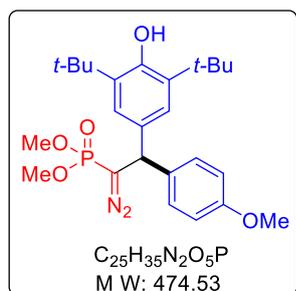


Following the general procedure, treatment of 2,6-di-tert-butyl-4-(4-(tert-butyl)benzylidene)cyclohexa-2,5-dien-1-one (105 mg, 0.30 mmol) with SGR (68 mg, 0.45 mmol) in the presence of Cs₂CO₃ (196 mg, 0.60 mmol) in CH₃CN (3.0 mL) at 25 °C for 45 minute followed by column chromatography afforded the product **3e** as yellow solid (143 mg, 95%). R_f (Ethyl acetate/Hexane: 30/70) = 0.42. **Mp** 140-142 °C. ¹³C NMR (100 MHz, ppm/CDCl₃): 152.9 (C), 150.1 (C), 138.2 (d, J_{C-P} = 4.0 Hz, C), 136.1 (C), 136.1 (C), 131.5 (d, J_{C-P} = 3.7 Hz, C), 128.0

(CH), 128.0 (CH), 125.6 (CH), 125.6 (CH), 124.9 (CH), 124.9 (CH), 53.0 (d, J_{C-P} = 2.8 Hz, CH₃), 52.9 (d, J_{C-P} = 2.7 Hz, CH₃), 46.8 (d, J_{C-P} = 229.7 Hz, C), 45.7 (d, J_{C-P} = 8.9 Hz, CH), 34.6 (C), 34.5 (C), 34.5 (C), 31.5 (CH₃), 31.5 (CH₃), 31.5 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃),

30.4 (CH₃), 30.4 (CH₃). ¹H NMR (400 MHz, ppm/CDCl₃): 7.34 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.00 (s, 2H), 5.15 (s, 1H), 4.59 (d, *J* = 8.8 Hz, 1H), 3.62 (d, *J* = 7.2 Hz, 3H), 3.59 (d, *J* = 7.2 Hz, 3H), 1.39 (s, 18H), 1.31 (s, 9H). ³¹P NMR (161.9 MHz, CDCl₃): 24.33. HRMS for C₂₈H₄₂N₂O₄P⁺: calcd. [M+H]⁺: 501.2877, found: 501.2877.

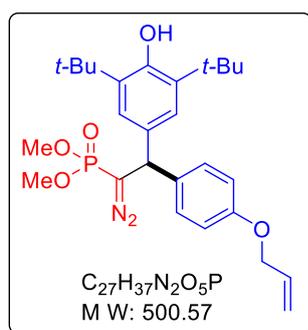
Dimethyl (2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-diazo-2-(4-methoxyphenyl)ethyl)phosphonate (3f)



Following the general procedure, treatment of 2,6-di-*tert*-butyl-4-(4-methoxybenzylidene)cyclohexa-2,5-dien-1-one (97 mg, 0.30 mmol) with SGR (68 mg, 0.45 mmol) in the presence of Cs₂CO₃ (196 mg, 0.60 mmol) in CH₃CN (3.0 mL) at 25 °C for 45 minute followed by column chromatography afforded the product **3f** as yellow solid (132 mg, 93%). *R_f* (Ethyl acetate/Hexane: 30/70) = 0.34. *Mp* 104-106 °C. ¹³C

NMR (100 MHz, ppm/CDCl₃): 158.7 (C), 152.9 (C), 136.2 (C), 136.2 (C), 133.5 (d, *J_{C-P}* = 3.7 Hz, C), 131.4 (d, *J_{C-P}* = 3.9 Hz, C), 129.4 (CH), 129.4 (CH), 124.8 (CH), 124.8 (CH), 114.1 (CH), 114.1 (CH), 55.4 (CH₃), 53.0 (d, *J_{C-P}* = 2.1 Hz, CH₃), 52.9 (d, *J_{C-P}* = 2.1 Hz, CH₃), 46.8 (d, *J_{C-P}* = 230.3 Hz, C), 45.4 (d, *J_{C-P}* = 8.9 Hz, CH), 34.5 (C), 34.5 (C), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃). ¹H NMR (400 MHz, ppm/CDCl₃): 7.16 (d, *J* = 8.8 Hz, 2H), 6.98 (s, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 5.15 (s, 1H), 4.59 (d, *J* = 9.2 Hz, 1H), 3.81 (s, 3H), 3.63 (d, *J* = 2.4 Hz, 3H), 3.60 (d, *J* = 2.4 Hz, 3H), 1.39 (s, 18H). ³¹P NMR (161.9 MHz, CDCl₃): 24.18. HRMS for C₂₅H₃₆N₂O₅P⁺: calcd. [M+H]⁺: 475.2356, found: 475.2360.

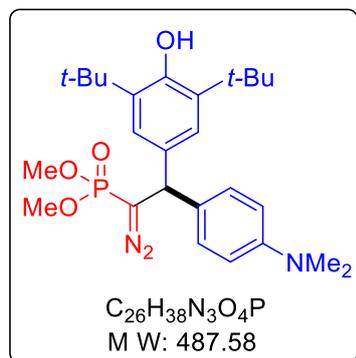
Dimethyl (2-(4-(allyloxy)phenyl)-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-diazoethyl)phosphonate (3g)



Following the general procedure, treatment of 4-(4-(allyloxy)benzylidene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one (105 mg, 0.30 mmol) with SGR (68 mg, 0.45 mmol) in the presence of Cs₂CO₃ (196 mg, 0.60 mmol) in CH₃CN (3.0 mL) at 25 °C for 45 minute followed by column chromatography afforded the product **3g** as yellow solid (141 mg, 94%). *R_f* (Ethyl acetate/Hexane: 30/70) = 0.31. *Mp* 112-114 °C. ¹³C NMR (100 MHz, ppm/CDCl₃): 157.7 (C), 152.9 (C), 136.2 (C), 136.2 (C), 133.7 (d, *J_{C-P}* = 3.6 Hz, C), 133.4 (CH),

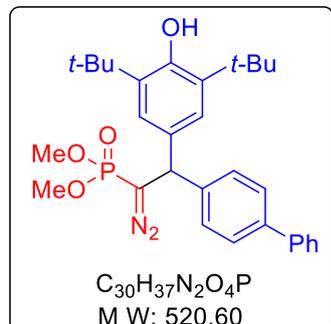
131.4 (d, *J_{C-P}* = 3.9 Hz, C), 129.4 (CH), 129.4 (CH), 124.9 (CH), 124.9 (CH), 117.8 (CH₂), 114.9 (CH), 114.9 (CH), 69.0 (CH₂), 53.0 (d, *J_{C-P}* = 2.1 Hz, CH₃), 53.0 (d, *J_{C-P}* = 2.0 Hz, CH₃), 46.8 (d, *J_{C-P}* = 230.3 Hz, C), 45.4 (d, *J_{C-P}* = 8.8 Hz, CH), 34.5 (C), 34.5 (C), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃). ¹H NMR (400 MHz, ppm/CDCl₃): 7.15 (d, *J* = 8.8 Hz, 2H), 6.98 (s, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.10-6.01 (m, 1H), 5.41 (d, *J* = 17.2 Hz, 1H), 5.28 (d, *J* = 10.8 Hz, 1H), 5.15 (s, 1H), 4.59 (d, *J* = 9.2 Hz, 1H), 4.53 (d, *J* = 5.2 Hz, 2H), 3.63 (d, *J* = 3.2 Hz, 3H), 3.60 (d, *J* = 3.2 Hz, 3H), 1.39 (s, 18H). ³¹P NMR (161.9 MHz, CDCl₃): 24.19. HRMS for C₂₇H₃₈N₂O₅P⁺: calcd. [M+H]⁺: 501.2513, found: 501.2508.

Dimethyl (2-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-diazo-2-(4-(dimethylamino)phenyl)ethyl)phosphonate (3h)



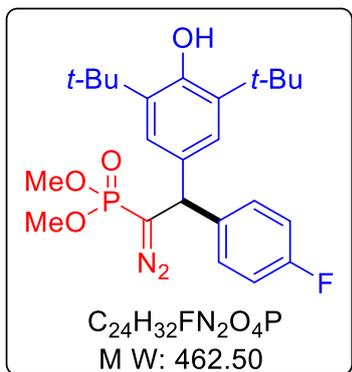
Following the general procedure, treatment of 2,6-di-tert-butyl-4-(4-(dimethylamino)benzylidene)cyclohexa-2,5-dien-1-one (101 mg, 0.30 mmol) with SGR (68 mg, 0.45 mmol) in the presence of Cs_2CO_3 (196 mg, 0.60 mmol) in CH_3CN (3.0 mL) at 25 °C for 45 minute followed by column chromatography afforded the product **3h** as yellow solid (139 mg, 95%). R_f (Ethyl acetate/Hexane: 30/70) = 0.31. **Mp** 126-128 °C. ^{13}C NMR (100 MHz, ppm/ $CDCl_3$): 152.8 (C), 149.7 (C), 136.1 (C), 136.1 (C), 131.9 (C), 131.9 (C), 129.0 (CH), 129.0 (CH), 124.8 (CH), 124.8 (CH), 112.7 (CH), 112.7 (CH), 52.9 (CH_3), 52.9 (CH_3), 46.8 (d, J_{C-P} = 229.9 Hz, C), 45.4 (d, J_{C-P} = 22.1 Hz, CH), 40.7 (CH_3), 40.7 (CH_3), 34.5 (C), 34.5 (C), 30.4 (CH_3), 30.4 (CH_3). 1H NMR (400 MHz, ppm/ $CDCl_3$): 7.10 (d, J = 8.8 Hz, 2H), 7.02 (s, 2H), 6.69 (d, J = 8.8 Hz, 2H), 5.14 (s, 1H), 4.54 (d, J = 8.8 Hz, 1H), 3.62 (d, J = 6.4 Hz, 3H), 3.59 (d, J = 6.4 Hz, 3H), 2.93 (s, 6H), 1.40 (s, 18H). ^{31}P NMR (161.9 MHz, $CDCl_3$): 24.60. **HRMS** for $C_{26}H_{39}N_3O_4P^+$: calcd. $[M+H]^+$: 488.2673, found: 488.2673.

Dimethyl (2-([1,1'-biphenyl]-4-yl)-2-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-diazoethyl)phosphonate (3i)



Following the general procedure, treatment of 4-([1,1'-biphenyl]-4-ylmethylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (111 mg, 0.30 mmol) with SGR (68 mg, 0.45 mmol) in the presence of Cs_2CO_3 (196 mg, 0.60 mmol) in CH_3CN (3.0 mL) at 25 °C for 45 minute followed by column chromatography afforded the product **3i** as yellow liquid (150 mg, 96%). R_f (Ethyl acetate/Hexane: 30/70) = 0.34. ^{13}C NMR (100 MHz, ppm/ $CDCl_3$): 153.0 (C), 140.7 (C), 140.6 (d, J_{C-P} = 1.6 Hz, C), 140.0 (C), 136.3 (C), 136.3 (C), 131.1 (d, J_{C-P} = 3.6 Hz, C), 128.9 (CH), 128.9 (CH), 128.7 (CH), 128.7 (CH), 127.5 (CH), 127.4 (CH), 127.4 (CH), 127.1 (CH), 127.1 (CH), 124.9 (CH), 124.9 (CH), 53.1 (d, J_{C-P} = 3.9 Hz, CH_3), 53.0 (d, J_{C-P} = 3.9 Hz, CH_3), 46.7 (d, J_{C-P} = 231.5 Hz, C), 45.9 (d, J_{C-P} = 8.8 Hz, CH), 34.5 (C), 34.5 (C), 30.4 (CH_3), 30.4 (CH_3). 1H NMR (400 MHz, ppm/ $CDCl_3$): 7.59 (t, J = 8.2 Hz, 4H), 7.46-7.42 (m, 2H), 7.36-7.32 (m, 3H), 7.03 (s, 2H), 5.18 (s, 1H), 4.69 (d, J = 8.8 Hz, 1H), 3.69 (d, J = 2.4 Hz, 3H), 3.63 (d, J = 2.4 Hz, 3H), 1.40 (s, 18H). ^{31}P NMR (161.9 MHz, $CDCl_3$): 24.05. **HRMS** for $C_{30}H_{38}N_2O_4P^+$: calcd. $[M+H]^+$: 521.2564, found: 521.2563.

Dimethyl (2-(3,5-di-tert-butyl-4-hydroxyphenyl)ethyl)phosphonate (3j)



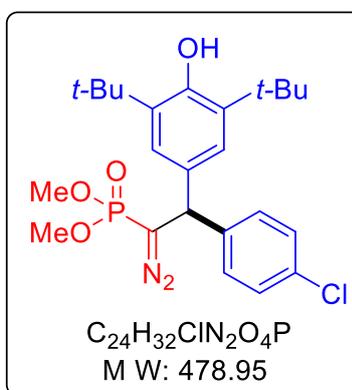
(2-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-diazo-2-(4-

fluorophenyl)ethyl)phosphonate (3j)

Following the general procedure, treatment of 2,6-di-tert-butyl-4-(4-fluorobenzylidene)cyclohexa-2,5-dien-1-one (94 mg, 0.30 mmol) with SGR (68 mg, 0.45 mmol) in the presence of Cs_2CO_3 (196 mg, 0.60 mmol) in CH_3CN (3.0 mL) at 25 °C for 45 minute followed by column chromatography afforded the product **3j** as yellow solid (119 mg, 86%). R_f (Ethyl acetate/Hexane: 30/70) = 0.31. **Mp** 142-144 °C. ^{13}C NMR (100 MHz, ppm/ $CDCl_3$): 162.0 (d, J_{C-F} = 244.3 Hz, C), 153.1 (C), 137.3 (C), 136.3 (C), 136.3 (C), 130.8 (d, J_{C-P} = 3.6 Hz, C), 130.0 (d, J_{C-F} = 7.9 Hz, CH), 130.0 (d, J_{C-F} = 7.9

Hz, CH), 124.8 (CH), 124.8 (CH), 115.6 (d, J_{C-F} = 21.3 Hz, CH), 115.6 (d, J_{C-F} = 21.3 Hz, CH), 53.0 (d, J_{C-P} = 5.2 Hz, CH_3), 53.0 (d, J_{C-P} = 5.2 Hz, CH_3), 47.8 (C), 45.5 (d, J_{C-P} = 8.8 Hz, CH), 34.5 (C), 34.5 (C), 30.4 (CH_3), 30.4 (CH_3). 1H NMR (400 MHz, ppm/ $CDCl_3$): 7.22 (t, J = 6.8 Hz, 2H), 7.03 (t, J = 8.6 Hz, 2H), 6.95 (s, 2H), 5.18 (s, 1H), 4.64 (d, J = 9.2 Hz, 1H), 3.64 (d, J = 5.2 Hz, 3H), 3.61 (d, J = 4.6 Hz, 3H), 1.39 (s, 18H). ^{31}P NMR (161.9 MHz, $CDCl_3$): 23.72. **HRMS** for $C_{24}H_{33}FN_2O_4P^+$: calcd. $[M+H]^+$: 463.2156, found: 463.2163

Dimethyl (2-(4-chlorophenyl)-2-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-diazoethyl)phosphonate (3k)



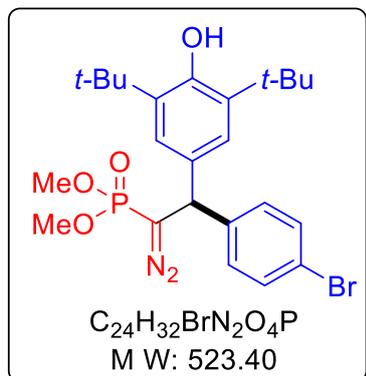
(2-(4-chlorophenyl)-2-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-

diazoethyl)phosphonate (3k)

Following the general procedure, treatment of 2,6-di-tert-butyl-4-(4-chlorobenzylidene)cyclohexa-2,5-dien-1-one (99 mg, 0.30 mmol) with SGR (68 mg, 0.45 mmol) in the presence of Cs_2CO_3 (196 mg, 0.60 mmol) in CH_3CN (3.0 mL) at 25 °C for 45 minute followed by column chromatography afforded the product **3k** as yellow solid (132 mg, 92%). R_f (Ethyl acetate/Hexane: 30/70) = 0.34. **Mp** 128-130 °C. ^{13}C NMR (100 MHz, ppm/ $CDCl_3$): 153.1 (C), 140.1 (d, J_{C-P} = 2.7 Hz, C), 136.4 (C), 136.4 (C), 133.1 (C), 130.6 (d, J_{C-P} = 3.2 Hz, C), 129.7 (CH), 129.7 (CH), 128.9 (CH), 128.9 (CH), 124.8 (CH), 124.8 (CH), 53.1 (d, J_{C-P} = 4.2 Hz, CH_3), 53.0 (d, J_{C-P} = 4.2 Hz, CH_3), 47.4 (C), 45.8 (d, J_{C-P} = 7.2 Hz, CH), 34.5 (C), 34.5 (C), 30.4 (CH_3), 30.4 (CH_3). 1H NMR (400 MHz, ppm/ $CDCl_3$): 7.31 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 6.95 (s, 2H), 5.18 (s, 1H), 4.62 (d, J = 9.2 Hz, 1H), 3.65 (d, J = 4.0 Hz, 3H), 3.62 (d, J = 4.0 Hz, 3H), 1.39 (s, 18H). ^{31}P NMR (161.9 MHz, $CDCl_3$): 23.60. **HRMS** for $C_{24}H_{33}ClO_4P^+$: calcd. $[M-N_2]^+$: 451.1800, found: 451.1793.

**Dimethyl
diazaoethyl)phosphonate (3l)**

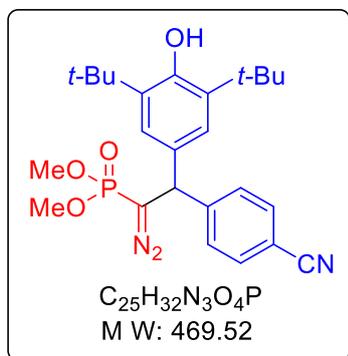
(2-(4-bromophenyl)-2-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-



Following the general procedure, treatment of 4-(4-bromobenzylidene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (112 mg, 0.30 mmol) with SGR (68 mg, 0.45 mmol) in the presence of Cs_2CO_3 (196 mg, 0.60 mmol) in CH_3CN (3.0 mL) at 25 °C for 45 minute followed by column chromatography afforded the product **3l** as yellow solid (149 mg, 95%). R_f (Ethyl acetate/Hexane: 30/70) = 0.29. **Mp** 136-138 °C. ^{13}C NMR (100 MHz, ppm/ $CDCl_3$): 153.1 (C), 140.6 (d, J_{C-P} = 3.5 Hz, C), 136.4 (C), 136.4 (C), 131.8 (CH), 131.8 (CH), 130.5 (d, J_{C-P} = 4.0 Hz, C), 130.0 (CH), 130.0 (CH), 124.8 (CH), 124.8 (CH), 121.1 (C), 53.1 (d, J_{C-P} = 5.3 Hz, CH_3), 52.9 (d, J_{C-P} = 5.3 Hz, CH_3), 46.4 (d, J_{C-P} = 231.4 Hz, C), 45.7 (d, J_{C-P} = 9.0 Hz, CH), 34.5 (C), 34.5 (C), 30.4 (CH_3), 30.4 (CH_3). 1H NMR (400 MHz, ppm/ $CDCl_3$): 7.46 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 6.94 (s, 2H), 5.20 (s, 1H), 4.61 (d, J = 8.8 Hz, 1H), 3.64 (d, J = 3.6 Hz, 3H), 3.62 (d, J = 3.2 Hz, 3H), 1.38 (s, 18H). ^{31}P NMR (161.9 MHz, $CDCl_3$): 23.55. **HRMS** for $C_{24}H_{33}BrN_2O_4P^+$: calcd. $[M+H]^+$: 523.1356, found: 523.1356.

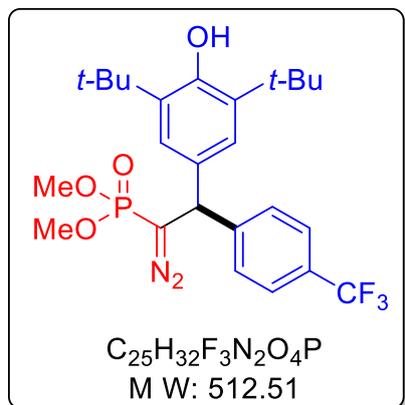
**Dimethyl
diazaoethyl)phosphonate (3m)**

(2-(4-cyanophenyl)-2-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-



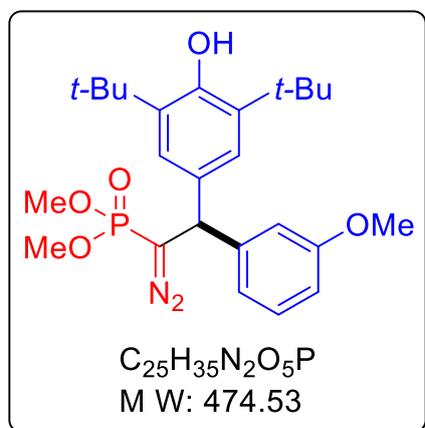
Following the general procedure, treatment of 4-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)benzocyanide (96 mg, 0.30 mmol) with SGR (68 mg, 0.45 mmol) in the presence of Cs_2CO_3 (196 mg, 0.60 mmol) in CH_3CN (3.0 mL) at 25 °C for 45 minute followed by column chromatography afforded the product **3m** as yellow solid (101 mg, 72%). R_f (Ethyl acetate/Hexane: 30/70) = 0.29. **Mp** 122-124 °C. ^{13}C NMR (100 MHz, ppm/ $CDCl_3$): 153.4 (C), 147.1 (d, J_{C-P} = 3.2 Hz, C), 136.6 (C), 136.6 (C), 132.6 (CH), 132.6 (CH), 129.7 (d, J_{C-P} = 4.1 Hz, C), 129.1 (CH), 129.1 (CH), 124.8 (CH), 124.8 (CH), 118.8 (C), 111.2 (C), 53.2 (d, J_{C-P} = 1.3 Hz, CH_3), 53.1 (d, J_{C-P} = 1.4 Hz, CH_3), 46.3 (d, J_{C-P} = 231.9 Hz, C), 46.3 (d, J_{C-P} = 9.1 Hz, CH), 34.6 (C), 34.6 (C), 30.3 (CH_3), 30.3 (CH_3). 1H NMR (400 MHz, ppm/ $CDCl_3$): 7.64 (d, J = 5.6 Hz, 2H), 7.38 (d, J = 5.2 Hz, 2H), 6.91 (s, 2H), 5.22 (s, 1H), 4.71 (d, J = 7.2 Hz, 1H), 3.66 (d, J = 1.0 Hz, 3H), 3.65 (d, J = 1.0 Hz, 3H), 1.38 (s, 18H). ^{31}P NMR (161.9 MHz, $CDCl_3$): 22.94. **HRMS** for $C_{25}H_{33}NO_4P^+$: calcd. $[M-N_2]^+$: 442.2142, found: 442.2155.

Dimethyl (2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-diazo-2-(4-(trifluoromethyl)phenyl)ethyl)phosphonate (3n)



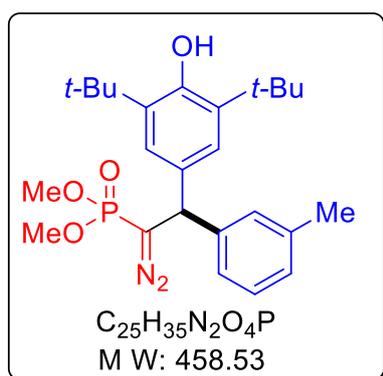
Following the general procedure, treatment of 2,6-di-*tert*-butyl-4-(4-(trifluoromethyl)benzylidene)cyclohexa-2,5-dien-1-one (109 mg, 0.30 mmol) with SGR (68 mg, 0.45 mmol) in the presence of Cs_2CO_3 (196 mg, 0.60 mmol) in CH_3CN (3.0 mL) at 25 °C for 45 minute followed by column chromatography afforded the product **3n** as yellow solid (145 mg, 94%). R_f (Ethyl acetate/Hexane: 30/70) = 0.31. M_p 136-138 °C. ^{13}C NMR (100 MHz, ppm/ $CDCl_3$): 153.2 (C), 145.7 (C), 136.2 (C), 136.2 (C), 130.1 (d, J_{C-P} = 3.8 Hz, C), 129.6 (C), 129.3 (C), 128.7 (CH), 128.7 (CH), 125.7 (CH), 125.6 (CH), 124.8 (CH), 124.8 (CH), 53.1 (d, J_{C-P} = 5.2 Hz, CH_3), 53.0 (d, J_{C-P} = 5.2 Hz, CH_3), 46.4 (d, J_{C-P} = 231.5 Hz, C), 46.0 (d, J_{C-P} = 9.0 Hz, CH), 34.5 (C), 34.5 (C), 30.3 (CH_3), 30.3 (CH_3), 30.3 (CH_3), 30.3 (CH_3). 1H NMR (400 MHz, ppm/ $CDCl_3$): 7.60 (d, J = 8.8 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 6.95 (s, 2H), 5.26 (s, 1H), 4.72 (d, J = 9.2 Hz, 1H), 3.65 (d, J = 4.0 Hz, 3H), 3.62 (d, J = 4.0 Hz, 3H), 1.39 (s, 18H). ^{31}P NMR (161.9 MHz, $CDCl_3$): 23.33. HRMS for $C_{25}H_{33}F_3N_2O_4P^+$: calcd. $[M+H]^+$: 513.2125, found: 513.2119.

Dimethyl (2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-diazo-2-(3-methoxyphenyl)ethyl)phosphonate (3o)



Following the general procedure, treatment of 2,6-di-*tert*-butyl-4-(3-methoxybenzylidene)cyclohexa-2,5-dien-1-one (97 mg, 0.30 mmol) with SGR (68 mg, 0.45 mmol) in the presence of Cs_2CO_3 (196 mg, 0.60 mmol) in CH_3CN (3.0 mL) at 25 °C for 45 minute followed by column chromatography afforded the product **3o** as yellow liquid (130 mg, 91%). R_f (Ethyl acetate/Hexane: 30/70) = 0.29. ^{13}C NMR (100 MHz, ppm/ $CDCl_3$): 159.9 (C), 152.9 (C), 143.1 (d, J_{C-P} = 3.6 Hz, C), 136.2 (C), 136.2 (C), 130.9 (d, J_{C-P} = 3.8 Hz, C), 129.6 (CH), 124.8 (CH), 124.8 (CH), 120.7 (CH), 114.1 (CH), 112.4 (CH), 55.3 (CH_3), 53.0 (d, J_{C-P} = 2.0 Hz, CH_3), 52.9 (d, J_{C-P} = 1.9 Hz, CH_3), 46.6 (d, J_{C-P} = 230.9 Hz, C), 46.1 (d, J_{C-P} = 3.9 Hz, CH), 34.4 (C), 34.4 (C), 30.3 (CH_3), 30.3 (CH_3), 30.3 (CH_3), 30.3 (CH_3), 30.3 (CH_3). 1H NMR (400 MHz, ppm/ $CDCl_3$): 7.27-7.23 (m, 1H), 6.99 (s, 2H), 6.85 (d, J = 7.6 Hz, 1H), 6.80-6.78 (m, 2H), 5.20 (s, 1H), 4.60 (d, J = 9.2 Hz, 1H), 3.77 (s, 3H), 3.63 (d, J = 2.0 Hz, 3H), 3.60 (d, J = 2.4 Hz, 3H), 1.38 (s, 18H). ^{31}P NMR (161.9 MHz, $CDCl_3$): 24.04. HRMS for $C_{25}H_{36}O_5P^+$: calcd. $[M-N_2]^+$: 447.2295, found: 447.2290.

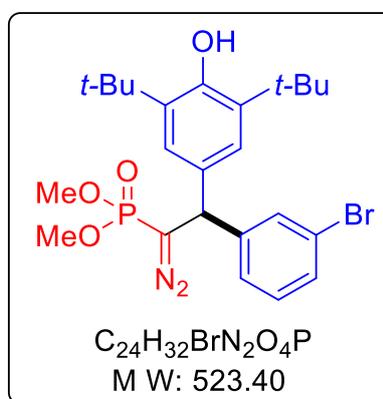
Dimethyl (2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-diazo-2-(*m*-tolyl)ethyl)phosphonate (**3p**)



Following the general procedure, treatment of 2,6-di-*tert*-butyl-4-(3-methylbenzylidene)cyclohexa-2,5-dien-1-one (92 mg, 0.30 mmol) with SGR (68 mg, 0.45 mmol) in the presence of Cs_2CO_3 (196 mg, 0.60 mmol) in CH_3CN (3.0 mL) at 25 °C for 45 minute followed by column chromatography afforded the product **3p** as yellow solid (131 mg, 95%). R_f (Ethyl acetate/Hexane: 30/70) = 0.35. **Mp** 130-132 °C. ^{13}C NMR (100 MHz, ppm/ $CDCl_3$): 152.9 (C), 141.4 (d, J_{C-P} = 3.5 Hz, C), 138.3 (C), 136.1 (C), 136.1 (C), 131.1 (d, J_{C-P} = 4.0 Hz, C), 129.1 (CH),

128.6 (CH), 128.0 (CH), 125.3 (CH), 124.9 (CH), 124.9 (CH), 53.0 (d, J_{C-P} = 5.2 Hz, CH_3), 53.0 (d, J_{C-P} = 5.2 Hz, CH_3), 46.7 (d, J_{C-P} = 230.4 Hz, C), 46.1 (d, J_{C-P} = 9.0 Hz, CH), 34.5 (C), 34.5 (C), 30.4 (CH_3), 21.6 (CH_3). 1H NMR (400 MHz, ppm/ $CDCl_3$): 7.24 (t, J = 7.8 Hz, 1H), 7.07 (s, 2H), 7.03 (s, 1H), 6.99 (s, 2H), 5.16 (s, 1H), 4.59 (d, J = 8.8 Hz, 1H), 3.63 (d, J = 9.6 Hz, 3H), 3.60 (d, J = 9.6 Hz, 3H), 2.33 (s, 3H), 1.39 (s, 18H). ^{31}P NMR (161.9 MHz, $CDCl_3$): 24.23. **HRMS** for $C_{25}H_{35}N_2O_4P^+$: calcd. $[M+H]^+$: 459.2407, found: 459.2407.

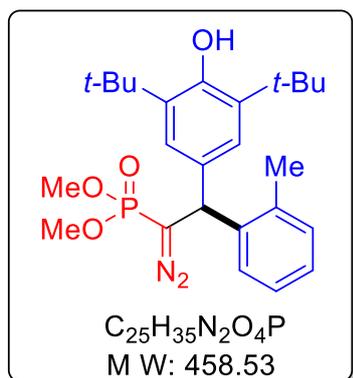
Dimethyl (2-(3-bromophenyl)-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-diazoethyl)phosphonate (**3q**)



Following the general procedure, treatment of 4-(3-bromobenzylidene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one (112.0 mg, 0.30 mmol) with SGR (68 mg, 0.45 mmol) in the presence of Cs_2CO_3 (196 mg, 0.60 mmol) in CH_3CN (3.0 mL) at 25 °C for 45 minute followed by column chromatography afforded the product **3q** as yellow solid (148 mg, 94%). R_f (Ethyl acetate/Hexane: 30/70) = 0.31. **Mp** 144-146 °C. ^{13}C NMR (100 MHz, ppm/ $CDCl_3$): 153.2 (C), 143.9 (d, J_{C-P} = 3.3 Hz, C), 136.4 (C), 136.4 (C), 131.5 (CH), 130.4 (CH), 130.3 (CH), 130.2 (d, J_{C-P} = 4.2 Hz, C), 126.9 (CH), 124.9

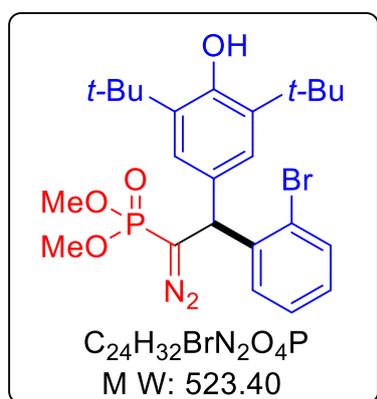
(CH), 124.9 (CH), 122.8 (C), 53.1 (d, J_{C-P} = 5.4 Hz, CH_3), 53.1 (d, J_{C-P} = 5.4 Hz, CH_3), 46.5 (d, J_{C-P} = 231.5 Hz, C), 45.9 (d, J_{C-P} = 9.0 Hz, CH), 34.5 (C), 34.5 (C), 30.4 (CH_3), 30.4 (CH_3). 1H NMR (400 MHz, ppm/ $CDCl_3$): 7.42-7.39 (m, 2H), 7.24-7.18 (m, 2H), 6.95 (s, 2H), 5.20 (s, 1H), 4.62 (d, J = 9.2 Hz, 1H), 3.65 (d, J = 6.0 Hz, 3H), 3.62 (d, J = 6.0 Hz, 3H), 1.39 (s, 18H). ^{31}P NMR (161.9 MHz, $CDCl_3$): 23.48. **HRMS** for $C_{24}H_{33}BrN_2O_4P^+$: calcd. $[M+H]^+$: 523.1356, found: 523.1361.

Dimethyl (2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-diazo-2-(*o*-tolyl)ethyl)phosphonate (**3r**)



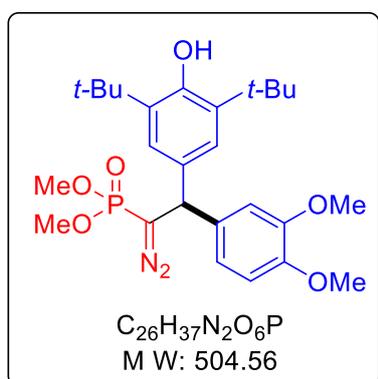
Following the general procedure, treatment of 2,6-di-*tert*-butyl-4-(2-methylbenzylidene)cyclohexa-2,5-dien-1-one (92 mg, 0.30 mmol) with SGR (68 mg, 0.45 mmol) in the presence of Cs_2CO_3 (196 mg, 0.60 mmol) in CH_3CN (3.0 mL) at 25 °C for 45 minute followed by column chromatography afforded the product **3r** as yellow solid (128 mg, 93%). R_f (Ethyl acetate/Hexane: 30/70) = 0.40. **Mp** 138-140 °C. ^{13}C NMR (100 MHz, ppm/ $CDCl_3$): 152.8 (C), 139.9 (d, J_{C-P} = 3.1 Hz, C), 136.2 (C), 136.1 (C), 136.1 (C), 130.8 (CH), 130.2 (d, J_{C-P} = 4.3 Hz, C), 127.9 (CH), 127.2 (CH), 126.2 (CH), 125.0 (CH), 125.0 (CH), 53.0 (d, J_{C-P} = 3.5 Hz, CH_3), 53.0 (d, J_{C-P} = 3.4 Hz, CH_3), 46.4 (d, J_{C-P} = 230.1 Hz, C), 42.9 (d, J_{C-P} = 9.0 Hz, CH), 34.5 (C), 34.5 (C), 30.4 (CH_3), 19.8 (CH_3). 1H NMR (400 MHz, ppm/ $CDCl_3$): 7.18 (s, 2H), 7.17 (s, 2H), 6.95 (s, 2H), 5.15 (s, 1H), 4.84 (d, J = 8.4 Hz, 1H), 3.65 (d, J = 11.6 Hz, 3H), 3.56 (d, J = 11.6 Hz, 3H), 2.31 (s, 3H), 1.38 (s, 18H). ^{31}P NMR (161.9 MHz, $CDCl_3$): 24.00. **HRMS** for $C_{25}H_{36}N_2O_4P^+$: calcd. $[M+H]^+$: 459.2407, found: 459.2409.

Dimethyl (2-(2-bromophenyl)-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-diazoethyl)phosphonate (**3s**)



Following the general procedure, treatment of 4-(2-bromobenzylidene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one (112 mg, 0.30 mmol) with SGR (68 mg, 0.45 mmol) in the presence of Cs_2CO_3 (196 mg, 0.60 mmol) in CH_3CN (3.0 mL) at 25 °C for 45 minute followed by column chromatography afforded the product **3s** as yellow solid (144 mg, 92%). R_f (Ethyl acetate/Hexane: 30/70) = 0.31. **Mp** 126-128 °C. ^{13}C NMR (100 MHz, ppm/ $CDCl_3$): 153.0 (C), 141.1 (d, J_{C-P} = 3.3 Hz, C), 136.2 (C), 136.2 (C), 133.4 (CH), 130.0 (CH), 129.3 (d, J_{C-P} = 4.1 Hz, C), 128.8 (CH), 127.7 (CH), 125.1 (CH), 125.1 (CH), 124.6 (C), 53.2 (d, J_{C-P} = 5.5 Hz, CH_3), 53.1 (d, J_{C-P} = 5.5 Hz, CH_3), 46.3 (d, J_{C-P} = 230.5 Hz, C), 45.9 (d, J_{C-P} = 9.4 Hz, CH), 34.5 (C), 34.5 (C), 30.4 (CH_3), 30.4 (CH_3). 1H NMR (400 MHz, ppm/ $CDCl_3$): 7.61 (d, J = 6.0 Hz, 1H), 7.35-7.26 (m, 2H), 7.16 (d, J = 6.0 Hz, 1H), 7.01 (s, 2H), 5.19 (s, 1H), 5.17 (s, 1H), 3.73 (d, J = 11.6 Hz, 3H), 3.60 (d, J = 11.6 Hz, 3H), 1.41 (s, 18H). ^{31}P NMR (161.9 MHz, $CDCl_3$): 23.20. **HRMS** for $C_{24}H_{33}BrN_2O_4P^+$: calcd. $[M+H]^+$: 523.1356, found: 523.1356.

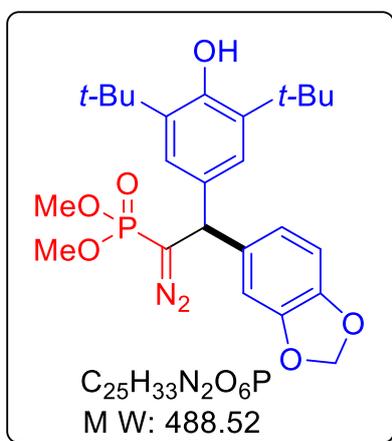
Dimethyl (2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-diazo-2-(3,4-dimethoxyphenyl)ethyl)phosphonate (3t)



Following the general procedure, treatment of 2,6-di-*tert*-butyl-4-(3,4-dimethoxybenzylidene)cyclohexa-2,5-dien-1-one (106 mg, 0.30 mmol) with SGR (68 mg, 0.45 mmol) in the presence of Cs_2CO_3 (196 mg, 0.60 mmol) in CH_3CN (3.0 mL) at 25 °C for 45 minute followed by column chromatography afforded the product **3t** as yellow liquid (141 mg, 93%). R_f (Ethyl acetate/Hexane: 40/60) = 0.31. ^{13}C NMR (100 MHz, ppm/ $CDCl_3$): 152.9 (C), 149.1 (C), 148.2 (C), 136.2 (C), 136.2 (C), 134.0 (d, J_{C-P} = 3.5 Hz, C), 131.1 (d, J_{C-P} = 3.9 Hz, C), 124.8 (CH), 124.8 (CH), 120.5 (CH), 111.7 (CH), 111.2 (CH), 56.0

(CH_3), 56.0 (CH_3), 53.0 (d, J_{C-P} = 3.9 Hz, CH_3), 53.0 (d, J_{C-P} = 4.9 Hz, CH_3), 46.8 (d, J_{C-P} = 230.6 Hz, C), 45.8 (d, J_{C-P} = 9.0 Hz, CH), 34.5 (C), 34.5 (C), 30.4 (CH_3), 30.4 (CH_3). 1H NMR (400 MHz, ppm/ $CDCl_3$): 7.00 (s, 2H), 6.84-6.77 (m, 3H), 5.16 (s, 1H), 4.60 (d, J = 9.2 Hz, 1H), 3.87 (s, 3H), 3.82 (s, 3H), 3.64 (d, J = 4.0 Hz, 3H), 3.61 (d, J = 4.0 Hz, 3H), 1.39 (s, 18H). ^{31}P NMR (161.9 MHz, $CDCl_3$): 24.11. HRMS for $C_{26}H_{38}O_6P^+$: calcd. $[M-N_2]^+$: 477.2401, found: 477.2394.

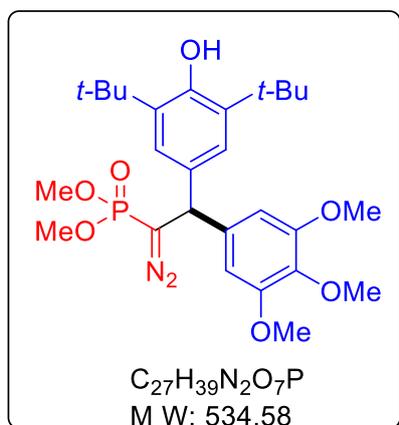
Dimethyl (2-(benzo[d][1,3]dioxol-5-yl)-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-diazoethyl)phosphonate (3u)



Following the general procedure, treatment of 4-(benzo[d][1,3]dioxol-5-ylmethylene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one (101 mg, 0.30 mmol) with SGR (68 mg, 0.45 mmol) in the presence of Cs_2CO_3 (196 mg, 0.60 mmol) in CH_3CN (3.0 mL) at 25 °C for 45 minute followed by column chromatography afforded the product **3u** as yellow liquid (136 mg, 93%). R_f (Ethyl acetate/Hexane: 40/60) = 0.31. ^{13}C NMR (100 MHz, ppm/ $CDCl_3$): 152.9 (C), 148.0 (C), 146.7 (C), 136.2 (C), 136.2 (C), 135.4 (d, J_{C-P} = 3.7 Hz, C), 131.1 (d, J_{C-P} = 3.8 Hz, C), 124.8 (CH), 124.8 (CH), 121.5 (CH), 108.9 (CH), 108.3 (CH), 101.2 (CH_2), 53.0 (d, J_{C-P} = 3.4

Hz, CH_3), 53.0 (d, J_{C-P} = 3.3 Hz, CH_3), 46.7 (d, J_{C-P} = 230.8 Hz, C), 45.9 (d, J_{C-P} = 9.0 Hz, CH), 34.5 (C), 34.5 (C), 30.4 (CH_3), 30.4 (CH_3). 1H NMR (400 MHz, ppm/ $CDCl_3$): 6.96 (s, 2H), 6.76-6.68 (m, 3H), 5.90 (s, 2H), 5.17 (s, 1H), 4.56 (d, J = 9.2 Hz, 1H), 3.65 (d, J = 6.8 Hz, 3H), 3.62 (d, J = 6.4 Hz, 3H), 1.39 (s, 18H). ^{31}P NMR (161.9 MHz, $CDCl_3$): 23.96. HRMS for $C_{25}H_{33}NaN_2O_6P^+$: calcd. $[M+Na]^+$: 511.1968, found: 511.1944.

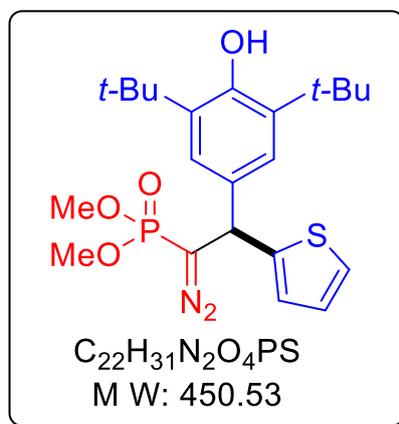
Dimethyl

(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-diazo-2-(3,4,5-trimethoxyphenyl)ethyl)phosphonate (3v)

Following the general procedure, treatment of 2,6-di-*tert*-butyl-4-(3,4,5-trimethoxybenzylidene)cyclohexa-2,5-dien-1-one (115.0 mg, 0.30 mmol) with SGR (68 mg, 0.45 mmol) in the presence of Cs_2CO_3 (196 mg, 0.60 mmol) in CH_3CN (3.0 mL) at 25 °C for 45 minute followed by column chromatography afforded the product **3v** as yellow solid (143 mg, 89%). R_f (Ethyl acetate/Hexane: 40/60) = 0.29. **Mp** 110-112 °C. ^{13}C NMR (100 MHz, ppm/ $CDCl_3$): 153.4 (C), 153.4 (C), 153.1 (C), 137.2 (C), 137.1 (d, J_{C-P} = 3.1 Hz, C), 136.2 (C), 136.2 (C), 130.8 (d, J_{C-P} = 3.5 Hz, C), 124.9 (CH), 124.9 (CH), 105.7 (CH), 105.7 (CH), 61.0 (CH₃), 56.3 (CH₃), 56.3

(CH₃), 53.1 (d, J_{C-P} = 4.0 Hz, CH₃), 53.1 (d, J_{C-P} = 4.2 Hz, CH₃), 46.8 (d, J_{C-P} = 230.7 Hz, C), 46.4 (d, J_{C-P} = 8.9 Hz, CH), 34.5 (C), 34.5 (C), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃). 1H NMR (400 MHz, ppm/ $CDCl_3$): 7.02 (s, 2H), 6.47 (s, 2H), 5.18 (s, 1H), 4.58 (d, J = 8.8 Hz, 1H), 3.84 (s, 3H), 3.80 (s, 6H), 3.64 (d, J = 11.6 Hz, 6H), 1.40 (s, 18H). ^{31}P NMR (161.9 MHz, $CDCl_3$): 23.94. **HRMS** for $C_{27}H_{40}N_2O_7P^+$: calcd. $[M+H]^+$: 535.2568, found: 535.2563.

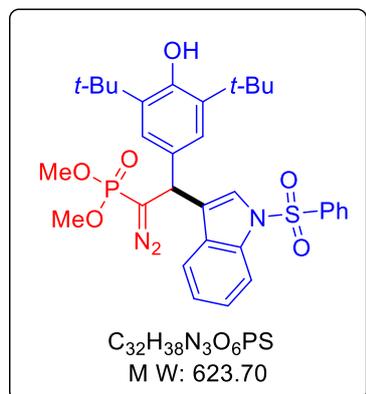
Dimethyl

(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-diazo-2-(thiophen-2-yl)ethyl)phosphonate (3w)

Following the general procedure, treatment of 2,6-di-*tert*-butyl-4-(thiophen-2-ylmethylene)cyclohexa-2,5-dien-1-one (90 mg, 0.30 mmol) with SGR (68 mg, 0.45 mmol) in the presence of Cs_2CO_3 (196 mg, 0.60 mmol) in CH_3CN (3.0 mL) at 25 °C for 45 minute followed by column chromatography afforded the product **3w** as yellow solid (128 mg, 95%). R_f (Ethyl acetate/Hexane: 30/70) = 0.29. **Mp** 120-122 °C. ^{13}C NMR (100 MHz, ppm/ $CDCl_3$): 153.3 (C), 145.4 (d, J_{C-P} = 4.8 Hz, C), 136.3 (C), 136.3 (C), 131.4 (d, J_{C-P} = 3.0 Hz, C), 126.9 (CH), 126.1 (CH), 125.1 (CH), 124.4 (CH), 124.4 (CH), 53.1 (d,

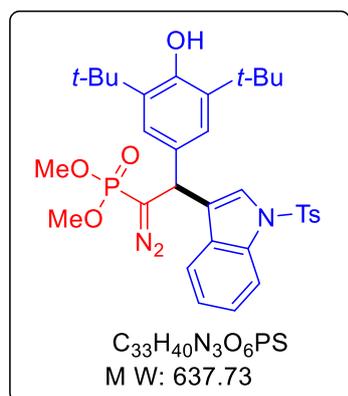
J_{C-P} = 5.1 Hz, CH₃), 53.0 (d, J_{C-P} = 5.0 Hz, CH₃), 47.9 (d, J_{C-P} = 230.2 Hz, C), 42.1 (d, J_{C-P} = 9.6 Hz, CH), 34.5 (C), 34.5 (C), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃). 1H NMR (400 MHz, ppm/ $CDCl_3$): 7.23 (d, J = 5.2 Hz, 1H), 7.08 (s, 2H), 6.96-6.94 (m, 1H), 6.86 (d, J = 3.6 Hz, 1H), 5.20 (s, 1H), 4.79 (d, J = 8.8 Hz, 1H), 3.68 (d, J = 12.0 Hz, 3H), 3.66 (d, J = 11.6 Hz, 3H), 1.41 (s, 18H). ^{31}P NMR (161.9 MHz, $CDCl_3$): 23.31. **HRMS** for $C_{22}H_{32}N_2O_4PS^+$: calcd. $[M+H]^+$: 451.1815, found: 451.1823.

Dimethyl (2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-diazo-2-(1-(phenylsulfonyl)-1H-indol-3-yl)ethyl)phosphonate (3x)



Following the general procedure, treatment of 2,6-di-*tert*-butyl-4-((1-(phenylsulfonyl)-1H-indol-3-yl)methylene)cyclohexa-2,5-dien-1-ol (143 mg, 0.30 mmol) with SGR (68 mg, 0.45 mmol) in the presence of CS_2CO_3 (196 mg, 0.60 mmol) in CH_3CN (3.0 mL) at 25 °C for 45 minute followed by column chromatography afforded the product **3x** as yellow liquid (174 mg, 93%). R_f (Ethyl acetate/Hexane: 30/70) = 0.42. ^{13}C NMR (100 MHz, ppm/ $CDCl_3$): 153.3 (C), 138.1 (C), 136.4 (C), 136.4 (C), 136.0 (C), 134.0 (CH), 129.8 (C), 129.4 (CH), 129.4 (CH), 126.7 (CH), 126.7 (CH), 125.4 (d, J_{C-P} = 9.0 Hz, C), 124.3 (CH), 124.3 (CH), 124.0 (d, J_{C-P} = 4.9 Hz, C), 123.7 (CH), 123.7 (CH), 120.4 (CH), 120.4 (CH), 114.1 (CH), 53.2 (d, J_{C-P} = 5.9 Hz, CH_3), 53.1 (d, J_{C-P} = 5.7 Hz, CH_3), 45.9 (d, J_{C-P} = 232.6 Hz, C), 38.4 (d, J_{C-P} = 9.4 Hz, CH), 34.5 (C), 34.5 (C), 30.4 (CH_3), 30.4 (CH_3). 1H NMR (400 MHz, ppm/ $CDCl_3$): 8.02 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 7.6 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.42 (t, J = 7.0 Hz, 3H), 7.33 (t, J = 7.8 Hz, 1H), 7.24 (s, 1H), 7.20 (t, J = 7.6 Hz, 1H), 7.00 (s, 2H), 5.20 (s, 1H), 4.75 (d, J = 8.4 Hz, 1H), 3.63 (d, J = 11.6 Hz, 3H), 3.58 (d, J = 11.6 Hz, 3H), 1.37 (s, 18H). ^{31}P NMR (161.9 MHz, $CDCl_3$): 23.10. HRMS for $C_{32}H_{38}N_3NaO_6PS^+$: calcd. $[M+Na]^+$: 646.2111, found: 646.2119.

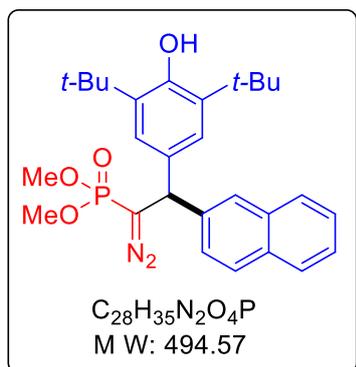
Dimethyl (2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-diazo-2-(1-tosyl-1H-indol-3-yl)ethyl)phosphonate (3y)



Following the general procedure, treatment of 2,6-di-*tert*-butyl-4-((1-tosyl-1H-indol-3-yl)methylene)cyclohexa-2,5-dien-1-ol (147 mg, 0.30 mmol) with SGR (68 mg, 0.45 mmol) in the presence of CS_2CO_3 (196 mg, 0.60 mmol) in CH_3CN (3.0 mL) at 25 °C for 45 minute followed by column chromatography afforded the product **3y** as yellow liquid (172 mg, 90%). R_f (Ethyl acetate/Hexane: 30/70) = 0.42. ^{13}C NMR (100 MHz, ppm/ $CDCl_3$): 153.3 (C), 145.1 (C), 136.4 (C), 136.4 (C), 136.0 (C), 135.1 (C), 130.0 (CH), 130.0 (C), 129.4 (CH), 126.8 (CH), 126.8 (CH), 125.4 (d, J_{C-P} = 8.0 Hz, C), 124.3 (CH), 124.3 (CH), 123.7 (d, J_{C-P} = 4.9 Hz, C), 123.6 (CH), 123.6 (CH), 120.3 (CH), 120.3 (CH), 114.1 (CH), 53.2 (d, J_{C-P} = 5.8 Hz, CH_3), 53.2 (d, J_{C-P} = 6.0 Hz, CH_3), 45.9 (d, J_{C-P} = 232.6 Hz, C), 38.3 (d, J_{C-P} = 9.6 Hz, CH), 34.5 (C), 34.5 (C), 30.4 (CH_3), 21.7 (CH_3). 1H NMR (400 MHz, ppm/ $CDCl_3$): 8.00 (d, J = 8.4 Hz, 1H), 7.68 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 7.6 Hz, 1H), 7.32 (t, J = 7.4 Hz, 1H), 7.24-7.18 (m, 4H), 7.00 (s, 2H), 5.20 (s, 1H), 4.75 (d, J = 8.0 Hz, 1H), 3.64 (d, J = 11.6 Hz, 3H), 3.60 (d, J = 11.6 Hz, 3H), 2.33 (s, 3H), 1.37 (s, 18H). ^{31}P NMR (161.9 MHz, $CDCl_3$): 23.16. HRMS for $C_{33}H_{40}N_3NaO_6PS^+$: calcd. $[M+Na]^+$: 660.2268, found: 660.2269.

Dimethyl
yl)ethyl)phosphonate (3z)

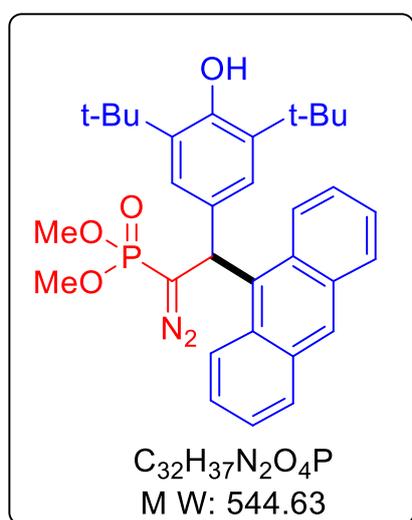
(2-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-diazo-2-(naphthalen-2-



Following the general procedure, treatment of 2,6-di-tert-butyl-4-(naphthalen-2-ylmethylene)cyclohexa-2,5-dien-1-one (103 mg, 0.30 mmol) with SGR (68 mg, 0.45 mmol) in the presence of Cs_2CO_3 (196 mg, 0.60 mmol) in CH_3CN (3.0 mL) at 25 °C for 45 minute followed by column chromatography afforded the product **3z** as yellow solid (125 mg, 84%). R_f (Ethyl acetate/Hexane: 30/70) = 0.39. **Mp** 154-156 °C. ^{13}C NMR (100 MHz, ppm/ $CDCl_3$): 153.1 (C), 138.9 (d, J_{C-P} = 3.3 Hz, C), 136.3 (C), 136.3 (C), 133.6 (C), 133.5 (C), 130.9 (d, J_{C-P} = 3.6 Hz, C), 128.5 (CH), 128.1 (CH), 127.8 (CH), 126.8 (CH), 126.7 (CH), 126.4 (CH), 126.1 (CH), 125.0 (CH), 125.0 (CH), 53.1 (d, J_{C-P} = 4.1 Hz, CH_3), 53.0 (d, J_{C-P} = 4.1 Hz, CH_3), 46.6 (d, J_{C-P} = 231.1 Hz, C), 46.3 (d, J_{C-P} = 8.9 Hz, CH), 34.5 (C), 34.5 (C), 30.4 (CH_3), 30.4 (CH_3). 1H NMR (400 MHz, ppm/ $CDCl_3$): 7.84-7.80 (m, 3H), 7.71 (s, 1H), 7.49-7.47 (m, 2H), 7.38 (d, J = 8.4 Hz, 1H), 7.04 (s, 2H), 5.20 (s, 1H), 4.82 (d, J = 9.2 Hz, 1H), 3.66 (d, J = 12.0 Hz, 3H), 3.61 (d, J = 11.6 Hz, 3H), 1.39 (s, 18H). ^{31}P NMR (161.9 MHz, $CDCl_3$): 24.06. **HRMS** for $C_{28}H_{36}N_2O_4P^+$: calcd. $[M+H]^+$: 495.2407, found: 495.2406.

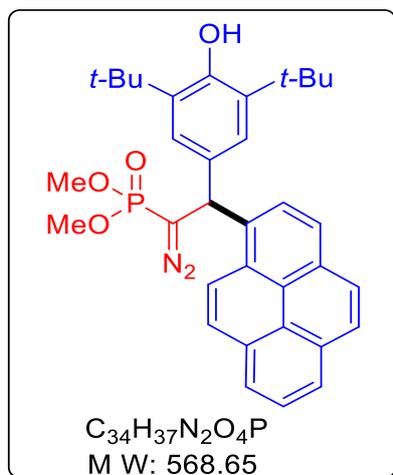
Dimethyl
diazoethyl)phosphonate (3aa)

(2-(anthracen-9-yl)-2-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-



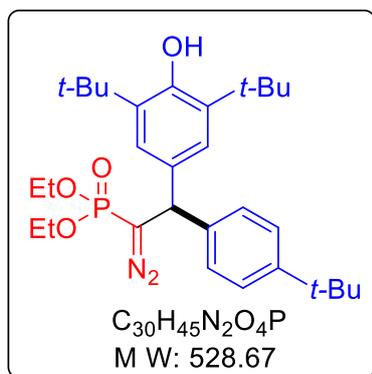
Following the general procedure, treatment of 4-(anthracen-9-ylmethylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (118 mg, 0.30 mmol) with SGR (68 mg, 0.45 mmol) in the presence of Cs_2CO_3 (196 mg, 0.60 mmol) in CH_3CN (3.0 mL) at 25 °C for 45 minute followed by column chromatography afforded the product **3aa** as yellow solid (147 mg, 90%). R_f (Ethyl acetate/Hexane: 30/70) = 0.39. **Mp** 150-152 °C. ^{13}C NMR (100 MHz, ppm/ $CDCl_3$): 152.7 (C), 136.2 (C), 136.2 (C), 132.7 (CH), 131.9 (C), 131.9 (C), 130.9 (C), 130.9 (C), 129.5 (CH), 129.5 (CH), 129.2 (d, J_{C-P} = 6.0 Hz, C), 128.2 (CH), 128.2 (CH), 125.7 (CH), 125.3 (C), 125.0 (CH), 124.9 (CH), 124.9 (CH), 124.9 (CH), 124.9 (CH), 52.9 (d, J_{C-P} = 5.6 Hz, CH_3), 52.4 (d, J_{C-P} = 5.2 Hz, CH_3), 47.1 (d, J_{C-P} = 230.1 Hz, C), 39.6 (d, J_{C-P} = 9.1 Hz, CH), 34.5 (C), 34.5 (C), 30.3 (CH_3), 30.3 (CH_3). 1H NMR (400 MHz, ppm/ $CDCl_3$): 8.46 (s, 1H), 8.09-8.02 (m, 4H), 7.46-7.39 (m, 4H), 7.08 (s, 2H), 6.46 (d, J = 8.8 Hz, 1H), 5.19 (s, 1H), 3.44 (d, J = 11.2 Hz, 3H), 3.00 (d, J = 12.0 Hz, 3H), 1.30 (s, 18H). ^{31}P NMR (161.9 MHz, $CDCl_3$): 24.28. **HRMS** for $C_{32}H_{38}N_2O_4P^+$: calcd. $[M+H]^+$: 545.2564, found: 545.2561.

Dimethyl (2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-diazo-2-(pyren-1-yl)ethyl)phosphonate (3ab)



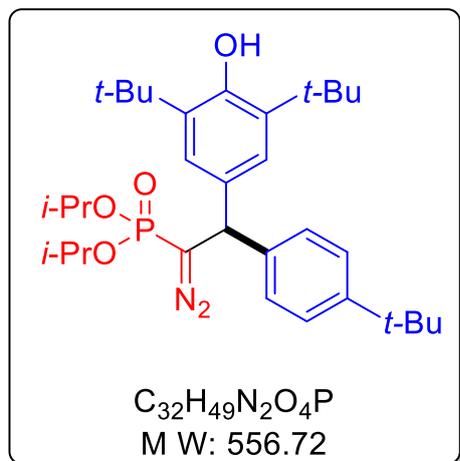
Following the general procedure, treatment of 2,6-di-*tert*-butyl-4-(pyren-1-ylmethyl)cyclohexa-2,5-dien-1-one (126 mg, 0.30 mmol) with SGR (68 mg, 0.45 mmol) in the presence of Cs_2CO_3 (196 mg, 0.60 mmol) in CH_3CN (3.0 mL) at 25 °C for 45 minute followed by column chromatography afforded the product **3ab** as yellow solid (138 mg, 81%). R_f (Ethyl acetate/Hexane: 30/70) = 0.39. **Mp** 160-162 °C. ^{13}C **NMR** (100 MHz, ppm/ $CDCl_3$): 153.0 (C), 136.3 (C), 136.3 (C), 135.0 (C), 131.5 (C), 131.1 (C), 130.8 (CH), 130.7 (C), 128.7 (C), 128.1 (CH), 127.5 (CH), 127.5 (CH), 126.2 (CH), 126.1 (CH), 125.5 (C), 125.3 (C), 125.2 (CH), 125.2 (CH), 125.2 (CH), 124.9 (C), 124.8 (CH), 123.1 (CH), 53.1 (CH₃), 53.1 (CH₃), 47.9 (d, J_{C-P} = 229.6 Hz, C), 42.9 (d, J_{C-P} = 8.9 Hz, CH), 34.5 (C), 34.5 (C), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃). 1H **NMR** (400 MHz, ppm/ $CDCl_3$): 8.49 (d, J = 9.2 Hz, 1H), 8.21-8.14 (m, 4H), 8.09-8.00 (m, 3H), 7.81 (d, J = 8.0 Hz, 1H), 7.15 (s, 2H), 5.85 (d, J = 8.4 Hz, 1H), 5.19 (s, 1H), 3.67 (d, J = 11.6 Hz, 3H), 3.58 (d, J = 11.6 Hz, 3H), 1.39 (s, 18H). ^{31}P **NMR** (161.9 MHz, $CDCl_3$): 23.63. **HRMS** for $C_{34}H_{38}N_2O_4P^+$: calcd. $[M+H]^+$: 569.2564, found: 569.2556.

Diethyl (2-(4-(*tert*-butyl)phenyl)-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-diazoethyl)phosphonate (3ac)



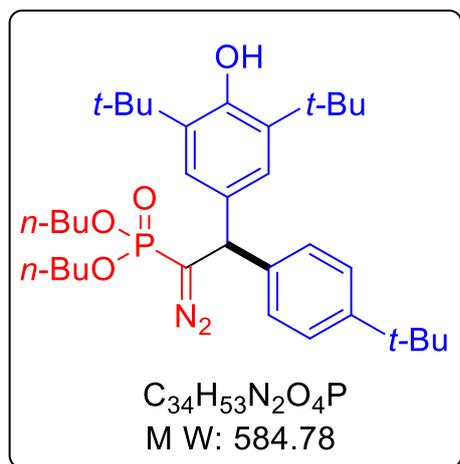
Following the general procedure, treatment of 2,6-di-*tert*-butyl-4-(4-(*tert*-butyl)benzylidene)cyclohexa-2,5-dien-1-one (105 mg, 0.30 mmol) with SGR (80 mg, 0.45 mmol) in the presence of Cs_2CO_3 (196 mg, 0.60 mmol) in CH_3CN (3.0 mL) at 25 °C for 45 minute followed by column chromatography afforded the product **3ac** as yellow liquid (135 mg, 85%). R_f (Ethyl acetate/Hexane: 20/80) = 0.30. ^{13}C **NMR** (100 MHz, ppm/ $CDCl_3$): 152.9 (C), 150.0 (C), 138.3 (d, J_{C-P} = 12.6 Hz, C), 136.1 (C), 136.1 (C), 131.5 (d, J_{C-P} = 12.6 Hz, C), 128.0 (CH), 128.0 (CH), 126.0 (CH), 126.0 (CH), 124.9 (CH), 124.9 (CH), 62.7 (d, J_{C-P} = 2.7 Hz, CH₂), 62.5 (d, J_{C-P} = 5.0 Hz, CH₂), 52.8 (C), 45.8 (d, J_{C-P} = 8.9 Hz, CH), 34.6 (C), 34.5 (C), 34.5 (C), 31.5 (CH₃), 31.5 (CH₃), 31.5 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 16.2 (CH₃), 16.2 (CH₃). 1H **NMR** (400 MHz, ppm/ $CDCl_3$): 7.34 (d, J = 8.4 Hz, 2H), 7.18-7.15 (m, 2H), 7.00 (d, J = 2.8 Hz, 2H), 5.15 (s, 1H), 4.59 (d, J = 8.8 Hz, 1H), 4.06-4.00 (m, 1H), 3.92-3.84 (m, 1H), 3.60 (q, J = 8.8 Hz, 2H), 1.39 (s, 18H), 1.26 (s, 9H), 1.19-1.17 (m, 6H). ^{31}P **NMR** (161.9 MHz, $CDCl_3$): 22.66. **HRMS** for $C_{30}H_{46}N_2O_4P^+$: calcd. $[M+H]^+$: 529.3190, found: 529.3188.

Diisopropyl (2-(4-(*tert*-butyl)phenyl)-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-diazoethyl)phosphonate (3ad)



Following the general procedure, treatment of 2,6-di-*tert*-butyl-4-(4-(*tert*-butyl)benzylidene)cyclohexa-2,5-dien-1-one (105 mg, 0.30 mmol) with SGR (93 mg, 0.45 mmol) in the presence of Cs_2CO_3 (196 mg, 0.60 mmol) in CH_3CN (3.0 mL) at 25 °C for 45 minute followed by column chromatography afforded the product **3ad** as yellow liquid (149 mg, 89%). R_f (Ethyl acetate/Hexane: 20/80) = 0.29. ^{13}C NMR (100 MHz, ppm/ $CDCl_3$): 152.8 (C), 149.8 (C), 138.6 (d, J_{C-P} = 3.8 Hz, C), 136.0 (C), 136.0 (C), 131.8 (d, J_{C-P} = 3.8 Hz, C), 128.0 (CH), 128.0 (CH), 125.4 (CH), 125.4 (CH), 125.0 (CH), 125.0 (CH), 71.5 (d, J_{C-P} = 5.3 Hz, CH), 71.5 (d, J_{C-P} = 5.3 Hz, CH), 48.2 (d, J_{C-P} = 229.4 Hz, C), 45.8 (d, J_{C-P} = 9.0 Hz, CH), 34.6 (C), 34.5 (C), 34.5 (C), 31.5 (CH₃), 31.5 (CH₃), 31.5 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 24.1 (CH₃), 24.1 (CH₃), 23.7 (CH₃), 23.7 (CH₃). 1H NMR (400 MHz, ppm/ $CDCl_3$): 7.32 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 7.00 (s, 2H), 5.13 (s, 1H), 4.61 (d, J = 9.2 Hz, 1H), 4.58-4.51 (m, 2H), 1.39 (s, 18H), 1.30 (s, 9H), 1.29-1.26 (m, 6H), 1.10 (s, 3H), 1.09 (s, 3H). ^{31}P NMR (161.9 MHz, $CDCl_3$): 18.43. HRMS for $C_{32}H_{50}N_2O_4P^+$: calcd. $[M+H]^+$: 557.3503, found: 557.3502.

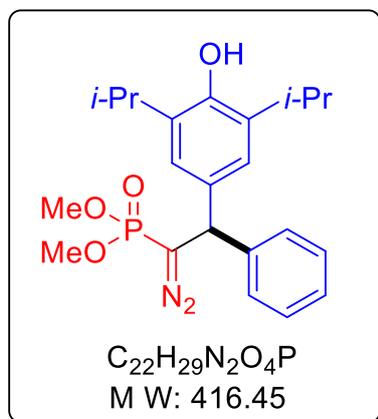
Dibutyl (2-(4-(*tert*-butyl)phenyl)-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-diazoethyl)phosphonate (3ae)



Following the general procedure, treatment of 2,6-di-*tert*-butyl-4-(4-(*tert*-butyl)benzylidene)cyclohexa-2,5-dien-1-one (105 mg, 0.30 mmol) with SGR (105 mg, 0.45 mmol) in the presence of Cs_2CO_3 (196 mg, 0.60 mmol) in CH_3CN (3.0 mL) at 25 °C for 45 minute followed by column chromatography afforded the product **3ae** as yellow liquid (163 mg, 93%). R_f (Ethyl acetate/Hexane: 20/80) = 0.29. ^{13}C NMR (100 MHz, ppm/ $CDCl_3$): 152.9 (C), 149.9 (C), 138.5 (d, J_{C-P} = 3.7 Hz, C), 136.1 (C), 136.1 (C), 131.6 (d, J_{C-P} = 3.7 Hz, C), 128.0 (CH), 128.0 (CH), 125.5 (CH), 125.5 (CH), 124.9 (CH), 124.9 (CH), 66.2 (d, J_{C-P} = 5.5 Hz, CH₂), 66.2 (d, J_{C-P} = 5.5 Hz, CH₂), 47.4 (d, J_{C-P} = 228.7 Hz, C), 45.7 (d, J_{C-P} = 8.9 Hz, CH), 34.6 (C), 34.5 (C), 34.5 (C), 32.4 (d, J_{C-P} = 3.0 Hz, CH₂), 32.3 (d, J_{C-P} = 3.1 Hz, CH₂), 31.5 (CH₃), 31.5 (CH₃), 31.5 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 18.8 (d, J_{C-P} = 1.8 Hz, CH₂), 18.8 (d, J_{C-P} = 1.8 Hz, CH₂), 13.7 (CH₃), 13.7 (CH₃). 1H NMR (400 MHz, ppm/ $CDCl_3$): 7.33 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 8.4 Hz, 2H), 6.99 (s, 2H), 5.14 (s, 1H), 4.58 (d, J = 8.8 Hz, 1H), 3.99-3.93 (m, 2H), 3.83-3.78 (m, 2H), 1.54-1.49

(m, 6H), 1.39 (s, 18H), 1.30 (s, 11H), 0.88-0.84 (m, 6H). ³¹P NMR (161.9 MHz, CDCl₃): 21.07. HRMS for C₃₄H₅₄N₂O₄P⁺: calcd. [M+H]⁺: 585.3816, found: 585.3817.

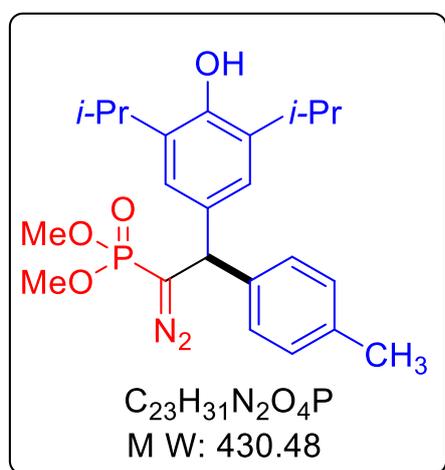
Dimethyl (1-diazo-2-(4-hydroxy-3,5-diisopropylphenyl)-2-phenylethyl)phosphonate (3af)



Following the general procedure, treatment of 4-benzylidene-2,6-diisopropylcyclohexa-2,5-dien-1-one (80 mg, 0.30 mmol) with SGR (68 mg, 0.45 mmol) in the presence of Cs₂CO₃ (196 mg, 0.60 mmol) in CH₃CN (3.0 mL) at 25 °C for 45 minute followed by column chromatography afforded the product **3af** as yellow solid (97 mg, 78%). R_f (Ethyl acetate/Hexane: 40/60) = 0.31. Mp 124-126 °C. ¹³C NMR (100 MHz, ppm/CDCl₃): 149.3(C), 141.3 (d, J_{C-P} = 3.7 Hz, C), 134.3 (C), 134.3 (C), 132.3 (d, J_{C-P} = 3.7 Hz, C), 128.7 (CH), 128.7 (CH), 128.3 (CH), 128.3 (CH), 127.2 (CH), 123.4 (CH), 123.4 (CH),

53.0 (d, J_{C-P} = 5.2 Hz, CH₃), 53.0 (d, J_{C-P} = 5.2 Hz, CH₃), 46.6 (d, J_{C-P} = 231.3 Hz, C), 45.9 (d, J_{C-P} = 8.9 Hz, CH), 27.3 (CH), 27.3 (CH), 22.8 (CH₃), 22.8 (CH₃), 22.8 (CH₃), 22.8 (CH₃). ¹H NMR (400 MHz, ppm/CDCl₃): 7.33 (t, J = 7.4 Hz, 2H), 7.27-7.23 (m, 3H), 6.86 (s, 2H), 5.14 (s, 1H), 4.66 (d, J = 9.2 Hz, 1H), 3.62 (d, J = 11.6 Hz, 6H), 3.19-3.12 (m, 2H), 1.20 (d, J = 6.8 Hz, 12H). ³¹P NMR (161.9 MHz, CDCl₃): 24.11. HRMS for C₂₂H₃₀O₄P⁺: calcd. [M-N₂]⁺: 389.1876, found: 389.1883.

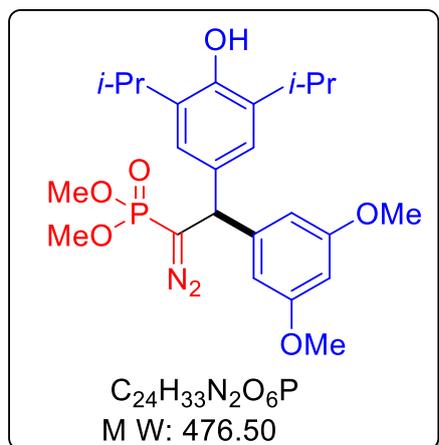
Dimethyl (1-diazo-2-(4-hydroxy-3,5-diisopropylphenyl)-2-(p-tolyl)ethyl)phosphonate (3ag)



Following the general procedure, treatment of 2,6-diisopropyl-4-(4-methylbenzylidene)cyclohexa-2,5-dien-1-one (84 mg, 0.30 mmol) with SGR (68 mg, 0.45 mmol) in the presence of Cs₂CO₃ (196 mg, 0.60 mmol) in CH₃CN (3.0 mL) at 25 °C for 45 minute followed by column chromatography afforded the product **3ag** as yellow liquid (94 mg, 73%). R_f (Ethyl acetate/Hexane: 40/60) = 0.31. 6.87 (s, 2H), 5.02 (s, 1H), 4.62 (d, J = 9.2 Hz, ¹³C NMR (100 MHz, ppm/CDCl₃): 149.2(C), 138.2 (d, J_{C-P} = 2.7 Hz, C), 136.8 (C), 136.8 (C), 134.2 (C), 132.7 (d, J_{C-P} = 3.6 Hz, C), 129.4 (CH), 129.4 (CH), 128.2 (CH), 128.2

(CH), 123.4 (CH), 123.4 (CH), 53.0 (d, J_{C-P} = 0.7 Hz, CH₃), 53.0 (d, J_{C-P} = 0.4 Hz, CH₃), 46.6 (d, J_{C-P} = 249.3 Hz, C), 45.6 (d, J_{C-P} = 8.8 Hz, CH), 27.3 (CH), 27.3 (CH), 22.8 (CH₃), 22.8 (CH₃), 22.8 (CH₃), 22.8 (CH₃), 21.2 (CH₃). ¹H NMR (400 MHz, ppm/CDCl₃): 7.16-7.10 (m, 4H), 6.87 (s, 2H), 5.02 (s, 1H), 4.62 (d, J = 9.2 Hz, 1H), 3.64 (d, J = 5.6 Hz, 3H), 3.61 (d, J = 5.6 Hz, 3H), 3.18-3.11 (m, 2H), 2.33 (s, 3H), 1.21 (d, J = 1.6 Hz, 6H), 1.20 (d, J = 1.6 Hz, 6H). ³¹P NMR (161.9 MHz, CDCl₃): 24.23. HRMS for C₂₃H₃₂O₄P⁺: calcd. [M-N₂]⁺: 403.2033, found: 403.2053.

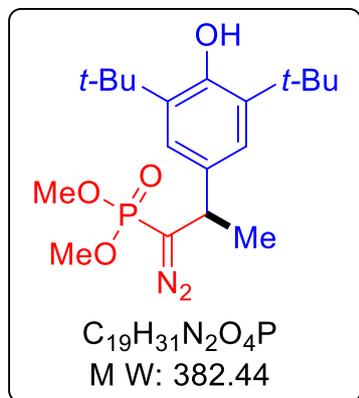
Dimethyl (1-diazo-2-(3,5-dimethoxyphenyl)-2-(4-hydroxy-3,5-diisopropylphenyl)ethyl)phosphonate (3ah)



Following the general procedure, treatment of 4-(3,5-dimethoxybenzylidene)-2,6-diisopropylcyclohexa-2,5-dien-1-one (98 mg, 0.30 mmol) with SGR (68 mg, 0.45 mmol) in the presence of Cs_2CO_3 (196 mg, 0.60 mmol) in CH_3CN (3.0 mL) at 25 °C for 45 minute followed by column chromatography afforded the product **3ah** as yellow liquid (107 mg, 75%). R_f (Ethyl acetate/Hexane: 40/60) = 0.28. ^{13}C NMR (100 MHz, ppm/ $CDCl_3$): 161.0 (C), 161.0 (C), 149.4 (C), 143.7 (d, J_{C-P} = 3.4 Hz, C), 134.4 (C), 134.4 (C), 131.9 (C), 123.2 (CH), 123.2 (CH), 106.6 (CH), 106.6 (CH), 97.0 (CH), 55.3 (CH₃), 55.3 (CH₃), 53.0 (CH₃),

53.0 (CH₃), 46.5 (d, J_{C-P} = 231.8 Hz, C), 46.0 (d, J_{C-P} = 8.9 Hz, CH), 27.1 (CH), 27.1 (CH), 22.9 (CH₃), 22.9 (CH₃), 22.9 (CH₃). 1H NMR (400 MHz, ppm/ $CDCl_3$): 6.87 (s, 2H), 6.39 (d, J = 2.4 Hz, 2H), 6.35 (d, J = 2.2 Hz, 1H), 5.48 (s, 1H), 4.57 (d, J = 9.2 Hz, 1H), 3.73 (s, 6H), 3.64 (d, J = 11.2 Hz, 3H), 3.61 (d, J = 11.2 Hz, 3H), 3.21-3.14 (m, 2H), 1.19 (d, J = 7.2 Hz, 12H). ^{31}P NMR (161.9 MHz, $CDCl_3$): 24.13. HRMS for $C_{24}H_{34}O_6P^+$: calcd. $[M-N_2]^+$: 449.2088, found: 449.2063.

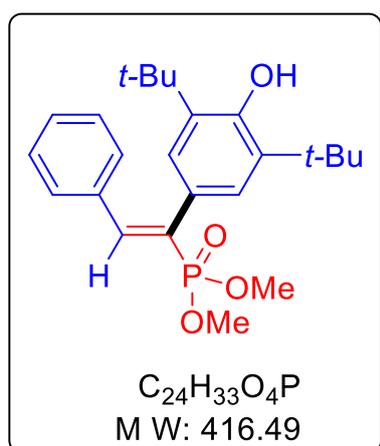
Dimethyl (2-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-diazopropyl)phosphonate (3ai)



Following the general procedure, treatment of 2,6-di-tert-butyl-4-ethylidenecyclohexa-2,5-dien-1-one (70 mg, 0.30 mmol) with SGR (68 mg, 0.45 mmol) in the presence of Cs_2CO_3 (196 mg, 0.60 mmol) in CH_3CN (3.0 mL) at 25 °C for 45 minute followed by column chromatography afforded the product **3ai** as a yellow liquid (52 mg, 45%). R_f (Ethyl acetate/Hexane: 30/70) = 0.37. ^{13}C NMR (100 MHz, ppm/ $CDCl_3$): 152.9 (C), 136.2 (C), 136.2 (C), 133.7 (d, J_{C-P} = 3.1 Hz, C), 123.3 (CH), 123.3 (CH), 52.9 (d, J_{C-P} = 5.4 Hz, CH₃), 52.8 (d, J_{C-P} = 6.6 Hz, CH₃), 35.0 (d, J_{C-P} = 8.6 Hz, C), 34.5 (C), 34.5 (C), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃),

30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 29.5 (d, J_{C-P} = 7.6 Hz, CH), 19.9 (d, J_{C-P} = 3.9 Hz, CH₃). 1H NMR (400 MHz, ppm/ $CDCl_3$): 7.16 (s, 1H), 6.95 (s, 2H), 5.04 (s, 1H), 3.57 (d, J = 9.2 Hz, 3H), 3.48 (d, J = 9.2 Hz, 3H), 1.42 (d, J = 5.6 Hz, 3H), 1.34 (s, 18H). ^{31}P NMR (161.9 MHz, $CDCl_3$): 24.49. HRMS for $C_{19}H_{32}N_2O_4P^+$: calcd. $[M+H]^+$: 383.2094, found: 383.2095.

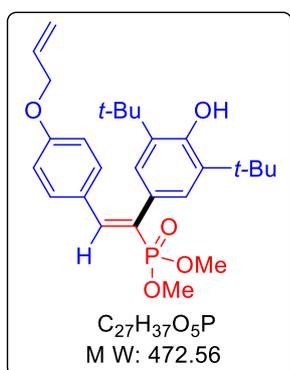
Dimethyl (*E*)-(1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-phenylvinyl)phosphonate (**4a**)



Following the general procedure, treatment of dimethyl (2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-diazo-2-phenylethyl)phosphonate (133 mg, 0.30 mmol) with $Rh_2(OAc)_4$ (13 mg, 0.03 mmol) in toluene (3.0 mL) at 100 °C for 6 h followed by column chromatography afforded the product **4a** as white solid (116 mg, 93%). R_f (Ethyl acetate/Hexane: 40/60) = 0.31. **Mp** 160-162 °C. ^{13}C NMR (100 MHz, ppm/ $CDCl_3$): 153.8 (d, J_{C-P} = 2.3 Hz, C), 143.9 (d, J_{C-P} = 12.1 Hz, C), 136.4 (d, J_{C-P} = 1.2 Hz, C), 136.4 (d, J_{C-P} = 1.2 Hz, C), 135.2 (d, J_{C-P} = 22.6 Hz, CH), 130.5 (d, J_{C-P} = 177.0 Hz, C), 130.3 (CH), 130.3 (CH), 128.8 (CH), 128.1 (CH), 128.1 (CH), 126.4 (d,

J_{C-P} = 5.7 Hz, CH), 126.4 (d, J_{C-P} = 5.7 Hz, CH), 125.6 (d, J_{C-P} = 8.4 Hz, C), 52.8 (d, J_{C-P} = 5.7 Hz, CH_3), 52.8 (d, J_{C-P} = 5.7 Hz, CH_3), 34.4 (C), 34.4 (C), 30.4 (CH_3), 30.4 (CH_3). 1H NMR (400 MHz, ppm/ $CDCl_3$): 7.56 (d, J = 24.0 Hz, 1H), 7.18-7.13 (m, 3H), 7.04-7.03 (m, 4H), 5.26 (s, 1H), 3.74 (d, J = 10.8 Hz, 6H), 1.36 (s, 18H). ^{31}P NMR (161.9 MHz, $CDCl_3$): 21.74. **HRMS** for $C_{24}H_{33}O_4P^+$: calcd. $[M+H]^+$: 417.2189, found: 417.2181.

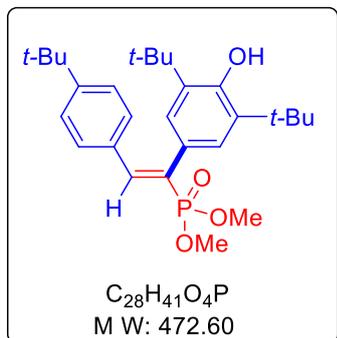
Dimethyl (*E*)-(2-(4-(allyloxy)phenyl)-1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)vinyl)phosphonate (**4b**)



Following the general procedure, treatment of dimethyl (2-(4-(allyloxy)phenyl)-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-diazoethyl)phosphonate (150 mg, 0.30 mmol) with $Rh_2(OAc)_4$ (13 mg, 0.03 mmol) in toluene (3.0 mL) at 100 °C for 6 h followed by column chromatography afforded the product **4b** as white solid (135 mg, 95%). R_f (Ethyl acetate/Hexane: 40/60) = 0.28. **Mp** 162-164 °C. ^{13}C NMR (100 MHz, ppm/ $CDCl_3$): 159.2 (C), 153.2 (d, J_{C-P} = 2.5 Hz, C), 143.7 (d, J_{C-P} = 12.5 Hz, C), 136.5 (d, J_{C-P} = 1.5 Hz, C), 136.5 (d, J_{C-P} = 1.5 Hz, C), 133.0 (CH_2), 132.1 (CH), 132.1 (CH), 128.6 (C), 128.0 (d, J_{C-P} = 23.1 Hz, CH), 127.7 (d, J_{C-P} = 178.5 Hz, C), 126.0 (d, J_{C-P} = 5.4 Hz, CH), 126.0 (d, J_{C-P} = 5.4 Hz, CH), 117.8 (CH), 114.3 (CH), 114.3 (CH), 68.8 (CH_2), 52.7 (d, J_{C-P} = 5.7 Hz, CH_3), 52.7 (d, J_{C-P} = 5.7 Hz, CH_3), 34.5 (C), 34.5 (C), 30.5 (CH_3), 30.5 (CH_3). 1H NMR (400 MHz, ppm/ $CDCl_3$): 7.50 (d, J = 24.4 Hz, 1H), 7.04 (d, J = 1.6 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 6.67 (d, J = 8.8 Hz, 2H), 6.04-5.94 (m, 1H), 5.38 (d, J = 17.6 Hz, 1H), 5.25 (t, J = 5.4 Hz, 2H), 4.48 (d, J = 4.8 Hz, 2H), 3.59 (d, J = 10.8 Hz, 6H), 1.38 (s, 18H). ^{31}P NMR (161.9 MHz, $CDCl_3$): 22.41. **HRMS** for $C_{27}H_{38}O_5P^+$: calcd. $[M+H]^+$: 473.2451, found: 473.2452.

Dimethyl
hydroxyphenyl)vinyl)phosphonate (4c)

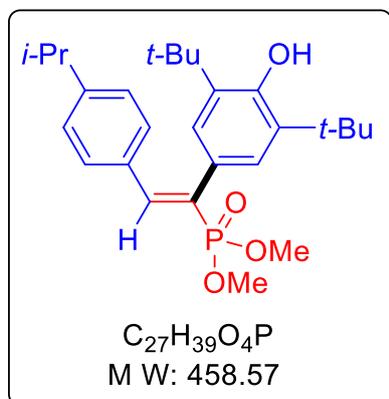
(E)-(2-(4-(tert-butyl)phenyl)-1-(3,5-di-tert-butyl-4-



Following the general procedure, treatment of dimethyl (2-(4-(tert-butyl)phenyl)-2-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-diazoethyl)phosphonate (150 mg, 0.30 mmol) with $Rh_2(OAc)_4$ (13 mg, 0.03 mmol) in toluene (3.0 mL) at 100 °C for 6 h followed by column chromatography afforded the product **4c** as white solid (135 mg, 95%). R_f (Ethyl acetate/Hexane: 40/60) = 0.33. **Mp** 170-172 °C. ^{13}C NMR (100 MHz, ppm/ $CDCl_3$): 153.7 (d, J_{C-P} = 2.4 Hz, C), 152.2 (C), 144.0 (d, J_{C-P} = 11.9 Hz, C), 136.3 (d, J_{C-P} = 1.5 Hz, C), 136.3 (d, J_{C-P} = 1.5 Hz, C), 132.5 (d, J_{C-P} = 22.7 Hz, CH), 130.1 (CH), 130.1 (CH), 129.5 (d, J_{C-P} = 177.4 Hz, C), 126.3 (CH), 126.2 (CH), 125.9 (d, J_{C-P} = 8.5 Hz, CH), 125.9 (d, J_{C-P} = 8.5 Hz, CH), 125.3 (d, J_{C-P} = 8.1 Hz, C), 123.1 (C), 52.7 (d, J_{C-P} = 6.4 Hz, CH_3), 52.7 (d, J_{C-P} = 6.4 Hz, CH_3), 34.5 (C), 34.5 (C), 31.3 (CH_3), 31.3 (CH_3), 31.3 (CH_3), 30.4 (CH_3). 1H NMR (400 MHz, ppm/ $CDCl_3$): 7.56 (t, J = 24.0 Hz, 1H), 7.17 (d, J = 6.8 Hz, 2H), 7.03 (d, J = 1.6 Hz, 2H), 6.97 (d, J = 8.4 Hz, 2H), 5.24 (s, 1H), 3.74 (d, J = 11.2 Hz, 6H), 1.36 (s, 18H), 1.25 (s, 9H). ^{31}P NMR (161.9 MHz, $CDCl_3$): 22.12. **HRMS** for $C_{28}H_{42}O_4P^+$: calcd. $[M+H]^+$: 473.2815, found: 473.2825.

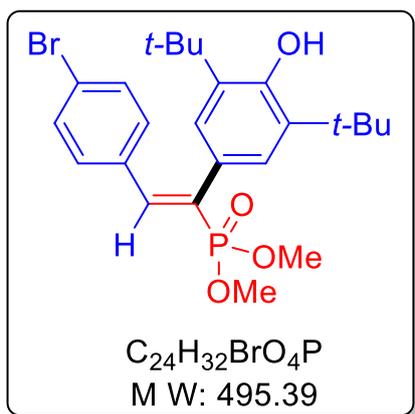
Dimethyl
isopropylphenyl)vinyl)phosphonate (4d)

(E)-(1-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(4-



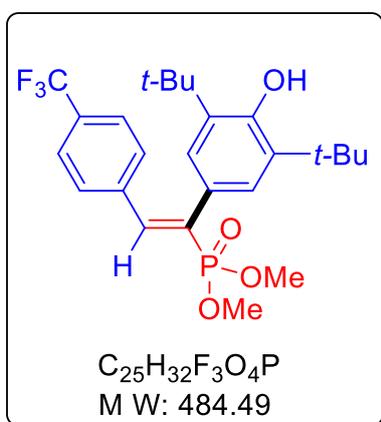
Following the general procedure, treatment of dimethyl (2-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-diazo-2-(4-isopropylphenyl)ethyl)phosphonate (146 mg, 0.30 mmol) with $Rh_2(OAc)_4$ (13 mg, 0.03 mmol) in toluene (3.0 mL) at 100 °C for 6 h followed by column chromatography afforded the product **4d** as white solid (125 mg, 91%). R_f (Ethyl acetate/Hexane: 40/60) = 0.32. **Mp** 164-166 °C. ^{13}C NMR (100 MHz, ppm/ $CDCl_3$): 153.7 (d, J_{C-P} = 2.3 Hz, C), 150.0 (C), 144.2 (d, J_{C-P} = 12.2 Hz, C), 136.4 (d, J_{C-P} = 1.2 Hz, C), 136.4 (d, J_{C-P} = 1.2 Hz, C), 136.9 (d, J_{C-P} = 22.6 Hz, CH), 130.4 (CH), 130.4 (CH), 129.4 (d, J_{C-P} = 177.4 Hz, C), 126.2 (CH), 126.2 (CH), 126.2 (CH), 126.2 (CH), 125.9 (d, J_{C-P} = 8.4 Hz, C), 52.7 (d, J_{C-P} = 5.7 Hz, CH_3), 52.7 (d, J_{C-P} = 5.7 Hz, CH_3), 34.4 (C), 34.4 (C), 34.1 (CH), 30.4 (CH_3), 23.9 (CH_3), 23.9 (CH_3). 1H NMR (400 MHz, ppm/ $CDCl_3$): 7.55 (d, J = 24.0 Hz, 1H), 7.03-6.95 (m, 6H), 5.24 (s, 1H), 3.74 (d, J = 11.2 Hz, 6H), 2.85-2.78 (m, 1H), 1.36 (s, 18H), 1.18 (d, J = 6.8 Hz, 6H). ^{31}P NMR (161.9 MHz, $CDCl_3$): 22.11. **HRMS** for $C_{27}H_{40}O_4P^+$: calcd. $[M+H]^+$: 459.2659, found: 459.2671.

Dimethyl (E)-(2-(4-bromophenyl)-1-(3,5-di-tert-butyl-4-hydroxyphenyl)vinyl)phosphonate (4e)



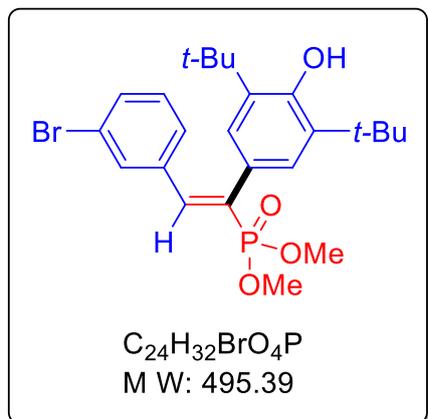
Following the general procedure, treatment of Dimethyl (2-(4-bromophenyl)-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-diazoethyl)phosphonate (157 mg, 0.30 mmol) with $Rh_2(OAc)_4$ (13 mg, 0.03 mmol) in toluene (3.0 mL) at 100 °C for 6 h followed by column chromatography afforded the product **4e** as white solid (137 mg, 92%). R_f (Ethyl acetate/Hexane: 40/60) = 0.33. **Mp** 166-168 °C. ^{13}C **NMR** (100 MHz, ppm/ $CDCl_3$): 154.1 (d, J_{C-P} = 2.4 Hz, C), 142.4 (d, J_{C-P} = 12.4 Hz, C), 136.6 (d, J_{C-P} = 1.5 Hz, C), 136.6 (d, J_{C-P} = 1.5 Hz, C), 134.1 (d, J_{C-P} = 22.9 Hz, CH), 131.8 (CH), 131.8 (CH), 131.6 (d, J_{C-P} = 177.2 Hz, C), 131.3 (CH), 131.3 (CH), 125.9 (d, J_{C-P} = 5.5 Hz, CH), 125.9 (d, J_{C-P} = 5.5 Hz, CH), 125.3 (d, J_{C-P} = 8.1 Hz, C), 123.1 (C), 52.9 (d, J_{C-P} = 6.4 Hz, CH_3), 52.9 (d, J_{C-P} = 6.4 Hz, CH_3), 34.5 (C), 34.5 (C), 30.4 (CH_3), 30.4 (CH_3). 1H **NMR** (400 MHz, ppm/ $CDCl_3$): 7.47 (d, J = 24.0 Hz, 1H), 7.27 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 2.0 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H), 5.28 (s, 1H), 3.74 (d, J = 10.8 Hz, 6H), 1.36 (s, 18H). ^{31}P **NMR** (161.9 MHz, $CDCl_3$): 21.14. **HRMS** for $C_{24}H_{33}BrO_4P^+$: calcd. $[M+H]^+$: 495.1294, found: 495.1298.

Dimethyl (E)-1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(4-(trifluoromethyl)phenyl)vinyl)phosphonate (4f)



Following the general procedure, treatment of dimethyl (2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-1-diazo-2-(4-(trifluoromethyl)phenyl)ethyl)phosphonate (154 mg, 0.30 mmol) with $Rh_2(OAc)_4$ (13 mg, 0.03 mmol) in toluene (3.0 mL) at 100 °C for 6 h followed by column chromatography afforded the product **4f** as white solid (131 mg, 90%). R_f (Ethyl acetate/Hexane: 40/60) = 0.29. **Mp** 178-180 °C. ^{13}C **NMR** (100 MHz, ppm/ $CDCl_3$): 154.1 (d, J_{C-P} = 2.3 Hz, C), 141.9 (d, J_{C-P} = 12.2 Hz, C), 139.0 (d, J_{C-P} = 22.8 Hz, CH), 136.6 (d, J_{C-P} = 1.1 Hz, C), 136.6 (d, J_{C-P} = 1.1 Hz, C), 133.6 (d, J_{C-P} = 217.5 Hz, C), 130.3 (CH), 130.3 (CH), 126.1 (CH), 126.1 (CH), 125.0 (CH), 125.0 (CH), 125.0 (C), 125.0 (C), 53.0 (d, J_{C-P} = 5.9 Hz, CH_3), 53.0 (d, J_{C-P} = 5.9 Hz, CH_3), 34.5 (C), 34.5 (C), 30.4 (CH_3), 30.4 (CH_3). 1H **NMR** (400 MHz, ppm/ $CDCl_3$): 7.57 (d, J = 24.0 Hz, 1H), 7.40 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 7.01 (d, J = 2.0 Hz, 2H), 5.29 (s, 1H), 3.76 (d, J = 11.2 Hz, 6H), 1.34 (s, 18H). ^{31}P **NMR** (161.9 MHz, $CDCl_3$): 20.57. **HRMS** for $C_{25}H_{33}F_3O_4P^+$: calcd. $[M+H]^+$: 485.2063, found: 485.2069.

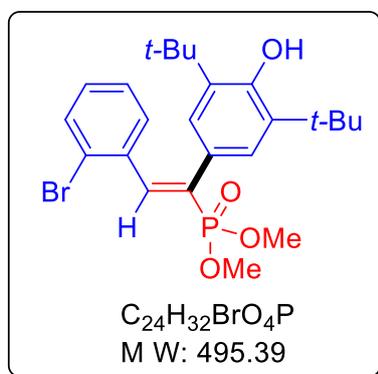
Dimethyl (E)-(2-(3-bromophenyl)-1-(3,5-di-tert-butyl-4-hydroxyphenyl)vinyl)phosphonate (4g)



Following the general procedure, treatment of dimethyl (2-(3-bromophenyl)-2-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-diazoethyl)phosphonate (157 mg, 0.30 mmol) with $Rh_2(OAc)_4$ (13 mg, 0.03 mmol) in toluene (3.0 mL) at 100 °C for 6 h followed by column chromatography afforded the product **4g** as white solid (140 mg, 94%). R_f (Ethyl acetate/Hexane: 40/60) = 0.31. **Mp** 170-172 °C. ^{13}C NMR (100 MHz, ppm/ $CDCl_3$): 154.2 (d, J_{C-P} = 2.0 Hz, C), 142.1 (d, J_{C-P} = 9.9 Hz, C), 137.3 (d, J_{C-P} = 18.3 Hz, CH), 136.8 (C), 136.8 (C), 132.8 (CH), 132.6 (d, J_{C-P} = 141. Hz, (C), 131.6

(CH), 129.7 (CH), 129.2 (CH), 125.9 (d, J_{C-P} = 4.4 Hz, CH), 125.9 (d, J_{C-P} = 4.4 Hz, CH), 125.9 (d, J_{C-P} = 6.5 Hz, C), 122.2 (C), 52.9 (d, J_{C-P} = 4.6 Hz, CH_3), 52.9 (d, J_{C-P} = 4.6 Hz, CH_3), 34.5 (C), 34.5 (C), 30.5 (CH_3), 30.4 (CH_3). 1H NMR (400 MHz, ppm/ $CDCl_3$): 7.46 (d, J = 24.0 Hz, 1H), 7.30 (d, J = 8.0 Hz, 1H), 7.07-7.01 (m, 5H), 5.30 (s, 1H), 3.73 (d, J = 11.2 Hz, 6H), 1.37 (s, 18H). ^{31}P NMR (161.9 MHz, $CDCl_3$): 20.80. **HRMS** for $C_{24}H_{33}BrO_4P^+$: calcd. $[M+H]^+$: 495.1294, found: 495.1295

Dimethyl (E)-(2-(2-bromophenyl)-1-(3,5-di-tert-butyl-4-hydroxyphenyl)vinyl)phosphonate (4h)

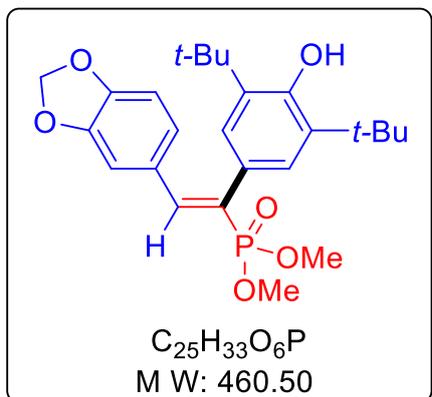


Following the general procedure, treatment of dimethyl (2-(2-bromophenyl)-2-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-diazoethyl)phosphonate (157 mg, 0.30 mmol) with $Rh_2(OAc)_4$ (13 mg, 0.03 mmol) in toluene (3.0 mL) at 100 °C for 6 h followed by column chromatography afforded the product **4h** as white solid (134 mg, 90%). R_f (Ethyl acetate/Hexane: 40/60) = 0.33. **Mp** 174-176 °C. ^{13}C NMR (100 MHz, ppm/ $CDCl_3$): 153.8 (d, J_{C-P} = 1.6 Hz, C), 142.4 (d, J_{C-P} = 10.0 Hz, C), 137.0 (d, J_{C-P} = 17.8 Hz, CH), 135.8 (C), 135.8 (C), 133.0 (d, J_{C-P} = 140.7 Hz, C),

131.1 (CH), 131.1 (CH), 129.3 (CH), 126.7 (CH), 126.7 (CH), 126.7 (CH), 124.8 (d, J_{C-P} = 140.7 Hz, C), 124.4 (C), 53.0 (d, J_{C-P} = 4.7 Hz, CH_3), 53.0 (d, J_{C-P} = 4.7 Hz, CH_3), 34.3 (C), 34.3 (C), 30.3 (CH_3), 30.3 (CH_3). 1H NMR (400 MHz, ppm/ $CDCl_3$): 7.62-7.54 (m, 2H), 7.03-6.96 (m, 4H), 6.74 (d, J = 7.6 Hz, 1H), 5.18 (s, 1H), 3.81 (d, J = 10.8 Hz, 6H), 1.28 (s, 18H). ^{31}P NMR (161.9 MHz, $CDCl_3$): 20.77. **HRMS** for $C_{24}H_{33}BrO_4P^+$: calcd. $[M+H]^+$: 495.1294, found: 495.1295.

Dimethyl
hydroxyphenyl)vinyl)phosphonate (4i)

(E)-(2-(benzo[d][1,3]dioxol-5-yl)-1-(3,5-di-tert-butyl-4-

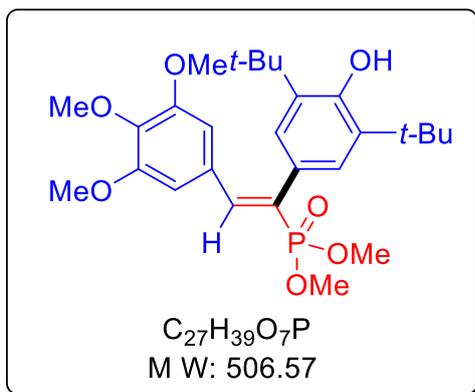


Following the general procedure, treatment of dimethyl (2-(benzo[d][1,3]dioxol-5-yl)-2-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-diazoethyl)phosphonate (146 mg, 0.30 mmol) with $Rh_2(OAc)_4$ (13 mg, 0.03 mmol) in toluene (3.0 mL) at 100 °C for 6 h followed by column chromatography afforded the product **4i** as white solid (131 mg, 95%). R_f (Ethyl acetate/Hexane: 40/60) = 0.25. **Mp** 158-160 °C. ^{13}C NMR (100 MHz, ppm/ $CDCl_3$): 153.9 (d, J_{C-P} = 2.3 Hz, C), 148.3 (C), 147.4 (C), 143.6 (d, J_{C-P} = 12.7 Hz, C), 136.6 (d, J_{C-P} = 0.9 Hz, C), 136.6 (d, J_{C-P} = 0.9 Hz, C), 129.4 (d, J_{C-P} =

23.3 Hz, CH), 128.2 (d, J_{C-P} = 178.5 Hz, C), 126.3 (CH), 126.0 (d, J_{C-P} = 10.0 Hz, CH), 126.0 (d, J_{C-P} = 10.0 Hz, CH), 125.7 (d, J_{C-P} = 8.0 Hz, C), 109.5 (CH), 108.0 (CH), 101.3 (CH₂), 52.7 (d, J_{C-P} = 5.7 Hz, CH₃), 52.7 (d, J_{C-P} = 5.7 Hz, CH₃), 34.5 (C), 34.5 (C), 30.5 (CH₃), 30.5 (CH₃), 30.5 (CH₃), 30.5 (CH₃), 30.5 (CH₃), 30.5 (CH₃). 1H NMR (400 MHz, ppm/ $CDCl_3$): 7.45 (d, J = 24.0 Hz, 1H), 7.39 (d, J = 2.0 Hz, 2H), 6.71 (d, J = 8.4 Hz, 1H), 6.58 (d, J = 8.0 Hz, 1H), 6.35 (s, 1H), 5.87 (s, 2H), 5.27 (s, 1H), 3.73 (d, J = 11.2 Hz, 6H), 1.39 (s, 18H). ^{31}P NMR (161.9 MHz, $CDCl_3$): 22.11. **HRMS** for $C_{25}H_{34}O_6P^+$: calcd. $[M+H]^+$: 461.2088, found: 461.2085

Dimethyl
trimethoxyphenyl)vinyl)phosphonate (4j)

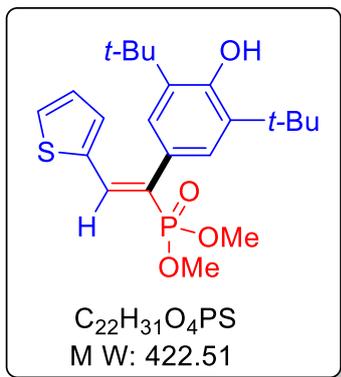
(E)-(1-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(3,4,5-



Following the general procedure, treatment of dimethyl (2-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-diazo-2-(3,4,5-trimethoxyphenyl)ethyl)phosphonate (160 mg, 0.30 mmol) with $Rh_2(OAc)_4$ (13 mg, 0.03 mmol) in toluene (3.0 mL) at 100 °C for 6 h followed by column chromatography afforded the product **4j** as white solid (144 mg, 95%). R_f (Ethyl acetate/Hexane: 40/60) = 0.27. **Mp** 164-166 °C. ^{13}C NMR (100 MHz, ppm/ $CDCl_3$): 153.7 (d, J_{C-P} = 2.5 Hz, C), 152.6 (C), 152.6 (C), 144.2 (d, J_{C-P} = 12.7 Hz, C), 138.7 (C), 136.9 (d, J_{C-P} =

1.5 Hz, C), 136.9 (d, J_{C-P} = 1.5 Hz, C), 130.3 (d, J_{C-P} = 23.2 Hz, CH), 129.7 (d, J_{C-P} = 177.0 Hz, C), 126.3 (d, J_{C-P} = 7.8 Hz, C), 125.9 (d, J_{C-P} = 5.2 Hz, CH), 125.9 (d, J_{C-P} = 5.2 Hz, CH), 107.7 (CH), 107.7 (CH), 60.9 (CH₃), 55.6 (CH₃), 55.6 (CH₃), 52.8 (d, J_{C-P} = 5.1 Hz, CH₃), 52.8 (d, J_{C-P} = 5.1 Hz, CH₃), 34.4 (C), 34.4 (C), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃), 30.4 (CH₃). 1H NMR (400 MHz, ppm/ $CDCl_3$): 7.48 (d, J = 24.0 Hz, 1H), 7.02 (d, J = 1.6 Hz, 2H), 6.27 (s, 2H), 5.26 (s, 1H), 3.77 (d, J = 8.0 Hz, 6H), 3.74 (s, 3H), 3.54 (s, 6H), 1.36 (s, 18H). ^{31}P NMR (161.9 MHz, $CDCl_3$): 21.46. **HRMS** for $C_{27}H_{40}O_7P^+$: calcd. $[M+H]^+$: 507.2506, found: 507.2508.

Dimethyl (E)-1-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(thiophen-2-yl)vinylphosphonate (4k)



Following the general procedure, treatment of dimethyl (2-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-diazo-2-(thiophen-2-yl)ethyl)phosphonate (135 mg, 0.30 mmol) with $Rh_2(OAc)_4$ (13 mg, 0.03 mmol) in toluene (3.0 mL) at 100 °C for 6 h followed by column chromatography afforded the product **4k** as white solid (118 mg, 93%). R_f (Ethyl acetate/Hexane: 40/60) = 0.29. **Mp** 168-170 °C. ^{13}C NMR (100 MHz, ppm/ $CDCl_3$): 154.5 (d, J_{C-P} = 2.7 Hz, C), 138.8 (d, J_{C-P} = 24.8 Hz, CH), 138.8(d, J_{C-P} = 15.1 Hz, C), 137.0 (d, J_{C-P} = 1.2 Hz, C), 137.0 (d, J_{C-P} = 1.2 Hz, C), 133.0 (CH), 130.2 (CH), 126.9 (d, J_{C-P} = 182.6 Hz, C), 126.3 (d, J_{C-P} = 4.8 Hz, CH), 126.3 (d, J_{C-P} = 4.8 Hz, CH), 124.9 (d, J_{C-P} = 7.5 Hz, C), 124.9 (d, J_{C-P} = 7.5 Hz, C), 52.7 (d, J_{C-P} = 5.6 Hz, CH_3), 52.7 (d, J_{C-P} = 5.6 Hz, CH_3), 34.6 (C), 34.6 (C), 30.5 (CH_3), 30.5 (CH_3). 1H NMR (400 MHz, ppm/ $CDCl_3$): 7.79 (d, J = 22.8 Hz, 1H), 7.19 (d, J = 5.2 Hz, 1H), 7.15 (d, J = 3.6 Hz, 1H), 7.01 (d, J = 2.0 Hz, 2H), 6.93-6.90 (m, 1H), 5.31 (s, 1H), 3.74 (d, J = 10.8 Hz, 6H), 1.43 (s, 18H). ^{31}P NMR (161.9 MHz, $CDCl_3$): 21.56. **HRMS** for $C_{22}H_{32}O_4PS^+$: calcd. $[M+H]^+$: 423.1753, found: 423.1754.

