Supporting Information for:

Nucleophile-Controlled Mono- and Diphosphonation of Amino-2-en-1-ones via Catalyst-Free C(sp³)-N Bond Cleavage

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CONTENTS

- 1 General experimental details and materials
- 2 General Procedure
- 3 Experimental characterization data for products
- 4 Copies of product ¹H NMR, ¹³C NMR and ³¹P NMR

1. General experiment detail and materials

Experimental: All non-aqueous reactions and manipulations were performed in air atmosphere using standard techniques. All solvents before use were dried and degassed by standard methods and stored under nitrogen. All reactions were monitored by TLC with silica gel-coated plates.

NMR spectra were recorded on Agilent Technologies 400 and AVANCE III 600 MHz spectrometers. Chemical shifts are reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard. Coupling constants (*J*) are reported in Hz and refer to apparent peak multiplications. High resolution mass spectra (HRMS) were recorded on Bruker Daltonics APEX II 47e Specification (ESI).

2. General Procedure



2-((diethylamino)methyl)-1-phenylprop-2-en-1-one (1a): Ketone 1(1 mmol) was mixed with silica gel (2.0 g) in a mortar. Then formaldehyde (0.18 g, 3 mmol, 37% in H₂O), and dialkylamine (2 mmol) were added and mixed. The mixture was placed into a flask with a cap, and stirred for 5–7 hours at room temperature. Then ether (20 ml) was added. After filtration and the removal of the solvent at the reduced pressure, the product was isolated. Further purification of the crude reaction mixture on silica gel column gave the pure product.



General procedure for 3a: To a 50 mL Schlenk tube with a stir bar added allylamine derivatives **1a** (65.1 mg, 0.3 mmol), diethyl phosphite (82.8 mg, 2 eq.) and DCE (2 mL), the mixture was stirred at 80 °C for 8h, and monitored by TLC. The solution was then evaporated under vacuum. The crude reaction mixture was purified by column chromatography on silica gel (petroleum ester/ethyl acetate = 20:1-2.5:1) to get product **3a** with 77.8 mg.



General procedure for 5: To a 50 mL Schlenk tube with a stir bar added allylamine derivatives **1** (81.9 mg, 0.3 mmol), diphenylphosphine oxygen (151.5 mg, 2.5 eq.) and DCE (2 mL), the mixture was stirred at 100 $^{\circ}$ C for 5h, and monitored by TLC. The solution was then evaporated under vacuum. The crude reaction mixture was purified by column chromatography on silica gel (petroleum ester/ethyl acetate = 20:1-pure EA) to get product **5** with 161 mg.



General procedure for 6: To a 50 mL Schlenk tube with a stir bar added allylamine derivatives **1e** (81.9 mg, 0.3 mmol), diethyl phosphite (82.8 mg, 2 eq.) and DCE (2 mL), the mixture was stirred at 100 °C for 8h. Then, diphenylphosphine oxygen (90.9 mg, 1.5 eq.) were added. the mixture was stirred at 100 °C for 5 h, and monitored by TLC. The solution was then evaporated under vacuum. The crude reaction mixture was purified by column chromatography on silica gel (petroleum ester/ethyl acetate = 20:1-pure EA) to get product **6ea** with 111.8 mg.



General Procedure for 1ab:

Step1: To the mixture of the corresponding aryl iodide (2 mmol), PdCl₂(PPh₃) (0.28 g, 0.4 mmol) and triethylamine (6 mmol) in tetrahydrofuran (5 mL) the corresponding prop-2-ynyl acetate (2.1 mmol) was added under argon atmosphere. After stirring of resulting mixture for 5 min at room temperature, copper (I) iodide (38 mg, 0.2 mmol) was added. The mixture was stirred under argon at room temperature for 1–4 h. When the completion of the reaction was observed by TLC, solvent was evaporated under reduced pressure, and crude residue was purified by Flash Column chromatography

eluting with hexane -ethyl acetate mixtures.

Step2: To the solution of the corresponding 3-arylprop-2-inylcarboxylate **9** (1 mmol) and aldehyde (1 mmol) in dry dichloromethane (5 mL) boron trifluoride etherate (0.142 g, 0.13 mL, 1 mmol) was added. The resulting solution was stirred at room temperature. When the completion of the reaction was observed by TLC, the solution was quenched with aqueous sodium bicarbonate. The organic layer was separated, washed with water (2*20 mL), dried over anhydrous Na₂SO₄. After the evaporation of solvent under reduced pressure, the residue was purified by Flash Column chromatography eluting with hexane – ethyl acetate mixtures.

Step3: The 1ab was synthesized by stirring a solution of the **1ab** adduct **11** (0.14 mmol) and appropriate amine (0.168 mmol) in dimethylformamide (2 mL) was stirred at room temperature till the reaction was completed (monitored by TLC). The mixture was then quenched with ethyl acetate (10 mL), and the organic solution was washed with water (2 x 20 mL) and dried over anhydrous Na₂SO₄. After evaporation of the solvent under reduced pressure, the residue was purified by Flash Column chromatography eluting with hexane – ethyl acetate mixtures.





3. Experimental characterization data for product

1. Diethyl (2-benzoylallyl)phosphonate (3a)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 92% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 6.8 Hz, 1H), 7.40 (t, *J* = 7.1 Hz, 2H), 6.08 (d, *J* = 3.8 Hz, 1H), 5.74 (d, *J* = 3.7 Hz, 1H), 4.10 – 3.97 (m, 4H), 3.08 (d, *J* = 21.5 Hz, 2H), 1.20 (t, *J* =

6.3 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 196.33, 138.99, 138.89, 137.05, 132.29, 129.59, 129.29, 129.19, 128.13, 61.95, 29.75, 28.37, 16.18. ³¹P NMR (162 MHz, CDCl₃) δ 25.92. HRMS (m/z): calcd for C₁₄H₂₀O₄P [M+H]⁺: 283.1094, found: 283.1094.

2. Diethyl (2-(4-methylbenzoyl)allyl)phosphonate (3b)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 90% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, *J* = 7.8 Hz, 2H), 7.20 (d, *J* = 7.5 Hz, 2H), 6.04 (d, *J* = 4.3 Hz, 1H), 5.72 (d, *J* = 4.7 Hz, 1H), 4.10 – 3.96 (m, 4H), 3.08 (d, *J* = 21.5 Hz, 2H), 2.37 (s, 3H), 1.20 (t, *J* = 6.9 Hz,

6H); ¹³C NMR (101 MHz, CDCl₃) δ 196.15, 143.19, 138.93, 138.83, 134.27, 129.88, 128.87, 128.72, 128.62, 62.02, 61.96, 29.89, 28.51, 21.58, 16.28, 16.22; ³¹P NMR (243 MHz, CDCl₃) δ 26.56. HRMS (m/z): calcd for C₁₅H₂₂O₄P [M+H]⁺: 297.1250, found: 297.1255.

3. Diethyl (2-(2,4-dimethylbenzoyl)allyl)phosphonate (3c)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 88% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.22 (d, J = 7.6 Hz, 1H), 7.08 – 6.96 (m, 2H),

6.18 (d, J = 4.5 Hz, 1H), 5.77 (d, J = 4.9 Hz, 1H), 4.12 (dd, J = 14.5, 7.3 Hz, 4H), 3.10 (d, J = 21.8 Hz, 2H), 2.34 (s, 3H), 2.30 (s, 3H), 1.29 (t, J = 7.0 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 198.19, 140.46, 140.38, 140.28, 136.97, 134.89, 132.01, 131.92, 131.70, 128.96, 62.07, 62.01, 27.92, 26.54, 21.31, 19.72, 16.37, 16.31; ³¹P NMR (243 MHz, CDCl₃) δ 26.80. HRMS (m/z): calcd for C₁₆H₂₄O₄P [M+H]⁺: 311.1407, found: 311.1412.

4. Diethyl (2-(3-methoxybenzoyl)allyl)phosphonate (3d)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 76% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.25 (m, 3H), 7.13 – 7.06 (m, 1H), 6.12 (d, J = 4.2 Hz, 1H), 5.81 (d, J = 4.8 Hz, 1H), 4.16 – 4.01 (m, 4H), 3.85 (s, 3H), 3.13 (d, J = 21.5 Hz, 2H), 1.25 (t, J = 7.0

Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 194.63, 151.52, 147.80, 138.94, 138.84, 131.25, 127.60, 127.50, 126.31, 109.58, 107.63, 101.76, 62.03, 61.97, 30.38, 29.00, 16.26, 16.20.³¹P NMR (243 MHz, CDCl₃) δ 26.59. HRMS (m/z): calcd for $C_{15}H_{22}O_5P$ [M+H]⁺: 313.1199, found: 313.1203.

5. Diethyl (2-(4-methoxybenzoyl)allyl)phosphonate (3e)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 55% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 4.1 Hz, 2H), 7.01 – 6.83 (m, 2H), 6.00 (s, 1H), 5.70 (t, *J* = 4.3 Hz, 1H), 4.05 (td, *J* = 7.0, 4.6 Hz, 4H), 3.86 (d, *J* = 4.5 Hz, 3H), 3.10 (dd, *J* = 21.4, 3.5 Hz, 2H),

1.21 (dd, J = 11.3, 6.8 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 195.22, 163.21, 138.92, 138.82, 132.17, 129.48, 127.60, 127.50, 113.45, 62.02, 61.95, 55.44, 30.28, 28.90, 16.27, 16.21. ³¹P NMR (243 MHz, CDCl₃) δ 26.58. HRMS (m/z): calcd for C₁₅H₂₂O₅P [M+H]⁺: 313.1199, found: 313.1200.

6. Diethyl (2-(benzo[d][1,3]dioxole-5-carbonyl)allyl)phosphonate (3f)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 70% yield.¹H NMR (400 MHz, CDCl₃) δ 7.44 – 7.36 (m, 1H), 7.30 (d, *J* = 1.5 Hz, 1H), 6.82 (dd, *J* = 8.1, 3.4 Hz, 1H), 6.03 (d, *J* = 3.6 Hz, 2H), 5.98 (d, *J* = 0.7 Hz, 1H), 5.69 (d, *J* = 4.3 Hz, 1H), 4.09 – 3.99 (m, 4H),

3.08 (d, J = 21.4 Hz, 2H), 1.21 (td, J = 6.9, 3.3 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 194.67, 151.52, 147.80, 138.94, 138.84, 131.25, 127.60, 127.50, 126.31, 109.58, 107.63, 101.76, 62.03, 61.97, 30.38, 29.00, 16.26, 16.20. ³¹P NMR (243 MHz, CDCl₃) δ 26.43. HRMS (m/z): calcd for C₁₅H₂₀O₆P [M+H]⁺: 327.0992, found: 327.0992.

7. Diethyl (2-(1-naphthoyl)allyl)phosphonate (3g)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 66% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.11 – 8.05 (m, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 9.0 Hz, 1H), 7.59 (d, *J* = 7.0 Hz, 1H), 7.55 – 7.44 (m, 3H), 6.24 (d, *J* = 4.5 Hz, 1H), 5.83 (d, *J* = 4.9 Hz,

1H), 4.24 – 4.05 (m, 4H), 3.22 (d, J = 21.8 Hz, 2H), 1.32 (t, J = 6.9 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 197.75, 197.71, 140.88, 140.78, 135.67, 133.58, 132.90, 132.80, 131.12, 130.85, 128.32, 127.50, 127.19, 126.42, 125.39, 124.22, 62.19, 62.13, 28.14, 26.77, 16.42, 16.36; ³¹P NMR (243 MHz, CDCl₃) δ 26.72. HRMS (m/z): calcd for C₁₈H₂₂O₄P [M+H]⁺: 333.1250, found: 333.1253.

8. Diethyl (2-(2-naphthoyl)allyl)phosphonate (3h)



The title compound was prepared according to the general procedure and purified by column chromatography to give a yellow oil, 77% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.31 (s, 1H), 7.91 (dt, J = 14.4, 8.1 Hz, 4H), 7.59 (dd, J = 17.8, 8.3 Hz, 2H), 6.17 (d, J = 3.8 Hz, 1H), 5.85 (d, J = 4.7 Hz, 1H), 4.18 – 4.02 (m, 4H), 3.19 (d,

J = 21.5 Hz, 2H), 1.25 (t, J = 7.0 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 196.42, 138.97, 135.25, 134.25, 132.18, 131.37, 129.37, 129.34, 129.24, 128.26, 128.21, 127.76, 126.77, 125.47, 62.11, 62.04, 29.98, 28.61, 16.33, 16.27. ³¹P NMR (243 MHz, CDCl₃) δ 26.61. HRMS (m/z): calcd for C₁₈H₂₂O₄P [M+H]⁺: 333.1250, found: 333.1254.

9. Diethyl (2-(4-nitrobenzoyl)allyl)phosphonate (3i)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 53% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.30 (d, *J* = 8.8 Hz, 2H), 7.90 (d, *J* = 8.8 Hz, 2H), 6.21 (d, *J* = 5.1 Hz, 1H), 5.75 (d, *J* = 5.0 Hz, 1H), 4.15 - 4.04 (m, 4H), 3.13 (d, *J* = 21.6 Hz, 2H), 1.27 (t, *J* = 7.1 Hz,

6H); ¹³C NMR (101 MHz, CDCl₃) δ 194.63, 149.84, 142.44, 139.07, 138.98, 130.65, 130.55, 130.38, 123.46, 62.21, 62.14, 29.64, 28.26, 16.35, 16.29. ³¹P NMR (162 MHz, D₂O) δ 26.06. HRMS (m/z): calcd for C₁₄H₁₉NO₆P [M+H]⁺: 328.0945, found: 328.0945.

10. Diethyl (2-(4-fluorobenzoyl)allyl)phosphonate (3j)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 85% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.92 – 7.77 (m, 2H), 7.13 (t, *J* = 8.5 Hz, 2H), 6.09 (d, *J* = 4.8 Hz, 1H), 5.74 (d, *J* = 4.9 Hz, 1H), 4.17 – 4.00 (m, 4H), 3.13 (d, *J* = 21.5 Hz, 2H), 1.25 (t, *J* = 7.0 Hz, 6H).¹³C NMR (101

MHz, CDCl₃) δ 194.92, 166.64, 164.11, 138.89, 138.80, 133.20, 133.17, 132.31, 132.22, 128.75, 128.65, 115.47, 115.25, 62.17, 62.11, 30.03, 28.65, 16.24, 16.18; ³¹P NMR (243 MHz, CDCl₃) δ 26.45. HRMS (m/z): calcd for C₁₄H₁₉FO₄P [M+H]⁺: 301.1000, found: 301.1003.

11. Diethyl (2-(4-bromobenzoyl)allyl)phosphonate (3k)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 82% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 6.10 (d, *J* = 4.5 Hz, 1H), 5.73 (d, *J* = 4.9 Hz, 1H), 4.15 – 3.97 (m, 4H), 3.10 (d, *J* = 21.5 Hz, 2H), 1.23 (t, *J* = 7.0 Hz, 6H); ¹³C NMR

(101 MHz, CDCl₃) δ 195.39, 138.85, 138.75, 135.74, 131.54, 131.21, 129.28, 129.18, 127.49, 62.11, 62.05, 29.89, 28.52, 16.32, 16.26; ³¹P NMR (243 MHz, CDCl₃) δ 26.27. HRMS (m/z): calcd for C₁₄H₁₉BrO₄P [M+H]⁺: 361.0199, found: 361.0201.

12. Diethyl (2-(3,4-dichlorobenzoyl)allyl)phosphonate (3l)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 72% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, *J* = 1.8 Hz, 1H), 7.61 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.52 (d, *J* = 8.3 Hz, 1H), 6.11 (d, *J* = 5.1 Hz, 1H), 5.74 (d, *J* = 5.0 Hz, 1H), 4.12 - 4.02 (m, 4H), 3.09 (d, *J* = 21.5 Hz, 2H),

1.25 (t, J = 7.1 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 193.96, 138.69, 137.02, 136.67, 132.91, 131.49, 130.38, 129.38, 129.28, 128.69, 62.15, 62.08, 29.99, 28.61, 16.30, 16.24; ³¹P NMR (243 MHz, CDCl₃) δ 193.96, 138.69, 137.02, 136.67, 132.91, 131.49, 130.38, 129.38, 129.28, 128.69, 62.15, 62.08, 29.99, 28.61, 16.30, 16.24; ³¹P NMR (243 MHz, CDCl₃) δ 193.96, 138.69, 137.02, 136.67, 132.91, 131.49, 130.38, 129.38, 129.28, 128.69, 62.15, 62.08, 29.99, 28.61, 16.30, 16.24; ³¹P NMR (243 MHz, CDCl₃) δ 193.96, 138.69, 137.02, 136.67, 132.91, 131.49, 130.38, 129.38, 129.28, 128.69, 62.15, 62.08, 29.99, 28.61, 16.30, 16.24; ³¹P NMR (243 MHz, CDCl₃) δ 193.96, 140.24; δ 140.24; δ

CDCl₃) δ 26.05. HRMS (m/z): calcd for C₁₄H₁₈Cl₂O₄P [M+H]⁺: 351.0314, found: 351.0316.

13. Diethyl (2-(2-bromobenzoyl)allyl)phosphonate (3m)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 74% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.59 (d, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.32 – 7.24 (m, 2H), 6.34 (d, *J* = 4.9 Hz, 1H), 5.82 (d, *J* = 5.1 Hz, 1H), 4.12 (p, *J* = 7.3 Hz, 4H), 3.09 (d, *J* = 21.8 Hz, 2H), 1.31 (t, *J* =

7.1 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 139.89, 139.10, 134.05, 133.96, 133.18, 131.03, 128.92, 126.86, 119.48, 62.17, 62.10, 27.12, 25.73, 16.38, 16.32; ³¹P NMR (162 MHz, D₂O) δ 26.58. HRMS (m/z): calcd for C₁₄H₁₉BrO₄P [M+H]⁺: 361.0199, found: 361.0199.

14. Diethyl (2-(3-bromobenzoyl)allyl)phosphonate (3n)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 80% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.88 (s, 1H), 7.74 – 7.59 (m, 2H), 7.37 – 7.23 (m, 1H), 6.13 (d, *J* = 4.7 Hz, 1H), 5.76 (d, *J* = 4.9 Hz, 1H), 4.18 – 3.96 (m, 4H), 3.09 (d, *J* = 21.2 Hz, 2H), 1.31 – 1.20 (m, 6H); ¹³C NMR

(101 MHz, CDCl₃) δ 138.93, 135.26, 132.43, 129.81, 128.18, 122.45, 109.99, 62.07, 29.76, 28.38, 16.32, 16.26.³¹P NMR (243 MHz, CDCl₃) δ 26.28. HRMS (m/z): calcd for C₁₄H₁₉BrO₄P [M+H]⁺: 361.0199, found: 361.0200.

15. Diethyl (2-(thiophene-2-carbonyl)allyl)phosphonate (30)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 91% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.68 (dd, *J* = 11.3, 3.6 Hz, 2H), 7.14 – 7.07 (m, 1H), 5.99 (t, *J* = 6.0 Hz, 2H), 4.04 (dq, *J* = 14.2, 7.1 Hz, 4H), 3.07 (d, *J* = 21.4 Hz, 2H), 1.20 (t, *J* = 7.0 Hz, 6H); ¹³C NMR (101 MHz,

CDCl₃) δ 188.01, 142.88, 139.42, 139.33, 134.56, 134.37, 128.02, 126.97, 126.87, 62.27, 62.21, 30.55, 29.17, 18.59, 16.40, 16.34; ³¹P NMR (162 MHz, D₂O) δ 26.18. HRMS (m/z): calcd for C₁₂H₁₈O₄PS [M+H]⁺: 289.0658, found: 289.0659.

16. Diethyl (2-(pyridine-2-carbonyl)allyl)phosphonate (3p)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 91% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.67 (s, 1H), 7.84 (s, 2H), 7.44 (s, 1H), 6.31 (d, *J* = 16.3 Hz, 2H), 4.08 (p, *J* = 7.1 Hz, 4H), 3.16 (d, *J* = 21.7 Hz, 2H),

1.25 (t, J = 7.0 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 129.58 (s), 127.07 (d, J = 7.6 Hz), 126.40 (s), 124.16 (s), 122.60 (s), 120.19 (s), 119.29 (s), 110.54 (s), 62.13 (s), 23.68 (s), 22.25 (s), 16.43 (s). HRMS (m/z): calcd for C₁₃H₁₈NO₄P [M+H]⁺:284.1046, found: 284.1044.

17. Diethyl (2-(4-morpholinobenzoyl)allyl)phosphonate (3q)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 68% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.97 (d, *J* = 4.4 Hz, 1H), 5.68 (d, *J* = 4.8 Hz, 1H), 4.05 (dt, *J* = 14.1, 6.9 Hz, 4H), 3.85 (s, 4H), 3.30 (s, 4H), 3.10 (d, *J* =

21.3 Hz, 2H), 1.21 (t, *J* = 7.0 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 194.92, 154.08, 138.78, 132.08, 127.14, 126.85, 126.75, 113.10, 66.56, 62.01, 61.95, 47.51, 30.39, 29.02, 16.29, 16.23; ³¹P NMR (243

MHz, CDCl₃) δ 26.72. HRMS (m/z): calcd for C₁₈H₂₇NO₅P [M+H]⁺: 368.1621, found: 368.1623.

18. Diethyl (2-([1,1'-biphenyl]-4-carbonyl)allyl)phosphonate (3i)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 90% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, *J* = 8.2 Hz, 2H), 7.63 (dd, *J* = 17.1, 7.8 Hz, 4H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 1H),

6.11 (d, J = 5.0 Hz, 1H), 5.81 (d, J = 5.0 Hz, 1H), 4.08 (p, J = 7.2 Hz, 4H), 3.13 (d, J = 21.5 Hz, 2H), 1.24 (t, J = 7.0 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 196.04, 145.21, 139.87, 138.95, 138.85, 135.66, 130.35, 129.18, 129.08, 128.93, 128.16, 127.23, 126.88, 62.13, 62.06, 29.89, 28.51, 16.34, 16.28; ³¹P NMR (243 MHz, CDCl₃) δ 26.51. HRMS (m/z): calcd for C₂₀H₂₄O₄P [M+H]⁺: 359.1407, found: 359.1410.

19. Dimethyl (2-benzoylallyl)phosphonate (3s)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 77% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, *J* = 7.9 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 6.14 (d, *J* = 4.5 Hz, 1H), 5.81 (d, *J* = 4.6 Hz, 1H), 3.72 (d, *J* = 10.2 Hz, 6H), 3.15 (d, *J* = 21.6 Hz, 2H); ¹³C

NMR (101 MHz, CDCl₃) δ 138.50, 137.01, 132.43, 130.04, 129.94, 129.61, 128.26, 52.75, 52.68, 28.78, 27.40. ³¹P NMR (162 MHz, CDCl₃) δ 28.75. HRMS (m/z): calcd for C₁₂H₁₆O₄P [M+H]⁺: 255.0781, found: 255.0782.

20. Diisopropyl (2-benzoylallyl)phosphonate (3t)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 62% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.72 (d, *J* = 7.3 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 6.04 (d, *J* = 5.1 Hz, 1H), 5.69 (d, *J* = 5.1 Hz, 1H), 4.62 (dq, *J* = 12.5, 6.2 Hz, 2H), 3.02 (d, *J* = 21.6 Hz, 2H),

1.19 (dd, J = 9.3, 6.2 Hz, 12H); ¹³C NMR (101 MHz, CDCl₃) δ 196.52, 139.33, 139.23, 137.13, 132.37, 129.78, 128.16, 70.72, 70.65, 31.07, 29.67, 23.92; ³¹P NMR (162 MHz, CDCl₃) δ 23.93. HRMS (m/z): calcd for C₁₆H₂₄O₄P [M+H]⁺: 311.1407, found: 311.1408.

21. Diisobutyl (2-benzoylallyl)phosphonate (3u)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 86% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.79 – 7.72 (m, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 6.12 (d, *J* = 5.0 Hz, 1H), 5.79 (d, *J* = 5.1 Hz, 1H), 3.77 (t, *J* = 6.5 Hz, 4H), 3.13 (d, *J* = 21.6 Hz, 2H), 1.83 (dt, *J* = 13.3, 6.6

Hz, 3H), 0.86 (d, J = 6.7 Hz, 12H); ¹³C NMR (101 MHz, CDCl₃) δ 196.48, 139.33, 139.23, 137.13, 132.37, 129.78, 128.95, 128.16, 70.72, 70.65, 31.07, 29.67, 23.97; ³¹P NMR (162 MHz, CDCl₃) δ 25.80. HRMS (m/z): calcd for C₁₈H₂₈O₄P [M+H]⁺: 339.1720, found: 339.1721.

22. Dibutyl (2-benzoylallyl)phosphonate (3v)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 75% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, *J* = 7.9 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.3 Hz, 2H), 6.10 (d, *J* = 4.7 Hz, 1H), 5.77 (d, *J* = 4.8 Hz, 1H), 3.99 (dd, *J* = 13.1, 6.5 Hz, 4H), 3.12 (d, *J* = 21.5 Hz, 2H), 1.58

-1.49 (m, 4H), 1.29 (dt, *J* = 14.4, 7.3 Hz, 4H), 0.84 (t, *J* = 7.3 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 138.85, 137.01, 132.40, 129.71, 129.38, 129.28, 128.17, 65.69, 32.37, 29.66, 28.28, 18.64, 13.54; ³¹P NMR (162 MHz, CDCl₃) δ 26.03. HRMS (m/z): calcd for C₁₈H₂₈O₄P [M+H]⁺: 339.1720, found: 339.1723.

23. Ethyl (2-benzoylallyl)(phenyl)phosphinate (3w)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 70% yield. ¹H NMR (400 MHz, CDCl3) δ 7.86 – 7.73 (m, 2H), 7.61 (d, J = 7.3 Hz, 2H), 7.50 (t, J = 7.3 Hz, 2H), 7.44 (dd, J = 7.4, 3.0 Hz, 2H), 7.37 (t, J = 7.6 Hz,

2H), 6.09 (d, J = 4.7 Hz, 1H), 5.75 (d, J = 4.9 Hz, 1H), 4.04 (dt, J = 9.8, 7.2 Hz, 1H), 3.91 – 3.77 (m, 1H), 3.38 - 3.20 (m, 2H), 1.18 (t, J = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl3) δ 196.29, 196.26, 196.20, 138.40, 138.32, 136.89, 132.44, 132.41, 132.18, 131.95, 131.85, 130.25, 130.16, 129.56, 128.59, 128.47, 128.05, 77.32, 77.00, 76.69, 61.00, 60.93, 33.42, 32.45, 16.32, 16.26; ³¹P NMR (243 MHz, Acetone) δ 39.06. HRMS (m/z): calcd for C₁₈H₂₀O₃P [M+H]⁺: 315.1145, found: 315.1149.

24. **3-(Diphenylphosphoryl)-2-((diphenylphosphoryl)methyl)-1-phenylpropan-1**one (5a)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 98% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.73 (dd, *J* = 11.0, 7.6 Hz, 4H), 7.61 – 7.49 (m, 6H), 7.45 (dt, *J* = 14.2, 7.1 Hz, 7H), 7.35 (dd, *J* = 11.6, 7.1 Hz, 6H), 7.21 (t, *J* = 7.7 Hz, 2H), 4.00 (ddd, *J* = 17.8, 11.5, 6.4 Hz, 1H), 3.08 – 2.92 (m, 2H),

2.83 – 2.65 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 199.34, 199.27, 199.20, 134.76, 133.16, 133.10, 132.58, 132.11, 131.92, 131.90, 131.82, 131.80, 131.59, 130.96, 130.91, 130.86, 130.82, 128.77, 128.65, 128.63, 128.52, 128.45, 77.35, 77.03, 76.71, 33.74, 33.71, 33.68, 32.56, 32.49, 31.87, 31.79; ³¹P NMR (243 MHz, Acetone) δ 28.23. HRMS (m/z): calcd for C₃₄H₃₁O₃P₂ [M+H]⁺: 549.1743, found: 549.1742.

25. 3-(Diphenylphosphoryl)-2-((diphenylphosphoryl)methyl)-1-(p-tolyl)propan-1 one (5b)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 97% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.73 (dd, *J* = 10.9, 7.8 Hz, 4H), 7.56 (dd, *J* = 11.1, 7.9 Hz, 4H), 7.50 (d, *J* = 6.8 Hz, 2H), 7.45 (d, *J* = 7.1 Hz, 6H), 7.34 (dd, *J* = 7.2, 5.2 Hz, 4H), 7.30 – 7.21 (m, 2H), 7.00 (d, *J*

= 7.9 Hz, 2H), 3.97 (ddd, J = 17.6, 11.5, 6.5 Hz, 1H), 3.06 – 2.91 (m, 2H), 2.82 – 2.66 (m, 2H), 2.32 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 198.88, 198.81, 198.73, 144.02, 133.23, 132.71, 132.25, 131.86, 131.84, 131.77, 131.74, 130.96, 130.92, 130.87, 130.82, 129.15, 77.35, 77.03, 76.71, 33.61, 33.59, 33.57, 32.60, 32.53, 31.91, 31.83, 21.57; ³¹P NMR (162 MHz, DMSO) δ 33.64. HRMS (m/z): calcd for C₃₅H₃₃O₃P₂ [M+H]⁺: 563.1899, found: 563.1899.

26. 3-(Diphenylphosphoryl)-2-((diphenylphosphoryl)methyl)-1-(4-methoxyphenyl)propan-1-o-ne (5c)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 98% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.70 (dd, *J* = 10.3, 8.3 Hz, 4H), 7.54 (dd, *J* = 10.6, 8.2 Hz, 4H), 7.50 – 7.36 (m, 8H), 7.32 (d, *J* = 8.7 Hz, 6H), 6.64 (d, J = 8.7 Hz, 2H), 4.01 – 3.88 (m, 1H), 3.75 (s, 3H), 3.04 – 2.89 (m, 2H), 2.80 – 2.64 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 197.87, 197.80, 197.76, 163.60, 133.13, 132.57, 131.88, 131.86, 131.77, 131.75, 130.96, 130.86, 130.84, 130.80, 128.74, 128.63, 128.58, 128.46, 127.79, 113.63, 77.37, 77.05, 76.73, 55.42, 33.29, 32.78, 32.70, 32.08, 32.01; ³¹P NMR (162 MHz, DMSO) δ 35.25. HRMS (m/z): calcd for C₃₅H₃₃O₄P₂ [M+H]⁺: 579.1849, found: 579.184

27. 3-(Diphenylphosphoryl)-2-((diphenylphosphoryl)methyl)-1-(4-ethoxyphenyl) propan-1-one (5d)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 89% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.72 (dd, *J* = 10.4, 8.1 Hz, 4H), 7.56 (dd, *J* = 10.6, 8.2 Hz, 4H), 7.49 (d, *J* = 6.4 Hz, 2H), 7.43 (t, *J* = 5.8 Hz, 6H), 7.32 (d, *J* = 8.5 Hz, 6H), 6.65 (d, *J* = 8.7 Hz, 2H), 4.01 (dd,

J = 13.9, 6.9 Hz, 2H), 3.99 - 3.90 (m, 1H), 3.03 - 2.89 (m, 2H), 2.81 - 2.62 (m, 2H), 1.38 (t, J = 6.9 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 197.81, 197.74, 197.67, 163.00, 133.27, 132.74, 132.28, 131.84, 131.81, 131.73, 131.70, 130.95, 130.89, 130.85, 130.83, 130.79, 114.06, 77.43, 77.11, 76.79, 63.68, 33.31, 33.29, 33.27, 32.78, 32.70, 32.08, 32.00, 14.61; ³¹P NMR (162 MHz, DMSO) δ 30.12. HRMS (m/z): calcd for C₃₆H₃₅O₄P₂ [M+H]⁺: 593.2005, found: 593.2002.

28. 1-(3,4-Dichlorophenyl)-3-(diphenylphosphoryl)-2-((diphenylphosphoryl)methyl)propan-1-on-e (5e)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 86% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.72 (dd, *J* = 10.5, 8.2 Hz, 4H), 7.60 – 7.50 (m, 6H), 7.47 (s, 6H), 7.40 – 7.23 (m, 7H), 3.97 – 3.78 (m, 1H), 3.08 – 2.92 (m, 2H), 2.81 – 2.62 (m, 2H). ¹³C NMR (101 MHz,

CDCl₃) δ 197.72, 137.74, 134.75, 133.04, 132.04, 132.02, 131.99, 131.96, 130.86, 130.82, 130.76, 130.72, 130.52, 130.29, 128.85, 128.73, 128.61, 127.60, 77.32, 77.00, 76.69, 33.87, 33.04, 32.97, 32.35, 32.27; ³¹P NMR (162 MHz, DMSO) δ 29.78. HRMS (m/z): calcd for C₃₄H₂₉Cl₂O₃P₂ [M+H]⁺: 617.0963, found: 617.0959.

29. 3-(Diphenylphosphoryl)-**2-**((diphenylphosphoryl)methyl)-**1-**(**4-**fluorophenyl)-propan-**1**-one (5f)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 97% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.72 (dd, *J* = 10.6, 8.0 Hz, 4H), 7.60 – 7.48 (m, 6H), 7.44 (t, *J* = 6.4 Hz, 6H), 7.42 – 7.28 (m, 6H), 6.86 (t, *J* = 8.5 Hz, 2H), 4.03 – 3.87 (m, 1H), 3.05 –

2.90 (m, 2H), 2.80 – 2.66 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 198.03, 197.96, 197.89, 167.00, 164.47, 133.13, 132.69, 132.15, 131.94, 131.91, 131.82, 131.79, 131.41, 131.38, 131.22, 131.13, 130.89, 130.87, 130.80, 130.78, 128.78, 128.66, 128.62, 128.51, 115.60, 115.38, 77.39, 77.07, 76.75, 33.70, 33.68, 33.66, 32.85, 32.77, 32.15, 32.08; ³¹P NMR (162 MHz, DMSO) δ 34.87. HRMS (m/z): calcd for C₃₄H₃₀FO₃P₂ [M+H]⁺: 567.1649, found: 567.1647.

30. 1-(3-Bromophenyl)-3-(diphenylphosphoryl)-2-((diphenylphosphoryl)methyl) -propan-1-one (5g)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 86% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.79 – 7.66 (m, 4H), 7.60 – 7.48 (m, 7H), 7.45 (dd, J = 7.4, 2.5 Hz, 6H), 7.35 (dd, J = 7.3, 4.9 Hz, 5H), 7.10 (t, J = 7.9 Hz, 1H), 3.90 (ddd, J = 17.4, 11.0, 6.5 Hz, 1H), 3.02 (ddd, J = 16.5, 10.4, 6.3 Hz, 2H), 2.79 – 2.62 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 198.36, 136.80, 136.02, 132.01, 131.98, 131.96, 131.33, 130.87, 130.86, 130.78, 130.77, 130.04, 128.83, 128.73, 128.71, 128.61, 127.14, 122.79, 77.31, 77.00, 76.68, 33.96, 33.95, 32.83, 32.76, 32.14, 32.06; ³¹P NMR (162 MHz, DMSO) δ 34.00. HRMS (m/z): calcd for C₃₄H₃₀BrO₃P₂ [M+H]⁺: 627.0848, found: 627.0843.

31. 3-(Diphenylphosphoryl)-2-((diphenylphosphoryl)methyl)-1-(4-nitrophenyl)p-ropan-1-one (5h)

The title compound was prepared according to the general procedure and purified by column



chromatography to give yellow oil, 45% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, J = 8.5 Hz, 2H), 7.72 (dd, J = 11.0, 8.0 Hz, 4H), 7.52 (dd, J = 19.9, 10.2 Hz, 14H), 7.42 – 7.31 (m, 4H), 4.06 – 3.91 (m, 1H), 3.10 – 2.91 (m, 2H), 2.83 – 2.64 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 198.60, 198.54, 198.47, 150.12, 139.91, 134.30,

132.14, 132.12, 132.03, 132.01, 130.85, 130.83, 130.76, 130.74, 129.47, 129.12, 128.90, 128.79, 128.75, 128.63, 123.52, 77.33, 77.01, 76.69, 34.39, 34.37, 34.34, 33.13, 33.05, 32.44, 32.36; ³¹P NMR (162 MHz, DMSO) δ 29.67. HRMS (m/z): calcd for C₃₄H₃₀NO₅P₂ [M+H]⁺: 594.1594, found: 594.1592.

32. 3-(Diphenylphosphoryl)-**2-**((diphenylphosphoryl)methyl)-**1-**(naphthalen-**2-**yl) propan-**1-**one (5i)

The title compound was prepared according to the general procedure and purified by column



chromatography to give yellow oil, 98% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, J = 8.0 Hz, 1H), 7.74 (dd, J = 12.6, 5.8 Hz, 6H), 7.67 – 7.56 (m, 5H), 7.49 (ddd, J = 26.4, 15.2, 7.9 Hz, 11H), 7.36 (dt, J = 7.3, 3.7 Hz, 4H), 4.17 (ddd, J = 17.7, 11.3, 6.4 Hz, 1H), 3.18 – 3.05 (m, 2H), 2.88 – 2.75 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 199.36, 199.28, 199.21, 135.65, 133.24, 132.79,

132.32, 132.25, 131.88, 131.85, 131.80, 131.78, 130.98, 130.93, 130.89, 130.84, 130.01, 129.64, 128.75, 128.67, 128.64, 128.55, 128.45, 128.42, 127.61, 126.40, 124.44, 77.34, 77.02, 76.70, 33.84, 33.81, 33.79, 32.80, 32.73, 32.11, 32.03; ³¹P NMR (243 MHz, CDCl₃) δ 30.56. HRMS (m/z): calcd for C₃₈H₃₃O₃P₂ [M+H]⁺: 599.1899, found: 599.1896.

33. 3-(Diphenylphosphoryl)-**2-**((diphenylphosphoryl)methyl)-**1-**(thiophen-**2-**yl)p-ropan-**1**-one (5j)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 80% yield.¹H NMR (400 MHz, CDCl₃) δ 7.79 – 7.66 (m, 4H), 7.61 – 7.47 (m, 7H), 7.44 (d, *J* = 5.5 Hz, 6H), 7.33 (s, 4H), 6.92 – 6.79 (m, 2H), 3.92 – 3.76 (m, 1H), 3.09 – 2.92 (m, 2H), 2.83 – 2.64 (m, 2H). ¹³C

NMR (101 MHz, CDCl₃) δ 192.30, 192.23, 192.15, 142.42, 134.85, 133.15, 132.44, 132.40, 132.17, 131.92, 131.89, 131.82, 131.79, 130.95, 130.86, 130.76, 128.76, 128.64, 128.59, 128.47, 127.90, 77.39, 77.07, 76.75, 35.66, 35.64, 35.62, 33.02, 32.94, 32.33, 32.25; ³¹P NMR (162 MHz, DMSO) δ 29.89. HRMS (m/z): calcd for C₃₂H₂₉O₃P₂S [M+H]⁺: 555.1307, found: 555.1308.

34. 3-(Di-p-tolylphosphoryl)-2-((di-p-tolylphosphoryl)methyl)-1-phenylpropan-1

one (5k)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 84% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.58 (dd, *J* = 11.3, 8.1 Hz, 4H), 7.48 – 7.36 (m, 7H), 7.23 (dd, *J* = 13.8, 5.8 Hz, 6H), 7.13 (d, *J* = 6.2 Hz, 4H), 4.00 (ddd, *J* = 17.6, 11.3, 6.5 Hz, 1H), 2.92 (ddd, *J* = 16.7, 10.6, 6.4 Hz, 2H), 2.75 – 2.61 (m, 2H), 2.36 (d, *J* = 13.7 Hz, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 199.60, 199.52, 199.46, 142.25, 142.22, 142.18, 142.15,

134.87, 133.02, 131.03, 130.93, 130.83, 129.43, 129.31, 129.28, 129.15, 128.58, 128.27, 77.32, 77.00, 76.69, 33.78, 32.83, 32.75, 32.13, 32.05, 21.57, 21.53; ³¹P NMR (162 MHz, DMSO) δ 36.17. HRMS (m/z): calcd for C₃₈H₃₉O₃P₂ [M+H]⁺: 605.2369, found: 605.2368.

35. 3-(Di(naphthalen-2-yl)phosphoryl)-2-((di(naphthalen-2-yl)phosphoryl)methy -l)-1-phenylpr-opan-1-one (5l)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 72% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.40 (d, *J* = 13.3 Hz, 2H), 8.20 (d, *J* = 13.3 Hz, 2H), 7.87 (t, *J* = 9.2 Hz, 6H), 7.74 (dd, *J* = 13.6, 8.7 Hz, 4H), 7.67 – 7.37 (m, 13H), 7.36 – 7.22 (m, 4H), 6.95 (t, *J* = 7.5 Hz, 2H), 4.16 (ddd, *J* = 15.2, 10.0, 5.3 Hz, 1H), 3.35 – 3.19 (m, 2H), 3.07 – 2.89 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 199.42, 199.35, 199.28, 134.75, 134.72, 134.70, 134.56, 134.54, 133.07,

132.95, 132.86, 132.60, 132.47, 132.40, 132.28, 130.20, 129.69, 129.21, 129.02, 128.78, 128.73, 128.61, 128.51, 128.47, 128.39, 128.29, 128.24, 128.13, 127.85, 127.68, 126.99, 126.85, 125.80, 125.69, 125.64, 125.54, 77.37, 77.06, 76.74, 33.93, 33.91, 33.89, 32.64, 32.56, 31.94, 31.86; ³¹P NMR (162 MHz, DMSO) δ 30.65. HRMS (m/z): calcd for C₅₀H₃₉O₃P₂ [M+H]⁺: 749.2369, found: 749.2364. **36. 3-(Dimethylphosphoryl)-2-((dimethylphosphoryl)methyl)-1-phenylpropan-1-one (5m)**



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 85% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.03 (d, *J* = 7.5 Hz, 2H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 4.40 (ddd, *J* = 18.7, 12.2, 6.8 Hz, 1H), 2.36 – 2.22 (m, 4H), 1.49 (t, *J* = 13.6 Hz, 12H); ¹³C NMR (101 MHz, CDCl₃) δ

200.71, 135.05, 133.79, 129.07, 128.73, 77.32, 77.01, 76.69, 35.06, 35.03, 35.00, 33.97, 33.89, 33.30, 33.23, 18.34, 17.65, 17.46, 16.78; ³¹P NMR (162 MHz, DMSO) δ 46.35. HRMS (m/z): calcd for C₁₄H₂₃O₃P₂ [M+H]⁺:301.1117, found: 301.1123.

37. Diethyl (2-((diphenylphosphoryl)methyl)-3-oxo-3-phenylpropyl)phosphonat-e(6)



The title compound was prepared according to the general procedure and purified by column chromatography to give yellow oil, 77% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.73 (dd, *J* = 12.6, 5.5 Hz, 4H), 7.66 (dd, *J* = 12.0, 7.7 Hz, 2H), 7.52 – 7.42 (m, 5H), 7.36 (dt, *J* = 15.5, 5.1 Hz, 4H), 4.19 (ddd, *J* = 18.7, 12.4, 6.0 Hz, 1H), 3.94 (tt, *J* = 15.6, 7.9 Hz, 4H), 2.71

(dt, J = 11.0, 6.6 Hz, 2H), 2.38 – 2.24 (m, 2H), 1.18 (t, J = 7.0 Hz, 3H), 1.09 (t, J = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 199.84, 199.77, 199.70, 135.23, 133.24, 131.93, 131.91, 131.85, 131.82,

131.04, 130.95, 130.72, 130.63, 128.76, 128.64, 128.61, 128.50, 128.48, 77.32, 77.01, 76.69, 61.76, 61.71, 61.65, 34.25, 34.22, 34.19, 32.88, 32.76, 32.18, 32.06, 29.28, 29.21, 27.88, 27.81, 16.25, 16.19, 16.11, 16.04; ³¹P NMR (243 MHz, Acetone) δ 29.00, 27.14. HRMS (m/z): calcd for C₂₆H₃₀O₅P₂ [M+H]⁺: 485.1641, found: 485.1642.

38. 1-(4-methoxyphenyl)-2-methylene-3-(4-nitrophenyl)hexane-1,5-dione (11)



The title compound was prepared according to the general procedure. ¹H NMR (400 MHz, CDCl₃) δ 8.17, 8.15, 7.71, 7.69, 7.62, 7.60, 6.89, 6.87, 6.85, 6.01, 5.82, 3.82, 2.13. HRMS (m/z): calcd for C₂₀H₁₉NO₅ [M+H]⁺: 354.1336, found: 354.1332.

39.(E)-2-((dibutylamino)methyl)-1-(4-methoxyphenyl)-3-(4-nitrophenyl)prop-2-e n-1-one (1ab)



¹H NMR (400 MHz, CDCl₃) δ 8.17, 8.15, 7.71, 7.69, 7.62, 7.60, 6.89, 6.87, 6.85, 6.01, 5.82, 3.82, 2.13. HRMS (m/z): calcd for C₂₅H₃₂N₂O₄ [M+H]⁺: 425.2435, found: 425.2440.

4. Copies of product ¹H NMR, ¹³C NMR and ³¹P NMR











































































f1 (ppm) -1



















2.36 4.29 13.69 ⁴ 1.30 2.30 2.33 2.33 --100 f1 (ppm) -1 -2































