Supporting Information for:

Rh(III)-Catalyzed Enaminone-Directed C-H Coupling with α-Diazo-α-phosphonoacetate for Reactivity Discovery: Fluoride-Mediated Dephosphonation for C-C Coupling Reactions

*Chao Song, Chen Yang, Hua Zeng, Wenjing Zhang, Shan Guo, and Jin Zhu**
Department of Polymer Science and Engineering, School of Chemistry and Chemical Engineering, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210023, China.

*Corresponding author. Email: jinz@nju.edu.cn

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1. General Methods

Materials:

All reagents and solvents were purchased from commercial available sources and used without further purification unless otherwise stated. Super dry solvents were used directly. Toluene was freshly distilled over Na/benzophenone before use. $[RhCp^*Cl_2]_2$ was purchased from Meryer and purified by flash column chromatography, stored and weighed in a nitrogen-filled glovebox. $AgSbF_6$ was purchased from Alfa Aesar and also stored and manipulated in the glovebox. TBAF (1M solution in THF) was purchased from Alfa Aesar. Diazophosphorylacetates were synthesised and characterized according to the literature.[1] The other chemicals were obtained from local suppliers. Abbreviations for the solvents and reagents: DCE, 1,2-dichloroethane; DMF, N,N-dimethylformamide; DCM, dichloromethane; TFE, 2,2,2-trifluoroethane; PE, petroleum ether; THF, tetrahydrofuran; EA, ethyl acetate; DMF-DMA, N,N-Dimethylformamide dimethyl acetal; DMAP, 4-dimethylaminopyridine; DIPEA, N,N-Diisopropylethylamine; DBU, 1,8-Diazabicyclo[5.4.0]undec-7-ene; TBAF, tetrabutylammonium fluoride; CPME, cyclopentyl methyl ether.

Methods:

All Rh(III)-catalyzed reactions were carried out without any particular precautions to extrude moisture or oxygen. All reactions conducted above room temperature (rt) were run in oil baths with the temperatures calibrated with a thermometer. Prior to an experiment, the oil bath was allowed to equilibrate to the desired temperature for 15 min. ^1H, ^{13}C spectra were recorded in DMSO-d_6 (with tetramethylsilane as internal standard) solutions on Bruker AVANCE 400 MHz or 500Mz facilities. The following notations were used: s - singlet, d - doublet, t - triplet, q - quartet, m - multiplet, dd - doublet of doublet, dt - doublet of triplet, td - triplet of doublet, dq –doublet of quartet, ddd - doublet of doublet of doublet. High-resolution mass spectra were obtained on a Waters Micromass GCT Premier facility.

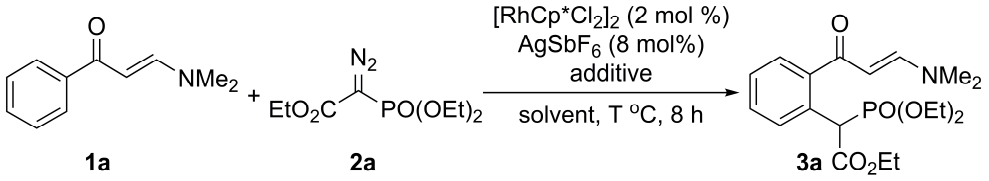
2. Reaction Development

General procedure for the C-H functionalization reaction development:

To a 13 × 150 mm test tube equipped with magnetic stir bar was added an additive, for example, KOAc (2.0 mg, 0.02 mmol, 10 mol %). Other additives include LiOAc (1.3 mg, 0.02 mmol, 10 mol %), NaOAc (1.6 mg, 0.02 mmol, 10 mol %), CsOAc (3.8 mg, 0.02 mmol, 10 mol %). The test tube was transferred to a glovebox, and added with $[RhCp^*Cl_2]_2$ (2.5 mg, 0.004 mmol, 2.0 mol %) and $AgSbF_6$ (5.5 mg, 0.016 mmol, 8.0 mol %). After the test tube was sealed with a rubber septum and removed from the glovebox, liquid additive such as HOAc (1.1 μL, 0.02 mmol, 10 mol %) was firstly injected in and then a solution of **1a** (35.0 mg, 0.2 mmol, 1 equiv) and **2a** (50 μL, 0.24 mmol, 1.2 equiv) in 1.0 mL of solvent was injected into the test tube *via* syringe. The reaction

mixture was placed in a pre-heated oil bath or at ambient temperature and stirred for 8 h, during which time a constant checking by TLC was performed every two hours. The reaction mixture was cooled to rt and filtered over celite. The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography on silica gel with DCM/MeOH (20 : 1) as the eluent.

Table S1. Optimization of Rh(III) Catalyzed C-H Functionalization Reaction[a,b]



1a **2a** **3a**

entry	solvent	additive (mol %)	T °C	yield (%)
1	DCE	KOAc (10)	60 °C	0
2	MeOH	KOAc (10)	60 °C	0
3	MeCN	KOAc (10)	60 °C	24
4	1,4-Dioxane	KOAc (10)	60 °C	68
5	DMF	KOAc (10)	60 °C	0
6	Toluene	KOAc (10)	60 °C	26
7	^{t}AmylOH	KOAc (10)	60 °C	36
8	DCM	KOAc (10)	60 °C	58
9	TFE	KOAc (10)	60 °C	76
10	**TFE**	**KOAc (10)**	**r.t.**	**92**
11	TFE	KOAc (100)	r.t.	60
12	TFE	LiOAc (10)	r.t.	83
13	TFE	NaOAc (10)	r.t.	82
14	TFE	CsOAc (10)	r.t.	85
15	TFE	HOAc (10)	r.t.	30
16	TFE	$Zn(OAc)_2$ (10)	r.t.	85

[a]Conditions: **1a** (0.2 mmol, 1 equiv), **2a** (1.2 equiv), solvent (1 mL). [b]Isolated yields.

General procedure for the cyclization reaction development:

To a 13 × 150 mm test tube equipped with magnetic stir bar was added the substrate **3a** (79.5 mg, 0.2 mmol, 1 equiv). The test tube was transferred to a glovebox, and added with solid base, for example, ^{t}BuOK (67.3 mg, 0.6 mmol, 3 equiv). Other solid reagents include ^{t}BuOK (48.0 mg, 0.6 mmol, 3 equiv), K_2CO_3 (82.9 mg, 0.6 mmol, 3 equiv), DMAP (73.3 mg, 0.6 mmol, 3 equiv), NaH (14.4 mg, 0.6 mmol, 3 equiv), MeONa (32.4 mg, 0.6 mmol, 3 equiv), EtONa (40.8 mg, 0.6 mmol, 3 equiv) and LiCl (17.0 mg, 0.6 mmol, 3 equiv). After the test tube was sealed with a rubber septum and removed from the glovebox, liquid bases such as DIPEA (104.5 μL, 0.6 mmol, 3 equiv) was injected in. Other liquid bases include DBU (149.5 μL, 1 mmol, 5 equiv), TBAF (0.6 mL, 1M in THF, 3 equiv). Finally, appropriate amount of THF was injected into the tube to make the solvent reach 2 mL. The reaction mixture was placed in a pre-heated oil bath or at ambient temperature and stirred for 8 h, during which time a constant checking by TLC was performed every two hours. The reaction mixture was cooled to rt and filtered over celite. The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography on silica gel with PE/EA (5 : 1) as the eluent.

3. Synthesis and Characterization of Enaminone Substrates

General procedure for the synthesis of enaminone substrates:

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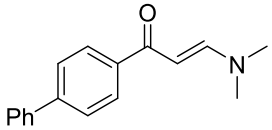
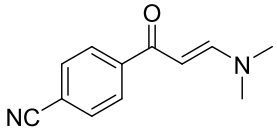
The majority of enaminone substrates were synthesized and characterized according to our previous work[2] except for the following compounds listed below. The specific procedure is: DMF-DMA (70 mmol) was added to the 50 mL toluene solvent of substituted acetophenones (50 mmol). Then the reaction was stirred in 110 °C oil bath until it completed in TLC observation. The mixture was cooled to room temperature and the solvent was removed by evaporation. The residue was recrystallized and a yellow solid was obtained.

(E)-1-([1,1'-biphenyl]-4-yl)-3-(dimethylamino)prop-2-en-1-one (1d): The title compound was



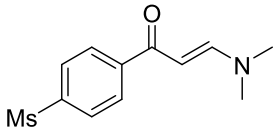
obtained as a yellow solid in 71% yield (8.89 g). $\mathbf{R_f}$ = 0.5 (DCM : MeOH, 50 : 1). **^{1}H NMR (500 MHz, DMSO)** δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.77 – 7.71 (m, 5H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.41 (d, *J* = 7.4 Hz, 1H), 5.89 (d, *J* = 12.2 Hz, 1H), 3.16 (s, 3H), 2.94 (s, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 185.6, 154.7, 142.8, 139.9, 139.5, 129.5, 128.4, 127.3, 126.9, 91.4, 45.0, 37.6. **HRMS (ESI)** Calcd. for $C_{17}H_{18}ON$: $[M + H]^+$, 252.1383. Found: *m/z* 252.1381.

(E)-4-(3-(dimethylamino)acryloyl)benzonitrile (1l): The title compound was obtained as a



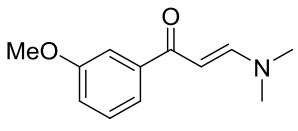
yellow solid in 82% yield (8.19 g). $\mathbf{R_f}$ = 0.4 (DCM : MeOH, 50 : 1). **^{1}H NMR (500 MHz, DMSO)** δ 8.04 (d, *J* = 8.3 Hz, 2H), 7.93 – 7.88 (m, 2H), 7.79 (d, *J* = 12.1 Hz, 1H), 5.86 (d, *J* = 12.2 Hz, 1H), 3.18 (s, 3H), 2.95 (s, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 184.3, 155.6, 144.5, 132.8, 128.3, 119.1, 113.3, 91.4, 45.2, 37.8. **HRMS (ESI)** Calcd. for $C_{12}H_{13}ON_2$: $[M + H]^+$, 201.1022. Found: *m/z* 201.1021.

(E)-3-(dimethylamino)-1-(4-(methylsulfonyl)phenyl)prop-2-en-1-one (1m): The title



compound was obtained as a yellow solid in 79% yield (9.97 g). $\mathbf{R_f}$ = 0.6 (DCM : MeOH, 20 : 1). **^{1}H NMR (500 MHz, DMSO)** δ 8.11 (d, *J* = 8.3 Hz, 2H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 12.1 Hz, 1H), 5.86 (d, *J* = 12.2 Hz, 1H), 3.26 (s, 3H), 3.18 (s, 3H), 2.95 (s, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 184.6, 155.5, 145.0, 142.7, 128.4, 127.4, 91.5, 45.1, 43.9, 37.8. **HRMS (ESI)** Calcd. for $C_{12}H_{16}N_2O_3S$: $[M + H]^+$, 254.0845. Found: *m/z* 254.0844.

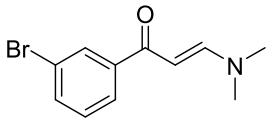
(E)-3-(dimethylamino)-1-(3-methoxyphenyl)prop-2-en-1-one (1o): The title compound was



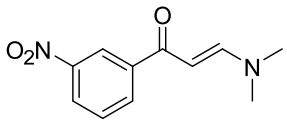
obtained as a yellow solid in 68% yield (7.01 g). $\mathbf{R_f}$ = 0.4 (DCM : MeOH, 50 : 1). **^{1}H NMR (500 MHz, DMSO)** δ 7.71 (d, *J* = 12.3 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.39 (d, *J* = 1.4 Hz, 1H), 7.35 (t, *J* = 7.9 Hz, 1H), 7.07 – 7.03 (m, 1H), 5.80 (d, *J* = 12.3 Hz, 1H), 3.80 (s, 3H),

3.14 (s, 3H), 2.91 (s, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 185.9, 159.7, 154.7, 142.3, 129.7, 120.0, 117.0, 112.6, 91.5, 55.6, 45.0, 37.6. **HRMS (ESI)** Calcd. for $C_{12}H_{16}O_2N$: $[M + H]^+$, 206.1176. Found: *m/z* 206.1176.

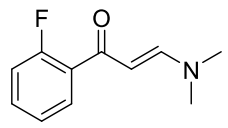
(E)-1-(3-bromophenyl)-3-(dimethylamino)prop-2-en-1-one (1r): The title compound was obtained as a yellow solid in 81% yield (10.31 g). **R_f** = 0.5 (DCM : MeOH, 50 : 1). **^{1}H NMR (500 MHz, DMSO)** δ 8.03 (t, *J* = 1.7 Hz, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.75 (d, *J* = 12.2 Hz, 1H), 7.68 (ddd, *J* = 7.9, 2.0, 0.9 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 5.84 (d, *J* = 12.2 Hz, 1H), 3.16 (s, 3H), 2.94 (s, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 184.2, 155.3, 142.9, 133.9, 130.9, 130.2, 126.6, 122.3, 91.0, 45.1, 37.7. **HRMS (ESI)** Calcd. for $C_{11}H_{13}ONBr$: $[M + H]^+$, 254.0175. Found: *m/z* 254.0173.



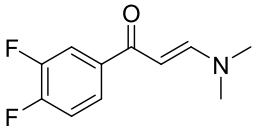
(E)-3-(dimethylamino)-1-(3-nitrophenyl)prop-2-en-1-one (1s): The title compound was obtained as a yellow solid in 68% yield (7.44 g). **R_f** = 0.4 (DCM : MeOH, 50 : 1). **^{1}H NMR (500 MHz, DMSO)** δ 8.61 (d, *J* = 1.7 Hz, 1H), 8.38 – 8.30 (m, 2H), 7.83 (d, *J* = 12.1 Hz, 1H), 7.73 (t, *J* = 7.9 Hz, 1H), 5.92 (d, *J* = 12.1 Hz, 1H), 3.19 (s, 3H), 2.97 (s, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 183.3, 155.8, 148.4, 142.1, 133.9, 130.4, 125.6, 122.0, 90.8, 45.2, 37.8. **HRMS (ESI)** Calcd. for $C_{11}H_{13}O_3N_2$: $[M + H]^+$, 221.0921. Found: *m/z* 221.0919.



(E)-3-(dimethylamino)-1-(2-fluorophenyl)prop-2-en-1-one (1t): The title compound was obtained as a yellow oil in 71% yield (6.87 g). **R_f** = 0.4 (DCM : MeOH, 50 : 1). **^{1}H NMR (500 MHz, DMSO)** δ 7.58 (s, 2H), 7.50 – 7.43 (m, 1H), 7.27 – 7.19 (m, 2H), 5.45 (d, *J* = 11.6 Hz, 1H), 3.12 (s, 3H), 2.85 (s, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 159.9 (d, *J* = 245.6 Hz), 154.8, 132.1, 130.3 (d, *J* = 3.4 Hz), 130.0 (d, *J* = 14.9 Hz), 124.8, 124.8, 116.5 (d, *J* = 23.2 Hz), 95.9, 45.0, 37.5. **HRMS (ESI)** Calcd. for $C_{11}H_{13}ONF$: $[M + H]^+$, 194.0976. Found: *m/z* 194.0975.

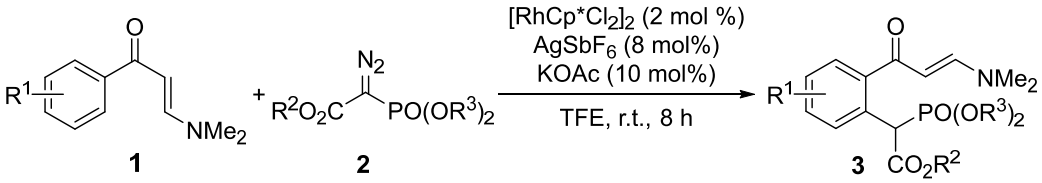


(E)-1-(3,4-difluorophenyl)-3-(dimethylamino)prop-2-en-1-one (1v): The title compound was obtained as a yellow solid in 83% yield (8.74 g). **R_f** = 0.4 (DCM : MeOH, 50 : 1). **^{1}H NMR (500 MHz, DMSO)** δ 7.92 (ddd, *J* = 11.8, 8.1, 2.0 Hz, 1H), 7.82 – 7.77 (m, 1H), 7.75 (d, *J* = 12.2 Hz, 1H), 7.48 (dt, *J* = 10.5, 8.4 Hz, 1H), 5.85 (d, *J* = 12.2 Hz, 1H), 3.16 (s, 3H), 2.94 (s, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 183.2, 155.3, 151.5 (dd, *J* = 249.7, 12.8 Hz), 149.7 (dd, *J* = 246.1, 12.9 Hz), 138.3 (t, *J* = 3.6 Hz), 124.8 (dd, *J* = 7.2, 3.2 Hz), 117.6 (d, *J* = 17.3 Hz), 116.7 (d, *J* = 17.3 Hz), 90.8, 45.1, 37.7. **HRMS (ESI)** Calcd. for $C_{11}H_{12}ONF_2$: $[M + H]^+$, 212.0881. Found: *m/z* 212.0881.



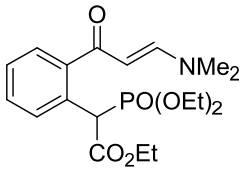
4. Synthesis and Characterization of C-H Functionalization Products

General procedure for the synthesis of C-H functionalization products:



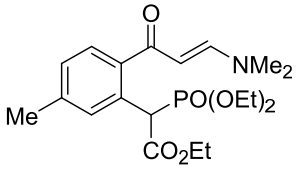
To a 13 × 150 mm test tube equipped with a magnetic stir bar was added KOAc (2.0 mg, 0.02 mmol, 10 mol %). The test tube was transferred to a glovebox, and added with $[RhCp^*Cl_2]_2$ (2.5 mg, 0.004 mmol, 2.0 mol %) and $AgSbF_6$ (5.5 mg, 0.016 mmol, 8.0 mol %). After the test tube was sealed with a rubber septum and removed from the glovebox, a solution of **1a-1v** (0.2 mmol, 1 equiv) and **2a**, **2w**, **2x** (0.24 mmol, 1.2 equiv) in 1.0 mL TFE was injected into the test tube *via* syringe. The reaction mixture was stirred for 8 h at ambient temperature. Then the reaction mixture was filtered over celite. The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography on silica gel with DCM/MeOH (50 : 1) as the eluent.

Ethyl (E)-2-(diethoxyphosphoryl)-2-(2-(3-(dimethylamino)acryloyl)phenyl)acetate (3a): The



title compound was obtained as an orange solid in 92% yield (73.3 mg). **R_f** = 0.5 (DCM : MeOH, 20 : 1). **^{1}H NMR (400 MHz, DMSO)** δ 7.77 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.47 – 7.38 (m, 2H), 7.37 – 7.32 (m, 1H), 7.90 – 7.10 (br, 1H), 5.34 (d, *J* = 12.4 Hz, 1H), 5.70 – 4.80 (br, 1H), 4.19 – 3.97 (m, 4H), 3.91 – 3.71 (m, 2H), 3.10 (s, 3H), 2.84 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 3H), 1.00 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, DMSO)** δ 190.1 (m), 167.3 (d, *J* = 3.3 Hz), 154.8 (m), 142.5, 130.7 (d, *J* = 4.1 Hz), 128.6, 128.5, 128.5, 127.4, 127.3, 95.6 (m), 62.5 (d, *J* = 6.7 Hz), 62.4 (d, *J* = 6.8 Hz), 61.2, 46.0 (d, *J* = 133.5 Hz), 44.5, 37.0, 16.1 (d, *J* = 5.8 Hz), 15.9 (d, *J* = 5.8 Hz), 13.9. **HRMS (ESI)** Calcd. for $C_{19}H_{29}O_6NP$: $[M + H]^+$, 398.1727. Found: *m/z* 398.1725.

Ethyl (E)-2-(diethoxyphosphoryl)-2-(2-(3-(dimethylamino)acryloyl)-5-methyl phenyl)acetate



(**3b**): The title compound was obtained as a brown oil in 92% yield (75.5 mg). **R_f** = 0.4 (DCM : MeOH, 20 : 1). **^{1}H NMR (400 MHz, DMSO)** δ 7.57 (s, 1H), 7.36 (m, 1H), 7.16 (d, *J* = 7.9 Hz, 1H), 7.66 – 7.25 (br, 1H), 5.34 (d, *J* = 12.4 Hz, 1H), 5.60 – 5.00 (br, 1H), 4.19 – 3.97 (m, 4H), 3.91 – 3.72 (m, 2H), 3.09 (s, 3H), 2.84 (s, 3H), 2.33 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 3H), 1.01 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, DMSO)** δ 190.5 (m), 167.9 (d, *J* = 3.3 Hz), 155.2 (m), 140.0 (d, *J* = 7.7 Hz), 138.3, 131.6 (d, *J* = 4.3 Hz), 129.2 (d, *J* = 6.8 Hz), 128.4, 128.2, 96.0 (m), 63.0 (d, *J* = 6.7 Hz), 62.8 (d, *J* = 6.8 Hz), 61.7, 46.1 (d, *J* = 131.7 Hz), 45.0, 37.4, 21.5, 16.6 (d, *J* = 5.8 Hz), 16.4 (d, *J* = 5.8 Hz), 14.4. **HRMS (ESI)** Calcd. for $C_{20}H_{31}O_6NP$: $[M + H]^+$, 412.1884. Found: *m/z* 412.1882.

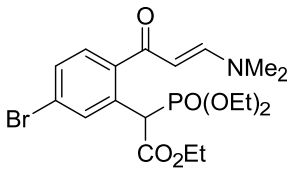
Ethyl (E)-2-(diethoxyphosphoryl)-2-(2-(3-(dimethylamino)acryloyl)-5-methoxyphenyl) acetate (3c): The title compound was obtained as an orange solid in 95% yield (81.0 mg). $\mathbf{R_f}$ = 0.4 (DCM : MeOH, 20 : 1). **^{1}H NMR (400 MHz, DMSO)** δ 7.49 (d, *J* = 8.3 Hz, 2H), 7.32 (t, *J* = 2.5 Hz, 1H), 6.92 (ddd, *J* = 8.6, 2.6, 1.5 Hz, 1H), 5.55 (d, *J* = 24.4 Hz, 1H), 5.38 (d, *J* = 12.4 Hz, 1H), 4.16 – 3.98 (m, 4H), 3.91 – 3.77 (m, 5H), 3.10 (s, 3H), 2.84 (s, 3H), 1.19 (td, *J* = 7.1, 4.2 Hz, 6H), 1.02 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, DMSO)** δ 189.5, 167.31 (d, *J* = 3.7 Hz), 159.0, 154.5, 134.5 (d, *J* = 7.6 Hz), 130.9 (d, *J* = 7.0 Hz), 129.6, 116.9 (d, *J* = 4.6 Hz), 111.9, 95.2, 62.5 (d, *J* = 6.7 Hz), 62.3 (d, *J* = 6.7 Hz), 61.2, 55.1, 45.5 (d, *J* = 130.9 Hz), 44.5, 37.0, 16.1 (d, *J* = 5.8 Hz), 15.9 (d, *J* = 5.8 Hz), 13.9. **HRMS (ESI)** Calcd. for $C_{20}H_{31}O_7NP$: $[M + H]^+$, 428.1833. Found: *m/z* 428.1829.

Ethyl (E)-2-(diethoxyphosphoryl)-2-(4-(3-(dimethylamino)acryloyl)-[1,1'-biphenyl]-3-yl) acetate (3d): The title compound was obtained as an orange solid in 99% yield (93.3 mg). $\mathbf{R_f}$ = 0.6 (DCM : MeOH, 20 : 1). **^{1}H NMR (400 MHz, DMSO)** δ 8.10 (t, *J* = 1.9 Hz, 1H), 7.68 – 7.62 (m, 3H), 7.58 – 7.48 (m, 3H), 7.45 – 7.38 (m, 1H), 7.61 – 7.45 (br, 1H), 5.42 (d, *J* = 12.3 Hz, 1H), 6.18 – 4.67 (br, 1H), 4.22 – 4.01 (m, 4H), 3.99 – 3.71 (m, 2H), 3.12 (s, 3H), 2.87 (s, 3H), 1.21 (t, *J* = 7.0 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H), 1.01 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, DMSO)** δ 189.8 (m), 167.4 (d, *J* = 3.4 Hz), 154.8 (m), 141.2 (d, *J* = 7.8 Hz), 140.0, 139.4, 129.4 (d, *J* = 6.8 Hz), 129.2, 129.1, 128.3, 127.9, 126.6, 125.5, 95.4 (m), 62.6 (d, *J* = 6.7 Hz), 62.5 (d, *J* = 6.8 Hz), 61.3, 45.8 (d, *J* = 131.5 Hz), 44.5, 37.0, 16.1 (d, *J* = 5.8 Hz), 15.9 (d, *J* = 5.8 Hz), 13.9. **HRMS (ESI)** Calcd. for $C_{25}H_{33}O_6NP$: $[M + H]^+$, 474.2040. Found: *m/z* 474.2037.

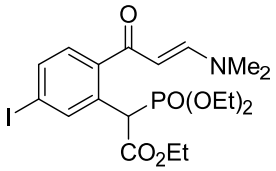
Ethyl (E)-2-(diethoxyphosphoryl)-2-(2-(3-(dimethylamino)acryloyl)-5-fluorophenyl) acetate (3e): The title compound was obtained as a brown solid in 98% yield (81.5 mg). $\mathbf{R_f}$ = 0.4 (DCM : MeOH, 20 : 1). **^{1}H NMR (400 MHz, DMSO)** δ 7.54 (dt, *J* = 10.8, 2.4 Hz, 2H), 7.27 – 7.17 (m, 1H), 7.80 – 7.31 (br, 1H), 5.35 (d, *J* = 12.4 Hz, 1H), 5.55 – 5.16 (br, 1H), 4.22 – 3.98 (m, 4H), 3.95 – 3.76 (m, 2H), 3.12 (s, 3H), 2.86 (s, 3H), 1.21 (t, *J* = 7.0 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H), 1.03 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, DMSO)** δ 189.5 (m), 167.4 (d, *J* = 3.8 Hz), 161.8 (d, *J* = 244.9 Hz), 155.7 (m), 139.4 (d, *J* = 6.4 Hz), 132.2 (d, *J* = 5.6 Hz), 130.3 (d, *J* = 8.2 Hz), 117.9 (d, *J* = 23.2 Hz), 114.8 (d, *J* = 21.0 Hz), 95.3 (m), 63.2 (m), 62.0, 46.2 (d, *J* = 130.2 Hz), 45.0, 37.5, 16.6 (d, *J* = 5.8 Hz), 16.4 (d, *J* = 5.8 Hz), 14.4. **HRMS (ESI)** Calcd. for $C_{19}H_{28}O_6NFP$: $[M + H]^+$, 416.1633. Found: *m/z* 416.1629.

Ethyl (E)-2-(5-chloro-2-(3-(dimethylamino)acryloyl)phenyl)-2-(diethoxyphosphoryl)acetate (3f): The title compound was obtained as an orange solid in 99% yield (85.5 mg). $\mathbf{R_f}$ = 0.4 (DCM : MeOH, 20 : 1). **^{1}H NMR (400 MHz, DMSO)** δ 7.79 (s, 1H), 7.44 (d, *J* = 7.9 Hz, 2H),7.73 – 7.15 (br,1H), 5.34 (d, *J* = 12.2 Hz, 1H), 5.72 – 4.80 (br, 1H), 4.21 – 4.00 (m, 4H), 3.86 (m, 2H), 3.12 (s, 3H), 2.86 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H), 1.19 (t, *J* = 7.2 Hz, 3H), 1.04 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, DMSO)** δ 188.4 (m), 166.9 (d,

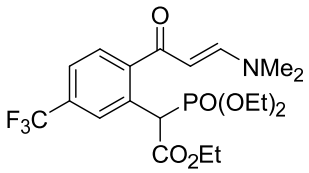
J = 3.4 Hz), 155.0 (m), 141.1 (d, *J* = 7.1 Hz), 132.8, 131.0 (d, *J* = 6.5 Hz), 130.4 (d, *J* = 3.5 Hz), 129.3, 127.4, 94.4 (m), 62.7 (d, *J* = 5.8 Hz), 61.5, 45.6 (d, *J* = 129.9 Hz), 44.6, 37.2, 16.1 (d, *J* = 5.8 Hz), 15.9 (d, *J* = 5.8 Hz), 13.8. **HRMS (ESI)** Calcd. for $C_{19}H_{28}O_6NClP$: $[M + H]^+$, 432.1337. Found: *m/z* 432.1334.

Ethyl (E)-2-(5-bromo-2-(3-(dimethylamino)acryloyl)phenyl)-2-(diethoxy phosphoryl)acetate (3g): 

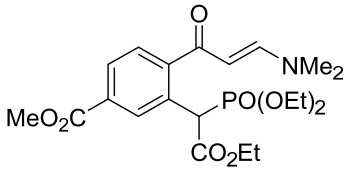
The title compound was obtained as a yellow solid in 92% yield (87.9 mg). $\mathbf{R_f}$ = 0.4 (DCM : MeOH, 50 : 1). **^{1}H NMR (400 MHz, DMSO)** δ 7.99 (t, *J* = 2.1 Hz, 1H), 7.65 – 7.60 (m, 1H), 7.47 (s, 1H), 7.93 – 7.56 (br, 1H), 5.39 (d, *J* = 12.2 Hz, 1H), 5.70 – 5.00 (br, 1H), 4.25 – 4.05 (m, 4H), 4.03 – 3.80 (m, 2H), 3.17 (s, 3H), 2.91 (s, 3H), 1.27 (t, 7.3 Hz, 3H), 1.25 (t, 7.3 Hz, 3H), 1.10 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, DMSO)** δ 188.7 (m), 166.9 (d, *J* = 3.2 Hz), 155.1 (m), 141.4 (d, *J* = 7.1 Hz), 133.3 (d, *J* = 2.9 Hz), 131.1 (d, *J* = 6.7 Hz), 130.3, 129.5, 121.5, 94.6 (m), 62.7 (d, *J* = 6.1 Hz), 61.6, 45.6 (d, *J* = 132.2 Hz), 44.6, 37.1, 16.1 (d, *J* = 5.8 Hz), 15.9 (d, *J* = 5.8 Hz), 13.9. **HRMS (ESI)** Calcd. for $C_{19}H_{28}O_6NBrP$: $[M + H]^+$, 476.0832. Found: *m/z* 476.0830.

Ethyl (E)-2-(diethoxyphosphoryl)-2-(2-(3-(dimethylamino)acryloyl)-5-iodophenyl)acetate (3h): 

The title compound was obtained as an orange solid in 92% yield (96.0 mg). $\mathbf{R_f}$ = 0.5 (DCM : MeOH, 20 : 1). **^{1}H NMR (400 MHz, DMSO)** δ 8.12 (t, *J* = 1.9 Hz, 1H), 7.73 (m, 1H), 7.24 (s, 1H), 8.03 – 7.37 (br, 1H), 5.32 (d, *J* = 12.2 Hz, 1H), 5.74 – 4.70 (br, 1H), 4.18 – 3.99 (m, 4H), 3.95 – 3.78 (m, 2H), 3.11 (s, 3H), 2.85 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.2 Hz, 3H), 1.05 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, DMSO)** δ 188.7 (m), 167.0 (d, *J* = 3.3 Hz), 155.1 (m), 141.7 (d, *J* = 7.4 Hz), 139.2 (d, *J* = 2.9 Hz), 136.0, 130.8 (d, *J* = 6.4 Hz), 129.4, 95.0, 94.7 (m), 62.7 (m), 61.5, 45.4 (d, *J* = 128.3 Hz), 44.6, 37.0, 16.1 (d, *J* = 5.8 Hz), 15.9 (d, *J* = 5.8 Hz), 13.9. **HRMS (ESI)** Calcd. for $C_{19}H_{28}O_6NIP$: $[M + H]^+$, 524.0693. Found: *m/z* 524.0689.

Ethyl (E)-2-(diethoxyphosphoryl)-2-(2-(3-(dimethylamino)acryloyl)-5-(trifluoromethyl) phenyl)acetate (3i): 

The title compound was obtained as a yellow solid in 94% yield (87.2 mg). $\mathbf{R_f}$ = 0.4 (DCM : MeOH, 20 : 1). **^{1}H NMR (400 MHz, DMSO)** δ 8.13 (s, 1H), 7.70 (m, 2H), 8.07 – 6.50 (br, 1H), 5.36 (d, *J* = 11.5 Hz, 1H), 5.76 – 4.65 (br, 1H), 4.20 – 4.01 (m, 4H), 3.88 (m, 2H), 3.14 (s, 3H), 2.87 (s, 3H), 1.21 (t, *J* = 6.9 Hz, 3H), 1.20 (t, *J* = 6.9 Hz, 3H), 1.04 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, DMSO)** δ 188.6 (m), 167.3 (d, *J* = 3.9 Hz), 155.4 (m), 146.8 (d, *J* = 6.5 Hz), 130.3 (d, *J* = 7.0 Hz), 129.0 (q, *J* = 32.9 Hz), 128.7, 127.9, 124.8, 124.4 (q, *J* = 272.2 Hz), 94.8 (m), 63.3 (d, *J* = 6.8 Hz), 63.3 (d, *J* = 6.8 Hz), 62.1, 47.1, 45.8, 45.1, 37.6, 16.5 (d, *J* = 5.9 Hz), 16.3 (d, *J* = 5.9 Hz), 14.3. **HRMS (ESI)** Calcd. for $C_{20}H_{28}O_6NF_3P$: $[M + H]^+$, 466.1601. Found: *m/z* 466.1598.

Methyl (E)-3-(1-(diethoxyphosphoryl)-2-ethoxy-2-oxoethyl)-4-(3-(dimethylamino)acryloyl) benzoate (3j): 

The title compound was obtained as an orange solid in 96% yield (87.2 mg). $\mathbf{R_f}$ = 0.4 (DCM : MeOH, 20 : 1).

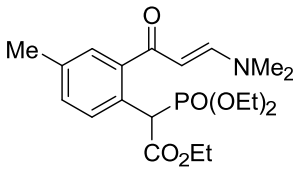
^{1}H NMR (400 MHz, DMSO) δ 8.44 (t, *J* = 1.9 Hz, 1H), 7.93 (dt, *J* = 8.0, 1.6 Hz, 1H), 7.55 (s, 1H), 7.89 – 7.20 (br, 1H), 5.35 (d, *J* = 11.2 Hz, 1H), 5.80 – 4.65 (br, 1H), 4.19 – 4.01 (m, 4H), 3.94 – 3.78 (m, 5H), 3.12 (s, 3H), 2.86 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H), 1.04 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, DMSO)** δ 188.8 (m), 167.0, 165.7, 154.8 (m), 146.8, 131.7, 129.2, 129.1, 128.2, 127.7, 94.3 (m), 62.7 (d, *J* = 6.0 Hz), 61.5, 52.3, 45.9 (d, *J* = 129.1 Hz), 44.6, 37.1, 16.1 (d, *J* = 5.8 Hz), 15.8 (d, *J* = 5.9 Hz), 13.8. **HRMS (ESI)** Calcd. for $C_{21}H_{31}O_8NP$: $[M + H]^+$, 456.1782. Found: *m/z* 456.1778.

Ethyl (E)-2-(diethoxyphosphoryl)-2-(2-(3-(dimethylamino)acryloyl)-5-nitrophenyl)acetate (3k): The title compound was obtained as a yellow solid in 92% yield (81.0 mg). **R_f** = 0.4 (DCM : MeOH, 20 : 1). **^{1}H NMR (400 MHz, DMSO)** δ 8.67 (t, *J* = 2.3 Hz, 1H), 8.22 (ddd, *J* = 8.5, 2.3, 1.5 Hz, 1H), 7.72 (s, 1H), 8.15 – 6.50 (br, 1H), 5.37 (d, *J* = 9.5 Hz, 1H), 5.90 – 4.30 (br, 1H), 4.22 – 4.03 (m, 4H), 3.97 – 3.83 (m, 2H), 3.17 (s, 3H), 2.88 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.07 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, DMSO)** δ 187.2 (m), 166.6, 154.9 (m), 148.6, 146.7 (d, *J* = 1.5 Hz), 130.5, 128.7, 125.5, 122.6, 94.07 (m), 63.0 (d, *J* = 3.7 Hz), 61.8, 45.9 (d, *J* = 128.9 Hz), 44.7, 37.1, 16.1 (d, *J* = 5.8 Hz), 15.9 (d, *J* = 5.8 Hz), 13.8. **HRMS (ESI)** Calcd. for $C_{19}H_{28}O_8N_2P$: $[M + H]^+$, 443.1578. Found: *m/z* 443.1577.

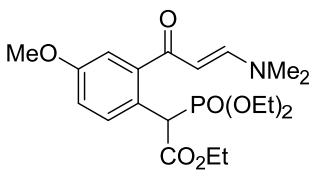
Ethyl (E)-2-(5-cyano-2-(3-(dimethylamino)acryloyl)phenyl)-2-(diethoxyphosphoryl)acetate (3l): The title compound was obtained as a yellow solid in 84% yield (71.1 mg). **R_f** = 0.4 (DCM : MeOH, 20 : 1). **^{1}H NMR (400 MHz, DMSO)** δ 8.10 (t, *J* = 1.8 Hz, 1H), 7.87 (dt, *J* = 8.0, 1.5 Hz, 1H), 7.64 (s, 1H), 8.04 – 7.20 (br, 1H), 5.34 (d, *J* = 11.7 Hz, 2H), 5.76 – 4.40 (br, 1H), 4.23 – 4.00 (m, 4H), 3.97 – 3.77 (m, 2H), 3.15 (s, 3H), 2.87 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 3H), 1.04 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, DMSO)** δ 187.6 (m), 166.7, 155.1 (m), 146.8, 134.2, 131.3, 130.0 (d, *J* = 5.6 Hz), 128.4, 118.4, 110.9, 93.9 (m), 63.1 – 62.7 (m), 61.8, 45.6 (d, *J* = 126.7 Hz), 44.7, 37.1, 16.1 (d, *J* = 5.8 Hz), 15.9 (d, *J* = 5.7 Hz), 13.8. **HRMS (ESI)** Calcd. for $C_{20}H_{28}O_6N_2P$: $[M + H]^+$, 423.1679. Found: *m/z* 423.1677.

Ethyl (E)-2-(diethoxyphosphoryl)-2-(2-(3-(dimethylamino)acryloyl)-5-(methylsulfonyl) phenyl)acetate (3m): The title compound was obtained as an orange oil in 94% yield (89.1 mg). **R_f** = 0.3 (DCM : MeOH, 20 : 1). **^{1}H NMR (400 MHz, DMSO)** δ 8.33 (t, *J* = 2.0 Hz, 1H), 7.93 (dt, *J* = 8.1, 1.6 Hz, 1H), 7.68 (s, 1H),7.89 – 7.40 (br, 1H), 5.35 (d, *J* = 11.8 Hz, 1H), 5.76 – 4.40 (br, 1H), 4.21 – 4.00 (m, 4H), 3.98 – 3.81 (m, 2H), 3.21 (s, 3H), 3.15(s, 3H), 2.87 (s, 3H), 1.21 (t, *J* = 6.9 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 1H), 1.06 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, DMSO)** δ 166.7, 154.8 (m), 147.2 (m), 140.3, 129.9 (d, *J* = 6.6 Hz), 129.0, 128.3, 126.2, 94.0 (m), 62.8 (d, *J* = 6.6 Hz), 61.7, 46.1 (d, *J* = 132.5 Hz), 44.7, 43.6, 37.1, 16.1 (d, *J* = 5.8 Hz), 15.9 (d, *J* = 5.7 Hz), 13.8. **HRMS (ESI)** Calcd. for $C_{20}H_{31}O_8NPS$: $[M + H]^+$, 476.1503. Found: *m/z* 476.1504.

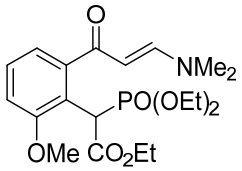
Ethyl (E)-2-(diethoxyphosphoryl)-2-(2-(3-(dimethylamino)acryloyl)-4-methylphenyl)acetate (3na): The title compound was obtained as a red oil in 97% yield (79.9 mg). $\mathbf{R_f}$ = 0.4 (DCM : MeOH, 20 : 1). **^{1}H NMR (400 MHz, DMSO)** δ 7.65 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.23 (d, *J* = 7.1 Hz, 2H), 7.60 – 7.04 (br, 1H), 5.33 (d, *J* = 12.3 Hz, 1H), 5.75 – 4.63 (br, 1H), 4.14 – 3.97 (m, 4H), 3.91 – 3.71 (m, 2H), 3.10 (s, 3H), 2.84 (s, 3H), 2.32 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 3H), 1.02 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, DMSO)** δ 190.5 (m), 167.4, 154.8 (m), 142.4 (d, *J* = 7.7 Hz), 136.6, 130.5, 129.1, 127.8, 125.5 (d, *J* = 6.4 Hz), 95.5 (m), 62.5 (d, *J* = 6.7 Hz), 62.3 (d, *J* = 6.7 Hz), 61.1, 45.7 (d, *J* = 131.5 Hz), 44.5, 37.0, 20.6, 16.1 (d, *J* = 5.8 Hz), 15.9 (d, *J* = 5.8 Hz), 13.9. **HRMS (ESI)** Calcd. for $C_{20}H_{31}O_6NP$: $[M + H]^+$, 412.1884. Found: *m/z* 412.1883.



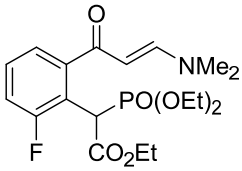
Ethyl (E)-2-(diethoxyphosphoryl)-2-(2-(3-(dimethylamino)acryloyl)-4-methoxyphenyl) acetate (3oa): The title compound was obtained as an orange solid in 32% yield (27.6 mg). $\mathbf{R_f}$ = 0.6 (DCM : MeOH, 20 : 1). **^{1}H NMR (400 MHz, DMSO)** δ 7.69 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.54 (s, 1H), 7.01 (dd, *J* = 8.7, 2.8 Hz, 1H), 6.90 (s, 1H), 5.32 (d, *J* = 12.1 Hz, 1H), 5.12 (s, 1H), 4.14 – 3.97 (m, 4H), 3.88 – 3.74 (m, 5H), 3.10 (s, 3H), 2.85 (s, 3H), 1.22 – 1.15 (m, 6H), 1.02 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, DMSO)** δ 189.5 (m), 167.5, 158.1, 154.6 (m), 143.9 (d, *J* = 3.5 Hz), 131.9 (d, *J* = 3.5 Hz), 120.2 (d, *J* = 6.8 Hz), 114.0, 112.6, 94.7 (m), 62.5 (d, *J* = 6.6 Hz), 62.3 (d, *J* = 6.8 Hz), 61.1, 55.2, 45.3 (d, *J* = 131.7 Hz), 44.5, 37.0, 16.1 (d, *J* = 5.8 Hz), 16.0 (d, *J* = 5.7 Hz), 13.9. **HRMS (ESI)** Calcd. for $C_{20}H_{31}O_7NP$: $[M + H]^+$, 428.1833. Found: *m/z* 428.1830.



Ethyl (E)-2-(diethoxyphosphoryl)-2-(2-(3-(dimethylamino)acryloyl)-6-methoxyphenyl) acetate (3ob): The title compound was obtained as an orange oil in 53% yield (45.2 mg). $\mathbf{R_f}$ = 0.5 (DCM : MeOH, 20 : 1). **^{1}H NMR (400 MHz, DMSO)** δ 7.49 (s, 1H), 7.31 (td, *J* = 8.0, 1.6 Hz, 1H), 7.06 (m, *J* = 8.2 Hz, 2H), 5.51 (br, 1H), 5.31 (d, *J* = 12.3 Hz, 1H), 4.15 – 4.00 (m, 2H), 4.00 – 3.76 (m, 4H), 3.72 (s, 3H), 3.04 (d, *J* = 32.9 Hz, 3H), 2.83 (s, 3H), 1.18 – 1.09 (m, 6H), 1.04 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, DMSO)** δ 190.4 (m), 167.4, 157.9 (d, *J* = 3.7 Hz), 154.9 (m), 143.3 (d, *J* = 6.7 Hz), 128.3, 119.9, 119.6 (d, *J* = 5.1 Hz), 112.3, 95.4, 61.6 (t, *J* = 6.0 Hz), 60.5, 55.7, 44.5, 44.3 (d, *J* = 148.1 Hz), 36.9, 16.2 (d, *J* = 5.7 Hz), 16.1 (d, *J* = 5.9 Hz), 13.9. **HRMS (ESI)** Calcd. for $C_{20}H_{31}O_7NP$: $[M + H]^+$, 428.1833. Found: *m/z* 428.1829.

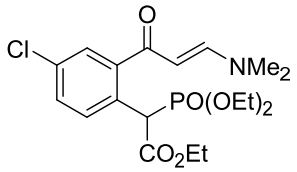


Ethyl (E)-2-(diethoxyphosphoryl)-2-(2-(3-(dimethylamino)acryloyl)-6-fluorophenyl)acetate (3pb): The title compound was obtained as an orange oil in 99% yield (82.0 mg). $\mathbf{R_f}$ = 0.4 (DCM : MeOH, 20 : 1). **^{1}H NMR (400 MHz, DMSO)** δ 7.85 – 6.86 (m, 4H), 5.37 (d, *J* = 12.0 Hz, 1H), 6.20 – 4.63 (br, 1H), 4.16 – 4.00 (m, 4H), 3.96 – 3.82 (m, 2H), 3.12 (s, 3H), 2.86 (s, 3H), 1.18 (t, *J* = 7.1Hz, 3H), 1.17 (t, *J* = 7.1Hz, 3H), 1.06 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, DMSO)** δ 189.0 (m), 166.5, 161.1 (dd, *J* = 249.1, 4.7 Hz), 155.0 (m), 144.73 – 142.51 (m), 129.2 (d, *J* = 8.3 Hz), 123.5, 118.5 (d, *J* = 18.6 Hz), 116.3 (d, *J* = 22.1 Hz), 95.0 (m), 62.3 (d, *J* = 6.4 Hz), 62.0 (d, *J* = 6.5 Hz), 61.2, 44.6, 43.7 (d, *J* = 149.0 Hz), 37.0, 16.1 (d, *J* = 5.7 Hz), 16.0



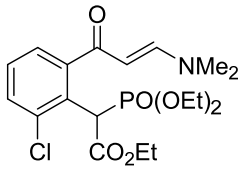
(d, J = 5.8 Hz), 13.8. **HRMS (ESI)** Calcd. for $C_{19}H_{28}O_6NFP$: $[M + H]^+$, 416.1633. Found: *m/z* 416.1631.

Ethyl (E)-2-(4-chloro-2-(3-(dimethylamino)acryloyl)phenyl)-2-(diethoxyphosphoryl)acetate



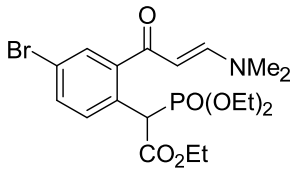
(3qa): The title compound was obtained as an orange solid in 34% yield (29.6 mg). $\mathbf{R_f}$ = 0.5 (DCM : MeOH, 20 : 1). **^{1}H NMR (400 MHz, DMSO)** δ 7.78 (dd, J = 8.5, 2.1 Hz, 1H), 7.60 – 7.30 (m, 2H), 5.35 (d, J = 11.7 Hz, 1H), 4.21 – 3.97 (m, 4H), 3.95 – 3.75 (m, 2H), 3.13 (s, 1H), 2.87 (s, 3H), 1.25 – 1.15 (m, 6H), 1.04 (t, J = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, DMSO)** δ 188.0 (m), 167.0, 154.9 (m), 144.3 (d, J = 6.3 Hz), 132.6, 132.2 (d, J = 2.1 Hz), 128.4, 127.6, 126.9, 94.2 (m), 62.6 (t, J = 7.0 Hz), 61.4, 45.6 (d, J = 131.2 Hz), 44.6, 37.1, 16.1 (d, J = 5.8 Hz), 15.9 (d, J = 5.7 Hz), 13.9. **HRMS (ESI)** Calcd. for $C_{19}H_{28}O_6NClP$: $[M + H]^+$, 432.1337. Found: *m/z* 432.1335.

Ethyl (E)-2-(2-chloro-6-(3-(dimethylamino)acryloyl)phenyl)-2-(diethoxyphosphoryl)acetate



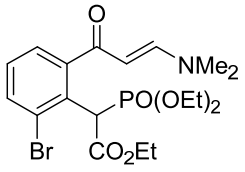
(3qb): The title compound was obtained as an orange solid in 64% yield (55.2 mg). $\mathbf{R_f}$ = 0.4 (DCM : MeOH, 20 : 1). **^{1}H NMR (400 MHz, DMSO)** δ 7.40 (m, 4H), 6.70 – 4.30 (br, 1H), 5.33 (d, J = 11.5 Hz, 1H), 4.17 – 4.00 (m, 4H), 3.84 (m, 2H), 3.11 (s, 3H), 2.85 (s, 3H), 1.16 (t, J = 7.0 Hz, 6H), 1.02 (t, J = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, DMSO)** δ 189.7 (m), 166.6, 154.9 (m), 145.0, 135.2, 130.6, 129.0, 128.7, 126.6, 94.4 (m), 62.2 (d, J = 6.5 Hz), 61.8 (d, J = 6.3 Hz), 61.2 (s), 46.2 (d, J = 165.1 Hz), 44.6, 37.0, 16.2 (d, J = 5.7 Hz), 16.0 (d, J = 5.7 Hz), 13.9. **HRMS (ESI)** Calcd. for $C_{19}H_{28}O_6NClP$: $[M + H]^+$, 432.1337. Found: *m/z* 432.1336.

Ethyl (E)-2-(4-bromo-2-(3-(dimethylamino)acryloyl)phenyl)-2-(diethoxyphosphoryl)acetate



(3ra): The title compound was obtained as an orange solid in 58% yield (55.0 mg). $\mathbf{R_f}$ = 0.6 (DCM : MeOH, 20 : 1). **^{1}H NMR (400 MHz, DMSO)** δ 7.68 (ddd, J = 22.5, 8.5, 2.0 Hz, 2H), 7.58 (s, 1H), 5.35 (d, J = 11.8 Hz, 1H), 4.20 – 3.98 (m, 4H), 3.95 – 3.75 (m, 2H), 3.13 (s, 3H), 2.87 (s, 3H), 1.20 (dd, J = 15.5, 7.1 Hz, 6H), 1.04 (t, J = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, DMSO)** δ 187.8 (m), 166.9, 155.1 (m), 144.6 (d, J = 4.9 Hz), 132.8, 131.3, 129.7, 128.0 (d, J = 4.4 Hz), 120.8 (d, J = 2.5 Hz), 94.3 (m), 62.8 – 62.5 (m), 61.4, 45.7 (d, J = 132.5 Hz), 44.6, 37.1, 16.1 (d, J = 5.7 Hz), 15.9 (d, J = 5.7 Hz), 13.9. **HRMS (ESI)** Calcd. for $C_{19}H_{28}O_6NBrP$: $[M + H]^+$, 476.0832. Found: *m/z* 476.0829.

Ethyl (E)-2-(2-bromo-6-(3-(dimethylamino)acryloyl)phenyl)-2-(diethoxyphosphoryl)acetate



(3rb): The title compound was obtained as an orange solid in 41% yield (38.8 mg). $\mathbf{R_f}$ = 0.5 (DCM : MeOH, 20 : 1). **^{1}H NMR (400 MHz, DMSO)** δ 7.65 (d, J = 7.9 Hz, 1H), 7.57 – 7.40 (m, 1H), 7.90 – 7.30 (br, 1H), 7.27 (t, J = 7.2 Hz, 1H), 6.15 (s, 1H), 5.32 (d, J = 10.9 Hz, 1H), 4.19 – 3.98 (m, 4H), 3.93 – 3.73 (m, 2H), 3.12 (s, 3H), 2.85 (s, 3H), 1.22 – 1.11 (m, 6H), 1.02 (t, J = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, DMSO)** δ 189.7 (m), 166.6, 154.6 (m), 145.5, 134.3, 130.5, 128.9, 127.1, 125.4, 94.7 (m), 62.2 (d, J = 6.1 Hz), 61.8 (d, J = 6.0 Hz), 61.2, 47.3 (d,

J = 141.4 Hz), 44.6, 37.0, 16.2 (d, J = 5.7 Hz), 16.0 (d, J = 5.6 Hz), 13.9. **HRMS (ESI)** Calcd. for $C_{19}H_{28}O_6NBrP$: $[M + H]^+$, 476.0832. Found: *m/z* 476.0833.

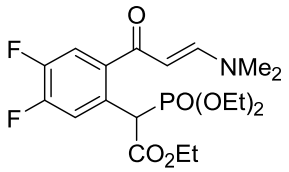
Ethyl (E)-2-(diethoxyphosphoryl)-2-(2-(3-(dimethylamino)acryloyl)-4-nitrophenyl)acetate (3sa): The title compound was obtained as a red oil in 42% yield (37.0 mg). $\mathbf{R_f}$ = 0.7 (DCM : MeOH, 20 : 1). **^{1}H NMR (400 MHz, DMSO)** δ 8.32 (dd, J = 8.7, 2.5 Hz, 1H), 8.18 (s, 1H), 8.03 (dd, J = 8.7, 2.1 Hz, 1H), 7.83 (s, 1H), 5.43 (s, 2H), 4.12 (m, 4H), 3.95 – 3.79 (m, 2H), 3.15 (s, 3H), 2.90 (s, 3H), 1.21 (m, 6H), 1.05 (t, J = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, DMSO)** δ 187.8 (m), 166.4, 155.2 (m), 146.5, 143.6, 136.1, 132.3, 123.0, 121.9, 93.6 (m), 62.9 (m), 61.7, 46.4 (d, J = 126.6 Hz), 44.7, 37.2, 16.1 (d, J = 5.8 Hz), 15.9 (d, J = 5.7 Hz), 13.8. **HRMS (ESI)** Calcd. for $C_{19}H_{28}O_8N_2P$: $[M + H]^+$, 443.1578. Found: *m/z* 443.1577.

Ethyl (E)-2-(diethoxyphosphoryl)-2-(2-(3-(dimethylamino)acryloyl)-6-nitrophenyl)acetate (3sb): The title compound was obtained as an orange solid in 39% yield (34.6 mg). $\mathbf{R_f}$ = 0.5 (DCM : MeOH, 20 : 1). **^{1}H NMR (400 MHz, DMSO)** δ 8.11 (d, J = 8.6 Hz, 1H), 7.80 (s, 1H), 7.64 (td, J = 8.0, 1.3 Hz, 1H), 5.85 (s, 1H), 5.35 (t, J = 11.2 Hz, 1H), 4.15 – 4.01 (m, 4H), 3.93 – 3.77 (m, 2H), 3.15 (s, 3H), 2.87 (s, 3H), 1.17 (dt, J = 11.2, 7.1 Hz, 6H), 1.04 (t, J = 6.9 Hz, 3H). **^{13}C NMR (101 MHz, DMSO)** δ 188.0 (m), 166.0, 154.8 (m), 148.7, 145.9, 132.8, 129.0, 125.7, 124.5 (d, J = 4.7 Hz), 94.4 (m), 62.6 (d, J = 6.3 Hz), 62.0 (d, J = 6.5 Hz), 61.2, 47.2 (d, J = 184.0 Hz), 44.7, 37.1, 16.1 (d, J = 5.9 Hz), 15.9 (d, J = 5.8 Hz), 13.8. **HRMS (ESI)** Calcd. for $C_{19}H_{28}O_8N_2P$: $[M + H]^+$, 443.1578. Found: *m/z* 443.1574.

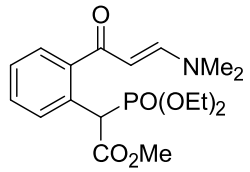
Ethyl (E)-2-(diethoxyphosphoryl)-2-(2-(3-(dimethylamino)acryloyl)-3-fluorophenyl)acetate (3t): The title compound was obtained as an orange oil in 99% yield (82.0 mg). $\mathbf{R_f}$ = 0.7 (DCM : MeOH, 20 : 1). **^{1}H NMR (400 MHz, DMSO)** δ 7.44 (d, J = 6.2 Hz, 1H), 7.21 (t, J = 8.7 Hz, 1H), 7.20 (dd, J = 374, 113.5 Hz, 1H), 5.25 (s, 1H), 4.47 (dd, J = 167.3, 23.7 Hz, 1H), 4.14 – 4.00 (m, 4H), 3.98 – 3.77 (m, 2H), 3.23 – 2.87 (m, 3H), 2.83 (s, 3H), 1.25 – 1.15 (m, 6H), 1.05 (s, 3H). **^{13}C NMR (101 MHz, DMSO)** δ 185.6 (d, J = 205.5 Hz), 166.7, 158.7 (d, J = 94.2 Hz), 157.1 (d, J = 59.8 Hz), 153.4 (m), 130.1, 129.1, 126.3, 114.9 (d, J = 21.8 Hz), 98.1 (d, J = 393.9 Hz), 62.7 (d, J = 5.8 Hz), 61.5, 46.9 (d, J = 102.0 Hz), 44.5, 36.9, 16.1 (d, J = 5.6 Hz), 15.9, 13.8. **HRMS (ESI)** Calcd. for $C_{19}H_{28}O_6NFP$: $[M + H]^+$, 416.1633. Found: *m/z* 416.1630.

Ethyl (E)-2-(diethoxyphosphoryl)-2-(2-(3-(dimethylamino)acryloyl)-4,5-dimethoxyphenyl) acetate (3u): The title compound was obtained as a yellow solid in 96% yield (87.7 mg). $\mathbf{R_f}$ = 0.4 (DCM : MeOH, 20 : 1). **^{1}H NMR (400 MHz, DMSO)** δ 7.51 (s, 1H), 7.36 (d, J = 1.9 Hz, 1H), 6.99 (s, 1H), 5.38 (d, J = 12.4 Hz, 2H), 4.19 – 3.97 (m, 4H), 3.97 – 3.81 (m, 2H), 3.80 (s, 3H), 3.77 (s, 3H), 3.11 (s, 3H), 2.86 (s, 3H), 1.23 – 1.15 (m, 6H), 1.05 (t, J = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, DMSO)** δ 189.5 (m), 167.5 (d, J = 2.7 Hz), 154.6 (m), 148.4, 147.5, 135.1 (d, J = 8.4 Hz), 121.3 (d, J = 5.9 Hz), 113.8 (d, J = 3.6 Hz),

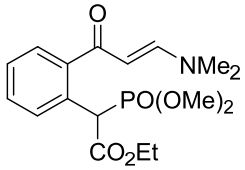
111.1, 95.4 (m), 62.5 (d, *J* = 6.6 Hz), 62.3 (d, *J* = 6.7 Hz), 61.1, 55.5, 55.4 45.3 (d, *J* = 132.2 Hz), 44.4, 37.0, 16.2 (d, *J* = 5.8 Hz), 16.0 (d, *J* = 5.8 Hz), 13.9. **HRMS (ESI)** Calcd. for $C_{21}H_{33}O_8NP$: $[M + H]^+$, 458.1938. Found: *m/z* 458.1934.

Ethyl (E)-2-(diethoxyphosphoryl)-2-(2-(3-(dimethylamino)acryloyl)-4,5-difluorophenyl) acetate (**3v**): 

The title compound was obtained as an orange solid in 96% yield (83.0 mg). $\mathbf{R_f}$ = 0.4 (DCM : MeOH, 20 : 1). **^{1}H NMR (400 MHz, DMSO)** δ 7.64 (s, 1H), 7.51 – 7.26 (m, 2H), 5.83 (s, 1H), 5.38 (d, *J* = 12.0 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 4.11 – 4.03 (m, 2H), 4.00 – 3.86 (m, 2H), 3.13 (s, 3H), 2.87 (s, 3H), 1.22 – 1.15 (m, 6H), 1.09 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, DMSO)** δ 187.8 (m), 166.0, 155.3, 149.9 (dd, *J* = 248.4, 13.7 Hz), 148.9 (ddd, *J* = 250.8, 13.3, 4.6 Hz), 139.1 (d, *J* = 3.3 Hz), 124.1, 121.5, 116.2 (d, *J* = 16.7 Hz), 94.7 (m), 62.6 (d, *J* = 6.5 Hz), 62.2 (d, *J* = 6.5 Hz), 61.4, 44.6, 43.2, 37.1, 16.1 (d, *J* = 5.8 Hz), 16.0 (d, *J* = 5.8 Hz), 13.8. **HRMS (ESI)** Calcd. for $C_{19}H_{27}O_6NF_2P$: $[M + H]^+$, 434.1539. Found: *m/z* 434.1536.

Methyl (E)-2-(diethoxyphosphoryl)-2-(2-(3-(dimethylamino)acryloyl)phenyl)acetate (**3w**): 

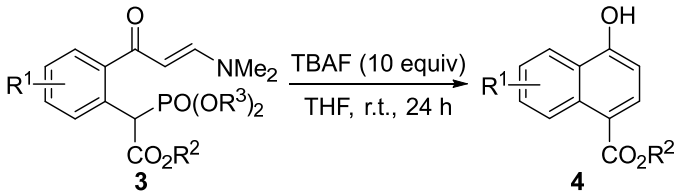
The title compound was obtained as a red oil in 92% yield (70.7 mg). $\mathbf{R_f}$ = 0.3 (DCM : MeOH, 20 : 1). **^{1}H NMR (400 MHz, DMSO)** δ 7.77 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.71 – 7.40 (m, 3H), 7.39 – 7.33 (m, 1H), 5.67 – 5.00 (m, 2H), 4.02 (dq, *J* = 14.1, 7.1 Hz, 2H), 3.92 – 3.72 (m, 2H), 3.66 (s, 3H), 3.11 (s, 3H), 2.85 (s, 3H), 1.19 (t, *J* = 7.0 Hz, 3H), 1.01 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, DMSO)** δ 190.0 (m), 167.87 (d, *J* = 3.0 Hz), 155.0 (m), 142.4 (d, *J* = 7.9 Hz), 130.6, 130.6, 128.5, 127.5, 127.4, 95.3 (m), 62.6 (d, *J* = 6.8 Hz), 62.4 (d, *J* = 6.9 Hz), 52.5, 45.9 (d, *J* = 131.6 Hz), 44.5, 37.0, 16.1 (d, *J* = 5.7 Hz), 15.9 (d, *J* = 5.7 Hz). **HRMS (ESI)** Calcd. for $C_{18}H_{27}O_6NP$: $[M + H]^+$, 384.1571. Found: *m/z* 384.1568.

Ethyl (E)-2-(dimethoxyphosphoryl)-2-(2-(3-(dimethylamino)acryloyl)phenyl)acetate (**3x**): 

The title compound was obtained as a red oil in 92% yield (68.0 mg). $\mathbf{R_f}$ = 0.3 (DCM : MeOH, 20 : 1). **^{1}H NMR (400 MHz, DMSO)** δ 7.75 (d, *J* = 7.4 Hz, 1H), 7.64 – 7.39 (m, 3H), 7.35 (dd, *J* = 10.5, 4.3 Hz, 1H), 5.68 – 4.97 (m, 2H), 4.20 – 4.04 (m, 2H), 3.66 (d, *J* = 11.0 Hz, 3H), 3.47 (d, *J* = 10.9 Hz, 3H), 3.10 (s, 3H), 2.85 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, DMSO)** δ 190.1 (m), 167.2, 154.8 (m), 142.3 (d, *J* = 7.9 Hz), 130.6 (d, *J* = 3.8 Hz), 128.6, 128.4 (d, *J* = 6.5 Hz), 127.5, 127.4, 95.5 (m), 61.4, 53.3 (d, *J* = 5.7 Hz), 45.4 (d, *J* = 131.3 Hz), 44.5, 37.0, 13.9. **HRMS (ESI)** Calcd. for $C_{17}H_{25}O_6NP$: $[M + H]^+$, 370.1414. Found: *m/z* 370.1412.

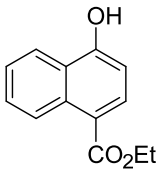
5. Synthesis and Characterization of Cyclization Products

General procedure for the synthesis of cyclization products:

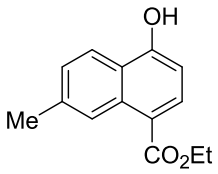


To a 13 × 150 mm test tube equipped with magnetic stir bar was added the substrate **3a**-**3x** (0.2 mmol, 1 equiv). The test tube was transferred to a glovebox. After the test tube was sealed with a rubber septum and removed from the glovebox, TBAF (2 mL, 1M in THF, 10 equiv) was then injected into the tube. The reaction mixture was stirred for 24 h at ambient temperature, during which time a constant checking by TLC was performed. The reaction mixture was quenched with HOAc and filtered over a thin layer of silica gel and then washed with EA (3 × 10 mL). The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography on silica gel with PE/EA (5 : 1) as the eluent.

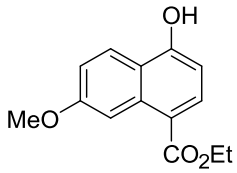
Ethyl 4-hydroxy-1-naphthoate (4a): The title compound was obtained as a white solid in 92% yield (39.9 mg). $\mathbf{R_f}$ = 0.6 (PE : EA, 5 : 1). **^{1}H NMR (500 MHz, DMSO)** δ 11.16 (s, 1H), 8.95 (d, *J* = 8.7 Hz, 1H), 8.30 – 8.22 (m, 1H), 8.14 (d, *J* = 8.2 Hz, 1H), 7.64 (ddd, *J* = 8.5, 6.8, 1.4 Hz, 1H), 7.52 (ddd, *J* = 8.1, 6.8, 1.0 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 166.9, 158.6, 133.3, 133.2, 128.6, 125.6, 125.4, 125.0, 123.0, 116.9, 107.5, 60.6, 14.7. **HRMS (ESI)** Calcd. for $C_{13}H_{13}O_3$: $[M + H]^+$, 217.0859. Found: *m/z* 217.0858.



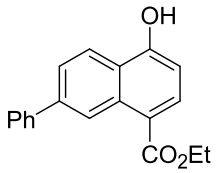
Ethyl 4-hydroxy-7-methyl-1-naphthoate (4b): The title compound was obtained as a white solid in 89% yield (40.8 mg). $\mathbf{R_f}$ = 0.5 (PE : EA, 5 : 1). **^{1}H NMR (500 MHz, DMSO)** δ 11.06 (s, 1H), 8.75 (s, 1H), 8.15 (d, *J* = 8.5 Hz, 1H), 8.09 (d, *J* = 8.2 Hz, 1H), 7.35 (dd, *J* = 8.6, 1.5 Hz, 1H), 6.87 (d, *J* = 8.2 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.49 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 167.0, 158.6, 138.0, 133.6, 133.2, 127.4, 124.7, 123.2, 123.0, 116.2, 106.8, 60.5, 22.3, 14.8. **HRMS (ESI)** Calcd. for $C_{14}H_{15}O_3$: $[M + H]^+$, 231.1016. Found: *m/z* 231.1014.



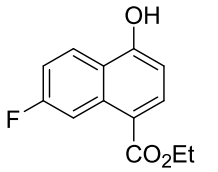
Ethyl 4-hydroxy-7-methoxy-1-naphthoate (4c): The title compound was obtained as a white solid in 80% yield (39.5 mg). $\mathbf{R_f}$ = 0.5 (PE : EA, 5 : 1). **^{1}H NMR (500 MHz, DMSO)** δ 11.08 (s, 1H), 8.49 (d, *J* = 2.6 Hz, 1H), 8.16 (t, *J* = 8.7 Hz, 2H), 7.17 (dd, *J* = 9.2, 2.6 Hz, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.88 (s, 3H), 1.36 (s, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 167.0, 159.6, 158.9, 135.3, 134.2, 124.8, 120.1, 117.3, 115.3, 106.0, 104.8, 60.4, 55.4, 14.8. **HRMS (ESI)** Calcd. for $C_{14}H_{15}O_4$: $[M + H]^+$, 247.0965. Found: *m/z* 247.0963.



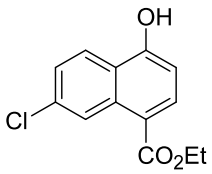
Ethyl 4-hydroxy-7-phenyl-1-naphthoate (4d): The title compound was obtained as a white solid in 97% yield (56.7 mg). $\mathbf{R_f}$ = 0.6 (PE : EA, 5 : 1). **^{1}H NMR (500 MHz, DMSO)** δ 11.24 (s, 1H), 9.30 (d, *J* = 1.6 Hz, 1H), 8.35 (d, *J* = 8.7 Hz, 1H), 8.19 (d, *J* = 8.2 Hz, 1H), 7.84 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.80 – 7.75 (m, 2H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 167.0, 158.6, 140.8, 140.1, 133.9, 133.7, 129.6, 128.3, 127.5, 124.5, 124.2, 123.9, 123.5, 116.9, 107.7, 60.6, 14.8. **HRMS (ESI)** Calcd. for $C_{19}H_{17}O_3$: $[M + H]^+$, 293.1172. Found: *m/z* 293.1169.



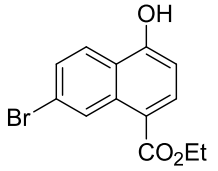
Ethyl 7-fluoro-4-hydroxy-1-naphthoate (4e): The title compound was obtained as a white solid in 86% yield (40.2 mg). $\mathbf{R_f}$ = 0.5 (PE : EA, 5 : 1). **^{1}H NMR (500 MHz, DMSO)** δ 11.38 (s, 1H), 8.71 (dd, *J* = 12.9, 2.6 Hz, 1H), 8.31 (dd, *J* = 9.3, 6.4 Hz, 1H), 8.22 (d, *J* = 8.3 Hz, 1H), 7.42 (ddd, *J* = 9.2, 8.1, 2.7 Hz, 1H), 6.93 (d, *J* = 8.3 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 166.6, 163.3, 161.3, 159.0, 134.9, 134.6 (d, *J* = 10.6 Hz), 126.4 (d, *J* = 9.8 Hz), 122.2, 115.8 (d, *J* = 5.1 Hz), 115.4, 115.2, 109.6, 109.4, 107.3 (d, *J* = 1.0 Hz), 60.7, 14.7. **^{13}C NMR (126 MHz, DMSO)** δ 166.6, 162.3 (d, *J* = 244.2 Hz), 159.0, 134.9, 134.6 (d, *J* = 10.6 Hz), 126.4 (d, *J* = 9.8 Hz), 122.2, 115.8 (d, *J* = 5.1 Hz), 115.3 (d, *J* = 25.2 Hz), 109.5 (d, *J* = 24.1 Hz), 107.3 (d, *J* = 1.0 Hz), 60.7, 14.7. **HRMS (ESI)** Calcd. for $C_{14}H_{15}O_3$: $[M + H]^+$, 235.0765. Found: *m/z* 235.0765.



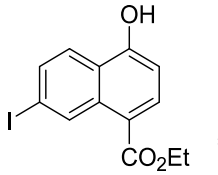
Ethyl 7-chloro-4-hydroxy-1-naphthoate (4f): The title compound was obtained as a white solid in 82% yield (41.0 mg). $\mathbf{R_f}$ = 0.5 (PE : EA, 5 : 1). **^{1}H NMR (500 MHz, DMSO)** δ 11.42 (s, 1H), 9.05 (d, *J* = 2.1 Hz, 1H), 8.25 (d, *J* = 9.0 Hz, 1H), 8.20 (d, *J* = 8.2 Hz, 1H), 7.53 (dd, *J* = 9.0, 2.2 Hz, 1H), 6.96 (d, *J* = 8.3 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 166.5, 158.9, 134.7, 134.0, 134.0, 125.9, 125.5, 124.5, 123.4, 115.6, 108.1, 60.8, 14.7. **HRMS (ESI)** Calcd. for $C_{13}H_{12}O_3Cl$: $[M + H]^+$, 251.0469. Found: *m/z* 251.0468.



Ethyl 7-bromo-4-hydroxy-1-naphthoate (4g): The title compound was obtained as a white solid in 81% yield (47.9 mg). $\mathbf{R_f}$ = 0.5 (PE : EA, 5 : 1). **^{1}H NMR (500 MHz, DMSO)** δ 11.42 (s, 1H), 9.22 (d, *J* = 2.0 Hz, 1H), 8.18 (t, *J* = 8.5 Hz, 2H), 7.65 (dd, *J* = 9.0, 2.0 Hz, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 166.5, 158.9, 134.6, 134.4, 128.4, 127.7, 125.5, 123.6, 123.0, 115.6, 108.2, 60.8, 14.7. **HRMS (ESI)** Calcd. for $C_{13}H_{12}O_3Br$: $[M + H]^+$, 294.9964. Found: *m/z* 294.9962.



Ethyl 4-hydroxy-7-iodo-1-naphthoate (4h): The title compound was obtained as a white solid in 71% yield (48.4 mg). $\mathbf{R_f}$ = 0.5 (PE : EA, 5 : 1). **^{1}H NMR (500 MHz, DMSO)** δ 11.37 (s, 1H), 9.43 (d, *J* = 1.7 Hz, 1H), 8.16 (d, *J* = 8.2 Hz, 1H), 8.00 (d, *J* = 8.8 Hz, 1H), 7.79 (dd, *J* = 8.8, 1.7 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 166.5,



158.9, 134.6, 134.3, 134.2, 133.7, 125.1, 123.8, 115.4, 108.2, 96.7, 60.7, 14.7. **HRMS (ESI)** Calcd. for $C_{13}H_{12}O_3I$: $[M + H]^+$, 342.9826. Found: *m/z* 342.9824.

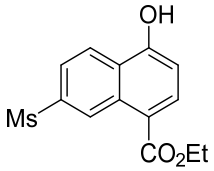
Ethyl 4-hydroxy-7-(trifluoromethyl)-1-naphthoate (4i): The title compound was obtained as a white solid in 82% yield (46.7 mg). $\mathbf{R_f}$ = 0.5 (PE : EA, 5 : 1). **^{1}H NMR (500 MHz, DMSO)** δ 11.58 (s, 1H), 9.42 (s, 1H), 8.43 (d, *J* = 8.8 Hz, 1H), 8.28 (d, *J* = 8.2 Hz, 1H), 7.75 (dd, *J* = 8.8, 1.7 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, DMSO) δ 166.44 (s), 158.61 (s), 134.84 (s), 132.12 (s), 128.98 (s), 128.73 (s), 128.48 (s), 128.20 (d, *J* = 8.0 Hz), 126.47 (s), 126.01 (s), 124.91 (s), 123.84 (s), 123.32 (q, *J* = 4.7 Hz), 121.68 (s), 120.60 (d, *J* = 3.0 Hz), 117.07 (s), 109.71 (s), 60.91 (s), 14.60 (s). **^{13}C NMR (126 MHz, DMSO)** δ 166.4, 158.6, 134.8, 132.1, 128.6 (q, *J* = 31.3 Hz), 126.5,124.9 (q, *J* = 272.3 Hz), 124.9, 123.3 (q, *J* = 4.7 Hz), 120.6 (q, *J* = 3.0 Hz), 117.1, 109.7, 60.9, 14.6. **HRMS (ESI)** Calcd. for $C_{14}H_{12}O_3F_3$: $[M + H]^+$, 285.0733. Found: *m/z* 285.0731.

1-Ethyl 7-methyl 4-hydroxynaphthalene-1,7-dicarboxylate (4j): The title compound was obtained as a white solid in 93% yield (51.1 mg). $\mathbf{R_f}$ = 0.5 (PE : EA, 5 : 1). **^{1}H NMR (500 MHz, DMSO)** δ 11.41 (s, 1H), 9.69 (d, *J* = 1.3 Hz, 1H), 8.32 (d, *J* = 8.8 Hz, 1H), 8.20 (d, *J* = 8.2 Hz, 1H), 7.97 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.06 (d, *J* = 8.2 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.92 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 166.9, 166.5, 158.5, 134.1, 132.4, 129.2, 128.4, 127.1, 124.3, 123.7, 117.7, 109.6, 60.8, 52.8, 14.7. **HRMS (ESI)** Calcd. for $C_{15}H_{15}O_5$: $[M + H]^+$, 275.0914. Found: *m/z* 275.0913.

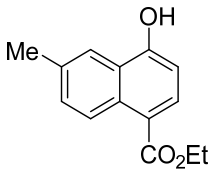
Ethyl 4-hydroxy-7-nitro-1-naphthoate (4k): The title compound was obtained as a yellow solid in 98% yield (51.3 mg). $\mathbf{R_f}$ = 0.4 (PE : EA, 5 : 1). **^{1}H NMR (500 MHz, DMSO)** δ 11.65 (s, 1H), 9.82 (d, *J* = 2.3 Hz, 1H), 8.31 (d, *J* = 9.2 Hz, 1H), 8.22 (d, *J* = 8.3 Hz, 1H), 8.11 (dd, *J* = 9.2, 2.4 Hz, 1H), 7.07 (d, *J* = 8.3 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 166.0, 158.6, 147.0, 135.3, 131.9, 127.3, 125.2, 122.1, 118.3, 117.7, 110.8, 61.0, 14.6. **HRMS (ESI)** Calcd. for $C_{13}H_{12}O_5N$: $[M + H]^+$, 262.0710. Found: *m/z* 262.0708.

Ethyl 7-cyano-4-hydroxy-1-naphthoate (4l): The title compound was obtained as a white solid in 91% yield (43.8 mg). $\mathbf{R_f}$ = 0.5 (PE : EA, 5 : 1). **^{1}H NMR (500 MHz, DMSO)** δ 11.60 (s, 1H), 9.35 (d, *J* = 1.2 Hz, 1H), 8.32 (d, *J* = 8.7 Hz, 1H), 8.22 (d, *J* = 8.3 Hz, 1H), 7.74 (dd, *J* = 8.7, 1.6 Hz, 1H), 7.07 (d, *J* = 8.3 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 166.2, 158.5, 134.9, 132.0, 131.7, 126.3, 125.8, 124.7, 119.7, 116.6, 111.1, 110.3, 61.0, 14.6. **HRMS (ESI)** Calcd. for $C_{14}H_{12}O_3N$: $[M + H]^+$, 242.0812. Found: *m/z* 242.0810.

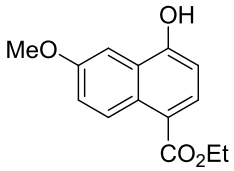
Ethyl 4-hydroxy-7-(methylsulfonyl)-1-naphthoate (4m): The title compound was obtained as a white solid in 89% yield (52.3 mg). $\mathbf{R_f}$ = 0.3 (PE : EA, 5 : 1). **^{1}H NMR (500 MHz, DMSO)** δ 11.62 (s, 1H), 9.63 (d, *J* = 1.7 Hz, 1H), 8.47 (d, *J* = 8.8 Hz, 1H), 8.30 (d, *J* = 8.2 Hz, 1H), 7.98 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.14 (d, *J* = 8.2 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.29 (s, 3H), 1.38 (s, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 166.4, 158.6, 140.5, 134.9, 132.0, 126.8, 126.0, 125.0, 122.0, 117.7, 110.3, 61.0, 44.0, 14.7. **HRMS (ESI)** Calcd. for $C_{14}H_{15}O_5S$: $[M + H]^+$, 295.0635. Found: *m/z* 295.0634.



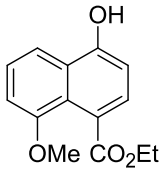
Ethyl 4-hydroxy-6-methyl-1-naphthoate (4na): The title compound was obtained as a white solid in 90% yield (41.5 mg). $\mathbf{R_f}$ = 0.5 (PE : EA, 5 : 1). **^{1}H NMR (500 MHz, DMSO)** δ 11.04 (s, 1H), 8.85 (d, *J* = 8.8 Hz, 1H), 8.06 (d, *J* = 8.1 Hz, 1H), 8.04 (s, 1H), 7.47 (dd, *J* = 8.9, 1.9 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.47 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 167.0, 158.1, 134.6, 132.2, 131.5, 130.6, 125.6, 125.2, 121.9, 116.8, 107.5, 60.5, 21.7, 14.7. **HRMS (ESI)** Calcd. for $C_{14}H_{15}O_3$: $[M + H]^+$, 231.1016. Found: *m/z* 231.1015.



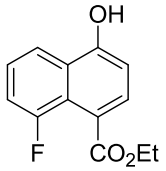
Ethyl 4-hydroxy-6-methoxy-1-naphthoate (4oa): The title compound was obtained as a white solid in 89% yield (43.7 mg). $\mathbf{R_f}$ = 0.5 (PE : EA, 5 : 1). **^{1}H NMR (500 MHz, DMSO)** δ 11.04 (s, 1H), 8.88 (d, *J* = 9.4 Hz, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.56 (d, *J* = 2.8 Hz, 1H), 7.29 (dd, *J* = 9.4, 2.8 Hz, 1H), 6.93 (d, *J* = 8.1 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 167.0, 157.4, 156.9, 130.6, 128.5, 127.5, 126.3, 120.7, 117.0, 107.9, 101.4, 60.5, 55.5, 14.7. **HRMS (ESI)** Calcd. for $C_{14}H_{15}O_4$: $[M + H]^+$, 247.0965. Found: *m/z* 247.0963.



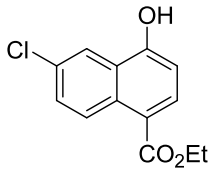
Ethyl 4-hydroxy-8-methoxy-1-naphthoate (4ob): The title compound was obtained as a white solid in 85% yield (42.0 mg). $\mathbf{R_f}$ = 0.5 (PE : EA, 5 : 1). **^{1}H NMR (500 MHz, DMSO)** δ 10.56 (s, 1H), 7.81 – 7.76 (m, 1H), 7.46 – 7.40 (m, 1H), 7.26 (d, *J* = 7.8 Hz, 1H), 7.04 (d, *J* = 7.3 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 171.1, 154.7, 126.2, 126.0, 122.9, 121.1, 115.0, 107.8, 107.2, 60.9, 56.3, 14.7. **HRMS (ESI)** Calcd. for $C_{14}H_{15}O_4$: $[M + H]^+$, 247.0965. Found: *m/z* 247.0964.



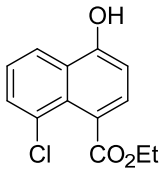
Ethyl 8-fluoro-4-hydroxy-1-naphthoate (4pb): The title compound was obtained as a white solid in 83% yield (38.7 mg). $\mathbf{R_f}$ = 0.5 (PE : EA, 5 : 1). **^{1}H NMR (500 MHz, DMSO)** δ 11.02 (s, 1H), 8.06 (dd, *J* = 8.4, 1.0 Hz, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.54 – 7.49 (m, 1H), 7.40 (ddd, *J* = 12.6, 7.7, 1.0 Hz, 1H), 6.97 (d, *J* = 7.9 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 169.5, 157.6 (d, *J* = 250.3 Hz), 155.7 (d, *J* = 4.3 Hz), 129.0, 126.7 (d, *J* = 5.1 Hz), 125.9 (d, *J* = 8.8 Hz), 121.1 (d, *J* = 15.1 Hz), 119.2 (d, *J* = 3.8 Hz), 118.6, 112.8 (d, *J* = 21.1 Hz), 108.3, 61.3, 14.5. **HRMS (ESI)** Calcd. for $C_{13}H_{12}O_3F$: $[M + H]^+$, 235.0765. Found: *m/z* 235.0763.



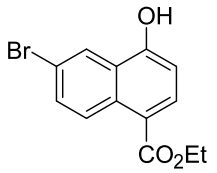
Ethyl 6-chloro-4-hydroxy-1-naphthoate (4qa): The title compound was obtained as a white solid in 98% yield (49.2 mg). $\mathbf{R_f}$ = 0.5 (PE : EA, 5 : 1). **^{1}H NMR (500 MHz, DMSO)** δ 11.41 (s, 1H), 8.97 (d, *J* = 9.3 Hz, 1H), 8.20 (d, *J* = 2.4 Hz, 1H), 8.15 (d, *J* = 8.2 Hz, 1H), 7.64 (dd, *J* = 9.3, 2.4 Hz, 1H), 6.99 (d, *J* = 8.2 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 166.6, 157.7, 133.6, 131.6, 130.4, 128.9, 128.1, 125.9, 121.8, 116.9, 108.6, 60.8, 14.7. **HRMS (ESI)** Calcd. for $C_{13}H_{12}O_3Cl$: $[M + H]^+$, 251.0469. Found: *m/z* 251.0467.



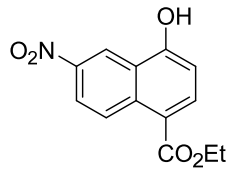
Ethyl 8-chloro-4-hydroxy-1-naphthoate (4qb): The title compound was obtained as a white solid in 86% yield (43.0 mg). $\mathbf{R_f}$ = 0.5 (PE : EA, 5 : 1). **^{1}H NMR (500 MHz, DMSO)** δ 11.05 (s, 1H), 8.26 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.73 (dd, *J* = 7.4, 1.1 Hz, 1H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.50 (dd, *J* = 8.3, 7.6 Hz, 1H), 6.98 (d, *J* = 7.9 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 170.2, 155.9, 130.1, 129.9, 129.5, 128.4, 126.8, 126.0, 122.6, 121.5, 108.0, 61.5, 14.3. **HRMS (ESI)** Calcd. for $C_{13}H_{12}O_3Cl$: $[M + H]^+$, 251.0469. Found: *m/z* 251.0469.



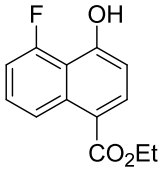
Ethyl 6-bromo-4-hydroxy-1-naphthoate (4ra): The title compound was obtained as a white solid in 95% yield (56.1 mg). $\mathbf{R_f}$ = 0.5 (PE : EA, 5 : 1). **^{1}H NMR (500 MHz, DMSO)** δ 11.42 (s, 1H), 8.89 (d, *J* = 9.3 Hz, 1H), 8.36 (d, *J* = 2.2 Hz, 1H), 8.16 (d, *J* = 8.2 Hz, 1H), 7.75 (dd, *J* = 9.3, 2.2 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 166.5, 157.6, 133.7, 131.8, 131.5, 128.2, 126.3, 125.1, 118.9, 116.9, 108.7, 60.8, 14.7. **HRMS (ESI)** Calcd. for $C_{13}H_{12}O_3Br$: $[M + H]^+$, 294.9964. Found: *m/z* 294.9962.



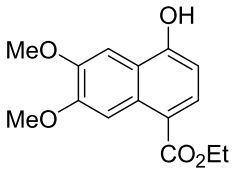
Ethyl 4-hydroxy-6-nitro-1-naphthoate (4sa): The title compound was obtained as a yellow solid in 99% yield (51.6 mg). $\mathbf{R_f}$ = 0.5 (PE : EA, 5 : 1). **^{1}H NMR (500 MHz, DMSO)** δ 11.92 (s, 1H), 9.01 (d, *J* = 9.5 Hz, 1H), 8.95 (d, *J* = 2.5 Hz, 1H), 8.26 (d, *J* = 8.3 Hz, 1H), 8.22 (dd, *J* = 9.5, 2.6 Hz, 1H), 7.03 (d, *J* = 8.3 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 166.1, 160.1, 144.2, 137.0, 135.7, 127.6, 123.8, 121.3, 119.6, 116.7, 109.4, 61.0, 14.6. **HRMS (ESI)** Calcd. for $C_{13}H_{12}O_5N$: $[M + H]^+$, 251.0469. Found: *m/z* 251.0467.



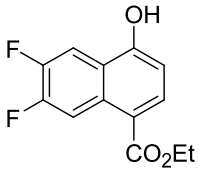
Ethyl 5-fluoro-4-hydroxy-1-naphthoate (4t): The title compound was obtained as a white solid in 68% yield (31.9 mg). $\mathbf{R_f}$ = 0.6 (PE : EA, 10 : 1). **^{1}H NMR (500 MHz, DMSO)** δ 11.11 (s, 1H), 8.73 (d, *J* = 8.7 Hz, 1H), 8.12 (d, *J* = 8.3 Hz, 1H), 7.60 – 7.54 (m, 1H), 7.23 (dd, *J* = 13.1, 7.7 Hz, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 166.9, 159.5 (d, *J* = 257.3 Hz), 158.6 (d, *J* = 3.6 Hz), 135.8 (d, *J* = 2.8 Hz), 133.9, 128.7 (d, *J* = 9.1 Hz), 121.7 (d, *J* = 4.6 Hz), 116.9 (d, *J* = 2.8 Hz), 115.1 (d, *J* = 9.8 Hz), 111.1 (d, *J* = 21.3 Hz), 109.5, 60.8, 14.7. **HRMS (ESI)** Calcd. for $C_{13}H_{12}O_3F$: $[M + H]^+$, 235.0765. Found: *m/z* 235.0763.



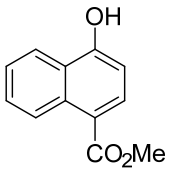
Ethyl 4-hydroxy-6,7-dimethoxy-1-naphthoate (4u): The title compound was obtained as a white solid in 97% yield (53.6 mg). $\mathbf{R_f}$ = 0.5 (PE : EA, 5 : 1). **^{1}H NMR (500 MHz, DMSO)** δ 10.95 (s, 1H), 8.51 (s, 1H), 8.02 (d, *J* = 8.3 Hz, 1H), 7.52 (s, 1H), 6.83 (d, *J* = 8.3 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 3.90 (m, 6H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 167.2, 157.5, 151.3, 148.6, 131.4, 129.8, 120.3, 115.2, 106.5, 105.2, 101.8, 60.4, 55.6, 55.6, 14.7. **HRMS (ESI)** Calcd. for $C_{15}H_{17}O_5$: $[M + H]^+$, 277.1071. Found: *m/z* 277.1069.



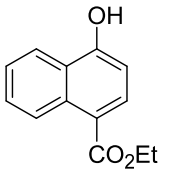
Ethyl 6,7-difluoro-4-hydroxy-1-naphthoate (4v): The title compound was obtained as a white solid in 97% yield (49.0 mg). $\mathbf{R_f}$ = 0.6 (PE : EA, 5 : 1). **^{1}H NMR (500 MHz, DMSO)** δ 11.25 (s, 1H), 8.09 (ddd, *J* = 9.1, 5.1, 1.2 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.61 (td, *J* = 9.7, 7.8 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 168.8, 156.2, 148.4 (dd, *J* = 245.6, 12.3 Hz), 144.2 (dd, *J* = 250.8, 13.3 Hz), 131.0, 122.7 (d, *J* = 3.5 Hz), 122.3 (d, *J* = 11.4 Hz), 120.6 (dd, *J* = 8.1, 4.7 Hz), 118.1 (d, *J* = 6.1 Hz), 116.3 (d, *J* = 20.5 Hz), 107.8, 61.4, 14.4. **HRMS (ESI)** Calcd. for $C_{13}H_{10}O_3F_2$: $[M + H]^+$, 253.0671. Found: *m/z* 253.0669.



Methyl 4-hydroxy-1-naphthoate (4w): The title compound was obtained as a white solid in 94% yield (38.1 mg). $\mathbf{R_f}$ = 0.6 (PE : EA, 5 : 1). **^{1}H NMR (500 MHz, DMSO)** δ 11.18 (s, 1H), 8.95 (d, *J* = 8.7 Hz, 1H), 8.27 (d, *J* = 8.3 Hz, 1H), 8.14 (d, *J* = 8.2 Hz, 1H), 7.64 (ddd, *J* = 8.5, 6.8, 1.4 Hz, 1H), 7.53 (ddd, *J* = 8.0, 6.9, 1.0 Hz, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 3.87 (s, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 167.4, 158.7, 133.3, 133.3, 128.7, 125.6, 125.4, 125.0, 123.0, 116.5, 107.5, 52.1. **HRMS (ESI)** Calcd. for $C_{12}H_{11}O_3$: $[M + H]^+$, 203.0703. Found: *m/z* 203.0701.

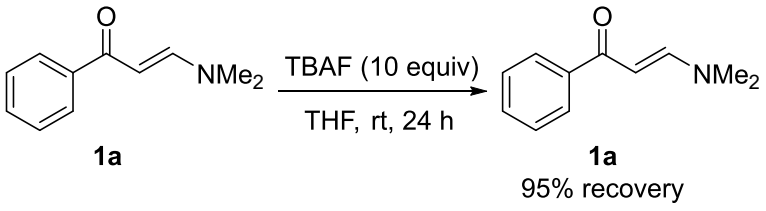


Ethyl 4-hydroxy-1-naphthoate (4x): The title compound was obtained as a white solid in 72% yield (31.2 mg). $\mathbf{R_f}$ = 0.6 (PE : EA, 5 : 1). **^{1}H NMR (500 MHz, DMSO)** δ 11.15 (s, 1H), 8.95 (d, *J* = 8.7 Hz, 1H), 8.26 (d, *J* = 8.1 Hz, 1H), 8.14 (d, *J* = 8.2 Hz, 1H), 7.64 (ddd, *J* = 8.5, 6.8, 1.3 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, DMSO)** δ 166.9, 158.5, 133.3, 133.2, 128.6, 125.6, 125.4, 125.0, 123.0, 116.9, 107.5, 60.6, 14.8.



6. Mechanism Studies of Cyclization

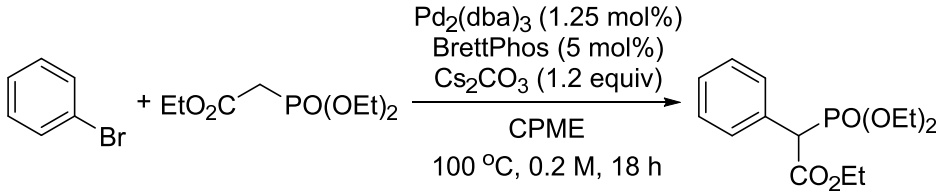
Control experiment of 1a with TBAF treatment:



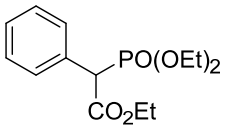
(S1)

To a 13 × 150 mm test tube equipped with magnetic stir bar was added the substrate **1a** (35 mg, 0.2 mmol, 1 equiv). The test tube was transferred to a glovebox. After the test tube was sealed with a rubber septum and removed from the glovebox, TBAF (2 mL, 1M in THF, 10 equiv) was then injected into the tube. The reaction mixture was stirred for 24 h at ambient temperature, during which time a constant checking by TLC was performed. The reaction mixture was quenched with HOAc and filtered over a thin layer of silica gel and then washed with EA (3 × 10 mL). The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography with PE/EA (1 : 1) as the eluent. and the eluates were analyzed by NMR experiments.

Procedure for the synthesis of 5:



Phosphoryl phenylacetate was synthesized and characterized according to the literature.[3] The specific procedure is: In a glovebox, a 100 mL flask containing a magnetic stir bar was charged with Cs_2CO_3 (3.9 g, 12 mmol), $Pd_2(dba)_3$ (115 mg, 0.125 mmol) and BrettPhos (290 mg, 0.5 mmol). The flask was capped and brought out of the glovebox. 50 mL CPME was added via syringe, followed by Bromobenzene (1.2 mL, 11 mmol) and triethyl phosphonoacetate (2.0 mL, 10 mmol). The flask was sparged with dry nitrogen and then heated to 100 °C in an oil bath with vigorous stirring for 18 h. The reaction mixture was allowed to cool to room temperature and then quenched with 50 mL of 1.0 M HCl. This mixture was diluted with H_2O and extracted with EtOAc (3 × 100 mL). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The resulting residue was purified by flash column chromatography with DCM/MeOH (50 : 1) as the eluent.



Ethyl 2-(diethoxyphosphoryl)-2-phenylacetate (5): The title compound was obtained as a yellow liquid in 78% yield (2.3 g). $\mathbf{R_f}$ = 0.4 (DCM : MeOH, 50 : 1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.55 – 7.49 (m, 2H), 7.39 – 7.27 (m, 3H), 4.28 – 4.16 (m, 3H), 4.11 – 3.95 (m, 4H), 1.31 – 1.23 (m, 6H), 1.20 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.7 (d, *J* = 3.5 Hz), 131.0 (d, *J* = 8.6 Hz), 129.6 (d, *J* = 6.3 Hz), 128.5 (d, *J* = 2.4 Hz), 128.0 (d, *J* = 2.9 Hz), 63.4 (d, *J* = 6.7 Hz), 63.1 (d, *J* = 7.1 Hz), 61.8, 52.3 (d, *J* = 134.7 Hz), 16.3 (d, *J* = 6.1 Hz), 16.3 (d, *J* = 6.0 Hz), 14.1. **^{31}P NMR (202 MHz, DMSO)** δ 18.86.

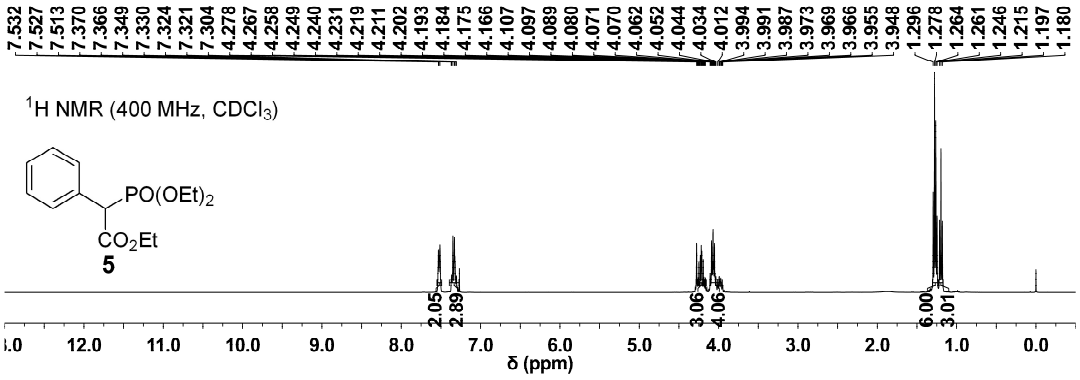


Figure S1. ^{1}H NMR spectrum of 5.

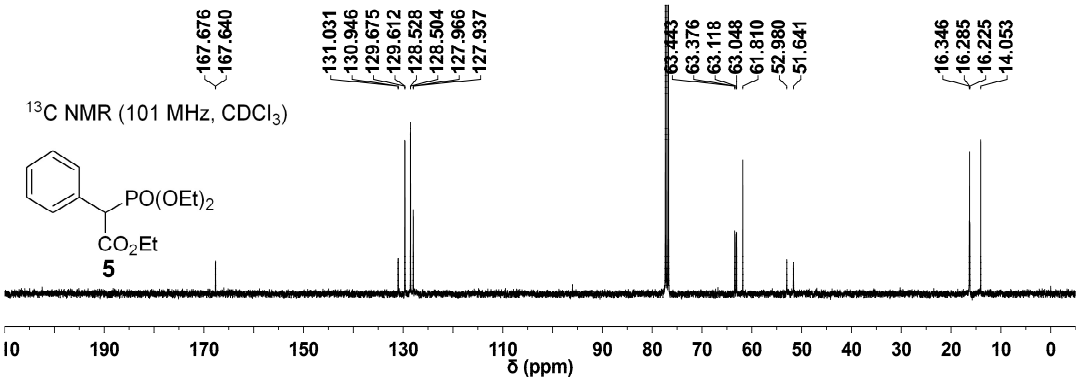


Figure S2. ^{13}C NMR spectrum of 5.

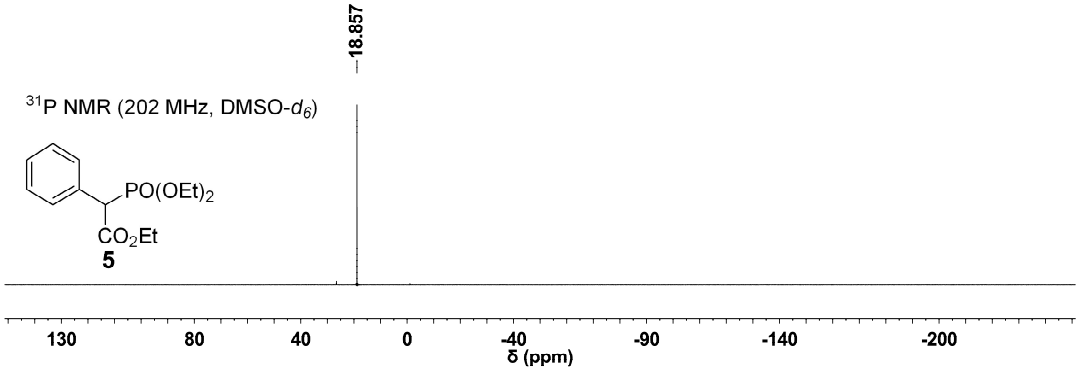
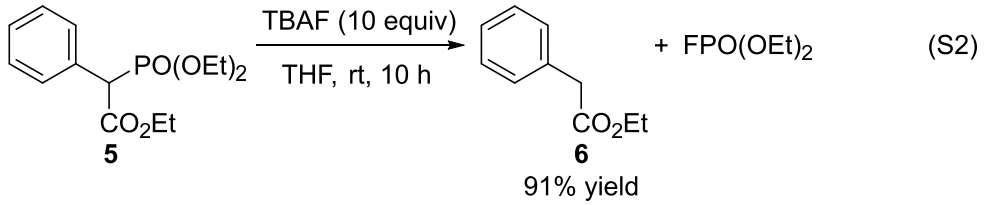


Figure S3. ^{31}P NMR spectrum of 5.

Dephosphonation reaction of 5:



(S2)

To a 13 × 150 mm test tube equipped with magnetic stir bar was added **5** (60 mg, 0.2 mmol, 1 equiv). The test tube was transferred to a glovebox. After the test tube was sealed with a rubber septum and removed from the glovebox, TBAF (2 mL, 1M in THF, 10 equiv) was then injected

into the tube. The reaction mixture was stirred for 10 h at ambient temperature, during which time a constant checking by TLC was performed. The reaction mixture was quenched with HOAc and filtered over a thin layer of silica gel and then washed with EA (3 × 10 mL). The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography and the eluates were analyzed by NMR experiments. In the case of phosphonate compound detection, the reaction solution (100 μL) was directly analyzed by NMR.

Ethyl 2-phenylacetate (6): The title compound was obtained as a colorless liquid in 91% yield (29.8 mg). $\mathbf{R_f}$ = 0.6 (PE : EA, 5 : 1). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.38 – 7.27 (m, 5H), 4.18 (d, *J* = 7.1 Hz, 2H), 3.64 (s, 2H), 1.28 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 171.6, 134.2, 129.3, 128.6, 127.1, 60.9, 41.5, 14.2.

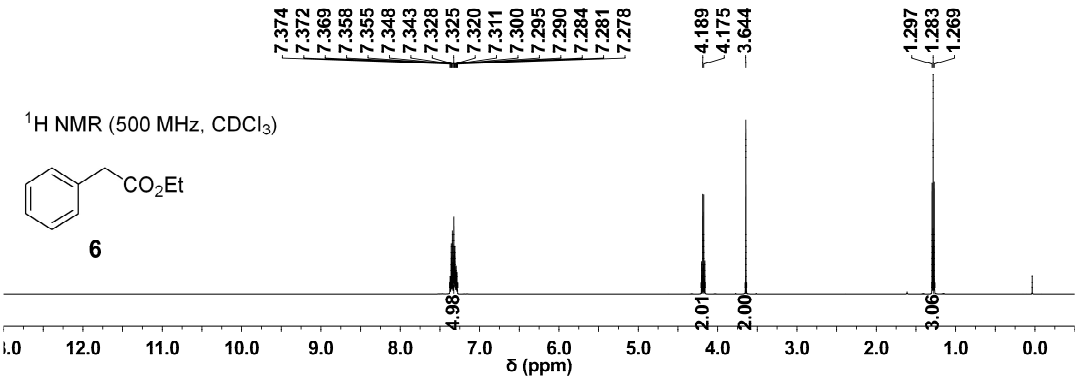


Figure S4. ^{1}H NMR spectrum of 6.

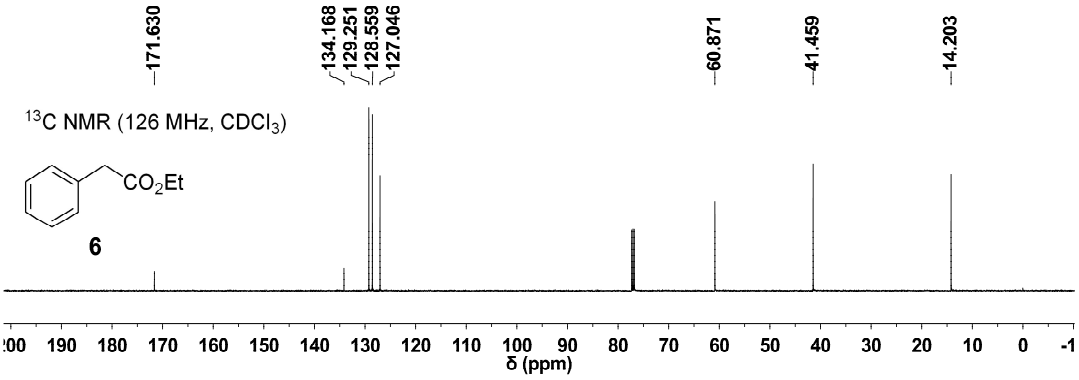


Figure S5. ^{13}C NMR spectrum of 6.

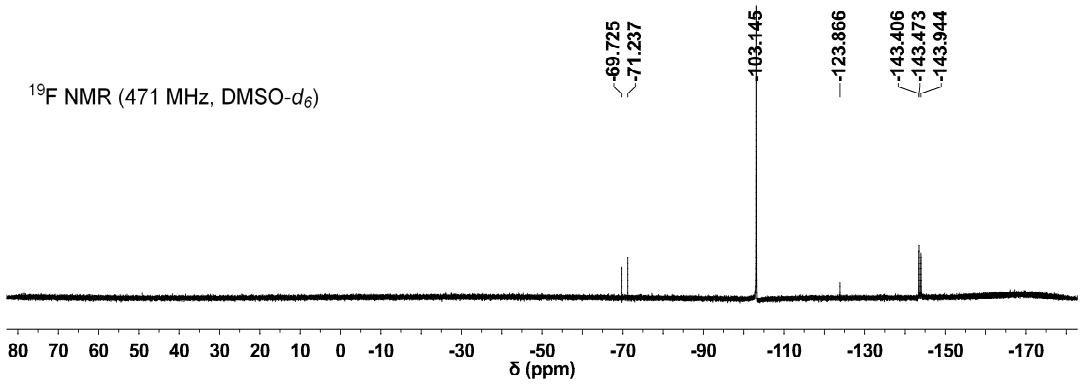


Figure S6. ^{19}F NMR spectrum of TBAF.

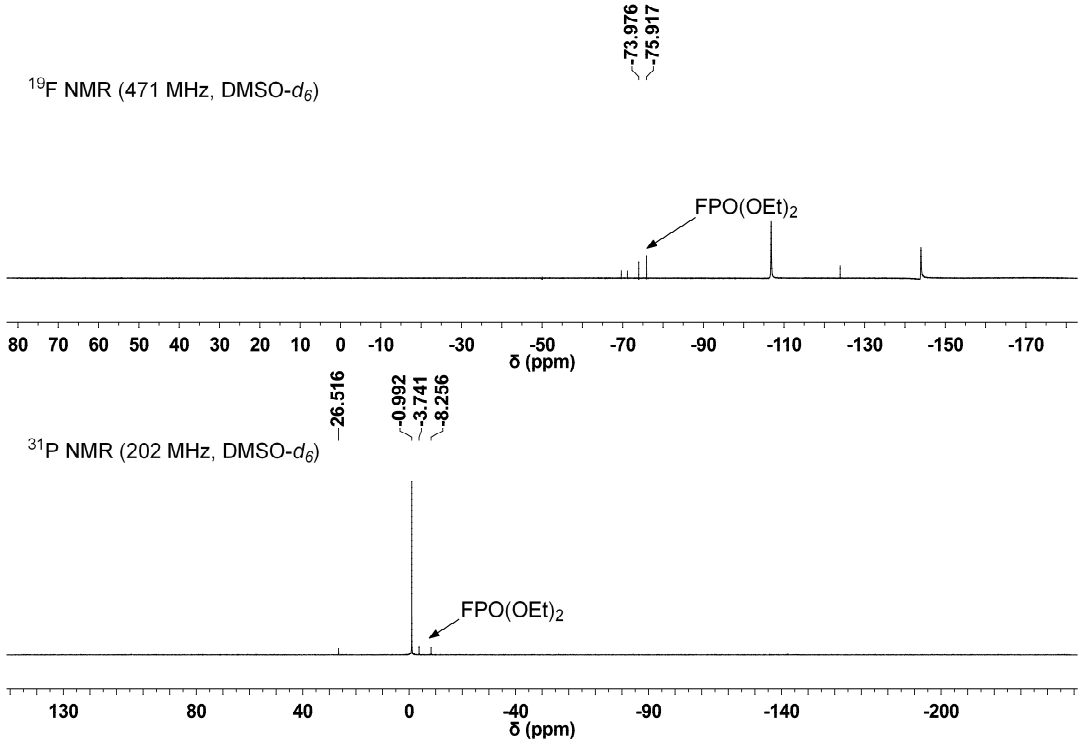
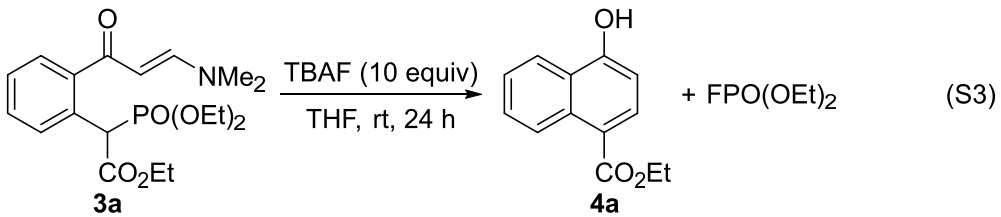


Figure S7. NMR spectra of the reaction solution from eq S1.

Cyclization reaction of 3a for phosphonate compound detection:



(S3)

To a 13 × 150 mm test tube equipped with magnetic stir bar was added **3a** (79 mg, 0.2 mmol, 1 equiv). The test tube was transferred to a glovebox. After the test tube was sealed with a rubber septum and removed from the glovebox, TBAF (2 mL, 1M in THF, 10 equiv) was then injected into the tube. The reaction mixture was stirred for 24 h at ambient temperature. The reaction solution (100 μL) was directly analyzed by NMR.

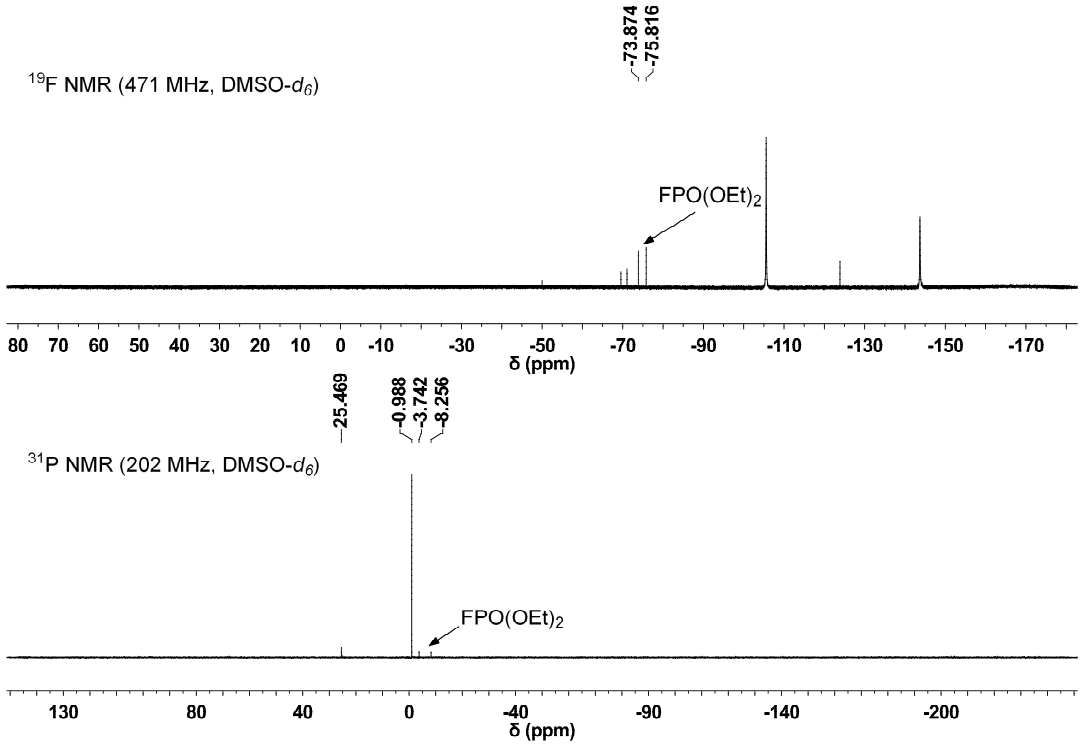
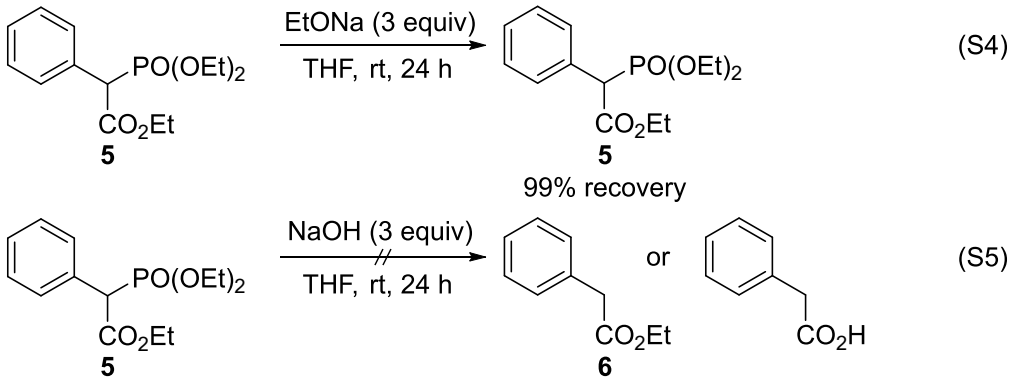


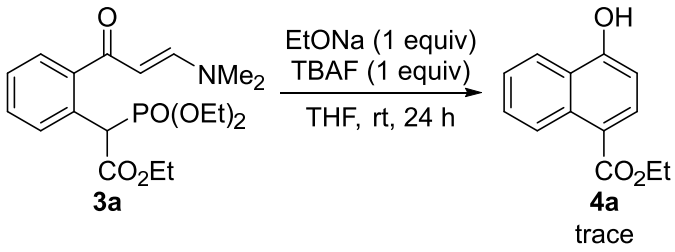
Figure S8. NMR spectra of the reaction solution from eq S2.

Procedure for the control experiments of 5:



To a 13 × 150 mm test tube equipped with magnetic stir bar was added **5** (60 mg, 0.2 mmol, 1 equiv). The test tube was transferred to a glovebox and EtONa (41 mg, 0.6 mmol, 3 equiv) or NaOH (24 mg, 0.6 mmol, 3 equiv) was added. After the test tube was sealed with a rubber septum and removed from the glovebox, 2 mL THF was then injected into the tube. The reaction mixture was stirred for 24 h at ambient temperature, during which time a constant checking by TLC was performed. The reaction mixture was quenched with HOAc and filtered over a thin layer of silica gel and then washed with EA (3 × 10 mL). The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography and the eluates were analyzed by NMR experiments. Under EtONa condition, the starting material **5** was recovered in 99%. Under, NaOH condition, the starting material **5** was consumed but no **6** or its hydrolysis product was observed.

Cyclization trials of 3a with combined reagents:

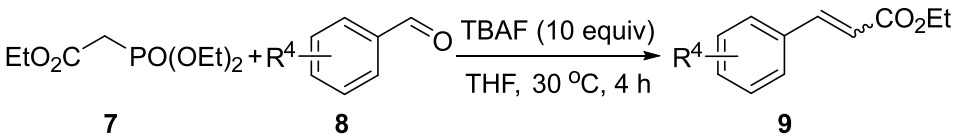


(S6)

To a 13 × 150 mm test tube equipped with magnetic stir bar was added **3a** (79 mg, 0.2 mmol, 1 equiv) and EtONa (14 mg, 0.2 mmol, 1 equiv). The test tube was transferred to a glovebox. After the test tube was sealed with a rubber septum and removed from the glovebox, TBAF (0.2 mL, 1 M in THF, 1 equiv) and 1.8 mL THF was then injected into the tube. The reaction mixture was stirred for 24 h at ambient temperature, during which time a constant checking by TLC was performed.

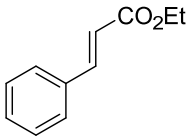
7. Synthesis and Characterization of Cinnamate Derivatives

General procedure for the synthesis of cinnamate derivatives:

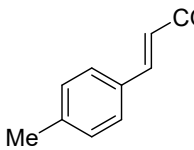


To a 13 × 150 mm test tube equipped with magnetic stir bar was added the substrate **7** (53.8 mg, 0.24 mmol, 1.2 equiv), **8a-8r** (0.2 mmol, 1 equiv) or both. The test tube was transferred to a glovebox. After the test tube was sealed with a rubber septum and removed from the glovebox, TBAF (2 mL, 1 M in THF, 10 equiv) was then injected into the tube. The reaction mixture was stirred for 4 h at 30 °C in oil bath, during which time a constant checking by TLC was performed. The reaction mixture was quenched with HOAc and filtered over a thin layer of silica gel and then washed with EA (3 × 10 mL). The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography with PE/EA (20 : 1) as the eluent. The NMR data of products were confirmed to be consistent with the literature.[4]

Ethyl cinnamate (9a): The title compound was obtained as a colorless liquid in 84% yield (29.5 mg). $\mathbf{R_f}$ = 0.5 (PE : EA, 20 : 1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.69 (d, *J* = 16.0 Hz, 1H), 7.54 – 7.50 (m, 2H), 7.42 – 7.33 (m, 3H), 6.44 (d, *J* = 16.0 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.0, 144.6, 134.5, 130.2, 128.9, 128.1, 118.3, 60.5, 14.3.

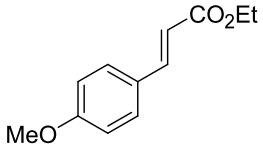


Ethyl (E)-3-(p-tolyl)acrylate (9b): The title compound was obtained as a colorless liquid in 92% yield (34.9 mg). $\mathbf{R_f}$ = 0.5 (PE : EA, 20 : 1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 (d, *J* = 16.0 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.39 (d, *J* = 16.0 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.36 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.2, 144.6, 140.6,

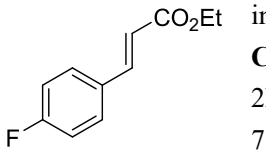


131.8, 129.6, 128.1, 117.2, 60.4, 21.5, 14.4.

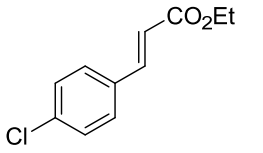
Ethyl (E)-3-(4-methoxyphenyl)acrylate (9c): The title compound was obtained as a colorless liquid in 99% yield (40.8 mg). $\mathbf{R_f}$ = 0.4 (PE : EA, 20 : 1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.64 (d, *J* = 16.0 Hz, 1H), 7.49 – 7.45 (m, 2H), 6.92 – 6.86 (m, 2H), 6.30 (d, *J* = 16.0 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.3, 161.3, 144.3, 129.7, 127.2, 115.7, 114.3, 60.3, 55.3, 14.4.



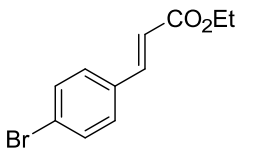
Ethyl (E)-3-(4-fluorophenyl)acrylate (9d): The title compound was obtained as a colorless liquid in 79% yield (30.7 mg). $\mathbf{R_f}$ = 0.6 (PE : EA, 20 : 1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.57 (d, *J* = 16.0 Hz, 1H), 7.47 – 7.39 (m, 2H), 7.04 – 6.93 (m, 2H), 6.28 (dd, *J* = 16.0, 0.4 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.0 (d, *J* = 177.6 Hz), 162.6, 143.3, 130.7 (d, *J* = 3.1 Hz), 129.9 (d, *J* = 8.5 Hz), 118.0, 116.0 (d, *J* = 21.9 Hz), 60.6, 14.3.



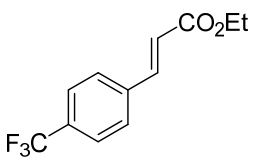
Ethyl (E)-3-(4-chlorophenyl)acrylate (9e): The title compound was obtained as a colorless liquid in 81% yield (34.0 mg). $\mathbf{R_f}$ = 0.5 (PE : EA, 20 : 1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.62 (d, *J* = 16.0 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.39 – 7.31 (m, 2H), 6.40 (d, *J* = 16.0 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.7, 143.1, 136.1, 133.0, 129.2, 129.2, 118.9, 60.6, 14.3.



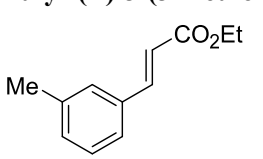
Ethyl (E)-3-(4-bromophenyl)acrylate (9f): The title compound was obtained as a colorless liquid in 99% yield (50.4 mg). $\mathbf{R_f}$ = 0.5 (PE : EA, 20 : 1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.61 (d, *J* = 16.0 Hz, 1H), 7.54 – 7.47 (m, 2H), 7.40 – 7.35 (m, 2H), 6.42 (d, *J* = 16.0 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.7, 143.2, 133.4, 132.1, 129.4, 124.5, 119.0, 60.6, 14.3.



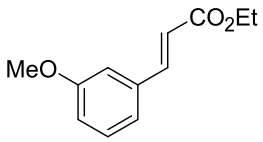
Ethyl (E)-3-(4-(trifluoromethyl)phenyl)acrylate (9g): The title compound was obtained as a colorless liquid in 55% yield (26.8 mg). $\mathbf{R_f}$ = 0.5 (PE : EA, 20 : 1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.69 (d, *J* = 16.1 Hz, 1H), 7.67 – 7.60 (m, 4H), 6.51 (d, *J* = 16.0 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.4, 142.7, 137.9, 131.7 (q, *J* = 32.7 Hz), 128.2, 125.9 (q, *J* = 3.6 Hz), 123.8 (q, *J* = 272.2 Hz), 120.9, 60.8, 14.3.



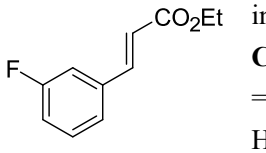
Ethyl (E)-3-(3-methoxyphenyl)acrylate (9h): The title compound was obtained as a colorless liquid in 83% yield (31.4 mg). $\mathbf{R_f}$ = 0.4 (PE : EA, 20 : 1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 (d, *J* = 16.0 Hz, 1H), 7.32 (m, *J* = 6.7 Hz, 2H), 7.27 (m, *J* = 10.9, 4.8 Hz, 1H), 7.18 (m, *J* = 7.5 Hz, 1H), 6.42 (d, *J* = 16.0 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.36 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.1, 144.8, 138.5, 134.4, 131.1, 128.8, 128.7, 125.3, 118.1, 60.5, 21.3, 14.3.



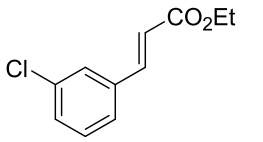
Ethyl (E)-3-(3-methoxyphenyl)acrylate (9i): The title compound was obtained as a colorless liquid in 98% yield (40.3 mg). $\mathbf{R_f}$ = 0.4 (PE : EA, 20 : 1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65 (d, *J* = 16.0 Hz, 1H), 7.29 (t, *J* = 7.9 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 7.05 – 7.02 (m, 1H), 6.92 (ddd, *J* = 8.2, 2.5, 0.6 Hz, 1H), 6.42 (d, *J* = 16.0 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.0, 159.9, 144.5, 135.8, 129.9, 120.8, 118.6, 116.1, 112.9, 60.5, 55.3, 14.3.



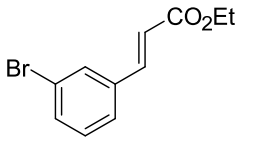
Ethyl (E)-3-(3-fluorophenyl)acrylate (9j): The title compound was obtained as a colorless liquid in 78% yield (30.4 mg). $\mathbf{R_f}$ = 0.6 (PE : EA, 20 : 1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.63 (d, *J* = 16.0 Hz, 1H), 7.35 (td, *J* = 7.9, 5.8 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.24 – 7.19 (m, 1H), 7.12 – 7.03 (m, 1H), 6.43 (d, *J* = 16.0 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.6, 163.0 (d, *J* = 246.7 Hz), 143.2 (d, *J* = 2.0 Hz), 136.7 (d, *J* = 7.6 Hz), 130.4 (d, *J* = 8.2 Hz), 124.0 (d, *J* = 2.4 Hz), 119.7 (s), 117.1 (d, *J* = 21.4 Hz), 114.3 (d, *J* = 21.9 Hz), 60.7, 14.3.



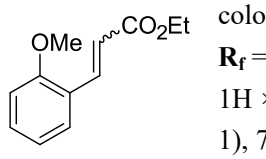
Ethyl (E)-3-(3-chlorophenyl)acrylate (9k): The title compound was obtained as a colorless liquid in 84% yield (35.3 mg). $\mathbf{R_f}$ = 0.5 (PE : EA, 20 : 1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.61 (d, *J* = 16.0 Hz, 1H), 7.50 (d, *J* = 1.8 Hz, 1H), 7.38 (dt, *J* = 6.9, 1.6 Hz, 1H), 7.36 – 7.26 (m, 2H), 6.43 (d, *J* = 16.0 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.6, 142.9, 136.3, 134.9, 130.1, 130.1, 127.8, 126.2, 119.8, 60.7, 14.3.

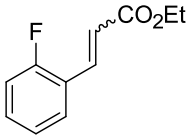


Ethyl (E)-3-(3-bromophenyl)acrylate (9l): The title compound was obtained as a colorless liquid in 71% yield (36.3 mg). $\mathbf{R_f}$ = 0.5 (PE : EA, 20 : 1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 (t, *J* = 1.7 Hz, 1H), 7.59 (d, *J* = 16.0 Hz, 1H), 7.52 – 7.47 (m, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.25 (t, *J* = 7.8 Hz, 1H), 6.42 (d, *J* = 16.0 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.5, 142.8, 136.6, 133.0, 130.7, 130.4, 126.6, 123.0, 119.8, 60.7, 14.3.

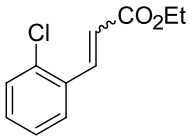


Ethyl 3-(2-methoxyphenyl)acrylate (9m): The title compound was obtained as an inseparable colorless liquid mixture of *E/Z* (1 : 0.34) isomers in 94% total yield (38.6 mg). $\mathbf{R_f}$ = 0.5 (PE : EA, 20 : 1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.99 (d, *J* = 16.2 Hz, 1H × 1), 7.54 (dd, *J* = 7.6, 1.4 Hz, 1H × 0.34), 7.50 (dd, *J* = 7.7, 1.6 Hz, 1H × 1), 7.37 – 7.27 (m, 1H × 1 + 1H × 0.34), 7.16 (d, *J* = 12.4 Hz, 1H × 0.34), 6.97 – 6.85 (m, 2H × 1 + 2H × 0.34), 6.52 (d, *J* = 16.2 Hz, 1H × 1), 5.96 (d, *J* = 12.4 Hz, 1H × 0.34), 4.26 (q, *J* = 7.1 Hz, 2H), 4.13 (q, *J* = 7.1 Hz, 2H × 0.34), 3.87 (s, 3H), 3.82 (s, 3H× 0.34), 1.33 (t, *J* = 7.1 Hz, 3H × 1), 1.20 (t, *J* = 7.1 Hz, 3H× 0.34). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.5, 166.4, 158.3, 157.1, 140.0, 139.0, 131.4, 130.7, 130.4, 128.9, 124.1, 123.4, 120.7, 120.0, 119.9, 118.8, 111.1, 110.3, 60.4, 60.1, 55.5, 14.4, 14.1.

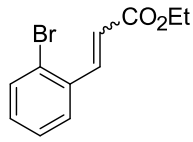


Ethyl 3-(2-fluorophenyl)acrylate (9n): The title compound was obtained as an inseparable colorless liquid mixture of *E/Z* (1 : 0.04) isomers in 75% total yield (29.3 mg). 

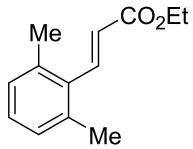
$\mathbf{R_f}$ = 0.5 (PE : EA, 20 : 1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.81 (d, *J* = 16.2 Hz, 1H × 1), 7.53 (td, *J* = 7.6, 1.6 Hz, 1H × 1), 7.40 – 7.31 (m, 1H × 1), 7.20 – 7.05 (m, 2H × 1), 6.54 (d, *J* = 16.2 Hz, 1H × 1), 6.07 (d, *J* = 12.4 Hz, 1H × 0.04), 4.27 (q, *J* = 7.1 Hz, 2H × 1), 4.16 (q, *J* = 7.1 Hz, 1H × 0.04), 1.34 (t, *J* = 7.1 Hz, 3H × 1), 1.22 (t, *J* = 7.1 Hz, 1H × 0.04). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.8, 161.3 (d, *J* = 253.9 Hz), 137.2 (d, *J* = 2.4 Hz), 131.6 (d, *J* = 8.7 Hz), 129.1 (d, *J* = 2.5 Hz), 124.4 (d, *J* = 3.4 Hz), 122.5 (d, *J* = 11.7 Hz), 120.9 (d, *J* = 6.5 Hz), 116.2 (d, *J* = 21.9 Hz), 60.6, 14.3.

Ethyl 3-(2-chlorophenyl)acrylate (9o): The title compound was obtained as an inseparable colorless liquid mixture of *E/Z* (1 : 0.44) isomers in 89% total yield (37.3 mg). 

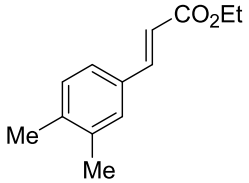
$\mathbf{R_f}$ = 0.5 (PE : EA, 20 : 1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.09 (d, *J* = 16.0 Hz, 1H × 1), 7.61 (dd, *J* = 7.2, 2.2 Hz, 1H × 1), 7.49 (dd, *J* = 7.2, 2.1 Hz, 1H × 0.44), 7.41 (dd, *J* = 7.7, 1.6 Hz, 1H × 1), 7.38 (dd, *J* = 7.7, 1.6 Hz, 1H × 0.44), 7.33 – 7.19 (m, 2H × 1 + 1H × 0.44), 7.13 (d, *J* = 12.2 Hz, 1H × 0.44), 6.43 (d, *J* = 16.0 Hz, 1H × 1), 6.08 (d, *J* = 12.2 Hz, 1H × 0.44), 4.28 (q, *J* = 7.1 Hz, 2H × 1), 4.11 (q, *J* = 7.1 Hz, 2H × 0.44), 1.35 (t, *J* = 7.1 Hz, 3H × 1), 1.17 (t, *J* = 7.1 Hz, 3H × 0.44). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.5, 165.6, 140.4, 134.9, 134.0, 133.2, 132.8, 131.0, 130.8, 130.2, 129.8, 129.1, 127.6, 127.1, 126.0, 122.0, 121.0, 60.7, 60.4, 14.3, 14.0.

Ethyl 3-(2-bromophenyl)acrylate (**9p)**: The title compound was obtained as an inseparable colorless liquid mixture of *E/Z* (1 : 0.46) isomers in 78% total yield (39.8 mg). 

$\mathbf{R_f}$ = 0.5 (PE : EA, 20 : 1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.05 (d, *J* = 15.9 Hz, 1H × 1), 7.63 – 7.55 (m, 2H × 1 + 1H × 0.46), 7.47 (dd, *J* = 7.7, 1.4 Hz, 1H × 0.46), 7.34 – 7.25 (m, 1H × 1 + 1H × 0.46), 7.25 – 7.15 (m, 1H × 1 + 1H × 0.46), 7.08 (d, *J* = 12.2 Hz, 1H × 0.46), 6.38 (d, *J* = 15.9 Hz, 1H × 1), 6.06 (d, *J* = 12.2 Hz, 1H × 0.46), 4.28 (q, *J* = 7.1 Hz, 2H × 1), 4.10 (q, *J* = 7.1 Hz, 2H × 0.46), 1.35 (t, *J* = 7.1 Hz, 3H × 1), 1.17 (t, *J* = 7.1 Hz, 3H × 0.46). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.4, 165.5, 142.9, 142.5, 135.9, 134.6, 133.4, 132.2, 131.2, 130.8, 129.9, 127.8, 127.7, 126.6, 125.3, 123.1, 121.8, 121.1, 60.7, 60.3, 14.3, 14.0.

Ethyl (E)-3-(2,6-dimethylphenyl)acrylate (9q): The title compound was obtained as a colorless liquid in 97% yield (39.7 mg). 

$\mathbf{R_f}$ = 0.5 (PE : EA, 20 : 1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.84 (d, *J* = 16.4 Hz, 1H), 7.12 (dd, *J* = 8.5, 6.4 Hz, 1H), 7.05 (d, *J* = 7.5 Hz, 2H), 6.06 (d, *J* = 16.4 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.34 (s, 6H), 1.34 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.3, 136.6, 134.0, 128.3, 128.2, 124.0, 60.6, 21.1, 14.3.

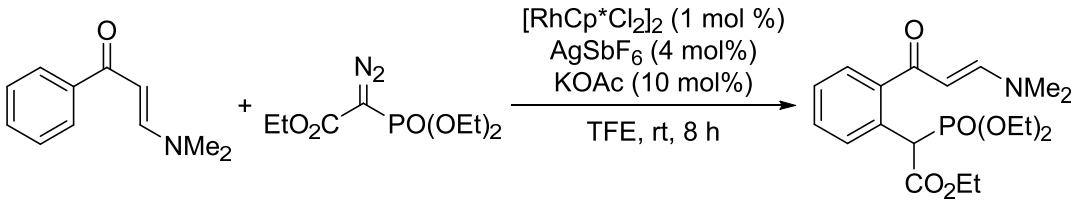
Ethyl (E)-3-(3,4-dimethylphenyl)acrylate (**9r)**: The title compound was obtained as a colorless liquid in 99% yield (40.5 mg). 

$\mathbf{R_f}$ = 0.5 (PE : EA, 20 : 1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.64 (d, *J* = 16.0 Hz, 1H), 7.31 – 7.23 (m, 2H), 7.13 (d, *J* = 7.8 Hz, 1H), 6.38 (d, *J* = 16.0 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.26 (s, 6H), 1.33 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.3,

144.8, 139.4, 137.1, 132.2, 130.2, 129.3, 125.7, 117.0, 60.4, 19.8, 19.7, 14.4.

8. Millimole Scale Reactions

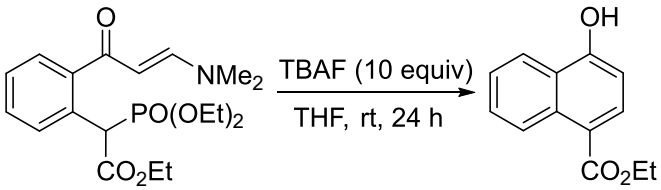
Procedure for 10 millimole scale synthesis of 3a:



1a **2a** **3a**

To a 100 mL round-bottomed flask equipped with a magnetic stir bar was added **1a** (1.75 g, 10 mmol, 1 equiv) and KOAc (100.0 mg, 1 mmol, 10 mol %). The flask was transferred to a glovebox, and added with $[RhCp^*Cl_2]_2$ (62 mg, 0.1 mmol, 1.0 mol %) and $AgSbF_6$ (138 mg, 0.4 mmol, 4.0 mol %). After the flask was sealed with a rubber septum and removed from the glovebox, **2a** (3.00 g, 12 mmol, 1.2 equiv) in 50 mL TFE was injected into the test tube *via* syringe. The reaction mixture was stirred for 8 h at ambient temperature. The reaction mixture was filtered over celite. The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography on silica gel with PE/EA (1 : 1), DCM/MeOH (50 : 1) and DCM/MeOH (20 : 1) as the eluents. The product **3a** was obtained in 87% yield (3.45 g) as an orange solid.

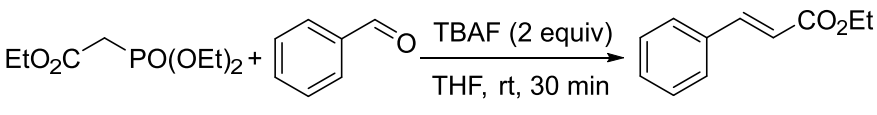
Procedure for 1 millimole scale synthesis of 4a:



3a **4a**

To a 25 mL round-bottomed flask equipped with a magnetic stir bar was added **3a** (397 mg, 1 mmol, 1 equiv). The flask was transferred to a glovebox. After the flask was sealed with a rubber septum and removed from the glovebox, TBAF (10 mL, 1M in THF, 10 equiv) was then injected into the tube. The reaction mixture was stirred for 24 h at ambient temperature. The reaction mixture was cooled to rt, filtered over a thin layer of silica gel and then washed with EA (3 × 100 mL). The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography on silica gel with PE/EA (5 : 1) as the eluent. The product **4a** was obtained in 87% yield (187 mg) as a white solid.

Procedure for 1 millimole scale synthesis of 9a:



7 **8a** **9a**

To a 25 mL round-bottomed flask equipped with magnetic stir bar was added the substrate **7** (269 mg, 1.2 mmol, 1.2 equiv), **8a** (106 mg, 1 mmol, 1 equiv). The flask was transferred to a glovebox. After the flask was sealed with a rubber septum and removed from the glovebox, TBAF (2 mL, 1 M in THF, 2 equiv) was then injected into the flask. The reaction mixture was stirred for 30 min. The reaction mixture was quenched with HOAc and filtered over a thin layer of silica gel and then washed with EA (3 × 10 mL). The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography with PE/EA (50 : 1) as the eluent. The product 9a was obtained in 81% yield (142.6 mg) as a colorless oil.

9. References

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10. NMR Spectra for All the Compounds