Supporting Information for

Synthesis of α -trifluoromethyl- β -keto phosphonates by electrophilic trifluoromethylation with tognol reagent

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1. General information.

^1H and ^{19}F NMR (CFCl_3 as external standard and low field is positive) spectra were recorded on a Bruker AM 400 spectrometer. ^{13}C NMR spectra were recorded on a Bruker AM 400 spectrometer. Chemical shifts (δ) were reported in ppm, and coupling constants (J) were in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. The NMR yield was determined by ^{19}F NMR using (trifluoromethyl)benzene as an internal standard before working up the reaction. High resolution mass spectra (HRMS) were performed using a GC/MS TOF high-resolution mass spectrometer equipped with a liquid chromatography system.

Materials: Unless otherwise noted, all reagents were obtained commercially and used without further purification. All solvents were dried according to standard procedures. Reactions were performed under an atmosphere of N_2 using glassware.

2. Preparation of substrates.

A typical procedure A^[1] (synthesis of **1a**) is shown below:

Diethyl (1-Oxo-1,2,3,4-tetrahydronaphthalen-2-yl) phosphonate (1a)^[1].

A solution of 1-tetralone (1.25 g, 8.5 mmol) in anhydrous THF (15.0 mL) was added dropwise to a stirred 1 M solution of lithium diisopropylamide (9.4 mmol, 9.4 mL) at -65°C under N_2 . After stirring for 45 min, the resulting enolate was treated with diethyl chlorophosphate (1.62 g, 9.4 mmol) and the mixture was allowed to warm to 0°C over the course of 50 min. After this mixture was cooled to -70°C , it was transferred to a 2 M solution of lithium diisopropylamide (18.8 mmol, 9.4 mL). The resulting solution was allowed to warm to 10°C over 2 h and was treated with a solution of acetic acid (2.0 mL) in Et_2O (30.0 mL). The resulting mixture was filtered and the filtrate concentrated. The oily residue was purified by silica gel column chromatography (petroleum ether/ ethyl acetate, 5:1) to give the phosphonate (1.63 g, 68%) as a brown oil. ^1H NMR (400 MHz, CDCl_3) δ 8.06 (d, $J = 7.8$ Hz, 1H), 7.50 (td, $J = 7.6$, 1.0 Hz, 1H), 7.32 (t, $J = 7.6$ Hz, 1H), 7.26 (d, $J = 7.7$ Hz, 1H), 4.26 – 4.10 (m, 4H), 3.35 – 3.18 (m, 2H), 2.94 (dt, $J = 16.8$, 5.5 Hz, 1H), 2.56 – 2.43 (m, 2H), 1.36 (t, $J = 7.1$ Hz, 3H), 1.23 (t, $J = 7.1$ Hz, 3H). MS (EI) m/z : 282 $[\text{M}]^+$.

Dimethyl (1-Oxo-1,2,3,4-tetrahydronaphthalen-2-yl) phosphonate (1b) ^[2].

Compound **1b** was prepared following the *procedure A* and obtained in 56% yield as a brown oil. ¹H NMR (400 MHz, CDCl₃) δ 8.05 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.49 (td, *J* = 7.5, 1.4 Hz, 1H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.25 (d, *J* = 7.7 Hz, 1H), 3.84 (d, *J* = 11.0 Hz, 6H), 3.79 (d, *J* = 11.0 Hz, 6H), 3.34 – 3.18 (m, 2H), 2.94 (dt, *J* = 16.8, 6.0 Hz, 1H), 2.53 – 2.40 (m, 2H). MS (EI) *m/z*: 254 [M]⁺.

Diethyl (1,2,3,4-tetrahydro-7-methoxy-1-oxo-2-naphthalenyl) phosphonate (1c) ^[3].

Compound **1c** was prepared following the *procedure A* and obtained in 65% yield as a brown oil. ¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, *J* = 2.8 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 7.08 (dd, *J* = 8.4, 2.8 Hz, 1H), 4.24 – 4.11 (m, 4H), 3.84 (s, 3H), 3.26 – 3.15 (m, 2H), 2.87 (dt, *J* = 16.6, 5.6 Hz, 1H), 2.54 – 2.39 (m, 2H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). MS (EI) *m/z*: 312 [M]⁺.

Dimethyl (1,2,3,4-tetrahydro-7-methoxy-1-oxo-2-naphthalenyl) phosphonate (1d).

Compound **1d** was prepared following the *procedure A* and obtained in 48% yield as a brown oil. ¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, *J* = 2.7 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 7.07 (dd, *J* = 8.4, 2.8 Hz, 1H), 3.85 – 3.77 (m, 9H), 3.28 – 3.12 (m, 2H), 2.87 (dt, *J* = 16.5, 5.9 Hz, 1H), 2.51 – 2.39 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 191.4 (d, *J* = 5.6 Hz), 157.4, 135.5, 131.7 (d, *J* = 3.3 Hz), 129.0, 121.4, 108.5, 54.5, 52.1 (dd, *J* = 32.1, 6.8 Hz), 45.7 (d, *J* = 134.4 Hz), 25.8 (d, *J* = 8.2 Hz), 23.6 (d, *J* = 4.6 Hz). IR (KBr)_{max} 2953, 1676, 1609, 1496, 1243, 1027, 882, 826, 567 cm⁻¹. MS (EI) *m/z*: 284 [M]⁺. HRMS (EI-TOF) *m/z*: [M]⁺ Calcd for C₁₃H₁₇O₅P: 284.0813; Found: 284.0808.

A typical procedure **B**^[4,5] (synthesis of **1e**) is shown below:

Diethyl(1-methyl-2-oxo-2-phenylethyl)phosphonate (**1e**)^[2]:

Styrene (1.04 g, 10.0 mmol) was added to a mixture of H-diethyl phosphonate (2.76 g, 20.0 mmol), CuCl_2 (33.6 mg, 0.25 mmol), FeCl_3 (81.3 mg, 0.5 mmol), and Et_3N (1.01 g, 10.0 mol) in DMSO (4 mL) at room temperature under O_2 (balloon). The reaction mixture was stirred at 55°C for 24 h. After completion of the reaction, water (8 mL) was added to the reaction mixture, and the resulting mixture was extracted with dichloromethane. The organic layer was washed with 0.1 M HCl (8 mL $\times$ 1), water (8 mL $\times$ 3), brine (8 mL $\times$ 1), and the separated aqueous phase was extracted with CH_2Cl_2 (8 mL $\times$ 2). The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 3:1) to afford the β -ketophosphonate as a light yellow oil (1.77 g, 69% yield).

To a solution of diethyl(2-oxo-2-phenyl-ethyl)phosphonate (1.35 g, 5.0 mmol) and K_2CO_3 (1.04 g, 7.5 mmol) in acetone (4.0 mL) was added MeI (1.06 g, 7.5 mmol) at 0°C . After stirring at 25°C for 20 h, the reaction mixture was quenched with 10% NH_4Cl aqueous solution and extracted with EtOAc for three times. The combined organic layer was dried over Na_2SO_4 , and the organic solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate, 3:1) to afford the desired phosphonate as a light yellow oil (0.86 g, 64% yield). ^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, $J = 7.5$ Hz, 2H), 7.58 (t, $J = 7.4$ Hz, 1H), 7.47 (t, $J = 7.7$ Hz, 2H), 4.26 – 3.97 (m, 5H), 1.54 (dd, $J = 18.1$, 7.0 Hz, 3H), 1.28 (t, $J = 7.1$ Hz, 3H), 1.19 (t, $J = 7.1$ Hz, 3H). MS (EI) m/z : 270 $[\text{M}]^+$.

Diethyl (1-benzoylpropyl) phosphonate (**1f**)^[6].

Compound **1f** was prepared following the *procedure B* and obtained in 43% yield over two steps as a yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, $J = 7.8$ Hz, 2H), 7.59 (t, $J = 7.3$ Hz, 1H), 7.48 (t, $J = 7.6$ Hz, 2H), 4.21 – 3.95 (m, 5H), 2.29 – 2.22 (m, 1H), 2.10 – 1.98 (m, 1H), 1.28 (t, $J = 7.0$ Hz, 3H), 1.18 (t, $J = 7.0$ Hz, 3H), 0.95 (t, $J = 7.4$ Hz, 3H). MS (EI) m/z : 284 $[\text{M}]^+$.

Diethyl [2-(4-methylphenyl)-1-methyl-2-oxoethyl] phosphonate (1g).

Compound **1g** was prepared following the *procedure B* and obtained in 52% yield over two steps as a yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, $J = 8.2$ Hz, 2H), 7.27 (d, $J = 8.1$ Hz, 2H), 4.20 – 4.02 (m, 5H), 2.41 (s, 3H), 1.52 (dd, $J = 18.1, 7.0$ Hz, 3H), 1.28 (t, $J = 7.1$ Hz, 3H), 1.21 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 195.0 (d, $J = 4.9$ Hz), 143.2, 133.3 (d, $J = 1.6$ Hz), 128.2, 128.0, 61.6 (t, $J = 6.5$ Hz), 40.1 (d, $J = 130.5$ Hz), 20.6, 15.3 (dd, $J = 11.5, 6.1$ Hz), 11.3 (d, $J = 6.6$ Hz). IR (KBr) $_{\text{max}}$ 2983, 1674, 1608, 1448, 1243, 1022, 950, 793, 537 cm^{-1} . MS (EI) m/z : 284 $[\text{M}]^+$. HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{14}\text{H}_{21}\text{O}_4\text{P}$: 284.1177; Found: 284.1180.

Diethyl [2-(4-chlorophenyl)-1-methyl-2-oxoethyl] phosphonate (1h) ^[2].

Compound **1h** was prepared following the *procedure B* and obtained in 45% yield over two steps as a yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, $J = 8.6$ Hz, 2H), 7.45 (d, $J = 8.6$ Hz, 2H), 4.19 – 4.00 (m, 5H), 1.52 (dd, $J = 17.9, 7.0$ Hz, 3H), 1.29 (t, $J = 7.1$ Hz, 3H), 1.21 (t, $J = 7.1$ Hz, 3H). MS (EI) m/z : 304 $[\text{M}]^+$.

Diethyl [2-(4-acetoxyphenyl)-1-methyl-2-oxoethyl] phosphonate (1i).

Compound **1i** was prepared following the *procedure B* and obtained in 47% yield over two steps as a yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 8.05 (d, $J = 8.7$ Hz, 2H), 7.21 (d, $J = 8.7$ Hz, 2H), 4.17 – 4.03 (m, 5H), 2.33 (s, 3H), 1.53 (dd, $J = 18.0, 7.0$ Hz, 3H), 1.29 (t, $J = 7.1$ Hz, 3H), 1.22 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 195.2 (d, $J = 4.9$ Hz), 168.7, 154.5, 134.3 (d, $J = 1.4$ Hz), 130.5, 121.7, 62.7 (t, $J = 7.5$ Hz), 41.4 (d, $J = 130.2$ Hz), 21.1, 16.3 (dd, $J = 12.5, 6.1$ Hz), 12.2 (d, $J = 6.5$ Hz). IR (KBr) $_{\text{max}}$ 2983, 1762, 1675, 1592, 1245, 1196, 1019, 949, 792, 539 cm^{-1} . MS (EI) m/z : 328 $[\text{M}]^+$. HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{15}\text{H}_{21}\text{O}_6\text{P}$: 328.1075; Found: 328.1079.

Dimethyl (1-oxo-1-phenylpropan-2-yl)phosphonate (1j) ^[5].

Compound **1j** was prepared following the *procedure B* and obtained in 35% yield over two steps as a light yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, *J* = 7.4 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 4.20 (dq, *J* = 22.8, 7.1 Hz, 1H), 3.77 (d, *J* = 10.9 Hz, 6H), 3.72 (d, *J* = 10.9 Hz, 6H), 1.55 (dd, *J* = 18.1, 7.1 Hz, 3H). MS (EI) *m/z*: 242 [M]⁺.

Diisopropyl (1-oxo-1-phenylpropan-2-yl)phosphonate (1k) ^[4].

Compound **1k** was prepared following the *procedure B* and obtained in 37% yield over two steps as a light yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, *J* = 7.4 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 4.77 – 4.58 (m, 2H), 4.13 (dq, *J* = 23.6, 7.0 Hz, 1H), 1.51 (dd, *J* = 18.0, 7.0 Hz, 3H), 1.31 (d, *J* = 6.2 Hz, 3H), 1.27 (d, *J* = 6.2 Hz, 3H), 1.24 (d, *J* = 6.2 Hz, 3H), 1.18 (d, *J* = 6.2 Hz, 3H). MS (EI) *m/z*: 298 [M]⁺.

Dibutyl (1-oxo-1-phenylpropan-2-yl)phosphonate (1l).

Compound **1l** was prepared following the *procedure B* and obtained in 41% yield over two steps as a light yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, *J* = 7.8 Hz, 2H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 4.21 (dq, *J* = 21.3, 6.9 Hz, 1H), 4.12 – 3.93 (m, 4H), 1.60 – 1.51 (m, 7H), 1.39 – 1.33 (m, 2H), 1.29 – 1.23 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 196.4 (d, *J* = 4.9 Hz), 136.9, 133.3, 128.8, 128.5, 66.4 (dd, *J* = 24.4, 7.0 Hz), 41.3 (d, *J* = 130.0 Hz), 32.4 (dd, *J* = 14.1, 6.1 Hz), 18.6 (d, *J* = 7.3 Hz), 13.6 (d, *J* = 5.3 Hz), 12.2 (d, *J* = 6.4 Hz). IR (KBr)_{max} 2959, 1682, 1457, 1377, 1242, 1019, 912, 742, 543 cm⁻¹. MS (EI) *m/z*: 326 [M]⁺. HRMS (EI-TOF) *m/z*: [M]⁺ Calcd for C₁₇H₂₇O₄P: 326.1647; Found: 326.1646.

3. Synthesis of α -trifluoromethyl- β -keto phosphonates.

A typical procedure C (synthesis of **2a**) is shown below:

Diethyl(2-trifluoromethyl-1,2,3,4-tetrahydro-1-oxonaphthalen-2-yl)phosphonate (**2a**).

A 25 mL Schlenk tube was charged with a stir bar, *t*-BuONa (28.8 mg, 0.3 mmol) under N₂ atmosphere. Phosphonate (56.4 mg, 0.2 mmol), HMPA (215.0 mg, 1.2 mmol) and CH₂Cl₂ (2.0 mL) were added to the tube. The reaction mixture was cooled 0 °C and stirred for 30 min. Then, Togni reagent (94.8 mg, 0.3 mmol) was added to the reaction mixture. After stirring at room temperature for 18 h, the reaction was quenched with 10% NH₄Cl aqueous solution and extracted with CH₂Cl₂ for three times. The combined organic layer was dried over Na₂SO₄, and the organic solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether/ ethyl acetate, 5:1) to afford the desired product as a light yellow oil (52.2 mg, 75% yield). ¹H NMR (400 MHz, CDCl₃) δ 8.07 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.51 (td, *J* = 7.5, 1.4 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 7.7 Hz, 1H), 4.28 – 4.12 (m, 4H), 3.45 – 3.35 (m, 1H), 3.03 (dt, *J* = 17.0, 5.1 Hz, 1H), 2.87 – 2.78 (m, 1H), 2.68 – 2.54 (m, 1H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 187.8 (d, *J* = 4.8 Hz), 143.2, 134.3, 131.8, 128.5, 128.4, 126.9, 124.5 (qd, *J* = 284.0, 3.4 Hz), 64.0 (dd, *J* = 40.9, 7.1 Hz), 57.8 (dq, *J* = 130.1, 23.5 Hz), 26.5 (dd, *J* = 4.2, 2.3 Hz), 25.2 (d, *J* = 3.7 Hz), 16.1 (dd, *J* = 14.0, 6.1 Hz). ¹⁹F NMR (377 MHz, CDCl₃) δ -64.6 (d, *J* = 6.7 Hz, 3F). IR (KBr)_{max} 2987, 1687, 1600, 1450, 1264, 1160, 1025, 970, 894, 781, 567 cm⁻¹. MS (EI) *m/z*: 350 [M]⁺. HRMS (EI-TOF) *m/z*: [M]⁺ Calcd for C₁₅H₁₈F₃O₄P: 350.0894; Found: 350.0890.

Dimethyl(2-trifluoromethyl-1,2,3,4-tetrahydro-1-oxonaphthalen-2-yl)phosphonate (**2b**).

Compound **2b** was prepared following the *procedure C* and obtained in 68% yield as a light yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, *J* = 7.9 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.26 (d, *J* = 8.6 Hz, 1H), 3.86 (d, *J* = 11.1 Hz,

3H), 3.84 (d, $J = 11.1$ Hz, 3H), 3.39 – 3.30 (m, 1H), 3.04 (dt, $J = 17.0, 5.4$ Hz, 1H), 2.87 – 2.78 (m, 1H), 2.69 – 2.55 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 187.7 (d, $J = 5.1$ Hz), 143.1, 134.5, 131.6, 128.6, 128.5, 127.1, 124.5 (qd, $J = 285.3, 3.5$ Hz), 57.7 (dq, $J = 131.3, 23.8$ Hz), 54.3 (dd, $J = 58.3, 7.0$ Hz), 26.5 (dd, $J = 4.2, 2.2$ Hz), 25.2 (d, $J = 4.3$ Hz). ^{19}F NMR (377 MHz, CDCl_3) δ -64.5 (d, $J = 7.0$ Hz, 3F). IR (KBr) $_{\text{max}}$ 2960, 1684, 1598, 1451, 1263, 1161, 1029, 893, 783, 564 cm^{-1} . MS (EI) m/z : 322 $[\text{M}]^+$. HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{13}\text{H}_{14}\text{F}_3\text{O}_4\text{P}$: 322.0581; Found: 322.0585.

Diethyl(2-trifluoromethyl-1,2,3,4-tetrahydro-7-methoxy-1-oxonaphthalen-2-yl) Phosphonate (2c).

Compound **2c** was prepared following the *procedure C* and obtained in 62% yield as a light yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.55 (d, $J = 2.7$ Hz, 1H), 7.16 (d, $J = 8.4$ Hz, 1H), 7.10 (dd, $J = 8.4, 2.7$ Hz, 1H), 4.29 – 4.13 (m, 4H), 3.83 (s, 3H), 3.36 – 3.24 (m, 1H), 2.97 (dt, $J = 16.8, 5.1$ Hz, 1H), 2.87 – 2.75 (m, 1H), 2.66 – 2.56 (m, 1H), 1.34 (t, $J = 7.1$ Hz, 3H), 1.25 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 187.8 (d, $J = 5.0$ Hz), 158.5, 135.9, 132.4, 129.8, 124.4 (qd, $J = 285.0, 3.4$ Hz), 122.9, 110.1, 64.0 (dd, $J = 46.9, 7.1$ Hz), 57.6 (dq, $J = 130.8, 23.4$ Hz), 55.5, 26.8 (dd, $J = 4.1, 2.2$ Hz), 24.4 (d, $J = 3.8$ Hz), 16.2 (dd, $J = 10.9, 6.1$ Hz). ^{19}F NMR (377 MHz, CDCl_3) δ -64.5 (d, $J = 6.6$ Hz, 3F). IR (KBr) $_{\text{max}}$ 2983, 1684, 1611, 1334, 1257, 1163, 1024, 970, 739, 566 cm^{-1} . MS (EI) m/z : 380 $[\text{M}]^+$. HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{16}\text{H}_{20}\text{F}_3\text{O}_5\text{P}$: 380.1000; Found: 380.1003.

Dimethyl(2-trifluoromethyl-1,2,3,4-tetrahydro-7-methoxy-1-oxonaphthalen-2-yl) Phosphonate (2d).

Compound **2d** was prepared following the *procedure C* and obtained in 61% yield as a light yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.55 (d, $J = 2.7$ Hz, 1H), 7.17 (d, $J = 8.5$ Hz, 1H), 7.11 (dd, $J = 8.4, 2.7$ Hz, 1H), 3.87 – 3.84 (m, 9H), 3.30 – 3.21 (m, 1H), 3.03 – 2.94 (m, 1H), 2.85 – 2.75 (m, 1H), 2.66 – 2.53 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 187.7 (d, $J = 5.1$ Hz), 158.5, 135.9, 132.2, 129.9, 124.5 (qd, $J = 285.3, 3.4$ Hz), 123.1, 110.2, 57.6 (dq, $J = 131.8, 24.1$ Hz), 55.5, 54.3 (dd, $J = 59.9, 7.0$ Hz), 26.7, 24.4 (d, $J = 4.4$ Hz). ^{19}F NMR (377 MHz, CDCl_3) δ -64.5 (d, $J = 6.9$ Hz, 3F). IR (KBr) $_{\text{max}}$ 2958, 1682, 1610, 1499, 1257, 1165, 1029, 832, 740, 566 cm^{-1} . MS (EI) m/z : 352 $[\text{M}]^+$. HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{14}\text{H}_{16}\text{F}_3\text{O}_5\text{P}$: 352.0687; Found:

352.0679.

Diethyl (1-trifluoromethyl-1-methyl-2-oxo-2-phenylethyl)phosphonate (2e).

Compound **2e** was prepared following the *procedure C* and obtained in 70% yield as a light yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, J = 7.7 Hz, 2H), 7.51 (t, J = 7.3 Hz, 1H), 7.42 (t, J = 7.6 Hz, 2H), 4.29 – 4.14 (m, 4H), 1.79 (d, J = 15.4 Hz, 3H), 1.34 (t, J = 6.9 Hz, 3H), 1.33 (t, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 195.3 (d, J = 3.2 Hz), 138.4, 131.8, 128.3, 128.0, 124.7 (qd, J = 284.5, 3.1 Hz), 64.2 (dd, J = 25.2, 7.0 Hz), 60.4 (dq, J = 130.1, 24.5 Hz), 16.9 (dd, J = 5.3, 2.8 Hz), 16.2 (d, J = 5.9 Hz). ^{19}F NMR (377 MHz, CDCl_3) δ -63.8 (d, J = 7.5 Hz, 3F). IR (KBr) $_{\text{max}}$ 2981, 1689, 1449, 1382, 1261, 1164, 1019, 914, 744 cm^{-1} . MS (EI) m/z : 338 $[\text{M}]^+$. HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{14}\text{H}_{18}\text{F}_3\text{O}_4\text{P}$: 338.0894; Found: 338.0903.

Diethyl (1-trifluoromethyl-1-ethyl-2-oxo-2-phenylethyl)phosphonate (2f).

Compound **2f** was prepared following the *procedure C* and obtained in 57% yield as a light yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.99 (d, J = 7.4 Hz, 2H), 7.52 (t, J = 7.4 Hz, 1H), 7.42 (t, J = 7.6 Hz, 2H), 4.28 – 4.11 (m, 4H), 2.80 – 2.66 (m, 1H), 2.37 – 2.24 (m, 1H), 1.34 (t, J = 7.1 Hz, 3H), 1.30 (t, J = 7.1 Hz, 3H), 0.89 (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 194.9 (d, J = 3.6 Hz), 139.2, 131.8, 128.1, 128.0, 124.9 (qd, J = 284.7, 3.4 Hz), 66.0 (dq, J = 126.0, 22.9 Hz), 64.2 (dd, J = 29.1, 7.1 Hz), 24.6, 16.2 (dd, J = 11.3, 6.0 Hz), 9.6 (d, J = 11.8 Hz). ^{19}F NMR (377 MHz, CDCl_3) δ -58.5 (d, J = 7.6 Hz, 3F). IR (KBr) $_{\text{max}}$ 2986, 1687, 1452, 1386, 1259, 1168, 1022, 975, 744, 579 cm^{-1} . MS (EI) m/z : 352 $[\text{M}]^+$. HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{15}\text{H}_{20}\text{F}_3\text{O}_4\text{P}$: 352.1051; Found: 352.1047.

Diethyl 1- trifluoromethyl -1-methyl-2-oxo-2-(4-methylphenyl)ethylphosphonate (2g).

Compound **2g** was prepared following the *procedure C* and obtained in 72% yield as

a light yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.89 (d, J = 8.1 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 4.27 – 4.12 (m, 4H), 2.39 (s, 3H), 1.80 (d, J = 15.4 Hz, 3H), 1.33 (t, J = 6.8 Hz, 3H), 1.31 (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 194.3 (d, J = 3.0 Hz), 142.7, 135.4, 128.9, 128.7, 124.8 (qd, J = 283.1, 2.9 Hz), 64.1 (dd, J = 21.7, 7.0 Hz), 60.4 (dq, J = 130.0, 24.2 Hz), 21.5, 17.0 (dd, J = 5.2, 2.8 Hz), 16.2 (d, J = 5.9 Hz). ^{19}F NMR (377 MHz, CDCl_3) δ -63.7 (d, J = 7.4 Hz, 3F). IR (KBr) $_{\text{max}}$ 2981, 1686, 1610, 1456, 1383, 1263, 1164, 1021, 913, 743, 579 cm^{-1} . MS (EI) m/z : 352 $[\text{M}]^+$. HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{15}\text{H}_{20}\text{F}_3\text{O}_4\text{P}$: 352.1051; Found: 352.1058.

Diethyl 1- trifluoromethyl -1-methyl-2-oxo-2-(4-chlorophenyl)ethylphosphonate (2h).

Compound **2h** was prepared following the *procedure C* and obtained in 64% yield as a light yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, J = 8.6 Hz, 2H), 7.40 (d, J = 8.6 Hz, 2H), 4.29 – 4.11 (m, 4H), 1.78 (d, J = 15.1 Hz, 3H), 1.34 (t, J = 7.1 Hz, 3H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 193.6 (d, J = 2.2 Hz), 138.5, 136.5, 130.3, 128.3, 124.6 (qd, J = 283.1, 2.4 Hz), 64.2 (dd, J = 25.7, 6.9 Hz), 60.7 (dq, J = 128.3, 24.2 Hz), 16.9 (dd, J = 5.0, 2.5 Hz), 16.2 (d, J = 3.6 Hz). ^{19}F NMR (377 MHz, CDCl_3) δ -63.6 (d, J = 7.4 Hz, 3F). IR (KBr) $_{\text{max}}$ 2981, 1694, 1588, 1457, 1383, 1264, 1169, 1020, 913, 835, 746 cm^{-1} . MS (EI) m/z : 372 $[\text{M}]^+$. HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{14}\text{H}_{17}\text{ClF}_3\text{O}_4\text{P}$: 372.0505; Found: 372.0511.

Diethyl 1- trifluoromethyl -1-methyl-2-oxo-2-(4-acetoxyphenyl)ethylphosphonate (2i).

Compound **2i** was prepared following the *procedure C* and obtained in 46% yield as a light yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 8.06 (d, J = 8.7 Hz, 2H), 7.16 (d, J = 8.7 Hz, 2H), 4.28 – 4.11 (m, 4H), 2.32 (s, 3H), 1.80 (d, J = 15.3 Hz, 3H), 1.33 (t, J = 7.2 Hz, 3H), 1.31 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 193.5 (d, J = 2.9 Hz), 168.8, 153.5, 135.5, 130.5, 124.7 (qd, J = 283.2, 2.8 Hz), 121.2, 64.2 (dd, J = 23.0, 7.0 Hz), 60.5 (dq, J = 129.2, 24.5 Hz), 21.2, 17.0 (dd, J = 5.3, 2.8 Hz), 16.2 (d, J = 4.8 Hz). ^{19}F NMR (377 MHz, CDCl_3) δ -63.7 (d, J = 7.4 Hz, 3F). IR (KBr) $_{\text{max}}$ 2989, 1766, 1689, 1597, 1375, 1263, 1198, 1167, 1018, 951, 745, 577 cm^{-1} . MS (EI) m/z : 396 $[\text{M}]^+$. HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{16}\text{H}_{20}\text{F}_3\text{O}_6\text{P}$: 396.0949; Found: 396.0949.

Dimethyl (1-trifluoromethyl-1-methyl-2-oxo-2-phenylethyl)phosphonate (2j).

Compound **2j** was prepared following the *procedure C* and obtained in 59% yield as a light yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, $J = 7.7$ Hz, 2H), 7.52 (t, $J = 7.3$ Hz, 1H), 7.43 (t, $J = 7.7$ Hz, 2H), 3.88 (d, $J = 11.1$ Hz, 3H), 3.85 (d, $J = 11.1$ Hz, 3H), 1.80 (d, $J = 15.5$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 195.2 (d, $J = 3.4$ Hz), 138.2, 131.9, 128.2, 128.1, 124.6 (qd, $J = 284.3$, 3.3 Hz), 60.3 (dq, $J = 130.2$, 24.7 Hz), 54.4 (dd, $J = 28.6$, 6.9 Hz), 16.9 (dd, $J = 5.3$, 2.8 Hz). ^{19}F NMR (377 MHz, CDCl_3) δ -64.0 (d, $J = 7.5$ Hz, 3F). IR (KBr) $_{\text{max}}$ 2960, 1690, 1456, 1380, 1262, 1166, 1028, 914, 744 cm^{-1} . MS (EI) m/z : 310 $[\text{M}]^+$. HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{12}\text{H}_{14}\text{F}_3\text{O}_4\text{P}$: 310.0581; Found: 310.0585.

Diisopropyl (1-trifluoromethyl-1-methyl-2-oxo-2-phenylethyl)phosphonate (2k).

Compound **2k** was prepared following the *procedure C* and obtained in 76% yield as a light yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, $J = 7.7$ Hz, 2H), 7.50 (t, $J = 7.3$ Hz, 1H), 7.41 (t, $J = 7.6$ Hz, 2H), 4.88 – 4.70 (m, 2H), 1.77 (d, $J = 15.2$ Hz, 3H), 1.37 – 1.33 (m, 9H), 1.28 (d, $J = 6.2$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 195.3 (d, $J = 3.1$ Hz), 138.6, 131.7, 128.5, 127.9, 124.7 (qd, $J = 283.9$, 3.0 Hz), 73.3 (dd, $J = 36.3$, 7.3 Hz), 60.7 (dq, $J = 131.0$, 24.2 Hz), 24.2 (dd, $J = 16.3$, 3.1 Hz), 23.3 (dd, $J = 7.8$, 6.2 Hz), 17.0 (dd, $J = 5.4$, 2.8 Hz). ^{19}F NMR (377 MHz, CDCl_3) δ -63.5 (d, $J = 7.6$ Hz, 3F). IR (KBr) $_{\text{max}}$ 2984, 1690, 1456, 1382, 1263, 1166, 1102, 996, 742, 578 cm^{-1} . MS (EI) m/z : 366 $[\text{M}]^+$. HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{16}\text{H}_{22}\text{F}_3\text{O}_4\text{P}$: 366.1207; Found: 366.1205.

Dibutyl (1-trifluoromethyl-1-methyl-2-oxo-2-phenylethyl)phosphonate (2l).

Compound **2l** was prepared following the *procedure C* and obtained in 67% yield as a light yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.93 (d, $J = 7.6$ Hz, 2H), 7.51 (t, $J = 7.4$ Hz, 1H), 7.42 (t, $J = 7.6$ Hz, 2H), 4.21 – 4.07 (m, 4H), 1.79 (d, $J = 15.3$ Hz, 3H), 1.69 – 1.60 (m, 4H), 1.41 – 1.33 (m, 4H), 0.91 (t, $J = 7.4$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 195.1 (d, $J = 3.3$ Hz), 138.3, 131.8, 128.4, 128.0, 124.7 (qd, $J = 284.0$,

3.0 Hz), 67.7 (dd, $J = 27.2, 7.3$ Hz), 60.4 (dq, $J = 130.3, 24.7$ Hz), 32.3 (dd, $J = 6.0, 1.9$ Hz), 18.6 (d, $J = 1.4$ Hz), 16.9 (dd, $J = 5.3, 2.8$ Hz), 13.5. ^{19}F NMR (377 MHz, CDCl_3) δ -63.8 (d, $J = 7.4$ Hz, 3F). IR (KBr) $_{\text{max}}$ 2962, 1690, 1459, 1382, 1264, 1165, 1021, 913, 742, 580 cm^{-1} . MS (EI) m/z : 394 $[\text{M}]^+$. HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{18}\text{H}_{26}\text{F}_3\text{O}_4\text{P}$: 394.1520; Found: 394.1517.

Diethyl(2-pentafluoroethyl-1,2,3,4-tetrahydro-1-oxonaphthalen-2-yl)phosphonate (3a).

Compound **3a** was prepared following the *procedure C* and obtained in 37% yield as a light yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 8.07 (d, $J = 7.9$ Hz, 1H), 7.51 (t, $J = 7.4$ Hz, 1H), 7.34 (t, $J = 7.6$ Hz, 1H), 7.24 (d, $J = 7.6$ Hz, 1H), 4.31 – 4.14 (m, 4H), 3.44 – 3.32 (m, 1H), 3.04 – 2.95 (m, 1H), 2.85 – 2.75 (m, 1H), 2.65 – 2.48 (m, 1H), 1.32 (t, $J = 7.1$ Hz, 3H), 1.22 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 187.8 (dd, $J = 5.6, 3.6$ Hz), 142.8, 134.1, 132.1, 128.5, 128.4, 127.1, 120.6-120.2 (m), 117.8-117.3 (m), 64.1 (dd, $J = 45.0, 7.1$ Hz), 57.0 (dt, $J = 127.3, 18.2$ Hz), 26.4 (dd, $J = 4.6, 2.4$ Hz), 25.5 (d, $J = 2.9$ Hz), 16.1 (dd, $J = 12.5, 6.3$ Hz). ^{19}F NMR (377 MHz, CDCl_3) δ -77.2 (s, 3F), -107.0 (dd, $J = 283.3, 13.5$ Hz, 1F), -109.0 (dd, $J = 283.3, 4.5$ Hz, 1F). IR (KBr) $_{\text{max}}$ 2987, 1689, 1603, 1449, 1259, 1215, 1019, 964, 744, 604 cm^{-1} . MS (EI) m/z : 400 $[\text{M}]^+$. HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{16}\text{H}_{18}\text{F}_5\text{O}_4\text{P}$: 400.0862; Found: 400.0870.

Diethyl (1- pentafluoroethyl -1-methyl-2-oxo-2-phenylethyl)phosphonate (3e).

Compound **3e** was prepared following the *procedure C* and obtained in 48% yield as a light yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, $J = 8.1$ Hz, 2H), 7.50 (t, $J = 7.4$ Hz, 1H), 7.41 (t, $J = 7.6$ Hz, 2H), 4.34 – 4.12 (m, 4H), 1.77 (d, $J = 15.4$ Hz, 3H), 1.36 (t, $J = 7.1$ Hz, 3H), 1.29 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 195.1 (t, $J = 4.4$ Hz), 138.8, 131.7, 128.7 (d, $J = 2.5$ Hz), 127.9, 120.5-119.6 (m), 117.9-117.1 (m), 64.2 (dd, $J = 78.1, 7.1$ Hz), 58.8 (dt, $J = 127.3, 19.2$ Hz), 17.1 (dd, $J = 6.2, 3.2$ Hz), 16.2 (dd, $J = 13.4, 6.0$ Hz). ^{19}F NMR (377 MHz, CDCl_3) δ -77.8 (s, 3F), -106.3 (dd, $J = 277.8, 6.7$ Hz, 1F), -109.5 (dd, $J = 277.8, 5.9$ Hz, 1F). IR (KBr) $_{\text{max}}$ 2988, 1690, 1453, 1257, 1207, 1012, 953, 742, 698, 558 cm^{-1} . MS (EI) m/z : 388 $[\text{M}]^+$. HRMS (EI-TOF) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{15}\text{H}_{18}\text{F}_5\text{O}_4\text{P}$: 388.0862; Found: 388.0859.

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4. Copies of ^1H , ^{19}F and ^{13}C NMR spectra for the new products