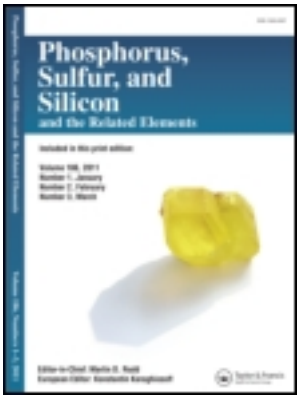

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A Synthesis of Phosphorylated 2,4-Dioxothiazolidine Derivatives

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A SYNTHESIS OF PHOSPHORYLATED 2,4-DIOXOTHIAZOLIDINE DERIVATIVES

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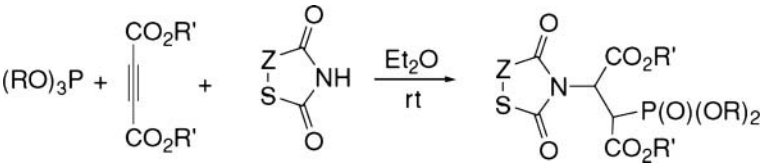
GRAPHICAL ABSTRACT



Abstract *The zwitterionic 1:1 intermediates generated from trialkyl phosphites and dialkyl acetylenedicarboxylates are trapped by 2,4-thiazolidinedione and 5-arylidene-2,4-thiazolidinediones to produce dialkyl 2-(2,4-dioxothiazolidin-3-yl)-3-(dialkoxyphosphoryl) succinates and dialkyl 2-(5-arylidene-2,4-dioxothiazolidin-3-yl)-3-(dialkoxyphosphoryl) succinates in good yields.*

Keywords Acetylenic esters; MCR; phosphites; phosphonates; 2,4-thiazolidinedione

INTRODUCTION

Multicomponent reactions (MCRs), with three or more reactants combining in a one-pot procedure to give a single product, are powerful building tools in organic synthesis.[1,2] Organophosphorus compounds are widely used in agriculture as insecticides and fungicides and to some extent as herbicides.[3,4] In research laboratories, organophosphorus compounds find important applications in organic synthesis (Wittig, Staudinger, organocatalysis).[5,6] Furthermore, organophosphorus compounds can be used as flame retardants for fabrics and plastics, plasticizing and stabilizing agents in the plastics industry, selective extractants for metal salts from ores, additives for petroleum products, and corrosion inhibitors.[7,8]

As part of our study on the development of new routes to heterocyclic and carbocyclic systems,[9–13] we now report an efficient synthesis of dialkyl 2-(2,4-dioxothiazolidin-3-yl)-3-(dialkoxyphosphoryl)succinates **4a–d** and dialkyl 2-(5-arylidene-2,4-dioxothiazolidin-3-yl)-3-(dialkoxyphosphoryl)succinates **4e–l** from the reaction of trialkyl phosphites

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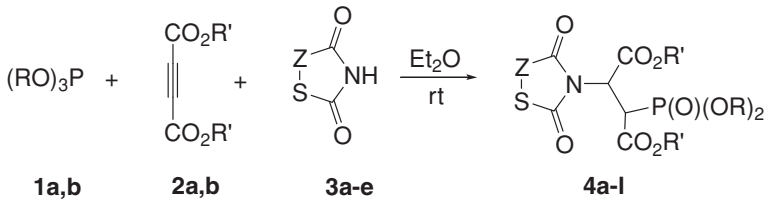
Table 1 Reaction of $(RO)_3P$, acetylenic esters, and 2,4-thiazolidinediones



Phosphite **1** R		Acetylenic ester **2** R'		Thiazolidinedione **3** Z		Product **4**	Yield (%)
1a	Me	**2a**	Me	**3a**	CH_2	**4a**	70
1a	Me	**2b**	Et	**3a**	CH_2	**4b**	73
1b	Ph	**2a**	Me	**3a**	CH_2	**4c**	82
1b	Ph	**2b**	Et	**3a**	CH_2	**4d**	84
1a	Me	**2a**	Me	**3b**	Ph−CH=C	**4e**	85
1a	Me	**2b**	Et	**3b**	Ph−CH=C	**4f**	83
1a	Me	**2a**	Me	**3c**	*p*-Tolyl−CH=C	**4g**	93
1a	Me	**2b**	Et	**3c**	*p*-Tolyl−CH=C	**4h**	91
1a	Me	**2a**	Me	**3d**	2-Thienyl−CH=C	**4i**	90
1a	Me	**2b**	Et	**3d**	2-Thienyl−CH=C	**4j**	88
1a	Me	**2a**	Me	**3e**	2-Furyl−CH=C	**4k**	90
1a	Me	**2b**	Et	**3e**	2-Furyl−CH=C	**4l**	86

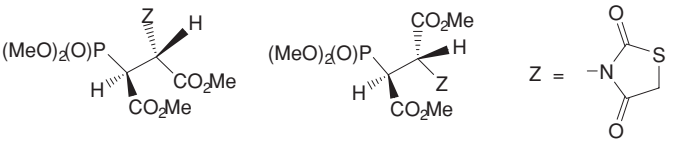
1, dialkyl acetylenedicarboxylates **2**, and 2,4-thiazolidinedione **3a** or 5-arylidene-2,4-thiazolidinediones **3b–e** in good yields (Table 1).

RESULTS AND DISCUSSION

The reactions were carried out by mixing phosphate **1** with **3** and then adding the acetylenic ester **2** slowly at r.t. The reactions were complete within 1–3 h. The structures of compounds **4a–l** as 1:1:1 adducts were apparent from their mass spectra, which displayed, in each case, the molecular ion peak at appropriate *m/z* values. The ^{1}H- and ^{13}C-NMR spectroscopic data, as well as infrared (IR) spectra, are in agreement with the proposed structures. The ^{1}H-NMR spectrum of **4a** exhibited two doublets readily recognized as arising from the two diastereotopic methoxy ($\delta = 3.73$ ppm, $^3J_{HP} = 11.0$ Hz and $\delta = 3.78$ ppm, $^3J_{HP} = 11.0$ Hz) groups. The two singlets at $\delta = 3.75$ and 3.85 ppm belong to the ester methoxy protons. The proton-decoupled ^{13}C-NMR spectrum of **4a** showed 11 distinct resonances in agreement with the proposed structure.

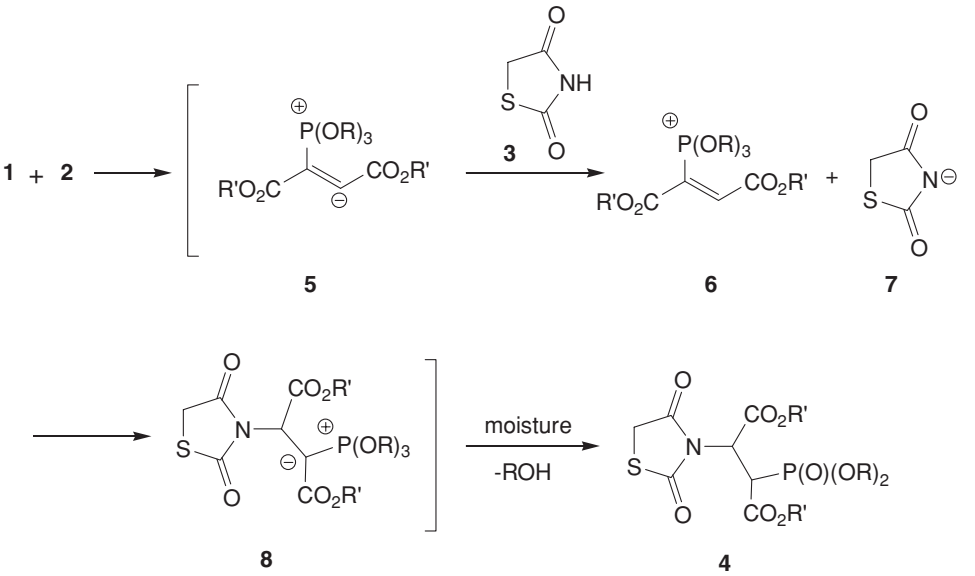
Observation of $^3J_{HH} = 11.4$ Hz for the vicinal methine protons in **4a** indicates the dominance of the *anti* arrangement. Because compound **4a** possesses two stereogenic centers, two diastereomers with *anti* HCCH arrangement are possible (Scheme 1). The observation of $^3J_{CP} = 17.6$ Hz for the carbonyl carbon atom of CO_2Me group is in agreement with the (2*S*,3*R*) or (2*R*,3*S*) diastereomer. However, as long as the coupling constant of at least one other diastereomer is not known, the assignment remains uncertain.

Although we have not established the mechanism of the reaction between phosphites **1**, dialkyl acetylenedicarboxylates **2**, and 2,4-thiazolidinedione in an experimental manner,



(2*S*, 3*R*)-**4a** *or* (2*R*, 3*S*)-**4a** (2*S*, 3*S*)-**4a** *or* (2*R*, 3*R*)-**4a**

Scheme 1 Diastereoisomers of compound **4a**.



Scheme 2 Plausible mechanism for formation of compounds **4**.

a possible explanation is proposed in Scheme 2. The first step may involve addition of phosphite to acetylenic ester and formation of the 1:1 adducts **5** and its subsequent protonation by 2,4-thiazolidinedione. Then, the positively charged ion **6** is attacked by the anion of the NH-acidic **7** to produce ylide **8**, which is hydrolyzed to give **4**. Because the reactions were carried out under an ordinary atmosphere, the conversion of **8** to **4** is presumably accomplished by the moisture from the air. When the reaction was carried out in the absence of air, a complex mixture was obtained.

The reaction of trimethyl phosphite (**1a**), acetylenedicarboxylates **2**, and 5-arylidene-2,4-thiazolidinediones **3b–e** (prepared by a Knoevenagel condensation of thiazolidine-2,4-dione with aromatic aldehydes)[14] proceeded smoothly to afford functionalized phosphonated **4e–l** in good yields. The structures of compounds were again confirmed by ^{1}H—, ^{13}C—, and ^{31}P-NMR data and IR spectra. Observation of $^{3}J_{HH} = 11.0$ Hz for the vicinal methine protons in **4e** indicates the dominance of the *anti* arrangement (see Scheme 1). The observation of $^{3}J_{CP} = 17.8$ Hz for the CO_2Me group is in agreement with the presence of a single diastereoisomer, namely, (2*S*,3*R*) and its enantiomer (2*R*,3*S*).

CONCLUSIONS

In summary, the reaction of dialkyl acetylenedicarboxylates with phosphites in the presence of 2,4-thiazolidinedione or 5-arylidene-2,4-thiazolidinediones provides a simple one-pot synthesis of stable dialkyl(aryl) phosphorylsuccinates of potential synthetic and pharmaceutical interest. The present procedure has the advantage that the reaction is performed under neutral conditions, and the starting material can be used without any activation or modification.

EXPERIMENTAL

5-Arylidene-2,4-thiazolidinediones **3b–e** were prepared according to the literature.[14] Other compounds were purchased from Merck and used without further purification. IR spectra were recorded on a Shimadzu IR-460 spectrometer. ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra were recorded on a Bruker DRX-300 Avance instrument with $CDCl_3$ as solvent at 300.1, 75.5, and 121.5 MHz, respectively. Electron impact–mass spectrometry (EI-MS) (70 eV) was used to obtain mass spectra (in *m/z*) using a Finnigan-MAT-8430 mass spectrometer. Elemental analyses (C, H, N) were obtained with a Heraeus CHN-O rapid analyzer.

General Procedure for the Preparation of Compounds 4

To a stirred solution of **1** (1 mmol) and **3** (1 mmol) in Et_2O (5 mL) was added a solution of **2** (1 mmol) in Et_2O (2 mL) at r.t. over 10 min. After completion of the reaction (1–3 h; thin-layer chromatography [TLC; AcOEt/hexane 1:1]), the reaction mixture was purified by column chromatography (silica gel [230–240 mesh; Merck], hexane/AcOEt 4:1).

Dimethyl 2-(dimethoxyphosphoryl)-3-(2,4-dioxothiazolidin-3-yl)succinate (4a). Pale yellow oil, yield: 0.26 g (70%). Anal. Calcd. for $C_{11}H_{16}NO_9PS$ (369.3): C, 35.78; H, 4.37; N, 3.79%. Found: C, 35.5; H, 4.3; N, 3.9%. IR (KBr, cm^{-1}): 1748 and 1695 (C=O), 1258 (P=O); ^{1}H-NMR (300 MHz, $CDCl_3$, δ/ppm): 3.73 (3 H, d, $^{3}J_{HP}$ = 11.0 Hz, MeO), 3.75 (3 H, s, MeO), 3.78 (3 H, d, $^{3}J_{HP}$ = 11.0 Hz, MeO), 3.85 (3 H, s, MeO), 4.03 (2 H, s, CH_2S), 4.17 (1 H, dd, $^{3}J_{HH}$ = 11.4 Hz, $^{2}J_{HP}$ = 20.4 Hz, CH), 5.61 (1 H, dd, $^{3}J_{HH}$ = 11.4 Hz, $^{3}J_{HP}$ = 4.4 Hz, CH); ^{13}C-NMR (75 MHz, $CDCl_3$, δ/ppm): 33.8 (CH_2S), 42.7 (d, $^{1}J_{CP}$ = 128.2 Hz, CH), 52.0 (d, $^{2}J_{CP}$ = 5.4 Hz, CH), 52.9 (MeO), 53.3 (MeO), 53.8 (d, $^{2}J_{PC}$ = 5.3 Hz, MeO), 54.5 (d, $^{2}J_{PC}$ = 5.9 Hz, MeO), 164.8 (C=O), 166.7 (d, $^{2}J_{CP}$ = 7.5 Hz, C=O), 167.0 (d, $^{3}J_{CP}$ = 17.6 Hz, C=O), 170.9 (C=O); ^{31}P-NMR (121 MHz, $CDCl_3$, δ/ppm): 18.7; MS (EI, 70 eV): *m/z* (%) = 369 (M^+, 8), 338 (18), 296 (27), 222 (35), 193 (20), 124 (16), 109 (86), 31 (80).

Diethyl 2-(dimethoxyphosphoryl)-3-(2,4-dioxothiazolidin-3-yl)succinate (4b). Pale yellow oil, yield: 0.29 g (73%). Anal. Calcd. for $C_{13}H_{20}NO_9PS$ (397.3): C, 39.30; H, 5.07; N, 3.53%. Found: C, 39.6; H, 5.0; N, 3.6%. IR (KBr, cm^{-1}): 1740 and 1705 (C=O), 1255 (P=O); ^{1}H-NMR (300 MHz, $CDCl_3$, δ/ppm): 1.23 (3 H, t, $^{3}J_{HH}$ = 7.2 Hz, Me), 1.34 (3 H, t, $^{3}J_{HH}$ = 7.2 Hz, Me), 3.74 (3 H, d, $^{3}J_{HP}$ = 11.1 Hz, MeO), 3.80 (3 H, d, $^{3}J_{HP}$ = 11.1 Hz, MeO), 4.02 (2 H, s, CH_2S), 4.18–4.34 (5 H, m, 2 CH_2O, CH), 5.58 (1 H, dd, $^{3}J_{HH}$ = 11.4 Hz, $^{3}J_{HP}$ = 4.5 Hz, CH); ^{13}C-NMR (75 MHz, $CDCl_3$, δ/ppm): 14.3 (Me), 14.4 (Me), 42.8 (d, $^{1}J_{CP}$ = 127.3 Hz, CH), 52.2 (d, $^{2}J_{CP}$ = 5.4 Hz, CH), 53.9 (d, $^{2}J_{PC}$ = 5.3 Hz, MeO), 54.4 (d, $^{2}J_{PC}$ = 5.8 Hz, MeO), 62.5 (CH_2O), 63.2 (CH_2O), 163.8 (C=O), 166.8 (d, $^{2}J_{CP}$ = 7.5 Hz, C=O), 167.2 (d, $^{3}J_{CP}$ = 17.6 Hz, C=O), 171.2 (C=O); ^{31}P-NMR

(121 MHz, $CDCl_3$, δ/ppm): 15.3; MS (EI, 70 eV): m/z (%) = 397 (M^+, 5), 348 (18), 324 (25), 235 (35), 207 (20), 135 (22), 109 (100), 44 (38).

Dimethyl 2-(2,4-dioxothiazolidin-3-yl)-3-(diphenoxyphosphoryl)succinate (4c). Colorless oil, yield: 0.40 g (82%). Anal. Calcd. for $C_{21}H_{20}NO_9PS$ (493.4): C, 51.12; H, 4.09; N, 2.84%. Found: C, 51.3; H, 4.0; N, 2.7%. IR (KBr, cm^{-1}): 1745 and 1710 (C=O), 1279 (P=O); ^{1}H-NMR (300 MHz, $CDCl_3$, δ/ppm): 3.78 (3 H, s, MeO), 3.90 (3 H, s, MeO), 4.02 (2 H, s, CH_2S), 4.46 (1 H, dd, $^3J_{HH}$ = 11.4 Hz, $^2J_{HP}$ = 21.1 Hz, CH), 5.88 (1 H, dd, $^3J_{HH}$ = 11.4 Hz, $^3J_{HP}$ = 4.5 Hz, CH), 7.12–7.23 (6 H, m, 6 CH), 7.29–7.34 (4 H, m, 4 CH); ^{13}C-NMR (75 MHz, $CDCl_3$, δ/ppm): 34.0 (CH_2S), 43.9 (d, $^1J_{CP}$ = 133.0 Hz, CH), 52.1 (d, $^2J_{CP}$ = 4.1 Hz, CH), 53.8 (MeO), 54.1 (MeO), 120.7 (d, $^3J_{CP}$ = 4.5 Hz, 2 CH_{ortho}), 121.0 (d, $^3J_{CP}$ = 4.5 Hz, 2 CH_{ortho}), 126.1 (CH_{para}), 126.2 (CH_{para}), 130.3 (m, 4 CH_{meta}), 149.7 (d, $^2J_{CP}$ = 8.5 Hz, C_{ipso}), 150.4 (d, $^2J_{CP}$ = 8.2 Hz, C_{ipso}), 165.5 (C=O), 166.7 (d, $^3J_{CP}$ = 9.4 Hz, C=O), 167.6 (d, $^2J_{CP}$ = 18.9 Hz, C=O), 171.2 (C=O); ^{31}P-NMR (121 MHz, $CDCl_3$, δ/ppm): 11.7; MS (EI, 70 eV): m/z (%) = 493 (M^+, 4), 462 (16), 420 (26), 346 (20), 318 (16), 233 (100), 93 (56).

Diethyl 2-(2,4-dioxothiazolidin-3-yl)-3-(diphenoxyphosphoryl)succinate (4d). Colorless oil, yield: 0.44 g (84%). Anal. Calcd. for $C_{23}H_{24}NO_9PS$ (521.5): C, 52.97; H, 4.64; N, 2.69%. Found: C, 52.7; H, 4.6; N, 2.6%. IR (KBr, cm^{-1}): 1740 and 1969 (C=O), 1282 (P=O); ^{1}H-NMR (300 MHz, $CDCl_3$, δ/ppm): 1.29 (3 H, t, $^3J_{HH}$ = 7.2 Hz, Me), 1.34 (3 H, t, $^3J_{HH}$ = 7.2 Hz, Me), 4.00 (2 H, s, CH_2S), 4.22 (2 H, q, $^3J_{HH}$ = 7.2 Hz, CH_2O), 4.32 (2 H, q, $^3J_{HH}$ = 7.2 Hz, CH_2O), 4.46 (1 H, dd, $^3J_{HH}$ = 11.4 Hz, $^2J_{HP}$ = 21.1 Hz, CH), 5.86 (1 H, dd, $^3J_{HH}$ = 11.4 Hz, $^3J_{HP}$ = 4.8 Hz, CH), 7.13–7.27 (6 H, m, 6 CH), 7.29–7.36 (4 H, m, 4 CH); ^{13}C-NMR (75 MHz, $CDCl_3$, δ/ppm): 14.3 (Me), 14.4 (Me), 34.0 (CH_2S), 44.1 (d, $^1J_{CP}$ = 132.6 Hz, CH), 52.2 (d, $^2J_{CP}$ = 4.4 Hz, CH), 62.9 (CH_2O), 63.4 (CH_2O), 120.7 (d, $^3J_{CP}$ = 4.3 Hz, 2 CH_{ortho}), 121.0 (d, $^3J_{CP}$ = 4.3 Hz, 2 CH_{ortho}), 126.0 (CH_{para}), 126.1 (CH_{para}), 130.2 (m, 4 CH_{meta}), 149.7 (d, $^2J_{CP}$ = 8.5 Hz, C_{ipso}), 150.3 (d, $^2J_{CP}$ = 8.2 Hz, C_{ipso}), 163.7 (C=O), 166.0 (d, $^3J_{CP}$ = 8.0 Hz, C=O), 167.2 (d, $^2J_{CP}$ = 19.2 Hz, C=O), 171.8 (C=O); ^{31}P-NMR (121 MHz, $CDCl_3$, δ/ppm): 11.1; MS (EI, 70 eV): m/z (%) = 521 (M^+, 8), 472 (23), 448 (20), 374 (35), 332 (28), 233 (100), 93 (86), 77 (42).

Dimethyl 2-(5-benzylidene-2,4-dioxothiazolidin-3-yl)-3-(dimethoxyphosphoryl)succinate (4e). Colorless oil, yield: 0.39 g (85%). Anal. Calcd. for $C_{18}H_{20}NO_9PS$ (457.4): C, 47.27; H, 4.41; N, 3.06%. Found: C, 47.0; H, 4.3; N, 3.1%. IR (KBr, cm^{-1}): 1746 and 1699 (C=O), 1269 (P=O); ^{1}H-NMR (300 MHz, $CDCl_3$, δ/ppm): 3.68 (3 H, d, $^3J_{HP}$ = 11.0 Hz, MeO), 3.73 (3 H, d, $^3J_{HP}$ = 11.0 Hz, MeO), 3.75 (3 H, s, MeO), 3.81 (3 H, s, MeO), 4.13 (1 H, dd, $^3J_{HH}$ = 11.7 Hz, $^2J_{HP}$ = 20.7 Hz, CH), 5.66 (1 H, dd, $^3J_{HH}$ = 11.7 Hz, $^3J_{HP}$ = 4.5 Hz, CH), 7.48–7.71 (5 H, m, 5 CH), 8.00 (1 H, s, CH); ^{13}C-NMR (75 MHz, $CDCl_3$, δ/ppm): 43.2 (d, $^1J_{CP}$ = 128.5 Hz, CH), 52.2 (d, $^2J_{CP}$ = 5.6 Hz, CH), 53.3 (MeO), 53.8 (d, $^2J_{PC}$ = 6.1 Hz, MeO), 54.0 (MeO), 54.3 (d, $^2J_{PC}$ = 6.2 Hz, MeO), 120.9 (C), 129.6 (2 CH), 130.7 (2 CH), 131.1 (CH), 133.4 (C), 135.2 (CH), 165.7 (C=O), 167.7 (d, $^2J_{CP}$ = 8.2 Hz, C=O), 167.9 (d, $^3J_{CP}$ = 17.8 Hz, C=O), 171.3 (C=O); ^{31}P-NMR (121 MHz, $CDCl_3$, δ/ppm): 20.1; MS (EI, 70 eV): m/z (%) = 457 (M^+, 3), 352 (27), 296 (33), 222 (21), 193 (18), 134 (100), 109 (18).

Diethyl 2-(5-benzylidene-2,4-dioxothiazolidin-3-yl)-3-(dimethoxyphosphoryl)succinate (4f). Pale yellow oil, yield: 0.40 g (83%). Anal. Calcd. for $C_{20}H_{24}NO_9PS$ (485.4): C, 49.48; H, 4.98; N, 2.89%. Found: C, 49.2; H, 5.1; N, 2.8%. IR (KBr, cm^{-1}): 1730 and 1695 (C=O), 1254 (P=O); ^{1}H-NMR (300 MHz, $CDCl_3$, δ/ppm): 1.22 (3 H, t, $^3J_{HH}$ = 7.2 Hz, Me), 1.35 (3 H, t, $^3J_{HH}$ = 7.2 Hz, Me), 3.72 (3 H, d, $^3J_{HP}$ =

11.1 Hz, MeO), 3.77 (3 H, d, $^3J_{HP}$ = 11.0 Hz, MeO), 4.19–4.35 (5 H, m, 2 CH_2O, CH), 5.58 (1 H, dd, $^3J_{HH}$ = 11.4 Hz, $^3J_{HP}$ = 4.5 Hz, CH), 7.46–7.52 (5 H, m, 5 CH), 7.94 (1 H, s, CH); ^{13}C-NMR (75 MHz, $CDCl_3$, δ/ppm): 14.3 (Me), 14.4 (Me), 43.4 (d, $^1J_{CP}$ = 128.2 Hz, CH), 52.4 (d, $^2J_{CP}$ = 6.4 Hz, CH), 53.9 (d, $^2J_{PC}$ = 6.5 Hz, MeO), 54.2 (d, $^2J_{PC}$ = 6.2 Hz, MeO), 62.6 (CH_2O), 63.5 (CH_2O), 121.0 (C), 129.6 (2 CH), 130.8 (2 CH), 131.1 (CH), 133.4 (C), 135.0 (CH), 165.6 (C=O), 167.2 (d, $^2J_{CP}$ = 7.2 Hz, C=O), 167.5 (d, $^3J_{CP}$ = 17.8 Hz, C=O), 170.7 (C=O); ^{31}P-NMR (121 MHz, $CDCl_3$, δ/ppm): 19.2; MS (EI, 70 eV): *m/z* (%) = 485 (M^+, 5), 436 (16), 380 (55), 235 (35), 207 (20), 134 (100), 109 (30).

Dimethyl 2-(dimethoxyphosphoryl)-3-(5-(4-methylbenzylidene)-2,4-dioxothiazolidin-3-yl)succinate (4g). Pale yellow oil, yield: 0.44 g (93%). Anal. Calcd. for $C_{19}H_{22}NO_9PS$ (471.4): C, 48.41; H, 4.70; N, 2.97%. Found: C, 48.6; H, 4.8; N, 2.9%. IR (KBr, cm^{-1}): 1724 and 1700 (C=O), 1246 (P=O); ^{1}H-NMR (300 MHz, $CDCl_3$, δ/ppm): 2.42 (3 H, s, Me), 3.68 (3 H, d, $^3J_{HP}$ = 11.1 Hz, MeO), 3.73 (3 H, d, $^3J_{HP}$ = 11.1 Hz, MeO), 3.75 (3 H, s, MeO), 3.80 (3 H, s, MeO), 4.07 (1 H, dd, $^3J_{HH}$ = 11.4 Hz, $^2J_{HP}$ = 20.5 Hz, CH), 5.67 (1 H, dd, $^3J_{HH}$ = 11.4 Hz, $^3J_{HP}$ = 4.5 Hz, CH), 7.42 (2 H, d, $^3J_{HH}$ = 8.1 Hz, 2 CH), 7.58 (2 H, d, $^3J_{HH}$ = 8.1 Hz, 2 CH), 7.95 (1 H, s, CH); ^{13}C-NMR (75 MHz, $CDCl_3$, δ/ppm): 22.0 (Me), 43.2 (d, $^1J_{CP}$ = 128.5 Hz, CH), 52.2 (d, $^2J_{CP}$ = 4.5 Hz, CH), 53.6 (MeO), 53.9 (d, $^2J_{PC}$ = 6.3 Hz, MeO), 54.0 (MeO), 54.3 (d, $^2J_{PC}$ = 6.3 Hz, MeO), 119.6 (C), 130.4 (2 CH), 130.6 (C), 130.8 (2 CH), 136.3 (C), 142.0 (CH), 165.7 (C=O), 167.7 (d, $^2J_{CP}$ = 7.2 Hz, C=O), 168.0 (d, $^3J_{CP}$ = 18.0 Hz, C=O), 170.9 (C=O); ^{31}P-NMR (121 MHz, $CDCl_3$, δ/ppm): 19.7; MS (EI, 70 eV): *m/z* (%) = 471 (M^+, 5), 439 (22), 352 (15), 222 (25), 148 (100), 124 (22), 109 (20).

Diethyl 2-(dimethoxyphosphoryl)-3-(5-(4-methylbenzylidene)-2,4-dioxothiazolidin-3-yl)succinate (4h). Pale yellow oil, yield: 0.45 g (91%). Anal. Calcd. for $C_{21}H_{26}NO_9PS$ (499.5): C, 50.50; H, 5.25; N, 2.80%. Found: C, 50.3; H, 5.1; N, 2.7%. IR (KBr, cm^{-1}): 1722 and 1700 (C=O), 1252 (P=O); ^{1}H-NMR (300 MHz, $CDCl_3$, δ/ppm): 1.24 (3 H, t, $^3J_{HH}$ = 7.2 Hz, Me), 1.35 (3 H, t, $^3J_{HH}$ = 7.2 Hz, Me), 2.41 (3 H, s, Me), 3.71 (3 H, d, $^3J_{HP}$ = 11.4 Hz, MeO), 3.81 (3 H, d, $^3J_{HP}$ = 11.4 Hz, MeO), 4.18–4.35 (5 H, m, 2 CH_2O, CH), 5.72 (1 H, dd, $^3J_{HH}$ = 11.4 Hz, $^3J_{HP}$ = 4.2 Hz, CH), 7.28 (2 H, d, $^3J_{HH}$ = 7.8 Hz, 2 CH), 7.42 (2 H, d, $^3J_{HH}$ = 7.8 Hz, 2 CH), 7.90 (1 H, s, CH); ^{13}C-NMR (75 MHz, $CDCl_3$, δ/ppm): 14.3 (Me), 14.4 (Me), 22.0 (Me), 43.6 (d, $^1J_{CP}$ = 127.7 Hz, CH), 52.3 (d, $^2J_{CP}$ = 7.1 Hz, CH), 53.8 (d, $^2J_{PC}$ = 6.7 Hz, MeO), 54.2 (d, $^2J_{PC}$ = 5.9 Hz, MeO), 62.6 (CH_2O), 63.2 (CH_2O), 119.8 (C), 130.4 (2 CH), 130.7 (C), 130.8 (2 CH), 135.1 (C), 141.9 (CH), 165.8 (C=O), 167.1 (d, $^2J_{CP}$ = 7.2 Hz, C=O), 167.5 (d, $^3J_{CP}$ = 22.4 Hz, C=O), 171.0 (C=O); ^{31}P-NMR (121 MHz, $CDCl_3$, δ/ppm): 20.8; MS (EI, 70 eV): *m/z* (%) = 499 (M^+, 6), 434 (12), 324 (14), 235 (14), 207 (16), 148 (100), 135 (12), 109 (13), 96 (14).

Dimethyl 2-(dimethoxyphosphoryl)-3-(2,4-dioxo-5-(thiophen-2-ylmethylene)thiazolidin-3-yl)succinate (4i). Pale yellow oil, yield: 0.41 g (90%). Anal. Calcd. for $C_{16}H_{18}NO_9PS_2$ (463.4): C, 41.47; H, 3.92; N, 3.02%. Found: C, 41.2; H, 3.8; N, 3.1%. IR (KBr, cm^{-1}): 1735 and 1691 (C=O), 1260 (P=O); ^{1}H-NMR (300 MHz, $CDCl_3$, δ/ppm): 3.72 (3 H, d, $^3J_{HP}$ = 11.7 Hz, MeO), 3.74 (3 H, s, MeO), 3.78 (3 H, d, $^3J_{HP}$ = 11.7 Hz, MeO), 3.87 (3 H, s, MeO), 4.26 (1 H, dd, $^3J_{HH}$ = 11.4 Hz, $^2J_{HP}$ = 20.3 Hz, CH), 5.73 (1 H, dd, $^3J_{HH}$ = 11.4 Hz, $^3J_{HP}$ = 4.5 Hz, CH), 7.20 (1 H, dd, $^3J_{HH}$ = 4.8 Hz, $^3J_{HH}$ = 3.6 Hz, CH), 7.42 (1 H, d, $^3J_{HH}$ = 3.6 Hz, CH), 7.68 (1 H, d, $^3J_{HH}$ = 4.8 Hz, CH), 8.01 (1 H, s, CH); ^{13}C-NMR (75 MHz, $CDCl_3$, δ/ppm): 43.2 (d, $^1J_{CP}$ = 128.6 Hz, CH), 52.3 (d, $^2J_{PC}$ = 7 Hz, CH), 53.2 (d, $^2J_{PC}$ = 5.3 Hz, MeO), 53.7 (MeO), 54.0 (MeO), 54.3 (d, $^2J_{PC}$ = 5.3

Hz, MeO), 118.8 (C), 127.7 (C), 129.0 (CH), 132.8 (CH), 134.1 (CH), 137.9 (CH), 165.3 (C=O), 167.2 (d, $^2J_{CP}$ = 7.4 Hz, C=O), 167.9 (d, $^3J_{CP}$ = 17.5 Hz, C=O), 171.0 (C=O); ^{31}P-NMR (121 MHz, $CDCl_3$, δ/ppm): 20.5; MS (EI, 70 eV): *m*/*z* (%) = 463 (M^+, 4), 296 (27), 193 (40), 139 (100), 109 (55).

Diethyl 2-(dimethoxyphosphoryl)-3-(2,4-dioxo-5-(thiophen-2-ylmethylene)thiazolidin-3-yl)succinate (4j). Pale yellow oil, yield: 0.43 g (88%). Anal. Calcd. for $C_{18}H_{22}NO_9PS_2$ (491.5): C, 43.99; H, 4.51; N, 2.85%. Found: C, 43.7; H, 4.4; N, 2.8%. IR (KBr, cm^{-1}): 1732 and 1690 (C=O), 1246 (P=O); ^{1}H-NMR (300 MHz, $CDCl_3$, δ/ppm): 1.23 (3 H, t, $^3J_{HH}$ = 7.2 Hz, Me), 1.36 (3 H, t, $^3J_{HH}$ = 7.2 Hz, Me), 3.72 (3 H, d, $^3J_{HP}$ = 11.0 Hz, MeO), 3.79 (3 H, d, $^3J_{HP}$ = 11.0 Hz, MeO), 4.19–4.33 (5 H, m, 2 CH_2O, CH), 5.72 (1 H, dd, $^3J_{HH}$ = 11.4 Hz, $^3J_{HP}$ = 4.5 Hz, CH), 7.20 (1 H, dd, $^3J_{HH}$ = 4.5 Hz, $^3J_{HH}$ = 3.2 Hz, CH), 7.42 (1 H, d, $^3J_{HH}$ = 3.2 Hz, CH), 7.68 (1 H, d, $^3J_{HH}$ = 4.5 Hz, CH), 8.11 (1 H, s, CH); ^{13}C-NMR (75 MHz, $CDCl_3$, δ/ppm): 14.3 (Me), 14.4 (Me), 43.4 (d, $^1J_{CP}$ = 128.1 Hz, CH), 52.5 (d, $^2J_{PC}$ = 6.6 Hz, CH), 53.9 (d, $^2J_{PC}$ = 6.9 Hz, MeO), 54.2 (d, $^2J_{CP}$ = 5.9 Hz, MeO), 62.6 (CH_2O), 63.2 (CH_2O), 118.9 (C), 127.5 (C), 129.0 (CH), 132.7 (CH), 134.1 (CH), 137.9 (CH), 165.4 (C=O), 167.1 (d, $^2J_{CP}$ = 7.4 Hz, C=O), 167.5 (d, $^3J_{CP}$ = 19.5 Hz, C=O), 170.6 (C=O); ^{31}P-NMR (121 MHz, $CDCl_3$, δ/ppm): 21.1; MS (EI, 70 eV): *m*/*z* (%) = 491 (M^+, 5), 442 (25), 380 (36), 324 (22), 235 (20), 139 (100), 109 (17).

Dimethyl 2-(dimethoxyphosphoryl)-3-(5-(furan-2-ylmethylene)-2,4-dioxothiazolidin-3-yl)succinate (4k). Pale yellow oil, yield: 0.40 g (90%). Anal. Calcd. for $C_{16}H_{18}NO_{10}PS$ (447.3): C, 42.96; H, 4.06; N, 3.13%. Found: C, 42.7; H, 4.1; N, 3.0%. IR (KBr, cm^{-1}): 1730 and 1705 (C=O), 1257 (P=O); ^{1}H-NMR (300 MHz, $CDCl_3$, δ/ppm): 3.75 (3 H, d, $^3J_{HP}$ = 11.7 Hz, MeO), 3.78 (3 H, s, MeO), 3.79 (3 H, d, $^3J_{HP}$ = 11.7 Hz, MeO), 3.87 (3 H, s, MeO), 4.25 (1 H, dd, $^3J_{HH}$ = 11.1 Hz, $^2J_{HP}$ = 20.6 Hz, CH), 5.72 (1 H, dd, $^3J_{HH}$ = 11.1 Hz, $^3J_{HP}$ = 4.5 Hz, CH), 6.60 (1 H, dd, $^3J_{HH}$ = 4.2 Hz, $^3J_{HH}$ = 3.2 Hz, CH), 6.81 (1 H, d, $^3J_{HH}$ = 3.2 Hz, CH), 7.68 (1 H, d, $^3J_{HH}$ = 4.2 Hz, CH), 7.80 (1 H, s, CH); ^{13}C-NMR (75 MHz, $CDCl_3$, δ/ppm): 43.2 (d, $^1J_{CP}$ = 128.5 Hz, CH), 52.2 (d, $^2J_{PC}$ = 4.3 Hz, CH), 53.2 (MeO), 53.9 (MeO), 54.2 (d, $^2J_{PC}$ = 6.2 Hz, MeO), 54.7 (d, $^2J_{CP}$ = 5.9 Hz, MeO), 113.6 (CH), 118.5 (C), 118.7 (C), 120.8 (CH), 147.1 (CH), 150.0 (CH), 165.5 (C=O), 167.7 (d, $^2J_{CP}$ = 7.2 Hz, C=O), 168.0 (d, $^3J_{CP}$ = 18.0 Hz, C=O), 170.9 (C=O); ^{31}P-NMR (121 MHz, $CDCl_3$, δ/ppm): 22.4; MS (EI, 70 eV): *m*/*z* (%) = 447 (M^+, 4), 416 (24), 352 (31), 296 (24), 193 (31), 124 (100), 109 (36), 31 (96).

Diethyl 2-(dimethoxyphosphoryl)-3-(5-(furan-2-ylmethylene)-2,4-dioxothiazolidin-3-yl)succinate (4l). Pale yellow oil, yield: 0.41 g (86%). Anal. Calcd. for $C_{18}H_{22}NO_{10}PS$ (475.4): C, 45.48; H, 4.66; N, 2.95%. Found: C, 45.3; H, 4.5; N, 2.8%. IR (KBr, cm^{-1}): 1725 and 1690 (C=O), 1262 (P=O); ^{1}H-NMR (300 MHz, $CDCl_3$, δ/ppm):1.22 (3 H, t, $^3J_{HH}$ = 7.2 Hz, Me), 1.34 (3 H, t, $^3J_{HH}$ = 7.2 Hz, Me), 3.72 (3 H, d, $^3J_{HP}$ = 11.4 Hz, MeO), 3.79 (3 H, d, $^3J_{HP}$ = 11.4 Hz, MeO), 4.18–4.36 (5 H, m, 2 CH_2O, CH), 5.70 (1 H, dd, $^3J_{HH}$ = 11.4 Hz, $^3J_{HP}$ = 4.2 Hz, CH), 6.59 (1 H, dd, $^3J_{HH}$ = 4.8 Hz, $^3J_{HH}$ = 3.3 Hz, CH), 6.80 (1 H, d, $^3J_{HH}$ = 3.3 Hz, CH), 7.68 (1 H, d, $^3J_{HH}$ = 4.8 Hz, CH), 7.78 (1 H, s, CH); ^{13}C-NMR (75 MHz, $CDCl_3$, δ/ppm): 14.3 (Me), 14.4 (Me), 43.4 (d, $^1J_{CP}$ = 128.2 Hz, CH), 52.3 (d, $^2J_{PC}$ = 4.8 Hz, CH), 53.8 (d, $^2J_{PC}$ = 6.6 Hz, MeO), 54.2 (d, $^2J_{CP}$ = 6.0 Hz, MeO), 62.5 (CH_2O), 63.2 (CH_2O), 113.6 (CH), 118.5 (C), 118.7 (C), 120.6 (CH), 147.0 (CH), 150.1 (CH), 165.3 (C=O), 167.1 (d, $^2J_{CP}$ = 7.4 Hz, C=O), 167.4 (d, $^3J_{CP}$ = 17.8 Hz, C=O), 169.3 (C=O); ^{31}P-NMR (121 MHz, $CDCl_3$, δ/ppm): 21.9; MS (EI, 70 eV): *m*/*z* (%) = 475 (M^+, 4), 426 (18), 380 (47), 235 (26), 124 (100), 109 (26).

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