Supporting Information for:

Phosphine-Catalyzed Synthesis of 1,3-Dioxan-4-ylidenes

Xue-Feng Zhu, Christopher E. Henry, Jay Wang, Travis Dudding, and Ohyun Kwon*

*Department of Chemistry and Biochemistry, University of California, Los Angeles, California
90095-1569, USA*

General Information: All reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. THF and diethyl ether were distilled over sodium / benzophenone ketyl; dichloromethane, benzene, toluene, and acetonitrile were freshly distilled from CaH₂. All other anhydrous solvents were packaged in Sure/Seal™ bottles and were used as received from *Aldrich Company*; chloroform was stabilized with amylene. All the aldehydes are commercially available and purchased from *Aldrich Company* or *Acros Organics*. The liquid aldehydes were distilled prior to use, the solid aldehydes were freshly opened and weighed and transferred under argon. All the phosphines are commercially available and purchased from *Aldrich Company* or *Strem Chemicals, Inc.* All other reagents were used as received from commercial sources. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60F-254) and visualized by UV or permanganate staining. Flash column chromatography was performed using E. Merck silica gel 60 (230–400 mesh) using compressed air. IR spectra were recorded on a Perkin-Elmer pargon 1600 FT-IR spectrometer. NMR spectra were obtained on Bruker Avance-500, ARX-500 or ARX-400 instruments as indicated and calibrated using residual undeuterated chloroform as an internal reference (7.24 ppm for ¹H NMR and 77.00 ppm for ¹³C NMR, respectively). Data for ¹H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. Data for ¹³C NMR spectra are reported in terms of chemical shift, multiplicities, and coupling constants (Hz) in the case of *J*_{CF} coupling. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, br = broad, and app = apparent. High resolution matrix assisted laser desorption/ionization (MALDI) mass spectra were recorded with a

dihydroxy-benzoic acid (DHB) matrix on an Applied Biosystems Voyager-DE STR run in reflector mode with external calibration at an accelerating voltage of 20000 V. High-resolution EI mass spectra were recorded by rapid thermal vaporization of samples deposited on desorption ionization filament that was directly inserted into the electron ionization (EI, 70 eV, 200°C) source of a triple sector high resolution instrument (VG/Micromass Autospec) tuned to 8000 static resolution (M/DM, 10% valley) using perflourinated kerosene (formula weight 705, Lancaster Synthesis, Inc., NH) as internal calibrant. High resolution chemical ionization (CI) mass spectra were performed on a Micromass GCT Gas Chromatograph EI/CI TOF. Atmospheric pressure chemical ionization (APCI) was performed on a SCIEX II instrument with an optional Applied Biosystems/MSD Sciex QSTAR-XL hybrid Quad-TOF. Data were analyzed using instrument supplied software. X-ray crystallographic data were collected using a Bruker SMART CCD based diffractometer equipped with low-temperature apparatus operating at 100K.

Screening of Solvents for the Phosphine-Catalyzed Reaction of 4-Pyridinecarboxaldehyde with Ethyl 2,3-butadienoate

Entry	Solvent	Yield(%) ^a	E/Z ^b	Entry	Solvent	Yield(%) ^a	E/Z ^b
1	CHCl ₃	94	9.0:1.0	9	Benzene	74	7.6:1.0
2	DCE	88	7.3:1.0	10	Toluene	72	6.8:1.0
3	CH ₂ Cl ₂	86	7.0:1.0	11	Ether	65	4.6:1.0
4	1,4-Dioxane	80	8.8:1.0	12	MeCCl ₃	40	7.2:1.0
5	AcOEt	80	7.4:1.0	13	Acetone	7	NA
6	THF	79	8.0:1.0	14	MeCN	0	NA
7	2-Me THF	78	7.0:1.0	15	Pentane	0	NA
8	DME	77	8.5:1.0	16	CCl ₄	0	NA

^a Isolated yields. ^b E/Z stereoisomer ratio determined based on isolated yields.

The results of solvent screening were summarized in the above table. Chloroform stands out as the best solvent for this reaction among 16 common solvents investigated in this study.

As an example, the experimental procedure for the reaction of 4-pyridinecarboxaldehyde with ethyl 2,3-butadienoate in chloroform is described here. To a solution of 4-pyridinecarboxaldehyde (5.0 mmol) and tributylphosphine (51.5 μ L, 0.2 mmol) in chloroform (10 mL) was added ethyl 2,3-butadienoate (1.0 mmol) dropwise within *ca.* 1 min using a micro syringe. After the addition, a rosy reddish solution was obtained. The mixture was then stirred at room temperature under argon and monitored by TLC (eluant: hexanes/EtOAc = 1/1). After the reaction was complete, the resulting mixture was concentrated and the residue was purified by flash column chromatography on silica gel (gradient elution: 33–50% EtOAc in hexanes then 1.0–8.0% methanol in dichloromethane) to give products.

E-([1,3]-dioxan-4-ylidene)-acetate 3. 84.6% yield (94% combined yield); as a slightly yellow oil: IR (film) $\nu_{\max}$ 3072, 2981, 2953, 1708, 1656, 1413, 1376, 1326, 1269, 1216, 1148, 1097, 1064, 1001, 813 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.72 (br s, 2H), 8.64 (br s, 2H), 7.50 (d, J = 7.2 Hz, 2H), 7.36 (d, J = 7.0 Hz, 2H), 6.01 (s, 1H), 5.65 (d, J = 2.4 Hz, 1H), 5.08 (dd, J = 13.8, 4.6 Hz, 1H), 4.15 (q, J = 8.9 Hz, 2H), 4.02 (dd, J = 20.2, 4.6 Hz, 1H), 2.79 (ddd, J = 20.2, 13.8, 2.8 Hz, 1H), 1.27 (t, J = 8.9 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.0, 165.3, 150.22 (2C), 150.20 (2C), 148.2, 144.2, 120.8, 120.2, 102.3 (2C), 99.1 (2C), 75.3, 60.0, 32.6, 14.3; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{17}\text{N}_2\text{O}_4$ [M^+] 326.1267, found 326.1269; calcd for $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_4$ [$(\text{M}+\text{H})^+$] 327.1345, found 327.1349;

Z-([1,3]-dioxan-4-ylidene)-acetate 3. 9.4% yield (94% combined yield); as a slightly yellow oil: IR (film) $\nu_{\max}$ 2956, 2925, 2855, 1705, 1648, 1606, 1562, 1465, 112, 1374, 1253, 1137, 1096, 1064, 1045, 1013, 811, 764 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.72 (br s, 2H), 8.67 (br s, 2H), 7.63 (br d, J = 6.9 Hz, 2H), 7.35 (br d, J = 6.7 Hz, 2H), 6.06 (s, 1H), 5.22 (d, J = 1.4 Hz, 1H), 5.11 (dd, J = 12.2, 5.7 Hz, 1H), 4.20 (q, J = 8.9 Hz, 2H), 2.74–2.63 (m, 2H), 1.30 (t, J = 8.9 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.3, 160.7, 150.3 (2C), 150.1 (2C), 147.9, 144.3, 120.7, 120.2, 101.4 (2C), 98.7 (2C), 76.0, 59.9, 36.1, 14.3; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_4$ [$(\text{M}+\text{H})^+$] 327.1345, found 327.1340.

Screening of Phosphines for the Phosphine-Catalyzed Reaction of Aldehyde with Ethyl 2,3-butadienoate

Entry	Ar ^a	Phosphine	Yield (%) ^b	E/Z ^c
1	4-Pyridyl	Me ₃ P	94	7.5:1.0
2	4-Pyridyl	Bu ₃ P	94	9:0:1.0
3	4-Pyridyl	Ph ₂ [4-(Me ₂ N)Ph]P	11	9.2:1.0
4	4-Pyridyl	Ph ₃ P	0	NA
5	4-Pyridyl	(<i>o</i> -Tolyl) ₃ P	0	NA
6	4-Pyridyl	(<i>i</i> -Pr) ₃ P	0	NA
7	4-Pyridyl	(Me ₂ N) ₃ P	0	NA
8	4-Pyridyl	(MeO) ₃ P	0	NA
9	3-ClC ₆ H ₄	Me ₃ P	61	6.8/1.0
10	3-ClC ₆ H ₄	Et ₃ P	28	6.7/1.0
11	3-ClC ₆ H ₄	Bu ₃ P	28	9.0/1.0
12	Ph	Me ₃ P	17	only E
13	Ph	Bu ₃ P	trace	NA

^a 5 equiv of aldehyde was used. ^b Isolated yields. ^c E/Z stereoisomer ratio determined based on isolated yields.

Using a similar experimental procedure described in solvent screening section, different alkyl or aryl phosphines were tested. The results are summarized in the above table. Trimethylphosphine represents the best catalyst for this reaction in terms of giving the best yield and requiring the shortest reaction time as well.

Allenolate Preparation

Ethyl 2,3-butadienoate **1a**,¹ 1-naphthyl 2,3-butadienoate **1b**,² phenyl 2,3-butadienoate **1c**,² benzyl 2,3-butadienoate **1f**,³ methyl 2,3-butadienoate **1g**,¹ *iso*-butyl 2,3-butadienoate **1h**,⁴ and *tert*-butyl 2,3-butadienoate **1m**⁴ were prepared by the reported methods.

2,2,2-Trifluoroethyl 2,3-butadienoate **1d**, 2-fluoroethyl 2,3-butadienoate **1e**, neopentyl 2,3-butadienoate **1i**, 2-trimethylsilylethyl 2,3-butadienoate **1j**, *iso*-propyl 2,3-butadienoate **1k** and trimethylsilylmethyl 2,3-butadienoate **1l** can be easily synthesized by a four-step procedure starting from bromoacetyl bromide and corresponding alcohols (See the below scheme). As new compounds, these allenates' physical data are reported here.

A typical experimental procedure for the synthesis of allenates **1d, **1e**, **1i**, **1j**, **1k** and **1l**.** As an example, the synthesis of 2-trimethylsilylethyl 2,3-butadienoate **1j** is described here. To a solution of bromoacetyl bromide (7.46 mL, 83.72 mmol) in 200 mL of dichloromethane was added a mixture of 2-trimethylsilylethanol (10.0 g, 83.72 mmol) and triethylamine (11.8 mL, 83.72 mmol) within 1 h at room temperature. After addition, a slightly yellow solution with a lot of suspended white solid was obtained. The resulting reaction mixture was further stirred overnight at rt. Water (100 mL) was added and the organic layer was separated. The aqueous layer was extracted with dichloromethane (50 mL x 2). The combined extract was washed with brine (50 mL) and dried over sodium sulfate and concentrated. The residue was then purified by reduced pressure distillation or by flash column chromatography on silica gel (elution 5% EtOAc in hexanes) to give bromoester (16.1 g, 67.31 mmol, 80% yield) as a colorless oil. Then the bromoester was dissolved in toluene (200 mL), triphenylphosphine (17.6 g, 67.31 mmol) was added, the resulting mixture was further stirred for 7 days at room temperature. The reaction mixture was then filtered and washed with toluene and hexane to give phosphonium salt as a white solid (33.8 g, 67.31 mmol, 100% yield). Phosphonium salt (13.9 g, 27.6 mmol) was dissolved in dichloromethane (250 mL), to this solution was added 10% sodium carbonate aqueous solution (50 mL) within 30 min at 0 °C. After the addition, the resulting mixture was

vigorously stirred for 30 min at 0 °C and then warmed to rt. The organic layer was separated. The aqueous layer was extracted with dichloromethane (50 mL x 2). The combined extract was washed with brine (50 mL) and dried over sodium sulfate and concentrated to give phosphorane (10.5 g, 24.98 mmol, 90.5% yield) as a slightly yellow oil. To this resulting phosphorane residue was added dichloromethane (100 mL) and 1.0 equivalent of triethylamine (3.5 mL). After stirred for about 10 min, 1.0 equivalent of acetyl chloride (1.82 mL) was added dropwise over 30 min at room temperature. Then the reaction mixture was stirred overnight. The resulting mixture was poured into a Büchner funnel packed with silica gel and was washed with dichloromethane several times. The combined filtrate was carefully evaporated to remove most of the solvent and the residue was subjected to a flash column chromatography (eluant 5% EtOAc in hexanes) to provide allenolate **1j** as a colorless oil (2.64 g, 14.3 mmol, 57% yield).

2,2,2-Trifluoroethyl 2,3-butadienoate 1d. 2% overall yield; as a colorless oil: IR (neat) $\nu_{\max}$ 3078, 3002, 2976, 2932, 2876, 1972, 1938, 1739, 1427, 1411, 1285, 1237, 1167, 1090, 1063, 978, 917, 856 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 5.71 (t, J = 6.5 Hz, 1H), 5.31 (d, J = 6.5 Hz, 2H), 4.53 (q, J = 8.4 Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 216.8, 164.0, 86.6, 80.0, 60.6 (q, J_{CF} = 37.0 Hz), 34.6 (q, J_{CF} = 16.3 Hz); HRMS (EI) calcd for $\text{C}_6\text{H}_5\text{F}_3\text{O}_2$ [M^+] 166.0242, found 166.0252.

2-Fluoroethyl 2,3-butadienoate 1e. 40% overall yield; as a colorless oil: IR (neat) $\nu_{\max}$ 3073, 2995, 2961, 1970, 1943, 1720, 1426, 1373, 1337, 1259, 1171, 1064, 959, 862, 777 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 5.67 (t, J = 6.5 Hz, 1H), 5.25 (d, J = 6.5 Hz, 2H), 4.61 (dt, J = 47.4, 4.2 Hz, 2H), 4.38 (dt, J = 28.6, 4.2 Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 216.1, 165.4, 87.5, 81.2 (d, J_{CF} = 170.6 Hz), 79.6, 63.7 (d, J_{CF} = 20.4 Hz); HRMS (CI) calcd for $\text{C}_6\text{H}_8\text{FO}_2$ [($\text{M}+\text{H}$) $^+$] 131.0508, found 131.0509.

Neopentyl 2,3-butadienoate 1i. 31% overall yield; as a colorless oil: IR (neat) $\nu_{\max}$ 3070, 2960, 2871, 1972, 1944, 1720, 1479, 1424, 1371, 1339, 1298, 1272, 1253, 1163, 1083, 1018, 858 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.64 (t, J = 6.5 Hz, 1H), 5.42 (d, J = 6.5 Hz, 2H), 3.81 (s, 2H), 0.94 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 215.9, 165.9, 88.1, 79.1, 74.1, 31.5, 26.4 (3C); HRMS (CI) calcd for $\text{C}_9\text{H}_{15}\text{O}_2$ $[(\text{M}+\text{H})^+]$ 155.1072, found 155.1074.

2-Trimethylsilylethyl 2,3-butadienoate 1j. 41% overall yield; as a colorless oil: IR (neat) $\nu_{\max}$ 3070, 2954, 2898, 1972, 1943, 1716, 1454, 1423, 1379, 1336, 1299, 1251, 1159, 1080, 1062, 1043, 988, 938, 839, 767 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 5.61 (t, J = 6.6 Hz, 1H), 5.20 (d, J = 6.6 Hz, 2H), 4.24 (dd, J = 9.6, 7.1 Hz, 2H), 1.01 (dd, J = 9.5, 7.2 Hz, 2H), 0.03 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 215.7, 165.8, 88.2, 79.2, 63.2, 17.2, -1.5 (3C); HRMS (CI) calcd for $\text{C}_9\text{H}_{16}\text{O}_2\text{Si}$ $[\text{M}^+]$ 184.0920, found 184.0915.

iso-Propyl 2,3-butadienoate 1k. 31% overall yield; as a colorless oil: IR (neat) $\nu_{\max}$ 3070, 2983, 2939, 2879, 1972, 1943, 1719, 1638, 1468, 1425, 1360, 1324, 1263, 1175, 1108, 975, 858 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 5.59 (t, J = 6.5 Hz, 1H), 5.19 (d, J = 6.5 Hz, 2H), 5.05 (sept, J = 6.3 Hz, 1H), 1.25 (d, J = 6.3 Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 215.6, 165.3, 88.4, 79.2, 68.4, 21.8 (2C); HRMS (CI) calcd for $[(\text{M}+\text{H})^+]$ $\text{C}_7\text{H}_{11}\text{O}_2$ 127.0759, found 127.0763.

Trimethylsilylmethyl 2,3-butadienoate 1l. 30% overall yield; as a colorless oil: IR (neat) $\nu_{\max}$ 3070, 2958, 2908, 1972, 1943, 1720, 1424, 1350, 1306, 1288, 1251, 1159, 1082, 1009, 858, 775

cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 5.62 (t, *J* = 6.5 Hz, 1H), 5.18 (d, *J* = 6.5 Hz, 2H), 3.82 (s, 2H), 0.06 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 215.6, 166.4, 87.9, 78.9, 58.3, -2.9 (3C); HRMS (CI) calcd for C₈H₁₅O₂Si [(M+H)⁺] 171.0841, found 171.0846.

Screening of Allenates for the Trimethylphosphine-Catalyzed Reaction of 3-Chlorobenzaldehyde with Different 2, 3-butadienoates

Results of this investigation were reported in **Table 1** of the paper. As an example, the experimental procedure for the reaction of 3-chlorobenzaldehyde with *iso*-propyl 2,3-butadienoate in chloroform is described here. To a solution of 3-chlorobenzaldehyde (5.0 mmol) and trimethylphosphine (21.3 μL, 0.2 mmol) in chloroform (10 mL) was added *iso*-propyl 2,3-butadienoate (1.0 mmol) dropwise within *ca.* 1.5 min using a micro syringe. After the addition, an orange solution was obtained. The mixture was then stirred at room temperature under argon and the progress of the reaction was monitored by TLC (eluant: hexanes/ethyl acetate = 4/1). After the reaction was complete, the resulting mixture was concentrated and the residue was purified by flash column chromatography on silica gel (gradient elution: 1–33% ethyl acetate in hexanes) to give products. Except [1,3]-dioxan-4-ylidene-acetate **3k**, only major isomer's spectral data are recorded here.

***E*-([1,3]-dioxan-4-ylidene)-acetate 3a.** 33.2% yield (37% combined yield); as a slightly yellow oil: IR (film) ν_{max} 3070, 2983, 2903, 1740, 1720, 1648, 1600, 1577, 1477, 1431, 1394, 1373,

1214, 1137, 1101, 1065, 885 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.59 (m, 1H), 7.47–7.31 (m, 7H), 5.97, (s, 1H), 5.60 (d, $J = 2.1$ Hz, 1H), 5.00 (dd, $J = 14.7, 3.5$ Hz, 1H), 4.15 (q, $J = 4.15$ Hz, 2H), 3.97 (dd, $J = 16.2, 3.5$ Hz, 1H), 2.78 (ddd, $J = 17.8, 9.7, 2.1$ Hz, 1H), 1.28 (t, $J = 7.14$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 167.2, 166.4, 141.6, 138.2, 134.5, 134.4, 129.9, 129.8, 128.5, 126.6, 125.9, 124.5, 124.5, 123.8, 101.5, 100.5, 76.3, 59.8, 33.1, 14.3; HRMS (MALDI-ICR) calcd for $\text{C}_{20}\text{H}_{18}\text{Cl}_2\text{O}_4\text{Na}$ [(M+Na) $^+$] 415.0474, found 415.0474.

***E*-([1,3]-dioxan-4-ylidene)-acetate 3e.** 19% yield (22% combined yield); as a slightly yellow oil: IR (film) ν_{max} 3071, 2957, 2894, 1747, 1704, 1645, 1601, 1577, 1479, 1433, 1378, 1343, 1271, 1214, 1195, 1138, 1073, 1018, 910 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.58 (m, 1H), 7.47–7.31 (m, 7H), 6.00, (s, 1H), 5.65 (d, $J = 2.0$ Hz, 1H), 5.01 (dd, $J = 11.2, 3.5$ Hz, 1H), 4.62 (dt, $J = 47.4, 4.2$ Hz, 2H), 4.3 (dm, $J = 13.2$ Hz, 2H), 3.93 (dd, $J = 16.3, 3.6$ Hz, 1H), 2.82 (ddd, $J = 16.3, 11.2, 2.1$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 167.4, 166.9, 141.6, 138.2, 134.6, 134.5, 130.0, 129.9, 129.8, 128.6, 126.6, 126.0, 124.6, 123.9, 100.6, 100.5, 81.5 (d, $J_{\text{CF}} = 81.5$ Hz), 76.1, 62.7 (d, $J_{\text{CF}} = 20.1$ Hz), 33.1; HRMS (MALDI) calcd for $\text{C}_{20}\text{H}_{17}\text{Cl}_2\text{FO}_4\text{Na}$ [(M+Na) $^+$] 433.0380, found 433.0387.

***E*-([1,3]-dioxan-4-ylidene)-acetate 3f.** 34% yield; as a slightly yellow oil: IR (film) ν_{max} 3067, 3033, 2955, 1703, 1705, 1645, 1601, 1577, 1478, 1431, 1382, 1343, 1268, 1214, 1131, 1102,

1065, 1027, 909, 864 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.58 (m, 1H), 7.44–7.30 (m, 12H) 5.98 (s, 1H), 5.66 (d, $J = 2.0$ Hz, 1H) 5.14 (s, 2H), 5.00 (dd, $J = 14.7, 3.5$ Hz, 1H), 3.97 (dd, $J = 16.3, 3.5$ Hz, 1H) 2.80 (ddd, $J = 16.3, 11.2, 2.2$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 167.2, 165.9, 141.6, 138.2, 134.2, 134.4, 129.9, 129.8, 129.8, 129.7, 128.5, 128.1, 128.1, 126.6, 125.9, 123.9, 101.1, 100.5, 76.2, 65.6, 58.3, 33.2, 30.2; HRMS (MALDI-ICR) calcd for $\text{C}_{25}\text{H}_{20}\text{Cl}_2\text{O}_4\text{Na}$ $[(\text{M}+\text{Na})^+]$ 477.0636, found 477.0631.

E-([1,3]-dioxan-4-ylidene)-acetate 3g, 44.7% yield (50% combined yield); as a slightly yellow oil: IR (film) ν_{max} 3071, 2997, 2950, 2900, 1708, 1650, 1601, 1479, 1435, 1395, 1367, 1346, 1271, 1192, 1140, 1065, 1040, 975, 909 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.59–7.58 (m, 1H), 7.47–7.31 (m, 7H), 5.98 (s, 1H), 5.61 (d, $J = 2.0$ Hz, 1H), 5.00 (dd, $J = 11.2, 3.4$ Hz, 1H), 3.96 (dd, $J = 16.2, 3.5$ Hz, 1H), 3.69 (s, 3H), 2.80 (ddd, $J = 16.3, 11.2, 2.1$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 167.6, 165.9, 141.6, 138.2, 134.6, 134.4, 129.9, 129.8, 128.5, 126.6, 125.9, 124.5, 123.8, 101.0, 100.5, 76.2, 51.0, 33.1, 30.8; HRMS (MALDI-ICR) calcd for $\text{C}_{19}\text{H}_{16}\text{Cl}_2\text{O}_4\text{Na}$ $[(\text{M}+\text{Na})^+]$ 401.0324, found 401.0318.

E-([1,3]-dioxan-4-ylidene)-acetate 3h, 60.8% yield (68% combined yield); as a slightly yellow oil: IR (film) ν_{max} 3071, 2963, 2874, 1703, 1649, 1601, 1578, 1470, 1432, 1396, 1379, 1246, 1214, 1136, 1102, 1064, 987, 909 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.59 (m, 1H), 7.45–7.31

(m, 7H), 5.97 (s, 1H), 5.64 (d, $J = 2.1$ Hz, 1H), 5.00 (dd, $J = 11.2, 3.5$ Hz, 1H), 3.97 (dd, $J = 16.1, 3.5$ Hz, 1H), 3.88 (d, $J = 6.7$ Hz, 2H), 2.80, (ddd, $J = 16.3, 11.1, 2.1$ Hz, 1H), 1.94, (sept, $J = 6.7$ Hz, 1H), 0.95 (d, $J = 6.7$ Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 167.2, 166.3, 141.7, 138.2, 134.4, 134.4, 130.1, 129.8, 129.8, 126.6, 125.9, 124.6, 123.8, 101.5, 100.4, 76.2, 70.0, 33.1, 30.9, 27.3, 19.1; HRMS (MALDI-ICR) calcd for $\text{C}_{22}\text{H}_{22}\text{Cl}_2\text{O}_4\text{Na}$ $[(\text{M}+\text{Na})^+]$ 443.0804, found 443.0787.

***E*-([1,3]-dioxan-4-ylidene)-acetate 3i.** 60.2% yield (68% combined yield); as a slightly yellow oil: IR (film) ν_{max} 3071, 2962, 1703, 1650, 1601, 1577, 1478, 1431, 1377, 1214, 1138, 1108, 1065, 1038, 909 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.59 (m, 1H), 7.45–7.31 (m, 7H), 5.98 (s, 1H), 5.66 (d, $J = 2.0$ Hz, 1H), 5.01 (dd, $J = 11.2, 3.5$ Hz, 1H), 3.97 (dd, $J = 16.2, 3.5$ Hz, 1H), 3.79 (s, 2H), 2.80, (ddd, $J = 16.2, 11.2, 2.1$ Hz, 1H), 0.94 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 167.3, 166.3, 141.7, 138.2, 134.5, 134.4, 129.9, 129.8, 128.5, 126.6, 125.9, 124.5, 123.8, 101.6, 100.4, 76.2, 73.2, 33.2, 31.3, 26.5, 19.1; HRMS (MALDI-ICR) calcd for $\text{C}_{23}\text{H}_{24}\text{Cl}_2\text{O}_4\text{Na}$ $[(\text{M}+\text{Na})^+]$ 434.1052, found 434.1052.

***E*-([1,3]-dioxan-4-ylidene)-acetate 3j.** 62.8% yield (71% combined yield); as a slightly yellow oil: IR (film) ν_{max} 3067, 2955, 2897, 1703, 1652, 1601, 1578, 1479, 1431, 1386, 1265, 1250, 1214, 1195, 1134, 1102, 1062, 971, 909 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.58 (m, 1H),

7.47–7.31 (m, 7H), 5.97, (s, 1H), 5.59 (d, $J = 2.1$, 1H), 5.00 (dd, $J = 14.7$, 3.5 Hz, 1H), 4.22–4.17 (m, 2H), 3.97 (dd, $J = 16.2$, 3.5 Hz, 1H), 2.78 (ddd, $J = 17.8$, 9.7, 2.1 Hz, 1H), 1.04–0.98 (m, 2H), 0.05 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 167.2, 166.4, 141.6, 138.2, 134.5, 134.4, 129.9, 129.8, 128.5, 126.6, 125.9, 124.5, 124.5, 123.8, 101.5, 100.5, 76.3, 59.8, 33.1, 14.3, –1.9 (3C); HRMS (EI) calcd for $\text{C}_{23}\text{H}_{26}\text{Cl}_2\text{O}_4\text{SiNa}$ $[(\text{M}+\text{Na})^+]$ 487.0875, found 487.0881.

E-([1,3]-dioxan-4-ylidene)-acetate 3k (major). 63.7% yield (72% combined yield); as a slightly yellow oil: IR (film) ν_{max} 3071, 2981, 2936, 1701, 1648, 1601, 1578, 1479, 1431, 1373, 1345, 1270, 1248, 1214, 1188, 1143, 1106, 1063, 1030, 967, 909 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.59–7.58 (m, 1H), 7.47–7.31 (m, 7H), 5.96 (s, 1H), 5.58 (d, $J = 2.0$ Hz, 1H), 5.02–4.98 (m, 2H), 3.98 (dd, $J = 16.2$, 3.5 Hz, 1H), 2.78 (ddd, $J = 16.1$, 11.2, 2.1 Hz, 1H), 1.26 (d, $J = 6.3$, 3H), 1.24 (d, $J = 6.3$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 166.7, 166.1, 141.7, 138.3, 134.5, 134.4, 129.9, 129.8, 128.4, 126.6, 125.9, 124.5, 123.8, 102.0, 100.4, 76.3, 67.0, 33.1, 30.8, 21.9 (2C); HRMS (MALDI-ICR) calcd for $\text{C}_{21}\text{H}_{20}\text{Cl}_2\text{O}_4\text{Na}$ $[(\text{M}+\text{Na})^+]$ 429.0641, found 429.0631.

Z-([1,3]-dioxan-4-ylidene)-acetate 3k (minor). 8.3% yield (72% combined yield); as a slightly yellow oil: IR (film) ν_{max} 3069, 2982, 2936, 2878, 1738, 1714, 1658, 1651, 1599, 1575, 1477, 1374, 1338, 1267, 1219, 1181, 1104, 1079, 988, 910 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ

7.69–7.67 (m, 1H), 7.58 (dtm, $J = 6.5, 2.0$ Hz, 1H), 7.43–7.28 (m, 6H), 6.03 (s, 1H), 5.14 (d, $J = 2.0$ Hz, 1H), 5.09 (sept, $J = 6.3$ Hz, 1H), 5.03 (dd, $J = 10.7, 3.7$ Hz, 1H) 2.70 (ddd, $J = 15.0, 10.8, 1.6$ Hz, 1H) 2.61 (dd, $J = 15.0, 3.7$ Hz, 1H) 1.28 (d, $J = 6.2$ Hz, 3H), 1.28 (d, $J = 6.2$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 164.2, 161.4, 141.6, 138.3, 134.7, 134.3, 130.1, 129.7, 129.5, 126.6, 125.9, 124.5, 123.8, 101.3, 99.9, 89.5 76.7, 67.0, 36.7, 22.0 (2C); HRMS (MALDI-ICR) calcd for $\text{C}_{21}\text{H}_{20}\text{Cl}_2\text{O}_4\text{Na}$ $[(\text{M}+\text{Na})^+]$ 429.0641, found 429.0631.

***E*-([1,3]-dioxan-4-ylidene)-acetate 3I.** 66.6% yield (75% combined yield); as a slightly yellow oil: IR (film) ν_{max} 3071, 2958, 2903, 2254, 1703, 1650, 1601, 1578, 1479, 1431, 1396, 1368, 1346, 1285, 1250, 1214, 1135, 1102, 1064, 1035, 972, 909 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.59 (m, 1H), 7.46–7.31 (m, 7H), 5.97 (s, 1H), 5.64 (d, $J = 2.0$ Hz, 1H), 5.00 (dd, $J = 11.2, 3.4$ Hz, 1H), 3.97 (dd, $J = 16.1, 3.5$ Hz, 1H), 3.79 (s, $J = 9.4$ Hz, 2H), 2.79 (ddd, $J = 16.1, 11.2, 2.1$ Hz, 1H), 0.08 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 167.9, 165.8, 141.7, 138.3, 134.5, 134.4, 134.3, 129.9, 129.8, 128.4, 126.5, 125.9, 124.5, 123.8, 101.5, 100.3, 76.3, 57.0, 33.1, -3.1 (3C); HRMS (MALDI-ICR) calcd for $\text{C}_{22}\text{H}_{24}\text{Cl}_2\text{O}_4\text{SiNa}$ $[(\text{M}+\text{Na})^+]$ 473.0726, found 473.0713.

***E*-([1,3]-dioxan-4-ylidene)-acetate 3m.** 57.2% yield (63% combined yield); as a slightly yellow oil: IR (film) ν_{max} 3072, 2962, 2254, 1704, 1653, 1602, 1578, 1478, 1431, 1377, 1138, 1108, 1065, 1039, 908 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.58–7.56 (m, 1H), 7.47–7.43 (m, 2H),

7.41–7.35 (m, 2H), 7.32–7.29 (m, 3H), 5.94 (s, 1H), 5.55 (d, $J = 2.0$ Hz, 1H), 4.99 (dd, $J = 14.2$, 4.2 Hz, 1H), 3.95 (dd, $J = 20.1$, 4.3 Hz, 1H) 2.73 (ddd, $J = 20.1$, 14.2, 2.7 Hz, 1H), 1.47 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 166.6, 165.4, 141.8, 138.4, 134.5, 134.4, 129.9, 129.8, 129.7, 129.1, 127.9, 126.6, 126.0, 124.5, 123.9, 103.4, 100.4, 76.4, 33.1, 28.3 (3C); HRMS (MALDI-ICR) calcd for $\text{C}_{22}\text{H}_{22}\text{Cl}_2\text{O}_4\text{Na}$ [(M+Na) $^+$] 443.0793, found 443.0785.

Reaction Scope of the Trimethylphosphine-Catalyzed Reaction of Aldehydes with *iso*-Propyl 2,3-butadienoate

Results of this investigation were reported in **Table 2** of the paper. As an example, the experimental procedure for the reaction of 4-cyanobenzaldehyde with *iso*-propyl 2,3-butadienoate in chloroform is described here. To a solution of 4-cyanobenzaldehyde (10.0 mmol) and Me_3P (21.3 μL , 0.2 mmol) in chloroform (10 mL) was added *iso*-propyl 2,3-butadienoate (1.0 mmol) dropwise within *ca.* 1.5 min using a micro syringe. After the addition, a clear orange solution was obtained. The mixture was then stirred at room temperature under argon and the progress of the reaction was monitored by TLC (eluant: hexanes/ethyl acetate = 4/1). After the reaction was complete (*ca.* 24 h), the resulting mixture was concentrated and the residue was purified by flash column chromatography on silica gel (gradient elution: 1–50% ethyl acetate in hexanes) to give products.

***E*-([1,3]-dioxan-4-ylidene)-acetate 4a.** 88.2% yield (99% combined yield); as a colorless oil: IR (film) $\nu_{\max}$ 3070, 2980, 2934, 1699, 1651, 1601, 1578, 1479, 1431, 1372, 1345, 1327, 1268, 1214, 1188, 1141, 1104, 1063, 1029, 967, 909 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.71 (dm, $J = 6.0$ Hz, 2H), 8.64 (dm, $J = 6.0$ Hz, 2H), 7.49 (dm, $J = 6.0$ Hz, 2H), 7.36 (dm, $J = 6.0$ Hz, 2H), 6.00 (s, 1H), 5.62 (d, $J = 2.0$ Hz, 1H), 5.08 (dd, $J = 11.1, 3.6$ Hz, 1H), 5.02 (sept, $J = 6.3$ Hz, 1H), 4.03, (dd, $J = 16.1, 3.7$ Hz, 1H) 2.77 (ddd, $J = 16.1, 11.1, 2.0$ Hz, 1H), 1.25 (t, $J = 6.2$ Hz, 3H) 1.23 (t, $J = 6.3$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 166.5, 165.0, 150.11 (2C), 150.05 (2C), 148.4, 144.4, 120.8 (2C), 120.3 (2C), 102.8, 99.1, 75.3, 67.3, 32.6, 21.89, 21.86; HRMS (MALDI-ICR) calcd for $\text{C}_{19}\text{H}_{21}\text{N}_2\text{O}_4$ $[(\text{M}+\text{H})^+]$ 341.1496, found 341.1490.

***Z*-([1,3]-dioxan-4-ylidene)-acetate 4a.** 10.8% yield (99% combined yield); as a colorless oil: IR (film) $\nu_{\max}$ 3042, 2978, 2929 1710, 1655, 1599, 1580, 1480, 1428, 1374, 1327, 1285, 1217, 1181, 1145, 1108, 1063, 1041, 1026, 988 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.72 (dm, $J = 6.0$ Hz, 2H), 8.66 (dm, $J = 6.1$ Hz, 2H), 7.63 (dm, $J = 6.0$ Hz, 2H), 7.34 (dm, $J = 6.0$ Hz, 2H), 6.06 (s, 1H), 5.20 (d, $J = 1.2$ Hz, 1H), 5.12–5.03 (m, 2H), 2.72–2.26 (m, 2H), 1.28 (d, $J = 6.1$ Hz, 3H) 1.27 (d, $J = 6.2$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 163.8, 160.5, 150.4 (2C), 150.2 (2C), 148.0, 144.3, 120.7 (2C), 120.2 (2C), 101.9, 98.7, 76.0, 67.1, 36.1, 22.0 (2C); HRMS (MALDI-ICR) calcd for $\text{C}_{19}\text{H}_{21}\text{N}_2\text{O}_4$ $[(\text{M}+\text{H})^+]$ 341.1496, found 341.1509.

***E*-([1,3]-dioxan-4-ylidene)-acetate 4c.** 86.8% yield (96% combined yield); as a slightly yellow oil: IR (film) $\nu_{\max}$ 3092, 3041, 2982, 2937, 2902, 2877, 1695, 1651, 1645, 1599, 1481, 1467, 1428, 1373, 1328, 1225, 1178, 1107, 1067, 1026, 948, 909, 885 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.75 (d, $J = 2.0$ Hz, 1H), 8.65 (d, $J = 2.2$ Hz, 1H), 8.62 (dd, $J = 4.8, 1.7$ Hz, 1H), 8.55 (dd, $J = 6.4, 1.6$ Hz, 1H), 7.86 (dt, $J = 6.4, 1.9$ Hz, 1H), 7.72 (dt, $J = 4.4, 2.1$, 1H) 7.33–7.26 (m, 2H), 5.05 (s, 1H), 5.57 (d, $J = 2.0$ Hz, 1H) 5.08 (dd, $J = 11.1, 3.5$ Hz, 1H), 4.98 (sept, $J = 6.2$ Hz, 1H), 3.97 (dd, $J = 11.0, 5.2$ Hz, 1H) 2.81 (ddd, $J = 16.1, 11.1, 2.0$ Hz, 1H) 1.21 (d, $J = 6.4$ Hz, 3H), 1.19 (d, $J = 6.3$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 166.4, 165.5, 150.8, 149.7, 147.8, 147.5, 135.1, 133.8, 133.3, 131.9, 123.4, 123.2, 102.4, 99.4, 74.9, 67.0, 32.8, 21.7 (2C); HRMS (MALDI-ICR) calcd for $\text{C}_{19}\text{H}_{21}\text{N}_2\text{O}_4$ $[(\text{M}+\text{H})^+]$ 341.1496, found 341.1512.

***Z*-([1,3]-dioxan-4-ylidene)-acetate 4c.** 9.2% yield (96% combined yield); as a slightly yellow oil: IR (film) $\nu_{\max}$ 3044, 2980, 2850, 1697, 1654, 1605, 1414, 1374, 1325, 1269, 1219, 1144, 1106, 1106, 1065, 993, 814 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.87 (br s, 8.87, 1H), 8.80–8.61 (m, 3H), 8.03 (dm, $J = 7.9$ Hz, 1H), 7.78 (dm, $J = 7.9$ Hz, 1H) 7.39–7.31 (m, 2H), 6.14 (s, 1H), 5.18 (d, $J = 1.4$ Hz, 1H), 5.15 (dd, $J = 10.4, 3.9$ Hz, 1H) 5.07 (sept, $J = 6.2$ Hz, 1H), 2.78–2.65 (m, 2H), 1.26 (d, $J = 6.2$ Hz, 3H) 1.25 (d, $J = 6.3$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 164.0, 160.9, 150.7, 150.0, 147.8, 147.4, 134.0, 133.4, 130.9, 128.8, 123.7, 123.3, 101.7, 99.2, 75.6, 67.1, 36.5, 22.0 (2C); HRMS (MALDI-ICR) calcd for $\text{C}_{19}\text{H}_{21}\text{N}_2\text{O}_4$ $[(\text{M}+\text{H})^+]$ 341.1496, found 341.1512.

E-([1,3]-dioxan-4-ylidene)-acetate 4d. 36.6% yield (47% combined yield); as a brown oil: IR (film) $\nu_{\max}$ 3066, 3015, 2980, 2935, 2902, 1701, 1646, 1593, 1574, 1473, 1437, 1374, 1329, 1292, 1266, 1224, 1180, 1141, 1067, 1029, 909 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.59 (ddm, $J = 28.5, 4.1$ Hz, 2H), 7.78 (td, $J = 7.7, 1.7$ Hz, 1H), 7.71 (app br d, $J = 5.0$ Hz, 1H), 7.67 (td, $J = 7.7, 1.8$ Hz, 1H), 7.49 (app br d, $J = 7.9$ Hz, 1H), 7.32 (ddd, $J = 7.5, 4.9, 1.3$ Hz, 1H) 7.20 (ddd, $J = 7.5, 4.8, 1.1$ Hz, 1H), 6.12 (s, 1H), 5.56 (d, $J = 1.8$ Hz, 1H), 5.20 (dd, $J = 10.6, 4.0$ Hz, 1H) 4.98 (sept, $J = 6.2$ Hz, 1H) 4.01 (dd, $J = 16.4, 4.0$ Hz, 1H), 3.08 (ddd, $J = 16.4, 10.6, 2.0$, 1H), 1.20 (t, $J = 6.6$ Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 166.6, 166.4, 158.5, 155.0, 149.13, 149.11, 137.0, 136.8, 124.5, 123.1, 121.2, 120.6, 101.8, 101.2, 77.6, 66.8, 31.6, 21.8 (2C); HRMS (MALDI-ICR) calcd for $\text{C}_{19}\text{H}_{21}\text{N}_2\text{O}_4$ $[(\text{M}+\text{H})^+]$ 341.1496, found 341.1512.

Z-([1,3]-dioxan-4-ylidene)-acetate 4d. 10.4% yield (47% combined yield); as a brown oil: IR (film) $\nu_{\max}$ 3071, 2980, 2931, 1708, 1654, 1594, 1474, 1437, 1373, 1340, 1267, 1215, 1150, 1107, 1064, 995, 900 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.65 (dm, $J = 4.1$ Hz, 1H), 8.56 (dm, $J = 4.1$ Hz, 1H), 7.92 (dm, $J = 7.9$ Hz, 1H), 7.82 (td, $J = 7.8, 1.7$ Hz, 1H), 7.69 (td, $J = 7.7, 1.7$ Hz, 1H), 7.55 (dm, $J = 7.9$ Hz, 1H), 7.34 (ddd, $J = 7.5, 4.8, 1.2$ Hz, 1H), 7.22 (ddd, $J = 7.5, 4.9, 0.97$ Hz, 1H), 6.24 (s, 1H), 5.33 (dd, $J = 8.9, 4.9$ Hz, 1H) 5.10 (d, $J = 0.73$ Hz, 1H), 5.03 (sept, $J = 6.3$ Hz, 1H), 3.04 (dd, $J = 15.5, 4.8$ Hz, 1H), 2.88 (ddd, $J = 15.4, 9.0, 1.4$ Hz, 1H) 1.22 (d, $J = 6.0$ Hz, 3H), 1.21 (d, $J = 5.9$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 164.2 162.2, 157.7, 154.9,

149.2, 149.0, 137.1, 136.9, 124.4, 123.1, 121.4, 120.6, 100.1, 100.0, 77.4, 66.7, 34.4, 21.9 (2C); HRMS (MALDI-ICR) calcd for $C_{19}H_{21}N_2O_4$ $[(M+H)^+]$ 341.1496, found 341.1511.

***E*-([1,3]-dioxan-4-ylidene)-acetate 4e.** 86.6% yield (99% combined yield); as a slightly yellow oil: IR (film) $\nu_{\max}$ 3075, 2983, 2939, 2880, 1703, 1651, 1523, 1468, 1416, 1374, 1324, 1268, 1250, 1218, 1018, 965 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.75–7.68 (m, 4H), 7.65 (dm, $J = 8.2$ Hz, 2H), 7.57 (dm, $J = 8.4$ Hz, 2H), 6.08 (s, 1H), 5.65 (d, $J = 2.0$ Hz, 1H), 5.12 (dd, $J = 11.1, 3.5$ Hz, 1H), 5.07 (sept, $J = 4.2$ Hz, 1H), 4.06 (dd, $J = 16.1, 3.6$ Hz, 1H), 3.52 (ddd, $J = 16.1, 11.1, 2.1$ Hz, 1H), 1.28 (d, $J = 6.2$ Hz, 3H), 1.26 (d, $J = 6.2$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 166.6, 165.8, 143.7, 140.0, 131.7 (q, $J_{\text{CF}} = 32.4$ Hz), 130.5 (q, $J_{\text{CF}} = 32.7$ Hz), 126.7 (2C), 125.6 (q, $J_{\text{CF}} = 4.2$ Hz), 125.4 (q, $J_{\text{CF}} = 3.9$ Hz), 125.0 (2C), 124.9 (2C), 122.9 (2C), 102.3, 100.2, 76.3, 67.1, 33.1, 21.7 (2C); HRMS (MALDI-ICR) calcd for $C_{23}H_{20}F_6O_4\text{Na}$ $[(M+\text{Na})^+]$ 497.1158, found 497.1137.

***Z*-([1,3]-dioxan-4-ylidene)-acetate 4e.** 12.4% yield (99% combined yield); as a slightly yellow oil: IR (film) $\nu_{\max}$ 3070, 2984, 2372, 1738, 1715, 1417, 1325, 1166, 1127, 1102, 1068, 1018, 938, 841 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.84 (dm, $J = 8.5$ Hz, 2H), 7.70 (dm, $J = 8.1$ Hz, 2H), 7.68 (dm, $J = 8.3$ Hz, 2H), 7.53 (dm, $J = 7.9$ Hz, 2H), 6.14 (s, 1H), 5.18–5.15 (m, 2H), 5.09

(sept, $J = 5.9$ Hz, 1H), 2.71–2.68 (m, 2H), 1.27 (d, $J = 6.2$ Hz, 3H), 1.26 (d, $J = 6.2$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 164.0, 161.2, 143.4, 139.9, 131.5 (q, $J_{\text{CF}} = 32.6$ Hz), 130.7 (q, $J_{\text{CF}} = 32.7$ Hz), 126.6 (2C), 126.0 (2C), 125.8 (q, $J_{\text{CF}} = 4.0$ Hz, 2C), 125.4 (q, $J_{\text{CF}} = 3.6$ Hz, 2C), 125.0 (q, $J_{\text{CF}} = 5.9$ Hz), 122.8 (q, $J_{\text{CF}} = 5.7$ Hz), 101.4, 99.7, 76.95, 67.0, 36.7, 22.0 (2C); HRMS (MALDI-ICR) calcd for $\text{C}_{23}\text{H}_{20}\text{F}_6\text{O}_4\text{Na}$ [(M+Na) $^+$] 497.1158, found 497.1137.

E-([1,3]-dioxan-4-ylidene)-acetate 4f. 80.3% yield (90% combined yield); as a slightly yellow oil: IR (film) ν_{max} 3077, 2983, 2939, 2879, 1702, 1649, 1494, 1467, 1453, 1421, 1375, 1328, 1280, 1249, 1208, 1166, 1130, 1104, 1073, 1030, 969, 902 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.86 (br s, 1H), 7.78 (dm, $J = 7.7$ Hz, 1H), 7.75–7.68 (m, 2H), 7.63–7.50 (m, 4H), 6.08 (s, 1H), 5.64 (d, $J = 2.0$ Hz, 1H), 5.12 (dd, $J = 11.2, 3.5$ Hz, 1H), 5.04 (sept, $J = 6.3$ Hz, 1H), 4.05 (dd, $J = 16.1, 3.5$ Hz, 1H), 2.84 (ddd, $J = 16.1, 11.3, 2.1$ Hz, 1H), 1.27 (d, $J = 6.2$ Hz, 3H), 1.25 (d, $J = 6.2$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 166.7, 165.8, 140.7, 137.3, 131.2 (q, $J_{\text{CF}} = 14.2$ Hz), 130.9 (q, $J_{\text{CF}} = 15.0$ Hz), 129.7, 129.2, 129.15, 129.07, 126.4 (q, $J_{\text{CF}} = 3.4$ Hz), 125.2 (q, $J_{\text{CF}} = 3.4$ Hz), 125.0, 123.3 (q, $J_{\text{CF}} = 3.2$ Hz), 122.8, 123.4 (q, $J_{\text{CF}} = 3.2$), 102.4, 100.4, 76.5, 67.2, 33.1, 21.8 (2C); HRMS (MALDI-ICR) calcd for $\text{C}_{23}\text{H}_{20}\text{F}_6\text{O}_4\text{Na}$ [(M+Na) $^+$] 497.1158, found 497.1149.

Z-([1,3]-dioxan-4-ylidene)-acetate 4f. 9.7% yield (90% combined yield); as a slightly yellow oil: IR (film); ν_{max} 3055, 2985, 2937, 2879, 1709, 1658, 1452, 1421, 1371, 1328, 1265, 1217,

1168, 1130, 1106, 1074, 990, 909; ^1H NMR (500 MHz, CDCl_3) δ 7.86 (s, 1H), 7.78 (dm, $J = 7.7$ Hz, 1H), 7.71–7.51 (m, 6H), 6.08, (s, 1H), 5.63 (d, $J = 2.0$ Hz, 1H), 5.12 (dd, $J = 11.2, 3.5$ Hz, 1H), 5.04 (sept, $J = 6.3$ Hz, 1H), 4.05 (dd, $J = 16.1, 3.5$ Hz, 1H), 2.84 (ddd, $J = 16.1, 11.2, 2.1$ Hz, 1H), 1.27 (d, $J = 6.2$ Hz, 3H), 1.25 (d, $J = 6.2$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 164.1, 161.0, 140.5, 137.2, 131.1 (q, $J_{\text{CF}} = 32.8$ Hz), 130.6 129.8, 129.4, 129.1, 129.0, 126.2 (q, $J_{\text{CF}} = 7.8$ Hz) 125.4 (q, $J_{\text{CF}} = 7.9$ Hz), 125.0, 125.0, 123.1 (q, $J_{\text{CF}} = 4.0$ Hz), 122.6 (q, $J_{\text{CF}} = 4.1$ Hz), 101.7, 99.9, 77.2, 67.1, 36.7, 21.9 (2C); HRMS (MALDI-ICR) calcd for $\text{C}_{23}\text{H}_{20}\text{F}_6\text{O}_4\text{Na}$ $[(\text{M}+\text{Na})^+]$ 497.1158, found 497.1140.

E-([1,3]-dioxan-4-ylidene)-acetate 4g. 56.2% yield (65% combined yield); as a white solid: IR (film) ν_{max} 3019, 2981, 2958, 2877, 1701, 1650, 1611, 1451, 1429, 1374, 1315, 1286, 1232, 1217, 1167, 1128, 1108, 1057, 1037, 945 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.03 (dm, $J = 7.9$ Hz, 1H), 7.86 (dm, $J = 8.2$ Hz, 1H), 7.73–7.60 (m, 4H), 7.53 (tm, $J = 7.6$ Hz, 1H), 7.4 (tm, $J = 7.7$ Hz, 1H), 6.38 (s, 1H), 5.57 (d, $J = 2.0$ Hz, 1H), 5.46 (dd, $J = 10.7, 3.5$ Hz, 1H), 5.01 (sept, $J = 6.3$ Hz, 1H), 3.95 (dd, $J = 16.3, 3.7$ Hz, 1H), 2.87 (ddd, $J = 16.1, 10.7, 2.0$ Hz, 1H), 1.23 (d, $J = 6.6$ Hz, 3H), 1.22 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 164.1, 161.0, 140.5, 137.2, 131.1 (q, $J_{\text{CF}} = 32.8$ Hz), 130.6 129.8, 129.4, 129.1, 129.0, 126.2 (q, $J_{\text{CF}} = 7.8$ Hz) 125.4 (q, $J_{\text{CF}} = 7.9$ Hz), 125.0, 125.0, 123.1 (q, $J_{\text{CF}} = 4.0$ Hz), 122.6 (q, $J_{\text{CF}} = 4.1$ Hz), 101.7, 99.9, 77.2, 67.1, 36.7, 21.9 (2C); HRMS (MALDI-ICR) calcd for $\text{C}_{23}\text{H}_{20}\text{F}_6\text{O}_4\text{Na}$ $[(\text{M}+\text{Na})^+]$ 497.1158, found 497.1147.

Z-([1,3]-dioxan-4-ylidene)-acetate 4g. 8.8% yield (65% combined yield); as a slightly yellow oil: IR (film) $\nu_{\max}$ 3068, 2981, 2930, 1715, 1659, 1456, 1373, 1314, 1290, 1219, 1165, 1110, 1075, 1058, 1037 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.18 (dm, J = 8.1 Hz, 1H), 7.81 (dm, J = 7.9 Hz, 1H), 7.71–7.63 (m, 3H), 7.60 (tm, J = 7.7 Hz, 1H), 7.52 (tm, J = 7.7 Hz, 1H), 7.43 (tm, J = 7.6 Hz, 1H), 6.46 (s, 1H), 5.55 (dd, J = 8.9, 4.6 Hz, 1H), 5.09 (d, J = 2.0 Hz, 1H), 5.02 (sept, J = 6.3 Hz, 1H), 2.85 (dd, J = 15.3, 4.7 Hz, 1H), 2.66 (ddd, J = 15.4, 8.9, 2.0 Hz, 1H), 1.21 (d, J = 6.3 Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 164.0, 160.9, 140.5, 136.2, 131.1 (q, J_{CF} = 33.7 Hz), 130.6, 129.7, 129.3, 129.2, 129.1, 126.2 (q, J_{CF} = 7.8 Hz), 125.4 (q, J_{CF} = 7.9 Hz), 125.0, 123.1 (q, J_{CF} = 4.0 Hz), 122.6 (q, J_{CF} = 4.1 Hz), 101.7, 99.9, 75.1, 66.9, 36.9, 31.6, 21.8 (2C); HRMS (MALDI-ICR) calcd for $\text{C}_{23}\text{H}_{20}\text{F}_6\text{O}_4\text{Na}$ $[(\text{M}+\text{Na})^+]$ 497.1158, found 497.1142.

E-([1,3]-dioxan-4-ylidene)-acetate 4h. 74.1% yield (84% combined yield); as a yellow oil: IR (film) $\nu_{\max}$ 2981, 1701, 1654, 1648, 1523, 1347, 1141, 1107, 1068, 1029, 953, 855, 739 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.27 (dm, J = 8.8 Hz, 2H), 8.22 (dm, J = 8.8 Hz, 2H), 7.75 (d, J = 8.7 Hz, 2H), 7.60 (d, J = 8.6 Hz, 2H), 6.10 (s, 1H), 5.62 (d, J = 1.9 Hz, 1H), 5.19 (dd, J = 11.0, 3.6 Hz, 1H), 4.99 (sept, J = 6.3 Hz, 1H), 4.05 (dd, J = 16.1, 3.6 Hz, 1H), 2.79 (ddd, J = 16.1, 11.0, 2.1 Hz, 1H), 1.23 (d, J = 6.3 Hz, 3H), 1.21 (d, J = 6.2 Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 166.4, 164.9, 148.6, 147.8, 146.5, 142.4, 127.4 (2C), 126.4 (2C), 123.9 (2C), 123.7 (2C), 102.9,

99.5, 76.0, 67.3, 32.9, 21.9, 21.8; HRMS (EI) calcd for C₂₁H₂₁N₂O₈ [(M+H)⁺] 429.1298, found 429.1312.

Z-([1,3]-dioxan-4-ylidene)-acetate 4h. 9.9% yield (84% combined yield); as a yellow oil: IR (film) ν_{max} 2981, 1709, 1659, 1607, 1522, 1347, 1223, 1211, 1147, 1108, 1063, 990 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.26 (d, *J* = 8.9 Hz, 2H), 8.25 (d, *J* = 8.8 Hz, 2H), 7.87 (d, *J* = 8.6 Hz, 2H), 7.59 (d, *J* = 8.6 Hz, 2H), 6.14 (s, 1H), 5.23 (dd, *J* = 10.1, 4.2 Hz, 1H), 5.19 (d, *J* = 1.3 Hz, 1H), 5.06 (sept, *J* = 6.3 Hz, 1H), 2.72 (dd, *J* = 15.0, 4.2 Hz, 1H), 2.67 (ddd, *J* = 14.9, 10.1, 2.6 Hz, 1H), 1.25 (d, *J* = 6.2 Hz, 3H), 1.24 (d, *J* = 6.2 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 163.8, 160.4, 148.5, 147.9, 146.3, 142.4, 127.3 (2C), 126.5 (2C), 124.0 (2C), 123.6 (2C), 102.1, 99.1, 76.7, 67.2, 36.4, 22.0 (2C); HRMS (EI) calcd for C₂₁H₂₀N₂O₈ [M⁺] 428.1220, found 428.1207.

E-([1,3]-dioxan-4-ylidene)-acetate 4i. 85.3% yield (97% combined yield); as a slightly yellow oil: IR (film) ν_{max} 2981, 1701, 1650, 1532, 1373, 1350, 1142, 1107, 1063, 1029, 978, 902 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.42 (m, 1H), 8.29–8.26 (m, 2H), 8.19 (dm, *J* = 8.2 Hz, 1H), 7.91 (d, *J* = 7.7 Hz, 1H), 7.77 (d, *J* = 7.7 Hz, 1H), 7.62 (t, *J* = 8.0 Hz, 1H), 7.57 (t, *J* = 8.0 Hz, 1H), 6.11 (s, 1H), 5.63 (d, *J* = 1.9 Hz, 1H), 5.18 (dd, *J* = 11.1, 3.5 Hz, 1H), 5.00 (sept, *J* = 6.3 Hz,

1H), 4.06 (dd, $J = 16.1, 3.5$ Hz, 1H), 2.83 (ddd, $J = 16.0, 11.2, 2.8$ Hz, 1H), 1.24 (t, $J = 6.3$ Hz, 3H), 1.22 (t, $J = 6.3$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 166.5, 165.0, 148.4, 148.2, 141.6, 138.1, 132.4, 131.8, 129.8, 129.7, 124.6, 123.4, 121.7, 120.9, 103.0, 99.7, 76.1, 67.3, 33.0, 21.9, 21.8; HRMS (MALDI) calcd for $\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_8\text{Na}$ $[(\text{M}+\text{Na})^+]$ 451.1112, found 451.1109.

Z-4i

Z-([1,3]-dioxan-4-ylidene)-acetate 4i. 11.7% yield (97% combined yield); as a slightly yellow oil: IR (film) ν_{max} 2981, 1709, 1659, 1531, 1349, 1215, 1147, 1105, 1060, 989, 905, 808, 735, 685 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.49 (m, 1H), 8.27–8.24 (m, 2H), 8.20 (ddd, $J = 8.2, 2.2, 0.9$ Hz, 1H), 8.05 (d, $J = 7.8$ Hz, 1H), 7.78 (d, $J = 7.7$ Hz, 1H), 7.62 (t, $J = 8.0$ Hz, 1H), 7.60 (t, $J = 8.0$ Hz, 1H), 6.15 (s, 1H), 5.22 (t, $J = 7.2$ Hz, 1H), 5.20 (s, 1H), 5.06 (sept, $J = 6.2$ Hz, 1H), 2.72 (d, $J = 6.7$ Hz, 2H), 1.25 (d, $J = 6.1$ Hz, 3H), 1.24 (d, $J = 6.1$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 163.9, 160.3, 148.4, 148.2, 141.3, 138.1, 132.4, 131.8, 130.0, 129.6, 124.4, 123.5, 121.5, 120.9, 102.2, 99.2, 76.7, 67.2, 36.5, 21.9 (2C); HRMS (EI) calcd for $\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_8$ $[\text{M}^+]$ 428.1220, found 428.1224.

E-4j

E-([1,3]-dioxan-4-ylidene)-acetate 4j. 86.1% yield (99% combined yield); as a slightly yellow oil: IR (film) ν_{max} 2981, 2230, 1703, 1699, 1651, 1645, 1373, 1141, 1106, 1067, 1029, 950 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.75–7.73 (m, 2H), 7.70–7.68 (m, 4H), 7.55 (dm, $J = 8.2$ Hz, 2H),

6.05 (s, 1H), 5.61 (d, $J = 2.0$ Hz, 1H), 5.12 (dd, $J = 11.0, 3.6$ Hz, 1H), 5.01 (sept, $J = 6.3$ Hz, 1H), 4.03 (dd, $J = 16.1, 3.6$ Hz, 1H), 2.77 (ddd, $J = 16.1, 11.1, 2.0$ Hz, 1H), 1.25 (d, $J = 6.2$ Hz, 3H), 1.24 (d, $J = 6.2$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 166.4, 165.0, 144.6, 140.7, 132.4 (2C), 132.3 (2C), 127.0 (2C), 126.2 (2C), 118.3, 118.2, 113.5, 112.2, 102.7, 99.7, 76.1, 67.2, 32.9, 21.82, 21.78; HRMS (MALDI) calcd for $\text{C}_{23}\text{H}_{20}\text{N}_2\text{O}_4\text{Na}$ $[(\text{M}+\text{Na})^+]$ 411.1315, found 411.1335.

Z-([1,3]-dioxan-4-ylidene)-acetate 4j. 12.9% yield (99% combined yield); as a slightly yellow oil: IR (film) ν_{max} 2981, 2230, 1713, 1699, 1694, 1660, 1652, 1373, 1223, 1147, 1108, 1063, 990 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.80 (dm, $J = 8.1$ Hz, 2H), 7.71 (dm, $J = 8.5$ Hz, 2H), 7.69 (dm, $J = 8.5$ Hz, 2H), 7.51 (dm, $J = 8.2$ Hz, 2H), 6.09 (s, 1H), 5.17 (d, $J = 0.8$ Hz, 1H), 5.14 (dd, $J = 9.4, 5.0$ Hz, 1H), 5.05 (sept, $J = 6.2$ Hz, 1H), 2.70–2.60 (m, 2H), 1.245 (t, $J = 6.2$ Hz, 3H), 1.236 (t, $J = 6.2$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 163.8, 160.6, 144.4, 140.7, 132.6 (2C), 132.3 (2C), 127.0 (2C), 126.3 (2C), 118.4, 118.3, 113.3, 112.5, 101.9, 99.2, 76.8, 67.1, 36.5, 22.0 (2C); HRMS (EI) calcd for $\text{C}_{23}\text{H}_{20}\text{N}_2\text{O}_4$ $[\text{M}^+]$ 388.1423, found 388.1413.

E-([1,3]-dioxan-4-ylidene)-acetate 4k. 85.1% yield (98% combined yield); as a colorless oil: IR (film) ν_{max} 2981, 2231, 1700, 1651, 1484, 1373, 1154, 1138, 1106, 1063, 1030 cm^{-1} ; ^1H NMR

(500 MHz, CDCl₃) δ 7.85 (m, 1H), 7.79 (dm, J = 7.9 Hz, 1H), 7.71 (m, 1H), 7.69 (dm, J = 7.8 Hz, 1H), 7.64 (dm, J = 7.9 Hz, 1H), 7.60 (dm, J = 7.8 Hz, 1H), 7.54 (t, J = 7.8 Hz, 1H), 7.49 (t, J = 7.8 Hz, 1H), 6.02 (s, 1H), 5.59 (d, J = 2.0 Hz, 1H), 5.08 (dd, J = 11.1, 3.5 Hz, 1H), 4.99 (sept, J = 6.3 Hz, 1H), 3.99 (dd, J = 16.1, 3.6 Hz, 1H), 2.75 (ddd, J = 16.1, 11.1, 2.0 Hz, 1H), 1.22 (d, J = 6.3 Hz, 3H), 1.21 (d, J = 6.3 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 166.4, 165.1, 141.0, 137.6, 133.1, 131.9, 130.6, 130.0, 129.97, 129.5, 129.4, 129.2, 118.3, 118.2, 112.8, 112.6, 102.7, 99.6, 75.8, 67.2, 32.9, 21.80, 21.77; HRMS (MALDI) calcd for C₂₃H₂₀N₂O₄Na [(M+Na)⁺] 411.1315, found 411.1316.

Z-4k

Z-([1,3]-dioxan-4-ylidene)-acetate 4k. 12.9% yield (98% combined yield); as a white solid: IR (film) ν_{max} 2977, 2230, 1703, 1645, 1631, 1486, 1400, 1344, 1217, 1104, 1063, 1031, 987, 824, 790 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.96 (m, 1H), 7.93 (dm, J = 7.9 Hz, 1H), 7.70–7.67 (m, 2H), 7.66–7.63 (m, 2H), 7.54 (t, J = 7.9 Hz, 1H), 7.52 (t, J = 7.8 Hz, 1H), 6.06 (s, 1H), 5.17 (s, 1H), 5.12 (t, J = 7.1 Hz, 1H), 5.06 (sept, J = 6.3 Hz, 1H), 2.69–2.61 (m, 2H), 1.25 (t, J = 6.3 Hz, 3H), 1.24 (t, J = 6.3 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 163.8, 160.4, 140.9, 137.6, 133.0, 132.2, 130.6, 130.0, 129.9, 129.7, 129.34, 129.28, 118.4, 118.3, 113.0, 112.6, 102.0, 99.1, 76.6, 67.1, 36.5, 21.9 (2C); HRMS (EI) calcd for C₂₃H₂₀N₂O₄ [M⁺] 388.1423, found 388.1428.

E-4l

***E*-([1,3]-dioxan-4-ylidene)-acetate 4l.** 56.7% yield (64% combined yield); as a slightly yellow oil: IR (film) $\nu_{\max}$ 3070, 2983, 2930, 1720, 1657, 1463, 1374, 1315, 1289, 1219, 1164, 1110, 1080, 1053, 1037, 769 cm^{-1} ; ^1H NMR (500 MHz, C_6D_6) δ 7.75 (dd, $J = 7.8, 1.7$ Hz, 1H), 7.47 (dd, $J = 7.8, 1.5$ Hz, 1H), 7.05 (ddd, $J = 13.4, 8.0, 1.0$ Hz, 2H), 6.90 (td, $J = 7.6, 1.0$ Hz, 1H), 6.84 (td, $J = 7.6, 1.0$ Hz, 1H), 6.77 (td, $J = 7.9, 1.7$ Hz, 1H), 6.71 (td, $J = 7.8, 1.7$ Hz, 1H), 6.77 (s, 1H), 5.87 (d, $J = 1.9$ Hz, 1H), 5.32 (dd, $J = 10.4, 3.8$ Hz, 1H), 5.09 (sept, $J = 6.2$ Hz, 1H), 4.32 (dd, $J = 16.2, 3.8$ Hz, 1H), 2.84 (ddd, $J = 16.1, 10.4, 2.1$ Hz, 1H), 1.07 (d, $J = 6.2$ Hz, 3H), 1.03 (d, $J = 6.2$ Hz, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 167.1, 166.6, 138.6, 134.9, 132.1, 130.0, 129.8, 129.5, 128.7, 128.4, 128.3, 128.1, 127.2, 127.1, 102.5, 99.9, 74.7, 67.0, 32.4, 22.2 (2C); HRMS (MALDI-ICR) calcd for $\text{C}_{21}\text{H}_{20}\text{Cl}_2\text{O}_4\text{Na}$ [(M+Na) $^+$] 429.0631, found 429.0620.

***Z*-([1,3]-dioxan-4-ylidene)-acetate 4l.** 7.3% yield (64% combined yield); as a slightly yellow oil: IR (film) $\nu_{\max}$ 3055, 2984, 2937, 2879, 1738, 1715, 1594, 1468, 1422, 1386, 1375, 1337, 1265, 1206, 1104, 1053, 1039, 1022, 928 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.95 (dd, $J = 7.4, 1.9$ Hz, 1H) 7.61 (dd, 7.6, 1.8, 1H) 7.48–7.26 (m, 6H), 6.48 (s, 1H), 5.56 (dd, $J = 9.2, 4.5$ Hz, 1H), 5.08 (d, $J = 1.2$ Hz, 1H) 5.04 (sept, $J = 6.3$ Hz, 1H), 2.97 (dd, $J = 15.2, 4.4$, 1H), 2.59 (ddd, $J = 15.2, 9.2, 1.4$ Hz, 1H), 1.220 (d, $J = 6.2$ Hz, 3H), 1.216 (d, $J = 6.3$ Hz, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 164.1, 161.6, 143.2, 137.6, 132.7, 131.7, 130.7, 129.7, 129.4, 129.3, 128.2, 126.9, 126.7, 100.2, 97.8, 74.0, 69.2, 66.6 35.4, 21.8 (2C); HRMS (MALDI-ICR) calcd for $\text{C}_{21}\text{H}_{20}\text{Cl}_2\text{O}_4\text{Na}$ [(M+Na) $^+$] 429.0631, found 429.0616.

E-4m

E-([1,3]-dioxan-4-ylidene)-acetate 4m. 71.7% yield (77% combined yield); as a slightly yellow oil: IR (film) $\nu_{\max}$ 3077, 2981, 2937, 2877, 1702, 1648, 1619, 1595, 1491, 1451, 1373, 1348, 1273, 1258, 1166, 1149, 1133, 1092, 1061, 1029 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.42–7.26 (m, 4H), 7.22–7.16 (m, 2H), 7.12 (tdd, J = 8.4, 2.5, 1.2 Hz, 1H), 7.02 (tdd, J = 8.4, 2.5, .81 Hz, 1H), 6.00 (s, 1H), 5.59 (d, J = 2.0 Hz, 1H), 5.07–5.01 (m, 2H), 3.99 (dd, J = 16.2, 3.5 Hz, 1H), 2.80 (ddd, J = 16.1, 11.2, 2.1 Hz, 1H), 1.27 (d, J = 6.2 Hz, 3H), 1.25 (d, J = 6.3 Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 166.7, 166.2, 163.8 (d, J_{CF} = 25.9 Hz), 161.8 (d, J_{CF} = 25.2 Hz), 142.3 (d, J_{CF} = 6.7 Hz), 138.8 (d, J_{CF} = 7.7 Hz), 130.2 (d, J_{CF} = 7.5 Hz), 130.1 (d, J_{CF} = 7.5 Hz), 122.0 (d, J_{CF} = 3.3 Hz), 121.2 (d, J_{CF} = 3.4 Hz), 116.6 (d, J_{CF} = 20.8 Hz), 115.2 (d, J_{CF} = 20.8 Hz), 113.5 (d, J_{CF} = 23.2 Hz), 112.8 (d, J_{CF} = 22.0 Hz), 102.0, 100.3, 76.2, 67.0, 33.2, 21.9 (2C); HRMS (MALDI-ICR) calcd for $\text{C}_{21}\text{H}_{20}\text{F}_2\text{O}_4\text{Na}$ [(M+Na) $^+$] 397.1222, found 397.1213.

Z-4m

Z-([1,3]-dioxan-4-ylidene)-acetate 4m. 5.3% yield (77% combined yield); as a slightly yellow oil: IR (film) $\nu_{\max}$ 3055, 2985, 2937, 2879, 1738, 1715, 1655, 1594, 1468, 1435, 1386, 1375, 1265, 1181, 1142, 1104, 1039, 1053, 982, 896, 739 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.49–7.35 (m, 4H), 7.19–7.05 (m, 4H), 6.07 (s, 1H), 5.14 (d, J = 1.5 Hz, 1H), 5.11–5.05 (m, 2H), 2.70 (ddd, J = 15.0, 10.5, 1.7 Hz, 1H), 2.63 (dd, J = 15.0, 3.9 Hz, 1H), 1.274 (d, J = 6.2 Hz, 3H), 1.266 (d, J = 6.2 Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 164.1, 163.8 (d, J_{CF} = 29.3 Hz), 161.8

(d, $J_{\text{CF}} = 27.7$ Hz), 161.5, 142.1 (d, $J_{\text{CF}} = 6.9$ Hz), 138.7 (d, $J_{\text{CF}} = 7.7$ Hz), 130.3 (d, $J_{\text{CF}} = 8.3$ Hz), 130.0 (d, $J_{\text{CF}} = 7.8$ Hz), 121.9 (d, $J_{\text{CF}} = 3.1$ Hz), 121.2 (d, $J_{\text{CF}} = 2.9$ Hz), 116.3 (d, $J_{\text{CF}} = 20.9$ Hz), 115.4 (d, $J_{\text{CF}} = 20.9$ Hz), 113.4 (d, $J_{\text{CF}} = 23.6$ Hz), 112.8 (d, $J_{\text{CF}} = 22.4$ Hz), 101.1, 99.8, 76.8, 66.9, 36.7, 21.9 (2C); HRMS (MALDI-ICR) calcd for $\text{C}_{21}\text{H}_{20}\text{F}_2\text{O}_4\text{Na}$ [(M+Na) $^+$] 397.1222, found 397.1214.

E-([1,3]-dioxan-4-ylidene)-acetate 4n. 54% yield; as a slightly yellow oil: IR (film) ν_{max} 3071, 2979, 2937, 2836, 1702, 1644, 1589, 1492, 1465, 1436, 1373, 1324, 1289, 1266, 1198, 1137, 1107, 1029, 972 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.63–7.58 (m, 2H), 7.47–7.38 (m, 7H), 7.37–7.31 (m, 1H) 6.03 (s, 1H), 5.18 (d, $J = 2.0$ Hz, 1H), 5.06–4.99 (m, 2H), 3.98 (dd, $J = 16.2$, 3.5 Hz, 1H), 2.84 (ddd, $J = 16.2$, 11.3, 2.1 Hz, 1H), 1.26 (d, $J = 6.3$ Hz, 3H) 1.24 (d, $J = 6.3$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 167.3, 167.0, 140.0, 136.7, 129.6, 128.5 (2C), 125.4 (2C), 128.2, 126.3 (2C), 125.8 (2C) 101.6, 101.3, 76.7, 66.8, 33.4, 21.9 (2C); HRMS (MALDI-TOF) calcd for $\text{C}_{21}\text{H}_{22}\text{O}_4\text{Na}$ [(M+Na) $^+$] 361.1410, found 361.1421.

E-([1,3]-dioxan-4-ylidene)-acetate 4o. 47% yield; as a slightly yellow oil: IR (film) ν_{max} 3070, 2978, 2937, 2837, 1700, 1644, 1604, 1491, 1465, 1436, 1372, 1324, 1288, 1198, 1157, 1107, 1029, 972 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.33 (t, $J = 7.9$ Hz, 1H), 7.29 (t, $J = 7.9$ Hz, 1H), 7.17–7.13 (m, 2H), 7.03–7.00 (m, 2H), 6.96 (dd, $J = 13.1$, 7.2 Hz, 1H), 6.86 (dd, $J = 8.2$, 2.2 Hz,

1H), 5.99 (s, 1H), 5.56 (d, $J = 1.9$ Hz, 1H), 5.05–4.99 (m, 2H), 3.96 (dd, $J = 16.2, 3.5$ Hz, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 2.83 (ddd, $J = 16.2, 11.3, 2.0$ Hz, 1H), 1.25 (d, $J = 6.3$ Hz, 3H) 1.24 (d, $J = 6.3$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 167.1, 166.9, 159.65, 159.77, 141.6, 138.1, 129.6, 129.5, 118.7, 118.1, 115.3, 113.7, 111.7, 111.4, 101.4, 101.3, 76.8, 66.8, 55.30, 55.25, 33.4, 21.9 (2C); HRMS (MALDI-ICR) calcd for $\text{C}_{23}\text{H}_{26}\text{O}_6\text{Na}$ $[(\text{M}+\text{Na})^+]$ 421.1622, found 421.1630.

Reactivity of dihydrofuran under reaction conditions: Dihydrofuran **5** was synthesized and subjected to optimized reaction conditions. No trace of dioxanylidene **3k** was detected and dihydrofuran **5** was recovered at 98% yield.

Dihydrofuran 5. White powder: IR (film) ν_{max} 2981, 2933, 1713, 1616, 1575, 1467, 1434, 1384, 1223, 1105, 1074, 1029, 935 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.42 (s, 1H), 7.32–7.28 (m, 3H), 5.38 (dd, $J = 12.2, 3.8$ Hz, 1H), 5.18 (s, 1H), 4.50 (sept, $J = 6.1$ Hz, 1H), 2.74, (ddd, $J = 17.1, 12.2, 1.0$ Hz, 1H), 2.54 (dd, $J = 17.1, 3.9$ Hz, 1H), 1.35 (d, $J = 6.1$ Hz, 3H), 1.30 (d, $J = 6.1$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 170.4, 166.9, 140.3, 134.6, 129.9, 128.6, 126.1, 124.0, 90.7, 76.1, 72.1, 35.5, 21.4, 21.2; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{15}\text{ClO}_3$ $[\text{M}^+]$ 266.0710, found 266.0715.

The Synthesis of δ -Hydroxy- β -Ketoester **11** (Deprotection):

Results of this investigation were reported in **Table 3** of the paper. Hydrolysis of the acetal functionality of differentially substituted [1,3]-dioxan-4-ylidene-acetates was accomplished under acidic conditions to access synthetically useful δ -hydroxy- β -ketoesters.

A typical experimental procedure for the deprotection of ([1,3]-dioxan-4-ylidene)-acetates to the corresponding δ -hydroxy- β -ketoesters is as follows; to a solution of [1,3]-dioxan-4-ylidene-acetate (1 mmol) in wet chloroform (50 mL) was added *conc.* HCl (12.1 M, 1 mmol, 83 μ L.) The mixture was then stirred at room temperature and monitored by TLC (eluent: hexanes/ethyl acetate = 4:1 to 2:1). After the reaction was complete, the resulting mixture was concentrated and the residue was purified by flash column chromatography on silica gel (eluant: hexanes/ethyl acetate 10:1 to 4:1) to yield the product.

δ -hydroxy- β -ketoester 11a. 97% yield; as a clear oil: IR (film) $\nu_{\max}$ 3479, 3072, 2980, 2940, 1733, 1712, 1647, 1596, 1574, 1468, 1403, 1388, 1375, 1317, 1275, 1191, 1150, 1105, 1080 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.37–7.33 (m, 5H), 5.21 (dd, J = 6.2, 3.0 Hz, 1H), 5.06 (sept, J = 6.3 Hz, 1H), 3.46 (s, 2H), 3.05–2.90 (m, 2H), 1.26 (d, J = 6.3 Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 202.1, 166.3, 142.4, 128.6 (2C), 127.8 (2C), 125.6, 69.8, 69.3, 51.5, 50.2, 21.7 (2C); HRMS (EI) calcd for $\text{C}_{14}\text{H}_{18}\text{O}_4$ [M^+] 250.1205, found 250.1209.

δ -hydroxy- β -ketoester 11b. 95.5% yield; as a clear oil: IR (film) $\nu_{\max}$ 3483, 3067, 2982, 2935, 1735, 1711, 1647, 1598, 1575, 1468, 1407, 1387, 1375, 1356, 1315, 1274, 1194, 1145, 1104, 1078, 967 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.40–7.37 (m, 1H), 7.30–7.21 (m, 3H), 5.30 (s, 1H), 5.17 (dd, J = 8.3, 3.9 Hz, 1H), 5.06 (sept, J = 6.3 Hz, 1H), 3.45 (s, 2H), 2.99–2.89 (m, 2H), 1.26 (d, J = 6.3 Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 202.9, 166.3, 144.5, 134.5, 129.9, 127.90, 127.85, 123.7, 69.4, 69.1, 51.4, 50.1, 21.7 (2C); HRMS (MALDI-ICR) calcd for $\text{C}_{14}\text{H}_{17}\text{ClO}_4\text{Na}$ [$(\text{M}+\text{Na})^+$] 307.0708, found 307.0709.

δ -hydroxy- β -ketoester 11c. 87% yield; as a clear oil: IR (film) $\nu_{\max}$ 3480, 3066, 2983, 2935, 2229, 1736, 1713, 1646, 1609, 1505, 1467, 1407, 1387, 1375, 1357, 1315, 1274, 1196, 1145, 1105, 1079, 1018, 967 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.64 (dm, $J = 6.6$ Hz, 2H), 7.48 (dm, $J = 8.2$ Hz, 2H), 5.25 (t, $J = 6.8$ Hz, 1H) 5.05 (sept, $J = 6.3$ Hz, 1H), 3.46 (s, $J = 6.3$ Hz, 2H) 2.95–2.89 (m, 2H), 1.25 (d, $J = 6.3$ Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 202.7, 166.3, 147.7, 132.4 (2C), 126.3 (2C), 118.7, 111.5, 69.5, 69.0, 51.2, 50.0, 21.8 (2C); HRMS (MALDI-ICR) calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_4\text{Na}$ $[(\text{M}+\text{Na})^+]$ 298.1050, found 298.1053.

δ -hydroxy- β -ketoester 11d. 88.2% yield; as a clear oil: IR (film) $\nu_{\max}$ 3483, 3068, 2983, 2936, 2230, 1736, 1712, 1647, 1584, 1482, 1467, 1408, 1387, 1375, 1357, 1316, 1275, 1205, 1181, 1147, 1105, 967, 901, 803 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.72–7.68 (m, 1H), 7.61–7.56 (m, 2H), 7.47–7.44 (m, 1H), 5.23 (t, $J = 6.1$ Hz, 1H), 5.05 (sept, $J = 6.3$ Hz, 1H), 3.46 (s, 2H), 2.94 (d, $J = 6.1$ Hz, 2H), 1.26 (d, $J = 6.3$ Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 202.7, 166.3, 144.0, 131.4, 131.3, 130.1, 129.2, 118.6, 112.6, 69.5, 68.7, 51.2, 50.0, 21.8 (2C); HRMS (MALDI-ICR) calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_4\text{Na}$ $[(\text{M}+\text{Na})^+]$ 298.1050, found 298.1054.

δ -hydroxy- β -ketoester 11e. 81.9% yield; as a clear oil: IR (film) $\nu_{\max}$ 3503, 2983, 2936, 1735, 1710, 1605, 1520, 1467, 1407, 1375, 1347, 1315, 1183, 1145, 1105, 1013, 968 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.19 (dm $J = 8.7$ Hz, 2H), 7.54 (dm, $J = 8.7$ Hz, 1H) 5.33–5.27 (br m, 1H) 5.05 (sept, $J = 6.3$ Hz, 1H) 3.47–3.44 (m, 2H), 3.00–2.95 (m, 2H), 1.25 (d, $J = 6.3$ Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 202.6, 166.3, 149.7, 147.4, 126.4 (2C), 123.8 (2C), 69.5, 68.8, 51.2,

50.0, 21.8 (2C); HRMS (MALDI-ICR) calcd for C₁₄H₁₇NO₆Na [(M+Na)⁺] 318.0948, found 318.0953.

δ-hydroxy-β-ketoester 11f. 88.5% yield; as a clear oil: IR (film) $\nu_{\max}$ 3501, 3091, 2983, 1736, 1712, 1643, 1583, 1531, 1468, 1454, 1408, 1374, 1351, 1198, 1146, 1104, 967 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.24 (s, 1H), 8.12 (d, *J* = 8.1 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.52 (t, *J* = 8.1 Hz, 1H) 5.31–5.28 (m, 1H), 5.05 (sept, *J* = 6.3 Hz, 1H), 3.47 (s, 2H), 2.99 (d, *J* = 6.4 Hz, 2H) 1.25 (d, *J* = 6.3 Hz, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 202.6, 166.2, 148.3, 144.6, 131.7, 129.4, 122.5, 120.6, 69.4, 68.6, 53.3, 51.1, 49.9, 21.7 (2C); HRMS (MALDI-ICR) calcd for C₁₄H₁₇NO₆Na [(M+Na)⁺] 318.0948, found 318.0950.

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