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Stereospecific synthesis of phosphono-(1*Z*,3*E*)-dienyl compounds from β-phenyltelluro-vinylphosphonates and -vinylphosphine oxides

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Abstract

Phosphono-1,3-dienyl compounds **2** can be prepared by palladium cross-coupling reaction of β-phenyltelluro-vinylphosphonates or -vinylphosphine oxides with alkenes in the presence of a catalytic amount of $PdCl_2$ and AcOAg as reoxidant agent at room temperature. The coupling reaction is stereospecific and the compounds **2** were obtained in good yields with total retention of configuration.

Keywords: Phosphine oxide; Phosphonates; Tellurium; Dienes; Palladium; Cross-coupling

1. Introduction

Unsaturated phosphono compounds containing electron-withdrawing substituents as well as other heteroatom-functionalized moieties have been widely utilized in organic synthesis during the last two decades, and have furnished many synthetic possibilities [1].

Stereodefined conjugated dienes and enynes represent a class of important synthetic intermediates and are a part of a variety of natural products of biological interest [2,3], such as sorbic acid and abscisic acid. These systems have also been found in several classes of pheromones like those from *Thysanoplusia intermixta* [4] and *Thaumetopoea processionea* [5]. Dienylphosphorus compounds containing a (*Z*)-olefinic moiety are synthetically useful due to their potential to act as dienophiles or as Michael acceptors, an could also be regarded as an analog of abscisic acid. On the other hand, vinylic tellurides have been used as vinyl carbocation equivalent in Heck [6] and Sonogashira type [7] cross-coupling reactions.

Thus, as part of our continuing interest in vinylic tellurides and vinylphosphono compounds [8], we have recently been investigating the hydrochalcogenation of 1-alkynylphosphonates [9] and hydrotelluration of 1-alkynylphosphine oxides [7a]. We have found that the β-*n*-butyltelluro-vinylphosphonates or -vinylphosphine oxides, obtained from 1-alkynylphosphono compounds, can be transformed into their correspondent enynephosphonates and enynephosphine oxides via a Palladium-catalyzed cross-coupling reaction (Scheme 1).

In connection with our continued studies in cross-coupling reactions catalyzed by palladium [7], now we wish to report that β-phenyltelluro vinylphosphine oxides and -vinylphosphonates **1** readily react with alkenes in a Heck-type reaction providing the phosphono-(1*Z*,3*E*)-dienyl compounds **2** with total regio and stereocontrol (Scheme 2).

2. Results and discussion

The required starting β-phenyltelluro vinylphosphono compounds **1** were prepared by addition of alkynylphosphine oxides or alkynylphosphonates to a solution of sodium phenyl tellurolate, prepared by reduction of diphenyl ditelluride with sodium borohydride in ethanol at room temperature [7a,9].

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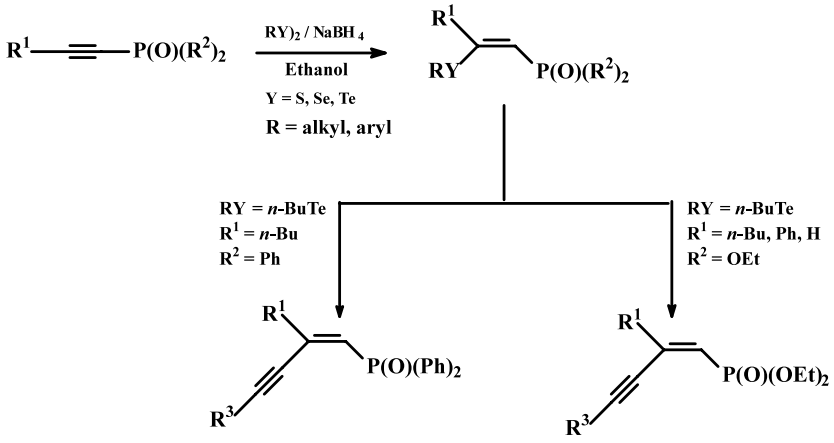
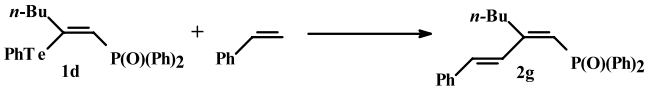


Scheme 1.

Our initial goal in the study of this reaction was to investigate the effects of a variety of reaction conditions including base, solvent, reoxidant, and palladium (II) salt. β-organotelluro vinylphosphine oxide **1d** and styrene were chosen as standards to optimize the reaction. The results are summarized in Table 1.

Initially, treatment of compound **1d** with styrene using a stoichiometric amount of $PdCl_2$ in methanol at room temperature for 24 h afforded the phosphono-1,3-dienyl compound **2g** in 99% yield (Entry 1, Table 1). In the search for a catalytic process, the amount of palladium chloride was reduced to 0.15 equivalents, but the desired compound **2g** was obtained in only 13% yield (Entry 2, Table 1). According to the reported mechanism in the literature for this reaction, the use of a reoxidant for palladium (II) is necessary [6]. The choice of the better reoxidant for this reaction started with silver acetate, which furnished the desired compound **2g** in a very good yield (Entry 3, Table 1). $CuCl_2$ and $FeCl_3$ were also tested, but they were not efficient in reoxidizing palladium to the active specie (see Entries 8 and 9). When potassium phosphate was used as a base in place of triethylamine, we obtained product **2g** in lower yield (75%, Entry 6, Table 1). Acetonitrile was tested as

Table 1
Reaction of β-phenyltelluro vinylphosphine oxide **1d** with styrene

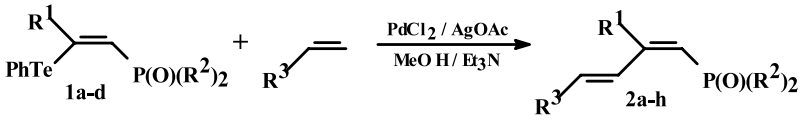


Entry	Pd^{II} salt (equivalents)	Base	Oxidant	Product **2g** Yield [a] (%)
1	$PdCl_2$ (1.00)	Et_3N	–	99
2	$PdCl_2$ (0.15)	Et_3N	–	13
3	$PdCl_2$ (0.15)	Et_3N	AcOAg	93
4	$PdCl_2$ (0.10)	Et_3N	AcOAg	60
5	$PdCl_2$ (0.15) [b]	Et_3N	AcOAg	45
6	$PdCl_2$ (0.15)	K_3PO_4	AcOAg	75
7	$PdCl_2$ (0.10)	K_3PO_4	AcOAg	50
8	$PdCl_2$ (0.15)	Et_3N	$FeCl_3$	13
9	$PdCl_2$ (0.15)	Et_3N	$CuCl_2$	–
10	$Pd(OAc)_2$ (0.15)	Et_3N	AcOAg	63

Carried out with compound **1d** (0.5 mmol), oxidant (2 mmol), styrene (2 mmol), methanol (5 ml) and Et_3N (2 mmol) at 25 °C for 24 h.

[a] Isolated yield after purification by column chromatography on silica gel (EtOAc:Hexane/3:7).

[b] Reaction solvent: acetonitrile.

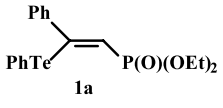
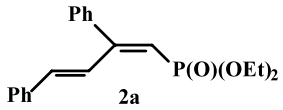
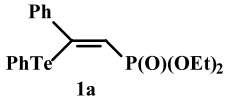
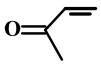
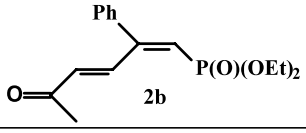
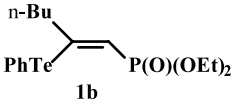
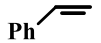
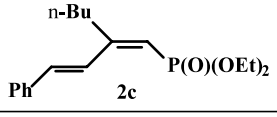
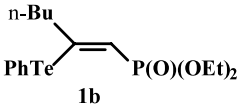
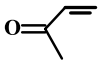
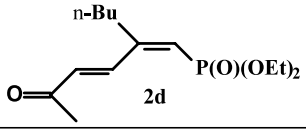
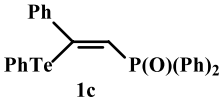
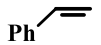
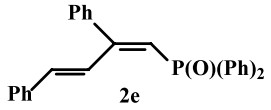
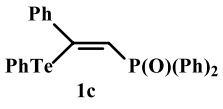
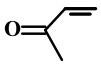
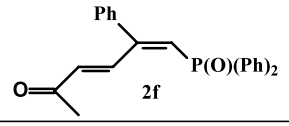
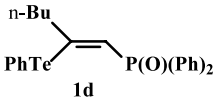
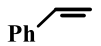
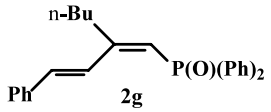
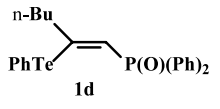
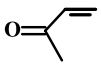
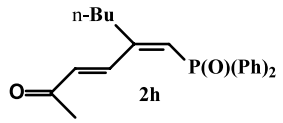


1a: R^1 = Ph, R^2 = OEt
1b: R^1 = *n*-Bu, R^2 = OEt
1c: R^1 = Ph, R^2 = Ph
1d: R^1 = *n*-Bu, R^2 = Ph

2a: R^1 = Ph, R^2 = OEt, R^3 = Ph
2b: R^1 = Ph, R^2 = OEt, R^3 = $COCH_3$
2c: R^1 = *n*-Bu, R^2 = OEt, R^3 = Ph
2d: R^1 = *n*-Bu, R^2 = OEt, R^3 = $COCH_3$
2e: R^1 = Ph, R^2 = Ph, R^3 = Ph
2f: R^1 = Ph, R^2 = Ph, R^3 = $COCH_3$
2g: R^1 = *n*-Bu, R^2 = Ph, R^3 = Ph
2h: R^1 = *n*-Bu, R^2 = Ph, R^3 = $COCH_3$

Scheme 2.

Table 2
Synthesis of phosphono-1,3-dienyl compounds **2** according to conditions described in Scheme 2

Entry	β-phenyltelluro vinylphosphono 1	Alkene	Product 2	Yield[a] (%)
1	 1a		 2a	83
2	 1a		 2b	71
3	 1b		 2c	86
4	 1b		 2d	81
5	 1c		 2e	61
6	 1c		 2f	59
7	 1d		 2g	93
8	 1d		 2h	76

[a] Isolated yield.

solvent yielding compound **2g** in 45%. From the analysis of the results summarized in Table 1, the $PdCl_2$–Et_3N–AcOAg system has revealed to be the best amongst those examined for the cross-coupling reaction. Then, the optimum conditions for this reaction was the use of $PdCl_2$ (15 mol.%), AcOAg (2 mmol), Et_3N (2 mmol), methanol (5 ml), β-phenyltelluro vinylphosphono compounds **1** (0.5 mmol) and the appropriate alkene (2 mmol) at room temperature for 24 h. On the base of these results, we applied this methodology to prepare several phosphono-1,3-dienyl compounds **2** (Table 2). In all cases studied, we observed the formation of a small amount of *trans*-stilbene or *trans*-styryl methyl ketone due to the coupling reaction of phenyl moiety of **1** with the alkene. The phosphono-(1*Z*,3*E*)-dienyl compounds **2** were isolated as oils or solids after column chromatography on silica gel, using as eluent a mixture of hexane and ethyl acetate. The regio- and stereochemistry

(1*Z*,3*E*) of products **2** were readily determined by ^{1}H-NMR spectral analysis. For example, the coupling constants for vinylic hydrogens of the new double bond formed are in agreement with typical values (15–17 Hz), for a *trans* relationship between them. There is no evidence of the presence of the (*Z*) isomer, comproving the highly stereoselective character of the coupling reaction. Moreover, the reaction proceeds with retention of the stereochemistry of the original double bond of the starting telluride **1**.

In summary, we have developed a simple and convenient catalytic method for the stereospecific preparation of phosphono-(1*Z*,3*E*)-dienyl compounds **2** from β-phenyltelluro vinylphosphono compounds **1**. The reaction proceeds cleanly under mild conditions and substituents such as phosphine oxides, ketone and phosphonates are tolerated quite well. Further studies of the dienylphosphono compounds as dienophile in Diels–Alder reactions are in progress in our group.

3. Experimental

3.1. General

^{1}H- and ^{13}C-NMR spectra of $CDCl_3$ solutions were recorded on a 200 MHz (Bruker DPX 200). Chemical shifts are expressed as parts per million with respect to tetramethylsilane as an internal standard. High-resolution mass spectra were obtained at 70 eV with a Bruker Bioapex. Reactions were conducted under argon atmosphere. Merck silica gel (230–400 mesh) was used for flash chromatography.

3.2. Preparation of β-organotelluro vinylphosphono compounds **1a–d** [7a,9]

To a solution of RTeNa [generated in situ from RTeTeR (1 mmol) and $NaBH_4$ (2.2 mmol)] in absolute ethanol (10 ml) the 1-alkynylphosphono compound was added dropwise at room temperature. The reaction mixture was stirred for 5 h. Then the mixture was poured into a saturated aqueous solution of NH_4Cl (10 ml) and the aqueous layer was extracted with ethyl acetate (2 × 25 ml). The organic layer was dried over $MgSO_4$ and filtered, and the solvent was removed under vacuum. The residue was purified by flash chromatography on silica gel using as eluent a mixture of ethyl acetate and hexane (3:7) to afford the products **1**. **1b**: ^{1}H-NMR (200 MHz, $CDCl_3$): δ 7.92 (d, $J = 7.6$ Hz, 2H), 7.42–7.21 (m, 3H), 6.27 (d, $^2J_{P-H} = 16.4$ Hz, 1H), 4.11 (dq, $^3J_{P-H} = 7.5$ Hz, $J = 7.2$ Hz, 4H), 2.21 (t, $J = 7.8$ Hz, 2H), 1.40–1.23 (m, 2H), 1.35 (t, $J = 7.2$ Hz, 6H), 1.00 (sext, $J = 7.4$ Hz, 2H), 0.66 (t, $J = 7$ Hz, 3H); ^{13}C-NMR (50 MHz, $CDCl_3$): δ 154.75 (d, $^2J_{P-C} = 6.3$ Hz), 141.43, 128.58, 128.27, 115.33 (d, $^1J_{P-C} = 192$ Hz), 115.29, 61.27 (d, $^2J_{P-C} = 5$ Hz), 41.67 (d, $^3J_{P-C} = 23$ Hz), 31.56, 21.16, 15.94 (d, $^3J_{P-C} = 6.2$ Hz), 13.05; MS *m/z* (relative intensity) 426(M + 2, 25), 347(15), 219(76), 163(80), 81(100); Anal. Calc. for $C_{16}H_{25}O_3PTe$: C, 45.33; H, 5.94. Found: C44.91; H, 5.80%. IR (film, cm^{-1}): 3064, 2956, 2870, 1559, 1433, 1391, 1292, 1231, 1163, 1027, 965, 848, 797, 737, 696.

3.3. Preparation of phosphono-1,3-dienyl compounds **2a–h**: general procedure

To a solution of $PdCl_2$ (15 mol.%, 13.3 mg, 0.075 mmol), AcOAg (334 mg, 2 mmol), Et_3N (202 mg, 2 mmol) in MeOH (5 ml) at 25 °C, β-phenyltelluro vinylphosphono **1** (0.5 mmol) and the appropriate alkene (2 mmol) were added. The reaction mixture was stirred for 24 h. Then, the mixture was filtered through a pad of celite. The filtrate was poured into a saturated aqueous solution of NH_4Cl (5 ml) and the aqueous layer was extracted with ethyl acetate (3 × 20 ml). The organic layer was dried over $MgSO_4$, filtered and the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel using as eluent a mixture of hexane and ethyl acetate (7:3) to afford the products **2**.

3.3.1. Compound **2a**: oil

^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 8.04$ (d, 1H, $J =$ 16.1 Hz); 7.36–7.13 (m, 10H); 6.47 (d, 1H, $J = 16.1$ Hz); 5.49 (d, 1H, $J_{P-H} = 15.8$ Hz); 4.16–3.98 (m, 4H); 1.17 (t, 6H, $J = 7.8$ Hz). ^{13}C-NMR (50 MHz, $CDCl_3$) $\delta =$ 158.66 (d, $J_{P-C} = 6.5$ Hz); 140.24 (d, $J_{P-C} = 22.1$ Hz); 138.57; 136.08; 132.33; 128.91; 128.44; 128.34; 127.65; 126.89; 125.99 (d, $J_{P-C} = 8.2$ Hz); 115.27 (d, $J_{P-C} =$ 182.8 Hz); 61.43 (d, $J_{P-C} = 5.5$ Hz); 16.13 (d, $J_{P-C} =$ 14.5 Hz). HRMS Calc. for $C_{20}H_{23}O_3P$: [M + Na] 365.1282; [M + Na] Found: 365.1268. IR (Film; cm^{-1}): 3065, 3018, 2984, 2927, 2908, 2188, 1617, 1574, 1555, 1493, 1445, 1388, 1245, 1154, 1016, 954, 826, 745, 692.

3.3.2. Compound **2b**: oil

^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 8.41$ (d, 1H, $J =$ 16.3 Hz); 7.31–7.17 (m, 5H); 5.97 (d, 1H, $J = 16.3$ Hz); 5.83 (d, 1H, $J_{P-H} = 14.5$ Hz); 4.17–4.02 (m, 4H); 2.3 (s, 3H); 1.29 (t, 6H, 7.1 Hz). ^{13}C-NMR (50 MHz, $CDCl_3$) $\delta = 198.90$; 156.18 (d, $J_{P-C} = 5.7$ Hz); 139.68 (d, $J_{P-C} =$ 8.3 Hz); 138.56 (d, $J_{P-C} = 21.3$ Hz); 135.68; 128.84; 128.33; 128.04; 122.54 (d, $J_{P-C} = 181.5$ Hz); 61.83 (d, $J_{P-C} = 5.6$ Hz); 26.55; 16.18 (d, $J_{P-C} = 6.2$ Hz); HRMS Calc. for $C_{16}H_{21}O_4P$ [M + Na] 331.1075; [M + Na] Found: 331.1066. IR (Film; cm^{-1}): 2951, 2918, 2856, 1669, 1450, 1245, 1054, 1021, 964.

3.3.3. Compound **2c**: oil

^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 7.84$ (d, 1H, $J =$ 16.2 Hz); 7.39 (d, 2H, $J = 7.1$ Hz); 7.24–7.10 (m, 3 H);

6.73 (d, 1H, $J = 16.2$ Hz); 5.38 (d, 1H, $J_{P-H} = 15.9$ Hz); 4.05–3.89 (m, 4H); 2.35 (t, 2H, $J = 7.1$ Hz); 1.52–1.15 (m, 4H); 1.20 (t, 6H, $J = 7.0$ Hz); 0.82 (t, 3H, $J = 7.1$ Hz). ^{13}C-NMR (50 MHz, $CDCl_3$) $\delta = 157.76$ (d, $J_{P-C} = 4.9$ Hz); 136.06; 133.22; 128.15; 128.01; 126.75; 125.38 (d, $J_{P-C} = 9.1$ Hz); 113.45 (d, $J_{P-C} = 184.3$ Hz); 60.83 (d, $J_{P-C} = 5.3$ Hz); 33.86 (d, $J_{P-C} = 20.8$ Hz); 30.51; 22.01; 15.86 (d, $J_{P-C} = 6.3$ Hz), 13.38. HRMS Calc. for $C_{18}H_{27}O_3P$: [M+Na] 345.1595; [M+Na] Found: 345.1585. IR (Film, cm^{-1}): 3056, 3022, 2979, 2956, 2922, 2875, 1631, 1583, 1450, 1388, 1240, 1159, 1021, 950, 749, 688.

*3.3.4. Compound **2d**: oil*

^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 8.24$ (d, 1H, $J = 16.5$ Hz); 6.22 (d, 1H, $J = 16.5$ Hz); 5.71 (d, 1H, $J_{P-H} = 14.5$ Hz); 4.1–3.96 (m, 4H); 2.35–2.28 (m, 5H); 1.42–1.23 (m, 10H); 0.84 (t, 3H, 6.9 Hz). ^{13}C-NMR (50 MHz, $CDCl_3$) $\delta = 198.86$; 155.65 (d, $J_{P-C} = 4.1$ Hz); 139.41 (d, $J_{P-C} = 8.9$ Hz); 139.04; 131.44; 129.31; 120.50 (d, $J_{P-C} = 182.8$ Hz); 119.01; 61.26 (d, $J_{P-C} = 5.5$ Hz); 33.75 (d, $J_{P-C} = 19.9$ Hz); 30.08, 25.85; 21.90; 15.85 (d, $J_{P-C} = 6.1$ Hz); 13.26. HRMS Calc. for $C_{14}H_{25}O_4P$ (M = Na): 311.1388; [M+Na] Found: 311.1376. IR (Film; cm^{-1}): 2956, 2927, 2865, 1674, 1569, 1459, 1359, 1231, 1016, 954, 830, 778.

*3.3.5. Compound **2e**: m.p. 101–102 °C*

^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 7.83$ (d, 1H, $J = 13.6$ Hz); 7.79 (d, 1H, $J = 13.6$ Hz); 7.63–7.01 (m, 20H); 6.85 (d, 1H, $J_{P-H} = 47.2$ Hz). ^{13}C-NMR (50 MHz, $CDCl_3$) $\delta = 161.74$ (d, $J_{P-C} = 3.0$ Hz); 141.52 (d, $J_{P-C} = 5.2$ Hz); 133.81 (d, $J_{P-C} = 146.9$ Hz); 130.88; 130.75; 130.66; 130.55; 128.61; 128.40; 128.35; 128.28; 128.06; 120.36 (d, $J_{P-C} = 102.7$ Hz); 105.27 (d, $J_{P-C} = 28.8$ Hz). HRMS Calc. for $C_{28}H_{23}OP$ [M+Na]: 429.1384; [M+Na] Found: 429.1378. IR (KBr; cm^{-1}): 3053, 3023, 2919, 2849, 2177, 1560, 1490, 1440, 1345, 1176, 1116, 828, 748, 723, 703, 529.

*3.3.6. Compound **2f**: m.p. 95–96 °C*

^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 7.93$–7.38 (m, 4H); 7.59–7.31 (m, 11H), 7.22 (d, 1H, 7.6 Hz); 7.09 (d, 1H, 7.6 Hz); 6.79 (d, 1H, $J_{P-H} = 18.4$ Hz), 2.03 (s, 3H). ^{13}C-NMR (50 MHz, $CDCl_3$) $\delta = 198.9$; 165.30 (d, $J_{P-C} = 2.7$ Hz); 141.12 (d, $J_{P-C} = 9.1$ Hz); 133.87 (d, $J_{P-C} = 105.6$ Hz); 132.00; 131.89 (d, $J_{P-C} = 9.9$ Hz); 131.77; 130.53; 130.42; 130.26; 129.79; 129.02; 128.43 (d, $J_{P-C} = 5.8$ Hz); 32.41. HRMS Calc. for $C_{24}H_{21}O_2P$ [M+Na]: 395.1176; [M+Na] Found: 395.1227. IR (KBr; cm^{-1}): 3083, 3063, 3023, 2182, 1719, 1589, 1485, 1440, 1206, 1126, 852, 748, 718, 683, 643, 554, 514.

*3.3.7. Compound **2g**: m.p. 114–115 °C*

^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 7.99$ (d, 1H, $J = 16.2$ Hz); 7.82–7.70 (m, 4H); 7.50–7.21 (m, 11H); 6.82 (d, 1H, $J = 16.2$ Hz); 5.97 (d, 1H, $J_{P-H} = 23.1$ Hz); 2.56 (t, 2H, $J = 7.0$ Hz); 1.61 (m, 2H, $J = 7.1$ Hz); 1.42 (m, 2H, $J = 7.3$ Hz); 0.95 (t, 3H, $J = 7.1$ Hz). ^{13}C-NMR (50 MHz, $CDCl_3$) $\delta = 159.14$; 135.90; 135.03 (d, $J_{P-C} = 139.3$ Hz); 133.82; 131.35 (d, $J_{P-C} = 2.6$ Hz); 130.93 (d, $J_{P-C} = 9.7$ Hz); 128.49 (d, $J_{P-C} = 12$ Hz); 128.46; 128.37; 127.29; 126.12 (d, $J_{P-C} = 9.5$ Hz); 118.46 (d, $J_{P-C} = 101.2$ Hz); 34.79 (d, $J_{P-C} = 15.1$ Hz); 31.21; 22.63; 13.87. HRMS Calc. for $C_{26}H_{27}OP$: [M+Na] 409.1697; [M+Na] Found: 409.1687. IR (KBr, cm^{-1}): 3048, 2954, 2924, 2889, 2859, 1634, 1555, 1440, 1171, 1116, 962, 887, 823, 748.

*3.3.8. Compound **2h**: m.p. 80–81 °C*

^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 8.46$ (d, 1H, $J = 16.5$ Hz); 7.64 (m, 4H); 7.32 (m, 6H); 6.2 (d, 1H, $J_{P-H} = 22.9$ Hz); 6.17 (d, 1H, $J = 16.5$ Hz); 2.37 (t, 2H, 7.0 Hz); 2.18 (s, 3H); 1.35 (m, 4H); 0.83 (t, 3H, 7.1 Hz). ^{13}C-NMR (50 MHz, $CDCl_3$) $\delta = 199.83$; 157.02; 140.23 (d, $J_{P-C} = 8.9$ Hz); 133.68 (d, $J_{P-C} = 105.0$ Hz); 131.91; 131.73; 130.83; 128.69; 125.70 (d, $J_{P-C} = 97.1$ Hz); 34.56 (d, $J_{P-C} = 14$ Hz); 30.62; 25.80; 22.32; 13.59. HRMS Calc. for $C_{22}H_{25}O_2P$ [M+Na]: 375.1489; [M+Na] Found: 375.1480. IR (KBr; cm^{-1}): 3060, 2956, 2927, 2851, 2188, 1707, 1669, 1555, 1431, 1255, 1174, 1112, 688.

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