

Supplementary Information.

Experimental preparations and spectroscopic and analytical data for the new compounds.

**Synthesis and derivatization of highly-functionalized  
 $\lambda^5$ -phospholes**

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## Experimental

**General Considerations** All reactions and manipulations were performed under an atmosphere of dry nitrogen by standard Schlenk techniques. Solvents were distilled over appropriate drying agents under dry nitrogen before use. The IR spectra were measured with Perkin-Elmer Paragon 1000 spectrophotometers. The C, H, and N analyses were performed on a Perkin-Elmer 240B elemental analyzer. NMR spectra were recorded on Bruker 300 and 400 MHz spectrometers. Coupling constants  $J$  are given in Hz. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, dd = doublet of doublets, q = quartet, hp = heptaplet, m = multiplet. Chemical shifts of the NMR spectra were referenced to internal SiMe<sub>4</sub> (<sup>1</sup>H and <sup>13</sup>C) or external H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P). The electronic absorption spectra were recorded in dichloromethane solution on a Perkin-Elmer Lambda 25 UV/Vis spectrometer. All reagents were obtained commercially and used without further purification.

Synthesis and characterization of the new compounds:

**Synthesis of Compound 2:** To a solution of (PPh<sub>2</sub>)<sub>2</sub>C=C=N*t*Bu (**1**) (40 mg, 0.08 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (12 mL) 11 μL of acrolein (0.16 mmol) were added. The resulting mixture was stirred for 30 min at room temperature. After this time, the color of the solution changed from colorless to yellow and the IR spectrum showed the disappearance of the ν(C=C=N) band of **1** (2002 cm<sup>-1</sup>). The solution was then concentrated to 2 mL and hexane (15 mL) added to obtain a yellow solid. Yield 38 mg (91%). IR (Nujol): ν(NH) 3396, ν(C=O) 1589 cm<sup>-1</sup>. <sup>31</sup>P{<sup>1</sup>H} NMR (121.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 32.1 (d, <sup>2</sup>J<sub>PP</sub> = 122 Hz, Ph<sub>2</sub>P=C), -33.4 ppm (d, <sup>2</sup>J<sub>PP</sub> = 122 Hz, PPh<sub>2</sub>); <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 9.14 (s, 1 H, CHO), 7.4–7.2 (20 H, Ph), 4.90 (s, 1 H, NH), 3.72 (dd, <sup>2</sup>J<sub>HP</sub> = 10 Hz, <sup>4</sup>J<sub>HP</sub> = 1 Hz, 2 H, CH<sub>2</sub>), 1.04 ppm (s, 9 H, *t*Bu); <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 176.2 (d, <sup>3</sup>J<sub>CP</sub> = 5 Hz, CHO), 169.2 (d, <sup>2</sup>J<sub>CP</sub> = 36 Hz, P<sub>2</sub>C–C), 94.8 (s, C-CHO), 54.3 (s, C(CH<sub>3</sub>)<sub>3</sub>), 49.6 (dd, <sup>1</sup>J<sub>CP</sub> = 106 Hz, <sup>1</sup>J<sub>CP</sub> = 16 Hz, P<sub>2</sub>C), 30.5 (s, C(CH<sub>3</sub>)<sub>3</sub>), 27.3 ppm (dd, <sup>1</sup>J<sub>CP</sub> = 55 Hz, <sup>3</sup>J<sub>CP</sub> = 5 Hz, CH<sub>2</sub>); elemental analysis calcd (%) for C<sub>33</sub>H<sub>33</sub>NOP<sub>2</sub>: C 75.98, H 6.38, N 2.69; found: C 75.21, H 6.30, N 2.48.

**Synthesis of Compound 3:** To a solution of **1** (50 mg, 0.10 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) acrylonitrile (66 μL, 1.00 mmol) was added and the mixture stirred for 2 d at room temperature, after what a yellow solution was formed. This was concentrated to 2 mL and hexane (10 mL) was added to obtain a yellow solid, which was washed with hexane (2 x 5 mL) and dried under vacuum. Yield 33 mg (64%). IR (Nujol): ν(NH) 3392, ν(CN) 2132 cm<sup>-1</sup>. <sup>31</sup>P{<sup>1</sup>H} NMR (121.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 32.1 (d, <sup>2</sup>J<sub>PP</sub> = 147 Hz, Ph<sub>2</sub>P=C), -34.1 ppm (d, <sup>2</sup>J<sub>PP</sub> = 147 Hz, PPh<sub>2</sub>); <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 7.8–7.2 (20 H, Ph), 4.63 (s, 1 H, NH), 3.63 (dd, <sup>2</sup>J<sub>HP</sub> = 11 Hz, <sup>4</sup>J<sub>HP</sub> = 2 Hz, 2 H, CH<sub>2</sub>), 1.05 ppm (s, 9 H, *t*Bu); <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 163.9 (d, <sup>2</sup>J<sub>CP</sub> = 36 Hz, P<sub>2</sub>C–C), 130.0 (s, CN), 53.0 (s, C(CH<sub>3</sub>)<sub>3</sub>), 47.0 (dd, <sup>2</sup>J<sub>CP</sub> = 7 Hz, <sup>3</sup>J<sub>CP</sub> = 3 Hz, C–CN), 38.2 (dd, <sup>1</sup>J<sub>CP</sub> = 111 Hz, <sup>1</sup>J<sub>CP</sub> = 14 Hz, P<sub>2</sub>C), 31.8 (dd, <sup>1</sup>J<sub>CP</sub> = 55 Hz, <sup>3</sup>J<sub>CP</sub> = 6 Hz, CH<sub>2</sub>), 31.0 ppm (s, C(CH<sub>3</sub>)<sub>3</sub>); elemental analysis calcd (%) for C<sub>33</sub>H<sub>32</sub>N<sub>2</sub>P<sub>2</sub>: C 76.42, H 6.22, N 5.40; found: C 76.12, H 6.21, N 5.11.

**Synthesis of Compound 4:** A solution containing compound **1** (40 mg, 0.08 mmol) and dimethyl maleate (30 μL, 0.24 mmol) in toluene (10 mL) was heated at the refluxing temperature for 8 h. The solvent was then evaporated to dryness under vacuum, and the residue dissolved in 2 mL of CH<sub>2</sub>Cl<sub>2</sub>. Addition of hexane (15 mL) causes the formation of a white precipitate of the compound. Crystals suitable for X-ray crystallography were obtained by crystallization from THF/hexane. Yield 38 mg (78%). In solution, compound **4** appears as a mixture of two isomers in a *ca.* 1:3 ratio, featuring almost identical spectroscopic data, with slight differences in the chemical shift of the P2 phosphorus atom (major isomer 33.9 ppm, <sup>2</sup>J<sub>PP</sub> = 114 Hz; minor isomer 36.4 ppm, <sup>2</sup>J<sub>PP</sub> = 115 Hz) and in the methyl signal of the carboxylate group bonded to C4 (major isomer 3.26 ppm, minor isomer 3.52 ppm). This can be tentatively explained by the existence of two conformers of **4** arising from the absence of free rotation around the C4-C10 bond, which is in agreement with its rather short bond length (1.429(4) Å). In fact, the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum at 90° C showed just two doublets, which indicates quick interconversion of both conformers at that temperature. <sup>31</sup>P{<sup>1</sup>H} NMR (121.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>): Major isomer (75%), δ = 33.9 (d, <sup>2</sup>J<sub>PP</sub> = 114 Hz, Ph<sub>2</sub>P=C), -36.6 ppm (d, <sup>2</sup>J<sub>PP</sub> = 114 Hz, PPh<sub>2</sub>), minor isomer (25%), δ = 36.4 (d, <sup>2</sup>J<sub>PP</sub> = 115 Hz,

Ph<sub>2</sub>P=C), -36.9 ppm (d, <sup>2</sup>J<sub>PP</sub> = 115 Hz, PPh<sub>2</sub>); <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>): Major isomer (75%): δ = 8.0–6.9 (20 H, Ph), 5.16 (s, 1 H, NH), 4.89 (d, <sup>3</sup>J<sub>HP</sub> = 14 Hz, 1 H, CH), 3.62 (s, 3 H, CH<sub>3</sub>O), 3.26 (s, 3 H, CH<sub>3</sub>O), 0.88 ppm (s, 9 H, *t*Bu), minor isomer (25%): δ = 8.0–6.9 (20 H, Ph), 5.16 (s, 1 H, NH), 4.89 (d, <sup>3</sup>J<sub>HP</sub> = 14 Hz, 1 H, CH), 3.64 (s, 3 H, CH<sub>3</sub>O), 3.52 (s, 3 H, CH<sub>3</sub>O), 0.88 ppm (s, 9 H, *t*Bu); <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>): Major isomer (75%), δ = 169.8 (dd, <sup>2</sup>J<sub>CP</sub> = 32 Hz, <sup>2</sup>J<sub>CP</sub> = 4 Hz, P<sub>2</sub>C–C), 172.8 (s, CO<sub>2</sub>CH<sub>3</sub>), 166.9 (s, CO<sub>2</sub>CH<sub>3</sub>), 79.3 (dd, <sup>1</sup>J<sub>CP</sub> = 104 Hz, <sup>1</sup>J<sub>CP</sub> = 28 Hz, P<sub>2</sub>C), 54.4 (s, C(CH<sub>3</sub>)<sub>3</sub>), 53.5 (d, <sup>2</sup>J<sub>CP</sub> = 15 Hz, CH–CO<sub>2</sub>CH<sub>3</sub>), 52.3 (s, OCH<sub>3</sub>), 49.4 (s, OCH<sub>3</sub>), 42.0 (d, <sup>1</sup>J<sub>CP</sub> = 120 Hz, C–CO<sub>2</sub>CH<sub>3</sub>), 30.7 ppm (s, C(CH<sub>3</sub>)<sub>3</sub>), minor isomer (25%), δ = 169.8 (dd, <sup>2</sup>J<sub>CP</sub> = 32 Hz, <sup>2</sup>J<sub>CP</sub> = 4 Hz, P<sub>2</sub>C–C), 172.8 (s, CO<sub>2</sub>CH<sub>3</sub>), 167.5 (s, CO<sub>2</sub>CH<sub>3</sub>), 79.3 (dd, <sup>1</sup>J<sub>CP</sub> = 104 Hz, <sup>1</sup>J<sub>CP</sub> = 28 Hz, P<sub>2</sub>C), 54.4 (s, C(CH<sub>3</sub>)<sub>3</sub>), 53.5 (d, <sup>2</sup>J<sub>CP</sub> = 15 Hz, CH–CO<sub>2</sub>CH<sub>3</sub>), 52.3 (s, OCH<sub>3</sub>), 50.0 (s, OCH<sub>3</sub>), 42.0 (d, <sup>1</sup>J<sub>CP</sub> = 120 Hz, C–CO<sub>2</sub>CH<sub>3</sub>), 30.7 ppm (s, C(CH<sub>3</sub>)<sub>3</sub>); elemental analysis calcd (%) for C<sub>36</sub>H<sub>37</sub>NO<sub>4</sub>P<sub>2</sub>: C 70.91, H 6.12, N 2.30; found: C 70.40, H 5.99, N 2.25.

**Synthesis of Compound 5:** A solution of compound **2** (35 mg, 0.07 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was treated with methyl propiolate (8 μL, 0.09 mmol) and the resulting solution stirred at room temperature for 1.5 h. The solution was then concentrated to 2 mL and hexane (15 mL) added forming a yellow precipitate, which was filtered and dried under vacuum. Crystals suitable for X-ray crystallography were obtained by crystallization from THF/hexane. Yield 37 mg (87%). <sup>31</sup>P{<sup>1</sup>H} NMR (121.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 33.5 (d, <sup>2</sup>J<sub>PP</sub> = 36 Hz, Ph<sub>2</sub>P=C), -17.2 ppm (d, <sup>2</sup>J<sub>PP</sub> = 36 Hz, PPh<sub>2</sub>); <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 9.06 (s, 1 H, CHO), 7.88 (d, <sup>3</sup>J<sub>HH</sub> = 13 Hz, 1 H, *t*BuN–CH=), 7.7–6.9 (20 H, Ph), 4.86 (d, <sup>3</sup>J<sub>HH</sub> = 13 Hz, 1 H, =CHCO<sub>2</sub>Me), 3.63 (s, 3 H, CH<sub>3</sub>O), 3.61 (m, 2 H, CH<sub>2</sub>), 1.58 ppm (s, 9 H, *t*Bu); <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 180.5 (d, <sup>3</sup>J<sub>CP</sub> = 12 Hz, CHO), 173.2 (dd, <sup>2</sup>J<sub>CP</sub> = 34 Hz, <sup>2</sup>J<sub>CP</sub> = 40 Hz, P<sub>2</sub>C–C), 170.0 (s, CO<sub>2</sub>CH<sub>3</sub>), 148.7 (s, *t*BuN–CH=), 107.9 (s, C–CHO), 90.6 (s, =CHCO<sub>2</sub>Me), 66.3 (dd, <sup>1</sup>J<sub>CP</sub> = 62 Hz, <sup>1</sup>J<sub>CP</sub> = 25 Hz, P<sub>2</sub>C), 59.8 (s, C(CH<sub>3</sub>)<sub>3</sub>), 50.9 (s, OCH<sub>3</sub>), 30.5 ppm (s, C(CH<sub>3</sub>)<sub>3</sub>), 29.2 (d, <sup>1</sup>J<sub>CP</sub> = 55 Hz, CH<sub>2</sub>); elemental analysis calcd (%) for C<sub>37</sub>H<sub>37</sub>NO<sub>3</sub>P<sub>2</sub>: C 73.36, H 6.16, N 2.31; found: C 73.40, H 6.01, N 2.41.

**Synthesis of Compound 6:** To a solution of **2** (32 mg, 0.06 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) methyl iodide (7 μL, 0.12 mmol) was added and the resulting mixture stirred for 8 h at room temperature, giving a yellow solution. This was concentrated to 2 mL and hexane (15 mL) added to obtain a yellow solid, which was washed with hexane (2 x 10 mL) and dried under vacuum. Yield 24 mg (64%). <sup>31</sup>P{<sup>1</sup>H} NMR (121.4 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 31.7 (d, <sup>2</sup>J<sub>PP</sub> = 44 Hz, Ph<sub>2</sub>P=C), 10.3 ppm (d, <sup>2</sup>J<sub>PP</sub> = 44 Hz, Ph<sub>2</sub>P–Me); <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 9.30 (s, 1 H, CHO), 7.9–7.4 (20 H, Ph), 4.37 (s, 1 H, NH), 3.76 (d, <sup>2</sup>J<sub>HP</sub> = 10 Hz, 2 H, CH<sub>2</sub>), 2.42 (d, <sup>2</sup>J<sub>HP</sub> = 13 Hz, 3 H, CH<sub>3</sub>), 1.10 ppm (s, 9 H, *t*Bu); <sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 180.8 (d, <sup>3</sup>J<sub>CP</sub> = 11 Hz, CHO), 164.6 (d, <sup>2</sup>J<sub>CP</sub> = 27 Hz, P<sub>2</sub>C–C), 97.2 (d, <sup>2</sup>J<sub>CP</sub> = 8 Hz, C–CHO), 55.9 (s, C(CH<sub>3</sub>)<sub>3</sub>), 34.2 (t, <sup>1</sup>J<sub>CP</sub> = 111 Hz, P<sub>2</sub>C), 31.4 (dd, <sup>1</sup>J<sub>CP</sub> = 57 Hz, <sup>3</sup>J<sub>CP</sub> = 5 Hz, CH<sub>2</sub>), 30.5 ppm (s, C(CH<sub>3</sub>)<sub>3</sub>); elemental analysis calcd (%) for C<sub>34</sub>H<sub>36</sub>INO<sub>2</sub>P<sub>2</sub>: C 61.53, H 5.47, N 2.11; found: C 61.37, H 5.32, N 2.21.

**Synthesis of Compound 7:** To a solution of compound **2** (50 mg, 0.096 mmol) in THF (10 mL) was added [Ru(*p*-cym)Cl<sub>2</sub>]<sub>2</sub> (59 mg, 0.096 mmol) and the resulting mixture stirred for 1 h at room temperature. An orange precipitate appeared that was filtered, washed with hexane (2 x 5 mL) and dried under vacuum. Crystals for X-ray diffraction study were obtained by slow diffusion of hexane into a dichloroethane solution of the compound. Yield (92 mg, 85%). IR (Nujol): ν(NH) 3266, ν(C=O) 1549 cm<sup>-1</sup>. <sup>31</sup>P{<sup>1</sup>H} NMR (162.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -80° C): δ = 26.9 (d, <sup>2</sup>J<sub>PP</sub> = 10 Hz, Ph<sub>2</sub>P=C), 22.0 ppm (d, <sup>2</sup>J<sub>PP</sub> = 10 Hz, PPh<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -80° C): δ = 8.1–7.1 (19 H, Ph, CHO), 6.39 (s, 1 H, Ph), 6.17 (s, 1 H, Ph), 5.78 (s, 1 H, NH), 5.63, 5.50, 5.46, 5.31, 5.23, 5.21 (d, <sup>3</sup>J<sub>HH</sub> = 6 Hz, 6 H, *p*-cym), 4.54 (d, <sup>3</sup>J<sub>HH</sub> = 4 Hz, 1 H, *p*-cym), 4.31 (dd, <sup>2</sup>J<sub>HH</sub> = 16 Hz, <sup>2</sup>J<sub>HP</sub> = 9 Hz, 1 H, CH<sub>2</sub>), 3.63 (d, <sup>3</sup>J<sub>HH</sub> = 4 Hz, 1 H, *p*-cym), 3.13 (dd, <sup>2</sup>J<sub>HH</sub> = 16 Hz, <sup>2</sup>J<sub>HP</sub> = 10 Hz, 1 H, CH<sub>2</sub>), 3.03 (hp, <sup>3</sup>J<sub>HH</sub> = 6 Hz, 1 H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.35 (hp, <sup>3</sup>J<sub>HH</sub> = 6 Hz, 1 H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.19 (s, 3 H, CH<sub>3</sub>), 1.90 (s, 3 H, CH<sub>3</sub>), 1.33 (d, <sup>3</sup>J<sub>HH</sub> = 6 Hz, 3 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.27 (d, <sup>3</sup>J<sub>HH</sub> = 6 Hz, 6 H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.19 (s, 9 H, *t*Bu), 1.01 ppm (d, <sup>3</sup>J<sub>HH</sub> = 6 Hz, 3 H, CH(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -80° C): δ = 174.4 (dd, <sup>2</sup>J<sub>CP</sub> = 30 Hz, <sup>2</sup>J<sub>CP</sub> = 7 Hz, P<sub>2</sub>C–C), 171.6 (d, <sup>3</sup>J<sub>CP</sub> = 9 Hz, CHO), 104.6, 100.1, 98.6, 96.2 (s, C<sub>ipso</sub> *p*-cym), 99.6 (d, <sup>2</sup>J<sub>CP</sub> = 6 Hz, C–CHO), 91.7 (br, CH *p*-cym), 86.9, 82.1, 81.6, 80.4, 79.2, 78.0 (s, CH *p*-cym), 62.5 (dd, <sup>1</sup>J<sub>CP</sub> = 98 Hz, <sup>1</sup>J<sub>CP</sub> = 45 Hz, P<sub>2</sub>C), 59.1 (s,

C(CH<sub>3</sub>)<sub>3</sub>), 31.7 (s, C(CH<sub>3</sub>)<sub>3</sub>), 31.2, 30.4 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 31.0 (d, <sup>1</sup>J<sub>CP</sub> = 53 Hz, CH<sub>2</sub>), 25.2, 22.5, 22.1, 20.3 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 19.1, 18.5 ppm (s, CH<sub>3</sub>); elemental analysis calcd (%) for C<sub>53</sub>H<sub>61</sub>Cl<sub>4</sub>NOP<sub>2</sub>Ru<sub>2</sub>: C 56.14, H 5.42, N 1.24; found: C 55.97, H 5.22, N 1.12.

**X-ray Crystallography.** Single crystals of compounds, [4]·C<sub>4</sub>H<sub>8</sub>O and 2[5]·C<sub>4</sub>H<sub>8</sub>O were studied at 293(1) K using a KAPPACCD diffractometer equipped with a graphite monochromated Cu Kα radiation (*l* = 1.5418 Å) while [7]·C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> was studied at 120(1) K using an Agilent XCALIBUR GEMINI diffractometer equipped with a graphite monochromated Mo Kα radiation (*λ* = 0.7107 Å). Preliminary RT data collection of compound 7 lead to sets of poor quality, but good enough for structure solution. New data collections at 120 K partially avoid the crystal deterioration, but the improvement was limited. These refinement troubles are due to the presence of solvent molecules, affecting to one of the two molecules of 7, in particular to the 4-isopropyltoluene group and one 1,2-dichloroethane molecule. Still some diffuse isolated electron density was removed by applying SQUEEZE,<sup>1</sup> as it could not be modeled to any reasonable structural model. As one of the two molecules of 7 present in the Asymmetric Unit is accurately determined, further structural discussions along the paper will refer to this particular molecule. Details of data collection, solution and refinement are shown in Table 1. Multi-scan absorption correction procedures were applied to all the data. The structures were solved, using the WINGX package,<sup>2</sup> by Patterson methods (DIRDIF2008<sup>3</sup>) and refined by using full-matrix least-squared against *F*<sup>2</sup> (SHELXL-97).<sup>4</sup> All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were geometrically placed and left riding on their parent atoms. Full-matrix least-squares refinements were carried out by minimizing *Sw*(*F*<sub>o</sub><sup>2</sup> – *F*<sub>c</sub><sup>2</sup>)<sup>2</sup> with the SHELXL-97 weighting scheme. CCDC 929248 (4), 929250 (5) and 929251 (7) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

Table 1. Crystallographic data for compounds [4]·C<sub>4</sub>H<sub>8</sub>O, 2[5]·C<sub>4</sub>H<sub>8</sub>O and [7]·C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>.

	[4]·C <sub>4</sub> H <sub>8</sub> O	2[5]·C <sub>4</sub> H <sub>8</sub> O	[7]·C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>
formula	C <sub>40</sub> H <sub>45</sub> NO <sub>5</sub> P <sub>2</sub>	C <sub>78</sub> H <sub>82</sub> N <sub>2</sub> O <sub>7</sub> P <sub>4</sub>	C <sub>55</sub> H <sub>65</sub> Cl <sub>6</sub> NOP <sub>2</sub> Ru <sub>2</sub>
FW	681.71	1283.34	1232.86
crystal size/mm	0.15 x 0.15 x 0.05	0.20 x 0.10 x 0.05	0.19 x 0.12 x 0.02
Wavelength/Å	1.5418	1.5418	0.7107
crystal system	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 21/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> /Å	17.454(1)	43.02(1)	61.933(2)
<i>b</i> /Å	11.108(5)	11.494(4)	17.1300(4)
<i>c</i> /Å	20.214(9)	34.049(7)	21.7555(7)
<i>α</i> /deg	90	90	90
<i>β</i> /deg	114.518(3)	122.46(1)	94.674(3)
<i>γ</i> /deg	90	90	90
<i>V</i> /Å <sup>3</sup>	3565.7(3)	14205(7)	23003.8(12)
<i>Z</i>	4	8	16
<i>T</i> /K	293(1)	293(1)	120(1)

$D_c/g\text{ cm}^{-3}$	1.270	1.200	1.424
$\mu/\text{mm}^{-1}$	1.467	1.411	0.897
$F(000)$	1448	5440	10080
$\theta$ range/deg	3.74 –69.48	4.08 – 68.65	3.18-31.07
rlns collected	6789	8340	104618
indep rlns/ $R_{\text{int}}$	6644/0.0409	8340/0.0805	34076/0.126
rlns observed ( $>2\sigma$ )	4547	3148	17273
Data/restraints/params	6644/0/545	8340/0/826	34076/0/1207
R1/wR2 ( $I > 2\sigma(I)$ )	0.057/0.157	0.063/0.133	0.113/0.226
R1/wR2 (all data)	0.088/0.199	0.199/0.165	0.208/0.274
GOF on $F^2$	1.112	1.039	1.045
Largest diff peak/hole ( $e\text{ \AA}^{-3}$ )	0.49, -0.55	0.18, -0.19	1.74, -2.70

## References

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## UV/Vis spectroscopic characterization.

**Table 1.** Electronic absorption spectra of compounds **2-6** in CH<sub>2</sub>Cl<sub>2</sub>.

Compound	$\lambda_{\max}$ (nm) (log $\epsilon$ )
<b>2</b>	260 (4.19), 352 (4.15)
<b>3</b>	275 (4.24), 322 (sh, 4.10)
<b>4</b>	260 (4.20)
<b>5</b>	268 (4.42), 397 (4.25)
<b>6</b>	345 (4.01)

## UV/Vis Absorption Spectra



