Palladium-Catalyzed Hydroarylation of Diazocarboxylates and Diazophosphonates

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Abstract
A simple synthetic procedure for the Pd-catalyzed hydroarylation of diazoacetic ester has been previously developed in our laboratory. Now we have applied this methodology for hydroarylation of \(-\)diazocarboxylates/\(-\)diazophosphonates. Diazocarboxylate reacted with aryl iodides and formic acid to afford diarylated esters or phosphonates in yields up to 71%.

Key words hydroarylation, diazo compounds, arylacetates, palladium catalysis, cross coupling, phosphonates

The transition-metal-catalyzed transformation of \(-\)diazocarbonyl compounds has become a standard method in organic synthesis. The approach has traditionally been used for carbene generation in reactions such as \(X-H\) insertion (\(X = C, N, O, S\)), cyclopropanation, and cycloaddition to nitriles and carbonyl compounds.\(^1\) More recently, the scope of their application was widened significantly to include Pd-catalyzed cross-coupling reactions, mostly due to the important contributions made by J. Wang and co-workers.\(^2\)

Depending on the reaction conditions, two types of cross-coupling reactions can be carried out: (i) with retention of diazo group leading to formation of aryl-substituted diazo compound;\(^3\) (ii) with the loss of diazo function (Scheme 1).\(^4\)

In the latter case, a organopalladium intermediate that is generated can be captured with a nucleophile.\(^4-6\) The hydride ion generated from formic acid is a suitable nucleophile for this type reaction. Our research group has elaborated Pd-catalyzed three-component hydroarylation coupling: aryl iodides reacted with \(-\)diazocarboxylates/\(-\)diazophosphonates and formic acid to generate mono- or diarylacetates and diarylphosphonates.

Recently, J. Wang and co-workers have reported Pd-catalyzed reductive coupling of ethyl diazoacetate (EDA) with aryl iodides leading to the formation of \(\alpha,\alpha\)-diarylacetates. Although their methodology provides high yield and wide scope of products, it requires a stoichiometric amount of silver carbonate.\(^7\)

The coupling of aryl iodides with EDA in the presence of formic acid and Et\(_3\)N was investigated previously by our research team (Scheme 2).\(^8\)

A number of aryl iodides were subjected to three-component hydroarylation under the optimized reaction conditions. Exploration of substrates containing electron-withdrawing groups (EWG) as well as iodobenzene allowed a range of ethyl arylacetates 2 to be synthesized in respectable yields (50–85%).

In this context, we have been interested in continuing our previous studies in an attempt to extend our method to a wider range of substrates. Herein we report a solution to this issue.
The coupling of methyl 4-iodobenzoate (1a) with phenyl diazoacetate (3a) in the presence of formic acid and Et₃N was investigated as a model reaction for the preparation of diarylated products (Table 1).

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<tr>
<th>Entry</th>
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<th>Yield (%)</th>
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<td>Et₃N</td>
<td>MeCN</td>
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<td>2</td>
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<td>MeCN</td>
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<td>3</td>
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<td>Et₃N</td>
<td>MeCN</td>
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<td>4</td>
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<td>42</td>
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<td>5</td>
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<td>Et₃N</td>
<td>1,2-DCE</td>
<td>60</td>
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<tr>
<td>6</td>
<td>PdCl₂(PPh₃)₂</td>
<td>Et₃N</td>
<td>benzene</td>
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<td>Et₃N</td>
<td>CHCl₃</td>
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<td>55</td>
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</table>

Optimization of Reaction Conditions in the Model Reaction

Table 1

The phosphonate (PO₃²⁻) moiety is a common structural fragment that is present in a wide range of biologically active compounds. Despite structural and electronic differences between phosphonate and carboxylic functionalities (in terms of size, shape, acidity, and geometry) the...
phosphonates followed by liberation of carbon dioxide (complex produced by substitution of halogen with formate anion described in several publications,13,14 would produce benzylic intermediate, which is now to this complex could generate carbene complex.

We also applied the above procedure for the synthesis of diarylmethylphosphonates 6a–e (Table 3). Diazophosphonates 5 exhibited comparable reactivity under analogous reaction conditions yielding the corresponding \( \alpha,\alpha \)-diarylphosphonates 6a–e in good yield.

Table 3 Hydroarylation of Diazophosphonates 5 with Aryl Iodides 1a

<table>
<thead>
<tr>
<th>Entry</th>
<th>R1</th>
<th>R</th>
<th>Product</th>
<th>Yield (%) b</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>p-MeO</td>
<td>p-MeO</td>
<td>6a</td>
<td>66</td>
</tr>
<tr>
<td>2</td>
<td>H</td>
<td>O2N</td>
<td>6b</td>
<td>60</td>
</tr>
<tr>
<td>3</td>
<td>H</td>
<td>p-MeO</td>
<td>6c</td>
<td>54</td>
</tr>
<tr>
<td>4</td>
<td>H</td>
<td>p-NC</td>
<td>6d</td>
<td>63</td>
</tr>
<tr>
<td>5</td>
<td>H</td>
<td>p-Ac</td>
<td>6e</td>
<td>71</td>
</tr>
</tbody>
</table>

a Reaction conditions: 1 (0.5 mmol), 5 (0.5 mmol), Et3N (1.25 mmol), HCO2H (0.5 mmol), Pd(PPh3)2Cl2 (0.025 mmol), DCE, reflux for 4 h.
b Isolated yield.

The proposed mechanism of hydroarylation is presented in Scheme 3. Palladium dichloride complex can be easily reduced by formic acid resulting in Pd(0) species. The catalytic cycle starts with oxidative addition to form arylpalladium iodide complex A. Then addition of diazo compound to this complex could generate carbene complex B.12 Migration of the aryl group to the carbene center, which is now described in several publications,13,14 would produce benzylic intermediate C. The exchange complex D can be easily produced by substitution of halogen with formate anion followed by liberation of carbon dioxide (complex E). Retructive elimination should provide the product simultaneously with regeneration of the Pd(0) species.

In conclusion, this report describes a simple method for palladium-catalyzed hydroarylation of diazocarboxylates and diarylphosphonates in the presence of formic acid. The proposed reaction can serve as a pathway for the preparation of diarylated carboxylic acid and phosphonic acid derivatives that are otherwise difficult to access. A range of arylated products were synthesized in 35–71% yield by applying this methodology.

All solvents were distilled prior to use. Acetonitrile and 1,2-dichloroethane were dried by distillation over P2O5. Chromatography was carried out using 230–400 mesh silica gel (Merck 40/60).1H NMR spectra were recorded with a commercial Agilent 400-MR (400 MHz) instrument. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl3, δ = 7.26 ppm).13C{1H} NMR spectra were collected with commercial Agilent 400-MR (162 MHz and 376 MHz respectively) instrument. HRMS (ESI) were recorded with a commercial apparatus. Published procedures were applied for the synthesis of aryldiazocarboxylates (3)a and aryldiazophosphonates (5).10

Pd-Catalyzed Cross-Coupling between Aryl Iodides and Aryldiazoacetates; Typical Procedure A

To a mixture of aryl iodide (1a–h; 0.5 mmol), aryldiazoacetate (3a–d; 0.75 mmol), and PdCl2(PPh3)2 (18 mg, 0.025 mmol) in a Schlenk flask under argon atmosphere, Et3N (127 mg, 1.25 mmol) and formic acid (23 mg, 0.5 mmol) in DCE (3 mL) were added. The mixture was stirred and heated at 80 °C until 1a–h disappeared (2–4 h, monitoring by TLC). Solvent was evaporated under reduced pressure. Pure product 4 was isolated by column chromatography (EtOAc/petrol ether, 1:5 v/v).

Pd-Catalyzed Cross-Coupling between Aryl Iodides and Aryldiazophosphonates; Typical Procedure B

To a mixture of aryl iodide (1; 0.5 mmol), aryldiazophosphonate (5a–b; 0.5 mmol), and PdCl2(PPh3)2 (18 mg, 0.025 mmol) in a Schlenk flask under argon atmosphere, Et3N (127 mg, 1.25 mmol) and formic acid (23 mg, 0.5 mmol) in DCE (3 mL) were added. The mixture was stirred and heated at 80 °C for 3 h. Solvent was evaporated under reduced pressure. Pure product 6 was isolated by column chromatography (EtOAc/petrol ether, 1:1 v/v).

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**Characterization of Synthesized Products**

**Ethyl [4-(Methoxycarbonyl)phenyl](phenyl)acetate (4a)**
Prepared according to general procedure A from methyl 4-iodobenzonitrile and phenyldiazoacetate. Reaction time 2 h.
Yield: 104 mg (70%); colorless oil.

1H NMR (400 MHz, CDCl3): δ = 7.99 (d, J = 8.4 Hz, 2 H), 7.39 (d, J = 8.3 Hz, 2 H), 7.26–7.38 (m, 5 H), 5.05 (s, 1 H), 4.26 (q, J = 7.1 Hz, 2 H), 3.94 (s, 3 H), 1.30 (t, J = 7.1 Hz, 3 H).

13C NMR (100 MHz, CDCl3): δ = 171.9, 166.8, 143.8, 138.0, 129.8, 129.2, 128.7, 128.5, 127.5, 127.2, 61.4, 57.1, 52.1, 14.1.

IR (film): 2230, 1738, 1612 cm⁻¹.

NMR spectral data for this compound were consistent with those in the literature.⁷

**Ethyl [3-(Methoxycarbonyl)phenyl](phenyl)acetate (4b)**
Prepared according to general procedure A from methyl 3-iodobenzonitrile and phenyldiazoacetate. Reaction time 2.5 h.
Yield: 67 mg (45%); colorless oil.

1H NMR (400 MHz, CDCl3): δ = 8.02 (bs, 1 H), 7.95 (dt, Jf = 7.7 Hz, J = 1.3 Hz, 1 H), 7.53 (dt, Jf = 7.7 Hz, J = 1.9 Hz, 1 H), 7.43–7.25 (m, 6 H), 5.06 (s, 1 H), 4.22 (q, J = 7.1 Hz, 2 H), 3.90 (s, 3 H), 1.26 (t, J = 7.1 Hz, 3 H).

13C NMR (100 MHz, CDCl3): δ = 172.1, 166.8, 139.2, 138.3, 133.1, 130.5, 129.8, 128.9, 128.7, 128.5, 127.5, 126.4, 56.9, 52.1, 14.1.

IR (film): 1740, 1610, 1281 cm⁻¹.


**Ethyl (Pyridin-3-yl)(phenyl)acetate (4c)**
Prepared according to general procedure A from 3-iodopyridine and phenyldiazoacetate. Reaction time 2.5 h.
Yield: 64 mg (53%); colorless oil.

1H NMR (400 MHz, CDCl3): δ = 8.57 (d, J = 2.0 Hz, 1 H), 8.50 (dd, Jf = 4.7 Hz, J = 1.5 Hz, 1 H), 7.68 (dt, Jf = 1.7 Hz, J = 8.0 Hz, 1 H), 7.21–7.36 (m, 6 H), 5.01 (s, 1 H), 4.21 (q, J = 7.1 Hz, 2 H), 1.25 (t, J = 7.1 Hz, 3 H).

13C NMR (100 MHz, CDCl3): δ = 171.7, 149.9, 148.7, 137.8, 136.1, 134.6, 128.9, 128.4, 127.6, 123.4, 61.6, 54.6, 14.1.

IR (film): 1730, 1600 cm⁻¹.


**Ethyl (4-Nitrophenyl)(phenyl)acetate (4e)**
Prepared according to general procedure A from 4-iodo-1-nitrobenzene and phenyldiazoacetate. Reaction time 1.5 h.
Yield: 100 mg (71%); yellow oil.

1H NMR (400 MHz, CDCl3): δ = 8.17 (d, J = 8.8 Hz, 2 H), 7.49 (d, J = 8.8 Hz, 2 H), 7.39–7.28 (m, 5 H), 5.10 (s, 1 H), 4.24 (q, J = 7.1 Hz, 2 H), 1.27 (t, J = 7.1 Hz, 3 H).

13C NMR (100 MHz, CDCl3): δ = 171.4, 146.0, 137.4, 129.6, 129.0, 128.9, 128.5, 127.8, 123.7, 61.7, 56.8, 14.1.

IR (film): 1735, 1520, 1355 cm⁻¹.

Anal. Calcd for C19H19NO4: C, 67.36; H, 5.30; N, 4.91. Found: C, 67.49; H, 5.31; N, 4.86.

NMR spectral data for this compound were consistent with those in the literature.⁷

**Ethyl [4-(Trifluoromethyl)phenyl](phenyl)acetate (4f)**
Prepared according to general procedure A from 4-trifluoromethyl-1-iodobenzene and phenyldiazoacetate. Reaction time 3 h.
Yield: 85 mg (55%); colorless oil.

1H NMR (400 MHz, CDCl3): δ = 7.57 (d, J = 8.2 Hz, 2 H), 7.44 (d, J = 8.6 Hz, 2 H), 7.38–7.28 (m, 5 H), 5.05 (s, 1 H), 4.23 (d, J = 7.0 Hz, 2 H), 1.25 (t, J = 7.0 Hz, 3 H).

13C NMR (100 MHz, CDCl3): δ = 171.8, 142.7, 137.9, 129.0, 128.8 (q, Jc,F = 33.4 Hz), 128.5, 127.6, 125.5 (q, Jc,F = 3.8 Hz), 123.9 (q, Jc,F = 244 Hz, CF3), 61.5, 56.8, 14.1.

19F NMR (376 MHz, CDCl3): δ = 62.6.


**Ethyl (4-Acetylphenyl)(phenyl)acetate (4g)**
Prepared according to general procedure A from 4-iodoacetophenone and phenyldiazoacetate. Reaction time 2 h.
Yield: 98 mg (69%); colorless oil.

1H NMR (400 MHz, CDCl3): δ = 7.92 (d, J = 8.4 Hz, 2 H), 7.44 (d, J = 8.5 Hz, 2 H), 7.36–7.26 (m, 5 H), 5.08 (s, 1 H), 4.23 (d, J = 7.1 Hz, 2 H), 2.58 (s, 3 H), 1.27 (t, J = 7.1 Hz, 3 H).

13C NMR (100 MHz, CDCl3): δ = 197.6, 171.7, 143.9, 137.9, 135.9, 128.9, 128.7, 128.5, 128.4, 127.4, 61.4, 56.9, 26.5, 14.0.


NMR spectral data for this compound were consistent with those in the literature.¹⁶

**Ethyl (4-Nitrophenyl)[4-cyanophenyl]acetate (4i)**
Prepared according to general procedure A from 4-iodo-1-nitrobenzene and phenyldiazoacetate. Reaction time 2 h.
Yield: 57 mg (37%); colorless oil.

1H NMR (400 MHz, CDCl3): δ = 8.19 (d, J = 8.2 Hz, 2 H), 7.64 (d, J = 8.1 Hz, 2 H), 7.48 (d, J = 8.2 Hz, 2 H), 7.42 (d, J = 8.1 Hz, 2 H), 5.14 (s, 1 H), 4.24 (q, J = 7.1 Hz, 2 H), 1.26 (t, J = 7.1 Hz, 3 H).

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Anal. Calcd for C_{19}H_{17}NO_{4}: C, 70.58; H, 5.30; N, 4.33. Found: C, 70.41; H, 4.73; N, 8.93.

Ethyl [3-(Methoxy-carboxyloxy)phenyl][4-cyanophenyl]acetate (4j)
Prepared according to general procedure A from methyl 4-iodobenzonitrile and (4-cyanophenyl)diazoacetate. Reaction time 4 h.
Yield: 89 mg (64%); colorless oil.

1^{13}C\{1H\} NMR (100 MHz, CDCl_3): \delta = 171.2, 166.5, 142.9, 129.4, 128.9, 128.7, 127.4, 126.9 (d, J = 6.7 Hz), 62.9 (d, J = 6.5 Hz), 62.6 (d, J = 6.5 Hz), 52.2, 51.3 (d, J = 138.2 Hz), 16.2.

Diethyl (4-Cyanophenyl)(phenyl)methylphosphonate (6d)
Prepared according to general procedure B from methyl 4-iodobenzonitrile and diethyl 1-diazo-phenylmethylphosphonate.
Yield: 86 mg (63%); colorless oil.

1^{1}H NMR (400 MHz, CDCl_3): \delta = 7.65 (d, J = 8.3 Hz, 2 H), 7.60 (d, J = 8.3 Hz, 2 H), 7.49 (d, J = 8.2 Hz, 2 H), 7.37–7.30 (m, 2 H), 7.30–7.24 (m, 1 H), 4.48 (d, J = 25.1 Hz, 1 H), 4.06–3.76 (m, 4 H), 1.14 (t, J = 7.0 Hz, 3 H), 1.09 (t, J = 7.0 Hz, 3 H).

31P NMR (162 MHz, CDCl_3): \delta = 24.2.

HRMS (ESI): m/z [M + H]^+ calcld for C_{13}H_{20}O_{3}P: 363.1361; found: 363.1361.

Diethyl (4-Cyanophenyl)(phenyl)methylphosphonate (6c)
Prepared according to general procedure B from methyl 4-iodobenzonitrile and diethyl 1-diazo-phenylmethylphosphonate.
Yield: 97 mg (54%); colorless oil.

1^{1}H NMR (400 MHz, CDCl_3): \delta = 7.97 (d, J = 8.1 Hz, 2 H), 7.60 (d, J = 7.7 Hz, 2 H), 7.51 (d, J = 7.3 Hz, 2 H), 7.35–7.27 (m, 2 H), 7.27–7.21 (m, 1 H), 4.48 (d, J = 25.0 Hz, 1 H), 4.03–3.92 (m, 2 H), 3.88 (s, 3 H), 3.89–3.79 (m, 2 H), 1.10 (q, J = 6.7 Hz, 6 H).

31P NMR (162 MHz, CDCl_3): \delta = 23.4.

Ethyl (3-Methylphenyl)[4-cyanophenyl]acetate (4l)
Prepared according to general procedure A from 4-iodo-1-nitrobenzene and diethyl 1-diazo-phenylmethylphosphonate.
Yield: 104 mg (60%); yellow oil.

1^{1}H NMR (400 MHz, CDCl_3): \delta = 8.15 (d, J = 8.7 Hz, 2 H), 7.70 (d, J = 8.7 Hz, 2 H), 7.49 (d, J = 8.0 Hz, 2 H), 7.35–7.30 (m, 2 H), 7.28–7.24 (m, 1 H), 4.52 (d, J = 25.1 Hz, 1 H), 4.06–3.75 (m, 4 H), 1.14 (t, J = 7.1 Hz, 3 H), 1.09 (t, J = 7.0 Hz, 3 H).

1^{13}C\{1H\} NMR (100 MHz, CDCl_3): \delta = 170.4, 144.6, 135.4, 130.3, 129.4, 128.9, 128.7, 123.7, 63.2 (d, J = 6.7 Hz), 62.7 (d, J = 6.7 Hz), 51.0 (d, J = 139.1 Hz), 16.2.

1^{31}P NMR (162 MHz, CDCl_3): \delta = 23.4.

NMR spectral data for this compound were consistent with those in the literature.\(^7\)

Ethyl Bis[4-(methoxy-carboxyloxy)phenyl]phosphonate (6a)
Prepared according to general procedure B from methyl 4-iodobenzonitrile and diethyl 1-diazo-phenylmethylphosphonate.
Yield: 97 mg (54%); colorless oil.

1^{1}H NMR (400 MHz, CDCl_3): \delta = 7.83 (d, J = 8.3 Hz, 2 H), 7.70 (d, J = 8.3 Hz, 2 H), 7.50–7.48 (m, 2 H), 7.45–7.41 (m, 3 H), 5.09 (s, 1 H), 4.24 (q, J = 7.1 Hz, 2 H), 3.91 (s, 3 H), 1.26 (t, J = 7.1 Hz, 3 H).

IR (film): 2235, 1739, 1542, 1347 cm\(^{-1}\).

1^{13}C\{1H\} NMR (100 MHz, CDCl_3): \delta = 171.5, 144.1, 138.7, 137.3, 132.3, 129.4, 129.1, 128.8, 128.5, 125.4, 118.7, 111.1, 61.6, 56.9, 21.4, 14.1.

IR (film): 2227, 1731, 1607 cm\(^{-1}\).

Anal. Calcd for C_{19}H_{17}NO_{4}: C, 70.58; H, 5.30; N, 4.33. Found: C, 70.41; H, 4.73; N, 8.93.

Diethyl [4-(Methoxy-carboxyloxy)phenyl][4-methoxyphenyl]methylphosphonate (6a)
Prepared according to general procedure B from methyl 4-iodobenzonitrile and diethyl 1-diazo-[4-(methylxyloxy)phenyl]methylphosphonate.
Yield: 129 mg (66%); colorless oil.

1^{1}H NMR (400 MHz, CDCl_3): \delta = 7.80 (d, J = 8.2 Hz, 2 H), 7.57 (d, J = 8.2 Hz, 2 H), 7.41 (d, J = 8.5 Hz, 2 H), 6.84 (d, J = 8.5 Hz, 2 H), 4.43 (d, J = 25.0 Hz, 1 H), 4.00–3.92 (m, 2 H), 3.87–3.79 (m, 2 H), 3.76 (s, 3 H), 1.11 (t, J = 7.1 Hz, 6 H).

1^{13}C\{1H\} NMR (100 MHz, CDCl_3): \delta = 166.8, 158.8, 142.5, 130.5, 129.8, 129.4, 128.8, 128.0, 114.1, 62.9 (d, J = 6.5 Hz), 62.6 (d, J = 6.5 Hz), 55.2, 52.1, 51.3 (d, J = 138.2 Hz), 16.2.

31P NMR (162 MHz, CDCl_3): \delta = 23.6.

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Diethyl (4-Acetylphenyl)(phenyl)methylphosphonate (6e)
Prepared according to general procedure B from 4-iodoacetophenone and diethyl 1-diazo-phenylmethylphosphonate.

Yield: 100 mg (71%); colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.90$ (d, $J = 8.2$ Hz, 2 H), 7.63 (d, $J = 8.4$ Hz, 2 H), 7.51 (d, $J = 8.2$ Hz, 2 H), 7.35–7.30 (m, 2 H), 7.28–7.23 (m, 1 H), 4.49 (d, $J = 25.0$ Hz, 1 H), 4.03–3.93 (m, 2 H), 3.92–3.77 (m, 2 H), 2.57 (s, 3 H), 1.13 (t, $J = 7.1$ Hz, 3 H), 1.10 (t, $J = 7.1$ Hz, 3 H).

$^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$): $\delta =$ 197.6, 142.3, 135.8, 129.6, 129.4, 129.3, 128.7, 128.5, 127.4, 62.9 (d, $J = 6.6$ Hz), 62.6 (d, $J = 6.6$ Hz), 51.2 (d, $J = 138.4$ Hz), 26.5, 16.1.

$^{31}$P NMR (162 MHz, CDCl$_3$): $\delta = 24.2$.

HRMS (ESI): $m/z$ [M + H]$^+$ calcd for C$_{19}$H$_{24}$O$_4$P: 347.1412; found: 347.1414.

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Supporting Information
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