Supporting Information for

Copper-Catalyzed Radical Coupling/Fragmentation Reaction: Efficient Access to β-Oxophosphine Oxides

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1. General information

Solvents were purified and dried by standard methods prior to use. All commercially available reagents were used without further purification unless otherwise noted. Oxygen- and moisture-sensitive reactions were carried out under argon atmosphere. Column chromatography was generally performed on silica gel (200-300 mesh) and reactions were monitored by thin layer chromatography (TLC) using silica gel GF254 plates with UV light to visualize the course of reaction. Melting points were determined with a digital Koffer apparatus and were uncorrected. $^1$H, $^{13}$C and $^{31}$P NMR data were recorded on a 400 MHz spectrometer using CDCl$_3$ as solvent at room temperature. The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. High-resolution mass spectra (HRMS) were obtained on a FT-ICR spectrometer.

2. Synthesis of the starting materials

Substrates 1a, 1c, 1d-1g, 1j, 1k, 1m, 1o, 1q-1s were prepared according to the Method A.\textsuperscript{[1-3]} 1h, 1i, 1l, 1n, 1p were prepared according to the Method B.\textsuperscript{[1-3]} 1b was prepared according to the Method C.\textsuperscript{[4]} 1t was prepared according to the Method d.\textsuperscript{[5]} Spectroscopy data of the known compounds matches with the data reported in the corresponding references.

Method A:

To a solution of alkenyl bromide (4.0 mmol) in dry THF was added a solution of t-BuLi (1.6 M in pentane, 8.0 mmol) at -78 °C under an argon atmosphere for 20 min. The solution was stirred at -78 °C for 1.5 h. A solution of ketone or aldehyde (5.2 mmol, 1.3 equiv) in dry THF was added to the reaction mixture and stirred at -78 °C for 1 h. Then the reaction was allowed to warm to room temperature. The reaction mixture was quenched with H$_2$O and extracted with ethyl acetate. The combined organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The crude reaction mixture was purified by flash column chromatography on silica gel to afford the corresponding product.

Method B:

A three-necked flask equipped with an addition funnel, a condenser and a stir bar was charged with Mg turnings (12.0 mmol) under an argon atmosphere. Dry THF (8 mL) and bromoethane (0.26 mmol) were added via syringe. Then iodine (8.0 mg) was added. After stirring at rt for 10 min, alkenyl bromide (4.0 mmol) in dry THF (5 mL) was then added dropwise over 40 min via the addition funnel. The reaction was then heated to reflux for 3 h and was cooled to room temperature and ketone (5.6 mmol) was added. The resulting reaction mixture was stirred at
room temperature for 6 h, then quenched with saturated aqueous NH₄Cl solution and extracted twice with ethyl acetate. The combined organic layer was washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The crude reaction mixture was purified by flash column chromatography on silica gel to afford the corresponding product.

**Method C:**
To a solution of Mg (10.0 mmol) in Et₂O, bromobenzene (10.0 mmol) was added at 0 °C. The reaction mixture was heated to reflux for 2 h, Cul (10% mmol) was then added at rt. The reaction mixture was allowed to stir at same temperature for 0.5 h, propargyl alcohol (4.0 mmol) in Et₂O was added dropwise at rt. Then, the reaction was heated to reflux for 24 h, after cooling to rt, quenched with saturated aqueous NH₄Cl solution and extracted twice with ethyl acetate. The combined organic layer was washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The crude reaction mixture was purified by flash column chromatography on silica gel to afford the corresponding product.

**Method D:**
To a solution of indene (1.0 equiv.) in anhydrous tetrahydrofuran at -78 °C was added n-butyllithium (1.0 equiv.) over 10 minutes. The mixture was allowed to warm to room temperature and stirred for a further 6 h, before it was cooled again to -78 °C. The appropriate ketone (1.0 equiv.) was then added dropwise into the solution over 15 minutes. The reaction was then allowed to warm slowly to room temperature and then stirred for a further 6 h before being quenched with water. The organic layer was then extracted three times with diethyl ether, combined, washed once with brine and dried (MgSO₄) before concentrating in vacuo. The product was purified by flash chromatography using silica gel and/or basic aluminium oxide, followed by recrystallization from hexane to afford the desired product in high purity.

**3. General procedure for the copper-catalyzed radical reaction.**
A mixture of allylic alcohols 1 (0.2 mmol), H-phosphine oxides 2 (0.4 mmol) and CuSO₄·5H₂O (10 mmol %), TBHP (2.0 equiv), 4 Å MS (40.0 mg) in DCE (2.0 mL) was stirred under an atomosphere of argon at 60 °C for 1 h. The resulting mixture was concentrated under vacuum and the crude product was purified by silica gel chromatography using petroleum ether–AcOEt (3:1-2:1, v/v) as the eluent to give the corresponding products.
4. The detail optimization of the reaction conditions\([a]\)

![Chemical structure diagram]

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<th>Entry</th>
<th>Catalyst</th>
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<th>Solvent</th>
<th>Additive</th>
<th>Yield [%]([b])</th>
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[a] Reaction conditions: 1a (0.2 mmol, 1.0 equiv.), 2a (0.4 mmol, 2.0 equiv.), catalyst (10 mol%), oxidant (0.4 mmol, 2.0 equiv.), 4 Å MS (40.0 mg), solvent (2.0 ml) at 60 °C under argon for 1 h. [b] Isolated yields. [c] 4 Å MS (10.0 mg). [d] 4 Å MS (30.0 mg). [e] 4 Å MS (100.0 mg). [f] CuSO\(_4\)·5H\(_2\)O (5 mol%). [g] In the air.

5. The failed substrates bearing heterocycle for this copper-catalyzed radical reaction.

A mixture of 1k (1.09 g, 5 mmol), 2a (2.02 g, 10 mmol) and CuSO$_4$·5H$_2$O (10 mmol %), TBHP (2.0 equiv), 4 Å MS (1.1 g) in DCE (25 mL) was stirred under an atomosphere of argon at 60 °C for 1 h. The resulting mixture was concentrated under vacuum and the crude product was purified by silica gel chromatography using petroleum ether–AcOEt (3:1-2:1, v/v) as the eluent to give the corresponding products.

7. Synthesis of 1-(4-butylphenyl)-3-phenylpropan-1-one 5.

A tube was charged with a magnetic stir-bar, 3ka (0.50 mmol), sodium methoxide (0.55 mmol), and anhydrous THF (10.0 mL). The tube was stirred vigorously under air at 70 °C. After 1 h benzyl bromide (0.55 mmol) was added and stirring was continued at 70 °C for 12 h. The reaction mixture was allowed to cool to ambient temperature, and then transferred to a round-bottom flask. Silica gel was added, and the solvent was removed under reduced pressure to afford a free-flowing powder. This powder was then dryloaded onto a silica gel column and purified by flash chromatography using petroleum ether: AcOEt (2:1, v/v) as the eluent to give the corresponding product 4 in 77% yield.

A tube was charged with a magnetic stir-bar, 4 (0.11 mmol), 4 M aqueous NaOH (2 mL), ethanol (2 mL). The reaction mixture was heated with stirring at 80 °C for 1 h. The reaction mixture was allowed to cool to ambient temperature, and then transferred to a round-bottom flask. Silica gel was added, and the solvent was removed under reduced pressure to afford a free-flowing powder. This powder was then dryloaded onto a silica gel column and purified by flash chromatography using petroleum ether as the eluent to give the corresponding product 5 in 83% yield.

\[ \text{S1} \quad \text{Br} + \text{S2} \quad \rightarrow \quad \text{S2} \quad \text{NHTs} \quad \rightarrow \quad \text{6} \quad \text{NHTs} \]

n-BuLi (2.5 M in THF, 1.5 eq.) was added dropwise to a solution of (1-bromovinyl)benzene S1 (1.0 eq.) in dry THF at -78 °C under argon. The resulting mixture was then stirred at the same temperature for 1.5 h. Imine S2 (2.0 eq.) was then condensed into the reaction mixture and it was stirred for an additional 0.5 h at -78 °C. The suspension was then slowly warmed to 22 °C and monitored by TLC analysis until start materials was disappeared completely. A saturated solution of NH₄Cl was then added and the mixture was extracted with EtOAc, and dried over MgSO₄. Concentration and purification by chromatography on silica gel (PE / EtOAc = 5 : 1) afforded the 6 as colorless oil.


![3aa](image)

White solid; Mp: 137−139°C. \(^1\)H NMR (400 MHz, CDCl₃) δ 8.02 − 7.97 (m, 2H), 7.85 − 7.77 (m, 4H), 7.54 (dd, \(J = 7.1, 5.2, 1.3 \text{ Hz}, 3H\)), 7.50 − 7.40 (m, 6H), 4.16 (d, \(J = 15.4 \text{ Hz}, 2H\)). \(^{13}\)C NMR (101 MHz, CDCl₃) δ (192.78, 192.72, d, \(J = 6.1 \text{ Hz}\)), 136.77, 133.57, (132.23, 131.20, d, \(J = 104.0 \text{ Hz}\)), (132.12, 132.10, d, \(J = 2.0 \text{ Hz}\)), (131.06, 130.96 d, \(J = 10.1 \text{ Hz}\)), 129.16, (128.61, 128.49, d, \(J = 12.1 \text{ Hz}\)), 128.46, (43.43, 42.85, d, \(J = 58.6 \text{ Hz}\)). \(^{31}\)P NMR (162 MHz, CDCl₃) δ 27.15. HRMS (ESI): m/z [M+H]⁺ calculated for C₂₀H₁₉O₂P: 321.1039, found: 321.1048.

![3ja](image)

White solid; Mp: 123−125°C. \(^1\)H NMR (400 MHz, CDCl₃) δ 7.89 (d, \(J = 8.2 \text{ Hz}, 2H\)), 7.85 − 7.76 (m, 4H), 7.56 − 7.50 (m, 2H), 7.50 − 7.43 (m, 4H), 7.22 (d, \(J = 8.0 \text{ Hz}, 2H\)), 4.12 (d, \(J = 15.3 \text{ Hz}, 2H\)), 2.38 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl₃) δ (192.31, 192.26, d, \(J = 5.1 \text{ Hz}\)), 144.61, 134.39, (132.36, 131.34, d, \(J = 103.0 \text{ Hz}\)), (132.09, 132.06, d, \(J = 3.0 \text{ Hz}\)), (131.10, 131.00, d, \(J = 10.1 \text{ Hz}\)), 129.36, 129.19, (128.61, 128.49, d, \(J = 12.1 \text{ Hz}\)), (43.39, 42.82, d, \(J = 57.6 \text{ Hz}\)), 21.68. \(^{31}\)P NMR (162 MHz,
$^{13}$C NMR (101 MHz, CDCl$_3$) δ 27.18. HRMS (ESI): m/z [M+H]$^+$ calculated for C$_{21}$H$_{20}$O$_2$: 335.1195, found: 335.1196.

White solid; Mp: 98–99°C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.90 (d, J = 8.3 Hz, 2H), 7.85 – 7.77 (m, 4H), 7.56 – 7.50 (m, 2H), 7.49 – 7.42 (m, 4H), 7.22 (d, J = 8.3 Hz, 2H), 4.13 (d, J = 15.4 Hz, 2H), 2.70 – 2.55 (m, 2H), 1.65 – 1.51 (m, 2H), 1.32 (dt, J = 14.7, 7.4 Hz, 2H), 0.92 (t, J = 7.3 Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ (192.25, 192.20, d, J = 5.1 Hz), 149.34, 134.64, (132.45, 131.43, d, J = 103.0 Hz), (132.00, 131.98, d, J = 2.0 Hz), (131.10, 131.00, d, J = 10.1 Hz), 129.31, 128.54, (128.50, 128.42, d, J = 8.1 Hz), (43.36, 42.78, d, J = 58.6 Hz), 35.59, 33.01, 22.17, 13.79. $^{31}$P NMR (162 MHz, CDCl$_3$) δ 27.17. HRMS (ESI): m/z [M+H]$^+$ calculated for C$_{26}$H$_{22}$O$_2$:397.1352, found: 397.1358.

White solid; Mp: 148–150°C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.07 (d, J = 8.3 Hz, 2H), 7.82 (dd, J = 12.0, 7.2 Hz, 4H), 7.61 (dd, J = 15.7, 7.8 Hz, 4H), 7.54 – 7.35 (m, 9H), 4.17 (d, J = 15.2 Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ (192.17, 192.12, d, J = 5.1 Hz), 146.01, 139.52, 135.43, (132.19, 131.16, d, J = 104.0 Hz), (132.06, 132.04, d, J = 2.0 Hz), (130.98, 130.89, d, J = 9.1 Hz), 129.77, 128.80, (128.56, 128.44, d, J = 12.1 Hz), 128.17, 127.12, 127.00, (43.43, 42.85, d, J = 58.6 Hz). $^{31}$P NMR (162 MHz, CDCl$_3$) δ 27.17. HRMS (ESI): m/z [M+H]$^+$ calculated for C$_{26}$H$_{22}$O$_2$:397.1352, found: 397.1358.

White solid; Mp: 105–107°C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.86 – 7.76 (m, 4H), 7.61 (d, J = 7.7 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.50 – 7.43 (m, 5H), 7.33 (t, J = 8.0 Hz, 1H), 7.09 (dd, J = 8.2, 2.1 Hz, 1H),
4.14 (d, J = 15.3 Hz, 2H), 3.81 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ (192.63, 192.58, d, J = 5.1 Hz), 159.57, 138.17, (132.31, 131.28, d, J = 104.0 Hz), (132.13, 132.10, d, J = 3.0 Hz), (131.10, 131.01, d, J = 9.1 Hz), 129.50, (128.63, 128.50, d, J = 13.1 Hz), 122.19, 120.57, 112.55, 55.37, (43.60, 43.02, d, J = 58.6 Hz). $^{31}$P NMR (162 MHz, CDCl$_3$) δ 27.12. HRMS (ESI): m/z [M+H]$^+$ calculated for C$_{21}$H$_{20}$O$_3$P: 351.1145, found: 351.1147.

White solid; Mp: 167–168°C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.96 (d, J = 8.6 Hz, 2H), 7.85 – 7.74 (m, 4H), 7.57 – 7.51 (m, 2H), 7.47 (ddd, J = 7.1, 5.4, 2.4 Hz, 4H), 7.39 (d, J = 8.6 Hz, 2H), 4.11 (d, J = 15.2 Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ (191.56, 191.51, d, J = 5.1 Hz), 140.12, 135.20, (132.19, 131.16, d, J = 104.0 Hz), (132.19, 132.16, d, J = 3.0 Hz), (131.00, 130.91, d, J = 9.1 Hz), 130.68, 128.74, (128.66, 128.54, d, J = 12.1 Hz), (43.80, 43.24, d, J = 56.6 Hz). $^{31}$P NMR (162 MHz, CDCl$_3$) δ 26.60. HRMS (ESI): m/z [M+H]$^+$ calculated for C$_{20}$H$_{17}$ClO$_2$P: 355.0649, found: 355.0648.

White solid; Mp: 164–165°C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.12 – 8.00 (m, 2H), 7.86 – 7.75 (m, 4H), 7.57 – 7.51 (m, 2H), 7.47 (ddd, J = 7.0, 5.4, 2.4 Hz, 4H), 7.09 (t, J = 8.6 Hz, 2H), 4.12 (d, J = 15.3 Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ (191.15, 191.10, d, J = 5.1 Hz), (167.27, 164.72, d, J = 257.6 Hz), (132.20, 132.17, d, J = 3.0 Hz), (132.16, 131.13, d, J = 104.0 Hz), (132.12, 132.03, d, J = 9.1 Hz), (131.04, 130.95, d, J = 9.1 Hz), (128.67, 128.54, d, J = 13.1 Hz), (115.69, 115.47, d, J = 22.2 Hz), (43.72, 43.15, d, J = 57.6 Hz). $^{31}$P NMR (162 MHz, CDCl$_3$) δ 26.95. HRMS (ESI): m/z [M+H]$^+$ calculated for C$_{20}$H$_{17}$FO$_2$P: 339.0945, found: 339.0944.
White solid; Mp: 95–96°C. $^1H$ NMR (400 MHz, CDCl$_3$) $\delta$ 7.88 – 7.75 (m, 5H), 7.68 – 7.61 (m, 1H), 7.58 – 7.51 (m, 2H), 7.51 – 7.44 (m, 4H), 7.44 – 7.38 (m, 1H), 7.27 – 7.21 (m, 1H), 4.13 (d, $J$ = 15.2 Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ (191.66, 191.61, d, $J$ = 5.1 Hz), (163.82, 161.36, d, $J$ = 248.5 Hz), (138.98, 138.92, d, $J$ = 6.1 Hz), (132.25, 132.22, d, $J$ = 3.0 Hz), (132.15, 131.12, d, $J$ = 104.0 Hz), (131.07, 130.97, d, $J$ = 10.1 Hz), (130.22, 130.14, d, $J$ = 8.1 Hz), (128.70, 128.57, d, $J$ = 13.1 Hz), (125.30, 125.27, d, $J$ = 3.0 Hz), (115.69, 115.47, d, $J$ = 22.2 Hz), (43.81, 43.24, d, $J$ = 57.6 Hz). $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 26.76. HRMS (ESI): m/z [M+H]$^+$ calculated for C$_{20}$H$_{17}$FO$_2$P: 339.0945, found: 339.0949.

Yellow oil. $^1H$ NMR (400 MHz, CDCl$_3$) $\delta$ 7.80 – 7.73 (m, 4H), 7.58 – 7.53 (m, 2H), 7.52 – 7.46 (m, 4H), 3.58 (d, $J$ = 15.0 Hz, 2H), 2.53 (d, $J$ = 6.8 Hz, 2H), 2.07 (dt, $J$ = 17.2, 6.7 Hz, 1H), 0.82 (d, $J$ = 6.7 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ (202.79, 202.74, d, $J$ = 5.1 Hz), (132.24, 131.22, d, $J$ = 103.0 Hz), (132.24, 132.22, d, $J$ = 2.0 Hz), (130.90, 130.80, d, $J$ = 10.1 Hz), (128.77, 128.65, d, $J$ = 12.1 Hz), 54.04, (47.52, 46.96, d, $J$ = 56.6 Hz), 24.02, 22.26. $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 26.78. HRMS (ESI): m/z [M+H]$^+$ calculated for C$_{18}$H$_{22}$O$_2$P: 301.1352, found: 301.1354.

Yellow oil. $^1H$ NMR (400 MHz, CDCl$_3$) $\delta$ 7.80 – 7.73 (m, 4H), 7.58 – 7.46 (m, 6H), 3.60 (d, $J$ = 15.0 Hz, 2H), 2.64 (t, $J$ = 7.3 Hz, 2H), 1.54 – 1.41 (m, 2H), 1.26 – 1.13 (m, 6H), 0.84 (t, $J$ = 7.0 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ (203.28, 203.22, d, $J$ = 6.1 Hz), (132.30, 131.27, d, $J$ = 104.0 Hz), (132.23, 132.20, d, $J$ = 3.0 Hz), (130.90, 130.80, d, $J$ = 10.1 Hz), (128.77, 128.65, d, $J$ = 12.1 Hz),...
(47.28, 46.72, d, \( J = 56.6 \) Hz), 45.33, 31.48, 28.45, 23.16, 22.42, 14.00. \(^{31}\text{P NMR (162 MHz, CDCl}_3\)) \( \delta 26.69. \) \( \text{HRMS (ESI): m/z [M+H]}^+ \text{ calculated for } C_{20}H_{26}O_2P:329.1665, \text{found: 329.1666.} \)

White solid; Mp: 91–93°C. \(^1\text{H NMR (400 MHz, CDCl}_3\)) \( \delta 7.99 (d, J = 7.5 \text{ Hz, 2H}), 7.67 \text{ (dd, } J = 12.0, 8.0 \text{ Hz, 4H}), 7.52 (t, J = 7.4 \text{ Hz, 1H}), 7.40 (t, J = 7.7 \text{ Hz, 2H}), 7.25 \text{ (dd, } J = 8.2, 2.7 \text{ Hz, 4H}), 4.11 \text{ (d, } J = 15.4 \text{ Hz, 2H}), 2.37 \text{ (s, 6H).} \) \(^{13}\text{C NMR (101 MHz, CDCl}_3\)) \( \delta (192.98, 192.93, \text{ d, } J = 5.1 \text{ Hz, } 142.57, 142.54, \text{ d, } J = 3.0 \text{ Hz, } 136.99, 133.40, \text{ (131.12, 131.01, d, } J = 11.1 \text{ Hz}), (129.33, 129.21, \text{ d, } J = 12.1 \text{ Hz), 129.21, (129.21, 128.18, d, } J = 104.0 \text{ Hz, } 128.40, \text{ (43.76, 43.19, d, } J = 57.6 \text{ Hz), 21.52.} \) \(^{31}\text{P NMR (162 MHz, CDCl}_3\)) \( \delta 27.63. \) \( \text{HRMS (ESI): m/z [M+H]}^+ \text{ calculated for } C_{26}H_{22}O_2P:397.1352, \text{found: 397.1358.} \) \( \text{HRMS (ESI): m/z [M+H]}^+ \text{ calculated for } C_{22}H_{22}O_2P:349.1352, \text{found: 349.1354.} \)

Yellow oil. \(^1\text{H NMR (400 MHz, CDCl}_3\)) \( \delta 8.05 – 7.96 \text{ (m, 2H), 7.65 – 7.58 (m, 1H), 7.50 (dd, } J = 10.6, 4.8 \text{ Hz, 2H), 3.81 (s, 3H), 3.78 (s, 3H), 3.67 \text{ (d, } J = 22.6 \text{ Hz, 2H).} \) \(^{13}\text{C NMR (101 MHz, CDCl}_3\)) \( \delta (191.76, 191.69, \text{ d, } J = 7.1 \text{ Hz, } 136.26, 133.85, 128.96, 128.70, \text{ (53.29, 53.22, d, } J = 7.1 \text{ Hz), (37.99, 36.68, d, } J = 132.3 \text{ Hz).} \) \(^{31}\text{P NMR (162 MHz, CDCl}_3\)) \( \delta 23.06. \) \( \text{HRMS (ESI): m/z [M+H]}^+ \text{ calculated for } C_{10}H_{14}O_3P:229.0624, \text{found: 229.0628.} \)

Yellow oil. \(^1\text{H NMR (400 MHz, CDCl}_3\)) \( \delta 8.02 \text{ (d, } J = 7.7 \text{ Hz, 2H), 7.59 \text{ (t, } J = 7.3 \text{ Hz, 1H), 7.48 \text{ (t, } J = 7.6 \text{ Hz, 2H), 3.89 – 3.79 (m, 4H), 3.66 \text{ (d, } J = 22.9 \text{ Hz, 2H), 1.87 \text{ (td, } J = 13.3, 6.6 \text{ Hz, 2H), 0.88 \text{ (d, } J} \)
= 6.7 Hz, 12H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ (191.89, 191.82, d, $J$ = 7.1 Hz), 136.44, 133.63, 129.03, 128.58, (72.40, 72.33, d, $J$ = 7.1 Hz), (38.74, 37.46, d, $J$ = 129.3 Hz), (29.13, 29.06, d, $J$ = 7.1 Hz), (18.57, 18.56, d, $J$ = 1.0 Hz). $^{31}$P NMR (162 MHz, CDCl$_3$) δ 19.73. HRMS (ESI): m/z [M+H]$^+$ calculated for C$_{16}$H$_{26}$O$_4$P: 313.1563, found: 313.1565.

White solid; Mp: 86–88°C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.94 (dd, $J$ = 12.0, 6.9 Hz, 2H), 7.71 (dd, $J$ = 11.9, 7.2 Hz, 2H), 7.62 (d, $J$ = 7.7 Hz, 1H), 7.59 – 7.49 (m, 4H), 7.48 – 7.42 (m, 2H), 7.38 (dd, $J$ = 12.6, 5.1 Hz, 2H), 7.31 (d, $J$ = 7.4 Hz, 1H), 3.96 (ddd, $J$ = 15.7, 8.4, 3.5 Hz, 1H), 3.70 – 3.55 (m, 1H), 3.49 – 3.36 (m, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ (199.87, 199.84, d, $J$ = 3.0 Hz ), (153.10, 153.05, d, $J$ = 5.1 Hz), (136.95, 136.94, d, $J$ = 1.0 Hz), 13 5.01, (132.40, 131.38, d, $J$ = 103.0 Hz), (132.19, 132.16, d, $J$ = 3.0 Hz), (132.09, 132.06, d, $J$ = 3.0 Hz), (131.66, 131.57, d, $J$ = 9.1 Hz), (131.41, 131.31, d, $J$ = 10.1 Hz), (130.35, 129.33, d, $J$ = 103.0 Hz), (128.74, 128.62, d, $J$ = 12.1 Hz), (128.31, 128.18, d, $J$ = 13.1 Hz), 127.61, 126.29, 124.11, (49.09, 48.46, d, $J$ = 63.6 Hz), 28.27. $^{31}$P NMR (162 MHz, CDCl$_3$) δ 32.22. HRMS (ESI) m/z: [M + H]$^+$ calcd for C$_{21}$H$_{18}$O$_2$P 333.1039, found 333.1045.

White solid; Mp: 133–135°C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.99 – 7.88 (m, 2H), 7.80 – 7.73 (m, 2H), 7.45 – 7.38 (m, 6H), 7.34 (ddd, $J$ = 7.1, 5.4, 2.4 Hz, 2H), 7.15 – 7.05 (m, 5H), 6.96 (d, $J$ = 8.2 Hz, 2H), 4.83 (ddd, $J$ = 15.8, 11.3, 2.4 Hz, 1H), 3.56 (ddd, $J$ = 13.9, 11.4, 4.8 Hz, 1H), 3.30 – 3.16 (m, 1H), 2.51 (t, $J$ = 7.6 Hz, 2H), 1.53 – 1.47 (m, 2H), 1.29 – 1.23 (m, 2H), 0.89 (t, $J$ = 7.3 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ (196.82, 196.79, d, $J$ = 3.0 Hz), 148.39, (139.15, 139.01, d, $J$ = 14.1 Hz), 135.94, (131.98, 131.96, d, $J$ = 2.0 Hz), (131.90, 131.88, d, $J$ = 2.0 Hz), (131.83, 131.74, d, $J$ = 9.1
(131.38, 131.29, \(d, J = 9.1 \text{ Hz}\)), (130.78, 129.79, \(d, J = 100.0 \text{ Hz}\)), 130.32, (128.44, 128.41, \(d, J = 3.0 \text{ Hz}\)), 128.30, 128.10, 126.39, (54.19, 53.65, \(d, J = 54.5 \text{ Hz}\)), 35.34, 33.79, 32.91, 22.00, 13.73.

\(^{31}\text{P NMR (162 MHz, CDCl}_3\)) \(\delta\) 29.34. HRMS (ESI): m/z \([\text{M+H}]^+\) calculated for C\(_{31}\)H\(_{32}\)O\(_2\)P: 467.2134, found: 467.2135.

![Structure 5](image)

Colorless oil. \(^1\text{H NMR (400 MHz, CDCl}_3\)) \(\delta\) 7.88 (\(d, J = 8.2 \text{ Hz}, 2\text{H}\)), 7.33 – 7.18 (m, 7H), 3.33 – 3.22 (m, 2H), 3.06 (dd, \(J = 10.1, 5.3 \text{ Hz}, 2\text{H}\)), 2.73 – 2.60 (m, 2H), 1.65 – 1.56 (m, 2H), 1.36 (dt, \(J = 14.9, 7.4 \text{ Hz}, 2\text{H}\)), 0.93 (t, \(J = 7.3 \text{ Hz}, 3\text{H}\)). \(^{13}\text{C NMR (101 MHz, CDCl}_3\)) \(\delta\) 198.9, 148.8, 141.4, 134.6, 128.6, 128.5, 128.4, 128.2, 126.1, 40.4, 35.7, 33.2, 30.2, 22.3, 13.9. HRMS (ESI): m/z \([\text{M+H}]^+\) calculated for C\(_{19}\)H\(_{23}\)O: 267.1743, found: 267.1746.

![Structure 6](image)

Viscous oil. \(^1\text{H NMR (400 MHz, CDCl}_3\)) \(\delta\) 7.58 (\(d, J = 8.3 \text{ Hz}, 2\text{H}\)), 7.21 – 7.14 (m, 5H), 7.14 – 7.03 (m, 4H), 6.76 – 6.69 (m, 2H), 5.41 (\(d, J = 7.6 \text{ Hz}, 1\text{H}\)), 5.36 (s, 1H), 5.19 (s, 1H), 5.11 (\(d, J = 7.6 \text{ Hz}, 1\text{H}\)), 3.73 (s, 3H), 2.39 (s, 3H). \(^{13}\text{C NMR (101 MHz, CDCl}_3\)) \(\delta\) 159.0, 147.3, 143.1, 138.9, 137.5, 131.1, 129.3, 128.6, 128.3, 127.8, 127.2, 126.8, 116.0, 113.9, 60.3, 55.2, 21.4. HRMS (ESI): m/z \([\text{M+H}]^+\) calculated for C\(_{23}\)H\(_{24}\)NO\(_3\)S: 394.1471, found: 394.1474.

![Structure 7](image)
White solid; Mp: 79–82°C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.21 (d, $J = 7.7$ Hz, 1H), 7.74 – 7.65 (m, 2H), 7.64 – 7.56 (m, 2H), 7.47 (dd, $J = 7.3$, 1.4 Hz, 1H), 7.44 – 7.38 (m, 3H), 7.38 – 7.30 (m, 4H), 7.23 – 7.16 (m, 2H), 7.05 (t, $J = 7.3$ Hz, 1H), 7.01 – 6.89 (m, 4H), 6.80 (d, $J = 8.6$ Hz, 2H), 6.38 (d, $J = 8.8$ Hz, 2H), 5.27 (d, $J = 8.9$ Hz, 1H), 3.67 (s, 3H), 3.37 (dd, $J = 15.4$, 11.4 Hz, 1H), 3.15 (dd, $J = 15.4$, 12.2 Hz, 1H), 2.28 (s, 3H), 1.01 (s, 9H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 158.41, 141.76, (138.64, 138.60, d, $J = 4.0$ Hz), 138.54, (134.47, 134.39, d, $J = 8.1$ Hz), (133.44, 133.38, d, $J = 6.1$ Hz), (131.42, 131.39, d, $J = 3.0$ Hz), (131.26, 131.23, d, $J = 3.0$ Hz), (130.90, 130.80, d, $J = 10.1$ Hz), 130.72, (130.62, 130.53, d, $J = 9.1$ Hz), 128.68, (128.52, 128.40, d, $J = 12.1$ Hz), (128.36, 128.24, d, $J = 12.1$ Hz), 127.92, 127.70, 127.29, 126.98, 126.82, 112.25, (86.56, 86.53, d, $J = 3.0$ Hz), 80.89, 63.41, 55.02, (35.35, 34.65, d, $J = 70.7$ Hz), 26.55, 21.25. HRMS (ESI): m/z [M+H]$^+$ calculated for C$_{39}$H$_{43}$NO$_6$PS: 684.2543, found: 684.2545.

White solid; Mp: 124–126°C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.93 (s, 1H), 7.87 (d, $J = 8.2$ Hz, 4H), 7.32 (d, $J = 8.1$ Hz, 2H), 6.96 (d, $J = 8.8$ Hz, 2H), 3.87 (s, 3H), 2.41 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 169.1, 165.2, 144.2, 135.7, 133.6, 129.6, 127.8, 125.1, 114.6, 55.6, 21.5. HRMS (ESI): m/z [M+H]$^+$ calculated for C$_{15}$H$_{16}$NO$_3$S: 290.0845, found: 290.0848.

References


GC-MS spectrum of cyclopentanone
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{31}\text{P NMR (162 MHz, CDCl}_3)$
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)

3ja
$^{31}$P NMR (162 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

**3ka**

![NMR spectrum of 3ka](image)
$^{13}$C NMR (101 MHz, CDCl$_3$)

3ka

nBu

$^{13}$C NMR (101 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{31}$P NMR (162 MHz, CDCl$_3$)

3ka

nBu

![Chemical structure of 3ka](image)

-27.16
$^1$H NMR (400 MHz, CDCl$_3$)
**3la**

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{31}$P NMR (162 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

3ma

Organic structure with chemical shifts marked on the NMR spectrum.
$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{31}$P NMR (162 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^3\text{P NMR (162 MHz, CDCl}_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

3oa
$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{31}$P NMR (162 MHz, CDCl$_3$)

$^{31}$P NMR (162 MHz, CDCl$_3$)
3pa

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{31}\text{P NMR (162 MHz, CDCl}_3\text{)}$
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{31}$P NMR (162 MHz, CDCl$_3$)

3ra

$\text{Ph}$
C₆H₁₃

3sa

¹H NMR (400 MHz, CDCl₃)
$^1$H NMR (300 MHz, CDCl$_3$)

$^1$C NMR (101 MHz, CDCl$_3$)

3sa

C$_6$H$_{13}$

OC

Ph

O

$^1$C NMR (101 MHz, CDCl$_3$)
$^{31}$P NMR (162 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{31}$P NMR (162 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

3ac
$^{13}$C NMR (101 MHz, CDCl$_3$)

3ac
$^{31}$P NMR (162 MHz, CDCl$_3$)
"$^1$H NMR (400 MHz, CDCl$_3$)"
$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{31}$P NMR (162 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)
\[ ^{31}\text{P NMR (162 MHz, CDCl}_3) \]

3ta
$^1$H NMR (400 MHz, CDCl₃)
$^{13}$C NMR (101 MHz, CDCl$_3$)

![Carbon NMR spectrum](image)
$^{31}$P NMR (162 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{31}$P NMR (162 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)