Supporting Information

Highly Chemo- and Regioselective C-P Cross-coupling reaction of Quinone Imine Kets with Ar₂P(O)H to Construct Ortho-amino Triarylphosphine Derivatives

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General Information

All compounds were fully characterised by spectroscopic data. The NMR spectra were recorded on a Bruker DRX400. Chemical shifts (δ) are expressed in ppm, J values are given in Hz, and deuterated CDCl₃ was used as solvent. The reactions were monitored by thin layer chromatography (TLC) using silica gel GF254. The melting points were determined on a XT-4A melting point apparatus and are uncorrected. HRMs were performed on an Agilent LC/Msd TOF instrument.

General Procedure for the Preparation raw material 1 and 2

Scheme 1. Synthesis of raw material 1

To a stirred solution of the corresponding aniline (10 mmol, 1.0 equiv) in pyridine (20 mL) at 0 °C, the corresponding sulfonyl chloride (11 mmol, 1.1 equiv) was added slowly. The reaction mixture was allowed to warm to ambient temperature and was stirred for overnight, monitored by TLC analysis. When the corresponding aniline was completely consumed, then the pyridine was evaporated under reduced pressure. The residue was quenched with EtOAc (10 mL) and 1N HCl (10 mL), then the mixture was extracted with EtOAc (3 x 20 mL) and saturated NaHCO₃ (3 x 10 mL). The combined organic layers were washed with brine, dried with anhydrous Na₂SO₄, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel to give the corresponding N-protected aniline (petroleum ether/EtOAc, 10:1-4:1).

To a solution of the corresponding N-protected aniline (2 mmol, 1.0 equiv) in distilled MeOH (20 mL) was added phenyliodoso diacetate (PIDA) (2.4 mmol, 1.2 equiv) under nitrogen atmosphere, and the mixture was stirred at room temperature and monitored by TLC analysis. When the corresponding N-protected aniline was completely consumed, the reaction was quenched with saturated NaHCO₃ (20 mL) and then extracted with EtOAc (3 × 20 mL). The combined organic layers were
washed with brine (20 mL) and dried with anhydrous Na$_2$SO$_4$, then the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel to give the corresponding quinine imine ketals 1 (petroleum ether/EtOAc, 15:1-6:1).

**Scheme 2. Synthesis of raw material 2**

The mixture of magnesium turnings (3.3 mmol, 3.3 equiv), a piece of iodine and small amount of 1-bromo-4-butylbenzene in THF (20 ml) was vigorously stirred under N$_2$. The flask was heated until the reaction was initiated (the solution become colorless). A solution of Aryl bromide (30.0 mmol, 3.0 equiv) in THF (30 ml) was added dropwise and stirred for 1 h. The flask was cooled to 0 °C by an ice-bath and diethyl phosphite (1.30 ml, 10.0 mmol, 1.0 equiv) in THF (10 ml) was added over 30 min. After stirring for additional 2 h at room temperature, the reaction was quenched by the addition of 2 M HCl (20 ml) at 0 °C, and stirred for 15 min. The mixture was filtrated through a celite pad, and the filtrate was extracted with EtOAc three times. The combined organic layer was washed with brine and dried over Na$_2$SO$_4$. After evaporation, the residue was purified by flash column chromatography on silica gel (PE/EtOAc 1:1) to afford desired product 2.

**General Procedure for the Preparation of Compound 3 and 6**

A 10 mL round-bottom flask was charged with quinone imine ketals (QIKs) 1 (0.1 mmol), Ar$_2$P(O)H 2 (0.11 mmol) and C$_2$CO$_3$ in EtOH (2 mL), and the solution was stirred for 8–12 h under 40 °C until quinone imine ketals (QIKs) 1 were completely consumed as indicated by TLC. Then, the crude products were condensed under the
reduced pressure. Then, the crude products was purified by flash column chromatography (petroleum ether/EtOAc = 10:1–2:1), afforded the pure products 3 in 82–95% yields.

Scheme 4. Synthesis of compound 6

A 10 mL round-bottom flask was charged with compound 3 (0.05 mmol), HSiCl₃ (0.5 mmol) and Et₃N (1.0 mmol) in toluene 2.0 mL under nitrogen atmosphere, and the solution was stirred for 2–6 h under 100 °C until compound 3 were completely consumed as indicated by TLC. Then, NaOH (1.0 mol/L) was added to solution, the solution was extracted with EtOAc (3 x 10 mL). The organic phases were washed with brine, dried by anhydrous Na₂SO₄ and condensed under the reduced pressure to give a residue, which was further purified by flash column chromatography (petroleum ether/EtOAc = 6:1–1:2), afforded the pure products 6 in 87–95% yields.
Spectroscopic Data of 3, 6 and 7-10

\( \text{N-}(2\text{-}(\text{diphenylphosphoryl})\text{-}4\text{-methoxyphenyl})\text{-}4\text{-methylbenzenesulfonamide} \)

\((3\text{aa})\)

White solid; Mp: 160-162 °C, \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 10.76 \) (br, 1H, NH), 7.84-7.88 (m, 1H, ArH), 7.51-7.57 (m, 5H, ArH), 7.37-7.44 (m, 7H, ArH), 7.00-7.03 (m, 1H, ArH), 6.87-6.89 (m, 2H, ArH), 6.37-6.41 (m, 1H, ArH), 3.64 (s, 3H, ArOCH\(_3\)), 2.25 (s, 3H, ArCH\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta = 155.0, 154.8, 142.9, 137.0, 136.5, 132.3, 132.0, 131.9, 131.8, 130.9, 129.2, 128.7, 128.6, 127.2, 123.9, 123.8, 118.8, 118.7, 118.0, 55.5, 21.6. HRMS (ESI-TOF): \( m/z \) calcd for C\(_{26}\)H\(_{24}\)NO\(_4\)PSNa [M + Na]\(^+\), 500.1056, found, 500.1056.

\( \text{N-}(2\text{-}(\text{diphenylphosphoryl})\text{-}4\text{-methoxyphenyl})\text{-}4\text{-methoxybenzenesulfonamide} \)

\((3\text{ab})\)

White solid; Mp: 160-162 °C, \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 11.65 \) (br, 1H, NH), 8.71-8.75 (m, 1H, ArH), 8.05-8.07 (m, 2H, ArH), 7.64-7.69 (m, 4H, ArH), 7.43-7.59 (m, 9H, ArH), 7.11-7.14 (m, 1H, ArH), 6.54-6.59 (m, 1H, ArH), 3.71 (s, 3H, ArOCH\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta = 165.2, 154.7, 154.5, 137.8, 134.4, 132.6, 132.5, 132.1, 132.0, 131.7, 131.6, 130.6, 128.9, 128.7, 128.6, 127.4, 124.0, 123.9, 119.8, 118.9, 118.7, 117.6, 55.5. HRMS (ESI-TOF): \( m/z \) calcd for C\(_{26}\)H\(_{22}\)NO\(_3\)PNa [M + Na]\(^+\), 450.1230, found, 450.1228.

\( \text{N-}(2\text{-}(\text{diphenylphosphoryl})\text{-}4\text{-methoxyphenyl})\text{-}4\text{-methoxybenzenesulfonamide} \)

\((3\text{ac})\)

White solid; Mp: 158-160 °C, \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 10.72 \) (br, 1H, NH),
7.85-7.88 (m, 1H, ArH), 7.53-7.57 (m, 4H, ArH), 7.38-7.41 (m, 8H, ArH), 7.00-7.03 (m, 1H, ArH), 6.54-6.56 (m, 2H, ArH), 6.38-6.42 (m, 1H, ArH), 3.74 (s, 3H, ArOCH₃), 3.64 (s, 3H, ArOCH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 162.5, 155.0, 154.9, 137.1, 137.0, 131.9, 131.8, 128.7, 128.5, 124.1, 124.0, 118.7, 118.6, 118.0, 113.7, 55.4, 55.3. HRMS (ESI-TOF): m/z calcd for C₂₆H₂₄NO₅PSNa [M + Na]⁺, 516.1005, found, 516.1004.

N-(2-(diphenylphosphoryl)-4-methoxyphenyl)[1,1'-biphenyl]-4-sulfonamide (3ad)

![Image of N-(2-(diphenylphosphoryl)-4-methoxyphenyl)-1,1'-biphenyl]-4-sulfonamide (3ad)

White solid; Mp: 201-203 °C, ¹H NMR (400 MHz, CDCl₃): δ = 10.85 (br, 1H, NH), 7.91-7.94 (m, 1H, ArH), 7.69-7.72 (m, 2H, ArH), 7.31-7.51 (m, 17H, ArH), 7.03-7.06 (m, 1H, ArH), 6.38-6.43 (m, 1H, ArH), 3.65 (s, 3H, ArOCH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 155.1, 155.0, 144.9, 139.0, 138.0, 136.8, 136.7, 132.5, 132.4, 131.9, 131.8, 131.7, 130.8, 129.0, 128.8, 128.6, 128.4, 127.7, 127.2, 127.0, 124.0, 123.9, 118.9, 118.7, 118.1, 118.0, 55.5. HRMS (ESI-TOF): m/z calcd for C₃₁H₂₇NO₅PS [M + H]⁺, 540.1393, found, 540.1393.

4-chloro-N-(2-(diphenylphosphoryl)-4-methoxyphenyl)benzenesulfonamide (3ae)

![Image of 4-chloro-N-(2-(diphenylphosphoryl)-4-methoxyphenyl)benzenesulfonamide (3ae)

White solid; Mp: 209-211 °C, ¹H NMR (400 MHz, CDCl₃): δ = 10.83 (br, 1H, NH), 7.88-7.91 (m, 1H, ArH), 7.56-7.60 (m, 2H, ArH), 7.51-7.54 (m, 2H, ArH), 7.33-7.43 (m, 8H, ArH), 7.03-7.06 (m, 1H, ArH), 6.97-7.00 (m, 2H, ArH), 6.37-6.42 (m, 1H, ArH), 3.66 (s, 3H, ArOCH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 155.4, 155.2, 138.8, 137.8, 136.3, 132.6, 132.5, 131.8, 131.7, 130.7, 129.4, 128.8, 128.7, 128.5, 128.0, 124.7, 124.6, 119.9, 119.0, 118.9, 118.1, 118.0, 55.5. HRMS (ESI-TOF): m/z calcd for C₂₅H₂₂ClNO₄PS [M + H]⁺, 498.0690, found, 498.0690.
**4-bromo-N-(2-(diphenylphosphoryl)-4-methoxyphenyl)benzenesulfonamide (3af)**

![Chemical Structure]

White solid; Mp: 212-214 °C, \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 10.86\) (br, 1H, NH), 7.88-7.91 (m, 1H, ArH), 7.57-7.61 (m, 2H, ArH), 7.33-7.46 (m, 10H, ArH), 7.13-7.16 (m, 2H, ArH), 7.03-7.06 (m, 1H, ArH), 6.37-6.42 (m, 1H, ArH), 3.66 (s, 3H, ArOCH\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 155.4, 155.3, 138.3, 136.3, 136.2, 132.6, 132.5, 131.8, 131.7, 131.6, 130.7, 128.9, 128.7, 128.6, 127.5, 124.6, 124.5, 119.9, 119.0, 118.9, 118.8, 118.1, 118.0, 55.5. HRMS (ESI-TOF): \(m/z\) calcd for C\(_{25}\)H\(_{22}\)BrNO\(_4\)PS [M + H]+, 542.0185, found, 542.0185.

**N-(2-(diphenylphosphoryl)-4-methoxyphenyl)-4-(trifluoromethyl)benzenesulfonamide (3ag)**

![Chemical Structure]

White solid; Mp: 156-158 °C, \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 10.98\) (br, 1H, NH), 7.90-7.94 (m, 1H, ArH), 7.73-7.75 (m, 2H, ArH), 7.53-7.57 (m, 2H, ArH), 7.30-7.42 (m, 10H, ArH), 7.04-7.07 (m, 1H, ArH), 6.38-6.42 (m, 1H, ArH), 3.66 (s, 3H, ArOCH\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 155.5, 155.3, 142.9, 136.0, 134.0, 133.7, 132.8, 132.7, 131.7, 131.6, 130.6, 128.8, 128.7, 127.6, 125.6 (q, J = 8.0 Hz), 124.5, 124.3, 124.2, 121.8, 119.9, 119.0, 118.9, 118.1, 55.5. HRMS (ESI-TOF): \(m/z\) calcd for C\(_{26}\)H\(_{21}\)F\(_3\)NO\(_4\)PS [M + Na]+, 554.0773, found, 554.0772.

**N-(2-(diphenylphosphoryl)-4-methoxyphenyl)-4-nitrobenzenesulfonamide (3ah)**

![Chemical Structure]

White solid; Mp: 177-179 °C, \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 11.00\) (br, 1H, NH), 7.90-7.94 (m, 1H, ArH), 7.69-7.78 (m, 4H, ArH), 7.47-7.52 (m, 2H, ArH), 7.27-7.37
N-(2-(diphenylphosphoryl)-4-methoxyphenyl)naphthalene-2-sulfonamide (3ai)

White solid; Mp: 206-208 °C, \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 10.90\) (br, 1H, NH), 8.24 (s, 1H, ArH), 7.94-7.98 (m, 1H, ArH), 7.70-7.85 (m, 4H, ArH), 7.43-7.59 (m, 6H, ArH), 7.16-7.38 (m, 6H, ArH), 7.02-7.06 (m, 1H, ArH), 6.32-6.36 (m, 1H, ArH), 3.62 (s, 3H, ArOCH\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 155.2, 155.0, 136.7, 136.6, 136.5, 134.7, 132.3, 132.2, 131.9, 131.7, 131.6, 131.5, 130.6, 129.4, 128.9, 128.7, 128.5, 128.4, 128.3, 127.9, 127.1, 124.3, 124.2, 122.6, 119.6, 118.8, 118.7, 118.6, 118.1, 118.0, 55.5. HRMS (ESI-TOF): \(m/z\) calcd for C\(_{29}\)H\(_{21}\)N\(_2\)O\(_5\)PSNa [M + Na]\(^+\), 536.1056, found, 536.1055.

N-(2-(diphenylphosphoryl)-4-methoxyphenyl)thiophene-2-sulfonamide (3aj)

White solid; Mp: 177-179 °C, \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 10.95\) (br, 1H, NH), 7.88-7.91 (m, 1H, ArH), 7.79-7.85 (m, 2H, ArH), 7.53-7.58 (m, 2H, ArH), 7.44-7.48 (m, 3H, ArH), 7.43-7.44 (m, 3H, ArH), 7.30-7.32 (m, 1H, ArH), 7.19-7.20 (m, 1H, ArH), 7.04-7.07 (m, 1H, ArH), 6.64-6.66 (m, 1H, ArH), 6.43-6.47 (m, 1H, ArH), 3.67 (s, 3H, ArOCH\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 155.3, 155.2, 139.8, 136.5, 136.4, 132.5, 132.4, 132.2, 132.1, 132.0, 131.9, 131.8, 131.7, 132.6, 130.8, 128.8, 128.7, 128.6, 128.5, 127.1, 124.0, 123.9, 120.0, 119.0, 118.9, 117.9, 55.5. HRMS (ESI-TOF): \(m/z\) calcd for C\(_{23}\)H\(_{21}\)NO\(_4\)PS \[M + H]\(^+\), 470.0644, found, 470.0644.
N-(2-(diphenylphosphoryl)-4-methoxyphenyl)ethanesulfonamide (3ak)

White solid; Mp: 154-156 °C, \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 9.99\) (br, 1H, NH), 7.76-7.84 (m, 2H, ArH), 7.60-7.68 (m, 5H, ArH), 7.46-7.54 (m, 4H, ArH), 7.04-7.07 (m, 1H, ArH), 6.51-6.55 (m, 1H, ArH), 3.68 (s, 3H, ArOCH\(_3\)), 2.77 (q, \(J = 8.0\) Hz, 2H, CH\(_2\)), 1.10 (t, \(J = 8.0\) Hz, 3H, CH\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 155.1, 154.9, 136.7, 136.6, 132.9, 132.8, 132.5, 132.4, 132.2, 132.1, 131.7, 131.6, 131.3, 130.2, 129.0, 128.9, 128.8, 128.7, 128.6, 122.8, 122.7, 119.3, 119.2, 118.2, 118.1, 55.5, 46.6, 7.9. HRMS (ESI-TOF): \(m/z\) calcd for C\(_{21}\)H\(_{22}\)NO\(_4\)PSNa [M + Na]\(^+\), 438.0899, found, 438.0899.

N-(2-(diphenylphosphoryl)-4-methoxyphenyl)butane-1-sulfonamide (3al)

White solid; Mp: 132-134 °C, \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 10.10\) (br, 1H, NH), 7.76-7.79 (m, 1H, ArH), 7.59-7.68 (m, 6H, ArH), 7.49-7.53 (m, 4H, ArH), 7.04-7.07 (m, 1H, ArH), 6.51-6.56 (m, 1H, ArH), 3.69 (s, 3H, ArOCH\(_3\)), 1.53-1.61 (m, 2H, ArH), 1.04-1.14 (m, 2H, ArH), 0.72 (t, \(J = 8.0\) Hz, 3H, CH\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 155.1, 154.9, 136.7, 132.8, 132.1, 132.0, 128.9, 128.8, 123.2, 123.1, 119.2, 119.1, 118.1, 55.6, 51.9, 25.0, 21.4, 13.5. HRMS (ESI-TOF): \(m/z\) calcd for C\(_{23}\)H\(_{26}\)NO\(_4\)PSNa [M + Na]\(^+\), 466.1212, found, 466.1212.

N-(2-(diphenylphosphoryl)-4-methoxyphenyl)-1-phenylmethanesulfonamide (3am)

White solid; Mp: 153-155 °C, \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 10.02\) (br, 1H, NH),
7.79-7.85 (m, 2H, ArH), 7.58-7.69 (m, 5H, ArH), 7.45-7.55 (m, 6H, ArH), 7.20-7.25 (m, 3H, ArH), 6.95-6.98 (m, 1H, ArH), 6.50-6.54 (m, 1H, ArH), 3.99 (s, 2H, ArCH₂), 3.68 (s, 3H, ArOCH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 155.0, 154.8, 136.6, 136.5, 133.0, 132.9, 132.5, 132.4, 132.2, 132.1, 131.7, 131.6, 131.1, 130.8, 130.7, 130.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.4, 122.8, 122.7, 120.0, 119.2, 119.1, 118.1, 118.0, 58.6, 55.6. HRMS (ESI-TOF): m/z calcd for C₁₉H₂₄NO₄PSNa [M + Na]⁺, 500.1056, found, 500.1056.

**N-(2-(diphenylphosphoryl)-4-methoxy-6-methylphenyl)-4-methylbenzenesulfonamide (3an)**

![Chemical Structure](image)

White solid; Mp: 166-168 °C; ¹H NMR (400 MHz, CDCl₃): δ = 10.01 (br, 1H, NH), 7.50-7.54 (m, 4H, ArH), 7.37-7.44 (m, 8H, ArH), 6.95-6.96 (m, 1H, ArH), 6.89-6.91 (m, 2H, ArH), 6.31-6.35 (m, 1H, ArH), 3.67 (s, 3H, ArOCH₃), 2.51 (s, 3H, ArCH₃), 2.21 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 156.1, 155.9, 142.8, 140.5, 140.4, 137.1, 134.4, 132.5, 132.1, 132.0, 131.9, 131.8, 131.5, 129.0, 128.5, 128.4, 127.5, 124.7, 123.8, 119.8, 117.7, 117.6, 55.4, 21.6, 20.8. HRMS (ESI-TOF): m/z calcd for C₂₅H₂₆NO₄PSNa [M + Na]⁺, 514.1212, found, 514.1212.

**N-(2-(diphenylphosphoryl)-4-methoxy-5-methylphenyl)-4-methylbenzenesulfonamide (3o)**

![Chemical Structure](image)

White solid; Mp: 128-130 °C; ¹H NMR (400 MHz, CDCl₃): δ = 10.76 (br, 1H, NH), 7.72-7.74 (m, 1H, ArH), 7.52-7.57 (m, 4H, ArH), 7.36-7.45 (m, 8H, ArH), 6.87 (d, J = 8.0 Hz, 2H, ArH), 6.20 (d, J = 16.0 Hz, 1H, ArH), 3.47 (s, 3H, ArOCH₃), 2.23-2.24 (m, 6H, ArCH₃, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 153.6, 153.4, 142.8, 137.2, 137.1, 136.5, 133.4, 133.3, 132.5, 132.2, 132.1, 131.9, 131.8, 131.6, 131.5, 131.4, 129.2, 129.1, 128.7, 128.6, 128.5, 127.5, 127.2, 125.1, 125.0, 115.4, 114.4, 113.2,
113.0, 55.3, 21.6, 16.7. HRMS (ESI-TOF): \( m/z \) calcd for \( \text{C}_{27}\text{H}_{26}\text{NO}_{4}\text{PSNa} [\text{M + Na}]^+ \), 514.1212, found, 514.1212.

**N-(2-(diphenylphosphoryl)-4,5-dimethoxyphenyl)-4-methylbenzenesulfonamide (3ap)**

White solid; Mp: 163-165 °C, \(^1\)H NMR (400 MHz, CDCl\_3): \( \delta = 10.93 \) (br, 1H, NH), 7.80-7.85 (m, 1H, ArH), 7.51-7.58 (m, 5H,ArH), 7.36-7.41 (m, 7H, ArH), 6.88 (d, \( J = 8.0 \) Hz, 2H, ArH), 6.22-6.26 (m, 1H, ArH), 3.96 (s, 3H, ArOCH\_3), 3.54 (s, 3H, ArOCH\_3), 2.26 (s, 3H, ArCH\_3); \(^{13}\)C NMR (100 MHz, CDCl\_3): \( \delta = 152.9, 144.9, 144.7, 143.1, 139.2, 139.1, 136.3, 132.5, 132.2, 131.8, 131.7, 131.6, 131.5, 129.2, 128.7, 128.6, 127.2, 114.5, 114.4, 107.9, 106.9, 105.9, 105.8, 56.3, 56.0, 21.6. HRMS (ESI-TOF): \( m/z \) calcd for \( \text{C}_{27}\text{H}_{26}\text{NO}_{5}\text{PSNa} [\text{M + Na}]^+ \), 530.1162, found, 530.1162.

**N-(5-chloro-2-(diphenylphosphoryl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3aq)**

White solid; Mp: 152-154 °C, \(^1\)H NMR (400 MHz, CDCl\_3): \( \delta = 10.84 \) (br, 1H, NH), 8.00 (d, \( J = 8.0 \) Hz, 1H, ArH), 7.53-7.61 (m, 4H, ArH), 7.37-7.45 (m, 8H,ArH), 6.90-6.92 (m, 2H, ArH), 6.31 (d, \( J = 16.0 \) Hz, 1H, ArH), 3.54 (s, 3H, ArOCH\_3), 2.27 (s, 3H, ArCH\_3); \(^{13}\)C NMR (100 MHz, CDCl\_3): \( \delta = 150.8, 150.7, 143.3, 137.8, 137.7, 137.5, 136.2, 132.6, 132.5, 131.8, 131.7, 130.7, 129.3, 128.9, 128.7, 128.4, 127.2, 124.2, 124.1, 117.1, 116.1, 115.4, 115.2, 56.2, 21.6. HRMS (ESI-TOF): \( m/z \) calcd for \( \text{C}_{26}\text{H}_{23}\text{ClNO}_{4}\text{PSNa} [\text{M + Na}]^+ \), 534.0666, found, 534.0665.

**N-(5-bromo-2-(diphenylphosphoryl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3ar)**
White solid; Mp: 174-176 °C, $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 12.31 (br, 1H, NH), 8.04-8.08 (m, 1H, ArH), 7.46-7.59 (m, 8H, ArH), 7.36-7.40 (m, 4H, ArH), 7.12 (d, $J$ = 8.0 Hz, 1H, ArH), 6.93 (d, $J$ = 8.0 Hz, 2H, ArH), 3.85 (s, 3H, ArOCH$_3$), 2.30 (s, 3H, ArCH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 152.7, 152.6, 143.1, 140.3, 143.2, 136.3, 132.3, 132.2, 132.1, 132.0, 131.6, 130.4, 129.8, 129.3, 128.4, 128.3, 127.5, 126.5, 124.1, 124.0, 119.1, 118.1, 116.1, 116.0, 115.8, 115.7, 56.6, 21.7. HRMS (ESI-TOF): $m/z$ calcd for C$_{26}$H$_{23}$BrNO$_4$PSNa [M + Na]$^+$, 578.0161, found, 578.0160.

$N$-([2-(diphenylphosphoryl)]-5-iodo-4-methoxyphenyl)-4-methylbenzenesulfonamide (3as)

White solid; Mp: 151-153 °C, $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 10.75 (br, 1H, NH), 8.38 (d, $J$ = 8.0 Hz, 1H, ArH), 7.53-7.59 (m, 4H, ArH), 7.37-7.44 (m, 8H, ArH), 6.90 (d, $J$ = 8.0 Hz, 2H, ArH), 6.16 (d, $J$ = 16.0 Hz, 1H, ArH), 3.51 (s, 3H, ArOCH$_3$), 2.26 (s, 3H, ArCH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 154.0, 153.8, 143.2, 138.0, 137.9, 136.2, 133.5, 133.4, 132.6, 132.5, 131.9, 131.8, 130.6, 129.3, 128.8, 128.7, 127.2, 118.9, 117.9, 113.4, 113.3, 93.1, 93.0, 56.4, 21.6. HRMS (ESI-TOF): $m/z$ calcd for C$_{26}$H$_{23}$INO$_4$PSNa [M + Na]$^+$, 626.0022, found, 626.0022.

$N$-([2-(diphenylphosphoryl)]-4-methoxynaphthalen-1-yl)-4-methylbenzenesulfonamide (3at)

White solid; Mp: 151-153 °C, $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 10.68 (br, 1H, NH), 8.70-8.73 (m, 1H, ArH), 8.18-8.21 (m, 1H, ArH), 7.61-7.66 (m, 2H, ArH), 7.35-7.54 (m, 12H, ArH), 6.80-6.82 (m, 2H, ArH), 6.18-6.22 (m, 1H, ArH), 3.68 (s, 3H, ArOCH$_3$), 2.16 (s, 3H, ArCH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 152.8, 152.6, 143.0,
132.1, 132.0, 131.9, 131.8, 130.0, 128.5, 128.4, 128.1, 127.7, 126.9, 121.3, 118.1, 117.1, 104.9, 104.8, 55.5, 21.7. HRMS (ESI-TOF): m/z calcd for C_{30}H_{26}NO_{4}PSNa [M + Na]^+, 550.1212, found, 550.1212.

*N*-\((2-\text{(diphenylphosphoryl)}\)-4-ethoxyphenyl)-4-methylbenzenesulfonamide (3au)

White solid; Mp: 150-152 °C, \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 10.77\) (br, 1H, NH), 7.83-7.87 (m, 1H, ArH), 7.51-7.57 (m, 4H, ArH), 7.37-7.43 (m, 8H, ArH), 6.99-7.02 (m, 1H, ArH), 6.86-6.88 (m, 2H, ArH), 6.36-6.41 (m, 1H, ArH), 3.84 (q, \(J = 8.0\) Hz, 2H, CH\(_2\)), 2.24 (s, 3H, ArCH\(_3\)), 1.30 (t, \(J = 8.0\) Hz, 3H, CH\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 154.4, 154.3, 142.9, 136.8, 136.7, 136.4, 132.3, 132.2, 132.0, 131.9, 131.8, 131.0, 129.2, 128.7, 128.6, 127.2, 124.0, 123.9, 119.3, 119.1, 119.0, 118.7, 118.6, 118.3, 63.8, 21.6, 14.6. HRMS (ESI-TOF): m/z calcd for C\(_{27}\)H\(_{26}\)NO\(_4\)PSNa [M + Na]^+, 514.1212, found, 514.1211.

*N*-\((2-\text{(diphenylphosphoryl)}\)-4-isopropoxyphenyl)-4-methylbenzenesulfonamide (3av)

White solid; Mp: 177-179 °C, \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 10.74\) (br, 1H, NH), 7.81-7.87 (m, 4H, ArH), 7.51-7.57 (m, 4H, ArH), 7.38-7.44 (m, 8H, ArH), 6.98-7.02 (m, 1H, ArH), 6.86-6.89 (m, 2H, ArH), 6.33-6.37 (m, 1H, ArH), 4.24-4.30 (m, 1H, CH), 2.25 (s, 3H, ArCH\(_3\)), 1.19 (s, 3H, CH\(_3\)), 1.17 (s, 3H, CH\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 153.3, 153.1, 142.9, 136.7, 136.5, 132.3, 132.2, 132.0, 131.9, 131.8, 131.0, 129.2, 128.7, 128.6, 127.2, 123.9, 123.8, 120.4, 120.3, 120.2, 70.5, 21.8, 21.6. HRMS (ESI-TOF): m/z calcd for C\(_{28}\)H\(_{26}\)NO\(_4\)PSNa [M + Na]^+, 528.1369, found, 528.1367.

*N*-\((2-\text{(di-p-tolylphosphoryl)}\)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3ba)
White solid; Mp: 194-196 °C, ¹H NMR (400 MHz, CDCl₃): δ = 10.84 (br, 1H, NH), 7.82-7.86 (m, 1H, ArH), 7.52-7.55 (m, 2H, ArH), 7.25-7.32 (m, 5H, ArH), 7.18-7.20 (m, 3H, ArH), 6.97-7.00 (m, 1H, ArH), 6.88-6.90 (m, 2H, ArH), 6.37-6.41 (m, 1H, ArH), 3.64 (s, 3H, ArOCH₃), 2.41 (s, 3H, 2ArCH₃), 2.26 (s, 3H, ArCH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 154.9, 154.8, 142.9, 142.8, 136.8, 136.5, 131.9, 131.8, 129.4, 129.3, 129.1, 127.3, 123.7, 118.9, 117.7, 55.5, 21.7, 21.6. HRMS (ESI-TOF): m/z calcd for C₂₈H₂₈NO₄PSNa [M + Na]⁺, 528.1369, found, 528.1368.

N-(2-(di-m-tolylphosphoryl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3bb)

White solid; Mp: 173-175 °C, ¹H NMR (400 MHz, CDCl₃): δ = 10.81 (br, 1H, NH), 7.82-7.87 (m, 1H, ArH), 7.52-7.54 (m, 2H, ArH), 7.23-7.35 (m, 6H, ArH), 7.08-7.13 (m, 2H, ArH), 6.99-7.02 (m, 1H, ArH), 6.87-6.89 (m, 2H, ArH), 6.38-6.43 (m, 1H, ArH), 3.65 (s, 3H, ArOCH₃), 2.33 (s, 3H, 2ArCH₃), 2.24 (s, 3H, ArCH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 154.9, 154.8, 142.8, 138.6, 138.5, 136.9, 136.8, 136.6, 133.1, 132.3, 132.2, 131.9, 130.9, 129.7, 129.1, 129.0, 128.9, 128.5, 128.3, 127.2, 126.5, 123.6, 123.5, 119.7, 119.0, 118.9, 118.7, 117.8, 55.5, 21.5, 21.4. HRMS (ESI-TOF): m/z calcd for C₂₈H₂₈NO₄PSNa [M + Na]⁺, 528.1369, found, 528.1368.

N-(2-(bis(3,5-dimethylphenyl)phosphoryl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3bc)
White solid; Mp: 154-156 °C, $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 10.85$ (br, 1H, NH), 7.82-7.86 (m, 1H, ArH), 7.58-7.59 (m, 1H, ArH), 7.52-7.54 (m, 2H, ArH), 7.15 (s, 2H, ArH), 6.99-7.02 (m, 5H, ArH), 6.88-6.90 (m, 2H, ArH), 6.40-6.44 (m, 1H, ArH), 3.66 (s, 3H, ArOCH$_3$), 2.28 (s, 12H, 4ArCH$_3$), 2.24 (s, 3H, ArCH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 154.8$, 154.6, 142.6, 138.3, 138.2, 138.1, 136.7, 136.6, 133.5, 134.1, 134.0, 131.8, 130.7, 129.7, 129.5, 129.4, 129.3, 129.2, 128.9, 127.3, 127.2, 126.5, 123.3, 123.2, 119.9, 119.2, 119.1, 118.9, 117.5, 117.4, 115.8, 111.3, 109.2, 55.5, 21.5, 21.3. HRMS (ESI-TOF): $m/z$ calcd for C$_{30}$H$_{32}$NO$_4$PSNa [M + Na]$^+$, 556.1682, found, 556.1680.

$N$-(2-(bis(4-fluorophenyl)phosphoryl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3bd)

\[
\begin{array}{c}
\text{Ts} \quad \text{NH} \quad \text{P} \quad \text{O} \quad \text{Ar} \\
\text{OMe} \quad \text{F} \quad \text{F} \\
\end{array}
\]

White solid; Mp: 132-134 °C, $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 10.54$ (br, 1H, NH), 7.88-7.91 (m, 1H, ArH), 7.49-7.51 (m, 2H, ArH), 7.35-7.42 (m, 4H, ArH), 7.03-7.12 (m, 5H, ArH), 6.90-6.92 (m, 2H, ArH), 6.31-6.35 (m, 1H, ArH), 3.67 (s, 3H, ArOCH$_3$), 2.28 (s, 3H, ArCH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 166.6$ (d, $J = 3.0$ Hz), 166.5 (d, $J = 4.0$ Hz), 164.1, 164.0, 155.2, 155.0, 143.2, 136.8, 136.7, 136.5, 134.5, 134.4, 134.3, 134.2, 129.1, 127.1, 119.3, 118.7, 118.6, 118.3, 118.2, 118.1, 116.4, 116.2, 116.1, 116.0, 55.5, 21.4. HRMS (ESI-TOF): $m/z$ calcd for C$_{26}$H$_{22}$F$_2$NO$_4$PSNa [M + Na]$^+$, 536.0867, found, 536.0867.

$N$-(2-(bis(4-chlorophenyl)phosphoryl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3be)

\[
\begin{array}{c}
\text{Ts} \quad \text{NH} \quad \text{P} \quad \text{O} \quad \text{Ar} \\
\text{OMe} \quad \text{Cl} \quad \text{Cl} \\
\end{array}
\]

White solid; Mp: 185-187 °C, $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 10.46$ (br, 1H, NH),
7.90-7.93 (m, 1H, ArH), 7.46-7.48 (m, 2H, ArH), 7.36-7.39 (m, 4H, ArH), 7.27-7.32 (m, 4H, ArH), 7.04-7.07 (m, 1H, ArH), 6.88-6.90 (m, 2H, ArH), 6.30-6.34 (m, 1H, ArH), 3.67 (s, 3H, ArOCH$_3$), 2.30 (s, 3H, ArCH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 155.2, 155.1, 143.4, 139.4, 139.3, 136.8, 136.7, 136.5, 133.2, 133.0, 130.2, 129.2, 129.1, 129.0, 127.1, 124.6, 124.5, 118.9, 118.7, 118.6, 118.2, 117.9, 55.5, 21.6. HRMS (ESI-TOF): $m/z$ calcd for C$_{26}$H$_{22}$Cl$_2$NO$_4$PSNa [M + Na]$^+$, 568.0276, found, 568.0276. 

$N$-(2-(bis(4-(trifluoromethyl)phenyl)phosphoryl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3bf)

White solid; Mp: 185-187 °C, $^1$H NMR (400 MHz, DMSO-$_d$$_6$): $\delta$ = 10.09 (br, 1H, NH), 7.90-7.92 (m, 4H, ArH), 7.70-7.75 (m, 4H, ArH), 7.49-7.51 (m, 2H, ArH), 7.38-7.41 (m, 1H, ArH), 7.31-7.35 (m, 3H, ArH), 7.08-7.12 (m, 1H, ArH), 3.50 (s, 3H, ArOCH$_3$), 2.31 (s, 3H, ArCH$_3$); $^{13}$C NMR (100 MHz, DMSO-$_d$$_6$): $\delta$ = 157.7, 157.6, 143.7, 138.0, 137.0, 136.6, 132.7, 132.6, 131.6, 131.5, 130.1, 129.2, 127.7, 127.6, 127.2, 126.0, 125.9 (q, $J$ = 8.0 Hz), 125.8, 125.6, 122.9, 119.5, 118.5, 113.8, 113.7, 56.1, 21.4. HRMS (ESI-TOF): $m/z$ calcd for C$_{28}$H$_{22}$F$_6$NO$_4$PSNa [M + Na]$^+$, 636.0804, found, 636.0804. 

$N$-(2-(bis(3-fluoro-5-methylphenyl)phosphoryl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3bg)

White solid; Mp: 185-187 °C, $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 9.32 (br, 1H, NH), 7.69-7.76 (m, 2H, ArH), 7.47-7.49 (m, 2H, ArH), 7.35-7.39 (m, 2H, ArH), 6.98-7.09 (m, 6H, ArH), 6.82-6.85 (m, 1H, ArH), 3.54 (s, 3H, ArOCH$_3$), 2.36 (s, 3H, 2ArCH$_3$),
2.32 (s, 3H, ArCH₃); $^{13}$C NMR (100 MHz, CDCl₃): $\delta = 163.5$ (d, $J = 19.0$ Hz), 163.3, 161.0 (d, $J = 19.0$ Hz), 160.8, 157.0, 143.3, 141.2, 141.1, 141.0, 140.9, 136.5, 134.7, 134.6, 133.7, 133.6, 132.0, 131.9, 129.4, 128.5, 128.4, 128.3, 128.1, 128.0, 127.2, 127.1, 119.8, 119.6, 119.5, 118.5, 115.8, 115.7, 115.6, 115.5, 112.2, 112.2, 55.4, 21.5, 21.4. HRMS (ESI-TOF): $m/z$ calcd for C$_{28}$H$_{26}$F$_{2}$NO$_{4}$PSNa [M + Na]$^+$, 564.1180, found, 564.1180.

$N$-(2-(di(thiophen-2-yl)phosphoryl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (3bh)

White solid; Mp: 185-187 °C, $^1$H NMR (400 MHz, CDCl₃): $\delta = 10.60$ (br, 1H, NH), 7.84-7.88 (m, 1H, ArH), 7.72-7.75 (m, 2H, ArH), 7.58-7.60 (m, 2H, ArH), 7.27-7.29 (m, 2H, ArH), 7.03-7.14 (m, 3H, ArH), 6.95-6.97 (m, 2H, ArH), 6.58-6.63 (m, 1H, ArH), 3.67 (s, 3H, ArOCH$_{3}$), 2.27 (s, 3H, ArCH$_{3}$); $^{13}$C NMR (100 MHz, CDCl₃): $\delta = 155.3, 155.1, 143.1, 137.5, 137.3, 136.4, 136.3, 136.2, 134.8, 134.7, 133.9, 132.7, 129.2, 128.5, 128.3, 127.3, 124.1, 124.0, 120.3, 119.2, 118.9, 117.9, 117.7, 55.5, 21.6. HRMS (ESI-TOF): $m/z$ calcd for C$_{22}$H$_{20}$NO$_{4}$PS$_{3}$Na [M + Na]$^+$, 512.0184, found, 512.0184.

$N$-(2-(diphenylphosphanyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (6a)

White solid; Mp: 101-103 °C, $^1$H NMR (400 MHz, CDCl₃): $\delta = 7.67-7.70$ (m, 1H, ArH), 7.48-7.50 (m, 2H,ArH), 7.23-7.41 (m, 7H,ArH), 6.97-7.01 (m, 6H, ArH), 6.88-6.91 (m, 1H,ArH), 6.35 (br,1H, NH), 3.59 (s, 3H, ArOCH$_{3}$), 2.30 (s, 3H, ArCH$_{3}$); $^{13}$C NMR (100 MHz, CDCl₃): $\delta = 157.0, 143.4, 135.8, 134.7, 134.6, 133.9, 133.6, 133.4, 133.2, 130.3, 130.2, 129.3, 129.0, 128.7, 128.6, 127.4, 124.4, 120.0, 115.7, 55.3, 21.6; $^{31}$P NMR (CDCl₃, 160 MHz): $\delta = -24.2$; HRMS (ESI-TOF): $m/z$ calcd for
C_{28}H_{24}NO_{3}PSNa [M + Na]^+, 484.1107, found, 484.1108.

*N-(2-(diphenylphosphanyl)-4-ethoxyphenyl)-4-methylbenzenesulfonamide (6b)*

![Chemical structure of 6b]

White solid; Mp: 134-136 °C, \( ^1H \) NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.66-7.69 \) (m, 1H, ArH), 7.47-7.55 (m, 2H, ArH), 7.38-7.42 (m, 1H, ArH), 7.29-7.34 (m, 2H, ArH), 7.23-7.27 (m, 5H, ArH), 6.96-7.02 (m, 5H, ArH), 6.86-6.90 (m, 1H, ArH), 6.34-6.36 (m, 1H, ArH), 3.75-3.81 (m, 2H, ArH), 2.30 (s, 3H, ArCH\(_3\)), 1.27 (t, \( J = 8.0 \) Hz, 3H, CH\(_3\)); \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)): \( \delta = 156.4, 143.4, 135.8, 134.7, 134.6, 133.4, 133.2, 129.3, 129.0, 128.7, 128.6, 127.4, 124.4, 120.3, 116.5, 63.5, 21.6, 14.6; \( ^{31}P \) NMR (CDCl\(_3\), 160 MHz): \( \delta = -24.3 \); HRMS (ESI-TOF): \( m/z \) calcd for C\(_{27}\)H\(_{26}\)NO\(_3\)PSNa [M + Na]^+, 498.1263, found, 498.1260.

*N-(2-(diphenylphosphanyl)-4-isopropoxyphenyl)-4-methylbenzenesulfonamide (6c)*

![Chemical structure of 6c]

White solid; Mp: 134-136 °C, \( ^1H \) NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.64-7.69 \) (m, 1H, ArH), 7.48-7.52 (m, 2H, ArH), 7.38-7.43 (m, 1H, ArH), 7.30-7.34 (m, 2H, ArH), 7.23-7.27 (m, 5H, ArH), 6.96-7.01 (m, 6H, ArH), 6.86-6.90 (m, 1H, ArH), 6.30-6.36 (m, 1H, ArH), 4.17-4.23 (m, 1H, ArH), 2.30 (s, 3H, ArCH\(_3\)), 1.15 (s, 3H, CH\(_3\)), 1.13 (s, 3H, CH\(_3\)); \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)): \( \delta = 155.3, 143.4, 135.8, 134.8, 134.7, 133.7, 133.5, 133.4, 133.3, 133.2, 133.1, 129.9, 129.8, 129.3, 129.0, 128.9, 128.7, 128.6, 127.4, 124.5, 124.4, 121.4, 120.4, 118.4, 116.5, 70.1, 21.7, 21.6; \( ^{31}P \) NMR (CDCl\(_3\), 160 MHz): \( \delta = -24.4 \); HRMS (ESI-TOF): \( m/z \) calcd for C\(_{28}\)H\(_{28}\)NO\(_3\)PSNa [M + Na]^+, 512.1420, found, 512.1421.

*N-(2-(diphenylphosphanyl)-4-methoxy-6-methylphenyl)-4-methylbenzenesulphonamide (6d)*

![Chemical structure of 6d]
White solid; Mp: 134-136 °C, $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.59$-7.61 (m, 2H, ArH), 7.24-7.33 (m, 7H, ArH), 7.18-7.20 (m, 2H, ArH), 6.94-6.98 (m, 4H, ArH), 6.78-6.79 (m, 1H, ArH), 6.11-6.13 (m, 2H, ArH), 3.60 (s, 3H, ArOCH$_3$), 2.46 (s, 3H, ArCH$_3$), 2.40 (s, 3H, ArCH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 158.2$, 143.4, 140.8, 140.7, 138.9, 138.8, 137.3, 137.2, 135.8, 135.7, 133.8, 133.6, 130.2, 130.0, 129.2, 129.0, 128.7, 128.6, 128.0, 127.9, 117.7, 116.9, 55.1, 21.7, 21.3; $^{31}$P NMR (CDCl$_3$, 160 MHz): $\delta = -15.7$; HRMS (ESI-TOF): $m/z$ calc'd for C$_{27}$H$_{26}$NO$_3$PSNa [M + Na]$^+$, 498.1263, found, 498.1263.

$N$-(2-(diphenylphosphanyl)-4-methoxy-5-methylphenyl)-4-methylbenzenesulfonamide (6e)

White solid; Mp: 175-177 °C, $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.56$-7.57 (m, 1H, ArH), 7.47-7.50 (m, 2H, ArH), 7.28-7.32 (m, 2H, ArH), 7.22-7.26 (m, 5H, ArH), 6.96-7.04 (m, 6H, ArH), 6.22-6.23 (m, 1H, ArH), 3.43 (s, 3H, ArOCH$_3$), 2.28 (s, 3H, ArCH$_3$), 2.22 (s, 3H, ArCH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 155.4$, 143.4, 135.8, 135.4, 135.3, 134.1, 133.8, 133.2, 133.0, 130.2, 129.4, 129.3, 128.8, 128.6, 128.5, 127.4, 125.9, 125.8, 125.5, 125.4, 115.3, 55.2, 21.6, 16.4; $^{31}$P NMR (CDCl$_3$, 160 MHz): $\delta = -25.1$; HRMS (ESI-TOF): $m/z$ calc'd for C$_{27}$H$_{26}$NO$_3$PSNa [M + Na]$^+$, 498.1263, found, 498.1263.

$N$-(2-(diphenylphosphanyl)-4,5-dimethoxyphenyl)-4-methylbenzenesulfonamide (6f)
White solid; Mp: 142-144 °C, $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.76$ (d, $J = 8.0$ Hz, 1H, ArH), 7.48-7.50 (m, 2H, ArH), 7.38-7.39 (m, 1H, ArH), 7.28-7.32 (m, 2H, ArH), 7.21-7.26 (m, 4H, ArH), 6.94-6.98 (m, 6H, ArH), 6.31 (d, $J = 4.0$ Hz, 1H, ArH), 3.95 (s, 3H, ArOCH$_3$), 3.50 (s, 3H, ArOCH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 151.0$, 146.7, 143.6, 135.8, 135.5, 135.4, 133.0, 132.8, 132.2, 131.8, 131.7, 129.4, 129.2, 128.7, 128.6, 128.5, 127.3, 127.2, 117.9, 117.8, 116.5, 106.1, 56.2, 55.7, 21.6. $^{31}$P NMR (CDCl$_3$, 160 MHz): $\delta = -27.2$; HRMS (ESI-TOF): $m/z$ calcd for C$_{27}$H$_{26}$NO$_4$PSNa [M + Na]$^+$, 514.1212, found, 514.1215.

$N$-(5-chloro-2-(diphenylphosphanyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (6g)

White solid; Mp: 132-134 °C, $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.82$ (d, $J = 8.0$ Hz, 1H, ArH), 7.50-7.52 (m, 2H, ArH), 7.32-7.36 (m, 2H, ArH), 7.25-7.30 (m, 5H, ArH), 6.97-7.02 (m, 6H, ArH), 6.30-6.31 (m, 1H, ArH), 3.49 (s, 3H, ArOCH$_3$), 2.31 (s, 3H, ArCH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 152.5$, 143.7, 135.5, 134.4, 134.3, 134.2, 133.2, 132.1, 129.4, 129.2, 128.8, 128.7, 127.9, 127.8, 127.4, 125.1, 124.5, 124.4, 117.2, 55.9, 21.6. $^{31}$P NMR (CDCl$_3$, 160 MHz): $\delta = -24.7$; HRMS (ESI-TOF): $m/z$ calcd for C$_{26}$H$_{23}$ClNO$_3$PSNa [M + Na]$^+$, 518.0717, found, 518.0716.

$N$-(2-(diphenylphosphanyl)-5-iodo-4-methoxyphenyl)-4-methylbenzenesulfonamide (6h)

White solid; Mp: 145-147 °C, $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.67$-7.71 (m, 1H, ArH), 7.48-7.50 (m, 2H, ArH), 7.37-7.42 (m, 2H, ArH), 7.30-7.32 (m, 2H, ArH), 7.23-7.26 (m, 2H, ArH), 6.97-7.01 (m, 6H, ArH), 6.88-6.91 (m, 1H, ArH), 6.33-6.35 (m, 1H, ArH), 3.60 (s, 3H, ArOCH$_3$), 2.31 (s, 3H, ArCH$_3$); $^{13}$C NMR (100 MHz,
CDCl$_3$): $\delta$ = 157.0, 143.4, 135.8, 134.7, 134.6, 133.6, 133.4, 133.2, 131.9, 131.8, 129.3, 129.0, 128.7, 127.6, 128.5, 127.4, 127.2, 124.4, 120.0, 115.7, 55.3, 21.6. $^{31}$P NMR (CDCl$_3$, 160 MHz): $\delta$ = -24.2; HRMS (ESI-TOF): $m/z$ calcd for C$_{28}$H$_{23}$INO$_3$PSNa [M + Na]$^+$, 610.0073, found, 610.0073.

$N$-(2-(diphenylphosphanyl)-4-methoxynaphthalen-1-yl)-4-methylbenzenesulfonamide (6i)

White solid; Mp: 120-122 ºC, $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.39-8.41 (m, 1H, ArH), 8.17-8.20 (m, 1H, ArH), 7.51-7.57 (m, 5H, ArH), 7.37-7.41 (m, 1H, ArH), 7.28-7.33 (m, 4H, ArH), 7.09-7.11 (m, 2H, ArH), 7.00-7.04 (m, 4H, ArH), 6.80-6.82 (m, 1H, ArH), 6.21-6.22 (m, 1H, ArH), 3.61 (s, 3H, ArOCH$_3$), 2.33 (s, 3H, ArCH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 154.6, 143.5, 136.1, 136.0, 133.5, 133.3, 129.2, 128.8, 128.6, 128.5, 128.2, 127.1, 126.8, 125.9, 121.6, 107.3, 55.3, 21.6; $^{31}$P NMR (CDCl$_3$, 160 MHz): $\delta$ = -16.8; HRMS (ESI-TOF): $m/z$ calcd for C$_{30}$H$_{26}$NO$_3$PSNa [M + Na]$^+$, 534.1263, found, 534.1263.

$N$-(2-(di-p-tolylphosphanyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (6j)

White solid; Mp: 125-127 ºC, $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.64-7.68 (m, 1H, ArH), 7.48-7.50 (m, 2H, ArH), 7.33-7.35 (m, 1H, ArH), 7.06-7.07 (m, 4H, ArH), 6.99-7.01 (m, 2H, ArH), 6.86-6.90 (m, 5H, ArH), 6.35-6.36 (m, 1H, ArH), 3.61 (s, 3H, ArOCH$_3$), 2.33 (s, 6H, 2ArCH$_3$), 2.31 (s, 3H, ArCH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 156.9, 143.4, 139.1, 135.8, 133.6, 133.5, 133.3, 133.4, 133.2, 131.2, 131.1, 131.0, 130.9, 129.5, 129.4, 129.2, 127.4, 124.3, 124.2, 120.0, 115.2, 55.3, 21.6, 21.4; $^{31}$P NMR (CDCl$_3$, 160 MHz): $\delta$ = -25.6; HRMS (ESI-TOF): $m/z$ calcd for C$_{28}$H$_{26}$NO$_3$PSNa [M
+ Na][, 512.1420, found, 512.1420.

**N-(2-(di-m-tolylphosphanyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (6k)**

![Chemical structure](image)

White solid; Mp: 145-147 °C, $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.66-7.69 (m, 1H, ArH), 7.49-7.51 (m, 2H, ArH), 7.35-7.37 (m, 1H, ArH), 7.11-7.16 (m, 4H, ArH), 7.00-7.03 (m, 2H, ArH), 6.87-6.90 (m, 1H, ArH), 6.83-6.86 (m, 2H, ArH), 6.73-6.78 (m, 2H, ArH), 6.34-6.36 (m, 1H, ArH), 3.61 (s, 3H, ArOCH$_3$), 2.31 (s, 3H, ArCH$_3$), 2.26 (s, 6H, 2ArCH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 156.9, 143.0, 138.3, 138.2, 135.9, 134.4, 134.3, 134.2, 134.0, 133.7, 133.4, 130.6, 130.5, 130.3, 129.9, 129.3, 128.6, 128.5, 127.5, 124.3, 124.2, 120.1, 115.4, 55.3, 21.6, 21.5; $^{31}$P NMR (CDCl$_3$, 160 MHz): $\delta$ = -24.0; HRMS (ESI-TOF): $m/z$ calcd for C$_{28}$H$_{28}$NO$_3$PSNa [M + Na]$^+$, 512.1420, found, 512.1420.

**N-(2-(bis(3,5-dimethylphenyl)phosphanyl)-4-methoxyphenyl)-4-methylbenzenesulfonamide (6l)**

![Chemical structure](image)

White solid; Mp: 166-168 °C, $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.63-7.67 (m, 1H, ArH), 7.49-7.51 (m, 3H, ArH), 7.01-7.04 (m, 3H, ArH), 6.94 (m, 3H, ArH), 6.85-6.89 (m, 1H, ArH), 6.61-6.63 (m, 2H, ArH), 6.35-6.38 (m, 2H, ArH), 3.63 (s, 3H, ArOCH$_3$), 2.21 (s, 3H, 5ArCH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 156.8, 156.2, 143.2, 143.1, 138.1, 138.0, 137.9, 135.9, 134.1, 134.0, 133.5, 133.3, 131.2, 131.0, 130.9, 130.8, 129.1, 127.5, 127.4, 124.1, 120.4, 120.1, 116.0, 115.1, 55.3, 21.5, 21.3; $^{31}$P NMR (CDCl$_3$, 160 MHz): $\delta$ = -23.5; HRMS (ESI-TOF): $m/z$ calcd for C$_{30}$H$_{32}$NO$_3$PSNa [M + Na]$^+$, 540.1733, found, 540.1733.
N-(2-(bis(4-chlorophenyl)phosphino)-4-methoxyphenyl)-4-methylbenzenesulfonamide (6m)

![Structure of 6m]

White solid; Mp: 160-162 °C, $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.71-7.74$ (m, 1H, ArH), 7.43-7.45 (m, 2H, ArH), 7.32-7.34 (m, 1H, ArH), 7.21-7.24 (m, 4H, ArH), 6.86-6.98 (m, 7H, ArH), 6.30 (t, $J = 4.0$ Hz, 1H, ArH), 3.64 (s, 3H, ArOCH$_3$), 2.32 (s, 3H, ArCH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 157.2$, 143.8, 135.8, 135.7, 134.6, 134.4, 133.9, 133.7, 132.9, 132.8, 129.3, 129.1, 129.0, 127.2, 124.8, 124.7, 120.1, 115.9, 55.4, 21.6; $^{31}$P NMR (CDCl$_3$, 160 MHz): $\delta = -26.3$; HRMS (ESI-TOF): $m/z$ calcd for C$_{26}$H$_{22}$Cl$_2$NO$_3$PSNa [M + Na]$^+$, 552.0327, found, 552.0326.

N-(2-(bis(4-fluorophenyl)phosphino)-4-methoxyphenyl)-4-methylbenzenesulfonamide (6n)

![Structure of 6n]

White solid; Mp: 146-148 °C, $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.69-7.72$ (m, 1H, ArH), 7.45-7.47 (m, 2H, ArH), 7.26-7.30 (m, 2H, ArH), 6.91-7.01 (m, 10H, ArH), 6.29 (m, 1H, ArH), 3.63 (s, 3H, ArOCH$_3$), 2.32 (s, 3H, ArCH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 164.8$ (d, $J = 249.0$ Hz), 162.3, 157.1, 143.6, 135.9, 135.4, 134.3, 135.2, 135.1, 133.7, 133.4, 129.9, 129.3, 127.3, 124.7, 123.2, 119.9, 116.2, 116.1, 116.0, 115.9, 115.7, 55.3, 21.5; $^{31}$P NMR (CDCl$_3$, 160 MHz): $\delta = -26.4$; HRMS (ESI-TOF): $m/z$ calcd for C$_{26}$H$_{22}$F$_2$NO$_3$PSNa [M + Na]$^+$, 520.0918, found, 520.0918.

N-(2-(bis(3-fluoro-5-methylphenyl)phosphino)-4-methoxyphenyl)-4-methylbenzenesulfonamide (6o)
White solid; Mp: 177-179 °C, \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.41\) - 7.43 (m, 2H, ArH), 7.25 - 7.27 (m, 1H, ArH), 7.19 - 7.21 (m, 2H, ArH), 6.81 - 6.87 (m, 5H, ArH), ArH), 6.31 - 6.35 (m, 2H, ArH), 6.25 (m, 1H, ArH), 5.99 (t, \(J = 8.0\) H, 1H, ArH), 3.71 (s, 3H, ArOCH\(_3\)), 2.35 (s, 3H, ArCH\(_3\)), 2.31 (s, 3H, 2ArCH\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 164.0\) (d, \(J = 7.0\) Hz), 163.9, 161.5 (d, \(J = 6.0\) Hz), 161.4, 159.4, 159.2, 143.9, 140.7, 140.6, 140.6, 140.5, 138.0, 137.9, 137.8, 135.3, 130.7, 130.6, 130.4, 130.3, 129.6, 129.4, 128.8, 127.3, 127.1, 125.9, 125.7, 125.5, 117.0, 116.8, 116.7, 116.6, 116.5, 111.0, 56.1, 21.4, 21.3; \(^{31}\)P NMR (CDCl\(_3\), 160 MHz): \(\delta = -16.6\); HRMS (ESI-TOF): \(m/z\) calcld for C\(_{28}\)H\(_{26}\)F\(_2\)NO\(_3\)PSNa [M + Na]+, 548.1231, found, 548.1231.

\(N\)-(2-(di(thiophen-2-yl)phosphino)-4-methoxyphenyl)-4-methylbenzenesulfonamide (6p)

White solid; Mp: 165-167 °C, \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.55\) - 7.58 (m, 3H, ArH), 7.50 - 7.52 (m, 2H, ArH), 7.04 - 7.10 (m, 6H, ArH), 6.86 - 6.90 (m, 2H, ArH), 6.63 - 6.65 (m, 1H, ArH), 3.67 (s, 3H, ArOCH\(_3\)), 2.35 (s, 3H, ArCH\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 157.4, 143.6, 136.2, 136.0, 135.9, 135.8, 135.6, 132.9, 132.8, 132.6, 132.1, 131.9, 129.4, 128.4, 128.3, 127.4, 127.3, 126.0, 118.4, 115.8, 55.3, 21.6; \(^{31}\)P NMR (CDCl\(_3\), 160 MHz): \(\delta = -47.9\); HRMS (ESI-TOF): \(m/z\) calcld for C\(_{22}\)H\(_{20}\)NO\(_3\)PS\(_3\)Na [M + Na]+, 496.0235, found, 496.0235.

\(N\)-(2-(diphenylphosphoryl)-4-hydroxyphenyl)-4-methylbenzenesulfonamide (7)
White solid; Mp: 179-181 °C, \(^1\)H NMR (400 MHz, CDOD): \(\delta = 7.73-7.76\) (m, 1H, ArH), 7.61-7.66 (m, 2H, ArH), 7.44-7.51 (m, 4H, ArH), 7.32-7.39 (m, 6H, ArH), 6.97-7.01 (m, 1H, ArH), 6.88-6.90 (m, 2H, ArH), 6.32-6.36 (m, 1H, ArH), 2.24 (s, 3H, ArCH\(_3\)); \(^{13}\)C NMR (100 MHz, CDOD): \(\delta = 153.7, 153.6, 143.6, 135.8, 135.0, 134.9, 132.6, 132.5, 131.5, 131.4, 131.3, 130.3, 129.1, 128.8, 128.6, 126.7, 124.1, 124.0, 120.6, 119.1, 119.0, 118.7, 117.7, 20.2; \(^{31}\)P NMR (CDCl\(_3\), 160 MHz): \(\delta = 39.1;\) HRMS (ESI-TOF): \(m/z\) calcd for C\(_{25}\)H\(_{22}\)NO\(_4\)PSNa [M + Na]\(^+\), 486.0899, found, 486.0899.

3-(diphenylphosphoryl)-4-((4-methylphenyl)sulphonamido)phenyltrifluoromethanesulfonate (8)

White solid; Mp: 163-165 °C, \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 11.19\) (br, 1H, NH), 7.91-7.95 (m, 1H, ArH), 7.58-7.63 (m, 4H, ArH), 7.43-7.48 (m, 8H, ArH), 7.31-7.34 (m, 1H, ArH), 6.99-7.01 (m, 2H, ArH), 6.74-6.79 (m, 1H, ArH), 2.31 (s, 3H, ArCH\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 144.0, 143.9, 143.8, 143.7, 136.2, 133.0, 132.9, 131.9, 131.8, 130.7, 129.6, 129.5, 129.1, 128.9, 127.1, 126.1, 125.9, 125.8, 123.3, 122.4, 122.3, 120.1, 120.0, 119.0, 117.0 (q, \(J = 319.0\) Hz), 113.8, 21.6; \(^{31}\)P NMR (CDCl\(_3\), 160 MHz): \(\delta = 35.9;\) F\(^{19}\) NMR (376 MHz, CDCl\(_3\)): \(\delta = -72.5;\) HRMS (ESI-TOF): \(m/z\) calcd for C\(_{26}\)H\(_{21}\)F\(_3\)NO\(_6\)PS\(_2\)Na [M + Na]\(^+\), 618.0392, found, 618.0392.

N-(2-(diphenylphosphoryl)phenyl)-4-methylbenzenesulphonamide (9)

White solid; Mp > 400 °C, \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 11.13\) (br, 1H, NH), 7.85-7.89 (m, 1H, ArH), 7.54-7.60 (m, 4H, ArH), 7.39-7.47 (m, 9H, ArH), 6.87-7.00 (m, 4H, ArH), 2.27 (s, 3H, ArCH\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 144.0, 143.1, 136.6, 133.4, 133.3, 133.2, 133.1, 132.4, 132.3, 132.1, 132.0, 131.9, 131.0, 129.3, 129.1, 128.8, 128.6, 126.7, 124.1, 124.0, 120.6, 119.1, 119.0, 118.7, 117.7, 20.2; \(^{31}\)P NMR (CDCl\(_3\), 160 MHz): \(\delta = 39.1;\) HRMS (ESI-TOF): \(m/z\) calcd for C\(_{25}\)H\(_{22}\)NO\(_4\)PSNa [M + Na]\(^+\), 486.0899, found, 486.0899.
128.7, 128.6, 127.2, 122.9, 122.8, 121.1, 121.0, 117.6, 116.6, 21.6; \(^{31}\)P NMR (CDCl\(_3\), 160 MHz): \(\delta = 37.1\); HRMS (ESI-TOF): \(m/z\) calcd for C\(_{25}\)H\(_{22}\)NO\(_3\)PSNa [M + Na]^+, 470.0950, found, 470.0950.

\textbf{N-(2-(diphenylphosphanyl)phenyl)-4-methylbenzenesulfonamide (10)}

White solid; Mp: 140-141 °C, \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.83-7.85\) (m, 1H, ArH), 7.55-7.60 (m, 1H, ArH), 7.47-7.51 (m, 2H, ArH), 7.41-7.46 (m, 1H, ArH), 7.31-7.36 (m, 3H, ArH), 7.28-7.29 (m, 1H, ArH), 7.24-7.25 (m, 1H, ArH), 6.93-7.05 (m, 7H, ArH), 6.85-6.89 (m, 1H, ArH), 2.29 (s, 3H, ArCH\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 153.4, 143.5, 135.8, 135.1, 134.5, 133.4, 133.2, 132.0, 131.9, 130.8, 129.4, 129.3, 128.9, 128.7, 128.6, 127.2, 127.1, 125.1, 121.0, 21.6; \(^{31}\)P NMR (CDCl\(_3\), 160 MHz): \(\delta = -26.6\); HRMS (ESI-TOF): \(m/z\) calcd for C\(_{25}\)H\(_{22}\)NO\(_3\)PSNa [M + Na]^+, 454.1001, found, 454.1001.
Copies of $^1$H and $^{13}$C spectra of 3, 6 and 7-10

**Figure S1.** $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 3aa

**Figure S2.** $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 3aa
**Figure S3.** $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 3ab

**Figure S4.** $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 3ab
Figure S5. $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 3ac

Figure S6. $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 3ac
Figure S7. $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 3ad

Figure S8. $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 3ad
Figure S9. $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 3ae

Figure S10. $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 3ae
Figure S11. $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 3af

Figure S12. $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 3af
Figure S13. $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 3ag

Figure S14. $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 3ag
Figure S15. $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 3ah

Figure S16. $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 3ah
Figure S17. $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 3ai

Figure S18. $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 3ai
Figure S19. $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 3aj

Figure S20. $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 3aj
Figure S21. $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 3ak

Figure S22. $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 3ak
Figure S23. $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 3al

Figure S24. $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 3al
Figure S25. $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 3am

Figure S26. $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 3am
Figure S27 $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 3an

Figure S28. $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 3an
Figure S29 $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 3ao

Figure S30 $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 3ao
Figure 31. $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 3ap

Figure 32. $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 3ap
Figure 33. $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 3aq

Figure 34. $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 3aq
Figure 35. $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 3ar

Figure 36. $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 3ar
Figure 37. $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 3as

Figure 38 $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 3as
Figure 39 $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 3at

Figure 40 $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 3at
Figure 41 $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 3au

Figure 42 $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 3au
Figure 43 $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 3av

Figure 44 $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 3av
**Figure 45** $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 3ba

**Figure 46** $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 3ba
Figure 47 $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 3bb

Figure 48 $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 3bb
Figure 49 $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 3bc

Figure 50 $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 3bc
Figure 51 $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 3bd

Figure 52 $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 3bd
**Figure 53** $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 3be

**Figure 54** $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 3be
Figure 55 $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 3bf

Figure 56 $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 3bf
Figure 57 $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 3bg

Figure 58 $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 3bg
**Figure 59** $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 3bh

**Figure 60** $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 3bh
Figure 61. $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 6a

Figure 62. $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 6a
**Figure 63.** $^{31}$P NMR (CDCl$_3$, 160 MHz) spectra of compound 6a

**Figure 64.** $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 6b
Figure 65. $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 6b

Figure 66. $^{31}$P NMR (CDCl$_3$, 160 MHz) spectra of compound 6b
Figure 67. $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 6c

Figure 68. $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 6c
Figure 69. $^{31}$P NMR (CDCl$_3$, 160 MHz) spectra of compound 6c

Figure 70. $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 6d
Figure 71. $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 6d

Figure 72. $^{31}$P NMR (CDCl$_3$, 160 MHz) spectra of compound 6d
Figure 73. $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 6e

Figure 74. $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 6e
Figure 75. $^{31}$P NMR (CDCl$_3$, 160 MHz) spectra of compound 6e

Figure 76. $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 6f
Figure 77. $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 6f

Figure 78. $^{31}$P NMR (CDCl$_3$, 160 MHz) spectra of compound 6f
Figure 79. $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 6g

Figure 80. $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 6g
Figure 81. $^{31}$P NMR (CDCl$_3$, 160 MHz) spectra of compound 6g

![Figure 81. $^{31}$P NMR (CDCl$_3$, 160 MHz) spectra of compound 6g](image)

Figure 82. $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 6h

![Figure 82. $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 6h](image)
Figure 83. $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 6h

Figure 84. $^{31}$P NMR (CDCl$_3$, 160 MHz) spectra of compound 6h
Figure 85. $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 6i

Figure 86. $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 6i
Figure 87. $^{31}$P NMR (CDCl$_3$, 160 MHz) spectra of compound 6i

Figure 88. $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 6j
Figure 89. $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 6j

Figure 90. $^{31}$P NMR (CDCl$_3$, 160 MHz) spectra of compound 6j
Figure 91. $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 6k

Figure 92. $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 6k
Figure 93. $^{31}$P NMR (CDCl$_3$, 160 MHz) spectra of compound 6k

Figure 94. $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 6l
Figure 95. $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 6l

Figure 96. $^{31}$P NMR (CDCl$_3$, 160 MHz) spectra of compound 6l
Figure 97. $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 6m

Figure 98. $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 6m
Figure 99. $^{31}$P NMR (CDCl$_3$, 160 MHz) spectra of compound 6m

Figure 100. $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 6n
**Figure 101.** $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 6n

**Figure 102.** $^{31}$P NMR (CDCl$_3$, 160 MHz) spectra of compound 6n
Figure 103. $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 6o

Figure 104. $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 6o
Figure 105. $^{31}$P NMR (CDCl$_3$, 160 MHz) spectra of compound 6o

Figure 106. $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 6p
Figure 107. $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 6p

Figure 108. $^{31}$P NMR (CDCl$_3$, 160 MHz) spectra of compound 6o
Figure 109. $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 7

Figure 110. $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 7
Figure 111. $^{31}$P NMR (CDCl$_3$, 160 MHz) spectra of compound 7

Figure 112. $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 8
Figure 113. $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 8

Figure 114. $^{31}$P NMR (CDCl$_3$, 160 MHz) spectra of compound 8
Figure 115. $^{19}$FNMR (CDCl$_3$, 160 MHz) spectra of compound 8

![Figure 115](image)

Figure 116. $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 9

![Figure 116](image)
Figure 117. $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 9

Figure 118. $^{31}$P NMR (CDCl$_3$, 160 MHz) spectra of compound 9
Figure 119. $^1$H NMR (400MHz, CDCl$_3$) spectra of compound 10

Figure 120. $^{13}$C NMR (100MHz, CDCl$_3$) spectra of compound 10
Figure 121. $^{31}$P NMR (CDCl$_3$, 160 MHz) spectra of compound 10

Figure 122. HRMS (ESI-TOF): spectra of compound 3aa