Electronic Supplementary Material (ESI) for ChemComm.

Multicomponent Reactions Involving Phosphines, Arynes and Aldehydes

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Supporting Information

1. General Information

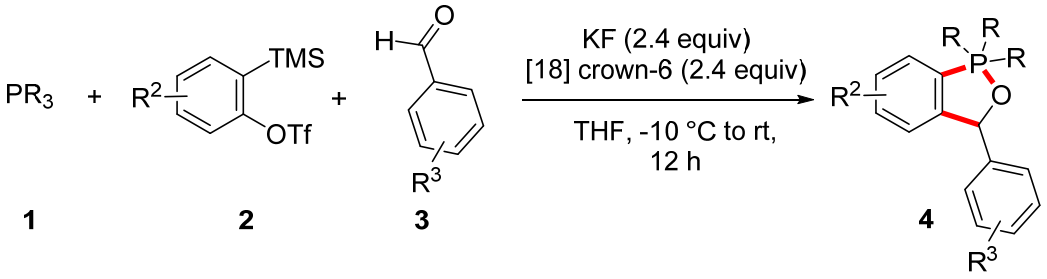
Unless otherwise specified, all reactions were carried out under an atmosphere of argon in flame-dried reaction vessels with Teflon screw caps. 30 °C corresponds to the room temperature of the lab when the experiments were carried out. THF was freshly purified by distillation over Na-benzophenone and was transferred under argon. [18] Crown 6 was recrystallized from dry CH_3CN and KF was dried by heating at 110 °C for 12 h and left to cool under argon. The aldehydes and trifluoroacetophenone were purchased from either Sigma Aldrich or Acros Organics. The aldehydes were purified either by distillation (for liquids) or washing with $NaHCO_3$ after dissolving in ether or dichloromethane (for solids), prior to use. Phosphines and triphenylarsine were purchased from Sigma Aldrich or Alfa Aesar and used as received. The 2(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** and the other symmetric and unsymmetric aryne precursors were synthesized following literature procedure.[1]

Analytical thin layer chromatography was performed on TLC Silica gel 60 F_{254}. Visualization was accomplished with short wave UV light or Iodine vapor. Chromatography was performed on silica gel (100-200 mesh) by standard techniques eluting with solvents as indicated.

All compounds were fully characterized. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV 400, 500 in solvents as indicated. Chemical shifts (δ) are given in ppm. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δH = 7.26 ppm, δC = 77.16 ppm). Infrared spectra were recorded on a Bruker Alpha-E Infrared Spectrophotometer. The wave numbers (n) of recorded IR-signals are quoted in cm^{-1}. HRMS data were recorded on either Thermo Scientific Q-Exactive, Accela 1250 pump or Waters SYNAPT G2 High Definition Mass Spectroscopy System. X-ray intensity data measurements were carried out on a Bruker SMART APEX II CCD diffractometer with graphite-monochromatized (MoK_α= 0.71073Å) radiation.

[1] (*a*) Y. Sato, T. Tamura, A. Kinbara and M. Morib, *Adv. Synth. Catal.* 2007, **349**, 647; (*b*) D. Peña, A. Cobas, D. Pérez and E. Guitián, *Synthesis* 2002, 1454.

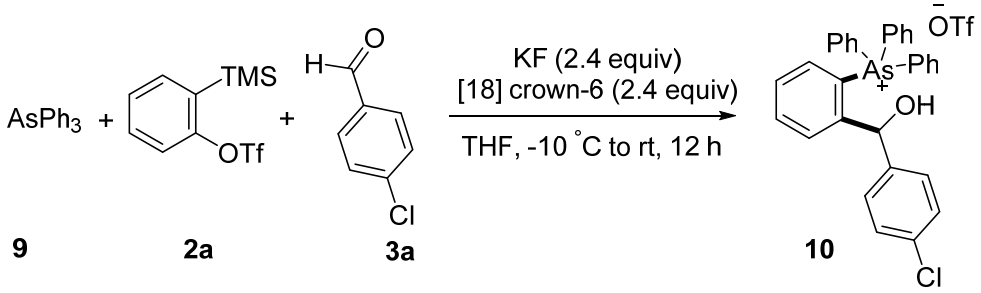
2. General Procedure for the MCR Involving Phosphine, Aryne and Aldehyde



1 **2** **3** **4**

To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the phosphine **1** (0.50 mmol), KF (70 mg, 1.20 mmol) and 18-crown-6 (0.317 mg, 1.20 mmol). Then the screw-capped tube was evacuated and backfilled with argon. The mixture was dissolved in THF (3.0 mL) under argon atmosphere and subsequently cooled the reaction mixture to -10 °C and kept stirring for five minutes. To the stirring solution aryne precursor **2** (0.60 mmol) was added and continued stirring for another five minutes followed by addition of the aldehyde **3** (0.75 mmol). Then the reaction mixture was slowly warmed to rt and kept stirring for 12 h. When TLC control showed the completion of the reaction (typically after 12 h), the reaction stopped and the solvent was evaporated and the crude residue was purified by column chromatography on silica gel (100-200 mesh) (Petroleum ether/EtOAc = 40/60) to afford the corresponding benzooxaphosphole derivatives **4** in moderate to good yields.

3. Procedure for the MCR Involving Triphenylarsine, Aryne and Aldehyde

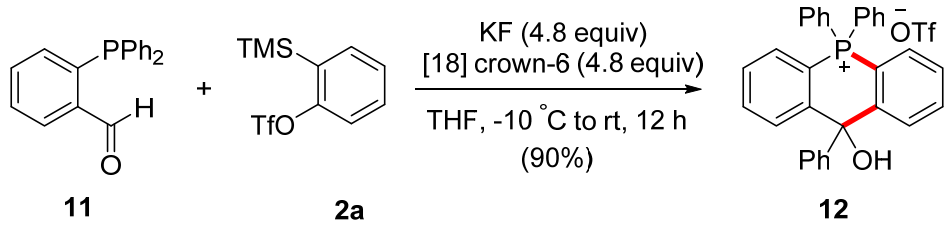


9 **2a** **3a** **10**

To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the triphenylarsine **9** (0.153 g, 0.50 mmol), KF (70 mg, 1.20 mmol) and 18-crown-6 (0.317 mg, 1.20

mmol). Then the screw-capped tube was evacuated and backfilled with argon. The mixture was dissolved in THF (3.0 mL) under argon atmosphere and subsequently cooled the reaction mixture to -10 °C and kept stirring for five minutes. To the stirring solution 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.179 g, 146 µL, 0.60 mmol) was added and continued stirring for another five minutes followed by addition of the 4-chlorobenzaldehyde **3a** (0.105 g, 0.75 mmol). Then the reaction mixture was slowly warmed to rt and kept stirring for 12 h. After 12 h the reaction stopped and the solvent was evaporated and the crude residue was purified by column chromatography on silica gel (EtOAc) followed by crystallization with EtOAc/Petroleum ether afforded the (2-((4-chlorophenyl)(hydroxy)methyl)phenyl) triphenylarsonium trifluoromethanesulfonate **10** in 52% yield.

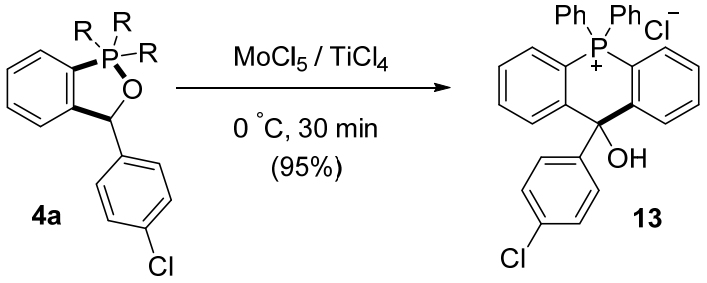
4. Procedure for the Intramolecular Reaction



11 **2a** **12**

To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the 2-(diphenylphosphanyl)benzaldehyde **11** (0.073 g, 0.25 mmol), KF (70 mg, 1.20 mmol) and 18-crown-6 (0.317 mg, 1.20 mmol). Then the screw-capped tube was evacuated and backfilled with argon. The mixture was dissolved in THF (3.0 mL) under argon atmosphere and subsequently cooled the reaction mixture to -10 °C and kept stirring for five minutes. To the stirring solution 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.179 g, 146 µL, 0.60 mmol) was added and continued stirring at 25° C for 12 h. After 12 h the reaction stopped and the solvent was evaporated and the crude residue was purified by column chromatography on silica gel (EtOAc) followed by crystallization with EtOAc/Petroleum ether afforded the (2-((4-chlorophenyl) (hydroxy)methyl)phenyl)triphenylarsonium trifluoromethanesulfonate **12** in 90% yield.

5. Procedure for the Molybdenum-Mediated C-C Coupling Reaction

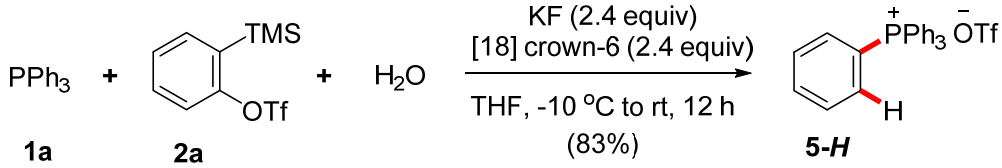


To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the **4a** (120 mg, 0.25 mmol) in dichloromethane (5.0 mL) and the mixture was cooled to 0 °C. To the cold solution was added a solution of $TiCl_4$ in dichloromethane (0.5 mL, 1.0 M, 0.50 mmol) at 0 °C and stirred for five minutes at this temperature under argon atmosphere. Then $MoCl_5$ (137 mg, 0.50 mmol) was added and the mixture was stirred for 30 min at 0 °C.[2] Subsequently, a saturated solution of sodium bicarbonate (10 mL) was added and it was stirred for further 5 minutes. The mixture was extracted with dichloromethane (3×50 mL), dried over sodium sulfate and the solvent was evaporated and the crude residue was purified by flash column chromatography on silica gel (DCM/MeOH = 90/10) afforded the 10-(4-chlorophenyl)-10-hydroxy-5,5-diphenyl-5,10-dihydroacridophosphin-5-ium chloride **13** in 95% yield.

6. Mechanistic Experiments

a. Deuterium Labeling Experiment

Experiment under Optimized Reaction Condition Using H_2O in the Absence of Aldehyde

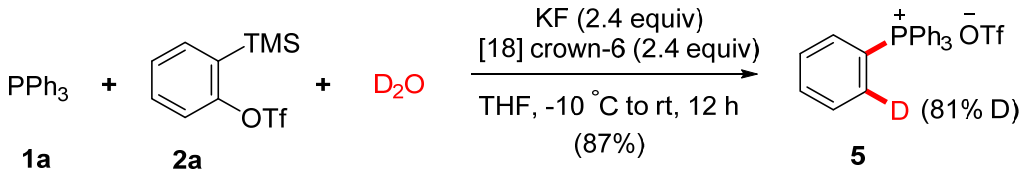


To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the triphenylphosphine **1a** (131 mg, 0.50 mmol) KF (70 mg, 1.20 mmol) and 18-crown-6 (0.317 mg,

[2] S. Trosien, P. Böttger and S. R. Waldvoge, *Org. Lett.* 2014, **16**, 402.

1.20 mmol). Then the screw-capped tube was evacuated and backfilled with argon. The mixture was dissolved in THF (3.0 mL) under argon atmosphere and subsequently cooled the reaction mixture to -10 °C and kept stirring for five minutes. To the stirring solution 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (179 mg, 146 µL, 0.60 mmol) was added and continued stirring for another five minutes followed by addition of the water (18 mg, 18 µL, 1.00 mmol). Then the reaction mixture was slowly warmed to rt and kept stirring for 12 h. When the reaction was complete, the solvent was evaporated and the crude residue was purified by flash column chromatography on silica gel (MeOH/DCM = 05/95) to afford the tetraphenyl phosphonium trifluoromethanesulfonate **5-*H*** as a white solid (202 mg, 83% yield).[3]

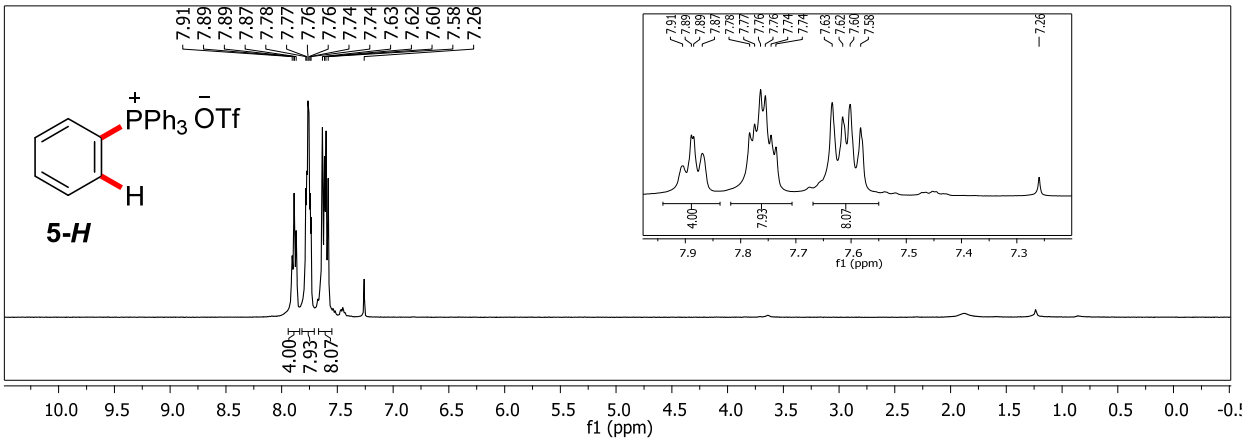
Experiment under Optimized Reaction Condition with D_2O in the Absence of Aldehyde



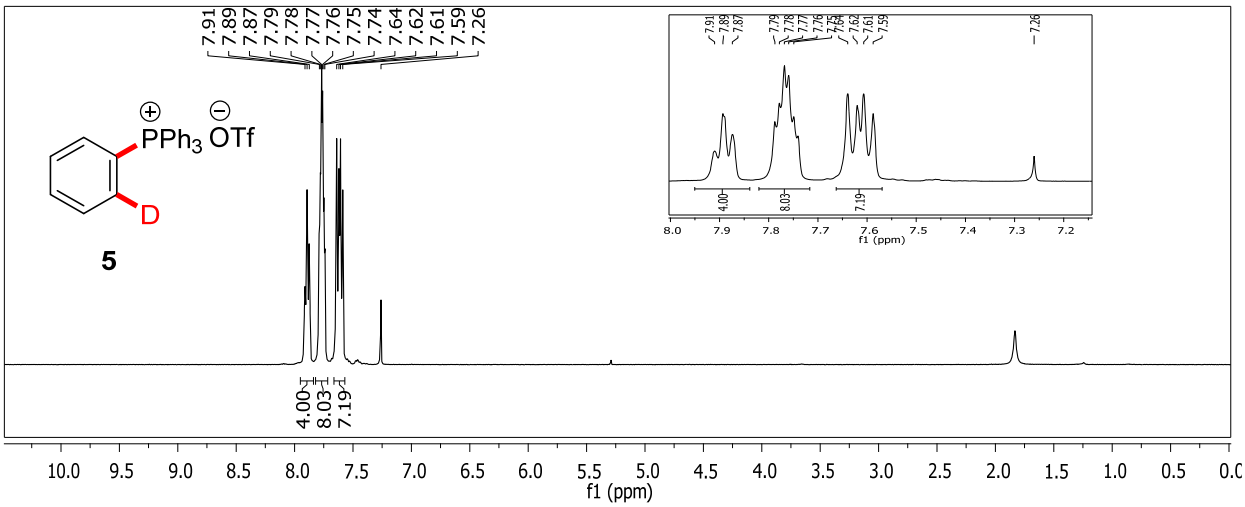
To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the triphenylphosphine **1a** (131 mg, 0.50 mmol) KF (70 mg, 1.20 mmol) and 18-crown-6 (0.317 mg, 1.20 mmol). Then the screw-capped tube was evacuated and backfilled with argon. The mixture was dissolved in THF (3.0 mL) under argon atmosphere and subsequently cooled the reaction mixture to -10 °C and kept stirring for five minutes. To the stirring solution 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (179 mg, 146 µL, 0.60 mmol) was added and continued stirring for another five minutes followed by addition of the Deuterium Oxide (20 mg, 18 µL, 1.00 mmol). Then the reaction mixture was slowly warmed to rt and kept stirring for 12 h. When the reaction was complete, the solvent was evaporated and the crude residue was purified by flash column chromatography on silica gel (MeOH/DCM = 05/95) to afford the triphenyl(phenyl-2-*d*)phosphonium trifluoromethanesulfonate **5** as a white solid (213 mg, 87% yield). *The incorporation of 81% deuterium at the 2-position of the ring indicates the initial formation of the zwitterionic intermediate from PPh_3 and aryne, which is subsequently quenched by D_2O leading to* ***5****.*

[3] E. Rémond, A. Tessier, F. R. Leroux, J. Bayardon and Jugé, S. *Org. Lett.* 2010, **12**, 1568.

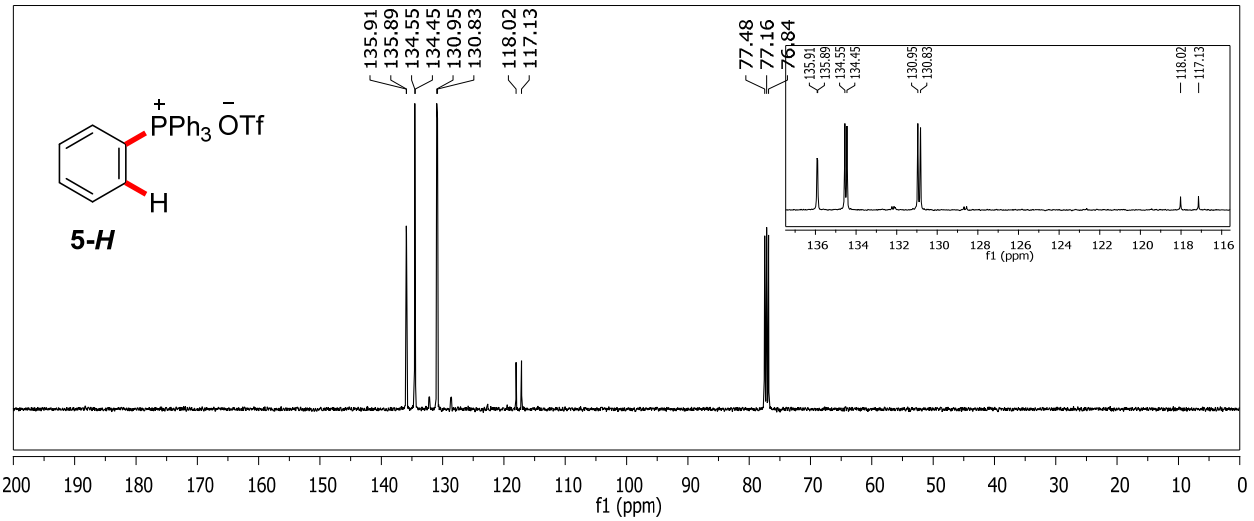
^{1}H-NMR Spectrum of Tetraphenylphosphonium Trifluoromethanesulfonate ($CDCl_3$) (5-*H*)



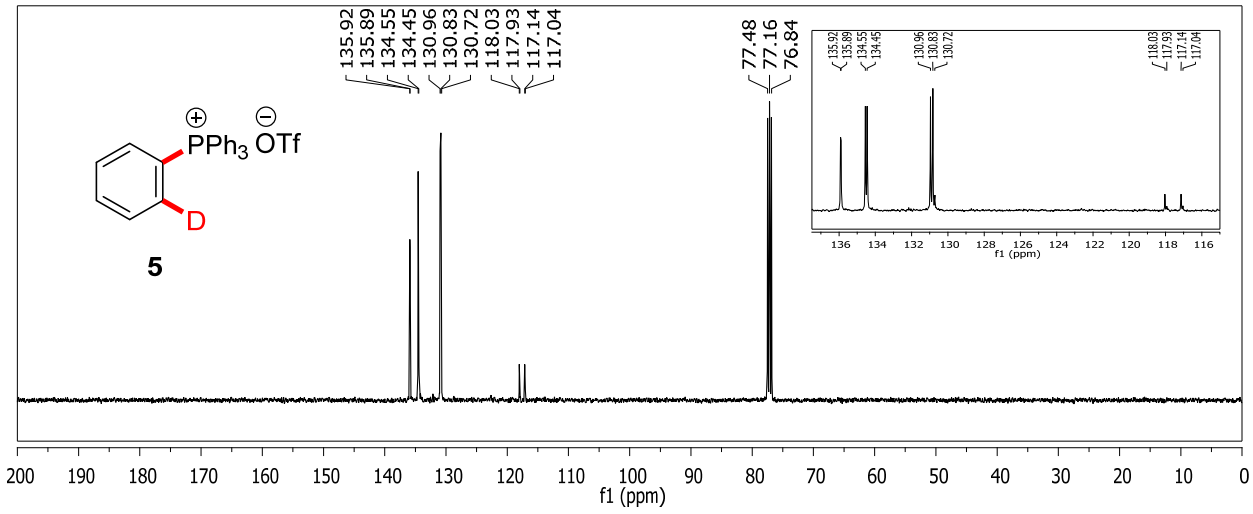
^{1}H-NMR of Triphenyl(phenyl-2-*d*)phosphonium Trifluoromethanesulfonate ($CDCl_3$) (5)



^{13}C-NMR Spectrum of Tetraphenylphosphonium Trifluoromethanesulfonate ($CDCl_3$) (5-*H*)

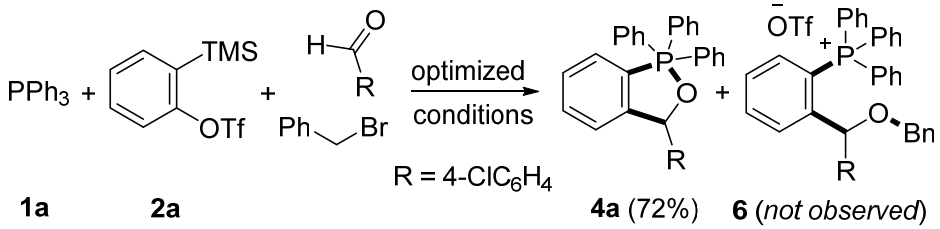


^{13}C-NMR of Triphenyl(phenyl-2-*d*)phosphonium Trifluoromethanesulfonate ($CDCl_3$) (5)



b. Zwitterion Trapping Experiments

Experiment to Intercept the Zwitterion with Benzylbromide

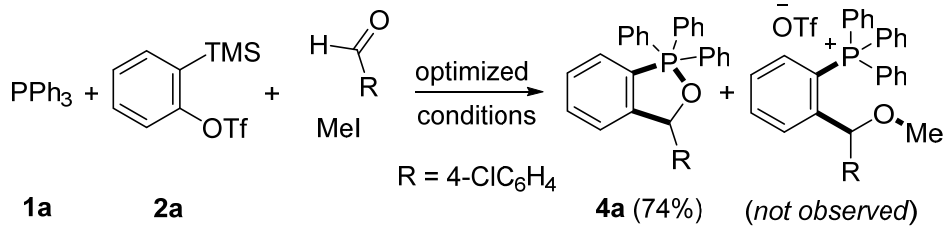


To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the triphenylphosphine **1a** (131 mg, 0.50 mmol) KF (70 mg, 1.2 mmol) and 18-crown-6 (0.317 mg, 1.2 mmol). Then the screw-capped tube was evacuated and backfilled with argon. The mixture was dissolved in THF (2.0 mL) under argon atmosphere and subsequently cooled the reaction mixture to -10 °C and kept stirring for five minutes. To the stirring solution 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (179 mg, 146 µL, 0.60 mmol) was added and continued stirring for another five minutes followed by addition of the mixture of 4-chlorobenzaldehyde (105 mg, 0.75 mmol) and benzyl bromide (257 mg, 179 µL, 1.50 mmol) in 1.0 ml THF. Then the reaction mixture was slowly warmed to rt and kept stirring for 12 h. After

12 h the reaction stopped and the solvent was evaporated and the crude residue was purified by column chromatography on silica gel to afford the 3-(4-chlorophenyl)-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole **4a** as a white solid (0.171 g, 72% yield) and recovery of 236 mg (92%) benzyl bromide. Interestingly, no detectable amounts of (2-((benzyloxy)(4-chlorophenyl)methyl)phenyl)triphenylphosphonium trifluoromethanesulfonate **6** was observed.

The formation of no benzyl incorporated product ***6*** *(92% benzyl bromide was recovered) indicates the concerted nature of this annulation reaction.*

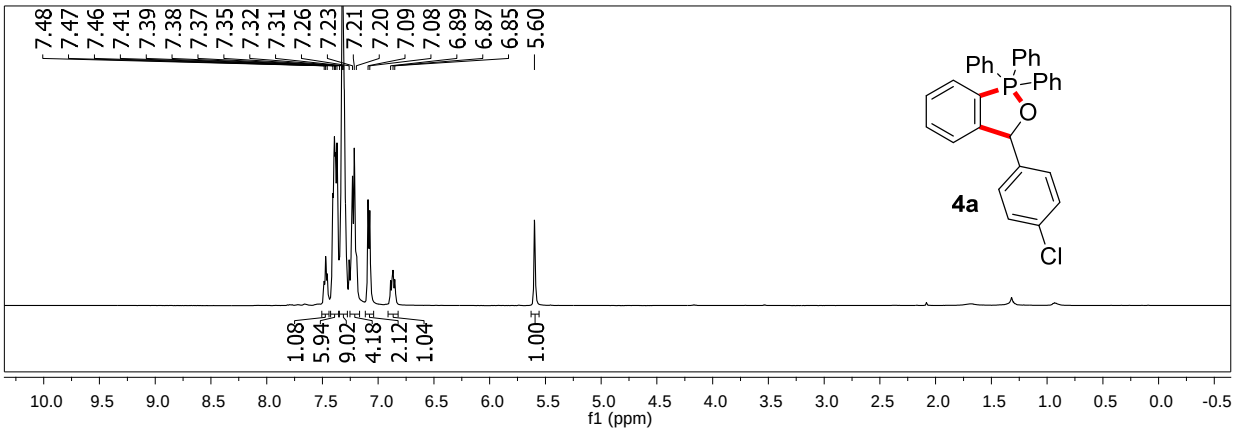
Experiment to Intercept the Zwitterion with Methyl Iodide



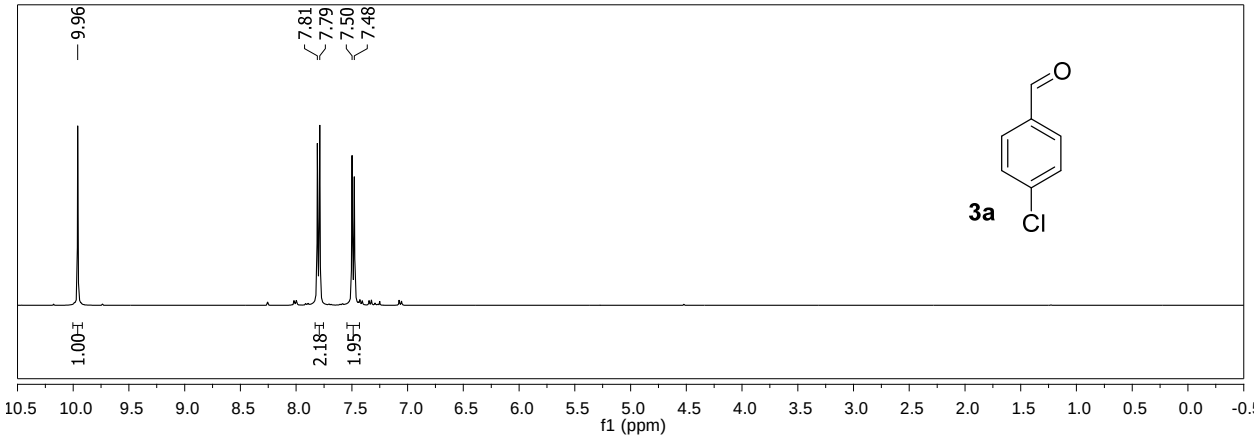
To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the triphenylphosphine **1a** (66 mg, 0.25 mmol) KF (35 mg, 0.60 mmol) and 18-crown-6 (0.159 mg, 0.60 mmol). Then the screw-capped tube was evacuated and backfilled with argon. The mixture was dissolved in THF (1.0 mL) under argon atmosphere and subsequently cooled the reaction mixture to -10 °C and kept stirring for five minutes. To the stirring solution 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (89 mg, 73 µL, 0.30 mmol) was added and continued stirring for another five minutes followed by addition of the mixture of 4-chlorobenzaldehyde (53 mg, 0.375 mmol) and MeI (71 mg, 32 µL, 0.50 mmol) in 1.0 ml THF. Then the reaction mixture was slowly warmed to rt and kept stirring for 12 h. When the reaction is complete, the mixture was diluted with DCM (2.0 mL) and filtered through a short pad of silica gel and eluted with 10% MeOH/DCM mixture (10 mL). The solvent was evaporated to obtain the crude product, which was analyzed using ^{1}H NMR using CH_2Br_2 (18.0 µL, 0.25 mmol) as the internal standard. ^{1}H NMR analysis showed that the crude mixture contains 74%

product **4a**, but there is no detectable amounts of (2-((4-chlorophenyl)(methoxy)methyl) phenyl)triphenylphosphonium trifluoromethanesulfonate .

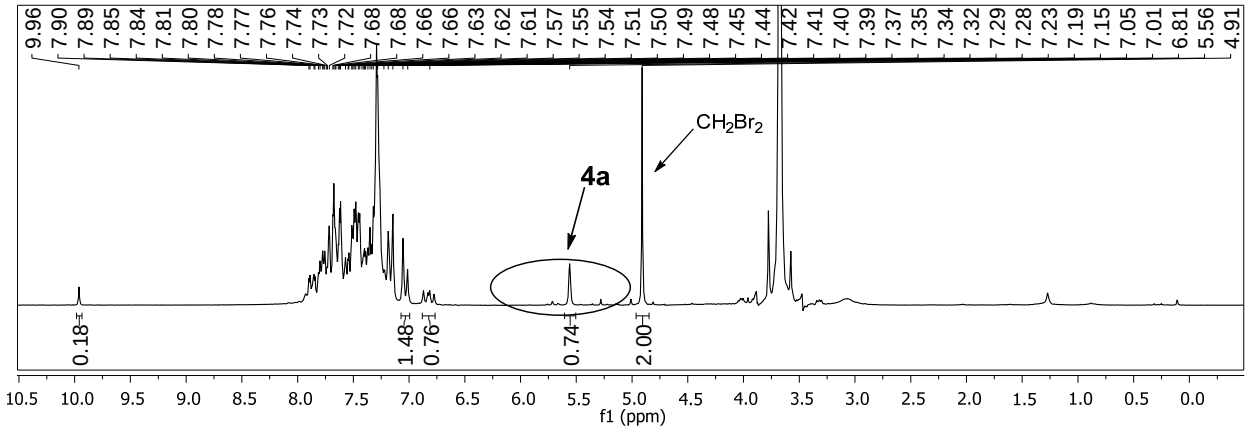
^{1}H-NMR Spectrum of 4a



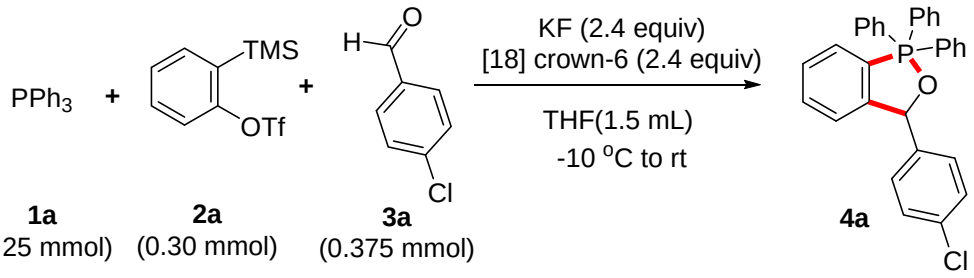
^{1}H-NMR Spectrum of 4-chlrobenzaldehyde (3a)



^{1}H-NMR of Crude Reaction Mixture after 12 h



c. Kinetics Study



1a (0.25 mmol) **2a** (0.30 mmol) **3a** (0.375 mmol) **4a**

Six reactions were carried out in parallel. To each of the flame-dried screw-capped test tube equipped with a magnetic stir bar was added the triphenylphosphine **1a** (66 mg, 0.25 mmol) KF (35 mg, 0.6 mmol) and 18-crown-6 (0.159 mg, 0.6 mmol). Then the screw-capped tube was evacuated and backfilled with argon. The mixture was dissolved in THF (1.5 mL) under argon atmosphere followed by cooling of the reaction mixture to -10 °C and continued stirring for five minutes. After five minutes of stirring 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (89 mg, 73 µL, 0.30 mmol) was added and continued stirring for another five minutes followed by addition of the 4-chlorobenzaldehyde **3a** (53 mg, 0.375 mmol). The reaction mixture was warmed to rt. After 5 minutes stirring the first reaction is quenched and the mixture was diluted with EtOAc (2.0 mL) and filtered through a short pad of silica gel and eluted with EtOAc (10 mL). The solvent was evaporated to obtain the crude product, which was analyzed using ^{1}H NMR using CH_2Br_2 (18.0 µL, 0.25 mmol) as the internal standard. The same procedure is followed for other five reactions and they were quenched after 15 min, 30 min, 45 min, 60 min, and 120 min respectively.

entry	Time (min)	Yield of **4a** (%)
1	5	10
2	15	29
3	30	46
4	45	58
5	60	69
6	120	74

The yields were determined by ^{1}H-NMR analysis of crude products using CH_2Br_2 as the internal standard.

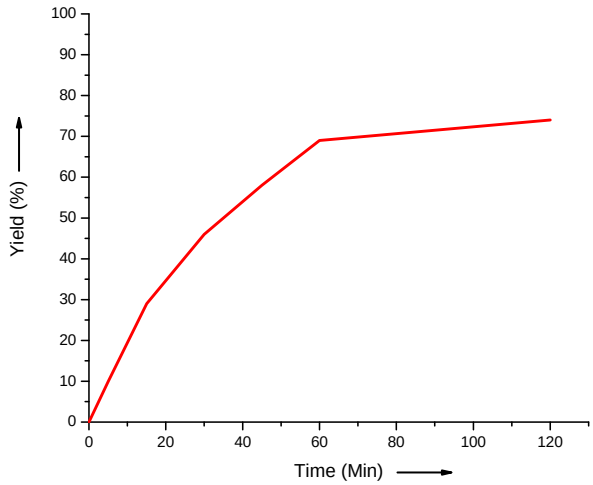
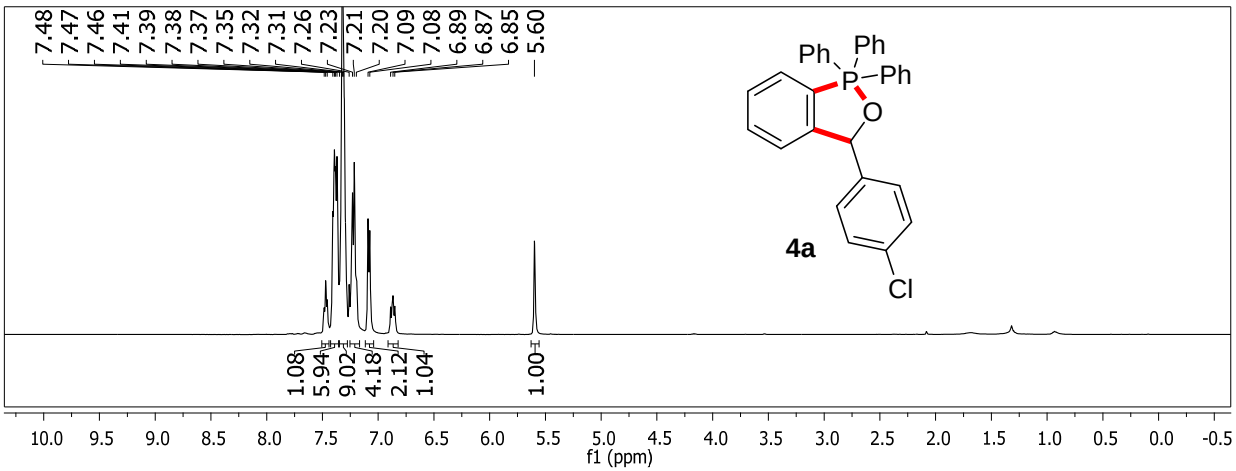
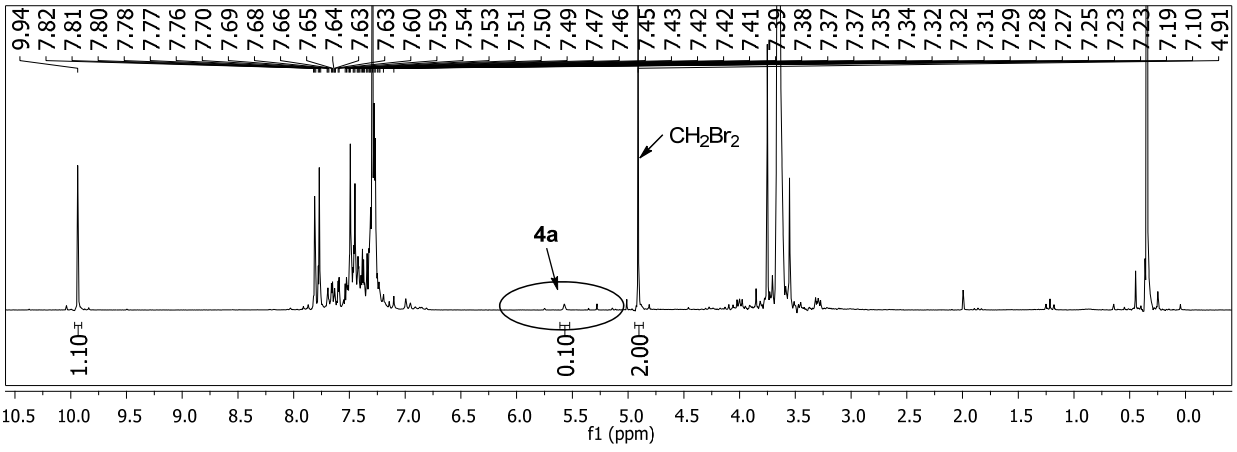


Figure 1. Kinetics Study of MCR Involving Phosphine, Aryne and Aldehyde

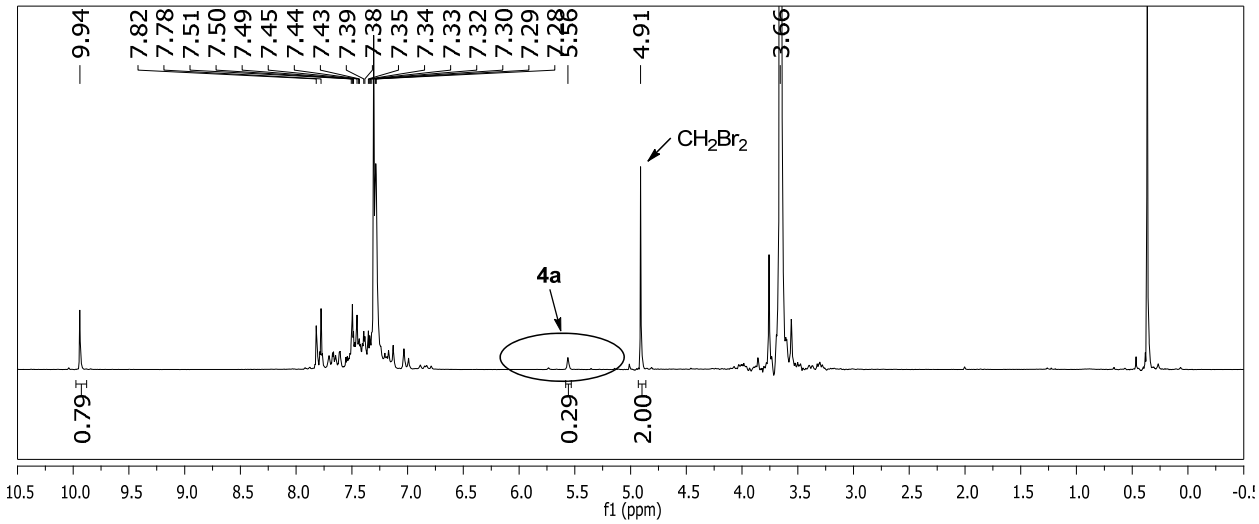
^{1}H-NMR Spectrum (4a)



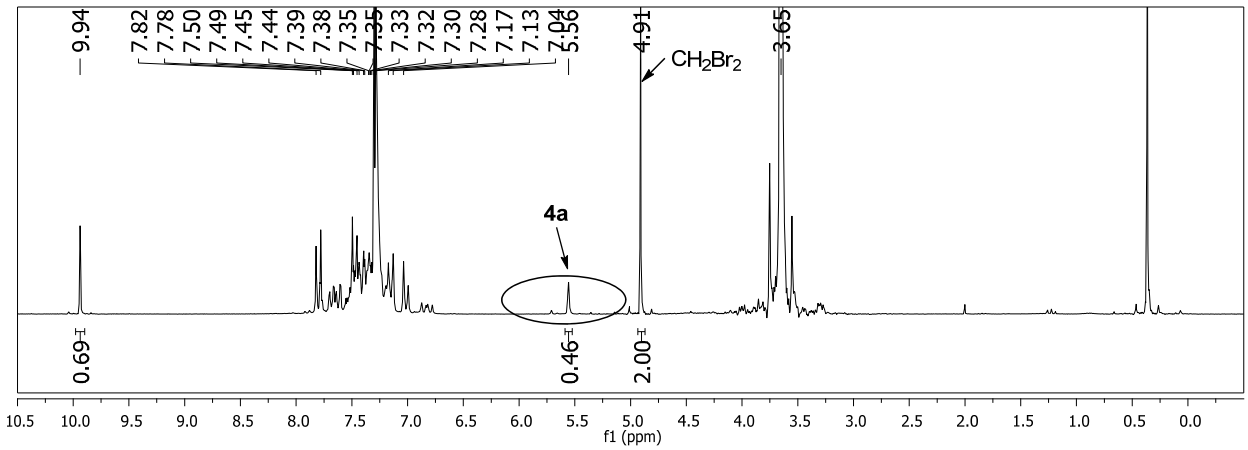
^{1}H-NMR of Crude Reaction Mixture after 5 minutes ($CDCl_3$)



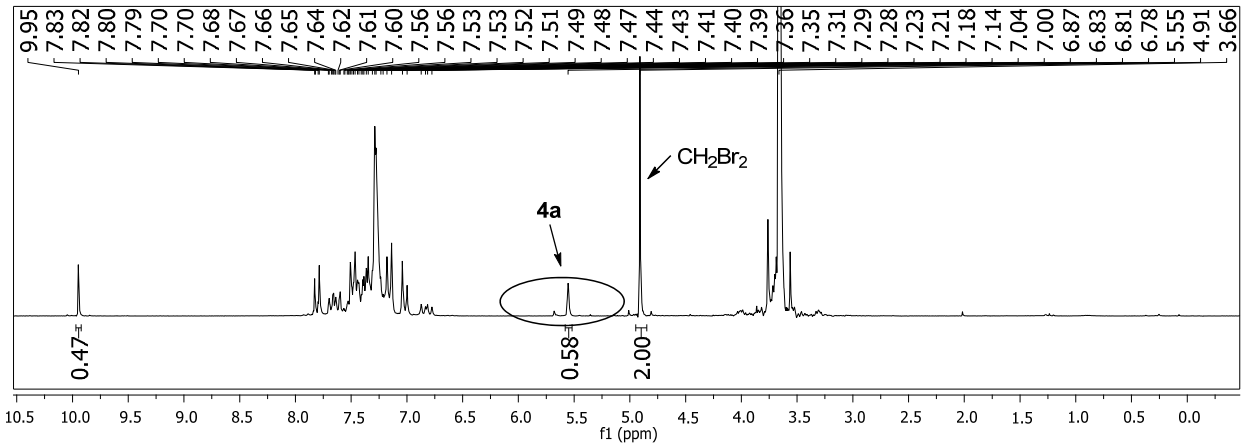
^{1}H-NMR of Crude Reaction Mixture after 15 minutes ($CDCl_3$)



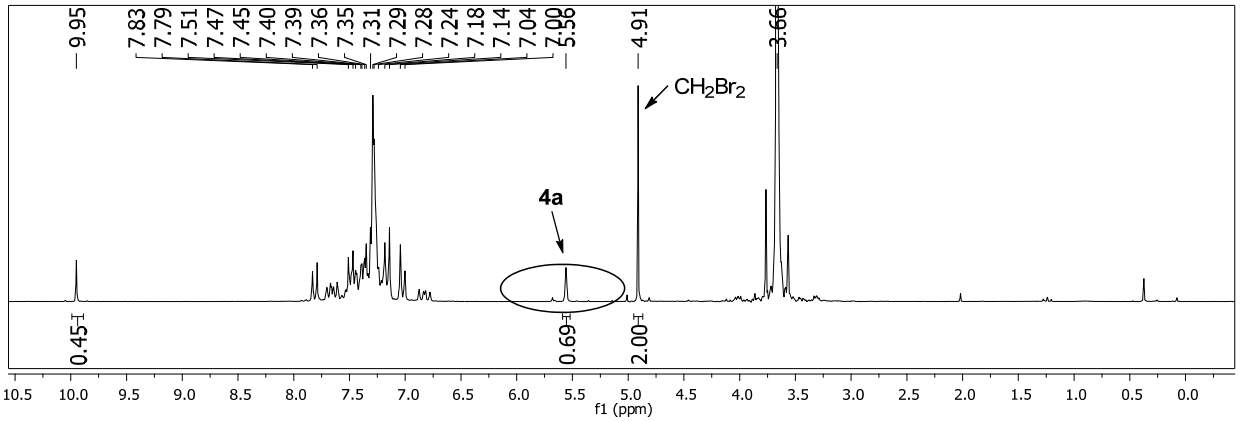
^{1}H-NMR of Crude Reaction Mixture after 30 minutes ($CDCl_3$)



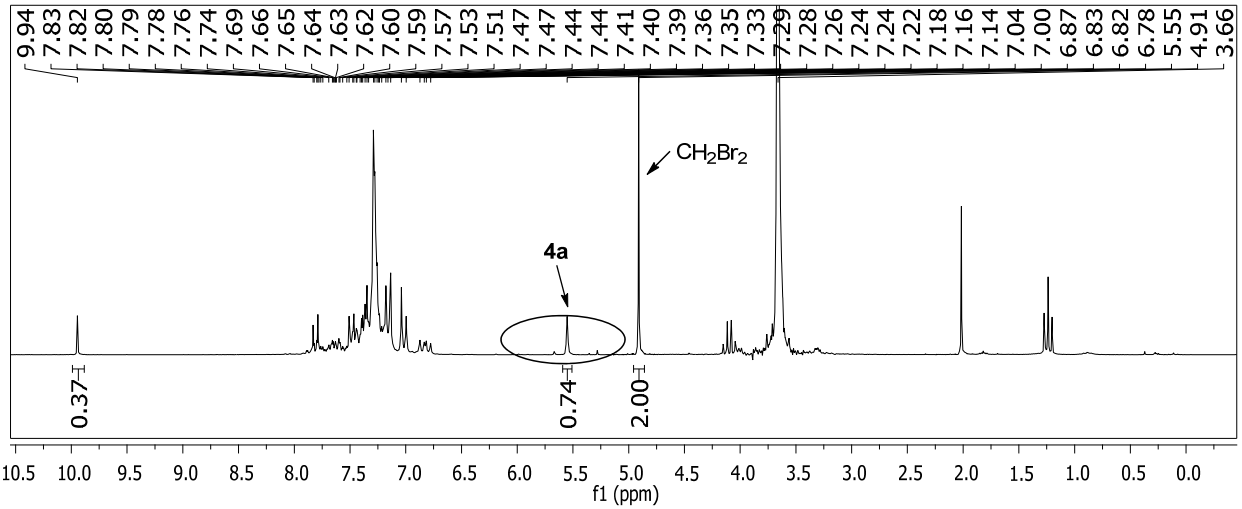
^{1}H-NMR of Crude Reaction Mixture after 45 minutes ($CDCl_3$)



^{1}H-NMR of Crude Reaction Mixture after 60 minutes ($CDCl_3$)

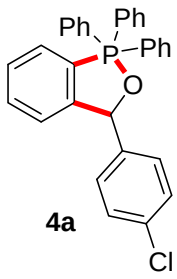


^{1}H-NMR of Crude Reaction Mixture after 120 minutes ($CDCl_3$)



7. Synthesis and Characterization of Benzooxaphospholes

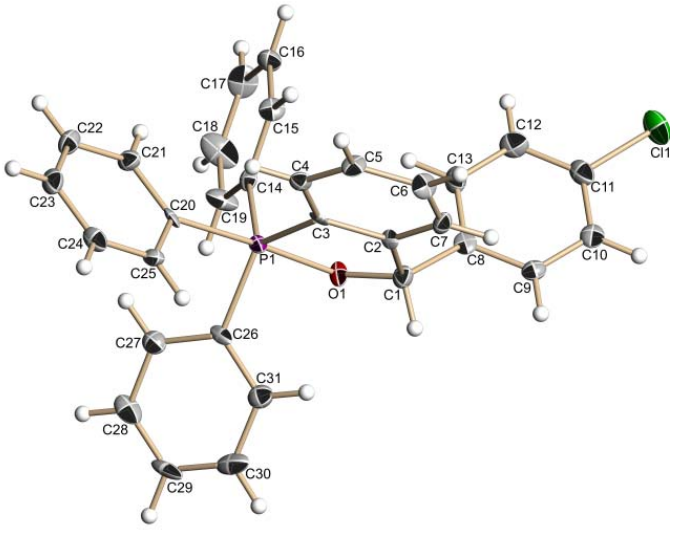
3-(4-Chlorophenyl)-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4a)



4a

Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.358 g, 292 µL, 1.20 mmol) and 4-chlorobenzaldehyde **3a** (0.211 g, 1.50 mmol) with triphenylphosphine **1a** (0.262 g, 1.0 mmol) in the presence of KF (0.140 g, 2.40 mmol) and 18-crown-6 (0.634 g, 2.40 mmol) in THF (6.0 mL) at -10 °C to rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 40/60) of the crude reaction mixture using silica gel afforded 3-(4-chlorophenyl)-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole **4a** as a white solid (0.389 g, 81% yield).

***R*$_f$** (EtOAc): 0.41; **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.47 (t, *J* = 6.6 Hz, 1H, H$_{ar}$), 7.41-7.37 (m, 6H, H$_{ar}$), 7.35-7.31 (m, 9H, H$_{ar}$), 7.23-7.20 (m, 4H, H$_{ar}$), 7.08 (d, *J* = 7.9 Hz, 2H, H$_{ar}$), 6.87 (t, *J* = 10.7 Hz, 1H, H$_{ar}$), 5.60 (s, 1H, CH). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 153.92 (d, *J* = 21.5 Hz), 143.72, 142.93, 136.56 (d, *J* = 21.5 Hz), 132.95, 132.31 (d, *J* = 2.4 Hz), 131.42 (d, *J* = 8.8 Hz), 129.16, 129.02, 128.38, 128.13, 127.96, 127.53, 127.43, 127.36, 124.77 (d, *J* = 15.4 Hz), 76.25. **^{31}P NMR (203 MHz, CDCl$_3$)** δ -51.41 **HRMS (ESI)** calculated [M+H]$^+$ for $C_{31}H_{25}ClOP$: 479.1326, found: 479.1327. **FTIR (cm^{-1})** 3829, 3743, 3618, 3058, 3005, 1897, 1588, 1485, 1437, 1406, 1257, 1229, 1183, 1112, 1078, 1020, 886, 847, 745, 695, 663.

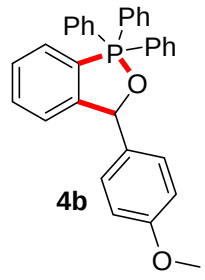


X-ray intensity data measurements of compound **4a** (crystallized from EtOAc-Petroleum ether) were carried out on a Bruker SMART APEX II CCD diffractometer with graphite-monochromatized (MoK$_\alpha$= 0.71073Å) radiation at room temperature 296(2) K. The X-ray generator was operated at 50 kV and 30 mA. A preliminary set of cell constants and an orientation matrix were calculated from three sets of 36 frames. Data were collected with ω scan width of 0.5° at

different settings of φ and 2θ with a frame time of 15 and 20 secs respectively keeping the sample-to-detector distance fixed at 5.00 cm. The X-ray data collection was monitored by APEX2 program (Bruker, 2006). All the data were corrected for Lorentzian, polarization and absorption effects using SAINT and SADABS programs (Bruker, 2006). SHELX-97 was used for structure solution and full matrix least-squares refinement on F^2. Hydrogen atoms were placed in geometrically idealized position and constrained to ride on their parent atoms.[4] CCDC-1001501 (**4a**), contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data of **4a** $C_{31}H_{24}ClOP$, M = 478.92, colorless block, 0.28 x 0.27 x 0.08 mm^3, triclinic, space group *P*-1, a = 10.1588(6) Å, b = 13.9351(8) Å, c = 18.4004(10) Å, α = 78.641(3)°, β = 75.556(3)°, γ = 73.465(3)°, V = 2395.8(2) $Å^3$, Z = 4, T = 296(2) K, $2\theta_{max}$ = 50.00°, D_{calc} (g cm^{-3}) = 1.328, $F(000)$ = 1000, μ (mm^{-1}) = 0.249, 24693 reflections collected, 7126 unique reflections (R_{int}=0.0496), 6406 observed ($I > 2\sigma(I)$) reflections, multi-scan absorption correction, T_{min} = 0.934, T_{max} = 0.980, 613 refined parameters, S = 1.349, $R1$ = 0.1043, $wR2$ = 0.1620 (all data R = 0.1171, $wR2$ = 0.1665), maximum and minimum residual electron densities; $\Delta\rho_{max}$ = 0.40, $\Delta\rho_{min}$= -0.37 ($eÅ^{-3}$).

3-(4-Methoxyphenyl)-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4b)



4b

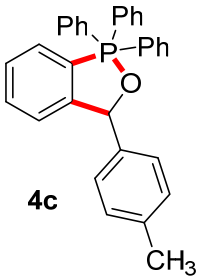
Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.179 g, 146 µL, 0.60 mmol) and 4-methoxybenzaldehyde **2b** (0.102 g, 91 µL, 0.75 mmol) with triphenylphosphine **1a** (0.131 g, 0.50 mmol) in the presence of KF (0.070 g, 1.20 mmol) and 18-crown-6 (0.317 g, 1.20 mmol) in THF (3.0 mL) at -10 °C to rt for 12 h followed by flash column chromatography (Pet. ether

[4] 1) Bruker (2006). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA. (2) G. M. Sheldrick, *Acta Crystallogr*. 2008, **A64**, 112.

/EtOAc = 40/60) of the crude reaction mixture using silica gel afforded 3-(4-methoxyphenyl)-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole **4b** as a white solid (0.182 g, 77% yield).

***R*$_f$** (EtOAc): 0.38; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.49-7.46 (m, 1H, H$_{ar}$), 7.42-7.39 (m, 6H, H$_{ar}$), 7.33-7.29 (m, 9H, H$_{ar}$), 7.23 (t, *J* = 5.8 Hz, 2H, H$_{ar}$), 7.11 (d, *J* = 8.4 Hz, 2H, H$_{ar}$), 6.86-6.81 (m, 3H, H$_{ar}$), 5.52 (s, 1H, CH), 3.79 (s, 3H, CH$_3$). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 158.98, 154.88 (d, *J* = 21.6 Hz), 144.17, 143.11, 136.46 (d, *J* = 6.5 Hz), 136.28, 132.15 (d, *J* = 3.1 Hz), 131.59 (d, *J* = 8.9 Hz), 129.12, 128.03, 127.41 (d, *J* = 12.3 Hz), 127.26, 127.12, 124.90 (d, *J* = 15.4 Hz), 113.69, 76.23, 55.32. **^{31}P NMR (162 MHz, CDCl$_3$)** δ -52.65. **HRMS (ESI)** calculated [M+H]$^+$ for $C_{32}H_{28}O_2P$: 475.1821, found: 475.1822. **FTIR (cm^{-1})** 3843, 3649, 3005, 2361, 1836, 1741, 1693, 1647, 1484, 1436, 1246, 1216, 1118, 1050, 742, 699, 665.

1,1,1-Triphenyl-3-(*p*-tolyl)-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4c)

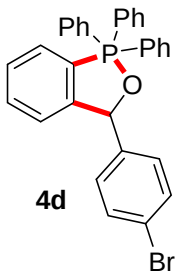


4c

Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.179 g, 146 µL, 0.6 mmol) and 4-methylbenzaldehyde **2c** (0.090 g, 88 µL , 0.75 mmol) with triphenylphosphine **1a** (0.131 g, 0.5 mmol) in the presence of KF (0.070 g, 1.20 mmol) and 18-crown-6 (0.317 g, 1.20 mmol) in THF (3.0 mL) at -10 °C to rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 40/60) of the crude reaction mixture using silica gel afforded 1,1,1-triphenyl-3-(p-tolyl)-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole **4c** as a white solid (0.154 g, 67% yield).

***R*$_f$** (EtOAc): 0.44; **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.44 (t, *J* = 6.2 Hz, 1H, H$_{ar}$), 7.39-7.35 (m, 6H, H$_{ar}$), 7.32-7.27 (m, 9H, H$_{ar}$), 7.22 (dd, J_1 = 6.6 Hz, J_2 = 13.0 Hz, 2H, H$_{ar}$), 7.0-7.03 (m, 4H, H$_{ar}$), 6.82 (dd, J_1 = 8.3 Hz, J_2 = 10.3 Hz, 1H, H$_{ar}$), 5.51 (s, 1H, CH), 2.30 (s, 3H, CH$_3$). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 154.75 (d, *J* = 21.8 Hz), 144.06, 143.22, 141.23, 136.83, 136.37 (d, *J* = 14.6 Hz), 132.17 (d, *J* = 2.5 Hz), 131.58 (d, *J* = 9.1 Hz), 128.96, 128.29, 128.0 (d, *J* = 1.8 Hz), 127.26, 127.41 (d, *J* = 12.5 Hz), 127.17 (d, *J* = 14.1 Hz), 124.88 (d, *J* = 15.6 Hz), 76.58. **^{31}P NMR (203 MHz, CDCl$_3$)** δ -52.08. **HRMS (ESI)** calculated [M+H]$^+$ for $C_{32}H_{28}OP$: 459.1872, found 459.1872. **FTIR (cm^{-1})** 3843, 3013, 2361, 1835, 1647, 1515, 1214, 1033, 742, 666.

3-(4-Bromophenyl)-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4d)

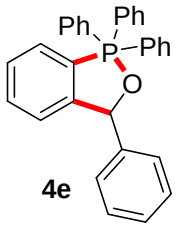


4d

Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.179 g, 146 µL, 0.60 mmol) and 4-bromobenzaldehyde **3d** (0.137 g, 0.75 mmol) with triphenylphosphine **1a** (0.131 g, 0.50 mmol) in the presence of KF (0.070 g, 1.20 mmol) and 18-crown-6 (0.317 g, 1.20 mmol) in THF (3.0 mL) at -10 °C to rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 40/60) of the crude reaction mixture using silica gel afforded 3-(4-bromophenyl)-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole **4d** as a white solid (0.223 g, 85% yield).

***R*$_f$** (EtOAc): 0.42; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.46 (t, *J* = 6.4 Hz, 1H, H$_{ar}$), 7.37-7.35 (m, 5H, H$_{ar}$), 7.33-7.26 (m, 12H, H$_{ar}$), 7.23-7.17 (m, 2H, H$_{ar}$), 6.98 (d, *J* = 8.3 Hz, 2H, H$_{ar}$), 6.84 (dd, J_1 = 8.2 Hz, J_2 = 11.2 Hz, 1H, H$_{ar}$), 5.56 (s, 1H, CH). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 153.82 (d, *J* = 21.2 Hz), 143.47, 142.38, 136.63 (d, *J* = 14.5 Hz), 132.41 (d, *J* = 2.7 Hz), 131.52 (d, *J* = 8.8 Hz), 131.35, 129.55, 128.29, 127.56 (d, *J* = 12.3 Hz), 127.40, 124.96 (d, *J* = 14.9 Hz), 121.17, 76.30. **^{31}P NMR (162 MHz, CDCl$_3$)** δ -51.38 **HRMS (ESI)** calculated [M+H]$^+$ for $C_{31}H_{25}BrOP$: 523.0821, found: 523.0825. **FTIR (cm^{-1})** 3894, 3843, 3743, 3619, 2982. 2360, 1835, 1707, 1615, 1467, 1435, 1249, 1180, 1046, 844, 743, 665.

1,1,1,3-Tetraphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4e)



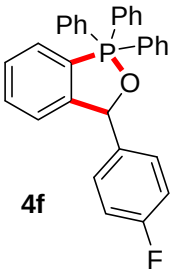
4e

Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.179 g, 146 µL, 0.60 mmol) and benzaldehyde **2e** (0.105 g, 0.75 mmol) with triphenylphosphine **1a** (0.080 g, 76 µL, 0.50 mmol) in the presence of KF (0.070 g, 1.20 mmol) and 18-crown-6 (0.317 g, 1.20 mmol) in THF (3.0 mL) at -10 °C to rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 40/60) of the crude reaction mixture using silica gel afforded 1,1,1,3-tetraphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole **4e** as a white solid (0.180 g, 81% yield).

***R*$_f$** (EtOAc): 0.40; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.45-7.36 (m, 7H, H$_{ar}$), 7.31 (bs, 9H, H$_{ar}$), 7.26-7.22 (m, 5H, H$_{ar}$), 7.15 (d, *J* = 7.1 Hz, 2H, H$_{ar}$), 6.83 (t, *J* = 8.4 Hz, 1H, H$_{ar}$), 5.56 (s, 1H, CH). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 154.44 (d, *J* = 21.4 Hz), 144.17, 143.62 (d, *J* = 12.5 Hz), 142.65, 142.55, 136.46 (d, *J* = 14.5 Hz), 132.27 (d, *J* = 2.3 Hz), 131.64 (d, *J* = 8.8 Hz), 128.28,

128.21, 127.92, 127.57, 127.44, 127.34, 127.21, 125.01 (d, J = 15.5 Hz), 76.74. **^{31}P NMR (162 MHz, $CDCl_3$)** δ -48.23 **HRMS (ESI)** calculated $[M+H]^+$ for $C_{31}H_{26}ClOP$: 445.1716, found: 445.1718. **FTIR (cm^{-1})** 3860, 3677, 3619, 3013, 2362, 1741, 1693, 1647, 1516, 1462, 1216, 1117, 1057, 741, 667, 633.

3-(4-Fluorophenyl)-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4f)

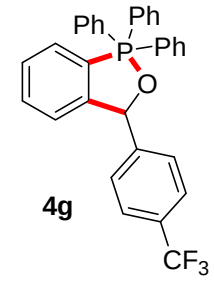


4f

Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.179 g, 146 µL, 0.6 mmol) and 4-fluorobenzaldehyde **3f** (0.093 g, 81 µL, 0.75 mmol) with triphenylphosphine **1a** (0.131 g, 0.5 mmol) in the presence of KF (0.070 g, 1.2 mmol) and 18-crown-6 (0.317 g, 1.2 mmol) in THF (3.0 mL) at -10 °C to rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 40/60) of the crude reaction mixture using silica gel afforded 3-(4-fluorophenyl)-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[c][1,2]oxaphosphole **4f** as a white solid (0.181 g, 78% yield).

***R*$_f$** (EtOAc): 0.53; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.49 (t, J = 6.5 Hz, 1H, H_{ar}), 7.40-7.36 (m, 6H, H_{ar}), 7.33-7.29 (m, 9H, H_{ar}), 7.27 (dd, J_1 = 7.2 Hz, J_2 = 12.9 Hz, 1H, H_{ar}), 7.20 (d, J = 7.2 Hz, 1H, H_{ar}), 7.14 (dd, J_1 = 5.7 Hz, J_2 = 8.5 Hz, 2H, H_{ar}), 6.94 (t, J = 8.8 Hz, 2H, H_{ar}), 6.88 (dd, J_1 = 8.1 Hz, J_2 = 11.0 Hz, 1H, H_{ar}), 5.57 (s, 1H, CH). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 162.25 (d, J = 244.6 Hz), 154.33 (d, J = 21.6 Hz), 140.13, 136.54 (d, J = 14.5 Hz), 132.28 (d, J = 2.6 Hz), 131.49 (d, J = 8.9 Hz), 29.46 (d, J = 8.2 Hz), 128.14, 127.54, 127.44, 127.32, 124.83 (d, J = 15.0 Hz), 115.17, 115.0, 76.19. **^{31}P NMR (203 MHz, $CDCl_3$)** δ -51.96 **HRMS (ESI)** calculated $[M+H]^+$ for $C_{31}H_{25}FOP$: 463.1622, found: 463.1649. **FTIR (cm^{-1})** 3677, 3060, 2805, 1646, 1507, 1437, 1260, 1103, 827, 742.

1,1,1-Triphenyl-3-(4-(trifluoromethyl)phenyl)-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4g)



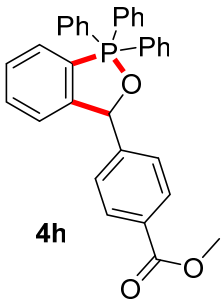
4g

Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.179 g, 146 µL, 0.6 mmol) and 4-(trifluoromethyl)benzaldehyde **3g** (0.131 g, 102 µL, 0.75 mmol) with triphenylphosphine **1a** (0.131 g, 0.5 mmol) in the presence of KF (0.070 g, 1.2 mmol) and 18-crown-6 (0.317 g, 1.2 mmol) in THF (3.0 mL) at -10 °C to rt

for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 40/60) of the crude reaction mixture using silica gel afforded 1,1,1-Triphenyl-3-(4-(trifluoromethyl)phenyl)-1,3-dihydro-1λ^5-benzo[c][1,2]oxaphosphole **4g** as a white solid (0.199 g, 78% yield).

***R*$_f$** (EtOAc): 0.58; **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.47 (d, *J* = 8.0 Hz, 3H, H$_{ar}$), 7.38-7.28 (m, 15H, H$_{ar}$), 7.24-7.19 (m, 4H, H$_{ar}$), 6.89 (dd, J_1 = 8.3 Hz, J_2 = 11.2 Hz, 1H, H$_{ar}$), 5.68 (s, 1H, CH). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 153.37 (d, *J* = 21.2 Hz), 148.43, 143.40, 142.55, 136.69 (d, *J* = 14.3 Hz), 132.38 (d, *J* = 2.9 Hz), 132.13 (d, *J* = 9.8 Hz), 132.00 (d, *J* = 2.4 Hz), 131.34 (d, *J* = 8.8 Hz), 129.35 (q, *J* = 31.83 Hz) , 128.20, 127.91, 127.49 (d, *J* = 13.4 Hz) , 125.15 (d, *J* = 3.5 Hz), 124.74 (d, *J* = 15.2 Hz), 76.46. **^{31}P NMR (203 MHz, CDCl$_3$)** δ -50.16. **HRMS (ESI)** calculated [M+H]$^+$ for $C_{32}H_{25}F_3OP$: 513.1590, found: 513.1602. **FTIR (cm^{-1})** 3842, 3062, 2360, 1916, 1583, 1486, 1198, 1027, 739, 664.

Methyl-4-(1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphol-3-yl)benzoate (4h)

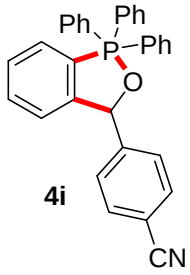


4h

Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.179 g, 146 µL, 0.60 mmol) and methyl 4-formylbenzoate **3h** (0.123 g, 0.75 mmol) with triphenylphosphine **1a** (0.131 g, 0.50 mmol) in the presence of KF (0.070 g, 1.20 mmol) and 18-crown-6 (0.317 g, 120 mmol) in THF (3.0 mL) at -10 °C to rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 40/60) of the crude reaction mixture using silica gel afforded methyl-4-(1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphol-3-yl)benzoate **4h** as a white solid (0.227 g, 90% yield).

***R*$_f$** (EtOAc): 0.47; **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.93 (d, *J* = 6.9 Hz, 2H, H$_{ar}$), 7.48 (t, *J* = 6.5 Hz, 1H, H$_{ar}$), 7.40-7.37 (m, 6H, H$_{ar}$), 7.33-7.29 (m, 9H, H$_{ar}$), 7.27-7.24 (m, 1H, H$_{ar}$), 7.21 (d, *J* = 7.2 Hz, 3H, H$_{ar}$), 6.87 (t, *J* = 9.2 Hz, 1H, H$_{ar}$), 5.70 (s, 1H, CH), 3.90 (s, 3H, CH$_3$). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 167.19, 153.56 (d, *J* = 21.5 Hz), 149.72, 143.72, 142.88, 136.71 (d, *J* = 14.6 Hz), 132.39 (d, *J* = 2.5 Hz), 131.43 (d, *J* = 8.7 Hz), 129.68, 129.06, 128.83, 128.19, 127.70, 127.58, 127.48, 124.75 (d, *J* = 15.2 Hz), 76.70, 52.09. **^{31}P NMR (203 MHz, CDCl$_3$)** δ -50.75 **HRMS (ESI)** calculated [M+H]$^+$ for $C_{33}H_{28}O_3P$: 503.1771, found: 503.1788. **FTIR (cm^{-1})** 3829, 3744, 3678, 3649, 3008, 2319, 1712, 1647, 1614. 1469. 1369. 1279, 1217, 1112, 1041, 986, 872, 834.

4-(1,1,1-Triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphol-3-yl)benzonitrile (4i)

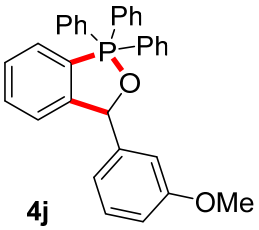


4i

Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.179 g, 146 µL, 0.60 mmol) and 4-formylbenzonitrile **3i** (0.098 g, 0.75 mmol) with triphenylphosphine **1a** (0.131 g, 0.50 mmol) in the presence of KF (0.070 g, 1.20 mmol) and 18-crown-6 (0.317 g, 1.20 mmol) in THF (3.0 mL) at -10 °C to rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 40/60) of the crude reaction mixture using silica gel afforded 4-(1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphol-3-yl)benzonitrile **4i** as a white solid (0.206 g, 83% yield).

***R*$_f$** (EtOAc): 0.51; **^{1}H NMR (400 MHz, CDCl$_3$) δ** 7.51 (d, *J* = 6.7 Hz, 3H, H$_{ar}$), 7.37-7.28 (m, 16H, H$_{ar}$), 7.20 (d, *J* = 7.2 Hz, 3H, H$_{ar}$), 6.90 (t, *J* = 8.5 Hz, 1H, H$_{ar}$), 5.73 (s, 1H, CH). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 152.84 (d, *J* = 21.4 Hz), 150.03, 143.56, 142.54, 136.93 (d, *J* = 14.6 Hz), 132.59, 132.15, 131.38 (d, *J* = 8.4 Hz), 128.39, 128.29, 127.80, 127.64 (d, *J* = 12.3 Hz), 124.75, 119.11, 110.95, 76.57. **^{31}P NMR (162 MHz, CDCl$_3$)** δ -50.08. **HRMS (ESI)** calculated [M+H] $^+$ for $C_{32}H_{25}NOP$: 470.1668, found: 470.1672. **FTIR (cm^{-1})** 3829, 3677, 3005, 1735, 1645, 1595, 1487, 1399, 1373, 1249, 1111, 1062, 846, 744, 699.

3-(3-Methoxyphenyl)-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4j)



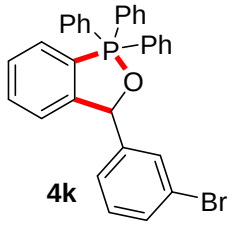
4j

Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.179 g, 146 µL, 0.6 mmol) and 3-methoxybenzaldehyde **3j** (0.102 g, 91 µL, 0.75 mmol) with triphenylphosphine **1a** (0.131 g, 0.5 mmol) in the presence of KF (0.070 g, 1.20 mmol) and 18-crown-6 (0.317 g, 1.20 mmol) in THF (3.0mL) at -10 °C to rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 40/60) of the crude reaction mixture using silica gel afforded 3-(3-methoxyphenyl)-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole **4j** as a white solid (0.192 g, 81% yield).

***R*$_f$** (EtOAc): 0.50; **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.46 (t, *J* = 7.2 Hz, 1H, H$_{ar}$), 7.40-7.38 (m, 6H, H$_{ar}$), 7.33-7.26 (m, 10H, H$_{ar}$), 7.23-7.16 (m, 2H, H$_{ar}$), 6.85-6.81 (m, 2H, H$_{ar}$), 6.74 (d, *J* = 8.0 Hz, 1H, H$_{ar}$), 6.59 (s, 1H, H$_{ar}$), 5.66 (s, 1H, CH), 3.58 (s, 3H, OCH$_3$). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 159.76, 154.33 (d, *J* = 21.9 Hz), 146.01, 144.10, 143.26, 136.55 (d, *J* = 14.5 Hz), 132.36, 131.43 (d, *J* = 8.8 Hz), 129.10, 128.05, 127.50 (d, *J* = 12.2 Hz), 127.27(d, *J* = 14.2 Hz),

124.86 (d, J = 15.4 Hz), 120.12, 113.83, 112.05, 77.23, 55.20. **^{31}P NMR (203 MHz, $CDCl_3$)** δ -51.37 **HRMS (ESI)** calculated $[M+H]^+$ for $C_{32}H_{28}O_2P$: 475.1821, found: 475.1852. **FTIR (cm^{-1})** 3678, 3015, 2361, 1647, 1462, 1215, 1052, 741, 667.

3-(3-Bromophenyl)-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4k)

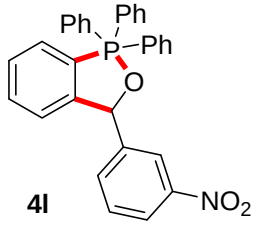


4k

Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.179 g, 146 µL, 0.60 mmol) and 3-bromobenzaldehyde **3k** (0.139 g, 88 µL, 0.75 mmol) with triphenylphosphine **1a** (0.131 g, 0.50 mmol) in the presence of KF (0.070 g, 1.20 mmol) and 18-crown-6 (0.317 g, 1.20 mmol) in THF (3.0 mL) at -10 °C to rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 40/60) of the crude reaction mixture using silica gel afforded 3-(3-bromophenyl)-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole **4k** as a white solid (0.194 g, 74% yield).

***R*$_f$** (EtOAc): 0.52; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.48 (t, J = 6.8 Hz, 1H, H_{ar}), 7.41-7.38 (m, 4H, H_{ar}), 7.36 (bs, 2H, H_{ar}), 7.33-7.29 (m, 10H, H_{ar}), 7.26-7.21 (m, 2H, H_{ar}), 7.16-7.08 (m, 3H, H_{ar}), 6.88 (dd, J_1 = 8.0 Hz, J_2 = 11.3 Hz, 1H, H_{ar}), 5.65 (s, 1H, CH). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 153.53 (d, J = 21.1 Hz), 146.78, 143.35, 142.32, 136.69 (d, J = 14.5 Hz), 132.46 (d, J = 2.9 Hz), 131.44 (d, J = 8.9 Hz), 130.75, 130.28, 129.74, 128.31 (d, J = 1.8 Hz), 127.61, 127.49, 126.22, 124.96 (d, J = 15.2 Hz), 122.51, 76.45. **^{31}P NMR (162 MHz, $CDCl_3$)** δ -49.87 **HRMS (ESI)** calculated $[M+H]^+$ for $C_{31}H_{25}BrOP$: 523.0821, found: 523.0826. **FTIR (cm^{-1})** 3894, 3860, 3743, 3678, 3619, 3012, 2362, 1836, 1741, 1693, 1647, 1516, 1479, 1429, 1217, 1184, 1065, 910, 742.

3-(3-Nitrophenyl)-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4l)



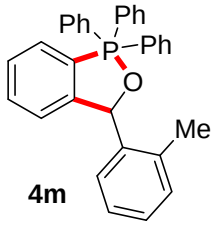
4l

Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.179 g, 146 µL, 0.6 mmol) and 3-nitrobenzaldehyde **3l** (0.113 g, 0.75 mmol) with triphenylphosphine **1a** (0.131 g, 0.5mmol) in the presence of KF (0.070 g, 1.2 mmol) and 18-crown-6 (0.317 g, 1.20 mmol) in THF (3.0 mL) at -10 °C to rt for 12 h

followed by flash column chromatography (Pet. ether /EtOAc = 40/60) of the crude reaction mixture using silica gel afforded 3-(3-nitrophenyl)-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[c][1,2]oxaphosphole **4l** as a white solid (0.186 g, 76% yield).

***R*$_f$** (EtOAc): 0.47; **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.06 (d, *J* = 8.0 Hz, 1H, H$_{ar}$), 7.96 (s, 1H, H$_{ar}$), 7.53-7.49 (m, 2H, H$_{ar}$), 7.40-7.34 (m, 16H, H$_{ar}$), 7.29-7.27 (m, 1H, H$_{ar}$), 7.24 (d, *J* = 7.0 Hz, 1H, H$_{ar}$), 6.93 (dd, J_1 = 8.2 Hz, J_2 = 11.3 Hz, 1H, H$_{ar}$), 5.81 (s, 1H, CH). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 153.95 (d, *J* = 20.6 Hz), 148.38, 146.98, 137.0 (d, *J* = 14.77 Hz), 133.76, 132.65 (d, *J* = 2.6 Hz), 131.30 (d, *J* = 8.8 Hz), 129.12, 128.42, 127.85, 127.74, 127.64, 124.79 (d, *J* = 15.2 Hz), 122.70, 122.32, 76.40. **^{31}P NMR (203 MHz, CDCl$_3$)** δ -49.49. **HRMS (ESI)** calculated [M+H]$^+$ for $C_{31}H_{25}NO_3P$: 490.1567, found: 490.1584. **FTIR (cm^{-1})** 3743, 3060, 2361, 1580, 1529, 1349, 1064, 999, 693.

1,1,1-Triphenyl-3-(*o*-tolyl)-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4m)

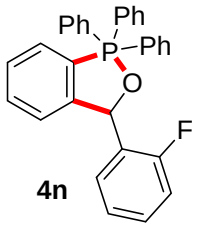


4m

Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.179 g, 146 µL, 0.6 mmol) and 2-methylbenzaldehyde **4m** (0.090 g, 87 µL, 0.75 mmol) with triphenylphosphine **1a** (0.131 g, 0.5 mmol) in the presence of KF (0.070 g, 1.2 mmol) and 18-crown-6 (0.317 g, 1.2 mmol) in THF (3.0 mL) at -10 °C to rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 40/60) of the crude reaction mixture using silica gel afforded 1,1,1-triphenyl-3-(o-tolyl)-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole **4m** as a white solid (0.147 g, 64% yield).

***R*$_f$** (EtOAc): 0.42; **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.45-7.37 (m, 7H, H$_{ar}$), 7.30-7.26 (m, 9H, H$_{ar}$), 7.24-7.20 (m, 1H, H$_{ar}$), 7.12-7.09 (m, 3H, H$_{ar}$), 7.06-7.03 (m, 1H, H$_{ar}$), 6.96 (d, *J* = 7.36 Hz, 1H, H$_{ar}$), 6.89 (dd, (dd, J_1 = 8.3 Hz, J_2 = 10.8 Hz, 1H, H$_{ar}$), 5.32 (s, 1H, CH), 2.31 (s, 3H, CH$_3$). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 154.74 (d, *J* = 20.1 Hz), 141.98, 136.49 (d, *J* = 14.3 Hz), 136.0, 132.18 (d, *J* = 2.6 Hz), 131.64 (d, *J* = 9.1 Hz), 130.28, 128.30, 128.14, 127.47 (d, *J* = 12.3 Hz), 127.21, 127.14, 127.10, 126.23, 124.77 (d, *J* = 15.0 Hz), 72.40, 19.74. **^{31}P NMR (203 MHz, CDCl$_3$)** δ -52.37. **HRMS (ESI)** calculated [M+H]$^+$ for $C_{32}H_{28}OP$: 459.1872, found: 459.1873. **FTIR (cm^{-1})** 3828, 3060, 2361, 1835, 1741, 1484, 1264, 1050, 742, 665.

3-(2-Fluorophenyl)-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4n)

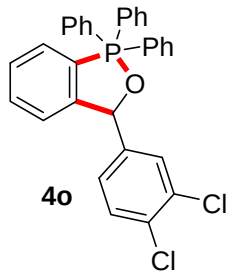


4n

Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.179 g, 146 µL, 0.60 mmol) and 2-fluorobenzaldehyde **2n** (0.093 g, 80 µL, 0.75 mmol) with triphenylphosphine **1a** (0.131 g, 0.50 mmol) in the presence of KF (0.070 g, 1.20 mmol) and 18-crown-6 (0.317 g, 1.20 mmol) in THF (3.0 mL) at -10 °C to rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 40/60) of the crude reaction mixture using silica gel afforded 3-(2-fluorophenyl)-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole **4n** as a white solid (0.199 g, 86% yield).

***R*$_f$** (EtOAc): 0.49; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.49 (t, *J* = 6.9 Hz, 1H, H$_{ar}$), 7.42-7.36 (m, 7H, H$_{ar}$), 7.33-7.29 (m, 9H, H$_{ar}$), 7.25-7.20 (m, 1H, H$_{ar}$), 7.18-7.13 (m, 1H, H$_{ar}$), 7.03 (t, *J* = 9.7 Hz, 1H, H$_{ar}$), 6.91-6.60 (m, 3H, H$_{ar}$), 6.06 (s, 1H, CH). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 160.65 (d, $J_{C\text{-}F}$ = 245.3 Hz), 153.91 (d, *J* = 20.1 Hz), 143.60, 142.53, 136.66 (d, *J* = 14.6 Hz), 132.60 (d, *J* = 2.8 Hz), 131.73, 131.60, 131.44 (d, *J* = 8.9 Hz), 129.42 (d, *J* = 4.2 Hz), 128.67 (d, *J* = 8.2 Hz), 128.23 (d, *J* = 1.2 Hz), 127.61, 127.49, 127.30, 124.78 (dd, J_1 = 2.6 Hz, J_2 = 15.2 Hz), 124.23 (d, *J* = 3.0 Hz), 115.10, 70.72. **^{31}P NMR (162 MHz, CDCl$_3$)** δ -51.40 **HRMS (ESI)** calculated [M+H]$^+$ for $C_{31}H_{25}FOP$: 463.1622, found: 463.1646. **FTIR (cm^{-1})** 3925, 3861, 3143, 3648, 3061, 3004, 2362, 1835, 1707, 1648, 1547, 1395, 1263, 1222, 1107, 1062, 808, 745, 667.

3-(3,4-Dichlorophenyl)-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4o)



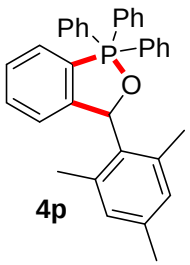
4o

Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.179 g, 146 µL, 0.60 mmol) and 3,4-dichlorobenzaldehyde **2o** (0.131 g, 0.75 mmol) with triphenylphosphine **1a** (0.131 g, 0.50 mmol) in the presence of KF (0.070 g, 1.20 mmol) and 18-crown-6 (0.317 g, 1.20 mmol) in THF (3.0 mL) at -10 °C to rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 40/60) of the crude reaction mixture using silica gel afforded 3-(3,4-dichlorophenyl)-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole **4o** as a white solid (0.210 g, 82% yield).

***R*$_f$** (EtOAc): 0.48; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.52-7.48 (m, 1H, H$_{ar}$), 7.37-7.29 (m, 15H, H$_{ar}$), 7.28-7.22 (m, 3H, H$_{ar}$), 7.07 (bs, 1H, H$_{ar}$), 6.98 (dd, J_1 = 1.9 Hz, J_2 = 8.3 Hz, 1H, H$_{ar}$), 6.87 (dd, J_1 = 8.0 Hz, J_2 = 11.7 Hz, 1H, H$_{ar}$), 5.64 (s, 1H, CH). **^{13}C NMR (100 MHz, CDCl$_3$)** δ

153.18 (d, J = 20.6 Hz), 144.96, 142.31, 136.85 (d, J = 14.5 Hz), 132.60, 132.29, 131.43 (d, J = 8.8 Hz), 131.02, 130.13, 129.68, 128.42, 127.64, (d, J = 12.3 Hz), 126.88, 124.91 (d, J = 14.5 Hz), 76.08. **^{31}P NMR (162 MHz, $CDCl_3$)** δ -49.64 **HRMS (ESI)** calculated $[M+H]^+$ for $C_{31}H_{24}Cl_2OP$: 513.0936, found: 513.0968. **FTIR (cm^{-1})** 3925, 3861, 2829, 3677, 3619. 3059, 2978, 2361, 1835, 1707, 1693, 1547, 1482, 1395, 1258, 1118, 894, 745, 716.

3-Mesityl-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4p)

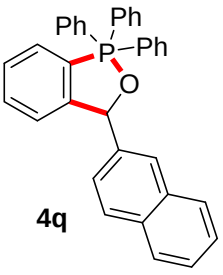


4p

Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.179 g, 146 µL, 0.60 mmol) and 2,4,6-trimethylbenzaldehyde **3p** (0.111 g, 111 µL, 0.75 mmol) with triphenylphosphine **1a** (0.131 g, 0.50 mmol) in the presence of KF (0.070 g, 1.20 mmol) and 18-crown-6 (0.317 g, 1.20 mmol) in THF (3.0 mL) at -10 °C to rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 40/60) of the crude reaction mixture using silica gel afforded 3-mesityl-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole **4p** as a white solid (0.151 g, 62% yield).

***R*$_f$** (EtOAc): 0.29; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.49-7.41 (m, 7H, H_{ar}), 7.32 (bs, 9H, H_{ar}), 7.27-7.17 (m, 1H, H_{ar}), 7.07-7.03 (m, 2H, H_{ar}), 6.76 (bs, 2H, H_{ar}), 5.62 (s, 1H, CH), 2.23 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 1.86 (s, 3H, CH_3),. **^{13}C NMR (100 MHz, $CDCl_3$)** δ 155.41 (d, J = 19.4 Hz), 141.84, 140.79, 138.04, 137.38, 136.90, 136.49 (d, J = 13.8 Hz), 134.05, 132.10, 131.71 (d, J = 8.7 Hz), 130.76, 128.87, 128.33, 127.52 (d, J = 12.3 Hz), 126.81 (d, J = 14.3 Hz), 123.47 (d, J = 14.6 Hz), 70.45, 21.13, 20.96, 20.53. **^{31}P NMR (162 MHz, $CDCl_3$)** δ -49.31 **HRMS (ESI)** calculated $[M+H]^+$ for $C_{34}H_{32}OP$: 487.2185, found: 487.2185. **FTIR (cm^{-1})** 3759, 3672, 3063, 3013, 2926, 2855, 1891, 1626, 1517, 1438, 1342, 1273, 1071, 987, 839, 744.

3-(Naphthalen-2-yl)-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4q)



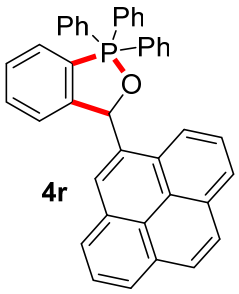
4q

Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.179 g, 146 µL, 0.60 mmol) and 2-naphthaldehyde **3q** (0.117 g, 0.75 mmol) with triphenylphosphine **1a** (0.131 g, 0.50 mmol) in the presence of KF (0.070 g, 1.20 mmol) and 18-crown-6 (0.317 g, 1.20 mmol) in THF (3.0 mL) at -10 °C to rt for 12 h followed by

flash column chromatography (Pet. ether /EtOAc = 40/60) of the crude reaction mixture using silica gel afforded 3-(naphthalen-2-yl)-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2] oxaphosphole **4q** as a white solid (0.195 g, 79% yield).

***R*$_f$** (EtOAc): 0.54; **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.65-7.64 (m, 1H, H$_{ar}$), 7.60 (d, *J* = 8.5 Hz, 1H, H$_{ar}$), 7.54-7.53 (m, 1H, H$_{ar}$), 7.43 (s, 1H, H$_{ar}$), 7.36-7.28 (m, 9H, H$_{ar}$), 7.20 (bs, 9H, H$_{ar}$), 7.15-7.07 (m, 3H, H$_{ar}$), 6.74 (d, *J* = 10.3 Hz, 2H, H$_{ar}$), 5.68 (s, 1H, CH). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 154.31 (d, *J* = 21.9 Hz), 143.96, 143.10, 141.63, 136.57 (d, *J* = 14.5 Hz), 133.37, 132.99, 132.30 (d, *J* = 2.1 Hz), 132.24, 131.59 (d, *J* = 8.9 Hz), 128.63 (d, *J* = 12.1 Hz), 128.12, 128.03 (d, *J* = 6.8 Hz), 127.66, 127.50 (d, *J* = 12.3 Hz), 127.28, 126.92, 125.81 (d, *J* = 8.9 Hz), 125.60, 125.02 (d, *J* = 15.5 Hz), 77.16 (merged with the $CDCl_3$ peak). **^{31}P NMR (203 MHz, CDCl$_3$)** δ -49.43 **HRMS (ESI)** calculated $[M+H]^+$ for $C_{35}H_{28}OP$: 495.1872, found: 495.1876. **FTIR (cm^{-1})** 3843, 3648, 3590, 3063, 2926, 2321, 1635, 1607, 1514, 1432, 1292, 1185, 1083, 889, 815, 751, 696.

1,1,1-Triphenyl-3-(pyren-4-yl)-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4r)



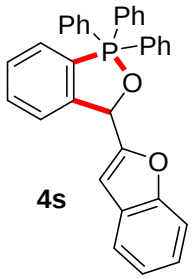
4r

Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.179 g, 146 µL, 0.60 mmol) and pyrene-4-carbaldehyde **2r** (0.173 g, 0.75 mmol) with triphenylphosphine **1r** (0.131 g, 0.50 mmol) in the presence of KF (0.070 g, 1.20 mmol) and 18-crown-6 (0.317 g, 1.20 mmol) in THF (3.0 mL) at -10 °C to rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 40/60) of the crude reaction mixture using silica gel afforded 1,1,1-triphenyl-3-(pyren-4-yl)-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole **4r** as a yellow solid (0.201 g, 71% yield).

***R*$_f$** (EtOAc): 0.53; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.46 (d, *J* = 9.4 Hz, 1H, H$_{ar}$), 8.19 (d, *J* = 7.6 Hz, 2H, H$_{ar}$), 8.11 (d, *J* = 9.4 Hz, 1H, H$_{ar}$), 8.07-8.04 (m, 3H, H$_{ar}$), 8.00 (d, *J* = 7.7 Hz, 1H, H$_{ar}$), 7.75 (d, *J* = 8.0 Hz, 1H, H$_{ar}$), 7.60-7.50 (m, 6H, H$_{ar}$), 7.40-7.34 (m, 10H, H$_{ar}$), 7.29-7.22 (m, 2H, H$_{ar}$), 7.04 (dd, J_1 = 8.3 Hz, J_2 = 11.2 Hz, 1H, H$_{ar}$), 6.77 (s, 1H, CH). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 154.84 (d, *J* = 21.0 Hz), 143.60, 142.55, 137.94, 136.72 (d, *J* = 14.4 Hz), 132.33 (d, *J* = 2.7 Hz), 132.22, 132.12, 131.62 (d, *J* = 8.9 Hz), 131.46, 130.80, 130.57, 129.46, 128.93, 128.66, 128.54, 128.25, 127.56 (d, *J* = 12.6 Hz), 127.44, 127.04, 125.96, 125.82, 125.23 (d, *J* = 15.9 Hz), 124.92 (d, *J* = 16.8 Hz), 123.60, 73.01. **^{31}P NMR (162 MHz, CDCl$_3$)** δ -50.44 **HRMS**

(ESI) calculated $[M+H]^+$ for $C_{41}H_{30}OP$: 569.2029, found: 569.2029. **FTIR (cm^{-1})** 2985, 1733, 1438, 1372, 1241, 1194, 1045, 939, 847, 754, 696, 654, 639.

3-(Benzofuran-2-yl)-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4s)

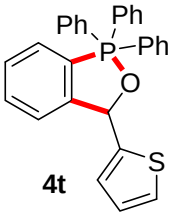


4s

Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.179 g, 146 µL, 0.60 mmol) and benzofuran-2-carbaldehyde **3s** (0.110 g, 91 µL, 0.75 mmol) with triphenylphosphine **1a** (0.131 g, 0.50 mmol) in the presence of KF (0.070 g, 1.20 mmol) and 18-crown-6 (0.317 g, 1.20 mmol) in THF (3.0 mL) at -10 °C to rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 40/60) of the crude reaction mixture using silica gel afforded 3-(benzofuran-2-yl)-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole **4s** as a white solid (0.203 g, 83% yield).

***R*$_f$** (EtOAc): 0.36; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65-7.63 (m, 1H, H_{ar}), 7.60-7.56 (m, 1H, H_{ar}), 7.52-7.43 (m, 8H, H_{ar}), 7.39-7.31 (m, 9H, H_{ar}), 7.29-7.25 (m, 2H, H_{ar}), 7.23-7.20 (m, 1H, H_{ar}), 6.83 (dd, J_1 = 8.0 Hz, J_2 = 11.3 Hz, 1H), 6.35 (s, 1H), 5.92 (s, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.23, 155.21, 150.81 (d, J = 20.4 Hz), 143.66, 142.60, 136.88 (d, J = 14.3 Hz), 132.52 (d, J = 3.0 Hz), 131.69 (d, J = 9.0 Hz), 128.43, 128.26 (d, J = 2.2 Hz), 127.99 (d, J = 14.2 Hz), 127.46 (d, J = 12.5 Hz), 124.82 (d, J = 15.1 Hz), 123.70, 122.47, 120.92, 111.91, 103.94, 70.49. **^{31}P NMR (162 MHz, $CDCl_3$)** δ -43.56 **HRMS (ESI)** calculated $[M+H]^+$ for $C_{33}H_{26}OP$: 485.1665, found: 485.1674. **FTIR (cm^{-1})** 3893, 3843, 3743, 3678, 3648, 3619, 3015, 2396, 1741, 1693, 1647, 1516, 1461, 1216, 1117, 741, 668.

1,1,1-Triphenyl-3-(thiophen-2-yl)-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4t)



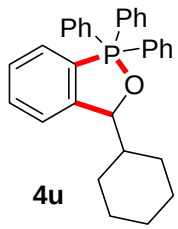
4t

Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.179 g, 146µL, 0.60 mmol) and thiophene-2-carbaldehyde **3t** (0.084 g, 70 µL, 0.75 mmol) with triphenylphosphine **1a** (0.131 g, 0.50 mmol) in the presence of KF (0.070 g, 1.2 mmol) and 18-crown-6 (0.317 g, 1.2 mmol) in THF (3.0 mL) at -10 °C to rt for 12 h followed by flash

column chromatography (Pet. ether /EtOAc = 40/60) of the crude reaction mixture using silica gel afforded 1,1,1-triphenyl-3-(thiophen-2-yl)-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole **4t** as a white solid (0.149 g, 66% yield).

***R*$_f$** (EtOAc): 0.39 **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.52 (t, *J* = 6.2 Hz, 1H, H$_{ar}$), 7.44-7.41 (m, 6H, H$_{ar}$), 7.39-7.34 (m, 10H, H$_{ar}$), 7.27-7.23 (m, 1H, H$_{ar}$), 7.20 (d, *J* = 4.7 Hz, 1H, H$_{ar}$), 7.02 (s, 1H, H$_{ar}$), 6.94 (bs, 1H), 6.84 (t, *J* = 8.6 Hz, 1H, H$_{ar}$), 5.83 (s, 1H, CH). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 153.78 (d, *J* = 20.6 Hz), 148.64, 143.40, 142.55, 136.36 (d, *J* = 14.4 Hz), 132.30 (d, *J* = 2.8 Hz), 131.56 (d, *J* = 9.1 Hz), 128.11, 127.66, 127.54, 127.38 (d, *J* = 12.1Hz), 126.09, 125.16 (d, *J* = 11.9 Hz), 124.75 (d, *J* = 15.7 Hz), 71.95. **^{31}P NMR (203 MHz, CDCl$_3$)** δ -51.66 **HRMS (ESI)** calculated [M+H]$^+$ for $C_{29}H_{24}OPS$: 451.1280, found: 451.1279. **FTIR (cm^{-1})** 3894, 3861, 3678, 3648, 3619, 3011, 2873, 2362, 1836, 1741, 1693, 1647, 1464, 1216, 1116. 1030. 948, 741, 656.

3-Cyclohexyl-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4u)

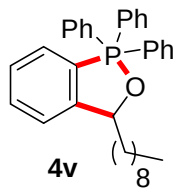


4u

Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.179 g, 146 µL, 0.60 mmol) and cyclohexanecarbaldehyde **3u** (0.084 g, 91 µL, 0.75 mmol) with triphenylphosphine **1a** (0.131 g, 0.50 mmol) in the presence of KF (0.070 g, 1.20 mmol) and 18-crown-6 (0.317 g, 1.20 mmol) in THF (3.0 mL) at -10 °C to rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 40/60) of the crude reaction mixture using silica gel afforded 3-cyclohexyl-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole **4u** as a white solid (0.191 g, 85% yield).

***R*$_f$** (EtOAc): 0.33; **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.55 (s, 2H, H$_{ar}$), 7.38-7.36 (m, 6H, H$_{ar}$), 7.30-7.26 (m, 9H, H$_{ar}$), 7.24 (bs, 1H, H$_{ar}$), 6.91-6.89 (m, 1H, H$_{ar}$), 4.64 (s, 1H, CH), 1.75 (bs, 2H), 1.63 (bs, 3H), 1.38-1.25 (m, 3H), 1.10-1.06 (m, 2H), 0.84-0.83 (m, 1H). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 154.05 (d, *J* = 24.2 Hz), 144.80, 143.96, 136.61 (d, *J* = 14.5 Hz), 131.59 (d, *J* = 8.8 Hz), 129.95, 127.64, 127.10 (d, *J* = 12.1 Hz), 126.77 (d, *J* = 14.1 Hz), 123.38 (d, *J* = 15.7 Hz), 77.84, 44.07, 30.69, 27.18, 26.87, 26.65, 26.54. **^{31}P NMR (203 MHz, CDCl$_3$)** δ -52.53 **HRMS (ESI)** calculated [M+H]$^+$ for $C_{31}H_{32}OP$: 451.2185, found: 451.2185. **FTIR (cm^{-1})** 3840, 3861, 3743, 3678, 3619, 3059, 3007. 2929, 2854, 2361, 1693, 1647, 1515, 1482, 1437, 1261, 1218, 1107, 1023, 860, 812, 743, 698.

3-Nonyl-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4v)

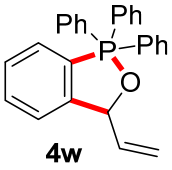


4v

Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.179 g, 146 µL, 0.60 mmol) and decanal **3v** (0.117 g, 141 µL, 0.75 mmol) with triphenylphosphine **1a** (0.131 g, 0.50 mmol) in the presence of KF (0.070 g, 1.20 mmol) and 18-crown-6 (0.317 g, 1.20 mmol) in THF (3.0 mL) at -10 °C to rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 40/60) of the crude reaction mixture using silica gel afforded 3-nonyl-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole **4v** as a white solid (0.146 g, 59% yield).

***R*$_f$** (EtOAc): 0.38; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.57-7.53 (m, 1H, H$_{ar}$), 7.51-7.49 (m, 1H, H$_{ar}$), 7.35-7.33 (m, 4H, H$_{ar}$), 7.31-7.25 (m, 11H, H$_{ar}$), 7.22-7.18 (m, 1H, H$_{ar}$), 6.74 (dd, J_1 = 8.2 Hz, J_2 = 11.3 Hz, 1H, H$_{ar}$), 4.78 (dd, J_1 = 4.1 Hz, J_2 = 6.0 Hz, 1H, CH), 1.77-1.72 (m, 1H), 1.61-1.56 (m, 1H), 1.39-1.28 (m, 4H), 1.23 (bs, 4H), 1.14 (bs, 6H), 0.90 (t, J = 6.8 Hz, 3H, CH$_3$). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 155.06 (d, J = 22.8 Hz), 143.32, 142.27, 136.62 (d, J = 14.5 Hz), 132.26 (d, J = 2.7 Hz), 131.81 (d, J = 8.9 Hz), 128.27, 127.42 (d, J = 12.3 Hz), 126.98 (d, J = 14.1 Hz), 123.76 (d, J = 15.4 Hz), 73.18 (d, J = 2.4 Hz), 37.13, 32.01, 29.91, 29.61, 29.56, 29.40, 25.21, 22.79, 14.24. **^{31}P NMR (162 MHz, CDCl$_3$)** δ -46.43 **HRMS (ESI)** calculated [M+H]$^+$ for $C_{34}H_{40}OP$: 495.2811, found: 495.2810. **FTIR (cm^{-1})** 3842, 3743, 3616, 1063, 2927. 2855. 2360, 1742, 16932, 1648. 1488, 1436, 1293, 1180, 1117, 1081, 1003, 836, 744, 697.

1,1,1-Triphenyl-3-vinyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4w)



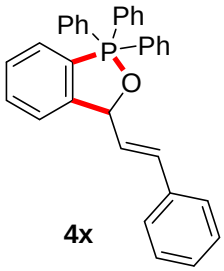
4w

Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.179 g, 146 µL, 0.60 mmol) and acrylaldehyde **3w** (0.042 g, 50 µL, 0.75 mmol) with triphenylphosphine **1a** (0.131 g, 0.50 mmol) in the presence of KF (0.070 g, 1.20 mmol) and 18-crown-6 (0.317 g, 1.20 mmol) in THF (3.0 mL) at -10 °C to rt for 24 h followed by flash column chromatography (Pet. ether /EtOAc = 40/60) of the crude reaction mixture using silica gel afforded 1,1,1-triphenyl-3-vinyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole **4w** as a yellow solid (0.132 g, 67% yield).

***R*$_f$** (EtOAc): 0.21; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.60-7.56 (m, 1H, H$_{ar}$), 7.50 (d, J = 7.2 Hz, 1H, H$_{ar}$), 7.38-7.36 (m, 4H, H$_{ar}$), 7.34-7.27 (m, 11H, H$_{ar}$), 7.25-7.22 (m, 1H, H$_{ar}$), 6.73 (dd, J_1 = 8.1 Hz, J_2 = 10.9 Hz, 1H, H$_{ar}$), 5.92-5.83 (m, 1H), 5.24 (d, J = 17.0 Hz, 1H), 5.16-5.14 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.81 (d, *J* = 22.7 Hz), 144.33, 143.28, 139.60, 136.68 (d, *J* = 14.5 Hz), 132.20 (d, *J* = 3.1 Hz), 131.52 (d, *J* = 9.0 Hz), 127.99 (d, *J* = 2.1 Hz), 127.36, 127.24, 124.34 (d, *J* = 15.5 Hz), 116.10, 75.95. **^{31}P NMR (162 MHz, $CDCl_3$)** δ -51.78 **HRMS (ESI)** calculated $[M+H]^+$ for $C_{27}H_{24}OP$: 395.1559, found: 395.1559. **FTIR (cm^{-1})** 3925, 3861, 3743, 3619, 3060, 2980, 2320, 1964, 1693, 1612, 1469, 1435, 1369, 1251, 1182, 1039, 938, 803, 692.

1,1,1-Triphenyl-3-styryl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4x)

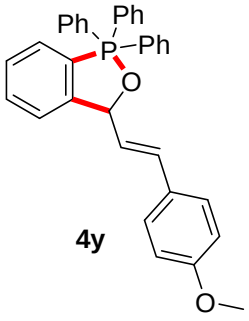


4x

Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.179 g, 146 µL, 0.60 mmol) and *trans* cinnamaldehyde **3x** (0.099 g, 94 µL, 0.75 mmol) with triphenylphosphine **1a** (0.131 g, 0.50 mmol) in the presence of KF (0.070 g, 1.20 mmol) and 18-crown-6 (0.317 g, 1.20 mmol) in THF (3.0 mL) at -10 °C to rt for 24 h followed by flash column chromatography (Pet. ether /EtOAc = 40/60) of the crude reaction mixture using silica gel afforded 1,1,1-triphenyl-3-styryl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole **4x** as a yellow solid (0.156 g, 66% yield).

***R*$_f$** (EtOAc): 0.30; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.60-7.53 (m, 2H, H_{ar}), 7.40-7.37 (m, 4H, H_{ar}), 7.53-7.29 (m, 15H, H_{ar}), 7.27-7.24 (m, 2H, H_{ar}), 6.75 (dd, J_1 = 8.2 Hz, J_2 = 10.8 Hz, 1H), 6.49 (d, *J* = 15.6 Hz, 1H), 6.23 (dd, J_1 = 7.0 Hz, J_2 = 15.7 Hz, 1H), 5.35 (s, 1H, CH). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 153.17 (d, *J* = 22.4 Hz), 144.59, 143.53, 137.23, 136.84 (d, *J* = 14.6 Hz), 132.28 (d, *J* = 2.9 Hz), 131.59 (d, *J* = 8.9 Hz), 131.18 (d, *J* = 9.9 Hz), 129.00, 128.45, 128.03, (d, *J* = 2.0 Hz), 127.66, 127.58, 127.39 (d, *J* = 12.3 Hz), 126.62, 124.45 (d, *J* = 15.4 Hz), 75.35. **^{31}P NMR (162 MHz, $CDCl_3$)** δ -51.56 **HRMS (ESI)** calculated $[M+H]^+$ for $C_{33}H_{28}OP$: 471.1872, found: 471.1896. **FTIR (cm^{-1})** 3829. 3743, 3678, 3648. 3061. 2980, 2320. 1738, 1647, 1609, 1469. 1433, 1370, 1250, 1195, 1112, 1039, 986, 872, 801, 742.

3-(4-Methoxystyryl)-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4y)



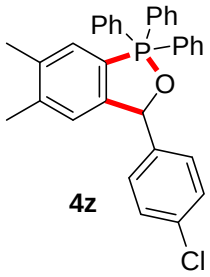
4y

Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.179 g, 146 µL, 0.60 mmol) and (*E*)-3-(4-methoxyphenyl)acrylaldehyde **3y** (0.122 g, 0.75 mmol) with triphenylphosphine **1a** (0.131 g, 0.50 mmol) in the presence of KF (0.070

g, 1.20 mmol) and 18-crown-6 (0.317 g, 1.20 mmol) in THF (3.0 mL) at -10 °C to rt for 24 h followed by flash column chromatography (Pet. ether /EtOAc = 40/60) of the crude reaction mixture using silica gel afforded 3-(4-methoxystyryl)-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole **4y** as a yellow solid (0.153 g, 61% yield).

***R*$_f$** (EtOAc): 0.27; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.73-7.64 (m, 1H, H$_{ar}$), 7.56-7.47 (m, 3H, H$_{ar}$), 7.36-7.33 (m, 4H, H$_{ar}$), 7.31-7.26 (m, 9H, H$_{ar}$), 7.22 (d, *J* = 7.9 Hz, 3H, H$_{ar}$), 6.82 (d, *J* = 8.5 Hz, 2H, H$_{ar}$), 6.71 (t, *J* = 9.1 Hz, 1H, H$_{ar}$), 6.41 (d, *J* = 15.8 Hz, 1H), 6.05 (d, J_1 = 8.5 Hz, J_2 = 15.7 Hz, 1H), 5.27 (d, *J* = 7.1 Hz, 1H, CH), 3.79 (s, 3H, CH$_3$). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 159.04, 153.35 (d, *J* = 22.7 Hz), 144.59, 143.54, 136.75 (d, *J* = 14.5 Hz), 132.22, 132.12, 132.04, 131.59 (d, *J* = 8.8 Hz), 130.85, 130.00, 128.93, 127.98 (d, *J* = 1.8 Hz), 127.75, 127.35, (d, *J* = 12.4 Hz), 124.47 (d, *J* = 15.4 Hz), 113.86, 75.46, 55.31. **^{31}P NMR (162 MHz, CDCl$_3$)** δ -51.80 **HRMS (ESI)** calculated [M+H] $^+$ for $C_{34}H_{30}OP$: 501.1978, found: 501.1995. **FTIR (cm^{-1})** 3861, 3744, 3678, 3619, 3060, 2981, 1736, 1647. 1608, 1469, 1434, 1370, 1249, 1195, 1113, 1079, 986, 872, 833, 745.

3-(4-Chlorophenyl)-5,6-dimethyl-1,1,1-triphenyl-1,3-dihydro-1λ^5 benzo[*c*][1,2]oxaphosphole (4z)



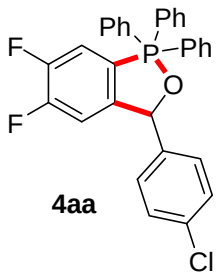
4z

Following the general procedure, treatment of 4,5-dimethyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2z** (0.196 g, 0.60 mmol) and 4-chlorobenzaldehyde **3a** (0.105 g, 0.75 mmol) with triphenylphosphine **1a** (0.131 g, 0.50 mmol) in the presence of KF (0.070 g, 1.2 mmol) and 18-crown-6 (0.317 g, 1.2 mmol) in THF (3.0 mL) at -10 °C to rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 40/60) of the crude reaction mixture using silica gel afforded 3-(4-chlorophenyl)-5,6-dimethyl-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole **4z** as a white solid (0.163 g, 64% yield).

***R*$_f$** (EtOAc): 0.39; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.42-7.37 (m, 6H), 7.32-7.26 (m, 9H), 7.22 (d, *J* =8.1 Hz, 2H), 7.07 (d, *J* = 7.8 Hz, 2H), 6.98 (bs, 1H), 6.59 (d, *J* = 11.3 Hz, 1H), 5.61 (s, 1H, CH), 2.27 (s, 3H), 2.13 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 151.96 (d, *J* = 21.2 Hz), 144.07, 143.33, 143.01, 142.08 (d, *J* = 3.1 Hz), 137.26 (d, *J* = 14.9 Hz), 135.96 (d, *J* = 14.8 Hz), 132.72, 131.35 (d, *J* = 8.6 Hz), 129.06, 128.60, 127.99 (d, *J* = 1.7 Hz), 127.38 (d, *J* = 12.3 Hz), 125.84 (d, *J* = 16.2 Hz), 76.24, 20.15, 20.11. **^{31}P NMR (162 MHz, CDCl$_3$)** δ -51.37 **HRMS (ESI)**

calculated $[M+H]^+$ for $C_{33}H_{29}ClOP$: 507.1639, found: 507.1643. **FTIR (cm^{-1})** 3925, 3861, 3829, 3648, 3566, 3058, 2979, 2360, 1835, 1741, 1707, 1647, 1485, 1436, 1265, 1225, 1081, 1018, 810, 745, 662.

3-(4-Chlorophenyl)-5,6-difluoro-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4aa)

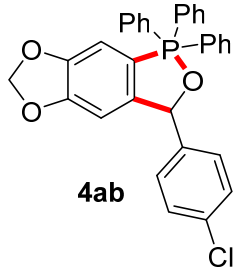


4aa

Following the general procedure, treatment of 4,5-difluoro-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2aa** (0.201 g, 0.60 mmol) and 4-chlorobenzaldehyde **3a** (0.105 g, 0.75 mmol) with triphenylphosphine **1a** (0.131 g, 0.50 mmol) in the presence of KF (0.070 g, 1.20 mmol) and 18-crown-6 (0.317 g, 1.20 mmol) in THF (3.0 mL) at -10 °C to rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 40/60) of the crude reaction mixture using silica gel afforded 3-(4-chlorophenyl)-5,6-difluoro-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole **4aa** as a white solid (0.193 g, 75% yield).

***R*$_f$** (EtOAc): 0.48; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.37-7.32 (m, 15H, H_{ar}), 7.22 (d, *J* = 8.0 Hz, 2H, H_{ar}), 7.04 (d, *J* = 8.0 Hz, 2H, H_{ar}), 6.93 (t, *J* = 6.9 Hz, 1H, H_{ar}), 6.62-6.55 (m, 1H, H_{ar}), 5.43 (s, 1H, CH). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 153.33 (d, *J* = 259.8 Hz), 153.20 (d, *J* = 257.5 Hz), 151.16-150.81 (m), 150.62 (d, *J* = 5.4 Hz), 148.51 (d, J_1 = 12.9 Hz, J_2 = 22.0 Hz), 142.99, 141.78, 133.46, 131.39 (d, *J* = 9.0 Hz), 129.03, 128.62 (d, *J* = 7.2 Hz), 127.93, 127.70 (d, *J* = 12.5 Hz), 124.57 (t, *J* = 18.7 Hz), 113.13 (t, *J* = 18.4 Hz), 75.45. **^{31}P NMR (162 MHz, $CDCl_3$)** δ -51.78 **HRMS (ESI)** calculated $[M+H]^+$ for $C_{31}H_{23}ClF_2OP$: 515.1138, found: 515.1165. **FTIR (cm^{-1})** 3894, 3861, 3744, 3678, 2928, 2361, 1741, 1693, 1647, 1614, 1516, 1488, 1430, 1293, 1215, 1084, 1006, 898, 742.

3-(4-Chlorophenyl)-1,1,1-triphenyl-1,3-dihydro-1λ^5-[1,3]dioxolo[4',5':4,5]benzo[1,2-*c*][1,2]oxaphosphole (4ab)



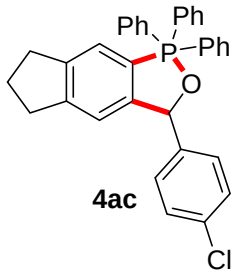
4ab

Following the general procedure, treatment of 6-(trimethylsilyl)benzo[*d*][1,3]dioxol-5-yl trifluoromethanesulfonate **2ab** (0.206 g, 0.60 mmol) and 4-chlorobenzaldehyde **3a** (0.105 g, 0.75 mmol) with triphenylphosphine **1a** (0.131 g, 0.50 mmol) in the presence of KF (0.070 g, 1.20 mmol) and 18-crown-6 (0.317 g, 1.20 mmol) in THF (3.0 mL) at -10 °C to rt for 12 h followed by flash column chromatography (Pet.

ether /EtOAc = 40/60) of the crude reaction mixture using silica gel afforded 3-(4-chlorophenyl)-1,1,1-triphenyl-1,3-dihydro-1λ^5-[1,3]dioxolo[4',5':4,5]benzo[1,2-*c*][1,2] oxaphosphole **4ab** as a white solid (0.201 g, 77% yield).

***R*$_f$** (EtOAc): 0.32; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.40-7.26 (m, 6H, H$_{ar}$), 7.32 (bs, 9H, H$_{ar}$), 7.22-7.20 (m, 2H, H$_{ar}$), 7.06-7.04 (m, 2H, H$_{ar}$), 6.59 (bs, 1H, H$_{ar}$), 6.21-6.17 (m, 1H, H$_{ar}$), 5.97 (d, *J* = 6.2 Hz, 2H, CH$_2$), 5.50 (s, 1H, CH). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 151.94, 150.23 (d, *J* = 23.0 Hz), 147.84 (d, *J* = 22.4 Hz), 143.31, 142.73, 142.25, 133.02, 131.41 (d, *J* = 8.9 Hz), 129.10, 128.37 (d, *J* = 9.3 Hz), 127.57 (d, *J* = 12.5 Hz), 120.74, 119.34, 114.56 (d, *J* = 19.3 Hz), 104.85 (d, *J* = 19.1 Hz), 102.28, 76.16. **^{31}P NMR (162 MHz, CDCl$_3$)** δ -49.02 **HRMS (ESI)** calculated [M+H]$^+$ for $C_{32}H_{25}ClO_3P$: 523.1224, found: 523.1228. **FTIR (cm^{-1})** 3829, 3744, 3619, 3061, 2981, 2899, 1736, 1609, 1469, 1432, 1250, 1079, 986, 832, 745, 661.

3-(4-Chlorophenyl)-1,1,1-triphenyl-3,5,6,7-tetrahydro-1*H*-1λ^5-indeno[5,6-*c*][1,2]oxaphosphole (4ac)



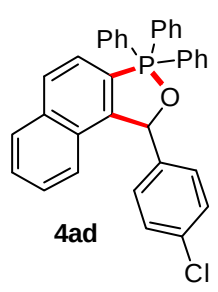
4ac

Following the general procedure, treatment of 6-(trimethylsilyl)-2,3-dihydro-1*H*-inden-5-yl trifluoromethanesulfonate **2ac** (0.201 g, 0.60 mmol) and 4-chlorobenzaldehyde **3a** (0.105 g, 0.75 mmol) with triphenylphosphine **1a** (0.131 g, 0.50 mmol) in the presence of KF (0.070 g, 1.20 mmol) and 18-crown-6 (0.317 g, 1.20 mmol) in THF (3.0 mL) at -10 °C to rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 40/60) of the crude reaction mixture using silica gel afforded 3-(4-chlorophenyl)-1,1,1-triphenyl-3,5,6,7-tetrahydro-1*H*-1λ^5-indeno[5,6-*c*][1,2]oxaphosphole **4ac** as a white solid (0.204 g, 79% yield).

***R*$_f$** (EtOAc): 0.43; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.42-7.37 (m, 6H, H$_{ar}$), 7.31-7.27 (m, 9H, H$_{ar}$), 7.21 (d, *J* = 8.3 Hz, 2H, H$_{ar}$), 7.08 (d, *J* = 8.4 Hz, 2H, H$_{ar}$), 7.03 (bs, 1H, H$_{ar}$), 6.69 (d, *J* = 11.3 Hz, 1H, H$_{ar}$), 5.59 (s, 1H, CH), 2.94-2.83 (m, 2H, CH$_2$), 2.77 (t, *J* = 7.3 Hz, 2H, CH$_2$), 2.12-2.04 (m, 2H, CH$_2$). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 152.89 (d, *J* = 22.5 Hz), 150.18 (d, *J* = 2.9 Hz), 144.23, 144.19, 144.08, 143.42, 143.12, 132.74, 131.84 (d, *J* = 15.4 Hz), 131.34 (d, *J* = 8.9 Hz), 129.10, 128.29, 127.96 (d, *J* = 1.8 Hz), 127.39 (d, *J* = 12.3 Hz), 120.53 (d, *J* = 17.0 Hz), 76.37, 32.71, 32.47, 25.85. **^{31}P NMR (162 MHz, CDCl$_3$)** δ -51.78 **HRMS (ESI)** calculated [M+H]$^+$ for $C_{34}H_{29}ClOP$: 519.1639, found: 519.1638. **FTIR (cm^{-1})** 3893, 3843, 3743, 3565,

3059, 3008, 2361, 1845, 1740, 1693, 1546, 1485, 1436, 1398, 1268, 1195, 1111, 1034, 803, 694, 633.

1-(4-Chlorophenyl)-3,3,3-triphenyl-1,3-dihydro-3λ^5-naphtho[2,1-*c*][1,2]oxaphosphole (4ad)

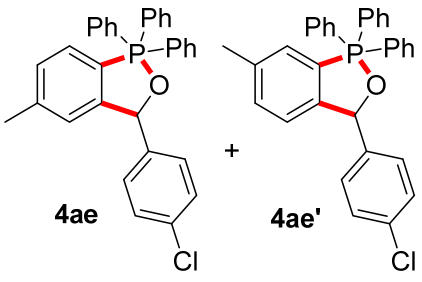


4ad

Following the general procedure, treatment of 2-(trimethylsilyl)naphthalen-1-yl trifluoromethanesulfonate **1ad** (0.209 g, 0.60 mmol) and 4-chlorobenzaldehyde **3a** (0.105 g, 0.75 mmol) with triphenylphosphine **1a** (0.131 g, 0.50 mmol) in the presence of KF (0.070 g, 1.20 mmol) and 18-crown-6 (0.317 g, 1.20 mmol) in THF (3.0 mL) at -10 °C to rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 40/60) of the crude reaction mixture using silica gel afforded 1-(4-chlorophenyl)-3,3,3-triphenyl-1,3-dihydro-3λ^5-naphtho[2,1-c][1,2]oxaphosphole **4ad** as a white solid (0.181 g, 68% yield).

***R*$_f$** (EtOAc): 0.45; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.81 (d, *J* = 8.2 Hz, 1H, H$_{ar}$), 7.71 (d, *J* = 8.3 Hz, 1H, H$_{ar}$), 7.50-7.42 (m, 8H, H$_{ar}$), 7.36 (d, *J* = 8.2 Hz, 2H, H$_{ar}$), 7.27-7.22 (m, 10H, H$_{ar}$), 7.19 (d, *J* = 7.5 Hz, 1H, H$_{ar}$), 7.05 (d, *J* = 8.6 Hz, 1H, H$_{ar}$), 6.91 (t, *J* = 7.3 Hz, 1H, H$_{ar}$), 6.23 (d, *J* = 8.2 Hz, 1H, H$_{ar}$). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 147.85, 147.00, 142.93, 141.47 (d, *J* = 2.0 Hz), 134.05 (d, *J* = 8.0 Hz), 133.55, 132.21 (d, *J* = 11.3 Hz), 131.83 (d, *J* = 9.9 Hz), 131.46, 128.79, 128.56, 128.32, 127.47 (d, *J* = 12.1 Hz), 125.29, 124.81, 121.00, 74.08. **^{31}P NMR (162 MHz, CDCl$_3$)** δ -49.36 **HRMS (ESI)** calculated [M+H]$^+$ for $C_{35}H_{27}ClOP$: 529.1483, found: 529.1483. **FTIR (cm^{-1})** 3894, 3648, 3619, 3011, 2362, 1836, 1707, 1648, 1646, 1467, 1429, 1282, 1217, 1009, 743, 668.

3-(4-Chlorophenyl)-5-methyl-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole & 3-(4-Chlorophenyl)-6-methyl-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4ae & 4ae')



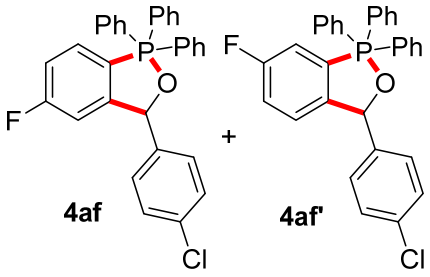
4ae **4ae'**

Following the general procedure, treatment of 5-methyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2e** (0.189 g, 0.60 mmol) and 4-chlorobenzaldehyde **3a** (0.105 g, 0.75 mmol) with triphenylphosphine **1a** (0.131 g, 0.50 mmol) in the presence of KF (0.070 g, 1.20 mmol) and 18-crown-6 (0.317 g, 1.20 mmol) in THF (3.0 mL) at -10 °C to rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 40/60) of the crude reaction

mixture using silica gel afforded 3-(4-chlorophenyl)-5-methyl-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole **4ae** and 3-(4-chlorophenyl)-6-methyl-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole **4ae'** as inseparable mixture of regioisomers in 1:1 ratio as a white solid (0.229 g, 93% yield, regioisomeric ratio was determined by ^{1}H NMR analysis of crude reaction mixture).

***R*$_f$** (EtOAc): 0.45; **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.42-7.36 (m, 6H, H$_{ar}$), 7.34-7.29 (m, 10H, H$_{ar}$), 7.25-7.22 (m, 2H, H$_{ar}$), 7.12-7.06 (m, 3H, H$_{ar}$), 6.78-6.73 (m, H$_{ar}$), 6.67-6.64 (m, H$_{ar}$), 5.61-5.59 (m, 1H, CH), 2.29 (s, CH$_3$), 2.25 (s, CH$_3$). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 154.35 (d, *J* = 21.6 Hz), 131.35 (d, *J* = 21.3 Hz), 143.93 (d, *J* = 5.2 Hz), 143.25, 143.21, 143.11, 142.84, 137.06 (d, *J* = 14.3 Hz), 136.84 (d, *J* = 14.4 Hz), 136.53 (d, *J* = 14.9 Hz), 133.43 (d, *J* = 2.7 Hz), 132.87, 131.42 (d, *J* = 8.8 Hz), 129.17, 129.11, 128.76, 128.61, 128.36 (d, *J* = 2.2 Hz), 128.10, 127.77, 127.46 (d, *J* = 12.4 Hz), 125.64, 125.52, 125.36, 124.06, 124.50, 124.28, 76.37, 76.15, 21.47. **^{31}P NMR (203 MHz, CDCl$_3$)** δ -50.95 & -51.49. **HRMS (ESI)** calculated [M+H]$^+$ for $C_{32}H_{27}ClOP$: 493.1483, found: 493.1480. **FTIR (cm^{-1})** 3054.42, 1733, 1659, 1589, 1484, 1435, 1402, 1255, 1184, 1116, 1087, 1073, 1053, 1028, 1013, 997, 966, 933, 848, 822, 794, 748, 721, 691, 665, 633.

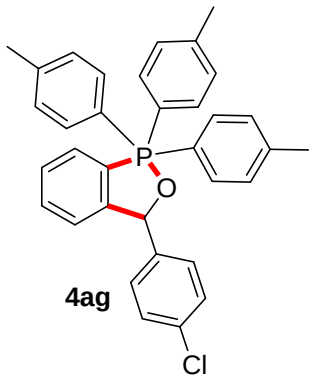
3-(4-Chlorophenyl)-5-fluoro-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole & 3-(4-Chlorophenyl)-6-fluoro-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4af & 4af')



Following the general procedure, treatment of 4-fluoro-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2f** (0.189 g, 0.60 mmol) and 4-chlorobenzaldehyde **3a** (0.105 g, 0.75 mmol) with triphenylphosphine **1a** (0.131 g, 0.50 mmol) in the presence of KF (0.070 g, 1.20 mmol) and 18-crown-6 (0.317 g, 1.20 mmol) in THF (3.0 mL) at -10 °C to rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 40/60) of the crude reaction mixture using silica gel afforded 3-(4-chlorophenyl)-5-fluoro-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole **4af** and 3-(4-chlorophenyl)-6-fluoro-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole **4af'** as inseparable mixture of regioisomers in 3:1 ratio as a white solid (0.216 g, 87% yield, regioisomeric ratio was determined by ^{1}H NMR analysis of crude reaction mixture).

***R*f** (EtOAc): 0.53; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.45-7.38 (m, 4H, H_{ar}), 7.37-7.34 (m, 11H, H_{ar}), 7.27 (d, J = 8.3 Hz, 3H, H_{ar}), 7.12-7.08 (m, 2H, H_{ar}), 6.98-6.80 (m, 2H, H_{ar}), 5.56 (s, 1H, CH). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 165.72 (d, $J_{C\text{-}F}$ = 256.2 Hz), 157.26 (dd, J_1 = 7.9 Hz, J_2 = 24.8 Hz), 143.58, 142.47, 142.28, 138.83-138.62 (m), 133.27, 131.41, 131.34, 129.05, 128.29, 127.59 (d, J = 12.4 Hz), 123.37, 122.63-122.31 (m), 115.10 (dd, J_1 = 17.2 Hz, J_2 = 20.4 Hz), 111.66 (t, J = 21.3 Hz), 76.00. **^{31}P NMR (203 MHz, $CDCl_3$)** δ -52.59. Representative Peaks of Minor Isomer: **^{1}H NMR** δ 7.22-7.14 (m), 6.56-6.50 (m), 5.51 (s). **^{13}C NMR** δ 149.33 (d, J = 20.0 Hz), 143.34, 142.73, 133.21, 131.47, 129.19, 128.58, 128.38, 125.86-125.66 (m), 124.48, 119.80 (d, J = 23.4 Hz), 75.64. **^{31}P NMR** δ -52.23. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{31}H_{24}ClFOP$: 497.1232, found: 497.1232. **FTIR (cm^{-1})** 3843, 3744, 3678, 3648, 3012, 2361, 1741, 1693, 1597, 1483, 1217, 1086, 1053, 955, 830, 742, 697, 636.

3-(4-Chlorophenyl)-1,1,1-tri-*p*-tolyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4ag)

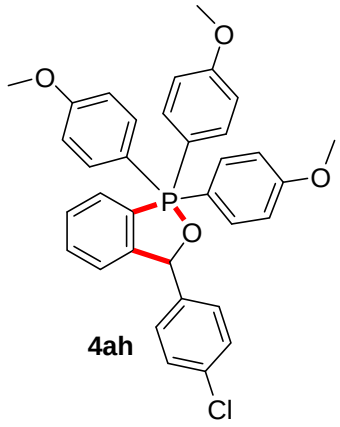


4ag

Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.179 g, 146 μL, 0.60 mmol) and 4-chlorobenzaldehyde **3a** (0.105 g, 0.75 mmol) with tri-*p*-tolylphosphane **1g** (0.152 g, 0.50 mmol) in the presence of KF (0.070 g, 1.20 mmol) and 18-crown-6 (0.317 g, 1.20 mmol) in THF (3.0 mL) at -10 °C to rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 40/60) of the crude reaction mixture using silica gel afforded 3-(4-chlorophenyl)-1,1,1-tri-*p*-tolyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole **4ag** as a white solid (0.193 g, 74% yield).

***R*f** (EtOAc): 0.30; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.47 (t, J = 5.5 Hz, 1H, H_{ar}), 7.32-7.27 (m, 6H, H_{ar}), 7.24-7.20 (m, 4H, H_{ar}), 7.15-7.11 (m, 8H, H_{ar}), 6.90 (dd, J_1 = 8.1 Hz, J_2 = 10.9 Hz, 1H, H_{ar}), 5.56 (s, 1H, CH), 2.39 (s, 9H, $3CH_3$). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 153.79 (d, J = 20.1 Hz), 143.18, 140.10, 139.02, 137.97 (d, J = 1.8 Hz), 136.49 (d, J = 14.5 Hz), 132.77, 132.11, 131.59 (d, J = 9.2 Hz), 129.38, 129.23, 128.23 (d, J = 6.5 Hz), 128.07, 127.24 (d, J = 14.1 Hz), 124.86 (d, J = 15.1 Hz), 75.81, 21.36. **^{31}P NMR (162 MHz, $CDCl_3$)** δ -49.23 **HRMS (ESI)** calculated $[M+H]^+$ for $C_{34}H_{31}ClOP$: 521.1796, found: 521.1797. **FTIR (cm^{-1})** 3743, 3056, 2983, 1733, 1589, 1484, 1437, 1317, 1245, 1184, 1111, 1051, 846, 813, 745, 694. 662

3-(4-Chlorophenyl)-1,1,1-tris(4-methoxyphenyl)-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4ah)

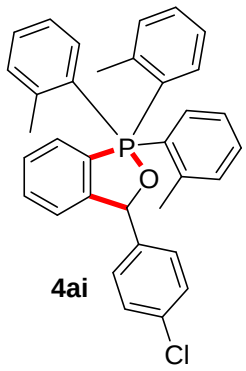


4ah

Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.179 g, 146 µL, 0.60 mmol) and 4-chlorobenzaldehyde **3a** (0.105 g, 0.75 mmol) with tris(4-methoxyphenyl)phosphane **1h** (0.176 g, 0.50 mmol) in the presence of KF (0.070 g, 1.20 mmol) and 18-crown-6 (0.317 g, 1.20 mmol) in THF (3.0 mL) at -10 °C to rt for 12 h followed by flash column chromatography (EtOAc) of the crude reaction mixture using silica gel afforded 3-(4-chlorophenyl)-1,1,1-tris(4-methoxyphenyl)-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole **4ah** as a white solid (0.166 g, 58% yield).

***R*$_f$** (EtOAc): 0.23; **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.65 (t, *J* = 7.0 Hz, 2H, H$_{ar}$), 7.35-7.31 (m, 7H, H$_{ar}$), 7.03-6.99 (m, 3H, H$_{ar}$), 6.92-6.91 (m, 6H, H$_{ar}$), 6.76 (bs, 2H, H$_{ar}$), 5.57 (s, 1H, CH), 3.82 (s, 9H, 3CH$_3$). **^{13}C NMR (125 MHz, CDCl$_3$)** δ 162.34 (d, *J* = 8.8 Hz), 150.63, 141.46, 135.99 (d, *J* = 13.3 Hz), 134.89 (d, *J* = 7.3 Hz), 133.88, 132.73, 129.10, 128.40, 128.29, 128.04, 114.60, 73.86, 55.61. **^{31}P NMR (203 MHz, CDCl$_3$)** δ -40.79. **HRMS (ESI)** calculated [M+H]$^+$ for $C_{34}H_{31}ClO_4P$: 569.1643, found: 569.1646. **FTIR (cm^{-1})** 3894, 3678, 3619, 3018, 2362, 1741, 1693, 1596, 1464, 1264, 1267, 1217, 1110, 1027, 740, 667.

3-(4-Chlorophenyl)-1,1,1-tri-o-tolyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4ai)



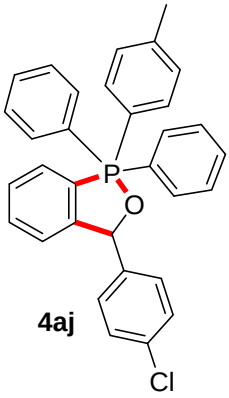
4ai

Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.179 g, 146 µL, 0.60 mmol) and 4-bromobenzaldehyde **3a** (0.137 g, 0.75 mmol) with tri-*o*-tolylphosphane **1i** (0.152 g, 0.50 mmol) in the presence of KF (0.070 g, 1.20 mmol) and 18-crown-6 (0.317 g, 1.20 mmol) in THF (3.0 mL) at -10 °C to rt for 12 h followed by flash column chromatography (EtOAc) of the crude reaction mixture using silica gel afforded 3-(4-chlorophenyl)-1,1,1-tri-*o*-tolyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole **4ai** as a white solid (0.167 g, 64% yield).

***R*$_f$** (EtOAc): 0.17; **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.12-8.07 (m, 1H, H$_{ar}$), 8.03 (t, *J* = 6.4 Hz, 1H, H$_{ar}$), 7.92-7.89 (m, 1H, H$_{ar}$), 7.72-7.69 (m, 2H, H$_{ar}$), 7.66-7.59 (m, 4H, H$_{ar}$), 7.48-7.46 (m,

2H, H_{ar}), 7.43-7.40 (m, 1H, H_{ar}), 7.34-7.30 (m, 2H, H_{ar}), 6.95-6.90 (m, 1H, H_{ar}), 6.86 (d, *J* = 8.1 Hz, 2H, H_{ar}), 6.42 (d, *J* = 7.9 Hz, 2H, H_{ar}), 5.58 (d, *J* = 3.5 Hz, 1H, H_{ar}), 5.31 (d, *J* = 4.0 Hz, 1H, CH), 1.82 (s, 6H, $2CH_3$), 1.75 (s, 3H, CH_3). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 148.45 (d, *J* = 8.3 Hz), 144.25 (d, *J* = 8.6 Hz), 143.68 (d, *J* = 8.5 Hz), 142.98 (d, *J* = 9.2 Hz), 139.12, 136.67 (d, *J* = 12.6 Hz), 135.76-135.68 (m), 135.55-135.49 (m), 135.39, 135.33, 134.76 (d, *J* = 13.8 Hz), 134.39 (d, *J* = 11.2 Hz), 133.92 (d, *J* = 11.5 Hz), 133.56 (d, *J* = 10.9 Hz), 133.25 (d, *J* = 10.4 Hz), 133.07, 129.76 (d, *J* = 13.0 Hz), 128.97 (d, *J* = 13.3 Hz), 128.65, 128.59, 128.26, 128.06, 127.9 (d, *J* = 12.9 Hz), 127.72, 121.89, 119.34, 116.33 (d, *J* = 11.8 Hz), 115.84, 115.68 (d, *J* = 10.8 Hz), 115.16, 114.73, 114.05, 72.19 (d, *J* = 4.5 Hz), 23.19, 23.15, 22.86. **^{31}P NMR (203 MHz, $CDCl_3$)** δ 22.33 **HRMS (ESI)** calculated $[M+H]^+$ for $C_{34}H_{31}ClOP$: 521.1796, found: 521.1795. **FTIR (cm^{-1})** 3893, 3843, 3678, 3619, 3019. 2362, 1836, 1741, 1693, 1646, 1516, 1464, 1215, 741, 668.

3-(4-Chlorophenyl)-1,1-diphenyl-1-(*p*-tolyl)-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4aj)



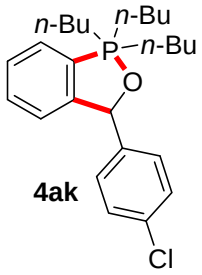
4aj

Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.179 g, 146 µL, 0.60 mmol) and 4-chlorobenzaldehyde **3a** (0.105 g, 0.75 mmol) with diphenyl(*p*-tolyl)phosphane **1j** (0.138 g, 0.50 mmol) in the presence of KF (0.070 g, 1.20 mmol) and 18-crown-6 (0.317 g, 1.20 mmol) in THF (3.0 mL) at -10 °C to rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 40/60) of the crude reaction mixture using silica gel afforded 3-(4-chlorophenyl)-1,1-diphenyl-1-(*p*-tolyl)-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole **4aj** as a white solid (0.198 g, 80% yield).

***R*$_f$** (EtOAc): 0.37; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.49-7.45 (m, 1H, H_{ar}), 7.40-7.35 (m, 4H, H_{ar}), 7.32-7.28 (m, 8H, H_{ar}), 7.24-7.21 (m, 4H, H_{ar}), 7.14-7.12 (m, 2H, H_{ar}), 7.08 (d, *J* = 8.2 Hz, 2H, H_{ar}), 6.88 (dd, J_1 = 8.4 Hz, J_2 = 11.0 Hz, 1H, H_{ar}), 5.59 (s, 1H, CH), 2.37 (s, 3H, CH_3). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 153.84 (d, *J* = 20.1 Hz), 142.99, 138.26 (d, *J* = 2.2 Hz), 136.55 (d, *J* = 14.4 Hz), 132.88, 132.28 (d, *J* = 2.8 Hz), 131.85 (d, *J* = 9.5 Hz), 131.47, 131.37 (d, *J* = 2.9 Hz), 131.26, 129.18, 128.33, 128.27, 128.14, 127.49 (d, *J* = 11.9 Hz), 127.30, 124.91 (d, *J* = 15.1 Hz), 76.05, 21.38. **^{31}P NMR (162 MHz, $CDCl_3$)** δ -44.49. **HRMS (ESI)** calculated $[M+H]^+$ for

$C_{32}H_{27}ClOP$: 493.1483, found: 493.1525. **FTIR (cm^{-1})** 3861, 3649, 3062, 3006, 2319, 1740, 1693, 1596, 1437, 1399, 1259, 1222, 1185, 1017, 812, 743, 664.

1,1,1-Tributyl-3-(4-chlorophenyl)-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4ak)

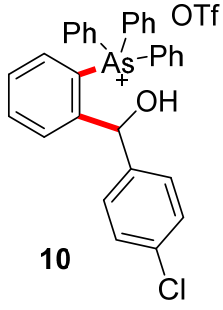


4ak

Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.179 g, 146 µL, 0.60 mmol) and 4-chlorobenzaldehyde **1a** (0.105 g, 0.75 mmol) with tri-*n*-butylphosphine **1k** (0.101 g, 125 µL, 0.50 mmol) in the presence of KF (0.070 g, 1.20 mmol) and 18-crown-6 (0.317 g, 1.20 mmol) in THF (3.0 mL) at -10 °C to rt for 12 h followed by flash column chromatography (Pet. ether /EtOAc = 40/60) of the crude reaction mixture using silica gel afforded 1,1,1-tributyl-3-(4-chlorophenyl)-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole **4ak** as a white solid (0.167 g, 79% yield).

***R*$_f$** (EtOAc): 0.21; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.68 (dd, J_1 = 7.6 Hz, J_2 = 13.4 Hz, 1H, H_{ar}), 7.59-7.50 (m, 2H, H_{ar}), 7.25 (d, J = 8.3 Hz, 2H, H_{ar}), 7.16 (d, J = 8.5 Hz, 3H, H_{ar}), 6.05 (s, 1H, CH), 2.47-2.44 (m, 6H, $3CH_2$), 1.50-1.21 (m, 12H, $6CH_2$), 0.84 (t, J = 6.5 Hz, 9H, $3CH_3$). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 143.38 (d, J = 6.4 Hz), 141.37, 134.33 (d, J = 8.8 Hz), 133.95 (d, J = 2.2 Hz), 133.75, 131.52 (d, J = 10.4 Hz), 128.85, 128.68 (d, J = 12.7 Hz), 115.78, 115.00, 73.47 (d, J = 1.8 Hz), 24.25 (d, J = 4.1 Hz), 23.63 (d, J = 16.3 Hz), 21.65 (d, J = 50.3 Hz), 13.36. **^{31}P NMR (162 MHz, $CDCl_3$)** δ 32.97 **HRMS (ESI)** calculated $[M+H]^+$ for $C_{25}H_{37}ClOP$: 419.2265, found: 419.2265. **FTIR (cm^{-1})** 3843, 3648, 3619, 3010, 2873, 2361, 1817, 1741, 1647, 1463, 1351, 1251, 1222, 1030, 949, 854, 742, 637.

(2-((4-Chlorophenyl)(hydroxy)methyl)phenyl)triphenylarsonium trifluoromethanesulfonate (10)



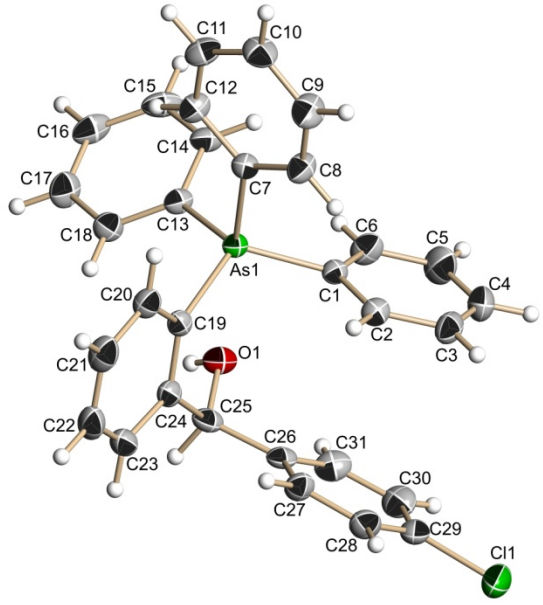
10

Treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.179 g, 146 µL, 0.60 mmol) and 4-chlorobenzaldehyde **3a** (0.105 g, 0.75 mmol) with triphenylarsane **9** (0.153 g, 0.50 mmol) in the presence of KF (0.070 g, 1.20 mmol) and 18-crown-6 (0.317 g, 1.20 mmol) in THF (3.0 mL) at -10 °C to rt for 12 h followed by flash column chromatography (EtOAc) of the crude reaction mixture using silica gel afforded (2-((4-

chlorophenyl)(hydroxy)methyl)phenyl)triphenylarsonium trifluoromethanesulfonate **10** as a white solid (0.172 g, 52% yield).

***R*f** (EtOAc): 0.13; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.69-7.64 (m, 4H, H_{ar}), 7.57 (t, *J* = 7.8 Hz, 6H, H_{ar}), 7.52-7.50 (m, 6H, H_{ar}), 7.44-7.37 (m, 2H, H_{ar}), 7.29-7.26 (m, 1H, H_{ar}), 7.07 (d, *J* = 8.5 Hz, 2H, H_{ar}), 6.87 (d, *J* = 8.5 Hz, 2H, H_{ar}), 6.46 (bs, 1H), 6.07 (s, 1H, CH). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 148.64, 140.88, 135.39, 133.90, 133.40, 133.15, 132.57, 132.45, 131.41, 130.96, 130.40, 129.11, 128.83, 128.39, 126.64, 117.85, 73.29. **^{19} F NMR (376 MHz, $CDCl_3$)** -77.04 **HRMS (ESI)** calculated $[M]^+$ for $C_{31}H_{25}ClOAs$: 523.0804, found: 523.0801. **FTIR (cm^{-1})** 3843, 3744, 3638, 3619, 3013, 2361, 1741, 1693, 1647, 1516, 1495, 1444, 1270, 1161, 1030, 837, 665.

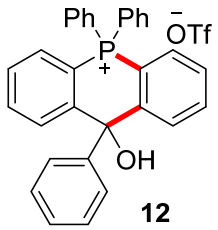
X-ray intensity data measurements of compound **10 (**crystallized from EtOAc-Petroleum ether) was carried out on a Bruker SMART APEX II CCD diffractometer with graphite-monochromatized (MoK_α= 0.71073Å) radiation at room temperatrure 296(2) K. The X-ray generator was operated at 50 kV and 30 mA. A preliminary set of cell constants and an orientation matrix were calculated from three sets of 36 frames. Data were collected with ω scan width of 0.5° at different settings of φ and 2θ with a frame time of 15, 20 and 20 secs respectively keeping the sample-to-detector distance fixed at 5.00 cm. The X-ray data collection was monitored by APEX2 program (Bruker, 2006). All the data were corrected for Lorentzian, polarization and absorption effects using SAINT and SADABS programs (Bruker, 2006). SHELX-97 was used for structure solution and full matrix least-squares refinement on F^2. CCDC- 1001503 (**10**), contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



Crystal data of **10** $C_{31}H_{25}AsClO$, SO_3CF_3, M = 672.95, colorless block, 0.45 x 0.42 x 0.39 mm^3, monoclinic, space group $P2_1/c$, a = 9.6419(2) Å, b = 14.7407(4) Å, c = 20.9802(5) Å, β = 91.8490(10)°, V = 2980.33(12) $Å^3$, Z = 8, T = 297(2) K, $2\theta_{max}$=50.00°, D_{calc} (g cm^{-3}) =

1.500, $F(000)$ = 1368, μ (mm^{-1}) = 1.355, 41767 reflections collected, 5255 unique reflections (R_{int}=0.0425), 4116 observed ($I > 2\sigma(I)$) reflections, multi-scan absorption correction, T_{min} = 0.581, T_{max} = 0.620, 410 refined parameters, S = 1.060, $R1$ = 0.0547, $wR2$ = 0.1273 (all data R = 0.0735, $wR2$ = 0.1385), maximum and minimum residual electron densities; $\Delta\rho_{max}$ = 1.00, $\Delta\rho_{min}$= -1.00 (eÅ^{-3}).

10-Hydroxy-5,5,10-triphenyl-5,10-dihydroacridophosphin-5-ium trifluoromethanesulfonate (12)

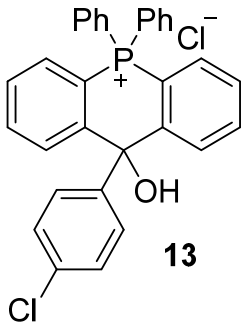


12

Treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** (0.179 g, 146 µL, 0.60 mmol) and 2-(diphenylphosphanyl)benzaldehyde **11** (0.073 g, 0.25 mmol) in the presence of KF (0.70 g, 1.20 mmol) and 18-crown-6 (0.317 g, 1.20 mmol) in THF (3.0 mL) at -10 °C to rt for 12 h followed by flash column chromatography (DCM /MeOH = 90/10) of the crude reaction mixture using silica gel afforded 10-hydroxy-5,5,10-triphenyl-5,10-dihydroacridophosphin-5-ium trifluoromethanesulfonate **12** as a white solid (0.134 g, 90% yield).

***R*$_f$** (DCM/MeOH = 95/05): 0.23; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.48-8.44 (m, 2H, H$_{ar}$), 7.86 (t, J = 7.7 Hz, 2H, H$_{ar}$), 7.79-7.76 (m, 1H, H$_{ar}$), 7.60-7.54 (m, 5H, H$_{ar}$), 7.49-7.40 (m, 4H, H$_{ar}$), 7.37-7.33 (m, 2H, H$_{ar}$), 7.22-7.17 (m, 2H, H$_{ar}$), 6.81-6.78 (m, 1H, H$_{ar}$), 6.70 (t, J = 7.8 Hz, 2H, H$_{ar}$), 6.51 (d, J = 7.9 Hz, 2H, H$_{ar}$), 5.95 (bs, 1H, OH) [exchangeable with D_2O]. **^{13}C NMR (100 MHz, CDCl$_3$)** δ 151.75 (d, J = 6.3 Hz), 143.52, 135.75 (d, J = 2.7 Hz), 135.47 (d, J = 1.8 Hz), 135.07 (d, J = 11.4 Hz), 134.59 (d, J = 2.7 Hz), 133.09 (d, J = 8.9 Hz), 132.89 (d, J = 10.7 Hz), 130.54 (d, J = 13.4 Hz), 130.15 (d, J = 13.1 Hz), 129.64 (d, J = 9.8 Hz), 129.14 (d, J = 12.5 Hz), 128.03, 127.86, 127.57, 122.21, 119.62, 118.70, 116.96 (d, J = 90.4 Hz), 113.60 (d, J = 88.1 Hz), 76.92. **^{31} P NMR (162 MHz, CDCl$_3$)** 10.30 **^{19} F NMR (376 MHz, CDCl$_3$)** -77.00 **HRMS (ESI)** calculated [M]$^+$ for $C_{31}H_{24}OP$: 443.1559, found: 443.1554. **FTIR (cm^{-1})** 3534, 2871, 1974, 1695, 1644, 1471, 1454, 1439, 1350, 1272, 1257, 1224, 1202, 1148, 1098, 1029, 993, 960, 836, 766, 754, 721, 706.

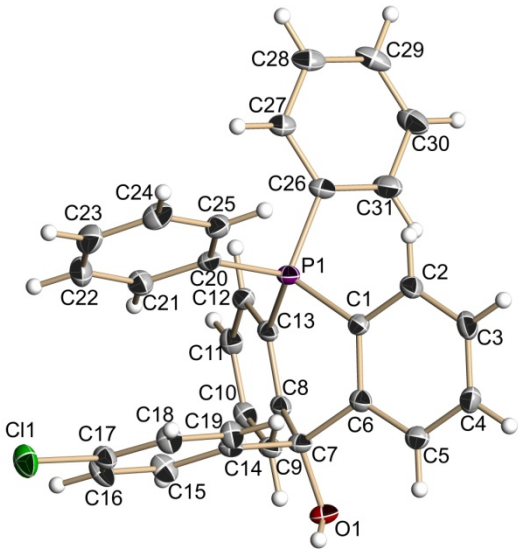
10-(4-Chlorophenyl)-10-hydroxy-5,5-diphenyl-5,10-dihydroacridophosphin-5-ium chloride (13)



Treatment of 3-(4-chlorophenyl)-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo [*c*][1,2]oxaphosphole **4a** (120 mg, 0.25 mmol) with 1.0 (M) $TiCl_4$ in dichloromethane (0.5 ml, 1M, 0.5 mmol) and $MoCl_5$ (137 mg, 0.5 mmol) in dichloromethane (5 mL) at 0 °C for 30 min followed by flash column chromatography on silica gel (DCM/MeOH = 90/10) afforded the 10-(4-chlorophenyl)-10-hydroxy-5,5-diphenyl-5,10-dihydroacridophosphin-5-ium chloride **13** as a yellow solid (122 mg, 95% yield).

***R*$_f$** (DCM/MeOH = 95/05): 0.17; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.67-8.63 (m, 2H, H_{ar}), 7.87 (t, *J* = 7.6 Hz, 2H, H_{ar}), 7.79 (t, *J* = 7.2 Hz, 1H, H_{ar}), 7.64-7.55 (m, 6H, H_{ar}), 7.45-7.34 (m, 6H, H_{ar}), 7.16-7.11 (m, 2H, H_{ar}), 6.58 (d, *J* = 8.7 Hz, 2H, H_{ar}), 6.41 (d, *J* = 8.6 Hz, 2H, H_{ar}). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 152.23 (d, *J* = 6.2 Hz), 142.76, 135.81 (d, *J* = 2.2 Hz), 135.52, 135.07 (d, *J* = 11.4 Hz), 134.24 (d, *J* = 2.3 Hz), 133.39, 132.85, 132.79, 132.74, 130.51 (d, *J* = 13.2 Hz), 130.19 (d, *J* = 12.3 Hz), 129.47, 128.94 (d, *J* = 12.8 Hz), 127.81, 119.03 (d, *J* = 91.4 Hz), 116.95 (d, *J* = 89.3 Hz), 113.52 (d, *J* = 87.2 Hz), 76.54 (d, *J* = 8.5 Hz). **^{31} P NMR (162 MHz, $CDCl_3$)** 17.56 **HRMS (ESI)** calculated $[M]^+$ for $C_{31}H_{23}ClOP$: 477.1170, found: 477.1167. **FTIR (cm^{-1})** 3058, 2954, 2922, 2853, 1731, 1667, 1586, 1486, 1463, 1437, 1398, 1373, 1268, 1236, 1162, 1139, 1106, 1092, 1044, 1012, 997, 925, 828, 739, 723, 686.

X-ray intensity data measurements of compound **13** (crystallized from EtOAc-CH_2Cl_2) was carried out on a Bruker SMART APEX II CCD diffractometer with graphite-monochromatized (MoK_α= 0.71073Å) radiation at room temperatrure 296(2) K. The X-ray generator was operated at 50 kV and 30 mA. A preliminary set of cell constants and an orientation matrix were calculated from three sets of 36 frames. Data were collected with ω scan width of 0.5° at different settings of φ and 2θ with a frame time of 15, 20 and 20 secs respectively keeping the

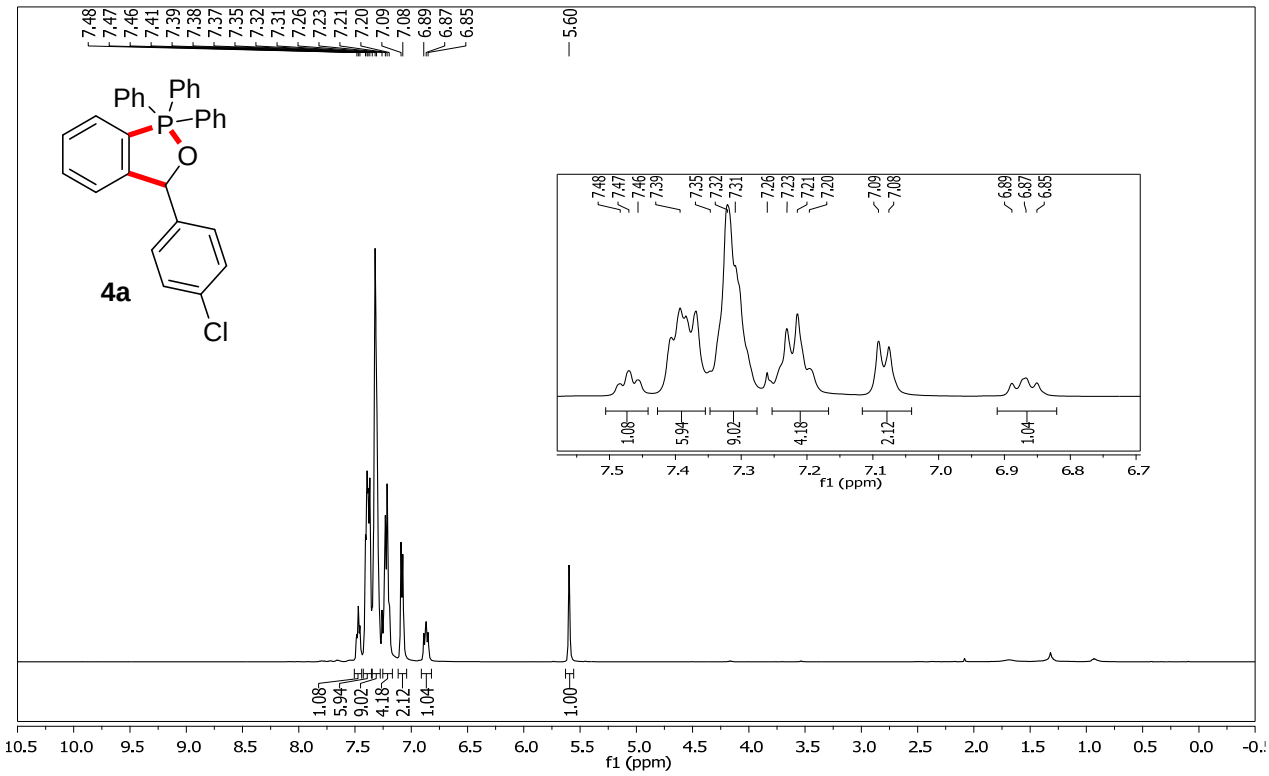


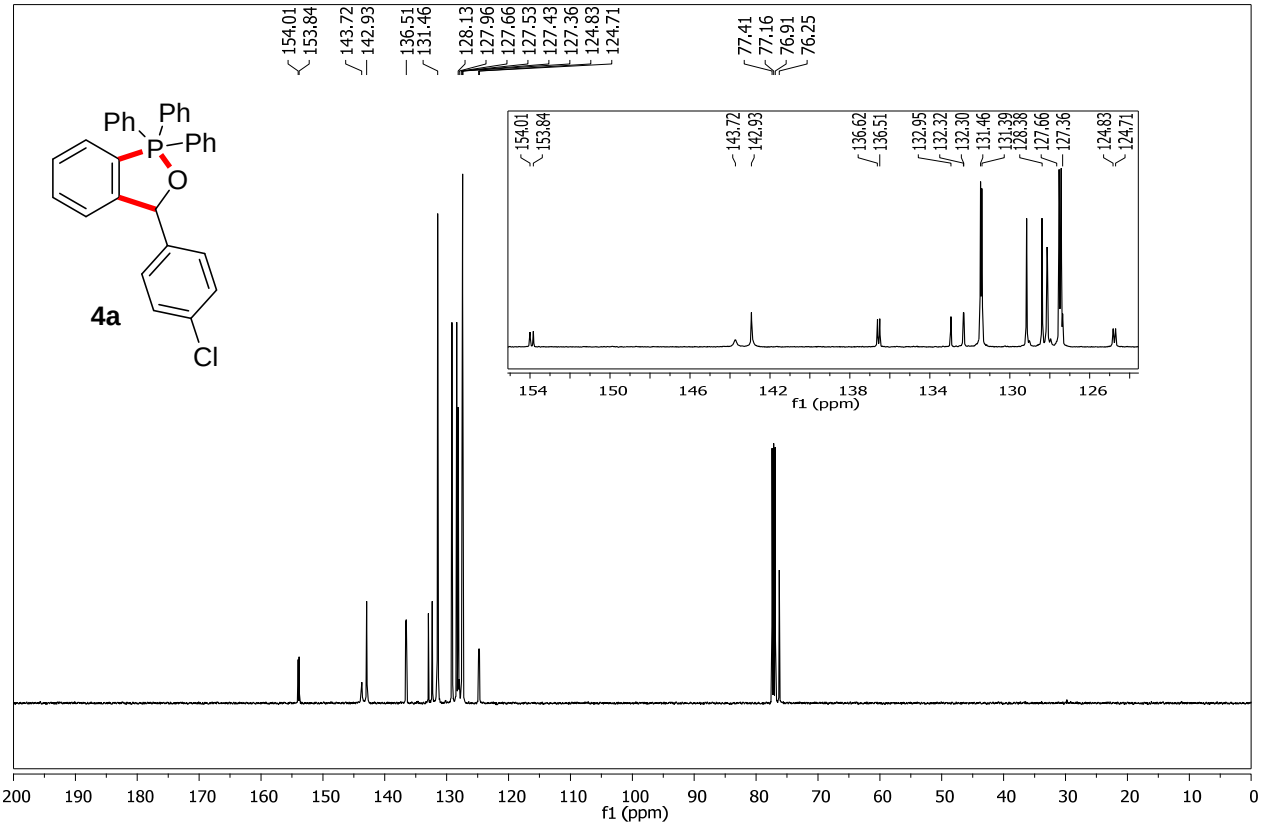
sample-to-detector distance fixed at 5.00 cm. The X-ray data collection was monitored by APEX2 program (Bruker, 2006). All the data were corrected for Lorentzian, polarization and absorption effects using SAINT and SADABS programs (Bruker, 2006). SHELX-97 was used for structure solution and full matrix least-squares refinement on F^2. All the hydrogen atoms were placed in geometrically idealized position and constrained to ride on their parent atoms except hydroxyl H-atoms of **13** which were located in the difference Fourier and refined isotropically. CCDC- 1001504 (**13**), contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data of **13** $C_{31}H_{23}Cl_2O1P$, 0.25 H_2O, M = 517.36, colorless block, 0.28 x 0.22 x 0.21 mm^3, monoclinic, space group $P2_1/c$, a = 14.2166(10) Å, b = 28.5677(19) Å, c = 12.5338(8) Å, β = 97.179(3)°, V = 5050.5(6) $Å^3$, Z = 8, T = 150(2) K, $2\theta_{max}$=50.00°, D_{calc} (g cm^{-3}) = 1.361, $F(000)$ = 2144, μ (mm^{-1}) = 0.345, 39982 reflections collected, 8870 unique reflections (R_{int}=0.0368), 7023 observed ($I > 2\sigma(I)$) reflections, multi-scan absorption correction, T_{min} = 0.910, T_{max} = 0.931, 648 refined parameters, S = 1.142, $R1$ = 0.0632, $wR2$ = 0.1396 (all data R = 0.0835, $wR2$ = 0.1490), maximum and minimum residual electron densities; $\Delta\rho_{max}$ = 0.47, $\Delta\rho_{min}$= -0.37 ($eÅ^{-3}$).

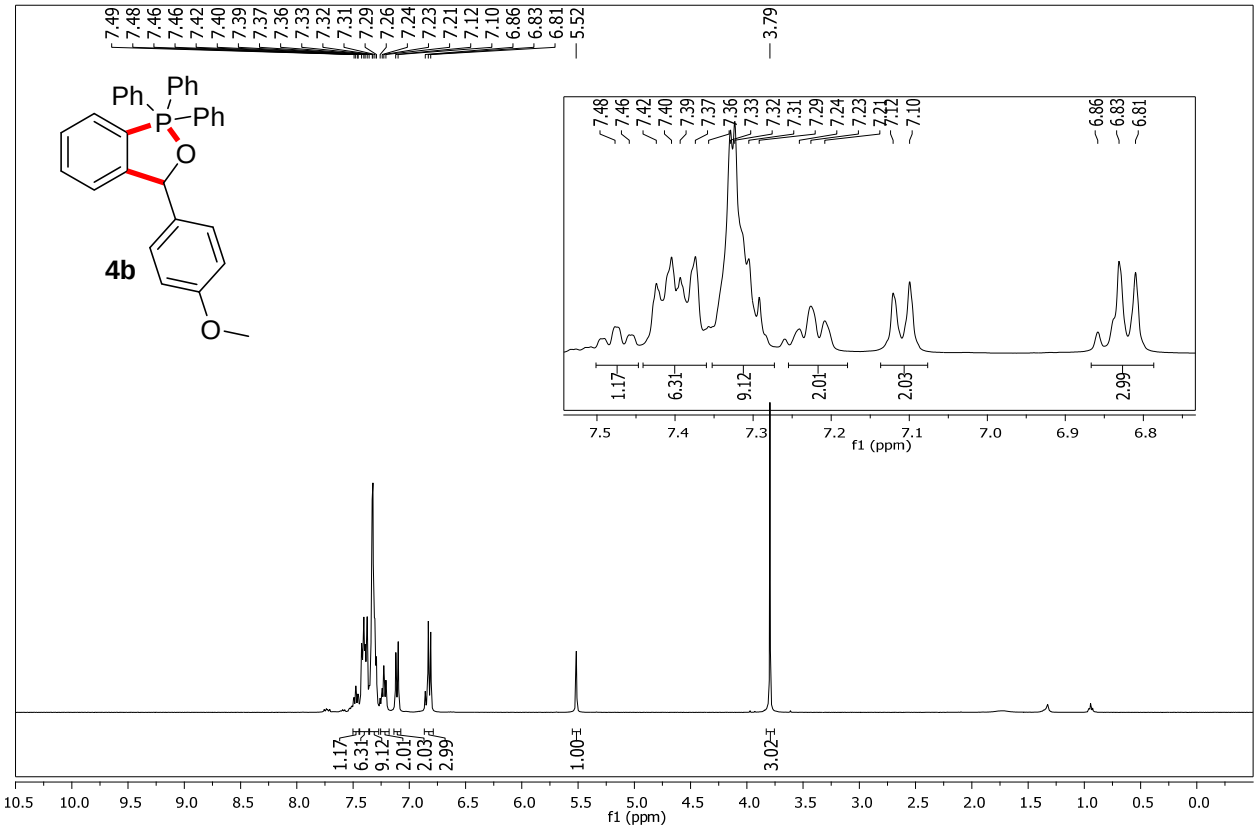
8. ^{1}H and ^{13}C NMR Spectra of Benzooxaphospholes

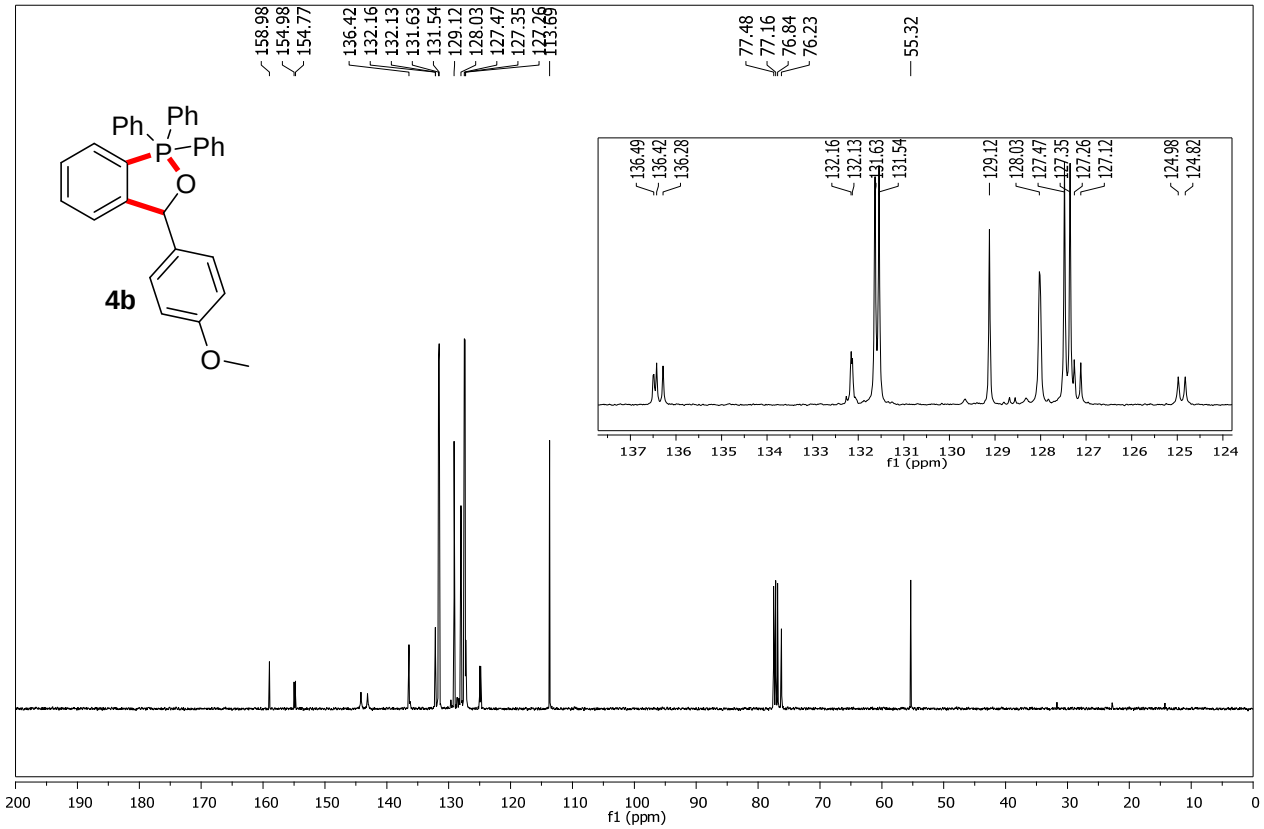
3-(4-Chlorophenyl)-1,1,1-triphenyl-1,3-dihydro-1λ^{5}-benzo[*c*][1,2]oxaphosphole (4a)



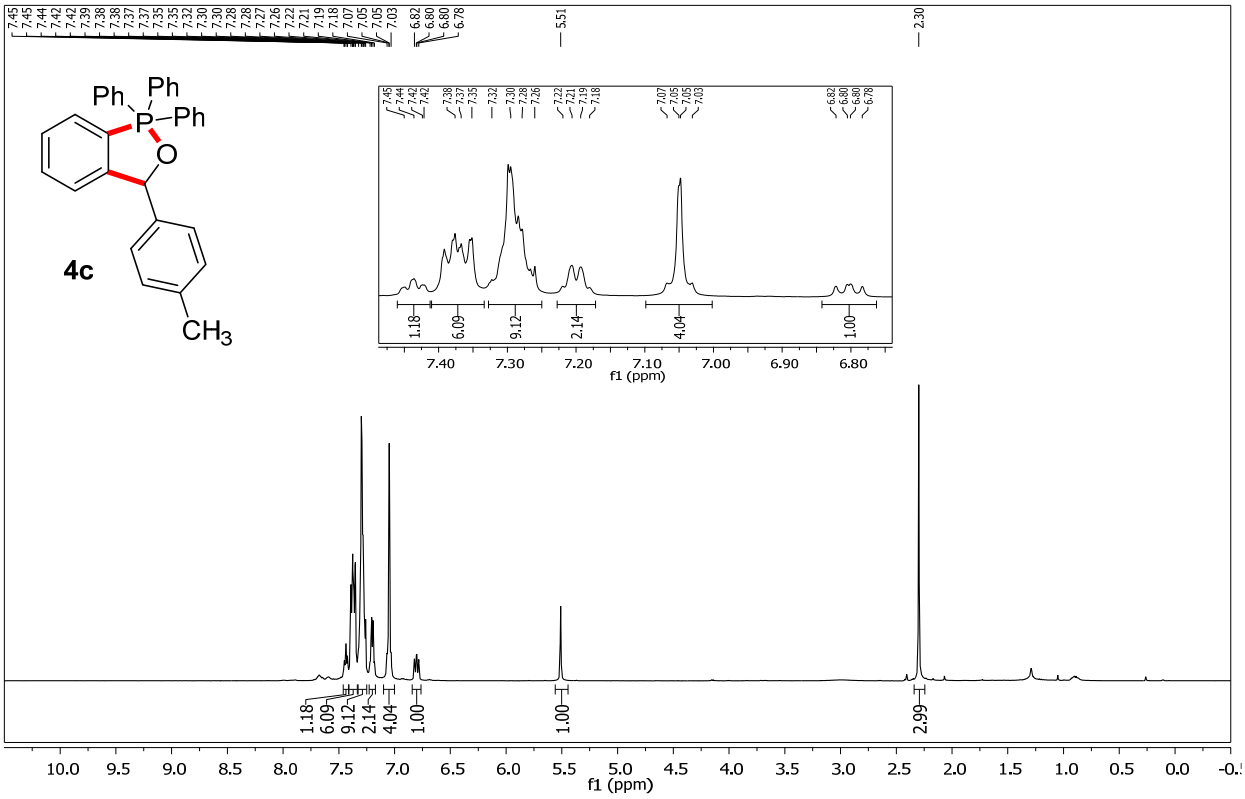


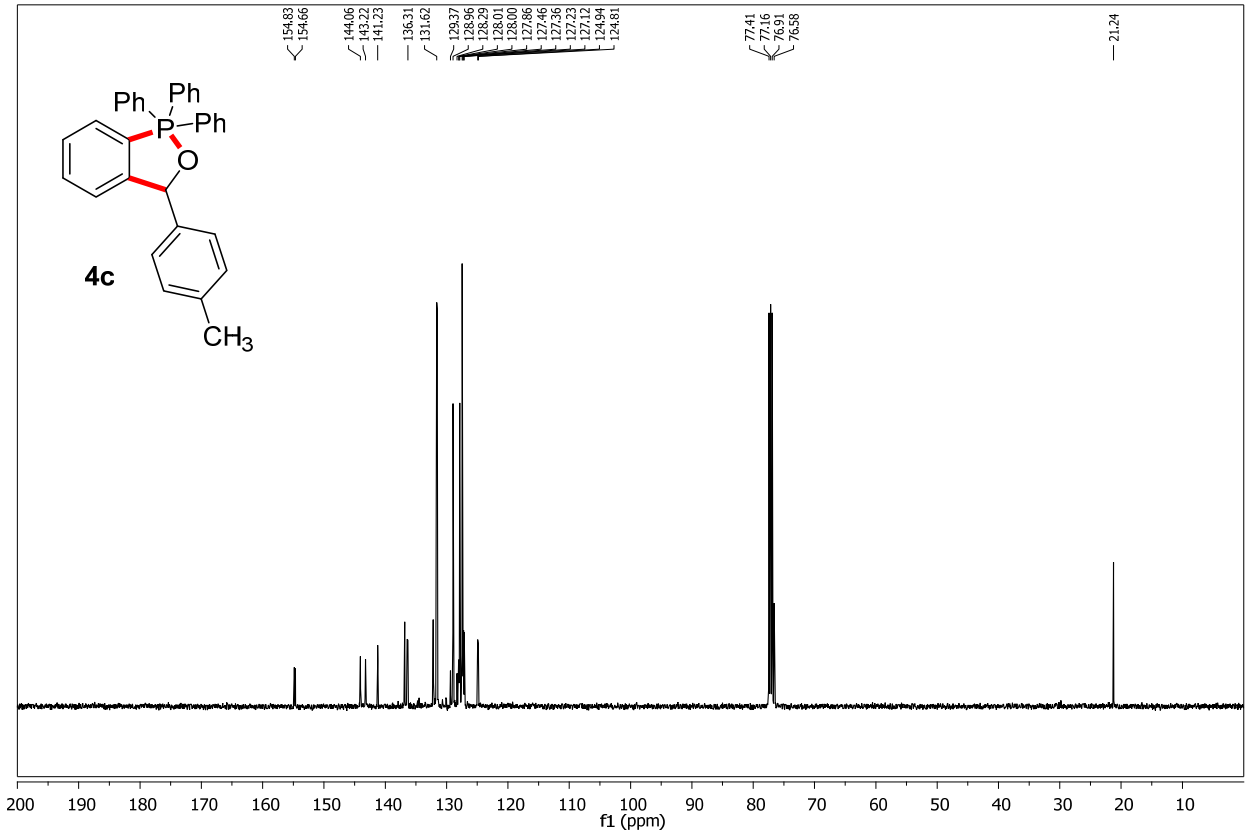
3-(4-Methoxyphenyl)-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4b)



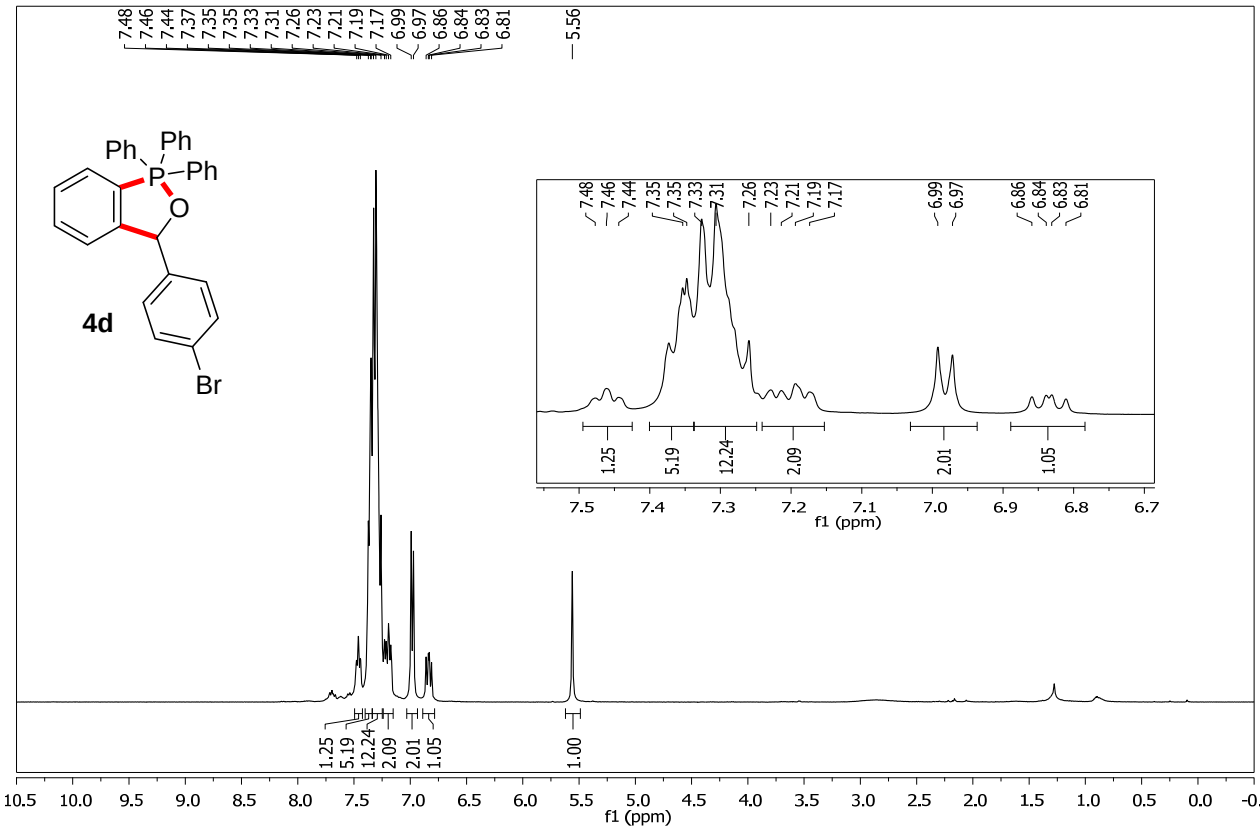


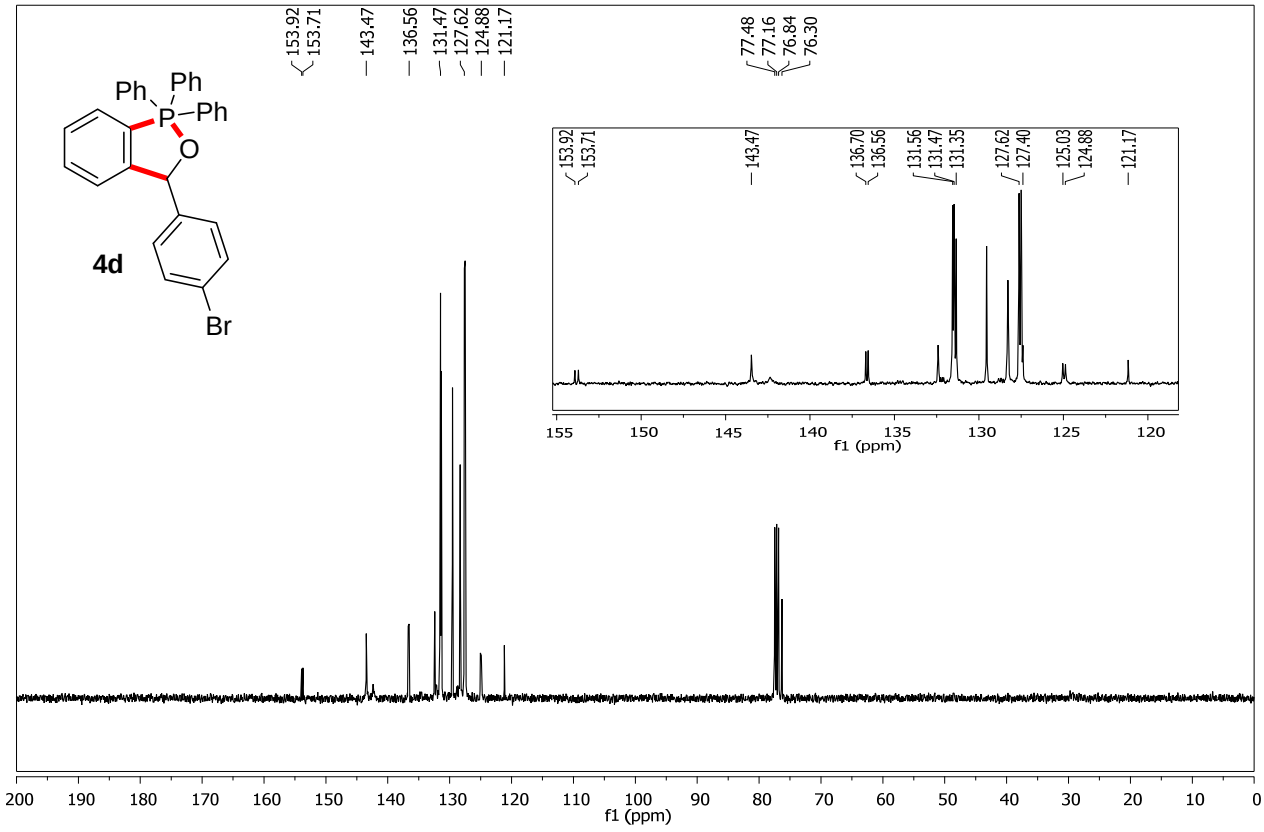
1,1,1-Triphenyl-3-(*p*-tolyl)-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4c)



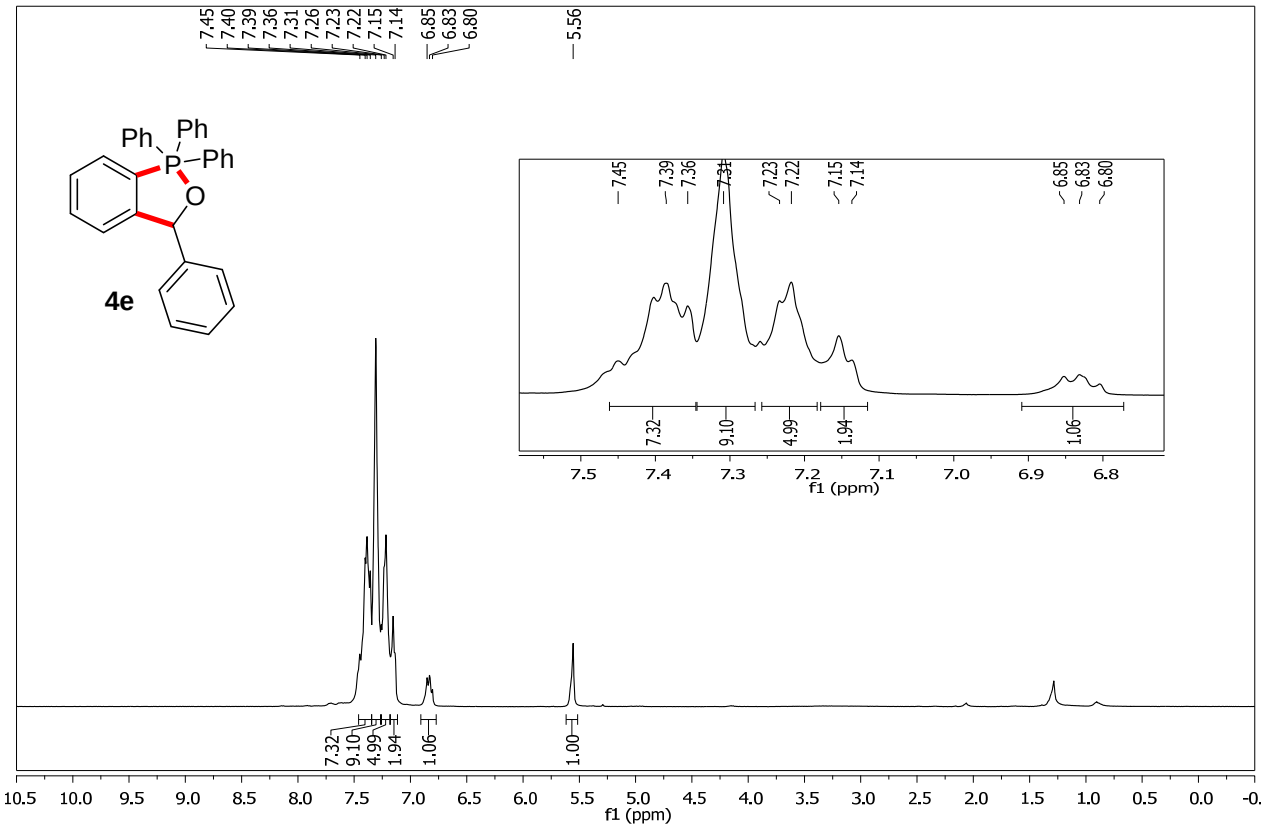


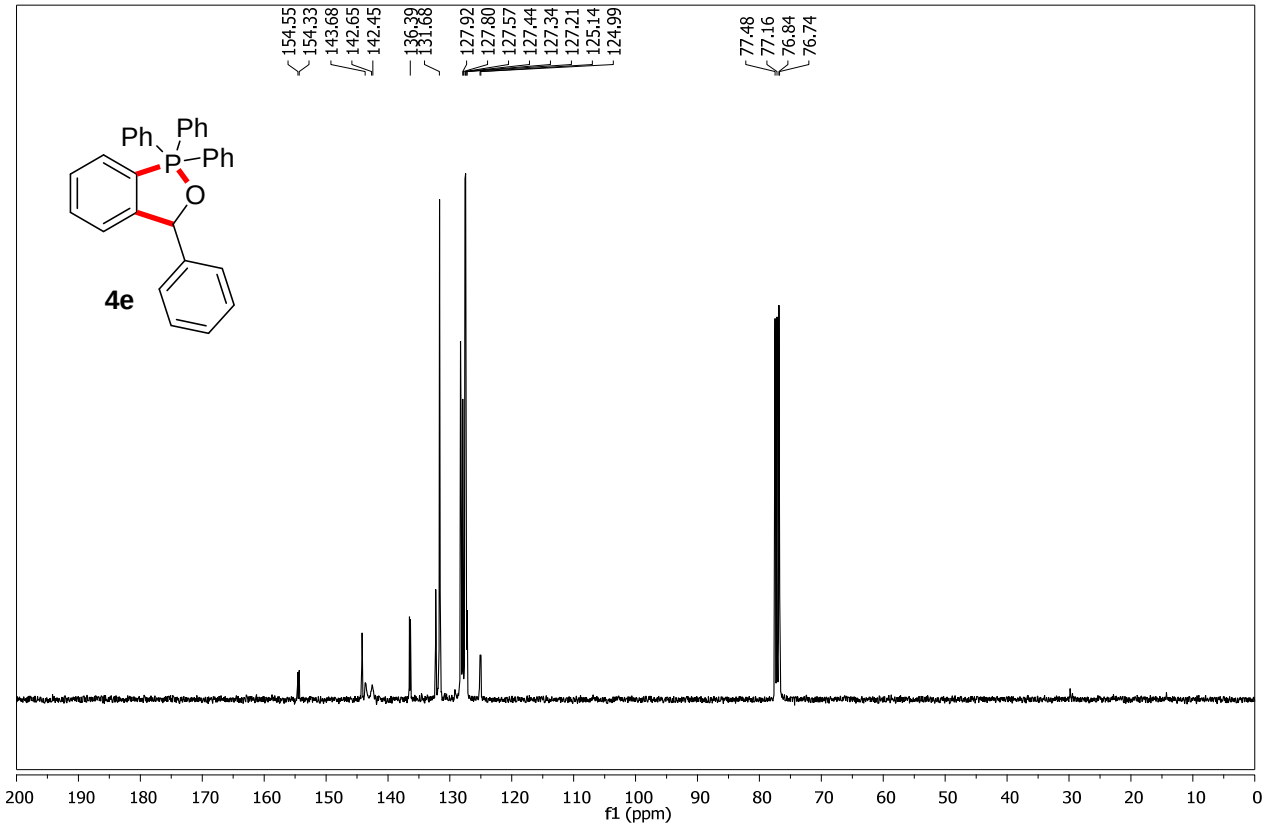
3-(4-Bromophenyl)-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4d)



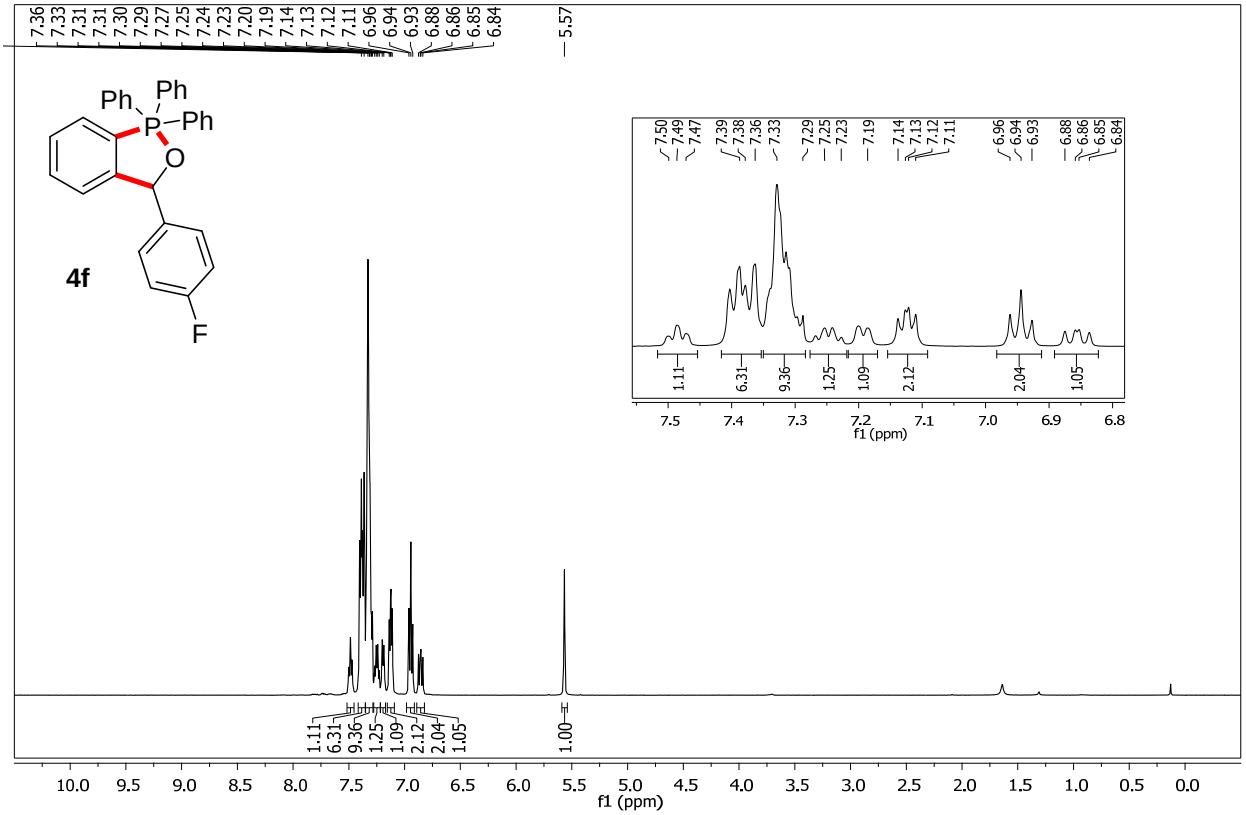


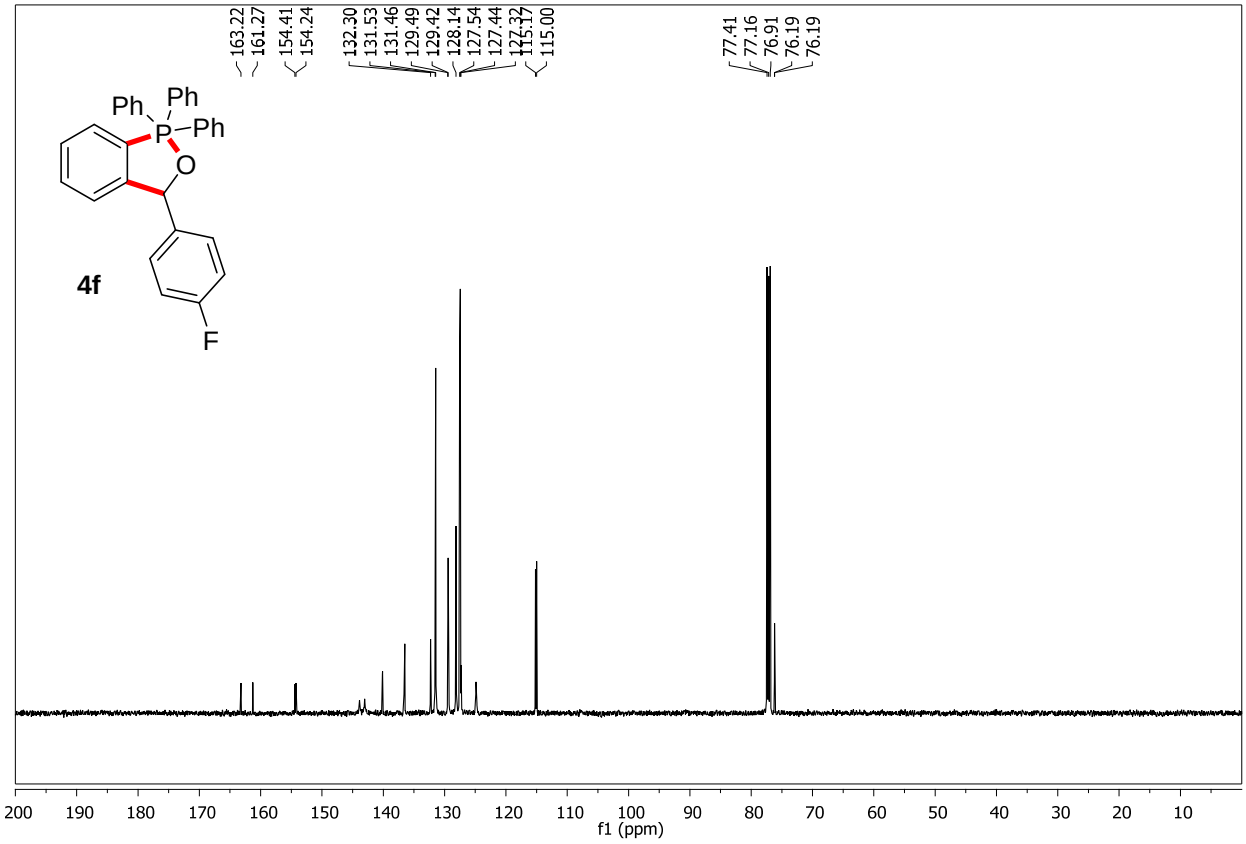
1,1,1,3-Tetraphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4e)



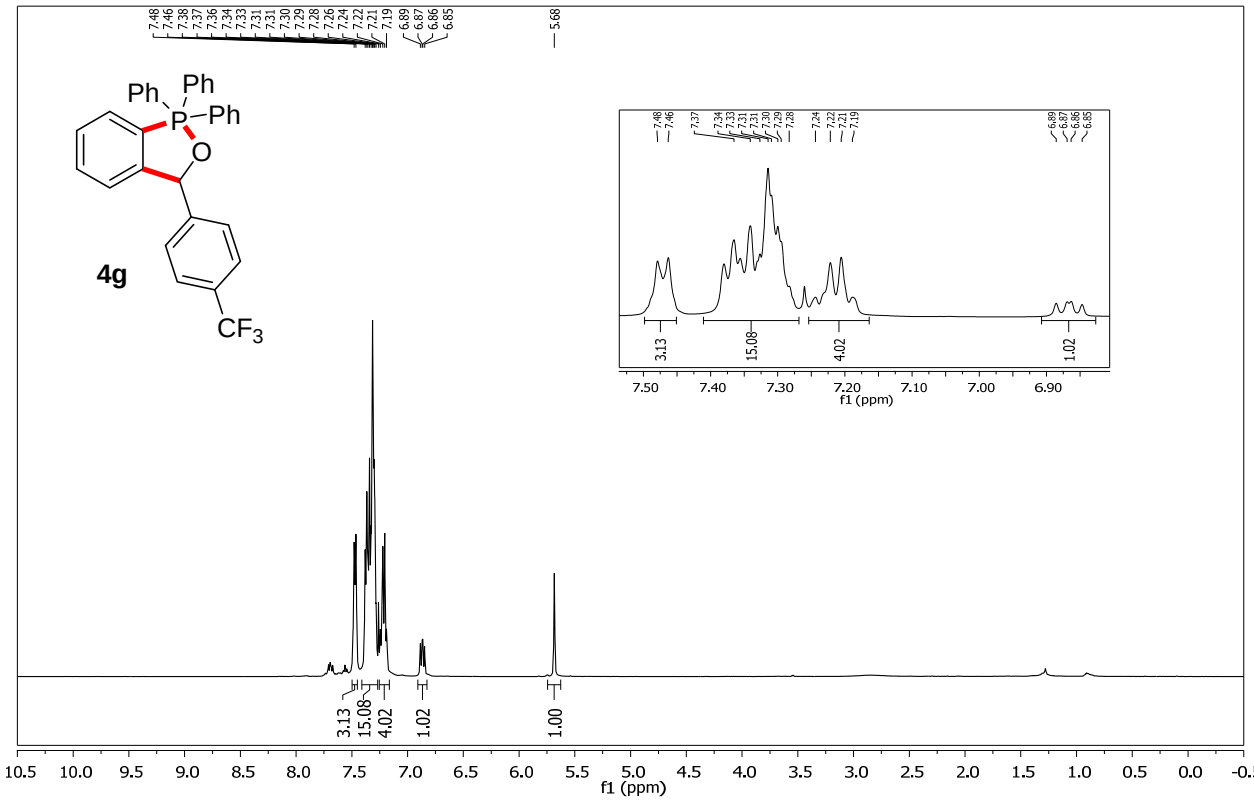


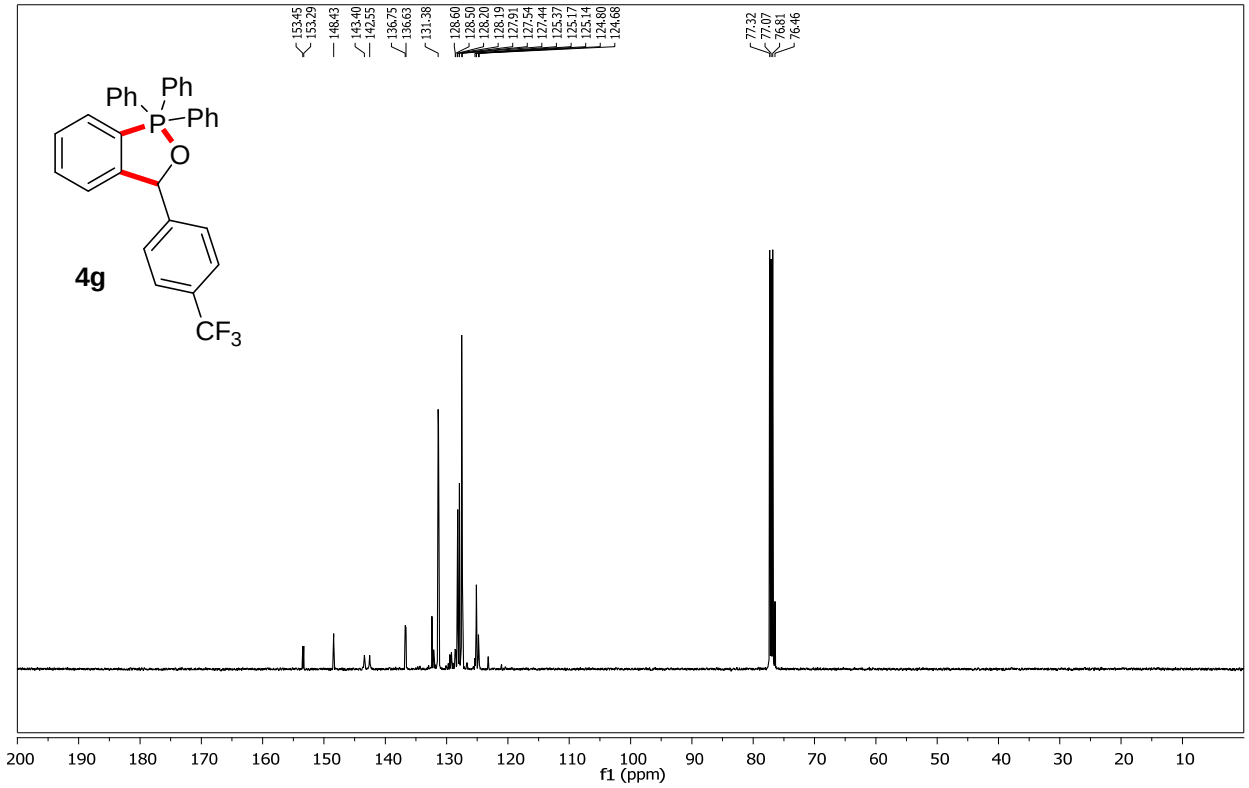
3-(4-Fluorophenyl)-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4f)



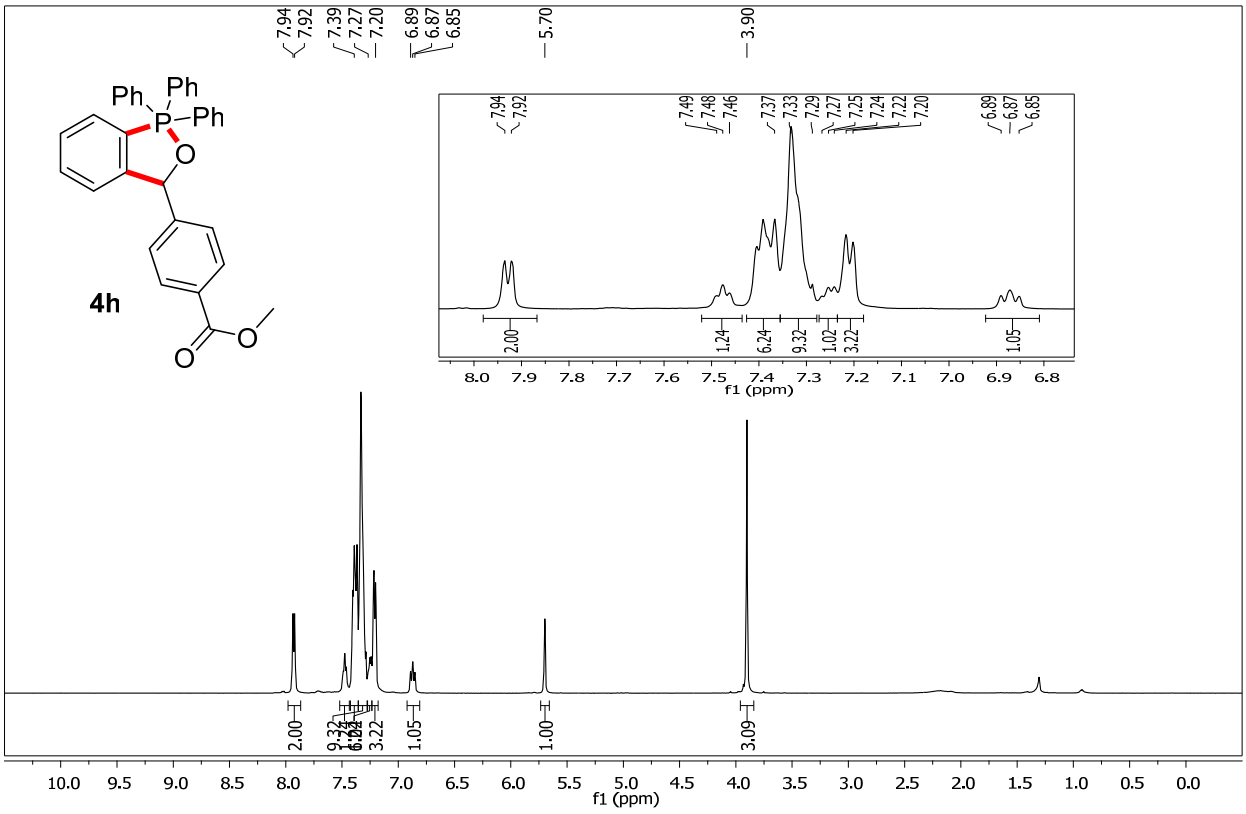


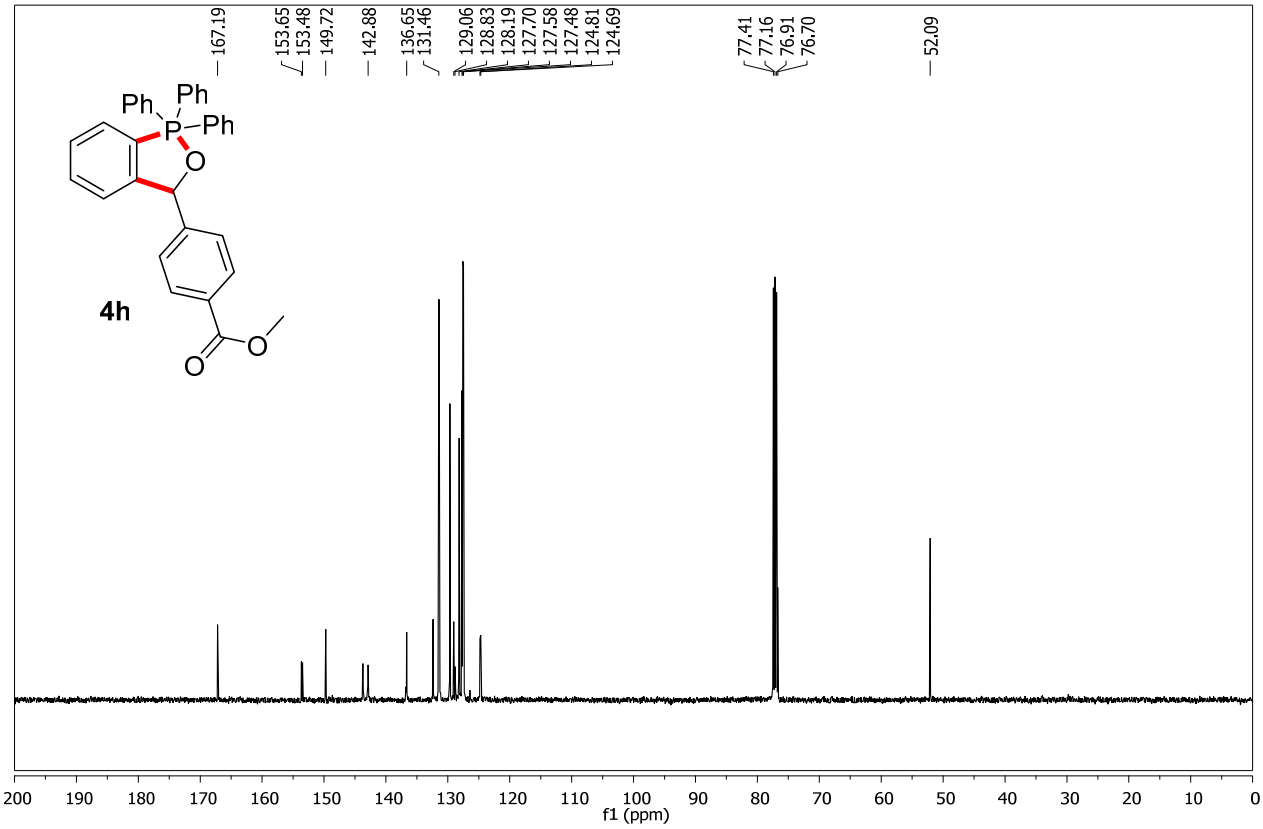
1,1,1-Triphenyl-3-(4-(trifluoromethyl)phenyl)-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4g)



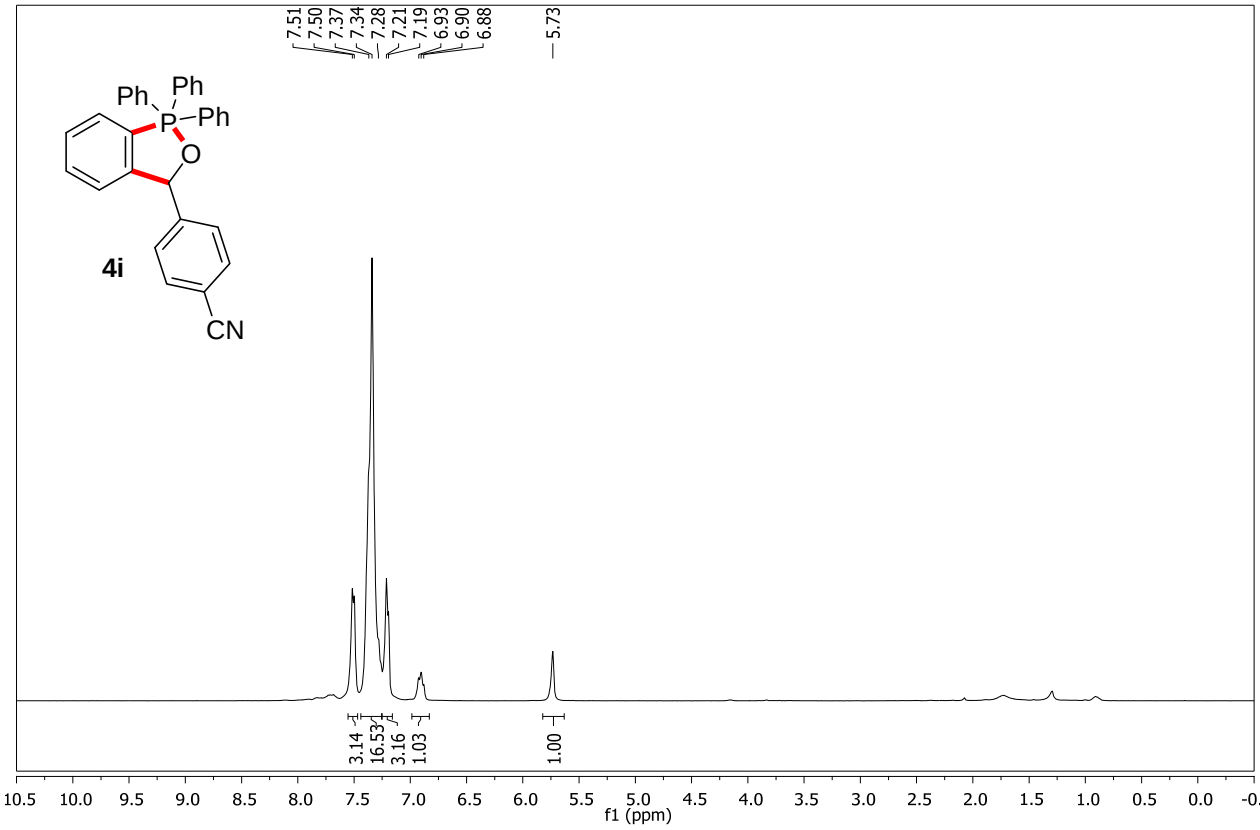


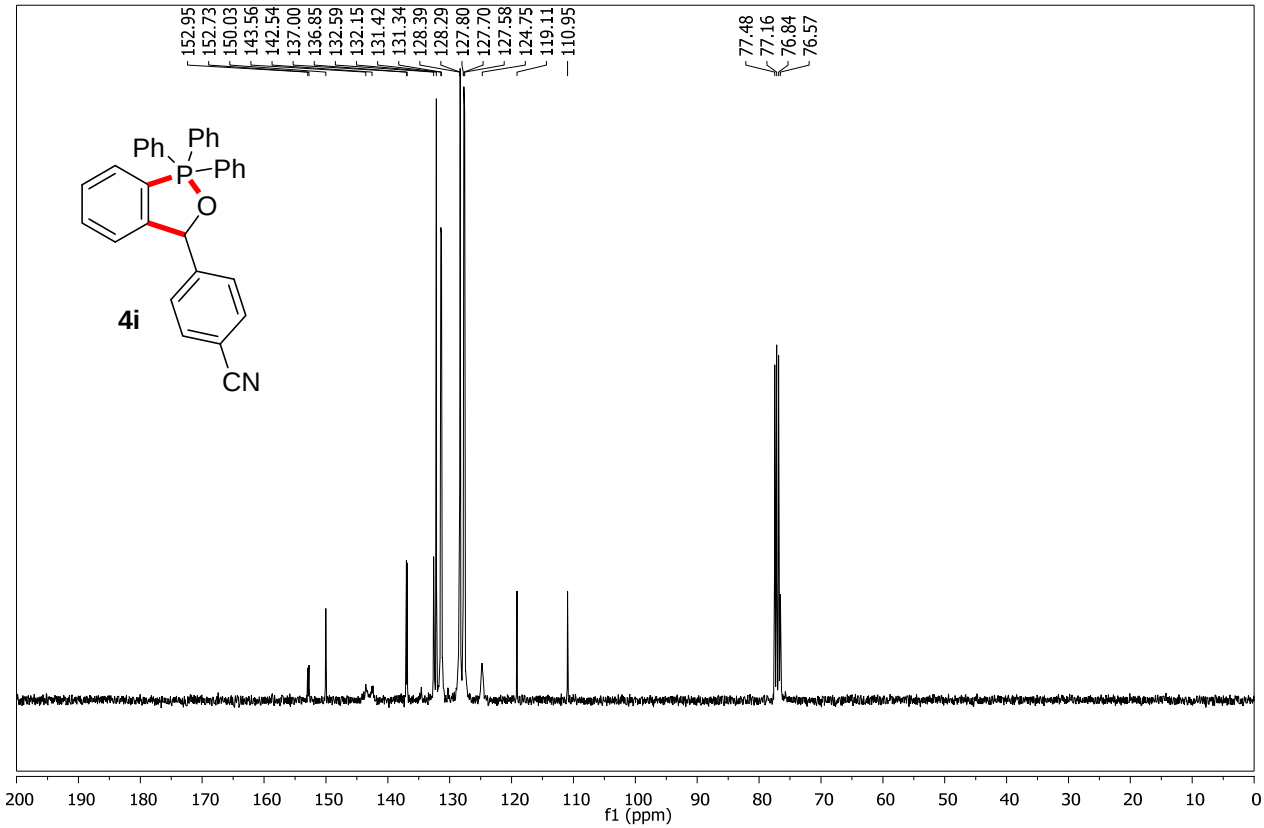
Methyl-4-(1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphol-3-yl)benzoate (4h)



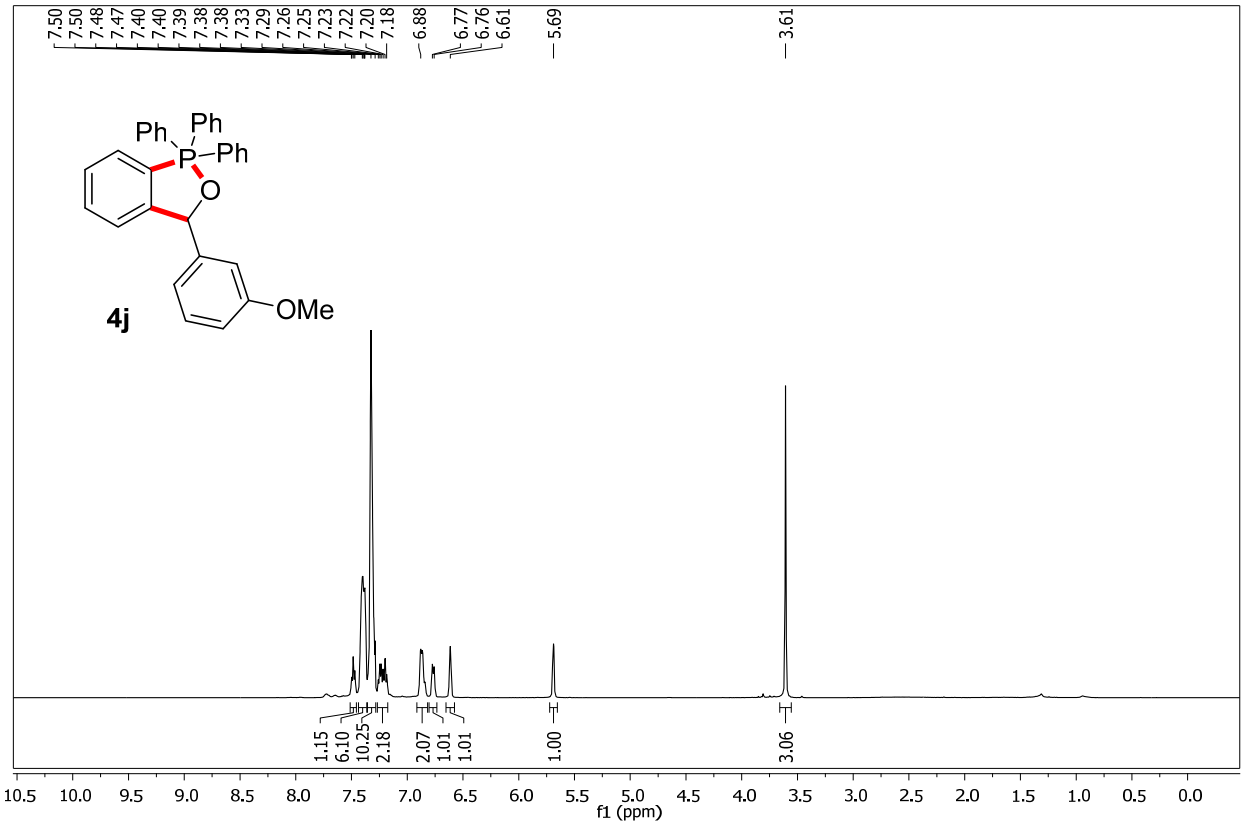


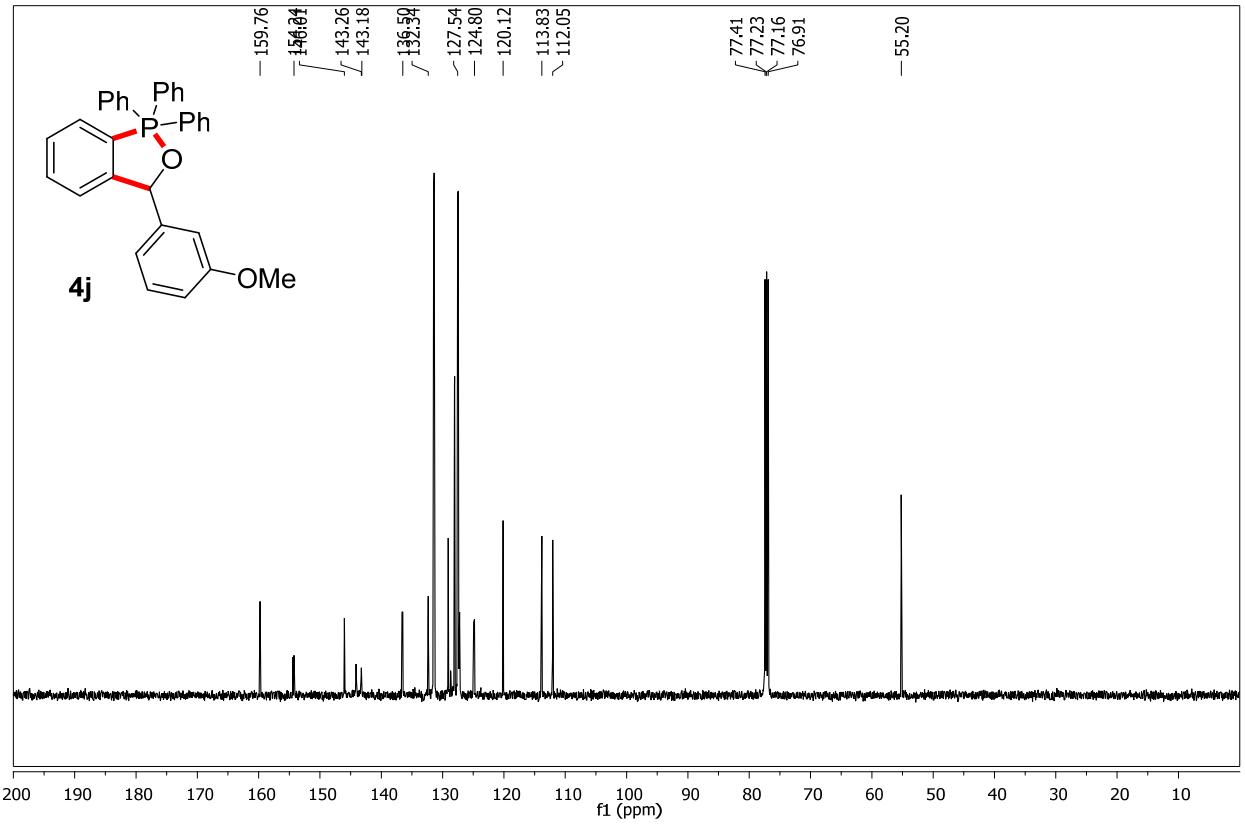
4-(1,1,1-Triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphol-3-yl)benzonitrile (4i)



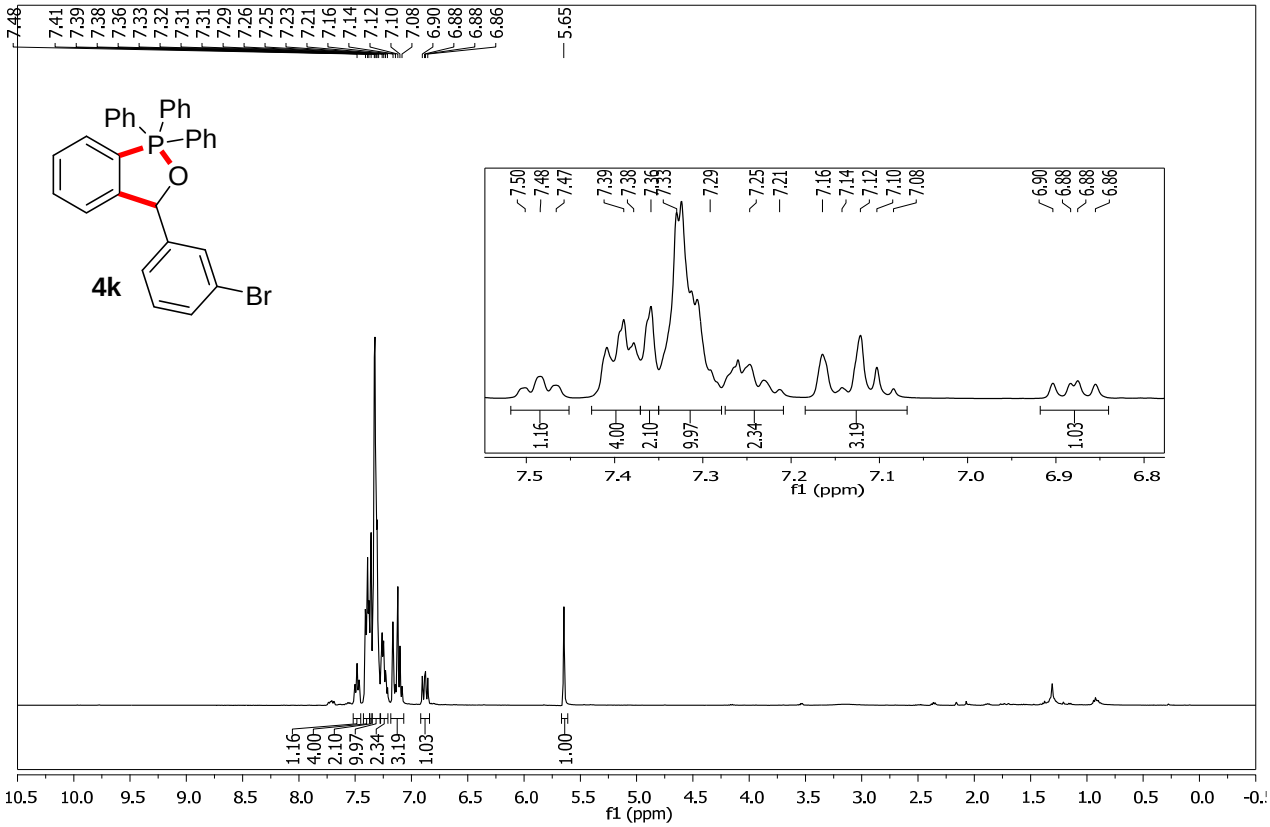


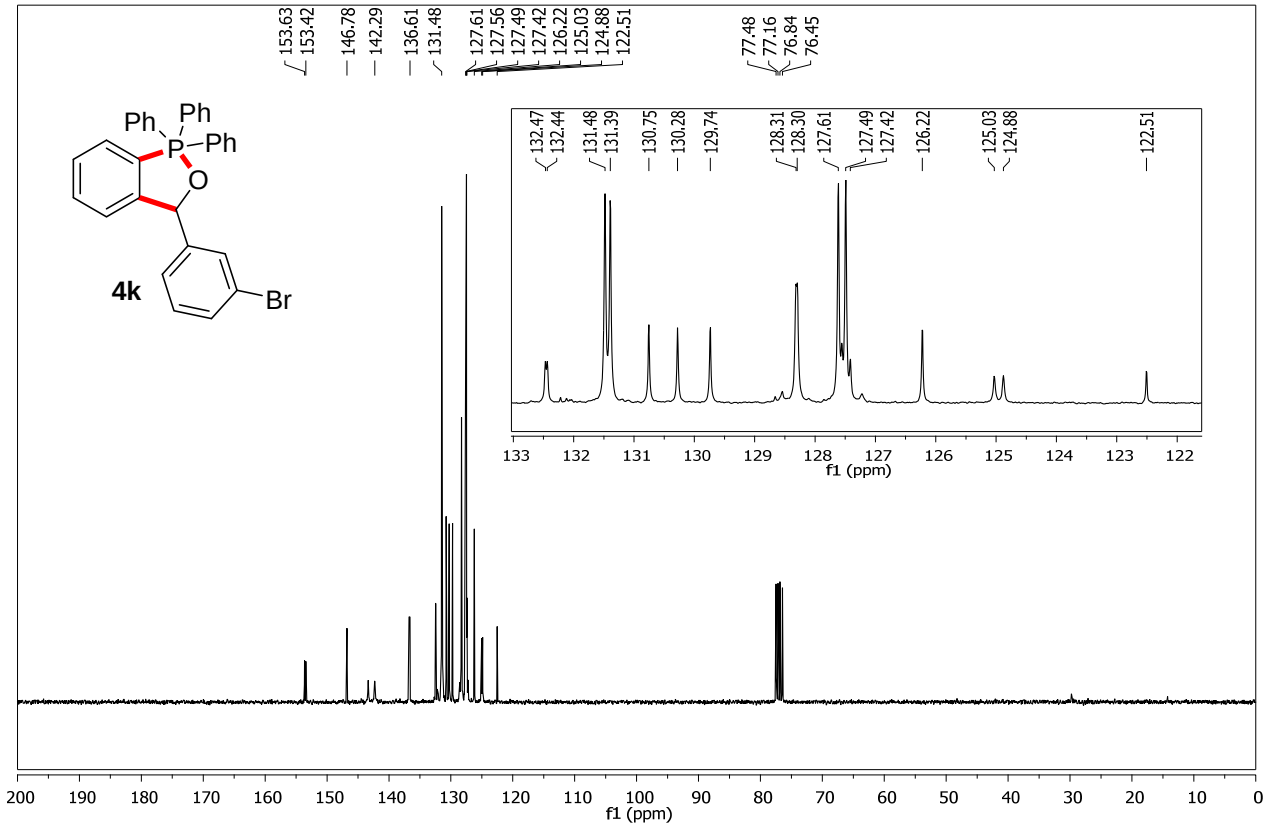
3-(3-Methoxyphenyl)-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4j)



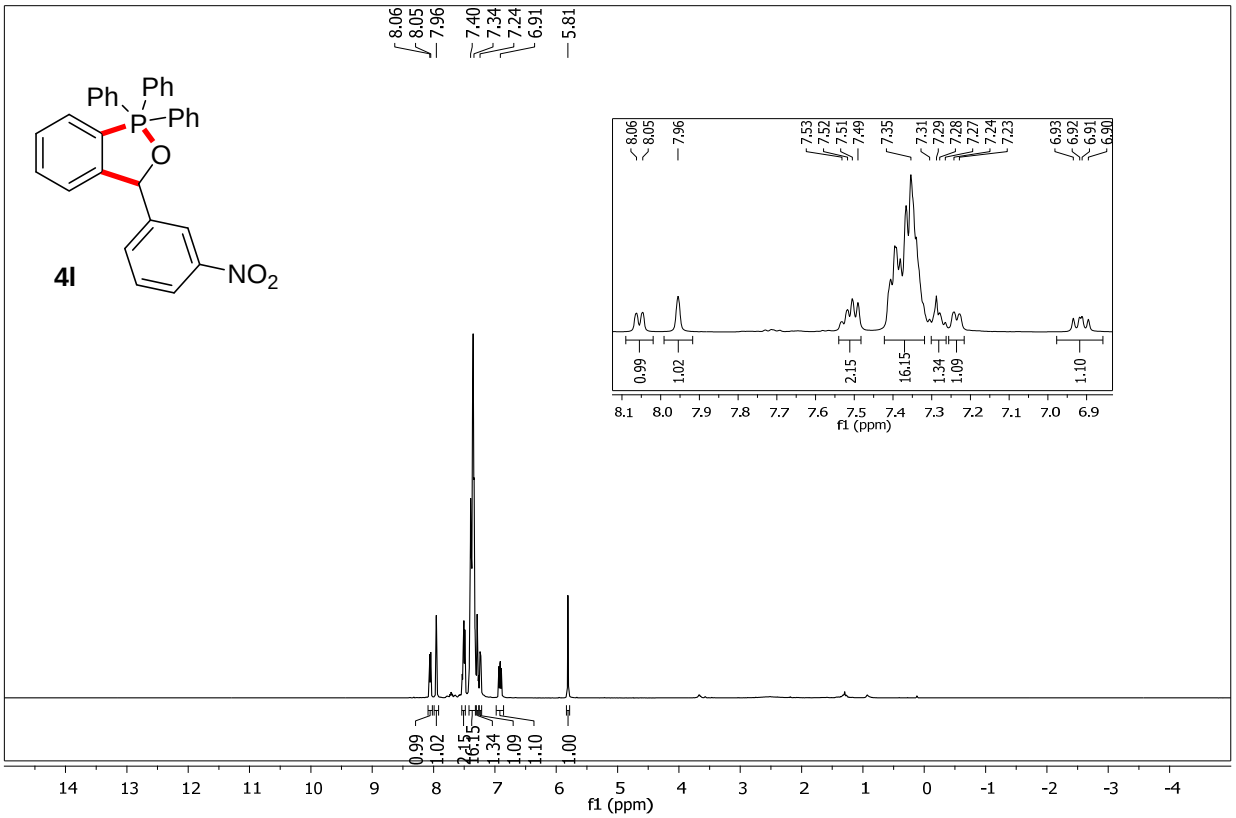


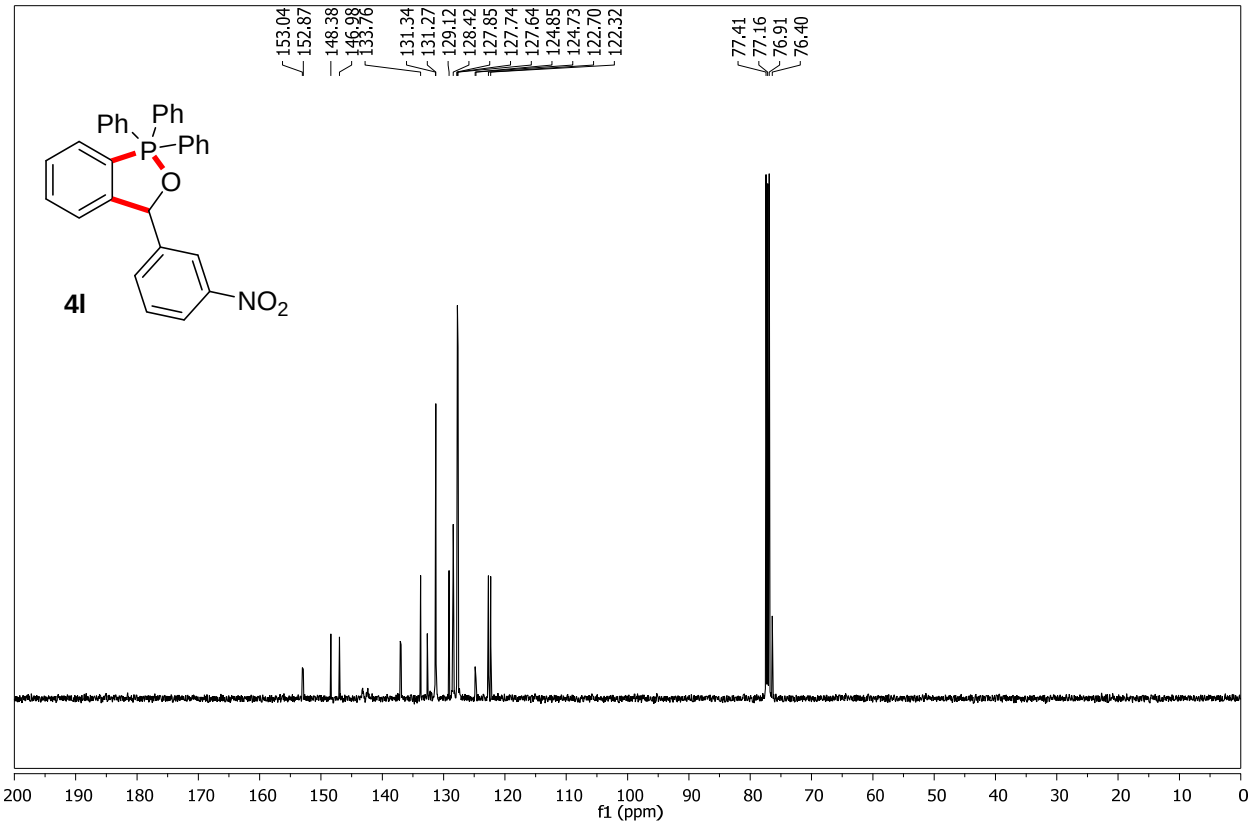
3-(3-Bromophenyl)-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4k)



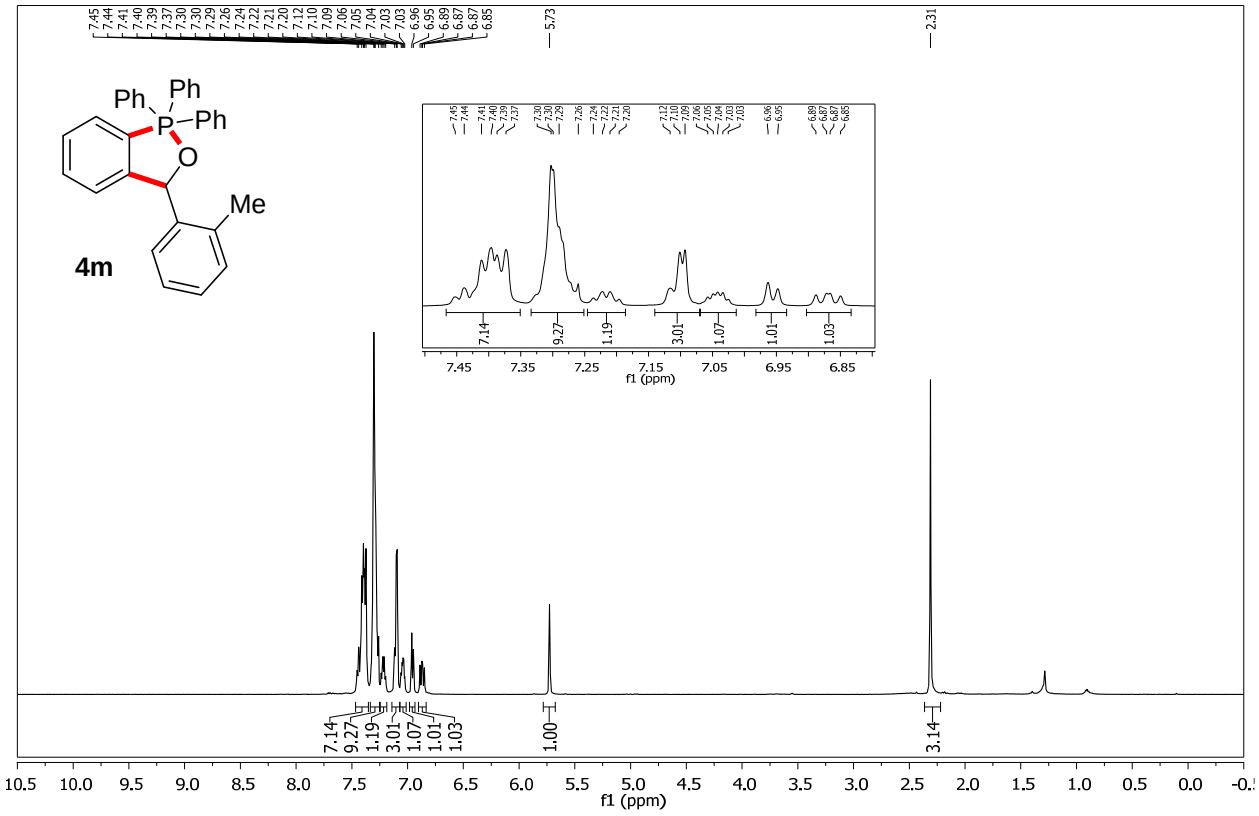


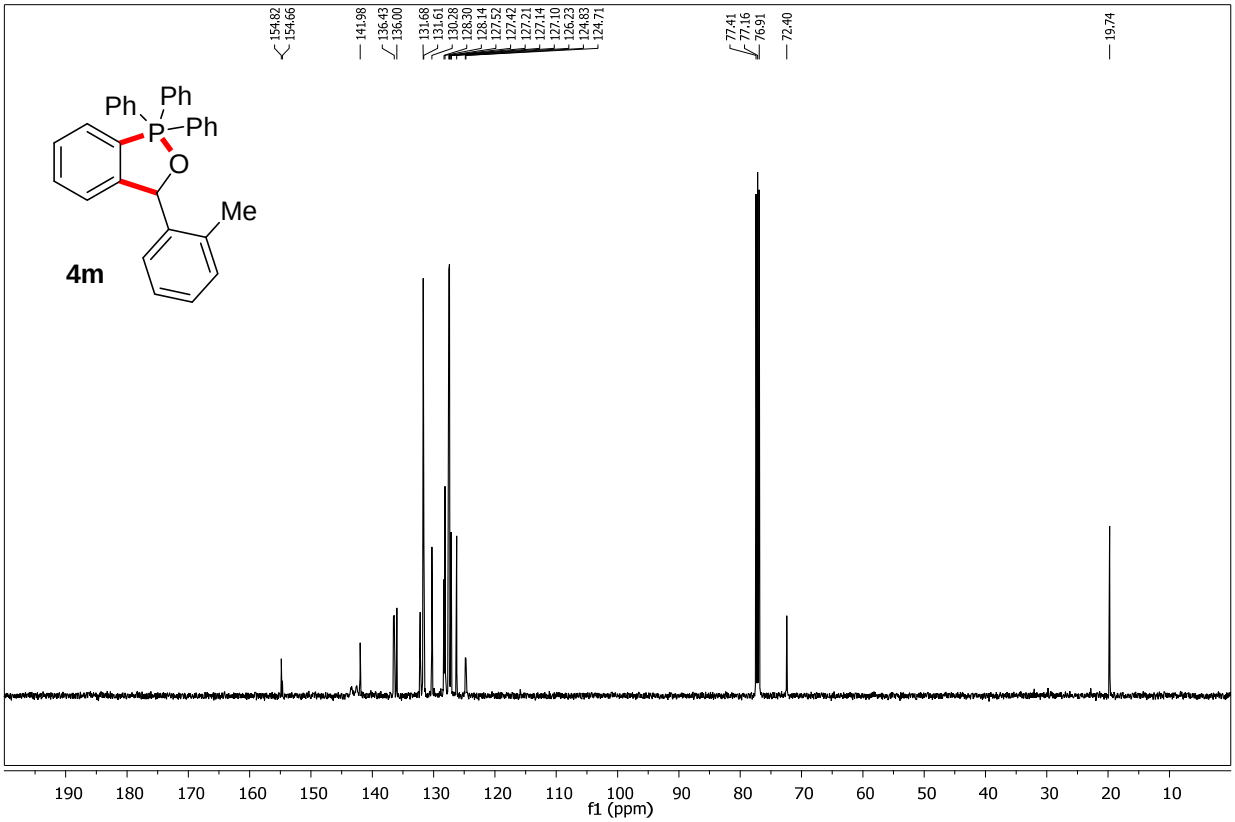
3-(3-Nitrophenyl)-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4l)



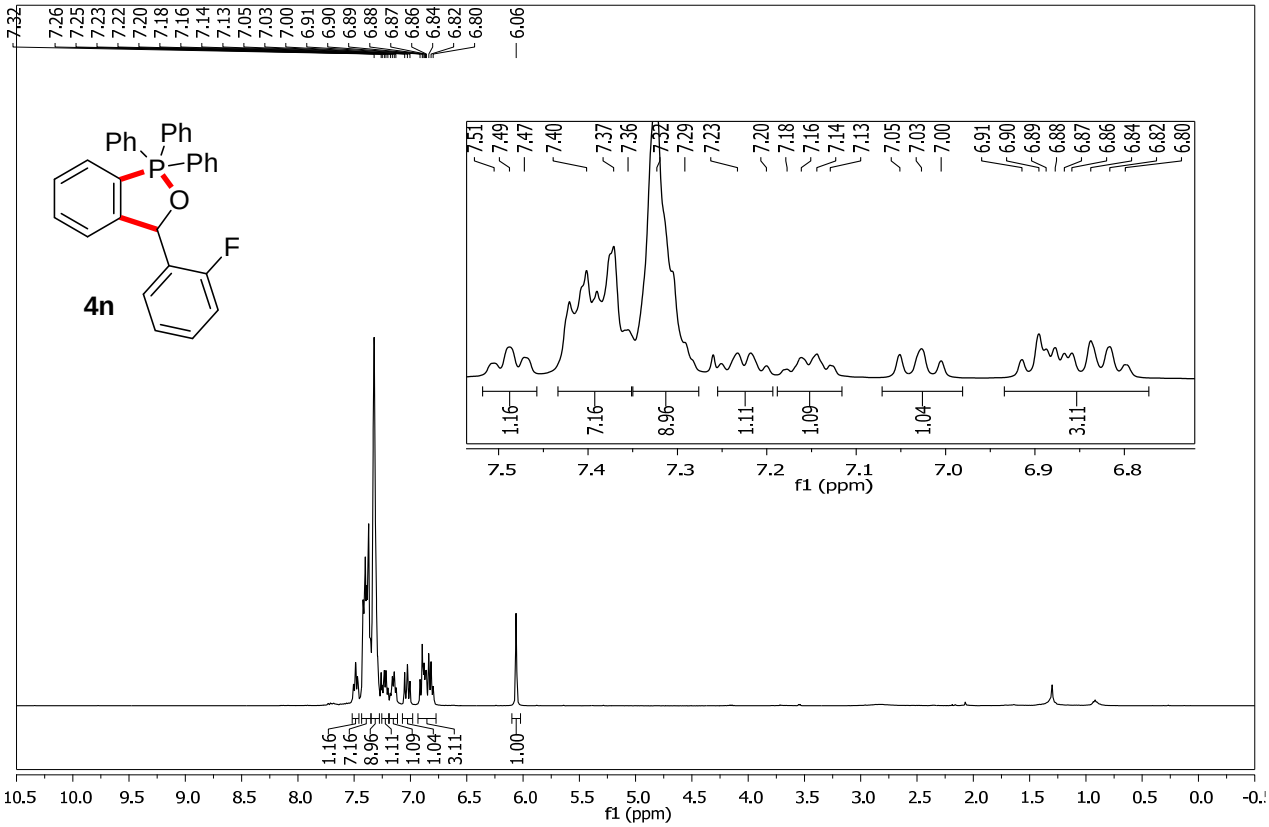


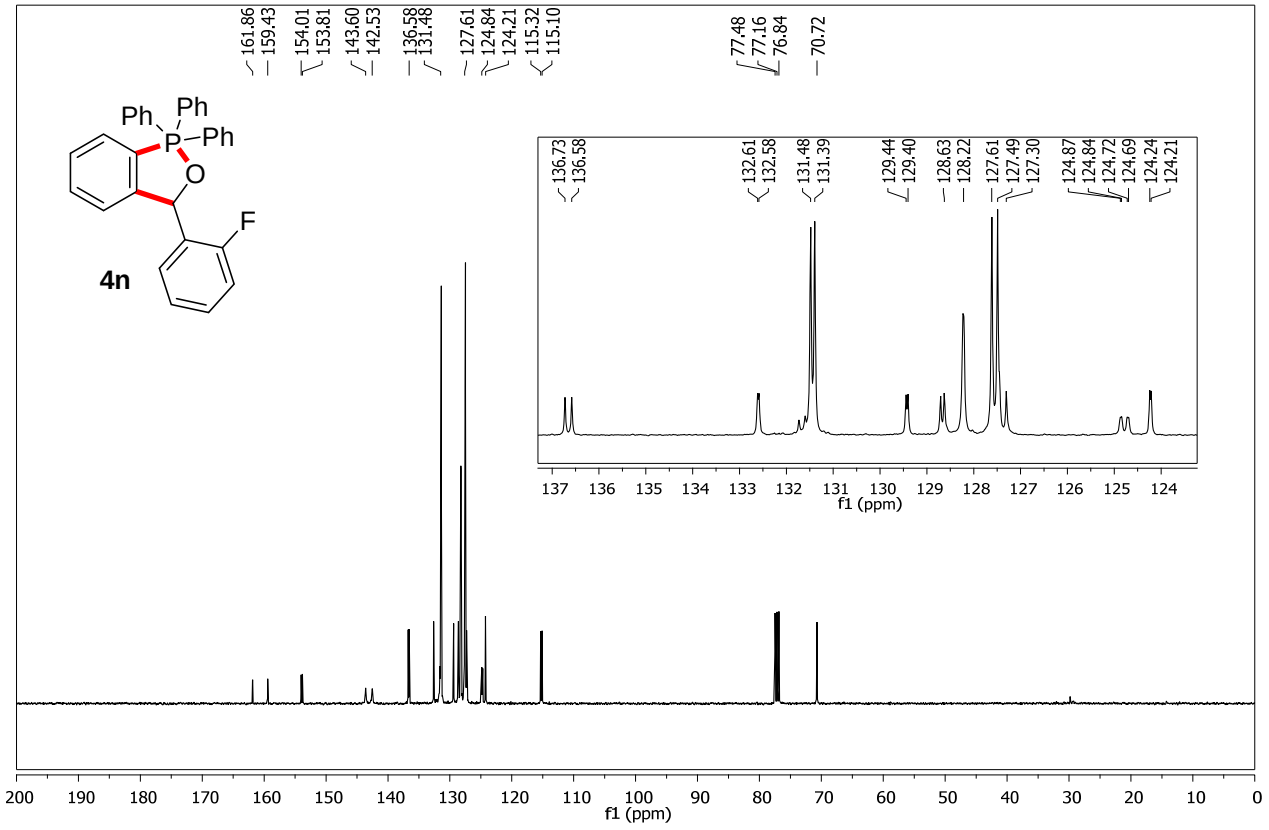
1,1,1-Triphenyl-3-(*o*-tolyl)-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4m)



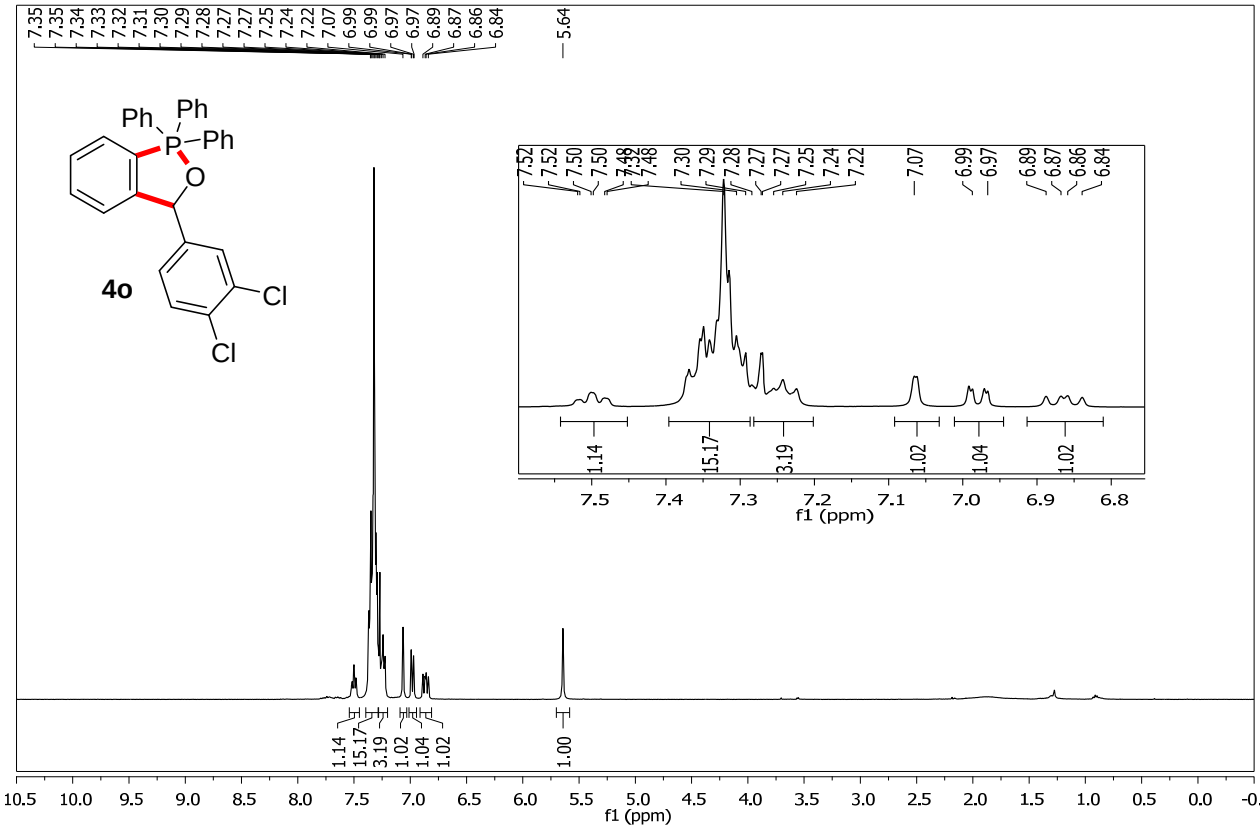


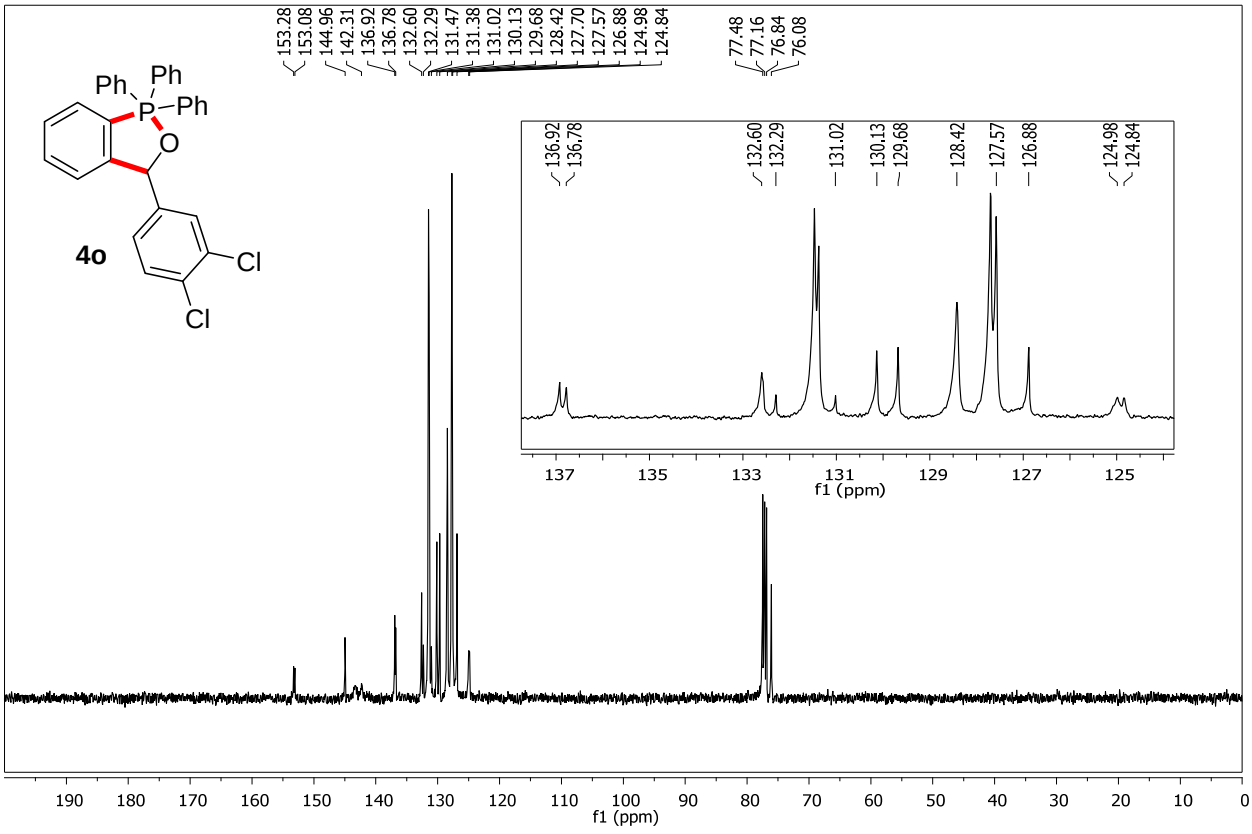
3-(2-Fluorophenyl)-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4n)



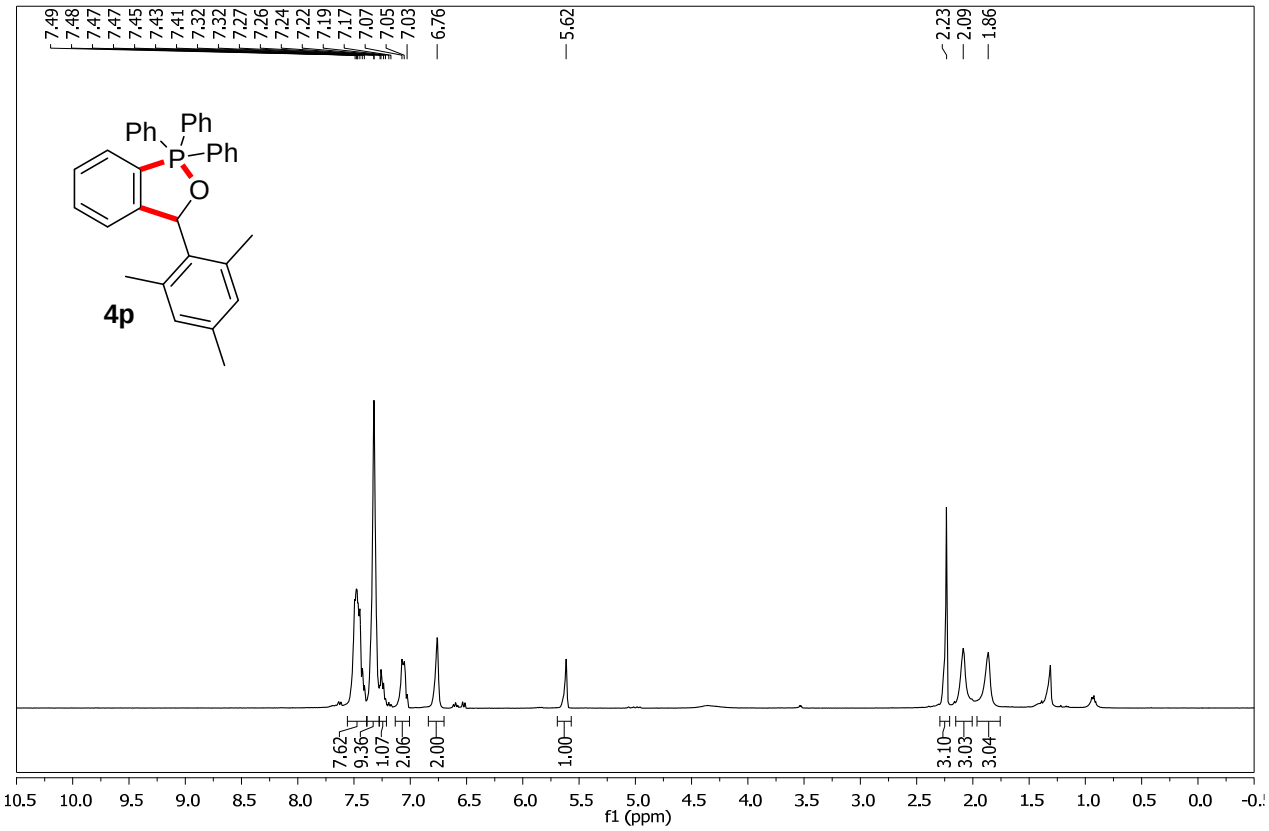


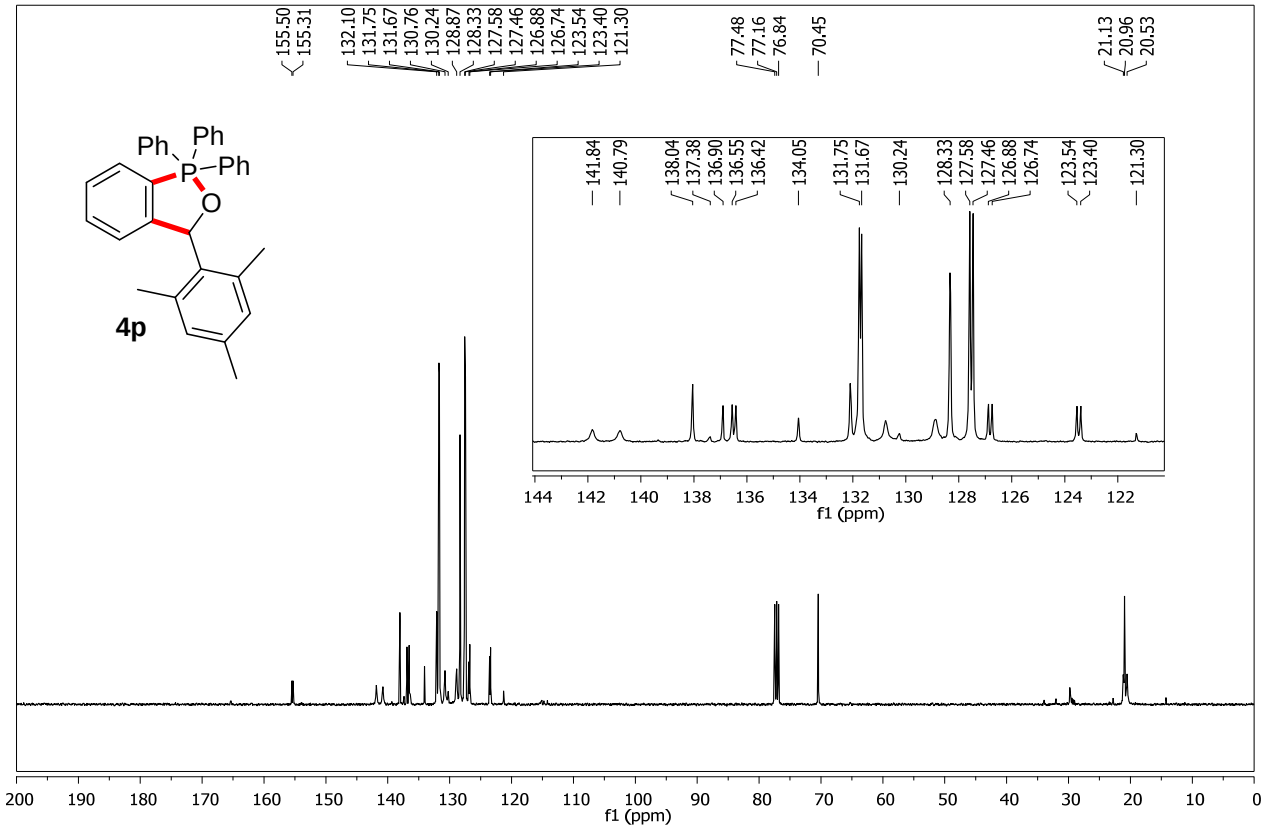
3-(3,4-Dichlorophenyl)-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4o)



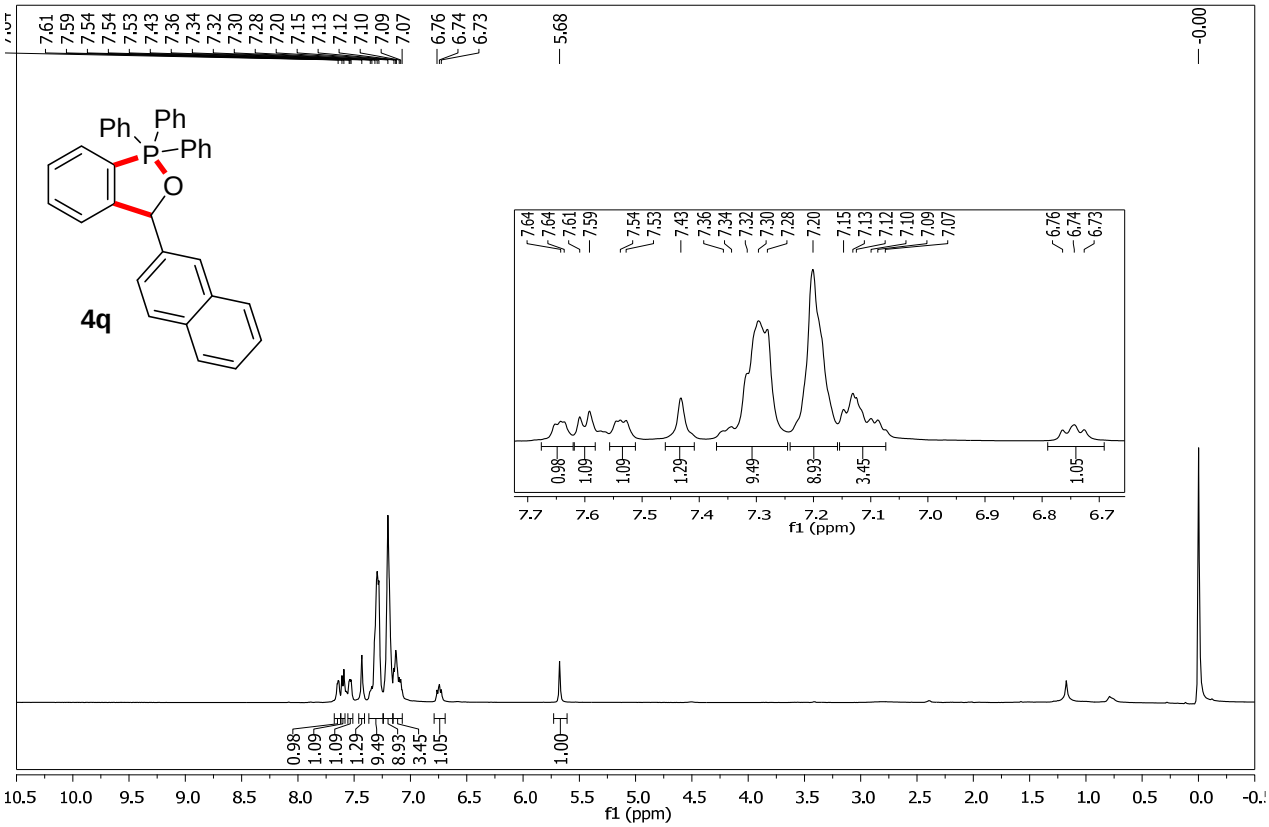


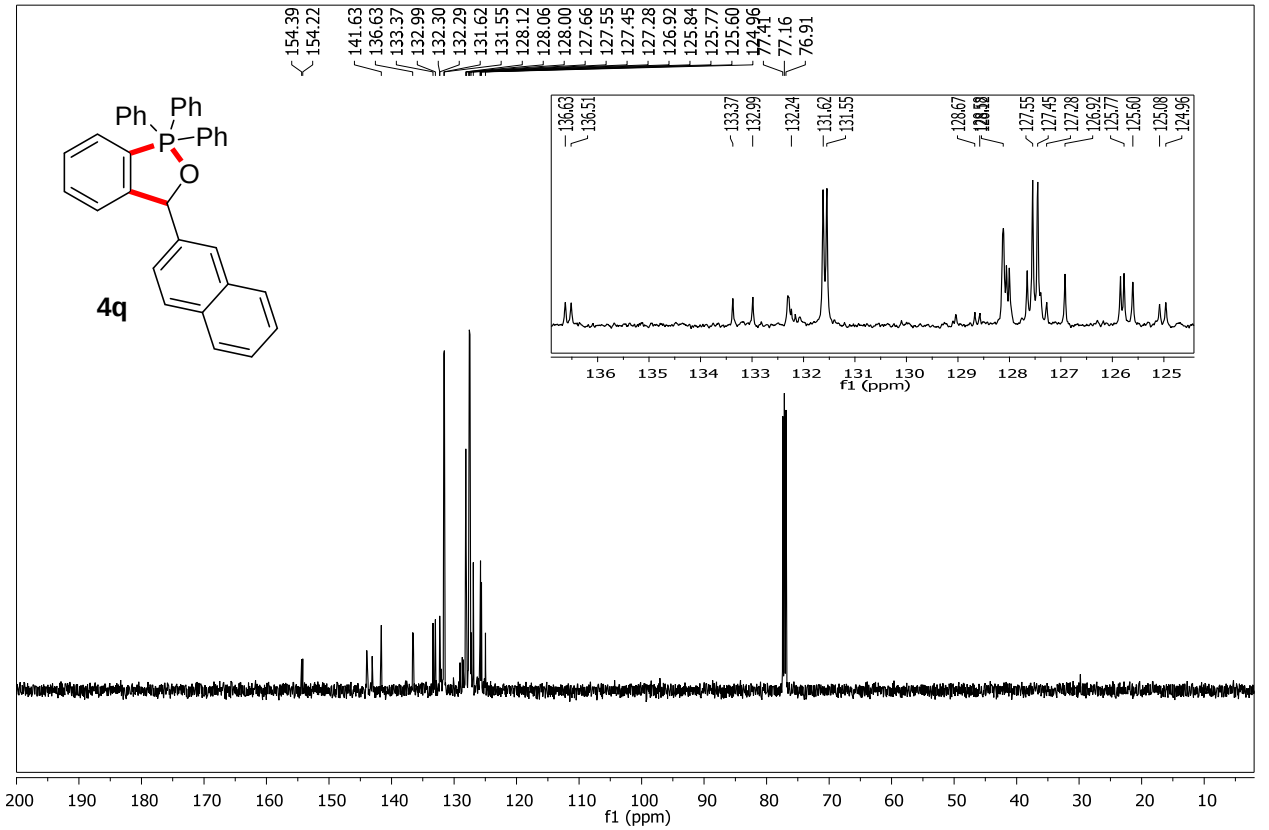
3-Mesityl-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4p)



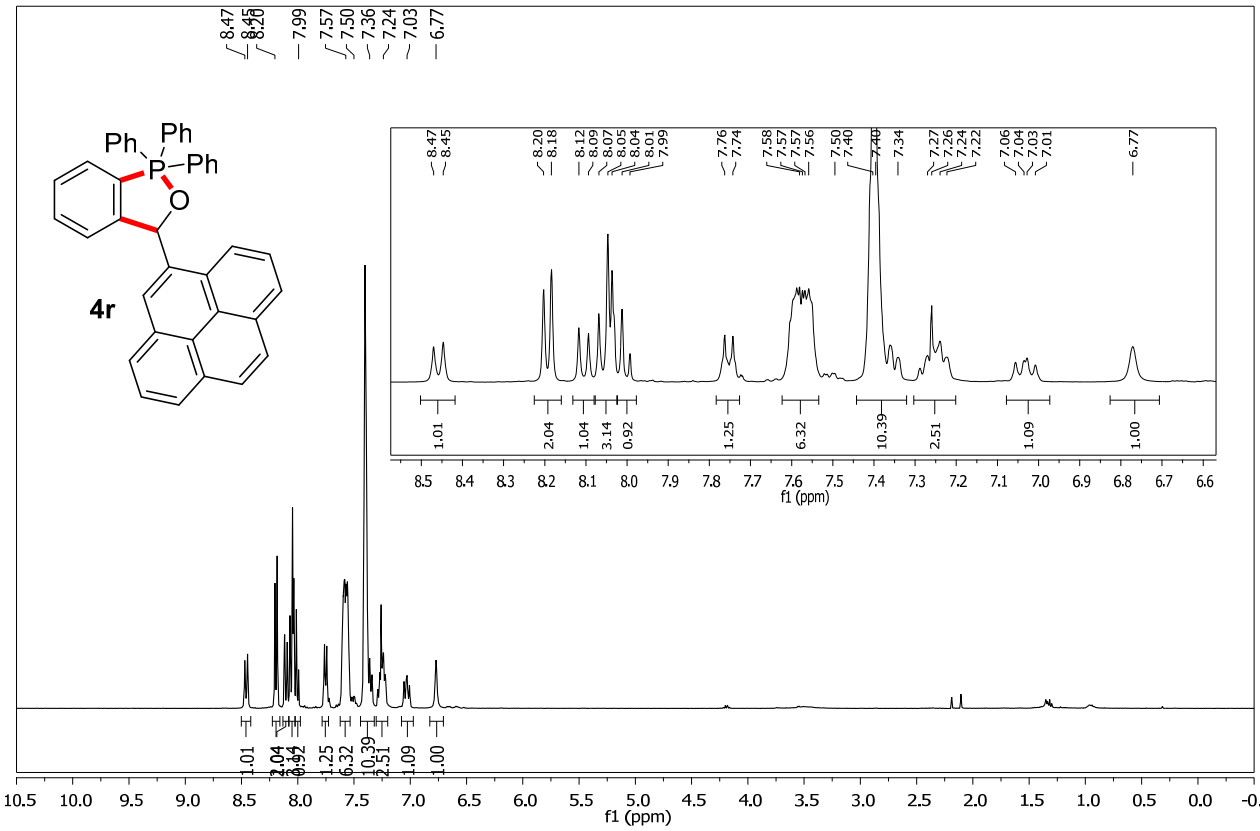


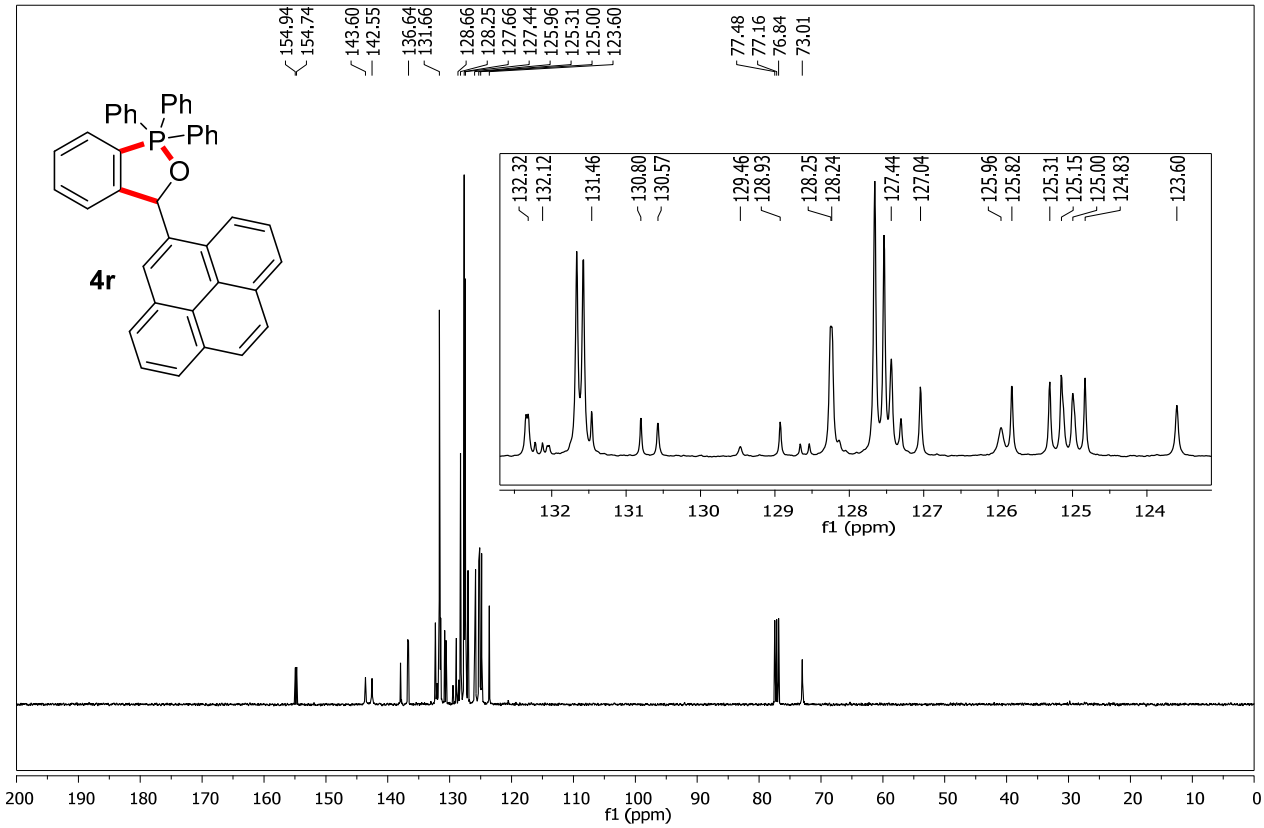
3-(Naphthalen-2-yl)-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4q)



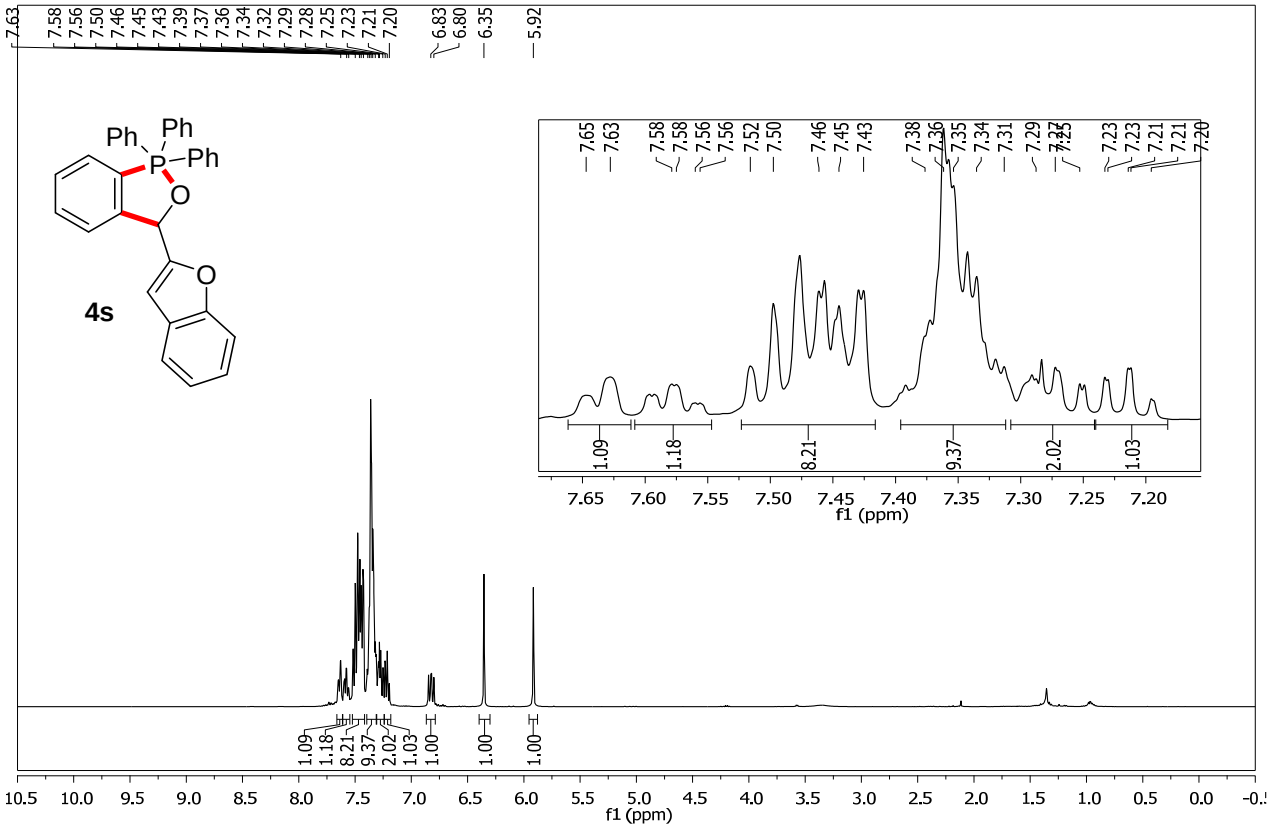


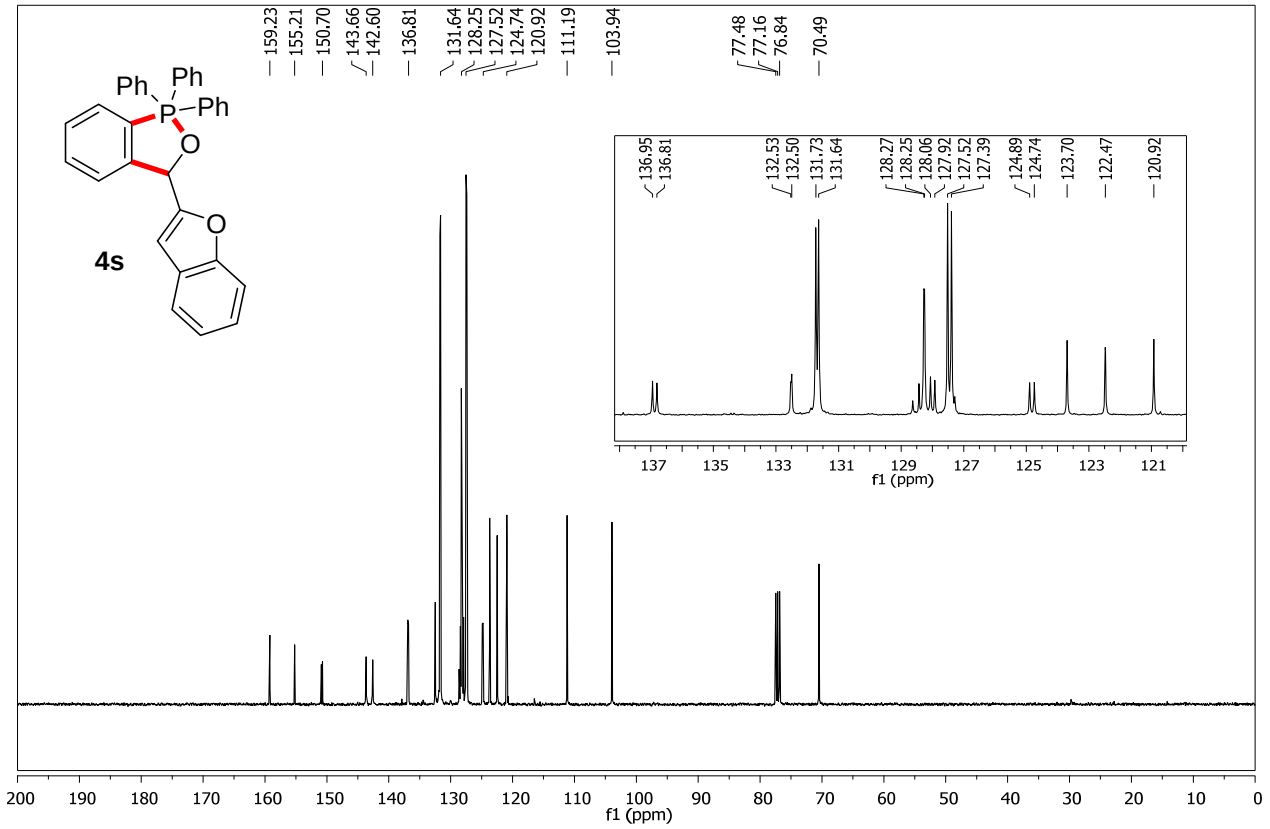
1,1,1-Triphenyl-3-(pyren-4-yl)-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4r)



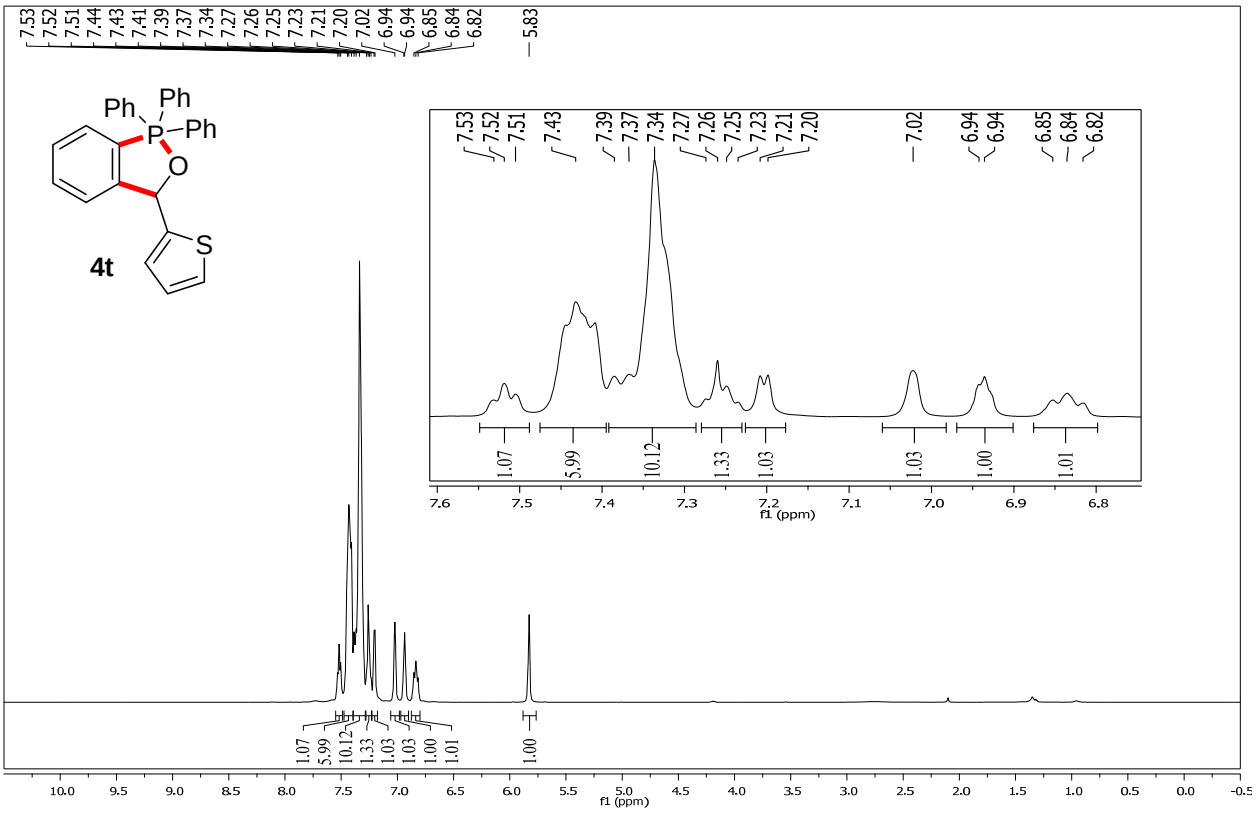


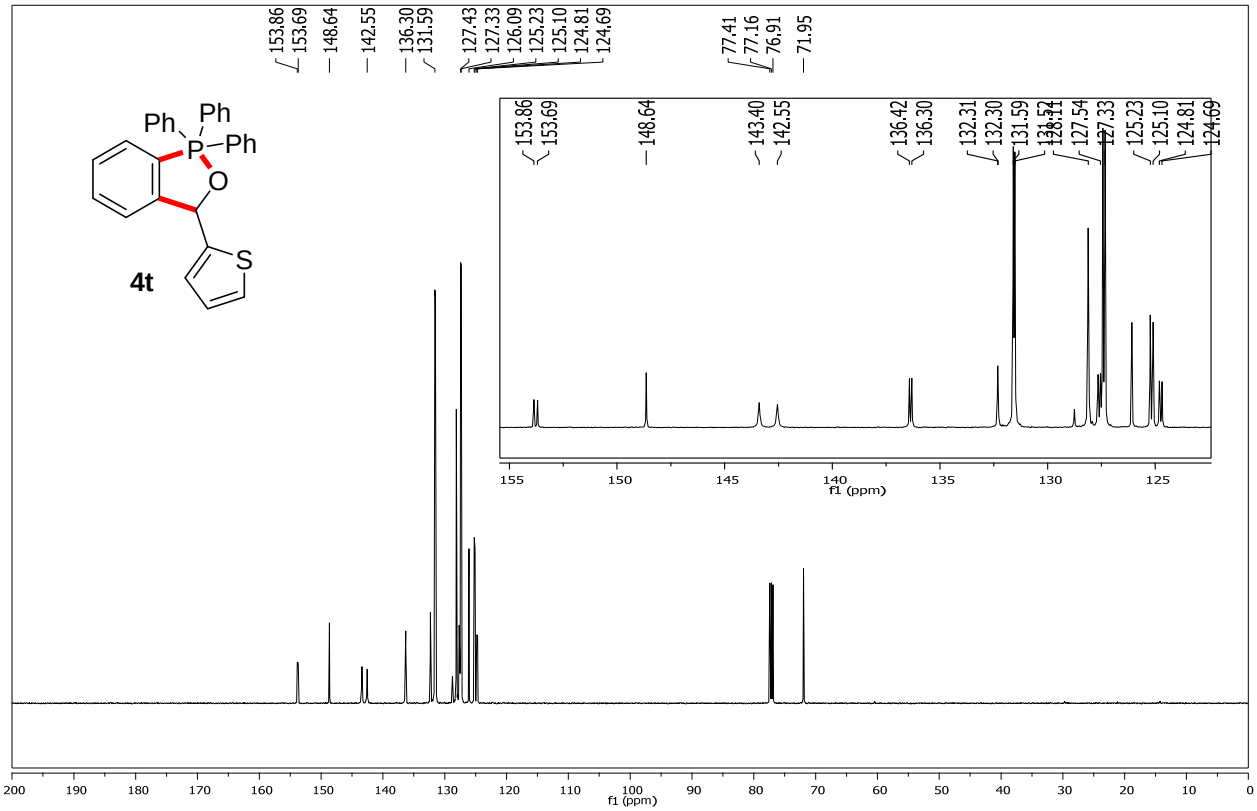
3-(Benzofuran-2-yl)-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4s)



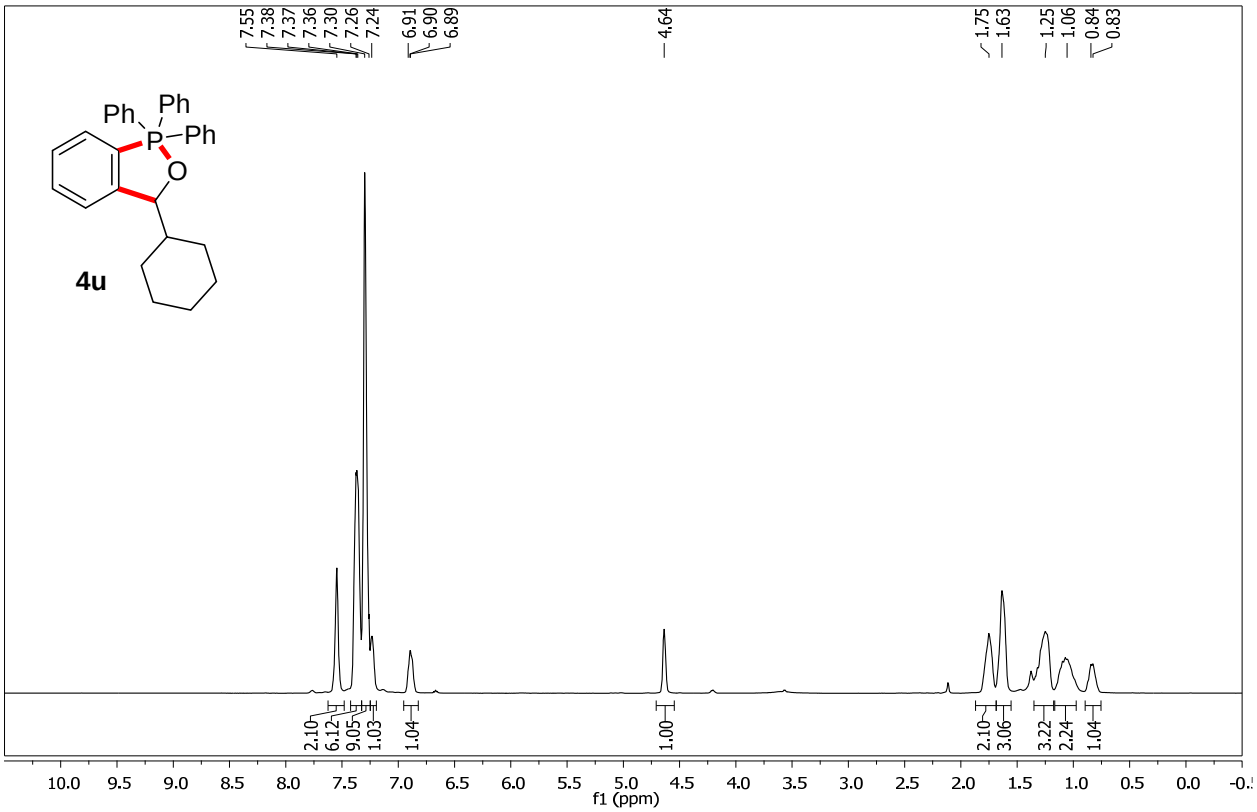


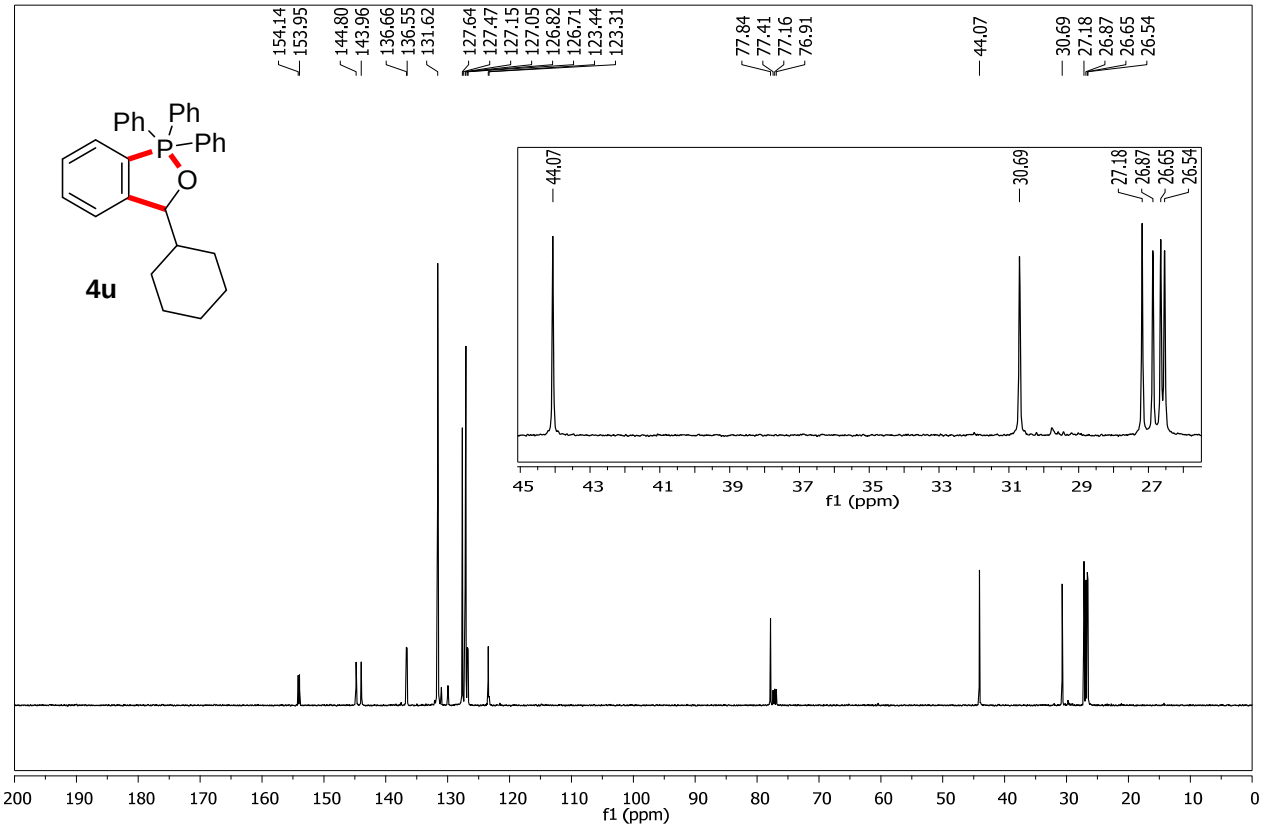
1,1,1-Triphenyl-3-(thiophen-2-yl)-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4t)



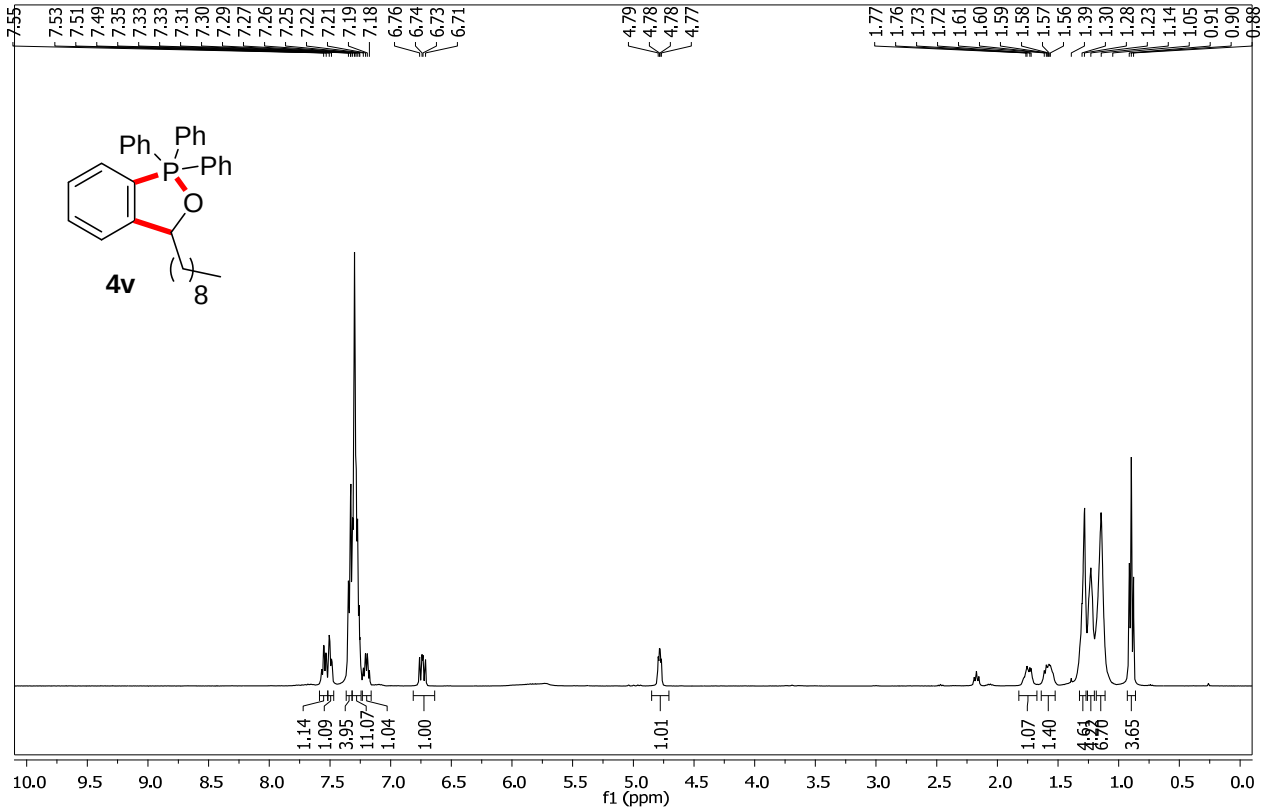


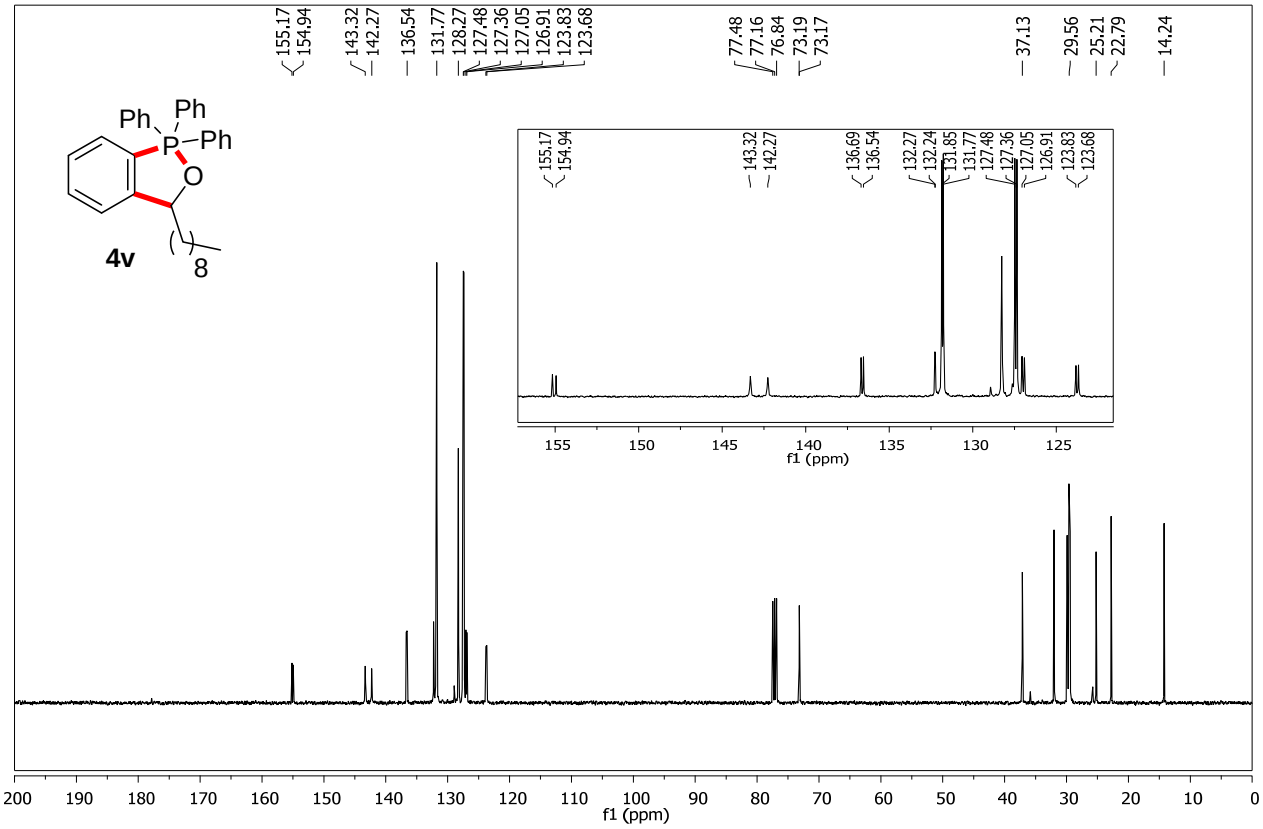
3-Cyclohexyl-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4u)



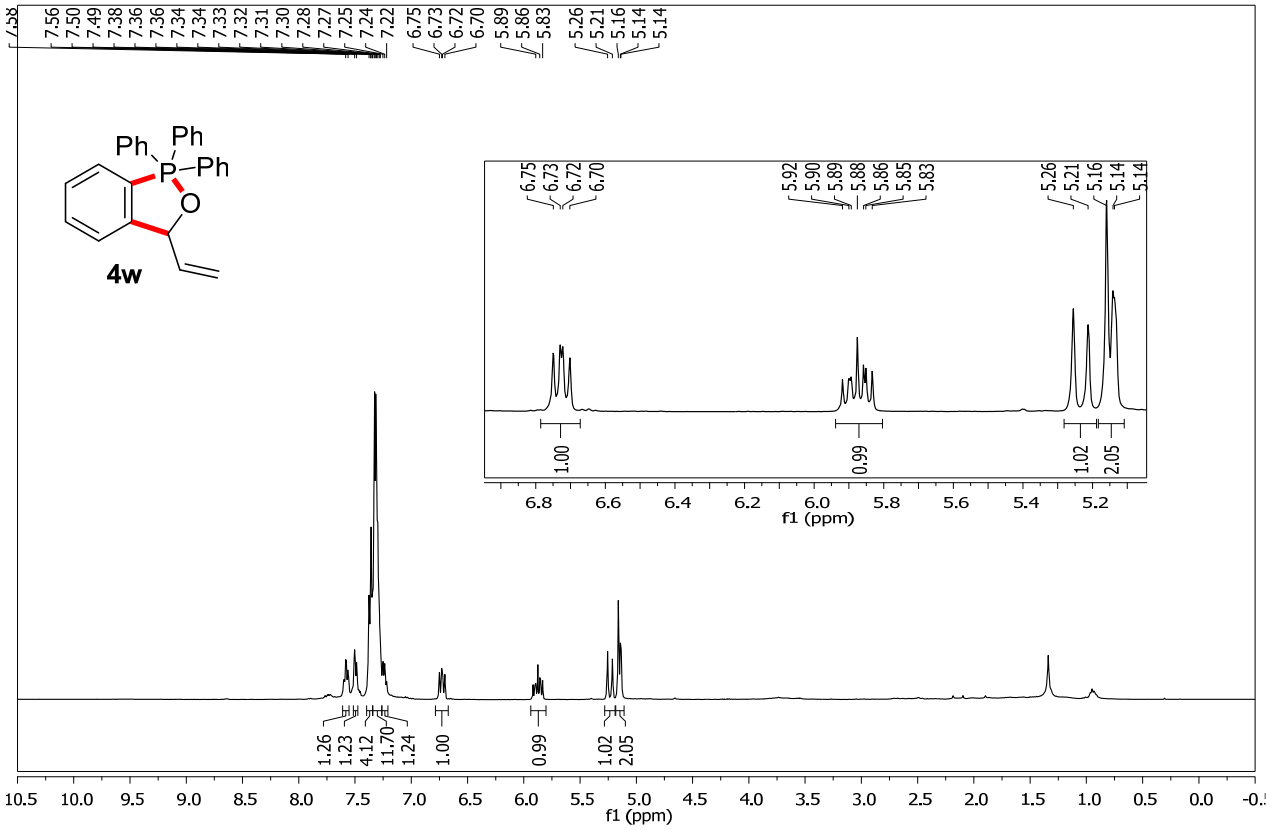


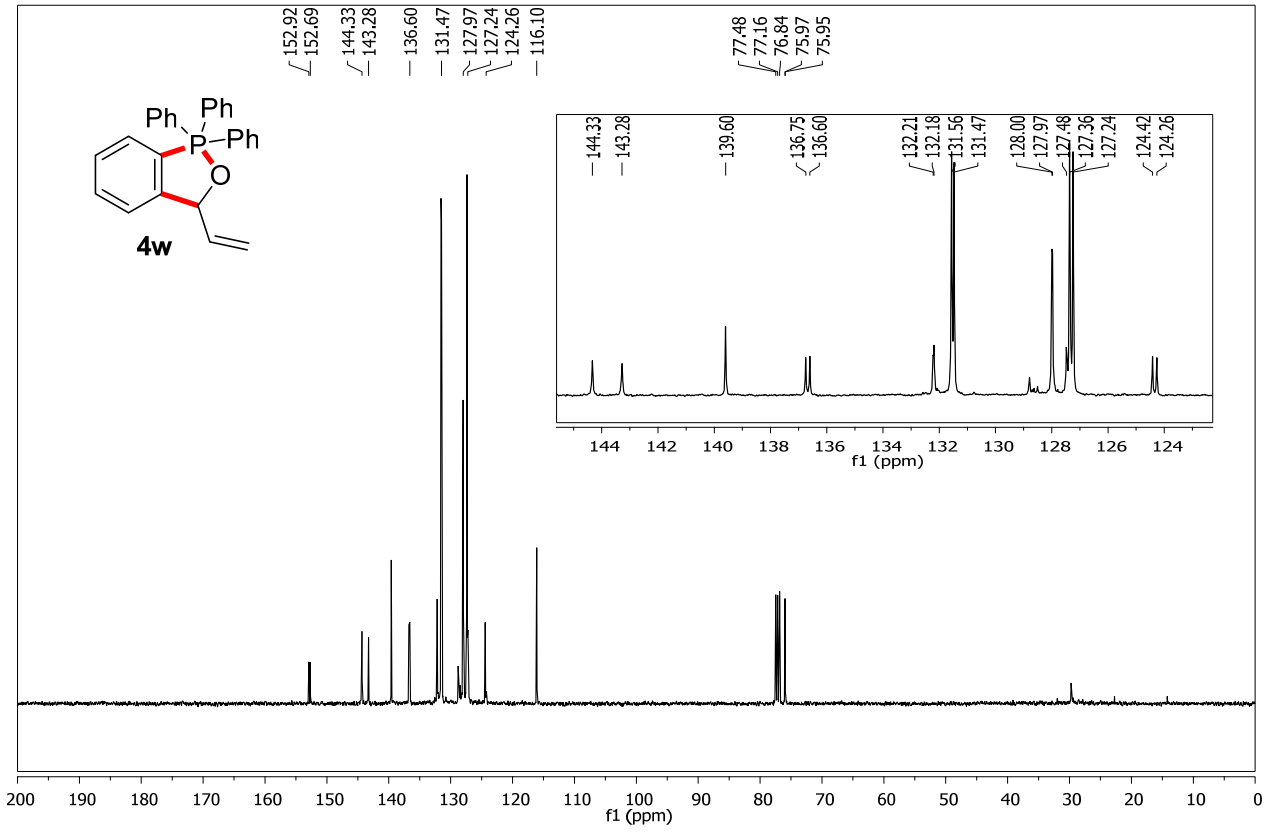
3-Nonyl-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4v)



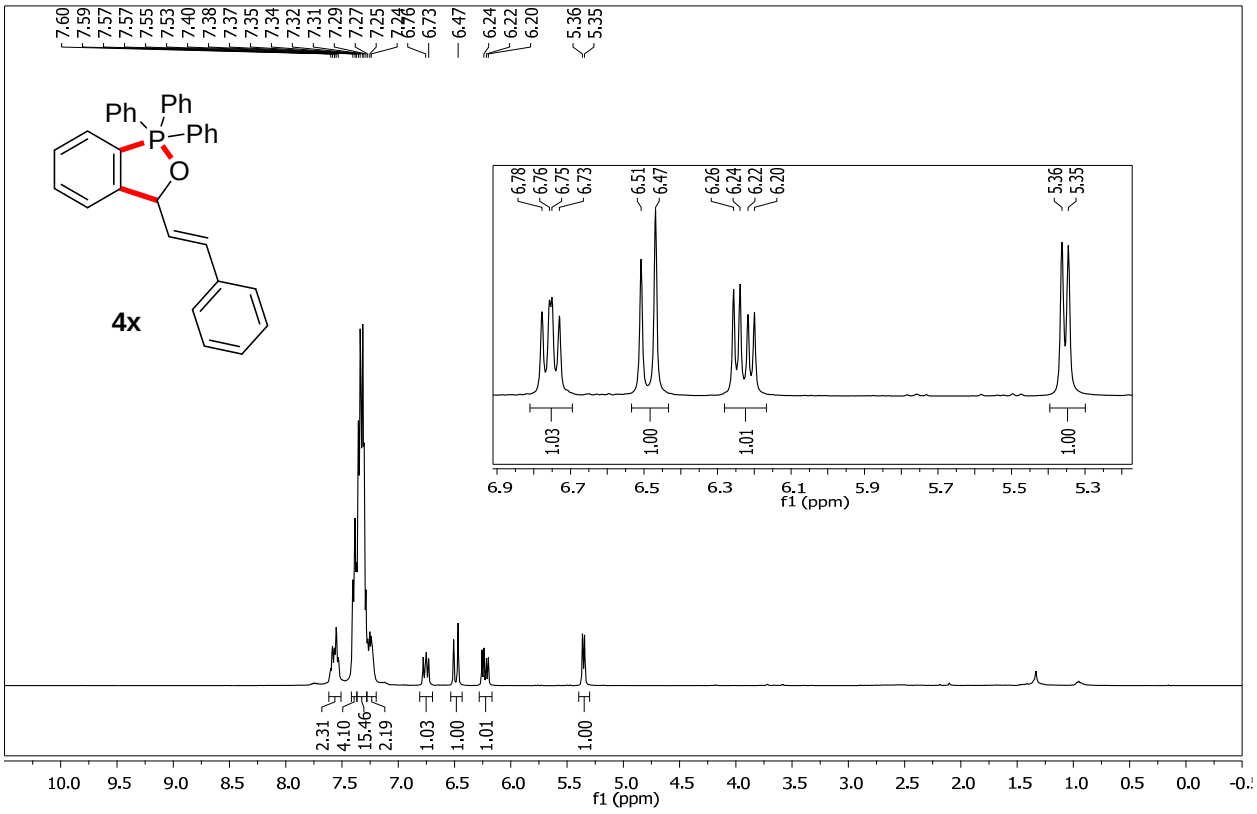


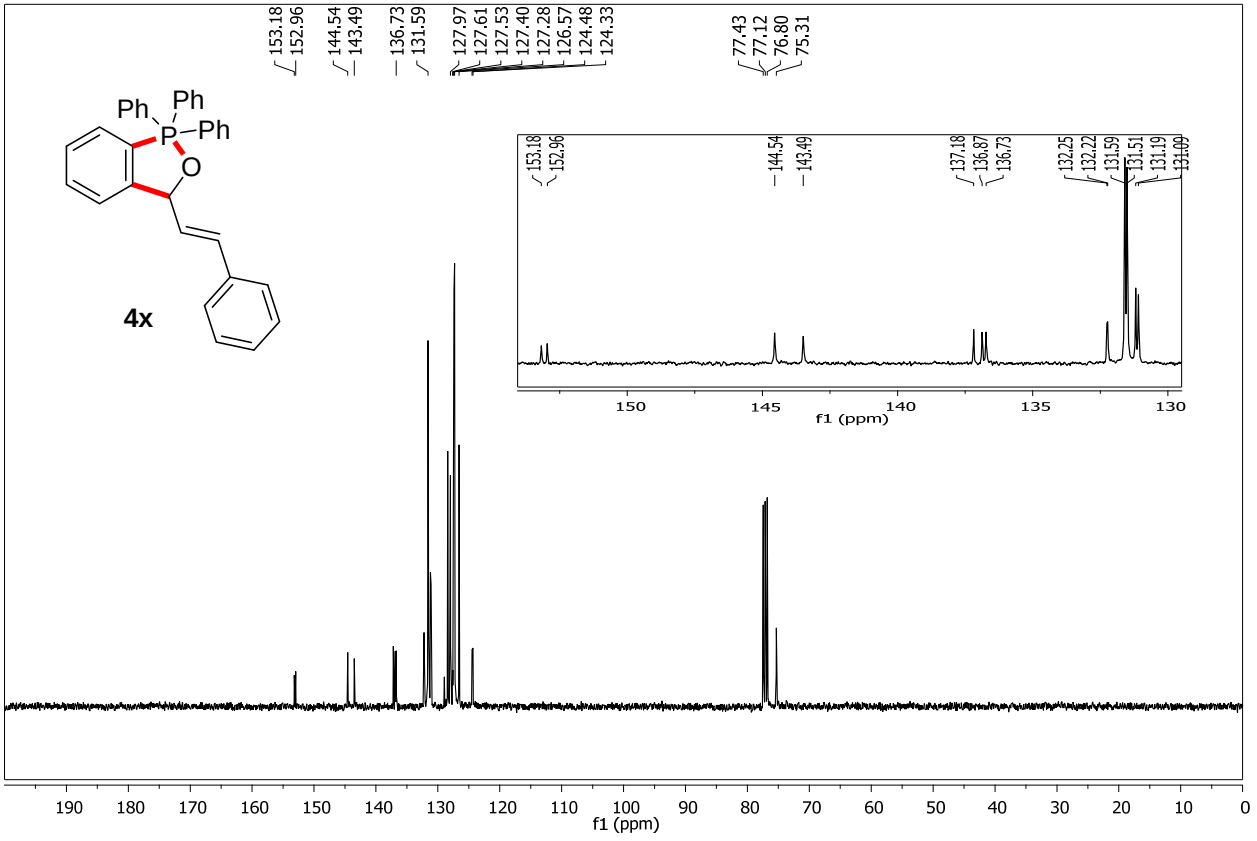
1,1,1-Triphenyl-3-vinyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4w)



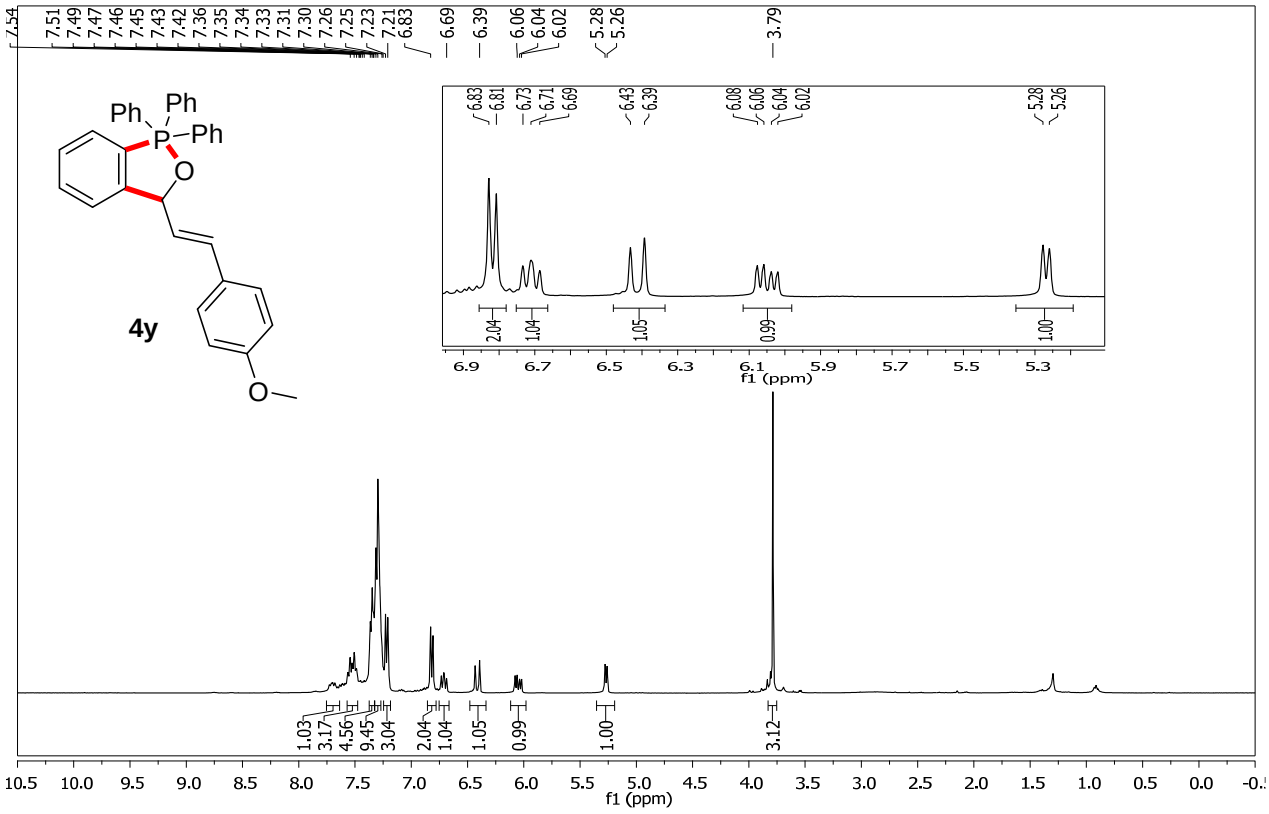


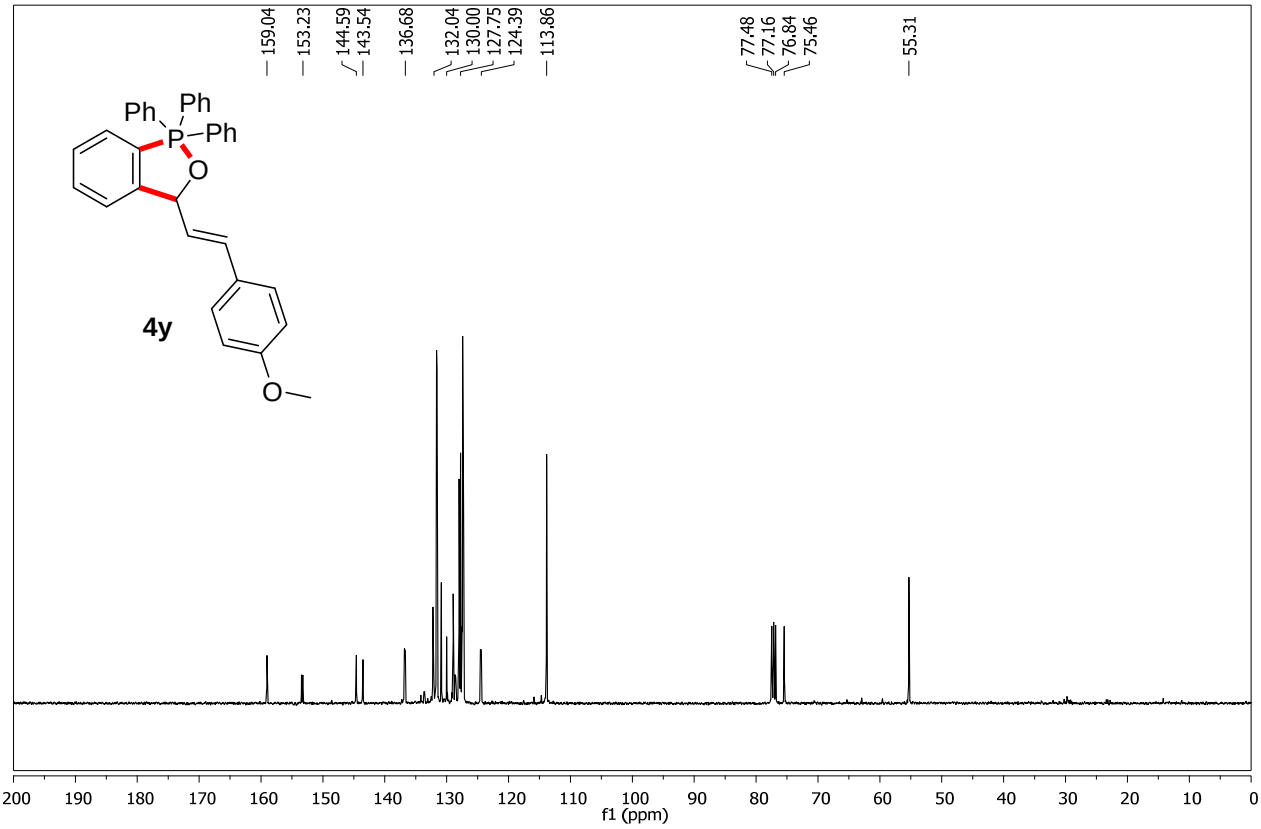
1,1,1-Triphenyl-3-styryl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4x)



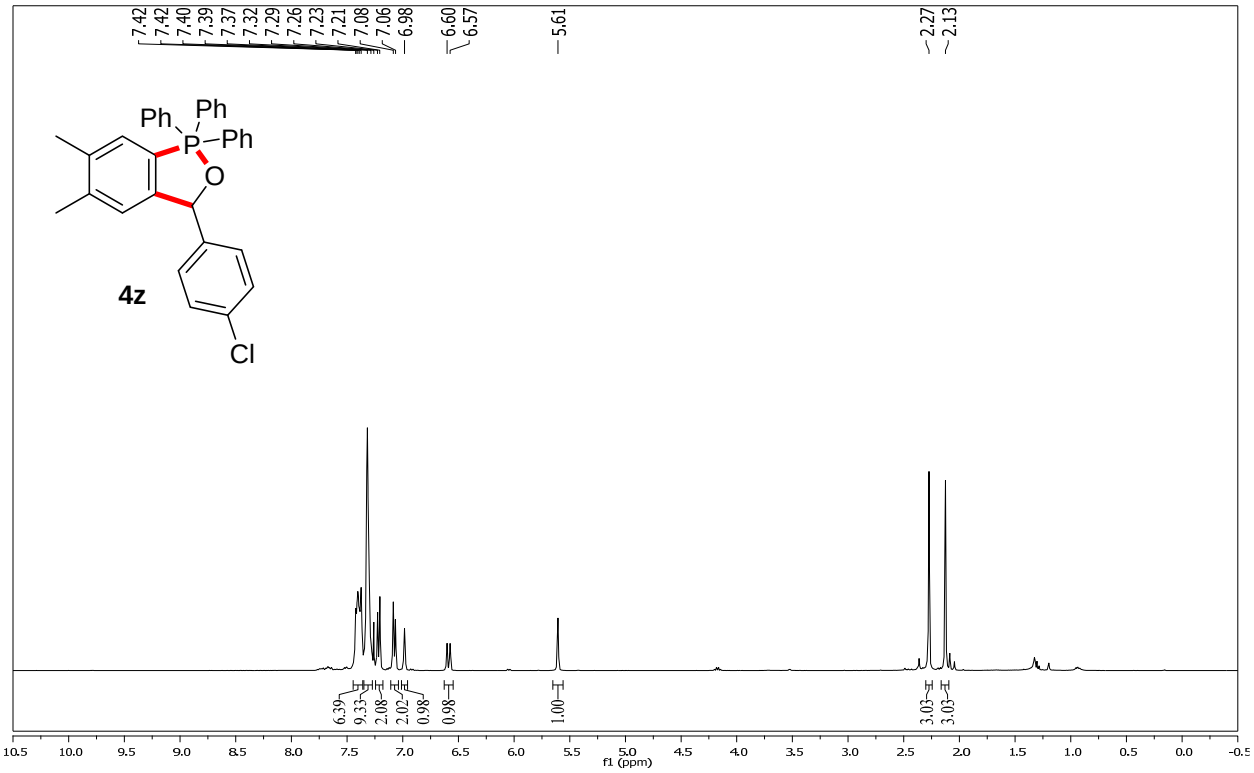


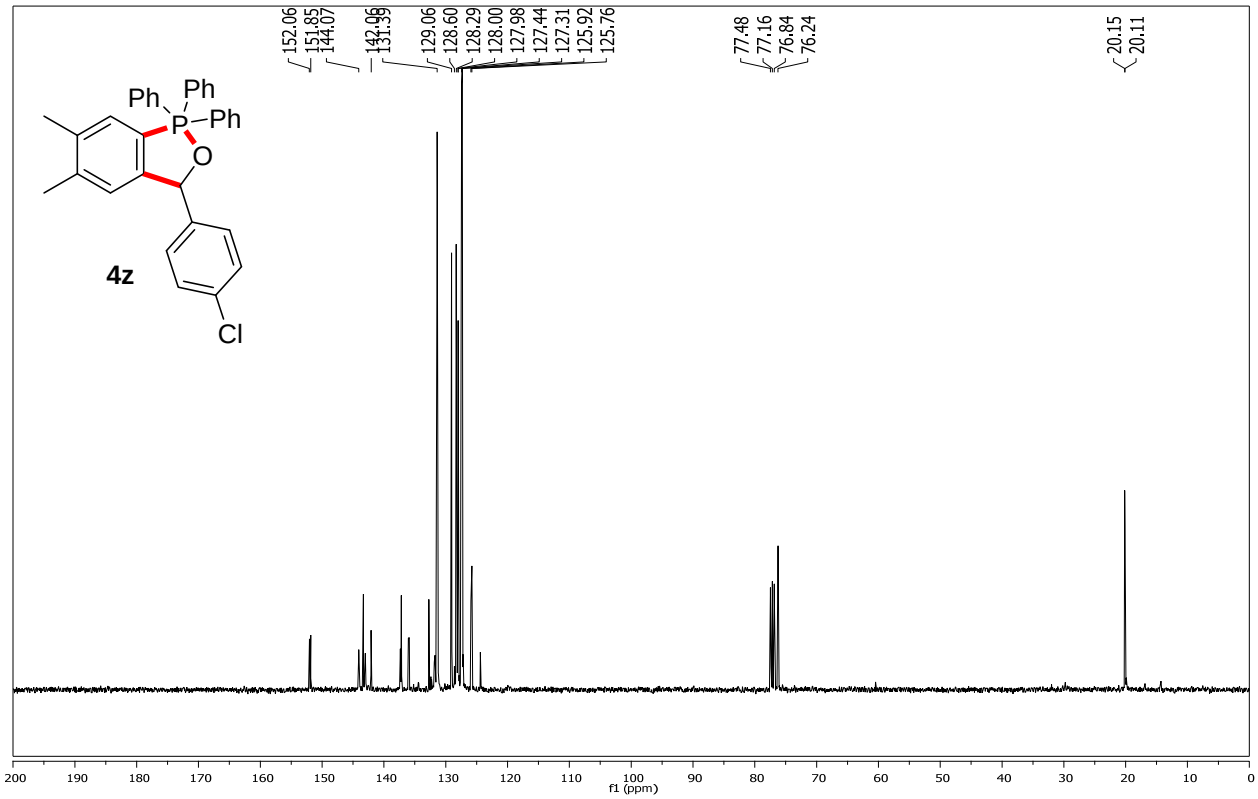
3-(4-Methoxystyryl)-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4y)



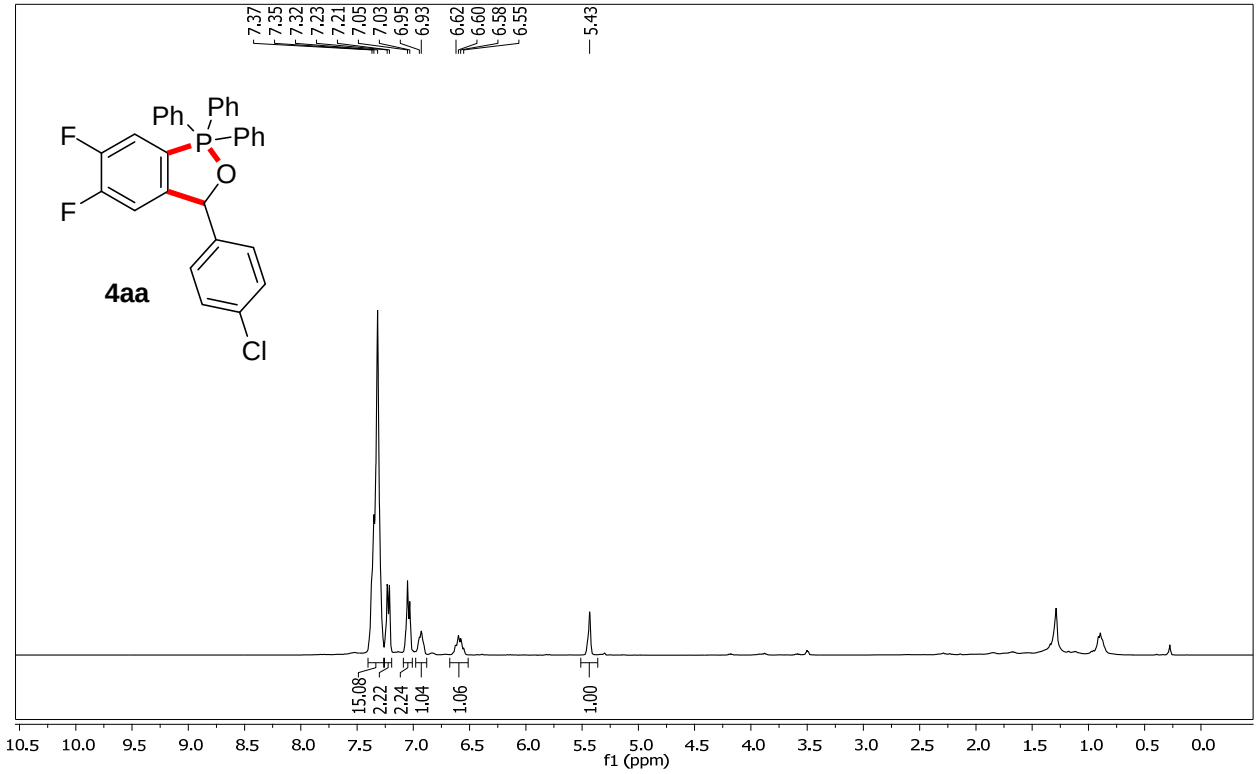


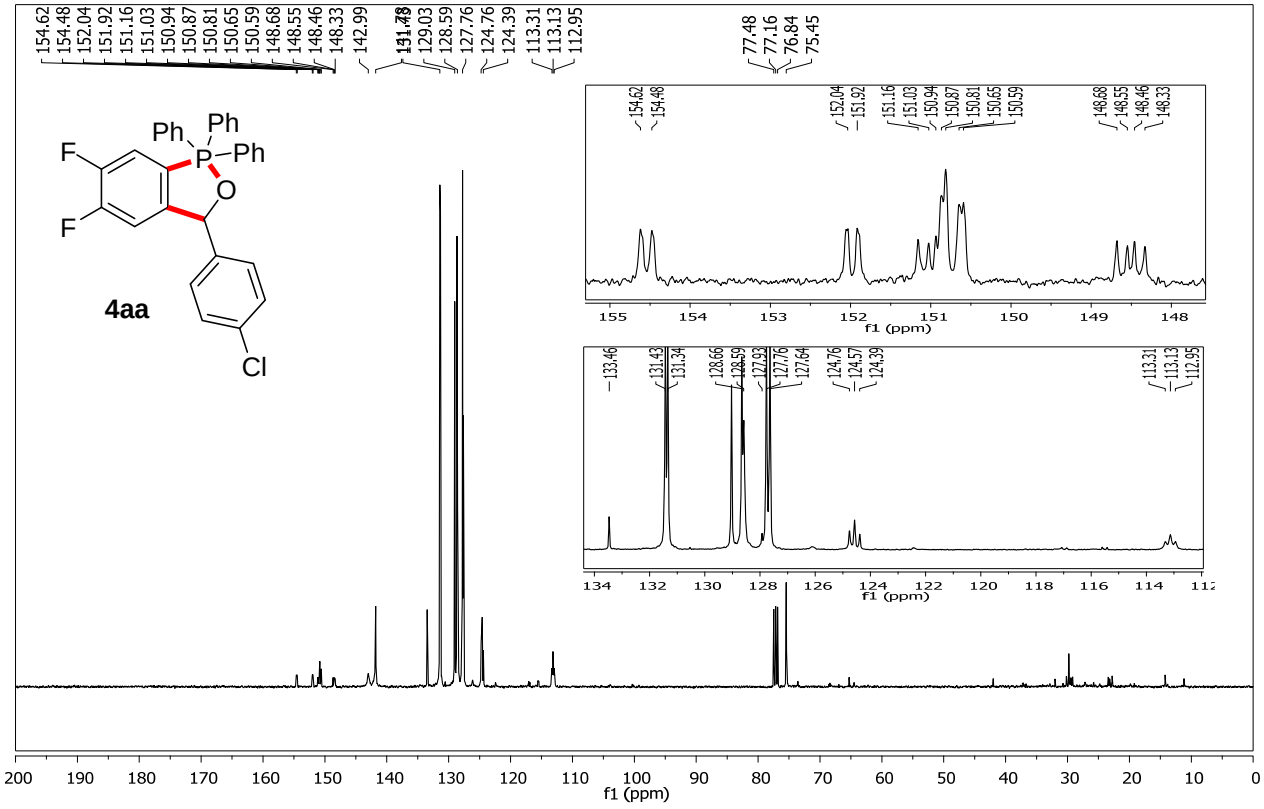
3-(4-Chlorophenyl)-5,6-dimethyl-1,1,1-triphenyl-1,3-dihydro-1λ^5 benzo[*c*][1,2]oxaphosphole (4z)



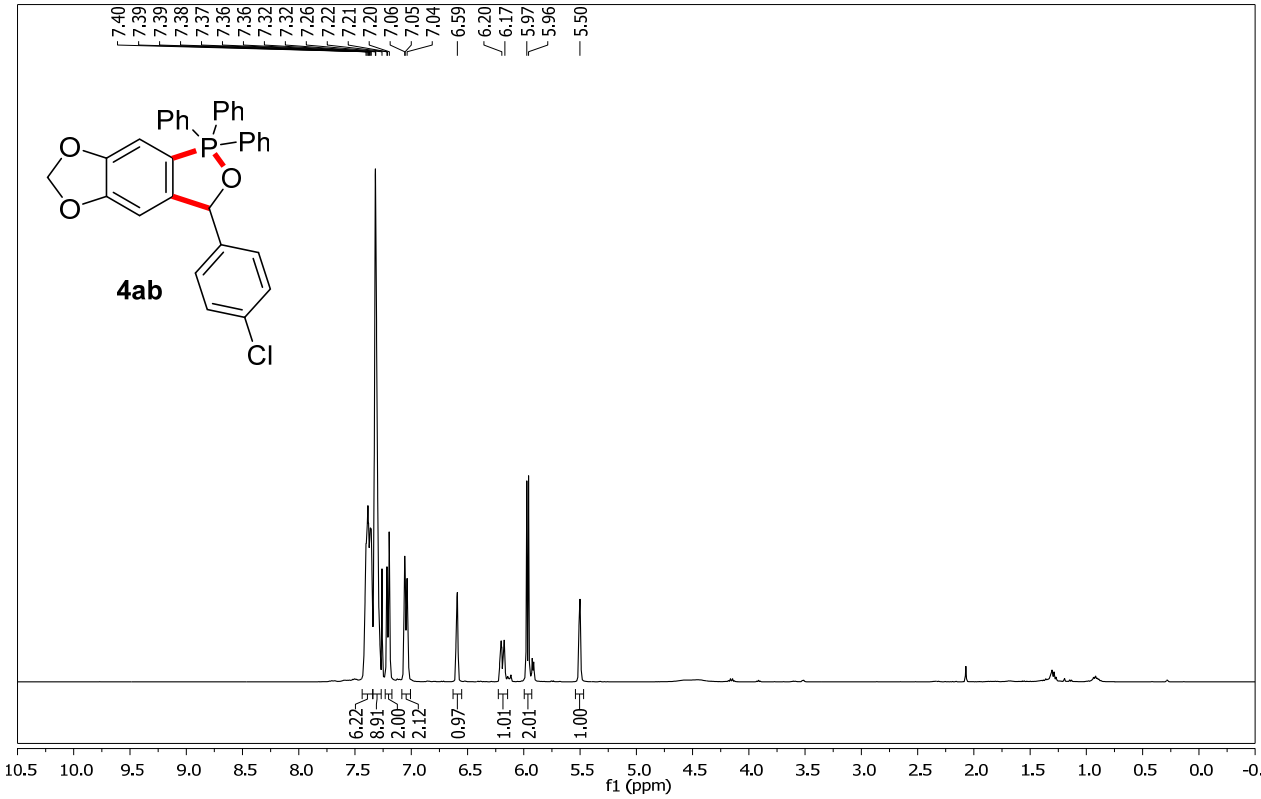


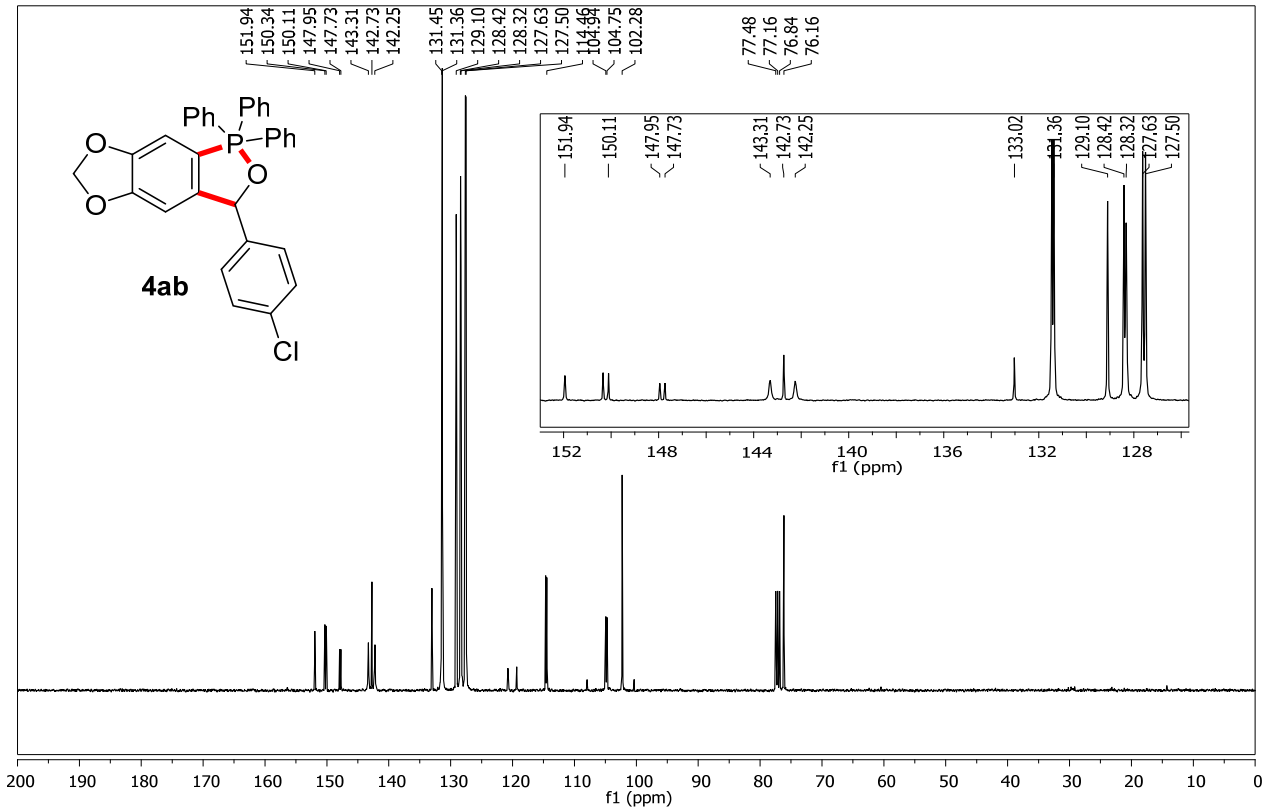
3-(4-Chlorophenyl)-5,6-difluoro-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4aa)



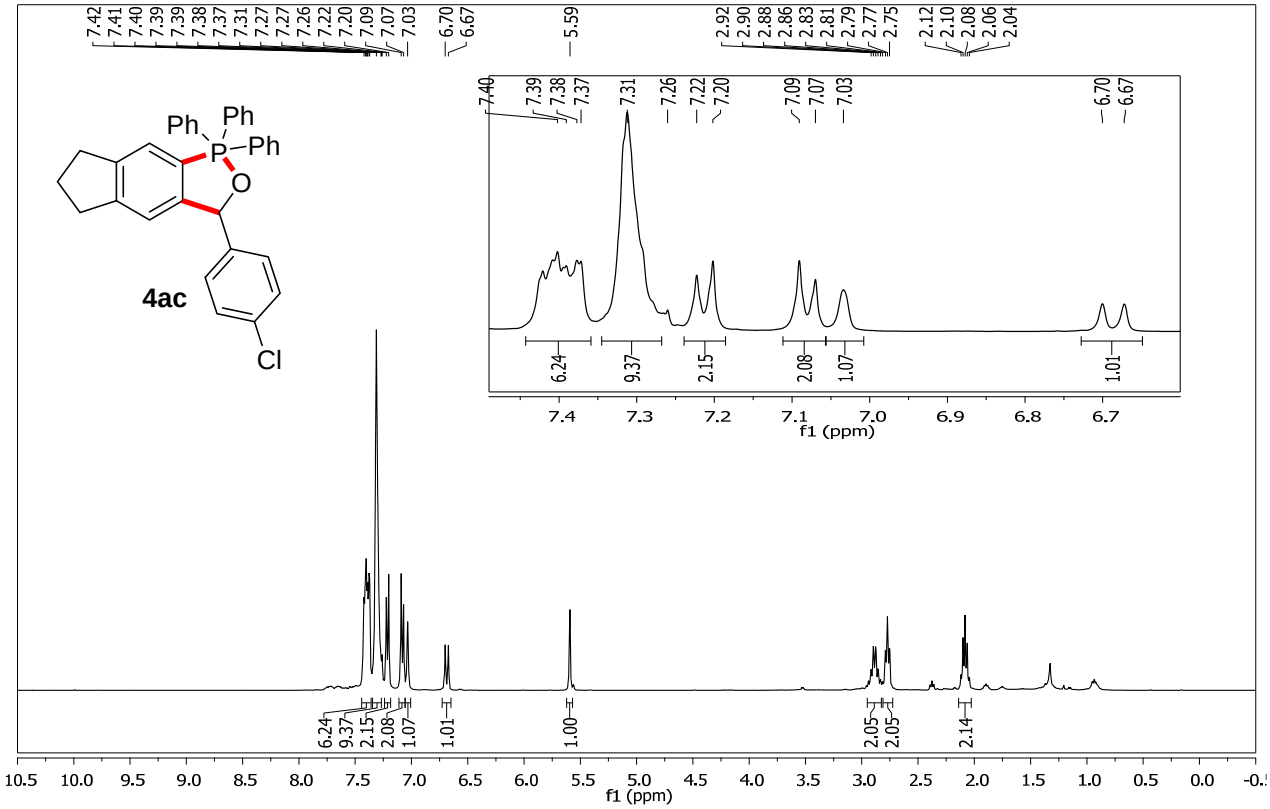


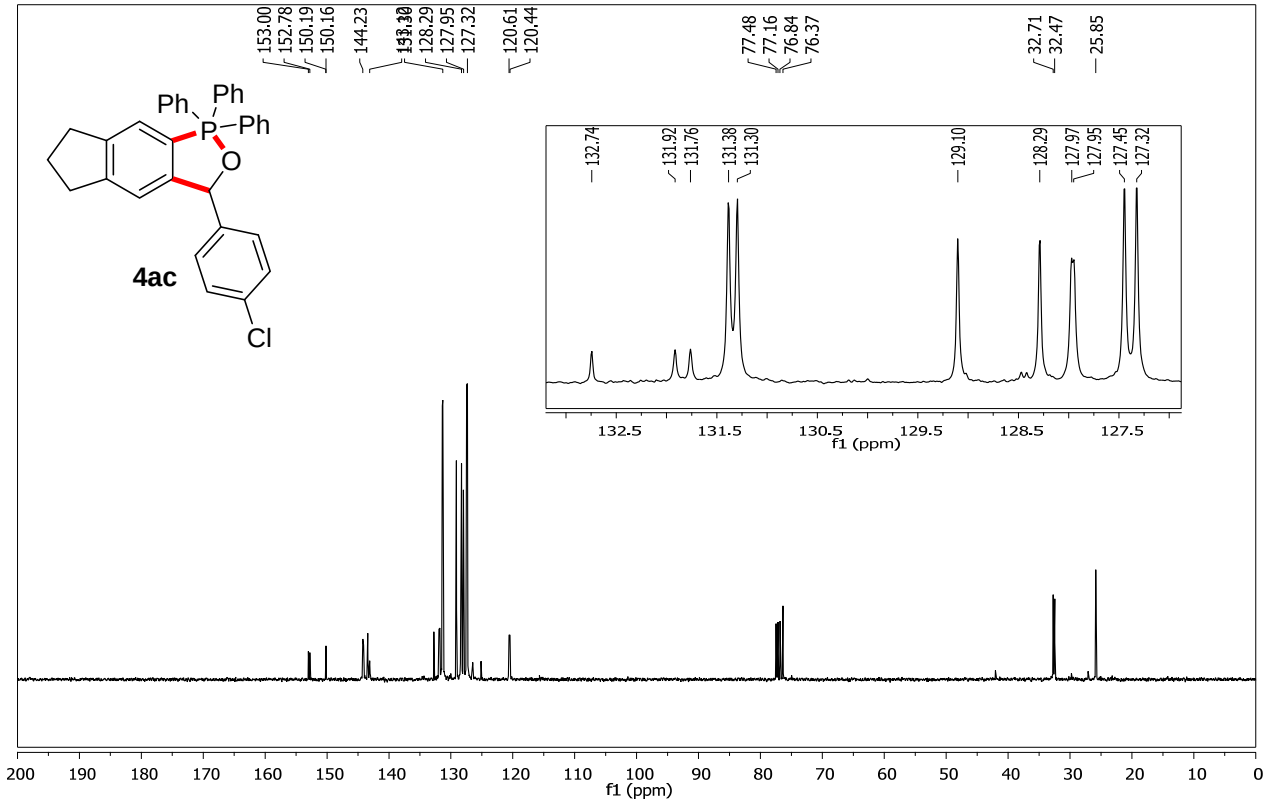
3-(4-Chlorophenyl)-1,1,1-triphenyl-1,3-dihydro-1λ^5-[1,3]dioxolo[4',5':4,5]benzo[1,2-*c*][1,2]oxaphosphole (4ab)



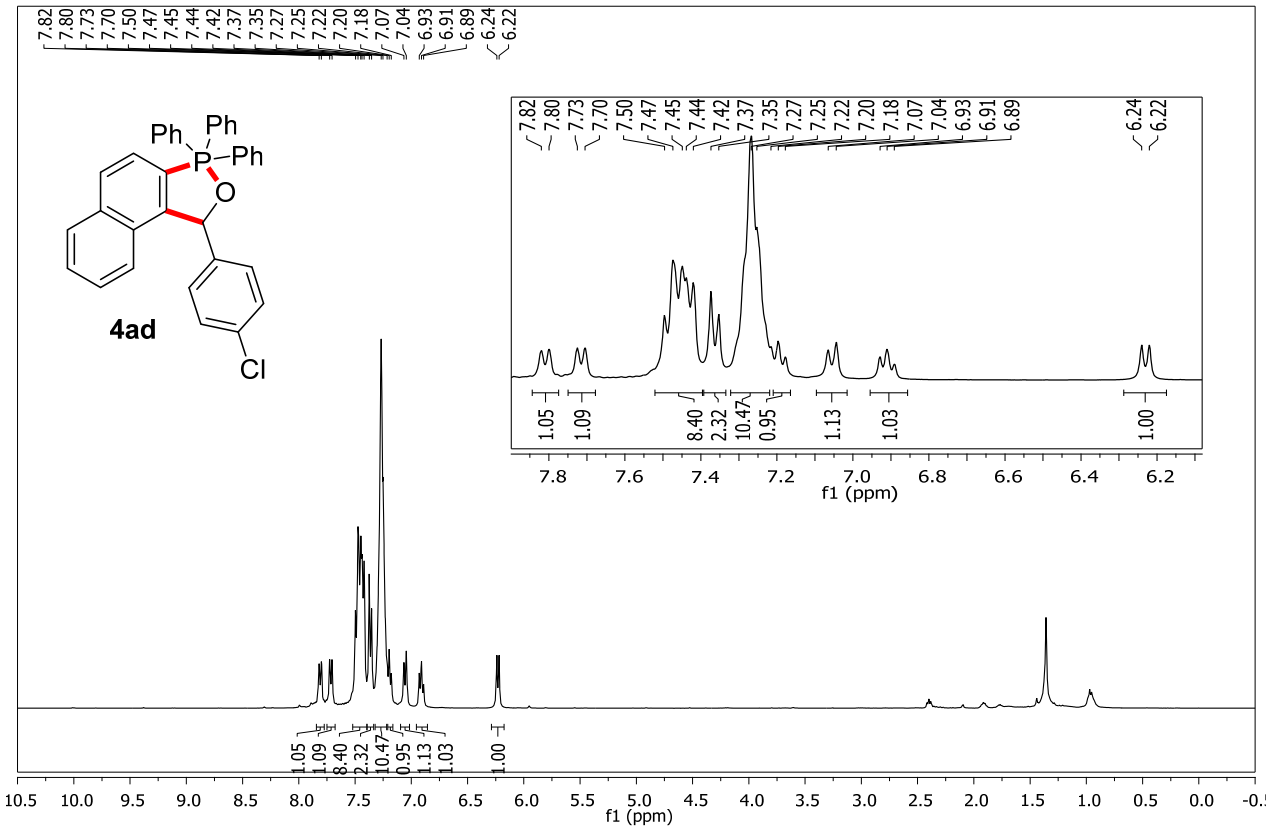


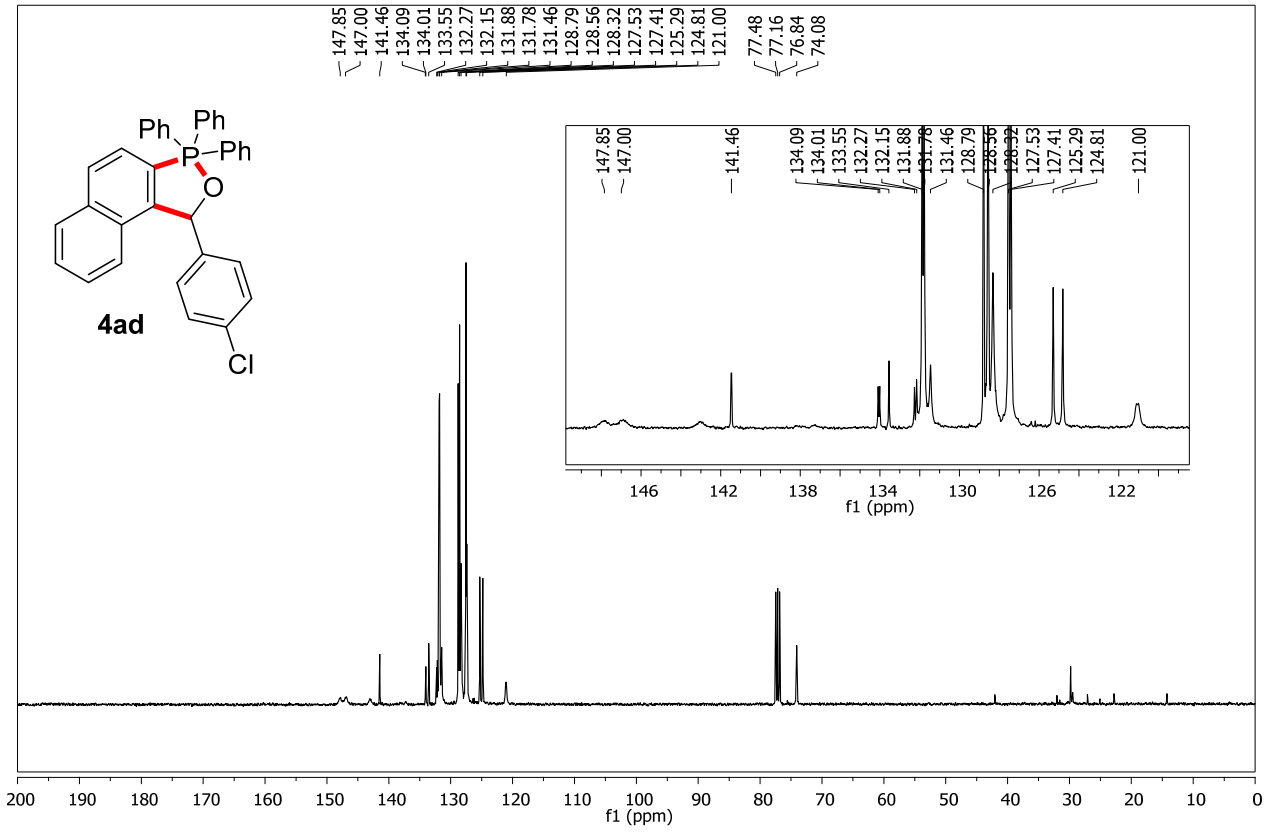
3-(4-Chlorophenyl)-1,1,1-triphenyl-3,5,6,7-tetrahydro-1*H*-1λ^5-indeno[5,6-*c*][1,2]oxaphosphole (4ac)



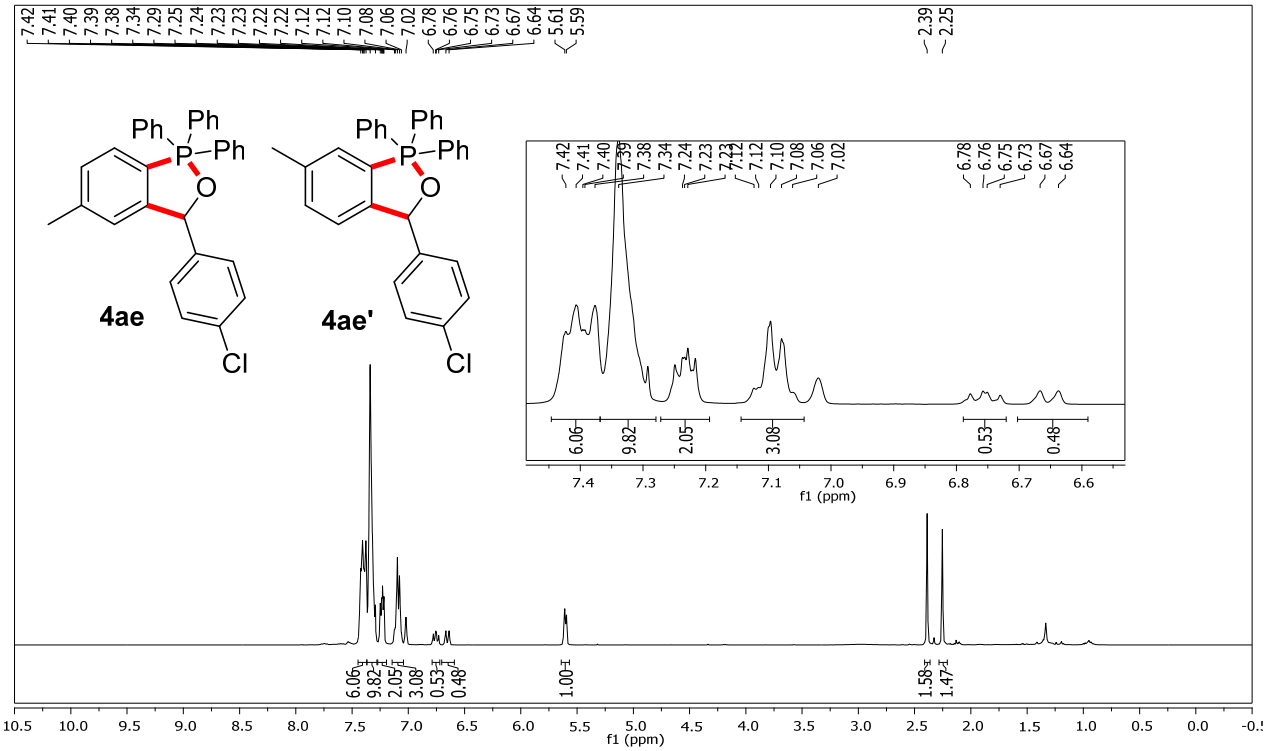


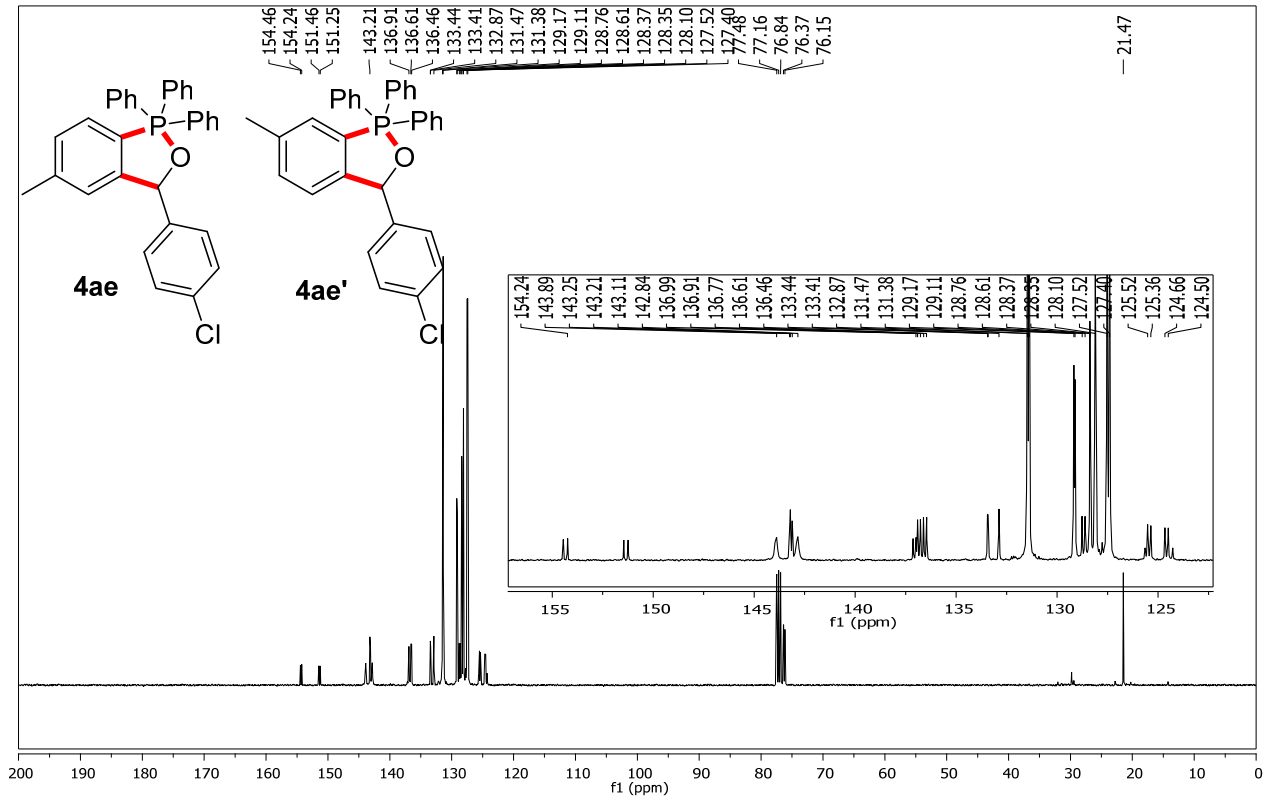
1-(4-Chlorophenyl)-3,3,3-triphenyl-1,3-dihydro-3λ^5-naphtho[2,1-c][1,2]oxaphosphole (4ad)



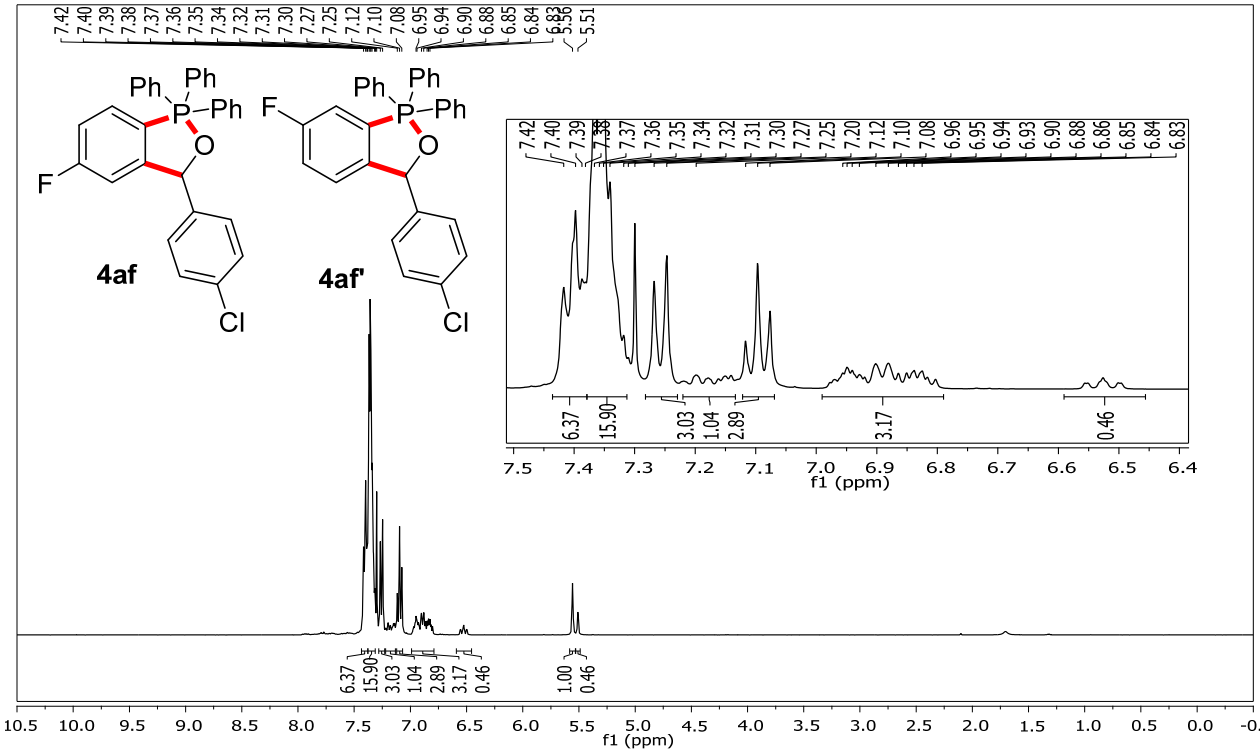


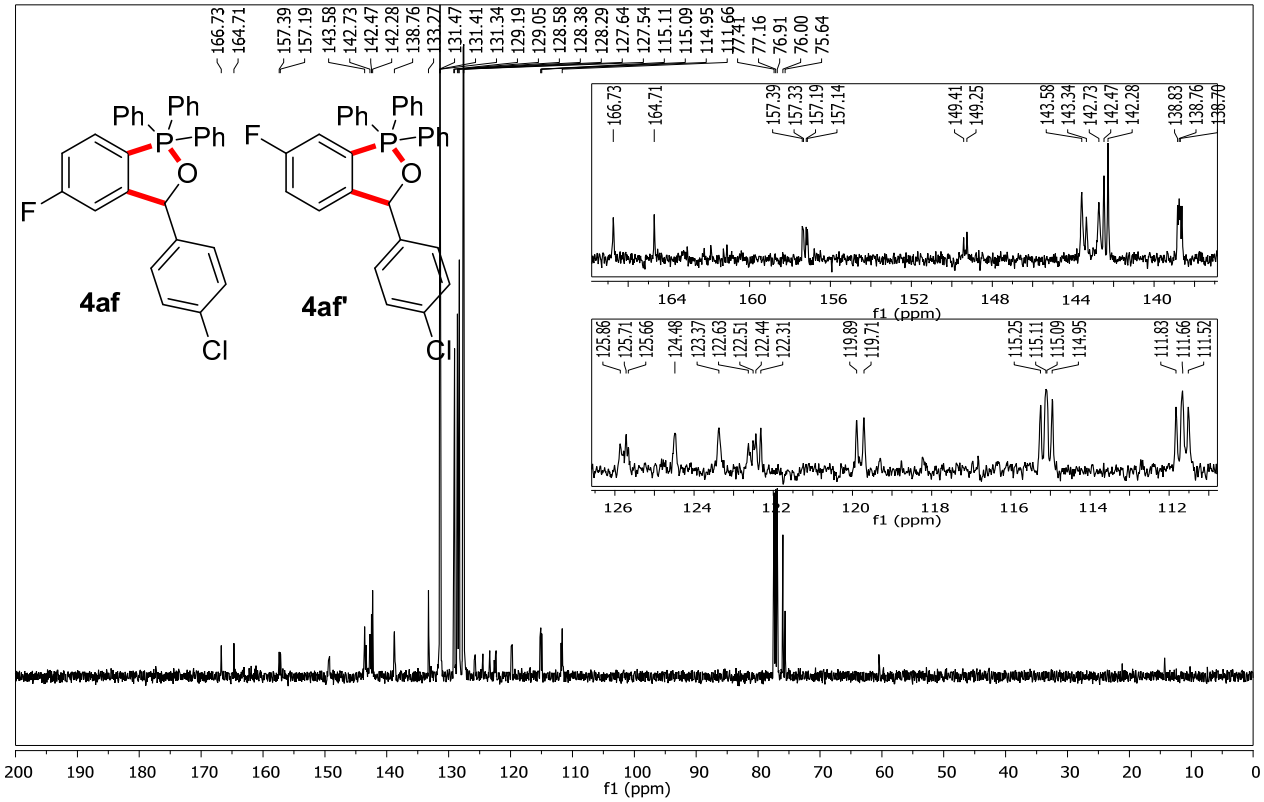
3-(4-Chlorophenyl)-5-methyl-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole & 3-(4-Chlorophenyl)-6-methyl-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4ae & 4ae')



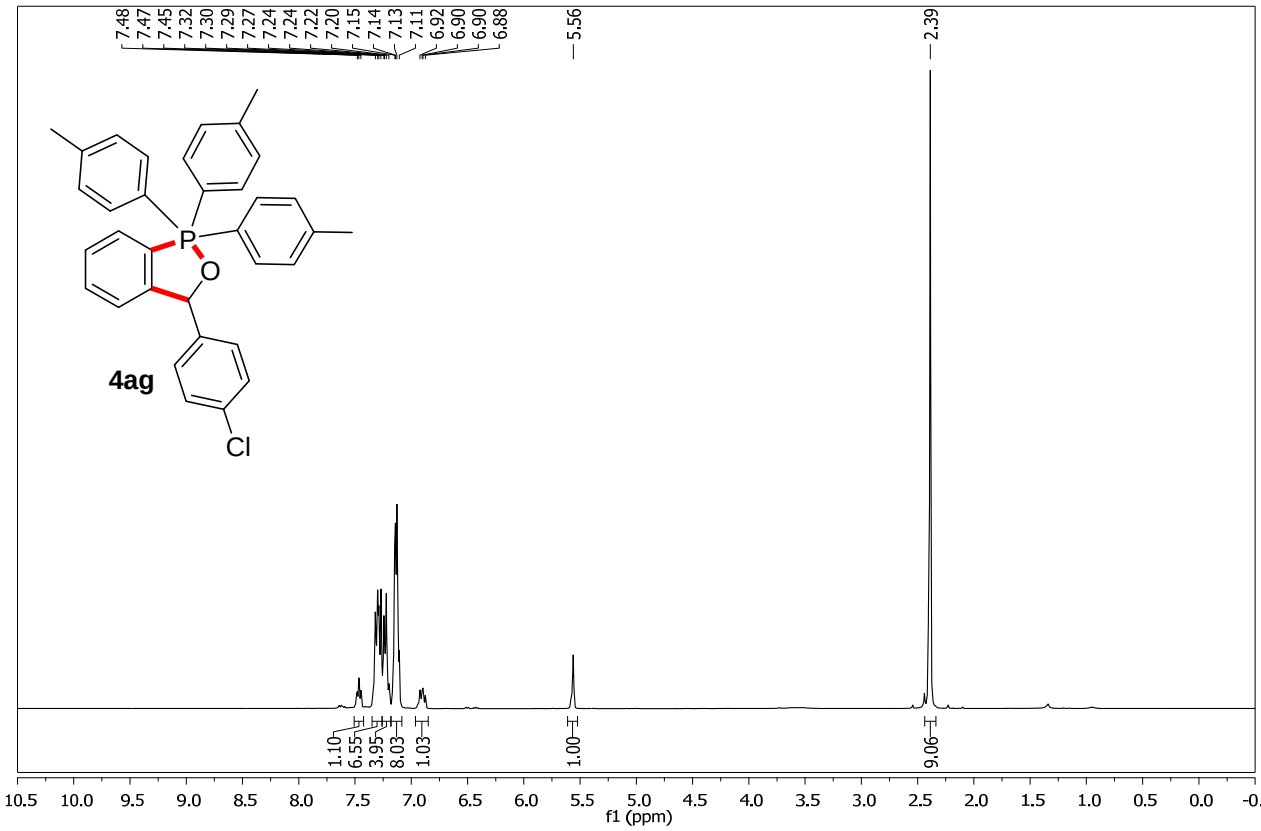


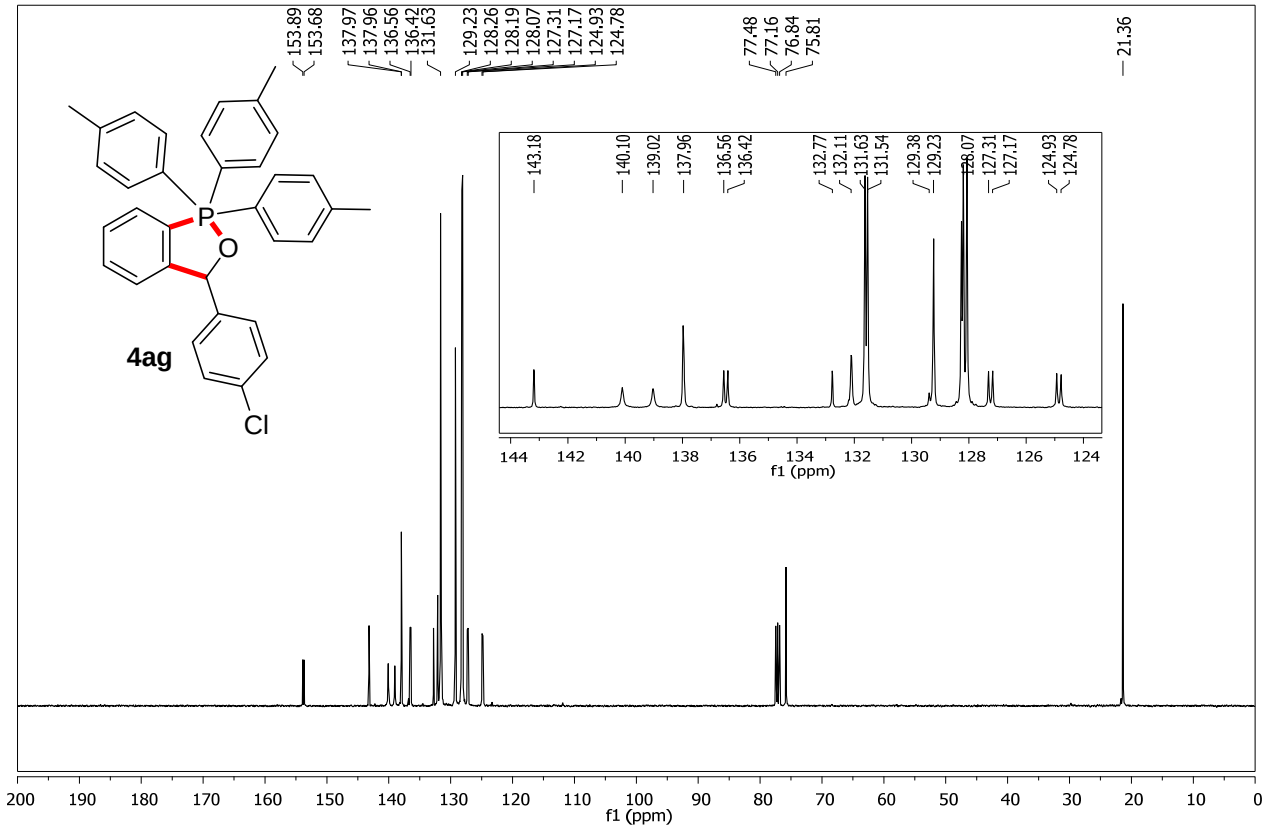
3-(4-Chlorophenyl)-5-fluoro-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole & 3-(4-Chlorophenyl)-6-fluoro-1,1,1-triphenyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4af & 4af')



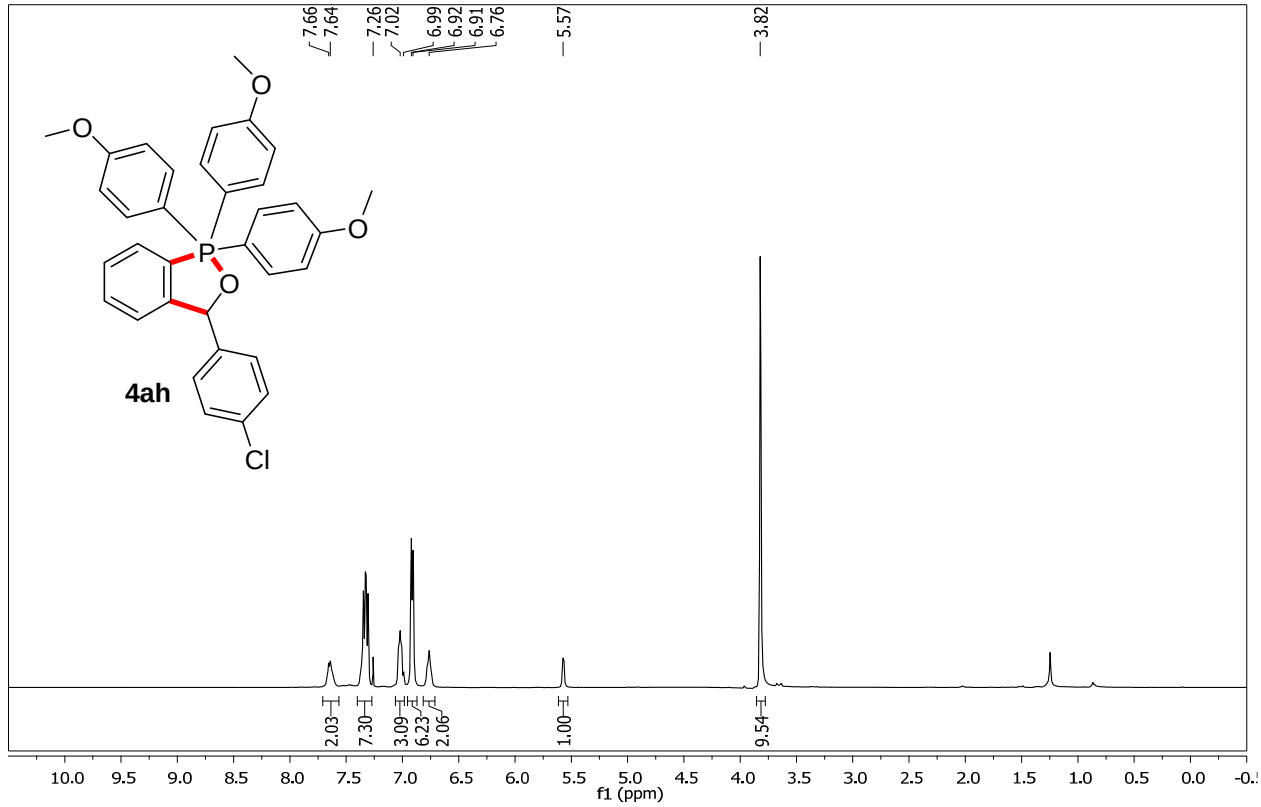


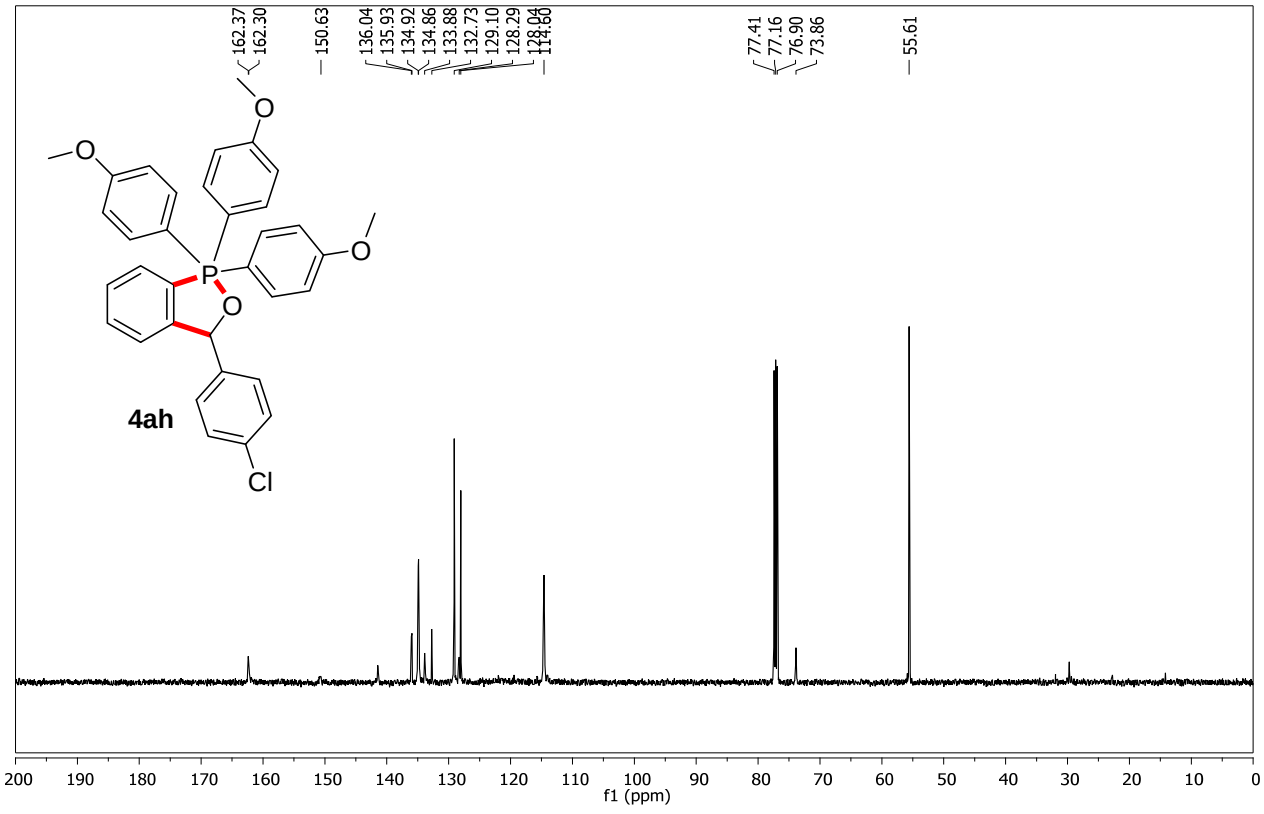
3-(4-Chlorophenyl)-1,1,1-tri-*p*-tolyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4ag)



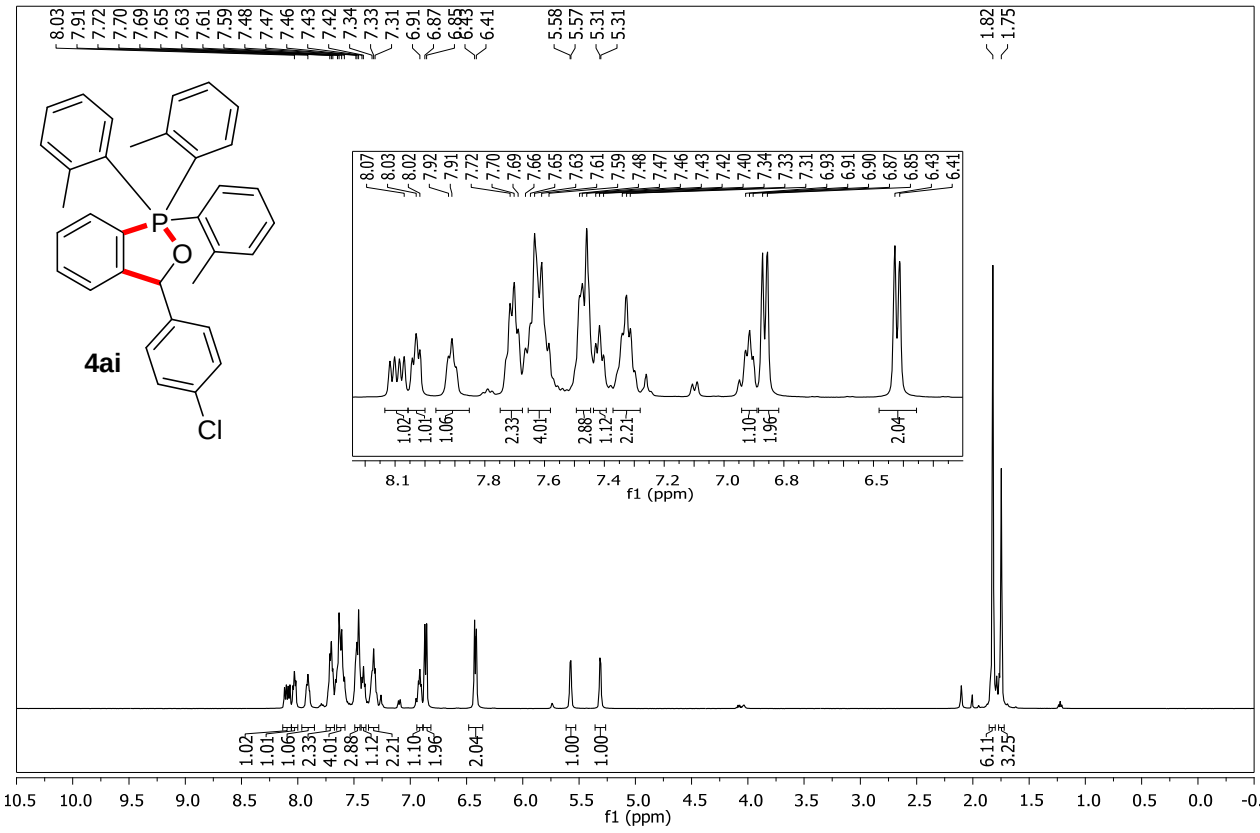


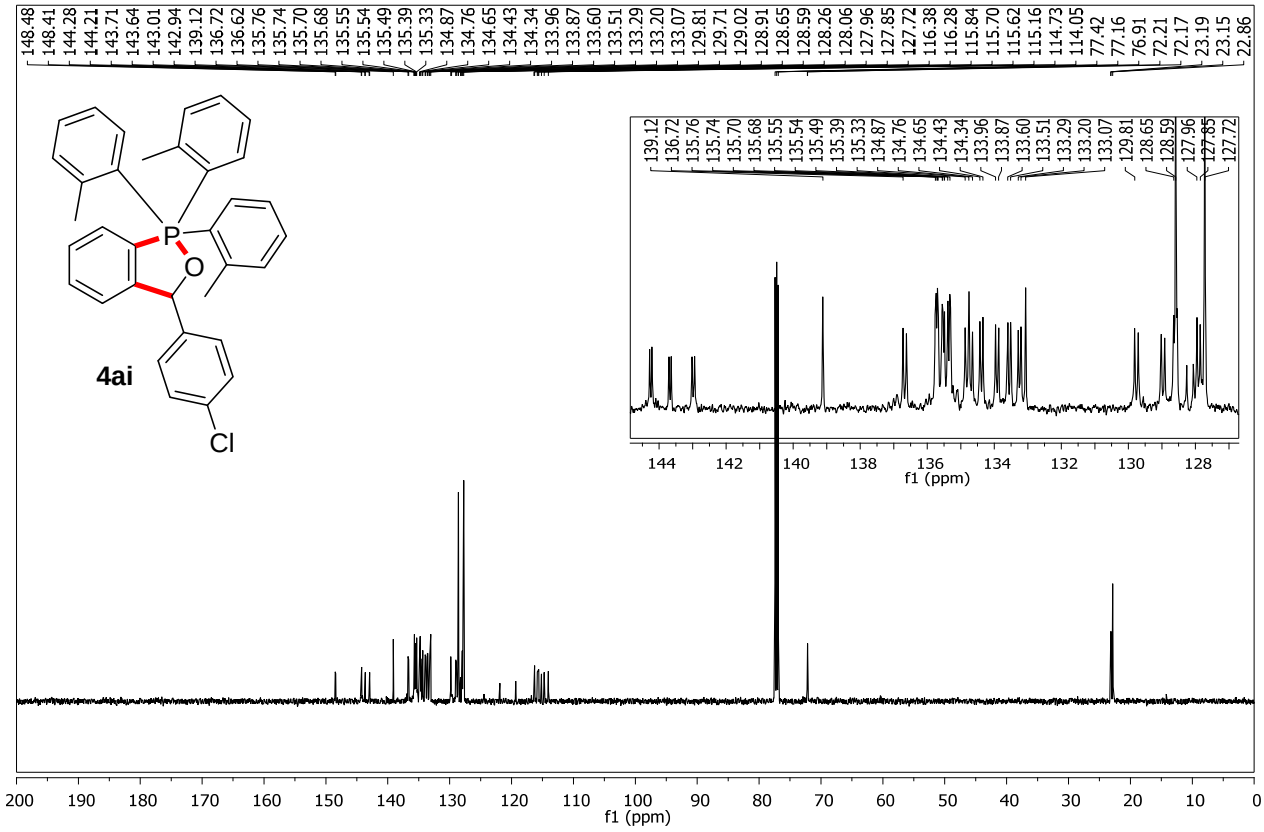
3-(4-Chlorophenyl)-1,1,1-tris(4-methoxyphenyl)-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4ah)



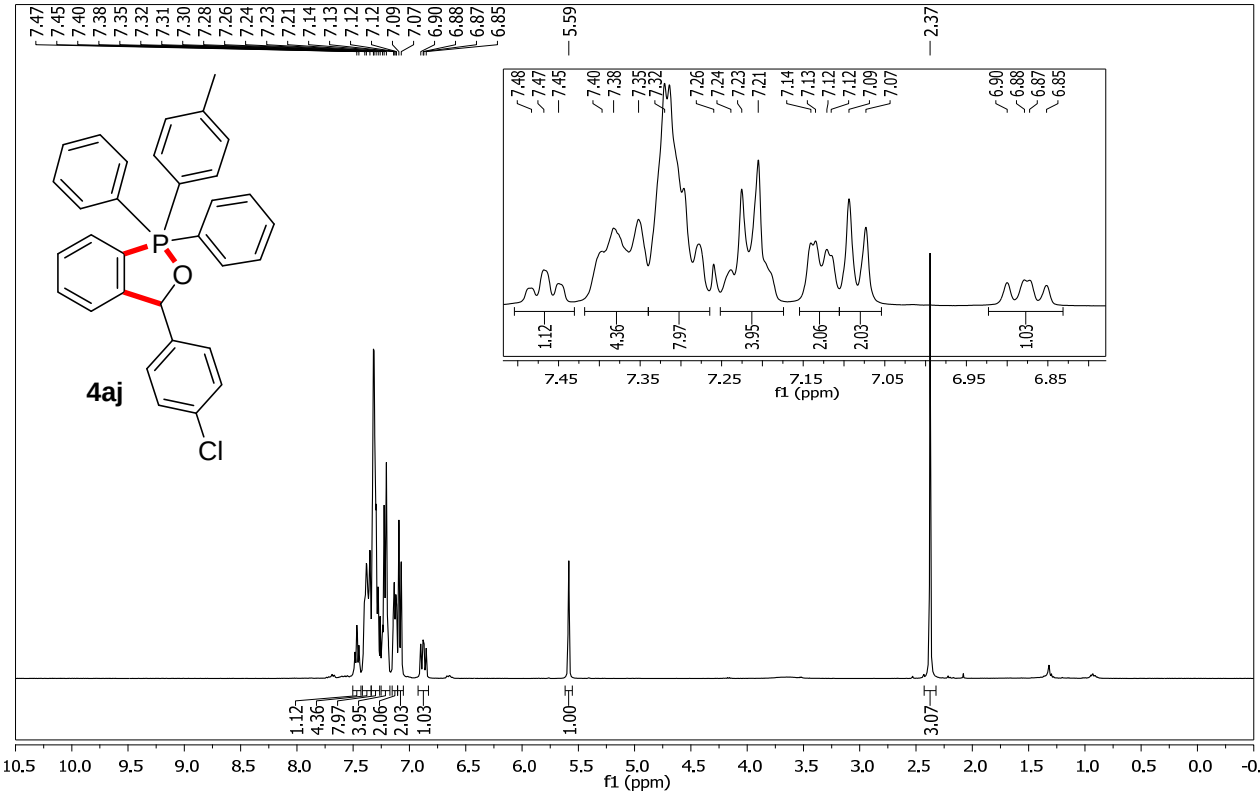


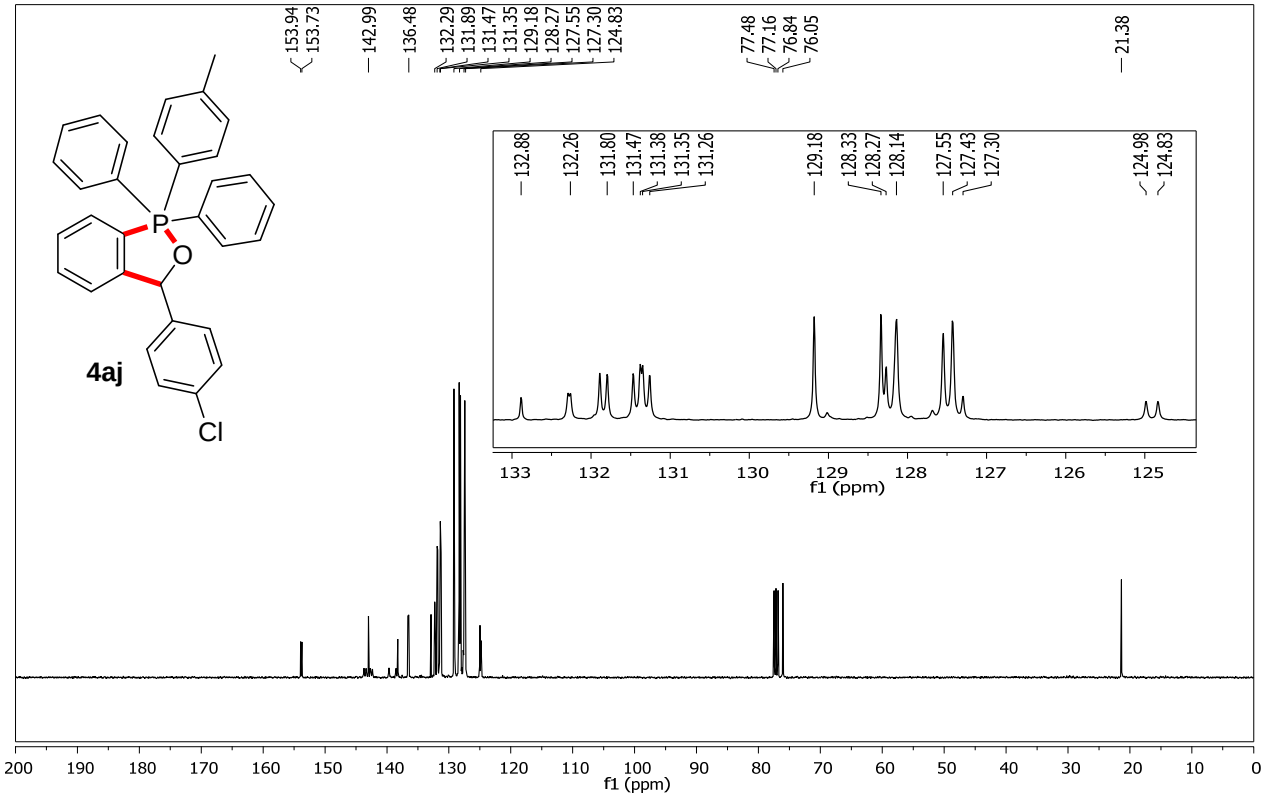
3-(4-Chlorophenyl)-1,1,1-tri-o-tolyl-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4ai)



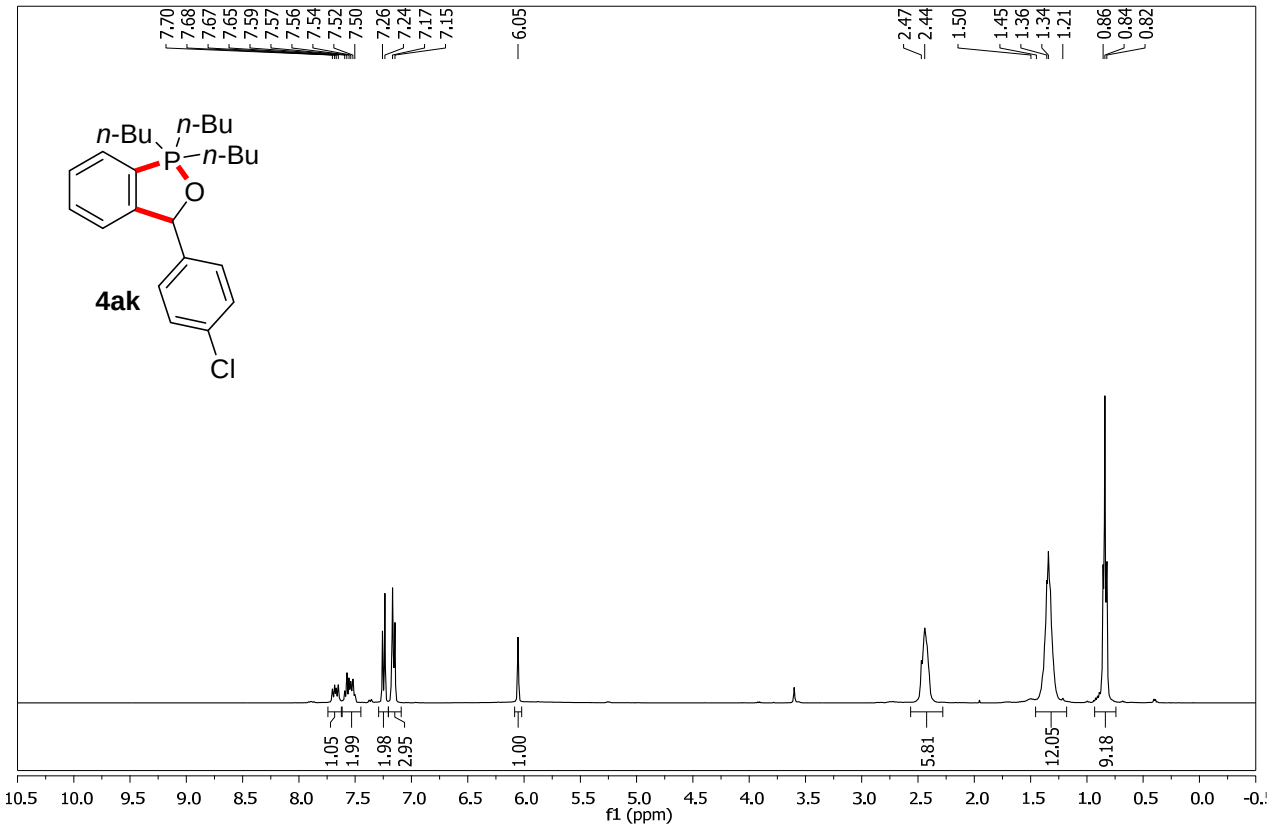


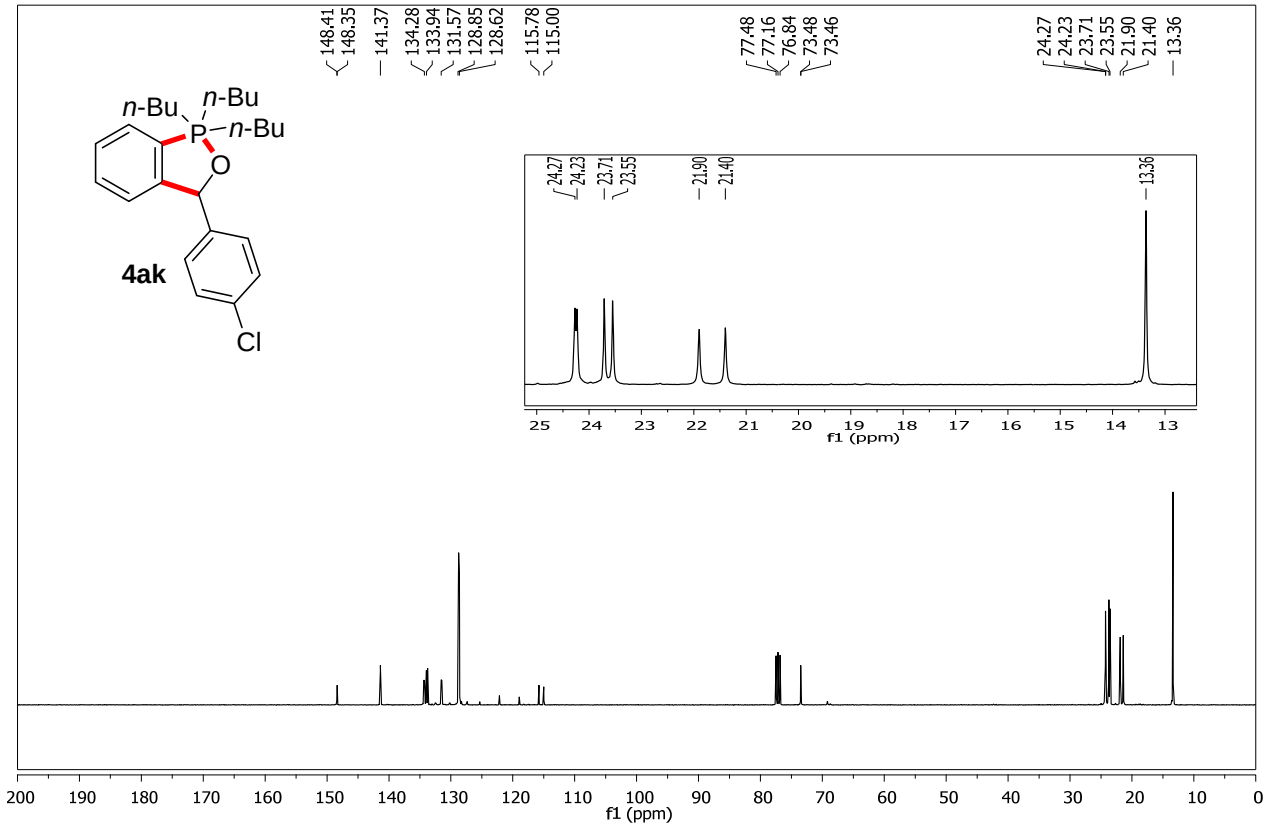
3-(4-Chlorophenyl)-1,1-diphenyl-1-(*p*-tolyl)-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4aj)



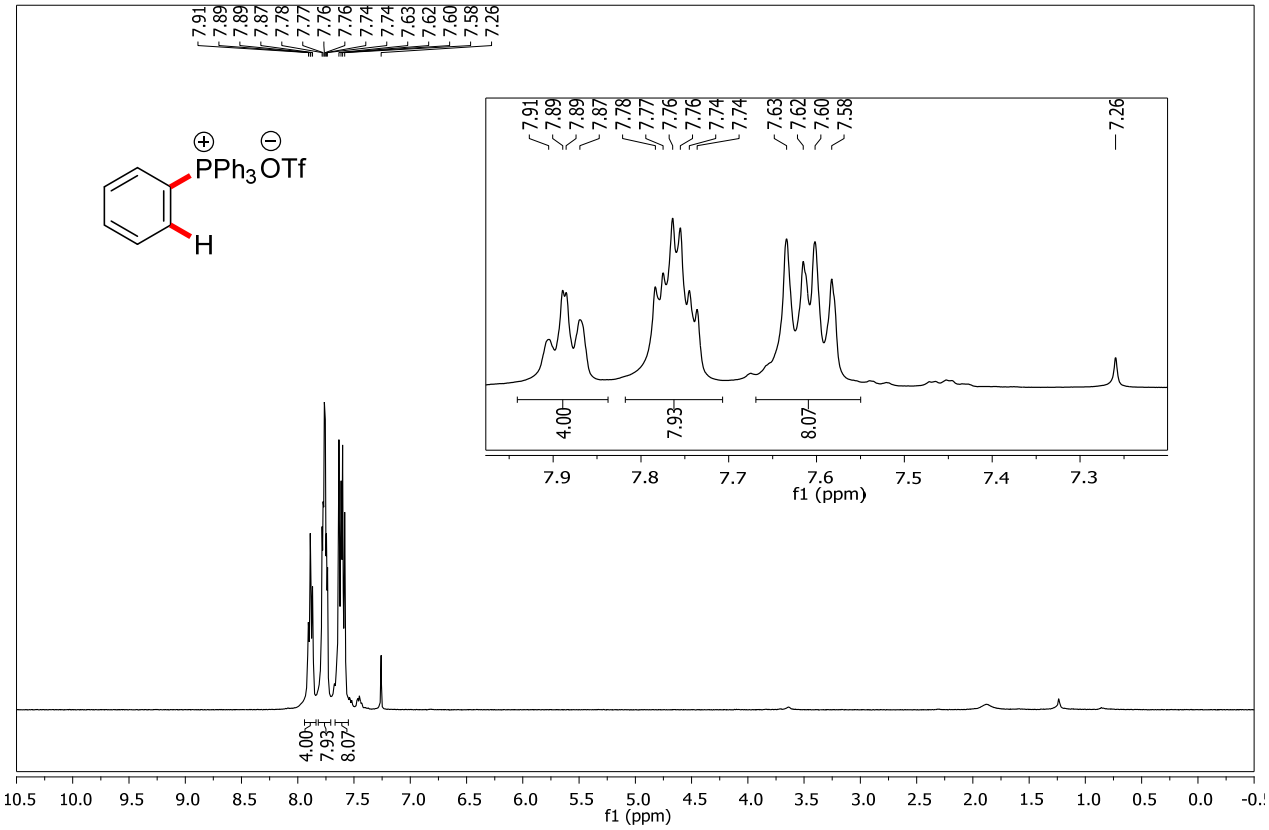


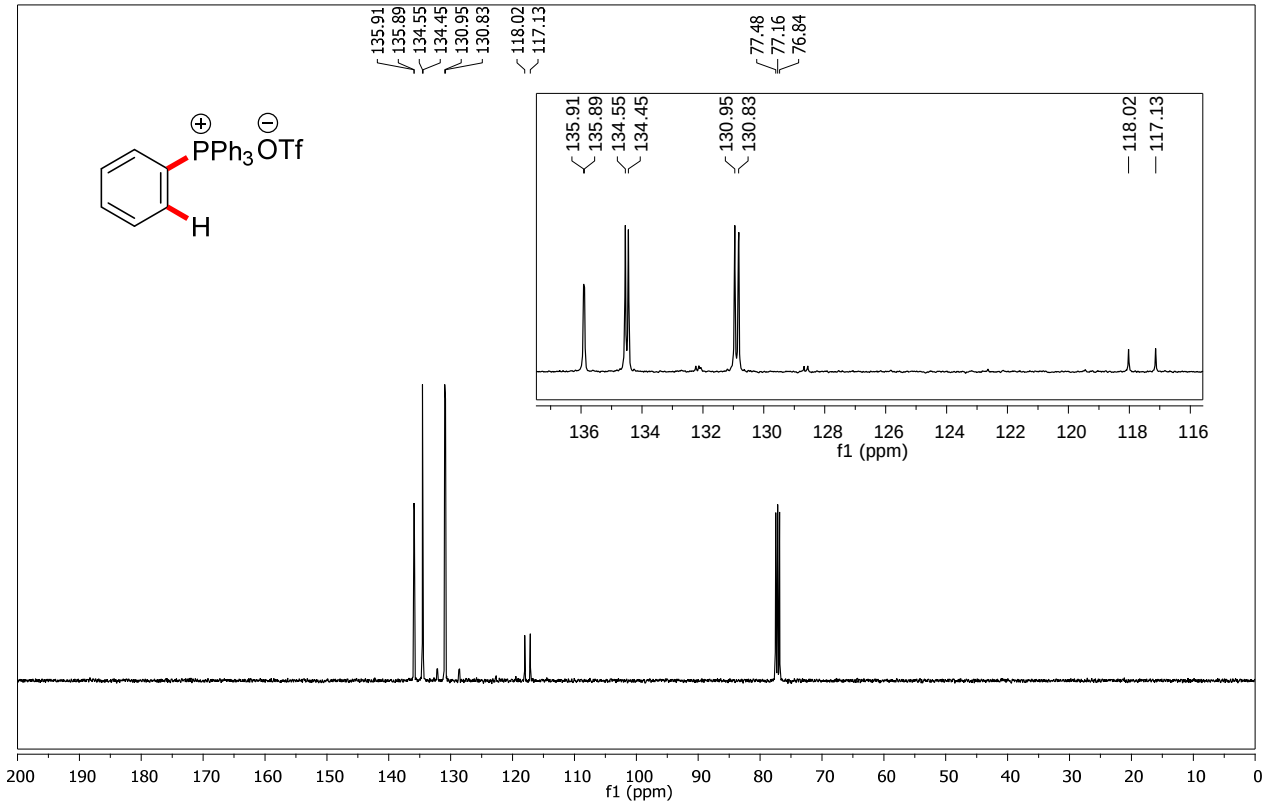
1,1,1-Tributyl-3-(4-chlorophenyl)-1,3-dihydro-1λ^5-benzo[*c*][1,2]oxaphosphole (4ak)



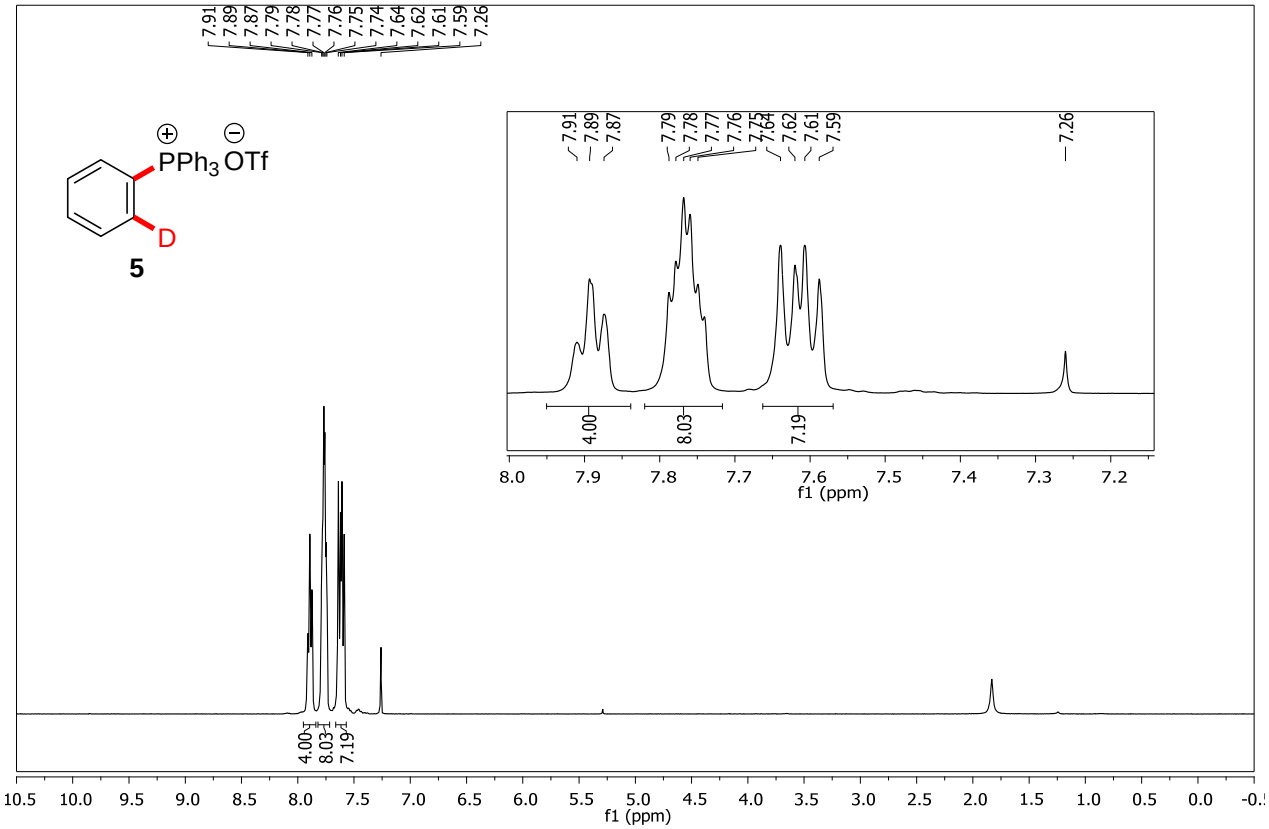


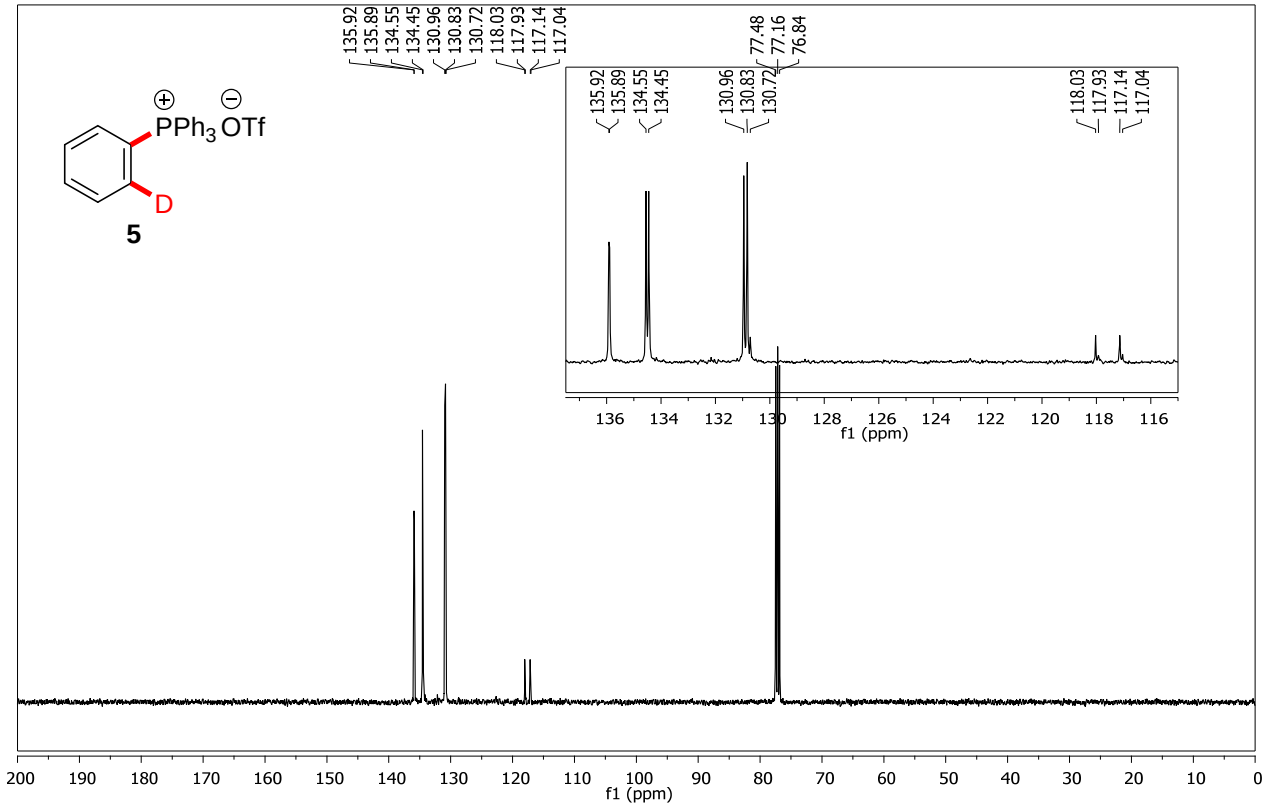
Tetraphenylphosphonium trifluoromethanesulfonate (5-*H*)



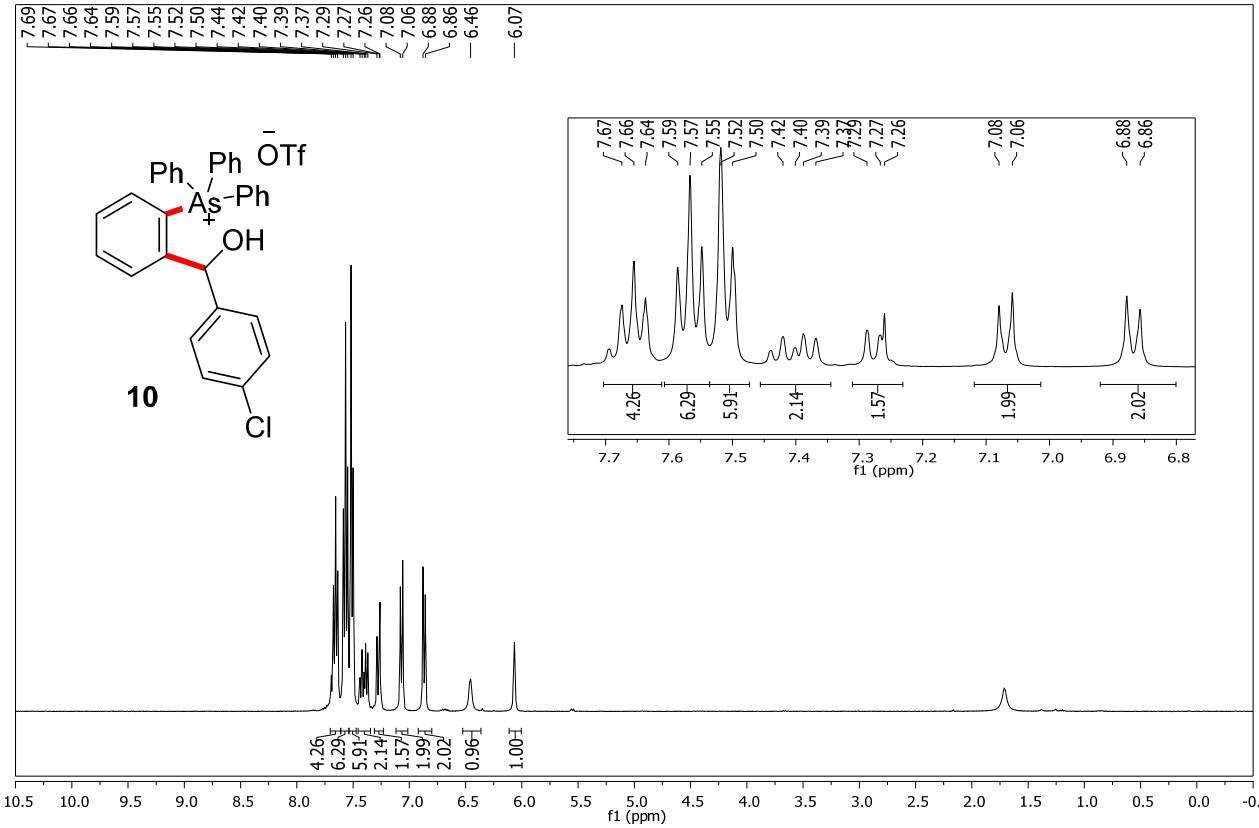


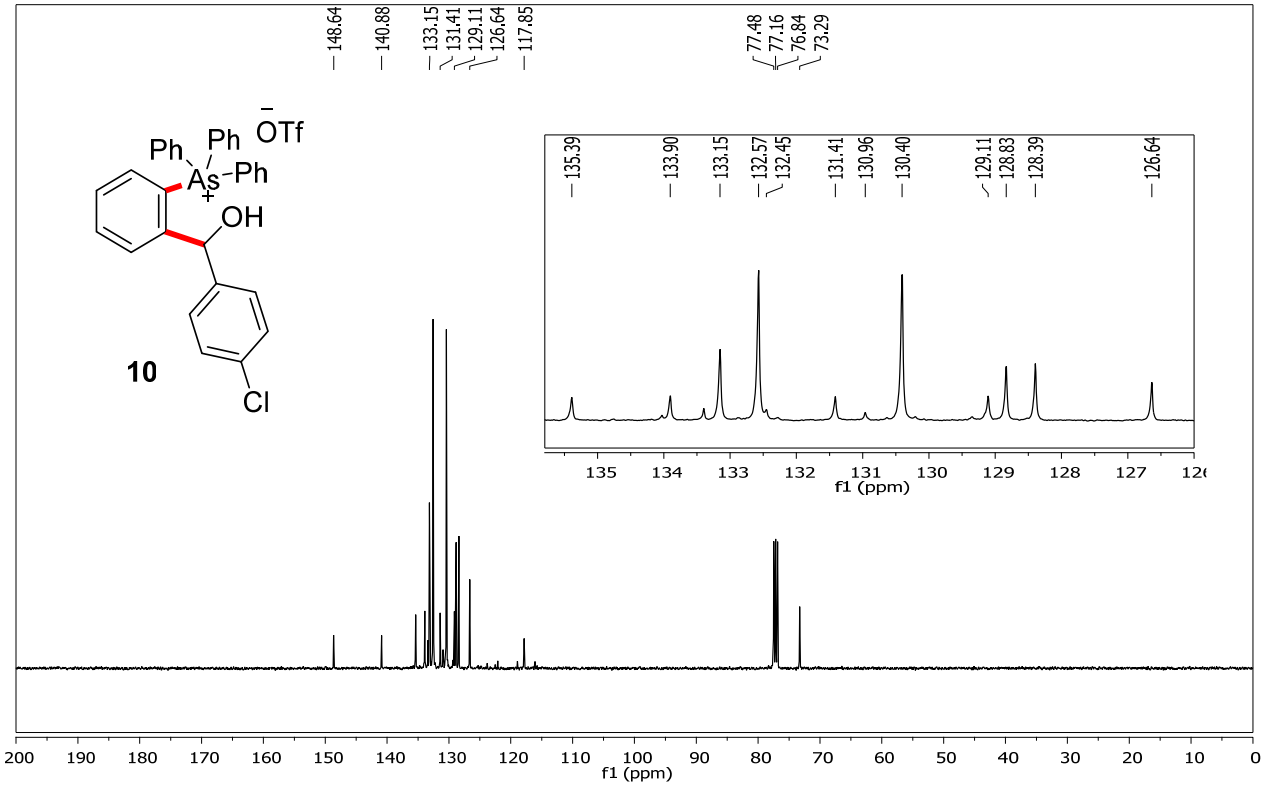
Triphenyl(phenyl-2-*d*)phosphonium trifluoromethanesulfonate (5)



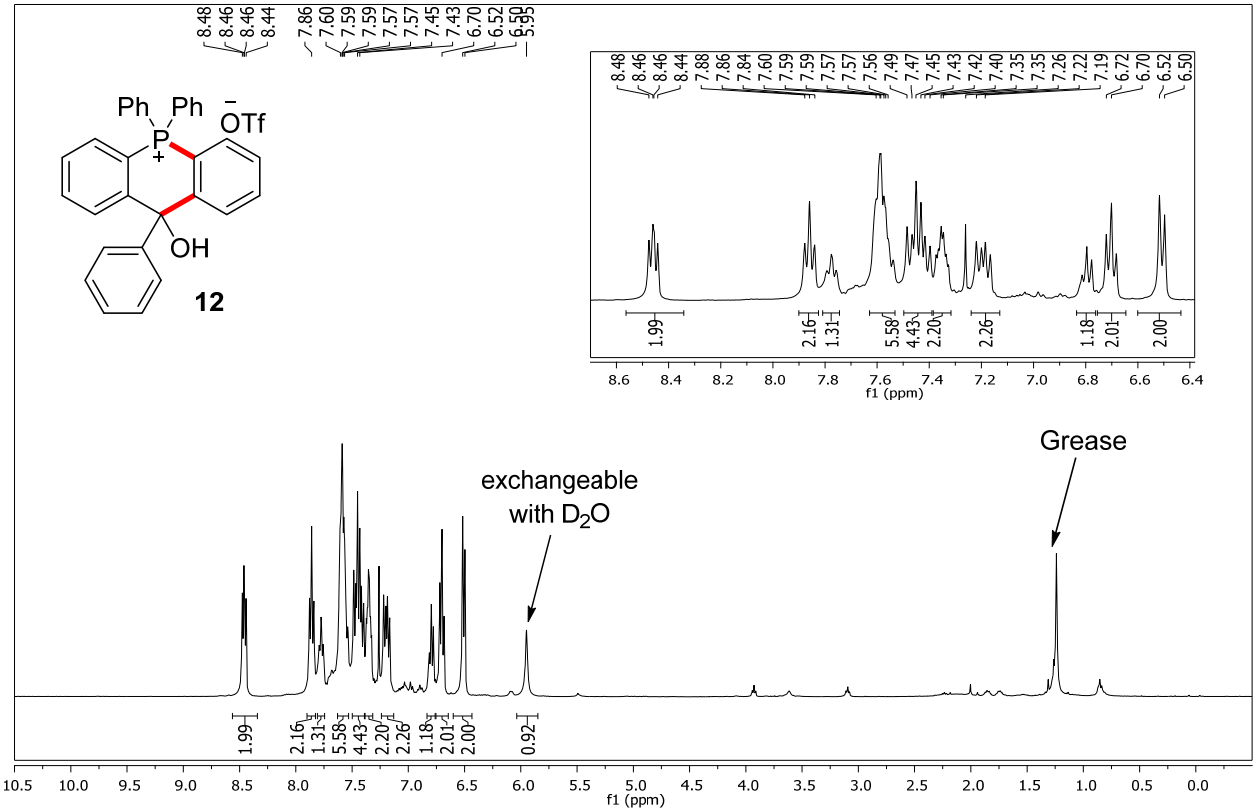


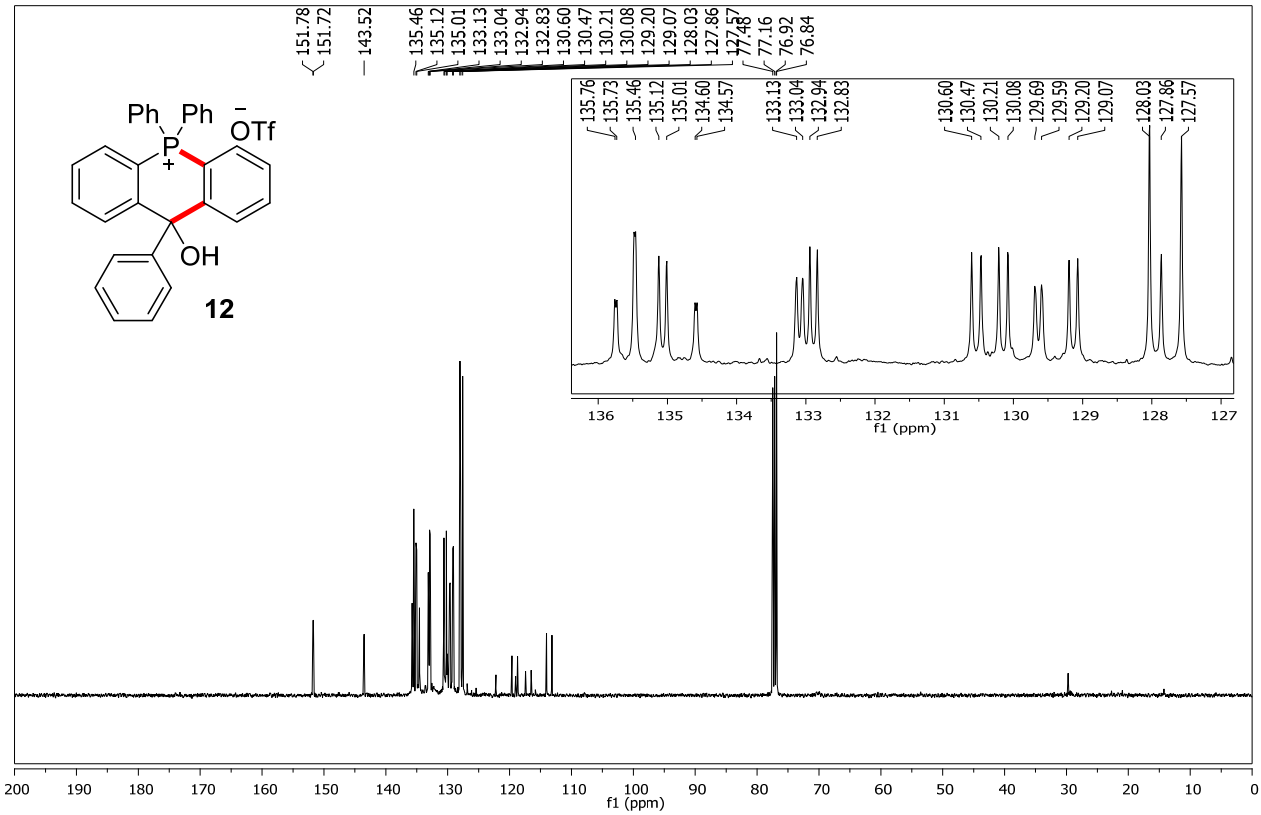
(2-((4-Chlorophenyl)(hydroxy)methyl)phenyl)triphenylarsonium trifluoromethanesulfonate (10)





10-Hydroxy-5,5,10-triphenyl-5,10-dihydroacridophosphin-5-ium trifluoromethanesulfonate (12)





10-(4-Chlorophenyl)-10-hydroxy-5,5-diphenyl-5,10-dihydroacridophosphin-5-ium chloride (13)