# Transition-Metal-Free Multicomponent Reactions Involving Arynes, Phosphines and Isatins

***Dissertation submitted for the partial fulfilment of the BS-MS Dual Degree Programme***

***By***


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# Certificate

This is to certify that this dissertation entitled "**Transition-Metal-Free Multicomponent Reactions Involving Arynes, Phosphines and Isatins**" towards the partial fulfilment of the BS-MS dual degree programme at the Indian Institute of Science Education and Research, Pune represents the original research work carried out by **Digvijay Porwal** at the Organic Chemistry Division, **CSIR-NATIONAL CHEMICAL LABORATORY, Pune, INDIA** under the supervision of Dr. Akkattu T. Biju, Senior Scientist, Organic Chemistry Division during the academic year 2013-2014.

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# Declaration

I, **Digvijay Porwal,** hereby declare that the matter embodied in the dissertation entitled "**Transition-Metal-Free Multicomponent Reactions Involving Arynes, Phosphines and Isatins**" are the results of the investigation carried out by me at the Organic Chemistry Division, **CSIR-NATIONAL CHEMICAL LABORATORY, Pune, INDIA** under the supervision of Dr. Akkattu T. Biju, Senior Scientist, Organic Chemistry Division and the same has not been submitted elsewhere for any other degree.

NCL, Pune
2nd April 2014 Digvijay Porwal

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**Digvijay Porwal**

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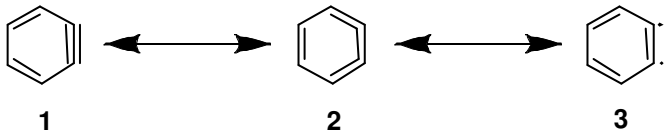
## Chapter 1a: History of Arynes

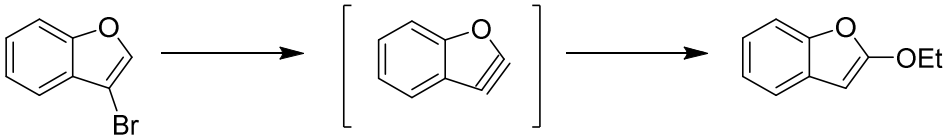
Arynes or benzynes are highly reactive intermediates in organic chemistry, and they are derived from an aromatic ring by the formal removal of two adjacent protons.[1,2] Arynes usually best described as having a strained C-C triple bond in a ring; however, they possess some diradical character as well (Scheme 1).



1 2 3

**Scheme 1.** Resonance in benzyne

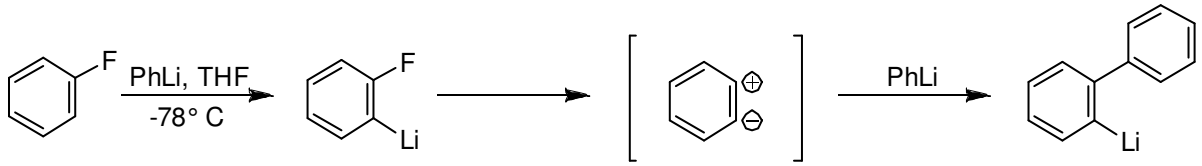
The very first hint on the existence of benzyne intermediate came from the work of Stoermer and Kahlert in 1902. They observed that upon treatment of 3-bromobenzofuran **4** with base in absolute ethanol resulted in the formation 2-ethoxybenzofuran **6**. Based on this observation, they postulated an aryne intermediate **5** (Scheme 2).[3]




4 5 6

**Scheme 2.** Aryne intermediate generated from 3-bromobenzofuran

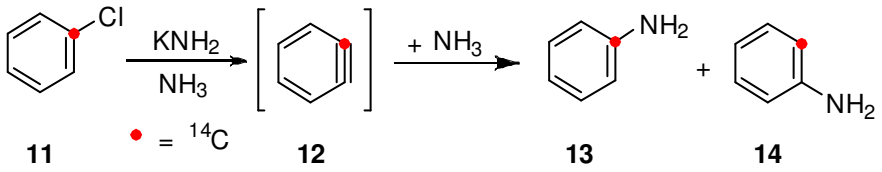
In 1942 Wittig and coworkers suggested the existence of benzyne based on experimental results on reaction between fluorobenzene **7** and phenyl lithium. They proposed that the reaction proceeded via a zwitterionic intermediate **9** generated from the aryl lithium **8**, which is a direct evidence supporting the existence of aryne (Scheme 3).[4]




7 8 9 10

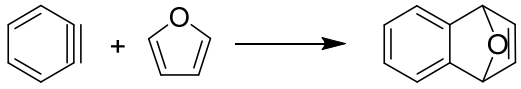
**Scheme 3.** Zwitterionic intermediate proposed by Wittig & coworkers

In 1953 Roberts and coworkers performed the classic $^{14}C$ labeling experiment, which provided strong support for benzyne formation (Scheme 4).[5] He performed the reaction of $^{14}C$ labeled chlorobenzene **11** with potassium amide, and analyzed the incorporation of $^{14}C$ in the resulting aniline. The observation of equal amounts of aniline with $^{14}C$ incorporation at C-1 and C-2 sheds light on the symmetrical intermediate **12**, which is now known as benzyne.




**Scheme 4.** $^{14}C$ labeling experiment by Roberts and coworkers

The existence of aryne intermediates were further confirmed experimentally by Wittig and coworkers by the [4+2] cycloaddition reaction between furan and in situ generated benzyne (Scheme 5),[6]

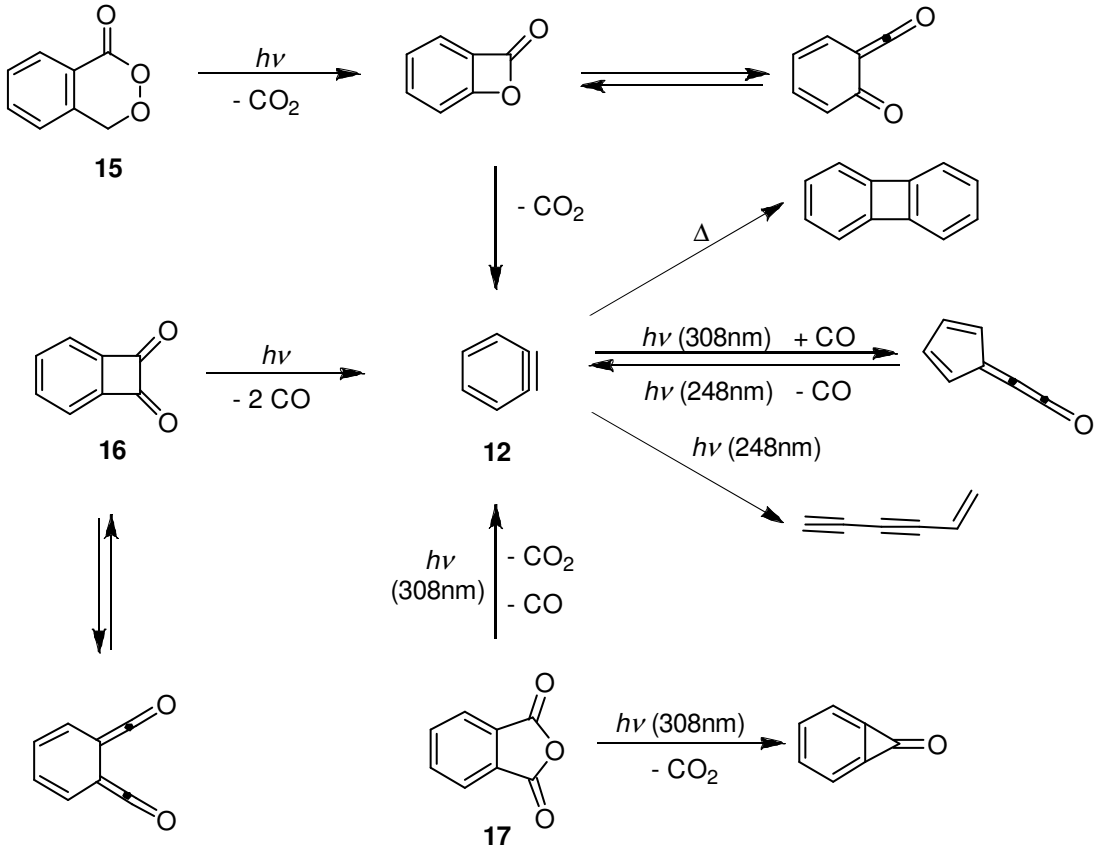



**Scheme 5.** [4+2] cycloaddition performed by Wittig and coworkers

In 1963 Fisher and Lossing investigated the pyrolysis of the three isomeric diiodobenzenes using mass spectrometry and identified **12** on the basis of the measured ionization potential.[7] At approximately the same time Berry and coworkers studied the photo-initiated decomposition of benzene diazonium carboxylates in the gas phase and characterized **12** by its UV and mass spectra.[8]

The first direct IR spectroscopic detection of *ortho*-benzyne was accomplished by Chapman and coworkers using matrix isolation spectroscopy at very low temperature to generate **12** starting from phthaloyl peroxide **15** and benzocyclobutenedione (**16**; Scheme 6).[9] High amount of **12** were also generated by using phthalic anhydride **17** as

a precursor. The comparatively complex reactions of the molecules involved in this photochemistry led to some controversy concerning the frequency of the C-C triple bond stretching vibration.[10] This was established in 1992 by Radziszewski and coworkers by assigning this vibration to an absorption at 1846 $cm^{-1}$ by thorough analysis of the spectra of **12** obtained from different isotopomers of phthalic anhydride.[11] As expected, the formal C-C triple bond stretching in **12** is significantly weaker than in unstrained alkynes, whose C-C triple bond stretching vibrations usually occur at about 2150 $cm^{-1}$. Nevertheless, *ortho*-benzyne is better described as a strained alkyne than as a biradical, which is evident from both the large singlet-triplet splitting of (37.5 ± 0.3) $KCalmol^{-1}$ and the alkyne-like reactivity (e.g. Diels-Alder reactions). The enthalpy of formation of **12** was determined to be (106.6 ± 3.0) $KCalmol^{-1}$ by Squires and Wenthold.[12] For the C-C triple bond length in **12** a value of (124 ± 2) pm was found experimentally,[13] which comes closer to a typical C-C triple bond (120.3 pm in acetylene) than to a C-C double bond (133.9 pm in ethylene).



**Scheme 6.** Photochemistry of **12** and the corresponding precursor.

Within 14 years of the seminal experiments of Roberts leading to the first proposal of the structure of benzyne as mentioned earlier, synthetic organic chemists recognized the potential to exploit this highly reactive intermediate (and its substituted variants) in the total synthesis of natural products as well as to generate various methodologies to obtain molecules of high importance. More specifically, it was recognized that arynes offered the prudent advantage of rapidly functionalizing an aromatic ring by forming multiple carbon–carbon or carbon–heteroatom bonds in a single operation, often in a regioselective manner. Initially, the scope of synthetic applications was somewhat limited due to the harsh conditions required to generate the aryne species.[2] Many of these methods required strong bases, such as *n*-BuLi, or high temperature. However, with the development of mild methods for the generation of arynes rapidly increased the interest in employing them in the synthesis of more complex polycyclic systems. All the methods for the generation of arynes have been discussed in chapter 2 in detail.

## Chapter 1b: Structure of Arynes

Of all arynes, the benzyne structure has been the most studied in the literature, but the general features of the benzyne structure discussed here also apply to other arynes. First, one should note that the formal triple bond drawn in benzyne is not conjugated. The orbitals of this bond are perpendicular to the π-system in benzene, so the interaction is localized (Figure 1).[14] The orbitals of the formally drawn triple bond are highlighted in black in Figure 1.

**Figure 1.** Benzyne, showing the delocalized π-system and the localized C-C triple bond

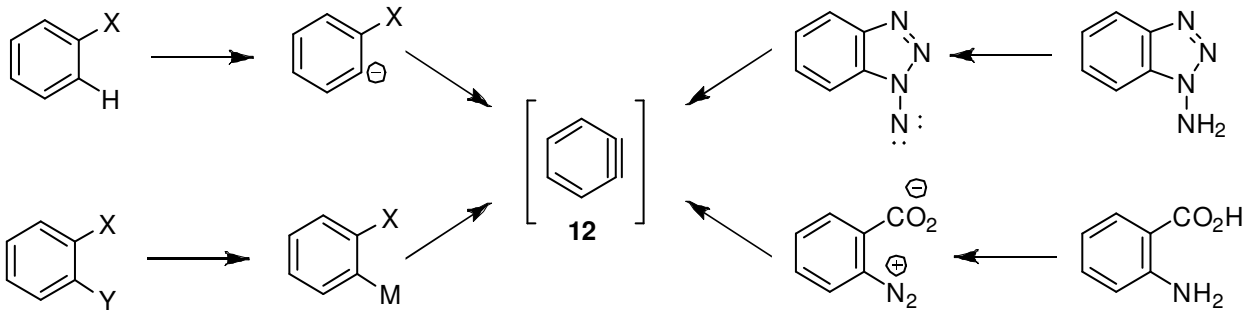
A great deal of computational work on the structure and orbital energies of benzyne has been done, the results seem to correlate with benzyne's high electrophilicity. Calculations have shown that benzyne has a very small HOMO-LUMO gap when compared to a linear alkyne. In a computational study by Rondan and coworkers using *ab initio* methods (4-31G), 2-butyne and distorted 2-butynes were compared with benzyne. The frontier orbitals were compared, showing a general decrease in the energy of the LUMO as the structure became more like benzyne, while the HOMO stayed at approximately the same energy (Figure 2).[15]

**Figure 2.** Frontier Orbital energies (in eV) for 2-butyne, distorted 2-butynes & benzyne.

Conclusively it can be assumed that the relatively low energy of the LUMO in benzyne has been attributed to mixing of the $\pi^*$ orbital with a $\sigma^*$ orbital which lies just slightly higher in energy[6] and also this low lying LUMO character in benzyne attribute to its electrophilic character too (and therefore, other arynes as well). This orbital will be much closer in energy, compared to linear alkynes, to the HOMO of a nucleophile, making nucleophilic reactions much more facile.[16]

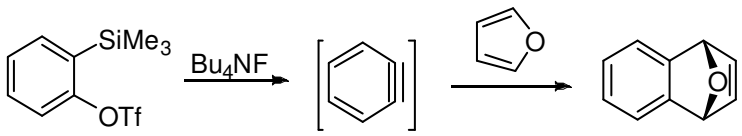
## Generation of Arynes

*ortho*-Benzyne is an important reactive intermediate and many studies on its generation and reactions have been known in the literature. Because of their extreme reactivity, arynes must be generated *in situ*. The important methods for the generation of arynes are summarized in (Scheme 7).



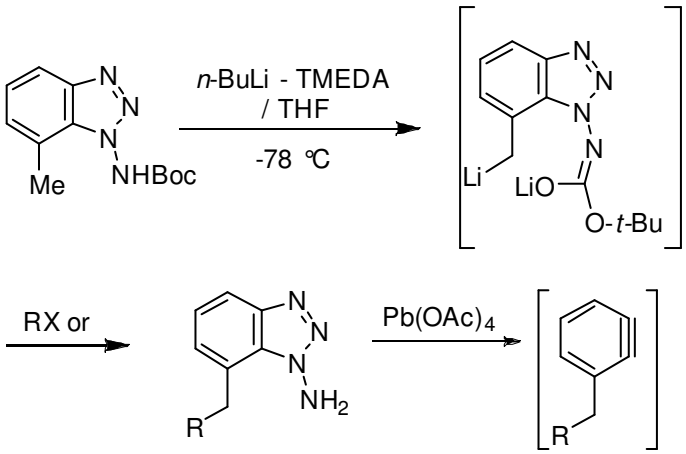

**Scheme 7.** Common methods for the generation of arynes.

An aromatic halide can be treated with a strong base such as sodium amide,[17] to remove the *ortho*-aromatic proton and generate benzyne via an elimination. The use of strong bases which may act as nucleophiles can be avoided by treatment of *ortho*-dihalosubstituted benzenes with a metal (lithium or magnesium) to give the desired aryne by elimination.[18] Aryl triflates have been used to generate arynes via other routes than metal-halogen exchange. For example, fluoride induced elimination of trimethylsilyl group from 2-(trimethylsilyl) aryl triflate developed by Kobayashi and coworkers provides a convenient route to benzyne generation under mild conditions (Scheme 8).[19] This is the most widely used method for the mild generation of arynes now, and this method is compatible with wide variety of functional groups, and is tolerable with various base sensitive substrates.



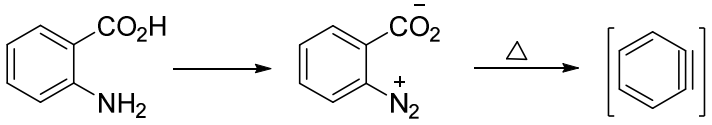

**Scheme 8.** Generation of arynes from triflates.

Moreover, oxidation of aminotriazole usually produces good yields of arynes in solution, but has the disadvantage of requiring the presence of an oxidant such as lead tetra acetate in the reaction medium.[20] The use of NBS was also developed by Campbell and coworkers.[20,21] Deprotonation of 7-methyl-1-aminobenzotriazole derivatives leads to 7-substituted-1-amino benzotriazoles, precursors of *ortho*-substituted benzynes (Scheme 9).[22]

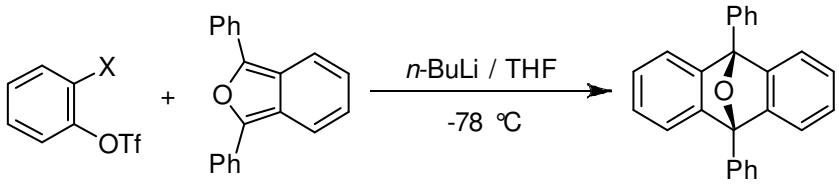



**Scheme 9.** Generation of arynes from aminobenzotriazoles.

Arynes are also generated from anthranilic acid, by decomposition of the benzenediazonium-2-carboxylate.[23,24] This method is often not recommended in view of the explosive nature of the diazo compounds (Scheme 10). In addition, metal–halogen exchange of *ortho*-halotriflates at -70° C with *n*-BuLi also generate arynes (Scheme 11).[25]

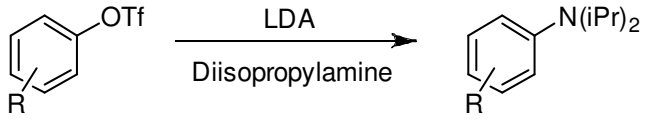



**Scheme 10**. Generation of arynes from benzenediazonium-2-carboxylate

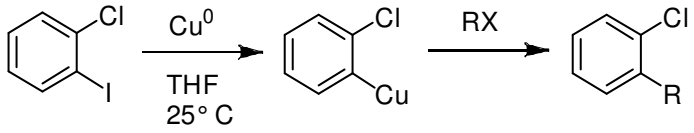



**Scheme 11.** Generation of arynes from *ortho*-halotriflates.

Aryl triflates generated from the corresponding phenols react with lithium diisopropylamide (LDA) in diisopropylamine to give the corresponding amines in good yields (Scheme 12) and this reaction proceeds via the generation of arynes.[26] Whereas *ortho*-halolithium or magnesium arenes readily undergo elimination to arynes, *ortho*-Cl- and *ortho*-F aryl copper reagents do not, and can be used in nucleophilic displacement reactions, as in the following example (Scheme 13).[27]

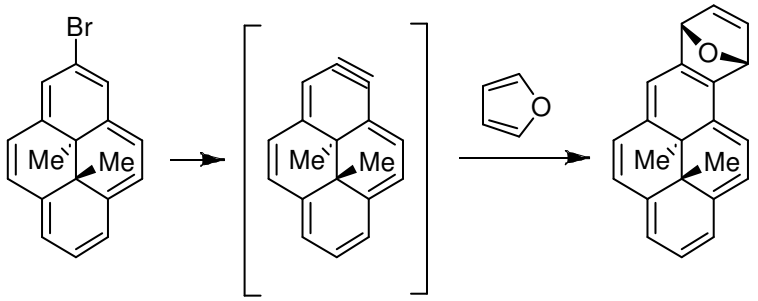



**Scheme 12.** Addition of arynes to lithium diisopropylamide.



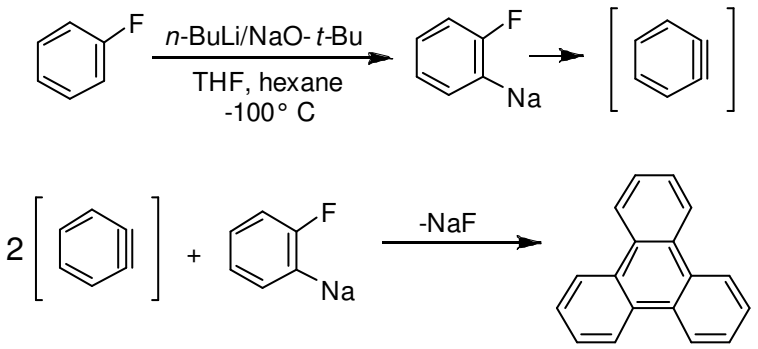

**Scheme 13.** Reactivity of *ortho*-Cl-copper reagents.

Annulyne has been generated from the corresponding pyrene bromide and sodamide, and has been trapped by various furans, followed by the removal of the oxygen bridge leading to the annulated annulenes (Scheme 14).[28]




**Scheme 14.** Generation of annulyne.

An efficient method for the synthesis of triphenylene can be accomplished using aryne chemistry.The synthesis involved *ortho*-sodiofluorobenzene as an intermediate. Its fast decomposition gave rise to the generation of benzyne and upon trimerization resulted in the high yield synthesis triphenylene (Scheme 15).[29]

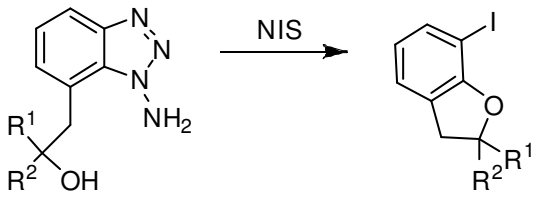



**Scheme 15.** Synthesis of triphenylene.

A remarkable and so far unique generation of a benzyne intermediate has been proposed in the thermal decomposition of azidoquinone in benzene which provided a cycloadduct by reaction with the solvent (Scheme 16).[30]

**Scheme 16.** Generation of arynes from azidoquinones.

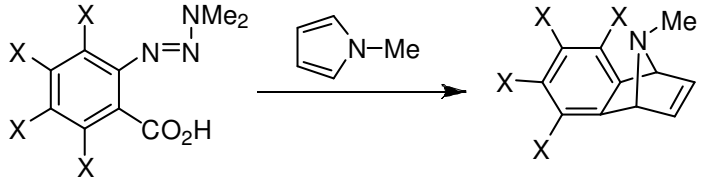
In 1994, Knight reported the generation of benzynes from 1-aminobenzotriazoles containing *ortho*-hydroxyethyl groups.[31] Intramolecular nucleophilic addition followed by trapping of iodine provided good yields of iododihydrobenzofurans (Scheme 171). The corresponding bromo-derivatives were previously obtained from NBS but in much lower yields than from NIS.[32]




$R^1$ = n-Pent, $R^2$ = H: 92%
$R^1$ = Ph, $R^2$ = H: 81%
$R^1$ = $R^2$ = Me: 95%
$R^1$ = $R^2$ = -$(CH_2)_4$-: 82%

**Scheme 17.** Synthesis of iodo-dihydrobenzofurans

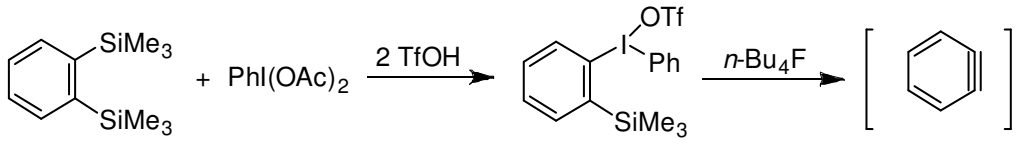
A study on the decomposition of 1-(2-carboxyphenyl)-3,3-dimethyltriazene and the tetrabromo- and tetrachloro analogues showed that the arenediazonium-2-carboxylates were intermediates in the formation of the corresponding arynes (Scheme 18).[33]




X = Cl: 28%
X = Br: 20%

**Scheme 18.** Generation of arynes from 1-(20-carboxyphenyl)-3,3-dimethyltriazene.

(Phenyl)[o-(trimethylsilyl)phenyl]iodonium triflate readily prepared from o-bis(trimethylsilyl)benzene and $PhI(OAc)_2$ was reported to be a new and efficient precursor for the generation of benzyne, reported by Kitamura in 1995 (Scheme 19).[34]




**Scheme 19.**Generation of arynes from (phenyl)[o-(trimethylsilyl)phenyl]iodonium triflate.

The above discussed methods are the most notable methods, which are widely used in the generation of arynes. However there are many other methods available in

the literature which are also been employed in the generation and the subsequent trapping of aryne. Various researchers around the globe have been working to develop methods for aryne generation, which are even more practical and efficient.

In summary, the various methods for the generation of arynes in solution can be represented as in Figure 3.

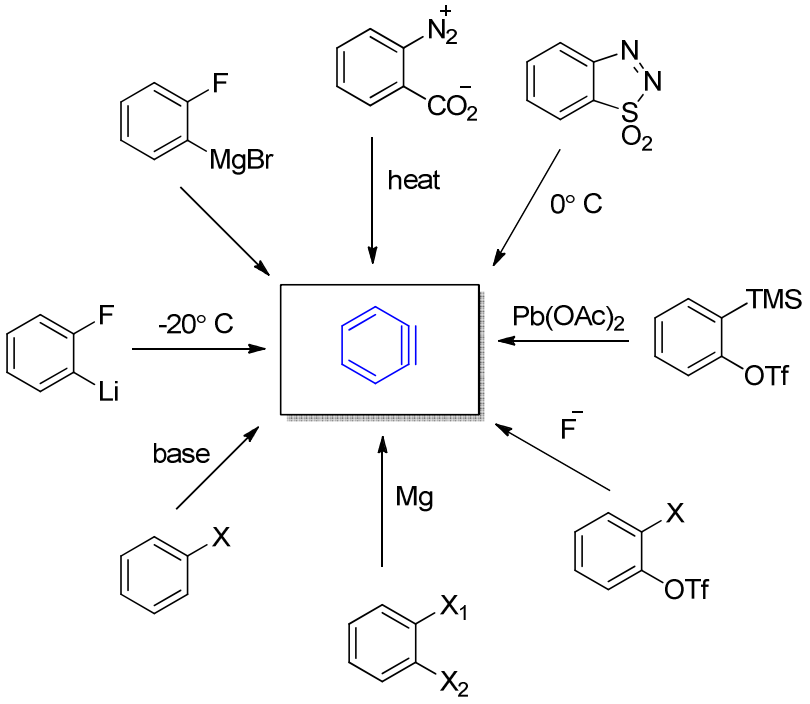
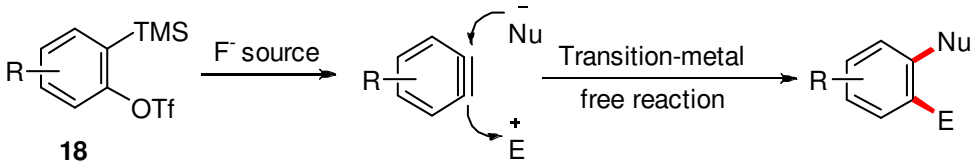



**Figure 3.** Methods for aryne generation

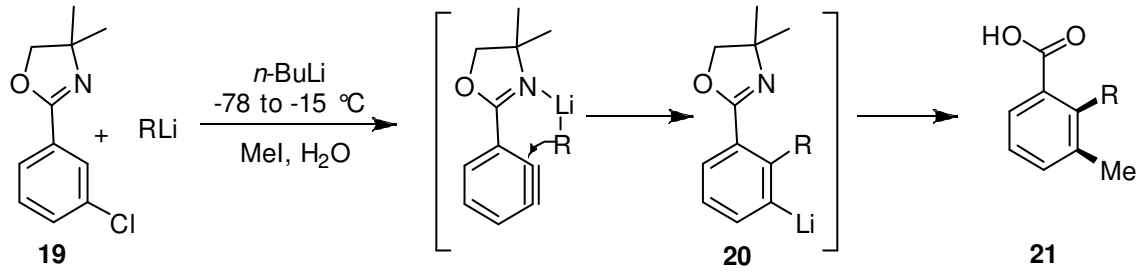
# Multicomponent Reactions of Arynes

From the last three decades, the chemistry of arynes has witnessed an renaissance of interest for the construction of various benzofused carbocycles and heterocycles, as well as for the synthesis of several 1,2-disubstituted arenes.[35] The resurgence of interest was mainly due to the development of a mild method for aryne generation from 2-(trimethylsilyl)aryl triflates **18** by the fluoride-induced 1,2-elimination reaction as discussed in the previous chapter (Scheme 8).[19,36] This mild method of aryne generation is compatible with a wide variety of functional groups. The important transition-metal-free reactivity profiles offered by arynes in various carbon–carbon and carbon–heteroatom bond-forming reactions include pericyclic reactions,[37] insertion reactions,[38] and multicomponent reactions (MCRs).[39] The MCR of arynes result when a nucleophile adds to aryne generating an aryl anion intermediate, which is subsequently intercepted by an electrophile (provided the nucleophile and electrophile are separate units, Scheme 20). In this chapter a discussion on some of the most notable works on aryne MCR, and the N-heterocycle-triggered aryne MCR developed in our laboratory has been attempted.[40]



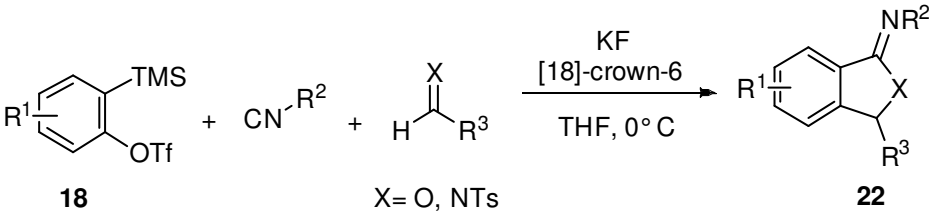

**Scheme 20.** Transition-metal-free MCR involving arynes.

Before 1983 there were few reports on employing anionic species as the nucleophilic trigger to carry out aryne MCR. It was in the year 1983, Meyers and Pansegrau reported the reaction of 2-(3-chlorophenyl) 2-oxazoline **19** with organolithium reagents followed by the trapping of the arylanion intermediate **20** using methyl iodide and subsequent hydrolysis leading to the formation of 2-substituted 3-methyl benzoic acid derivative **21** (Scheme 21).[41]




**Scheme 21.** Transition-metal-free MCR involving arynes

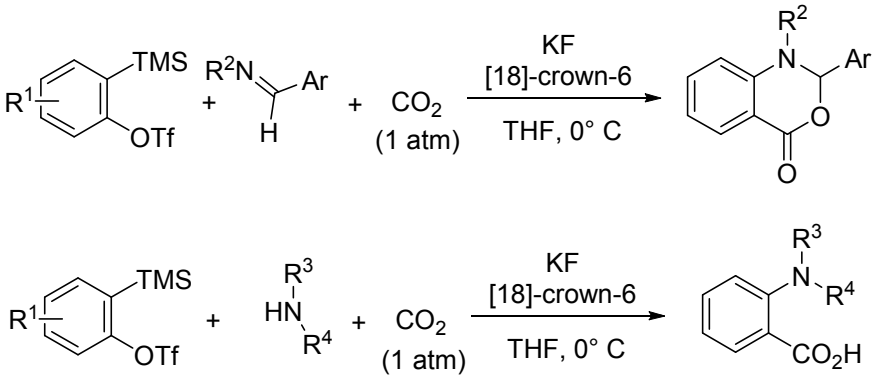
Isocyanide was first employed as a neutral nucleophile in aryne MCR by Yoshida, Kunai, and coworkers in 2004. They reported an unprecedented three-component reaction of arynes with isocyanides and aldehydes, and the reaction furnished the iminoisobenzofurans **22** in good yields (Scheme 22).[42] Subsequent studies from the same group revealed that these reactions worked well with activated imines, ketones, and 1,4-benzoquinones as the electrophilic component instead of aldehydes.




**Scheme 22.** MCR involving arynes, isocyanides, and electrophiles.

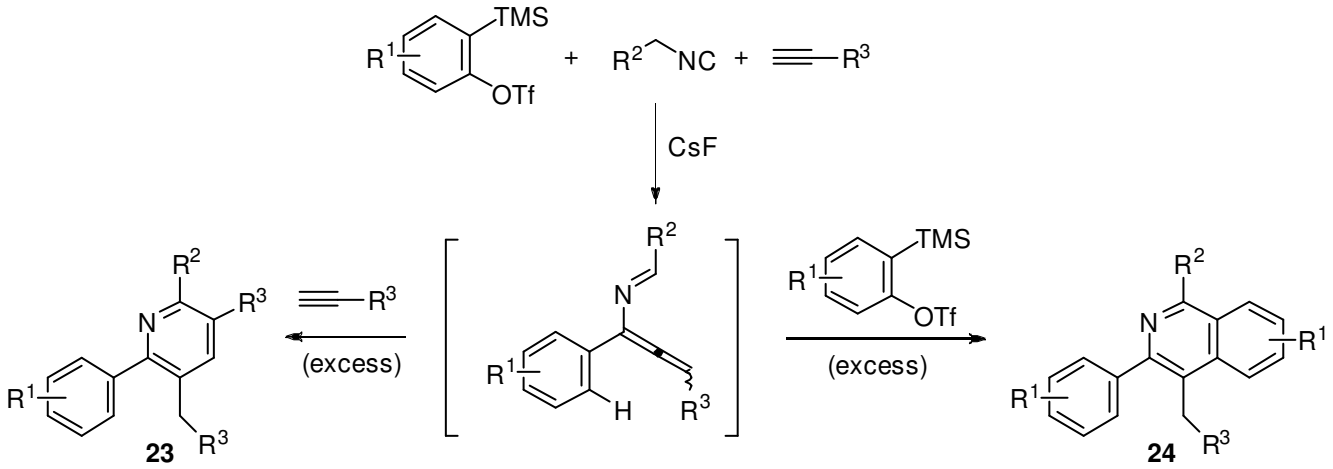
Recently, Stoltz and coworkers extended the isocyanide-initiated aryne MCR using phenyl esters as the electrophilic component, and the reaction furnished the phenoxy iminoisobenzofuran derivatives in good yield.[43] Moreover, carbocyclic imino indenones were formed when activated alkynes were used as the electrophile. It should be also noted that the Yoshida group, very recently, utilized alkynyl (or polyfluorinated aryl) bromides as the third component in aryne MCR initiated by isocyanides.[44] The Yoshida group also demonstrated the synthetic utility of $CO_2$ as one-carbon source in aryne MCR. The 1,4-dipolar intermediate from arynes and imines can be trapped using $CO_2$ to afford biologically significant benzoxazinone derivatives (Scheme 23).[45a]

Interestingly, the use of amines as nucleophilic trigger followed by quenching with $CO_2$ resulted in the formation of anthranilic acid derivatives.[45b]




**Scheme 23.** Aryne MCR initiated by imines/amines using $CO_2$ as electrophile

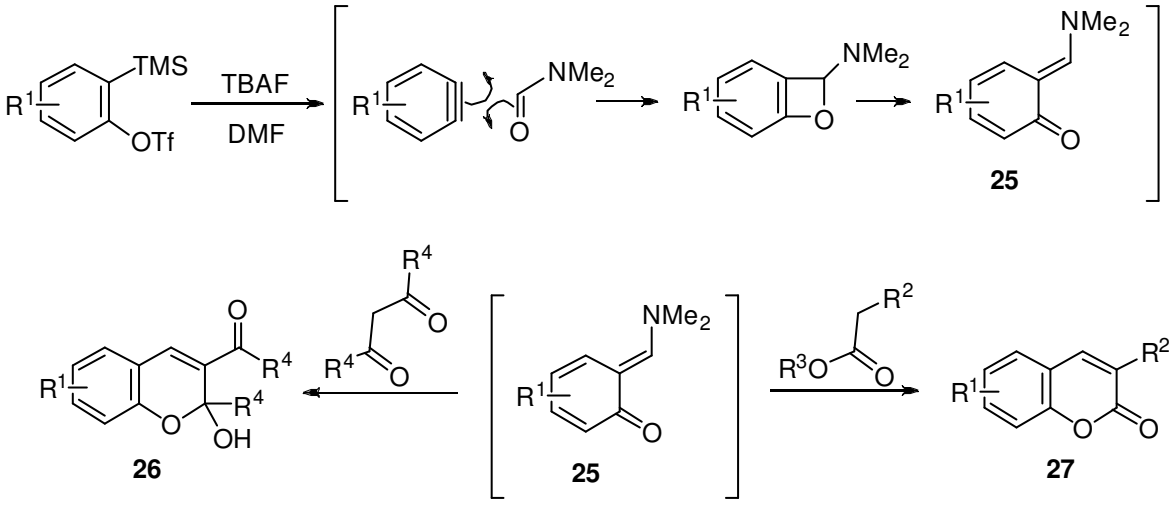
Sha and Huang recently reported the aryne MCR of isocyanides with terminal alkynes. Highly selective synthesis of either substituted pyridines or isoquinolines depending on the reaction conditions were obtained.[46] When the terminal alkyne was used in excess, the reaction afforded pyridines **23**, whereas isoquinolines **24** were formed with excess of arynes (Scheme 24).




**Scheme 24.** Aryne MCR with isocyanides and terminal alkynes.

Recently, the use of dimethyl formamide (DMF) as the nucleophilic trigger was developed independently by the Miyabe and Yoshida groups. The three-component

coupling reaction between aryne, DMF, and an active methylene compound resulted in the formation of either 2*H*chromenes **26** or coumarine derivatives **27**.[47] The insertion of the carbonyl group of DMF to the aryne generates the *ortho*-quinonemethide intermediate **25**. Subsequent reaction of **25** with cyclic or acyclic 1,3-diketones as the third component resulted in the formation of 2*H*-chromenes **26**. Interestingly, the use of β-ketoester or α-(hetero)aryl esters as the third component furnished coumarin derivatives **27** (Scheme 25). Subsequently, the Miyabe group reported the insertion of arynes into formamides generating the *ortho*-quinonemethides followed by trapping with zinc enolates leading to the synthesis of dihydrobenzofurans.[48]




**Scheme 25.** Aryne MCR triggered by DMF.

Jeganmohan and Cheng in 2006, demonstrated the synthetic potential of N-heterocycles such as pyridine, quinoline, and isoquinoline as nucleophiles in aryne reactions with nitriles possessing an α-hydrogen.[49a] In this case, the nitriles act as solvent as well as the third component, and the reaction resulted in the construction of a new C–C and C–N bonds in one-pot (Scheme 26). The reaction proceeds via the initial formation of 1,4-zwitterionic intermediate **28** from isoquinoline and aryne, which is protonated by the nitrile, thus generating the isoquinolinium salt **29**. The nitrile anion then undergoes a nucleophilic attack on **29** forming the desired product **30**. Inspired by this work, they further used terminal alkynes as the third component in aryne MCR with N-heterocycles, and the reaction affords 1,2-dihydroaromatic alkynes **31** in good

yields.[49b] Notably, methyl ketones can also be used as the third component in this reaction.

**Scheme 26.** Aryne MCR induced by N-heterocycles

Apart from the reports of the Cheng group, the utility of N-heterocycles in aryne MCR has not been well studied. Though, the generation of 1,4-zwitterionic intermediate from N-heterocycles and activated alkynes such as dimethyl acetylenedicarboxylate (DMAD) followed by the interception of the zwitterion with various electrophiles are reported by the Nair group.[50] the analogous aryne MCRs by replacing DMAD with highly electrophilic arynes has not been explored. In the contect of our general interest in developing a new MCR with highly electrophilic arynes, we got success and recently reported a novel aryne MCR involving isoquinoline **32** and N-substituted isatins **33** with aryne generated in situ from 2-(trimethylsilyl)aryl triflate **18** using KF and [18]crown-6, and the reaction resulted in the formation of the spirooxazino isoquinoline derivatives **34** as an inseparable mixture of diastereomers (Scheme 27).[40a] The reaction was found to be general with a variety of N-substituted isatins containing electron-rich and electron-poor functional groups, as well as various electronically different arynes were well tolerated.

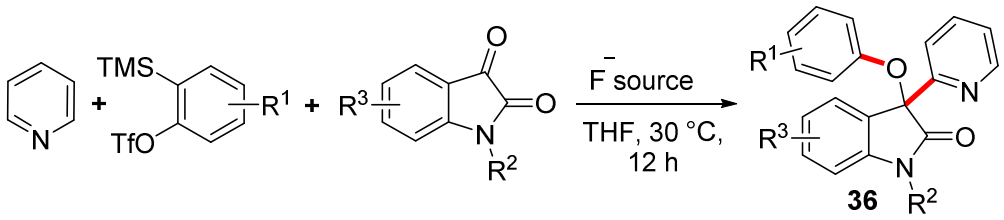
**Scheme 27.** MCR involving isoquinoline, arynes, and N-substituted isatin

In order to expand the scope of this aryne MCR, various carbonyl compounds as the electrophilic trapping agents were examined. The reaction of quinoline and arynes with aldehydes resulted in the formation of benzoxazino quinoline derivatives **35** as an inseparable mixture of diastereomers in good yield and excellent diastereoselectivity.[40b] A wide variety of (hetero)aromatic and aliphatic aldehydes are well tolerated under the optimized reaction conditions (Scheme 28). In addition, various

carbonyl compounds such as benzophenone 1,4-benzoquinone, di-aryl 1,2-dione, as well as α-ketoester were also used as the carbonyl component in this reaction.

**Scheme 28.** Aryne MCR involving quinoline and various carbonyl compounds.

In view of the interesting results obtained on aryne MCRs initiated by isoquinoline and quinoline, we then investigated the reactivity using other N-heterocycles as the nucleophilic trigger. when pyridine is used as nucleophilic trigger, the reaction afforded indolin 2-one derivative **36** (Scheme 29).[40a] Interestingly, no oxazino pyridine derivative resulting from the interception of pyridine-aryne zwitterion with electrophilic carbonyl group of isatin (analogous to isoquinoline-aryne zwitterion reactivity, Scheme 27, 28) was observed in this case. The preliminary mechanistic studies shed light on a pyridylidene as a key intermediate in this reaction.

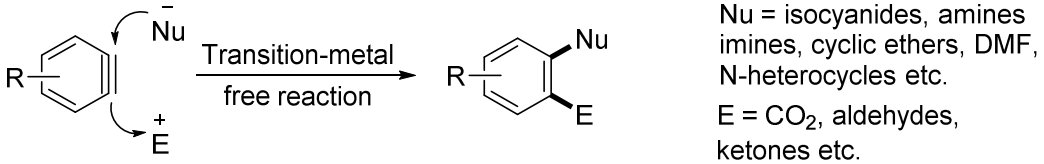



**Scheme 29.** MCR involving pyridine, arynes and N-substituted isatins

So, as discussed above, there are considerable amount of work has been done on MCR's involving arynes, various electrophiles and nucleophiles, the nucleophilic component in most of the aryne MCRs include isocyanides, amines, imines or N-heterocycles. Herein, we report for the first time MCR involving phosphines, arynes, and various carbonyl compounds, leading to synthesis of benzoxaphosphole derivatives, which are not only new members of heterophosphole family but are also molecules of high biological utility and chemical importance.

## Statement of the Problem

Arynes have been recognized as highly reactive intermediates and they have played significant role in various fundamental organic transformations. Due to the pronounced electrophilicity of arynes as well as the highly strained triple bond in the ring system, arynes have found widespread applications in various bond-forming reactions including pericyclic reactions, insertion reactions, transition-metal catalyzed reactions and multicomponent reactions (MCRs). Interestingly, recent developments in aryne chemistry have been dedicated to transition-metal free reactions, especially the MCRs. The commonly used nucleophile in aryne MCRs is isocyanides, however, the utility of imines, amines, cyclic ethers, DMF, and N-heterocyles etc. as nucleophiles is also known and the trapping agents used are usually carbonyl compounds including carbon dioxide (Scheme 30).

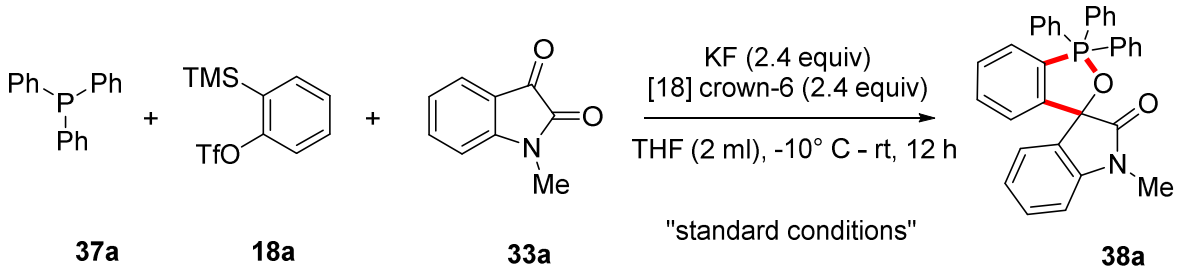



**Scheme 30.** Transition-metal-free aryne MCRs, state-of-the-art.

Although several nucleophiles as the initiator for aryne MCRs are known, surprisingly, however, the synthetic utility of phosphines as nucleophiles in the realm of aryne MCRs, to the best of our knowledge is unknown. Notably, if successful, these reactions could give direct access to various benzo-fused phosphorus heterocycles of interesting biological properties. We have carried out a systematic investigation on the aryne MCRs where phosphines are used as the nucleophilic trigger and N-substituted isatins as the electrophilic trapping reagent, and these reactions allowed the straightforward synthesis of spirobenzophosphole derivatives. In addition, the feasibility of this reaction with various acyclic activated carbonyl compounds was tested. These results are presented in the following pages.

## Results and Discussion

Our present study was initiated with the treatment of triphenylphosphine **37a** and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **18a** with 1-methylindoline-2,3-dione **33a** in the presence of KF and 18-crown-6 in THF at -10 °C to rt for 12h. Interestingly, a facile reaction occurred leading to the formation of 1'-methyl-1,1,1-triphenyl-1*H*-1λ$^5$-spiro[benzo[c][1,2]oxaphosphole-3,3'-indolin]-2'-one **38a** in 23% yield (Table 1, entry 1). With this result, we have carried out an extensive optimization of reaction conditions to examine the effects of varying the amount of all the reactants. Interestingly, with 1.0 equiv of triphenylphosphine and increasing amount of both 1-methylindoline-2,3-dione and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate to 1.5 equiv, the yield of spirobenzooxaphosphole **38** was increased to 47% (Table 1, entry 4).




**37a** **18a** **33a** **38a**

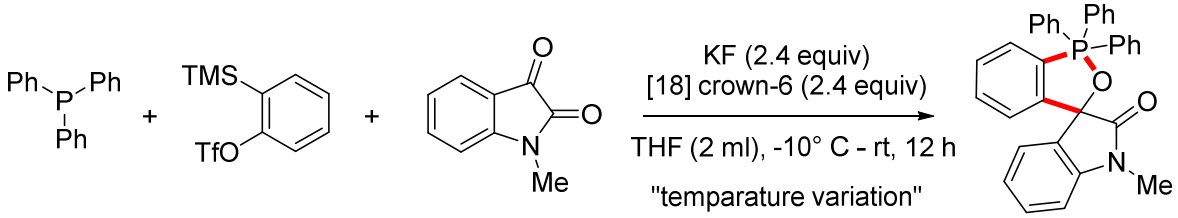
| Entry | Variation of the standard conditions[a] | Yield of **38a** (%) |
|---|---|---|
| 1 | 1 equiv of **37a**, 1.2 equiv of **18a** and 1 equiv of **33a** | 23 |
| 2 | 1 equiv of **37a**, 1.5 equiv of **18a** and 1 equiv of **33a** | 30 |
| 3 | 1.5 equiv of **37**, 1.5 equiv of **18a** and 1 equiv of **33a** | 42 |
| 4 | 1 equiv of **37a**, 1.5 equiv of **18a** and 1.5 equiv of **33a** | 47 |

[a] Standard conditions: **37a** (0.25 mmol), **18a** (0.30 mmol), **33a** (0.25 mmol), THF (2 mL), -10° C to rt and 12 h. [b]Isolated yield of product is given.

**Table 1.** Optimization of the reaction conditions: screening of reactants amount.

In order to investigate the effect of temperature, the reaction was carried out at various temperatures ranging from rt to 70 °C. Pleasingly, a gradual increase in the

yield was observed with a maximum isolated yield of 67% at 70° C (Table 2, entry 4). Additionally, increasing the temperature above 70° C resulted in the decrease in the yield of product (Table 2, entry 5). These results are summarized in Table 2.



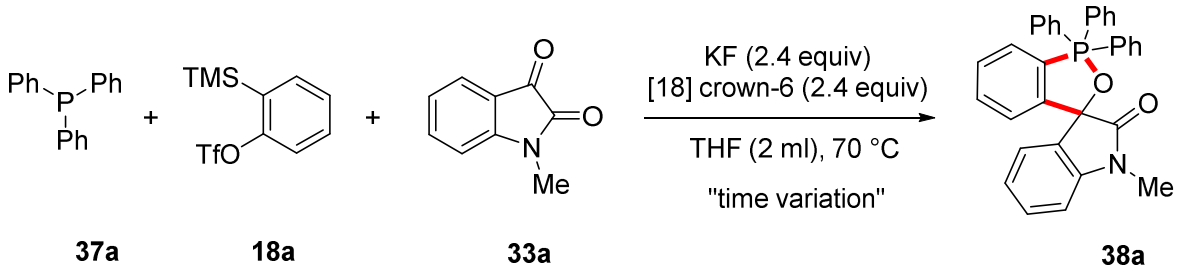

**37a** **18a** **33a** **38a**

| Entry | Variation of temperature[a] | Yield of **38a** (%) |
|---|---|---|
| 1 | -10 °C to rt | 47 |
| 2 | rt | 52 |
| 3 | 60 °C | 59 |
| 4 | 70 °C | 67 |
| 5 | 80 °C | 20 |

[a] Standard conditions: **37a** (0.25 mmol), **18a** (0.375 mmol), **33a** (0.375 mmol), THF (2.0 mL), -10° C to rt and 12 h. [b]Isolated yield of pure product is given.

**Table 2.** Optimization of the reaction conditions, variation of temperature

During the optimization studies, we observed that the increasing the reaction time improves the yield of the benzooxaphosphole **38a**. Delightfully, a reaction time of 20 hours resulted in the formation of **38a** in a high yield of 89% (Table 3, entry 2) with triphenylphosphine almost completely consumed. However, further increase in the reaction time did not improve the yield of **38a**. These results are summarized in Table 3.



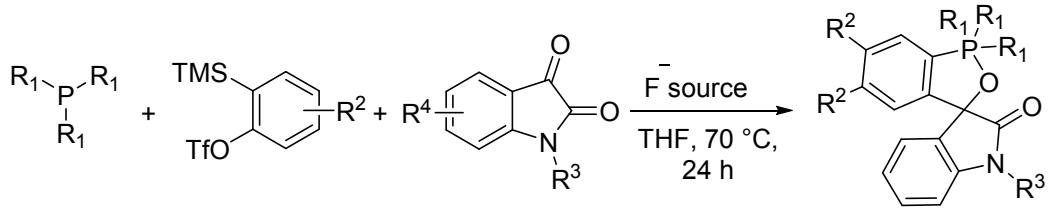

**37a** **18a** **33a** **38a**

| Entry | Variation of time[a] | Yield of **38a** (%) |
|---|---|---|
| 1 | 12 h | 47 |
| 2 | 20 h | 89 |
| 3 | 24 h | 89 |

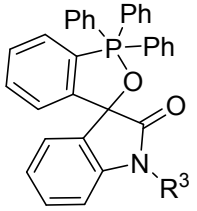
[a] Standard conditions: **37a** (0.25 mmol), **18a** (0.375 mmol), **33a** (0.375 mmol), THF (2.0 mL), 70° C. [b]Isolated yield of pure product is given.

**Table 3.** Optimization of the reaction conditions, variation of the reaction time.

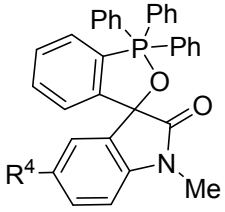
With these optimized reaction conditions in hand, we then examined the substrate scope of this phosphine-triggered aryne MCR (Scheme 31). The reaction was well tolerated by various substituents on the nitrogen atom of N-substituted isatin leading to the formation of benzoxaphosphole derivatives in 56-71% yield (**38a-38d**). Moreover, electron-withdrawing groups at the carbocyclic ring of N-substituted isatin resulted in the smooth conversion to the product (**38e-38g**). Additionally, electronically different 4,5-disubstituted symmetrical arynes readily afforded the benzoxophosphole derivatives in good yield (**38h-38j**). Interestingly, an unsymmetric aryne generated from 1-(trimethylsilyl)-2-naphthyltriflate furnished the desired product in 49% yield (**38k**). Furthermore, this unique MCR is not limited to triphneylphosphine. Gratifyingly, tri-*p*-tolylphosphane, tris(4-methoxyphenyl)phosphane as well as diphenyl(*p*-tolyl)phosphane worked well leading to the formation of the desired products in moderate to good yields (**38l-38n**). Moreover the reaction also works well with triphenylarsene giving **38o** in 62% yield demonstrating the versatility of the present reaction.



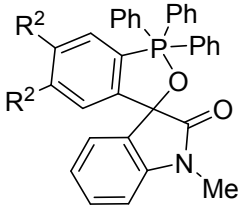

**37** **18** **33** **38**



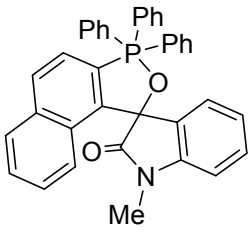
$R^3$ = Me, **38a**, 89%
$R^3$ = Bn, **38b**, 71%
$R^3$ = allyl, **38c**, 56%
$R^3$ = Ph, **38d**, 63%



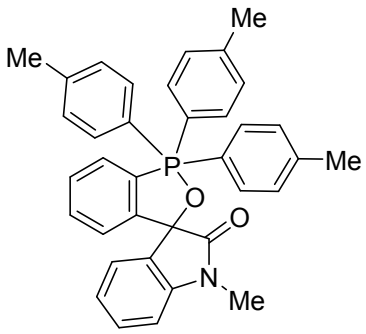
$R^4$ = Br, **38e**, 82%
$R^4$ = Cl, **38f**, 67%
$R^4$ = F, **38g**, 87%



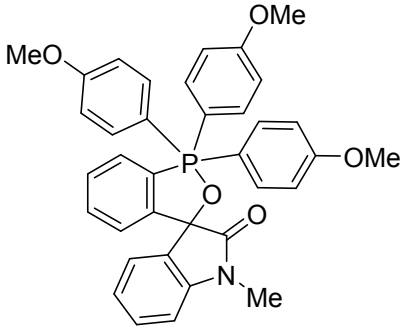
$R^2$ = Me, **38h**, 59%
$R^2$ = $O(CH_2)O$, **38i**, 61%
$R^2$ = F, **38j**, 63%



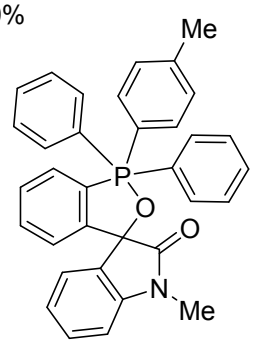
**38k**, 49%



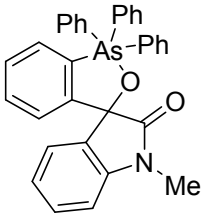
**38l**, 67%



**38m**, 65%



**38n**, 65%



**38o**, 62%

General conditions: **37a** (0.5 mmol), **18a** (0.75 mmol), **33a** (0.75 mmol) KF (1.5 mmol), [18] crown-6 (1.5 mmol), THF (4.0 mL), 70 °C, 20 h. Yields of isolated products are given.

**Scheme 31.** Substrate scope of the MCR involving phosphines, arynes and N-substituted isatins

In view of these interesting results, we next evaluated the effect of varying the N-substituted isatins component of this reaction (Scheme 32). Delightfully, benzil and 2 ,2'-thenil underwent efficient cyclization with triphenylphosphine and aryne leading to the formation of the phenyl(1,1,1,3-tetraphenyl-1,3-dihydro-1λ$^5$-benzo[*c*][1,2] oxaphosphol-3-yl)methanone **40a** in 51% yield and thiophen-2-yl(1,1,1-triphenyl-3-(thiophen-2-yl)-1,3-dihydro-11λ$^5$-benzo[*c*][1,2]oxaphosphol-3-yl)methanone **40b** in 42% yield respectively. Moreover, ethyl phenyl glyoxylate can be used as an effective carbonyl surrogate in this reaction, and the reaction afforded the ethyl 1,1,1,3-tetraphenyl-1,3-dihydro-1λ$^5$-benzo[*c*][1,2]oxaphosphole-3-carboxylate derivative **40c** in 58% yield. Notably, these reactions worked efficiently at lower temperature.

General conditions: **33a** (0.5 mmol), **18a** (0.75 mmol), **39** (0.75 mmol) KF (1.5 mmol), [18] crown-6 (1.5 mmol), THF (4.0 mL), -10 ℃ to rt, 20 h. Yields of isolated products are given.

**Scheme 32.** Substrate scope of the MCR involving phosphines, arynes and ketones.

The mechanistic rationale for this aryne MCR may be advanced as follows (Scheme 33). The reaction proceeds via the initial generation of the 1,4-dipolar intermediate **41** from phosphine and aryne (generated from **18**). The zwitterion **41** can add to the electrophilic carbonyl group of isatin in a concerted manner leading to the formation of **38** (Scheme 3). Alternatively, in a step-wise pathway, **41** can add to isatin generating the intermediate **42** which undergoes cyclization leading to **38.**

**Scheme 33.** Plausible Reaction Mechanism

## Conclusion

In summary, we have developed a conceptually new MCR involving phosphines, arynes, and N-substituted isatins. The three-component reaction involving phosphines, arynes and isatins resulted in the formation of benzooxaphosphole derivatives in good yields. The reaction proceeds via the generation of 1,3-zwitterionic intermediates from arynes and phosphines. Moreover, the synthetic utility of this reaction with acyclic activated ketones was examined. Given the widespread application of organophosphorus compounds in different areas, the method presented herein is likely to find potential applications in organic chemistry.

# Experimental Section

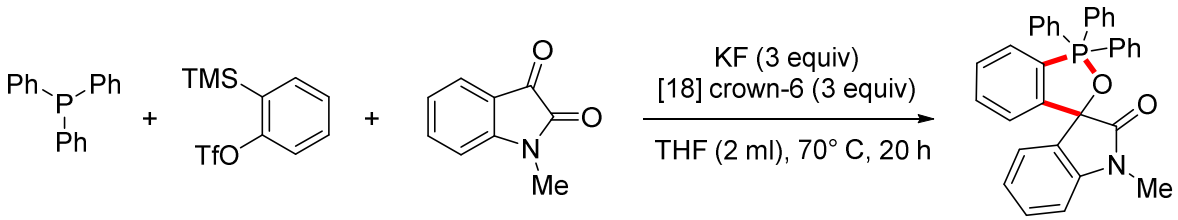
### General Information

Unless otherwise specified, all reactions were carried out under an atmosphere of argon in flame-dried reaction vessels with Teflon screw caps. Reaction temperature is reported as the temperature of the bath surrounding the reaction vessel. 30 ℃ 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 ℃ for 12 h and left to cool under argon. The isatin derivatives were purchased from Sigma Aldrich or Acros and the N-alkylation was carried out by treating with the corresponding alkyl halides under basic condition following the known procedure.[35] Phosphines were purchased from Aldrich. The 2(trimethylsilyl)phenyl trifluoromethane sulfonate **18a** and the other symmetric and unsymmetric aryne precursors were synthesized following literature procedure.[36]

Analytical thin layer chromatography was performed on TLC Silica gel 60 F254. Visualization was accomplished with short wave UV light or Iodine vapours as staining reagent. 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 (CDCl3: δH = 7.26 ppm, δC = 77.16 ppm). Infrared spectra were recorded on a Perkin-Elmer 1615 FT Infrared Spectrophotometer Model 60B. The wave numbers (n) of recorded IR-signals are quoted in $cm^{-1}$. HRMS data were recorded on a Thermo Scientific Q-Exactive, Accela 1250 pump.

**General Procedure for the Optimisation of Reaction Conditions**




**37a** **18a** **33a** **38a**

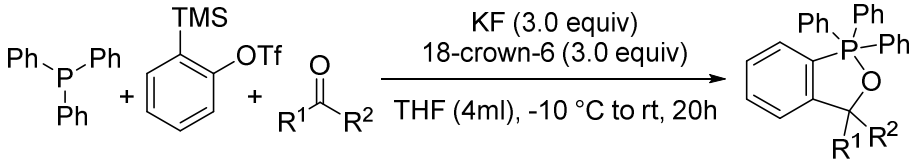
To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added 18-crown-6 (0.198 g, 0.75 mmol), KF (0.043 g, 0.75 mmol) and 1-methylindoline-2,3-dione **33a** (0.375 mmol). Then the screw-capped tube was evacuated and backfilled with argon. The mixture was dissolved in THF (2.0 mL) under argon atmosphere. The resultant reaction mixture was kept stirring at 30 °C for 5 min. To the stirring solution was then added triphenylphosphine **37a** (0.25 mmol) and the aryne precursor **18a** (0.375 mmol). Then the reaction mixture was placed in preheated oil bath at 70° C. When TLC control showed the completion of the reaction (typically after 20 h), the reaction mixture cooled to room temperature and the solvent was evaporated and the crude residue was subsequently purified by flash column chromatography on silica gel to afford the corresponding product **38a** as a yellow solid in moderate to good yields.

**General Procedure for the MCR involving Phosphines, Arynes and Isatins**

To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added 18-crown-6 (0.396 g, 1.5 mmol), KF (0.087 g, 1.5 mmol), 1-methylindoline-2,3-dione **33** (0.75 mmol) and triphneylphosphine **37** (0.50 mmol). Then the screw-capped tube was evacuated and backfilled with argon. The mixture was dissolved in THF (4.0 mL) under argon atmosphere. The resultant reaction mixture was kept stirring at 30 °C for 5 min. To the stirring solution was then added the aryne precursor **18** (0.75 mmol). Then the reaction mixture was placed in preheated oil bath at 70° C. When TLC control showed the completion of the reaction (typically after 20 h), the reaction mixture cooled

to room temperature and the solvent was evaporated and the crude residue was subsequently purified by flash column chromatography on silica gel to afford the corresponding product **38** in moderate to good yields.

**General Procedure for the MCR involving Phosphines, Arynes and Ketones**




**37a** **18a** **39** **40**

To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added 18-crown-6 (0.396 g, 1.5 mmol), KF (0.087 g, 1.5 mmol), diketones **39** (0.75 mmol) and triphneylphosphine **37a** (0.50 mmol). Then the screw-capped tube was evacuated and backfilled with argon. The mixture was dissolved in THF (4.0 mL) under argon atmosphere. The resultant reaction mixture was kept stirring at -10 ℃ for 5 min. To the stirring solution was then added and the aryne precursor **18a** (0.75 mmol). Then the reaction mixture was placed in ice bath and left stirring. When TLC control showed the completion of the reaction (typically after 20 h), the reaction mixture cooled to room temperature and the solvent was evaporated and the crude residue was subsequently purified by flash column chromatography on silica gel to afford the corresponding product **40** as a white solid in moderate to good yields.

## Synthesis and Characterization of Benzooxaphospholes

**1'-Methyl-1,1,1-triphenyl-1*H*-1λ$^5$-spiro[benzo[*c*][1,2]oxaphosphole-3,3'-indolin]-2'-one (38a)**

Following the general procedure, treatment of triphenylphosphine **37a** (0.132 g, 0.5 mmol) and 1-methylindoline-2,3-dione **33a** (0.121 g, 0.75 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **18a** (0.224 g, 182 µL, 1.5 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at 70 °C for 20 h followed by silica gel flash column chromatography (Pet. ether/EtOAc = 50/50) of the crude reaction mixture afforded 1'-methyl-1,1,1-triphenyl-1*H*-1λ$^5$-spiro[benzo[*c*][1,2]oxaphosphole-3,3'-indolin]-2'-one **38a** as a yellow solid (0.223 g, 89%).

***R*$_f$** (Pet. ether /EtOAc = 50/50): 0.55; **$^1$H NMR (400 MHz, CDCl$_3$)** $\delta_H$ 7.61-7.58 (m, 6H ), 7.44 (d, *J* = 6.39 Hz, 1H ), 7.33 (s, 10H), 7.13-6.98 (m, 3H), 6.76 (d, *J* = 7.6 Hz, 1H), 6.57 (t, *J* = 14.6 Hz, 1H), 5.54 (s, 1H), 3.24 (s, 3H), **$^{13}$C NMR (400 MHz, CDCl$_3$)** $\delta_C$ 177.59, 148.47 (d, *J* = 19.91), 142.98, 136.88 (d, *J* = 14.42), 1336.80, 135.26, 133.05 (d, *J* = 2.47), 132.28 (d, *J* = 8.99), 131.38, 128.40 (d, *J* = 14.06), 127.56 (t, *J* = 12.33), 115.60, 109.33, 18.65, 26.56 **HRMS** calculated $[M+H]^+$ for $C_{33}H_{26}NO_2P$: 500.1774, found: 500.1774. **FTIR (cm$^{-1}$)** 3783.99, 3704.30, 3009.70, 2360.96, 1718.06, 1610.26, 1473.03, 1440.32, 1370.39, 1220.96, 1194.89, 1111.05, 1039.84, 959.20, 911.32, 771.57, 742.49, 696.65, 661.80

**1'-Benzyl-1,1,1-triphenyl-1*H*-1λ$^5$-spiro[benzo[*c*][1,2]oxaphosphole-3,3'-indolin]-2'-one (38b)**

Following the general procedure, treatment of triphenylphosphine **37a** (0.132 g, 0.5 mmol) and 1-benzylindoline-2,3-dione **33b** (0.180 g, 0.75 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **18a** (0.224 g, 182 µL, 1.5 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at 70 °C for 20 h followed by silica gel flash column chromatography (Pet. ether/EtOAc = 50/50) of the crude reaction mixture afforded 1'-benzyl-1,1,1-triphenyl-1*H*-1λ$^5$-spiro[benzo[*c*][1,2]oxaphosphole-3,3'-indolin]-2'-one **38b** as a yellow solid (0.204g, 71%).

***R*$_f$** (Pet. ether /EtOAc = 50/50): 0.46 **$^1$H NMR (400 MHz, CDCl$_3$)** $\delta_H$ 7.62-7.56 (m, 6H), 7.45-7.41 (m, 3H), 7.37-7.26 (m, 14H), 17.06 (t, *J* = 19.38, 1H), 6.99 (t, *J* = 15.13, 1H), 6.94 (d, *J* = 7.32, 1H), 6.69 (d, *J* = 17.73, 1H), 6.52 (t, *J* = 14.84, 1H), 5.53 (d, *J* = 6.14, 1H), 5.31 (d, *J* = 15.34, 1H), 4.50 (d, *J* = 15.47. 1H). **$^{13}$C NMR (400 MHz, CDCl$_3$)** $\delta_C$ 178.23, 149.56 (d. *J* = 20.08), 143.09, 136.98 (d, *J* = 14.53), 136.50, 133.42, 133.11, 132.45 (d, *J* = 8.93), 128.89, 128.71, 128.28 (d, *J* = 14.39), 127.66 (t, *J* = 22.03), 124.34, 123.00, 108.98, 81.02, 44.26. **HRMS** calculated $[M+H]^+$ for $C_{39}H_{30}NO_2P$: 576.2087, found: 576.2100. **FTIR (cm$^{-1}$)** 3733.69, 3734.40, 3429.50, 2120.16, 1768.91, 1651.34, 1482.31, 1480.12, 1395.47, 1232.06, 1151.32, 1021.05, 1038.34, 936.10, 753.49, 613.13

**1'-Allyl-1,1,1-triphenyl-1*H*-1λ$^5$-spiro[benzo[*c*][1,2]oxaphosphole-3,3'-indolin]-2'-one (38c)**

Following the general procedure, treatment of triphenylphosphine **37a** (0.132 g, 0.5 mmol) and 1-allylindoline-2,3-dione **33c** (0.137 g, 0.75 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **18a** (0.224 g, 182 µL, 1.5 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at 70 ℃ for 20 h followed by silica gel flash column chromatography (Pet. ether/EtOAc = 50/50) of the crude reaction mixture afforded 1'-allyl-1,1,1-triphenyl-1*H*-1λ$^5$-spiro[benzo[*c*][1,2]oxaphosphole-3,3'-indolin]-2'-one **38c** as a white solid (0.147 g, 56%).

***R*$_f$** (Pet. ether /EtOAc = 50/50): 0.51; **$^1$H NMR (400 MHz, CDCl$_3$)** $\delta_H$ 7.59-7.55 (m, 6H), 7.44 (t, *J*=13.61, 1H), 7.30-7.26 (m, 11H), 7.10-6.95 (m, 3H), 6.76 (d, *J* = 7.88, 1H), 6.53 (t, *J* = 14.86, 1H), 5.95-5.85 (m, 1H), 5.50 (d, *J* = 7.01, 1H), 5.36 (d, *J* = 17.17, 1H), 5.26 (d, *J* = 10.16, 1H), 4.54 (dd, $J_1$ = 15.00, $J_2$ = 4.06, 1H), 4.16-4.12 (m, 1H) **$^{13}$C NMR (400 MHz, CDCl$_3$)** $\delta_C$ 177.83, 149.52 (d, *J* = 20.65), 143.22, 136.95 (d, *J* = 14.78), 133.44, 133.08, 132.45 (d, *J* = 9.19), 131.99, 128.70, 128.25 (t, *J* = 14.02), 127.59 (d, *J* = 12.51), 124.38, 122.93, 118.00, 108.92, 42.90 **HRMS** calculated $[M+H]^+$ for $C_{35}H_{28}NO_2P$: 526.1930, found: 526.1937. **FTIR (cm$^{-1}$)** 3006, 2973, 2925, 2856, 1716, 1612, 1488, 1466, 1354, 1285, 1196, 1175, 1101, 1023, 999, 933, 750, 692, 598.

**1,1,1,1'-tetraphenyl-1*H*-1λ$^5$-spiro[benzo[*c*][1,2]oxaphosphole-3,3'-indolin]-2'-one (38d)**

Following the general procedure, treatment of triphenylphosphine **37a** (0.132 g, 0.5 mmol) and 1-phenylindoline-2,3-dione **33d** (0.167 g, 0.75 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **18a** (0.224 g, 182 µL, 1.5 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at 70 °C for 20 h followed by silica gel flash column chromatography (Pet. ether/EtOAc = 50/50) of the crude reaction mixture afforded 1,1,1,1'-tetraphenyl-1*H*-1λ$^5$-spiro[benzo[*c*][1,2]oxaphosphole-3,3'-indolin]-2'-one **38d** as a white solid (0.177 g, 63%).

***R*$_f$** (Pet. ether /EtOAc = 50/50): 0.63; **$^1$H NMR (400 MHz, CDCl$_3$)** $\delta_H$ 7.64-7.59 (m, 6H), 7.54-7.47 (m, 5H), 7.39 (t, *J* = 14.3, 1H), 7.32-7.26 (m, 11H), 7.16 (dd, $J_1$ = 7.53, $J_2$ = 1.91, 1H), 7.09-7.00 (m, 2H), 7.76 (d, *J* = 7.90, 1H), 6.58 (t, *J* = 15.07, 1H), 5.5 (d, *J* = 7.22, 1H). **$^{13}$C NMR (400 MHz, CDCl$_3$)** $\delta_C$ 177.52, 149.65 (d, *J* = 20.06), 143.72, 137.01 (d, *J* = 14.68), 134.69.80, 133.18 (d, *J* = 2.75), 132.45 (d, *J* = 9.07), 129.69, 128.63, 128.36 (t, *J* = 14.09), 128.02, 127.64 (d, *J* = 12.56), 126.96, 124.64, 123.44, 109.32, 81.18 **HRMS** calculated $[M+H]^+$ for $C_{38}H_{28}NO_2P$: 562.1930, found: 562.1934. **FTIR (cm$^{-1}$)** 3893.85, 3860.53, 3828.74, 3743.93, 3678.75, 3648.52, 3619.59, 3565.40, 3056.96, 2314.05, 1834.71, 1726.30, 1646.87, 1603.70, 1499.20, 1462.25, 1433.25, 1366.40, 1318.63, 1265.53, 1184.47, 1115.47, 1071.43, 996.73, 963.65, 832.97, 730.00, 701.07, 670.84.

**5'-Bromo-1'-methyl-1,1,1-triphenyl-1*H*-1λ$^5$-spiro[benzo[*c*][1,2]oxaphosphole-3,3' indolin]-2'-one (38e)**

Following the general procedure, treatment of triphenylphosphine **37a** (0.132 g, 0.5 mmol) and 5-bromo-1-methylindoline-2,3-dione **33e** (0.180 g, 0.75 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **18a** (0.224 g, 182 µL, 1.5 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at 70 °C for 20 h followed by silica gel flash column chromatography (Pet.

ether/EtOAc = 50/50) of the crude reaction mixture afforded 5'-bromo-1'-methyl-1,1,1-triphenyl-1*H*-1λ$^5$-spiro[benzo[*c*][1,2]oxaphosphole-3,3' indolin]-2'-one **38e** as a yellow solid (0.237 g, 82%).

***R*$_f$** (Pet. ether /EtOAc = 50/50): 0.49; **$^1$H NMR (500 MHz, CDCl$_3$)** $\delta_H$ 7.58 -7.53 (m, 6H ), 7.48-7.43 (m, 1H ), 7.32 (s, 10H), 7.19 (dd, $J_1$=8.23 Hz, $J_2$=1.97 Hz,1H), 7.09-7.04 (m, 1H), 6.96 (dd, $J_1$=7.42 Hz, $J_2$=2.11 Hz,1H), 6.60 (d, $J$ = 8.26 Hz, 1H), 5.43 (s, 1H), 3.19 (s, 3H) **$^{13}$C NMR (500 MHz, CDCl$_3$** $\delta_C$ 177.59, 148.47 (d, $J$ = 19.91), 142.98, 136.88 (d, $J$ = 14.42), 1336.80, 135.26, 133.05 (d, $J$ = 2.47), 132.28 (d, $J$ = 8.99), 131.38, 128.40 (d, $J$ = 14.06), 127.56 (t, $J$ = 12.33), 115.60, 109.33, 18.65, 29.72, 26.56. **HRMS** calculated $[M+H]^+$ for $C_{33}H_{25}BrNO_2P$: 578.0879, found: 578.0887. **FTIR (cm$^{-1}$)** 3767.41, 3694.99, 3382.64, 3064.85, 3010.30, 2361.65, 1720.93, 1608.02, 1479.36, 1433.23, 1352.06, 1227.42, 1190.22, 1103.88, 1036.49, 959.64, 888.33, 851.41, 811.78, 770.69, 742.80, 696.73, 665.08.

**5'-Chloro-1'-methyl-1,1,1-triphenyl-1*H*-λ$^5$-spiro[benzo[*c*][1,2]oxaphosphole-3,3'-indolin]-2'-one (38f)**

Following the general procedure, treatment of triphenylphosphine **37a** (0.132 g, 0.5 mmol) and 5-chloro-1-methylindoline-2,3-dione **33f** (0.147 g, 0.75 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **18a** (0.224 g, 182 µL, 1.5 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at 70 ℃ for 20 h followed by silica gel flash column chromatography (Pet. ether/EtOAc = 50/50) of the crude reaction mixture afforded 5'-chloro-1'-methyl-1,1,1-triphenyl-1*H*-λ$^5$-spiro[benzo[*c*][1,2]oxaphosphole-3,3'-indolin]-2'-one **38f** as a yellow solid (0.179 g, 67%).

***R*$_f$** (Pet. ether /EtOAc = 50/50): 0.43; **$^1$H NMR (400 MHz, CDCl$_3$)** $\delta_H$ 7.58 (s, 6H ), 7.46 (s, 1H ), 7.33 (s, 10H), 7.10-7.05 (m, 2H), 6.97-6.96 (m, 1H), 6.65 (d, $J$ = 8.07 Hz, 1H), 5.33 (s, 1H), 3.19 (s, 3H). **$^{13}$C NMR (400 MHz, CDCl$_3$)** $\delta_C$ 177.76, 148.60 (d, $J$ = 19.31 Hz), 142.59, 136.98 (d, $J$ = 14.55 Hz), 134.97, 133.16, 132.42 (d, $J$ = 8.17 Hz), 128.49 (d, $J$ = 14.52 Hz), 128.18, 127.7 (d, $J$ = 12.07 Hz), 124.92, 108.90, 80.81, 29.80, 26.68. **HRMS** calculated $[M+H]^+$ for $C_{33}H_{25}ClNO_2P$: 534.1384, found: 534.1387. **FTIR (cm$^{-1}$)**

3828.81, 3743.96, 3678.79, 3648.67, 3620.47, 3057.57, 1720.67, 1646.99, 1608.88, 1480.69, 1428.16, 1349.61, 1264.32, 1236.13, 1190.05, 1106.64, 1037.75, 958.20, 897.82, 855.42, 809.80, 729.43, 698.62.

**5'-Fluoro-1'-methyl-1,1,1-triphenyl-1*H*-λ$^5$-spiro[benzo[*c*][1,2]oxaphosphole-3,3'-indolin]-2'-one (38g)**

Following the general procedure, treatment of triphenylphosphine **37a** (0.132 g, 0.5 mmol) and 5-fluoro-1-methylindoline-2,3-dione **33g** (0.147 g, 0.75 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **18a** (0.224 g, 182 µL, 1.5 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at 70 °C for 20 h followed by silica gel flash column chromatography (Pet. ether/EtOAc = 50/50) of the crude reaction mixture afforded 5'-fluoro-1'-methyl-1,1,1-triphenyl-1*H*-λ$^5$-spiro[benzo[*c*][1,2]oxaphosphole-3,3'-indolin]-2'-one **38g** as a yellow solid (0.225 g, 87%).

***R*$_f$** (Pet. ether /EtOAc = 50/50): 0.41; **$^1$H NMR (400 MHz, CDCl$_3$)** $\delta_H$ 7.58 - 7.55 (m, 6H), 7.46 (t, *J* = 14.38, 1H), 7.33-7.27 (m, 10H), 7.06 (t, *J* = 19.98, 1H), 6.96 (dd, $J_1$ = 7.10, $J_2$ = 1.83, 1H), 6.81 - 6.76 (m, 1H), 6.66 - 6.63 (m, 1H), 5.18 (s, 1H), 3.20 (s, 3H) **$^{13}$C NMR (400 MHz, CDCl$_3$)** $\delta_C$ 177.81, 160.46, 158.07, 148.67 (d, *J* = 18.83), 139.86, 136.93 (d, *J* = 14.54), 134.86 (d, *J* = 6.84), 133.07, 132.37, 128.35 (d, *J* = 14,52), 127.63 (d, *J* = 9.25), 114.86 (d, *J* = 22.86), 112.30 (d, *J* = 25.59), 108.28, 29.70, 26.62. **HRMS** calculated $[M+H]^+$ for $C_{33}H_{25}FNO_2P$: 518.1680, found: 518.1677. **FTIR (cm$^{-1}$)** 3783.64, 3695.04, 3006.70, 2361.31, 1718.96, 1618.80, 1490.29, 1441.07, 1353.86, 1266.60, 1220.07, 1113.03, 910.78, 771.59, 741.51, 696.64, 665.19.

**1',5,6-Trimethyl-1,1,1-triphenyl-1*H*-1λ$^5$-spiro[benzo[*c*][1,2]oxaphosphole-3,3'-indolin]-2'-one (38h)**

Following the general procedure, treatment of 4,5-dimethyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **18b** (0.245 g, 0.75 mmol) and 1-methylindoline-2,3-dione **33a** (0.120 g, 0.75 mmol) with triphenylphosphine **37a** (0.131 g, 0.50 mmol) in the presence of KF (0.087 g, 1.50 mmol) and 18-crown-6 (0.396 g, 1.50 mmol) in THF (4.0 mL) at

70 ℃ for 20 h followed by silica gel flash column chromatography (Pet. ether/EtOAc = 50/50) of the crude reaction mixture afforded 1',5,6-trimethyl-1,1,1-triphenyl-1*H*-1λ$^5$-spiro[benzo[*c*][1,2]oxaphosphole-3,3'-indolin]-2'-one **38h** as a yellow solid (0.155 g, 59%).

***R*$_f$** (EtOAc): 0.57; **$^1$H NMR (400 MHz, CDCl$_3$)** $\delta_H$ 7.62-7.60 (m, 6H, H), 7.33 (s, 10H, H), 7.13 (t, *J* =7.66 Hz 1H, H), 6.77 (t, *J* = 8.56 Hz, 3H, H), 6.59 (t, *J* = 7.43 Hz, 1H, H), 5.58 (d, *J* = 7.42, 1H, H), 3.26 (s, 3H), 2.23 (s, 3H), 2.15 (s, 3H). **$^{13}$C NMR (400 MHz, CDCl$_3$)** $\delta_C$ 178.39, 147.36 (d, *J* = 20.35 Hz), 144.15, 144.10, 143.10, 142.78 (d, *J* = 3.20 Hz), 143.50 (d, *J* = 14.81 Hz), 136.99 (d, *J* = 14.88 Hz), 133.61, 132.40 (d, *J* = 9.11 Hz), 128.63, 128.05 (d, *J* = 1.71 Hz), 127.43 (d, *J* = 12.60 Hz), 126.13, 125.00 (d, *J* = 16.30 Hz), 124.74, 124.35, 122.87, 107.91, 80.86, 26.54, 20.35, 20.08. **HRMS** calculated [M+H] $^+$ for $C_{35}H_{30}NO_2P$: 528.2087, found: 528.2096. **FTIR (cm$^{-1}$)** 3783, 3695, 3663, 2927, 2361, 1718, 1608, 1473, 1440, 1355, 1219, 1112, 771, 740, 696, 668.

**1-Methyl-1',1',1'-triphenyl-1'*H*-1'1λ$^5$-spiro[indoline-3,3' [1,3]dioxolo[4',5':4,5] benzo [1,2-*c*][1,2]oxaphosphol]-2-one (38i)**

Following the general procedure, treatment of triphenylphosphine **37a** (0.132 g, 0.5 mmol) and 1-methylindoline-2,3-dione **33a** (0.121 g, 0.75 mmol) with 6-(trimethylsilyl)benzo[d][1,3]dioxol-5-yl trifluoromethanesulfonate **18c** (0.256 g, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (4.0 mL) at 70 ℃ for 20 h followed by silica gel flash column chromatography (Pet. ether/EtOAc = 50/50) of the crude reaction mixture afforded 1-methyl-1',1',1'-triphenyl-1'*H*-1'1λ$^5$-spiro[indoline-3,3' [1,3]dioxolo[4',5':4,5] benzo [1,2-*c*][1,2]oxaphosphol]-2-one **(38i)** as a yellow solid (0.165 g, 61%).

***R*$_f$** (Pet. ether /EtOAc = 50/50): 0.61; **$^1$H NMR (500 MHz, CDCl$_3$)** $\delta_H$ 7.58-7.55 (m, 6H), 7.30 (s, 9H), 7.09 (t, *J* = 7.63 Hz, 1H), 6.72 (d, *J* = 7.78 Hz, 1H), 6.56 (t, *J* = 7.41 Hz, 1H), 6.36-6.31 (m, 2H), 5.97 (d, *J* = 3.62 Hz, 2H), 5.56 (d, *J* = 5.10 Hz, 1H), 3.20 (s, 3H), **$^{13}$C NMR (500 MHz, CDCl$_3$)** $\delta_C$ 177.83, 152.40, 148.60 (d, *J* = 22.87 Hz), 145.40 (d, *J* = 22.21 Hz), 143.96, 132.95, 132.36 (d, *J* = 8.83 Hz), 128.93, 128.24, 127.57 (d, *J*

= 12.55 Hz), 124.35, 123.02, 114.86 (d, *J* = 19.77 Hz), 108.08, 103.64, 102.52, 80.95, 26.56. **HRMS** calculated $[M+H]^+$ for $C_{34}H_{26}NO_4P$: 544.1677, found: 544.1672. **FTIR ($cm^{-1}$)** 3779.56, 3715.24, 3008.56, 2359.51, 1716.91, 1610.02, 1470.99, 1434.96, 1369.28, 1261.78, 1220.23, 1113.21, 1042.17, 998.75, 940.65, 911.00, 841.60, 770.08, 740.67, 698.14, 664.89, 628.77.

**5,6-Difluoro-1'-methyl-1,1,1-triphenyl-1*H*-1λ$^5$-spiro[benzo[*c*][1,2]oxaphosphole-3,3'-indolin]-2'-one (38j)**

Following the general procedure, treatment of 4,5-difluoro-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **18d** (0.251 g, 0.75 mmol) and 1-methylindoline-2,3-dione **33a** (0.120 g, 0.75 mmol) with triphenylphosphine **37a** (0.131 g, 0.50 mmol) in the presence of KF (0.087 g, 1.50 mmol) and 18-crown-6 (0.396 g, 1.50 mmol) in THF (4.0 mL) at 70 °C for 20 h followed by silica gel flash column chromatography (Pet. ether/EtOAc = 50/50) of the crude reaction mixture afforded 5,6-difluoro-1'-methyl-1,1,1-triphenyl-1*H*-1λ$^5$-spiro[benzo[*c*][1,2]oxaphosphole-3,3'-indolin]-2'-one **38j** as a white solid (0.179 g, 63% yield).

***R*$_f$** (Pet. ether /EtOAc = 50/50): 0.48; **$^1$H NMR (400 MHz, $CDCl_3$)** $\delta_H$ 7.59-7.54 (m, 6H, $H_{ar}$), 7.33 (bs, 9H, H), 7.14-7.10 (m, 1H, H), 6.82-6.71 (m, 3H, H), 6.58 (t, *J* = 7.6 Hz, 1H, H), 5.51 (d, *J* = 6.7 Hz, 1H, H), 3.22 (s, 3H, $CH_3$). **$^{13}$C NMR (400 MHz, $CDCl_3$)** $\delta_C$ 172.21, 153.75 (dd, $J_1$ = 14.1 Hz, $J_2$ = 259.01), 150.39 (dd, $J_1$ = 14.7 Hz, $J_2$ = 249.7), 149.14-148.79 (m), 143.92, 143.27, 142.21, 132.18 (d, *J* = 9.1 Hz), 132.13, 129.29, 128.56, 127.75 (d, *J* = 12.5 Hz), 124.98-124.60 (m), 124.28, 123.17, 112.59-112.20 (m), 108.29, 80.38, 26.62. **HRMS** calculated $[M+H]^+$ for $C_{33}H_{24}F_2NO_2P$: 536.1585, found: 536.1588. **FTIR ($cm^{-1}$)** 3894, 3861, 3744, 3678, 3648, 3619, 2927, 2362, 1836, 1741, 1693, 1647, 1547, 1516, 1643, 1426, 1215, 742, 669.

**1-Methyl-3',3',3'-triphenyl-3'H-3'1λ$^5$-spiro[indoline-3,1'-naphtho[2,1-c][1,2] oxaphosphol]-2-one (38k)**

Following the general procedure, treatment of 1-(trimethylsilyl)naphthalen-2-yl trifluoromethanesulfonate **18e** (0.261 g, 0.75 mmol) and 1-methylindoline-2,3-dione **33a** (0.120 g, 0.75 mmol) with triphenylphosphine **37a** (0.131 g, 0.50 mmol) in the presence of KF (0.087 g, 1.50 mmol) and 18-crown-6 (0.396 g, 1.50 mmol) in THF (4.0 mL) at 70 °C for 20 h followed by silica gel flash column chromatography (Pet. ether/EtOAc = 50/50) of the crude reaction mixture afforded 1-methyl-3',3',3'-triphenyl-3'*H*-3'λ$^5$-spiro[indoline-3,1'-naphtho[2,1-*c*][1,2]oxaphosphol]-2-on **38k** as a yellow solid (0.135 g, 49% yield).

***R*$_f$** (Pet. ether /EtOAc = 50/50): 0.55; **$^1$H NMR (500 MHz, CDCl$_3$)** $\delta_H$ 7.87 (d, *J* = 8.25, H), 7.79-7.75 (m, 1H, H), 7.28 (s, 10 H, H), 7.21-7.19 (m, 1H, H), 7.14-7.09 (m, 2H, H), 6.83 (d, *J* =7.77 Hz 1H, H), 6.47 (t, *J* = 7.37 Hz, 1H, H), 5.60 (d, *J* = 6.44 Hz, 1H, H), 3.33 (s, 3H). **$^{13}$C NMR (500 MHz, CDCl$_3$)** $\delta_C$ 176.51, 147.25, 147.04, 144.80, 143.94, 143.75, 135.86 ( d, *J* = 2.20 Hz), 132.89, 132.42 (d, *J* = 8.69), 130.64 (d, *J* = 15.73), 129.32 (d, *J* = 14.90), 128.97, 128.68, 128.11 (d, *J* = 5.06), 127.55 (d, *J* = 12.32), 127.35, 124.46., 124.05, 122.98, 108.51, 80.54. 26.71. **HRMS** calculated $[M+H]^+$ for $C_{37}H_{28}NO_2P$: 550.1930, found: 550.1942. **FTIR (cm$^{-1}$** 3055, 1738, 1609, 1468, 1366, 1329, 1252, 1185, 1088, 1025, 855, 814, 696, 651.

**1'-methyl-1,1,1-tri-p-tolyl-1*H*-1λ$^5$-spiro[benzo[*c*][1,2]oxaphosphole-3,3'-indolin]-2'-one (38l)**

Following the general procedure, treatment of tristri-p-tolylphosphine **37b** (0.152 g, 0.5 mmol) and 1-methylindoline-2,3-dione **33a** (0.121 g, 0.75 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **18a** (0.224 g, 182 µL, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (4.0 mL) at 70 °C for 20 h followed by silica gel flash column chromatography (Pet. ether/EtOAc = 50/50) of the crude reaction mixture afforded 1'-methyl-1,1,1-tri-p-tolyl-1*H*-1λ$^5$-spiro[benzo[*c*][1,2]oxaphosphole-3,3'-indolin]-2'-one **38l** as a yellow solid (0.181 g, 67%).

***R*f** (Pet. ether /EtOAc = 50/50): 0.55; **$^1$H NMR (400 MHz, CDCl$_3$)** $\delta_H$ 7.49-7.38 (m, 7H), 7.28-7.25 (m, 1H), 7.12-7.03 (m, 1H), 6.95 (dd, $J_1$=1.85, $J$2=7.30), 1H), 6.74 (d, $J$ = 7.73 Hz, 1H), 6.55 (t, $J$ = 7.50 Hz, 1H), 5.54 (d, $J$ = 7.33 Hz, 1H), 3.22 (s, 3H), 2.35 (s, 9H), **$^{13}$C NMR (400 MHz, CDCl$_3$)** $\delta_C$ 178.27, 149.33 (d, $J$ = 20.35 Hz), 144.04, 140.85, 139.80, 137.82, 136.79 (d, $J$ = 14.71 Hz), 133.65, 132.70 (d, $J$ = 2.75 Hz), 132.42 (d, $J$ = 9.53 Hz), 128.59, 128.09 (d, $J$ = 13.03 Hz), 127.92, 124.39, 124.05 (d, $J$ = 15.29 Hz), 122.73, 107.83, 80.91, 26.47, 21.36. **HRMS** calculated $[M+H]^+$ for $C_{36}H_{32}NO_2P$: 542.2243, found: 542.2239. **FTIR (cm$^{-1}$)** 2919.98, 1716.86, 1609.59, 1468.51, 1344.79, 1222.69, 1190.27, 1109.91, 1042.12, 773.47, 735.48, 689.39, 659.58, 637.56, 615.06.

**1,1,1-Tris(4-methoxyphenyl)-1'-methyl-1*H*1λ$^5$spiro[benzo[*c*][1,2]oxaphosphole-3,3'-indolin]-2'-one (38m)**

Following the general procedure, treatment of tris(4-methoxyphenyl)phosphine **37c** (0.176 g, 0.5 mmol) and 1-methylindoline-2,3-dione **33a** (0.121 g, 0.75 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **18a** (0.224 g, 182 µL, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (4.0 mL) at 70 °C for 20 h followed by silica gel flash column chromatography (Pet. ether/EtOAc = 50/50) of the crude reaction mixture afforded 1,1,1-tris(4-methoxyphenyl)-1'-methyl-1*H*1λ$^5$spiro[benzo[*c*][1,2]oxaphosphole-3,3'-indolin]-2'-one **38m** (0.191 g, 65%).

***R*f** (EtOAc): 0.62; **$^1$H NMR (400 MHz, CDCl$_3$)** $\delta_H$ 7.49-7.38 (m, 7H), 7.27-7.24 (m, 1H), 7.09 (t, $J$ = 7.67 Hz, 1H), 7.03-6.98 (m, 1H), 6.94-6.92 (m, 1H), 6.83-6.81 (m, 6H), 6.74 (d, $J$ = 7.70 Hz, 1H) 6.58 (t, $J$ = 7.55 Hz, 1H), 5.63 (d, $J$ = 7.28 Hz, 1H), 3.80 (s, 9H), 3.21 (s, 3H),**$^{13}$C NMR (400 MHz, CDCl$_3$)** $\delta_C$ 178.52, 159.39, 149.27 (d, $J$ = 20.20 Hz), 144.08, 136.81 (d, $J$ = 14.80 Hz), 134.10 (d, $J$ = 10.75 Hz), 133.79, 132.79, 128.69, 128.08 (d, $J$ = 14.50 Hz), 124.41, 124.12 (d, $J$ = 12.95 Hz), 122.97, 112.88 (d, $J$ = 13.84 Hz), 107.96, 80.92, 55.32, 26.54. **HRMS** calculated $[M+H]^+$ for $C_{36}H_{32}NO_5P$: 590.2091, found: 590.2095. **FTIR (cm$^{-1}$)** 3878.48, 3740.05, 3054.18, 2938.99, 2838.33, 1713.85, 1596.79, 1497.73, 1464.89, 1351.16, 1253.47, 1182.60, 1113.51, 1076.71, 1030.61, 957.49, 832.96, 799.70, 730.30

**1'-methyl-1,1-diphenyl-1-(p-tolyl)-1H-1λ$^5$-spiro[benzo[c][1,2]oxaphosphole-3,3'-indolin]-2'-one (38n)**

Following the general procedure, treatment of diphenyl(p-tolyl)phosphine **37d** (0.138 g, 0.5 mmol) and 1-methylindoline-2,3-dione **33a** (0.121 g, 0.75 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **18a** (0.224 g, 182 µL, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (4.0 mL) at 70 °C for 20 h followed by silica gel flash column chromatography (Pet. ether/EtOAc = 50/50) of the crude reaction mixture afforded 1'-methyl-1,1-diphenyl-1-(p-tolyl)-1*H*-1λ$^5$-spiro[benzo[*c*][1,2]oxaphosphole-3,3'-indolin]-2'-one **38n** as a yellow solid (0.167 g, 65%).

***R*$_f$** (Pet. ether /EtOAc = 50/50): 0.58; **$^1$H NMR (400 MHz, CDCl$_3$)** $\delta_H$ 7.56-7.40(m, 7H), 7.36-7.24 (m, 7H), 7.12-7.01 (m, 4H), 6.96-6.94 (m, 1H), 6.74 (d, *J* = 7.72 Hz, 1H), 6.54 (t, *J* = 7.47 Hz, 1H), 5.53 (s, 1H), 3.21 (s, 3H), 2.34 (s, 3H), **$^{13}$C NMR (400 MHz, CDCl$_3$)** $\delta_C$ 178.11, 149.42 (d, *J* = 20.02 Hz), 144.08, 136.87 (d, *J* = 14.57 Hz), 133.43, 132.93, 132.70 (d, *J* = 9.22 Hz), 132.36 (t, *J* = 9.03 Hz), 128.79, 128.73, 128.23 (t, *J* = 10.17 Hz), 127.55 (d, *J* = 11.43 Hz), 125.45, 124.35, 122.90, 108.80, 107.98, 80.98, 26.55, 21.41. **HRMS** calculated $[M+H]^+$ for $C_{34}H_{28}NO_2P$: 514.1930, found: 514.1930. **FTIR (cm$^{-1}$)** 3782.97, 3695.37, 3008.44, 2361.21, 1716.90, 1608.67, 1472.41, 1440.11, 1349.00, 1220.20, 1111.58, 1039.61, 958.09, 848.23, 771.60, 743.18, 696.68, 665.36.

**1'-methyl-1,1,1-triphenyl-1*H*-1λ$^5$-spiro[benzo[*c*][1,2]oxarsole-3,3'-indolin]-2'-one (38o)**

Following the general procedure, treatment of triphenylarsine (0.153 g, 0.5 mmol) and 1-methylindoline-2,3-dione **33a** (0.121 g, 0.75 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **18a** (0.223 g, 182 µL, 0.75 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (4.0 mL) at 70 °C for 20 h followed by silica gel flash column chromatography (Pet. ether/EtOAc = 50/50) of

the crude reaction mixture afforded 1'-methyl-1,1,1-triphenyl-1*H*-1λ$^5$-spiro[benzo[*c*][1,2]oxarsole-3,3'-indolin]-2'-one **38o** as a yellow solid (0.167 g, 62%).
***R*$_f$** (EtOAc): 0.42; **$^1$H NMR (400 MHz, CDCl$_3$)** $\delta_H$ 7.65 (d, *J* = 5.39 Hz, 6H), 7.43-7.36 (m, 10H), 7.29-7.25 (m, 1H), 7.10-7.07 (m, 2H), 7.01 (d, *J* = 7.59 Hz, 1H), 6.75 (d, *J* = 7.69 Hz, 1H), 6.61 (t, *J* = 7.55 Hz, 1H), 5.88 (d, *J* = 7.34 Hz, 1H) 3.22 (s, 3H), **$^{13}$C NMR (400 MHz, CDCl$_3$)** $\delta_C$ 180.44, 147.91, 144.13, 140.99, 136.38, 133.64, 132.75, 132.53, 129.38, 128.45, 128.23, 128.20, 126.56, 125.81, 123.98, 122.81, 107.86, 80.85, 26.48. **HRMS** calculated [M+H] $^+$ for $C_{33}H_{26}A_sNO_2$: 544.1252, found: 544.1256. **FTIR (cm$^{-1}$)** 3893.02, 3860.58, 3843.34,3828.53, 3743.07, 3677.75, 3648.10, 3619.33, 3589.04, 3564.44, 2921.96, 2853.35,1707.49, 1463.83, 1363.37, 1280.47, 1110.56, 745.84, 684.38

**Phenyl(1,1,1,3-tetraphenyl-1,3-dihydro-1λ$^5$-benzo[c][1,2]oxaphosphol-3-yl)methanone (40a)**

Following the general procedure, treatment of triphenylphosphine **37a** (0.132 g, 0.5 mmol) and benzil **39a** (0.158 g, 0.75 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **18a** (0.224 g, 182 µL, 1.5 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at 70 ℃ for 20 h followed by silica gel flash column chromatography (Pet. ether/EtOAc = 80/20) of the crude reaction mixture afforded phenyl(1,1,1,3-tetraphenyl-1,3-dihydro-1λ$^5$-benzo[c][1,2]oxaphosphol-3-yl)methanone **40a** as a white solid (0.140 g, 51%).
***R*$_f$** (Pet. ether /EtOAc = 80/20): 0.53; **$^1$H NMR (400 MHz, CDCl$_3$)** $\delta_H$ 7.85 (dd, *J1* = 7.68, *J2* = 2.42, 1H), 7.72 (d, *J* = 7.87, 2H), 7.61 (t, *J* = 13.77, 1H), 7.35 (d, *J* = 7.01, 2H), 7.31-7.14 (m, 21H), 7.05-6.98 (m, 3H) **$^{13}$C NMR (400 MHz, CDCl$_3$)** $\delta_C$ 199.56, 1552.56 (d, *J* = 20.34), 144.38, 143.61, 142.54, 136.50 (d, *J* = 14.89), 134.81, 133.91 (d, *J* = 3.02), 131.52, 131.31 (d, *J* = 8.82), 131.13, 128.62, 128.46, 128.29, 127.67 (d, *J* = 2.21), 127.53, 127.39, 127.21, 127.06 (d, *J* = 4.78), 126.93, 125.75. 87.54. **HRMS** calculated [M+H] $^+$ for $C_{38}H_{29}O_2P$: 549.1978, found: 549.1976. **FTIR (cm$^{-1}$)** 3782.72, 3009.77, 2360.85, 1668.16, 1590.98, 1486.62, 1441.15, 1222.74, 1177.01, 1107.62, 1068.15, 998.07, 847.16, 771.38, 696.21, 660.16

**Thiophen-2-yl(1,1,1-triphenyl-3-(thiophen-2-yl)-1,3-dihydro-1λ$^5$-benzo[c][1,2] oxaphosphol-3-yl)methanone (40b)**

Following the general procedure, treatment of triphenylphosphine **37a** (0.132 g, 0.5 mmol) and 1,2-di(thiophen-2-yl)ethane-1,2-dione **39b** (0.170 g, 0.75 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **18a** (0.224 g, 182 µL, 1.5 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at 70 °C for 20 h followed by silica gel flash column chromatography (Pet. ether/EtOAc = 80/20) of the crude reaction mixture afforded thiophen-2-yl(1,1,1-triphenyl-3-(thiophen-2-yl)-1,3-dihydro-1λ$^5$-benzo[c][1,2] oxaphosphol -3-yl)methanone **40b** as a white solid (0.118 g, 42%).

***R*$_f$** (Pet. ether /EtOAc = 80/20): 0.61; **$^1$H NMR (400 MHz, CDCl$_3$)** $\delta_H$ 8.14 (dd, J1=7.53, J2=2.31, 1H), 7.84 (d, J=3.14), 7.76 (t, J=13.61, 1H), 7.43-7.37 (m, 8H), 7.32-7.26 (m, 9H), 7.18 (d, J=4.55, 1H), 7.06-7.00 (m, 2H), 6.94-6.91 (m, 1H), 6.81 (t, J=8.66, 1H) **$^{13}$C NMR (400 MHz, CDCl$_3$)** $\delta_C$ 192.14, 151.44, 151.26, 150.79, 142.99, 141.92, 140.38, 136.54, 136.39, 136.12, 133.25, 132.24 (d, J=2.94), 131.54 (d, J=8.82), 128.90 (d, j=15.49), 128.14, 128.03 (d, J=2.00), 127.32 (d, J=12.57), 126.80 (d, J=16.91), 125.55, 124.78, 124.02, 84.99. **HRMS** calculated $[M+H]^+$ for $C_{34}H_{26}O_2PS_2$: 561.1106, found: 561.1097. **FTIR (cm$^{-1}$)** 3829.00, 3743.46, 3678.34, 3620.90, 3067.95, 1949.72, 1890.78, 1822.30, 1709.18, 1650.02, 1582.21, 1508.65, 1482.39, 1434.60, 1408.24, 1350.98, 1310.33, 1279.25, 1242.55, 1159.15, 1116.39, 1072.02, 991.88, 908.01, 851.90, 823.18, 793.75, 759.60, 713.11, 693.29, 665.01.

**Ethyl-1,1,1,3-tetraphenyl-1,3-dihydro-1λ$^5$-benzo[c][1,2]oxaphosphole-3-carboxylate(40c)**

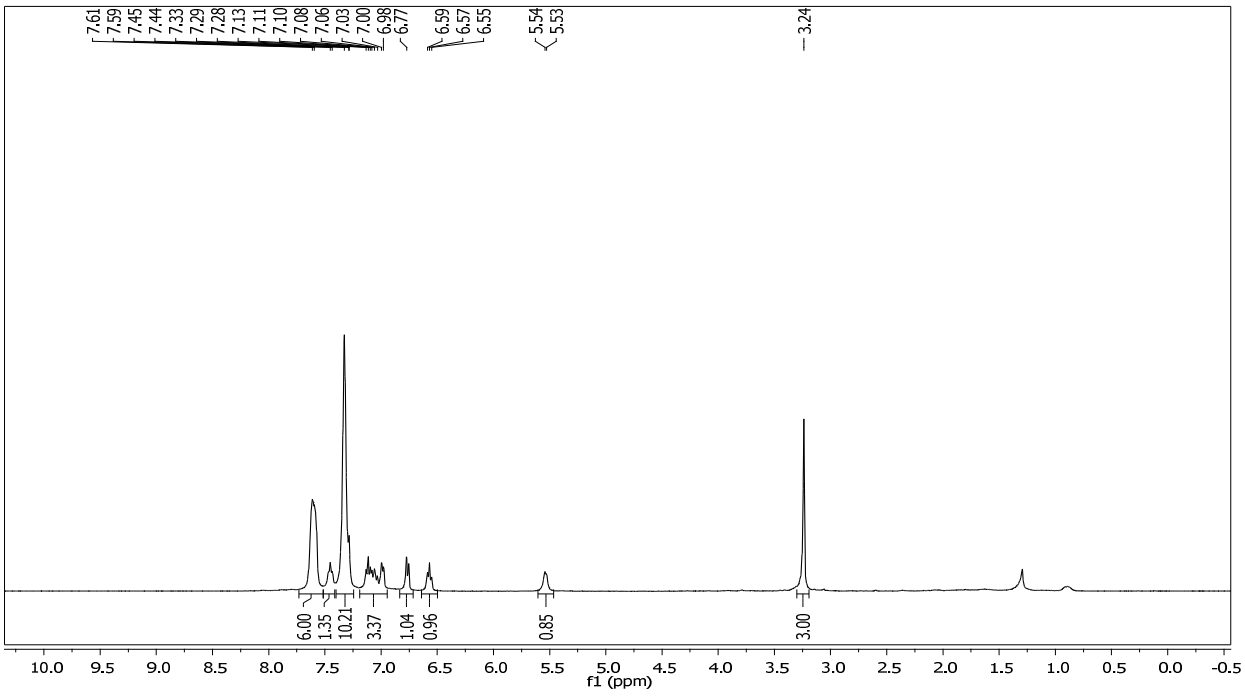
Following the general procedure, treatment of triphenylphosphine **37a** (0.132 g, 0.5 mmol) and ethyl 2-oxo-2-phenylacetate **39c** (0.134 g, 0.75 mmol) with 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **18a** (0.134 g, 182 µL, 1.5 mmol) in the presence of KF (0.087 g, 1.5 mmol) and 18-crown-6 (0.396 g, 1.5 mmol) in THF (2.0 mL) at 70 °C for 20 h followed by silica gel flash column chromatography (Pet.

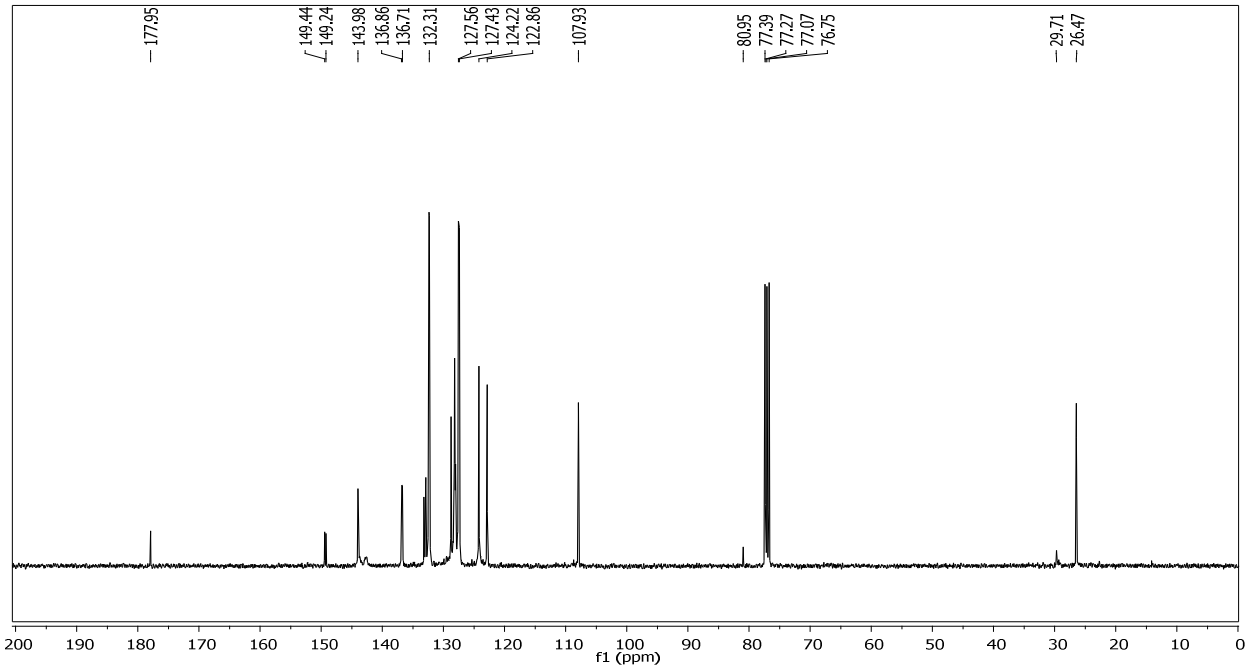
ether/EtOAc = 80/20) of the crude reaction mixture afforded ethyl-1,1,1,3-tetraphenyl-1,3-dihydro-1λ$^5$-benzo[c][1,2]oxaphosphole-3-carboxylate **40c** as a yellow solid (0.149 g, 58%).

***R*$_f$** (Pet. ether /EtOAc = 80/20): 0.56; **$^1$H NMR (400 MHz, CDCl$_3$)** $\delta_H$ 8.07 (d, *J* = 6.59, 1H), 7.74 (t, *J* = 13.30, 1H), 7.46-7.26 (m, 21H), 6.97 (t, *J* = 19.87, 1H), 4.17-4.11 (m, 1H), 3.91-3.86 (m, 1H), 1.222 (t, J = 14.08, 3H). **$^{13}$C NMR (400 MHz, CDCl$_3$)** $\delta_C$ 173.64, 143.56 (d, *J* = 25.84), 142.62, 136.67 (d, *J* = 14.55), 132.21 (d, *J* = 2.83), 131.75 (d, *J* = 8.99), 128.20, 127.99 (t, *J* = 7.32), 127.86, 127.35 (d, *J* = 12.53), 127.10, 126.59, 83.10, 61.46, 14.06. **HRMS** calculated $[M+H]^+$ for $C_{34}H_{29}O_3P$: 517.1927, found: 517.1932. **FTIR (cm$^{-1}$)** 3783.86, 3695.20, 3004.20, 2361.78, 1718.27, 1591.67, 1473.89, 1440.01, 1219.61, 1070.93, 1029.38, 771.56, 742.72, 695.37, 664.09.

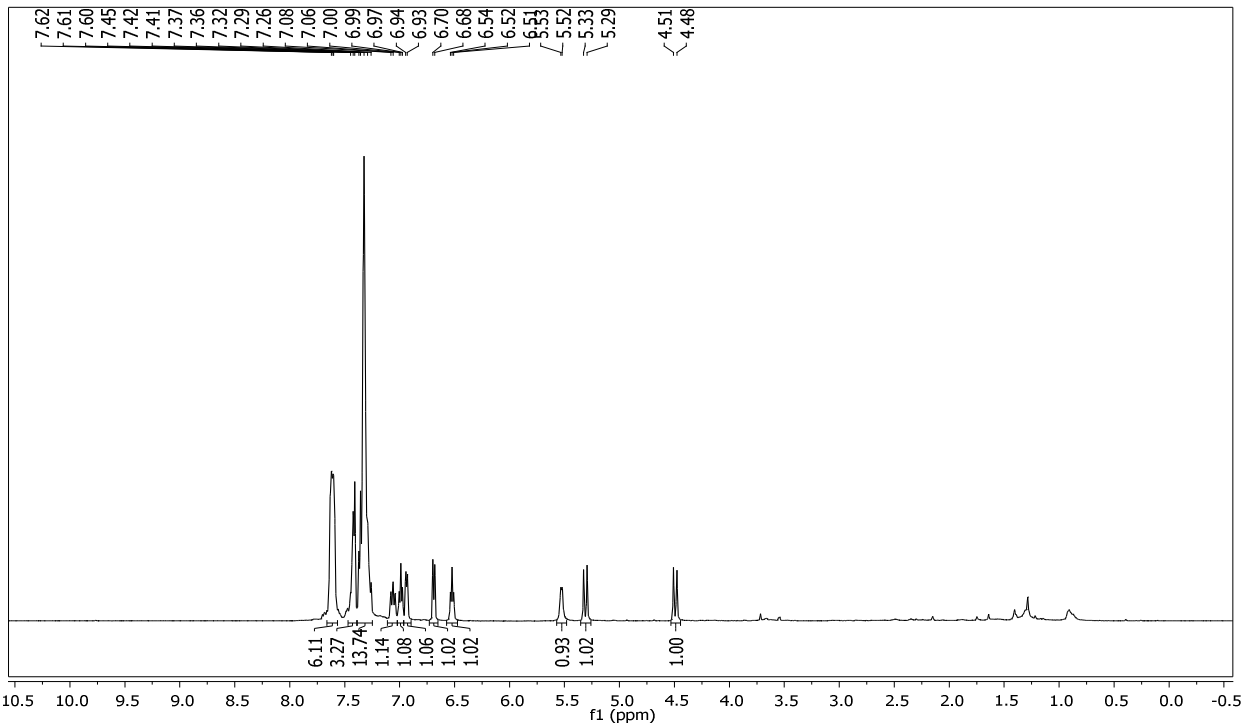
**$^{1}$H and $^{13}$C NMR Spectra of Benzoxophospholes**

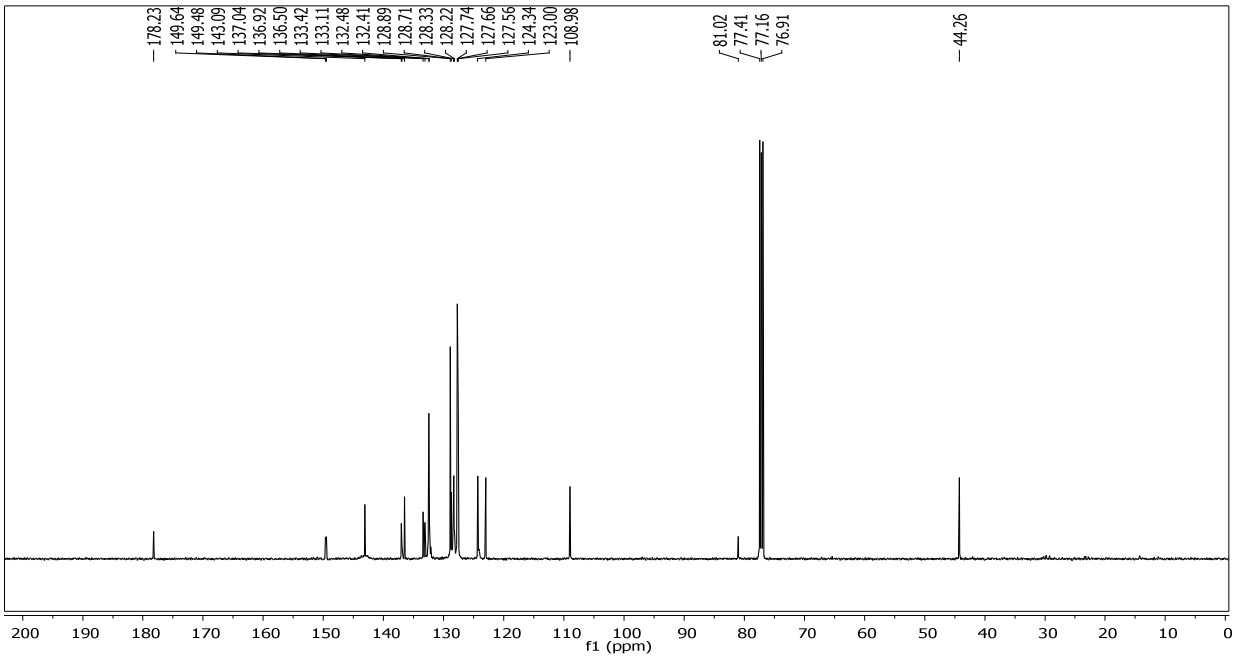
**1'-Methyl-1,1,1-triphenyl-1*H*-1λ$^{5}$-spiro[benzo[*c*][1,2]oxaphosphole-3,3'-indolin]-2'-one (38a)**



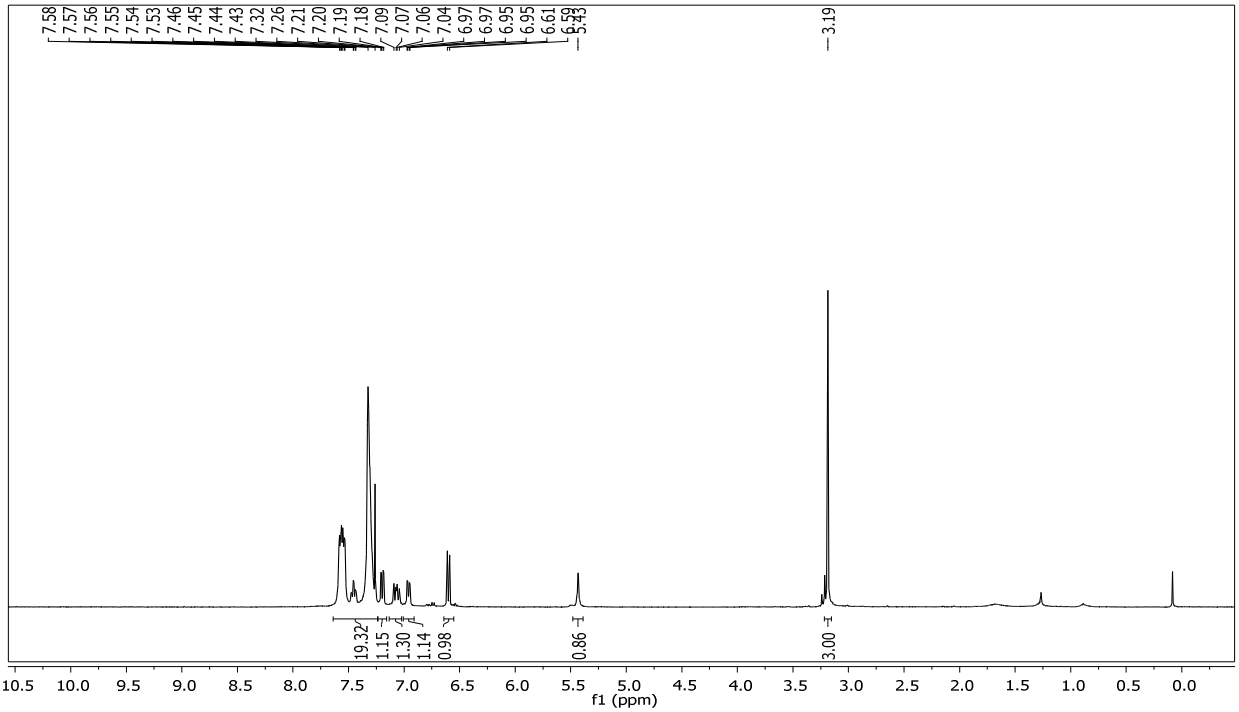


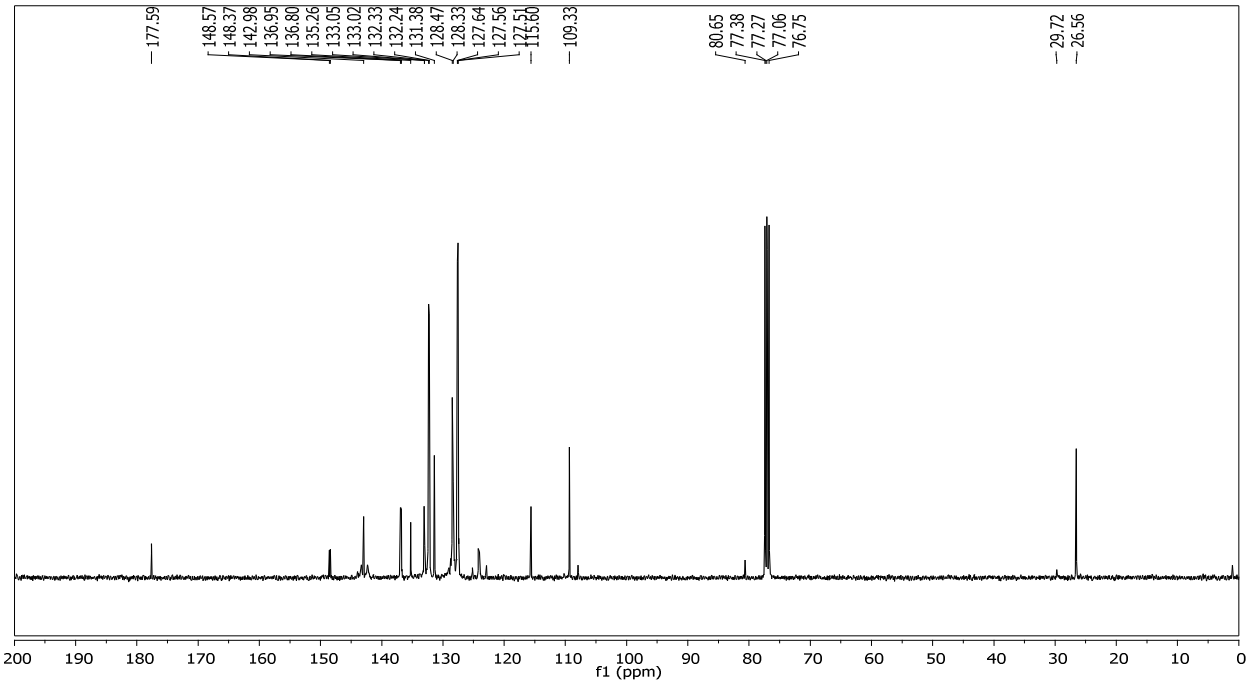

**1'-Benzyl-1,1,1-triphenyl-1*H*-1λ$^5$-spiro[benzo[*c*][1,2]oxaphosphole-3,3'-indolin]-2'-one (38b)**



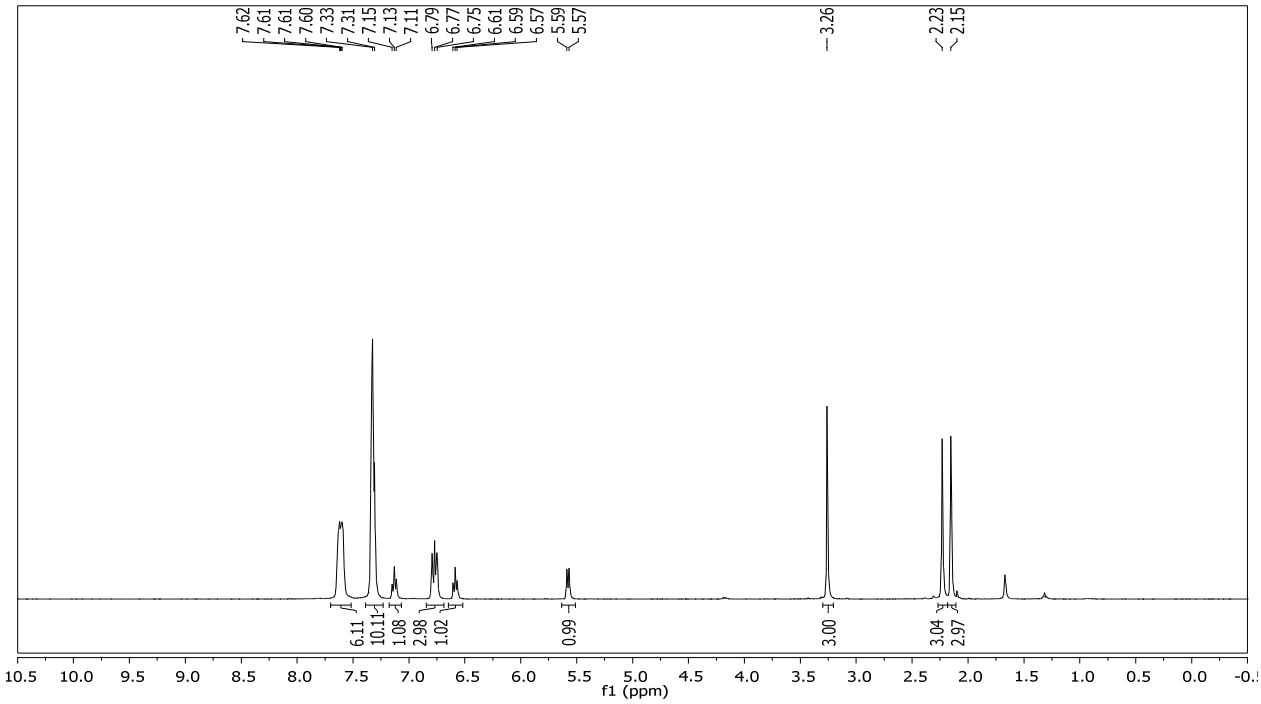



**5'-Bromo-1'-methyl-1,1,1-triphenyl-1*H*-1λ$^5$-spiro[benzo[*c*][1,2]oxaphosphole-3,3'-indolin]-2'-one (38e)**






**1',5,6-Trimethyl-1,1,1-triphenyl-1*H*-1λ$^5$-spiro[benzo[*c*][1,2]oxaphosphole-3,3'-indolin]-2'-one**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7.61
7.60
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7.31
7.15
7.13
7.11
6.79
6.77
6.75
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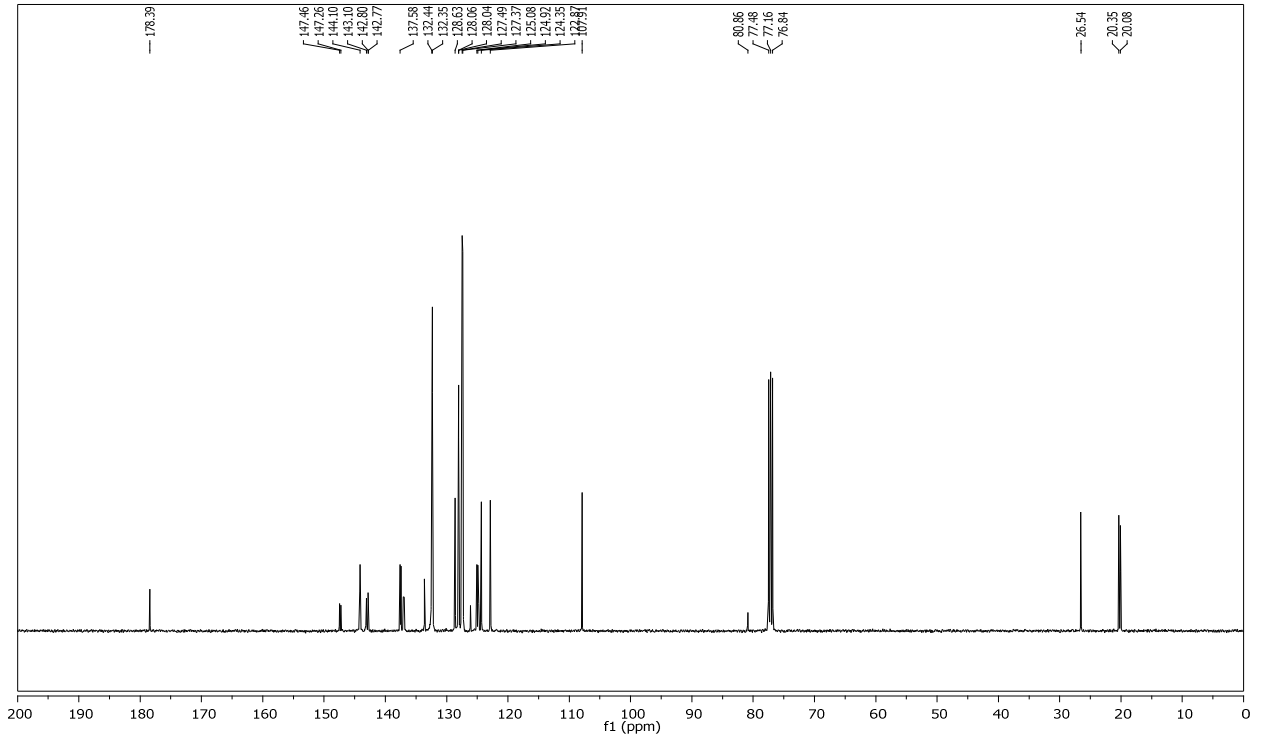
6.59
6.57
5.59
5.57
3.26
2.23
2.15
6.11
10.11
1.08
2.98
1.02
0.99
3.00
3.04
2.97
f1 (ppm)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137.58
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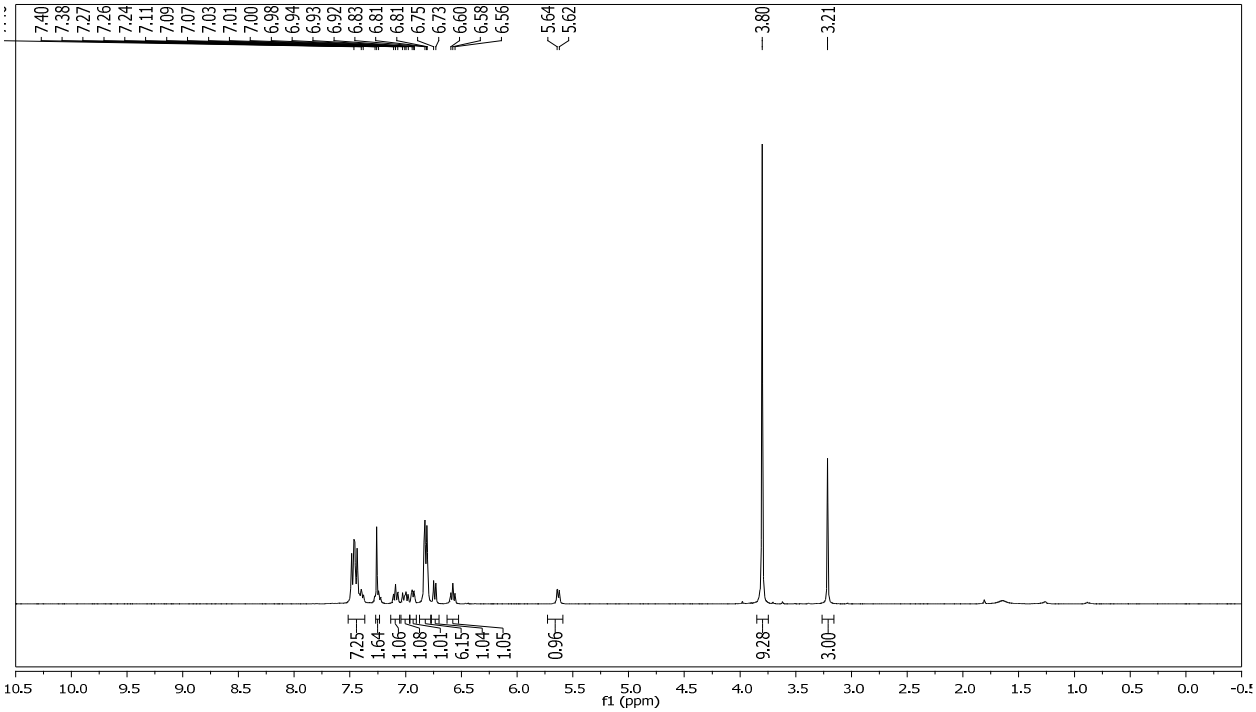
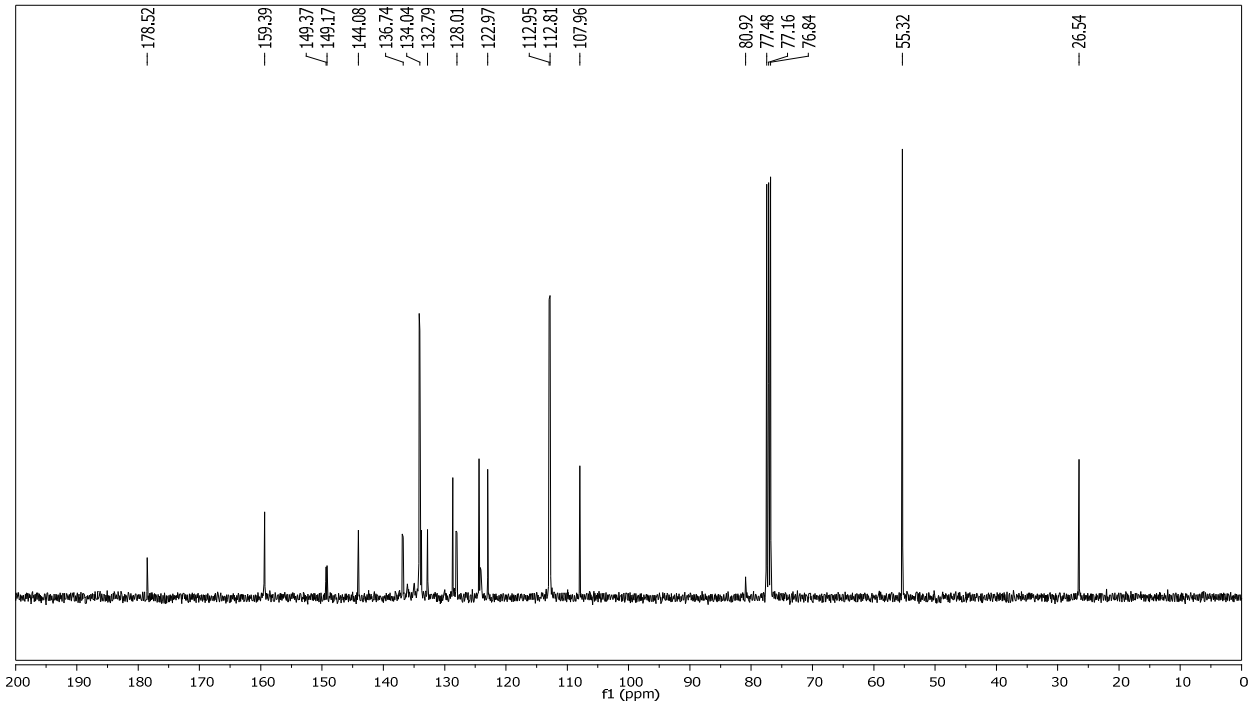
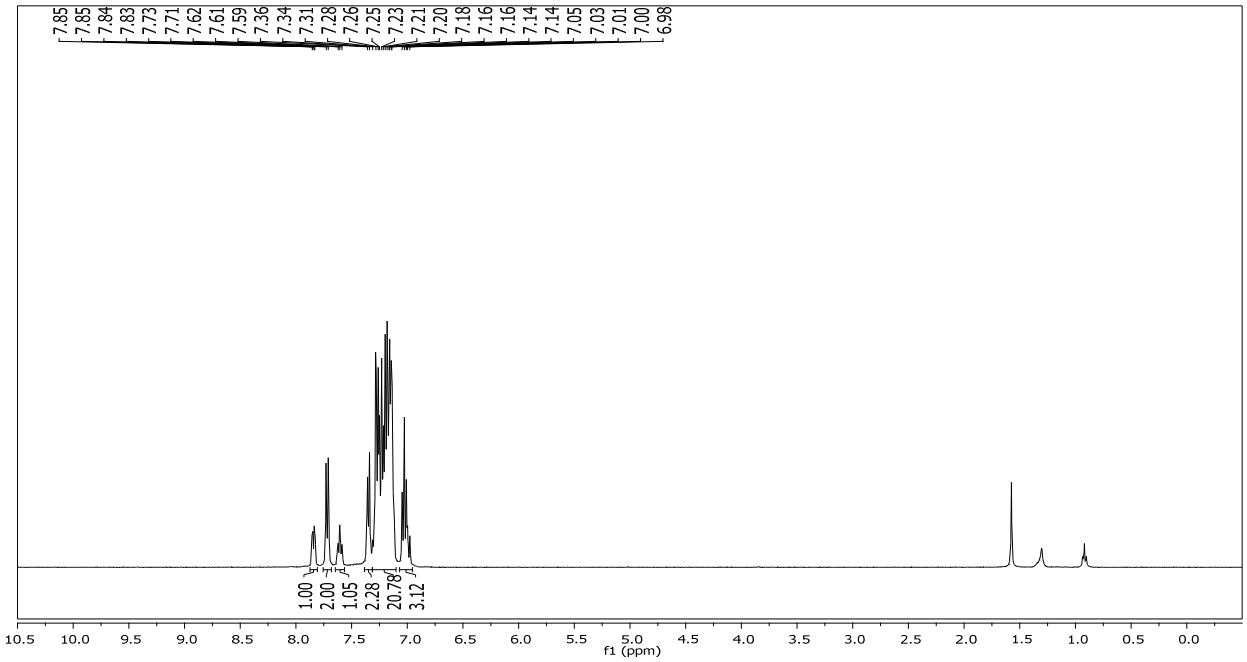
128.04
127.49
127.37
125.08
124.92
124.35
107.91
80.86
77.48
77.16
76.84
26.54
20.35
20.08
f1 (ppm)

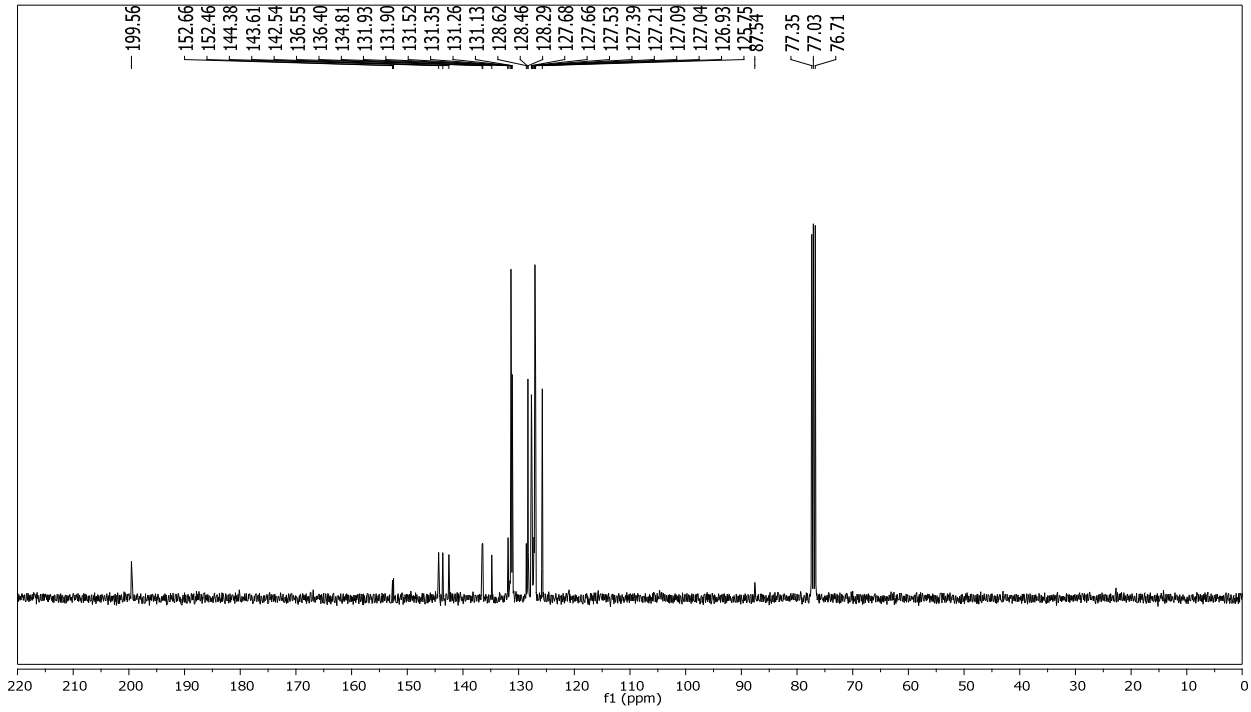
**1,1,1-tris(4-methoxyphenyl)-1'-methyl-1*H*-1λ$^5$spiro[benzo[*c*][1,2]oxaphosphole-3,3'-indolin]-2'-one(38m)**



**Phenyl(1,1,1,3-tetraphenyl-1,3-dihydro-1λ$^5$-benzo[*c*][1,2]oxaphosphol-3-yl)methanone (40a)**



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