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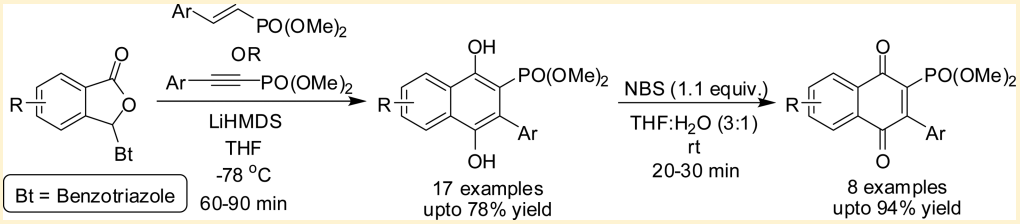
Unsaturated Phosphonates as Hauser Acceptors for the Synthesis of Phosphonylated Dihydroxynaphthalenes and Naphthoquinones

Atul Kumar Chaturvedi and Namrata Rastogi*

Medicinal & Process Chemistry Division, CSIR-Central Drug Research Institute, B.S. 10/1, Sector 10, Jankipuram extension, Sitapur Road, Lucknow 226031, India

Supporting Information



ABSTRACT: The unsaturated phosphonates were utilized as Hauser acceptors successfully for the first time. The products phosphonylated 1,4-dihydroxynaphthalenes were isolated in good yields in short reaction time and were further oxidized to the corresponding 1,4-naphthoquinones in quantitative yields. The reaction provides an efficient and straightforward approach for the synthesis of pharmacologically privileged disubstituted naphthalene-1,4-diols and naphtha-1,4-diones bearing a phosphonate group at the 2-position and various (het)aryl groups at the 3-position.

INTRODUCTION

Hauser−Kraus annulation of 3-(nucleofugal) isobenzofuranones (commonly known as phthalides) with activated multiple bonds is a general method for the synthesis of hydroxylated naphthalenes and naphthoquinones.[1] Both of these moieties are widely distributed in nature and considered privileged structures[2] due to their antibacterial,[3] antifungal,[4] anticancer,[5] antiviral,[6] anti-inflammatory, and antiallergic[7] properties (Figure 1).

The biological properties of these dihydroxynaphthalenes and naphthoquinones can be modulated greatly by varying substituents in the quinone ring. In principal, the substitution at 2- and 3-positions of the 1,4-dihydroxynaphthalene and 1,4-naphthoquinone scaffold can be varied by modifying the Hauser acceptor component in the Hauser−Kraus annulation. Although several first-generation and second-generation Hauser donors are known, the acceptors are usually multiple bonds activated by carbonyl derivatives with only few exceptions.[8] However, to the best of our knowledge, the reactivity of unsaturated phosphonates as Hauser acceptors remains hitherto unexplored.[1b] The reason for failure to employ unsaturated phosphonates as Hauser acceptors so far could be their low electrophilicity, which makes them poor Michael acceptors and hence poor Hauser acceptors.[9] Recently, Han and co-workers reported the synthesis of phosphoryl hydroquinones via 1,4-addition of various P(O)-H compounds to *p*-quinones; however, the reaction demonstrated limited success for the synthesis of phosphorylated naphthoquinones.[10] Our continued interest in phosphonate group chemistry,[11] combined with the fact that the phosphonate group as bioisostere of the carboxylate group[12] influences the pharmacological properties of molecules significantly,[13] prompted us to evaluate the potential of unsaturated phosphonates as Hauser acceptors. Herein, we report the first successful application of unsaturated phosphonates in Hauser−Kraus annulation, yielding phosphonylated dihydroxynaphthalenes and their oxidation to the corresponding naphthoquinones (Scheme 1).

RESULTS AND DISCUSSION

After our initial unsuccessful attempt to utilize common Hauser donors 3-phenylsulfonylphthalide and 3-cyanophthalide with dimethyl styrylphosphonate **2a** as acceptor,[14] the reactivity of 3-benzotriazolylphthalide **1a** as donor[15] was evaluated under the influence of bases commonly employed in Hauser annulation (Table 1). The advantages of using 3-benzotriazolylphthalide as Hauser donor are: (i) it is a simple synthesis as compared to the synthesis of 3-phenylsulfonylphthalides and 3-cyanophthalides, which involves use of KCN or NaCN, and (ii) benzotriazole recovered in the reaction can be reused for the synthesis of starting 3-benzotriazolylphthalide **1**, improving the reaction economy.

Although NaH, LDA, and lithium *tert*-butoxide failed to provide the desired product, NaHMDS could afford the phosphonylated dihydroxynaphthalene product **3a**, albeit in traces (entry 4). However, LiHMDS proved to be a better choice since the reaction using LiHMDS as base yielded product **3a** in 41% yield (entry 5). Further optimization revealed that 2.5 equiv of LiHMDS is the best condition for the

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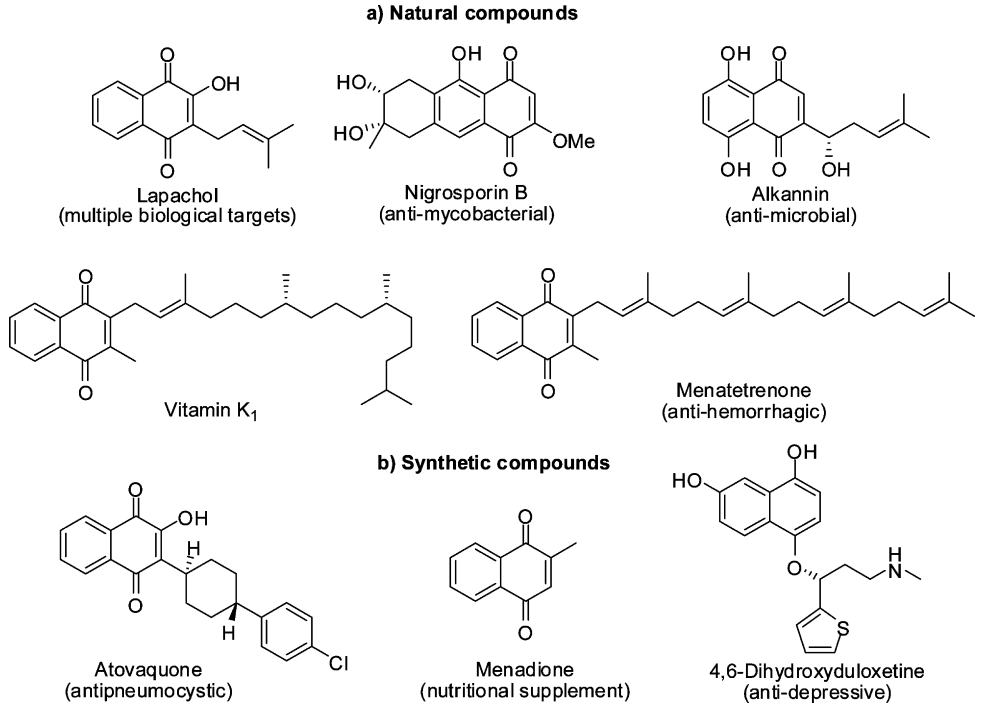
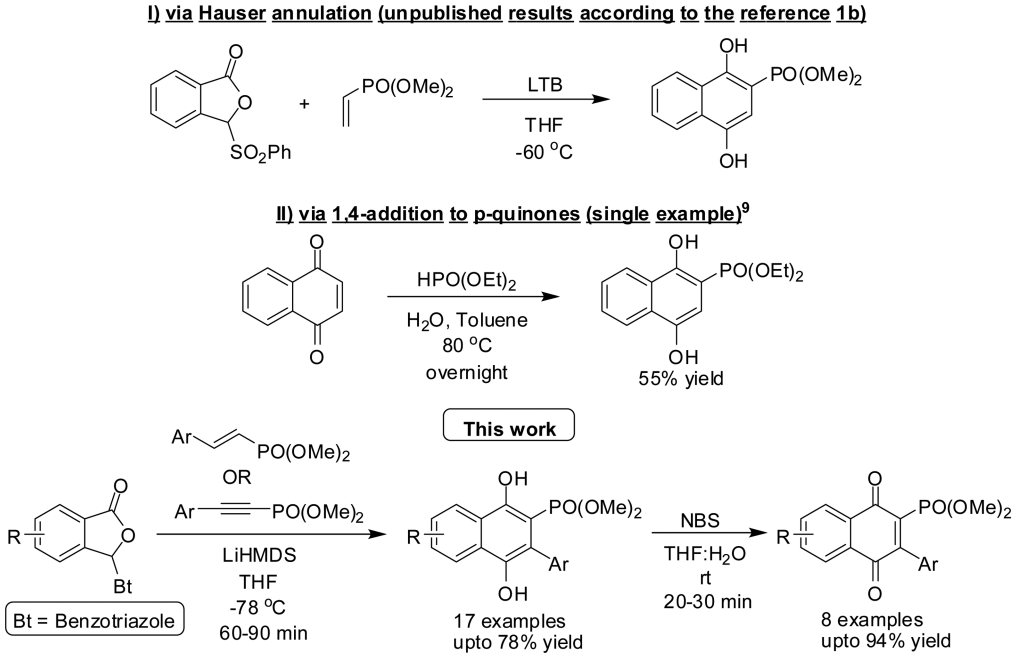


Figure 1. Representative examples of biologically active dihydroxynaphthalene and naphthoquinone.

Scheme 1. Schematic Representation of the Present Work vs Earlier Work



annulation of 3-benzotriazolylphthalide **1a** with styrylphosphonate **2a** (entry 7).

After successfully utilizing styrylphosphonate **2a** in the Hauser annulation, we subjected alkynylphosphonate **4a** to the same reaction conditions for annulation with **1a**, anticipating the isolation of 1,4-naphthoquinone product **5a**. The reaction with **4a** works smoothly under optimized conditions, but the product isolated was characterized to be **3a** instead of **5a** (Scheme 2).

Therefore, in order to access the scope of the reaction in terms of Hauser donor and acceptor components, both styrylphosphonates **2** and alkynylphosphonates **4** were employed for a comparative assessment of their utility in the reaction with 3-benzotriazolylphthalides **1a–d** (Table 2).

The results in Table 2 make following reaction attributes particularly evident: (i) the reactivity of both styrylphosphonates **2** and alkynylphosphonates **4** as Hauser acceptors is essentially the same since both provide the annulation product **3** in comparable yields; (ii) the reaction shows great leeway in terms of the unsaturated phosphonates since both styryl- and alkynylphosphonates with electron-rich as well as electron-poor aromatic or heteroaromatic rings have been successfully used in

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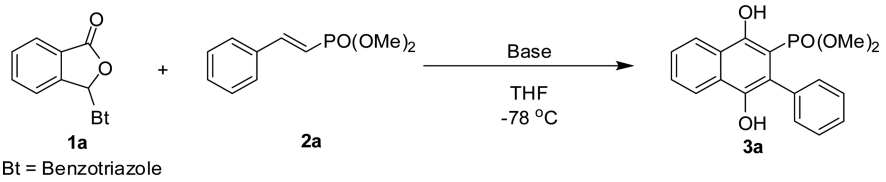
Table 1. Optimization of Reaction Conditions[a]

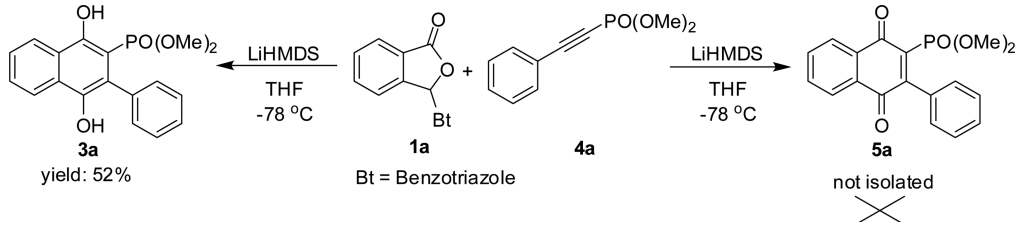


Bt = Benzotriazole

entry	base (equiv)	yield of **3a** (%)[b]
1	NaH (1.5)	no reaction
2	LDA (1.5)	complex mixture
3	LTB (1.5)	complex mixture
4	NaHMDS (1.5)	<10
5	LiHMDS (1.5)	41
6	LiHMDS (2.0)	46
7	LiHMDS (2.5)	56
8	LiHMDS (3.0)	53

[a]All reactions were performed with 1 mmol of **1a**, 1 mmol of **2a** and base in 10 mL of anhyd. THF. [b]Isolated yields.

Scheme 2. Reaction of 1a with Alkynylphosphonate 4a under Optimized Conditions



Bt = Benzotriazole

the reaction; and (iii) the substitution on the Hauser donor component, i.e., phthalide, is less tolerated as compared to the substitutions on the acceptor component, an observation concurrent with earlier reports.[16]

Interestingly, none of the products exhibit tautomerism in solid as well as in solution phase since formation of the corresponding 1,4-dihydroquinones was not detected in any case. This observation suggests that substitution at 2- and 3-positions of 1,4-dihydroxynaphthalenes by phosphonate and aryl groups, respectively, imparts stability to the enolic form over the keto form.[17] While the outcome of annulation of 3-benzotriazolylphthalides **1** with styrylphosphonates **2** can be explained on the basis of the established Hauser−Kraus mechanism initiated by deprotonation of **1** (Figure 2; Eq. I), in order to explain the formation of 1,4-dihydroxynaphthalenes with alkynylphosphonates **4** we invoke the formation of 3-isobenzofuranone anion **A′** (Figure 2; Eq. II).

The LiHMDS assisted generation of 3-isobenzofuranone anion **A** and **A′** is followed by their Michael addition with unsaturated phosphonates **2**/**4** leading to the anions **B** and **B′**, respectively. The phosphonate-stabilized anions **B** and **B′** undergo Dieckmann-like condensation,[18] resulting into the intermediates **C** and **C′** respectively. While intermediate **C** tautomerizes to the final product **3**, the intermediate **C′** undergoes hydrolysis to afford the final product **3**.

Although phosphonylated 1,4-naphthoquinones could not be obtained via the Hauser annulation strategy, they can be synthesized from the corresponding 1,4-dihydroxynaphthalenes **3**.[19] Therefore, we subjected 1,4-dihydroxynaphthalenes **3** to the NBS mediated oxidation for the synthesis of the corresponding 1,4-naphthoquinone products **5** (Table 3).[20] We were pleased to note that the reaction affords phosphonylated 1,4-naphthoquinones **5** in quantitative yields within under 30 min. The mild conditions employed for oxidation tolerated not only the phosphonate group but also various substituents in the aryl rings.

CONCLUSION

To summarize, we successfully employed unsaturated phosphonates as acceptors with 3-benzotriazolylphthalides as donors in the Hauser−Kraus annulation. Both alkenyl- and alkynylphosphonates provided the 1,4-dihydroxynaphthalenes in good yields, which were further oxidized into the corresponding 1,4-naphthoquinones in quantitative yields.

EXPERIMENTAL SECTION

General Information. All reactions were monitored by TLC; visualization was effected with UV and/or by developing in iodine. Chromatography refers to open column chromatography on silica gel (Merck, 100−200 mesh). Melting points were recorded on a Precision melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded as film or a KBr pellet. NMR spectra were recorded at 400 MHz (^{1}H), 100 MHz (^{13}C), and 162 MHz (^{31}P) spectrometers. Chemical shifts are reported in δ (ppm) relative to TMS as the internal standard for ^{1}H and ^{13}C and phosphoric acid as the external standard for ^{31}P. To describe spin multiplicity, standard abbreviations such as s, d, t, q, m, and dd referring to singlet, doublet, triplet, quartet, multiplet, and doublet of doublets respectively, are used. The coupling constants (J) are given in Hz. High-resolution mass spectra were recorded with a Q-TOF microspectrometer using ESI. All reactions were conducted in oven-dried glassware under nitrogen. THF was dried over sodium benzophenone ketyl. The unsaturated phosphonates **2**/**4** were synthesized following the literature protocols.[21] The 3-benzotriazolylphthalide **1a** was synthesized by Katritzki's method,[15] and **1b−d** were synthesized from the corresponding 3-bromophthalides[22] following the procedure described below. The characterization data for all the new compounds have been provided herewith.

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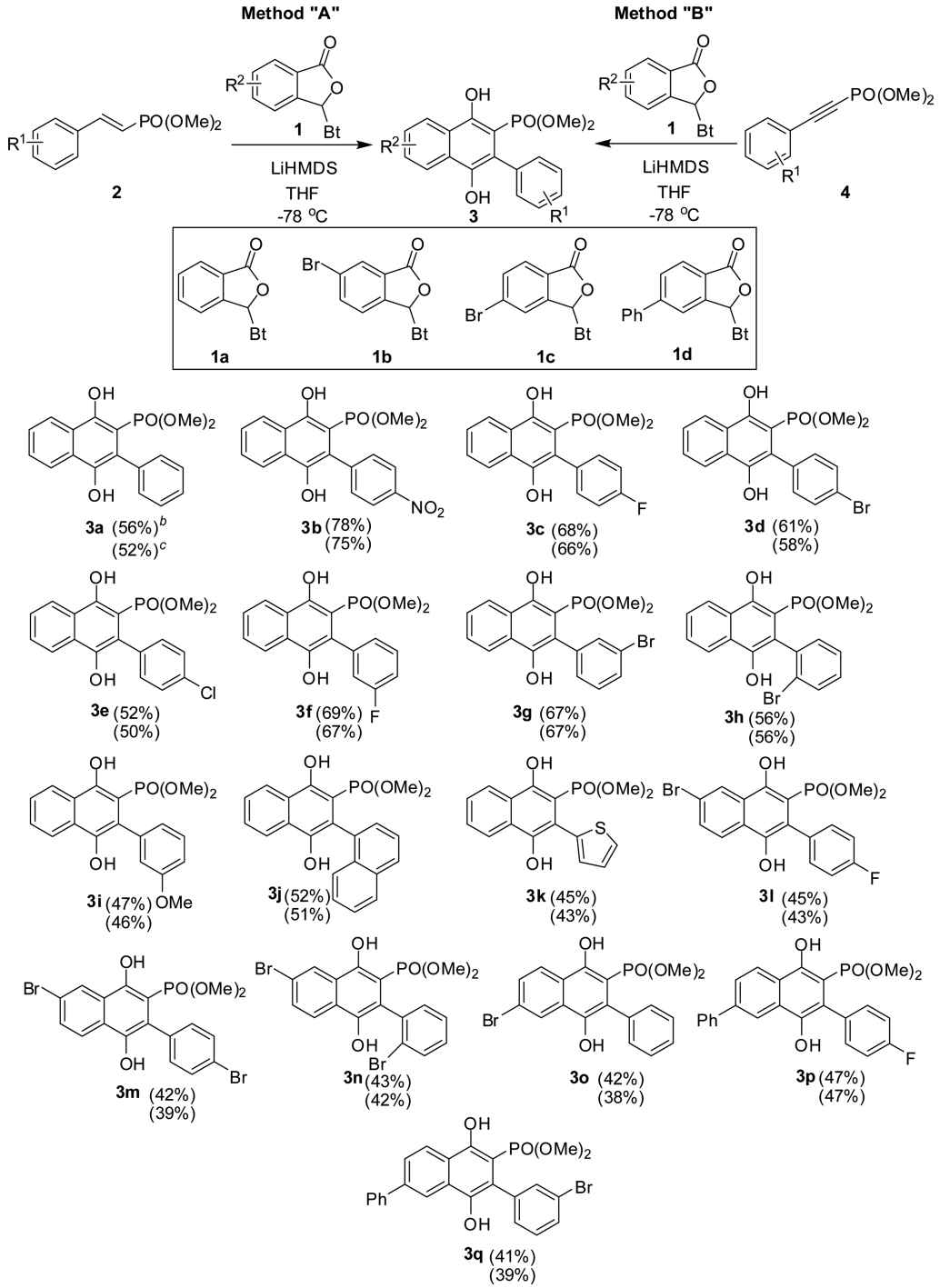
Table 2. Scope of the Reaction[a]



[a]All reactions were performed with 1 mmol of **1**, 1 mmol of **2**/**4**, and 2.5 mmol of LiHMDS in 10 mL of anhyd. THF. [b]Isolated yields by **Method "A"**. [c]Isolated yields by **Method "B"** (same notation is followed for all the cases).

General Procedure for the Synthesis of Benzotriazolylphthalides 1b–d. Triethyl amine (1.7 mL, 12 mmol) was added dropwise into a solution of benzotriazole (1.2 g, 10 mmol) and substituted 3-bromophthalide (10 mmol) in acetonitrile (50 mL) at room temperature. The reaction mixture was stirred until completion of the reaction (45–60 min; TLC monitoring), followed by dilution with water and extraction with ethyl acetate (3 × 25 mL). The combined organic layers were washed with brine (3 × 25 mL), dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by column chromatograpy on silica gel using hexane/ethyl acetate as eluent to afford the corresponding 3-benzotriazolylphthalide **1**.

General Procedure for Hauser–Kraus Annulation. 3-Benzotriazolylphthalide **1** (1 mmol) dissolved in anhydrous THF (10 mL) was added into a solution of LiHMDS (2.5 mL in THF, 2.5 mmol) in anhydrous THF (5 mL) at −78 °C under nitrogen. After 10–15 min of 3-benzotriazolylphthalide addition, unsaturated phosphonate **2**/**4** (1 mmol) was added into the reaction mixture. The reaction upon completion (60–90 min; TLC monitoring) was quenched with 20% aqueous acetic acid (5 mL) at −78 °C. The reaction mixture was further diluted with water (15 mL) and extracted with ethyl acetate (3

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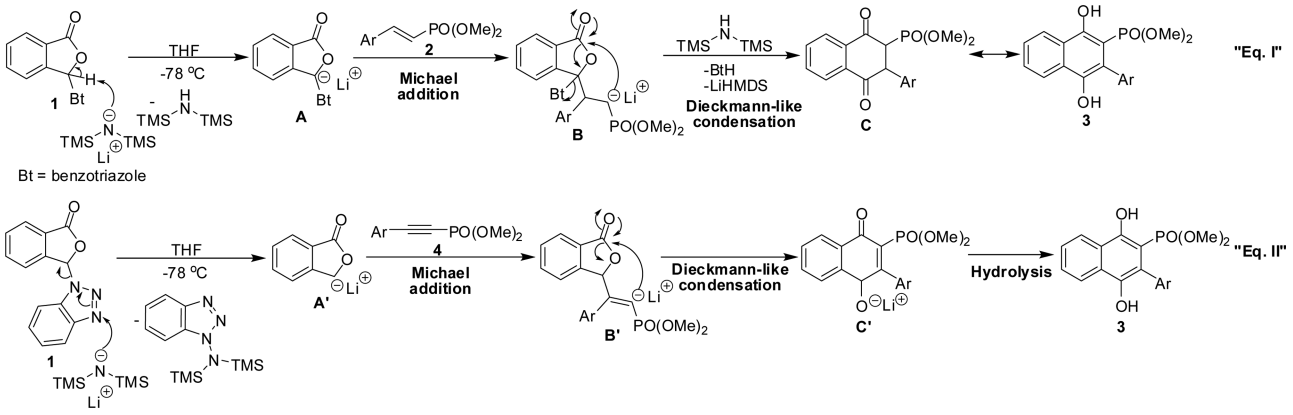
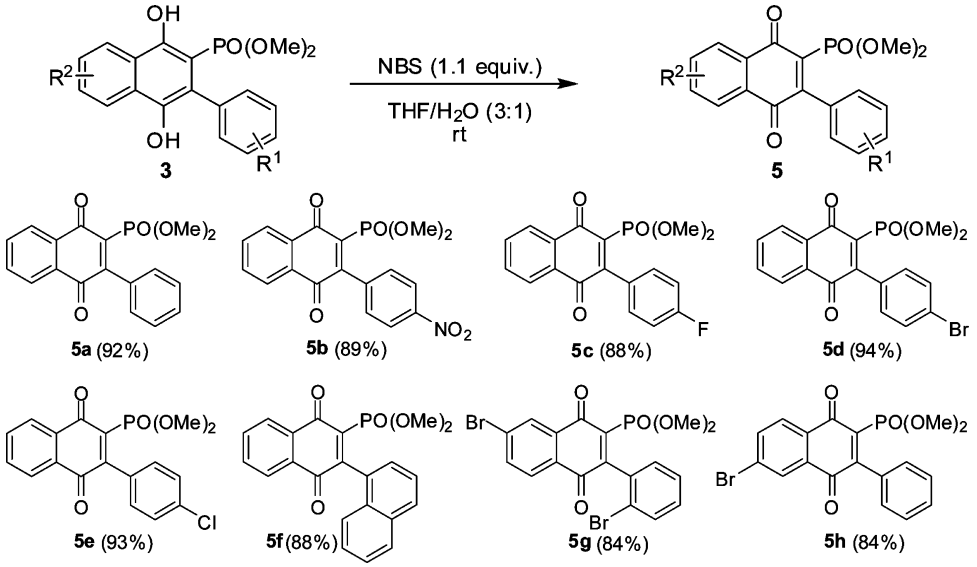


Figure 2. Mechanism of the reaction.

Table 3. Oxidation of 1,4-Dihydroxynaphthalenes 3 to 1,4-Naphthoquinones 5[a]



[a]All reactions were performed with 0.1 mmol of **3** and 0.11 mmol of NBS in 4 mL of THF:H_2O mixture.

× 15 mL). The combined organic layers were washed with brine (3 × 15 mL), dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatograpy on silica gel using hexane/ethyl acetate as eluent to afford product **3**, which was further recrystallized from dichloromethane−hexane (1:4).

General Procedure for Oxidation of 1,4-Dihydroxynaphthalenes 3. To a stirred solution of 1,4-dihydroxynaphthalene **3** (0.1 mmol) in a 3:1 THF:H_2O mixture (4 mL) was added NBS (20 mg, 0.11 mmol), and the reaction mixture was stirred at room temperature until the completion of the reaction (20−30 min; TLC monitoring). The reaction mixture was further diluted with water (15 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with brine (3 × 10 mL), dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel using hexane/ethyl acetate as eluent to afford the pure 1,4-naphthoquinone **5**.

3-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)-6-bromoisobenzofuran-1(3*H*)-one (1b). White solid; yield 66%. R_f 0.50 (30% EtOAc/hexane); mp 181−183 °C; IR (KBr, cm^{-1}): 1060, 1216, 1645, 1794; ^1H NMR (400 MHz, DMSO-d_6) δ 8.48 (s, 1H), 8.35 (d, J = 1.7 Hz, 1H), 8.18−8.21 (m, 1H), 8.13 (dd, J = 8.2 Hz, 1.8 Hz, 1H), 7.78 (d, J = 8.2 Hz, 1H), 7.61−7.65 (m, 1H), 7.50−7.54 (m, 1H), 7.43−7.45 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.7, 146.1, 142.6, 138.8, 132.7, 129.5, 128.8, 128.7, 127.3, 125.7, 125.3, 120.5, 110.8, 84.6; HRMS for $C_{14}H_8BrN_3O_2$: calcd. (MH^+): 329.9873, found: 329.9872.

3-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)-5-bromoisobenzofuran-1(3*H*)-one (1c). White solid; yield 75%. R_f 0.50 (30% EtOAc/hexane); mp 236−238 °C; IR (KBr, cm^{-1}): 1032, 1295, 1580, 1625, 3020, 3427; ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.0 Hz, 1H), 7.66−7.69 (m, 1H), 7.59−7.60 (br m, 1H), 7.53−7.56 (m, 2H), 7.35−7.45 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.0, 150.8, 150.3, 140.2, 137.6, 134.8, 134.3, 133.3, 132.6, 130.5, 130.4, 125.2, 115.5, 88.8; HRMS for $C_{14}H_8BrN_3O_2$: calcd. (MH^+): 329.9873, found: 329.9873.

3-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)-5-phenylisobenzofuran-1(3*H*)-one (1d). White solid; yield 74%. R_f 0.50 (30% EtOAc/hexane); mp 111−112 °C; IR (KBr, cm^{-1}): 1053, 1287, 1616, 1786; ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.0 Hz, 1H), 8.03−8.06 (m, 1H), 7.98 (s, 1H), 7.93 (dd, J = 8.0 Hz, 1.1 Hz, 1H), 7.61 (br t, J = 0.6 Hz, 1H), 7.48−7.50 (m, 2H), 7.26−7.40 (m, 5H), 6.66−6.69 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 149.0, 146.9, 143.4, 138.6, 131.4, 131.0, 129.2 ($C_{Ar}H$ × 2 merged with $C_{Ar}H$), 128.7, 127.5 ($C_{Ar}H$ × 2), 126.7, 125.2, 124.9, 122.2, 120.7, 109.7, 85.4; HRMS for $C_{20}H_{13}N_3O_2$: calcd. (MH^+): 328.1081, found: 328.1081.

(*E*)-Dimethyl 4-Bromostyrylphosphonate (2d). Yellow oil; yield 69%. R_f 0.50 (50% EtOAc/hexane); IR (Film, cm^{-1}): 909, 1037, 1156, 1643; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43−7.46 (m, 2H), 7.38−7.40 (m, 1H), 7.24−7.33 (m, 2H), 6.14 (dd appearing as t, J = 17.4 Hz, 1H), 3.70 (d, $^3J_{H\text{-}P}$ = 11.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2 (d, $J_{C\text{-}P}$ = 6.9 Hz, β-CH), 132.1($C_{Ar}H$ × 2), 129.1 ($C_{Ar}H$ × 2), 128.9, 127.8, 113.4 (d, $J_{C\text{-}P}$ = 191.3 Hz, α-CH), 52.5 (d,

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$^{2}J_{C\text{-}P}$ = 5.6 Hz, {PO}OCH_3 × 2); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 21.78; HRMS for $C_{10}H_{12}BrO_3P$: calcd. (MH^+): 290.9780, found: 290.9779.

(*E*)-Dimethyl 4-Chlorostyrylphosphonate (2e). Colorless oil; yield 42%. R_f 0.50 (50% EtOAc/hexane); IR (Film, cm^{-1}): 928, 1035, 1216, 1667; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.45 (m merged with d at 7.37, 1H), 7.37 (d, J = 8.5 Hz, 2H), 7.29 (d, J = 8.5 Hz, 2H), 6.13 (dd appearing as t, J = 17.4 Hz, 1H), 3.71 (d, $^{3}J_{H\text{-}P}$ = 11.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1 (d, $J_{C\text{-}P}$ = 6.9 Hz, β-CH), 136.4, 133.2 (d, $J_{C\text{-}P}$ = 23.7 Hz), 129.2 ($C_{Ar}H$ × 2), 128.9 ($C_{Ar}H$ × 2), 113.2 (d, $J_{C\text{-}P}$ = 191.4 Hz, α-CH), 52.5 (d, $^{2}J_{C\text{-}P}$ = 5.1 Hz, {PO}OCH_3 × 2); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 21.83; HRMS for $C_{10}H_{12}ClO_3P$: calcd. (MH^+): 247.0285, found: 247.0280.

(*E*)-Dimethyl 3-Fluorostyrylphosphonate (2f). Colorless oil; yield 62%. R_f 0.50 (50% EtOAc/hexane); IR (Film, cm^{-1}): 929, 1060, 1216, 1621; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.46 (m, 1H), 7.27−7.32 (m, 1H), 7.21 (s, 1H), 7.12−7.15 (m, 1H), 7.00−7.04 (m, 1H), 6.16 (dd appearing as t, J = 17.4 Hz, 1H), 3.71 (d, $^{3}J_{H\text{-}P}$ = 11.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0 (d, $^{1}J_{C\text{-}F}$ = 245.5 Hz), 148.1 (d, $J_{C\text{-}P}$ = 6.8 Hz, β-CH), 136.9 (dd, $J_{C\text{-}F}$ = 23.3 Hz, $J_{C\text{-}P}$ = 7.3 Hz), 130.5 (d, $J_{C\text{-}F}$ = 8.2 Hz), 123.8, 117.3 (d, $J_{C\text{-}F}$ = 21.2 Hz), 114.3 (d, $J_{C\text{-}P}$ = 191.0 Hz, α-CH), 114.0 (d, $J_{C\text{-}F}$ = 21.8 Hz), 52.5 (d, $^{2}J_{C\text{-}P}$ = 5.5 Hz, {PO}OCH_3 × 2); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 21.43; HRMS for $C_{10}H_{12}FO_3P$: calcd. (MH^+): 231.0581, found: 231.0577.

(*E*)-Dimethyl 2-(Naphthalene-1-yl)vinylphosphonate (2j). Yellow oil; yield 64%. R_f 0.50 (50% EtOAc/hexane); IR (Film, cm^{-1}): 929, 1061, 1216, 1644; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (dd, $J_{H\text{-}P}$ = 22.5 Hz, J = 17.3 Hz, 1H), 8.11 (d, J = 8.2 Hz, 1H), 7.82 (t, J = 8.6 Hz, 2H), 7.66 (d, J = 7.1 Hz, 1H), 7.40−7.52 (m, 3H), 6.27 (dd appearing as t, J = 17.7 Hz, 1H), 3.76 (d, $^{3}J_{H\text{-}P}$ = 11.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8 (d, $J_{C\text{-}P}$ = 7.1 Hz, β-CH), 133.6, 131.1, 130.6, 128.7, 126.9, 126.3, 125.4, 124.8, 123.3, 115.6 (d, $J_{C\text{-}P}$ = 189.4 Hz, α-CH), 115.4, 52.6 (d, $^{2}J_{C\text{-}P}$ = 5.6 Hz, {PO}OCH_3 × 2); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 21.69; HRMS for $C_{14}H_{15}O_3P$: calcd. (MH^+): 263.0832, found: 263.0830.

Dimethyl (4-Fluorophenyl)ethynylphosphonate (4c). Yellow oil; yield 90%. R_f 0.50 (50% EtOAc/hexane); IR (Film, cm^{-1}): 1038, 1236, 1268, 2189; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49−7.53 (m, 2H), 6.98−7.04 (m, 2H), 3.79 (d, $^{3}J_{H\text{-}P}$ = 12.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0 (d, $^{1}J_{C\text{-}F}$ = 252.2 Hz), 135.0 (d, $J_{C\text{-}P}$ = 8.4 Hz, $C_{Ar}H$ × 2), 116.2 (d, $J_{C\text{-}P}$ = 22.3 Hz, $C_{Ar}H$ × 2), 115.4, 98.8 (d, $^{2}J_{C\text{-}P}$ = 52.7 Hz, C≡C), 76.9 (d, $^{1}J_{C\text{-}P}$ = 300.9 Hz, C≡C), 53.4 (d, $^{2}J_{C\text{-}P}$ = 5.1 Hz, {PO}OCH_3 × 2); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ −2.97; HRMS for $C_{10}H_{10}FO_3P$: calcd. (MH^+): 229.0424, found: 229.0424.

Dimethyl (4-Bromophenyl)ethynylphosphonate (4d). Yellow oil; yield 89%. R_f 0.50 (50% EtOAc/hexane); IR (Film, cm^{-1}): 1040, 1267, 2189; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45−7.48 (m, 2H), 7.35−7.38 (m, 2H), 3.79 (d, $^{3}J_{H\text{-}P}$ = 12.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.0 (d, $J_{C\text{-}P}$ = 2.6 Hz, $C_{Ar}H$ × 2), 132.0 ($C_{Ar}H$ × 2), 125.7, 118.2 (d, $J_{C\text{-}P}$ = 5.7 Hz), 98.6 (d, $^{2}J_{C\text{-}P}$ = 52.7 Hz, C≡C), 78.5 (d, $^{1}J_{C\text{-}P}$ = 242.7 Hz, C≡C), 53.5 (d, $^{2}J_{C\text{-}P}$ = 5.7 Hz, {PO}OCH_3 × 2); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ −3.13; HRMS for $C_{10}H_{10}BrO_3P$: calcd. (MH^+): 288.9624, found: 288.9625.

Dimethyl (4-Chlorophenyl)ethynylphosphonate (4e). Colorless oil; yield 90%. R_f 0.50 (50% EtOAc/hexane); IR (Film, cm^{-1}): 913, 1045, 1279; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43−7.46 (m, 2H), 7.28−7.32 (m, 2H), 3.79 (d, $^{3}J_{H\text{-}P}$ = 12.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 133.9 (d, $J_{C\text{-}P}$ = 2.6 Hz, $C_{Ar}H$ × 2), 129.1 ($C_{Ar}H$ × 2), 117.8 (d, $J_{C\text{-}P}$ = 5.8 Hz), 98.5 (d, $^{2}J_{C\text{-}P}$ = 52.8 Hz, C≡C), 78.4 (d, $^{1}J_{C\text{-}P}$ = 231.8 Hz, C≡C), 53.5 (d, $^{2}J_{C\text{-}P}$ = 5.7 Hz, {PO}OCH_3 × 2); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ −3.13; HRMS for $C_{10}H_{10}ClO_3P$: calcd. (MH^+): 245.0129, found: 245.0125.

Dimethyl (3-Fluorophenyl)ethynylphosphonate (4f). Colorless oil; yield 75%. R_f 0.50 (50% EtOAc/hexane); IR (Film, cm^{-1}): 911, 958, 1216, 2402; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28−7.33 (m, 2H), 7.21 (br s, 1H), 7.09−7.13 (m, 1H), 3.79 (d, $^{3}J_{H\text{-}P}$ = 12.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2 (d, $^{1}J_{C\text{-}F}$ = 247.0 Hz), 130.4 (d, $J_{C\text{-}F}$ = 8.4 Hz), 128.6, 121.1 (dd, $J_{C\text{-}F}$ = 9.0 Hz, $J_{C\text{-}P}$ = 6.0 Hz), 119.4 (dd, $J_{C\text{-}F}$ = 23.4 Hz, $J_{C\text{-}P}$ = 1.5 Hz), 118.4 (d, $J_{C\text{-}F}$ = 21.1 Hz), 98.0 (dd, $J_{C\text{-}F}$ = 3.3 Hz, $^{2}J_{C\text{-}P}$ = 52.6 Hz, C≡C), 77.9 (d, $^{1}J_{C\text{-}P}$ = 298.8 Hz, C≡C), 53.5 (d, $^{2}J_{C\text{-}P}$ = 5.5 Hz, {PO}OCH_3 × 2); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ −3.39; HRMS for $C_{10}H_{10}FO_3P$: calcd. (MH^+): 229.0424, found: 229.0423.

Dimethyl (3-Bromophenyl)ethynylphosphonate (4g). Yellow oil; yield 76%. R_f 0.50 (50% EtOAc/hexane); IR (Film, cm^{-1}): 1042, 1268, 2192; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (t, J = 1.4 Hz, 1H), 7.52−7.54 (m, 1H), 7.43−7.45 (m, 1H), 7.22 (t merged with $CDCl_3$ peak, J = 6.4 Hz, 1H), 3.79 (d, $^{3}J_{H\text{-}P}$ = 12.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.3 (d, $J_{C\text{-}P}$ = 2.4 Hz), 134.1, 131.2 (d, $J_{C\text{-}P}$ = 2.5 Hz), 130.1, 122.4, 121.3 (d, $J_{C\text{-}P}$ = 5.7 Hz), 97.7 (d, $^{2}J_{C\text{-}P}$ = 52.4 Hz, C≡C), 78.5 (d, $^{1}J_{C\text{-}P}$ = 251.8 Hz, C≡C), 53.5 (d, $^{2}J_{C\text{-}P}$ = 5.5 Hz, {PO}OCH_3 × 2); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ −3.42; HRMS for $C_{10}H_{10}BrO_3P$: calcd. (MH^+): 288.9624, found: 288.9623.

Dimethyl (2-Bromophenyl)ethynylphosphonate (4h). Colorless oil; yield 87%. R_f 0.50 (50% EtOAc/hexane); IR (Film, cm^{-1}): 1041, 1269, 2191; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52−7.57 (m, 2H), 7.22−7.29 (m, 2H), 3.82 (d, $^{3}J_{H\text{-}P}$ = 12.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.6, 132.8, 131.9, 127.3, 126.2, 121.9 (d, $J_{C\text{-}P}$ = 5.7 Hz), 97.6 (d, $^{2}J_{C\text{-}P}$ = 52.4 Hz, C≡C), 81.2 (d, $^{1}J_{C\text{-}P}$ = 296.1 Hz, C≡C), 53.7 (d, $^{2}J_{C\text{-}P}$ = 5.4 Hz, {PO}OCH_3 × 2); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ −3.41; HRMS for $C_{10}H_{10}BrO_3P$: calcd. (MH^+): 288.9624, found: 288.9617.

Dimethyl (3-Methoxyphenyl)ethynylphosphonate (4i). Colorless oil; yield 77%. R_f 0.50 (50% EtOAc/hexane); IR (Film, cm^{-1}): 947, 1038, 1265, 2183; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19−7.23 (m, 1H), 7.10 (d, J = 7.6 Hz, 1H), 7.01 (br s, 1H), 6.93−6.95 (m, 1H), 3.79 (d, $^{3}J_{H\text{-}P}$ = 12.3 Hz, 6H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 129.8, 125.2 (d, $J_{C\text{-}P}$ = 2.5 Hz), 120.2 (d, $J_{C\text{-}P}$ = 5.7 Hz), 117.7, 117.2 (d, $J_{C\text{-}P}$ = 2.3 Hz), 99.9 (d, $^{2}J_{C\text{-}P}$ = 53.0 Hz, C≡C), 76.6 (d, $^{1}J_{C\text{-}P}$ = 300.8 Hz, C≡C), 55.4, 53.5 (d, $^{2}J_{C\text{-}P}$ = 5.6 Hz, {PO}OCH_3 × 2); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ −2.78; HRMS for $C_{11}H_{13}O_4P$: calcd. (MH^+): 241.0624, found: 241.0620.

Dimethyl Naphthalene-1-ylethynylphosphonate (4j). Red oil; yield 71%. R_f 0.50 (50% EtOAc/hexane); IR (Film, cm^{-1}): 888, 1043, 1263, 2181; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.2 Hz, 1H), 7.87 (d, J = 8.3 Hz, 1H), 7.75−7.81 (m, 2H), 7.46−7.56 (m, 2H), 7.36−7.40 (m, 1H), 3.84 (d, $^{3}J_{H\text{-}P}$ = 12.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.3 (d, $J_{C\text{-}P}$ = 1.8 Hz), 133.0, 132.9 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.6, 128.6, 127.8, 127.0, 125.5, 125.0, 116.8 (d, $J_{C\text{-}P}$ = 5.8 Hz), 98.5 (d, $^{2}J_{C\text{-}P}$ = 52.9 Hz, C≡C), 81.5 (d, $^{1}J_{C\text{-}P}$ = 299.8 Hz, C≡C), 53.5 (d, $^{2}J_{C\text{-}P}$ = 5.6 Hz, {PO}OCH_3 × 2); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ −2.71; HRMS for $C_{14}H_{13}O_3P$: calcd. (MH^+): 261.0675, found: 261.0675.

Dimethyl Thiophen-2-ylethynylphosphonate (4k). Yellow oil; yield 58%. R_f 0.50 (50% EtOAc/hexane); IR (Film, cm^{-1}): 816, 1045, 1216, 2177; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.41 (m, 2H), 6.98 (dd, J = 5.0 Hz, 3.8 Hz, 1H), 3.79 (d, $^{3}J_{H\text{-}P}$ = 12.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.3, 130.9, 127.4, 118.9 (d, $J_{C\text{-}P}$ = 6.4 Hz), 93.4 (d, $^{2}J_{C\text{-}P}$ = 54.2 Hz, C≡C), 81.0 (d, $^{1}J_{C\text{-}P}$ = 301.1 Hz, C≡C), 53.5 (d, $^{2}J_{C\text{-}P}$ = 5.3 Hz, {PO}OCH_3 × 2); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ −4.23; HRMS for $C_8H_9O_3PS$: calcd. (MH^+): 217.0083, found: 217.0071.

Dimethyl 1,4-Dihydroxy-3-phenylnaphthalen-2-ylphosphonate (3a). Compound **3a** was synthesized according to the general procedure from 3-benzotriazolylphthalide **1a** and **2a** (**Method A**) or **4a** (**Method B**). White solid; yield 56% (**Method A**) and 52% (**Method B**). R_f 0.50 (25% EtOAc/hexane); mp 198−200 °C; IR (KBr, cm^{-1}): 1032, 1295, 1580, 1625, 3020, 3427; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.62 (s, 1H), 8.36 (d, J = 8.1 Hz, 1H), 8.11 (d, J = 8.1 Hz, 1H), 7.58−7.62 (m, 1H), 7.50−7.54 (m, 1H), 7.38−7.46 (m, 3H), 7.25−7.27 (m, 2H), 4.72 (s, 1H), 3.43 (d, $^{3}J_{H\text{-}P}$ = 11.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6 (d, $J_{C\text{-}P}$ = 6.6 Hz), 141.3 (d, $J_{C\text{-}P}$ = 16.3 Hz), 134.5 (d, $J_{C\text{-}P}$ = 3.6 Hz), 131.0 ($C_{Ar}H$ × 2), 129.2, 128.8, 128.7 ($C_{Ar}H$ × 2), 127.9, 126.5, 125.6 (d, $J_{C\text{-}P}$ = 15.8 Hz), 123.9, 122.2, 119.2 (d, $J_{C\text{-}P}$ = 7.5 Hz), 97.9 (d, $^{1}J_{C\text{-}P}$ = 181.3 Hz), 52.3 (d, $^{2}J_{C\text{-}P}$ = 5.1 Hz, {PO}OCH_3 × 2); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 26.70; HRMS for $C_{18}H_{17}O_5P$: calcd. (MH^+): 345.0886, found: 345.0891.

Dimethyl 1,4-Dihydroxy-3-(4-nitrophenyl)naphthalen-2-ylphosphonate (3b). Compound **3b** was synthesized according to the general procedure from 3-benzotriazolylphthalide **1a** and **2b**

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(**Method A**) or **4b** (**Method B**). Yellow solid; yield 78% (**Method A**) and 75% (**Method B**). R_f 0.50 (25% EtOAc/hexane); mp 202−204 °C; IR (KBr, cm^{-1}): 1061, 1397, 1632, 1709; ^1H NMR (400 MHz, $CDCl_3$) δ 11.56 (d, J = 1.0 Hz, 1H), 8.38 (d, J = 8.2 Hz, 1H), 8.29 (d, J = 8.7 Hz, 2H), 8.11 (d, J = 8.2 Hz, 1H), 7.55−7.66 (m, 2H), 7.48 (d, J = 8.7 Hz, 2H), 4.48 (br s, 1H), 3.46 (d, $^3J_{H\text{-}P}$ = 11.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$ + CD_3OD) δ 156.6 (d, $J_{C\text{-}P}$ = 5.0 Hz), 147.7, 143.3, 141.4 (d, $J_{C\text{-}P}$ = 16.5 Hz), 132.2 ($C_{Ar}H \times 2$), 129.5, 128.9, 126.9, 125.7 (d, $J_{C\text{-}P}$ = 16.0 Hz), 123.9, 123.0 ($C_{Ar}H \times 2$), 122.1, 118.7 (d, $J_{C\text{-}P}$ = 7.0 Hz), 97.3 (d, $^1J_{C\text{-}P}$ = 179.2 Hz), 52.3 (d, $^2J_{C\text{-}P}$ = 5.3 Hz, {PO}$OCH_3 \times 2$); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 26.15; HRMS for $C_{18}H_{16}NO_7P$: calcd. (MH^+): 390.0737, found: 390.0732.

Dimethyl 3-(4-Fluorophenyl)-1,4-dihydroxynaphthalen-2-ylphosphonate (3c). Compound **3c** was synthesized according to the general procedure from 3-benzotriazolylphthalide **1a** and **2c** (**Method A**) or **4c** (**Method B**). White solid; yield 68% (**Method A**) and 66% (**Method B**). R_f 0.50 (25% EtOAc/hexane); mp 219−220 °C; IR (KBr, cm^{-1}): 1041, 1216, 1403, 1582, 3021, 3412; ^1H NMR (400 MHz, $CDCl_3$) δ 11.60 (s, 1H), 8.36 (d, J = 8.2 Hz, 1H), 8.11 (d, J = 8.1 Hz, 1H), 7.52−7.63 (m, 2H), 7.11−7.26 (m, 4H), 4.65 (s, 1H), 3.45 (d, $^3J_{H\text{-}P}$ = 11.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0 (d, $^1J_{C\text{-}F}$ = 247.3 Hz), 156.7 (d, $J_{C\text{-}P}$ = 6.6 Hz), 141.5 (d, $J_{C\text{-}P}$ = 16.3 Hz), 133.0 (d, $J_{C\text{-}F}$ = 8.1 Hz, $C_{Ar}H \times 2$), 130.2 (dd appearing as t, $J_{C\text{-}P}$ = 3.9 Hz, $J_{C\text{-}F}$ = 4.3 Hz), 129.3, 127.8 (d, $J_{C\text{-}P}$ = 2.5 Hz), 126.7, 125.7 (d, $J_{C\text{-}P}$ = 15.8 Hz), 123.9 (d, $J_{C\text{-}P}$ = 1.6 Hz), 122.2, 118.0 (d, $J_{C\text{-}P}$ = 7.4 Hz), 115.8 (d, $J_{C\text{-}F}$ = 21.3 Hz, $C_{Ar}H \times 2$), 97.9 (d, $^1J_{C\text{-}P}$ = 181.4 Hz), 52.3 (d, $^2J_{C\text{-}P}$ = 5.2 Hz, {PO}$OCH_3 \times 2$); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 26.68; HRMS for $C_{18}H_{16}FO_5P$: calcd. (MH^+): 363.0792, found: 363.0794.

Dimethyl 3-(4-Bromophenyl)-1,4-dihydroxynaphthalen-2-ylphosphonate (3d). Compound **3d** was synthesized according to the general procedure from 3-benzotriazolylphthalide **1a** and **2d** (**Method A**) or **4d** (**Method B**). White solid; yield 61% (**Method A**) and 58% (**Method B**). R_f 0.50 (25% EtOAc/hexane); mp 230−231 °C; IR (KBr, cm^{-1}): 1058, 1299, 1491, 1626, 2400, 3019, 3400; ^1H NMR (400 MHz, $CDCl_3$) δ 11.59 (s, 1H), 8.36 (d, J = 8.2 Hz, 1H), 8.11 (d, J = 8.2 Hz, 1H), 7.53−7.61 (m, 4H), 7.14 (d, J = 8.3 Hz, 2H), 4.62 (s, 1H), 3.46 (d, $^3J_{H\text{-}P}$ = 11.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7 (d, $J_{C\text{-}P}$ = 6.6 Hz), 141.2 (d, $J_{C\text{-}P}$ = 16.0 Hz), 133.5 (d, $J_{C\text{-}P}$ = 4.3 Hz), 132.8 ($C_{Ar}H \times 2$), 131.9 ($C_{Ar}H \times 2$), 129.4, 127.9, 126.8, 125.7 (d, $J_{C\text{-}P}$ = 16.1 Hz), 123.9, 123.2, 122.2, 117.9 (d, $J_{C\text{-}P}$ = 7.4 Hz), 97.6 (d, $^1J_{C\text{-}P}$ = 181.8 Hz), 52.4 (d, $^2J_{C\text{-}P}$ = 5.1 Hz, {PO}$OCH_3 \times 2$); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 26.51; HRMS for $C_{18}H_{16}BrO_5P$: calcd. (MH^+): 422.9991, found: 422.9996.

Dimethyl 3-(4-Chlorophenyl)-1,4-dihydroxynaphthalen-2-ylphosphonate (3e). Compound **3e** was synthesized according to the general procedure from 3-benzotriazolylphthalide **1a** and **2e** (**Method A**) or **4e** (**Method B**). White solid; yield 52% (**Method A**) and 50% (**Method B**). R_f 0.50 (25% EtOAc/hexane); mp 224−225 °C; IR (KBr, cm^{-1}): 1037, 1216, 1400, 1630, 3021; ^1H NMR (400 MHz, $CDCl_3$) δ 11.58 (d, J = 1.1 Hz, 1H), 8.35 (d, J = 8.3 Hz, 1H), 8.11 (d, J = 8.3 Hz, 1H), 7.58−7.62 (m, 1H), 7.51−7.55 (m, 1H), 7.41 (d, J = 8.3 Hz, 2H), 7.20 (d, J = 8.4 Hz, 2H), 4.64 (s, 1H), 3.45 (d, $^3J_{H\text{-}P}$ = 11.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7 (d, $J_{C\text{-}P}$ = 6.5 Hz), 141.3 (d, $J_{C\text{-}P}$ = 16.0 Hz), 135.0, 132.9 (d, $J_{C\text{-}P}$ = 3.9 Hz), 132.5 ($C_{Ar}H \times 2$), 129.4, 128.9 ($C_{Ar}H \times 2$), 127.9, 126.8, 125.7 (d, $J_{C\text{-}P}$ = 16.1 Hz), 123.9, 122.2, 117.9 (d, $J_{C\text{-}P}$ = 7.6 Hz), 97.7 (d, $^1J_{C\text{-}P}$ = 181.7 Hz), 52.4 (d, $^2J_{C\text{-}P}$ = 5.2 Hz, {PO}$OCH_3 \times 2$); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 26.54; HRMS for $C_{18}H_{16}ClO_5P$: calcd. (MH^+): 379.0497, found: 379.0496.

Dimethyl 3-(3-Fluorophenyl)-1,4-dihydroxynaphthalen-2-ylphosphonate (3f). Compound **3f** was synthesized according to the general procedure from 3-benzotriazolylphthalide **1a** and **2f** (**Method A**) or **4f** (**Method B**). White solid; yield 69% (**Method A**) and 67% (**Method B**). R_f 0.50 (25% EtOAc/hexane); mp 177−179 °C; IR (KBr, cm^{-1}): 1032, 1216, 1402, 1580, 3404; ^1H NMR (400 MHz, $CDCl_3$) δ 11.60 (s, 1H), 8.36 (d, J = 8.3 Hz, 1H), 8.12 (d, J = 8.2 Hz, 1H), 7.52−7.63 (m, 2H), 7.39−7.44 (m, 1H), 6.99−7.14 (m, 3H), 4.68 (s, 1H), 3.50 (d, $^3J_{H\text{-}P}$ = 11.5 Hz, 3H), 3.43 (d, $^3J_{H\text{-}P}$ = 11.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8 (d, $^1J_{C\text{-}F}$ = 246.5 Hz), 156.7 (d, $J_{C\text{-}P}$ = 6.7 Hz), 141.2 (d, $J_{C\text{-}P}$ = 16.1 Hz), 136.8 (dd, $J_{C\text{-}P}$ = 3.7 Hz, $J_{C\text{-}F}$ = 7.5 Hz), 130.2 (d, $J_{C\text{-}F}$ = 8.4 Hz), 129.4, 127.9 (d, $J_{C\text{-}P}$ = 2.1 Hz), 126.8, 126.7 (d, $J_{C\text{-}F}$ = 3.0 Hz), 125.7 (d, $J_{C\text{-}P}$ = 15.6 Hz), 123.9 (d, $J_{C\text{-}P}$ = 1.8 Hz), 122.2, 118.4 (d, $J_{C\text{-}F}$ = 21.2 Hz), 117.8 (d, $J_{C\text{-}P}$ = 8.0 Hz), 115.8 (d, $J_{C\text{-}F}$ = 20.8 Hz), 97.6 (d, $^1J_{C\text{-}P}$ = 182.0 Hz), 52.4 (two d merged to appear as q, $^2J_{C\text{-}P}$ = 5.2 Hz, 5.1 Hz, {PO}$OCH_3 \times 2$); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 26.44; HRMS for $C_{18}H_{16}FO_5P$: calcd. (MH^+): 363.0792, found: 363.0801.

Dimethyl 3-(3-Bromophenyl)-1,4-dihydroxynaphthalen-2-ylphosphonate (3g). Compound **3g** was synthesized according to the general procedure from 3-benzotriazolylphthalide **1a** and **2g** (**Method A**) or **4g** (**Method B**). White solid; yield 67% (**Method A**) and 67% (**Method B**). R_f 0.50 (25% EtOAc/hexane); mp 194−196 °C; IR (KBr, cm^{-1}): 1033, 1215, 1577, 1625, 1799, 3400; ^1H NMR (500 MHz, $CDCl_3$) δ 11.57 (s, 1H), 8.35 (d, J = 8.3 Hz, 1H), 8.11 (d, J = 8.3 Hz, 1H), 7.60 (t, J = 7.5 Hz, 1H), 7.51−7.54 (m, 2H), 7.44 (s, 1H), 7.30 (t, J = 7.9 Hz, 1H), 7.20 (d, J = 7.6 Hz, 1H), 4.72 (s, 1H), 3.49 (d, $^3J_{H\text{-}P}$ = 11.5 Hz, 3H), 3.41 (d, $^3J_{H\text{-}P}$ = 11.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8 (d, $J_{C\text{-}P}$ = 6.5 Hz), 141.2 (d, $J_{C\text{-}P}$ = 16.0 Hz), 136.7 (d, $J_{C\text{-}P}$ = 3.6 Hz), 134.4, 131.8, 130.1, 129.6, 129.4, 127.9, 126.8, 125.7 (d, $J_{C\text{-}P}$ = 15.8 Hz), 123.9, 122.5, 122.2, 117.8 (d, $J_{C\text{-}P}$ = 7.5 Hz), 97.6 (d, $^1J_{C\text{-}P}$ = 182.1 Hz), 52.4 (two d merged to appear as t, $^2J_{C\text{-}P}$ = 5.5 Hz, {PO}$OCH_3 \times 2$); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 26.24; HRMS for $C_{18}H_{16}BrO_5P$: calcd. (MH^+): 422.9991, found: 422.9988.

Dimethyl 3-(2-Bromophenyl)-1,4-dihydroxynaphthalen-2-ylphosphonate (3h). Compound **3h** was synthesized according to the general procedure from 3-benzotriazolylphthalide **1a** and **2h** (**Method A**) or **4h** (**Method B**). White solid; yield 56% (**Method A**) and 56% (**Method B**). R_f 0.50 (25% EtOAc/hexane); mp 208−210 °C; IR (KBr, cm^{-1}): 1046, 1218, 1404, 1582, 3389; ^1H NMR (400 MHz, $CDCl_3$) δ 11.63 (d, J = 1.2 Hz, 1H), 8.38 (d, J = 8.2 Hz, 1H), 8.15 (d, J = 8.0 Hz, 1H), 7.68−7.70 (m, 1H), 7.60−7.64 (m, 1H), 7.53−7.57 (m, 1H), 7.36−7.40 (m, 1H), 7.25−7.29 (m, 2H), 4.53 (s, 1H), 3.53 (d, $^3J_{H\text{-}P}$ = 11.4 Hz, 3H), 3.46 (d, $^3J_{H\text{-}P}$ = 11.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8 (d, $J_{C\text{-}P}$ = 6.6 Hz), 141.1 (d, $J_{C\text{-}P}$ = 15.9 Hz), 135.3 (d, $J_{C\text{-}P}$ = 4.2 Hz), 133.7, 132.9, 130.5, 129.2, 127.9, 127.2, 126.8, 126.4, 125.9 (d, $J_{C\text{-}P}$ = 15.8 Hz), 123.9, 122.3, 118.4 (d, $J_{C\text{-}P}$ = 6.3 Hz), 97.7 (d, $^1J_{C\text{-}P}$ = 183.1 Hz), 53.8 (d, $^2J_{C\text{-}P}$ = 5.2 Hz, {PO}OCH_3), 52.1 (d, $^2J_{C\text{-}P}$ = 5.4 Hz, {PO}OCH_3); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 26.19; HRMS for $C_{18}H_{16}BrO_5P$: calcd. (MH^+): 422.9991, found: 422.9981.

Dimethyl 1,4-Dihydroxy-3-(3-methoxyphenyl)naphthalen-2-ylphosphonate (3i). Compound **3i** was synthesized according to the general procedure from 3-benzotriazolylphthalide **1a** and **2i** (**Method A**) or **4i** (**Method B**). White solid; yield 47% (**Method A**) and 46% (**Method B**). R_f 0.50 (25% EtOAc/hexane); mp 181−182 °C; IR (KBr, cm^{-1}): 1068, 1216, 1403, 1644, 3409; ^1H NMR (400 MHz, $CDCl_3$) δ 11.65 (s, 1H), 8.37 (d, J = 8.1 Hz, 1H), 8.13 (d, J = 8.3 Hz, 1H), 7.52−7.64 (m, 2H), 7.37 (t, J = 7.9 Hz, 1H), 6.96 (dd, J = 8.2 Hz, 2.0 Hz, 1H), 6.83−6.87 (m, 2H), 4.85 (s, 1H), 3.79 (s, 3H), 3.50 (d, $^3J_{H\text{-}P}$ = 11.5 Hz, 3H), 3.45 (d, $^3J_{H\text{-}P}$ = 11.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 156.6 (d, $J_{C\text{-}P}$ = 6.5 Hz), 141.2 (d, $J_{C\text{-}P}$ = 16.2 Hz), 135.8 (d, $J_{C\text{-}P}$ = 3.5 Hz), 129.8, 129.2, 127.9, 126.5, 125.6 (d, $J_{C\text{-}P}$ = 15.7 Hz), 123.9, 123.0, 122.2, 119.0 (d, $J_{C\text{-}P}$ = 7.5 Hz), 116.6, 114.4, 97.7 (d, $^1J_{C\text{-}P}$ = 181.4 Hz), 55.3, 52.4 (two d merged to appear as t, $^2J_{C\text{-}P}$ = 4.6 Hz, {PO}$OCH_3 \times 2$); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 26.79; HRMS for $C_{19}H_{19}O_6P$: calcd. (MH^+): 375.0992, found: 375.0994.

Dimethyl 1′,4′-Dihydroxy-1,2′-binaphthyl-3′-ylphosphonate (3j). Compound **3j** was synthesized according to the general procedure from 3-benzotriazolylphthalide **1a** and **2j** (**Method A**) or **4j** (**Method B**). White solid; yield 52% (**Method A**) and 51% (**Method B**). R_f 0.50 (25% EtOAc/hexane); mp 168−169 °C; IR (KBr, cm^{-1}): 1031, 1216, 1401, 1623, 3398; ^1H NMR (400 MHz, $CDCl_3$) δ 11.67 (s, 1H), 8.41 (d, J = 8.0 Hz, 1H), 8.13 (d, J = 7.8 Hz, 1H), 7.84−7.91 (m, 2H), 7.50−7.63 (m, 3H), 7.38−7.42 (m, 3H), 7.29−7.32 (m, 1H), 4.62 (s, 1H), 3.45 (d, $^3J_{H\text{-}P}$ = 11.5 Hz, 3H), 2.81 (d, $^3J_{H\text{-}P}$ = 11.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9 (d, $J_{C\text{-}P}$ = 6.5 Hz), 141.7 (d, $J_{C\text{-}P}$ = 16.1 Hz), 133.7, 132.9, 131.5 (d, $J_{C\text{-}P}$ =

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3.4 Hz), 129.8, 129.4, 129.2, 128.4, 127.9, 126.6, 126.5, 126.3, 125.8 (d, J_{C-P} = 16.0 Hz), 125.7, 125.2, 123.9, 122.3, 116.8 (d, J_{C-P} = 7.5 Hz), 98.9 (d, $^{1}J_{C-P}$ = 182.5 Hz), 52.7 (d, $^{2}J_{C-P}$ = 5.3 Hz, {PO}OCH_3), 52.2 (d, $^{2}J_{C-P}$ = 5.2 Hz, {PO}OCH_3); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 26.21; HRMS for $C_{22}H_{19}O_5P$: calcd. (MH^+): 395.1043, found: 395.1038.

Dimethyl 1,4-Dihydroxy-3-(thiophen-2-yl)naphthalen-2-ylphosphonate (3k). Compound **3k** was synthesized according to the general procedure from 3-benzotriazolylphthalide **1a** and **2k** (**Method A**) or **4k** (**Method B**). Brown solid; yield 45% (**Method A**) and 43% (**Method B**). R_f 0.50 (25% EtOAc/hexane); mp 165−167 °C; IR (KBr, cm^{-1}): 1031, 1310, 1403, 1627, 2400, 3019, 3400; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.69 (s, 1H), 8.35 (d, J = 8.1 Hz, 1H), 8.13 (d, J = 8.0 Hz, 1H), 7.53−7.62 (m, 2H), 7.47 (d, J = 4.8 Hz, 1H), 7.12−7.14 (m, 1H), 7.01 (s, 1H), 5.17 (s, 1H), 3.52 (d, $^{3}J_{H-P}$ = 11.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8 (d, J_{C-P} = 6.4 Hz), 143.7 (d, J_{C-P} = 15.4 Hz), 134.1 (d, J_{C-P} = 4.5 Hz), 130.5, 129.4, 128.3, 127.5, 127.2, 126.3 (d, J_{C-P} = 15.7 Hz), 123.9, 122.4, 110.5 (d, J_{C-P} = 6.4 Hz), 98.3 (d, $^{1}J_{C-P}$ = 180.7 Hz), 52.6 (d, $^{2}J_{C-P}$ = 4.6 Hz, {PO}OCH_3 × 2); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 26.68; HRMS for $C_{16}H_{15}O_5PS$: calcd. (MH^+): 351.0451, found: 351.0449.

Dimethyl 7-Bromo-3-(4-fluorophenyl)-1,4-dihydroxynaphthalen-2-ylphosphonate (3l). Compound **3l** was synthesized according to the general procedure from 3-benzotriazolylphthalide **1b** and **2c** (**Method A**) or **4c** (**Method B**). White solid; yield 45% (**Method A**) and 43% (**Method B**). R_f 0.50 (25% EtOAc/hexane); mp 177−178 °C; IR (KBr, cm^{-1}): 1056, 1219, 1398, 1638, 3404; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.58 (s, 1H), 8.50 (s, 1H), 7.97 (d, J = 8.7 Hz, 1H), 7.66 (d, J = 8.7 Hz, 1H), 7.11−7.23 (m, 4H), 4.67 (s, 1H), 3.45 (d, $^{3}J_{H-P}$ = 11.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1 (d, $^{1}J_{C-F}$ = 247.5 Hz), 155.5 (d, J_{C-P} = 6.7 Hz), 141.5 (d, J_{C-P} = 14.3 Hz), 132.9 (d, J_{C-F} = 8.1 Hz, $C_{Ar}H$ × 2), 132.5, 129.8, 126.8 (d, J_{C-P} = 15.7 Hz), 126.4, 126.3, 124.1, 121.1, 118.7 (d, J_{C-P} = 7.2 Hz), 115.9 (d, J_{C-F} = 21.3 Hz, $C_{Ar}H$ × 2), 99.4 (d, $^{1}J_{C-P}$ = 181.0 Hz), 52.4 (d, $^{2}J_{C-P}$ = 5.1 Hz, {PO}OCH_3 × 2); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 25.91; HRMS for $C_{18}H_{15}BrFO_5P$: calcd. (MH^+): 440.9897, found: 440.9894.

Dimethyl 7-Bromo-3-(4-bromophenyl)-1,4-dihydroxynaphthalen-2-ylphosphonate (3m). Compound **3m** was synthesized according to the general procedure from 3-benzotriazolylphthalide **1b** and **2d** (**Method A**) or **4d** (**Method B**). White solid; yield 42% (**Method A**) and 39% (**Method B**). R_f 0.50 (25% EtOAc/hexane); mp 224−225 °C; IR (KBr, cm^{-1}): 1034, 1216, 1414, 1522, 2401, 3398, 3683; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.57 (s, 1H), 8.50 (d, J = 1.7 Hz, 1H), 7.97 (d, J = 8.9 Hz, 1H), 7.66 (dd, J = 8.9 Hz, 1.8 Hz, 1H), 7.57 (d, J = 8.3 Hz, 2H), 7.13 (d, J = 8.3 Hz, 2H), 4.63 (s, 1H), 3.45 (d, $^{3}J_{H-P}$ = 11.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5 (d, J_{C-P} = 6.7 Hz), 141.3 (d, J_{C-P} = 16.0 Hz), 133.1 (d, J_{C-P} = 4.1 Hz), 132.7 ($C_{Ar}H$ × 2), 132.5, 132.0 ($C_{Ar}H$ × 2), 126.8 (d, J_{C-P} = 16.3 Hz), 126.4, 126.3, 124.2, 123.4, 121.2, 118.5 (d, J_{C-P} = 7.1 Hz), 99.1 (d, $^{1}J_{C-P}$ = 181.3 Hz), 52.5 (d, $^{2}J_{C-P}$ = 5.2 Hz, {PO}OCH_3 × 2); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 25.75; HRMS for $C_{18}H_{15}Br_2O_5P$: calcd. (MH^+): 500.9097, found: 500.9095.

Dimethyl 7-Bromo-3-(2-bromophenyl)-1,4-dihydroxynaphthalen-2-ylphosphonate (3n). Compound **3n** was synthesized according to the general procedure from 3-benzotriazolylphthalide **1b** and **2h** (**Method A**) or **4h** (**Method B**). White solid; yield 43% (**Method A**) and 42% (**Method B**). R_f 0.50 (25% EtOAc/hexane); mp 178−179 °C; IR (KBr, cm^{-1}): 1065, 1156, 1385, 1404, 1645, 3401; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.62 (s, 1H), 8.52 (d, J = 1.7 Hz, 1H), 8.01 (d, J = 8.9 Hz, 1H), 7.65−7.70 (m, 2H), 7.36−7.40 (m, 1H), 7.26−7.30 (m, 2H), 4.55 (s, 1H), 3.53 (d, $^{3}J_{H-P}$ = 11.4 Hz, 3H), 3.46 (d, $^{3}J_{H-P}$ = 11.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6 (d, J_{C-P} = 6.7 Hz), 141.1 (d, J_{C-P} = 16.0 Hz), 134.9 (d, J_{C-P} = 3.6 Hz), 133.6, 132.9, 132.4, 130.7, 127.3, 127.0 (d, J_{C-P} = 16.2 Hz), 126.5, 126.3, 124.3, 121.3, 119.0 (d, J_{C-P} = 6.5 Hz), 99.2 (d, $^{1}J_{C-P}$ = 180.3 Hz), 53.9 (d, $^{2}J_{C-P}$ = 5.2 Hz, {PO}OCH_3), 52.2 (d, $^{2}J_{C-P}$ = 5.8 Hz, {PO}OCH_3); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 25.45; HRMS for $C_{18}H_{15}Br_2O_5P$: calcd. (MH^+): 500.9097, found: 500.9095.

Dimethyl 6-Bromo-1,4-dihydroxy-3-phenylnaphthalen-2-ylphosphonate (3o). Compound **3o** was synthesized according to the general procedure from 3-benzotriazolylphthalide **1c** and **2a** (**Method A**) or **4a** (**Method B**). White solid; yield 42% (**Method A**) and 38% (**Method B**). R_f 0.50 (25% EtOAc/hexane); mp 168−170 °C; IR (KBr, cm^{-1}): 1059, 1403, 1522, 1623, 2399, 3391, 3681; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.65 (s, 1H), 8.27 (d, J = 1.8 Hz, 1H), 8.21 (d, J = 8.9 Hz, 1H), 7.59 (dd, J = 8.9 Hz, 1.9 Hz, 1H), 7.42−7.46 (m, 3H), 7.23−7.25 (m, 2H), 4.71 (s, 1H), 3.43 (d, $^{3}J_{H-P}$ = 11.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4 (d, J_{C-P} = 6.7 Hz), 140.4 (d, J_{C-P} = 16.2 Hz), 134.0 (d, J_{C-P} = 4.1 Hz), 130.9 ($C_{Ar}H$ × 2), 129.9, 129.0, 128.9 (d, J_{C-P} = 2.7 Hz), 128.8 ($C_{Ar}H$ × 2), 125.8 (d, J_{C-P} = 2.2 Hz), 124.8, 124.1, 124.0, 120.7 (d, J_{C-P} = 7.6 Hz), 98.6 (d, $^{1}J_{C-P}$ = 181.6 Hz), 52.4 (d, $^{2}J_{C-P}$ = 5.2 Hz, {PO}OCH_3 × 2); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 26.12; HRMS for $C_{18}H_{16}BrO_5P$: calcd. (MH^+): 422.9991, found: 422.9984.

Dimethyl 3-(4-Fluorophenyl)-1,4-dihydroxy-6-phenylnaphthalen-2-ylphosphonate (3p). Compound **3p** was synthesized according to the general procedure from 3-benzotriazolylphthalide **1d** and **2c** (**Method A**) or **4c** (**Method B**). White solid; yield 47% (**Method A**) and 47% (**Method B**). R_f 0.50 (25% EtOAc/hexane); mp 232−233 °C; IR (KBr, cm^{-1}): 1069, 1216, 1403, 1640, 3020, 3401; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.60 (s, 1H), 8.42 (d, J = 8.7 Hz, 1H), 8.32 (d, J = 1.3 Hz, 1H), 7.79 (dd, J = 8.7 Hz, 1.6 Hz, 1H), 7.69 (d, J = 7.4 Hz, 2H), 7.40−7.44 (m, 2H), 7.33 (t, J = 7.4 Hz, 1H), 7.24−7.28 (m, 2H), 7.14 (t, J = 8.6 Hz, 2H), 4.70 (s, 1H), 3.46 (d, $^{3}J_{H-P}$ = 11.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0 (d, $^{1}J_{C-F}$ = 246.2 Hz), 156.7 (d, J_{C-P} = 6.4 Hz), 142.0, 141.7 (d, J_{C-P} = 15.9 Hz), 140.7, 133.0 (d, J_{C-F} = 8.1 Hz, $C_{Ar}H$ × 2), 130.2, 128.9 ($C_{Ar}H$ × 2), 128.2, 127.9, 127.6 ($C_{Ar}H$ × 2), 126.2, 124.7, 124.6, 120.1, 118.5 (d, J_{C-P} = 7.7 Hz), 115.8 (d, J_{C-F} = 21.3 Hz, $C_{Ar}H$ × 2), 97.9 (d, $^{1}J_{C-P}$ = 180.3 Hz), 52.4 (d, $^{2}J_{C-P}$ = 5.1 Hz, {PO}OCH_3 × 2); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 26.65; HRMS for $C_{24}H_{20}FO_5P$: calcd. (MH^+): 439.1105, found: 439.1106.

Dimethyl 3-(3-Bromophenyl)-1,4-dihydroxy-6-phenylnaphthalen-2-ylphosphonate (3q). Compound **3q** was synthesized according to the general procedure from 3-benzotriazolylphthalide **1d** and **2g** (**Method A**) or **4g** (**Method B**). White solid; yield 41% (**Method A**) and 39% (**Method B**). R_f 0.50 (25% EtOAc/hexane); mp 162−164 °C; IR (KBr, cm^{-1}): 929, 1068, 1216, 1404, 1644, 3684; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.60 (s, 1H), 8.42 (d, J = 8.7 Hz, 1H), 8.32 (d, J = 1.2 Hz, 1H), 7.80 (dd, J = 8.7 Hz, 1.5 Hz, 1H), 7.69 (d, J = 7.3 Hz, 2H), 7.56 (d, J = 7.9 Hz, 1H), 7.41−7.47 (m, 3H), 7.31−7.35 (m, 2H), 7.23 (d, J = 7.6 Hz, 1H), 4.71 (s, 1H), 3.51 (d, $^{3}J_{H-P}$ = 11.5 Hz, 3H), 3.43 (d, $^{3}J_{H-P}$ = 11.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8 (d, J_{C-P} = 6.5 Hz), 142.1, 141.4 (d, J_{C-P} = 15.9 Hz), 140.7, 136.7 (d, J_{C-P} = 4.0 Hz), 134.4, 131.9, 130.1, 129.6, 128.9 ($C_{Ar}H$ × 2), 128.2, 127.9, 127.6 ($C_{Ar}H$ × 2), 126.3, 124.8, 124.7, 122.6, 120.1, 118.2 (d, J_{C-P} = 7.6 Hz), 97.6 (d, $^{1}J_{C-P}$ = 182.4 Hz), 52.4 (two d appearing as t, $^{2}J_{C-P}$ = 5.9 Hz, {PO}OCH_3 × 2); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 26.20; HRMS for $C_{24}H_{20}BrO_5P$: calcd. (MH^+): 499.0304, found: 499.0298.

Dimethyl 1,4-Dioxo-3-phenyl-1,4-dihydronaphthalen-2-ylphosphonate (5a). Compound **5a** was synthesized via oxidation of 1,4-dihydroxynaphthalene **3a** according to the general procedure. Yellow solid; yield 92%. R_f 0.50 (60% EtOAc/hexane); mp 149−151 °C; IR (KBr, cm^{-1}): 926, 1036, 1216, 1402, 1668, 2400; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (m appearing as br d, J = 14.0 Hz, 2H), 7.73 (br s, 2H), 7.30−7.40 (m, 5H), 3.47 (d, $^{3}J_{H-P}$ = 10.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.5 (d, $^{3}J_{C-P}$ = 6.3 Hz), 183.9 (d, $^{2}J_{C-P}$ = 18.4 Hz), 154.4, 136.6 (d, $^{1}J_{C-P}$ = 181.4 Hz), 134.5, 134.2, 133.3 (d, J_{C-P} = 6.5 Hz), 132.2 (d, J_{C-P} = 9.5 Hz), 131.5, 129.5 ($C_{Ar}H$ × 2), 127.6 ($C_{Ar}H$ × 2), 126.9, 126.6, 53.2 (d, $^{2}J_{C-P}$ = 6.2 Hz, {PO}OCH_3 × 2); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 13.01; HRMS for $C_{18}H_{15}O_5P$: calcd. (MH^+): 343.0730, found: 343.0732.

Dimethyl 3-(4-Nitrophenyl)-1,4-dioxo-1,4-dihydronaphthalen-2-ylphosphonate (5b). Compound **5b** was synthesized via oxidation of 1,4-dihydroxynaphthalene **3b** according to the general procedure. Yellow solid; yield 89%. R_f 0.50 (60% EtOAc/hexane); mp 174−175 °C; IR (KBr, cm^{-1}): 1058, 1218, 1280, 1399, 1639; ^{1}H

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NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 8.6 Hz, 2H), 8.03−8.11 (m, 2H), 7.73−7.80 (m, 2H), 7.44 (d, J = 8.6 Hz, 2H), 3.56 (d, $^3J_{H\text{-}P}$ = 11.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.8 (d, $^3J_{C\text{-}P}$ = 5.9 Hz), 183.2 (d, $^2J_{C\text{-}P}$ = 17.6 Hz), 152.5, 148.2, 140.1 (d, $J_{C\text{-}P}$ = 6.2 Hz), 137.4 (d, $^1J_{C\text{-}P}$ = 179.9 Hz), 134.9, 134.6, 132.0 (d, $J_{C\text{-}P}$ = 9.2 Hz), 131.2, 130.4 ($C_{Ar}H$ × 2), 127.1, 126.8 (d, $J_{C\text{-}P}$ = 2.2 Hz), 122.7 ($C_{Ar}H$ × 2), 53.4 (d, $^2J_{C\text{-}P}$ = 6.4 Hz, {PO}OCH_3 × 2); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 11.77; HRMS for $C_{18}H_{14}NO_7P$: calcd. (MH^+): 388.0581, found: 388.0581.

Dimethyl 3-(4-Fluorophenyl)-1,4-dioxo-1,4-dihydronaphthalen-2-ylphosphonate (5c). Compound **5c** was synthesized via oxidation of 1,4-dihydroxynaphthalene **3c** according to the general procedure. Yellow solid; yield 88%. R_f 0.50 (60% EtOAc/hexane); mp 88−90 °C; IR (KBr, cm^{-1}): 1042, 1258, 1399, 1663, 2925; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03−8.09 (m, 2H), 7.74 (br s, 2H), 7.31 (br s, 2H), 7.10 (t, J = 8.1 Hz, 2H), 3.53 (d, $^3J_{H\text{-}P}$ = 11.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.4 (d, $^3J_{C\text{-}P}$ = 6.2 Hz), 183.8 (d, $^2J_{C\text{-}P}$ = 18.2 Hz), 163.6 (d, $^1J_{C\text{-}F}$ = 248.6 Hz), 153.4, 136.7 (d, $^1J_{C\text{-}P}$ = 181.3 Hz), 134.6, 134.3, 132.1 (d, $J_{C\text{-}P}$ = 9.7 Hz), 131.8 (d, $J_{C\text{-}F}$ = 8.4 Hz, $C_{Ar}H$ × 2), 131.4, 129.1, 127.0, 126.6, 114.9 (d, $J_{C\text{-}F}$ = 21.8 Hz, $C_{Ar}H$ × 2), 53.3 (d, $^2J_{C\text{-}P}$ = 6.3 Hz, {PO}OCH_3 × 2); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 12.88; HRMS for $C_{18}H_{14}FO_5P$: calcd. (MH^+): 361.0636, found: 361.0667.

Dimethyl 3-(4-Bromophenyl)-1,4-dioxo-1,4-dihydronaphthalen-2-ylphosphonate (5d). Compound **5d** was synthesized via oxidation of 1,4-dihydroxynaphthalene **3d** according to the general procedure. Yellow solid; yield 94%. R_f 0.50 (60% EtOAc/hexane); mp 157−159 °C; IR (KBr, cm^{-1}): 1055, 1216, 1284, 1403, 1670, 2400, 3020, 3401; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03−8.09 (m, 2H), 7.71−7.78 (m, 2H), 7.54 (d, J = 8.2 Hz, 2H), 7.17 (d merged with $CDCl_3$ peak, 2H), 3.53 (d, $^3J_{H\text{-}P}$ = 11.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.3 (d, $^3J_{C\text{-}P}$ = 6.0 Hz), 183.6 (d, $^2J_{C\text{-}P}$ = 17.9 Hz), 153.3 (d, $J_{C\text{-}P}$ = 2.0 Hz), 136.8 (d, $^1J_{C\text{-}P}$ = 180.4 Hz), 134.6, 134.4, 132.1, 132.0 (d, $J_{C\text{-}P}$ = 3.7 Hz), 131.4, 131.2 ($C_{Ar}H$ × 2), 130.9 ($C_{Ar}H$ × 2), 127.0, 126.6 (d, $J_{C\text{-}P}$ = 2.3 Hz), 124.2, 53.3 (d, $^2J_{C\text{-}P}$ = 6.2 Hz, {PO}OCH_3 × 2); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 12.66; HRMS for $C_{18}H_{14}BrO_5P$: calcd. (MH^+): 420.9835, found: 420.9836.

Dimethyl 3-(4-Chlorophenyl)-1,4-dioxo-1,4-dihydronaphthalen-2-ylphosphonate (5e). Compound **5e** was synthesized via oxidation of 1,4-dihydroxynaphthalene **3e** according to the general procedure. Yellow solid; yield 93%. R_f 0.50 (60% EtOAc/hexane); mp 176−177 °C; IR (KBr, cm^{-1}): 1068, 1157, 1385, 1667, 1720, 2400; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02−8.09 (m, 2H), 7.70−7.77 (m, 2H), 7.36−7.40 (m, 2H), 7.22−7.26 (m, 2H), 3.53 (d, $^3J_{H\text{-}P}$ = 11.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.3 (d, $^3J_{C\text{-}P}$ = 6.0 Hz), 183.6 (d, $^2J_{C\text{-}P}$ = 17.7 Hz), 153.3, 136.8 (d merged with peak at 135.9, $^1J_{C\text{-}P}$ = 180.9 Hz), 135.9 (peak merged with d at 136.8), 134.6, 134.3, 132.1 (d, $J_{C\text{-}P}$ = 9.4 Hz), 131.6 (d, $J_{C\text{-}P}$ = 6.5 Hz), 131.4, 131.0 ($C_{Ar}H$ × 2), 127.9 ($C_{Ar}H$ × 2), 127.0, 126.6, 53.3 (d, $^2J_{C\text{-}P}$ = 6.3 Hz, {PO}OCH_3 × 2); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 12.68; HRMS for $C_{18}H_{14}ClO_5P$: calcd. (MH^+): 377.0340, found: 377.0338.

Dimethyl 1′,4′-Dioxo-1′,4′-dihydro-1,2′-binaphthyl-3′-ylphosphonate (5f). Compound **5f** was synthesized via oxidation of 1,4-dihydroxynaphthalene **3j** according to the general procedure. Yellow solid; yield 88%. R_f 0.50 (60% EtOAc/hexane); mp 193−195 °C; IR (KBr, cm^{-1}): 1065, 1220, 1399, 1637, 3402; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 7.4 Hz, 1H), 8.00 (d, J = 7.6 Hz, 1H), 7.81−7.86 (m, 2H), 7.70−7.78 (m, 2H), 7.46−7.50 (m, 1H), 7.34−7.42 (m, 3H), 7.30 (d, J = 6.8 Hz, 1H), 3.42 (d, $^3J_{H\text{-}P}$ = 11.4 Hz, 3H), 3.04 (d, $^3J_{H\text{-}P}$ = 11.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.2 (d, $^3J_{C\text{-}P}$ = 6.6 Hz), 183.7 (d, $^2J_{C\text{-}P}$ = 18.2 Hz), 154.7 (d, $J_{C\text{-}P}$ = 2.3 Hz), 138.7 (d, $^1J_{C\text{-}P}$ = 181.9 Hz), 134.6, 134.4, 134.3, 132.9, 132.3 (d, $J_{C\text{-}P}$ = 9.4 Hz), 132.0 (d, $J_{C\text{-}P}$ = 6.4 Hz), 131.5 (d, $J_{C\text{-}P}$ = 9.7 Hz), 129.4, 128.4, 127.1, 126.8 (d, $J_{C\text{-}P}$ = 2.3 Hz), 126.6, 126.3 (d, $J_{C\text{-}P}$ = 2.1 Hz), 126.1, 125.4, 124.9, 53.7 (d, $^2J_{C\text{-}P}$ = 6.3 Hz, {PO}OCH_3), 52.7 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, {PO}OCH_3); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 12.34; HRMS for $C_{22}H_{17}O_5P$: calcd. (MH^+): 393.0886, found: 393.0884.

7-Bromo-3-(2-bromophenyl)-1,4-dioxo-1,4-dihydronaphthalen-2-ylphosphonate (5g). Compound **5g** was synthesized via oxidation of 1,4-dihydroxynaphthalene **3n** according to the general procedure. Yellow solid; yield 84%. R_f 0.50 (60% EtOAc/hexane); mp 109−110 °C; IR (KBr, cm^{-1}): 1061, 1275, 1403, 1583, 1673, 2399, 3400; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.84−7.91 (m, 2H), 7.59 (d, J = 6.4 Hz, 1H), 7.35−7.38 (m, 1H), 7.19−7.28 (m, 2H), 3.71 (d, $^3J_{H\text{-}P}$ = 11.0 Hz, 3H), 3.37 (d, $^3J_{H\text{-}P}$ = 11.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.9 (d, $^3J_{C\text{-}P}$ = 5.7 Hz), 181.9 (d, $^2J_{C\text{-}P}$ = 18.5 Hz), 154.6, 137.8, 137.4, 133.1, 132.1, 130.5, 130.3, 130.1, 129.9, 129.8, 128.7, 126.9, 126.6, 122.0, 54.1 (d, $^2J_{C\text{-}P}$ = 6.5 Hz, {PO}OCH_3), 52.9 (d, $^2J_{C\text{-}P}$ = 6.3 Hz, {PO}OCH_3); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 11.18; HRMS for $C_{18}H_{13}Br_2O_5P$: calcd. (MH^+): 498.8940, found: 498.8939.

Dimethyl 6-Bromo-1,4-dioxo-3-phenyl-1,4-dihydronaphthalen-2-ylphosphonate (5h). Compound **5h** was synthesized via oxidation of 1,4-dihydroxynaphthalene **3o** according to the general procedure. Yellow solid; yield 84%. R_f 0.50 (60% EtOAc/hexane); mp 162−164 °C; IR (KBr, cm^{-1}): 1073, 1384, 1403, 1519, 1630, 1720, 2400, 2963, 3391, 3670, 3745, 3848; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.95 (d, J = 8.2 Hz, 1H), 7.87 (d, J = 8.2 Hz, 1H), 7.41 (br s, 3H), 7.29 (br s, 2H), 3.47 (d, $^3J_{H\text{-}P}$ = 11.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.8 (d, $^3J_{C\text{-}P}$ = 6.3 Hz), 182.9 (d, $^2J_{C\text{-}P}$ = 18.4 Hz), 154.1 (d, $J_{C\text{-}P}$ = 2.6 Hz), 137.5, 136.7 (d, $^1J_{C\text{-}P}$ = 181.8 Hz), 133.0 (d, $J_{C\text{-}P}$ = 6.4 Hz), 132.4, 130.7 (d, $J_{C\text{-}P}$ = 9.9 Hz), 129.9, 129.8, 129.7, 129.5 ($C_{Ar}H$ × 2), 128.3 (d, $J_{C\text{-}P}$ = 2.3 Hz), 127.7 ($C_{Ar}H$ × 3), 53.3 (d, $^2J_{C\text{-}P}$ = 6.3 Hz, {PO}OCH_3 × 2); ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 12.60; HRMS for $C_{18}H_{14}BrO_5P$: calcd. (MH^+): 420.9835, found: 420.9837.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00312.

Copies of ^{1}H, ^{13}C, and ^{31}P NMR spectra of all new compounds (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*Tel.: +91-522-277-4681. Fax: +91-522-277-1941. E-mail: namrata.rastogi@cdri.res.in.

Notes

The authors declare no competing financial interest.

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