JOC The Journal of Organic Chemistry

Note

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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.7b01595 • Publication Date (Web): 15 Aug 2017

Just Accepted

ACS Publications

The Journal of Organic Chemistry is published by the American Chemical Society.
1155 Sixteenth Street N.W., Washington, DC 20036

Carbon-Phosphorous Bond Formation on Anilines Mediated by a Hypervalent Iodine Reagent

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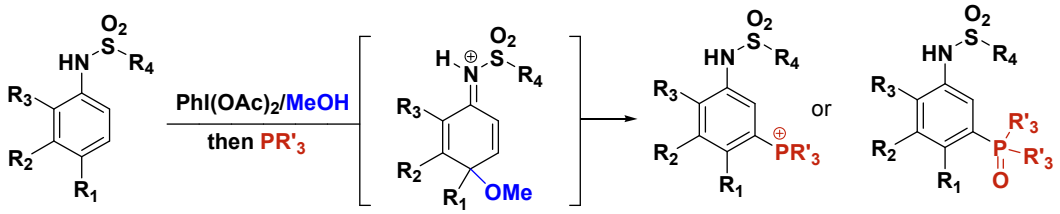
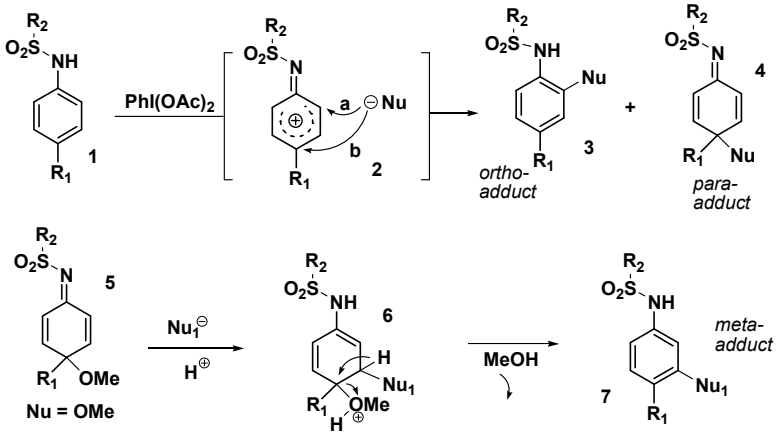


Abstract: Substituted anilines containing a sulfonyl group may be oxidized *in situ* in the presence of methanol and a hypervalent iodine reagent to form an active iminium species. Subsequent addition of phosphines or phosphites in the same pot produces *meta*-substituted anilines in good yields. This formal C-H bond functionalization is a direct and efficient means of selectively substituting the *meta*-position of anilines to produce aromatic phosphonium ions or phosphonates.

Methods for selective and mild activation of aromatic C-H bonds have elicited strong interest in the scientific community since these methods enable one-step formation of more highly-functionalized

systems without pre-activation. However, most of these efficient processes are restricted in scope and require catalytic amounts of a heavy metal.[1] Therefore, the discovery of novel, efficient, and environmentally benign methodologies enabling similar transformations remains an active field of research. As an alternative to methods requiring metal catalysts, formal C-H bond activation methods mediated by hypervalent iodine reagents[2] have been developed for electron-rich aromatic systems. Several methods using iodanes have recently been reported in the literature, examples of which include the noteworthy work of Kita,[3] Gaunt,[4] and Fan[5] and co-workers. Indeed, aromatic sulfonamides appear to be competent substrates, enabling selective coupling or nucleophilic addition at any position on the aromatic ring. The direct oxidation of anilines containing a sulfonyl group **1** in the presence of a nucleophile may occur at the *para* or the *ortho* positions depending on the nature of the nucleophile. With a hindered carbon-based nucleophile, the reaction occurs at the most accessible *ortho* position,[6] leading to **3**. In contrast, with smaller nucleophiles such as alcohols (methanol) the attack occurs at the most substituted position (*para*) to yield the dienimide[7] **4**. This functionalized system (Nu = MeO) may be strategically involved in a further 1,4-addition-rearomatization to produce a *meta*-substituted aromatic in an indirect manner.[8] Depending on the strategy and the nucleophile used, any position of an aniline may be selectively attacked, Scheme 1.



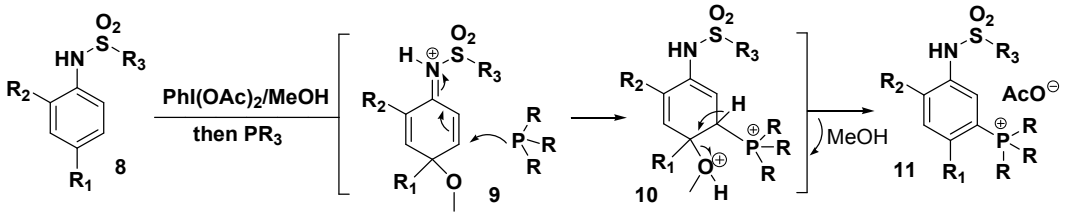
Scheme 1. Selective Substitution of Aniline derivatives

One interesting avenue would be to develop a method for one-pot *meta*-activation of the aniline derivative **7**. For this purpose, a reactive nucleophile stable under acidic and protic conditions (in the

presence of methanol and acetic acid) is required. Candidates of choice include elements in the third period of the periodic table, which are recognized for their nucleophilicity and poor basicity. In addition, metal-free direct carbon-phosphorous bond formation on unactivated aromatics is not often reported in the literature. Phosphonium salts are interesting reagents involved in noteworthy transformations[9] such as the Wittig reaction; they may also be employed as phase transfer catalysts[10] or as potentially chiral cationic counterions.[11]

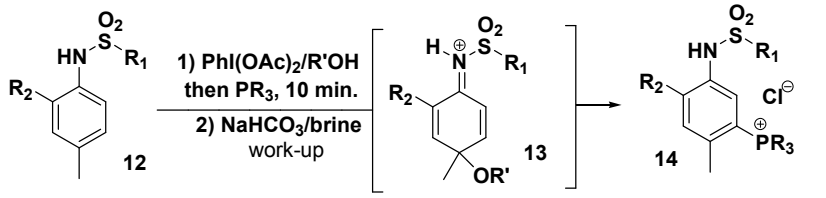
In this paper, we describe a formal C-H bond functionalization mediated by an iodane-(III) species and methanol to selectively produce good yields of *meta*-substituted anilines through a phosphorous moiety. This oxidative process involves the *in-situ* formation of a dienimine intermediate, which is trapped by a phosphorous nucleophile followed by a domino rearomatization. This transformation represents an aromatic variant of the Michaelis-Arbuzov reaction[12] on an unactivated aromatic sp^2 center.

Iodanes[13] catalyze remarkable transformations in electron-rich aromatic systems, including dearomatization processes and cross coupling transformations. Our interest in producing carbon-carbon bonds[6c] in such systems led us to explore new coupling routes with the formation of carbon-heteroatom bonds. Carbon-oxygen and carbon-nitrogen bond formation has been extensively reported in the literature,[13] and we were therefore motivated to investigate less well-explored techniques such as the direct functionalization of aromatic C-H bonds using a phosphorous group.[14] However, due to the direct reactivity of phosphines with iodanes to produce phosphonium oxides, it was obvious that these reagents could not be mixed. A previous report indicated that activation of aniline derivatives with iodanes in the presence of methanol would generate a dienimine species[7] that could readily be transformed into an iminium species by the acid released from the hypervalent iodine reagent reduction. This intermediate **9** appears to be an excellent Michael acceptor. A nucleophilic species insensitive to the acidic conditions generated during the oxidation could be added to the same pot to initiate a 1,4- addition process with the dearomatized species **9**. Phosphines and phosphites are valuable nucleophiles in this process, leading to enamines **10** which may subsequently be transformed into phosphonium ions **11** through a rearomatization process beginning with methanol elimination, Scheme 2.



Scheme 2. *meta*-Carbon-Phosphorous Bond Formation

Several conditions including a variety of phosphines, sulfonamides, solvents, and iodanes were investigated. DIB was chosen as the hypervalent iodine reagent of choice but PIFA (a perfluorinated and more expensive analog) may also be used with similar yields. However, DIB appears to be a milder and safer reagent in the presence of sensitive functional groups. Methanol was selected as the solvent of choice but the reaction may also be performed in ethanol or TFE at the cost of slightly lower yields. A series of representative experimental conditions is summarized in Table 1.



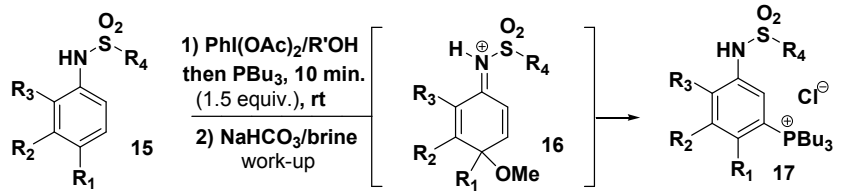
entry	R_1	R_2	R'	R	yield (%)
a	Me	H	Me	Ph*	**36**
b	*2*-NO_2-Ph	Me	Me	Ph*	**56**
c	Me	Me	Me	*n*-Bu	**85**
d	*4*-Tol	Me	Me	*n*-Bu	**78**
e	***2*-NO_2-Ph**	Me	Me	***n*-Bu**	**94**
f	***4*-NO_2-Ph**	Me	Me	***n*-Bu**	**95**
g	Me	Me	Et	*n*-Bu	**88**
h	Me	Me	CF_3CH_2	*n*-Bu	**84**

*48 h are required

Table 1. Conditions Optimization

The best results were obtained using electron-poor sulfonamides such as nosylamides, probably due to their electron-withdrawing effect on the Michael-acceptor moiety. A positive point is these sulfonamildes can be easily removed using a Fukuyama's process.[15] Aliphatic phosphines such as PBu_3 were much more reactive than the less nucleophilic aromatic derivative PPh_3. Phosphites were also competent reagents for this transformation. In our trials methanol was the best and least expensive solvent for this transformation, enabling direct functionalization of the *meta*-position. With these

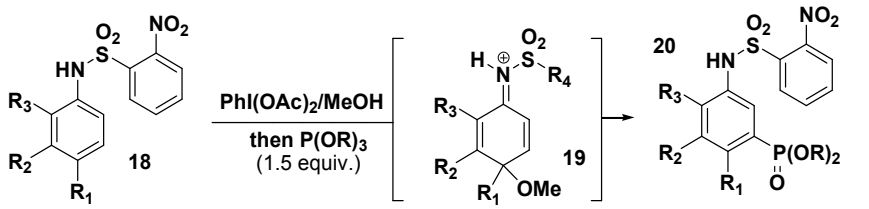
conditions in hand, several substituted nosylamides were transformed into phosphonium salts in good to excellent yields. In the case of non-symmetrical anilines, coupling occurred on the less hindered alkene for steric reasons, Table 2.



entry	R_1	R_2	R_3	R_4	yield (%)
a	Me	H	H	*2*-NO_2-Ph	**84**
b	Me	H	Me	*2*-NO_2-Ph	**94**
c	Me	H	Me	*4*-NO_2-Ph	**95**
d	OMe	H	H	*2*-NO_2-Ph	**95**
e	Et	H	H	*2*-NO_2-Ph	**79**
f	*n*-Bu	H	H	*2*-NO_2-Ph	**75**
g	Me	Br	H	Me	**90**
h	CH_2CO_2Me	H	H	Me	**65**
i	CH_2-CH_2-OTBS	H	H	Me	**68**
j	OMe	CH=CH=CH=CH		*2*-NO_2-Ph	**82**

Table 2. Phosphonium Salt Formation

As the process appears quite efficient in generating aromatic phosphonium ions, we were interested in extending the transformation to the formation of phosphonates. The introduction of phosphites to the reaction resulted in formation of the expected aryl phosphonates in good yields. In the case of compounds with structure **20b**, the reaction was carried out in ethanol rather than methanol. This change avoided partial trans-esterification of the phosphonate moiety, but reduced the yield. Representative experimental conditions are described in Table 3.

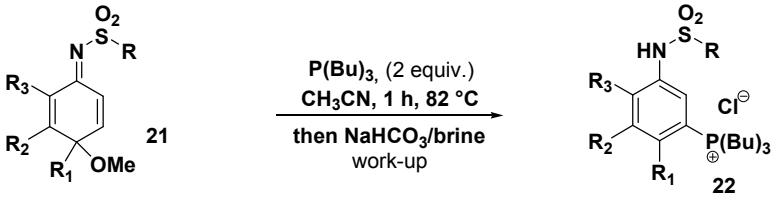


entry	R_1	R_2	R_3	R	yield (%)
a	Me	H	Me	Me	95
b*	Me	H	Me	Et	70
c	OMe	H	H	Me	95
d	OMe	CH=CH=CH=CH		Me	71

* EtOH has been used instead of MeOH to avoid partial trans-esterification

Table 3. Phosphonate Formation Conditions

In order to confirm the mechanism of this transformation and the efficiency of the one pot process, the results were compared to a two-step approach in which dienimine **21** was isolated and the 1,4-addition rearomatization representing the second part of the cascade was carried out separately under aprotic conditions (acetonitrile) at 82 °C. The expected *meta*-substituted anilines were obtained in fair to good yields. While the same products were formed in each protocol, the one-pot transformation occurred more rapidly and in better yield (examples **22a**, **22b** and **22e**), demonstrating that the process is more efficient under protic conditions mediated by an iminium species **16** as Michael acceptor, Table 4.



entry	R_1	R_2	R_3	R	yield (%)
a	Me	H	Me	Me	66
b	Me	H	Me	*2*-NO_2-Ph	79
c	Et	H	H	Me	60
d	Me	H	H	Et	72
e	Me	H	H	*2*-NO_2-Ph	81
f	Me	H	H	Me	59
g	Me	H	H	Tol.	56
h	OMe	CH=CH=CH=CH		Me	80

Table 4. Tributyl-phosphine 1,4-addition-Rearomatization Domino Process

We have developed a selective oxidative method enabling production of a carbon-phosphorous bond at the *meta*-position of aniline derivatives. This process occurs in one pot via the formation of a dieniminium intermediate that is readily transformed into the substituted aromatic system through a domino 1,4-addition and rearomatization process. This transformation is equivalent to a C-H bond functionalization without the need for metal catalysts.

Experimental Section:

Unless otherwise indicated, ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, in $CDCl_3$ solutions. Chemical shifts are reported in ppm on the δ scale. Multiplicities are described as s (singlet), d (doublet), dd, ddd, etc. (doublet of doublets, doublet of doublets of doublets, etc.), t (triplet), q (quartet), quin (quintuplet), m (multiplet), and further qualified as app (apparent), br (broad). Coupling

constants, J, are reported in Hz. HRMS were measured in the electrospray (ESI) mode on a LC-MSD TOF mass analyzer.

a) General procedure for the preparation of sulfonamide products 12/15

To a solution of the corresponding aniline (1 mmol, 1.0 equiv.) and pyridine (2.4 mmol, 2.4 equiv.) in CH_2Cl_2 (10 mL) at 0 °C the corresponding sulfonyl chloride or nitrobenzenesulfonyl chloride (1.1 mmol, 1.1 equiv.) was added slowly. The reaction mixture was allowed to warm to room temperature and stirred overnight. After complete conversion of the starting material (followed by TLC), the reaction was quenched with a solution of HCl (1M). The phases were separated and the aqueous phase extracted with CH_2Cl_2. The organic layers was washed with brine then, the organic phases were dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by silica gel chromatography (DCM/hexanes or EtOAc/hexanes)/recrystallization in ethanol or without purification to give the desired sulfonamides products **12**/**15**.

b) General procedure for the formation of phosphonium/phosphonate product 14/17/20:

Iodobenzene diacetate ("DIB", 0.15 mmol, 1.5 equiv.) was added to a vigorously stirred solution of sulfonamide **12/15/18** (0.1 mmol, 1 equiv.) in a minimum of MeOH (0.5 mL) at room temperature. The mixture was then stirred for 5 min, and phosphine or phosphite (0.15 mmol, 1.5 equiv.) was added (the reaction was followed by TLC with a mixture of ethyl acetate/hexane, 10 min. with PBu_3 or phosphite and 48 hours with PPh_3). The crude was concentrated under vacuum and the residue was quenched with a saturated solution of $NaHCO_3$. The phases were separated and the aqueous phase extracted with CH_2Cl_2. The organic layers was washed with brine then, the organic phases were dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by silica gel chromatography with a mixture of CH_2Cl_2/MeOH excepted for compounds **20a-d** (mixture of ethyl acetate/hexane) to give corresponding phosphonium/phosphonate products **14/17/20**.

c) General procedure for the formation of compounds 21:

Iodobenzene diacetate («DIB», 2 mmol, 2 equiv.) was added to a vigorously stirred solution of sulfonamide (1 mmol, 1 equiv.) in MeOH (5 mL) at 0°C. The mixture was then stirred for 5 min. (followed by TLC with a mixture of ethylacetate/hexane) and then concentrated under vacuum. The

residue was purified by silica gel chromatography with a mixture of ethyl acetate/hexane to give product **21**.

d) General procedure for the formation of phosphonium product 22:

To a solution of **21** (0.1 mmol, 1 equiv.) in acetonitrile (1 mL) was added tributylphosphine (2.0 mmol, 2.0 equiv.). The mixture was then stirred at 82°C between 20 min. and 2 hours. After completion, the reaction mixture was concentrated under reduced pressure. The residue was purified by silica gel chromatography with a mixture of CH_2Cl_2/MeOH or by recrystallization in diethyl ether to afford **22**.

N-p-tolylmethanesulfonamide (12a)[16]**:** was obtained without purification as a white solid: 0.9 mmol, 167 mg, 90% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (br, 4H), 7.08 (s, 1H), 2.98 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.6, 134.2, 130.3, 121.7, 39.0, 20.9.

N-(2,4-dimethylphenyl)-2-nitrobenzenesulfonamide (12b): was obtained without purification as a brown solid: 0.95 mmol, 291 mg, 95% yield; Mp: 102-104 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, J = 7.2 Hz, 1H), 7.82 – 7.67 (m, 2H), 7.61 (dt, J = 7.6, 3.8 Hz, 1H), 7.05 (br, 1H), 7.03 (s, 1H), 6.97 (br, 1H), 6.91 (d, J = 8.0 Hz, 1H), 2.27 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.0, 137.5, 133.9, 133.5, 132.8, 131.9, 131.5, 131.1, 127.5, 126.2, 125.3, 20.98, 17.83; LRMS (ESI): Calc. for $C_{14}H_{15}N_2O_4S$ $(M+H)^+$: 307; found: 307.

N-(2,4-dimethylphenyl)methanesulfonamide (12c)[17]**:** was obtained without purification as a white solid : 0.94 mmol, 187 mg, 94% yield; Mp: 131-133 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (d, J = 8.0 Hz, 1H), 7.04 (s, 1H), 7.01 (d, J = 8.2 Hz, 1H), 6.67 (s, 1H), 2.98 (s, 3H), 2.31 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.5, 132.0, 131.9, 127.8, 124.5, 39.7, 20.9, 18.1.

N-(2,4-dimethylphenyl)-4-methylbenzenesulfonamide (12d)[18]: was obtained by silica gel chromatography with a mixture of EtOAc/Hexane (1:1) as a white solid: 0.88 mmol, 242 mg, 88% yield; Mp: 93-94 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, J = 8.3 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.0 Hz, 1H), 6.95 – 6.87 (m, 2H), 6.75 (s, 1H), 2.38 (s, 3H), 2.25 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.7, 136.9, 136.3, 132.3, 131.8, 131.5, 129.6, 127.5, 127.3, 125.3, 21.6, 20.9, 17.6.

N-(2,4-dimethylphenyl)-4-nitrobenzenesulfonamide (12f): was obtained by recrystallization in ethanol as a white solid : 0.95 mmol, 291 mg, 95% yield; Mp: 133-134 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.8 Hz, 2H), 7.90 (d, *J* = 8.8 Hz, 2H), 7.08 (d, *J* = 8.7 Hz, 1H), 7.00 – 6.89 (m, 2H), 6.77 (s, 1H), 2.27 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.2, 145.5, 137.6, 133.0, 132.0, 130.6, 128.6, 127.9, 125.9, 124.3, 21.0, 17.7. LRMS (ESI): Calc. for $C_{14}H_{15}N_2O_4S$ $(M+H)^+$: 307; found: 307.

(2-methyl-5-(methylsulfonamido)phenyl)triphenylphosphonium chloride (14a): was obtained by silica gel chromatography with a mixture of CH_2Cl_2/MeOH (9:1) as a brown solid: 0.036 mmol, 16.1 mg, 36% yield; Mp: 67-69 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (t, *J* = 6.9 Hz, 3H), 7.71 – 7.51 (m, 13H), 7.20 (t, *J* = 7.9 Hz, 1H), 6.94 (dd, *J* = 18.0, 1.9 Hz, 1H), 2.83 (s, 3H), 1.78 (s, 3H); ^{13}C $\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 150.5, 150.3, 135.0, 135.0, 134.4, 134.3, 134.2, 134.1, 130.6, 130.4, 129.1, 129.0, 128.3, 128.2, 126.8, 126.8, 120.0, 118.9, 114.0, 112.8, 39.7, 22.1, 22.0; ^{31}P NMR (122 MHz, $CDCl_3$) δ 22.6 (br); HRMS (ESI): Calc. for $C_{26}H_{25}NO_2PS^+$ $(M)^+$: 446.1338; found: 446.1324.

(2,4-dimethyl-5-(2-nitrophenylsulfonamido)phenyl)triphenylphosphonium chloride (14b): was obtained by silica gel chromatography with a mixture of CH_2Cl_2/MeOH (97:03) as an yellow solid: 0.056 mmol, 31.8 mg, 56% yield; Mp: 247-249 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 – 7.70 (m, 4H), 7.68 – 7.57 (m, 6H), 7.55 (s, 2H), 7.54 – 7.48 (m, 4H), 7.31 – 7.25 (m, 2H), 7.24 – 7.16 (m, 2H), 7.11 (d, *J* = 7.3 Hz, 1H), 3.28 (s, 1H), 2.29 (s, 3H), 1.75 (s, 3H); ^{13}C $\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 148.1, 147.2, 147.0, 141.6, 139.9, 135.1, 134.9, 134.8, 134.8, 134.2, 134.1, 131.0, 130.8, 130.5, 130.4, 130.2, 129.9, 128.6, 128.4, 122.7, 120.3, 119.1, 110.2, 109.0, 22.1, 19.4; ^{31}P NMR (122 MHz, $CDCl_3$) δ 21.8 (br); HRMS (ESI): Calc. for $C_{32}H_{28}N_2O_4PS^+$ $(M)^+$: 567.1502; found: 567.1496.

Tributyl(2,4-dimethyl-5-(methylsulfonamido)phenyl)phosphonium chloride (14c): was obtained by silica gel chromatography with a mixture of CH_2Cl_2/MeOH (97:03) as an orange solid: 0.085 mmol, 34 mg, 85% yield; Mp: 162-163 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, *J* = 15.2 Hz, 1H), 7.04 (d, *J* = 6.2 Hz, 1H), 4.13 (br, 1H), 2.82 (s, 3H), 2.51 – 2.37 (m, 6H), 2.35 (s, 3H), 2.28 (s, 3H), 1.56 – 1.30 (m, 12H), 0.89 (br, 9H); ^{13}C $\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 147.2, 147.0, 139.9, 139.8, 135.2, 135.0, 129.2, 129.1, 124.5, 124.4, 109.9, 108.9, 40.0, 24.2, 24.1, 24.1, 24.0, 23.8, 21.1, 21.1, 21.0, 20.9, 20.5, 20.5, 19.3, 19.3, 13.5; ^{31}P NMR (122 MHz, $CDCl_3$) δ 30.0 (br); HRMS (ESI): Calc. for $C_{21}H_{39}NO_2PS^+$ $(M)^+$: 400.2434; found: 400.2415.

Tributyl(2,4-dimethyl-5-(4-methylphenylsulfonamido)phenyl)phosphonium chloride (14d): was obtained by silica gel chromatography with a mixture of CH_2Cl_2/MeOH (9:1) as a yellow solid: 0.078 mmol, 37.2 mg, 78% yield; Mp: 163-164 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 15.3 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 6.5 Hz, 1H), 2.33 (s, 3H), 2.31 – 2.22 (m, 12H), 1.44 – 1.30 (m, 6H), 1.29 – 1.16 (m, 6H), 0.87 (t, *J* = 7.2 Hz, 9H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 147.0, 146.9, 143.2, 139.6, 139.6, 134.8, 134.6, 128.7, 128.6, 127.2, 124.5, 124.3, 109.6, 108.6, 23.9, 23.8, 23.7, 23.7, 21.4, 20.7, 20.7, 20.6, 19.9, 19.3, 13.5; ^{31}P NMR (122 MHz, $CDCl_3$) δ 29.5 (br); HRMS (ESI): Calc. for $C_{27}H_{43}NO_2PS^+$ $(M)^+$: 476.2747; found: 476.2726.

Tributyl(2,4-dimethyl-5-(2-nitrophenylsulfonamido)phenyl)phosphonium chloride (14e): was obtained as an yellow solid: 0.095 mmol, 48.2 mg, 95% yield; Mp: 159-161 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (d, *J* = 6.7 Hz, 1H), 7.43 – 7.27 (m, 4H), 6.99 (d, *J* = 6.2 Hz, 1H), 2.32 (m, 12H), 1.51 – 1.14 (m, 12H), 0.84 (t, *J* = 7.0 Hz, 9H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 149.3, 147.2, 147.1, 139.5, 139.4, 139.3, 134.9, 134.7, 130.6, 130.6, 130.1, 129.1, 129.0, 123.8, 123.7, 122.5, 109.8, 108.8, 23.8, 23.6, 20.8, 20.8, 20.5, 19.9, 19.2, 13.5; HRMS (ESI): Calc. for $C_{26}H_{40}N_2O_4PS^+$ $(M)^+$: 507.2441; found: 507.2418.

Tributyl(2,4-dimethyl-5-(4-nitrophenylsulfonamido)phenyl)phosphonium chloride (14f): was obtained by silica gel chromatography with a mixture of CH_2Cl_2/MeOH (97:03) as a dark orange solid: 0.095 mmol, 48.2 mg, 95% yield; Mp: 152-154 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.7 Hz, 2H), 8.02 (d, *J* = 8.8 Hz, 2H), 7.54 (d, *J* = 15.4 Hz, 1H), 7.04 (d, *J* = 6.6 Hz, 1H), 2.27 (br, 12H), 1.51 – 1.28 (m, 12H), 0.91 (t, *J* = 7.0 Hz, 9H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 153.4, 148.2, 146.7, 146.5, 140.3, 135.3, 135.1, 129.8, 129.7, 127.7, 125.0, 124.9, 123.4, 109.6, 108.6, 23.9, 23.9, 23.7, 20.9, 20.8, 20.2, 19.1, 13.4; ^{31}P NMR (122 MHz, $CDCl_3$) δ 29.6 (br); HRMS (ESI): Calc. for $C_{26}H_{40}N_2O_4PS^+$ $(M)^+$: 507.2441; found: 507.2445.

2-nitro-N-(p-tolyl)benzenesulfonamide (15a)[19]: was obtained by silica gel chromatography with a mixture of EtOAc/Hexane (1:9) as an orange solid: 0.90 mmol, 263 mg, 90% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 – 7.75 (m, 2H), 7.68 (td, *J* = 7.8, 1.4 Hz, 1H), 7.56 (td, *J* = 7.7, 1.2 Hz, 1H), 7.17 (s, 1H),

7.06 (s, 4H), 2.28 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.3, 136.8, 134.0, 132.8, 132.6, 132.3, 131.9, 130.1, 125.3, 123.8, 21.0.

N-(4-methoxyphenyl)-2-nitrobenzenesulfonamide (15d)[20]: was obtained by silica gel chromatography with a mixture of CH_2Cl_2/Hexane (5:5) as an yellow solid: 0.85 mmol, 262 mg, 85% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.75 – 7.64 (m, 2H), 7.55 (td, *J* = 7.7, 1.2 Hz, 1H), 7.13 (s, 1H), 7.10 – 7.04 (m, 2H), 6.80 – 6.72 (m, 2H), 3.74 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.7, 148.3, 134.0, 132.6, 132.2, 131.9, 127.9, 126.3, 125.3, 114.6, 55.5.

N-(4-ethylphenyl)-2-nitrobenzenesulfonamide (15e)[21]: was obtained without purification as a brown solid : 0.95 mmol, 291 mg, 95% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 – 7.77 (m, 2H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.08 (br, 4H), 2.58 (q, *J* = 7.6 Hz, 2H), 1.17 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.3, 143.1, 134.0, 133.0, 132.6, 132.4, 131.9, 128.9, 125.3, 123.8, 28.3, 15.4.

N-(4-butylphenyl)-2-nitrobenzenesulfonamide (15f): was obtained without purification as a dark red solid : 0.95 mmol, 317 mg, 95% yield; Mp: 100-102 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 – 7.77 (m, 2H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.26 (br, 1H), 7.09 (br, 4H), 2.55 (t, *J* = 7.5 Hz, 2H), 1.53 (dd, *J* = 14.5, 7.3 Hz, 2H), 1.31 (dd, *J* = 14.3, 7.1 Hz, 2H), 0.91 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.3, 141.8, 134.0, 133.0, 132.6, 132.4, 131.9, 129.5, 125.3, 123.7, 35.1, 33.5, 22.3, 14.0; LRMS (ESI): Calc. for $C_{16}H_{19}N_2O_4S$ $(M+H)^+$: 319; found: 319.

N-(3-bromo-4-methylphenyl)methanesulfonamide (15g)[6d]: was obtained without purification as a brown solid : 0.95 mmol, 250 mg, 95% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (d, *J* = 2.2 Hz, 1H), 7.23 – 7.16 (m, 2H), 7.12 (dd, *J* = 8.2, 2.2 Hz, 1H), 3.02 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.6, 135.3, 131.6, 125.4, 124.9, 120.2, 39.4, 22.4.

Methyl 2-(4-(methylsulfonamido)phenyl)acetate (15h)[2f]: was obtained without purification as a brown solid: 0.90 mmol, 218 mg, 90%; Mp: 114-116 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.7

Hz, 2H), 7.18 (d, *J* = 8.6 Hz, 2H), 7.13 (br, 1H), 3.70 (s, 3H), 3.60 (s, 2H), 2.98 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.2, 136.0, 131.2, 130.7, 121.1, 52.3, 40.5, 39.3.

N-(4-(2-((tert-butyldimethylsilyl)oxy)ethyl)phenyl)methanesulfonamide (15i)[6c]: was obtained by silica gel chromatography with a mixture of EtOAc/Hexane (2:8) as an yellow oil: 0.95 mmol, 313 mg, 95% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 – 7.11 (m, 4H), 6.83 (s, 1H), 3.78 (t, *J* = 6.8 Hz, 2H), 2.97 (s, 3H), 2.79 (t, *J* = 6.8 Hz, 2H), 0.85 (s, 9H), -0.03 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.1, 134.8, 130.5, 121.4, 64.4, 53.6, 39.0, 39.2, 29.8, 26.0, 18.4, -5.3.

N-(4-methoxynaphthalen-1-yl)-2-nitrobenzenesulfonamide (15j)[22]: was obtained without purification as a brown solid: 0.95 mmol, 311 mg, 95% yield; ^{1}H NMR (300 MHz, Acetone-d6) δ 9.17 (br, 1H), 8.21 (d, *J* = 7.7 Hz, 1H), 8.08 – 7.72 (m, 7.3 Hz, 4H), 7.75 – 7.54 (m, 2H), 7.57 – 7.27 (m, 4H); ^{13}C NMR (75 MHz, Acetone-d6) δ 149.0, 135.3, 135.2, 133.4, 133.2, 132.4, 131.7, 131.3, 129.0, 128.9, 127.3, 127.2, 126.3, 126.1, 125.8, 123.6.

Tributyl(2-methyl-5-(2-nitrophenylsulfonamido)phenyl)phosphonium) chloride (17a): was obtained by silica gel chromatography with a mixture of CH_2Cl_2/MeOH (97:03) as a brown solid: 0.084 mmol, 41.5 mg, 84% yield; Mp: 37-40 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.48 – 7.34 (m, 3H), 7.34 – 7.34 (m, 1H), 7.28 (s, 1H), 7.04 (t, *J* = 7.3 Hz, 1H), 4.13 (s, 1H), 2.49 – 2.36 (m, 6H), 2.34 (s, 3H), 1.49 – 1.22 (m, 12H), 0.85 (t, *J* = 7.0 Hz, 9H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 149.2, 147.4, 147.3, 138.2, 133.8, 133.6, 130.9, 130.7, 130.6, 130.2, 130.1, 127.8, 125.9, 125.8, 122.8, 114.1, 113.1, 23.8, 23.6, 20.9, 20.4, 19.7, 13.5; ^{31}P NMR (122 MHz, $CDCl_3$) δ 30.4 (br); HRMS (ESI): Calc. for $C_{25}H_{38}N_2O_4PS^+$ $(M)^+$: 493.2284; found: 493.2312.

Tributyl(2-methoxy-5-(2-nitrophenylsulfonamido)phenyl)phosphonium chloride (17d): was obtained by silica gel chromatography with a mixture of CH_2Cl_2/MeOH (97:03) as an orange solid: 0.095 mmol, 48.4 mg, 95% yield; Mp: 45-47 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.54 – 7.37 (m, 3H), 7.35 (d, *J* = 1.2 Hz, 1H), 7.32 (dd, *J* = 5.9, 1.9 Hz, 1H), 6.82 (dd, *J* = 9.0, 6.4 Hz, 1H), 3.81 (s, 3H), 2.45 – 2.09 (m, 6H), 1.47 – 1.18 (m, 12H), 0.83 (t, *J* = 6.9 Hz, 9H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 155.5, 149.0, 140.7, 140.5, 137.1, 131.2, 131.1, 130.9, 130.7, 126.7, 126.6,

122.8, 112.5, 112.4, 103.7, 102.6, 56.2, 23.8, 23.7, 23.6, 19.6, 18.9, 13.4; ^{31}P NMR (122 MHz, $CDCl_3$) δ 29.7 (br); HRMS (ESI): Calc. for $C_{25}H_{38}N_2O_5PS^+$ $(M)^+$: 509,2234; found: 509.2235.

Tributyl(2-ethyl-5-(2-nitrophenylsulfonamido)phenyl)phosphonium chloride (17e): was obtained by silica gel chromatography with a mixture of CH_2Cl_2/MeOH (97:03) as a brown solid: 0.079 mmol, 40.1 mg, 79% yield; Mp: 130-131 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 6.2, 2.1 Hz, 1H), 7.46 – 7.34 (m, 3H), 7.31 (d, *J* = 8.5 Hz, 1H), 7.18 (dd, *J* = 15.5, 2.3 Hz, 1H), 7.14 – 7.08 (m, 1H), 3.47 (s, 1H), 2.57 (q, *J* = 7.3 Hz, 2H), 2.45 – 2.30 (m, *J* = 15.9, 11.8 Hz, 6H), 1.47 – 1.23 (m, 12H), 1.18 (t, *J* = 7.4 Hz, 3H), 0.84 (t, *J* = 7.0 Hz, 9H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 149.2, 148.1, 147.9, 138.67, 136.3, 136.2, 131.5, 131.3, 130.9, 130.6, 128.2, 128.1, 125.3, 125.1, 122.8, 113.2, 112.2, 26.4, 26.3, 23.9, 23.9, 23.8, 23.6, 21.0, 20.3, 15.7, 13.5; ^{31}P NMR (122 MHz, $CDCl_3$) δ 29.9 (br); HRMS (ESI): Calc. for $C_{26}H_{40}N_2O_4PS^+$ $(M)^+$: 507.2441; found: 507.2447.

Tributyl(2-butyl-5-(2-nitrophenylsulfonamido)phenyl)phosphonium chloride (17f): was obtained by silica gel chromatography with a mixture of CH_2Cl_2/MeOH (97:03) as a brown oil: 0.075 mmol, 40.2 mg, 75% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 6.2, 1.7 Hz, 1H), 7.47 – 7.34 (m, 3H), 7.31 (d, *J* = 8.5 Hz, 1H), 7.20 (dd, *J* = 15.2, 1.7 Hz, 1H), 7.11 (dd, *J* = 8.3, 6.6 Hz, 1H), 3.34 (s, 1H), 2.50 (t, *J* = 7.3 Hz, 2H), 2.43 – 2.29 (m, 6H), 1.54 – 1.24 (m, 16H), 0.97 – 0.74 (m, 12H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 149.2, 148.0, 147.8, 138.6, 135.1, 135.0, 132.0, 131.8, 130.9, 130.6, 130.5, 128.1, 125.4, 125.3, 122.8, 113.3, 112.3, 34.0, 33.3, 24.0, 23.9, 23.9, 23.6, 22.8, 21.1, 20.5, 14.1, 13.5; ^{31}P NMR (122 MHz, $CDCl_3$) δ 30.2 (br); HRMS (ESI): Calc. for $C_{28}H_{44}N_2O_4PS^+$ $(M)^+$: 535.2754; found: 535.2730.

(3-bromo-2-methyl-5-(methylsulfonamido)phenyl)tributylphosphonium chloride (17g): was obtained by silica gel chromatography with a mixture of CH_2Cl_2/MeOH (98:02 to 95:05) as an yellow solid: 0.090 mmol, 41.9 mg, 90% yield; Mp: 50-52 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.83 (d, *J* = 14.2 Hz, 1H), 5.77 (br, 1H), 3.00 (s, 3H), 2.69 – 2.55 (m, 6H), 2.52 (s, 3H), 1.56 – 1.35 (m, 12H), 0.92 (t, *J* = 6.9 Hz, 9H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 142.9, 142.7, 132.4, 132.3, 129.4, 129.2, 128.9, 125.6, 125.5, 117.9, 116.9, 39.8, 24.2, 24.1, 23.9, 23.7, 21.7, 21.7, 20.9, 20.3, 13.5; ^{31}P NMR (122 MHz, $CDCl_3$) δ 33.1 (br); HRMS (ESI): Calc. for $C_{20}H_{36}BrNO_2PS^+$ $(M)^+$: 464.1382; found: 464.1376.

Tributyl(2-(2-methoxy-2-oxoethyl)-5-(methylsulfonamido)phenyl)phosphonium chloride (17h): by silica gel chromatography with a mixture of CH_2Cl_2/MeOH (98:02 to 95:05) as a brown foam: 0.065 mmol, 28.9 mg, 65% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, *J* = 14.9 Hz, 1H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.40 (dd, *J* = 8.6, 5.9 Hz, 1H), 6.23 (br, 1H), 3.74 (s, 2H), 3.70 (s, 3H), 3.01 (s, 3H), 2.65 – 2.53 (m, 6H), 1.54 – 1.36 (m, 12H), 0.91 (t, *J* = 6.9 Hz, 9H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 170.6, 143.3, 143.1, 134.6, 134.5, 129.9, 129.8, 126.1, 126.0, 125.4, 116.8, 115.8, 52.8, 39.8, 39.3, 29.8, 24.1, 24.0, 23.9, 23.7, 21.1, 20.5, 13.5; ^{31}P NMR (122 MHz, $CDCl_3$) δ 31.9 (br); HRMS (ESI): Calc. for $C_{22}H_{39}NO_4PS^+$ $(M)^+$: 444.2332; found: 444.2318.

Tributyl(2-(2-((tert-butyldimethylsilyl)oxy)ethyl)-5-(methylsulfonamido)-phenyl)-phosphonium chloride (17i): was obtained was obtained by silica gel chromatography with a mixture of CH_2Cl_2/MeOH (98:02 to 95:05) as an yellow foam: 0.068 mmol, 36.1 mg, 68% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.72 (s, 1H), 8.49 (d, *J* = 15.3 Hz, 1H), 7.93 (d, *J* = 8.6 Hz, 1H), 7.43 (dd, *J* = 8.6, 5.8 Hz, 1H), 3.89 (t, *J* = 6.2 Hz, 2H), 3.10 (s, 3H), 2.89 (t, *J* = 6.1 Hz, 2H), 2.64 – 2.51 (m, 6H), 1.63 – 1.46 (m, 12H), 0.97 (t, *J* = 6.8 Hz, 9H), 0.84 (s, 9H), 0.01 (s, 6H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 139.4, 139.2, 138.0, 137.9, 132.9, 132.8, 125.9, 125.7, 125.3, 117.1, 116.0, 63.1, 39.7, 36.7, 34.8, 31.7, 29.8, 29.2, 26.0, 25.8, 25.4, 24.2, 24.0, 23.8, 23.6, 22.7, 21.5, 20.8, 18.4, 14.2, 13.6, 11.5, -3.46, -5.27; ^{31}P NMR (122 MHz, $CDCl_3$) δ 31.5 (br); HRMS (ESI): Calc. for $C_{27}H_{53}NO_3PSSi^+$ $(M)^+$: 530.3248; found: 530.3228.

Tributyl(1-methoxy-4-(2-nitrophenylsulfonamido)naphthalen-2-yl)phosphonium chloride (17j): was obtained by recrystallization in diethyl ether as an yellow solid: 0.082 mmol, 45.9 mg, 82% yield; Mp: 51-52 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.89 (dd, *J* = 6.9, 2.7 Hz, 1H), 8.14 (dd, *J* = 6.1, 1.9 Hz, 1H), 7.86 (dd, *J* = 6.7, 2.6 Hz, 1H), 7.58 – 7.48 (m, 2H), 7.38 – 7.28 (m, 3H), 7.15 (d, *J* = 13.7 Hz, 1H), 3.98 (s, 3H), 2.46 – 2.25 (m, 6H), 1.52 – 1.24 (m, 12H), 0.88 (t, *J* = 7.0 Hz, 9H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 152.0, 149.5, 145.3, 145.1, 139.1, 134.7, 130.6, 130.5, 130.1, 127.4, 127.3, 126.9, 126.9, 122.5, 121.8, 110.3, 110.2, 103.9, 102.8, 63.8, 23.9, 23.8, 23.8, 23.7, 20.3, 19.6, 13.5; ^{31}P NMR (122 MHz, $CDCl_3$) δ 29.7 (br); HRMS (ESI): Calc. for $C_{29}H_{40}N_2O_5PS^+$ $(M)^+$: 559.2390; found: 559.2389.

Dimethyl (2,4-dimethyl-5-(2-nitrophenylsulfonamido)phenyl)phosphonate (20a): was obtained by silica gel chromatography with a mixture of ethyl acetate/hexane (4:6 to 78:22) as an yellow solid: 0.095 mmol, 39.4 mg, 95% yield; Mp: 137-139 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.7 Hz, 1H), 7.82 – 7.69 (m, 2H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.52 (d, *J* = 15.0 Hz, 1H), 7.09 (d, *J* = 6.0 Hz, 1H), 3.70 (s, 3H), 3.66 (s, 3H), 2.46 (s, 3H), 2.24 (s, 3H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 148.1, 141.5, 141.3, 139.9, 139.8, 134.6, 134.4, 134.1, 133.2, 132.7, 131.7, 131.6, 131.6, 131.5, 131.4, 125.6, 125.5, 123.2, 52.7, 52.7, 20.7, 20.7, 18.1; ^{31}P NMR (122 MHz, $CDCl_3$) δ 20.9 (br); HRMS (ESI): Calc. for $C_{16}H_{23}N_3O_7PS$ $(M+NH_4)^+$: 432.0989; found: 432.0988.

Diethyl (2,4-dimethyl-5-(2-nitrophenylsulfonamido)-phenyl)phosphonate (20b): was obtained by silica gel chromatography with a mixture of ethyl acetate/hexane (4:6 to 6:4) as a white solid: 0.070 mmol, 31.0 mg, 70% yield; Mp: 155-157 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.80 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.73 (td, *J* = 7.8, 1.4 Hz, 1H), 7.61 (td, *J* = 7.7, 1.1 Hz, 1H), 7.53 (d, *J* = 14.9 Hz, 1H), 7.15 (s, 1H), 7.09 (d, *J* = 6.0 Hz, 1H), 4.12 – 3.91 (m, 4H), 2.49 (s, 3H), 2.27 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 6H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 148.2, 141.4, 141.2, 139.6, 134.6, 134.4, 134.1, 133.3, 132.8, 131.6, 131.6, 131.4, 131.3, 131.3, 127.1, 125.6, 124.6, 124.6, 62.2, 62.2, 20.8, 20.8, 18.1, 16.5, 16.4; ^{31}P NMR (122 MHz, $CDCl_3$) δ 17.9 (br); HRMS (ESI): Calc. for $C_{18}H_{24}N_2O_7PS^+$ $(M+H)^+$: 443,1036; found: 443.1046.

Dimethyl (2-methoxy-5-(2-nitrophenylsulfonamido)phenyl)-phosphonate (20c): was obtained by silica gel chromatography with a mixture of ethyl acetate/hexane (75:25 to 95:05) as a white solid: 0.095 mmol, 39.6 mg, 95% yield; Mp: 147-148 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (td, *J* = 9.1, 0.9 Hz, 3H), 7.68 (td, *J* = 7.8, 1.2 Hz, 1H), 7.60 – 7.52 (m, 1H), 7.50 – 7.41 (m, 1H), 6.90 – 6.84 (m, 1H), 3.85 (s, 3H), 3.75 (s, 3H), 3.71 (s, 3H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 160.0, 148.4, 134.1, 132.6, 132.4, 131.7, 130.7, 130.6, 128.5, 128.3, 125.4, 117.9, 115.4, 112.3, 112.2, 56.4, 53.2, 53.2; ^{31}P NMR (122 MHz, $CDCl_3$); HRMS (ESI): Calc. for $C_{15}H_{18}N_2O_8PS$ $(M+H)^+$: 417.0516; found: 417.0511.

Dimethyl (1-methoxy-4-(2-nitrophenylsulfonamido)naphthalen-2-yl)phosphonate (20d): was obtained by silica gel chromatography with a mixture of ethyl acetate/hexane (4:6 to 6:4) as a white solid: 0.069 mmol, 32.2 mg, 69% yield; Mp: 51-53 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24 – 8.09 (m, 2H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.77 – 7.63 (m, 3H), 7.62 – 7.44 (m, 4H), 4.09 (s, 3H), 3.80 (s, 3H), 3.76

(s, 3H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 160.7, 148.3, 134.6, 134.1, 133.0, 132.8, 131.6, 129.6, 128.9, 128.7, 127.4, 127.3, 125.5, 123.7, 123.6, 118.0, 115.5, 64.2, 53.2, 53.1; ^{31}P NMR (122 MHz, $CDCl_3$) δ 29.7 (br); HRMS (ESI): Calc. for $C_{19}H_{19}N_2NaO_8PS$ $(M+Na)^+$: 489.0492; found: 489.0499.

(E)-N-(4-methoxy-2,4-dimethylcyclohexa-2,5-dien-1-ylidene)methanesulfonamide (21a)[8]: was obtained by silica gel chromatography with a mixture of EtOAc/Hexane (15:85) as a white foam: 0.86 mmol, 197 mg, 86% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (dd, J = 10.2, 2.7 Hz, 1H), 6.66 (dd, J = 10.2, 2.4 Hz, 1H), 6.48 (s, 1H), 3.16 (d, J = 2.6 Hz, 3H), 3.09 (d, J = 2.7 Hz, 3H), 1.92 (s, 3H), 1.32 (d, J = 2.4 Hz, 3H).

(E)-N-(4-methoxy-2,4-dimethylcyclohexa-2,5-dien-1-ylidene)-2-nitrobenzenesulfonamide (21b): was obtained by silica gel chromatography with a mixture of EtOAc/Hexane (15:85) as a white foam: 0.69 mmol, 232 mg, 69% yield, ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.35 – 8.22 (m, 1H), 7.85 (d, J = 8.8 Hz, 1H), 7.80 – 7.67 (m, 2H), 7.49 (d, J = 10.2 Hz, 1H), 6.80 (dd, J = 10.2, 2.4 Hz, 1H), 6.57 (s, 1H), 3.16 (s, 3H), 1.89 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9, 153.6, 149.1, 136.4, 135.0, 133.8, 132.6, 129.8, 124.9, 124.6, 73.2, 53.7, 26.0, 17.6; LRMS Calc. for $C_{15}H_{17}N_2O_5S$ $(M+H)^+$: 337; found: 337.

N-(4-ethyl-4-methoxycyclohexa-2,5-dien-1-ylidene)methanesulfonamide (21c)[8]: was obtained by silica gel chromatography with a mixture of EtOAc/Hexane (15:85) as an yellow oil: 0.85 mmol, 194 mg, 85% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (dd, J = 10.6, 1.8 Hz, 1H), 6.74 – 6.57 (m, 2H), 6.43 (dd, J = 10.3, 1.8 Hz, 1H), 3.16 (s, 6H), 1.73 (q, J = 7.6 Hz, 2H), 0.80 (t, J = 7.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.4, 152.0, 150.5, 131.4, 125.3, 76.5, 53.5, 43.1, 32.5, 7.9.

N-(4-methoxy-4-methylcyclohexa-2,5-dien-1-ylidene)ethanesulfonamide (21d): was obtained by silica gel chromatography with a mixture of EtOAc/Hexane (1:9) as a white solid: 0.86 mmol, 197 mg, 86% yield; Mp: 79-80 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (dd, J = 10.5, 2.0 Hz, 1H), 6.74 – 6.61 (m, 2H), 6.36 (dd, J = 10.2, 2.0 Hz, 1H), 3.20 (q, J = 7.4 Hz, 2H), 3.13 (s, 3H), 1.44 (t, J = 7.4 Hz, 3H), 1.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.4, 152.2, 150.8, 130.3, 124.2, 72.7, 53.6, 49.3, 26.0, 8.1; LRMS Calc. for $C_{10}H_{16}NO_3S$ $(M+H)^+$: 230; found: 230.

N-(4-methoxy-4-methylcyclohexa-2,5-dien-1-ylidene)-2-nitrobenzenesulfonamide (21e): was obtained by silica gel chromatography with a mixture of EtOAc/Hexane (15:85) as a white solid: 0.71 mmol, 228 mg, 71% yield; Mp: 151-152 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.33 – 8.27 (m, 1H), 7.89 – 7.82 (m, 1H), 7.79 – 7.73 (m, 2H), 7.55 (d, *J* = 9.9 Hz, 1H), 6.86 – 6.75 (m, 2H), 6.41 (d, *J* = 9.3 Hz, 1H), 3.20 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.6, 154.0, 152.5, 148.0, 134.5, 134.0, 132.7, 130.1, 124.9, 124.2, 73.0, 53.8, 26.0; LRMS Calc. for $C_{14}H_{15}N_2O_5S$ $(M+H)^+$: 323; found: 323.

N-(4-methoxy-4-methylcyclohexa-2,5-dien-1-ylidene)methanesulfonamide (21f)[8]: was obtained by silica gel chromatography with a mixture of EtOAc/Hexane (15:85) as a colorless oil: 0.95 mmol, 204 mg, 95% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, *J* = 9.5 Hz, 1H), 6.76 – 6.64 (m, 2H), 6.44 – 6.31 (m, 1H), 3.17 (s, 3H), 3.16 (s, 3H), 1.39 (s, 3H).

N-(4-methoxy-4-methylcyclohexa-2,5-dien-1-ylidene)-4-methylbenzenesulfonamide (21g): was obtained by silica gel chromatography with a mixture of EtOAc/Hexane (1:9) as a white solid: 0.89 mmol, 259 mg, 89 % yield; Mp: 123-124 °C, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.1 Hz, 2H), 7.60 (d, *J* = 10.2 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.74 (dd, *J* = 10.3, 2.2 Hz, 1H), 6.65 (dd, *J* = 10.0, 2.2 Hz, 1H), 6.35 (d, *J* = 10.0 Hz, 1H), 3.13 (s, 3H), 2.40 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.7, 152.6, 150.9, 143.8, 138.2, 130.5, 129.6, 127.2, 123.9, 72.7, 53.6, 26.0, 21.6; LRMS Calc. for $C_{15}H_{18}NO_3S$ $(M+H)^+$: 292; found: 292.

(E)-N-(4,4-dimethoxynaphthalen-1(4H)-ylidene)methanesulfonamide (21h)[2g]**:** was obtained by silica gel chromatography with a mixture of EtOAc/Hexane (1:9) as an brown oil: 0.95 mmol, 267 mg, 95% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.75 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.71 (d, *J* = 10.7 Hz, 1H), 7.66 (td, *J* = 7.6, 1.3 Hz, 1H), 7.52 – 7.44 (m, 1H), 6.86 (d, *J* = 10.7 Hz, 1H), 3.30 (s, 3H), 3.18 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.4, 143.9, 139.4, 133.6, 130.9, 129.2, 126.9, 126.4, 94.4, 51.3, 43.3.

Tributyl(2-ethyl-5-(methylsulfonamido)phenyl)phosphonium chloride (22c): was obtained by silica gel chromatography with a mixture of CH_2Cl_2/MeOH (95:05) as a brown oil: 0.060 mmol, 24.0 mg, 60% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.6 Hz, 1H), 7.43 (dd, *J* = 15.2, 1.8 Hz, 1H), 7.24

– 7.18 (m, 1H), 4.51 (br, 1H), 2.92 (s, 3H), 2.62 (q, *J* = 7.3 Hz, 2H), 2.54 – 2.39 (m, 6H), 1.50 – 1.37 (m, 12H), 1.24 (t, *J* = 7.5, 3H), 0.90 (t, *J* = 6.8 Hz, 9H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 147.5, 135.9, 131.9, 131.8, 126.5, 125.5, 125.4, 113.4, 112.4, 39.8, 29.8, 26.6, 26.6, 24.2, 24.1, 24.0, 23.8, 21.4, 20.7, 16.0, 14.2, 13.6; ^{31}P NMR (122 MHz, $CDCl_3$) δ 29.7 (br); HRMS (ESI): Calc. for $C_{21}H_{39}NO_2PS^+$ $(M)^+$: 400,2434; found: 400.2440.

Tributyl(5-(ethylsulfonamido)-2-methylphenyl)phosphonium chloride (22d): was obtained by recrystallization in diethyl ether as a white solid: 0.072 mmol, 28.8 mg, 72% yield; Mp: 61-63 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, *J* = 13.8 Hz, 2H), 7.08 (t, *J* = 7.5 Hz, 1H), 3.04 (q, *J* = 7.4 Hz, 2H), 2.37 – 2.25 (m, 9H), 1.54 – 1.43 (m, *J* = 3.6 Hz, 12H), 1.39 (t, *J* = 7.4 Hz, 3H), 0.96 (t, *J* = 6.8 Hz, 9H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 150.8, 150.6, 133.7, 133.5, 126.5, 126.4, 125.9, 125.1, 125.0, 113.2, 112.2, 45.8, 23.9, 23.8, 23.7, 23.5, 20.6, 19.9, 13.3, 9.2; ^{31}P NMR (122 MHz, $CDCl_3$) δ 29.7 (br); HRMS (ESI): Calc. for $C_{21}H_{39}NO_2PS^+$ $(M)^+$: 400,2434; found: 400.2428.

Tributyl(2-methyl-5-(methylsulfonamido)phenyl)phosphonium chloride (22f): was obtained by silica gel chromatography with a mixture of CH_2Cl_2/MeOH (9:1) as a yellow solid: 0.059 mmol, 22.8 mg, 59% yield; Mp: 86-89 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.8 Hz, 1H), 7.36 – 7.29 (m, 1H), 7.11 (t, *J* = 7.7 Hz, 1H), 2.96 (s, 3H), 2.39 – 2.26 (m, 9H), 1.54 – 1.41 (m, *J* = 3.7 Hz, 12H), 0.96 (t, *J* = 6.7 Hz, 9H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 150.9, 150.7, 133.8, 133.7, 126.3, 126.2, 125.3, 125.2, 113.3, 112.3, 39.2, 23.9, 23.8, 23.7, 23.5, 20.6, 19.9, 13.3; ^{31}P NMR (122 MHz, $CDCl_3$) δ 29.6 (br); HRMS (ESI): Calc. for $C_{20}H_{37}NO_2PS^+$ $(M)^+$: 386,2277; found: 386.2271.

Tributyl(2-methyl-5-(4-methylphenylsulfonamido)phenyl)phosphonium chloride (22g): was obtained by recrystallization in diethyl ether as a white solid: 0.056 mmol, 25.9 mg, 56% yield; Mp: 114-117 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.18 (d, *J* = 15.7 Hz, 1H), 7.10 (d, *J* = 7.9 Hz, 2H), 7.04 – 6.95 (m, 1H), 2.41 – 2.26 (m, 12H), 1.44 – 1.25 (m, 12H), 0.87 (t, *J* = 7.0 Hz, 9H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 150.1, 149.9, 143.5, 139.6, 133.7, 133.5, 128.8, 127.1, 127.0, 125.2, 125.1, 113.1, 112.1, 23.9, 23.7, 21.4, 20.6, 20.0, 13.5; ^{31}P NMR (122 MHz, $CDCl_3$) δ 30.0 (br); HRMS (ESI): Calc. for $C_{26}H_{41}NO_2PS^+$ $(M)^+$: 462,2590; found: 462.2598.

Tributyl(1-methoxy-4-(methylsulfonamido)naphthalen-2-yl)phosphonium chloride (22h): was obtained by recrystallization in diethyl ether as a brown solid: 0.080 mmol, 36.2 mg, 80% yield; Mp: 157-159 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.85 – 8.78 (m, 1H), 7.89 – 7.82 (m, 1H), 7.57 – 7.49 (m, 2H), 7.37 (d, *J* = 14.1 Hz, 1H), 4.01 (s, 3H), 3.01 (s, 3H), 2.45 – 2.33 (m, 6H), 1.56 – 1.47 (m, 12H), 0.96 (t, *J* = 6.7 Hz, 9H); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 152.4, 144.8, 144.7, 144.6, 134.8, 134.8, 127.5, 127.4, 127.4, 127.2, 126.9, 126.79, 126.8, 121.8, 110.7, 63.8, 63.8, 39.3, 24.1, 24.0, 23.9, 23.7, 20.7, 20.1, 13.4; ^{31}P NMR (122 MHz, $CDCl_3$) δ 29.6 (br); HRMS (ESI): Calc. for $C_{24}H_{39}NO_3PS^+$ $(M)^+$: 452.2383; found: 452.2393.

Acknowledgment: We are very grateful to the Natural Sciences and Engineering Research Council of Canada (NSERC), the Canada Foundation for Innovation (CFI), and the provincial government of Quebec (FQRNT and CCVC) for their precious financial support in this research. We thank Dr. D. Warschawski for helpful discussion in NMR. S. Coulibali thanks the "Programme Canadien de Bourses de la Francophonie" for a scholarship.

Supporting Information Available: The Supporting Information is available free of charge on the ACS Publications website ^{1}H and ^{13}C NMR spectral data of all compounds.

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