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LETTER

Phosphovanadomolybdic acid catalyzed direct C–H trifluoromethylation of (hetero)arenes using $NaSO_2CF_3$ as the CF_3 source and O_2 as the terminal oxidant

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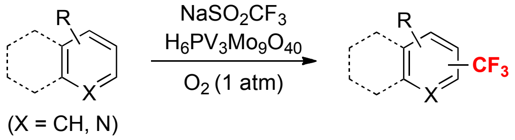
Chifeng Li, Kosuke Suzuki, Kazuya Yamaguchi* and Noritaka Mizuno*

A direct C–H trifluoromethylation of (hetero)arenes using $NaSO_2CF_3$ (Langlois' reagent) as the CF_3 source and O_2 as the terminal oxidant has been developed. In the presence of catalytic amounts of phosphovanadomolybdic acids, such as $H_6PV_3Mo_9O_{40}$, various kinds of substituted benzenes and heteroaromatic compounds could be converted into the corresponding trifluoromethylated products.

The trifluoromethyl (CF_3) group is becoming of increasing importance in pharmaceuticals, agrochemicals, polymers, and liquid crystals because the physical and chemical properties of molecules, such as metabolic stability, membrane permeability, and bioactivity, can be remarkably modified by installation of CF_3 group(s).[1] Therefore, the development of efficient trifluoromethylation methods has attracted considerable attention and become one of the most important subjects in extensive research fields.[2] In particular, catalytic direct C–H trifluoromethylation of (hetero)arenes is quite important.[2d,3] Recently, significant progress has been achieved in radical-based C–H trifluoromethylation using various kinds of CF_3 sources.[4] Sodium trifluoromethanesulfinate ($NaSO_2CF_3$, Langlois' reagent) is one of the most preferable trifluoromethylation reagents because it is relatively stable, easy-to-handle, and inexpensive in comparison with other reagents.[5] Although efforts have been devoted to develop the catalytic direct C–H trifluoromethylation of (hetero)arenes using $NaSO_2CF_3$ as the source of CF_3 radical,[6] the previously reported C–H trifluoromethylation systems typically require superstoichiometric amounts of organic or inorganic oxidants, such as *tert*-butylhydroperoxide, hypervalent iodine, and sodium persulfate.[6] With regard to the photocatalytic C–H trifluoromethylation of arenes using $NaSO_2CF_3$ as the CF_3 source, two methods with the use of acetone as the oxidant[7a] or under oxidant-free conditions[7b] have been recently reported. The $NaSO_2CF_3$-based trifluoromethylation of (hetero)arenes using O_2 as the terminal oxidant, which is regarded as the "greenest" oxidant, has been remained unexplored until now, to the best of our knowledge.



Scheme 1 A direct C–H trifluoromethylation of (hetero)arenes using $NaSO_2CF_3$ as the CF_3 radical source and O_2 as the terminal oxidant.

Herein, we report for the first time that phosphovanadomolybdic acids can act as efficient catalysts for oxidative direct C–H trifluoromethylation of (hetero)arenes using $NaSO_2CF_3$ as the CF_3 source and O_2 as the terminal oxidant (Scheme 1). In the presence of catalytic amounts of phosphovanadomolybdic acids, such as $H_6PV_3Mo_9O_{40}$, various kinds of substituted benzenes and heteroaromatic compounds could be converted into the corresponding trifluoromethylated products. Although various aerobic oxidation reactions have been reported using phosphovanadomolybdic acids,[8,9] the trifluoromethylation systems which utilize heteropoly acid catalysts (HPAs) have never been reported to date, to the best of our knowledge.

To begin with, we optimized the reaction conditions for the trifluoromethylation of 1,4-dimethoxybenzene (**1a**, model substrate) in the presence of a catalytic amount of $H_5PV_2Mo_{10}O_{40}$ using $NaSO_2CF_3$ as the CF_3 source in 1 atm of O_2. The solvent screening revealed that acetonitrile gave better yields of the trifluoromethylated products than other organic solvents examined, such as dimethyl sulfoxide, *N,N*-dimethylformamide, *N*-methylpyrrolidone, 1,2-dichloroethane, and ethanol (Table S1, entry 1 versus entries 6–10, ESI†). Addition of water into the acetonitrile-based reaction media could significantly improve the yields of the products, which is likely because of an increase in the solubility of $NaSO_2CF_3$ in the reaction media (Table S1, entries 2–5, ESI†). In particular, the trifluoromethylation in the 8/2 (v/v) mixture of acetonitrile and water gave the best result (Table S1, entry 3, ESI†). However, the further increase in the water contents

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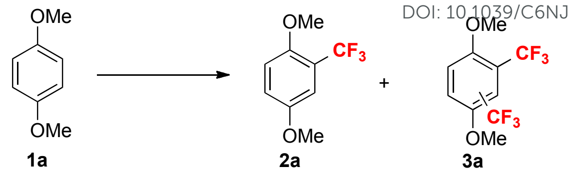
(acetonitrile/water = 6/4 and 4/6 v/v) resulted in a decrease in the yields of the trifluoromethylated products likely because of the poor solubility of **1a** in these water-rich media (Table S1, entries 4 and 5, ESI†). The yields of the trifluoromethylated products increased with an increase in the reaction temperature (bath temperature) up to 120 °C (Table S2, ESI†). The effect of amounts of $NaSO_2CF_3$ on the total yield and the **2a**/**3a** ratio is summarized in Table S3 (ESI†).

Next, we investigated the catalytic activities of various HPAs for the trifluoromethylation of **1a** using $NaSO_2CF_3$ in the mixture of acetonitrile/water (8/2 v/v) at 120 °C (bath temperature). The reaction hardly proceeded in the absence of catalysts (Table 1, entry 1). Although the trifluoromethylation also significantly proceeded in air (1 atm), the reaction was slower than that in O_2 (Table 1, entry 8 versus entry 9). When using vanadium-free HPAs, such as $H_3PMo_{12}O_{40}$, $H_3PW_{12}O_{40}$, $H_4SiMo_{12}O_{40}$, and $H_4SiW_{12}O_{40}$, the reactions were not efficient and gave the trifluoromethylated products **2a** and **3a** in quite low yields (Table 1, entries 2–5). The catalytic activities increased with an increase in the vanadium content ($H_3PMo_{12}O_{40} \ll H_4PV_1Mo_{11}O_{40} < H_5PV_2Mo_{10}O_{40} < H_6PV_3Mo_9O_{40} \approx H_7PV_4Mo_8O_{40}$ for phosphomolybdic acids, Table 1, entries 2, 6–8, and 12; $H_3PW_{12}O_{40} \ll H_4PV_1W_{11}O_{40} < H_5PV_2W_{10}O_{40} < H_6PV_3W_9O_{40} \approx H_7PV_4W_8O_{40}$ for phosphotungstic acids, Table 1, entries 3 and 13–16). These results show that vanadium is an indispensable component for this reaction. Regarding the polyatoms of vanadium-containing HPAs, molybdenum exhibited better catalytic activities than tungsten (Table 1, entries 6–8 versus entries 13–16). It is well known that molybdic acids possess the higher oxidation potentials than tungstic acids.[10]

Table 1 Effect of catalysts on the oxidative trifluoromethylation of **1a**[a]



Entry	Catalyst	Atmosphere	Total yield (%) (**2a**/**3a**)
1	w/o	O_2	6 (6/<1)
2	$H_3PMo_{12}O_{40}$	O_2	8 (8/<1)
3	$H_3PW_{12}O_{40}$	O_2	<1
4	$H_4SiMo_{12}O_{40}$	O_2	4 (4/<1)
5	$H_4SiW_{12}O_{40}$	O_2	3 (3/<1)
6	$H_4PV_1Mo_{11}O_{40}$	O_2	69 (57/12)
7	$H_5PV_2Mo_{10}O_{40}$	O_2	79 (62/17)
8	$\mathbf{H_6PV_3Mo_9O_{40}}$	$\mathbf{O_2}$	**90 (61/29)**
9[b]	$H_6PV_3Mo_9O_{40}$	Air	65 (59/6)
10[c]	$H_6PV_3Mo_9O_{40}$	Ar	20 (19/1)
11[d]	$H_6PV_3Mo_9O_{40}$ + TEMPO	O_2	2 (2/<1)
12	$H_7PV_4Mo_8O_{40}$	O_2	89 (61/28)
13	$H_4PV_1W_{11}O_{40}$	O_2	15 (15/<1)
14	$H_5PV_2W_{10}O_{40}$	O_2	49 (46/3)
15	$H_6PV_3W_9O_{40}$	O_2	70 (58/12)
16	$H_7PV_4W_8O_{40}$	O_2	74 (60/14)
17[e]	V_2O_5	O_2	19 (19/<1)
18[e]	$NaVO_3$	O_2	24 (24/<1)
19[e]	$VO(acac)_2$	O_2	27 (26/1)
20[f]	$V_2O_5 + H_3PMo_{12}O_{40}$	O_2	60 (55/5)
21[f]	$NaVO_3 + H_3PMo_{12}O_{40}$	O_2	69 (60/9)
22[f]	$VO(acac)_2 + H_3PMo_{12}O_{40}$	O_2	74 (63/11)

[a] Reaction conditions: **1a** (0.2 mmol), $NaSO_2CF_3$ (0.6 mmol), catalyst (10 mol% with respect to **1a**), acetonitrile/water (2 mL, 4/1 v/v), 120 °C (bath temp.), O_2 (1 atm), 6 h. Yields were determined by GC using biphenyl as an internal standard. [b] Air (1 atm). [c] Ar (1 atm). [d] TEMPO (0.6 mmol, 1 equiv with respect to $NaSO_2CF_3$), 23 h. [e] Vanadium (30 mol%). [f] Vanadium (30 mol%) + $H_3PMo_{12}O_{40}$ (10 mol%).

As above-mentioned, vanadium plays important role on the present trifluoromethylation. However, simple vanadium compounds, such as V_2O_5, $NaVO_3$, and $VO(acac)_2$ (acac = acetylacetonate), gave much lower yields of the trifluoromethylated products (Table 1, entries 17–19). Although the performance of these vanadium compounds was significantly improved by addition of $H_3PMo_{12}O_{40}$, $H_6PV_3Mo_9O_{40}$ exhibited higher catalytic activity in comparison with the mixtures of $V_2O_5 + H_3PMo_{12}O_{40}$, $NaVO_3 + H_3PMo_{12}O_{40}$, and $VO(acac)_2 + H_3PMo_{12}O_{40}$ (Table 1, entry 8 versus entries 20–22). Other transition metal compounds, such as $MnCl_2$, $Mn(acac)_2$, $Mn(acac)_3$, $Co(acac)_2$, $Ni(acac)_2$, $Pd(OAc)_2$ (OAc = acetate), and Ag(acac) generally exhibited lower catalytic activities than vanadium compounds (Table S4, ESI†). Notably, the catalytic performance of these transition metal compounds was unchanged even when the reaction was performed in the presence of $H_3PMo_{12}O_{40}$ (Table S4, ESI†). The aforementioned results support the synergetic effect of vanadium and HPAs. In particular, the substitution of vanadium into HPA frameworks can improve the intrinsic catalytic performance of vanadium for the present C–H trifluoromethylation.[8,9]

When the mixture of $H_6PV_3Mo_9O_{40}$ and $NaSO_2CF_3$ in acetonitrile was heated at 120 °C (bath temperature), the color of the solution immediately (within 5 min) changed from orange (the color of the fully oxidized form of $H_6PV_3Mo_9O_{40}$, Fig. S1a, ESI†) to dark green, and a new broad absorption band around 780 nm likely due to the intervalence charge-transfer (IVCT) of V^{4+}/Mo^{6+}, V^{5+}/Mo^{5+}, and/or Mo^{5+}/Mo^{6+} appeared (Fig. S1b, ESI†).[11] These results indicate that $H_6PV_3Mo_9O_{40}$ is reduced by $NaSO_2CF_3$. At the initial stage of the present trifluoromethylation, the color of the reaction solution also changed from orange to dark green, suggesting the reduction of $H_6PV_3Mo_9O_{40}$ during the reaction. At the end of the reaction, the color of the reaction solution again became close to the original color, and the IVCT band almost disappeared (Fig. S1c, ESI†). When the reaction was carried out under an Ar atmosphere, the yields of the products significantly decreased (Table 1, entry 10), and the color of the reaction solution remained dark green even when prolonging the reaction time, thus indicating that O_2 acts as the terminal oxidant for the present trifluoromethylation. Consequently, $H_6PV_3Mo_9O_{40}$ oxidizes $NaSO_2CF_3$, resulting in the formation of the reduced $H_6PV_3Mo_9O_{40}$, and then the reduced $H_6PV_3Mo_9O_{40}$ is reoxidized by O_2. When a radical scavenger of 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO, 1 equiv with respect to $NaSO_2CF_3$) was added to the reaction solution, the reaction was

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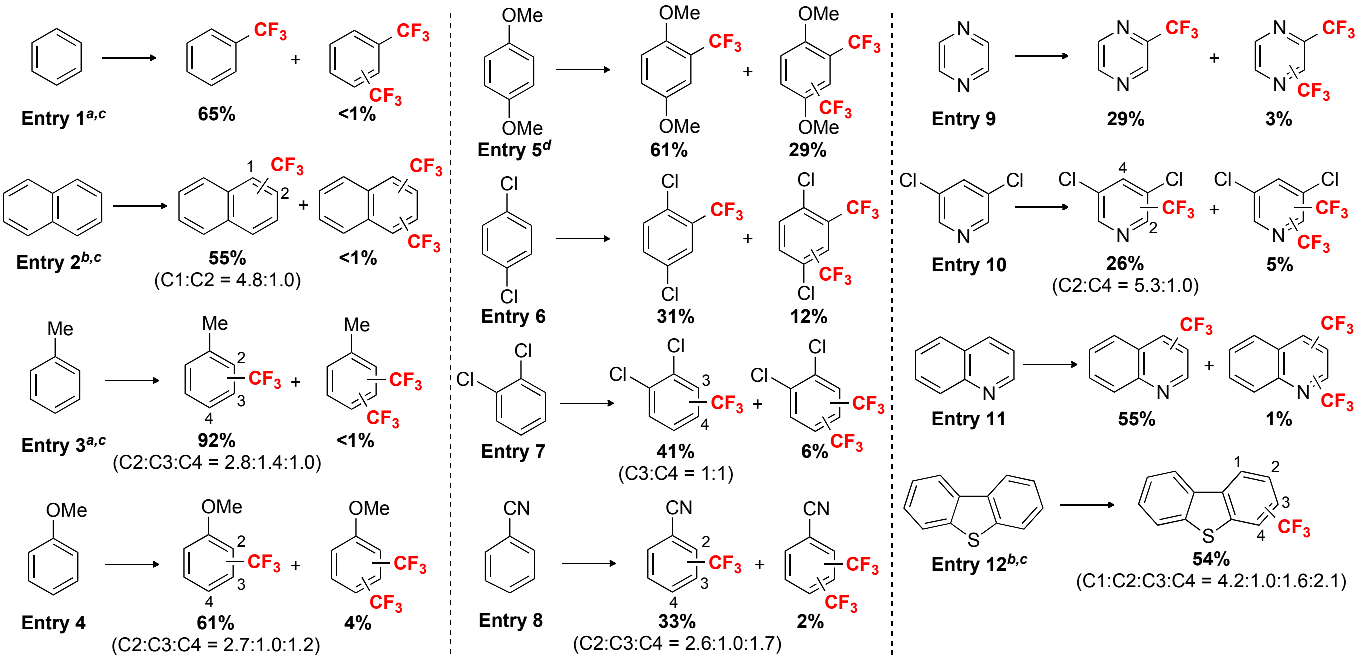
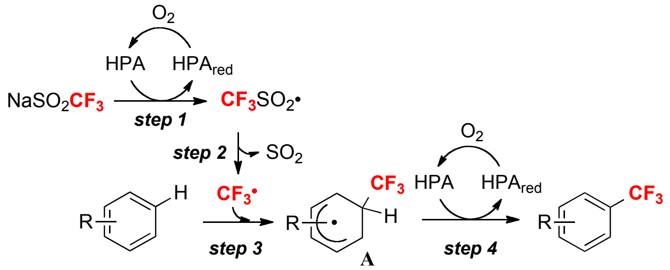
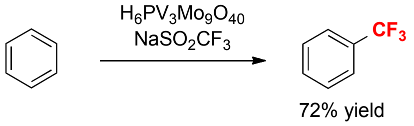


Fig. 1 Substrate scope for the $H_6PV_3Mo_9O_{40}$-catalyzed C–H trifluoromethylation. Reaction conditions: substrate (0.2 mmol), $NaSO_2CF_3$ (0.6 mmol), $H_6PV_3Mo_9O_{40}$ (10 mol% with respect to substrate), acetonitrile/water (2 mL, 4/1 v/v), 120 °C (bath temp.), O_2 (1 atm), 23 h. Yields were determined by GC with biphenyl as an internal standard. Ratios of regioisomers were determined by GC and ^{19}F NMR. [a]Substrate (4 mmol), $NaSO_2CF_3$ (0.2 mmol), $H_6PV_3Mo_9O_{40}$ (10 mol% with respect to $NaSO_2CF_3$). [b]Naphthalene (1 mmol), $NaSO_2CF_3$ (0.2 mmol), $H_6PV_3Mo_9O_{40}$ (10 mol% with respect to $NaSO_2CF_3$). [c]Yields were calculated based on $NaSO_2CF_3$. [d]6 h.



Scheme 2 A possible reaction mechanism for the present HPA-catalyzed trifluoromethylation. The reduced HPA (HPA_{red}) formed in step 1 and step 4 is reoxidized by O_2.



Scheme 3 A larger-scale trifluoromethylation of benzene. Reaction conditions: benzene (40 mmol), $NaSO_2CF_3$ (2.0 mmol), $H_6PV_3Mo_9O_{40}$ (10 mol% with respect to $NaSO_2CF_3$), acetonitrile/water (20 mL, 4/1 v/v), 120 °C (bath temp.), O_2 (1 atm), 44 h. Yields were calculated based on $NaSO_2CF_3$.

significantly suppressed, and the total yield of the trifluoromethylated products was only 2% (Table 1, entry 11). Therefore, we consider that the involvement of radical intermediates is most likely in the present trifluoromethylation.[12,13] The formation of SO_2 during the reaction was also confirmed by the gas phase GC-MS analysis (m/z 64 $[M]^+$ and 48).

Based on the above-mentioned experimental results, we here propose a possible reaction mechanism for the present HPA-catalyzed trifluoromethylation (Scheme 2). Firstly, the single-electron transfer from $NaSO_2CF_3$ to HPA proceeds to give the reduced HPA and CF_3SO_2• intermediate (step 1), immediately followed by its disproportion into CF_3• and SO_2 (step 2). Then, CF_3• reacts with an arene to afford the radical intermediate **A** (step 3), and subsequently, HPA accepts the electron and proton from the intermediate **A** to afford the corresponding trifluoromethylated product (step 4). The reduced HPA formed in step 1 and step 4 is reoxidized by O_2.[9]

Finally, we turned our attention to the examination of the substrate scope for the present aerobic C–H trifluoromethylation using $H_6PV_3Mo_9O_{40}$ under the optimized reaction conditions. As summarized in Fig. 1, various kinds of (hetero)arenes could be converted into the corresponding trifluoromethylated products. As mentioned above, the trifluoromethylation of **1a** gave the corresponding trifluoromethylated products in high yields (Fig. 1, entry 5; 90% total yield; 61% yield of **2a**; 29% yield of **3a**). Notably, benzene and naphthalene could be efficiently converted into trifluoromethylbenzene (65% yield based on $NaSO_2CF_3$) and trifluoromethylnaphthalenes (55% total yield based on $NaSO_2CF_3$), respectively (Fig. 1, entries 1 and 2). A larger-scale trifluoromethylation of benzene (ten-fold scale up) was also effective and gave trifluoromethylbenzene in 72% yield (based on $NaSO_2CF_3$, Scheme 3). The trifluoromethylation of benzenes possessing electron-donating as well as electron-withdrawing substituents on the phenyl rings efficiently proceeded to give the corresponding trifluoromethylated products (Fig. 1, entries 3–8). In the case of 1,4-dichlorobenzene and 1,2-dichlorobenzene, the reaction proceeded without any dechlorination (Fig. 1, entries 6 and 7). No hydration and hydrolytic decomposition proceeded for benzonitrile (Fig. 1, entry 8). Heteroarenes, such as pyrazine, 3,5-dichloropyridine, quinoline, and dibenzothiophene, could be also converted into the corresponding trifluoromethylated products (Fig. 1, entries 9–12).

In conclusion, we have successfully developed for the first time the efficient direct C–H trifluoromethylation of (hetero)arenes catalyzed by vanadium-containing heteropoly acids using $NaSO_2CF_3$ as the CF_3 source and O_2 as the terminal oxidant. The reaction proceeds *via* radical pathway. Various kinds of structurally diverse (hetero)arenes, such as substituted benzenes, naphthalene, pyrazine, pyridine, quinoline, and thiophene, could be converted into the corresponding trifluoromethylated products.

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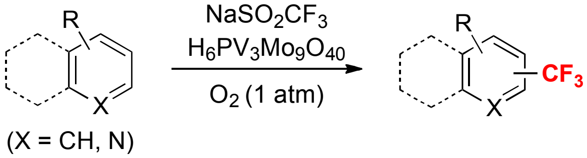
Graphical abstract



In the presence of phosphovanadomolybdic acids, a direct C–H trifluoromethylation of (hetero)arenes efficiently proceeded by utilizing $NaSO_2CF_3$ as the CF_3 source and O_2 as the terminal oxidant.