

*Electronic Supplementary Information (ESI) for*

## **Phosphanomolybdic acid catalyzed direct C–H trifluoromethylation of (hetero)arenes using NaSO<sub>2</sub>CF<sub>3</sub> as the CF<sub>3</sub> source and O<sub>2</sub> as the terminal oxidant**

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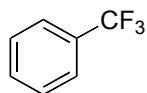
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**General:** Benzene (Kanto Chemical), toluene (Kanto Chemical), naphthalene (Wako), anisole (TCI), 1,4-dimethoxybenzene (TCI), 1,2-dichlorobenzene (Kanto Chemical), 1,4-dichlorobenzene (TCI), benzonitrile (Kanto Chemical), pyrazine (TCI), 3,5-dichloropyridine (TCI), quinoline (TCI), dibenzothiophene (TCI), sodium trifluoromethanesulfinate (TCI), ethyl acetate (Kanto Chemical), dimethyl sulfoxide (Kanto Chemical), *N,N*-dimethylformamide (Kanto Chemical), 1,2-dichloroethane (Kanto Chemical), ethanol (Kanto Chemical), *N*-methylpyrrolidone (Kanto Chemical), and acetonitrile (Kanto Chemical) were used as received. H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>, H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>, and H<sub>4</sub>SiMo<sub>12</sub>O<sub>40</sub> were obtained from Wako, and other heteropoly acids were obtained from Nippon Inorganic Colour & Chemical. The numbers of water of crystallization in heteropoly acids were 20–30 per molecule, and the molecular weights of heteropoly acids were calculated as triacontahydrates. UV/Vis spectra were measured on Jasco V-570 with a quartz cell of 1 cm path length. GC analyses were performed on Shimadzu GC-2014 with a FID detector equipped with an InertCap 1, InertCAP FFAP, and Stabilwax capillary column. GCMS spectra were recorded on Shimadzu GCMS-QP2010 at an ionization voltage of 70 eV equipped with an InertCap 5MS/Sil capillary column. NMR spectra were recorded on JEOL ECA-500 (<sup>1</sup>H, 500.0 MHz; <sup>19</sup>F, 470.6 MHz) by using 5 mm tubes. Chemical shifts were reported on the δ scale with resonances upfield of TMS (δ = 0 ppm) for <sup>1</sup>H NMR spectra and trifluoroacetic acid (δ = –76.55 ppm) for <sup>19</sup>F NMR spectra.

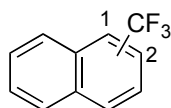
**Typical procedure for aerobic trifluoromethylation:** Substrate (0.2 mmol), CF<sub>3</sub>SO<sub>2</sub>Na (0.6 mmol), H<sub>6</sub>PV<sub>3</sub>Mo<sub>9</sub>O<sub>40</sub> (20 μmol, 10 mol% with respect to substrate), acetonitrile

(1.6 mL), and water (0.4 mL) were placed into a pyrex-glass screw-cap vial with a magnetic stir bar. Then, the reaction mixture was vigorously stirred at 120 °C (bath temperature) in 1 atm of O<sub>2</sub> for 6 h or 23 h. After the reaction, biphenyl (internal standard for GC analysis) was added to the reaction solution as an internal standard. The products were confirmed by GC-MS, <sup>19</sup>F NMR, and/or <sup>1</sup>H NMR, and the yields of products were determined by GC.

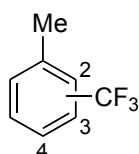
### **Compound data:**



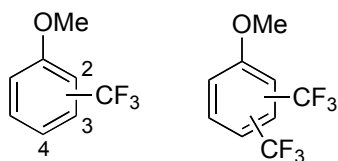
**Trifluoromethylbenzene**<sup>S1</sup> (**Fig. 1, Entry 1**): 65% yield (based on NaSO<sub>2</sub>CF<sub>3</sub>). <sup>19</sup>F NMR (470.6 MHz, CD<sub>3</sub>CN)  $\delta$  -62.5 (s) ppm. MS (EI) *m/z* (%): 146 (100) [*M*]<sup>+</sup>, 145 (48), 127 (49), 96 (47), 77 (20), 75 (14), 69 (15), 51 (36), 50 (25).



**Trifluoromethylnaphthalene**,<sup>S2</sup> **mixture of isomers** (**Fig. 1, Entry 2**): 55% yield (based on NaSO<sub>2</sub>CF<sub>3</sub>; C1:C2 = 4.8:1.0). <sup>19</sup>F NMR (470.6 MHz, CD<sub>3</sub>CN)  $\delta$  -59.6 (s, C1), -62.0 (s, C2) ppm. MS (EI) *m/z* (%): 196 (100) [*M*]<sup>+</sup>, 197 (13), 195 (27), 177 (15), 146 (41).

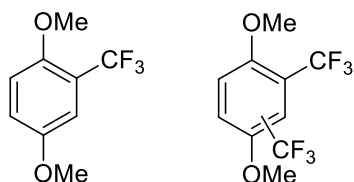


**(Trifluoromethyl)toluene**,<sup>S3</sup> **mixture of isomers** (**Fig. 1, Entry 3**): 92% yield (based on CF<sub>3</sub>SO<sub>2</sub>Na; C2:C3:C4 = 2.8:1.4:1.0). <sup>19</sup>F NMR (470.6 MHz, CD<sub>3</sub>CN)  $\delta$  -61.4 (s, C2), -62.0 (s, C3), -62.4 (s, C4) ppm. MS (EI) *m/z* (%): 160 (52) [*M*]<sup>+</sup>, 140 (11), 109 (10), 91 (100).

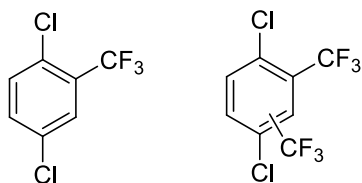


**Trifluoromethylanisole**,<sup>S4</sup> **mixture of isomers** (**Fig. 1, Entry 4**): 65% yield (61/4 mono-CF<sub>3</sub>/bis-CF<sub>3</sub>; isomer ratio of mono-CF<sub>3</sub>, C2:C3:C4 = 2.7:1.0:1.2). <sup>19</sup>F NMR (470.6 MHz, CD<sub>3</sub>CN)  $\delta$  -62.1 (s, C2), -62.5 (s, C3), -61.2 (s, C4), -60.6 (s, bis-CF<sub>3</sub>), -61.6 (s,

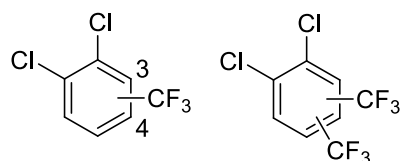
bis-CF<sub>3</sub>), -62.8 (s, bis-CF<sub>3</sub>), -63.0 (s, bis-CF<sub>3</sub>), -63.2 (s, bis-CF<sub>3</sub>) ppm. MS (EI) *m/z* (%): mono-CF<sub>3</sub>, 176 (100) [*M*]<sup>+</sup>, 146 (23), 145 (25), 133 (34), 127 (30), 126 (10), 114 (33), 109 (16), 96 (16), 83 (24), 77 (10), 75 (16), 63 (27), 57 (13), 50 (15); bis-CF<sub>3</sub>, 244 (100) [*M*]<sup>+</sup>, 225 (21), 214 (13), 210 (14), 201 (10), 195 (20), 194 (13), 182 (28), 181 (21), 177 (20), 176 (13), 163 (26), 145 (38), 132 (42), 127 (16), 113 (10), 75 (16), 69 (22), 63 (17).



**(Trifluoromethyl)1,4-dimethoxybenzene,<sup>S5</sup> mixture of isomers (Fig. 1, Entry 5):** 90% yield (61/29 mono-CF<sub>3</sub>/bis-CF<sub>3</sub>). <sup>19</sup>F NMR (470.6 MHz, CD<sub>3</sub>CN) δ -62.1 (s, mono-CF<sub>3</sub>), -54.9 (s, bis-CF<sub>3</sub>), -62.7 (s, bis-CF<sub>3</sub>) ppm. MS (EI) *m/z* (%): mono-CF<sub>3</sub>, 206 (82) [*M*]<sup>+</sup>, 191 (100), 163 (21), 129 (23), 101 (12), 63 (11); bis-CF<sub>3</sub>, 274 (100) [*M*]<sup>+</sup>, 275 (11), 260 (10), 259 (96), 255 (11), 225 (20), 197 (58), 169 (27), 119 (11), 75 (11).

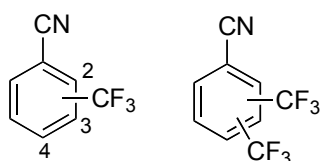


**(Trifluoromethyl)1,4-dichlorobenzene,<sup>S6</sup> mixture of isomers (Fig. 1, Entry 6):** 43% yield (31/12 mono-CF<sub>3</sub>/bis-CF<sub>3</sub>). <sup>19</sup>F NMR (470.6 MHz, CD<sub>3</sub>CN) δ -62.8 (s, mono-CF<sub>3</sub>), -62.6 (s, bis-CF<sub>3</sub>), -63.4 (s, bis-CF<sub>3</sub>) ppm. MS (EI) *m/z* (%): mono-CF<sub>3</sub>, 214 (100) [*M*]<sup>+</sup>, 218 (11), 216 (64), 197 (12), 195 (18), 181 (20), 179 (65), 166 (10), 164 (16), 144 (14), 143 (12), 125 (11), 109 (16), 75 (29), 74 (29), 73 (10), 69 (19), 50 (14); bis-CF<sub>3</sub>, 282 (100) [*M*]<sup>+</sup>, 286 (10), 284 (62), 283 (10), 265 (16), 263 (23), 249 (14), 247 (46), 232 (13), 213 (14), 199 (10), 197 (30), 143 (22), 120 (10), 105 (16), 74 (13), 69 (24).

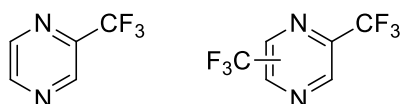


**(Trifluoromethyl)1,2-dichlorobenzene,<sup>S7</sup> mixture of isomers (Fig. 1, Entry 7):** 47% yield (41/6 mono-CF<sub>3</sub>/bis-CF<sub>3</sub>; isomer ratio of mono-CF<sub>3</sub>, C3:C4 = 1:1). <sup>19</sup>F NMR (470.6 MHz, CD<sub>3</sub>CN) δ -62.6 (s, C3 or C4), -62.7 (s, C3 or C4), -63.6 (s, bis-CF<sub>3</sub>) ppm. MS (EI) *m/z* (%):

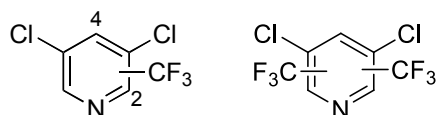
mono-CF<sub>3</sub>, 214 (100) [M]<sup>+</sup>, 218 (11), 216 (64), 197 (17), 195 (26), 181 (14), 179 (43), 166 (13), 164 (19), 144 (11), 143 (10), 109 (16), 75 (27), 74 (27), 69 (27), 50 (20); bis-CF<sub>3</sub>, 282 (96) [M]<sup>+</sup>, 286 (16), 284 (59), 283 (16), 265 (20), 263 (29), 249 (12), 247 (31), 234 (12), 232 (16), 215 (18), 213 (24), 212 (11), 197 (13), 178 (10), 162 (16), 143 (35), 123 (11), 109 (12), 105 (10), 99 (13), 93 (10), 85 (10), 75 (21), 74 (21), 69 (100), 50 (13).



**Trifluoromethylbenzonitrile,<sup>S8</sup> mixture of isomers (Fig. 1, Entry 8)** : 35% yield (33/2 mono-CF<sub>3</sub>/bis-CF<sub>3</sub>; isomer ratio of mono-CF<sub>3</sub>, C2:C3:C4 = 2.6/1.0/1.7). <sup>19</sup>F NMR (470.6 MHz, CD<sub>3</sub>CN) δ -61.8 (s, C2), -63.0 (s, C3), -63.4 (s, C4), -57.9 (s, bis-CF<sub>3</sub>), -61.9 (s, bis-CF<sub>3</sub>), -62.1 (s, bis-CF<sub>3</sub>), -62.3 (s, bis-CF<sub>3</sub>), -63.4 (s, bis-CF<sub>3</sub>), -63.5 (s, bis-CF<sub>3</sub>) ppm. MS (EI) *m/z* (%): mono-CF<sub>3</sub>, 171 (100) [M]<sup>+</sup>, 170 (26), 152 (49), 121 (51), 102 (13), 76 (16), 75 (34), 74 (10), 69 (25), 51 (21), 50 (25); bis-CF<sub>3</sub>, 239 (100) [M]<sup>+</sup>, 240 (14), 221 (10), 220 (68), 194 (13), 189 (44), 188 (12), 170 (100), 151 (11), 150 (18), 143 (14), 139 (17), 125 (12), 120 (11), 113 (10), 100 (25), 99 (19), 93 (13), 91 (11), 75 (39), 74 (13), 69 (66), 63 (10), 51 (11), 50 (24).

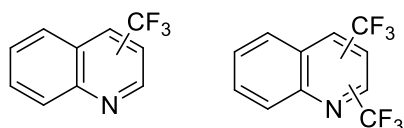


**Trifluoromethylpyrazine,<sup>S9</sup> mixture of isomers (Fig. 1, Entry 11)**: 32% yield (29/3 mono-CF<sub>3</sub>/bis-CF<sub>3</sub>). <sup>19</sup>F NMR (470.6 MHz, CD<sub>3</sub>CN) δ -67.9 (s, mono-CF<sub>3</sub>), -67.6 (s, bis-CF<sub>3</sub>), -67.8 (s, bis-CF<sub>3</sub>), -68.0 (s, bis-CF<sub>3</sub>) ppm. MS (EI) *m/z* (%): mono-CF<sub>3</sub>, 148 (20) [M]<sup>+</sup>, 80 (100), 75 (9), 53 (58), 52 (36), 51 (16); bis-CF<sub>3</sub>, 216 (100) [M]<sup>+</sup>, 197 (30), 147 (41), 127 (14), 121 (28), 120 (24), 94 (26), 75 (27), 69 (31), 52 (16).



**(Trifluoromethyl)3,5-dichloropyridine,<sup>S10</sup> mixture of isomers (Fig. 1, Entry 10)** : 31% yield (26/5 mono-CF<sub>3</sub>/bis-CF<sub>3</sub>; isomer ratio of mono-CF<sub>3</sub>, C2:C4 = 5.3/1.0). <sup>19</sup>F NMR (470.6 MHz, CD<sub>3</sub>CN) δ -57.9 (s, C4), -65.9 (s, C2), -57.5 (s, bis-CF<sub>3</sub>), -58.5 (s, bis-CF<sub>3</sub>), -66.3 (s,

bis-CF<sub>3</sub>) ppm. MS (EI) *m/z* (%): mono-CF<sub>3</sub>, 215 (89) [*M*]<sup>+</sup>, 217 (58), 180 (11), 167 (25), 165 (39), 148 (32), 146 (52), 130 (15), 112 (18), 110 (57), 99 (19), 87 (11), 85 (29), 84 (20), 76 (27), 75 (30), 69 (100), 68 (11), 62 (12), 60 (17), 51 (10), 50 (49); bis-CF<sub>3</sub>, 283 (13) [*M*]<sup>+</sup>, 215 (100), 285 (10), 219 (11), 217 (63), 216 (11), 214 (11), 182 (19), 180 (53), 160 (14), 153 (23), 99 (18), 86 (11), 85 (19), 84 (28), 75 (21), 69 (93), 68 (11), 60 (12), 50 (10).



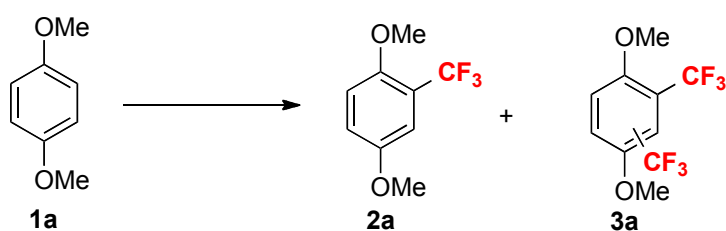
**Trifluoromethylquinoline,<sup>S11</sup> mixture of isomers (Fig. 1, Entry 11):** 56% yield (55/1 mono-CF<sub>3</sub>/bis-CF<sub>3</sub>). <sup>19</sup>F NMR (470.6 MHz, CD<sub>3</sub>CN)  $\delta$  -59.2 (s, mono-CF<sub>3</sub>), -59.9 (s, mono-CF<sub>3</sub>), -61.5 (s, mono-CF<sub>3</sub>), -61.8 (s, mono-CF<sub>3</sub>), -62.3 (s, mono-CF<sub>3</sub>), -62.5 (s, mono-CF<sub>3</sub>), -67.5 (s, mono-CF<sub>3</sub>) ppm. MS (EI) *m/z* (%): mono-CF<sub>3</sub>, 197 (100) [*M*]<sup>+</sup>, 198 (12), 178 (10), 176 (11), 147 (22), 75 (11), 69 (13); bis-CF<sub>3</sub>, 265 (100) [*M*]<sup>+</sup>, 266 (14), 246 (23), 215 (34), 197 (16), 196 (17), 176 (21), 169 (16), 129 (69), 128 (14), 102 (17), 99 (11), 86 (17), 76 (14), 75 (19), 74 (14), 69 (28), 63 (13), 58 (12), 51 (21), 50 (23).



**(Trifluoromethyl)dibenzothiophene,<sup>S12</sup> mixture of isomers (Fig. 1, Entry 12):** 54 % GC yield (based on CF<sub>3</sub>SO<sub>2</sub>Na, isomer ratio of mono-CF<sub>3</sub>, C1:C2:C3:C4 = 4.2/1.0/1.6/2.1). <sup>19</sup>F NMR (470.6 MHz, CD<sub>3</sub>CN)  $\delta$  -60.8 (s, C1), -61.2 (s, C2), -61.5 (s, C3), -62.9 (s, C4) ppm. MS (EI) *m/z* (%): 252 (100) [*M*]<sup>+</sup>, 254 (6), 253 (15), 251 (10), 233 (9), 231 (7), 202 (11), 188 (6), 139 (9), 126 (9), 101 (6).

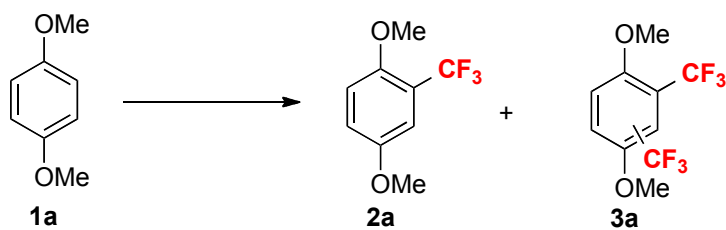
### Additional references

- S1 (a) S. Seo, J. B. Taylor and M. F. Greaney, *Chem. Commun.*, 2013, **49**, 6385; (b) A. Sato, J. Han, T. Ono, A. Wzorek, J. L. Aceña and V. A. Soloshonok, *Chem. Commun.*, 2015, **51**, 5967; (c) L. He, K. Natte, J. Rabeah, C. Taeschler, H. Neumann, A. Brückner and M. Beller, *Angew. Chem., Int. Ed.*, 2015, **54**, 4320.
- S2 (a) S. Arimori and N. Shibata, *Org. Lett.*, 2015, **17**, 1632; (b) J. Xu, D. F. Luo, B. Xiao, Z. J. Liu, T. J. Gong, Y. Fu and L. Liu, *Chem. Commun.*, 2011, **47**, 4300; (c) B. A. Khan, A. E. Buba and L. J. Gooßen, *Chem. –Eur. J.*, 2012, **18**, 1577.
- S3 (a) T. Knauber, F. Arikian, G. V. Rösenthaller and L. J. Gooßen, *Chem. –Eur. J.*, 2011, **17**, 2689; (b) B. Bayarmagnai, C. Matheis, E. Risto and L. J. Gooßen, *Adv. Synth. Catal.*, 2014, **356**, 2343.
- S4 (a) P. Novák, A. Lishchynskiy and V. V. Grushin, *Angew. Chem., Int. Ed.*, 2012, **51**, 7767; (b) S. Mizuta, I. S. R. Stenhagen, M. O’Duill, J. Wolstenhulme, A. K. Kirjavainen, S. J. Forsback, M. Tredwell, G. Sandford, P. R. Moore, M. Huiban, S. K. Luthra, J. Passchier, O. Solin and V. Gouverneur, *Org. Lett.*, 2013, **15**, 2648.
- S5 (a) L. Li, X. Mu, W. Liu, Y. Wang, Z. Mi and C. Li, *J. Am. Chem. Soc.*, 2016, **138**, 5809; (b) Y. Ye, S. H. Lee and M. S. Sanford, *Org. Lett.*, 2011, **13**, 5464.
- S6 Y. Tanabe, N. Matsuo and N. Ohno, *J. Org. Chem.*, 1988, **53**, 4582.
- S7 (a) H. Kondo, M. Oishi, K. Fujikawa and H. Amii, *Adv. Synth. Catal.*, 2011, **353**, 1247; (b) X. Lin, C. Hou, H. Li and Z. Weng, *Chem. –Eur. J.* 2016, **22**, 2075.
- S8 (a) G. Shi, C. Shao, S. Pan, J. Yu and Y. Zhang, *Org. Lett.*, 2015, **17**, 38.
- S9 (a) M. G. Mormino, P. S. Fier and J. F. Hartwig, *Org. Lett.* 2014, **16**, 1744; (b) K. Aikawa, Y. Nakamura, Y. Yokota, W. Toya, and K. Mikami, *Chem. –Eur. J.*, 2015, **21**, 96.
- S10 E. Mejía and A. Togni, *ACS Catal.*, 2012, **2**, 521.
- S11 (a) G. Danoun, B. Bayarmagnai, M. F. Grünberg and L. J. Gooßen, *Angew. Chem., Int. Ed.*, 2013, **52**, 7972; (b) Y. Liu, X. Shao, P. Zhang, L. Lu and Q. Shen, *Org. Lett.*, 2015, **17**, 2752.
- S12 B. Wang, D. C. Xiong and X. S. Ye, *Org. Lett.*, 2015, **17**, 5698.

**Table S1** Aerobic oxidative C–H trifluoromethylation of **1a** in various solvents<sup>a</sup>

Entry	Solvent	Total yield (%)	2a/3a ratio
1	Acetonitrile	45	45/<1
2	Acetonitrile/H <sub>2</sub> O (9/1 v/v)	63	60/3
3	Acetonitrile/H <sub>2</sub> O (8/2 v/v)	83	55/28
4	Acetonitrile/H <sub>2</sub> O (6/4 v/v)	69	39/30
5	Acetonitrile/H <sub>2</sub> O (4/6 v/v)	74	44/30
6	Dimethyl sulfoxide	24	24/<1
7	<i>N,N</i> -Dimethylformamide	5	5/<1
8	<i>N</i> -Methylpyrrolidone	<1	<1/<1
9	1,2-Dichloroethane	20	20/<1
10	Ethanol	12	12/<1

<sup>a</sup>Reaction conditions: **1a** (0.2 mmol), NaSO<sub>2</sub>CF<sub>3</sub> (0.6 mmol), H<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub> (10 mol% with respect to **1a**), solvent (2 mL), 120 °C (bath temp.), O<sub>2</sub> (1 atm), 23 h.

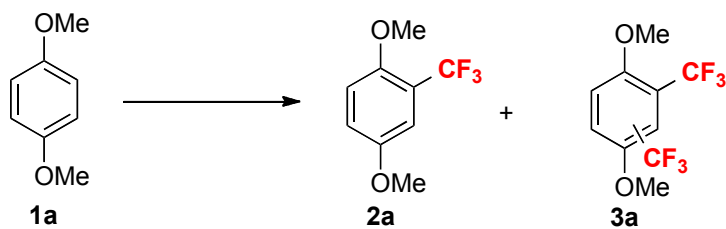
**Table S2** Aerobic oxidative C–H trifluoromethylation of **1a** at various temperatures<sup>a</sup>

Entry	Bath temperature (°C)	Total yield (%)	<b>2a/3a</b> ratio
1	80	26	26/<1
2	90	44	41/3
3	100	74	63/11
4	110	69	57/12
5	120	82	62/20
6	130	81	61/20

<sup>a</sup>Reaction conditions: **1a** (0.2 mmol), NaSO<sub>2</sub>CF<sub>3</sub> (0.6 mmol), H<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub> (10 mol% with respect to **1a**), acetonitrile/water (2 mL, 4/1 v/v), 80–130 °C (bath temp.), O<sub>2</sub> (1 atm), 23 h.

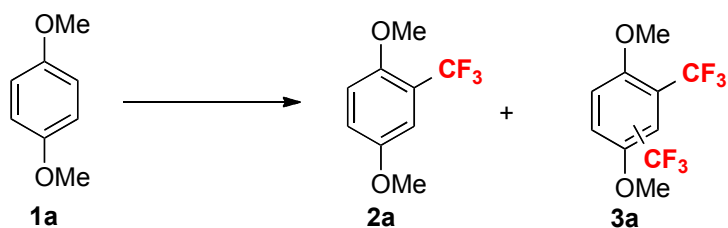


**Table S3** Aerobic oxidative C–H trifluoromethylation of **1a** with various amounts of NaSO<sub>2</sub>CF<sub>3</sub><sup>a</sup>



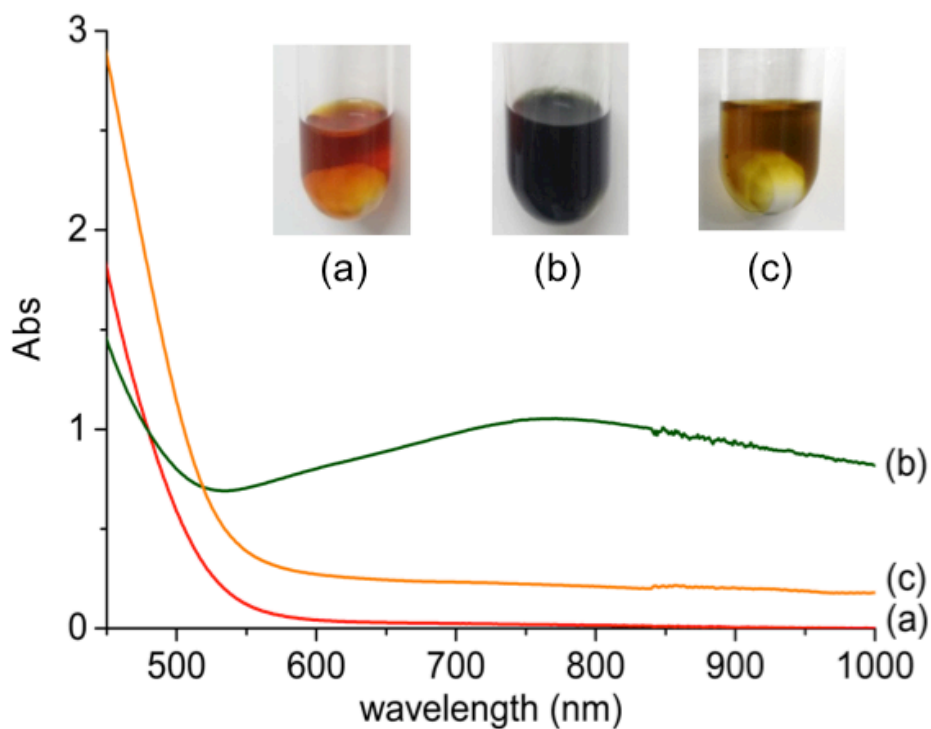
Entry	NaSO <sub>2</sub> CF <sub>3</sub> (equiv)	Total yield (%)	<b>2a/3a</b> ratio
1	1	45	43/2
2	2	61	53/8
3	3	82	62/20
4	4	91	57/34

<sup>a</sup>Reaction conditions: **1a** (0.2 mmol), NaSO<sub>2</sub>CF<sub>3</sub> (0.2–0.8 mmol, 1–4 equiv with respect to **1a**), H<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub> (10 mol% with respect to **1a**), acetonitrile/water (2 mL, 4/1 v/v), 120 °C (bath temp.), O<sub>2</sub> (1 atm), 23 h.

**Table S4** Aerobic oxidative C–H trifluoromethylation of **1a** with various catalysts<sup>a</sup>

Entry	Catalyst	Conv. of <b>1a</b> (%)	Total yield (%)	<b>2a/3a</b> ratio
<b>1</b>	<b>H<sub>6</sub>PV<sub>3</sub>Mo<sub>9</sub>O<sub>40</sub></b>	<b>92</b>	<b>90</b>	<b>61/29</b>
2 <sup>b</sup>	V <sub>2</sub> O <sub>5</sub>	25	19	19/<1
3 <sup>c</sup>	V <sub>2</sub> O <sub>5</sub> + H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>	64	60	55/5
4 <sup>b</sup>	NaVO <sub>3</sub>	36	24	24/<1
5 <sup>c</sup>	NaVO <sub>3</sub> + H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>	80	69	60/9
6 <sup>b</sup>	VO(acac) <sub>2</sub>	33	27	26/1
7 <sup>c</sup>	VO(acac) <sub>2</sub> + H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>	82	74	63/11
8 <sup>d</sup>	MnCl <sub>2</sub>	9	1	1/<1
9 <sup>e</sup>	MnCl <sub>2</sub> + H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>	5	1	1/<1
10 <sup>d</sup>	Mn(acac) <sub>2</sub>	6	1	1/<1
11 <sup>e</sup>	Mn(acac) <sub>2</sub> + H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>	5	2	2/<1
12 <sup>d</sup>	Mn(acac) <sub>3</sub>	7	4	4/<1
13 <sup>e</sup>	Mn(acac) <sub>3</sub> + H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>	6	6	6/<1
14 <sup>d</sup>	Fe(acac) <sub>3</sub>	38	25	25/<1
15 <sup>e</sup>	Fe(acac) <sub>3</sub> + H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>	37	32	32/<1
16 <sup>d</sup>	Co(acac) <sub>2</sub>	13	16	16/<1
17 <sup>e</sup>	Co(acac) <sub>2</sub> + H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>	8	3	3/<1
18 <sup>d</sup>	Ni(acac) <sub>2</sub>	21	15	15/<1
19 <sup>e</sup>	Ni(acac) <sub>2</sub> + H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>	1	1	1/<1
20 <sup>d</sup>	Pd(OAc) <sub>2</sub>	14	2	2/<1
21 <sup>e</sup>	Pd(OAc) <sub>2</sub> + H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>	<1	<1	1/<1
22 <sup>d</sup>	Ag(acac)	8	9	9/<1
23 <sup>e</sup>	Ag(acac) + H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub>	2	2	2/<1

<sup>a</sup>Reaction conditions: **1a** (0.2 mmol), NaSO<sub>2</sub>CF<sub>3</sub> (0.6 mmol), catalyst (10 mol% with respect to **1a**), acetonitrile/water (2 mL, 4/1 v/v), 120 °C (bath temp.), O<sub>2</sub> (1 atm), 6 h. Yields were determined by GC using biphenyl added as an internal standard. <sup>b</sup>Vanadium (30 mol%). <sup>c</sup>Vanadium (30 mol%) + H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> (10 mol%). <sup>d</sup>Transition metal compound (30 mol%). <sup>e</sup>Transition metal compound (30 mol%) + H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> (10 mol%).



**Fig. S1** UV/Vis spectra of the acetonitrile solution of the mixture of  $\text{H}_6\text{PV}_3\text{Mo}_9\text{O}_{40}$  and  $\text{NaSO}_2\text{CF}_3$  (30 equiv with respect to  $\text{H}_6\text{PV}_3\text{Mo}_9\text{O}_{40}$ ) (a) before and (b) after heating at  $120\text{ }^\circ\text{C}$  for 5 min. (c) UV/Vis spectrum of the solution after the trifluoromethylation of 1,4-dimethoxybenzene under the conditions described in Table 1.