Electronic Supplementary Information (ESI) for

An efficient H_2O_2-based oxidative bromination of alkenes, alkynes, and aromatics by a divanadium-substituted phosphotungstate

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Experimental Section

General. GC analyses were performed on Shimadzu GC-2014 with a FID detector equipped with a TC-WAX capillary column (0.25 mm × 30 m, GL Science Inc.). Mass spectra were recorded on a Shimadzu GCMS-QP2010 equipped with a TC-5HT capillary column (0.25 mm × 30 m, GL Science Inc.) at an ionization voltage of 70 eV. NMR spectra were recorded at room temperature on JEOL JNM-EX-270 (^{1}H, 270 MHz; ^{13}C, 67.8 MHz; ^{51}V, 70.9 MHz; and ^{31}P, 109 MHz). Chemical shifts (δ) were reported in ppm downfield from TMS (internal, in $CDCl_3$), TMS (internal, in $CDCl_3$), neat $VOCl_3$ (external), and 85% H_3PO_4 (external) for ^{1}H, ^{13}C, ^{51}V, and ^{31}P NMR spectra, respectively. Vanadium salts and complexes were obtained from Wako, Aldrich, or Kanto (reagent grade), and used as received. Solvents and substrates were obtained from Tokyo Kasei or Aldrich (reagent grade), and purified prior to the use.[S1]

Synthesis and Characterization of $TBA_4[\gamma\text{-}HPV_2W_{10}O_{40}]$ (1). The cesium salt of deprotonated divanadium-substituted phosphotungstate $Cs_5[\gamma\text{-}PV_2W_{10}O_{40}]$ was synthesized according to the published literature procedures[S2] and characterized by IR spectroscopy. The tetra-*n*-butylammonium (TBA) salt of the monoprotonated derivative $TBA_4[\gamma\text{-}HPV_2W_{10}O_{40}]$ (**1**) was prepared by the cation exchange reaction.[10] Sodium metavanadate (1.2 mmol) was dissolved in 120 mL of hot water. Upon cooling, the pH of the solution was adjusted to 2.0 with 3 M HCl. Cs5[γ-$PV_2W_{10}O_{40}]\cdot 6H_2O$ (3.8 g, 1.1 mmol) was dissolved into the solution and the insoluble materials were removed by filtration. TBABr (1.8 g, 5.6 mmol) was added with vigorous stirring. The precipitate was collected by filtration, washed with 400 mL of water, and dried in vacuo. Recrystallization from acetone/diethyl ether gave analytically pure orange crystals of **1**. Yield: 60%. ^{51}V NMR (CD_3CN): δ −581 ppm. ^{1}H NMR (CD_3CN): δ 4.38 ppm (1H per anion). ^{31}P NMR (CD_3CN): δ −14.1 ppm. Anal. calcd for $[(C_4H_9)_4N]_4[HPV_2W_{10}O_{40}]\cdot H_2O$; C, 21.4; H, 4.12; N, 1.56; P, 0.86; V, 2.83; W, 51.1. Found: C, 21.3; H, 3.96; N, 1.61; P, 0.84; V, 2.92; W, 49.0. IR (KBr): 1096, 1062, 1039, 1001, 952, 870, 803, 752, 534, 489, 399, 358, 333, 282, 256 cm^{-1}.

Additional References

S1 *Purification of Laboratory Chemicals*, 3rd ed., ed. by D. D. Perrin, W. L. F. Armarego, Pergamon Press, Oxford, U.K., 1988.

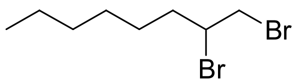
S2 P. J. Domaille and R. L. Harlow, *J. Am. Chem. Soc.*, 1986, **108**, 2108.

S3 N. B. Barhate, A. S. Gajare, R. D. Wakharkar and A. V. Bedekar, *Tetrahedron*, 1999, **55**, 11127.
S4 T. Ying, W. Bao and Y. Zhang, *J. Chem. Res.*, 2004, 806.
S5 N. Narender, P. Srinivasu, S. J. Kulkarni and K. V. Raghavan, *Synth. Commun.* 2000, **30**, 3669.
S6 A. Podgoršek, S. Stavber, M. Zupan and J. Iskra, *Tetrahedron*, 2009, **65**, 4429.
S7 K. V. V. K. Mohan, N. Narender, P. Srinivasu, S. J. Kulkarni and K. V. Raghavan, *Synth. Commun.*, 2004, **34**, 2143.

Compound Data

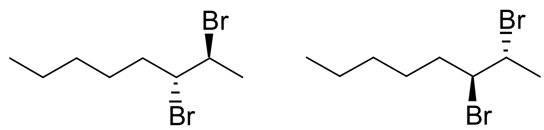
Conversions of substrates, yields of products, and selectivities to products are also summarized below.

Compound 3a (Conv. 99%, Yield 90%, Select. 91%)



GC (TC-WAX capillary column, 0.25 mm × 30 m, GL Science Inc.): carrier gas (N_2, 130 kPa), initial column temperature (50°C), initial time (5 min), final column temperature (220°C), progress rate (10°C/min), injection temperature (250°C), detection temperature (250°C), retention time (15.51 min).
MS (EI): *m/z* (%): 151(8), 149 (10), 137 (7), 135 (8), 112 (8), 111 (69), 71 (10), 70 (11), 69 (100), 67 (7), 57 (46), 56 (8), 55 (49), 53 (7).
^{1}H NMR ($CDCl_3$, TMS): δ 4.22−4.12 (m, 1H), 3.85 (dd, J = 10.0, 4.5 Hz, 1H), 3.63 (dd, J = 10.0, 10.0 Hz, 1H), 2.20−2.07 (m, 1H), 1.85−1.71 (m, 1H), 1.57−1.27 (m, 8H), 0.90 (t, J = 6.6 Hz, 3H).
$^{13}C\{^1H\}$ NMR ($CDCl_3$, TMS): δ 53.1, 36.4, 36.2, 31.5, 28.5, 26.7, 22.5, 14.0.

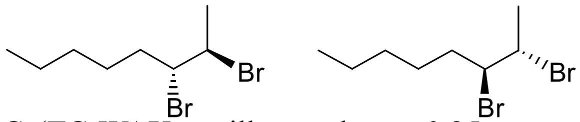
Compound *erythro*-3b (2*R3*S**) (Conv. 99%, Yield 87%, Select. 88%)**



GC (TC-WAX capillary column, 0.25 mm × 30 m, GL Science Inc.): carrier gas (N_2, 130 kPa), initial column temperature (50°C), initial time (5 min), final column temperature (220°C), progress rate (10°C/min), injection temperature (250°C), detection temperature (250°C), retention time (14.31 min).
MS (EI): *m/z* (%): 191 (5), 112 (8), 111 (60), 70 (10), 69 (100), 67 (6), 57 (10), 56 (8), 55 (59), 53 (7).
^{1}H NMR ($CDCl_3$, TMS): δ 4.23 (dq, J = 7.5, 6.5 Hz, 1H), 4.11 (ddd, J = 8.2, 7.5, 3.0 Hz, 1H), 2.16−2.04 (m, 1H), 1.96−1.89 (m, 1H), 1.86 (d, J = 6.5 Hz, 3H), 1.69−0.93 (m, 6H), 0.91 (t, J = 6.6, 3H).

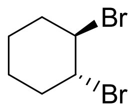
$^{13}C\{^1H\}$ NMR ($CDCl_3$, TMS): δ 61.8, 52.4, 37.1, 31.0, 26.6, 25.0, 22.4, 14.0.

Compound *threo*-3b (2*R3*R**) (Conv. >99%, Yield 76%, Select. 76%)**



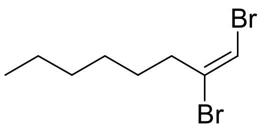
GC (TC-WAX capillary column, 0.25 mm × 30 m, GL Science Inc.): carrier gas (N_2, 130 kPa), initial column temperature (50°C), initial time (5 min), final column temperature (220°C), progress rate (10°C/min), injection temperature (250°C), detection temperature (250°C), retention time (14.56 min).
MS (EI): *m/z* (%): 112 (15), 111 (55), 83 (8), 81 (5), 70 (21), 69 (100), 67 (9), 57 (14), 56 (22), 55 (83), 54 (7), 53 (9).
^1H NMR ($CDCl_3$, TMS): δ 4.45 (dq, J = 3.0, 6.8 Hz, 1H), 4.20 (ddd, J = 10.3, 3.0, 3.0 Hz, 1H), 2.13−2.01 (m, 1H), 1.87−1.81 (m, 1H), 1.76 (d, J = 6.8 Hz, 3H), 1.67−1.54 (m, 1H), 1.34 (m, 6H), 0.91 (t, J = 6.6 Hz, 3H).
$^{13}C\{^1H\}$ NMR ($CDCl_3$, TMS): δ 60.1, 52.3, 33.9, 30.9, 27.4, 22.4, 21.5, 13.9.

Compound 3c (Conv. 93%, Yield 82%, Select. 88%)



GC (TC-WAX capillary column, 0.25 mm × 30 m, GL Science Inc.): carrier gas (N_2, 130 kPa), initial column temperature (50°C), initial time (5 min), final column temperature (220°C), progress rate (10°C/min), injection temperature (250°C), detection temperature (250°C), retention time (14.79 min).
MS (EI): *m/z* (%): 244 (0.5), 242 (1.1), 240 (0.6), 163 (14), 161 (15), 82 (9), 81 (100), 79 (18), 67 (8), 54 (7), 53 (10).
^1H NMR ($CDCl_3$, TMS): δ 4.46 (brs, 2H), 2.52−2.40 (m, 2H), 1.95−1.74 (m, 4H), 1.61−1.26 (m, 2H).
$^{13}C\{^1H\}$ NMR ($CDCl_3$, TMS): δ 55.2, 32.0, 22.4.

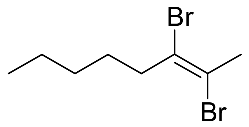
Compound 3d (Conv. 92%, Yield 92%, Select. >99%)



GC (TC-WAX capillary column, 0.25 mm × 30 m, GL Science Inc.): carrier gas (N_2, 130 kPa), initial column temperature (50°C), initial time (5 min), final column temperature (220°C), progress rate (10°C/min), injection temperature (250°C), detection temperature (250°C), retention time (13.34 min).

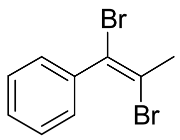
MS (EI): *m*/*z* (%): 272 (7), 270 (13), 268 (7), 199 (5), 134 (6), 133 (6), 132 (7), 121 (8), 119 (14), 117 (6), 110 (9), 109 (100), 81 (13), 79 (8), 77 (5), 71 (11), 70 (37), 69 (48), 68 (14), 67 (89), 66 (6), 65 (11), 55 (43), 53 (16), 52 (6), 51 (14).
^{1}H NMR ($CDCl_3$, TMS): δ 6.40 (s, 1H), 2.59 (t, J = 7.3 Hz, 2H), 1.63−1.52 (m, 2H), 1.31 (m, 6H), 0.90 (t, J = 6.8 Hz, 3H).
$^{13}C\{^1H\}$ NMR ($CDCl_3$, TMS): δ 127.0, 102.1, 36.9, 31.5, 28.0, 27.0, 22.5, 14.0.

Compound 3e (Conv. 99%, Yield 96%, Select. 97%)



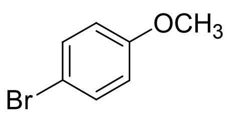
GC (TC-WAX capillary column, 0.25 mm × 30 m, GL Science Inc.): carrier gas (N_2, 130 kPa), initial column temperature (50°C), initial time (5 min), final column temperature (220°C), progress rate (10°C/min), injection temperature (250°C), detection temperature (250°C), retention time (12.27 min).
MS (EI): m/z (%): 272 (7), 270 (14), 268 (8), 148 (6), 146 (6), 135 (26), 134 (6), 133 (34), 131 (8), 110 (9), 109 (100), 81 (8), 79 (7), 77 (6), 67 (30), 66 (5), 65 (9), 57 (33), 56 (7), 55 (22), 54 (5), 53 (34), 52 (7), 51 (16).
^{1}H NMR ($CDCl_3$, TMS): δ 2.65 (t, J = 7.6Hz, 2H), 2.41 (s, 3H), 1.63−1.52 (m, 2H), 1.35−1.28 (m, 4H), 0.91 (t, J = 6.9 Hz, 3H).
$^{13}C\{^1H\}$ NMR ($CDCl_3$, TMS): δ 122.2, 115.1, 40.6, 30.7, 28.8, 27.1, 22.4, 14.0.

Compound 3f (Conv. 94%, Yield 94%, Select. >99%)



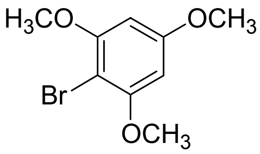
GC (TC-WAX capillary column, 0.25 mm × 30 m, GL Science Inc.): carrier gas (N_2, 130 kPa), initial column temperature (100°C), initial time (5 min), final column temperature (250°C), progress rate (10°C/min), injection temperature (250°C), detection temperature (250°C), retention time (12.97 min).
MS (EI): m/z (%): 278 (11), 276 (24), 274 (12), 197 (24), 195 (26), 117 (6), 116 (66), 115 (100), 89 (15), 65 (5), 63 (13), 62 (6), 58 (21), 51 (7), 50 (5).
^{1}H NMR ($CDCl_3$, TMS): δ 7.41−7.26 (m, 5H), 2.61 (s, 3H).
$^{13}C\{^1H\}$ NMR ($CDCl_3$, TMS): δ 140.8, 129.1, 128.6, 128.2, 117.2, 116.8, 29.3.

Compound 3g (Conv. 96%, Yield 96%, Select. >99%)



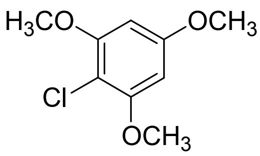
GC (TC-WAX capillary column, 0.25 mm × 30 m; GL Science Inc.): carrier gas (N_2, 130 kPa), initial column temperature (50°C), initial time (5 min), final column temperature (220°C), progress rate (10°C/min), injection temperature (250°C), detection temperature (250°C), retention time (15.93 min).
MS (EI): m/z (%): 189 (8), 188 (97), 187 (8), 186 (100), 173 (45), 171 (47), 145 (37), 143 (38), 92 (11), 79 (7), 77 (16), 76 (8), 75 (10), 74 (8), 64 (16), 63 (25), 62 (7), 51 (6), 50 (15).
^{1}H NMR ($CDCl_3$, TMS): δ 7.35 (d, J = 9.2 Hz, 2H), 6.75 (d, J = 9.2, 2H), 3.76 (s, 3H).
^{13}C{^{1}H} NMR ($CDCl_3$, TMS): δ 158.7, 132.2, 115.7, 112.7, 55.4.

Compound 3h (Conv. 98%, Yield 95%, Select. 97%)



GC (TC-WAX capillary column, 0.25 mm × 30 m, GL Science Inc.): carrier gas (N_2, 130 kPa), initial column temperature (100°C), initial time (5 min), final column temperature (250°C) , progress rate (10°C/min), injection temperature (250°C), detection temperature (250°C), retention time (20.20 min).
MS (EI): m/z (%): 248 (98), 247 (12), 246 (100), 205 (15), 203 (16), 190 (6), 188 (7), 173 (5), 167 (5), 159 (5), 157 (6), 152 (9), 139 (30), 138 (66), 137 (75), 124 (11), 123 (7), 122 (24), 109 (30), 108 (10), 107 (19), 96 (6), 94 (6), 93 (5), 92 (5), 81 (6), 79 (14), 78 (8), 77 (20), 69 (21), 66 (9), 65 (8), 63 (12), 62 (10), 59 (16), 53 (17), 51 (12), 50 (14).
^{1}H NMR ($CDCl_3$, TMS): δ 6.17 (s, 2H), 3.87 (s, 6H), 3.81 (s, 3H).
^{13}C{^{1}H} NMR ($CDCl_3$, TMS): δ 160.4, 157.4, 91.6, 56.3, 55.4.

Compound 4h (Conv. 96%, Yield 88%, Select. 92%)



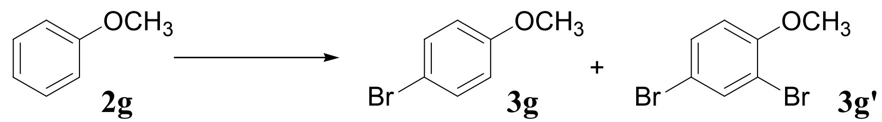
GC (TC-WAX capillary column, 0.25 mm × 30 m, GL Science Inc.): carrier gas (N_2, 130 kPa), initial column temperature (100°C), initial time (5 min), final column temperature (250°C), progress rate (10°C/min), injection temperature (250°C), detection temperature (250°C), retention time (18.92 min).
MS (EI): m/z (%):204 (33), 203 (12), 202 (100), 175 (8), 173 (28), 172 (5), 161 (9), 159 (29), 144 (11), 143 (6), 139 (16), 138 (27), 137 (14), 129 (10), 122 (5), 113 (9), 109 (20), 108 (5), 107 (5), 101 (5), 86 (7), 85 (6), 79 (6), 77 (8), 73 (5), 69 (13), 65 (7), 63 (7), 62 (6), 59 (10), 53 (8), 51 (6), 50 (6).
^{1}H NMR ($CDCl_3$, TMS): δ 6.19 (s, 2H), 3.88 (s, 6H), 3.81 (s, 3H).
^{13}C{1H} NMR ($CDCl_3$, TMS): δ 159.4, 156.6, 91.6, 56.3, 55.5.

Table S1. Oxidative bromination of terminal alkenes with H_2O_2 (comparison)

Alkene	Catalyst /Acid	Bromo source	Solvent	Temp. /°C	Time /min	Total yield /%	Selectivity /% dibromoalkane	bromohydrin	TON	TOF /h^{-1}	Ref.
2a	**1** /AcOH	NaBr	1,2-DCE/AcOH (v/v = 1/2)	20	10	90	>99	–	1800	10800	this work
2a	$PhEt_3NCl$ /HBr	$HBr/CaBr_2$	CCl_4/H_2O	r.t.	20	92	>99	–	105	315	6b
1-heptene	WO_4^{2-}–LDH /–	NH_4Br	CH_3OH/H_2O (v/v = 19/1)	25	667	60†	46	–	120	11	6c
1-heptene	WO_4^{2-}–LDH /–	NH_4Br	CH_3CN/H_2O (v/v = 1/4)	25	1180	81	17	83	182	9.3	6c
2a	NH_4VO_3 /$HClO_4$	KBr	$H_2O/CHCl_3$ (v/v = 1/1)	25	–	95	>99	–	0.95	–	6a
1-decene	– /HBr	HBr	CCl_4	r.t.	120	95	>99	–	–	–	S3
1-tetradecene	– /H_2SO_4	NaBr	[bmim]CCl_3COO	r.t.	480	90	>99	–	–	–	S4

Yields were based on **2a**. LDH = Ni, Al- layered double hydroxide. [bmim] = 1-butyl-3-methylimidazolium. r.t. = room temperature.
† 1-Bromo-2-methoxyheptane and 2-bromo-1-methoxyheptane were formed in 9% and 23% yields, respectively.

Table S2. Oxidative bromination of **2g** with H_2O_2 (comparison)



Catalyst/Acid	Bromo source	Solvent	Temp. /°C	Time /min	Total yield /%	Selectivity /% 3g	3g'	TON	TOF /h^{-1}	Ref.
1 /AcOH	KBr	1,2-DCE/AcOH (v/v = 1/2)	20	30	96	>99	–	1920	3840	this work
$(NH_4)_6Mo_7O_{24}$ /AcOH	KBr	AcOH	r.t.	20	99	>99	–	74	222	6f
NH_4VO_3 /HBr	HBr/KBr	H_2O	r.t.	1440	96	50	50	9.6	0.4	6d
NH_4VO_3 /HBr	HBr/KBr	$H_2O/CHCl_3$ (v/v = 1/1)	r.t.	1440	94	>99	–	9.4	0.4	6d
V_2O_5 /HBr	HBr/KBr	H_2O	25	100	68	>99	–	68	41	6e
V_2O_5 /HBr	KBr	H_2O	25	90	85	93	7	57	38	6e
V_2O_5 /HBr	KBr	H_2O	25	140	30	>99	–	12	5.1	6e
– /HBr	HBr/KBr	H_2O	25	100	15	>99	–	–	–	6e
HZSM-5 /AcOH	KBr	AcOH	r.t.	120	99	98	–	–	–	S5
– /HBr	HBr	H_2O	r.t.	480	100	>99	–	–	–	S6
– /AcOH	NH_4Br	AcOH	r.t.	180	99	99	–	–	–	S7

Yields were based on **2g**. r.t. = room temperature.