Electronic Supplementary Information (ESI) for

A highly negatively charged γ-Keggin germanodecatungstate efficient for Knoevenagel condensation

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Experimental Section

Materials. Acetonitrile (Kanto Chemical) was purified by The Ultimate Solvent System (GlassContour Company) prior to use.[S1] Substrates and other solvents were purified according to reported procedures.[S2] $Na_2WO_4 \cdot 2H_2O$ (Nippon Inorganic Colour & Chemical), GeO_2 (Wako Chemical), tetra-*n*-butylammonium bromide (TBABr) (TCI), tetra-*n*-butylammonium hydroxide 30-hydrate ($TBAOH \cdot 30H_2O$) (Aldrich), tetramethylammonium chloride (TCI), and deuterated solvents ($CDCl_3$ and dimethyl sulfoxide (DMSO)-d_6) (ACROS) were used as received. Divacant polyoxodecatungstates, $TBA_4[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]$[S3a] and $K_8[\gamma\text{-}GeW_{10}O_{36}] \cdot 6H_2O$,[S3b] were synthesized according to literature procedures.

Instruments. IR spectra were measured on a JASCO FTIR-460 spectrometer using KBr disks. NMR spectra were recorded on a JEOL JNM-EX-270 spectrometer (^{1}H, 270.0 MHz; ^{13}C, 67.80 MHz; ^{29}Si, 53.45 MHz; ^{183}W, 11.20 MHz) by using 5 mm (for ^{1}H and ^{13}C) or 10 mm (for ^{29}Si and ^{183}W) tubes. Chemical shifts (δ) were reported in ppm downfield from $SiMe_4$ (solvent, $CDCl_3$) for ^{1}H, ^{13}C, and ^{29}Si NMR spectra and from 2 M Na_2WO_4 (solvent, D_2O) for ^{183}W NMR spectra. GC analyses were performed on Shimadzu GC-2014 with a flame ionization detector equipped with a TC-WAX capillary column (internal diameter = 0.25 mm, length = 30 m) or an InertCap 5 capillary column (internal diameter = 0.25 mm, length = 30 m). Mass spectra were recorded on Shimadzu GCMS-QP2010 equipped with a TC-5HT capillary column at an ionization voltage of 70 eV. Cold-spray ionization mass spectra were measured on a JEOL JMS-T100CS spectrometer in the negative ion mode by direct infusion with a syringe pump (0.05 mL min^{-1}).

X-ray Crystallography. X-ray diffraction measurements were made on a Rigaku AFC-10 Saturn 724 CCD detector with graphite monochromated Mo Kα radiation (λ = 0.71069 Å). The data of $TBA_6 \cdot$**I** were collected using CrystalClear[S4] at 153 K, and indexing, integration, and absorption correction were performed with HKL2000[S5] software for Linux. Neutral scattering factors were obtained from the standard source. In the data reduction, corrections for Lorentz and polarization effects were made. The structural analysis was performed using CrystalStructure[S6] and Win-GX for Windows software.[S7] The

molecular structures of $[(CH_3)_4N]_4[\gamma\text{-}GeW_{10}O_{34}(H_2O)_2]$ and $TBA_6\cdot\mathbf{I}$ were solved by combination of SHELXS-97 (direct methods) and SHELXH-97 (Fourier and least squares refinement).[S8] Tungsten, silicon, and oxygen atoms were refined anisotropically, and carbon and nitrogen atoms were refined isotropically. There are class A alerts (PLAT306_ALERT_2_A) in our CIF of $[(CH_3)_4N]_4[\gamma\text{-}GeW_{10}O_{34}(H_2O)_2]\cdot 8H_2O$ because the hydrogen atoms of water molecules were not included in the refinement.

Synthesis and Characterization of $[(n\text{-}C_4H_9)_4N]_4[\gamma\text{-}GeW_{10}O_{34}(H_2O)_2]$. Into water (60 mL), $K_8[\gamma\text{-}GeW_{10}O_{36}]\cdot 6H_2O$ (6 g, 2 mmol) was dissolved and the pH value of the aqueous solution was carefully adjusted to 2.0 with HNO_3. After stirring the solution for 3 min at room temperature, an excess amount of TBABr (6.5 g, 20 mmol) was added in a single step. The resulting white precipitate of $TBA_4[\gamma\text{-}GeW_{10}O_{34}(H_2O)_2]$ was collected by filtration, washed with an excess amount of H_2O, and evacuated at ambient temperature. The analytically pure $TBA_4[\gamma\text{-}GeW_{10}O_{34}(H_2O)_2]$ was obtained as a white powder. Yield 2.8 g (39 %). ^{183}W NMR (11.20 MHz, DMSO-d_6, 298 K, Na_2WO_4) δ = –72.1 ($\Delta\nu_{1/2}$ = 4.1 Hz), –76.1 ($\Delta\nu_{1/2}$ = 4.1 Hz), –83.9 ($\Delta\nu_{1/2}$ = 5.6 Hz), –99.6 ($\Delta\nu_{1/2}$ = 6.1 Hz), and –183.7 ppm ($\Delta\nu_{1/2}$ = 5.2 Hz) with an integrated intensity ratio of 1:1:1:1:1, respectively; UV-Vis (CH_3CN) λ_{max} (ε) 259 nm (26200 $mol^{-1}dm^3cm^{-1}$); IR (KBr), 957, 883, 859, 819, 752, 688, 543, 495, 464, 437, 356 cm^{-1}; positive ion MS (CSI, DMSO), *m/z* 2033 ($[TBA_6GeW_{10}O_{34}(DMSO)_2]^{2+}$) and 3824 ($[TBA_5GeW_{10}O_{34}(DMSO)_2]^{+}$); elemental analysis calcd (%) for $C_{64}H_{148}N_4O_{36}GeW_{10}$ ($[(n\text{-}C_4H_9)_4N]_4[\gamma\text{-}GeW_{10}O_{34}(H_2O)_2]$), C 22.21, H 4.31, N 1.62, Ge 2.10, W 53.12; found, C 22.26, H 4.45, N 1.67, Ge 2.01, W 53.00.

Synthesis and Characterization of $[(n\text{-}C_4H_9)_4N]_6[\gamma\text{-}H_2GeW_{10}O_{36}]$ (I). Into the acetonitrile solution (2 mL) containing $TBA_4[\gamma\text{-}GeW_{10}O_{34}(H_2O)_2]$ (0.37 g, 0.10 mmol), $TBAOH\cdot 30H_2O$ (162 mg, 0.20 mmol) was added at 273 K. After stirring the solution for 2 h at 273 K, an excess amount of diethyl ether (60 mL) was added in a single step and the solution was kept for 1 day at ambient temperature. The solution was separated by decantation and the resulting white precipitates of **I** were evacuated at ambient temperature. The analytically pure **I** was obtained as a white powder. Yield 0.27 g (69%). ^{1}H NMR (270.0 MHz, DMSO-d_6, 298 K, TMS) δ = 5.37 ppm ($\Delta\nu_{1/2}$ = 1.6 Hz); ^{183}W NMR (11.20 MHz, DMSO-d_6, 298 K, Na_2WO_4) δ = –97.8 ($\Delta\nu_{1/2}$ = 4.8 Hz), –114.7 ($\Delta\nu_{1/2}$ = 3.2 Hz), and –168.3 ppm ($\Delta\nu_{1/2}$ = 5.0 Hz) with an integrated intensity ratio of 2:2:1, respectively, indicating the fast proton-exchange between the two bridging oxygens (i.e., O20/O22 and O25/O27); UV-Vis (CH_3CN) λ_{max} (ε) 268 nm (19500 $mol^{-1}dm^3cm^{-1}$); IR (KBr), 949, 891, 860, 806, 736, 540, 466, 443, 354, 292 cm^{-1}; positive ion MS (CSI, acetone), *m/z* 2214 ($[TBA_8H_2GeW_{10}O_{36}]^{2+}$) and 4186 ($[TBA_7H_2GeW_{10}O_{36}]^{+}$); elemental analysis calcd (%) for $C_{96}H_{218}N_6O_{36}GeW_{10}$ ($[(n\text{-}C_4H_9)_4N]_6[\gamma\text{-}H_2GeW_{10}O_{36}]$), C 29.24, H 5.57, N 2.13, Ge 1.84, W 46.61; found, C 28.61, H 5.84, N 2.25, Ge 1.77, W 46.10.

Synthesis and Characterization of $[(CH_3)_4N]_4[\gamma\text{-}GeW_{10}O_{34}(H_2O)_2]\cdot 8H_2O$. The pH value of the aqueous solution (8 mL) containing $K_8[\gamma\text{-}GeW_{10}O_{36}]\cdot 6H_2O$ (2.77 g, 0.8 mmol) was carefully adjusted to 1.9 with HNO_3, followed by addition of the aqueous solution (0.5 mL) containing $[(CH_3)_4N]Cl$ (1.08 g, 10 mmol). After stirring the solution for 3 min at room temperature, the resulting white precipitates

were collected by filtration, washed with water, and evacuated at ambient temperature. The analytically pure $[(CH_3)_4N]_4[\gamma\text{-}GeW_{10}O_{34}(H_2O)_2]$ was obtained as a white powder. Yield 0.63 g (24 %). An aqueous solution (1 mL) containing $[(CH_3)_4N]_4[\gamma\text{-}GeW_{10}O_{34}(H_2O)_2]$ (51.6 mg, 18 μmol) was kept at 277 K and single crystals suitable for X-ray structure analysis were obtained. IR (KBr), 1484, 1449, 1417, 1384, 1288, 1211, 1154, 957, 859, 809, 787, 744, 696, 653, 593, 546, 493, 480, 460, 435, 396, 354, 325 cm^{-1}; elemental analysis calcd (%) for $C_{16}H_{68}N_4O_{44}GeW_{10}$ ($[(CH_3)_4N]_4[\gamma\text{-}GeW_{10}O_{34}(H_2O)_2]\cdot 8H_2O$), Ge 2.48, W 62.71, C 6.56, H 2.34, N 1.91; found, Ge 2.45, W 63.74, C 6.74, H 2.09, N 1.79.

A Typical Procedure for Catalytic Knoevenagel Condensation. Catalytic reactions were carried out with a glass tube (30 mL) containing a magnetic stir bar. A typical procedure for the catalytic reaction was as follows: active methylene compound (1.0 mmol), aldehyde (1.5 mmol), acetonitrile (1 mL), and internal standard (naphthalene, ca. 0.3 mmol) were charged in the reaction vessel. The reaction was initiated by the addition of **I** (10 μmol) and the reaction solution was periodically analyzed by GC, GC-MS and NMR. All products were known compounds and identified by comparison of their ^1H and ^{13}C NMR signals with the literature data.

Data of products

Ethyl (2E)-2-cyano-3-phenyl-2-propenoate (3a). ^1H NMR (270 MHz, $CDCl_3$, 298 K, TMS): δ = 8.26 (s, 1H), 8.02–7.98 (m, 2H), 7.60–7.47 (m, 3H), 4.39 (q, J = 7.11 Hz, 2H), 1.40 (t, J = 7.16 Hz, 3H); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$, 298 K, TMS): δ = 162.4, 155.0, 133.2, 131.4, 131.0, 129.2, 115.4, 103.0, 62.7, 14.1; MS (70 eV, EI): *m/z* (%): 202 (13), 201 (94) [M^+], 200 (67), 173 (59), 172 (82), 157 (14), 156 (100), 146 (11), 129 (41), 128 (87), 127 (18), 107 (11), 102 (55), 101 (33), 78 (10), 77 (54), 76 (13), 75 (15), 51 (36), 50 (13).

2-Benzylidenemalononitrile (3b). ^1H NMR (270 MHz, $CDCl_3$, 298 K, TMS): δ = 7.94–7.89 (m, 2H), 7.79 (s, 1H), 768–7.51 (m, 3H); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$, 298 K, TMS): δ = 159.9, 134.6, 130.9, 130.7, 129.6, 113.7, 112.5, 82.8; MS (70 eV, EI): *m/z* (%): 155 (12), 154 (100) [M^+], 153 (10), 128 (11), 127 (82), 103 (50), 100 (12), 76 (15), 51 (14), 50 (13).

Ethyl (2E)-2-cyano-3-(4-methylphenyl)-2-propenoate (3d). ^1H NMR (270 MHz, $CDCl_3$, 298 K, TMS): δ = 8.21 (s, 1H), 7.92–7.89 (m, 2H), 7.32–7.27 (m, 2H), 4.38 (q, J = 7.11 Hz, 2H), 2.44 (s, 3H), 1.40 (t, J = 7.16 Hz, 3H); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$, 298 K, TMS): δ = 162.7, 154.9, 144.6, 131.2, 130.0, 128.8, 115.7, 101.5, 62.5, 21.8, 14.1; MS (70 eV, EI): *m/z* (%): 216 (15), 215 (100) [M^+], 214 (26), 200 (26), 187 (36), 186 (23), 172 (39), 170 (69), 169 (10), 143 (27), 142 (41), 141 (20), 140 (23), 116 (35), 115 (77), 114 (10), 91 (14), 89 (14), 65 (20), 63 (10).

Ethyl (2E)-3-(4-chlorophenyl)-2-cyano-2-propenoate (3e). ^1H NMR (270 MHz, $CDCl_3$, 298 K, TMS): δ = 8.20 (s, 1H), 7.95–7.92 (m, 2H), 7.50–7.27 (m, 2H), 4.39 (q, J = 7.11 Hz, 2H), 1.40 (t, J = 7.16 Hz, 3H); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$, 298 K, TMS): δ = 162.2, 153.4, 139.6, 132.2, 129.8, 129.6, 115.2, 103.5, 62.8, 14.1; MS (70 eV, EI): *m/z* (%): 237 (34), 236 (25), 235 (100) [M^+], 234 (37), 209 (22), 208 (15), 207 (65), 206 (23), 200 (27), 192 (27), 191 (12), 190 (80), 182 (10), 180 (12), 172

(29), 165 (10), 164 (21), 163 (35), 162 (56), 161 (17), 141 (15), 138 (11), 136 (34), 128 (24), 127 (61), 126 (48), 111 (14), 101 (13), 100 (22) , 99 (21), 76 (15), 75 (47), 74 (13), 51 (15), 50 (19).

Ethyl (2E)-2-cyano-2-heptenoate (3f). ^{1}H NMR (270 MHz, $CDCl_3$, 298 K, TMS): δ = 7.66 (t, J = 7.83 Hz, 1H), 4.32 (q, J = 7.11 Hz, 2H), 2.57 (m, 2H), 1.61–1.50 (m, 2H), 1.47–1.33 (m, 5H), 0.95 (t, J = 7.16 Hz, 3H); ^{13}C{^{1}H} NMR (67.5 MHz, $CDCl_3$, 298 K, TMS): δ = 163.8, 161.3, 113.6, 109.7, 62.3, 31.6, 29.7, 22.3, 14.0, 13.6; MS (70 eV, EI): *m/z* (%): 181 (1)[M^+], 136 (16), 126 (48), 124 (14), 111 (16), 108 (10), 107 (13), 98 (100), 83 (28), 81 (14), 80 (22), 68 (11), 67 (11), 56 (68), 55 (16), 52 (13).

Ethyl 2-cyano-5-phenyl-2,4-pentadienoate (3g). ^{1}H NMR (270 MHz, $CDCl_3$, 298 K, TMS): δ = 8.02–8.00 (m, 1H), 7.61–7.57 (m, 2H), 7.44–7.41 (m, 3H), 7.30–7.26 (m, 2H), 4.34 (q, J = 7.11 Hz, 2H), 1.38 (t, J = 7.16 Hz); ^{13}C{^{1}H} NMR (67.5 MHz, $CDCl_3$, 298 K, TMS): δ = 162.3, 155.4, 148.8, 134.6, 131.1, 129.1, 128.5, 123.0, 114.5, 104.5, 62.3, 14.1; MS (70 eV, EI): *m/z* (%): 202 (30)[M^+], 173 (36), 159 (11), 158 (100), 157 (68), 156 (12), 130 (28), 129 (40), 128 (18), 103 (26), 102 (28), 79 (17), 78 (17), 76 (25), 75 (25), 51 (29), 50 (16).

Ethyl (2E)-2-cyano-3-(3-pyridinyl)-2-propenoate (3h). ^{1}H NMR (270 MHz, $CDCl_3$, 298 K, TMS): δ = 8.93–8.92 (m, 1H), 8.78–8.75 (m, H), 8.61–8.56 (m, H), 8.27 (s, H), 7.51–7.46 (m, 1H), 4.42 (q, J = 7.11 Hz, 2H), 1.42 (t, J = 7.16 Hz, 3H); ^{13}C{^{1}H} NMR (67.5 MHz, $CDCl_3$, 298 K, TMS): δ = 161.7, 153.4, 152.9, 151.2, 135.9, 127.5, 124.0, 114.8, 105.6, 63.0, 14.1; MS (70 eV, EI): *m/z* (%): 202 (30) [M^+], 159 (11), 158 (100), 157 (68), 156 (12), 130 (28), 129 (40), 128 (18), 103 (26), 102 (28), 79 (17), 78 (17), 76 (25), 75 (25), 51 (29), 50 (16).

Ethyl cyano(cyclopentylidene)acetate (3i). ^{1}H NMR (270 MHz, $CDCl_3$, 298 K, TMS): δ = 4.27 (q, J = 7.11 Hz, 2H), 2.99 (t, J = 6.62 Hz, 2H), 2.80 (t, J = 6.48 Hz, 2H), 1.88–1.78 (m, 4H), 1.34 (t, J = 7.16 Hz, 3H); ^{13}C{^{1}H} NMR (67.5 MHz, $CDCl_3$, 298 K, TMS): δ = 187.4, 161.9, 115.6, 100.8, 61.5, 37.7, 35.4, 26.5, 22.3, 14.1; MS (70 eV, EI): *m/z* (%): 179 (15) [M^+], 151 (40), 134 (25), 133 (16), 123 (100), 122 (17), 106 (20), 105 (18), 104 (13), 95 (13), 80 (10), 79 (24), 78 (15), 77 (22), 67 (23), 51 (11).

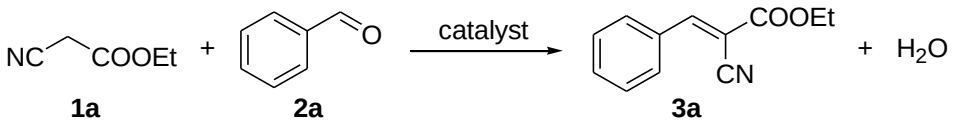
Ethyl cyano(cyclohexylidene)acetate (3j). ^{1}H NMR (270 MHz, $CDCl_3$, 298 K, TMS): δ = 4.27 (q, J = 7.20 Hz, 2H), 2.98 (t, J = 6.08 Hz, 2H), 2.66 (t, J = 6.21 Hz, 2H), 1.85–1.61 (m, 6H), 1.35 (t, J = 7.16 Hz, 3H); ^{13}C{^{1}H} NMR (67.5 MHz, $CDCl_3$, 298 K, TMS): δ = 179.9, 161.9, 115.5, 102.0, 61.6, 36.8, 31.5, 28.5, 28.2, 25.6, 14.0; MS (70 eV, EI): *m/z* (%): 193 (36)[M^+], 165 (60), 148 (54), 147 (57), 146 (19), 138 (11), 137 (100), 136 (16), 122 (16), 121 (79), 120 (43), 119 (42), 118 (20), 111 (16), 109 (35), 106 (17), 104 (13), 94 (14), 93 (47), 91 (31), 81 (26), 80 (30), 79 (27), 78 (17), 77 (22), 68 (13), 67 (21), 66 (15), 65 (24), 64 (11), 55 (26), 53 (15), 52 (14), 51 (14).

(2-Amino-3-cyano-4*H*-chromene-4-yl)malononitrile. ^{1}H NMR (270 MHz, DMSO-d_6, 298 K, TMS): δ = 7.54–7.37 (m, 4H), 7.29 (dd, J = 7.43 Hz, 1H), 7.15 (d, J = 8.10 Hz, 1H), 5.09 (d, J = 3.78 Hz, 1H), 4.61 (d, J = 3.78 Hz, 1H); ^{13}C{^{1}H} NMR (67.5 MHz, DMSO-d_6, 298 K, TMS): δ = 163.5, 149.8, 130.2, 128.9, 125.1, 119.4, 118.0, 116.4, 113.1, 112.9, 48.9, 37.1, 32.4.

Table S1. Crystallographic Data for $[(CH_3)_4N]_4[\gamma\text{-}GeW_{10}O_{34}(H_2O)_2]\cdot 8H_2O$ and $TBA_6\cdot$**I**

	$[(CH_3)_4N]_4[\gamma\text{-}GeW_{10}O_{34}(H_2O)_2]\cdot 8H_2O$	$TBA_6\cdot$**I**
formula	$C_{16}GeN_4O_{44}W_{10}$	$C_{102}GeN_9O_{36}W_{10}$
fw	2863.27	3838.20
crystal system	Monoclinic	Orthorhombic
space group	$P2_1/n$(#14)	*Pbca*(#61)
a (Å)	11.62520(10)	17.74710(10)
b (Å)	22.3313(2)	31.6276(2)
c (Å)	21.6699(2)	48.1971(3)
β (deg)	91.85	90.00
V (Å^3)	5622.71(9)	27052.9(3)
Z	4	8
gof	1.539	1.271
D_{calcd} (g cm^{-3})	3.322	1.885
R [$I > 2\sigma(I)$]	0.0493 (for 14389 data)	0.0866 (for 33132 data)
R_w (all data)	0.1829	0.2543

Table S2. Effect of Catalysts on Knoevenagel Condensation of **1a** with **2a**[a]

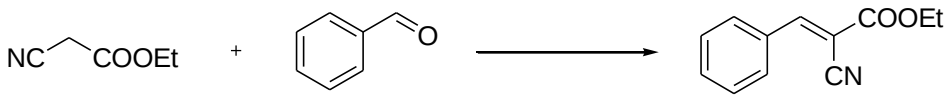


1a **2a** **3a**

Entry	Catalyst	Yield (%)
1	TBA_6·**I**	98 (95)
2[b]	TBA_6·**I**	91
3	$TBA_4[\gamma\text{-}GeW_{10}O_{34}(H_2O)_2]$	35
4	$K_8[\gamma\text{-}GeW_{10}O_{36}]\cdot 6H_2O$	4
5	$TBA_4[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]$	18
6	$TBA_4[\alpha\text{-}SiW_{12}O_{40}]$	1
7	$Na_2WO_4\cdot 2H_2O$	2
8[c]	GeO_2	<1
9[d]	TBABr	2
10	$TBA_8H_2[(\gamma\text{-}SiYW_{10}O_{36})_2]$	12
11	without	<1

[a] Reaction conditions: Catalyst (W: 10 mol% with respect to **1a**), **1a** (1.0 mmol), **2a** (1.5 mmol), CH_3CN (1 mL), 305 K, 2 h. Yield (%) = **3a** (mol)/initial **1a** (mol) × 100. The value in the parenthesis was isolated yield. [b] **2a** (1.0 mmol), 4 h. [c] GeO_2 (1 mol% with respect to **1a**). [d] TBABr (6 mol% with respect to **1a**).

Table S3. Various Catalytic Systems for Knoevenagel Condensation of **1a** with **2a** (Selected Examples)[a]



1a **2a** **3a**

Entry	Catalyst	**1a**/**2a**/C	Solvent	Temp. (K)	Time (min)	Yield (%)	TON	TOF (h^{-1})	Ref.
1	***TBA_6·I***	***100/150/1***	***–***	***313***	***5***	***85***	***85***	***1020 (3000)***	***This work***
2[b]	LDH-DA	53/53/1	DMF	rt	120	95	50	25	S9
3[c]	bovine serum albumin	1/1/–	[bmim]Br	333	240	93	–	–	S10
4[d]	HAP/BTEAC	1.5/1.5/–/0.13	water	rt	60	90	–	–	S11
5	Zn^{2+} ion-exchanged β zeolite	1/1/–	–	433	360	98	–	–	S12
6[e]	ASCPEI	1/1/–	ethanol	316	90	97	–	–	S13
7	$ZrCl_4$-SiO_2	11/10/1	CH_3CN	358	180	90	9	3	S14
8[f]	$MgBr_2$.OEt_2/TEA	5/5/1/5	THF	rt	60–120	95	10	–	S15
9	Na_2CO_3/MS 4A	24/24/1/–	–	363	15	93	–	–	S16
10[g]	amine-grafted PE-MCM-41	200/200/1	cyclohexane	355	60	>99 (98)	198	198	S17
11	$[H_3N^+(CH_2)_2OH][CH_3COO^-]$	1/1/–	–	rt	12	93	–	–	S18
12	poly[*N*-(6-aminohexyl)acrylamide]	5/5/1	–	353	10	100	5	30	S19
13	cyclic guanidinium lactate ionic liquid	0.4/0.4/1	–	rt	2	93	0.4	11	S20
14	perfluoroalkylated pyridine	20/20/1	*n*-octane	353	480	(97)	19	2	S21
15	Ni-nanoparticles	12/10/1	ethanol	298	35	(97)	10	17	S22
16	KOH/La_2O_3-MgO	80/80/1	–	rt	180	(95)	76	25	S23
17[h]	[2-aemim]PF_6	125/125/1	water	rt	180	91	114	38	S24

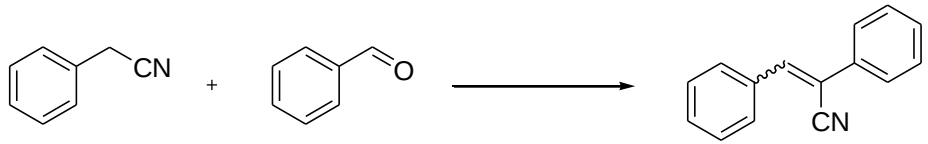
18	aminopropylsilyl-tethered MCM-41	9.5/9.9/1	toluene	rt	60	(99)	9	9	S25
19	aminopropyl-functionalized MCM	67/67/1	cyclohexane	355	2160	94	63	2	S26
20[i]	polystyryl supported-TBD	10/10/1	–	303	60	93	9	9	S27
21	Pd_{nano}/hydrotalcite	1/1/–	toluene	353	60	99	–	–	S28
22[j]	[diamine-A]BF_4	5/5/1	–	rt	1	100	5	300	S29
23	$Ru(C_2H_4)(PPh_3)_3$	50/50/1	benzene	rt	1020	98	49	3	S30
24[k]	($HDTMA^+$)-[Si]-MCM-41	2.6/2.5/–	benzene	293	360	97	–	–	S31
25	nano-silica dendrimer	10/10/1	*n*-hexane	rt	360	90	9	2	S32
26	layered Ni-Zn mixed basic salt	1.5/1/–	water	323	360	91	–	–	S33
27	urea	10/10/1	–	373	60	96	10	10	S34
28	triphenylphosphane/microwave irradiation	6.5/5/1	–		3	90	5	90	S35
29	[bmim]OH	5/5/1	–	rt	12	(93)	5	23	S36
30	polystyrene-supported poly(amidoamine) dendrimer	200/200/1	ethanol	323	15	(99)	198	792	S37
31	sulfonated nitrocoal acid	50/50/1	benzene	reflux	600	91	46	5	S38
32	LDH-F	1/1/–	DMF	333	120	92	–	–	S39
33	organic-inorganic hybrid silica material	83/92/1	–	403	120	(100)	83	42	S40
34[l]	[C_4dabco]BF_4	6.7/6.7/1	water	373	40	(96)	6	10	S41
35[m]	PAN_pF-3	7/7/1	ethanol	reflux	90	(97)	7	5	S42
36	$RuH_2(PPh_3)_4$	33/37/1	THF	rt	1440	(91)	30	1	S43
37	RuHAP	20/24/1	water	rt	240	>99	20	5	S44
38	functionalized (PS(N_3))-PEG	100/100/1	water	293	1440	97	97	4	S45
39	IRMOF-3_{DEF}	35/40/1	DMSO	313	120	99	35	17 (174)	S46
40	$CaCl_2$/Et_3N	10/10/0.5/1	ethanol	rt	30	90	9	18	S47
41	NaOH	10/10/1	ethanol	rt	30	90	9	18	S47
42	L-proline/microwave irradiation	2/1.7/1	–		5	100	2	24	S48

43	imidazole	4/4/1	DCE	reflux	40	(97)	4	6	S49
44[n]	DBU	5/5/1	water	rt	120	(93)	5	2	S50
45	DBU acetate	5/5/1	water	rt	120	(95)	5	2	S50
46	diethylamine-modified PEG-600	10/10/1	–	rt	6	(93)	9	93	S51
47	silicon oxynitride	1/1/1	toluene	323	1200	100	1	<1	S52
48[o]	FDU-ED	28/28/1	ethanol	353	60	99	28	28	S53
49	diamino-functionalized MCM-41	1/1/–	toluene	323	15	100	–	–	S54
50	$NbCl_5$	12/10/1	CH_3CN	reflux	150	(90)	9	4	S55
51	$CoFe_2O_4$	20/20/1	water/ethanol	323	20	(93)	19	56	S56
52	KF	4/4/1	ethanol	298	60	100	4	4	S57
53	reconstructed hydrotalcite	17/17/–	water	333	600	94 (90)	–	–	S58
54[p]	VAp	41667/45833/1	water	303	300	(95)	39583	7917	S59
		767/843/1					728	146	
55	aminopropyl-functionalized SBA-15	55/55/1	cyclohexane	355	60	>99	55	55	S60
		9/9/1	toluene	rt	60	(99)	9	9	S61
56	aminopropyl-functionalized MCM-41	10/10/1	toluene	rt	60	(99)	9	9	S61
57	aminopropyl-functionalized SBA-1	9/9/1	toluene	rt	360	(96)	8	1	S61
58[q]	AP-IL-SBA-15	74/74/1	water	323	60	94	70	70	S62
59[r]	NAP	10/10/1	water	rt	120	(91)	9	5	S63
60	3-hydroxyethylammonium-*n*-propanesulfonate	10/10/1	water	rt	15	(95)	10	38	S64
61	LaHAP	50/75/1	toluene	333	1440	>99	50	2	S65
62[s]	DMAN/SiO_2	10000/11400/1	ethanol	333	360	100	10000	1667 (7680)	S66
63[t]	NPm	1/1/–	methanol	rt	60	(96)	–	–	S67
64	2-hydroxyethylammonium formate	1/1/–	–	rt	180	(91)	–	–	S68

65	ammonium acetate/microwave irradiation	1/1/1	–		5	(97)	1	12	S69
66	$NaNO_3$/fluorapatite	2/2/6/1	–	rt	15	(94)	2	7	S70
67	Al_2O_3-OK	12/10/–	ethanol	reflux	30	(98)	–	–	S71
68	proline	20/10/1	DMSO	rt	960	(94)	9	<1	S72
69	NaF or LiCl/microwave irradiation	1/1/1	–		1.5	94	1	38	S73
70	K_2O-Al_2O_3	1.05/1/–	–	296	90	(94)	–	–	S74
71	*N*-methylpiperazine	5/5/1	–	rt	45	92	5	6	S75
72	MgO	0.3/0.3/1	CH_3CN	reflux	10	90	<1	2	S76
73[u]	IL-$OPPh_2$	12/10/1	–	333	23	(90)	9	23	S77
74	CoHAP	1/1/–	–	353	5	96	–	–	S78
75	morpholine	22/20/1	water	rt	120	90	18	9	S79
76[v]	EDDA	5/5/1	[bmim]BF_4	rt	10	(95)	5	29	S80
77	piperidine/microwave irradiation	50/50/1	–		3	(96)	48	960	S81
78	Mg-Al-O-*t*-Bu hydrotalcite	1/1/–	DMF	rt	20	(98)	–	–	S82
79[w]	$NaNO_3$/NP	1/1/–	methanol	rt	60	(94)	–	–	S83
80	hydrotalcite	1/1/–	[bmim]PF_6	rt	30	(94)	–	–	S84
81	ionic liquid functionalized silicagel	1/1/–	–	373	300	95	–	–	S85
82	KF-Al_2O_3/ultrasound irradiation	6/5/–	–	313	120	(99)	–	–	S86

[a] **1a**/**2a**/C = molar ratio of **1a**/**2a**/catalyst. The yield values in the parentheses were the isolated yields. TOF (h^{-1}) = TON/reaction time (h). The TOF values in the parentheses were determined by the initial rates. [b] LDH-DA = layered double hydroxides-supported diiospropylamide. [c] [bmim]Br = 1-butyl-3-methylimidazolium bromide. [d] BTEAC = benzyltriethylammonium chloride. [e] ASCPEI = silica grafted polyethylenimine. [f] TEA = triethylamine. [g] PE-MCM-41 = pore-expanded MCM-41. [h] [2-aemim]PF_6 = 1-aminoethyl-3-methylimidazolium hexafluorophosphate. [i] TBD = 1,5,7-triazabicyclo[4.4.0]dec-5-ene. [j] diamine-A = dipiperidinomethane. [k] $HDTMA^+$ = hexadecyltrimethylammonium. [l] [C_4dabco]BF_4 = 1-butyl-4-aza-1-azoniabicyclo[2.2.2]-octane tetrafluoroborate. [m] PAN_pF-3 = tertiary-amine functionalized polyacrylonitrile fiber. [n] DBU = 1,8-diazabicyclo[5.4.0]-undec-7-ene. [o] ED = ethylene diamine. [p] VAp = calcium vanadate apatite. [q] AP-IL-SBA-15 = ionic liquid immobilized on SBA-15. [r] NAP = 3-aminopropylated silicagel. [s] DMAN/SiO_2 = 1,8-bis(dimethylamino)naphthalene functionalized SiO_2. [t] NPm = natural microphosphate. [u] IL-$OPPh_2$ = imidazolium-based phosphinite ionic liquid. [v] EDDA = ethylenediammonium diacetate. [w] NP = natural phosphate.

Table S4. Various Catalytic Systems for Knoevenagel Condensation of **1c** with **2a**[a]



1c **2a** **3c**

Entry	Catalyst	**1c**/**2a**/C	Solvent	Temp. (K)	Time (min)	Yield (%)	TON	TOF (h^{-1})	Ref.
1	***TBA_6·I***	***20/30/1***	***CH_3CN***	***353***	***120***	***96***	***18***	***9***	***This work***
2	$NaOCH_3$	10/10/1	ethanol	rt	60	95	10	10	S87
3	NaOH/TBABr	10/10/1/1	toluene	303	20	97	10	29	S88
4	K_2CO_3/18-crown-6	10/10/1/1	toluene	303	90	80	8	5	S88
5	hydrotalcite	1/1.5/–	toluene	453	420	98	–	–	S28
6	poly-*N*-isopropyl acrylamide	20/20/1	10% NaOHaq	rt	120	86	15	8	S89
7	reconstructed hydrotalcite	3/6/–	water/DMF	353	60	98	–	–	S58
8[b]	VAp	1.5/1/0.05 g	water	383	720	89	20	2	S59
9	KF/Al_2O_3/microwave irradiation	2/2/–	neat	–	4	90	–	–	S90
10	*p*-(trimethylammoniomethyl)calyx[*n*]arene methyl ether/NaOH	100/200/1/375	5N NaOHaq	rt	120	91	<0.1	<0.1	S91
11	$P(MeNCH_2CH_2)_3N$	33/33/1	neat	323	360	98	33	5	S92
12	cetyltrimethylammonium chloride/NaOH	10/10/1/1.25	0.025 M NaOHaq	rt	60	86	0.7	0.7	S93
13	$RuH_2(PPh_3)_4$/dppe	33/37/1/2	THF	333	overnight	87	29	<5	S94
14	K_2CO_3	–/–/1	–			95	1	–	S95
15	NaOH/PEG	20/20/20/1	toluene	293	60	71	0.7	0.7	S96

[a] **1c**/**2a**/C = molar ratio of **1c**/**2a**/catalyst. The yield values in parentheses were isolated yields. TOF (h^{-1}) = TON/reaction time (h). [b] VAp = calcium vanadate apatite.

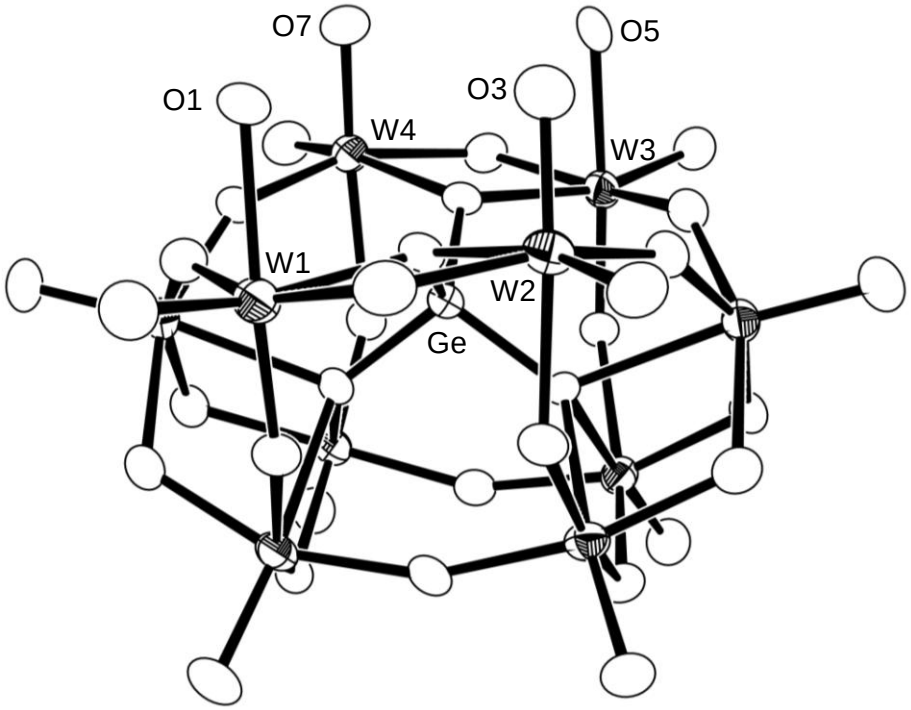


Fig. S1 Molecular structure of the anion part of $[(CH_3)_4N]_4[\gamma\text{-}GeW_{10}O_{34}(H_2O)_2]$. Thermal ellipsoids set at 50% probability.

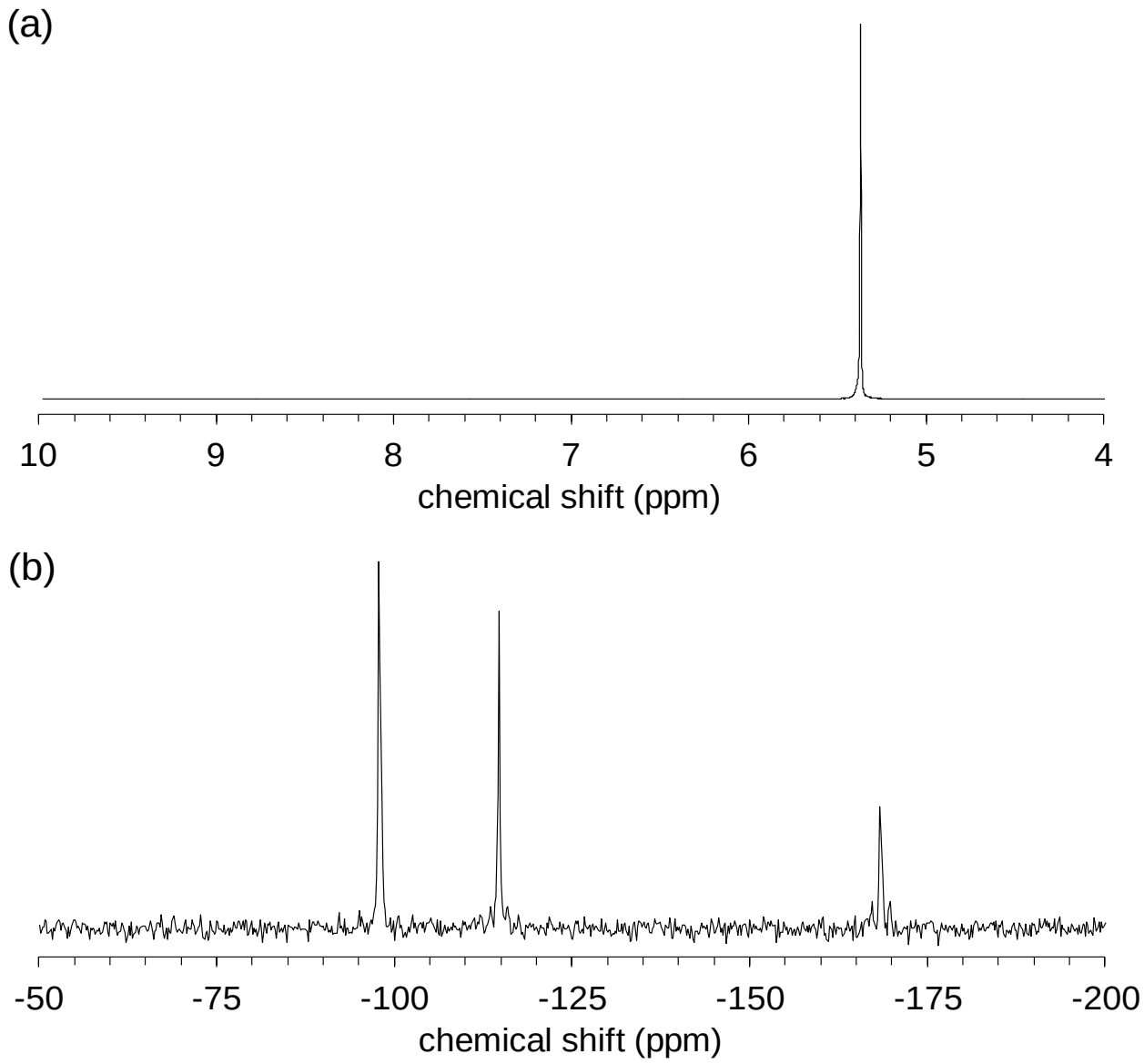


Fig. S2. (a) ^{1}H and (b) ^{183}W NMR spectra of $TBA_6 \cdot$**I** (Solvent: DMSO-d_6, 298 K).

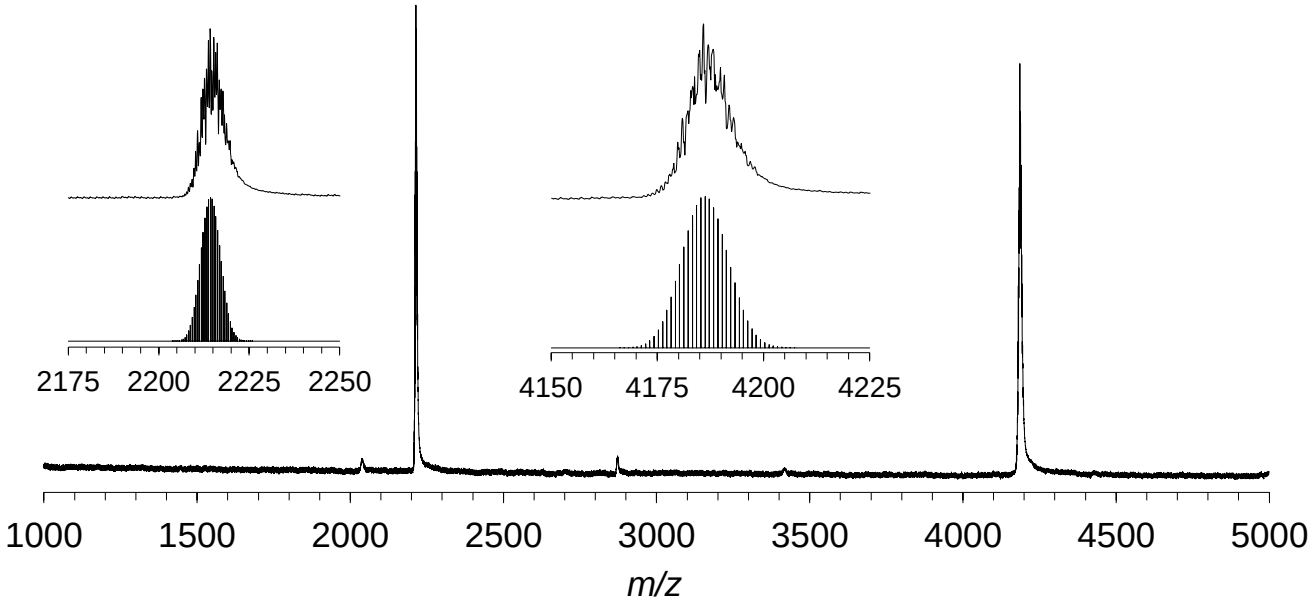


Fig. S3. CSI-MS spectrum (*m/z* = 1000–5000) of TBA_6·**I** (Solvent: acetone). Inset: CSI-MS spectra (*m/z* = 2175–2250 and 4150–4225) of TBA_6·**I** and calculated patterns of $TBA_8H_2GeW_{10}O_{36}^{2+}$ (*m/z* = 2214) and $TBA_7H_2GeW_{10}O_{36}^{+}$ (*m/z* = 4186).

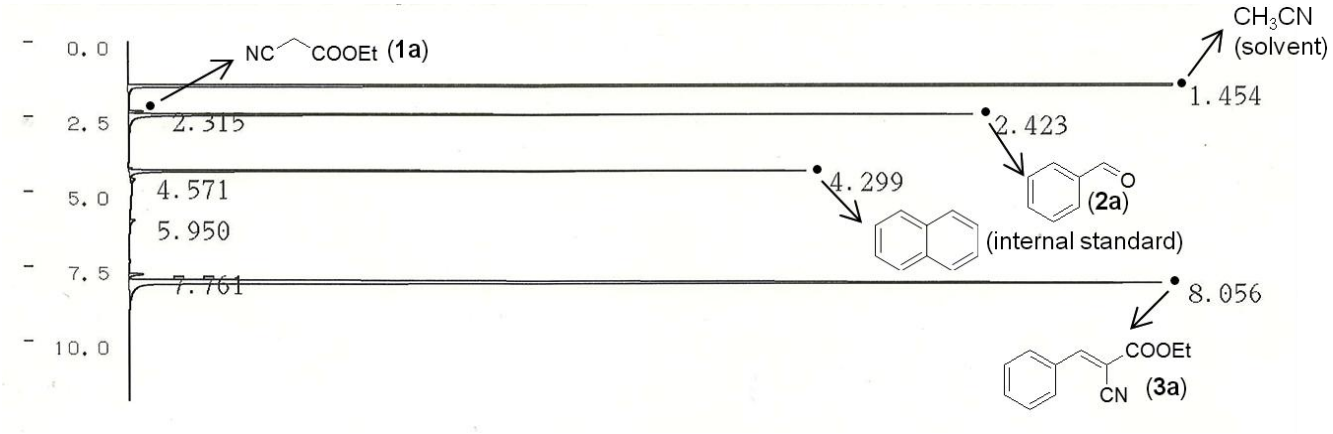


Fig. S4. GC chart of the reaction of **1a** with **2a**. The reaction was carried out under the same conditions as those of entry 1 in Table 1.

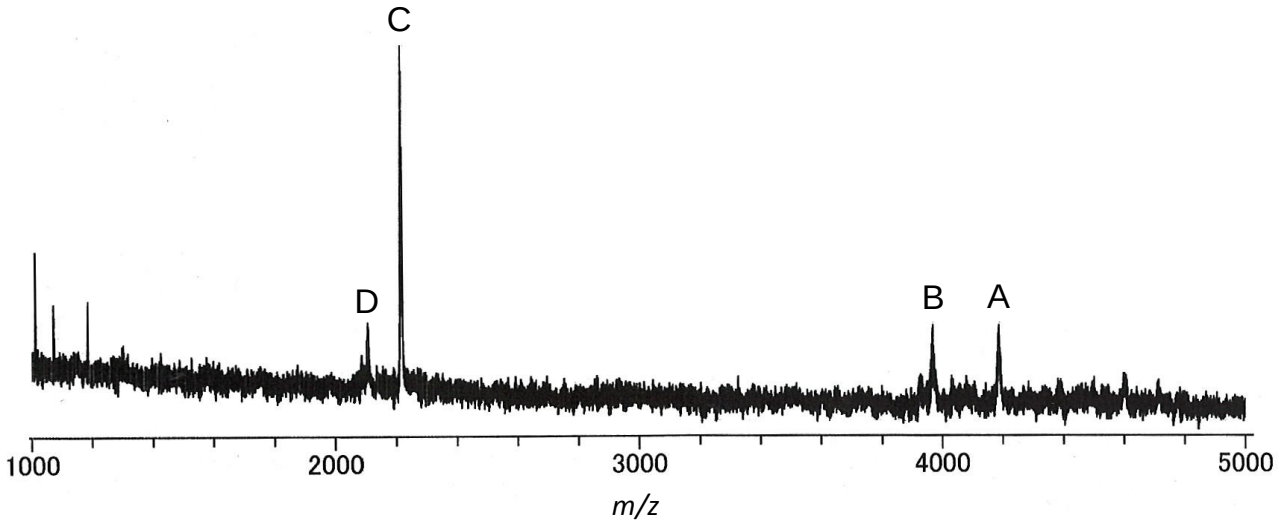


Fig. S5. CSI-MS spectrum (*m/z* = 1000–5000) of **I** after the reaction of **1a** with **2a** (Solvent: CH_3CN). The reaction was carried out under the same conditions as those of entry 1 in Table 1. The peaks A, B, C, and D are assignable to $[TBA_7H_2GeW_{10}O_{36}]^+$, $[TBA_6HGeW_{10}O_{35}(CH_3CN)]^+$, $[TBA_8H_2GeW_{10}O_{36}]^{2+}$, and $[TBA_7HGeW_{10}O_{35}(CH_3CN)]^{2+}$, respectively.

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