Supporting Materials

Novel hexagonal $\{V{=}O\}_6$-containing sandwich-type cluster accompanied by *In Situ* carbon-carbon bond formation of organic cation

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List of Figures and Table:

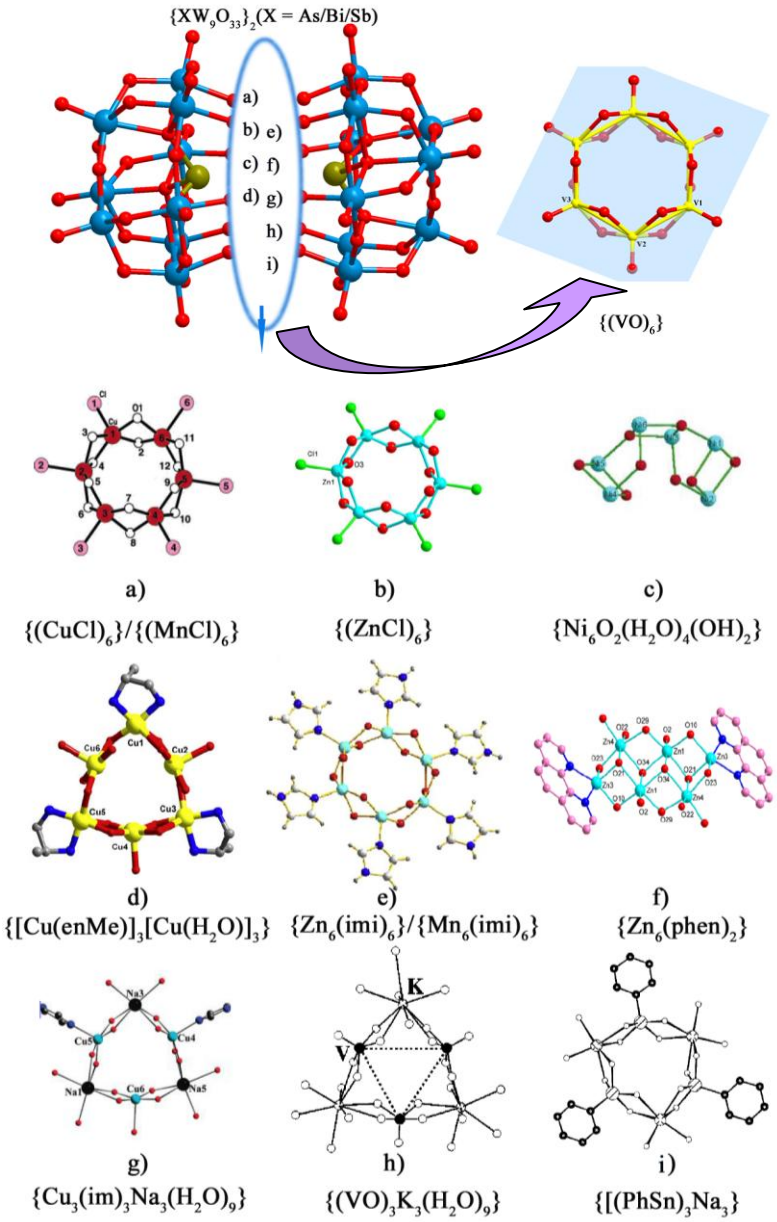


Fig. s1. Structures of six transition-metal cations in sandwich-type POMs.

Reference:

a) T. Yamase, K. Fukay, H. Nojiri, Y. Ohshima, *Inorg. Chem.* **2006**, 45(19), 7698-7704.

b) S. Chang, Y.F. Qi, E.B. Wang, Z.M. Zhang, *Inorg. Chim. Acta*, **2009**, 362, 453-457.

c) Z.M. Zhang, Y.G. Li, E.B. Wang, X.L. Wang, C. Qin, H.Y. An, *Inorg. Chem.* **2006**, 45, 4313.

d) S. Yao, Z.M. Zhang, Y.G. Li, E.B. Wang, *Inorg. Chem. Commun.* **2009**, 12, 937-940

e) Z. Zhao, B. Zhou, S. Zheng, Z. Su, C. Wang, *Inorg. Chim. Acta*, **2009**, 362, 5038-5042.

f) See reference b).

g) H. Liu, C. Qin, Y.G. Wei, L. Xu, G.G. Gao, F.Y. Li, X.S. Qu, *Inorg. Chem.* **2008**, *47*, 4166–4172; Robert, F.; Leyrie, M.; Hervé, G. *Acta Crystallogr.* **1982**, *B38*, 358; Kortz, U.; Nellutla, S.; Stowe, A. C.; Dalal, N. S.; Tol, J. V.; Bassil, B. S. *Inorg. Chem.* **2004**, *43*, 144–154.

h) T. Yamse, E. Ishikawa, K. Fukaya, H. Nojiri, T. Taniguchi, T. Atake, *Inorg. Chem.* **2004**, 43(25), 43, 8150-8157

i) Michael, G. S.; Dickman, H.; Pope, M. T. *Inorg. Chem.* **2000**, *39*, 939–943.

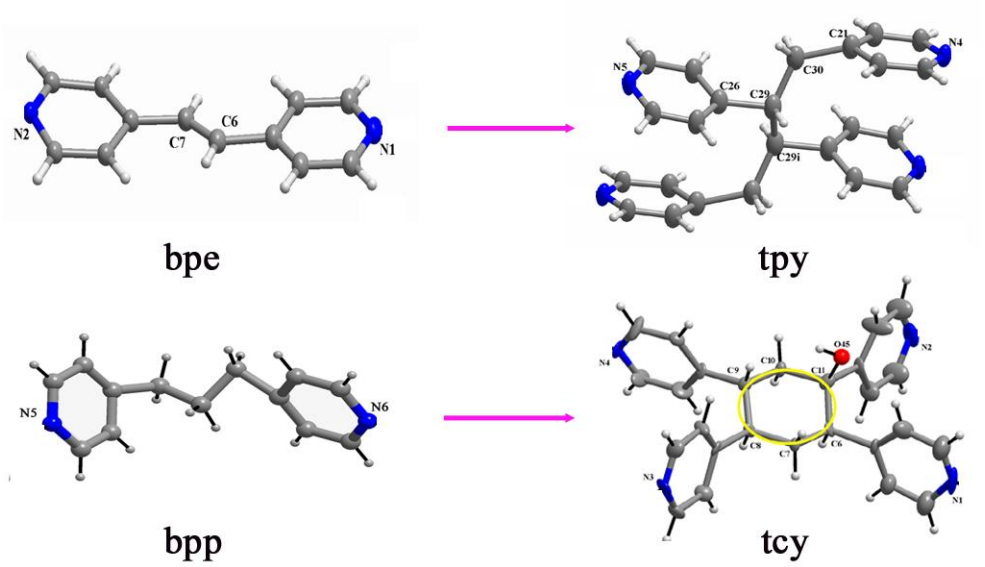


Fig. s2 In situ C-C bond formation in compounds **1** and **2**.

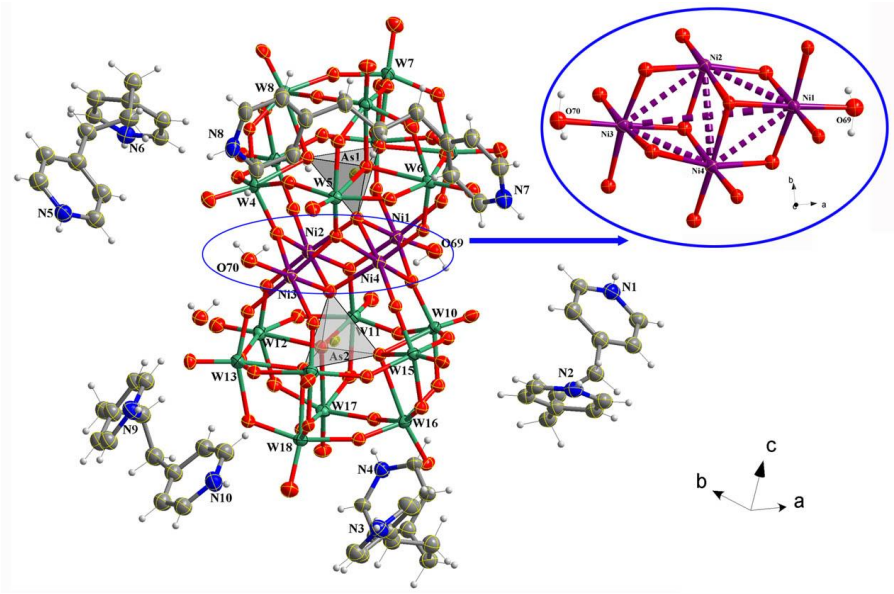


Fig. s3 ORTEP view of the asymmetric unit in compound **3**, showing the atom labeling scheme; the inset figure showing the sandwich tetra-metal cluster of $\{Ni_4O_{14}(H_2O)_2\}$.

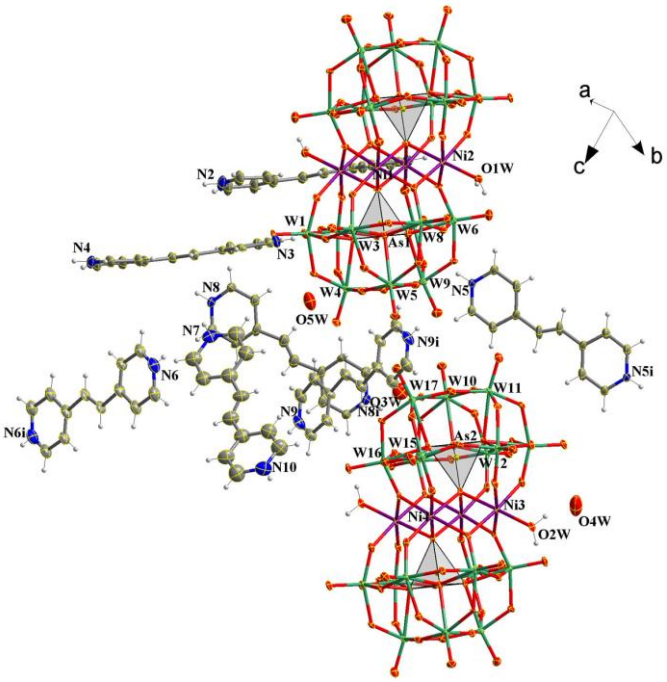


Fig. s4 ORTEP view with atom-label of compound **4**. The thermal ellipsoids are drawn at the 30% probability level. Tetrahedra represented {AsO_4}.

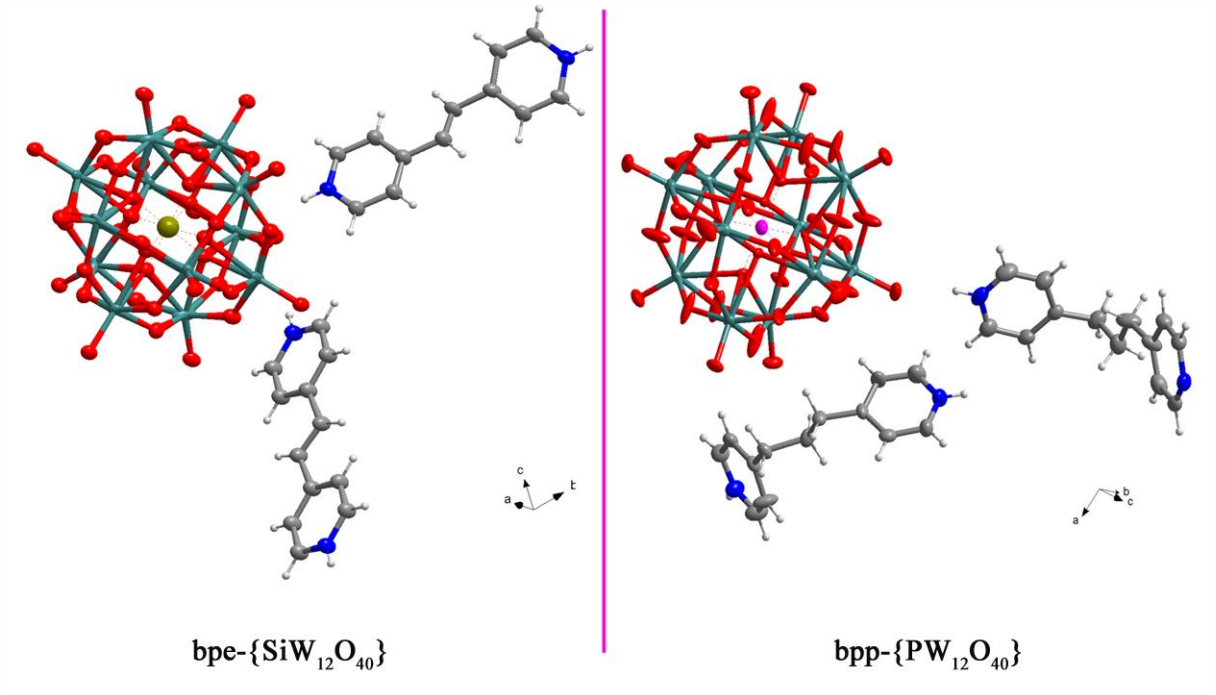
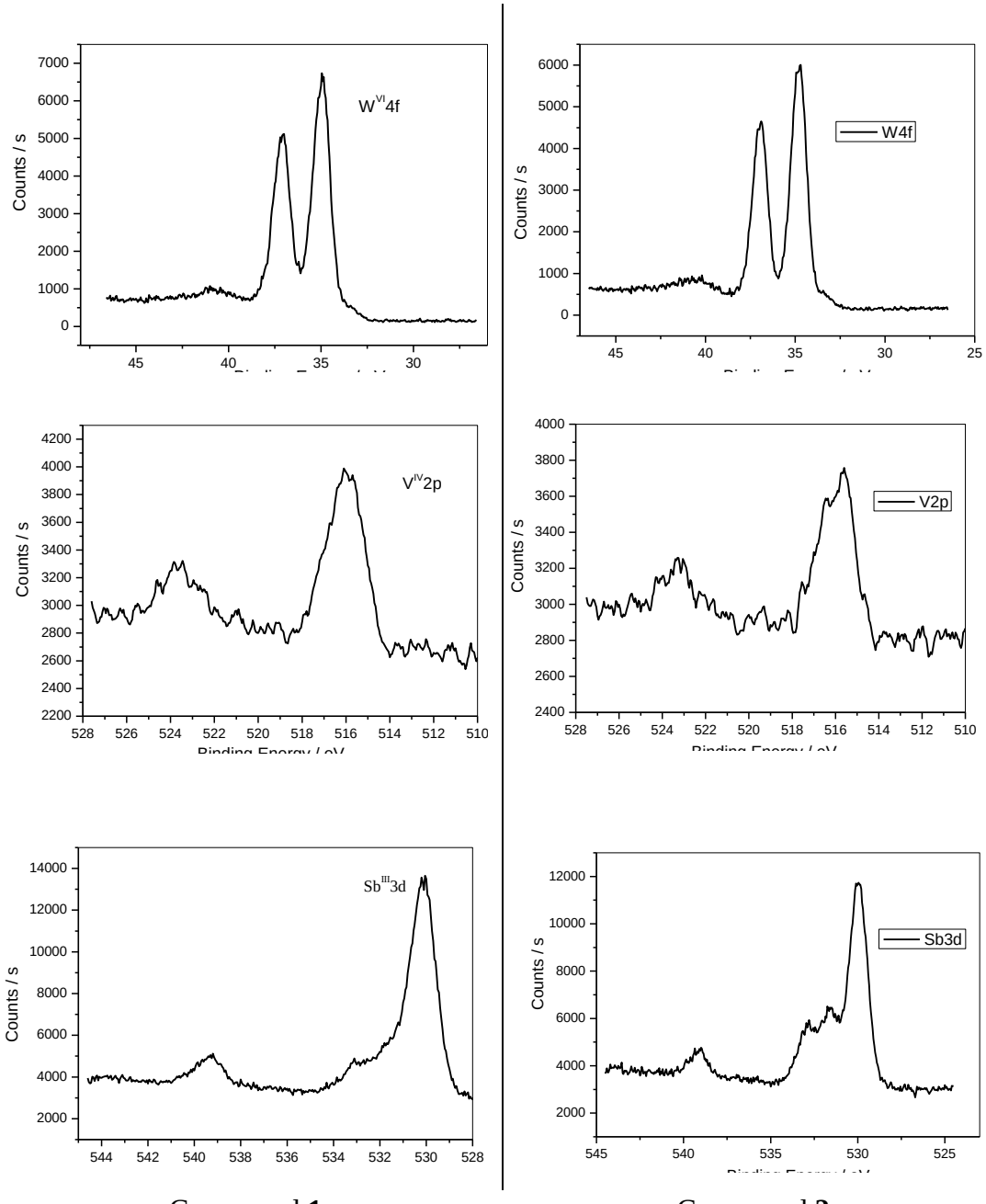


Fig. s5 The supramolecular assemblies **5** and **6** based protonated bpe or bpp cations and the closed α-Keggin $[XW_{12}O_{40}]^{n-}$ (X= P/Si, n= 3 or 4) anions.



Compound **1** Compound **2**

Fig. s6 XPS of compounds **1** and **2**.

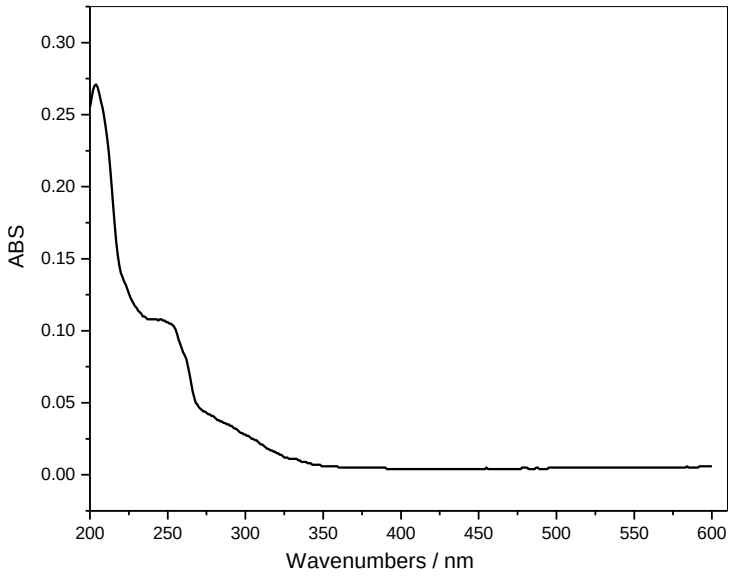


Fig. s7 UV-vis spectrum of **2** in menthol.

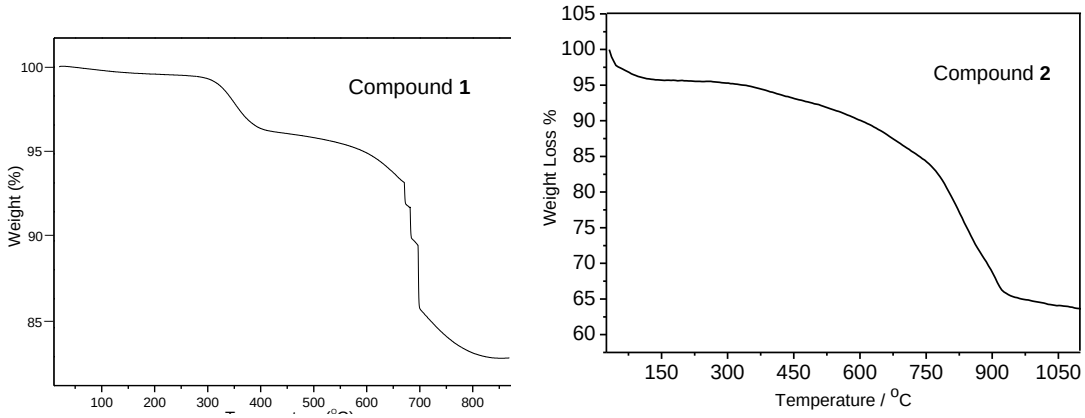


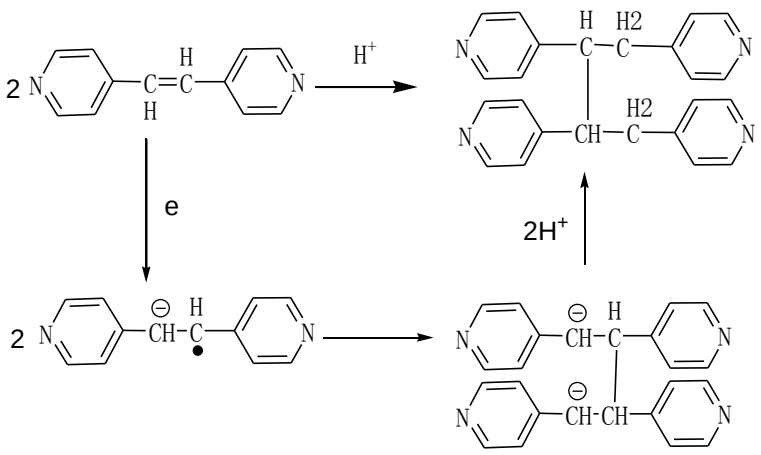
Fig. s8 TG curves of **1**-**2**.

Table s1 Representive hydrogen bonding distances in **1-2**.

D -H...A(Å)	**D-H(Å)**	**H...A(Å)**	**D...A(Å)**	**∠D– H...A (°)**
Compound **1**				
N(1)-H(1B)...O(13^{i})	0.86	1.91	2.72(3)	156
N(2)-H(2)...O(14^{ii})	0.86	2.01	2.848(19)	163
N(3)-H(3A)...O(30)	0.86	1.95	2.80(2)	168
N(4)-H(4B)...O(33)	0.86	1.96	2.80(2)	165
N(5)-H(5B)...O(22^{iii})	0.86	2.09	2.88(2)	152
O(37)-H(37A)...O(9^{iv})	0.85	2.05	2.79(3)	145
O(37)-H(37B)...N(5^{iii})	0.90	2.43	3.25(3)	151
C(5)-H(5A)...O(4^{v})	0.93	2.58	3.51(3)	172
C(7)-H(7A)...O(25)	0.93	2.39	3.25(3)	153
C(11)-H(11A)...O(7^{vi})	0.93	2.27	3.11(3)	149
C(13)-H(13A)...O(22)	0.93	2.48	3.27(3)	143
C(14)-H(14A)...O(34^{iv})	0.93	2.54	3.35(3)	147
C(20)-H(20A)...O(3^{vii})	0.93	2.34	3.24(4)	163
C(24)-H(24A)...O(20^{iii})	0.93	2.33	3.25(3)	169
C(28)-H(28A)...O(5^{vii})	0.93	2.23	3.05(3)	145
Symmetry codes: i = x,1+y,z; ii = 2-x,1-y,2-z; iii = 1-x,1-y,2-z; iv = 1-x,1-y,1-z; v = 2-x,2-y,1-z; vi = 2-x,2-y,2-z; vii = x,y,1+z				
Compound **2**				
N1-H1B...O5^{i}	0.86	1.89	2.71(3)	159
O1W-H1WA...O4^{ii}	0.85	2.11	2.96(3)	171
N2-H2B ...O27^{iii}	0.86	1.87	2.66(3)	152
O2W-H2WB...N1^{iv}	0.85	2.05	2.84(3)	152
N3-H3A...O39^{v}	0.86	1.97	2.82(3)	169
O2W-H2WA...O2W^{iv}]	0.85	2.17	3.02(2)	172
N4-H4B...O23^{vi}	0.86	1.86	2.69(2)	160
O3W-H3WA...O22^{vii}	0.85	1.96	2.81(3)	178
N6-H6B...O14^{viii}	0.86	2.13	2.98(2)	166
O5W-H5WA...O5W^{ix}	0.85	1.92	2.76(3)	168
O45-H45A...O21^{x}	0.82	1.98	2.78(3)	165
C2-H2A...O6^{vii}	0.93	2.50	3.29(3)	142
C5-H5A...O26^{i}	0.93	2.37	3.29(3)	172
C6-H6A...O34^{xi}	0.98	2.34	3.28(2)	162
C7-H7B...O21^{x}	0.97	2.39	3.27(3)	150
C19-H19A...O8^{xi}	0.93	2.37	3.25(3)	159
C24-H24A...O22^{vi}	0.93	2.43	3.30(2)	155
C26-H26A...O36^{x}	0.93	2.47	3.36(2)	161
C28--H28A...O14^{xii}	0.93	2.54	3.44(2)	164
Symmetry codes: i = 1/3-y,2/3+x-y,2/3+z ; ii = 2/3-x,1/3-y,1/3-z; iii = x,1+y,z; iv = 1/3-x,5/3-y,2/3-z; v = 1/3+y,5/3-x+y,2/3-z; vi = 1/3+x-y,2/3+x,-1/3-z; vii = y,1-x+y,-z; viii = -x+y,1-x,z; ix = y,-x+y,2-z; x = 1/3+x-y,2/3+x,2/3-z; xi = 1/3-y,2/3+x-y,-1/3+z				

Scheme 1 The proposed formation mechanism of organic reaction: a) **1** and b) **2**.

a)



b)