Electronic Supplementary Information (ESI)

H-bonded and metal(II)-organic architectures assembled from an unexplored aromatic tricarboxylic acid: Structural variety and functional properties

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*†Electronic Supplementary Information (ESI) available: synthesis and analytical data for **1**−**9**, additional structural representations (Figs. S1−S3), PXRD patterns (Fig. S4), catalysis data (Fig. S5−S8), and bonding parameters (Tables S1 and S2). CCDC-1984462–1984470.*

Synthesis and analytical data for 1–9

[Co(Hdcna)(phen)$_2$(H$_2$O)]·H$_2$O (1). A mixture of $CoCl_2·6H_2O$ (0.2 mmol, 47.6 mg), H_3dcna (0.2 mmol, 72.6 mg), phen (0.2 mmol, 40.0 mg), and NaOH (0.4 mmol, 16.0 mg) in H_2O (10 mL) was stirred for 15 min at ambienttemperature. It was then sealed in a Teflon-lined stainless steel reactor (25 mL) and heated at 160 °C for 3 days, followed by a slow cooling to ambienttemperature (10 °C/h). Pink block-shaped crystals were isolated manually, washed with distilled water, and dried in air to give product **1**. Yield: 27% (based on H_3dcna). Calcd for $C_{44}H_{31}CoN_5O_8$: C 64.71, H 3.83, N 8.58%. Found: C 64.49, H 3.81, N 8.62%. IR (KBr, cm^{-1}): 3395w, 3054 w, 1694 s, 1593 s, 1565 s, 1521 m, 1427 s, 1375 s, 1276 w, 1181 w, 1147 w, 1108 w, 1013 w, 918 w, 851 m, 778 m, 728 m, 644 w, 566 w.

[Ni(Hdcna)(phen)$_2$(H$_2$O)]·H$_2$O (2). A mixture of $NiCl_2·6H_2O$ (47.4 mg, 0.2 mmol), H_3dcna (72.6 mg, 0.2 mmol), phen (40.0 mg, 0.2 mmol), NaOH (16.0 mg, 0.4 mmol), and H_2O (10 mL) was stirred at room temperature for 15 min, then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 °C·h^{-1}. Purple crystals of **2** isolated manually, and washed with distilled water. Yield: 25% (based on H_3dcna). Anal. Calcd for $C_{44}H_{31}NiN_5O_8$: C 64.73, H 3.83, N 8.58%. Found: C 64.87, H 3.81, N 8.53%. IR (KBr, cm^{-1}): 3456 w, 3038 w, 1694 m, 1627 w, 1599 w, 1575 s, 1548 s, 1515 s, 1427 s, 1398 w, 1360 m, 1298 w, 1224 w, 1153 w, 1103 w, 1008 w, 946 w, 847 m, 784 m, 724 m, 640 w.

[Zn(μ-Hdcna)(phen)]$_n$ (3). A mixture of $ZnCl_2$ (27.3 mg, 0.20 mmol), H_3dcna (72.6 mg, 0.20 mmol), phen (40.0 mg, 0.2 mmol), NaOH (16.0 mg, 0.4 mmol), and H_2O (10 mL) was stirred at room temperature for 15 min, then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 °C·h^{-1}. Colourless block-shaped crystals of **3** were isolated manually, washed with distilled water and dried (yield 48% based on H_3dcna). Anal. Calcd for $C_{32}H_{19}ZnN_3O_6$: C, 63.33; H, 3.16; N, 6.92. Found: C, 53.17; H, 3.15; N, 6.94%. IR (KBr, cm^{-1}): 1694 w, 1588 s, 1515 m, 1420 m, 1381 s, 1298 w, 1213 w, 1175 w, 1142 w, 1097 w, 1008 w, 918 w, 847 m, 773 m, 724 m, 640 w.

[Co(μ-Hdcna)(bipy)(H_2O)$_2$]$_n$·$n$$H_2O$ (4). A mixture of $CoCl_2·6H_2O$ (47.6 mg, 0.20 mmol), H_3dcna (72.6 mg, 0.20 mmol), bipy (31.2 mg, 0.2 mmol), NaOH (16.0 mg, 0.4 mmol), and H_2O (10 mL) was stirred at room temperature for 15 min, then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 °C·h^{-1}. Pink block-shaped crystals of **4** were isolated manually, washed with distilled water and dried (yield 46% based on H_3dcna). Anal. Calcd for $C_{30}H_{25}CoN_3O_9$: C, 57.15; H, 4.00; N, 6.66. Found: C, 56.89; H, 3.98; N, 6.67%. IR (KBr, cm^{-1}): 3328 w, 3061 w, 1670 m, 1604 s, 1565 m, 1521 w, 1470 w, 1427 w, 1386 s, 1287 m, 1186 w, 1153 w, 1125 w, 1097 w, 1052 w, 1013 w, 914 w, 857 w, 802 w, 767 m, 7707 w, 645 w.

[Zn$_2$(μ-Hdcna)$_2$(bipy)$_2$(H_2O)$_4$]·6H_2O (5). Synthesis of **5** was similar to **3** except using bipy (31.2 mg, 0.20 mmol) instead of phen. Colorless block-shaped crystals of **5** were isolated manually, washed with distilled water and dried (yield 41% based on H_3dcna). Anal. Calcd for $C_{60}H_{58}Zn_2N_6O_{22}$: C, 53.54; H, 4.34; N, 6.24. Found: C, 53.72; H, 4.36; N, 6.28%. IR (KBr, cm^{-1}): 3412 w, 3071 w, 1705 m, 1599 s, 1560 m, 1442 m,1386 s, 1308 w, 1248 w, 1181 w, 1153 w, 1114 w, 1058 w, 1019 w, 896 w, 862 w, 773 m, 735 w, 717 w, 650 w.

[Zn(μ$_3$-Hdcna)(H_2biim)]$_n$ (6). Synthesis of **6** was similar to **3** except using H_2biim (26.8 mg, 0.20 mmol) instead of phen. Colorless block-shaped crystals of **6** were isolated manually, washed with distilled water and dried (yield 43% based on H_3dcna). Anal. Calcd for $C_{26}H_{17}ZnN_5O_6$: C, 55.68; H, 3.06; N, 12.49. Found: C, 55.43; H, 3.05; N, 12.60%. IR (KBr, cm^{-1}): 1693 m, 1605 s, 1579 s, 1428 m,1376 s, 1324 w, 1273 w, 1180 w, 1122 w, 1114 w, 1055 w, 988 w, 920 w, 874 w, 847 w, 770 m, 713 w, 687 w, 521 w.

[Ni$_2$(Hdcna)$_2$(μ-bpb)(bpb)$_2$(H_2O)$_4$] (7). A mixture of $NiCl_2·6H_2O$ (47.4 mg, 0.20 mmol), H_3dcna (72.6 mg, 0.20 mmol), bpb (46.5 mg, 0.20 mmol), NaOH (16.0 mg, 0.40 mmol), and H_2O (10 mL) was stirred at room temperature for 15 min, then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 °C·h^{-1}. Green block-shaped crystals of **7** were isolated manually, washed with distilled water and dried (yield 31%

based on H_3dcna). Anal. Calcd for $C_{88}H_{66}Ni_2N_8O_{16}$: C, 65.69; H, 4.13; N, 6.96. Found: C, 65.43; H, 4.15; N, 6.93%. IR (KBr, cm^{-1}): 3322 w, 3066 w, 1694 w, 1604 s, 1543 s, 1481 s, 1442 w, 1392 s, 1319 w, 1280 w, 1224 w, 1181 w, 1103 w, 1063 w, 996 w, 968 w, 901 w, 868 w, 80m w, 756 w, 711 w, 616 w.

[Fe(μ$_4$-Hdcna)(μ-H_2O)]$_n$·$n$$H_2O$ (8). A mixture of $FeSO_4·7H_2O$ (55.6 mg, 0.2 mmol), H_3dcna (72.6 mg, 0.20 mmol), NaOH (16.0 mg, 0.40 mmol), and H_2O (10 mL) was stirred at room temperature for 15 min, then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 °C·h^{-1}. Yellow block-shaped crystals of **8** were isolated manually, washed with distilled water and dried (yield 45% based on H_3dcna). Anal. Calcd for $C_{20}H_{15}FeNO_8$: C, 53.01; H, 3.34; N, 3.09. Found: C, 53.26; H, 3.37; N, 3.07%. IR (KBr, cm^{-1}): 3500 w, 2977 w, 1677 m, 1610 w, 1543 s, 1504 w, 1403 s, 1360 w, 1270 w, 1198 w, 1164 w, 1103 w, 1008 w, 914 w, 858 w, 767 m, 707 w, 662 w.

[Mn$_3$(μ$_5$-dcna)$_2$(bipy)$_2$(H_2O)$_2$]$_n$·2$n$$H_2O$ (9). A mixture of $MnCl_2·4H_2O$ (59.4 mg, 0.3 mmol), H_3dcna (72.6 mg, 0.20 mmol), 2,2′-bipy (46.8 mg, 0.30 mmol), NaOH (24.0 mg, 0.60 mmol), and H_2O (10 mL) was stirred at room temperature for 15 min, then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 °C·h^{-1}. Yellow block-shaped crystals of **9** were isolated manually, washed with distilled water and dried (yield 40% based on H_3dcna). Anal. Calcd for $C_{60}H_{44}Mn_3N_6O_{16}$: C, 56.75; H, 3.49; N, 6.62. Found: C, 56.95; H, 3.47; N, 6.65%. IR (KBr, cm^{-1}): 3250 w, 3055 w, 1599 m, 1582 s, 1521 m, 1465 w, 1438 w, 1386 s, 1315 w, 1241 w, 1164 w, 1114 w, 1052 w, 924 w, 858 w, 784 w, 763 m, 711 w, 645 w.

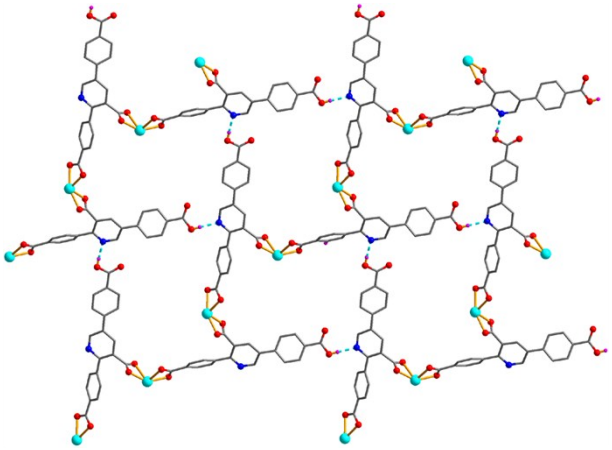


Fig. S1. 2D H-bonded network in **3** viewed along the *bc* plane (blue dashed lines represent the H-bonds).

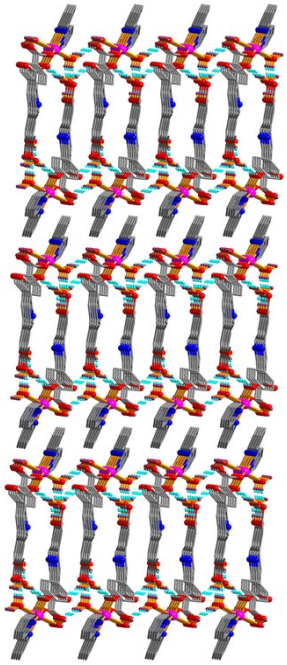


Fig. S2. 2D H-bonded layers in **4** viewed along the *ac* plane (blue dashed lines represent the H-bonds).

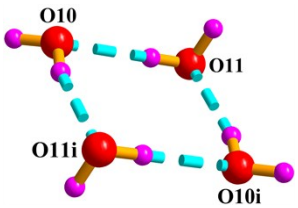
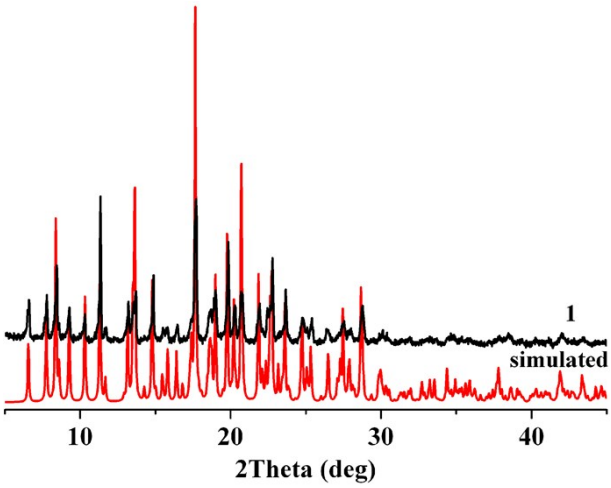
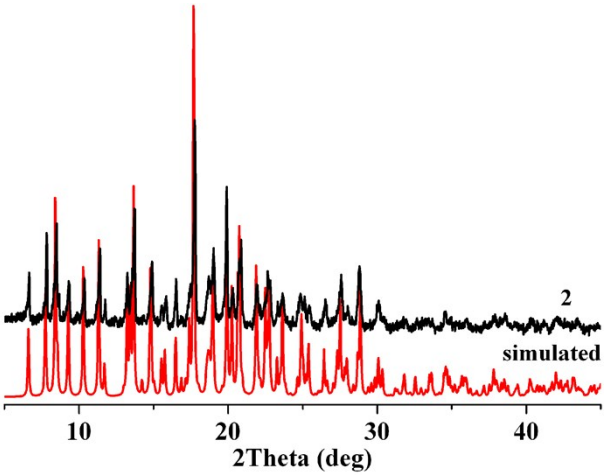


Fig. S3. Cyclic $(H_2O)_4$ cluster in **5**. Symmetry code: i = $–x + 1, –y + 1, –z + 1$ (blue dashed lines represent the H-bonds).


1
simulated
10
20
30
40
2Theta (deg)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simulated
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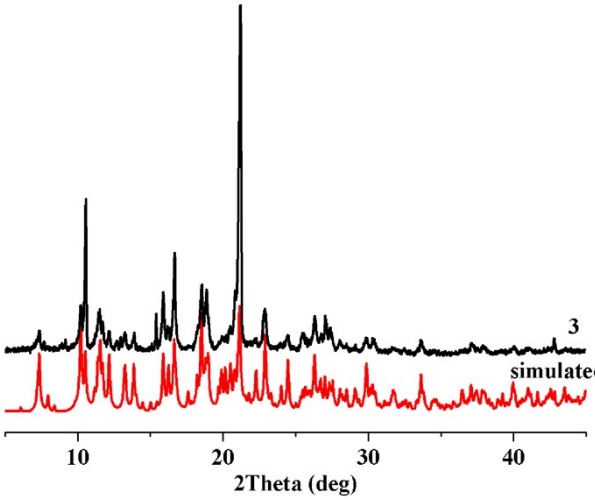
30
40
2Theta (deg)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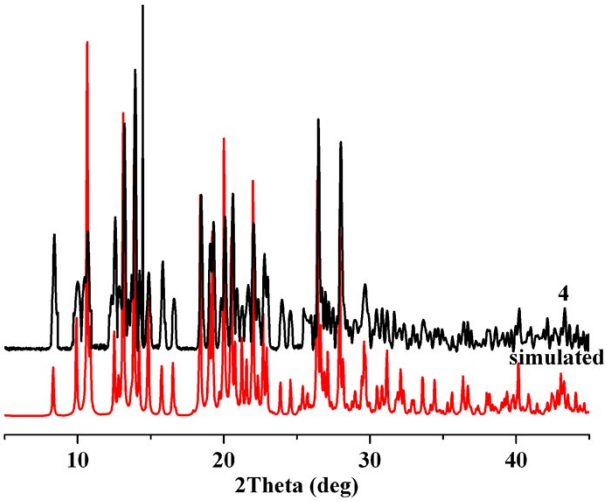
30
40
2Theta (deg)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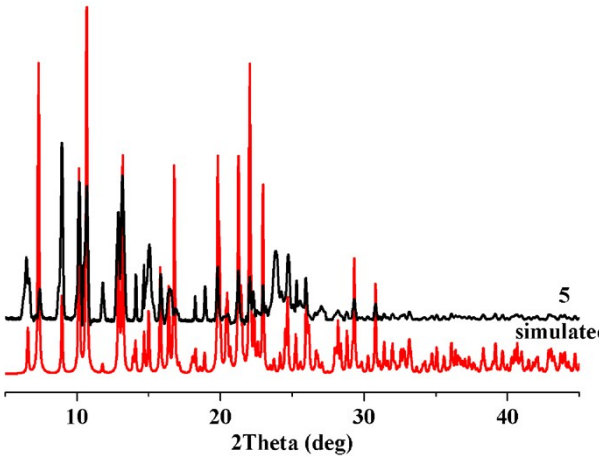
simulated
10
20
30
40
2Theta (deg)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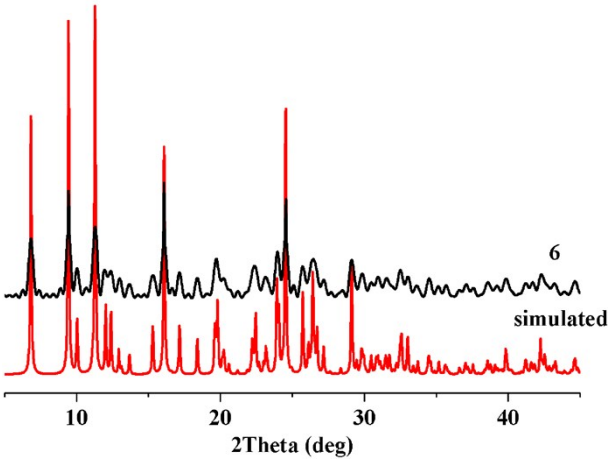
2Theta (deg)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simulated
10
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30
40
2Theta (deg)

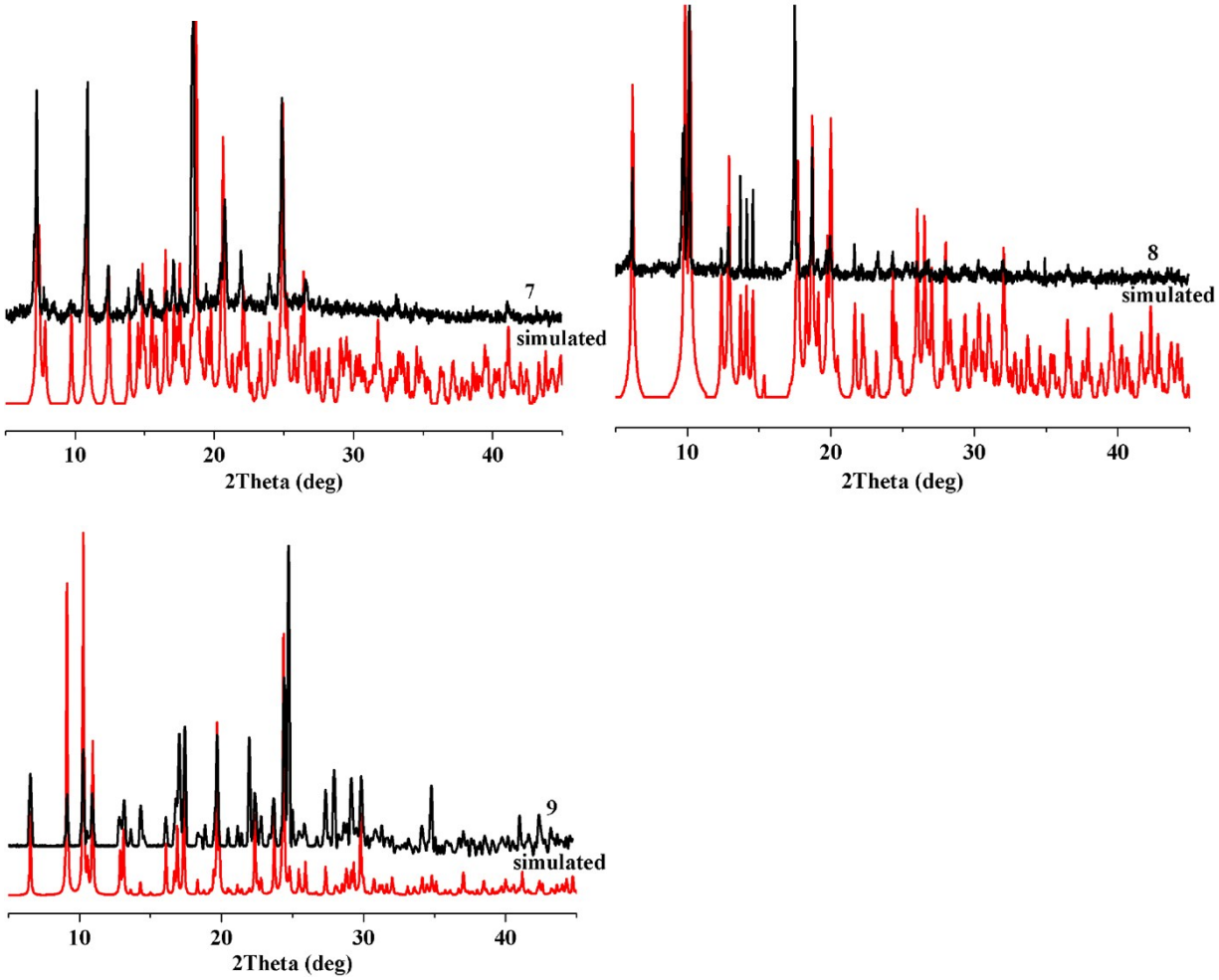

Fig. S4. PXRD patterns of compounds **1**–**9** at room temperature. Black paterns correspnond to the experimental data obtained using the as-synthesized bulk samples. Red patterns were simulated from the single crystal X-ray data.

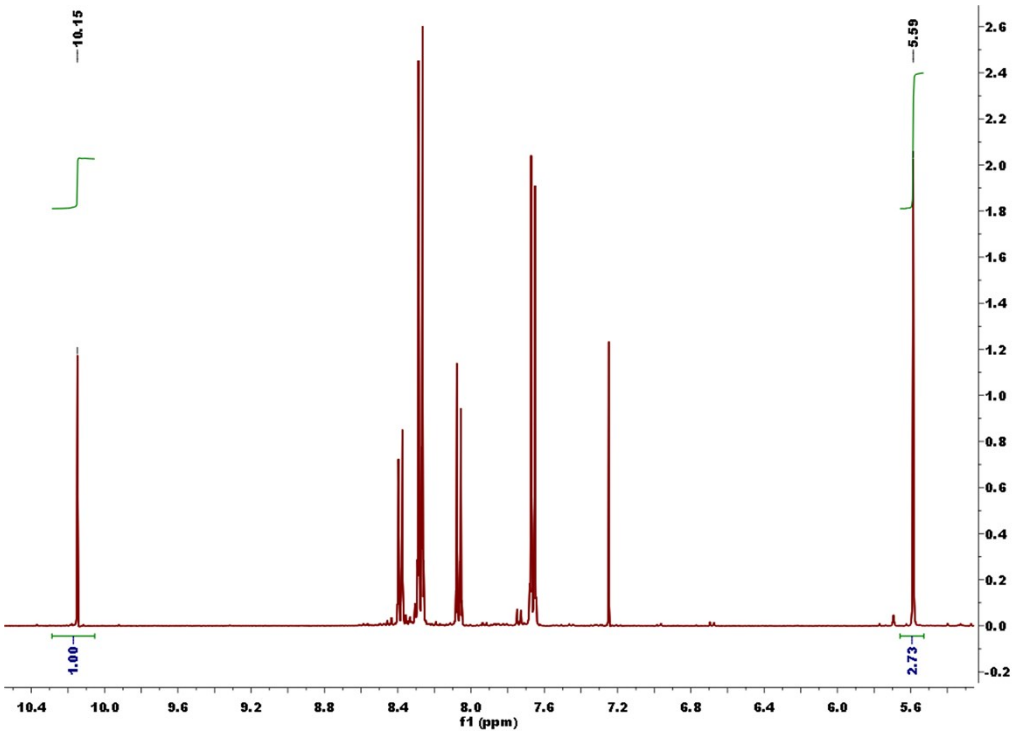

Fig. S5. Example of the ^{1}H NMR spectrum of the reaction mixture with integration of signals for determination of cyanosilylation reaction product (Table 3, entry 7, 4-nitrobenzaldehyde substrate).

Example of the product yield calculation in the cyanosilylation reaction

The –CH peak of 4-nitrobenzaldehyde (substrate) appears at 10.15 ppm while that of 2-(4-nitrophenyl)-2-((trimethylsilyl)oxy)acetonitrile (product) can be seen at 5.59 ppm.

Total amount: unreacted substrate (4-nitrobenzaldehyde) + formed product (2-(4-nitrophenyl)-2-((trimethylsilyl)oxy)acetonitrile) = 1+2.73 = 3.73

Percentage of the unreacted substrate: 100%/3.73 = 26.8%

Conversion of 4-nitrobenzaldehyde = yield of 2-(4-nitrophenyl)-2-((trimethylsilyl)oxy)acetonitrile = 100%−26.8% = 73.2%.

The accurateness of this procedure was confirmed by repeating a number of the ^{1}H NMR analyses in the presence of an internal standard (1,2-dimethoxyethane, 1.5% v/v), which was added to the $CDCl_3$ solution. These experiments gave product yields similar to those obtained by using the above-described method.

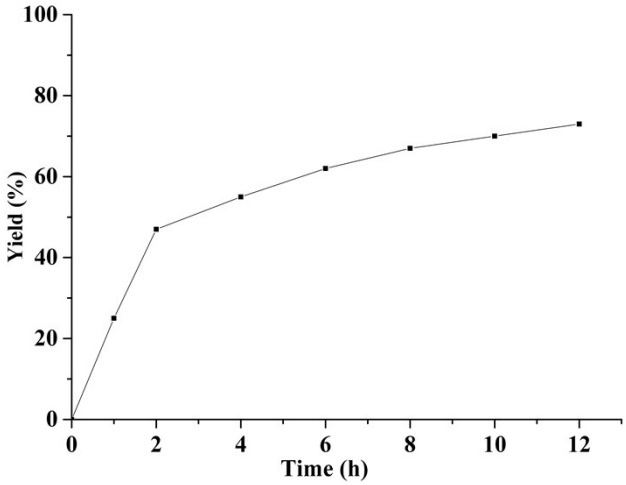

Fig. S6. Accumulation of 2-(4-nitrophenyl)-2-[(trimethylsilyl)oxy]acetonitrile vs. time in the cyanosilylation of 4-nitrobenzaldehyde with TMSCN catalysed by **5**. Reaction conditions are those of Table 3, entries 1−7.

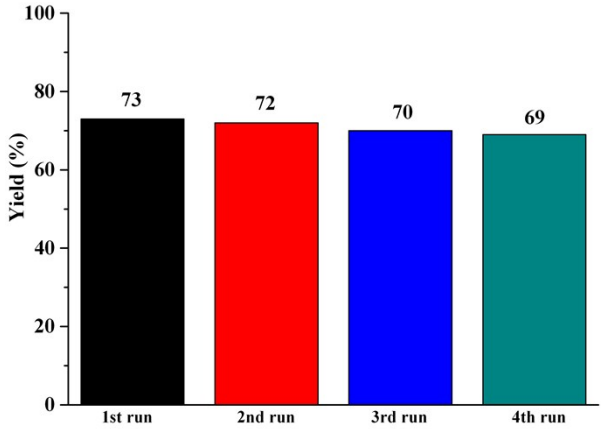

Fig. S7. Catalyst recycling experiments (four reaction runs) in the cyanosilylation of 4-nitrobenzaldehyde with TMSCN and catalyst **5**. Reaction conditions are those of Table 2 (entry 7). Figures above the bars correspond to product yields in %.

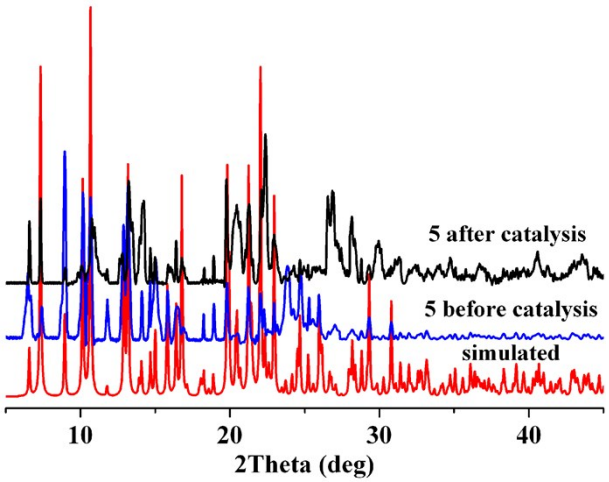

Fig. S8. PXRD patterns for **5**: simulated (red), before (blue) and after (black) catalysis.

Table S1. Selected bond lengths [Å] and angles [°] for the compounds **1**–**9**[a].

1					
Co(1)-O(1)	2.054(3)	Co(1)-O(7)	2.135(2)	Co(1)-N(2)	2.117(3)
Co(1)-N(3)	2.132(3)	Co(1)-N(4)	2.151(3)	Co(1)-N(5)	2.117(3)
O(1)-Co(1)-N(5)	85.55(11)	O(1)-Co(1)-N(2)	174.18(11)	N(2)-Co(1)-N(5)	95.11(12)
O(1)-Co(1)-N(3)	95.61(11)	N(3)-Co(1)-N(5)	94.64(12)	N(2)-Co(1)-N(3)	78.57(12)
O(7)-Co(1)-O(1)	88.43(10)	O(7)-Co(1)-N(5)	172.85(11)	N(2)-Co(1)-O(7)	91.27(11)
N(3)-Co(1)-O(7)	89.77(10)	N(24)-Co(1)-O(1)	91.46(11)	N(5)-Co(1)-N(4)	78.23(12)
N(2)-Co(1)-N(4)	94.34(12)	N(3)-Co(1)-N(4)	169.56(11)	N(4)-Co(1)-O(7)	98.10(11)
2					
Ni(1)-O(1)	2.046(2)	Ni(1)-O(7)	2.112(2)	Ni(1)-N(2)	2.074(2)
Ni(1)-N(3)	2.080(2)	Ni(1)-N(4)	2.098(2)	Ni(1)-N(5)	2.074(2)
O(1)- Ni(1)-N(2)	175.84(8)	O(1)- Ni(1)-N(5)	85.38(7)	N(2)-Ni(1)-N(5)	94.42(8)
O(1)- Ni(1)-N(3)	95.46(7)	N(3)- Ni(1)-N(2)	80.41(8)	N(5)-Ni(1)-N(3)	94.08(8)
O(1)- Ni(1)-N(4)	90.32(7)	N(2)-Ni(1)-N(4)	93.74(8)	N(4)-Ni(1)-N(5)	80.04(8)
N(3)-Co(1)-N(4)	171.42(8)	O(1)-Co(1)-O(7)	89.28(6)	N(2)-Ni(1)-O(7)	91.08(7)
N(5)-Co(1)-O(7)	174.16(7)	N(3)-Co(1)-O(7)	88.76(7)	N(4)-Ni(1)-O(7)	97.67(7)
3					
Zn(1)-O(1)	2.004(3)	Zn(1)-O(2)	2.480(4)	Zn(1)-O(7)	2.082(2)
Zn(1)-O(8)	2.208(2)	Zn(1)-N(3)	2.115(3)	Zn(1)-N(4)	2.122(3)
Zn(2)-O(5)i	2.103(3)	Zn(2)-O(6)i	2.211(3)	Zn(2)-O(9)	2.177(2)
Zn(2)-O(10)	2.159(2)	Zn(2)-N(5)	2.131(3)	Zn(2)-N(6)	2.105(3)
O(1)-Zn(1)-O(7)	141.65(11)	O(1)-Zn(1)-N(3)	113.43(11)	O(7)-Zn(1)-N(3)	97.92(10)
O(1)-Zn(1)-N(4)	102.09(10)	O(7)-Zn(1)-N(4)	105.35(10)	N(3)-Zn(1)-N(4)	78.74(11)
O(8)-Zni(1)-O(1)	95.98(9)	O(7)-Zn(1)-O(8)	61.00(9)	N(3)-Zn(1)-O(8)	90.34(11)
N(4)-Zn(1)-O(8)	161.46(10)	O(1)-Zn(1)-O(2)	57.48(11)	O(2)-Zn(1)-O(7)	98.31(10)
N(3)-Zn(1)-O(2)	160.03(11)	N(4)-Zn(1)-O(2)	85.79(12)	O(2)-Zn(1)-O(8)	107.72(12)
N(6)-Zn(2)-O(5)i	95.14(12)	N(5)-Zn(2)-O(5)i	161.36(10)	N(5)-Zn(2)-N(6)	78.71(12)
O(10)-Zn(2)-O(5)i	101.90(11)	N(6)-Zn(2)-O(10)	156.72(11)	N(5)-Zn(2)-O(10)	89.43(11)
O(9)-Zn(2)-O(5)i	98.56(10)	N(6)-Zn(2)-O(9)	101.75(10)	N(5)-Zn(2)-O(9)	99.92(10)
O(9)-Zn(2)-O(10)	60.32(9)	O(6)i-Zn(2)-O(5)i	60.60(10)	N(6)-Zn(2)-O(6)i	96.17(10)
N(5)-Zn(2)-O(6)i	102.24(10)	O(10)-Zn(2)-O(6)i	105.96(9)	O(9)-Zn(2)-O(6)i	153.79(10)
4					
Co(1)-O(1)	2.034(5)	Co(1)-O(3)i	2.064(5)	Co(1)-O(7)	2.076(4)
Co(1)-O(8)	2.197(4)	Co(1)-N(2)	2.095(6)	Co(1)-N(3)	2.124(6)
O(1)-Co(1)-O(3)i	94.2(2)	O(1)-Co(1)-O(7)	89.8(2)	O(3)i-Co(1)-O(7)	86.71(19)
O(1)-Co(1)-N(2)	166.8(2)	O(3)i-Co(1)-N(2)	99.0(2)	O(7)-Co(1)-N(2)	90.9(2)
O(1)-Co(1)-N(3)	90.7(2)	O(3)i-Co(1)-N(3)	174.4(2)	O(7)-Co(1)-N(3)	90.60(19)
N(3)-Co(1)-N(2)	76.1(2)	O(8)-Co(1)-O(1)	89.50(19)	O(8)-Co(1)-O(3)i	87.46(18)
O(8)-Co(1)-O(7)	174.06(18)	O(8)-Co(1)-N(2)	91.2(2)	O(8)-Co(1)-N(3)	95.31(19)
5					
Zn(1)-O(1)	2.066(2)	Zn(1)-O(3)i	2.091(2)	Zn(1)-O(7)	2.196(2)
Zn(1)-O(8)	2.146(2)	Zn(1)-N(2)	2.127(2)	Zn(1)-N(3)	2.146(2)
O(1)-Zn(1)-O(3)i	88.88(6)	O(1)-Zn(1)-N(2)	176.70(6)	O(3)i-Zn(1)-N(2)	92.55(7)
N(3)-Zn(1)-O(1)	101.83(7)	N(3)-Zn(1)-O(3)i	169.18(7)	N(2)-Zn(1)-N(3)	76.85(7)
O(8)-Zn(1)-O(1)	90.96(6)	O(3)i-Zn(1)-O(8)	95.55(6)	N(2)-Zn(1)-O(8)	85.94(6)
N(3)-Zn(1)-O(8)	85.94(7)	O(7)-Zn(1)-O(1)	91.44(6)	O(3)i-Zn(1)-O(7)	88.89(6)
N(2)-Zn(1)-O(7)	91.56(7)	O(7)-Zn(1)-N(3)	89.27(7)	O(7)-Zn(1)-O(8)	174.99(6)
6					
Zn(1)-O(1)	2.142(2)	Zn(1)-O(1)i	2.046(2)	Zn(1)-O(4)ii	1.951(2)

Zn(1)-N(2)	2.145(2)	Zn(1)-N(5)	2.066(2)		
O(4)ii-Zn(1)-O(1)i	101.37(7)	O(4)ii-Zn(1)-N(5)	143.81(8)	O(1)i-Zn(1)-N(5)	114.82(6)
O(4)i-Zn(1)-O(1)	90.72(7)	O(1)-Zn(1)-O(1)i	77.08(6)	N(5)-Zn(1)-O(1)	97.36(6)
N(2)-Zn(1)-O(4)ii	89.58(7)	O(1)i-Zn(1)-N(2)	108.74(6)	N(5)-Zn(1)-N(2)	78.96(6)
N(2)-Zn(1)-O(1)	173.99(6)	Zn(1)i-O-(1)-Zn(1)	102.92(6)		
7					
Ni(1)-O(1)	2.180(4)	Ni(1)-O(2)	2.116(3)	Ni(1)-O(7)	2.052(4)
Ni(1)-O(8)	2.033(3)	Ni(1)-N(2)	2.085(4)	Ni(1)-N(4)	2.094(4)
O(8)-Ni(1)-O(7)	90.97(17)	O(8)-Ni(1)-N(2)	91.66(15)	N(2)-Ni(1)-O(7)	93.63(15)
O(8)-Ni(1)-N(4)	92.42(15)	O(7)-Ni(1)-N(4)	90.40(16)	N(2)-Ni(1)-N(4)	174.22(17)
O(8)-Ni(1)-O(2)	100.58(14)	O(7)-Ni(1)-O(2)	168.22(16)	O(2)-Ni(1)-N(2)	88.37(15)
N(4)-Ni(1)-O(2)	86.85(15)	O(8)-Ni(1)-O(1)	162.19(14)	O(7)-Ni(1)-O(1)	106.63(16)
N(2)-Ni(1)-O(1)	89.93(15)	O(1)-Ni(1)-N(4)	84.94(15)	O(2)-Ni(1)-O(1)	61.73(13)
8					
Fe(1)-O(2)	2.048(2)	Fe(1)-O(2)i	2.048(2)	Fe(1)-O(3)ii	2.003(2)
Fe(1)-O(3)iii	2.003(2)	Fe(1)-O(7)	1.964(2)	Fe(1)-O(7)i	1.964(2)
Fe(2)-O(1)i	2.055(2)	Fe(2)-O(1)iv	2.055(2)	Fe(2)-O(4)iii	2.020(2)
Fe(2)-O(4)v	2.020(2)	Fe(2)-O(7)	1.955(2)	Fe(2)-O(7)vi	1.955(2)
O(7)-Fe(1)-O(3)iii	89.53(9)	O(7)i-Fe(1)-O(3)iii	90.47(9)	O(7)-Fe(1)-O(3)ii	90.62(9)
O(7)-Fe(1)-O(2)	88.01(8)	O(7)i-Fe(1)-O(2)	91.99(8)	O(3)iii-Fe(1)-O(2)	90.85(9)
O(3)ii-Fe(1)-O(2)	89.15(9)	O(7)vi-Fe(2)-O(4)iii	88.23(9)	O(7)-Fe(2)-O(4)iii	91.77(9)
O(7)vi-Fe(2)-O(1)iv	91.37(9)	O(7)-Fe(2)-O(1)iv	88.63(9)	O(4)iii-Fe(2)-O(1)iv	92.65(8)
Fe(1)-O(7)-Fe(2)	123.55(10)				
9					
Mn(1)-O(1)	2.187(4)	Mn(1)-O(3)i	2.280(3)	Mn(1)-O(4)i	2.495(4)
Mn(1)-O(5)ii	2.276(3)	Mn(1)-O(6)ii	2.412(4)	Mn(1)-N(2)	2.280(4)
Mn(1)-N(3)	2.258(4)	Mn(2)-O(2)	2.147(3)	Mn(2)-O(2)iii	2.147(3)
Mn(2)-O(3)i	2.202(3)	Mn(2)-O(3)iv	2.202(3)	Mn(2)-O(7)	2.231(3)
Mn(2)-O(7)iii	2.231(3)				
O(1)-Mn(1)-N(3)	90.01(14)	O(1)-Mn(1)-O(5)ii	93.80(13)	N(3)-Mn(1)-O(5)ii	159.48(14)
O(1)-Mn(1)-O(3)i	81.55(12)	N(3)-Mn(1)-O(3)i	119.18(15)	O(5)ii-Mn(1)-O(3)i	81.34(13)
N(2)-Mn(1)-O(1)	93.43(14)	N(3)-Mn(1)-N(2)	72.05(15)	N(2)- Mn(1)-O(5)ii	87.59(14)
N(2)-Mn(1)-O(3)i	167.47(15)	O(1)-Mn(1)-O(6)ii	146.98(13)	N(3)-Mn(1)-O(6)ii	122.99(14)
O(5)ii-Mn(1)-O(6)ii	55.90(12)	O(3)i-Mn(1)-O(6)ii	81.10(12)	N(2)-Mn(1)-O(6)ii	97.56(14)
O(1)-Mn(1)-O(4)i	116.95(13)	N(3)-Mn(1)-O(4)i	78.49(13)	O(5)ii-Mn(1)-O(4)i	117.12(12)
O(3)i-Mn(1)-O(4)i	54.27(12)	N(2)-Mn(1)-O(4)i	137.42(14)	O(6)ii-Mn(1)-O(4)i	73.50(13)
O(2)-Mn(2)-O(7)	89.50(13)	O(2)iii-Mn(2)-O(7)	90.50(13)	O(2)-Mn(2)-O(3)iv	86.23(13)
O(2)iii-Mn(2)-O(3)iv	93.77(13)	O(7)-Mn(2)-O(3)iv	86.97(12)	O(7)iii-Mn(2)-O(3)iv	93.03(12)

[a] Symmetry transformations used to generate equivalent atoms: i *x*, *y*, *z*+1 for **3** ; i *x*, *y*+1, *z* for **4**; i –*x*+2, –*y*+1, –*z*+2 for **5**; i –*x*+1, –*y*+2, –*z*+1; ii *x*, *y*+1, *z* for **6**; i –*x*+1, –*y*+1, –*z*+1; ii –*x*+1, –*y*, –*z*+1; iii *x*, *y*+1, *z* ; iv *x*+1, *y*, *z*; v *x*+1, *y*+1, *z*; vi –*x*+2, –*y*+1, –*z*+1 for **8**; i *x*+1, *y*+1, *z*; ii *x*+2, *y*+1, *z*; iii –*x*+2, –*y*+2, *z*; iv –*x*+1, –*y*+1, –*z* for **9**.

Table S2. Hydrogen bonds in crystal packing [Å, °] of **1–9**.

Complexes	D-H…A	*d*(D-H)	*d*(H…A)	*d*(D…A)	∠DHA	Symmetry code
1	O(4)-H(4)···O(5)	0.82	1.65	2.457(3)	169	*x*+1, *y*-1, *z*+1
	O(7)-H(1W)···O(2)	0.86	2.08	2.783(3)	138	-*x*+2, -*y*+2, -*z*+1
	O(7)-H(2W)···O(2)	0.82	1.92	2.665(4)	152	
	O(8)-H(3W)···O(3)	0.87	2.15	2.986(7)	160	*x*-1, *y*, *z*-1
2	O(4)-H(4)···O(5)	1.04(4)	1.41(4)	2.452(2)	178(6)	*x*+1, *y*-1, *z*+1
	O(7)-H(2W)···O(2)	0.82	1.90	2.657(3)	153	
	O(8)-H(3W)···O(3)	0.88	2.17	3.023(3)	162	*x*-1, *y*, *z*-1
	O(8)-H(4W)···O(3)	0.88	2.17	3.022(3)	163	-*x*+2, -*y*+1, -*z*+1
3	O(4)-H(4)···N(2)	0.82	1.89	2.697(3)	169	*x*, *y*+1, *z*
	O(11)-H(11)···N(1)	0.82	1.85	2.665(3)	178	*x*, *y*-1, *z*+1
4	O(6)-H(6)···O(9)	0.82	1.80	2.617(8)	177	*x*, *y*+1, *z*+1
	O(7)-H(1W)···O(4)	0.84	1.99	2.826(6)	173	*x*+1, *y*+1, *z*
	O(7)-H(2W)···O(5)	0.82	1.96	2.722(7)	155	-*x*+1, -*y*+2, -*z*+2
	O(8)-H(3W)···O(4)	0.82	1.95	2.669(8)	145	*x*, *y*+1, *z*
	O(8)-H(4W)···O(2)	0.85	2.15	2.731(6)	125	
	O(9)-H(5W)···O(1)	0.93	2.02	2.949(6)	175	-*x*+1, -*y*+1, -*z*+1
	O(9)-H(6W)···O(2)	0.85	2.00	2.851(6)	179	-*x*, -*y*+1, -*z*+1
5	O(5)-H(5)···O(9)	0.82	1.75	2.570(2)	176	*x*, *y*-1, *z*+1
	O(7)-H(1W)···O(4)	0.82	1.90	2.666(2)	156	-*x*+2, -*y*+1, -*z*+2
	O(7)-H(2W)···O(10)	0.82	2.06	2.823(2)	155	
	O(8)-H(3W)···N(1)	0.84	1.98	2.776(2)	157	*x*, *y*+1, *z*
	O(8)-H(4W)···O(2)	0.82	1.99	2.711(2)	146	
	O(9)-H(5W)···O(4)	0.85	1.88	2.710(2)	164	*x*, *y*, *z*-1
	O(9)-H(6W)···O(2)	0.88	1.90	2.763(2)	168	-*x*+1, -*y*+1, -*z*+1
	O(10)-H(7W)···O(6)	0.83	2.07	2.836(3)	152	*x*, *y*+1, *z*-1
	O(10)-H(8W)···O(11)	0.82	2.01	2.814(3)	165	-*x*+1, -*y*+1, -*z*+1
	O(11)-H(9W)···O(1)	0.85	2.05	2.898(2)	180	
	O(11)-H(10W)···O(10)	0.85	1.97	2.822(3)	180	
6	O(5)-H(5)···O(6)	0.82	1.80	2.618(2)	173	-*x*+2, -*y*+3, -*z*+2
	N(3)-H(1)···O(2)	0.86	1.97	2.706(2)	142	-*x*, -*y*+2, -*z*+1
	N(4)-H(2)···O(3)	0.86	2.13	2.839(3)	139	-*x*, -*y*+1, -*z*+1
7	O(6)-H(6)···N(3)	0.82	1.83	2.647(7)	175	-*x*+2, -*y*, -*z*+2
	O(8)-H(1W)···O(4)	0.85	1.83	2.681(5)	174	*x*, *y*-1, *z*
	O(8)-H(2W)···O(3)	0.82	1.83	2.602(5)	157	*x*+1, *y*-1, *z*
8	O(5)-H(5)···O(8)	0.82	1.86	2.666(3)	167	*x*, *y*+1, *z*-1
	O(8)-H(1W)···O(1)	0.85	2.17	3.016(3)	180	-*x*, -*y*+1, -*z*+1
	O(8)-H(2W)···O(2)	0.85	2.05	2.897(3)	180	-*x*+1, -*y*+1, -*z*+1
9	O(8)-H(1W)···O(6)	0.85	2.03	2.880(7)	173	*x*+1, *y*, *z*
	O(8)-H(2W)···O(8)	0.81	2.43	2.944(7)	122	-*x*+1, -*y*+1, -*z*+1