Supporting Information

Four Hybrid Materials Based on Preyssler P_5W_{30} Polyoxometalate and First-Row Transition-Metal Complex

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1. X-ray Crystallography

Single crystals of **1-4** with appropriate dimensions were chosen under an optical microscope and quickly coated with high vacuum grease (Dow Corning Corporation) before being mounted on a glass fiber for data collection. Single-crystal X-ray diffraction data were collected using a Bruker SMART APEX II diffractometer with a CCD area detector (graphite monochromatic Mo Kα radiation, λ = 0.71073 Å, ω-scans with a 0.5° step in ω) for **1-4**. Indexing was performed using APEX2 (Difference Vectors method).[1] Data integration and reduction were performed using SaintPlus 6.01.[2] Absorption correction was performed by multi-scan method implemented in SADABS.[3] Space groups were determined using XPREP implemented in APEX2.[4] Structures of **1-4** were solved using SHELXS-97 (direct methods) and refined using SHELXL-97 (full-matrix least-squares on F^2).[4] Hydrogen atoms were placed in calculated positions and included as riding atoms with isotropic displacement parameters 1.2-1.5 times U_{eq} of the attached C atoms. All structures were examined using the Addsym subroutine of PLATON[5] to assure that no additional symmetry could be applied to the models. Selected bond lengths and angles are collated in Table S1.

2. Table S1. Selected bond lengths and angles for 1-4.

Complex 1

Cu1—N5	1.985 (11)	Cu5—N12	1.968 (11)
Cu1—N1	1.998 (12)	Cu5—N10	2.032 (12)
Cu1—N8	2.006 (11)	Cu5—N7	2.034 (12)
Cu1—O48^{i}	2.023 (9)	Cu5—O47	2.362 (10)
Cu1—O31	2.197 (10)	Cu6—O56	1.892 (11)
Cu2—O19	1.927 (10)	Cu6—O4W	1.965 (12)
Cu2—O57	1.932 (10)	Cu6—O5W	2.002 (12)
Cu2—N11^{ii}	1.971 (11)	Cu6—N3^{iv}	2.033 (12)
Cu2—N14^{ii}	2.044 (12)	Cu6—O6W	2.427 (15)
Cu2—O7W	2.330 (16)	Na1—O9W^{v}	2.43 (4)
Cu3—O57	1.917 (10)	Na1—O2	2.588 (17)
Cu3—O8W	1.977 (11)	Na1—O30	2.633 (18)
Cu3—N9^{ii}	1.982 (12)	Na1—O25^{v}	2.656 (18)
Cu3—O12^{iii}	1.985 (10)	Na1—O54	2.668 (18)
Cu3—O3W	2.255 (13)	Na1—O29^{v}	2.685 (18)
Cu4—O56	1.885 (11)	Na1—O33	2.869 (18)
Cu4—O2W	1.963 (12)	Na1—O9^{v}	2.902 (18)
Cu4—N2^{iv}	1.995 (12)	Na1—O43	2.979 (19)
Cu4—O1W	2.000 (12)	Na1—O24^{v}	3.019 (18)
Cu4—O40	2.316 (10)	Na1—Na1^{v}	3.13 (3)
Cu5—N6	1.896 (12)		
N5—Cu1—N1	80.7 (5)	O9W—Na1—O30	81 (3)
N5—Cu1—N8	91.4 (5)	O9W^{v}—Na1—O30	83.6 (8)
N1—Cu1—N8	165.2 (5)	O2—Na1—O30	73.7 (5)
N5—Cu1—O48^{i}	166.2 (4)	O9W—Na1—O25^{v}	85 (3)
N1—Cu1—O48^{i}	93.3 (4)	O9W^{v}—Na1—O25^{v}	82.1 (7)
N8—Cu1—O48^{i}	91.5 (4)	O2—Na1—O25^{v}	141.6 (7)
N5—Cu1—O31	106.2 (4)	O30—Na1—O25^{v}	139.5 (7)
N1—Cu1—O31	99.0 (4)	O9W—Na1—O54	84 (3)
N8—Cu1—O31	95.2 (4)	O9W^{v}—Na1—O54	83.5 (8)
O48^{i}—Cu1—O31	87.0 (4)	O2—Na1—O54	70.9 (5)
O19—Cu2—O57	91.2 (4)	O30—Na1—O54	143.3 (7)
O19—Cu2—N11^{ii}	168.4 (5)	O25^{v}—Na1—O54	71.8 (5)
O57—Cu2—N11^{ii}	93.6 (4)	O9W—Na1—O29^{v}	84 (3)
O19—Cu2—N14^{ii}	92.9 (5)	O9W^{v}—Na1—O29^{v}	83.0 (8)
O57—Cu2—N14^{ii}	174.2 (5)	O2—Na1—O29^{v}	143.1 (7)
N11^{ii}—Cu2—N14^{ii}	81.6 (5)	O30—Na1—O29^{v}	70.4 (5)
O19—Cu2—O7W	90.6 (6)	O25^{v}—Na1—O29^{v}	70.4 (5)
O57—Cu2—O7W	96.4 (6)	O54—Na1—O29^{v}	141.2 (7)
N11^{ii}—Cu2—O7W	99.4 (7)	O9W—Na1—O33	129 (3)

N14^{ii}—Cu2—O7W	87.7 (6)	O9W^{v}—Na1—O33	132.0 (8)
O57—Cu3—O8W	89.7 (5)	O2—Na1—O33	58.4 (4)
O57—Cu3—N9^{ii}	93.2 (5)	O30—Na1—O33	58.6 (4)
O8W—Cu3—N9^{ii}	173.0 (6)	O25^{v}—Na1—O33	145.9 (7)
O57—Cu3—O12^{iii}	157.9 (4)	O54—Na1—O33	108.5 (6)
O8W—Cu3—O12^{iii}	86.4 (4)	O29^{v}—Na1—O33	107.6 (6)
N9^{ii}—Cu3—O12^{iii}	88.6 (4)	O9W—Na1—O9^{v}	131 (3)
O57—Cu3—O3W	105.6 (5)	O9W^{v}—Na1—O9^{v}	128.4 (9)
O8W—Cu3—O3W	90.1 (6)	O2—Na1—O9^{v}	108.1 (6)
N9^{ii}—Cu3—O3W	95.2 (5)	O30—Na1—O9^{v}	147.8 (7)
O12^{iii}—Cu3—O3W	96.2 (4)	O25^{v}—Na1—O9^{v}	56.6 (4)
O56—Cu4—O2W	91.6 (6)	O54—Na1—O9^{v}	56.9 (4)
O56—Cu4—N2^{iv}	87.9 (5)	O29^{v}—Na1—O9^{v}	106.8 (6)
O2W—Cu4—N2^{iv}	171.8 (6)	O33—Na1—O9^{v}	94.1 (5)
O56—Cu4—O1W	175.8 (6)	O9W—Na1—O43	129 (3)
O2W—Cu4—O1W	86.9 (6)	O9W^{v}—Na1—O43	129.5 (10)
N2^{iv}—Cu4—O1W	93.0 (5)	O2—Na1—O43	109.9 (6)
O56—Cu4—O40	101.6 (5)	O30—Na1—O43	57.5 (4)
O2W—Cu4—O40	87.0 (5)	O25^{v}—Na1—O43	106.2 (6)
N2^{iv}—Cu4—O40	101.1 (5)	O54—Na1—O43	146.8 (7)
O1W—Cu4—O40	82.2 (5)	O29^{v}—Na1—O43	55.9 (4)
N6—Cu5—N12	163.4 (5)	O33—Na1—O43	54.2 (4)
N6—Cu5—N10	90.1 (5)	O9^{v}—Na1—O43	93.6 (5)
N12—Cu5—N10	81.6 (5)	O9W—Na1—O24^{v}	131 (3)
N6—Cu5—N7	80.1 (5)	O9W^{v}—Na1—O24^{v}	128.3 (7)
N12—Cu5—N7	103.1 (5)	O2—Na1—O24^{v}	147.0 (7)
N10—Cu5—N7	159.9 (5)	O30—Na1—O24^{v}	106.8 (6)
N6—Cu5—O47	97.5 (4)	O25^{v}—Na1—O24^{v}	56.8 (4)
N12—Cu5—O47	97.9 (5)	O54—Na1—O24^{v}	108.2 (6)
N10—Cu5—O47	98.3 (4)	O29^{v}—Na1—O24^{v}	56.0 (4)
N7—Cu5—O47	100.3 (4)	O33—Na1—O24^{v}	92.9 (5)
O56—Cu6—O4W	174.5 (5)	O9^{v}—Na1—O24^{v}	53.8 (4)
O56—Cu6—O5W	90.2 (5)	O43—Na1—O24^{v}	52.3 (4)
O4W—Cu6—O5W	85.6 (5)	O9W—Na1—Na1^{v}	2 (2)
O56—Cu6—N3^{iv}	87.6 (5)	O9W^{v}—Na1—Na1^{v}	0.7 (7)
O4W—Cu6—N3^{iv}	96.4 (5)	O2—Na1—Na1^{v}	84.0 (6)
O5W—Cu6—N3^{iv}	176.2 (6)	O30—Na1—Na1^{v}	83.6 (5)
O56—Cu6—O6W	95.4 (6)	O25^{v}—Na1—Na1^{v}	82.6 (6)
O4W—Cu6—O6W	88.4 (7)	O54—Na1—Na1^{v}	83.2 (4)
O5W—Cu6—O6W	93.0 (6)	O29^{v}—Na1—Na1^{v}	83.6 (5)
N3^{iv}—Cu6—O6W	90.3 (5)	O33—Na1—Na1^{v}	131.5 (8)
O9W—Na1—O9W^{v}	3 (3)	O9^{v}—Na1—Na1^{v}	128.5 (6)
O9W—Na1—O2	82 (3)	O43—Na1—Na1^{v}	129.9 (4)
O9W^{v}—Na1—O2	84.7 (7)	O24^{v}—Na1—Na1^{v}	129.0 (8)

Symmetry codes: (i) −*x*+1, −*y*+2, −*z*+1; (ii) *x*+1/2, *y*+1/2, *z*; (iii) −*x*+3/2, −*y*+5/2, −*z*+1; (iv) *x*, −*y*+2, *z*−1/2; (v) −*x*+1, *y*, −*z*+1/2.

Complex 2

Cu1—O16	1.845(18)	Cu4—N21	2.031(19)
Cu1—O42	2.277(17)	Cu5—O75	2.06(2)
Cu1—O43	2.38(2)	Cu5—O76	1.964(16)
Cu1—N4^{ii}	2.09(2)	Cu5—O77	2.09(2)
Cu1—N7	1.98(2)	Cu5—N1	2.23(2)
Cu1—N8	2.26(2)	Cu5—N14	1.97(2)
Cu2—O16	1.867(17)	Cu5—N18^{v}	2.45(2)
Cu2—O76^{iii}	2.015(16)	K1—O22^{i}	2.68(3)
Cu2—N9	1.931(18)	K1—O23^{i}	2.61(3)
Cu2—N19^{iv}	1.90(2)	K1—O26^{i}	2.80(4)
Cu3—O13	2.315(19)	K1—O27^{i}	2.50(4)
Cu3—O14	1.883(16)	K1—O30^{i}	2.73(4)
Cu3—O76^{iii}	2.052(16)	K1—O44	2.57(3)
Cu3—N2^{iii}	1.97(2)	K1—O45	2.77(3)
Cu3—N10	1.96(2)	K1—O46	2.69(4)
Cu4—O14	1.985(17)	K1—O47	2.62(4)
Cu4—O15	2.186(19)	K1—O48	2.60(3)
Cu4—N11	2.12(2)	K1—O1W^{i}	2.51(6)
Cu4—N15^{v}	1.95(2)		
O16—Cu1—O42	90.7(7)	O23^{i}—K1—O26^{i}	36.5(10)
O16—Cu1—O43	96.1(8)	O23^{i}—K1—O30^{i}	107.7(12)
O16—Cu1—N4^{ii}	92.4(9)	O23^{i}—K1—O45	163.0(12)
O16—Cu1—N7	174.6(9)	O23^{i}—K1—O46	134.9(14)
O16—Cu1—N8	80.3(8)	O23^{i}—K1—O47	105.4(14)
O42—Cu1—O43	173.2(6)	O27^{i}—K1—O22^{i}	105.3(12)
N4^{ii}—Cu1—O42	85.3(8)	O27^{i}—K1—O23^{i}	72.8(12)
N4^{ii}—Cu1—O43	95.2(9)	O27^{i}—K1—O26^{i}	36.5(10)
N4^{ii}—Cu1—N8	169.6(9)	O27^{i}—K1—O30^{i}	35.1(11)
N7—Cu1—O42	86.3(8)	O27^{i}—K1—O44	74.5(12)
N7—Cu1—O43	86.9(9)	O27^{i}—K1—O45	105.5(12)
N7—Cu1—N4^{ii}	91.8(9)	O27^{i}—K1—O46	145.4(15)
N7—Cu1—N8	95.1(8)	O27^{i}—K1—O47	163.1(14)
N8—Cu1—O42	87.2(8)	O27^{i}—K1—O48	140.2(12)
N8—Cu1—O43	93.0(8)	O27^{i}—K1—O1W^{i}	79.6(14)
O16—Cu2—O76^{iii}	167.4(8)	O30^{i}—K1—O26^{i}	71.6(11)
O16—Cu2—N9	83.7(9)	O30^{i}—K1—O45	71.0(11)
O16—Cu2—N19^{iv}	93.9(9)	O44—K1—O22^{i}	166.1(12)
N9—Cu2—O76^{iii}	89.2(7)	O44—K1—O23^{i}	145.6(13)
N19^{iv}—Cu2—O76^{iii}	93.1(7)	O44—K1—O26^{i}	110.8(12)
N19^{iv}—Cu2—N9	177.7(8)	O44—K1—O30^{i}	39.5(11)
O14—Cu3—O13	95.9(8)	O44—K1—O45	31.7(10)

O14—Cu3—O76^{iii}	168.2(7)	O44—K1—O46	73.0(14)
O14—Cu3—N2^{iii}	95.0(8)	O44—K1—O47	102.7(14)
O14—Cu3—N10	87.6(8)	O44—K1—O48	140.4(12)
O76^{iii}—Cu3—O13	74.8(8)	O45—K1—O26^{i}	140.7(11)
N2^{iii}—Cu3—O13	97.9(9)	O46—K1—O26^{i}	164.7(12)
N2^{iii}—Cu3—O76^{iii}	93.4(7)	O46—K1—O30^{i}	112.2(14)
N10—Cu3—O13	95.5(9)	O46—K1—O45	41.3(13)
N10—Cu3—O76^{iii}	86.2(7)	O47—K1—O22^{i}	73.3(13)
N10—Cu3—N2^{iii}	166.1(10)	O47—K1—O26^{i}	140.7(13)
O14—Cu4—O15	95.3(7)	O47—K1—O30^{i}	140.7(15)
O14—Cu4—N11	86.9(7)	O47—K1—O45	71.1(13)
O14—Cu4—N21	89.7(7)	O47—K1—O46	30.1(14)
N11—Cu4—O15	95.4(12)	O48—K1—O22^{i}	35.7(10)
N15^{v}—Cu4—O14	170.5(8)	O48—K1—O23^{i}	68.3(11)
N15^{v}—Cu4—O15	93.9(8)	O48—K1—O26^{i}	104.8(11)
N15^{v}—Cu4—N11	90.2(9)	O48—K1—O30^{i}	167.5(12)
N15^{v}—Cu4—N21	90.3(9)	O48—K1—O45	109.1(11)
N21—Cu4—O15	102.3(11)	O48—K1—O46	68.1(13)
N21—Cu4—N11	162.2(9)	O48—K1—O47	38.1(13)
O75—Cu5—O77	174.0(11)	O1W—K1—O22^{i}	62(4)
O75—Cu5—N1	92.9(11)	O1W^{i}—K1—O22^{i}	89.6(16)
O75—Cu5—N18^{v}	97.6(10)	O1W—K1—O23^{i}	65(4)
O76—Cu5—O75	83.5(10)	O1W^{i}—K1—O23^{i}	87.2(15)
O76—Cu5—O77	94.0(8)	O1W—K1—O26^{i}	77(4)
O76—Cu5—N1	87.3(7)	O1W^{i}—K1—O26^{i}	84.9(14)
O76—Cu5—N14	168.1(8)	O1W—K1—O27^{i}	89(4)
O76—Cu5—N18^{v}	83.4(7)	O1W—K1—O30^{i}	101(5)
O77—Cu5—N1	81.6(9)	O1W^{i}—K1—O30^{i}	77.7(13)
O77—Cu5—N18^{v}	87.4(9)	O1W—K1—O44	105(4)
N1—Cu5—N18^{v}	165.1(8)	O1W^{i}—K1—O44	76.6(14)
N14—Cu5—O75	90.9(11)	O1W^{i}—K1—O45	75.9(13)
N14—Cu5—O77	92.5(9)	O1W—K1—O45	98(4)
N14—Cu5—N1	103.4(8)	O1W^{i}—K1—O46	81.6(14)
N14—Cu5—N18^{v}	87.0(8)	O1W—K1—O46	87(4)
O22^{i}—K1—O26^{i}	69.2(11)	O1W—K1—O47	75(4)
O22^{i}—K1—O30^{i}	139.7(12)	O1W^{i}—K1—O47	83.5(15)
O22^{i}—K1—O45	142.8(12)	O1W—K1—O48	67(4)
O22^{i}—K1—O46	103.4(14)	O1W^{i}—K1—O48	90.1(16)
O23^{i}—K1—O22^{i}	32.7(11)	O1W—K1—O1W^{i}	28(5)

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) −*x*, −*y*+1, −*z*+1; (iii) *x*+1/2, −*y*+1/2, *z*+1/2; (iv) −*x*+1/2, *y*+1/2, −*z*+3/2; (v) −*x*, −*y*, −*z*+1.

Complex 3

Ni1—O5W	2.070 (16)	Ni3—O4W	2.117 (18)
Ni1—O6W	2.131 (19)	Ni3—N3	2.030 (18)

Ni1—O19^{i}	2.049 (14)	Ni3—N6^{iv}	2.06 (2)
Ni1—O43	2.050 (14)	Na1—O13	2.66 (4)
Ni1—N8	2.081 (18)	Na1—O14	2.99 (3)
Ni1—N10	2.039 (17)	Na1—O16	2.65 (4)
Ni2—O7W	2.071 (17)	Na1—O23	2.93 (3)
Ni2—O8W	2.130 (16)	Na1—O24	2.96 (4)
Ni2—O9W	2.079 (16)	Na1—O28	3.00 (4)
Ni2—O37	2.086 (18)	Na1—O29	2.61 (4)
Ni2—N2^{ii}	2.06 (2)	Na1—O31	2.93 (3)
Ni2—N12^{iii}	2.04 (2)	Na1—O32	2.59 (4)
Ni3—O2W	2.126 (15)	Na1—O42	2.66 (4)
Ni3—O3	2.092 (14)	Na1—O10W^{v}	2.58 (6)
Ni3—O3W	2.040 (16)		
O5W—Ni1—O6W	88.7 (7)	O16—Na1—O31	109.9 (11)
O5W—Ni1—N8	89.5 (7)	O16—Na1—O42	142.2 (16)
O19^{i}—Ni1—O5W	86.9 (6)	O23—Na1—O14	53.8 (6)
O19^{i}—Ni1—O6W	89.3 (6)	O23—Na1—O24	94.3 (8)
O19^{i}—Ni1—O43	171.1 (6)	O23—Na1—O28	95.0 (7)
O19^{i}—Ni1—N8	95.7 (6)	O24—Na1—O14	54.6 (7)
O43—Ni1—O5W	87.8 (6)	O24—Na1—O28	54.5 (7)
O43—Ni1—O6W	83.4 (7)	O29—Na1—O13	72.0 (10)
O43—Ni1—N8	91.4 (6)	O29—Na1—O14	109.3 (13)
N8—Ni1—O6W	174.6 (7)	O29—Na1—O16	140.9 (14)
N10—Ni1—O5W	176.2 (7)	O29—Na1—O23	147.9 (12)
N10—Ni1—O6W	90.4 (7)	O29—Na1—O24	57.8 (8)
N10—Ni1—O19^{i}	96.8 (6)	O29—Na1—O28	57.0 (8)
N10—Ni1—O43	88.4 (6)	O29—Na1—O31	107.5 (12)
N10—Ni1—N8	91.0 (7)	O29—Na1—O42	70.4 (9)
O7W—Ni2—O8W	88.5 (7)	O31—Na1—O14	95.2 (8)
O7W—Ni2—O9W	87.6 (7)	O31—Na1—O23	54.7 (6)
O7W—Ni2—O37	88.2 (7)	O31—Na1—O24	94.0 (8)
O9W—Ni2—O8W	89.0 (7)	O31—Na1—O28	53.2 (6)
O9W—Ni2—O37	88.7 (6)	O32—Na1—O13	141.3 (15)
O37—Ni2—O8W	176.0 (6)	O32—Na1—O14	108.7 (11)
N2^{ii}—Ni2—O7W	174.6 (8)	O32—Na1—O16	72.5 (10)
N2^{ii}—Ni2—O8W	93.8 (7)	O32—Na1—O23	58.0 (8)
N2^{ii}—Ni2—O9W	87.6 (7)	O32—Na1—O24	147.9 (9)
N2^{ii}—Ni2—O37	89.4 (7)	O32—Na1—O28	107.9 (11)
N12^{iii}—Ni2—O7W	88.1 (9)	O32—Na1—O29	140.2 (15)
N12^{iii}—Ni2—O8W	91.0 (8)	O32—Na1—O31	57.8 (8)
N12^{iii}—Ni2—O9W	175.7 (9)	O32—Na1—O42	71.3 (10)
N12^{iii}—Ni2—O37	91.0 (8)	O42—Na1—O13	141.0 (14)
N12^{iii}—Ni2—N2ii	96.7 (9)	O42—Na1—O14	148.4 (10)
O3—Ni3—O2W	88.5 (6)	O42—Na1—O23	109.0 (11)

O3—Ni3—O4W	86.3 (6)	O42—Na1—O24	108.0 (12)
O3W—Ni3—O2W	83.9 (6)	O42—Na1—O28	56.3 (7)
O3W—Ni3—O3	171.1 (7)	O42—Na1—O31	57.1 (7)
O3W—Ni3—O4W	89.4 (7)	O10W—Na1—O13	79 (7)
O3W—Ni3—N6^{iv}	91.7 (8)	O10W^{v}—Na1—O13	83.4 (15)
O4W—Ni3—O2W	91.8 (7)	O10W^{v}—Na1—O14	129 (2)
N3—Ni3—O2W	176.1 (7)	O10W—Na1—O14	128 (8)
N3—Ni3—O3	94.4 (6)	O10W—Na1—O16	85 (7)
N3—Ni3—O3W	93.0 (7)	O10W^{v}—Na1—O16	81.6 (15)
N3—Ni3—O4W	85.9 (8)	O10W^{v}—Na1—O23	128.2 (11)
N3—Ni3—N6^{iv}	91.1 (8)	O10W—Na1—O23	134 (8)
N6^{iv}—Ni3—O2W	91.3 (7)	O10W—Na1—O24	125 (8)
N6^{iv}—Ni3—O3	93.0 (7)	O10W^{v}—Na1—O24	130.9 (11)
N6^{iv}—Ni3—O4W	176.9 (7)	O10W^{v}—Na1—O28	129.5 (19)
O13—Na1—O14	57.2 (8)	O10W—Na1—O28	126 (8)
O13—Na1—O23	108.3 (11)	O10W—Na1—O29	78 (8)
O13—Na1—O24	57.8 (8)	O10W^{v}—Na1—O29	83.9 (12)
O13—Na1—O28	109.3 (13)	O10W—Na1—O31	133 (8)
O13—Na1—O31	148.0 (12)	O10W^{v}—Na1—O31	128.7 (19)
O14—Na1—O28	96.0 (9)	O10W—Na1—O32	87 (8)
O16—Na1—O13	70.3 (9)	O10W^{v}—Na1—O32	81.2 (10)
O16—Na1—O14	56.6 (8)	O10W—Na1—O42	83 (7)
O16—Na1—O23	57.9 (8)	O10W^{v}—Na1—O42	82.7 (18)
O16—Na1—O24	108.2 (12)	O10W—Na1—O10W^{v}	6 (8)
O16—Na1—O28	148.8 (10)		

Symmetry codes: (i) $-x+1/2, y+1/2, -z+1/2$; (ii) $x, -y+1, z+1/2$; (iii) $x+1/2, -y+3/2, z+1/2$; (iv) $-x+1/2, -y+3/2, -z$; (v) $-x+1, y, -z+1/2$.

Complex 4

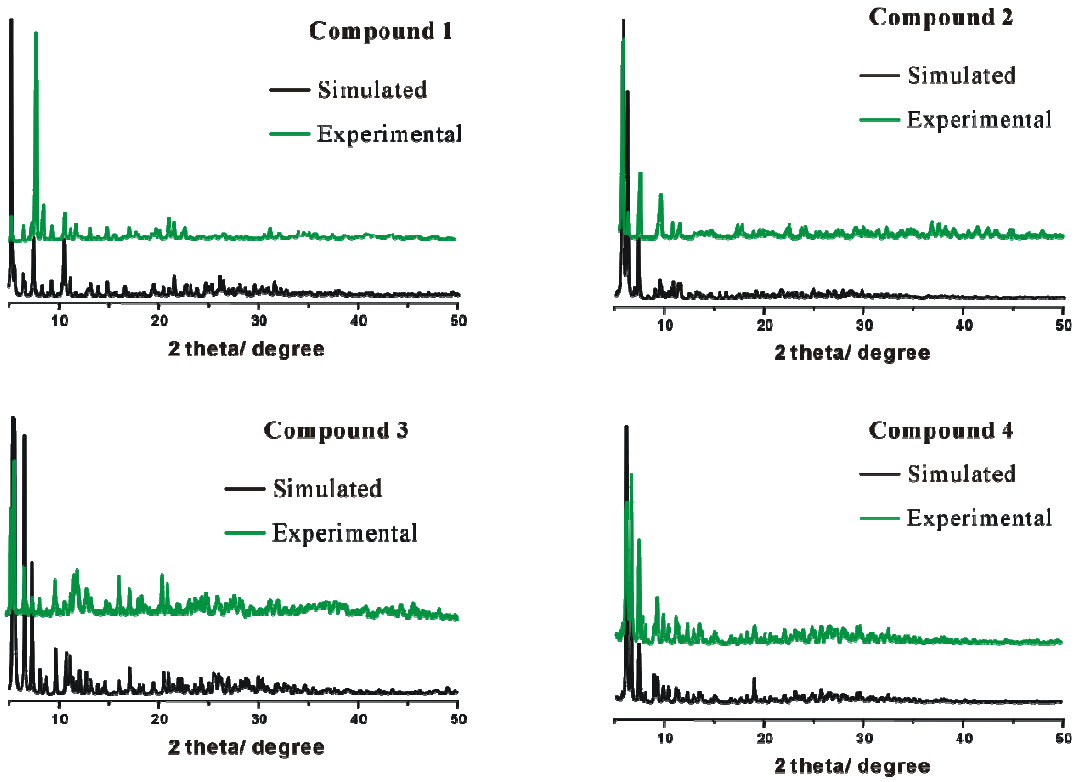
Co1—O2W	2.10 (3)	Co3—N22	2.12 (3)
Co1—O3W	2.06 (3)	Co4—O11W	2.16 (3)
Co1—O4W	2.10 (3)	Co4—O12W	2.17 (3)
Co1—O34^{i}	2.09 (2)	Co4—O13W	2.11 (3)
Co1—O61	2.04 (2)	Co4—N15	2.09 (3)
Co1—N23^{ii}	2.107 (18)	Co4—N18	2.11 (3)
Co2—O6W	2.08 (2)	K1—O1WA	2.431 (16)
Co2—O49	2.147 (19)	K1—O27	2.59 (2)
Co2—O64^{ii}	2.102 (18)	K1—O29	2.78 (3)
Co2—N4	2.08 (2)	K1—O33	2.68 (2)
Co2—N5	2.127 (17)	K1—O44	2.96 (2)
Co2—N10^{iii}	2.03 (9)	K1—O45	2.95 (2)
Co3—O9W	2.13 (3)	K1—O56	2.63 (2)
Co3—O10W	2.19 (3)	K1—O60	2.87 (3)
Co3—O19	2.074 (18)	K1—O62	2.66 (3)
Co3—N12	2.15 (3)	K1—O66	2.75 (2)

Co3—N19	2.13 (3)	K1—O68	2.66 (2)
O2W—Co1—N23 ^{i}	177(8)	O3W—Co1—O2W	89.3(14)
O3W—Co1—O4W	174.5(11)	O3W—Co1—O34 ^{ii}	97.0(10)
O3W—Co1—N23 ^{i}	91(8)	O4W—Co1—O2W	89.0(16)
O4W—Co1—N23 ^{i}	90(8)	O34 ^{ii}—Co1—O2W	87.0(9)
O34 ^{ii}—Co1—O4W	88.1(10)	O34 ^{ii}—Co1—N23 ^{i}	96(9)
O61—Co1—O2W	85.4(9)	O61—Co1—O3W	90.7(10)
O61—Co1—O4W	84.0(10)	O61—Co1—O34 ^{ii}	169.1(9)
O61—Co1—N23 ^{i}	92(9)	O6W—Co2—O49	86.1(10)
O6W—Co2—O64 ^{i}	88.0(10)	O6W—Co2—N4	91.4(11)
O6W—Co2—N5	91.3(10)	O64 ^{i}—Co2—O49	173.9(9)
O64 ^{i}—Co2—N5	92.3(8)	N4—Co2—O49	91.0(9)
N4—Co2—O64 ^{i}	90.8(9)	N4—Co2—N5	176.0(10)
N5—Co2—O49	86.2(9)	N10 ^{iii}—Co2—O6W	173(4)
N10 ^{iii}—Co2—O49	87(4)	N10 ^{iii}—Co2—O64 ^{i}	99(4)
N10 ^{iii}—Co2—N4	89(5)	N10 ^{iii}—Co2—N5	88(5)
O9W—Co3—O10W	87.3(12)	O9W—Co3—N12	92.6(12)
O9W—Co3—N19	174.8(11)	O19—Co3—O9W	87.7(10)
O19—Co3—O10W	174.3(11)	O19—Co3—N12	81.5(10)
O19—Co3—N19	87.1(10)	O19—Co3—N22	89.3(9)
N12—Co3—O10W	101.5(13)	N19—Co3—O10W	97.8(12)
N19—Co3—N12	86.4(12)	N22—Co3—O9W	88.4(10)
N22—Co3—O10W	87.8(13)	N22—Co3—N12	170.7(12)
N22—Co3—N19	91.8(11)	O11W—Co4—O12W	87.0(10)
O13W—Co4—O11W	169.2(13)	O13W—Co4—O12W	82.2(13)
O13W—Co4—N18	89.1(13)	N15—Co4—O11W	88.8(11)
N15—Co4—O12W	87.9(11)	N15—Co4—O13W	90.0(12)
N15—Co4—N18	176.1(12)	N18—Co4—O11W	91.4(12)
N18—Co4—O12W	88.2(11)	O1W—K1—O1WA	5.4(17)
O1W—K1—O27	79.5(17)	O1W—K1—O29	125.4(18)
O1W—K1—O33	77.0(16)	O1W—K1—O44	124.4(16)
O1W—K1—O45	131.0(17)	O1W—K1—O56	84.4(16)
O1W—K1—O60	131.9(17)	O1W—K1—O62	83.6(17)
O1W—K1—O66	130.2(18)	O1W—K1—O68	78.9(16)
O1WA—K1—O27	84.0(8)	O1WA—K1—O29	130.8(9)
O1WA—K1—O33	81.2(8)	O1WA—K1—O44	125.9(8)
O1WA—K1—O45	133.0(8)	O1WA—K1—O56	82.9(8)
O1WA—K1—O60	127.5(8)	O1WA—K1—O62	78.1(8)
O1WA—K1—O66	125.8(8)	O1WA—K1—O68	77.1(8)
O27—K1—O29	58.9(7)	O27—K1—O33	72.1(7)
O27—K1—O44	109.5(7)	O27—K1—O45	59.8(6)
O27—K1—O56	71.2(6)	O27—K1—O60	110.4(7)
O27—K1—O62	139.9(8)	O27—K1—O66	150.3(7)
O27—K1—O68	138.7(7)	O29—K1—O44	54.1(6)

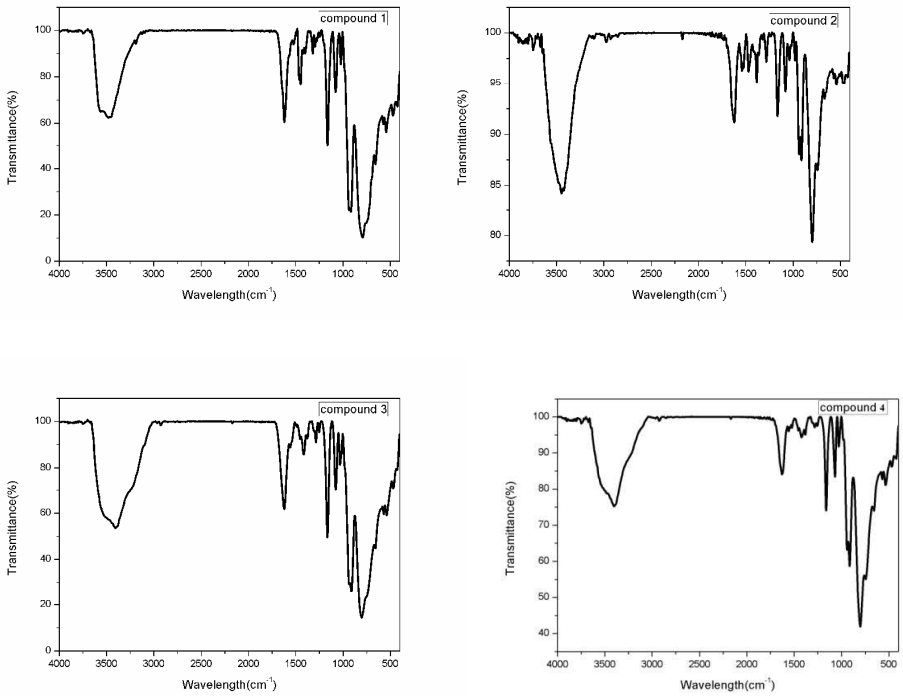
O29—K1—O45	55.1(6)	O29—K1—O60	97.1(7)
O33—K1—O29	58.6(7)	O33—K1—O44	56.7(6)
O33—K1—O45	111.0(7)	O33—K1—O60	151.1(7)
O33—K1—O66	108.6(7)	O45—K1—O44	95.8(6)
O56—K1—O29	110.2(7)	O56—K1—O33	141.2(7)
O56—K1—O44	151.1(7)	O56—K1—O45	58.8(6)
O56—K1—O60	57.8(6)	O56—K1—O62	71.2(7)
O56—K1—O66	109.5(7)	O56—K1—O68	140.1(7)
O60—K1—O44	97.4(6)	O60—K1—O45	54.5(6)
O62—K1—O29	150.9(8)	O62—K1—O33	138.1(8)
O62—K1—O44	110.1(7)	O62—K1—O45	109.8(7)
O62—K1—O60	58.1(6)	O62—K1—O66	58.9(6)
O62—K1—O68	71.0(7)	O66—K1—O29	95.2(7)
O66—K1—O44	55.1(6)	O66—K1—O45	94.3(7)
O66—K1—O60	54.5(6)	O68—K1—O29	109.0(7)
O68—K1—O33	69.0(7)	O68—K1—O44	58.1(6)
O68—K1—O45	150.0(7)	O68—K1—O60	110.3(6)
O68—K1—O66	59.5(6)		

Symmetry codes: (i) $x-1/2, -y+3/2, -z+1$; (ii) $-x+1, -y+1, -z+1$; (iii) $-x+1, y, -z+1/2$; (iv) $x+1/2, -y+3/2, -z+1$

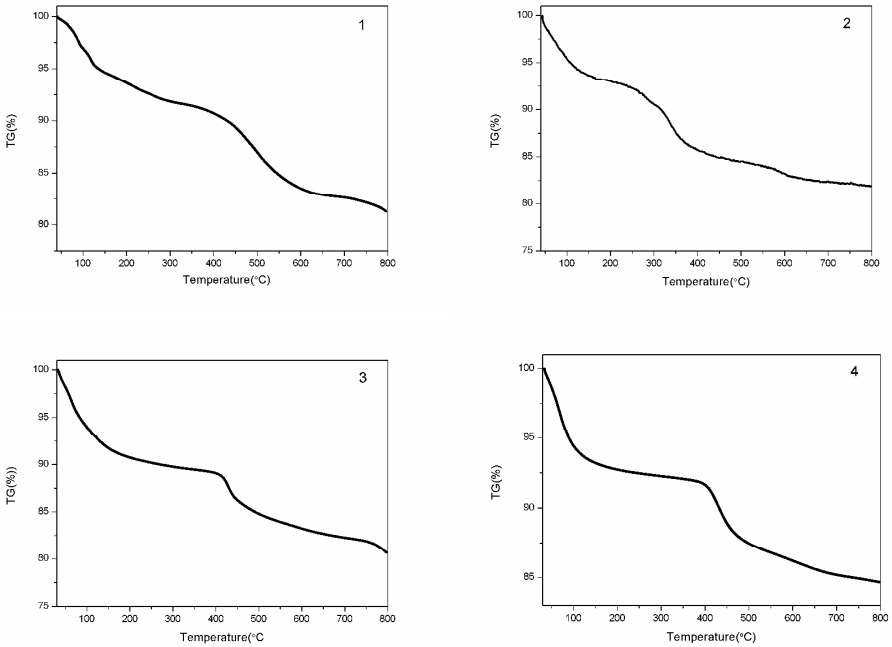
3. Figure S1. The XRD patterns of 1-4.



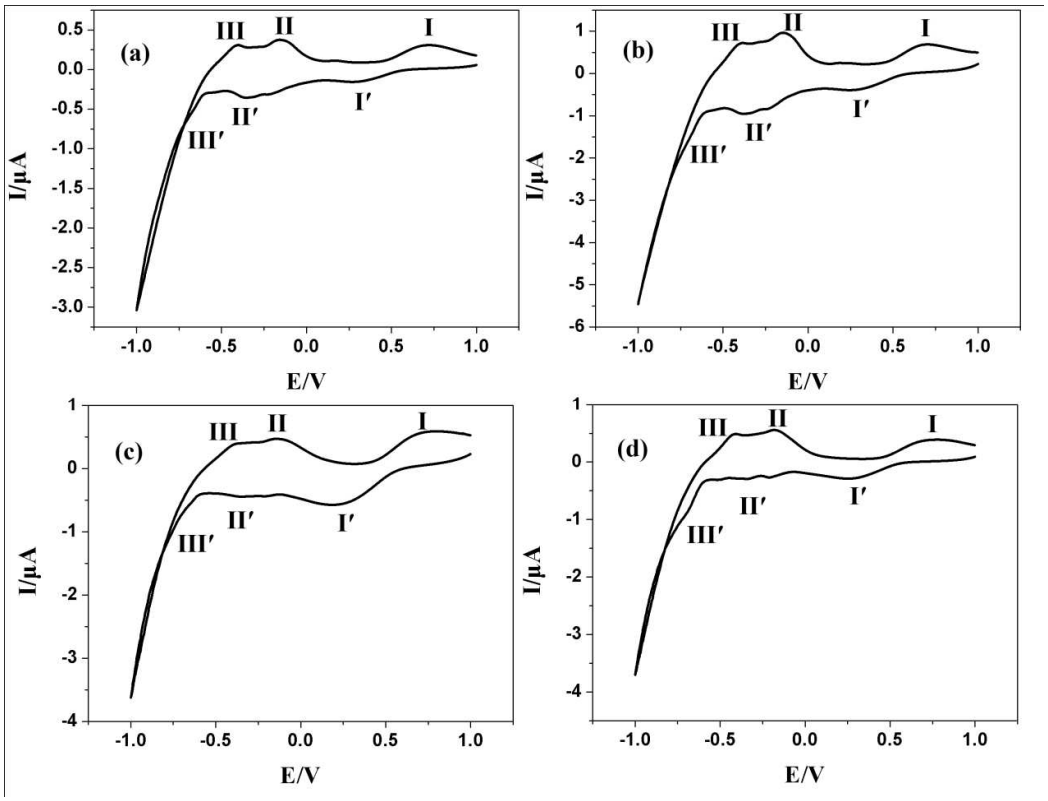
4. Figure S2. IR of 1-4.



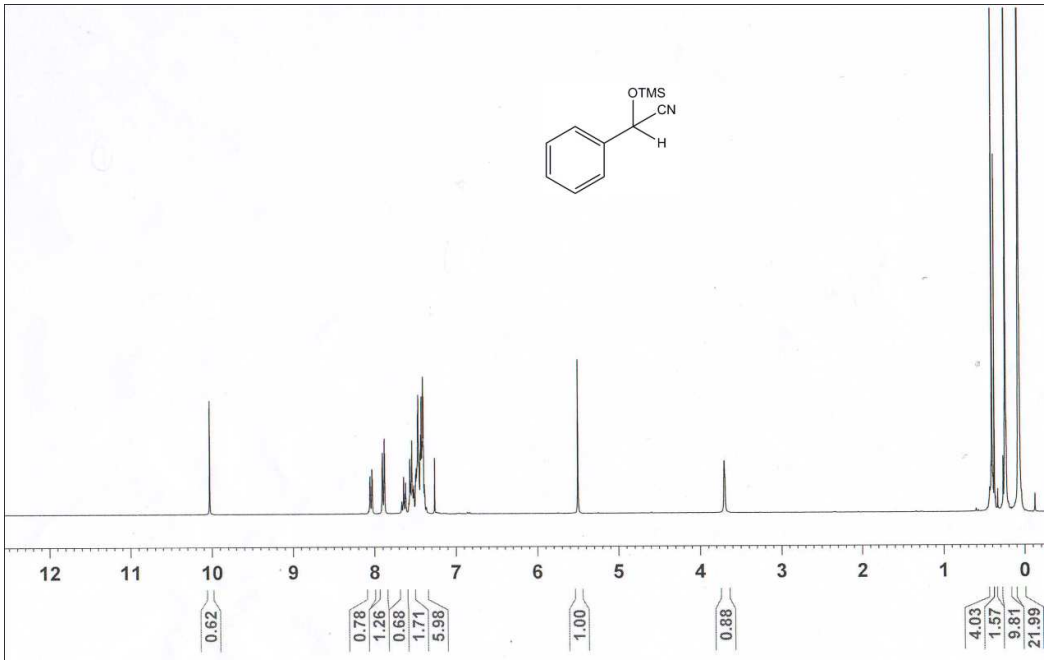
5. Figure S3. The TGA for 1- 4.



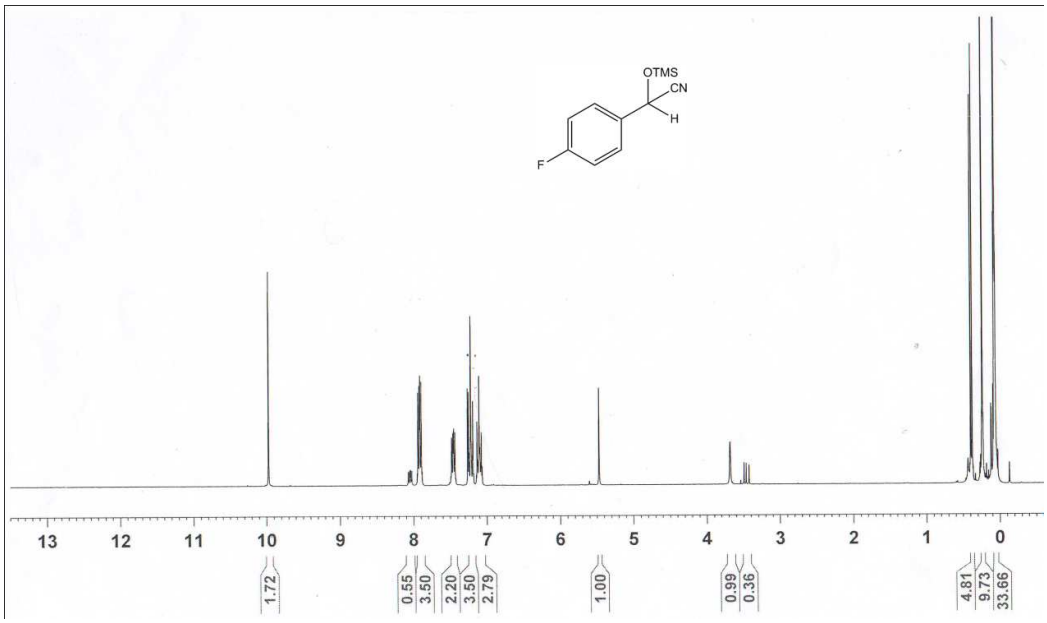
6. Figure S4. Cyclic voltammograms of the 1- to 4-CPEs in 1 M H_2SO_4 solution at 100 mV s^{-1}scan rate.



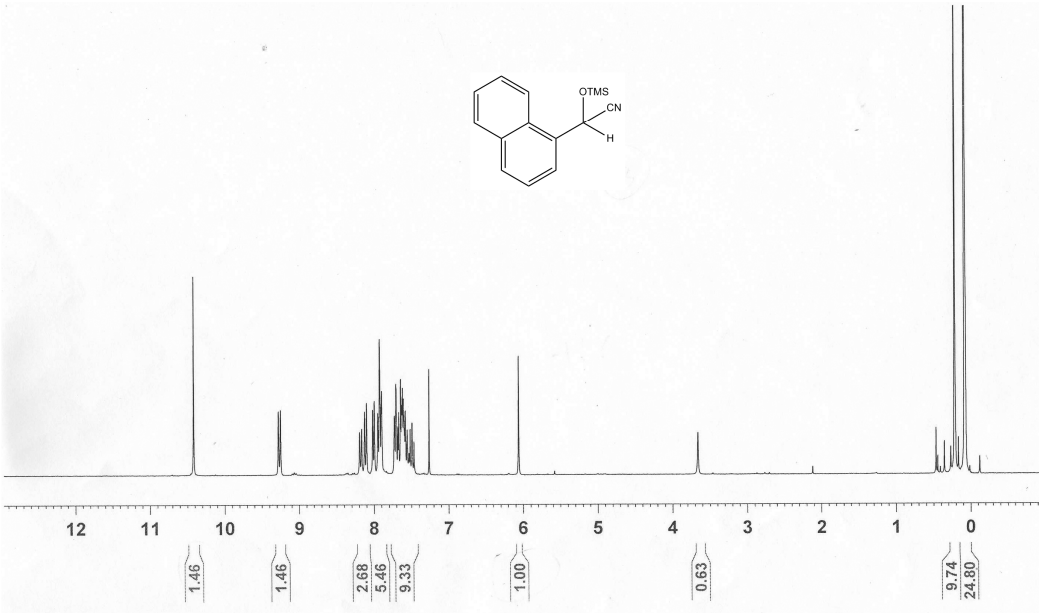
7. Figure S5. ^{1}H NMR spectra for reaction mixtures showing the conversion.



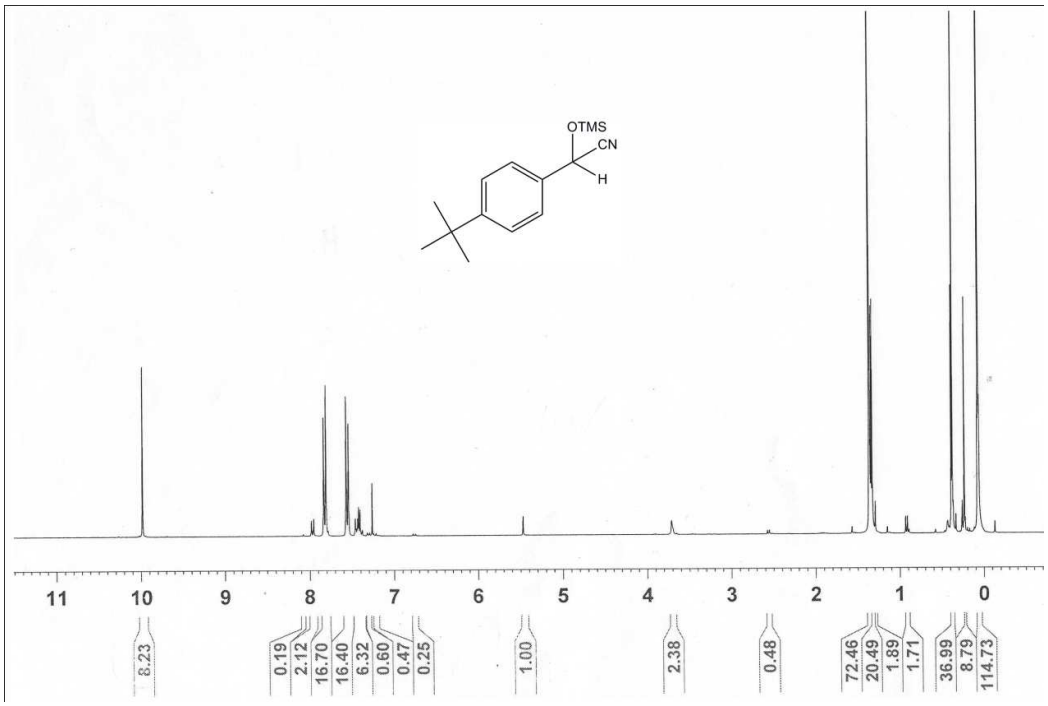
(a) ^{1}H NMR of crude reaction mixture corresponding to Table1, entry 1.



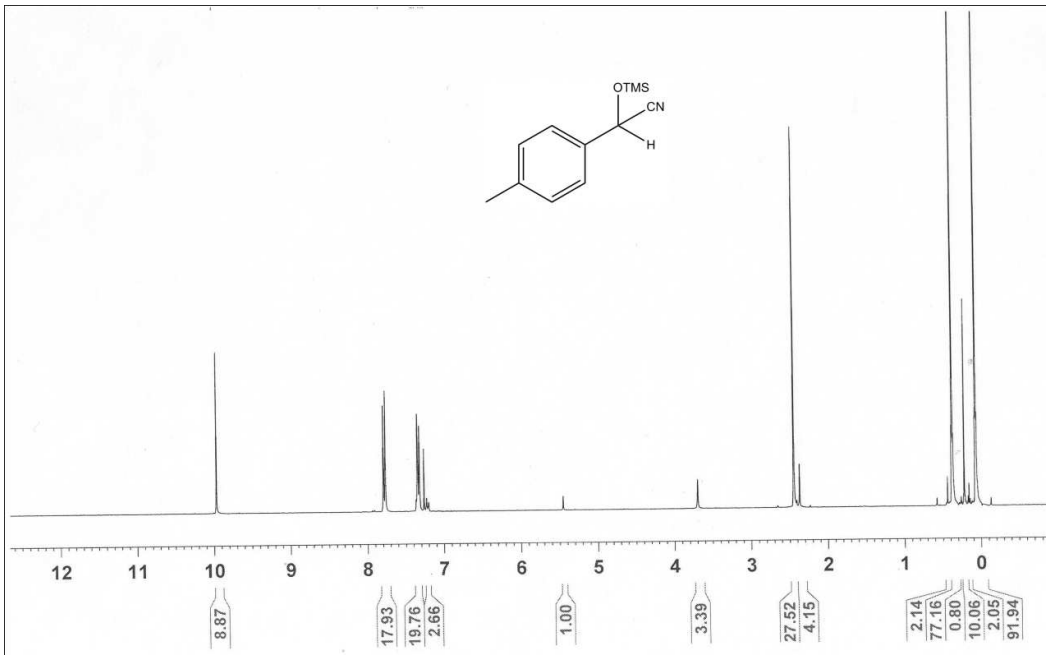
(b) ^{1}H NMR of crude reaction mixture corresponding to Table1, entry 2.



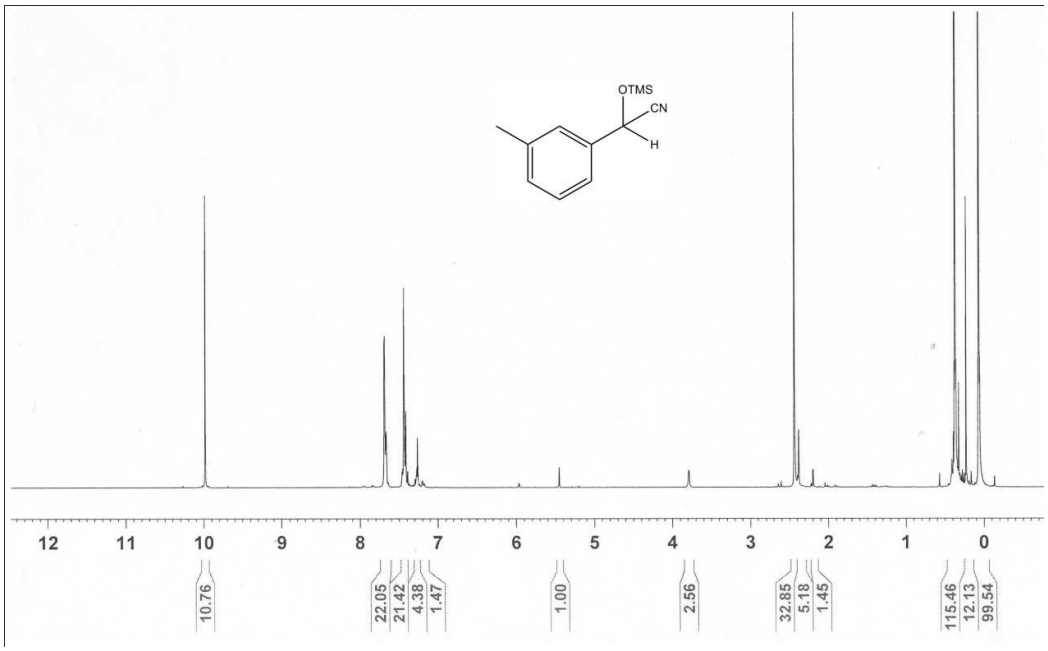
(c) ^{1}H NMR of crude reaction mixture corresponding to Table1, entry 3.



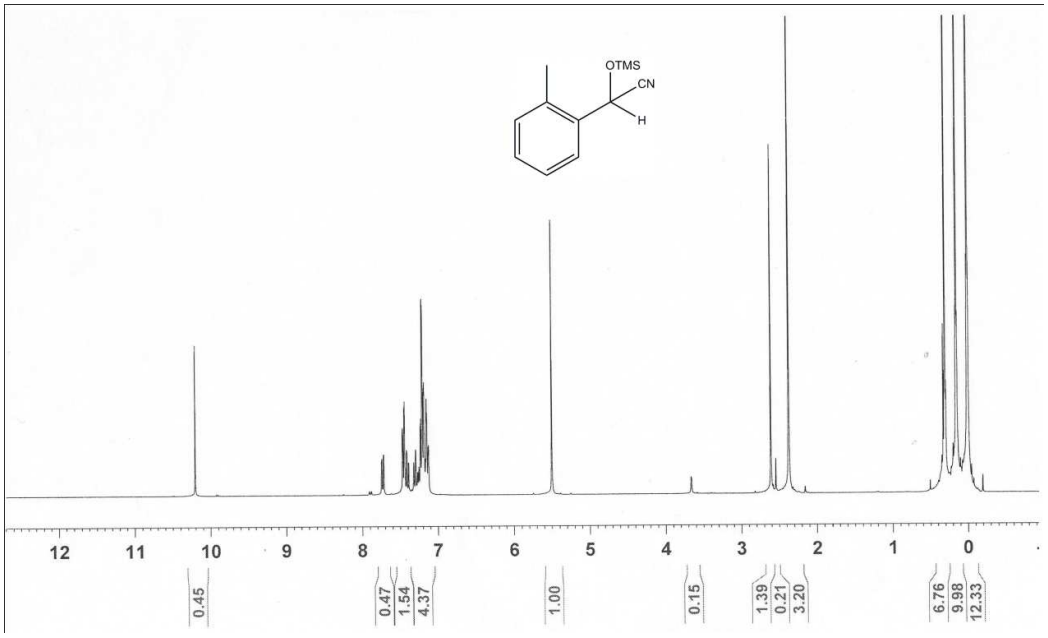
(d) ^{1}H NMR of crude reaction mixture corresponding to Table1, entry 4.



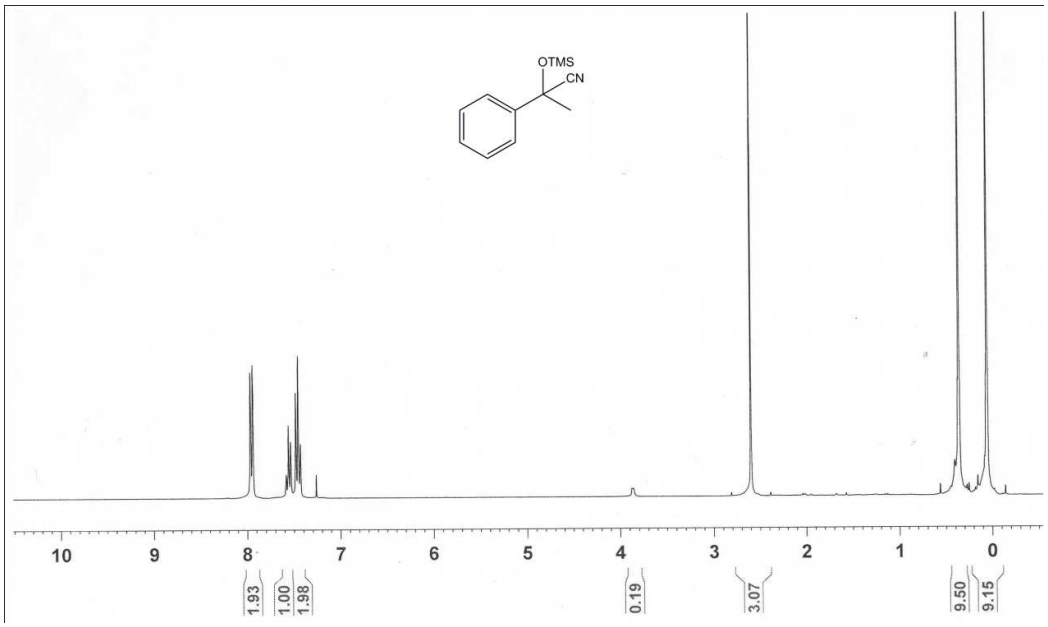
(e) ^{1}H NMR of crude reaction mixture corresponding to Table1, entry 5.



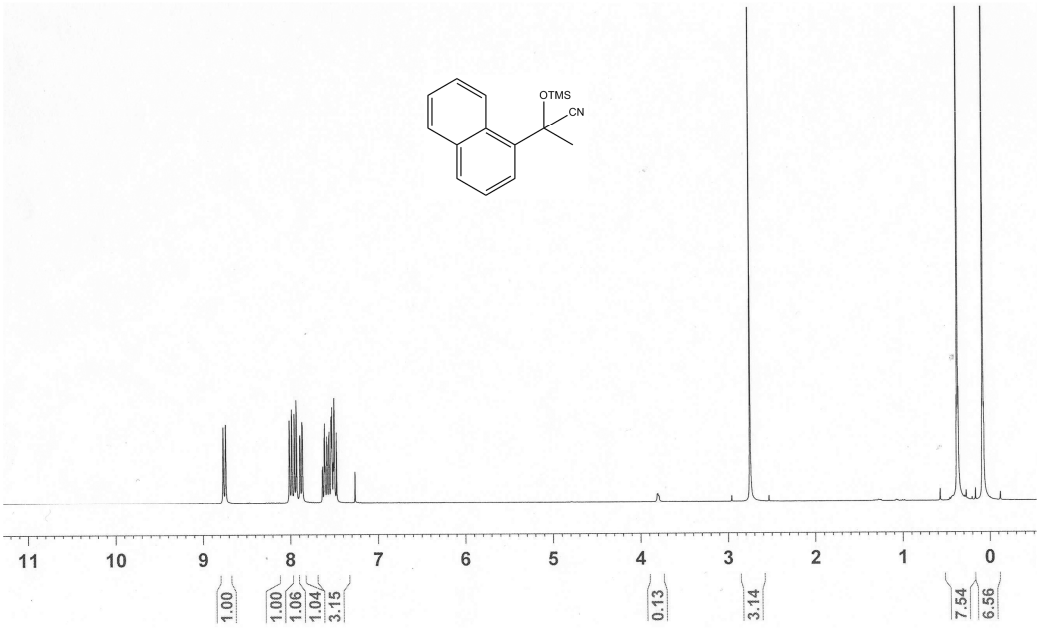
(f) ^{1}H NMR of crude reaction mixture corresponding to Table1, entry 6.



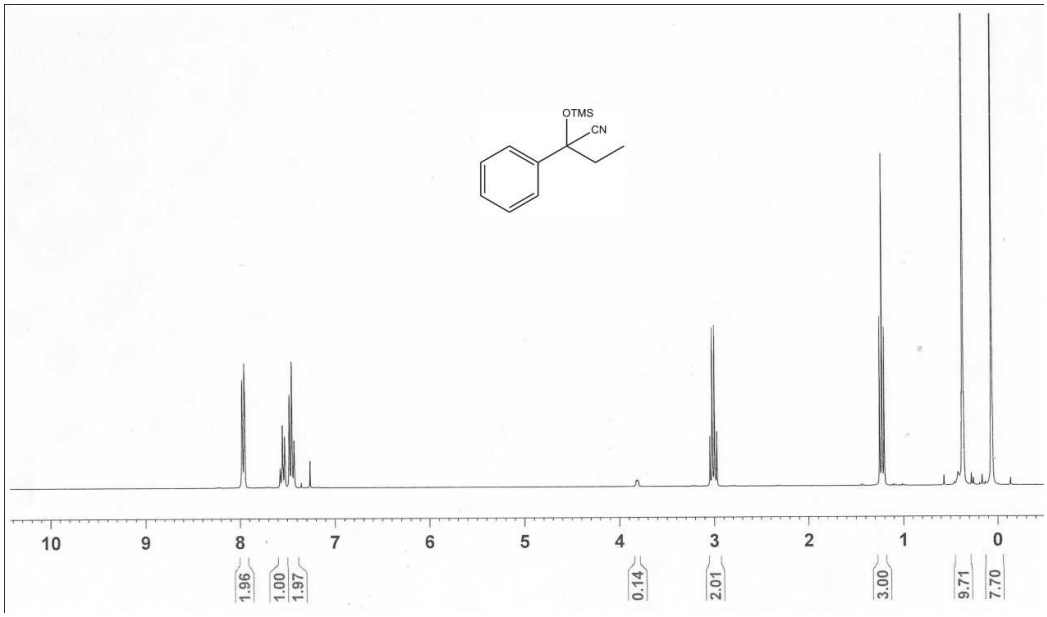
(g) ^{1}H NMR of crude reaction mixture corresponding to Table1, entry 7.



(h) ^{1}H NMR of crude reaction mixture corresponding to Table1, entry 8.



(i) ^{1}H NMR of crude reaction mixture corresponding to Table1, entry 9.



(j) ^{1}H NMR of crude reaction mixture corresponding to Table1, entry 10.

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