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Hypercoordiniate germanium complexes with phenanthrene-9,10-diolate ligands: synthesis, structure, and electronic properties

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Contents

Experimental

General. Experiments were performed under inert atmosphere of argon by standard vacuum-line techniques. The resulting compounds were stored in AS-ONE SGV-65V type glove box under argon atmosphere. All solvents were dried and degassed prior to use. The NMR spectra were obtained using JEOL ECX-500 (^{1}H: 500 MHz, ^{13}C: 125 MHz) NMR spectrometer. UV-vis spectra were obtained using Shimadzu UV-1600PCS spectrometer and the sample were measured in a quartz cell with 1.0 cm width. Emission spectra were obtained using Shimadzu RF-5300PC spectrometer and the sample were measured in a quartz cell with 1.0 cm width. X-ray crystallographic data and diffraction intensities were collected on Rigaku Rapid-S diffractometer utilizing graphite-monochromated Mo-*K*α (λ = 0.71073 Å) radiation at -123 °C. The structures were solved by the program system of Rigaku CrystalStructure with direct methods using SIR-92[S1] and the refinement methods using SHELXL program.[S2]

[S1] A. Altomare, M. C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Guagliardi, G. Polidoro, *J. Appl. Crystallogr.*, 1994, **27**, 435.
[S2] G. M. Sheldrick, *Acta Crystallogr. C*, 2015, **71**, 3-8.

*Sodium tris(phenanthrene-9,10-diolato)germanate **1**.* 9,10-Phenanthrenequinone (PQ, 0.628 g, 3.02 mmol) and 10% palladium charcoal (13 mg) were mixed in MeOH (7 ml). The orange suspension was exposed to hydrogen gas atmosphere at room temperature and was stirred until the mixture became a clear pale green solution to give phenanthrene-9,10-diol. After removal of palladium charcoal, sodium metal (102 mg, 4.44 mmol) and germanium oxide (212 mg, 2.03 mmol) were added to the pale green solution of phenanthrene-9,10-diol, and the resulting suspension was heated under methanol refluxing condition until it became a clear brown solution. After removal of methanol, the title compound was obtained as a greenish brown solid in 85% yield (0.746 g, 0.848 mmol as **1**·4MeOH). ^{13}C{^{1}H} NMR (THF, δ) 49.8 (MeOH), 121.5, 122.3, 122.8, 124.8, 125.2, 127.8, 140.0.

When a methanol solution of compound **1** was exposed to air, dark green crystals precipitated immediately. The crystals were collected by filtration. These crystals contained 9,10-phenanthrenequinone (PQ) and MeOH, as determined by NMR spectroscopy. ^{1}H NMR (THF-d_8, 500 MHz, δ) 7.20 (t, J = 7 Hz, 6H), 7.29 (t, J = 7 Hz, 6H), 7.38 (t, J = 7 Hz, 4H, PQ), 7.66 (broad, 4H, PQ), 8.05-8.15 (m, 8H, PQ), 8.16 (d, J = 7 Hz, 6H), 8.54 (d, J = 7 Hz, 6H) ; ^{13}C NMR (THF-d_8, 125 MHz, δ) 121.8, 122.5, 123.1, 124.8 (PQ), 125.0, 125.5, 128.1, 129.9 (PQ), 130.1 (PQ), 132.8 (PQ), 135.9 (PQ), 136.6 (PQ), 140.2, 179.9 (PQ); Anal. Calcd for **1**·2(PQ)·2(MeOH)·2H_2O (%): C 68.64, H 4.16, Found: C 68.48, H 4.00.

***1**·2(phen)·2(THF).* Sodium metal (0.050 g, 2.17 mmol) was added to 9,10-phenanthrenequinone (0.630 g, 3.03 mmol) in THF (30 ml) to give the corresponding sodium phenanthrene-9,10-diolate as a green suspension. Tetrachlorogermane (0.216 g, 1.01 mmol) was added, and the mixture was stirred overnight. Phenanthroline (0.360 g, 2.00 mmol) in THF (6 ml) was added to afford ***1**·2(phen)·2(THF)* as yellow crystals, yield: 0.952 g (0.863 mmol, 86%). ^{13}C{^{1}H} NMR (THF, δ) 121.2, 122.1, 122.6, 123.8 (phen), 124.5, 125.1, 127.1 (phen), 127.8, 129.5 (phen), 136.7 (phen), 140.3, 146.6 (phen), 151.2 (phen). Anal. Calcd for **1**·2(phen)·2(THF) (%): C 71.22, H 4.52, N 4.49, Found: C 70.99, H 4.23, N 4.78.

X-ray diffraction analysis

Table S1
Crystallographic data for germanate complexes **1**·2(PQ)·(DMSO)·3(MeOH) and **1**·2(phen)·2(THF)

	1·2(PQ)·(DMSO)·3(MeOH)	**1**·2(phen)·2(THF)
Formula	$C_{75}H_{58}Ge_2Na_2O_{14}S$	$C_{74}H_{56}GeN_4Na_2O_8$
Mol. weight	1333.90	1247.85
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$ (No.14)	$P2_1/c$ (No.14)
Unit cell dimensions		
a (Å)	16.159(5)	23.3472(16)
b (Å)	19.029(6)	12.9426(9)
c (Å)	19.759(5)	23.3144(18)
β (°)	94.804(8)	124.728(3)
V (Å^3)	5983(3)	5790.0(7)
Z	4	4
$D_{calc.}$ (g cm^{-3})	1.481	1.431
Unique reflections	13581	13101
No. variables	835	802
R ($I > 2\sigma(I)$)	0.0654	0.0732
wR_2 (all data)	0.1633	0.1053
GOF	0.835	0.956

1·2(PQ)·(DMSO)·3(MeOH)

Table S2 Bond lengths (Å) for **1**·2(PQ)·(DMSO)·3(MeOH)

atom	atom	distance	atom	atom	distance
Ge1	Na1	3.103(2)	Ge1	O1	1.887(3)
Ge1	O2	1.914(3)	Ge1	O3	1.907(3)
Ge1	O4	1.881(3)	Ge1	O5	1.885(3)
Ge1	O6	1.899(3)	S1	O11	1.429(4)
S1	C72	1.700(7)	S1	C73	1.805(8)
Na1	Na2[1]	3.567(3)	Na1	O1	2.457(4)
Na1	O3	2.454(3)	Na1	O5	2.570(4)
Na1	O7[1]	2.441(4)	Na1	O9	2.288(5)
Na1	O11	2.272(5)	Na2	O2	2.493(4)
Na2	O6	2.475(4)	Na2	O7	2.620(4)
Na2	O8	2.403(4)	Na2	O10[2]	2.479(4)
Na2	O11[2]	2.663(6)	Na2	O12	2.480(8)
O1	C1	1.357(6)	O2	C2	1.371(6)
O3	C15	1.367(5)	O4	C16	1.357(5)
O5	C29	1.364(6)	O6	C30	1.348(6)
O7	C43	1.225(6)	O8	C44	1.214(6)
O9	C57	1.215(7)	O10	C58	1.223(6)
O12	C71	1.444(15)	O13	C74	1.409(9)
O14	C75	1.373(11)	C1	C2	1.355(7)
C1	C14	1.438(7)	C2	C3	1.434(7)
C3	C4	1.410(7)	C3	C8	1.426(8)
C4	C5	1.377(9)	C5	C6	1.391(11)
C6	C7	1.376(10)	C7	C8	1.424(9)
C8	C9	1.443(8)	C9	C10	1.400(8)
C9	C14	1.414(8)	C10	C11	1.366(9)
C11	C12	1.404(10)	C12	C13	1.374(7)
C13	C14	1.413(7)	C15	C16	1.351(7)
C15	C28	1.430(6)	C16	C17	1.437(6)
C17	C18	1.415(8)	C17	C22	1.421(7)
C18	C19	1.359(7)	C19	C20	1.387(8)
C20	C21	1.367(9)	C21	C22	1.424(7)
C22	C23	1.453(8)	C23	C24	1.401(7)
C23	C28	1.428(6)	C24	C25	1.379(8)
C25	C26	1.389(8)	C26	C27	1.376(7)
C27	C28	1.394(7)	C29	C30	1.379(7)
C29	C42	1.422(7)	C30	C31	1.429(7)
C31	C32	1.404(7)	C31	C36	1.426(8)
C37	C42	1.414(7)	C38	C39	1.364(9)
C39	C40	1.397(8)	C40	C41	1.386(8)
C41	C42	1.413(7)	C43	C44	1.536(7)

Table S2 *(finished)*

C43	C56	1.456(7)	C44	C45	1.473(7)
C45	C46	1.395(7)	C45	C50	1.401(7)
C46	C47	1.364(8)	C47	C48	1.371(9)
C48	C49	1.383(8)	C49	C50	1.412(8)
C50	C51	1.486(7)	C51	C52	1.382(7)
C51	C56	1.404(7)	C52	C53	1.376(9)
C53	C54	1.392(9)	C54	C55	1.367(8)
C55	C56	1.400(7)	C57	C58	1.537(8)
C57	C70	1.450(8)	C58	C59	1.466(7)
C59	C60	1.400(8)	C59	C64	1.423(7)
C60	C61	1.370(8)	C61	C62	1.395(10)
C62	C63	1.370(9)	C63	C64	1.381(8)
C64	C65	1.483(8)	C65	C66	1.425(8)
C65	C70	1.394(8)	C66	C67	1.373(11)
C67	C68	1.377(12)	C68	C69	1.377(12)
C69	C70	1.397(9)			

Symmetry Operators:

(1) -X+1/2,Y+1/2,-Z+1/2

(2) -X+1/2,Y+1/2-1,-Z+1/2

Table S3 Bond angles for **1**·2(PQ)·(DMSO)·3(MeOH) (°)

atom	atom	atom	angle	atom	atom	atom	angle
Na1	Ge1	O1	52.35(10)	Na1	Ge1	O2	124.48(10)
Na1	Ge1	O3	52.26(9)	Na1	Ge1	O4	125.56(11)
Na1	Ge1	O5	55.80(11)	Na1	Ge1	O6	127.99(10)
O1	Ge1	O2	86.63(14)	O1	Ge1	O3	87.28(13)
O1	Ge1	O4	172.67(13)	O1	Ge1	O5	88.18(14)
O1	Ge1	O6	97.37(13)	O2	Ge1	O3	96.93(13)
O2	Ge1	O4	90.08(14)	O2	Ge1	O5	171.84(12)
O2	Ge1	O6	87.68(14)	O3	Ge1	O4	86.61(13)
O3	Ge1	O5	89.11(13)	O3	Ge1	O6	173.66(14)
O4	Ge1	O5	95.77(14)	O4	Ge1	O6	89.04(13)
O5	Ge1	O6	86.73(14)	O11	S1	C72	104.7(3)
O11	S1	C73	106.6(4)	C72	S1	C73	95.7(4)
Ge1	Na1	$Na2^{1}$	162.15(8)	Ge1	Na1	O1	37.46(8)
Ge1	Na1	O3	37.93(7)	Ge1	Na1	O5	37.35(8)
Ge1	Na1	$O7^{1}$	115.87(11)	Ge1	Na1	O9	101.21(12)
Ge1	Na1	O11	133.20(15)	$Na2^{1}$	Na1	O1	126.85(11)
$Na2^{1}$	Na1	O3	138.12(11)	$Na2^{1}$	Na1	O5	157.00(10)
$Na2^{1}$	Na1	$O7^{1}$	47.26(9)	$Na2^{1}$	Na1	O9	95.60(12)
$Na2^{1}$	Na1	O11	48.22(14)	O1	Na1	O3	64.46(10)
O1	Na1	O5	62.91(11)	O1	Na1	$O7^{1}$	89.96(13)
O1	Na1	O9	137.30(15)	O1	Na1	O11	106.01(16)
O3	Na1	O5	63.92(11)	O3	Na1	$O7^{1}$	99.33(13)
O3	Na1	O9	88.03(14)	O3	Na1	O11	170.35(17)
O5	Na1	$O7^{1}$	151.98(14)	O5	Na1	O9	76.02(14)
O5	Na1	O11	111.15(16)	$O7^{1}$	Na1	O9	128.09(15)
$O7^{1}$	Na1	O11	81.66(16)	O9	Na1	O11	98.95(17)
$Na1^{2}$	Na2	O2	127.78(11)	$Na1^{2}$	Na2	O6	132.80(10)
$Na1^{2}$	Na2	O7	43.17(9)	$Na1^{2}$	Na2	O8	100.80(12)
$Na1^{2}$	Na2	$O10^{2}$	54.17(10)	$Na1^{2}$	Na2	$O11^{2}$	39.51(10)
$Na1^{2}$	Na2	O12	104.8(2)	O2	Na2	O6	64.23(12)
O2	Na2	O7	163.08(13)	O2	Na2	O8	130.04(14)
O2	Na2	$O10^{2}$	90.11(13)	O2	Na2	$O11^{2}$	110.20(15)
O2	Na2	O12	78.4(2)	O6	Na2	O7	110.09(13)
O6	Na2	O8	92.92(14)	O6	Na2	$O10^{2}$	83.88(12)
O6	Na2	$O11^{2}$	166.37(15)	O6	Na2	O12	122.2(2)
O7	Na2	O8	64.30(13)	O7	Na2	$O10^{2}$	73.19(12)
O7	Na2	$O11^{2}$	71.43(14)	O7	Na2	O12	116.3(2)

Table S3 *(continued)*

atom	atom	atom	angle	atom	atom	atom	angle
O8	Na2	O10^{2}	133.28(15)	O8	Na2	O11^{2}	99.68(15)
O8	Na2	O12	78.5(2)	O10^{2}	Na2	O11^{2}	83.70(13)
O10^{2}	Na2	O12	140.7(2)	O11^{2}	Na2	O12	66.0(2)
Ge1	O1	Na1	90.18(13)	Ge1	O1	C1	109.4(3)
Na1	O1	C1	139.8(3)	Ge1	O2	Na2	95.47(14)
Ge1	O2	C2	108.9(3)	Na2	O2	C2	120.3(3)
Ge1	O3	Na1	89.81(11)	Ge1	O3	C15	108.4(3)
Na1	O3	C15	127.6(3)	Ge1	O4	C16	108.7(3)
Ge1	O5	Na1	86.85(13)	Ge1	O5	C29	109.8(3)
Na1	O5	C29	145.4(3)	Ge1	O6	Na2	96.43(13)
Ge1	O6	C30	109.3(3)	Na2	O6	C30	137.8(3)
Na1^{2}	O7	Na2	89.57(13)	Na1^{2}	O7	C43	148.5(3)
Na2	O7	C43	114.7(3)	Na2	O8	C44	122.6(3)
Na1	O9	C57	128.5(4)	Na2^{1}	O10	C58	157.9(3)
S1	O11	Na1	131.2(3)	S1	O11	Na2^{1}	127.0(3)
Na1	O11	Na2^{1}	92.26(16)	Na2	O12	C71	129.5(7)
O1	C1	C2	118.3(4)	O1	C1	C14	120.5(4)
C2	C1	C14	121.2(5)	O2	C2	C1	116.4(4)
O2	C2	C3	121.4(4)	C1	C2	C3	122.1(4)
C2	C3	C4	121.3(5)	C2	C3	C8	117.7(5)
C4	C3	C8	120.8(5)	C3	C4	C5	120.2(6)
C4	C5	C6	119.8(6)	C5	C6	C7	121.3(7)
C6	C7	C8	121.1(6)	C3	C8	C7	116.8(5)
C3	C8	C9	120.2(5)	C7	C8	C9	123.0(5)
C8	C9	C10	122.6(5)	C8	C9	C14	119.6(5)
C10	C9	C14	117.7(5)	C9	C10	C11	121.6(6)
C10	C11	C12	120.4(6)	C11	C12	C13	120.3(5)
C12	C13	C14	119.3(5)	C1	C14	C9	118.8(5)
C1	C14	C13	120.6(5)	C9	C14	C13	120.7(5)
O3	C15	C16	116.4(4)	O3	C15	C28	121.4(4)
C16	C15	C28	122.1(4)	O4	C16	C15	118.1(4)
O4	C16	C17	120.5(4)	C15	C16	C17	121.4(4)
C16	C17	C18	121.0(4)	C16	C17	C22	118.8(5)
C18	C17	C22	120.2(4)	C17	C18	C19	120.5(5)
C18	C19	C20	120.4(6)	C19	C20	C21	120.7(5)
C20	C21	C22	121.5(5)	C17	C22	C21	116.6(5)
C17	C22	C23	119.6(4)	C21	C22	C23	123.8(5)

Table S3 *(continued)*

atom	atom	atom	angle	atom	atom	atom	angle
C22	C23	C24	122.7(4)	C22	C23	C28	119.6(4)
C24	C23	C28	117.7(5)	C23	C24	C25	121.5(5)
C24	C25	C26	120.2(5)	C25	C26	C27	119.9(5)
C26	C27	C28	121.0(5)	C15	C28	C23	118.4(4)
C15	C28	C27	122.0(4)	C23	C28	C27	119.6(4)
O5	C29	C30	116.0(4)	O5	C29	C42	122.4(4)
C30	C29	C42	121.6(5)	O6	C30	C29	117.5(4)
O6	C30	C31	122.0(4)	C29	C30	C31	120.5(5)
C30	C31	C32	121.2(5)	C30	C31	C36	119.5(5)
C32	C31	C36	119.3(5)	C31	C32	C33	120.3(5)
C32	C33	C34	120.4(5)	C33	C34	C35	120.5(6)
C34	C35	C36	121.4(6)	C31	C36	C35	117.9(5)
C31	C36	C37	119.4(5)	C35	C36	C37	122.7(5)
C36	C37	C38	123.3(5)	C36	C37	C42	119.0(5)
C38	C37	C42	117.7(5)	C37	C38	C39	122.4(5)
C38	C39	C40	119.9(5)	C39	C40	C41	119.9(5)
C40	C41	C42	120.3(5)	C29	C42	C37	119.9(5)
C29	C42	C41	120.4(5)	C37	C42	C41	119.8(5)
O7	C43	C44	117.0(4)	O7	C43	C56	124.3(4)
C44	C43	C56	118.6(4)	O8	C44	C43	118.7(4)
O8	C44	C45	123.3(4)	C43	C44	C45	118.0(4)
C44	C45	C46	119.2(5)	C44	C45	C50	120.0(4)
C46	C45	C50	120.8(5)	C45	C46	C47	120.9(5)
C46	C47	C48	119.1(5)	C47	C48	C49	121.8(6)
C48	C49	C50	120.0(5)	C45	C50	C49	117.4(4)
C45	C50	C51	120.8(5)	C49	C50	C51	121.8(4)
C50	C51	C52	122.1(5)	C50	C51	C56	120.9(4)
C52	C51	C56	117.0(5)	C51	C52	C53	122.1(6)
C52	C53	C54	120.6(5)	C53	C54	C55	118.6(5)
C54	C55	C56	121.0(5)	C43	C56	C51	120.0(4)
C43	C56	C55	119.4(5)	C51	C56	C55	120.5(4)
O9	C57	C58	118.0(5)	O9	C57	C70	123.4(5)
C58	C57	C70	118.6(5)	O10	C58	C57	117.6(4)
O10	C58	C59	123.5(5)	C57	C58	C59	118.9(5)
C58	C59	C60	119.4(5)	C58	C59	C64	119.5(5)
C60	C59	C64	121.0(5)	C59	C60	C61	119.6(5)
C60	C61	C62	119.7(6)	C61	C62	C63	120.8(6)

Table S3 *(finished)*

atom	atom	atom	angle	atom	atom	atom	angle
C62	C63	C64	121.6(6)	C59	C64	C63	117.2(5)
C59	C64	C65	120.5(5)	C63	C64	C65	122.3(5)
C64	C65	C66	121.0(5)	C64	C65	C70	121.9(5)
C66	C65	C70	117.1(6)	C65	C66	C67	119.8(6)
C66	C67	C68	122.0(8)	C67	C68	C69	119.5(8)
C68	C69	C70	119.6(6)	C57	C70	C65	120.5(5)
C57	C70	C69	117.6(5)	C65	C70	C69	121.9(6)

Symmetry Operators:

(1) -X+1/2,Y+1/2,-Z+1/2 (2) -X+1/2,Y+1/2-1,-Z+1/2

Table S4 Intramolecular contacts less than 3.60 Å for **1**·2(PQ)·(DMSO)·3(MeOH)

atom	atom	distance	atom	atom	distance
S1	O12[1]	2.807(10)	S1	C71[1]	2.955(14)
Na1	C58	3.485(5)	Na1	C72	3.486(6)
Na2	O4	3.030(4)	O1	C13	2.847(6)
O1	C29	3.417(6)	O1	C30	3.494(6)
O1	C72	3.580(7)	O2	C4	2.882(7)
O2	C15	3.584(6)	O2	C16	3.502(5)
O3	C1	3.363(5)	O3	C2	3.487(6)
O3	C27	2.881(5)	O3	C55[1]	3.542(7)
O4	O8	3.271(5)	O4	O12	3.056(9)
O4	C18	2.854(6)	O4	C29	3.296(5)
O4	C30	3.225(5)	O5	C15	3.175(5)
O5	C16	3.218(5)	O5	C41	2.867(7)
O5	C72	3.538(7)	O6	C1	3.351(6)
O6	C2	3.267(6)	O6	C32	2.872(6)
O6	C60[2]	3.434(6)	O7	C13[2]	3.388(6)
O7	C32	3.429(6)	O7	C55	2.841(6)
O8	C46	2.839(7)	O8	C71	3.228(13)
O9	O10	2.675(6)	O9	C5[1]	3.280(7)
O9	C15	3.429(6)	O9	C27	3.584(6)
O9	C28	3.543(6)	O9	C41	3.534(7)
O9	C65	3.591(7)	O9	C69	2.777(9)
O10	C2[1]	3.447(6)	O10	C3[1]	3.401(6)
O10	C4[1]	3.411(6)	O10	C27	3.563(6)
O10	C60	2.837(6)	O11	C4[1]	3.470(8)
O11	C71[1]	3.476(14)	O12	C73[2]	3.057(12)
C1	C8	2.821(8)	C1	C55[1]	3.334(7)
C1	C60[2]	3.215(7)	C2	C9	2.822(7)
C2	C55[1]	3.524(7)	C2	C60[2]	3.556(7)
C3	C6	2.778(9)	C3	C14	2.863(7)
C3	C58[2]	3.332(7)	C3	C59[2]	3.597(7)
C4	C7	2.791(9)	C4	C58[2]	3.515(7)
C5	C8	2.834(8)	C5	C57[2]	3.457(8)
C6	C57[2]	3.474(9)	C7	C10	2.977(9)
C8	C58[2]	3.592(8)	C8	C59[2]	3.438(7)
C9	C12	2.809(8)	C9	C59[2]	3.585(8)
C10	C13	2.788(9)	C11	C14	2.775(8)
C11	C45[1]	3.512(8)	C11	C50[1]	3.428(8)

Table S4 *(finished)*

atom	atom	distance	atom	atom	distance
C12	C43[1]	3.580(7)	C12	C44[1]	3.328(8)
C12	C45[1]	3.274(8)	C13	C43[1]	3.112(7)
C13	C44[1]	3.432(7)	C13	C56[1]	3.466(7)
C13	C61[2]	3.360(8)	C14	C43[1]	3.525(7)
C14	C55[1]	3.539(7)	C14	C56[1]	3.329(7)
C14	C60[2]	3.320(7)	C14	C61[2]	3.314(7)
C15	C22	2.827(6)	C16	C23	2.830(7)
C17	C20	2.778(7)	C17	C28	2.860(7)
C18	C21	2.772(7)	C18	C71	3.501(15)
C19	C22	2.820(8)	C21	C24	3.002(8)
C23	C26	2.811(7)	C23	C69	3.558(8)
C24	C27	2.769(7)	C25	C28	2.787(7)
C25	C64	3.523(8)	C25	C65	3.450(8)
C26	C58	3.376(7)	C26	C59	3.288(7)
C26	C64	3.428(8)	C27	C57	3.202(7)
C27	C58	3.217(7)	C27	C70	3.587(8)
C28	C57	3.403(7)	C28	C70	3.512(8)
C29	C36	2.832(7)	C29	C72	3.520(8)
C30	C37	2.849(7)	C31	C34	2.789(8)
C31	C42	2.850(7)	C32	C35	2.775(8)
C32	C43	3.369(7)	C33	C36	2.800(8)
C33	C43	3.513(7)	C33	C56	3.394(7)
C35	C38	3.000(9)	C37	C40	2.815(8)
C38	C41	2.769(8)	C39	C42	2.796(8)
C43	C50	2.906(7)	C44	C51	2.898(7)
C45	C48	2.748(9)	C45	C56	2.934(7)
C46	C49	2.764(8)	C47	C50	2.812(7)
C49	C52	2.973(8)	C51	C54	2.818(7)
C52	C55	2.746(8)	C53	C56	2.754(7)
C57	C64	2.913(8)	C58	C65	2.898(8)
C59	C62	2.752(8)	C59	C70	2.941(8)
C60	C63	2.776(8)	C61	C64	2.809(8)
C63	C66	2.955(9)	C65	C68	2.813(11)
C66	C69	2.784(9)	C67	C70	2.745(10)
C71	C73[2]	3.420(17)			

Symmetry Operators:

(1) -X+1/2,Y+1/2,-Z+1/2 (2) -X+1/2,Y+1/2-1,-Z+1/2

Table S5 Intermolecular contacts less than 3.60 Å for **1**·2(PQ)·(dmso)·3(MeOH)

atom	atom	distance	atom	atom	distance
O2	O13[1]	2.864(7)	O12	O13[1]	2.805(11)
O12	C74[1]	3.437(12)	O13	O2[2]	2.864(7)
O13	O12[2]	2.805(11)	O13	O14[3]	3.314(11)
O13	C2[2]	3.538(7)	O13	C4[2]	3.396(8)
O13	C54	3.501(8)	O13	C73[4]	3.597(10)
O13	C75[3]	3.265(13)	O14	O13[3]	3.314(11)
O14	C53[3]	3.441(9)	O14	C54[3]	3.543(9)
C2	O13[1]	3.538(7)	C4	O13[1]	3.396(8)
C6	C67[5]	3.269(11)	C7	C67[5]	3.492(10)
C7	C68[5]	3.322(10)	C11	C39[5]	3.455(8)
C15	C74[1]	3.412(9)	C16	C74[1]	3.597(9)
C18	C49[6]	3.407(8)	C19	C49[6]	3.583(8)
C20	C39[7]	3.583(7)	C20	C52[6]	3.561(8)
C21	C72[7]	3.580(8)	C25	C61[8]	3.357(8)
C26	C61[8]	3.423(7)	C34	C66[9]	3.556(8)
C36	C47[6]	3.557(7)	C39	C11[10]	3.455(8)
C39	C20[9]	3.583(7)	C45	C47[6]	3.545(8)
C46	C47[6]	3.348(8)	C46	C48[6]	3.500(8)
C47	C36[6]	3.557(7)	C47	C45[6]	3.545(8)
C47	C46[6]	3.348(8)	C47	C47[6]	3.587(8)
C48	C46[6]	3.500(8)	C49	C18[6]	3.407(8)
C49	C19[6]	3.583(8)	C52	C20[6]	3.561(8)
C53	O14[3]	3.441(9)	C54	O13	3.501(8)
C54	O14[3]	3.543(9)	C61	C25[8]	3.357(8)
C61	C26[8]	3.423(7)	C66	C34[7]	3.556(8)
C67	C6[10]	3.269(11)	C67	C7[10]	3.492(10)
C68	C7[10]	3.322(10)	C71	C73[7]	3.576(15)
C72	C21[9]	3.580(8)	C73	O13[11]	3.597(10)
C73	C71[9]	3.576(15)	C74	O12[2]	3.437(12)
C74	C15[2]	3.412(9)	C74	C16[2]	3.597(9)
C75	O13[3]	3.265(13)			

Symmetry Operators:

(1) -X+1/2,Y+1/2,-Z+1/2
(2) -X+1/2,Y+1/2-1,-Z+1/2
(3) -X+1,-Y,-Z+1
(4) X,Y-1,Z
(5) X,-Y+1,Z+1
(6) -X+1,-Y,-Z
(7) X,-Y+1,Z
(8) -X,-Y+1,-Z
(9) X+1,-Y+1,Z+1
(10) X+1,-Y+1,Z
(11) X,Y+1,Z

1·2(phen)·2(THF)

Table S6 Bond lengths (Å) for **1**·2(phen)·2(THF)

atom	atom	distance	atom	atom	distance
Ge1	Na1	3.1275(13)	Ge1	Na2	3.0967(12)
Ge1	O1	1.897(3)	Ge1	O2	1.906(2)
Ge1	O3	1.889(3)	Ge1	O4	1.890(3)
Ge1	O5	1.904(2)	Ge1	O6	1.893(3)
Na1	O2	2.464(3)	Na1	O6	2.355(2)
Na1	O8	2.358(4)	Na1	N1	2.501(3)
Na1	N2	2.474(5)	Na2	O1	2.445(3)
Na2	O4	2.498(2)	Na2	O5	2.520(3)
Na2	O7	2.345(3)	Na2	N3	2.460(3)
Na2	N4	2.553(4)	O1	C1	1.364(5)
O2	C2	1.366(6)	O3	C15	1.359(5)
O4	C16	1.355(5)	O5	C29	1.358(5)
O6	C30	1.356(4)	O7	C67	1.432(4)
O7	C70	1.429(7)	O8	C71	1.418(6)
O8	C74	1.419(5)	N1	C43	1.322(5)
N1	C54	1.368(7)	N2	C52	1.316(5)
N2	C53	1.362(5)	N3	C55	1.317(5)
N3	C66	1.352(6)	N4	C64	1.320(6)
N4	C65	1.367(5)	C1	C2	1.364(4)
C1	C14	1.429(7)	C2	C3	1.435(6)
C3	C4	1.408(4)	C3	C8	1.416(7)
C4	C5	1.371(6)	C5	C6	1.393(8)
C6	C7	1.384(5)	C7	C8	1.421(6)
C8	C9	1.449(4)	C9	C10	1.409(7)
C9	C14	1.427(6)	C10	C11	1.363(5)
C11	C12	1.397(7)	C12	C13	1.370(7)
C13	C14	1.396(4)	C15	C16	1.374(4)
C15	C28	1.411(6)	C16	C17	1.424(6)
C17	C18	1.413(5)	C17	C22	1.415(6)
C18	C19	1.370(7)	C19	C20	1.388(7)
C20	C21	1.372(5)	C21	C22	1.410(6)
C22	C23	1.464(5)	C23	C24	1.394(7)
C23	C28	1.422(7)	C24	C25	1.382(5)
C25	C26	1.385(7)	C26	C27	1.364(7)
C27	C28	1.410(5)	C29	C30	1.370(6)
C29	C42	1.422(5)	C30	C31	1.425(6)
C31	C32	1.411(5)	C31	C36	1.411(4)

Table S6 *(finished)*

atom	atom	distance	atom	atom	distance
C32	C33	1.377(6)	C33	C34	1.391(5)
C34	C35	1.366(6)	C35	C36	1.413(6)
C36	C37	1.451(6)	C37	C38	1.406(5)
C37	C42	1.428(6)	C38	C39	1.367(7)
C39	C40	1.402(8)	C40	C41	1.362(5)
C41	C42	1.417(6)	C43	C44	1.404(5)
C44	C45	1.361(8)	C45	C46	1.388(6)
C46	C47	1.435(8)	C46	C54	1.408(5)
C47	C48	1.334(6)	C48	C49	1.424(5)
C49	C50	1.386(6)	C49	C53	1.415(8)
C50	C51	1.373(5)	C51	C52	1.398(8)
C53	C54	1.437(6)	C55	C56	1.396(5)
C56	C57	1.359(7)	C57	C58	1.399(6)
C58	C59	1.426(7)	C58	C66	1.416(5)
C59	C60	1.338(6)	C60	C61	1.424(6)
C61	C62	1.398(6)	C61	C65	1.405(7)
C62	C63	1.371(7)	C63	C64	1.388(7)
C65	C66	1.454(6)	C67	C68	1.512(8)
C68	C69	1.536(7)	C69	C70	1.501(7)
C71	C72	1.455(10)	C72	C73	1.512(5)
C73	C74	1.530(9)			

Table S7 Bond angles (°) for **1**·2(phen)·2(THF)

atom	atom	atom	angle	atom	atom	atom	angle
Na1	Ge1	Na2	173.53(6)	Na1	Ge1	O1	121.73(9)
Na1	Ge1	O2	51.97(7)	Na1	Ge1	O3	59.93(9)
Na1	Ge1	O4	131.04(7)	Na1	Ge1	O5	126.37(7)
Na1	Ge1	O6	48.67(6)	Na2	Ge1	O1	52.14(9)
Na2	Ge1	O2	125.95(7)	Na2	Ge1	O3	126.42(9)
Na2	Ge1	O4	53.75(7)	Na2	Ge1	O5	54.39(7)
Na2	Ge1	O6	127.26(7)	O1	Ge1	O2	86.92(10)
O1	Ge1	O3	173.47(11)	O1	Ge1	O4	87.44(12)
O1	Ge1	O5	87.06(10)	O1	Ge1	O6	98.02(12)
O2	Ge1	O3	90.01(11)	O2	Ge1	O4	97.33(11)
O2	Ge1	O5	170.35(14)	O2	Ge1	O6	86.95(11)
O3	Ge1	O4	87.23(12)	O3	Ge1	O5	96.72(11)
O3	Ge1	O6	87.57(12)	O4	Ge1	O5	89.93(11)
O4	Ge1	O6	173.26(13)	O5	Ge1	O6	86.42(10)
Ge1	Na1	O2	37.55(5)	Ge1	Na1	O6	37.14(7)
Ge1	Na1	O8	112.65(9)	Ge1	Na1	N1	151.26(9)
Ge1	Na1	N2	103.02(8)	O2	Na1	O6	65.67(8)
O2	Na1	O8	146.48(14)	O2	Na1	N1	113.71(10)
O2	Na1	N2	86.25(12)	O6	Na1	O8	98.46(10)
O6	Na1	N1	150.97(16)	O6	Na1	N2	83.93(12)
O8	Na1	N1	94.48(11)	O8	Na1	N2	122.77(14)
N1	Na1	N2	67.26(12)	Ge1	Na2	O1	37.77(7)
Ge1	Na2	O4	37.61(7)	Ge1	Na2	O5	37.91(5)
Ge1	Na2	O7	117.63(9)	Ge1	Na2	N3	111.47(7)
Ge1	Na2	N4	149.85(12)	O1	Na2	O4	63.94(10)
O1	Na2	O5	63.62(9)	O1	Na2	O7	96.32(12)
O1	Na2	N3	98.31(11)	O1	Na2	N4	163.86(12)
O4	Na2	O5	64.61(8)	O4	Na2	O7	155.20(12)
O4	Na2	N3	83.47(9)	O4	Na2	N4	115.57(13)
O5	Na2	O7	93.83(10)	O5	Na2	N3	147.58(9)
O5	Na2	N4	131.89(13)	O7	Na2	N3	115.73(11)
O7	Na2	N4	87.65(11)	N3	Na2	N4	66.05(11)
Ge1	O1	Na2	90.08(13)	Ge1	O1	C1	109.66(19)
Na2	O1	C1	140.7(2)	Ge1	O2	Na1	90.48(10)
Ge1	O2	C2	108.58(17)	Na1	O2	C2	127.8(3)
Ge1	O3	C15	109.48(19)	Ge1	O4	Na2	88.64(11)
Ge1	O4	C16	109.10(19)	Na2	O4	C16	140.8(2)

Table S7 *(continued)*

atom	atom	atom	angle	atom	atom	atom	angle
Ge1	O5	Na2	87.70(9)	Ge1	O5	C29	109.3(2)
Na2	O5	C29	136.0(2)	Ge1	O6	Na1	94.19(11)
Ge1	O6	C30	110.2(2)	Na1	O6	C30	142.5(2)
Na2	O7	C67	133.8(3)	Na2	O7	C70	121.19(18)
C67	O7	C70	104.9(3)	Na1	O8	C71	133.4(3)
Na1	O8	C74	121.0(2)	C71	O8	C74	105.5(4)
Na1	N1	C43	125.8(4)	Na1	N1	C54	115.0(2)
C43	N1	C54	117.6(3)	Na1	N2	C52	123.6(3)
Na1	N2	C53	116.1(3)	C52	N2	C53	117.4(5)
Na2	N3	C55	121.8(3)	Na2	N3	C66	120.0(2)
C55	N3	C66	117.1(3)	Na2	N4	C64	126.6(3)
Na2	N4	C65	116.8(3)	C64	N4	C65	116.4(4)
O1	C1	C2	116.7(4)	O1	C1	C14	121.0(3)
C2	C1	C14	122.3(4)	O2	C2	C1	117.9(4)
O2	C2	C3	121.4(3)	C1	C2	C3	120.7(4)
C2	C3	C4	121.3(4)	C2	C3	C8	118.8(3)
C4	C3	C8	119.9(4)	C3	C4	C5	121.1(4)
C4	C5	C6	120.1(3)	C5	C6	C7	119.9(4)
C6	C7	C8	121.6(5)	C3	C8	C7	117.4(3)
C3	C8	C9	120.3(4)	C7	C8	C9	122.3(4)
C8	C9	C10	124.1(4)	C8	C9	C14	119.3(4)
C10	C9	C14	116.5(3)	C9	C10	C11	122.4(5)
C10	C11	C12	120.0(5)	C11	C12	C13	119.9(3)
C12	C13	C14	120.7(4)	C1	C14	C9	118.3(3)
C1	C14	C13	121.3(4)	C9	C14	C13	120.4(4)
O3	C15	C16	116.6(4)	O3	C15	C28	121.8(3)
C16	C15	C28	121.5(4)	O4	C16	C15	117.5(4)
O4	C16	C17	122.1(3)	C15	C16	C17	120.3(4)
C16	C17	C18	120.7(4)	C16	C17	C22	119.6(3)
C18	C17	C22	119.5(4)	C17	C18	C19	120.2(4)
C18	C19	C20	120.5(3)	C19	C20	C21	120.5(4)
C20	C21	C22	120.8(4)	C17	C22	C21	118.3(3)
C17	C22	C23	119.7(4)	C21	C22	C23	121.9(4)
C22	C23	C24	123.6(4)	C22	C23	C28	118.0(4)
C24	C23	C28	118.5(3)	C23	C24	C25	121.4(5)
C24	C25	C26	120.4(5)	C25	C26	C27	119.4(4)
C26	C27	C28	122.0(4)	C15	C28	C23	120.1(3)

Table S7 *(finished)*

atom	atom	atom	angle	atom	atom	atom	angle
C15	C28	C27	121.6(4)	C23	C28	C27	118.2(4)
O5	C29	C30	117.3(3)	O5	C29	C42	123.0(4)
C30	C29	C42	119.7(4)	O6	C30	C29	116.6(3)
O6	C30	C31	121.1(3)	C29	C30	C31	122.3(3)
C30	C31	C32	120.5(3)	C30	C31	C36	119.2(3)
C32	C31	C36	120.3(4)	C31	C32	C33	119.9(3)
C32	C33	C34	120.2(4)	C33	C34	C35	120.6(4)
C34	C35	C36	121.4(3)	C31	C36	C35	117.6(4)
C31	C36	C37	119.1(4)	C35	C36	C37	123.3(3)
C36	C37	C38	122.5(4)	C36	C37	C42	119.3(3)
C38	C37	C42	118.1(4)	C37	C38	C39	121.5(4)
C38	C39	C40	120.4(4)	C39	C40	C41	119.6(4)
C40	C41	C42	121.5(4)	C29	C42	C37	119.8(4)
C29	C42	C41	121.7(4)	C37	C42	C41	118.5(3)
N1	C43	C44	124.2(5)	C43	C44	C45	117.7(4)
C44	C45	C46	120.6(4)	C45	C46	C47	122.4(4)
C45	C46	C54	118.1(5)	C47	C46	C54	119.5(4)
C46	C47	C48	120.8(4)	C47	C48	C49	121.9(5)
C48	C49	C50	122.7(5)	C48	C49	C53	119.1(4)
C50	C49	C53	118.2(4)	C49	C50	C51	120.2(5)
C50	C51	C52	117.4(4)	N2	C52	C51	125.0(4)
N2	C53	C49	121.8(4)	N2	C53	C54	118.8(5)
C49	C53	C54	119.3(3)	N1	C54	C46	121.7(4)
N1	C54	C53	118.9(3)	C46	C54	C53	119.3(5)
N3	C55	C56	124.5(4)	C55	C56	C57	118.4(4)
C56	C57	C58	120.0(4)	C57	C58	C59	123.3(4)
C57	C58	C66	117.1(4)	C59	C58	C66	119.7(4)
C58	C59	C60	121.4(4)	C59	C60	C61	121.2(5)
C60	C61	C62	122.8(4)	C60	C61	C65	119.8(4)
C62	C61	C65	117.5(4)	C61	C62	C63	119.7(5)
C62	C63	C64	118.2(4)	N4	C64	C63	125.1(4)
N4	C65	C61	123.1(4)	N4	C65	C66	117.5(4)
C61	C65	C66	119.4(3)	N3	C66	C58	122.9(4)
N3	C66	C65	118.6(3)	C58	C66	C65	118.5(4)
O7	C67	C68	106.5(4)	C67	C68	C69	104.4(3)
C68	C69	C70	102.8(5)	O7	C70	C69	104.8(3)
O8	C71	C72	107.5(4)	C71	C72	C73	104.2(5)
C72	C73	C74	104.2(5)	O8	C74	C73	106.1(3)

Table S8 Intramolecular contacts less than 3.60 Å for **1**·2(phen)·2(THF)

atom	atom	distance	atom	atom	distance
O1	C13	2.859(6)	O1	C29	3.271(4)
O1	C30	3.389(4)	O2	C4	2.879(5)
O2	C15	3.336(6)	O2	C16	3.393(6)
O3	O8	3.427(4)	O3	C27	2.870(6)
O3	C29	3.445(4)	O3	C30	3.350(5)
O3	C74	3.537(5)	O4	C1	3.361(6)
O4	C2	3.466(6)	O4	C18	2.867(6)
O4	C55	3.530(4)	O5	C15	3.467(4)
O5	C16	3.403(5)	O5	C41	2.907(4)
O6	C1	3.382(4)	O6	C2	3.251(4)
O6	C32	2.842(5)	O6	C52	3.211(6)
N1	C45	2.783(5)	N2	C2	3.434(5)
N2	C3	3.437(5)	N2	C4	3.422(5)
N2	C50	2.788(7)	N3	C18	3.537(6)
N3	C57	2.790(5)	N4	C62	2.798(6)
N4	C67	3.571(7)	C1	C8	2.816(6)
C2	C9	2.839(7)	C2	C52	3.390(6)
C3	C6	2.798(6)	C3	C14	2.863(4)
C3	C52	3.488(6)	C4	C7	2.771(7)
C4	C49	3.547(7)	C4	C53	3.167(6)
C4	C54	3.368(5)	C5	C8	2.823(5)
C5	C48	3.516(7)	C5	C49	3.445(6)
C5	C53	3.501(5)	C5	C54	3.579(5)
C7	C10	3.001(5)	C9	C12	2.818(5)
C10	C13	2.763(7)	C11	C14	2.780(7)
C15	C22	2.817(6)	C16	C23	2.846(7)
C17	C20	2.784(7)	C17	C28	2.837(5)
C18	C21	2.780(7)	C19	C22	2.801(5)
C21	C24	2.990(5)	C23	C26	2.809(5)
C24	C27	2.754(7)	C25	C28	2.793(7)
C29	C36	2.850(6)	C30	C37	2.812(4)
C31	C34	2.779(6)	C31	C42	2.838(6)
C32	C35	2.779(5)	C32	C52	3.491(6)
C32	C74	3.583(8)	C33	C36	2.810(6)
C35	C38	2.985(6)	C37	C40	2.812(6)
C38	C41	2.769(7)	C39	C42	2.797(5)
C42	C70	3.585(6)	C43	C46	2.721(8)
C44	C54	2.746(6)	C46	C49	2.820(6)
C47	C53	2.819(5)	C48	C54	2.813(8)
C49	C52	2.715(5)	C51	C53	2.746(6)
C55	C58	2.723(6)	C56	C66	2.724(6)
C58	C61	2.819(6)	C59	C65	2.816(6)
C60	C66	2.826(7)	C61	C64	2.721(6)
C63	C65	2.727(6)	C64	C67	3.588(9)

Table S9 Intermolecular contacts less than 3.60 Å for **1**·2(phen)·2(THF)

atom	atom	distance	atom	atom	distance
O5	C60[1]	3.470(7)	N3	C68[2]	3.481(5)
C2	C44[3]	3.599(5)	C3	C43[3]	3.594(6)
C3	C44[3]	3.252(6)	C4	C43[3]	3.320(6)
C4	C44[3]	3.444(6)	C5	C43[3]	3.338(7)
C8	C44[3]	3.595(8)	C10	C34[4]	3.576(6)
C11	C73[5]	3.587(9)	C13	C26[5]	3.570(7)
C16	C60[1]	3.541(6)	C17	C47[3]	3.426(5)
C18	C47[3]	3.596(4)	C20	C40[6]	3.516(5)
C21	C35[7]	3.566(6)	C22	C47[3]	3.498(6)
C24	C70[7]	3.560(7)	C25	C70[7]	3.570(7)
C26	C13[7]	3.570(7)	C26	C51[7]	3.527(4)
C34	C10[8]	3.576(6)	C35	C21[5]	3.566(6)
C35	C56[8]	3.416(8)	C36	C56[8]	3.559(7)
C37	C56[8]	3.528(6)	C37	C57[8]	3.415(7)
C38	C56[8]	3.471(6)	C38	C57[8]	3.242(7)
C39	C57[8]	3.497(6)	C40	C20[1]	3.516(5)
C43	C3[3]	3.594(6)	C43	C4[3]	3.320(6)
C43	C5[3]	3.338(7)	C44	C2[3]	3.599(5)
C44	C3[3]	3.252(6)	C44	C4[3]	3.444(6)
C44	C8[3]	3.595(8)	C47	C17[3]	3.426(5)
C47	C18[3]	3.596(4)	C47	C22[3]	3.498(6)
C51	C26[5]	3.527(4)	C56	C35[4]	3.416(8)
C56	C36[4]	3.559(7)	C56	C37[4]	3.528(6)
C56	C38[4]	3.471(6)	C57	C37[4]	3.415(7)
C57	C38[4]	3.242(7)	C57	C39[4]	3.497(6)
C59	C64[6]	3.550(6)	C60	O5[6]	3.470(7)
C60	C16[6]	3.541(6)	C64	C59[1]	3.550(6)
C66	C68[2]	3.421(7)	C68	N3[2]	3.481(5)
C68	C66[2]	3.421(7)	C70	C24[5]	3.560(7)
C70	C25[5]	3.570(7)	C73	C11[7]	3.587(9)

Symmetry Operators:

(1) -X,Y+1/2-1,-Z+1/2-1
(2) -X,-Y,-Z-1
(3) -X+1,-Y,-Z
(4) X,Y+1,Z
(5) X,-Y,Z
(6) -X,Y+1/2,-Z+1/2-1
(7) X,-Y,Z+1
(8) X,Y-1,Z

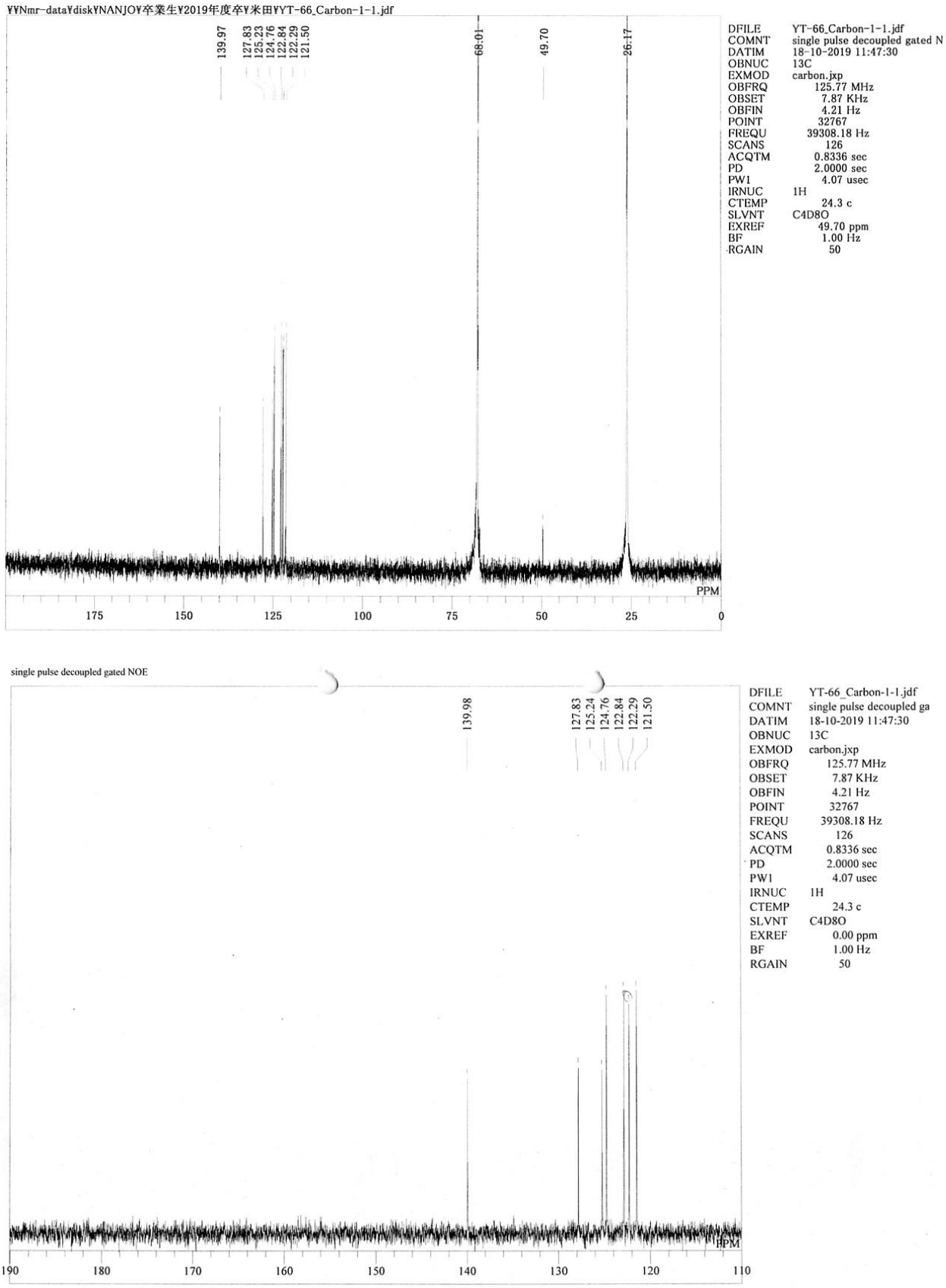

Figure S1 $^{13}C\{^{1}H\}$ NMR spectra of **1** in THF-d_8. Lower: expansion ranging from 110- 190 ppm.

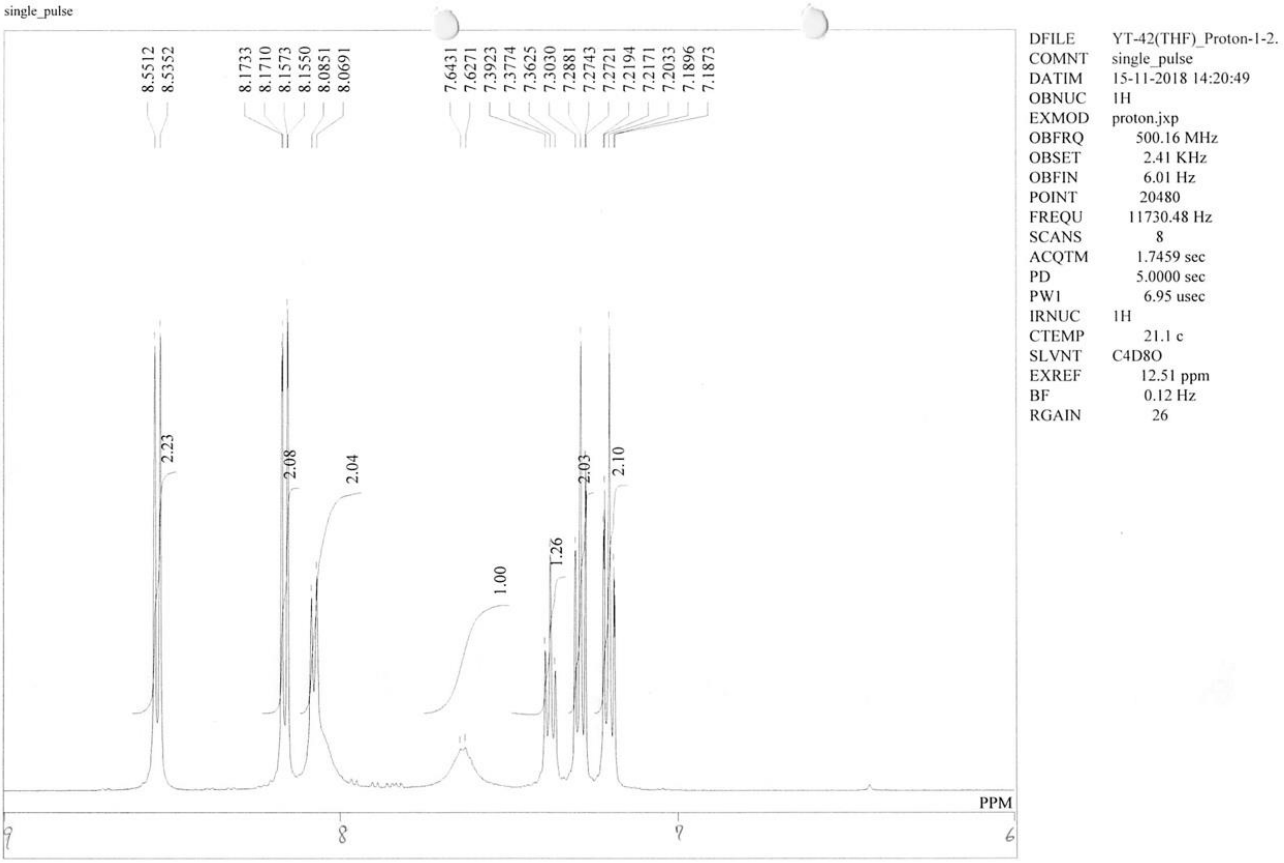

Figure S2 ^{1}H NMR spectrum of **1**·2(PQ) in THF-d_8.

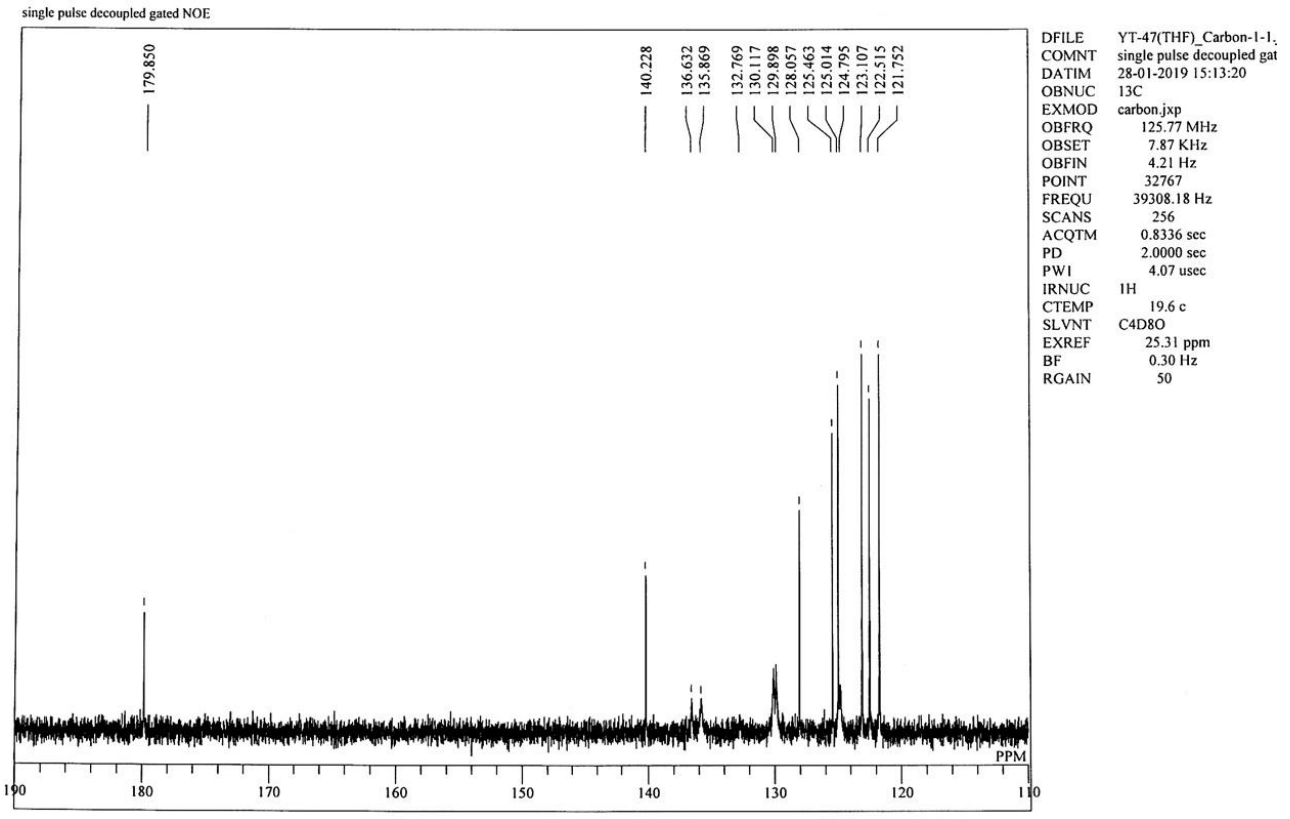

Figure S3 $^{13}C\{^{1}H\}$ NMR spectrum of **1**·2(PQ) in THF-d_8.

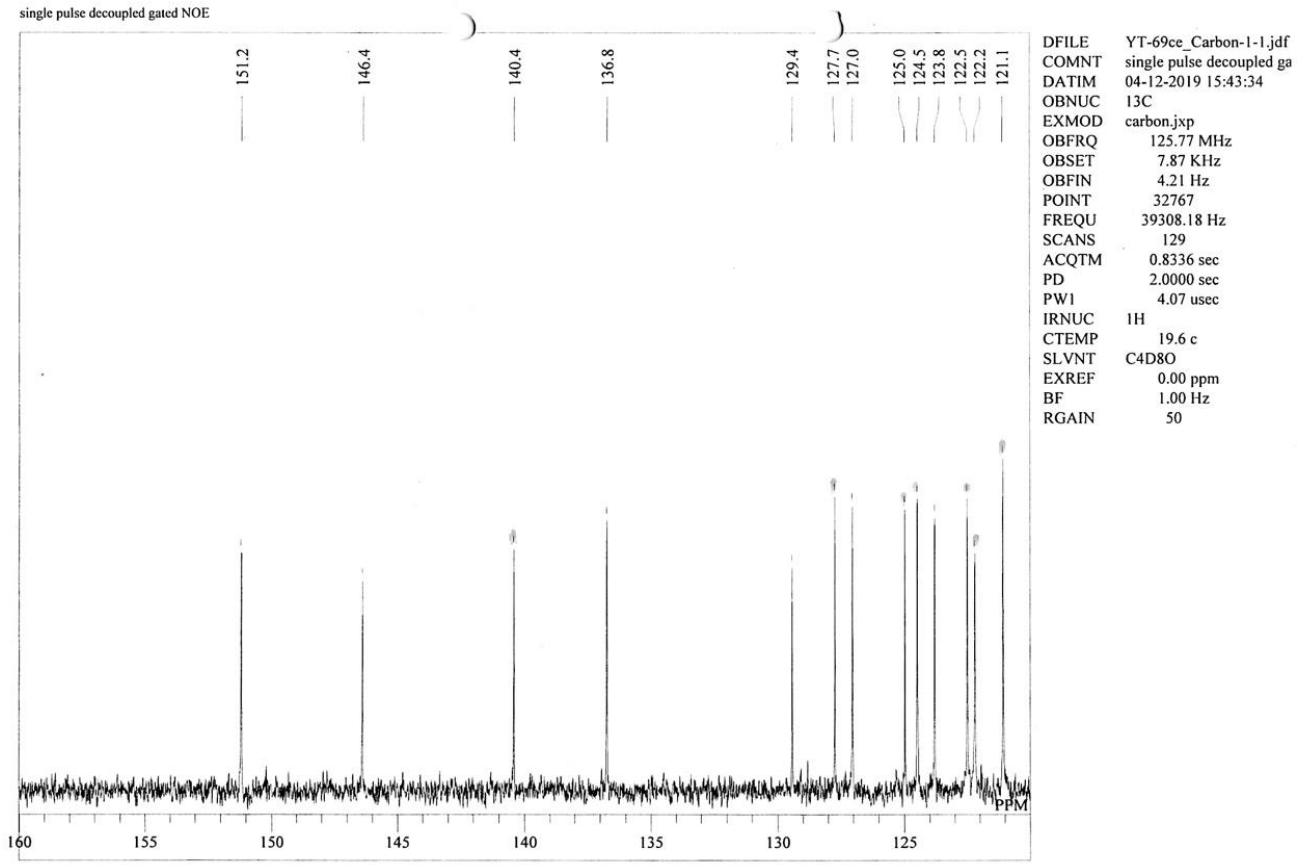

Figure S4 $^{13}C\{^{1}H\}$ NMR spectrum of **1**·2(phen)·2(THF) in THF-d_8.

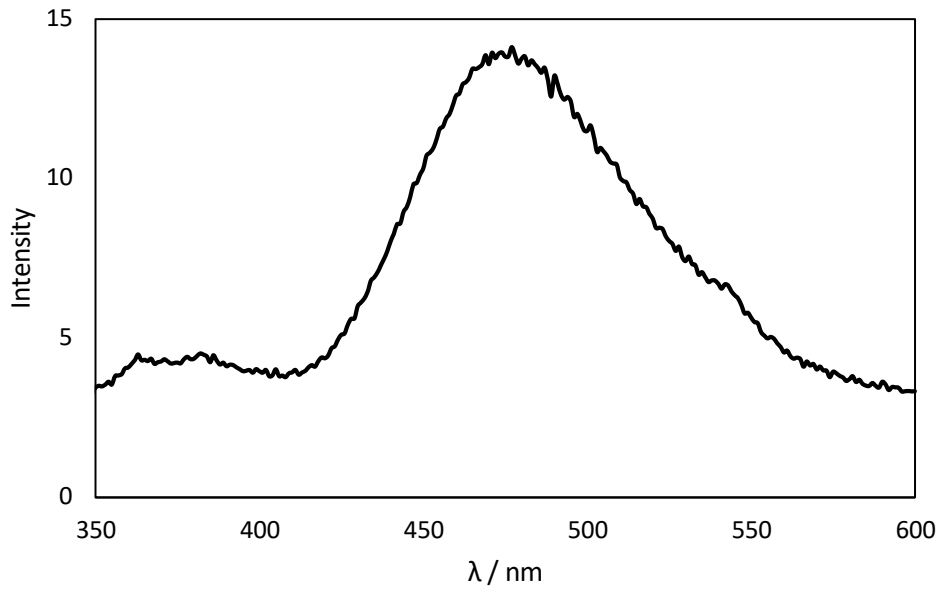

Figure S5 Fluorescence spectrum of **1** without PQ in THF at room temperature. Excitation wavelength is 330 nm. The sample was prepared by dissolving the greenish brown solid, which was synthesized by the methods of ii and iii in Scheme 1(see main text), in THF in a glove box under argon atmosphere.