Supporting Information for

Reactivity Studies Involving a Lewis Base Supported Terminal Uranium Phosphinidene Metallocene [η^5-1,3-$(Me_3C)_2C_5H_3]_2U(=P\text{-}2,4,6\text{-}{}^{i}Pr_3C_6H_2)(OPMe_3)$

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1. Figures

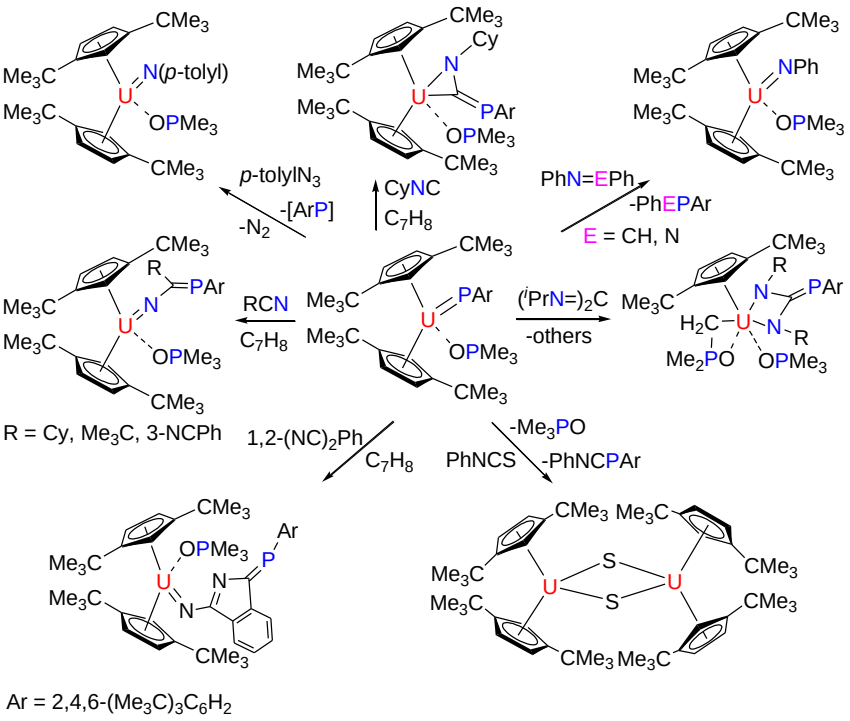

Figure S1. Selected reactivity of [η^5-1,3-$(Me_3C)_2C_5H_3]_2$U(=P-2,4,6-^{t}Bu$_3$Ph)(OPMe$_3$).

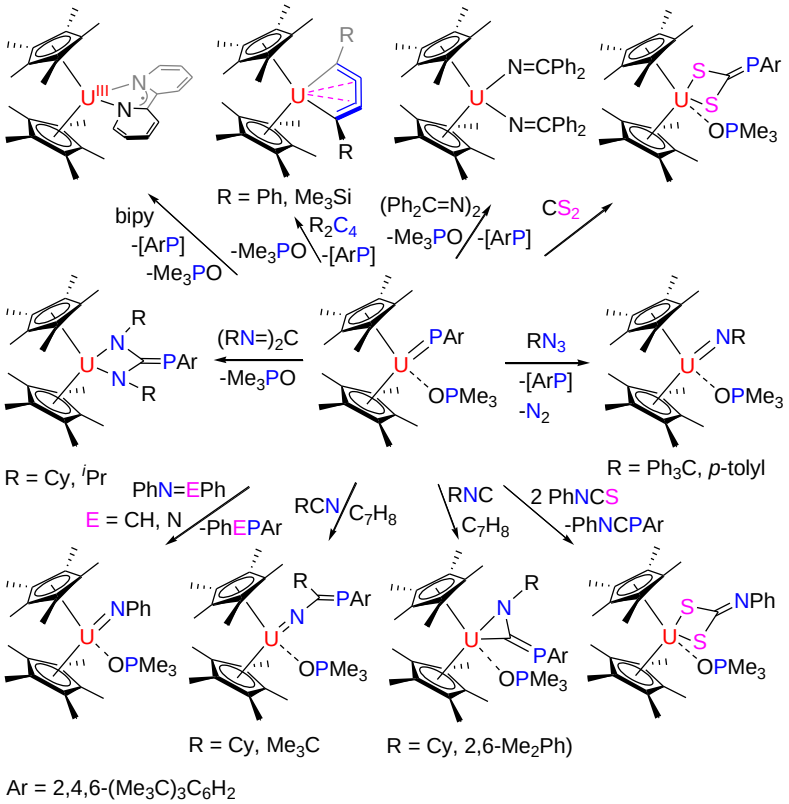

Figure S2. Selected reactivity of (η^5-$C_5Me_5)_2$U(=P-2,4,6-^{t}Bu$_3$Ph)(OPMe$_3$).

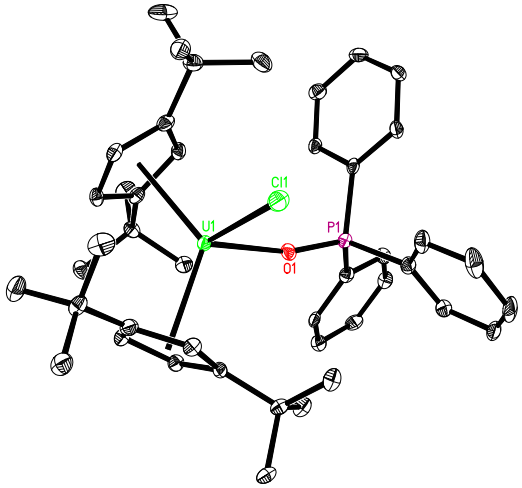

Figure S3. Molecular structure of **5** (thermal ellipsoids drawn at the 35% probability level).

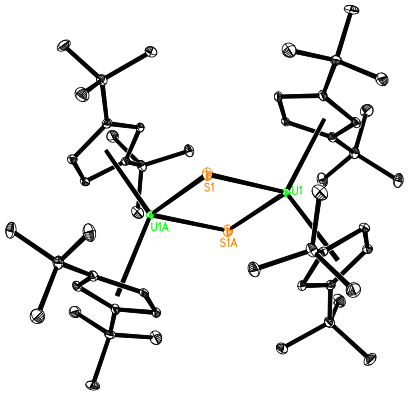

Figure S4. Molecular structure of **8** (thermal ellipsoids drawn at the 35% probability level). Selected bond lengths (Å) and angles (º): U-C(Cp) (av.) 2.774(4), U-C(Cp) (range) 2.707(4) to 2.827(4), U-Cp (cent) (av.) 2.523(4), U-S(1) 2.598(1), U-S(1A) 2.598(1), Cp(cent)-U-Cp(cent) 121.4(2), S(1)-U-S(1A) 85.5(1).

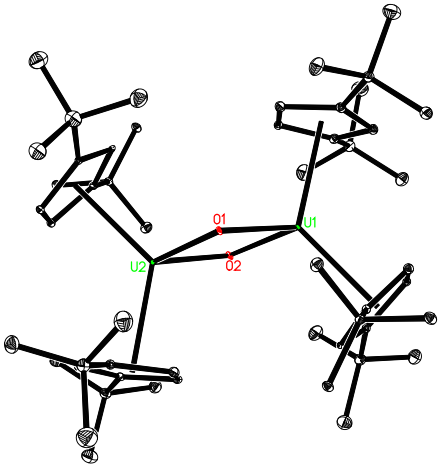

Figure S5. Molecular structure of **9** (thermal ellipsoids drawn at the 35% probability level). Selected bond lengths (Å) and angles (º): U-C(Cp) (av.) 2.801(6), U-C(Cp) (range) 2.720(6) to 2.859(6), U-Cp (cent) (av.) 2.528(6), U-O(1) 2.117(4), U-O(2) 2.128(4), Cp(cent)-U-Cp(cent) 123.8(2), O(1)-U-O(2) 73.7(2).

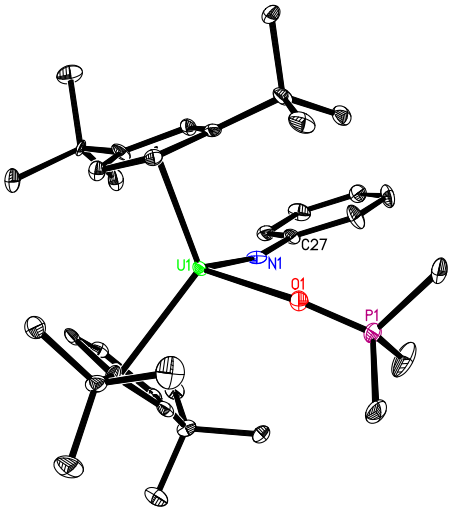

Figure S6. Molecular structure of **10** (thermal ellipsoids drawn at the 35% probability level). Selected bond lengths (Å) and angles (º): U-C(Cp) (av.) 2.807(9), U-C(Cp) (range) 2.760(9) to 2.860(9), U-Cp (cent) (av.) 2.534(9), U-N(1) 2.018(7), U-O(1) 2.381(6), Cp(cent)-U-Cp(cent) 120.9(2), N(1)-U-N(3) 93.2(3).

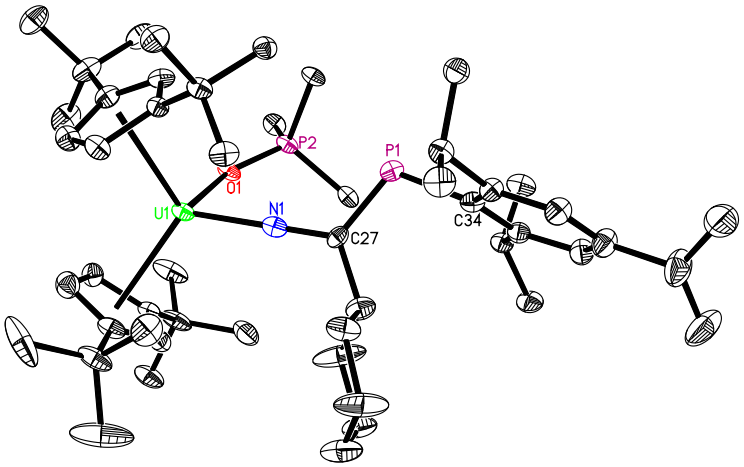

Figure S7. Molecular structure of **13** (thermal ellipsoids drawn at the 35% probability level).

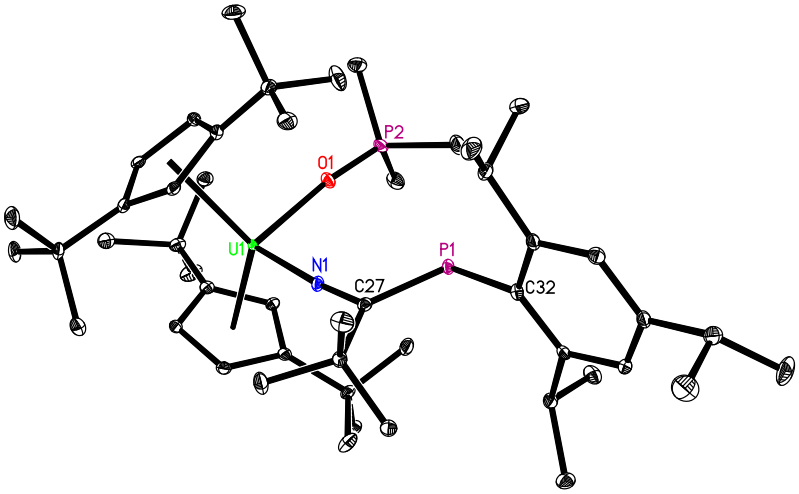

Figure S8. Molecular structure of **14** (thermal ellipsoids drawn at the 35% probability level).

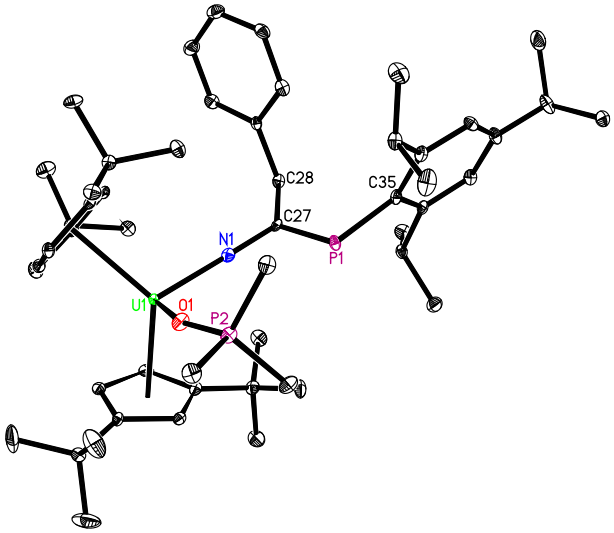

Figure S9. Molecular structure of **15** (thermal ellipsoids drawn at the 35% probability level).

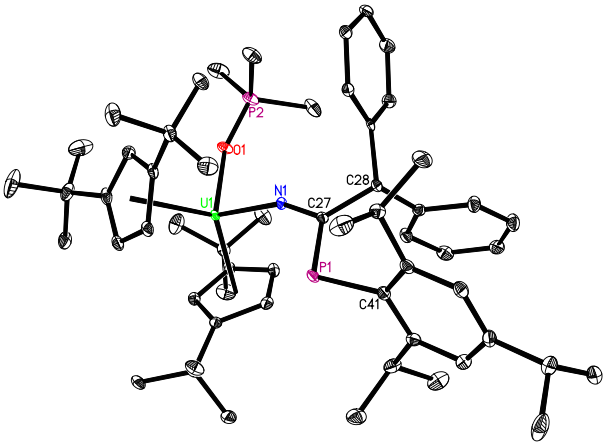

Figure S10. Molecular structure of **16** (thermal ellipsoids drawn at the 35% probability level).

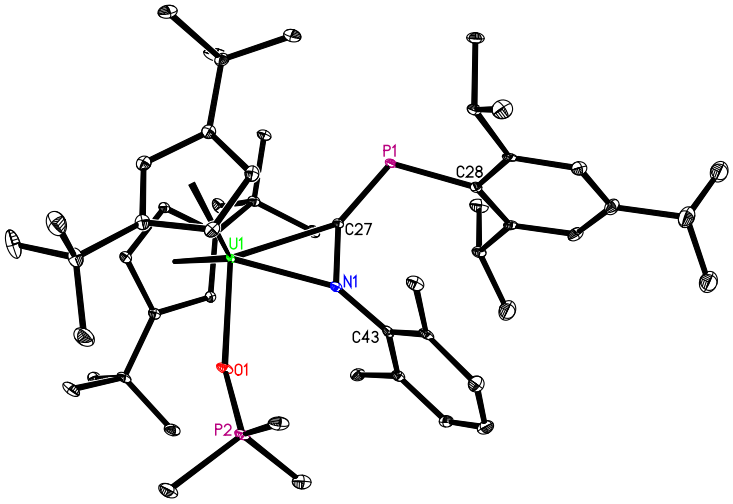

Figure S11. Molecular structure of **19** (thermal ellipsoids drawn at the 35% probability level).

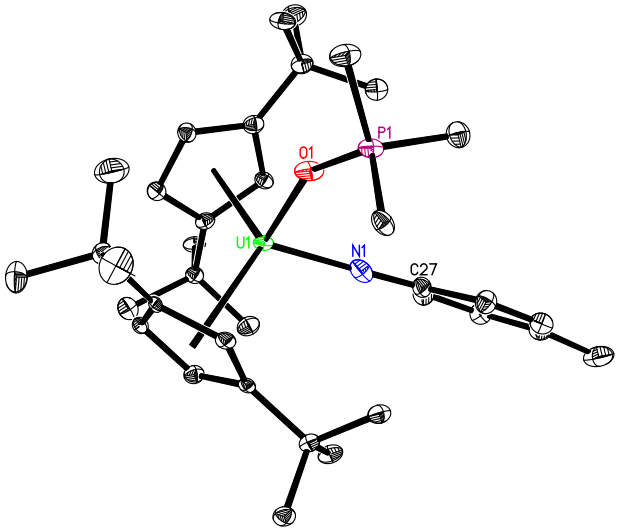

Figure S12. Molecular structure of **21** (thermal ellipsoids drawn at the 35% probability level). Selected bond lengths (Å) and angles (°): U-C(Cp) (av.) 2.813(14), U-C(Cp) (range) 2.764(14) to 2.857(13), U-Cp (cent) (av.) 2.543(14), U-N(1) 2.017(15), U-O(1) 2.366(9), Cp(cent)-U-Cp(cent) 123.2(4), N(1)-U-O(1) 92.0(5).

2. Crystallographic details

Table S1. Crystal Data and Experimental Parameters for Compounds 2-5 and 7

Compound	**2**	**3**	**4**	**5**	**7**
Formula	$C_{44}H_{74}OP_2U$	$C_{29}H_{51}ClOPU$	$C_{44}H_{75}OP_2U$	$C_{44}H_{57}ClOPU$	$C_{45}H_{74}OP_2S_2U$
Fw	919.00	720.14	920.01	906.34	995.13
crystal system	triclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	*P*(-1)	$P2_1/c$	*P*(-1)	$P2_1/c$	$P2_1/c$
a (Å)	11.247(1)	10.301(1)	11.251(1)	12.347(1)	15.280(1)
b (Å)	13.893(1)	11.966(1)	14.129(1)	14.211(1)	13.768(1)
c (Å)	15.359(1)	29.155(1)	15.855(1)	22.653(1)	25.981(1)
α (deg)	77.53(1)	90	75.74(1)	90	90
β (deg)	76.19(1)	90.58(1)	75.71(1)	95.04(1)	100.72(1)
γ (deg)	75.64(1)	90	70.89(1)	90	90
V (Å^3)	2226.10(18)	3593.41(9)	2269.78(18)	3959.52(15)	5370.41(16)
Z	2	4	2	4	4
D_{calc} (g/cm^3)	1.371	1.331	1.346	1.520	1.231
μ(Mo/Kα)$_{calc}$ (cm^{-1})	11.147	13.922	10.932	12.771	9.988
size (mm)	0.20 × 0.20 × 0.20	0.22 × 0.20 × 0.20	0.20 × 0.15 × 0.15	0.15 × 0.10 × 0.10	0.25 × 0.20 × 0.20
F(000)	936	1428	938	1812	2024
2θ range (deg)	8.20 to 144.27	7.99 to 146.82	8.08 to 146.53	7.19 to 146.58	7.29 to 146.67
no. of reflns, collected	15665	14337	15817	16232	22019
no of obsd reflns	8521	7007	8808	7706	10456
no of variables	448	344	458	445	481
abscorr (T_{max}, T_{min})	1.00, 0.28	1.00, 0.20	1.00, 0.74	1.00, 0.95	1.00, 0.58
R	0.036	0.028	0.033	0.039	0.031
R_w	0.088	0.072	0.078	0.081	0.073
R_{all}	0.040	0.030	0.036	0.056	0.033
Gof	1.04	1.05	1.03	1.01	1.06
CCDC	2043085	2043084	2043082	2043083	2043090

Table S2. Crystal Data and Experimental Parameters for Compounds 8-12

Compound	**8** C_6H_6	**9**	**10**	**11** $2C_6H_6$	**12**
Formula	$C_{58}H_{90}S_2U_2$	$C_{52}H_{84}O_2U_2$	$C_{35}H_{56}NOPU$	$C_{62}H_{104}N_4O_2P_4U$	$C_{51}H_{79}NOP_2U$
Fw	1327.47	1217.25	775.80	1299.40	1022.12
crystal system	triclinic	triclinic	monoclinic	monoclinic	triclinic
space group	*P*(-1)	*P*(-1)	$P2_1/n$	*C*2/*c*	*P*(-1)
a (Å)	10.450(1)	10.634(1)	12.970(1)	19.940(1)	11.667(1)
b (Å)	10.809(1)	12.116(1)	18.103(1)	11.201(1)	15.266(1)
c (Å)	14.090(1)	30.283(1)	14.668(1)	31.836(1)	15.515(1)
α (deg)	102.13(1)	94.38(1)	90	90	91.56(1)
β (deg)	105.06(1)	97.42(1)	95.73(1)	104.18(1)	101.18(1)
γ (deg)	107.47(1)	105.27(1)	90	90	105.64(1)
V (Å^3)	1392.50(9)	3707.4(2)	3426.83(18)	6893.96(19)	2601.23(10)
Z	1	3	4	4	2
D_{calc} (g/cm^3)	1.583	1.636	1.504	1.252	1.305
μ(Mo/Kα)$_{calc}$ (cm^{-1})	17.179	18.558	13.953	7.802	9.601
size (mm)	0.15 × 0.10 × 0.10	0.20 × 0.15 × 0.15	0.20 × 0.10 × 0.10	0.10 × 0.10 × 0.10	0.22 × 0.20 × 0.20
F(000)	654	1788	1552	2688	1044
2θ range (deg)	6.84 to 146.36	7.61 to 144.21	7.78 to 144.25	9.12 to 143.93	8.03 to 146.76
no. of reflns, collected	9560	26527	13003	13953	18305
no of obsd reflns	5400	14188	6534	6609	10143
no of variables	292	787	367	343	526
abscorr (T_{max}, T_{min})	1.00, 0.70	1.00, 0.26	1.00, 0.19	1.00, 0.84	1.00, 0.63
R	0.024	0.052	0.049	0.026	0.021
R_w	0.058	0.139	0.127	0.062	0.052
R_{all}	0.027	0.057	0.062	0.027	0.022
Gof	1.05	1.08	1.08	1.06	1.03
CCDC	2043100	2043098	2043097	2043089	2043086

Table S3. Crystal Data and Experimental Parameters for Compounds 13-17

Compound	**13**	**14**	**15** C_6H_6	**16**	**17** C_6H_6
Formula	$C_{51}H_{85}NOP_2U$	$C_{49}H_{83}NOP_2U$	$C_{58}H_{87}NOP_2U$	$C_{58}H_{85}NOP_2U$	$C_{58}H_{84}N_2OP_2U$
Fw	1028.16	1002.13	1114.25	1112.23	1125.24
crystal system	triclinic	triclinic	triclinic	triclinic	triclinic
space group	*P*(-1)	*P*(-1)	*P*(-1)	*P*(-1)	*P*(-1)
a (Å)	11.606(1)	11.356(1)	12.586(1)	11.262(1)	10.546(1)
b (Å)	15.480(1)	13.680(1)	13.482(1)	12.890(1)	16.111(1)
c (Å)	15.806(1)	17.553(1)	17.716(1)	20.103(1)	17.255(1)
α (deg)	92.42(1)	71.81(1)	88.64(1)	101.40(1)	97.18(1)
β (deg)	101.44(1)	79.05(1)	88.14(1)	105.08(1)	101.00(1)
γ (deg)	106.28(1)	89.35(1)	66.66(1)	93.69(1)	104.74(1)
V (Å^3)	2657.10(14)	2540.2(3)	2758.48(15)	2741.27(12)	2736.20(13)
Z	2	2	2	2	2
D_{calc} (g/cm^3)	1.285	1.310	1.342	1.347	1.366
μ(Mo/Kα)$_{calc}$ (cm^{-1})	9.400	9.818	9.100	9.157	9.186
size (mm)	0.25 × 0.15 × 0.15	0.25 × 0.20 × 0.20	0.25 × 0.20 × 0.20	0.20 × 0.20 × 0.20	0.20 × 0.10 × 0.10
F(000)	1056	1028	1144	1140	1152
2θ range (deg)	3.85 to 146.86	6.81 to 144.05	7.14 to 144.25	7.54 to 144.24	7.09 to 144.07
no. of reflns, collected	18901	18481	19743	20261	19818
no of obsd reflns	10311	9733	10577	10521	10479
no of variables	526	511	620	589	597
abscorr (T_{max}, T_{min})	1.00, 0.51	1.00, 0.20	1.00, 0.17	1.00, 0.60	1.00, 0.31
R	0.042	0.027	0.035	0.029	0.046
R_w	0.099	0.070	0.091	0.076	0.115
R_{all}	0.046	0.028	0.036	0.031	0.051
Gof	1.03	1.04	1.04	1.05	1.03
CCDC	2043087	2043095	2043088	2043091	2043096

Table S4. Crystal Data and Experimental Parameters for Compounds 18-21

Compound	**18**	**19**	**20**	**21**
Formula	$C_{51}H_{85}NOP_2U$	$C_{53}H_{83}NOP_2U$	$C_{44}H_{74}NOP_2U$	$C_{36}H_{58}NOPU$
Fw	1028.16	1050.17	933.01	789.83
crystal system	triclinic	monoclinic	monoclinic	triclinic
space group	*P*(-1)	$P2_1/c$	$P2_1/n$	*P*(-1)
a (Å)	11.752(1)	15.553(1)	10.994(1)	14.784(1)
b (Å)	13.649(1)	16.812(1)	27.269(1)	15.469(1)
c (Å)	18.397(1)	21.001(1)	15.125(1)	16.204(1)
α (deg)	102.13(1)	90	90	106.61(1)
β (deg)	96.59(1)	106.74(1)	90.18(1)	96.41(1)
γ (deg)	108.99(1)	90	90	94.75(1)
V (Å^3)	2674.04(11)	5258.50(11)	4534.12(6)	3503.3(3)
Z	2	4	4	4
D_{calc} (g/cm^3)	1.277	1.326	1.367	1.498
μ(Mo/Kα)$_{calc}$ (cm^{-1})	9.340	9.513	10.961	13.659
size (mm)	0.22 ×0.20 ×0.20	0.20 ×0.20 ×0.20	0.25 ×0.20 ×0.20	0.10 ×0.10 ×0.10
F(000)	1056	2152	1900	1584
2θ range (deg)	7.10 to 146.76	7.93 to 144.15	8.67 to 144.69	6.97 to 144.28
no. of reflns, collected	19244	20189	30427	25957
no of obsd reflns	10417	10088	8686	13410
no of variables	526	539	463	741
abscorr (T_{max}, T_{min})	1.00, 0.55	1.00, 0.30	1.00, 0.42	1.00, 0.26
R	0.025	0.030	0.024	0.085
R_w	0.060	0.079	0.061	0.217
R_{all}	0.027	0.032	0.025	0.107
Gof	1.02	1.06	1.11	1.03
CCDC	2043093	2043092	2043094	2043099