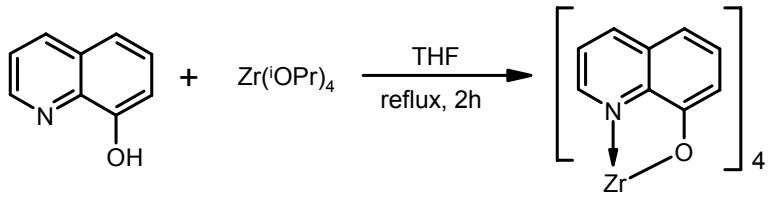
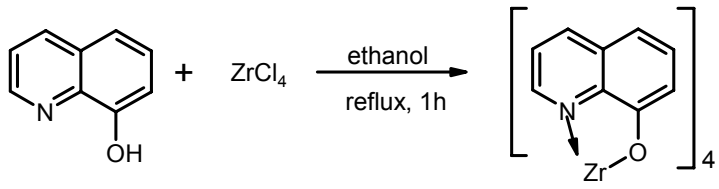
Preparation of Zirconium tetrakis(8-hydroxyquinolinate) [α-ZrQ_4]



8-Hydroxyquinoline, 99+% (Aldrich) (100 g; 0.69 mole) was dissolved in tetrahydrofuran, 99+% (ACS reagent) (400 ml). To the magnetically stirred solution was added zirconium isopropoxide (66.8 g; 0.17 mole) in tetrahydrofuran (175 ml), all at once. A yellow precipitate formed immediately. The reaction mixture was magnetically stirred and refluxed under nitrogen for 2 hours. After cooling the reaction mixture in the refrigerator the product was filtered off under suction, washed with fresh tetrahydrofuran and dried under vacuum at 80 °C for 10 hours. Yield 101 g (88 %), mp 388 °C (DSC, onset). The product was sublimed at 340 °C (2 x 10^{-6} Torr) to give a sublimation yield of 91 %. Overall yield was 81%. Found: C; 64.49, H; 3.57, N; 8.33, Zr; 13.79, Cl < 0.10. $C_{36}H_{24}N_4O_4Zr$ requires, C; 64.75, H; 3.62, N; 8.39, Zr; 13.66 %. The trace elements analysis: Fe <1 ppm, Cr<1 ppm, Co<1 ppm, Co <1 ppm, Ni< 1 ppm, Al<1 ppm, Cu <1 ppm, Mo < 1 ppm, Ta < 25 ppm , Pt < 1 ppm, Ti < 2 ppm, Hf 5 ppm and W < 1ppm.

Preparation of Zirconium tetrakis(8-hydroxyquinolinate) [β-ZrQ_4]



Ethanol was dried over potassium hydroxide and distilled before use.
To a solution of 8-hydroxyquinoline (100.0 g; 0.69 mol) in ethanol, 95% (700 ml) was carefully added zirconium (IV) chloride (40.2 g; 0.17 mol) in ethanol (200 ml) at 10 °C (The solution was cooled in an ice-water bath). After 10 minutes, the solution was warmed to 50 °C and piperidine (75 ml; 0.76 mole) was slowly added, during which time a yellow precipitate separated out. The suspension was refluxed for 1h, and allowed to cool to room temperature. The precipitate was collected by suction filtration on a Buchner funnel, washed thoroughly with ethanol, tetrahydrofuran and finally with diethyl ether. The product was dried under vacuum at 80 °C. Crude yield 106.5 g (93 %). Further purification of the product (65 g) was performed by Soxhlet extraction (65 g) with 1,4-dioxane for 24 h. Concentration of the extract yielded a yellow precipitate which was collected on a Buchner funnel and washed with ethanol, (95%; 100 ml). The product was dried under vacuum at 80 °C for 8h. Yield, 50 g (77 %), mp., 388 °C (DSC, onset). The product was further purified by sublimation to give a sublimed yield of 92 %. Overall yield was 66 %. Found C 64.42, H 3.58, N 8.16 ,Zr 13.54 , Cl < 0.10. $C_{36}H_{24}N_4O_4Zr$ requires, C 64.75, H 3.62, N 8.39 and Zr13.66 %. The trace elements analysis: Fe 5ppm, Cr<1ppm, Co<1ppm, Ni <1ppm, Al <1ppm, Cu < 1ppm, Mo<1 ppm, Ta 23 ppm, Pt < 1ppm, Ti<1 ppm, Hf 6ppm, W< 1ppm.

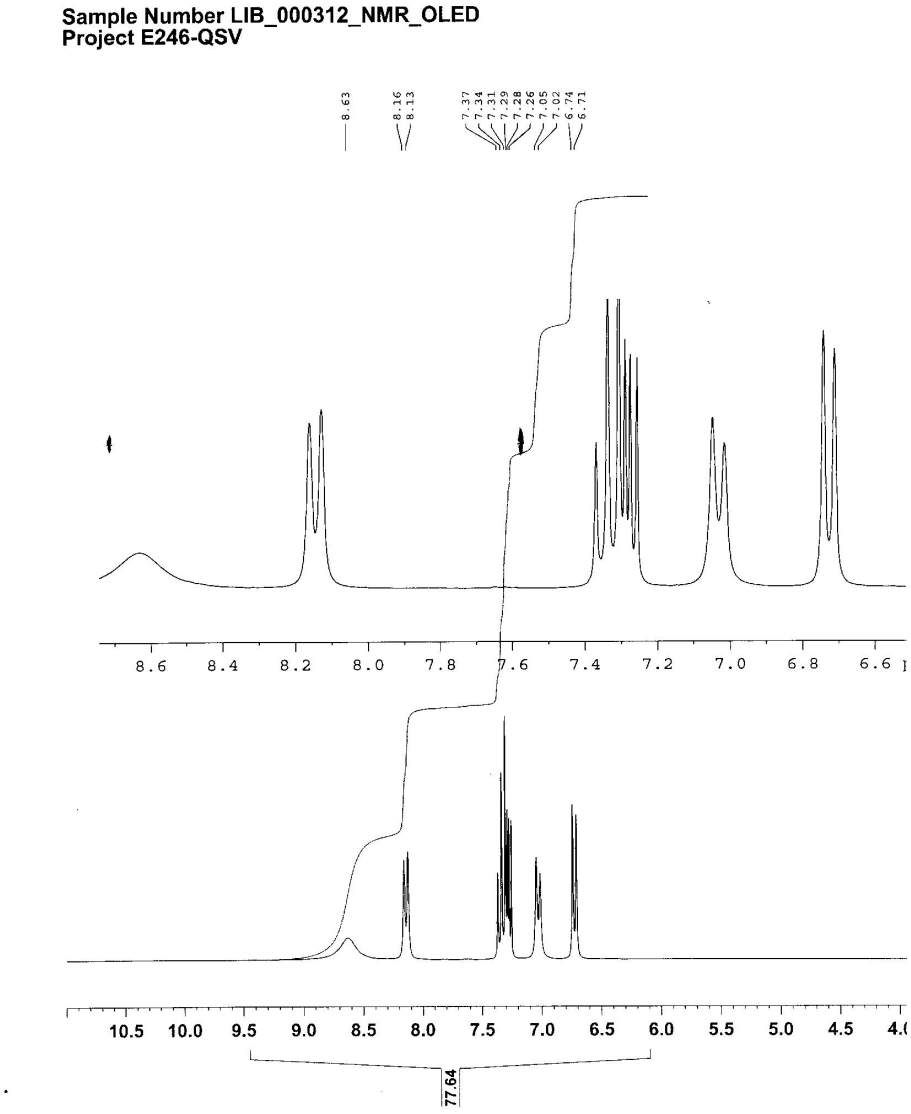


Fig. 16: ^{1}H NMR of α-Zrq_4 in DMSO-d^6

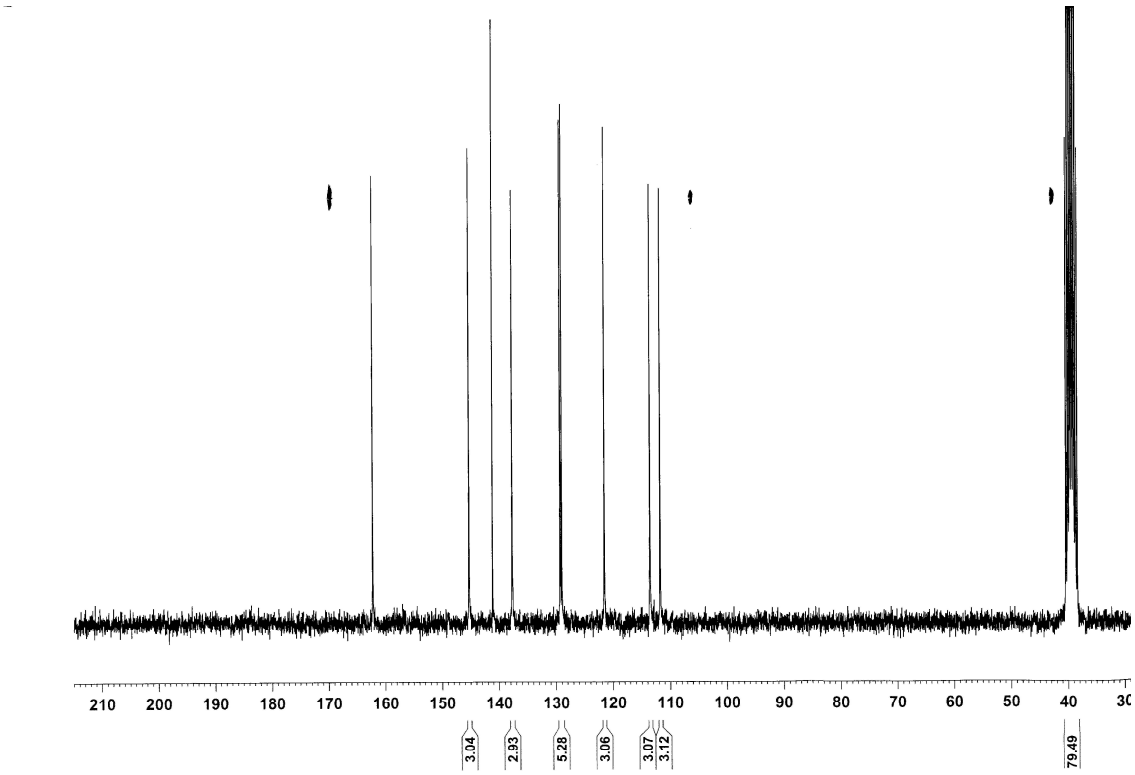


Fig. 17: ^{13}C NMR of α-Zrq_4 in DMSO-d^6

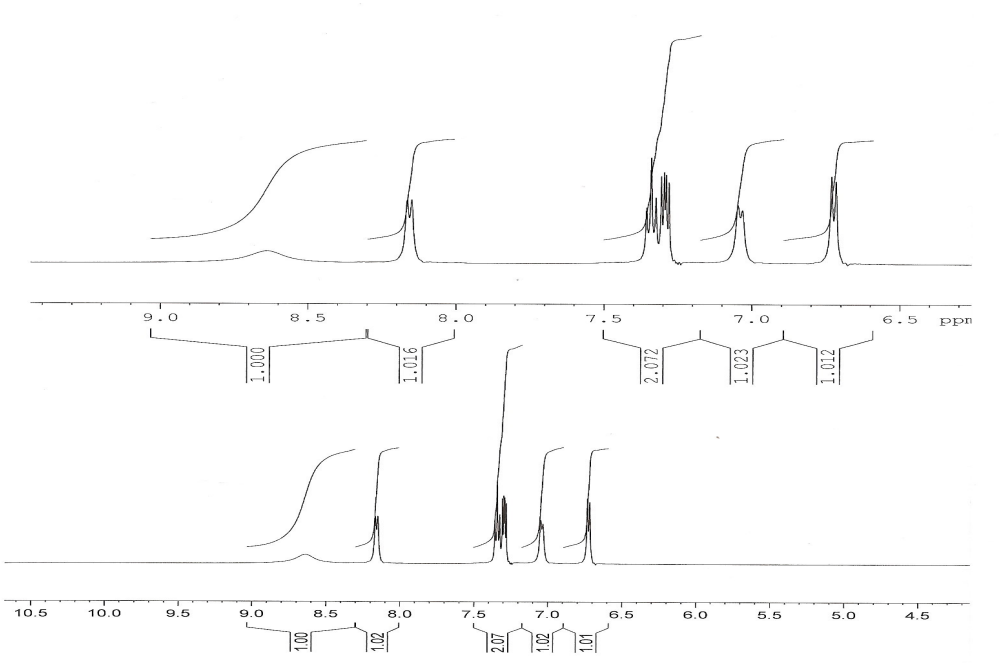


Fig. 18: ^{1}H NMR of β-Zrq_4 in DMSO-d^6

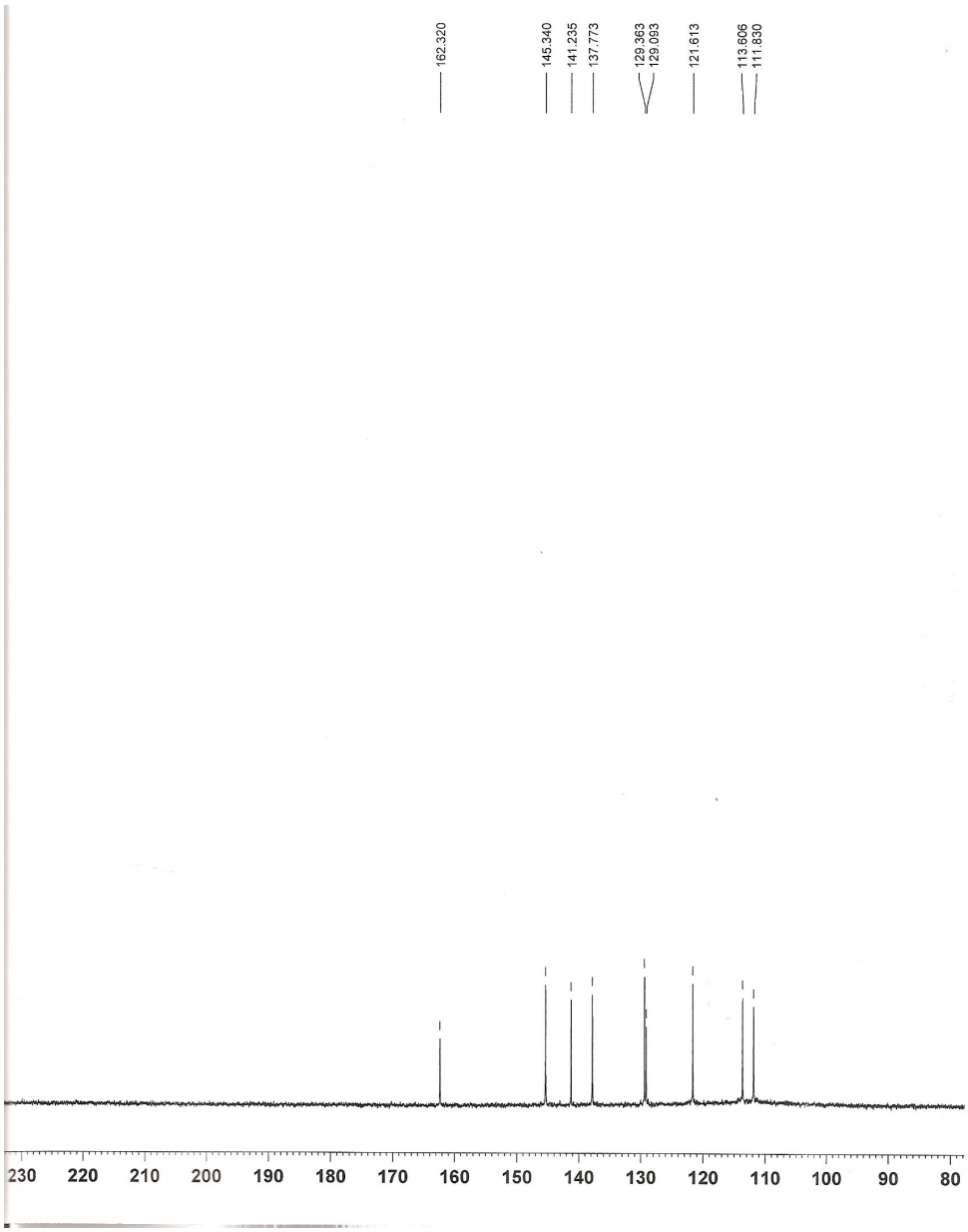


Fig. 19: ^{13}C NMR of β-Zrq_4 in DMSO-d^6

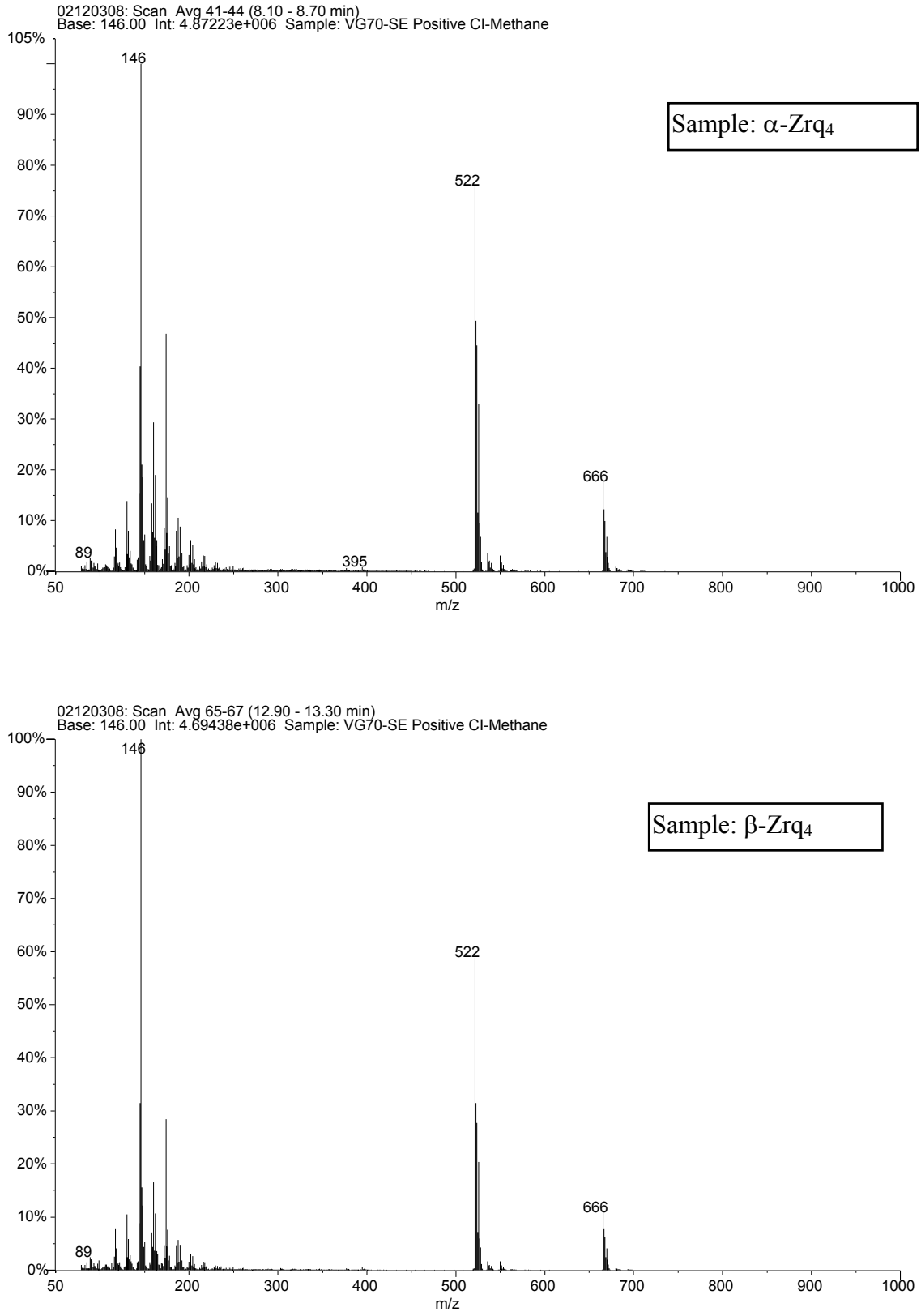


Fig. 20: Chemical ionization mass spectra of α-Zrq_4 and β- Zrq_4

Table S.1. Selected hydrogen-bond and contact parameters

α-form:

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
C7—H7···O4^{i}	0.95	2.49	3.430 (3)	171

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Cg(I) Res(I)   Cg(J)  [   ARU(J)]       Cg-Cg Transformed J-Plane P, Q, R, S     Alpha  Beta Gamma    CgI_Perp
CgJ_Perp  Slippage
Cg(6)  [ 1] -> Cg(6)  [  3755.01]  3.4983(14) -0.2617-0.9035-0.3394  -1.1877         0  2.14  2.14 -3.4958(10) -
3.4958(10)   0.130
[3755] = 2-X,-Y,-Z


Analysis of X-H...Cg(Pi-Ring) Interactions (H..Cg < 3.0 Ang. - Gamma <  30.0 Deg)
================================================================================================================
==========

   X--H(I)    Res(I)   Cg(J)  [   ARU(J)]     H..Cg  Transformed J-Plane P, Q, R, S  H-Perp Gamma      X-H..Cg
X..Cg    X-H,Pi

C(5)   -H(5)   [ 1] -> Cg(3)  [2655.01]        2.93   0.6763 0.1501-0.7212  -1.1311   2.92   3.82           111
3.386(3)   17
C(16)  -H(16)  [ 1] -> Cg(7)  [3755.01]        2.99  -0.7067 0.1607 0.6890 -12.3309   2.67  26.85           141
3.776(3)   61
C(35)  -H(35)  [ 1] -> Cg(5)  [4555.01]        2.91  -0.3223 0.2219 0.9203   9.5782  -2.73  20.25           131
3.608(3)   61
                                          ----------                                 ------------------------------
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                                   Min or Max  2.910                                -2.730   3.82           141
3.386      61

[2655] = 1-X,1/2+Y,1/2-Z
[3755] = 2-X,-Y,-Z
[4555] = X,1/2-Y,1/2+Z
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β-form:

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No centroid-centroid distances below 3.95 Å.


Analysis of X-H...Cg(Pi-Ring) Interactions (H..Cg < 3.0 Ang. - Gamma <  30.0 Deg)
================================================================================================================
=========

   X--H(I)    Res(I)   Cg(J)  [   ARU(J)]        H..Cg  Transformed J-Plane P, Q, R, S  H-Perp Gamma      X-H..Cg
X..Cg X-H,Pi

C(4)   -H(4)   [ 1] -> Cg(6)  [  4575.01]        2.94  -0.6483-0.2435 0.7214  -8.4560   2.81  17.28          143
3.727(3)     44
C(16)  -H(16)  [ 1] -> Cg(7)  [  3554.01]        2.91  -0.8843 0.0226-0.4664  -1.6284  -2.74  20.13          144
3.704(3)     72
C(24)  -H(24)  [ 1] -> Cg(3)  [  2675.01]        2.94  -0.1214 0.2262 0.9665  16.2743  -2.60  27.67          117
3.457(3)     54
C(27)  -H(27)  [ 1] -> Cg(8)  [  4575.01]        2.95   0.5336 0.0718 0.8427  16.4543  -2.89  12.10          121
3.521(3)     26
C(35)  -H(35)  [ 1] -> Cg(7)  [  4475.01]        2.92   0.8843-0.0226-0.4664  -6.0585   2.64  24.98          157
3.790(3)     65
                                          ----------                                 ------------------------------
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                                   Min or Max  2.910                                 -2.889  12.10          157
3.457        72

[4575] = 1/2+X,2-Y,Z
[3554] = 1/2-X,Y,-1/2+Z
[2675] = 1-X,2-Y,1/2+Z
[4475] = -1/2+X,2-Y,Z
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