Electronic Supplementary Information (ESI):

Synthesis of a Labile Sulfur-Centred Ligand, $[S(H)C(PPh_2S)_2]^-$: Structural Diversity in Lithium(I), Zinc(II) and Nickel(II) Complexes

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X-ray powder diffraction data (XRPD):

Experimental

The bulk powder sample of {Ni[S(H)C(PPh_2S)$_2$]$_2$} (**5b**) was examined by X-ray powder diffraction (XRPD) using a PANalytical X´Pert PRO diffractometer at room temperature. Primary beam Johansson monochromator was used to produce $CuK_{\alpha1}$ radiation (1.5406 Å; 45kV, 40mA). Each sample was prepared on to a silicon-made sample holder (producing zero-background signal) using petrolatum jelly as an adhesive. Diffraction pattern was collected with a position sensitive X´Celerator detector in a continuous scanning mode using 2θ-range of 3-70° with a step size of 0.017° and recording time of 40 s per step. HighScore Plus (v. 4.1)[1] program was used to examine the data and the DASH program[2] for the auto-indexing (with sub-program DICVOL)[3] and whole-pattern Pawley refinement of the patterns.

Results

Truncated 2θ-range of 5-50° with first 25 diffraction peak positions were used as an input for the auto-indexing procedure in order to search the best fitting unit cell parameters. As the result all the peaks were indexed by triclinic unit cell settings a = 12.4580(38) Å, b = 11.5306(38) Å, c = 9.3914(29) Å, α = 66.128(25)° β= 96.716(24)°, γ = 103.724(22)° and V = 1198.1 Å^3 with reasonable figure of merits (M_{25} = 36.7, F_{25} = 133.6 (0.0060, 31).[4] Prior to Pawley refinement *P*-1 space group was assigned based on the settings determined by single crystal analysis, and the unit cell settings afforded by the indexing were converted to correspond settings of the single crystal structure. Extraction of individual diffraction intensities by Pawley refinement process lead to good agreement between observed and calculated pattern with χ^2 = 1.40 (413 reflections; R_{wp} = 14.95 % and R_{exp}= 12.63 %) with refined unit cell setting shown in the Table S1.

Table S1. Crystallographic parameters of **5b** and its bulk powder.

Parameters	single crystal	powder
a (Å)	9.9297(5)	9.3821
b (Å)	11.399(5)	11.5244
c (Å)	12.389(5)	12.4515
α (°)	75.706(5)	76.266
β (°)	83.003(5)	83.335
γ (°)	66.213(5)	66.121
V (Å^3)	1163.85	1195.57
T (^{o}C)	-150	25

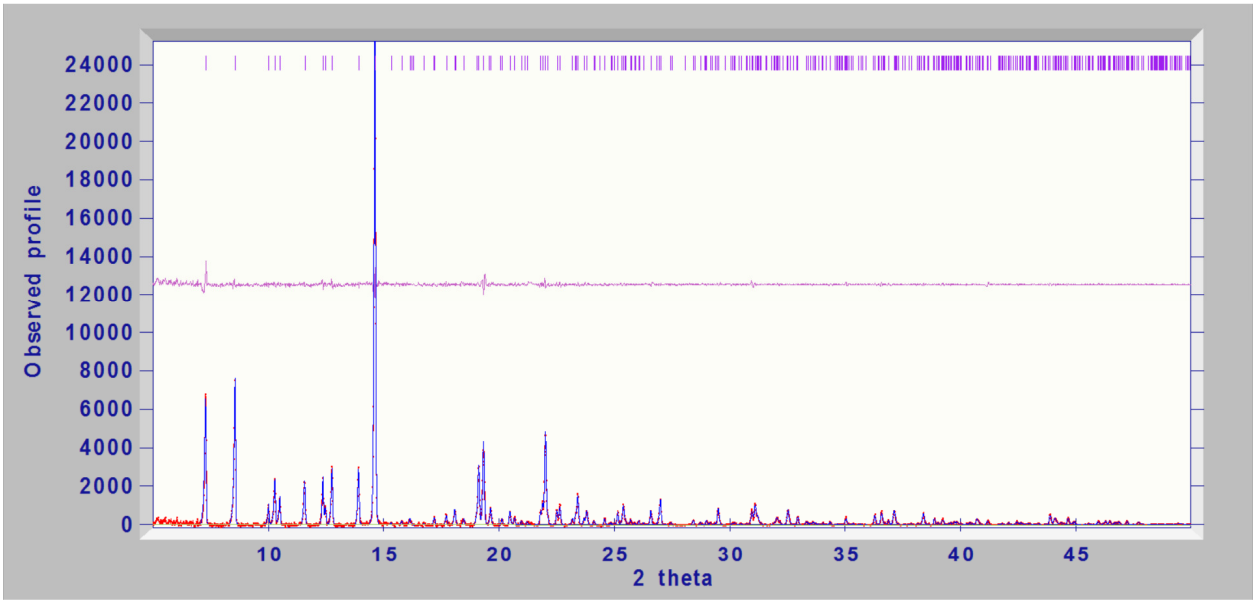

Figure S1. Whole-pattern Pawley refinement plot, Bragg peak positions are indicated by the bars on top. Experimental pattern is shown in red, calculated in blue and residual in light purple colour.

References:

1. HighScore plus 4.1, PANalytical BV. Almelo, Netherlands, 2014.

2. W. I. F. Shankland, J. van de Streek, E. Pidcock, W. D. S. Motherwell and J. C. Cole, *J. Appl. Cryst.*, 2006, **39**, 910.

3. *A. Boultif,* and *D. Louër*, Powder pattern indexing with the dichotomy method, *J. Appl. Cryst.*, 2004, **37**, 724.

4. P. M. De Wolff, A simplified criterion for the reliability of a powder pattern indexing, *J. Appl. Crystallogr.*, 1968, **1**, 108.

UV-Vis spectroscopic data:

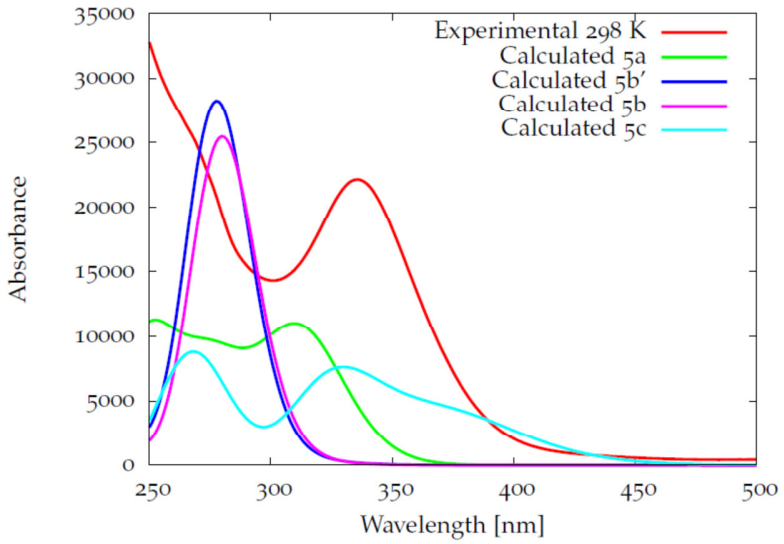

Figure S2. Comparison of the measured (**5b**) and calculated (**5a**, **5b**, **5b'** and **5c**) UV-Vis spectra.

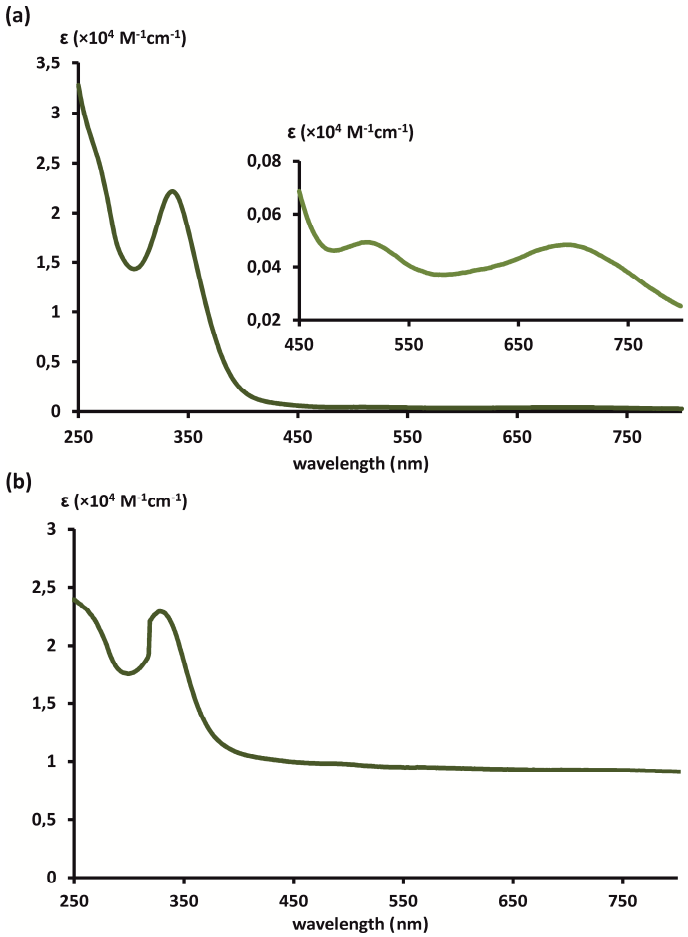

Figure S3. UV-Vis spectra of the square-planar Ni(II) isomer **5b** measured at (a) 23 °C, and (b) -50 °C.

Table S2. Calculated TDDFT excitation wavelengths and oscillator strengths greater than 0.001.

5a		**5b**		**5b'**		**5c**	
λ [nm]	f_{osc}	λ [nm]	f_{osc}	λ [nm]	f_{osc}	λ [nm]	f_{osc}
321.89	0.0195	312.11	0.0046	316.90	0.0048	674.13	0.0013
316.70	0.0055	280.01	0.4677	277.84	0.5172	614.27	0.0011
313.04	0.1006	242.49	0.0202	267.98	0.0023	411.70	0.0045
309.09	0.0700			242.89	0.0037	387.78	0.0285
279.18	0.1216			241.79	0.0264	369.87	0.0174
274.79	0.0010					364.21	0.0305
266.88	0.0170					344.47	0.0041
265.54	0.0040					327.25	0.1238
261.39	0.0291					310.87	0.0065
259.77	0.0065					283.90	0.0028
259.18	0.0182					276.89	0.0289
248.53	0.0849					274.95	0.0013
246.82	0.0766					273.05	0.0124
						270.51	0.0550
						266.40	0.0259
						263.80	0.0078
						261.57	0.0044
						259.35	0.0012
						258.88	0.0381
						256.05	0.0048

Additional computational data:

Table S3. Absolute energies, enthalpies and Gibbs' free energies of optimized structures at 298 K (in Hartree atomic units).

	E	*H*	*G*
5a	-7191.79230798	-7190.936610	-7191.094592
5b	-7191.79073323	-7190.934207	-7191.087285
5b'	-7191.78783420	-7190.931183	-7191.088359
5c	-7191.78320570	-7190.927359	-7191.094176

Optimized Cartesian coordinates:

5a

Ni	0.00000000	0.00000100	-0.00000100
P	-3.01671100	-1.56608700	-0.13822800
P	-3.00209800	1.57482100	-0.17826800
S	-1.45921100	-1.74363300	1.04489800
S	-1.49587600	1.73359500	1.06697100
S	-1.36044600	-0.02741000	-1.92996300
C	-3.11426800	-2.86037600	-1.39802000
C	-2.54176500	-4.08801600	-1.10538000
H	-2.00645100	-4.21849600	-0.17233500
C	-2.63710100	-5.13441200	-2.00420200
H	-2.18359300	-6.08926700	-1.76679800
C	-3.29969600	-4.95789800	-3.20371400
H	-3.36925200	-5.77536100	-3.91172000
C	-3.86834400	-3.73241300	-3.50401600
H	-4.38174400	-3.58601000	-4.44671100
C	-3.77833900	-2.68788500	-2.60563900
H	-4.22693900	-1.73757700	-2.86704500
C	-4.55754500	-1.70586200	0.79924100
C	-5.70939800	-2.22347400	0.22142400
H	-5.70107400	-2.57231700	-0.80381300
C	-6.87529300	-2.31408400	0.95763500
H	-7.76795400	-2.72547000	0.50168800
C	-6.89783700	-1.89040800	2.27362500
H	-7.81146500	-1.96683500	2.85165700
C	-5.75243200	-1.37699300	2.85500600
H	-5.76506900	-1.04941000	3.88759000
C	-4.58516200	-1.28749700	2.12280000
H	-3.68203600	-0.90134100	2.57998200
C	-4.59917200	1.80833100	0.63534200
C	-5.77969400	1.33086200	0.08072200
H	-5.77023900	0.73260700	-0.82228400
C	-6.99103900	1.59751100	0.68761600
H	-7.90566800	1.21451400	0.25148100
C	-7.03401600	2.34555800	1.85029000
H	-7.98563400	2.55479100	2.32473300
C	-5.86202200	2.81841300	2.41068200
H	-5.89006600	3.39882700	3.32509300
C	-4.64829800	2.54940200	1.80725300
H	-3.72837300	2.91135300	2.25053000
C	-2.98072700	2.82475000	-1.48711600
C	-4.04219600	2.94813800	-2.37432700
H	-4.90715900	2.30007800	-2.30109500
C	-4.01097900	3.91134900	-3.36282300
H	-4.84128500	4.00118100	-4.05302700
C	-2.92411200	4.76266100	-3.46608600
H	-2.90227600	5.52060400	-4.24047600
C	-1.86917400	4.64604600	-2.58122100
H	-1.01564500	5.30875400	-2.66055500
C	-1.89596700	3.67784600	-1.59409900
H	-1.06843700	3.57066800	-0.90289300
C	-2.95162700	-0.00671700	-1.08227400
H	-3.77238700	0.00288800	-1.80290500
P	3.01671300	1.56609000	0.13822300
P	3.00209700	-1.57481700	0.17826900
S	1.45921300	1.74363400	-1.04490400
S	1.49587800	-1.73359300	-1.06697300
S	1.36044700	0.02741700	1.92996100
C	3.11426800	2.86038000	1.39801300
C	2.54175400	4.08801600	1.10537700
H	2.00643300	4.21849300	0.17233600
C	2.63708800	5.13441200	2.00420000
H	2.18357300	6.08926500	1.76679800
C	3.29969200	4.95790200	3.20370700
H	3.36924800	5.77536600	3.91171300
C	3.86835000	3.73242200	3.50400500
H	4.38175800	3.58602200	4.44669700
C	3.77834700	2.68789300	2.60562800
H	4.22695500	1.73758800	2.86703100
C	4.55754700	1.70586200	-0.79924400
C	5.70939900	2.22347600	-0.22142700
H	5.70107400	2.57232100	0.80380900
C	6.87529600	2.31408300	-0.95763700
H	7.76795700	2.72547000	-0.50168900
C	6.89784200	1.89040300	-2.27362500
H	7.81147100	1.96682800	-2.85165600
C	5.75243800	1.37698700	-2.85500600
H	5.76507600	1.04940100	-3.88758900
C	4.58516700	1.28749300	-2.12280200
H	3.68204100	0.90133600	-2.57998500
C	4.59917200	-1.80833700	-0.63533600
C	5.77969400	-1.33087300	-0.08071100
H	5.77023900	-0.73261700	0.82229400
C	6.99104100	-1.59752900	-0.68760000
H	7.90566900	-1.21453600	-0.25146100
C	7.03401900	-2.34557800	-1.85027200
H	7.98563700	-2.55481600	-2.32471200
C	5.86202400	-2.81842700	-2.41066900
H	5.89006900	-3.39884400	-3.32507800
C	4.64829900	-2.54940900	-1.80724500
H	3.72837500	-2.91135700	-2.25052500
C	2.98072000	-2.82474400	1.48712000
C	4.04216100	-2.94809100	2.37437200
H	4.90710100	-2.29999600	2.30117400
C	4.01094500	-3.91130400	3.36286500
H	4.84122700	-4.00110300	4.05310100
C	2.92410800	-4.76266000	3.46608500
H	2.90227200	-5.52060500	4.24047300
C	1.86919800	-4.64608600	2.58118000
H	1.01569300	-5.30882800	2.66048100
C	1.89599100	-3.67788200	1.59406100
H	1.06848200	-3.57073400	0.90282500
C	2.95162800	0.00672200	1.08227200
H	3.77238800	-0.00288000	1.80290300

5b'

Ni	0.00174200	-0.08162500	0.09140800
P	2.75855700	1.42467100	-0.04949800
P	4.26215400	-1.36332800	0.26699600
S	1.31441000	1.20816500	1.29067400
S	3.62845500	-1.81273100	2.04173800
S	1.62079500	-0.98648200	-1.08367800
C	2.24163700	2.34236500	-1.51045000
C	1.01402900	2.98331100	-1.51546200
H	0.36376200	2.90695500	-0.65181200
C	0.61116200	3.69522900	-2.63054800
H	-0.35480200	4.18498300	-2.63257200
C	1.43145000	3.76922400	-3.73942900
H	1.11196600	4.32315600	-4.61428000
C	2.66039400	3.13116100	-3.73787300
H	3.30517600	3.18568200	-4.60654900
C	3.06543900	2.41976300	-2.62750800
H	4.03386900	1.93280600	-2.64197700
C	4.11709000	2.32616200	0.70996400
C	4.66556000	3.45779500	0.12308000
H	4.29509100	3.82063700	-0.82665000
C	5.68395800	4.14147400	0.76077100
H	6.10587700	5.02647700	0.30006600
C	6.15460600	3.70120100	1.98314700
H	6.95202600	4.23979500	2.48166300
C	5.60334500	2.57836300	2.57602600
H	5.96635600	2.23537200	3.53723100
C	4.58480400	1.89368100	1.94627500
H	4.15015700	1.01705100	2.41433500
C	5.94702700	-0.68820100	0.26608500
C	6.43697400	0.13383000	-0.74038200
H	5.81005400	0.44792500	-1.56527600
C	7.74619900	0.57519300	-0.70892000
H	8.11304600	1.22181000	-1.49695600
C	8.58160500	0.19372300	0.32459500
H	9.60808600	0.54031700	0.34813700

C	8.10264700	-0.62720300	1.32887500
H	8.75137100	-0.92758100	2.14304600
C	6.79185400	-1.06220600	1.30174100
H	6.40887500	-1.69143000	2.09617300
C	4.34994300	-2.79311100	-0.84340700
C	5.01021600	-2.71359200	-2.06231800
H	5.50175700	-1.79764400	-2.36808600
C	5.06141500	-3.81222300	-2.89731100
H	5.57915600	-3.74312400	-3.84652700
C	4.45804200	-4.99859800	-2.51769000
H	4.50116000	-5.86128800	-3.17229000
C	3.80418800	-5.08323400	-1.30282700
H	3.33143400	-6.01066300	-1.00222000
C	3.74920500	-3.98268100	-0.46769500
H	3.23931800	-4.03880800	0.48651100
C	3.20896900	-0.20459600	-0.69265000
H	3.72440600	-0.03903200	-1.64131400
P	-2.82941100	-1.49792200	0.18464200
P	-4.10307800	1.36305000	-0.34568000
S	-1.30328300	-1.40768800	-1.07880500
S	-3.28824300	1.69795900	-2.06994500
S	-1.61522500	0.86110800	1.23478900
C	-2.45441400	-2.39794300	1.69973100
C	-1.29484600	-3.15193500	1.76959600
H	-0.61370700	-3.16713400	0.92730900
C	-1.00111500	-3.86512100	2.91740500
H	-0.08851100	-4.44624100	2.96782400
C	-1.86222400	-3.82644000	3.99668700
H	-1.62835400	-4.38162800	4.89740100
C	-3.02264800	-3.07400700	3.93129100
H	-3.69930000	-3.03948800	4.77644400
C	-3.31951200	-2.36219500	2.78733400
H	-4.23712900	-1.78630300	2.75563400
C	-4.19732700	-2.34160300	-0.62288900
C	-4.87020100	-3.39344600	-0.01735900
H	-4.58607800	-3.73372200	0.96985400
C	-5.90431100	-4.02552500	-0.68234600
H	-6.42383700	-4.84856300	-0.20675500
C	-6.26739000	-3.61261200	-1.95019600
H	-7.07784200	-4.11022300	-2.46984600
C	-5.59163400	-2.57054100	-2.56140300
H	-5.87014000	-2.25011500	-3.55793000
C	-4.55638600	-1.93832100	-1.90449300
H	-4.02431300	-1.12480100	-2.38567600
C	-5.82414800	0.80101500	-0.47483700
C	-6.44748600	0.02980400	0.49689800
H	-5.91155400	-0.30994200	1.37372400
C	-7.77412000	-0.33190100	0.35947000
H	-8.24538900	-0.94152400	1.12102200
C	-8.49416200	0.08151800	-0.74601200
H	-9.53451200	-0.20243200	-0.85277200
C	-7.88215100	0.85379000	-1.71622800
H	-8.44011500	1.17847800	-2.58641000
C	-6.55348700	1.20754400	-1.58351800
H	-6.06575700	1.79570200	-2.35159700
C	-4.19139200	2.83641200	0.70617600
C	-4.91762200	2.82459100	1.88968200
H	-5.45357000	1.93633000	2.20324500
C	-4.97623100	3.95545000	2.67963800
H	-5.54455700	3.93911800	3.60189700
C	-4.31499900	5.10719100	2.28921800
H	-4.36385000	5.99537200	2.90833700
C	-3.59567400	5.12454200	1.10917300
H	-3.07735900	6.02466500	0.80071000
C	-3.53272900	3.99105600	0.31953500
H	-2.97056100	3.99299800	-0.60669700
C	-3.21944200	0.17582800	0.74171600
H	-3.82099500	0.08535100	1.64878400

5c

Ni	-0.08442100	-0.35483100	0.53183700
S	1.40663400	-1.93720200	-0.28598500
S	5.96669400	0.92837300	-0.36132300
S	1.45564400	1.18874300	1.09579700
P	2.92968500	-1.32424700	0.82802300
P	4.06179700	1.26310200	-0.57447900
C	4.43490400	-2.16381300	0.31828700
C	4.55673900	-2.65841100	-0.97082000
H	3.73673700	-2.55377500	-1.67073100
C	5.72355200	-3.28912700	-1.35868900
H	5.81656700	-3.67506500	-2.36663000
C	6.76466900	-3.43121500	-0.46045900
H	7.67764500	-3.92926800	-0.76538600
C	6.64145900	-2.94662800	0.83049400
H	7.45499500	-3.06260400	1.53623100
C	5.47982200	-2.31388100	1.22099200
H	5.38869700	-1.93769500	2.23316400
C	2.71163500	-1.77858400	2.56080200
C	2.49218800	-3.12761400	2.81557900
H	2.43656000	-3.83253900	1.99318700
C	2.34136800	-3.57431400	4.11157600
H	2.17239900	-4.62718400	4.30216500
C	2.40483000	-2.67586400	5.16336000
H	2.28402800	-3.02519500	6.18200600
C	2.61672000	-1.33387600	4.91425000
H	2.65911700	-0.62712000	5.73402800
C	2.77017400	-0.88232400	3.61538100
H	2.91083000	0.17615600	3.44098400
C	3.39533800	0.73642100	-2.16321700
C	2.04654800	0.88693000	-2.46706300
H	1.36515100	1.30746900	-1.73700800
C	1.57176000	0.49212300	-3.70134900
H	0.51839300	0.60338700	-3.92710800
C	2.43538200	-0.04952700	-4.63824300
H	2.05818200	-0.35693100	-5.60687400
C	3.77682400	-0.19851600	-4.34042300
H	4.45514200	-0.62114800	-5.07201900
C	4.25662900	0.19414800	-3.10448300
H	5.30568100	0.08099700	-2.85813100
C	3.69392900	3.02399700	-0.39808500
C	3.99492900	3.63448100	0.81416000
H	4.38660200	3.04872500	1.63840600
C	3.81329200	4.99130600	0.97391200
H	4.04514000	5.45783400	1.92389300
C	3.34289300	5.75596300	-0.08179500
H	3.20531000	6.82382400	0.04198500
C	3.05705100	5.15711300	-1.29195600
H	2.69701100	5.75183500	-2.12305700
C	3.23008300	3.79227800	-1.45155700
H	3.00622200	3.33520300	-2.40692600
C	3.09298300	0.48428500	0.79042600
H	3.73452300	0.71580800	1.64754900
S	-1.78411300	0.12411700	2.04582900
S	-6.02726500	-0.44526200	-0.92994400
S	-1.30278900	-0.07304200	-1.35510100
P	-2.86217400	1.17781500	0.76110700
P	-4.17954200	-1.04197400	-1.04071700
C	-4.47186000	1.54860600	1.47228400
C	-4.96966900	0.79379900	2.52208800
H	-4.38273000	-0.02110500	2.92785400
C	-6.21259600	1.08512900	3.05149800
H	-6.59930900	0.49415500	3.87295000
C	-6.95671200	2.12946500	2.53554000
H	-7.93092600	2.35710300	2.95219200
C	-6.45632400	2.89250600	1.49423500
H	-7.03522600	3.71652000	1.09516000
C	-5.21518700	2.60652700	0.96505700
H	-4.82484400	3.21399100	0.15663100
C	-2.13073300	2.79395500	0.43645300
C	-1.81181400	3.55531200	1.55426300
H	-1.95956900	3.14708800	2.54803700
C	-1.30118000	4.82783900	1.40488700
H	-1.05386500	5.41489600	2.28093900
C	-1.10265400	5.34738500	0.13754400
H	-0.69820800	6.34562600	0.01886700
C	-1.41117100	4.59076000	-0.97630500
H	-1.24784700	4.99107200	-1.96953500

C	-1.92554400	3.31519100	-0.83067600
H	-2.14102700	2.73197000	-1.71610600
C	-3.74722500	-2.32387100	0.15172800
C	-2.55594500	-3.03579800	0.05681800
H	-1.87345700	-2.84523000	-0.76128500
C	-2.24274800	-3.98575100	1.00790000
H	-1.31278800	-4.53624300	0.93025200
C	-3.11494200	-4.23588400	2.05379200
H	-2.86644400	-4.98353100	2.79818800
C	-4.30668000	-3.54179400	2.14286900
H	-4.99639600	-3.74404100	2.95362400
C	-4.62401200	-2.58972300	1.19157700
H	-5.55986300	-2.04597800	1.24639000
C	-3.81616000	-1.70564900	-2.68209900
C	-3.61901600	-0.84041600	-3.75105400
H	-3.58451100	0.23130800	-3.59515600
C	-3.46724100	-1.33675300	-5.02895600
H	-3.30746400	-0.65435400	-5.85520300
C	-3.52154600	-2.70219400	-5.25436400
H	-3.40216200	-3.09107500	-6.25881100
C	-3.73379500	-3.56601300	-4.19808500
H	-3.78568900	-4.63462100	-4.36918800
C	-3.88306600	-3.06990800	-2.91475400