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Trans-Cis C-Pd-C Rearrangement in Hemichelates

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cis-**I**: 40

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X-ray diffraction analyses.

Table S1. Acquisition and refinement data for structural X-ray diffraction analyses.

cmpd	**1**	*trans*-**3a**	*cis*-**3a**	*cis*-**3a•2a**	*cis*-**3b**	*trans*-**3c**	*cis*-**3c**
formula	$C_{16}H_{10}CrO_3$	$2(C_{25}H_{21}CrNO_3Pd)\cdot CH_2Cl_2$	$2(C_{25}H_{21}CrNO_3Pd)\cdot CH_2Cl_2$	$C_{25}H_{21}CrNO_3Pd$ $0.5(C_{18}H_{24}Cl_2N_2Pd_2)$ $\cdot 0.5(C_7H_{16})$	$C_{25}H_{20}CrFNO_3Pd$	$C_{33}H_{30}Cl_2CrNO_3Pd$	$C_{32}H_{27}CrNO_3Pd\cdot C_7H_8$
mol. wt	302.24	1168.58	1168.58	1735.94	559.82	687.64	724.08
habit	block, yellow	plate, orange	prism, yellow	plate, orange	needle, yellow	plate, orange	plate, orange
cryst. size (mm)	0.20× 0.16× 0.16	0.32× 0.12× 0.02	0.40× 0.15× 0.05	0.22× 0.20× 0.14	0.46 × 0.06 × 0.04	0.22× 0.22× 0.12	0.16× 0.16× 0.04
cryst. syst.	orthorhombic	monoclinic	triclinic	triclinic	monoclinic	orthorhombic	monoclinic
space group	$P2_12_12_1$	$C2/c$	$P\text{-}1$	$P\text{-}1$	$P2_1/c$	$Pca2_1$	$P2_1/c$
a (Å)	8.291(1)	35.116(5)	11.0027(7)	9.139(1)	15.9303 (9)	21.301(1)	12.275(1)
b (Å)	10.275(1)	8.321(1)	13.4372(7)	11.832(1)	10.3330 (6)	10.594(1)	20.459(1)
c (Å)	15.137(1)	17.156(3)	16.1063(6)	15.967(1)	13.6837 (8)	13.040(1)	12.392(1)
α (deg)			81.693(3)	88.424(1)			
β (deg)		115.285(6)	82.094(3)	88.469(1)	106.737 (2)		91.707(1)
γ (deg)			76.169(3)	84.314(1)			
V (Å^3)	1289.5(2)	4532.7(12)	2274.8(2)	1716.9(3)	157.0 (2)	2942.6(4)	3110.7(4)
Z	4	4	2	1	4	4	4
D_x (Mg m^{-3})	1.557	1.712	1.706	1.679	1.724	1.552	1.546
T (K)	150	150	173	150	173	150	150
θ_{max}, θ_{min} (°)	30.1, 2.8	27.5, 2.4	27.4, 1.3	30.0, 2.6	28.0, 1.3	30.0, 3.1	30.0, 1.9
μ (mm^{-1})	0.89	1.42	1.41	1.46	1.37	1.20	0.97
h,k,l range	-11/11, -14/14, -21/17	-45/32 -10/9 -21/22	-10/14 -15/17 -20/20	-12/12 -16/16 -22/22	-19/21 -13/13 -18/13	-29/29 -14/12 -18/10	-17/16 -28/28 -17/17
measd refln s	10021	12993	24085	27572	15410	21140	26638
indept refln s	3750	5040	10255	9772	5157	6182	8884
refln s ($I>2\sigma(I)$)		4544	6358	8528	3595	5877	7497
params	211	299	590	392	291	377	363
R_{int}	0.038	0.035	0.122	0.050	0.063	0.048	0.058
$R[F^2 > 2\sigma(F^2)]$	0.039	0.047	0.084	0.044	0.039	0.040	0.066
w$R(F^2)$	0.095	0.108	0.208	0.090	0.074	0.103	0.140
S	1.04	1.17	1.07	1.07	0.97	1.05	1.10
x (Flack)	0.073(16)					0.11(2)	

Table S1 (*continued*)

cmpd	*trans*-**3d**	*cis*-**3d**	*cis*-**3e**
formula	$C_{33}H_{30}CrN_2O_3Pd{\cdot}CH_2Cl_2$	$C_{33}H_{30}CrN_2O_3Pd$	$C_{26}H_{17}CrNO_3Pd$
mol. wt	745.92	660.99	549.80
habit	plate, red	block, yellow	prism, orange
cryst. size (mm)	0.10 × 0.05 × 0.02	0.20 × 0.18 × 0.16	0.35× 0.10× 0.05
cryst. syst.	triclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2_1/c$	*P*bca
a (Å)	10.4931 (3)	12.3542 (4)	16.0540(4)
b (Å)	11.8295 (3)	20.8076 (7)	7.7396(2)
c (Å)	13.8875 (3)	12.4042 (4)	33.1509(8)
α (deg)	92.884 (2)		
β (deg)	106.314 (2)	90.367 (1)	
γ (deg)	111.707 (2)		
V (Å^3)	1513.94 (7)	3188.57 (18)	4119.05(18)
Z	2	4	8
D_x (Mg m^{-3})	1.636	1.377	1.773
T (K)	173	173	173
θ_{max}, θ_{min} (°)	66.6, 3.4	29.0, 1.9	28.0, 1.2
μ (mm^{-1})	9.69	0.94	1.43
h,k,l range	-12/12 -14/13 -16/15	-16/16 -28/27 -12/16	-21/21 -10/10 -43/43
measd reflns	10878	26158	33880
indept reflns	5156	8473	4984
reflns ($I>2\sigma(I)$)	3961	6757	4289
params	393	366	289
R_{int}	0.056	0.029	0.029
$R[F^2 > 2\sigma(F^2)]$	0.046	0.030	0.025
w$R(F^2)$	0.111	0.077	0.076
S	0.99	1.04	1.16
x (Flack)			

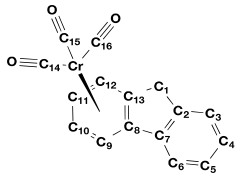


Figure S1 Atom numbering scheme for compound 1

Synthesis of tricarbonyl(η^6-fluorene)chromium, 1.

$Cr(CO)_6$ (5.0 g, 22.7 mmol), fluorene (11.330 g, 68.1 mmol), THF (15 mL), and *n*-dibutylether (150 mL) were gently refluxed for 116 h under a permanent flow of argon. The resulting orange/red solution was evaporated to dryness and the resulting residue was adsorbed on silica gel. Chromatographic separation was performed on silica gel using a mixture of CH_2Cl_2 and pentane (1:1 to 1:0) as eluent. The product was eluted as a yellow solution, which afforded 1 as a yellow solid upon removal of the solvents under reduced pressure (4.624 g, 15.30 mmol, 67 %). Anal. calcd for $C_{16}H_{10}CrO_3 \bullet 0.1CH_2Cl_2$: C, 62.23; H, 3.31. Found: C, 62.61; H, 3.36. HRMS-ESI (*m/z*): $[M+1Na]^+$ calcd for $C_{16}H_{10}CrO_3$, 324.9927; found, 324.9886. IR (cm^{-1}) ν(CO): 1942 (s), 1885 (s) 1850 (vs). ^{1}H NMR (300 MHz, C_6D_6, 298 K) δ 7.10 – 6.94 (m, 4H, H_3, H_6, H_5, H_4), 5.23 (dd, J = 4.7, 2.7 Hz, 1H, H_9), 4.90 (dd, J = 4.4, 2.8 Hz, 1H, H_{12}), 4.49 (dd, J = 4.7, 2.7 Hz, 2H, H_{10}, H_{11}), 3.39 (d, J = 21.4 Hz, 1H, H_{1a}), 3.08 (d, J = 21.5 Hz, 1H, H_{1b}). ^{13}C NMR (126 MHz, C_6D_6, 293 K) δ 233.7 (C_{15}, C_{16}, C_{14}), 142.2 (C_7), 138.8 (C_2), 128.6 (C_4), 127.5 (C_6), 125.1 (C_5), 120.2 (C_3), 112.5 (C_{13}), 110.7 (C_8), 91.1 (C_{10}), 90.6 (C_{11}), 90.1 (C_9), 86.1 (C_{12}), 36.6 (C_1).

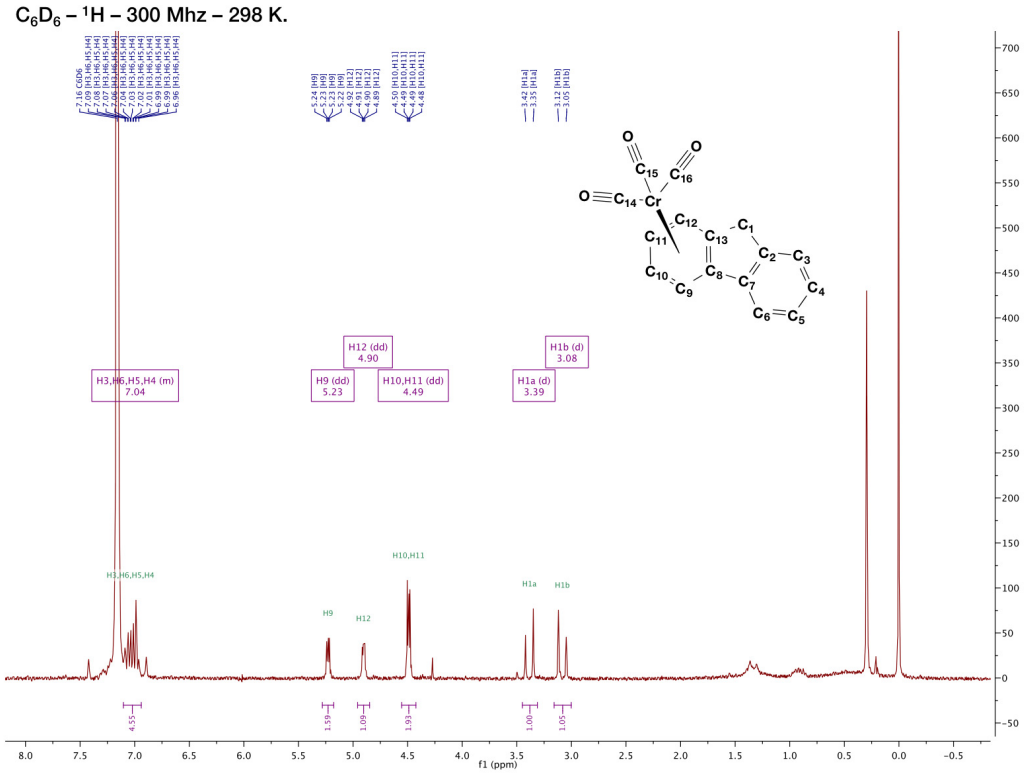


Figure S2

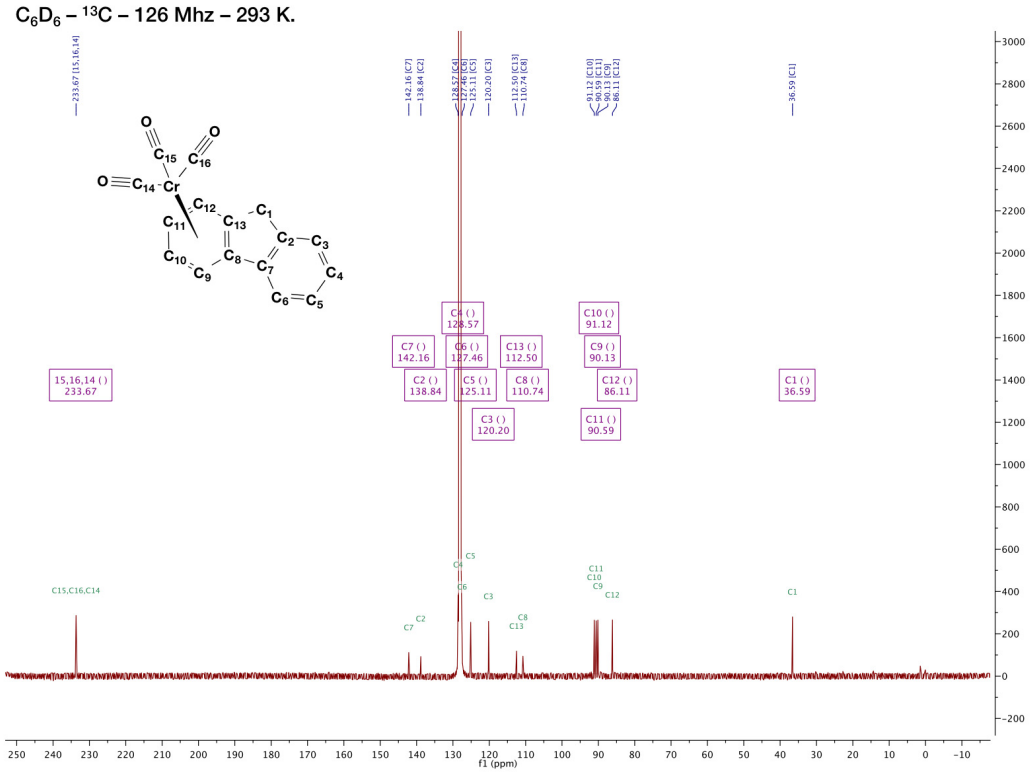


Figure S3

NMR data for *trans*/*cis*-3a-e

Complexes *trans*-3a and *cis*-3a.

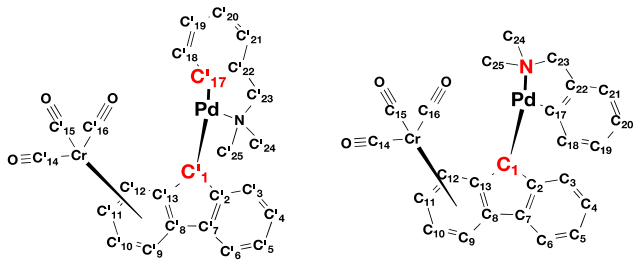


Figure S4 Atom numbering scheme for *trans*-3a and *cis*-3a

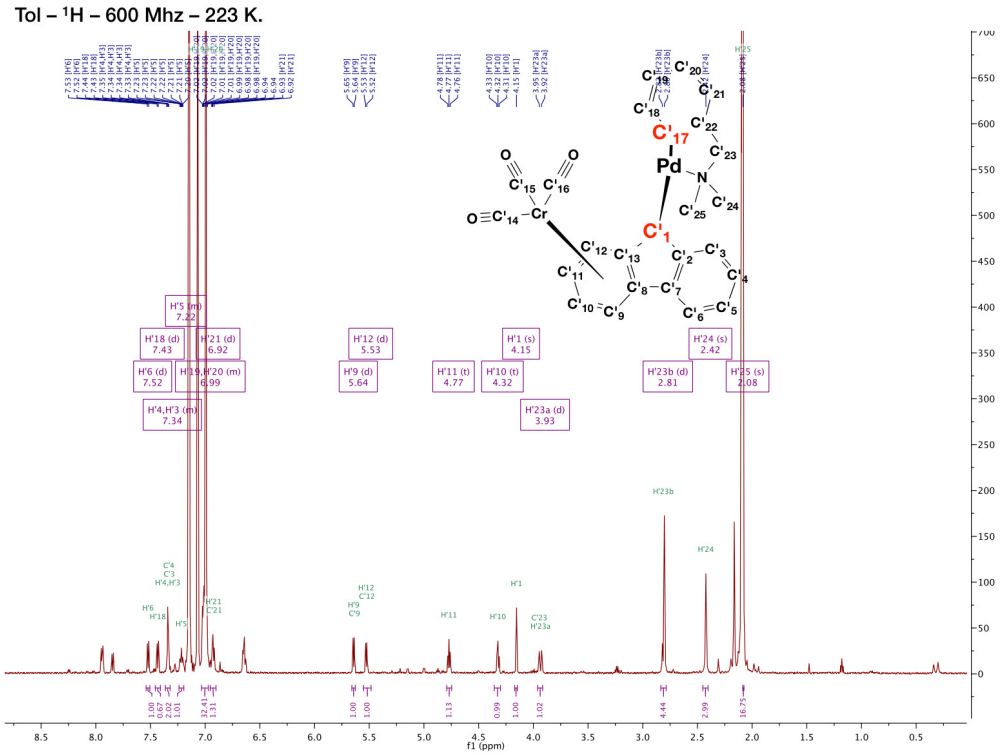


Figure S5

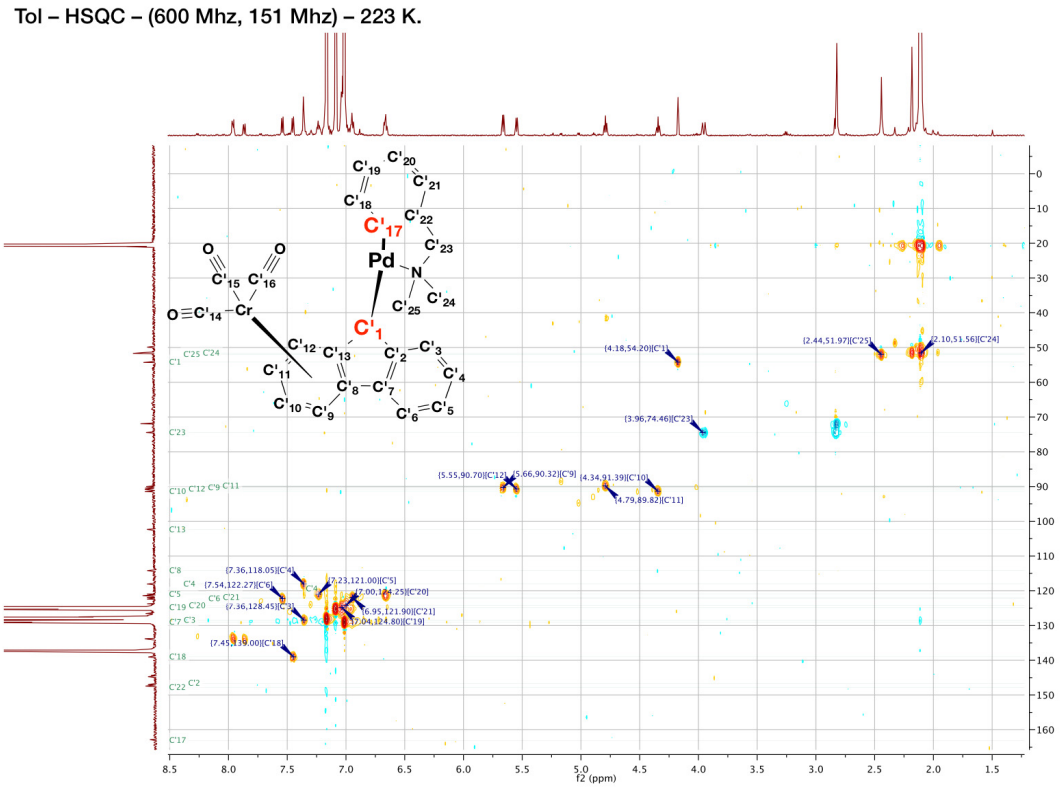
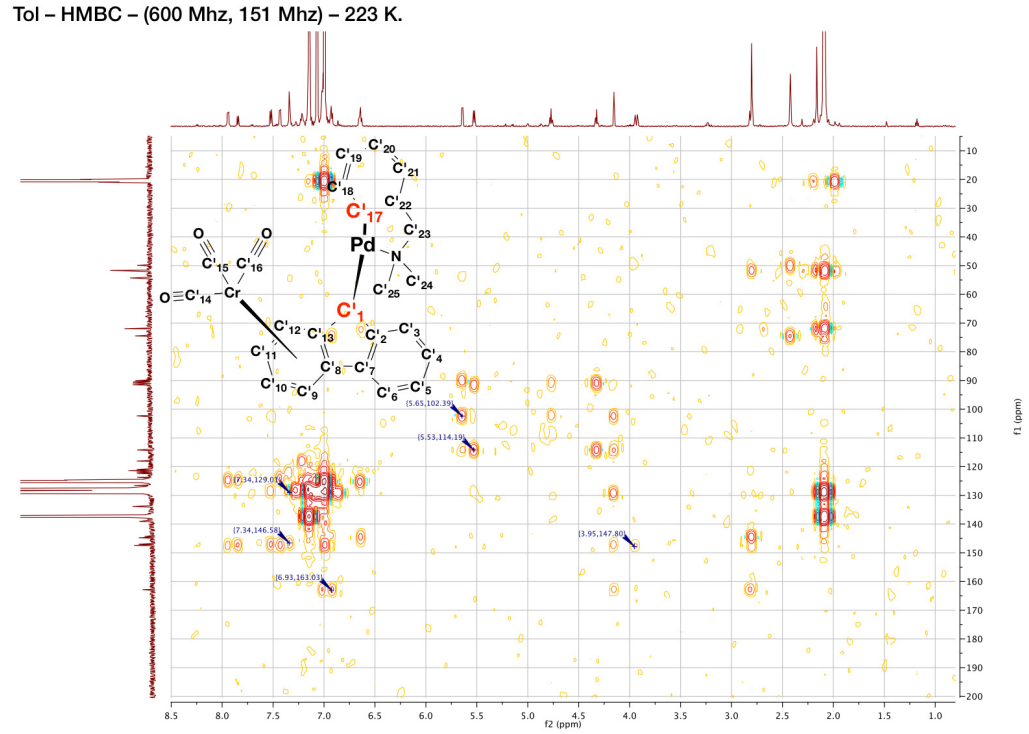


Figure S6



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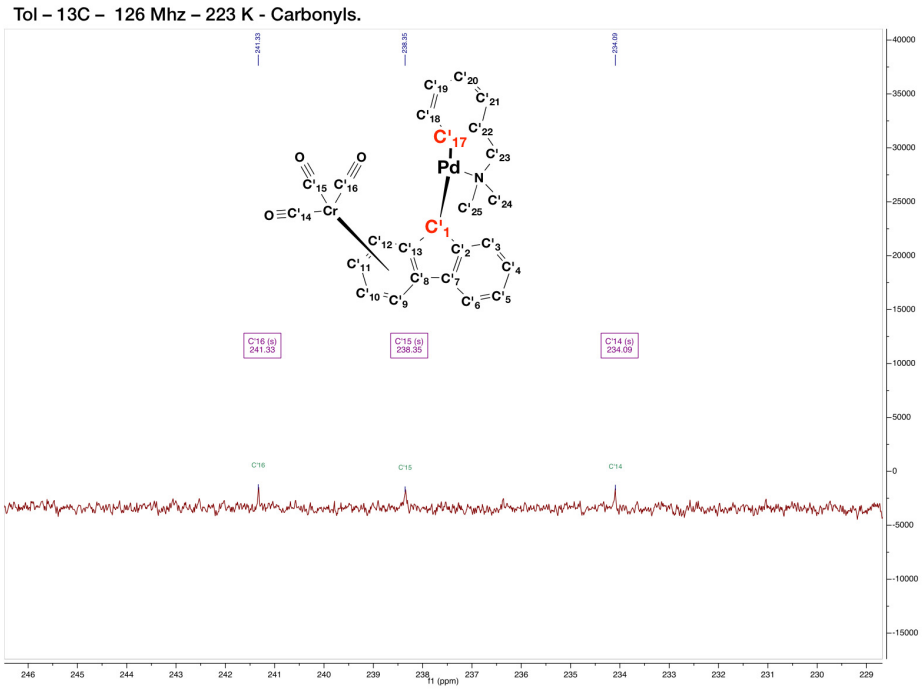

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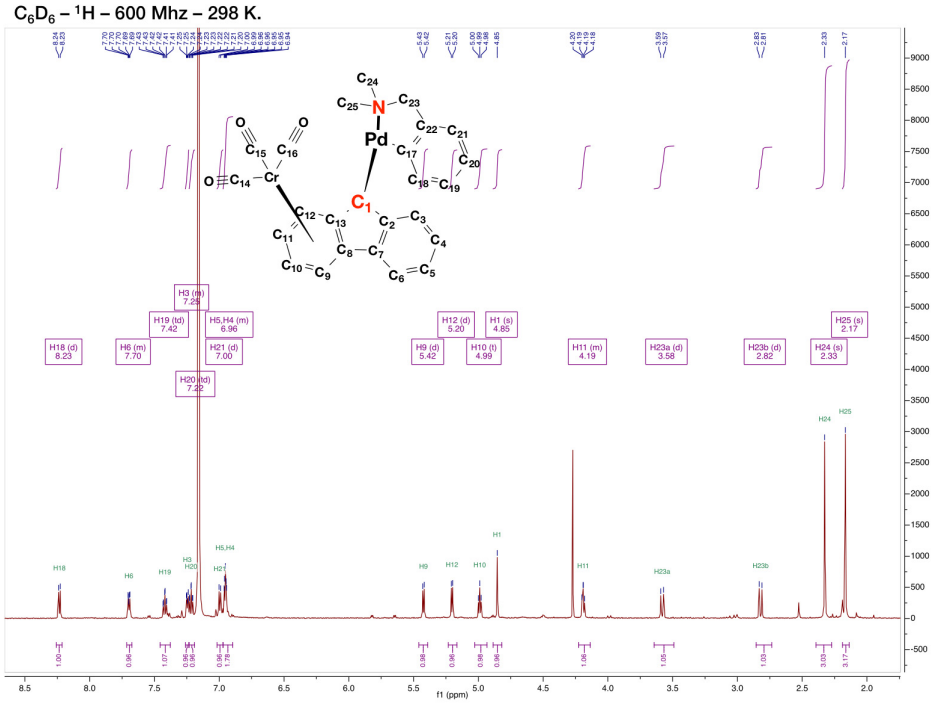


Figure S9

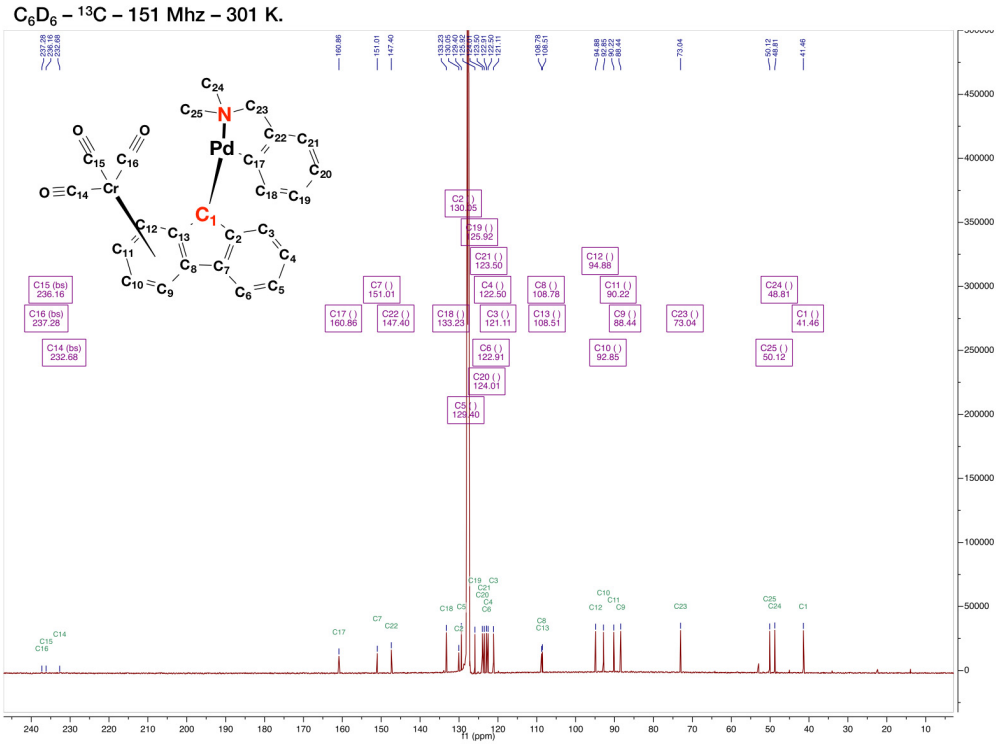


Figure S10

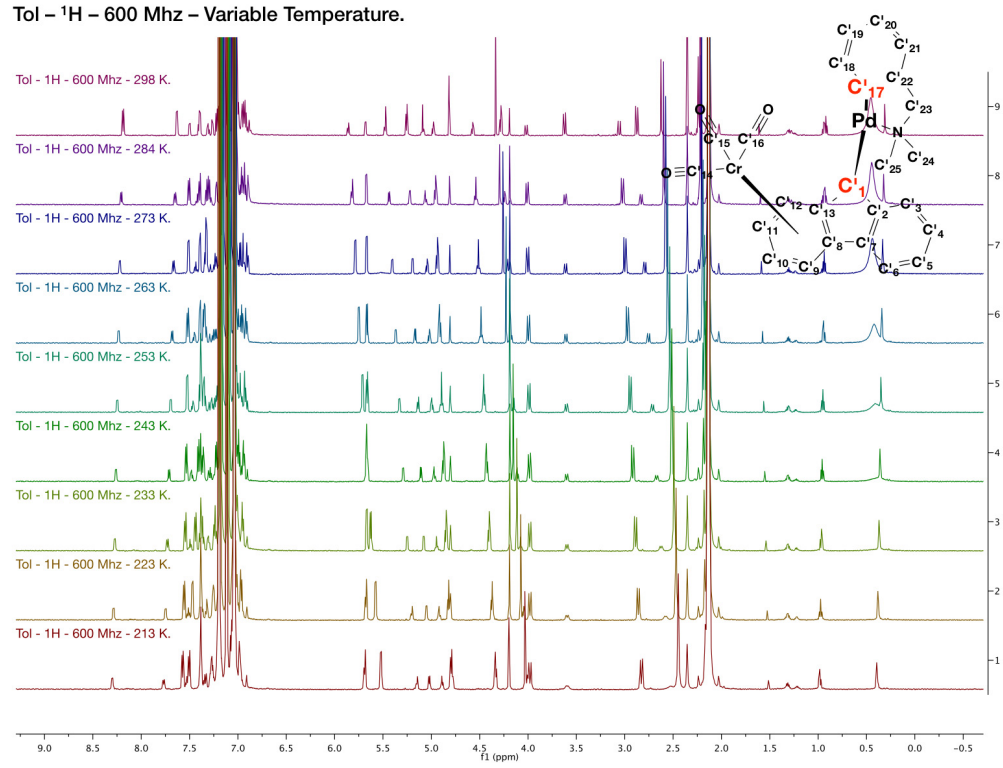


Figure S11

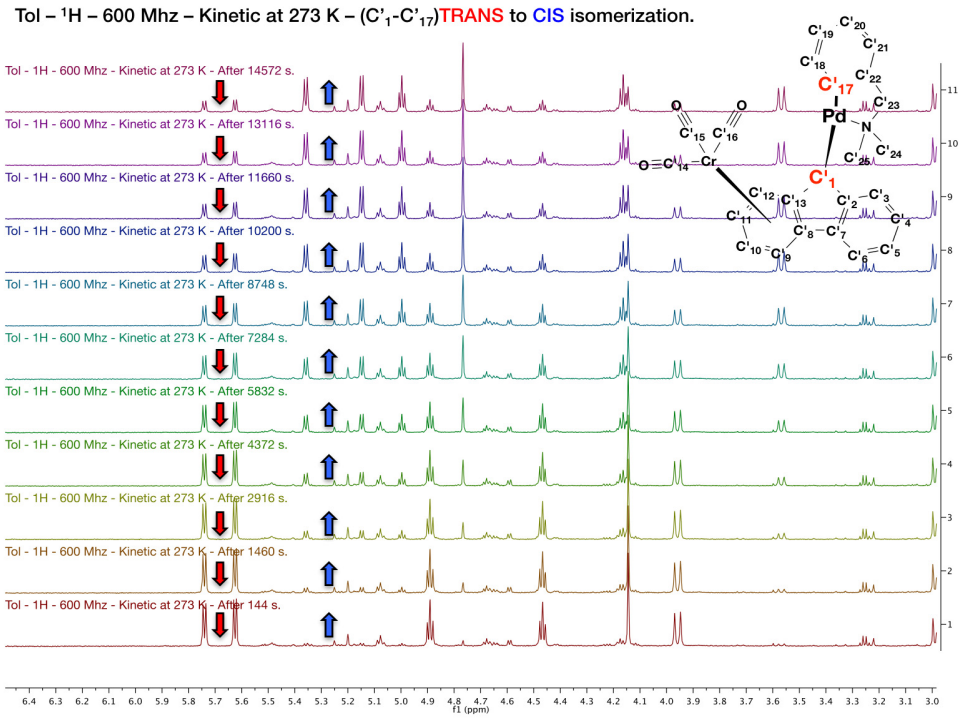


Figure S12

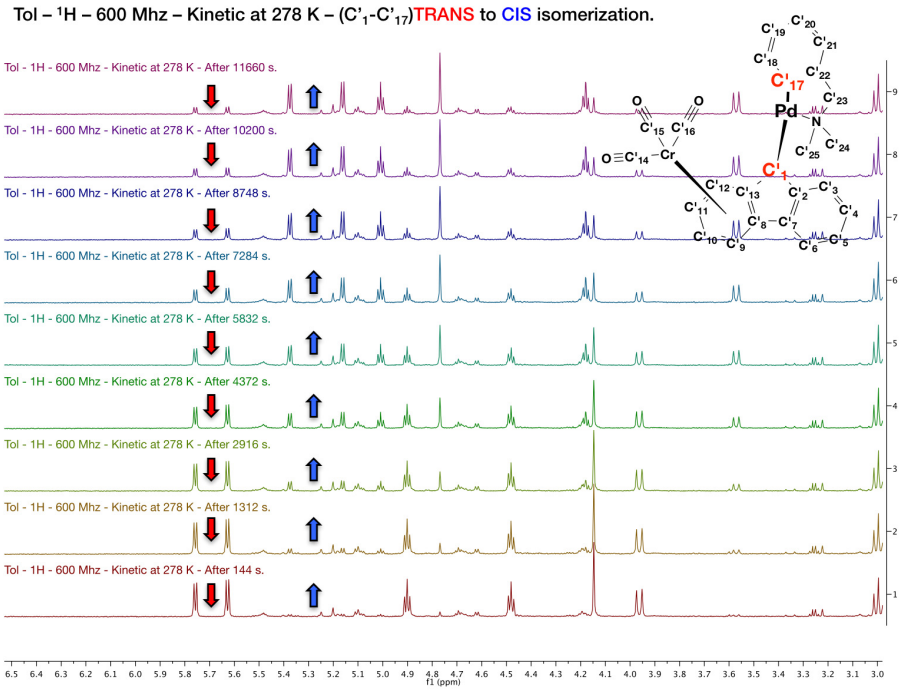


Figure S13

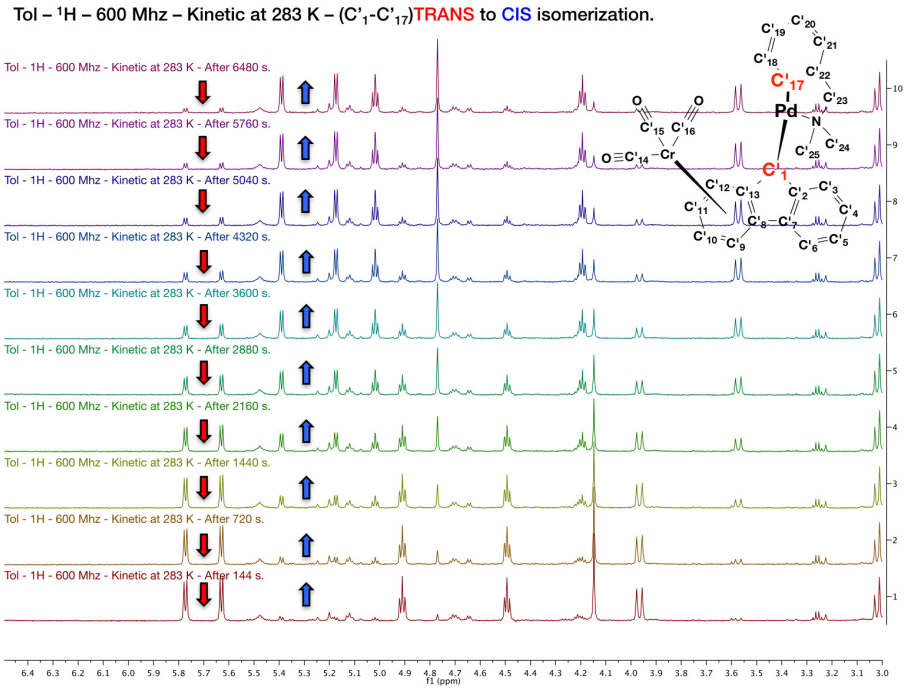


Figure S14

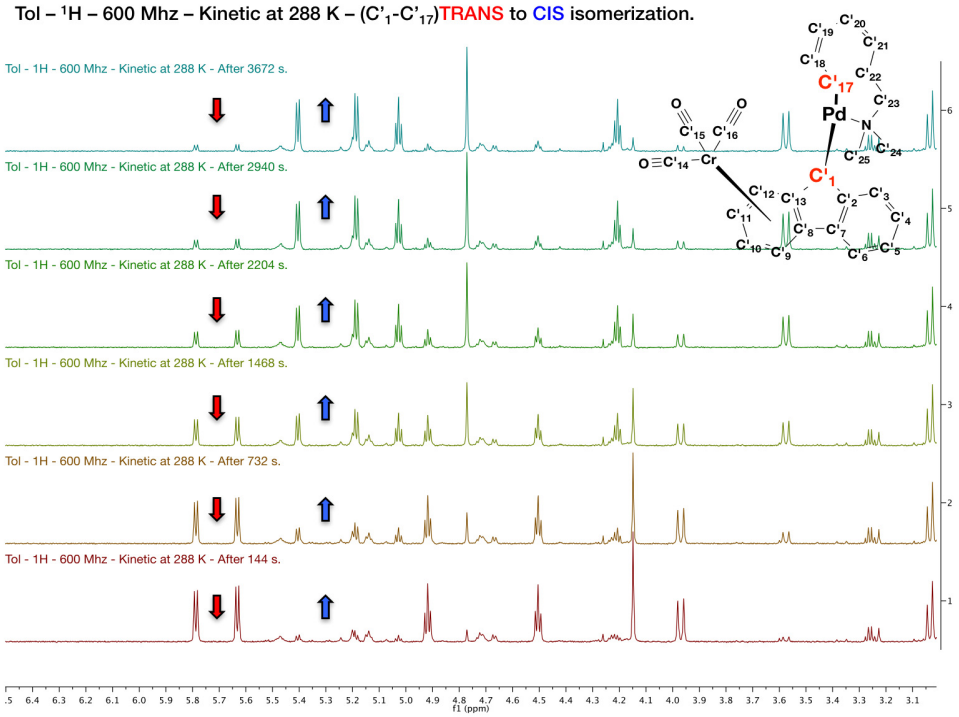


Figure S15

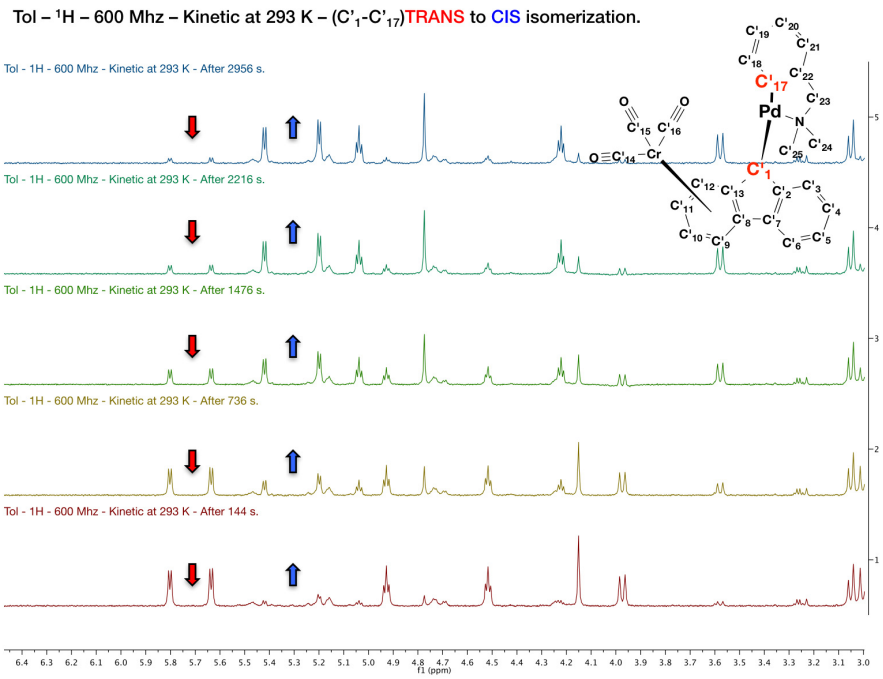


Figure S16

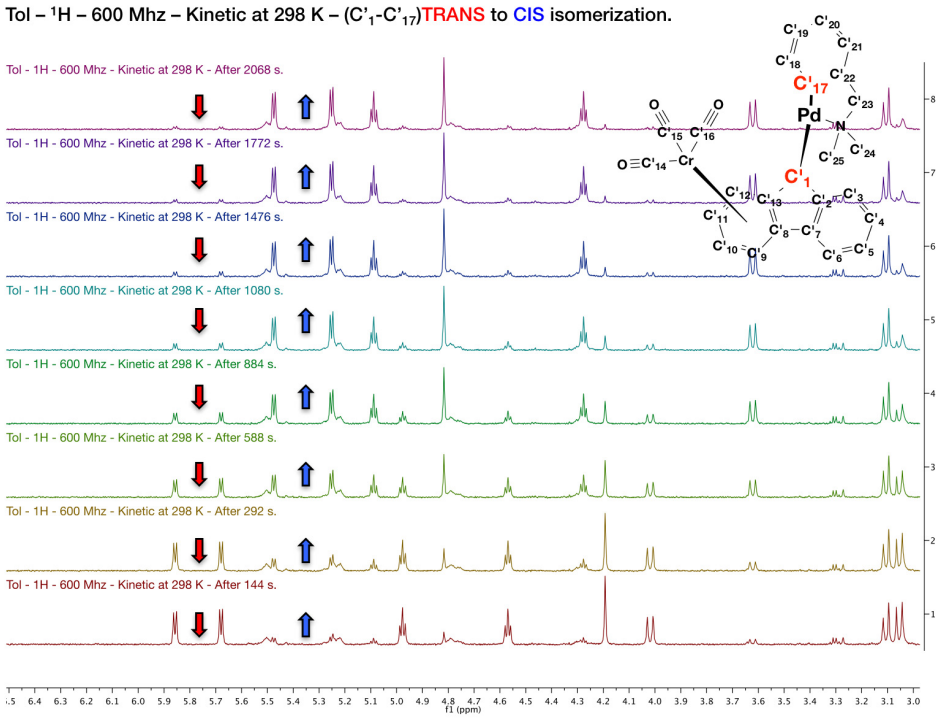


Figure S17

Complexes *trans*-3b and *cis*-3b

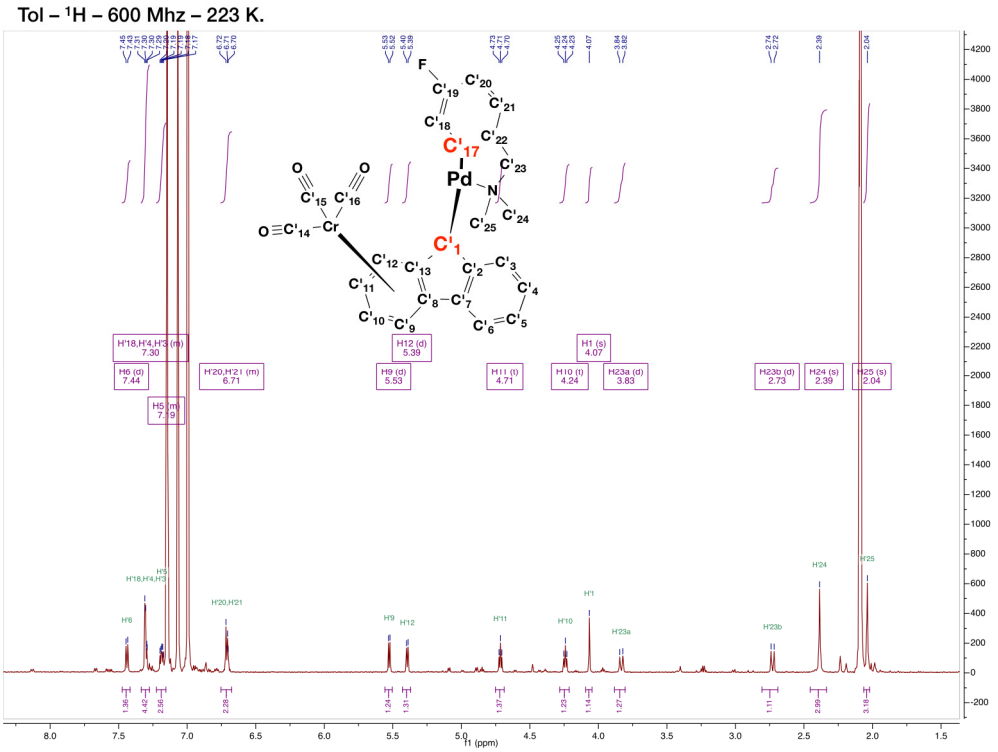


Figure S18

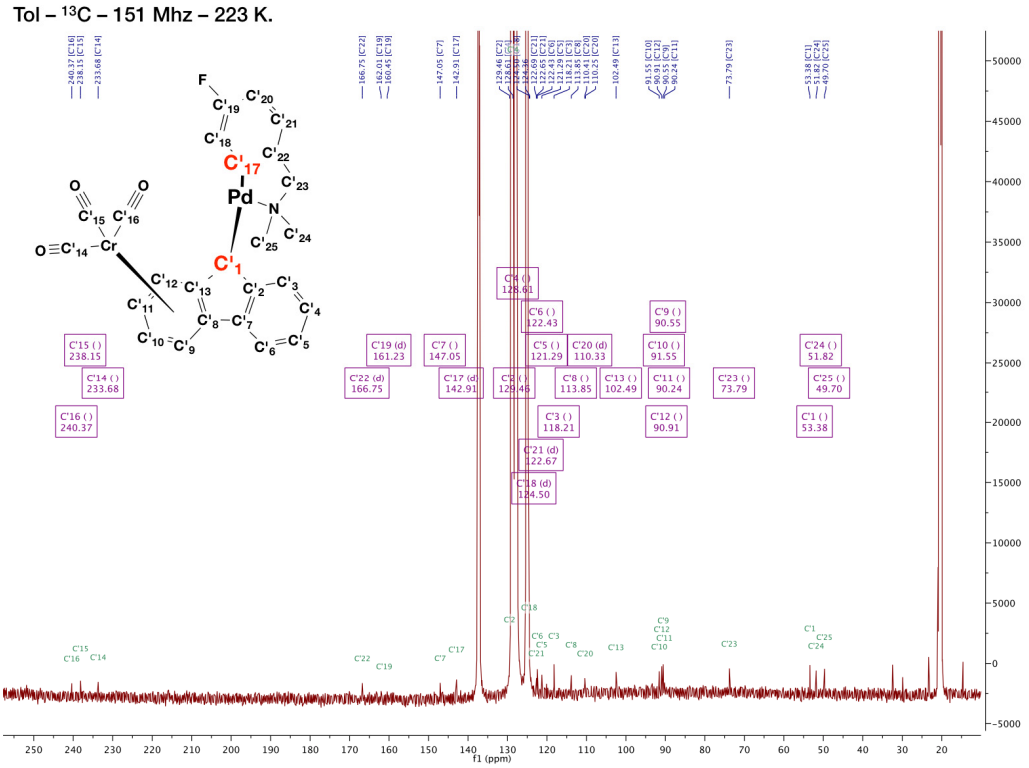


Figure S19

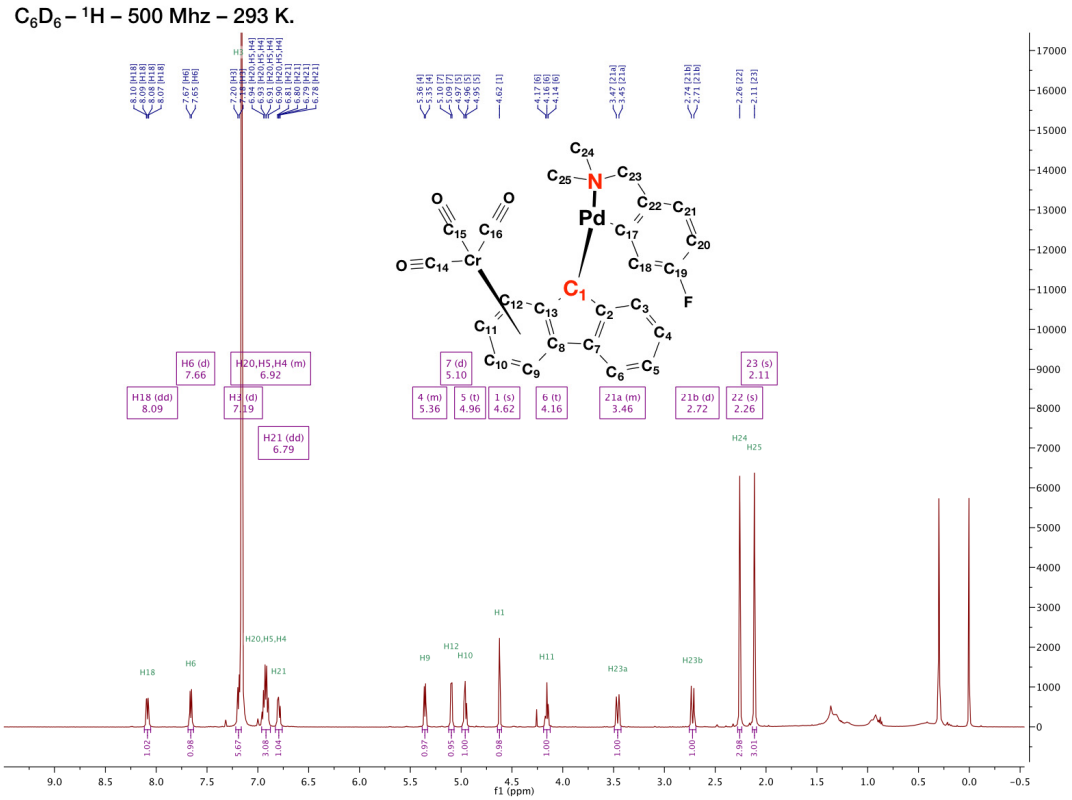


Figure S20

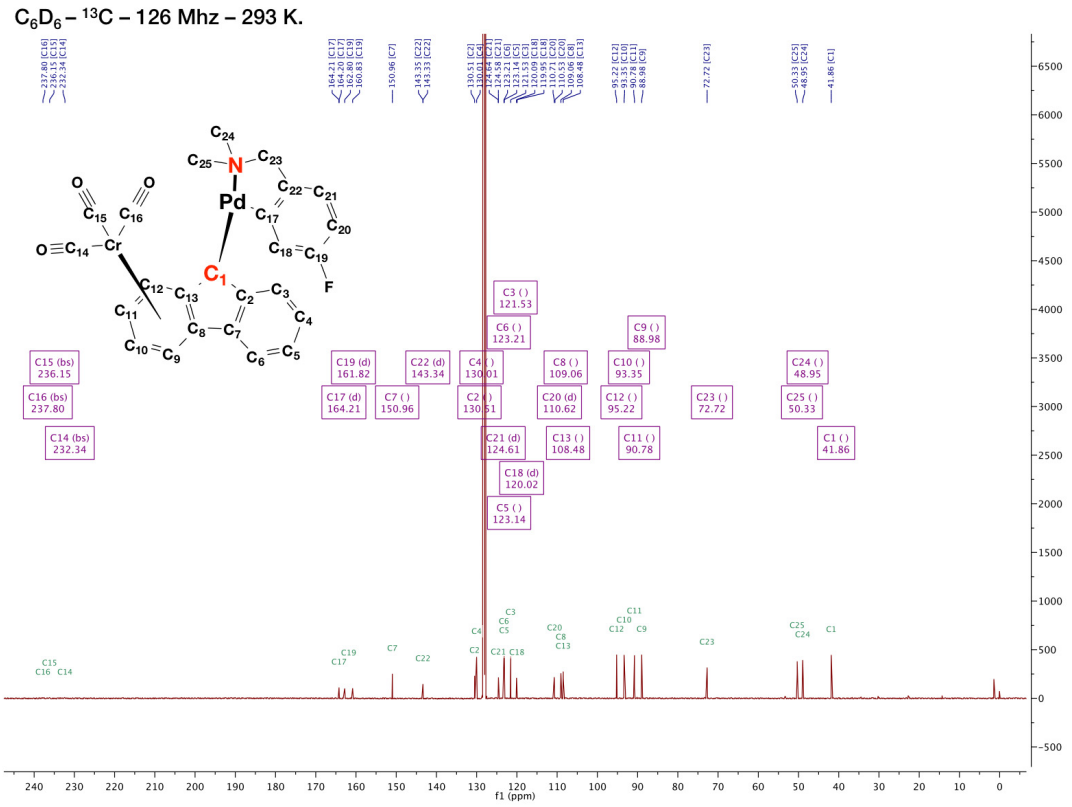
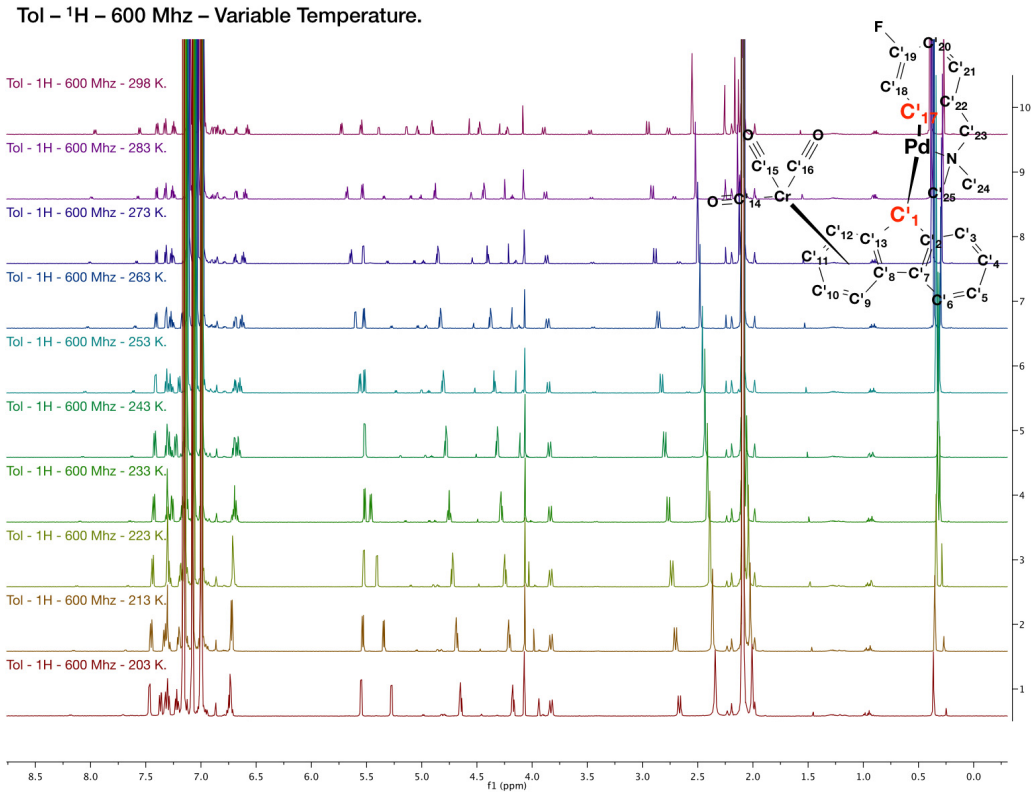


Figure S21



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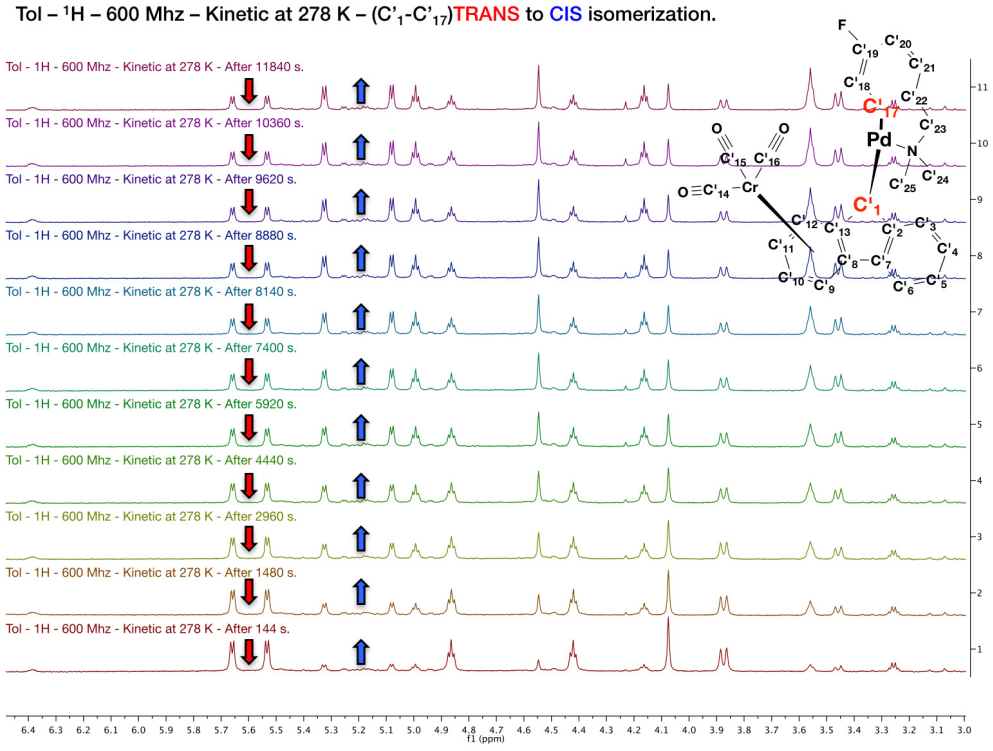

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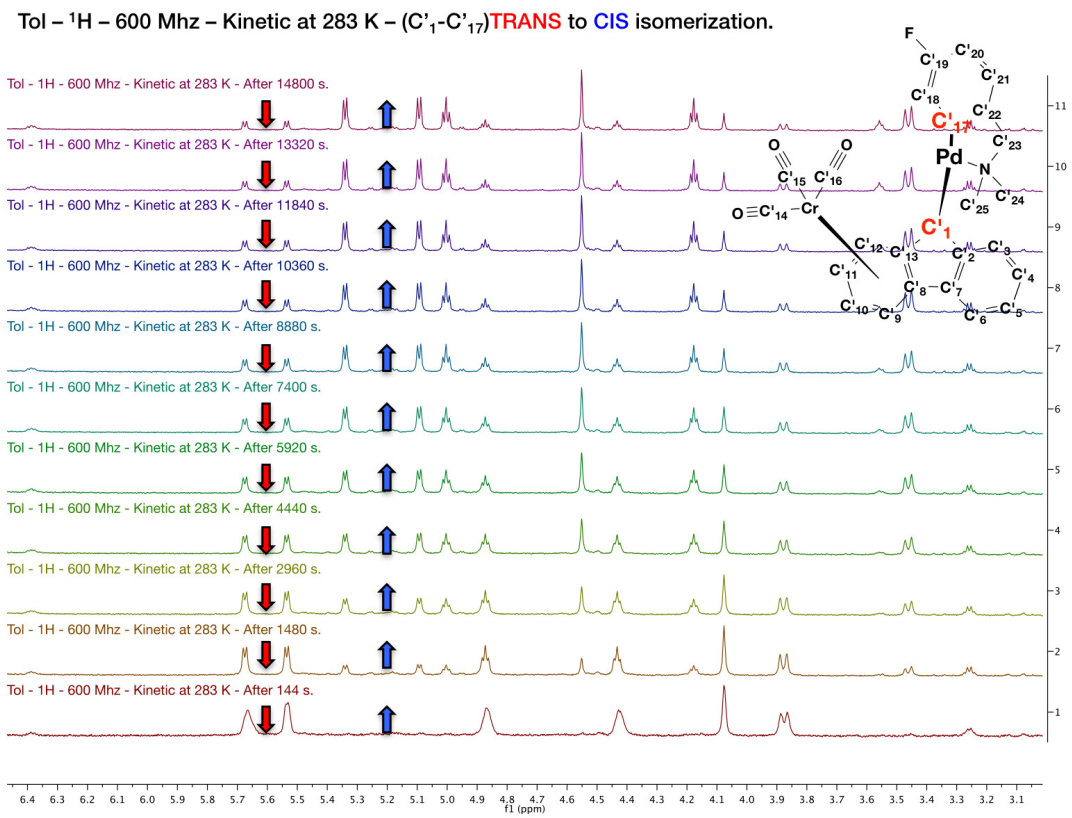

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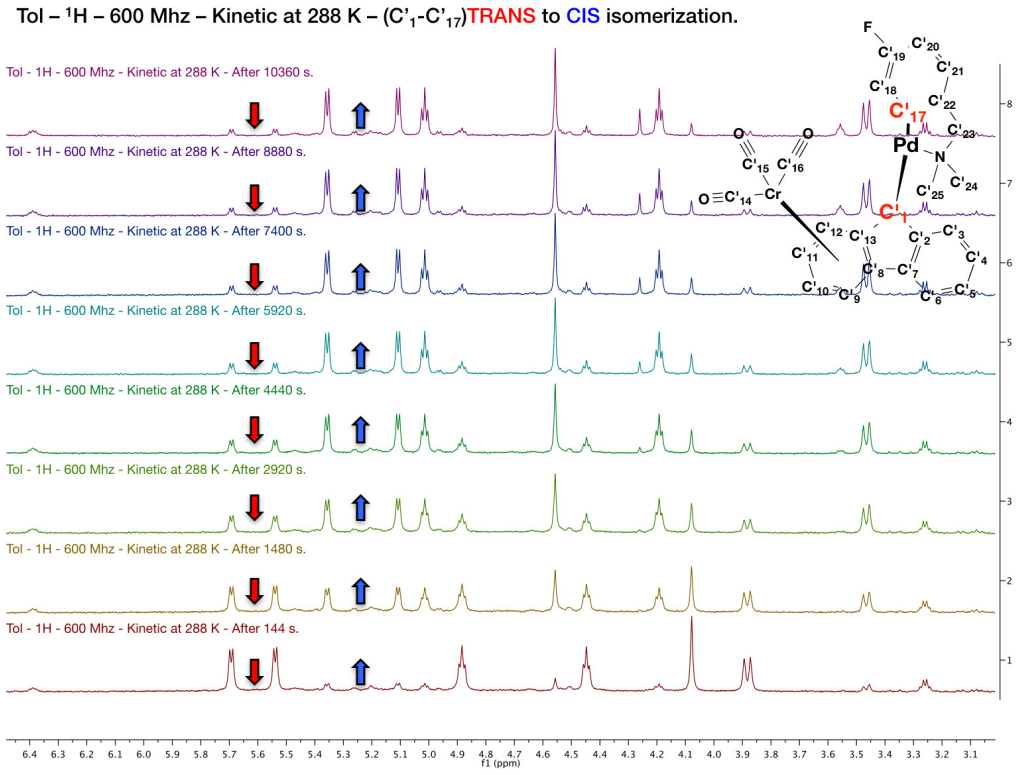


Figure 25

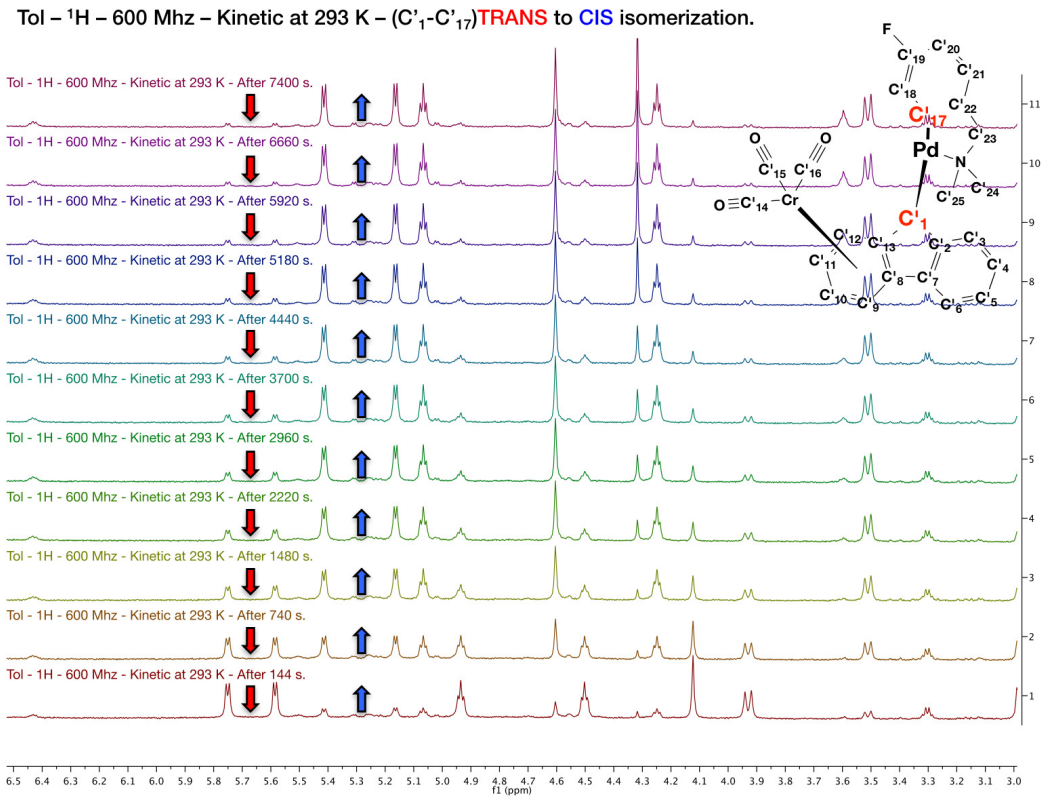


Figure S26

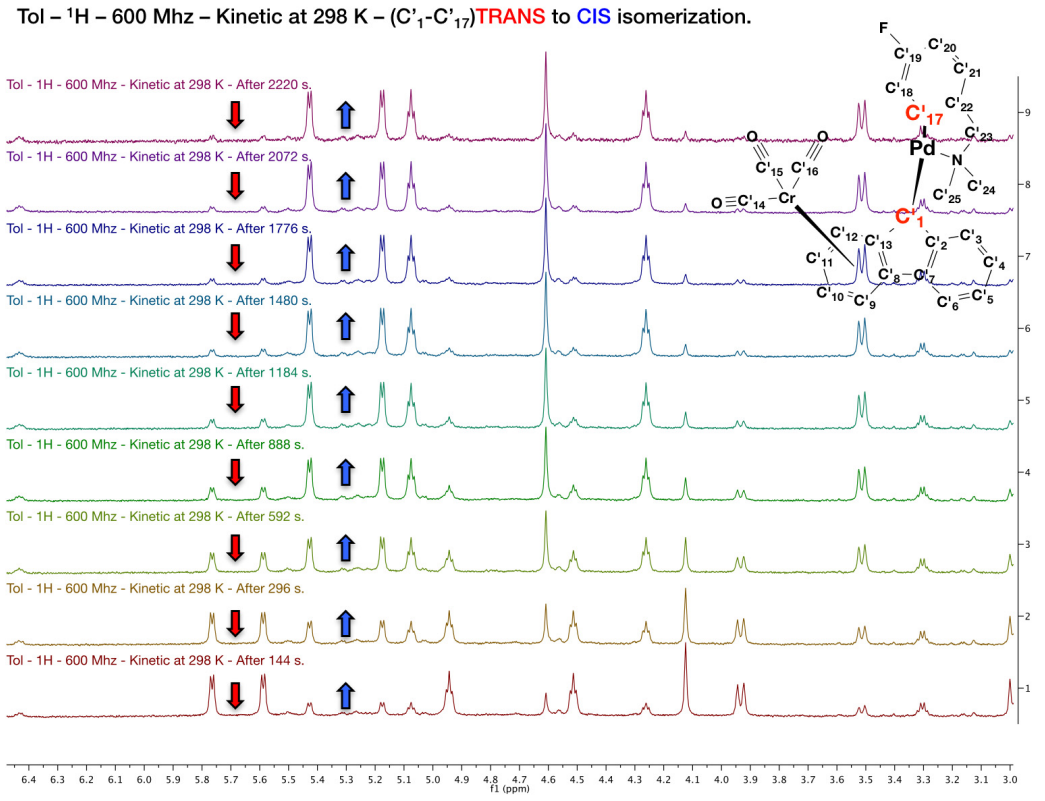


Figure 27

Complexes *trans*-3c and *cis*-3c.

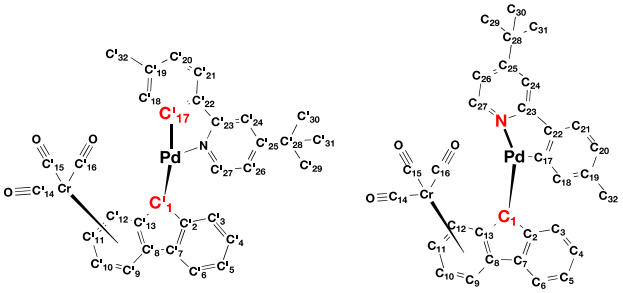


Figure S28 Atom numbering scheme for compound *trans*-3c and *cis*-3c.

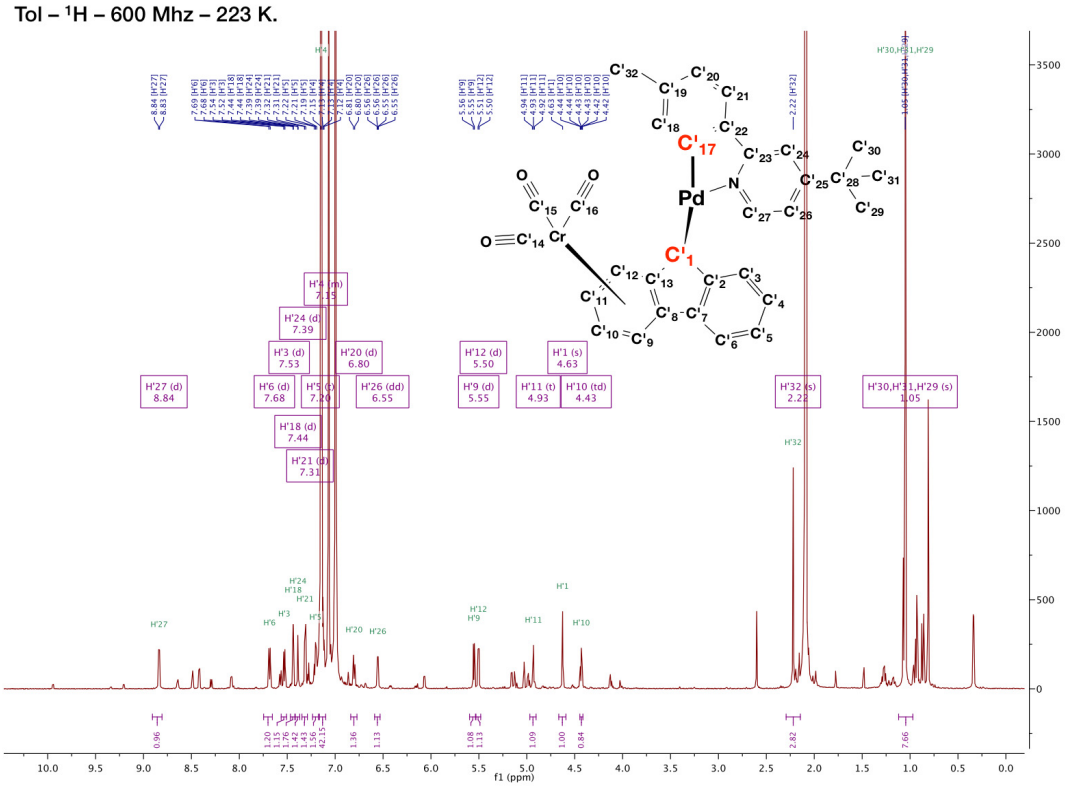


Figure S29

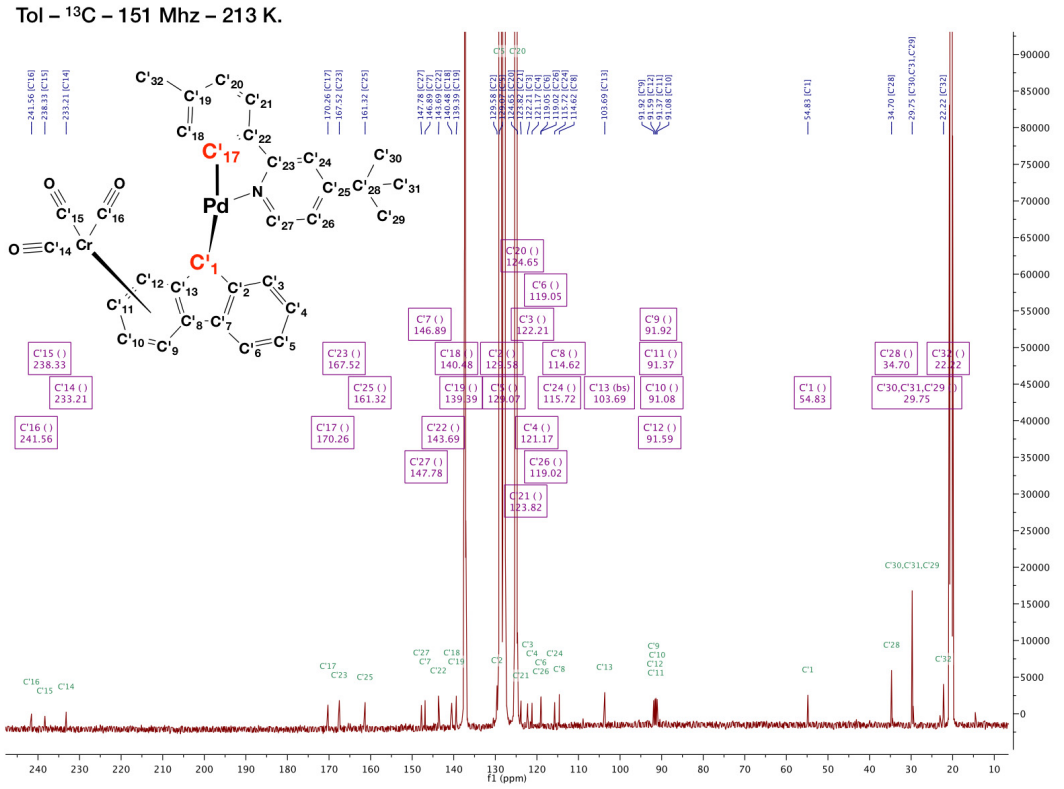


Figure S30

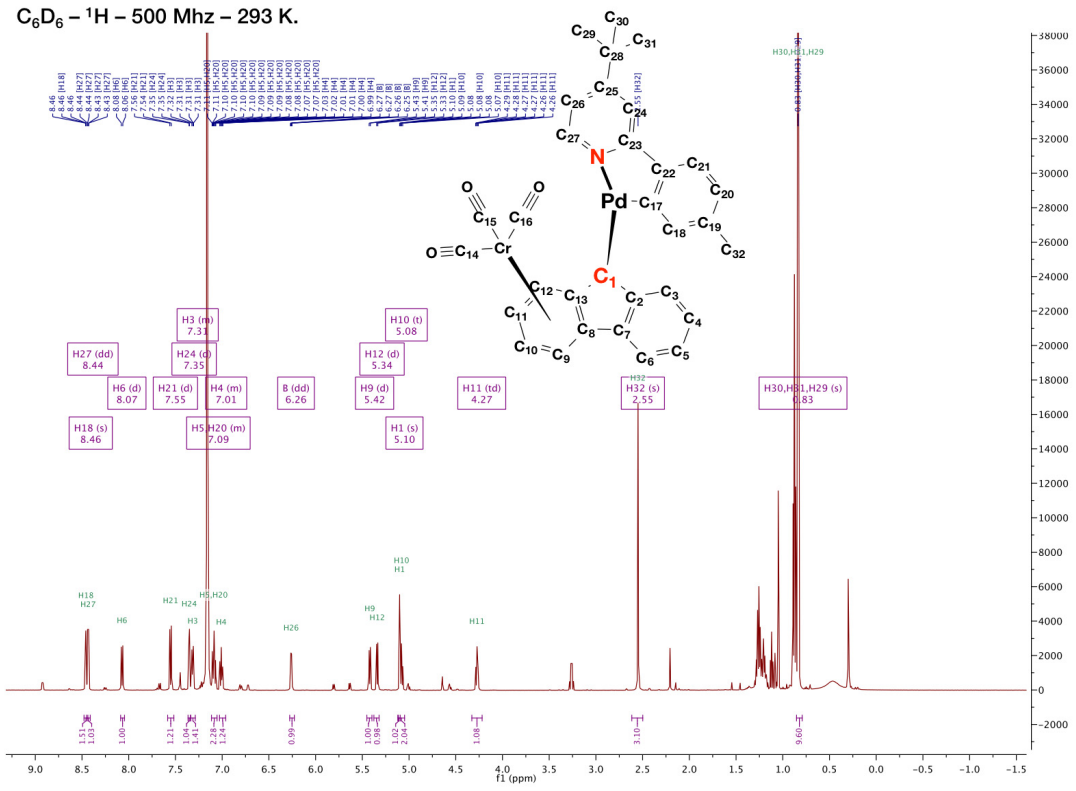


Figure S31

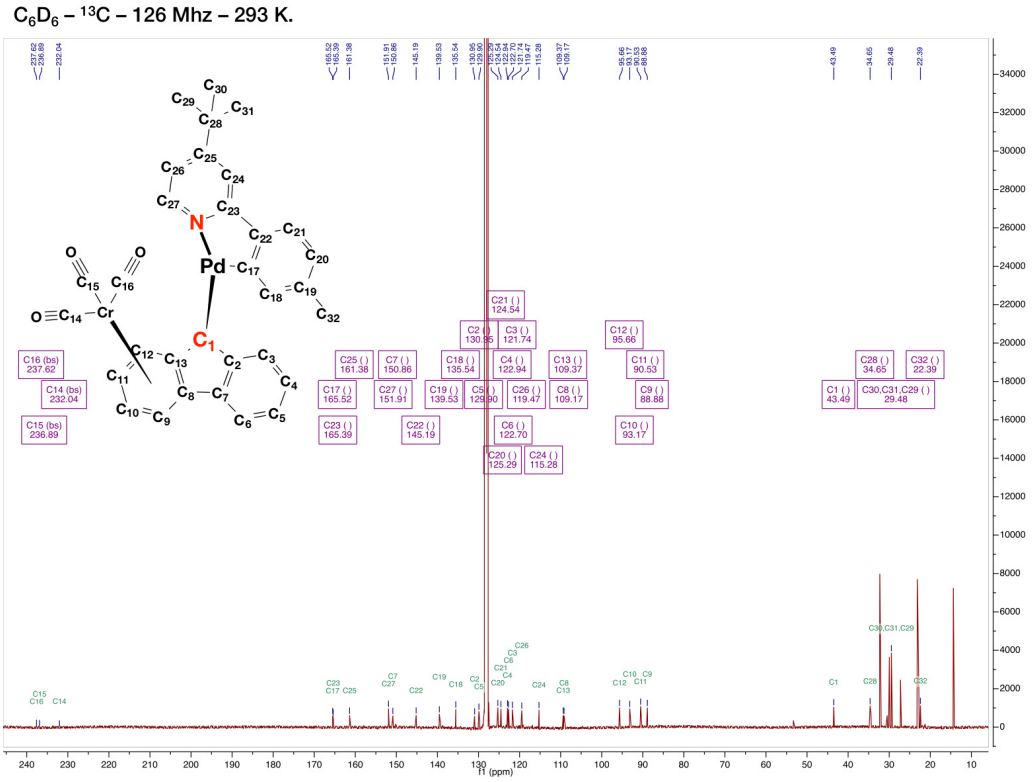


Figure S32

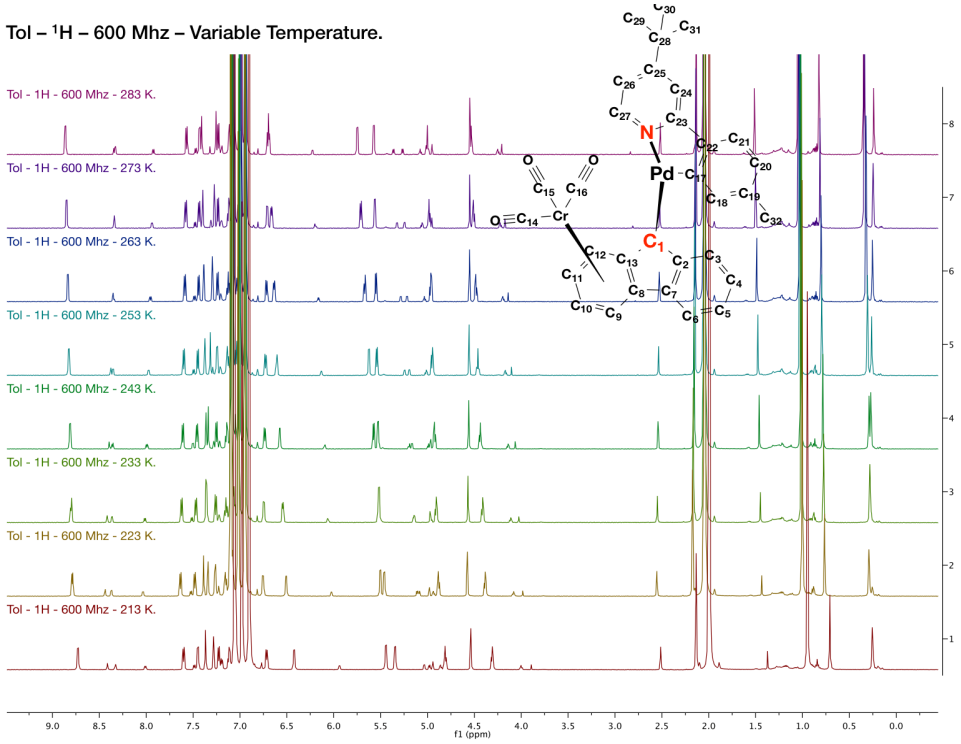
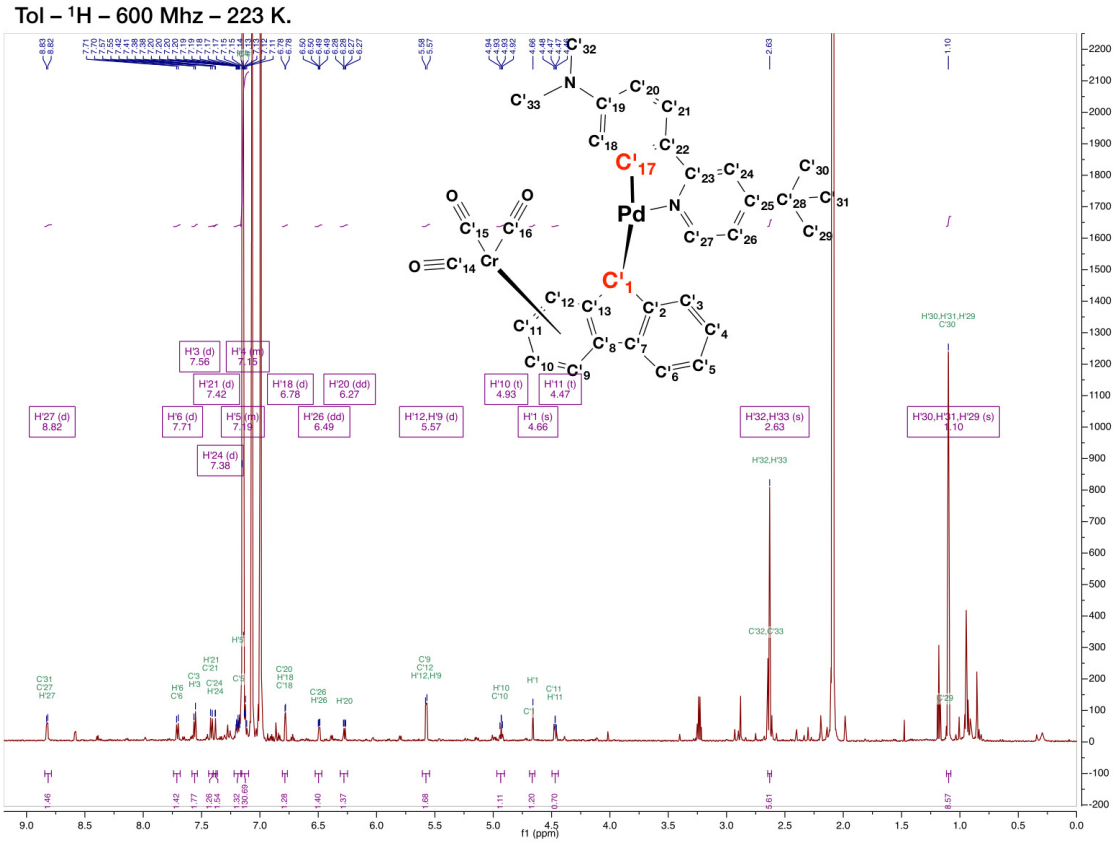


Figure S33

Complexes *trans*-3d and *cis*-3d



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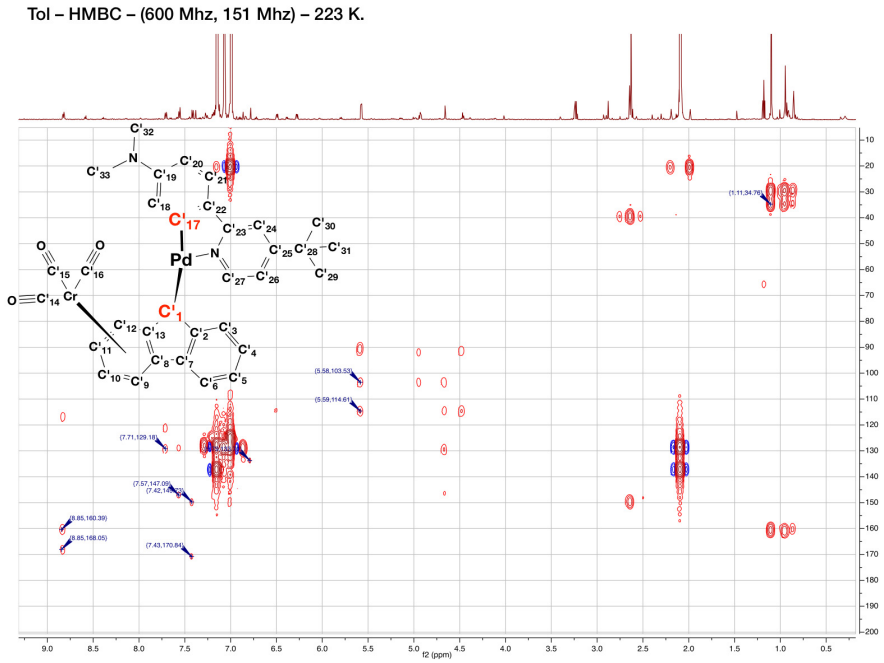

Figure S35

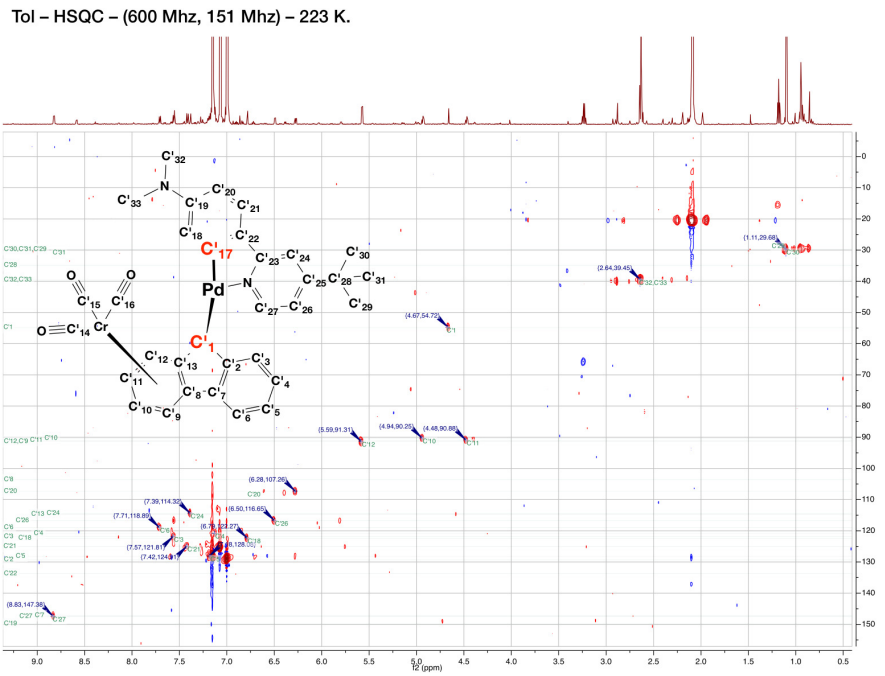

Figure S36

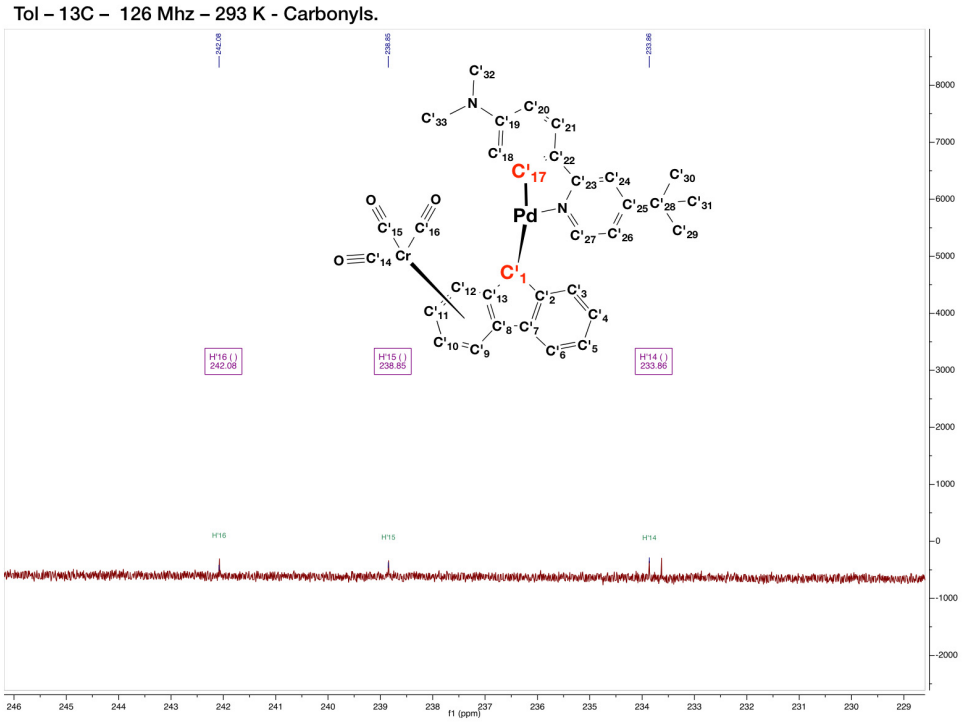

Figure S37

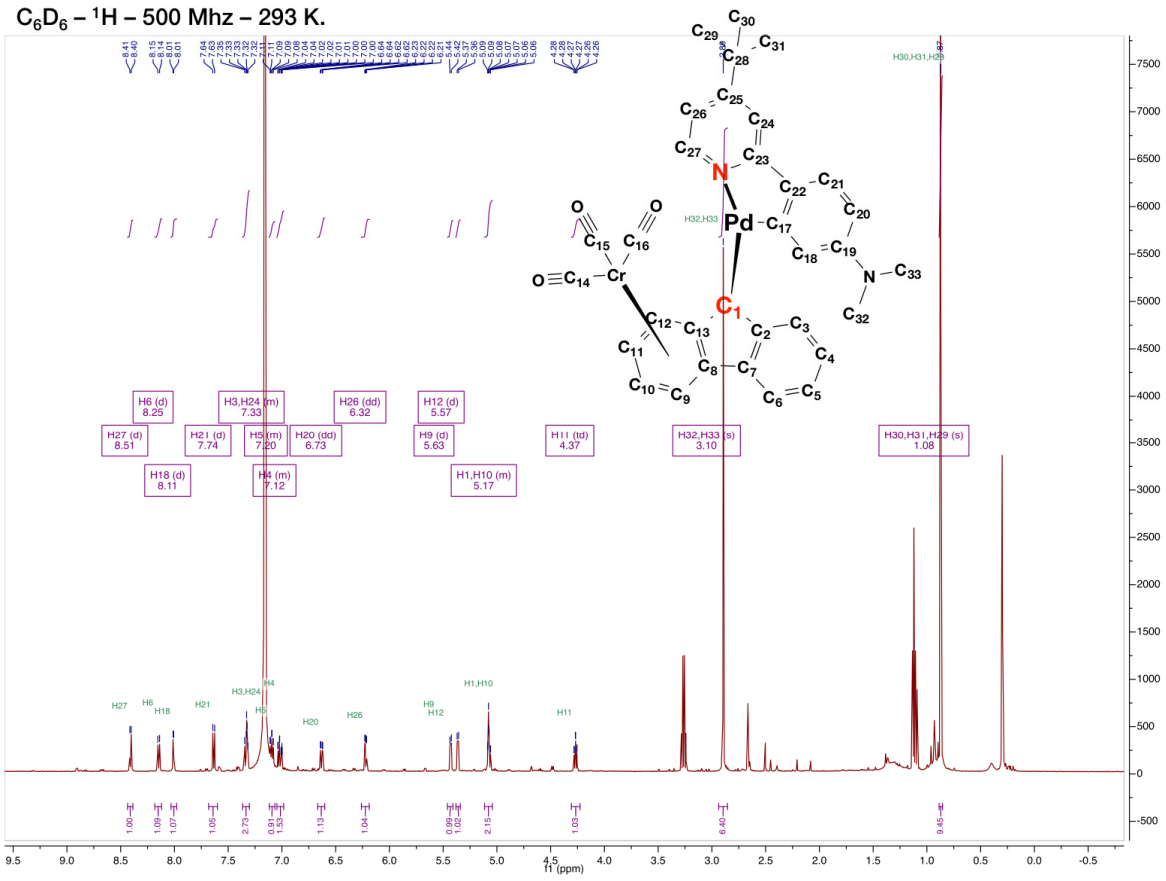
C6D6 – 1H – 500 Mhz – 293 K.
H6 (d) 8.25
H3,H24 (m) 7.33
H26 (dd) 6.32
H12 (d) 5.57
H27 (d) 8.51
H21 (d) 7.74
H5 (m) 7.20
H20 (dd) 6.73
H9 (d) 5.63
H11 (td) 4.37
H32,H33 (s) 3.10
H30,H31,H29 (s) 1.08
H18 (d) 8.11
H4 (m) 7.12
H1,H10 (m) 5.17
f1 (ppm)

Figure S38

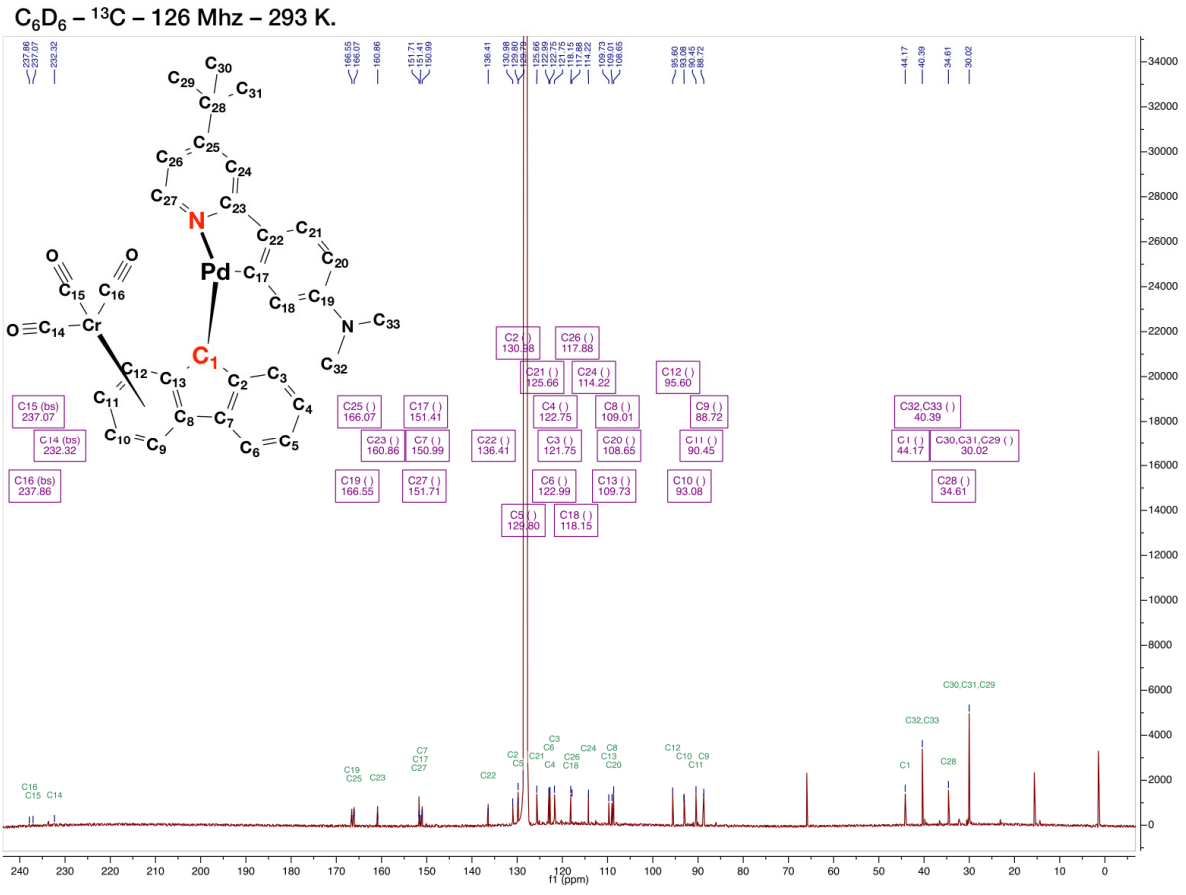

Figure S39

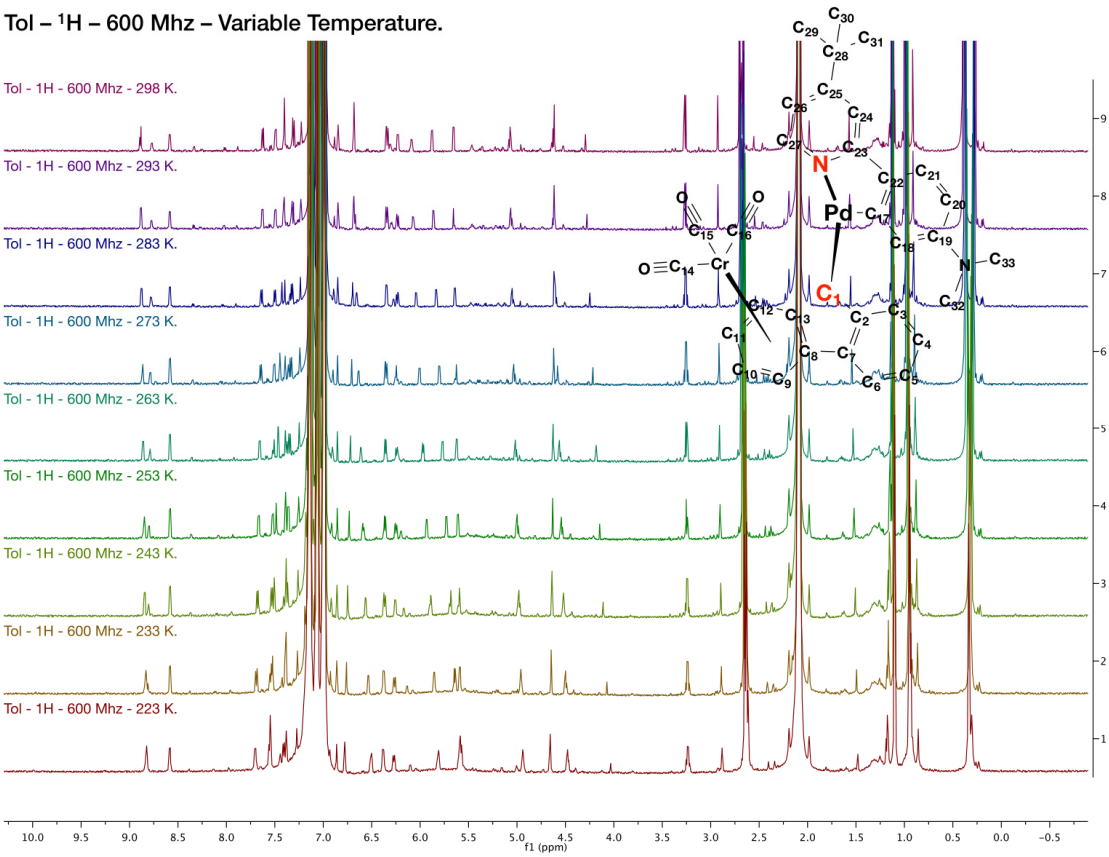
Tol – ¹H – 600 Mhz – Variable Temperature.
Tol - 1H - 600 Mhz - 298 K.
Tol - 1H - 600 Mhz - 293 K.
Tol - 1H - 600 Mhz - 283 K.
Tol - 1H - 600 Mhz - 273 K.
Tol - 1H - 600 Mhz - 263 K.
Tol - 1H - 600 Mhz - 253 K.
Tol - 1H - 600 Mhz - 243 K.
Tol - 1H - 600 Mhz - 233 K.
Tol - 1H - 600 Mhz - 223 K.
f1 (ppm)

Figure S40

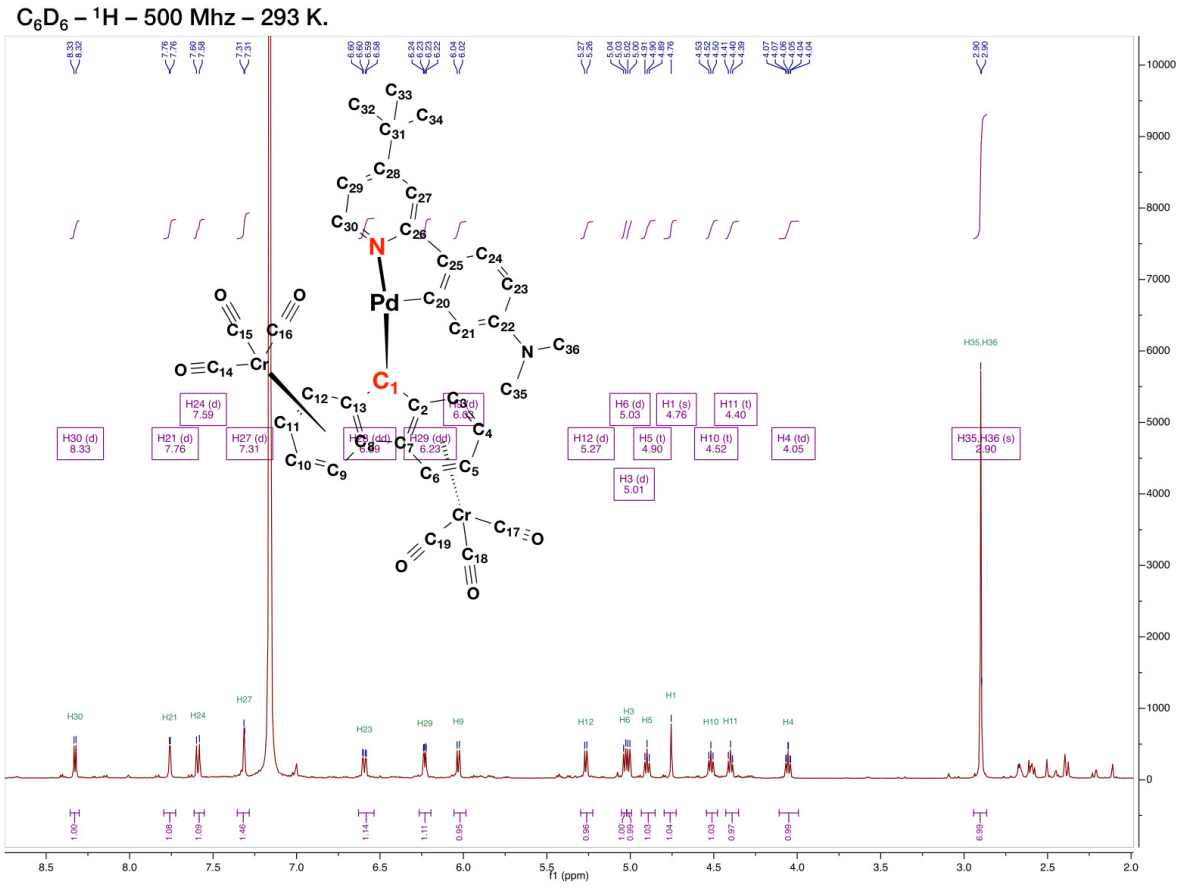

Figure S41

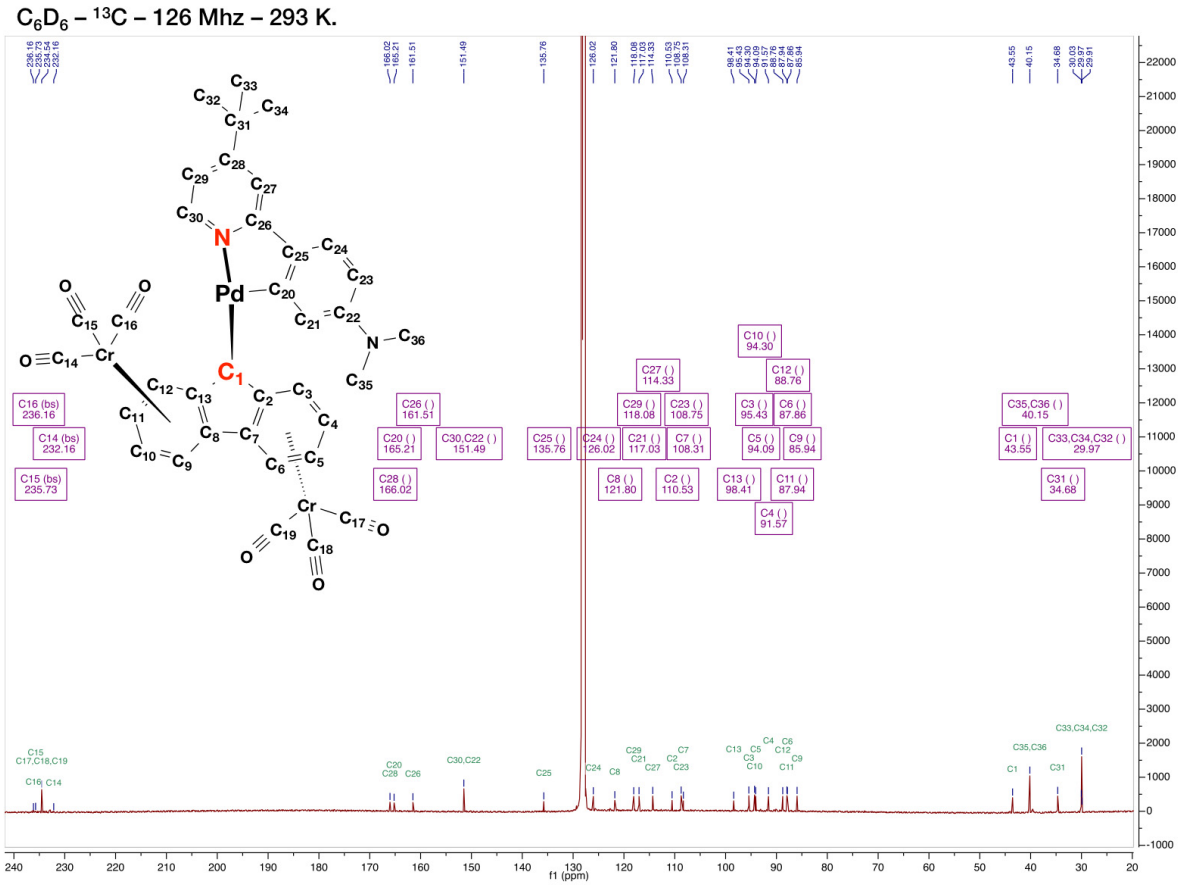

Figure S42

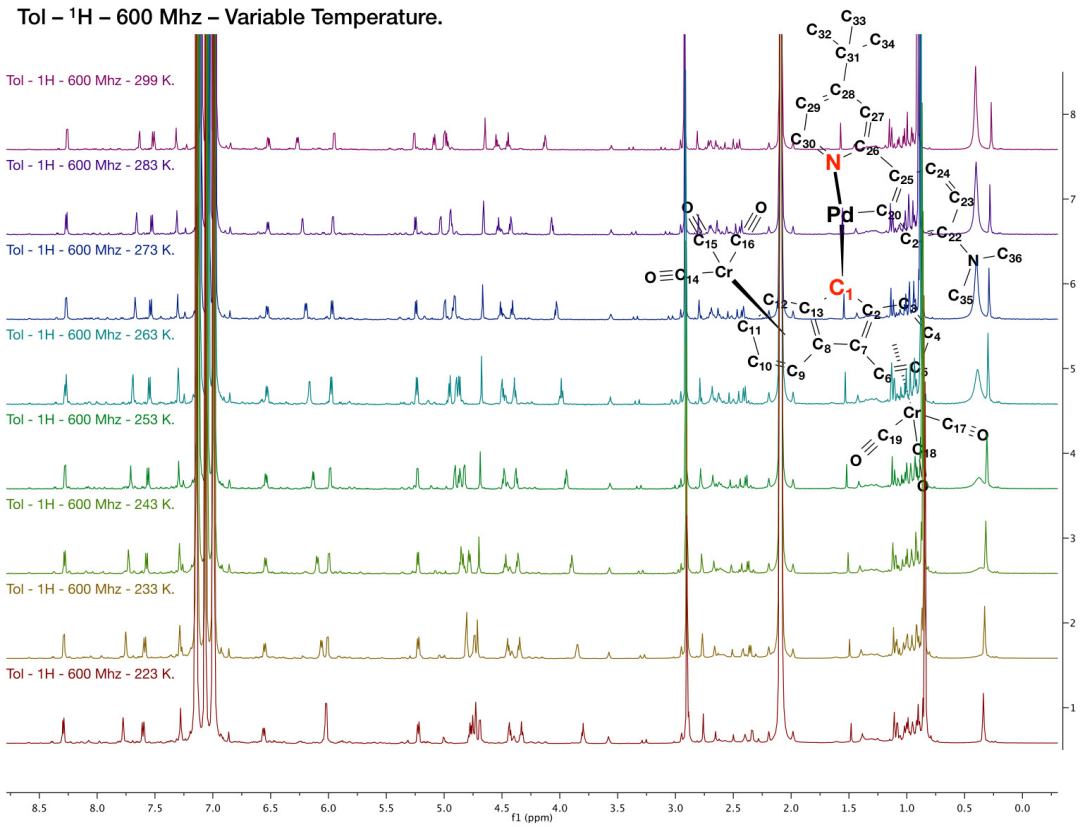
Tol – ¹H – 600 Mhz – Variable Temperature.
Tol - 1H - 600 Mhz - 299 K.
Tol - 1H - 600 Mhz - 283 K.
Tol - 1H - 600 Mhz - 273 K.
Tol - 1H - 600 Mhz - 263 K.
Tol - 1H - 600 Mhz - 253 K.
Tol - 1H - 600 Mhz - 243 K.
Tol - 1H - 600 Mhz - 233 K.
Tol - 1H - 600 Mhz - 223 K.
f1 (ppm)

Figure S43

Compound *cis*-3e.

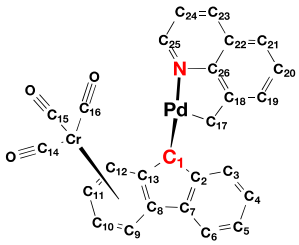

Figure S44 Atom numbering scheme for cis-3e

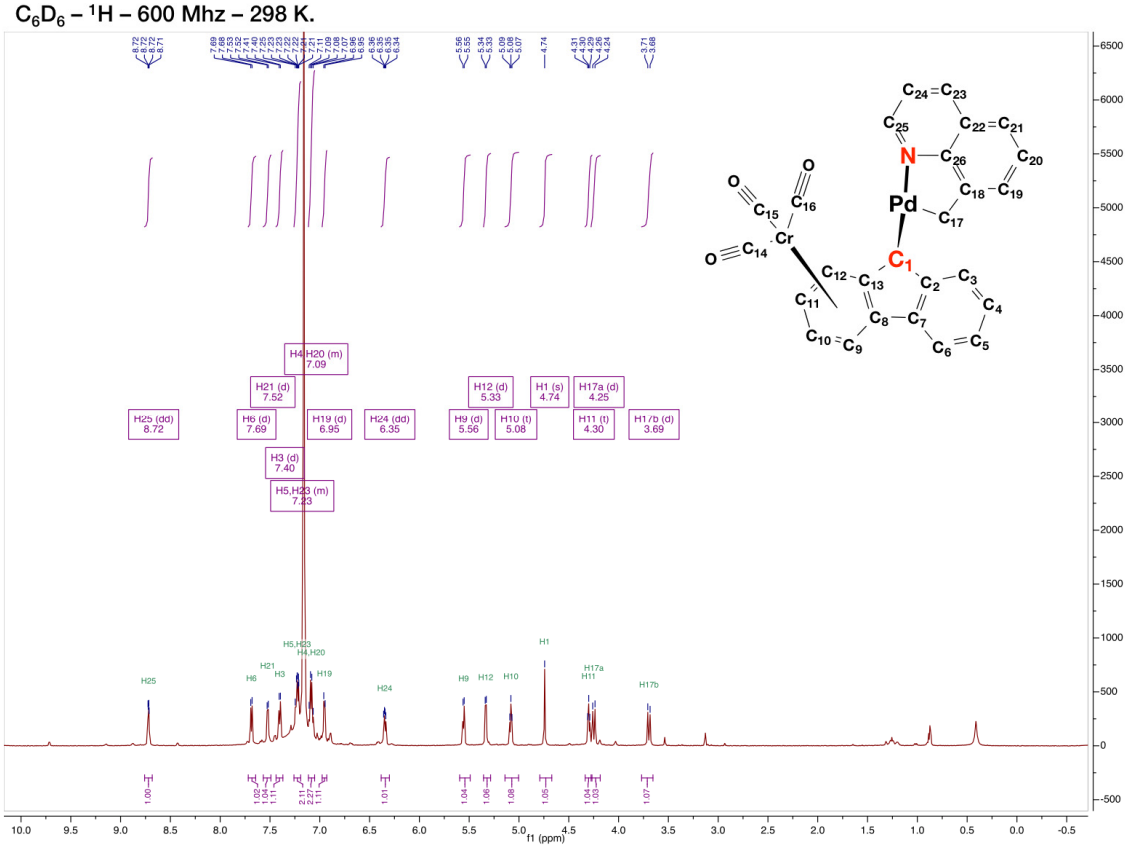

Figure S45

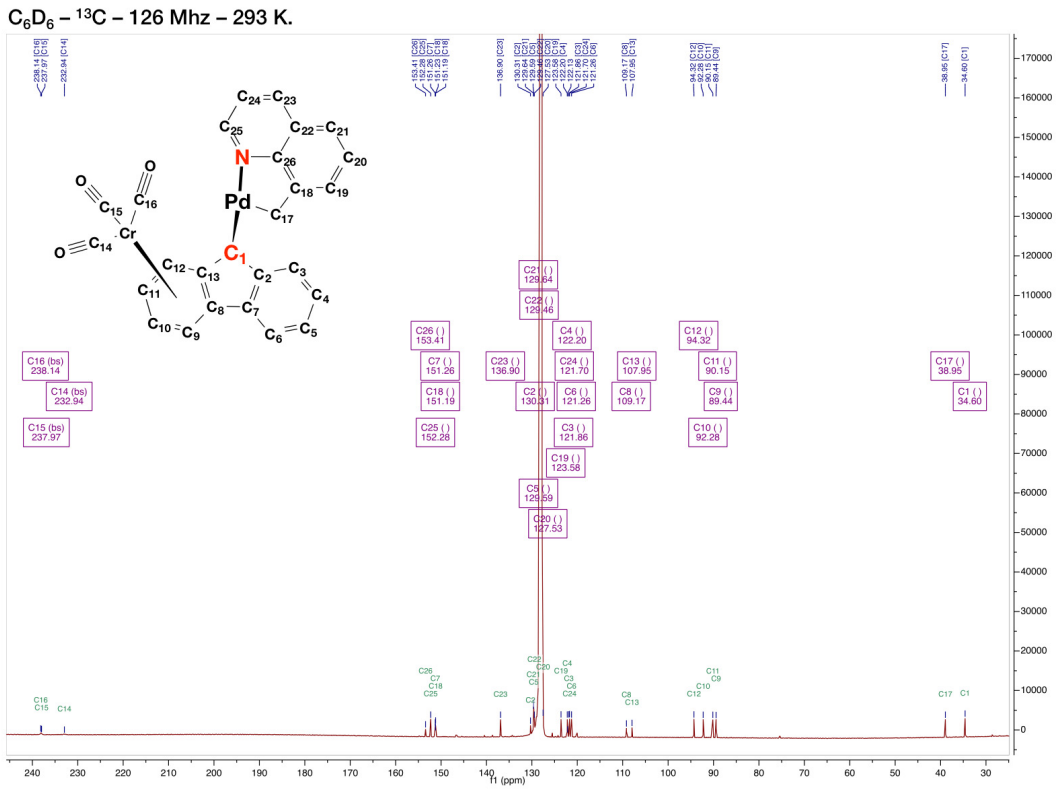

Figure S46

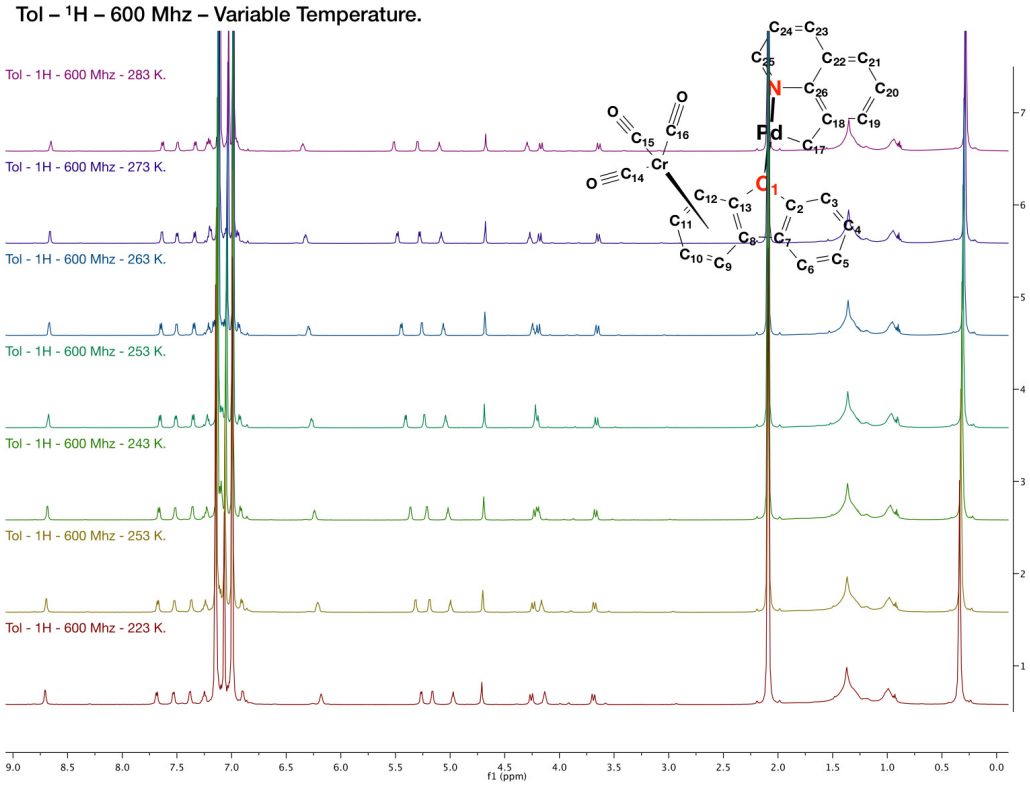

Figure S47

Computational Material

Computational ETS-NOCV analysis with an alternative fragmentation scheme.

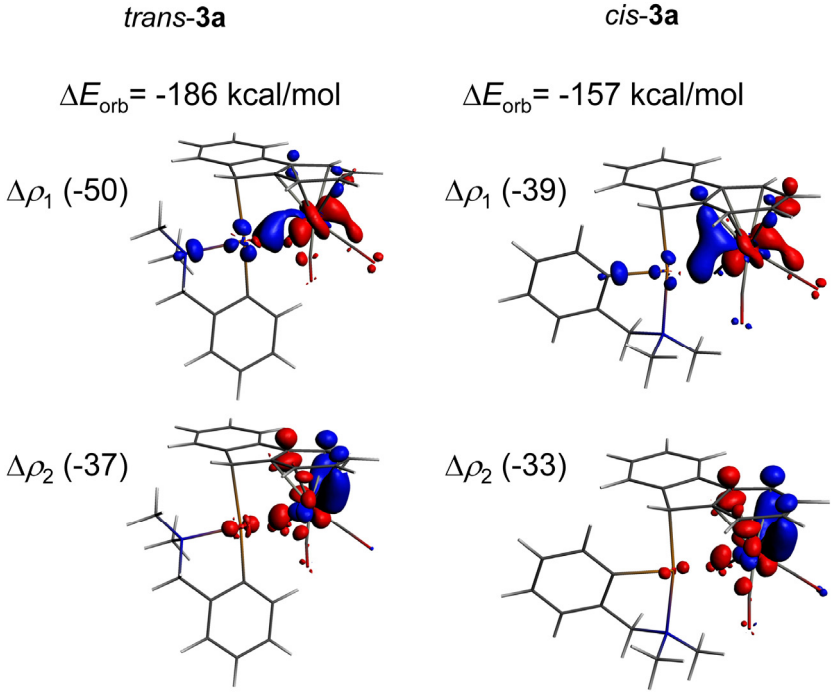

Figure S48 ETS-NOCV analyses of the interfragment orbital interactions within *trans*-**3a** (left hand side) and *cis*-**3a** (right hand side) where the arbitrary fragments are the $Cr(CO)_3$ moiety and the η^1-palladated fluorenyl ligand in their so-called prepared geometry. The isosurfaces (0.005 e/bohr^3) depict electron deformation densities, the red and blue colors being assigned to electron density donating and electron density receiving orbitals respectively. One can notice readily that the orbital component of the interfragment bonding interaction is by 30 kcal/mol larger in the trans isomer.

For the palladofluorenyl/$Cr(CO)_3$ fragmentation scheme where the main orbital interactions arise between the Cr centre, the arene and the neighbouring palladium. The strongest orbital energies are associated to electron deformation density $\Delta\rho_1$, which are associated to the Cr-arene and Cr-Pd interaction (see Figure S48); it suggests that the orbital donor-acceptor Cr→Pd interaction is stronger in *trans*-**3a** than in *cis*-**3a** ($\Delta\Delta\rho_1$= -10 kcal/mol). Using this fragmentation scheme for *trans*-**3a** and *cis*-**3a**, a Ziegler-Rauk Energy Decomposition Analysis[28] (EDA) was carried out. The total interaction energy ($\Delta E_{int}= \Delta E_{Pauli} + \Delta E_{electrostatic} + \Delta E_{orbital} + \Delta E_{dispersion}$) indicates an interfragment interaction stronger by -14 kcal/mol in *trans*-**3a** compared to *cis*-**3a**. The contribution of medium/long range dispersion forces (arising from the damped D3(BJ) correction[29]) is the same in the two cases. Further decomposition indicates however that the repulsive steric interaction ($\Delta E_{steric}= \Delta E_{Pauli} + \Delta E_{electrostatic}$) is also stronger in *trans*-**3a** by +14 kcal/mol, which can be explained by a lower compensation of Pauli repulsion by attractive electrostatic interactions. The orbital interaction is more favorable in *trans*-**3a** by -29 kcal/mol, thus making the overall interaction between $Cr(CO)_3$ and the rest of the complex more attractive in *trans*-**3a** (as compared to *cis*-**3a**) by 15 kcal/mol.

Quantum Theory of Atoms in Molecules (QTAIM) and NCIplots calculations.

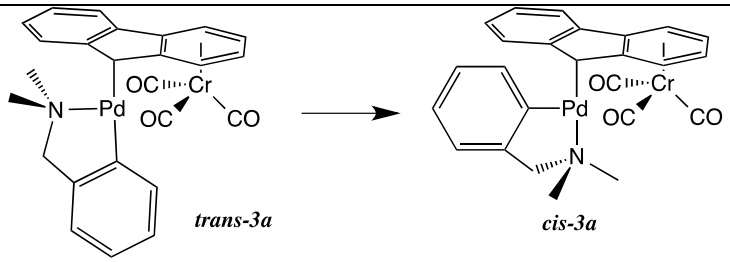

Figure 49 Schematic representation of the *trans*-**3a** → *cis*-**3a** isomerization process under study.

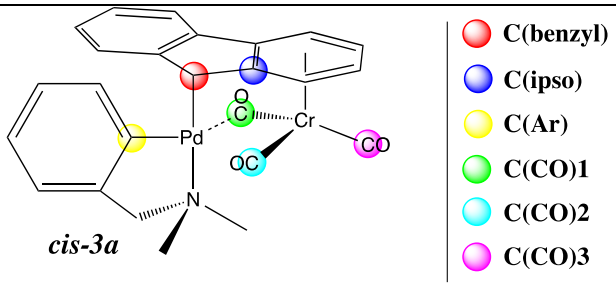

Figure 50 Definition of "C(benzyl)", "C(ipso)", "C(Ar)" and "C(CO)1-3".

Table S3: Interatomic distances (δ in Å), QTAIM analyses (densities ρ in a.u., delocalization indices **δ**, bond ellipticities **ε**, and Laplacian of the electron density $\nabla^2\rho$) dipole moments (μ in D) and relative energies (ΔE in kcal/mol) of complexes *trans*-**3a**, **TS-3a**, and *cis*-**3a**. See Scheme S2 for definition of the C atoms.

		Trans-3a	***TS-3a***	***Cis-3a***
δ(Å)	**Pd-Cr**	2.687	2.860	2.952
	Pd-C(benzyl)	2.264	2.374	2.081
	Pd-C(Ar)	2.028	1.995	2.000
	Pd-N	2.171	2.169	2.219
	Pd-C(ipso)	2.709	2.329	2.697
	Pd-C(CO)1	2.410	2.993	2.698
	Pd-C(CO)2	2.677	3.338	2.952
	Pd-C(CO)3	4.124	4.618	4.462
ρ	**Pd-Cr**	a	0.0294	a
	Pd-C(benzyl)	0.0726	a	0.1103
	Pd-C(Ar)	0.1301	0.1392	0.1372
	Pd-N	0.0824	0.0833	0.0728
	Pd-C(ipso)	a	a	a
	Pd-C(CO)1	0.0561	a	0.0321
	Pd-C(CO)2	a	a	a
	Pd-C(CO)3	a	a	a
δ	**Pd-Cr**	0.37	0.24	0.20
	Pd-C(benzyl)	0.51	0.40	0.75
	Pd-C(Ar)	0.88	0.94	0.94
	Pd-N	0.53	0.54	0.48
	Pd-C(ipso)	0.06	0.25	0.12
	Pd-C(CO)1	0.34	0.13	0.18
	Pd-C(CO)2	0.21	0.06	0.15
	Pd-C(CO)3	0.02	0.01	0.01
ε	**Pd-Cr**	a	0.59	a
	Pd-C(benzyl)	0.13	a	0.04
	Pd-C(Ar)	0.06	0.06	0.05
	Pd-N	0.08	0.08	0.04
	Pd-C(ipso)	a	a	a
	Pd-C(CO)1	0.34	a	0.82
	Pd-C(CO)2	a	a	a
	Pd-C(CO)3	a	a	a
$\nabla^2\rho$	**Pd-Cr**	a	0.0469	a
	Pd-C(benzyl)	0.1647	a	0.1751
	Pd-C(Ar)	0.1830	0.1656	0.1797
	Pd-N	0.3223	0.3232	0.2898
	Pd-C(ipso)	a	a	a
	Pd-C(CO)1	0.1134	a	0.0644
	Pd-C(CO)2	a	a	a
	Pd-C(CO)3	a	a	a
μ(D)[b]		4.91	4.97	1.26
ΔE[c]	(kcal/mol)	0.0	13.9	-5.5

a. No bond critical point found between these two centres.
b. Computed at the PBE0/SDD level with Gaussian09.
c. Single points at the PBE-D3(bj)/SDD/def2-TZVPP level.

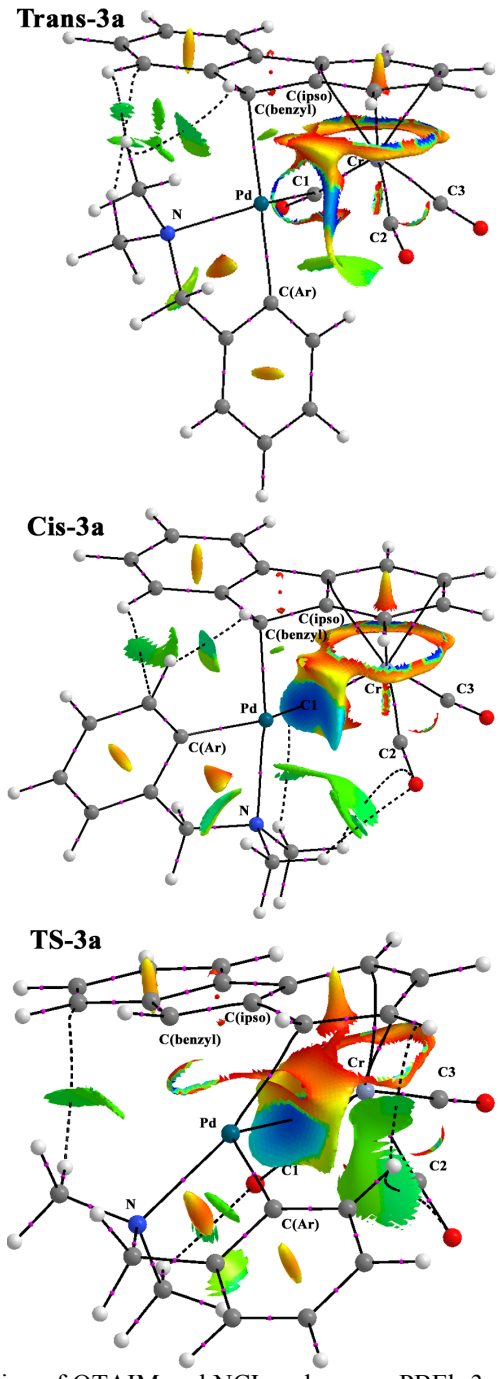

Figure 51 Combined representation of QTAIM and NCI analyses on PBEh-3c-optimized structures of *trans*-**3a**, *cis*-**3a** and **TS-3a**. Bond critical points are shown as purple spheres and bond paths are shown as black lines. NCI isosurfaces (s = 0.4 a.u.) are superimposed on the QTAIM structures, in the range of $-0.04 < \text{sign}(\lambda_2)\rho < +0.04$ a.u.. The colour code (according to the value of $\text{sign}(\lambda_2)\rho$ is: red +0.04, yellow +0.02, green 0.00, cyan -0.02 and blue -0.04 a.u. The labeling of selected atoms is shown in black.

Full reference for Gaussian 09

Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

Geometries

Optimized structures (XYZ coordinates in Å)

cis-**3a**:

```
52
Level: PBEh3c
Pd   -0.1592873   -0.1978781   -0.6362882
Cr   -1.7517307   -1.6506413    1.3807912
O    -1.7583632   -4.3956350    2.5646848
O    -2.0828335   -2.9624040   -1.2792771
O     1.1812064   -1.5667565    1.9926096
N     1.1624682   -1.6070112   -1.7285651
C     0.6037856   -1.8855199   -3.0594673
C     1.5214959   -2.8791762   -1.1009993
C     2.3764870   -0.7754992   -1.8685880
C     1.9915950    0.6003966   -2.3179324
C     2.7938324    1.3383320   -3.1760851
C     2.3966006    2.6035246   -3.5841526
C     1.1834576    3.1064159   -3.1439636
C     0.3818061    2.3591262   -2.2868685
C     0.7717553    1.0990952   -1.8416575
C    -1.7341005   -3.3520036    2.0984844
C    -1.8633116   -2.4344189   -0.2822343
C     0.0848326   -1.5967781    1.6577553
C     0.7154836    2.8150048    1.2488985
C     1.4459421    3.1117266    2.3861258
C     1.1810971    2.4861610    3.6060729
C     0.1624802    1.5566876    3.7031905
C    -0.5856532    1.2718475    2.5686036
C    -0.3125281    1.8812660    1.3327851
C    -1.2082119    1.3454241    0.2850493
C    -2.1541601    0.5178392    1.0309771
C    -3.2576521   -0.2288564    0.5873882
C    -3.9148310   -1.0973254    1.4724747
C    -3.4293262   -1.2702174    2.7789875
C    -2.3315003   -0.5285886    3.2484761
C    -1.7181863    0.3842033    2.3845018
H     1.3303447   -2.4330808   -3.6729368
H    -0.2940133   -2.4902264   -2.9686812
H     0.3484122   -0.9611805   -3.5708097
H     1.9921035   -2.7087747   -0.1369185
H     0.6381628   -3.4962950   -0.9561299
H     2.2252632   -3.4380775   -1.7295705
H     2.8642937   -0.7357173   -0.8904556
H     3.0840882   -1.2513923   -2.5630582
H     3.7304873    0.9251185   -3.5342160
H     3.0212536    3.1824633   -4.2517673
H     0.8517761    4.0839013   -3.4720446
H    -0.5623728    2.7892980   -1.9758867
H     0.9541209    3.2862014    0.3047025
H     2.2452289    3.8392880    2.3275171
H     1.7746350    2.7320523    4.4762363
H    -0.0480051    1.0706650    4.6481182
H    -1.6232529    2.0471555   -0.4361600
H    -3.5901237   -0.1472587   -0.4400961
H    -4.7589805   -1.6798335    1.1313074
H    -3.9062127   -1.9893747    3.4315709
H    -1.9698590   -0.6732723    4.2575010
```

trans-**3a**:

```
52
Level: PBEh3c
Pd    0.3564853    0.3493583    0.3356189
Cr    1.5035278   -1.0846178   -1.6258393
O     2.8138358   -3.7744719   -1.5650365
O     3.6845768   -0.0951657    0.1886769
O    -0.7918088   -2.4436779   -0.2314729
N    -0.5513697    1.6315282    1.8333689
C     2.3105696   -2.7496877   -1.5585145
C     2.7888747   -0.4925637   -0.4011705
C     0.1017538   -1.8443312   -0.6302896
C     0.4813333    0.7778596   -2.3360386
C     1.8664428    0.8991672   -2.5702949
C     2.5339024   -0.0651172   -3.3354874
C     1.8449138   -1.1894792   -3.8231954
C     0.4619262   -1.3265270   -3.6219577
C    -0.2241087   -0.3331196   -2.9185908
C    -1.6129149   -0.1999639   -2.5449750
C    -2.7226715   -0.9682024   -2.8728175
C    -3.9650960   -0.5778739   -2.4112970
C    -4.0924205    0.5764000   -1.6340284
C    -2.9906325    1.3355197   -1.2869324
C    -1.7232366    0.9423069   -1.7218746
C    -0.4033742    1.4974121   -1.4613712
C    -0.8024201    3.0179206    1.4472401
C    -1.8176068    1.0077541    2.2453927
C     0.4107039    1.6019317    2.9541126
C     0.9304414    0.2117311    3.1449296
C     1.2996750   -0.2511370    4.4006349
C     1.8194058   -1.5282788    4.5436047
C     1.9546363   -2.3316767    3.4230792
C     1.5718177   -1.8635561    2.1716821
C     1.0507893   -0.5833617    1.9974675
H     2.4194567    1.7260022   -2.1421658
H     3.5987381    0.0228384   -3.5002284
H     2.3882659   -1.9571420   -4.3573619
H    -0.0564520   -2.1974685   -4.0010358
H    -2.6231226   -1.8535238   -3.4891677
H    -4.8432691   -1.1576907   -2.6604325
H    -5.0756268    0.8845914   -1.3020473
H    -3.1213342    2.2344055   -0.6967383
H    -0.2602229    2.5583537   -1.2789669
H     0.1144680    3.4821785    1.0882709
H    -1.5443786    3.0615661    0.6540961
H    -1.1780774    3.6002807    2.2973819
H    -2.2943062    1.5932623    3.0417209
H    -2.4979879    0.9464397    1.3978919
H    -1.6394995    0.0003859    2.6135250
H     1.2321142    2.2778919    2.6979824
H    -0.0591011    2.0016189    3.8640863
H     1.1829847    0.3849443    5.2715951
H     2.1100594   -1.8932161    5.5200327
H     2.3578192   -3.3321890    3.5196683
H     1.7015206   -2.5296095    1.3272690
```

TS-**3a**:

```
52
Level: PBEh3c
Pd   -0.7153504   -0.3088312   -0.2081998
Cr    2.0754308   -0.7854116   -0.6156435
O     4.9257253   -0.1935657   -1.2724184
O     1.6725022   -0.3135546   -3.5649615
O     1.8812851    2.1153283    0.1430071
N    -1.9676059    1.4620243   -0.1972949
C    -1.2803550    2.5610910   -0.8912383
C    -2.3531667    1.9096808    1.1418635
C    -3.1503844    1.0591850   -0.9808130
C    -2.7268695    0.2196469   -2.1486300
C    -3.5017836    0.1377401   -3.2975589
C    -3.1505910   -0.7419805   -4.3103030
C    -2.0299928   -1.5430656   -4.1581325
C    -1.2477693   -1.4448383   -3.0134688
C    -1.5634625   -0.5476260   -1.9982026
C     3.8284661   -0.4078321   -1.0243359
C     1.7529682   -0.5205522   -2.4459094
C     1.8991610    1.0190680   -0.1836951
C     0.3554516    0.9896991    3.9342256
C     1.4058858    1.6081237    4.5916410
C     2.7294616    1.3128038    4.2645673
C     3.0218971    0.3868183    3.2766554
C     1.9761846   -0.2433840    2.6187561
C     0.6357454    0.0627511    2.9351893
C    -0.2510562   -0.7113276    2.0852459
C     0.5657733   -1.5396354    1.2971395
C     0.2245261   -2.2901716    0.1282223
C     1.3250744   -2.8762784   -0.6065277
C     2.6298912   -2.8437700   -0.1259432
C     2.9692209   -1.9813895    0.9450800
C     1.9587636   -1.2316181    1.5571731
H    -1.9709454    3.3972798   -1.0523722
H    -0.4448956    2.9158319   -0.2954485
H    -0.9064156    2.2298934   -1.8571070
H    -2.8978754    1.1213254    1.6588043
H    -1.4636871    2.1509489    1.7213670
H    -2.9923013    2.7994001    1.0952629
H    -3.7992413    0.4710529   -0.3251185
H    -3.7266337    1.9437806   -1.2854883
H    -4.3880687    0.7541501   -3.4012980
H    -3.7517808   -0.8063096   -5.2076826
H    -1.7563793   -2.2447576   -4.9361566
H    -0.3836276   -2.0903902   -2.9270028
H    -0.6687108    1.2229146    4.2004522
H     1.1992748    2.3302759    5.3707824
H     3.5333498    1.8122519    4.7881149
H     4.0517769    0.1662276    3.0235371
H    -1.2888447   -0.9035064    2.3339789
H    -0.7393529   -2.7925735    0.0410341
H     1.0984322   -3.4828532   -1.4729601
H     3.4060724   -3.4006383   -0.6328615
H     3.9948271   -1.9134323    1.2846730
```

cis-**I**:

45
Level:PBEh3c

Pd	0.0086188	0.0571738	-0.0878572
N	1.6811660	-0.0026465	-1.6370044
C	1.5448456	0.6630644	-2.9256451
C	2.8082759	0.5910418	-0.9090082
C	1.9355916	-1.4290722	-1.8529212
C	1.6873196	-2.2318712	-0.6132203
C	2.2845353	-3.4820609	-0.4994702
C	1.9157661	-4.3470125	0.5166939
C	0.9165239	-3.9541279	1.3908186
C	0.3472640	-2.6912809	1.2861962
C	0.7490423	-1.7634562	0.3228100
H	0.6621526	0.2959016	-3.4481774
H	1.4475773	1.7374002	-2.7878409
H	2.4192209	0.4861655	-3.5643422
H	2.5937973	1.6299275	-0.6602905
H	2.9880111	0.0499283	0.0171852
H	3.7240482	0.5601946	-1.5144468
H	1.2446603	-1.7688755	-2.6309588
H	2.9503356	-1.5824836	-2.2507665
H	3.0281777	-3.7905810	-1.2268395
H	2.3813845	-5.3199068	0.6062364
H	0.5696312	-4.6332715	2.1598100
H	-0.4562809	-2.4529652	1.9659929
C	-1.7884823	1.5753282	1.5842078
C	-2.5216325	2.0002821	2.6863881
C	-2.4201941	1.3348921	3.8957728
C	-1.5478388	0.2637818	3.9916776
C	-0.8404500	-0.1695711	2.8772626
C	-0.9750208	0.4293033	1.6231873
H	-2.2913156	0.2831635	-2.1256005
H	-2.6932530	2.9931988	0.2174671
H	-3.1608820	2.8730855	2.6030735
H	-2.9917409	1.6633198	4.7540862
H	-1.4090706	-0.2403038	4.9402170
H	-0.1430258	-0.9809407	3.0185534
H	-1.7712723	3.3627871	-2.0823962
C	-0.9943619	2.6128613	-1.8871106
H	-0.8163410	2.0715046	-2.8135989
C	-2.5620615	0.9252961	-1.2880445
H	-3.3678848	1.5977845	-1.6113022
H	-2.9386820	0.2960623	-0.4847747
H	-0.0802415	3.1351278	-1.6057849
C	-1.7480234	2.4501596	0.3691577
N	-1.3955176	1.6909284	-0.8329672
H	-0.9743729	3.2107631	0.5135745

trans-**I**:

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45
Level:PBEh3c
Pd    0.0122082    0.0481281   -0.0767559
N     2.1136296   -0.0966374    0.0121561
C     2.8039137    1.1994245    0.0030368
C     2.5210628   -0.8587342    1.2015760
C     2.5072070   -0.8401452   -1.2123933
C     1.5814917   -1.9952105   -1.4212359
C     2.0229861   -3.2022762   -1.9438297
C     1.1278442   -4.2506411   -2.1046900
C    -0.1896554   -4.0779011   -1.7121524
C    -0.6092813   -2.8606590   -1.1839823
C     0.2503927   -1.7708729   -1.0407477
H     2.4700290    1.7917749   -0.8459018
H     2.5875004    1.7584966    0.9067347
H     3.8876636    1.0530527   -0.0702096
H     2.1854474   -0.3491924    2.1022592
H     2.0788626   -1.8518649    1.1791634
H     3.6121871   -0.9595920    1.2397577
H     2.4382983   -0.1403077   -2.0500525
H     3.5602645   -1.1437173   -1.1354624
H     3.0636569   -3.3344486   -2.2208057
H     1.4605569   -5.1962525   -2.5128219
H    -0.8924045   -4.8970112   -1.8068523
H    -1.6457318   -2.7899992   -0.8659017
C    -1.4787809    2.3665956    0.8428191
C    -1.9591165    3.4202654    1.6068734
C    -1.2252569    3.8711123    2.6949861
C    -0.0350396    3.2379065    3.0140898
C     0.4248271    2.1790035    2.2374284
C    -0.2637981    1.7209467    1.1138983
H    -2.6616791   -1.3792976    0.5916901
H    -3.3114276    2.0584695   -0.2841109
H    -2.9073142    3.8887008    1.3645104
H    -1.5894546    4.6931517    3.2975133
H     0.5334448    3.5615552    3.8778031
H     1.3486916    1.7006144    2.5502106
H    -3.5470645    0.2168383   -1.9052260
C    -2.5035995   -0.0789450   -1.7462063
H    -2.4278248   -1.1565848   -1.8427720
C    -2.8414831   -0.3065589    0.6169939
H    -3.9112524   -0.1248470    0.4586940
H    -2.5650291    0.0688012    1.5994118
H    -1.8877895    0.3715301   -2.5213067
C    -2.2374521    1.8307975   -0.3291031
N    -2.0442941    0.3607144   -0.4225954
H    -1.8588654    2.2649522   -1.2587601
```

TS-**I**:

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Level:PBEh3c

Pd	-0.7089517	-0.3370594	-0.1741172
N	1.9838081	0.1322915	-0.3371092
C	2.2202300	1.5038137	-0.7229332
C	2.7934727	-0.2413815	0.8007582
C	2.1582294	-0.7964105	-1.4428881
C	1.5758372	-2.1532168	-1.1299060
C	2.3381046	-3.2939911	-1.3449657
C	1.8100024	-4.5496293	-1.0732205
C	0.5206362	-4.6515445	-0.5764709
C	-0.2281438	-3.4992403	-0.3580192
C	0.2632090	-2.2167231	-0.6305774
H	1.5683639	1.7733568	-1.5557232
H	1.9870165	2.1678031	0.1105227
H	3.2590161	1.6973827	-1.0333424
H	2.6156860	0.4487229	1.6254596
H	2.5329018	-1.2465933	1.1309639
H	3.8711016	-0.2274964	0.5743297
H	1.6415985	-0.3761551	-2.3124128
H	3.2210836	-0.8853408	-1.7269011
H	3.3526023	-3.2090152	-1.7212567
H	2.4060783	-5.4382245	-1.2398506
H	0.1005053	-5.6261268	-0.3569820
H	-1.2339328	-3.6154094	0.0322548
C	-1.3423951	2.2012573	0.9656927
C	-1.3632090	3.2086640	1.9186500
C	-0.7048811	3.0240479	3.1268488
C	-0.0474761	1.8288706	3.3821044
C	-0.0289133	0.8162942	2.4286768
C	-0.6642843	1.0073184	1.2120872
H	-3.7701771	-0.6079401	-0.2679220
H	-2.9124799	2.8951322	-0.3741695
H	-1.8955349	4.1335101	1.7275368
H	-0.7179223	3.8062697	3.8742351
H	0.4495453	1.6791910	4.3322458
H	0.4779222	-0.1182395	2.6404705
H	-3.4029358	1.3896347	-2.5138785
C	-2.5630925	0.7621826	-2.1931773
H	-2.7790672	-0.2711718	-2.4583753
C	-3.5651072	0.4364343	-0.0431709
H	-4.4252782	1.0408538	-0.3551996
H	-3.4353802	0.5385350	1.0314157
H	-1.6685209	1.0720899	-2.7299176
C	-2.0148555	2.2634105	-0.3652808
N	-2.3491857	0.8707501	-0.7480378
H	-1.3327714	2.6614279	-1.1220442

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