Supporting Information

Pd-Catalyzed Hydroamination of Alkoxyallenes with Azole Heterocycles: Examples and Mechanistic Proposal

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Contents

General methods

The structures were optimized by using density functional theory (DFT) at the M06/6-311+G** (SDD for Pd) level of theory[1] as implemented in Gaussian 09.[2] The stationary points were characterized by frequency calculations in order to verify that they have the right number of imaginary frequencies. Solvent effects were taken into account at the same levels of theory by applying the conductor-like polarizable continuum model (CPCM, Solvent = Acetonitrile).[3,4] For verification purposes the following theoretical levels were also applied in special cases: M06/def2TZVPP[5,6] and B3LYP-D3/6-31G** (LANL2DZ for Pd).[7,8]

[1] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215.

[2] Gaussian09, 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**.

[3] V. Barone, M. Cossi, *J. Phys. Chem. A* **1998**, *102*, 1995.

[4] M. Cossi, N. Rega, G. Scalmani, V. Barone, *J. Comp. Chem.* **2003**, *24*, 669.

[5] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.

[6] F. Weigend, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057.

[7] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104.

[8] P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 270.

Complex formation and binding energies

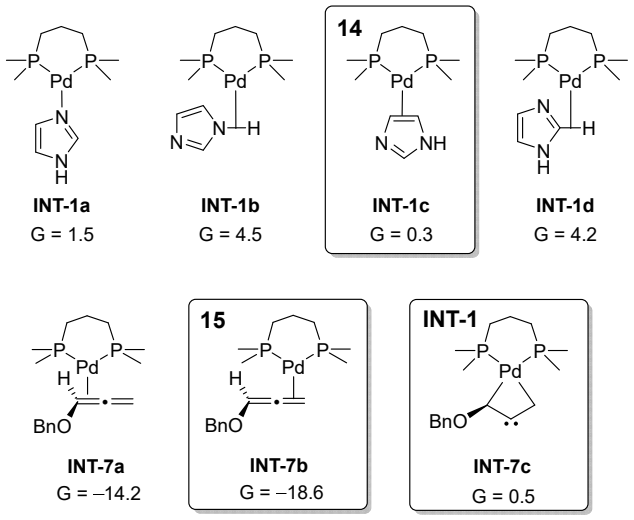


Figure S1. Possible coordination complexes of (dppp)-Pd(0) and imidazole (top) and (dppp)-Pd(0) and benzoxyallene (bottom). The structures highlighted with frames appeared in the main text and the numbers in the upper left corners are the structure numbers in the main text.

Mechanism A. Pd–H insertion into the allene

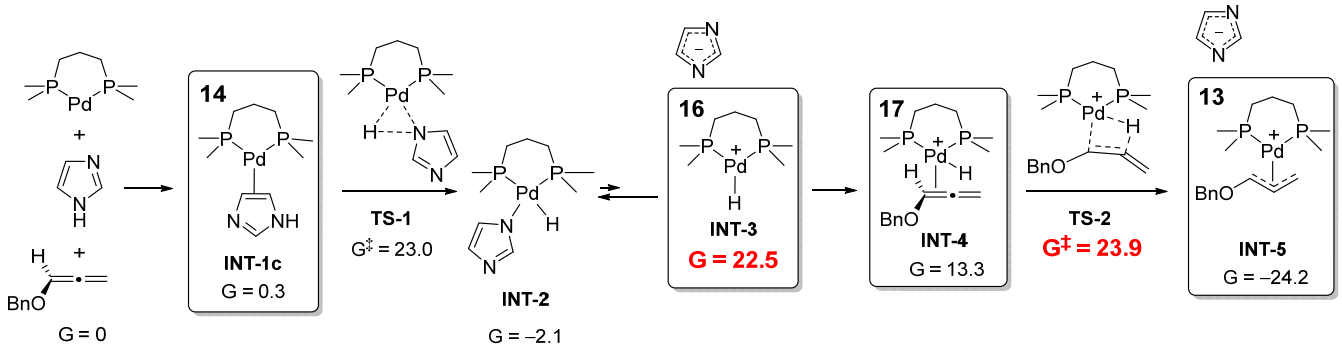


Figure S2. Mechanistic scenario, involving N–H oxidative addition, formation of **16** (**INT-3**), and Pd–H insertion into the allene. The key hydrido-palladium cationic complex (**16**) is too unstable (22.5 kcal/mol). The structures highlighted with frames appeared in the main text and the numbers in the upper left corners are the structure numbers in the main text.

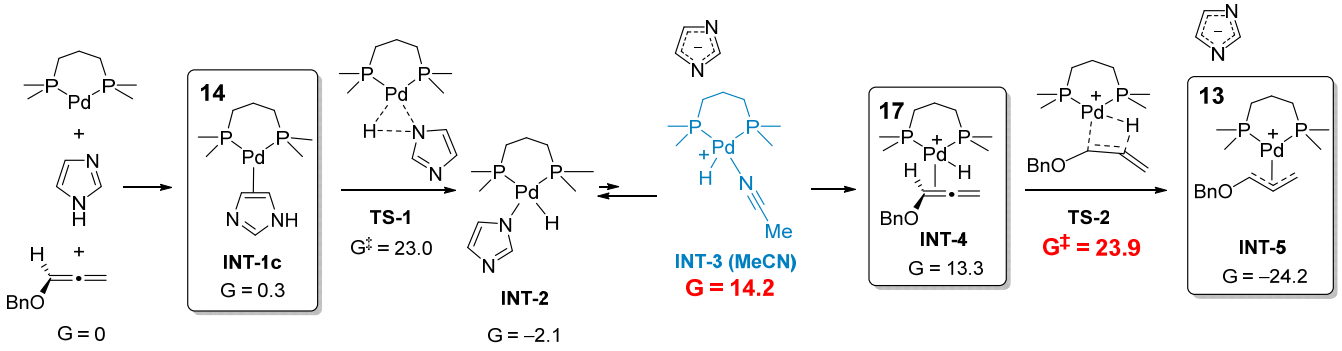


Figure S3. Mechanistic scenario, involving N–H oxidative addition, formation of solvent stabilized **INT-3 (MeCN)**, and Pd–H insertion into the allene. The key hydrido-palladium cationic complex (**INT-3 (MeCN)**) is still too unstable (14.2 kcal/mol). The structures highlighted with frames appeared in the main text and the numbers in the upper left corners are the structure numbers in the main text.

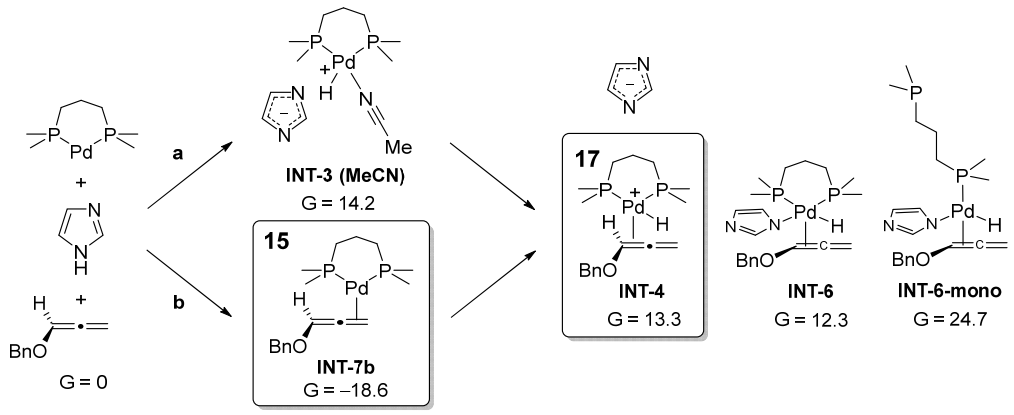


Figure S4. The most probable initial complex (**15**/**INT-7b**) and **INT-3 (MeCN)**. The energy difference in favor of **15**/**INT-7b** by 32.8 kcal/mol. Route b (**15**/**INT-7b** to **17**/**INT-4**) involves an exceedingly high energy increase (31.9 kcal/mol) which makes it unfeasible. The coordination of imidazole to palladium at that point, forming the pentacoordinated **INT-6** species does not seem to ease the situation. On the other hand, the option of a decoordination of one of the phosphines from palladium to form a monodentate dppp ligand is not energetically feasible. The structures highlighted with frames appeared in the main text and the numbers in the upper left corners are the structure numbers in the main text.

Mechanism B. Pd(0)-allene complex as active species

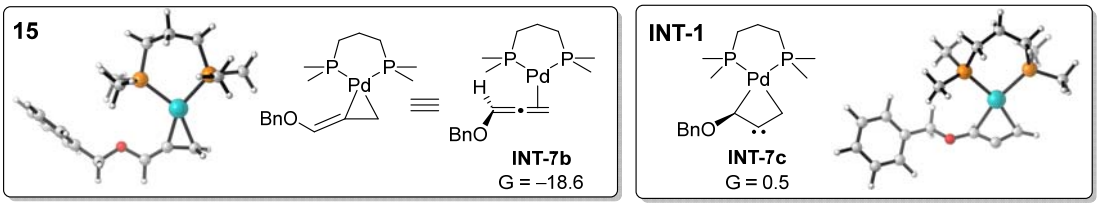


Figure S5. Structural and energetic comparison of allene-Palladium(0) intermediates: **15**/**INT-7b** and **INT-1**/**INT-7c**. The structures highlighted with frames appeared in the main text and the numbers in the upper left corners are the structure numbers in the main text. **INT-1**/**INT-7c** is the precursor of the protonation step, bearing a bent π-allyl-type structure wherein the metal is bound to the two terminal carbon atoms of the allene, whereas the central carbon shows the typical structure of a carbene.

The energy of **INT-1**/**INT-7c** is 19.1 kcal/mol higher than that of **15**/**INT-7b**, and thus, it can be regarded as a very unstable and reactive isomer, comparing to the regular allene-palladium complex **15**/**INT-7b**. Its participation in a hypothetical equilibrium between the different allene-complexes would be almost negligible, but its significance comes from the fact that its protonation with a soft acid like imidazole occurs almost barrierless (see **Figure 2** in the main text, **TS-1** vs **INT-1** $\Delta G^{\#} = 0.6$ *kcal/mol*). These data seem to indicate that **INT-1**/**INT-7c** is a transient intermediate, which in the presence of acids gets protonated very easily to form the very stable complex **13**/**INT-5**. The structure and energy of **INT-1**/**INT-7c** are actually closer to a transition state than to a minimum (although it is in fact a local minimum in the potential energy surface), and it becomes significant only when protonated *acidic* species participate in the reaction.

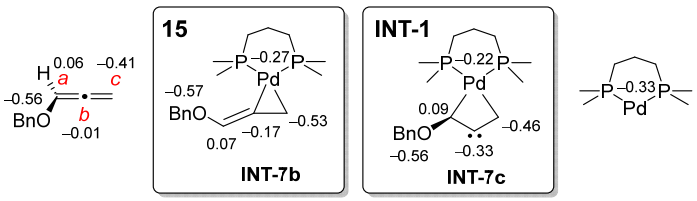


Figure S6. The charge of the different atoms computed by Natural Population Analyses. The allene is becoming more electron rich by the coordination in the complexes, especially in **INT-1**/**INT-7c**.

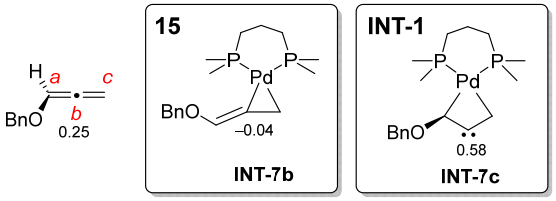
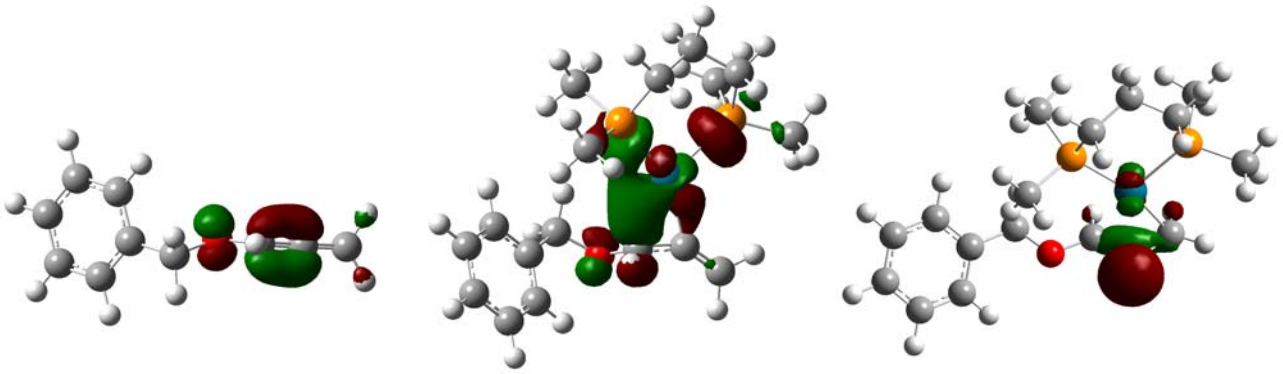


Figure S7. Fukui nuclepohilicity indexes of the central carbon C_b.

The computed Fukui nucleophilicity indexes at the central allene C_b atom indicate that it presents a medium/low nucleophilicity (+0.25) in the free allene, that becomes insignificant (-0.04) when coordinated to the Pd atom in **15**/**INT-7b**. However, the formation of the *carbene*-like structure in **INT-1**/**INT-7c** induces a severe increase in its nucleophilicity to reach a maximum of +0.58, confirming our idea that the central carbon becomes very basic and reactive in this high-in-energy complex. Noteworthy, the Fukui electrophilicity indexes at that specific carbon do not show any change between the three species.



free allene
-6.8 eV

INT-7b
-5.6 eV

INT-7c
-5.2 eV

Figure S8. 3-D representation of the HOMO orbitals and their energies in eV for the free allene and the complexes (**15**/**INT-7b** and **INT-1**/**INT-7c**).

The HOMO energies in the different compounds show a clear trend, increasing from the free allene (-6.8 eV) to 18 / INT-7b (-5.6 eV), and even more to **INT-1**/**INT-7c** (-5.2 eV). More interestingly, in the benzyloxyallene, the HOMO is centered in an oxygen lone pair and especially in the π-system of the C=C closer to the oxygen, as would be the case in any enol ether. In **15**/**INT-7b**, the major contribution of the HOMO comes from one of the d-orbitals in the Palladium, probably the one involved in binding the Ca atom of the allene. And noteworthy, in **INT-1 INT-7c**, the HOMO corresponds to an electron lone pair, located in a sp^2 orbital of the C_b atom, coplanar to the other two carbons, C_a and C_c. In our opinion, that orbital is a clear confirmation of the carbene nature of the central carbon atom in **INT-1**/**INT-7c**.

In conclusion, the free benzyloxyallene presents a HOMO orbital similar to that of an enol-ether, but its low energy makes a protonation event unfeasible. After coordination of the allene to a Pd(0) complex (**15**/**INT-7b**), the protonation would take place in the palladium atom, to form the type of species proposed by Trost, Amatore, and others, but due to the low energy of its HOMO (its low basicity), the protonation can only take place with relatively acidic species, which must be at least carboxylic-type of acids. Finally, the formation of a transient intermediate (**INT-1**/**INT-7c**) with a carbene structure and higher basicity, facilitates the protonation of the allene at the central carbon by even slightly acidic species, to irreversibly form a π-allyl system (**13**/**INT-5**).

Cartesian coordinates of the structures involved in the computational study

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INT-1a

C	-2.67973	-1.31441	-0.87916
H	-3.39516	-2.14371	-0.77592
H	-2.44035	-1.23618	-1.94912
C	-3.33046	-0.01898	-0.39521
H	-4.36987	-0.02154	-0.74749
H	-3.40675	-0.02299	0.70252
C	-2.68835	1.28386	-0.87148
H	-3.41166	2.10653	-0.77019
H	-2.44185	1.21100	-1.94022
P	-1.11860	-1.81946	-0.00942
P	-1.13737	1.79909	0.00904
Pd	0.36133	-0.00365	0.04957
C	-1.81153	-2.33644	1.62064
H	-1.05142	-2.89873	2.17131
H	-2.07956	-1.46058	2.21859
H	-2.69810	-2.97034	1.49107
C	-0.92379	-3.48996	-0.77570
H	-0.11752	-4.03028	-0.27108
H	-1.84842	-4.07718	-0.70245
H	-0.65412	-3.38057	-1.83040
C	-1.84442	2.30563	1.63640
H	-1.09121	2.87069	2.19368
H	-2.73431	2.93437	1.50414
H	-2.11006	1.42560	2.22913
C	-0.94970	3.47297	-0.75113
H	-1.88025	4.05141	-0.68412
H	-0.15291	4.01907	-0.23777
H	-0.66970	3.36912	-1.80370
C	4.76734	-0.09061	-0.71686
C	3.45350	-0.13872	-1.07815
C	3.47774	0.14931	1.04881
N	4.76712	0.09263	0.64219
H	5.58137	0.17365	1.23444
H	5.67865	-0.16812	-1.28736
H	3.03021	-0.26999	-2.06341
H	3.19191	0.29083	2.08099
N	2.65583	0.01138	0.03270

INT-1b

C	-2.69532	-0.53339	-0.84383
H	-3.68206	-1.01922	-0.81405
H	-2.37912	-0.52956	-1.89630
C	-2.82214	0.90407	-0.33262
H	-3.78756	1.28634	-0.68731
H	-2.90525	0.91128	0.76419
C	-1.75001	1.89808	-0.78729
H	-2.15238	2.92095	-0.74047
H	-1.48731	1.71125	-1.83789
P	-1.51627	-1.65128	0.05983
P	-0.15769	1.89106	0.16841
Pd	0.39110	-0.37114	0.26406
C	-2.46684	-1.96549	1.60561

H	-1.98923	-2.77251	2.16863
H	-2.46959	-1.07063	2.23486
H	-3.50116	-2.25209	1.37836
C	-1.86836	-3.22036	-0.84001
H	-1.36963	-4.05159	-0.33351
H	-2.94628	-3.42101	-0.88083
H	-1.47772	-3.15577	-1.85953
C	-0.68260	2.74472	1.71180
H	0.19996	2.98380	2.31196
H	-1.22488	3.67147	1.48649
H	-1.32398	2.08500	2.30356
C	0.71323	3.26944	-0.68569
H	0.09340	4.17387	-0.72301
H	1.64590	3.49298	-0.15894
H	0.96417	2.96264	-1.70553
C	3.21834	-0.59174	-1.18487
C	3.90516	0.57515	-1.00599
C	3.61845	-0.23475	0.94913
N	3.04589	-1.10595	0.07820
H	2.57707	-1.97285	0.31319
H	2.84942	-1.09689	-2.06370
H	4.23311	1.27197	-1.76469
H	3.61869	-0.40891	2.01628
N	4.15235	0.79063	0.32850

INT-1c / **14 (in the main text)**

C	-2.29560	1.37307	1.18076
H	-3.00758	2.21034	1.21366
H	-1.82146	1.32258	2.17083
C	-3.04679	0.07338	0.89751
H	-3.96367	0.08374	1.49964
H	-3.39498	0.05955	-0.14578
C	-2.29222	-1.21593	1.21909
H	-3.00207	-2.04826	1.32922
H	-1.77033	-1.11421	2.18095
P	-0.96827	1.83310	-0.03055
P	-1.02097	-1.72100	-0.02826
Pd	0.55267	0.03950	-0.39417
C	-1.99185	2.30896	-1.48553
H	-1.35775	2.81194	-2.22147
H	-2.41765	1.41948	-1.95941
H	-2.80396	2.98551	-1.19188
C	-0.55058	3.50535	0.61741
H	0.14281	3.99757	-0.07067
H	-1.44736	4.12727	0.72882
H	-0.05840	3.41088	1.58979
C	-2.09702	-2.34726	-1.38326
H	-1.47676	-2.85260	-2.12913
H	-2.84376	-3.05359	-1.00072
H	-2.60689	-1.51610	-1.87902
C	-0.46975	-3.31101	0.71301
H	-1.31763	-3.96314	0.95641
H	0.19064	-3.82654	0.00884
H	0.10153	-3.10554	1.62372
C	2.72540	0.58558	-0.66102
C	2.60661	-0.81794	-0.75932
C	3.61178	-0.44041	1.10465

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N          3.41184        0.77853        0.54453
H          3.62053        1.66764        0.97308
H          2.79796        1.32897       -1.44346
H          2.47011       -1.39301       -1.66736
H          4.07928       -0.54430        2.07632
N          3.18160       -1.42439        0.36652
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INT-1d
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C          2.43545        1.39345       -1.35810
H          3.12220        2.18587       -1.69057
H          2.11343        0.85865       -2.26249
C          3.17482        0.43333       -0.42130
H          4.21122        0.36780       -0.77504
H          3.24885        0.86719        0.58718
C          2.63092       -0.99570       -0.34242
H          3.43173       -1.68074       -0.02679
H          2.30942       -1.32715       -1.33967
P          0.92539        2.23414       -0.67456
P          1.19020       -1.27008        0.79553
Pd        -0.23630        0.55784        0.41039
C          1.71017        3.53475        0.36629
H          0.94556        4.24110        0.70211
H          2.16392        3.08128        1.25220
H          2.47883        4.07844       -0.19680
C          0.47206        3.24446       -2.14674
H         -0.31904        3.94948       -1.87609
H          1.33671        3.80433       -2.52456
H          0.09442        2.59208       -2.93919
C          2.04564       -1.33259        2.42468
H          1.33482       -1.65795        3.19104
H          2.89357       -2.02854        2.40264
H          2.40262       -0.33501        2.69703
C          0.92724       -3.07133        0.51317
H          1.86452       -3.63278        0.61481
H          0.20263       -3.44826        1.24117
H          0.52026       -3.23133       -0.48944
C         -2.41119       -1.51780        3.01032
C         -2.95213       -1.84880        1.79938
C         -2.49740        0.23698        1.68776
N         -2.13575       -0.17901        2.93023
H         -1.70378        0.38910        3.64535
H         -2.43211        1.27778        1.37918
N         -3.01299       -0.74904        0.98123
H         -3.30319       -2.81877        1.47572
H         -2.20414       -2.09645        3.89653
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INT-2
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C          3.14900        0.29100       -0.68900
H          4.09700        0.81300       -0.52400
H          3.00900        0.22400       -1.77300
C          3.22600       -1.12100       -0.08400
H          4.19600       -1.54200       -0.36600
H          3.23800       -1.07100        1.01000
C          2.14100       -2.10000       -0.57000
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H	2.41700	-3.12300	-0.29600
H	2.08100	-2.06800	-1.66200
P	1.81800	1.40900	-0.05200
P	0.43200	-1.77700	0.06900
Pd	-0.30600	0.54500	-0.06100
C	2.38500	1.88200	1.63200
H	1.71700	2.64600	2.03100
H	2.35100	1.01600	2.29400
H	3.40500	2.27300	1.59900
C	2.07800	2.92800	-1.04900
H	1.45200	3.72800	-0.65300
H	3.12600	3.23500	-1.02000
H	1.78600	2.73700	-2.08300
C	0.46300	-2.48300	1.77200
H	-0.54000	-2.43100	2.19900
H	0.79300	-3.52500	1.75900
H	1.13300	-1.90000	2.40500
C	-0.59000	-2.98400	-0.87000
H	-0.19900	-3.99900	-0.76200
H	-1.61400	-2.94800	-0.49700
H	-0.59500	-2.71100	-1.92600
C	-3.25400	0.19300	-1.11200
C	-4.48100	-0.28400	-0.69500
C	-3.09100	-0.56200	0.90600
N	-2.36300	0.00900	-0.08100
H	-0.73000	2.06600	-0.14400
H	-2.95900	0.64200	-2.04800
H	-5.41600	-0.30800	-1.23700
H	-2.66300	-0.82300	1.86400
N	-4.37600	-0.76100	0.59100

INT-3 / **16 (in the main text)**

C	3.13100	0.27300	-0.56100
C	3.09500	-1.12500	0.07900
C	2.08500	-2.09900	-0.55300
C	2.24200	2.04500	1.59900
C	2.15100	2.91300	-1.18000
C	0.09700	-2.55400	1.51900
C	-0.61700	-2.86300	-1.27000
H	4.07300	0.77000	-0.30500
H	3.10500	0.18900	-1.65100
H	4.09100	-1.55800	-0.04600
H	2.94100	-1.05300	1.16100
H	2.31700	-3.12400	-0.25200
H	2.16500	-2.05800	-1.64400
P	1.81500	1.48300	-0.09000
P	0.31700	-1.76200	-0.12900
Pd	-0.25000	0.62700	-0.18500
H	1.56100	2.84400	1.89300
H	2.13800	1.22000	2.30400
H	3.27000	2.41400	1.61800
H	1.53900	3.75700	-0.86400
H	3.20900	3.18400	-1.12500
H	1.89600	2.65600	-2.20800
H	-0.94600	-2.46400	1.82600
H	0.37200	-3.61100	1.48300
H	0.71700	-2.04600	2.25900

H	-0.26600	-3.89500	-1.19300
H	-1.67800	-2.82700	-1.01900
H	-0.49000	-2.51400	-2.29600
H	-0.48700	2.18400	-0.17700

INT-3 (MeCN)

C	3.27820	0.24466	-0.64656
C	-3.29118	0.38898	0.24006
N	-2.16159	0.56948	0.14175
C	-4.70696	0.16467	0.36387
H	-4.98656	-0.75071	-0.16136
H	-5.25577	1.00555	-0.06449
H	-4.97357	0.06554	1.41790
C	3.17335	-1.17361	-0.09237
C	2.01752	-1.98667	-0.66684
C	2.69503	1.82516	1.70076
C	2.51945	2.97828	-0.92276
C	0.26494	-2.23928	1.60534
C	-0.77642	-2.50439	-1.04394
H	4.27655	0.65680	-0.44687
H	3.15154	0.23726	-1.73708
H	4.10705	-1.69427	-0.33011
H	3.12587	-1.15838	1.00557
H	2.14467	-3.05254	-0.43758
H	1.99908	-1.89277	-1.76033
P	2.09878	1.48211	0.01716
P	0.36482	-1.48515	-0.05342
Pd	-0.07714	0.87045	0.02755
H	2.12494	2.65918	2.11724
H	2.54890	0.95151	2.34089
H	3.75860	2.08490	1.67237
H	2.00364	3.83354	-0.47971
H	3.60136	3.14488	-0.89714
H	2.19192	2.86920	-1.95920
H	-0.73475	-2.06572	2.01432
H	0.45464	-3.31668	1.55307
H	0.99286	-1.77228	2.27446
H	-0.49778	-3.56162	-0.98050
H	-1.79413	-2.37597	-0.66530
H	-0.74946	-2.18400	-2.08829
H	-0.21940	2.46486	0.13760

INT-4 / 17 **(in the main text)**

C	3.78000	-1.91100	-1.09400
C	4.40600	0.38400	-0.06400
C	1.83000	-3.87100	-0.31300
C	4.28600	-0.47800	-1.33200
C	2.38300	2.44100	-0.49100
C	3.40100	1.89400	2.17100
C	1.16400	-1.93700	-2.35400
C	-3.81500	-0.01800	-0.46500
C	-6.29500	0.63500	0.66300
C	-4.02400	1.24000	0.10900
C	-1.32800	-1.04400	0.91300

C	-2.48200	-0.37600	-1.06600
C	-0.49000	-1.83500	1.63300
C	-0.29600	-2.82400	2.47800
C	-4.86500	-0.94600	-0.47500
C	-6.09600	-0.62300	0.08900
C	-5.26000	1.56700	0.66900
H	3.98300	-2.52500	-1.97700
H	0.69200	-3.13600	2.79500
H	-1.14200	-3.36200	2.90000
H	-7.25600	0.88600	1.09900
H	-6.90200	-1.34800	0.07700
H	-5.41100	2.54600	1.10900
H	-4.71600	-1.92100	-0.92600
H	-3.22100	1.97000	0.11300
H	-1.83200	0.49600	-1.15400
H	-2.59300	-0.83600	-2.04600
H	-1.69300	-0.10500	1.31900
H	0.61500	0.65500	1.90800
H	3.71200	1.14200	2.89700
H	2.57500	2.46800	2.59300
H	4.23900	2.56100	1.95700
H	2.11600	2.04700	-1.47300
H	3.22000	3.13500	-0.59400
H	1.52000	2.96900	-0.08400
H	4.32800	-2.36100	-0.26000
H	0.09600	-2.13000	-2.23800
H	5.05000	1.24700	-0.26300
P	1.97700	-2.08200	-0.70800
Pd	1.10100	-0.46800	0.91400
H	5.28700	-0.55300	-1.76700
H	1.59000	-2.65100	-3.06200
H	4.88500	-0.19200	0.73500
H	3.67700	0.02700	-2.08800
H	1.29000	-0.92500	-2.74100
H	0.77900	-4.13600	-0.19600
P	2.83600	1.06400	0.63600
O	-1.77300	-1.40400	-0.29400
H	2.27000	-4.47700	-1.10900
H	2.34800	-4.08200	0.62400

INT-5 / **15 (in the main text)**

H	0.33100	2.61600	1.06400
H	-0.94000	0.78600	3.58900
H	-3.17300	1.96800	2.83900
H	-4.18900	-1.84200	-2.83800
H	-1.37000	-0.75100	2.79900
H	-4.78000	-0.17900	-2.67600
H	-1.16300	3.39700	0.52800
H	-4.77200	-2.98700	0.22700
H	-1.76900	-0.95400	-3.51500
H	-5.13400	0.93600	-0.11900
H	-5.77600	-0.55400	0.56100
H	-0.83500	3.21300	2.26900
H	-3.94200	-0.44500	2.36100
H	-3.18800	-3.31500	-0.51700
H	-3.26800	-2.60500	1.10100
H	-5.69800	-1.52100	-1.95000

H	-3.62200	2.38200	1.19000
H	-0.20800	0.95000	-3.18100
C	4.93600	4.03300	-0.26300
C	-3.27800	1.56200	1.82800
C	4.71500	1.66900	-1.72300
C	3.92000	3.12300	0.03000
C	5.84000	3.76300	-1.28900
C	3.80000	1.93500	-0.69700
C	2.69900	0.95600	-0.39600
O	1.66300	1.10000	-1.40700
C	-1.05400	-1.00500	-2.70500
C	-0.11500	0.05400	-2.57500
C	0.81600	0.06200	-1.54500
C	-3.74500	-2.62800	0.12100
C	-4.69700	-1.14300	-2.17200
C	5.72800	2.57800	-2.02000
P	-3.72000	-0.94700	-0.62800
Pd	-1.54700	-0.07600	-0.82400
C	-4.86200	0.03800	0.44500
C	-4.32300	0.43300	1.83100
C	-0.85400	0.20100	2.67000
P	-1.57800	1.11200	1.24200
C	-0.72800	2.74400	1.28700
H	-5.17600	0.78100	2.42200
H	6.63100	4.46800	-1.51700
H	5.02100	4.95000	0.31000
H	6.43200	2.36100	-2.81500
H	4.63500	0.74600	-2.28700
H	3.22000	3.33700	0.83100
H	2.25800	1.14400	0.58600
H	3.07000	-0.07200	-0.42700
H	0.19800	-0.00500	2.47100
H	-0.77100	-2.00900	-2.40100
H	1.06300	-0.84500	-0.99900

INT-6

H	1.23929	3.40783	-1.21487
H	-5.74383	2.16527	-1.01042
H	-5.20528	0.09009	2.70503
H	-3.95472	-1.69373	1.52287
H	-4.48833	0.38127	-2.18437
H	-3.52754	-2.80713	-0.72870
H	-3.44606	-1.76868	-2.17567
H	-1.41229	-3.36157	-1.49967
H	2.11438	-2.98192	-0.71071
H	1.32123	0.08801	-2.32619
H	2.05988	-2.38610	-2.45373
H	0.60530	-3.11068	1.60625
H	2.34244	-2.80848	1.84829
H	-1.95869	2.43879	0.70974
H	-0.22547	3.96262	-0.35913
H	1.12064	3.21602	0.54654
H	-0.62905	2.05080	-2.94986
H	-1.78073	0.85564	-2.30704
H	2.14191	-0.06120	3.66804
H	-6.09101	2.02684	1.43820
H	-1.74894	1.35600	2.81914

H	-1.25232	-0.98643	1.85751
H	-0.45304	-0.54915	3.37897
H	-1.98049	2.59005	-1.90964
H	-0.12317	1.82428	2.39716
H	3.32174	-0.11036	2.31802
H	2.19532	1.24626	2.44970
H	1.20102	-2.55173	3.19336
H	-2.17899	0.71333	0.39927
C	-5.35347	1.31983	-0.45217
C	-5.05033	0.15521	1.63238
C	-4.35519	-0.84619	0.97029
C	-4.65367	0.31641	-1.11123
C	-5.54784	1.24193	0.92077
C	-4.14672	-0.76939	-0.40551
C	-3.29884	-1.79315	-1.08718
O	-1.93895	-1.47990	-0.77844
C	-1.02196	-2.37707	-1.23338
C	0.26072	-2.10298	-1.32384
C	1.58356	-2.41752	-1.47643
C	2.30500	0.17019	2.60970
C	1.33546	-2.47014	2.10956
C	-1.44666	1.46627	0.71239
C	-1.25342	1.78998	-2.09103
P	-0.19116	1.54205	-0.62803
C	0.55455	3.19369	-0.38938
C	-0.93811	1.14270	2.11218
C	-0.51244	-0.31074	2.30864
Pd	1.29504	-0.31205	-0.79774
P	1.11273	-0.74085	1.57067
H	5.94194	2.33732	0.29111
H	3.32956	2.54832	-0.54670
H	4.33517	-1.48591	-0.17263
N	5.55513	0.22672	0.19672
C	4.43358	-0.40383	-0.15665
C	5.22861	1.55004	0.07561
C	3.92163	1.66435	-0.34601
N	3.41339	0.40505	-0.49498

INT-6-mono

H	-8.07624	1.04133	-0.27154
H	-7.40057	-0.33253	-1.16031
H	-2.14646	-1.10981	0.31738
H	-7.06870	-0.15421	0.58125
H	-0.24638	0.36306	-3.02444
H	-0.74674	1.79273	-2.07735
H	-2.80647	1.32869	0.04255
H	-2.14079	-1.28345	-1.43189
H	-2.89774	1.08418	-1.69748
C	2.24315	4.43854	0.40899
H	2.35771	4.86017	2.51214
H	0.96976	1.34414	-2.17528
C	3.42387	3.06568	1.99426
C	2.64646	4.18461	1.71272
C	3.38796	2.45120	-0.33914
C	3.74060	1.47711	-1.41567
O	3.01539	0.27127	-1.14316
H	3.45812	1.86414	-2.40385

C	3.79546	2.20633	0.97143
C	2.60872	3.57012	-0.61296
C	-3.00551	0.57410	-0.73092
H	4.40133	1.32874	1.18511
C	-5.49216	2.25276	0.84275
P	-5.71088	1.39487	-0.78087
H	-6.33024	2.93681	1.00657
C	-7.20305	0.38885	-0.36197
H	2.28409	3.76174	-1.63320
H	1.63738	5.31155	0.18649
H	3.74282	2.86692	3.01282
C	2.97456	-0.63464	-2.14782
C	-1.99383	-0.55797	-0.61982
C	-4.43107	0.06146	-0.58903
C	-0.01931	1.07289	0.73922
C	2.22815	-1.71216	-2.07916
C	-0.04827	0.95180	-2.12405
C	1.65176	-2.90438	-2.33269
H	-0.34240	0.59185	1.66792
H	-5.45376	1.53594	1.67226
H	2.20032	-3.83650	-2.22840
H	-4.63509	-0.69325	-1.36106
H	1.03949	1.33648	0.83238
H	-4.56542	-0.43126	0.38596
H	-0.59952	1.98580	0.57119
H	-4.57376	2.84639	0.84215
P	-0.20992	-0.10698	-0.64295
Pd	1.08884	-2.17416	-0.31591
H	1.81219	-3.53202	0.05369
H	0.70502	-2.96289	-2.87060
H	3.57305	-0.42450	-3.03458
H	4.81574	1.25199	-1.42583
N	0.43047	-2.15412	1.65248
C	1.13950	-1.61404	2.69227
H	-1.52152	-3.00795	1.59739
C	0.34064	-1.68348	3.80824
H	0.56190	-1.35181	4.81516
H	2.13822	-1.21908	2.55676
C	-0.74870	-2.52746	2.18726
N	-0.85570	-2.26565	3.48576

INT-7a

C	1.03163	-1.77249	-0.21336
O	1.77938	-1.92283	0.96018
C	2.38844	-0.75162	1.44300
C	3.56041	-0.26383	0.63263
C	3.97604	1.05982	0.76364
C	4.27561	-1.11321	-0.20602
C	5.08619	1.52701	0.07405
C	5.38212	-0.64582	-0.90466
C	5.79210	0.67404	-0.76632
C	-0.11288	-2.56374	-0.34458
C	-0.56650	-3.78923	-0.54664
C	-3.86647	1.10847	-0.73628
C	-3.20852	2.42528	-0.32966
C	-1.81752	2.66404	-0.91269
P	-3.15979	-0.41134	0.03925

P	-0.43574	1.74215	-0.09955
Pd	-0.78731	-0.63508	-0.08841
C	-3.77280	-0.26609	1.76346
C	-4.29625	-1.68678	-0.62723
C	-0.24223	2.68816	1.46336
C	0.97917	2.37234	-1.08141
H	1.61921	-1.48567	-1.08994
H	2.72429	-0.98812	2.46081
H	1.63322	0.04945	1.52116
H	3.42242	1.73119	1.41840
H	3.96048	-2.14760	-0.31047
H	5.39788	2.56110	0.18775
H	5.92848	-1.31797	-1.55988
H	6.65706	1.03776	-1.31251
H	0.10828	-4.63266	-0.70808
H	-1.63047	-4.01771	-0.56194
H	-4.93732	1.13246	-0.49061
H	-3.79214	0.97503	-1.82427
H	-3.85996	3.24059	-0.66670
H	-3.18510	2.51778	0.76606
H	-1.56751	3.73299	-0.86586
H	-1.80409	2.38165	-1.97462
H	-3.61271	-1.21718	2.27938
H	-3.21372	0.50606	2.29915
H	-4.84149	-0.02192	1.78190
H	-4.09072	-2.64170	-0.13458
H	-5.34441	-1.41290	-0.45837
H	-4.12447	-1.81032	-1.70021
H	0.66465	2.36043	1.98019
H	-0.16928	3.76326	1.26107
H	-1.09206	2.50348	2.12672
H	0.99226	3.46850	-1.10426
H	1.91858	2.00649	-0.65447
H	0.90032	1.99229	-2.10450

INT-7b / **15 (in the main text)**

H	1.58800	-0.23200	-3.78500
H	-1.86800	-1.21300	-3.58400
H	3.09100	-0.25100	3.58000
C	-0.39400	-1.92200	1.69200
P	0.26600	-0.33100	1.05700
C	1.32700	0.21700	2.47000
Pd	1.34500	-0.61600	-1.05200
P	3.55800	-0.59200	-0.14800
C	1.21100	-1.04200	-3.16000
H	4.74500	-0.15800	1.90700
H	2.61000	-1.53300	2.50300
C	3.72800	0.07700	1.56500
C	-0.03400	-0.93500	-2.54200
C	2.70100	-0.43900	2.57200
H	-0.89200	1.80600	1.08400
H	5.88700	0.12900	-0.39800
H	3.54600	-2.90900	0.61600
H	5.20900	-2.25500	0.58400
H	-1.97600	0.46800	0.64500
H	1.44300	1.30500	2.37400
H	0.75300	0.04300	3.39200

H	-5.02100	-1.87700	2.77300
H	-5.96600	1.71200	0.62200
H	-4.73100	0.85100	-1.34600
H	-3.78600	-2.72900	0.80200
H	-6.10400	0.34900	2.68900
H	-3.92400	-1.33300	-2.50700
H	-3.11700	-2.52500	-1.46000
H	1.62300	-2.02300	-3.40200
C	-4.95800	-1.27500	1.87200
C	-5.48600	0.73800	0.66500
C	-4.79900	0.25500	-0.43800
C	-4.26600	-1.75300	0.76500
C	-5.56400	-0.02700	1.82500
C	-4.17900	-0.99200	-0.39500
C	-3.37000	-1.45900	-1.56300
C	-1.34700	-0.98000	-2.65000
C	4.96100	0.25500	-0.97100
C	4.24800	-2.28100	0.05800
C	-1.17200	0.77500	1.31600
H	4.74400	1.32100	-1.07200
H	5.09800	-0.16500	-1.97200
H	-0.86900	-1.79000	2.67200
H	4.39000	-2.73000	-0.92900
H	-1.51600	0.72000	2.35600
H	0.41600	-2.65300	1.77700
H	-1.12900	-2.31300	0.98200
H	3.66200	1.17100	1.49400
O	-2.18400	-0.68000	-1.60000

INT-7c / **INT-1 (in the main text)**

C	1.56489	2.62076	-0.89072
C	1.32596	-2.93073	-0.03621
C	3.86184	1.48375	-0.68596
C	0.06972	-2.65758	-0.63866
C	2.95979	2.64182	-0.26912
C	-5.63120	1.43233	0.36637
C	-6.03295	-0.62974	-0.80072
C	-4.81044	-1.11777	-0.36276
C	-4.40336	0.94489	0.79733
C	-6.44773	0.64595	-0.43468
C	-3.98452	-0.33353	0.44071
C	-2.68071	-0.86796	0.94509
C	-0.73823	-1.97375	0.26623
C	4.69256	-1.22969	-0.74428
C	4.03614	-0.03251	1.74293
C	-1.11672	1.76550	-1.14417
C	-0.04718	2.33421	1.44640
H	-4.48729	-2.11546	-0.64580
H	2.12973	-3.38932	-0.61494
H	-0.64263	-2.06261	1.36418
H	3.45132	3.57390	-0.57072
P	0.36224	1.46121	-0.11149
Pd	1.15393	-0.76954	-0.04446
P	3.42504	-0.15857	0.02208
H	4.90277	1.69032	-0.40137
H	2.89048	2.69866	0.82665
H	-0.90234	1.44928	-2.16937

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H          5.69100       -0.79436       -0.62173
H          3.43409        0.68351        2.30876
H          5.08625        0.28063        1.75953
H         -1.96680        1.18067       -0.78146
H          1.62956        2.34263       -1.95140
H          1.11612        3.62245       -0.85126
H         -5.94612        2.43179        0.65080
H         -6.66785       -1.24817       -1.42808
H         -3.75918        1.56682        1.41594
H         -7.40512        1.02687       -0.77702
H         -2.84880       -1.58594        1.76435
H         -2.06920       -0.05156        1.36193
H          1.43626       -3.09366        1.04990
H          4.48007       -1.35470       -1.80920
H          4.66915       -2.21347       -0.26753
H         -0.30901        3.37881        1.24378
H          3.94290       -1.01069        2.22373
H         -1.37982        2.82944       -1.14201
H          0.80465        2.29959        2.13102
H         -0.89166        1.84300        1.93749
H          3.84638        1.37379       -1.77864
O         -1.97904       -1.50858       -0.10350
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TS-1
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C         -1.30400        1.93200       -1.65300
H         -2.04600        2.71600       -1.47000
H         -1.35700        1.68900       -2.72000
C          0.10000        2.47000       -1.31400
H          0.15300        3.49300       -1.69900
H          0.21900        2.56400       -0.22900
C          1.28700        1.69400       -1.91700
H          2.18100        2.32800       -1.90200
H          1.08000        1.46500       -2.96800
P         -1.86800        0.41900       -0.73100
P          1.71300        0.08100       -1.09100
Pd        -0.32000       -1.30700       -0.79100
C         -2.23100        1.08200        0.95400
H         -2.72200        0.30600        1.54400
H         -1.30100        1.35200        1.45600
H         -2.88000        1.96000        0.90000
C         -3.56300        0.18900       -1.42500
H         -4.07700       -0.59200       -0.86300
H         -4.14500        1.11400       -1.37200
H         -3.48900       -0.12800       -2.46700
C          2.57600        0.65200        0.44400
H          2.99500       -0.21200        0.96400
H          3.38200        1.35400        0.21100
H          1.86300        1.13600        1.11400
C          3.14100       -0.47800       -2.12600
H          3.90200        0.30200       -2.21900
H          3.59200       -1.36300       -1.67100
H          2.78500       -0.75000       -3.12200
C         -0.02800       -4.39400       -1.84000
C          0.41500       -5.60900       -1.37400
C          0.15100       -4.34400        0.33600
N         -0.17900       -3.57600       -0.73800
H         -1.21800       -2.63900       -0.65800
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H	-0.23800	-4.04600	-2.83800
H	0.65700	-6.49700	-1.94000
H	0.10600	-3.96600	1.34700
N	0.52600	-5.57300	0.00100

TS-2

H	0.09400	-0.60800	4.11000
H	-1.72400	-0.81400	3.80200
H	-7.45700	0.35300	0.64200
H	-6.71000	-1.84200	1.53000
H	-5.96800	1.64500	-0.86600
H	-4.48900	-2.73800	0.91500
H	-3.74400	0.75200	-1.47500
H	-2.13700	-0.99600	-1.46400
H	-2.67700	-2.62900	-1.03000
H	-1.47300	0.38900	0.33100
H	0.84100	0.65400	2.08200
H	3.99900	0.13900	3.12000
H	3.31400	1.77400	3.10900
H	4.98000	1.50500	2.53200
H	3.07900	2.39500	-0.94400
H	4.39400	2.87100	0.16100
H	2.69200	3.13100	0.61700
H	1.22400	-3.69100	-0.51200
H	1.18300	-3.59600	-2.29000
H	3.54200	-2.26900	-2.47600
H	3.69300	-2.58000	-0.75300
H	0.09700	-0.44200	-2.86900
H	5.56100	0.48700	0.10400
H	5.37500	-0.95100	-1.77300
H	1.45500	-1.24000	-3.69900
H	4.87900	-1.01300	0.72200
H	4.09400	0.20800	-1.99300
H	1.67400	0.35100	-2.92900
H	-0.19800	-3.02200	-1.32300
O	-1.71000	-1.68200	0.46500
P	3.31200	0.80200	0.88700
P	1.64100	-1.42300	-1.26000
Pd	1.14300	-0.14200	0.75900
C	3.43900	-1.81000	-1.48800
C	4.67200	-0.15300	0.07800
C	0.88800	-3.09700	-1.36400
C	4.41400	-0.62800	-1.36200
C	3.38200	2.46300	0.10100
C	3.97200	1.08500	2.57700
C	1.17300	-0.61500	-2.84800
C	-3.96000	-1.04900	-0.31600
C	-6.48100	-0.03700	0.37500
C	-4.38900	0.18400	-0.81300
C	-1.17800	-0.50000	0.88100
C	-2.60300	-1.59900	-0.68100
C	-0.57500	-0.40300	2.11300
C	-0.72900	-0.62300	3.40800
C	-4.80900	-1.77500	0.53000
C	-6.06000	-1.27200	0.87600
C	-5.64600	0.68800	-0.47100

TS-3

C	0.06412	-2.81990	1.46894
C	1.49408	-0.57287	2.61094
C	1.38905	0.78713	-2.78806
C	3.82107	-0.17783	1.51794
C	0.10505	1.12310	-2.26206
C	2.96309	-1.01484	2.48694
C	-5.61090	-1.58400	0.93194
C	-5.93094	0.46899	-0.30306
C	-4.72794	0.25301	-0.97706
C	-4.40190	-1.79498	0.26294
C	-6.37692	-0.45102	0.65094
C	-3.95392	-0.88097	-0.69806
C	-2.66291	-1.12695	-1.43906
C	-0.71993	-0.00091	-2.14806
C	4.68506	0.71119	-1.07506
C	4.23811	-2.09682	-0.61106
C	-1.19093	-0.22592	1.77694
N	0.42401	3.25111	1.99794
N	-0.17098	2.80910	-0.12706
C	0.81702	2.80612	0.80394
C	-0.91200	3.55208	1.81894
C	-1.28999	3.27608	0.51894
H	-4.37695	0.96902	-1.71406
H	2.16404	1.55014	-2.85506
H	-0.59391	-0.92091	-2.73906
H	3.41809	-0.92884	3.47994
P	0.36709	-1.01889	1.20294
Pd	1.22307	-0.25788	-0.87006
P	3.48608	-0.44383	-0.28606
H	4.88408	-0.38481	1.68794
H	3.02711	-2.07984	2.22994
H	-1.03395	0.85408	1.82294
H	5.69906	0.55021	-0.69706
H	3.66512	-2.86983	-0.09406
H	5.27811	-2.12580	-0.27106
H	-2.00492	-0.42194	1.07994
H	1.43406	0.51813	2.70494
H	1.05509	-0.99988	3.52094
H	-5.94689	-2.29901	1.67694
H	-6.51996	1.35498	-0.52306
H	-0.10797	2.22510	-1.13906
H	-3.80088	-2.66997	0.49494
H	-7.31393	-0.28203	1.17494
H	-2.85990	-1.54995	-2.43606
H	-2.03490	-1.84594	-0.89606
H	1.53307	-0.04187	-3.49506
O	-1.96293	0.11306	-1.58106
H	4.38004	1.74118	-0.87306
H	4.67006	0.55319	-2.15706
H	-0.26588	-3.01491	2.49394
H	4.20211	-2.30182	-1.68406
H	-1.46592	-0.59993	2.76894
H	0.98213	-3.37988	1.27194
H	-0.70387	-3.16791	0.77194
H	3.66605	0.89017	1.71494
H	-1.51801	3.94807	2.62494

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H         -2.24199        3.36606        0.01594
H          1.81502        2.45813        0.57394
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benzyloxyallene
-----------------------------------------------
C         -2.63825        0.23441        0.48907
H         -2.74262        0.59612        1.51338
O         -1.36122        0.02682        0.05701
C         -0.38017        0.79037        0.76055
H         -0.52660        0.64394        1.84167
H         -0.51346        1.85825        0.54161
C          0.97554        0.32432        0.34103
C          1.82143        1.15097       -0.38999
C          1.40180       -0.95984        0.67742
C          3.07988        0.70535       -0.77767
H          1.49201        2.15237       -0.65577
C          2.65332       -1.40978        0.28630
H          0.74172       -1.60618        1.25124
C          3.49596       -0.57522       -0.44145
H          3.73441        1.35925       -1.34574
H          2.97749       -2.41107        0.55289
H          4.47807       -0.92531       -0.74440
C         -3.68684       -0.01714       -0.24755
C         -4.75305       -0.28491       -0.94208
H         -5.20526       -1.27562       -0.94142
H         -5.24136        0.46850       -1.55808
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imidazole
-----------------------------------------------
C          0.60589        0.97931       -0.00005
C          1.13519       -0.27865        0.00003
C         -0.98337       -0.53795       -0.00003
N         -0.75393        0.79822        0.00004
H          1.05544        1.95948       -0.00008
H          2.17924       -0.55855        0.00006
H         -1.98332       -0.94917       -0.00004
N          0.13545       -1.22206       -0.00001
H         -1.45436        1.52601        0.00007
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dppp-Pd
-----------------------------------------------
C         -1.30434        1.67521       -0.60494
H         -2.10673        2.40481       -0.41915
H         -1.19148        1.60587       -1.69589
C         -0.00000        2.17854        0.02128
H         -0.00000        3.27189       -0.07175
H         -0.00003        1.98835        1.10493
C          1.30437        1.67522       -0.60488
H          2.10675        2.40482       -0.41904
H          1.19157        1.60589       -1.69583
P         -1.93559        0.01945       -0.03381
P          1.93560        0.01946       -0.03373
Pd         0.00001       -1.23512       -0.03902
C         -2.67395        0.48219        1.58773
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H         -3.23919       -0.36446        1.98744
H         -1.88150        0.72642        2.30102
H         -3.34463        1.34387        1.48272
C         -3.46239       -0.07261       -1.05972
H         -4.07292       -0.91957       -0.73426
H         -4.05221        0.84813       -0.97145
H         -3.19227       -0.22596       -2.10825
C          2.67386        0.48219        1.58786
H          3.23908       -0.36446        1.98759
H          3.34454        1.34387        1.48290
H          1.88136        0.72640        2.30110
C          3.46246       -0.07257       -1.05955
H          4.05227        0.84817       -0.97123
H          4.07298       -0.91953       -0.73406
H          3.19241       -0.22592       -2.10810
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TS-2a
-----------------------------------------------
N                  3.69700000   -3.56200000    1.04400000
 N                  2.50900000   -2.44700000   -0.42600000
 C                  2.48100000   -3.05400000    0.76000000
 C                  4.54600000   -3.28800000   -0.01200000
 C                  2.87800000    1.93300000    2.30800000
 C                 -1.79400000    1.26800000   -1.77500000
 C                 -1.43800000    1.96600000    1.04100000
 C                  2.62400000    3.35000000   -0.24500000
 C                  3.79400000   -2.59800000   -0.92300000
 C                  4.49500000    1.14600000    0.01500000
 C                  1.21400000    3.95900000   -0.16800000
 C                  0.16400000    3.27700000   -1.06200000
 C                 -1.23400000   -2.06400000   -0.25300000
 C                  0.70800000   -2.29400000   -1.59600000
 C                 -0.09900000   -1.49100000   -0.78500000
 H                  1.28700000    5.00100000   -0.49700000
 H                 -0.75700000    2.23800000    1.84900000
 H                 -2.15200000    2.78100000    0.88000000
 H                  3.69300000    2.62000000    2.55600000
 H                  1.93900000    2.35200000    2.67900000
 H                  4.57300000    1.07500000   -1.07300000
 H                 -2.40700000    0.43100000   -1.43700000
 H                 -1.32100000    1.01300000   -2.72500000
 H                  3.05000000    0.98200000    2.81900000
 H                  5.22600000    1.87700000    0.37400000
 H                  1.61700000   -3.15300000    1.40000000
 H                 -2.43300000    2.14600000   -1.91300000
 H                  4.72900000    0.17000000    0.44600000
H                  3.93900000   -4.08400000    1.87700000
 P                 -0.52100000    1.64900000   -0.51400000
 H                  4.08300000   -2.21800000   -1.89100000
 H                  5.57600000   -3.60800000   -0.02200000
 P                  2.79000000    1.66100000    0.48800000
 H                  2.94200000    3.27500000   -1.29200000
 H                  0.55400000    3.13700000   -2.07600000
 H                  0.86700000    4.00800000    0.87100000
 H                  3.34300000    4.00700000    0.25800000
 H                 -1.98000000    1.06100000    1.32000000
 H                  0.51900000   -3.36300000   -1.71900000
 H                 -0.71600000    3.92800000   -1.15200000
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 H                 -1.52100000   -3.08800000   -0.52200000
 Pd                 1.09800000    0.07300000   -0.20900000
 H                  1.33300000   -1.86200000   -2.37100000
 O                 -2.05800000   -1.42200000    0.53400000
 C                 -3.32700000   -2.08200000    0.96800000
 H                 -3.36400000   -3.06400000    0.48800000
 H                 -3.21700000   -2.20400000    2.04700000
 C                 -4.49300000   -1.21700000    0.60900000
 C                 -6.67000000    0.40700000   -0.06300000
 C                 -5.05400000   -1.28200000   -0.67600000
 C                 -5.03500000   -0.33600000    1.55500000
 C                 -6.12100000    0.47300000    1.22000000
 C                 -6.13700000   -0.47100000   -1.01100000
 H                 -4.66200000   -1.98600000   -1.40700000
 H                 -4.62400000   -0.30000000    2.56100000
 H                 -6.54800000    1.14100000    1.96100000
 H                 -6.57900000   -0.53700000   -2.00000000
 H                 -7.52300000    1.02800000   -0.31900000

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TS-2b
-----------------------------------------------
N                  1.13100000    4.04100000    0.59500000
 N                 1.11200000    1.88200000    0.95100000
 C                 0.63100000    3.05800000    1.36500000
 C                 3.90900000   -1.15200000    0.29000000
 C                 1.97500000    3.48400000   -0.34800000
 C                 3.25900000   -0.82100000    1.59500000
 C                -3.21800000    2.08700000   -1.89600000
 C                 5.16800000   -1.79200000   -2.12800000
 C                -1.69900000   -2.89200000    1.68100000
 C                -3.99000000   -1.06200000    1.56900000
 C                 3.71500000   -2.41200000   -0.29600000
 C                -2.66100000   -0.64500000   -2.77400000
 C                 5.37800000   -0.54200000   -1.54400000
 C                 4.33600000   -2.72700000   -1.50300000
 C                 4.74900000   -0.22100000   -0.34000000
 C                 1.96000000    2.13600000   -0.11500000
 C                -0.61900000    1.40200000   -3.01900000
 C                -3.63200000   -1.50900000   -1.95000000
 C                -2.96300000   -2.36200000   -0.85900000
 C                -0.83800000    0.22500000    3.48100000
 C                 1.15000000    0.24700000    2.11000000
 C                -0.30600000    0.11900000    2.25500000
 H                -4.12600000   -2.20100000   -2.64000000
 H                -4.54400000   -0.32100000    0.99000000
 H                -4.61400000   -1.95100000    1.70600000
 H                -3.52300000    2.30300000   -2.92400000
 H                -4.09400000    1.76400000   -1.32700000
 H                 0.16400000    0.64800000   -3.13700000
 H                -1.47000000   -2.55200000    2.69100000
 H                -0.77500000   -3.22400000    1.20400000
 H                -2.83800000    3.00500000   -1.44000000
 H                -1.05300000    1.62000000   -3.99900000
 H                -0.03700000    3.20900000    2.20000000
H                 -2.40300000   -3.73000000    1.72600000
 H                 -0.16700000    2.31400000   -2.62200000
 H                  0.94000000    5.03000000    0.70700000
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H	-1.90500000	0.14400000	3.66600000
P	-2.44000000	-1.52900000	0.70600000
H	2.49900000	1.34300000	-0.61300000
H	2.50400000	4.08200000	-1.07400000
P	-1.91600000	0.78300000	-1.86400000
H	-1.83300000	-1.26200000	-3.14100000
H	3.09200000	-3.15100000	0.20200000
H	-2.07900000	-2.87300000	-1.25900000
H	3.65000000	0.10000000	2.03500000
H	-4.43800000	-0.89800000	-1.52700000
H	-3.17400000	-0.24700000	-3.65700000
H	3.33600000	-1.63600000	2.31900000
O	1.78000000	-0.64700000	1.40200000
H	-3.76500000	-0.63800000	2.55000000
H	1.72100000	0.73400000	2.90800000
H	4.94000000	0.74200000	0.12900000
H	4.19100000	-3.70600000	-1.94700000
H	6.04400000	0.17500000	-2.01500000
H	5.66500000	-2.04600000	-3.05900000
H	-3.65500000	-3.14800000	-0.53100000
H	-0.22500000	0.38100000	4.37000000
Pd	-1.09700000	0.28600000	0.37800000