Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Reductive Activation of Pd^{II}-Precatalysts *via* Decarboxylation of Pivalate in Direct C–H Arylation Reactions

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I. Experimental

Materials and Methods

^{1}H NMR spectra were recorded on a Bruker AVHD-400 (400 MHz). ^{1}H chemical shifts are reported in parts per million (ppm) referenced to the appropriate residual solvent peak (*N*, *N*,-Dimethylformamide-d_7 (DMF-d_7): δ = 8.03 (s) ppm, Acetonitrile-d_3 (CD_3CN): δ = 1.94 (q) ppm). The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad signal, s = singlet, d = doublet, t = triplet, q = quintet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets. Coupling constants, *J*, are reported in Hertz (Hz). $^{13}C\{^{1}H\}$ NMR spectra were recorded on Bruker AVHD-400 (100 MHz) and fully decoupled by broad band proton decoupling. ^{13}C chemical shifts were reported in ppm referenced to the appropriate solvent peak (DMF-d_7: δ = 163.2 (t) ppm, CD_3CN: δ = 118.7 (s) ppm). Commercial grade reagents and solvents were used without further purification.

Experimental Procedures

Reduction of Pd(II) by sodium pivalate

An NMR tube equipped with a J. Young valve was loaded with $PdCl_2$ (8.9 mg, 0.05 mmol), sodium pivalate (24.8 mg, 0.2mmol), and CD_3CN (0.7 mL). The tube was sealed and heated in an oil bath at 100 °C for 40 hours. During this time, a black precipitate presumed to be Pd black had formed in the tube. The tube was removed from the hot oil bath and allowed to cool to room temperature and NMR spectra were recorded without unsealing the tube.

^{1}H NMR (400 MHz, CD_3CN) δ 4.66 (septet, $^{4}J_{HH}$ = 1.2 Hz, 2H, $\mathbf{H}_{2,}CC(CH_3)_2$), 1.71 (t, $^{4}J_{HH}$ = 1.2 Hz, 6H, $H_{2,}CC(C\mathbf{H}_3)_2$)

$^{13}C\{^{1}H\}$ NMR (100 MHz, CD_3CN) δ 111.4 ($H_{2,}\mathbf{C}C(CH_3)_2$), 24.5 ($H_{2,}CC(\mathbf{C}H_3)_2$). Resonance of internal vinyl carbon was not detected.

Reduction of Pd(II) by the combination of pivalic acid and potassium carbonate

An NMR tube equipped with a J. Young valve was loaded with $PdCl_2$ (8.9 mg, 0.05 mmol), pivalic acid (20.4 mg, 0.2 mmol), potassium carbonate (27.5 mg, 0.2 mmol) and DMF-d_7 (0.7 mL). The tube was sealed and heated in an oil bath at 120 °C for 14 hours. During this time, a black precipitate presumed to be Pd black had formed in the tube. The tube was removed from the hot oil bath and allowed to cool to room temperature and NMR spectra were recorded without unsealing the tube.

^{1}H NMR (400 MHz, DMF-d_7) δ 4.65 (septet, $^{4}J_{HH}$ = 1.2 Hz, 2H, $\mathbf{H}_{2,}CC(CH_3)_2$), 1.70 (t, $^{4}J_{HH}$ = 1.2 Hz, 6H, $H_{2,}CC(C\mathbf{H}_3)_2$)

Reductive homocoupling of bromotoluene with pivalic acid

An NMR tube equipped with a J. Young valve was loaded with $PdCl_2$ (3.5 mg, 0.02 mmol), pivalic acid (14.3 mg, 0.14 mmol), potassium carbonate (27.5 mg, 0.2 mmol), 4-bromotoluene (12.3 µL, 0.1 mmol) and DMF-d_7 (0.7 mL). The tube was sealed and heated in an oil bath at 120 °C for 30 hours. During this time, a black precipitate presumed to be Pd black had formed in the tube. The tube was removed from the hot oil bath and allowed to cool to room temperature and NMR spectra were recorded without unsealing the tube.

^{1}H NMR (400 MHz, DMF-d_7) δ 7.57 (d, $^{3}J_{HH}$ = 8.1 Hz, 4H, $[C(C\mathbf{H})_2(CH)_2CCH_3]_2$), 7.29 (d, $^{3}J_{HH}$ = 7.8 Hz, 4H, $[C(CH)_2(C\mathbf{H})_2CCH_3]_2$), 2.36 (s, 6H, $[C(CH)_2(CH)_2CC\mathbf{H}_3]_2$), and δ 7.29-7.15 (m, 5H, $(C\mathbf{H})_5CCH_3$), 2.32 (s, 3H, $(CH)_5CC\mathbf{H}_3$)

$^{13}C\{^{1}H\}$ NMR (100 MHz, DMF-d_7) δ 137.7 ($[C(CH)_2(CH)_2\mathbf{C}CH_3]_2$), 130.6 ($[C(\mathbf{C}H)_2(CH)_2CCH_3]_2$) , 127.5 ($[C(CH)_2(\mathbf{C}H)_2CCH_3]_2$), 21.3 ($[C(CH)_2(CH)_2C\mathbf{C}H_3]_2$), and δ 138.7 ($CH(CH)_2(CH)_2\mathbf{C}CH_3$), 130.0

($CH(\mathbf{C}H)_2(CH)_2CCH_3$), 129.3 ($CH(CH)_2(\mathbf{C}H)_2CCH_3$), 126.4 ($\mathbf{C}H(CH)_2(CH)_2CCH_3$), 21.7 ($CH(CH)_2(CH)_2C\mathbf{C}H_3$). Resonance of one quaternary carbon in 4,4'-dimethylbiphenyl was not detected

Reductive homocoupling of bromotoluene with acetic acid

An NMR tube equipped with a J. Young valve was loaded with $PdCl_2$ (3.5 mg, 0.02 mmol), acetic acid (8.0 µL, 0.14 mmol), potassium carbonate (27.5 mg, 0.2 mmol), 4-bromotoluene (12.3 µL, 0.1 mmol) and DMF-d_7 (0.7 mL). The tube was sealed and heated in an oil bath at 120 °C for 30 hours. The tube was removed from the hot oil bath and allowed to cool to room temperature and NMR spectra were recorded without unsealing the tube.

^{1}H NMR (400 MHz, DMF-d_7) δ 7.46 (d, $^3J_{HH}$ = 8.2 Hz, 2H, $CBr(C\mathbf{H})_2(CH)_2CCH_3$), 7.19 (d, $^3J_{HH}$ = 8.6 Hz, 2H, $CBr(CH)_2(C\mathbf{H})_2CCH_3$), 2.29 (s, 3H, $CBr(CH)_2(C\mathbf{H})_2CCH_3$)

II. Compound Characterization

4,4'-Dimethylbiphenyl

^{1}H NMR (400 MHz, DMF-d_7) δ 7.57 (d, $^3J_{HH}$ = 8.1 Hz, 4H, $[C(C\mathbf{H})_2(CH)_2CCH_3]_2$), 7.29 (d, $^3J_{HH}$ = 7.8 Hz, 4H, $[C(CH)_2(C\mathbf{H})_2CCH_3]_2$), 2.36 (s, 6H, $[C(CH)_2(CH)_{2z}CC\mathbf{H}_3]_2$)

^{13}C NMR (100 MHz, DMF-d_7) δ 138.9 ($[\mathbf{C}(CH)_2(CH)_2CCH_3]_2$), 137.8 ($[C(CH)_2(CH)_2\mathbf{C}CH_3]_2$), 130.6 ($[C(CH)_2(\mathbf{C}H)_2CCH_3]_2$), 127.5 ($[C(CH)_2(\mathbf{C}H)_2CCH_3]_2$), and 21.3 ($[C(CH)_2(CH)_2C\mathbf{C}H_3]_2$).

Toluene

^{1}H NMR (400 MHz, DMF-d_7) δ 7.29-7.15 (m, 5H, $(C\mathbf{H})_5CCH_3$), and 2.32 (s, 3H, $(CH)_5CC\mathbf{H}_3$).

^{13}C NMR (100 MHz, DMF-d_7) δ 138.8 ($CH(CH)_2(CH)_2\mathbf{C}CH_3$), 130.1 ($CH(\mathbf{C}H)_2(CH)_2CCH_3$), 129.3 ($CH(CH)_2(\mathbf{C}H)_2CCH_3$), 126.4 ($\mathbf{C}H(CH)_2(CH)_2CCH_3$), and 21.7 ($CH(CH)_2(CH)_2C\mathbf{C}H_3$).

III. NMR spectra

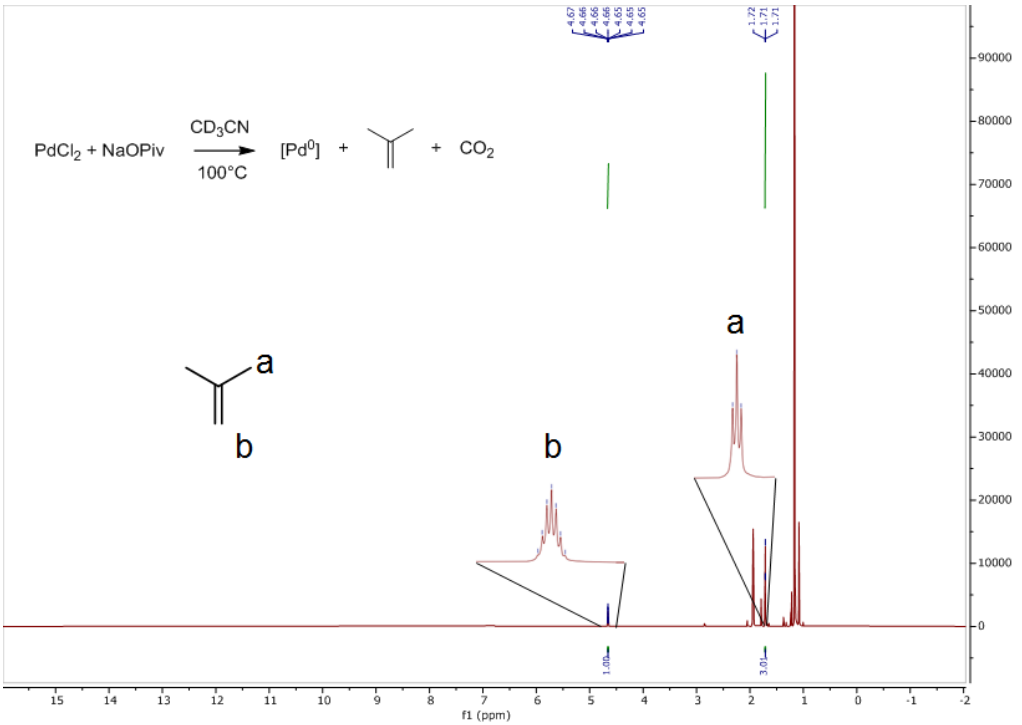

Figure S1. ^{1}H NMR spectrum of reaction of $PdCl_2$ with sodium pivalate.

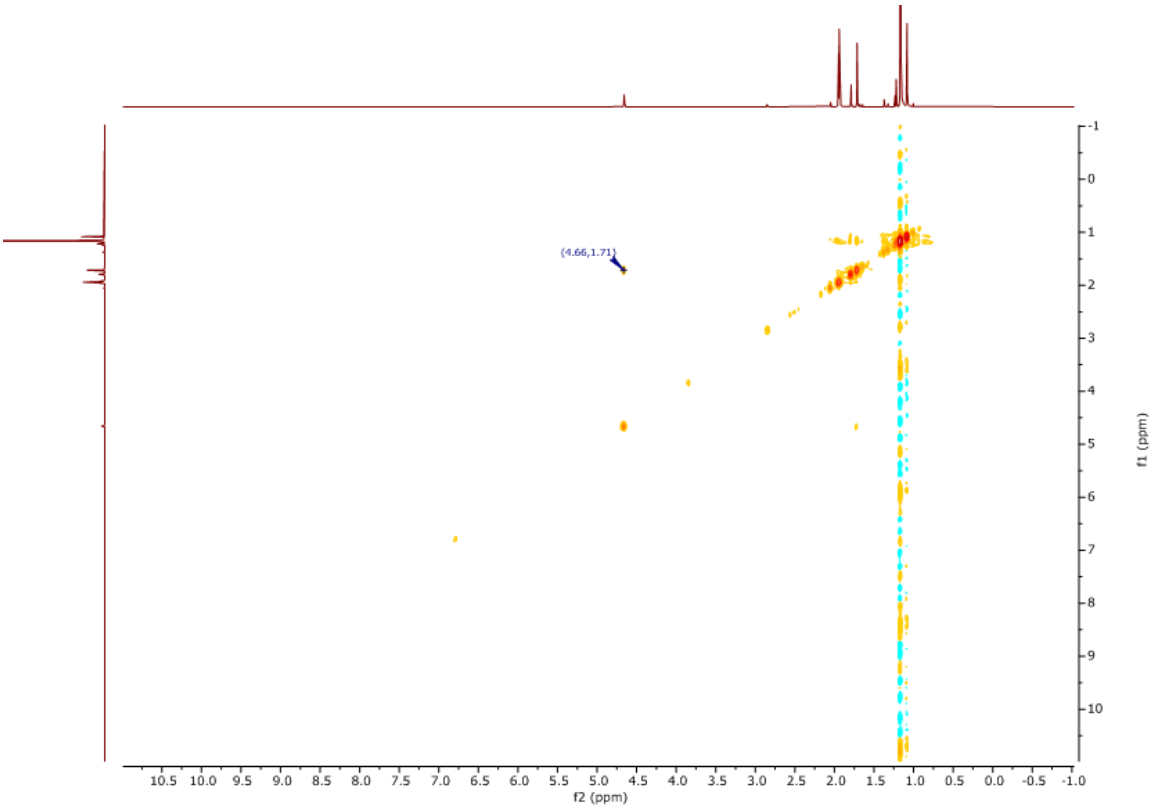

Figure S2. ^{1}H-^{1}H Correlation Spectroscopy (COSY) spectrum of reaction of $PdCl_2$ with sodium pivalate.

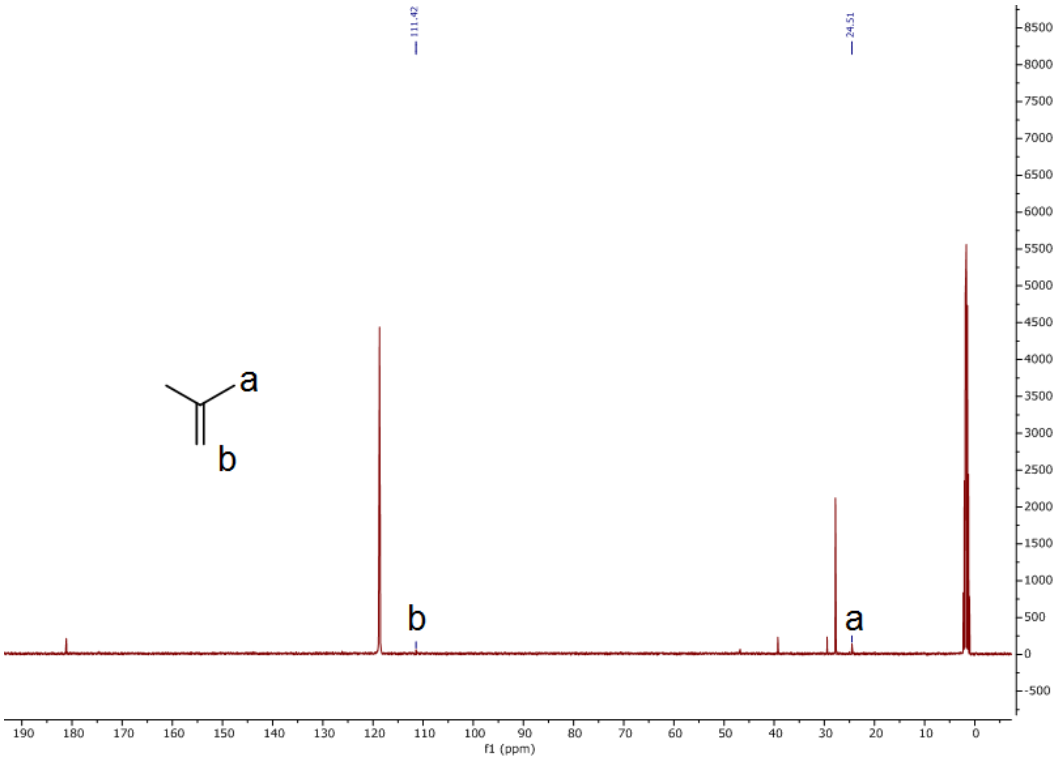

Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of reaction of $PdCl_2$ with sodium pivalate.

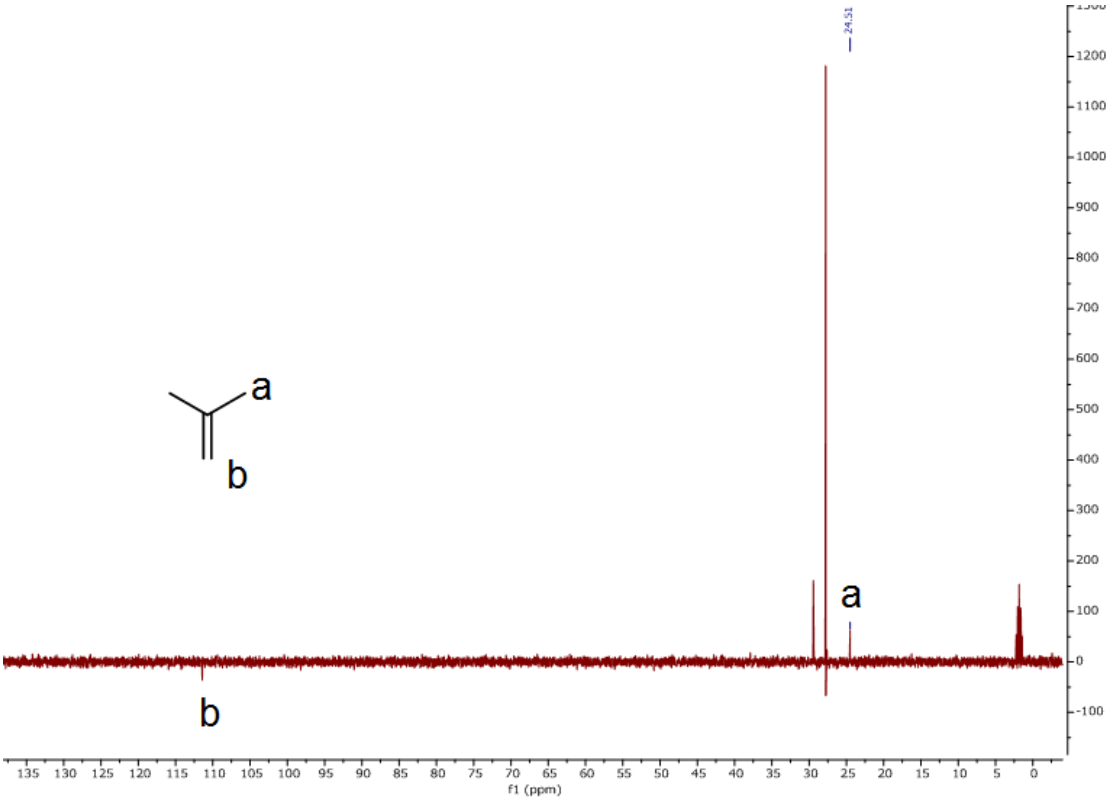

Figure S4. Distortionless enhancement by polarization transfer (DEPT) -135 spectrum

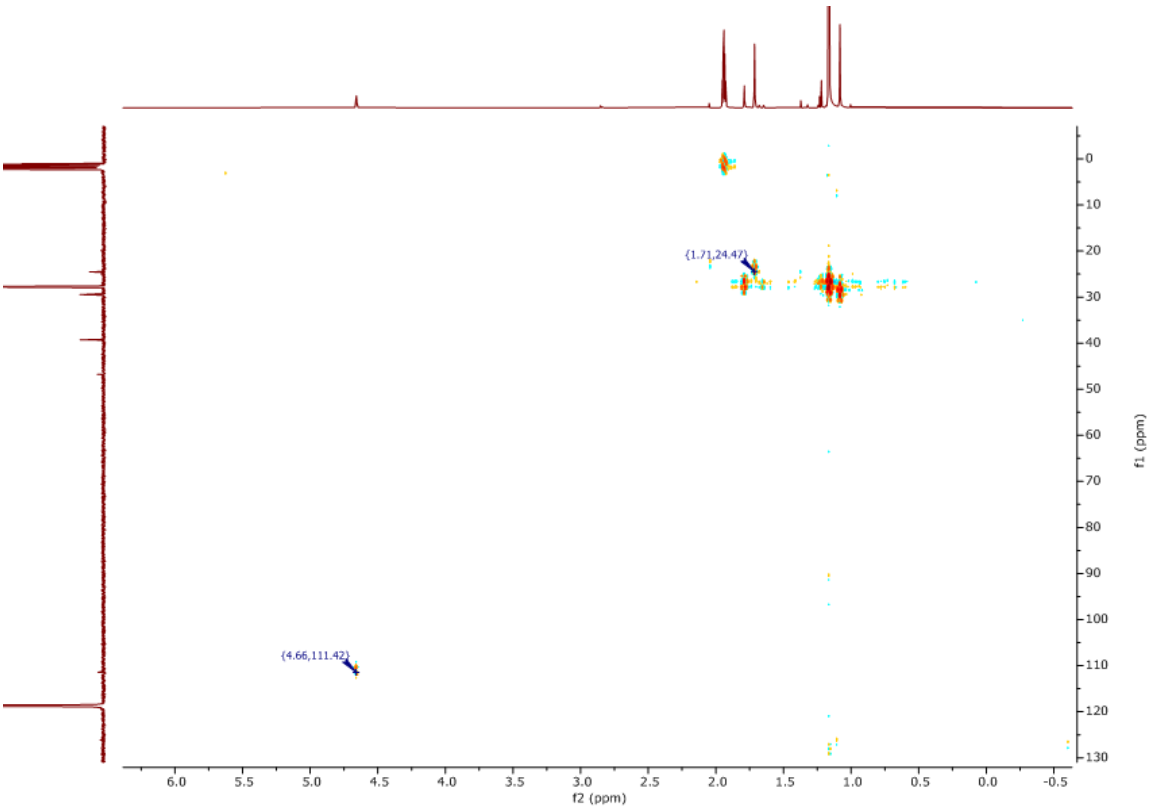

Figure S5. Heteronuclear single quantum coherence (HSQC) spectrum

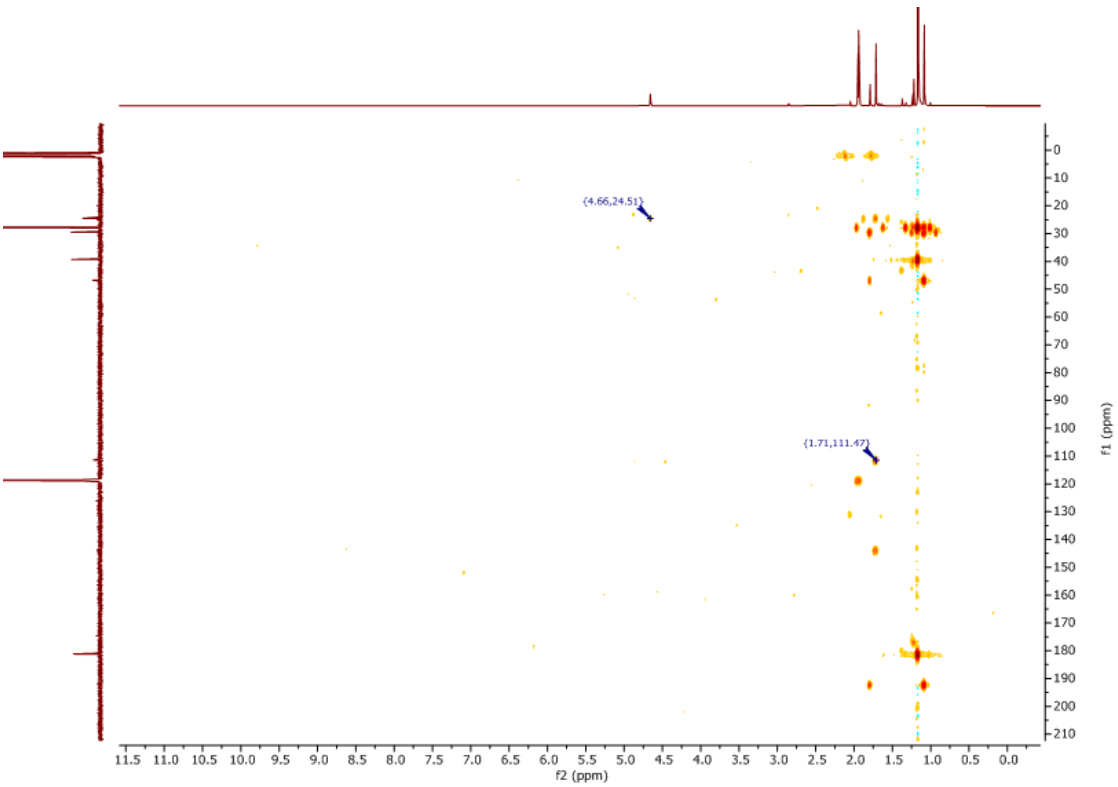

Figure S6. Heteronuclear multiple bond correlation (HMBC) spectrum

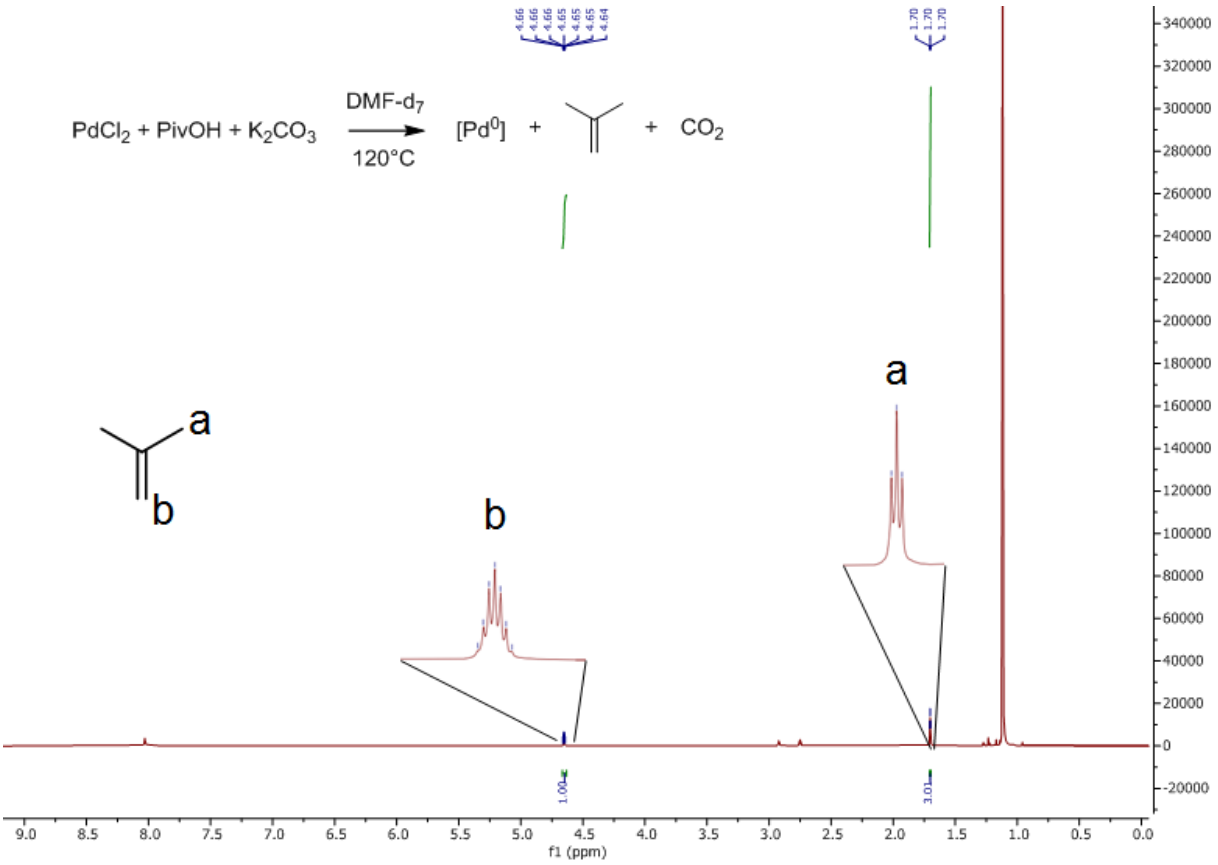

Figure S7. ^{1}H NMR spectrum of the isobutylene detection reaction with pivalic acid and potassium carbonate

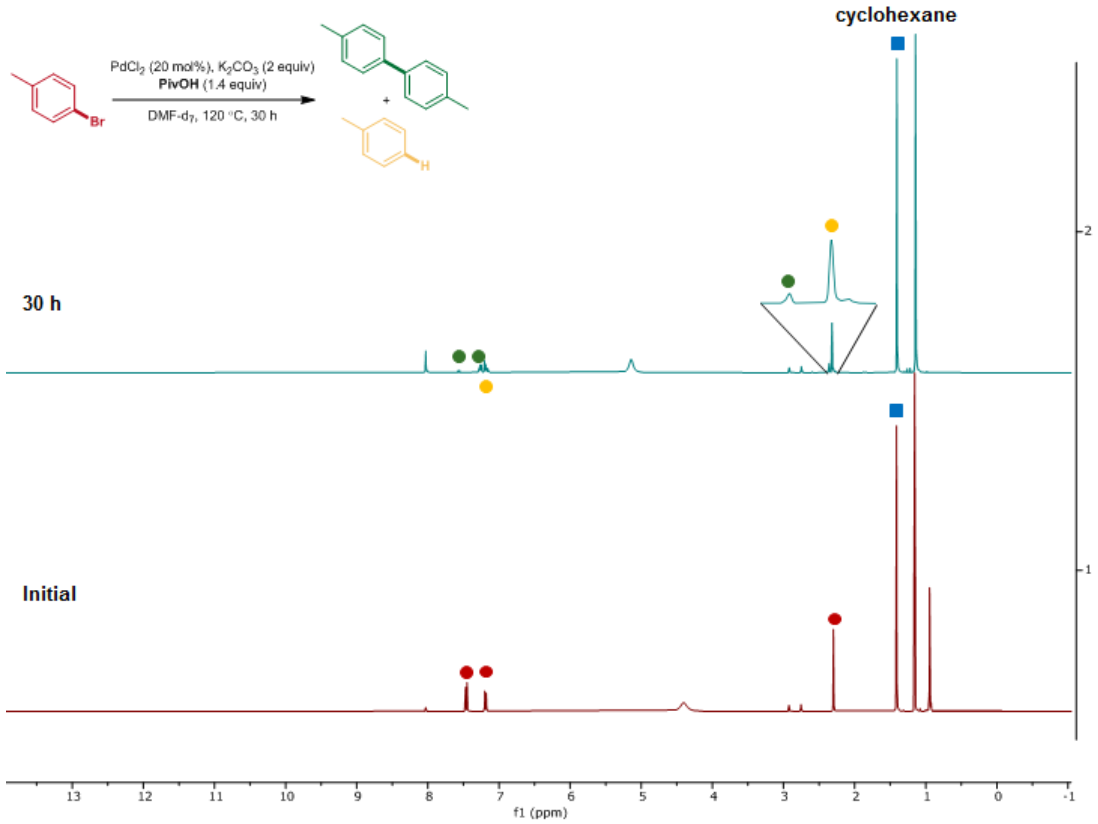

Figure S8. ^{1}H NMR spectra of the homocoupling reaction with PivOH varying time

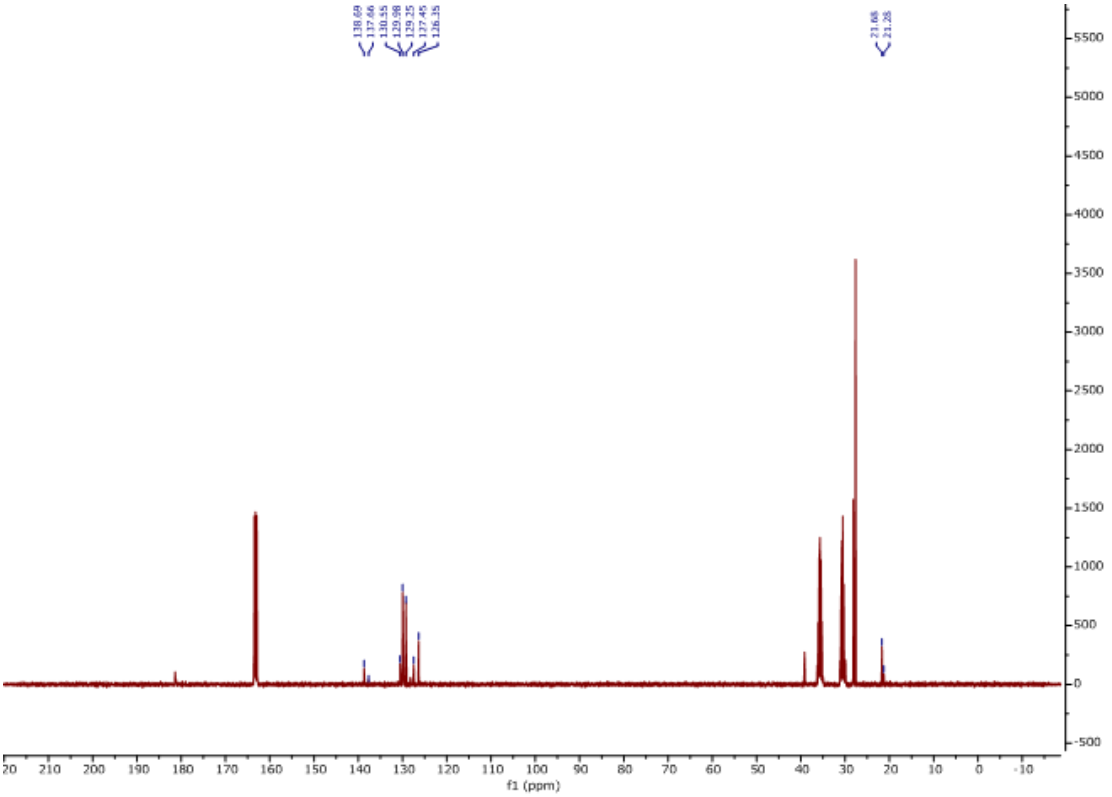

Figure S9. ^{13}C NMR spectrum of the homocoupling reaction with PivOH after 30 h

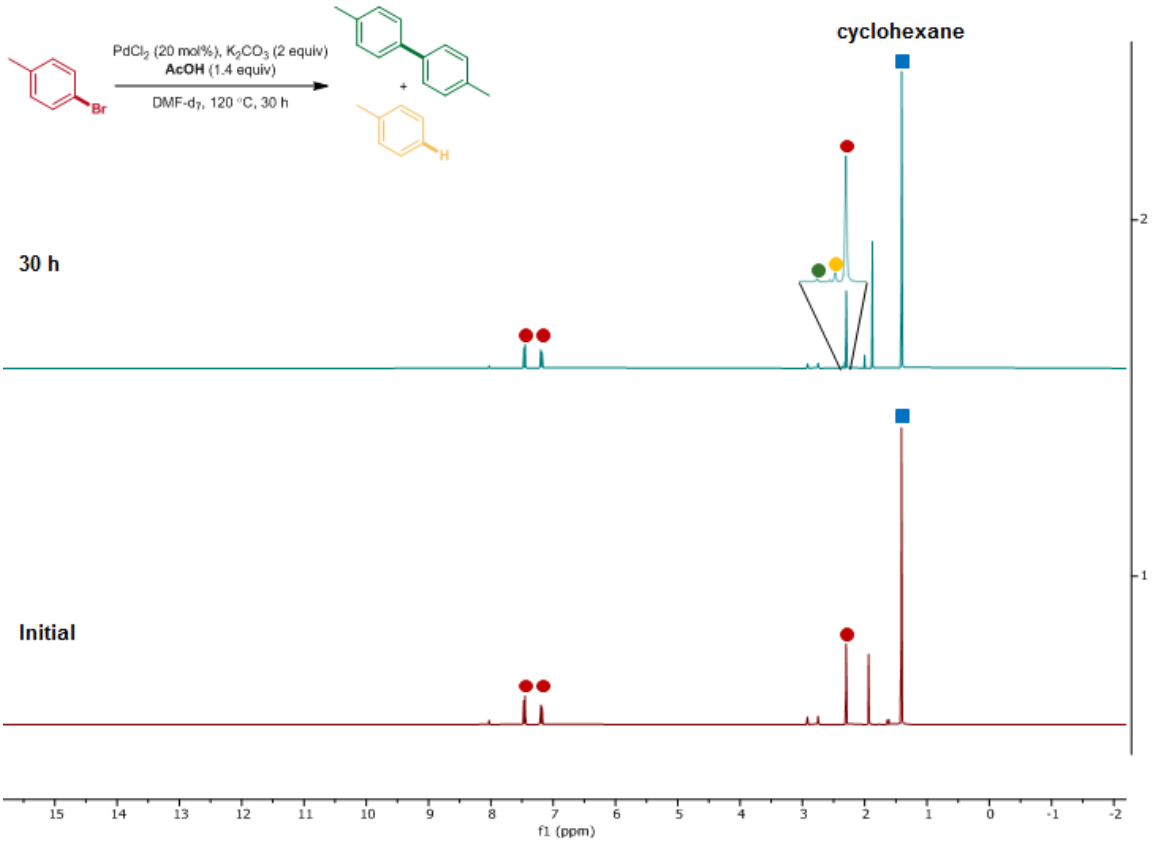

Figure S10. ^{1}H NMR spectra of the homocoupling reaction with AcOH varying time

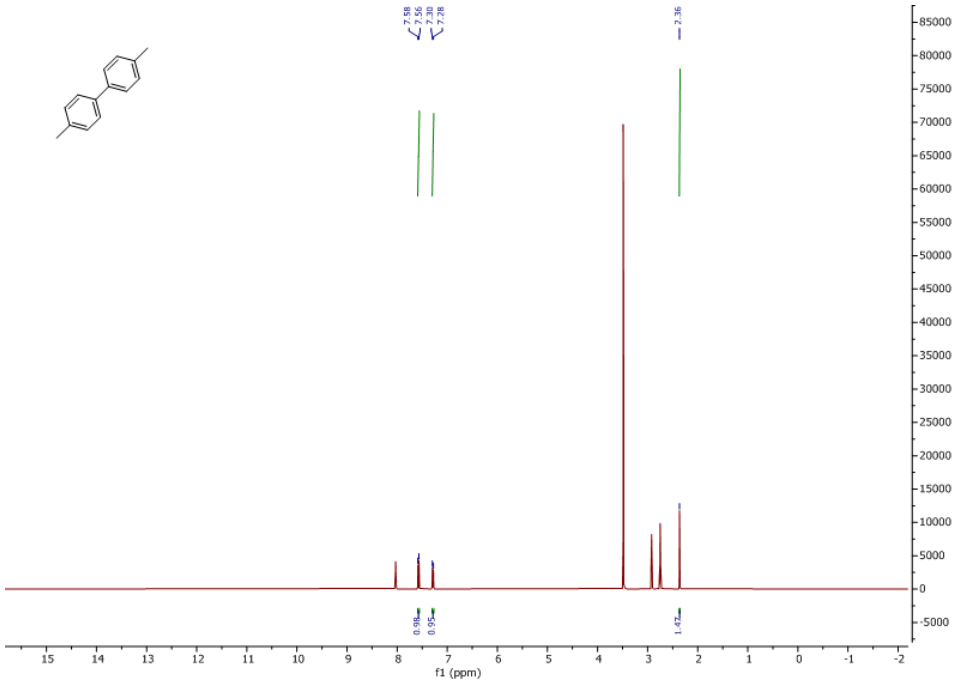

Figure S11. ^{1}H NMR spectrum of 4,4'-dimethylbiphenyl

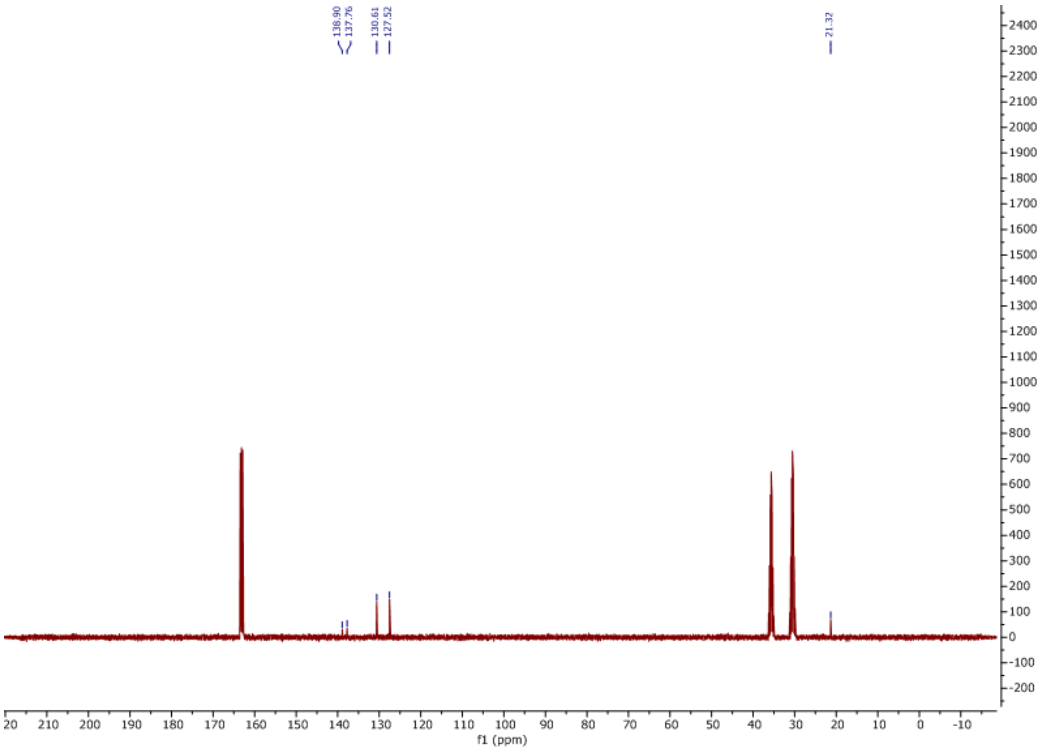

Figure S12. ^{13}C NMR spectrum of 4,4'-dimethylbiphenyl

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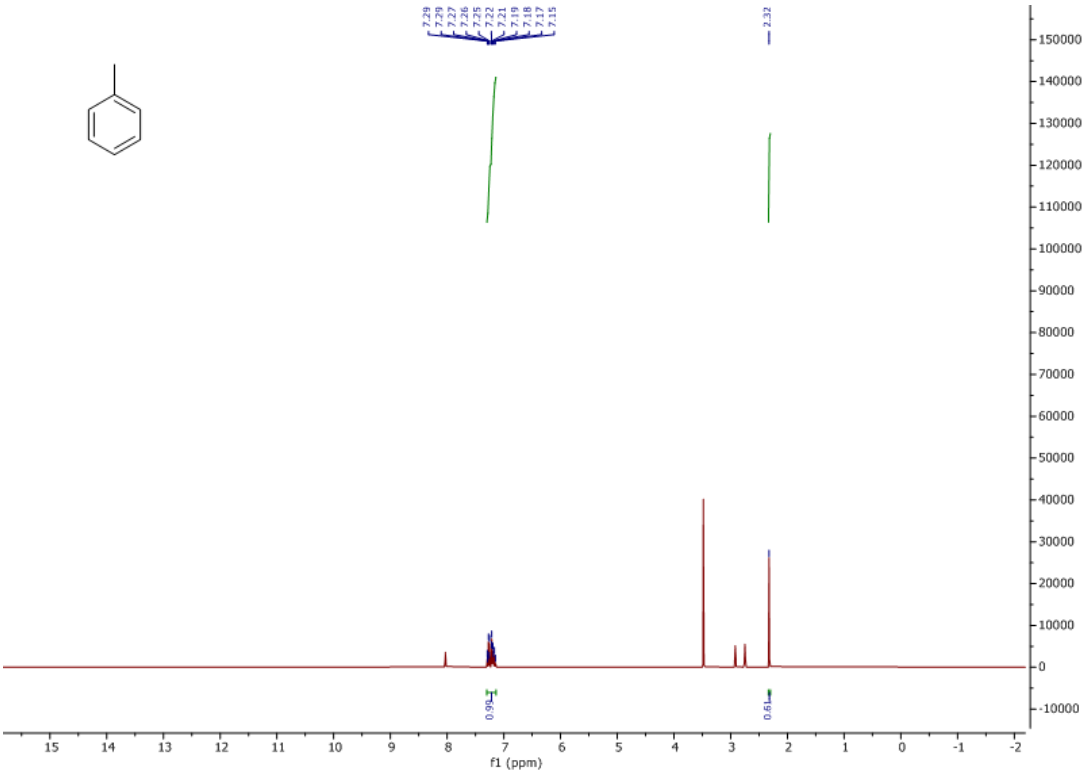


Figure S13. ^{1}H NMR spectrum of toluene

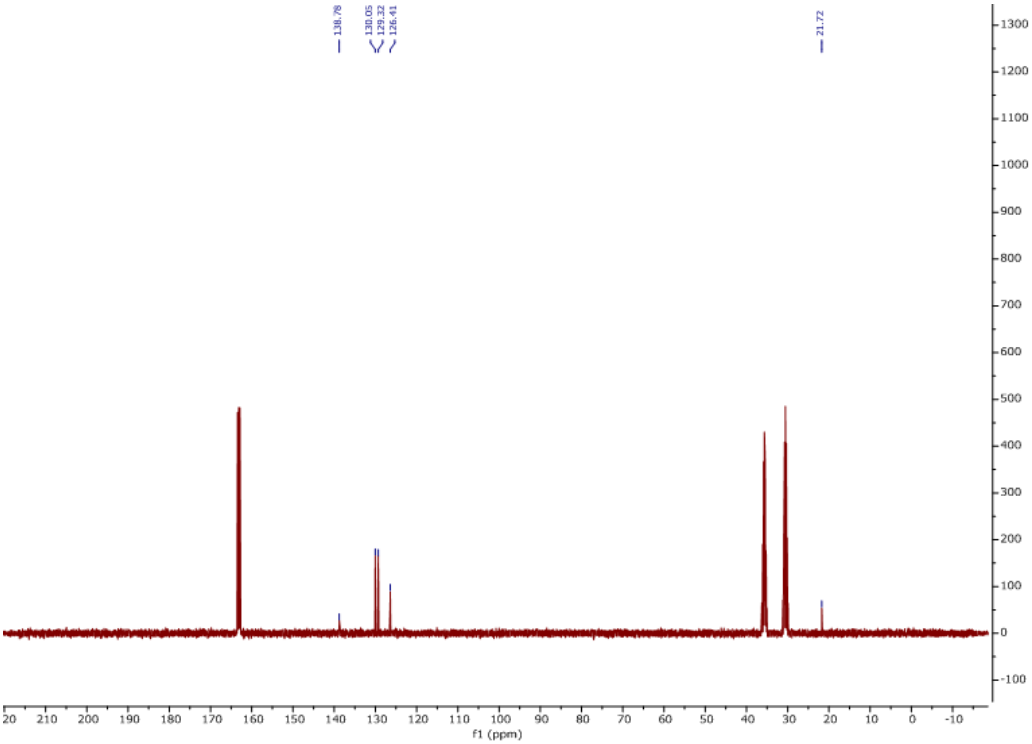


Figure S14. ^{13}C NMR spectrum of toluene

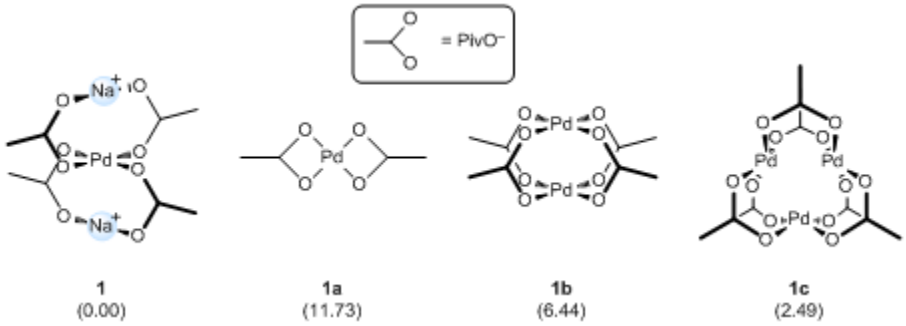
IV. Computational Details

Computational Methods

All density functional theory (DFT) calculations were performed using the Jaguar 9.1 quantum chemistry program.[1] Electronic exchange and correlation energy contribution to the total electronic energy was approximated with B3LYP hybrid functional[2,3] along with Grimme's D3[4] dispersion correction (B3LYP-D3). All intermediate and transition state geometries were optimized with 6-31G** basis set[5–7] for main group atoms. Pd atom was described by Los Alamos relativistic effective core potentials (ECP)[8–10] and its corresponding LACVP basis set. While these basis sets are adequate for obtaining accurate geometries, more reliable energies were obtained from single point calculations using Dunning's correlation-consistent triple-ζ basis set, cc-pVTZ(-f),[11] for main group and larger LACV3P** for Pd and Na.[12] The zero-point energy (ZPE), entropic and solvation contributions to the Gibbs energy are obtained from the same level of theory as the geometry optimizations (B3LYP-D3/6-31G**/LACVP). The optimized geometries characterized as the local minima on the potential energy surfaces do not contain any imaginary frequency, while each of the transition states contain one imaginary frequency. The solvation calculations utilized self-consistent reaction field (SCRF) approach on the gas phase geometry to model the solvation shell of dielectric constant ε = 37.8[13]

Energies of potential starting materials

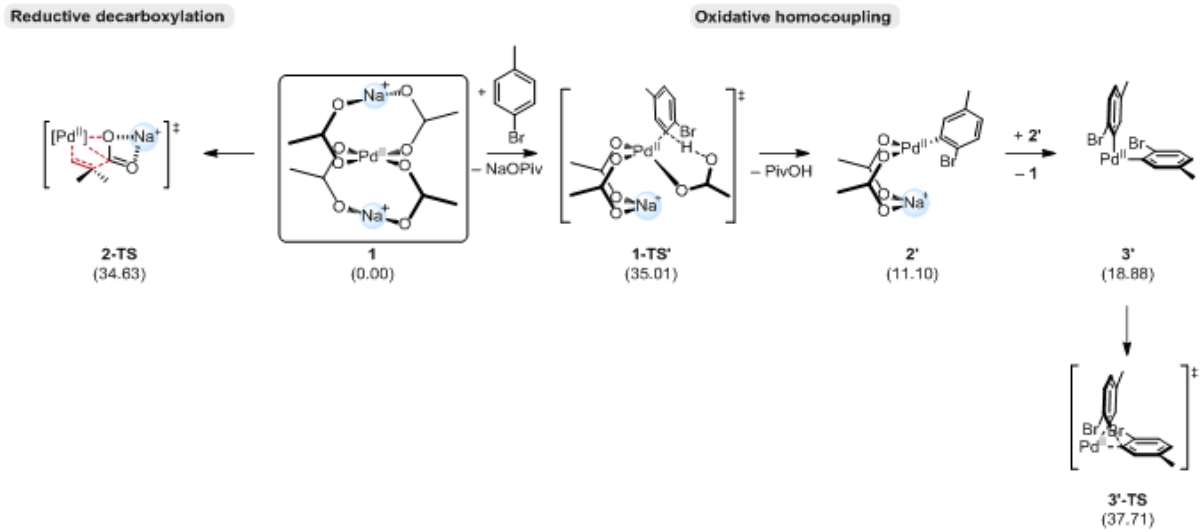
The free energies of potential starting materials are compared. The calculation results show that the tetra-carboxylate complex **1** is located lower in energy than other potential starting materials including Pd trimer **1c**.



Scheme S1. DFT calculated free energy of potential starting materials

Pd reduction *via* oxidative homocoupling

The mechanism of Pd^{II} reduction *via* oxidative homocoupling is summarized in Scheme S2. The starting material **1** performs concerted metalation deprotonation (CMD) with 4-bromotoluene and generates Pd-aryl complex **2'**. After that, the Pd-aryl complex would carry out transmetalation with another **2'** to form a Pd-diaryl complex. And subsequent reductive elimination yields Pd^0 and biaryl product. Whereas the calculated barrier difference between the CMD transition state **1-TS'** and the C–C cleavage step **2-TS** is only 0.4 kcal/mol, **2-TS** is expected to be faster than **1-TS'** since **2-TS** is an intramolecular reaction while **1-TS'** occurs intermolecularly. In addition, the high reductive elimination barrier of **3'-TS** which requires 37.7 kcal/mol would make this process less likely happen and the reductive decarboxylation would be a dominant Pd^0 generation process under the given condition.



Scheme S2. Proposed mechanism of oxidative homocoupling

Proposed Pd reduction mechanism with acetate

The proposed reductive decarboxylation mechanism is also examined with acetate. The calculation results demonstrate that the generation of strained 4-membered palladacycle complex **A2** through the CMD of acetate and the formation of Pd-methylene intermediate **A3** *via* subsequent C–C bond cleavage step are improbable with an insurmountable barrier of 37.0 and 62.2 kcal/mol, respectively.

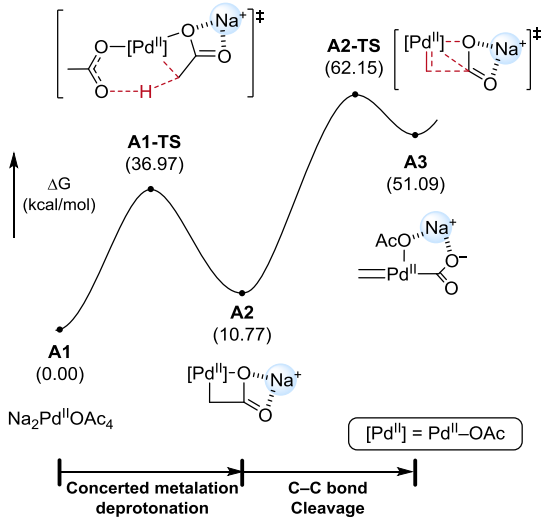


Figure S15. DFT calculated energy profile of the proposed reduction mechanism with acetate

Compute Energies of DFT-optimized structures

	E(SCF)/(eV)	ZPE/(kcal/mol)	S(gas)/(cal/mol)	G(solv)/(kcal/mol)
	cc-pVTZ(-f)/LACV3P	6-31G**/LACVP	6-31G**/LACVP	6-31G**/LACVP
1	-50011.816	344.63	241.983	-34.94

1-TS	-36159.816	255.166	188.24	-29.18
2	-26712.549	164.796	148.435	-43.73
2-TS	-26711.701	162.767	148.687	-28.57
3	-26712.939	163.05	156.991	-32.27
4	-12863.286	76.284	103.326	-5.88
4-TS	-12863.177	76.106	95.6	-2.43
5	-11344.076	97.789	112.423	-8.36
1-TS'	-43894.852	329.497	233.625	-26.35
2'	-34447.633	239.33	203.869	-30.84
3'	-18884.232	134.225	148.864	-7.09
3'-TS	-18883.305	133.812	143.531	-11.11
1a	-22310.650	171.331	144.225	-11.62
1b	-44623.125	345.424	229.822	-15.20
1c	-66936.102	518.728	314.717	-13.22
A1	-37168.836	130.869	180.462	-42.2
A1-TS	-26527.482	94.716	137.424	-32.81
A2	-20290.84	57.792	113.302	-45.7
A2-TS	-20288.932	54.672	117.126	-33.85
A3	-20289.215	54.874	123.244	-36.42
PivOH	-9446.947	92.537	86.755	-7.93
AcOH	-6236.253	38.912	68.414	-8.63
Acetonitrile	-3613.765	28.481	57.932	-8.12
NaOPiv	-13848.581	85.445	94.771	-34.55
NaOAc	-10637.875	31.854	78.253	-35.91
CO_2	-5133.564	7.277	51.155	-2.63
4-Bromotoluene	-7734.216	73.942	90.331	-3.28

Cartesian Coordinates of the Optimized Geometries

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PivOH

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O -2.738964558 0.314569861 -0.710036635

C -1.840463161 -0.391107142 -0.305904180

O -1.362970352 -1.432062864 -1.037590146

C -1.117935300 -0.253359228 1.034834623

C -1.698171377 0.951897860 1.788072586

H -1.196483016 1.062452912 2.754922628

H -1.562494755 1.874708772 1.217497468

H -2.770147562 0.827395797 1.963006616

C -1.336540699 -1.550279737 1.845347166

H	-0.941262245	-2.419838190	1.314284682
H	-0.825582445	-1.470292449	2.810628176
H	-2.400908470	-1.719075918	2.040088177
C	0.389846742	-0.049665008	0.771918595
H	0.918458879	0.048019528	1.726007462
H	0.814184785	-0.895202398	0.224905282
H	0.569834411	0.861608744	0.191896960
H	-1.879445553	-1.441984057	-1.860579729

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AcOH

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O	-4.729286194	4.227903366	-2.556911945
C	-3.391342163	4.273378849	-2.781358242
O	-2.727810383	3.279906750	-2.974946499
C	-2.880803347	5.691988468	-2.750711679
H	-3.087592840	6.137281418	-1.772802234
H	-1.809394598	5.697072983	-2.946557522
H	-3.405414820	6.293214321	-3.499115705
H	-4.976533890	3.288596630	-2.591031313

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Acetonitrile

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C	-0.585849881	0.000000196	0.156206951
N	-0.585991085	0.000000347	-1.003841400
C	-0.585862815	-0.000000549	1.617369771
H	0.439926416	0.000000028	1.997313857
H	-1.098801851	-0.888363302	1.997129440
H	-1.098801494	0.888362646	1.997127533

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NaOPiv

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O	-5.010547161	-1.091299295	-3.104804277
C	-5.911948681	-0.484650135	-3.770146847
O	-6.119926453	0.769350529	-3.696131229
C	-6.822066784	-1.303133965	-4.714177132
C	-6.424330235	-2.784296513	-4.725450993
H	-7.082797527	-3.347622395	-5.397692680
H	-5.392314911	-2.909959078	-5.064328194
H	-6.494612694	-3.216885805	-3.723992586
C	-8.272995949	-1.143092275	-4.215426445
H	-8.547193527	-0.085916631	-4.174353600
H	-8.967360497	-1.662787557	-4.886134148
H	-8.391731262	-1.569166780	-3.212522030
C	-6.700417995	-0.704158127	-6.129695415
H	-7.378179550	-1.217198372	-6.822106838
H	-6.948441505	0.359853923	-6.115198135
H	-5.680199623	-0.813390970	-6.515288830
Na	-4.530184746	0.838864326	-2.211190939

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NaOAc

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O	-4.733372688	4.171658516	-2.859133959
C	-3.470122814	4.293519497	-2.770725012
O	-2.665408373	3.314808369	-2.649651527
Na	-4.416845798	2.019132137	-2.748165607
C	-2.883904219	5.701420307	-2.778366566
H	-2.811662197	6.057180405	-1.744114399
H	-1.877898335	5.694705486	-3.202685118
H	-3.533712626	6.385539532	-3.327573061

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CO_2

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O	-4.377183914	-2.714765549	-0.035200581
O	-2.507269382	-1.383602619	-0.490785629
C	-3.442470074	-2.049233437	-0.263213098

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4-Bromotoluene

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C	-5.582464695	0.070968576	-3.015634060
C	-4.874389648	-0.218215674	-1.853556275
C	-5.371880054	-0.645649791	-4.189691067
C	-3.935481071	-1.250704050	-1.877827406
C	-4.428144932	-1.673416972	-4.190353394
C	-3.692612171	-1.990865946	-3.041841745
H	-5.050867081	0.348085761	-0.945909798
H	-5.932620049	-0.410133094	-5.087323189
H	-3.382709742	-1.481261253	-0.970560968
H	-4.264238834	-2.237074375	-5.105693340
C	-2.660265684	-3.093136787	-3.062590599
H	-2.444560766	-3.457861185	-2.053990126
H	-2.999343157	-3.944710493	-3.661482573

H	-1.715797067	-2.744578838	-3.497499943
Br	-6.910317421	1.520180106	-2.997437716

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Pd	-3.851111174	-0.361118913	-1.575319171
O	-5.020950794	-1.167715549	-3.096630096
C	-5.778898716	-0.369244725	-3.774355650
O	-5.812325954	0.870003879	-3.644342899
C	-6.730677605	-1.044655800	-4.784183025
C	-6.410038471	-2.536072493	-4.971839905
H	-7.118721485	-2.986522198	-5.675307274
H	-5.402571678	-2.673741341	-5.383042336
H	-6.478566647	-3.076982260	-4.023404598
C	-8.158373833	-0.885952473	-4.215314388
H	-8.395994186	0.170348808	-4.063860893
H	-8.889868736	-1.313533306	-4.910135746
H	-8.257377625	-1.403577447	-3.254862785
C	-6.617035389	-0.303374469	-6.129843235
H	-7.326809883	-0.720172346	-6.852797985
H	-6.830012798	0.760058463	-6.000669956
H	-5.609284878	-0.402230889	-6.550456524
O	-1.994098067	-1.365754604	-3.810201645
C	-1.997053146	-0.121702477	-3.803096294
O	-2.688047171	0.613929033	-2.988663673
C	-1.128253698	0.682241201	-4.792650700
C	-0.405715466	-0.270049930	-5.755700588
H	0.231662169	0.301164448	-6.439486027
H	0.218989715	-0.979809880	-5.207844734
H	-1.120604038	-0.847143173	-6.349764824
C	-2.035786629	1.643551350	-5.589405060
H	-2.476483107	2.402708769	-4.935726643
H	-1.451694369	2.163683891	-6.356206417
H	-2.849249125	1.105470300	-6.088614941
C	-0.103084460	1.494451046	-3.972230911
H	0.515605748	2.105091810	-4.639262676
H	-0.609522879	2.151947021	-3.260142088
H	0.560503900	0.830577075	-3.407700062
O	-5.037503242	-1.306789875	-0.228060484
O	-4.371685028	-3.307560682	-1.040523410
C	-6.271003723	-3.231790304	0.458450109
C	-5.107019901	-2.590457439	-0.325277418
C	-6.578152180	-2.449003458	1.745761156
C	-7.487353802	-3.167343378	-0.497013360
C	-5.942601204	-4.696501255	0.788278818
H	-7.423732281	-2.908777237	2.270346880
H	-5.716063499	-2.452555418	2.420910597
H	-6.824848175	-1.408720255	1.524076581
H	-7.283267021	-3.714042425	-1.424226403
H	-8.366924286	-3.615221262	-0.021008076
H	-7.724246502	-2.129438400	-0.753153205
H	-6.794464111	-5.166915894	1.292376399
H	-5.714696884	-5.260144711	-0.119109921
H	-5.074667454	-4.764285564	1.452638388
Na	-3.448564529	-2.849756718	-2.981831789
C	-2.671305895	1.728723049	-0.036297724
O	-2.711738586	0.439361006	-0.101932913
O	-3.353417158	2.516276360	-0.726898193
C	-1.646366239	2.265648365	0.985783279
C	-1.929687738	1.634119511	2.363372326
C	-0.245152608	1.839551568	0.494908959
C	-1.732832193	3.795655966	1.071749449
H	-1.191552758	1.981354237	3.095432997
H	-2.924474716	1.915306568	2.726496935
H	-1.883881688	0.544365525	2.306054592
H	-0.033008806	2.255295753	-0.497079372
H	0.523514807	2.203713417	1.186001182
H	-0.173864722	0.750853717	0.431390256
H	-0.999155045	4.170192719	1.794674873
H	-1.530503750	4.256558895	0.100899421
H	-2.728595257	4.116892815	1.390495777
Na	-4.322141647	2.216739655	-2.688962460

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O	-5.841691017	-1.191077709	-0.849278390
O	-7.676759720	-1.904828906	-1.854206800
C	-5.520982742	-2.829195261	-2.581895828
C	-6.440923214	-1.941843748	-1.739558578
C	-4.317342281	-1.982864738	-3.054822683
C	-5.030201435	-3.977200270	-1.670035005
C	-6.284115314	-3.395398617	-3.787262678

H	-4.622477531	-1.176298141	-3.732118607
H	-3.682030201	-2.632603168	-3.673453331
H	-5.870049953	-4.593751907	-1.333780885
H	-4.336476803	-4.618231773	-2.224579334
H	-4.510624886	-3.584733725	-0.791913629
H	-5.638482094	-4.066564560	-4.363585949
H	-7.165462017	-3.951148987	-3.456244469
H	-6.626004696	-2.593332529	-4.448305130
O	-2.142285585	0.191663280	-1.909610152
Pd	-4.012581348	-0.498361230	-1.399851918
C	-1.340611339	-0.737415612	-2.256516218
O	-1.706700325	-1.941633582	-2.420028687
C	0.123197272	-0.339549869	-2.479233503
C	0.663173318	0.216386497	-1.144026995
C	0.949406683	-1.552472353	-2.929855824
C	0.155445725	0.765568793	-3.556294441
H	1.701745391	0.539946616	-1.272013783
H	0.066552527	1.068264008	-0.809140146
H	0.640775859	-0.549400628	-0.361182213
H	0.565557420	-1.966013074	-3.866562366
H	1.991428852	-1.251997828	-3.083884239
H	0.924175203	-2.348105431	-2.180528402
H	1.188243985	1.090790153	-3.720969915
H	-0.238845602	0.398088872	-4.510194778
H	-0.440008372	1.627556086	-3.246357441
H	-3.060828924	-1.904052258	-2.432298660
O	-6.137576103	1.737198234	-0.313271016
C	-5.033314228	1.736888289	0.281815916
O	-4.039360046	0.964071214	0.045637853
C	-4.815926552	2.759083271	1.424497962
C	-5.898937225	2.492492676	2.491127968
C	-3.418176174	2.634358644	2.047483206
C	-5.011128902	4.168649197	0.829837561
H	-5.813645840	3.217692852	3.308025837
H	-6.898251057	2.578942776	2.054483175
H	-5.791308880	1.489162564	2.919682503
H	-2.639452457	2.802039623	1.298827291
H	-3.298162937	3.373861551	2.847954988
H	-3.260931730	1.637564301	2.468178749
H	-4.925688744	4.925804615	1.617531538
H	-4.250007629	4.382237434	0.071365692
H	-5.994939804	4.256489754	0.361814827
Na	-7.592862129	0.184764042	-0.697379112

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Pd	-3.985553980	-0.102687977	-1.578519940
O	-5.399180889	-1.275457025	-0.594729900
O	-6.576115608	-3.151355505	-0.738312483
C	-5.243616581	-2.485876083	-2.679684162
C	-5.812466145	-2.316658020	-1.272653222
C	-4.717187881	-1.120824337	-3.158086538
C	-4.083487034	-3.503239870	-2.548922062
C	-6.320341110	-3.050884962	-3.622217894
H	-5.524756432	-0.491852283	-3.553448200
H	-3.930410147	-1.218258142	-3.912551641
H	-4.446065426	-4.458041668	-2.155608654
H	-3.640524864	-3.677674770	-3.534887552
H	-3.297593832	-3.119566202	-1.890574098
H	-5.895187855	-3.213901758	-4.618100643
H	-6.706669331	-4.000827312	-3.241007328
H	-7.160170078	-2.355363607	-3.721571207
C	-2.144184828	1.648108602	-1.403036118
O	-2.703510046	1.387699723	-0.302055806
O	-2.517687321	1.054033041	-2.483052969
C	-1.013580441	2.680855989	-1.470956326
C	-1.589328051	4.030839920	-0.993644893
C	0.099560842	2.226234198	-0.504759669
C	-0.464849323	2.809815168	-2.899170160
H	-0.800623477	4.791781902	-0.975312233
H	-2.381163597	4.379228115	-1.665969729
H	-2.009507656	3.934346676	0.010771325
H	0.532469869	1.272351146	-0.825928509
H	0.902997971	2.971289158	-0.477819264
H	-0.298517317	2.099108458	0.504940212
H	0.338599563	3.555192471	-2.925626516
H	-0.065595791	1.855807900	-3.254774332
H	-1.249221325	3.118717194	-3.595428467
Na	-6.321857452	-2.101658821	1.210221291

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Pd	-4.054972172	-0.337482870	-2.129648924
O	-5.694073200	-1.351170540	-0.125813738
O	-3.885735512	-2.638091803	-0.576353073
C	-5.568882465	-2.303632259	-2.595020056
C	-4.919559002	-1.994080186	-0.872250319
C	-5.087247849	-1.291295290	-3.563537836
C	-5.032454967	-3.710659027	-2.872118235
C	-7.081292152	-2.248965502	-2.362844706
H	-5.830471992	-0.594203889	-3.959170103
H	-4.373990059	-1.630879164	-4.319003582
H	-5.322612762	-4.407827854	-2.082338572
H	-5.440249443	-4.070164680	-3.824368954
H	-3.942646980	-3.705435514	-2.927666426
H	-7.597886562	-2.527851582	-3.288988352
H	-7.385610104	-2.938899040	-1.572070360
H	-7.391559124	-1.245461464	-2.067129135
C	-2.486018658	1.603649497	-1.360858083
O	-2.858941078	0.767937601	-0.463485330
O	-2.870902061	1.481829166	-2.561968088
C	-1.563211083	2.772634983	-0.998326838
C	-2.299074650	4.082994938	-1.351209760
C	-1.206654787	2.747942686	0.495467246
C	-0.285175145	2.649753571	-1.855293870
H	-1.653928518	4.943149090	-1.140972733
H	-2.571680307	4.097391129	-2.409109592
H	-3.214229822	4.192818165	-0.758941412
H	-0.689743459	1.821209788	0.762782395
H	-0.547684848	3.589530230	0.735881269
H	-2.103780270	2.827306032	1.117011666
H	0.382465690	3.495135546	-1.655650973
H	0.257629633	1.726625085	-1.623906851
H	-0.535581470	2.642639875	-2.918757439
Na	-3.627099514	-0.795130730	0.893100083

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Pd	-3.918021441	-0.745268583	-2.178705454
O	-4.581094742	-3.308325768	-1.114289522
O	-2.520814180	-2.401809931	-0.643820286
C	-5.867049694	-1.011429906	-3.357978344
C	-3.669907331	-2.508208752	-1.132227182
C	-4.872412205	-1.850696087	-3.846421480
C	-6.942255497	-1.521102309	-2.427491188
C	-6.130051613	0.337193191	-3.990295172
H	-4.298391819	-1.562156439	-4.724892139
H	-4.856246948	-2.899952173	-3.570692062
H	-7.218327522	-0.755424261	-1.694955826
H	-7.844319820	-1.751692295	-3.011506557
H	-6.619716644	-2.419738054	-1.900120735
H	-7.060877323	0.285485744	-4.572251320
H	-6.251985073	1.113590002	-3.229790926
H	-5.319631577	0.646281421	-4.654359341
C	-3.123628855	1.810303569	-1.276648045
O	-2.799048185	0.685779393	-0.718931496
O	-3.826367140	1.868930340	-2.298249245
C	-2.622779846	3.122561932	-0.630768955
C	-3.871043205	3.920680285	-0.197942063
C	-1.719010592	2.870474815	0.584395587
C	-1.852250338	3.913980007	-1.706292152
H	-3.579573870	4.893044949	0.215428725
H	-4.527737141	4.083657742	-1.055630207
H	-4.437906742	3.381334543	0.569554269
H	-0.814811885	2.319332600	0.297594517
H	-1.397787333	3.821918249	1.023038626
H	-2.247041464	2.304349661	1.359188795
H	-1.541581511	4.890027523	-1.316069365
H	-0.952397048	3.374931335	-2.025452852
H	-2.483870268	4.067577839	-2.583936453
Na	-1.636341214	-0.714709580	0.363320589

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Pd	-3.835379601	-1.108097911	-2.438071728
O	-4.621857166	-2.877530575	-0.138227597
O	-2.801797867	-1.429893374	-0.450175315
C	-5.882379532	-0.832625628	-3.337834358
C	-3.819275856	-2.100742817	-0.545256197
C	-5.080741882	-1.656443834	-4.122998238
C	-6.908143520	-1.408483863	-2.385354519
C	-6.068768978	0.630868018	-3.677620649
H	-4.589502811	-1.258399129	-5.010078430
H	-5.193751812	-2.737260818	-4.085062027

H	-6.967224121	-0.819758356	-1.464725018
H	-7.900515079	-1.374105215	-2.856958628
H	-6.683545589	-2.442181826	-2.114553452
H	-7.039774418	0.767945707	-4.173732758
H	-6.078643322	1.251262784	-2.775890589
H	-5.288576126	1.002178192	-4.347466946

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Pd	-4.286954403	-1.070236325	-2.000540972
O	-2.974761248	-3.645077467	-0.010043431
O	-2.836944342	-1.310369253	-0.217215657
C	-5.924649239	-0.843461752	-3.429766893
C	-2.962189198	-2.489702702	-0.174453348
C	-4.979492188	-1.747310400	-3.921967983
C	-7.222883701	-1.325899005	-2.813891649
C	-5.952017784	0.593462408	-3.914736271
H	-4.245420456	-1.431781530	-4.660989285
H	-5.156053543	-2.819174528	-3.860503912
H	-7.513891697	-0.703126371	-1.961211324
H	-8.034431458	-1.258812428	-3.553422451
H	-7.152784824	-2.362477541	-2.474553585
H	-6.731850624	0.713317752	-4.681001186
H	-6.195426941	1.284708738	-3.100495100
H	-4.996347427	0.897470772	-4.349958897

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Pd	-3.178100109	-0.473945290	-2.814508438
C	-4.684387684	-1.085188150	-4.331579208
C	-3.447139025	-1.651987195	-4.613607407
C	-5.777883053	-1.883478880	-3.650948524
C	-5.168563843	0.147563800	-5.068200111
H	-2.797643423	-1.214243531	-5.369261742
H	-3.236182928	-2.685228348	-4.345163345
H	-6.326200962	-1.268047333	-2.929718733
H	-6.505977631	-2.233702183	-4.398294926
H	-5.378668308	-2.754012108	-3.124660015
H	-5.875530243	-0.143098384	-5.860071659
H	-5.699502945	0.828596473	-4.394510746
H	-4.343502045	0.696897805	-5.528715134
C	-1.796720982	0.911712408	-0.240438312
N	-2.344517946	0.441295981	-1.148511052
C	-1.110743642	1.501786232	0.901905477
H	-0.657805800	0.716839850	1.515388489
H	-1.821097851	2.063452721	1.516062737
H	-0.324253619	2.182295561	0.561432421

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Pd	-4.003958702	-0.310295075	-2.270485640
O	-5.571269035	-0.971172631	-3.465815306
C	-6.142879486	-1.488610864	-2.443348885
O	-5.543659687	-1.325819492	-1.320609450
C	-7.444220543	-2.261496782	-2.535262585
C	-7.929210186	-2.314484358	-3.992710829
H	-8.868484497	-2.874832153	-4.045285702
H	-8.104085922	-1.311686754	-4.392032146
H	-7.197745800	-2.807686567	-4.638727665
C	-7.184199333	-3.686582804	-1.992822170
H	-6.813506126	-3.653504372	-0.965253949
H	-8.116801262	-4.260038853	-2.008706570
H	-6.449578285	-4.217279911	-2.607367039
C	-8.482393265	-1.547133088	-1.638398886
H	-9.422677040	-2.108016253	-1.648285031
H	-8.128949165	-1.479779959	-0.606277585
H	-8.688473701	-0.534043312	-1.999207735
O	-2.422849655	0.320971876	-1.079411387
C	-1.841620803	0.824645042	-2.102967024
O	-2.461681128	0.706044257	-3.219633341
C	-0.493224651	1.514971018	-2.022913933
C	-0.007069801	1.564737201	-0.565547645
H	0.970567405	2.056054354	-0.522689164
H	-0.700786233	2.124600172	0.067927375
H	0.093251996	0.561013699	-0.143844515
C	0.495192081	0.708529830	-2.899144411
H	0.141782016	0.643381119	-3.931446075
H	1.472905993	1.201524615	-2.896478891
H	0.627566755	-0.308159083	-2.514635324
C	-0.651370347	2.941004276	-2.597200871
H	0.319619894	3.446975946	-2.593675852

H	-1.024610877	2.912032127	-3.623906851
H	-1.345478177	3.536694288	-1.995256186

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1b

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Pd	-0.414150447	-4.471967697	-1.878846169
O	0.601058483	-2.902239323	-4.482447147
O	-0.235826686	-4.941480637	-3.874122858
C	0.234444112	-4.099351883	-4.709122181
C	0.380916297	-4.619616508	-6.149419308
O	0.388584405	-1.666479707	-0.571915805
C	-0.091034278	-2.505199671	0.261247426
O	-0.466792464	-3.699074268	0.032369114
C	-0.233238474	-1.985104561	1.702160954
Pd	0.560329139	-2.129886866	-2.570860386
O	2.405144215	-2.986634493	-2.222588778
O	1.552825928	-5.017777443	-1.609621644
C	2.501340151	-4.200071812	-1.851576805
C	3.917494535	-4.774717808	-1.675717831
O	-1.407517314	-1.577108622	-2.834745884
C	-2.352169514	-2.397150755	-2.598617077
O	-2.253188133	-3.616706610	-2.239940643
C	-3.790054560	-1.861639619	-2.703113556
C	-3.811268806	-0.442777663	-3.288159609
H	-3.227624893	0.248710096	-2.675660133
H	-3.391262531	-0.426605731	-4.298358917
H	-4.844618320	-0.083251156	-3.337852716
C	-4.350525856	-1.854481578	-1.260624766
H	-5.390237808	-1.510168791	-1.268204451
H	-4.315808296	-2.857035875	-0.825676084
H	-3.773735523	-1.176701427	-0.621545970
C	-4.616025448	-2.820711851	-3.582352877
H	-4.221621037	-2.855425835	-4.603897095
H	-4.602580547	-3.834092140	-3.175551891
H	-5.653830051	-2.474822283	-3.633193016
C	0.891055763	-3.514103413	-7.084856510
H	1.866900325	-3.140891075	-6.762901783
H	0.988739789	-3.911281347	-8.101086617
H	0.202690929	-2.665180922	-7.108348846
C	1.384577036	-5.792945862	-6.111481667
H	1.038776517	-6.580271721	-5.437504768
H	1.502470851	-6.210962296	-7.116940022
H	2.369689226	-5.455090523	-5.769345760
C	-1.000761986	-5.124873638	-6.615886688
H	-0.924807489	-5.526458740	-7.632064342
H	-1.371464491	-5.910531044	-5.953693390
H	-1.732530355	-4.309494019	-6.628558159
C	4.984519482	-3.715454817	-1.988376975
H	4.892651558	-2.851504087	-1.324959517
H	5.981758118	-4.149851799	-1.858399391
H	4.895534992	-3.354301453	-3.016506433
C	4.051705360	-5.971700191	-2.641846180
H	5.045667171	-6.420037746	-2.539067984
H	3.296691895	-6.731414318	-2.427788496
H	3.932452917	-5.651693821	-3.683211327
C	4.052363396	-5.259261608	-0.216581702
H	3.285582066	-6.000710487	0.019556895
H	5.039269447	-5.709725857	-0.066382498
H	3.953042030	-4.422832489	0.484720170
C	1.153319478	-1.494050622	2.169452429
H	1.079942226	-1.091459513	3.185425520
H	1.876489520	-2.317085266	2.183753252
H	1.533178568	-0.712471485	1.507566810
C	-1.224949360	-0.801914394	1.665850282
H	-0.875167191	-0.021767093	0.985230088
H	-2.215679407	-1.133275628	1.334238410
H	-1.330072522	-0.377013534	2.669755936
C	-0.755258977	-3.085957050	2.636262655
H	-1.733918548	-3.449599743	2.311842680
H	-0.074859343	-3.941280842	2.661098003
H	-0.851719260	-2.688225746	3.652400255

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1c

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Pd	-0.181619361	-4.364183903	-2.154557705
Pd	-2.009055853	-6.520009995	-0.615044534
O	-0.991083682	-5.362781048	2.255672693
O	-2.857588053	-5.596832752	0.986170113
C	-2.240552187	-5.299601555	2.054703951
C	-3.089545250	-4.734043121	3.204958677
Pd	0.515088141	-5.189559460	0.878707230
O	0.183137029	-3.187061548	1.013945222

C	0.265554070	-2.376242876	0.041279018
O	0.423533559	-2.667592287	-1.182374835
C	0.082905881	-0.885666311	0.370428920
O	-2.025968313	-3.501336575	-2.174055099
C	-3.117931366	-4.135709763	-2.049432039
O	-3.258275747	-5.357775211	-1.744919658
C	-4.410923004	-3.319875956	-2.216207027
O	-1.313247800	-7.566117764	-2.216049194
C	-0.901461661	-7.039380550	-3.294755459
O	-0.695448101	-5.807676315	-3.511687994
C	-0.542676747	-8.003868103	-4.437596321
O	0.960316300	-7.174980164	0.894288778
C	0.101971857	-8.104936600	0.795374334
O	-1.128642797	-7.978239059	0.518663228
C	0.620588124	-9.544610023	0.946211338
O	1.699483514	-5.120945454	-2.302417755
C	2.526257753	-5.188308239	-1.341833472
O	2.290256262	-4.966094494	-0.116672866
C	3.946526051	-5.663028240	-1.690201879
C	0.915264785	-0.025838813	-0.596921861
H	1.984991193	-0.230357543	-0.483557314
H	0.638480544	-0.221409768	-1.634726048
H	0.747837245	1.034926891	-0.380822420
C	-1.425091743	-0.611256123	0.152211010
H	-1.719660282	-0.869587362	-0.869280040
H	-2.032284260	-1.200200200	0.846955419
H	-1.638025641	0.449369609	0.323700279
C	0.474973232	-0.592500329	1.826642513
H	-0.117467776	-1.186267018	2.526436090
H	1.531101942	-0.819852412	2.003761530
H	0.312108576	0.468568087	2.045233250
C	4.299697876	-5.318708897	-3.145057440
H	5.303281307	-5.690845966	-3.378083706
H	3.590402603	-5.767656803	-3.843599558
H	4.291316032	-4.235796928	-3.306427479
C	4.965773582	-5.033353329	-0.724820137
H	4.728855610	-5.278882504	0.312343627
H	5.969350338	-5.406467915	-0.955761492
H	4.977986813	-3.942717791	-0.822159708
C	3.910845995	-7.198825359	-1.493792653
H	3.599686861	-7.449406624	-0.475187451
H	3.209315777	-7.664180279	-2.193970919
H	4.906195164	-7.619537830	-1.672672153
C	-1.355567217	-9.304255486	-4.334051132
H	-1.067489743	-9.983820915	-5.143456936
H	-1.183739424	-9.806894302	-3.379515409
H	-2.428946018	-9.105662346	-4.420637131
C	0.965975165	-8.297885895	-4.256957054
H	1.150418162	-8.811320305	-3.307227373
H	1.318290591	-8.941825867	-5.069800854
H	1.544807434	-7.369245529	-4.265783310
C	-0.786558211	-7.323324680	-5.795820236
H	-0.198707327	-6.407894135	-5.888247967
H	-0.501578450	-8.006361961	-6.603812218
H	-1.843266010	-7.067410469	-5.923389435
C	1.921856165	-9.582017899	1.760935187
H	1.759205580	-9.213739395	2.778963327
H	2.286882401	-10.613047600	1.825238347
H	2.697364807	-8.966025352	1.300753713
C	-0.456358016	-10.423709869	1.606556654
H	-1.381691575	-10.413941383	1.026883841
H	-0.095691048	-11.455526352	1.677313089
H	-0.684099376	-10.073389053	2.618757248
C	0.877585232	-10.026824951	-0.503031433
H	1.672140002	-9.438075066	-0.973608732
H	1.188370824	-11.077320099	-0.494380713
H	-0.028838867	-9.930968285	-1.108375549
C	-5.523883343	-4.210566044	-2.794828892
H	-5.255329609	-4.578467846	-3.790510654
H	-5.710295677	-5.073664665	-2.152703762
H	-6.448625565	-3.630509853	-2.884234905
C	-4.178003311	-2.095490456	-3.115940571
H	-3.392866373	-1.450423360	-2.715375185
H	-3.879824877	-2.399069786	-4.125006199
H	-5.103045940	-1.513879180	-3.193767786
C	-4.787648201	-2.871538639	-0.782760441
H	-5.739361763	-2.329747438	-0.800966024
H	-4.888213158	-3.737871647	-0.121915959
H	-4.021772385	-2.207334757	-0.369645149
C	-2.488448381	-5.151904106	4.557926178
H	-3.082198858	-4.721830845	5.371671200
H	-2.494862795	-6.240900993	4.671315670
H	-1.457250595	-4.806579590	4.653682232
C	-4.548036098	-5.205431938	3.093639135

H	-4.988551617	-4.915452957	2.136977196
H	-4.616910458	-6.295029640	3.177447557
H	-5.141207218	-4.762240410	3.900867939
C	-3.006861925	-3.196547270	3.045567989
H	-3.545889139	-2.709227324	3.865092039
H	-1.964866042	-2.862928391	3.061420441
H	-3.458604097	-2.879172802	2.100507736

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1-TS'

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Na	-0.685461760	-4.454552650	-1.669745922
O	0.993747234	-2.073765755	-0.483916461
C	-0.109023049	-2.214985371	0.157243013
O	-1.094049215	-2.894545794	-0.226858109
C	-0.215371266	-1.461942792	1.500874877
O	2.504389763	-3.706907272	-2.431712627
O	1.090630651	-5.466515541	-2.408451080
C	2.239626884	-4.963467598	-2.411391258
C	3.494450808	-5.863505363	-2.379032850
C	4.367032528	-5.536066532	-3.608415604
H	4.632824421	-4.476636410	-3.624122143
H	5.285817623	-6.132964134	-3.584856749
H	3.837257147	-5.763285160	-4.539153099
C	3.090389013	-7.344011784	-2.395777702
H	3.986187935	-7.974575043	-2.369373322
H	2.465100288	-7.593329430	-1.534009695
H	2.522932053	-7.588168144	-3.298805475
C	4.275469780	-5.536452293	-1.088202834
H	3.672272921	-5.749830246	-0.198455125
H	5.184109211	-6.146633148	-1.034669876
H	4.557371140	-4.481186867	-1.064975619
C	1.122202277	-0.825483799	1.903246880
H	1.009474277	-0.291528851	2.853822470
H	1.900336266	-1.584742785	2.023409367
H	1.465452194	-0.119246550	1.143384457
C	-1.281747937	-0.363617808	1.292606592
H	-0.978637099	0.326313436	0.498025745
H	-2.242944717	-0.805676639	1.015980005
H	-1.412910581	0.212579012	2.215468168
C	-0.690412700	-2.449698925	2.583081245
H	-1.629166365	-2.924017429	2.286665916
H	0.055118881	-3.235322714	2.752048016
H	-0.845400214	-1.924604416	3.532313108
Pd	1.057316065	-2.276425600	-2.553556919
O	-0.337875187	-0.777912021	-2.524212122
C	1.250699997	-2.538626671	-4.699584961
C	-0.977492452	-0.414898574	-3.559751034
O	-0.754361391	-0.853846014	-4.729063034
C	-2.114220619	0.590951085	-3.328057289
C	-3.164433956	-0.127302229	-2.449497700
C	-1.541397333	1.806140661	-2.570903540
C	-2.734460592	1.029937744	-4.661303043
H	-3.972599506	0.567196190	-2.196422815
H	-3.606157064	-0.976470649	-2.983764410
H	-2.712352276	-0.498211890	-1.526407003
H	-0.776675224	2.316317320	-3.166262865
H	-2.343498945	2.522254705	-2.362826824
H	-1.090733409	1.498932481	-1.624766827
H	-3.553703547	1.731974363	-4.472428322
H	-1.994372010	1.524157405	-5.296937943
H	-3.129961014	0.174378961	-5.215094566
C	0.828552485	-3.813635111	-5.136753082
C	1.565446973	-4.596734524	-6.026563644
C	2.754819393	-4.058045864	-6.534707069
H	3.349552870	-4.639880180	-7.234726429
C	3.197289467	-2.782475710	-6.170286179
C	2.447663069	-2.054567814	-5.257184029
H	4.112844944	-2.377302885	-6.587258339
H	0.248154834	-1.668749452	-4.649370670
H	-0.109903574	-4.206285954	-4.753868580
Br	3.086730957	-0.267830163	-4.748528957
C	1.114725351	-5.994259834	-6.376005173
H	1.675562382	-6.403862000	-7.220973969
H	1.258968830	-6.662584782	-5.518166065
H	0.049948480	-6.019254684	-6.631903172

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2'

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Na	1.215825915	-4.062407017	0.551003397
O	0.282035261	-2.375021696	-0.318479121
C	-0.462645859	-1.518086433	-0.895282149
O	-0.387642890	-1.328859925	-2.149827003

C	-1.466658711	-0.678495169	-0.098333053
O	2.429639816	-4.258367062	-3.083361864
O	2.296490908	-5.020074368	-0.971643984
C	2.780053616	-5.035961628	-2.134137869
C	3.912039042	-6.019424915	-2.488213062
C	3.564652205	-6.738443375	-3.806303978
H	3.402131081	-6.013992310	-4.607002258
H	4.381139755	-7.409959316	-4.095141888
H	2.654747248	-7.339725971	-3.698969126
C	4.112982273	-7.039113045	-1.358143210
H	4.928350925	-7.725227833	-1.612825751
H	4.362307549	-6.540211201	-0.417329848
H	3.206245184	-7.629711628	-1.193171263
C	5.191051483	-5.174415112	-2.680375576
H	5.454783440	-4.646709442	-1.756354809
H	6.032371998	-5.822269917	-2.951417208
H	5.045433998	-4.431457520	-3.468533754
C	-1.486858010	-1.106389403	1.376210213
H	-2.202891350	-0.493115723	1.933695078
H	-1.786600709	-2.154877424	1.479030609
H	-0.501487732	-0.986195326	1.836579919
C	-1.039292812	0.800660551	-0.218515426
H	-0.050518651	0.962821066	0.224313974
H	-0.998677135	1.103531361	-1.267371774
H	-1.756466985	1.440974236	0.306813657
C	-2.861788034	-0.868513167	-0.729151487
H	-2.846979856	-0.588392496	-1.784702182
H	-3.189838886	-1.911678553	-0.656069040
H	-3.597180367	-0.245548025	-0.208316356
Pd	1.068191409	-2.761352777	-2.673280478
C	1.044476986	-2.362458706	-4.592051029
C	-0.169442073	-2.550108194	-5.261471272
C	-0.300637513	-2.290949106	-6.632515430
C	0.818029583	-1.820832014	-7.330407619
H	0.742001653	-1.604887009	-8.393176079
C	2.032531977	-1.614621043	-6.677931309
C	2.136146545	-1.887823343	-5.314198971
H	2.891765356	-1.232684851	-7.219494820
H	-1.035997510	-2.895247698	-4.703525543
Br	3.872600317	-1.522344351	-4.450889587
C	-1.613624096	-2.539191961	-7.338419437
H	-1.735787630	-1.876583695	-8.201146126
H	-1.674525380	-3.571129322	-7.707320213
H	-2.464210749	-2.382354021	-6.667463303

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3'

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Pd	1.032051802	-3.316265106	-3.216808796
C	0.657556057	-2.284176826	-4.875473022
C	-0.530082405	-1.938946605	-5.526763916
C	-0.521646202	-1.274049997	-6.763544083
C	0.706821620	-0.957338095	-7.356577396
H	0.728712261	-0.434643894	-8.309309959
C	1.912498116	-1.319065094	-6.750475883
C	1.839046478	-1.976863742	-5.533612728
H	2.867990732	-1.095893621	-7.212889194
H	-1.483074427	-2.204333305	-5.083070278
Br	3.509156942	-2.628292561	-4.635448456
C	-1.822831154	-0.942293704	-7.457869053
H	-1.719522119	-0.068000466	-8.107852936
H	-2.156582594	-1.778648973	-8.084429741
H	-2.620796680	-0.737190068	-6.737552166
C	-1.794937253	-2.278213263	-2.440153837
C	-0.728529692	-3.171974897	-2.302960396
C	-0.812888384	-4.084423065	-1.262353778
C	-2.911332846	-2.333050728	-1.590439916
H	-1.757300377	-1.510123372	-3.204596281
C	-2.950777054	-3.302846670	-0.580212474
C	-4.034004688	-1.332216382	-1.740916252
H	-3.811984539	-3.361221552	0.080068156
C	-1.887277007	-4.189678192	-0.394116908
H	-1.899993181	-4.931071281	0.397547126
Br	0.804124713	-5.245878220	-1.016566515
H	-4.999175072	-1.767267346	-1.462994695
H	-3.870335340	-0.460725635	-1.094981790
H	-4.110220909	-0.966254354	-2.769257545

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3'-TS

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Pd	1.038381934	-3.071933985	-2.753007174
C	0.682158411	-2.095836401	-4.553121090
C	-0.325006723	-2.485636473	-5.463038921

C	-0.205157682	-2.341686249	-6.846549988
C	0.971352041	-1.785525918	-7.361164093
H	1.086077332	-1.643521786	-8.432765961
C	2.007147551	-1.415460348	-6.506916523
C	1.856651783	-1.572207451	-5.132673740
H	2.931483269	-1.013674021	-6.907742977
H	-1.249038100	-2.885226727	-5.065967083
Br	3.459533930	-1.091417074	-4.053408146
C	-1.318668485	-2.778017998	-7.769665718
H	-1.479139805	-2.047548056	-8.569869995
H	-1.080033422	-3.735605001	-8.248469353
H	-2.261924505	-2.903270483	-7.230966568
C	0.332343161	-0.066552088	-2.724683762
C	-0.147950590	-1.375051022	-2.948565960
C	-1.493998170	-1.597179413	-2.590973139
C	-0.456699640	0.964419723	-2.211397648
H	1.357119799	0.156432211	-2.992177248
C	-1.794409156	0.691813290	-1.903767824
C	0.123767361	2.341222525	-1.987624764
H	-2.439218283	1.478277922	-1.520401001
C	-2.308027029	-0.591136098	-2.079562187
H	-3.336168528	-0.811144650	-1.813286543
Br	-2.340522766	-3.396551609	-2.686069489
H	-0.586702466	3.123765945	-2.274229765
H	0.368754953	2.497005463	-0.929757297
H	1.041438818	2.488514185	-2.563904047

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A1

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Pd	-3.862118244	-0.361262262	-1.603365779
O	-5.085346222	-1.119763017	-3.110930443
C	-5.751012802	-0.275833279	-3.837254524
O	-5.719922066	0.961141527	-3.720762014
O	-2.112330675	-1.436140776	-3.920036316
C	-2.068807840	-0.193880990	-3.899198771
O	-2.686978579	0.568693161	-3.051150322
O	-5.017482758	-1.264911413	-0.200398609
O	-4.375929356	-3.288316488	-0.990132511
C	-5.019832611	-2.555066109	-0.208886936
Na	-3.590455294	-2.841134548	-2.999869347
C	-2.695052862	1.665659666	0.018071996
O	-2.675858736	0.384192526	-0.135661095
O	-3.349416018	2.481029034	-0.666854620
Na	-4.212219238	2.243923426	-2.680686712
C	-6.586771488	-0.924105644	-4.928319931
H	-5.926695824	-1.193624854	-5.761064529
H	-7.058983326	-1.839007258	-4.562739849
H	-7.340967178	-0.225471005	-5.292440414
C	-5.934933186	-3.185623169	0.826909781
H	-6.878512859	-3.452215433	0.337857902
H	-5.481119633	-4.103634834	1.206260085
H	-6.147852898	-2.494976282	1.643750548
C	-1.852372408	2.163742304	1.180095196
H	-2.497696161	2.249433994	2.061248541
H	-1.045295000	1.466969728	1.411340952
H	-1.455504298	3.154839993	0.951285541
C	-1.198519111	0.555202544	-4.894228935
H	-0.224950016	0.743869722	-4.428787231
H	-1.042474151	-0.050760251	-5.788055897
H	-1.637088656	1.520227194	-5.158844948

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A1-TS

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O	-5.768948078	-1.727808714	-0.952302396
O	-6.665698051	-2.050709486	-2.980244160
C	-5.708652020	-2.155482292	-2.204972506
C	-4.316224575	-2.621697187	-2.568920612
H	-4.255774975	-2.819129229	-3.642585754
H	-4.037444592	-3.509091377	-1.995746374
O	-2.021629572	-0.163857192	-1.417528749
Pd	-3.899249315	-0.899312079	-1.083025455
C	-1.445076704	-0.643379569	-2.452761412
O	-1.957048416	-1.504572511	-3.222936869
H	-3.196732283	-1.889265776	-2.715578556
O	-6.057874680	1.307443857	-0.583740652
C	-5.144430161	1.335208297	0.270126730
O	-4.131175518	0.543688178	0.337421507
Na	-7.282414913	-0.174352825	-1.599679708
C	-0.049842052	-0.144758746	-2.751848221
H	0.654114187	-0.969921350	-2.606056929
H	0.007340371	0.155417576	-3.801072359
H	0.217218101	0.686323762	-2.099817276
C	-5.162680626	2.411048889	1.344730496

H	-6.177212715	2.516616821	1.737059236
H	-4.461618900	2.186336994	2.148768663
H	-4.883583069	3.363931417	0.882697165

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A2

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Pd	-3.864088058	-0.080041923	-1.313447595
O	-5.345175743	-1.207261324	-0.297165960
O	-6.447282314	-2.869834185	-1.329396367
C	-4.719964981	-1.498455882	-2.481938362
C	-5.601150990	-1.955828667	-1.354121685
C	-2.118105412	1.744378090	-1.515392184
O	-2.651034355	1.659844398	-0.376956493
O	-2.461491108	0.938661158	-2.461111069
Na	-6.826199055	-2.360850096	0.826229453
H	-5.277946949	-1.085758090	-3.326868534
H	-4.012532234	-2.264109135	-2.812367201
C	-1.077866077	2.793693781	-1.829217672
H	-0.771581650	3.307566881	-0.917120099
H	-0.214814380	2.328246832	-2.313049555
H	-1.499444127	3.518347740	-2.533637524

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A2-TS

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Pd	-4.069510937	-0.309938461	-2.060966969
O	-5.930899620	-1.702050447	-0.168794870
O	-3.937350750	-2.793586731	-0.567480206
C	-5.191257954	-1.647816777	-2.824752569
C	-4.944934845	-2.097724438	-0.785646141
C	-2.484793186	1.680746078	-1.420829296
O	-2.773258448	0.846995652	-0.485341996
O	-2.950899839	1.529833198	-2.582845926
Na	-3.381477594	-0.849060476	0.779605329
H	-6.262014866	-1.490109444	-2.990827084
H	-4.804818153	-2.483920097	-3.417804718
C	-1.580757976	2.846701860	-1.107160449
H	-2.037375927	3.455871582	-0.320962518
H	-0.627073467	2.472779751	-0.722327828
H	-1.410629392	3.455521107	-1.995282531

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A3

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Pd	-3.837996483	-0.763367712	-2.245823383
O	-4.465780258	-3.449552298	-1.207267046
O	-2.604298115	-2.395498991	-0.390194923
C	-3.627235413	-2.596615314	-1.072329283
C	-4.780114651	-1.725750327	-3.549410343
H	-5.008679867	-1.331325889	-4.550501347
H	-5.221148968	-2.715434313	-3.383922338
C	-3.178557396	1.841348648	-1.381105065
O	-2.972338200	0.688309669	-0.786446333
O	-3.732786655	1.934164524	-2.475444555
Na	-1.967011333	-0.594233990	0.561660945
C	-2.677921772	3.063371181	-0.629050910
H	-3.102762222	3.082259417	0.379704505
H	-1.587648511	3.013485193	-0.530595541
H	-2.949872971	3.975072145	-1.161438227

Vibrational Frequencies (in cm^{-1}) of the Optimized Geometries

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PivOH

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44.81 218.17 243.69 263.05 288.02 296.10
357.46 367.77 385.89 516.37 575.91 608.72
729.93 786.18 870.63 951.45 960.54 984.03
1056.55 1062.73 1157.62 1239.88 1252.98 1281.05
1366.12 1414.44 1422.72 1451.56 1492.34 1499.92
1505.83 1515.11 1520.06 1539.92 1837.99 3043.59
3045.30 3053.40 3113.56 3115.05 3126.98 3135.13
3136.72 3139.41 3755.87

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AcOH

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89.36 422.86 540.77 583.88 677.48 867.12
1003.63 1069.92 1218.70 1354.98 1422.22 1482.92
1488.41 1858.31 3065.68 3132.05 3185.45 3755.9

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Acetonitrile

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386.53 386.70 932.39 1061.26 1061.26 1420.16
1482.72 1483.05 2378.66 3058.51 3135.64 3136.11

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NaOPiv

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46.11 75.50 182.42 230.24 258.56 278.20
294.70 296.61 324.65 385.94 392.69 419.99
532.90 614.24 796.43 814.18 904.37 949.58
955.65 976.73 1058.73 1060.29 1240.35 1254.36
1267.37 1403.06 1404.57 1418.79 1456.05 1489.95
1497.34 1505.44 1512.49 1516.35 1540.57 1600.50
3031.13 3033.02 3041.21 3095.92 3098.25 3113.13
3131.33 3133.12 3136.96

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NaOAc

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37.15 106.43 255.45 344.71 463.89 610.01
680.12 935.14 1030.02 1063.80 1375.00 1447.45
1476.10 1495.35 1622.42 3052.64 3125.10 3161.12

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CO_2

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644.54 644.57 1368.70 2432.48

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4-Bromotoluene

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27.66 107.15 212.32 275.99 289.69 375.33
419.66 491.69 582.37 643.05 705.17 798.18
818.66 840.93 958.47 966.84 1016.08 1019.32
1066.30 1085.79 1149.25 1220.49 1235.37 1333.53
1339.80 1428.67 1437.82 1501.47 1506.64 1531.23
1629.64 1650.00 3039.12 3099.68 3123.17 3177.71
3180.32 3218.97 3219.74

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1

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7.87 12.52 15.14 18.96 22.90 23.28
28.07 47.30 48.10 59.79 65.08 74.08
80.28 100.96 109.31 114.62 125.48 134.34
153.45 161.22 164.35 169.45 175.48 184.57
203.45 207.28 213.29 220.69 223.45 228.64
230.07 235.26 241.82 256.02 260.19 269.34
278.28 282.37 283.06 287.29 288.64 293.17
293.88 302.05 310.93 315.86 318.76 322.47
325.52 326.48 329.65 383.75 387.91 391.93
393.68 395.52 396.47 397.75 398.83 436.52
440.79 453.99 457.67 568.88 569.59 573.49
573.98 627.54 632.10 640.36 649.57 784.93
788.09 789.31 790.15 804.11 806.00 811.88
812.29 900.46 901.46 907.32 909.35 948.21
948.94 949.93 950.53 952.58 954.89 956.32
956.62 977.52 978.74 979.91 979.96 1054.42
1055.84 1058.14 1059.02 1059.29 1060.19 1061.79
1062.58 1234.95 1238.80 1238.95 1239.89 1248.99
1250.42 1252.44 1257.56 1258.97 1262.53 1263.95
1265.45 1378.18 1381.79 1386.38 1394.56 1407.09
1407.98 1408.41 1409.39 1409.50 1415.57 1417.07
1419.10 1446.66 1447.54 1448.16 1450.74 1489.26
1489.99 1490.61 1491.35 1495.05 1497.98 1499.26
1500.50 1501.54 1503.95 1504.41 1505.32 1512.56
1513.06 1513.39 1513.91 1515.15 1515.62 1516.38
1516.73 1533.61 1537.21 1538.38 1541.15 1636.38
1643.28 1673.64 1687.08 3030.13 3033.12 3034.26
3036.30 3036.92 3037.69 3039.12 3039.50 3041.69
3045.03 3045.36 3048.26 3096.00 3100.53 3103.62
3103.95 3105.90 3106.52 3109.12 3109.92 3110.06
3111.06 3112.00 3115.70 3116.12 3118.84 3120.86
3129.27 3129.48 3133.09 3134.33 3136.21 3138.94
3141.89 3142.26 3143.93

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1-TS

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-1269.16 16.35 22.38 26.73 35.93 41.54
57.01 73.92 88.07 98.48 111.44 130.75
144.00 152.35 165.78 173.80 209.10 218.91
230.50 232.69 234.98 242.42 244.50 256.17
271.32 279.36 285.39 291.19 293.46 295.23
306.45 310.46 316.20 329.42 335.09 351.22
378.69 389.41 394.94 396.96 404.44 431.83
447.04 451.36 528.28 566.77 572.01 583.42
624.62 639.27 648.46 712.26 788.94 790.97
792.30 803.14 820.45 842.35 900.33 911.32
920.87 949.36 951.25 955.08 958.30 965.09
977.53 978.26 983.29 1028.07 1044.57 1055.89
1062.07 1062.84 1063.86 1088.09 1214.18 1234.57
1239.38 1240.37 1252.71 1255.97 1262.16 1266.29
1267.44 1343.95 1370.48 1395.82 1404.62 1406.66
1412.01 1414.13 1414.46 1422.01 1432.54 1443.23
1450.49 1464.08 1491.07 1491.42 1495.33 1498.86
1499.50 1500.22 1504.70 1505.08 1512.44 1513.75
1514.49 1516.42 1517.65 1526.27 1538.51 1540.36
1579.54 1636.13 1649.95 1686.49 3029.00 3033.36
3037.60 3041.22 3042.68 3043.03 3044.44 3047.85
3050.52 3077.92 3102.36 3106.31 3109.47 3112.14

3115.29 3117.05 3119.83 3120.80 3123.01 3133.66
3133.79 3134.96 3135.21 3135.64 3139.10 3142.84
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2
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15.32 26.30 40.60 64.26 73.52 80.28
130.85 136.14 175.37 180.19 194.06 227.64
232.18 245.09 263.01 268.38 272.50 285.43
292.97 294.90 321.42 342.86 347.41 376.99
385.23 392.56 428.45 445.40 544.84 560.01
610.79 624.25 661.98 755.75 785.56 788.61
817.93 845.77 912.21 918.57 950.45 956.02
957.07 969.74 979.10 1028.07 1059.38 1061.15
1065.29 1120.09 1209.41 1239.80 1243.42 1251.20
1254.46 1267.19 1382.83 1406.37 1406.51 1411.92
1424.92 1426.59 1462.32 1476.74 1490.22 1499.12
1499.48 1501.91 1505.03 1512.05 1512.72 1516.35
1526.22 1540.25 1593.54 1644.82 3035.27 3036.98
3037.06 3039.49 3044.17 3044.47 3102.96 3105.00
3110.71 3114.89 3116.03 3118.73 3122.83 3127.63
3131.89 3133.52 3137.35
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2-TS
==========
-263.20 17.25 25.12 42.35 63.73 81.98
98.46 141.41 142.62 144.74 161.31 200.77
223.08 232.14 238.70 250.66 267.13 267.40
285.08 287.81 290.25 300.11 320.97 343.53
353.12 378.54 391.23 398.00 427.99 439.90
540.68 589.69 606.33 633.43 728.84 745.79
785.33 809.75 815.22 912.92 950.38 953.33
956.19 980.44 1004.10 1014.45 1052.54 1052.83
1058.94 1060.88 1112.20 1235.53 1239.32 1254.74
1261.29 1264.38 1303.81 1410.26 1411.31 1412.79
1427.95 1429.81 1470.12 1485.07 1489.31 1491.09
1499.28 1499.44 1504.46 1512.11 1513.79 1514.76
1516.99 1541.56 1579.72 1691.39 3039.06 3039.15
3041.40 3044.98 3045.59 3069.19 3106.80 3107.90
3115.27 3121.13 3121.20 3124.96 3138.39 3142.26
3147.78 3155.60 3156.52
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3
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17.23 28.04 28.86 48.29 56.35 75.82
91.67 107.37 119.96 128.60 164.15 188.44
198.83 206.41 236.69 238.37 255.05 267.83
277.04 280.59 296.21 303.17 315.08 317.11
365.89 374.83 392.84 402.54 423.33 446.94
472.50 544.30 609.75 625.41 725.97 785.77
809.51 813.45 817.21 908.31 948.47 953.99
955.88 965.10 977.32 993.88 1037.77 1054.82
1060.26 1084.22 1107.21 1239.41 1249.23 1259.02
1265.69 1306.11 1394.36 1405.57 1408.82 1410.95
1423.99 1435.58 1445.65 1481.52 1488.93 1491.16
1502.70 1503.16 1505.35 1514.64 1516.76 1518.49
1540.03 1585.87 1677.77 1872.22 3020.62 3023.79
3026.06 3033.87 3038.67 3089.65 3090.11 3098.93
3100.80 3106.55 3106.62 3138.30 3139.43 3143.37
3144.35 3164.39 3242.07
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4
==========
29.04 56.81 88.48 168.31 173.69 215.58
225.76 242.10 274.50 343.38 396.49 431.97
469.11 596.03 608.32 789.92 808.35 937.72
955.48 986.12 1035.43 1077.24 1103.58 1239.30
1296.72 1411.20 1424.08 1437.36 1480.88 1496.13
1498.60 1515.10 1582.33 2108.09 3021.07 3025.95
3093.08 3098.46 3125.06 3131.13 3147.43 3215.84
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4-TS
==========
-31.46 2.77 70.99 80.33 180.28 190.36
207.16 226.74 252.26 356.07 393.14 427.37
467.44 540.46 604.49 776.03 804.81 926.39
953.64 982.14 1036.35 1072.11 1102.83 1286.36
1313.43 1407.31 1420.47 1434.48 1483.71 1498.64
1499.85 1515.25 1574.08 2365.28 3010.54 3015.31
3081.51 3084.56 3125.41 3127.77 3130.66 3210.83
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5
==========
28.38 37.60 41.01 85.01 134.43 169.90
190.42 228.31 239.60 250.24 341.00 364.41
366.98 391.57 428.71 462.66 767.11 807.85
902.65 951.54 955.75 981.88 1036.79 1053.62
1054.96 1075.27 1102.45 1287.59 1411.33 1417.14
1418.70 1433.77 1476.81 1479.12 1482.58 1497.63
1498.32 1514.30 1587.36 2364.07 3003.07 3007.82
3053.44 3080.91 3083.58 3123.47 3129.38 3131.07
3131.35 3133.37 3207.81
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1a

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12.78 22.32 28.98 46.06 81.49 152.86
154.56 182.90 185.31 212.99 214.14 216.52
245.21 259.50 268.62 271.62 275.04 277.55
289.49 320.78 343.97 376.09 379.20 391.56
418.88 456.82 471.86 540.47 559.68 616.78
624.59 778.28 781.36 812.61 815.18 915.31
920.29 944.68 945.02 953.77 953.87 975.74
975.75 1052.81 1052.95 1053.49 1053.72 1231.97
1232.30 1250.10 1250.70 1259.53 1262.36 1407.86
1407.88 1411.45 1411.79 1435.27 1435.97 1484.92
1490.03 1490.06 1490.29 1493.21 1497.57 1503.03
1503.06 1504.69 1507.96 1511.69 1511.94 1515.28
1515.33 1544.08 1546.51 3046.83 3047.00 3048.58
3048.62 3055.11 3055.25 3117.43 3117.72 3118.64
3118.93 3126.55 3126.87 3136.23 3136.34 3137.50
3137.56 3141.16 3141.34

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1b

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10.69 16.64 20.34 21.73 28.74 33.25
40.29 54.58 64.97 86.78 96.29 113.86
117.48 140.39 146.95 155.12 158.06 163.43
169.81 173.96 190.47 218.16 222.65 229.84
231.80 236.73 239.87 247.77 248.69 250.24
254.02 256.73 273.85 288.35 288.98 291.45
292.30 294.89 298.78 298.98 308.55 319.62
323.03 323.68 328.07 329.90 332.16 336.60
392.87 397.48 398.69 399.28 431.03 431.60
437.98 439.09 443.64 458.59 467.64 468.26
603.09 615.92 616.43 618.59 635.20 636.77
637.32 647.23 774.31 781.98 782.28 785.29
801.97 802.54 812.22 814.75 902.37 902.81
908.08 914.43 949.26 949.90 950.20 950.30
957.92 958.68 958.85 959.99 982.73 983.43
984.00 985.00 1058.88 1060.17 1060.55 1060.63
1062.89 1063.55 1063.89 1064.68 1236.49 1238.43
1238.85 1238.96 1248.64 1250.33 1251.39 1256.97
1264.14 1265.33 1266.00 1268.23 1389.35 1395.09
1395.60 1400.77 1410.51 1411.07 1411.61 1412.11
1419.15 1419.83 1420.05 1421.10 1453.22 1454.46
1454.75 1456.73 1490.00 1490.41 1491.13 1491.50
1496.88 1497.48 1498.51 1499.67 1501.26 1503.45
1504.95 1506.06 1513.55 1513.87 1514.13 1514.84
1515.03 1515.76 1517.00 1517.57 1527.35 1528.30
1537.20 1539.39 1539.65 1540.77 1543.95 1656.77
3039.49 3039.73 3040.26 3041.02 3042.22 3042.32
3042.52 3043.65 3050.23 3050.25 3050.39 3050.65
3107.20 3108.28 3108.61 3109.99 3110.07 3110.43
3110.70 3112.72 3121.31 3122.92 3123.07 3123.27
3133.89 3136.22 3136.33 3136.50 3137.77 3138.37
3139.63 3140.47 3143.27 3143.78 3144.55 3145.25

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22.95 25.79 27.86 31.83 32.26 34.04
38.07 40.64 41.97 44.21 51.26 55.49
59.15 60.18 62.69 63.14 74.08 91.93
98.95 106.96 107.04 116.25 129.30 129.97
133.28 133.65 136.35 151.36 151.56 166.68
168.87 175.30 184.06 184.44 192.98 193.35
211.71 212.23 213.14 225.63 226.20 231.19
231.57 232.30 234.78 241.43 246.66 247.40
250.52 250.61 267.18 267.92 268.15 279.61
281.31 281.56 282.46 283.20 284.21 285.58
287.48 300.84 301.67 303.76 304.36 309.30
309.56 310.17 315.42 330.07 330.59 332.40
333.01 334.99 336.02 394.51 394.77 395.48
396.83 397.33 397.57 429.65 432.22 433.04
433.58 434.35 434.66 455.93 456.31 460.15
469.11 469.24 476.60 604.64 613.65 613.92
620.50 622.49 622.61 634.95 635.10 640.18
644.25 644.34 645.06 779.07 779.17 781.67
783.24 783.38 784.96 805.34 807.09 807.27
810.89 811.05 811.93 908.04 909.47 909.78
913.06 913.49 917.22 949.68 949.91 949.96
950.07 950.41 950.84 959.47 959.62 959.97
960.21 961.55 961.82 985.00 985.04 985.29
985.89 987.03 987.68 1056.92 1057.07 1057.16
1057.26 1057.67 1057.97 1064.99 1065.10 1065.19
1065.33 1066.37 1066.57 1233.68 1233.88 1233.96
1234.27 1234.68 1235.20 1255.97 1256.22 1257.03
1257.16 1259.52 1264.99 1265.27 1265.40 1265.63
1266.21 1269.25 1270.43 1402.58 1402.72 1403.72
1404.98 1405.18 1405.23 1415.49 1415.67 1416.02
1416.56 1416.93 1416.94 1419.00 1419.21 1420.01
1420.21 1420.91 1422.73 1456.32 1456.54 1457.03
1457.88 1458.10 1459.18 1489.42 1489.48 1489.53
1489.64 1490.49 1490.63 1499.58 1499.82 1499.86
1500.05 1500.30 1500.40 1503.00 1503.22 1503.43
1503.55 1504.22 1504.67 1512.87 1512.91 1513.87

1513.87 1514.21 1514.25 1515.79 1516.00 1516.04
1516.27 1517.31 1517.85 1539.16 1539.54 1539.79
1539.90 1540.04 1540.24 1554.56 1569.33 1570.01
1579.07 1664.52 1665.17 3039.12 3040.74 3041.69
3041.74 3041.83 3042.80 3043.40 3044.01 3044.03
3044.06 3044.11 3044.35 3049.17 3049.55 3049.74
3049.86 3050.05 3050.58 3110.89 3111.03 3111.05
3111.12 3111.18 3111.50 3113.02 3114.94 3115.48
3115.57 3115.81 3116.30 3117.14 3118.21 3118.99
3119.19 3119.52 3121.14 3127.75 3129.42 3129.72
3129.91 3130.22 3131.31 3140.85 3140.96 3141.16
3141.81 3142.66 3143.62 3145.77 3146.50 3146.53
3146.89 3147.61 3147.75

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-1056.40 8.38 16.86 18.68 20.56 27.63
38.57 41.92 50.79 57.83 63.63 64.44
68.45 80.57 91.94 98.02 101.47 104.03
110.38 119.06 129.08 144.16 155.94 180.26
185.66 203.59 210.79 228.20 231.45 235.04
245.43 247.58 261.38 267.07 276.63 278.43
284.02 287.12 290.62 293.69 294.35 303.67
307.14 312.77 321.64 323.75 325.89 332.00
389.84 391.08 393.09 396.07 398.04 412.27
413.46 436.91 443.82 450.85 470.82 535.61
569.17 575.85 585.22 599.97 620.71 638.21
644.59 674.48 734.46 784.65 787.83 791.91
806.13 806.59 811.69 831.02 840.21 898.51
900.10 903.59 910.34 949.62 949.78 950.02
956.77 956.92 959.66 970.86 979.45 980.55
983.88 1015.25 1022.24 1056.02 1060.42 1060.86
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1225.44 1236.00 1238.47 1239.74 1240.53 1251.62
1253.19 1255.90 1264.31 1267.40 1269.43 1306.68
1337.33 1357.53 1392.64 1396.53 1406.01 1410.96
1412.53 1412.95 1414.32 1416.57 1418.02 1426.81
1437.65 1450.03 1452.58 1473.98 1483.80 1489.44
1490.37 1491.29 1495.78 1496.86 1498.11 1500.17
1503.10 1504.01 1505.17 1506.58 1513.05 1513.24
1514.26 1515.00 1517.13 1517.69 1536.92 1537.56
1542.17 1606.04 1619.04 1626.54 1644.93 1668.56
3035.92 3036.20 3037.19 3038.64 3038.82 3040.64
3044.72 3045.93 3046.80 3050.89 3096.45 3101.85
3103.66 3105.92 3110.56 3110.64 3113.08 3116.88
3117.08 3123.28 3124.00 3127.83 3128.68 3135.18
3135.72 3137.41 3139.30 3143.21 3143.67 3147.67
3173.23 3179.25 3214.42

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13.48 17.02 18.98 21.79 28.37 32.16
47.01 60.66 64.09 76.12 81.43 89.37
95.76 122.84 137.26 142.77 157.42 171.40
202.74 211.40 231.08 235.10 247.25 263.60
268.39 275.10 281.36 288.51 292.72 295.43
302.33 305.04 314.60 325.52 330.97 376.95
390.75 392.50 397.78 410.34 433.80 443.27
457.14 549.02 553.36 573.57 583.10 623.62
638.78 679.69 701.72 784.63 786.64 808.96
814.61 817.37 849.25 880.13 911.34 921.48
949.38 950.25 950.65 956.96 957.45 980.74
980.80 1006.55 1023.02 1058.28 1059.06 1061.67
1062.84 1063.79 1118.90 1174.25 1234.44 1239.12
1239.20 1256.39 1258.42 1264.90 1266.51 1285.79
1319.81 1408.82 1409.81 1410.49 1411.41 1411.55
1423.44 1426.17 1431.44 1462.24 1480.16 1485.93
1491.30 1491.46 1498.86 1499.68 1502.34 1503.41
1504.43 1505.06 1514.26 1514.52 1517.29 1517.36
1541.17 1543.57 1584.93 1601.12 1626.11 1653.06
3032.14 3033.67 3037.31 3037.38 3039.29 3044.12
3044.70 3092.66 3099.95 3102.55 3104.46 3108.47
3111.34 3113.30 3119.04 3119.19 3123.36 3137.35
3140.76 3145.04 3145.93 3176.58 3178.38 3207.10

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3'

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18.16 32.00 45.17 47.65 49.52 85.33
88.05 95.87 103.01 142.95 173.61 178.40
207.07 259.61 268.25 287.09 289.14 303.26
306.11 400.12 410.74 435.11 455.74 528.96
538.44 571.39 573.89 673.46 679.77 696.55
701.12 810.34 810.76 826.43 834.26 893.13
921.75 948.67 950.54 988.48 994.50 1022.34
1024.19 1063.83 1064.48 1099.68 1107.76 1166.45
1167.74 1230.22 1233.84 1281.31 1295.33 1333.55
1335.77 1412.71 1417.72 1426.69 1427.24 1473.14
1478.08 1502.21 1502.90 1503.58 1504.48 1607.07
1608.40 1621.25 1624.07 3037.33 3037.63 3098.45
3098.72 3123.33 3123.43 3182.14 3183.50 3206.03
3212.03 3214.04 3214.57

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3'-TS

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-331.40 34.74 45.64 48.83 60.85 64.85
86.99 91.05 102.80 113.12 119.37 177.30
182.17 243.37 275.85 278.40 280.12 309.34
309.62 391.46 401.89 435.83 457.77 503.68
543.27 572.39 577.61 650.07 660.97 689.64
697.90 806.24 817.97 818.57 825.88 892.08
901.49 954.00 954.60 995.88 1006.83 1021.67
1022.77 1065.52 1065.71 1073.56 1085.42 1172.64
1176.35 1235.99 1236.64 1287.52 1300.26 1307.03
1319.17 1405.47 1408.18 1428.13 1428.31 1477.96
1479.55 1500.10 1500.50 1504.06 1504.87 1594.98
1600.27 1624.16 1625.20 3037.50 3037.77 3096.55
3097.00 3126.55 3127.22 3180.60 3182.33 3211.87
3212.38 3229.76 3231.13

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A1

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25.07 31.95 36.79 41.46 44.32 47.25
59.96 65.94 75.20 80.65 88.72 94.50
99.74 121.27 131.86 140.21 158.85 164.83
183.73 206.29 212.04 222.44 235.57 246.35
248.76 266.87 270.43 273.81 277.39 350.05
350.21 516.99 519.31 528.93 531.58 605.91
612.43 614.85 615.58 681.01 682.08 692.33
702.50 939.46 940.71 948.52 948.72 1037.71
1038.75 1039.05 1039.49 1062.91 1064.00 1064.78
1065.89 1368.06 1371.67 1374.14 1381.88 1416.47
1416.84 1417.17 1428.04 1477.74 1478.43 1480.66
1482.01 1493.65 1493.87 1494.39 1494.74 1652.00
1658.50 1692.43 1707.14 3053.20 3057.69 3058.18
3059.05 3126.78 3129.72 3131.97 3133.09 3163.19
3167.55 3168.55 3169.48

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A1-TS

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-1113.61 35.62 36.92 43.52 58.68 68.36
83.93 97.48 129.03 137.13 165.76 173.10
200.51 213.60 234.77 251.45 286.60 307.93
331.86 385.40 411.11 482.64 519.25 552.71
611.65 616.76 651.05 679.00 687.73 712.26
740.34 925.25 942.73 957.44 1040.21 1041.60
1046.37 1057.60 1063.20 1070.10 1270.53 1322.17
1378.41 1392.17 1414.62 1436.39 1444.42 1483.09
1484.66 1492.32 1493.49 1559.79 1656.82 1670.20
1713.09 3060.26 3067.03 3084.01 3131.40 3137.96
3159.05 3171.97 3180.41

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A2

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27.06 46.61 67.25 76.57 95.10 155.38
159.22 182.51 265.56 287.79 326.75 380.52
435.94 487.93 549.02 600.46 605.76 689.72
712.52 737.24 929.52 948.60 1022.34 1050.52
1065.29 1087.94 1322.68 1380.45 1423.01 1466.30
1477.04 1488.25 1617.37 1676.90 3058.72 3079.80
3128.38 3147.57 3166.31

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A2-TS

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-216.04 28.54 57.46 61.96 81.64 105.53
120.86 135.47 169.33 185.54 209.34 220.00
281.64 286.93 461.09 482.20 565.37 604.57
655.46 657.32 682.34 714.59 948.65 972.92
1030.50 1067.30 1215.81 1385.39 1414.96 1470.08
1476.78 1488.17 1611.11 1813.78 3060.42 3062.29
3127.97 3157.64 3172.95

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A3

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21.26 43.10 56.93 59.95 71.29 104.34
118.12 123.07 181.40 205.90 230.31 253.19
292.47 299.36 323.00 466.14 599.02 609.96
658.67 670.78 694.86 748.49 929.10 945.53
1026.48 1062.46 1265.18 1347.86 1406.53 1422.04
1479.16 1494.64 1732.62 1933.87 3033.02 3047.85
3112.88 3146.57 3167.87

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12 LACV3P**: a triple-zeta contraction of the LACVP basis set developed by Schrodinger Inc. The main group elements (H-Ar) are calculated employing 6-311G**

13 Approximate dielectric environment offered by acetonitrile (MeCN) solvent.