

Supporting Information

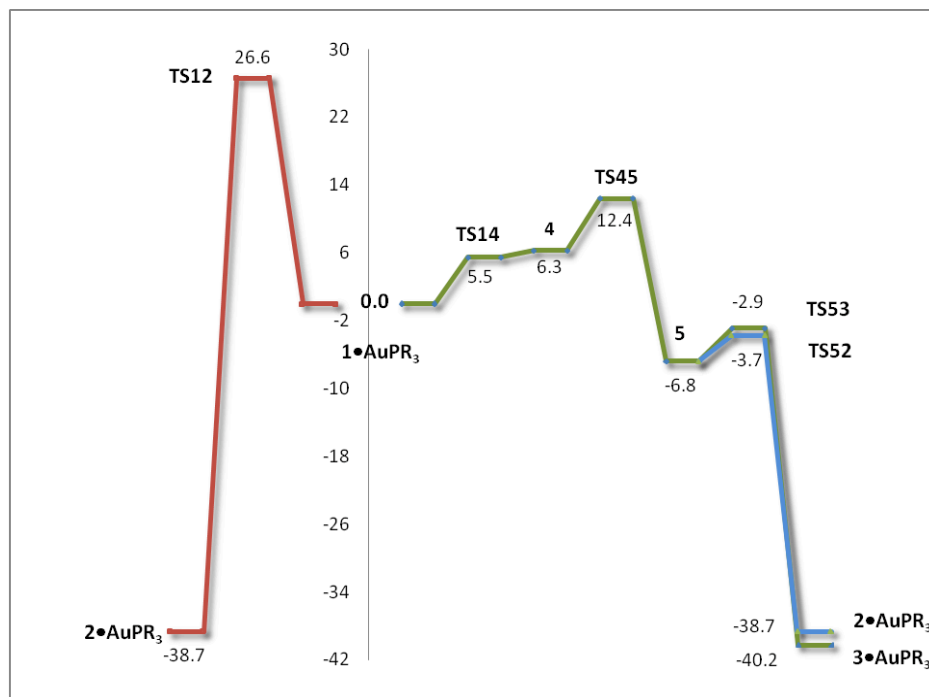
On the Impact of Steric and Electronic Properties of Ligands on Gold(I)-Catalyzed Cycloaddition Reactions

Diego Benitez,[‡] Ekaterina Tkatchouk,[‡] Ann Z. Gonzalez,[†]
William A. Goddard III^{‡,*} and F. Dean Toste,^{†,*}

*Materials and Process Simulation Center, California Institute of Technology, Pasadena, CA 91125 and
Department of Chemistry, University of California, Berkeley, CA 94720*

Contents	Page
1. Potential energy surface for P(Me) ₃	2
2. Reaction free energies (ΔG) at 298 K	2
3. Natural charges for TS52 (top) and TS53 (bottom)	2
4. Electronic energies, solvation and thermodynamic corrections	
AuP(Me) ₃ AuP(Ph) ₃ AuP(OPh) ₃	3
AuP(<i>t</i> Bu) ₂ (<i>o</i> -biPh)	4
5. Methods	4
6. XYZ coordinates	
AuP(Me) ₃	5
AuP(Ph) ₃	8
AuP(OPh) ₃	12
AuP(<i>t</i> Bu) ₂ (<i>o</i> -biPh)	16
7. Experimental	20

1. Potential energy surface for P(Me)₃ ligand with B3LYP and M06.

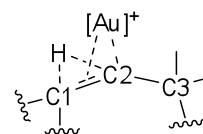
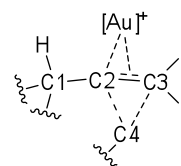


2. Reaction free energies (ΔG) at 298 K

	PMe ₃	P(OPh) ₃	PPh ₃	P(<i>t</i> Bu) ₂ (<i>o</i> -biPh)
TS45	12.4	4.5	11.7	15.1
5	-6.8	-10.7	-9.8	10.1
TS52	-3.7	-4.7	-4.1	-4.0
TS53	-2.8	-3.8	-3.8	-7.5
2•AuPR₃	-38.7	-39.2	-36.2	-34.9
3•AuPR₃	-40.2	-41.2	-38.6	-38.5
TS12	26.6	23.0	25.4	~16
Pred. 2:3	81:19	81:19	63:37	1:99
Exp. 2:3	NA	100:0	67:33	4:96

3. Natural charges for **TS52** (top) and **TS53** (bottom).

Ligand	H	C1	C2	C3	C4
P(OPh) ₃	0.22	-0.30	-0.06	-0.03	-0.42
PPh ₃	0.21	-0.28	-0.23	0.17	-0.37
P(<i>t</i> Bu) ₂ (<i>o</i> -biPh)	0.22	-0.31	-0.02	-0.08	-0.46
P(OPh) ₃	0.35	0.05	-0.27	-0.10	-0.44
PPh ₃	0.35	0.05	-0.26	-0.10	-0.44
P(<i>t</i> Bu) ₂ (<i>o</i> -biPh)	0.37	0.02	-0.29	-0.10	-0.44



4. Electronic energies, solvation and thermodynamic corrections

Au Ligand P(Me) ₃	Single Point Gas Phase M06 LACV3P**++(2f)	LACVP** CH ₃ Cl ₂	LACVP** gas phase Optimization M06			G(kcal/mol)
	E _{SCF}	V _{solv}	H _{vib}	ZPE	S _{vib}	
1·AuP(Me) ₃	-1519.73495	-41.18830	19.62900	292.80700	128.17638	-953411.66294
TS14	-1519.72316	-41.14450	19.25800	292.10300	131.20797	-953406.19918
4	-1519.72865	-38.72310	19.16600	293.37600	128.98822	-953405.38350
TS45	-1519.72367	-37.40500	18.37900	293.77600	122.01968	-953399.25197
5	-1519.75950	-38.50590	17.51100	296.92600	115.06144	-953418.48045
TS12	-1519.699958	-38.1073	18.358	293.692	121.5047494	-953385.02482
2·AuP(Me) ₃	-1519.81065	-38.32280	17.64200	297.33300	116.62973	-953450.32294
TS52	-1519.75331	-37.82220	17.55500	295.63200	115.87295	-953415.40548
3·AuP(Me) ₃	-1519.81355	-37.96630	17.57300	297.04900	115.72941	-953451.87178
TS53	-1519.74764	-39.47090	17.42300	294.32800	114.56164	-953414.54226

Au Ligand P(Ph) ₃	Single Point Gas Phase M06 LACV3P**++(2f)	LACVP** CH ₃ Cl ₂	LACVP** gas phase Optimization M06			G(kcal/mol)
	E _{SCF}	V _{solv}	H _{vib}	ZPE	S _{vib}	
1·Au P(Ph) ₃	-2094.63072	-36.20330	25.50300	393.87800	174.73417	-1314066.22569
4	-2094.62241	-35.22640	25.23500	394.09400	183.59200	-1314062.72289
TS45	-2094.61565	-36.74340	24.29300	394.84100	164.39102	-1314054.47500
5	-2094.65737	-35.56400	22.94800	397.78500	158.18833	-1314076.02894
TS12	-2094.59564	-35.19370	24.34700	394.41700	164.51026	-1314040.77285
2·Au P(Ph) ₃	-2094.69969	-36.02340	23.66700	398.15600	159.70024	-1314102.40096
TS52	-2094.64383	-37.55970	23.50200	396.72100	158.25538	-1314070.05561
3·Au P(Ph) ₃	-2094.70356	-35.54800	22.94600	398.00900	158.23801	-1314104.78885
TS53	-2094.64037	-37.97210	22.83900	395.12400	157.60378	-1314070.36298

Au Ligand P(OPh) ₃	Single Point Gas Phase M06 LACV3P**++(2f)	LACVP** CH ₃ Cl ₂	LACVP** gas phase Optimization M06			G(kcal/mol)
	E _{SCF}	V _{solv}	H _{vib}	ZPE	S _{vib}	
1·Au P(OPh) ₃	-2320.30462	-37.86810	25.55600	401.59300	182.61400	-1455675.01159
4	-2320.30721	-36.80340	26.40600	401.95700	192.83800	-1455677.40163
TS45	-2320.29636	-38.95260	25.57500	402.38300	184.13000	-1455670.55186
5	-2320.33063	-36.99960	24.74100	405.38900	176.90800	-1455685.78048
TS12	-2320.27163	-35.62540	25.59700	402.08100	184.08600	-1455651.97642
2·Au P(OPh) ₃	-2320.37470	-37.55610	24.94600	405.80800	179.59000	-1455714.16815
TS52	-2320.32157	-35.28910	24.66900	402.76300	169.45474	-1455678.86266
3·Au P(OPh) ₃	-2320.37811	-36.88530	25.21200	405.79100	182.49800	-1455716.25332
TS53	-2320.31994	-37.94710	24.86100	404.09500	171.95096	-1455679.71366

Au Ligand P(<i>t</i> Bu) ₂ (<i>o</i> -biPh)	Single Point Gas Phase M06 LACV3P++*(2f)	LACVP** CH ₂ Cl ₂	LACVP** gas phase Optimization M06			G(kcal/mol)
	E _{SCF}	V _{solv}	H _{vib}	ZPE	S _{vib}	
1·Au(<i>t</i> Bu) ₂ (<i>o</i> -biPh)	-2178.0515	-33.89	29.38	484.49	205.32	-1366325.90042
4	-2178.0422	-35.05	29.13	484.44	202.68	-1366320.73092
TS45	-2178.034098	-35.52	27.29	485.70	183.01	-1366310.82569
5	-2178.07685	-34.73860	27.47100	488.13900	188.81300	-1366335.97573
TS12	-2178.0294	-35.68	27.39	487.41	190.95	-1366308.61375
2·Au(<i>t</i> Bu) ₂ (<i>o</i> -biPh)	-2178.11737	-35.41650	27.48000	488.83400	186.83400	-1366360.78449
TS52	-2178.066869	-35.3678	26.817	487.284	182.323	-1366329.91558
3·Au(<i>t</i> Bu) ₂ (<i>o</i> -biPh)	-2178.12450	-34.51720	27.40900	488.57000	185.69500	-1366364.35464
TS53	-2178.06866	-35.39160	27.20200	485.52700	185.57700	-1366333.40244

5. Methods

Calculations were performed using density functional theory (DFT) with the M06 functional, as implemented in Jaguar 7.6.¹ All calculations used the Hay and Wadt small core-valence relativistic effective-core-potential² (ECP). The LACVP** basis set was used for all geometry optimizations and LACV3P++*(2f) for energies. LACV3P++*(2f) utilizes the LACV3P++* basis set as implemented in Jaguar plus a double-zeta f-shell with exponents from Martin and Sundermann.³ All electrons were described for all other atoms using the 6-31G** or 6-311++G** basis sets.^{4,5} For each optimized structure, the M06 analytic Hessian was calculated to obtain the vibrational frequencies, which in turn were used to obtain the zero point energies and free energy corrections (without translational or rotational components). Solvent corrections were based on single point self-consistent Poisson-Boltzmann continuum solvation calculations for CH₂Cl₂ ($\epsilon = 8.93$ and $R_0 = 2.33$ Å using the PBF⁶ module in Jaguar.

1. Jaguar 7.6, Schrodinger, LLC, New York, NY (2006).
2. Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299–310.
3. Martin, J. M. L.; Sundermann, A. *J. Chem. Phys.* **2001**, *114*, 3408–3420.
4. Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650–654.
5. Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265–3269.
6. Tannor, D. J. *et al. J. Am. Chem. Soc.* **1994**, *116*, 11875–11882.

TS52

C1	0.0084903770	-0.2669885806	0.0207815568
C2	-0.0113623290	0.0273742659	1.3971384188
C10	1.3113137120	-0.3036703232	-0.7170891675
C14	-1.1586220128	-0.8233767623	-0.7437861079
C5	-1.2336979518	-0.2505366331	2.2350723182
Au29	1.7503974911	0.2566687328	2.5846192137
C4	-1.6894445342	1.0154746481	2.9804815166
C6	-1.0593998390	-1.3148660362	3.3376276110
P30	3.4932226539	0.3652632263	4.1871770996
C18	-2.6082536498	0.4519434720	4.0521296370
C23	-2.2521205598	1.9706851747	1.9860456903
C19	-1.8183961915	-0.7624843504	4.5752453473
C31	3.1852907933	1.6179849683	5.4759533255
C35	5.1939087844	0.6889671439	3.6120413667
C39	3.5991266371	-1.2005926587	5.1146682455
C24	-1.6558025256	2.1442915521	0.8023607635
C43	-2.7390194960	-1.8296534117	5.1509699811
C46	-0.8393736427	-0.2986104506	5.6491307769
C3	-0.3294211863	1.5711983739	0.4289598731
O44	-3.9331471441	-1.8693912647	5.0021991430
O45	-2.0180580518	-2.7589168423	5.7884861922
O47	0.3648658766	-0.2082749819	5.5258938354
O48	-1.4974277882	0.0524115795	6.7502224380
C49	-2.7724747594	-3.8433952174	6.3415787913
C53	-0.7044437061	0.5146072627	7.8459240070
H11	1.6564173069	-1.3462399838	-0.7147798825
H12	1.2070277076	0.0061177939	-1.7629845520
H13	2.0830924972	0.2936750360	-0.2206829341
H15	-1.0618523209	-0.6229386933	-1.8152911857
H16	-1.1633905202	-1.9130715233	-0.6110009640
H17	-2.1236952865	-0.4432287087	-0.3993860702
H22	-2.0928171879	-0.5563389600	1.6208279902
H25	-0.8028931565	1.4642039973	3.4655070137
H7	-1.4766338596	-2.2754381433	3.0175931426
H8	-0.0095658940	-1.4896636021	3.6008119258
H20	-3.5472042102	0.0852680840	3.6163869718
H21	-2.8688358771	1.1589126647	4.8459098793
H28	-3.1936136163	2.4757804557	2.1963773484
H32	2.2123151802	1.40299737207	5.9303811213
H33	3.9693296217	1.5777753315	6.2414311536
H34	3.1621730122	2.6185058950	5.0342604437
H36	5.4938649797	-0.0766115140	2.8902296136
H37	5.2413493611	1.6655645604	3.1210798042
H38	5.8913013970	0.6781590570	4.4579009488
H40	2.6159420885	-1.4062402364	5.5506018444
H41	3.8678370768	-2.0193310831	4.4403486035
H42	4.3491612550	-1.1270823529	5.9111206352
H27	-2.1113557586	2.7860211918	0.0508944175
H9	-0.2231648408	1.6133709527	-0.6641455684
H26	0.5347699251	2.1178536523	0.8154828123
H50	-3.4947815422	-3.4706075042	7.0726929104
H51	-3.3121205575	-4.3743699973	5.5525440580
H52	-2.0469885033	-4.5010502477	6.8195518234
H54	0.0262307100	-0.2454991928	8.1354532458
H55	-0.1786644815	1.4358234497	7.5765822057
H56	-1.4015448680	0.7037373011	8.6610361437

TS12

C1	-0.0013209833	-0.0124414634	-0.0007383457
C2	0.0050097509	-0.0041412401	1.3707705402
C3	2.2912839050	0.0521413256	2.1693492829
C4	0.3161509067	0.5494924578	4.1768024062
C5	-0.7602911284	-0.3088812405	2.4667578159
C6	-2.0096995683	0.3877133129	2.9322713561
H7	-2.8913973108	-0.0724418461	2.4611392077
H8	-2.0134566617	1.4438604226	2.6307240151
H9	2.9297639380	-0.2742147699	1.3523202618
C10	1.2137693376	0.2144329832	-0.8653756839
H11	0.9403010069	0.7063431368	-1.8062247009
H12	1.6491905860	-0.7585791037	-1.1331373136
H13	1.9891153267	0.8090612772	-0.3766695034
C14	-1.1867879859	-0.5826545802	-0.7478380614
H15	-2.0688835261	-0.6838382263	-0.1087666853
H16	-0.9234989231	-1.5773876226	-1.1336968503
C18	-1.4474644092	0.0342696340	-1.6164952497
C19	-0.8251257821	0.7944011175	5.1129031595
H20	-2.1572512915	0.3365231904	4.4565814498
H21	-0.6967669469	0.2585881196	6.0591002706
H22	-0.8900406979	1.8680114358	5.3371667412
H23	-0.6565900973	-1.3444193047	2.8076998679
C24	1.2472961372	-0.4582100096	4.3137531769
H25	2.1817656838	-0.7228204127	3.2962197451
H26	0.5687251058	1.3946111748	3.5359893765
H27	2.0542060102	1.1135448151	2.1778493305
H28	2.7085648488	-1.6754096202	3.3255330051
Au29	1.0984821547	-1.1940406876	5.1046546220
P30	-0.5290044743	2.1955398719	0.6895217459
C31	-1.2822100115	4.3659190847	1.1941570566
H32	-3.0539610957	4.5656623964	0.8291110137
H33	-3.6138516029	3.8149456538	1.3989639238
H34	-3.2469873438	4.4224589694	-0.2371633285
C35	-3.3899773057	5.5653773700	1.1291430646
H36	-1.1658821679	4.6394647258	2.9921291644
H37	-1.8019306947	3.9038884446	3.5037194268
H38	-1.5178087889	5.6476877548	3.2416719463
C39	-0.1306001199	4.5247593312	3.3292583373
H40	-0.4318465186	5.7682852412	0.4061932999
H41	0.6320388969	5.7494987636	0.6609923880
H42	-0.8691303339	6.7119877245	0.7527370352
C43	-0.5314617818	5.7037885977	-0.6814727153
C44	-3.2373111201	1.3134077163	4.8907256099
C45	-2.4600487083	-1.1006541564	4.8693026832
O46	-3.5251255438	2.3169194079	4.2725704921
O47	-1.6849582988	-1.8275301293	5.4425653852
O48	-3.7359573273	0.9917996093	6.0763772328
C49	-3.6682081130	-1.4711655833	4.4414005137
H50	-4.7019547811	1.9006798281	6.6207901305
H51	-5.5649554962	1.9780834618	5.9544337632
H52	-4.2595737021	2.8920843100	6.7502202858
C53	-4.9956733883	1.4826086029	7.5828399169
H54	-4.0478485137	-2.8139888305	4.7692088300
H55	-4.0601929755	-2.9486721422	5.8540202466
H56	-3.3435362243	-3.5277512986	4.3332214634
H57	-5.0453348312	-2.9539845769	4.3536897748

O48	2.0250570399	3.8446010714	-1.0851211257
C49	1.8877366116	5.3655845741	3.0479768683
H50	2.6354269839	6.0771255265	2.6860878390
H51	2.2321037160	4.9443542296	3.9967775261
H52	0.9205146824	5.8528076936	3.1714052042
C53	1.1630950289	4.4755173486	-2.0377050788
H54	0.4072387068	5.0785571416	-1.5268271613
H55	0.6547509338	3.7222177883	-2.6507621372
H56	1.8071729811	5.1029225714	-2.6541383326
X57	1.1897188004#	-0.7663303073#	0.2058480330#
C54	-1.7508818259	3.8472209852	-4.7826127195
C55	-2.6542099182	4.2294323442	-3.7956831859
C56	-2.9514798803	3.3650283981	-2.7432287053
C57	-2.3375262914	2.1134733299	-2.6786452915
C58	-1.4217240190	1.7357959320	-3.6687257334
C59	-1.1343770964	2.5972199969	-4.7202645399
H60	-1.5255826921	4.5228838644	-5.6048740778
H61	-3.1350610132	5.2038312004	-3.8451095288
H62	-3.6610709218	3.6662409174	-1.9732766829
H63	-0.9387196160	0.7578233866	-3.6127792597
H64	-0.4310172359	2.2954731881	-5.4936581388
C61	-5.1040362102	3.2054242381	1.8216167304
C62	-5.7752743409	2.4323244926	0.8786212831
C63	-5.0592722902	1.7279149790	-0.0850818195
C64	-3.6634399256	1.7978005246	-0.1008570711
C65	-2.9892112927	2.5730809607	0.8508090094
C66	-3.7127827082	3.2779003494	1.8057231157
H67	-5.6677186481	3.7515125233	2.5748482157
H68	-6.8612258613	2.3744076041	0.8935610056
H69	-5.5877755402	1.1215647865	-0.8198518479
H70	-1.8997293051	2.6309630691	0.8312594722
H71	-3.1891994585	3.8809954104	2.5442704721
C68	-5.4008681844	-2.3466211369	-3.0875066255
C69	-5.3532886636	-1.1012184395	-3.7080338244
C70	-4.5289936000	-0.0999171729	-3.2031938927
C71	-3.7434122195	-0.3483275909	-2.0736105685
C72	-3.7911770429	-1.6038299309	-1.4563855516
C73	-4.6226521944	-2.5975805131	-1.9595384301
H74	-6.0448273927	-3.1272240840	-3.4863541125
H75	-5.9596644968	-0.9080336803	-4.5899511490
H76	-4.4948601086	0.8744052400	-3.6903523528
H77	-3.1732474135	-1.8010354629	-0.5777648382
H78	-4.6594902873	-3.5710716411	-1.4756677025

C24	2.4911137793	0.2340195888	2.9157389570
H25	0.4505956080	1.8085235192	3.6207857828
H26	1.7100233252	2.0484597225	2.0518951386
H27	3.2503949093	-0.5312337233	2.7609285655
H28	1.8418764021	-0.6924447887	4.7555253578
Au29	-1.1288127750	2.2850363476	0.5129202978
F30	-2.6638216824	4.0443504691	0.6427583594
C31	-3.0247154706	0.7580755135	5.1938655648
C32	-1.8552711253	-1.4124135944	4.7229820418
O33	-3.7113490839	1.6156118162	4.6858251234
O34	-0.9054003002	-2.0897324287	5.0335218742
O35	-3.1646369022	0.3237060481	6.4449612766
O36	-3.0599779285	-1.8972502688	4.4139752034
C37	-4.2265162483	0.9146581002	7.1998045836
H38	-5.1876118170	0.7353051140	6.7103420942
H39	-4.0720431684	1.9937138637	7.2963161797
H40	-4.2004860163	0.4371734166	8.1789757960
C41	-3.1941857027	-3.3200849554	4.5227235912
H42	-2.9838558875	-3.6434261329	5.5457283842
H43	-2.4985023044	-3.8224635986	3.8447128814
H44	-4.2253692506	-3.5461208212	4.2526105621
O45	-2.9752416167	4.8322985502	-0.7245358983
O46	-4.0629646601	3.4687071286	1.1236088727
O47	-2.2603161015	5.2489856072	1.6349159371
C48	-0.0490352032	4.3135836401	5.0263510120
C49	0.5982372194	4.7220038430	3.8621179167
C50	-0.1413275072	5.0241073095	2.7231406284
C51	-1.5247007088	4.9090375864	2.7782242165
C52	-2.1907351850	4.4872384753	3.9185813123
C53	-1.4357808711	4.1949463261	5.0511005964
H54	0.5325519610	4.0862491979	5.9171476567
H55	1.6815574234	4.8144941569	3.8423115935
H56	0.3313001997	5.3601944065	1.8014671225
H57	-3.2764772901	4.4054434597	3.9190863978
H58	-1.9436527405	3.8767399201	5.9599105479
C59	0.2989432109	5.0441982533	-3.2777467115
C60	-0.6588947185	4.0490455191	-3.4531782494
C61	-1.7596825046	3.9806480933	-2.6052097911
C62	-1.8773645668	4.9274166948	-1.5965928834
C63	-0.9396343863	5.9298062344	-1.4030914163
C64	0.1565894877	5.9822182719	-2.2597107493
H65	1.1553029912	5.0948956499	-3.9452171601
H66	-0.5543517705	3.3259712201	-4.2584874033
H67	-2.5302380187	3.2204189244	-2.7205017339
H68	-1.0834248467	6.6556601006	-0.6058489564
H69	0.9000571543	6.7649095957	-2.1326695238
C70	-7.2169439392	5.5860989275	2.8025767489
C71	-6.6881455919	4.4702192220	3.4442007931
C72	-5.6248931209	3.7731995033	2.8805336270
C73	-5.1208543337	4.2227880160	1.6706298647
C74	-5.6288004001	5.3240748616	1.0021818979
C75	-6.6884633285	6.0095096597	1.5877887403
H76	-8.0464032267	6.1270756747	3.2501868702
H77	-7.1028088987	4.1372367406	4.3922603352
H78	-5.1803308087	2.9017340086	3.3589308957
H79	-5.2130102490	5.6314891560	0.0459028284
H80	-7.1043082089	6.8782641378	1.0843093498
X81	0.0558781024	0.3870650304	0.5965470159

Table of numerical data with 4 columns and 55 rows (H21 to H91).

Table of numerical data with 4 columns and 55 rows (C38 to C93).

2•AuP(tBu)2(o-biPh)

Table of numerical data for 2•AuP(tBu)2(o-biPh) with 4 columns and 31 rows (C1 to C45).

5

Table of numerical data for 5 with 4 columns and 31 rows (C1 to C45).

H72	2.3784199579	-3.1598112456	3.1958261277	C71	1.9275320332	6.7645199916	5.2569350720
H73	1.6044277978	0.6275353138	3.1069201817	C72	0.5658490285	6.9903045055	5.410407515
H74	2.2469885093	2.2733250893	3.2196350551	C73	-0.3379671626	6.0327756627	4.9763926802
H75	1.2322377907	1.8175872111	1.8342239867	C74	0.0811348416	4.8267271155	4.3920890116
H76	4.1679720285	0.1357368531	3.5281926343	C75	1.4641305195	4.5842856368	4.2730452204
H77	5.3705755414	0.6107390908	2.3028567659	C76	2.3611711522	5.5729001169	4.6982919517
H78	4.5750877169	1.8335006751	3.2863916500	H77	2.6515129458	7.5078430018	5.5813000171
H79	4.6132935124	2.0838127677	0.3161897453	H78	0.2041555398	7.9117867845	5.8593717788
H80	3.7330330054	3.1556379972	1.4119916410	H79	-1.3974923598	6.2381702093	5.0906826335
C81	-0.3153158664	-0.5438838749	-3.8592230215	H80	3.4274910200	5.3755474216	4.6022296756
C82	0.3643396427	0.6675103104	-3.7541456483	C81	3.6831744026	1.1299722328	3.0721961018
C83	1.6006473546	0.7227917449	-3.1201959211	C82	3.6965855390	2.2804223824	2.2863175941
C84	2.1771466482	-0.4320848735	-2.5792858162	C83	2.9172451608	3.3768550935	2.6407219708
C85	1.4829511217	-1.6437499315	-2.6797813363	C84	2.1055479319	3.3360491711	3.7804040578
C86	0.2440584302	-1.6988690390	-3.3169202103	C85	2.0796943349	2.1674124729	4.5486149495
H87	-1.2718933156	-0.5905748109	-4.3761234015	C86	2.8682427687	1.0758919227	4.1996500369
H88	-0.0652058015	1.5750899862	-4.1756947125	H87	4.3123287168	0.2809414999	2.8092124251
H89	2.1406141181	1.6660923310	-3.0515685709	H88	4.3351454199	2.3325424894	1.4062674528
H90	1.9373798778	-2.5564335468	-2.2945120056	H89	2.9532695043	4.2910547422	2.0485487722
H91	-0.2715941418	-2.6528714685	-3.4127633073	H90	1.4709313397	2.1212660358	5.4503020826
H92	2.8786554870	2.4031266322	0.0471322882	H91	2.8489997831	0.1911775134	4.8333250460

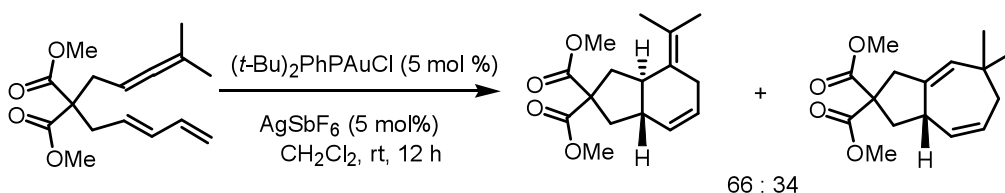
TS12

C1	-0.2654008511	0.0540562241	-0.1064991485
C2	-0.1112230834	-0.0419970175	1.2556931320
C3	2.1667487768	0.1303349427	1.8068049818
C4	0.7112317152	-0.5431542657	4.1292081696
C5	-0.7354904572	-0.6877021560	2.2831116599
C6	-1.9125989251	-0.2767033038	3.1348183397
H7	-2.6536486836	-1.0684995157	3.0472559451
H8	-2.3710481933	0.6173339950	2.7417922574
H9	2.7144647497	0.3072908879	0.8766310062
C10	0.8005939952	0.3802543964	-1.1169618036
H11	0.3724313745	0.8677981478	-1.9936743317
H12	1.2386561302	-0.5641607481	-1.4635242184
H13	1.6092795504	1.0050771306	-0.7355196610
C14	-1.5330448725	-0.4805363205	-0.7373470147
H15	-1.2929322839	-1.3827784097	-1.3066791882
H16	-1.9516523773	0.2365056946	-1.4435183317
H17	-2.2948303167	-0.7210588892	0.0006104110
C18	-0.3884631841	-0.8599354178	5.0815706747
C19	-1.6194340557	-0.0599983961	4.6403037310
H20	-0.6227720536	-1.9264869629	5.0615571815
H21	-0.1528320168	-0.6000473526	6.1275551274
H22	-0.5451867124	-1.7582300941	2.2899124702
C23	1.6451327663	-1.3974105103	3.6157795067
C24	2.3737815764	-1.0413962431	2.4607004516
H25	0.8356756289	0.5086590666	3.9038742774
H26	1.8185746116	1.0287005932	2.3256627438
H27	2.9769895984	-1.8066954251	1.9729153358
H28	1.6653089936	-2.4279231320	3.9518488111
Au29	-0.5990908412	2.2284378147	0.9559264518
F30	-0.3594444092	4.6153114886	0.7711258059
C31	0.5859256601	5.2803033128	2.2832725196
C32	-0.4413824027	5.4713018306	3.3871253081
C33	1.3506329839	6.5796098376	2.0827138613
C34	1.5911643191	4.2245942908	2.7528864772
C35	0.5595574633	4.8513212767	-0.8789864372
C36	-0.2877115216	4.1259832116	-1.9345973632
C37	1.9414061780	4.1994783033	-0.7881669416
C38	0.7252857584	6.2902267315	-1.3736196847
C39	-2.8886379137	-0.3541571552	5.4299708952
O40	-3.9547880516	0.1823555552	5.2330880114
O41	-2.6685196595	-1.2522220390	6.3399088373
C42	-1.3825887347	1.4252203532	4.8967506315
O43	-1.2242083476	2.2759262521	4.0460050582
O44	-1.3671039547	1.6576590392	6.2154645523
C45	-3.7947080076	-1.5503612173	7.1773504750
H46	-4.6567146990	-1.9047021223	6.5770761763
H47	-4.1207689610	-0.6598041323	7.7513446619
H48	-3.4304649318	-2.3314679628	7.8440431474
C49	-1.1460191604	3.0225184276	6.5872315723
H50	-1.9349733230	3.6642194575	6.2064067351
H51	-0.1690989133	3.3655990538	6.1920655777
H52	-1.1379985536	3.0139956050	7.6682799560
H53	-1.146940069	6.2687495026	3.1567120747
H54	-0.9906304512	4.5484043487	3.5800961174
H55	0.0888476711	5.7439786583	4.3211730499
H56	2.3374728352	3.9623149544	1.9831555836
H57	2.1506540231	4.6194477008	3.6285864334
H58	1.0661538402	3.3103317220	3.0764775837
H59	0.7070510920	7.4046013490	1.8117387714
H60	1.8315679116	6.8524847170	3.0320384556
H61	2.1439892536	6.4925418297	1.3520828382
H62	-0.2394982565	6.7540504345	-1.6327596488
H63	1.2494931889	6.9295541878	-0.6557788501
H64	1.3347622633	6.2727776801	-2.2948508552
H65	2.6375680905	4.7710462928	-0.1669786149
H66	1.8930888134	3.1804882002	-0.3925346713
H67	2.3835293050	4.1492320631	-1.7883588162
H68	-1.2936674492	4.5408649253	-2.0123575409
H69	0.1810967640	4.2503429671	-2.9134036057
H70	-0.3825096858	3.0591721801	-1.7342894690
C71	-4.1422857412	7.2199840843	0.1511761857
C72	-2.8755896570	7.8023166097	0.2265827481
C73	-1.7700666453	6.9960076661	0.4387407117
C74	-1.8863303624	5.6020245288	0.5925514275
C75	-3.1740544912	5.0230546274	0.5473216024
C76	-4.2795596022	5.8501359381	0.3125735538
H77	-5.0200080039	7.8312094189	-0.0220515865
H78	-2.7445138067	8.8769134580	0.1164320791
H79	-0.7925270975	7.4682855473	0.4855567232
H80	-5.2688341952	5.3880001807	0.2740672184
C81	-4.7240029065	1.1205001082	1.2742447097
C82	-4.3962908516	1.9486753094	2.3455080171
C83	-3.8057620062	3.1833356348	2.1077222835
C84	-3.5396329456	3.6001876498	0.8007166419
C85	-3.8625630812	2.7598449499	-0.2670389963
C86	-4.4507102340	1.5229170561	-0.0293298210
H87	-5.2040187643	0.1634864028	1.4590100928
H88	-4.5975708829	1.6339843657	3.3675089737
H89	-3.5718552534	3.8487784867	2.9414261529
H90	-3.6951869615	3.1021775647	-1.2897312703
H91	-4.7214082673	0.8818592515	-0.8679993511

6. Experimental

(*t*-Bu)₂PhPAuCl Synthesized via a modification of a procedure reported by Puddephat.¹ In a 20 mL screw-top vial was dissolved (SMe₂)AuCl (1 equiv) in CH₂Cl₂ (1 M). To the resulting suspension a solution of the ligand (1.0 equiv) in CH₂Cl₂ (1 M) was then added dropwise. The mixture was allowed to react for 1 h after which time the solvent was removed in a rotatory evaporator to yield the desired gold(I) complex as a white powder (97%).

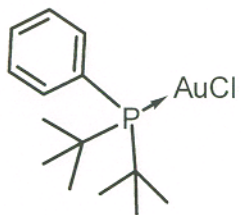
¹H NMR (400 MHz, CDCl₃): δ 1.39 (s, 9H), 1.42 (s, 9H), 7.46-7.56 (m, 3H), 7.99 (bs, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 30.2, 30.2, 36.3, 36.5, 127.3, 127.8, 128.5, 128.6, 131.9, 132.0. ³¹P NMR (166 MHz, CDCl₃): δ 79.0.



To a small vial was added AgSbF₆ (0.004 mmol, 1.0 mg, 0.05 equiv) and (*t*-Bu)₂PhPAuCl (0.004 mmol, 2.0 mg, 0.05 equiv) in CH₂Cl₂ (0.2 mL). The mixture was allowed to react for five minutes at room temperature, and then the suspension was filtered through glass fiber and added to a solution of the corresponding allene-diene (0.08 mmol, 1.0 equiv) in CH₂Cl₂ (0.8 mL). ¹H NMR analysis of the reaction crude after 12 hrs showed the formation of a 66:34 mixture of the corresponding [4+2] and [4+3] cycloadducts respectively. The spectroscopic data for this mixture was in complete agreement with the reported literature values.²

¹ Brandys, M.-C.; Jennings, M. C.; Puddephat, R. J. *Dalton* **2000**, 4601.

² Maulcon, P.; Zeldin, R. M.; Gonzalez, A. Z.; Toste, F. D. *J. Am. Chem. Soc.* **2009**, *131*, 6348-6349.



7.985
7.564
7.550
7.545
7.528
7.493
7.475
7.456
7.269

1.424
1.385

```

NAME      08-01-09-AG02-p102
EXPNO     1
PROCNO    1
Date_     20090801
Time      12.58
INSTRUM   AVQ-400
PROBHD    5 mm QNP 1H/13
PULPROG   zg30
TD        65536
SOLVENT   CDCl3
NS        8
DS        0
SWH       8012.820 Hz
FIDRES    0.122266 Hz
AQ        4.0899586 sec
RG        161.3
DW        62.400 usec
DE        6.00 usec
TE        293.2 K
D1        1.00000000 sec
TDO       1

```

```

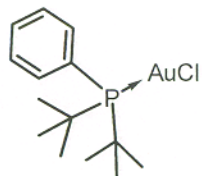
===== CHANNEL f1 =====
NUC1      1H
P1        12.80 usec
PL1       0.00 dB
PL1W      9.54516888 W
SFO1      400.1324700 MHz
SI        65536
SF        400.1300142 MHz
WDW       EM
SSB       0
LB        0.30 Hz
GB        0
PC        4.00

```



1.90
3.35

18.00



78.99

```

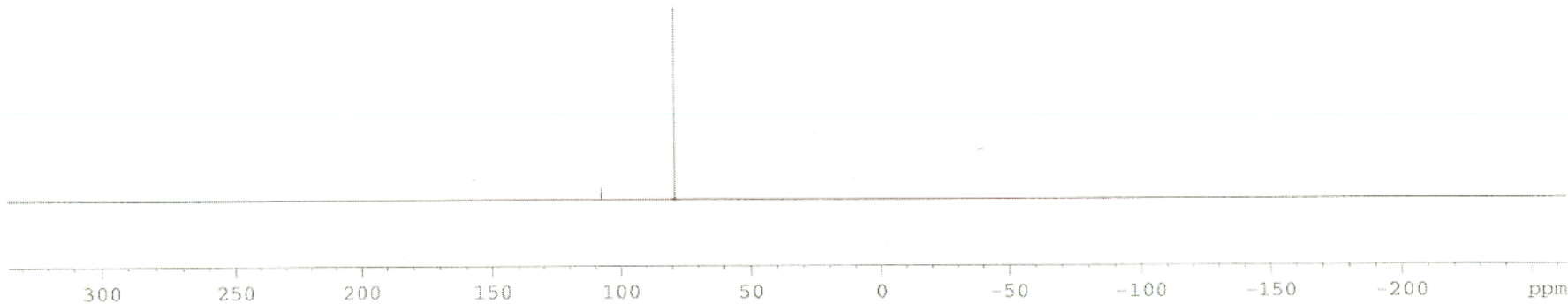
NAME      08-01-09-AG02-p102
EXPNO     2
PROCNO    1
Date_     20090801
Time      13.00
INSTRUM   AVQ-400
PROBHD    5 mm QNP 1H/13
PULPROG   zgpg30
TD        65536
SOLVENT   CDCl3
NS        23
DS        0
SWH       97087.375 Hz
FIDRES    1.481436 Hz
AQ        0.3375655 sec
RG        8192
DW        5.150 usec
DE        6.00 usec
TE        293.3 K
D1        2.00000000 sec
D11       0.03000000 sec
TDO       1
  
```

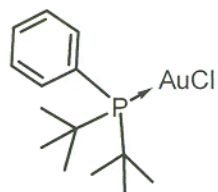
```

===== CHANNEL f1 =====
NUC1      31P
P1        7.70 usec
PL1       -2.00 dB
PL1W      16.27507401 W
SFO1      161.9814041 MHz
  
```

```

===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2      1H
PCPD2     70.00 usec
PL2       0.00 dB
PL12      15.00 dB
  
```

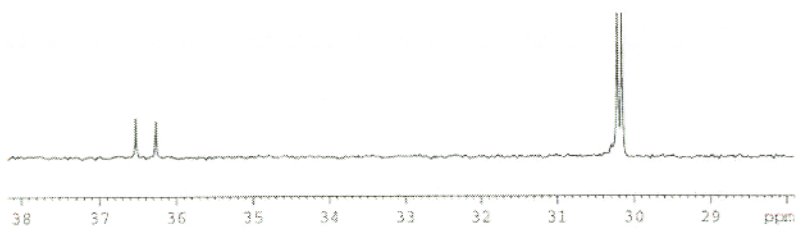
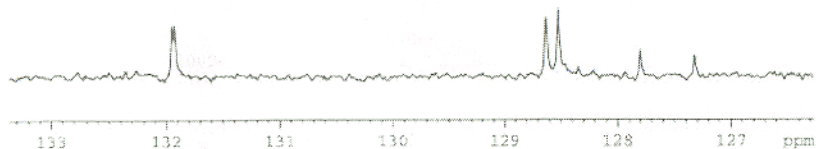




131.95
131.92
128.63
128.52
127.80
127.32

77.33
77.01
76.70

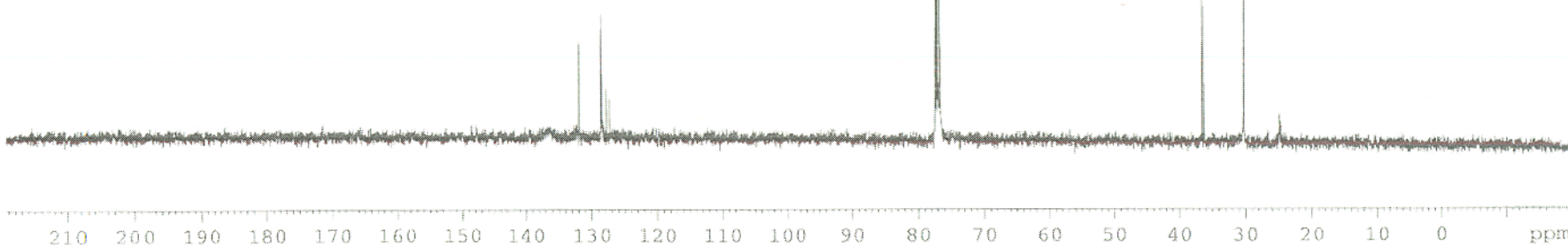
36.52
36.26
30.21
30.15

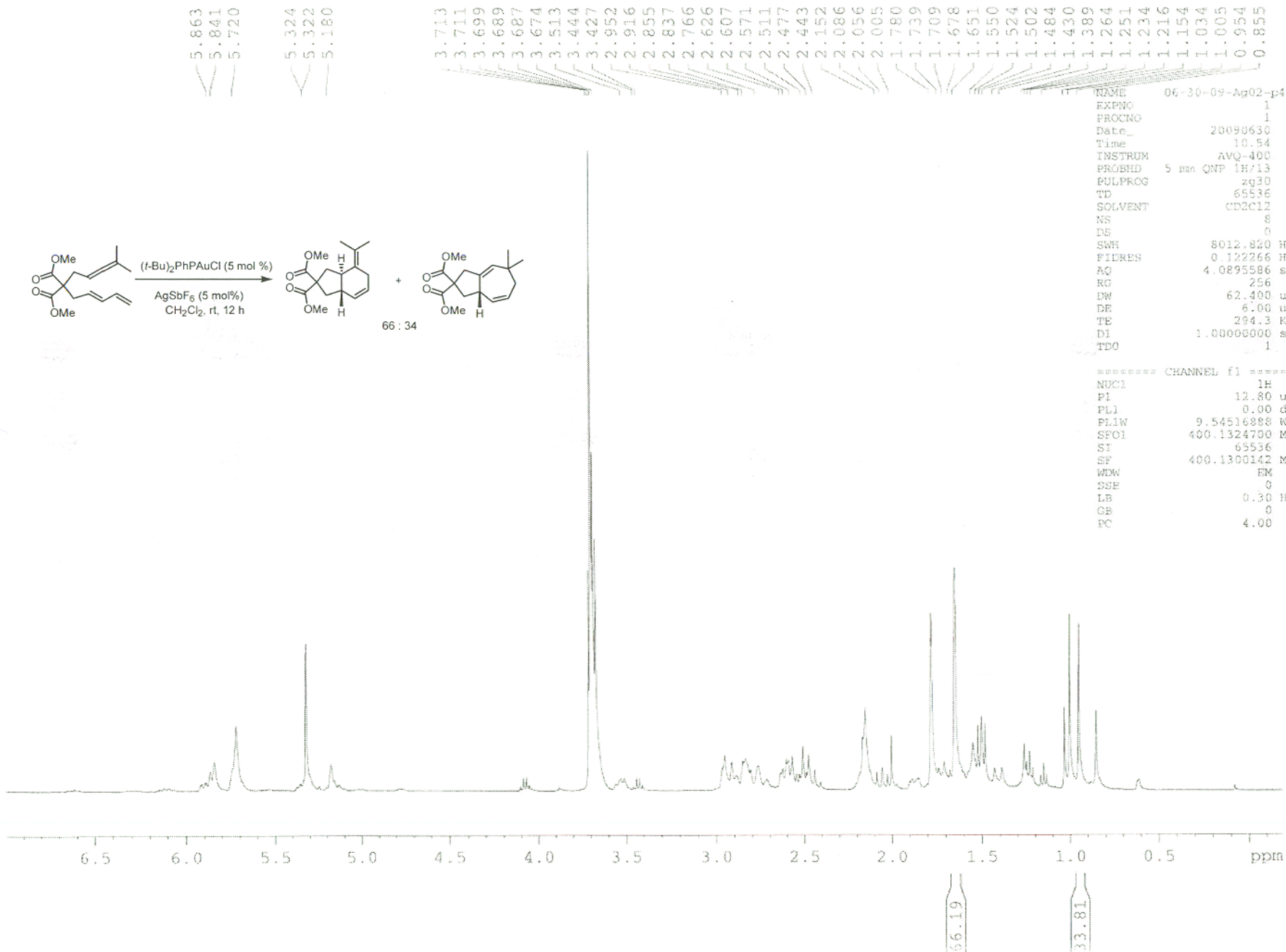
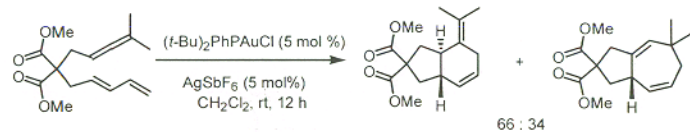


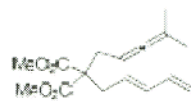
NAME 08-01-09-AG02-p102
EXPNO 3
PROCNO 1
Date_ 20090801
Time 13.29
INSTRUM AVQ-400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 500
DS 0
SWH 34038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3632196 sec
RG 16384
DW 20.800 usec
DE 6.00 usec
TE 293.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

==== CHANNEL f1 =====
NUC1 13C
P1 6.50 usec
PL1 -2.00 dB
PL1W 47.77286148 W
SFO1 100.6228298 MHz

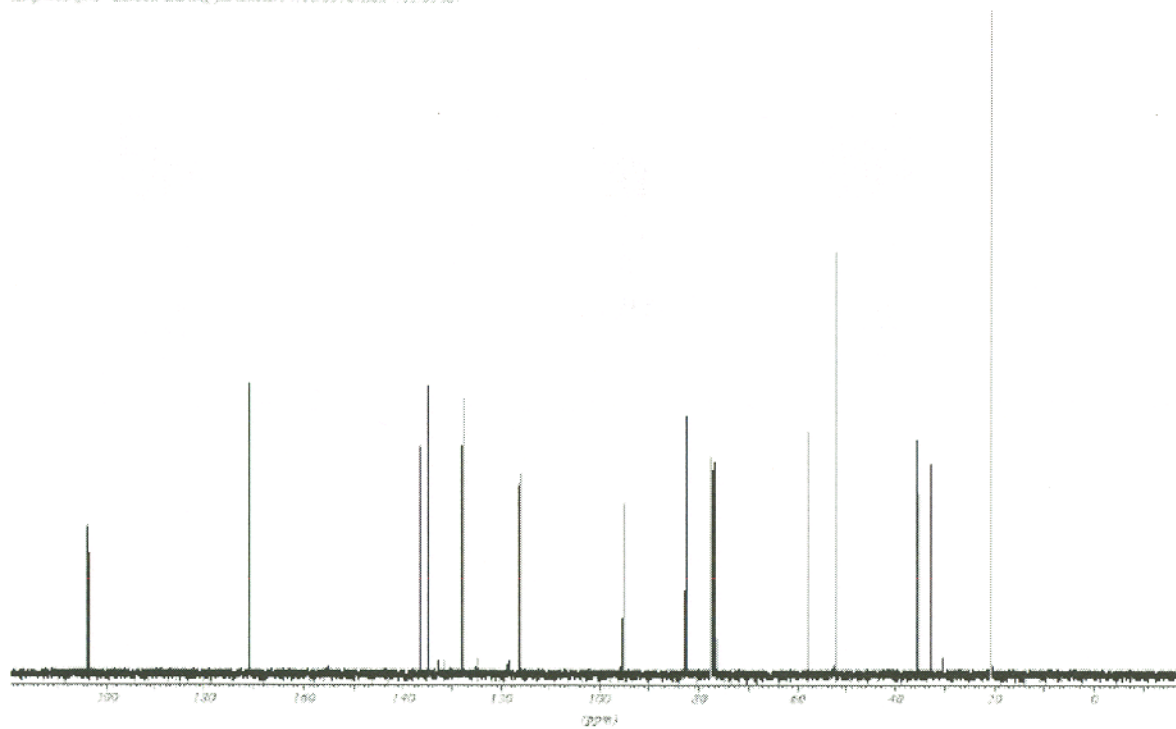
==== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 70.00 usec
PL2 0.00 dB
PL12 15.00 dB

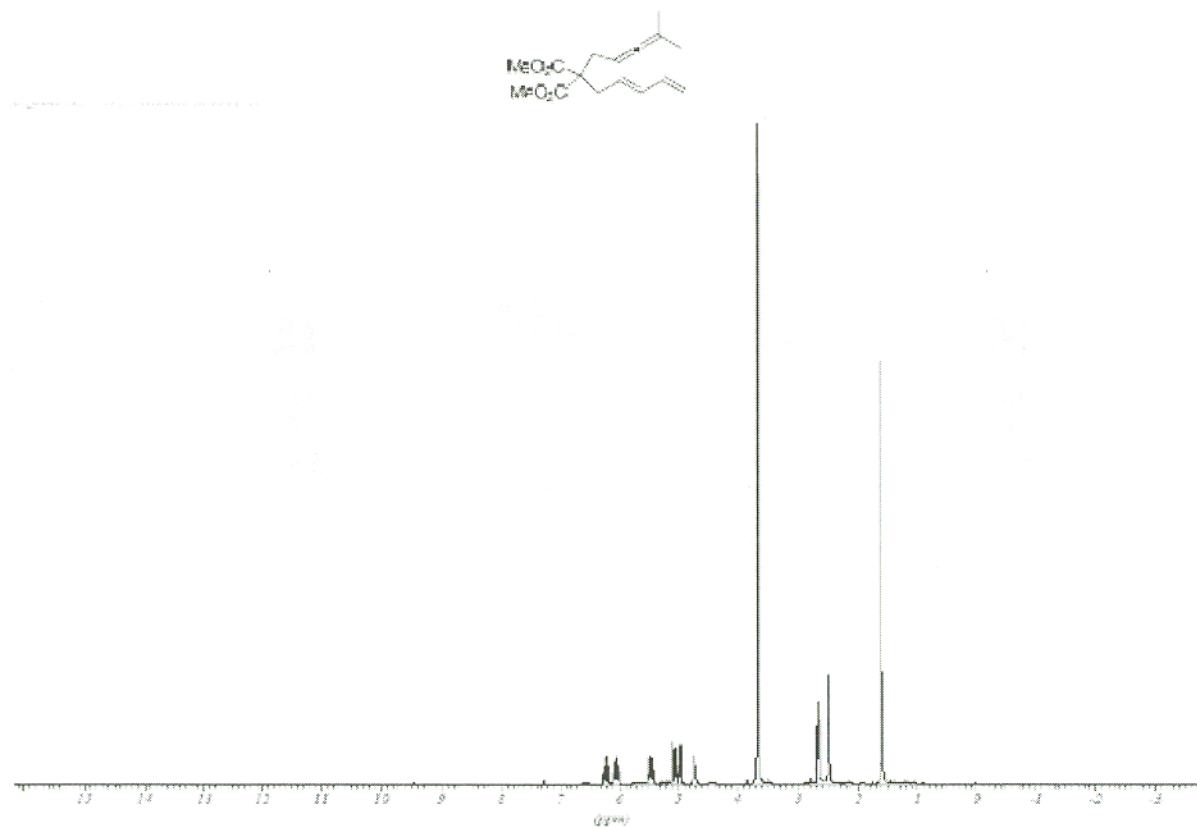


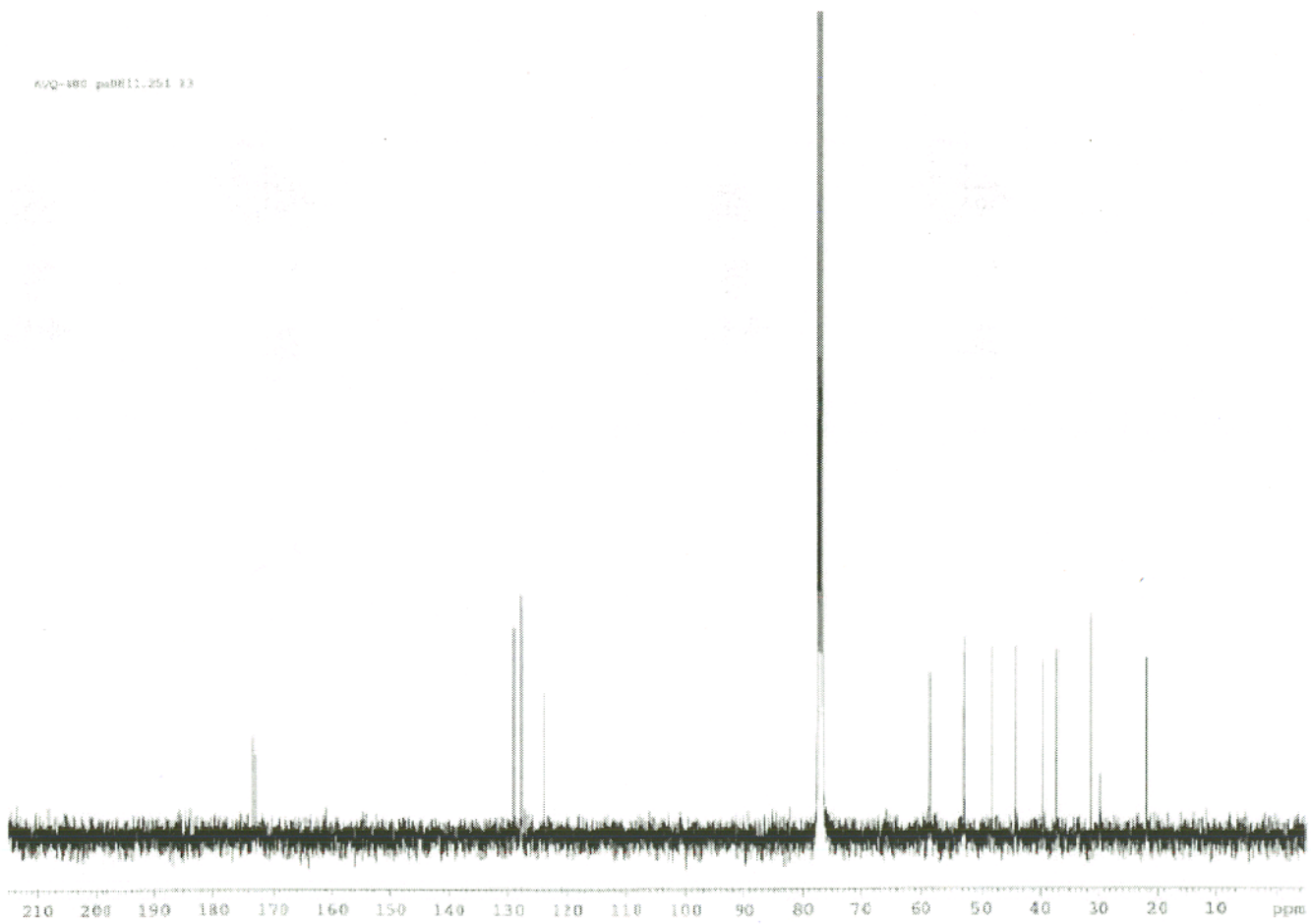
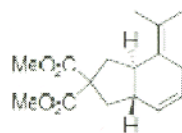


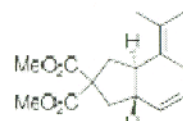


ATQ-100 QM9 - Carbon NMR parameters: 7/16/08 revised 7/22/08 JDT









AVC-400 ps0811.252

