

## “Supporting Information”

### Different roles of a cationic gold(I) complex in catalysing hydroarylation of alkynes and alkenes with a heterocycle

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**Table S1.** Cartesian coordinates and total energies for all of the calculated structures.

**5**

E (M06/BS1) = -806.319424 au

H(M06/BS1) = -806.105756 au

G(M06/BS1) = -806.163867 au

E(M06/BS2//M06/BS1) = -806.810764 au

E(M06-D3/BS2//M06/BS1) = -806.813432 au

Au	0.11906700	-0.27544300	0.02984700
P	-2.15084500	0.23425100	-0.02772500
C	-2.96693200	-0.27956400	-1.57143500
H	-4.03121000	-0.01309800	-1.53979600
H	-2.49189500	0.22050700	-2.42254000
H	-2.86750600	-1.36284600	-1.69996000
C	-3.10374700	-0.56002500	1.30390800
H	-2.72463400	-0.22816100	2.27672100
H	-4.16450900	-0.29242200	1.21646000
H	-2.99718100	-1.64818800	1.23714400
C	-2.50808400	2.01282200	0.12692600
H	-3.59207900	2.18016700	0.08587000
H	-2.11843100	2.38815000	1.07939100
H	-2.02490900	2.55869200	-0.69073000
C	2.29119900	-0.90628700	-0.03845500
C	2.57949200	-0.11186700	1.09006700
H	2.14096700	-1.98383500	-0.00437100
C	2.74302600	-0.15148700	-1.18502800
N	3.12983500	1.03986900	0.65266900
C	3.23414400	1.03704100	-0.72240400
H	2.70712200	-0.47430100	-2.21789900
H	3.64111700	1.89189700	-1.24579700
H	3.38407500	1.81845900	1.24864000
H	2.47203300	-0.33170800	2.14471700

**CH<sub>3</sub>CCH**

E (M06/BS1) = -116.552729 au

H(M06/BS1) = -116.492289 au

G(M06/BS1) = -116.521318 au

E(M06/BS2//M06/BS1) = -116.606770 au

E(M06-D3/BS2//M06/BS1) = -116.606917 au

C	-0.21585500	-0.00075300	0.00048400
C	-1.42431500	0.00020100	-0.00020000
C	1.23760500	0.00030300	-0.00015900
H	1.63584200	0.99526100	-0.23483000
H	1.63699800	-0.29396800	0.97858800
H	1.63673200	-0.70051900	-0.74429700
H	-2.49417900	0.00072500	-0.00020600

**TS<sub>5-6</sub>**

E (M06/BS1) = -922.873042 au  
 H(M06/BS1) = -922.598036 au  
 G(M06/BS1) = -922.665864 au  
 E(M06/BS2//M06/BS1) = -923.412805 au  
 E(M06-D3/BS2//M06/BS1) = -923.4181806 au

Au	0.15886700	-0.33541700	-0.22005600
P	-2.13712500	-0.18007200	0.15132200
C	-2.95623800	1.01421000	-0.95512000
H	-4.02737700	1.07413600	-0.72223400
H	-2.50000700	2.00230200	-0.82342800
H	-2.82840200	0.70452200	-1.99815500
C	-3.09593400	-1.71851100	-0.02843300
H	-2.72422500	-2.46785000	0.67903400
H	-4.15829400	-1.52574100	0.17027500
H	-2.98238700	-2.10985900	-1.04529400
C	-2.51978500	0.41783900	1.82994000
H	-3.60545800	0.51317900	1.96197500
H	-2.12304500	-0.28306800	2.57262400
H	-2.04521500	1.39436800	1.98152900
C	2.12138500	-2.22291900	-0.02392700
C	1.78128400	-2.08076100	-1.18481900
H	1.57704700	-2.06414300	-2.23771500
C	2.52390500	-2.37362300	1.36300800
H	1.67070800	-2.65868300	1.99052900
H	3.29255300	-3.14980500	1.45870700
H	2.93982600	-1.43693400	1.75644200
C	2.10631500	1.28904500	-0.12352700
C	1.45068400	2.07888700	-1.06617500
H	2.87083700	0.55190600	-0.34738400
C	1.76903400	1.81589600	1.16618500
N	0.75298300	3.03310400	-0.39031700
C	0.93008400	2.88450600	0.96194800
H	2.12559300	1.45568800	2.12416400
H	0.44273600	3.54975500	1.66286700
H	0.16408100	3.73227800	-0.82369400
H	1.48211000	2.05786400	-2.14792600

## 6

E (M06/BS1) = -712.859295 au  
 H(M06/BS1) = -712.674109 au  
 G(M06/BS1) = -712.729327 au  
 E(M06/BS2//M06/BS1) = -713.320184 au  
 E(M06-D3/BS2//M06/BS1) = -713.32239 au

Au	-0.42771600	-0.22457700	-0.00066700
P	1.86638500	0.18434200	0.00022400
C	2.28725800	1.92735300	-0.30392500
H	3.37754100	2.05163600	-0.28677100
H	1.90091100	2.23798600	-1.28058400
H	1.83718200	2.55720800	0.47085400

C	2.66773700	-0.24082900	1.57678500
H	2.52373200	-1.30569600	1.78953700
H	3.74180700	-0.02239500	1.51958000
H	2.22010900	0.34410200	2.38743800
C	2.75649000	-0.76283200	-1.27169700
H	3.82887700	-0.53494400	-1.22266400
H	2.60458000	-1.83517600	-1.10817100
H	2.37349700	-0.49960300	-2.26356000
C	-2.85434900	0.10402000	0.00201700
C	-2.51800200	-1.07779100	0.00456200
H	-2.52568900	-2.15311200	0.00770400
C	-3.30329800	1.48385400	-0.00094500
H	-4.40008200	1.50275000	0.00717500
H	-2.94524700	2.01963200	0.88531800
H	-2.95843700	2.01137700	-0.89731700

pyrrole

E (M06/BS1) = -210.005274 au

H(M06/BS1) = -209.918050 au

G(M06/BS1) = -209.949362 au

E(M06/BS2//M06/BS1) = -210.092827 au

E(M06-D3/BS2//M06/BS1) = -210.093194 au

C	-0.98029600	0.71326800	0.00008400
C	0.33378900	1.12039900	-0.00012100
H	-1.84610400	1.36574900	0.00016100
C	-0.98351400	-0.70880900	-0.00002000
N	1.11949700	-0.00251400	0.00007500
C	0.32863700	-1.12192400	-0.00005600
H	-1.85233900	-1.35735700	-0.00001500
H	0.76560300	-2.11257900	-0.00008700
H	2.12927300	-0.00482800	0.00029600
H	0.77539600	2.10900400	-0.00020500

TS<sub>6-7</sub>

E (M06/BS1) = -922.8632244 au

H(M06/BS1) = -922.588399 au

G(M06/BS1) = -922.657023 au

E(M06/BS2//M06/BS1) = -923.4009972 au

E(M06-D3/BS2//M06/BS1) = -923.4051979 au

C	2.04732600	0.15047500	-0.12581500
C	1.21665100	-0.82100700	-0.18125300
H	1.44259000	-1.87786900	-0.29579000
C	2.35751700	1.56281000	0.03452100
H	2.54704800	2.05646000	-0.92594200
H	1.50008000	2.04875500	0.51911300
H	3.22914700	1.71518100	0.68666700
Au	-0.81302600	-0.26676600	-0.06376500
P	-3.10216200	0.24994700	0.08249000

C	-4.08383900	-0.30983800	-1.34745500
H	-5.13892900	-0.04127200	-1.20721700
H	-3.70808600	0.16030500	-2.26282600
H	-3.99723400	-1.39699200	-1.45139300
C	-3.46527000	2.03103300	0.21994000
H	-4.54944400	2.18997300	0.28472100
H	-2.98521500	2.43847300	1.11646300
H	-3.07360500	2.55661700	-0.65785500
C	-3.92583000	-0.50172000	1.52427700
H	-3.45371000	-0.14578000	2.44654300
H	-4.99027500	-0.23407300	1.53379800
H	-3.82650600	-1.59187000	1.47835200
C	4.23384400	-0.96643400	0.66572600
C	4.08605300	-0.65800700	-0.69382600
H	3.72276400	-1.77056000	1.18156800
H	3.66714900	-1.24141100	-1.50310100
C	5.14153100	-0.04701100	1.21693500
N	4.94411800	0.38441700	-0.95948800
C	5.55944200	0.77776900	0.18619400
H	5.45260300	0.02360100	2.25149400
H	6.23620100	1.62310800	0.19311600
H	5.07355100	0.81332800	-1.86669500

7

E (M06/BS1) = -922.8926457 au

H(M06/BS1) = -922.614673 au

G(M06/BS1) = -922.682717 au

E(M06/BS2//M06/BS1) = -923.4255049 au

E(M06-D3/BS2//M06/BS1) = -923.4296418 au

C	-2.25682500	0.00182500	-0.07084200
C	-1.19767800	-0.82073000	-0.11200000
C	-2.20601400	1.49843100	0.03217300
H	-2.78455900	1.87635400	0.88883900
H	-1.16979800	1.83504200	0.15325900
H	-2.61630800	1.98453200	-0.86602300
Au	0.79344700	-0.29385200	-0.04265700
P	3.10537600	0.26835600	0.04652900
C	3.57062800	1.37096300	1.42702100
H	4.64778700	1.58204600	1.40332800
H	3.01578100	2.31291400	1.35166000
H	3.31735500	0.89305300	2.38013600
C	3.75073500	1.12716800	-1.43066800
H	4.81967000	1.34598100	-1.30981700
H	3.60824700	0.49708200	-2.31573600
H	3.20492300	2.06555200	-1.57983400
C	4.22546400	-1.16129300	0.24146400
H	4.09589200	-1.84935300	-0.60138100
H	5.27050100	-0.82733800	0.27917500
H	3.98276600	-1.69557600	1.16702600
C	-4.56851800	0.00967000	-1.16103800

C	-3.67053700	-0.57933300	-0.13624500
H	-4.32446100	-0.00477900	-2.21835700
C	-5.66705800	0.54691500	-0.58181400
N	-4.43771400	-0.31885200	1.08791700
C	-5.54305800	0.32043200	0.82689400
H	-6.49847100	1.05392100	-1.05449600
H	-6.23239600	0.61264300	1.61350300
H	-4.11932100	-0.58622900	2.01525200
H	-3.60778400	-1.67054300	-0.26713200
H	-1.43158000	-1.88866600	-0.19247800

**TS<sub>7-8</sub>**

E (M06/BS1) = -1151.847455 au

H(M06/BS1) = -1151.505923 au

G(M06/BS1) = -1151.585341 au

E(M06/BS2//M06/BS1) = -1152.480402 au

E(M06-D3/BS2//M06/BS1) = -1152.487029 au

C	-1.72470600	-0.75122100	0.48223000
C	-0.76412500	-0.71829900	-0.46754900
C	-1.47462600	-0.47946200	1.93826000
H	-1.69993500	-1.36403000	2.55072500
H	-0.42636600	-0.20518600	2.10375100
H	-2.11016300	0.33647400	2.31869300
Au	1.25107500	-0.34995700	-0.19267800
P	3.56971500	0.08486300	0.09091700
C	4.50778500	-1.25075200	0.90920900
H	5.56525000	-0.97162900	1.00325800
H	4.09190100	-1.43460400	1.90623100
H	4.42808400	-2.17317500	0.32308800
C	3.94337100	1.55962900	1.10156300
H	5.02886400	1.69865800	1.18942300
H	3.50120100	2.44755200	0.63575200
H	3.51186800	1.43938400	2.10168000
C	4.48626400	0.37680500	-1.46119900
H	4.04931800	1.22949200	-1.99291400
H	5.54229300	0.58602500	-1.24665500
H	4.41667400	-0.50786900	-2.10389900
C	-4.21677000	-1.30773000	1.05968400
C	-3.17427400	-0.90580000	0.16675500
H	-4.18993200	-1.15351800	2.13304200
C	-5.26468700	-1.83385800	0.32610400
N	-3.63238600	-1.32107200	-1.10478800
C	-4.86329500	-1.82489900	-1.01322200
H	-6.22341000	-2.17387800	0.69579800
H	-5.41480700	-2.12061600	-1.89814000
H	-3.13275000	-1.17822200	-1.97470400
H	-3.47491900	0.39962200	0.16427000
H	-1.09051800	-0.91693800	-1.49615700
C	-2.79584400	2.51969400	-0.08417900
O	-3.70064100	1.68420200	0.10176800

H	-1.34951800	1.24244800	-0.24556100
O	-1.53881900	2.22548400	-0.25894600
C	-3.09435800	3.97346500	-0.11574100
H	-2.54797200	4.47250800	0.69281900
H	-2.73610800	4.39957100	-1.05923300
H	-4.16572700	4.14617800	-0.00403700

**TS<sub>7-water</sub>**

E (M06/BS1) = -1075.668907 au

H(M06/BS1) = -1075.340452 au

G(M06/BS1) = -1075.416706 au

E(M06/BS2//M06/BS1) = -1076.287160 au

E(M06-D3/BS2//M06/BS1) = -1076.293697 au

C	-1.97155000	-0.17760900	0.48344800
C	-1.00913700	-0.41721800	-0.42813500
C	-1.71067400	0.34353300	1.86754200
H	-2.01364700	-0.38485800	2.63351100
H	-0.64283000	0.55290900	2.00399700
H	-2.27157200	1.26935600	2.07396000
Au	1.03167900	-0.23110200	-0.16954700
P	3.38931900	-0.06803400	0.10051600
C	4.11427200	-1.37817100	1.14645500
H	5.20041500	-1.24360300	1.23121600
H	3.66650300	-1.34064000	2.14597000
H	3.90478200	-2.36041400	0.70799600
C	3.97635700	1.47718700	0.87681600
H	5.06934200	1.46271700	0.97817200
H	3.68164500	2.33556400	0.26269000
H	3.52330500	1.58613400	1.86874700
C	4.34609600	-0.16834100	-1.45206800
H	4.05047700	0.64738400	-2.12133200
H	5.42150400	-0.09478500	-1.24440900
H	4.13929100	-1.12155000	-1.95164300
C	-4.48341200	-0.56607900	1.11906300
C	-3.43170300	-0.30339400	0.18293400
H	-4.45275200	-0.27235200	2.16296500
C	-5.54252700	-1.16258100	0.45938800
N	-3.90105900	-0.87585500	-1.02270800
C	-5.14123600	-1.33737900	-0.86941000
H	-6.50852400	-1.43048000	0.86758000
H	-5.69943800	-1.73384900	-1.70957600
H	-3.40053800	-0.85157000	-1.90361700
H	-3.71445300	0.97653100	-0.00079500
H	-1.33969800	-0.78536100	-1.40665400
O	-3.79629900	2.26375300	-0.35985200
H	-2.84327200	2.57794300	-0.43487500
H	-4.20967600	2.77604900	0.35499400
O	-1.18174900	2.73991700	-0.57066100
H	-0.88546400	1.80623200	-0.54782200
H	-0.76494500	3.14818800	0.20227400

H<sub>2</sub>O

E (M06/BS1) = -76.3803362 au

H(M06/BS1) = -76.355065 au

G(M06/BS1) = -76.376501 au

E(M06/BS2//M06/BS1) = -76.4283146 au

E(M06-D3/BS2//M06/BS1) = -76.4283147 au

O	0.00000000	0.00000000	0.11947700
H	0.00000000	0.75818700	-0.47790700
H	0.00000000	-0.75818700	-0.47790700

**TS<sub>7-pyrrole</sub>**

E (M06/BS1) = -1132.887483 au

H(M06/BS1) = -1132.525269 au

G(M06/BS1) = -1132.602991 au

E(M06/BS2//M06/BS1) = -1133.503079 au

E(M06-D3/BS2//M06/BS1) = -1133.510943 au

C	-1.57540500	-0.65647500	0.51559400
C	-0.58509900	-0.89689700	-0.36182000
C	-1.39500300	0.03966700	1.83437800
H	-1.59192500	-0.63620400	2.67988800
H	-0.36833200	0.41255200	1.93115900
H	-2.07978500	0.89581500	1.94322800
Au	1.39759500	-0.38448200	-0.14829500
P	3.69538100	0.19795700	0.08738100
C	4.61385400	-0.82371000	1.29222900
H	5.66244700	-0.50311100	1.34692500
H	4.15415700	-0.72572700	2.28228300
H	4.57275500	-1.87700000	0.99269200
C	4.00245800	1.90636400	0.65725700
H	5.08069200	2.09088700	0.74958800
H	3.57388500	2.61796900	-0.05743400
H	3.52525800	2.06082200	1.63163700
C	4.69137400	0.06888900	-1.43892600
H	4.28837700	0.74641600	-2.20017100
H	5.73770300	0.33287700	-1.23664900
H	4.64559100	-0.95545000	-1.82534300
C	-4.04148000	-1.26542100	1.18270100
C	-3.00416900	-0.98562200	0.22998700
H	-4.06494500	-0.85460300	2.18663200
C	-5.02880900	-2.01455800	0.57088100
N	-3.38620800	-1.72580700	-0.91204400
C	-4.58600800	-2.28114500	-0.73030900
H	-5.97388400	-2.33301100	0.99172800
H	-5.08527500	-2.81434300	-1.53104100
H	-2.86393500	-1.74999300	-1.78023200
H	-3.47635400	0.20951900	-0.08663800
H	-0.85907900	-1.42059400	-1.28590800



C	-4.24168100	2.30734000	0.28984900
C	-3.18524700	3.17876500	0.56227200
C	-2.20303200	2.94187400	-0.39587900
H	-5.17399400	2.21733100	0.83609100
H	-3.11925300	3.90010400	1.36714900
H	-1.21865800	3.38023400	-0.50946100
H	-2.09182100	1.58532900	-1.99001500
H	-4.52898100	0.99771600	-1.50991300
C	-3.87094900	1.49563500	-0.79915000
N	-2.63239100	1.97423300	-1.22738500

**8**

E (M06/BS1) = -1151.859305 au

H(M06/BS1) = -1151.513586 au

G(M06/BS1) = -1151.595277 au

E(M06/BS2//M06/BS1) = -1152.495344 au

E(M06-D3/BS2//M06/BS1) = -1152.502044 au

C	-1.69229000	-0.98017600	0.47238300
C	-0.76367700	-0.66793100	-0.47205200
C	-1.37908800	-1.01159300	1.94329100
H	-1.64131800	-1.98346400	2.38263000
H	-0.31276900	-0.82591700	2.11470000
H	-1.95038900	-0.25018400	2.49729600
Au	1.25013800	-0.29256500	-0.19913800
P	3.57558600	0.11225800	0.06817800
C	4.33024600	-0.73009800	1.50220200
H	5.40480300	-0.51086600	1.55132800
H	3.84965900	-0.38946500	2.42622100
H	4.18585400	-1.81262900	1.41264800
C	4.03681900	1.86370300	0.30230000
H	5.12409300	1.95974100	0.41894700
H	3.71326700	2.45104500	-0.56431400
H	3.54143500	2.25890900	1.19627800
C	4.60304900	-0.42522000	-1.34263700
H	4.29553100	0.10833000	-2.24905600
H	5.66270500	-0.21874700	-1.14333700
H	4.46903100	-1.50007100	-1.50859400
C	-4.21539500	-1.23652200	0.99124000
C	-3.10058300	-1.21419300	0.15076800
H	-4.18757700	-1.13707500	2.07102800
C	-5.36702800	-1.41809900	0.19021400
N	-3.58230200	-1.37670300	-1.13356000
C	-4.93908800	-1.50941500	-1.11549400
H	-6.39340900	-1.47343600	0.53072600
H	-5.49409100	-1.65275400	-2.03375900
H	-3.00673900	-1.45000300	-1.96252500
H	-1.12869300	-0.64405300	-1.50800200
C	-2.79257900	2.43846700	0.05370200
O	-3.81044400	1.67066000	0.16327400
C	-3.04931200	3.88111300	-0.10377800

O	-1.58068300	2.04809500	0.05227100
H	-3.03985400	4.11286200	-1.17715000
H	-2.25076700	4.45771800	0.36960700
H	-4.02744000	4.14540100	0.30215300
H	-1.39513800	1.03739100	0.03320400
H	-3.63422500	0.69267200	0.32696100

## 9

E (M06/BS1) = -922.9481266 au

H(M06/BS1) = -922.669647 au

G(M06/BS1) = -922.736169 au

E(M06/BS2//M06/BS1) = -923.4831873 au

E(M06-D3/BS2//M06/BS1) = -923.487428 au

Au	0.51952700	-0.46178700	-0.27836900
P	2.50906500	0.65259400	0.26761300
C	2.47264700	1.49227300	1.88354300
H	3.43393400	1.98937000	2.06698800
H	1.66952500	2.23701000	1.89685200
H	2.28635800	0.75906300	2.67576300
C	3.95293000	-0.45503800	0.34671300
H	4.09970000	-0.94026100	-0.62455800
H	4.85227100	0.11837300	0.60613100
H	3.78504700	-1.22832400	1.10429900
C	2.97786800	1.94623200	-0.92493600
H	3.91430300	2.42373700	-0.60904200
H	3.11431400	1.50235300	-1.91722200
H	2.18661800	2.70142400	-0.98309500
C	-2.04293600	-1.13776500	0.14134900
C	-1.27124600	-1.56749400	-0.94556700
C	-2.04798100	-1.94503500	1.40273100
H	-3.04567900	-2.37557300	1.56245200
H	-1.32392900	-2.76370500	1.34963300
H	-1.81527400	-1.32738900	2.27845400
C	-3.69579400	0.55099000	1.10427700
C	-2.85111600	0.03387400	0.11769600
H	-3.85958900	0.10948500	2.08095400
C	-4.29092600	1.71374500	0.60110300
N	-2.94240900	0.89114700	-0.96699000
C	-3.79676800	1.89897300	-0.68226500
H	-5.00230800	2.35589200	1.10461400
H	-3.99723100	2.67942500	-1.40554000
H	-2.42816400	0.80499100	-1.83386300
H	-0.92311800	-2.60277800	-0.92959400
H	-1.46860400	-1.17337300	-1.94517900

AcOH

E (M06/BS1) = -228.9599498 au

H(M06/BS1) = -228.892416 au

G(M06/BS1) = -228.924721 au

E(M06/BS2//M06/BS1) = -229.0620771 au

E(M06-D3/BS2//M06/BS1) = -229.0623695 au

C	0.09243400	0.12138700	-0.00018400
O	0.65177500	1.19431900	0.00000300
C	-1.38635000	-0.10035900	-0.00006300
O	0.76262000	-1.04402500	0.00009400
H	-1.67833700	-0.68042900	0.88280800
H	-1.67828400	-0.68352700	-0.88088000
H	-1.90700800	0.85930600	-0.00166600
H	1.71195600	-0.82386700	0.00044300

### TS<sub>9-10</sub>

E (M06/BS1) = -1132.935999 au

H(M06/BS1) = -1132.56919 au

G(M06/BS1) = -1132.64526 au

E(M06/BS2//M06/BS1) = -1133.549346 au

E(M06-D3/BS2//M06/BS1) = -1133.557112 au

C	1.79832500	-0.00513300	0.67138300
C	1.06341600	-0.91984000	-0.21035300
H	1.34917300	-0.85340600	-1.27001100
H	1.16742100	-1.96316000	0.10894700
C	3.72663200	-0.44564400	0.52680100
C	3.87899000	-1.83407400	0.81615200
C	4.04840000	-2.51617600	-0.37052900
C	4.10864000	-1.54747300	-1.38967500
N	4.00671300	-0.33540000	-0.84549400
H	3.98134500	0.53470100	-1.36509300
H	4.09583700	0.34540200	1.17415800
H	3.80172900	-2.26383400	1.80874400
H	4.12010000	-3.58616700	-0.51912300
H	4.21431300	-1.67913600	-2.46035500
C	1.60170000	-0.23142600	2.15725700
H	2.40033600	0.21392900	2.76285100
H	0.65603300	0.23305000	2.46828200
H	1.54509600	-1.30212000	2.38424700
C	2.18029300	2.52853200	1.04261400
C	2.09767700	3.66033500	0.20203000
H	2.47250500	2.52247300	2.08742500
C	1.71156100	3.21382500	-1.04401500
H	1.18784300	1.28661200	-1.72710200
H	2.29889700	4.68944100	0.47401100
H	1.51399300	3.75369100	-1.96144800
C	1.83689800	1.41212000	0.29525800
N	1.57616900	1.85674400	-0.98638500
Au	-1.01964300	-0.45955400	-0.10482500
P	-3.33987400	-0.00652400	-0.00253500
C	-3.83845800	1.06350900	1.39009800
H	-3.32996700	2.03104300	1.31307600
H	-4.92472500	1.22199400	1.37893800

H	-3.55178400	0.59285000	2.33724400
C	-4.02222300	0.83442100	-1.47205300
H	-3.84719600	0.22206000	-2.36367000
H	-5.10093300	0.99808200	-1.35100600
H	-3.52416600	1.80090300	-1.60849400
C	-4.38640200	-1.48938000	0.18500400
H	-5.44580500	-1.20502400	0.22723500
H	-4.22675200	-2.16468800	-0.66296400
H	-4.11626000	-2.01706700	1.10661600

## 10

E (M06/BS1) = -1132.941925 au

H(M06/BS1) = -1132.573768 au

G(M06/BS1) = -1132.650347 au

E(M06/BS2//M06/BS1) = -1133.554207 au

E(M06-D3/BS2//M06/BS1) = -1133.561861 au

C	1.93294300	-0.06749600	0.68620800
C	1.02738300	-0.92552800	-0.19609100
H	1.36108600	-0.89200700	-1.24655300
H	1.13385300	-1.97545600	0.11728300
C	3.45208400	-0.51052900	0.52054900
C	3.75833800	-1.94717200	0.66963500
C	4.32974000	-2.42468000	-0.46238300
C	4.42510900	-1.32398400	-1.37046400
N	3.95011800	-0.24105500	-0.81751100
H	3.88676500	0.67289100	-1.25942200
H	4.04606300	0.08501400	1.23330700
H	3.54051900	-2.50833400	1.57261400
H	4.66184000	-3.43266800	-0.67536200
H	4.82311000	-1.32013200	-2.38055300
C	1.59435800	-0.25980600	2.16556600
H	2.30426600	0.25451900	2.82695600
H	0.59389300	0.14562900	2.36153700
H	1.58211700	-1.32515500	2.43324700
C	2.47994200	2.47995700	0.96696400
C	2.23618700	3.63118500	0.17378700
H	3.02939600	2.44937700	1.90313300
C	1.52561100	3.22195100	-0.93015500
H	0.77149500	1.30785500	-1.45300000
H	2.54756100	4.64651800	0.39015200
H	1.12648200	3.77789000	-1.76898600
C	1.90290900	1.39584800	0.33249700
N	1.34763300	1.86708000	-0.83565700
Au	-1.03120100	-0.47148900	-0.10196100
P	-3.36532300	-0.00101400	-0.01404300
C	-3.87685200	1.09483400	1.35604800
H	-3.35924300	2.05714000	1.27178200
H	-4.96145000	1.26291300	1.32872500
H	-3.60683900	0.63750700	2.31467200
C	-4.03927900	0.82646300	-1.49768400

H	-3.86202800	0.20336600	-2.38158100
H	-5.11790500	0.99772000	-1.38605200
H	-3.53542700	1.78876300	-1.64336700
C	-4.43899200	-1.46540500	0.18543200
H	-5.49480400	-1.16613900	0.21498300
H	-4.28253600	-2.15537800	-0.65144000
H	-4.18465500	-1.98496800	1.11625100

**TS<sub>10-11</sub>**

E (M06/BS1) = -1361.887440 au

H(M06/BS1) = -1361.454881 au

G(M06/BS1) = -1361.543008 au

E(M06/BS2//M06/BS1) = -1362.600535 au

E(M06-D3/BS2//M06/BS1) = -1362.611806 au

C	1.17864700	-0.57944200	0.36412500
C	0.02670800	-1.39211500	-0.25931800
H	0.22133200	-1.56707300	-1.33060600
H	0.03910400	-2.39310700	0.20090700
C	2.51566800	-1.27009500	0.04677100
C	3.08652900	-2.41085600	0.66092300
C	3.94598000	-3.03383000	-0.24473100
C	3.85091200	-2.32961900	-1.43980000
N	2.98776300	-1.31231400	-1.27730200
H	2.73468000	-0.63572000	-1.99038900
H	3.50829200	-0.45335100	0.67311800
H	2.92610000	-2.68778700	1.69803200
H	4.58761700	-3.88606500	-0.06003000
H	4.37868100	-2.47393900	-2.37526100
C	1.01839400	-0.53653900	1.88384300
H	1.88608600	-0.09026200	2.38896600
H	0.12919600	0.04984000	2.14735100
H	0.87851700	-1.55045800	2.28050900
C	1.57450400	2.02106200	0.41047400
C	1.53641500	3.03560500	-0.58881500
H	1.83502800	2.15716400	1.45530300
C	1.17198800	2.43336000	-1.76731200
H	0.53427900	0.45461600	-2.14927900
H	1.75125800	4.08932400	-0.45190400
H	1.00348200	2.84100000	-2.75601100
C	1.22864000	0.82553000	-0.18249600
N	1.01142200	1.08983900	-1.52072600
Au	-1.87923200	-0.52475500	-0.04131400
P	-4.04899300	0.44745300	0.17845700
C	-4.06920400	2.27417300	0.24490500
H	-3.63343300	2.67974100	-0.67533700
H	-5.09684200	2.64515700	0.35277200
H	-3.46932400	2.61879600	1.09484700
C	-5.20916100	0.06002000	-1.17994900
H	-5.34634700	-1.02500200	-1.25092400
H	-6.18248500	0.53666600	-1.00404600

H	-4.79779900	0.42066100	-2.12973100
C	-4.96953400	-0.04336700	1.67943100
H	-5.95000600	0.44981700	1.70910800
H	-5.11155500	-1.13005500	1.68670200
H	-4.39686900	0.23762200	2.57062800
C	4.88223000	1.19467500	0.70398900
O	4.28069700	0.26489200	1.28105000
C	4.84025400	1.47877100	-0.74595000
O	5.60987600	2.01203200	1.41020300
H	5.66335300	2.13609700	-1.03275500
H	3.88584100	1.98325000	-0.96924300
H	4.88127900	0.54460300	-1.31367900
H	5.56203800	1.77021400	2.35754800

## 11

E (M06/BS1) = -1361.892102 au

H(M06/BS1) = -1361.454504 au

G(M06/BS1) = -1361.542048 au

E(M06/BS2//M06/BS1) = -1362.607621 au

E(M06-D3/BS2//M06/BS1) = -1362.618628 au

C	1.15104900	-0.93564600	-0.79878800
C	0.46753600	0.43602900	-0.96798700
H	0.97240700	1.19795400	-0.34860700
H	0.58571000	0.77524700	-2.00982400
C	2.65488100	-0.82249500	-0.95539900
C	3.69049300	-1.47184500	-0.30453200
C	4.92113000	-1.09820700	-0.93721700
C	4.61612600	-0.22570400	-1.94238000
N	3.23976400	-0.01984500	-1.91874900
H	2.71707900	0.43375400	-2.66222300
H	3.69356500	0.00783600	0.88219200
H	3.55563300	-2.20153400	0.48891500
H	5.91546100	-1.42528100	-0.65841200
H	5.24065700	0.30884600	-2.64652600
C	0.65658900	-1.89779400	-1.88863700
H	1.17170200	-2.86551300	-1.83527800
H	-0.42294700	-2.06601400	-1.77975000
H	0.83831200	-1.47217200	-2.88481400
C	0.69777900	-2.84013400	0.95544000
C	0.53117100	-2.84885200	2.36872400
H	0.70007800	-3.70690200	0.30330500
C	0.61580100	-1.54720900	2.79666100
H	0.78393600	0.25068200	1.69847700
H	0.37133300	-3.71720200	2.99752100
H	0.52676000	-1.11219700	3.78427700
C	0.87480800	-1.53248900	0.55712300
N	0.85085800	-0.75862600	1.69737100
Au	-1.58197400	0.41273200	-0.46915900
P	-3.86525100	0.32246100	0.19590300
C	-4.11383500	-0.67122700	1.70982700

H	-3.53618100	-0.23477200	2.53310300
H	-5.17568200	-0.70037700	1.98742600
H	-3.75411300	-1.69282400	1.54058300
C	-4.65018300	1.92239400	0.60037500
H	-4.64267900	2.57284100	-0.28148800
H	-5.68716300	1.76786400	0.92589000
H	-4.09012300	2.41647100	1.40247600
C	-5.01867400	-0.42646500	-1.00728200
H	-6.03549100	-0.46038400	-0.59454500
H	-5.02340900	0.16419300	-1.93039300
H	-4.69242000	-1.44469700	-1.24742900
C	3.96189100	1.93264400	1.05989000
O	3.90565200	0.75476300	1.54030200
C	4.32300600	3.03610900	1.96287100
O	3.74260900	2.21944300	-0.16898200
H	3.93756100	3.98434700	1.58309800
H	5.41913100	3.09579400	2.00069900
H	3.96215100	2.83077000	2.97339600
H	3.52555100	1.45150300	-0.77006600

### TS<sub>11-9</sub>

E (M06/BS1) = -1361.875476 au

H(M06/BS1) = -1361.443466 au

G(M06/BS1) = -1361.530334 au

E(M06/BS2//M06/BS1) = -1362.591181 au

E(M06-D3/BS2//M06/BS1) = -1362.602733 au

C	1.21680200	0.77219900	0.74292000
C	0.85098800	-0.68351300	0.35955400
H	0.91729500	-1.00433600	-0.69088900
H	0.81905700	-1.44213400	1.15516900
C	2.69904200	1.06363000	0.56761700
C	3.39298300	1.78232000	-0.39686100
C	4.77514800	1.77061800	-0.04674300
C	4.89390600	1.03971500	1.10691000
N	3.63843700	0.61437100	1.46644300
H	3.44019400	0.06066500	2.28997600
H	3.60251600	-0.15757500	-1.07330900
H	2.94173300	2.31964100	-1.22382300
H	5.58358600	2.24461500	-0.58997900
H	5.75979900	0.77559300	1.70028000
C	0.85813300	0.98539800	2.21916100
H	1.17721500	1.97672600	2.56447500
H	-0.22484700	0.89216000	2.36800900
H	1.33472900	0.22928300	2.85652100
C	-0.47354500	2.73312300	0.28155300
C	-1.02752500	3.29541700	-0.90126900
H	-0.70879000	3.02048400	1.30033300
C	-0.45973800	2.64235900	-1.96809700
H	0.94730300	1.06780200	-2.04024900
H	-1.74955200	4.10196100	-0.95964000

H	-0.58856700	2.76762700	-3.03572100
C	0.41538300	1.74539600	-0.09169200
N	0.41756900	1.71227200	-1.46906400
Au	-1.34948300	-0.70922800	0.17430000
P	-3.65313700	-0.39688400	-0.07110600
C	-4.01529900	0.65802200	-1.51405400
H	-3.73034100	0.13568800	-2.43443800
H	-5.08362700	0.90778600	-1.55292400
H	-3.42245700	1.57877700	-1.43893100
C	-4.72268800	-1.85806000	-0.27689800
H	-4.63609100	-2.50890900	0.59997700
H	-5.76848500	-1.54576100	-0.39370000
H	-4.41216600	-2.42113100	-1.16400900
C	-4.37277900	0.51672700	1.33381100
H	-5.43456500	0.72682200	1.15044700
H	-4.27198300	-0.06963100	2.25383900
H	-3.83226100	1.46281800	1.46004500
C	3.89149300	-2.04765300	-0.74218100
O	4.06821400	-0.96773300	-1.43124400
C	4.77745700	-3.17897400	-1.09383600
O	3.04874200	-2.16822200	0.18037300
H	4.37760700	-4.11562000	-0.70213900
H	5.76527300	-2.99671900	-0.65195800
H	4.90918000	-3.22966300	-2.17872900
H	2.16824900	-1.41392000	0.27416500

### prod1

E (M06/BS1) = -326.6296701 au

H(M06/BS1) = -326.477729 au

G(M06/BS1) = -326.518562 au

E(M06/BS2//M06/BS1) = -326.76133 au

E(M06-D3/BS2//M06/BS1) = -326.762753 au

C	-1.39979400	0.12146200	-0.00001100
C	-2.03924400	1.30107800	-0.00006200
C	-2.16467200	-1.16991700	0.00006200
H	-1.91724700	-1.77758100	0.88170100
H	-3.24507100	-0.98943000	0.00001800
H	-1.91719100	-1.77771400	-0.88146600
C	0.83370600	-1.15317700	-0.00004300
C	0.05007800	-0.00990800	-0.00001500
H	0.45930600	-2.17102100	-0.00011100
C	2.19233900	-0.75577100	-0.00000200
N	0.91781200	1.06155900	-0.00004200
C	2.21175200	0.62072200	0.00004600
H	3.06125400	-1.40349800	-0.00006700
H	3.03767400	1.32091700	0.00002300
H	0.64334000	2.03385400	0.00049300
H	-3.12663000	1.34497300	-0.00004300
H	-1.52510400	2.26166100	-0.00010400



**prod2**

E (M06/BS1) = -536.673831 au

H(M06/BS1) = -536.431054 au

G(M06/BS1) = -536.482238 au

E(M06/BS2//M06/BS1) = -536.8849063 au

E(M06-D3/BS2//M06/BS1) = -536.8890818 au

C	-0.01857500	0.96076800	0.01697400
C	-0.04648400	1.77858000	1.31972000
H	-0.06725600	1.13294700	2.20753800
H	0.84855300	2.41132600	1.37727000
H	-0.91988000	2.44516300	1.36217100
C	1.26619200	0.17751900	-0.04135600
C	2.37972800	0.29456800	-0.84561900
C	3.33377200	-0.66846800	-0.41338800
C	2.77750700	-1.34763800	0.64328600
N	1.53183200	-0.82032100	0.86744900
H	0.85637700	-1.17959100	1.52900100
H	2.50270400	1.00386900	-1.65672900
H	4.31794900	-0.84038600	-0.83454100
H	3.15597900	-2.16100000	1.24966700
C	-0.08483700	1.93029500	-1.16897700
H	-0.02746400	1.38803400	-2.12139200
H	-1.03085500	2.48731000	-1.14938400
H	0.73813600	2.65740900	-1.12832900
C	-1.30024000	-1.25248500	-0.59155800
C	-2.65676100	-1.66198100	-0.48232600
H	-0.48077000	-1.81626300	-1.02502500
C	-3.34416500	-0.63751000	0.12203800
H	-2.68531500	1.24647700	0.82556300
H	-3.07827100	-2.60723200	-0.80533100
H	-4.38508600	-0.54326100	0.40507900
C	-1.19216000	0.01182500	-0.04927500
N	-2.45021300	0.37208500	0.37645400

**TS<sub>9-12</sub>**

E (M06/BS1) = -1151.907896 au

H(M06/BS1) = -1151.561119 au

G(M06/BS1) = -1151.639650 au

E(M06/BS2//M06/BS1) = -1152.5392 au

E(M06-D3/BS2//M06/BS1) = -1152.547205 au

Au	-0.66599000	0.35669800	-0.30887200
P	0.90819600	2.00992500	0.06348900
C	2.26747200	1.98844400	-1.14728000
H	2.96023200	2.81495300	-0.94220500
H	2.80366000	1.03445000	-1.06014300
H	1.87034700	2.08871400	-2.16340500
C	0.25576500	3.70929700	0.02072900
H	-0.50950700	3.83154200	0.79495700
H	1.06840800	4.42688500	0.19424400

H	-0.19813100	3.90464100	-0.95700000
C	1.73155900	1.85094400	1.67814500
H	2.46729800	2.65673700	1.79958200
H	0.99013200	1.91254300	2.48230300
H	2.24371100	0.88122600	1.73634800
C	0.97855000	-1.97213300	-0.95760800
C	-0.30308800	-2.24533700	-0.59769500
C	1.34711700	-1.82998300	-2.40447700
H	2.09137000	-2.58522100	-2.69064800
H	0.47005000	-1.94804100	-3.04924700
H	1.79439500	-0.84736200	-2.60884500
C	3.39372400	-1.49128000	-0.23491400
C	2.05709900	-1.79237100	-0.00612900
H	3.85277500	-1.37548800	-1.21133800
C	4.03771900	-1.38039600	1.01760500
N	1.89611100	-1.86394700	1.36197300
C	3.08429900	-1.61779500	1.98589100
H	5.08344700	-1.16141200	1.19625600
H	3.16084000	-1.64077100	3.06565700
H	1.02831600	-2.06482500	1.84055700
H	-1.06194000	-2.42706800	-1.35668200
H	-0.59842600	-2.44914500	0.43308300
O	-2.85153400	-0.48668800	-0.43524500
C	-3.54797600	-0.70252500	0.55262500
O	-3.15693800	-0.44250700	1.79009100
H	-2.26700700	-0.03532500	1.77695900
C	-4.91656200	-1.28237500	0.48415900
H	-5.17299500	-1.52354000	-0.54850000
H	-4.96765300	-2.18240400	1.10671700
H	-5.63811300	-0.56482200	0.89102800

## 12

E (M06/BS1) = -825.261754 au

H(M06/BS1) = -825.069069 au

G(M06/BS1) = -825.126916 au

E(M06/BS2//M06/BS1) = -825.769396 au

E(M06-D3/BS2//M06/BS1) = -825.771679 au

Au	-0.08691700	-0.23033400	-0.00496100
P	2.15997300	0.16435100	0.00385300
C	2.56718600	1.92894100	-0.15346000
H	3.65618800	2.06338600	-0.13402000
H	2.16899600	2.31721700	-1.09712200
H	2.11626000	2.48538900	0.67531800
C	2.97220000	-0.39153300	1.53192200
H	2.83056500	-1.47078200	1.65392700
H	4.04559700	-0.16756600	1.48558500
H	2.52910200	0.12203600	2.39200600
C	3.03992400	-0.66618900	-1.35222500
H	4.11240300	-0.44134400	-1.29148400
H	2.89036200	-1.74891300	-1.28142300

H	2.64862200	-0.31728600	-2.31406100
C	-3.10313600	0.17944100	-0.00042300
O	-2.22948700	-0.68620500	-0.00269200
O	-2.74357800	1.44907000	-0.00982800
C	-4.55429100	-0.14968700	0.01922200
H	-5.00972000	0.24422600	0.93600500
H	-5.06042400	0.32033400	-0.83215500
H	-4.69491100	-1.23066000	-0.02073600
H	-3.51297100	2.04631100	-0.00778100

### TS<sub>12-13</sub>

E (M06/BS1) = -1151.891482 au

H(M06/BS1) = -1151.549517 au

G(M06/BS1) = -1151.633687 au

E(M06/BS2//M06/BS1) = -1152.523292 au

E(M06-D3/BS2//M06/BS1) = -1152.529047 au

Au	-1.78345800	0.50028600	-0.11898200
P	-2.93311700	-1.45290700	0.15673700
C	-1.85005600	-2.87001100	0.51949900
H	-2.44754100	-3.78570600	0.61493700
H	-1.12019100	-2.99365400	-0.28796600
H	-1.31040500	-2.68842600	1.45553100
C	-4.13246800	-1.41293900	1.52455000
H	-4.87831700	-0.63214700	1.34020900
H	-4.63570700	-2.38446100	1.61072900
H	-3.61302300	-1.18822600	2.46249100
C	-3.89416100	-1.95019500	-1.30617100
H	-4.40207200	-2.90420000	-1.11481600
H	-4.63958700	-1.18122100	-1.53674800
H	-3.22505600	-2.06037200	-2.16639100
C	0.46246300	2.39700900	-0.24780200
O	-0.78851000	2.36690200	-0.40434000
O	1.13199700	1.36618700	0.07212900
C	1.16535400	3.70802100	-0.44995400
H	1.66911200	4.00406500	0.47807300
H	1.93800800	3.60092600	-1.22076800
H	0.46144400	4.48851100	-0.74486500
C	4.05401800	0.38873500	0.89328800
C	3.73890800	1.63843100	0.33486000
C	3.92629100	0.21516500	2.37078700
H	4.92544100	0.13037800	2.82044300
H	3.42348500	1.07333500	2.82683000
H	3.37671400	-0.69663500	2.63057900
C	4.66382500	-2.05835100	0.54522000
C	4.40529500	-0.74268600	0.12861500
H	4.61800500	-2.40924700	1.56983300
C	4.99301200	-2.81496200	-0.57767900
N	4.58434700	-0.73095700	-1.24984700
C	4.92999800	-1.96047300	-1.67482600
H	5.25170800	-3.86554700	-0.60899300

H	5.11183700	-2.15830500	-2.72392500
H	4.46504300	0.07061000	-1.85514400
H	3.81299100	2.49023600	1.01659600
H	4.07806800	1.86482200	-0.67935700
H	2.41682900	1.52182100	0.20554300

### 13

E (M06/BS1) = -327.067704 au

H(M06/BS1) = -326.902916 au

G(M06/BS1) = -326.944431 au

E(M06/BS2//M06/BS1) = -327.191772 au

E(M06-D3/BS2//M06/BS1) = -327.193396 au

C	-1.29104200	0.01270600	-0.00296900
C	-2.05943700	-1.25525200	0.00062900
C	-2.09955500	1.25483300	-0.00067700
H	-2.63257000	1.33410400	-0.95948700
H	-2.87656600	1.18782900	0.77258400
H	-1.52082200	2.16759900	0.15330700
C	0.96376200	1.17732600	0.00419700
C	0.07685500	0.05506400	-0.00005000
H	0.65516200	2.21549100	0.00495700
C	2.25425700	0.71089900	0.00112900
N	0.90847500	-1.07722700	-0.00488400
C	2.18009400	-0.69867300	-0.00120600
H	3.16827200	1.28962800	0.00085200
H	2.98330300	-1.42610200	0.00079900
H	0.60096900	-2.04286300	0.00500000
H	-2.88506200	-1.19199600	-0.71962100
H	-1.47549600	-2.15220700	-0.21940900
H	-2.52611500	-1.38230800	0.98888700

### TS<sub>13-14</sub>

E (M06/BS1) = -537.0780351 au

H(M06/BS1) = -536.824291 au

G(M06/BS1) = -536.874618 au

E(M06/BS2//M06/BS1) = -537.2826119 au

E(M06-D3/BS2//M06/BS1) = -537.2877039 au

C	-0.49123600	1.28975400	0.09599300
C	-0.82948700	2.13890400	-1.09476700
H	-0.57521500	1.68091500	-2.05574400
H	-1.89687700	2.38617100	-1.11149000
H	-0.28041600	3.08922800	-1.01311100
C	-1.91841600	-0.33625600	-0.21300400
C	-1.34293400	-0.97539100	-1.33341300
C	-0.57500600	-2.03347200	-0.87467500
C	-0.76007600	-2.10180000	0.51282600
N	-1.62835800	-1.14427300	0.87827300
H	-1.94543100	-0.97959300	1.82567900

H	-2.80124500	0.29466400	-0.19317700
H	-1.43434300	-0.63001300	-2.35718700
H	0.06636900	-2.68513000	-1.45484000
H	-0.34057900	-2.78984800	1.23677400
C	-1.05526300	1.80837200	1.38768600
H	-0.83892500	1.17085100	2.24994200
H	-0.59420300	2.78814700	1.58324700
H	-2.13697400	1.97190100	1.32337300
C	1.40968600	-0.01974300	1.21185800
C	2.64005000	-0.49935000	0.75069200
H	1.02107500	-0.11345600	2.21951200
C	2.73558100	-0.14380900	-0.58607700
H	1.45718000	0.92247300	-1.85733800
H	3.38307700	-1.04622700	1.31671000
H	3.53141600	-0.31349900	-1.30053000
C	0.76886100	0.64442500	0.14962300
N	1.61329000	0.51907500	-0.94288400

## 14

E (M06/BS1) = -537.0937949 au

H(M06/BS1) = -536.838242 au

G(M06/BS1) = -536.889391 au

E(M06/BS2//M06/BS1) = -537.2976511 au

E(M06-D3/BS2//M06/BS1) = -537.3022084 au

C	0.10420500	0.92990400	0.19690200
C	0.52759100	0.96295300	1.66390000
H	0.68641300	-0.03903400	2.08558000
H	1.46193300	1.52449900	1.78518000
H	-0.23910500	1.47046800	2.26282800
C	1.14062400	0.10424900	-0.64487100
C	2.57527300	0.42490200	-0.46729700
C	3.25668400	-0.68018200	-0.08260400
C	2.30517600	-1.74617400	-0.00199300
N	1.11464500	-1.31368300	-0.31490700
H	0.26578500	-1.87390700	-0.33819900
H	0.85894500	0.20840400	-1.70651100
H	2.98817800	1.41429500	-0.63627100
H	4.31366200	-0.77852000	0.12880000
H	2.48162600	-2.78236000	0.27055500
C	0.08481400	2.35180000	-0.36422700
H	-0.19937600	2.36948200	-1.42369900
H	-0.64773100	2.94994700	0.19071900
H	1.06388700	2.83812700	-0.26130400
C	-2.04306400	0.21736300	-1.11308900
C	-3.16967000	-0.58385000	-0.79716800
H	-1.84059500	0.69549500	-2.06650300
C	-3.02388000	-0.99648500	0.50594200
H	-1.52526800	-0.58007100	1.93535800
H	-3.99738500	-0.82759000	-1.45254200

H	-3.65961300	-1.60340200	1.13781900
C	-1.23934000	0.28112100	0.00851100
N	-1.84633700	-0.48338000	0.98121500

## 15

E (M06/BS1) = -824.8298689 au

H(M06/BS1) = -824.650044 au

G(M06/BS1) = -824.705736 au

E(M06/BS2//M06/BS1) = -825.3382711 au

E(M06-D3/BS2//M06/BS1) = -825.3404651 au

Au	-0.15395400	-0.24711700	0.00303000
P	2.09444500	0.16247500	-0.00083700
C	2.49775800	1.93326800	0.14626700
H	3.58542400	2.07973800	0.12803400
H	2.04163000	2.48199300	-0.68525900
H	2.09290600	2.32563200	1.08575900
C	3.01613400	-0.63254400	1.35464400
H	2.89311400	-1.71963900	1.29682300
H	4.08262500	-0.38228700	1.28548100
H	2.62318600	-0.28653200	2.31718700
C	2.94852800	-0.37584600	-1.51777800
H	4.01580900	-0.12504500	-1.46277200
H	2.83502400	-1.45863400	-1.64027000
H	2.50135400	0.12261200	-2.38503400
C	-2.95349400	0.34597600	-0.00148000
O	-2.20718200	-0.71413800	-0.00478200
O	-2.53696000	1.50535800	0.00597500
C	-4.43538100	0.04098600	-0.00700100
H	-4.69774200	-0.55812100	0.87317300
H	-5.02374200	0.96279500	-0.00862800
H	-4.69200600	-0.55820600	-0.88873900

## TS<sub>14-12</sub>

E (M06/BS1) = -1361.935809 au

H(M06/BS1) = -1361.502734 au

G(M06/BS1) = -1361.586289 au

E(M06/BS2//M06/BS1) = -1362.642814 au

E(M06-D3/BS2//M06/BS1) = -1362.655776 au

Au	1.65582700	-1.01007500	-0.03064900
P	2.99144200	0.79677700	0.39116200
C	2.05811500	2.12468500	1.21791800
H	2.71037100	2.98999100	1.39461800
H	1.21329800	2.42558200	0.58325700
H	1.67379600	1.75841900	2.17697100
C	4.41200900	0.46424700	1.47851100
H	5.07218000	-0.27453600	1.01131700
H	4.97294200	1.39020900	1.65949600
H	4.05535900	0.06256000	2.43338200

C	3.69290600	1.57775500	-1.09560600
H	4.29801700	2.44797500	-0.81033500
H	4.31794200	0.86072700	-1.63854900
H	2.87267000	1.90287900	-1.74636500
C	-0.85856400	-2.39388000	-0.13756300
O	0.32147200	-2.66142200	-0.49588600
O	-1.11330900	-1.41241000	0.62834200
C	-1.97974700	-3.22899500	-0.67988800
H	-1.65534300	-4.26088100	-0.83935800
H	-2.84958600	-3.20216000	-0.01491000
H	-2.27723300	-2.82139000	-1.65640000
C	-2.50011600	1.51773200	0.64460500
C	-3.57820400	2.61197600	0.69660700
H	-4.10155800	2.70723000	-0.26350300
H	-4.31681600	2.37652700	1.47363800
H	-3.14912600	3.59081300	0.94960300
C	-3.19341400	0.17238200	0.39822600
C	-4.08795300	-0.45947100	1.32206700
C	-5.09143400	-1.10217000	0.62249100
C	-4.89077000	-0.80667300	-0.73375600
N	-3.81414900	-0.03582500	-0.86024500
H	-3.44284900	0.32487300	-1.73411500
H	-2.24943200	-0.73576500	0.49774400
H	-3.92961600	-0.48575600	2.39547300
H	-5.87661500	-1.73191500	1.02091900
H	-5.44918800	-1.14311400	-1.59999500
C	-1.76816000	1.46412600	1.99252200
H	-1.00520100	0.67502600	2.00111700
H	-1.27061900	2.42425200	2.18211600
H	-2.46991400	1.29085900	2.81959000
C	-0.88489900	0.98356100	-1.38851500
C	0.01164300	1.78296400	-2.14851800
H	-1.03725100	-0.08248600	-1.50758100
C	-0.08188000	3.06604000	-1.66791200
H	-1.27530900	3.88572200	-0.12796900
H	0.63785200	1.44818100	-2.96842800
H	0.41209100	3.98140900	-1.96849100
C	-1.50991900	1.79781900	-0.46251100
N	-1.00381800	3.06398600	-0.65134800

## 17

E (M06/BS1) = -805.856189 au

H(M06/BS1) = -805.656292 au

G(M06/BS1) = -805.711070 au

E(M06/BS2//M06/BS1) = -806.351293 au

E(M06-D3/BS2//M06/BS1) = -806.353648 au

Au	-0.04089400	-0.01968400	-0.00027500
P	2.33787700	0.00913800	0.00091700
C	3.12344800	-0.44302800	1.58815600
H	4.21703600	-0.38793300	1.50731200

H	2.78262900	0.24174700	2.37300300
H	2.83197900	-1.46211700	1.86663200
C	3.13455900	-1.11121100	-1.20339400
H	2.81124500	-0.85038600	-2.21759200
H	4.22754100	-1.03035500	-1.13903500
H	2.83625400	-2.14582000	-0.99966900
C	3.07225900	1.63784700	-0.38530500
H	4.16851500	1.58194500	-0.36364300
H	2.74574600	1.96222100	-1.37989900
H	2.73285400	2.37728900	0.34897800
C	-2.08771200	-0.06641200	-0.00039700
C	-2.96791800	-1.14328800	0.00107100
C	-4.30152600	-0.65285300	0.00167400
H	-2.66946900	-2.18802600	0.00174400
H	-5.21702500	-1.23556500	0.00280600
H	-4.99630600	1.48068800	0.00035800
H	-2.54590700	2.00683600	-0.00150000
N	-2.89483300	1.05901300	-0.00068400
C	-4.22291000	0.72133400	0.00040600

## 18

E (M06/BS1) = -904.013281 au

H(M06/BS1) = -903.781724 au

G(M06/BS1) = -903.845151 au

E(M06/BS2//M06/BS1) = -904.542003 au

E(M06-D3/BS2//M06/BS1) = -904.544970 au

Au	-0.32309300	0.00070300	0.00027600
P	2.03342700	-0.00046500	-0.00024400
C	2.79807900	1.11086900	1.23025500
H	3.89267700	1.05244500	1.17069400
H	2.47938900	2.14250200	1.04269300
H	2.47264500	0.82434000	2.23658700
C	2.79517800	-1.62360400	0.34696600
H	2.46758300	-2.35100700	-0.40425500
H	3.89017500	-1.54622000	0.32493200
H	2.47544400	-1.97576500	1.33410900
C	2.79892700	0.50922700	-1.57795500
H	3.89354000	0.48468100	-1.49701600
H	2.47899400	-0.16785400	-2.37793300
H	2.47680800	1.52510900	-1.83243600
C	-3.56585200	0.00002300	-0.00020600
C	-2.34123600	-0.00046300	0.00039600
C	-5.02201300	-0.00131500	-0.00128300
H	-5.42627700	-0.54797400	-0.86421500
H	-5.42753800	-0.47551700	0.90267100
H	-5.42900800	1.01826900	-0.04304200

## 17'

E (M06/BS1) = -805.851901 au



H(M06/BS1) = -805.652083 au

G(M06/BS1) = -805.707107 au

E(M06/BS2//M06/BS1) = -806.346605 au

E(M06-D3/BS2//M06/BS1) = -806.348994 au

Au	-0.03292300	-0.00981200	-0.00142400
P	2.35108600	0.00458700	0.00119400
C	3.13356100	-0.44341100	1.59213400
H	4.22771000	-0.39772100	1.51225900
H	2.79763500	0.24858100	2.37281200
H	2.83367100	-1.45840200	1.87685900
C	3.14504200	-1.13152500	-1.19147900
H	2.82693600	-0.87759500	-2.20912600
H	4.23850400	-1.05851700	-1.12477700
H	2.83844000	-2.16224400	-0.97995700
C	3.10650700	1.62221100	-0.39482300
H	4.20210200	1.55487700	-0.36848700
H	2.78742900	1.94276500	-1.39310800
H	2.77228800	2.37112100	0.33225500
C	-2.08114000	-0.01686200	-0.00084700
C	-2.91039100	1.09297100	-0.00019100
C	-2.96857400	-1.14538200	0.00120700
N	-4.22142300	0.68192900	0.00208000
C	-4.26622400	-0.68910100	0.00290700
H	-2.67565300	-2.19149100	0.00145300
H	-5.21464600	-1.21364100	0.00475900
H	-5.02820300	1.28976500	0.00275400
H	-2.67432000	2.15189400	-0.00111000

### LAuOH

E (M06/BS1) = -672.231395 au

H(M06/BS1) = -672.093572 au

G(M06/BS1) = -672.141902 au

E(M06/BS2//M06/BS1) = -672.685540 au

E(M06-D3/BS2//M06/BS1) = -672.687074 au

Au	0.76600600	-0.00046600	-0.00008900
P	-1.52785700	0.00185800	-0.00020500
C	-2.28436300	1.65745900	-0.10870200
H	-3.37923800	1.57847500	-0.09816300
H	-1.95678100	2.26800200	0.74024400
H	-1.96432300	2.14724700	-1.03528300
C	-2.28045200	-0.92213600	-1.38169100
H	-1.95014300	-1.96651900	-1.34803500
H	-3.37578400	-0.88507900	-1.31863200
H	-1.95517700	-0.48547300	-2.33276500
C	-2.28115200	-0.73224300	1.49065600
H	-3.37622500	-0.70809500	1.41881400
H	-1.94618800	-1.76989200	1.59901300
H	-1.96218000	-0.16946600	2.37533300
O	2.78178600	-0.10383100	0.00480200

H 3.09094900 0.81190400 -0.03037600

**17"**

E (M06/BS1) = -805.863634 au

H(M06/BS1) = -805.664663 au

G(M06/BS1) = -805.719392 au

E(M06/BS2//M06/BS1) = -806.361442 au

E(M06-D3/BS2//M06/BS1) = -806.363795 au

Au	0.03002800	0.00061800	-0.00021200
P	-2.28422700	-0.00120400	0.00005500
C	-3.03494200	-0.91378400	1.38910200
H	-4.13000000	-0.86593600	1.32879400
H	-2.71521200	-1.96137300	1.35718500
H	-2.70307700	-0.47713200	2.33765500
C	-3.03190200	1.65886500	0.09723500
H	-2.70352300	2.26260600	-0.75605400
H	-4.12689300	1.58228200	0.08776000
H	-2.71041400	2.15428900	1.02012500
C	-3.03815900	-0.74512300	-1.48470200
H	-4.13286500	-0.70652000	-1.41382000
H	-2.71214700	-0.19757200	-2.37605700
H	-2.71615500	-1.78810400	-1.57858800
C	4.22358000	0.70768400	0.00058400
C	2.89992200	1.10366600	0.00062900
H	5.09077800	1.36122300	0.00109100
C	4.22214500	-0.71149200	-0.00033900
N	2.08466800	0.00029800	-0.00022000
C	2.89769400	-1.10474300	-0.00079200
H	5.08799200	-1.36682900	-0.00070700
H	2.46786400	-2.10249000	-0.00149500
H	2.47211300	2.10227500	0.00128500

**TS<sub>9,6</sub>**

E (M06/BS1) = -1039.501868 au

H(M06/BS1) = -1039.162189 au

G(M06/BS1) = -1039.239386 au

E(M06/BS2//M06/BS1) = -1040.085659 au

E(M06-D3/BS2//M06/BS1) = -1040.093563 au

Au	-0.90650300	-0.02957000	-0.20636800
P	0.09254700	2.08269100	0.00347800
C	1.25134600	2.47117200	-1.34890000
H	1.66576800	3.47874100	-1.21353800
H	2.06831500	1.73893900	-1.33434000
H	0.73850000	2.41485100	-2.31543200
C	-1.06299900	3.49227400	0.04684000
H	-1.73669900	3.39033900	0.90470600
H	-0.50598700	4.43464800	0.13177800
H	-1.66270200	3.50685500	-0.86991600

C	1.09993700	2.26026200	1.51166900
H	1.50173700	3.28039800	1.57183400
H	0.48946500	2.05844800	2.39858800
H	1.93336800	1.54615300	1.48293100
C	1.18036400	-1.75444400	-0.92600700
C	0.04440000	-2.36602300	-0.47822600
C	1.38997900	-1.53514100	-2.39520900
H	2.27215700	-2.08879000	-2.74378500
H	0.52185500	-1.87017500	-2.97244000
H	1.56535500	-0.47496300	-2.62261000
C	3.41594700	-0.62648400	-0.37173100
C	2.23851100	-1.29157300	-0.05323600
H	3.75139800	-0.38667500	-1.37522900
C	4.09427100	-0.33804400	0.83263500
N	2.20658000	-1.40464400	1.32150600
C	3.31931800	-0.83229200	1.86217200
H	5.04861500	0.16296500	0.93988300
H	3.47939400	-0.83098500	2.93295000
H	1.46667900	-1.83638000	1.85866700
H	-0.66768800	-2.78200600	-1.18925800
H	-0.09283200	-2.66332000	0.56261000
C	-3.12913900	-1.28953900	0.64467100
C	-3.12307600	-1.15040900	-0.56675500
H	-3.27439600	-1.10791400	-1.62843500
C	-3.12132000	-1.45929700	2.08623300
H	-3.12240400	-0.48967100	2.59841800
H	-4.00995200	-2.01600500	2.40729000
H	-2.23575300	-2.02008600	2.41077200

### TS<sub>6-13</sub>

E (M06/BS1) = -1039.480848 au

H(M06/BS1) = -1039.145256 au

G(M06/BS1) = -1039.221617 au

E(M06/BS2//M06/BS1) = -1040.061742 au

E(M06-D3/BS2//M06/BS1) = -1040.069186 au

Au	0.05622100	0.80622400	0.00386700
P	-2.28891700	0.80280100	0.14210800
C	-3.00222200	-0.24255900	1.45434400
H	-4.09310100	-0.12315900	1.47974600
H	-2.75918700	-1.29274800	1.25847800
H	-2.58163000	0.04230100	2.42524300
C	-2.96510400	2.46386300	0.47223000
H	-2.65512500	3.15162900	-0.32239200
H	-4.06132700	2.42678900	0.51360100
H	-2.57867900	2.83683300	1.42731400
C	-3.13091900	0.26382700	-1.38214900
H	-4.21961700	0.31891300	-1.25354600
H	-2.83053200	0.90707400	-2.21670300
H	-2.84216000	-0.76805800	-1.61309900

C	1.85274300	-2.10372300	0.76772800
C	3.00497500	-1.59944000	0.17819500
C	1.70095700	-2.02091400	2.25056700
H	1.28142900	-2.94288700	2.67004000
H	2.65891800	-1.81896800	2.73842300
H	1.00670600	-1.20339600	2.50539200
C	-0.56395100	-2.85475400	0.46401200
C	0.71201900	-2.48407000	0.01671100
H	-0.86299000	-2.92028200	1.50473800
C	-1.35595400	-3.13283500	-0.65426900
N	0.66882500	-2.54462300	-1.37024800
C	-0.55980000	-2.92741900	-1.77523200
H	-2.38970700	-3.45718400	-0.66235600
H	-0.79202000	-3.03589400	-2.82736200
H	1.43619000	-2.33413500	-1.99518700
H	3.88947300	-1.47510300	0.80340400
H	3.21859300	-1.78136800	-0.87678300
H	2.54963100	-0.25534100	0.07162200
C	2.11824400	1.01312000	-0.15270600
C	2.98814200	1.86522600	-0.38169100
C	4.02509700	2.83697500	-0.64497400
H	4.72116100	2.92484300	0.19846700
H	4.59490700	2.58838600	-1.54897300
H	3.57422000	3.82660200	-0.80203600

### TS<sub>14-6</sub>

E(M06/BS1) = -1249.518289 au

H(M06/BS1) = -1249.093912 au

G(M06/BS1) = -1249.175625 au

E(M06/BS2//M06/BS1) = -1250.180867 au

E(M06-D3/BS2//M06/BS1) = -1250.192868 au

Au	0.92513800	-1.01224700	-0.04258100
P	3.02724900	-0.05244100	0.34811200
C	3.47279800	0.03441000	2.11485900
H	4.44327200	0.53234300	2.23851100
H	2.70575100	0.59879300	2.65809500
H	3.52746300	-0.97551500	2.53597800
C	4.46145300	-0.84750600	-0.44668100
H	4.31696500	-0.86929300	-1.53231100
H	5.37804400	-0.29089000	-0.21286000
H	4.56111600	-1.87690400	-0.08519300
C	3.08124000	1.68206200	-0.21020600
H	4.04739500	2.13832800	0.04149500
H	2.92212600	1.72737000	-1.29365600
H	2.26946200	2.24185600	0.27265500
C	-1.69249600	1.71904900	0.82039800
C	-2.70577400	2.82422800	1.17221200
H	-3.37444700	3.03747000	0.32879500
H	-3.31612100	2.52120500	2.03329000
H	-2.19616800	3.75813100	1.44376600

C	-2.46671200	0.42617400	0.59102600
C	-3.08336600	-0.36499400	1.61599000
C	-4.17368100	-1.01710400	1.08006400
C	-4.31896300	-0.55032300	-0.23707800
N	-3.38279500	0.36217900	-0.48525200
H	-3.23103200	0.82119200	-1.37811100
H	-1.65358900	-0.58282800	0.21610900
H	-2.66150200	-0.51360400	2.60448100
H	-4.79929000	-1.76232300	1.55487100
H	-5.04092200	-0.83915500	-0.99283600
C	-0.73876300	1.53062700	2.00759000
H	-0.06467900	0.67386900	1.85767200
H	-0.11816900	2.42577400	2.14206000
H	-1.29394200	1.37682700	2.94224200
C	-0.70745500	1.45435200	-1.63059000
C	0.07416400	2.31130100	-2.45292500
H	-1.03782800	0.45440200	-1.89248000
C	0.30791600	3.45812500	-1.73754200
H	-0.30638100	4.03630300	0.19945500
H	0.41865900	2.10319400	-3.45908600
H	0.85216400	4.35967800	-1.98854900
C	-0.93009600	2.10009400	-0.42731800
N	-0.30032000	3.32093500	-0.51547200
C	-0.97383100	-1.76501300	-0.36570100
C	-1.82265100	-2.56362000	-0.77835300
C	-2.77905300	-3.54292600	-1.26400100
H	-3.39768400	-3.14506900	-2.07820600
H	-2.24627900	-4.42057800	-1.65440300
H	-3.44562900	-3.89184300	-0.46494500

### 15'

E (M06/BS1) = -1122.478402 au

H(M06/BS1) = -1122.319032 au

G(M06/BS1) = -1122.381024 au

E(M06/BS2//M06/BS1) = -1123.116104 au

E(M06-D3/BS2//M06/BS1) = -1123.118312 au

Au	-0.15395400	-0.24711700	0.00303000
P	2.09444500	0.16247500	-0.00083700
C	2.49775800	1.93326800	0.14626700
H	3.58542400	2.07973800	0.12803400
H	2.04163000	2.48199300	-0.68525900
H	2.09290600	2.32563200	1.08575900
C	3.01613400	-0.63254400	1.35464400
H	2.89311400	-1.71963900	1.29682300
H	4.08262500	-0.38228700	1.28548100
H	2.62318600	-0.28653200	2.31718700
C	2.94852800	-0.37584600	-1.51777800
H	4.01580900	-0.12504500	-1.46277200
H	2.83502400	-1.45863400	-1.64027000
H	2.50135400	0.12261200	-2.38503400

C	-2.95349400	0.34597600	-0.00148000
O	-2.20718200	-0.71413800	-0.00478200
O	-2.53696000	1.50535800	0.00597500
C	-4.43538100	0.04098600	-0.00700100
H	-4.69774200	-0.55812100	0.87317300
H	-5.02374200	0.96279500	-0.00862800
H	-4.69200600	-0.55820600	-0.88873900

TFA

E (M06/BS1) = -526.595429 au

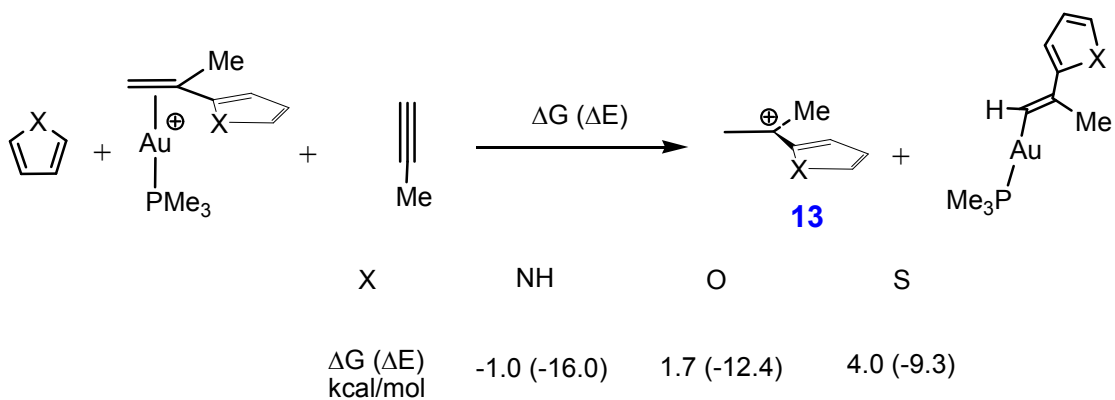
H(M06/BS1) = -526.548512 au

G(M06/BS1) = -526.586668 au

E(M06/BS2//M06/BS1) = -526.8270838 au

E(M06-D3/BS2//M06/BS1) = -526.827388 au

C	0.93399000	0.15589300	0.00022000
O	1.49374200	1.21754500	-0.00006500
C	-0.59552500	0.00141900	-0.00002300
O	1.49478100	-1.04488000	-0.00004900
H	2.46432900	-0.93207800	-0.00008400
F	-0.98938100	-0.67322800	-1.07783900
F	-0.98965700	-0.67042200	1.07945600
F	-1.17688400	1.18885900	-0.00163800



**Scheme S1.** Comparison of the stability of the carbocation **13** for different heterocycles calculated based on the reaction shown above (a part of the mechanism illustrated in Figure 4). It follows that the replacement of pyrrole by less-nucleophilic substrates, such as furan and thiophene, decreases the stability of carbocation **13** by about 2.0-5.0 kcal/mol.

## Computational details

Gaussian 09<sup>S1</sup> was used to fully optimize all the structures reported in this paper at the M06 level of density functional theory (DFT)<sup>S2</sup> in acetic acid using the CPCM<sup>S3</sup> solvation model. The effective-core potential of Hay and Wadt with a double- $\xi$  valence basis set (LANL2DZ)<sup>S4</sup> was chosen to describe Au. The 6-31G(d) basis set was used for other atoms.<sup>S5</sup> A Polarization function of  $\xi_f = 1.050$  was also added for Au.<sup>S6</sup> This basis set combination will be referred to as BS1. Frequency calculations were carried out at the same level of theory as those for the structural optimization. Transition structures were located using the Berny algorithm. Intrinsic reaction coordinate (IRC)<sup>S7</sup> calculations were used to confirm the connectivity between transition structures and minima. To further refine the energies obtained from the M06/BS1 calculations, we carried out single-point energy calculations for all of the structures with a larger basis set (BS2) in acetic acid using the CPCM solvation model. BS2 utilizes def2-TZVP for all atoms along with the effective core potential including scalar relativistic effects<sup>S8</sup> for Au. We also performed single-point energy calculations employing the D3 empirical dispersion correction by Grimme. The potential and Gibbs free energies obtained from the M06-D3/BS2//M06/BS1 calculations in acetic acid are used for interpreting the obtained results.

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