This is the peer reviewed version of the following article: Dalton Trans. 2017, 46, 12257, which has been published in final form at http://pubs.rsc.org/en/content/articlelanding/2017/dt/c7dt03154h#!divAbstract

Journal Name

COMMUNICATION

Gold-Catalyzed Domino Cyclization-Alkynylation Reactions with EBX Reagents: New Insights into the Reaction Mechanism

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

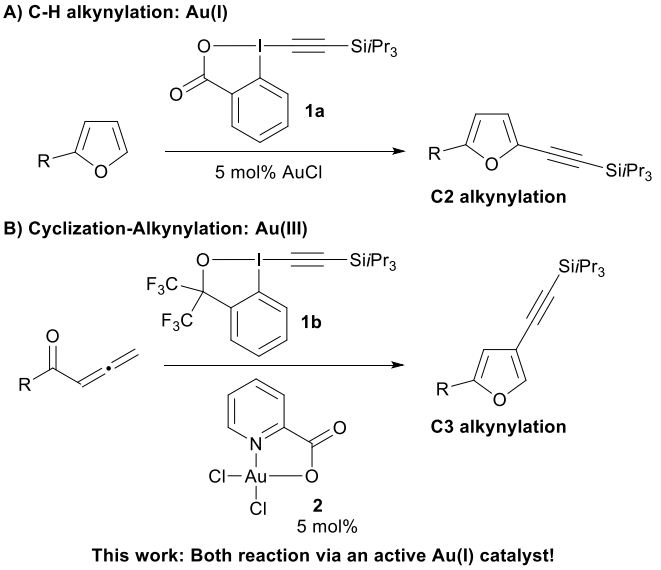
www.rsc.org/

Hossein Ghari,[a] Yifan Li,[b] Roohollah Roohzadeh,[a] Paola Caramenti,[b] Jerome Waser*[b] and Alireza Ariafard*[a,c]

Gold-catalyzed domino processes constitute a useful alternative to C-H functionalization for the synthesis of functionalized (hetero)arenes. Herein, we report computational studies on the gold-catalyzed cyclization alkynylation of keto-allenes with ethynylbenziodoxole (EBX) reagents, which identified a gold(I) picolinate complex as the active catalyst, giving first mechanistic insights into this transformation.

Alkynyl substituted heterocycles are interesting building blocks for synthetic chemistry, due to the preponderance of heterocycles in drugs, agrochemicals and organic materials, as well as the multiple transformations available for the functionalization of the alkyne group.[1] These compounds are usually accessed using the Sonogashira cross coupling reaction,[2] but this transformation is based on the availability of the corresponding aryl halides. In order to develop more efficient synthetic methods, direct C-H alkynylation reactions have been introduced in the last decades.[3] Nevertheless, these approaches are usually based on the use of directing groups, or are limited to the most reactive position of heterocycles.

In order to increase the flexibility and efficiency for the synthesis of alkynylated heterocycles, Waser and co-workers turned to the use of domino cyclization-alkynylation reactions.[4,5] This approach gave access to alkynylated heterocycles, which could not be synthesized via C-H functionalization. In particular, the gold(III)-catalyzed cyclization-alkynylation of keto allenes using EthynylBenziodoXole (EBX) reagent **1b** gave access to C3-alkynylated poly-substituted furans, whereas C2-alkynylated furans were obtained via C-H alkynylation with TIPS-EBX (**1a**) and a gold (I) catalyst (Scheme 1).[4b] The use of gold(III) dichloride picolinate catalyst **2** was crucial for success, as well as the use of bistrifluoromethyl benziodoxole **1b**. As the reaction mechanism was not known, it was very difficult to rationalize the differences between the two catalytic processes.



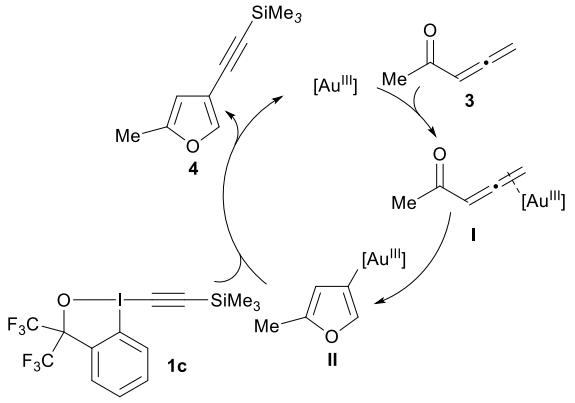
Scheme 1 C-H- vs domino cyclization-alkynylation: two different active catalysts?

Herein, we report computational studies on the domino cyclization-alkynylation reaction, which indicated that an *in situ* formed gold(I) complex is in fact the active catalyst. The picolinate ligand was found to significantly diminish the activation energy for the oxidative addition of EBX reagents on a gold(I) intermediate. These first insights into the reaction mechanism will be useful for the development of domino processes using gold catalysts and EBX reagents.[6]

As no gold complex relevant to the catalytic cycle could be isolated, proposing a mechanism for the domino alkynylation process was especially challenging. Based on the work of Hashmi and co-workers on the gold-catalyzed cyclization of

[a] *Department of Chemistry, Islamic Azad University, Central Tehran Branch, Shahrak Gharb, Tehran, Iran.*
[b] *Laboratory of Catalysis and Organic Synthesis, Ecole Polytechnique Fédérale de Lausanne, EPFL SB ISIC LCSO, BCH 4306, 1015 Lausanne (CH), Fax: (+) 41 21 693 97 00, E-mail: jerome.waser@epfl.ch, Homepage: http://lcso.epfl.ch*
[c] *School of Physical Science (Chemistry), University of Tasmania, Private Bag 75, Hobart TAS 7001, Australia. E-mail: alirezaa@utas.edu.au.*
Electronic Supplementary Information (ESI) available: details of computational methods and experimental procedures. See DOI: 10.1039/x0xx00000x

allenes,[7] activation of the π-system of allene **3** by the gold catalyst (**I**) followed by cyclization to give aurated furan **II** can be reasonably expected (Scheme 2).[8] At this point, alkynylation with EBX **1c** would close the catalytic cycle. The alkynylation step was particularly intriguing, as the superiority of Au(III) catalyst **2** seemed to exclude a redox mediated process. We initially hypothesized an activation of the triple bond of **1c** by the gold catalyst, followed by insertion, α-elimination and 1,2-silyl shift to give the observed product. Ariafard showed later by computation that an iodine to gold alkyne exchange was possible on gold(I) complexes.[9a] If this transformation can also be achieved for gold(III) intermediates, other mechanisms would need to be considered for the alkynylation step.



Scheme 2 Working model for the reaction mechanism with methyl allene **3** and reagent **1c**.

In order to investigate this possibility, we setup to perform computation using B3LYP-D3-CPCM/def2-QZVP:6-311+G(2d,p)//B3LYP-CPCM/LANL2DZ:6-31G(d) calculations in ^{i}PrOH.[10] An energetically accessible cyclization pathway was identified for the reaction of complex **2** with allene **3** in presence of sodium bicarbonate to give organogold intermediate **9** (Fig. 1). This process involved ligand exchange to give allene complex **6**, cyclization via transition state $\mathbf{TS_{6\text{-}7}}$ and deprotonation. The energy barriers for ligand exchange and cyclization were higher (27.6 and 27.0 kcal/mol respectively) than for deprotonation. The more challenging alkynylation step was investigated next (Fig. 2). Ligand exchange between chloride and EBX reagent **1c** via associative transition state $\mathbf{TS_{9\text{-}10}}$ required only 17.4 kcal/mol and gave π-bond alkyne complex **10**. As observed previously on gold(I) intermediates,[9a] alkyne shift from iodine to gold was easy, with a barrier of only 2.8 kcal/mol, and led to the formation of the more stable gold alkynyl complex **11**. However, in contrast to related gold(I) and palladium(II) complexes,[9] the favoured reaction pathway for **11** was not 1,2-aryl shift, but reductive elimination on gold via low lying three-atom transition state $\mathbf{TS_{11\text{-}12}}$ to give gold(I) complex **12** and iodonium bound alkyne **13**. This result was unexpected, and did not allow to close the catalytic cycle, as a stoichiometric amount of gold(III) complex would be needed.

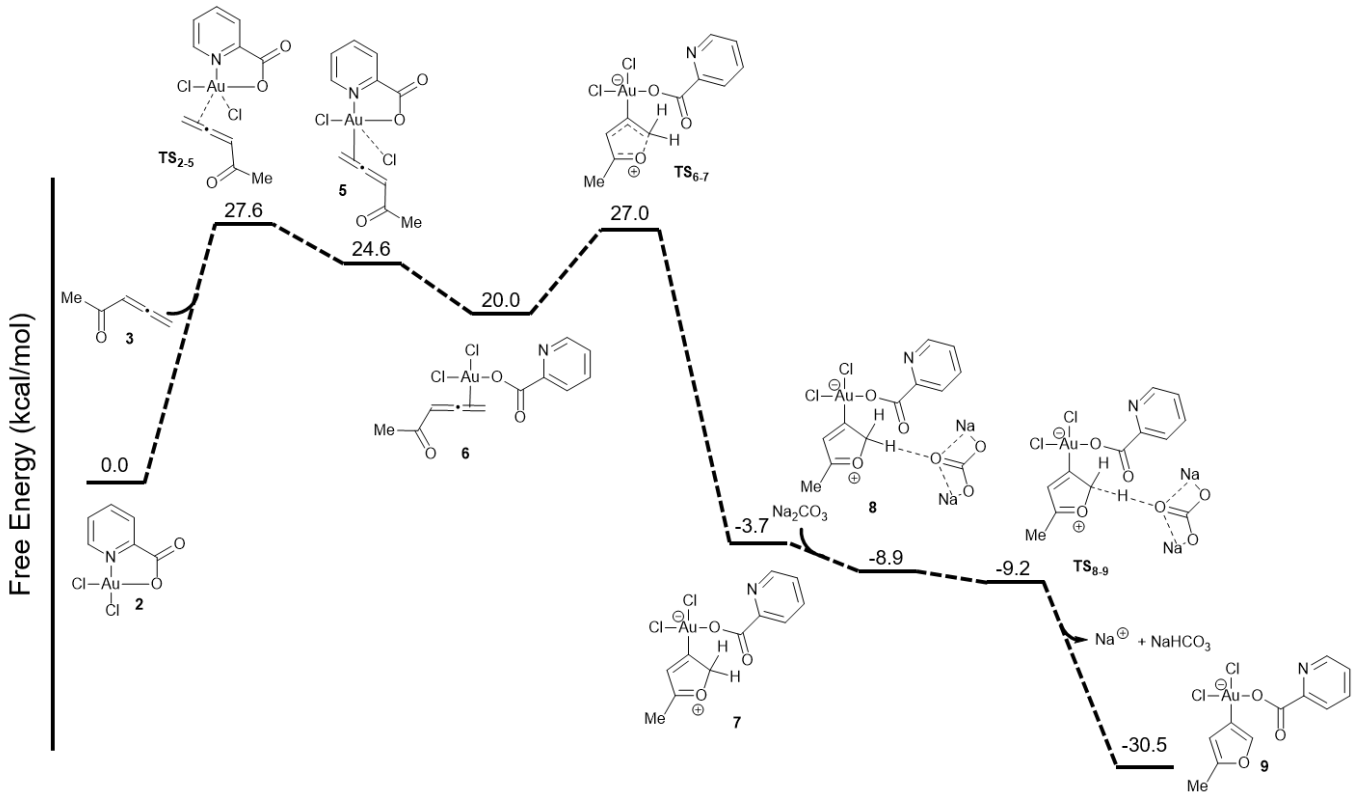


Fig. 1 Gibbs energy profile for the cyclization of allene **3** mediated by gold(III) complex **2**.

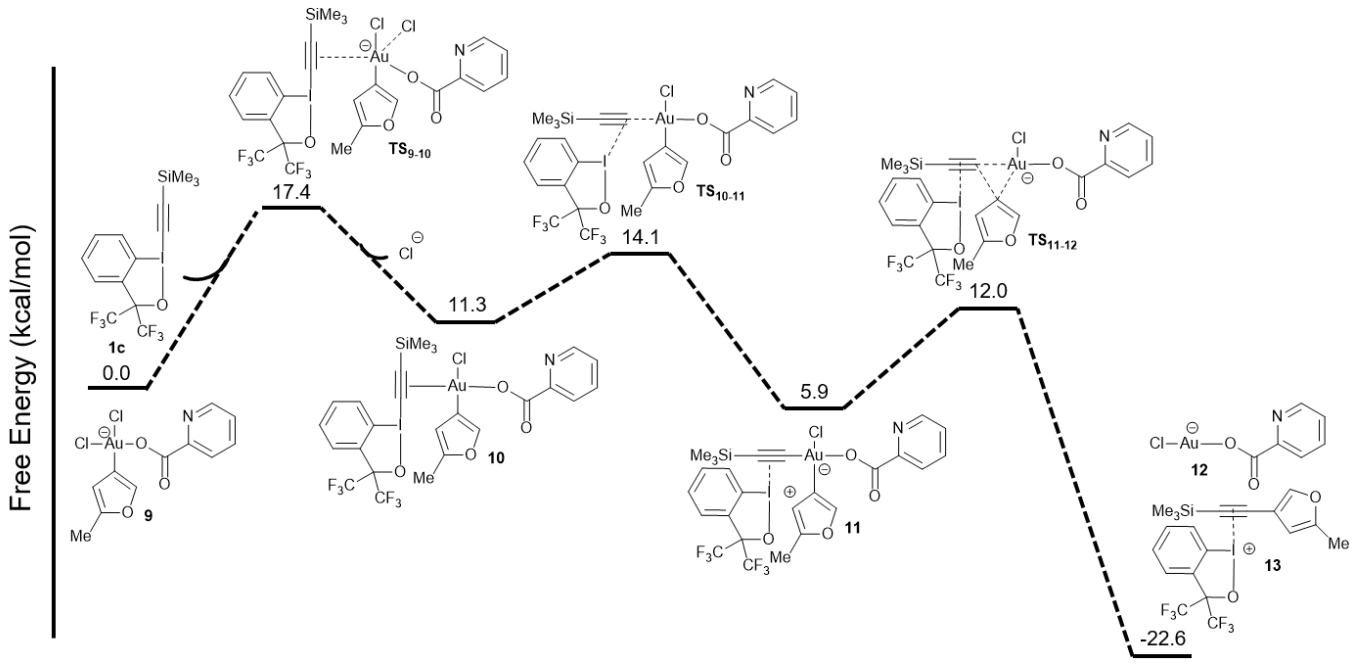


Fig. 2 Gibbs energy profile for the reaction of gold(III) intermediate **9** with EBX **1c**.

We wondered if complex **12** could also be a competent catalyst. In fact, **12** was efficient to promote the cyclization of allene **3** to organogold(I) furan complex **18** (Gibss energy barriers for ligand exchange, cyclization and deprotonation of 5.9, 17.0 and 1.9 kcal/mol respectively, Fig. 3). The reaction of **18** with reagent **1c** was then examined (Fig. 4). After a reorientation of the picolinic acid ligand to give complex **19**, an oxidative addition transition state $\mathbf{TS_{19\text{-}20}}$ was observed, with an energy of only 21.7 kcal/mol.[11] The formed gold(III) complex **20** can then undergo reductive elimination via three-atom transition state $\mathbf{TS_{20\text{-}22}}$ (15.8 kcal/mol) to give the gold π-complex **22** of the product **4**, which is in equilibrium with linear complex **23**. Importantly, complex **18** needs to rearrange to **19** for accessing transition state $\mathbf{TS_{19\text{-}20}}$ in which the nitrogen atom of the picolinate ligand is capable of interacting with the gold centre. When the nitrogen atom was not involved in the transition state, the energy was found to be 6.9 kcal/mol higher (Fig. 5, $\mathbf{TS^{II}_{19\text{-}20}}$).

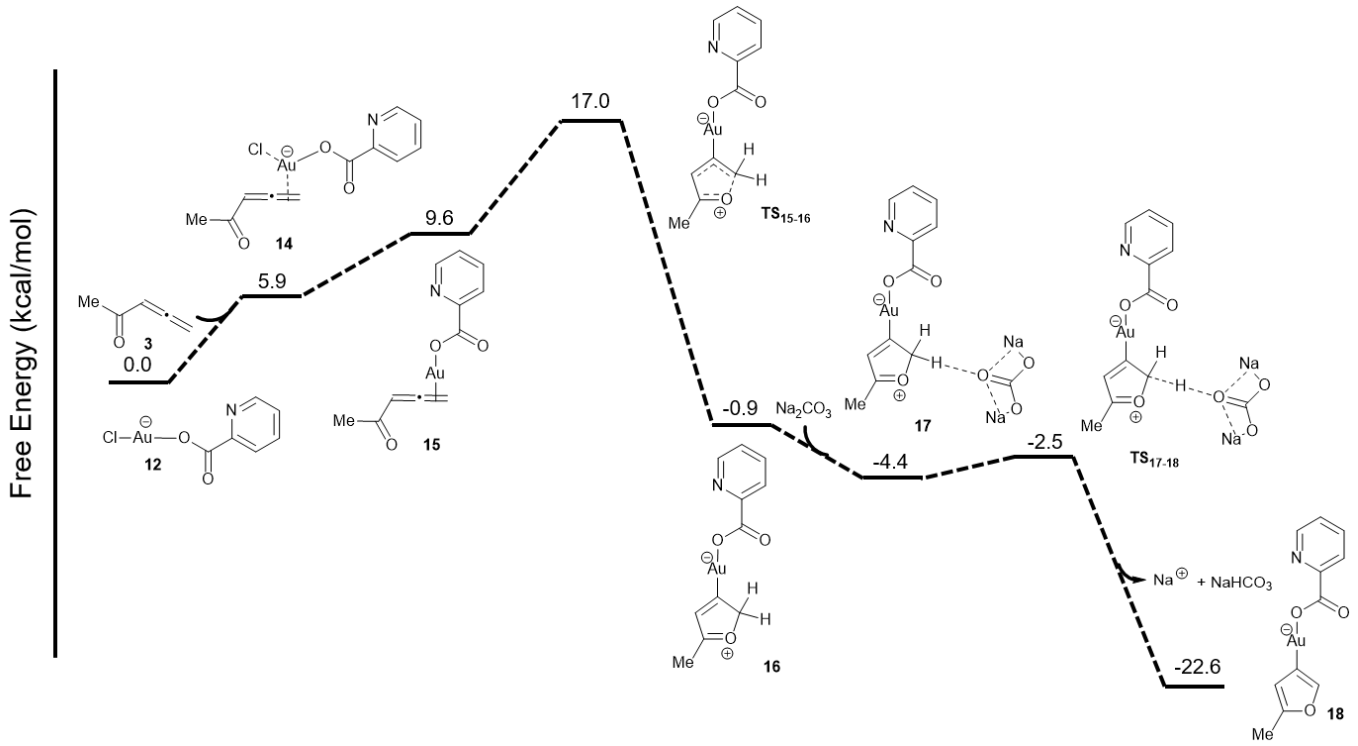


Fig. 3 Gibbs energy profile for the cyclization of allene **3** mediated by gold(I) complex **12**.

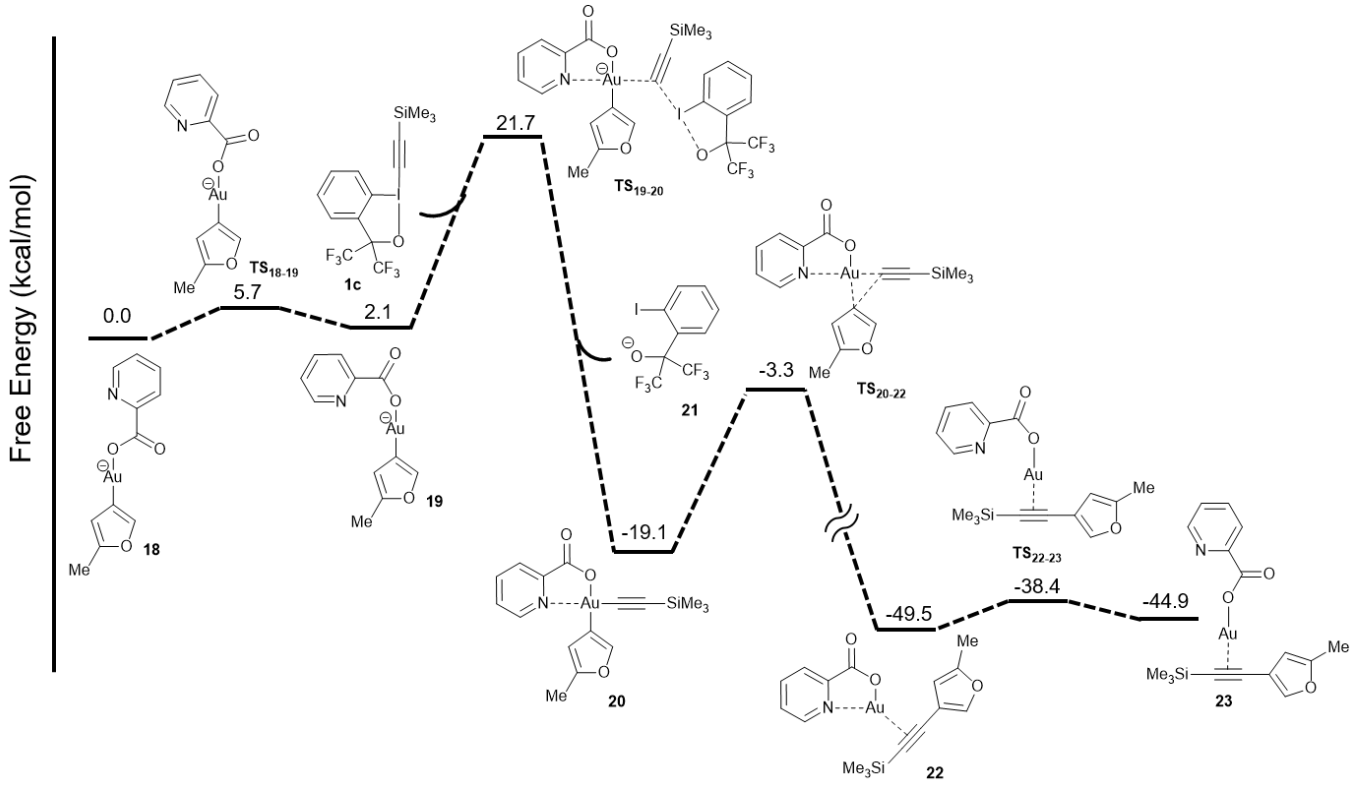


Fig. 4 Gibbs energy profile for the reaction of gold(I) intermediate **18** with EBX **1c**.

The transition states $\mathbf{TS^{III}_{11\text{-}12}}$ bearing a carbonate ligand or $\mathbf{TS^{IV}_{11\text{-}12}}$ with no extra ligand were also higher in energy. This result is in accordance with the importance of the picolinic acid ligand observed experimentally.

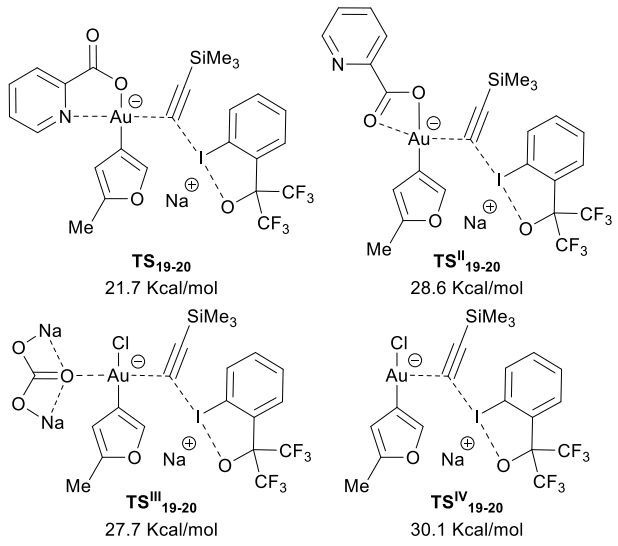
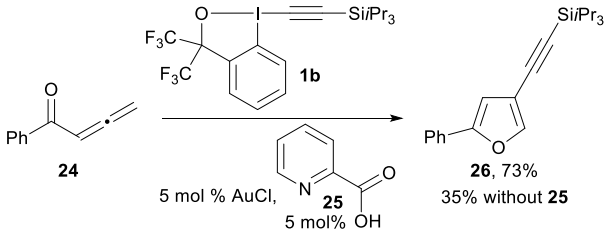


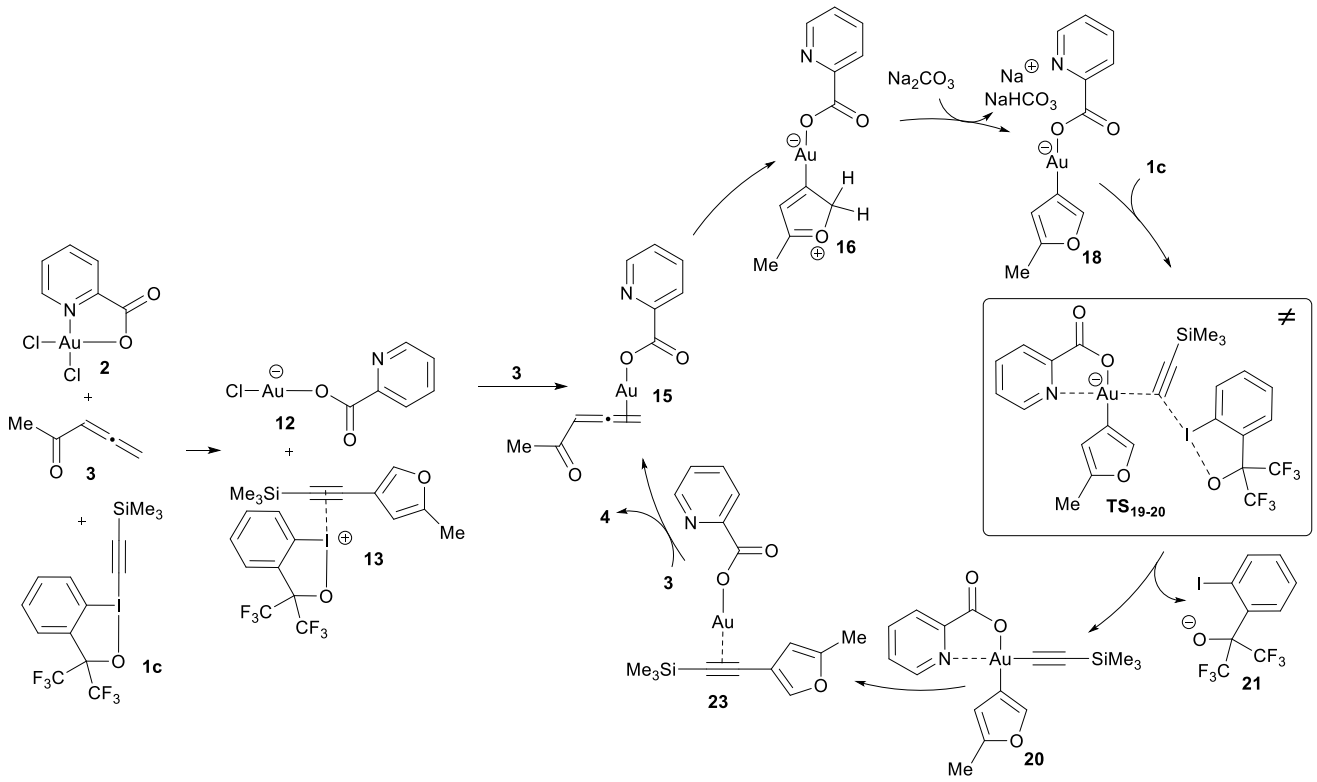
Fig. 5 Compared transition states for the oxidative addition step.

In retrospect, it appears surprizing that gold(I) catalysts had been found inactive in our original work.[4b] However, preliminary catalyst screening experiments were performed with another hypervalent iodine reagent (TIPS-EBX (**1a**)), which was less efficient in this process. We decided therefore to re-investigated the reaction of phenyl-allene ketone **24** in presence of a gold(I) catalyst, but with EBX reagent **1b**. When Au(I)Cl was used as catalyst with picolinic acid (**25**) as additive, the cyclization alkynylation product **26** was obtained in yield and reaction time comparable to those with gold(III) complex **2** (Scheme 3). When **25** was omitted, **26** could be obtained only in moderate yield.



Scheme 3 Gold(I) catalyzed cyclization-alkynylation process.

Based on the computational results and this experimental confirmation, a refined mechanism can be proposed (Scheme 4). In an initiation step, allene **3** and EBX **1c** react with gold complex **2** to give gold(I) complex **12** and iodonium **13**. The former then reacts with allene **3** to initiate a gold (I/III) catalytic cycle via complex **15**. Cyclization followed by deprotonation gives then organogold intermediate **18**. Oxidative addition proceeds via key transition state $\mathbf{TS_{19\text{-}20}}$, for which the picolinic acid ligand plays an essential role in lowering the energy The resulting gold(III) complex **20** then undergoes reductive elimination to give π-complex **23**. Ligand exchange with allene **3** via a three coordinate intermediate (**27**) lying 9.6 kcal/mol above **23** closes the catalytic cycle.



Scheme 4 Refined catalytic cycle for the cyclization-alkynylation of allene **3**.

In summary, we have performed computational studies of the gold-catalyzed cyclization-alkynylation domino process of keto-allenes. Our results showed that the used gold(III) complex was a precursor of an active gold(I) catalyst, and that the picolinic acid ligand was essential for lowering the energy of the key oxidative addition transition state. These mechanism insights will be highly useful for developing new transformations based on gold catalysis and hypervalent iodine reagents.

Computational Details

Gaussian 09[12] was used to fully optimize all the structures reported in this paper at the B3LYP level of density functional theory (DFT)[13] in ^{i}PrOH using the CPCM[14] solvation model. The effective-core potential of Hay and Wadt with a double-ξ valence basis set (LANL2DZ)[15] was chosen to describe Au and I. The 6-31G(d) basis set was used for other atoms.[16] Polarization functions were also added for Au (ξ_f =1.050) and I (ξ_f = 0.289).[17] 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)[18] calculations were used to confirm the connectivity between transition structures and minima. To further refine the energies obtained from the B3LYP/BS1 calculations, we carried out single-point energy calculations by employing the D3 empirical dispersion correction[19] for all of the structures with a larger basis set (BS2) in ^{i}PrOH using the CPCM solvation model. BS2 utilizes the quadruple-ζ valence def2-QZVP basis set[20] on Au and I and 6-311+G(2d,p) basis set for other atoms. The relative Gibbs free energies obtained from the B3LYP-D3-CPCM/def2-QZVP:6-311+G(2d,p)//B3LYP-CPCM/LANL2DZ:6-31(G) calculations are adjusted by the method proposed by Okuno[21] and finally used for interpretation.

Acknowledgments

We thank the Swiss National Science Foundation (Grant No. 200021_159920) for financial support.

Notes and references

1 F. Diederich, P. J. Stang and R. R. Tykwinski, *Acetylene Chemistry: Chemistry, Biology and Material Science*, Wiley-VCH, 2005.

2 R. Chinchilla and C. Najera, *Chem. Rev.*, 2007, **107**, 874.

3 Review: (a) J. P. Brand and J. Waser, *Chem. Soc. Rev.*, 2012, **41**, 4165. Selected examples: (b) I. V. Seregin, V. Ryabova and V. Gevorgyan, *J. Am. Chem. Soc.*, 2007, **129**, 7742. (c) M. Tobisu, Y. Ano and N. Chatani, *Org. Lett.*, 2009, **11**, 3250. (d) Y. H. Gu and X. M. Wang, *Tetrahedron Lett.*, 2009, **50**, 763. (e) J. P. Brand, J. Charpentier and J. Waser, *Angew. Chem., Int. Ed.*, 2009, **48**, 9346. (f) F. Besselievre and S. Piguel, *Angew. Chem., Int. Ed.*, 2009, **48**, 9553. (g) X. Jie, Y. Shang, P. Hu and W. Su, *Angew. Chem., Int. Ed.*, 2013, **52**, 3630. (h) C. Feng and T.-P. Loh, *Angew. Chem., Int. Ed.*, 2014, **53**, 2722. (i) F. Xie, Z. Qi, S. Yu and X. Li, *J. Am. Chem. Soc.*, 2014, **136**, 4780. (j) M. Shang, H. L. Wang, S. Z. Sun, H. X. Dai and J. Q. Yu, *J. Am. Chem. Soc.*, 2014, **136**, 11590. (k) P. Wang, G. C. Li, P. Jain, M. E. Farmer, J. He, P. X. Shen and J. Q. Yu, *J. Am. Chem. Soc.*, 2016, **138**, 14092.

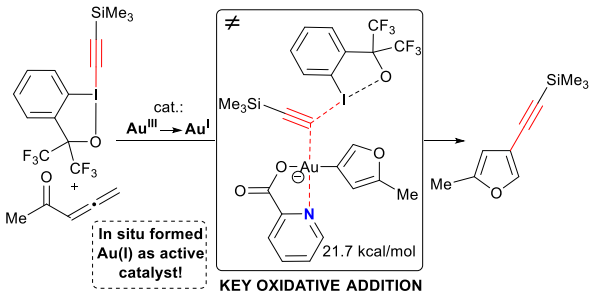
4 (a) J. P. Brand, C. Chevalley and J. Waser, *Beilstein J. Org. Chem.*, 2011, **7**, 565. (b) Y. Li, J. P. Brand and J. Waser, *Angew. Chem., Int. Ed.*, 2013, **52**, 6743. (c) Y. Li and J. Waser, *Angew. Chem., In.t Ed.*, 2015, **54**, 5438.

5 Selected examples of domino cyclization-alkynylation reactions for the synthesis of alkynylated heterocycles: (a) A. Arcadi, S. Cacchi, G. Fabrizi, F. Marinelli and L. M. Parisi, *J.*

Org. Chem., 2005, **70**, 6213. (b) B. Yao, Q. Wang and J. P. Zhu, *Angew. Chem., Int. Ed.*, 2012, **51**, 12311.
6 Y. Li, D. P. Hari, M. V. Vita and J. Waser, *Angew. Chem., Int. Ed.*, 2016, **55**, 4436.
7 (a) A. S. K. Hashmi, L. Schwarz, J.-H. Choi and T. M. Frost, *Angew. Chem., Int. Ed.*, 2000, **39**, 2285. (b) A. Hossein Bagi, Y. Khaledi, H. Ghari, S. Arndt, A. S. K. Hashmi, B. F. Yates, A. Ariafard*, J. Am. Chem. Soc.* 2016, **138**, 14599.
8 To simplify computations, the mechanism was studied with smaller allene ketone **3** and trimethylsilyl EBX reagent **1c**.
9 (a) A. Ariafard, *ACS Catalysis*, 2014, **4**, 2896. (b) A. Ariafard *Organometallics* 2014, **33**, 7318.
10 See computational details. For Cartesian coordinates see table S1 in the ESI.
11 For review on reactions involving Au(I)/Au(III), see: (a) P. Garcia, M. Malacria, C. Aubert, V. Gandon and L. Fensterbank, *Chemcatchem*, 2010, **2**, 493. (b) H. A. Wegner and M. Auzias, *Angew. Chem., Int. Ed.*, 2011, **50**, 8236. (c) M. N. Hopkinson, A. D. Gee and V. Gouverneur, *Chem. Eur. J.*, 2011, **17**, 8248. (d) T. C. Boorman and I. Larrosa, *Chem. Soc. Rev.*, 2011, **40**, 1910. (e) T. de Haro and C. Nevado, *Synthesis*, 2011, 2530. Selected examples: (f) X. Yao and C.-J. Li, *Org. Lett.*, 2006, **8**, 1953. (g) M. N. Hopkinson, J. E. Ross, G. T. Giuffredi, A. D. Gee and V. Gouverneur, *Org. Lett.*, 2010, **12**, 4904. (h) L. T. Ball, G. C. Lloyd-Jones and C. A. Russell, *Science*, 2012, **337**, 1644. (i) Y. Ma, S. Zhang, S. Yang, F. Song and J. You, *Angew. Chem., Int. Ed.*, 2014, **53**, 7870. (j) M. Joost, A. Zeineddine, L. Estévez, S. Mallet−Ladeira, K. Miqueu, A. Amgoune and D. Bourissou, *J. Am. Chem. Soc.*, 2014, **136**, 14654. (k) X. C. Cambeiro, N. Ahlsten and I. Larrosa, *J. Am. Chem. Soc.*, 2015, **137**, 15636. (l) C. Y. Wu, T. Horibe, C. B. Jacobsen and F. D. Toste, *Nature*, 2015, **517**, 449. (m) M. Hofer, A. Genoux, R. Kumar and C. Nevado, *Angew. Chem., Int. Ed.*, 2017, **56**, 1021.
12 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision D.01; Gaussian, Inc.: Wallingford, CT, 2009.
13 (a) Y. Zhao, N. E. Schultz and D. G. Truhlar, *J. Chem. Theory Comput*. 2006, **2**, 364. (b) Y. Zhao and D. G. Truhlar, *J. Chem. Phys*. 2006, **125**, No. 194101. (c) Y. Zhao and D. G. Truhlar, *J. Phys. Chem. A* 2006, **110**, 13126.
14 V. Barone and M. Cossi, *J. Phys. Chem. A*. 1998, **102**, 1995.
15 P. J. Hay and W. R. Wadt, *J. Chem. Phys*. 1985, **82**, 270. (b) W. R. Wadt and P. J. Hay, *J. Chem. Phys*. 1985, **82**, 284.
16 P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta* 1973, **28**, 213.
17 (a) A. W. Ehlers, M. Böhme, S. Dapprich, A. Gobbi, A. Höllwarth, V. Jonas, K. F. Köhler, R. Stegmann, A. Veldkamp and G. Frenking, *Chem. Phys. Lett*. 1993, **208**, 111. (b) A. Höllwarth, M. Böhme, S. Dapprich, A. W. Ehlers, A. Gobbi, V. Jonas, K. F. Köhler, R. Stegmenn, A. Veldkamp and G. Frenking, *Chem. Phys. Lett*. 1993, **208**, 237.
18 (a) K. *J.* Fukui, *Phys. Chem*. 1970, **74**, 4161. (b) K. Fukui, *Acc. Chem. Res*. 1981, **14**, 363.
19 (a) S. Ehrlich, J. Moellmann and S. Grimme, *Acc. Chem. Res*. 2013, **46**, 916. (b) J. Antony, R. Sure and S. Grimme, *Chem. Commun*. 2015, **51**, 1764.
20 F. Weigend, F. Furche and R. Aldrichs, *J. Chem. Phys*. 2003, **119**, 12753.
21 Y. Okuno, *Chem. Eur. J*. 1997, **3**, 212.

Graphical Abstract:

New insights into the mechanism of gold-catalyzed domino reactions with hypervalent iodine reagents revealed by computation and confirmed by experiments.



Supporting Information

Table of content

1. Cartesian coordinates (Table S1)

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

1c
E (B3LYP/BS1) = -1516.353872 au
H (B3LYP/BS1) = -1516.085771 au
G (B3LYP/BS1) = -1516.171915 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -1803.264903 au

Si	5.48013600	0.02578200	-0.00318200
C	6.22416800	-1.03476900	-1.37591600
H	6.02566200	-2.09998900	-1.21166000
H	5.81769600	-0.76057000	-2.35602200
H	7.31194600	-0.89739800	-1.41215700
C	6.16016200	-0.47668300	1.68433700
H	5.71723900	0.12320500	2.48749100
H	5.95850400	-1.53249900	1.89824000
H	7.24685900	-0.32934900	1.71447700
C	5.77414600	1.86110800	-0.33210900
H	5.35920400	2.16533400	-1.29970600
H	5.31879400	2.48542600	0.44500700
H	6.85030800	2.07330000	-0.34593500
C	3.64306300	-0.26053800	0.00566500
C	2.43174700	-0.44487600	0.00883600
I	0.44287400	-1.08163300	0.01167700
O	-1.73812700	-1.37646200	0.01325200
C	0.56588000	2.02192500	0.00594900
C	-0.29516100	0.93491100	0.00560100
C	-1.68001700	1.04123800	0.00101500
C	-2.22010500	2.33659100	-0.00410300
C	-1.38424300	3.45355600	-0.00374100
C	0.00303500	3.30094000	0.00132800
H	1.64152200	1.88330300	0.00969800
H	-3.29401400	2.47161300	-0.00801600
H	-1.82214000	4.44685400	-0.00747700
H	0.65366100	4.17001200	0.00170900
C	-2.52111700	-0.25231900	0.00056000
C	-3.41695800	-0.29580200	1.27271200
C	-3.39475500	-0.30769900	-1.28655000
F	-2.60081300	-0.23756300	-2.37275900
F	-4.08510600	-1.45908800	-1.35950200
F	-4.29250300	0.70143800	-1.37332600
F	-4.31880100	0.71180800	1.33231500
F	-4.10583900	-1.44801200	1.34598900
F	-2.64288500	-0.21163000	2.37200200

2
E (B3LYP/BS1) = -1492.154034 au

H (B3LYP/BS1) = -1492.044729 au
G (B3LYP/BS1) = -1492.097347 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -1492.721413 au

Au	0.73053200	0.02404600	-0.00005900
Cl	2.90945000	0.90398900	-0.00015900
Cl	1.59766100	-2.17065100	-0.00026500
C	-2.07895100	0.56687300	0.00011300
C	-3.45653300	0.41760600	0.00019900
C	-3.99359300	-0.87149700	0.00018000
C	-3.13277800	-1.96817600	0.00017500
C	-1.75504400	-1.75805700	0.00015400
N	-1.26244200	-0.51097600	0.00009600
H	-5.06853800	-1.01652400	0.00029400
H	-4.07458300	1.30815900	0.00030200
H	-3.51082600	-2.98381500	0.00015700
H	-1.03586700	-2.56723600	0.00008000
O	-0.07897800	1.88197300	0.00014400
C	-1.40443600	1.91077600	0.00023500
O	-2.03076900	2.95361800	0.00036300

3
E (B3LYP/BS1) = -269.304946 au
H (B3LYP/BS1) = -269.203365 au
G (B3LYP/BS1) = -269.24184 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -269.405829 au

C	-1.49102200	-0.34385300	0.00000500
C	-0.24220700	-0.76161800	-0.00002500
C	-2.72363700	0.07746700	0.00002100
C	0.91727600	0.18028300	-0.00005100
O	0.77702700	1.39629300	-0.00000700
H	-0.02762000	-1.82924300	-0.00011200
H	-3.26060700	0.26073300	0.92890800
H	-3.26060000	0.26078400	-0.92886300
C	2.28482100	-0.47251100	0.00000500
H	2.39856000	-1.11513400	0.88195900
H	2.39785000	-1.11734000	-0.88040300
H	3.06482300	0.29123700	-0.00117400

4
E (B3LYP/BS1) = -754.183717 au
H (B3LYP/BS1) = -753.957304 au
G (B3LYP/BS1) = -754.017641 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -754.382046 au

C	0.15485700	-0.13673000	0.00179000
C	-1.06456000	-0.04877700	0.00185500
Si	-2.90546600	0.07370600	0.00040900
C	-3.54962300	-0.41358300	1.70967100

H	-3.15905200	0.25166100	2.48841300
H	-4.64494200	-0.35496300	1.73630400
H	-3.26248500	-1.43981200	1.96666600
C	-3.38714200	1.85707700	-0.39933200
H	-3.01835800	2.15840200	-1.38658600
H	-4.47895200	1.96470600	-0.40137000
H	-2.98268700	2.55707300	0.34090400
C	-3.58749800	-1.10069400	-1.31452900
H	-3.30250000	-2.13928500	-1.11033800
H	-4.68332100	-1.05193100	-1.33800600
H	-3.21867300	-0.83919700	-2.31310400
C	1.57055400	-0.22148900	0.00121700
C	2.52180000	0.87065800	0.00156300
C	2.32767400	-1.36551000	-0.00008800
C	3.76298200	0.31366200	0.00038700
H	2.07544400	-2.41480000	-0.00081600
O	3.65008900	-1.05819700	-0.00062000
H	2.28716000	1.92556500	0.00253200
C	5.14316000	0.87128000	-0.00002500
H	5.70598400	0.54819200	0.88411200
H	5.70496200	0.54934800	-0.88523200
H	5.09999700	1.96336700	0.00071200

$TS_{2\text{-}5}$
E (B3LYP/BS1) = -1761.426245 au
H (B3LYP/BS1) = -1761.214859 au
G (B3LYP/BS1) = -1761.288004 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -1762.097573 au

Au	0.04817100	-0.26274800	0.01003200
Cl	-0.73491400	-0.37642200	2.48885400
Cl	-0.29105200	-2.58096100	-0.28020700
C	2.70669800	1.02004600	-0.09480700
C	4.06580800	1.29186500	-0.17999500
C	4.94782100	0.22696700	-0.37508500
C	4.44243000	-1.06905000	-0.47826500
C	3.06478300	-1.27203800	-0.38439200
N	2.23945900	-0.23765500	-0.19781300
H	6.01529000	0.40705000	-0.44569400
H	4.40220800	2.31886100	-0.09318300
H	5.09632800	-1.92019500	-0.63038600
H	2.60989200	-2.25340400	-0.45685200
O	0.41226700	1.71888700	0.19105600
C	1.68377100	2.10197500	0.11393600
O	1.98483900	3.27755500	0.21069200
C	-2.23323900	0.20372100	-0.85646000
C	-3.22481700	0.27438400	-0.00523600
C	-1.38812500	0.19915900	-1.90252500
C	-4.62627500	0.58886500	-0.48245500
O	-4.87717400	0.75272900	-1.66301500

H	-3.04698600	0.11302800	1.05590300
H	-1.24333500	-0.70036500	-2.49700000
H	-0.94505700	1.12793400	-2.25760100
C	-5.66420700	0.68348200	0.60989800
H	-5.71305400	-0.26080600	1.16585300
H	-5.38292100	1.46299400	1.32863400
H	-6.64004300	0.91143000	0.17796200

5

E (B3LYP/BS1) = -1761.428196 au
H (B3LYP/BS1) = -1761.215632 au
G (B3LYP/BS1) = -1761.290335 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -1762.102023 au

Au	-0.05160700	-0.22904800	-0.12578800
Cl	0.06840200	-0.37086100	2.50735400
Cl	-0.43302700	-2.55692700	-0.32988100
C	2.63764200	0.99378200	-0.12802800
C	4.00496900	1.23605000	-0.11071800
C	4.87520000	0.14715800	-0.19549800
C	4.34959400	-1.14091800	-0.29546200
C	2.96445200	-1.31104200	-0.30675100
N	2.14841100	-0.25608800	-0.22542400
H	5.94875300	0.30291000	-0.18283000
H	4.35798000	2.25792100	-0.03158900
H	4.99399900	-2.00996500	-0.36330300
H	2.49557500	-2.28591000	-0.37889000
O	0.34424100	1.75775500	-0.04894200
C	1.63015900	2.10519900	-0.03884100
O	1.95007200	3.27707600	0.03539600
C	-2.17051400	0.15256300	-0.56041700
C	-3.13856300	0.23682000	0.32383400
C	-1.59230300	0.19091400	-1.80294200
C	-4.53976300	0.55255100	-0.15658300
O	-4.77954200	0.71679800	-1.33933900
H	-2.95599700	0.08853300	1.38327600
H	-1.57345600	-0.69427300	-2.43470100
H	-1.25716600	1.13629000	-2.22551200
C	-5.58527800	0.64577600	0.92741300
H	-5.63972600	-0.30067400	1.47910500
H	-5.30768900	1.42201600	1.65094100
H	-6.55729400	0.87680800	0.48872900

6

E (B3LYP/BS1) = -1761.428212 au
H (B3LYP/BS1) = -1761.216206 au
G (B3LYP/BS1) = -1761.293022 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -1762.101171 au

Au	-0.88421300	-0.86733600	0.00903900

Cl	-0.27957300	-2.80657700	-1.21211700
Cl	-3.09150800	-1.66601700	0.30346000
C	3.22710100	0.24502700	0.21164500
C	3.53278000	0.54554000	-1.11994900
C	4.82786900	0.96632300	-1.42361900
C	5.75601500	1.07345300	-0.39021600
C	5.34743800	0.75197400	0.90868700
N	4.11266000	0.34325600	1.21437700
H	5.10296000	1.20428000	-2.44666900
H	2.77638200	0.44559100	-1.88895600
H	6.77470400	1.39752800	-0.57750400
H	6.04765400	0.82710900	1.73832100
O	0.96471800	-0.09395100	-0.36302800
C	1.84788000	-0.23512800	0.61293300
O	1.59211900	-0.68908000	1.72051100
C	-1.58505000	1.40960900	0.48065800
C	-1.90991300	2.21773300	-0.48838100
C	-1.28515400	0.72448700	1.60729800
C	-2.32081900	3.65359500	-0.17142300
O	-2.34952100	4.06232500	0.97137700
H	-1.89777600	1.89516200	-1.52555300
H	-0.30055400	0.80772000	2.06499100
H	-2.08393300	0.27301100	2.19351400
C	-2.67547800	4.48480100	-1.37817000
H	-1.82058400	4.53466600	-2.06345500
H	-3.50163400	4.01700600	-1.92734800
H	-2.95918800	5.48993700	-1.06257200

$TS_{6\text{-}7}$

E (B3LYP/BS1) = -1761.424306 au
H (B3LYP/BS1) = -1761.213267 au
G (B3LYP/BS1) = -1761.288286 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -1762.096228 au

Au	1.04178200	-0.77912900	-0.10472100
Cl	0.60460900	-3.04344200	0.50572000
Cl	3.36699700	-1.04529700	0.25088700
C	-3.12662800	0.00470700	0.15553500
C	-3.62296200	-0.42854900	-1.07877600
C	-4.98836700	-0.29155500	-1.32978700
C	-5.79621900	0.27300500	-0.34507700
C	-5.20050400	0.67651200	0.85467600
N	-3.89543400	0.54821400	1.11109400
H	-5.40921000	-0.61984000	-2.27534800
H	-2.95472100	-0.86111200	-1.81350300
H	-6.86343000	0.40091800	-0.49510800
H	-5.80328400	1.12231400	1.64346000
O	-0.93196000	-0.51431600	-0.53671800
C	-1.65746900	-0.12263600	0.50107300
O	-1.20272300	0.11431000	1.61102900

C	1.30399000	1.34157300	-0.29611800
C	1.20023500	2.29723600	0.60403900
C	1.53377200	1.15366600	-1.63270200
C	1.41753600	3.67203000	0.01399700
O	1.65941400	3.79506900	-1.17784100
H	2.53526700	0.94562500	-2.00572300
H	0.70117300	1.10889800	-2.33383800
H	0.97236000	2.15540200	1.65225200
C	1.30974400	4.83585500	0.96273500
H	0.31205100	4.84777300	1.41823200
H	2.03297100	4.71764900	1.77841900
H	1.49014500	5.77309000	0.43476400

7

E (B3LYP/BS1) = -1761.487266 au
H (B3LYP/BS1) = -1761.272135 au
G (B3LYP/BS1) = -1761.345432 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -1762.151007 au

Au	-1.04563100	-0.75997100	-0.07744900
Cl	-0.76210700	-3.17372000	-0.14720500
Cl	-3.39097300	-0.94008400	0.21872900
C	3.14215300	0.02384300	0.21755900
C	3.65787900	-0.62214800	-0.91158500
C	5.03284100	-0.56622000	-1.14052300
C	5.83348800	0.13274300	-0.23969600
C	5.21972700	0.74692000	0.85678200
N	3.90515400	0.69845400	1.09217700
H	5.46671800	-1.05969900	-2.00502700
H	2.99549600	-1.15348600	-1.58392600
H	6.90788100	0.20421600	-0.37572300
H	5.81612800	1.30198600	1.57852300
O	0.95406600	-0.55773800	-0.43518400
C	1.65975200	-0.00924900	0.53533500
O	1.19870300	0.42950100	1.58231900
C	-1.24539900	1.22679200	-0.02146500
C	-1.05395200	2.12292400	-1.03115600
C	-1.61877000	1.98053200	1.19961700
C	-1.30436800	3.41576700	-0.49191100
O	-1.62828500	3.37621600	0.77058400
H	-0.76803000	1.93308400	-2.05597400
H	-0.87694600	1.88680400	1.99693500
H	-2.61657000	1.74894000	1.58159700
C	-1.24846400	4.72950700	-1.16504000
H	-0.26630400	4.85768200	-1.63378800
H	-1.99179000	4.74995200	-1.97148200
H	-1.44063600	5.54142800	-0.46303000

8

E (B3LYP/BS1) = -2350.085874 au

H (B3LYP/BS1) = -2349.845699 au
G (B3LYP/BS1) = -2349.941239 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -2350.873977 au

Au	0.01862800	-1.47197700	-0.20215000
C	0.97872900	-0.51351900	1.27610200
C	1.59878900	-1.04540300	2.37696100
C	1.17466200	0.93884300	1.29041600
C	2.14715200	0.04071100	3.09842500
O	1.90260900	1.19087000	2.52083700
H	1.80910300	1.29015800	0.40625600
H	0.27036200	1.55237600	1.30047400
H	1.68786500	-2.08333900	2.66364300
C	2.95609800	0.03673600	4.33879500
H	2.90015500	1.00434800	4.84162700
H	2.62327900	-0.76105800	5.00726000
H	4.00500000	-0.16173500	4.08087800
O	2.53450200	1.70106500	-1.08350000
C	2.46388000	3.02484800	-1.32228100
O	1.39756000	3.48365700	-1.86195100
O	3.47244800	3.74795000	-1.00758000
Na	0.52933400	1.42826100	-2.21470400
Na	4.73145900	1.95851600	-0.50522900
C	-3.43011700	1.01631700	0.25444300
C	-4.29270600	0.23949900	1.03540300
C	-5.54568800	0.76033200	1.35964400
C	-5.88308500	2.02979500	0.89574500
C	-4.94841600	2.72660700	0.12241900
N	-3.74640000	2.24011700	-0.19864400
H	-6.24141100	0.18413900	1.96196500
H	-3.98566100	-0.74265400	1.37348700
H	-6.84561400	2.47687000	1.12248300
H	-5.18016500	3.72058200	-0.25468900
O	-1.75476600	-0.63916600	0.41615100
C	-2.06139700	0.50728300	-0.13927600
O	-1.32655600	1.13602900	-0.90212700
Cl	2.06253800	-2.49025900	-0.79577000
Cl	-1.17502200	-2.60764900	-1.99241800

TS$_{8\text{-}9}$
E (B3LYP/BS1) = -2350.085214 au
H (B3LYP/BS1) = -2349.848455 au
G (B3LYP/BS1) = -2349.941575 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -2350.873543 au

Au	0.02600800	-1.50858600	-0.10472000
C	1.09687100	-0.41129800	1.19295200
C	1.91219700	-0.86032600	2.21490400
C	1.20185800	1.02775200	1.12969700
C	2.45661600	0.28085500	2.82313100

O	2.03169400	1.39048900	2.24724600
H	1.78781200	1.34667100	0.10637300
H	0.30091300	1.64211700	1.12776400
H	2.12440300	-1.87957800	2.50290300
C	3.42893800	0.40392400	3.93688600
H	3.13541600	1.21248000	4.61304100
H	3.49889900	-0.53451400	4.48995300
H	4.42155600	0.64638900	3.53618300
O	2.39574400	1.66675700	-1.18187400
C	2.20739200	2.97357000	-1.53612200
O	1.17819600	3.24860000	-2.23105200
O	3.08338900	3.81526600	-1.15651600
Na	0.44762300	1.11444400	-2.39026400
Na	4.49484200	2.24583500	-0.37676000
C	-3.38709700	1.02951300	0.30699400
C	-4.19800700	0.35069200	1.22285600
C	-5.42548700	0.91578400	1.57003500
C	-5.78920600	2.13124300	0.99477400
C	-4.90552900	2.73137700	0.09135600
N	-3.72918700	2.20072200	-0.25396500
H	-6.08157400	0.41460800	2.27517000
H	-3.87177200	-0.59229500	1.64431200
H	-6.73336500	2.60975800	1.23424900
H	-5.15847000	3.68170100	-0.37432700
O	-1.69642600	-0.60155200	0.55143200
C	-2.05035300	0.46579300	-0.12052500
O	-1.37979400	0.98816300	-1.01241000
Cl	2.01472900	-2.59524600	-0.75908200
Cl	-1.30489700	-2.81841700	-1.67409100

9

E (B3LYP/BS1) = -1761.050522 au
H (B3LYP/BS1) = -1760.847577 au
G (B3LYP/BS1) = -1760.919790 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -1761.716561 au

Au	-1.11974000	-0.65499900	-0.11691600
Cl	-0.80638000	-3.12157300	-0.34461500
Cl	-3.45709500	-0.90848600	0.16615800
C	3.11212500	-0.21331600	0.25705100
C	3.53618700	-0.06745200	-1.06916200
C	4.89927400	0.08494100	-1.32282000
C	5.78444800	0.08608100	-0.24660000
C	5.26164700	-0.06598900	1.04117800
N	3.95854300	-0.21327200	1.29977700
H	5.25998500	0.19976900	-2.34076700
H	2.81023400	-0.07499000	-1.87281700
H	6.85375200	0.20100800	-0.39335300
H	5.92507200	-0.06952600	1.90438000
O	0.87788800	-0.39128300	-0.47025200

C	1.64200300	-0.38467100	0.60086900
O	1.25033100	-0.50028600	1.75624700
C	-1.28349000	1.34541500	0.03576100
C	-0.42458100	2.30403200	-0.60690900
C	-2.18216300	2.05984000	0.76709600
C	-0.86443300	3.53639400	-0.22181900
O	-1.93784300	3.39973500	0.62351500
H	0.41263600	2.09514800	-1.25575800
C	-0.42079000	4.92599200	-0.52327000
H	0.43461500	4.90194100	-1.20361700
H	-1.21958000	5.50951700	-0.99778600
H	-0.11968000	5.45905600	0.38718600
H	-3.01266700	1.79394000	1.39989900

$TS_{9\text{-}10}$

E (B3LYP/BS1) = -3277.375153 au
H (B3LYP/BS1) = -3276.903816 au
G (B3LYP/BS1) = -3277.040416 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -3564.971615 au

Au	2.32800200	-0.28025000	-0.78904400
Cl	4.38645400	-1.41979200	-1.77358300
Cl	1.13443000	-0.40326400	-2.98734300
Si	1.86503900	-3.95784900	0.48674600
C	0.60903900	-5.01300100	1.42457500
H	0.36969700	-4.57515600	2.40004400
H	-0.32536300	-5.13402200	0.86564100
H	1.02824000	-6.01218000	1.59709000
C	3.42952300	-3.71755400	1.50183500
H	4.13709600	-3.06072500	0.98763200
H	3.20656900	-3.28148700	2.48156200
H	3.91047500	-4.69037200	1.66313200
C	2.22542100	-4.66405500	-1.22107500
H	1.30650100	-4.78616600	-1.80555500
H	2.90472600	-4.00779700	-1.77523700
H	2.69886700	-5.64914900	-1.12587000
C	1.01177600	-2.29672800	0.25128800
C	0.26881100	-1.30522800	0.15941000
I	-1.38260200	0.07307600	0.24263700
O	-3.27994800	1.13657900	0.31945500
C	-2.41879500	-2.79598300	-0.46505700
C	-2.79399300	-1.49339700	-0.16254800
C	-4.12602600	-1.08421000	-0.11362100
C	-5.11320100	-2.05008300	-0.35755500
C	-4.76142400	-3.36659300	-0.65404300
C	-3.41876700	-3.73938800	-0.71374000
H	-1.37541300	-3.07841600	-0.51733700
H	-6.15826300	-1.77094600	-0.32023700
H	-5.54049000	-4.09874800	-0.84240500
H	-3.13919400	-4.76071100	-0.95348500

C	-4.42838500	0.39108500	0.19930500
C	1.61816200	4.09419600	-0.20069200
C	2.71290500	4.68243800	-0.84590300
C	2.80747000	6.07343000	-0.87432000
C	1.80418200	6.82525600	-0.26520600
C	0.74963200	6.14490800	0.35004900
N	0.64960200	4.81193500	0.39133200
H	3.64717000	6.55839700	-1.36375600
H	3.46501400	4.05533300	-1.30883400
H	1.83162200	7.91040600	-0.26306700
H	-0.05220200	6.70088500	0.83339400
O	2.30711800	1.94929300	-0.89885100
C	1.47494900	2.57654800	-0.13604800
O	0.61896000	2.06865700	0.60236200
C	3.26831700	-0.08237800	0.98205400
C	4.61102600	-0.04814500	1.19534500
C	3.64616400	0.25556100	3.16454400
O	4.85843200	0.15836400	2.52778700
C	3.67790500	0.49227000	4.63485200
H	2.65768200	0.54158300	5.02458300
H	4.20721100	-0.31227800	5.16038600
H	4.18380900	1.43460400	4.87983200
C	2.63637300	0.11575500	2.25788200
H	1.57910700	0.16668400	2.46438300
H	5.47192500	-0.16141700	0.55906900
C	-5.25648600	1.02546400	-0.95585200
C	-5.20202500	0.49494800	1.54581600
F	-4.59678800	0.87843600	-2.11995800
F	-5.44411300	2.34141200	-0.75558100
F	-6.48107100	0.46842800	-1.10772000
F	-6.39758900	-0.13803300	1.52641700
F	-4.46640400	-0.05860600	2.52983000
F	-5.43555300	1.77534300	1.88278300

10

E (B3LYP/BS1) = -2817.014209 au
H (B3LYP/BS1) = -2816.54406 au
G (B3LYP/BS1) = -2816.676625 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -3104.563024 au

I	-1.98041900	-0.18309800	-1.07952000
C	-2.76135100	-0.13988300	0.90892900
O	-3.82219100	0.84227600	-1.39330700
C	-4.67830100	0.94054700	-0.31062600
C	-4.02666500	0.43089800	0.98411600
C	-4.62771800	0.48822100	2.24996300
C	-2.06930700	-0.64018700	2.00011600
C	-3.96006000	-0.00425900	3.37153800
H	-5.61421100	0.92002100	2.35868600
C	-2.68739400	-0.56378100	3.25125100

H	-1.07947300	-1.06840200	1.89918800
H	-4.43965900	0.05153100	4.34354200
H	-2.16559300	-0.94310300	4.12414400
C	-0.21297600	-1.29316400	-0.45715100
C	0.61743900	-2.22859400	-0.50149400
Si	1.59341500	-3.85099900	-0.73196100
C	3.21414200	-3.71679900	0.20894300
H	3.05412000	-3.63913100	1.28926400
H	3.80765800	-4.61996400	0.02061500
H	3.79847900	-2.84870900	-0.11437200
C	0.45216700	-5.17992700	-0.04090100
H	-0.50938700	-5.19543200	-0.56520300
H	0.92303500	-6.16233200	-0.16896500
H	0.26171000	-5.03283700	1.02759900
C	1.85420600	-4.00956100	-2.58735900
H	2.39861800	-3.14673200	-2.98458900
H	2.43779500	-4.91392800	-2.79865600
H	0.89995500	-4.08855300	-3.11931500
Au	1.76342100	-0.18388800	-0.37941900
Cl	1.66935200	0.00142000	-2.85364000
C	1.83293800	-0.22888500	1.64054200
C	2.20611500	0.83955700	2.39899900
C	1.71131900	-0.78840700	3.81105000
H	2.54096400	1.83715500	2.16870100
O	2.13156500	0.51400500	3.72421000
C	1.57013800	-1.36021900	5.17846700
H	2.52532600	-1.34551500	5.71737200
H	0.84462200	-0.79481000	5.77575000
H	1.22893200	-2.39658000	5.11390000
C	1.51137900	-1.29023400	2.55715200
H	1.17653000	-2.29027300	2.32771000
C	-5.04296000	2.44662200	-0.17625300
C	-5.93831400	0.08903200	-0.63756400
F	-6.51962800	0.49140900	-1.77945100
F	-5.49737200	2.94382700	-1.33709600
F	-5.99304400	2.67224500	0.75850700
F	-3.94851000	3.14648300	0.17211400
F	-6.87404400	0.13975600	0.33411900
F	-5.57531900	-1.19876800	-0.79108900
C	5.43000800	1.98211200	-0.29936100
C	5.04097300	3.32424200	-0.22036900
C	6.03225400	4.30548600	-0.19148500
C	7.36713500	3.91009300	-0.24281900
C	7.65194100	2.54303200	-0.32095400
N	6.71399900	1.59169900	-0.34927300
H	5.76439400	5.35606200	-0.13009800
H	3.99023700	3.58439700	-0.18274000
H	8.17329200	4.63653000	-0.22320800
H	8.68423100	2.20024700	-0.36276100
O	3.16520500	1.31283500	-0.31752900

C	4.40579700	0.86443800	-0.33044600
O	4.72285200	-0.31876800	-0.36378400

$TS_{10\text{-}11}$

E (B3LYP/BS1) = -2817.013651 au
H (B3LYP/BS1) = -2816.544655 au
G (B3LYP/BS1) = -2816.675679 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -3104.558952 au

I	-1.82474800	0.42626200	0.80804500
C	-2.37586900	-0.03470500	-1.20212300
O	-3.60982000	-0.67736600	1.14013300
C	-4.22954100	-1.21668800	0.02115500
C	-3.52929200	-0.80928600	-1.28124200
C	-3.96895200	-1.17438800	-2.56119800
C	-1.64883500	0.38910200	-2.30370600
C	-3.26390200	-0.76455000	-3.69315100
H	-4.86056600	-1.77799800	-2.67153200
C	-2.11085200	0.01054700	-3.56807500
H	-0.74678800	0.98147800	-2.20435600
H	-3.61950800	-1.05634000	-4.67613900
H	-1.56002600	0.32664000	-4.44831500
C	-0.01374700	1.58402000	0.13439500
C	0.18245800	2.82211000	0.06842200
Si	0.51114000	4.68230000	-0.05741400
C	0.10064000	5.20312600	-1.81533800
H	-0.95472200	5.02349500	-2.04738300
H	0.29719200	6.27489500	-1.93963900
H	0.71195500	4.65820700	-2.54230400
C	-0.62666100	5.45981500	1.22653700
H	-0.39215400	5.10577000	2.23573300
H	-0.49310400	6.54836600	1.20641000
H	-1.67980100	5.24513800	1.01726000
C	2.33581100	4.87344700	0.36778800
H	2.97075100	4.33689100	-0.34484600
H	2.60172700	5.93682500	0.32937200
H	2.55194100	4.50270000	1.37519600
Au	1.82833300	0.61543900	-0.12395000
Cl	2.00639900	1.25791500	-2.51561700
C	1.75293400	0.11615900	1.82960700
C	1.60236700	0.97087400	2.87956000
C	1.80546800	-1.05749900	3.73844400
H	1.47125400	2.03739700	2.96729500
O	1.63719900	0.26856400	4.05305100
C	1.86608400	-2.01354200	4.87845900
H	2.70199900	-1.78288900	5.55015500
H	0.94556800	-1.98573700	5.47432400
H	1.99979100	-3.03082200	4.50168900
C	1.88275000	-1.20384100	2.38406800
H	2.01418100	-2.12776900	1.84111600

C	-5.69267200	-0.68807900	0.03625800
C	-4.19137100	-2.76353900	0.18523000
F	-2.91155300	-3.17981800	0.18446200
F	-4.74873000	-3.14606000	1.34543900
F	-4.83691900	-3.41062200	-0.80829700
F	-6.28726800	-0.93438200	1.21412100
F	-5.69124400	0.64311800	-0.15543400
F	-6.45828700	-1.24423700	-0.92784000
C	4.89052700	-2.29215400	-0.79732300
C	6.07443600	-1.54577600	-0.81645400
C	7.28333100	-2.21638300	-1.00267800
C	7.26383500	-3.60119400	-1.15616800
C	6.02857700	-4.25546000	-1.11900300
N	4.86187100	-3.62619500	-0.94791000
H	8.21950300	-1.66650100	-1.02660100
H	6.03943300	-0.47044200	-0.69097800
H	8.17842400	-4.16713200	-1.30205500
H	5.97794200	-5.33675700	-1.23385100
O	3.64539100	-0.35624000	-0.27500700
C	3.54189200	-1.62064500	-0.61338700
O	2.48348000	-2.22511000	-0.76727300

11

E (B3LYP/BS1) = -2817.027374 au
H (B3LYP/BS1) = -2816.556838 au
G (B3LYP/BS1) = -2816.687601 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -3104.573796 au

I	1.82355400	-0.12232800	-1.04787900
C	2.37685600	-0.00676000	1.01370500
O	3.28180600	-1.60532500	-0.97724800
C	4.12830200	-1.56756500	0.13747500
C	3.49898800	-0.78412800	1.28947000
C	3.98552000	-0.76539400	2.60269700
C	1.70520300	0.75275900	1.95815400
C	3.33609100	-0.01187200	3.58116000
H	4.86342600	-1.34415200	2.86092400
C	2.20247300	0.73739700	3.26576800
H	0.82585600	1.33446800	1.71137800
H	3.72037100	-0.01444500	4.59587100
H	1.69365600	1.31584800	4.03007800
C	-0.35498300	1.28560600	-0.71689500
C	0.58808000	2.07616200	-0.93303400
Si	1.63259500	3.61701900	-1.31551600
C	0.48087600	5.06557100	-0.97113300
H	0.17807000	5.09711000	0.08099600
H	0.99694000	6.00529700	-1.20303900
H	-0.42151900	5.01313100	-1.58957200
C	3.13140800	3.60283200	-0.17855000
H	3.77631900	2.73428700	-0.35098200

H	3.73022000	4.50179900	-0.36956500
H	2.84001900	3.61211700	0.87703200
C	2.12073000	3.50257800	-3.12862300
H	1.23849000	3.45216500	-3.77584000
H	2.69548600	4.39399500	-3.40818100
H	2.74635100	2.62612500	-3.33010500
Au	-1.97871200	0.20461600	-0.46503900
Cl	-1.66119100	-0.77417000	-2.72492400
C	-2.23826300	0.96573600	1.38766800
C	-2.79873400	0.26881200	2.41454300
C	-2.28573000	2.26400600	3.21950200
H	-3.21121300	-0.72244300	2.50498500
O	-2.83274200	1.04702400	3.53875300
C	-2.23268200	3.28214400	4.30481200
H	-3.23680200	3.53583300	4.66631200
H	-1.65396000	2.92151200	5.16394200
H	-1.76172800	4.19591100	3.93324500
C	-1.90087300	2.26278400	1.90963100
H	-1.44835300	3.08832800	1.38014300
C	4.35204100	-3.05885100	0.51996300
C	5.46380600	-0.89506900	-0.29563800
F	6.04368600	-1.55645200	-1.30691600
F	4.72340200	-3.77927700	-0.54700800
F	5.30960300	-3.19910700	1.46125400
F	3.21412200	-3.58157400	1.00176900
F	6.34784500	-0.82029700	0.71588600
F	5.21064400	0.36305100	-0.71650500
C	-5.95638200	-1.35668300	-0.27835200
C	-5.80083800	-2.60344700	0.33906800
C	-6.92825400	-3.40290200	0.52770600
C	-8.16435100	-2.92999200	0.09176500
C	-8.21561700	-1.67129600	-0.51515700
N	-7.14495500	-0.89302700	-0.70054400
H	-6.84061200	-4.37464000	1.00479900
H	-4.81865600	-2.92854000	0.65956200
H	-9.06990500	-3.51558500	0.21514400
H	-9.16526200	-1.27249900	-0.86794800
O	-3.62566900	-0.98127100	-0.15293500
C	-4.76922300	-0.44058800	-0.50793500
O	-4.89828000	0.68566100	-0.98003100

$TS_{11\text{-}12}$

E (B3LYP/BS1) = -2817.016007 au
H (B3LYP/BS1) = -2816.547017 au
G (B3LYP/BS1) = -2816.677551 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -3104.562761 au

I	2.08826400	0.42504500	-0.91683100
C	2.49217500	-0.35100000	1.03525600
O	3.77302700	-0.84086400	-1.30979900

C	4.49758400	-1.22868500	-0.19215400
C	3.67658500	-1.07968500	1.09506000
C	4.04873100	-1.60174700	2.34096000
C	1.65929100	-0.14251700	2.12460500
C	3.23514300	-1.40943400	3.45792300
H	4.96890500	-2.16435600	2.43605700
C	2.04526800	-0.68894000	3.35269500
H	0.73836900	0.41982500	2.03770600
H	3.53474400	-1.82795200	4.41333900
H	1.40864200	-0.54557900	4.21994700
C	-0.61745500	1.21972100	-0.20831300
C	0.45030200	1.90524800	-0.11923800
Si	1.12305600	3.66065900	0.25139400
C	-0.26504100	4.67647300	1.00955600
H	-0.62075300	4.24464300	1.95052400
H	0.10737700	5.68617800	1.22290300
H	-1.11432400	4.76800900	0.32524400
C	2.57334100	3.47933400	1.44055400
H	3.39361900	2.88716400	1.02069600
H	2.96905100	4.47777900	1.66472700
H	2.26871500	3.02122700	2.38768800
C	1.67794600	4.36254700	-1.40658000
H	0.85094800	4.40211300	-2.12393000
H	2.04738700	5.38509100	-1.26018600
H	2.49086700	3.77739700	-1.85040600
Au	-2.01002800	-0.12007200	-0.43733100
Cl	-0.91982000	-2.23034900	-1.00001200
C	-2.60366400	1.78418000	0.01761800
C	-2.84412500	2.25283100	1.28802700
C	-3.74327300	3.71212000	-0.11041700
H	-2.59894400	1.88021100	2.27036800
O	-3.53077400	3.41036400	1.22617300
C	-4.50633700	4.95656400	-0.39407100
H	-5.51271300	4.91077600	0.03845600
H	-4.00290400	5.83574500	0.02445600
H	-4.60022200	5.09253300	-1.47415100
C	-3.18332000	2.74620800	-0.88709500
H	-3.18653900	2.70552500	-1.96633100
C	4.88234600	-2.71500400	-0.44330800
C	5.76952300	-0.33624500	-0.10014300
F	3.78404300	-3.48668900	-0.39561800
F	5.75975200	-3.18440400	0.47219900
F	5.44552100	-2.86986100	-1.65108700
F	6.51572300	-0.42251000	-1.21259000
F	5.39696000	0.95351600	0.04552600
F	6.55450200	-0.65549500	0.94845200
C	-5.71217200	-2.17931000	0.32183400
C	-6.32148700	-2.30976600	-0.93202500
C	-7.56429700	-2.93774600	-1.01302500
C	-8.15246600	-3.41082800	0.15847600

C	-7.46513200	-3.23198700	1.36265300
N	-6.27359300	-2.63309400	1.45572700
H	-8.06118800	-3.05446600	-1.97179900
H	-5.82427500	-1.92560000	-1.81424000
H	-9.11810500	-3.90652100	0.14726400
H	-7.89653600	-3.58926500	2.29642200
O	-3.86479800	-1.06923300	-0.65986100
C	-4.35824900	-1.50685000	0.46777200
O	-3.80675900	-1.40372500	1.56541700

12

E (B3LYP/BS1) = -1032.137413 au
H (B3LYP/BS1) = -1032.032244 au
G (B3LYP/BS1) = -1032.084622 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -1032.658932 au

Au	-1.54487300	-0.12888000	-0.03607000
Cl	-3.86546500	0.13102600	0.19994300
C	2.74282200	0.19855000	-0.04238400
C	3.13844800	-1.14416500	0.00542700
C	4.49740200	-1.44369100	0.09671900
C	5.41337100	-0.39350300	0.13014100
C	4.92160800	0.91331200	0.06791900
N	3.62150700	1.21580100	-0.01311000
H	4.83241200	-2.47602900	0.14336400
H	2.38765900	-1.92417600	-0.02264300
H	6.48117900	-0.57468900	0.20384700
H	5.60965500	1.75731700	0.08796300
O	0.48254800	-0.45436100	-0.22640400
C	1.26942300	0.57891800	-0.09551600
O	0.91719900	1.75492300	-0.00410400

13

E (B3LYP/BS1) = -1784.940995 au
H (B3LYP/BS1) = -1784.576486 au
G (B3LYP/BS1) = -1784.675262 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -2071.940733 au

I	-0.04456100	0.23402400	-0.96004500
C	0.64047400	-0.29546900	0.99567700
O	1.92030700	-0.43935300	-1.39520400
C	2.77702700	-0.51152200	-0.30014500
C	2.00019700	-0.59342000	1.01832400
C	2.56476300	-0.91812300	2.25875400
C	-0.17973000	-0.33379300	2.11242100
C	1.77000200	-0.96259200	3.40475600
H	3.62136900	-1.14392100	2.32775300
C	0.40616800	-0.67804700	3.33479500
H	-1.23770600	-0.11235600	2.05218500
H	2.22226200	-1.22403800	4.35586500

H	-0.21286700	-0.72179700	4.22506800
C	-2.94759700	0.18891400	-0.21132600
C	-2.07308200	1.09168400	-0.12523200
Si	-2.08905500	2.97541800	0.29782400
C	-3.74130300	3.31556400	1.12819500
H	-3.84938200	2.74049200	2.05429800
H	-3.81443000	4.38017900	1.38152700
H	-4.57971300	3.06770100	0.46811800
C	-0.63259400	3.32203500	1.43748100
H	0.33049600	3.08516200	0.97221300
H	-0.62663500	4.39203800	1.67997000
H	-0.70709600	2.76760200	2.37878300
C	-1.91312000	3.86453700	-1.35150700
H	-2.73006000	3.60965100	-2.03504900
H	-1.94093200	4.94780800	-1.18003500
H	-0.96353900	3.63155000	-1.84542600
C	-3.88003400	-0.81929600	-0.31243400
C	-4.31480900	-1.78787900	0.67989600
C	-4.63111000	-1.09074700	-1.45644400
C	-5.26284900	-2.54831900	0.08602100
H	-4.65223200	-0.63271800	-2.43471200
O	-5.44732700	-2.10574500	-1.23169800
H	-3.94828300	-1.87734700	1.69138700
C	-6.10678500	-3.69205800	0.51207200
H	-7.17168500	-3.44427900	0.43738200
H	-5.92158100	-4.57259200	-0.11347700
H	-5.87993700	-3.94704500	1.54961500
C	3.67416400	0.76008900	-0.29933000
C	3.62745600	-1.79317800	-0.53362400
F	4.64060500	-1.90259700	0.35319700
F	4.16583200	-1.79745400	-1.76146300
F	2.85249100	-2.88311400	-0.41489700
F	4.36787300	0.87584700	-1.44152100
F	2.89010600	1.85234400	-0.18031800
F	4.55233600	0.77111600	0.72194600

14

E (B3LYP/BS1) = -1301.439746 au
H (B3LYP/BS1) = -1301.231036 au
G (B3LYP/BS1) = -1301.30516 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -1302.069834 au

Au	-0.67168400	0.22119100	-0.12686200
C	-2.58615400	-0.51089500	-0.13754800
C	-3.79862700	-0.02003600	0.09854400
C	-1.79417100	-1.59951100	-0.49454600
C	-5.01224200	-0.88313300	-0.02032200
O	-4.95024900	-2.06478500	-0.33424600
H	-3.93818800	1.01931000	0.38056200
H	-1.53095200	-2.35437100	0.24418000

H	-1.70200300	-1.89363000	-1.53859600
C	-6.33154300	-0.19679600	0.27254300
H	-6.33102800	0.20440200	1.29368300
H	-6.47334600	0.65557100	-0.40344200
H	-7.15686100	-0.90152300	0.15475300
C	3.69156800	-0.38989500	0.14885100
C	4.21868100	0.27073000	-0.96855400
C	5.59512400	0.23786500	-1.18782600
C	6.40022700	-0.45394300	-0.28385100
C	5.78282200	-1.08178600	0.80103600
N	4.46383500	-1.05825700	1.02376300
H	6.02940200	0.74183100	-2.04684200
H	3.54941100	0.79339300	-1.64078300
H	7.47709500	-0.50946200	-0.41016100
H	6.38160600	-1.63107900	1.52655400
O	1.50327200	0.27424300	-0.45737000
C	2.18905100	-0.38036600	0.42057400
O	1.73504700	-0.96790300	1.41222000
Cl	-0.64246500	2.70137800	0.49632900

15

E (B3LYP/BS1) = -841.062686 au
H (B3LYP/BS1) = -840.85658 au
G (B3LYP/BS1) = -840.924859 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -841.646072 au

Au	-0.66753800	-0.58110000	0.03071300
C	-2.75792200	-0.18947800	0.06446200
C	-3.38232400	0.88861900	-0.37186300
C	-2.61574500	-1.42051100	0.63034000
C	-4.88012900	0.98586000	-0.25009900
O	-5.54539200	0.08875700	0.24103800
H	-2.84242800	1.71714700	-0.81873000
H	-2.58152400	-1.53222200	1.71299700
H	-2.76125800	-2.32364600	0.03963800
C	-5.48722500	2.26649600	-0.77685400
H	-5.06448500	3.12957000	-0.24789300
H	-5.24143900	2.39130500	-1.83863600
H	-6.57067300	2.24771000	-0.64734400
C	3.52187500	0.38680500	0.09374600
C	4.01140600	-0.30528400	-1.02071600
C	5.37340900	-0.23175800	-1.31253400
C	6.19494700	0.52934800	-0.48338600
C	5.61138900	1.18460300	0.60533500
N	4.30863400	1.12257400	0.89806400
H	5.78233300	-0.75866900	-2.16981400
H	3.33241500	-0.88339800	-1.63506000
H	7.26082500	0.61769600	-0.66878900
H	6.22478400	1.78796100	1.27263900
O	1.33591300	-0.38045500	-0.37854800

C	2.04875800	0.33743400	0.45920200
O	1.61021600	0.92453000	1.44531200

$TS_{15\text{-}16}$
E (B3LYP/BS1) = -841.055018 au
H (B3LYP/BS1) = -840.849835 au
G (B3LYP/BS1) = -840.91791 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -841.633567 au

Au	0.65114100	-0.32344200	0.00000600
C	2.63456300	0.00647400	-0.00008800
C	3.51048100	1.01589100	-0.00019500
C	2.93504800	-1.35078000	0.00020700
C	4.91604900	0.52947100	0.00005700
O	5.14321800	-0.68413000	0.00027300
H	2.98455500	-1.91669200	0.92821300
H	2.98461700	-1.91709100	-0.92755100
H	3.27665800	2.07319800	-0.00038600
C	6.02760400	1.54488900	0.00005000
H	5.93651900	2.19078300	-0.88127200
H	5.93590900	2.19151800	0.88076600
H	7.00090800	1.05258200	0.00057500
C	-3.57990900	0.30363000	-0.00004200
C	-4.17151100	-0.96559400	-0.00049300
C	-5.56309500	-1.05861500	-0.00037800
C	-6.31188800	0.11680800	0.00024800
C	-5.62871800	1.33658300	0.00071600
N	-4.29599000	1.44145400	0.00055000
H	-6.05065900	-2.02922800	-0.00076700
H	-3.54509100	-1.84910300	-0.00094600
H	-7.39720700	0.09690900	0.00037200
H	-6.18353400	2.27351100	0.00123500
O	-1.42003800	-0.67317800	0.00044400
C	-2.07016600	0.45386600	-0.00028100
O	-1.53588600	1.56976000	-0.00113300

16
E (B3LYP/BS1) = -841.094933 au
H (B3LYP/BS1) = -840.886277 au
G (B3LYP/BS1) = -840.952952 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -841.666961 au

Au	0.66794500	-0.23913900	-0.00003200
C	2.63073300	-0.12547800	0.00002300
C	3.47120300	0.97593200	0.00012500
C	3.53301000	-1.31038100	-0.00003300
C	4.80408900	0.52624600	0.00010700
O	4.89747400	-0.78363900	-0.00001700
H	3.43191700	-1.93798400	0.89064500
H	3.43190600	-1.93800400	-0.89068700

H	3.18942100	2.01974800	0.00023700
C	6.06725700	1.30176100	0.00013200
H	5.86581300	2.37349100	0.00056500
H	6.66207300	1.03974600	0.88274100
H	6.66156800	1.04048900	-0.88305800
C	-3.63511200	0.28866500	-0.00000800
C	-4.09634500	-1.03378400	0.00005400
C	-5.47099700	-1.26923200	0.00012000
C	-6.33677600	-0.17685800	0.00012500
C	-5.78090300	1.10565000	0.00004600
N	-4.46562200	1.34626300	-0.00000600
H	-5.85663400	-2.28479400	0.00016600
H	-3.38274100	-1.84841400	0.00003700
H	-7.41446800	-0.30734300	0.00018800
H	-6.42842300	1.98136700	0.00005300
O	-1.39558500	-0.47148300	-0.00005600
C	-2.14419300	0.59692300	-0.00008600
O	-1.74195500	1.76177000	-0.00016600

17

E (B3LYP/BS1) = -1429.695439 au
H (B3LYP/BS1) = -1429.460972 au
G (B3LYP/BS1) = -1429.548175 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -1430.389768 au

Au	0.06978600	-1.17016500	-0.09989900
C	-1.88205000	-1.42671300	-0.17300100
C	-2.69760900	-2.41227600	0.36566200
C	-2.79254200	-0.43319500	-0.77799100
C	-4.03515800	-2.07266700	0.10172100
O	-4.14588700	-0.94959400	-0.57114600
H	-2.72570400	0.56603600	-0.27569000
H	-2.66292000	-0.28933500	-1.85538900
H	-2.39608400	-3.29668100	0.90984200
C	-5.28714500	-2.77270200	0.48208400
H	-5.06881100	-3.74513800	0.92558000
H	-5.84146000	-2.16551000	1.20820900
H	-5.92877200	-2.90153100	-0.39584800
O	-2.39400300	2.20604200	0.54492400
C	-2.47659400	3.17985800	-0.36900300
O	-1.40815400	3.52776000	-0.98995400
O	-3.62011300	3.72627500	-0.57875800
Na	-0.10825600	2.16959100	0.24886500
Na	-4.55633900	2.61922100	1.12806100
C	4.16350900	0.30810300	0.12172000
C	4.90169000	-0.87419300	-0.01253300
C	6.29426900	-0.80059400	-0.02381200
C	6.89915700	0.44884400	0.09947100
C	6.07694700	1.57200700	0.22960000
N	4.74121600	1.51602200	0.24155100

H	6.89274700	-1.70101200	-0.12758900
H	4.38502800	-1.82135500	-0.10597700
H	7.97907000	0.55822300	0.09531500
H	6.51639700	2.56308900	0.32826200
O	2.14224600	-0.91237400	0.02451300
C	2.64492400	0.27508800	0.13031200
O	2.00129200	1.33161200	0.23328300

$TS_{17\text{-}18}$
E (B3LYP/BS1) = -1429.690452 au
H (B3LYP/BS1) = -1429.461047 au
G (B3LYP/BS1) = -1429.544651 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -1430.385191 au

Au	0.09254400	-1.13767500	-0.14942100
C	-1.87948400	-1.31870800	-0.19255200
C	-2.73134500	-2.20926800	0.48908100
C	-2.74518700	-0.36795500	-0.82782200
C	-4.04357200	-1.85748300	0.19846700
O	-4.09710000	-0.80976200	-0.61955700
H	-2.61218700	0.74248500	-0.17336400
H	-2.60610800	-0.05648700	-1.86315800
H	-2.44556100	-3.02730500	1.13635900
C	-5.33541300	-2.42327600	0.67240400
H	-5.16639700	-3.34758600	1.22849500
H	-5.84684600	-1.70868500	1.32909200
H	-6.00007600	-2.62837500	-0.17370100
O	-2.45380500	1.90487600	0.48146300
C	-2.55941100	2.96505700	-0.39206800
O	-1.47912600	3.43293100	-0.86277300
O	-3.72843700	3.39251400	-0.63985100
Na	-0.09363000	2.11327300	0.35957900
Na	-4.71357000	2.22494300	1.02046100
C	4.19653200	0.32002200	0.14130500
C	4.94655700	-0.84443700	-0.06464500
C	6.33840600	-0.75774900	-0.06468700
C	6.93121300	0.48682200	0.14024500
C	6.09800300	1.59187400	0.33707100
N	4.76270200	1.52311500	0.33983300
H	6.94570700	-1.64439500	-0.22214900
H	4.43879200	-1.78829200	-0.22017700
H	8.01008100	0.60600600	0.14836200
H	6.52780700	2.57878700	0.49980300
O	2.18449400	-0.90506800	-0.05819900
C	2.67775700	0.27131600	0.14442800
O	2.02644100	1.31335200	0.33242300

18
E (B3LYP/BS1) = -840.638155 au
H (B3LYP/BS1) = -840.441873 au

G (B3LYP/BS1) = -840.507465 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -841.214661 au

Au	0.69897400	-0.25354000	0.00026900
C	2.69536000	-0.18721200	-0.00006300
C	3.56542100	0.97556200	-0.00097600
C	3.56459200	-1.24397800	0.00062300
C	4.85858100	0.54173200	-0.00079200
O	4.87922700	-0.82862700	0.00020500
H	3.25596700	2.01317300	-0.00172800
C	6.17969900	1.23250100	-0.00145400
H	6.03193000	2.31614900	-0.00187200
H	6.77616600	0.97089200	0.88231100
H	6.77570200	0.97016100	-0.88532000
C	-3.65765600	0.29790300	0.00012600
C	-4.11467300	-1.02661900	-0.00067800
C	-5.48755400	-1.26992600	-0.00132000
C	-6.35980600	-0.18216600	-0.00116100
C	-5.80984900	1.10230900	-0.00034300
N	-4.49527000	1.35024800	0.00028400
H	-5.86775400	-2.28774400	-0.00193900
H	-3.39550100	-1.83637600	-0.00078800
H	-7.43691800	-0.31821600	-0.00165400
H	-6.46198500	1.97491600	-0.00021700
O	-1.41741000	-0.45234400	0.00058600
C	-2.16215100	0.60810900	0.00079900
O	-1.77356400	1.78121100	0.00146100
H	3.43250600	-2.31625100	0.00141700

$TS_{18\text{-}19}$
E (B3LYP/BS1) = -840.629546 au
H (B3LYP/BS1) = -840.434398 au
G (B3LYP/BS1) = -840.496513 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -841.207920 au

Au	-0.51027300	-0.64377300	-0.26540600
C	-2.36061000	0.00515200	0.08987000
C	-2.93242300	1.31496000	-0.16487000
C	-3.38835100	-0.69798400	0.65651800
C	-4.22879100	1.30207100	0.25903200
O	-4.52915500	0.06609300	0.76974700
H	-2.43011000	2.16396400	-0.61085400
C	-5.32105900	2.31650000	0.27414400
H	-4.96237400	3.25506000	-0.15769700
H	-6.19166600	1.98507400	-0.30661300
H	-5.66980500	2.52271400	1.29443300
C	3.18914400	0.05200600	0.13391200
C	2.96268600	0.97512500	-0.89541000
C	3.67037300	2.17665400	-0.89772400
C	4.57341100	2.42260000	0.13558500

C	4.72990900	1.44345900	1.12028700
N	4.06808400	0.28073400	1.12710400
H	3.51857100	2.90561100	-1.68909000
H	2.24727800	0.73796900	-1.67342500
H	5.14505800	3.34442300	0.18221300
H	5.42579200	1.60380900	1.94295200
O	1.44499800	-1.38037300	-0.67031600
C	2.44941100	-1.28644100	0.15565900
O	2.85582800	-2.19352600	0.88373800
H	-3.48334400	-1.70788500	1.02804600

19

E (B3LYP/BS1) = -840.633896 au
H (B3LYP/BS1) = -840.437695 au
G (B3LYP/BS1) = -840.502645 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -841.211298 au

Au	0.37727600	-0.74419400	0.06972300
C	-3.01198900	0.23720100	0.03829700
C	-4.29512200	0.64620100	-0.34947300
C	-4.57133100	2.00773700	-0.45142200
C	-3.56046300	2.92149000	-0.15072700
C	-2.31586700	2.42251100	0.23691400
N	-2.03990600	1.11552100	0.32879400
H	-5.55594900	2.35026700	-0.75748300
H	-5.04372200	-0.10747500	-0.56095800
H	-3.72696200	3.99247300	-0.21185900
H	-1.50283600	3.10282200	0.48473800
O	-1.51710000	-1.66702500	0.33295100
C	-2.72781300	-1.26163600	0.15216900
O	-3.70145800	-2.02674000	0.07592800
C	2.23291400	-0.04883600	-0.17670700
C	3.02809100	0.74390000	0.74477700
C	3.04715800	-0.19470600	-1.26630300
C	4.22885900	1.00906400	0.15454400
O	4.26033200	0.43804900	-1.09052800
H	2.73315600	1.07537900	1.73248600
C	5.44592800	1.75699100	0.58140000
H	5.29931300	2.16139400	1.58698900
H	6.33404700	1.11187500	0.60053500
H	5.66678400	2.59451400	-0.09312100
H	2.93436300	-0.69231000	-2.21859700

TS$_{19\text{-}20}$

E (B3LYP/BS1) = -2356.951957 au
H (B3LYP/BS1) = -2356.487563 au
G (B3LYP/BS1) = -2356.614233 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -2644.465872 au

I	1.35484400	1.37337000	-0.42207600

C	1.77302200	-0.64536300	-1.10111700
O	3.73192900	1.09040300	-0.31032900
C	4.13189400	-0.20266000	-0.31633200
C	3.05075500	-1.15569100	-0.89202800
C	3.28316900	-2.49050600	-1.25829600
C	0.75784000	-1.37683000	-1.71382200
C	2.27533000	-3.25545600	-1.84761300
H	4.26140100	-2.92837800	-1.10231800
C	1.01941200	-2.69776600	-2.09020300
H	-0.21316400	-0.93730200	-1.91604000
H	2.48056600	-4.28339900	-2.13188800
H	0.24116000	-3.28060500	-2.57472200
C	-0.94064100	1.60917700	-0.24069900
C	-1.38961900	2.77916000	-0.29184700
Si	-2.17549100	4.42773600	-0.32054900
C	-4.05852100	4.30052000	-0.11833000
H	-4.32620000	3.83906600	0.83984300
H	-4.52181400	5.29529500	-0.15306400
H	-4.50489400	3.69641200	-0.91755500
C	-1.47231200	5.45829500	1.10683000
H	-0.38769700	5.58664400	1.01326500
H	-1.92923700	6.45598000	1.12078100
H	-1.67270500	4.98574700	2.07580600
C	-1.80697300	5.28641000	-1.97029000
H	-2.18379500	4.69987400	-2.81693700
H	-2.28699700	6.27274200	-2.00882500
H	-0.72978700	5.42997800	-2.11493600
C	5.42054200	-0.28299400	-1.19385500
C	4.47219900	-0.65296700	1.13915100
F	5.44414400	0.10615400	1.68322600
F	3.37901100	-0.52279800	1.92812700
F	4.87615100	-1.94299000	1.23859800
F	6.31768300	0.65214500	-0.82858400
F	6.06729200	-1.47782700	-1.13281700
F	5.11553000	-0.06320200	-2.48869100
Au	-1.96321800	-0.21337800	0.13679200
C	-3.98653700	-2.20320500	-1.22938700
C	-4.88510800	-3.22742600	-1.53287900
C	-5.31240000	-4.07522500	-0.51166300
C	-4.82995600	-3.87590600	0.78320100
C	-3.93351700	-2.83139500	1.00604400
N	-3.52991500	-2.02139000	0.02052600
H	-6.01080000	-4.87991800	-0.72132300
H	-5.22667600	-3.33656500	-2.55520700
H	-5.13755600	-4.51296300	1.60573700
H	-3.52163000	-2.62657200	1.99069400
O	-2.65283200	-0.33332800	-1.95826200
C	-3.48935300	-1.25206700	-2.31418100
O	-3.91162600	-1.41638200	-3.46473700
C	-1.32687000	-0.34495900	2.06692800

C	-0.00019500	-0.63557800	2.55952100
C	-2.09427900	-0.22533500	3.18963400
C	-0.06189700	-0.67530700	3.92142500
O	-1.34587300	-0.42418500	4.33059400
H	0.89329200	-0.79544300	1.97345200
C	0.95588800	-0.92316800	4.98155500
H	1.93847500	-1.05536400	4.51937100
H	1.01907100	-0.08292900	5.68467900
H	0.72832600	-1.82332400	5.56716100
H	-3.13795700	-0.00726500	3.36218800

$TS^{II}_{19\text{-}20}$

E (B3LYP/BS1) = -2356.943454 au
H (B3LYP/BS1) = -2356.479282 au
G (B3LYP/BS1) = -2356.610527 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -2644.450105 au

I	1.30627000	0.65637800	-1.08039400
C	1.55856400	-1.39921800	-0.44690000
O	3.70407600	0.14852200	-1.18477000
C	4.04059000	-0.92050200	-0.42935200
C	2.83941000	-1.86553900	-0.16019400
C	2.95628900	-3.17350900	0.33448200
C	0.42145700	-2.19444000	-0.31649600
C	1.83102600	-3.98396000	0.49266900
H	3.93456800	-3.56804400	0.58014300
C	0.56573700	-3.50202000	0.15613000
H	-0.56061700	-1.82084300	-0.58813600
H	1.94857500	-4.99649200	0.86773100
H	-0.31121500	-4.13533500	0.25611000
C	-0.95834500	1.60798700	-0.73323400
C	-1.18317400	2.62569300	-1.41038600
Si	-1.56281700	4.12651900	-2.39466200
C	-1.01669700	3.87617500	-4.19070900
H	-1.52668600	3.01898100	-4.64618800
H	-1.25123000	4.76342600	-4.79263500
H	0.06313400	3.69955000	-4.25857200
C	-3.42758700	4.45855700	-2.35181700
H	-3.77716400	4.63081100	-1.32702800
H	-3.67767000	5.34626900	-2.94678800
H	-3.99141400	3.61189700	-2.76125300
C	-0.63286800	5.59245000	-1.63906800
H	0.45042800	5.42484500	-1.64332900
H	-0.83301700	6.50804000	-2.20977300
H	-0.94269800	5.76878600	-0.60235200
C	5.15975700	-1.69159100	-1.19780700
C	4.59812400	-0.43854700	0.94729000
F	5.67043200	0.36604400	0.79991700
F	3.65205900	0.27476700	1.60043200
F	4.97224900	-1.44467400	1.77655700

F	6.14166200	-0.85743800	-1.59008200
F	5.76326900	-2.67826200	-0.48030700
F	4.65214700	-2.26494800	-2.30793300
Au	-1.87339400	0.44502800	0.70540900
C	-4.36808300	-2.84478600	-0.21429400
C	-5.04643100	-3.60311500	0.74690400
C	-5.83489300	-4.67188000	0.32280700
C	-5.91693800	-4.94062300	-1.04254400
C	-5.20254400	-4.12379500	-1.92433800
N	-4.44164600	-3.09653900	-1.53253400
H	-6.37315600	-5.28068100	1.04334700
H	-4.94720800	-3.34866500	1.79535100
H	-6.51771700	-5.76107900	-1.42220800
H	-5.24617000	-4.30681500	-2.99660900
O	-2.86671900	-1.01966900	-0.65695100
C	-3.51060300	-1.68480500	0.23066200
O	-3.44492200	-1.40487800	1.45681300
C	-1.13025200	1.53082400	2.24481000
C	0.22522900	1.57510500	2.74151900
C	-1.84277100	2.34190900	3.07995800
C	0.22967000	2.38416700	3.83974300
O	-1.03628700	2.86495300	4.06235900
H	1.08615600	1.06147400	2.33494800
C	1.28877700	2.81820100	4.79377400
H	2.24936200	2.38444600	4.50258800
H	1.39660600	3.91021200	4.80723400
H	1.06641700	2.49834900	5.81977000
H	-2.87867200	2.64283200	3.12573100

$TS^{III}_{19\text{-}20}$

E (B3LYP/BS1) = -2969.505893 au
H (B3LYP/BS1) = -2969.11398 au
G (B3LYP/BS1) = -2969.248058 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -3257.024144 au

I	1.14230700	1.54989700	-0.15405300
C	1.93216600	-0.21270800	-1.15361200
O	3.44852500	1.44544800	0.39952700
C	4.03493900	0.24660600	0.16414200
C	3.21948700	-0.62573000	-0.82325300
C	3.69944700	-1.79795000	-1.42757000
C	1.14367200	-0.87558300	-2.08957300
C	2.92087600	-2.49517200	-2.35292800
H	4.69235500	-2.15811200	-1.18792500
C	1.65019300	-2.03022600	-2.69444400
H	0.16031500	-0.50703700	-2.36039900
H	3.31715000	-3.39375100	-2.81699500
H	1.04950100	-2.55522500	-3.43177800
C	-1.11534400	1.60579800	-0.46136500
C	-1.65419100	2.73461300	-0.34320400

Si	-2.65092100	4.25104100	-0.15251300
C	-2.18238500	5.09299400	1.48158800
H	-1.12626600	5.38664000	1.49282700
H	-2.78489500	5.99766600	1.63330500
H	-2.35562200	4.43009500	2.33792100
C	-2.29847100	5.43171800	-1.59380000
H	-2.54430600	4.96966700	-2.55755300
H	-2.89836700	6.34604300	-1.49997800
H	-1.24216700	5.72388500	-1.62173300
C	-4.51037700	3.86568300	-0.12492500
H	-4.76312100	3.19634100	0.70659900
H	-5.10147100	4.78361500	-0.00873700
H	-4.82808000	3.37776100	-1.05441000
C	5.44995100	0.53429500	-0.42588500
C	4.17891500	-0.53097100	1.50836400
F	4.90243600	0.16068500	2.41208900
F	2.95756400	-0.73863800	2.04714300
F	4.76632500	-1.74720100	1.38219900
F	6.12539800	1.41460100	0.33745500
F	6.24544700	-0.56288800	-0.53997000
F	5.33858100	1.07257200	-1.65709900
Au	-2.02058200	-0.34280700	-0.54998000
C	-1.66421700	-0.62768300	1.45607300
C	-1.90987900	0.29577600	2.54190900
C	-1.12433300	-1.72903300	2.05793200
C	-1.51420500	-0.30516800	3.70187100
O	-1.02573000	-1.55609600	3.42546300
H	-2.32003100	1.29309000	2.45490500
C	-1.50609900	0.11645300	5.13155900
H	-1.90272400	1.13153000	5.22125400
H	-2.12037200	-0.54599700	5.75480100
H	-0.49065800	0.10856500	5.54770600
H	-0.76535100	-2.67976000	1.69292700
O	-1.83696800	-3.83358100	-1.36530400
C	-2.72254400	-3.50747800	-0.50367000
O	-3.35021800	-2.35226700	-0.55284300
O	-3.02870200	-4.31274200	0.48092600
Na	-3.87894800	-2.53334700	1.65109500
Na	-1.42282300	-5.75878300	-0.24218000
Cl	-2.48837400	-0.05321300	-3.01683600

$TS^{IV}_{19\text{-}20}$

E (B3LYP/BS1) = -2380.907830 au
H (B3LYP/BS1) = -2380.541745 au
G (B3LYP/BS1) = -2380.658846 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -2668.299476 au

I	0.59861600	-0.63305600	0.06597900
C	1.99865300	0.90183600	-0.43793600
O	2.92290400	-1.65055900	0.24140400

C	3.88128700	-0.70653500	0.18646400
C	3.36794300	0.67831900	-0.30664800
C	4.22338400	1.74666400	-0.62453400
C	1.47187800	2.11636400	-0.87927100
C	3.72204000	2.96934600	-1.06963100
H	5.29392000	1.61648900	-0.53182400
C	2.34545300	3.15646100	-1.20075400
H	0.39932100	2.24908300	-0.96378500
H	4.41022400	3.77323400	-1.31420400
H	1.94612900	4.10414100	-1.55054100
C	-1.82654800	0.91052600	-0.00612700
C	-1.94730400	1.97637000	0.59953000
Si	-2.04131000	3.57327300	1.51163500
C	-3.57835900	3.56269200	2.61490600
H	-3.54619100	2.73793400	3.33647300
H	-3.65156900	4.50016500	3.18058400
H	-4.49388600	3.45601300	2.02142300
C	-0.48920100	3.77130100	2.57601400
H	0.41869700	3.76140500	1.96187400
H	-0.51597500	4.72143200	3.12433900
H	-0.40682700	2.96201100	3.31101300
C	-2.15539100	4.98176200	0.25410000
H	-3.04167500	4.87600200	-0.38236500
H	-2.22337800	5.94937200	0.76693800
H	-1.27392000	5.00843200	-0.39707400
C	4.48922000	-0.51560800	1.61396200
C	4.99236700	-1.22441600	-0.78564500
F	5.34559600	-2.48941300	-0.48743900
F	4.53646900	-1.22384200	-2.05534300
F	6.14286500	-0.49646800	-0.77532400
F	4.99555900	-1.67117400	2.09381400
F	5.48496900	0.40432200	1.68723500
F	3.52292700	-0.11589300	2.46767500
Au	-2.67882200	-0.50276500	-1.18814800
C	-3.35222600	-1.55437000	0.40481100
C	-2.86444500	-2.82240400	0.89709300
C	-4.39043300	-1.22157200	1.22759500
C	-3.65822500	-3.17624500	1.94865600
O	-4.60207400	-2.20069500	2.16092800
H	-2.04748300	-3.40769300	0.49835400
C	-3.70463200	-4.35987700	2.85150800
H	-2.89583800	-5.05052400	2.59853100
H	-3.58944500	-4.06684200	3.90254200
H	-4.65615200	-4.89889200	2.76261800
H	-5.04776000	-0.36788900	1.28986100
Cl	-2.26908300	0.31289900	-3.48174300

20

E (B3LYP/BS1) = -1325.899941 au

H (B3LYP/BS1) = -1325.569479 au

G (B3LYP/BS1) = -1325.65583 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -1326.591313 au

C	-1.55800000	-0.46366500	0.00589100
C	-2.77421300	-0.60801600	-0.00636800
Si	-4.60455000	-0.85025000	-0.02542400
C	-5.37788600	0.30909400	1.25207300
H	-5.15622000	1.35843900	1.02549900
H	-6.46864800	0.19124500	1.26479500
H	-5.00577900	0.09541200	2.26083000
C	-5.24467400	-0.44148200	-1.75673700
H	-4.79731800	-1.09737900	-2.51256800
H	-6.33337100	-0.56961000	-1.80286200
H	-5.01688900	0.59499700	-2.03139400
C	-4.98531700	-2.64939900	0.41028600
H	-4.61082800	-2.90477300	1.40842300
H	-6.06842300	-2.82408500	0.40318800
H	-4.52891700	-3.33987000	-0.30838900
Au	0.39013100	-0.28718100	0.02371000
C	3.04787200	-1.49945500	-0.05200100
C	4.42538400	-1.68273800	-0.05046500
C	5.25801200	-0.56747200	0.04265800
C	4.68554100	0.70160600	0.13169100
C	3.29865600	0.81901400	0.12657900
N	2.50814200	-0.26301500	0.03603000
H	6.33672400	-0.68607500	0.04562700
H	4.81136600	-2.69244700	-0.12212500
H	5.29644300	1.59407400	0.20486300
H	2.79825100	1.77756000	0.19177700
O	0.81848300	-2.36835700	-0.14457200
C	2.08618600	-2.67134500	-0.15223700
O	2.53502900	-3.81089000	-0.23391600
C	0.11114300	1.69348400	0.16814300
C	0.23346600	2.65256700	-0.89876300
C	-0.14660500	2.40660700	1.29842800
C	0.05588400	3.88344000	-0.33543400
O	-0.17582100	3.74494300	1.00906400
H	0.43311900	2.45078500	-1.94173800
C	0.06667100	5.27062500	-0.87717700
H	0.25646600	5.24593300	-1.95338100
H	-0.89342400	5.77390100	-0.70927700
H	0.84623800	5.88068000	-0.40462100
H	-0.32669500	2.14038900	2.32801400

21
E (B3LYP/BS1) = -1031.105014 au
H (B3LYP/BS1) = -1030.970813 au
G (B3LYP/BS1) = -1031.0317 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -1317.923469 au

I	2.47595500	-0.87838700	-0.11832600
C	1.22614000	0.87908700	0.00163700
O	-0.39817800	-1.53483300	-0.38667600
C	-1.04841200	-0.43450200	-0.09473900
C	-0.17231100	0.88610100	0.01340500
C	-0.78629000	2.14998500	0.13608500
C	1.97396300	2.06077300	0.09212700
C	-0.05911800	3.33477400	0.22316200
H	-1.86628700	2.20568400	0.15881700
C	1.33442100	3.29371300	0.19900900
H	3.05821800	2.01446500	0.08019100
H	-0.58282100	4.28303500	0.31139800
H	1.92284600	4.20481300	0.26544400
C	-2.15271600	-0.19564000	-1.20082800
C	-1.77966200	-0.60062300	1.29148300
F	-2.59953700	-1.67872200	1.28411800
F	-0.86634900	-0.80943800	2.26841000
F	-2.54812200	0.44762700	1.70840400
F	-2.82666200	-1.33789300	-1.45644800
F	-3.11814300	0.73712700	-0.93042100
F	-1.57321500	0.18387500	-2.36508800

$TS_{20\text{-}22}$

E (B3LYP/BS1) = -1325.877352 au
H (B3LYP/BS1) = -1325.548889 au
G (B3LYP/BS1) = -1325.633937 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -1326.565396 au

C	-1.48043600	-0.21088800	0.08780100
C	-2.63449400	-0.64213900	0.03589500
Si	-4.36696200	-1.27619800	-0.04196000
C	-5.12573800	-1.14458400	1.68404200
H	-5.14376500	-0.10646100	2.03513500
H	-6.15852500	-1.51479400	1.67582400
H	-4.56235700	-1.73895500	2.41263700
C	-5.33260600	-0.22169400	-1.27855900
H	-4.88813700	-0.27431200	-2.27917300
H	-6.36851200	-0.57552100	-1.35249600
H	-5.35766700	0.83087000	-0.97400500
C	-4.33085300	-3.07925000	-0.60840500
H	-3.76573100	-3.70548700	0.09154200
H	-5.35025400	-3.48019000	-0.67133300
H	-3.86957300	-3.17692900	-1.59794900
Au	0.49930700	-0.25324800	0.05208400
C	3.39759700	-1.08173500	-0.08004900
C	4.78935500	-1.05742400	-0.11539500
C	5.44567100	0.17162900	-0.05723800
C	4.69059700	1.34212100	0.03530800
C	3.30218700	1.24258800	0.06657500
N	2.68060600	0.05474700	0.00918000

H	6.52994400	0.21751700	-0.08322900
H	5.32413000	-1.99664900	-0.18713400
H	5.16194300	2.31744900	0.08312600
H	2.66463100	2.11776600	0.13911700
O	1.32965300	-2.28319300	-0.09512400
C	2.61799600	-2.38842000	-0.13875600
O	3.24878100	-3.44491100	-0.22225200
C	-0.61758100	1.48206100	0.17893500
C	-0.81926600	2.41408500	-0.90726100
C	-0.70885600	2.21940800	1.33338600
C	-1.02355600	3.63344200	-0.33887400
O	-0.96008400	3.52211700	1.03288200
H	-0.81891400	2.18673700	-1.96329000
C	-1.28588700	4.99261000	-0.88577600
H	-1.32609900	4.95037300	-1.97709400
H	-2.23950000	5.39228600	-0.52046100
H	-0.49797600	5.69857100	-0.59663600
H	-0.65727400	1.96488700	2.38016900

22

E (B3LYP/BS1) = -1325.952084 au
H (B3LYP/BS1) = -1325.621282 au
G (B3LYP/BS1) = 1325.706654 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -1326.641128 au

C	-1.65753500	0.10289800	0.03930000
C	-1.44590600	-1.15030500	0.00571700
Si	-1.68605700	-3.00766900	-0.01012100
C	-0.54525700	-3.73672200	1.30205200
H	-0.81480400	-3.38338500	2.30411100
H	-0.61008700	-4.83168100	1.30133700
H	0.49593600	-3.45404500	1.10902100
C	-3.50390700	-3.34273500	0.37499100
H	-4.16296400	-2.87776700	-0.36702300
H	-3.69770400	-4.42249500	0.36737500
H	-3.77865700	-2.95835300	1.36376700
C	-1.22092800	-3.62894200	-1.73035900
H	-0.17985000	-3.38325800	-1.96950900
H	-1.33117500	-4.71908300	-1.78427700
H	-1.86116700	-3.18657300	-2.50207600
Au	0.45270600	-0.18742700	-0.00536600
C	3.40025900	0.58719200	-0.00082800
C	4.58357300	1.32418200	-0.01135900
C	4.52122000	2.71423600	-0.08335000
C	3.27087300	3.33086800	-0.14537300
C	2.13032500	2.53303400	-0.12716300
N	2.19721900	1.19281800	-0.05251500
H	5.43027700	3.30772800	-0.09356700
H	5.52378400	0.78851700	0.03470500
H	3.17226100	4.40906100	-0.20688000

H	1.13820900	2.96658100	-0.17810100
O	2.28706200	-1.52683300	0.01986600
C	3.42748100	-0.93909000	0.05830700
O	4.53369000	-1.49074500	0.13099200
C	-2.48450300	1.26751500	0.06962700
C	-3.90708700	1.32158700	-0.19176900
C	-2.11356200	2.55301300	0.36425900
C	-4.28399100	2.61915900	-0.03874200
O	-3.18627300	3.37839100	0.30474900
H	-4.54235400	0.48987300	-0.46065100
C	-5.58102300	3.33770000	-0.16457200
H	-6.36841700	2.63158400	-0.43983000
H	-5.86391200	3.81959100	0.77897400
H	-5.53255200	4.11774100	-0.93378800
H	-1.17236900	3.00231900	0.64033800

$TS_{22\text{-}23}$
E (B3LYP/BS1) = -1325.933638 au
H (B3LYP/BS1) = -1325.604537 au
G (B3LYP/BS1) = -1325.691702 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -1326.619813 au

C	2.09919000	0.53028400	0.25296600
C	1.19562400	1.38964000	0.12970800
Si	0.48796800	3.13977800	0.15967200
C	-1.07895800	3.10115600	1.20453200
H	-0.86422100	2.78294200	2.23108700
H	-1.52720100	4.10128300	1.24904200
H	-1.82245700	2.41458800	0.78389600
C	1.81147400	4.24279300	0.92606300
H	2.73434400	4.22623200	0.33556300
H	1.45754100	5.28012800	0.97085700
H	2.05281500	3.92474200	1.94649800
C	0.12816700	3.61497200	-1.62786100
H	-0.60348600	2.93651100	-2.08092200
H	-0.28007600	4.63205100	-1.67221000
H	1.03889300	3.59018800	-2.23686100
Au	0.00577200	-0.28935900	-0.42815800
C	-3.51868300	-1.35337800	0.07863200
C	-3.82703300	-0.22571600	-0.69265400
C	-4.98844800	0.49158400	-0.40497100
C	-5.79459800	0.06403000	0.64837200
C	-5.40210900	-1.07241000	1.36194900
N	-4.29851300	-1.77660600	1.08961100
H	-5.25652000	1.36561200	-0.99170300
H	-3.16785300	0.06742400	-1.50063800
H	-6.70569900	0.59076900	0.91443000
H	-6.00860700	-1.43295700	2.19143100
O	-2.13350400	-3.29430100	0.27867100
C	-2.27214400	-2.17915700	-0.20946700

O	-1.42109100	-1.63019000	-1.05918900
C	3.22632000	-0.30487200	0.42733300
C	4.15259300	-0.77850300	-0.57947600
C	3.67576000	-0.81589300	1.62259500
C	5.08183200	-1.52562600	0.07160900
O	4.78869600	-1.54601500	1.42316200
H	4.11034400	-0.57261800	-1.63907900
C	6.28691600	-2.28339700	-0.35870400
H	6.41136300	-2.19304000	-1.44046400
H	7.19217200	-1.90099300	0.12733500
H	6.19810700	-3.34694400	-0.10785800
H	3.31435000	-0.73616700	2.63652300

23

E (B3LYP/BS1) = -1325.943912 au
H (B3LYP/BS1) = -1325.613654 au
G (B3LYP/BS1) = -1325.705712 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -1326.626461 au

C	-2.38017000	0.17252900	0.11710400
C	-2.00104500	-1.01800000	0.04004100
Si	-2.36443400	-2.87319000	0.02899000
C	-1.35157300	-3.64944100	1.41465900
H	-1.62596100	-3.23178400	2.39003100
H	-1.52580600	-4.73177400	1.45029100
H	-0.27912500	-3.48266700	1.26266600
C	-4.21635500	-3.07228300	0.32359200
H	-4.79969800	-2.58136700	-0.46345800
H	-4.48446000	-4.13603600	0.32901900
H	-4.51469900	-2.64479600	1.28743800
C	-1.85441300	-3.52735200	-1.66299800
H	-0.78849300	-3.35482100	-1.85029300
H	-2.03915000	-4.60695200	-1.72221200
H	-2.42394600	-3.04367500	-2.46476500
Au	-0.00610200	-0.31095700	-0.17852800
C	4.22017100	0.46180900	0.19689000
C	4.66640700	0.41857600	-1.12987600
C	6.02142300	0.62063300	-1.39156900
C	6.88158800	0.85792500	-0.32099300
C	6.34103600	0.88142400	0.96796400
N	5.04491100	0.68980800	1.23396200
H	6.39586300	0.59282400	-2.41085700
H	3.95905600	0.23003900	-1.92794700
H	7.94396900	1.02108200	-0.47291400
H	6.98485900	1.06360200	1.82712700
O	2.35898200	0.28607400	1.70304100
C	2.75278800	0.24824900	0.53782000
O	2.00792100	0.03231700	-0.51566000
C	-2.90121000	1.47829500	0.20194000
C	-3.31392400	2.35396000	-0.87589500

C	-3.14857500	2.17287600	1.36533900
C	-3.77420600	3.49162400	-0.29484000
O	-3.67252400	3.37679800	1.08168900
H	-3.26501500	2.13809000	-1.93317000
C	-4.33686000	4.76648800	-0.81360900
H	-4.36130600	4.74034400	-1.90563500
H	-5.35753900	4.92862900	-0.44775200
H	-3.73041900	5.62451100	-0.50079800
H	-3.00392000	1.93097900	2.40740700

27

E (B3LYP/BS1) = -1595.241941 au
H (B3LYP/BS1) = -1594.808855 au
G (B3LYP/BS1) = -1594.914555 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -1596.036855 au

C	1.20295700	1.72438100	-0.18790800
C	2.22678900	1.14363300	0.21970000
Si	3.92818000	0.82175100	0.93219400
C	4.99035900	-0.05197100	-0.35678500
H	5.06024800	0.53961600	-1.27660900
H	6.00633800	-0.18795700	0.03390500
H	4.59836700	-1.04033400	-0.61724200
C	4.61994600	2.53767400	1.31319700
H	3.98731000	3.07356900	2.02933900
H	5.62317100	2.44985900	1.74843300
H	4.69856900	3.14541400	0.40476200
C	3.74770300	-0.19413900	2.50943500
H	3.30118100	-1.17622900	2.32047500
H	4.73317300	-0.35513500	2.96340600
H	3.12046300	0.32662200	3.24176100
Au	0.70912500	-0.63359400	-0.23195800
C	0.31431300	2.75891000	-0.59997200
C	0.65330400	4.16854300	-0.62244000
C	-0.97637000	2.67630200	-1.05760200
C	-0.44333800	4.82456100	-1.08445100
H	-1.64895600	1.84326800	-1.19180700
O	-1.44210900	3.91356300	-1.35145300
H	1.59655600	4.60650200	-0.32917800
C	-0.75682400	6.25605400	-1.34351200
H	-1.01123900	6.42479200	-2.39678700
H	-1.60717700	6.59414800	-0.73917100
H	0.10894800	6.87502500	-1.09537500
C	-3.54470300	0.05523600	0.79535400
C	-4.23031700	-0.08040600	2.00879700
C	-5.60133400	0.16713500	2.04045600
C	-6.23869900	0.54938800	0.86037800
C	-5.46861200	0.66456700	-0.29969200
N	-4.15296400	0.42276800	-0.34587300

H	-6.15987500	0.06568500	2.96664600
H	-3.68144700	-0.37401300	2.89542600
H	-7.30416600	0.75532200	0.83313900
H	-5.93379000	0.96490800	-1.23725100
O	-1.45568200	-0.42011400	1.83937400
C	-2.04613700	-0.21542200	0.76385200
O	-1.49933200	-0.20722100	-0.40307100
C	1.97561100	-2.48905700	-0.39798800
H	2.58677100	-2.39271100	-1.29239000
H	2.49409200	-2.65110900	0.54427900
C	0.62950300	-2.73455100	-0.50183700
C	-0.42663000	-3.51333200	-0.67796100
H	-1.43149500	-3.10259400	-0.67985000
C	-0.25787400	-4.98920400	-0.88580200
O	0.84091300	-5.52455400	-0.89032200
C	-1.54100000	-5.76592300	-1.08993300
H	-2.20213500	-5.63725500	-0.22404500
H	-2.08145800	-5.37965400	-1.96308500
H	-1.32028000	-6.82538000	-1.23165000

Cl

E (B3LYP/BS1) = -460.361274 au
H (B3LYP/BS1) = -460.358914 au
G (B3LYP/BS1) = -460.376297 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -460.410349 au

Cl	0.00000000	0.00000000	0.00000000

Na_2CO_3

E (B3LYP/BS1) = -588.573952 au
H (B3LYP/BS1) = -588.549592 au
G (B3LYP/BS1) = -588.589351 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -588.700665 au

O	1.12878500	1.18976200	0.00220700
C	-0.00002900	0.56642200	0.00212000
O	-1.12905500	1.18954500	-0.00322800
O	0.00009500	-0.75968600	0.00671300
Na	-2.24862400	-0.74348200	-0.00165600
Na	2.24876800	-0.74338200	-0.00364000

HNa_2CO_3

E (B3LYP/BS1) = -589.055772 au
H (B3LYP/BS1) = -589.018985 au
G (B3LYP/BS1) = -589.060652 au
E (B3LYP-D3/BS2// B3LYP/BS1) = -589.177302 au

O	1.10485800	1.22183500	-0.00019500
C	-0.10426700	0.53932100	0.00030400

O	-1.16307800	1.19860600	0.00053300
O	0.03213800	-0.71917300	-0.00083600
Na	-2.33044500	-0.84150300	-0.00008000
Na	2.32316500	-0.88772900	0.00026700
H	0.91434700	2.17548300	0.00010000

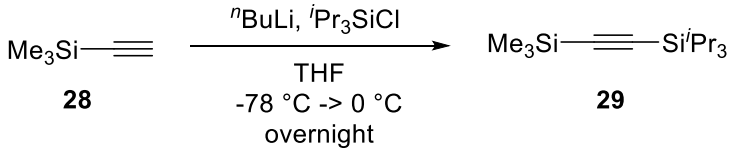
2. General method

All reactions were carried out in oven dried glassware under an atmosphere of nitrogen, unless stated otherwise. For quantitative flash chromatography technical grade solvents were used. For flash chromatography for analysis, HPLC grade solvents from Sigma-Aldrich were used. THF, Et_2O, CH_3CN, toluene, hexane and CH_2Cl_2 were dried by passage over activated alumina under nitrogen atmosphere (H_2O content < 10 ppm, *Karl-Fischer* titration). NEt_3 and pyridine were distilled under nitrogen from KOH. Gold chloride was purchased from Aldrich and kept in desiccator under anhydrous condition (decrease of reactivity has been observed for catalyst if prolonged exposition to air (*ca* 1 month). All chemicals were purchased from Acros, Aldrich, Fluka, VWR, Aplichem or Merck and used as such unless stated otherwise. Chromatographic purification was performed as flash chromatography using Macherey-Nagel silica 40-63, 60 Å, using the solvents indicated as eluent with 0.1-0.5 bar pressure.TLC was performed on Merck silica gel 60 F_{254} TLC glass plates or aluminium plates and visualized with UV light, permanganate stain, CAN stain or Anisaldehyde stain. Melting points were measured on a Büchi B-540 melting point apparatus using open glass capillaries, the data is uncorrected. ^{1}H-NMR spectra were recorded on a Brucker DPX-400 400 MHz spectrometer in chloroform-d, DMSO-d_6 or CD_3OD, all signals are reported in ppm with the internal chloroform signal at 7.26 ppm, the internal DMSO signal at 2.50 ppm or the internal methanol signal at 3.30 ppm as standard. The data is being reported as (s = singlet, d = doublet, t = triplet, q = quadruplet, qi = quintet, m = multiplet or unresolved, br = broad signal, app = apparent, coupling constant(s) in Hz, integration, interpretation).^{13}C-NMR spectra were recorded with ^{1}H-decoupling on a Brucker DPX-400 100 MHz spectrometer in chloroform-d, DMSO-d_6 or CD_3OD, all signals are reported in ppm with the internal chloroform signal at 77.0 ppm, the internal DMSO signal at 39.5 ppm or the internal methanol signal at 49.0 ppm as standard. Infrared spectra were recorded on a JASCO FT-IR B4100 spectrophotometer with an ATR PRO410-S and a ZnSe prisma and are reported as cm^{-1} (w = weak, m = medium, s = strong, br = broad). Gas chromatographic and low resolution mass spectrometric measurements were performed on a Perkin-Elmer Clarus 600 gas chromatographer and mass spectrometer using a Perkin-Elemer Elite fused silica column (length: 30 m, diameter: 0.32 mm) and Helium as carrier gas. High resolution mass spectrometric measurements were performed by the mass spectrometry service of ISIC at the EPFL on a MICROMASS (ESI) Q-TOF Ultima API. HPLC measurement were done on a JASCO HPLC system with an AS2055 Autosampler, a PU 2089 Pump, a UV 2075 detector and a SEDEX 85 (SEDERE) detector using a CHIRALPAK IC column from DAICEL Chemical Industries Ltd. HPLC grade solvents from Sigma-Aldrich were used.

3. Domino cyclization-alkynylation reaction

The synthesis of reagents and starting materials has been reported in our previous publication[1] and is re-copied here for easier reproduction of the results.

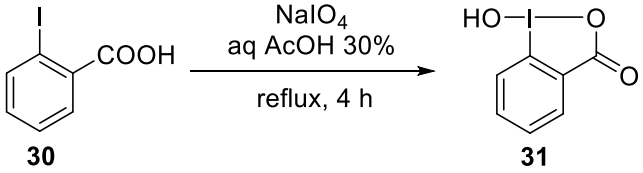
Tri*iso*propylsilyl trimethylsilylacetylene (29)



Following a reported procedure,[2] *n*-butyllithium (2.5 M in hexanes, 12.0 mL, 29.9 mmol, 0.98 equiv) was added dropwise to a stirred solution of ethynyltrimethylsilane (**28**) (3.0 g, 30 mmol, 1.0 equiv) in THF (48 mL) at -78 °C. The mixture was then warmed to 0 °C and stirred for 5 min. The mixture was then cooled back to -78 °C and chlorotri*iso*propylsilane (6.4 mL, 30 mmol, 1.0 equiv) was added dropwise. The mixture was then allowed to warm to room temperature and stirred overnight. A saturated solution of ammonium chloride (40 mL) was added, and the reaction mixture was extracted with diethyl ether (2 x 60 mL). The organic layer was washed with water and brine, then dried over $MgSO_4$, filtered and concentrated under reduced pressure to obtain a colorless liquid which was further purified by Kugelrohr distillation (56-57°C/0.25 mmHg) to yield **29** (7.16 g, 28.0 mmol, 92% yield) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.08 (m, 21 H, TIPS), 0.18 (s, 9 H, TMS). IR ν 2959 (m), 2944 (m), 2896 (w), 2867 (m), 1464 (w), 1385 (w), 1250 (m), 996 (w), 842 (s), 764 (s), 675 (m), 660 (m). Characterization data of **21** corresponded to the literature values. [S12]

1-Hydroxy-1,2-benziodoxol-3-(1*H*)-one (31)

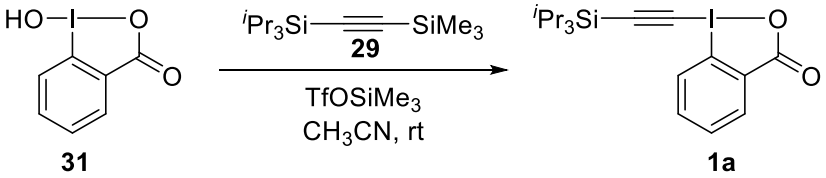


Following the reported procedure,[3] $NaIO_4$ (7.24 g, 33.8 mmol, 1.05 equiv) and 2-iodobenzoic acid (**30**) (8.00 g, 32.2 mmol, 1.00 equiv) were suspended in 30% (v:v) aq. AcOH (48 mL). The mixture was vigorously stirred and refluxed for 4 h. The reaction mixture was then diluted with cold water (180 mL) and allowed to cool to rt, protecting it from light. After 1 h, the crude product was collected by filtration, washed on the filter with ice water (3 x 20 mL) and acetone (3 x 20 mL), and air-dried in the dark to give the pure product **31** (8.3 g, 31 mmol, 98%) as a colorless solid.

[1] Y. Li, J. P. Brand, J. Waser, *Angew. Chem., Int. Ed.* **2013**, *52*, 6743-6747.
[2] C J. Helal, P. A. Magriotis, E. J. Corey, *J. Am. Chem. Soc.* **1996**, *118*, 10938.
[3] L. Kraszkiewicz, L. Skulski, *Arkivoc*. **2003**, *6*, 120.

^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.02 (dd, 1 H, *J* = 7.7, 1.4 Hz, Ar*H*), 7.97 (m, 1 H, Ar*H*), 7.85 (dd, 1 H, *J* = 8.2, 0.7 Hz, Ar*H*), 7.71 (td, 1 H, *J* = 7.6, 1.2 Hz, Ar*H*); ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ 167.7, 134.5, 131.5, 131.1, 130.4, 126.3, 120.4; IR ν 3083 (w), 3060 (w), 2867 (w), 2402 (w), 1601 (m), 1585 (m), 1564 (m), 1440 (m), 1338 (s), 1302 (m), 1148 (m), 1018 (w), 834 (m), 798 (w), 740 (s), 694 (s), 674 (m), 649 (m); the reported values correspond to the ones in literature. [S13]

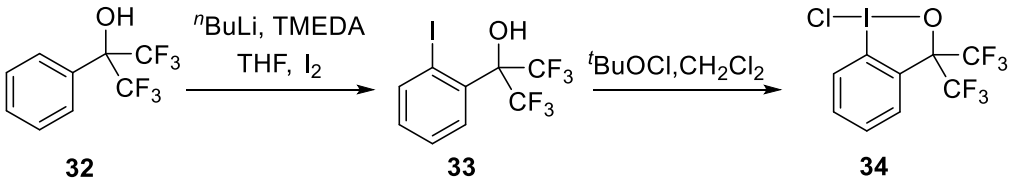
1-[(Tri*iso*-propylsilyl)ethynyl]-1,2-benziodoxol-3(1*H*)-one (TIPS-EBX, 1a)



Following a reported procedure, [4] 2-iodosylbenzoic acid (**31**) (21.7 g, 82.0 mmol, 1.0 equiv) was charged in oven-dried three-neck 1L flask equipped with a magnetic stirrer. After 3 vacuum/nitrogen cycles, anhydrous acetonitrile (500 mL) was added via canula and cooled to 0 °C. Trimethylsilyltriflate (16.4 mL, 90.0 mmol, 1.1 equiv) was added dropwise via a dropping funnel over 30 min (no temperature increase was observed). After 15 min, (trimethylsilyl)(tri*iso*propylsilyl)acetylene (**29**) (23.0 g, 90.0 mmol, 1.1 equiv) was added via canula over 15 min (no temperature increase was observed). After 30 min, the suspension became an orange solution. After 10 min, pyridine (7.0 mL, 90 mmol, 1.1 equiv) was added via syringe. After 15 min, the reaction mixture was transferred in a one-neck 1L flask and reduced under vacuum until a solid was obtained. The solid was dissolved in DCM (200 mL) and transferred in a 1L separatory funnel. The organic layer was added and washed with 1 M HCl (200 mL) and the aqueous layer was extracted with CH_2Cl_2 (200 mL). The organic layers were combined, washed with a saturated solution of $NaHCO_3$ (2 x 200 mL), dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. Recrystallization from acetonitrile (*ca* 120 mL) afforded **1a** (30.1 g, 70.2 mmol, 86%) as colorless cristals.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (m, 1 H, Ar*H*), 8.29 (m, 1 H, Ar*H*), 7.77 (m, 2 H, Ar*H*), 1.16 (m, 21 H, TIPS). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 134.6, 132.3, 131.4, 131.4, 126.1, 115.6, 114.1, 64.6, 18.4, 11.1. IR ν 2943 (m), 2865 (m), 1716 (m), 1618 (m), 1604 (s), 1584 (m), 1557 (m), 1465 (m), 1439 (w), 1349 (m), 1291 (m), 1270 (w), 1244 (m), 1140 (m), 1016 (m), 999 (m), 883 (m), 833 (m), 742 (m), 702 (s), 636 (m); Melting point (Dec.) 170-176°C; Characterization data of **6** corresponded to the literature values. [4]

1-Chloro-1,3-dihydro-3,3-bis(trifluoromethyl)-1,2-benziodoxole (34)

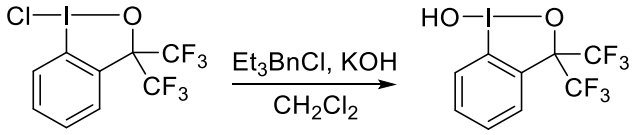


[4] J. P. Brand, J. Charpentier, J. Waser, *Angew. Chem., Int. Ed.* **2009**, *48*, 9346-9349.

Following a reported procedure,[5] TMEDA (distilled over KOH) (1.26 mL, 8.20 mmol, 0.2 equiv) was added to a solution of ^{n}BuLi (2.5 M in hexanes, 36.6 mL, 91.6 mmol, 2.2 equiv). After 15 min, the cloudy solution was cooled to 0 °C and **32** (7.0 mL, 42 mmol, 1 equiv) in THF (6 mL) was added dropwise. The reaction was stirred 30 min at 0 °C and then at RT overnight. I_2 (11.2 g, 44.0 mmol, 1.06 equiv) was then added portions wise at 0 °C and the mixture stirred at 0 °C for 30 min and 4 h at RT. The reaction was quenched with saturated NH_4Cl. Et_2O (100 mL) was added and the layers were separated. The aqueous layer was then extracted twice with Et_2O (3 x 50 mL). The organic layers were combined, washed twice with saturated NaS_2O_3 (2 x 50 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure to afford 15.6 g of crude **33** as an brown oil which was used without further purification.

The crude oil was dissolved in wet CH_2Cl_2 (40 mL) in the dark under air. ^{t}BuOCl (5.2 mL, 44 mmol, 1.05 equiv) was then added dropwise at 0 °C. After 30 min, the resulting suspension was filtered to afford **33** (7.30 g, 18.1 mmol, 43%) as a yellow solid. The mother liquors were carefully reduced to one third and filtered to afford more **34** (3.51 g, 8.71 mmol, 21%) as a yellow solid. Combined yield: 64%. Mp 167 – 169 °C, Lit: 166-168 °C.[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, 1 H, *J* = 8.4 Hz, ArH), 7.85 (m, 1 H, ArH), 7.73 (m, 2 H, ArH). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.8, 132.1, 131.6, 129.7, 128.5, 122.8 (q, 289 Hz), 113.4, 84.8. The melting point and the ^{1}H NMR correspond to the reported values.[5]

1-Hydroxy-3,3-bis(trifluoromethyl)-3-(*1H*)-1,2-benziodoxole (35)

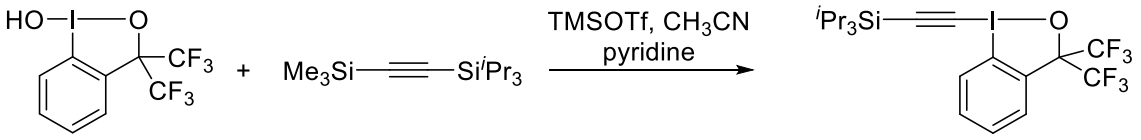


34 **35**

Following a preported procedure,[6] Et_3BnNCl (83 mg, 0.36 mmol, 0.05 equiv) was added to a stirring solution of **34** (10.7 g, 26.5 mmol, 1 equiv) in CH_2Cl_2 (150 mL) and KOH (1.48 g, 26.5 mmol, 1 equiv) in water (28 mL). The reaction was stirred overnight under air. The organic layer was separated and dried over $MgSO_4$. The resulting solid was purified over a silica plug eluting with EtOAc,then recristallized in EtOAC (about 50 mL) and washed with pentane to afford **35** (7.42 g, 19.2 mmol, 73%) as a white solid. ^{1}H NMR (400 MHz, DMSO) δ 7.96 (m, 2 H, ArH), 7.73 (m, 2 H, ArH). ^{13}C NMR (101 MHz, DMSO) δ 133.3, 131.0, 130.8, 128.9, 127.9, 123.4 (q, *J* = 290 Hz), 117.2, 83.7 (m). IR 1464 (w), 1435 (w), 1290 (w), 1263 (m), 1185 (s), 1139 (s), 1103 (m), 1041 (w), 1021 (w), 952 (s), 760 (m), 730 (m), 692 (m).

1-[(Tri*iso*propylsilyl)ethynyl]-3,3-bis(trifluoromethyl)-3(*1H*)-1,2-benziodoxole (1b)

[5] E. F. Perozzi, R. S. Michalak, G. D. Figuly, W. H. Stevenson, D. B. Dess, M. R. Ross, J. C. Martin, *J. Org. Chem.* **1981**, *46*, 1049.
[6] A. J. Blake, A. Novak, M. Davies, R. I. Robinson, S. Woodward, *Synth. Commun.* **2009,** *39*, 1065.



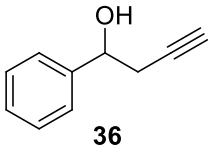
35 **29** **1b**

TMSOTf (3.80 g, 17.1 mmol, 1.1 equiv) was added to **35** (6.00 g, 15.5 mmol, 1.0 equiv) in CH_2Cl_2 (200 mL) at RT. After 20 min, the solution was concentrated under reduced pressure at 0 °C and the reaction flask was refilled with Ar. Then the resulting yellow solid was dissolved in dry CH_3CN (200 mL). (Trimethylsilyl)(tri*iso*-propylsilyl)acetylene (**29**) (5.14 g, 20.2 mmol, 1.3 equiv) was added and after 20 min a few drops of pyridine were added. The reaction was then concentrated under vacuum, the residues were dissolved in Et_2O and the solutions filtered through a silica plug (eluant Et_2O). The resulting solid was recrystallized in pentane to afford **1b** (5.43 g, 9.87 mmol, 64%) as a white crystalline solid. R_f (PET/Et_2O 95/5): 0.4. Mp 131 – 132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (*ca* 0.10 mmol/mL) δ 8.36 (dd, 1 H, *J* = 7.9, 1.7 Hz, ArH), 7.84 (d, 1 H, *J* = 6.7 Hz, ArH), 7.68 (m, 2H, ArH), 1.15 (m, 21 H, TIPS). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.7, 131.1, 129.9, 129.9 (m), 128.2, 123.6 (q, 288 Hz), 112.1, 110.8, 81.4 (m), 69.7, 18.5, 11.2. IR 2947 (m), 2868 (m), 2249 (w), 1566 (w), 1465 (m), 1438 (w), 1387 (w), 1264 (s), 1218 (m), 1184 (s), 1149 (s), 1071 (w), 994 (w), 951 (s), 910 (m), 873 (w), 732 (s), 696 (s), 655 (s), 655 (s). HRMS(ESI) calcd for $C_{20}H_{26}OF_6ISi^+$ (M+H) 551.0702, found 551.0723.

General procedure for the preparation of propargylic alcohols:

A 50 mL two-necked flask was charged with Mg (321 mg, 13.2 mmol, 1.32 equiv), $HgCl_2$ (2.7 mg, 0.10 mmol, 0.01 equiv) and dry diethyl ether (30 mL), then propargyl bromide was added dropwise (2.86 g, 12.0 mmol, 1.20 equiv). When the solution became homogeneous, the aldehyde (10.0 mmol, 1.00 equiv) was added dropwise. The reaction was quenched with a sat NH_4Cl solution (30 mL) when TLC (Pentane/EtOAc: 5/1) indicated that the benzaldehyde was completely consumed. The aqueous and organic layers were separated, the aqueous layer was extracted with diethyl ether (3×20 mL). The combined organic layers were dried over $MgSO_4$, concentrated under vaccum and purified by column chromatography (Pentane/EtOAc: 5/1).

Phenylbut-3-yn-1-ol (36) was obtained as a transparent oil (1.09 g, 7.46 mmol, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.30 (m, 5 H, *ArH*), 4.82 (m, 1 H, *CH*Ph), 3.23 (d, 1 H, *J* = 3.8 Hz, *OH*), 2.62 (m, 2 H, *CH_2*), 2.09 (t, 1 H, *J* = 2.6 Hz, alkyne *CH*) . ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.3, 128.1, 127.6, 125.6, 80.6, 72.0, 70.7, 28.9. The ^{1}H NMR data corresponds to the literature [7]



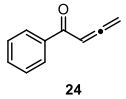
36

Typical procedure to prepare ketone allene:

Following a reported procedure,[8] a solution of **36** (1.31 g, 9.00 mmol, 1 equiv) and CH_3CN (40 mL) was added into a solution of H_5IO_6 (2.15 g, 9.45 mmol, 1.05 equiv) and CH_3CN (40 mL) by an addition funnel at 0 °C. Then, pyridiniumchlorochromat (PDC) (38 mg, 0.18 mmol, 0.02 equiv) was added into the mixture in three portions. The ice bath was removed and the

[7] J. Chen, B. Captain, N. Takenaka, *Org. Lett*. **2011**, *13*, 1654.
[S18] M. Hunsen, *Tetrahedron Lett*. **2005**, *46*, 1651.

reaction was diluted with EtOAc (100 mL) when TLC (Pentane/EtOAc: 10/1) showed that all starting material was consumed. The organic layer was washed with a mixture of brine and water (25 mL / 25 mL), sat $Na_2S_2O_3$ (50 mL), brine (50 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (Pentane/EtOAc: 10/1).


24

1-Phenylbuta-2,3-dien-1-one (24) was obtained following as a brown solid (0.73 g, 5.5 mmol, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (m, 2 H, *ArH*), 7.54 (m, 1 H, *ArH*), 7.44 (m, 2 H, *ArH*), 6.43 (t, 1 H, *J* = 6.5 Hz, *CH*), 5.25 (d, 2 H, *J* = 6.5 Hz, *CH_2*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 217.0, 190.9, 137.4, 132.7, 128.6, 128.3, 93.2, 79.2. The NMR data corresponds to the literature.[9]

Domino cyclization-alkynylation reaction:

The optimization data from our previous publication is copied again here for information. New experiments are given in bold (entry 16 and 17 in table S3).

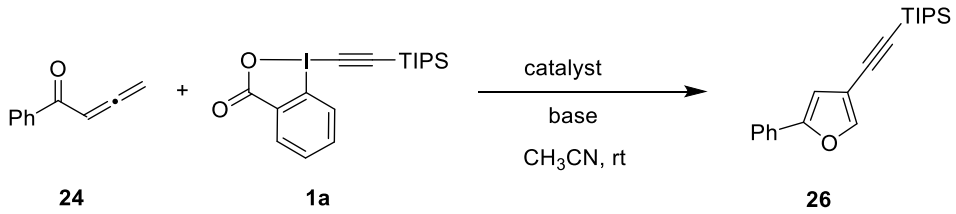
Optimization of the reaction with TIPS-EBX (1a):

TIPS-EBX (**1a**) (51 mg, 0.12 mmol, 1.2 equiv), base (0.12 mmol, 1.2 equiv) and catalyst (0.005 mmol, 0.050 equiv) were added into a solution of 1-phenylbuta-2,3-dien-1-one (**24**) (15 mg, 0.10 mmol, 1.0 equiv) and CH_3CN (5 mL). The reaction was stopped after 72 h. Isolated yields after column chromatography (SiO_2, pentane) are given.

The complete list of experiments for the optimization of the domino alkynylation with TIPS-EBX (**1a**) reagent is shown in Table S2.

[9] X. Fan, Y. Qu, Y. Wang, X. Zhang, J. Wang, *Tetrahedron Lett*. **2010**, *51*, 2123.

Table S2: Optimization with TIPS-EBX (**1a**) reagent:



24 **1a** **26**

Entry	Catalyst	Base	Yield (%)
1	**2**	NEt_3	0
2	**2**	Py	0
3	**2**	DBU	<5
4	**2**	KO*t*Bu	0
5	**2**	Cs_2CO_3	<5
6	**2**	K_2CO_3	10
7	**2**	Na_2CO_3	31
8	**2**	Li_2CO_3	<5
9	**2**	$NaHCO_3$	22
10	AuCl	Na_2CO_3	0
11	Au(IPr)Cl + 5mol % AgOTs	Na_2CO_3	0
12	$AuCl_3$	Na_2CO_3	0[a]
13	$NaAuCl_4$	Na_2CO_3	<5
14	$Au(OAc)_3$	Na_2CO_3	0
15	$InCl_3$	Na_2CO_3	0
16	$PtCl_2$	Na_2CO_3	<5
17	$PdCl_2(CH_3CN)_2$	Na_2CO_3	<5

[a] Only cyclization product without alkynylation was obtained

Optimization of the reaction with 1b:

General procedure: 1-[(tri*iso*propylsilyl)ethynyl]-3,3-bis(trifluoromethyl)-3(*1H*)-1,2-benziodoxole (**1b**) (110 mg, 0.200 mmol, 2.00 equiv)**,** Na_2CO_3 (21 mg, 0.20 mmol, 2.0 equiv) and catalyst (0.005 mmol, 0.050 equiv) were added into a solution of 1-phenylbuta-2,3-dien-1-one (**24**) (15 mg, 0.10 mmol, 1.0 equiv) and *iso*-propanol (5 mL). The reaction was stopped after 72 h. 1 mL of mixture was mixed with 0.16 mL n-decane solution (0.125 M in CH_3CN) and injected into the GC-MS chromatographer. The following oven program was used: Initial temperature: 50 °C, Ramp: 10.0 °C/min to 250 °C, hold 25 min at 250 °C). Yields were determined by GC-MS, based on the following calibration.

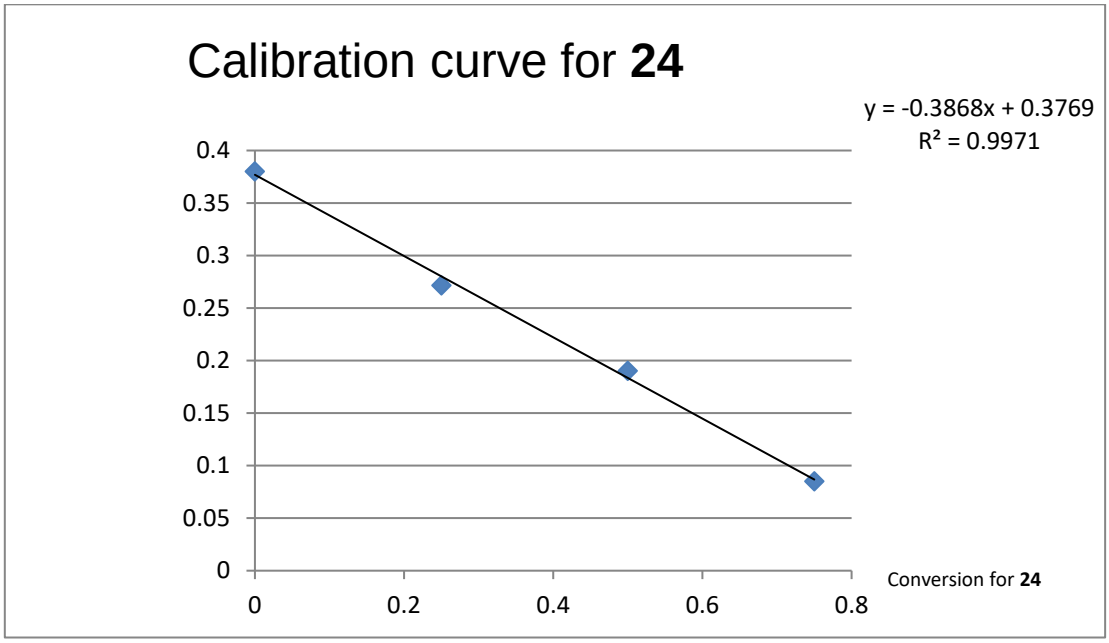
A 0.125 M standard solution was prepared by dissolving n-decane (0.242 mL, 1.25 mmol) in CH_3CN (10 mL).

1-Phenylbuta-2,3-dien-1-one (**24**) (7.2 mg, 0.054 mmol) was dissolved in CH_2Cl_2 (1.0 mL) (solution O).

- 25 µL of solution O were mixed with 160 µL of the standard solution 0.125 M and diluted by adding CH_2Cl_2 (600 µL) to obtain solution A;
- 50 µL of solution O were mixed with 160 µL of the standard solution 0.125 M and diluted by adding CH_2Cl_2 (600 µL) to obtain solution B;
- 75 µL of solution O were mixed with 160 µL of the standard solution 0.125 M and diluted by adding CH_2Cl_2 (600 µL) to obtain solution C;

- 100 µL of solution O were mixed with 160 µL of the standard solution 0.125 M and diluted by adding CH_2Cl_2 (600 µL) to obtain solution D;

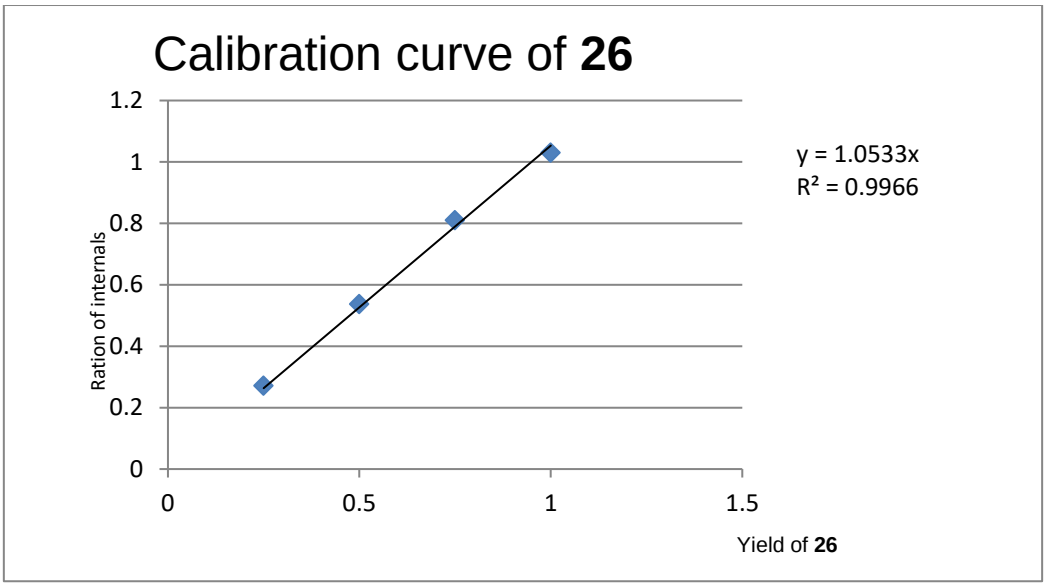
GC-MS chromatograms were acquired for solutions A, B, C and D and in each of them the ratio between the integrals of the signals corresponding to compound **24** (retention time: 13.8 min) and to the internal standard (retention time: 15.9 min) was calculated. These observed ratios by integration of the chromatogram peaks and the ratios (mmol **24**/mmol n-decane) were used as the axis of the calibration graph.



Triisopropyl((5-phenylfuran-3-yl)ethynyl)silane **(26)** (16.2 mg, 0.0500 mmol) was dissolved in CH_2Cl_2 (1.0 mL) (solution P).

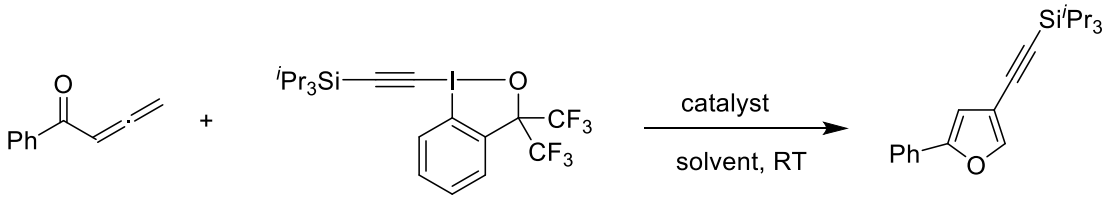
- 25 µL of solution P were mixed with 160 µL of the standard solution 0.125 M and diluted by adding CH_2Cl_2 (600 µL) to obtain solution E;
- 50 µL of solution P were mixed with 160 µL of the standard solution 0.125 M and diluted by adding CH_2Cl_2 (600 µL) to obtain solution F;
- 75 µL of solution P were mixed with 160 µL of the standard solution 0.125 M and diluted by adding CH_2Cl_2 (600 µL) to obtain solution G;
- 100 µL of solution P were mixed with 160 µL of the standard solution 0.125 M and diluted by adding CH_2Cl_2 (600 µL) to obtain solution H;

GC-MS chromatograms were acquired for solutions E, F, G and H and in each of them the ratio between the integrals of the signals corresponding to compound **26** (retention time: 30.7 min) and to the internal standard (retention time: 15.9 min) was calculated. These observed ratios by integration of the chromatogram peaks and the ratios (mmol **26**/mmol n-decane) were used as the axis of the calibration graph.



The complete list of experiments for the optimizationof the domino alkynylation with benziodoxole reagent **1b** is shown in Table S3:

Table S3: Optimization with bistrifluoromethyl benziodoxole reagent **1b**:

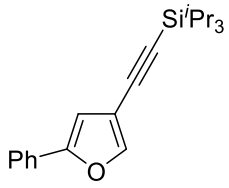


24 **1b** **26**

Entry	Catalyst	Base	Solvent	Yield (%)
1	**2**	-	CH_3CN	50[a]
2	**2**	-	CH_3CN	<5
3	**2**	-	CH_3CN	<5
4	**2**	Na_2CO_3	CH_3CN	33
5	**2**	Na_2CO_3	CH_3CN	73
6	**2**	Na_2CO_3	CH_2Cl_2	11
7	**2**	Na_2CO_3	THF	6
8	**2**	Na_2CO_3	EtOH	23
9	**2**	Na_2CO_3	^{i}PrOH	93
10	$AuCl_3$	Na_2CO_3	^{i}PrOH	0
11	$AuCl_3$·Pyridine	Na_2CO_3	^{i}PrOH	0
12	$AuCl_3$+benzoic acid	Na_2CO_3	^{i}PrOH	0
13	$AuCl_3$+isonicotinic acid	Na_2CO_3	^{i}PrOH	0
14	$AuCl_3$·Pyridine+benzoic acid	Na_2CO_3	^{i}PrOH	0
15	$AuCl_3$+ picolinic acid (**25**)	Na_2CO_3	^{i}PrOH	81
16	**AuCl + picolinic acid (25)**	**Na_2CO_3**	**^{i}PrOH**	**73**[b]
17	**AuCl**	**Na_2CO_3**	**^{i}PrOH**	**35**[b]

[a] 14 % cyclization product without alkynylation was obtained. [b] Isolated yield after column chromatography.

Triisopropyl((5-phenylfuran-3-yl)ethynyl)silane (26)



26

R_f (Pentane): 0.7.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (app d, 3 H, *J* = 8.1 Hz, *ArH* + *FuranH*), 7.39 (t, 2 H, *J* = 7.5 Hz, *ArH*), 7.29 (d, 1 H, *J* = 7.5 Hz, *ArH*), 6.69 (s, 1 H, *FuranH*), 1.12 (m, 21 H, *TIPS*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 145.6, 130.1, 128.7, 127.9, 123.9, 109.8, 107.8, 97.7, 92.9, 18.6, 11.3. IR 2943 (s), 2923 (m), 2865 (s), 2157 (m), 1746 (w), 1463 (m), 1384 (w), 1253 (w), 1228 (w), 1191 (w), 1144 (m), 1072 (w), 1016 (m), 992 (s), 883 (s), 808 (m). HRMS (ESI) calcd for $C_{21}H_{29}OSi^+$ $[M+H]^+$ 325.1982; found 325.1987.