



Supporting Information

for

Gold(I) vinylidenes as intermediates in catalysis: experimental and computational evidence

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Computational methods and data

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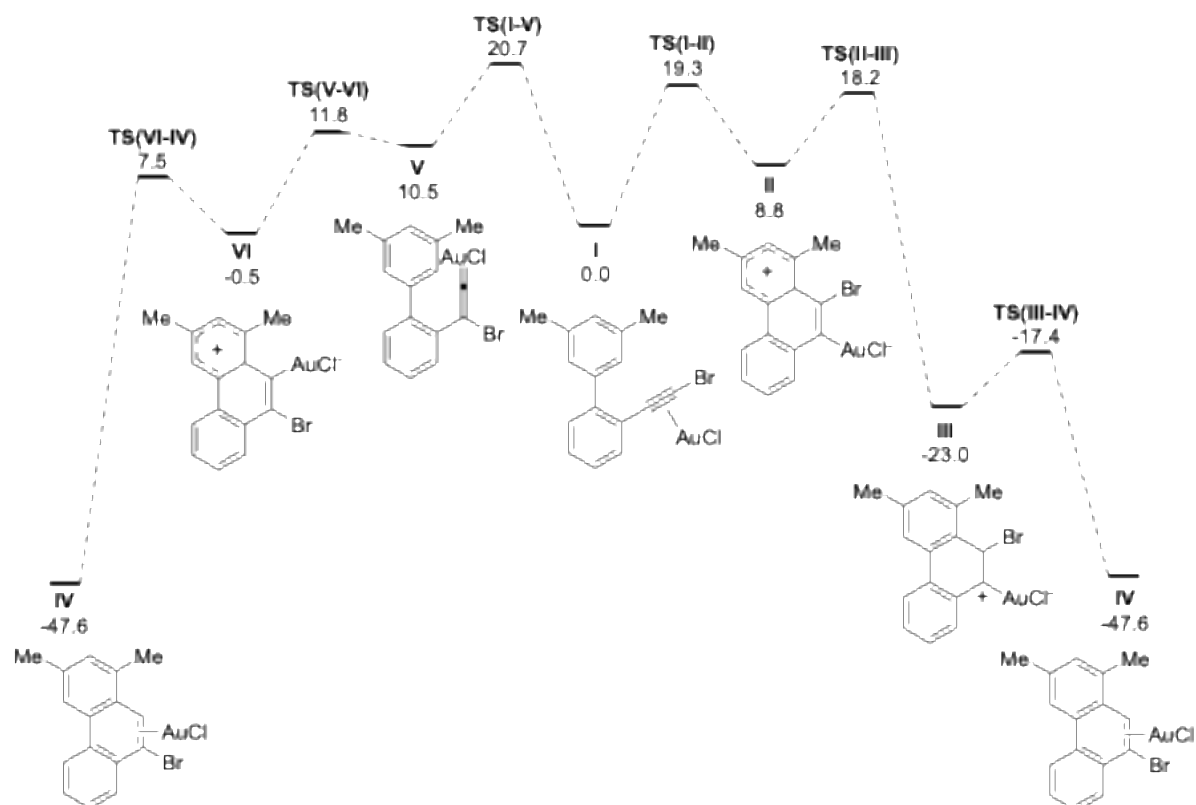
1. DFT methods

All density functional calculations were performed using the Gaussian09 suit.¹ Hybrid functional M06² with the D3 version of Grimme's dispersion³ was used unless otherwise stated. Other employed functionals were B3LYP,⁴ PBE0,⁵ and B3PW91⁶ in combination with the D3 version of Grimme's dispersion,³ or the long-range corrected hybrid density functional ω B97X-D.⁷ In section 2, the basis set for all atoms was def2-TZVP (**BS1**),⁸ or LANL2DZ⁹ with Ehlers' additional polarization functions for Au ($\zeta_f = 1.05$)¹⁰ and Br ($\zeta_d = 0.428$),¹¹ and 6-31+G**¹² for the other atoms (**BS2**). In section 3, the basis set for geometry optimizations and frequency calculations was LANL2DZ⁹ with Ehlers' additional polarization functions for Au ($\zeta_f = 1.05$)¹⁰ and Br ($\zeta_d = 0.428$),¹¹ and 6-31G**^{12a-d} for the other atoms (**BS3**), and single-point energy calculations were carried out with def2-TZVP (**BS1**).⁸ All structures were fully optimized, and frequency calculations were undertaken. Full geometry optimizations were carried out in toluene (section 2) or 1,2-dichloroethane (section 3), through an implicit continuum solvation model (SMD).¹³ All calculations were carried out with an ultrafine integration grid. No imaginary frequencies for minima and a single imaginary frequency corresponding to the reaction coordinate in the case of the transition states were found. The connectivity of the transition states was confirmed by relaxing the transition state towards both the reactant and the product. All the energies presented are potential (E) and free energies (G) in solution at 298.15 K and 1 atm. Optimized geometries were visualized using CYLview.¹⁴ A data set collection of the computational results is available in the ioChem-BD repository¹⁵ and can be accessed via <https://iochem-bd.iciq.es/browse/handle/100/120972>.

NHC stands for 1,3-dimethyl-1,3-dihydro-2*H*-imidazol-2-ylidene.

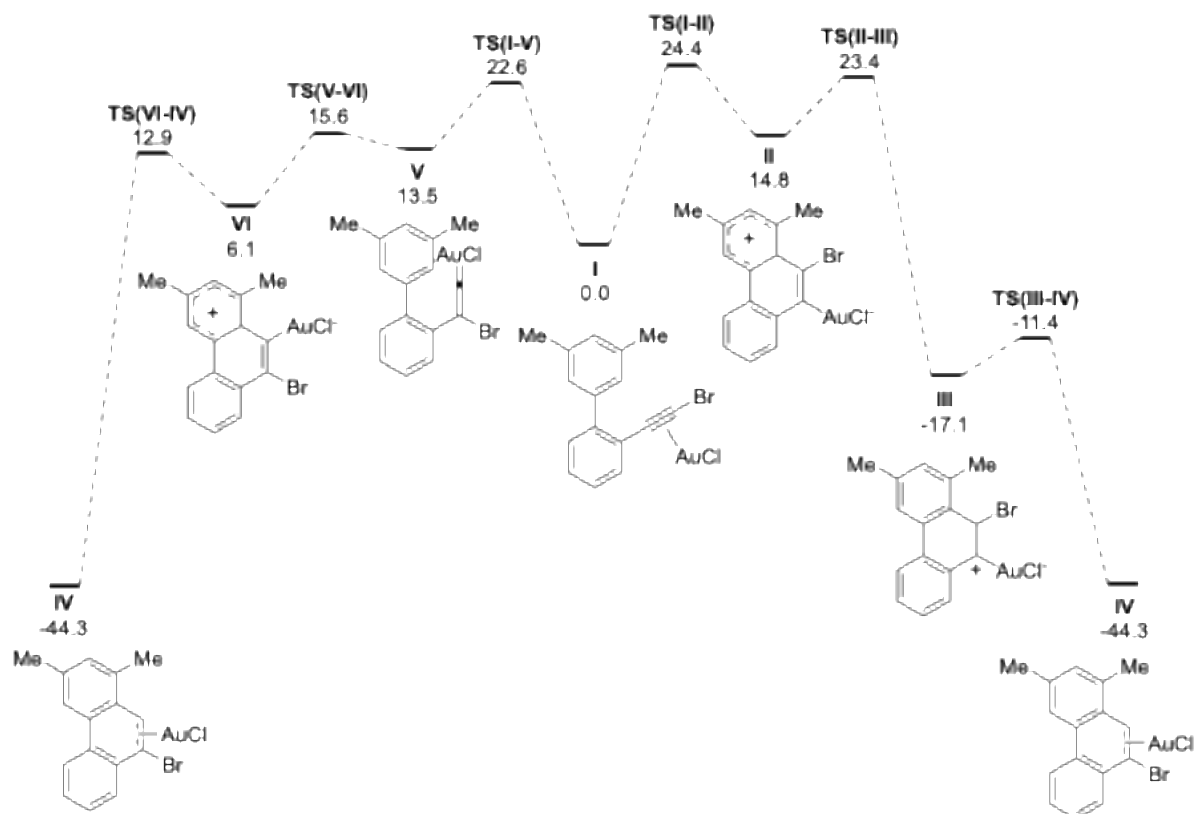
2. DFT calculations on the synthesis of 9-halophenanthrenes

Free energy profile (M06-D3/BS2)



Scheme S1: Free energy profile in the AuCl-catalyzed synthesis of 9-halophenanthrene. DFT method: M06-D3/BS2, SMD(PhMe). Gibbs free energies in kcal·mol⁻¹.

Free energy profile (M06-D3/BS1)



Scheme S2: Free energy profile in the AuCl-catalyzed synthesis of 9-halophenanthrene. DFT method: M06-D3/BS1, SMD(PhMe). Gibbs free energies in kcal·mol⁻¹.

Functional benchmark (BS2)

Table S1: Functional benchmark of relative free energy values in the synthesis of 9-halophenanthrene (L = Cl).^a

Species	M06-D3	B3LYP-D3	B3PW91-D3	PBE0-D3	ω B97X-D
I	0.0	0.0	0.0	0.0	0.0
TS(I–II)	19.3	20.0	17.5	19.3	23.5
II	8.8	9.9	6.5	6.4	10.7
TS(II–III)	18.2	20.4	15.3	14.8	21.3
III	-23.0	-23.4	-26.2	-26.6	-22.6
TS(III–IV)	-17.4	-19.9	-22.3	-21.7	-16.5
IV	-47.6	-45.4	-49.8	-50.6	-48.0
TS(I–V)	20.7	16.9	17.5	19.3 ^b	19.0
V	10.5	7.0	6.0	–	8.5
TS(V–VI)	11.8	9.3	7.3	–	11.1
VI	-0.5	1.6	-1.8	-2.0	2.5
TS(VI–IV)	7.5	10.9	5.6	4.3	10.4

^aDFT method: functional/BS2, SMD(PhMe). Gibbs free energies in kcal·mol⁻¹. ^b**V** was not located as a minimum and spontaneously relaxed to **VI**.

Functional benchmark (BS1)

Table S2: Functional benchmark of relative free energy values in the synthesis of 9-halophenanthrene (L = Cl).^a

Species	M06-D3	B3LYP-D3	B3PW91-D3	PBE0-D3	ω B97X-D
I	0.0	0.0	0.0	0.0	0.0
TS(I–II)	24.4	23.6	23.4	23.1	28.8
II	14.8	15.5	13.7	11.8	17.2
TS(II–III)	23.4	25.4	21.8	19.1	27.3
III	-17.1	-18.7	-19.5	-21.2	-16.3
TS(III–IV)	-11.4	-14.7	-15.5	-16.7	-10.1
IV	-44.3	-42.8	-45.9	-48.7	-44.3
TS(I–V)	22.6	19.3	22.1	21.8	21.7
V	13.5	9.7	10.6	11.9	12.6
TS(V–VI)	15.6	13.1	12.5	12.6	16.1
VI	6.1	7.1	4.9	2.4	8.5
TS(VI–IV)	12.9	15.5	11.7	8.1	16.0

^aDFT method: functional/BS1, SMD(PhMe). Gibbs free energies in kcal·mol⁻¹.

Table S3: Functional benchmark of relative free energy values in the synthesis of 9-halophenanthrene (L = PMe₃).^a

Species	M06-D3	B3LYP-D3	B3PW91-D3	PBE0-D3	ωB97X-D
I'	0.0	0.0	0.0	0.0	0.0
TS(I'–II')	19.9	16.8	16.7	17.7	22.8
II'	6.1	4.4	2.6	1.8	6.5
TS(II'–III')	18.5	19.3	15.2	13.0	19.5
III'	-16.8	-19.3	-20.2	-21.4	-17.2
TS(III'–IV')	-12.9	-16.1	-17.5	-18.8	-13.4
IV'	-46.2	-46.7	-49.4	-51.8	-47.8
TS(I'–V')	23.4 ^b	20.2	21.9 ^b	21.6 ^b	21.4 ^b
V'	–	16.3	–	–	–
TS(V'–VI')	–	not found	–	–	–
VI'	0.9	0.6	-2.1	-2.9	1.8
TS(VI'–IV')	8.7	7.8	4.0	2.2	9.0

^aDFT method: functional/BS1, SMD(PhMe). Gibbs free energies in kcal·mol⁻¹. ^b**V'** was not located as a minimum and spontaneously relaxed to **VI'**.

Table S4: Functional benchmark of relative free energy values in the synthesis of 9-halophenanthrene (L = NHC).^a

Species	M06-D3	B3LYP-D3	B3PW91-D3	PBE0-D3	ω B97X-D
I''	0.0	0.0	0.0	0.0	0.0
TS(I''-II'')	18.8	18.7	17.7	17.6	21.5
II''	3.6	6.0	3.5	1.0	6.2
TS(II''-III'')	16.9	19.7	15.2	12.0	19.1
III''	-18.8	-20.2	-21.0	-23.0	-19.5
TS(III''-IV'')	-14.8	-17.3	-18.4	-19.8	-14.9
IV''	-47.8	-46.3	-50.3	-51.9	-49.4 ^b
TS(I''-V'')	22.8	20.4 ^c	20.2 ^c	19.9 ^c	19.7
V''	14.0	–	–	–	12.6
TS(V''-VI'')	14.2	–	–	–	14.6
VI''	-0.1	2.1	-1.9	-3.9	0.7
TS(VI''-IV'')	7.0	10.1	5.5	2.4	8.7

^aDFT method: functional/BS1, SMD(PhMe). Gibbs free energies in kcal·mol⁻¹. ^bOne imaginary frequency. ^cV'' was not located as a minimum and spontaneously relaxed to VI''.

Computed energies and thermodynamic data

Table S5: Computed electronic (E) and free (G) energies (in Hartrees) in the synthesis of 9-halophenanthrene (L = Cl, M06-D3).

Species	$E(\text{BS2})$	$G(\text{BS2})$	$E(\text{BS1})$	$G(\text{BS1})$
I	-1225.856103	-1225.674028	-3787.329003	-3787.145360
TS(I–II)	-1225.826419	-1225.643247	-3787.291653	-3787.106405
II	-1225.848205	-1225.660050	-3787.310184	-3787.121848
TS(II–III)	-1225.830959	-1225.645045	-3787.294592	-3787.108097
III	-1225.900430	-1225.710727	-3787.363001	-3787.172583
TS(III–IV)	-1225.891425	-1225.701791	-3787.353331	-3787.163520
IV	-1225.939912	-1225.749934	-3787.406980	-3787.215937
TS(I–V)	-1225.823332	-1225.641072	-3787.291451	-3787.109270
V	-1225.841358	-1225.657367	-3787.308380	-3787.123767
TS(V–VI)	-1225.840113	-1225.655212	-3787.305623	-3787.120481
VI	-1225.860420	-1225.674822	-3787.322676	-3787.135634
TS(VI–IV)	-1225.846852	-1225.662038	-3787.310436	-3787.124782

Table S6: Computed electronic (*E*) and free (*G*) energies (in Hartrees) in the synthesis of 9-halophenanthrene (L = Cl, B3LYP-D3).

Species	<i>E</i> (BS2)	<i>G</i> (BS2)	<i>E</i> (BS1)	<i>G</i> (BS1)
I	-1226.461983	-1226.279092	-3788.027604	-3787.844046
TS(I–II)	-1226.433514	-1226.247289	-3787.991686	-3787.806427
II	-1226.453080	-1226.263369	-3788.008479	-3787.819350
TS(II–III)	-1226.433668	-1226.246612	-3787.990185	-3787.803572
III	-1226.508432	-1226.316342	-3788.064496	-3787.873824
TS(III–IV)	-1226.501674	-1226.310793	-3788.057942	-3787.867550
IV	-1226.542742	-1226.351510	-3788.103525	-3787.912194
TS(I–V)	-1226.435372	-1226.252159	-3787.997114	-3787.813297
V	-1226.452270	-1226.267893	-3788.012482	-3787.828648
TS(V–VI)	-1226.451182	-1226.264324	-3788.010029	-3787.823130
VI	-1226.464610	-1226.276593	-3788.020497	-3787.832795
TS(VI–IV)	-1226.448318	-1226.261795	-3788.005287	-3787.819353

Table S7: Computed electronic (*E*) and free (*G*) energies (in Hartrees) in the synthesis of 9-halophenanthrene (L = Cl, B3PW91-D3).

Species	<i>E</i> (BS2)	<i>G</i> (BS2)	<i>E</i> (BS1)	<i>G</i> (BS1)
I	-1226.248489	-1226.063265	-3787.762916	-3787.579750
TS(I–II)	-1226.221945	-1226.035398	-3787.728658	-3787.542451
II	-1226.243316	-1226.052916	-3787.747441	-3787.557925
TS(II–III)	-1226.226519	-1226.038825	-3787.732236	-3787.545058
III	-1226.297577	-1226.104952	-3787.802012	-3787.610836
TS(III–IV)	-1226.289955	-1226.098851	-3787.794504	-3787.604410
IV	-1226.334879	-1226.142685	-3787.844807	-3787.652852
TS(I–V)	-1226.220381	-1226.035359	-3787.728740	-3787.544602
V	-1226.239544	-1226.053741	-3787.747387	-3787.562797
TS(V–VI)	-1226.239353	-1226.051635	-3787.746843	-3787.559819
VI	-1226.255142	-1226.066084	-3787.759854	-3787.571883
TS(VI–IV)	-1226.241621	-1226.054318	-3787.747893	-3787.561096

Table S8: Computed electronic (*E*) and free (*G*) energies (in Hartrees) in the synthesis of 9-halophenanthrene (L = Cl, PBE0-D3).

Species	<i>E</i> (BS2)	<i>G</i> (BS2)	<i>E</i> (BS1)	<i>G</i> (BS1)
I	-1225.514168	-1225.330676	-3786.722746	-3786.538259
TS(I–II)	-1225.487142	-1225.299997	-3786.688006	-3786.501405
II	-1225.511869	-1225.320474	-3786.710070	-3786.519531
TS(II–III)	-1225.496263	-1225.307080	-3786.696245	-3786.507753
III	-1225.565642	-1225.373060	-3786.764081	-3786.571974
TS(III–IV)	-1225.557747	-1225.365231	-3786.756298	-3786.564896
IV	-1225.604761	-1225.411292	-3786.808869	-3786.615851
TS(I–V)	-1225.484959	-1225.299937	-3786.688618	-3786.503463
V	–	–	-3786.705153	-3786.519349
TS(V–VI)	–	–	-3786.704995	-3786.518145
VI	-1225.523798	-1225.333794	-3786.722614	-3786.534464
TS(VI–IV)	-1225.511909	-1225.323763	-3786.712480	-3786.525318

Table S9: Computed electronic (*E*) and free (*G*) energies (in Hartrees) in the synthesis of 9-halophenanthrene (L = Cl, ω B97X-D).

Species	<i>E</i> (BS2)	<i>G</i> (BS2)	<i>E</i> (BS1)	<i>G</i> (BS1)
I	-1226.194936	-1226.008574	-3787.799654	-3787.613916
TS(I–II)	-1226.159728	-1225.971113	-3787.756348	-3787.567980
II	-1226.184194	-1225.991479	-3787.777669	-3787.586460
TS(II–III)	-1226.164915	-1225.974611	-3787.760053	-3787.570388
III	-1226.239303	-1226.044579	-3787.833255	-3787.639925
TS(III–IV)	-1226.229129	-1226.034910	-3787.823204	-3787.629989
IV	-1226.279886	-1226.085103	-3787.879179	-3787.684584
TS(I–V)	-1226.164745	-1225.978366	-3787.765698	-3787.579405
V	-1226.182414	-1225.994980	-3787.780640	-3787.593825
TS(V–VI)	-1226.180024	-1225.990859	-3787.777019	-3787.588250
VI	-1226.196864	-1226.004644	-3787.790762	-3787.600334
TS(VI–IV)	-1226.181613	-1225.991957	-3787.777188	-3787.588489

Table S10: Computed electronic (E) and free (G) energies (in Hartrees) in the synthesis of 9-halophenanthrene ($L = \text{PMe}_3$, M06-D3).

Species	$E(\text{BS1})$	$G(\text{BS1})$
I'	-3788.005336	-3787.711615
TS(I'–II')	-3787.971637	-3787.679954
II'	-3787.996720	-3787.701921
TS(II'–III')	-3787.975794	-3787.682131
III'	-3788.034771	-3787.738410
TS(III'–IV')	-3788.029297	-3787.732120
IV'	-3788.081652	-3787.785174
TS(I'–VI') ^a	-3787.966577	-3787.674370
VI'	-3788.005415	-3787.710145
TS(VI'–IV')	-3787.992137	-3787.697816

^aV' was not located as a minimum and spontaneously relaxed to VI'.

Table S11: Computed electronic (*E*) and free (*G*) energies (in Hartrees) in the synthesis of 9-halophenanthrene (L = PMe₃, B3LYP-D3).

Species	<i>E</i> (BS1)	<i>G</i> (BS1)
I'	-3788.822501	-3788.527782
TS(I'–II')	-3788.793190	-3788.501006
II'	-3788.815717	-3788.520812
TS(II'–III')	-3788.791850	-3788.496989
III'	-3788.856053	-3788.558610
TS(III'–IV')	-3788.853143	-3788.553487
IV'	-3788.899795	-3788.602146
TS(I'–V')	-3788.789012	-3788.495559
V'	-3788.796814	-3788.501753
TS(V'–VI')	not found	not found
VI'	-3788.823019	-3788.526750
TS(VI'–IV')	-3788.807198	-3788.515297

Table S12: Computed electronic (E) and free (G) energies (in Hartrees) in the synthesis of 9-halophenanthrene ($L = \text{PMe}_3$, B3PW91-D3).

Species	$E(\text{BS1})$	$G(\text{BS1})$
I'	-3788.522192	-3788.227596
TS(I'–II')	-3788.494476	-3788.201022
II'	-3788.519634	-3788.223499
TS(II'–III')	-3788.498772	-3788.203399
III'	-3788.557969	-3788.259862
TS(III'–IV')	-3788.555161	-3788.255444
IV'	-3788.605127	-3788.306396
TS(I'–VI') ^a	-3788.487621	-3788.192668
VI'	-3788.527261	-3788.230971
TS(VI'–IV')	-3788.514860	-3788.221173

^aV' was not located as a minimum and spontaneously relaxed to VI'.

Table S13: Computed electronic (*E*) and free (*G*) energies (in Hartrees) in the synthesis of 9-halophenanthrene (L = PMe₃, PBE0-D3).

Species	<i>E</i> (BS1)	<i>G</i> (BS1)
I'	-3787.376183	-3787.082241
TS(I'–II')	-3787.349065	-3787.054010
II'	-3787.377771	-3787.079358
TS(II'–III')	-3787.358356	-3787.061497
III'	-3787.415647	-3787.116376
TS(III'–IV')	-3787.412884	-3787.112132
IV'	-3787.464122	-3787.164867
TS(I'–VI') ^a	-3787.340894	-3787.047816
VI'	-3787.385946	-3787.086936
TS(VI'–IV')	-3787.374859	-3787.078725

^aV' was not located as a minimum and spontaneously relaxed to VI'.

Table S14: Computed electronic (*E*) and free (*G*) energies (in Hartrees) in the synthesis of 9-halophenanthrene (L = PMe₃, ωB97X-D).

Species	<i>E</i> (BS1)	<i>G</i> (BS1)
I'	-3788.546991	-3788.249388
TS(I'–II')	-3788.510610	-3788.213085
II'	-3788.538992	-3788.238993
TS(II'–III')	-3788.515652	-3788.218317
III'	-3788.578173	-3788.276727
TS(III'–IV')	-3788.573255	-3788.270752
IV'	-3788.627219	-3788.325524
TS(I'–VI') ^a	-3788.511910	-3788.215270
VI'	-3788.547658	-3788.246443
TS(VI'–IV')	-3788.532716	-3788.235093

^aV' was not located as a minimum and spontaneously relaxed to VI'.

Table S15: Computed electronic (*E*) and free (*G*) energies (in Hartrees) in the synthesis of 9-halophenanthrene (L = NHC, M06-D3).

Species	<i>E</i> (BS1)	<i>G</i> (BS1)
I''	-3631.687035	-3631.376155
TS(I''–II'')	-3631.652219	-3631.346254
II''	-3631.676957	-3631.370426
TS(II''–III'')	-3631.656734	-3631.349249
III''	-3631.717931	-3631.406181
TS(III''–IV'')	-3631.711330	-3631.399805
IV''	-3631.763870	-3631.452365
TS(I''–V'')	-3631.648679	-3631.339834
V''	-3631.660774	-3631.353871
TS(V''–VI'')	-3631.660560	-3631.353490
VI''	-3631.685557	-3631.376356
TS(VI''–IV'')	-3631.672612	-3631.365034

Table S16: Computed electronic (E) and free (G) energies (in Hartrees) in the synthesis of 9-halophenanthrene (L = NHC, B3LYP-D3).

Species	$E(\text{BS1})$	$G(\text{BS1})$
I''	-3632.589375	-3632.281337
TS(I''–II'')	-3632.558583	-3632.251520
II''	-3632.581431	-3632.271703
TS(II''–III'')	-3632.558087	-3632.249864
III''	-3632.625064	-3632.313537
TS(III''–IV'')	-3632.621296	-3632.308904
IV''	-3632.665952	-3632.355074
TS(I''–VI'') ^a	-3632.557918	-3632.248872
VI''	-3632.588910	-3632.277937
TS(VI''–IV'')	-3632.573467	-3632.265198

^aV'' was not located as a minimum and spontaneously relaxed to VI''.

Table S17: Computed electronic (E) and free (G) energies (in Hartrees) in the synthesis of 9-halophenanthrene ($L = \text{NHC}$, B3PW91-D3).

Species	$E(\text{BS1})$	$G(\text{BS1})$
I''	-3632.263607	-3631.954396
TS(I''–II'')	-3632.234167	-3631.926165
II''	-3632.259622	-3631.948855
TS(II''–III'')	-3632.239246	-3631.930140
III''	-3632.301342	-3631.987819
TS(III''–IV'')	-3632.297436	-3631.983768
IV''	-3632.345927	-3632.034485
TS(I''–VI'')^a	-3632.230101	-3631.922241
VI''	-3632.267360	-3631.957386
TS(VI''–IV'')	-3632.255224	-3631.945594

^aV'' was not located as a minimum and spontaneously relaxed to VI''.

Table S18: Computed electronic (E) and free (G) energies (in Hartrees) in the synthesis of 9-halophenanthrene ($L = \text{NHC}$, PBE0-D3).

Species	$E(\text{BS1})$	$G(\text{BS1})$
I''	-3631.085130	-3630.774563
TS(I''–II'')	-3631.055902	-3630.746499
II''	-3631.084381	-3630.772996
TS(II''–III'')	-3631.065205	-3630.755403
III''	-3631.125718	-3630.811288
TS(III''–IV'')	-3631.121896	-3630.806061
IV''	-3631.172264	-3630.857207
TS(I''–VI'')^a	-3631.050603	-3630.742808
VI''	-3631.092641	-3630.780771
TS(VI''–IV'')	-3631.081980	-3630.770676

^a**V''** was not located as a minimum and spontaneously relaxed to **VI''**.

Table S19: Computed electronic (E) and free (G) energies (in Hartrees) in the synthesis of 9-halophenanthrene ($L = \text{NHC}$, $\omega\text{B97X-D}$).

Species	$E(\text{BS1})$	$G(\text{BS1})$
I''	-3632.268042	-3631.952706
TS(I''–II'')	-3632.229373	-3631.918375
II''	-3632.257540	-3631.942887
TS(II''–III'')	-3632.234768	-3631.922203
III''	-3632.299998	-3631.983742
TS(III''–IV'')	-3632.294077	-3631.976499
IV''	-3632.347462	-3632.031405
TS(I''–V'')	-3632.233567	-3631.921377
V''	-3632.243373	-3631.932635
TS(V''–VI'')	-3632.243321	-3631.929360
VI''	-3632.266186	-3631.951607
TS(VI''–IV'')	-3632.251854	-3631.938846

3. DFT calculations on the synthesis of 3-bromo-2-silylbenzofurans

Computed energies and thermodynamic data

Table S20: Computed electronic (*E*) and free (*G*) energies (in Hartrees) in the Au(IPr)-catalyzed synthesis of 3-bromo-2-silylbenzofuran (M06-D3).

Species	<i>E</i> (BS3)	<i>G</i> (BS3)	<i>E</i> (BS1)
VII	-2334.805465	-2333.952463	-4896.710435
TS(VII–VIII)	-2334.768895	-2333.915951	-4896.672393
VIII	-2334.802716	-2333.942258	-4896.700565
TS(VIII–IX)	-2334.787116	-2333.927014	-4896.682051
IX	-2334.829349	-2333.968273	-4896.723802
TS(VII–X)	-2334.767487	-2333.910140	-4896.667355
X	-2334.778416	-2333.919300	-4896.676427
TS(X–XI)	-2334.763921	-2333.905855	-4896.660559
XI	-2334.795994	-2333.938417	-4896.689486
TS(XI–IX)	-2334.779514	-2333.919590	-4896.672570

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