Supplementary Information

Distinctive C–N Cleavage/C–C Formation Mechanism in Au-Catalyzed Reactions of N-(o-Alkynylphenyl)imines and Vinyldiazo Ketones

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† Electronic supplementary information (ESI) available: Additional computational results and Cartesian coordinates of all optimized structures located in this work (PDF).

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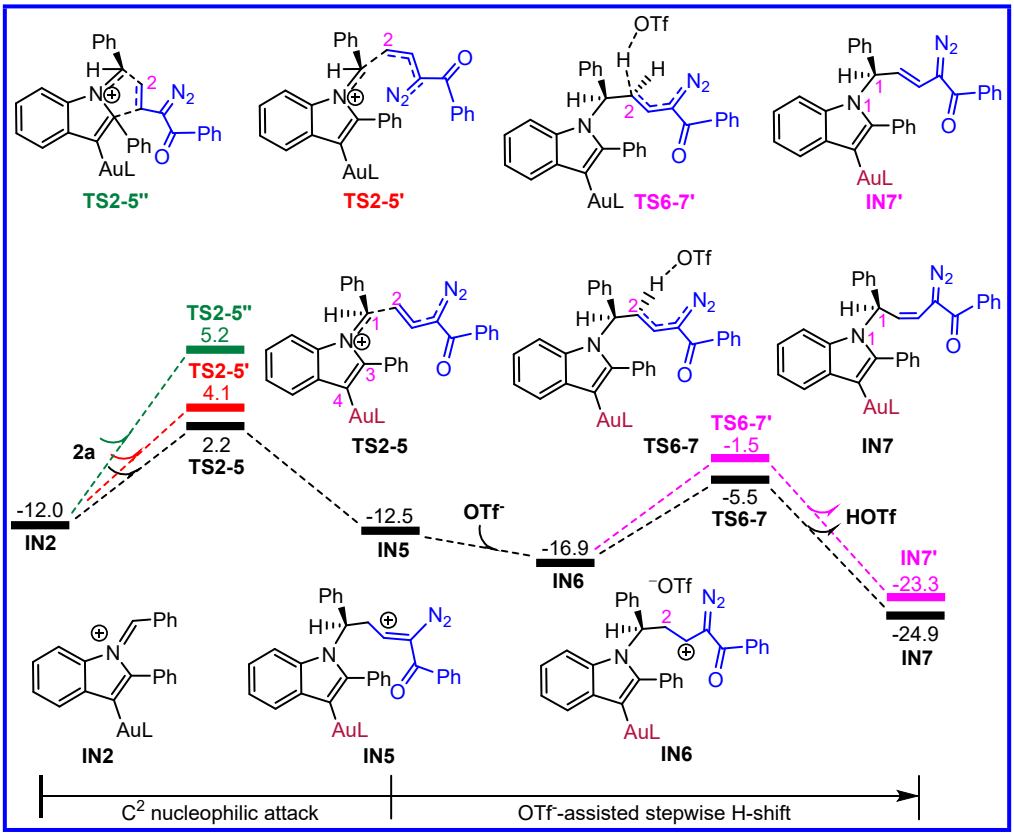
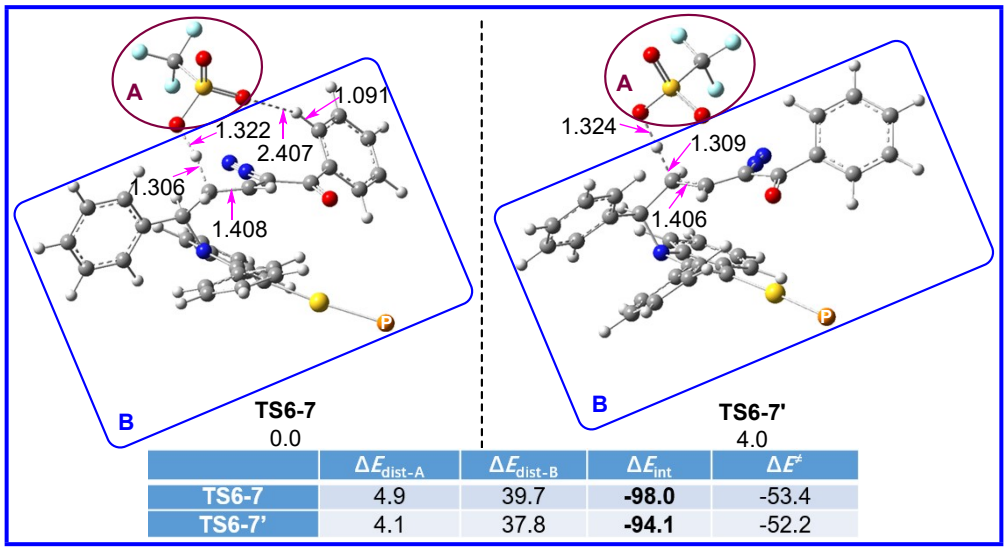


Fig. S1 Calculated free energy profiles in DCE solvent along other possible pathways from **IN2**. The relative free energies are given in kcal mol^{-1}. L=PPh_3



	$\Delta E_{dist\text{-}A}$	$\Delta E_{dist\text{-}B}$	ΔE_{int}	$\Delta E^{\ddagger}$
TS6-7	4.9	39.7	**-98.0**	-53.4
TS6-7'	4.1	37.8	**-94.1**	-52.2

Fig. S2 Distortion/interaction analyses for **TS6-7** and **TS6-7'** in Fig. S1. The phenyl groups attached to P atom are omitted for clarity. The free energies and bond distances are given in kcal mol^{-1} and Å, respectively.

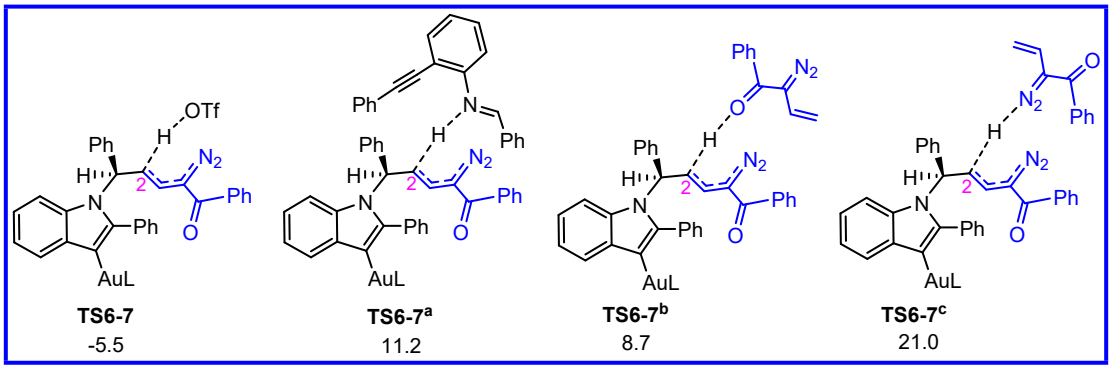


Fig. S3 Other possible H-shift transition states from **IN6**. The relative free energies are given in kcal mol^{-1}. L=PPh_3

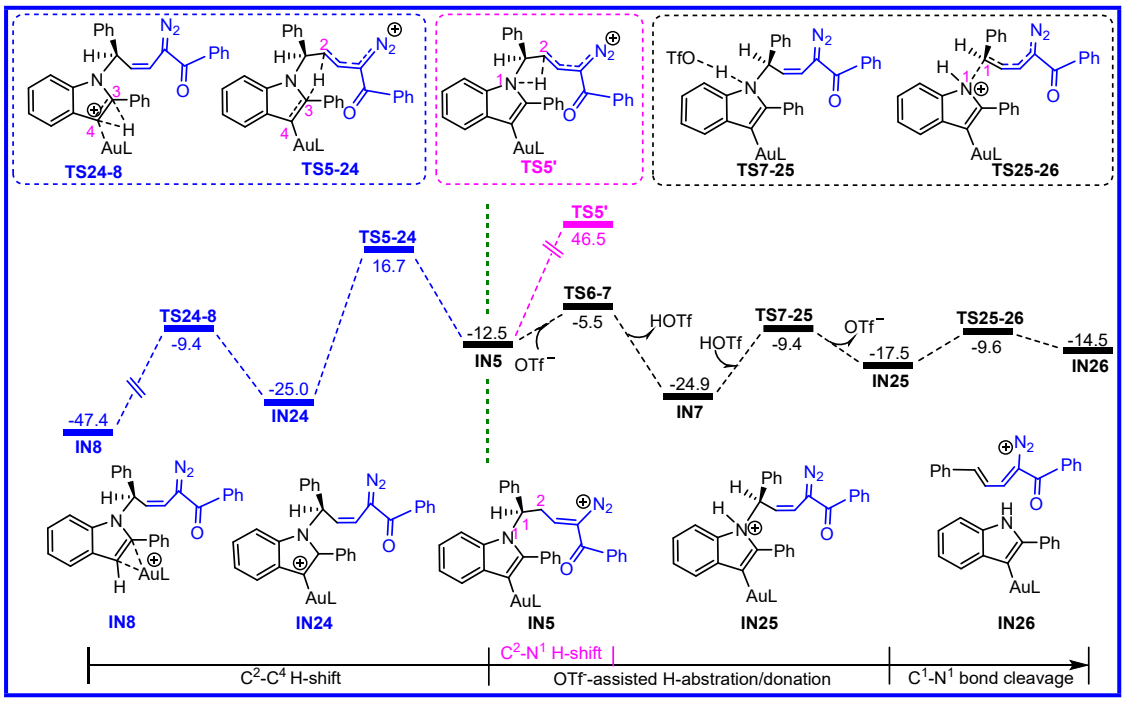


Fig. S4 Calculated free energy profile in DCE solvent for other possible H-shift pathways starting from **IN5**. The relative free energies are given in kcal mol^{-1}. L=PPh_3

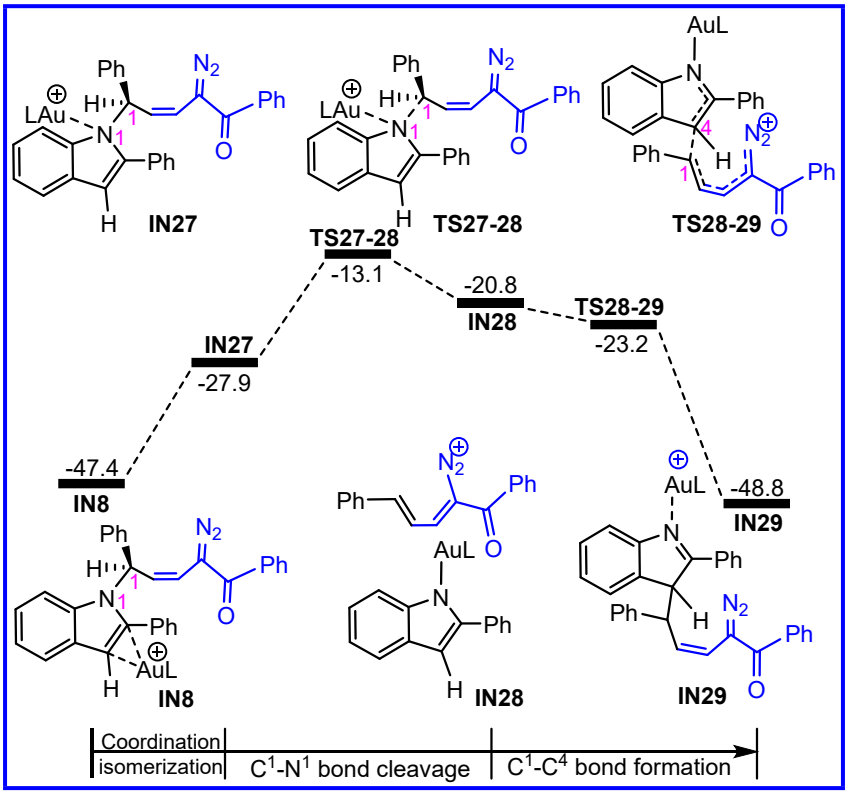


Fig. S5 Calculated free energy profile in DCE solvent for other possible C^1-N^1 cleavage pathway from **IN8**. The relative free energies are given in kcal mol^{-1}. L=PPh_3

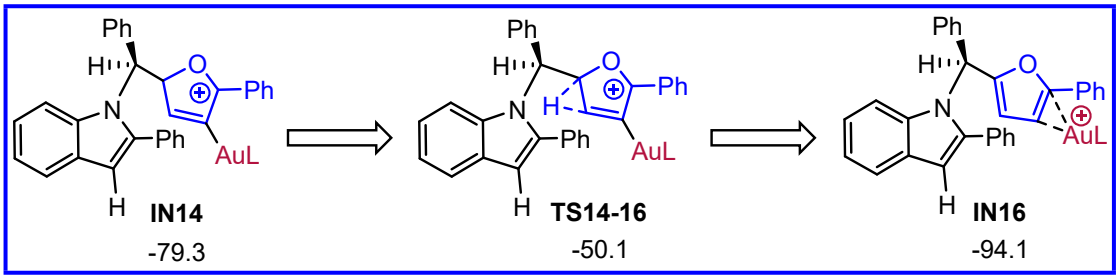


Fig. S6 Calculated direct 1,2-H-shift pathway in DCE solvent from **IN14**. The relative free energies are given in kcal mol^{-1}. L=PPh_3

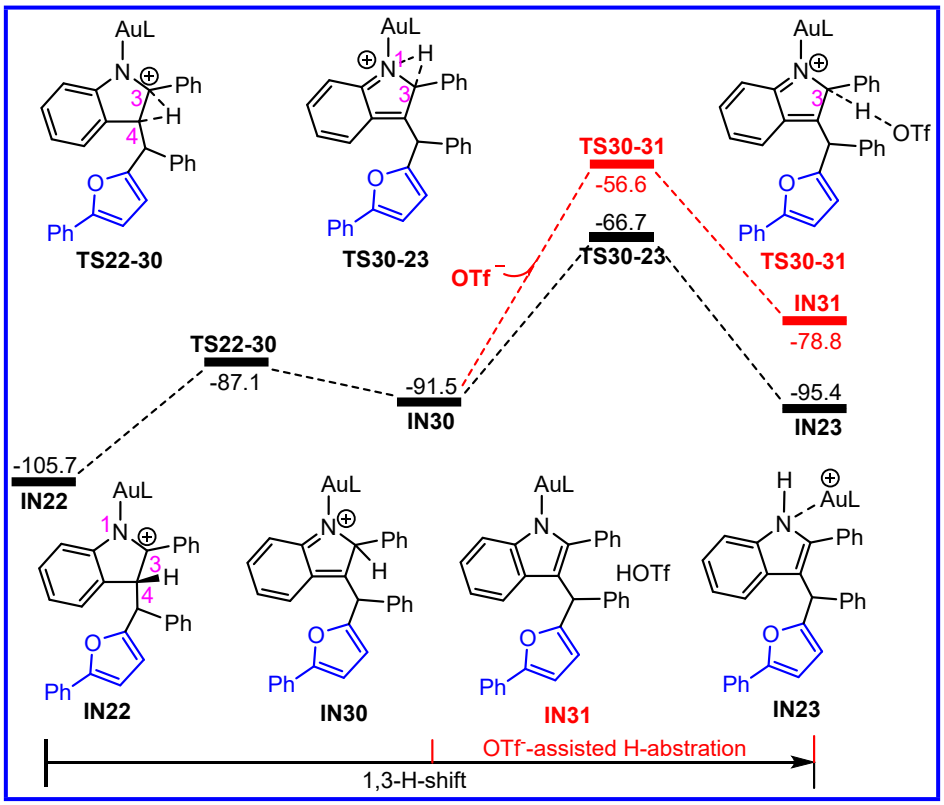


Fig. S7 Calculated free energy profile in DCE solvent for other possible pathways from **IN22**. The relative free energies are given in kcal mol^{-1}. L=PPh_3

Table S1. Calculated Gibbs free energies in the gas-phase using M06 functional, single-point HF energies in DCE solvent using M06 functional, and imaginary frequencies for all structures in the present work. The relative energies and the imaginary frequencies are given in Hartree and cm^{-1}, respectively.

Structure	Gibbs Free Energy (M06 gas-phase optimized calculation)	Solvation HF Energy (M06 single-point calculation)	Imaginary Frequency
[LAu(DCE)]$^+$	-2169.904494	-2170.49362480	
AuL$^+$	-1171.024051	-1171.4980612	
1	-863.043478	-863.51966134	
IN1	-2034.121943	-2035.05566396	
TS1-2	-2034.118460	-2035.04800838	-211.40
IN2	-2034.144204	-2035.07993738	
2	-570.014299	-570.29042518	
IN3	-1741.075537	-1741.81794134	
TS3-4	-1741.061068	-1741.80270127	-456.03
IN4	-1631.634470	-1632.34313470	
IN5	-2604.158471	-2605.39497016	
IN6	-3565.380766	-3566.74779574	
TS6-7	-3565.368877	-3566.72668485	-1606.70
IN7	-2603.784162	-2604.97549152	
TS7-8	-3565.404591	-3566.95844672	-1062.88
IN8	-2604.206597	-2605.43965179	

TS8-9	-2604.173113	-2605.40479735	-147.75
IN9	-2604.175038	-2605.40834373	
TS9-10	-2604.154344	-2605.38726851	-191.26
IN10	-2604.181805	-2605.41770415	
IN11	-2604.189529	-2605.42397216	
TS11-12	-2604.176082	-2605.40786596	-464.10
IN12	-2494.755520	-2495.94975043	
TS12-13	-2494.739379	-2495.93332160	-58.66
IN13	-2494.738353	-2495.93336448	
TS13-14	-2494.728822	-2495.92504403	-277.91
IN14	-2494.791973	-2495.98696294	
TS14-15	-3455.994171	-3457.51168190	-1592.00
IN15	-2494.403646	-2495.55656403	
TS15-16	-3456.019652	-3457.53538870	-1263.40
IN16	-2494.811572	-2496.01223636	
IN17	-2494.829348	-2496.02588061	
TS17-18	-2494.791716	-2495.98607584	-179.72
IN18	-2494.792631	-2495.98354475	
TS18-19	-2494.780661	-2495.96764391	-181.32
IN19	-2494.807333	-2496.00627374	
IN20	-2494.809835	-2496.00970561	
TS20-21	-2494.796037	-2495.99275791	-294.53

IN21	-2494.810760	-2496.00593402	
TS21-22	-2494.805487	-2496.00051100	-22.40
IN22	-2494.828696	-2496.02585881	
TS22-23	-2571.149621	-2572.40344267	-271.71
IN23	-2494.810837	-2496.01623111	
P	-1323.746625	-1324.48525759	
TS2-5''	-2604.142020	-2605.36987919	-410.46
TS2-5'	-2604.141585	-2605.37387808	-414.40
TS6-7'	-3565.361449	-3566.72580764	-1536.51
IN7'	-2603.778068	-2604.96847862	
TS6-7[a]	-3467.178861	-3468.90954359	-1032.56
TS6-7[b]	-3174.149734	-3175.67543339	-845.26
TS6-7[c]	-3174.123099	-3175.65723119	-133.30
TS5-24	-2604.111680	-2605.34191210	-953.79
IN24	-2604.168195	-2605.39943451	
TS24-8	-2604.149347	-2605.37644586	-885.37
TS5'	-2604.059315	-2605.2865983	-1644.92
TS7-25	-3565.373920	-3566.94405887	-31.01
IN25	-2604.149808	-2605.38548864	
TS25-26	-2604.148309	-2605.38076344	-310.45
IN26	-2604.158483	-2605.39520425	

IN27	-2604.182400	-2605.42199745	
TS27-28	-2604.167931	-2605.40606828	-255.03
IN28	-2604.177814	-2605.41722130	
TS28-29	-2604.185154	-2605.41759739	-259.21
IN29	-2604.203658	-2605.44265811	
TS14-16	-2494.742600	-2495.93714313	-1093.15
TS22-30	-2494.781782	-2495.97582708	-1021.55
IN30	-2494.804848	-2495.99886308	
TS30-31	-3456.226394	-3457.55267418	-1389.45
IN31	-3456.028566	-3457.55138584	
TS30-23	-2494.758711	-2495.95295649	-1480.36