Tandem Pseudopericyclic Reactions: [1,5]-X Sigmatropic Shift / 6 π -Electrocyclic Ring Closure Converting *N*-(2-X-Carbonyl)phenyl Ketenimines into 2-X-Quinolin-4(3*H*)-ones

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COMPUTATIONAL DATA

TABLE S1. Electronic energy including the zero point vibrational correction (in hartrees), relative energy (E. relat. in kcal·mol⁻¹) and first frequency (cm⁻¹) of the stationary points found in the transformations **8a-f** → **9a-f** and **8a-f** → **11a-f**.

Method	HF/6-31G*			B3LYP/6-31+G*		
	Electronic E.	E. relat.	Freq	Electronic E.	E. relat.	Freq
X = F, 8a → 9a / 11a						
8a	-420.267391	0.00	58.0	-422.631821	0.00	45.5
TS1a	-420.207953	37.30	-739.5	-422.597612	21.47	-497.2
10a	-420.255595	7.40	35.4	-422.621729	6.33	37.7
TS2a	-420.231468	22.54	-720.3	-422.613444	11.53	-300.8
9a	-420.305902	-24.17	83.0	-422.663840	-20.09	70.4
TS3a	-420.237361	18.84	-540.9	-422.616492	9.62	-318.5
11a	-420.269754	-1.48	83.1	-422.632178	-0.22	70.8
X = Cl, 8b → 9b / 11b						
8b	-780.3014030	0.00	43.2	-782.9787230	0.00	38.7
TS1b	-780.2516030	31.25	-446.4	-782.9536100	15.76	-319.6
10b	-780.2980390	2.11	34.5	-782.9698910	5.54	30.6
TS2b	-780.2719320	18.49	-818.0	-782.9643090	9.04	-337.3
9b	-780.3463910	-28.23	71.2	-783.0131720	-21.62	59.6
TS3b	-780.2727560	17.98	-562.4	-782.9642920	9.06	-310.0
11b	-780.3103520	-5.62	67.3	-782.9826940	-2.49	53.7
X = OH, 8c → 9c / 11c						
8c	-396.265241	0.00	57.7	-398.604388	0.00	53.5
TS1c	-396.209397	35.04	-538.8	-398.567888	22.90	-417.6
10c	-396.246000	12.07	24.9	-398.5880800	10.23	10.2

TS2c	-396.2273880	23.75	-612.5	-398.5836870	12.990	-179.6
9c	-396.308970	-27.44	74.4	-398.642864	-24.14	57.8
TS3c	-396.236951	17.75	-559.5	-398.590839	8.50	-338.3
11c	-396.269657	-2.77	83.7	-398.608614	-2.65	69.8

X = SH, 8d → 9d / 11d

8d	-718.899521	0.00	43.2	-721.559537	0.00	43.1
TS1d	-718.843473	35.17	-550.2	-721.532846	16.75	-296.6
10d	-718.898405	0.70	42.3	-721.553866	3.56	39.5
TS2d	-718.876854	14.22	-728.3	-721.551462	5.07	-238.4
9d	-718.948946	-31.01	47.3	-721.599953	-25.36	31.3
TS3d	-718.873339	16.43	-586.3	-721.547395	7.62	-339.1
11d	-718.913272	-8.63	58.4	-721.569144	-6.03	41.3

X = NH₂, 8e → 9e / 11e

8e	-376.418224	0.00	50.6	-378.722472	0.00	51.5
TS1 ^A e	-376.371007	29.63	-615.6	-378.693639	18.09	-417.8
INTe	-376.394719	14.75	96.7	-378.713278	5.77	91.2
TS1 ^B e	-376.393694	15.39	-302.7	--	--	--
10e	-376.405021	8.29	42.1	--	--	--
TS2e	-376.395421	14.31	-504.4	--	--	--
TS4e	--	--	--	-378.707784	9.22	-57.4
9e	-376.466690	-30.41	50.0	-378.766422	-27.58	15.1
TS3e	-376.394979	14.59	-543.6	-378.712351	6.35	-331.7
11e	-376.430657	-7.80	78.3	-378.733777	-7.09	61.2

X = PH₂, 8f → 9f / 11f

8f	-662.665141	0.00	45.2	-665.296916	0.00	45.1
TS1 ^A f	-662.613416	32.46	-582.3	-665.274000	14.38	-329.0

INTf	-662.642567	14.17	30.7	-665.294042	1.80	18.1
TS1^Bf	-662.638143	16.94	-327.7	-665.288426	5.33	-158.9
10f	-662.672201	-4.43	45.9	-665.300790	-2.43	40.0
TS2f	-662.645104	12.57	-819.8	-665.294217	1.69	-348.0
9f	-662.717258	-32.70	46.2	-665.340646	-27.44	47.6
TS3f	-662.638968	16.42	-598.2	-665.286600	6.47	-328.3
11f	-662.687626	-14.11	62.3	-665.315797	-11.85	42.7

Cartesian coordinates of the stationary points found in the transformations **8a-f** $\rightarrow$ **9a-f** and **8a-f** $\rightarrow$ **11a-f** optimized at the B3LYP/6-31+G* theoretical level, and cartesian coordinates of **TS1^A**, **TS1^B**, **10e** and **TS2e** optimized at the HF/6-31G* theoretical level.

8a (B3LYP/6-31+G*)			TS1a (B3LYP/6-31+G*)			10a (B3LYP/6-31+G*)		
C,-1.4027769513,-0.0651846638,-1.4998997913	C,-0.1840997887,0.0665684934,1.4997182583	C,-0.1947708367,-0.2717637847,-1.4041987284						
C,-2.3402199357,-0.9447822631,-1.7631250244	C,-1.1308684303,0.0592054937,2.4244003959	C,-0.6778864506,-0.4920354436,-2.6324158165						
N,-0.599350452,0.824413067,-1.2694703272	N,1.064718474,0.1269510897,1.2444463083	N,1.1194419421,-0.2754541332,-1.0563849098						
C,0.7433684519,0.9089625197,-1.0054801191	C,1.6916074018,0.1024126376,0.0890292214	C,1.6112584606,-0.0662152456,0.1189217624						
C,1.3765939337,0.5358822629,0.1344169426	C,1.1526647276,0.0043811201,-1.2014201553	C,1.0524487541,0.2293106879,1.4304491528						
C,0.7230518833,-0.138850731,1.2472066487	C,-0.1917272481,-0.0904765604,-1.539863892	C,-0.2079327651,0.3832999677,1.8454960377						
F,1.6182787037,-0.3288516507,2.2781689142	F,-1.0540640867,-0.0652763953,-0.0682667627	F,-1.1177607066,-0.0163817401,-0.3931365209						
H,-2.8184771801,-1.476852503,-0.9468331305	H,-2.1765048757,-0.0145024922,2.1612041596	H,-1.7434456455,-0.4709439879,-2.8245205209						
H,-2.6282973096,-1.1633118123,-2.7859717694	H,-0.8319704143,0.1289974836,3.4652500413	H,0.0114772558,-0.693774037,-3.4420127153						
H,1.3051559287,1.4372970704,-1.7733941238	H,2.7755653552,0.1687738196,0.1559949149	H,2.6999380447,-0.1198774562,0.1591858975						
H,2.4287585963,0.7697878315,0.2429361701	H,1.8280631213,-0.0003244688,-2.0503312783	H,1.7703255107,0.3507783057,2.2395345452						
O,-0.407037437,-0.5193134531,1.3709153721	O,-0.9483832123,-0.1795826698,-2.4325030127	O,-1.25165556719,0.5392318348,2.3314026752						

TS2a (B3LYP/6-31+G*)			9a (B3LYP/6-31+G*)			TS3a (B3LYP/6-31+G*)		
C,0.1066378798,0.3361250412,-1.1858632744	C,0.3132453916,-0.6188025457,0.98439224642	C,-1.323171224,0.1657126852,-0.8085780516						
C,-0.8533760561,-0.6004981366,-0.9527790946	C,-0.9448961904,0.0666385058,0.5655316668	C,-2.5846463263,-0.2116543993,-0.6878510609						
N,1.3952513162,0.3132828991,-0.7841769048	N,1.4082948444,-0.7092340646,0.3544299645	N,-0.4033545313,0.7673951957,-1.4361420274						
C,1.6157176432,-0.0466126257,0.455302303	C,1.4578527005,-0.0863358372,-0.9055466243	C,0.8840354292,0.9222400857,-1.1683623819						
C,0.6710841375,-0.3545930139,1.4802085161	C,0.4431400315,0.5927197599,-1.4908005983	C,1.5218605586,0.40013742,-0.0453962745						
C,-0.6790589095,-0.4972811394,1.3357606652	C,-0.8474678558,0.7326037891,-0.8138013453	C,0.7631171995,-0.343216988,0.8755383713						
F,-0.2370551679,1.4687060704,-1.8315014017	F,0.2304768675,-1.2036924569,2.1937424927	F,1.4454554862,-0.8238578731,1.9435316177						
H,-1.871890487,-0.4432222887,-1.2895223518	H,-1.7744729015,-0.6537875046,0.5604486194	H,-2.917137977,-0.8019622021,0.1539625582						
H,-0.5525681129,-1.615031993,-0.7131821617	H,-1.220227534,0.8234590318,1.312946761	H,-3.2859604991,0.0867520349,-1.4607936449						
H,2.6619958292,-0.0711252053,0.7580685977	H,2.417976844,-0.1940829534,-1.4019164275	H,1.4494429747,1.4996514787,-1.8954146038						
H,1.0165474536,-0.3784900719,2.5109668476	H,0.5562702968,1.0484234596,-2.4650229789	H,2.5782920086,0.5565529398,0.1225576792						
O,-1.7566719443,-0.7407882653,1.7388306657	O,-1.8053933609,1.3316145625,-1.2832251923	O,-0.4471782707,-0.6121690732,0.8310996913						

11a (B3LYP/6-31+G*)			8b (B3LYP/6-31+G*)			TS1b (B3LYP/6-31+G*)		
C,-1.1291298155,0.0655836118,-0.5632788358	C,1.7231979252,1.0626490496,1.5373355067	C,-0.0014341401,0.2232593726,1.6775501879						
C,-2.4395410942,-0.153421106,-0.7290438238	C,1.708210352,1.3142894251,2.8257316658	C,-0.7746936599,0.5341860928,2.7107655275						
N,-0.3231706465,0.7819931437,-1.4230440588	N,1.8241178303,0.7804574008,0.3562696372	N,1.1743342575,-0.0823190809,1.3147330976						
C,0.9342993042,0.9215082781,-1.1471167725	C,1.1502222986,0.9886462853,-0.8137700368	C,1.8039372192,-0.365432275,0.2010382934						
C,1.5752400369,0.3683178678,0.0256727917	C,0.0210404988,0.3603444567,-1.2349620088	C,1.3532941374,-0.4391817954,-1.1240552401						
C,0.7487768681,-0.3226548315,0.835059173	C,-0.7263151083,-0.583514458,-0.4161776121	C,0.0949704449,-0.2375051284,-1.6866859897						
F,1.1367202742,-0.9097404903,1.9619446132	Cl,-2.1507453162,-1.2914837036,-1.3284603312	Cl,-1.3156683642,0.2503341506,-0.161355064						
H,-3.0102407634,-0.7273995176,-0.009899459	H,1.125214664,0.6827858013,3.4886307416	H,-1.8273808647,0.7510381706,2.6031338621						
H,-2.9291317383,0.2557801147,-1.6027772838	H,2.2535993266,2.1582479104,3.2345894141	H,-0.3151635939,0.5674335155,3.6949653223						
H,1.536676566,1.4947757709,-1.85388534485	H,1.6657663299,1.6577992961,-1.5007016536	H,2.8629062092,-0.5788118999,0.3360965573						
H,2.6263033458,0.4906258865,0.2469110461	H,-0.3330600987,0.5558445327,-2.2386983597	H,2.0978858382,-0.6975864171,-1.8721697851						
O,-0.5407197801,-0.5095090962,0.6244701662	O,-0.521976307,-0.9271431173,0.7146466172	O,-0.4410836511,-0.2516847453,-2.7367035283						

10b (B3LYP/6-31+G*)	TS2b (B3LYP/6-31+G*)	9b (B3LYP/6-31+G*)
C,-0.9051725153,-0.096287666,-0.4956436876	C,-0.747036591,-0.0564804934,-0.5583268805	C,0.3703125165,0.1001351133,-0.7239742136
C,-1.7047641933,-0.0019336354,0.5759662336	C,-1.1145068374,-0.0192776582,0.7588148822	C,-0.9822442587,0.2791751589,-0.0974093697
N,-0.3191165559,0.9569320719,-1.1833653043	N,-0.1286244999,0.9431298744,-1.2249090076	N,1.4241099296,-0.3250016955,-0.1537079659
C,0.6878478651,1.5771214952,-0.6783668077	C,0.8864478189,1.5102782845,-0.6177347018	C,1.3314869956,-0.6685012487,1.2071671235
C,1.4237094383,1.3479060349,0.5571698999	C,1.467841009,1.1668727367,0.6375793033	C,0.2143172071,-0.5858760547,1.9662537389
C,1.1988123752,0.4378727368,1.5092131651	C,0.9438518086,0.3008018827,1.5576474417	C,-1.0402686896,-0.1059511863,1.3854277629
Cl,-0.6023118171,-1.6686714661,-1.2513748789	Cl,-0.9670745959,-1.5361749582,-1.479871418	Cl,0.4653423673,0.5347031637,-2.4252735246
H,-2.1779758419,-0.8740702524,1.0108060025	H,-1.5619072879,-0.8786446916,1.2445882201	H,-1.7268342832,-0.3121596219,-0.647269362
H,-1.9174753831,0.9733348386,1.0037445618	H,-1.2688197365,0.9503167224,1.2262583609	H,-1.3059337909,1.3231450838,-0.2059529012
H,1.0758368503,2.4106518825,-1.2649819459	H,1.3717026293,2.3159818486,-1.1671259027	H,2.269636504,-1.0227251892,1.624772733
H,2.296717374,1.9680566784,0.7472693288	H,2.4619725706,1.5385892128,0.8724703369	H,0.2163831732,-0.8692909872,3.0138903481
O,1.1241769953,-0.2996479399,2.4062574132	O,0.9647635257,-0.2282933048,2.6110132344	O,-2.0868079974,-0.0059752368,2.0119218261

TS3b (B3LYP/6-31+G*)	11b (B3LYP/6-31+G*)	8c (B3LYP/6-31+G*)
C,1.2855907479,0.8673974869,1.2078898108	C,1.1205463437,-0.2015809892,1.1134177732	C,-0.1891164173,1.9857706821,0.340901504
C,1.3768617951,0.8625082812,2.5260887279	C,1.6999171728,-1.0101878247,2.0104956821	C,-1.2675893519,2.6463066835,0.6919978507
N,1.6802585217,1.2307674567,0.0642688748	N,1.498387275,1.1020489014,0.8636425133	N,0.8698992192,1.432713652,0.0823011167
C,1.1836412703,1.0291313011,-1.1465255168	C,0.858582801,1.7834459614,-0.0306553427	C,1.244995324,0.4824966372,-0.8456121538
C,0.0719278071,0.2357291659,-1.4249459881	C,-0.2496985822,1.2668757406,-0.8054941639	C,0.8620765825,-0.8136094711,-0.8935372835
C,-0.5922090118,-0.4082336412,-0.3619463569	C,-0.5944883793,-0.0109150162,-0.5369479183	C,-0.1274828078,-1.4347170807,-0.0056066937
Cl,-1.9681116827,-1.4623360664,-0.8090220086	Cl,-1.8821576935,-0.8569558774,-1.3248124545	O,-0.2321567755,-2.7721661605,-0.25418085
H,0.7024018086,0.2758178927,3.1336307223	H,1.3549034718,-2.0256496451,2.1592439037	H,-1.9873982882,2.1772430456,1.35511393
H,2.1475308539,1.4693956552,2.9913321974	H,2.5290269532,-0.6317034142,2.593661261	H,-1.4625649366,3.6418023951,0.3074012575
H,1.7187535826,1.5139748579,-1.9595937944	H,1.1870622365,2.8086026479,-0.1991289947	H,2.0191332741,0.8304279793,-1.5266792213
H,-0.2564307105,0.0913218723,-2.4443732264	H,-0.7678202831,1.8585516042,-1.5476566889	H,1.338960576,-1.4605363731,-1.6213920329
O,-0.3213802789,-0.3281706137,0.8473915077	O,0.0237660385,-0.7652151023,0.3706623088	H,-0.9039713866,-3.1186786931,0.3622432252

TS1c (B3LYP/6-31+G*)	10c (B3LYP/6-31+G*)	TS2c (B3LYP/6-31+G*)
C,-0.465588703,-0.9589591654,-0.9656008147	C,-0.0508869635,1.4426645234,0.1254333824	C,-0.6681092848,1.0254022101,-0.2533615547
C,-0.3671420525,-2.231795797,-1.3505618735	C,-0.1290822542,2.7834664566,0.0245555646	C,-0.6111032088,0.7831915147,1.0874748586
N,-0.9727464075,0.1703778759,-1.3322763543	N,0.1476657247,0.8218185602,1.3389951182	N,0.4414461478,1.1729956551,-1.0530734546
C,-0.8057386501,1.3375111331,-0.7228210547	C,0.2342826616,-0.4523052908,1.526489093	C,1.3314036725,0.2313808223,-1.0044186846
C,-0.0599166686,1.6026240393,0.4263188565	C,0.1724721624,-1.6387518183,0.6796823333	C,1.3217025426,-0.999914467,-0.2547803362
C,0.655479354,0.609161625,1.1211784509	C,-0.0030405886,-1.8011719244,-0.6340953642	C,0.4605140617,-1.3729246982,0.7194260801
O,0.3089899729,-0.7535366497,0.5787019534	O,-0.1618774717,0.5960731706,-0.963866057	O,-1.8204876097,1.1072067405,-0.9620208833
H,0.1401790791,-2.9885736262,-0.7679951845	H,-0.2853705352,3.2831491623,-0.92671336775	H,-1.5094863725,0.6552970147,1.685247605
H,-0.8405889369,-2.5162815038,-2.2834659704	H,-0.0337219032,3.3870275534,0.9174262274	H,0.3173876952,0.9417754726,1.6236982901
H,-1.3021248124,2.1765590566,-1.2064094674	H,0.3929704533,-0.7325092185,2.5694697046	H,2.2044164605,0.3706107438,-1.6427937456
H,0.0388734105,2.6177984952,0.7898910244	H,0.2892474163,-2.5922267088,1.1925069767	H,2.0465878689,-1.7663365175,-0.5207862921
O,1.4436797297,0.5970770736,2.0335516951	O,-0.1430053035,-2.1207016973,-1.7452368671	O,-0.0015712254,-2.046182784,1.5638945117
H,1.0087898169,-1.381721955,0.844803503	H,-0.3001934088,1.09544458245,-1.7845217204	H,-2.5790047047,1.0966797565,-0.3548817772

9c (B3LYP/6-31+G*)		TS3c (B3LYP/6-31+G*)		11c (B3LYP/6-31+G*)	
C, 0.1068069526, 1.1872629501, 0.2150460545		C, 0.673569242, 0.3866802724, -1.3548816087		C, 0.5239897343, 0.0196624138, 1.1517528496	
C, 0.0979085691, 0.3675960714, -1.0403634167		C, 0.2611671981, 0.5745324706, -2.5984411461		C, 0.535471903, 0.0218291932, 2.4924924828	
N, -0.0081794495, 0.7459959412, 1.4185546771		N, 1.5985655263, 0.2801706028, -0.4990666155		N, 1.6347632042, 0.0567668217, 0.3411333165	
C, -0.1564515012, -0.6337647239, 1.5792521228		C, 1.560029728, -0.2306276369, 0.7339054392		C, 1.4735765523, 0.0493879555, -0.9484714823	
C, -0.1906281788, -1.155458135, 0.5827265479		C, 0.401919954, -0.5054455139, 1.4382409273		C, 0.2021278987, 0.0046662298, -1.6147740878	
C, -0.0670930411, -1.1392981489, -0.8101457357		C, -0.8606411827, -0.2305651239, 0.8476351178		C, -0.8796994475, -0.0313860728, -0.7958324443	
O, 0.2519476486, 2.5054638865, 0.0034576519		O, -1.9355711673, -0.3889015141, 1.6491841003		O, -2.1458197963, -0.0755474681, -1.2233579319	
H, 1.0270974995, 0.5439302134, -1.598525003		H, -0.7884468175, 0.6761783932, -2.8339293174		H, -0.3824585853, -0.008997657, 3.0660275905	
H, -0.707069954, 0.7182535692, -1.6999776711		H, 1.0054638123, 0.6161700822, -3.3873518682		H, 1.4878602146, 0.0552620021, 3.0047151336	
H, -0.2483198157, -0.9410686383, 2.6178899646		H, 2.5283832496, -0.3691775694, 1.2087493752		H, 2.3810910244, 0.0798124776, -1.5505748794	
H, -0.3093738325, -2.6123805842, 0.7929488946		H, 0.4429579201, -0.8350946713, 2.4678350384		H, 0.0957837516, -0.0005265349, -2.6907826008	
O, -0.0885554217, -1.9099110571, -1.7634575663		O, -1.047909362, 0.1586566345, -0.334292219		O, -0.7816066297, -0.026078658, 0.5388826548	
H, 0.2445276306, 2.9415824246, 0.8786869534		H, -2.726742251, -0.1747582271, 1.120275654		H, -2.739007271, -0.0948656485, -0.45077761504	

8d (B3LYP/6-31+G*)		TS1d (B3LYP/6-31+G*)		10d (B3LYP/6-31+G*)	
C, -1.4437412776, 2.0320700209, 0.1047052217		C, 1.169083648, -0.8089185849, -0.8947983192		C, 0.164279171, -0.8058331452, 0.0252788529	
C, -2.6570363761, 2.126972854, 0.59648298		C, 2.0856246034, -1.7548001469, -0.7050452241		C, -0.1071098854, 0.2768838665, -0.9935783888	
N, -0.2929954859, 2.0323511165, -0.3036505354		N, 0.5060259426, -0.1363324076, -1.7372129298		N, 0.1953397486, -0.6338212768, 1.3018602151	
C, 0.4358969648, 1.2522047831, -1.1713637996		C, -0.6518806198, 0.5200626334, -1.6864297166		C, -0.0397715495, 0.6545713823, 1.7936297202	
C, 0.8440542435, -0.0260830087, -0.9808782481		C, -1.4188298866, 0.8795294159, -0.5980984512		C, -0.3013794414, 1.7591582375, 1.0510133911	
C, 0.485744158, -0.8646936275, 0.1692195463		C, -1.1849217391, 0.6094225265, 0.7902579993		C, -0.3580528697, 1.6689805164, -0.4032109947	
S, 1.3490711124, -2.4704230026, 0.1371336917		S, 0.6364356851, 0.1050550734, 1.2276635923		S, 0.4543031591, -2.4141830072, -0.6531119764	
H, -2.9395148722, 1.5101079977, 1.443611407		H, 2.4741885075, -2.0082305755, 0.2705821411		H, 0.7348494565, 0.3486842139, -1.6955778308	
H, -3.3882972024, 2.7939616539, 0.1523008323		H, 2.4562659332, -2.2867890779, -1.5778230806		H, -0.9759549613, 0.0028609102, -1.6074715465	
H, 0.7965722509, 1.7984428084, -2.0411514761		H, -1.0268536681, 0.8219182926, -2.6623751514		H, 0.0039794364, 0.714604543, 2.8783147832	
H, 1.512948125, -0.4510969028, -1.7230269843		H, -2.3546185589, 1.3932939725, -0.7870815772		H, -0.4733151541, 2.7267318382, 1.5117434264	
O, -0.2837308858, -0.570042243, 1.0652880025		O, -1.933966213, 0.705927761, 1.7283689976		O, -0.5888630564, 2.6198439339, -1.1416596233	
H, 0.7644631122, -2.9135935176, 1.2683826808		H, 0.25113388958, -0.9659440844, 1.9523009899		H, 0.6366843374, -3.0105210696, 0.5442427888	

TS2d (B3LYP/6-31+G*)		9d (B3LYP/6-31+G*)		TS3d (B3LYP/6-31+G*)	
C, 0.3058318726, 0.8915695817, -0.0618284466		C, 0.164279171, -0.80583331452, 0.0252788529		C, -1.2117281758, 1.5425393302, 0.1331078702	
C, 0.7129710096, 0.2459781854, -1.1953861711		C, -0.1071098854, 0.2768838665, -0.9935783888		C, -2.3573085227, 1.6739065977, 0.7792779467	
N, 0.8015571809, 0.6023290566, 1.189608203		N, 0.1953397486, -0.6338212768, 1.3018602151		N, -0.3189209252, 1.9699199469, -0.653570135	
C, 0.776251423, -0.6504847028, 1.5476435106		C, -0.0397715495, 0.6545713823, 1.7936297202		C, 0.5894490021, 1.2771006648, -1.3473728096	
C, 0.2642426925, -1.780854478, 0.8269405127		C, -0.3013794414, 1.7591582375, 1.0510133911		C, 0.9654475631, -0.0270705135, -1.0754720625	
C, -0.1175913795, -1.8104458893, -0.4767360418		C, -0.3580528697, 1.6689805164, -0.4032109947		C, 0.3966921272, -0.715145748, 0.033969008	
S, -0.9593793077, 2.135093436, -0.1388130426		S, 0.4543431591, -2.4141830072, -0.6531119764		S, 1.1866266523, -2.2615842463, 0.4956584237	
H, 0.2766851606, 0.4678064017, -2.1641391607		H, 0.7348494565, 0.3486842139, -1.6955778308		H, -2.6667105801, 0.9570595642, 1.5267638303	
H, 1.6518129805, -0.300208999, -1.1913851016		H, -0.9759549613, 0.0028609102, -1.6074715465		H, -2.9969216216, 2.5156994567, 0.5323492721	
H, 1.1628154066, -0.8646162217, 2.5440790787		H, 0.0039794364, 0.714604543, 2.8783147822		H, 1.1064594766, 1.8388470296, -2.1223772333	
H, 0.0924575053, -2.7076603606, 1.3694296984		H, -0.4733151541, 2.7267318382, 1.5117434264		H, 1.7849221193, -0.4751607161, -1.6241982938	
O, -0.5006089458, -2.3258633419, -1.4632302918		O, -0.5888630564, 2.6198439339, -1.1416596233		O, -0.5712197682, -0.2997733675, 0.7158730705	
H, -1.0899645371, 2.2592113621, 1.1978088974		H, 0.6366843374, -3.0105210696, 0.5442427888		H, 0.2931168287, -2.5503320692, 1.4638747309	

11d (B3LYP/6-31+G*)	8e (B3LYP/6-31+G*)	TS1 ^a (B3LYP/6-31+G*)
C, 1.0280813812, -0.7541624698, -0.9607590469	C, 1.2828623166, 0.9669598455, 1.2139910606	C, 0.2708330487, 1.4013713518, 0.5274493361
C, 1.269248877, -1.8144078853, -1.7455162866	C, 1.2542057329, 0.9840903575, 2.5259295446	C, -0.4894071451, 2.3718652139, 1.0238010134
N, 1.8884151694, 0.3099923496, -0.7875181116	N, 1.4230302604, 0.9549202293, -0.0018279917	N, 1.4032048153, 0.8544785162, 0.3999714342
C, 1.5041417858, 1.3109361281, -0.0582860437	C, 0.513578787, 1.096000316, -1.0367582755	C, 1.6598602839, -0.4558947812, 0.1970434132
C, 0.225595306, 1.391596767, 0.6015171119	C, -0.5132547091, 0.2753411605, -1.3475897638	C, 0.7631450096, -1.4125109801, -0.2230624616
C, -0.5817658733, 0.3078571747, 0.4702294604	C, -0.938225134, -0.9134203078, -0.5710284411	C, -0.6295510308, -1.1495847678, -0.489425481
S, -2.158089168, 0.1488994, 1.2492957352	N, -1.9171766215, -1.6672761861, -1.1787697387	N, -0.9490782139, 0.2700908664, -0.7071528153
H, 0.5510845373, -2.6189080599, -1.8444284429	H, 0.9561294315, 0.0887717489, 3.0616762551	H, -1.5310745146, 2.4880760283, 0.7617728156
H, 2.2059838574, -1.8612716964, -2.2851827518	H, 1.4870036102, 1.8886437563, 3.0778091043	H, -0.0387806497, 3.069017809, 1.7245516403
H, 2.2074677997, 2.1363562954, 0.0509192872	H, 0.7624666803, 1.9114071657, -1.7133138686	H, 2.6910245881, -0.7476232314, 0.3832911158
H, -0.0690048243, 2.2587875507, 1.1789351732	H, -1.0482983048, 0.4956152828, -2.268098496	H, 1.0843633879, -2.4451624869, -0.295780944
O, -0.2213660103, -0.7657715089, -0.2535083284	O, -0.4965352561, -1.2198205422, 0.5361591315	O, -1.5345032134, -1.9681060752, -0.5425941219
H, -2.4858929927, -0.9920471546, 0.6086072076	H, -2.1668392166, -2.5421515288, -0.7367095882	H, -1.9624663488, 0.3903276629, -0.68622383964
	H, -2.1541413852, -1.5510586196, -2.1537170939	H, -0.5952079627, 0.5867509223, -1.61140851

INTE (B3LYP/6-31+G*)	TS4 (B3LYP/6-31+G*)	9e (B3LYP/6-31+G*)
C, 0.4295458139, -0.2868341058, 1.1869487753	C, -1.8523576228, -0.7524351565, -1.027646591	C, -0.0377107565, -0.511801795, -1.1050421801
C, 0.3650377463, -0.0929305287, 2.5149682811	C, -1.2789651434, -0.1513040789, 0.0314804106	C, -1.0692648072, 0.0917025618, -0.1767024939
N, 1.5667700063, -0.4112917253, 0.4361164342	N, -0.8287184383, -0.8259912016, 1.1885599624	N, 1.2364474909, -0.6012423658, -0.8434447053
C, 1.4897884839, -0.1109617944, -0.8435198773	N, -1.0373027158, 1.2368903027, 0.0744980388	C, 1.6704431807, -0.1044240414, 0.3727596481
C, 0.3635540699, 0.3414056284, -1.5823816208	C, 0.1687065966, 1.6768747634, 0.0320179912	C, 0.9090540512, 0.47764262575, 1.3433624599
C, -0.9110202057, 0.352914417, -1.0402790289	C, 1.4409738113, 0.9785715713, -0.1150080495	C, -0.5192133988, 0.6278377778, 1.1542465534
N, -0.8558805246, -0.3996572255, 0.4295548632	C, 1.6667084853, -0.3367799539, -0.1553896765	N, -0.4900590126, -0.9892963095, -2.2894289931
H, -0.5772401733, 0.0025849243, 3.0447145243	O, 1.988888073, -1.4530364966, -0.2087391095	H, -1.5894448898, 0.9169886624, -0.6811866807
H, 1.2847938758, -0.0256873372, 3.083878774	H, -2.057185271, -1.8187301496, -1.0300685029	H, -1.8416551076, -0.6534289905, 0.0570369228
H, 2.4308808088, -0.1907013913, -1.3883768211	H, -2.1047649628, -0.1787170267, -1.9111269686	H, 2.7427394835, -0.2125148671, 0.5240714326
H, 0.4821472626, 0.6932458663, -2.6007139089	H, 0.2834431358, 2.7610635624, 0.0899755155	H, 1.3498058386, 0.8377117861, 2.2671160689
O, -2.038771749, 0.6745433435, -1.3489641583	H, 2.3414078426, 1.5784554893, -0.2249627632	O, -1.2893472577, 1.1385617701, 1.9643526901
H, -1.0545060976, -1.3848686433, 0.2215596984	H, -1.0054190086, -0.30693288, 2.0444738144	H, 0.1726455367, -1.4002622327, -2.9342496841
H, -1.6535523975, -0.0358392107, 0.9565327417	H, -1.1768350033, -1.7765860079, 1.2674912101	H, -1.4638817649, -0.9488499054, -2.5492376159

TS3e (B3LYP/6-31+G*)	11e (B3LYP/6-31+G*)	TS1 ^a (HF/6-31G*)
C, 0.9709682249, 0.6461374327, 1.0758271514	C, 0.8669357749, 0.2041889651, 0.9158537181	C, 0.2538497637, 1.3441817705, 0.4468400785
C, 1.0587678829, 0.5704054704, 2.3937391535	C, 1.5710384723, -0.0892648758, 2.0206414186	C, -0.5194897654, 2.2325825639, 1.0233008591
N, 1.2807013662, 1.1578972423, -0.0370727938	N, 1.0155724319, 1.3430761476, 0.1584117288	N, 1.4260023471, 0.8821000183, 0.2857584661
C, 0.5278254314, 1.1798015488, -1.1544774474	C, 0.2702642811, 1.4853582362, -0.900044205	C, 1.6452227249, -0.4430005378, 0.1690719921
C, -0.4999510203, 0.3107933938, -1.4297724072	C, -0.7059060646, 0.5410979394, -1.3457669739	C, 0.7485799563, -1.4082814153, -0.1484107614
C, -0.8249880817, -0.7560958, -0.5139057277	C, -0.8470873978, -0.5933972524, -0.5768063184	C, -0.6373340591, -1.1142944917, -0.4306945789
N, -1.7036586281, -1.7165212484, -0.924470434	N, -1.6716074305, -1.6423921359, -0.8201754861	N, -0.881682029, 0.2969504673, -0.7139019243
H, 0.6251360613, -0.2568019884, 2.9375851587	H, 1.4043251155, -1.008282441, 2.5686406696	H, -1.5523221029, 2.3569149868, 0.7795245597
H, 1.5623147394, 1.3708381318, 2.9267727205	H, 2.3195948432, 0.6126270734, 2.3636072709	H, -0.0705177331, 2.8651854732, 1.76522218638
H, 0.8430688495, 1.9001529343, -1.906425139	H, 0.41707439, 2.4001682229, -1.4743773017	H, 2.668450622, -0.73376352, 0.3297747822
H, -0.9784865641, 0.342702379, -2.4024395363	H, -1.2949855508, 0.6966816861, -2.24106947	H, 1.0397502622, -2.439384242, -0.1715045525
O, -0.3328237603, -0.8551006641, 0.6452433666	O, -0.1127261874, -0.7716810562, 0.5311566728	O, -1.5549270365, -1.8696719395, -0.4671045739
H, -1.8511797908, -2.5141652754, -0.3207933655	H, -1.8488974168, -2.2721728113, -0.0482018791	H, -1.8726575442, 0.462709176, -0.7013740276
H, -1.9732970031, -1.7978051002, -1.8943085116	H, -2.4345272866, -1.5082594374, -1.4687722076	H, -0.5285011607, 0.52523229047, -1.6284473633

INTE (HF/6-31G*)		TS1 ^b (HF/6-31G*)		10e (HF/6-31G*)	
C, 0.418729542, -0.2778079774, 1.1667838947		C, 0.3176194505, 0.1618131435, 1.26452229641		C, 0.0602836563, 0.4707003297, 1.1753992579	
C, 0.3521209717, -0.0825787342, 2.4702320624		C, 0.2846425118, 0.8960214489, 2.3610535839		C, 0.1104870263, -0.7728652481, 1.6416427086	
N, 1.5573652336, -0.4287243444, 0.4180459834		N, 1.4862172341, -0.2920761714, 0.6727950412		N, 1.0856619205, 1.0461585567, 0.4103914869	
C, 1.4808256404, -0.1071402139, -0.8294023926		C, 1.4933152176, -0.4618264378, -0.5913400411		C, 1.2706654905, 0.7070213936, -0.7859103985	
C, 0.3577684419, 0.3490098329, -1.562947924		C, 0.4603162755, -0.2719327502, -1.5721087038		C, 0.5667727014, -0.2358770861, -1.6533567467	
C, -0.9021741485, 0.3408442066, -1.0089408405		C, -0.8425697776, -0.0294256774, -1.2991366955		C, -0.4738943872, -1.0039800588, -1.3674696311	
N, -0.8458947054, -0.3806811543, 0.4088056601		N, -0.8917969014, -0.2248335799, 0.5786513583		N, -0.9876948614, 1.3608017205, 1.3906975123	
H, -0.5808767501, 0.0197840908, 2.9928306929		H, -0.6387633545, 1.2272065182, 2.7992847419		H, -0.6655975638, -1.1643481777, 2.2736547793	
H, 1.2611274216, -0.0210524927, 3.0345931028		H, 1.2036845129, 1.1831282836, 2.8322394335		H, 0.9465819779, -1.4071667622, 1.4193958124	
H, 2.4075272968, -0.1831112139, -1.3751287929		H, 2.4397294653, -0.7767468541, -1.0033429585		H, 2.085016257, 1.1994797438, -1.2947640785	
H, 0.4660219193, 0.7036361391, -2.5678257152		H, 0.7106880795, -0.3119464181, -2.6147773254		H, 0.8837021564, -0.3174817067, -2.6766346851	
O, -2.0130975423, 0.6487546189, -1.3036386091		O, -1.9235265759, 0.1818325526, -1.6689684084		O, -1.3622957448, -1.7003112566, -1.2475016988	
H, -1.0412443624, -1.3528015204, 0.2146726219		H, -1.0725745893, -1.2072586977, 0.7054688944		H, -1.5558074904, 1.1407933484, 2.1810533898	
H, -1.6316915695, -0.0246161468, 0.9276566584		H, -1.6990359026, 0.2814266448, 0.8946481383		H, -0.6871857166, 2.3124956855, 1.4078578365	

TS2e (HF/6-31G*)		8f (B3LYP/6-31+G*)		TS1 ^a (B3LYP/6-31+G*)	
C, -0.2582473289, 0.6373756874, -1.0229096984		C, 0.1084142526, 0.0073956991, 2.5270209294		C, -1.6177178642, 0.6288450213, 0.0636269751	
C, -0.5648829997, -0.6952807906, -1.0422108132		C, -0.0342061981, -0.0476425074, 3.8297960141		C, -2.8641159112, 0.2173164818, -0.171141692	
N, 0.9938111479, 1.090999773, -0.6745313483		N, 0.142971209, 0.0398707429, 1.2938988236		N, -0.8397481669, 1.6213102185, 0.1619043537	
C, 1.4968440386, 0.5905524235, 0.3898397758		C, 1.3145178062, 0.2657948547, 0.5586340964		C, 0.4522446155, 1.8177856781, -0.1527956591	
C, 0.9564786784, -0.368561893, 1.3019188372		C, 1.34343943, -0.2452148782, -0.7872785466		C, 1.4915657598, 0.9131067538, -0.2607009753	
C, -0.1598687027, -1.1152650708, 1.1161065539		C, 0.233445048, -0.0240656569, -1.7387802533		C, 1.4623608846, -0.5149554548, -0.0845661077	
N, -1.1575640683, 1.615970198, -1.2408689831		P, -1.5623401555, -0.2185902617, -1.183075163		P, -0.2338477666, -1.3113690642, 0.2908050752	
H, -1.558235551, -1.0215699013, -1.2939397467		H, -0.2505568145, 0.8498063528, 4.401994938		H, -3.181906252, -0.8022681374, -0.009121087	
H, 0.2305420888, -1.3958320111, -1.2167265311		H, 0.064196662, -0.9917770747, 4.357640502		H, -3.5803751976, 0.9419806873, -0.5519975319	
H, 2.4622758041, 0.9800749797, 0.6712174577		H, 2.2293927972, 0.4524956488, 1.1237315354		H, 0.7098845423, 2.8710409968, -0.2499209118	
H, 1.4120256884, -0.4877697786, 2.267680521		H, 2.2987447639, 0.4067055967, -1.2812261844		H, 2.4810469177, 1.3252021667, -0.4437428945	
O, -0.9231857766, -1.9118245688, 1.4348205127		O, 0.5097708062, -0.2079716572, -2.9179821386		O, 2.4477247776, -1.2442085867, -0.1130039784	
H, -0.8348333689, 2.5560076293, -1.2282816416		H, -2.076289791, 0.2571017053, -2.4184412833		H, 0.2079713155, -2.3348455111, 1.1706281765	
H, -2.0019601197, 1.4219722661, -1.7271797726		H, -1.7030122304, 1.0090161488, -0.48736016		H, -0.3784907867, -2.0986679562, -0.8744367751	

INTf (B3LYP/6-31+G*)		TS1 ^b (B3LYP/6-31+G*)		10f (B3LYP/6-31+G*)	
C, -0.6049465072, -0.067861314, -2.7080421084		C, -1.4403900593, 0.0755744909, -0.3566846215		C, -1.0334151136, 0.0911088378, -0.1186273274	
C, -0.0460308968, -0.0374718004, -1.4773738708		C, -2.7577553496, -0.0543746092, -0.1011582662		C, -1.3837511386, 0.0075951557, 1.178949484	
N, 1.3081982878, -0.0613728712, -1.2554246368		N, -0.9217334697, 1.2921773557, -0.7900884569		N, -0.5666637483, 1.2738997516, -0.7075915717	
C, 1.8391933332, -0.0449588416, -0.0501893067		C, 0.305205525, 1.6694228221, -0.6041125395		C, 0.6361809642, 1.676406696, -0.512739135	
C, 1.2826653212, -0.0027503207, 1.2631512429		C, 1.4601331915, 1.1243097212, 0.0777613188		C, 1.7157486372, 1.0801623451, 0.2698710034	
C, -0.0717087405, 0.0386198468, 1.597606508		C, 1.7316889163, -0.0544224193, 0.6980059175		C, 1.6926428591, -0.0100696324, 1.0391276898	
P, -1.1467262591, 0.0392771157, 0.0082888682		P, -0.2559427301, -1.3132277098, -0.1098176765		P, -1.1175049673, -1.3199409946, -1.331874118	
H, -1.6794757204, -0.0487202057, -2.8608354872		H, -3.1917078264, -0.9877073583, 0.2414686571		H, -1.8051347458, -0.9000831501, 1.5987841966	
H, 0.0368234496, -0.113480501, -3.5837332517		H, -3.4164234589, 0.8012464681, -0.2262860567		H, -1.2866495574, 0.8659589063, 1.8402930678	
H, 2.9297264523, -0.0699195369, -0.0668823574		H, 0.523685676, 2.6537744942, -1.0226892149		H, 0.9221232501, 2.6058351539, -1.0075381733	
H, 1.9810708389, -0.0017980892, 2.0964842228		H, 2.3167442782, 1.7963902859, 0.1440017987		H, 2.6920405966, 1.5580098919, 0.2277100636	
O, -0.6955513617, 0.0766329076, 2.6572598633		O, 2.4310986806, -0.7515681301, 1.3435543094		O, 1.8237366311, -0.9327521853, 1.7395068434	
H, -1.9854812041, 1.1698632649, 0.0094199448		H, -1.076825472, -2.3299908002, 0.4307663694		H, -2.0443339963, -2.1175254453, -0.6053236343	
H, -2.0697821093, -1.022020251, 0.0601926675		H, -0.1062807453, -1.8310539259, -1.4205025385		H, -2.1031505187, -0.7395816299, -2.1782177837	

TS2f (B3LYP/6-31+G*)		9f (B3LYP/6-31+G*)		TS3f (B3LYP/6-31+G*)	
C,-0.8876222353,0.0821694372,-0.2792466491		C,0.3640916131,0.143689103,-0.7071846485		C,1.6381947518,0.0235885363,1.1897774001	
C,-0.8186406444,0.0057746812,1.092557235		C,-0.9730614955,0.3481403173,-0.0294912562		C,1.8955868758,-0.7165480057,2.2517665149	
N,-0.3921268967,1.1562664629,-0.9661352295		N,1.4215414349,-0.2824043835,-0.1027010553		N,1.8668020666,0.958782021,0.3762566744	
C,0.813687894,1.5573129003,-0.6508891236		C,1.3312495485,-0.5951466917,1.2618205104		C,0.9934068543,1.6455066013,-0.376513035	
C,1.7020102796,0.9755292885,0.3047779225		C,0.2065553029,-0.5487136325,2.0168532384		C,-0.2591961671,1.1914645169,-0.7437666444	
C,1.354089933,0.0335776727,1.23383332457		C,-1.0606414558,-0.1339200263,1.4192935148		C,-0.7005434405,-0.1215836317,-0.3853576117	
P,-1.3813575961,-1.3452527555,-1.355159893		P,0.4579185124,0.3791163011,-2.5419840747		P,-2.2827652012,-0.7869549804,-1.1538069673	
H,-1.1773822621,-0.8677927821,1.6288776676		H,-1.7835037263,-0.1117212181,-0.6103561594		H,1.3467801578,-1.6280437167,2.4449759234	
H,-0.7405455558,0.9207777842,1.6766958887		H,-1.201141404,1.425752279,-0.0273497363		H,2.6572962129,-0.3807008662,2.9491599388	
H,1.1980681694,2.4040038407,-1.2190228673		H,2.2764503631,-0.9136541699,1.6948105009		H,1.3777308823,2.576126155,-0.7897887128	
H,2.75943542,1.2230872565,0.2631351172		H,0.209986914,-0.8405703702,3.0626439796		H,-0.8384473289,1.7720054694,-1.4530438914	
O,1.6368339517,-0.6401638962,2.1652826153		O,-2.1307471868,-0.1395896261,2.0165946359		O,-0.118789583,-0.8488043999,0.4561557856	
H,-2.4580734229,-1.8219399463,-0.5581815814		H,-0.2408622009,1.6177021381,-2.5983538702		H,-1.8402569876,-2.1308111906,-1.237527995	
H,-2.1921271053,-0.5780827696,-2.2296159292		H,1.7563187378,0.9450000988,-2.5732314478		H,-1.9836159673,-0.459858195,-2.5051535023	

11f (B3LYP/6-31+G*)	
C,1.1442630762,-0.178393531,1.1244081253	
C,1.7400981713,-0.9700278127,2.0290015077	
N,1.5305284117,1.1293324895,0.8798682542	
C,0.8925074525,1.812608797,-0.0132221505	
C,-0.2166164655,1.2853171235,-0.7834910897	
C,-0.5862487932,0.0066608916,-0.5374246929	
P,-1.977668982,-0.83224625681,-1.4230239697	
H,1.4080513059,-1.9881276792,2.1908749386	
H,2.5678771429,-0.5765234012,2.604172466	
H,1.2228844143,2.8378777443,-0.1798888623	
H,-0.7299509655,1.8854240638,-1.5248896124	
O,0.060247747,-0.7389574806,0.3916172006	
H,-2.5817420832,-1.3712061509,-0.2520266423	
H,-1.2617865901,-2.0311664478,-1.7005283252	

Table S2. Second order perturbation theory analysis (selected interactions)

Transition structure	Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis				
	Threshold for printing: 0.50 kcal/mol				
	Donor NBO (i)	Acceptor NBO (j)	E(2) kcal/mol	E(j)-E(i) a.u.	F(i,j) a.u.
<p>TS1a</p> <p>The Lp(4) at the fluorine atom interacts with the LUMO orbital of the ketenimine moiety, the BD(2)*C1-N3 natural localized orbital.</p>	within unit 1				
	2. BD (2) C 1- C 2	/ 24. LP (1) N 3	42.94	0.08	0.091
	4. BD (2) C 1- N 3	/160. BD* (3) C 6- O12	0.68	0.38	0.015
	9. BD (2) C 4- C 5	/ 24. LP (1) N 3	55.86	0.06	0.075
	9. BD (2) C 4- C 5	/159. BD* (2) C 6- O12	44.37	0.27	0.100
	14. BD (2) C 6- O12	/154. BD* (2) C 4- C 5	3.36	0.42	0.037
	24. LP (1) N 3	/147. BD* (2) C 1- C 2	67.06	0.25	0.128
	24. LP (1) N 3	/154. BD* (2) C 4- C 5	92.97	0.21	0.132
	29. LP (1) O12	/156. BD* (1) C 5- C 6	6.80	1.24	0.082
	149. BD* (2) C 1- N 3	/160. BD* (3) C 6- O12	9.33	0.04	0.032
	160. BD* (3) C 6- O12	/153. BD* (1) C 4- C 5	1.69	0.53	0.067
	160. BD* (3) C 6- O12	/156. BD* (1) C 5- C 6	5.29	0.51	0.116
	from unit 2 to unit 1				
	25. LP (1) F 7	/149. BD* (2) C 1- N 3	13.17	0.88	0.104
	25. LP (1) F 7	/160. BD* (3) C 6- O12	15.51	0.92	0.115
	26. LP (2) F 7	/147. BD* (2) C 1- C 2	2.81	0.43	0.032
	26. LP (2) F 7	/159. BD* (2) C 6- O12	5.66	0.40	0.046
	27. LP (3) F 7	/149. BD* (2) C 1- N 3	61.68	0.69	0.190
	27. LP (3) F 7	/160. BD* (3) C 6- O12	45.15	0.73	0.166
	28. LP (4) F 7	/149. BD* (2) C 1- N 3	33.35	0.36	0.098
	28. LP (4) F 7	/160. BD* (3) C 6- O12	86.40	0.40	0.167
<p>TS1b</p> <p>The Lp(3) at the chlorine atom [not the BD(1) C 6- Cl7 natural orbital] interacts with the LUMO orbital of the ketenimine moiety, the BD(2)*C1-N3 natural localized orbital.</p>	2. BD (2) C 1- C 2	/157. BD* (2) N 3- C 4	14.76	0.28	0.063
	8. BD (2) N 3- C 4	/ 28. LP (1) C 5	10.72	0.20	0.061
	8. BD (2) N 3- C 4	/151. BD* (2) C 1- C 2	33.82	0.37	0.101
	13. BD (1) C 6-Cl 7	/153. BD* (2) C 1- N 3	2.14	0.43	0.030
	15. BD (2) C 6- O12	/ 28. LP (1) C 5	5.08	0.28	0.055
	28. LP (1) C 5	/157. BD* (2) N 3- C 4	127.80	0.13	0.123
	28. LP (1) C 5	/164. BD* (2) C 6- O12	120.65	0.14	0.129
	29. LP (1) Cl 7	/153. BD* (2) C 1- N 3	8.37	0.77	0.080
	30. LP (2) Cl 7	/164. BD* (2) C 6- O12	4.40	0.30	0.036
	31. LP (3) Cl 7	/153. BD* (2) C 1- N 3	94.10	0.29	0.148
	31. LP (3) Cl 7	/162. BD* (1) C 6-Cl 7	2.00	0.29	0.022
	31. LP (3) Cl 7	/163. BD* (1) C 6- O12	1.47	0.97	0.037
	33. LP (2) O12	/160. BD* (1) C 5- C 6	6.48	0.83	0.072
	33. LP (2) O12	/162. BD* (1) C 6-Cl 7	118.68	0.25	0.155
	33. LP (2) O12	/163. BD* (1) C 6- O12	2.84	0.94	0.051
	157. BD* (2) N 3- C 4	/151. BD* (2) C 1- C 2	58.95	0.05	0.082
	157. BD* (2) N 3- C 4	/164. BD* (2) C 6- O12	2.35	0.01	0.008

<p>TS1c</p> <p>Only a Lp on the migrating oxygen atom.</p>	...	2. BD (2) C 1- C 2	/154. BD* (2) N 3- C 4	10.92	0.29	0.056
	...	8. BD (2) N 3- C 4	/ 26. LP (1) C 5	12.51	0.19	0.063
	...	8. BD (2) N 3- C 4	/148. BD* (2) C 1- C 2	37.10	0.34	0.101
	...	25. LP (1) N 3	/150. BD* (1) C 1- O 7	53.14	0.34	0.121
	...	25. LP (1) N 3	/155. BD* (1) C 4- C 5	9.64	0.88	0.088
	...	26. LP (1) C 5	/154. BD* (2) N 3- C 4	135.41	0.12	0.124
	...	26. LP (1) C 5	/161. BD* (2) C 6- O12	115.84	0.13	0.122
	...	27. LP (1) O 7	/148. BD* (2) C 1- C 2	3.72	0.48	0.039
	...	27. LP (1) O 7	/161. BD* (2) C 6- O12	12.37	0.46	0.073
	...	28. LP (1) O12	/157. BD* (1) C 5- C 6	4.88	1.22	0.069
	...	29. LP (2) O12	/157. BD* (1) C 5- C 6	12.51	0.79	0.093
	...	29. LP (2) O12	/159. BD* (1) C 6- O 7	57.28	0.44	0.142
	...	150. BD* (1) C 1- O 7	/159. BD* (1) C 6- O 7	4.37	0.15	0.046
	...	150. BD* (1) C 1- O 7	/162. BD* (1) O 7- H13	1.12	0.35	0.044
	...	154. BD* (2) N 3- C 4	/148. BD* (2) C 1- C 2	86.36	0.03	0.075
	...	154. BD* (2) N 3- C 4	/150. BD* (1) C 1- O 7	0.50	0.02	0.004
	...	161. BD* (2) C 6- O12	/150. BD* (1) C 1- O 7	4.12	0.01	0.011
	...					
	...					
	...

<p>TS1d</p> <p>The Lp(2) at the sulphur atom [not the BD(1)C6-S7] interacts with the LUMO orbital of the ketenimine moiety, the BD(2)*C1-N3 natural localized orbital.</p>	...	2. BD (2) C 1- C 2	/ 29. LP (1) N 3	40.08	0.08	0.089
	...	9. BD (2) C 4- C 5	/ 29. LP (1) N 3	51.76	0.05	0.076
	...	9. BD (2) C 4- C 5	/165. BD* (2) C 6- O12	31.83	0.27	0.084
	...	13. BD (1) C 6- S 7	/154. BD* (2) C 1- N 3	1.71	0.51	0.030
	...	15. BD (2) C 6- O12	/159. BD* (2) C 4- C 5	4.39	0.40	0.041
	...	29. LP (1) N 3	/152. BD* (2) C 1- C 2	70.84	0.24	0.129
	...	29. LP (1) N 3	/154. BD* (2) C 1- N 3	6.55	0.17	0.030
	...	29. LP (1) N 3	/159. BD* (2) C 4- C 5	71.90	0.23	0.122
	...	30. LP (1) S 7	/154. BD* (2) C 1- N 3	5.74	0.56	0.057
	...	31. LP (2) S 7	/154. BD* (2) C 1- N 3	88.72	0.24	0.131
	...	33. LP (2) O12	/161. BD* (1) C 5- C 6	12.88	0.78	0.094
	...	33. LP (2) O12	/163. BD* (1) C 6- S 7	52.75	0.33	0.119
	...	159. BD* (2) C 4- C 5	/152. BD* (2) C 1- C 2	1.27	0.02	0.008
	...	159. BD* (2) C 4- C 5	/163. BD* (1) C 6- S 7	1.22	0.05	0.013
	...	165. BD* (2) C 6- O12	/159. BD* (2) C 4- C 5	152.30	0.01	0.076
	...					
	...					
	...					
	...					
	...					
	...

<p>TS2a</p> <p>Interaction between the BD(2)C1-C2 and BD*(2)C6-O12 natural orbitals</p>	...	2. BD (2) C 1- C 2	/153. BD*(2) N 3- C 4	6.14	0.30	0.039
		2. BD (2) C 1- C 2	/157. BD*(2) C 5- C 6	2.33	0.29	0.024
		2. BD (2) C 1- C 2	/160. BD*(2) C 6- O12	21.42	0.29	0.071
	...	8. BD (2) N 3- C 4	/147. BD*(2) C 1- C 2	15.36	0.34	0.066
		8. BD (2) N 3- C 4	/149. BD*(1) C 1- F 7	6.37	0.59	0.055
	...	8. BD (2) N 3- C 4	/157. BD*(2) C 5- C 6	5.97	0.33	0.042
	...	12. BD (2) C 5- C 6	/153. BD*(2) N 3- C 4	30.91	0.30	0.086
	...	12. BD (2) C 5- C 6	/160. BD*(2) C 6- O12	2.31	0.28	0.023
	...	15. BD (2) C 6- O12	/147. BD*(2) C 1- C 2	2.78	0.44	0.033
	...	15. BD (2) C 6- O12	/157. BD*(2) C 5- C 6	0.51	0.43	0.015
	...	24. LP (1) N 3	/147. BD*(2) C 1- C 2	11.22	0.36	0.058
		24. LP (1) N 3	/149. BD*(1) C 1- F 7	2.50	0.61	0.036
		24. LP (1) N 3	/153. BD*(2) N 3- C 4	0.77	0.37	0.015
		24. LP (1) N 3	/154. BD*(1) C 4- C 5	11.32	0.86	0.091
	...	27. LP (3) F 7	/147. BD*(2) C 1- C 2	23.95	0.42	0.093
		28. LP (1) O12	/156. BD*(1) C 5- C 6	8.11	1.29	0.091
		29. LP (2) O12	/156. BD*(1) C 5- C 6	1.13	0.87	0.031
		29. LP (2) O12	/157. BD*(2) C 5- C 6	105.18	0.30	0.159
		29. LP (2) O12	/160. BD*(2) C 6- O12	2.43	0.31	0.025
	...	157. BD*(2) C 5- C 6	/147. BD*(2) C 1- C 2	3.64	0.01	0.010
		157. BD*(2) C 5- C 6	/153. BD*(2) N 3- C 4	123.43	0.02	0.073
	...

<p>TS2b</p>	...	2. BD (2) C 1- C 2	/157. BD*(2) N 3- C 4	6.00	0.31	0.039
		2. BD (2) C 1- C 2	/161. BD*(2) C 5- C 6	2.64	0.29	0.026
		2. BD (2) C 1- C 2	/164. BD*(2) C 6- O12	25.35	0.30	0.078
	...	8. BD (2) N 3- C 4	/151. BD*(2) C 1- C 2	14.53	0.33	0.063
		8. BD (2) N 3- C 4	/153. BD*(1) C 1- Cl 7	5.62	0.46	0.046
	...	8. BD (2) N 3- C 4	/161. BD*(2) C 5- C 6	6.06	0.33	0.043
	...	12. BD (2) C 5- C 6	/157. BD*(2) N 3- C 4	31.19	0.30	0.087
	...	12. BD (2) C 5- C 6	/164. BD*(2) C 6- O12	2.12	0.28	0.022
	...	15. BD (2) C 6- O12	/151. BD*(2) C 1- C 2	3.94	0.42	0.039
	...	28. LP (1) N 3	/151. BD*(2) C 1- C 2	11.00	0.35	0.056
		28. LP (1) N 3	/153. BD*(1) C 1- Cl 7	0.76	0.48	0.018
		28. LP (1) N 3	/157. BD*(2) N 3- C 4	1.02	0.37	0.018
	...	31. LP (3) Cl 7	/151. BD*(2) C 1- C 2	16.52	0.31	0.067
	...	33. LP (2) O12	/161. BD*(2) C 5- C 6	105.97	0.30	0.160
	...	33. LP (2) O12	/164. BD*(2) C 6- O12	1.05	0.31	0.016
	...	151. BD*(2) C 1- C 2	/157. BD*(2) N 3- C 4	36.31	0.02	0.047
		157. BD*(2) N 3- C 4	/153. BD*(1) C 1- Cl 7	2.26	0.11	0.033
	...	161. BD*(2) C 5- C 6	/157. BD*(2) N 3- C 4	128.19	0.02	0.072
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<p>TS2f</p>	...	2. BD (2) C 1- C 2	/159. BD*(2) N 3- C 4	5.39	0.32	0.037
	...	2. BD (2) C 1- C 2	/163. BD*(2) C 5- C 6	3.07	0.29	0.027
	...	2. BD (2) C 1- C 2	/166. BD*(2) C 6- O12	33.05	0.29	0.088
	...	8. BD (2) N 3- C 4	/153. BD*(2) C 1- C 2	12.00	0.35	0.059
	...	8. BD (2) N 3- C 4	/163. BD*(2) C 5- C 6	5.63	0.35	0.043
	...	12. BD (2) C 5- C 6	/159. BD*(2) N 3- C 4	28.77	0.31	0.086
	...	12. BD (2) C 5- C 6	/166. BD*(2) C 6- O12	1.86	0.28	0.021
	...	15. BD (2) C 6- O12	/153. BD*(2) C 1- C 2	4.78	0.42	0.042
	...	30. LP (1) N 3	/153. BD*(2) C 1- C 2	11.22	0.35	0.057
	...	31. LP (1) P 7	/153. BD*(2) C 1- C 2	3.38	0.44	0.036
	...	33. LP (2) O12	/163. BD*(2) C 5- C 6	104.78	0.30	0.159
	...	153. BD*(2) C 1- C 2	/159. BD*(2) N 3- C 4	17.76	0.04	0.046
	...	163. BD*(2) C 5- C 6	/159. BD*(2) N 3- C 4	61.56	0.04	0.072
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<p>TS3a</p> <p>Interaction between a Lp at O12 with the BD*(2)C1-N3 natural orbital</p>	...	2. BD (2) C 1- C 2	/ 25. LP (1) N 3	45.51	0.07	0.091
	...	9. BD (2) C 4- C 5	/ 25. LP (1) N 3	62.55	0.05	0.077
	...	9. BD (2) C 4- C 5	/159. BD*(2) C 6- O12	42.73	0.24	0.094
	...	11. BD (1) C 5- C 6	/157. BD*(1) C 6- F 7	63.40	1.44	0.272
	...	11. BD (1) C 5- C 6	/158. BD*(1) C 6- O12	1.66	1.17	0.040
	...	11. BD (1) C 5- C 6	/160. BD*(3) C 6- O12	102.04	1.50	0.362
	...	13. BD (1) C 6- F 7	/155. BD*(1) C 5- C 6	15.32	1.41	0.136
	...	13. BD (1) C 6- F 7	/157. BD*(1) C 6- F 7	30.21	1.62	0.203
	...	13. BD (1) C 6- F 7	/160. BD*(3) C 6- O12	246.06	1.67	0.583
	...	15. BD (2) C 6- O12	/153. BD*(2) C 4- C 5	2.77	0.40	0.033
	...	15. BD (2) C 6- O12	/159. BD*(2) C 6- O12	1.29	0.37	0.022
	...	16. BD (3) C 6- O12	/148. BD*(2) C 1- N 3	63.65	0.33	0.130
	...	16. BD (3) C 6- O12	/155. BD*(1) C 5- C 6	8.95	0.96	0.087
	...	16. BD (3) C 6- O12	/157. BD*(1) C 6- F 7	37.57	1.16	0.196
	...	25. LP (1) N 3	/146. BD*(2) C 1- C 2	71.27	0.26	0.133
	...	25. LP (1) N 3	/153. BD*(2) C 4- C 5	80.13	0.22	0.126
	...	26. LP (1) F 7	/160. BD*(3) C 6- O12	15.40	1.93	0.164
	...	27. LP (2) F 7	/158. BD*(1) C 6- O12	10.34	0.96	0.089
	...	28. LP (3) F 7	/159. BD*(2) C 6- O12	28.50	0.39	0.103
	...	29. LP (1) O12	/148. BD*(2) C 1- N 3	10.83	0.65	0.080
	...	29. LP (1) O12	/155. BD*(1) C 5- C 6	7.25	1.28	0.086
	...	159. BD*(2) C 6- O12	/153. BD*(2) C 4- C 5	113.33	0.03	0.081
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<p>TS3b</p>	...	2. BD (2) C 1- C 2	/ 28. LP (1) N 3	46.81	0.07	0.091
	...	9. BD (2) C 4- C 5	/ 28. LP (1) N 3	69.77	0.05	0.078
	...	9. BD (2) C 4- C 5	/164. BD*(2) C 6- O12	42.24	0.24	0.092
	...	15. BD (2) C 6- O12	/151. BD*(2) C 1- C 2	0.99	0.43	0.020
	...	15. BD (2) C 6- O12	/158. BD*(2) C 4- C 5	2.91	0.40	0.033
	...	28. LP (1) N 3	/151. BD*(2) C 1- C 2	71.12	0.26	0.133
	...	28. LP (1) N 3	/158. BD*(2) C 4- C 5	77.77	0.22	0.125
	...	31. LP (3) Cl 7	/164. BD*(2) C 6- O12	18.56	0.28	0.070
	...	32. LP (1) O12	/153. BD*(2) C 1- N 3	9.77	0.65	0.076
	...	33. LP (2) O12	/153. BD*(2) C 1- N 3	64.28	0.31	0.128
	...	33. LP (2) O12	/162. BD*(1) C 6-Cl 7	31.18	0.44	0.110
	...	164. BD*(2) C 6- O12	/151. BD*(2) C 1- C 2	0.82	0.07	0.012
	...	164. BD*(2) C 6- O12	/158. BD*(2) C 4- C 5	87.77	0.04	0.080
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<p>TS3c</p>	...	2. BD (2) C 1- C 2	/ 25. LP (1) N 3	41.26	0.07	0.088
	...	9. BD (2) C 4- C 5	/ 25. LP (1) N 3	49.42	0.06	0.075
	...	9. BD (2) C 4- C 5	/161. BD*(2) C 6- O12	36.87	0.24	0.089
	...	15. BD (2) C 6- O12	/150. BD*(2) C 1- N 3	1.85	0.38	0.025
	...	15. BD (2) C 6- O12	/155. BD*(2) C 4- C 5	2.54	0.40	0.031
	...	25. LP (1) N 3	/148. BD*(2) C 1- C 2	71.99	0.25	0.132
	...	25. LP (1) N 3	/150. BD*(2) C 1- N 3	4.04	0.20	0.027
	...	25. LP (1) N 3	/155. BD*(2) C 4- C 5	71.75	0.22	0.121
	...	27. LP (2) O 7	/161. BD*(2) C 6- O12	44.87	0.32	0.115
	...	28. LP (1) O12	/150. BD*(2) C 1- N 3	9.87	0.65	0.077
	...	29. LP (2) O12	/150. BD*(2) C 1- N 3	66.20	0.33	0.134
	...	29. LP (2) O12	/157. BD*(1) C 5- C 6	5.62	0.84	0.066
	...	29. LP (2) O12	/159. BD*(1) C 6- O 7	21.40	0.70	0.115
	...	161. BD*(2) C 6- O12	/155. BD*(2) C 4- C 5	80.43	0.04	0.079
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<p>TS3d</p>	...	2. BD (2) C 1- C 2	/ 29. LP (1) N 3	42.72	0.07	0.088
	...	9. BD (2) C 4- C 5	/ 29. LP (1) N 3	51.40	0.06	0.076
	...	9. BD (2) C 4- C 5	/165. BD*(2) C 6- O12	35.87	0.24	0.087
	...	15. BD (2) C 6- O12	/154. BD*(2) C 1- N 3	2.69	0.38	0.031
	...	15. BD (2) C 6- O12	/159. BD*(2) C 4- C 5	2.97	0.40	0.033
	...	29. LP (1) N 3	/152. BD*(2) C 1- C 2	68.62	0.25	0.130
	...	29. LP (1) N 3	/154. BD*(2) C 1- N 3	6.84	0.20	0.035
	...	29. LP (1) N 3	/157. BD*(1) N 3- C 4	1.49	0.72	0.034
	...	29. LP (1) N 3	/159. BD*(2) C 4- C 5	69.71	0.22	0.120
	...	31. LP (2) S 7	/165. BD*(2) C 6- O12	25.55	0.23	0.074
	...	33. LP (2) O12	/154. BD*(2) C 1- N 3	57.55	0.33	0.125
	...	33. LP (2) O12	/161. BD*(1) C 5- C 6	6.35	0.84	0.070
	...	33. LP (2) O12	/163. BD*(1) C 6- S 7	22.28	0.50	0.099
	...	33. LP (2) O12	/165. BD*(2) C 6- O12	4.45	0.32	0.035
	...	154. BD*(2) C 1- N 3	/152. BD*(2) C 1- C 2	1.24	0.06	0.014
	...	165. BD*(2) C 6- O12	/154. BD*(2) C 1- N 3	23.27	0.02	0.027
	...	165. BD*(2) C 6- O12	/159. BD*(2) C 4- C 5	68.58	0.04	0.077
	...

<p>TS3e</p>	...	2. BD (2) C 1- C 2	/ 26. LP (1) N 3	38.60	0.07	0.085
	...	9. BD (2) C 4- C 5	/ 26. LP (1) N 3	35.70	0.07	0.073
	...	9. BD (2) C 4- C 5	/162. BD*(2) C 6- O12	28.69	0.27	0.084
	...	15. BD (2) C 6- O12	/149. BD*(2) C 1- C 2	0.71	0.43	0.016
	...	15. BD (2) C 6- O12	/151. BD*(2) C 1- N 3	1.76	0.38	0.025
	...	15. BD (2) C 6- O12	/156. BD*(2) C 4- C 5	2.57	0.40	0.031
	...	26. LP (1) N 3	/149. BD*(2) C 1- C 2	69.19	0.25	0.129
	...	26. LP (1) N 3	/150. BD*(1) C 1- N 3	0.82	0.86	0.028
	...	26. LP (1) N 3	/151. BD*(2) C 1- N 3	10.35	0.20	0.043
	...	26. LP (1) N 3	/154. BD*(1) N 3- C 4	2.62	0.70	0.045
	...	26. LP (1) N 3	/156. BD*(2) C 4- C 5	65.05	0.22	0.116
	...	27. LP (1) N 7	/162. BD*(2) C 6- O12	53.84	0.28	0.115
	...	28. LP (1) O12	/151. BD*(2) C 1- N 3	8.88	0.65	0.073
	...	29. LP (2) O12	/151. BD*(2) C 1- N 3	60.20	0.33	0.128
	...	29. LP (2) O12	/162. BD*(2) C 6- O12	4.76	0.33	0.037
	...	151. BD*(2) C 1- N 3	/149. BD*(2) C 1- C 2	1.97	0.05	0.017
	...	151. BD*(2) C 1- N 3	/156. BD*(2) C 4- C 5	0.58	0.02	0.006
	...	162. BD*(2) C 6- O12	/149. BD*(2) C 1- C 2	0.59	0.05	0.009
	...	162. BD*(2) C 6- O12	/156. BD*(2) C 4- C 5	109.57	0.02	0.076
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<p>TS3f</p>	...	2. BD (2) C 1- C 2	/ 30. LP (1) N 3	43.33	0.07	0.087
	...	9. BD (2) C 4- C 5	/ 30. LP (1) N 3	50.04	0.06	0.075
	...	9. BD (2) C 4- C 5	/166. BD*(2) C 6- O12	33.56	0.26	0.086
	...	15. BD (2) C 6- O12	/153. BD*(2) C 1- C 2	0.54	0.43	0.014
	...	15. BD (2) C 6- O12	/155. BD*(2) C 1- N 3	1.14	0.38	0.020
	...	15. BD (2) C 6- O12	/160. BD*(2) C 4- C 5	3.36	0.40	0.035
	...	30. LP (1) N 3	/153. BD*(2) C 1- C 2	66.49	0.26	0.129
	...	30. LP (1) N 3	/154. BD*(1) C 1- N 3	0.73	0.87	0.026
	...	30. LP (1) N 3	/155. BD*(2) C 1- N 3	10.56	0.20	0.044
	...	30. LP (1) N 3	/158. BD*(1) N 3- C 4	2.26	0.71	0.042
	...	30. LP (1) N 3	/160. BD*(2) C 4- C 5	65.25	0.23	0.117
	...	31. LP (1) P 7	/166. BD*(2) C 6- O12	5.59	0.43	0.047
	...	32. LP (1) O12	/155. BD*(2) C 1- N 3	7.14	0.64	0.066
	...	33. LP (2) O12	/155. BD*(2) C 1- N 3	46.92	0.33	0.113
	...	155. BD*(2) C 1- N 3	/153. BD*(2) C 1- C 2	2.23	0.05	0.019
	...	166. BD*(2) C 6- O12	/153. BD*(2) C 1- C 2	0.53	0.06	0.009
	...	166. BD*(2) C 6- O12	/160. BD*(2) C 4- C 5	94.63	0.03	0.077
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Figure S1. B3LYP/6-31+G*-optimized geometries of transition states **TS1a-d** and **TS1ref** (two views) showing the points used to evaluate the NICS.

Figure S2. B3LYP/6-31+G*-optimized geometries of transition states **TS2a-f** showing the points used to evaluate the NICS. In the case of **TS2e** the geometry was optimized at the HF/6-31G* theoretical level, see text for details.

Figure S3. B3LYP/6-31+G*-optimized geometries of transition states **TS2ref** and **TS3a-f** showing the points used to evaluate the NICS.

EXPERIMENTAL DATA

General Methods

Melting points are uncorrected. Infrared (IR) spectra were recorded neat or as nujol. ^1H NMR spectra were recorded in CDCl_3 at 300 or 400 MHz. ^{13}C NMR spectra were recorded in CDCl_3 at 75 or 100 MHz. The chemical shifts are expressed in ppm, relative to Me_4Si at $\delta = 0.00$ ppm for ^1H , while the chemical shifts for ^{13}C are reported relative to the resonance of CDCl_3 $\delta = 77.10$ ppm. Mass spectra were determined at an ionizing voltage of 70 eV.

Materials: 2-azidobenzoyl chloride **1a**,² 2-azido-5-chlorobenzoyl chloride **1b**,² bis(4-methoxyphenyl) diselenide,³ 2-azido-*N,N*-dimethylbenzamide **2o**,⁴ *N,N*-dimethyl-2-(triphenylphosphoranylideneamino)benzamide **3o**,⁵ diphenylketene,⁶ and methylphenylketene⁷ were prepared by published procedures.

The experimental details for the synthesis of compounds **2a-j**, **3a-j**, and **5a-l** and their characterization (NMR, IR, MS and elemental analyses) have been reported in a preliminary paper.⁸

Preparation of *Se*-aryl 2-azidoselenobenzoates **2k,l**

An orange solution of the corresponding diaryl diselenide (5 mmol) in anhydrous ethanol (30 mL) was stirred at 0°C under an atmosphere of nitrogen. Powdered sodium borohydride was added in small portions, of 0.04 g each, until the solution became colorless. Then, a solution of 2-azidobenzoyl chloride **1a** (1.82 g, 10 mmol) in anhydrous ethanol was added dropwise over 5 min. The mixture was stirred at 0°C for 30 min and at room temperature for 3 hours. The solvent was removed under reduced pressure and diethyl ether (50 mL) and saturated sodium hydrogen carbonate solution (50 mL) were added to the residue. The organic phase was separated and dried over anhydrous magnesium sulfate. The diethyl ether was removed under reduced pressure and the

residue was purified by column chromatography on silica gel, using hexanes/dichloromethane (3:2, v/v) as eluent.

In this reaction the major product is ethyl 2-azidobenzoate.

Se-Phenyl 2-azidoselenobenzoate 2k: yield 17%; yellow oil; IR (neat) 2127 (vs), 2101 (vs), 1704 (s), 1666 (s), 1590 (m), 1481 (s), 1443 (s), 1298 (s), 1190 (s), 1141 (w), 1095 (w), 1022 (w), 880 (vs), 759 (s), 693 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.21 (t, 1 H, $J = 7.6$ Hz), 7.25 (d, 1 H, $J = 8.1$ Hz), 7.40-7.43 (m, 3 H), 7.52-7.60 (m, 3 H), 7.81 (dd, 1 H, $J = 7.8, 1.4$ Hz); ^{13}C NMR (CDCl_3 , 100 MHz) δ 119.6, 124.8, 127.2 (s), 129.1, 129.4, 129.6, 130.4 (s), 133.7, 136.2, 138.0 (s), 191.4 (s). Anal. Calcd for $\text{C}_{13}\text{H}_9\text{N}_3\text{OSe}$ (302.19): C, 51.67; H, 3.00; N, 13.90. Found: C, 51.46; H, 2.85; N, 13.67.

Se-(4-Methoxyphenyl) 2-azidoselenobenzoate 2l: yield 15%; yellow oil; IR (neat) 2125 (vs), 2101 (vs), 1705 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 3.83 (s, 3 H), 6.92-6.96 (m, 2 H), 7.20 (td, 1 H, $J = 7.8, 1.0$ Hz), 7.25 (dd, 1 H, $J = 8.1, 0.8$ Hz), 7.46-7.50 (m, 2 H), 7.54 (ddd, 1 H, $J = 8.5, 7.5, 1.5$ Hz), 7.80 (dd, 1 H, $J = 7.8, 1.5$ Hz); ^{13}C NMR (CDCl_3 , 100 MHz) δ 55.3, 115.1, 117.8 (s), 119.6, 124.8, 129.6, 131.0 (s), 133.6, 137.7, 138.0 (s), 160.5 (s), 192.4 (s). Anal. Calcd for $\text{C}_{14}\text{H}_{11}\text{N}_3\text{O}_2\text{Se}$ (332.22): C, 50.61; H, 3.34; N, 12.65. Found: C, 50.37; H, 3.07; N, 12.38.

Preparation of aryl 2-azidobenzoates 2m,n

To a solution of 2-azidobenzoyl chloride **1a** (0.91 g, 5 mmol) in anhydrous dichloromethane (50 mL) DMAP (0.79 g, 6.5 mmol) and the corresponding phenol (5 mmol) were added. The reaction mixture was stirred at room temperature for 5 hours. Then *n*-hexane (50 mL) was added and the resulting solid was filtered and washed with *n*-hexane (3 x 15 mL). From the filtrate the solvent was

removed under reduced pressure, and the resulting material was purified by column chromatography on silica gel, using hexanes/diethyl ether as eluent.

4-Methylphenyl 2-azidobenzoate 2m: column chromatography: hexanes/diethyl ether (7:3, v/v); yield 94%; colorless oil; IR (neat) 2123 (vs), 1746 (vs), 1600 (s), 1578 (s), 1511 (vs), 1484 (vs), 1445 (s), 1300 (vs), 1249 (vs), 1196 (vs), 1165 (vs), 1116 (vs), 1047 (vs), 879 (m), 797 (m), 752 (vs) cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 2.36 (s, 3 H), 7.07-7.12 (m, 2 H), 7.18-7.23 (m, 2 H), 7.25 (dd, 1 H, $J = 5.5, 1.1$ Hz), 7.28 (dd, 1 H, $J = 8.1, 0.8$ Hz), 7.57 (ddd, 1 H, $J = 8.6, 8.1, 1.6$ Hz), 8.05 (dd, 1 H, $J = 7.8, 1.6$ Hz); ^{13}C NMR (CDCl_3 , 75 MHz) δ 20.9, 120.1, 121.3, 122.0 (s), 124.6, 130.0, 132.3, 133.8, 135.7 (s), 140.7 (s), 148.5 (s), 163.8 (s); MS (EI, 70eV) m/z (rel int) 253 (M^+ , 2), 146 (100). Anal. Calcd for $\text{C}_{14}\text{H}_{11}\text{N}_3\text{O}_2$ (253.26): C, 66.39; H, 4.38; N, 16.59. Found: C, 66.47; H, 4.24; N, 16.39.

3,4-Dimethoxyphenyl 2-azidobenzoate 2n: column chromatography: hexanes/diethyl ether (2:3, v/v); yield 83%; colorless oil; IR (neat) 2125 (vs), 1748 (vs), 1606 (s), 1513 (vs), 1298 (vs), 1235 (vs), 1153 (vs), 1126 (s), 1040 (vs), 911 (m), 881 (m), 762 (s), 739 (s), 690 (m), 614 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 3.88 (s, 3 H), 3.89 (s, 3 H), 6.76-6.80 (m, 2 H), 6.87-6.90 (m, 1 H), 7.25 (td, 1 H, $J = 7.8, 1.0$ Hz), 7.30 (dd, 1 H, $J = 8.1, 1.0$ Hz), 7.59 (ddd, 1 H, $J = 8.6, 8.1, 1.6$ Hz), 8.07 (dd, 1 H, $J = 7.8, 1.6$ Hz); ^{13}C NMR (CDCl_3 , 75 MHz) δ 56.0, 56.2, 105.8, 111.1, 112.9, 120.0, 121.7 (s), 124.6, 132.3, 133.9, 140.7 (s), 144.3 (s), 146.9 (s), 149.4 (s), 163.9 (s); MS (EI, 70eV) m/z (rel int) 299 (M^+ , 14), 90 (100). Anal. Calcd for $\text{C}_{15}\text{H}_{13}\text{N}_3\text{O}_4$ (299.28): C, 60.20; H, 4.38; N, 14.04. Found: C, 60.03; H, 4.27; N, 14.22.

Preparation of 2-azidobenzamides 2p,q

A solution of the corresponding amine (10 mmol) in anhydrous pyridine (20 mL) was cooled at 0°C and 2-azidobenzoyl chloride **1a** (1.82 g, 10 mmol) was added dropwise. The reaction mixture was stirred at 0°C for 1.5 hours. Then water (300 mL) was added and the resulting suspension was extracted with diethyl ether (3 x 100 mL). The combined extracts were washed with 2N hydrochloric acid (300 mL), and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the resulting material was purified by column chromatography on silica gel using hexanes/diethyl ether (1:4, v/v) as eluent.

2-Azido-*N*-methyl-*N*-phenylbenzamide 2p: yield 63%; mp 74-75°C (colorless prisms, Et₂O/*n*-hexane); IR (nujol) 2131 (vs), 2090 (vs), 1647 (vs), 1595 (vs), 1493 (vs), 1428 (vs), 1309 (vs), 1176 (m), 1114 (s), 1090 (s), 1031 (m), 759 (vs), 706 (vs), 676 (vs) cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 3.49 (s, 3 H), 6.92-6.99 (m, 2 H), 7.06-7.23 (m, 7 H); ¹³C NMR (CDCl₃, 75 MHz) δ 37.2, 118.3, 124.4, 126.8, 127.0, 128.8, 129.0, 129.1 (s), 130.1, 136.5 (s), 143.5 (s), 168.2 (s); MS (EI, 70eV) *m/z* (rel int) 252 (M⁺, 31), 224 (100). Anal. Calcd for C₁₄H₁₂N₄O (252.27): C, 66.65; H, 4.79; N, 22.21. Found: C, 66.47; H, 4.74; N, 22.38.

2-Azido-*N,N*-bis(4-methylphenyl)benzamide 2q: yield 54%; mp 124-125°C (colorless prisms, Et₂O/*n*-hexane); IR (nujol) 2134 (vs), 2108 (vs), 1666 (vs), 1580 (m), 1512 (vs), 1450 (s), 1298 (vs), 1111 (w), 1037 (w), 962 (w), 819 (s), 758 (m), 749 (m), 719 (w), 678 (m), 587 (s) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 2.22 (br s, 3 H), 2.32 (br s, 3 H), 6.94-7.26 (m, 11 H), 7.35 (dd, 1 H, *J* = 7.6, 1.4 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 21.0, 118.4, 124.6, 126.5 (br), 127.9 (br), 129.4, 129.6 (s), 130.4, 136.5 (s), 136.6 (s), 140.2 (s), 168.2 (s); MS (EI, 70eV) *m/z* (rel int) 342 (M⁺, 44), 314 (100). Anal. Calcd for C₂₁H₁₈N₄O (342.39): C, 73.67; H, 5.30; N, 16.36. Found: C, 73.45; H, 5.14; N, 16.29.

Preparation of 2-(triphenylphosphoranylideneamino)benzoates **3m,n and 2-(triphenylphosphoranylideneamino)benzamides **3p,q****

To a solution of the corresponding 2-azidobenzoate **2** (4 mmol) or 2-azidobenzamide **2** (4 mmol) in anhydrous diethyl ether (40 mL) triphenylphosphine (1.05 g, 4 mmol) was added in five portions. The reaction mixture was stirred at room temperature under nitrogen for 16 hours. Then, the precipitated compounds **3** were isolated by filtration.

These compounds were used in the following step without further purification. For analytical samples compounds **3** were recrystallized from diethyl ether.

4-Methylphenyl 2-(triphenylphosphoranylideneamino)benzoate **3m:** yield 96%; mp 189-190°C (colorless prisms, Et₂O); IR (nujol) 1734 (vs), 1595 (s), 1546 (s), 1508 (s), 1448 (vs), 1193 (vs), 1168 (vs), 1114 (vs), 1062 (s), 1019 (vs), 752 (s), 725 (s), 698 (vs) cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 2.35 (s, 3 H), 6.53 (dt, 1 H, *J* = 8.2, 1.2 Hz), 6.63-6.68 (m, 1 H), 6.98 (ddd, 1 H, *J* = 8.6, 8.2, 1.8 Hz), 7.08-7.11 (m, 2 H), 7.15-7.19 (m, 2 H), 7.37-7.44 (m, 6 H), 7.46-7.52 (m, 3 H), 7.77-7.87 (m, 7 H); ¹³C NMR (CDCl₃, 75 MHz) δ 21.0, 116.6, 121.9, 123.4 (d, *J* = 10.9 Hz), 124.7 (d, *J* = 21.7 Hz) (s), 128.6 (d, *J* = 12.1 Hz), 129.8, 131.1 (d, *J* = 99.1 Hz) (s), 131.6 (d, *J* = 2.0 Hz), 131.7 (d, *J* = 2.7 Hz), 132.0, 132.8 (d, *J* = 9.8 Hz), 134.6 (s), 149.5 (s), 152.3 (s), 167.4 (s); ³¹P NMR (CDCl₃, H₃PO₄, 121.4 Hz) δ 2.4; MS (EI, 70 eV) *m/z* (rel int) 487 (M⁺, 5), 380 (100). Anal. Calcd for C₃₂H₂₆NO₂P (487.54): C, 78.83; H, 5.37; N, 2.87. Found: C, 78.97; H, 5.21; N, 2.74.

3,4-Dimethoxyphenyl 2-(triphenylphosphoranylideneamino)benzoate **3n:** yield 83%; mp 167-169°C (colorless prisms, Et₂O); IR (nujol) 1728 (vs), 1595 (s), 1551 (s), 1511 (vs), 1267 (s), 1236 (s), 1111 (vs), 1059 (s), 1017 (vs), 871 (m), 748 (m), 720 (s), 697 (s) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 3.79 (s, 3 H), 3.88 (s, 3 H), 6.54 (d, 1 H, *J* = 8.2 Hz), 6.67 (t, 1 H, *J* = 7.3 Hz), 6.77-6.79

(m, 2 H), 6.85-6.88 (m, 1 H), 6.99 (ddd, 1 H, $J = 8.6, 8.4, 1.8$ Hz), 7.39-7.43 (m, 6 H), 7.48-7.52 (m, 3 H), 7.78-7.83 (m, 6 H), 7.87 (dt, 1 H, $J = 7.9, 2.1$ Hz); ^{13}C NMR (CDCl_3 , 100 MHz) δ 55.9, 56.2, 106.5, 111.2, 113.5, 116.6, 123.4 (d, $J = 10.9$ Hz), 124.3 (d, $J = 21.7$ Hz) (s), 128.7 (d, $J = 12.1$ Hz), 131.0 (d, $J = 100.4$ Hz) (s), 131.8 (d, $J = 2.7$ Hz), 132.2, 132.8 (d, $J = 9.8$ Hz), 145.5 (s), 146.4 (s), 149.3 (s), 152.4 (s), 167.4 (d, $J = 1.2$ Hz) (s); ^{31}P NMR (CDCl_3 , H_3PO_4 , 121.4 Hz) δ 2.3; MS (EI, 70 eV) m/z (rel int) 533 (M^+ , 6), 380 (100). Anal. Calcd for $\text{C}_{33}\text{H}_{28}\text{NO}_4\text{P}$ (533.56): C, 74.29; H, 5.29; N, 2.62. Found: C, 74.11; H, 5.23; N, 2.81.

***N*-Methyl-*N*-phenyl-2-(triphenylphosphoranylideneamino)benzamide 3p**: yield 89%; mp 166-168°C (colorless prisms, Et_2O); IR (nujol) 1628 (vs), 1590 (vs), 1480 (vs), 1448 (vs), 1330 (vs), 1305 (s), 1251 (w), 1182 (w), 1160 (w), 1114 (vs), 1050 (m), 1029 (m), 876 (w), 720 (s), 700 (vs) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 3.35-3.56 (m, 3 H), 6.11 (br s, 1 H), 6.49 (br s, 1 H), 6.68 (br s, 1 H), 6.92-7.00 (m, 4 H), 7.16 (br s, 1 H), 7.38-7.42 (m, 7 H), 7.47-7.51 (m, 3 H), 7.71-7.73 (m, 6 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 37.0, 116.4, 120.9 (d, $J = 10.4$ Hz), 125.5, 126.6, 128.0, 128.6 (d, $J = 12.0$ Hz), 128.8, 131.0 (d, $J = 100.0$ Hz) (s), 131.6 (d, $J = 2.3$ Hz), 132.6 (d, $J = 9.8$ Hz), 133.2 (s), 144.6 (s), 147.3 (s), 172.9 (s); ^{31}P NMR (CDCl_3 , H_3PO_4 , 121.4 Hz) δ 0.7; MS (EI, 70 eV) m/z (rel int) 486 (M^+ , 23), 380 (100). Anal. Calcd for $\text{C}_{32}\text{H}_{27}\text{N}_2\text{OP}$ (486.54): C, 78.99; H, 5.59; N, 5.76. Found: C, 78.81; H, 5.41; N, 5.64.

***N,N*-Bis(4-methylphenyl)-2-(triphenylphosphoranylideneamino)benzamide 3q**: yield 93%; mp 239-240°C (yellow prisms, Et_2O); IR (nujol) 1650 (vs), 1589 (s), 1510 (vs), 1480 (vs), 1337 (vs), 1250 (m), 1109 (vs), 1052 (m), 1024 (m), 1000 (w), 958 (w), 865 (w), 823 (m), 752 (vs), 720 (vs), 695 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 2.25 (s, 6 H), 6.11 (d, 1 H, $J = 8.0$ Hz), 6.51 (t, 1 H, $J = 7.2$ Hz), 6.68 (td, 1 H, $J = 8.0, 1.7$ Hz), 6.90 (br s, 4 H), 7.12 (br s, 4 H), 7.23-7.25 (m, 1 H), 7.34-7.38 (m, 6 H), 7.44-7.48 (m, 3 H), 7.61-7.66 (m, 6 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 21.0, 116.4,

121.3 (d, $J = 10.8$ Hz), 127.6 (br), 128.5 (d, $J = 12.0$ Hz), 128.7, 128.8, 128.9, 131.3 (d, $J = 99.8$ Hz) (s), 131.6 (d, $J = 2.6$ Hz), 132.8 (d, $J = 9.7$ Hz), 133.4 (d, $J = 25.8$ Hz) (s), 135.0 (s), 141.8 (s), 147.8 (s), 172.7 (s); ^{31}P NMR (CDCl_3 , H_3PO_4 , 121.4 Hz) δ 2.1; MS (EI, 70 eV) m/z (rel int) 576 (M^+ , 6), 380 (100). Anal. Calcd for $\text{C}_{39}\text{H}_{33}\text{N}_2\text{OP}$ (576.66): C, 81.23; H, 5.77; N, 4.86. Found: C, 81.02; H, 5.62; N, 4.68.

Preparation of *N*-[2-(4-methylphenylthiocarbonyl)]phenyl-*C,C*-diphenylketenimine 4a

To a solution of *S*-(4-methylphenyl) 2-(triphenylphosphoranylideneamino)thiobenzoate **3a** (0.5 g, 1 mmol) in anhydrous dichloromethane (25 mL) a solution of diphenylketene (0.19 g, 1 mmol) in the same solvent (5 mL) was added. After stirring at room temperature for 30 min the solvent was removed under reduced pressure, and the resulting material was chromatographed on a silica gel column using hexanes/diethyl ether (4:1, v/v) as eluent.

***N*-[2-(4-methylphenylthiocarbonyl)]phenyl-*C,C*-diphenylketenimine 4a:** yield 85%; mp 125-127°C (yellow needles, $\text{Et}_2\text{O}/n$ -hexane); IR (nujol) 2022 (vs), 1675 (vs), 1587 (s), 1569 (m), 1494 (s), 1270 (w), 1196 (s), 1182 (s), 1162 (w), 905 (s), 811 (m), 785 (m), 766 (s), 694 (vs) cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 2.38 (s, 3 H), 7.21-7.25 (m, 4 H), 7.27-7.37 (m, 12 H), 7.49 (t, 1 H, $J = 8.0$ Hz), 7.86 (d, 1 H, $J = 8.0$ Hz); ^{13}C NMR (CDCl_3 , 75 MHz) δ : 21.4, 78.1 (s), 123.6, 124.5 (s), 126.7, 127.2, 128.1, 128.9, 129.1, 130.1, 132.7 (s), 133.0, 133.5 (s), 134.8, 138.9 (s), 139.8 (s), 190.1 (s), 191.3 (s); MS (EI, 70 eV) m/z (rel int) 419 (M^+ , 29), 296 (100). Anal. Calcd for $\text{C}_{28}\text{H}_{21}\text{NOS}$ (419.55): C, 80.16; H, 5.05; N, 3.34. Found: C, 80.38; H, 5.21; N, 3.21.

Spectroscopic data for the quinolin-4(3*H*)-ones 5n,o, 5q,r and 5s-v

3-Methyl-3-phenyl-2-phenylselenoquinolin-4(3*H*)-one 5n: yield 60%; IR (nujol) 1685 (vs), 1593 (vs), 1574 (vs), 1268 (vs), 1217 (s), 1157 (m), 1072 (m), 768 (vs), 737 (vs), 690 (vs) cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 1.97 (s, 3 H), 7.18-7.42 (m, 10 H), 7.57 (dd, 1 H, $J = 7.8, 1.6$ Hz), 7.59-7.63 (m, 2 H), 7.87 (dd, 1 H, $J = 7.8, 1.6$ Hz); ^{13}C NMR (CDCl_3 , 75 MHz) δ 23.3, 61.1 (s), 121.1 (s), 126.7, 127.6, 127.7 (s), 128.2, 128.3, 128.4, 128.7, 129.0, 129.1, 136.1, 136.4, 138.1 (s), 146.7 (s), 181.3 (s), 197.8 (s); MS (EI, 70eV) m/z (rel int) 391 (M^+ for ^{80}Se , 11), 389 (M^+ for ^{78}Se , 6), 234 (100). Anal. Calcd for $\text{C}_{22}\text{H}_{17}\text{NOSe}$ (390.34): C, 67.69; H, 4.39; N, 3.59. Found: C, 67.50; H, 4.22; N, 3.31.

2-(4-Methoxyphenylseleno)-3,3-diphenylquinolin-4(3*H*)-one 5o: yield 36%; mp 182-183°C (yellow prisms, Et_2O); IR (nujol) 1685 (vs), 1579 (vs), 1565 (vs), 1493 (vs), 1293 (s), 1252 (vs), 1117 (s), 1115 (s), 1029 (s), 890 (w), 826 (m), 749 (m), 700 (vs) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 3.85 (s, 3 H), 6.93-6.98 (m, 2 H), 7.16-7.20 (m, 2 H), 7.33-7.37 (m, 10 H), 7.49 (ddd, 1 H, $J = 8.5, 8.0, 1.6$ Hz), 7.53-7.57 (m, 2 H), 7.76 (ddd, 1 H, $J = 7.5, 1.6, 0.8$ Hz); ^{13}C NMR (CDCl_3 , 100 MHz) δ 55.4, 72.1 (s), 114.8, 119.2 (s), 121.8 (s), 126.5, 127.3, 127.7, 128.5, 128.6, 130.4, 135.8, 137.5 (s), 137.9, 146.3 (s), 160.3 (s), 179.7 (s), 197.3 (s); MS (EI, 70eV) m/z (rel int) 483 (M^+ for ^{80}Se , 12), 481 (M^+ for ^{78}Se , 6), 296 (100). Anal. Calcd for $\text{C}_{28}\text{H}_{21}\text{NO}_2\text{Se}$ (482.44): C, 69.71; H, 4.39; N, 2.90. Found: C, 69.55; H, 4.26; N, 2.80.

3-Methyl-2-(4-methylphenoxy)-3-phenylquinolin-4(3*H*)-one 5q: column chromatography: hexanes/diethyl ether (9:1, v/v); yield 28%; IR (nujol) 1688 (vs), 1641 (vs), 1599 (vs), 1505 (vs), 1275 (vs), 1198 (vs), 1163 (s), 1121 (s), 1074 (m) cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 2.04 (s, 3 H), 2.36 (s, 3 H), 6.99-7.03 (m, 2 H), 7.17-7.39 (m, 9 H), 7.53 (td, 1 H, $J = 7.8, 1.5$ Hz), 7.89 (dd, 1

H, $J = 7.8, 1.5$ Hz); ^{13}C NMR (CDCl_3 , 75 MHz) δ 20.9, 21.0, 55.7 (s), 121.5, 121.6 (s), 126.2, 126.3, 127.3, 127.6, 127.9, 129.1, 129.8, 135.0 (s), 136.1, 138.4 (s), 147.2 (s), 150.2 (s), 170.8 (s), 196.7 (s); MS (EI, 70eV) m/z (rel int) 341 (M^+ , 26), 77 (100). Anal. Calcd for $\text{C}_{23}\text{H}_{19}\text{NO}_2$ (341.41): C, 80.91; H, 5.61; N, 4.10. Found: C, 80.77; H, 5.47; N, 4.22.

2-(3,4-Dimethoxyphenyloxy)-3,3-diphenylquinolin-4(3H)-one 5r: column chromatography: hexanes/diethyl ether (1:1, v/v); yield 36%; IR (nujol) 1688 (vs), 1634 (vs), 1598 (vs), 1508 (vs), 1261 (vs), 1227 (vs), 1184 (vs), 1154 (s), 1124 (s), 1033 (s), 941 (m), 853 (w), 768 (s), 704 (s), 653 (m) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 3.81 (s, 3 H), 3.86 (s, 3 H), 6.56 (s, 1 H, $J = 2.6$ Hz), 6.62 (dd, 1 H, $J = 8.7, 2.6$ Hz), 6.81 (d, 1 H, $J = 8.7$ Hz), 7.24 (td, 1 H, $J = 7.6, 1.1$ Hz), 7.29 (dd, 1 H, $J = 8.0, 0.8$ Hz), 7.32-7.39 (m, 10 H), 7.56 (td, 1 H, $J = 7.6, 1.6$ Hz), 7.96 (dd, 1 H, $J = 7.6, 1.4$ Hz); ^{13}C NMR (CDCl_3 , 100 MHz) δ 56.1, 56.2, 67.1 (s), 106.1, 111.0, 112.9, 122.1 (s), 126.6, 127.3, 127.7, 128.0, 128.6, 129.6, 136.3, 138.8 (s), 146.2 (s), 146.5 (s), 146.6 (s), 149.2 (s), 168.5 (s), 196.6 (s); MS (EI, 70eV) m/z (rel int) 449 (M^+ , 44), 296 (100). Anal. Calcd for $\text{C}_{29}\text{H}_{23}\text{NO}_4$ (449.51): C, 77.49; H, 5.16; N, 3.12. Found: C, 77.55; H, 5.29; N, 3.01.

3-Methyl-2-(3,4-dimethoxyphenyloxy)-3-phenylquinolin-4(3H)-one 5s: column chromatography: hexanes/diethyl ether (2:3, v/v); yield 25%; IR (nujol) 1687 (vs), 1644 (vs), 1601 (vs), 1512 (vs), 1259 (vs), 1190 (vs), 1116 (vs), 1030 (vs), 958 (s), 913 (s), 843 (m), 772 (s), 738 (vs), 707 (s), 645 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 2.04 (s, 3 H), 3.85 (s, 3 H), 3.89 (s, 3 H), 6.67-6.70 (m, 2 H), 6.85 (d, 1 H, $J = 8.7$ Hz), 7.22 (td, 1 H, $J = 7.6, 1.1$ Hz), 7.28-7.39 (m, 6 H), 7.56 (td, 1 H, $J = 7.9, 1.6$ Hz), 7.90 (dd, 1 H, $J = 7.7, 1.6$ Hz); ^{13}C NMR (CDCl_3 , 100 MHz) δ 20.8, 55.6 (s), 56.0, 56.2, 106.1, 111.0, 113.0, 121.5 (s), 126.2, 126.4, 127.3, 127.6, 128.0, 129.1, 136.2, 138.3 (s), 146.0 (s), 146.6 (s), 147.1 (s), 149.3 (s), 170.9 (s), 196.6 (s); MS (EI, 70eV) m/z (rel int)

387 (M^+ , 77), 154 (100). Anal. Calcd for $C_{24}H_{21}NO_4$ (387.43): C, 74.40; H, 5.46; N, 3.61. Found: C, 74.21; H, 5.37; N, 3.42.

2-(*N*-Methyl-*N*-phenyl)amino-3,3-diphenylquinolin-4(3*H*)-one 5u: column chromatography: hexanes/diethyl ether (4:1, v/v); yield 30%; mp 193-195°C (yellow prisms, Et_2O); IR (nujol) 1675 (s), 1601 (m), 1537 (vs), 1500 (s), 1297 (m), 1284 (m), 1234 (m), 1148 (w), 1135 (w), 1022 (w), 856 (w), 769 (w), 743 (w), 700 (m) cm^{-1} ; 1H NMR ($CDCl_3$, 400 MHz) δ 3.35 (s, 3 H), 6.55 (d, 2 H, $J = 7.7$ Hz), 6.89 (t, 2 H, $J = 7.7$ Hz), 6.91-6.99 (m, 2 H), 7.15-7.18 (m, 5 H), 7.22-7.25 (m, 5 H), 7.27 (d, 1 H, $J = 8.3$ Hz), 7.46 (td, 1 H, $J = 8.3, 1.4$ Hz), 7.64 (d, 1 H, $J = 7.6$ Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 43.1, 67.6 (s), 119.1 (s), 123.3, 126.0, 126.3, 127.1, 127.4, 127.8, 128.2, 128.7, 129.6, 136.1, 137.6 (s), 145.5 (s), 150.4 (s), 165.4 (s), 197.3 (s); MS (EI, 70eV) m/z (rel int) 402 (M^+ , 88), 401 (100). Anal. Calcd for $C_{28}H_{22}N_2O$ (402.49): C, 83.56; H, 5.51; N, 6.96. Found: C, 83.45; H, 5.77; N, 6.84.

2-[*N,N*-Bis(4-methylphenyl)amino]-3,3-diphenylquinolin-4(3*H*)-one 5v: column chromatography: hexanes/diethyl ether (3:2, v/v); yield 25%; mp 230-231°C (yellow prisms, Et_2O); IR (nujol) 1688 (m), 1599 (m), 1578 (m), 1548 (vs), 1508 (s), 1340 (s), 1287 (m), 1269 (m), 1230 (m), 1148 (w), 818 (w), 762 (w), 735 (w), 701 (w) cm^{-1} ; 1H NMR ($CDCl_3$, 400 MHz) δ 2.21 (s, 6 H), 6.67 (d, 4 H, $J = 8.2$ Hz), 6.78 (d, 4 H, $J = 8.2$ Hz), 6.92 (t, 1 H, $J = 7.4$ Hz), 7.08 (d, 1 H, $J = 8.2$ Hz), 7.11-7.16 (m, 5 H), 7.23-7.25 (m, 5 H), 7.39 (td, 1 H, $J = 8.2, 1.4$ Hz), 7.58 (dd, 1 H, $J = 7.4, 1.2$ Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.0, 69.3 (s), 119.7 (s), 123.9, 126.6, 127.0, 127.4, 127.9, 128.0, 129.3, 129.9, 135.3 (s), 135.8, 137.6 (s), 142.9 (s), 149.6 (s), 166.4 (s), 197.4 (s); MS (EI, 70eV) m/z (rel int) 492 (M^+ , 83), 165 (100). Anal. Calcd for $C_{35}H_{28}N_2O$ (492.61): C, 85.34; H, 5.73; N, 5.69. Found: C, 85.21; H, 5.59; N, 5.50.

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