Supporting Information for

Time-Resolved IR Studies of Cyclic Enone Triplet Excited States and their Reactions with Alkenes

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Table S-1. Optimized geometry of 3-phenyl-2-cyclohexenone (**1**)

Theory: B3LYP/6-31G*
Energy with zero point correction (Hartrees): -539.515601

Cartesian Coordinates:

Atomic	Coordinates (Angstroms)		
Number	X	Y	Z
1	-0.381824	1.118545	4.141513
6	0.937561	0.831129	2.484146
8	1.968863	0.97042	3.129153
6	0.964733	0.325555	1.099593
6	-0.140596	0.142733	0.336718
1	1.960657	0.141318	0.706625
6	-1.516678	0.449427	0.902367
6	-0.048919	-0.332109	-1.06427
6	-1.549893	0.374739	2.434293
1	-2.252616	-0.241272	0.475179
1	-1.821996	1.456889	0.577101
6	-0.424667	1.210754	3.051907
1	-2.526395	0.708608	2.803883
1	-1.43513	-0.673019	2.742035
1	-0.586408	2.276949	2.82841
6	0.126931	-1.204784	-3.742514
6	1.015999	-1.146682	-1.493503
6	-1.031458	0.019467	-2.008131
6	-0.939936	-0.404236	-3.333079
6	1.102395	-1.577386	-2.814447
1	1.766431	-1.467503	-0.777714
1	-1.865352	0.648303	-1.711512
1	-1.705079	-0.108147	-4.045696
1	1.929198	-2.213695	-3.118379
1	0.194776	-1.541983	-4.773144

Table S-2. Optimized geometry of the triplet excited state of 3-phenyl-2-cyclohexenone (**1**)

Theory: B3LYP/6-31G*
Energy with zero point correction (Hartrees) = -539.433254
$<S^2> = 2.04$

Cartesian Coordinates:

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	3.187721	0.529955	0.387185
6	2.616713	-0.832962	-0.005092
8	3.369365	-1.827868	-0.094860
6	1.237582	-0.931678	-0.363473
6	0.310586	0.223793	-0.378389
1	0.924041	-1.904949	-0.729951
6	-1.073293	0.056777	-0.168249
6	1.021172	1.546964	-0.486574
1	0.340122	2.393983	-0.380863
1	1.495343	1.642757	-1.477311
1	1.659410	1.509603	1.581240
1	3.879755	0.820527	-0.415742
1	3.806197	0.397015	1.282178
6	2.126435	1.619007	0.594360
1	2.598082	2.608806	0.575217
6	-3.876036	-0.318349	0.234315
6	-2.000302	1.155438	-0.202032
6	-1.641749	-1.241743	0.083356
6	-3.000018	-1.412754	0.281711
6	-3.354555	0.964465	-0.012612
1	-1.635901	2.158055	-0.395212
1	-0.991211	-2.107674	0.130653
1	-3.389373	-2.409240	0.473625
1	-4.024483	1.819487	-0.054857
1	-4.942440	-0.458906	0.382864

Table S-3. B3LYP/6-31G* calculated IR frequencies[a] (cm^{-1}) and intensities (in parentheses) for 3-phenyl-2-cyclohexenone (**1**)

Singlet		^{18}O-Labeled Singlet		Triplet		^{18}O-Labeled Triplet	
3087	(11)	3087	(11)	3097	(7)	3097	(7)
3083	(26)	3083	(26)	3093	(24)	3093	(24)
3076	(15)	3076	(15)	3082	(32)	3082	(32)
3072	(13)	3072	(13)	3073	(2)	3073	(2)
3064	(7)	3064	(7)	3062	(14)	3062	(14)
3057	(2)	3057	(2)	3057	(6)	3057	(6)
2987	(21)	2987	(21)	3000	(15)	3000	(15)
2966	(39)	2966	(39)	2973	(27)	2973	(27)
2959	(27)	2959	(27)	2962	(32)	2962	(32)
2924	(34)	2924	(34)	2926	(31)	2926	(31)
2900	(11)	2900	(11)	2919	(19)	2919	(19)
2888	(15)	2888	(15)	2875	(26)	2875	(26)
1697	(299)	1664	(301)	1541	(11)	1541	(10)
1601	(48)	1600	(35)	1512	(5)	1512	(5)
1592	(20)	1592	(19)	1479	(1)	1478	(0)
1566	(17)	1566	(15)	1463	(8)	1463	(5)
1484	(5)	1484	(5)	1446	(23)	1446	(7)
1465	(3)	1465	(3)	1442	(30)	1434	(4)
1449	(6)	1449	(6)	1432	(6)	1419	(39)
1434	(9)	1434	(9)	1415	(0)	1415	(3)
1430	(9)	1430	(9)	1410	(17)	1410	(22)
1352	(2)	1352	(2)	1335	(5)	1335	(5)
1337	(31)	1337	(30)	1316	(3)	1316	(3)
1317	(1)	1317	(1)	1308	(1)	1307	(1)
1314	(21)	1313	(24)	1299	(2)	1299	(3)
1304	(25)	1303	(22)	1284	(10)	1284	(9)
1266	(14)	1265	(13)	1267	(7)	1267	(7)
1242	(4)	1241	(4)	1230	(3)	1230	(3)
1233	(96)	1232	(96)	1224	(32)	1222	(29)
1214	(9)	1213	(10)	1186	(29)	1184	(32)
1174	(8)	1174	(8)	1172	(5)	1171	(6)
1170	(50)	1170	(50)	1146	(7)	1146	(6)
1148	(0)	1148	(0)	1134	(2)	1134	(2)
1120	(19)	1120	(19)	1117	(4)	1117	(4)
1074	(4)	1074	(4)	1068	(4)	1068	(4)
1044	(1)	1043	(1)	1021	(2)	1021	(2)
1033	(0)	1033	(0)	1016	(2)	1016	(2)
1021	(2)	1021	(2)	999	(0)	999	(0)
977	(0)	977	(0)	956	(2)	956	(2)
966	(6)	965	(7)	942	(0)	942	(0)
960	(0)	960	(0)	936	(38)	934	(38)
933	(7)	933	(2)	920	(0)	920	(0)

Table S-3. (continued)

Singlet		^{18}O-Labeled Singlet		Triplet		^{18}O-Labeled Triplet	
933	(6)	933	(11)	904	(8)	904	(8)
904	(1)	904	(1)	860	(7)	859	(8)
890	(16)	890	(16)	841	(5)	841	(5)
872	(1)	871	(1)	832	(2)	832	(2)
843	(1)	843	(1)	787	(4)	786	(4)
825	(1)	825	(1)	773	(0)	772	(0)
796	(1)	794	(1)	741	(18)	741	(18)
746	(34)	746	(34)	723	(33)	723	(33)
734	(5)	733	(5)	703	(1)	703	(1)
681	(22)	681	(22)	643	(26)	643	(26)
646	(3)	643	(3)	617	(11)	614	(10)
609	(0)	609	(0)	595	(0)	595	(0)
593	(1)	591	(0)	510	(1)	507	(1)
560	(2)	560	(2)	500	(9)	497	(10)
500	(10)	493	(8)	478	(13)	474	(11)
462	(2)	460	(3)	449	(8)	447	(9)
458	(3)	453	(2)	421	(2)	418	(2)
414	(5)	412	(5)	392	(1)	392	(1)
399	(0)	399	(0)	375	(7)	375	(7)
335	(5)	332	(6)	361	(3)	356	(3)
279	(1)	277	(1)	293	(1)	291	(1)
246	(1)	246	(1)	237	(1)	236	(1)
213	(2)	212	(2)	178	(2)	177	(2)
122	(2)	120	(2)	131	(1)	130	(1)
112	(1)	111	(1)	102	(2)	100	(2)
77	(0)	77	(0)	60	(1)	59	(1)
50	(1)	49	(1)	35	(0)	35	(0)

[a]Scaled by 0.96

Table S-4. Optimized geometry of 3-phenyl-2-cyclopentenone (**2**)

Theory: B3LYP/6-31G*
Energy with zero point correction (Hartrees): -500.231971

Cartesian Coordinates:

Atomic	Coordinates (Angstroms)		
Number	X	Y	Z
6	2.819547	1.098812	0.000059
6	1.318245	1.440100	-0.000032
6	0.604413	0.093097	-0.000013
6	1.494535	-0.927203	0.000021
6	2.882053	-0.436011	0.000040
8	3.899013	-1.107217	-0.000077
6	-0.862533	-0.005242	-0.000003
6	-1.657712	1.155387	-0.000013
6	-3.049443	1.074393	-0.000008
6	-3.678815	-0.170228	0.000000
6	-2.904627	-1.334647	0.000006
6	-1.516601	-1.253510	0.000011
1	3.346745	1.484010	0.879380
1	3.346934	1.484208	-0.879077
1	1.027072	2.030792	-0.877851
1	1.027006	2.030897	0.877681
1	1.273768	-1.988257	0.000090
1	-1.185660	2.132571	-0.000028
1	-3.641304	1.985608	-0.000008
1	-4.763374	-0.235341	0.000001
1	-3.386157	-2.308688	0.000008
1	-0.931500	-2.167752	0.000023

Table S-5. Optimized geometry of the triplet excited state of 3-phenyl-2-cyclopentenone (**2**)

Theory: B3LYP/6-31G*
Energy with zero point correction (Hartrees) = -500.144688
S^2 = <2.04>

Cartesian Coordinates:

Atomic	Coordinates (Angstroms)		
Number	X	Y	Z
6	2.816898	1.089360	0.092321
6	1.322679	1.473229	-0.053045
6	0.545509	0.164182	-0.037087
6	1.525180	-0.937098	-0.051466
6	2.862983	-0.443333	0.006838
8	3.900058	-1.129178	0.000072
6	-0.835924	0.032743	-0.015666
6	-1.487621	-1.261127	0.006737
6	-2.861905	-1.369421	0.026962
6	-3.676860	-0.221569	0.025078
6	-3.073549	1.056278	0.002731
6	-1.705010	1.190457	-0.016290
1	3.236155	1.404644	1.055334
1	3.451977	1.527365	-0.684451
1	1.145233	2.012936	-0.994536
1	0.992638	2.146602	0.747804
1	1.299443	-1.994796	-0.106578
1	-0.880458	-2.159705	0.009699
1	-3.320954	-2.354452	0.044212
1	-4.758232	-0.315901	0.039965
1	-3.700312	1.944337	0.000330
1	-1.260230	2.180189	-0.035039

Table S-6. B3LYP/6-31G* calculated IR frequencies[a] (cm^{-1}) and intensities (in parentheses) for 3-phenyl-2-cyclopentenone (**2**)

Singlet		^{18}O-Labeled Singlet		Triplet		^{18}O-Labeled Triplet	
3111	(6)	3111	(6)	3123	(8)	3123	(8)
3089	(7)	3089	(7)	3092	(13)	3092	(13)
3085	(22)	3085	(22)	3087	(25)	3087	(25)
3077	(24)	3077	(24)	3082	(15)	3082	(15)
3066	(7)	3066	(7)	3063	(11)	3063	(11)
3058	(1)	3058	(1)	3058	(6)	3058	(6)
2993	(12)	2993	(12)	2986	(16)	2986	(16)
2955	(14)	2955	(14)	2947	(26)	2947	(26)
2952	(10)	2952	(10)	2936	(12)	2936	(12)
2924	(23)	2924	(23)	2902	(16)	2902	(16)
1731	(420)	1698	(408)	1557	(3)	1555	(2)
1596	(3)	1596	(2)	1519	(46)	1519	(44)
1590	(89)	1590	(88)	1499	(16)	1499	(15)
1565	(37)	1565	(35)	1464	(45)	1453	(5)
1486	(7)	1486	(7)	1453	(5)	1440	(42)
1457	(7)	1457	(7)	1432	(1)	1432	(3)
1435	(17)	1435	(17)	1415	(1)	1415	(0)
1425	(4)	1425	(4)	1395	(6)	1395	(6)
1323	(8)	1323	(8)	1312	(0)	1312	(0)
1311	(25)	1311	(24)	1291	(34)	1291	(33)
1285	(6)	1285	(6)	1280	(12)	1279	(12)
1249	(76)	1248	(75)	1256	(4)	1254	(4)
1238	(5)	1236	(4)	1232	(12)	1232	(12)
1207	(1)	1207	(1)	1206	(11)	1206	(10)
1202	(1)	1202	(1)	1180	(20)	1179	(13)
1175	(24)	1175	(23)	1170	(73)	1168	(79)
1159	(102)	1158	(101)	1138	(20)	1138	(20)
1147	(11)	1147	(12)	1116	(14)	1116	(14)
1128	(0)	1128	(0)	1108	(1)	1108	(1)
1073	(4)	1073	(4)	1058	(13)	1058	(14)
1020	(3)	1020	(3)	983	(0)	983	(0)
989	(5)	988	(5)	974	(6)	973	(6)
987	(3)	987	(3)	952	(0)	952	(0)
977	(1)	977	(1)	946	(2)	946	(2)
960	(0)	960	(0)	939	(1)	938	(1)
942	(0)	942	(0)	919	(0)	919	(0)
930	(0)	930	(0)	863	(25)	863	(26)
899	(0)	899	(0)	845	(8)	844	(8)
860	(16)	860	(16)	824	(3)	824	(4)
835	(5)	833	(5)	793	(5)	793	(5)
818	(0)	818	(0)	777	(3)	776	(3)

Table S-6. (continued)

Singlet		^{18}O-Labeled Singlet		Triplet		^{18}O-Labeled Triplet	
811	(0)	811	(0)	757	(0)	757	(0)
806	(6)	806	(7)	726	(33)	726	(33)
749	(43)	749	(43)	685	(11)	684	(11)
674	(22)	674	(22)	627	(26)	627	(26)
640	(1)	640	(1)	619	(5)	618	(4)
617	(5)	612	(2)	602	(15)	594	(13)
603	(4)	596	(8)	584	(2)	581	(6)
553	(1)	553	(1)	480	(7)	474	(5)
519	(0)	517	(0)	472	(0)	472	(2)
491	(5)	483	(4)	423	(5)	422	(5)
405	(3)	405	(3)	390	(0)	390	(0)
394	(0)	394	(0)	370	(4)	366	(4)
367	(8)	364	(8)	318	(5)	317	(5)
308	(0)	305	(0)	302	(1)	299	(1)
190	(2)	189	(2)	165	(3)	164	(3)
144	(2)	142	(2)	136	(1)	135	(1)
109	(1)	109	(1)	110	(0)	110	(0)
82	(0)	82	(0)	67	(2)	66	(2)
16	(1)	16	(1)	27	(0)	27	(0)

[a]Scaled by 0.96