Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting information for:

Between a Reactant Rock and a Solvent Hard-Place – Molecular Corrals Guide Aromatic Substitutions

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Table S1 The optimized Cartesian geometries(Å) for the reaction of **1**+et-MgBr(THF)$_2$→**2a**+MeO-MgBr(THF)$_2$ at CAM-B3LYP+IDSCRF/DZVP level.

Species	Cartesian coordinates			Species	Cartesian coordinates		
1	C	-3.70978	0.27806	-0.02421	**EtMgBr(THF)$_2$**	Mg	0.10857	-0.24932	0.08572
	C	-2.75273	1.27232	0.01877		C	1.86377	-1.08165	-0.76267
	C	-3.32220	-1.08729	-0.05643		H	2.66817	-0.32983	-0.70362
	H	-3.04687	2.32026	0.03398		H	2.21308	-1.89915	-0.11208
	H	-4.08486	-1.86173	-0.10256		C	1.79564	-1.60928	-2.20928
	C	-1.36773	0.94765	0.03766		H	1.49286	-0.82716	-2.91924
	C	-1.98624	-1.43466	-0.03621		H	1.06215	-2.41998	-2.31114
	H	-1.68917	-2.47813	-0.07741		Br	-0.38490	0.07005	2.51462
	C	-0.97770	-0.43032	0.02006		O	-1.68540	-1.02367	-0.61757
	H	-4.76624	0.53805	-0.04026		C	-2.01942	-1.02530	-2.03375
	C	-0.35730	1.95035	0.06351		C	-2.66950	-1.79061	0.13530
	H	-0.64896	2.99861	0.07769		C	-3.11117	-2.07542	-2.18429
	C	0.97110	1.60285	0.05852		H	-2.37456	-0.02401	-2.29708
	C	0.41435	-0.76889	0.05300		H	-1.11017	-1.24568	-2.59580
	H	1.73337	2.37465	0.06235		C	-3.82491	-1.99975	-0.83215
	C	1.38696	0.23449	0.05745		H	-2.20651	-2.73697	0.43089
	C	2.84343	-0.07909	0.03734		H	-2.92200	-1.21952	1.02878
	O	3.36023	-1.16335	0.26651		H	-2.67023	-3.06592	-2.33056
	O	3.59707	1.00913	-0.27446		H	-3.76659	-1.86200	-3.03131
	H	4.53877	0.71981	-0.25065		H	-4.39479	-2.90067	-0.59540
	O	0.73317	-2.10295	0.00013		H	-4.50599	-1.14387	-0.80461
	C	0.94436	-2.73936	1.27720		O	-0.24946	1.61759	-0.74872
	H	1.81588	-2.31248	1.77991		C	-1.34372	2.50249	-0.37580
	H	0.05244	-2.64224	1.90783		C	0.76262	2.35160	-1.49547
	H	1.12691	-3.79386	1.06032		C	-0.83748	3.90669	-0.67374
						H	-2.21050	2.24059	-0.99104
						H	-1.57388	2.32247	0.67540
						C	0.10040	3.67218	-1.86094
						H	1.63023	2.49494	-0.84464
						H	1.05373	1.74261	-2.35280
						H	-0.28187	4.30091	0.18221
						H	-1.65479	4.59473	-0.90005
						H	0.83347	4.47032	-1.99553
						H	-0.47164	3.56980	-2.78806
						H	2.75165	-2.00886	-2.58059

COMa				**TSa**			
	C	-6.38384	-1.54412	-0.90527	C	5.42468	1.82009	-0.76132
	C	-6.07361	-0.24916	-1.23996	C	5.47342	0.43744	-0.70430
	C	-5.48822	-2.31662	-0.12520	C	4.22200	2.50085	-0.45990
	H	-6.75724	0.34383	-1.84332	H	6.40075	-0.08729	-0.92823
	H	-5.74182	-3.34373	0.12422	H	4.18753	3.58730	-0.50460
	C	-4.85613	0.33814	-0.80712	C	4.32911	-0.32232	-0.34449
	C	-4.30374	-1.77562	0.30893	C	3.08915	1.78321	-0.11293
	H	-3.60530	-2.36635	0.89304	H	2.16111	2.30154	0.11020
	C	-3.96384	-0.43627	-0.01852	C	3.11200	0.36731	-0.05120
	H	-7.31903	-1.98452	-1.24224	H	6.31324	2.38580	-1.03490
	C	-4.50915	1.67754	-1.13609	C	4.38064	-1.75107	-0.23112
	H	-5.19463	2.27044	-1.73669	H	5.31513	-2.26581	-0.44343
	C	-3.32826	2.21301	-0.70727	C	3.26622	-2.45499	0.14078
	C	-2.73771	0.14622	0.42204	C	1.93089	-0.38774	0.30745
	H	-3.06418	3.23363	-0.96443	H	3.30198	-3.53841	0.20989
	C	-2.41321	1.44359	0.06799	C	2.02666	-1.80058	0.42558
	C	-1.12551	2.05711	0.46262	C	0.82379	-2.57235	0.63687
	O	-0.05857	1.48136	0.62932	O	-0.33827	-2.11187	0.57509
	O	-1.21253	3.38582	0.60951	O	0.99885	-3.89369	0.86356
	H	-0.32041	3.72607	0.85250	H	0.10442	-4.29603	0.95373
	O	-1.91063	-0.61253	1.19637	O	0.97362	0.31051	1.09391
	Mg	1.25379	-0.22750	0.02749	Mg	-0.87318	-0.12317	0.14571
	C	0.13982	-0.85019	-1.69566	C	0.56798	-0.07696	-1.75350
	H	0.58840	-1.76667	-2.11642	H	-0.45320	0.09583	-2.14056
	H	-0.86147	-1.16776	-1.36377	H	1.10330	0.86682	-1.90168
	C	-0.04108	0.16270	-2.84404	C	1.19617	-1.21889	-2.54725
	H	0.92142	0.47384	-3.27406	H	0.83534	-2.20210	-2.21020
	H	-0.53305	1.08316	-2.50027	H	2.28599	-1.23640	-2.44004
	O	2.64846	1.33063	-0.28316	O	-2.56617	-0.80673	-1.00716
	C	3.77076	1.58510	0.60156	C	-3.97169	-0.54010	-0.69837
	C	2.48490	2.42356	-1.21868	C	-2.46987	-1.92835	-1.94282
	C	4.52449	2.74120	-0.04043	C	-4.76254	-1.27323	-1.77913
	H	3.37563	1.84692	1.58751	H	-4.17564	-0.92450	0.30444
	H	4.34190	0.65924	0.68541	H	-4.11021	0.54348	-0.69326
	C	3.39561	3.53252	-0.70629	C	-3.88218	-2.50594	-2.04137
	H	2.78820	2.07145	-2.21008	H	-2.12063	-1.53462	-2.90348
	H	1.42761	2.69286	-1.24679	H	-1.73033	-2.62898	-1.55086
	H	5.22781	2.37156	-0.79322	H	-4.84588	-0.65989	-2.68345
	H	5.08405	3.32294	0.69537	H	-5.77137	-1.52858	-1.44278
	H	3.73931	4.18476	-1.51214	H	-4.06547	-2.96920	-3.01495
	H	2.87264	4.14628	0.03365	H	-4.04331	-3.26165	-1.26507
	O	3.07080	-1.46336	-0.51116	O	-1.35635	1.94357	-0.32990
	C	3.05582	-2.88731	-0.24611	C	-1.24139	3.04490	0.62834
	C	3.68193	-1.20915	-1.79544	C	-1.74432	2.46656	-1.63323

	C	3.43382	-3.55707	-1.56157		C -1.46456	4.32742	-0.17897
	H	3.78416	-3.09302	0.54496		H -2.00315	2.88859	1.39577
	H	2.06284	-3.15882	0.11623		H -0.25311	2.98840	1.09230
	C	4.35561	-2.51550	-2.19935		C -2.33775	3.84342	-1.34830
	H	2.89521	-0.92314	-2.50148		H -0.85118	2.53292	-2.26492
	H	4.37888	-0.37541	-1.68105		H -2.44477	1.75849	-2.08153
	H	2.54449	-3.70824	-2.18049		H -0.51349	4.72129	-0.55354
	H	3.91537	-4.52551	-1.40676		H -1.94305	5.10599	0.42153
	H	4.44064	-2.61634	-3.28389		H -2.29037	4.49966	-2.22202
	H	5.35984	-2.57809	-1.76853		H -3.38482	3.75409	-1.03872
	Br	1.59907	-0.94405	2.45960		Br -2.26292	0.05708	2.40853
	C	-2.07250	-0.42365	2.60803		C 1.32993	0.39847	2.50267
	H	-1.89843	0.62190	2.88306		H 0.51043	0.93008	2.98434
	H	-3.07881	-0.72351	2.92264		H 1.42192	-0.60207	2.93411
	H	-1.31603	-1.04542	3.08355		H 2.27210	0.94408	2.60752
	H	-0.64710	-0.21191	-3.68464		H 0.98368	-1.16586	-3.62736
INTa	C	5.76052	1.54111	0.01877	**TS1a**	C 5.74376	1.57254	0.05206
	C	5.66398	0.15428	0.08664		C 5.62819	0.21813	0.32316
	C	4.59960	2.31327	-0.14617		C 4.62501	2.28956	-0.42005
	H	6.56249	-0.44545	0.22584		H 6.48685	-0.33882	0.69520
	H	4.65970	3.39867	-0.19008		H 4.70354	3.35560	-0.62259
	C	4.41588	-0.50647	-0.01028		C 4.40234	-0.47133	0.13402
	C	3.36226	1.67338	-0.25089		C 3.41896	1.62985	-0.61862
	H	2.46521	2.27836	-0.36322		H 2.56255	2.20339	-0.96029
	C	3.24628	0.27595	-0.19027		C 3.27243	0.24825	-0.35499
	H	6.73268	2.02436	0.10000		H 6.69276	2.08243	0.20817
	C	4.32551	-1.94996	0.08925		C 4.29656	-1.87735	0.41983
	H	5.23941	-2.52383	0.22573		H 5.17061	-2.41309	0.78316
	C	3.11072	-2.56874	0.05448		C 3.09994	-2.51361	0.25980
	C	1.86291	-0.36408	-0.33213		C 1.96589	-0.42389	-0.55949
	H	3.05794	-3.64832	0.17172		H 3.01046	-3.56702	0.50913
	C	1.87405	-1.86380	-0.11382		C 1.92656	-1.83602	-0.21211
	C	0.65520	-2.54050	-0.04951		C 0.67848	-2.52658	-0.18617
	O	-0.52283	-2.01639	-0.09373		O -0.47410	-2.00139	-0.25081
	O	0.68494	-3.90330	0.08930		O 0.73280	-3.87340	-0.03020
	H	-0.24818	-4.18580	0.19952		H -0.19287	-4.18398	0.09014
	O	0.93279	0.28060	0.68463		O 0.80712	0.41988	0.70010
	Mg	-1.16985	-0.19633	0.37547		Mg -1.12272	-0.15559	0.39496
	C	1.23967	0.03942	-1.69546		C 1.19032	0.03688	-1.79888
	H	0.23514	-0.39059	-1.77899		H 0.21084	-0.44410	-1.82915
	H	1.13168	1.12845	-1.72817		H 1.01970	1.11473	-1.75148
	C	2.05619	-0.43809	-2.90349		C 1.92035	-0.31439	-3.10843
	H	2.17256	-1.52636	-2.89444		H 2.07509	-1.39482	-3.19695
	H	3.05465	0.00969	-2.91363		H 2.89819	0.17281	-3.16787

	O	-2.90572	-0.61644	-0.81463	O	-2.78143	-0.52222	-0.94849
	C	-4.26327	-0.26160	-0.38594	C	-4.16135	-0.24596	-0.53027
	C	-2.96944	-1.55873	-1.93477	C	-2.78862	-1.34581	-2.15654
	C	-5.19092	-0.82709	-1.46118	C	-5.04918	-0.78044	-1.65563
	H	-4.43014	-0.71522	0.59436	H	-4.32482	-0.76270	0.41883
	H	-4.31026	0.82551	-0.28282	H	-4.25524	0.83028	-0.36548
	C	-4.41262	-2.05545	-1.96008	C	-4.20021	-1.91957	-2.24218
	H	-2.71321	-1.01211	-2.85069	H	-2.56411	-0.69734	-3.01274
	H	-2.22441	-2.33289	-1.75086	H	-2.00437	-2.09474	-2.04694
	H	-5.32931	-0.10502	-2.27357	H	-5.22609	-0.00728	-2.41158
	H	-6.17474	-1.07679	-1.05452	H	-6.01897	-1.11672	-1.27868
	H	-4.71526	-2.37973	-2.95967	H	-4.47598	-2.17790	-3.26848
	H	-4.53930	-2.89755	-1.27117	H	-4.28295	-2.82011	-1.62421
	O	-1.38736	1.80257	-0.30885	O	-1.63189	1.89937	-0.02099
	C	-1.03185	2.92945	0.56362	C	-1.31456	2.92176	0.98244
	C	-1.84524	2.30191	-1.60199	C	-1.87237	2.53350	-1.31071
	C	-1.15363	4.18054	-0.30928	C	-1.22353	4.24306	0.21627
	H	-1.73783	2.92507	1.39871	H	-2.12504	2.91905	1.71717
	H	-0.02279	2.75182	0.94045	H	-0.38053	2.63283	1.46647
	C	-2.19904	3.76610	-1.35773	C	-2.14603	4.00092	-0.98966
	H	-1.02633	2.19769	-2.32389	H	-0.97590	2.41859	-1.93225
	H	-2.68457	1.68186	-1.92020	H	-2.70638	2.01605	-1.78873
	H	-0.19775	4.40724	-0.79346	H	-0.19667	4.42380	-0.11928
	H	-1.45551	5.05346	0.27562	H	-1.53537	5.09127	0.83183
	H	-2.14541	4.35788	-2.27567	H	-1.92622	4.65388	-1.83895
	H	-3.21194	3.85088	-0.94964	H	-3.19566	4.14082	-0.70898
	Br	-2.22054	-0.07503	2.66305	B	-2.24954	-0.49307	2.63604
	C	1.40978	0.19147	2.04707	C	1.36685	0.34615	2.00361
	H	0.61108	0.56854	2.68640	H	0.63814	0.70491	2.74055
	H	1.62626	-0.84869	2.31268	H	1.62898	-0.68787	2.27572
	H	2.31051	0.79862	2.17078	H	2.27153	0.96529	2.07422
	H	1.55087	-0.15812	-3.83440	H	1.32547	0.01352	-3.96848

CPLa	C	7.38430	0.51565	0.33799	**2a**	C	-3.68747	-1.86680	-0.07660
	C	6.79084	-0.51668	-0.34194		C	-3.62725	-0.52005	-0.36724
	C	6.58516	1.42104	1.07537		C	-2.52207	-2.54270	0.36586
	H	7.39263	-1.22096	-0.91203		H	-4.51493	0.01120	-0.70632
	H	7.05592	2.24033	1.61276		H	-2.56940	-3.60546	0.59392
	C	5.38181	-0.69041	-0.31786		C	-2.40954	0.20408	-0.23129
	C	5.22134	1.27211	1.11737		C	-1.32852	-1.86370	0.50904
	H	4.64229	1.98636	1.69096		H	-0.45900	-2.41671	0.84749
	C	4.56734	0.21248	0.42311		C	-1.22284	-0.46882	0.21714
	H	8.46390	0.64152	0.31397		H	-4.62303	-2.41182	-0.18411
	C	4.77292	-1.76062	-1.02426		C	-2.35085	1.59289	-0.52984
	H	5.39855	-2.45097	-1.58507		H	-3.25099	2.10331	-0.86717
	C	3.41921	-1.91699	-0.99861		C	-1.17208	2.28026	-0.39450
	C	3.13839	0.04676	0.44554		C	0.01629	0.25709	0.34930
	H	2.95271	-2.73414	-1.53737		H	-1.13200	3.34008	-0.62276
	C	2.59079	-1.00720	-0.27857		C	0.02225	1.62081	0.03078
	C	1.12648	-1.24391	-0.35924		C	1.26472	2.44865	0.09419
	O	0.27013	-0.37753	-0.16819		O	2.41629	2.04201	0.00918
	O	0.79641	-2.48380	-0.69310		O	0.99902	3.77342	0.24002
	Mg	-1.78461	-0.17772	0.40471		C	1.25284	-0.47583	0.84031
	C	2.30302	1.01318	1.25833		H	1.94102	0.22721	1.30836
	H	1.36812	0.54879	1.56245		H	0.96345	-1.18861	1.61856
	H	2.83608	1.25666	2.18054		C	2.00746	-1.21920	-0.28124
	C	1.98063	2.30548	0.49625		H	2.37035	-0.51166	-1.03202
	H	1.38796	2.08257	-0.39434		H	1.37016	-1.95524	-0.78278
	H	2.88634	2.83065	0.17862		H	1.86594	4.24213	0.23152
	Br	-2.41129	-2.30233	-0.93601		H	2.87310	-1.74827	0.13315
	O	-1.74394	1.45517	-0.88506	**BrMgOMe(THF)$_2$**	Mg	-3.12762	0.15623	-0.49204
	C	-1.25534	1.44735	-2.25113		Br	-2.06986	-1.99959	-1.04716
	C	-1.95610	2.81877	-0.42888		O	-2.57222	0.58535	1.42762
	C	-1.58660	2.83188	-2.78585		C	-2.52354	-0.31454	2.56948
	H	-0.17761	1.26002	-2.23086		C	-2.09563	1.91037	1.80065
	H	-1.75290	0.62915	-2.77480		C	-1.77239	0.45403	3.64974
	C	-1.41029	3.70701	-1.54142		H	-3.55400	-0.53575	2.86394
	H	-3.03039	2.95607	-0.27658		H	-2.03137	-1.23496	2.25060
	H	-1.44257	2.94343	0.52703		C	-2.11515	1.91009	3.32094
	H	-2.62159	2.86686	-3.13916		H	-1.08237	2.03017	1.40472
	H	-0.93077	3.11994	-3.61017		H	-2.75355	2.64017	1.32823
	H	-1.94650	4.65637	-1.60254		H	-0.69536	0.28547	3.55874
	H	-0.35100	3.92236	-1.37443		H	-2.08325	0.15344	4.65248
	C	-4.82632	0.45524	-0.29891		H	-1.40149	2.62390	3.73785
	O	-3.79953	0.42850	0.72630		H	-3.11335	2.16386	3.69052
	C	-4.41653	0.37373	2.04050		C	-6.06819	0.84364	-0.23385
	C	-5.80705	-0.18159	1.78483		O	-5.11161	-0.25816	-0.23647

	C	-6.16178	0.46745	0.44384		C	-5.79705	-1.52138	-0.48500
	H	-4.67030	1.33974	-0.92239		C	-7.28232	-1.18425	-0.44142
	H	-4.70309	-0.43981	-0.91309		C	-7.30875	0.27563	-0.90269
	H	-3.76363	-0.22769	2.67092		H	-6.25891	1.11937	0.80853
	H	-4.45925	1.39335	2.44091		H	-5.59606	1.67563	-0.75832
	H	-5.76929	-1.27111	1.68992		H	-5.48224	-1.88574	-1.46598
	H	-6.50768	0.07331	2.58352		H	-5.47977	-2.23372	0.27826
	H	-6.93610	-0.07076	-0.10727		H	-7.86566	-1.84988	-1.08105
	H	-6.50672	1.49400	0.60048		H	-7.66476	-1.26789	0.58020
	H	-0.19505	-2.53582	-0.78830		H	-7.21713	0.33852	-1.99115
	O	-1.40495	-0.11902	2.23879		H	-8.21510	0.80490	-0.60059
	C	-0.55354	-0.83947	3.06526		O	-3.15296	1.79534	-1.33942
	H	0.00644	-0.18248	3.75542		C	-2.32067	2.74047	-1.92792
	H	-1.10048	-1.56242	3.69824		H	-1.59023	2.29649	-2.62634
	H	0.20637	-1.42903	2.51598		H	-2.89985	3.48032	-2.50679
	H	1.40106	2.98387	1.13023		H	-1.73728	3.31288	-1.18326

Table S2 The optimized Cartesian geometries(Å) for the reaction of **1**+et-MgBr(THF)$_2$→**2a**+MeO-MgBr(THF)$_2$ at CAM-B3LYP+IDSCRF/6-311++G(d,p) level.

Species	Cartesian coordinates			Species	Cartesian coordinates		
1	C	-3.67693	0.26706	-0.01750	**EtMgBr(THF)$_2$**	Mg	0.02767	-0.32013	0.17310
	C	-2.73377	1.25571	0.02957		C	1.77604	-1.26495	-0.58719
	C	-3.28643	-1.08882	-0.05645		H	2.60270	-0.54001	-0.55025
	H	-3.02865	2.29918	0.04933		H	2.07553	-2.05274	0.11826
	H	-4.04326	-1.86291	-0.10631		C	1.71449	-1.87002	-1.99942
	C	-1.35424	0.93832	0.04715		H	1.45856	-1.12003	-2.75745
	C	-1.96200	-1.42783	-0.03752		H	0.95221	-2.65396	-2.07086
	H	-1.65875	-2.46527	-0.08253		Br	-0.50941	0.13678	2.57161
	C	-0.96434	-0.42388	0.02446		O	-1.76460	-1.07585	-0.53042
	H	-4.73049	0.52157	-0.03219		C	-2.06838	-1.13103	-1.94975
	C	-0.35332	1.94150	0.07191		C	-2.78726	-1.77265	0.23471
	H	-0.65172	2.98358	0.08619		C	-3.18198	-2.15633	-2.07490
	C	0.96415	1.60302	0.06434		H	-2.39254	-0.13616	-2.26429
	C	0.42244	-0.75369	0.05755		H	-1.15548	-1.39882	-2.48013
	H	1.72473	2.37158	0.06585		C	-3.92356	-1.99324	-0.74787
	C	1.37784	0.24312	0.06676		H	-2.36186	-2.71578	0.58509
	C	2.82883	-0.07067	0.06589		H	-3.04106	-1.15250	1.09169
	O	3.33630	-1.10730	0.41988		H	-2.76588	-3.16277	-2.15952
	O	3.56716	0.96116	-0.37719		H	-3.81014	-1.97037	-2.94577
	H	4.50873	0.70268	-0.32907		H	-4.52629	-2.86170	-0.48331
	O	0.75118	-2.07453	-0.00329		H	-4.57692	-1.11825	-0.77937
	C	0.91083	-2.72986	1.25840		O	-0.23040	1.51462	-0.74645
	H	1.76364	-2.31479	1.79466		C	-1.30616	2.44723	-0.45623
	H	-0.00009	-2.63883	1.85609		C	0.81746	2.17049	-1.51185

	H 1.09642 -3.77822 1.03407		C -0.74792 3.81356 -0.81430 H -2.16119 2.17925 -1.08179 H -1.57084 2.33225 0.59374 C 0.20591 3.48539 -1.96349 H 1.67446 2.32378 -0.85246 H 1.10483 1.50650 -2.32567 H -0.19844 4.23338 0.03124 H -1.53414 4.51419 -1.09460 H 0.96413 4.25125 -2.12501 H -0.34902 3.34966 -2.89472 H 2.65790 -2.32720 -2.32729
COMa	C -6.36520 -1.55475 -0.93017 C -6.06245 -0.25817 -1.24171 C -5.47055 -2.33294 -0.16429 H -6.74529 0.34060 -1.83447 H -5.71868 -3.36222 0.06688 C -4.85227 0.32730 -0.79881 C -4.29431 -1.79630 0.28030 H -3.59637 -2.39112 0.85471 C -3.95995 -0.45412 -0.02318 H -7.29481 -1.99273 -1.27517 C -4.51110 1.66938 -1.10463 H -5.19724 2.26597 -1.69485 C -3.33853 2.20162 -0.66643 C -2.74004 0.12612 0.42637 H -3.07933 3.22474 -0.90430 C -2.42288 1.42623 0.09475 C -1.14121 2.03821 0.50337 O -0.07301 1.47444 0.63506 O -1.24571 3.35293 0.70565 H -0.36664 3.70489 0.95326 O -1.90996 -0.63698 1.18556 Mg 1.23308 -0.20940 0.00094 C 0.09820 -0.77722 -1.74176 H 0.52044 -1.70071 -2.16756 H -0.91173 -1.06456 -1.41815 C -0.03721 0.25745 -2.87191 H 0.93607 0.53041 -3.29784 H -0.48504 1.19271 -2.51510 O 2.63270 1.33883 -0.29581 C 3.81398 1.51088 0.52680 C 2.45326 2.47676 -1.16831 C 4.55864 2.67979 -0.09551 H 3.48916 1.72466 1.54698	**TSa**	C 5.34824 1.83219 -0.76551 C 5.40972 0.46326 -0.70949 C 4.14946 2.49986 -0.45918 H 6.33520 -0.05361 -0.93950 H 4.10651 3.58171 -0.50563 C 4.28019 -0.30159 -0.34451 C 3.03549 1.78051 -0.10741 H 2.10567 2.28559 0.12015 C 3.07366 0.37299 -0.04621 H 6.22645 2.40337 -1.04459 C 4.34288 -1.72489 -0.23673 H 5.27752 -2.22784 -0.45473 C 3.24604 -2.42905 0.13596 C 1.90599 -0.38834 0.31749 H 3.28546 -3.50848 0.20601 C 2.01157 -1.78393 0.42957 C 0.81462 -2.55576 0.64151 O -0.33139 -2.09953 0.58172 O 0.99307 -3.86209 0.86254 H 0.11422 -4.27949 0.95437 O 0.95040 0.29722 1.09339 Mg -0.86782 -0.11785 0.13894 C 0.56936 -0.10227 -1.71986 H -0.44270 0.07180 -2.12019 H 1.11166 0.83008 -1.88964 C 1.19317 -1.25852 -2.48090 H 0.84453 -2.23101 -2.11004 H 2.28043 -1.26647 -2.37917 O -2.52806 -0.79766 -0.98872 C -3.92330 -0.50701 -0.71689 C -2.42069 -1.90181 -1.92405 C -4.69246 -1.22729 -1.80972 H -4.15937 -0.88445 0.27821

	H	4.35925	0.56854	0.52217	H	-4.04628	0.57546	-0.71681
	C	3.41668	3.53205	-0.64983	C	-3.82701	-2.46510	-2.04321
	H	2.69853	2.16801	-2.18769	H	-2.05874	-1.50482	-2.87529
	H	1.40606	2.77243	-1.13045	H	-1.69138	-2.60610	-1.52834
	H	5.20610	2.33671	-0.90627	H	-4.74068	-0.61762	-2.71555
	H	5.17430	3.20612	0.63369	H	-5.71067	-1.46485	-1.50182
	H	3.73081	4.22054	-1.43415	H	-3.99644	-2.93610	-3.01144
	H	2.95282	4.11214	0.15149	H	-4.00882	-3.20774	-1.26298
	O	3.01001	-1.45223	-0.55646	O	-1.33207	1.91142	-0.31993
	C	3.14294	-2.83929	-0.17160	C	-1.23585	3.00152	0.63392
	C	3.58006	-1.24421	-1.86589	C	-1.71376	2.42057	-1.61767
	C	3.54701	-3.57539	-1.43904	C	-1.43373	4.27304	-0.17918
	H	3.91047	-2.90633	0.60342	H	-2.01447	2.85231	1.38142
	H	2.19528	-3.16998	0.25033	H	-0.26244	2.94144	1.12100
	C	4.35717	-2.51352	-2.18149	C	-2.30311	3.79080	-1.34004
	H	2.76140	-1.08134	-2.57071	H	-0.82101	2.48303	-2.24455
	H	4.20169	-0.34934	-1.82819	H	-2.41042	1.71212	-2.06361
	H	2.66221	-3.85232	-2.01693	H	-0.47733	4.64557	-0.55348
	H	4.11436	-4.48132	-1.22464	H	-1.89980	5.06232	0.41035
	H	4.42939	-2.69448	-3.25409	H	-2.25783	4.44197	-2.21302
	H	5.36984	-2.45404	-1.77514	H	-3.34658	3.70271	-1.02810
	Br	1.60065	-0.91206	2.44032	Br	-2.25305	0.05200	2.38279
	C	-2.08297	-0.49605	2.59863	C	1.30401	0.40234	2.48695
	H	-1.94752	0.54499	2.90274	H	0.48267	0.92568	2.96683
	H	-3.07673	-0.83965	2.89948	H	1.40936	-0.59059	2.92540
	H	-1.30790	-1.10215	3.05819	H	2.23757	0.95757	2.58588
	H	-0.65874	-0.07531	-3.71594	H	0.97602	-1.24320	-3.55688
INTa	C	5.68531	1.53556	0.04509	**TS1a**	C	5.67965	1.51261	0.19858
	C	5.59932	0.15741	0.07345		C	5.57002	0.14966	0.32126
	C	4.52727	2.29893	-0.08231		C	4.56494	2.27045	-0.18623
	H	6.49880	-0.43962	0.18282		H	6.42642	-0.44208	0.62691
	H	4.58097	3.38120	-0.09698		H	4.64198	3.34816	-0.26997
	C	4.36397	-0.50183	-0.02685		C	4.35172	-0.51334	0.06412
	C	3.30257	1.66085	-0.18989		C	3.37073	1.64155	-0.44983
	H	2.40168	2.25735	-0.27750		H	2.51290	2.24109	-0.72402
	C	3.19954	0.27083	-0.16789		C	3.23124	0.24571	-0.33835
	H	6.65176	2.02040	0.12743		H	6.62429	2.00330	0.40512
	C	4.28432	-1.94786	0.03292		C	4.24814	-1.93619	0.20025
	H	5.20270	-2.51305	0.13750		H	5.12206	-2.50268	0.49855
	C	3.08696	-2.56626	0.00099		C	3.06193	-2.54432	-0.01915
	C	1.82377	-0.36977	-0.31501		C	1.93641	-0.39930	-0.60345
	H	3.03943	-3.64528	0.08708		H	2.96859	-3.61443	0.11379
	C	1.84630	-1.86656	-0.12891		C	1.89498	-1.81925	-0.41214
	C	0.64250	-2.53985	-0.05944		C	0.64554	-2.50122	-0.43277

O	-0.52473 -2.01928 -0.08199	O	-0.48629 -1.97079 -0.40005
O	0.67153 -3.89202 0.05784	O	0.69774 -3.84065 -0.43549
H	-0.24899 -4.18411 0.17495	H	-0.21309 -4.17495 -0.32791
O	0.91172 0.24113 0.70368	O	0.79266 0.30097 0.81333
M	-1.16754 -0.20284 0.37413	Mg	-1.11296 -0.19298 0.43317
C	1.20516 0.05168 -1.66278	C	1.11432 0.22205 -1.72343
H	0.20902 -0.38930 -1.75547	H	0.15068 -0.27845 -1.79711
H	1.08791 1.13711 -1.67002	H	0.91987 1.26981 -1.50063
C	2.03081 -0.39249 -2.86502	C	1.81114 0.09070 -3.07986
H	2.16424 -1.47554 -2.86727	H	1.99648 -0.95688 -3.32476
H	3.01915 0.06978 -2.85953	H	2.76906 0.61230 -3.08962
O	-2.87368 -0.60778 -0.79489	O	-2.79558 -0.48561 -0.84146
C	-4.20865 -0.18533 -0.40235	C	-4.15694 -0.29894 -0.37023
C	-2.95360 -1.57868 -1.87363	C	-2.80178 -1.08368 -2.16260
C	-5.13018 -0.72591 -1.48243	C	-5.02976 -0.49832 -1.59649
H	-4.41881 -0.61317 0.57809	H	-4.35024 -1.04259 0.40345
H	-4.20864 0.90132 -0.31688	H	-4.22569 0.69225 0.07697
C	-4.41031 -2.00328 -1.91347	C	-4.23485 -1.53322 -2.39201
H	-2.65480 -1.07881 -2.79972	H	-2.50117 -0.31691 -2.88291
H	-2.25054 -2.37539 -1.64636	H	-2.07308 -1.89058 -2.16383
H	-5.19823 -0.02627 -2.31921	H	-5.12040 0.43178 -2.16344
H	-6.13631 -0.90387 -1.10338	H	-6.03168 -0.83492 -1.33082
H	-4.70652 -2.35269 -2.90244	H	-4.49112 -1.55490 -3.45111
H	-4.59272 -2.80610 -1.19546	H	-4.39096 -2.53268 -1.97980
O	-1.35410 1.76405 -0.31298	O	-1.50917 1.85400 0.05348
C	-0.97909 2.88060 0.54329	C	-0.99591 2.84983 0.98082
C	-1.79648 2.24976 -1.60331	C	-2.04360 2.49724 -1.12668
C	-1.02887 4.10756 -0.35367	C	-0.94033 4.14067 0.18306
H	-1.70440 2.92512 1.35669	H	-1.69289 2.91477 1.81929
H	0.00835 2.66956 0.95007	H	-0.02939 2.49293 1.32812
C	-2.08832 3.72280 -1.38584	C	-2.11282 3.97632 -0.78291
H	-0.98855 2.10196 -2.32508	H	-1.36134 2.30843 -1.96046
H	-2.65776 1.65908 -1.90729	H	-3.01061 2.05353 -1.35376
H	-0.06429 4.26661 -0.84129	H	0.00163 4.21087 -0.36644
H	-1.28045 5.00795 0.20616	H	-1.02932 5.01931 0.82177
H	-2.01617 4.29427 -2.31103	H	-2.03524 4.60491 -1.66996
H	-3.09187 3.85620 -0.97516	H	-3.05542 4.20612 -0.28074
Br	-2.21750 -0.04722 2.64324	Br	-2.22876 -0.65180 2.64102
C	1.38504 0.12195 2.05205	C	1.39726 0.09368 2.06356
H	0.59511 0.49322 2.69961	H	0.70236 0.34996 2.86900
H	1.59048 -0.92339 2.29218	H	1.68884 -0.95659 2.20466
H	2.29119 0.71279 2.18495	H	2.29595 0.71221 2.17178
H	1.53116 -0.10994 -3.79371	H	1.18563 0.51610 -3.86761

CPLa	C	7.37359	0.51515	0.21916
	C	6.76070	-0.50496	-0.45086
	C	6.60509	1.39930	1.00358
	H	7.33905	-1.19398	-1.05679
	H	7.09279	2.20903	1.53382
	C	5.35892	-0.68879	-0.37078
	C	5.25026	1.24267	1.10103
	H	4.69084	1.93964	1.70871
	C	4.57472	0.19508	0.41778
	H	8.44722	0.64770	0.15155
	C	4.72614	-1.74754	-1.06530
	H	5.32920	-2.42216	-1.66253
	C	3.38112	-1.91251	-0.98296
	C	3.15215	0.02049	0.49781
	H	2.89670	-2.72105	-1.51243
	C	2.58112	-1.02231	-0.21573
	C	1.11751	-1.26222	-0.24007
	O	0.27327	-0.40054	-0.02680
	O	0.78281	-2.50007	-0.55168
	Mg	-1.80317	-0.15304	0.43830
	C	2.34915	0.96598	1.36047
	H	1.43360	0.48669	1.69199
	H	2.92088	1.19188	2.26175
	C	1.98833	2.26914	0.64076
	H	1.35693	2.05990	-0.22313
	H	2.87639	2.80080	0.29343
	Br	-2.38942	-2.31522	-0.87033
	O	-1.68027	1.42001	-0.90980
	C	-1.12119	1.35427	-2.24475
	C	-1.95885	2.79523	-0.54116
	C	-1.44465	2.70204	-2.86304
	H	-0.04510	1.18931	-2.15761
	H	-1.57529	0.50437	-2.75255
	C	-1.35770	3.63755	-1.65614
	H	-3.04206	2.91120	-0.47289
	H	-1.51842	2.98174	0.43845
	H	-2.45596	2.70014	-3.27623
	H	-0.74883	2.96404	-3.65978
	H	-1.89996	4.57237	-1.79599
	H	-0.31532	3.87717	-1.43532
	C	-4.80670	0.44159	-0.42958
	O	-3.82438	0.46287	0.63496
	C	-4.49349	0.49604	1.92040
	C	-5.85446	-0.11102	1.64640

2a	C	-3.66089	-1.85453	-0.07443
	C	-3.60388	-0.52163	-0.36652
	C	-2.50209	-2.52421	0.36894
	H	-4.48741	0.00721	-0.70740
	H	-2.54838	-3.58238	0.59885
	C	-2.39367	0.20154	-0.23196
	C	-1.32116	-1.84951	0.51073
	H	-0.45072	-2.39332	0.84958
	C	-1.22050	-0.46294	0.21539
	H	-4.59176	-2.39942	-0.18127
	C	-2.33645	1.58319	-0.53376
	H	-3.23495	2.08726	-0.87172
	C	-1.16972	2.26572	-0.39986
	C	0.01144	0.26191	0.34653
	H	-1.12623	3.32180	-0.62736
	C	0.01620	1.60893	0.02571
	C	1.25708	2.42850	0.08797
	O	2.38864	2.02126	-0.03401
	O	1.00024	3.73364	0.27792
	C	1.24088	-0.46669	0.83679
	H	1.92761	0.23732	1.29883
	H	0.94750	-1.17087	1.61695
	C	1.98042	-1.21064	-0.27983
	H	2.34591	-0.50498	-1.02622
	H	1.33404	-1.93494	-0.77944
	H	1.85117	4.21473	0.26620
	H	2.83960	-1.74866	0.12637
MeOMg Br(THF)$_2$	Mg	-3.19561	0.25105	-0.39466
	Br	-2.12801	-1.89376	-0.99301
	O	-2.61826	0.61038	1.52729
	C	-2.49001	-0.35089	2.60838
	C	-2.09877	1.90862	1.93260
	C	-1.58934	0.32582	3.62721
	H	-3.48890	-0.54028	3.00872
	H	-2.08372	-1.27060	2.18995
	C	-1.93398	1.80374	3.43805
	H	-1.14350	2.06164	1.42594
	H	-2.80494	2.66667	1.60023
	H	-0.53943	0.14460	3.38655
	H	-1.77658	-0.03423	4.63855
	H	-1.16039	2.47544	3.80952
	H	-2.87156	2.04628	3.94362
	C	-6.15307	0.89618	-0.53329
	O	-5.18670	-0.14574	-0.21862

	C	-6.17032	0.44744	0.25789		C	-5.84058	-1.44613	-0.19097
	H	-4.64581	1.31013	-1.07045		C	-7.31363	-1.16348	-0.46150
	H	-4.63879	-0.46566	-1.00989		C	-7.27570	0.15766	-1.23215
	H	-3.85143	-0.03552	2.61749		H	-6.48790	1.34441	0.40624
	H	-4.57893	1.54070	2.23666		H	-5.62657	1.63892	-1.12999
	H	-5.78351	-1.20087	1.61863		H	-5.37994	-2.05997	-0.96503
	H	-6.59272	0.16927	2.39810		H	-5.65628	-1.90076	0.78239
	H	-6.90146	-0.14596	-0.29089		H	-7.78256	-1.97355	-1.01938
	H	-6.55477	1.46648	0.34139		H	-7.85818	-1.03665	0.47668
	H	-0.20308	-2.56176	-0.64083		H	-7.02225	-0.01208	-2.28116
	O	-1.54136	-0.04781	2.29768		H	-8.21749	0.70455	-1.18809
	C	-0.68116	-0.58054	3.23919		O	-3.18844	1.90336	-1.22936
	H	-0.16454	0.20199	3.82028		C	-2.44650	2.83562	-1.93177
	H	-1.21084	-1.21277	3.97188		H	-1.77949	2.37769	-2.68012
	H	0.11166	-1.21597	2.80401		H	-3.09480	3.53932	-2.47732
	H	1.43737	2.93187	1.31153		H	-1.80663	3.44655	-1.27248

Table S3 The optimized Cartesian geometries(Å) for the reaction of **1**+et-MgBr(THF)$_2$→**2a**+MeO-MgBr(THF)$_2$ at B3LYP+IDSCRF/DZVP level.

Species	Cartesian coordinates			Species	Cartesian coordinates
1	C	-3.69236	0.27207	-0.01815	**EtMgBr(THF)$_2$**	
	C	-2.74241	1.26219	0.02488		
	C	-3.30387	-1.08986	-0.05425		
	H	-3.03662	2.30916	0.04358		
	H	-4.06513	-1.86441	-0.10016		
	C	-1.36021	0.93914	0.04031		
	C	-1.97469	-1.43247	-0.03827		
	H	-1.67313	-2.47391	-0.08232		
	C	-0.97254	-0.42697	0.01820		
	H	-4.74848	0.52989	-0.03122		
	C	-0.35403	1.94273	0.06660		
	H	-0.64891	2.98917	0.08229		
	C	0.96752	1.59875	0.06007		
	C	0.41650	-0.76283	0.04713		
	H	1.73105	2.36858	0.06453		
	C	1.37963	0.23367	0.05648		
	C	2.83293	-0.08118	0.04279		
	O	3.34265	-1.15609	0.30004		
	O	3.58313	0.98940	-0.29297		
	H	4.52470	0.70481	-0.26268		
	O	0.73659	-2.09078	-0.00636		
	C	0.92880	-2.72057	1.26660		
	H	1.78737	-2.28616	1.78290		
	H	0.02651	-2.62892	1.88148		

	H	1.12326	-3.77354	1.05855			
COMa	C	-6.50335	-1.56695	-0.95729	**TSa**	C	5.35609	1.85268	-0.76364
	C	-6.18703	-0.25888	-1.26676		C	5.42024	0.47811	-0.71739
	C	-5.61047	-2.35809	-0.18734		C	4.15109	2.51776	-0.45098
	H	-6.86829	0.34661	-1.86191		H	6.34999	-0.03565	-0.95199
	H	-5.86696	-3.39035	0.04092		H	4.10550	3.60310	-0.48920
	C	-4.96776	0.31964	-0.81696		C	4.28862	-0.29317	-0.35681
	C	-4.42001	-1.82585	0.26555		C	3.03534	1.78943	-0.10344
	H	-3.72661	-2.43239	0.84046		H	2.10130	2.29188	0.12868
	C	-4.07228	-0.47790	-0.03323		C	3.07779	0.37751	-0.05276
	H	-7.43893	-1.99858	-1.30712		H	6.23567	2.42963	-1.03920
	C	-4.61471	1.66658	-1.11744		C	4.35567	-1.72060	-0.25852
	H	-5.29583	2.27493	-1.70905		H	5.29303	-2.22293	-0.48262
	C	-3.42693	2.19364	-0.67269		C	3.25611	-2.43162	0.11369
	C	-2.84400	0.09510	0.42488		C	1.90853	-0.38786	0.30960
	H	-3.16055	3.21823	-0.91372		H	3.29772	-3.51462	0.17533
	C	-2.51049	1.40756	0.09164		C	2.01810	-1.78801	0.41450
	C	-1.21407	2.01029	0.48854		C	0.82268	-2.56871	0.62313
	O	-0.14278	1.42747	0.63556		O	-0.33391	-2.11485	0.56810
	O	-1.29967	3.34714	0.66096		O	1.00655	-3.88072	0.83510
	H	-0.40247	3.67808	0.90244		H	0.11887	-4.29529	0.92473
	O	-2.01651	-0.68325	1.18842		O	0.95598	0.29691	1.09609
	Mg	1.29918	-0.23086	-0.00105		Mg	-0.86367	-0.13280	0.14332
	C	0.18397	-0.89290	-1.72088		C	0.56164	-0.08914	-1.71211
	H	0.63969	-1.81741	-2.11954		H	-0.44928	0.08748	-2.12234
	H	-0.81354	-1.20946	-1.37260		H	1.09958	0.84913	-1.88409
	C	-0.01243	0.09175	-2.89843		C	1.18784	-1.23576	-2.49610
	H	0.94646	0.40410	-3.33895		H	0.83066	-2.21512	-2.14682
	H	-0.51697	1.01488	-2.57730		H	2.27703	-1.25197	-2.39049
	O	2.64528	1.40980	-0.26630		O	-2.53532	-0.79159	-0.99068
	C	3.79311	1.66203	0.60413		C	-3.92747	-0.49152	-0.70451
	C	2.43975	2.53818	-1.16666		C	-2.44755	-1.89655	-1.93113
	C	4.50049	2.87153	-0.00574		C	-4.70916	-1.16530	-1.82126
	H	3.41579	1.86659	1.61136		H	-4.16881	-0.89973	0.27947
	H	4.39361	0.75051	0.62894		H	-4.03369	0.59420	-0.66684
	C	3.33380	3.65633	-0.62884		C	-3.87114	-2.41941	-2.08052
	H	2.73532	2.22715	-2.17508		H	-2.05464	-1.50482	-2.87425
	H	1.37499	2.78114	-1.16751		H	-1.74591	-2.62791	-1.52771
	H	5.20685	2.55540	-0.78135		H	-4.73654	-0.52973	-2.71215
	H	5.05103	3.44403	0.74595		H	-5.73676	-1.38634	-1.52412
	H	3.64804	4.34452	-1.41847		H	-4.04175	-2.85945	-3.06556
	H	2.80723	4.23254	0.14000		H	-4.08159	-3.17993	-1.32272
	O	3.19544	-1.41341	-0.55961		O	-1.35176	1.90559	-0.30234
	C	3.33557	-2.82126	-0.20447		C	-1.25184	2.99070	0.66043

	C	3.77427	-1.18021	-1.87274	C	-1.70995	2.43227	-1.60206
	C	3.83151	-3.52778	-1.46850	C	-1.44753	4.27388	-0.14164
	H	4.05744	-2.89073	0.61688	H	-2.03093	2.83643	1.40907
	H	2.36824	-3.18298	0.15121	H	-0.27618	2.92522	1.14753
	C	4.62108	-2.41657	-2.17905	C	-2.30469	3.80228	-1.31842
	H	2.95848	-1.05659	-2.59408	H	-0.80535	2.50246	-2.21462
	H	4.35285	-0.25338	-1.82579	H	-2.40074	1.72872	-2.07020
	H	2.98560	-3.84920	-2.08584	H	-0.48750	4.65554	-0.50226
	H	4.43872	-4.40733	-1.23542	H	-1.92361	5.05556	0.45429
	H	4.73276	-2.58396	-3.25431	H	-2.24867	4.46250	-2.18690
	H	5.62049	-2.31541	-1.74118	H	-3.35345	3.70984	-1.01967
	Br	1.63400	-0.97175	2.44618	Br	-2.23769	0.01908	2.39288
	C	-2.15405	-0.50948	2.61362	C	1.31126	0.37321	2.49406
	H	-2.01824	0.54091	2.89478	H	0.51233	0.93164	2.97764
	H	-3.13997	-0.85497	2.94908	H	1.36901	-0.62850	2.92640
	H	-1.35975	-1.10489	3.06345	H	2.27044	0.88639	2.60003
	H	-0.61558	-0.31292	-3.72998	H	0.97514	-1.19574	-3.57459
INTa	C	5.70506	1.52638	0.04479	**TS1a**	C	7.38430	0.51565	0.33799
	C	5.61350	0.14300	0.06355		C	6.79084	-0.51668	-0.34194
	C	4.54396	2.29694	-0.06982		C	6.58516	1.42104	1.07537
	H	6.51470	-0.45878	0.16381		H	7.39263	-1.22096	-0.91203
	H	4.60070	3.38248	-0.07538		H	7.05592	2.24033	1.61276
	C	4.37144	-0.51248	-0.03438		C	5.38181	-0.69041	-0.31786
	C	3.31268	1.66007	-0.17522		C	5.22134	1.27211	1.11737
	H	2.41073	2.26275	-0.25011		H	4.64229	1.98636	1.69096
	C	3.20503	0.26597	-0.16388		C	4.56734	0.21248	0.42311
	H	6.67640	2.00908	0.12553		H	8.46390	0.64152	0.31397
	C	4.28821	-1.96213	0.01684		C	4.77292	-1.76062	-1.02426
	H	5.20718	-2.53421	0.11352		H	5.39855	-2.45097	-1.58507
	C	3.08314	-2.57722	-0.01275		C	3.41921	-1.91699	-0.99861
	C	1.82460	-0.36854	-0.30995		C	3.13839	0.04676	0.44554
	H	3.03148	-3.65958	0.06726		H	2.95271	-2.73414	-1.53737
	C	1.84218	-1.86823	-0.13340		C	2.59079	-1.00720	-0.27857
	C	0.63473	-2.54314	-0.06715		C	1.12648	-1.24391	-0.35924
	O	-0.54055	-2.01899	-0.08734		O	0.27013	-0.37753	-0.16819
	O	0.66065	-3.90048	0.04487		O	0.79641	-2.48380	-0.69310
	H	-0.27060	-4.18424	0.15222		Mg	-1.78461	-0.17772	0.40471
	O	0.91633	0.24330	0.71130		C	2.30302	1.01318	1.25833
	Mg	-1.16877	-0.21063	0.38383		H	1.36812	0.54879	1.56245
	C	1.20572	0.06120	-1.65762		H	2.83608	1.25666	2.18054
	H	0.20436	-0.37230	-1.75261		C	1.98063	2.30548	0.49625
	H	1.09348	1.14926	-1.66480		H	1.38796	2.08257	-0.39434
	C	2.02762	-0.38572	-2.86515		H	2.88634	2.83065	0.17862
	H	2.15520	-1.47150	-2.87098		Br	-2.41129	-2.30233	-0.93601

	H	3.02040	0.07182	-2.86310	O	-1.74394	1.45517	-0.88506
	O	-2.88841	-0.60491	-0.78692	C	-1.25534	1.44735	-2.25113
	C	-4.22498	-0.19478	-0.37854	C	-1.95610	2.81877	-0.42888
	C	-2.97295	-1.55423	-1.88741	C	-1.58660	2.83188	-2.78585
	C	-5.15205	-0.70741	-1.47163	H	-0.17761	1.26002	-2.23086
	H	-4.43213	-0.64962	0.59258	H	-1.75290	0.62915	-2.77480
	H	-4.22513	0.89129	-0.26312	C	-1.41029	3.70701	-1.54142
	C	-4.43374	-1.97557	-1.93757	H	-3.03039	2.95607	-0.27658
	H	-2.67117	-1.03541	-2.80425	H	-1.44257	2.94343	0.52703
	H	-2.27157	-2.36060	-1.67820	H	-2.62159	2.86686	-3.13916
	H	-5.22198	0.01545	-2.29055	H	-0.93077	3.11994	-3.61017
	H	-6.15903	-0.89460	-1.09258	H	-1.94650	4.65637	-1.60254
	H	-4.73110	-2.29813	-2.93782	H	-0.35100	3.92236	-1.37443
	H	-4.61737	-2.79848	-1.24035	C	-4.82632	0.45524	-0.29891
	O	-1.35205	1.76102	-0.31319	O	-3.79953	0.42850	0.72630
	C	-0.97059	2.87937	0.54158	C	-4.41653	0.37373	2.04050
	C	-1.80203	2.24962	-1.60333	C	-5.80705	-0.18159	1.78483
	C	-0.99356	4.10370	-0.36404	C	-6.16178	0.46745	0.44384
	H	-1.70475	2.93963	1.34882	H	-4.67030	1.33974	-0.92239
	H	0.01124	2.65630	0.96105	H	-4.70309	-0.43981	-0.91309
	C	-2.06200	3.73349	-1.39483	H	-3.76363	-0.22769	2.67092
	H	-1.00558	2.07761	-2.33516	H	-4.45925	1.39335	2.44091
	H	-2.68228	1.67555	-1.89338	H	-5.76929	-1.27111	1.68992
	H	-0.02358	4.23872	-0.85213	H	-6.50768	0.07331	2.58352
	H	-1.22727	5.01420	0.19166	H	-6.93610	-0.07076	-0.10727
	H	-1.97713	4.29669	-2.32667	H	-6.50672	1.49400	0.60048
	H	-3.06409	3.89153	-0.98494	H	-0.19505	-2.53582	-0.78830
	Br	-2.21708	-0.04443	2.64766	O	-1.40495	-0.11902	2.23879
	C	1.38820	0.10622	2.06280	C	-0.55354	-0.83947	3.06526
	H	0.60510	0.49399	2.71271	H	0.00644	-0.18248	3.75542
	H	1.57058	-0.94604	2.30038	H	-1.10048	-1.56242	3.69824
	H	2.30856	0.67831	2.19879	H	0.20637	-1.42903	2.51598
	H	1.52504	-0.09737	-3.79327	H	1.40106	2.98387	1.13023

CPLa					**2a**			
	C	7.47145	0.43637	0.19227		C	-3.68747	-1.86680	-0.07660
	C	6.82096	-0.54198	-0.52993		C	-3.62725	-0.52005	-0.36724
	C	6.72853	1.29070	1.04590		C	-2.52207	-2.54270	0.36586
	H	7.37993	-1.20677	-1.18618		H	-4.51493	0.01120	-0.70632
	H	7.24200	2.06157	1.61662		H	-2.56940	-3.60546	0.59392
	C	5.41091	-0.70687	-0.43289		C	-2.40954	0.20408	-0.23129
	C	5.35964	1.15202	1.15901		C	-1.32852	-1.86370	0.50904
	H	4.82719	1.82605	1.82128		H	-0.45900	-2.41671	0.84749
	C	4.64680	0.15361	0.42596		C	-1.22284	-0.46882	0.21714
	H	8.55015	0.55407	0.11203		H	-4.62303	-2.41182	-0.18411
	C	4.74435	-1.72132	-1.17346		C	-2.35085	1.59289	-0.52984
	H	5.32429	-2.37530	-1.82188		H	-3.25099	2.10331	-0.86717
	C	3.38637	-1.87407	-1.06939		C	-1.17208	2.28026	-0.39450
	C	3.21576	0.00103	0.51982		C	0.01629	0.25709	0.34930
	H	2.88161	-2.65155	-1.63288		H	-1.13200	3.34008	-0.62276
	C	2.60806	-1.00886	-0.23837		C	0.02225	1.62081	0.03078
	C	1.13606	-1.24090	-0.24558		C	1.26472	2.44865	0.09419
	O	0.28501	-0.37926	0.01726		O	2.41629	2.04201	0.00918
	O	0.79313	-2.48017	-0.60113		O	0.99902	3.77342	0.24002
	Mg	-1.83417	-0.12220	0.45838		C	1.25284	-0.47583	0.84031
	C	2.43511	0.92469	1.43818		H	1.94102	0.22721	1.30836
	H	1.50387	0.45464	1.74768		H	0.96345	-1.18861	1.61856
	H	3.01185	1.09392	2.35257		C	2.00746	-1.21920	-0.28124
	C	2.10071	2.28220	0.78674		H	2.37035	-0.51166	-1.03202
	H	1.47016	2.13533	-0.09470		H	1.37016	-1.95524	-0.78278
	H	3.00212	2.82014	0.47494		H	1.86594	4.24213	0.23152
	B	-2.41350	-2.33354	-0.80894		H	2.87310	-1.74827	0.13315

	O	-1.70295	1.45908	-0.91867	**MeOMg Br(THF)$_2$**	Mg	-3.20763	0.29563	-0.40888
	C	-1.16528	1.38913	-2.27499		Br	-2.11012	-1.84240	-1.05181
	C	-1.90555	2.85457	-0.52533		O	-2.63723	0.63791	1.54763
	C	-1.43473	2.76717	-2.87415		C	-2.43406	-0.35618	2.60369
	H	-0.09434	1.17027	-2.20883		C	-2.18224	1.95956	1.99867
	H	-1.67131	0.56747	-2.78722		C	-1.52088	0.32701	3.61941
	C	-1.29103	3.68927	-1.65091		H	-3.41418	-0.59775	3.03025
	H	-2.98335	3.01814	-0.42662		H	-2.00694	-1.24770	2.13959
	H	-1.43037	3.00431	0.44762		C	-1.93731	1.80290	3.49888
	H	-2.45140	2.81705	-3.27874		H	-1.26507	2.20138	1.45217
	H	-0.73245	3.00801	-3.67682		H	-2.95626	2.68318	1.73702
	H	-1.80431	4.64696	-1.77257		H	-0.47086	0.19881	3.33579
	H	-0.23429	3.89120	-1.44702		H	-1.65754	-0.07651	4.62638
	C	-4.87555	0.47264	-0.49302		H	-1.17120	2.49509	3.85861
	O	-3.91226	0.47977	0.60459		H	-2.85940	1.98885	4.06008
	C	-4.62568	0.42623	1.87753		C	-6.21351	0.90869	-0.54592
	C	-5.95986	-0.22971	1.54004		O	-5.22076	-0.12030	-0.21185
	C	-6.26536	0.36556	0.15411		C	-5.85763	-1.44391	-0.19941
	H	-4.74560	1.39096	-1.07453		C	-7.34356	-1.18833	-0.47329
	H	-4.64224	-0.38830	-1.12487		C	-7.33260	0.14435	-1.24280
	H	-3.98354	-0.11263	2.57357		H	-6.55430	1.36603	0.39063
	H	-4.76232	1.45377	2.23928		H	-5.69924	1.65409	-1.15523
	H	-5.84363	-1.31725	1.47940		H	-5.38033	-2.04345	-0.97889
	H	-6.73263	-0.00390	2.28078		H	-5.66548	-1.90210	0.77435
	H	-6.94226	-0.25395	-0.44075		H	-7.79488	-2.00706	-1.04007
	H	-6.71866	1.35701	0.26003		H	-7.89488	-1.07956	0.46663
	H	-0.20463	-2.53083	-0.66338		H	-7.08479	-0.01707	-2.29749
	O	-1.59907	0.10184	2.31051		H	-8.28732	0.67493	-1.18865
	C	-0.79702	-0.49012	3.28319		O	-3.21169	1.95312	-1.24538
	H	-0.26924	0.26327	3.90023		C	-2.35557	2.79145	-1.96219
	H	-1.38540	-1.11050	3.98794		H	-1.74291	2.25237	-2.70884
	H	-0.01213	-1.15641	2.87152		H	-2.92158	3.56145	-2.51843
	H	1.55470	2.91521	1.49496		H	-1.64774	3.33596	-1.30761

Table S4 The optimized Cartesian geometries(Å) for the reaction of **1**+Ph-MgBr(THF)$_2$→**2b**+MeO-MgBr(THF)$_2$ at CAM-B3LYP+IDSCRF/DZVP level.

Species	Cartesian coordinates			Species	Cartesian coordinates		
1	C	-3.70978	0.27806	-0.02421	**PhMgBr(THF)$_2$**	Mg	0.09665	0.62772	0.54353
	C	-2.75273	1.27232	0.01877		Br	0.21127	2.68180	-0.84198
	C	-3.32220	-1.08729	-0.05643		O	1.53197	-0.61949	-0.25391
	H	-3.04687	2.32026	0.03398		C	1.74760	-0.81949	-1.68173
	H	-4.08486	-1.86173	-0.10256		C	2.61774	-1.21944	0.51019
	C	-1.36773	0.94765	0.03766		C	3.16108	-1.37393	-1.79725

	C	-1.98624	-1.43466	-0.03621	H	0.99598	-1.53274	-2.03397
	H	-1.68917	-2.47813	-0.07741	H	1.60065	0.14034	-2.17929
	C	-0.97770	-0.43032	0.02006	C	3.32938	-2.13098	-0.47724
	H	-4.76624	0.53805	-0.04026	H	3.26976	-0.41532	0.86523
	C	-0.35730	1.95035	0.06351	H	2.17876	-1.73183	1.36707
	H	-0.64896	2.99861	0.07769	H	3.88615	-0.55775	-1.86559
	C	0.97110	1.60285	0.05852	H	3.27631	-2.01066	-2.67688
	C	0.41435	-0.76889	0.05300	H	4.37415	-2.29028	-0.20239
	H	1.73337	2.37465	0.06235	H	2.83239	-3.10460	-0.52469
	C	1.38696	0.23449	0.05745	C	-1.74748	-1.80148	0.05725
	C	2.84343	-0.07909	0.03734	O	-1.50984	-0.39624	-0.24086
	O	3.36023	-1.16335	0.26651	C	-2.63141	0.16014	-0.98974
	O	3.59707	1.00913	-0.27446	C	-3.45207	-1.04709	-1.41851
	H	4.53877	0.71981	-0.25065	C	-3.21530	-2.03237	-0.27092
	O	0.73317	-2.10295	0.00013	H	-1.08633	-2.39701	-0.58024
	C	0.94436	-2.73936	1.27720	H	-1.49126	-1.97164	1.10478
	H	1.81588	-2.31248	1.77991	H	-3.18929	0.81984	-0.31880
	H	0.05244	-2.64224	1.90783	H	-2.22335	0.74669	-1.81301
	H	1.12691	-3.79386	1.06032	H	-4.50496	-0.79264	-1.55655
					H	-3.07004	-1.45448	-2.35931
					H	-3.84287	-1.77933	0.58873
					H	-3.41137	-3.07070	-0.54646
					C	0.08176	0.44940	2.65600
					C	-1.11009	0.13629	3.34285
					C	1.21041	0.63170	3.48230
					C	-1.18138	0.01107	4.73377
					C	1.16504	0.51155	4.87411
					C	-0.03731	0.19837	5.50872
					H	-2.03445	-0.01492	2.78067
					H	2.17402	0.88345	3.03493
					H	-2.12879	-0.23065	5.21323
					H	2.06688	0.66399	5.46512
					H	-0.08199	0.10411	6.59183
COMb	C	-5.64502	1.73498	0.24908	**TSb**	C	-5.37223	1.85445	0.30704
	C	-5.63101	0.37470	0.06961		C	-5.41445	0.49518	0.08988
	C	-4.46899	2.49638	0.03557		C	-4.16043	2.55851	0.14878
	H	-6.52815	-0.21486	0.24394		H	-6.34946	-0.04952	0.20129
	H	-4.48824	3.57073	0.19942		H	-4.13146	3.63235	0.31463
	C	-4.44511	-0.28920	-0.34044		C	-4.25294	-0.21784	-0.29155
	C	-3.30920	1.88345	-0.36485		C	-3.01497	1.88276	-0.20994
	H	-2.40226	2.46257	-0.50499		H	-2.07919	2.42023	-0.32346
	C	-3.27270	0.47872	-0.57155		C	-3.03420	0.48873	-0.42924
	H	-6.55781	2.23398	0.56485		H	-6.27448	2.38835	0.59571
	C	-4.40071	-1.69868	-0.51766		C	-4.29866	-1.62091	-0.57775

	H	-5.30054	-2.28275	-0.34108	H	-5.23967	-2.15311	-0.46620
	C	-3.24084	-2.31603	-0.88897	C	-3.18372	-2.26440	-1.01908
	C	-2.08555	-0.18875	-0.98377	C	-1.82630	-0.23099	-0.78062
	H	-3.20367	-3.39405	-1.00350	H	-3.21927	-3.32352	-1.25424
	C	-2.05429	-1.56307	-1.11717	C	-1.93753	-1.58499	-1.16544
	C	-0.80013	-2.28358	-1.41970	C	-0.74043	-2.33398	-1.45264
	O	0.33518	-1.87769	-1.18851	O	0.41585	-1.92990	-1.23531
	O	-0.99525	-3.48856	-1.95564	O	-0.92341	-3.57001	-1.93939
	H	-0.11457	-3.91213	-2.09034	H	-0.03629	-3.98070	-2.05244
	O	-0.97622	0.58255	-1.27877	O	-0.79986	0.56340	-1.34568
	Mg	1.01720	-0.10015	-0.18601	Mg	0.96620	-0.11001	-0.39005
	O	2.81144	-1.06726	0.52685	O	2.52051	-1.03168	0.71386
	C	4.18829	-0.83428	0.13846	C	3.93581	-0.96095	0.39421
	C	2.73012	-2.25839	1.35464	C	2.28647	-2.11450	1.65932
	C	5.01225	-1.58938	1.16847	C	4.62455	-1.62785	1.57204
	H	4.33706	-1.21837	-0.87419	H	4.10917	-1.49436	-0.54432
	H	4.35505	0.24345	0.12387	H	4.19173	0.08808	0.24392
	C	4.14597	-2.82680	1.41157	C	3.64923	-2.75915	1.90267
	H	2.35806	-1.95552	2.33573	H	1.86084	-1.67312	2.56315
	H	2.00859	-2.94106	0.90134	H	1.55617	-2.79752	1.22335
	H	5.11269	-1.00116	2.08635	H	4.70979	-0.93069	2.41183
	H	6.01276	-1.82742	0.79977	H	5.62529	-1.98203	1.31431
	H	4.34826	-3.31827	2.36587	H	3.74499	-3.12869	2.92592
	H	4.29992	-3.55765	0.61203	H	3.80289	-3.60036	1.22054
	O	1.58935	1.86864	0.50064	O	1.49382	1.81045	0.39627
	C	1.45518	3.12754	-0.20691	C	1.31752	3.03740	-0.36409
	C	2.36495	2.06008	1.70593	C	2.24461	2.08326	1.60360
	C	2.15955	4.17191	0.65861	C	1.91085	4.14842	0.49729
	H	1.92605	2.99998	-1.18389	H	1.84695	2.90897	-1.31037
	H	0.38916	3.33173	-0.34208	H	0.25025	3.16484	-0.56125
	C	3.16147	3.33004	1.45324	C	2.95244	3.40108	1.33361
	H	1.67980	2.16980	2.55303	H	1.54335	2.16213	2.44070
	H	2.96911	1.16516	1.85939	H	2.90980	1.23907	1.78316
	H	1.44968	4.65366	1.33767	H	1.14633	4.58541	1.14681
	H	2.63226	4.94852	0.05339	H	2.33883	4.94763	-0.11165
	H	3.48404	3.80715	2.38160	H	3.21915	3.92140	2.25634
	H	4.04696	3.11090	0.84855	H	3.86406	3.23207	0.75255
	Br	2.33208	0.45524	-2.46792	Br	2.50134	0.38002	-2.48984
	C	-1.02466	1.12438	-2.62141	C	-1.01961	0.88850	-2.73603
	H	-0.21011	1.84002	-2.69711	H	-0.20649	1.55250	-3.02176
	H	-0.86545	0.32420	-3.34791	H	-0.98165	-0.01571	-3.34751
	H	-1.98932	1.60896	-2.79020	H	-1.98721	1.38282	-2.85001
	C	-0.21055	-0.44782	1.60417	C	-0.75736	-0.37148	1.24225
	C	-0.75080	0.63991	2.32387	C	-0.84944	0.72394	2.12047

	C	-0.56920	-1.70750	2.13110		C -1.03417	-1.62340	1.81287
	C	-1.55448	0.50177	3.46056		C -1.14950	0.58176	3.47731
	C	-1.36903	-1.88066	3.26480		C -1.32128	-1.79620	3.16744
	C	-1.86759	-0.76834	3.94374		C -1.37859	-0.68643	4.01167
	H	-0.54569	1.65661	1.98287		H -0.68721	1.73191	1.74120
	H	-0.21765	-2.61744	1.63841		H -1.04170	-2.51392	1.18127
	H	-1.94122	1.38539	3.96777		H -1.20699	1.46020	4.11851
	H	-1.60637	-2.88365	3.61868		H -1.51409	-2.79199	3.56358
	H	-2.49127	-0.88968	4.82749		H -1.61496	-0.80711	5.06679
INTb	C	-5.66344	1.61845	0.62597	**TS1b**	C 5.72025	-1.49739	0.82610
	C	-5.55088	0.71595	-0.41797		C 5.53192	-0.94696	-0.42282
	C	-4.54135	1.91609	1.40717		C 4.70328	-1.39607	1.79277
	H	-6.41920	0.48471	-1.03174		H 6.31617	-1.01438	-1.17389
	H	-4.61306	2.62361	2.22922		H 4.84567	-1.82214	2.78260
	C	-4.32686	0.08627	-0.72046		C 4.32835	-0.28524	-0.76240
	C	-3.33262	1.29301	1.12742		C 3.52394	-0.74970	1.48203
	H	-2.46981	1.52801	1.74285		H 2.75409	-0.67927	2.24083
	C	-3.20003	0.38157	0.07336		C 3.29686	-0.19066	0.20582
	H	-6.61912	2.09338	0.83592		H 6.65274	-2.00311	1.06609
	C	-4.23220	-0.83793	-1.83419		C 4.16711	0.30334	-2.06171
	H	-5.12245	-1.04093	-2.42317		H 4.97392	0.22341	-2.78512
	C	-3.04396	-1.40942	-2.13892		C 3.01118	0.94570	-2.36529
	C	-1.83517	-0.26037	-0.19308		C 2.01084	0.45967	-0.12300
	H	-2.97131	-2.08282	-2.98846		H 2.87282	1.38572	-3.34810
	C	-1.84581	-1.16621	-1.39520		C 1.93600	1.05173	-1.43000
	C	-0.64333	-1.74726	-1.77502		C 0.69363	1.60047	-1.86612
	O	0.49813	-1.52723	-1.23795		O -0.41749	1.42590	-1.30662
	O	-0.65573	-2.63238	-2.80603		O 0.72159	2.33305	-2.99318
	H	0.27914	-2.87134	-2.97703		H -0.20921	2.54430	-3.22775
	O	-0.82790	0.83811	-0.41384		O 0.75534	-0.99267	-0.20779
	Mg	1.20808	0.17178	-0.50695		Mg -1.11979	-0.31634	-0.46764
	O	2.72705	-1.00224	0.34442		O -2.71108	0.95562	0.13961
	C	3.91256	-1.32871	-0.43367		C -3.86806	1.17952	-0.71227
	C	2.40679	-2.10651	1.24241		C -2.46098	2.13806	0.95151
	C	4.58746	-2.44700	0.34161		C -4.59349	2.35768	-0.08393
	H	3.59503	-1.65295	-1.42904		H -3.51538	1.40539	-1.72261
	H	4.50655	-0.41927	-0.53143		H -4.44578	0.25505	-0.74212
	C	3.38657	-3.21961	0.89119		C -3.43085	3.19880	0.44597
	H	2.54307	-1.74397	2.26511		H -2.65286	1.86793	1.99407
	H	1.36211	-2.37967	1.08936		H -1.41326	2.41652	0.83705
	H	5.19083	-2.03673	1.15727		H -5.23309	2.02042	0.73769
	H	5.23490	-3.05216	-0.29678		H -5.21490	2.88687	-0.80983
	H	3.62935	-3.83538	1.75992		H -3.72259	3.89368	1.23648
	H	2.96474	-3.86755	0.11748		H -2.97565	3.77256	-0.36656

	O	1.67909	1.65143	0.92809		O	-1.77780	-1.58330	1.10657
	C	1.05169	2.96000	0.95144		C	-1.15232	-2.87219	1.33413
	C	3.00524	1.74308	1.52867		C	-3.11723	-1.58625	1.67351
	C	1.70639	3.67110	2.12149		C	-1.86676	-3.43116	2.55163
	H	1.25951	3.46459	0.00144		H	-1.31155	-3.49666	0.44804
	H	-0.02296	2.80862	1.05493		H	-0.08465	-2.69812	1.46230
	C	3.15379	3.18700	2.00907		C	-3.30388	-2.96334	2.31092
	H	3.03725	1.01924	2.34590		H	-3.16185	-0.77655	2.40612
	H	3.74534	1.46966	0.77554		H	-3.83458	-1.38674	0.87624
	H	1.25549	3.34429	3.06346		H	-1.45962	-2.98965	3.46663
	H	1.60941	4.75650	2.04872		H	-1.77407	-4.51734	2.62074
	H	3.70067	3.24467	2.95245		H	-3.90016	-2.90991	3.22437
	H	3.69298	3.78092	1.26610		H	-3.80785	-3.63946	1.61456
	Br	2.35766	1.35250	-2.40432		Br	-2.21400	-1.55347	-2.37668
	C	-1.21946	1.77165	-1.43735		C	1.27467	-2.01741	-1.02905
	H	-0.34648	2.38024	-1.67011		H	0.50385	-2.77174	-1.22242
	H	-1.53186	1.23766	-2.33900		H	1.60280	-1.62721	-2.00284
	H	-2.03455	2.40330	-1.07783		H	2.12863	-2.50945	-0.54561
	C	-1.36894	-0.97202	1.08609		C	1.36284	1.20270	1.02942
	C	-0.65150	-0.32981	2.09909		C	1.59501	2.58174	1.11649
	C	-1.76575	-2.29730	1.29635		C	0.65758	0.58903	2.07031
	C	-0.33259	-0.99374	3.28462		C	1.13458	3.32308	2.20163
	C	-1.45023	-2.96145	2.47771		C	0.19961	1.32873	3.15999
	C	-0.73023	-2.31211	3.48160		C	0.43615	2.69862	3.23439
	H	-0.33517	0.69900	1.97713		H	2.15465	3.07831	0.32862
	H	-2.33122	-2.81142	0.52479		H	0.46842	-0.47628	2.02833
	H	0.22868	-0.47133	4.05596		H	1.32946	4.39214	2.24221
	H	-1.77055	-3.99137	2.61650		H	-0.34524	0.82513	3.95521
	H	-0.48437	-2.83013	4.40534		H	0.08072	3.27449	4.08537

CPLb				**2b**			
	C	7.23279	-0.37409	0.79874	C	5.97414	-2.04556	1.31003
	C	6.55074	-1.48511	0.37332	C	5.30552	-2.61291	0.25538
	C	6.54813	0.85430	0.96259	C	5.51158	-0.82901	1.86828
	H	7.06487	-2.43529	0.24721	H	5.65654	-3.54341	-0.18531
	H	7.09146	1.73053	1.30710	H	6.05035	-0.37981	2.69878
	C	5.16078	-1.41977	0.09107	C	4.14627	-1.99648	-0.28599
	C	5.20585	0.94582	0.69250	C	4.39168	-0.21406	1.36709
	H	4.69917	1.89460	0.82833	H	4.05218	0.71947	1.80263
	C	4.46607	-0.18726	0.24519	C	3.66757	-0.78094	0.27939
	H	8.29686	-0.43256	1.01399	H	6.86183	-2.52329	1.71722
	C	4.44805	-2.56646	-0.34335	C	3.46135	-2.56455	-1.39140
	H	4.97861	-3.50822	-0.46262	H	3.82971	-3.49220	-1.82340
	C	3.11152	-2.48986	-0.60407	C	2.35750	-1.95072	-1.91042
	C	3.05840	-0.11549	-0.03270	C	2.49180	-0.15931	-0.25723
	H	2.56879	-3.36888	-0.93137	H	1.83938	-2.38284	-2.75948
	C	2.39922	-1.26553	-0.44181	C	1.85643	-0.74695	-1.33916
	C	0.93396	-1.31560	-0.70570	C	0.61113	-0.16747	-1.92512
	O	0.11191	-0.50975	-0.26726	O	-0.19067	0.54188	-1.34956
	O	0.57216	-2.35630	-1.44044	O	0.43245	-0.53868	-3.21012
	H	-0.42546	-2.40819	-1.47096	H	-0.42021	-0.14976	-3.51094
	O	-1.62951	-0.42884	2.13125	C	2.02734	1.12748	0.34492
	Mg	-1.97147	-0.43819	0.28836	C	1.31314	1.13619	1.54554
	O	-2.18430	1.13367	-1.04627	C	2.34538	2.34293	-0.26434
	C	-3.15247	1.11863	-2.13359	C	0.90742	2.33918	2.11780
	C	-1.26500	2.24957	-1.20446	C	1.94142	3.54836	0.30764
	C	-2.98878	2.46401	-2.82587	C	1.21912	3.55019	1.49955
	H	-2.90529	0.28172	-2.79238	H	0.34534	2.33113	3.04862
	H	-4.13853	0.94828	-1.69922	H	2.19393	4.48750	-0.17889
	C	-1.50113	2.75925	-2.61830	H	0.90283	4.48967	1.94620
	H	-1.51831	3.00287	-0.45214	H	2.91103	2.34688	-1.19350
	H	-0.25773	1.88112	-1.02033	H	1.06401	0.19457	2.02944
	H	-3.60240	3.22618	-2.33558	**MeOMg**	Mg	-3.15240	0.28100	-0.41792
	H	-3.27738	2.41570	-3.87815	**Br(THF)$_2$**	Br	-2.05064	-1.83792	-1.11142
	H	-1.25285	3.81817	-2.71657		O	-2.57125	0.61675	1.52730
	H	-0.89475	2.19523	-3.33356		C	-2.51278	-0.35756	2.61695
	O	-4.03114	-0.01139	0.74294		C	-2.02515	1.90417	1.96505
	C	-4.74054	-1.04501	1.48161		C	-1.67557	0.31003	3.70379
	C	-4.26584	1.27587	1.36427		H	-3.53760	-0.54821	2.94703
	C	-5.39464	-0.34220	2.66759		H	-2.07998	-1.27558	2.21907
	H	-5.47242	-1.48602	0.79895		C	-1.96783	1.80236	3.48323
	H	-4.01865	-1.80491	1.78320		H	-1.03117	2.01565	1.52366
	C	-5.54349	1.09687	2.16842		H	-2.67914	2.68439	1.57921
	H	-3.41224	1.50581	2.01025		H	-0.61339	0.10176	3.55010
	H	-4.33973	2.02020	0.56838		H	-1.95153	-0.03839	4.70005

	H	-4.72920	-0.37291	3.53434	H	-1.20154	2.45395	3.90584
	H	-6.34551	-0.80417	2.94281	H	-2.93132	2.07502	3.92278
	H	-5.62671	1.82755	2.97641	C	-6.14404	0.90296	-0.44289
	H	-6.42030	1.19577	1.52063	O	-5.15525	-0.15246	-0.20536
	Br	-2.59107	-2.50187	-1.14406	C	-5.80340	-1.46662	-0.25172
	C	-0.59166	-0.89643	2.92431	C	-7.28868	-1.18209	-0.48292
	H	-0.89540	-1.76625	3.53569	C	-7.28062	0.19586	-1.16398
	H	0.29636	-1.21800	2.34813	H	-6.46029	1.29531	0.52869
	H	-0.23652	-0.12767	3.63651	H	-5.63531	1.68202	-1.00959
	C	2.41218	1.22807	0.09640	H	-5.34709	-2.02533	-1.07017
	C	2.57075	2.16650	-0.92714	H	-5.60006	-1.97904	0.68963
	C	1.76092	1.61041	1.27172	H	-7.75629	-1.95733	-1.09148
	C	2.09650	3.46966	-0.77561	H	-7.82271	-1.12993	0.46957
	C	1.28944	2.91160	1.42526	H	-7.05447	0.10129	-2.22963
	C	1.46201	3.84830	0.40574	H	-8.22791	0.72703	-1.05831
	H	3.08527	1.88146	-1.84219	O	-3.17010	1.95814	-1.22853
	H	1.62055	0.88673	2.06919	C	-2.48081	2.83571	-2.05467
	H	2.23193	4.18926	-1.57950	H	-1.92314	2.32565	-2.85989
	H	0.78647	3.19445	2.34671	H	-3.16456	3.54675	-2.54946
	H	1.09885	4.86561	0.53008	H	-1.74368	3.44509	-1.50095

Table S5 The optimized Cartesian geometries(Å) for the reaction of **1**+2MeO-Ph-MgBr(THF)$_2$→**2c**+MeO-MgBr(THF)$_2$ at CAM-B3LYP+IDSCRF/DZVP level(path a).

Species	Cartesian coordinates			Species	Cartesian coordinates		
1	C	-3.70978	0.27806	-0.02421	**2-MeOPhMgBr(THF)$_2$**	Mg	-0.28813	0.10206	0.39395
	C	-2.75273	1.27232	0.01877		Br	-1.17377	-0.87013	2.50453
	C	-3.32220	-1.08729	-0.05643		O	-1.95971	1.00083	-0.44204
	H	-3.04687	2.32026	0.03398		C	-3.26337	0.35770	-0.51429
	H	-4.08486	-1.86173	-0.10256		C	-2.05363	2.38679	-0.87322
	C	-1.36773	0.94765	0.03766		C	-4.25394	1.49711	-0.70330
	C	-1.98624	-1.43466	-0.03621		H	-3.25307	-0.32602	-1.36887
	H	-1.68917	-2.47813	-0.07741		H	-3.40289	-0.21106	0.40613
	C	-0.97770	-0.43032	0.02006		C	-3.43417	2.51305	-1.50284
	H	-4.76624	0.53805	-0.04026		H	-1.94586	3.02480	0.00933
	C	-0.35730	1.95035	0.06351		H	-1.23027	2.58153	-1.56214
	H	-0.64896	2.99861	0.07769		H	-4.54331	1.91460	0.26559
	C	0.97110	1.60285	0.05852		H	-5.15775	1.16990	-1.22167
	C	0.41435	-0.76889	0.05300		H	-3.82115	3.53174	-1.43183
	H	1.73337	2.37465	0.06235		H	-3.39905	2.23103	-2.55941
	C	1.38696	0.23449	0.05745		C	0.18079	-1.27226	-2.28544
	C	2.84343	-0.07909	0.03734		O	-0.37113	-1.46316	-0.95155
	O	3.36023	-1.16335	0.26651		C	-0.29576	-2.86685	-0.57261
	O	3.59707	1.00913	-0.27446		C	0.00722	-3.60666	-1.86700

	H	4.53877	0.71981	-0.25065		C	0.85826	-2.59019	-2.63214
	O	0.73317	-2.10295	0.00013		H	-0.65148	-1.04701	-2.95964
	C	0.94436	-2.73936	1.27720		H	0.86323	-0.42078	-2.25001
	H	1.81588	-2.31248	1.77991		H	0.50568	-2.97788	0.16311
	H	0.05244	-2.64224	1.90783		H	-1.24575	-3.13698	-0.11015
	H	1.12691	-3.79386	1.06032		H	0.52434	-4.55092	-1.68354
						H	-0.91779	-3.82076	-2.41083
						H	1.88725	-2.59559	-2.26168
						H	0.87776	-2.76774	-3.70956
						C	1.38987	1.37758	0.11000
						C	1.56687	2.75205	-0.08726
						C	2.57688	0.62967	0.17749
						C	2.82942	3.35044	-0.21197
						C	3.85367	1.17862	0.05856
						C	3.96950	2.55899	-0.13889
						H	0.69501	3.40498	-0.14128
						H	2.91800	4.42462	-0.36108
						H	4.75210	0.57185	0.11532
						H	4.95756	3.00449	-0.23213
						O	2.36500	-0.73201	0.37147
						C	3.49083	-1.56799	0.57570
						H	4.13650	-1.59815	-0.31013
						H	4.07979	-1.24080	1.44040
						H	3.10278	-2.56959	0.76856
COMca	C	6.28422	1.39712	0.26252	**TSca**	C	5.31718	-2.20754	0.44199
	C	5.98330	0.20903	-0.35702		C	5.38407	-0.91910	-0.06170
	C	5.34376	2.01357	1.12378		C	4.07256	-2.87169	0.51218
	H	6.70215	-0.26364	-1.02255		H	6.34366	-0.41005	-0.13738
	H	5.59070	2.95881	1.60029		H	4.01944	-3.89083	0.88918
	C	4.73073	-0.42192	-0.14201		C	4.21858	-0.24410	-0.50993
	C	4.12381	1.42639	1.35080		C	2.91814	-2.22240	0.10157
	H	3.39103	1.90166	1.99495		H	1.96492	-2.73848	0.15782
	C	3.79208	0.19540	0.72638		C	2.95672	-0.90103	-0.40036
	H	7.24675	1.87259	0.09036		H	6.22283	-2.71279	0.77228
	C	4.39352	-1.65609	-0.76380		C	4.29639	1.05144	-1.12175
	H	5.11450	-2.13109	-1.42468		H	5.26219	1.54641	-1.19562
	C	3.17968	-2.23722	-0.53582		C	3.17407	1.62280	-1.65856
	C	2.52977	-0.43257	0.95133		C	1.73429	-0.20321	-0.80947
	H	2.92523	-3.17763	-1.01290		H	3.23884	2.58620	-2.15561
	C	2.21814	-1.62258	0.31803		C	1.89241	1.00099	-1.56845
	C	0.90584	-2.27598	0.49749		C	0.71954	1.70828	-2.01083
	O	-0.15099	-1.73904	0.80874		O	-0.45870	1.41109	-1.71175
	O	0.95138	-3.59742	0.28519		O	0.93907	2.79988	-2.77966
	H	0.04744	-3.96046	0.43003		H	0.05877	3.19292	-2.97820

	O	1.66167	0.17411	1.81066	O	0.65418	-1.08051	-1.16507
	Mg	-1.33380	0.03686	0.40579	Mg	-1.10203	-0.10039	-0.44495
	O	-2.77696	-1.33311	-0.29849	O	-2.58581	1.15633	0.44374
	C	-4.06030	-1.52630	0.35256	C	-4.01495	1.14488	0.11916
	C	-2.58619	-2.32163	-1.34150	C	-2.25821	2.38158	1.18008
	C	-4.83326	-2.45783	-0.57003	C	-4.63756	2.19819	1.03126
	H	-3.88126	-1.97336	1.33489	H	-4.12645	1.39319	-0.94008
	H	-4.51182	-0.54291	0.49001	H	-4.38691	0.13105	0.27798
	C	-3.71819	-3.32507	-1.15893	C	-3.51783	3.24629	1.12499
	H	-2.63911	-1.80832	-2.30631	H	-2.00288	2.09234	2.20504
	H	-1.58787	-2.74402	-1.22878	H	-1.38520	2.83078	0.70645
	H	-5.33401	-1.88849	-1.35941	H	-4.85467	1.77620	2.01911
	H	-5.58868	-3.03323	-0.03021	H	-5.56779	2.59622	0.61592
	H	-3.99410	-3.80528	-2.10042	H	-3.60469	3.89428	2.00179
	H	-3.42842	-4.10488	-0.44784	H	-3.51212	3.87883	0.23056
	O	-2.98468	1.48131	-0.08790	O	-1.74647	-1.74704	0.81037
	C	-3.27517	2.71515	0.61269	C	-1.65272	-3.14775	0.39668
	C	-3.43181	1.57498	-1.46062	C	-2.42804	-1.65633	2.09518
	C	-3.64893	3.72014	-0.46909	C	-2.19576	-3.96862	1.56999
	H	-4.10267	2.52795	1.30468	H	-2.25175	-3.25522	-0.51115
	H	-2.39638	2.99473	1.19498	H	-0.60572	-3.36281	0.16472
	C	-4.29952	2.82633	-1.52675	C	-3.16183	-2.98592	2.25198
	H	-2.54796	1.65275	-2.10090	H	-1.67472	-1.50798	2.87720
	H	-3.96987	0.65594	-1.70547	H	-3.08282	-0.78434	2.06455
	H	-2.75041	4.19554	-0.87381	H	-1.38847	-4.24680	2.25628
	H	-4.31346	4.50123	-0.09203	H	-2.68488	-4.88561	1.22994
	H	-4.30497	3.26877	-2.52563	H	-3.35195	-3.22842	3.30143
	H	-5.33229	2.59407	-1.24804	H	-4.12078	-2.95850	1.72336
	Br	-1.91777	0.33760	2.87679	Br	-2.71455	-1.03779	-2.36260
	C	1.72176	-0.30912	3.15866	C	0.83334	-1.75480	-2.44017
	H	1.49482	-1.37934	3.19841	H	-0.06470	-2.35380	-2.58531
	H	2.71358	-0.12556	3.58777	H	0.92069	-1.02556	-3.24997
	H	0.95554	0.23492	3.70817	H	1.72588	-2.38504	-2.40526
	C	-0.06066	0.98283	-1.05694	C	0.78229	0.38478	1.07094
	C	0.21042	2.35851	-1.01378	C	0.88390	-0.62308	2.05383
	C	0.53149	0.30738	-2.13761	C	1.12113	1.68953	1.51879
	C	1.00793	3.02800	-1.95309	C	1.25855	-0.38469	3.38101
	C	1.33238	0.93178	-3.09838	C	1.53226	1.95785	2.83664
	C	1.56924	2.30632	-2.99896	C	1.59528	0.91649	3.76868
	H	1.18621	4.09824	-1.86543	H	1.30126	-1.20239	4.09897
	H	1.77717	0.38051	-3.92077	H	1.79503	2.96335	3.15209
	H	2.19242	2.79834	-3.74289	H	1.90877	1.12800	4.78959
	O	0.25843	-1.05607	-2.19976	O	0.98887	2.70236	0.59051
	C	0.77470	-1.79447	-3.28914	C	1.53248	3.98723	0.88595

	H	0.40436	-1.41422	-4.24955		H	0.98293	4.48349	1.69638
	H	1.87151	-1.78927	-3.30140		H	2.59438	3.92208	1.15293
	H	0.42851	-2.82228	-3.15842		H	1.42674	4.57427	-0.02876
	H	-0.21448	2.95844	-0.20612		H	0.66672	-1.65125	1.77111
INTca	C	5.18053	-2.49769	0.77150	**TS1ca**	C	5.27393	-2.40760	0.97280
	C	5.09868	-1.87656	-0.46452		C	5.13105	-1.99660	-0.33522
	C	4.13167	-2.36171	1.68730		C	4.30924	-2.04163	1.92836
	H	5.91314	-1.98093	-1.17877		H	5.87647	-2.27147	-1.07864
	H	4.18315	-2.84213	2.66104		H	4.41581	-2.35879	2.96260
	C	3.97624	-1.10800	-0.83030		C	4.02558	-1.21538	-0.74581
	C	3.02290	-1.59915	1.34163		C	3.22542	-1.27495	1.54723
	H	2.21200	-1.49138	2.05691		H	2.49022	-1.00045	2.29497
	C	2.92244	-0.97384	0.09491		C	3.04717	-0.85287	0.21328
	H	6.05786	-3.08752	1.02772		H	6.13121	-3.00945	1.26597
	C	3.90596	-0.47045	-2.13061		C	3.90913	-0.77763	-2.10822
	H	4.73684	-0.59564	-2.81993		H	4.67506	-1.06081	-2.82510
	C	2.81649	0.25629	-2.47121		C	2.84373	-0.02105	-2.47611
	C	1.65651	-0.18146	-0.23285		C	1.85190	-0.07051	-0.17797
	H	2.76576	0.72225	-3.45142		H	2.74118	0.31075	-3.50486
	C	1.69002	0.43406	-1.60739		C	1.81969	0.35071	-1.55582
	C	0.57772	1.13927	-2.03058		C	0.68468	1.05609	-2.02958
	O	-0.53333	1.25003	-1.39362		O	-0.41495	1.16305	-1.42192
	O	0.63374	1.77617	-3.23267		O	0.78286	1.62660	-3.24532
	H	-0.26696	2.12178	-3.40170		H	-0.10880	1.96635	-3.47822
	O	0.47881	-1.12778	-0.17773		O	0.41764	-1.28884	-0.07890
	Mg	-1.45831	-0.20878	-0.43438		Mg	-1.34820	-0.36570	-0.42889
	O	-2.85177	1.25955	0.15845		O	-2.75149	1.16887	0.02748
	C	-4.02131	1.53859	-0.66095		C	-3.86543	1.45362	-0.86102
	C	-2.41042	2.48299	0.81898		C	-2.34603	2.38673	0.71460
	C	-4.57112	2.84710	-0.11968		C	-4.44767	2.75886	-0.34563
	H	-3.70120	1.62695	-1.70309		H	-3.48096	1.54951	-1.88064
	H	-4.70043	0.69002	-0.57257		H	-4.54738	0.60363	-0.82328
	C	-3.29150	3.59421	0.26126		C	-3.19269	3.50328	0.11417
	H	-2.55420	2.34223	1.89406		H	-2.54771	2.24423	1.78018
	H	-1.34935	2.61822	0.60822		H	-1.27437	2.52360	0.56622
	H	-5.19164	2.66557	0.76336		H	-5.11794	2.57143	0.49907
	H	-5.17375	3.37359	-0.86306		H	-5.00676	3.28998	-1.11922
	H	-3.45562	4.38793	0.99332		H	-3.39871	4.29251	0.84054
	H	-2.83013	4.03576	-0.62679		H	-2.68086	3.95057	-0.74293
	O	-2.10967	-1.34950	1.23012		O	-2.18040	-1.35976	1.25442
	C	-1.58532	-2.65392	1.59471		C	-1.72694	-2.67186	1.67738
	C	-3.46511	-1.21224	1.75460		C	-3.49869	-1.09893	1.81225
	C	-2.35551	-3.03522	2.84552		C	-2.48680	-2.93939	2.96438
	H	-1.78052	-3.35201	0.77354		H	-1.98326	-3.39921	0.89900

	H	-0.50934	-2.55045	1.73492	H	-0.64341	-2.62582	1.78038
	C	-3.75274	-2.50089	2.52391	C	-3.85373	-2.32729	2.65038
	H	-3.47384	-0.32730	2.39428	H	-3.42349	-0.18984	2.41358
	H	-4.14455	-1.05897	0.91507	H	-4.19707	-0.92839	0.99164
	H	-1.93324	-2.53020	3.71961	H	-2.00910	-2.42211	3.80231
	H	-2.33807	-4.11239	3.02501	H	-2.53658	-4.00511	3.19866
	H	-4.35762	-2.31353	3.41354	H	-4.42227	-2.05806	3.54317
	H	-4.29057	-3.21073	1.88944	H	-4.45393	-3.02805	2.06327
	Br	-2.75785	-1.53614	-2.12955	Br	-2.58946	-1.62544	-2.23115
	C	0.67815	-2.31222	-0.97211	C	0.74877	-2.47190	-0.77910
	H	-0.29149	-2.79611	-1.08166	H	-0.14008	-3.10327	-0.88009
	H	1.05264	-2.04522	-1.96392	H	1.11178	-2.25086	-1.79183
	H	1.38092	-2.98460	-0.47567	H	1.52187	-3.03698	-0.24350
	C	1.41033	0.82586	0.89977	C	1.37812	0.89466	0.89936
	C	0.46925	0.62546	1.90492	C	1.93675	2.19456	0.94143
	C	2.24162	1.96497	1.00259	C	0.52807	0.53064	1.94305
	C	0.29740	1.52757	2.95806	C	1.59058	3.08189	1.96341
	C	2.06421	2.88057	2.04073	C	0.19249	1.40653	2.97622
	C	1.08956	2.66338	3.01585	C	0.71940	2.68908	2.97886
	H	-0.13765	-0.27147	1.89530	H	0.13428	-0.47671	1.95588
	H	-0.45043	1.33219	3.72211	H	2.00998	4.08097	1.98792
	H	2.69270	3.76124	2.11032	H	-0.47404	1.07736	3.76896
	H	0.97058	3.38260	3.82250	H	0.46931	3.39182	3.76993
	O	3.22159	2.08726	0.07143	O	2.83228	2.51718	-0.03175
	C	4.09992	3.19730	0.13860	C	3.43350	3.80234	-0.00733
	H	3.55991	4.14429	0.02563	H	2.68684	4.59738	-0.11260
	H	4.66316	3.20772	1.07889	H	4.00858	3.95939	0.91218
	H	4.79216	3.07692	-0.69489	H	4.10890	3.82938	-0.86275

CPLca				**2c**			
	C	6.91007	-1.29099	1.07116	C	5.96490	-2.04976	1.31429
	C	6.15034	-2.21728	0.40377	C	5.32105	-2.60040	0.23550
	C	6.33614	-0.05646	1.46027	C	5.47516	-0.85496	1.89650
	H	6.57933	-3.16971	0.10048	H	5.69091	-3.51620	-0.22042
	H	6.94135	0.67360	1.99178	H	5.99105	-0.42286	2.75030
	C	4.78983	-1.95340	0.09474	C	4.16096	-1.98747	-0.30833
	C	5.02366	0.22277	1.17356	C	4.35705	-0.24185	1.38967
	H	4.60025	1.17160	1.48456	H	3.99351	0.67491	1.84238
	C	4.20556	-0.71570	0.48198	C	3.66189	-0.78951	0.27469
	H	7.95108	-1.50049	1.30450	H	6.85221	-2.52580	1.72437
	C	3.99857	-2.90507	-0.59850	C	3.49154	-2.54390	-1.42956
	H	4.44420	-3.85163	-0.89544	H	3.87579	-3.45786	-1.87672
	C	2.69328	-2.63616	-0.88824	C	2.38025	-1.93782	-1.94198
	C	2.82788	-0.44513	0.18097	C	2.48688	-0.17016	-0.26281
	H	2.09107	-3.36531	-1.41776	H	1.87172	-2.36219	-2.80074
	C	2.09074	-1.40612	-0.49224	C	1.86111	-0.75040	-1.35281
	C	0.64896	-1.24364	-0.82660	C	0.60983	-0.17604	-1.92767
	O	-0.13611	-0.50306	-0.23090	O	-0.19241	0.52423	-1.34104
	O	0.25764	-2.01964	-1.82531	O	0.42357	-0.53858	-3.21426
	H	-0.73442	-1.95522	-1.92469	H	-0.43379	-0.15259	-3.50503
	O	-1.97067	-1.01123	2.04159	C	2.02105	1.11709	0.33600
	Mg	-2.23170	-0.44053	0.27877	C	1.19119	1.12290	1.46944
	O	-2.28484	1.49544	-0.48024	C	2.43731	2.33079	-0.19958
	C	-3.25725	1.92884	-1.45859	C	0.78771	2.33062	2.03836
	C	-1.17050	2.40511	-0.60580	C	2.03654	3.54591	0.35994
	C	-2.43007	2.33663	-2.68111	C	1.21182	3.53758	1.47783
	H	-3.94381	1.10176	-1.63133	H	0.14347	2.34848	2.91042
	H	-3.80575	2.77770	-1.03433	H	2.37023	4.48413	-0.07480
	C	-1.02233	2.63547	-2.11055	H	0.88997	4.47326	1.92842
	H	-1.42807	3.32867	-0.07494	O	0.82847	-0.10256	1.94372
	H	-0.31073	1.94154	-0.13035	C	-0.00267	-0.15775	3.09355
	H	-2.87163	3.20247	-3.17938	H	0.48082	0.30933	3.95885
	H	-2.38990	1.51793	-3.40200	H	-0.96959	0.32364	2.91017
	H	-0.69213	3.65490	-2.32196	H	-0.16155	-1.21673	3.29874
	H	-0.28267	1.94914	-2.52867	H	3.08653	2.32398	-1.07242
	O	-4.27669	-0.01760	0.77398	**MeOMg**			
	C	-5.16598	-1.14111	0.99275	**Br(THF)$_2$**	Mg	-3.15240	0.28100	-0.41792
	C	-4.44930	0.95558	1.84093		Br	-2.05064	-1.83792	-1.11142
	C	-6.26527	-0.59645	1.88948		O	-2.57125	0.61675	1.52730
	H	-5.50627	-1.48489	0.01560		C	-2.51278	-0.35756	2.61695
	H	-4.59943	-1.93815	1.48521		C	-2.02515	1.90417	1.96505
	C	-5.48437	0.36101	2.79288		C	-1.67557	0.31003	3.70379
	H	-3.48052	1.11464	2.31733		H	-3.53760	-0.54821	2.94703
	H	-4.79548	1.88568	1.37961		H	-2.07998	-1.27558	2.21907
						C	-1.96783	1.80236	3.48323

	H	-6.77617	-1.38896	2.44124	H	-1.03117	2.01565	1.52366
	H	-7.00807	-0.05391	1.29611	H	-2.67914	2.68439	1.57921
	H	-4.98382	-0.19669	3.58891	H	-0.61339	0.10176	3.55010
	H	-6.10972	1.13116	3.25022	H	-1.95153	-0.03839	4.70005
	Br	-2.91684	-1.87230	-1.77062	H	-1.20154	2.45395	3.90584
	C	-0.93436	-1.61419	2.73877	H	-2.93132	2.07502	3.92278
	H	-0.57505	-0.98537	3.57562	C	-6.14404	0.90296	-0.44289
	H	-1.24391	-2.57632	3.18682	O	-5.15525	-0.15246	-0.20536
	H	-0.04823	-1.83380	2.11449	C	-5.80340	-1.46662	-0.25172
	C	2.29390	0.88825	0.59643	C	-7.28868	-1.18209	-0.48292
	C	1.66907	1.06205	1.82742	C	-7.28062	0.19586	-1.16398
	C	2.54150	2.01717	-0.20430	H	-6.46029	1.29531	0.52869
	C	1.30104	2.32891	2.27996	H	-5.63531	1.68202	-1.00959
	C	2.18280	3.29106	0.24314	H	-5.34709	-2.02533	-1.07017
	C	1.56936	3.43974	1.48754	H	-5.60006	-1.97904	0.68963
	H	0.81427	2.44213	3.24459	H	-7.75629	-1.95733	-1.09148
	H	2.37772	4.16947	-0.36202	H	-7.82271	-1.12993	0.46957
	H	1.29574	4.43533	1.82820	H	-7.05447	0.10129	-2.22963
	O	3.14921	1.77510	-1.40098	H	-8.22791	0.72703	-1.05831
	C	3.48607	2.88431	-2.22242	O	-3.17010	1.95814	-1.22853
	H	2.59252	3.43591	-2.53513	C	-2.48081	2.83571	-2.05467
	H	4.17606	3.56400	-1.71055	H	-1.92314	2.32565	-2.85989
	H	3.97670	2.46737	-3.10214	H	-3.16456	3.54675	-2.54946
	H	1.47076	0.18878	2.44232	H	-1.74368	3.44509	-1.50095

Table S6 The optimized Cartesian geometries(Å) for the reaction of 1+2-MeO-Ph-MgBr(THF)$_2$→2c+MeO-MgBr(THF)$_2$ at CAM-B3LYP+IDSCRF/DZVP level(path b).

Species	Cartesian coordinates			Species	Cartesian coordinates		
1	C	-3.70978	0.27806	-0.02421	**2-MeOPh MgBr(THF)$_2$**	Mg	-0.28813	0.10206	0.39395
	C	-2.75273	1.27232	0.01877		Br	-1.17377	-0.87013	2.50453
	C	-3.32220	-1.08729	-0.05643		O	-1.95971	1.00083	-0.44204
	H	-3.04687	2.32026	0.03398		C	-3.26337	0.35770	-0.51429
	H	-4.08486	-1.86173	-0.10256		C	-2.05363	2.38679	-0.87322
	C	-1.36773	0.94765	0.03766		C	-4.25394	1.49711	-0.70330
	C	-1.98624	-1.43466	-0.03621		H	-3.25307	-0.32602	-1.36887
	H	-1.68917	-2.47813	-0.07741		H	-3.40289	-0.21106	0.40613
	C	-0.97770	-0.43032	0.02006		C	-3.43417	2.51305	-1.50284
	H	-4.76624	0.53805	-0.04026		H	-1.94586	3.02480	0.00933
	C	-0.35730	1.95035	0.06351		H	-1.23027	2.58153	-1.56214
	H	-0.64896	2.99861	0.07769		H	-4.54331	1.91460	0.26559
	C	0.97110	1.60285	0.05852		H	-5.15775	1.16990	-1.22167
	C	0.41435	-0.76889	0.05300		H	-3.82115	3.53174	-1.43183
	H	1.73337	2.37465	0.06235		H	-3.39905	2.23103	-2.55941

	C	1.38696	0.23449	0.05745	C	0.18079	-1.27226	-2.28544
	C	2.84343	-0.07909	0.03734	O	-0.37113	-1.46316	-0.95155
	O	3.36023	-1.16335	0.26651	C	-0.29576	-2.86685	-0.57261
	O	3.59707	1.00913	-0.27446	C	0.00722	-3.60666	-1.86700
	H	4.53877	0.71981	-0.25065	C	0.85826	-2.59019	-2.63214
	O	0.73317	-2.10295	0.00013	H	-0.65148	-1.04701	-2.95964
	C	0.94436	-2.73936	1.27720	H	0.86323	-0.42078	-2.25001
	H	1.81588	-2.31248	1.77991	H	0.50568	-2.97788	0.16311
	H	0.05244	-2.64224	1.90783	H	-1.24575	-3.13698	-0.11015
	H	1.12691	-3.79386	1.06032	H	0.52434	-4.55092	-1.68354
					H	-0.91779	-3.82076	-2.41083
					H	1.88725	-2.59559	-2.26168
					H	0.87776	-2.76774	-3.70956
					C	1.38987	1.37758	0.11000
					C	1.56687	2.75205	-0.08726
					C	2.57688	0.62967	0.17749
					C	2.82942	3.35044	-0.21197
					C	3.85367	1.17862	0.05856
					C	3.96950	2.55899	-0.13889
					H	0.69501	3.40498	-0.14128
					H	2.91800	4.42462	-0.36108
					H	4.75210	0.57185	0.11532
					H	4.95756	3.00449	-0.23213
					O	2.36500	-0.73201	0.37147
					C	3.49083	-1.56799	0.57570
					H	4.13650	-1.59815	-0.31013
					H	4.07979	-1.24080	1.44040
					H	3.10278	-2.56959	0.76856
COMcb	C	6.26044	1.15032	0.23083	**TScb**	C	-5.50210	1.09254	-0.74280
	C	5.98303	0.06079	-0.55718		C	-5.39754	-0.14564	-0.14692
	C	5.31057	1.61158	1.17563		C	-4.36735	1.69563	-1.32088
	H	6.70874	-0.29153	-1.28674		H	-6.27525	-0.62461	0.28161
	H	5.53952	2.48100	1.78659		H	-4.45629	2.66365	-1.80755
	C	4.74525	-0.62325	-0.43655		C	-4.15942	-0.82727	-0.09901
	C	4.10558	0.96969	1.31624		C	-3.14535	1.05930	-1.26580
	H	3.36640	1.32674	2.02631		H	-2.26471	1.52330	-1.69315
	C	3.79816	-0.16272	0.51635		C	-3.01262	-0.19974	-0.64399
	H	7.21138	1.66760	0.12967		H	-6.46331	1.59994	-0.77912
	C	4.43050	-1.75547	-1.23743		C	-4.06102	-2.15512	0.43301
	H	5.15785	-2.10935	-1.96397		H	-4.94696	-2.62357	0.85356
	C	3.22768	-2.38818	-1.10200		C	-2.88583	-2.83476	0.35142
	C	2.55228	-0.84515	0.64445		C	-1.72356	-0.86766	-0.56434
	H	2.98779	-3.24661	-1.72085		H	-2.81661	-3.85491	0.71599
	C	2.25913	-1.92740	-0.16448		C	-1.70870	-2.23243	-0.18596

	C	0.94848	-2.60832	-0.09597	C	-0.45248	-2.92570	-0.10426
	O	-0.12364	-2.10685	0.21930	O	0.66559	-2.38155	-0.17550
	O	1.01540	-3.89783	-0.45216	O	-0.52130	-4.24886	0.10961
	H	0.10702	-4.27615	-0.40215	H	0.39999	-4.58685	0.17901
	O	1.67239	-0.40346	1.58878	O	-0.75431	-0.41027	-1.48995
	Mg	-1.30262	-0.21684	0.26270	Mg	1.06280	-0.35101	-0.36846
	O	-2.75897	-1.44871	-0.65829	O	2.64173	-0.62813	1.03334
	C	-4.02583	-1.78957	-0.04000	C	4.04587	-0.54124	0.67973
	C	-2.60912	-2.14130	-1.92026	C	2.50256	-1.30295	2.31368
	C	-4.84516	-2.42820	-1.15202	C	4.77480	-0.61552	2.00975
	H	-3.83016	-2.48628	0.78077	H	4.29550	-1.38026	0.02423
	H	-4.44812	-0.87088	0.36911	H	4.18938	0.38502	0.12243
	C	-3.76797	-3.13071	-1.98266	C	3.92281	-1.63304	2.77271
	H	-2.65747	-1.39852	-2.72282	H	1.99063	-0.61518	2.98991
	H	-1.62601	-2.61604	-1.93423	H	1.87926	-2.18688	2.16780
	H	-5.34942	-1.66053	-1.74738	H	4.75995	0.35786	2.51064
	H	-5.60246	-3.11188	-0.76190	H	5.81511	-0.92734	1.89165
	H	-4.07658	-3.33364	-3.01052	H	4.02596	-1.55666	3.85731
	H	-3.48687	-4.07935	-1.51538	H	4.19591	-2.64978	2.47582
	O	-2.95218	1.26242	0.11636	O	1.69464	1.66273	-0.46298
	C	-3.16622	2.33717	1.06406	C	1.44473	2.47516	-1.64236
	C	-3.43501	1.65098	-1.19053	C	2.15890	2.49959	0.61755
	C	-3.52160	3.55516	0.22309	C	1.83899	3.90275	-1.26220
	H	-3.98483	2.04487	1.73010	H	2.05900	2.06183	-2.44417
	H	-2.25625	2.45359	1.65068	H	0.38895	2.37755	-1.90306
	C	-4.24318	2.92413	-0.96950	C	2.78542	3.69817	-0.07599
	H	-2.56992	1.81898	-1.83869	H	1.30489	2.78832	1.23728
	H	-4.02529	0.82430	-1.59412	H	2.85155	1.91219	1.22023
	H	-2.61086	4.06176	-0.10875	H	0.96196	4.47486	-0.94836
	H	-4.13770	4.27061	0.77321	H	2.30626	4.42974	-2.09702
	H	-4.25560	3.56078	-1.85735	H	2.84753	4.56942	0.58029
	H	-5.27782	2.68244	-0.70598	H	3.79386	3.45126	-0.42184
	Br	-1.81034	-0.45657	2.75222	Br	2.54144	-0.84879	-2.51005
	C	1.78725	-1.06193	2.85736	C	-0.96646	-0.89413	-2.83423
	H	1.60331	-2.13644	2.75335	H	-0.23645	-0.38176	-3.45716
	H	2.78269	-0.89885	3.28599	H	-0.79318	-1.97151	-2.88326
	H	1.01555	-0.63004	3.49151	H	-1.98425	-0.66014	-3.15436
	C	-0.09503	0.74957	-1.23773	C	-0.73765	0.15285	1.18176
	C	0.33089	2.07045	-1.01175	C	-1.04159	1.50932	1.42160
	C	0.31234	0.20831	-2.46299	C	-0.80812	-0.67326	2.30845
	C	1.09824	2.80537	-1.91842	C	-1.34442	2.00309	2.69536
	C	1.07742	0.90819	-3.40886	C	-1.08596	-0.21617	3.59854
	C	1.46980	2.21085	-3.12990	C	-1.35621	1.13475	3.78788
	H	1.41683	3.82223	-1.71102	H	-1.57225	3.05172	2.85640

	H	1.36579	0.43675	-4.34667	H	-1.11095	-0.90818	4.43761
	H	2.06779	2.77538	-3.84243	H	-1.59346	1.52012	4.77706
	O	-0.07543	2.60621	0.20378	O	-1.01956	2.34137	0.32372
	C	0.37232	3.89985	0.55444	C	-1.56992	3.63982	0.45198
	H	1.46759	3.95072	0.59876	H	-2.59713	3.60488	0.83265
	H	0.00941	4.66308	-0.14591	H	-0.96382	4.27986	1.10550
	H	-0.03252	4.10885	1.54671	H	-1.57848	4.06985	-0.55151
	H	0.03135	-0.81691	-2.71366	H	-0.65750	-1.74639	2.18291
INTcb	C	-5.58842	1.97001	-0.00909	**TS1cb**	C	-5.52032	-2.14487	-0.37894
	C	-5.34542	1.16767	-1.11163		C	-5.21118	-1.73863	0.89988
	C	-4.63848	2.05237	1.01679		C	-4.70940	-1.74486	-1.46135
	H	-6.08441	1.10194	-1.90783		H	-5.83477	-2.04527	1.73711
	H	-4.82058	2.67617	1.88817		H	-4.94930	-2.07020	-2.47046
	C	-4.15166	0.42766	-1.23529		C	-4.08219	-0.92270	1.15764
	C	-3.46223	1.32294	0.91046		C	-3.61261	-0.94281	-1.23276
	H	-2.72159	1.38024	1.70526		H	-2.98260	-0.64009	-2.06418
	C	-3.20029	0.51698	-0.20209		C	-3.27074	-0.51875	0.07013
	H	-6.51678	2.53263	0.05987		H	-6.38953	-2.77419	-0.55601
	C	-3.91000	-0.41290	-2.39322		C	-3.77121	-0.48942	2.48868
	H	-4.66906	-0.46686	-3.16888		H	-4.41136	-0.79563	3.31172
	C	-2.75177	-1.11132	-2.49491		C	-2.67354	0.28427	2.70232
	C	-1.86347	-0.22088	-0.26585		C	-2.07946	0.30135	0.28835
	H	-2.57462	-1.73747	-3.36557		H	-2.41567	0.60645	3.70683
	C	-1.72029	-1.06149	-1.50774		C	-1.82549	0.69408	1.62981
	C	-0.52712	-1.75803	-1.65304		C	-0.61918	1.42027	1.90343
	O	0.47706	-1.67105	-0.86537		O	0.35375	1.49216	1.12313
	O	-0.39814	-2.60204	-2.71033		O	-0.54196	2.02388	3.09875
	H	0.53499	-2.90018	-2.71209		H	0.37422	2.36605	3.19877
	O	-0.78591	0.81295	-0.24890		O	-0.61581	-1.08680	-0.04046
	Mg	1.20612	0.07208	-0.17209		Mg	1.13771	-0.19657	0.11974
	O	2.94480	-0.93662	0.55897		O	2.81557	1.11543	-0.32893
	C	4.32237	-0.68505	0.18080		C	4.17536	0.96056	0.13645
	C	2.87006	-2.33609	0.91616		C	2.65028	2.53321	-0.54648
	C	4.86983	-2.01381	-0.37036		C	4.43832	2.16487	1.04529
	H	4.31096	0.11677	-0.55538		H	4.23965	0.00547	0.65290
	H	4.86393	-0.36296	1.07669		H	4.83479	0.96113	-0.73990
	C	3.73608	-3.02797	-0.12364		C	3.37550	3.20324	0.61974
	H	3.27711	-2.45817	1.92823		H	3.11705	2.78722	-1.50668
	H	1.82235	-2.63097	0.89356		H	1.58428	2.74674	-0.58553
	H	5.78230	-2.29795	0.15879		H	5.45834	2.53418	0.91735
	H	5.10965	-1.93356	-1.43201		H	4.30959	1.88312	2.09186
	H	4.10055	-3.99692	0.22504		H	3.81383	4.15689	0.31685
	H	3.15061	-3.18329	-1.03231		H	2.67371	3.39439	1.43346
	O	1.71466	1.93033	.79870		O	2.01931	-1.69995	-1.16809

	C	0.78549	2.80611	1.49566	C	1.20540	-2.65098	-1.90375
	C	3.02788	2.55813	0.73844	C	3.40431	-2.13733	-1.17072
	C	1.66143	3.80638	2.23233	C	2.18752	-3.37924	-2.80586
	H	0.15316	3.30206	0.75481	H	0.73204	-3.33238	-1.19238
	H	0.15560	2.18904	2.13588	H	0.42472	-2.09204	-2.41884
	C	2.83046	3.97525	1.26038	C	3.42168	-3.47527	-1.90612
	H	3.70233	1.98211	1.38038	H	3.99082	-1.37615	-1.69464
	H	3.37426	2.50701	-0.29398	H	3.73864	-2.20628	-0.13425
	H	2.00700	3.39113	3.18455	H	2.40413	-2.78560	-3.70021
	H	1.12990	4.73841	2.43682	H	1.80788	-4.35324	-3.12309
	H	3.73538	4.36345	1.73274	H	4.35212	-3.62356	-2.45858
	H	2.55360	4.64814	0.44344	H	3.31002	-4.30120	-1.19768
	Br	2.27594	0.84986	-2.40389	Br	2.22504	-1.18766	2.27074
	C	-0.98339	1.83237	-1.24745	C	-0.94265	-2.21976	0.72267
	H	-0.04146	2.36965	-1.34583	H	-0.07378	-2.88358	0.82331
	H	-1.22692	1.38078	-2.21221	H	-1.24763	-1.95621	1.74587
	H	-1.77922	2.51314	-0.93869	H	-1.75782	-2.79272	0.25697
	C	-1.74890	-1.11253	0.99435	C	-1.83665	1.34392	-0.80416
	C	-0.73526	-1.18826	1.95800	C	-0.80007	1.54221	-1.73123
	C	-2.83136	-1.98896	1.15485	C	-2.89115	2.27341	-0.84021
	C	-0.83325	-2.07482	3.03647	C	-0.85984	2.60383	-2.64349
	C	-2.93919	-2.87777	2.21412	C	-2.95483	3.33124	-1.73563
	C	-1.93066	-2.91436	3.17119	C	-1.92576	3.49285	-2.65427
	H	-0.04620	-2.12759	3.77820	H	-0.05855	2.75631	-3.35503
	H	-3.80434	-3.53071	2.29125	H	-3.80013	4.01356	-1.71358
	H	-1.98565	-3.59491	4.01686	H	-1.93875	4.30663	-3.37470
	O	0.39899	-0.39163	1.82650	O	0.31080	0.71404	-1.74112
	C	1.21042	-0.20494	2.99401	C	1.09777	0.68671	-2.93984
	H	0.59294	0.13262	3.83097	H	0.45590	0.51034	-3.80731
	H	1.73588	-1.12330	3.26464	H	1.65812	1.61515	-3.07279
	H	1.94096	0.55632	2.73314	H	1.79980	-0.13320	-2.81564
	H	-3.62295	-1.96226	0.41194	H	-3.70124	2.14614	-0.12801
INT1cb	C	6.58711	-0.54751	1.06756	**TS2cb**	C	6.76418	-0.68622	0.61373
	C	5.97342	-1.54034	0.34855		C	6.06504	-1.58707	-0.14788
	C	5.91173	0.67591	1.29388		C	6.13796	0.50851	1.04371
	H	6.47577	-2.48967	0.17667		H	6.53248	-2.51174	-0.47886
	H	6.39278	1.45580	1.87875		H	6.69186	1.21585	1.65575
	C	4.66754	-1.35747	-0.17903		C	4.71690	-1.33611	-0.51643
	C	4.65464	0.88340	0.78453		C	4.83836	0.77834	0.69557
	H	4.15690	1.82691	0.97755		H	4.37691	1.69829	1.03697
	C	3.98992	-0.12088	0.02086		C	4.08397	-0.13085	-0.10135
	H	7.58535	-0.69789	1.47111		H	7.79551	-0.88704	0.89301
	C	4.02159	-2.39660	-0.89547		C	3.98549	-2.27376	-1.29010
	H	4.54348	-3.33806	-1.05018		H	4.47055	-3.19461	-1.60542

	C	2.75363	-2.22203	-1.36606	C	2.68740	-2.02541	-1.62654
	C	2.66724	0.06706	-0.51209	C	2.71775	0.12523	-0.46496
	H	2.24820	-3.02252	-1.89305	H	2.12474	-2.74575	-2.20857
	C	2.06418	-0.99336	-1.17480	C	2.04092	-0.82511	-1.21645
	C	0.66920	-0.91840	-1.66899	C	0.61590	-0.66540	-1.59179
	O	-0.07819	0.05080	-1.49261	O	-0.12876	0.21495	-1.14637
	O	0.26044	-1.97250	-2.35687	O	0.18410	-1.55016	-2.47489
	H	-0.72993	-1.91780	-2.42198	H	-0.80520	-1.47618	-2.54154
	O	-0.34418	-1.87448	0.64029	O	-0.68653	-1.95703	0.50412
	Mg	-1.38937	-0.37034	0.11519	Mg	-1.75319	-0.47311	-0.01045
	O	-2.39659	1.46566	-0.40624	O	-2.54194	1.49452	-0.12286
	C	-3.84232	1.53794	-0.37822	C	-3.99084	1.66024	-0.05108
	C	-1.98079	2.40757	-1.42042	C	-1.98494	2.60621	-0.87125
	C	-4.28843	1.84411	-1.81641	C	-4.33473	2.84880	-0.95486
	H	-4.20945	0.58601	0.00097	H	-4.43827	0.72833	-0.39825
	H	-4.12576	2.34302	0.30979	H	-4.26746	1.82546	0.99216
	C	-2.98404	2.21751	-2.55007	C	-3.08959	3.00119	-1.83303
	H	-2.03627	3.41607	-0.99222	H	-1.75525	3.41373	-0.16801
	H	-0.95158	2.18217	-1.68632	H	-1.06465	2.26343	-1.33764
	H	-5.01106	2.66377	-1.82588	H	-4.48967	3.75253	-0.35849
	H	-4.75481	0.96925	-2.27048	H	-5.24398	2.66436	-1.53082
	H	-3.08164	3.11938	-3.15929	H	-2.96013	4.01549	-2.21829
	H	-2.66131	1.39715	-3.19391	H	-3.11900	2.30570	-2.67633
	O	-2.57041	-0.25224	1.86051	O	-3.00361	-0.55078	1.69615
	C	-3.04069	-1.49451	2.45607	C	-3.45681	-1.87606	2.07181
	C	-2.66560	0.83050	2.81720	C	-2.60390	0.17901	2.89245
	C	-3.19204	-1.19382	3.94102	C	-2.73986	-2.16654	3.37706
	H	-3.99751	-1.74595	1.98840	H	-4.54538	-1.84420	2.19839
	H	-2.30640	-2.26406	2.22051	H	-3.20117	-2.55507	1.25898
	C	-3.54558	0.29556	3.93850	C	-2.77085	-0.79605	4.06058
	H	-1.65813	1.07015	3.17115	H	-1.56752	0.49540	2.75652
	H	-3.07653	1.70233	2.30633	H	-3.23954	1.06397	2.98139
	H	-2.24593	-1.36131	4.46499	H	-1.71275	-2.47290	3.16252
	H	-3.95740	-1.81764	4.40797	H	-3.23406	-2.94691	3.96059
	H	-3.34186	0.79192	4.89001	H	-1.98269	-0.67086	4.80631
	H	-4.60285	0.43811	3.69482	H	-3.73348	-0.64054	4.55643
	Br	-2.99365	-1.73246	-1.60575	Br	-3.10031	-1.38439	-2.05460
	C	-0.39328	-3.25699	0.63465	C	-0.71957	-3.33683	0.38740
	H	-0.38782	-3.68154	1.65873	H	-1.03532	-3.83814	1.32403
	H	-1.28750	-3.66116	0.12696	H	-1.40604	-3.69042	-0.40378
	H	0.48258	-3.69834	0.12149	H	0.27703	-3.75055	0.14370
	C	2.07007	1.43626	-0.36658	C	2.14375	1.45776	-0.08713
	C	1.01860	1.76609	0.49944	C	1.23739	1.69123	0.95992
	C	2.65801	2.48086	-1.08856	C	2.59500	2.56365	-0.81993

	C	0.60812	3.08398	0.66700		C	0.82736	2.99582	1.24978
	C	2.23686	3.80094	-0.94839		C	2.17168	3.85947	-0.54664
	C	1.21644	4.10852	-0.05294		C	1.28367	4.07571	0.50540
	H	-0.21158	3.28626	1.35131		H	0.13094	3.13563	2.07228
	H	2.71372	4.58457	-1.53130		H	2.53893	4.68947	-1.14423
	H	0.88544	5.13565	0.07741		H	0.94792	5.08095	0.74821
	O	0.29263	0.78699	1.16311		O	0.63356	0.72001	1.71379
	C	0.92897	0.22365	2.32403		C	1.40785	-0.37931	2.21725
	H	1.93308	-0.12691	2.07718		H	2.45038	-0.08316	2.36049
	H	0.97696	0.97912	3.11593		H	0.97395	-0.63304	3.18756
	H	0.32448	-0.63387	2.61202		H	1.31098	-1.23819	1.55269
	H	3.46992	2.24786	-1.77336		H	3.29723	2.39091	-1.63241
CPLc	C	7.10973	-0.86467	0.76113	**2c**	C	5.96490	-2.04976	1.31429
	C	6.33876	-1.91980	0.34593		C	5.32105	-2.60040	0.23550
	C	6.54940	0.43385	0.83165		C	5.47516	-0.85496	1.89650
	H	6.75973	-2.92048	0.27894		H	5.69091	-3.51620	-0.22042
	H	7.16675	1.26873	1.15340		H	5.99105	-0.42286	2.75030
	C	4.97771	-1.72790	-0.01090		C	4.16096	-1.98747	-0.30833
	C	5.23612	0.64575	0.49597		C	4.35705	-0.24185	1.38967
	H	4.82770	1.64840	0.55137		H	3.99351	0.67491	1.84238
	C	4.40276	-0.42841	0.07230		C	3.66189	-0.78951	0.27469
	H	8.15145	-1.01922	1.03121		H	6.85221	-2.52580	1.72437
	C	4.18242	-2.81050	-0.46675		C	3.49154	-2.54390	-1.42956
	H	4.62331	-3.80242	-0.53276		H	3.87579	-3.45786	-1.87672
	C	2.88119	-2.60873	-0.82506		C	2.38025	-1.93782	-1.94198
	C	3.02284	-0.23414	-0.27350		C	2.48688	-0.17016	-0.26281
	H	2.27615	-3.43664	-1.17690		H	1.87172	-2.36219	-2.80074
	C	2.28557	-1.31942	-0.71799		C	1.86111	-0.75040	-1.35281
	C	0.83047	-1.24179	-1.03040		C	0.60983	-0.17604	-1.92767
	O	0.04261	-0.44493	-0.52141		O	-0.19241	0.52423	-1.34104
	O	0.43804	-2.17351	-1.88715		O	0.42357	-0.53858	-3.21426
	H	-0.55860	-2.16904	-1.94375		H	-0.43379	-0.15259	-3.50503
	O	-1.34494	-0.73751	1.91823		C	2.02105	1.11709	0.33600
	Mg	-2.02045	-0.50048	0.19209		C	1.19119	1.12290	1.46944
	O	-2.29474	1.34913	-0.68130		C	2.43731	2.33079	-0.19958
	C	-3.25749	1.61478	-1.73791		C	0.78771	2.33062	2.03836
	C	-1.38411	2.47440	-0.52893		C	2.03654	3.54591	0.35994
	C	-3.13335	3.10605	-2.01406		C	1.21182	3.53758	1.47783
	H	-2.98404	1.00998	-2.60730		H	0.14347	2.34848	2.91042
	H	-4.23908	1.29908	-1.38051		H	2.37023	4.48413	-0.07480
	C	-1.65121	3.36550	-1.73310		H	0.88997	4.47326	1.92842
	H	-1.62729	2.97451	0.41400		O	0.82847	-0.10256	1.94372
	H	-0.37130	2.07970	-0.48077		C	-0.00267	-0.15775	3.09355
	H	-3.76159	3.67797	-1.32405		H	0.48082	0.30933	3.95885

	H	-3.42955	3.35549	-3.03531		H	-0.96959	0.32364	2.91017
	H	-1.42851	4.41324	-1.52153		H	-0.16155	-1.21673	3.29874
	H	-1.03796	3.04911	-2.58183		H	3.08653	2.32398	-1.07242
	O	-4.08185	-0.26843	0.81058					
	C	-5.05001	-1.34083	0.95298					
	C	-4.43852	0.84344	1.66732					
	C	-5.94540	-0.93400	2.11805					
	H	-5.60272	-1.41916	0.01229					
	H	-4.50832	-2.27331	1.11956					
	C	-5.88732	0.59447	2.06288					
	H	-3.76863	0.84233	2.53266					
	H	-4.28682	1.76466	1.10070					
	H	-5.53143	-1.29654	3.06346					
	H	-6.95722	-1.33163	2.01227					
	H	-6.14115	1.07131	3.01225					
	H	-6.56450	0.97746	1.29316					
	Br	-2.72912	-2.19993	-1.61736					
	C	-1.83652	-1.10428	3.16101					
	H	-1.30386	-1.98011	3.57369					
	H	-1.72878	-0.29516	3.90767					
	H	-2.90977	-1.37688	3.15144					
	C	2.48879	1.16098	-0.24450					
	C	2.26917	1.88032	0.94160					
	C	2.35405	1.83576	-1.46436					
	C	1.95320	3.24145	0.88150					
	C	2.04039	3.18942	-1.52460					
	C	1.85052	3.89826	-0.33878					
	H	1.80017	3.76927	1.81910					
	H	1.95758	3.68681	-2.48723					
	H	1.61381	4.95921	-0.36280					
	O	2.43582	1.36615	2.19722					
	C	1.83741	0.10083	2.52979					
	H	2.48682	-0.72823	2.23572					
	H	1.74350	0.10387	3.61786					
	H	0.84439	-0.01569	2.08396					
	H	2.53539	1.28454	-2.38448					

Table S7 The optimized Cartesian geometries(Å) for the reaction of **1**+2,6-diMeO-Ph-MgBr(THF)$_2$→**2d**+MeO-MgBr(THF)$_2$ at CAM-B3LYP+IDSCRF/DZVP level.

Species	Cartesian coordinates			Species	Cartesian coordinates		
1	C	-3.70978	0.27806	-0.02421	**2,6-diMeOPhMgBr(THF)$_2$**	Mg	0.38887	-0.08650	0.45162
	C	-2.75273	1.27232	0.01877		Br	1.56460	-0.37599	2.62170
	C	-3.32220	-1.08729	-0.05643		O	1.53738	-1.04981	-0.96255
	H	-3.04687	2.32026	0.03398		C	2.99379	-1.04360	-0.96661

	H	-4.08486	-1.86173	-0.10256		C	1.03174	-1.93647	-2.00173
	C	-1.36773	0.94765	0.03766		C	3.39203	-2.18602	-1.89075
	C	-1.98624	-1.43466	-0.03621		H	3.32327	-0.07202	-1.34796
	H	-1.68917	-2.47813	-0.07741		H	3.33130	-1.15975	0.06431
	C	-0.97770	-0.43032	0.02006		C	2.23329	-2.21925	-2.89041
	H	-4.76624	0.53805	-0.04026		H	0.64892	-2.83749	-1.51742
	C	-0.35730	1.95035	0.06351		H	0.20911	-1.42531	-2.50458
	H	-0.64896	2.99861	0.07769		H	3.44421	-3.12609	-1.33372
	C	0.97110	1.60285	0.05852		H	4.36228	-2.00987	-2.35993
	C	0.41435	-0.76889	0.05300		H	2.13853	-3.17619	-3.40815
	H	1.73337	2.37465	0.06235		H	2.35048	-1.43170	-3.64112
	C	1.38696	0.23449	0.05745		C	0.89131	2.17478	-1.55630
	C	2.84343	-0.07909	0.03734		O	1.09551	1.75570	-0.17720
	O	3.36023	-1.16335	0.26651		C	1.18272	2.91892	0.68753
	O	3.59707	1.00913	-0.27446		C	1.60510	4.04460	-0.24073
	H	4.53877	0.71981	-0.25065		C	0.84460	3.70067	-1.52493
	O	0.73317	-2.10295	0.00013		H	1.73698	1.79556	-2.13720
	C	0.94436	-2.73936	1.27720		H	-0.03609	1.72652	-1.91837
	H	1.81588	-2.31248	1.77991		H	0.19539	3.10009	1.12459
	H	0.05244	-2.64224	1.90783		H	1.89647	2.68314	1.47724
	H	1.12691	-3.79386	1.06032		H	1.34617	5.02683	0.16066
						H	2.68595	4.01282	-0.40800
						H	-0.19047	4.04478	-1.45653
						H	1.29222	4.13882	-2.41955
						C	-1.68263	-0.28658	0.06341
						C	-2.62314	0.72194	-0.15534
						C	-2.18507	-1.58884	0.07517
						C	-3.98721	0.46556	-0.36112
						C	-3.53448	-1.90720	-0.12292
						C	-4.42369	-0.85726	-0.34170
						H	-4.70676	1.25889	-0.53051
						H	-3.90145	-2.92779	-0.10791
						H	-5.47828	-1.07315	-0.49741
						O	-1.22157	-2.56004	0.30480
						C	-1.63292	-3.91247	0.40111
						H	-2.34970	-4.05692	1.21793
						H	-2.07837	-4.26766	-0.53595
						H	-0.73298	-4.49271	0.61156
						O	-2.11624	2.01187	-0.15390
						C	-3.02661	3.08643	-0.30425
						H	-3.53089	3.06014	-1.27780
						H	-3.78120	3.09149	0.49114
						H	-2.43646	4.00228	-0.23583
COMd	C	6.22449	1.16409	0.24387	**TSd**	C	-5.45483	1.61448	-0.54181

	C	5.91920	-0.05132	-0.31778	C	-5.36944	0.24873	-0.36839
	C	5.28563	1.82632	1.07265	C	-4.30563	2.34966	-0.88500
	H	6.63690	-0.55851	-0.95872	H	-6.26066	-0.33147	-0.13840
	H	5.53691	2.79233	1.50307	H	-4.37644	3.42065	-1.05832
	C	4.66334	-0.66577	-0.07464	C	-4.13878	-0.42950	-0.51758
	C	4.06271	1.25640	1.32603	C	-3.08730	1.70947	-1.00353
	H	3.33063	1.76444	1.94552	H	-2.19939	2.27210	-1.26284
	C	3.72728	-0.00237	0.76199	C	-2.97121	0.32181	-0.79515
	H	7.18947	1.62619	0.05028	H	-6.41229	2.11923	-0.43531
	C	4.31961	-1.92585	-0.63849	C	-4.07233	-1.86315	-0.47614
	H	5.03903	-2.43504	-1.27517	H	-4.97213	-2.42964	-0.25106
	C	3.10112	-2.48825	-0.38733	C	-2.91539	-2.49180	-0.81562
	C	2.46135	-0.61174	1.01170	C	-1.67273	-0.35964	-0.88570
	H	2.84053	-3.44772	-0.82156	H	-2.87529	-3.57589	-0.85713
	C	2.14293	-1.82710	0.43372	C	-1.71916	-1.76936	-1.09660
	C	0.82059	-2.45185	0.63834	C	-0.49223	-2.47866	-1.29105
	O	-0.22831	-1.88007	0.91053	O	0.64712	-1.97902	-1.21114
	O	0.84823	-3.78393	0.50033	O	-0.59984	-3.79465	-1.54895
	H	-0.06244	-4.12491	0.65547	H	0.31289	-4.14782	-1.63731
	O	1.59187	0.04072	1.83490	O	-0.67984	0.37938	-1.59073
	Mg	-1.32018	-0.05389	0.39349	Mg	1.13470	-0.08365	-0.55211
	O	-2.82179	-1.43385	-0.23280	O	2.67503	-0.97865	0.62646
	C	-4.12075	-1.49714	0.41300	C	4.08796	-0.73709	0.39625
	C	-2.67371	-2.52970	-1.16873	C	2.50802	-2.13503	1.49154
	C	-4.92674	-2.48912	-0.41315	C	4.79103	-1.44291	1.54364
	H	-3.97300	-1.83972	1.44105	H	4.35792	-1.15829	-0.57573
	H	-4.52800	-0.48575	0.43528	H	4.23790	0.34242	0.35798
	C	-3.84547	-3.46195	-0.88835	C	3.91237	-2.68138	1.73102
	H	-2.70813	-2.11768	-2.18198	H	2.03588	-1.78806	2.41541
	H	-1.69330	-2.97819	-1.01127	H	1.83618	-2.83341	0.99472
	H	-5.39432	-1.98934	-1.26746	H	4.78019	-0.82013	2.44415
	H	-5.71198	-2.96815	0.17610	H	5.82936	-1.68189	1.30231
	H	-4.13400	-4.03438	-1.77296	H	4.00884	-3.13637	2.71941
	H	-3.59198	-4.16690	-0.09038	H	4.16229	-3.43772	0.98099
	O	-2.91402	1.36383	-0.22716	O	1.88344	1.73123	0.26603
	C	-3.20355	2.63152	0.40917	C	1.90171	2.98575	-0.46963
	C	-3.28892	1.41193	-1.62325	C	2.20584	1.97622	1.65164
	C	-3.45780	3.60683	-0.73132	C	2.31335	4.05975	0.53802
	H	-4.08916	2.50192	1.04096	H	2.62094	2.86574	-1.28086
	H	-2.35339	2.89234	1.03719	H	0.90715	3.14626	-0.89048
	C	-4.08409	2.70162	-1.79420	C	3.02520	3.25575	1.62959
	H	-2.37213	1.40947	-2.22038	H	1.27909	2.09967	2.22034
	H	-3.86368	0.51069	-1.85225	H	2.73637	1.10137	2.02827
	H	-2.51110	4.01957	-1.09176	H	1.43415	4.56005	0.95296

	H	-4.10597	4.43362	-0.43041	H	2.95029	4.82015	0.08071
	H	-4.00376	3.10063	-2.80813	H	3.03316	3.75852	2.59955
	H	-5.14330	2.53298	-1.57518	H	4.05907	3.04100	1.34172
	Br	-1.97466	0.33280	2.84451	Br	2.65190	0.32655	-2.67808
	C	1.63665	-0.37685	3.20461	C	-0.86388	0.39244	-3.02105
	H	0.87341	0.20258	3.72107	H	-0.13232	1.09787	-3.40994
	H	1.39630	-1.44117	3.29466	H	-0.67220	-0.59697	-3.44206
	H	2.62787	-0.18498	3.63164	H	-1.87915	0.71376	-3.26323
	C	0.03914	0.64061	-1.13963	C	-0.78250	-0.07224	1.01155
	C	0.45811	1.97434	-1.14567	C	-1.09270	1.18114	1.58973
	C	0.54994	-0.13679	-2.18088	C	-0.95600	-1.16928	1.88456
	C	1.31200	2.52446	-2.11230	C	-1.55032	1.33920	2.90040
	C	1.40718	0.35283	-3.17777	C	-1.42192	-1.05323	3.20191
	C	1.77823	1.69335	-3.12794	C	-1.71954	0.20844	3.69524
	H	1.62100	3.56385	-2.09088	H	-1.77014	2.31584	3.31546
	H	1.79009	-0.27569	-3.97420	H	-1.54417	-1.91979	3.84138
	H	2.44330	2.09564	-3.88903	H	-2.07797	0.31758	4.71619
	O	0.14919	-1.46835	-2.16926	O	-0.60983	-2.39344	1.37695
	C	0.58873	-2.31148	-3.21562	C	-1.00263	-3.56519	2.07237
	H	0.25166	-1.95309	-4.19624	H	-0.45334	-3.67873	3.01429
	H	1.68105	-2.41052	-3.22717	H	-2.07932	-3.56682	2.27441
	H	0.14769	-3.29292	-3.02730	H	-0.76019	-4.40158	1.41487
	O	-0.04324	2.74348	-0.10504	O	-0.90379	2.27288	0.77982
	C	0.38297	4.08740	0.00512	C	-1.38136	3.53324	1.21749
	H	1.47073	4.15848	0.12838	H	-2.45139	3.49877	1.45008
	H	0.08344	4.68525	-0.86501	H	-0.83004	3.89581	2.09342
	H	-0.10164	4.49172	0.89608	H	-1.21966	4.22483	0.38837
INTd	C	-5.01760	2.79435	0.13083	**TS1d**	C	-4.89358	-3.00599	-0.44057
	C	-4.81421	2.12774	-1.06922		C	-4.66316	-2.55629	0.84266
	C	-4.14820	2.57538	1.20420		C	-4.13055	-2.49953	-1.51012
	H	-5.49273	2.29564	-1.90301		H	-5.25114	-2.94552	1.67149
	H	-4.29833	3.09003	2.14945		H	-4.30535	-2.85678	-2.52194
	C	-3.74451	1.22902	-1.23860		C	-3.66721	-1.58903	1.11276
	C	-3.08683	1.68948	1.04841		C	-3.15638	-1.55241	-1.26528
	H	-2.40623	1.51932	1.87927		H	-2.55785	-1.17021	-2.08745
	C	-2.86998	1.01794	-0.15516		C	-2.90117	-1.08334	0.03751
	H	-5.85244	3.48312	0.23528		H	-5.66291	-3.75192	-0.62731
	C	-3.54943	0.52380	-2.49203		C	-3.44350	-1.10653	2.44703
	H	-4.24486	0.70555	-3.30708		H	-4.05144	-1.49391	3.26051
	C	-2.51606	-0.34237	-2.63547		C	-2.46251	-0.19506	2.67696
	C	-1.64384	0.11333	-0.27610		C	-1.83611	-0.10066	0.27118
	H	-2.37719	-0.86262	-3.57961		H	-2.26738	0.15787	3.68543
	C	-1.55903	-0.59258	-1.60412		C	-1.65087	0.31991	1.62086
	C	-0.45819	-1.41054	-1.80195		C	-0.55832	1.19097	1.90796

	O	0.52411	-1.54566	-0.99105	O	0.40014	1.41179	1.13015
	O	-0.38755	-2.13523	-2.95446	O	-0.55142	1.77602	3.11847
	H	0.50230	-2.52708	-2.96311	H	0.31809	2.22152	3.22122
	O	-0.44838	1.00966	-0.14691	O	-0.22953	-1.25835	-0.03232
	Mg	1.43570	0.04056	-0.14308	Mg	1.39902	-0.13963	0.13722
	O	3.01978	-1.22635	0.50551	O	2.86805	1.38995	-0.34965
	C	4.41676	-1.15455	0.12738	C	4.21911	1.48099	0.15716
	C	2.75703	-2.62201	0.78433	C	2.47298	2.75272	-0.61837
	C	4.73352	-2.47860	-0.58574	C	4.24818	2.74136	1.02785
	H	4.53618	-0.27944	-0.50813	H	4.42634	0.56644	0.70871
	H	5.00632	-1.03452	1.04255	H	4.89636	1.56557	-0.70123
	C	3.50325	-3.36910	-0.31153	C	3.03468	3.56780	0.54463
	H	3.15740	-2.85440	1.77870	H	2.92030	3.05429	-1.57411
	H	1.67873	-2.76927	0.77010	H	1.38818	2.78185	-0.69273
	H	5.64995	-2.91715	-0.18528	H	5.19286	3.27613	0.90588
	H	4.87619	-2.32271	-1.65617	H	4.14428	2.47677	2.08167
	H	3.77253	-4.38046	0.00032	H	3.30949	4.57586	0.22579
	H	2.87012	-3.43785	-1.19800	H	2.28526	3.65070	1.33342
	O	2.17613	1.76228	0.91988	O	2.49947	-1.53221	-1.10416
	C	1.37754	2.71122	1.68264	C	1.87547	-2.67366	-1.74591
	C	3.57279	2.17798	0.93189	C	3.94384	-1.66028	-1.18075
	C	2.38047	3.49442	2.51388	C	2.92622	-3.18451	-2.71673
	H	0.85029	3.36245	0.98153	H	1.64107	-3.42179	-0.98327
	H	0.64469	2.14823	2.25955	H	0.94442	-2.32965	-2.19532
	C	3.58571	3.55868	1.57422	C	4.21424	-2.97193	-1.91751
	H	4.13230	1.45024	1.52787	H	4.32131	-0.79364	-1.73181
	H	3.93451	2.16212	-0.09625	H	4.34055	-1.64496	-0.16423
	H	2.63272	2.95103	3.42981	H	2.93098	-2.58292	-3.63172
	H	1.99555	4.47777	2.79168	H	2.75800	-4.22810	-2.99260
	H	4.52774	3.75627	2.08949	H	5.10774	-2.91043	-2.54261
	H	3.43812	4.33369	0.81690	H	4.35376	-3.78829	-1.20318
	Br	2.60011	0.82679	-2.34780	Br	2.62851	-0.96454	2.28923
	C	-0.50185	2.13591	-1.04519	C	-0.39895	-2.41803	0.74701
	H	0.50506	2.54597	-1.10057	H	0.56375	-2.92267	0.89374
	H	-0.80103	1.81637	-2.04580	H	-0.78342	-2.18671	1.74996
	H	-1.19517	2.88908	-0.66642	H	-1.08877	-3.12517	0.26518
	C	-1.64791	-0.90066	0.89752	C	-1.74813	0.97740	-0.81088
	C	-0.66387	-1.12661	1.87089	C	-0.75391	1.27660	-1.75395
	C	-2.80270	-1.72236	0.98361	C	-2.90513	1.80613	-0.84096
	C	-0.83810	-2.05797	2.90130	C	-0.91992	2.29957	-2.69679
	C	-2.98720	-2.65030	2.00804	C	-3.07597	2.82338	-1.77858
	C	-2.00103	-2.80527	2.97056	C	-2.07669	3.05821	-2.71076
	H	-0.06824	-2.21689	3.64323	H	-0.14268	2.52026	-3.41581
	H	-3.88609	-3.25151	2.05565	H	-3.97200	3.43159	-1.78437

	H	-2.13218	-3.52526	3.77317		H	-2.19412	3.84907	-3.44690
	O	-3.72521	-1.55310	0.00628		O	-3.84499	1.54655	0.10461
	C	-4.94572	-2.27590	0.06489		C	-5.07370	2.25459	0.07314
	H	-4.77541	-3.35507	-0.01105		H	-4.92488	3.32607	0.24714
	H	-5.49881	-2.05344	0.98352		H	-5.59791	2.10556	-0.87720
	H	-5.52593	-1.94256	-0.79536		H	-5.67181	1.83916	0.88432
	O	0.53963	-0.43272	1.80040		O	0.44109	0.57714	-1.74944
	C	1.35486	-0.40211	2.98310		C	1.20644	0.58095	-2.96278
	H	0.76425	-0.06420	3.83774		H	0.56856	0.31968	-3.81108
	H	1.79077	-1.38091	3.19066		H	1.67930	1.55088	-3.13443
	H	2.15472	0.30306	2.77648		H	1.97996	-0.16908	-2.82670
CPLd	C	-6.84782	-1.42567	-0.93711	**2d**	C	6.00515	-1.99818	1.27171
	C	-6.05060	-2.32501	-0.27759		C	5.32914	-2.58262	0.23101
	C	-6.34274	-0.14374	-1.26454		C	5.53390	-0.78355	1.82756
	H	-6.42899	-3.30980	-0.01265		H	5.68348	-3.51451	-0.20414
	H	-6.98098	0.56968	-1.77976		H	6.07442	-0.32443	2.65154
	C	-4.71775	-1.98856	0.08018		C	4.15642	-1.98348	-0.30094
	C	-5.05680	0.20375	-0.93667		C	4.40254	-0.18544	1.33255
	H	-4.69054	1.19143	-1.19290		H	4.05194	0.74579	1.76573
	C	-4.19664	-0.70826	-0.26054		C	3.67680	-0.76509	0.25407
	H	-7.86778	-1.68979	-1.20543		H	6.90284	-2.46289	1.67213
	C	-3.89897	-2.90480	0.78762		C	3.45225	-2.57491	-1.38186
	H	-4.29729	-3.88315	1.04633		H	3.81784	-3.50709	-1.80656
	C	-2.62943	-2.55762	1.15037		C	2.33193	-1.97862	-1.88515
	C	-2.84529	-0.37170	0.08668		C	2.49376	-0.15402	-0.27507
	H	-2.00856	-3.25461	1.70174		H	1.79925	-2.43127	-2.71348
	C	-2.09009	-1.29052	0.79480		C	1.83888	-0.76174	-1.33335
	C	-0.67786	-1.03837	1.18915		C	0.60362	-0.17301	-1.92699
	O	0.09915	-0.28640	0.59980		O	-0.06989	0.72334	-1.45524
	O	-0.29999	-1.75513	2.23820		O	0.26617	-0.75598	-3.09817
	H	0.68023	-1.63680	2.37941		H	-0.56117	-0.32246	-3.40702
	O	1.49930	-1.43864	-1.53776		C	2.03547	1.12973	0.33439
	Mg	2.15924	-0.54412	-0.03568		C	1.18286	1.12499	1.44368
	O	2.38688	1.49736	0.12993		C	2.48306	2.35521	-0.16937
	C	3.28505	2.13894	1.07545		C	0.78144	2.32010	2.04645
	C	1.48462	2.47611	-0.45915		C	2.08961	3.56109	0.41963
	C	3.17361	3.62446	0.76875		C	1.24163	3.52380	1.52152
	H	2.94384	1.90025	2.08698		H	0.12054	2.32550	2.90513
	H	4.28028	1.71639	0.92754		H	2.43022	4.51503	0.03493
	C	1.71137	3.75577	0.33437		H	0.93178	4.45738	1.98436
	H	1.76184	2.59155	-1.51179		O	3.30961	2.27594	-1.25227
	H	0.47245	2.08232	-0.39016		C	3.81482	3.48439	-1.80210
	H	3.84506	3.89826	-0.05108		H	3.00539	4.12453	-2.16961
	H	3.42276	4.23868	1.63685		H	4.41472	4.03617	-1.07018

	H	1.51788	4.64652	-0.26674		H	4.44900	3.19038	-2.63887
	H	1.05234	3.78230	1.20700		O	0.78999	-0.10854	1.87071
	O	4.21856	-0.49374	-0.69782		C	-0.08086	-0.18765	2.98988
	C	5.06091	-1.67597	-0.64435		H	0.38003	0.24109	3.88652
	C	4.58037	0.32401	-1.83621		H	-1.03271	0.31644	2.79024
	C	5.87464	-1.66384	-1.93396		H	-0.26360	-1.25016	3.15270
	H	5.69055	-1.59395	0.24614					
	H	4.41734	-2.55149	-0.54161					
	C	5.95500	-0.17109	-2.26311					
	H	3.83052	0.18035	-2.62119					
	H	4.56743	1.36829	-1.51756					
	H	5.34424	-2.20065	-2.72534					
	H	6.85434	-2.12836	-1.80145					
	H	6.15362	0.02848	-3.31852					
	H	6.73526	0.31314	-1.66797					
	Br	2.88070	-1.50788	2.24795					
	C	1.96200	-2.23637	-2.57141					
	H	2.85151	-1.82384	-3.08574					
	H	2.24163	-3.25329	-2.23835					
	H	1.19277	-2.36794	-3.35429					
	C	-2.35986	0.99609	-0.26557					
	C	-2.13218	1.40251	-1.58494					
	C	-2.28148	1.96773	0.75428					
	C	-1.88226	2.74816	-1.88498					
	C	-2.03162	3.30711	0.46248					
	C	-1.84755	3.68715	-0.86826					
	H	-1.72387	3.02483	-2.92305					
	H	-1.98869	4.05458	1.24580					
	H	-1.65865	4.73176	-1.10286					
	O	-2.49463	1.50086	2.01762					
	C	-2.45649	2.42602	3.09492					
	H	-1.47292	2.90121	3.17727					
	H	-3.22841	3.19568	2.98678					
	H	-2.65140	1.84355	3.99561					
	O	-2.22426	0.56825	-2.66272					
	C	-1.55799	-0.70691	-2.63824					
	H	-2.21316	-1.47952	-2.22740					
	H	-1.34790	-0.94329	-3.68375					
	H	-0.61679	-0.67465	-2.08048					

Table S8 The obtained frequencies for the stationary points of reactions (a)-(d) at CAM-B3LYP+IDSCRF/DZVP level.

Species	Frequencies (cm^{-1})
1	28 70 109 133 152 188 197 236 308 329 339 410 449 489 495 545 579 593 616 619 699 720 746 762 796 837 867 884 910 922 1001 1013 1027 1034 1055 1128 1166 1174 1178 1183 1214 1217 1243 1261 1297 1361 1395 1427 1446 1472 1492 1505 1519 1520 1568 1651 1681 1710 1802 3071 3169 3203 3205 3212 3216 3227 3245 3253 3557
EtMgBr $(THF)_2$	22 29 31 40 47 51 69 73 81 96 131 141 149 162 178 226 248 258 261 289 333 508 525 584 585 698 699 869 870 887 888 904 913 917 935 936 943 950 951 984 985 1016 1061 1063 1087 1088 1178 1179 1201 1213 1214 1221 1221 1267 1277 1278 1285 1287 1337 1338 1374 1374 1396 1398 1419 1420 1422 1477 1504 1506 1514 1515 1519 1531 1535 1538 1546 1548 2999 3014 3039 3069 3094 3097 3099 3100 3101 3102 3103 3106 3106 3165 3165 3170 3171 3180 3181 3185 3194
COMa	15 24 30 38 46 47 59 63 69 77 82 90 91 95 101 103 113 123 127 136 141 143 147 153 174 195 197 213 218 234 255 260 264 271 309 324 336 359 418 445 451 493 504 518 548 582 586 589 602 619 626 695 699 709 722 749 764 794 835 857 863 865 884 890 892 908 909 919 923 935 935 938 941 952 953 981 986 1000 1012 1016 1017 1027 1056 1059 1063 1105 1107 1113 1168 1176 1178 1178 1183 1194 1196 1211 1212 1216 1223 1224 1226 1245 1254 1270 1275 1276 1280 1282 1296 1333 1334 1368 1369 1375 1389 1390 1412 1414 1414 1420 1430 1450 1475 1485 1494 1498 1504 1504 1509 1516 1517 1519 1524 1532 1535 1542 1550 1553 1568 1655 1682 1712 1770 2967 2999 3003 3065 3087 3092 3092 3096 3096 3097 3105 3108 3110 3115 3156 3157 3162 3164 3175 3176 3179 3180 3183 3206 3214 3217 3228 3242 3243 3248 3523
TSa	-333i 21 32 37 42 51 60 67 76 79 85 90 100 100 111 115 129 137 145 148 159 161 162 174 183 198 212 222 253 262 266 272 273 314 328 337 348 359 381 424 447 484 504 526 557 569 585 588 606 617 624 693 695 697 719 749 756 790 821 835 863 867 877 889 892 900 905 913 919 935 938 944 946 952 954 982 986 993 1000 1015 1021 1043 1060 1061 1063 1088 1094 1099 1140 1165 1171 1177 1178 1181 1183 1205 1212 1214 1220 1221 1224 1236 1243 1271 1275 1278 1283 1284 1292 1335 1336 1353 1371 1372 1391 1392 1394 1412 1416 1418 1424 1462 1473 1481 1493 1496 1503 1504 1505 1510 1515 1515 1516 1525 1535 1542 1548 1553 1556 1614 1674 1689 1708 2990 3020 3068 3088 3095 3097 3097 3099 3100 3103 3106 3119 3120 3135 3160 3161 3166 3167 3176 3182 3183 3185 3186 3201 3211 3213 3224 3230 3237 3238 3558
INTa	15 23 31 38 44 59 68 72 77 80 87 97 102 107 112 118 144 148 156 157 170 181 194 196 205 213 244 260 265 269 295 317 320 332 336 383 393 409 427 437 455 488 535 547 584 585 588 592 622 633 693 695 697 734 752 775

	782 796 813 849 867 869 888 889 898 906 909 917 922 936 937 952 953 976 983 987 988 993 1012 1056 1061 1064 1074 1077 1086 1089 1107 1118 1156 1171 1177 1178 1179 1181 1189 1213 1214 1221 1222 1230 1240 1246 1277 1278 1280 1282 1285 1300 1322 1337 1337 1345 1351 1373 1375 1377 1395 1397 1418 1418 1428 1443 1459 1481 1504 1505 1505 1507 1509 1515 1515 1516 1527 1529 1535 1537 1543 1549 1554 1610 1654 1686 1688 3074 3081 3083 3088 3096 3096 3100 3101 3101 3117 3119 3134 3159 3162 3165 3170 3171 3171 3173 3182 3188 3192 3194 3202 3203 3205 3213 3213 3225 3227 3622
TS1a	-281i 17 23 33 38 48 55 57 66 74 79 81 94 103 106 107 115 127 140 149 152 160 174 187 195 207 211 233 258 263 268 276 299 311 334 338 357 361 407 421 447 493 501 543 555 586 586 590 597 606 664 692 696 711 745 757 790 805 816 824 868 869 873 888 889 901 909 915 921 935 936 952 953 981 984 988 992 993 1016 1061 1065 1068 1076 1090 1093 1096 1113 1118 1169 1173 1177 1178 1186 1186 1200 1207 1210 1213 1221 1224 1228 1244 1276 1279 1284 1286 1287 1303 1336 1337 1350 1356 1373 1373 1390 1395 1396 1397 1418 1420 1426 1459 1468 1485 1496 1504 1506 1512 1513 1514 1516 1522 1523 1531 1536 1539 1547 1551 1555 1601 1653 1684 1695 3010 3072 3080 3085 3093 3095 3096 3100 3101 3103 3112 3118 3125 3156 3162 3162 3163 3167 3169 3178 3182 3183 3192 3197 3202 3209 3210 3222 3238 3239 3570
CPLa	12 19 24 27 31 38 44 49 55 59 69 73 85 89 94 97 107 111 113 126 137 145 161 172 185 191 198 211 225 233 259 260 272 283 311 336 359 382 432 447 498 500 553 554 584 587 594 600 612 683 694 703 721 753 758 787 803 823 833 856 866 867 874 890 891 906 910 914 924 935 940 950 951 976 983 984 998 1013 1024 1060 1062 1063 1087 1095 1096 1104 1121 1167 1170 1178 1179 1191 1192 1206 1207 1212 1214 1214 1223 1230 1248 1273 1276 1280 1281 1284 1302 1307 1334 1338 1369 1372 1374 1385 1393 1394 1416 1419 1422 1429 1430 1454 1476 1504 1505 1506 1514 1514 1516 1516 1517 1519 1522 1537 1542 1549 1550 1552 1576 1649 1683 1707 1754 2936 2979 2994 3072 3084 3096 3099 3100 3102 3104 3107 3108 3115 3153 3156 3161 3165 3167 3169 3174 3175 3183 3204 3205 3205 3210 3214 3227 3251 3254 3292
MgBrOMe $(THF)_2$	12 22 24 31 37 42 51 57 66 69 106 130 143 150 165 170 230 260 267 321 331 573 584 585 701 702 868 869 888 888 908 920 936 936 948 950 981 984 1059 1061 1080 1088 1179 1179 1183 1191 1210 1213 1213 1221 1226 1276 1278 1282 1288 1336 1338 1373 1374 1396 1399 1418 1422 1504 1505 1506 1515 1515 1517 1520 1536 1537 1547 1548 2955 3003 3019 3095 3100 3101 3101 3102 3103 3105 3116 3164 3165 3171 3171 3181 3185 3188 3193
2a	50 73 99 120 186 203 209 238 314 335 369 417 444 491 497 548 581 590 591 614 686 713 738 759 795 800 831 864

	873 902 905 983 997 1012 1023 1061 1081 1100 1119 1167 1184 1190 1213 1221 1248 1294 1301 1366 1377 1393 1422 1429 1445 1475 1513 1514 1522 1543 1575 1652 1683 1708 1795 3073 3112 3153 3172 3190 3203 3209 3214 3227 3251 3251 3556
PhMgBr $(THF)_2$	17 19 24 33 37 40 47 56 70 74 113 130 146 149 160 169 174 255 261 309 321 389 401 451 583 585 636 663 700 701 723 745 869 871 883 886 888 905 916 932 935 937 950 950 983 984 1006 1016 1020 1048 1061 1063 1083 1084 1089 1098 1169 1177 1178 1213 1214 1216 1221 1221 1277 1279 1284 1285 1286 1338 1339 1360 1374 1375 1396 1399 1420 1421 1456 1504 1506 1514 1515 1519 1534 1536 1546 1547 1635 1653 3097 3100 3102 3102 3102 3103 3105 3109 3139 3146 3165 3166 3170 3172 3179 3183 3186 3188 3194 3194 3213
COMb	16 26 29 33 38 43 47 58 62 66 77 79 89 94 98 106 112 121 126 137 139 148 154 157 175 181 184 189 206 219 251 262 267 278 301 322 337 337 360 407 419 452 457 491 505 549 583 588 588 602 620 626 637 649 694 697 707 723 726 745 750 763 794 833 861 861 862 882 884 891 893 908 915 922 932 934 937 938 951 953 983 983 999 1008 1010 1014 1016 1021 1026 1040 1057 1061 1063 1086 1090 1099 1103 1112 1165 1168 1176 1179 1180 1185 1195 1212 1212 1214 1217 1225 1225 1228 1245 1255 1272 1275 1280 1282 1285 1297 1335 1335 1356 1370 1370 1376 1390 1391 1415 1415 1416 1431 1451 1454 1475 1498 1499 1506 1506 1512 1513 1517 1518 1525 1533 1545 1549 1556 1569 1630 1647 1655 1683 1712 1766 3091 3094 3096 3096 3098 3098 3106 3113 3117 3130 3144 3157 3158 3164 3165 3175 3175 3181 3181 3185 3185 3187 3205 3206 3214 3216 3228 3242 3244 3248 3520
TSb	-330i 14 18 31 34 43 51 55 69 71 81 84 95 96 100 108 116 119 130 138 138 150 156 170 178 187 194 201 209 235 256 265 276 278 317 331 342 360 370 410 411 429 453 496 510 543 559 585 586 592 613 626 632 633 661 695 696 716 724 742 751 759 790 820 835 859 862 877 878 889 892 906 910 919 933 938 941 943 952 953 982 982 993 1000 1010 1012 1015 1016 1021 1030 1061 1063 1064 1074 1087 1089 1096 1098 1163 1167 1170 1174 1179 1182 1184 1203 1208 1213 1213 1218 1225 1227 1237 1244 1274 1275 1281 1284 1292 1296 1336 1336 1347 1352 1371 1372 1389 1393 1394 1409 1416 1419 1459 1463 1474 1485 1495 1500 1504 1506 1512 1514 1515 1518 1530 1542 1548 1555 1557 1613 1636 1643 1676 1690 1707 3092 3094 3097 3099 3100 3102 3113 3114 3120 3147 3160 3160 3167 3168 3174 3179 3187 3188 3188 3192 3193 3194 3201 3211 3213 3213 3224 3232 3239 3243 3554
INTb	22 27 31 33 45 52 54 59 64 68 82 85 89 95 101 103 111 141 143 159 161 167 186 193 200 219 235 249 266 278 278 294 308 324 330 342 358 389 405 423 429 441 464 499 521 549 572 585 590 592 600 635 645 663 692 694

	703 727 737 751 769 779 789 803 842 857 865 879 888 890 895 905 912 918 932 934 941 952 956 969 973 984 985 991 991 1011 1019 1025 1028 1061 1063 1067 1070 1077 1081 1088 1110 1131 1152 1171 1174 1175 1177 1181 1185 1206 1215 1215 1218 1221 1222 1233 1243 1252 1275 1278 1283 1288 1290 1302 1328 1338 1340 1341 1352 1360 1372 1373 1396 1399 1419 1425 1451 1459 1483 1491 1504 1505 1506 1509 1513 1517 1526 1527 1534 1535 1541 1541 1550 1605 1651 1662 1685 1687 1689 3087 3094 3098 3099 3102 3105 3107 3110 3120 3163 3164 3170 3171 3179 3187 3188 3191 3192 3195 3201 3206 3208 3210 3211 3220 3223 3228 3231 3234 3264 3614
TS1b	-291i 25 29 34 42 44 47 60 63 65 71 81 82 92 100 106 109 118 140 146 158 161 166 175 179 191 219 236 246 268 269 272 280 298 310 316 337 350 363 391 415 431 447 498 518 541 550 574 586 589 590 624 637 642 659 694 701 717 730 745 756 779 798 814 823 859 861 866 885 888 892 902 909 918 933 935 939 953 955 973 985 986 988 990 994 1016 1021 1026 1038 1064 1066 1067 1071 1087 1095 1102 1111 1135 1168 1174 1174 1177 1178 1187 1192 1202 1203 1215 1215 1218 1223 1228 1240 1254 1274 1282 1285 1290 1301 1318 1328 1336 1339 1355 1371 1373 1382 1388 1393 1399 1416 1426 1460 1462 1487 1490 1499 1504 1504 1512 1513 1517 1526 1527 1536 1538 1541 1551 1551 1597 1654 1660 1683 1685 1694 3026 3093 3097 3097 3100 3102 3102 3105 3111 3113 3123 3160 3162 3168 3170 3183 3187 3194 3197 3198 3202 3209 3209 3211 3220 3223 3228 3235 3257 3269 3572
CPLb	10 23 25 29 33 42 43 52 56 59 66 69 74 84 89 90 95 101 110 114 124 141 145 154 171 173 191 206 225 237 245 262 267 271 289 309 316 333 369 405 415 449 490 526 541 553 574 585 586 595 626 632 641 690 692 699 720 722 751 756 786 787 820 836 858 860 869 871 874 888 891 910 911 920 920 934 936 951 953 959 983 988 1000 1002 1007 1017 1025 1027 1027 1061 1062 1064 1065 1089 1098 1110 1149 1169 1170 1174 1176 1178 1192 1194 1203 1207 1207 1214 1218 1222 1224 1241 1266 1279 1281 1283 1287 1288 1316 1318 1337 1338 1358 1363 1372 1372 1398 1399 1422 1425 1429 1430 1450 1472 1487 1503 1504 1504 1512 1514 1517 1518 1519 1526 1536 1541 1547 1550 1572 1651 1659 1681 1689 1705 1754 2941 2982 2987 3094 3096 3097 3100 3104 3104 3109 3113 3158 3163 3165 3170 3172 3185 3188 3200 3204 3208 3211 3215 3216 3217 3227 3227 3238 3248 3250 3258
2b	28 45 59 72 91 168 175 222 256 288 321 343 388 417 448 479 520 537 570 578 604 612 634 640 695 713 719 735 762 785 796 835 856 869 870 910 913 954 998 1001 1005 1015 1022 1026 1026 1060 1064 1109 1145 1168 1174 1178 1191 1202 1217 1242 1267 1308 1318 1356 1358 1391 1431 1442 1473 1488 1517 1548 1573 1653 1660 1680 1691 1707 1810 3200 3203 3204 3209 3212 3214 3220 3227 3229

	3245 3250 3554
2MeOPhMgBr(THF)$_2$	20 20 26 32 36 42 53 62 69 76 83 88 118 136 148 154 161 202 223 257 259 270 290 297 323 389 445 483 546 577 583 585 661 696 701 736 781 802 866 872 876 887 888 906 918 935 936 950 950 962 983 987 1002 1045 1061 1062 1065 1086 1089 1101 1144 1176 1177 1179 1184 1209 1213 1214 1221 1222 1255 1278 1278 1285 1286 1303 1336 1337 1338 1373 1374 1396 1397 1420 1421 1465 1493 1502 1504 1505 1513 1514 1514 1526 1533 1537 1544 1548 1644 1651 3051 3097 3100 3101 3101 3102 3104 3105 3113 3132 3162 3164 3165 3168 3171 3178 3182 3183 3186 3190 3195 3212 3231
COMca	14 18 28 30 34 38 47 51 54 59 63 71 74 75 87 95 97 103 108 120 122 130 136 146 150 156 166 186 189 191 208 232 240 249 254 258 283 297 310 313 331 352 368 414 449 454 478 491 499 546 550 581 583 584 587 601 619 634 653 687 695 711 721 734 749 765 781 794 806 836 862 863 864 872 885 887 889 911 914 921 932 933 933 950 953 956 981 983 996 1001 1011 1027 1038 1045 1056 1059 1062 1066 1097 1107 1107 1129 1141 1167 1177 1177 1178 1180 1182 1182 1192 1208 1212 1213 1217 1220 1221 1222 1244 1256 1263 1276 1276 1280 1282 1300 1301 1333 1334 1335 1368 1370 1371 1390 1394 1407 1415 1417 1429 1450 1462 1473 1491 1496 1503 1503 1505 1507 1512 1513 1515 1516 1523 1529 1533 1538 1545 1550 1569 1640 1647 1652 1682 1710 1773 3043 3062 3093 3095 3096 3096 3098 3101 3105 3108 3120 3141 3146 3154 3160 3161 3167 3169 3169 3180 3186 3189 3192 3204 3207 3211 3215 3221 3227 3230 3244 3247 3547
TSca	-310i 20 35 38 42 48 53 55 59 70 76 81 84 90 97 103 104 119 119 129 132 142 150 152 166 175 182 189 194 202 217 218 255 258 264 271 284 289 309 324 339 356 373 414 425 445 471 490 505 532 541 547 570 580 583 587 604 620 626 652 684 687 701 725 739 747 764 771 795 804 813 850 851 854 862 870 875 878 885 888 920 921 923 934 935 948 967 971 972 974 976 982 992 995 1041 1042 1046 1047 1050 1052 1054 1073 1130 1145 1162 1165 1166 1168 1169 1172 1174 1176 1195 1198 1200 1204 1207 1208 1218 1236 1251 1266 1270 1273 1275 1277 1281 1314 1321 1324 1324 1354 1356 1361 1378 1380 1382 1404 1408 1434 1444 1448 1464 1471 1478 1487 1492 1496 1498 1506 1507 1508 1511 1515 1526 1527 1537 1541 1547 1570 1596 1604 1630 1646 1661 3024 3065 3067 3068 3069 3070 3072 3077 3084 3093 3104 3128 3128 3136 3136 3149 3158 3160 3161 3161 3161 3172 3173 3175 3183 3185 3186 3197 3202 3206 3215 3216 3537
INTca	21 30 34 36 42 48 50 62 64 68 72 79 86 88 93 102 108 127 138 146 157 158 166 172 186 194 200 210 231 258 264 266 277 278 287 300 318 324 331 340 353 381 403 424 440 462 485 494 531 539 566 581 586 588 590 594

	603 645 659 690 694 701 733 749 762 771 782 789 804 819 839 858 865 884 888 889 894 905 912 916 936 937 941 953 956 972 984 984 986 988 990 1009 1015 1061 1064 1070 1075 1082 1084 1086 1096 1126 1147 1156 1170 1174 1176 1178 1183 1184 1185 1211 1215 1216 1220 1223 1223 1231 1244 1249 1275 1278 1284 1289 1290 1301 1307 1326 1339 1339 1340 1348 1353 1373 1374 1395 1400 1419 1426 1442 1459 1482 1485 1504 1505 1505 1506 1509 1513 1515 1518 1520 1526 1528 1534 1536 1541 1548 1550 1608 1654 1665 1681 1687 1689 3055 3088 3095 3098 3099 3102 3104 3106 3111 3120 3137 3163 3163 3170 3172 3181 3188 3189 3192 3193 3193 3198 3202 3205 3206 3211 3214 3222 3225 3226 3250 3266 3622
TS1ca	-310i 23 26 32 35 41 44 50 63 65 70 76 80 85 94 99 103 104 117 140 145 155 162 163 173 176 185 189 208 233 246 264 268 274 279 283 294 312 313 331 343 345 370 394 406 445 481 502 510 536 548 568 578 586 586 589 600 628 643 659 694 701 712 743 755 766 785 797 811 813 824 858 864 864 887 890 893 902 909 918 935 937 940 953 954 983 984 986 989 992 994 1015 1030 1063 1067 1070 1081 1088 1092 1094 1098 1129 1154 1168 1174 1175 1176 1182 1184 1185 1190 1202 1214 1215 1216 1219 1223 1230 1239 1246 1275 1281 1286 1288 1293 1304 1317 1320 1335 1337 1338 1371 1372 1376 1385 1394 1398 1416 1425 1461 1465 1482 1488 1498 1504 1504 1505 1511 1513 1516 1518 1521 1524 1527 1535 1541 1542 1549 1551 1594 1651 1659 1680 1682 1692 3034 3058 3092 3097 3097 3100 3102 3105 3110 3110 3115 3133 3141 3161 3162 3169 3169 3184 3188 3190 3196 3197 3197 3207 3208 3210 3222 3223 3234 3249 3252 3280 3582
CPLca	12 22 27 33 35 40 43 50 51 53 57 65 70 76 82 84 91 98 101 104 108 118 121 149 150 156 174 181 189 201 221 229 242 263 269 271 284 291 314 326 332 336 369 407 434 481 495 506 536 553 558 571 587 590 603 629 641 654 662 693 695 715 751 756 771 781 788 812 819 826 836 860 860 871 873 879 892 911 915 928 932 936 952 954 971 977 985 988 998 1001 1010 1016 1026 1061 1065 1075 1084 1091 1096 1099 1138 1157 1162 1169 1173 1176 1182 1185 1193 1193 1206 1209 1217 1217 1224 1239 1243 1258 1259 1280 1281 1282 1289 1299 1304 1313 1322 1339 1339 1341 1342 1363 1371 1394 1399 1418 1426 1428 1430 1451 1472 1483 1503 1504 1505 1507 1512 1516 1517 1519 1520 1520 1522 1526 1527 1542 1542 1554 1572 1653 1663 1682 1686 1706 1751 2941 2981 2990 3060 3085 3089 3095 3097 3101 3106 3106 3117 3145 3159 3159 3166 3177 3178 3188 3200 3204 3206 3210 3210 3214 3224 3227 3236 3238 3245 3248 3254 3257
2c	26 48 58 69 82 98 142 164 177 215 241 264 298 314 330 343 390 434 473 492 507 534 551 570 580 590 611 619 640 697 709 733 761 768 780 796 812 834 859 869 876 909

	921 969 996 999 1004 1013 1024 1058 1075 1092 1136 1155 1167 1178 1182 1186 1190 1217 1218 1241 1258 1297 1310 1319 1344 1358 1391 1431 1442 1473 1483 1505 1516 1519 1523 1556 1573 1654 1667 1680 1687 1707 1808 3059 3143 3197 3202 3203 3209 3213 3213 3225 3229 3240 3247 3249 3556
COMcb	14 26 29 33 42 44 47 51 62 64 72 78 81 85 94 97 105 105 111 116 129 135 138 148 153 165 169 182 190 195 207 227 234 241 254 260 272 298 303 311 330 351 378 417 450 452 482 491 500 547 552 579 583 584 586 600 615 632 655 688 699 712 720 734 748 766 782 796 806 836 862 864 867 873 885 888 889 911 916 924 932 933 934 950 953 955 984 986 995 1000 1010 1028 1038 1043 1055 1059 1061 1066 1103 1106 1108 1128 1141 1167 1176 1177 1178 1180 1183 1184 1191 1208 1210 1213 1216 1220 1221 1222 1243 1257 1262 1274 1278 1281 1283 1299 1299 1334 1334 1336 1368 1370 1370 1390 1393 1407 1417 1418 1430 1449 1463 1473 1492 1494 1502 1504 1504 1507 1513 1513 1515 1515 1524 1527 1532 1537 1548 1551 1569 1640 1647 1653 1681 1711 1774 3040 3061 3092 3095 3096 3097 3099 3101 3104 3105 3115 3139 3144 3152 3160 3161 3164 3170 3174 3175 3187 3188 3200 3204 3206 3212 3215 3225 3227 3228 3242 3243 3540
TScb	-339i 22 32 37 44 50 56 61 71 74 81 85 91 97 99 112 112 121 127 133 138 145 151 161 166 177 185 191 197 204 227 236 259 270 276 287 294 307 312 333 344 364 373 419 431 455 479 495 512 539 549 562 573 587 590 595 613 626 636 661 697 705 715 738 751 760 779 790 810 818 833 853 855 873 878 889 894 905 913 924 935 940 941 952 953 969 980 984 992 999 1004 1006 1017 1018 1062 1065 1067 1076 1087 1094 1100 1102 1148 1163 1169 1174 1175 1177 1181 1182 1187 1200 1210 1212 1214 1219 1228 1230 1235 1244 1272 1273 1275 1282 1287 1293 1296 1327 1335 1337 1344 1369 1369 1384 1392 1395 1404 1418 1420 1459 1466 1473 1482 1490 1496 1501 1504 1505 1506 1514 1514 1515 1517 1526 1531 1541 1546 1553 1554 1610 1638 1645 1675 1687 1705 3047 3093 3093 3097 3100 3106 3112 3113 3120 3122 3128 3157 3159 3159 3166 3168 3177 3185 3187 3187 3190 3194 3196 3199 3210 3212 3212 3223 3233 3233 3238 3263 3558
INTcb	22 31 36 39 48 54 59 60 69 77 83 87 92 109 112 117 126 140 145 153 160 170 181 187 197 205 210 226 239 243 272 277 286 299 306 316 329 334 339 347 357 384 390 421 441 464 487 494 529 539 563 573 586 592 600 613 615 641 657 691 692 703 733 745 759 774 776 787 804 815 816 848 868 877 885 889 895 908 933 935 938 941 948 953 970 971 982 983 986 989 990 1010 1014 1056 1061 1064 1072 1081 1085 1090 1101 1118 1147 1160 1164 1167 1176 1177 1182 1185 1191 1206 1212 1213 1221 1223 1238 1239 1244 1264 1272 1274 1276 1280 1286 1301

	1315 1322 1336 1337 1339 1342 1350 1353 1372 1396 1398 1419 1424 1450 1459 1480 1485 1497 1502 1505 1507 1509 1513 1516 1519 1521 1524 1532 1534 1539 1544 1552 1553 1600 1651 1666 1679 1688 1689 3070 3089 3090 3091 3094 3096 3101 3108 3117 3119 3163 3163 3170 3178 3179 3185 3187 3193 3197 3199 3203 3205 3207 3211 3212 3213 3223 3224 3225 3234 3241 3262 3622
TS1cb	-220i 26 31 40 47 49 53 65 65 74 80 84 91 94 101 110 114 116 130 135 144 157 169 174 182 189 193 202 220 227 243 255 262 274 283 294 297 326 331 334 337 343 371 393 421 461 484 495 523 535 547 562 577 588 594 609 620 641 649 660 666 695 712 738 757 765 776 798 807 817 818 832 863 864 876 879 891 902 915 935 937 939 949 953 975 982 983 988 989 990 995 1014 1016 1060 1062 1063 1090 1094 1097 1101 1114 1127 1160 1160 1168 1177 1180 1182 1184 1190 1193 1200 1211 1214 1218 1227 1229 1240 1244 1262 1276 1277 1280 1284 1296 1302 1314 1327 1335 1344 1344 1346 1371 1390 1393 1395 1402 1416 1422 1461 1466 1477 1489 1495 1498 1503 1505 1512 1516 1517 1519 1523 1524 1534 1540 1544 1551 1554 1558 1599 1663 1672 1682 1685 1698 3011 3070 3077 3081 3088 3088 3091 3096 3101 3108 3119 3122 3160 3162 3166 3174 3178 3180 3197 3199 3208 3210 3211 3212 3214 3219 3221 3229 3233 3233 3244 3266 3571
INT1cb	24 29 38 40 45 51 57 60 63 66 69 82 87 92 95 100 102 107 114 118 125 129 134 148 153 167 171 184 195 203 211 214 228 254 260 264 268 277 317 325 343 357 371 397 433 472 496 506 513 536 544 575 585 590 611 626 628 641 672 689 696 706 717 748 767 774 791 793 810 819 834 864 868 869 879 889 900 909 918 930 934 935 947 952 971 985 985 989 999 1001 1017 1018 1026 1055 1062 1062 1080 1085 1093 1098 1127 1151 1160 1169 1175 1178 1179 1182 1194 1195 1207 1208 1213 1218 1221 1237 1242 1256 1263 1274 1277 1278 1279 1284 1297 1311 1313 1324 1336 1339 1349 1361 1372 1394 1395 1419 1419 1427 1430 1454 1465 1473 1491 1502 1502 1503 1506 1515 1515 1516 1518 1520 1522 1523 1538 1541 1548 1551 1573 1648 1655 1682 1688 1705 1732 2927 2965 2998 3074 3076 3080 3097 3098 3104 3107 3108 3117 3161 3166 3168 3174 3181 3182 3203 3203 3205 3206 3210 3214 3215 3224 3227 3228 3231 3233 3249 3260 3387
TS2cb	-26i 14 20 26 30 40 47 50 53 63 68 73 79 85 87 91 94 102 117 125 127 135 141 147 156 163 165 177 186 197 203 219 231 254 262 271 281 304 312 323 340 349 369 405 442 470 493 511 516 537 547 574 582 587 591 609 628 640 685 691 696 708 740 750 771 776 783 802 808 837 842 850 863 871 891 893 894 908 912 914 929 942 946 951 956 981 982 985 999 1003 1011 1019 1028 1057 1061 1063 1069 1083 1085 1090 1128 1151 1169 1173 1173 1175 1180 1189 1193 1194 1205 1208

	1210 1217 1218 1236 1238 1242 1257 1275 1280 1282 1283 1292 1296 1301 1319 1337 1338 1339 1363 1369 1371 1398 1400 1422 1428 1428 1431 1455 1470 1474 1489 1501 1503 1503 1506 1515 1516 1520 1521 1521 1528 1530 1537 1543 1549 1550 1572 1649 1653 1682 1688 1705 1736 2932 2971 2992 3079 3085 3097 3098 3100 3104 3107 3111 3122 3157 3159 3171 3172 3173 3179 3189 3197 3203 3204 3205 3210 3211 3215 3223 3226 3227 3231 3246 3259 3370
CPLcb	17 22 26 30 32 41 47 50 58 61 62 72 78 81 84 89 93 99 104 111 117 123 133 143 150 154 163 170 183 193 204 212 225 244 258 260 268 275 287 312 316 341 361 406 440 468 487 509 537 551 555 574 583 585 585 608 632 640 690 694 701 711 749 754 772 784 787 813 819 834 862 864 869 870 887 888 894 910 913 923 930 934 934 951 952 982 984 985 998 1000 1012 1015 1026 1050 1061 1062 1063 1080 1091 1102 1126 1151 1169 1172 1174 1178 1178 1183 1193 1193 1206 1207 1210 1214 1215 1221 1221 1239 1259 1276 1278 1279 1282 1285 1287 1300 1317 1335 1336 1336 1364 1371 1372 1393 1398 1417 1422 1426 1430 1449 1471 1483 1502 1504 1505 1507 1514 1514 1515 1520 1521 1524 1534 1537 1539 1546 1548 1553 1571 1646 1657 1681 1686 1707 1754 2939 2979 2994 3063 3096 3097 3100 3101 3102 3104 3107 3108 3159 3163 3164 3167 3172 3172 3179 3180 3183 3202 3204 3210 3211 3215 3219 3223 3227 3231 3251 3253 3271
2,6-diMeOMg $(THF)_2$	11 22 32 35 37 42 52 55 62 69 78 88 101 107 135 139 154 159 181 198 224 252 258 265 285 289 300 321 329 374 390 509 521 585 589 600 615 657 700 705 727 752 793 860 866 869 887 893 909 910 919 935 939 950 951 974 983 986 1048 1062 1066 1085 1091 1099 1137 1159 1176 1178 1183 1183 1196 1202 1214 1215 1216 1222 1226 1262 1276 1278 1284 1288 1301 1338 1338 1352 1371 1375 1395 1398 1418 1422 1469 1481 1495 1503 1505 1505 1514 1515 1515 1516 1525 1527 1531 1537 1545 1548 1642 1654 3049 3051 3099 3100 3101 3101 3103 3104 3111 3122 3129 3130 3163 3164 3169 3170 3177 3180 3184 3184 3190 3193 3205 3238 3242
COMd	25 26 31 35 43 45 54 55 57 62 70 71 77 82 84 95 102 106 108 119 122 129 136 143 147 156 157 169 188 193 197 201 209 225 235 246 258 264 269 279 304 308 314 329 331 352 368 379 415 450 491 500 514 524 546 583 584 587 601 602 606 619 635 655 688 694 710 721 724 749 752 765 791 795 837 862 863 864 865 885 889 890 909 912 916 923 932 933 934 952 953 967 982 985 1001 1011 1027 1038 1041 1055 1060 1062 1100 1103 1110 1129 1141 1159 1167 1177 1178 1180 1182 1182 1183 1192 1195 1203 1212 1213 1214 1217 1221 1221 1222 1243 1257 1263 1276 1276 1280 1284 1298 1300 1334 1335 1350 1369 1370 1371 1391 1393 1409 1416 1418 1429 1450 1469 1473 1478 1494 1496 1501 1503 1503 1507 1512 1513 1513 1514 1515 1523 1525 1528 1532 1536 1546 1552

	1569 1639 1651 1653 1681 1710 1774 3042 3044 3061 3091 3092 3094 3096 3099 3102 3105 3111 3118 3122 3145 3151 3159 3160 3166 3169 3169 3175 3189 3195 3200 3203 3203 3211 3215 3221 3226 3236 3241 3244 3245 3549
TSd	-380i 21 35 36 50 52 55 66 67 70 79 86 87 94 98 108 112 119 125 135 140 141 158 161 164 169 184 192 197 202 206 217 219 245 253 269 272 283 285 296 308 313 333 334 349 367 373 386 428 447 478 505 516 519 543 559 581 586 590 599 607 614 630 658 669 695 702 713 732 750 756 761 786 800 821 826 855 860 865 877 890 894 904 913 924 926 935 940 941 952 954 978 983 984 992 993 999 1017 1022 1060 1066 1068 1085 1093 1097 1102 1146 1154 1159 1168 1174 1177 1181 1181 1181 1188 1194 1201 1208 1213 1214 1216 1221 1225 1230 1235 1246 1272 1274 1277 1281 1287 1295 1313 1328 1333 1335 1336 1369 1370 1375 1391 1392 1393 1417 1418 1447 1465 1468 1476 1486 1493 1498 1502 1504 1505 1506 1515 1516 1516 1517 1518 1524 1528 1533 1542 1547 1551 1556 1607 1638 1646 1673 1686 1701 3052 3055 3092 3094 3096 3098 3105 3107 3110 3116 3125 3135 3139 3158 3159 3167 3167 3180 3187 3187 3189 3190 3192 3197 3201 3207 3208 3210 3222 3230 3237 3244 3247 3266 3575
INTd	11 29 37 42 47 51 53 58 63 73 80 84 90 91 107 111 117 125 137 146 148 158 166 174 177 186 199 206 222 225 244 251 261 278 287 290 298 303 317 331 334 344 348 361 367 381 390 406 423 447 471 507 526 538 563 575 589 591 601 617 623 628 642 650 689 691 692 731 744 746 757 783 790 803 813 814 841 868 876 878 890 893 906 917 933 936 940 942 947 954 971 972 983 984 987 988 991 1009 1051 1061 1073 1078 1082 1084 1088 1115 1144 1148 1156 1161 1167 1176 1179 1180 1183 1183 1198 1203 1212 1223 1223 1226 1229 1238 1239 1247 1265 1271 1276 1279 1285 1290 1302 1311 1329 1335 1337 1339 1345 1347 1350 1374 1394 1397 1418 1422 1443 1460 1479 1484 1490 1500 1505 1507 1510 1511 1513 1515 1516 1516 1519 1520 1523 1526 1534 1536 1538 1544 1551 1605 1654 1669 1676 1681 1688 3063 3077 3092 3095 3097 3098 3100 3105 3111 3122 3122 3148 3166 3166 3173 3183 3188 3189 3189 3198 3200 3203 3204 3205 3209 3210 3216 3217 3225 3228 3230 3247 3268 3281 3784
TS1d	-246i 26 31 41 46 47 53 55 62 67 69 81 86 87 92 99 111 112 115 126 129 140 155 163 171 175 179 187 191 207 216 231 243 255 268 274 278 285 292 309 318 329 337 339 352 358 372 385 413 423 460 498 523 533 541 557 574 582 589 608 620 622 646 647 667 669 697 704 735 748 755 769 794 811 816 817 824 860 861 874 877 892 901 916 931 937 939 940 950 953 976 982 983 985 989 990 991 1012 1062 1066 1080 1092 1094 1098 1108 1119 1153 1157 1160 1167 1177 1177 1179 1183 1184 1191 1198 1200 1212 1219 1221 1226 1230 1235 1241 1244 1263 1274 1280 1285 1290 1296 1303 1314 1332 1335 1345 1346 1346 1370 1382 1392 1394 1396 1415 1422 1460 1468 1479 1489 1492 1498 1503 1506

	1512 1513 1516 1517 1518 1518 1522 1523 1526 1531 1538 1540 1549 1551 1552 1599 1660 1668 1678 1680 1694 3020 3059 3070 3078 3090 3092 3093 3099 3102 3104 3108 3114 3119 3144 3159 3162 3166 3176 3178 3180 3194 3199 3200 3205 3207 3209 3215 3217 3219 3227 3231 3250 3260 3274 3582
CPLd	17 20 27 28 35 38 39 48 53 56 63 67 70 77 82 86 88 96 98 100 110 113 120 125 138 147 149 150 162 171 188 200 204 218 226 236 248 259 268 270 276 297 298 314 328 357 371 415 430 447 484 503 537 542 545 550 574 586 586 603 617 636 659 683 694 702 703 747 752 756 768 784 817 823 835 860 862 869 870 887 888 888 908 911 922 927 934 934 950 951 953 983 985 993 998 1001 1015 1026 1060 1061 1064 1065 1091 1102 1110 1144 1146 1169 1175 1177 1178 1179 1186 1192 1192 1193 1207 1212 1214 1215 1216 1220 1222 1224 1239 1259 1277 1279 1280 1282 1285 1291 1307 1315 1336 1336 1359 1367 1371 1372 1393 1398 1418 1422 1424 1431 1449 1473 1480 1495 1503 1504 1506 1513 1515 1516 1516 1517 1519 1521 1523 1525 1534 1535 1538 1542 1546 1551 1571 1650 1663 1678 1682 1707 1753 2940 2979 2993 3061 3065 3096 3096 3098 3101 3103 3104 3108 3108 3146 3159 3163 3164 3169 3172 3172 3178 3180 3183 3199 3203 3210 3212 3214 3216 3226 3233 3250 3253 3255 3288
2d	17 42 59 60 65 76 103 141 147 147 204 206 220 262 284 295 296 331 347 360 376 409 439 491 516 528 538 571 572 589 612 624 631 640 692 701 729 748 760 762 797 813 835 859 867 871 910 920 945 986 995 1000 1015 1024 1058 1097 1121 1147 1167 1169 1176 1185 1185 1190 1208 1215 1216 1222 1241 1260 1297 1303 1347 1348 1357 1388 1431 1442 1474 1482 1494 1515 1516 1516 1522 1522 1527 1553 1573 1653 1674 1678 1681 1707 1806 3061 3061 3145 3146 3197 3197 3202 3208 3212 3215 3225 3238 3253 3255 3256 3561

Table S9 The total energies (E:a.u.), zero-point energies (ZPE:a.u.) and Gibbs free energies (G:a.u.) for the stationary points of reaction (a), computed at CAM-B3LYP+IDSCRF/DZVP level.

	E	E+ZPE .	G(195)	G(273)	G(298)
1	-688.74777	-688.55156	-688.57422[a] -688.56690[b]	-688.58669 -688.57615	-688.59104 -688.57945
$MgBrEt(THF)_2$	-3317.89465	-3317.58884	-3317.61840 -3317.61190	-3317.63567 -3317.62627	-3317.64168 -3317.63134
1+ $MgBrEt(THF)_2$	-4006.64242	-4006.14040	-4006.19262 -4006.17880	-4006.22236 -4006.20242	-4006.23272 -4006.21079
COMa	-4006.64296	-4006.13957	-4006.17608 -4006.16925	-4006.19956 -4006.18970	-4006.20794 -4006.19710
TSa	-4006.62939	-4006.12576	-4006.16016 -4006.15338	-4006.18233 -4006.17254	-4006.19026 -4006.17950

INTa	-4006.70780	-4006.20023	-4006.23516 -4006.22912	-4006.25747 -4006.24872	-4006.26545 -4006.25582
TS1a	-4006.69529	-4006.18982	-4006.22506 -4006.21949	-4006.24757 -4006.23948	-4006.25561 -4006.24669
CPLa	-4006.72864	-4006.22280	-4006.26114 -4006.25525	-4006.28537 -4006.27684	-4006.29398 -4006.28458
MgBrOMe(THF)$_2$	-3353.87417	-3353.59133	-3353.62268 -3353.61599	-3353.64077 -3353.63134	-3353.64703 -3353.63665
2a	-652.83939	-652.61829	-652.64061 -652.63276	-652.65291 -652.64109	-652.65720 -652.64422
MgBrOMe(THF)$_2$+2a	-4006.71356	-4006.20962	-4006.26329 -4006.24891	-4006.29368 -4006.27243	-4006.30423 -4006.28087

(a) From G09 output with idea-gas translational entropy; (b) Using cavity volume(*V1*) and the solute volume(*V2*), it can be transferred to the displacement along each axis(mass-centre movement), and then the free-volume of could be easily calculated with the cubic of the displacement.

Table S10 The total energies (E:a.u.), zero-point energies (ZPE:a.u.) and Gibbs free energies (G:a.u.) for the stationary points for reaction (a), computed at CAM-B3LYP+IDSCRF/6-311++G(d,p) level in THF.

	E	E+ZPE .	G(195)	G(273)	G(298)
1	-688.85468	-688.65934	-688.68178[a] -688.67491[b]	-688.69416 -688.68424	-688.69847 -688.68756
MgBrEt(THF)$_2$	-3318.47168	-3318.16812	-3318.19757 -3318.19151	-3318.21478 -3318.20600	-3318.22077 -3318.21111
1+ MgBrEt(THF)$_2$	-4007.32636	-4006.82746	-4006.87935 -4006.86642	-4006.90894 -4006.89024	-4006.90958 -4006.89867
COMa	-4007.32674	-4006.82611	-4006.86390 -4006.85792	-4006.88802 -4006.87935	-4006.89660 -4006.88706
TSa	-4007.31334	-4006.81278	-4006.84701 -4006.84038	-4006.86910 -4006.85953	-4006.87701 -4006.86649
INTa	-4007.39051	-4006.88589	-4006.92069 -4006.91358	-4006.94294 -4006.93270	-4006.95090 -4006.93964
TS1a	-4007.37872	-4006.87633	-4006.91224 -4006.90598	-4006.93504 -4006.92598	-4006.94317 -4006.93320
CPLa	-4007.41308	-4006.91033	-4006.94884 -4006.94220	-4006.97314 -4006.96355	-4006.98177 -4006.97122
MgBrOMe(THF)$_2$	-3354.45383	-3354.17300	-3354.20373 -3354.19761	-3354.22153 -3354.21268	-3354.22769 -3354.21795
2a	-652.94531	-652.72529	-652.74761 -652.74038	-652.75992 -652.74950	-652.76422 -652.75276
MgBrOMe(THF)$_2$+2a	-4007.39914	-4006.89829	-4006.95134	-4006.98145	-4006.99191

			-4006.93799	-4006.96218	-4006.97071

See the footnote of **Table S9**

Table S11 The total energies (E:a.u.), zero-point energies (ZPE:a.u.) and Gibbs free energies (G:a.u.) for the stationary points for reaction (a), computed at B3LYP+IDSCRF/DZVP level in THF.

	E	E+ZPE .	G(195)	G(273)	G(298)
1	-689.08369	-688.89008	-688.91270	-688.92519	-688.92954
			-688.90547	-688.91478	-688.91810
MgBrEt(THF)$_2$	-3318.10637	-3317.80430	-3317.83511	-3317.85301	-3317.85923
			-3317.82811	-3317.84292	-3317.84813
1+ MgBrEt(THF)$_2$	-4007.19006	-4006.69438	-4006.74781	-4006.7782	-4006.78877
			-4006.73358	-4006.7577	-4006.76623
COMa	-4007.18518	-4006.68855	-4006.72683	-4006.75130	-4006.76000
			-4006.72020	-4006.74172	-4006.74946
TSa	-4007.17185	-4006.67447	-4006.70880	-4006.73104	-4006.73901
			-4006.70151	-4006.72055	-4006.72747
INTa	-4007.24187	-4006.74081	-4006.77626	-4006.79893	-4006.80703
			-4006.76963	-4006.78935	-4006.79650
TS1a	-4007.23514	-4006.73525	-4006.76979	-4006.79200	-4006.79996
			-4006.76289	-4006.78206	-4006.78902
CPLa	-4007.26991	-4006.77034	-4006.80886	-4006.83329	-4006.84197
			-4006.80260	-4006.82423	-4006.83200
MgBrOMe(THF)$_2$	-3354.07950	-3353.79975	-3353.83010	-3353.84778	-3353.85391
			-3353.82358	-3353.83835	-3353.84354
2a	-653.18049	-652.96222	-652.98466	-652.99705	-653.00138
			-652.97730	-652.98646	-652.98974
MgBrOMe(THF)$_2$+2a	-4007.25999	-4006.76197	-4006.81476	-4006.84483	-4006.85529
			-4006.80088	-4006.82481	-4006.83328

See the footnote of **Table S9**

Table S12 The total energies (E:a.u.), total energies+zero-point energies (E+ZPE:a.u.) and Gibbs free energies (G: a.u.) for the stationary points of reaction (b), computed at CAM-B3LYP+IDSCRF/DZVP level.

	E	E+ZPE .	G(195)	G(273)	G(298)
1	-688.74777	-688.55156	-688.57422[a]	-688.58669	-688.59104
			-688.56690[b]	-688.57615	-688.57945
MgBrPh(THF)$_2$	-3470.25624	-3469.92437	-3469.95630	-3469.97493	-3469.98142
			-3469.94989	-3469.96487	-3469.97035

1+ MgBrPh(THF)$_2$	-4159.00401	-4158.47593	-4158.53052 -4158.51611	-4158.56162 -4158.54102	-4158.57246 -4158.54962
COMb	-4159.00747	-4158.47749	-4158.51495 -4158.50807	-4158.53909 -4158.52917	-4158.54773 -4158.53682
TSb	-4158.98849	-4158.45921	-4158.49563 -4158.48875	-4158.51904 -4158.50911	-4158.52742 -4158.51650
INTb	-4159.05593	-4158.52391	-4158.55989 -4158.55193	-4158.58303 -4158.57160	-4158.59133 -4158.57877
TS1b	-4159.04692	-4158.51673	-4158.55238 -4158.54485	-4158.57537 -4158.56455	-4158.58362 -4158.57173
CPLb	-4159.07659	-4158.54679	-4158.58585 -4158.57837	-4158.61077 -4158.60001	-4158.61965 -4158.60782
MgBrOMe(THF)$_2$	-3353.87417	-3353.59133	-3353.62268 -3353.61615	-3353.64077 -3353.63134	-3353.64703 -3353.63665
2b	-805.19003	-804.94538	-804.96989 -804.96110	-804.98358 -804.97097	-804.98838 -804.97453
MgBrOMe(THF)$_2$+2b	-4159.0642	-4158.53671	-4158.59257 -4158.57725	-4158.62435 -4158.60231	-4158.63541 -4158.61118

See the footnote of **Table S9**

Table S13 The total energies (E:a.u.), total energies+zero-point energies (E+ZPE:a.u.) and Gibbs free energies (G: a.u.) for the stationary points of reaction (c), computed at CAM-B3LYP+IDSCRF/DZVP level.

	E	E+ZPE .	G(195)	G(273)	G(298)
1	-688.74777	-688.55156	-688.57422[a] -688.56680[b]	-688.58669 -688.57615	-688.59104 -688.57945
MgBrPhOMe (THF)$_2$	-3584.76293	-3584.39783	-3584.43053 -3584.42381	-3584.45007 -3584.44038	-3584.45692 -3584.44627
1+ MgBrPhOMe(THF)$_2$	-4273.51070	-4272.94939	-4273.00475 -4272.99061	-4273.03676 -4273.01653	-4273.04796 -4273.02572
COMca	-4273.51219	-4272.94976	-4272.98953 -4272.98276	-4273.01538 -4273.00562	-4273.02463 -4273.01389
Tsca	-4273.49017	-4272.92734	-4272.96413 -4272.95728	-4272.98825 -4272.97837	-4272.99693 -4272.98605
INTca	-4273.54774	-4272.98255	-4273.01954 -4273.01337	-4273.04371 -4273.03479	-4273.05241 -4273.04258
TS1ca	-4273.54001	-4272.97669	-4273.01380 -4273.00768	-4273.03804 -4273.02918	-4273.04675 -4273.03700
CPLca	-4273.57494	-4273.01160	-4273.05190 -4273.04549	-4273.07797 -4273.06872	-4273.08729 -4273.07710
COMcb	-4273.51185	-4272.94921	-4272.98806	-4273.01347	-4273.02258

			-4272.98083	-4273.00306	-4273.01113
TScb	-4273.48974	-4272.92666	-4272.96272	-4272.98647	-4272.99502
			-4272.95341	-4272.97315	-4272.98040
INTcb	-4273.55241	-4272.98618	-4273.02202	-4273.04552	-4273.05400
			-4273.01574	-4273.03643	-4273.04400
TS1cb	-4273.53721	-4272.97298	-4273.00871	-4273.03222	-4273.04069
			-4273.00137	-4273.02164	-4273.02907
CPLcb	-4273.57522	-4273.01172	-4273.05044	-4273.07556	-4273.08455
			-4273.04338	-4273.06539	-4273.07337
MgBrOMe(THF)$_2$	-3353.87417	-3353.59133	-3353.62268	-3353.64077	-3353.64703
			-3353.61615	-3353.63134	-3353.63665
2c	-919.68969	-919.41181	-919.43753	-919.45235	-919.45757
			-919.42969	-919.44108	-919.44519
MgBrOMe(THF)$_2$+2c	-4273.56386	-4273.00314	-4273.06021	-4273.08369	-4273.1046
			-4273.04584	-4273.07242	-4273.08184

see footnote of **Table S9**

Table S14 The total energies (E:a.u.), total energies+zero-point energies (E+ZPE:a.u.) and Gibbs free energies (G: a.u.) for the stationary points of reaction (d), computed at CAM-B3LYP+IDSCRF/DZVP level.

	E	E+ZPE .	G(195)	G(273)	G(298)
1	-688.74777	-688.55156	-688.57422[a]	-688.58669	-688.59104
			-688.56690[b]	-688.57615	-688.57945
MgBrPh2OMe (THF)$_2$	-3699.26825	-3698.86989	-3698.90392	-3698.92464	-3698.93194
			-3698.89739	-3698.91521	-3698.92156
1+ MgBrPh2OMe(THF)$_2$	-4388.01602	-4387.42145	-4387.47814	-4387.51133	-4387.52298
			-4387.46429	-4387.49136	-4387.50101
COMd	-4388.01752	-4387.42139	-4387.46066	-4387.48682	-4387.49623
			-4387.45466	-4387.47812	-4387.48666
TSd	-4387.98928	-4387.39258	-4387.42921	-4387.45372	-4387.46258
			-4387.42241	-4387.44391	-4387.45179
INTd	-4388.04706	-4387.44702	-4387.48442	-4387.50918	-4387.51812
			-4387.47415	-4387.49451	-4387.50202
TS1d	-4388.03076	-4387.43347	-4387.47051	-4387.49520	-4387.50412
			-4387.46421	-4387.48609	-4387.49409
CPLd	-4388.07450	-4387.47765	-4387.51860	-4387.54552	-4387.55517
			-4387.51175	-4387.53564	-4387.54430
MgBrOMe(THF)$_2$	-3353.87417	-3353.59133	-3353.62268	-3353.64077	-3353.64703
			-3353.61615	-3353.63134	-3353.63665
2d	-1034.18888	-1033.87786	-1033.90526	-1033.92144	-1033.92717
			-1033.89876	-1033.91204	-1033.91683

MgBrOMe(THF)$_2$+2d	-4388.06305	-4387.46919	-4387.52794 -4387.51491	-4387.56221 -4387.54338	-4387.57420 -4387.55348

See the footnote of **Table S9**

Table S15 The total energies (E:a.u.), total energies+zero-point energies (E+ZPE:a.u.) and Gibbs free energies (G: a.u.) for the stationary points of other reactions in Table 1 , computed at CAM-B3LYP+IDSCRF/DZVP level.

	E	E+ZPE .	G(195)	G(273)	G(298)
1	-688.74777	-688.55156	-688.57422[a] -688.56690[b]	-688.58669 -688.57615	-688.59104 -688.57945
MgBrPhOMe-4 (THF)$_2$	-3584.75702	-3584.39191	-3584.42505 -3584.41787	-3584.44477 -3584.43442	-3584.45168 -3584.44030
1+ MgBrPhOMe-4(THF)$_2$	-4273.50479	-4272.94347	-4272.99927 -4272.98430	-4273.03146 -4273.00991	-4273.04272 -4273.01903
TSe	-4273.48884	-4272.92630	-4272.96387 -4272.95712	-4272.98839 -4272.97865	-4272.99717 -4272.98648
MgBrPhOMe-2,5 (THF)$_2$	-3699.26163	-3698.86347	-3698.89867 -3698.89211	-3698.91989 -3698.91042	-3698.92735 -3698.91693
1+ MgBrPhOMe-2,5(THF)$_2$	-4388.0094	-4387.41503	-4387.47289 -4387.45854	-4387.50658 -4387.48591	-4387.51839 -4387.49566
TSf	-4387.98887	-4387.39293	-4387.43118 -4387.42498	-4387.45656 -4387.44759	-4387.46571 -4387.45584
MgBrMe-2,5(THF)$_2$	-3548.84657	-3548.45914	-3548.49332 -3548.48667	-3548.51378 -3548.50417	-3548.52094 -3548.51037
1+MgBrMe-2,5(THF)$_2$	-4237.59434	-4237.01070	-4237.06754 -4237.05357	-4237.10047 -4237.08032	-4237.11198 -4237.08982
TSg	-4237.57502	-4236.98925	-4237.02641 -4237.01977	-4237.05089 -4237.04130	-4237.05970 -4237.04904
MgBrPh-Me-2(THF)$_2$	-3509.55074	-3509.19109	-3509.22360 -3509.21680	-3509.24288 -3509.23308	-3509.24963 -3509.23885
1+ MgBrPh-Me-2(THF)$_2$	-4198.29851	-4197.74265	-4197.79782 -4197.78370	-4197.82957 -4197.80923	-4197.84067 -4197.81830
TSh	-4198.27899	-4197.72078	-4197.75632 -4197.74938	-4197.77961 -4197.76961	-4197.78800 -4197.77699
MgBrPh-Me-2,5(THF)$_2$	-3548.84450	-3548.45687	-3548.48993 -3548.48363	-3548.50983 -3548.50072	-3548.51681 -3548.50680
1+ MgBrPh-Me-2,5(THF)$_2$	-4237.59227	-4237.00843	-4237.06415 -4237.05053	-4237.09652 -4237.07687	-4237.10785 -4237.08625
TSi	-4237.55779	-4236.97053	-4237.00643 -4236.99957	-4237.03012 -4237.02024	-4237.03868 -4237.02780

See the footnote of **Table S9**

Table S16 The total energies (E:a.u.), zero-point energies (ZPE:a.u.) and Gibbs free energies (G:a.u.) for the stationary points of reaction (a), computed at CAM-B3LYP+IDSCRF/DZVP level.

	E	E+ZPE .	G(195)	G(273)	G(298)
1...THF	-921.12719	-920.81042	-920.83875[a] -920.83206[b]	-920.85522 -920.84555	-920.86100 -920.85036
$MgBrEt(THF)_2$	-3317.89465	-3317.58884	-3317.61840 -3317.61190	-3317.63567 -3317.62627	-3317.64168 -3317.63134
1...THF+ $MgBrEt(THF)_2$	-4239.02184	-4238.39926	-4238.45715 -4238.44396	-4238.49089 -4238.47182	-4238.50268 -4238.4817
COMa	-4239.02329	-4238.40024	-4238.44413 -4238.43760	-4238.47248 -4238.46306	-4238.48258 -4238.47221
TSa	-4239.00894	-4238.38454	-4238.42317 -4238.41660	-4238.44869 -4238.43920	-4238.45785 -4238.44741
INTa	-4239.08473	-4238.45691	-4238.49731 -4238.49063	-4238.52360 -4238.51396	-4238.53301 -4238.52240
TS1a	-4239.07540	-4238.44949	-4238.49080 -4238.48418	-4238.51753 -4238.50796	-4238.52707 -4238.51655
CPLa	-4239.09683	-4238.47144	-4238.51460 -4238.50796	-4238.54260 -4238.53301	-4238.55257 -4238.54202
$MgBrOMe(THF)_2$	-3353.87417	-3353.59133	-3353.62268 -3353.61599	-3353.64077 -3353.63134	-3353.64703 -3353.63665
2a...THF	-885.21870	-884.87712	-884.90552 -884.89874	-884.92200 -884.91222	-884.92779 -884.91703
$MgBrOMe(THF)_2$+2a...THF	-4239.09287	-4238.46845	-4238.52820 -4238.51473	-4238.56277 -4238.54356	-4238.57482 -4238.55368

See the footnote of **Table S9**

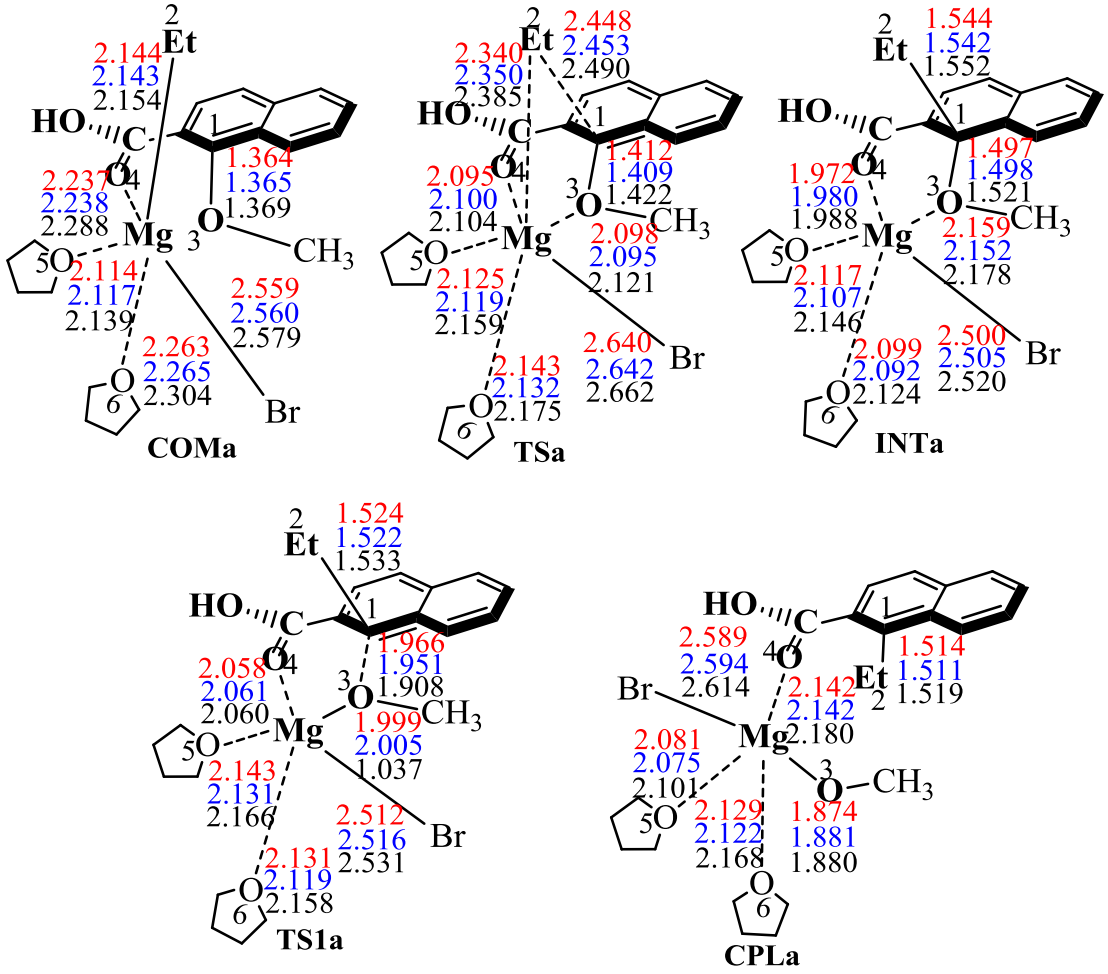

Figure S1 The main geometric parameters for the stationary points along reaction a, obtained with CAM-B3LYP+IDSCRF/dzvp(in red), CAM-B3LYP+IDSCRF/6-311++G**(in blue) and B3LYP/DZVP(in black).

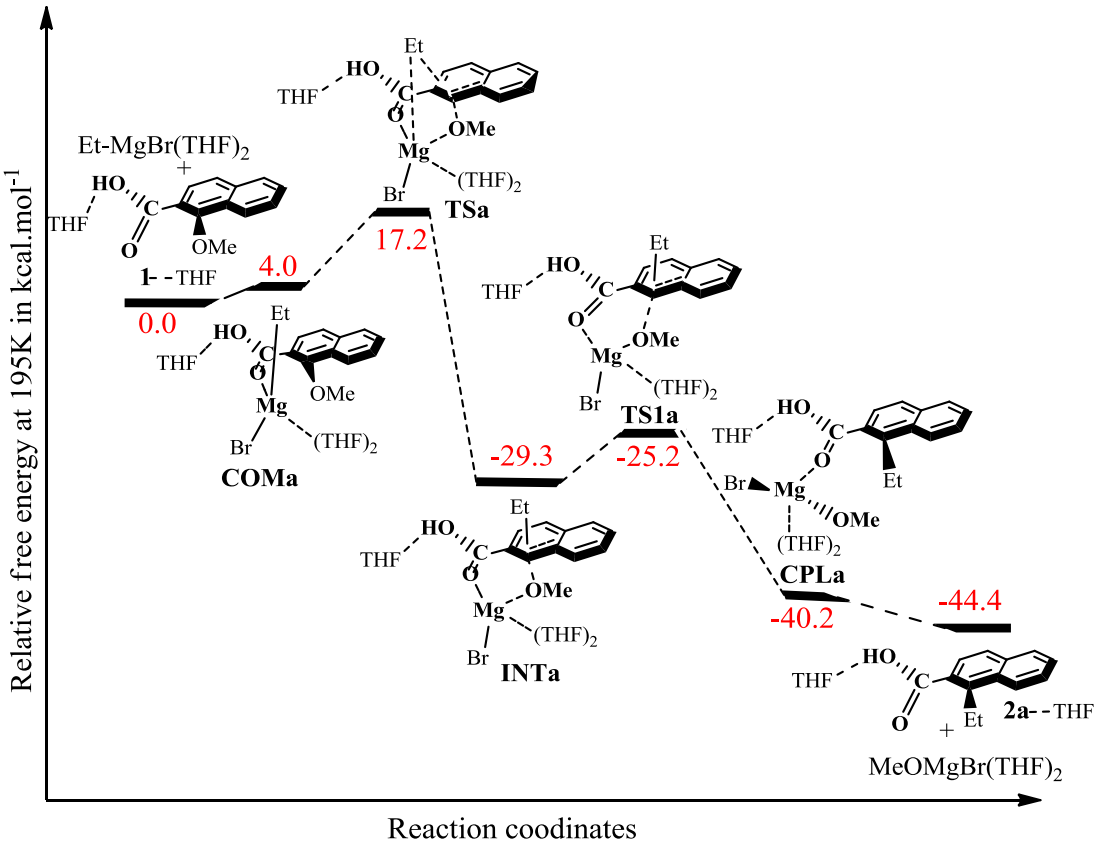

Figure S2 Free energy profile (kcal•mol^{-1}) for the reaction of **1…THF**+Et-MgBr(THF)$_2$→**2a…THF**+MeO-MgBr(THF)$_2$ at 195K