Synthetic Studies Towards the Mulberry Diels-Alder Adducts: H-Bond Accelerated Cycloadditions of Chalcones

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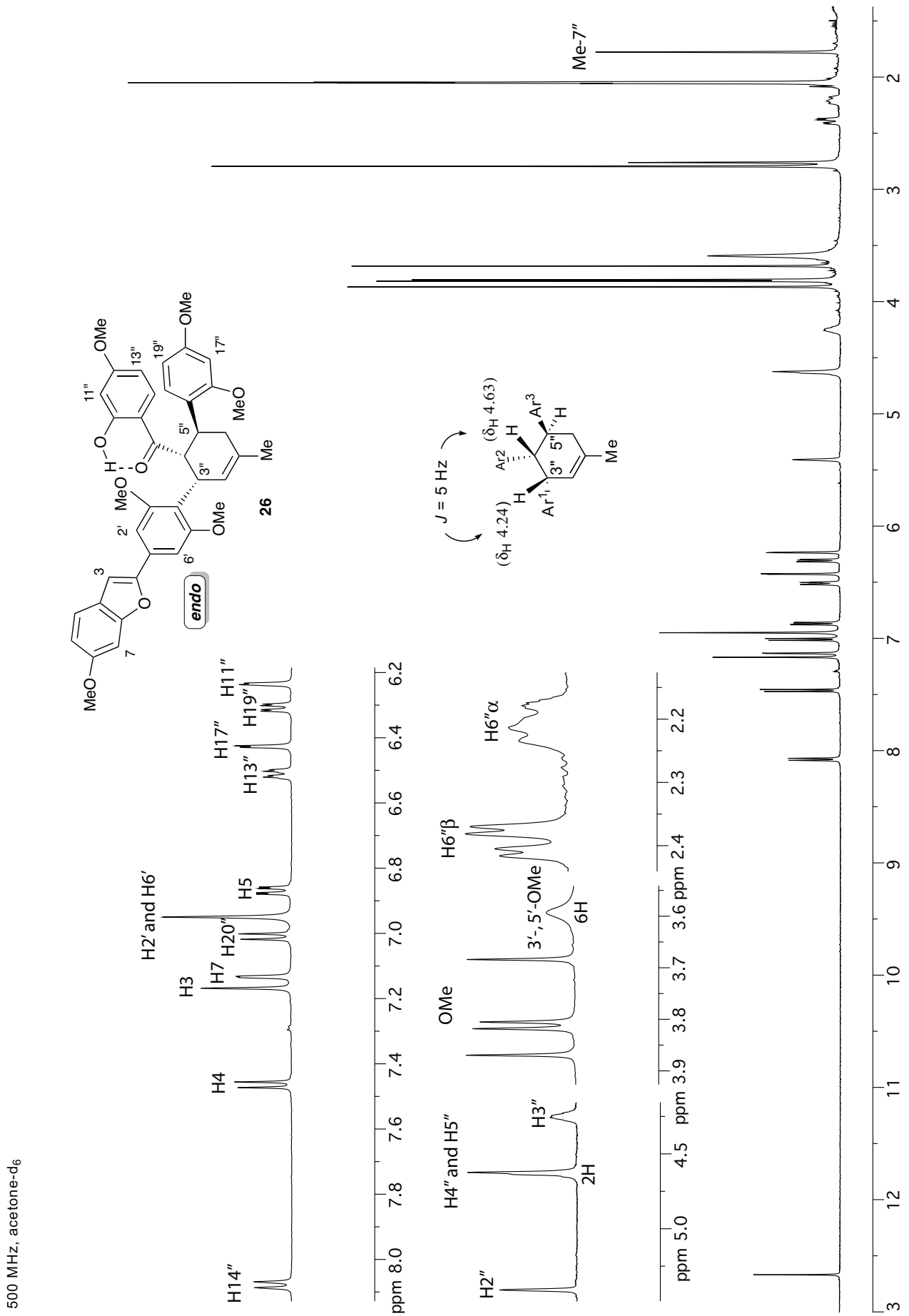
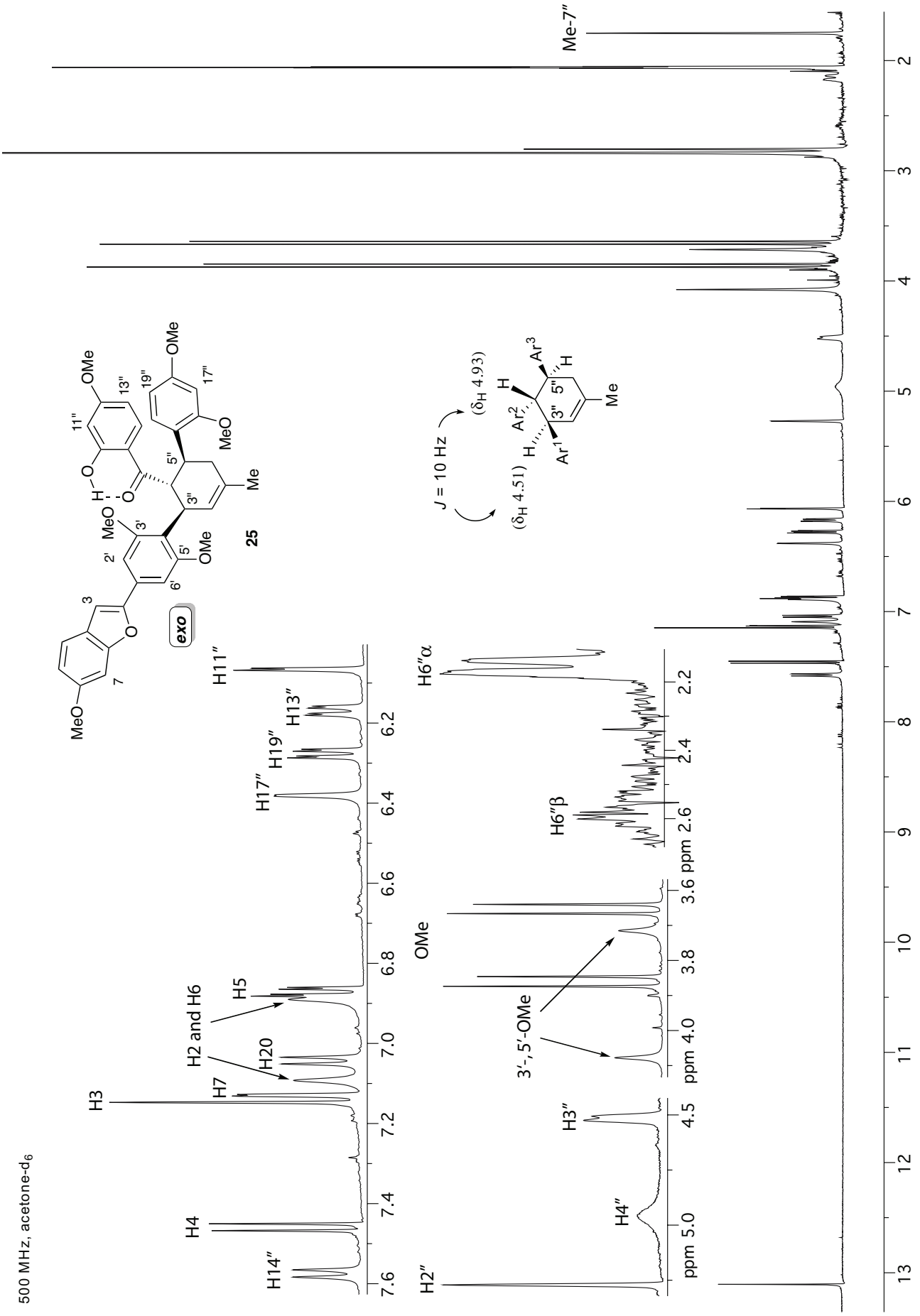
Electronic Supporting Information

Contents

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H4″
H2″
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2.2
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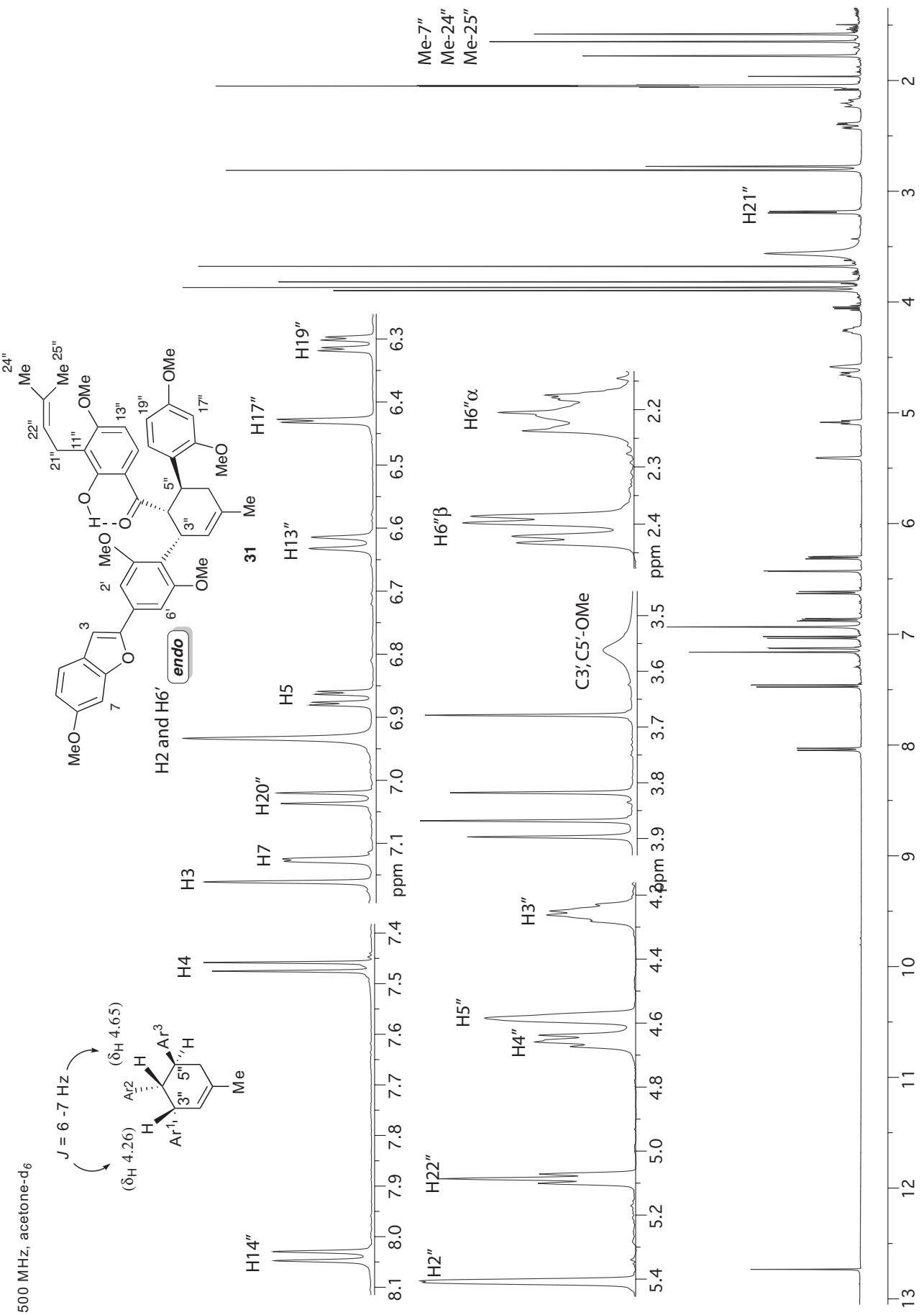
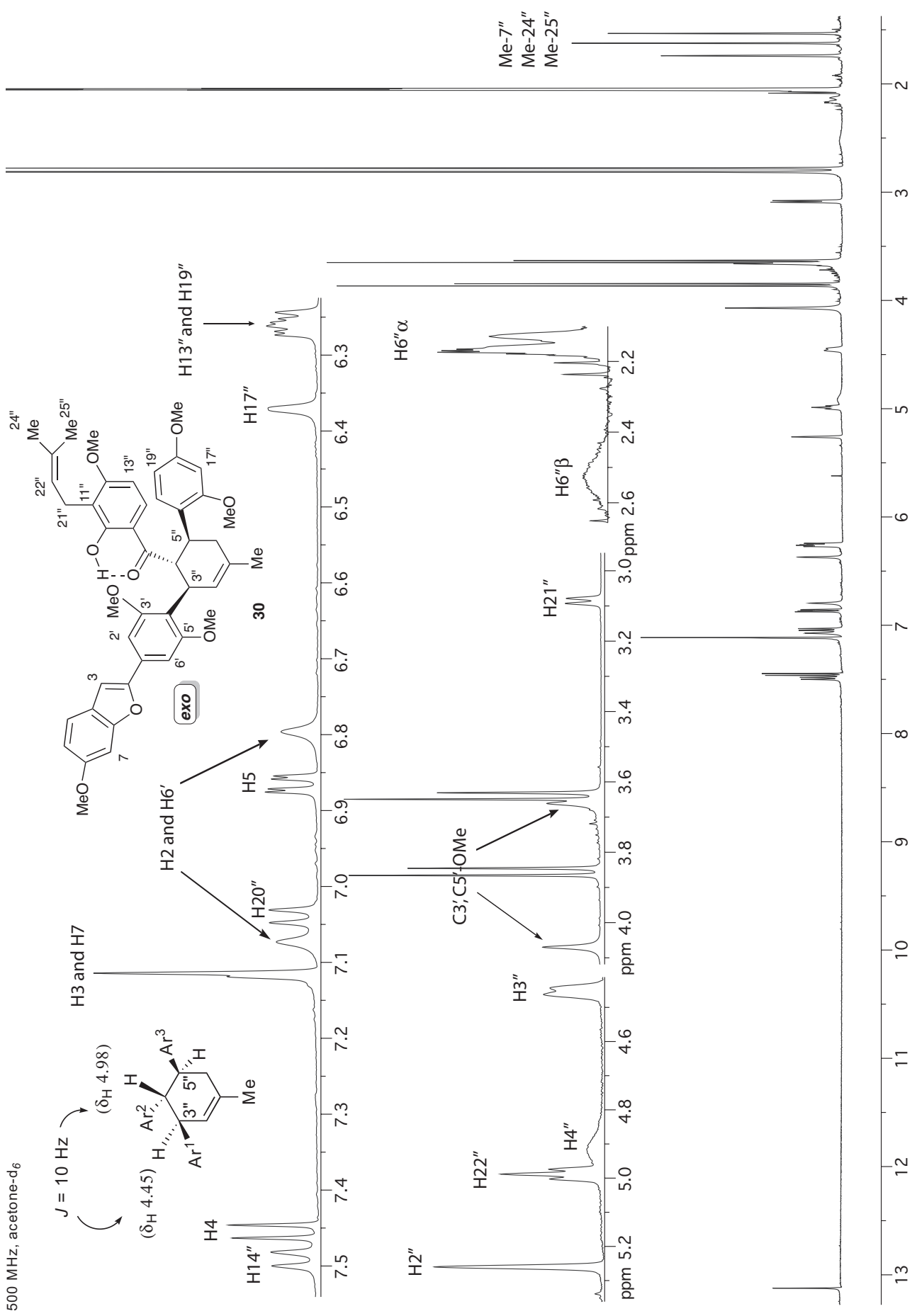
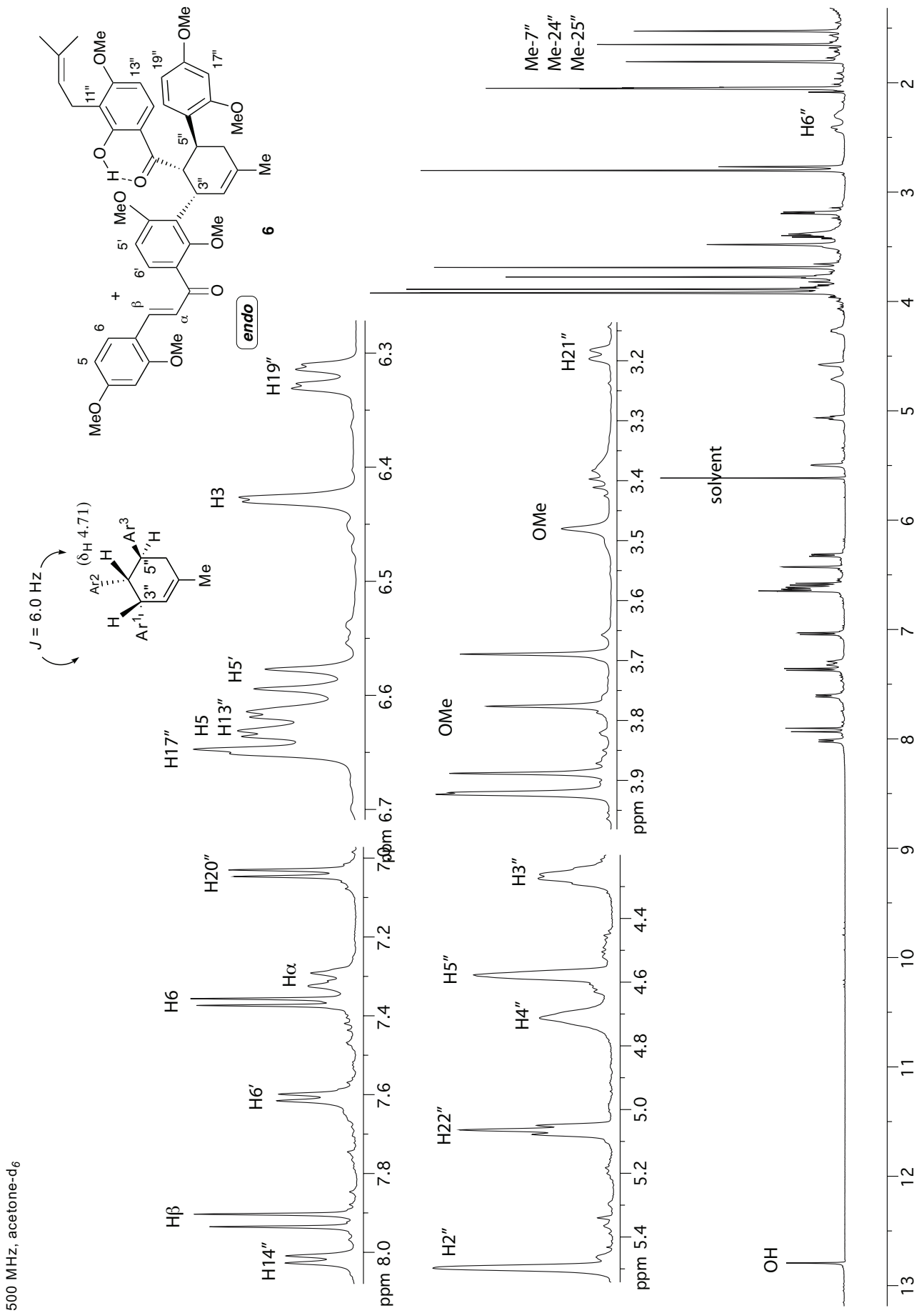
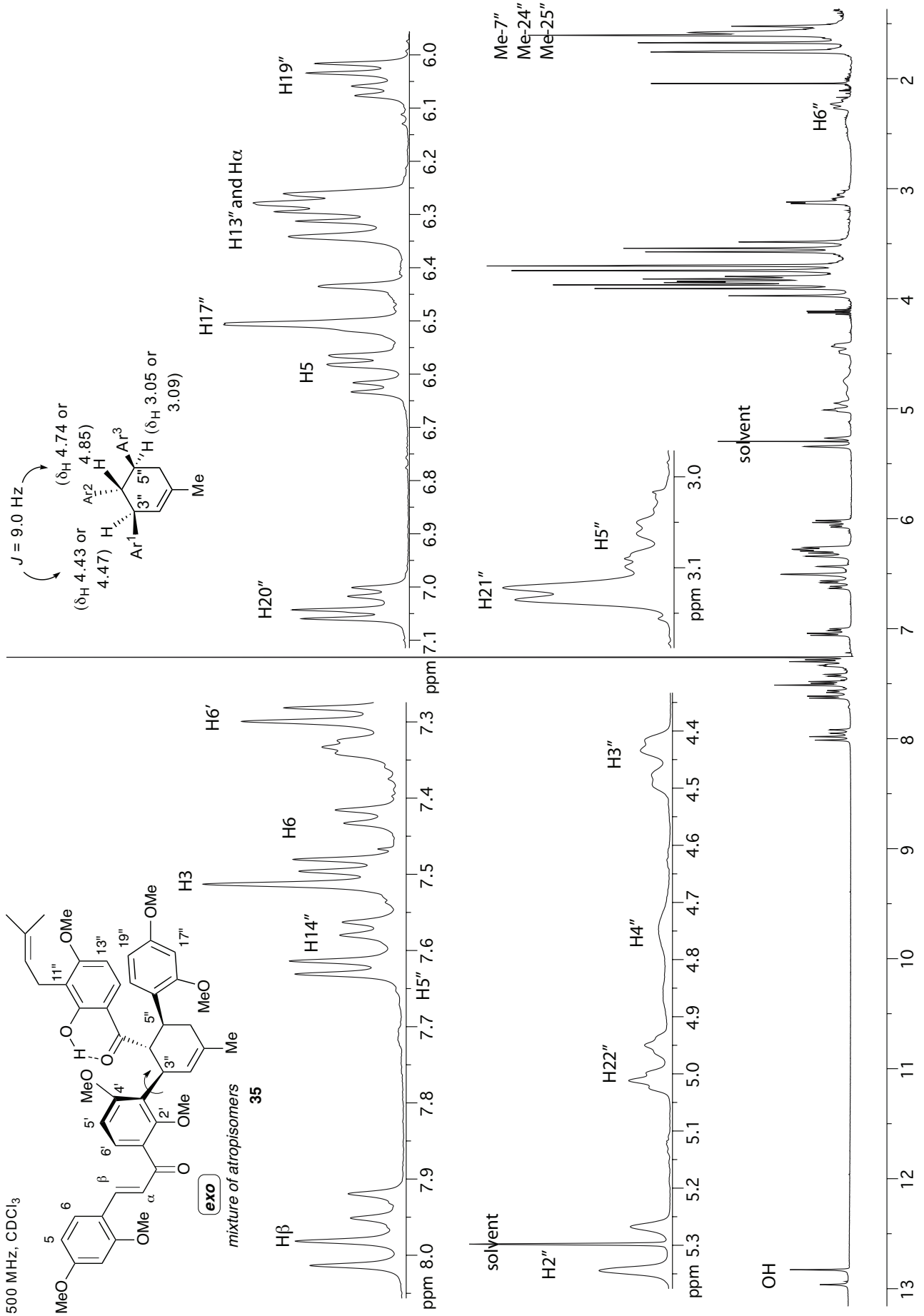
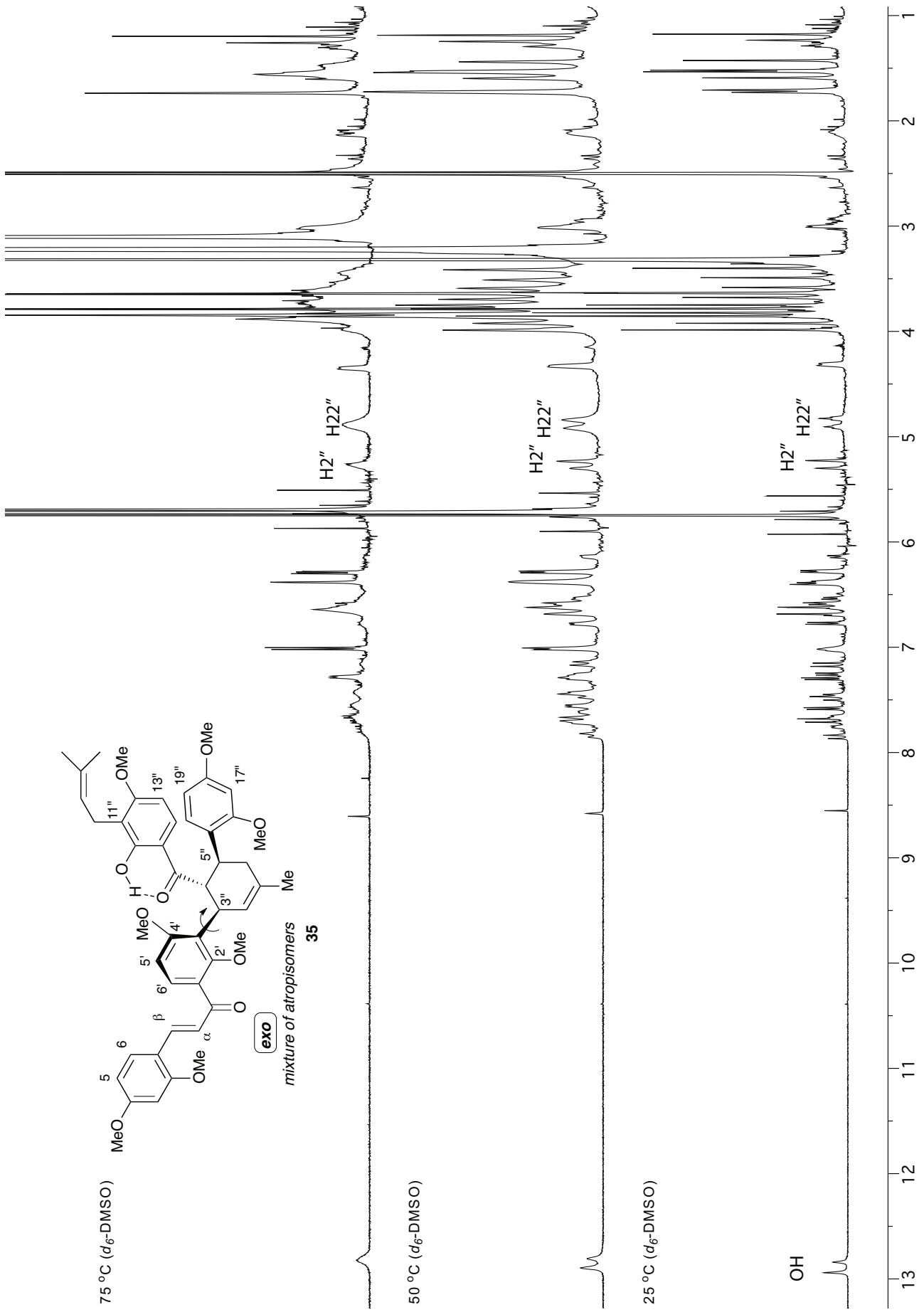










Calculated Geometries and Energies

The B3LYP/6-31G(d) optimized geometry of the lowest-energy conformer of each species is given below, along with the following energies:
B3LYP/6-31G(d) electronic energy (E)
B3LYP/6-31G(d) zero-point energy (ZPE)
B3LYP/6-31G(d) free energy at 298.15 K and 1 atm (G)
B3LYP-D dispersion energy (E_{disp})
M06-2X/6-311+G(d,p) single-point electronic energy ($E_{M06-2X,LBS}$)
M06-2X/6-31G(d) single-point electronic energy (E_{M06-2X})
M06-2X/6-31G(d) single-point energy in toluene ($E_{M06-2X,toluene}$)
All energies are in Hartree, except for E_{disp}, which is given in kcal/mol.

A comparison of the activation energies predicted by M06-2X, B3LYP, and B3LYP-D in the gas phase, together with M06-2X activation energies in solution, is provided in Table S1.

Table S1. Activation Energies for **TS1**–**TS4** Computed by Different Methods.[a]

	$\Delta G^{\ddagger}$			
	OH		OMe	
	endo (**TS1**)	*exo* (**TS2**)	*endo* (**TS3**)	*exo* (**TS4**)
M06-2X/6-311+G(d,p)	26.4	25.3	28.7	27.9
B3LYP/6-31G(d)	38.8	38.7	41.3	41.3
B3LYP-D	18.8	17.5	20.1	19.1
M06-2X/6-311+G(d,p), toluene[b]	23.1	22.1	25.4	24.6

[a] All calculations use the B3LYP/6-31G(d) optimized geometries and incorporate thermochemical corrections computed from the B3LYP/6-31G(d) frequencies. [b] Incorporates CPCM solvation energy computed at the M06-2X/6-31G(d) level (UAKS radii).

OH-substituted Chalcone 24

H	-8.502529	-0.695818	0.000000
C	-7.614900	-0.061075	0.000000
O	-6.504405	-0.948223	0.000000
C	-5.252976	-0.415540	0.000000
C	-4.966680	0.953441	0.000000
C	-3.633358	1.351017	0.000000
C	-2.553643	0.451287	0.000000
C	-2.881777	-0.937168	0.000000
C	-4.209154	-1.354008	0.000000
H	-4.479595	-2.401945	0.000000
H	-5.752715	1.698418	0.000000
H	-3.406407	2.413874	0.000000
O	-1.839074	-1.810954	0.000000
C	-2.110592	-3.206198	0.000000
H	-1.136262	-3.697583	0.000000
C	-1.213503	1.013325	0.000000
H	-1.187867	2.102503	0.000000
C	0.000000	0.413149	0.000000
H	0.085095	-0.661846	0.000000
C	1.217762	1.242784	0.000000
O	1.117929	2.494828	0.000000

C	2.547504	0.611803	0.000000
C	2.752570	-0.788218	0.000000
H	1.896749	-1.453519	0.000000
C	4.011045	-1.350789	0.000000
H	4.156766	-2.425484	0.000000
C	5.145685	-0.510934	0.000000
C	4.995852	0.871898	0.000000
H	5.838901	1.551174	0.000000
C	3.710691	1.438803	0.000000
O	3.635609	2.774644	0.000000
H	2.655623	2.988823	0.000000
O	6.343281	-1.151714	0.000000
C	7.529832	-0.368710	0.000000
H	8.356410	-1.081277	0.000000
H	-7.621044	0.573745	0.895092
H	-7.621044	0.573745	-0.895092
H	-2.669520	-3.504798	0.895497
H	-2.669520	-3.504798	-0.895497
H	7.592052	0.263466	0.894610
H	7.592052	0.263466	-0.894610

0 imaginary frequencies
E = -1072.842856
ZPE = 0.328881
G = -1072.566432
E_{disp} = -30.51573
$E_{M06-2X,LBS}$ = -1072.700836
E_{M06-2X} = -1072.395777
$E_{M06-2X,toluene}$ = -1072.413519

OMe-substituted Chalcone 12

C	1.164557	0.993946	0.069225
C	-0.056620	0.418064	0.003502
H	1.184342	2.068285	0.224984
C	2.459925	0.336361	-0.044607
C	3.656558	1.099094	0.088667
C	4.907295	0.496516	-0.018682
C	5.007309	-0.880561	-0.262180
C	3.850556	-1.657170	-0.399159
C	2.609373	-1.036302	-0.288936
O	3.491921	2.428883	0.325104
C	4.640359	3.250570	0.463053
H	5.251408	3.243583	-0.448743
H	4.262887	4.259204	0.638927
H	5.257671	2.938509	1.315303
H	5.826884	1.059144	0.080169
O	6.279289	-1.361375	-0.347986
C	6.459779	-2.748284	-0.593148
H	6.022101	-3.358655	0.207303
H	6.023805	-3.047183	-1.555114
H	7.539102	-2.908184	-0.620445
H	3.904257	-2.722111	-0.590166
H	1.717120	-1.644686	-0.400296
H	-0.187473	-0.647437	-0.131910
C	-1.271989	1.255298	0.107408
O	-1.193558	2.483356	0.187139
C	-2.637841	0.626231	0.034439
C	-2.984292	-0.711134	0.363798
C	-4.302034	-1.150990	0.241055
C	-5.305801	-0.279737	-0.203925

```
C    -4.995229    1.047633   -0.516622
C    -3.675972    1.468657   -0.381882
O    -1.991305   -1.524631    0.829828
C    -2.316404   -2.846156    1.233538
H    -1.381831   -3.284636    1.588236
H    -2.703504   -3.441608    0.396675
H    -3.050917   -2.846783    2.048572
H    -3.408534    2.496252   -0.604470
H    -5.752615    1.743138   -0.857442
H    -4.593441   -2.162915    0.490887
O    -6.549490   -0.828939   -0.289863
C    -7.621155   -0.000748   -0.718127
H    -7.454431    0.379447   -1.734114
H    -8.509377   -0.635062   -0.710558
H    -7.772546    0.845617   -0.036081
0 imaginary frequencies
E = -1112.128088
ZPE = 0.356764
G = -1111.827194
E_disp = -33.46185
E_M06-2X,LBS = -1111.972019
E_M06-2X = -1111.662495
E_M06-2X,toluene = -1111.681463
```

Diene 38

```
C    -1.363228    0.897390    0.000000
C     0.000000    0.502356    0.000000
C     0.962550    1.550595    0.000000
C     0.593154    2.898756    0.000000
C    -0.758028    3.233833    0.000000
C    -1.738178    2.246316    0.000000
C     0.487537   -0.876971    0.000000
C    -0.196063   -2.046054    0.000000
C     0.435760   -3.365977    0.000000
C     1.943514   -3.473974    0.000000
O     2.270403    1.149189    0.000000
C     3.289807    2.133200    0.000000
O    -2.282238   -0.112094    0.000000
C    -3.663016    0.211354    0.000000
C    -0.333007   -4.472381    0.000000
H     1.570025   -0.936576    0.000000
H    -1.278658   -2.046624    0.000000
H     1.341872    3.681027    0.000000
H    -1.051524    4.279983    0.000000
H    -2.783213    2.529404    0.000000
H    -4.190877   -0.744205    0.000000
H    -3.944660    0.780742    0.895133
H    -3.944660    0.780742   -0.895133
H     4.233018    1.583459    0.000000
H     3.240572    2.767384   -0.894843
H     3.240572    2.767384    0.894843
H     0.096458   -5.470339    0.000000
H    -1.418346   -4.408774    0.000000
H     2.262908   -4.520209    0.000000
H     2.378192   -2.985412    0.881103
H     2.378192   -2.985412   -0.881103
0 imaginary frequencies
E = -655.413378
ZPE = 0.261884
```

G = -655.194452
E_{disp} = -22.56575
$E_{M06-2X,LBS}$ = -655.301191
E_{M06-2X} = -655.118727
$E_{M06-2X,toluene}$ = -655.128064

TS1 (OH, *endo*)

C	-0.684116	-0.598669	0.341065
C	-1.913181	-1.047602	-0.206870
H	-0.643203	0.316880	0.915776
C	0.466155	-1.450639	0.268807
H	-1.957818	-2.124843	-0.328712
C	-3.192328	-0.434074	0.253987
C	-0.813905	-1.098326	-2.777590
C	0.370384	-0.344976	-2.622307
C	0.435613	0.797816	-1.846364
C	-2.016312	-0.706178	-2.152592
H	-2.216204	0.355951	-2.055285
H	-2.908406	-1.282944	-2.389177
C	-0.754128	-2.436813	-3.470642
H	-1.520648	-2.522294	-4.251046
H	-0.925995	-3.240493	-2.743928
H	0.224610	-2.610349	-3.927941
H	1.280144	-0.757190	-3.037459
H	-0.498886	1.257853	-1.557632
C	1.591888	1.599454	-1.485093
C	1.366624	2.889490	-0.923156
C	2.419085	3.720154	-0.534861
C	3.729394	3.269990	-0.685776
C	4.002197	2.011566	-1.211374
C	2.946496	1.180507	-1.603484
O	3.146590	-0.062564	-2.111648
C	4.453444	-0.625299	-2.084144
H	5.128513	-0.098366	-2.770808
H	4.864538	-0.610820	-1.068949
H	4.331379	-1.660607	-2.403194
H	5.028237	1.681098	-1.311229
H	4.552096	3.912717	-0.384827
H	2.232567	4.701519	-0.117366
O	0.053633	3.252531	-0.792640
C	-0.252143	4.536648	-0.273081
H	0.117288	4.656657	0.753560
H	0.163209	5.334139	-0.902230
H	-1.341571	4.606069	-0.275735
C	-4.374187	-1.215668	0.323949
C	-5.574507	-0.665849	0.767478
C	-5.636257	0.685816	1.136497
C	-4.495448	1.486220	1.052647
C	-3.300421	0.911038	0.610498
H	-2.419823	1.544013	0.536457
H	-4.519252	2.535525	1.321386
O	-6.863564	1.115016	1.556529
C	-6.997690	2.470230	1.951570
H	-6.344117	2.709930	2.800811
H	-6.776983	3.156636	1.123211
H	-8.039793	2.592949	2.252789
H	-6.482986	-1.250581	0.838960
O	-4.250525	-2.518301	-0.070175
C	-5.383830	-3.366970	0.014975

H	-5.048799	-4.346357	-0.331273
H	-5.746395	-3.450456	1.047617
H	-6.201585	-3.013885	-0.626954
O	0.426321	-2.483592	-0.470945
C	1.697882	-1.162360	1.044716
C	2.852335	-1.967351	0.843431
C	4.030764	-1.732925	1.574034
C	4.073676	-0.707457	2.515592
C	2.941610	0.098593	2.736324
C	1.789157	-0.139355	2.010250
O	2.872637	-2.972001	-0.048549
H	1.930462	-3.016418	-0.406074
H	4.871995	-2.389256	1.387210
O	5.164435	-0.410463	3.278819
H	2.995099	0.886278	3.480078
H	0.921666	0.480706	2.209567
C	6.327504	-1.208109	3.128275
H	7.059687	-0.806540	3.831561
H	6.731221	-1.145671	2.108898
H	6.129023	-2.260267	3.370257

1 imaginary frequency

E = -1728.221535

ZPE = 0.591553

G = -1727.702015

E_{disp} = -73.13923

$E_{M06-2X,LBS}$ = -1727.987102

E_{M06-2X} = -1727.499893

$E_{M06-2X,toluene}$ = -1727.532298

TS2 (OH, *exo*)

C	-1.956761	0.756796	-2.365195
C	-1.784338	-0.641535	-2.397283
H	-0.813233	-1.068776	-2.633723
H	-2.616588	-1.230975	-2.779557
C	-3.327384	1.331941	-2.633252
H	-3.388320	2.388790	-2.353975
H	-3.583030	1.252594	-3.698793
H	-4.100332	0.787720	-2.077325
C	-0.935361	1.605290	-1.895392
H	-1.204395	2.631162	-1.667454
C	0.353776	1.176346	-1.620553
H	0.687289	0.254542	-2.077992
C	1.424745	1.949141	-1.008414
C	1.229780	3.003733	-0.077810
C	2.311845	3.681945	0.491420
C	3.610511	3.311582	0.147157
C	3.852843	2.276071	-0.750030
C	2.769484	1.599124	-1.318318
O	-0.068247	3.290813	0.241907
C	-0.328090	4.314261	1.190445
H	0.115642	4.081963	2.167060
H	0.044553	5.287514	0.846474
H	-1.414477	4.358209	1.287657
H	2.154401	4.485420	1.199662
H	4.449463	3.841250	0.590113
H	4.870378	2.004829	-1.000978
O	2.912573	0.588487	-2.215480
C	4.217037	0.101723	-2.508192
H	4.731982	-0.223464	-1.597606

H	4.068836	-0.759464	-3.159902
H	4.815673	0.862878	-3.025098
C	-1.686152	-1.254747	-0.520348
C	-0.431436	-0.881956	0.028508
H	-1.713978	-2.281509	-0.873611
C	-2.943717	-0.814092	0.140871
H	-0.384923	-0.156726	0.828268
C	0.750095	-1.620836	-0.326943
C	-3.047782	0.383205	0.851760
H	-2.180599	1.034358	0.911127
C	-4.230561	0.793733	1.475438
H	-4.252903	1.732165	2.016539
C	-5.359749	-0.021352	1.384159
O	-6.573077	0.255475	1.949137
C	-6.704971	1.457089	2.689949
H	-6.018392	1.481245	3.546655
H	-6.527054	2.340706	2.062426
H	-7.734590	1.474441	3.052506
C	-5.300677	-1.224877	0.665582
H	-6.199201	-1.826735	0.613226
C	-4.113439	-1.612619	0.049395
O	-3.992061	-2.762652	-0.679587
C	-5.110646	-3.629241	-0.778052
H	-5.429090	-3.987951	0.209214
H	-4.778948	-4.476016	-1.381600
H	-5.958597	-3.138597	-1.273838
O	0.726085	-2.385075	-1.342015
C	1.997850	-1.507836	0.463150
C	3.168487	-2.183126	0.016169
C	4.366148	-2.110394	0.749063
C	4.413618	-1.379322	1.933432
C	3.266649	-0.708300	2.399080
C	2.095320	-0.783409	1.670017
O	3.184783	-2.903286	-1.116232
H	2.233255	-2.877332	-1.452353
H	5.219758	-2.654803	0.364099
H	3.325979	-0.151355	3.327861
H	1.218782	-0.274857	2.055887
O	5.522120	-1.258684	2.716647
C	6.701565	-1.943434	2.324394
H	7.445714	-1.721321	3.091635
H	7.067591	-1.592035	1.350698
H	6.539823	-3.027928	2.276439

1 imaginary frequency
E = -1728.222038
ZPE = 0.591597
G = -1727.702156
E_{disp} = -74.35026
$E_{M06-2X,LBS}$ = -1727.98923
E_{M06-2X} = -1727.501979
$E_{M06-2X,toluene}$ = -1727.534183

TS3 (OMe, *endo*)

C	1.988741	-1.250826	2.042016
C	1.924673	-1.240148	0.075409
C	0.694200	-0.721592	-0.405026
C	-0.388470	0.374977	1.950872
H	2.231466	-0.197728	2.144327
H	2.853743	-1.895352	2.187844

C	0.761722	-1.694690	2.584570
C	0.651828	-3.112528	3.087556
H	0.954581	-3.814438	2.302294
H	1.301823	-3.281399	3.956886
H	-0.374657	-3.360073	3.373423
C	-0.384541	-0.869124	2.554361
H	-1.313484	-1.293968	2.909594
H	0.569336	0.811096	1.708789
C	-1.491903	1.296058	1.722913
C	-1.183627	2.608347	1.261419
C	-2.176750	3.552672	0.990768
C	-3.514268	3.202917	1.169135
C	-3.868124	1.933105	1.612642
C	-2.870355	0.990558	1.888911
O	0.149098	2.880651	1.105281
C	0.539991	4.187187	0.720124
H	0.160202	4.447478	-0.276733
H	0.199223	4.939445	1.443107
H	1.631417	4.176325	0.697973
H	-1.922108	4.548662	0.650400
H	-4.291255	3.933547	0.961505
H	-4.913349	1.682434	1.741741
O	-3.157595	-0.261006	2.337921
C	-4.509867	-0.691208	2.375321
H	-5.100202	-0.106964	3.093207
H	-4.477289	-1.732542	2.700499
H	-4.971576	-0.635536	1.382524
H	1.979968	-2.322389	0.017824
C	3.200321	-0.542831	-0.260767
C	3.285831	0.841968	-0.411876
H	2.386861	1.436308	-0.271750
C	4.478922	1.500267	-0.727064
H	4.485279	2.578375	-0.836207
C	5.640548	0.744523	-0.892583
O	6.870043	1.256168	-1.204903
C	6.982893	2.658027	-1.378438
H	6.349181	3.016290	-2.200870
H	6.720765	3.202068	-0.460947
H	8.030224	2.847362	-1.622074
C	5.601029	-0.647943	-0.731359
H	6.525143	-1.197329	-0.860143
C	4.402106	-1.281061	-0.411861
O	4.300409	-2.630958	-0.219594
C	5.458262	-3.431742	-0.386280
H	5.140114	-4.458611	-0.196861
H	5.856262	-3.356563	-1.406660
H	6.245727	-3.156910	0.327997
H	0.626308	0.256683	-0.852953
C	-0.447723	-1.597743	-0.399468
O	-0.360666	-2.707338	0.172392
C	-1.768766	-1.238129	-1.042045
C	-2.784853	-2.189294	-0.899330
C	-4.063387	-2.043247	-1.434620
C	-4.351934	-0.883557	-2.158469
C	-3.366434	0.096358	-2.328599
C	-2.091251	-0.071594	-1.785698
H	-2.525863	-3.081507	-0.339345
H	-4.800563	-2.825061	-1.293390
O	-5.555501	-0.604043	-2.742930

H	-3.633518	0.978039	-2.896500
O	-1.114437	0.868164	-1.958602
C	-6.587535	-1.570664	-2.637299
H	-6.296632	-2.524916	-3.095631
H	-7.442442	-1.157135	-3.176090
H	-6.870695	-1.748370	-1.591030
C	-1.418457	2.053597	-2.673895
H	-2.209666	2.628939	-2.177178
H	-1.716518	1.837375	-3.707973
H	-0.495542	2.637415	-2.682134

1 imaginary frequency

E = -1767.505022

ZPE = 0.620070

G = -1766.958919

E_{disp} = -77.13841

$E_{M06-2X,LBS}$ = -1767.256752

E_{M06-2X} = -1766.765203

$E_{M06-2X,toluene}$ = -1766.798853

TS4 (OMe, *exo*)

C	1.817260	-0.803816	2.499707
C	1.693074	-1.354055	0.611220
C	0.429241	-0.963397	0.097552
C	-0.286274	1.063449	1.760309
C	1.007640	1.465100	2.057240
C	2.013221	0.592148	2.511131
H	0.841649	-1.226881	2.727429
H	2.642267	-1.417377	2.859722
C	3.392433	1.138320	2.797835
H	4.155947	0.615139	2.209121
H	3.462671	2.206948	2.569358
H	3.656815	1.005251	3.855900
H	1.294181	2.491743	1.852627
H	-0.650028	0.150352	2.211787
C	-1.332059	1.887029	1.160702
C	-1.100450	2.918934	0.215812
C	-2.156847	3.642184	-0.349358
C	-3.468170	3.339495	0.014474
C	-3.745181	2.330332	0.931849
C	-2.685386	1.615773	1.500182
O	-2.861853	0.639582	2.431718
C	-4.178882	0.202324	2.730922
H	-4.775185	1.005698	3.183237
H	-4.061433	-0.608620	3.451618
H	-4.685067	-0.177958	1.835910
H	-4.770660	2.111880	1.202141
H	-4.286988	3.903951	-0.423483
H	-1.968485	4.432969	-1.064751
O	0.206113	3.142856	-0.122635
C	0.504796	4.168653	-1.054616
H	0.048577	3.973733	-2.034270
H	0.174677	5.151433	-0.694001
H	1.591687	4.168519	-1.156869
H	1.725987	-2.391394	0.931708
C	2.939245	-0.890980	-0.056936
C	3.024432	0.318570	-0.748919
C	4.197149	0.750389	-1.378681
C	5.334498	-0.054944	-1.314070
C	5.294398	-1.271292	-0.616356

C	4.117283	-1.679941	0.006042
H	2.148992	0.959685	-0.789402
H	4.204874	1.698026	-1.904387
O	6.540127	0.242974	-1.888428
C	6.651642	1.459042	-2.606961
H	5.954929	1.493389	-3.455382
H	6.472104	2.329197	-1.961073
H	7.676791	1.494225	-2.981176
H	6.198722	-1.865971	-0.584819
O	4.015123	-2.844835	0.715582
C	5.143332	-3.700005	0.787512
H	4.827723	-4.560513	1.380393
H	5.455692	-4.039167	-0.208801
H	5.991853	-3.208854	1.282219
H	0.349742	-0.240041	-0.696069
C	-0.737536	-1.734408	0.477449
O	-0.674348	-2.524873	1.441257
C	-2.057139	-1.625392	-0.255325
C	-2.365774	-0.841485	-1.400818
C	-3.643170	-0.878663	-1.963053
C	-4.642670	-1.695027	-1.420343
C	-4.366799	-2.483111	-0.299030
C	-3.088039	-2.427094	0.250214
O	-1.378286	-0.064837	-1.933143
H	-3.901066	-0.286126	-2.831002
O	-5.845546	-1.645210	-2.063947
H	-5.115026	-3.133745	0.138440
H	-2.838617	-3.030915	1.116229
C	-1.663615	0.736663	-3.067778
H	-1.975734	0.126755	-3.925274
H	-0.728124	1.244650	-3.310746
H	-2.436643	1.482820	-2.846436
C	-6.898080	-2.461993	-1.576147
H	-7.167849	-2.199981	-0.544464
H	-6.635763	-3.527064	-1.618492
H	-7.751280	-2.273802	-2.230739

1 imaginary frequency
E = -1767.504877
ZPE = 0.619931
G = -1766.958865
E_{disp} = -78.25830
$E_{M06-2X,LBS}$ = -1767.257999
E_{M06-2X} = -1766.766344
$E_{M06-2X,toluene}$ = -1766.79985

Product: OH-substituted chalcone 24 + 38 (*endo*)

C	-1.291439	2.738353	-1.682460
C	-1.643376	1.510174	-2.486822
C	-0.731135	2.659242	-0.470008
C	-1.552227	4.062180	-2.355564
H	-0.473730	3.573688	0.061212
C	-0.472642	1.361635	0.265550
C	-1.524112	0.163861	-1.735873
C	-0.332160	0.147006	-0.720144
H	-2.664136	1.608508	-2.883953
H	-0.980958	1.481484	-3.359543
C	0.606946	1.463847	1.336762
C	-2.810245	-0.265792	-1.038844
H	-1.302622	-0.605756	-2.481545

H	-0.445047	-0.756414	-0.117698
C	1.007410	0.062829	-1.445940
H	-1.389829	1.124481	0.816940
H	-1.004487	4.134262	-3.306035
H	-2.616701	4.187619	-2.600512
H	-1.247531	4.904511	-1.725575
C	-3.073500	-1.644066	-0.837960
C	-4.245565	-2.077278	-0.223999
C	-5.190614	-1.140571	0.221687
C	-4.955665	0.222450	0.050702
C	-3.771125	0.630465	-0.576913
O	-2.104434	-2.502247	-1.286919
H	-4.463921	-3.127223	-0.073689
O	-6.303293	-1.677454	0.809984
H	-5.666093	0.967587	0.388372
H	-3.594921	1.694742	-0.701960
O	1.140799	0.635569	-2.545735
C	2.122589	-0.720904	-0.889968
C	2.036275	-1.475166	0.304048
C	3.100445	-2.199490	0.798681
C	4.327718	-2.191714	0.104072
C	4.464569	-1.460767	-1.072652
C	3.374709	-0.731810	-1.574278
H	1.107489	-1.484443	0.861380
H	3.022083	-2.773769	1.715209
O	5.319248	-2.932751	0.664245
H	5.387067	-1.431053	-1.638738
O	3.574203	-0.047543	-2.710443
H	2.688797	0.364513	-2.931863
C	6.583011	-2.974411	0.015729
H	7.212945	-3.618166	0.632045
H	6.502347	-3.399648	-0.992582
H	7.033754	-1.975999	-0.048386
C	-2.321264	-3.898059	-1.164870
H	-1.441149	-4.376114	-1.599133
H	-2.417870	-4.201516	-0.114000
H	-3.217185	-4.216122	-1.713890
C	-7.307678	-0.787689	1.266729
H	-8.098334	-1.415198	1.683058
H	-6.929244	-0.115815	2.048912
H	-7.717814	-0.184894	0.445519
C	1.863337	2.055766	1.099582
C	2.820357	2.183058	2.115196
C	2.528226	1.697479	3.386140
C	1.308893	1.083109	3.658565
C	0.361852	0.965135	2.632460
O	2.072656	2.478330	-0.179988
H	3.779408	2.646657	1.919213
H	3.267069	1.791792	4.177521
H	1.107206	0.701051	4.651759
O	-0.850701	0.349401	2.808436
C	3.356276	2.953911	-0.553040
H	3.299847	3.136149	-1.627140
H	3.606091	3.889041	-0.034543
H	4.133590	2.206081	-0.353559
C	-1.197035	-0.124624	4.098206
H	-2.199847	-0.544748	4.000171
H	-0.508128	-0.908163	4.440814
H	-1.212942	0.687467	4.836942

0 imaginary frequencies
E = -1728.280991
ZPE = 0.597174
G = -1727.753545
E_{disp} = -76.09040
$E_{M06-2X,LBS}$ = -1728.064535
E_{M06-2X} = -1727.580676
$E_{M06-2X,toluene}$ = -1727.615365

Product: OH-substituted chalcone 24 + 38 (*exo*)

C	-1.115250	-3.846277	0.153123
C	-2.069962	-2.993718	-0.234139
C	-1.836679	-1.564916	-0.684266
C	-0.423398	-1.058673	-0.265603
C	0.636701	-2.149656	-0.599504
C	0.340070	-3.440222	0.192163
C	-1.425352	-5.256075	0.587053
H	-0.928964	-5.992902	-0.060466
H	-1.060621	-5.445504	1.607049
H	-2.501266	-5.459138	0.569928
H	-3.108015	-3.325389	-0.251550
C	-2.964128	-0.635077	-0.236882
H	-1.852886	-1.552408	-1.779084
C	-0.099072	0.221558	-1.029694
H	-0.414181	-0.895110	0.808334
C	2.081479	-1.694436	-0.442256
H	0.504029	-2.379249	-1.663293
H	0.660735	-3.322473	1.236172
H	0.959981	-4.250505	-0.219192
C	-3.286597	-0.440010	1.120551
C	-4.342267	0.391940	1.515781
C	-5.089405	1.047161	0.541124
C	-4.803673	0.885764	-0.810810
C	-3.746969	0.046642	-1.192243
C	-2.855122	-1.091931	3.389285
H	-2.787534	-0.084005	3.820437
H	-3.870901	-1.479169	3.541509
H	-2.140255	-1.746496	3.891990
O	-2.493087	-1.105804	2.019037
H	-4.576712	0.536013	2.563289
H	-5.907790	1.696254	0.841055
H	-5.398918	1.402991	-1.553088
O	-3.414287	-0.173820	-2.499907
C	-4.100025	0.541269	-3.512753
H	-5.168325	0.287322	-3.537409
H	-3.989419	1.625945	-3.385800
H	-3.636258	0.239298	-4.453566
O	0.014619	0.134641	-2.269851
C	0.087525	1.508856	-0.354700
C	-0.072532	1.689414	1.039960
C	0.128604	2.909165	1.650389
C	0.507448	4.022550	0.869763
C	0.667568	3.896284	-0.506805
C	0.455736	2.653438	-1.124279
H	-0.376125	0.847797	1.650676
H	-0.002068	3.042600	2.718844
O	0.689624	5.179490	1.557865
C	1.074500	6.342819	0.837432
H	0.316884	6.622782	0.094806

H	1.165393	7.136746	1.580716
H	2.039024	6.200895	0.334053
H	0.950907	4.726638	-1.141231
O	0.617041	2.597156	-2.451875
H	0.424260	1.648468	-2.707492
C	2.936255	-1.717502	-1.543028
C	4.281305	-1.336758	-1.481979
C	4.797481	-0.907192	-0.260606
C	3.971931	-0.864383	0.872507
C	2.636854	-1.251386	0.783330
H	2.532534	-2.040512	-2.499105
H	4.891440	-1.374853	-2.376342
H	4.410104	-0.520060	1.800612
O	1.788421	-1.226702	1.861971
C	2.278126	-0.733394	3.098561
H	3.109013	-1.343023	3.476770
H	1.440948	-0.795135	3.796870
H	2.603985	0.310882	3.011894
O	6.087587	-0.504637	-0.051800
C	6.971746	-0.510019	-1.160063
H	7.931397	-0.153688	-0.780290
H	6.624963	0.161225	-1.956932
H	7.097903	-1.520227	-1.572145

0 imaginary frequencies
E = -1728.287646
ZPE = 0.596862
G = -1727.761966
E_{disp} = -73.24190
$E_{M06-2X,LBS}$ = -1728.066609
E_{M06-2X} = -1727.582603
$E_{M06-2X,toluene}$ = -1727.617815

Product: OMe-substituted chalcone 12 + 38 (*endo*)

C	-1.339144	3.004338	-1.396208
C	-1.718756	1.896972	-2.348598
C	-0.738811	2.758903	-0.226084
C	-1.622724	4.407597	-1.869220
H	-0.465592	3.593243	0.418078
C	-0.453342	1.374188	0.318258
C	-1.593937	0.464380	-1.782920
C	-0.371790	0.293414	-0.820711
H	-2.746877	2.054997	-2.706473
H	-1.072074	1.976182	-3.229956
C	0.673933	1.356203	1.345750
C	-2.865262	-0.039929	-1.109518
H	-1.406815	-0.200175	-2.631245
H	-0.466886	-0.674343	-0.332421
C	0.939958	0.279375	-1.611275
H	-1.343142	1.071095	0.882389
H	-1.112321	4.612650	-2.821290
H	-2.695686	4.561726	-2.053945
H	-1.292655	5.156355	-1.141218
C	-3.162357	-1.426057	-1.113240
C	-4.319267	-1.922683	-0.518025
C	-5.215776	-1.045730	0.111197
C	-4.949063	0.321453	0.139728
C	-3.780326	0.794633	-0.472438
O	-2.243272	-2.226987	-1.738103
H	-4.562869	-2.977855	-0.522174

O	-6.317581	-1.642805	0.664184
H	-5.622556	1.021760	0.619429
H	-3.577269	1.861053	-0.442384
O	1.025241	0.894364	-2.669180
C	2.148577	-0.508226	-1.156949
C	2.227283	-1.490541	-0.130952
C	3.438125	-2.126838	0.148306
C	4.595839	-1.816366	-0.574160
C	4.546145	-0.864777	-1.598739
C	3.329907	-0.245595	-1.865532
O	1.089373	-1.805221	0.545126
H	3.519691	-2.876865	0.924086
O	5.712673	-2.501797	-0.201439
H	5.422811	-0.610206	-2.182321
H	3.258910	0.485476	-2.663635
C	6.920319	-2.252093	-0.905480
H	7.670514	-2.901518	-0.450616
H	6.823656	-2.498665	-1.970569
H	7.236704	-1.205891	-0.804592
C	-2.495758	-3.618204	-1.817759
H	-1.650851	-4.044827	-2.361968
H	-2.554346	-4.076773	-0.821440
H	-3.424617	-3.830162	-2.363840
C	-7.272231	-0.810586	1.299181
H	-8.060531	-1.475752	1.657873
H	-6.837493	-0.271657	2.152019
H	-7.703402	-0.081913	0.599559
C	1.913184	1.991020	1.128859
C	2.914697	2.010043	2.109933
C	2.681415	1.384063	3.330145
C	1.473360	0.740121	3.585688
C	0.483454	0.727999	2.593162
O	2.058004	2.580455	-0.092382
H	3.861958	2.501950	1.926336
H	3.453725	1.396137	4.094766
H	1.310449	0.258126	4.542088
O	-0.725008	0.101550	2.766921
C	3.297684	3.174719	-0.433607
H	3.173766	3.543190	-1.453362
H	3.541041	4.015005	0.230543
H	4.113240	2.440847	-0.408108
C	-1.072972	-0.363522	4.058695
H	-2.098172	-0.730267	3.976605
H	-0.422614	-1.185871	4.387185
H	-1.031812	0.442138	4.803482
C	1.146442	-2.726766	1.622273
H	0.130917	-2.770199	2.018554
H	1.452057	-3.725079	1.283342
H	1.830877	-2.379448	2.405653

0 imaginary frequencies

E = -1767.564918

ZPE = 0.625077

G = -1767.011280

E_{disp} = -80.62273

$E_{M06-2X,LBS}$ = -1767.335351

E_{M06-2X} = -1766.847084

$E_{M06-2X,toluene}$ = -1766.882387

Product: OMe-substituted chalcone 12 + 38 (*exo*)

C	-2.018333	-3.463238	-0.121850
C	-0.529233	-3.321349	0.086661
C	0.067344	-2.136182	-0.698047
C	-0.759264	-0.832901	-0.442442
C	-2.230838	-1.055885	-0.904339
C	-2.753439	-2.436651	-0.560212
C	-2.619469	-4.807756	0.197580
H	-2.417744	-5.095793	1.239864
H	-2.187219	-5.600293	-0.430179
H	-3.704823	-4.812810	0.050804
H	-0.307966	-3.215517	1.157217
H	-0.020647	-4.241876	-0.235841
C	1.568115	-1.996336	-0.478838
H	-0.063285	-2.359407	-1.764032
C	-0.108309	0.280159	-1.277122
H	-0.731305	-0.595731	0.617678
C	-3.186473	0.034379	-0.416252
H	-2.217066	-0.976678	-1.996534
H	-3.825593	-2.572954	-0.705205
C	2.151849	-1.663887	0.768236
C	3.533580	-1.567348	0.915984
C	4.378986	-1.801503	-0.178374
C	3.837063	-2.129553	-1.419617
C	2.444874	-2.217959	-1.539375
O	1.281680	-1.444119	1.804082
C	1.801340	-0.994912	3.043308
H	2.470727	-1.737937	3.497021
H	2.340068	-0.045199	2.929608
H	0.936135	-0.848041	3.693005
H	3.994054	-1.311618	1.861973
O	5.716255	-1.678681	0.086757
C	6.625420	-1.908817	-0.975504
H	6.474348	-1.198111	-1.799242
H	7.622722	-1.765463	-0.554476
H	6.540881	-2.931667	-1.366482
H	4.463747	-2.311373	-2.284633
H	2.022862	-2.464020	-2.510546
O	-0.136515	0.193901	-2.500064
C	0.692574	1.384434	-0.651829
C	1.762826	1.873693	-1.410362
C	2.623899	2.869676	-0.959614
C	2.398881	3.421745	0.305498
C	1.319700	2.982539	1.085041
C	0.469494	1.979942	0.616880
H	1.915062	1.428965	-2.387948
H	3.448368	3.194086	-1.582789
O	3.161630	4.397275	0.874574
C	4.261850	4.906385	0.134936
H	4.998201	4.122070	-0.082344
H	3.935333	5.366106	-0.806693
H	4.720678	5.667381	0.768873
H	1.167664	3.460482	2.044347
O	-0.618741	1.563303	1.318468
C	-0.933583	2.199387	2.545565
H	-1.861495	1.737144	2.882816
H	-1.092428	3.276443	2.409175
H	-0.147669	2.041817	3.296167
C	-3.596257	0.127413	0.927804
C	-4.516023	1.095064	1.355181

C	-5.027228	2.000386	0.428844
C	-4.641395	1.951473	-0.906865
C	-3.729680	0.969085	-1.322046
O	-3.029393	-0.777895	1.785570
C	-3.604679	-0.956456	3.066367
H	-3.096726	-1.818228	3.504380
H	-4.680980	-1.162242	3.000504
H	-3.449662	-0.083374	3.716330
H	-4.828188	1.147136	2.391646
H	-5.738376	2.755574	0.753558
H	-5.052508	2.661821	-1.613547
O	-3.323293	0.841398	-2.620014
C	-3.760068	1.789642	-3.576080
H	-4.849728	1.758025	-3.713131
H	-3.461349	2.809411	-3.299868
H	-3.270208	1.512390	-4.511163

0 imaginary frequencies

E = -1767.569272

ZPE = 0.624478

G = -1767.018145

E_{disp} = -78.77788

$E_{M06-2X,LBS}$ = -1767.337324

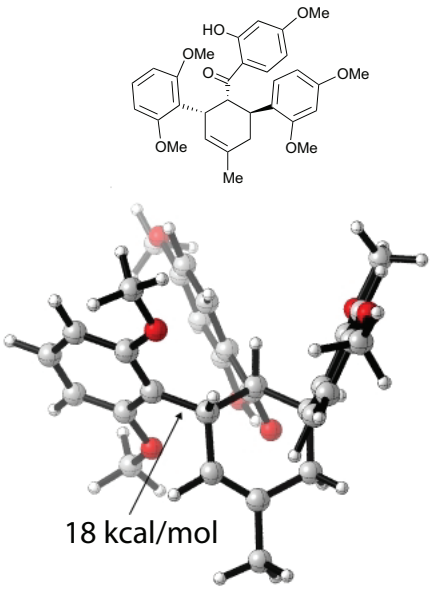
E_{M06-2X} = -1766.848498

$E_{M06-2X,toluene}$ = -1766.885456

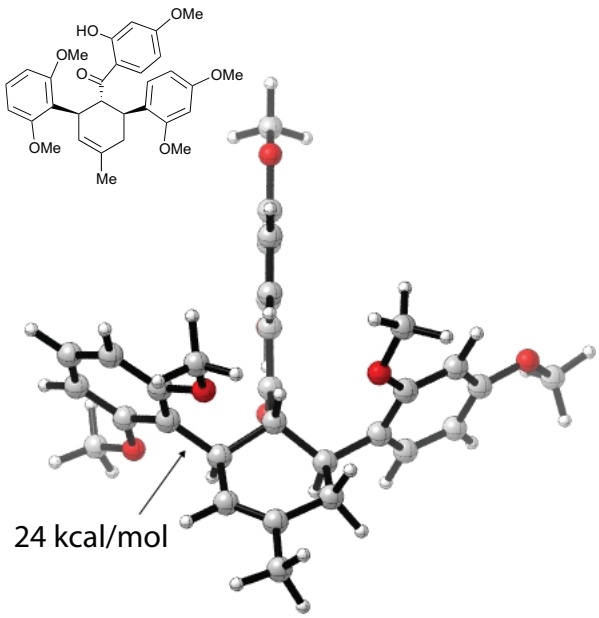
Transition States for Rotation about C–Ar^3 Bonds in Cycloadducts

Rotational barriers in the *endo* and *exo* products from cycloaddition of **24** + **38** were computed by a rotational scan. The C–Ar^3 dihedral angle was scanned in 10° steps (in both positive and negative directions) with MMFF94 optimizations at each step. Single-point energies at each step were then computed at the M06-2X/6-31G(d) level. The lowest-energy rotational transition state for each of the two compounds is reported below.

Endo



Exo



TS for rotation about C–Ar^3 bond in *endo* product from 24 + 38

C	1.474367	1.233955	2.902210
C	1.315252	2.001285	1.808808
C	0.848022	1.446460	0.491509
C	0.044464	0.122197	0.597720
C	0.796907	-0.883689	1.531572
C	1.172797	-0.249880	2.903232
C	1.939076	1.805709	4.210127
H	2.122139	2.883513	4.147589
H	2.872373	1.326495	4.522870
H	1.184867	1.639944	4.986149
H	1.551284	3.061955	1.851745
C	0.523887	2.553287	-0.542623
H	0.015987	-0.301389	-0.408929
C	-1.383542	0.191362	1.142390
O	-1.651376	0.626037	2.266907
C	-2.510719	-0.426277	0.370396
C	-2.466988	-0.584442	-1.019417
C	-3.538618	-1.178684	-1.696002
C	-4.671483	-1.615231	-1.005141
C	-4.734415	-1.439850	0.375034
C	-3.667776	-0.840970	1.051412
O	-3.832789	-0.686118	2.404727
H	-3.087505	-0.128722	2.727898
H	-1.628589	-0.231441	-1.610705
H	-3.491705	-1.295556	-2.776464
H	-5.595739	-1.747324	0.957241
O	-5.638054	-2.178869	-1.790727
C	-6.808993	-2.643997	-1.129154
H	-7.342400	-1.819217	-0.645241
H	-7.473314	-3.070558	-1.886899

H	-6.569371	-3.436279	-0.412336
H	0.109893	-1.700686	1.800955
C	1.948968	-1.570264	0.782972
C	1.672991	-2.624542	-0.115578
C	2.719917	-3.240819	-0.810152
C	4.042640	-2.822772	-0.638283
C	4.319182	-1.775248	0.234178
C	3.281698	-1.154131	0.935684
H	3.535129	-0.324933	1.592400
H	5.327892	-1.408733	0.391333
O	4.960691	-3.512109	-1.383532
C	6.323435	-3.133868	-1.234050
H	6.922631	-3.780430	-1.882406
H	6.665305	-3.285722	-0.204898
H	6.483337	-2.099637	-1.556357
H	2.539476	-4.055625	-1.503383
O	0.349818	-2.964288	-0.248940
C	0.025179	-4.014439	-1.150432
H	0.308893	-3.755844	-2.175817
H	-1.060962	-4.146628	-1.130286
H	0.481252	-4.959149	-0.837121
H	2.007584	-0.797614	3.357977
C	-0.812042	3.000992	-0.781472
C	-1.068113	3.937355	-1.789294
C	-0.026580	4.477191	-2.536757
C	1.286849	4.091430	-2.285944
C	1.574079	3.138901	-1.301446
O	-1.801297	2.502522	0.008389
C	-2.956057	3.311125	0.206527
H	-2.689973	4.345096	0.451028
H	-3.510104	2.899352	1.055619
H	-3.611227	3.268026	-0.669043
H	2.066893	4.552643	-2.882346
H	-0.238407	5.209696	-3.311605
H	-2.078060	4.265607	-2.013950
O	2.849330	2.722745	-1.006970
C	3.920761	3.236382	-1.785775
H	4.021823	4.318292	-1.652250
H	4.844790	2.770718	-1.429622
H	3.803582	2.974460	-2.842453
H	1.785706	1.056497	0.070302
H	0.325066	-0.397327	3.586663

E_{M06-2X} = -1727.552516

TS for rotation about C–Ar[3] bond in *exo* product from 24 + 38

C	2.565997	2.613636	-1.011953
C	3.047894	1.409072	-1.348895
C	2.498246	0.021723	-0.980449
C	0.955245	0.178133	-0.558091
C	0.339014	1.604073	-0.760535
C	1.277134	2.716108	-0.272221
C	3.243705	3.895972	-1.390279
H	2.596157	4.492145	-2.041177
H	3.471104	4.481374	-0.493495
H	4.185207	3.723291	-1.922148
H	3.926392	1.389954	-1.990612
H	2.575975	-0.588726	-1.888536
C	3.406108	-0.717313	0.061979
C	0.107524	-0.793232	-1.399406

O	0.390970	-1.057685	-2.573463
C	-1.195155	-1.336192	-0.892687
C	-2.200640	-1.678943	-1.813351
O	-2.024941	-1.605555	-3.173481
H	-1.070131	-1.429648	-3.335721
C	-3.463248	-2.100486	-1.389382
H	-4.201623	-2.340384	-2.146941
C	-3.740393	-2.202456	-0.029066
C	-2.735226	-1.910507	0.894125
C	-1.472725	-1.478999	0.469644
H	-0.736421	-1.242790	1.230099
H	-2.942504	-1.995348	1.958296
O	-4.933171	-2.583705	0.521188
C	-6.047482	-2.639934	-0.361568
H	-6.199386	-1.683125	-0.873133
H	-6.939772	-2.839923	0.239541
H	-5.938299	-3.459463	-1.079012
H	0.861478	-0.045769	0.501888
C	-1.059478	1.808021	-0.164095
C	-2.126893	2.036724	-1.053438
C	-3.433063	2.209256	-0.590336
C	-3.696525	2.166862	0.773981
C	-2.643469	1.962010	1.670312
C	-1.331225	1.774539	1.218354
H	-1.950953	2.068481	-2.127717
H	-4.215703	2.373926	-1.322880
O	-4.924428	2.315388	1.359912
C	-6.046754	2.357808	0.487597
H	-6.026808	3.258848	-0.134021
H	-6.948698	2.400272	1.105768
H	-6.106926	1.453139	-0.126982
H	-2.888327	1.940986	2.727120
O	-0.266099	1.529318	2.042923
C	-0.518507	1.403491	3.436037
H	0.432719	1.177464	3.927502
H	-1.202380	0.573022	3.640531
H	-0.894739	2.342204	3.855149
H	0.233499	1.742562	-1.849092
H	0.810764	3.690829	-0.466552
H	1.482031	2.669967	0.802206
C	2.858059	-1.667759	0.975671
C	3.605420	-2.176327	2.047650
C	4.947605	-1.862130	2.174500
C	5.555132	-1.072622	1.206500
C	4.811184	-0.515789	0.150140
O	5.428368	0.156227	-0.873987
C	6.740165	0.659401	-0.656322
H	7.473462	-0.153216	-0.656943
H	6.983837	1.324222	-1.490734
H	6.798026	1.248267	0.265172
H	6.626044	-0.919552	1.291487
H	5.532451	-2.273103	2.992481
H	3.149761	-2.838970	2.777440
O	1.591553	-2.152082	0.769780
C	1.519856	-3.579770	0.747378
H	2.386126	-4.030738	0.250309
H	0.626265	-3.862144	0.182955
H	1.408331	-3.969530	1.764006

E_{M06-2X} = -1727.541985