Supplementary Data

Geminal Repulsion Disrupts Diels–Alder Reactions of Geminally Substituted Cyclopentadienes and 4*H*-Pyrazoles

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M06-2X/6-31+G(d) Optimized Coordinates and M06-2X/6-311++G(d,p) Gibbs Free Energies

Ethylene

C	0.00000000	0.66519200	0.00000000
H	0.92502300	1.23512000	0.00000000
H	-0.92498400	1.23516200	0.00000000
C	0.00000000	-0.66519200	0.00000000
H	-0.92502300	-1.23512000	0.00000000
H	0.92498400	-1.23516200	0.00000000

G: −78.533482
H: −78.507974

Cyclopentadiene

C	0.01190700	1.21588100	-0.00040000
C	-1.17508100	0.29332700	0.00037800
C	1.18062500	0.27034800	0.00021200
H	2.21681800	0.58775100	0.00079200
H	-2.20488300	0.63085700	-0.00009200
H	0.01799900	1.87482700	-0.87997400
H	0.01861900	1.87389400	0.87983900
C	-0.74497200	-0.98278600	0.00007800
H	-1.36963500	-1.86920600	-0.00044800
C	0.72563400	-0.99714100	-0.00020100
H	1.33240700	-1.89589700	-0.00052400

G: −193.991995
H: −193.960317

Cyclopentadiene + Ethylene TS

C	0.36698800	0.00003400	1.32487500
C	0.45985500	1.15459300	0.36203400
C	1.17857400	0.70337200	-0.74264800
C	0.45966900	-1.15459100	0.36209700
C	1.17847400	-0.70354000	-0.74260300
C	-1.61292700	0.69144700	-0.33531700
C	-1.61301600	-0.69134300	-0.33526600
H	-2.05012000	1.23951900	0.49468100
H	-2.05025200	-1.23926500	0.49480700
H	0.39103900	-2.19306100	0.66958700
H	1.55701100	-1.33052600	-1.54273900
H	1.55719800	1.33025100	-1.54282800
H	0.39130000	2.19309200	0.66944000
H	-1.54332300	-1.24162000	-1.26672000
H	-1.54319600	1.24167200	-1.26679800

H	-0.49703200	0.00013200	1.99113700
H	1.28167700	-0.00002500	1.94039900

G: −272.477148
H: −272.440793

Cyclopentadiene + Ethylene Adduct

C	-0.03020600	0.00031000	1.37650100
C	-0.08570300	-1.12552400	0.32451400
C	-0.08458400	1.12569700	0.32407600
C	1.18074900	-0.77844100	-0.52124700
C	1.18170300	0.77724400	-0.52129800
H	2.07969400	-1.17467900	-0.03745800
H	2.08082600	1.17261600	-0.03694000
H	-0.11385300	2.15344200	0.69091000
H	-0.11563300	-2.15310200	0.69176500
H	1.12793600	1.20226400	-1.52701200
H	1.12612900	-1.20347800	-1.52697600
H	0.89768800	-0.00003800	1.96086100
H	-0.89577900	0.00089200	2.04486700
C	-1.27675600	-0.66917600	-0.50010800
H	-1.92166500	-1.32553200	-1.07573200
C	-1.27606500	0.67002500	-0.50041000
H	-1.92016700	1.32680900	-1.07644300

G: −272.544735
H: −272.510120

5,5-Dimethylcyclopentadiene

C	0.54613900	0.00000000	0.00000000
C	-0.40673800	-1.17241000	0.00000000
C	-0.40673800	1.17241000	0.00000000
H	-0.06990300	2.20468000	-0.00000100
H	-0.06990300	-2.20468000	0.00000000
C	-1.67860400	0.73704500	0.00000000
H	-2.57109400	1.35350600	0.00000000
C	-1.67860400	-0.73704500	0.00000000
H	-2.57109400	-1.35350600	0.00000000
C	1.42720900	0.00000000	-1.26158600
H	2.07054700	-0.88673300	-1.27900600
H	0.81028800	-0.00000100	-2.16535100
H	2.07054700	0.88673200	-1.27900700
C	1.42720900	0.00000000	1.26158600
H	2.07054700	-0.88673200	1.27900700
H	2.07054700	0.88673300	1.27900600
H	0.81028800	0.00000100	2.16535100

G: −272.547797
H: −272.509996

5,5-Dimethylcyclopentadiene + Ethylene TS

C	-0.80997200	-0.27391900	-0.00012100
C	-0.05764800	0.37213300	-1.14991900
C	0.40565900	1.60573000	-0.70411300
C	-0.05793200	0.37203100	1.14988800
C	0.40551800	1.60565800	0.70435700
C	-2.25790300	0.30446700	-0.00015400
H	-2.80041100	-0.04665300	-0.88461400
H	-2.79987600	-0.04516400	0.88522500
H	-2.25195900	1.39573700	-0.00106100
C	1.82906200	-0.78424700	-0.69051600
C	1.82909600	-0.78421900	0.69048500
H	1.49390000	-1.65123900	-1.25232100
H	1.49398500	-1.65117000	1.25239000
H	-0.26755900	0.13013000	2.18909800
H	0.81934200	2.38611900	1.33379900
H	0.81960400	2.38626800	-1.33338000
H	-0.26719400	0.13060400	-2.18923300
H	2.47858100	-0.10929300	1.23586700
H	2.47863800	-0.10950700	-1.23602000
C	-0.96856200	-1.79442500	0.00003400
H	-1.53831000	-2.10802100	-0.88236600
H	-0.02579200	-2.33931500	-0.00055400
H	-1.53685200	-2.10774600	0.88352100

G: −351.027574
H: −350.985654

5,5-Dimethylcyclopentadiene + Ethylene Adduct

C	0.83721900	-0.00616200	-0.00002200
C	-0.23897100	0.09482600	1.12207900
C	-1.02159200	1.31473400	0.66940300
C	-0.23892700	0.09516000	-1.12202200
C	-1.02154300	1.31500700	-0.66897200
C	1.85112000	1.14187800	0.00001100
H	2.49741200	1.07415200	0.88336900
H	2.49659700	1.07450400	-0.88396700
H	1.37546000	2.12366900	0.00047200
C	-1.16875800	-1.11240500	0.77815500
C	-1.16895000	-1.11199000	-0.77850100
H	-0.77168900	-2.04798900	1.18406500
H	-0.77256100	-2.04759300	-1.18495100
H	0.13294700	0.10673000	-2.15065600
H	-1.56501200	1.98561000	-1.32705400

H	-1.56522600	1.98512100	1.32757500
H	0.13295900	0.10594200	2.15068700
H	-2.16854700	-0.97026500	-1.19748900
H	-2.16820800	-0.97137000	1.19762800
C	1.63534000	-1.31347300	-0.00005200
H	2.28285000	-1.35540900	0.88414200
H	1.01920300	-2.21388400	-0.00101800
H	2.28418400	-1.35465700	-0.88327600

G: −351.099675
H: −351.059216

2,3-Diazacyclopentadiene

C	0.00000000	-1.19041000	0.00000000
C	0.00000000	-0.20408700	-1.12456600
C	0.00000000	-0.20408700	1.12456600
H	0.00000000	-0.43655900	2.18409900
H	0.00000000	-0.43655900	-2.18409900
N	0.00000000	1.01006400	0.71717000
N	0.00000000	1.01006400	-0.71717000
H	-0.88517500	-1.83813900	0.00000000
H	0.88517600	-1.83813900	0.00000000

G: −226.084086
H: −226.052802

2,3-Diazacyclopentadiene + Ethylene TS

C	-0.57920200	-0.00037100	1.26549800
C	-0.52409800	-1.10756200	0.25666300
C	-0.52500900	1.10733500	0.25721300
C	1.59576000	-0.69010900	-0.15868400
C	1.59554800	0.69073800	-0.15885900
H	1.92219700	-1.23924600	0.72062700
H	1.92177100	1.24033800	0.72024100
H	-0.54790000	2.16988500	0.47333900
H	-0.54683600	-2.17018600	0.47245800
H	1.61778200	1.23936500	-1.09346300
H	1.61859800	-1.23892000	-1.09316500
H	0.17647400	-0.00020300	2.04900800
H	-1.58061400	-0.00092800	1.72683900
N	-0.99731300	0.66877200	-0.91034500
N	-0.99689700	-0.66881300	-0.91063700

G: −304.570333
H: −304.534433

2,3-Diazacyclopentadiene + Ethylene Adduct

C	-0.31829000	0.00127200	1.34421200
C	-0.17095900	-1.09421100	0.28823700
C	-0.16874100	1.09502600	0.28716000
C	1.21890700	-0.77704500	-0.32594800
C	1.22026500	0.77486000	-0.32696400
H	2.01212800	-1.18933400	0.30339500
H	2.01467600	1.18647100	0.30147900
H	-0.35199600	2.13470900	0.55195900
H	-0.35520300	-2.13332500	0.55466700
H	1.31654200	1.20316500	-1.32719400
H	1.31500400	-1.20673900	-1.32567200
N	-1.13088600	-0.62039000	-0.75541600
N	-1.13016100	0.62072400	-0.75619700
H	0.48398000	0.00076900	2.08672000
H	-1.29490000	0.00253500	1.83574500

G: −304.639135
H: −304.604891

5,5-Dimethyl-2,3-diazacyclopentadiene

C	0.53141500	0.00000000	0.00000000
C	-0.47067000	-0.00000900	1.11844000
C	-0.47067000	0.00000900	-1.11844000
H	-0.22957800	0.00001700	-2.17852500
H	-0.22957800	-0.00001700	2.17852500
C	1.39996100	-1.26878500	-0.00001000
H	2.04243300	-1.28578000	0.88613300
H	0.78186100	-2.17109800	-0.00001700
H	2.04243300	-1.28576700	-0.88615200
C	1.39996100	1.26878500	0.00001000
H	2.04243300	1.28576700	0.88615200
H	2.04243300	1.28578000	-0.88613300
H	0.78186100	2.17109800	0.00001700
N	-1.68673400	0.00000600	-0.72056500
N	-1.68673400	-0.00000600	0.72056500

G: −304.64065
H: −304.602863

5,5-Dimethyl-2,3-diazacyclopentadiene + Ethylene TS

C	0.81200800	0.29193500	-0.00000400
C	0.04843100	-0.39842000	-1.10270400
C	0.04842500	-0.39840300	1.10270300
C	2.25374000	-0.30110300	0.00000500
H	2.79534300	0.04581200	-0.88559000
H	2.79535300	0.04586100	0.88557400
H	2.23962600	-1.39293100	0.00003400

C	-1.84866300	0.67946400	-0.68949500
C	-1.84864800	0.67948800	0.68949300
H	-1.53924800	1.55769800	-1.24988900
H	-1.53921500	1.55774300	1.24984700
H	0.21597000	-0.25239000	2.16667300
H	0.21597700	-0.25242100	-2.16667600
H	-2.45515600	-0.03451600	1.23432300
H	-2.45517600	-0.03456700	-1.23428500
C	0.94054900	1.81008300	-0.00001100
H	-0.01671000	2.33078600	-0.00009800
H	1.50228000	2.13553000	0.88242100
H	1.50242500	2.13550900	-0.88235800
N	-0.40689300	-1.57288900	-0.67103200
N	-0.40689600	-1.57287900	0.67104700

G: −383.123567
H: −383.081911

5,5-Dimethyl-2,3-diazacyclopentadiene + Ethylene Adduct

C	-0.83310300	0.10859100	-0.00001900
C	0.22878800	-0.14301400	1.09098900
C	0.22871800	-0.14307200	-1.09098200
C	-1.96791200	-0.92026400	-0.00000300
H	-2.60037800	-0.78281300	0.88417600
H	-2.60026500	-0.78281100	-0.88426600
H	-1.60285700	-1.94945300	0.00002600
C	1.33317600	0.90098100	0.77594400
C	1.33318100	0.90088800	-0.77607900
H	1.08043800	1.87711500	1.19748400
H	1.08060500	1.87702400	-1.19767500
H	-0.08978400	-0.21258600	-2.13188900
H	-0.08970000	-0.21235400	2.13190700
H	2.28967400	0.58756000	-1.20076700
H	2.28968900	0.58783900	1.20068300
C	-1.44468900	1.50846000	0.00002100
H	-2.08083300	1.63762000	0.88318200
H	-0.70796200	2.31379600	-0.00032300
H	-2.08138700	1.63745800	-0.88275800
N	0.84602100	-1.41807000	0.62128100
N	0.84595100	-1.41819000	-0.62113800

G: −383.123567
H: −383.155418

5-Methyl-5-*tert*-butylcyclopentadiene

C	-0.25455300	0.46841800	0.01023500
C	-1.12619500	0.08679100	-1.16843700

C	-1.12779600	0.04711000	1.17443200
H	-0.84377200	0.18791200	2.21209600
H	-0.83273200	0.24526100	-2.20159800
C	-2.29417100	-0.45136300	0.72928400
H	-3.11919500	-0.80136800	1.34060600
C	-2.29225000	-0.42856900	-0.74288200
H	-3.11236400	-0.76674200	-1.36720500
C	-0.11007000	2.00751400	0.02969000
H	0.36114700	2.37302800	-0.88719900
H	-1.10083400	2.46537400	0.10734000
H	0.48799800	2.34472100	0.88234800
C	1.13482600	-0.26798500	-0.00436100
C	2.04526700	0.31206300	-1.09594600
H	2.37526200	1.32837100	-0.85652100
H	2.94170300	-0.31082500	-1.19609500
H	1.54745600	0.33437300	-2.07225600
C	1.84564000	-0.12204200	1.34951200
H	2.86286100	-0.52412900	1.27614100
H	1.92903900	0.92338200	1.66563100
H	1.32653000	-0.67908400	2.13624500
C	0.93198500	-1.76520000	-0.28055700
H	0.61010900	-1.94351900	-1.31127800
H	1.87338200	-2.30468100	-0.12290400
H	0.17731400	-2.19249100	0.38882700

G: −390.378106
H: −390.332444

5-Methyl-5-*tert*-butylcyclopentadiene + Ethylene TS

C	-0.01820400	-0.38695700	0.01182400
C	0.69166100	0.28783800	-1.15361700
C	1.05748500	1.56897400	-0.75024000
C	0.68884300	0.35857400	1.13774700
C	1.05095600	1.61401700	0.65379400
C	-1.58775400	-0.00283500	0.00618700
C	2.65655300	-0.67022500	-0.67110100
C	2.69061800	-0.57002500	0.71009300
H	2.40970700	-1.61038600	-1.15558100
H	2.49996900	-1.43009900	1.34438400
H	0.52089900	0.13332700	2.18740000
H	1.41024000	2.43945000	1.25985600
H	1.41631800	2.35596800	-1.40532300
H	0.51674900	-0.00146000	-2.18734900
H	3.27105900	0.21515200	1.18125200
H	3.23073100	0.01836100	-1.27993000
C	0.07200500	-1.92231600	0.02691500
H	-0.11266000	-2.32199000	-0.97559900

H	1.04456700	-2.28584600	0.34789800
H	-0.66918600	-2.36625300	0.69580700
C	-2.31944300	-0.85621400	-1.04768900
H	-2.35623800	-1.91627700	-0.78277400
H	-3.35405100	-0.50758800	-1.14063200
H	-1.84987200	-0.76442400	-2.03410300
C	-2.20437100	-0.28563400	1.38827600
H	-3.29652400	-0.21472300	1.32333800
H	-1.96544000	-1.28193700	1.77214100
H	-1.86799500	0.45160600	2.12475100
C	-1.91185600	1.46348800	-0.32250500
H	-1.43383800	2.16254000	0.36637300
H	-1.61634400	1.73398200	-1.34016500
H	-2.99705600	1.59849400	-0.23985300

G: −468.848043
H: −468.798963

5-Methyl-5-*tert*-butylcyclopentadiene + Ethylene Adduct

C	-0.01230000	-0.44824500	0.01147700
C	0.91167500	0.10207200	-1.12383000
C	1.12499800	1.54068000	-0.69397900
C	0.92883200	0.13935000	1.11847000
C	1.11786200	1.56752400	0.64205200
C	-1.50872200	0.06540300	0.00750400
C	2.27087900	-0.59032200	-0.78270800
C	2.30453000	-0.52496400	0.77203700
H	2.29574100	-1.62168000	-1.14774100
H	2.41646200	-1.51365900	1.22581600
H	0.61725900	0.00249500	2.15677400
H	1.33167700	2.41525200	1.28597700
H	1.33461500	2.36462300	-1.36926900
H	0.57059100	-0.05659800	-2.15143900
H	3.12615500	0.09340500	1.14270500
H	3.10707900	-0.05792800	-1.24339000
C	-0.04029900	-1.99147600	0.02570500
H	-0.27583900	-2.38381700	-0.96954500
H	0.90712000	-2.43413000	0.32763000
H	-0.79690300	-2.37343600	0.71637400
C	-2.33774400	-0.76790000	-0.99402200
H	-2.45416500	-1.81037400	-0.68736500
H	-3.34286900	-0.34184300	-1.08247900
H	-1.88419200	-0.75480000	-1.99296500
C	-2.11821700	-0.10125800	1.41053300
H	-3.19096600	0.12352000	1.38016200
H	-2.00654000	-1.11618600	1.80555200
H	-1.65597300	0.59176000	2.12230200

C	-1.74464600	1.53525400	-0.39521700
H	-1.32332100	2.24602500	0.31640400
H	-1.32982200	1.76420700	-1.38313900
H	-2.82720000	1.70646100	-0.44049300

G: −468.916452
H: −468.869291

5-Methylcyclopentadiene

C	0.69672200	0.00006200	0.46349000
C	-0.20560900	-1.17468800	0.19087600
C	-0.20574100	1.17472500	0.19084200
H	0.11493400	2.20734000	0.27887000
H	0.11526000	-2.20727100	0.27857600
H	0.98379700	0.00018400	1.52753200
C	-1.42366500	-0.73610400	-0.17666100
H	-2.27774400	-1.35140100	-0.43816400
C	-1.42369900	0.73597200	-0.17686300
H	-2.27776800	1.35131800	-0.43828400
C	1.97313400	0.00000900	-0.39011300
H	2.58069100	0.88631900	-0.18239500
H	2.58064200	-0.88632200	-0.18233600
H	1.71334800	-0.00001600	-1.45322300

G: −233.269216
H: −233.234196

5-Methylcyclopentadiene + Ethylene TS (*syn*)

C	0.59005700	-0.94441200	-0.00051600
C	-0.26983900	-0.48866000	-1.15302800
C	-1.58852800	-0.49517600	-0.70319500
C	-0.26950200	-0.48991800	1.15268700
C	-1.58831700	-0.49586800	0.70328000
C	0.18981500	1.67166500	-0.68951700
C	0.19034600	1.67108600	0.69058200
H	1.12116500	1.64065200	-1.24807600
H	1.12208000	1.63936500	1.24845700
H	0.03100100	-0.59864600	2.19104700
H	-2.46593300	-0.38895200	1.33168400
H	-2.46633300	-0.38760600	-1.33122300
H	0.03021000	-0.59652100	-2.19161200
H	-0.66017000	2.05946800	1.23896000
H	-0.66100100	2.06068900	-1.23697700
H	0.46062400	-2.04392200	-0.00122100
C	2.08804700	-0.67944000	-0.00033300
H	2.55090400	-1.13111900	-0.88437800
H	2.33408500	0.38381500	0.00076800

H	2.55089100	-1.13288800	0.88281200

G: −311.754167
H: –311.714886

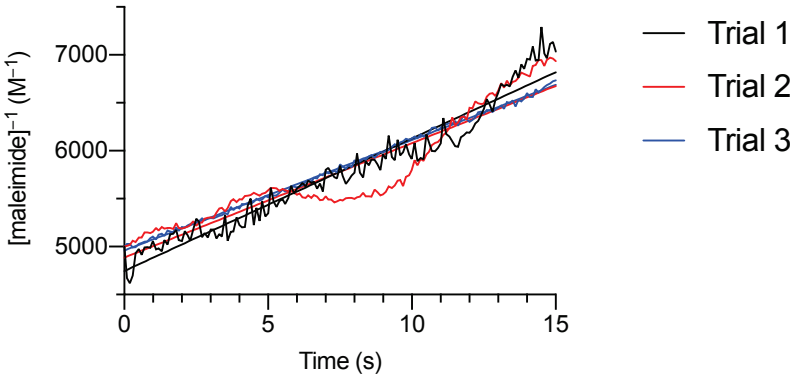
5-Methylcyclopentadiene + Ethylene Adduct (*syn*)

C	0.70526300	-0.81894800	0.00031800
C	-0.15755700	-0.19391400	-1.12392100
C	-0.15791400	-0.19337800	1.12400500
C	-0.05906800	1.32616500	-0.77749700
C	-0.05966000	1.32654000	0.77690300
H	0.86247300	1.75939500	-1.17999800
H	0.86142500	1.76026200	1.17989200
H	0.11688800	-0.44146600	2.15226000
H	0.11768500	-0.44253300	-2.15192900
H	-0.89896100	1.88553000	1.19875100
H	-0.89788100	1.88520600	-1.20023800
C	2.18978900	-0.47958700	0.00030200
H	2.67870500	-0.90352700	0.88464100
H	2.67866000	-0.90351300	-0.88407600
H	2.38106700	0.59729100	0.00031700
H	0.58145200	-1.90820100	0.00052700
C	-1.53909600	-0.62614200	-0.66999700
H	-2.38789900	-0.78926600	-1.32664000
C	-1.53930700	-0.62583000	0.66990700
H	-2.38831500	-0.78861700	1.32637300

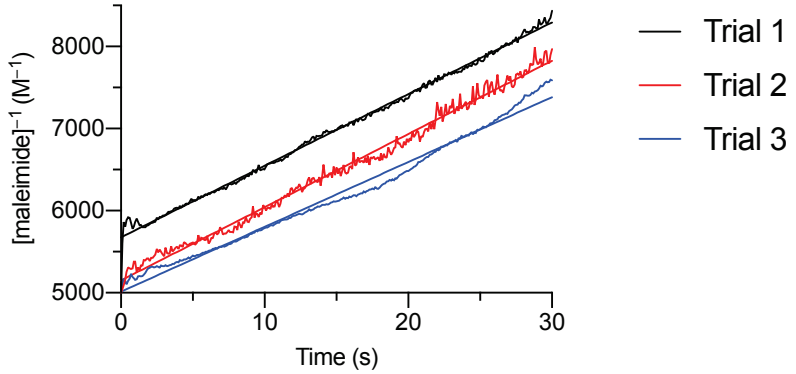
G: −311.823403
H: –311.785688

Kinetic Traces

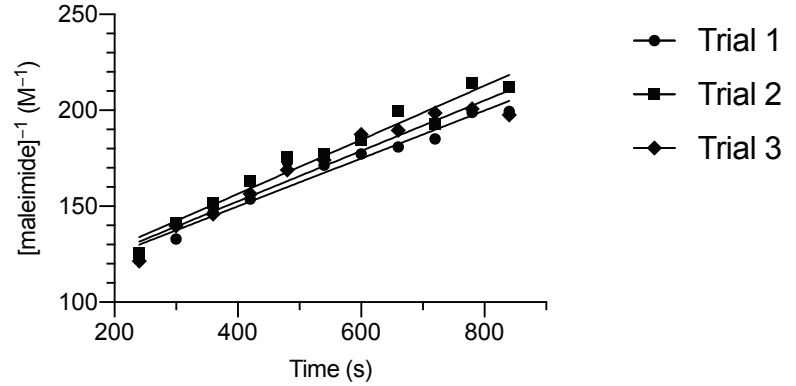
Kinetic Traces for the Reaction of Maleimide with 1,2,3,4-Tetramethylcyclopentadiene



Kinetic Traces for the Reaction of Maleimide with 1,2,3,4,5-Pentamethylcyclopentadiene

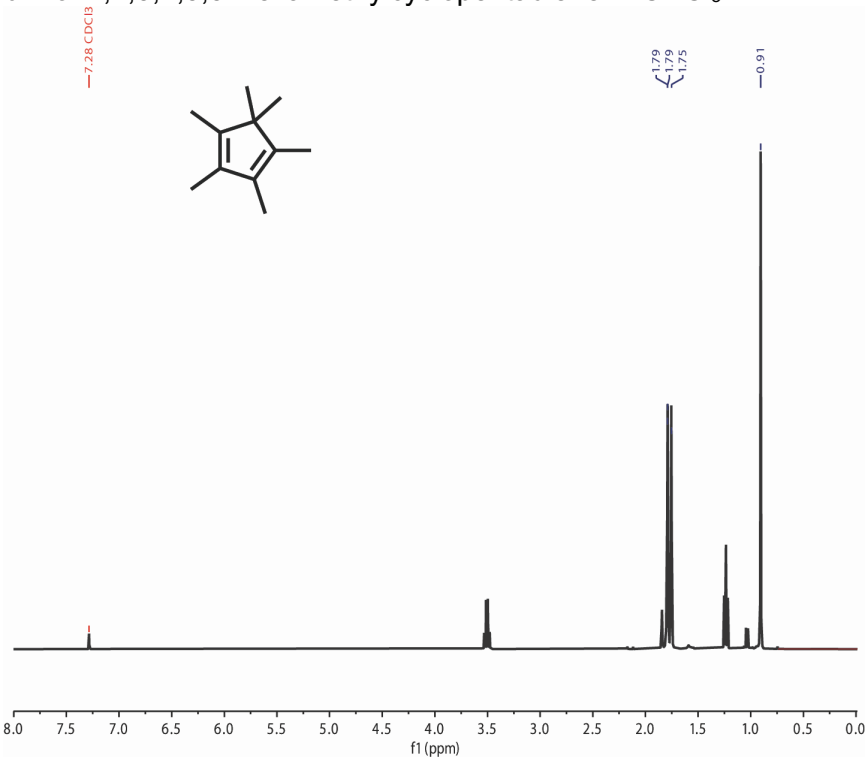


Kinetic Traces for the Reaction of Maleimide with 1,2,3,4,5,5-Hexamethylcyclopentadiene



NMR Spectra

^{1}H NMR Spectrum of 1,2,3,4,5,5-Hexamethylcyclopentadiene in $CDCl_3$



^{13}C NMR Spectrum of 1,2,3,4,5,5-Hexamethylcyclopentadiene in $CDCl_3$