

Supporting Information

Additional Computational Details

The MECP was searched and optimized on the PES using the SurfCrossOpt strategy in ORCA. The complete active space self-consistent field (CASSCF) wave function,^[1] with a 11-electron/11-orbital active space (11,11), was used to calculate the spin-orbit coupling (SOC) constant at the minimum energy crossing point (MECP).^[2] For the S^+/C_6H_6 system, five $3p(S)$ electrons and six electrons from the phenyl ring are included in the active space; for the S_2^+/C_6H_6 and S_3^+/C_6H_6 systems, basically nine $3p(S)$ electrons and two electrons from the phenyl ring are included in the active space. Note that the CASSCF calculation here is only for qualitative examination of the intersystem crossing probability, and larger active space should be employed if more accurate results are needed. However, even with the accurate SOC constants, the Landau-Zener treatment employed in this work can only generate an approximately qualitative result.^[3]

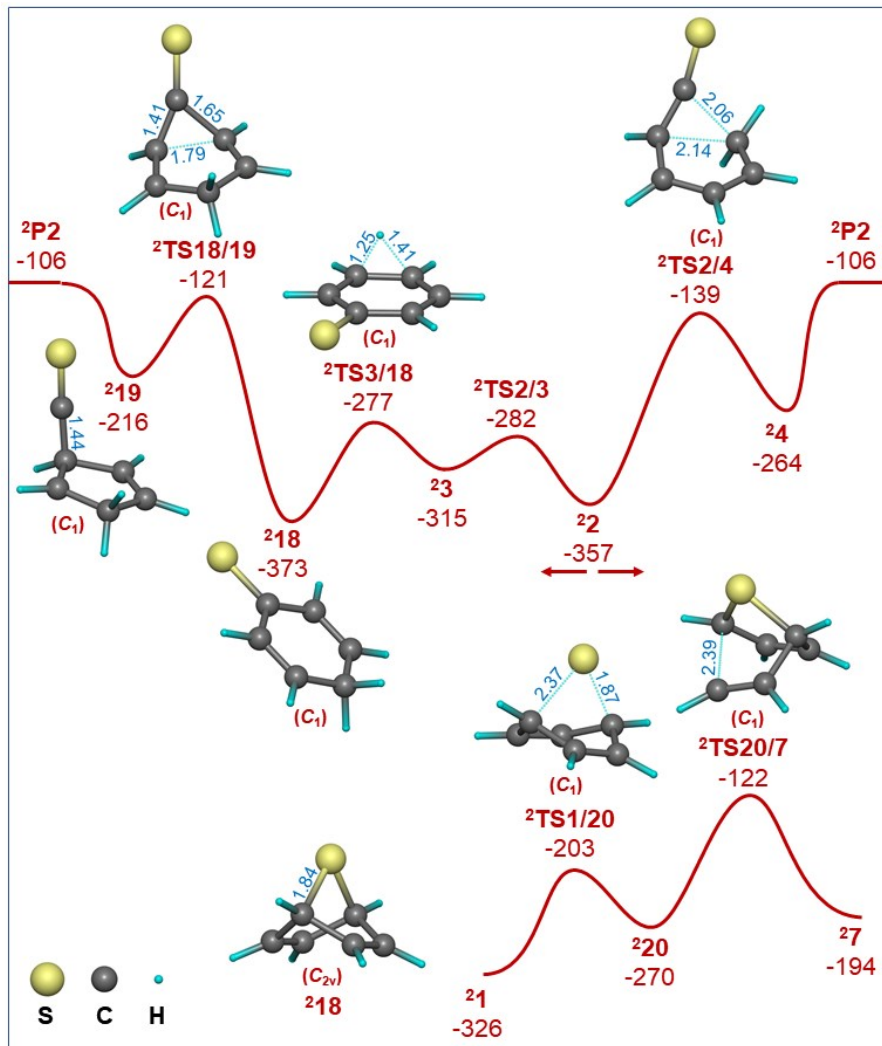


Figure S1. Simplified PES and selected structural information of alternative pathways for the reactions of S^+ with benzene as calculated at the B2GP-PLYP-D3(BJ)/AVQZ//B3LYP-D3(BJ)/def2-TZVP level of theory. Zero-point corrected, relative energies are given in kJ mol^{-1} and bond lengths in \AA ; charges are omitted for the sake of clarity.

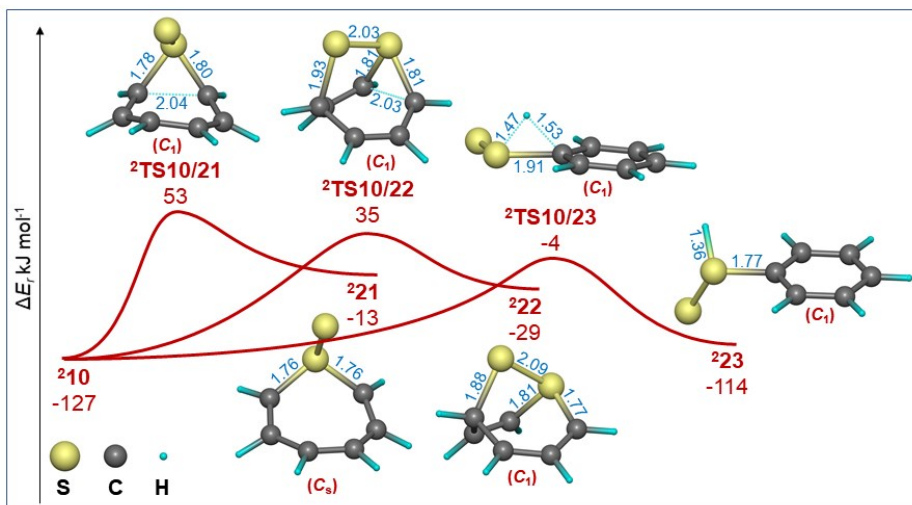


Figure S2. Simplified PES and selected structural information of alternative pathways for the reactions of S_2^+ with benzene as calculated at the B2GP-PLYP-D3(BJ)/AVQZ//B3LYP-D3(BJ)/def2-TZVP level of theory. Zero-point corrected, relative energies are given in kJ mol^{-1} and bond lengths in \AA ; charges are omitted for the sake of clarity.

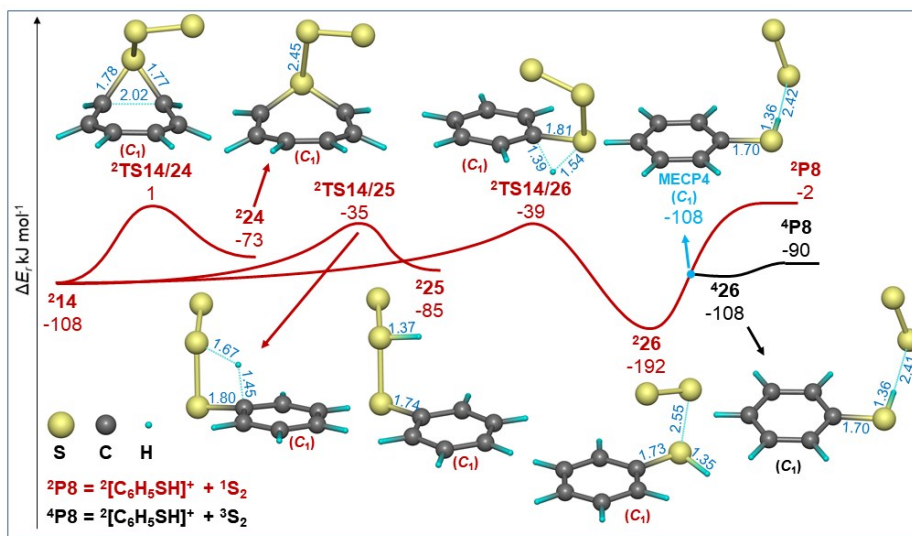
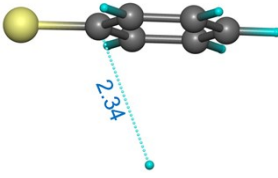
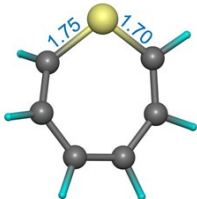
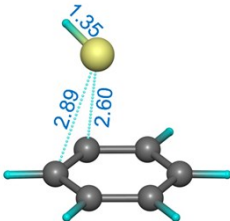
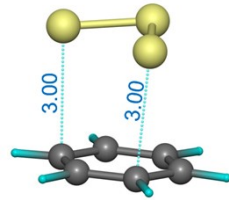
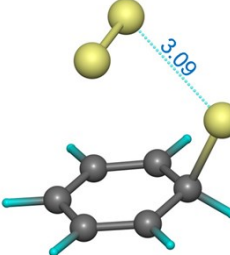


Figure S3. Simplified PES and selected structural information of alternative pathways for the reactions of S_3^+ with benzene as calculated at the B2GP-PLYP-D3(BJ)/AVQZ//B3LYP-D3(BJ)/def2-TZVP level of theory. Zero-point corrected, relative energies are given in kJ mol^{-1} and bond lengths in \AA ; charges are omitted for the sake of clarity.

As shown in Figure S3, the sequence ${}^2\mathbf{14} \rightarrow {}^2\mathbf{26} \rightarrow \mathbf{MECP4} \rightarrow {}^4\mathbf{P8}$ is also energetically favorable when comparing with the generation of ${}^4\mathbf{P7}$ (see Figure 5 in the main text). However, according to the calculation, the SOC constant at $\mathbf{MECP4}$ is only 5 cm^{-1} , suggesting a rather low ISC probability herein ($< 0.01^{[4]}$). Thus, the reaction proceeds along the spin-conserving path, i.e. ${}^2\mathbf{14} \rightarrow {}^2\mathbf{26} \rightarrow {}^2\mathbf{P8}$, which is relatively much less competing.

Table S1. The relative energies and selected structural information for the triplet electromers of key intermediates in the S_n^+/C_6H_6 ($n = 1 - 3$) systems.

<p>${}^4\mathbf{2}$, -94 kJ mol^{-1}</p> 	<p>${}^4\mathbf{5}$, -73 kJ mol^{-1}</p> 	<p>${}^4\mathbf{9}$, -62 kJ mol^{-1}</p> 
<p>${}^4\mathbf{13}$, -29 kJ mol^{-1}</p> 	<p>${}^4\mathbf{14}$, 40 kJ mol^{-1}</p> 	

As shown in Table S1, these triplet species are of much higher energy as compared to their doublet electromers. Though not all triplet electromers of the intermediates involved in the transformations are listed here, it is conceivable that upon more covalent interaction of the benzene molecule with the sulfur atom(s) a higher-spin state is even less favored.

Optimized Coordinates of Key Structures (in Å)

²TS1/2:

C	-1.60922500	-1.18050200	-0.03092800
C	-2.24262100	0.04336100	-0.07745300
C	-1.50463600	1.24190500	-0.02952000
C	-0.13686100	1.22898300	0.06934300
C	0.57334200	-0.01929600	0.08166800
C	-0.20704700	-1.24162600	0.01081600
H	-2.17281200	-2.10311000	-0.04773400
H	-3.32216500	0.08623200	-0.13554800
H	-2.02630400	2.18972000	-0.04952800
H	0.43117500	2.14699300	0.13195900
H	0.24455000	-0.57337600	1.16738000
H	0.32297800	-2.18522200	-0.00260100
S	2.33030400	0.00011400	-0.07546800

²TS1/5:

C	-1.62576400	-0.79097200	-0.31719100
C	-1.74689300	0.59106900	-0.29279500
C	-0.77208800	1.43194200	0.26857900
C	0.56580800	1.13949500	0.39927000
C	0.69816600	-0.90802500	0.66414900
C	-0.56851200	-1.45018200	0.28391800
H	-2.46240300	-1.38184700	-0.66351300
H	-2.68661400	1.03448000	-0.59821000
H	-1.09255300	2.37769800	0.69282400
H	1.19387800	1.77043700	1.01914100
H	1.24246600	-1.30633000	1.51332400
H	-0.66722100	-2.51537600	0.48485600
S	1.57300900	-0.00368900	-0.53025000

²TS1/9:

C	-1.55216000	-1.23105600	-0.03974700
C	-2.23917200	-0.00825700	-0.09933400
C	-1.56313400	1.22505100	-0.02287300
C	-0.20151300	1.25178200	0.09720900
C	0.52329200	0.01078600	0.11971500
C	-0.18981300	-1.24000900	0.10146100
H	-2.09892900	-2.16224100	-0.09534900
H	-3.31793500	-0.01267700	-0.19153000
H	-2.12381800	2.14865100	-0.06671500
H	0.35005800	2.18015600	0.15018400
H	1.34337000	-0.10858400	1.11171300
H	0.37250400	-2.16106300	0.17444500
S	2.30060900	0.00412400	-0.12633400

²TS2/3:

C	-0.11886400	1.21963000	0.01553300
C	-0.11855700	-1.19053600	-0.04741500
C	0.60796700	0.02323800	-0.00509800
C	-1.56543900	-1.16882900	-0.03829900
C	-2.25082400	0.06580300	-0.03452000
C	-1.51438200	1.23367000	-0.00223700
H	0.41372800	2.16136400	0.04717000
H	0.37942400	-2.15060700	-0.08674200
H	-0.98207500	-1.27333500	1.05975900
H	-3.33076900	0.07792500	-0.05439200
H	-2.02298800	2.18858000	0.00891800
S	2.33717300	0.00028700	-0.00835400
H	-2.09149800	-2.10637900	-0.16883800

²TS2/4:

C	1.44780800	1.16326500	-0.22596100
C	1.94801300	-0.00249200	-0.73083600
C	1.44064300	-1.18034800	-0.14511000
C	0.25155900	-1.05439600	0.62735000
C	-0.85787300	-0.34302200	0.20355000
C	0.49328900	1.05902600	0.88468800
H	1.72961400	2.14421000	-0.58755600
H	2.74270900	-0.02510600	-1.46347100
H	1.98848900	-2.11225000	-0.12180700
H	0.10770500	-1.64807700	1.53144600
H	0.90955300	0.84868200	1.87007200
H	-0.33575300	1.75612700	0.93392500
S	-2.21768500	0.07401300	-0.36529300

²TS3/4:

C	-0.14194200	0.90394300	0.58108400
C	-0.25298000	-0.99399200	0.50357200
C	0.74827200	-0.13340000	0.02920800
C	-1.62623200	-1.11382700	-0.10042100
C	-2.15212000	0.22267000	-0.46690400
C	-1.39816400	1.24551800	-0.02341700
H	0.33575500	1.56258800	1.29832400
H	0.03859700	-1.69736900	1.27792400
H	-2.28987500	-1.59213900	0.62649800
H	-3.07808500	0.33658400	-1.01243800
H	-1.67729400	2.28870900	-0.09423500
S	2.32464600	0.00668100	-0.26695000
H	-1.58444200	-1.79073600	-0.96359900

²TS3/18:

C	0.29659100	-0.84119000	0.83133400
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C	0.28490800	0.94431500	0.71845100
C	-0.79598000	0.21207200	0.19543800
C	1.42529900	1.16150700	-0.14227200
C	1.97115500	-0.09320400	-0.72165600
C	1.31983300	-1.20227900	0.01941900
H	-0.16192500	-1.43172200	1.61155400
H	0.11348900	1.53261900	1.61714100
H	1.85840000	-0.20318900	-1.81056600
H	1.67707200	-2.22313000	-0.04134800
S	-2.21736600	-0.04624800	-0.37752400
H	3.05680700	-0.14029100	-0.55928800
H	1.92316400	2.11836100	-0.18139400

²TS5/6:

C	-0.02273400	1.29349900	0.50883300
C	1.10942700	1.20885800	-0.47086900
C	1.57059300	-0.02077800	-0.60986600
C	-0.85491500	-1.23019500	-0.36257000
C	-1.72423000	-0.18536600	-0.45983500
C	-1.36939600	1.02148500	0.17591100
H	0.14331100	1.95438200	1.35858600
H	1.46984700	2.10141600	-0.97062700
H	2.33627800	-0.45518600	-1.23359100
S	0.60241200	-0.95708200	0.58659600
H	-1.01071500	-2.20722200	-0.80090700
H	-2.68682500	-0.30929200	-0.94008400
H	-2.14296800	1.70418800	0.51145500

²TS6/7:

C	0.36845500	0.64903900	0.67702500
C	1.66505800	0.77296000	-0.08125400
C	2.03126900	-0.31294200	-0.70963900
C	-1.46974700	-0.75535100	-0.34366900
C	-1.74057500	0.63735600	-0.45772900
C	-0.77246200	1.40747800	0.09055800
H	0.46741500	0.83077600	1.75418600
H	2.21129800	1.71451000	-0.09445800
H	2.78643200	-0.74900700	-1.34308900
S	-0.02613800	-1.13411600	0.38426400
H	-2.10816400	-1.54277400	-0.72248600
H	-2.63830900	1.01269600	-0.92764100
H	-0.79245400	2.48841100	0.13351000

²TS7/8:

C	0.26869700	0.30101600	-0.87611300
C	2.06588000	0.46602300	0.01227300
C	2.34912500	-0.40986500	0.83542400

C	-1.59408700	-0.31548300	0.62252200
C	-1.41535100	1.06823800	0.56041500
C	-0.40209200	1.42190800	-0.30686000
H	0.70298000	0.30318200	-1.86756900
H	2.44519700	1.34194800	-0.47866700
H	2.43689900	-1.23629200	1.50681900
H	-2.01591400	1.76577900	1.12483000
H	-0.10942600	2.43952800	-0.52467700
S	-0.54831700	-1.18542500	-0.37976100
H	-2.31970700	-0.83837700	1.22947800

²TS10/11:

C	-2.81699000	-0.00051200	-0.32433100
C	-2.15728300	-1.21984600	-0.14554700
C	-0.82882100	-1.23674400	0.21319700
C	-0.11525900	0.00044900	0.29999300
C	-0.82935500	1.23716400	0.21157700
C	-2.15780600	1.21925500	-0.14748700
H	-3.86458300	-0.00093700	-0.59652800
H	-2.69373900	-2.15051000	-0.26931500
H	-0.30138500	-2.16850100	0.36877100
H	0.52208200	-0.00068600	-0.86836300
H	-0.30236300	2.16934100	0.36615700
H	-2.69456800	2.14955500	-0.27262700
S	1.58327200	0.00125100	0.95126400
S	2.33970500	-0.00105400	-0.91204600

²TS10/12:

C	-2.89297700	0.47987000	-0.07057100
C	-1.91748300	1.45101800	-0.03436400
C	-0.56248300	1.07946100	0.02305700
C	-0.20646900	-0.31616900	0.08129100
C	-1.24920900	-1.29250700	0.04329000
C	-2.55697000	-0.88966100	-0.02714500
H	-3.93426300	0.76777700	-0.13013100
H	-2.17113200	2.50150000	-0.06680400
H	0.24316000	1.80448400	0.02473500
H	-0.33941500	0.30144800	1.16523800
H	-0.98624000	-2.34233800	0.06257000
H	-3.34365300	-1.63186400	-0.05586000
S	1.50070300	-0.91707800	-0.05312700
S	2.67711400	0.63751100	-0.01519200

²TS10/21:

C	0.36629400	-1.44125000	-0.63072700
C	0.74421900	0.18256400	1.58669800
C	1.23605200	1.06672600	0.60382100

C	1.63616600	0.62877400	-0.67936900
C	1.38288800	-0.64695800	-1.13554100
H	0.25607700	-2.49914200	-0.83108500
H	2.28732900	1.27955100	-1.24712200
H	2.00097900	-1.07876700	-1.91450100
H	1.59199500	2.03427500	0.93323100
S	-1.19074000	-0.72709000	-0.06407600
S	-1.23321900	1.25151800	-0.42235400
C	-0.05082600	-0.91427400	1.29466400
H	1.04301200	0.33120900	2.61843200
H	-0.28480800	-1.71146000	1.98664100

²TS10/22:

C	0.34632200	0.91135200	1.28491600
C	-0.36608900	-0.19840200	1.64030200
C	-0.72717500	-1.13499200	0.53207200
C	-1.74118900	-0.53881600	-0.37877100
C	-1.58265600	0.73386300	-0.80752800
C	-0.41955300	1.48537300	-0.50455900
H	0.64781800	1.74727800	1.89653300
H	-0.78820000	-0.32356400	2.62765500
H	-0.96893800	-2.14107100	0.86162100
H	-2.58615000	-1.13983500	-0.68326500
H	-2.34675600	1.22731600	-1.39568400
H	-0.32473200	2.54963900	-0.67697400
S	0.88592100	-1.29473100	-0.52303700
S	1.19589100	0.70285400	-0.30374300

²TS10/23:

C	2.93252900	0.47569900	-0.04903900
C	2.60609400	-0.88066800	-0.04011300
C	1.28099100	-1.27241200	0.02122000
C	0.30723800	-0.26259600	0.04307100
C	0.60401000	1.09931800	0.05631200
C	1.93821800	1.45845400	-0.00068000
H	3.97176400	0.77317100	-0.08893800
H	3.38384700	-1.63082900	-0.07546800
H	1.00655900	-2.31955600	0.03874600
H	-0.66912600	-0.67261700	1.14319000
H	-0.18285500	1.84101900	0.08316000
H	2.20870700	2.50533600	-0.01446300
S	-1.49569100	-0.88832400	-0.05264000
S	-2.73764500	0.62561800	-0.02678900

²TS13/14:

C	-2.20057900	-0.60874300	-1.21921000
C	-1.72779700	0.68729000	-1.22689000

C	-1.44819500	1.34310800	0.00050600
C	-1.72755900	0.68632700	1.22744100
C	-2.20034000	-0.60969700	1.21882800
C	-2.43614100	-1.25235400	-0.00042300
H	-2.40624900	-1.11985500	-2.14942200
H	-1.55596100	1.21010100	-2.15781900
H	-1.28776900	2.41640200	0.00091200
H	-1.55554900	1.20840700	2.15874800
H	-2.40583700	-1.12154200	2.14867700
H	-2.81677900	-2.26577200	-0.00078200
S	0.88065400	1.03986800	0.00014800
S	1.22981400	-0.96804600	-0.00010000
S	3.04402000	-0.18453000	-0.00016200

²TS14/15:

C	-2.11447800	1.17880100	0.75625400
C	-0.94676600	0.44794100	1.06813700
C	-0.62258400	-0.75405900	0.31527100
C	-1.50016500	-1.14144500	-0.73877500
C	-2.62126600	-0.40027100	-1.01010200
C	-2.93006600	0.75793700	-0.26523600
H	-2.33951000	2.07040600	1.32454500
H	-0.27148200	0.75183400	1.85508900
H	-1.29618300	-0.78788500	1.41971500
H	-1.24836700	-2.01828600	-1.31844500
H	-3.27840700	-0.70383300	-1.81436400
H	-3.82293500	1.31961700	-0.50543400
S	0.91774700	-1.56686200	0.60578400
S	2.19785600	-0.16511700	-0.50536300
S	1.67619900	1.65915000	-0.20757100

²TS14/24:

C	-0.79522100	1.13232400	1.31572900
C	-0.88104000	-0.25529100	1.47418200
C	-1.83116700	-1.03115400	-0.12686200
C	-2.14615800	0.01372500	-1.00227900
C	-1.58411600	1.27152200	-0.99179300
C	-0.94151400	1.81515500	0.13071600
H	-0.68832600	1.69508100	2.23617100
H	-1.02940700	-0.70003800	2.45034600
H	-2.49045800	-1.88182000	-0.00481200
H	-2.96844900	-0.18489300	-1.68076600
H	-1.83804900	1.94564700	-1.79917600
H	-0.74315500	2.87880200	0.12790100
S	-0.17838300	-1.45089400	0.36830100
S	1.34176000	-0.40217800	-0.97051600
S	2.51369500	0.51366800	0.21922600

²TS14/25:

C	2.93294700	-0.48950500	-0.86012400
C	1.73427700	-1.07614600	-0.52033900
C	0.80838600	-0.36809300	0.30453800
C	1.19128000	0.89626900	0.85685900
C	2.39563400	1.45953700	0.50167600
C	3.26234100	0.77041400	-0.35176600
H	3.62598200	-1.01086800	-1.50594800
H	1.46609800	-2.05795800	-0.88628900
H	0.50914000	1.40342700	1.52602300
H	2.67817700	2.42499700	0.89817800
H	4.21057300	1.21861000	-0.61897000
S	-0.61892700	-1.23391900	0.98087900
S	-1.69969200	-0.29995300	-0.66505500
S	-3.07768800	0.95211200	-0.21053500
H	-0.09825800	0.17509200	-0.68268200

²TS14/26:

C	-2.04956800	0.97642400	1.01473200
C	-0.88455800	0.23491000	1.13793100
C	-0.61256700	-0.79469500	0.19516500
C	-1.50131100	-1.03093400	-0.88479100
C	-2.65022100	-0.28266200	-0.97445900
C	-2.92746200	0.71507900	-0.02691600
H	-2.27258500	1.74527100	1.74130700
H	-0.21797700	0.38075000	1.97709500
H	-0.31561100	-1.78558300	1.11621900
H	-1.26801700	-1.79532200	-1.61220300
H	-3.34213800	-0.46025800	-1.78641000
H	-3.84217700	1.28657000	-0.11157800
S	0.96998000	-1.67309900	0.27473200
S	2.42143600	0.15257700	-0.09219200
S	1.29687400	1.62801200	-0.43844000

²TS15/16:

C	1.60963000	1.09815900	-0.71991000
C	0.82500000	-0.45875800	0.94528000
C	0.60803500	0.70602200	0.15807400
C	2.06609400	-1.18155400	0.82958800
C	3.05231700	-0.74173200	-0.08189600
C	2.81718700	0.39224500	-0.82742700
H	1.44786300	1.96854600	-1.34220200
H	0.08010300	-0.81494800	1.64159100
H	1.91106200	-0.25148600	1.70570300
H	3.97112600	-1.30154500	-0.18115100
H	3.56598000	0.74064100	-1.52629900
S	-0.85774000	1.63909100	0.28676100
H	2.18317300	-2.09911400	1.39181700

S	-2.40953800	0.08960400	0.08756700
S	-1.67202700	-1.54922000	-0.59381000

²TS16/17:

C	-1.97172000	1.12029500	0.42857600
C	-0.85734200	-0.83144400	-0.46988100
C	-0.78991500	0.48958200	-0.05500300
C	-2.08944300	-1.52422600	-0.42739500
C	-3.27220700	-0.87306200	0.07615900
C	-3.17957800	0.47185600	0.48027300
H	-1.91153700	2.14957100	0.76107100
H	0.01611900	-1.35223500	-0.83019300
H	-2.87261000	-1.00401300	-1.25818600
H	-4.19687200	-1.43098500	0.13732600
H	-4.05963300	0.97903800	0.84990600
S	0.64086600	1.49321800	-0.05485700
H	-2.12640300	-2.58449200	-0.64524300
S	2.22850100	0.18814500	-0.66708400
S	2.63764300	-1.04854400	0.77125000

MECP1:

C	-1.48918285317009	0.91854333634088	0.28229237741629
C	-1.68109456090096	-0.45950258714690	0.41523537573350
C	-0.77496540479988	-1.35245807068933	-0.16239277287311
C	0.34111673831745	-0.85683450079960	-0.87196516135579
C	0.52063841700751	0.53720271353126	-1.01423050541805
C	-0.39498505415001	1.41665724117053	-0.43080484373035
H	-2.19452587120585	1.60490243306410	0.73168871854808
H	-2.53441006349690	-0.83757055434248	0.96233833857091
H	-0.92223371150504	-2.42059145309178	-0.07110137522931
H	1.02481600007625	-1.54346961077100	-1.35414514087513
H	1.36501275880055	0.91519350592000	-1.57526003613968
H	-0.25713117867567	2.48475557773064	-0.53570922450389
S	1.30790237370265	-0.47278408091632	1.41635221985653

MECP2:

C	2.72401916	0.06954162	-0.68315057
C	2.41314795	-1.15355247	-0.00631776
C	1.39200367	-1.20247426	0.90526026
C	0.69293516	-0.01399316	1.19618594
C	0.97551937	1.20505988	0.47442913
C	1.99571918	1.23412528	-0.45304553
H	3.54134583	0.07412749	-1.39409104
H	3.00751259	-2.03305093	-0.21699323
H	1.16274581	-2.11328315	1.44070289
H	0.00358689	0.02529024	2.02810709
H	0.40260987	2.09046537	0.71271350
H	2.22752392	2.14461845	-0.98747892

S	-1.26319240	-0.01953260	-1.33343593
S	-2.21639599	0.39728526	0.32017618

MECP3:

C	0.91822359035304	-0.89723701481404	0.01393460052761
C	2.25258685778617	1.20157705112602	0.00701473136737
C	0.97803699146958	0.53646384292819	0.01933165331421
C	3.39173157109815	0.48019983941872	-0.00436027574725
C	3.39134498349186	-0.99399123189582	-0.00488009411782
C	2.05674929756827	-1.61998325437914	0.00368959634992
H	-0.04640370046953	-1.38224136497122	0.01922475634397
H	2.27995578001544	2.28303816222130	0.00923634145371
H	3.97089596992348	-1.36698314680033	-0.86549095213705
H	2.00632197915864	-2.70235339225862	-0.00036143232401
S	-0.40938725225863	1.48349669099097	0.03975196983719
H	4.34900840230112	0.98747909345021	-0.01201701671137
S	-2.72581965241222	-0.34938334194803	0.91982664356111
S	-2.83344542908738	-0.45409078569264	-0.99270272173391
H	3.98123961106199	-1.36661614737556	0.84899920001634

MECP4:

C	1.82948566039654	-1.71376415604814	-0.43584066365334
C	0.89103664812975	-0.71432441090350	-0.43386189454987
C	1.27668952961780	0.59724931029982	-0.04284965855309
C	2.62086489017889	0.86982310306849	0.34273474438864
C	3.54236054460175	-0.14590003909653	0.33433320922541
C	3.15469593155421	-1.43892055093894	-0.05352208109637
H	1.55243484801749	-2.71615257086849	-0.73247347055422
H	-0.13127956112193	-0.91221382692508	-0.72401209810860
H	-0.93181423061095	1.24044845527849	-0.41016732600756
H	2.90067915289107	1.87270788731813	0.63858049041409
H	4.56572844374340	0.04658362963594	0.62572366780155
H	3.88650634297311	-2.23651763088134	-0.05842390053349
S	0.18863495836846	1.90779968985345	-0.01026507870823
S	-2.97806530914343	-0.75662056519729	0.96034425430312
S	-2.95535684959617	-0.02644532459501	-0.80022719436804

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