Supporting Information belonging to the manuscript:

Regioselective and Stepwise [8+2] Cycloaddition Reaction between Alkynyl-Fischer Carbene Complexes and Tropothione

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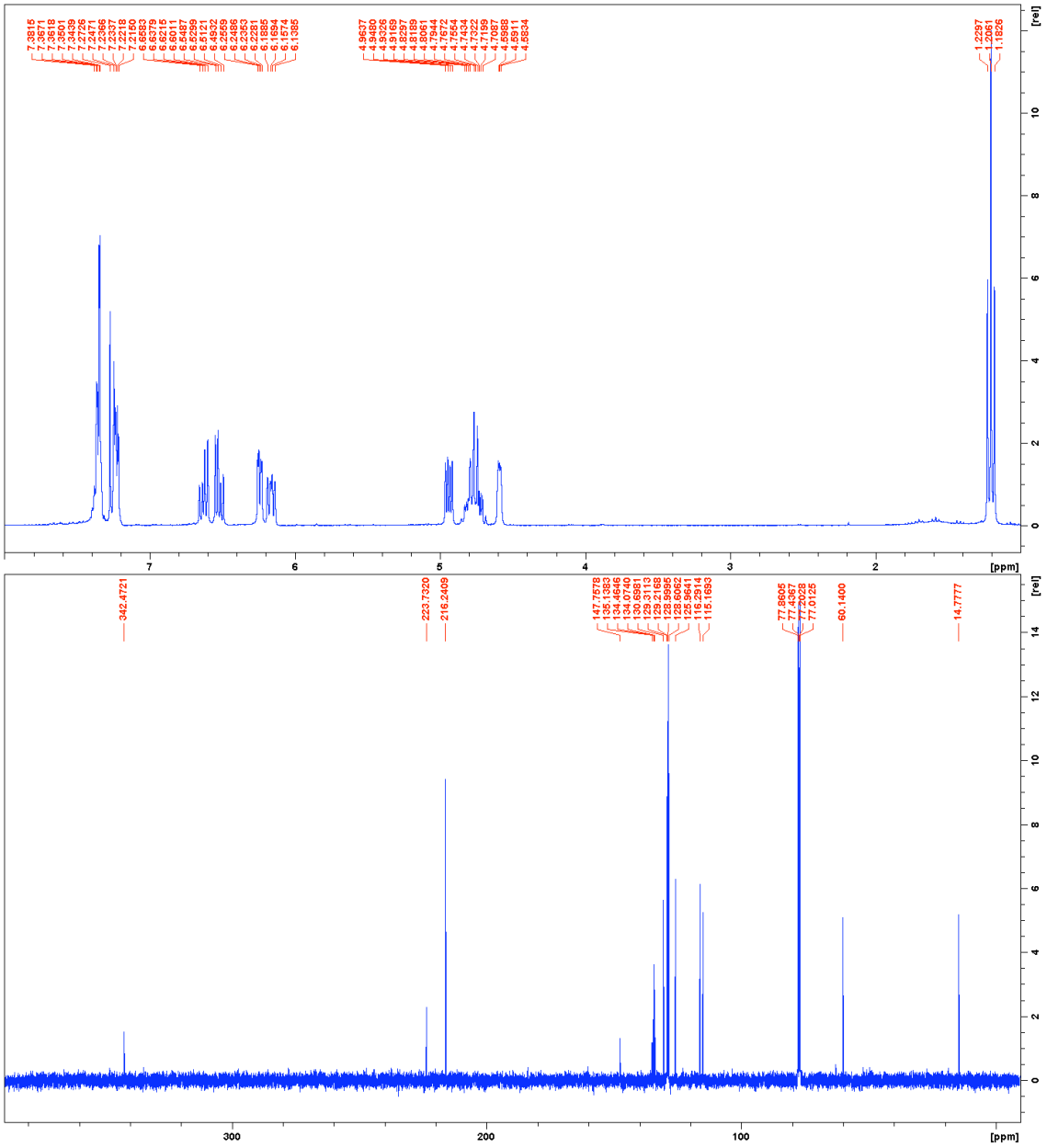
CONTENTS:

Compound 3a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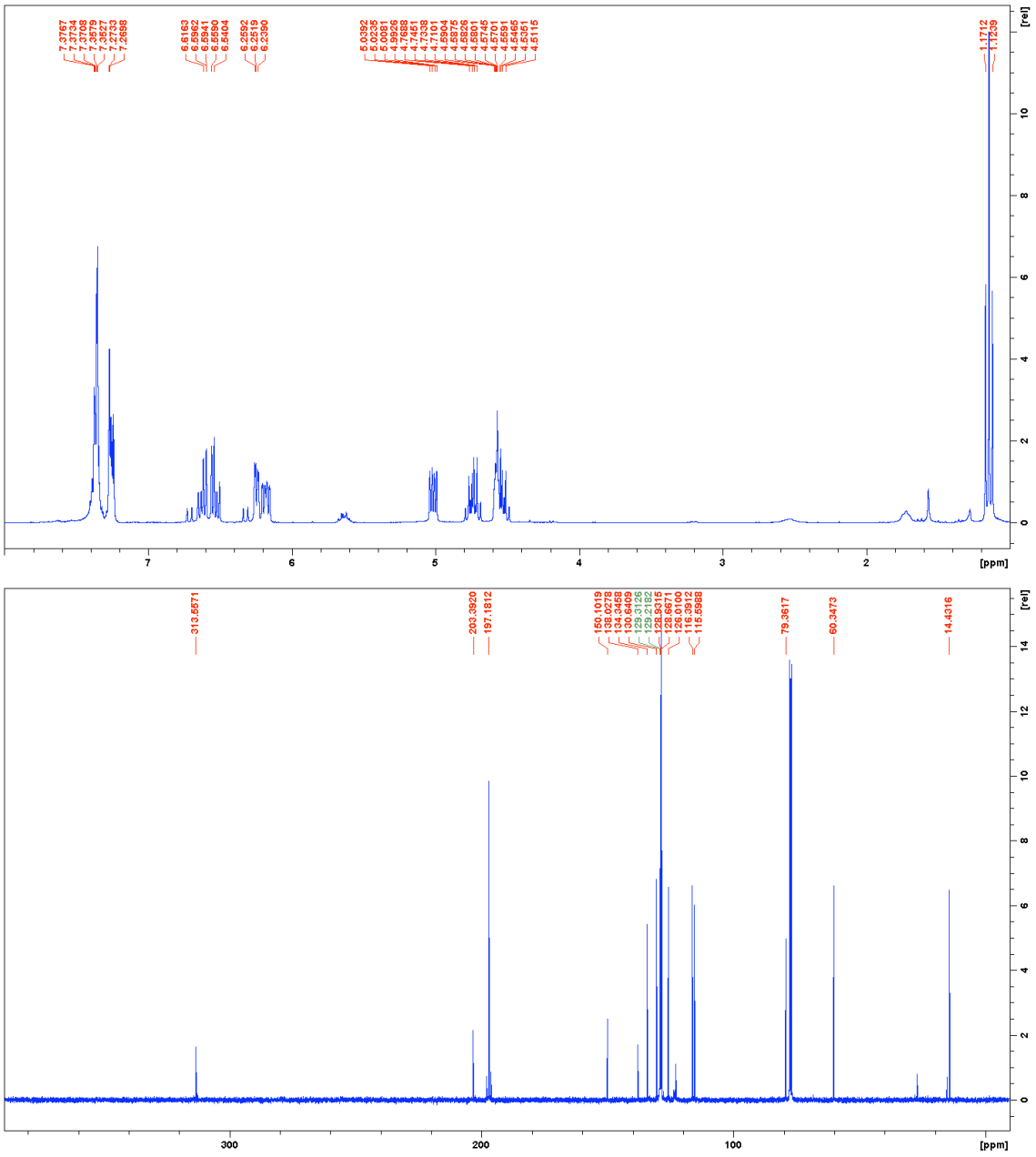
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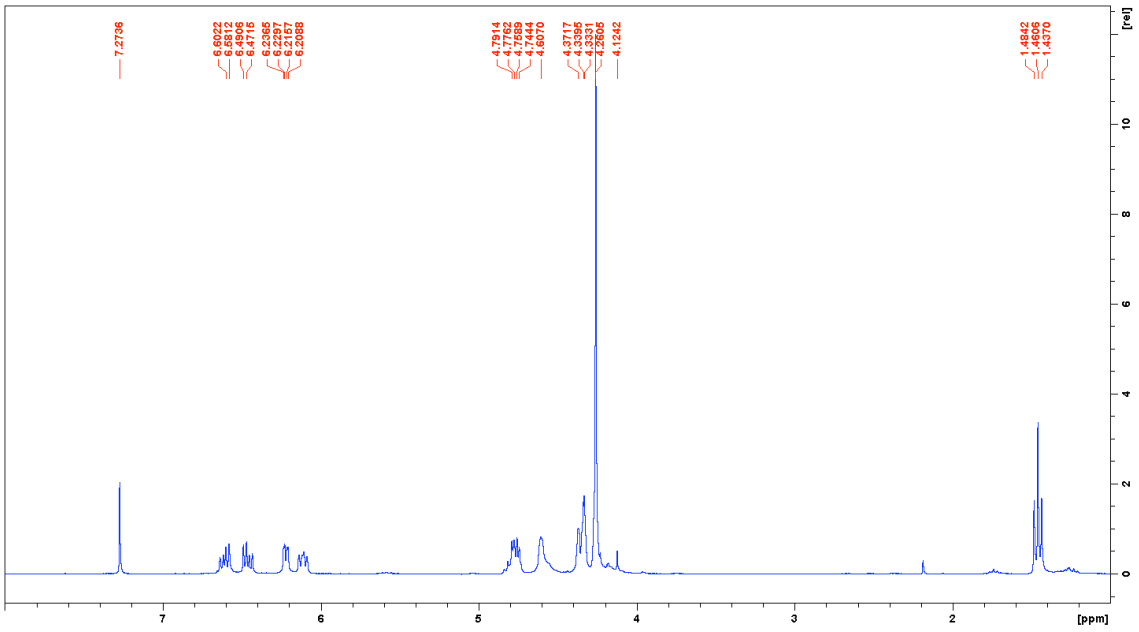
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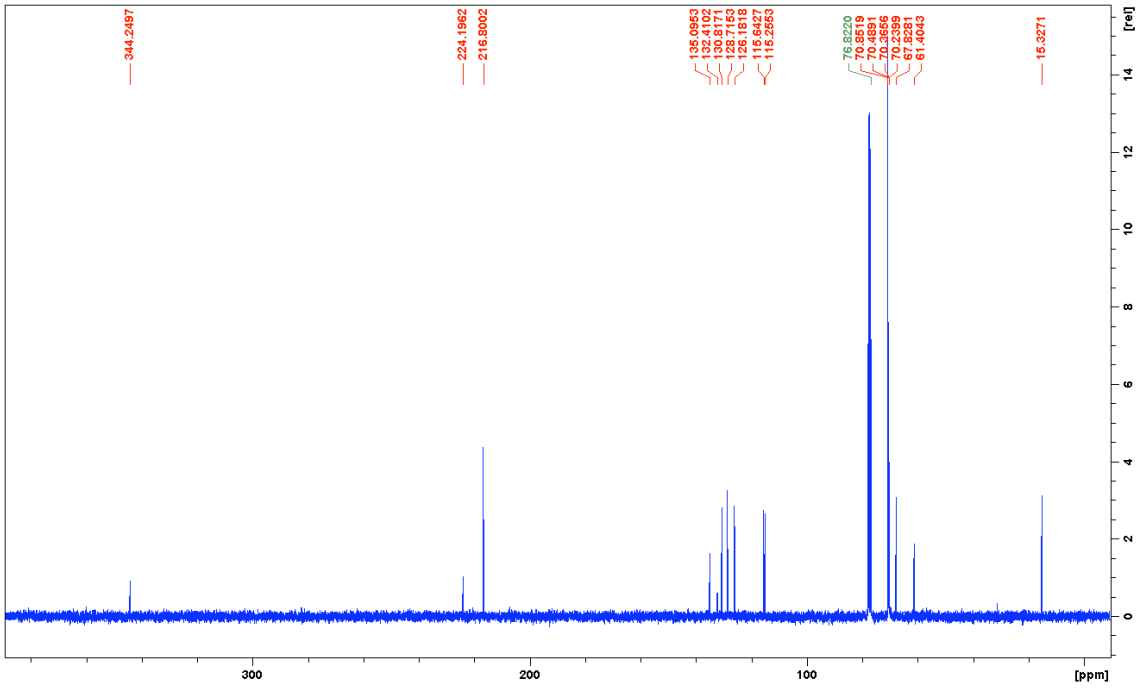
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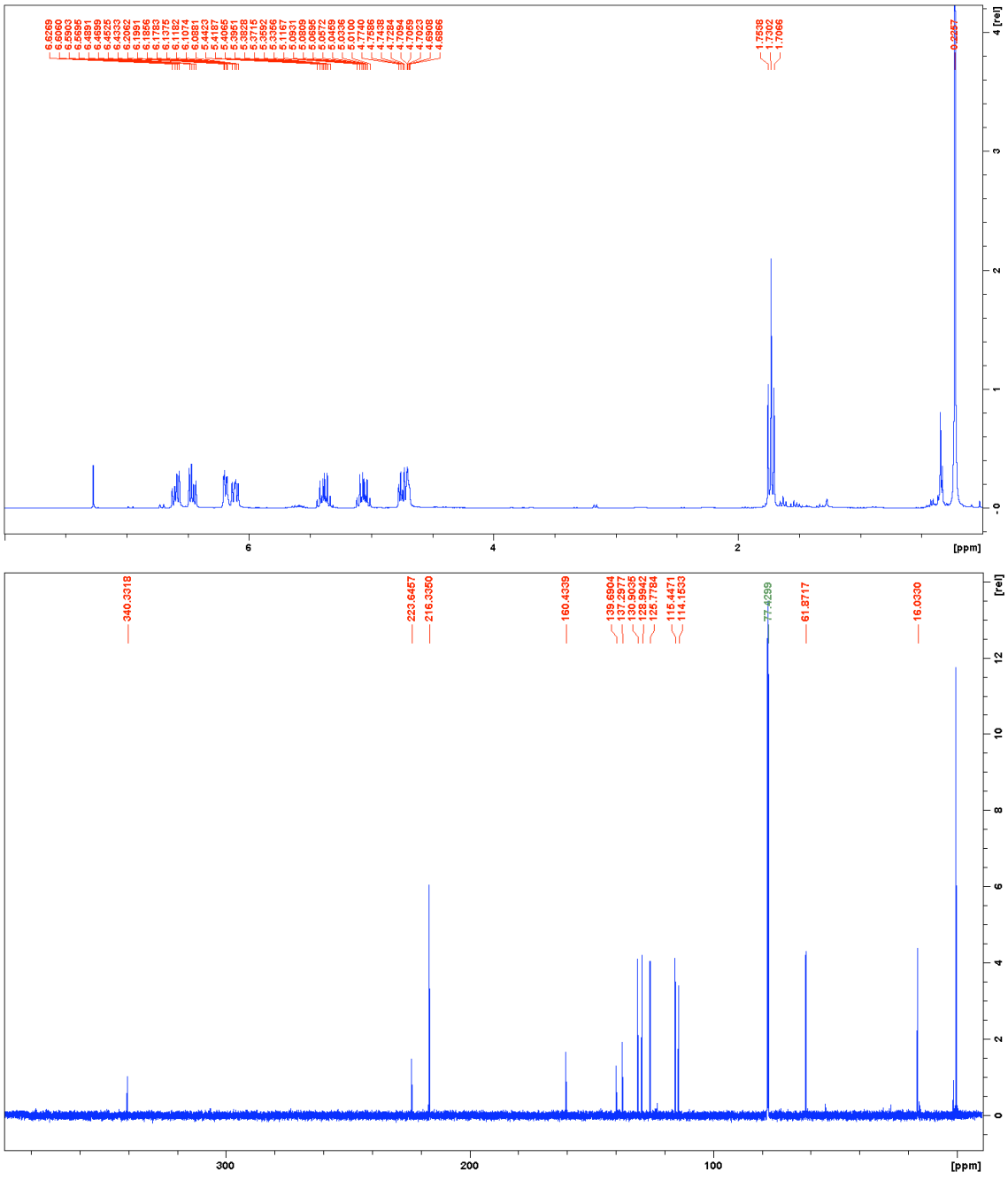
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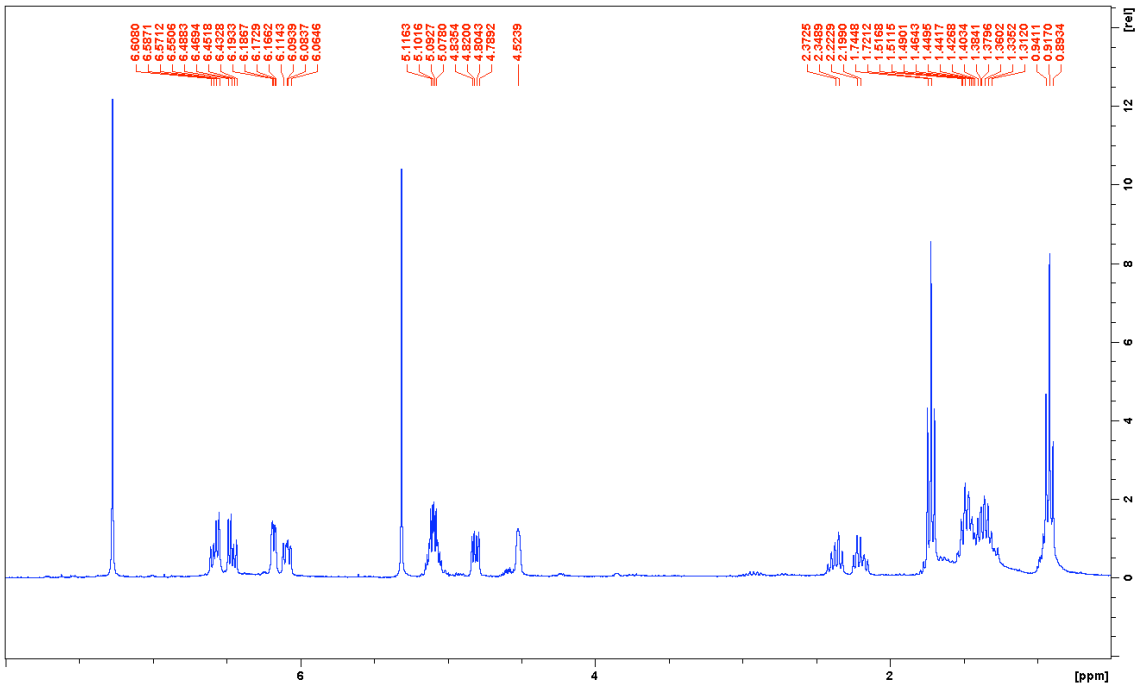
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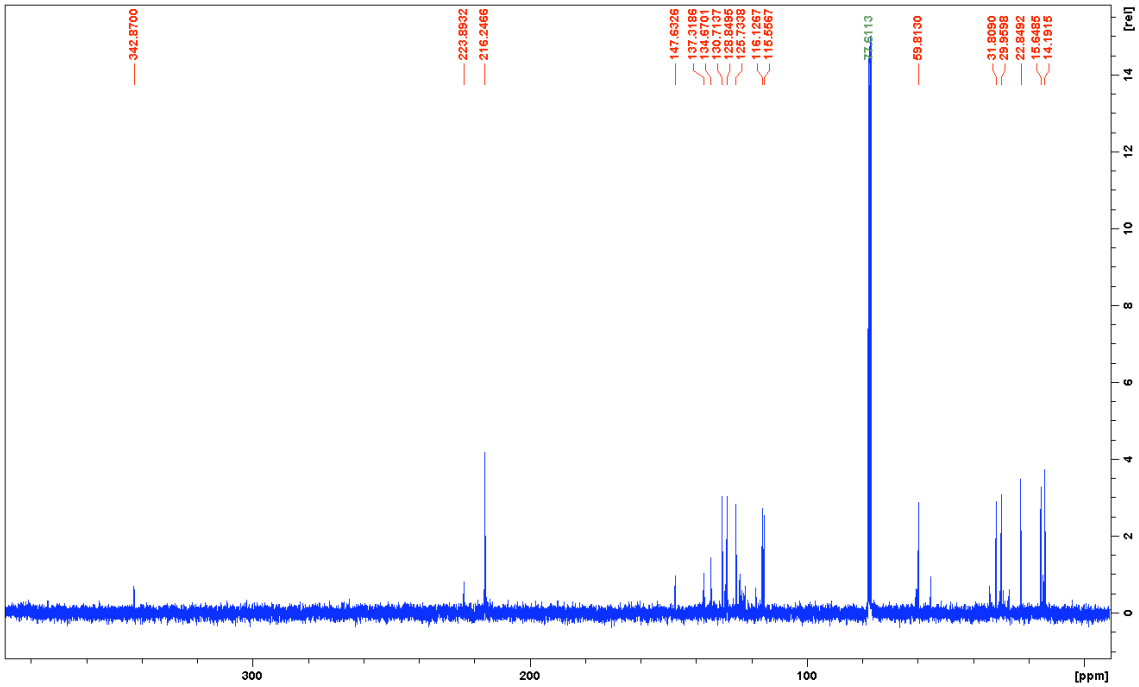
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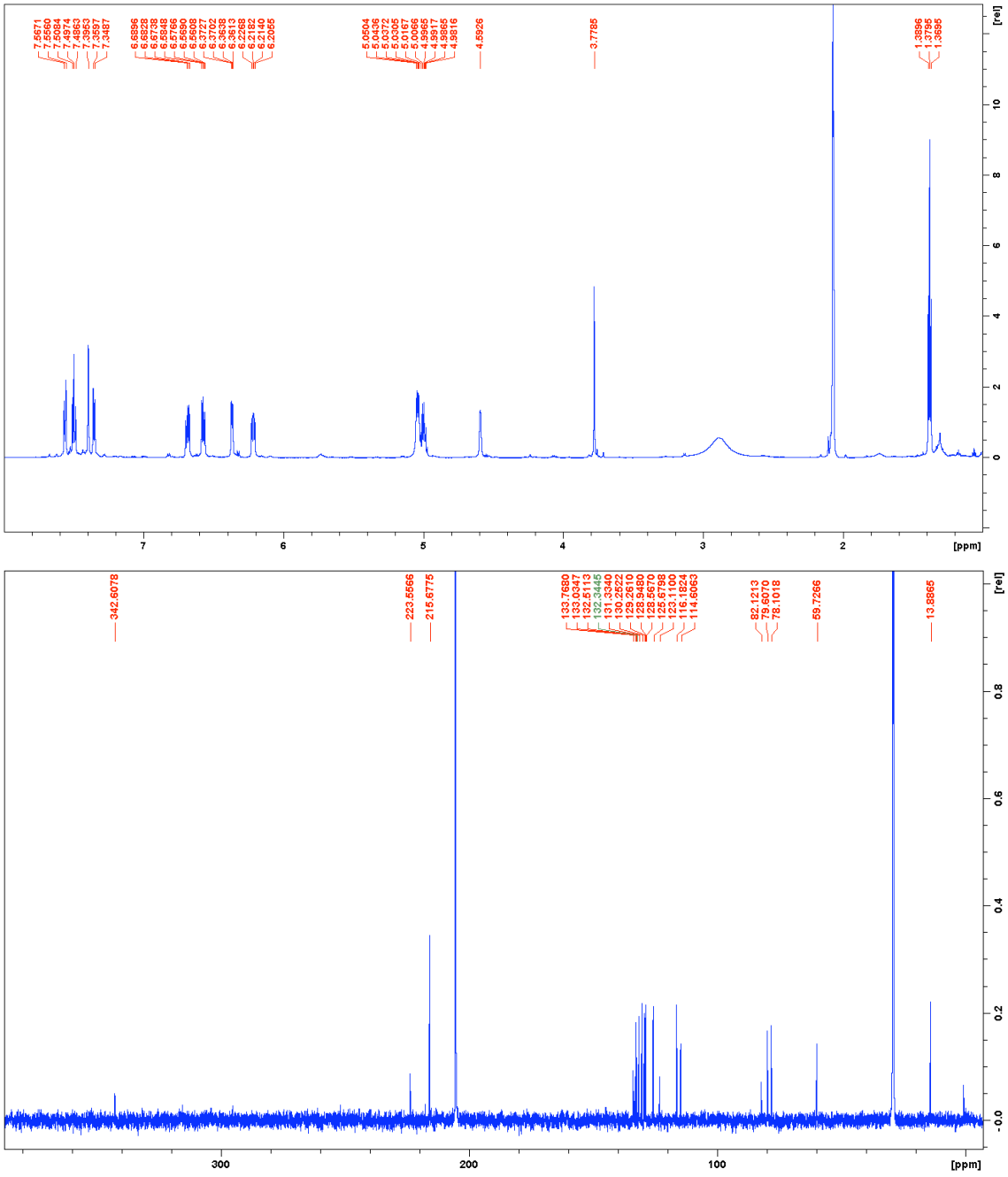
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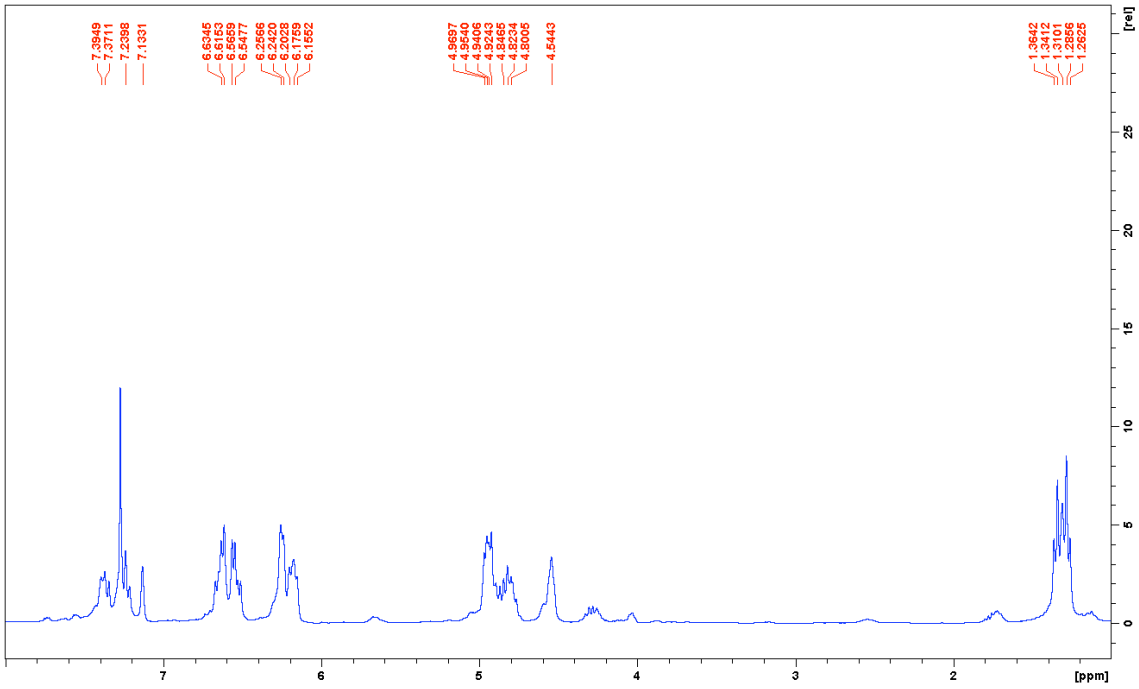
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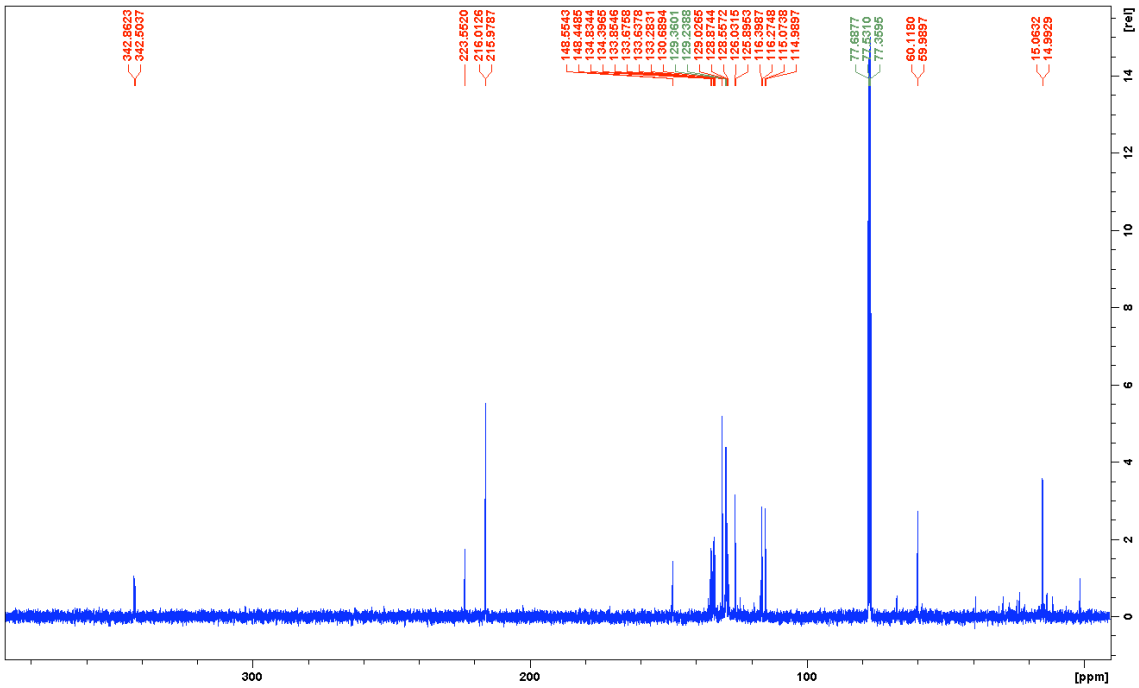
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Computational Details

All the calculations reported in this paper were obtained with the GAUSSIAN 09 suite of programs.[1] All reactants, transition states and cycloadducts were optimized using the hybrid functional B3LYP[2] with the standard double-ζ quality def2-SVP basis-set.[3] Reactants and products were characterized by frequency calculations,[4] and have positive definite Hessian matrices. Transition structures (TS's) show only one negative eigenvalue in their diagonalized force constant matrices, and their associated eigenvectors were confirmed to correspond to the motion along the reaction coordinate under consideration using the Intrinsic Reaction Coordinate (IRC) method.[5] Solvents effects were taken into account using the Polarizable Continuum Model (PCM).[6] Single point calculations on the gas-phase B3LYP/def2-SVP optimized geometries were performed to estimate the change in the Gibbs energies in the presence of dichloromethane as solvent using the Truhlar's meta hybrid exchange-correlation functional M06.[7] This level is denoted as PCM-M06/def2-SVP//B3LYP/def2-SVP. NICS values have been computed using the gauge invariant atomic orbital (GIAO) method[8] at the GIAO-B3LYP/def2-SVP level.

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[1] Gaussian 09, Revision B.1, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

[2] (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1998**, *37*, 785.

[3] Weigend, F.; Alhrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.

[4] McIver, J. W.; Komornicki, A. K. *J. Am. Chem. Soc.* **1972**, *94*, 2625.

[5] González, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523.

[6] (a) Miertuš, S.; Scrocco, E.; Tomasi, J. *Chem. Phys.* **1981**, *55*, 117. (b) Pascual-Ahuir, J. L.; Silla, E.; Tuñón, I. *J. Comp. Chem.* **1994**, *15*, 1127. (c) Barone, V.; Cossi, M. *J. Phys. Chem. A*, **1998**, *102*, 1995.

[7] Zhao, Y.; Truhlar, D. G. *Acc. Chem. Res.* **2008**, *41*, 157.

[8] Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251.

Cartesian coordinates (in Å) and free energies (in a.u., computed at 298K) of all stationary points discussed in the text. All calculations have been performed at the PCM(CH2Cl2)-M06-2X/def2-SVP//B3LYP/def2-SVP level.

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Cr	-1.912727000	-0.325245000	0.000055000
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C	-1.881652000	-0.289489000	-1.913560000
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C	-0.555075000	-1.651057000	-0.000006000
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C	0.855667000	0.918943000	-0.000307000
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C	3.391404000	0.150343000	-0.000066000
C	3.690099000	-1.232546000	-0.000415000
C	4.452296000	1.084711000	0.000380000
H	2.869726000	-1.952738000	-0.000734000
H	4.223509000	2.152363000	0.000651000
C	5.016216000	-1.660062000	-0.000327000
C	5.774039000	0.645407000	0.000467000
H	5.239975000	-2.729487000	-0.000598000
H	6.588728000	1.373499000	0.000812000
C	6.058485000	-0.725550000	0.000110000
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H	-1.395337000	2.626244000	0.000072000
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C	0.189510000	-1.271919000	0.000183000
H	0.867506000	-2.130124000	0.000301000

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C	1.839233000	4.101914000	0.320212000
C	1.826350000	2.683701000	0.017994000
H	-1.161733000	5.688125000	-0.444354000
H	-1.736818000	3.950334000	-2.031367000
H	0.009479000	1.992101000	-2.190825000
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H	2.814478000	4.555756000	0.521067000
C	0.611343000	-0.074554000	0.631197000
C	1.755572000	-0.494907000	0.365318000
S	3.163269000	1.792330000	-0.384513000
C	2.852529000	-1.376029000	0.102058000
C	3.886435000	-1.561410000	1.045301000
C	2.883966000	-2.107215000	-1.105773000
C	4.915879000	-2.463866000	0.788947000
H	3.871880000	-0.987545000	1.974034000
C	3.921707000	-3.004106000	-1.354895000
H	2.089626000	-1.957040000	-1.839371000
C	4.937890000	-3.186139000	-0.410645000
H	5.709430000	-2.604902000	1.526890000
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H	5.749450000	-3.890593000	-0.609262000
C	-0.744357000	-0.171217000	1.031526000
Cr	-2.213488000	-1.031442000	-0.115221000
O	-1.032681000	0.249881000	2.257691000
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H	0.560935000	1.519854000	2.763492000
H	-0.552879000	1.003184000	4.082351000
H	0.660583000	-0.147213000	3.415830000
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O	-0.552269000	-0.693124000	-2.647704000
C	-3.571672000	-1.879369000	-1.131834000
O	-4.395636000	-2.391733000	-1.750754000
C	-3.045581000	0.667131000	-0.359036000
O	-3.561369000	1.685794000	-0.494243000
C	0.407534000	2.320534000	-0.050431000
H	-0.161478000	2.732582000	0.791919000

TS2, E = -2738.352532

C	1.214403000	4.853424000	-0.473806000
C	1.850331000	4.175733000	-1.484477000
C	2.362789000	2.844908000	-1.456198000
C	0.913042000	4.381618000	0.837795000
C	1.179994000	3.166384000	1.422015000
C	1.856882000	2.005935000	0.902074000
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C	1.441062000	-1.163021000	0.712393000
S	2.006523000	0.675653000	1.952765000

C	2.607482000	-1.764862000	0.077237000
C	3.941668000	-1.483584000	0.423451000
C	2.365125000	-2.719509000	-0.938363000
C	4.997280000	-2.137364000	-0.216914000
H	4.144240000	-0.745771000	1.201253000
C	3.423080000	-3.367930000	-1.571899000
H	1.334116000	-2.942760000	-1.219765000
C	4.746236000	-3.081316000	-1.215696000
H	6.025796000	-1.905422000	0.071703000
H	3.211500000	-4.101016000	-2.354589000
H	5.574453000	-3.589202000	-1.716010000
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C	-0.929236000	-2.423225000	3.067042000
H	-0.343678000	-3.246076000	2.625836000
H	-0.240111000	-1.697563000	3.527792000
H	-1.619578000	-2.817328000	3.823903000
C	-2.480305000	-1.989096000	-1.289581000
O	-2.502430000	-3.012804000	-1.811938000
C	-0.926656000	0.186887000	-1.492412000
O	-0.053493000	0.501389000	-2.178131000
C	-2.211197000	1.314799000	0.578836000
O	-2.081597000	2.291204000	1.177992000
C	-3.562475000	0.504915000	-1.657002000
O	-4.272719000	0.998184000	-2.420101000
C	-3.910484000	-0.777046000	0.667665000
O	-4.842410000	-1.042021000	1.282343000
C	2.372526000	1.919656000	-0.440059000
H	2.836189000	0.961477000	-0.684198000

TS3, E = -2738.359518

C	-2.704958000	3.807457000	-0.431865000
C	-2.783942000	2.962661000	0.694457000
C	-1.744510000	2.390527000	1.416365000
C	-1.571635000	4.200739000	-1.129765000
C	-0.234152000	3.791521000	-0.950813000
C	0.317470000	2.985635000	0.041809000
H	-3.657572000	4.197079000	-0.802493000
H	-3.788815000	2.772873000	1.081834000
H	-2.040674000	1.850346000	2.320552000
H	-1.740972000	4.865868000	-1.981650000
H	0.469369000	4.132733000	-1.715774000
C	0.777640000	0.243314000	0.699065000
C	1.911192000	0.760478000	0.273085000
S	2.016639000	2.599398000	-0.091990000
C	3.187477000	0.049689000	0.005634000
C	4.348688000	0.712288000	-0.434907000
C	3.262317000	-1.345225000	0.205463000
C	5.536537000	0.011727000	-0.662445000
H	4.337679000	1.789547000	-0.612383000
C	4.445255000	-2.042436000	-0.027511000
H	2.374253000	-1.884045000	0.539098000
C	5.592855000	-1.368257000	-0.461409000
H	6.422006000	0.553909000	-1.004100000
H	4.470359000	-3.123786000	0.129290000
H	6.520618000	-1.916361000	-0.642743000
C	-0.192453000	-0.657659000	1.017000000
Cr	-1.549122000	-1.506208000	-0.363935000
O	-0.363555000	-1.015248000	2.313976000

C	0.596960000	-0.640636000	3.298680000
H	1.609260000	-0.970041000	3.014706000
H	0.615076000	0.450474000	3.457609000
H	0.294337000	-1.135188000	4.231371000
C	-0.086470000	-2.208324000	-1.369061000
O	0.782953000	-2.637221000	-1.986741000
C	-1.529642000	0.039764000	-1.453868000
O	-1.543184000	0.967461000	-2.140607000
C	-2.947239000	-0.783987000	0.692751000
O	-3.793809000	-0.336317000	1.336857000
C	-2.789419000	-2.313790000	-1.525049000
O	-3.557836000	-2.804265000	-2.232423000
C	-1.542368000	-3.071010000	0.735908000
O	-1.549382000	-4.020445000	1.381652000
C	-0.358324000	2.409053000	1.166931000
H	0.278595000	2.142335000	2.006526000

INT1, E = -2738.371031

C	1.846091000	4.779240000	-0.374381000
C	1.647418000	4.014177000	-1.501990000
C	1.664610000	2.597204000	-1.609565000
C	2.105394000	4.330299000	0.949208000
C	2.202154000	3.046754000	1.440427000
C	2.086055000	1.794861000	0.761488000
H	1.794509000	5.864277000	-0.502953000
H	1.453078000	4.555584000	-2.432399000
H	1.481041000	2.198012000	-2.611347000
H	2.230151000	5.123320000	1.692764000
H	2.381128000	2.966898000	2.517890000
C	0.168757000	-1.109896000	1.008300000
C	1.476576000	-0.987328000	0.836881000
S	2.199286000	0.410387000	1.792338000
C	2.398850000	-1.860047000	0.074023000
C	3.786436000	-1.635101000	0.008569000
C	1.873001000	-2.964909000	-0.630411000
C	4.619584000	-2.483911000	-0.726572000
H	4.223891000	-0.789386000	0.544473000
C	2.705126000	-3.806017000	-1.364711000
H	0.797271000	-3.149934000	-0.594057000
C	4.085674000	-3.572994000	-1.417614000
H	5.694803000	-2.288307000	-0.756789000
H	2.272441000	-4.653440000	-1.902967000
H	4.736212000	-4.235578000	-1.993752000
C	-1.153062000	-1.092144000	1.118208000
Cr	-2.351960000	-0.079449000	-0.361161000
O	-1.818212000	-1.723155000	2.114281000
C	-1.057270000	-2.404658000	3.100750000
H	-0.448879000	-3.206680000	2.646781000
H	-0.383659000	-1.709258000	3.631904000
H	-1.771403000	-2.840833000	3.812473000
C	-2.896260000	-1.836981000	-0.875521000
O	-3.200046000	-2.902619000	-1.179933000
C	-1.004911000	-0.114340000	-1.674780000
O	-0.190452000	-0.093795000	-2.498326000
C	-1.670545000	1.557639000	0.286383000
O	-1.224365000	2.550562000	0.677045000
C	-3.503557000	0.755360000	-1.576088000
O	-4.211002000	1.275432000	-2.327770000
C	-3.746002000	-0.023342000	0.955273000
O	-4.601120000	0.039847000	1.718039000

C	1.858771000	1.637874000	-0.637984000
H	1.802101000	0.605324000	-0.987623000

3M, E = -2738.408662

C	0.520786000	4.878479000	-0.076363000
C	-0.023166000	3.935502000	-1.024254000
C	0.168832000	2.593426000	-1.009282000
C	1.739065000	4.760876000	0.547979000
C	2.656384000	3.661220000	0.403685000
C	2.265233000	2.388744000	0.120445000
H	0.000159000	5.836784000	0.021911000
H	-0.609692000	4.357813000	-1.848123000
H	-0.116488000	1.985768000	-1.868615000
H	2.107285000	5.634092000	1.097269000
H	3.725702000	3.880432000	0.488432000
C	0.849902000	0.400838000	0.237002000
C	2.067450000	-0.140052000	-0.074883000
S	3.339049000	1.074496000	-0.367019000
C	2.446551000	-1.556632000	-0.238061000
C	3.726930000	-2.012100000	0.141166000
C	1.542132000	-2.483497000	-0.790692000
C	4.075458000	-3.355442000	-0.003944000
H	4.446393000	-1.307768000	0.565349000
C	1.891434000	-3.827072000	-0.929180000
H	0.568202000	-2.139820000	-1.137139000
C	3.157977000	-4.268714000	-0.534326000
H	5.069845000	-3.691312000	0.300441000
H	1.169629000	-4.527177000	-1.356129000
H	3.433052000	-5.320255000	-0.647405000
C	-0.339587000	-0.355249000	0.706302000
Cr	-2.254259000	-0.431286000	-0.052290000
O	-0.150842000	-1.092272000	1.789195000
C	1.011582000	-1.117904000	2.638134000
H	1.715615000	-1.885615000	2.289751000
H	1.512565000	-0.140960000	2.667734000
H	0.634215000	-1.386147000	3.633396000
C	-2.023433000	-2.302218000	-0.317337000
O	-1.881394000	-3.433235000	-0.468190000
C	-1.650129000	-0.100463000	-1.819658000
O	-1.322755000	0.063107000	-2.911552000
C	-2.533314000	1.424016000	0.318300000
O	-2.766892000	2.517039000	0.581855000
C	-4.029222000	-0.538587000	-0.718063000
O	-5.103333000	-0.603808000	-1.124347000
C	-2.886821000	-0.828747000	1.709789000
O	-3.285568000	-1.075037000	2.756811000
C	0.823007000	1.928688000	0.184760000
H	0.364908000	2.346057000	1.101103000