Supporting Information for

Experimental and theoretical studies of the [3,3]-sigmatropic rearrangement of isoprenylazides.

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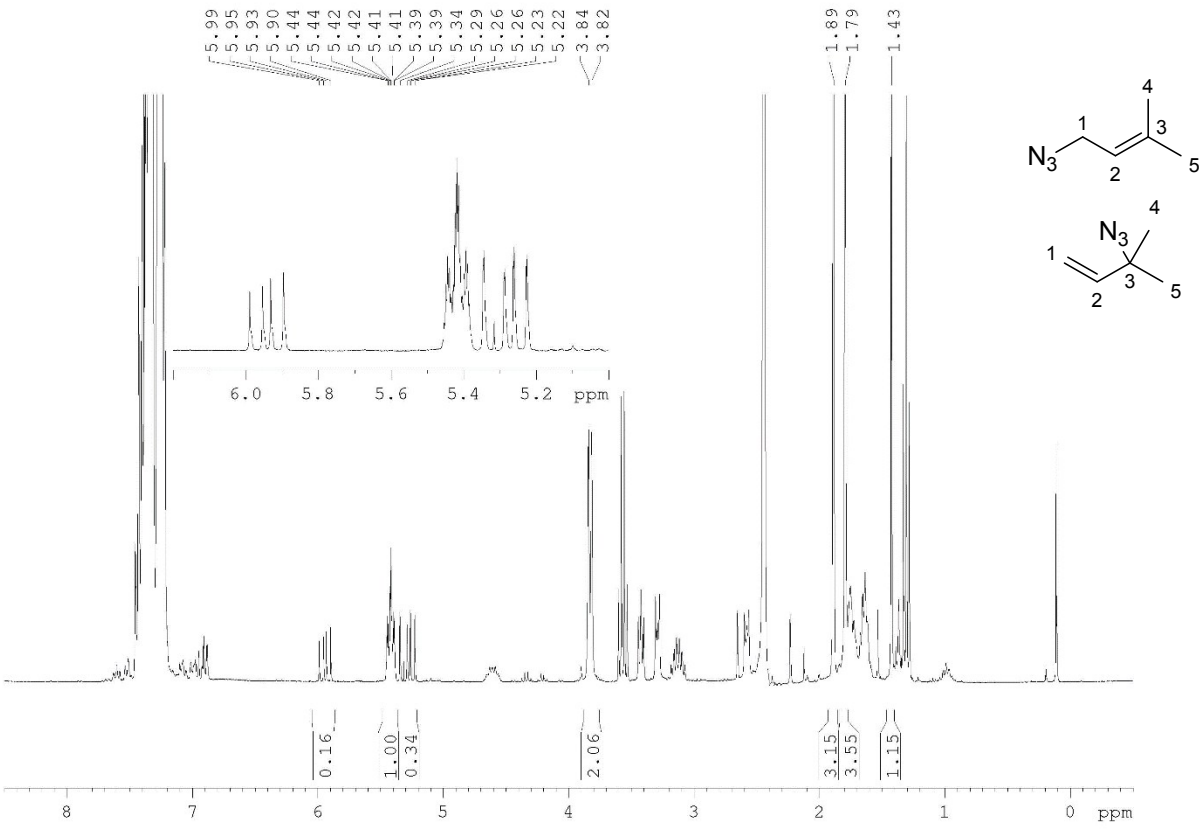
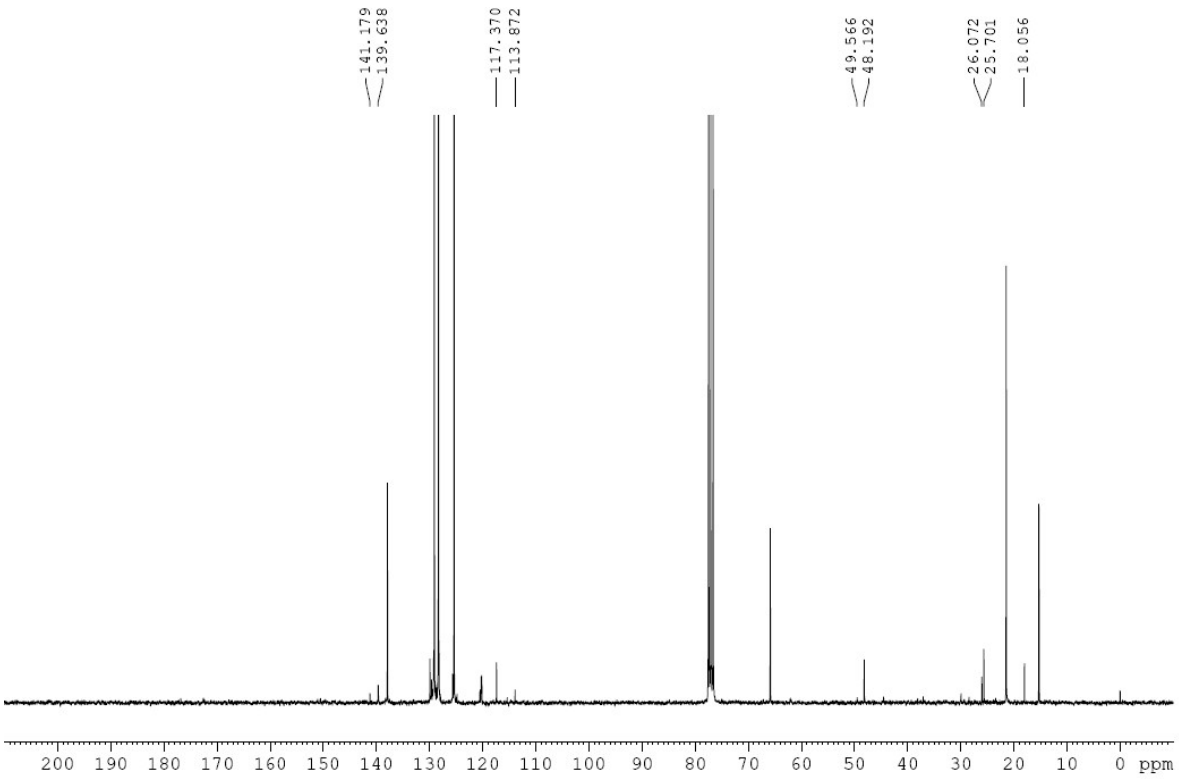
List of Supporting Information

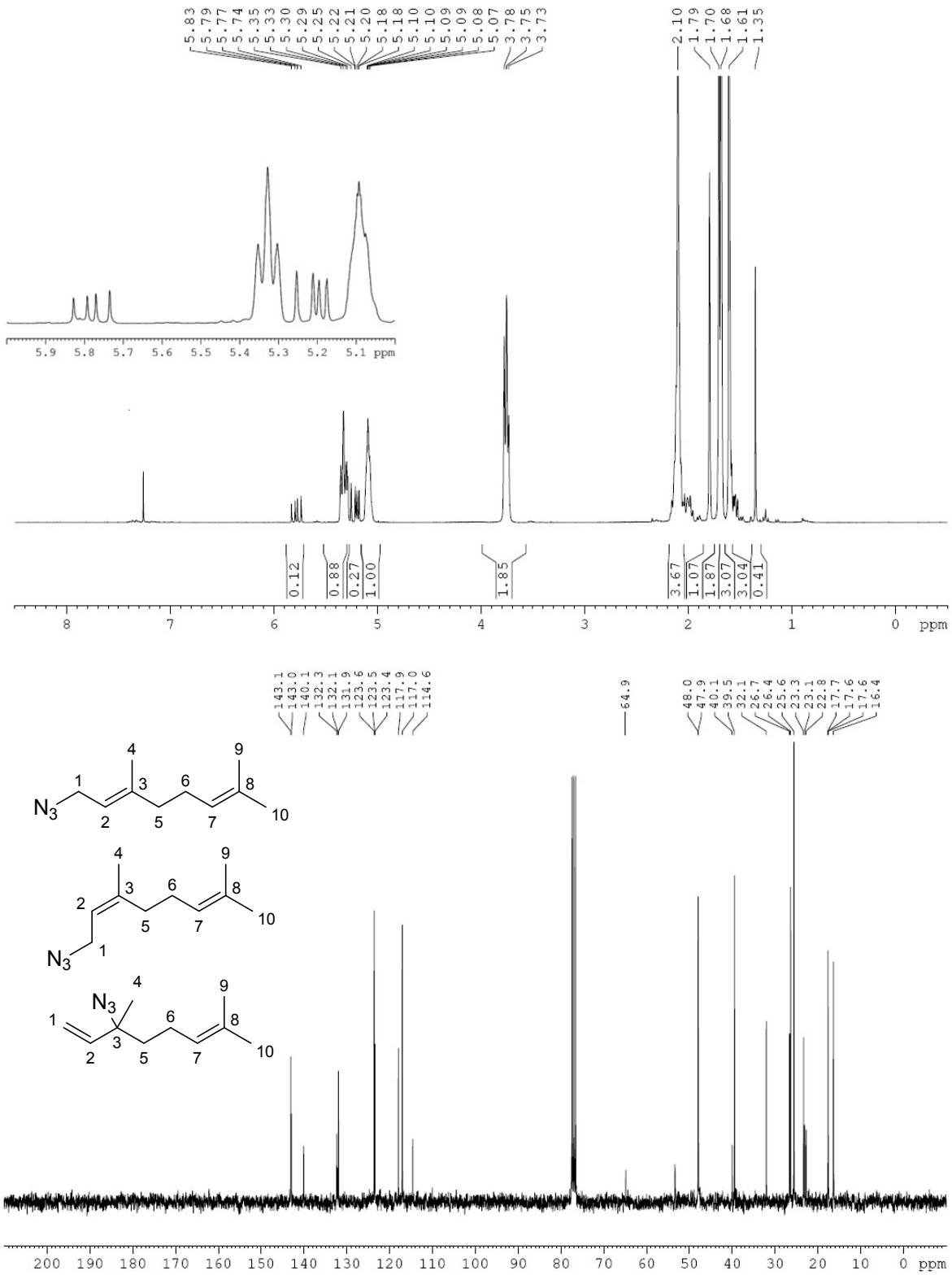
Supplementary Material

Spectral data of 1-azido-3-methylbut-2-ene **(6a)** and 3-azido-3-methylbut-1-ene **(6a rearr)** 6.4% w/w in Toluene/Ethyl Ether.

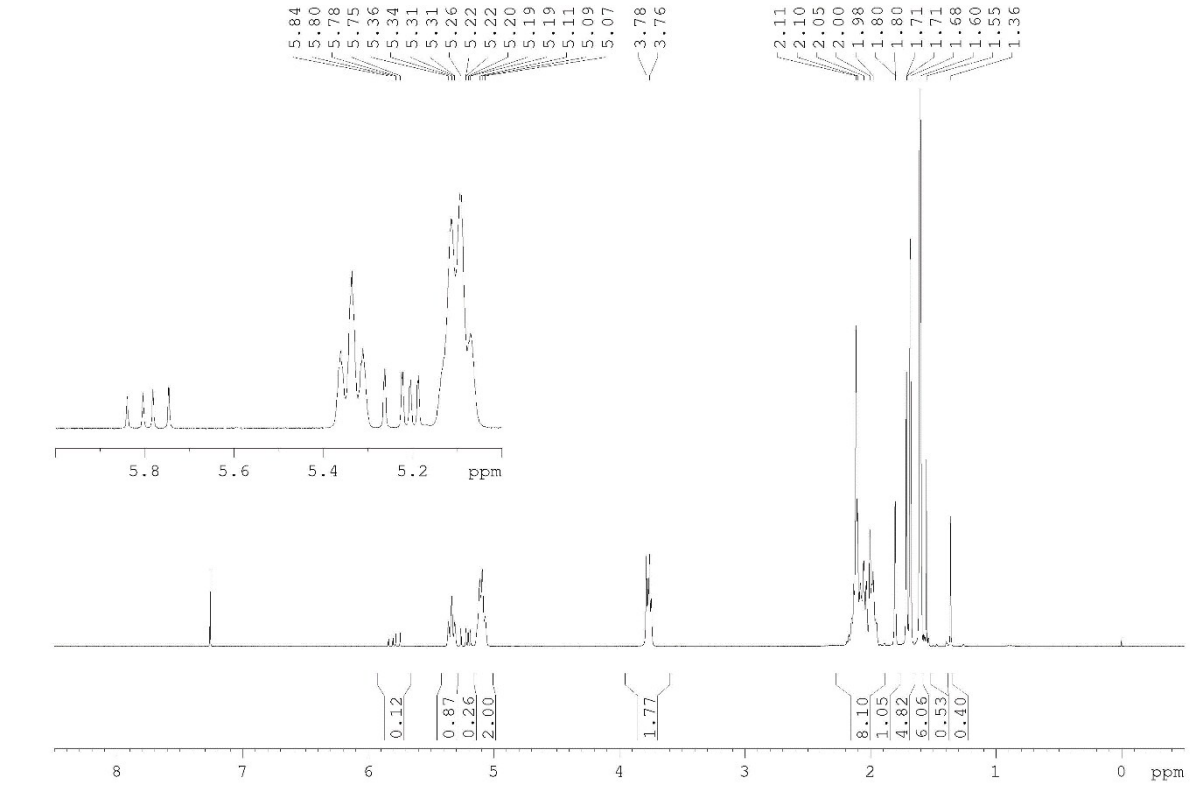


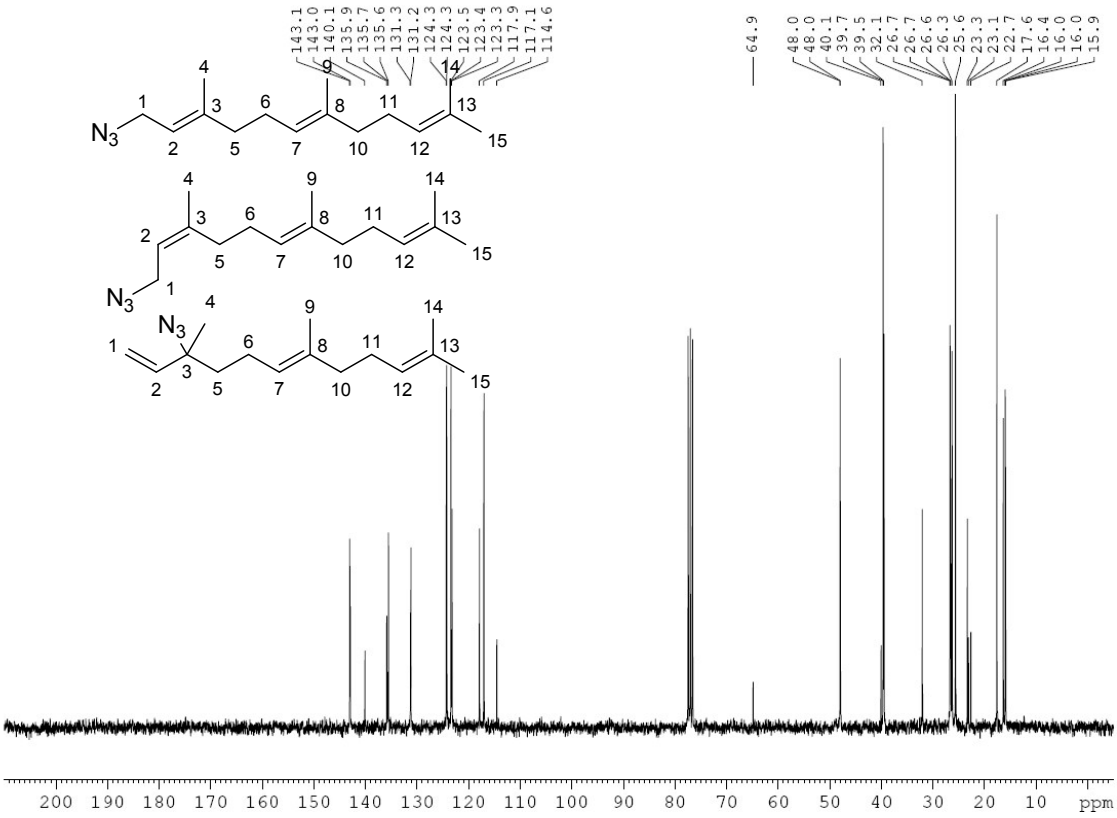


Spectral data of (*E*)-1-azido-3,7-dimethylocta-2,6-diene **(6a-*E*)**; (*Z*)-1-azido-3,7-dimethylocta-2,6-diene **(6b-*Z*)** and 3-azido-3,7-dimethylocta-1,6-diene **(6a-*t*)**

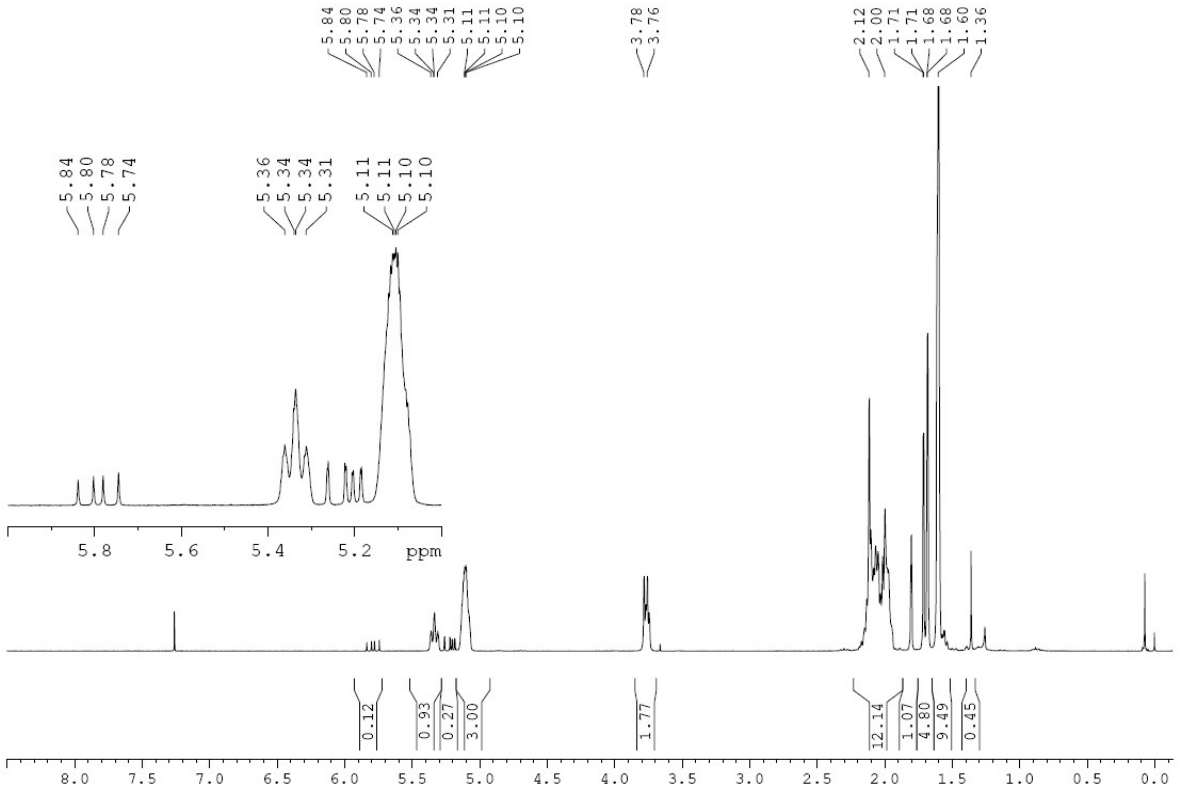


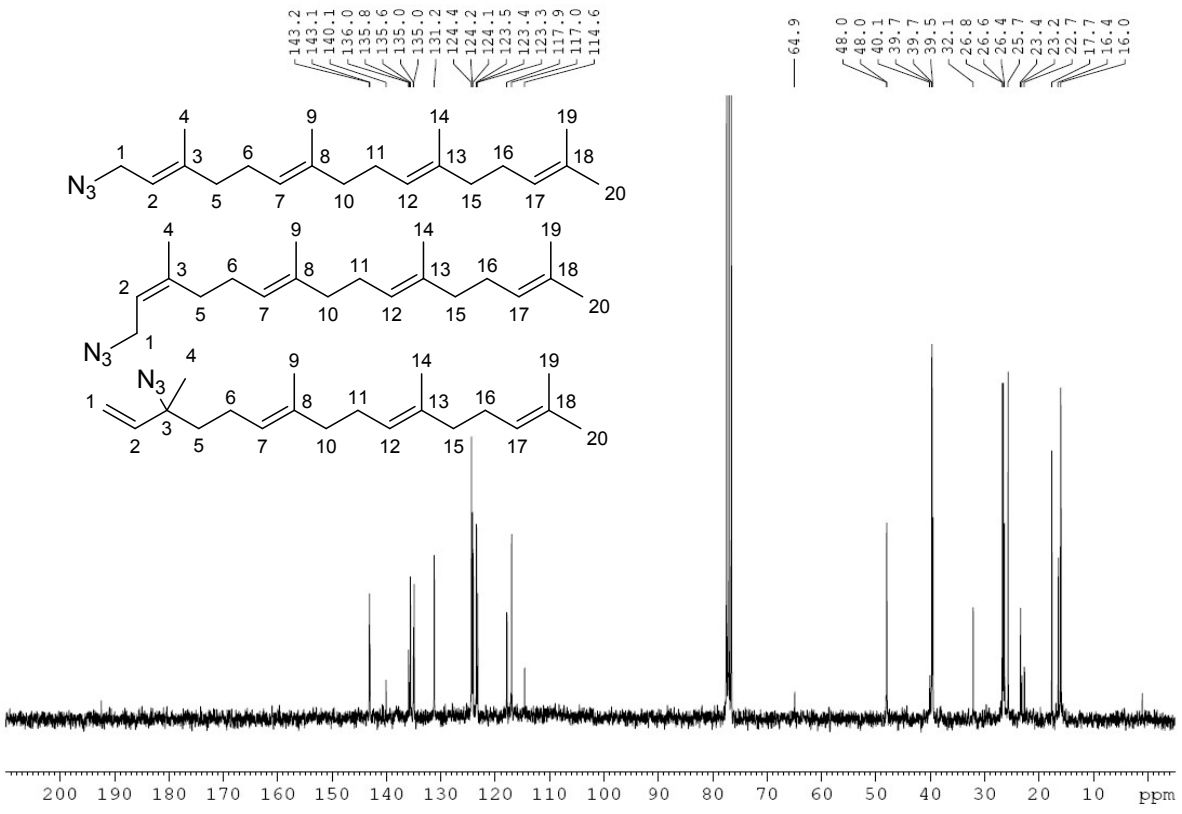
Spectral data of (2*E*,6*E*)-1-azido-3,7,11-trimethyldodeca-2,6,10-triene **(6c-*E*)**; (2*Z*,6*E*)-1-azido-3,7,11-trimethyldodeca-2,6,10-triene **(6c-*Z*)** and (*E*)-3-azido-3,7,11-trimethyldodeca-1,6,10-triene **(6c-*t*)**



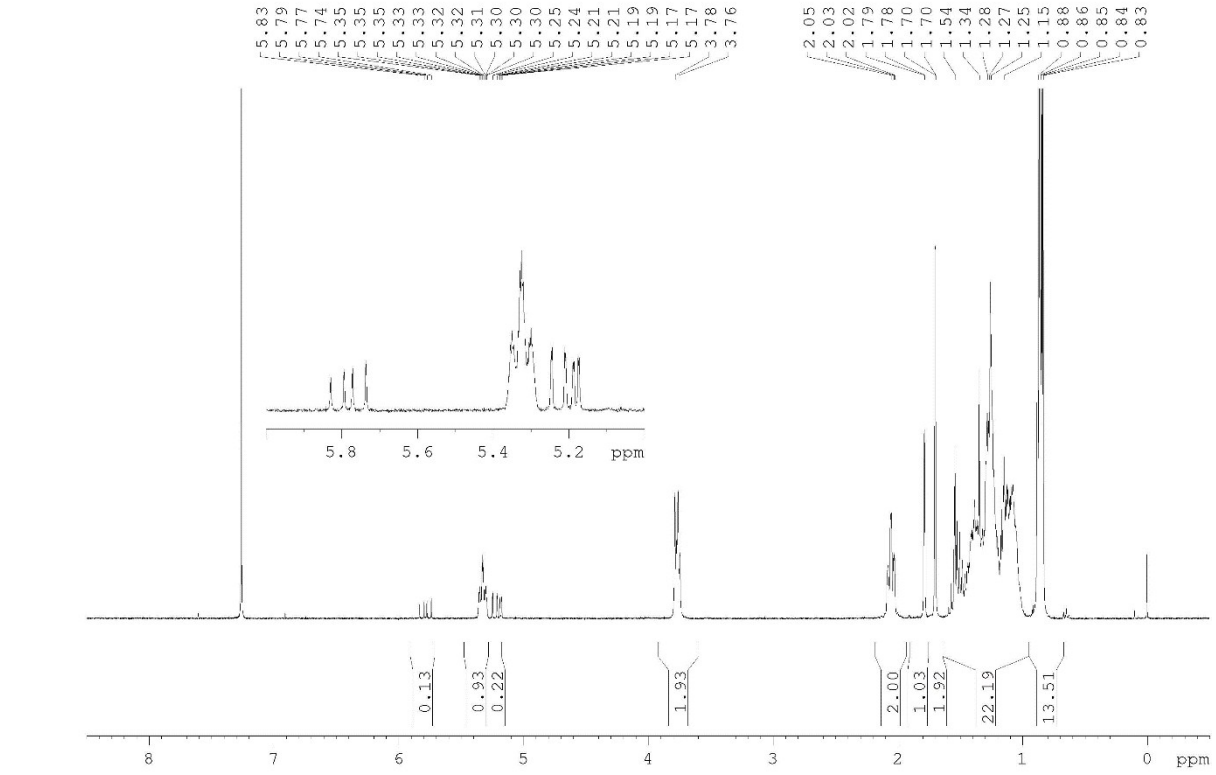


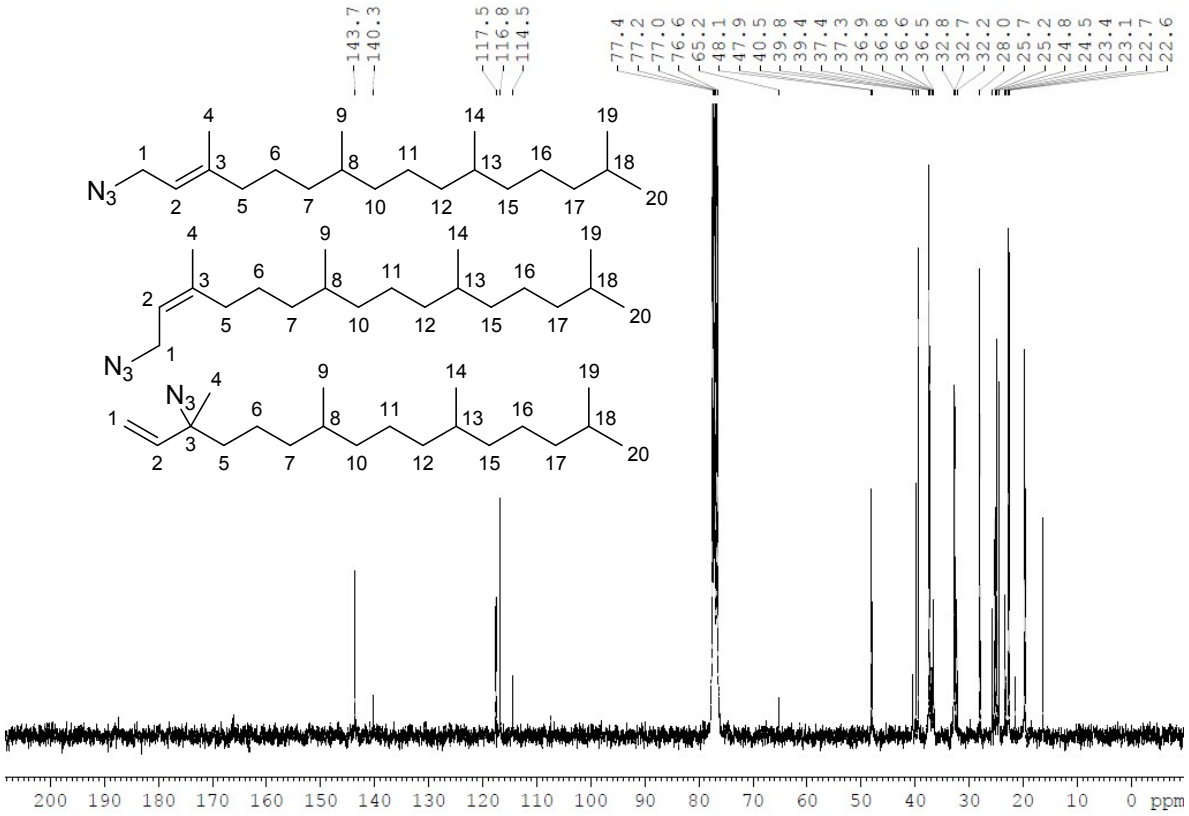
Spectral data of (2*E*,6*E*,10*E*)-1-azido-3,7,11,15-tetramethylhexadeca-2,6,10,14-tetraene **(6d-*E*)**; (2*Z*,6*E*,10*E*)-1-azido-3,7,11,15-tetramethylhexadeca-2,6,10,14-tetraene **(6d-*Z*)** and (6*E*,10*E*)-3-azido-3,7,11,15-tetramethylhexadeca-1,6,10,14-tetraene **(6d-*t*)**



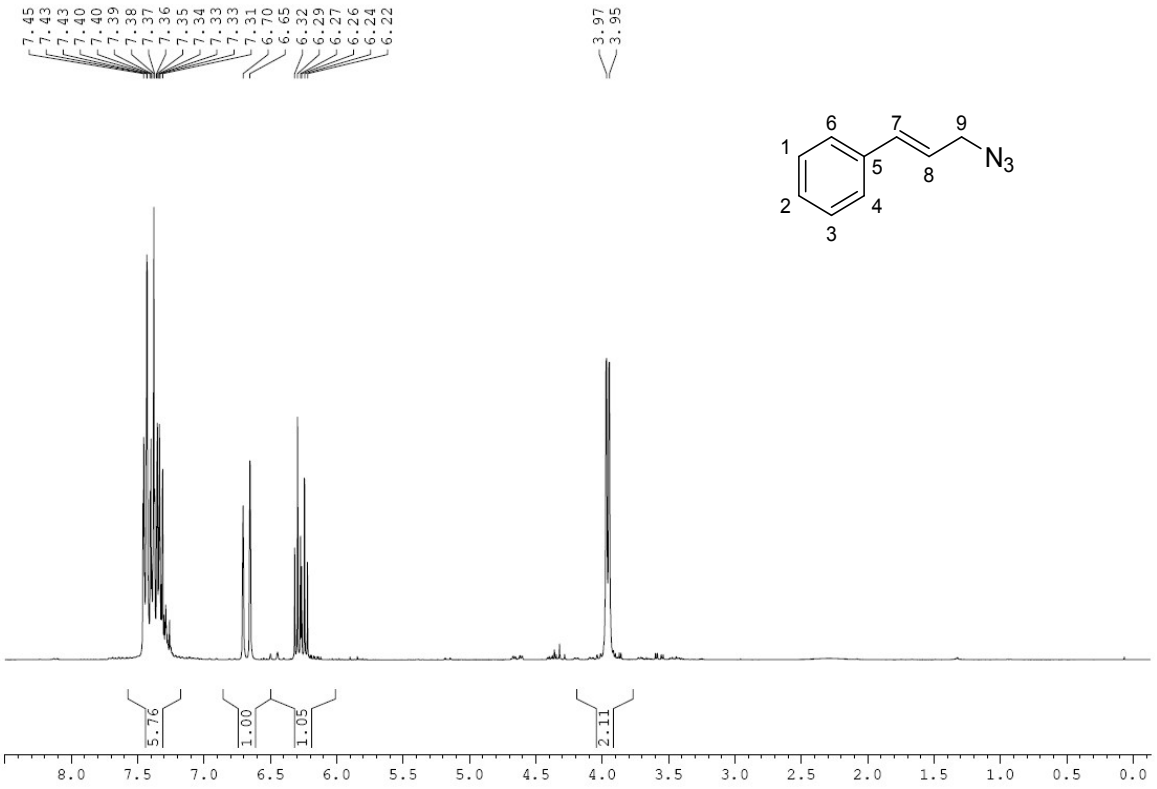


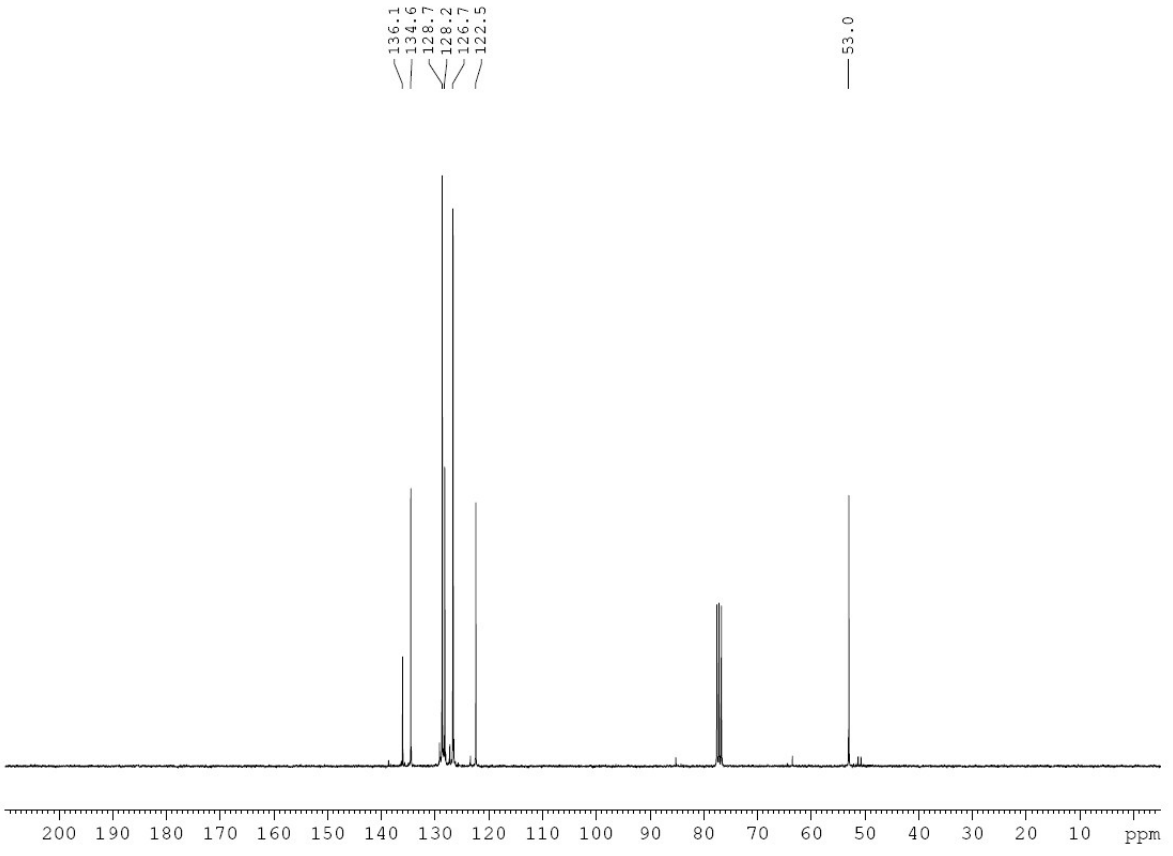
Spectral data of (*E*)-1-azido-3,7,11,15-tetramethylhexadec-2-ene (**6e-*E***); (*Z*)-1-azido-3,7,11,15-tetramethylhexadec-2-ene (**6e-*Z***) and (3R)-3-azido-3,7,11,15-tetramethylhexadec-1-ene (**6e-*t***)



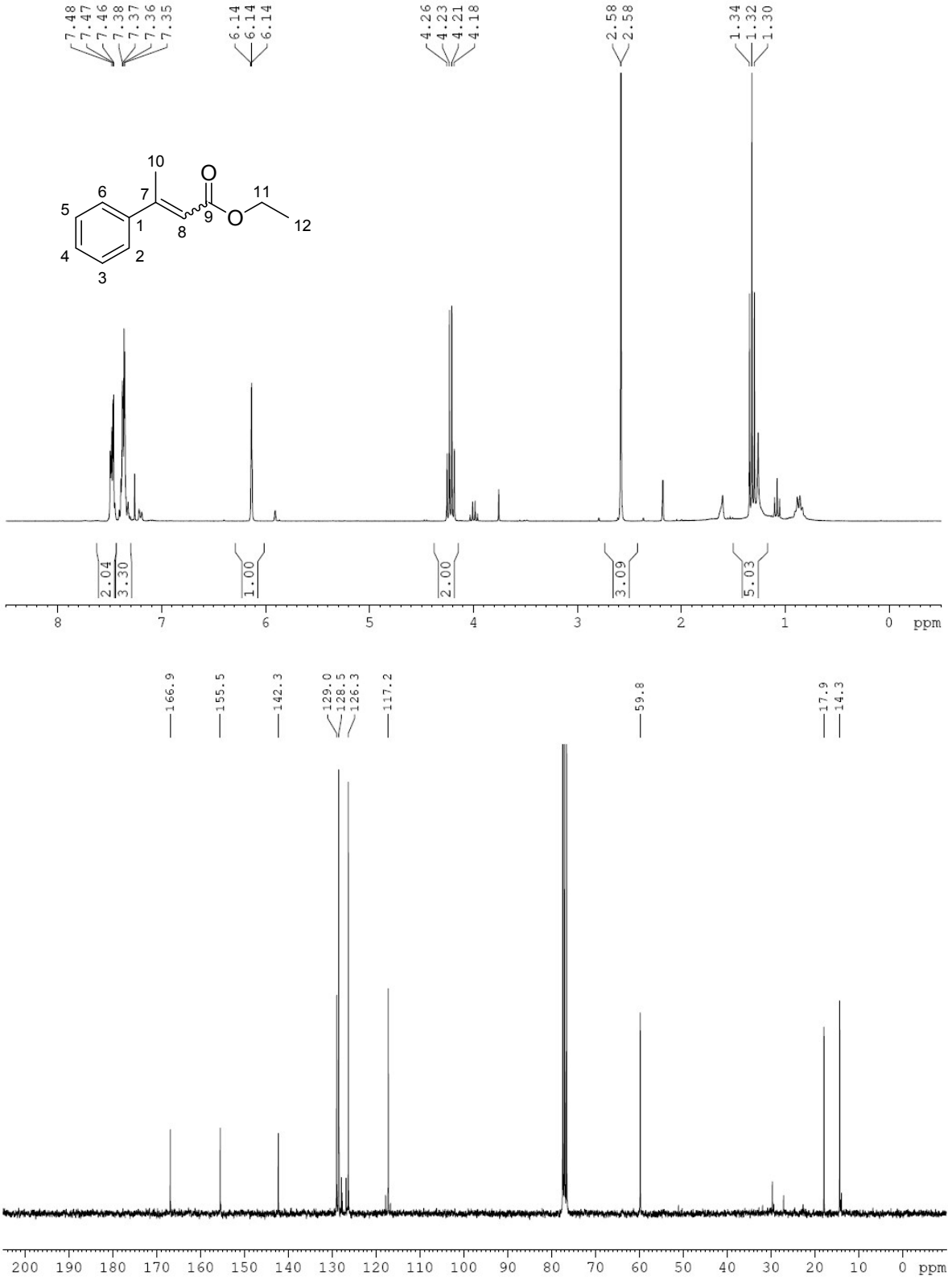


Spectral data of (*E*)-(3-azidoprop-1-en-1-yl) benzene **(8)**

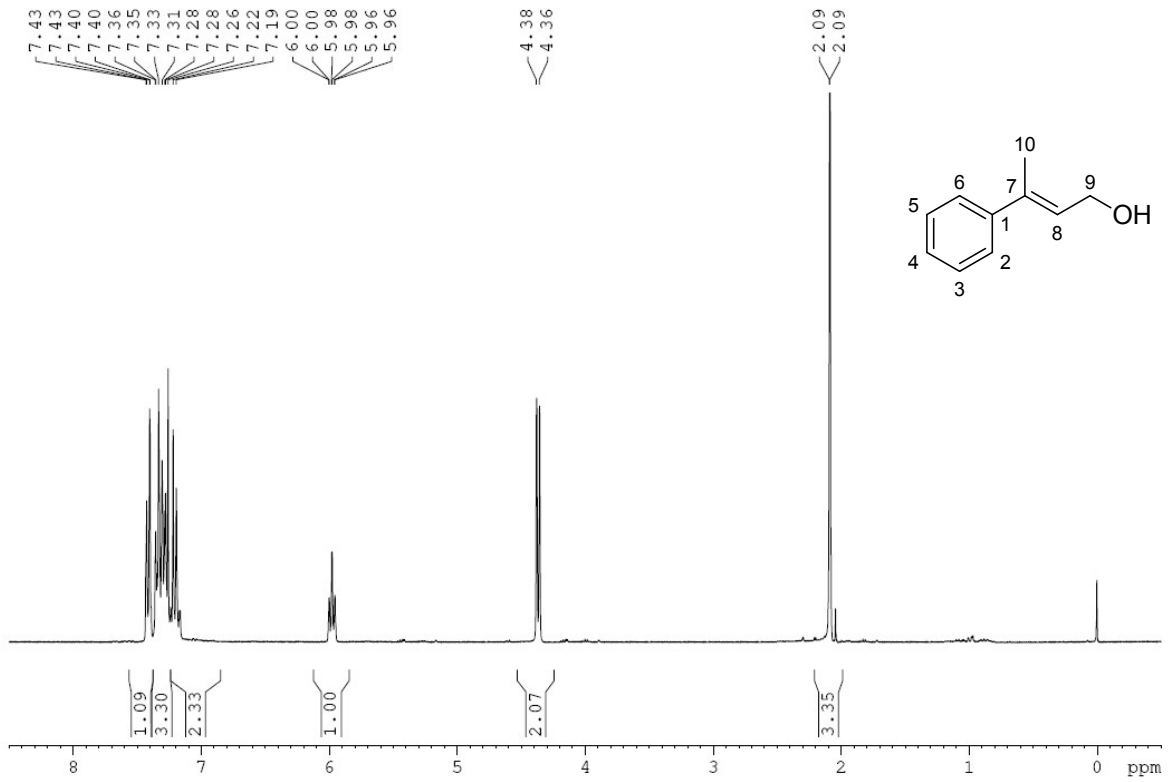


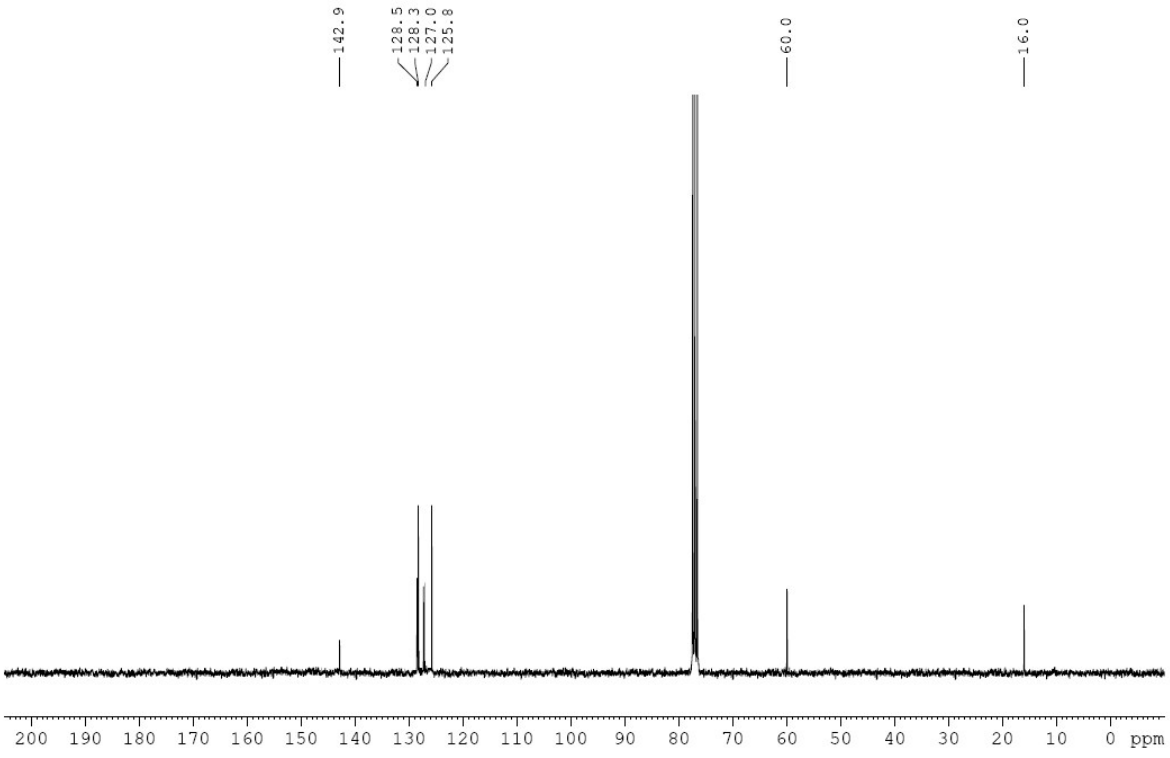


Spectral data of (*E*)-ethyl 3-phenylbut-2-enoate **(10*E*)** and (*Z*)-ethyl 3-phenylbut-2-enoate **(10*Z*)**



Spectral data of (*E*)-3-Phenylbut-2-en-1-ol **(11)**





Spectral data of (*E*)-(4-azidobut-2-en-2-yl) bencene **(12)**

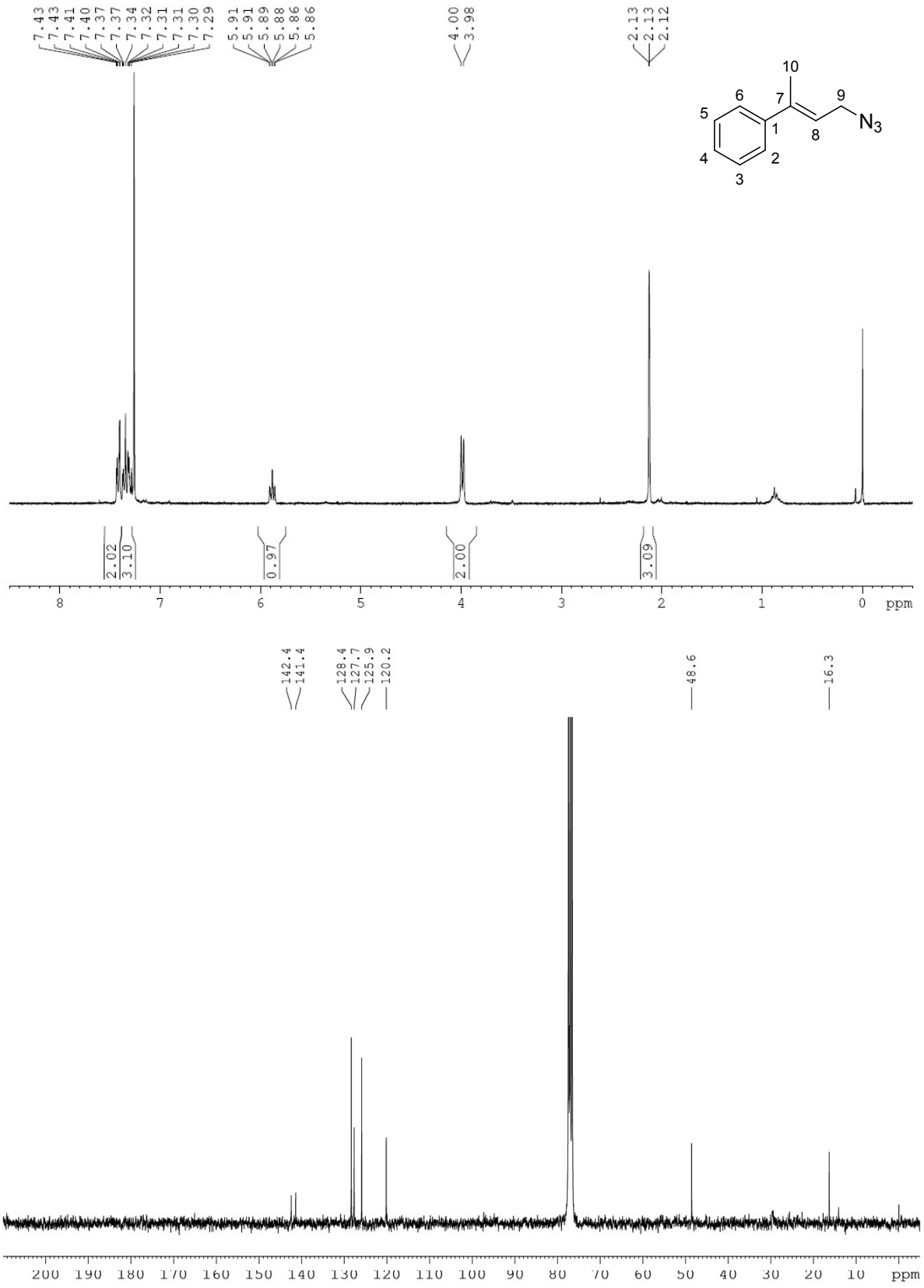


Table S1.Bond distances, local topological properties for the selected bond critical calculated at the TSs under study.[a]

Species	Bonds	R	ρ_b	$\nabla^2\rho_b$	ε	H_b	DI
TS-6a	C1-C2	1.39	0.314	-0.908	0.194	-0.330	1.31
	C2-C3	1.37	0.322	-0.952	0.218	-0.350	1.43
	N1-N2	1.16	0.530	-1.466	0.179	-0.870	2.02
	N2-N3	1.16	0.529	-1.464	0.183	-0.868	2.03
TS-8	C1-C2	1.39	0.313	-0.911	0.175	-0.329	1.31
	C2-C3	1.37	0.326	-0.971	0.224	-0.356	1.45
	N1-N2	1.17	0.526	-1.445	0.192	-0.861	2.01
	N2-N3	1.16	0.534	-1.488	0.185	-0.883	2.05
TS-12	C1-C2	1.40	0.309	-0.886	0.179	-0.320	1.28
	C2-C3	1.37	0.325	-0.967	0.226	-0.356	1.46
	N1-N2	1.17	0.527	-1.447	0.185	-0.866	2.01
	N2-N3	1.16	0.533	-1.480	0.179	-0.881	2.05

[a]Bond distances (R) in Å;ρ_b, $\nabla^2\rho_b$, H_b in au. ε and $DI$are dimensionless

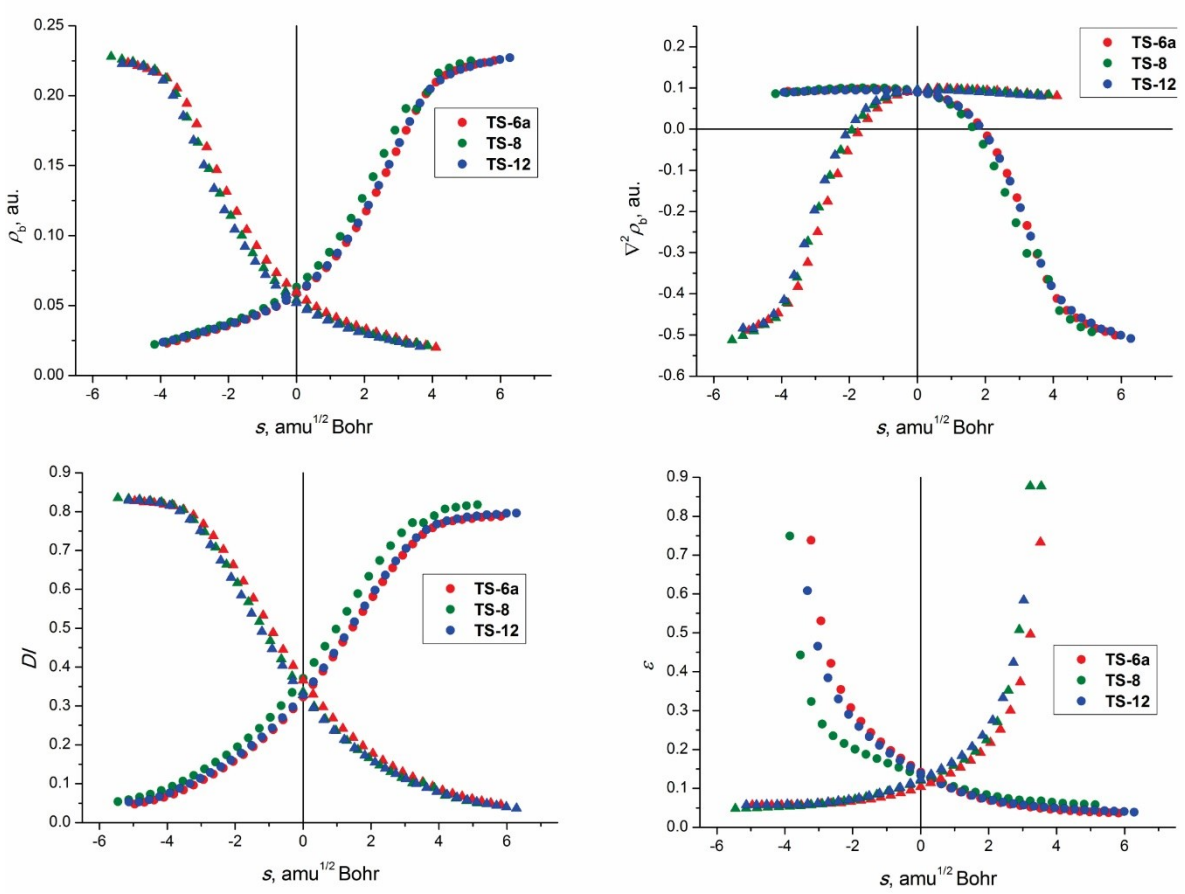


Figure S1. Topological properties and delocalization index at the C1-N1 (circle) and C3-N3 (triangle) bcps, along the IRC path corresponding to **TS-6a**, **TS-8** and **TS-12**. TSs are located at s = 0.0 amu$^{1/2}$ Bohr.

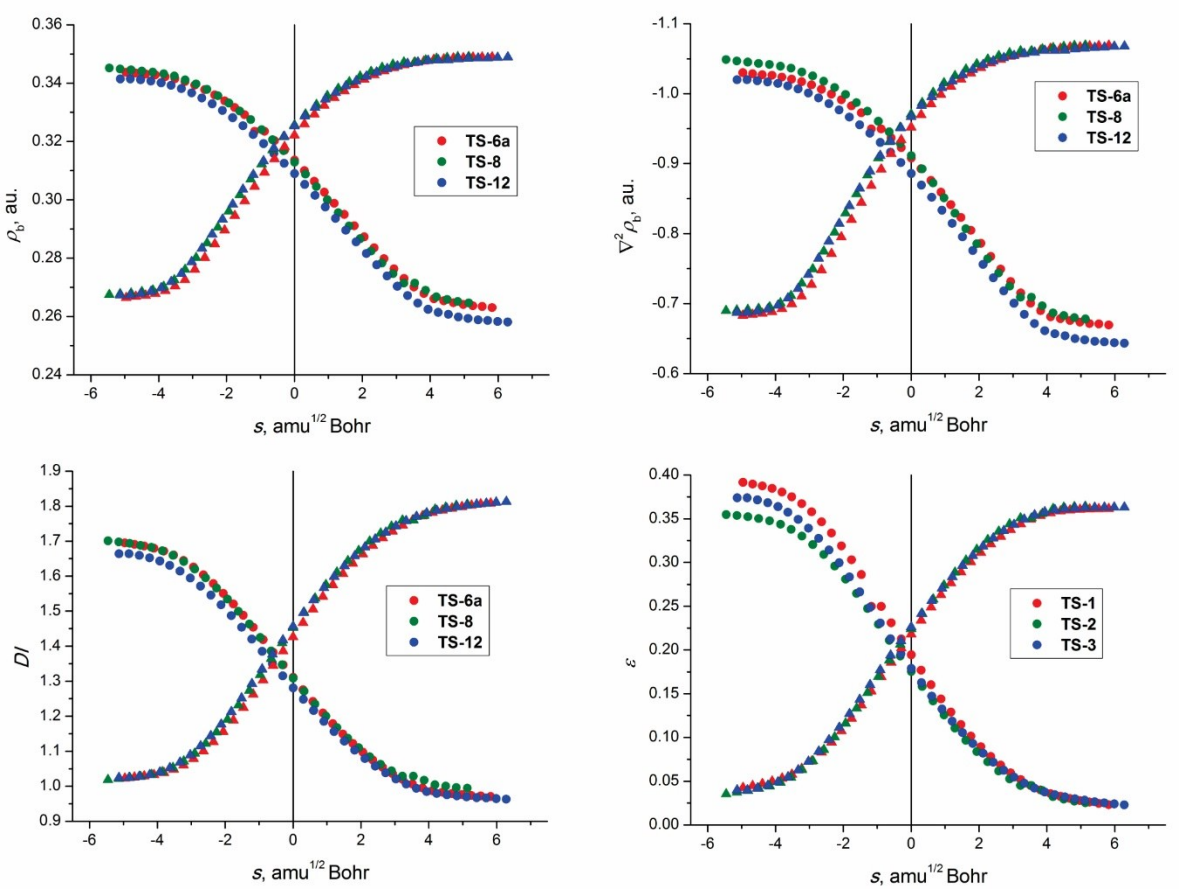


Figure S2. Topological properties and delocalization index at the C1-C2 (circle) and C2-C3 (triangle) bcps, along the IRC path corresponding to **TS-6a**, **TS-8** and **TS-12**. TSs are located at*s* = 0.0 amu$^{1/2}$ Bohr.

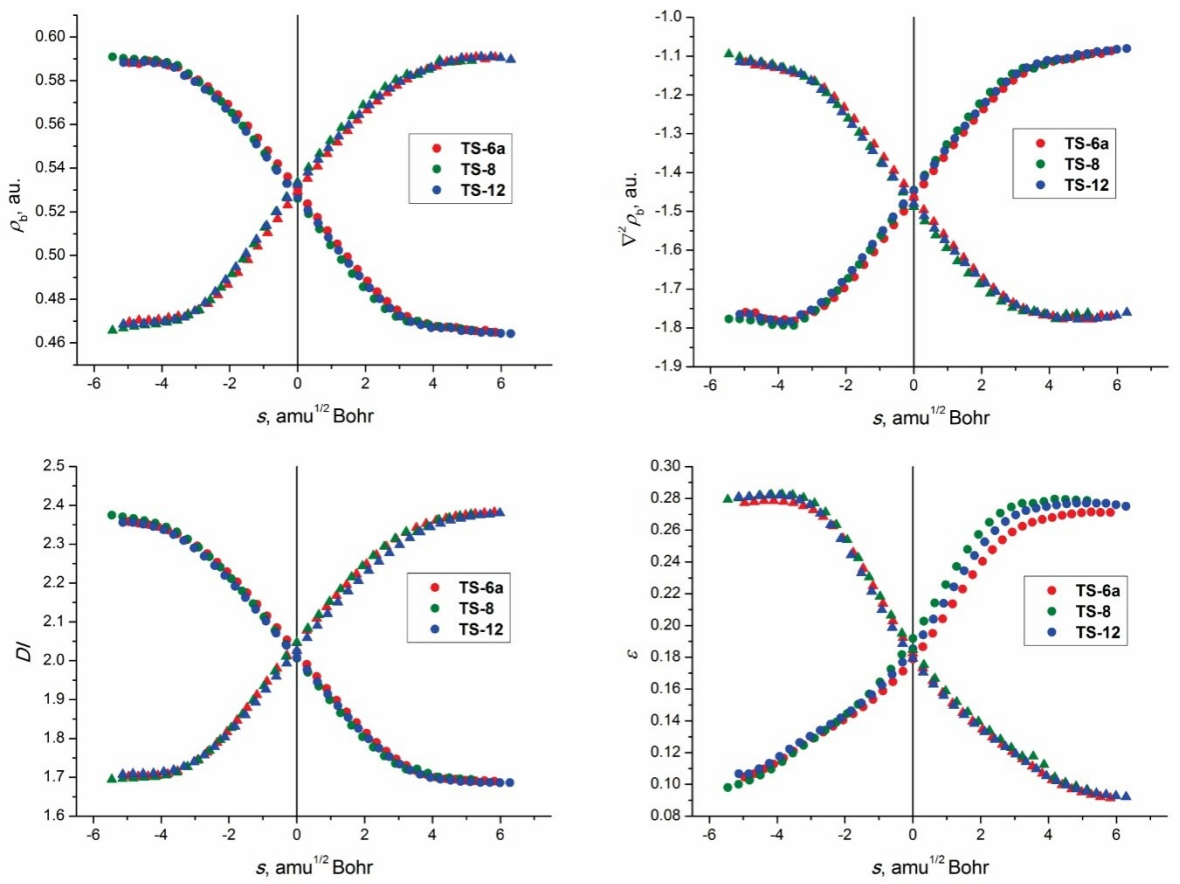


Figure S3. Topological properties and delocalization index at the N1-N2 (circle) and N2-N3 (triangle) bcps, along the IRC path corresponding to **TS-6a**, **TS-8** and **TS-12**. TSs are located at *s* = 0.0 amu$^{1/2}$ Bohr.

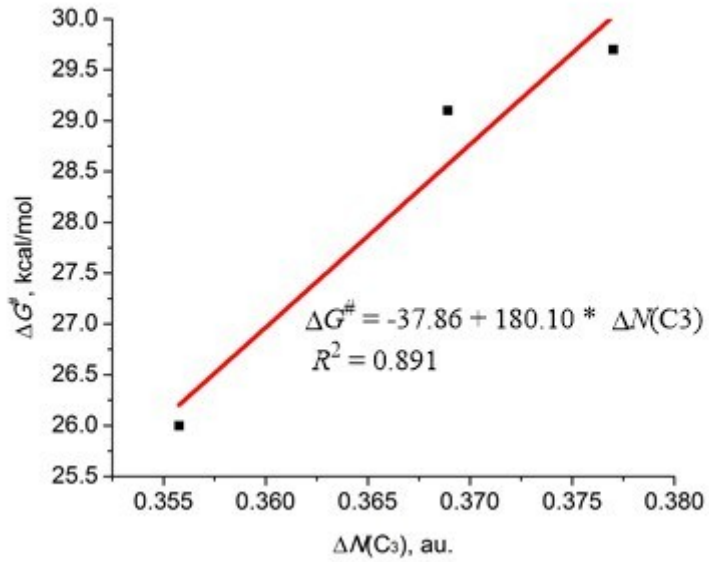


Figure S4. Relationship between $\Delta G^{\#}$ for the [3,3]-sigmatropic reactions under study and ΔN(C3).

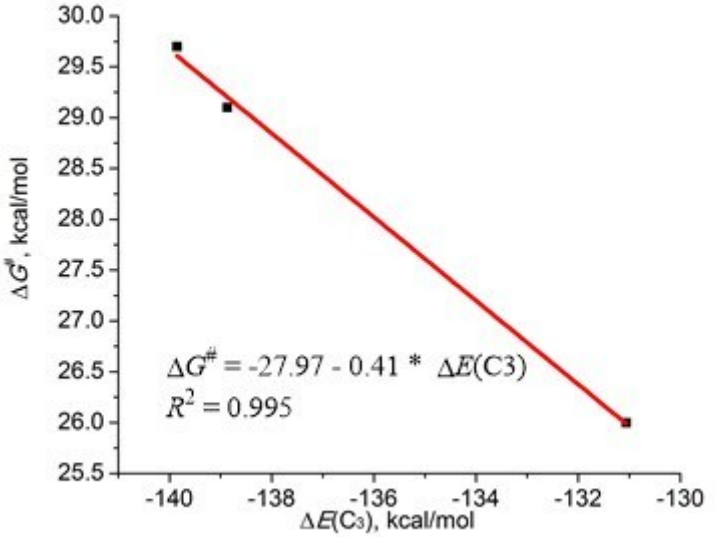


Figure S5. Relationship between $\Delta G^{\#}$ for the [3,3]-sigmatropic reactions under study and ΔE(C3).

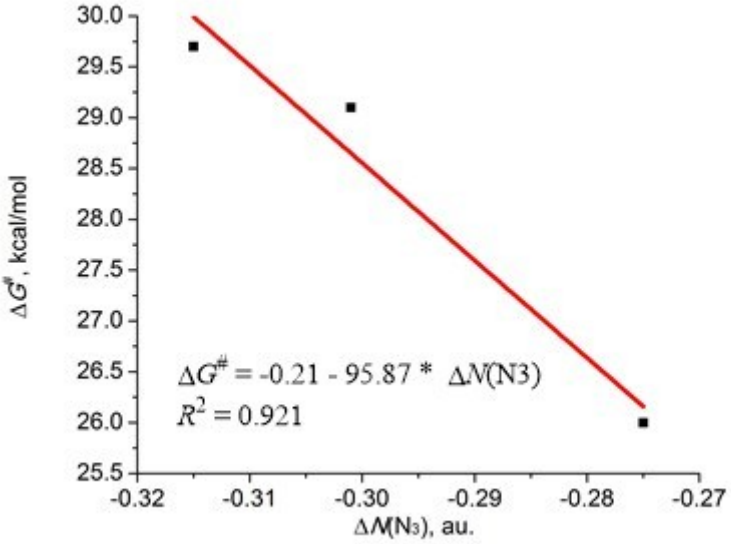


Figure S6. Relationship between $\Delta G^{\#}$ for the [3,3]-sigmatropic reactions under study and ΔN(N3).

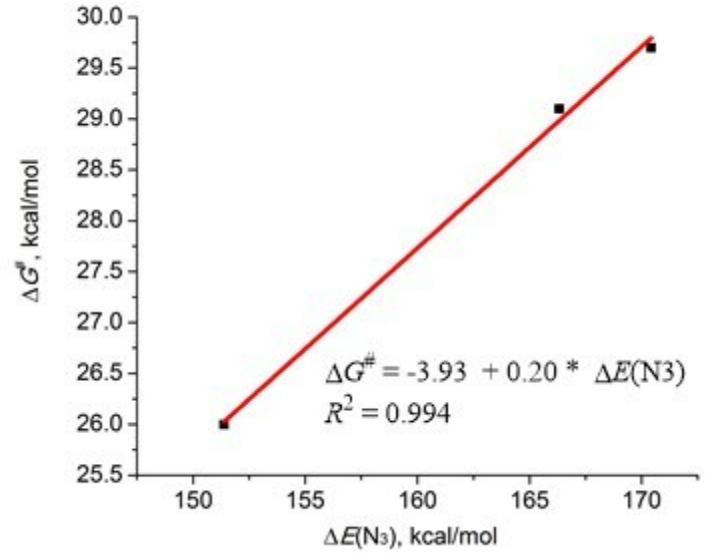


Figure S7. Relationship between $\Delta G^{\#}$ for the [3,3]-sigmatropic reactions under study and ΔE(N3).

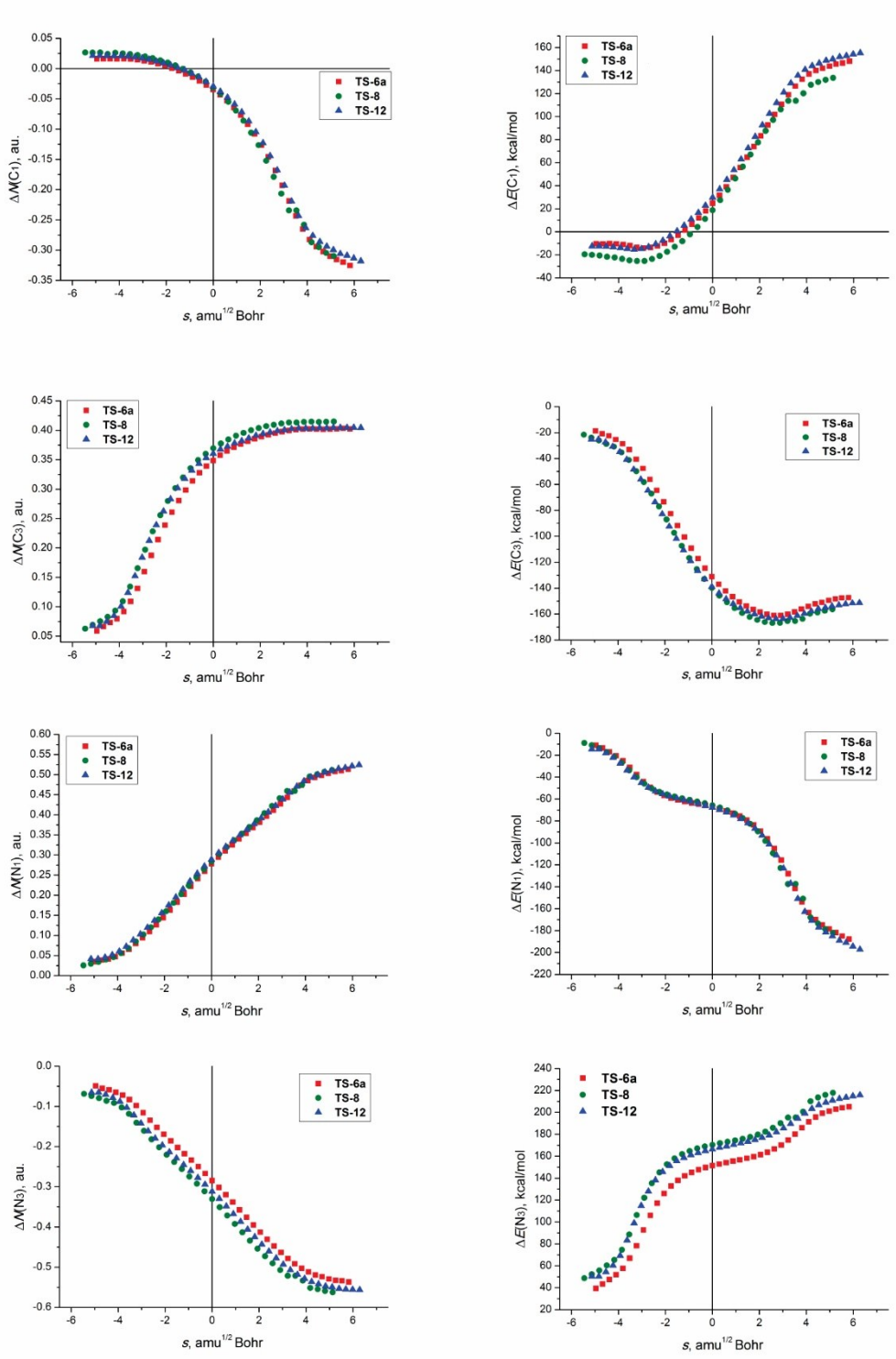


Figure S8. Changes in electron population and atomic energy for the C1, C2, N1 and N3 atoms along the IRC path corresponding **TS-6a**, **TS-8** and **TS-12**. TSs are located at s = 0.0 amu$^{1/2}$ Bohr.

Cartesian coordinates, unique frequency imaginary, and computed absolute electronic energies (including zero-point energy -ZPE- corrections) and free energy of the stationary points involved in reactions under study.

6a

C	-1.834306	-0.025759	0.023523
C	-3.046317	-0.874595	-0.168101
C	-0.660476	-0.584615	0.296548
C	0.627673	0.108592	0.541770
N	1.619506	-0.372199	-0.436529
N	2.768129	-0.071014	-0.189330
N	3.853339	0.160058	-0.043129
C	-2.081491	1.437847	-0.117599
H	-3.469096	-0.720669	-1.159928
H	-3.822348	-0.604801	0.546948
H	-2.823356	-1.929955	-0.049942
H	-0.610307	-1.663152	0.363392
H	0.987212	-0.119043	1.545838
H	0.536696	1.187170	0.457768
H	-1.186224	2.042990	-0.044242
H	-2.780638	1.777552	0.645259
H	-2.549249	1.643179	-1.079023

Sum of electronic and zero-point Energies = -359.871115 au.
Sum of electronic and thermal Free Energies =-359.906278 au.

8

C	-4.092403	-0.231199	0.004039
C	-3.321917	-1.377019	0.017988
C	-1.943957	-1.283299	0.010826
C	-1.305886	-0.048734	-0.007692
C	-2.095868	1.097770	-0.024969
C	-3.47107	1.006128	-0.018295
C	0.155437	-0.024897	-0.009883
C	0.932929	1.047185	0.031765
C	2.416169	1.020898	0.029622
N	2.907662	-0.351018	-0.029315
N	4.114209	-0.470973	-0.013026
N	5.211797	-0.684115	-0.002890
H	-5.168338	-0.297688	0.008671
H	-3.793041	-2.346705	0.033906
H	-1.345038	-2.180961	0.021728
H	-1.634722	2.072007	-0.048078
H	-4.064563	1.906384	-0.032888
H	0.632663	-0.994037	-0.044187
H	0.512469	2.041450	0.074374
H	2.791321	1.587303	-0.824774
H	2.792954	1.514001	0.927465

Sum of electronic and zero-point Energies = -512.241193 au.
Sum of electronic and thermal Free Energies = -512.281160 au.

12

N	-3.216071	-0.783040	-0.199780
C	-2.351448	0.370221	0.057323
C	-0.934889	-0.085320	-0.022923
C	0.123318	0.698539	0.160589
C	1.493345	0.159422	0.062434
C	-0.016533	2.160723	0.437205
N	-4.407053	-0.554452	-0.161866
N	-5.519783	-0.443067	-0.149217
C	1.782460	-1.162467	0.387075
C	3.065311	-1.657113	0.275345
C	4.094636	-0.839502	-0.155120
C	3.826474	0.479122	-0.465312
C	2.541512	0.974224	-0.350972
H	-2.555083	1.149422	-0.678274
H	-2.576622	0.784468	1.041346
H	-0.804622	-1.127029	-0.273363
H	-1.020841	2.419072	0.755466
H	0.676287	2.479126	1.211813
H	0.203387	2.750507	-0.451736
H	0.997374	-1.804581	0.752499
H	3.265201	-2.683456	0.538867
H	5.097731	-1.225445	-0.237635
H	4.620448	1.128874	-0.797322
H	2.351975	2.005865	-0.599482

Sum of electronic and zero-point Energies = -551.511466 au.
Sum of electronic and thermal Free Energies = -551.553171 au.

TS-6a

1 imaginary frequency : -373.2 cm^{-1}

C	0.949933	0.239388	0.001293
C	0.039980	1.065156	-0.652867
C	2.171674	-0.209363	-0.716679
C	-1.134841	1.471786	-0.073336
C	1.007323	0.154839	1.489130
H	0.146782	1.161646	-1.723146
H	2.032578	-0.199407	-1.791866
H	2.995237	0.459909	-0.467546
H	2.455920	-1.208153	-0.402927
H	-1.858109	2.016323	-0.656914
H	-1.236758	1.559143	0.993816
H	1.582723	0.999034	1.868632
H	0.028248	0.178054	1.954132
H	1.509339	-0.756097	1.795272
N	-0.219290	-1.520455	-0.217798
N	-1.281207	-1.064562	-0.078174
N	-2.193842	-0.349452	0.031015

Sum of electronic and zero-point Energies = -359.832707 au.
Sum of electronic and thermal Free Energies = -359.864810 au.

TS-8

1 imaginary frequency : -366.2 cm^{-1}

C	-3.493824	-0.140564	-0.283284
C	-3.015013	0.952312	0.412386
C	-1.667980	1.049595	0.698125
C	-0.787855	0.050511	0.305298
C	-1.277050	-1.039955	-0.403730
C	-2.621109	-1.134008	-0.693677
C	0.624040	0.185475	0.650379
C	1.494191	-0.885170	0.831951
C	2.800748	-0.650585	1.157117
H	-4.544246	-0.217634	-0.513085
H	-3.689239	1.731501	0.728516
H	-1.289781	1.905293	1.235346
H	-0.603027	-1.808563	-0.745296
H	-2.991244	-1.981402	-1.247555
H	0.886936	1.111850	1.138344
H	1.197935	-1.871604	0.511120
H	3.506335	-1.460294	1.232505
H	3.089233	0.283103	1.611469
N	1.401720	0.952193	-1.123295
N	2.514464	0.615027	-1.027097
N	3.526705	0.144507	-0.706573

Sum of electronic and zero-point Energies = -512.197275 au.
Sum of electronic and thermal Free Energies = -512.233836 au.

TS-12

1 imaginary frequency : -345.9 cm-1

C	-3.565006	-0.488680	0.001566
C	-3.183682	0.830610	-0.139133
C	-1.845909	1.175935	-0.099504
C	-0.875385	0.205167	0.102732
C	-1.268905	-1.120926	0.236136
C	-2.601666	-1.465831	0.183260
C	0.550608	0.571663	0.201354
C	1.308853	-0.014989	1.221147
C	0.984505	1.845316	-0.444111
C	2.646336	0.214257	1.377394
H	-4.608126	-0.757812	-0.039298
H	-3.927932	1.596923	-0.283866
H	-1.563314	2.209818	-0.211057
H	-0.515944	-1.885446	0.343139
H	-2.890966	-2.500317	0.273576
H	0.861478	-0.835000	1.761165
H	2.056079	1.873952	-0.602197
H	0.498061	1.972969	-1.403827
H	0.717798	2.687578	0.193030
H	3.200918	-0.341820	2.114619
H	3.123132	1.102757	1.004037
N	1.322937	-0.660019	-1.348726
N	2.422206	-0.781177	-0.980578
N	3.419189	-0.792910	-0.384177

Sum of electronic and zero-point Energies = -551.470094 au.

Sum of electronic and thermal Free Energies = -551.506832 au.

6a rearr

N	-0.466785	-0.834309	-0.000043
N	-1.665196	-0.654938	-0.000012
N	-2.782575	-0.587993	0.000010
C	0.360474	0.392829	-0.000001
C	0.068257	1.207939	-1.249116
C	0.068271	1.207867	1.249164
C	1.791352	-0.042243	-0.000012
C	2.228352	-1.286503	-0.000007
H	0.708786	2.084724	-1.283232
H	0.243390	0.616068	-2.142194
H	-0.964587	1.550576	-1.251119
H	0.708829	2.084628	1.283331
H	-0.964561	1.550537	1.251188
H	0.243391	0.615938	2.142206
H	2.494482	0.780000	-0.000019
H	3.285602	-1.499340	-0.000012
H	1.546328	-2.121782	0.000001

Sum of electronic and zero-point Energies = -359.869885 au.
Sum of electronic and thermal Free Energies = -359.903369 au.

8 rearr

C	-3.066899	-0.294305	-0.301301
C	-2.630641	0.402973	0.807015
C	-1.281942	0.436904	1.115340
C	-0.365043	-0.229131	0.321915
C	-0.809009	-0.924748	-0.792860
C	-2.152711	-0.956798	-1.102724
C	1.108088	-0.156881	0.638212
C	1.751286	-1.502280	0.651409
N	1.817245	0.691381	-0.335082
N	1.408309	1.832884	-0.403270
N	1.095205	2.897517	-0.533942
C	2.753955	-1.877812	-0.118794
H	-4.117043	-0.322790	-0.543568
H	-3.337737	0.922645	1.433249
H	-0.939814	0.982538	1.981637
H	-0.094052	-1.441502	-1.414475
H	-2.490346	-1.501224	-1.969886
H	1.217132	0.287742	1.629058
H	1.318222	-2.190533	1.363247
H	3.160336	-2.874079	-0.047953
H	3.195488	-1.202807	-0.834530

Sum of electronic and zero-point Energies = -512.233128 au.
Sum of electronic and thermal Free Energies = -512.270931 au.

12 rearr

C	2.389673	-2.071887	-0.564356
C	1.551402	-1.612635	0.344225
C	1.040856	-0.206530	0.441310
C	-0.466957	-0.207269	0.234635
C	1.467920	0.387267	1.771758
C	-0.967057	-0.680891	-0.971798
C	-2.322975	-0.690614	-1.217541
C	-3.205601	-0.230341	-0.255060
C	-2.718331	0.240150	0.945856
C	-1.354767	0.253962	1.189889
N	1.682486	0.561111	-0.653692
N	1.291703	1.705179	-0.766589
N	0.989618	2.766533	-0.944631
H	2.704070	-3.103375	-0.549208
H	2.783588	-1.437082	-1.341719
H	1.166575	-2.266584	1.114363
H	1.119131	1.411884	1.877443
H	1.076226	-0.195299	2.600064
H	2.551280	0.382155	1.830616
H	-0.278397	-1.042009	-1.720175
H	-2.694172	-1.059736	-2.160100
H	-4.266830	-0.238772	-0.444545
H	-3.397423	0.602451	1.700796
H	-0.995671	0.629333	2.133341

Sum of electronic and zero-point Energies = -551.505665 au.
Sum of electronic and thermal Free Energies = -551.543911 au.