Supporting information for:

One-step synthesis of conjugated enynenitriles from bromocyanoacetylene

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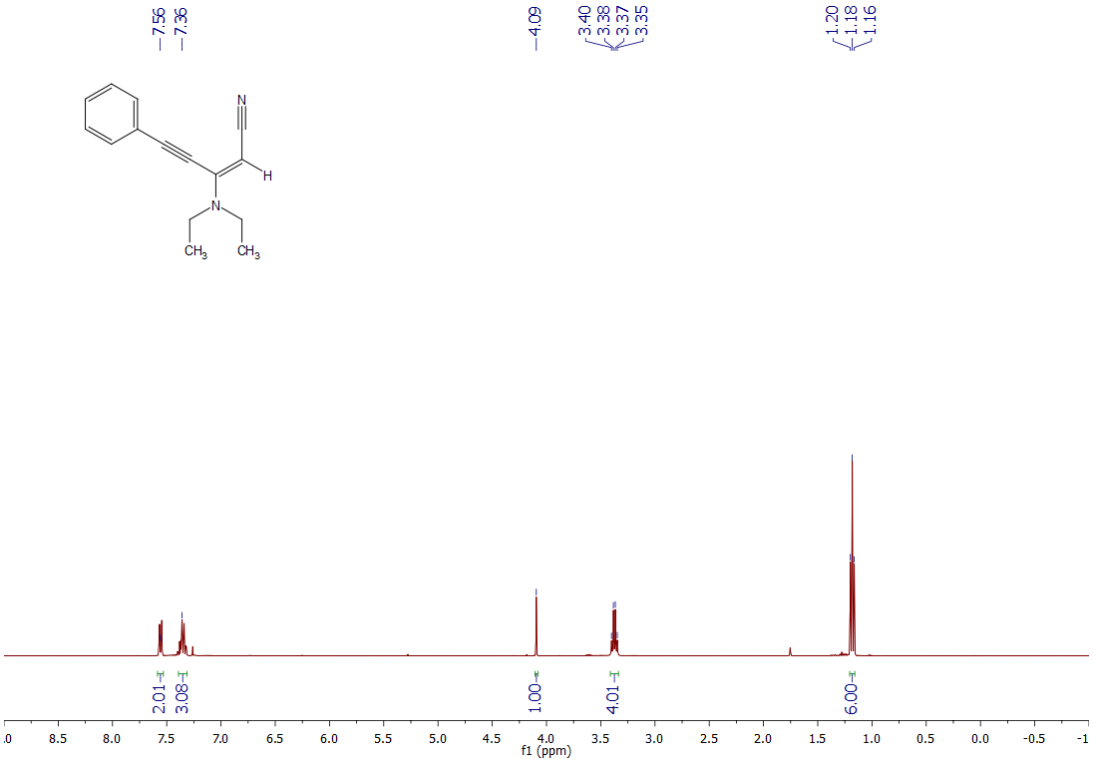
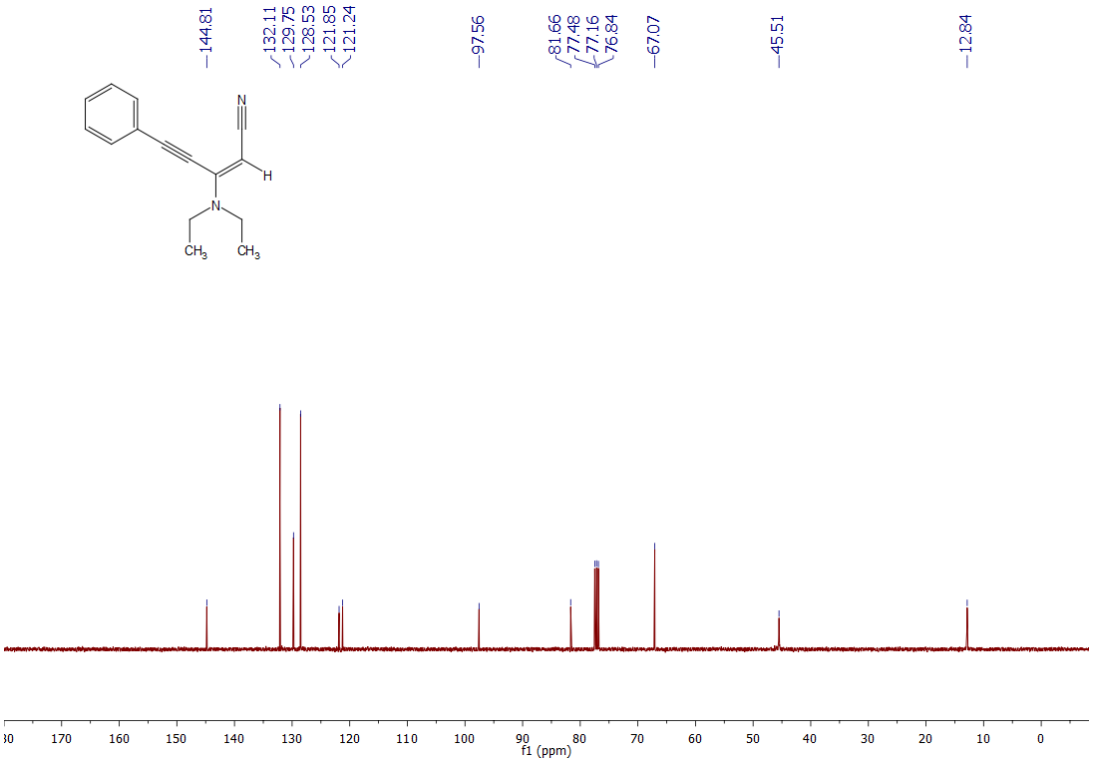
NMR Section

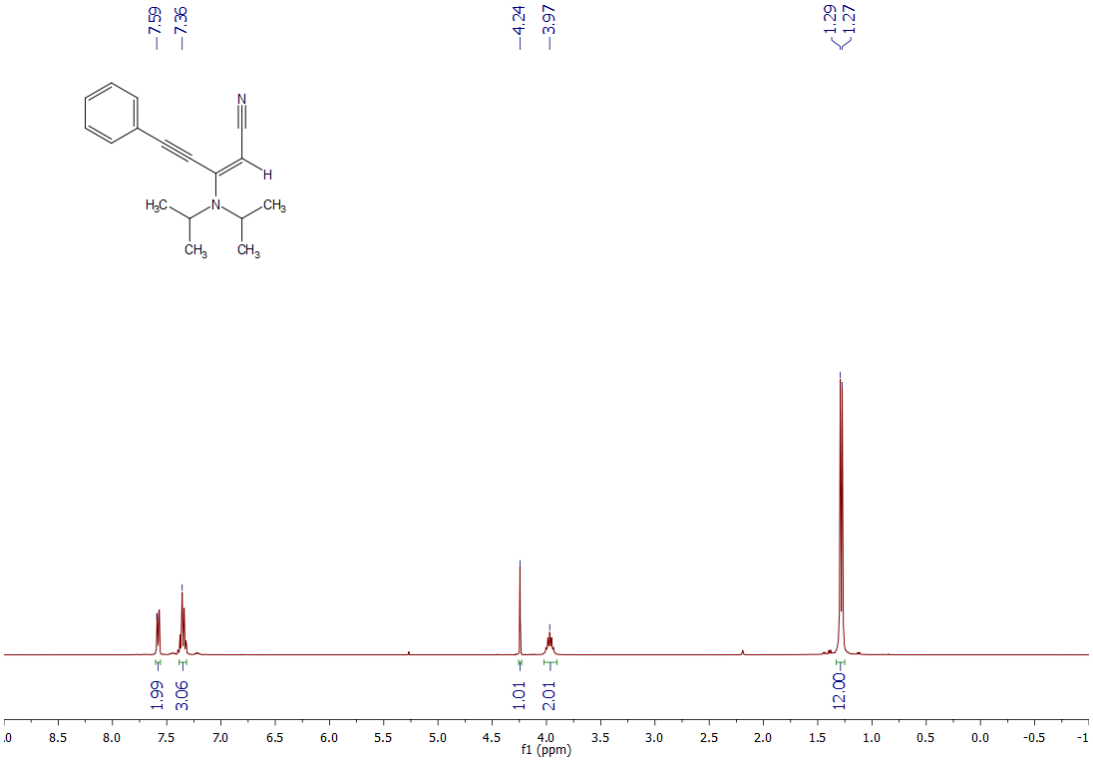
^{1}H spectrum of compound **5** ($CDCl_3$, 400 MHz)



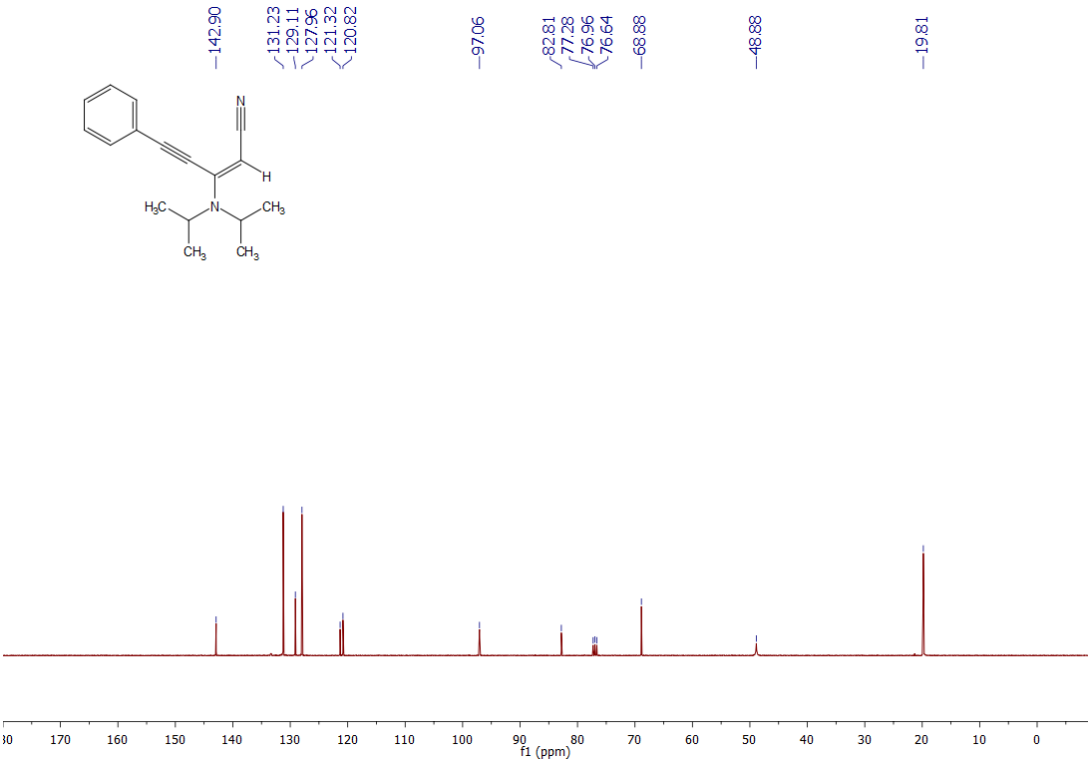
^{13}C spectrum of compound **5** ($CDCl_3$, 125 MHz)



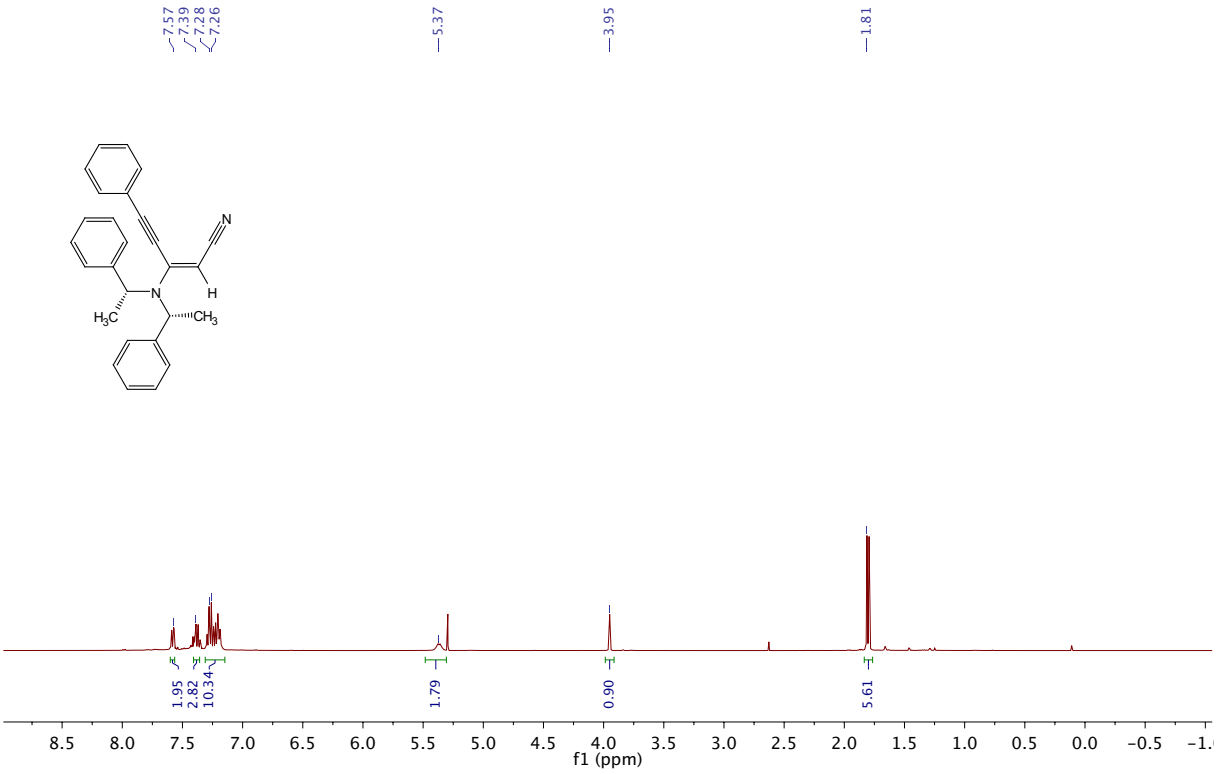
^{1}H spectrum of compound **6** ($CDCl_3$, 400 MHz)



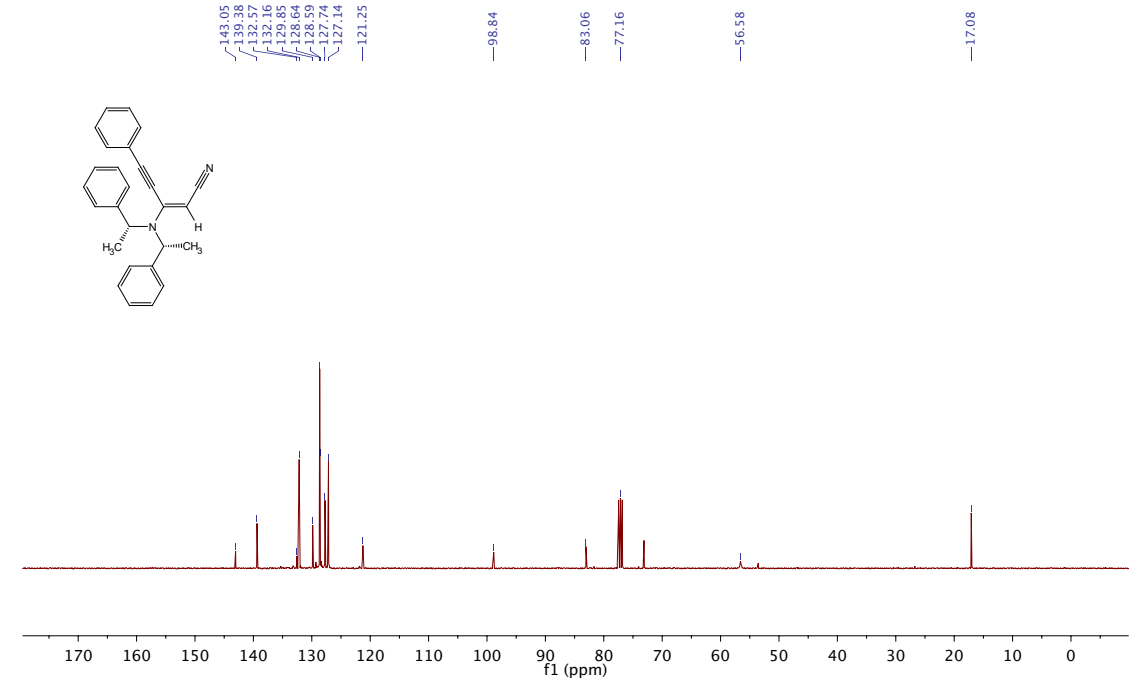
^{13}C spectrum of compound **6** ($CDCl_3$, 125 MHz)



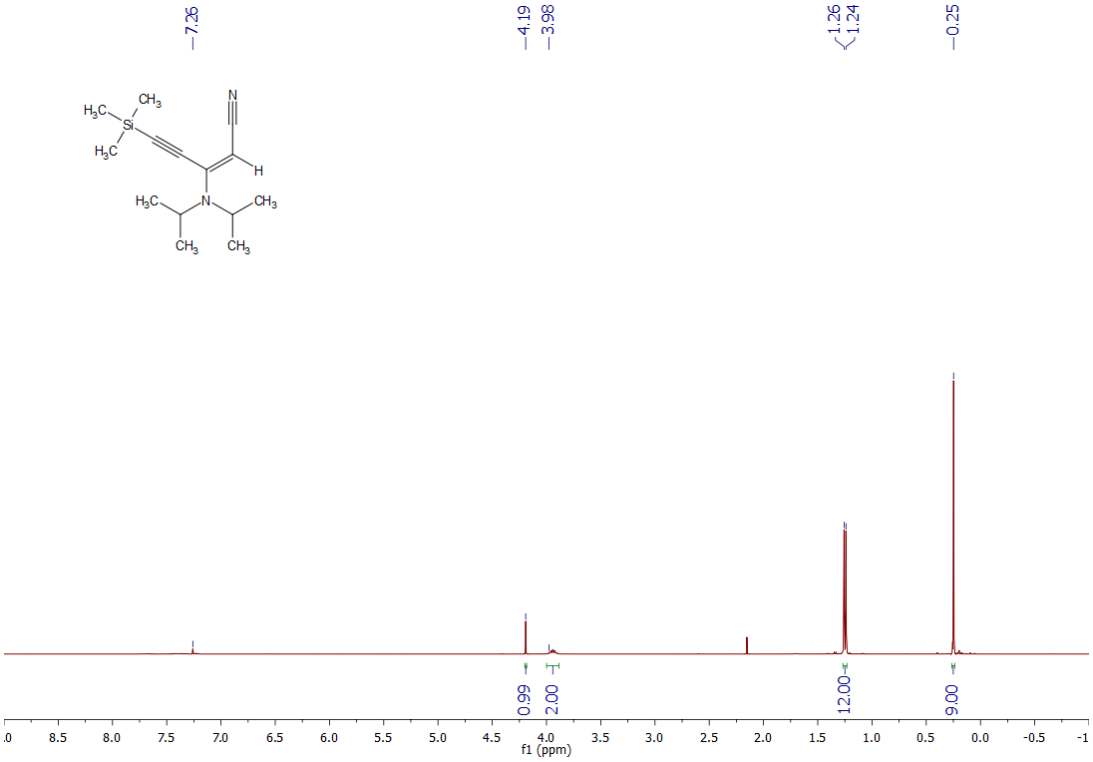
^{1}H spectrum of compound **7** ($CDCl_3$, 400 MHz)



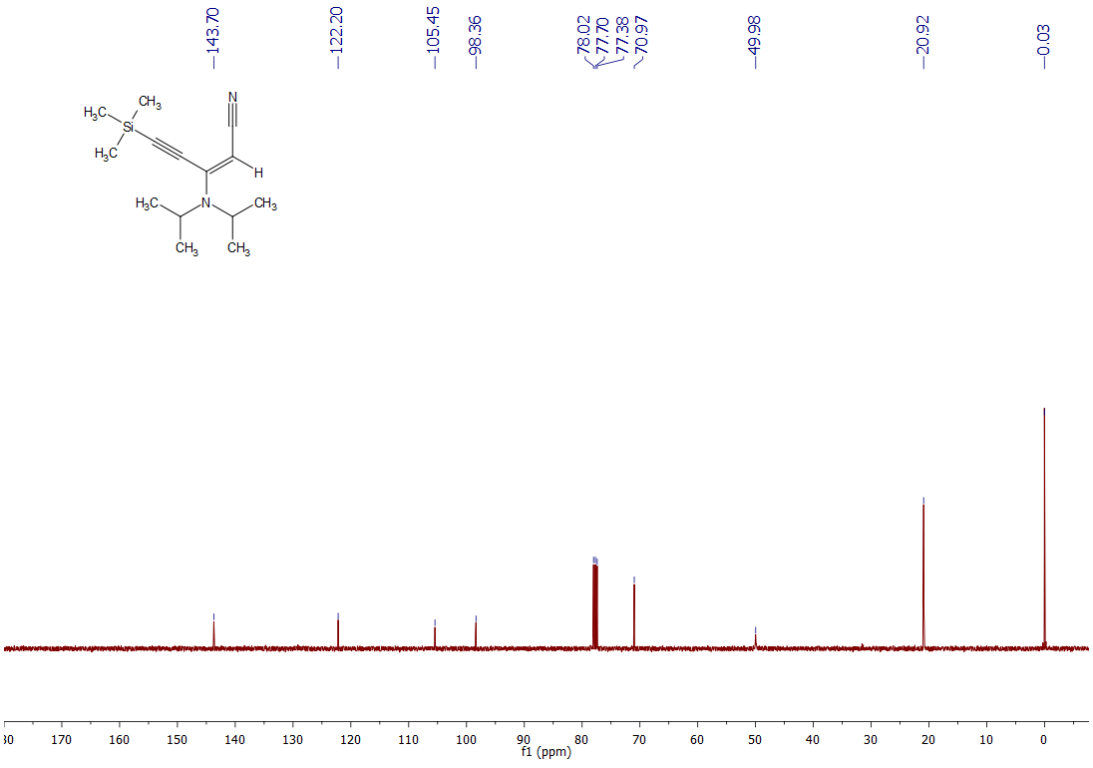
^{13}C{^{1}H} spectrum of compound **7** ($CDCl_3$, 125 MHz)



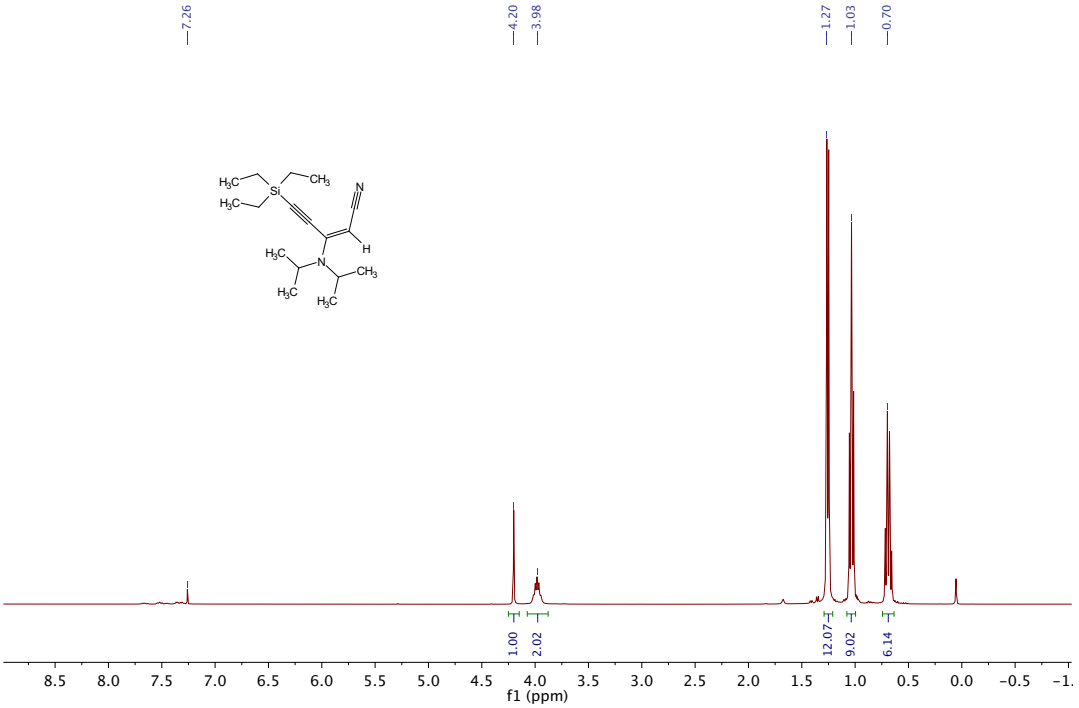
^{1}H spectrum of compound **8** ($CDCl_3$, 400 MHz)



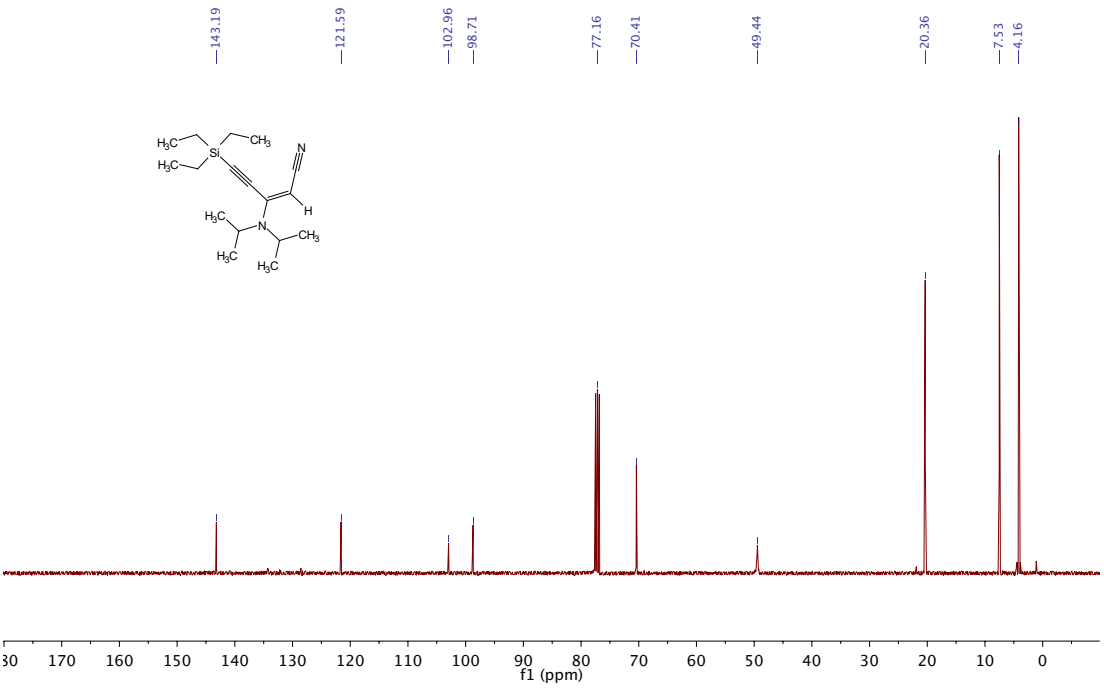
^{13}C spectrum of compound **8** ($CDCl_3$, 125 MHz)



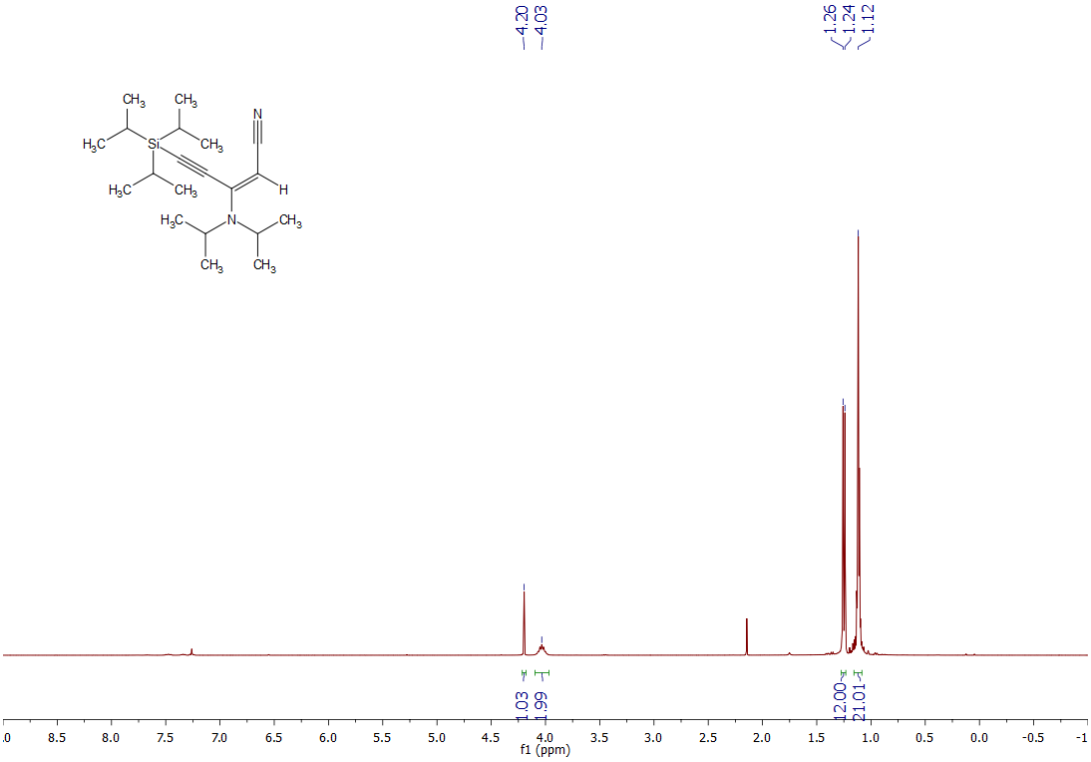
^{1}H spectrum of compound **9** ($CDCl_3$, 400 MHz)



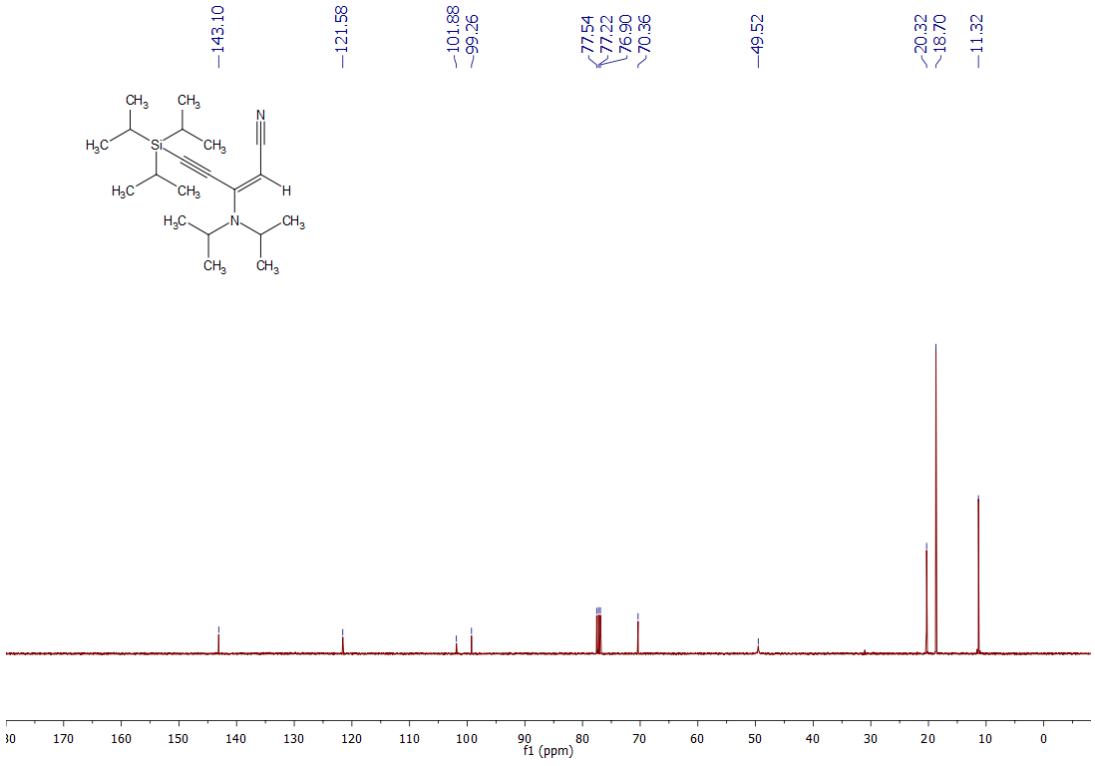
^{13}C spectrum of compound **9** ($CDCl_3$, 125 MHz)



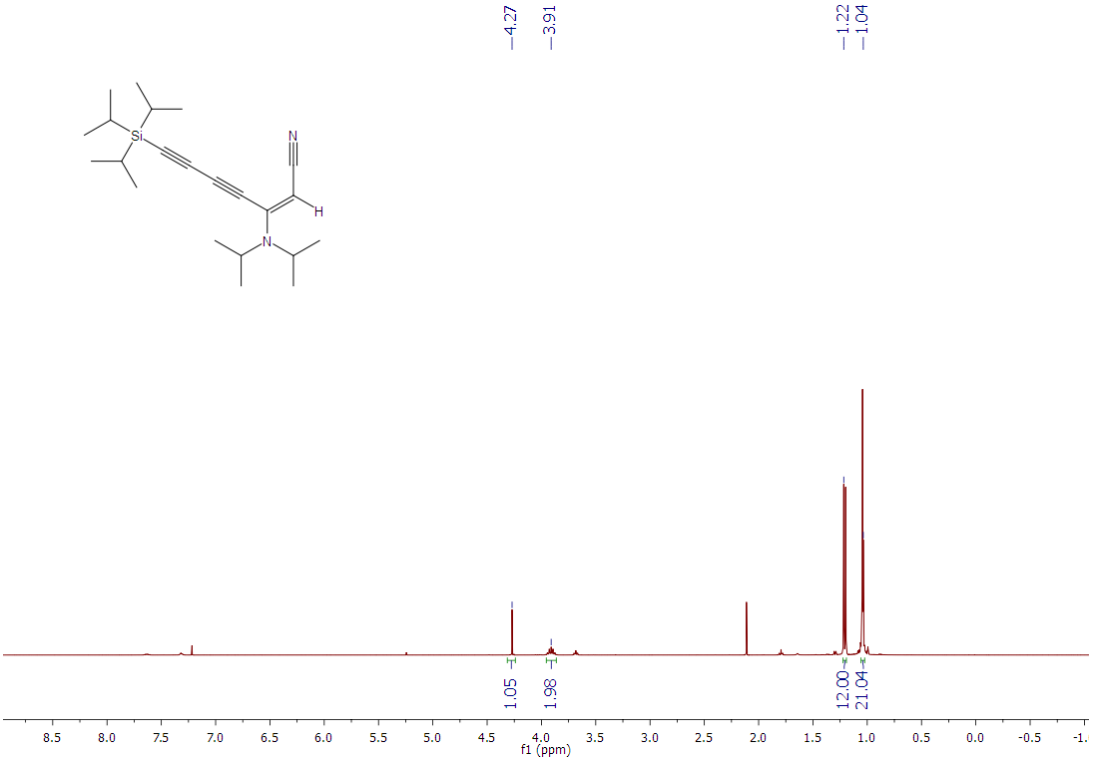
^{1}H spectrum of compound **10** ($CDCl_3$, 400 MHz)



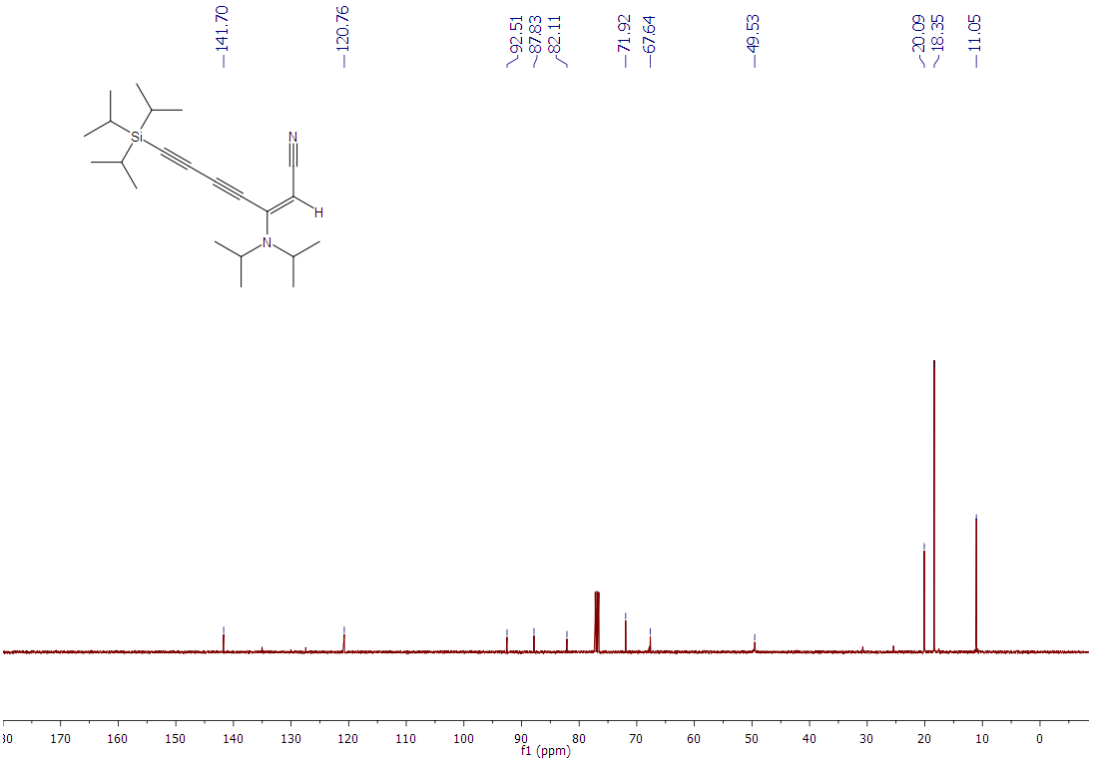
^{13}C spectrum of compound **10** ($CDCl_3$, 125 MHz)



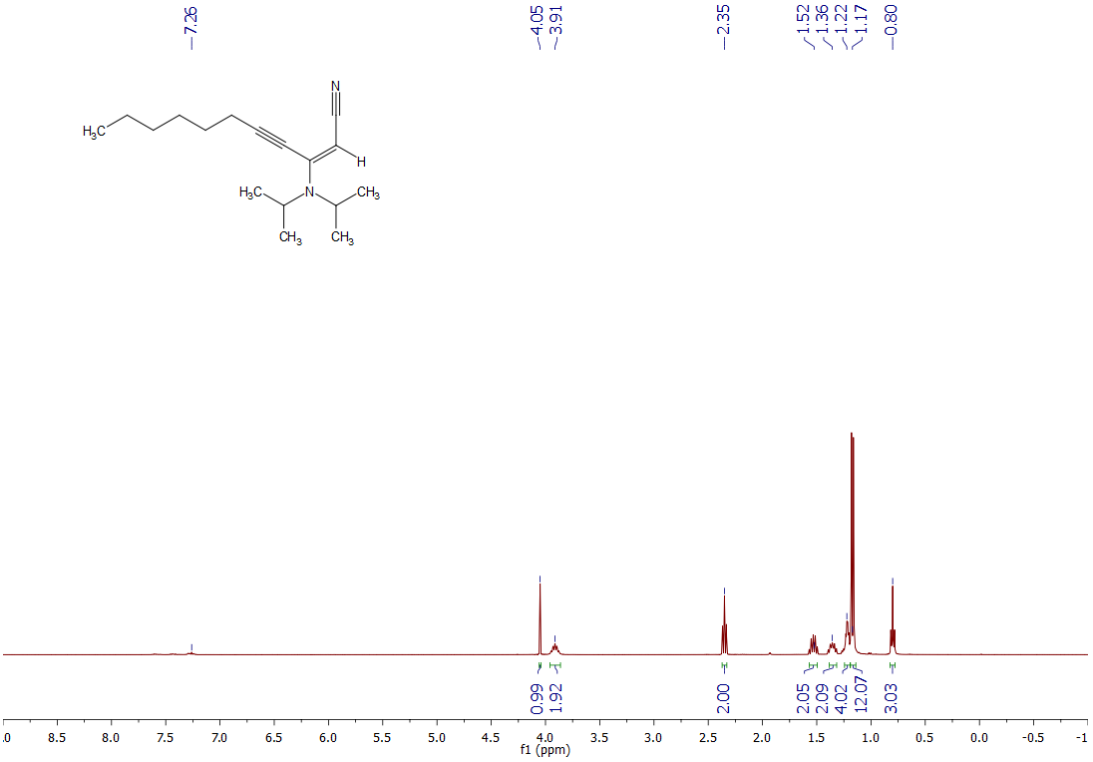
^{1}H spectrum of compound **11** ($CDCl_3$, 400 MHz)



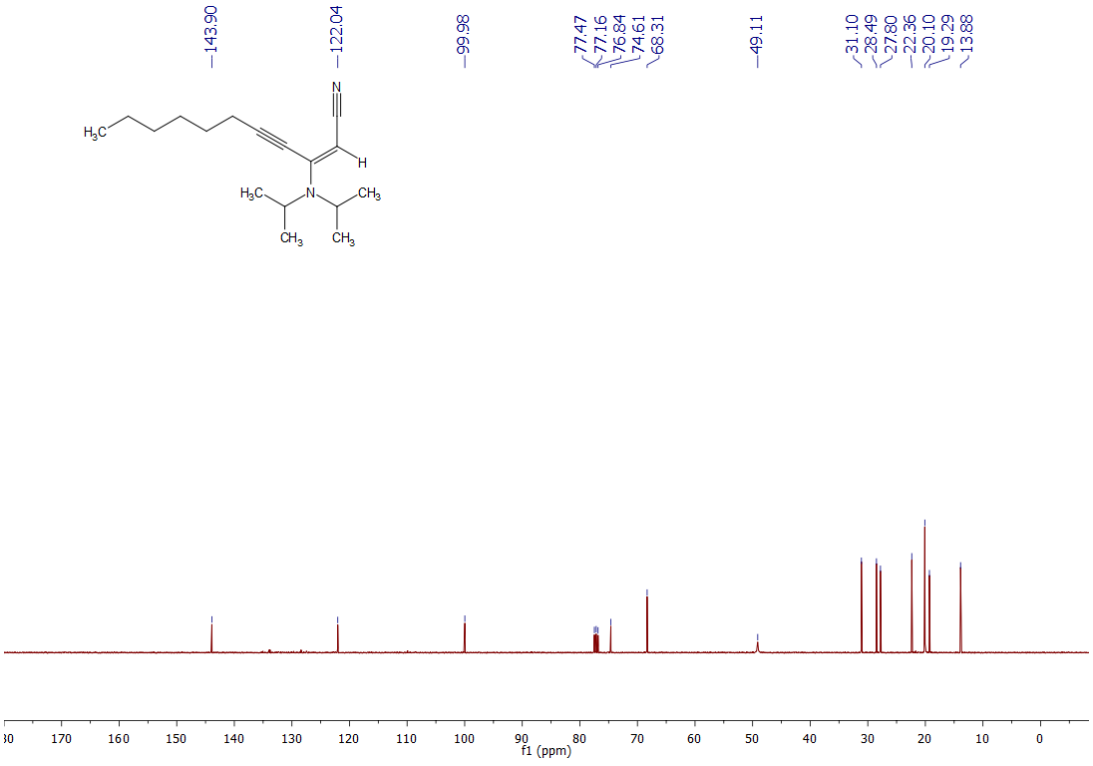
^{13}C spectrum of compound **11** ($CDCl_3$, 125 MHz)



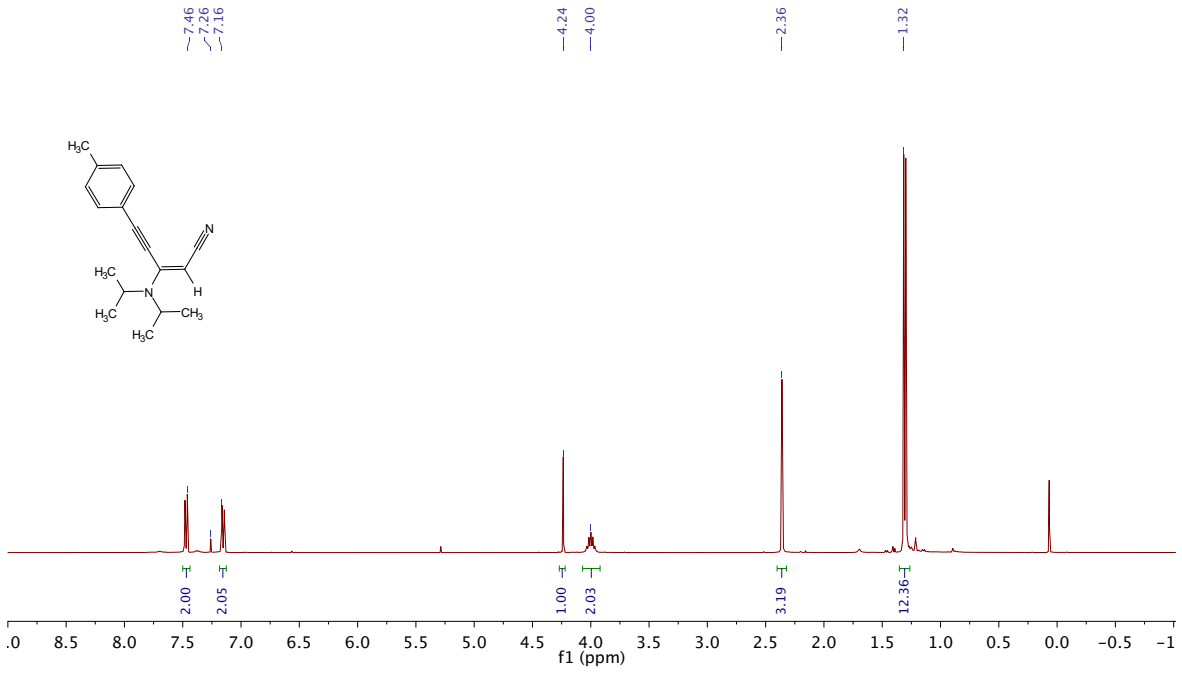
^{1}H spectrum of compound **12** ($CDCl_3$, 400 MHz)



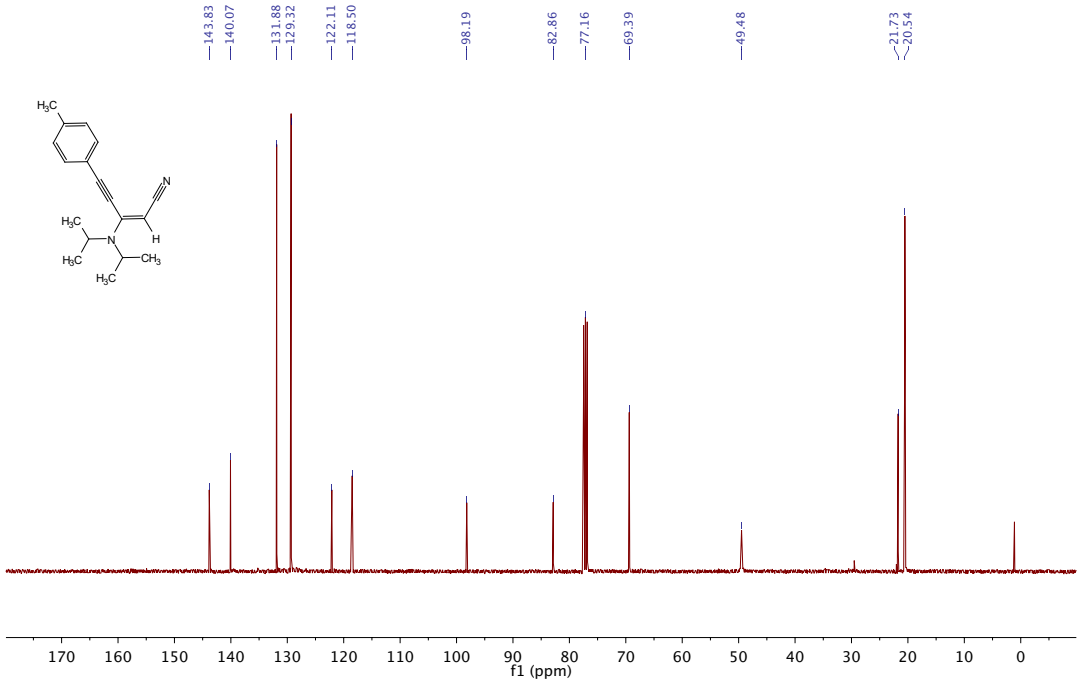
^{13}C spectrum of compound **12** ($CDCl_3$, 125 MHz)



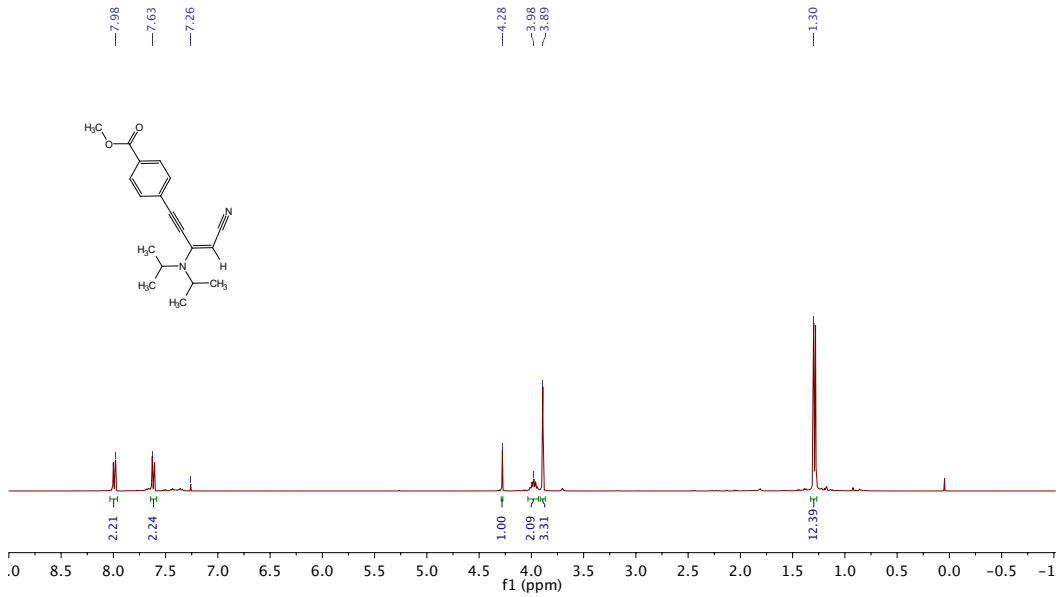
^{1}H spectrum of compound **14** ($CDCl_3$, 400 MHz)



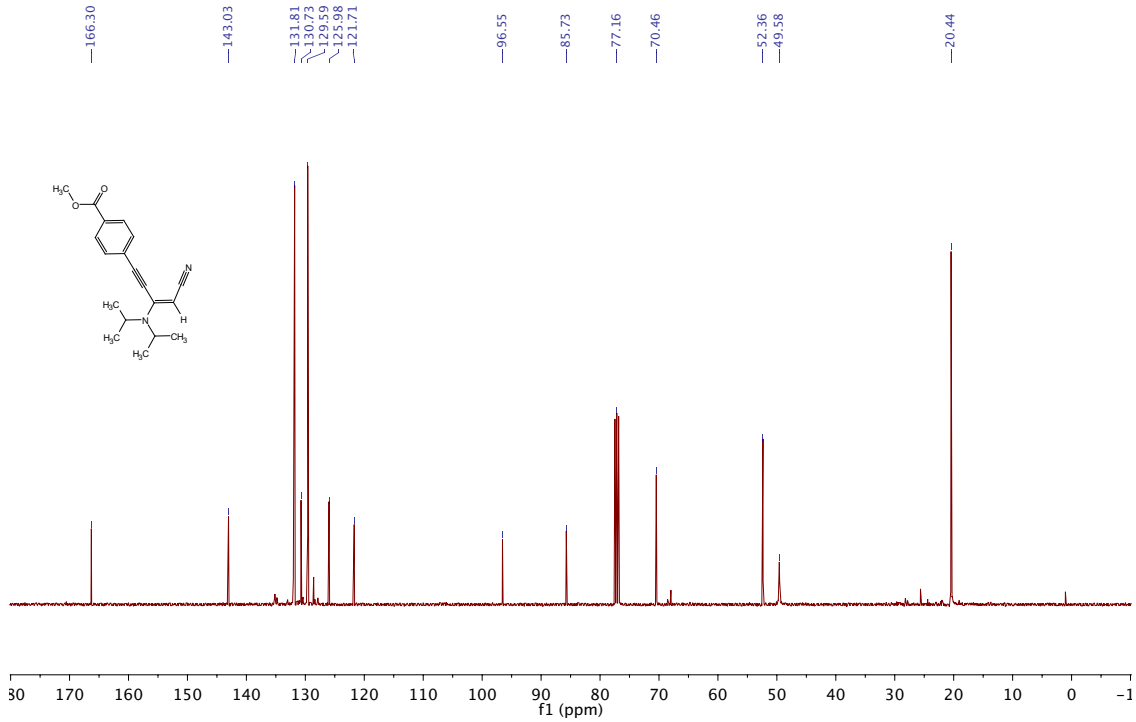
^{13}C spectrum of compound **14** ($CDCl_3$, 125 MHz)



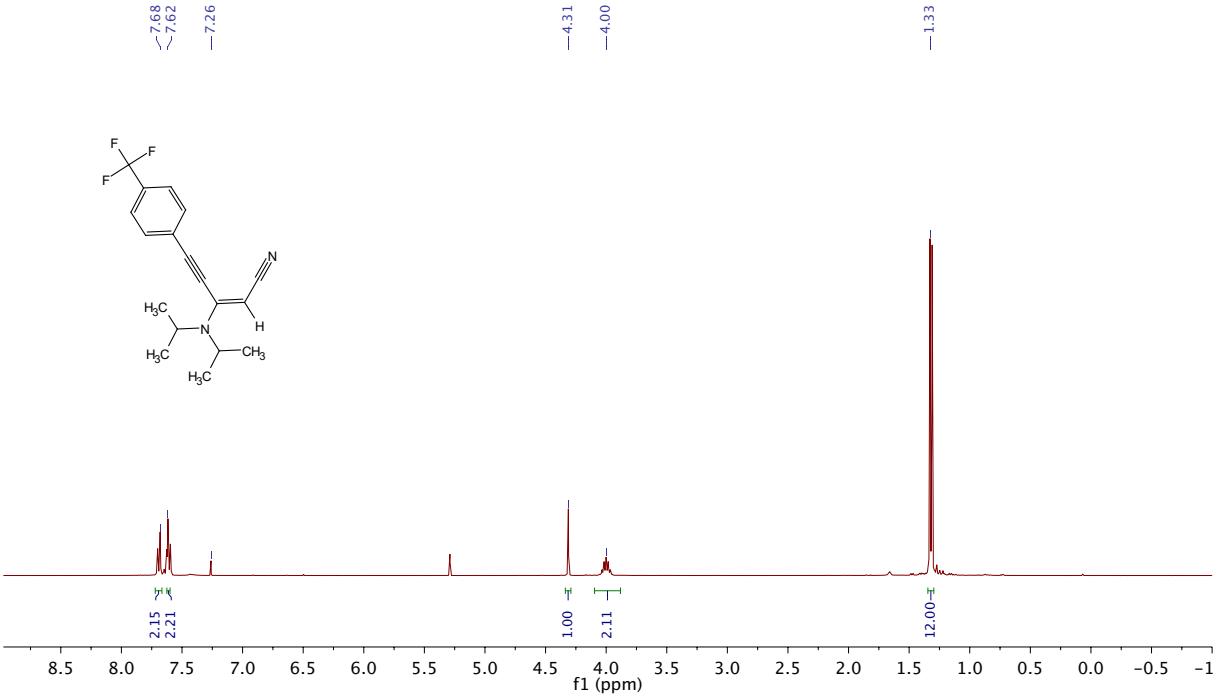
^{1}H spectrum of compound **17** ($CDCl_3$, 400 MHz)



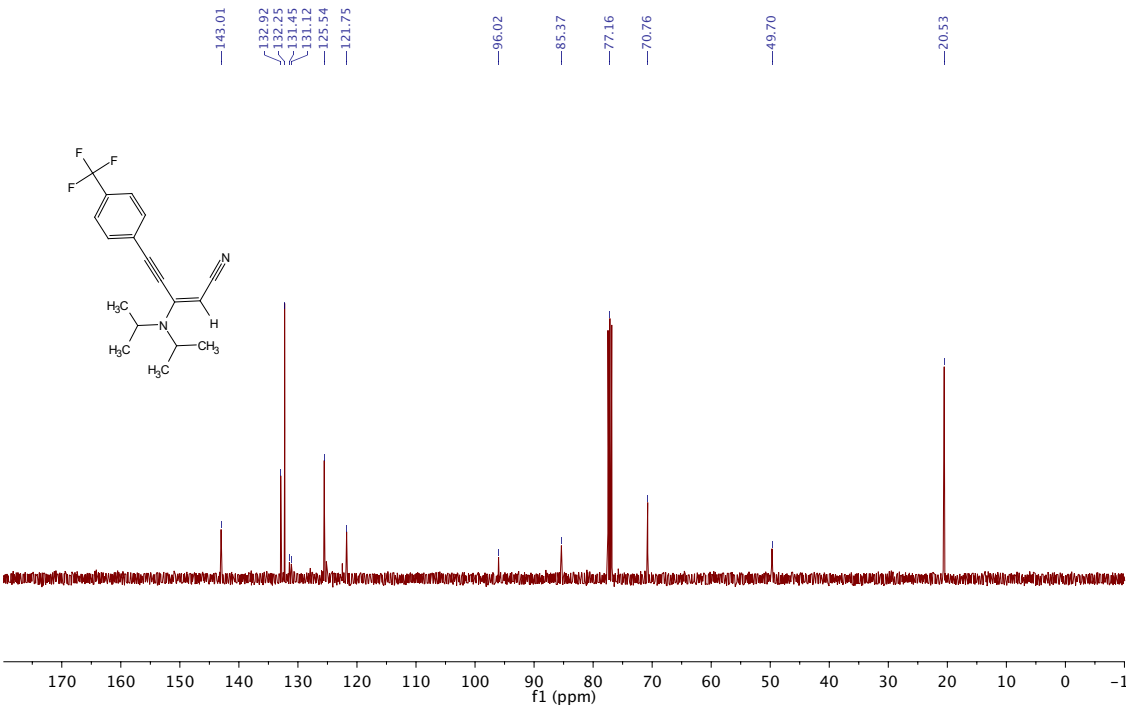
^{13}C spectrum of compound **17** ($CDCl_3$, 125 MHz)



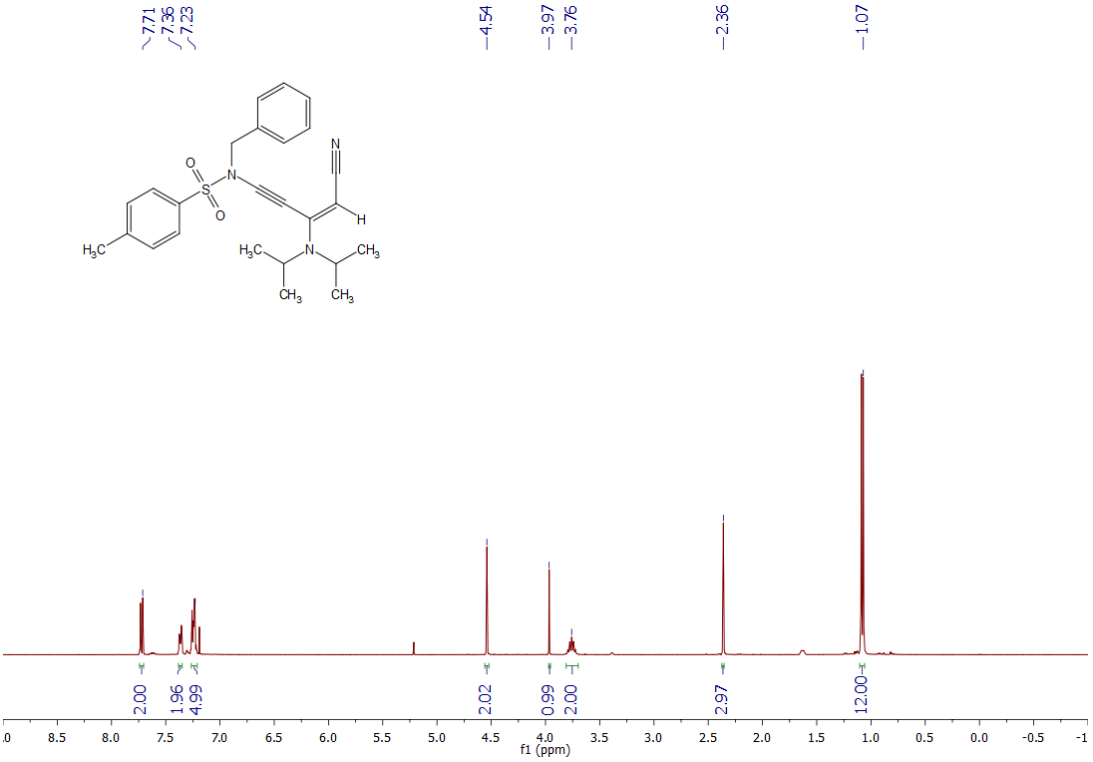
^{1}H spectrum of compound **18** ($CDCl_3$, 400 MHz)



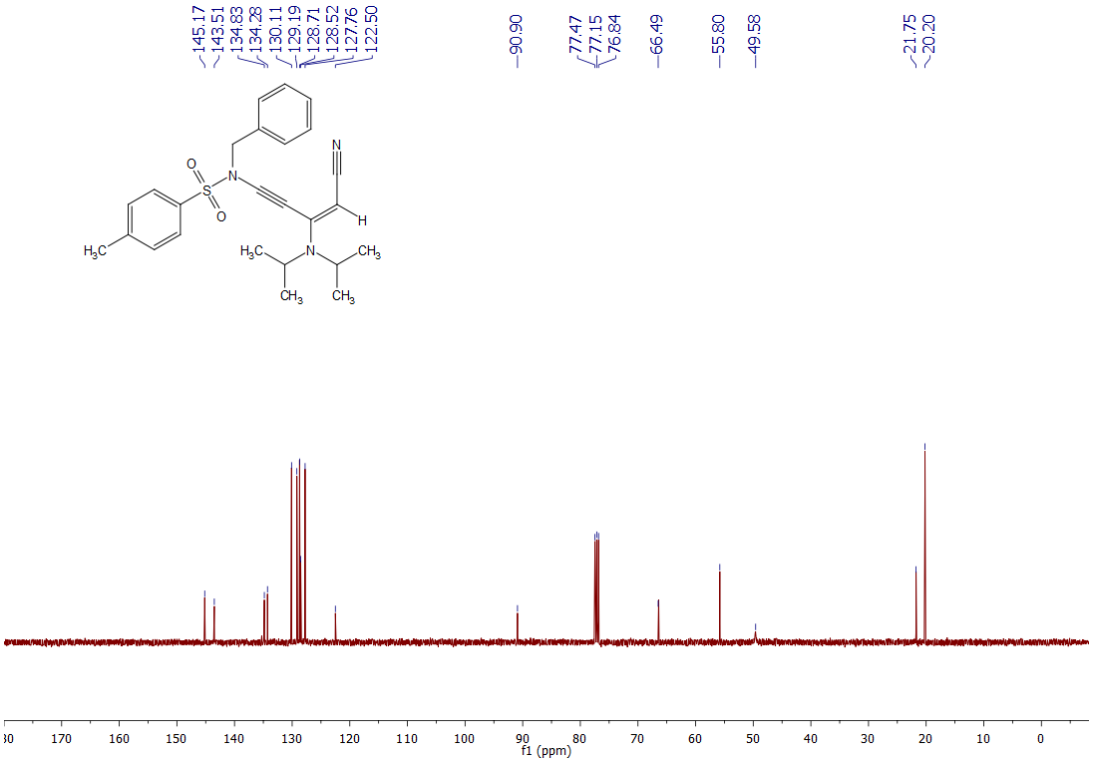
^{13}C spectrum of compound **18** ($CDCl_3$, 125 MHz)



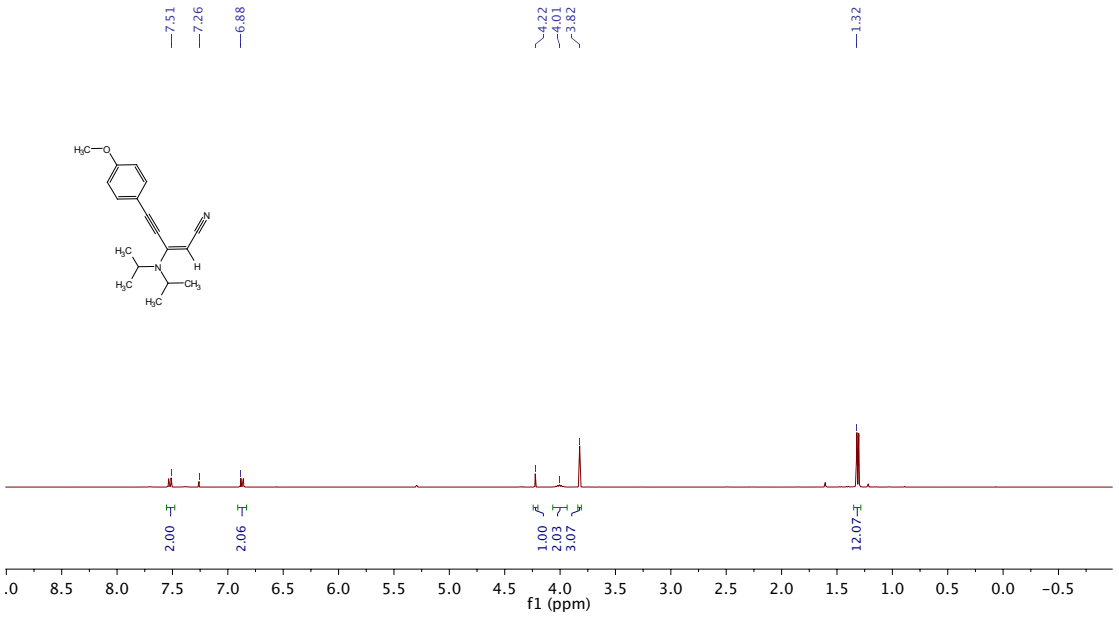
^{1}H spectrum of compound **20** ($CDCl_3$, 400 MHz)



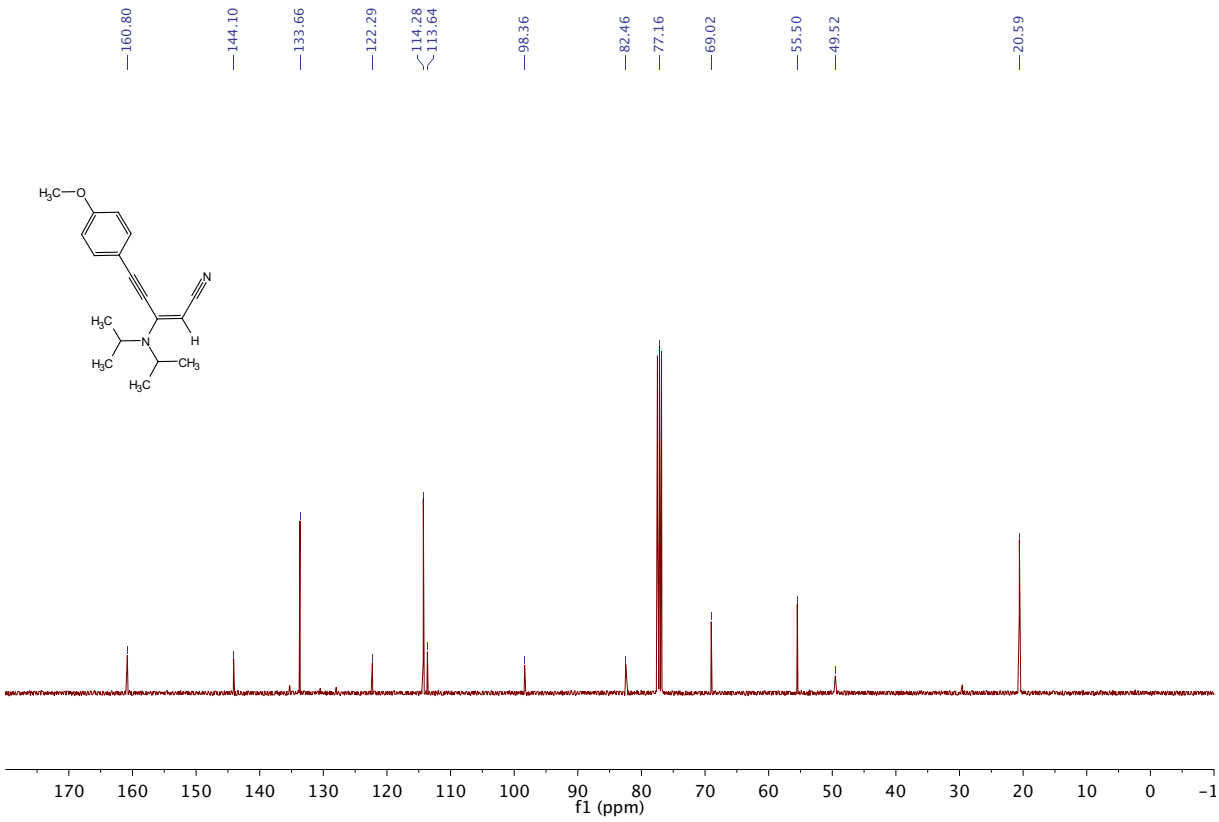
^{13}C spectrum of compound **20** ($CDCl_3$, 125 MHz)



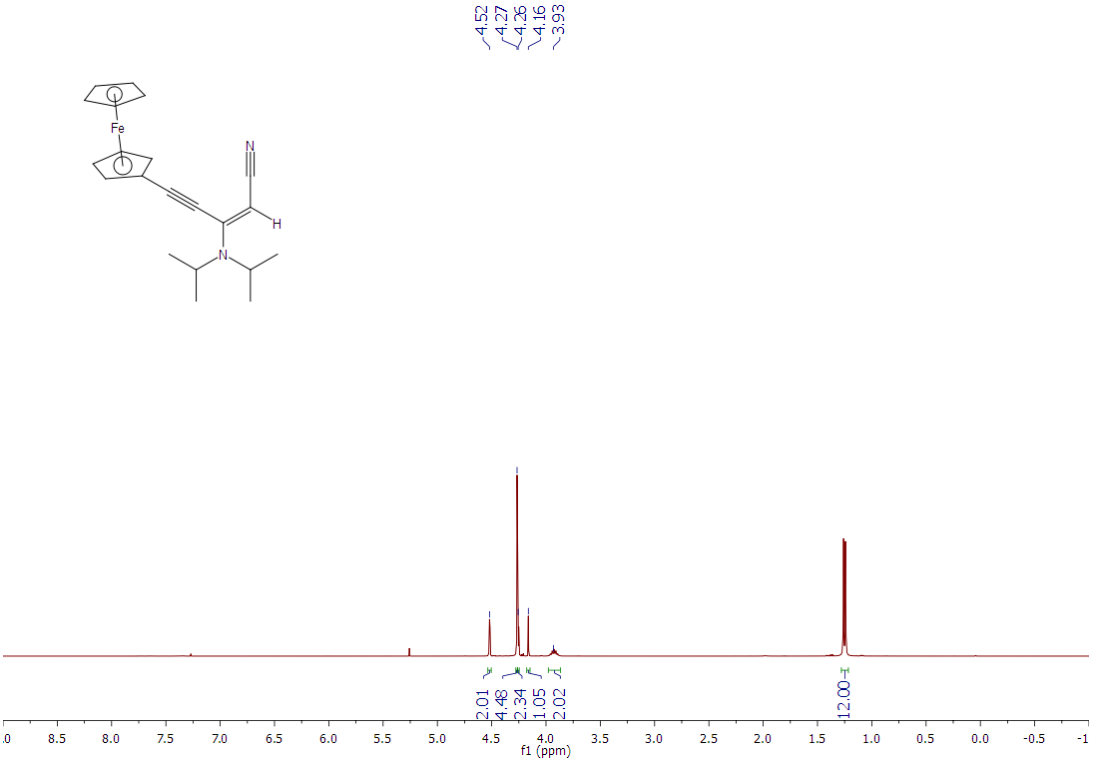
^{1}H spectrum of compound **21** ($CDCl_3$, 400 MHz)



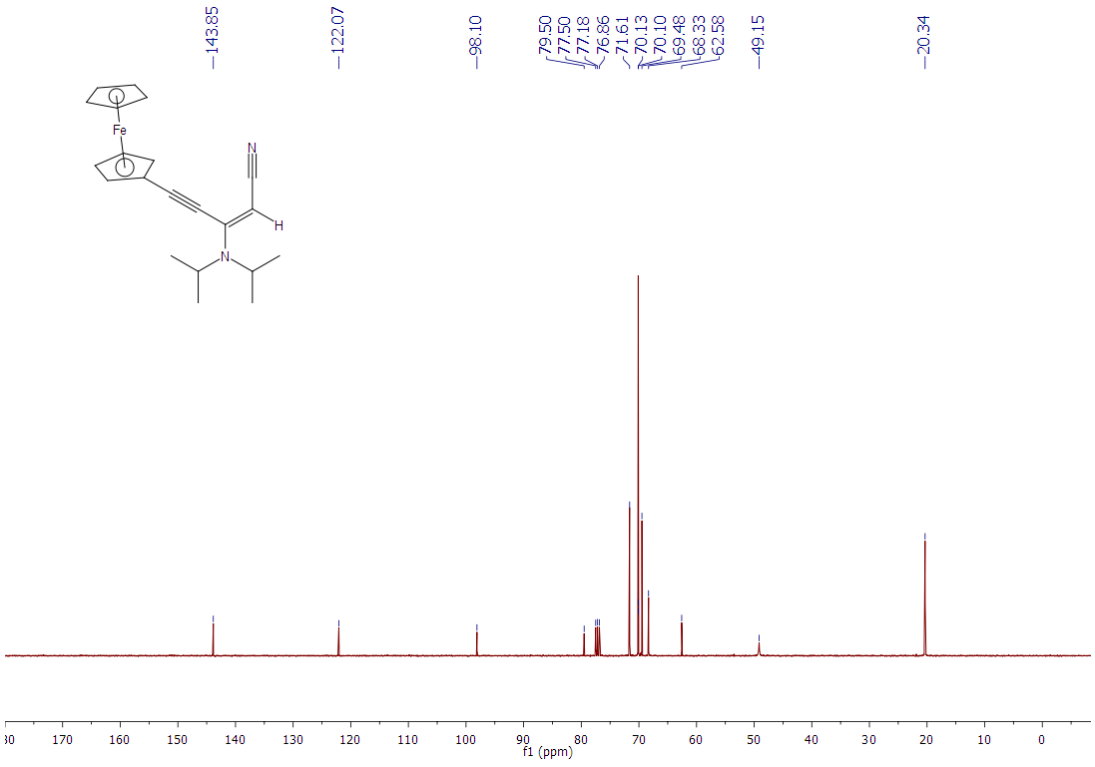
^{13}C spectrum of compound **21** ($CDCl_3$, 125 MHz)



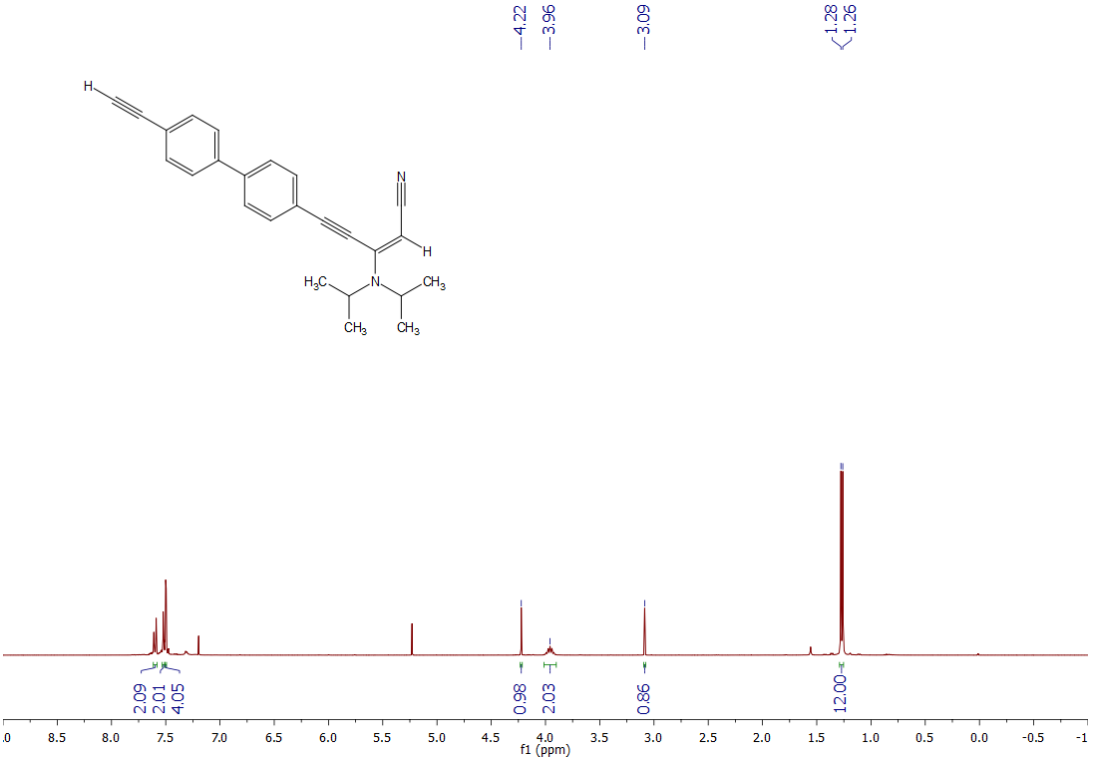
^{1}H spectrum of compound **22** ($CDCl_3$, 400 MHz)



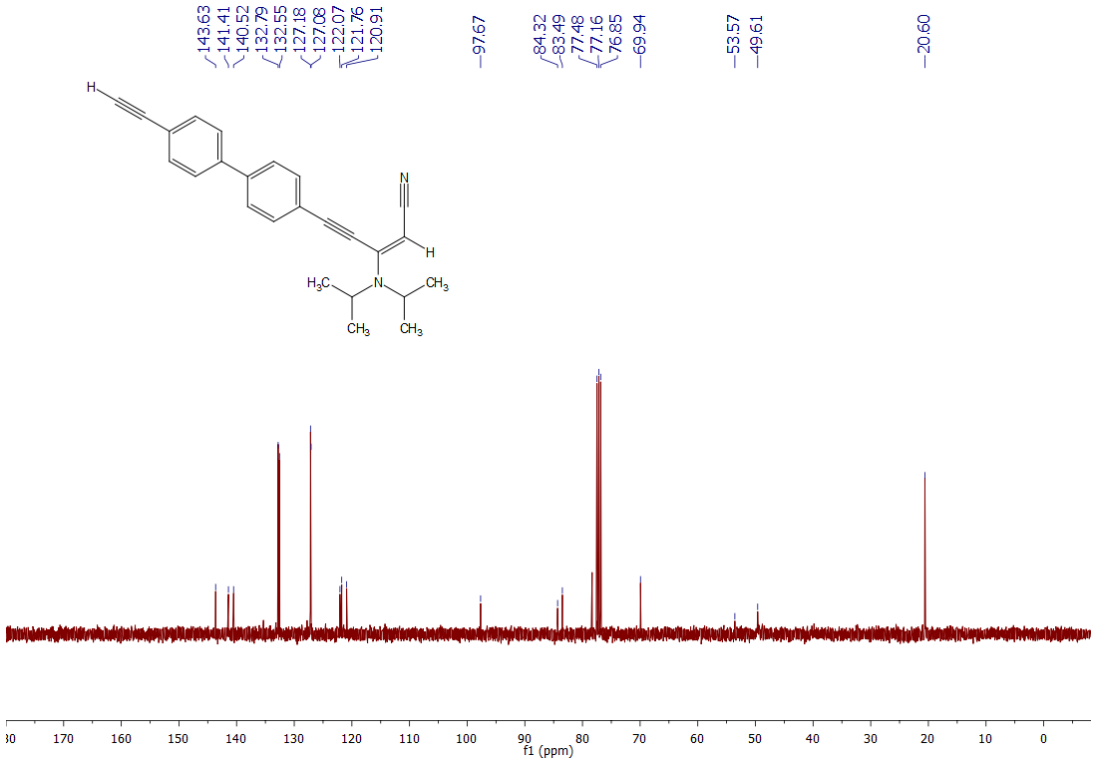
^{13}C spectrum of compound **22** ($CDCl_3$, 125 MHz)



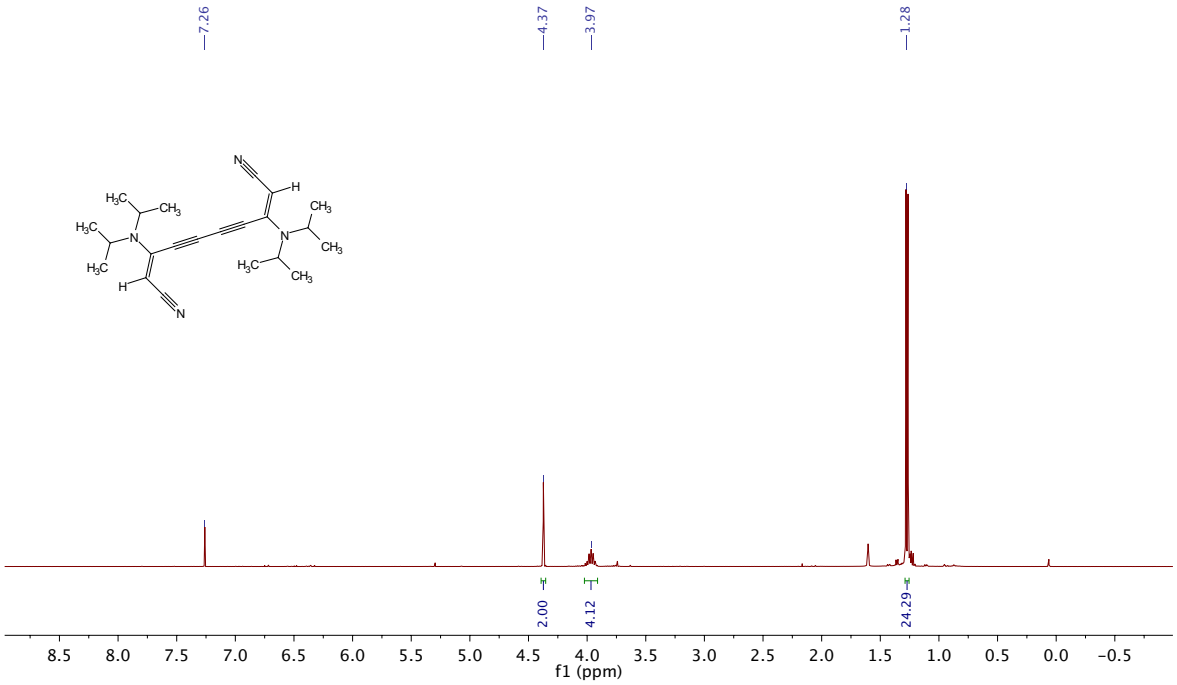
^{1}H spectrum of compound **23** ($CDCl_3$, 400 MHz)



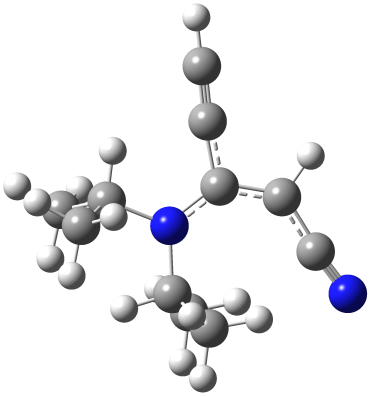
^{13}C spectrum of compound **23** ($CDCl_3$, 125 MHz)



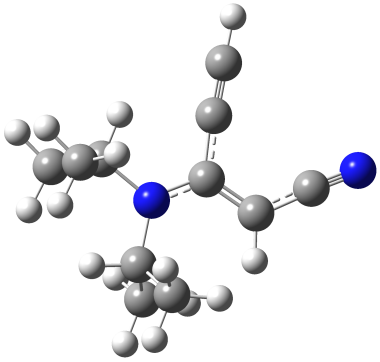
^{1}H spectrum of compound **24** ($CDCl_3$, 400 MHz)



Theoretical calculations of E/Z conformers of enynes systems



Model Z



Model E

Gas-Phase

	Model Z	Model E	Differences (kj/mol)
B3LYP/6-31+g(d,p)			
Enthalpy	-537.977805 (a.u.)	-537.982753 (a.u.)	13.0
Free energy	-538.035818	-538.041625	15.2
High-level (G4MP2)			
Enthalpy	-537.331187 (a.u.)	-537.335201	10.5
Free energy	-537.335201	-537.394459	11.6
In THF (B3lyp/6-31+G(d,p))			
Enthalpy	-537.987174	-537.995100	20.8
Free energy	-538.045144	-538.054451	24.4

Model Z – B3LYP/6-31+G(d,p) calculations

Optimized geometry (cartesian coordinates in Å)

6	-3.320832	0.597983	-0.123011
6	-2.550485	1.461513	0.641866
7	-4.611898	0.153251	0.016322
6	-5.185513	-0.791826	-0.981815
6	-6.366896	-0.176319	-1.748087
6	-5.535205	-2.151216	-0.356130
1	-4.395608	-0.971771	-1.709105
1	-6.077281	0.769414	-2.215699
1	-6.685303	-0.863968	-2.538740
1	-7.235364	0.007715	-1.106886
1	-4.665165	-2.583589	0.146895
1	-6.354039	-2.083935	0.367903
1	-5.852331	-2.843142	-1.143558
6	-5.529841	0.544056	1.118638
6	-5.925949	2.030690	1.085604
6	-5.082637	0.028301	2.497806
1	-6.446204	-0.003520	0.889475
1	-6.313856	2.297942	0.097965
1	-6.720892	2.200631	1.819943
1	-5.107332	2.704696	1.332884
1	-4.903874	-1.050544	2.459536
1	-4.186040	0.517231	2.875464
1	-5.884149	0.214157	3.221066
6	-2.581747	0.104014	-1.264019
6	-1.889181	-0.257746	-2.189654
1	-1.285663	-0.581935	-3.007223
6	-2.819076	2.182204	1.823484
7	-2.939414	2.818652	2.797391
1	-1.545295	1.621073	0.268761

Enthalpy = -537.977805 hartrees
Free energy = -538.035818 hartrees

Model E – B3LYP/6-31+G(d,p) calculations
Optimized geometry (cartesian coordinates in Å)

6	0.765850	-0.111765	-0.123861
6	1.625667	0.964855	-0.213069
1	1.268036	1.981480	-0.161581
6	3.023334	0.820341	-0.376683
7	4.182423	0.762330	-0.511674
7	-0.599649	-0.037651	0.035103
6	-1.418693	-1.272941	0.118564
6	-2.405700	-1.393390	-1.053493
6	-2.110862	-1.417491	1.483291
1	-0.713583	-2.098891	0.028744
1	-1.881136	-1.332427	-2.011633
1	-2.915744	-2.361257	-1.005240
1	-3.178590	-0.617334	-1.032390
1	-1.380391	-1.373398	2.296547
1	-2.866247	-0.642811	1.654531
1	-2.620527	-2.385370	1.535146
6	-1.331547	1.248367	0.132570
6	-1.287656	2.082035	-1.161964
6	-0.990299	2.057478	1.398180
1	-2.374566	0.947209	0.250908
1	-1.598450	1.476924	-2.018369
1	-1.982020	2.924000	-1.070024
1	-0.300272	2.490467	-1.383865
1	-1.095939	1.435011	2.291237
1	0.021814	2.465647	1.394773
1	-1.686790	2.898251	1.484803
6	1.362853	-1.418132	-0.205807
6	1.943440	-2.477610	-0.283502
1	2.470002	-3.402735	-0.353648

Enthalpy = -537.982753 hartrees
Free energy = -538.041625 hartrees

Model Z – G4MP2 calculations
Optimized geometry (cartesian coordinates in Å)

6	-0.165294	1.091130	-0.000215
6	-1.490822	1.473623	-0.000343
7	0.430301	-0.141720	-0.000061
6	1.909884	-0.248707	-0.000217
6	2.442682	-0.918230	-1.275613
6	2.443033	-0.916827	1.275765
1	2.282366	0.773794	-0.000855
1	2.081248	-0.398159	-2.167018
1	3.536475	-0.879179	-1.277842
1	2.154340	-1.971289	-1.351048
1	2.082030	-0.395627	2.166686
1	2.154470	-1.969729	1.352544
1	3.536835	-0.878019	1.277558
6	-0.294985	-1.434103	0.000481
6	-1.087558	-1.694592	-1.291206
6	-1.087528	-1.693494	1.292404
1	0.507860	-2.173574	0.000795
1	-0.446985	-1.552543	-2.166242
1	-1.432070	-2.733846	-1.288681
1	-1.966828	-1.061068	-1.393298
1	-0.446938	-1.550670	2.167303
1	-1.966823	-1.059920	1.393988
1	-1.432010	-2.732759	1.290777
6	0.710793	2.235730	-0.000234
6	1.364479	3.246713	-0.000217
1	1.949893	4.133312	-0.000223
6	-2.690738	0.743559	-0.000460
7	-3.733246	0.226709	-0.000567
1	-1.645362	2.545505	-0.000401

Enthalpy = -537.331187 hartrees
Free Energy = -537.335201 hartrees

Model E – G4MP2 calculations
Optimized geometry (cartesian coordinates in Å)

6	-0.762907	0.195193	-0.000107
6	-1.714774	-0.795555	-0.000115
1	-1.445162	-1.839008	-0.000015
6	-3.098747	-0.524750	-0.000225
7	-4.247788	-0.353318	-0.000298
7	0.597109	0.004567	-0.000001
6	1.519476	1.160060	0.000168
6	2.374407	1.219865	-1.274539
6	2.374061	1.219764	1.275110
1	0.882769	2.043869	0.000110
1	1.741845	1.220634	-2.166455
1	2.967493	2.139637	-1.275977
1	3.075049	0.381848	-1.349167
1	1.741256	1.220501	2.166856
1	3.074647	0.381711	1.349876
1	2.967182	2.139512	1.276767
6	1.218792	-1.336024	0.000087
6	0.954193	-2.136452	-1.287654
6	0.953633	-2.136577	1.287636
1	2.291035	-1.130206	0.000332
1	1.236001	-1.550167	-2.166281
1	1.561392	-3.046955	-1.276432
1	-0.088313	-2.433726	-1.407525
1	1.234882	-1.550312	2.166455
1	-0.088886	-2.434040	1.406939
1	1.560987	-3.046979	1.276664

6	-1.249573	1.543904	-0.000205
6	-1.732643	2.645909	-0.000227
1	-2.172927	3.612908	0.000382

Enthalpy = -537.335201 hartrees
Free Energy = -537.394459 hartrees

Model Z – B3LYP/6-31+G(d,p) calculations in THF solvent
Optimized geometry (cartesian coordinates in Å)

6	-0.166797	1.082805	-0.000189
6	-1.506081	1.466889	-0.000238
7	0.431509	-0.143451	-0.000057
6	1.921731	-0.250640	-0.000207
6	2.447524	-0.920965	-1.277991
6	2.447863	-0.919606	1.278146
1	2.292287	0.772676	-0.000824
1	2.085716	-0.400264	-2.169585
1	3.541479	-0.879632	-1.279112
1	2.160072	-1.974876	-1.350639
1	2.086428	-0.397850	2.169276
1	2.160237	-1.973382	1.352063
1	3.541825	-0.878463	1.278868
6	-0.295408	-1.441421	0.000455
6	-1.082022	-1.694800	-1.296998
6	-1.081991	-1.693785	1.298121
1	0.505169	-2.182273	0.000742
1	-0.422809	-1.594763	-2.164131
1	-1.467548	-2.719677	-1.280100
1	-1.931905	-1.026823	-1.429757
1	-0.422755	-1.593063	2.165159
1	-1.931886	-1.025726	1.430397
1	-1.467501	-2.718679	1.282027
6	0.706305	2.236617	-0.000280

6	1.355315	3.259526	-0.000328
1	1.943162	4.151299	-0.000349
6	-2.709894	0.740618	-0.000279
7	-3.772540	0.246751	-0.000328
1	-1.667983	2.538979	-0.000298

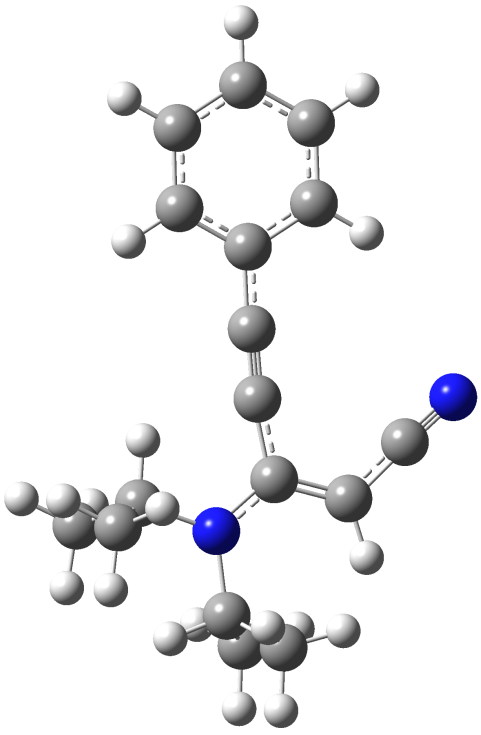
Enthalpy = -537.987174 hartrees
Free energy = -538.045144 hartrees

Model E – B3LYP/6-31+G(d,p) calculations in THF solvent
Optimized geometry (cartesian coordinates in Å)

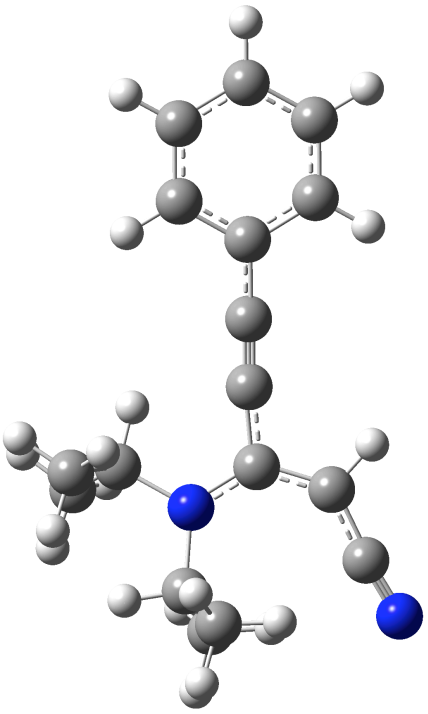
6	-0.758870	0.201113	-0.000054
6	-1.718119	-0.801637	-0.000081
1	-1.451124	-1.846697	-0.000008
6	-3.100396	-0.529979	-0.000206
7	-4.259902	-0.364006	-0.000324
7	0.592686	0.007717	0.000010
6	1.526889	1.167653	0.000191
6	2.377987	1.217529	-1.277428
6	2.377540	1.217470	1.278109
1	0.894571	2.054629	0.000093
1	1.743740	1.219284	-2.168841
1	2.971919	2.137101	-1.278694
1	3.076126	0.377152	-1.349654
1	1.742978	1.219261	2.169298
1	3.075586	0.377036	1.350573
1	2.971541	2.136998	1.279595
6	1.220114	-1.341600	0.000006
6	0.955897	-2.140348	-1.288990
6	0.955719	-2.140542	1.288853
1	2.290118	-1.129011	0.000114

1	1.197929	-1.539354	-2.170007
1	1.600439	-3.025240	-1.293102
1	-0.075518	-2.483821	-1.387240
1	1.197068	-1.539486	2.170014
1	-0.075551	-2.484580	1.386644
1	1.600719	-3.025100	1.293184
6	-1.249314	1.555523	-0.000126
6	-1.740904	2.662307	-0.000193
1	-2.169289	3.640925	-0.000256

Enthalpy = -537.995100 hartrees
Free energy = -538.054451 hartrees



Compound **6**, isomer Z



Compound **6**, isomer E

Gas-Phase

	Isomer Z	Isomer E	Differences (kj/mol)
B3LYP/6-31+g(d,p)			
Enthalpy	-768.972698 (a.u.)	-768.979158 (a.u.)	17.0

Free energy	-769.044194	-769.050500	16.5

Compound **6**, Isomer Z – B3LYP/6-31+G(d,p) calculations

Optimized geometry (cartesian coordinates in Å)

6	1.031393	-0.626451	0.075245
6	1.358378	-1.975818	0.056732
7	1.825892	0.496125	0.099580
6	1.195468	1.832848	0.277426
6	1.176205	2.642800	-1.028781
6	1.814371	2.619514	1.443716
1	0.159824	1.635761	0.552225
1	0.674302	2.083995	-1.824223
1	0.633284	3.581744	-0.875004
1	2.183776	2.900234	-1.372354
1	1.785446	2.036002	2.368591
1	2.851124	2.915756	1.253870
1	1.238266	3.537250	1.602368
6	3.287188	0.514122	-0.177489
6	3.660923	-0.121583	-1.527440
6	4.149565	0.039081	1.005834
1	3.506563	1.577945	-0.292950
1	3.047282	0.299522	-2.330040
1	4.709376	0.109918	-1.743948
1	3.559953	-1.205944	-1.543153
1	3.891498	0.592430	1.913205
1	4.050300	-1.026447	1.207474
1	5.203707	0.233964	0.778465
6	-0.393680	-0.416530	0.059212
6	-1.607995	-0.339448	0.027676
6	2.595008	-2.647941	0.120558
7	3.566269	-3.298097	0.173540
1	0.510001	-2.648539	0.005917
6	-3.031430	-0.245036	-0.003893
6	-3.824772	-1.401762	0.143821
6	-3.666652	1.001135	-0.183871
6	-5.214907	-1.309319	0.112144
1	-3.340657	-2.363002	0.282538
6	-5.057376	1.083767	-0.213101
1	-3.061847	1.894611	-0.301227
6	-5.835772	-0.068837	-0.065599
1	-5.815043	-2.207095	0.226621
1	-5.535180	2.049011	-0.352454
1	-6.919262	-0.000686	-0.089584

Enthalpy = -768.972698 hartrees
Free energy = -769.044194 hartrees

Compound **6**, Isomer E – B3LYP/6-31+G(d,p) calculations
Optimized geometry (cartesian coordinates in Å)

6	-1.181218	0.584152	0.057796
6	-1.439765	1.941515	0.144668
1	-2.445438	2.330819	0.170328
6	-0.406266	2.903907	0.205254
7	0.419898	3.729467	0.257061
7	-2.134717	-0.407621	-0.004598
6	-1.728135	-1.831119	-0.095885
6	-2.176192	-2.479036	-1.415783
6	-2.172046	-2.641314	1.132610
1	-0.637969	-1.821662	-0.097120
1	-1.812138	-1.905652	-2.273472
1	-1.767817	-3.492899	-1.484832
1	-3.265893	-2.561964	-1.492673
1	-1.804966	-2.181373	2.054911
1	-3.261534	-2.733293	1.201913
1	-1.763895	-3.655747	1.071130
6	-3.591142	-0.135141	0.014953
6	-4.093206	0.625268	-1.227199
6	-4.089384	0.460777	1.345294
1	-4.044735	-1.126728	-0.047823
1	-3.768743	0.120471	-2.141717
1	-5.188277	0.643667	-1.218635
1	-3.744667	1.658369	-1.275662
1	-3.763187	-0.156887	2.187037
1	-3.739576	1.478962	1.524331
1	-5.184453	0.480912	1.342011
6	0.198817	0.200266	0.032125
6	1.402918	0.025712	0.020065
6	2.820958	-0.123915	0.009335
6	3.638852	1.023436	0.081592
6	3.421133	-1.396629	-0.072049
6	5.025982	0.890833	0.072026
1	3.173315	2.001940	0.144236
6	4.809555	-1.516617	-0.080836
1	2.793316	-2.280387	-0.127693
6	5.615130	-0.375436	-0.008963

1	5.648844	1.778609	0.127972
1	5.263842	-2.501088	-0.143764
1	6.696794	-0.472719	-0.016052

Enthalpy = -768.979158 hartrees
Free energy = -769.050500 hartrees