

SUPPORTING INFORMATION

***pseudo*-Multicomponent 1,3-dipolar cycloaddition involving a metal-free generation of unactivated azomethine ylides**

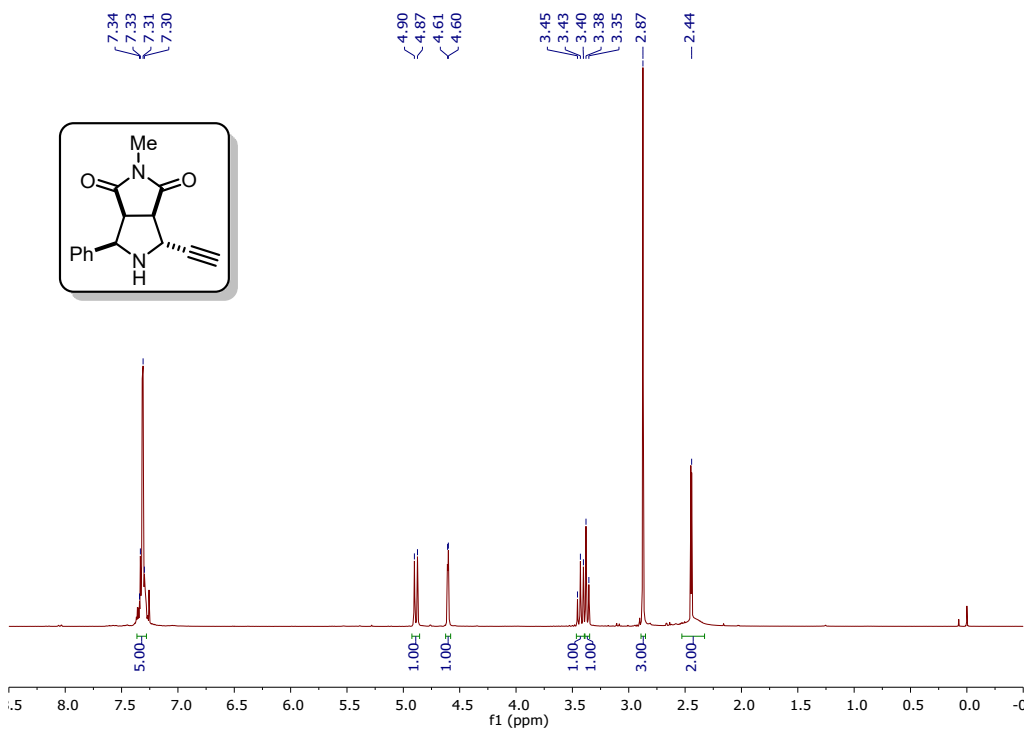
Asmaa Belabbes, María Gracia Retamosa, Francisco Foubelo, Ana Sirvent, Carmen Nájera, Miguel Yus, and José M. Sansano.

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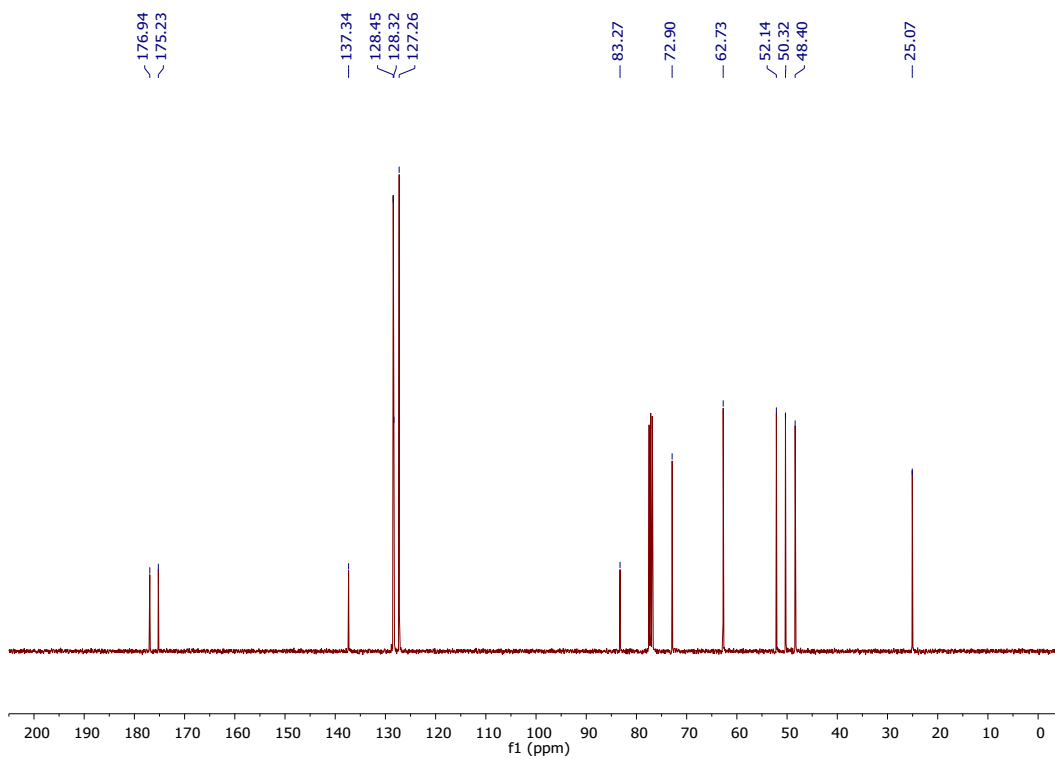
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1. NMR SPECTRA

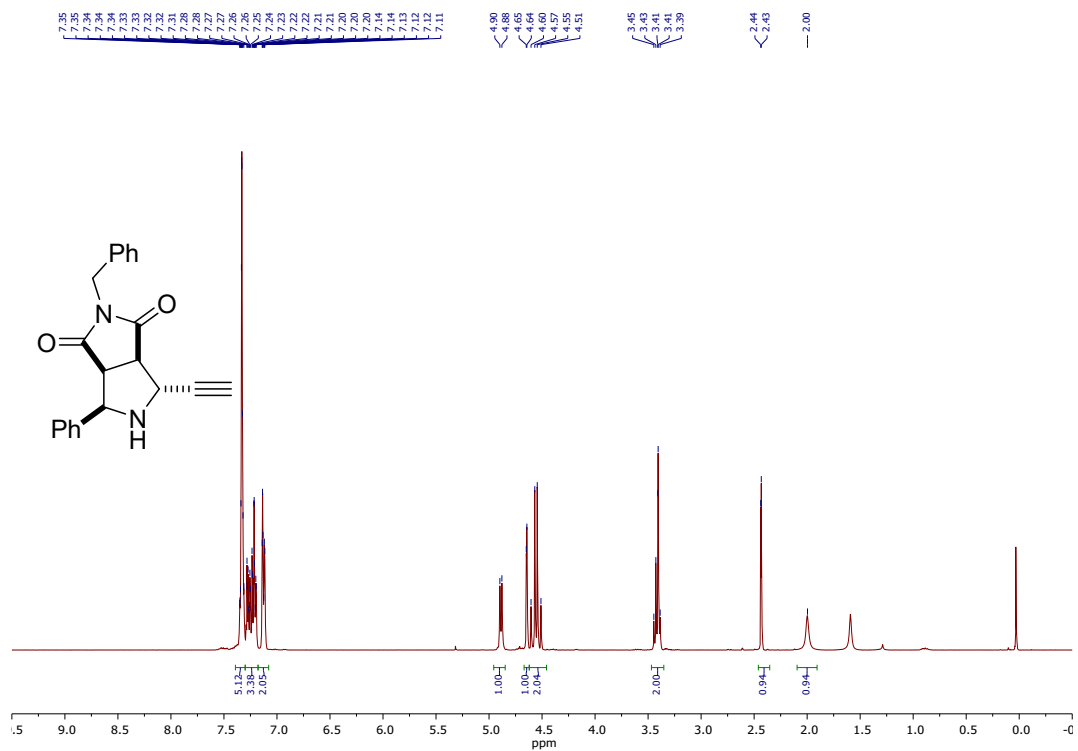
^1H NMR of **2aa**



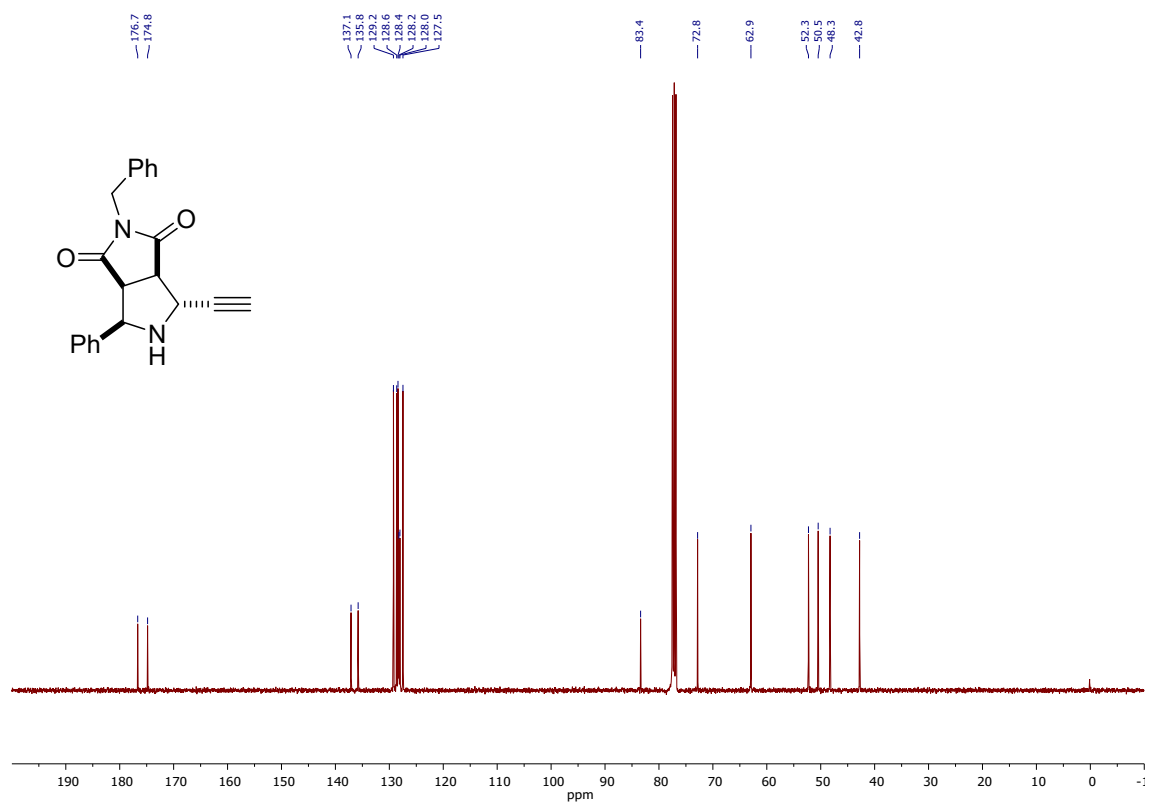
$^{13}\text{C}\{\text{H}\}$ NMR of **2aa**



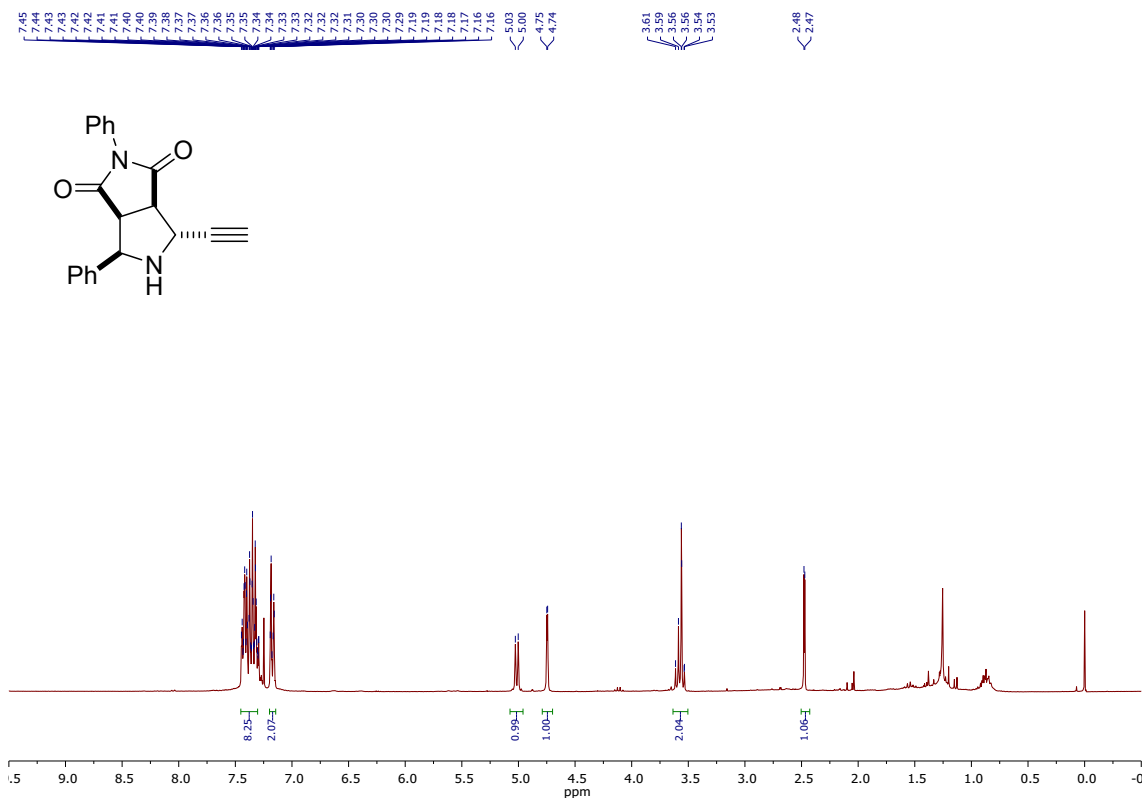
^1H NMR of **2ab**



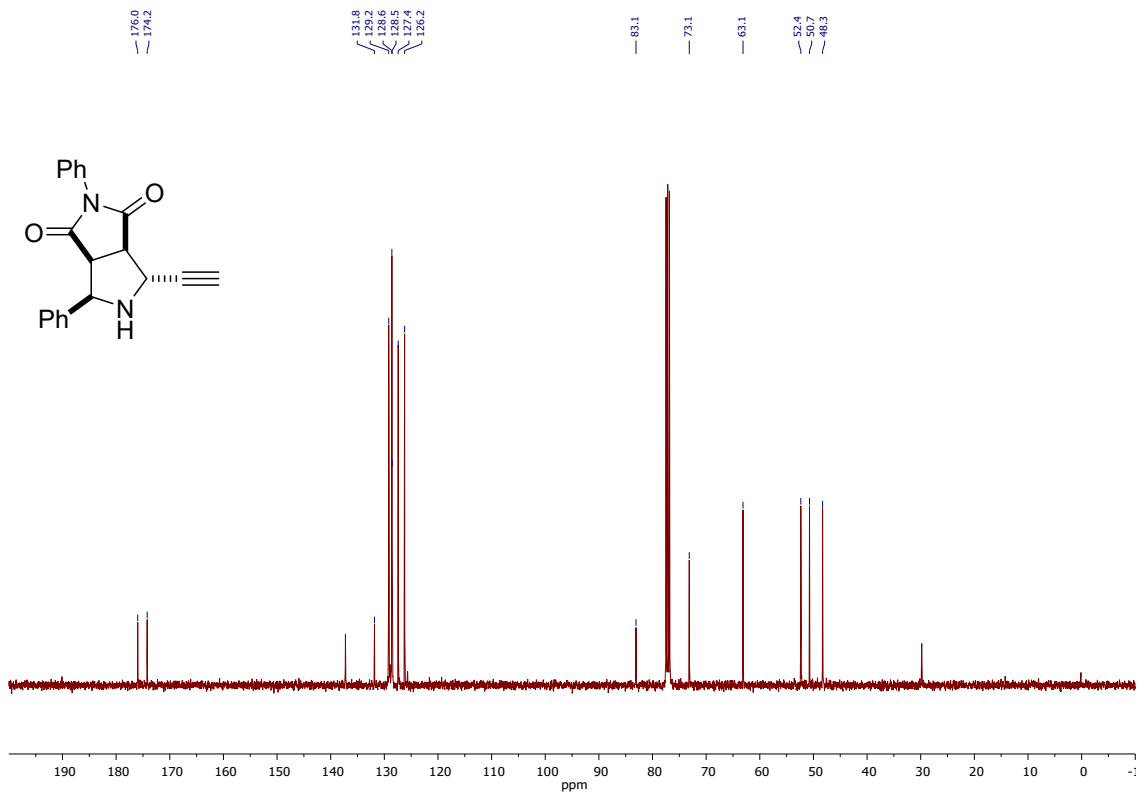
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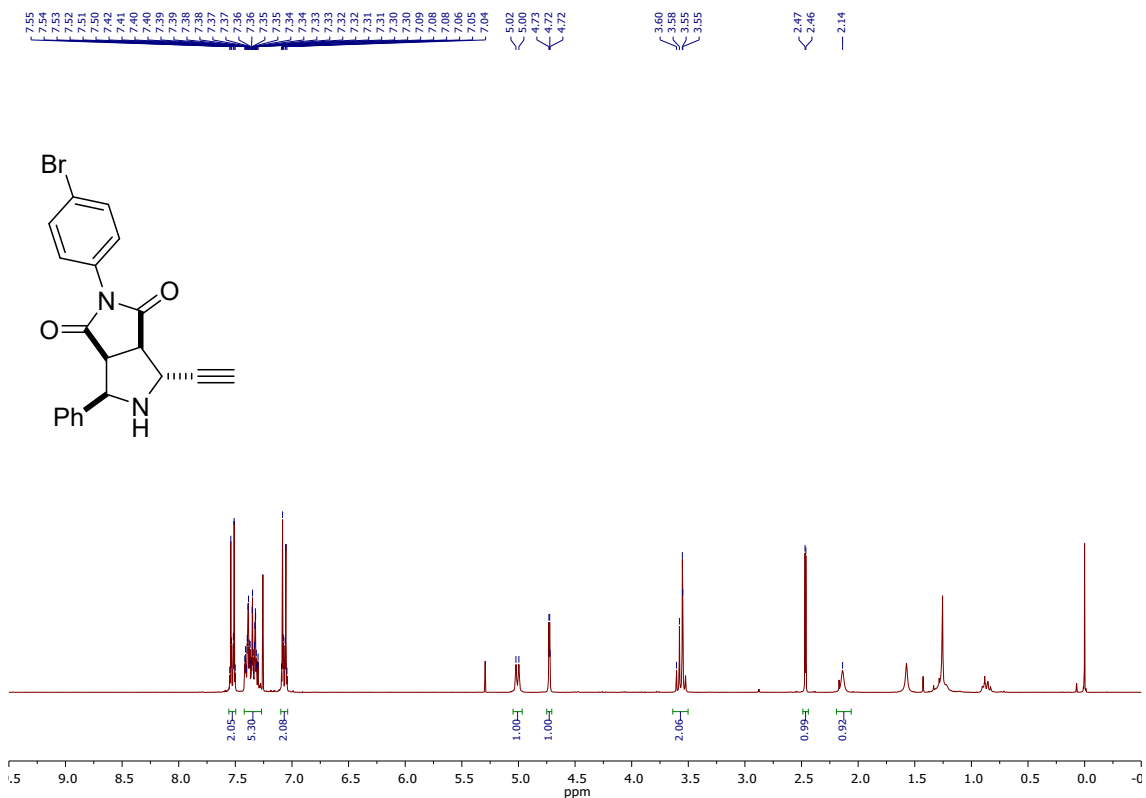
¹H NMR of 2ac



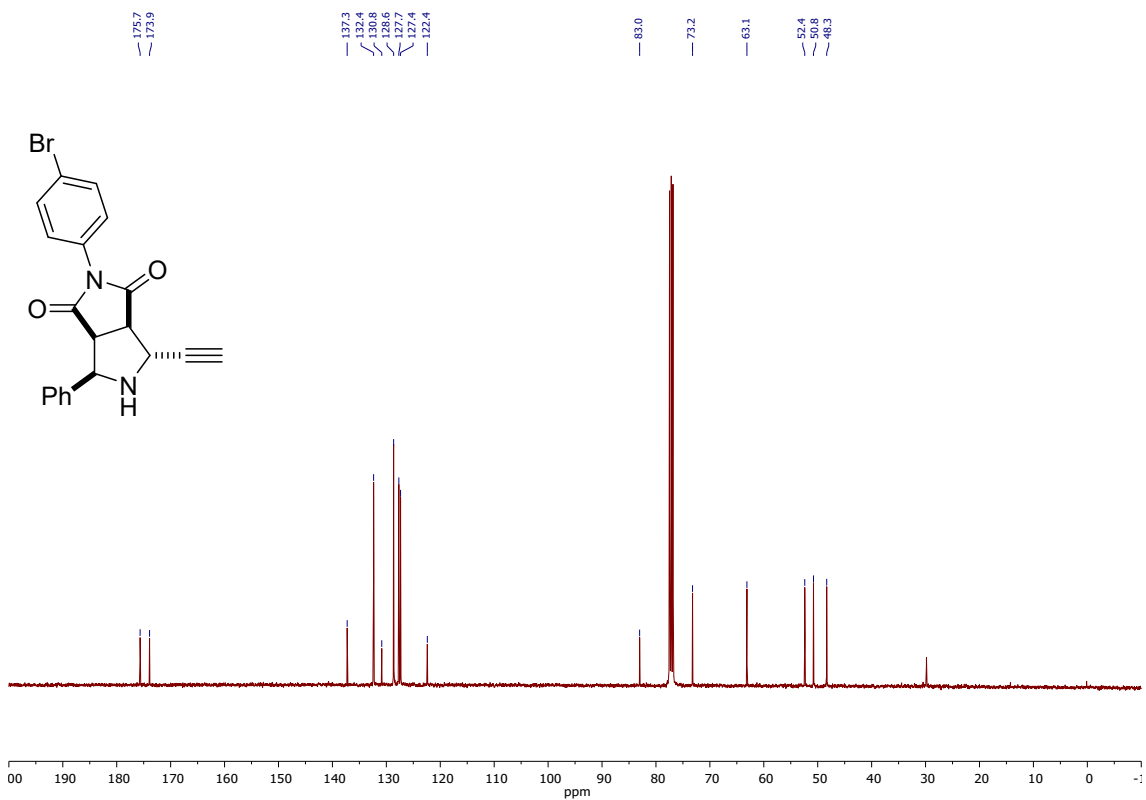
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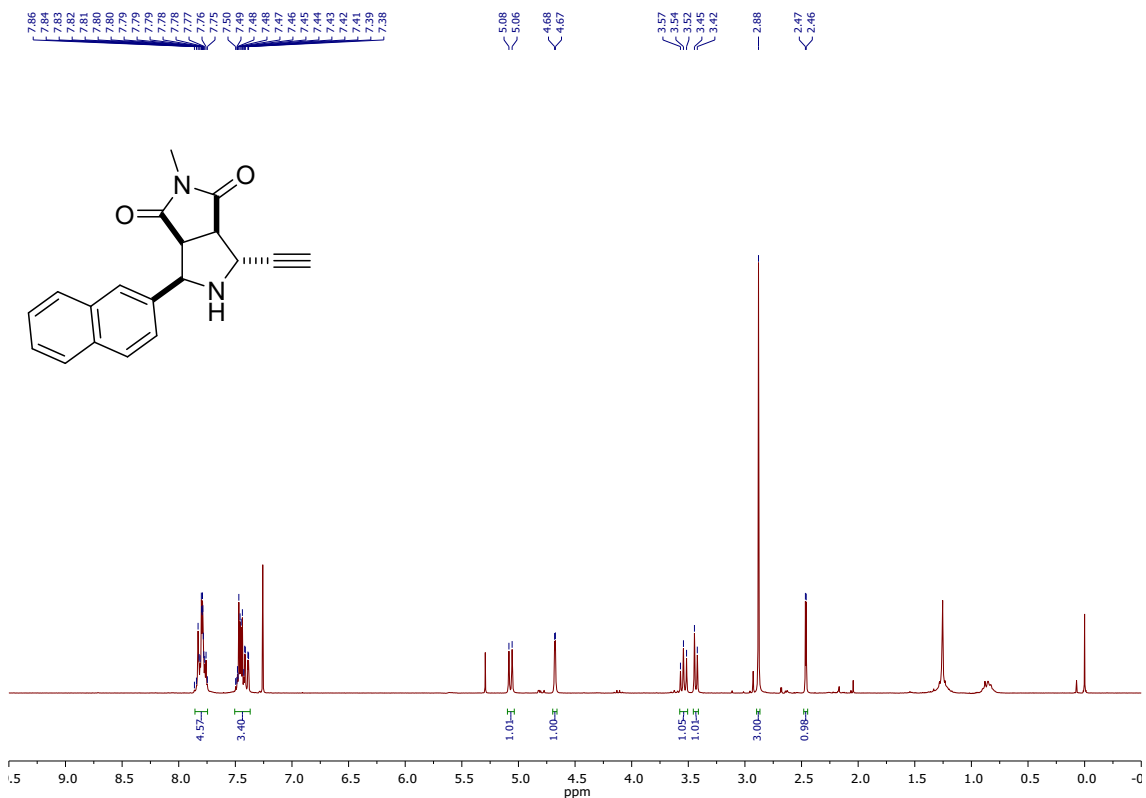
^1H NMR of **2ad**



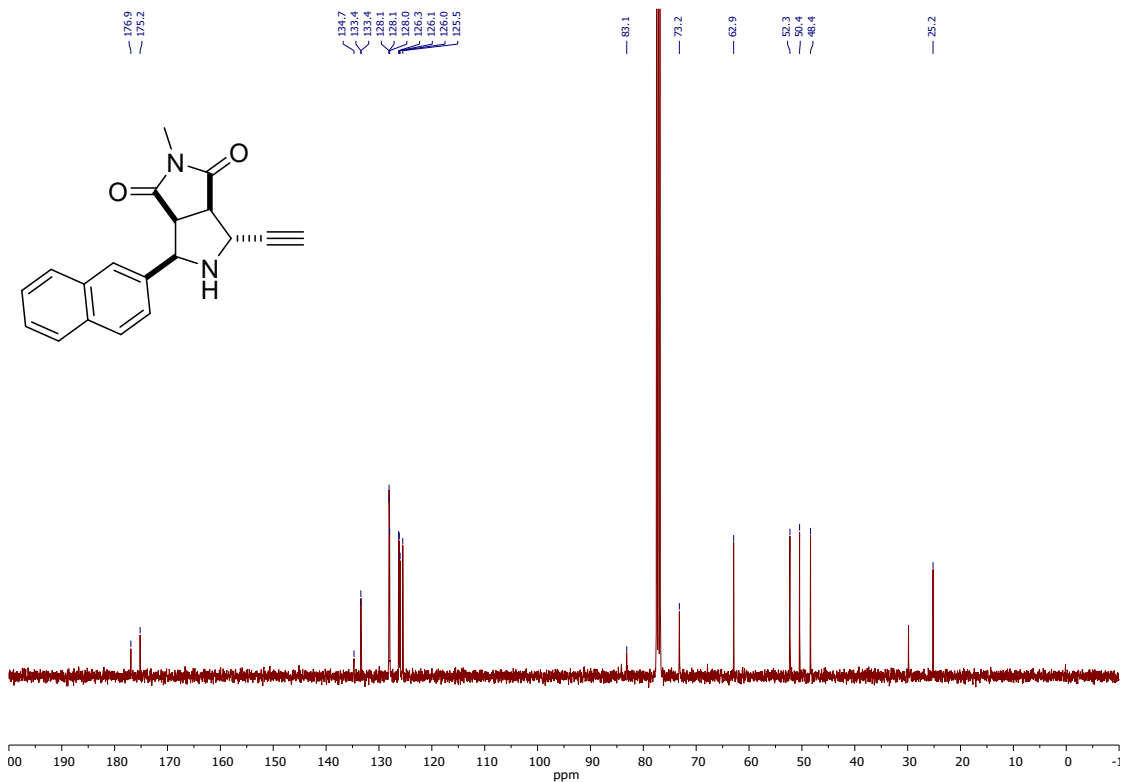
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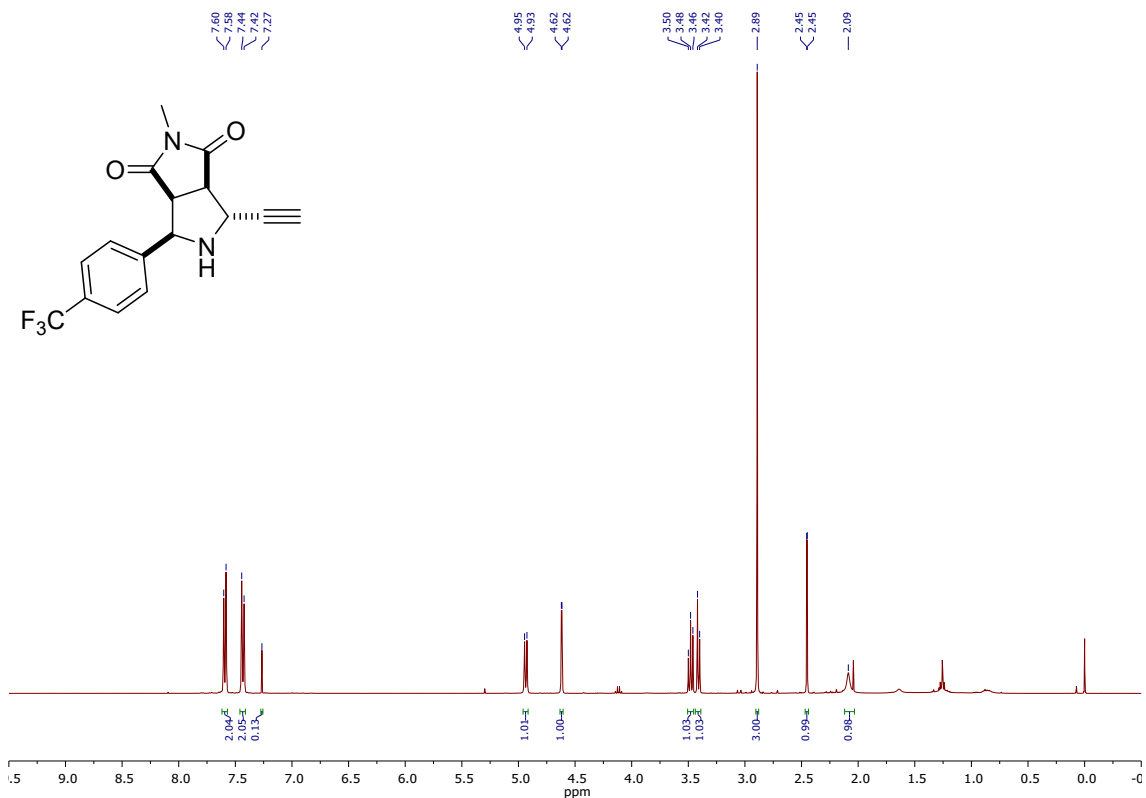
¹H NMR of 2ba



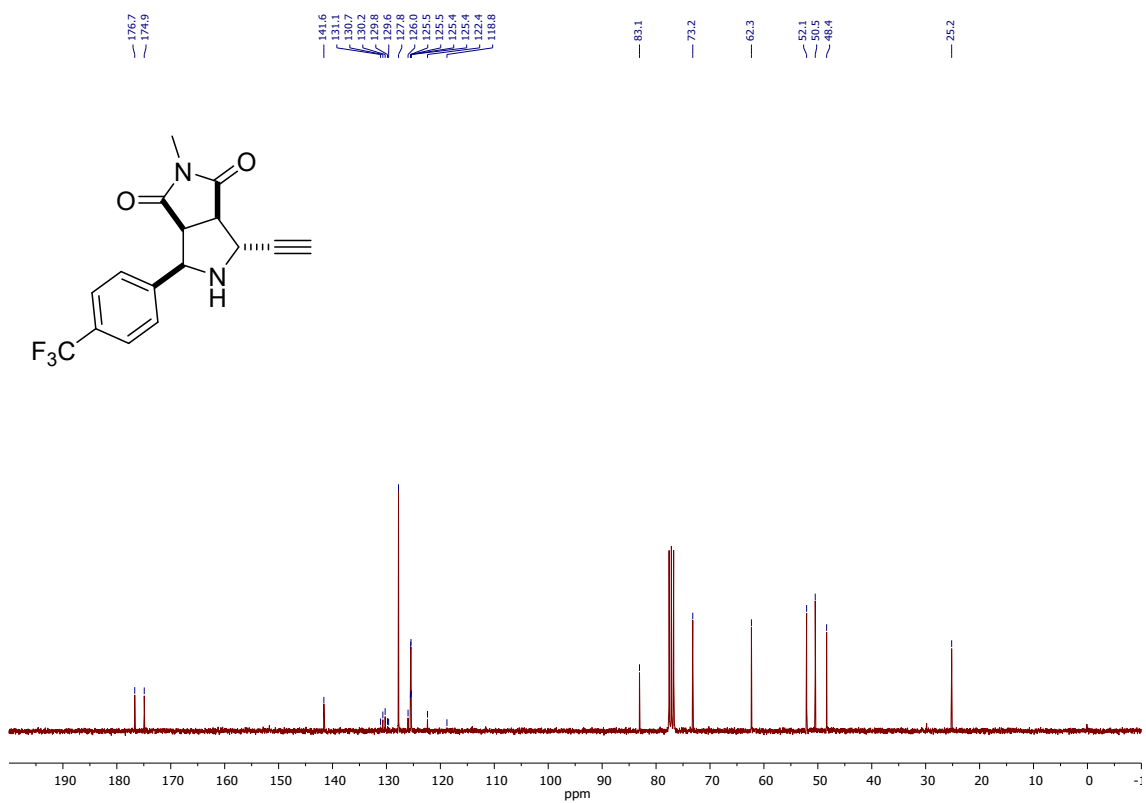
¹³C{H} NMR of 2ba



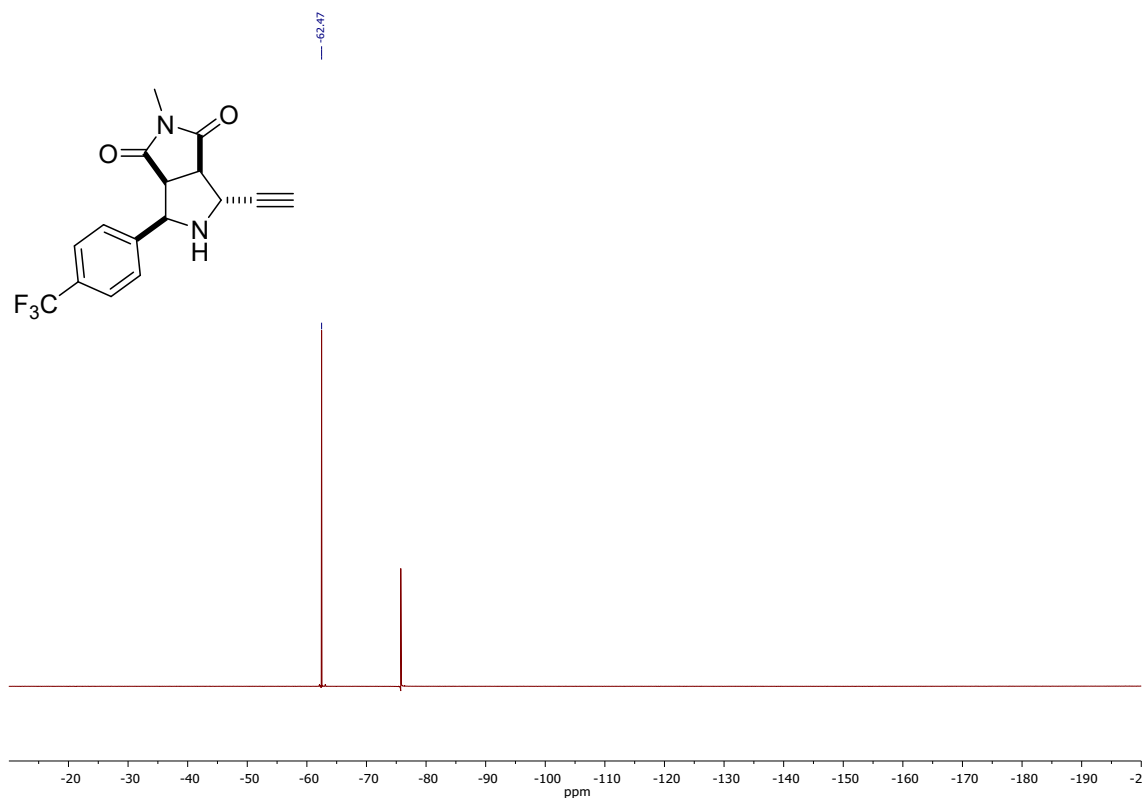
¹H NMR of 2ca



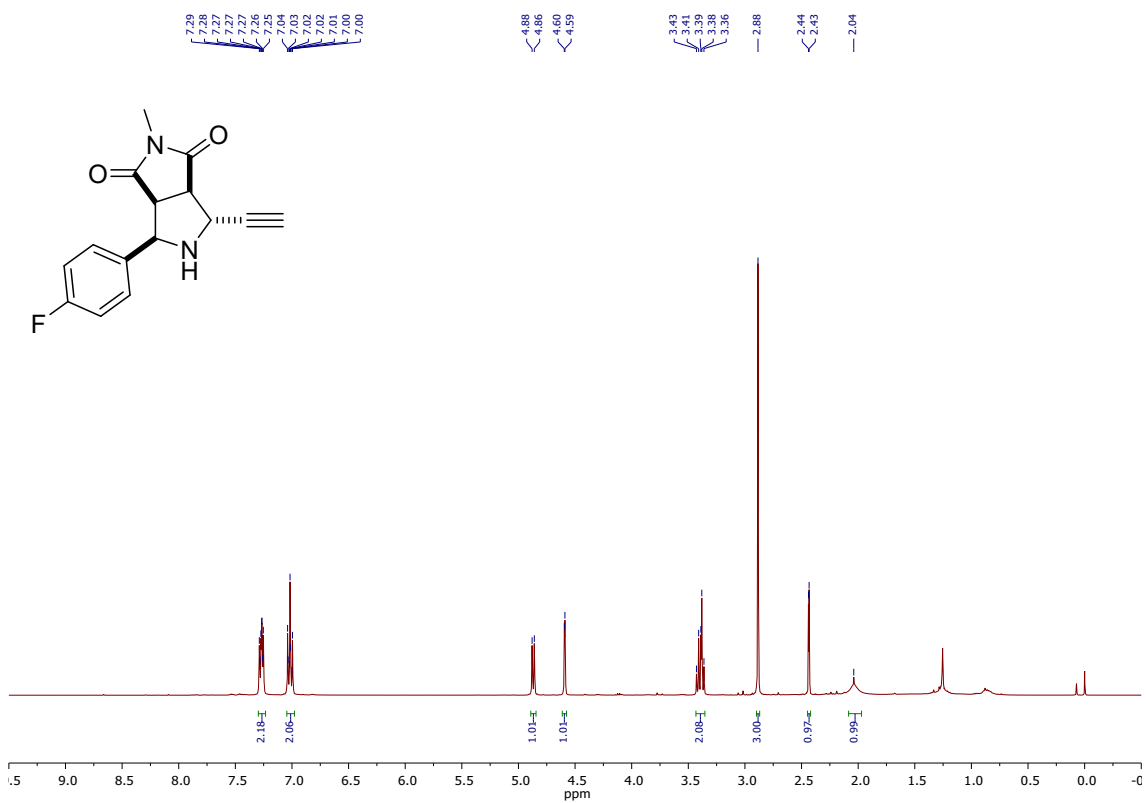
¹³C{¹H} NMR of 2ca



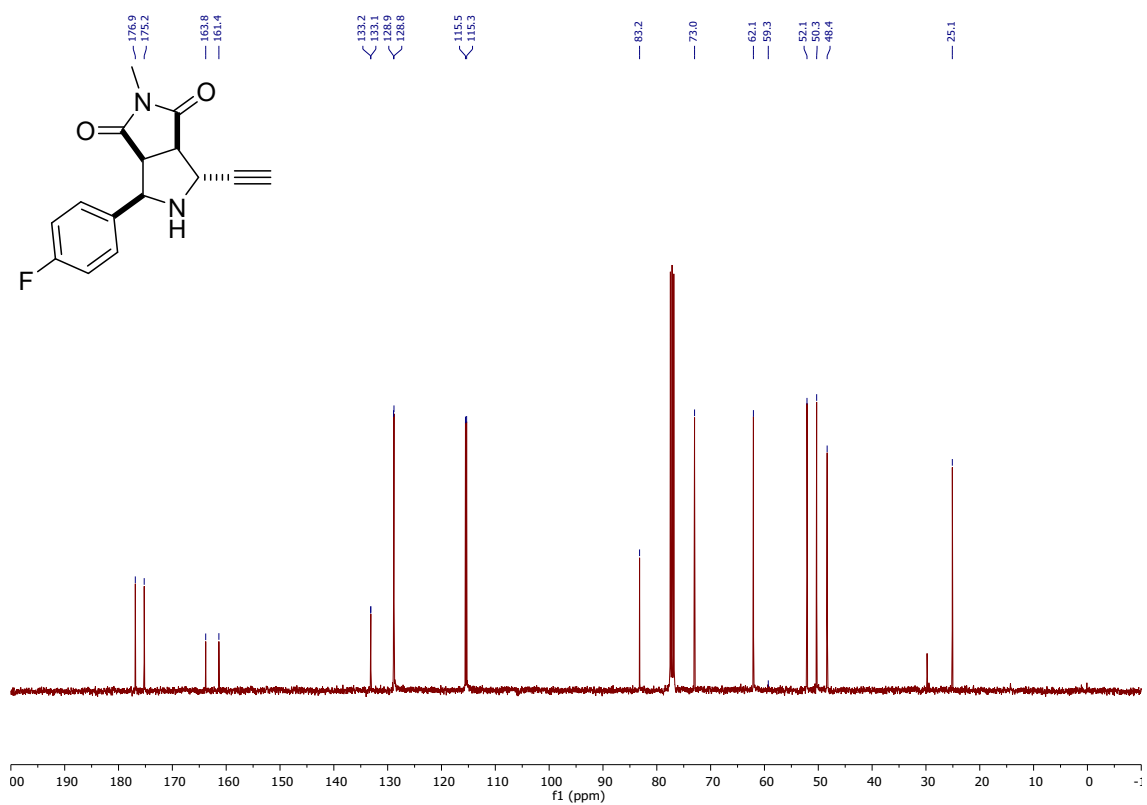
^{19}F NMR of **2ca**



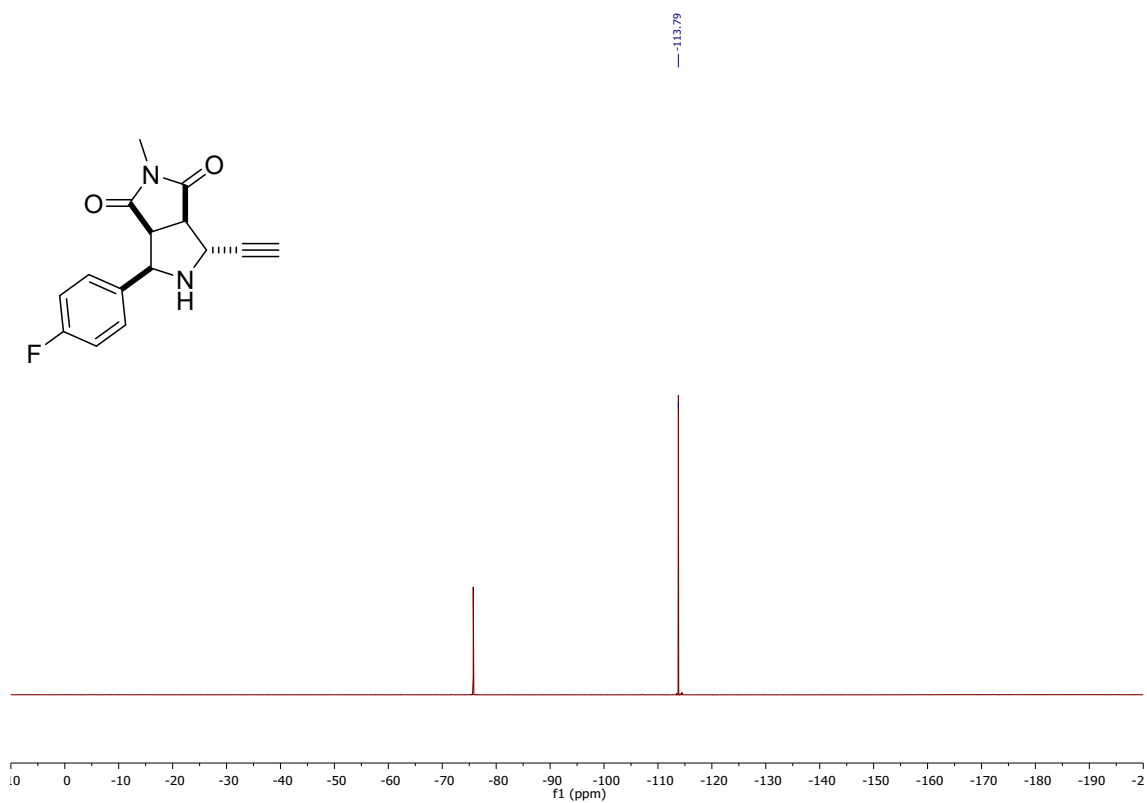
^1H NMR of **2da**



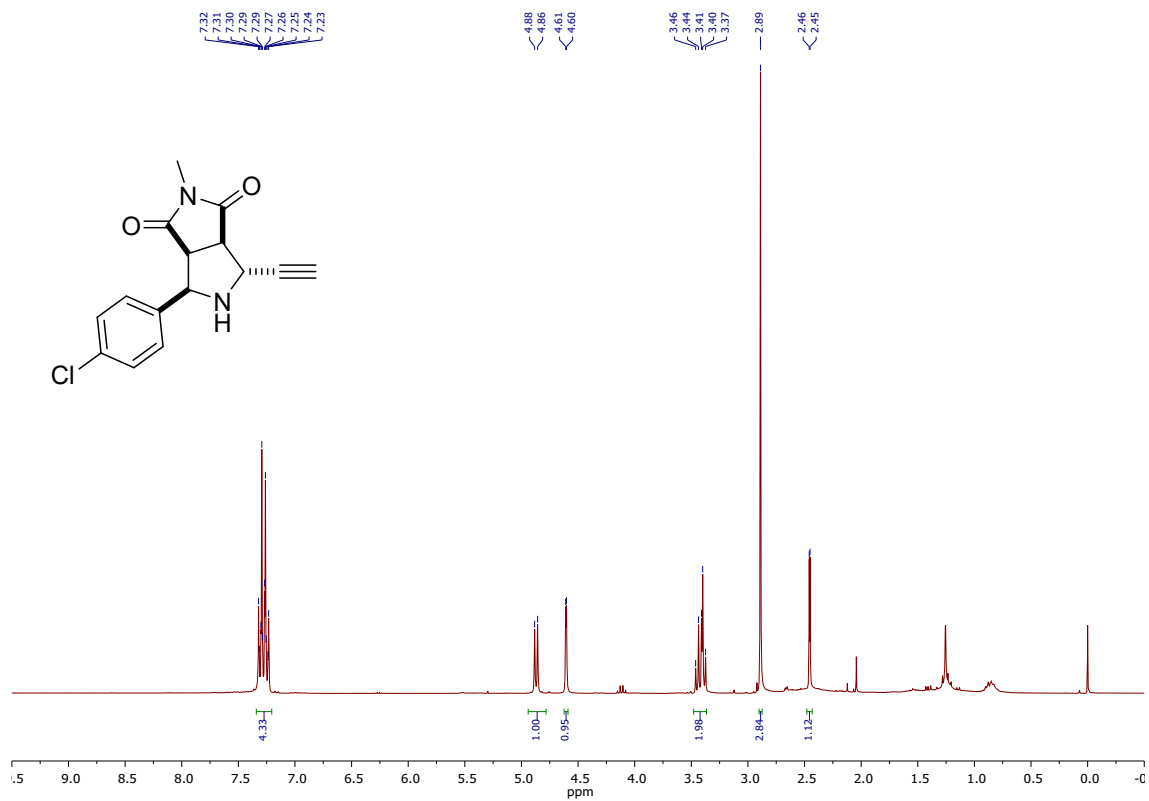
$^{13}\text{C}\{\text{H}\}$ NMR of **2da**



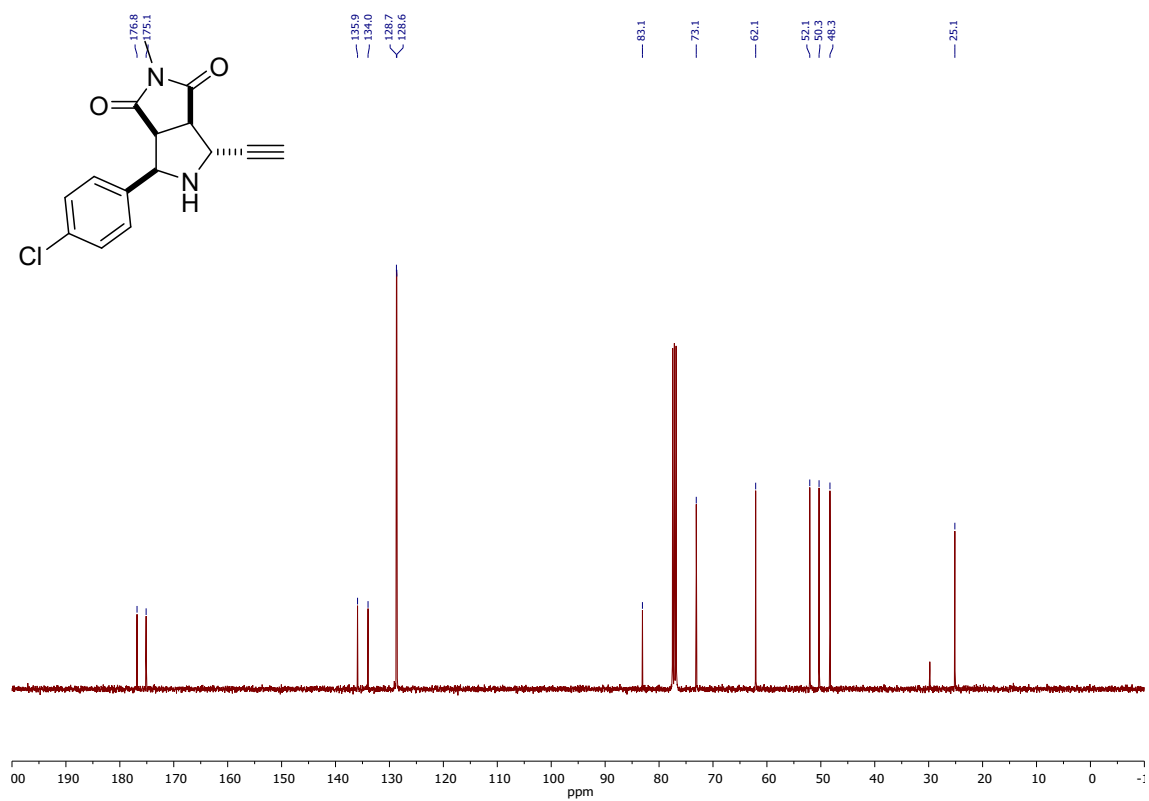
^{19}F NMR of **2da**



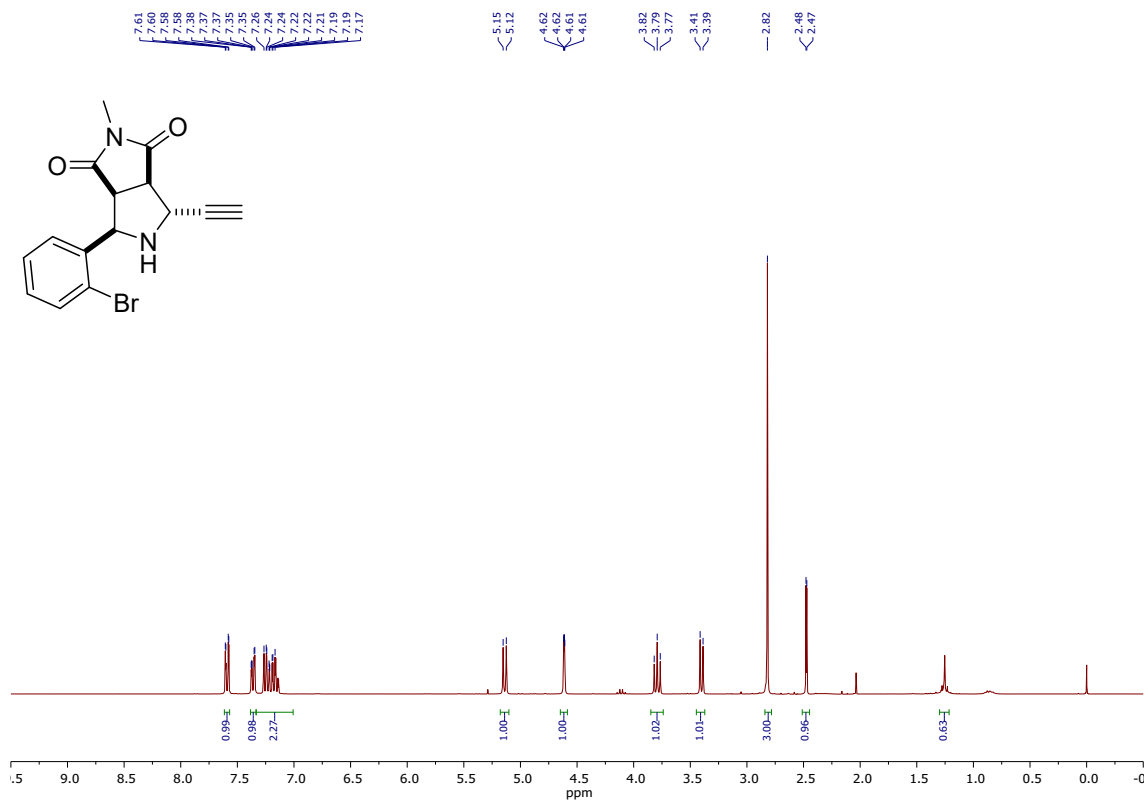
^1H NMR of **2ea**



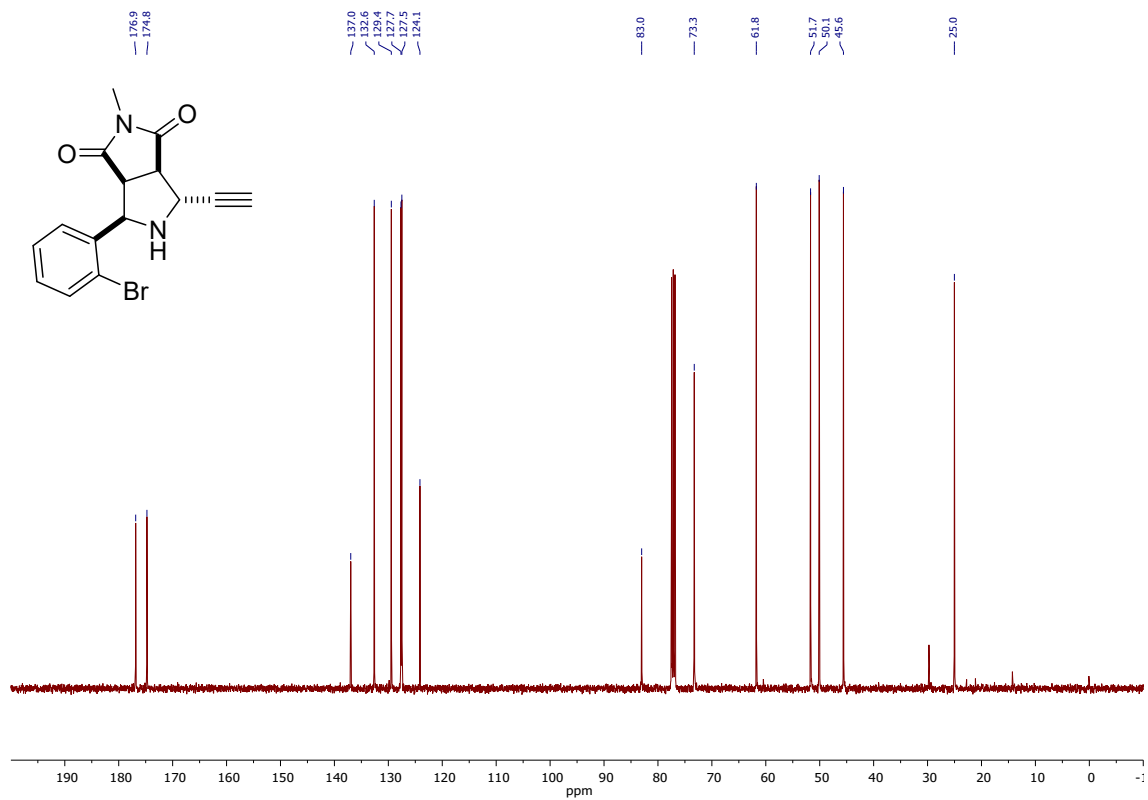
¹³C{¹H} NMR of 2ea



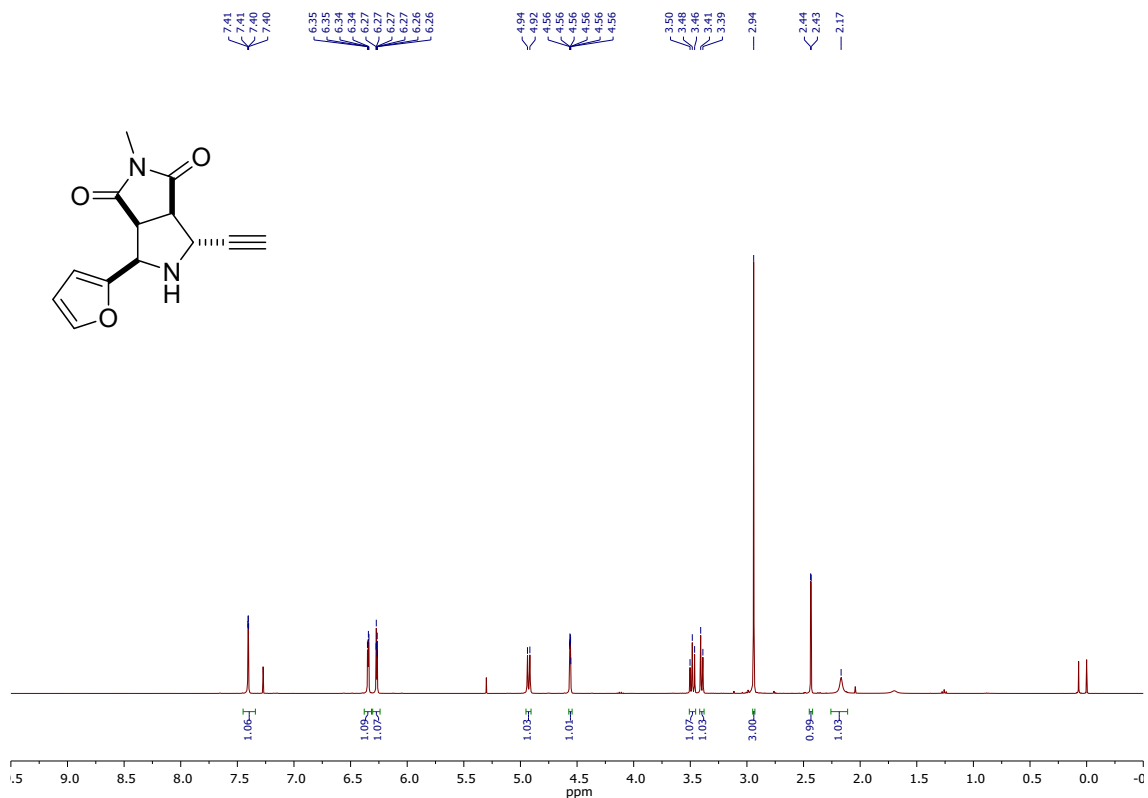
^1H NMR of **2fa**



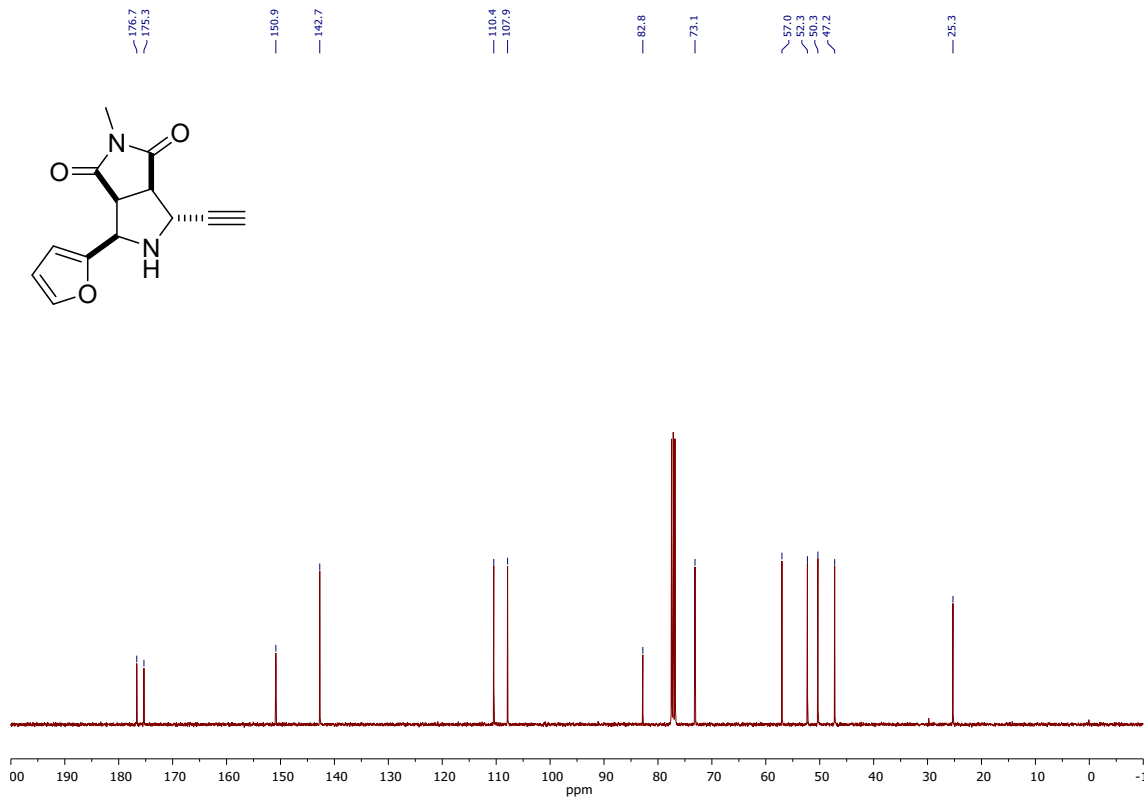
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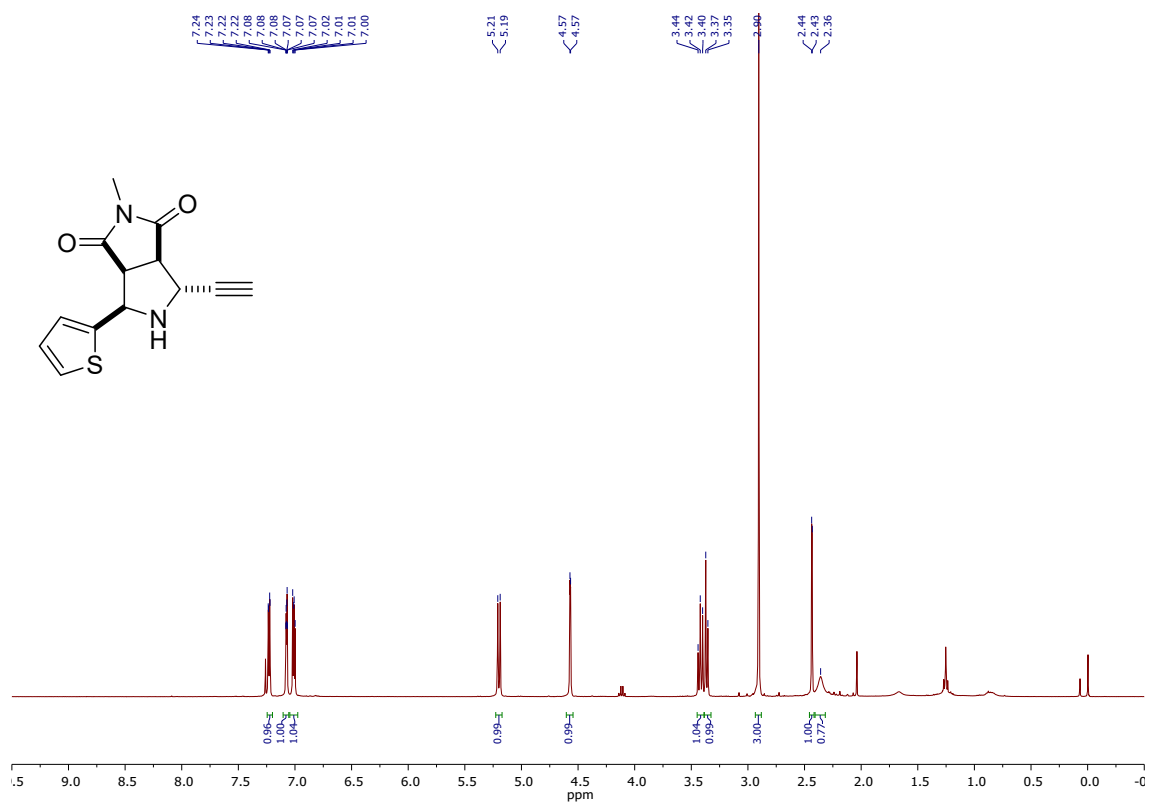
¹H NMR of 2ga



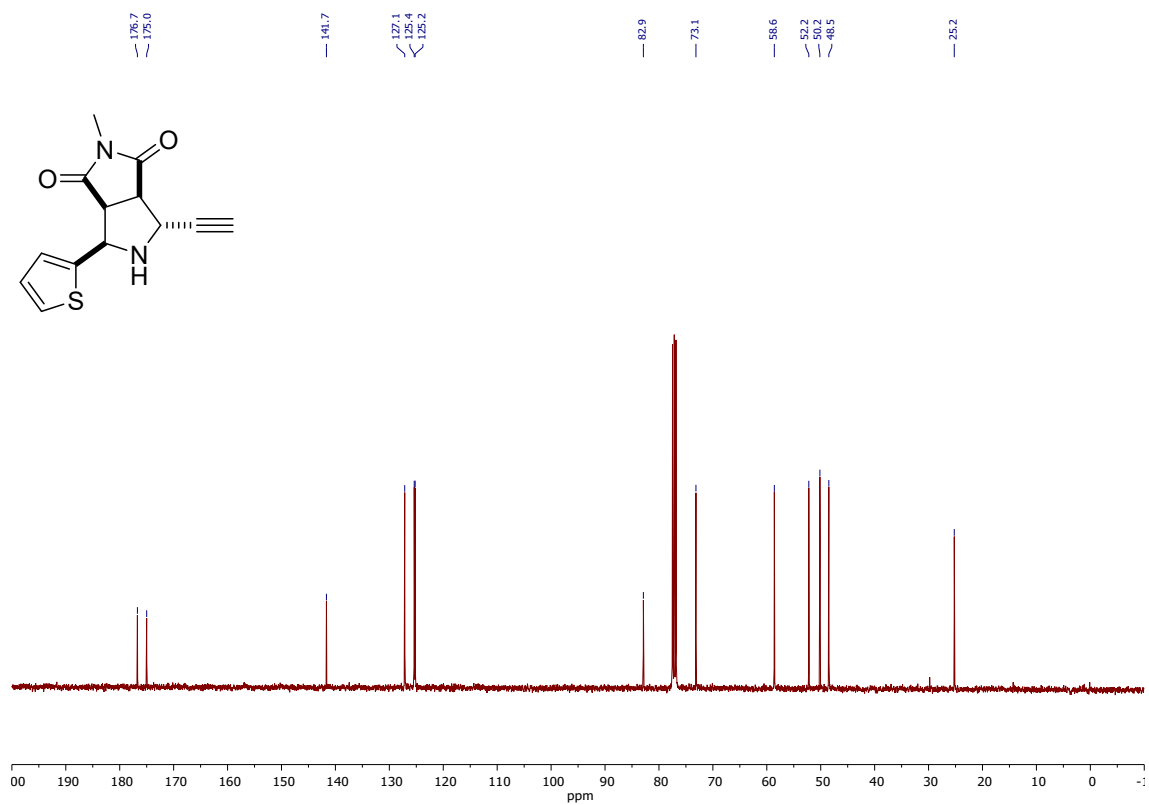
¹³C{¹H} NMR of 2ga



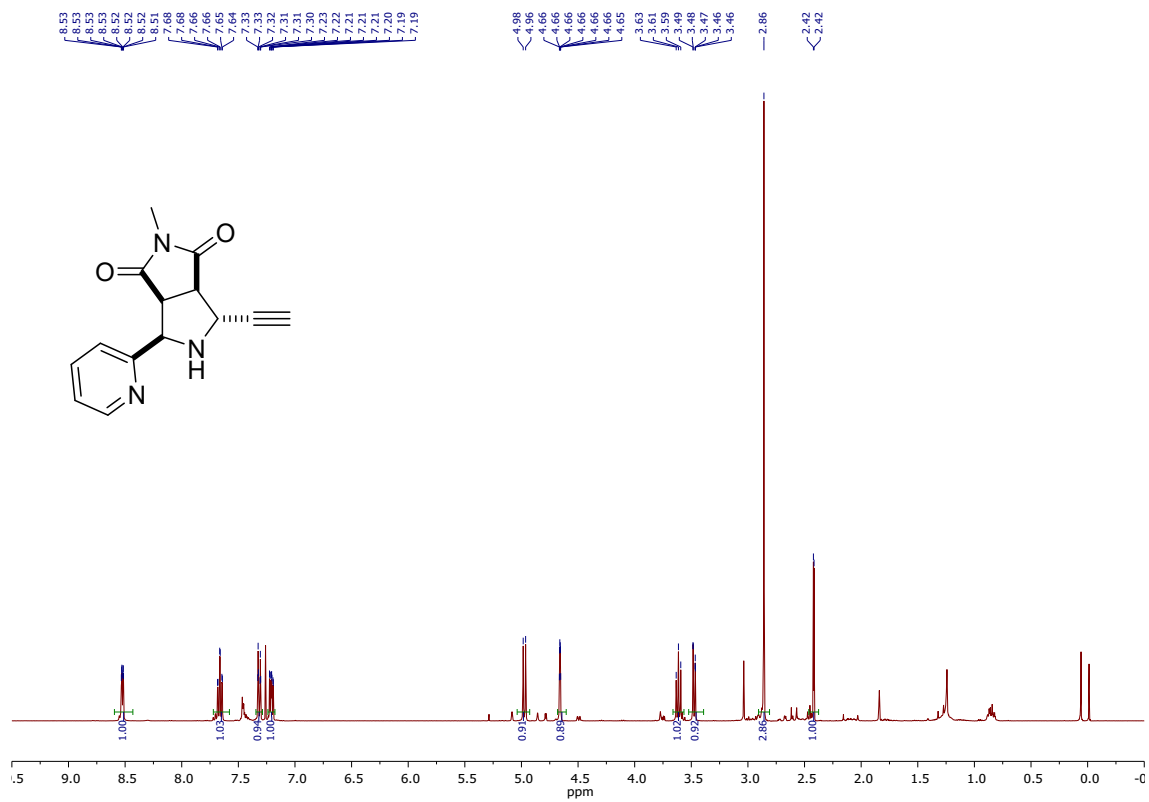
¹H NMR of 2ha



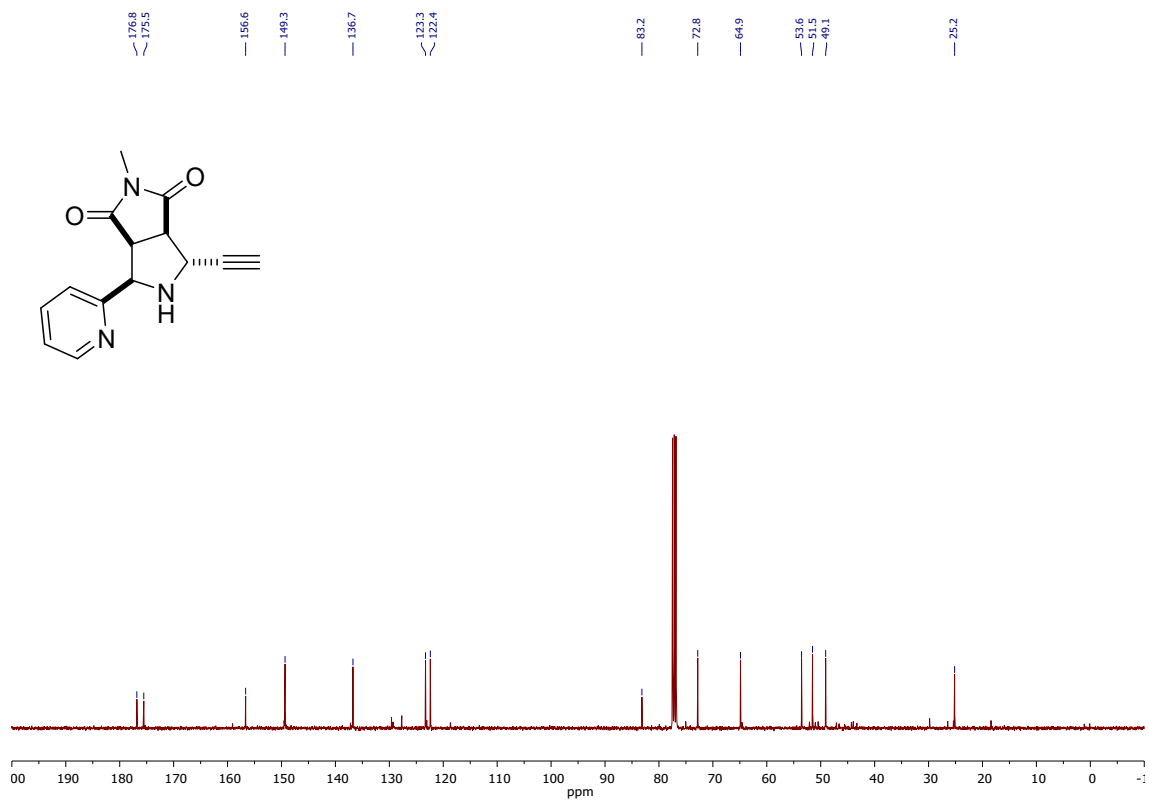
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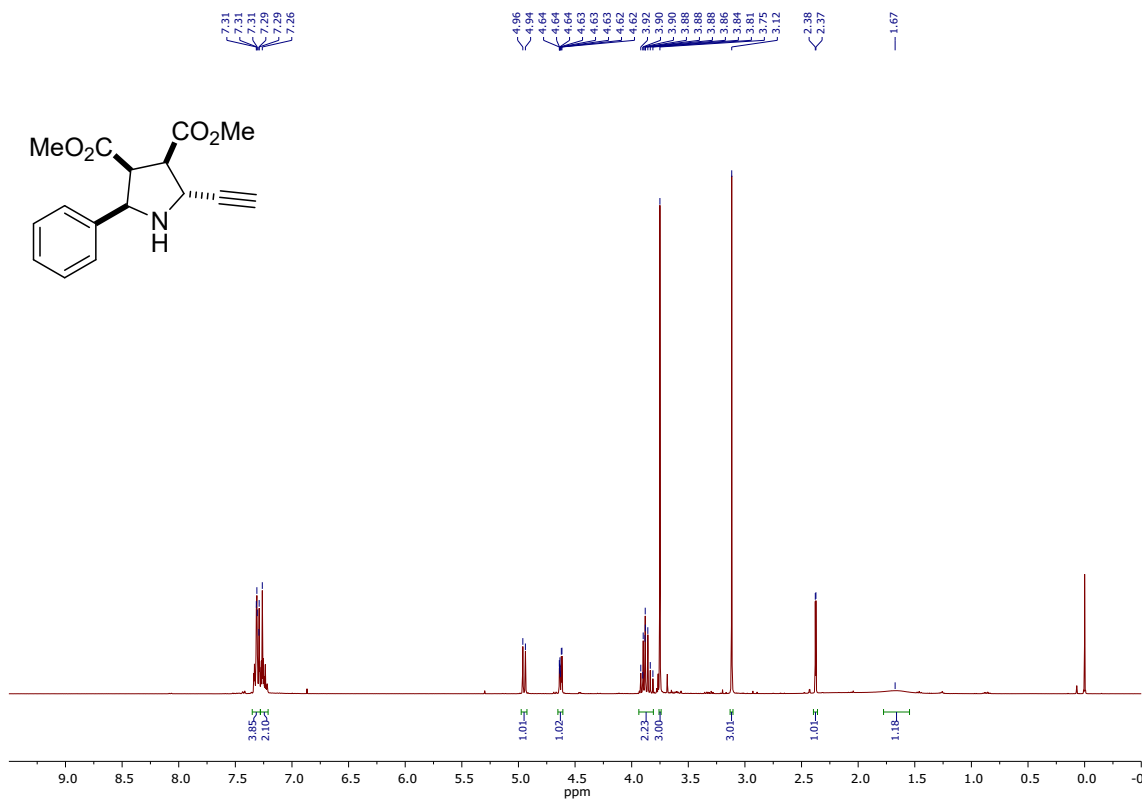
¹H NMR of 2ia



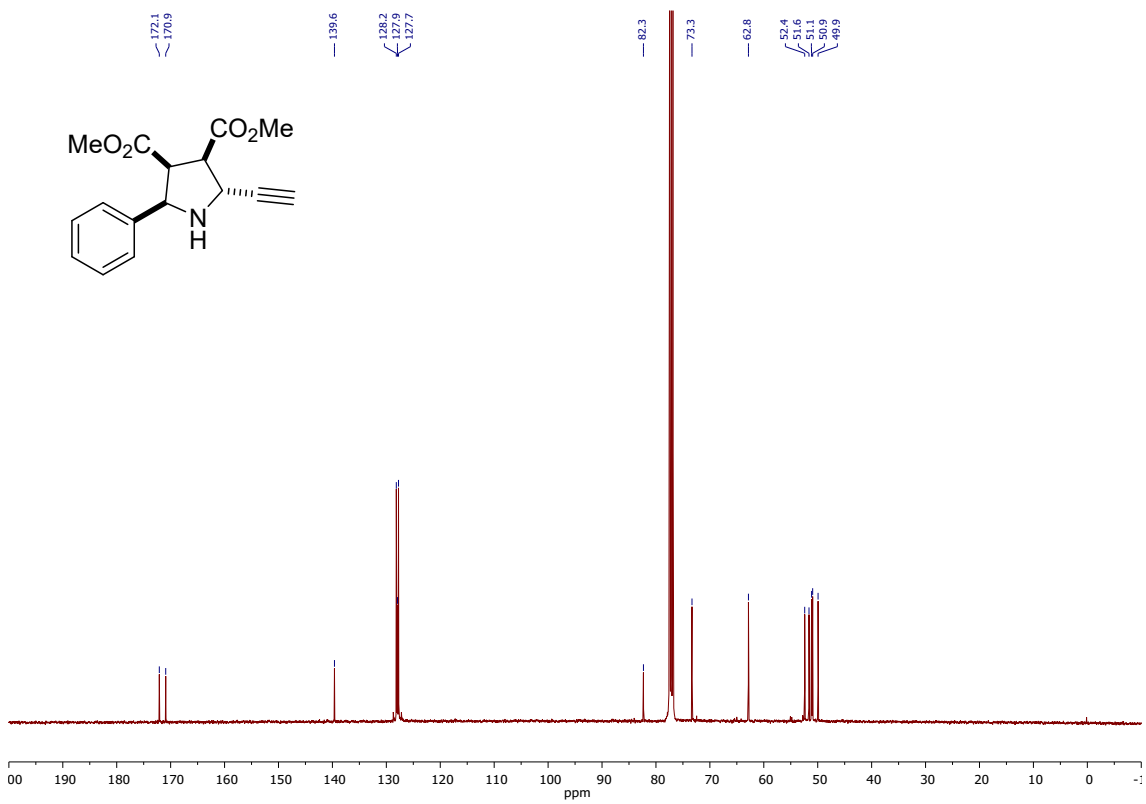
$^{13}\text{C}\{\text{H}\}$ NMR of **2ia**



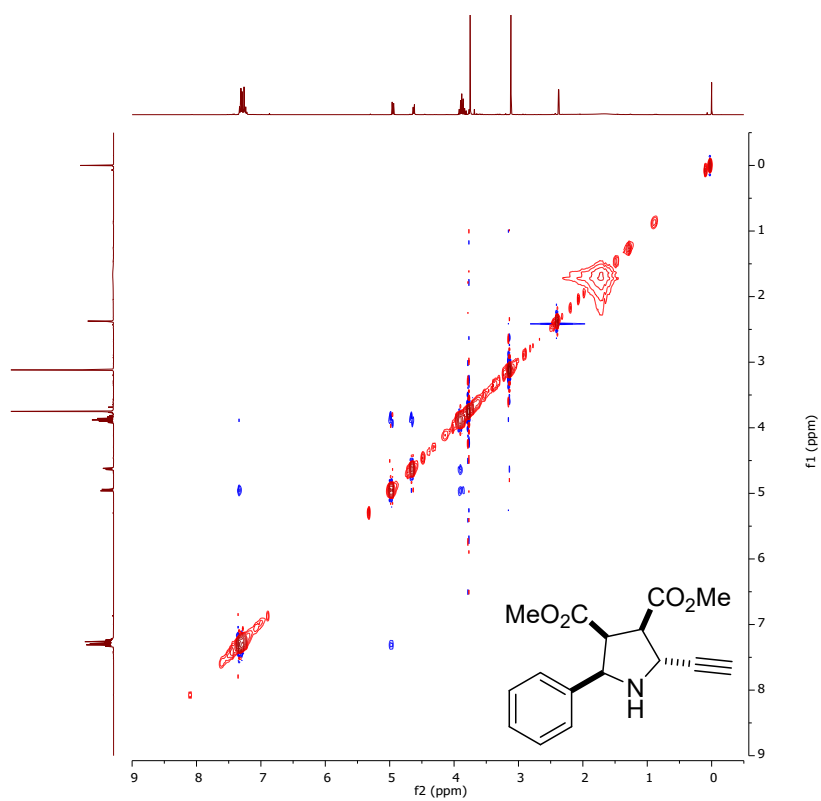
^1H NMR of **2ae**



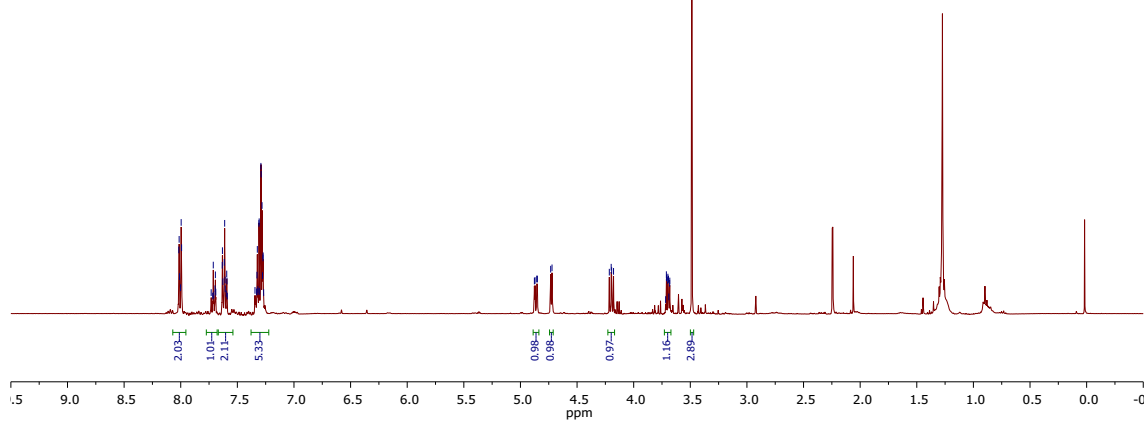
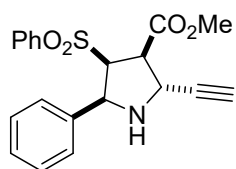
¹³C{H} NMR of 2ae



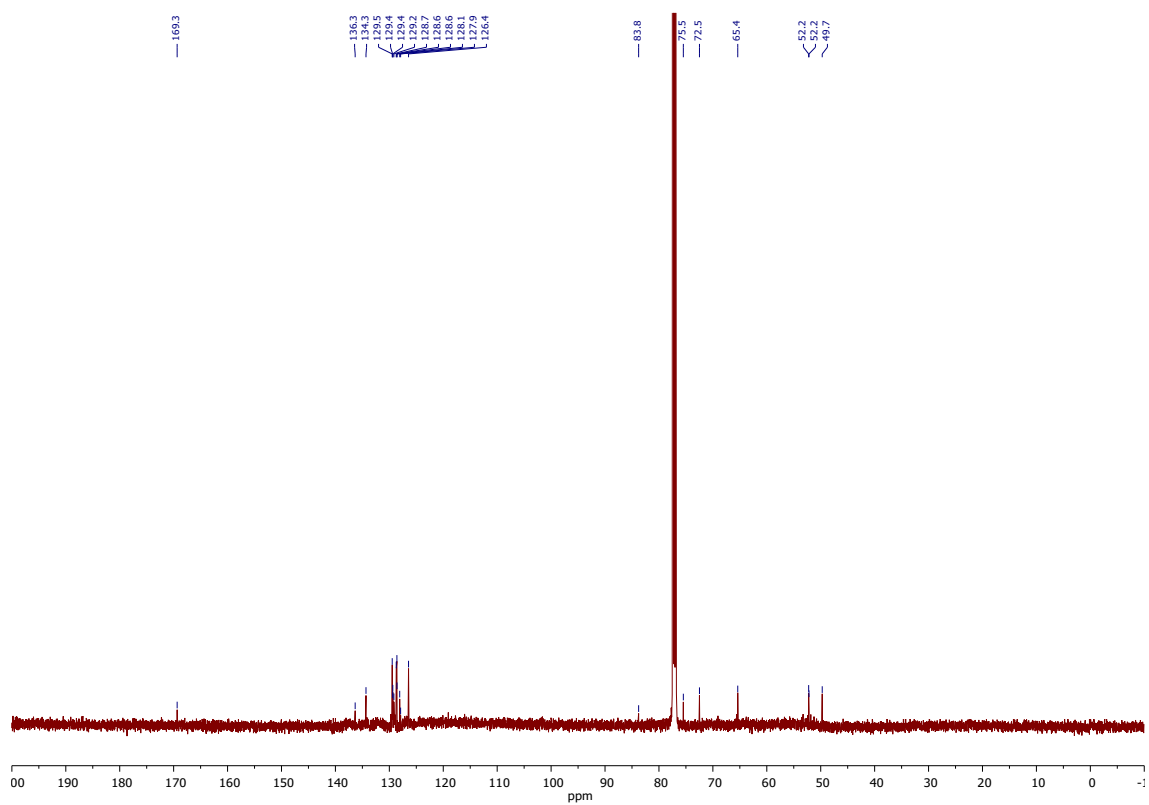
NOESY of 2ae



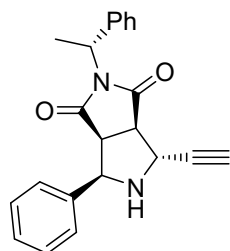
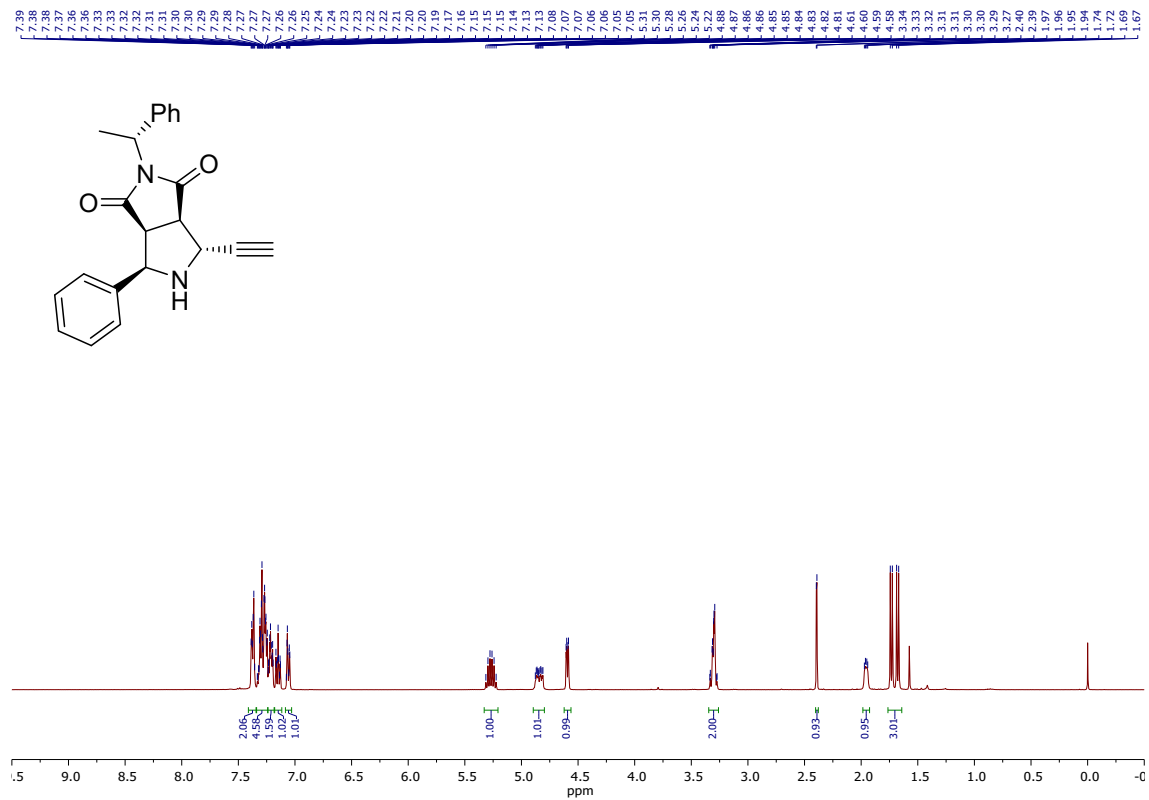
¹H NMR of 2af



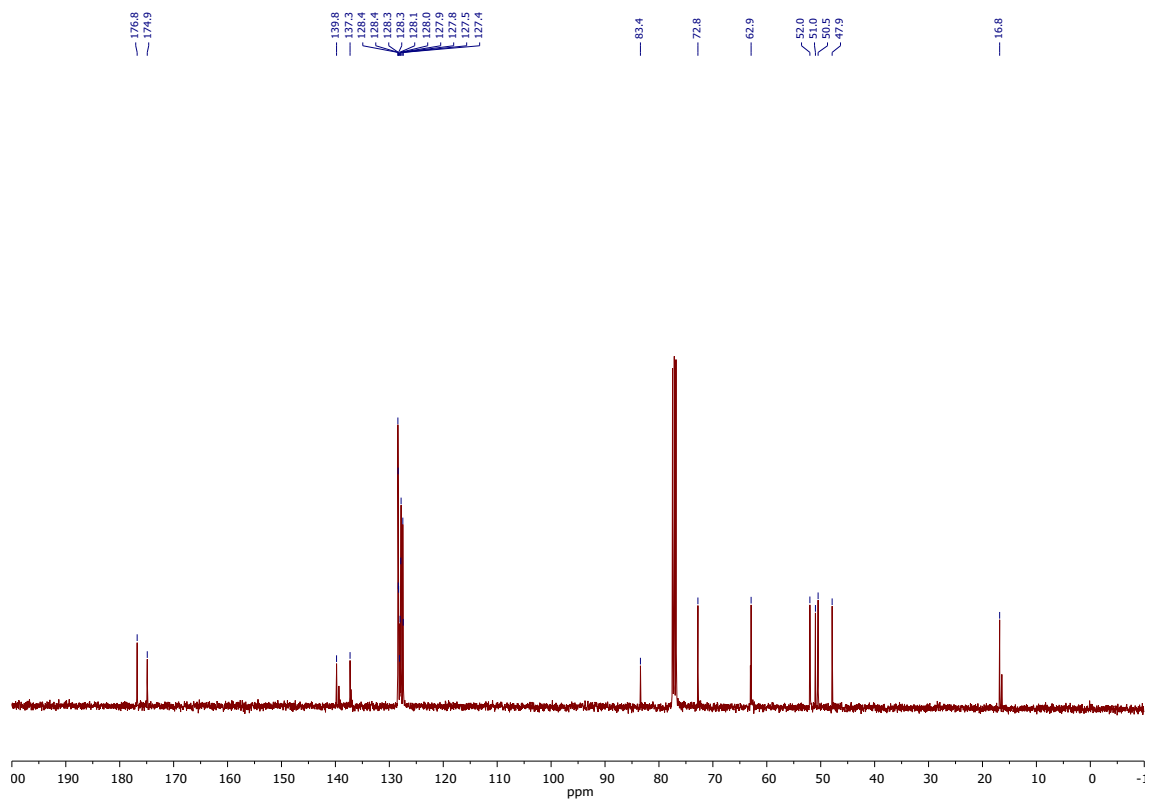
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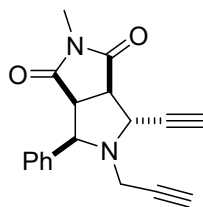
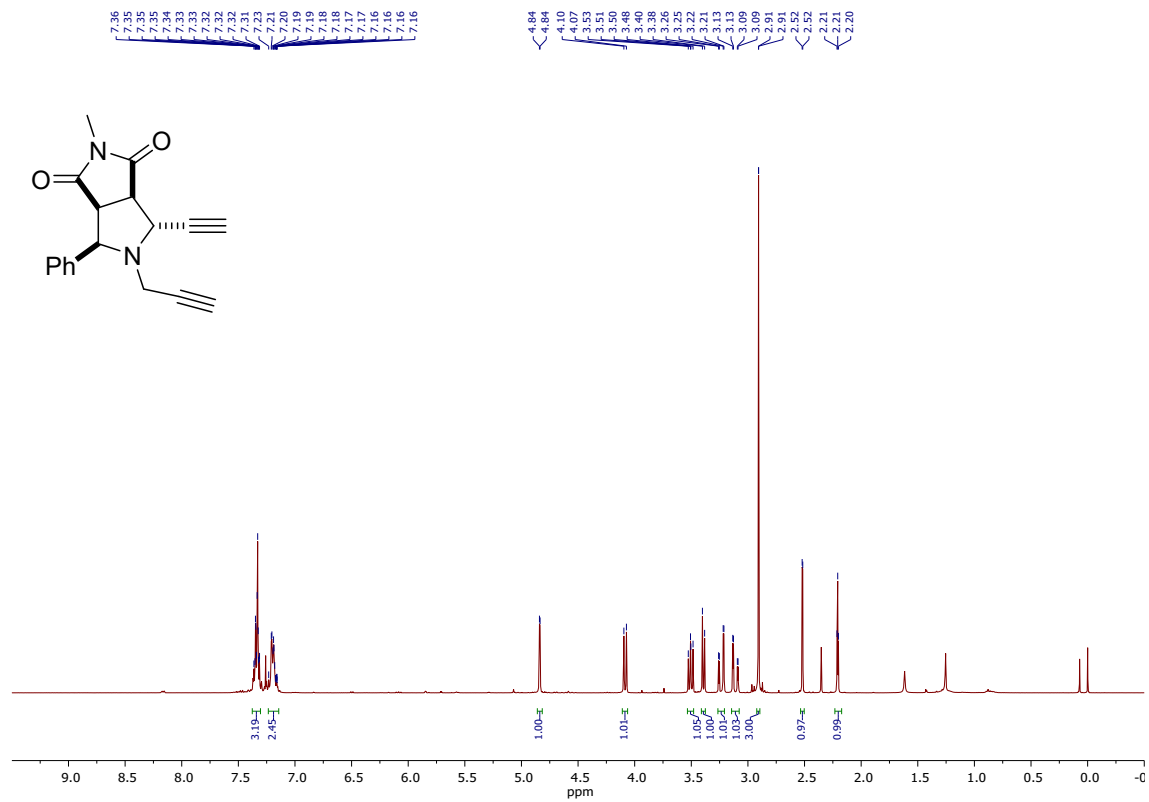
¹H NMR of 2ag



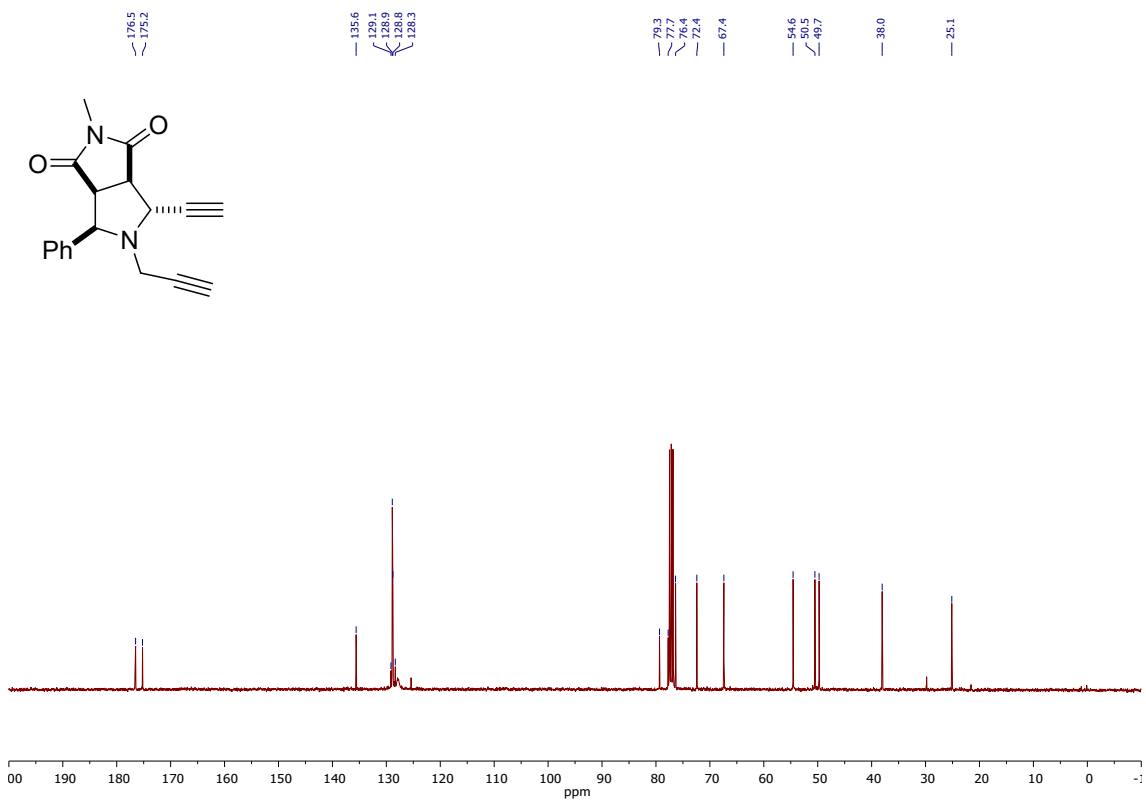
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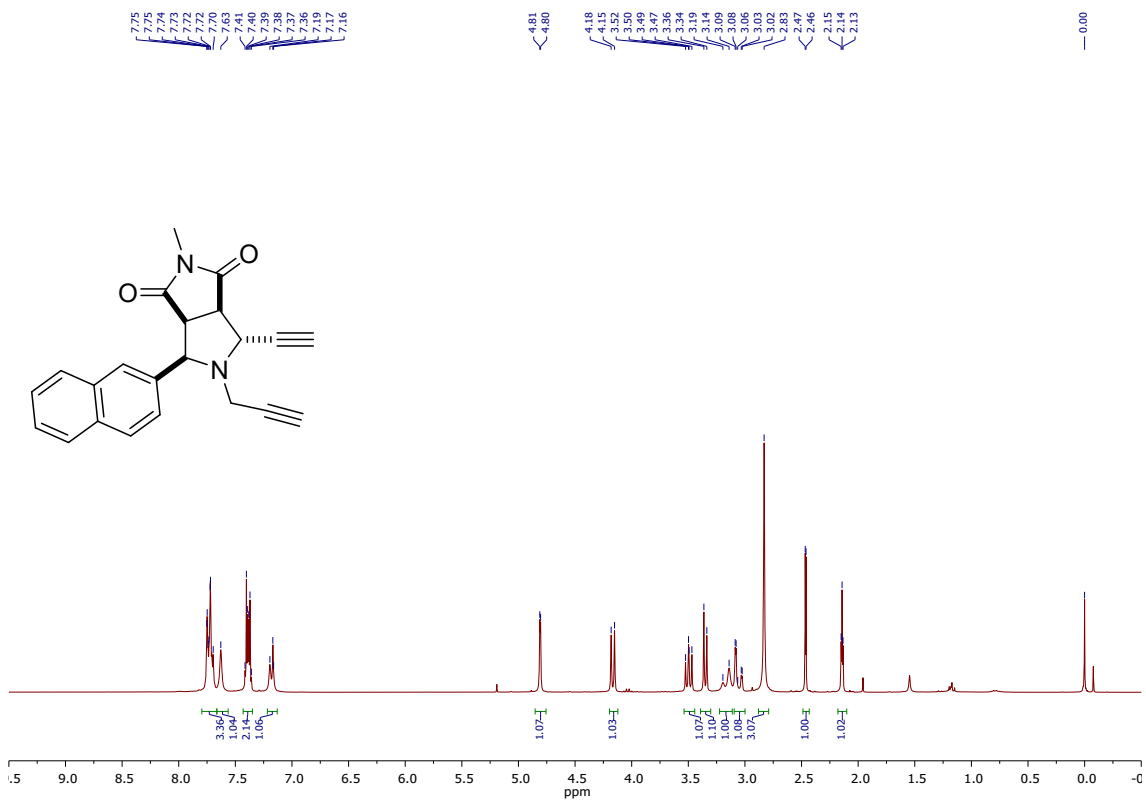
¹H NMR of 3aa



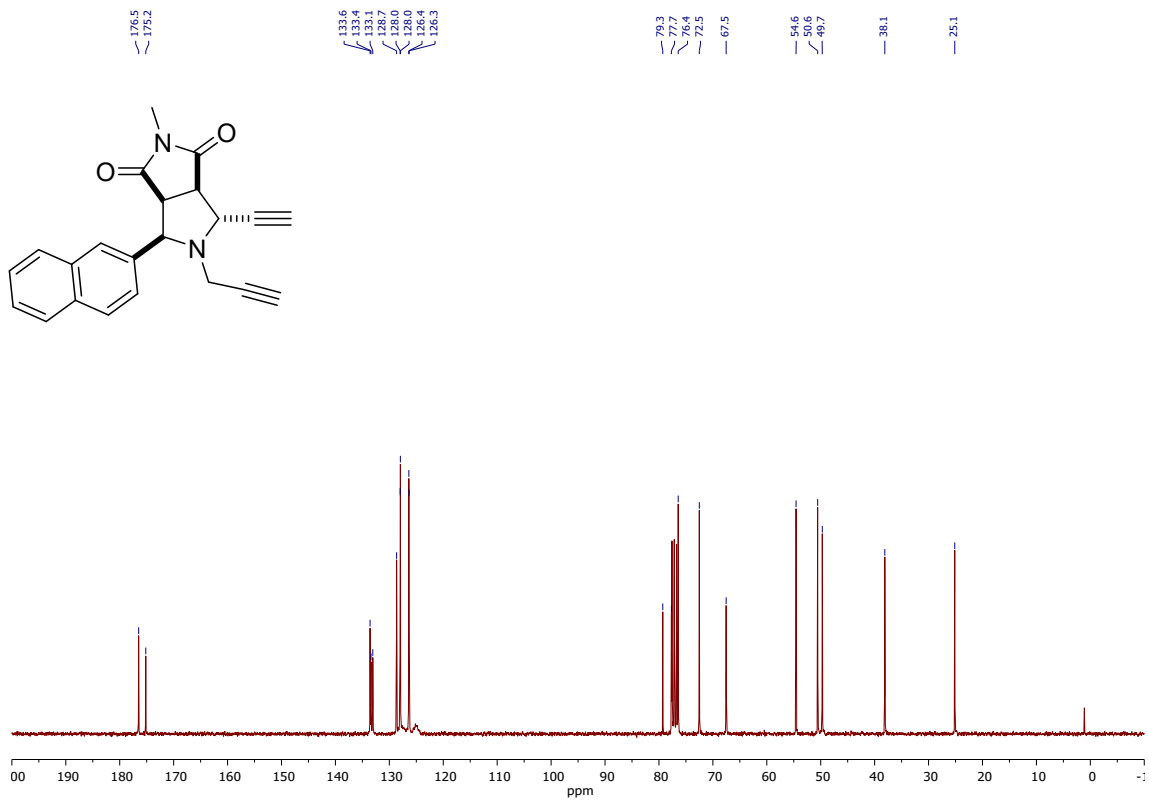
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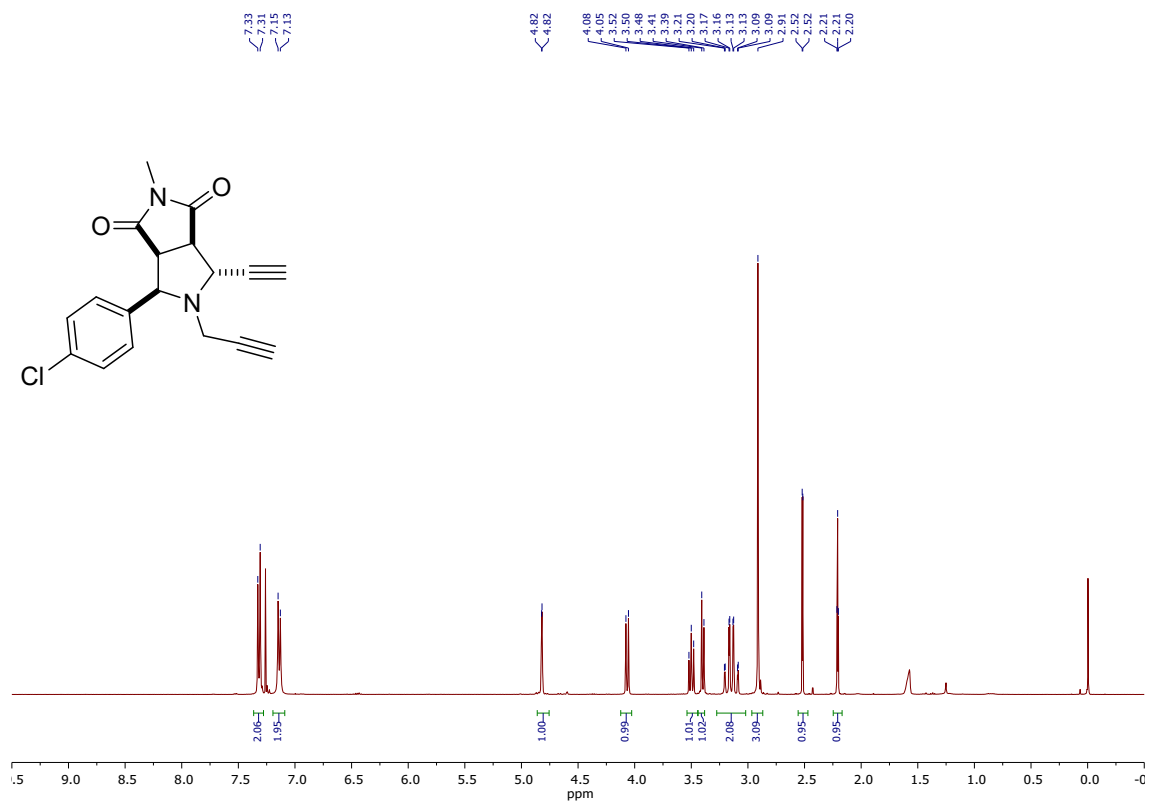
¹H NMR of 3ba



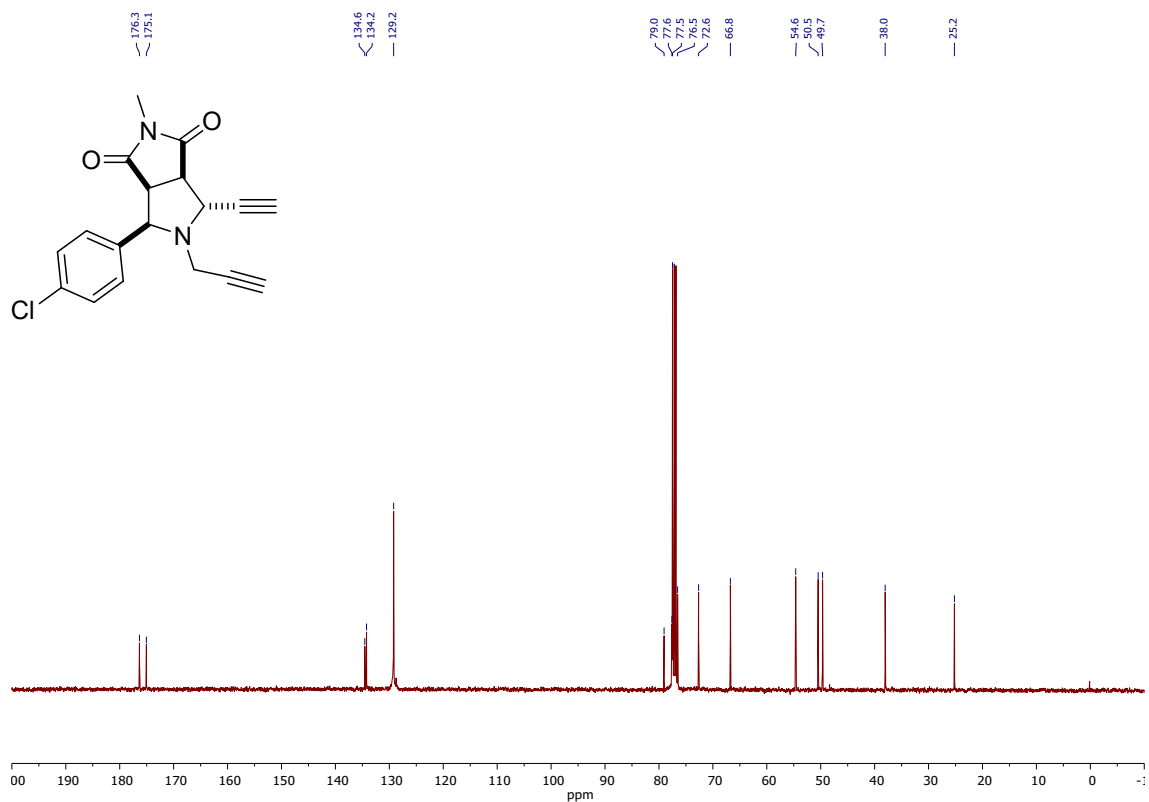
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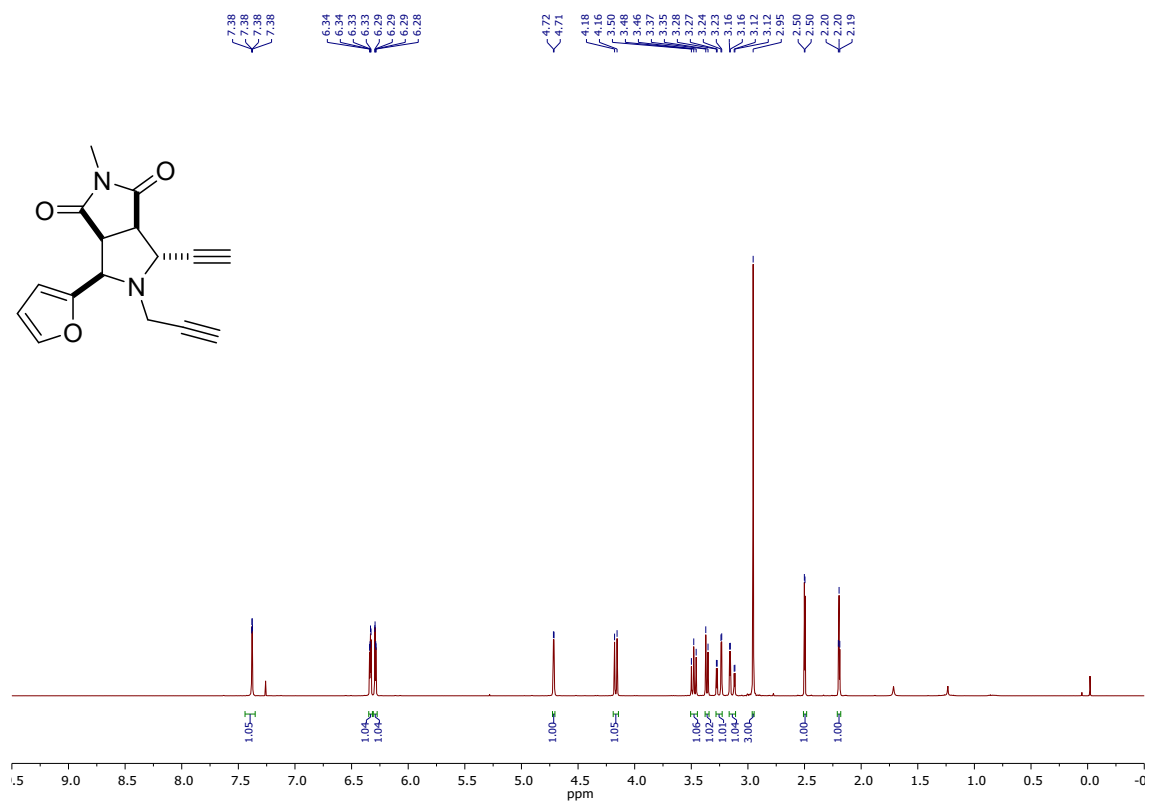
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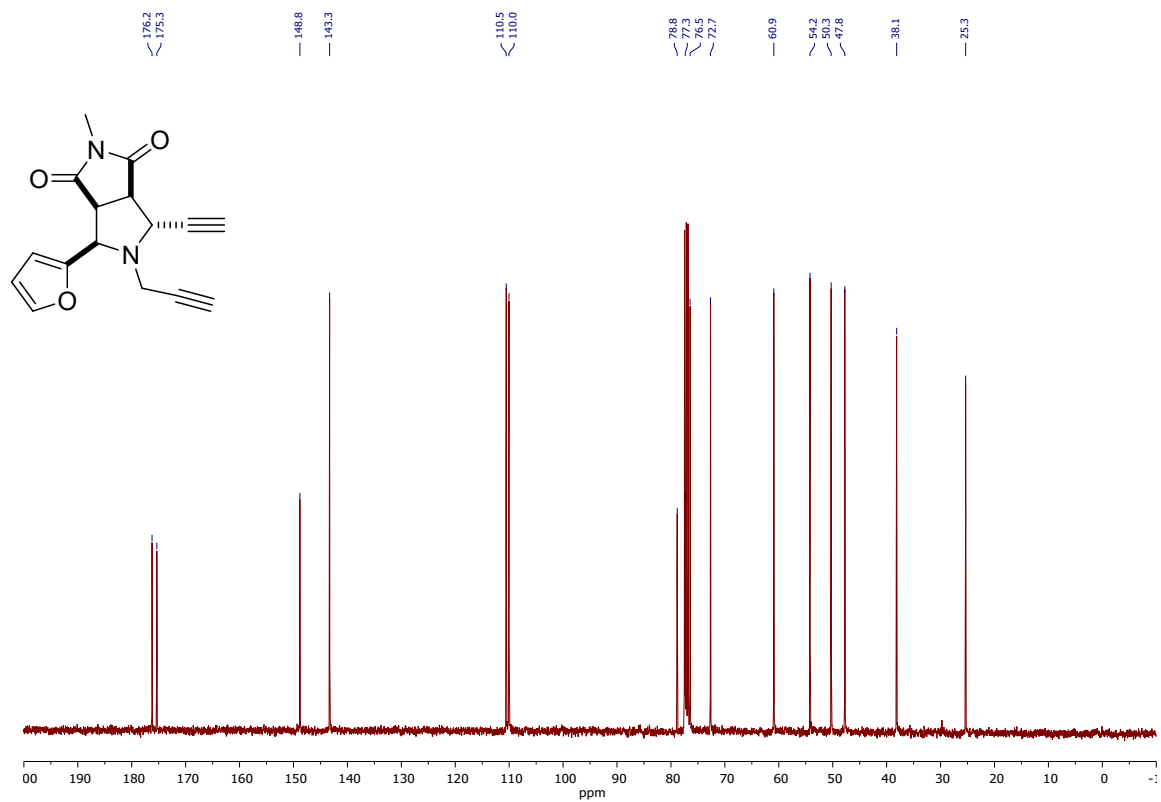
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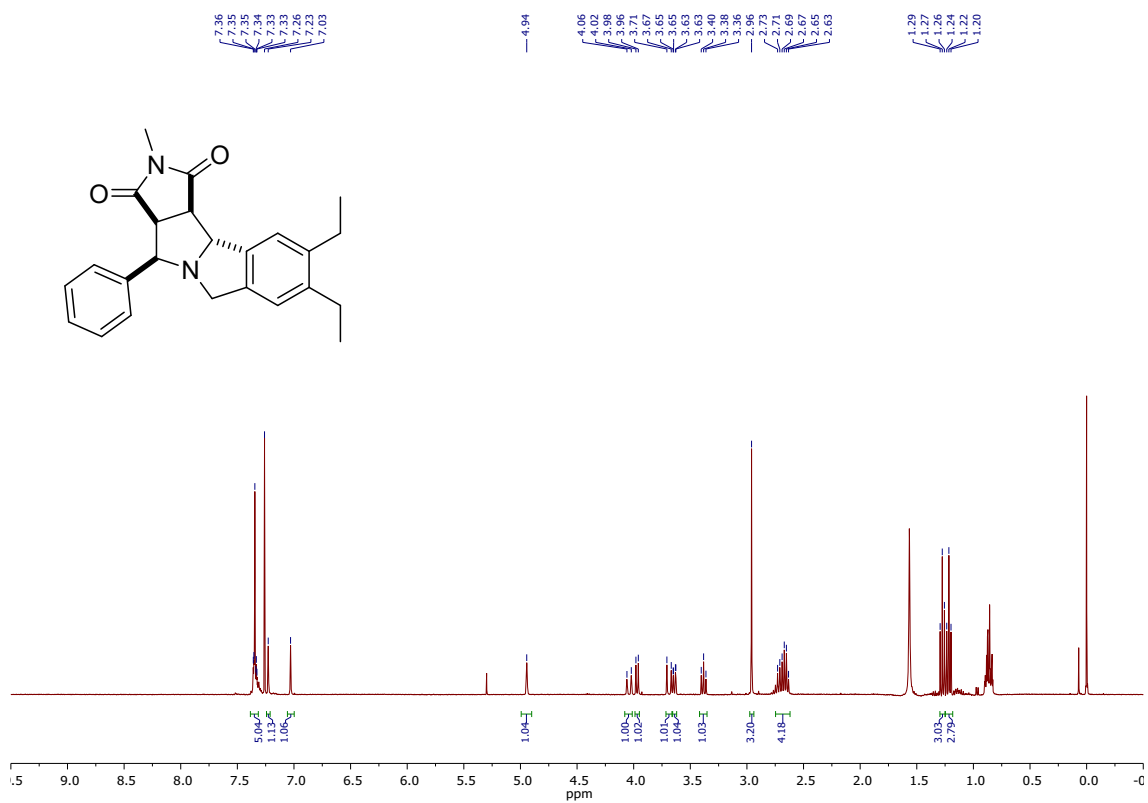
¹H NMR of 3ga



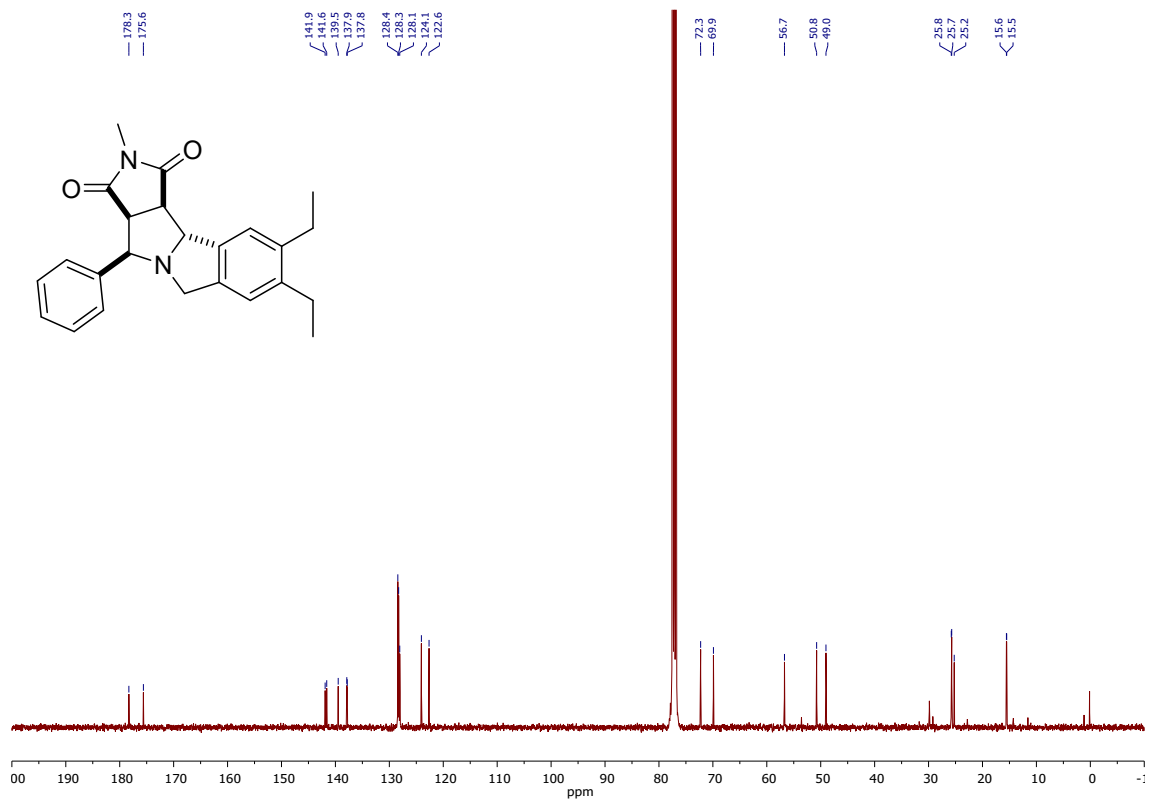
¹³C{¹H} NMR of 3ga



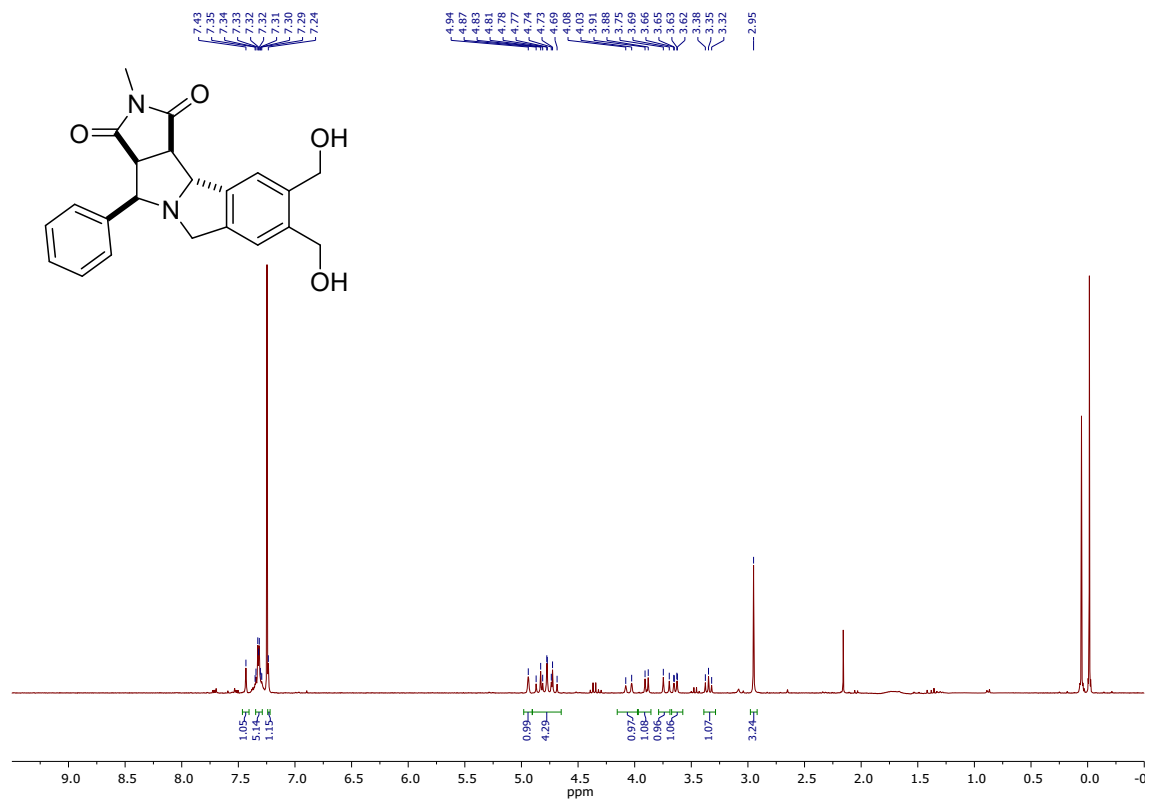
¹H NMR of 4aa



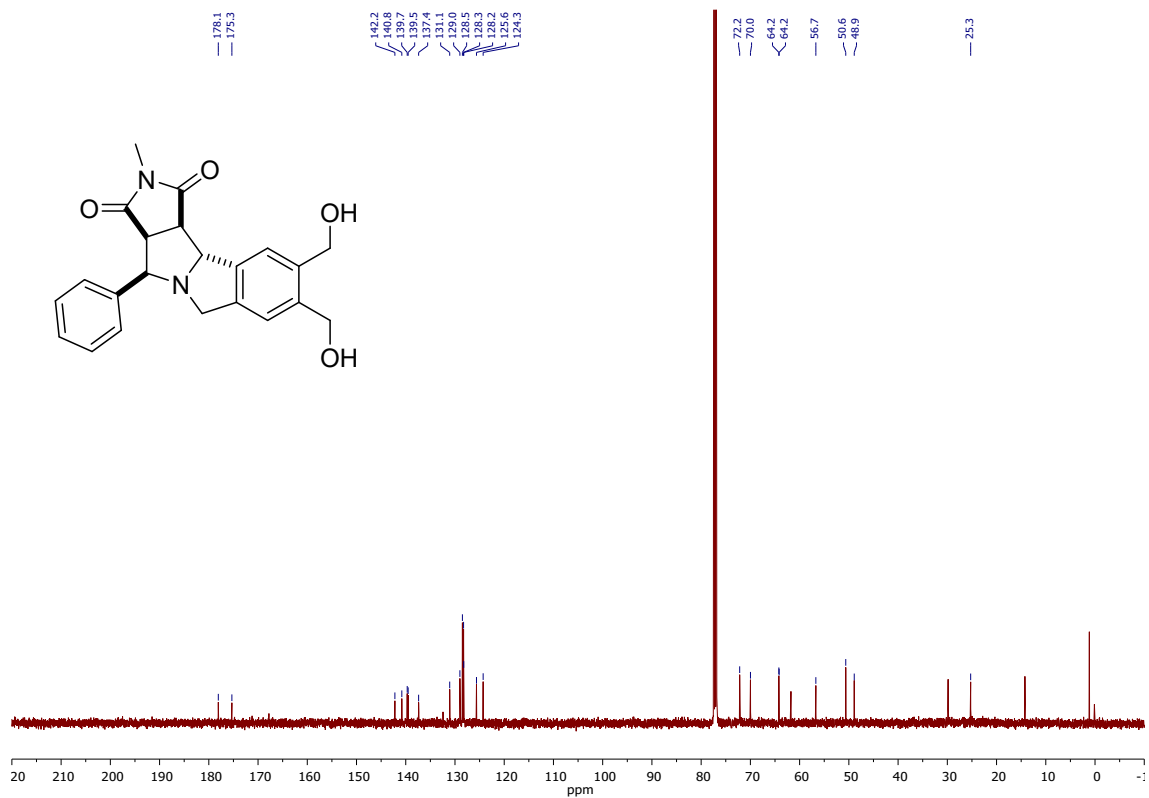
¹³C{¹H} NMR of 4aa



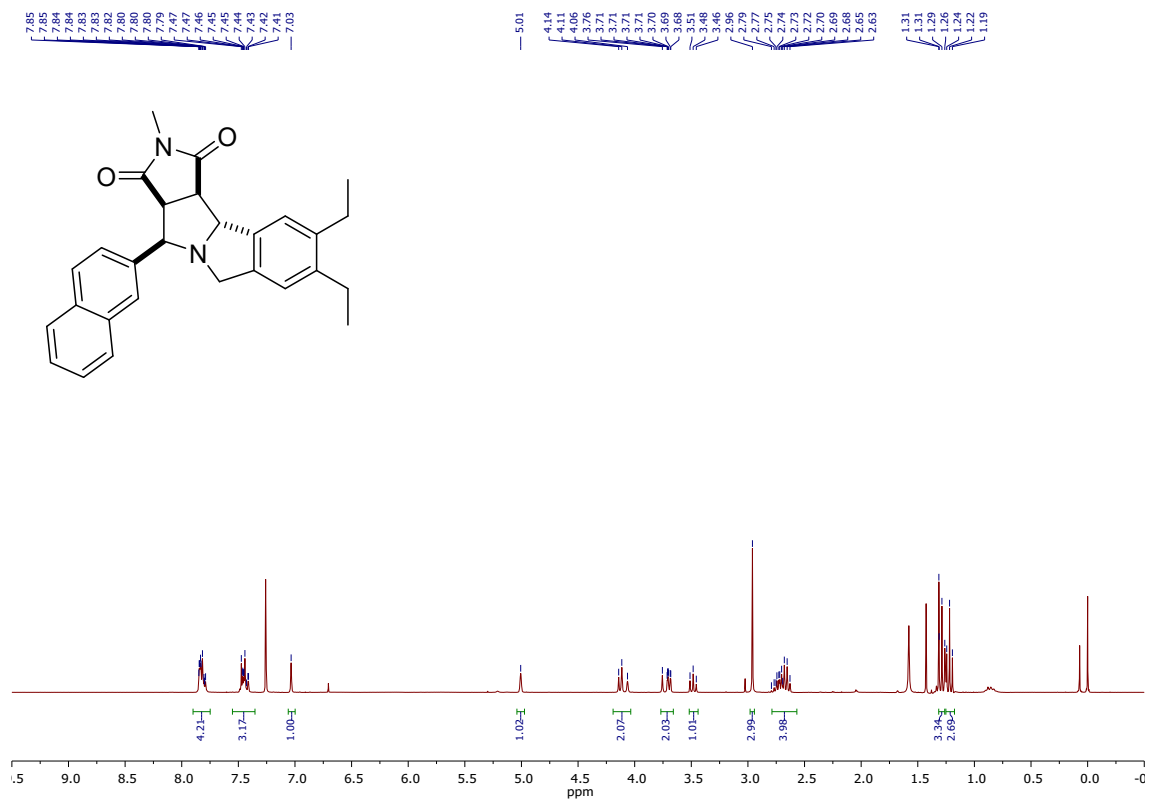
¹H NMR of 4ab



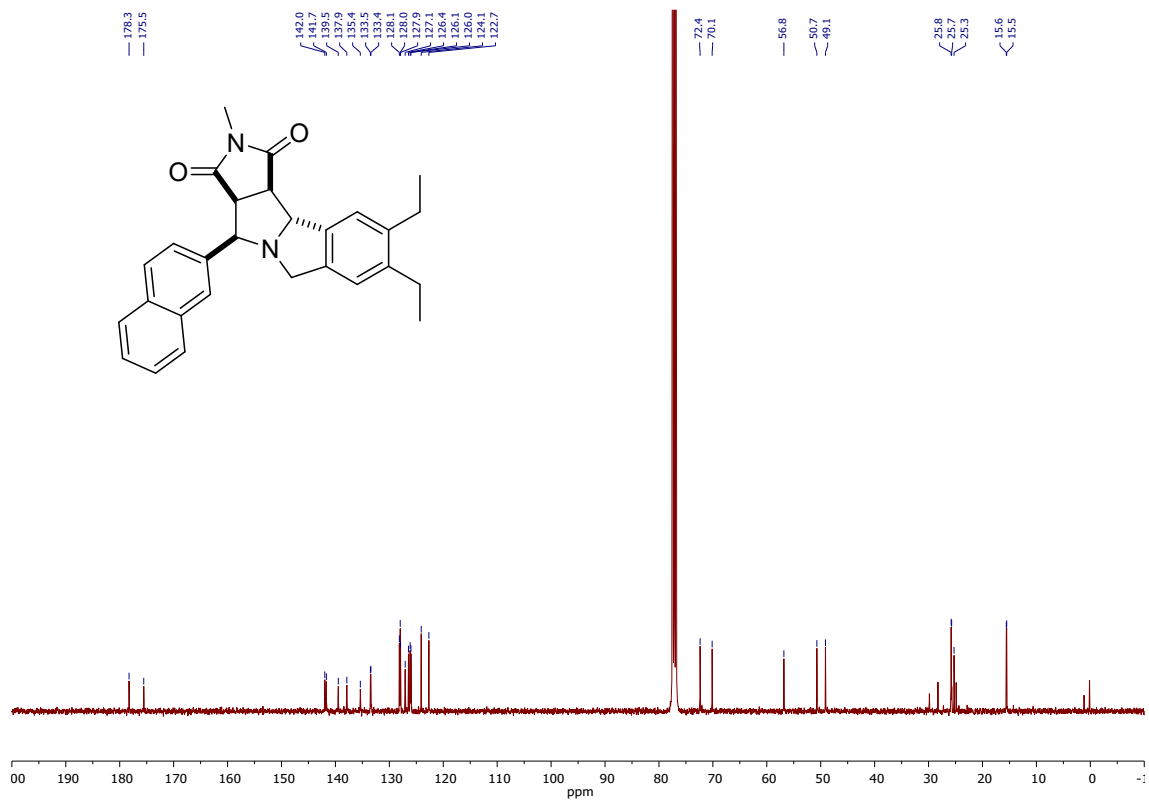
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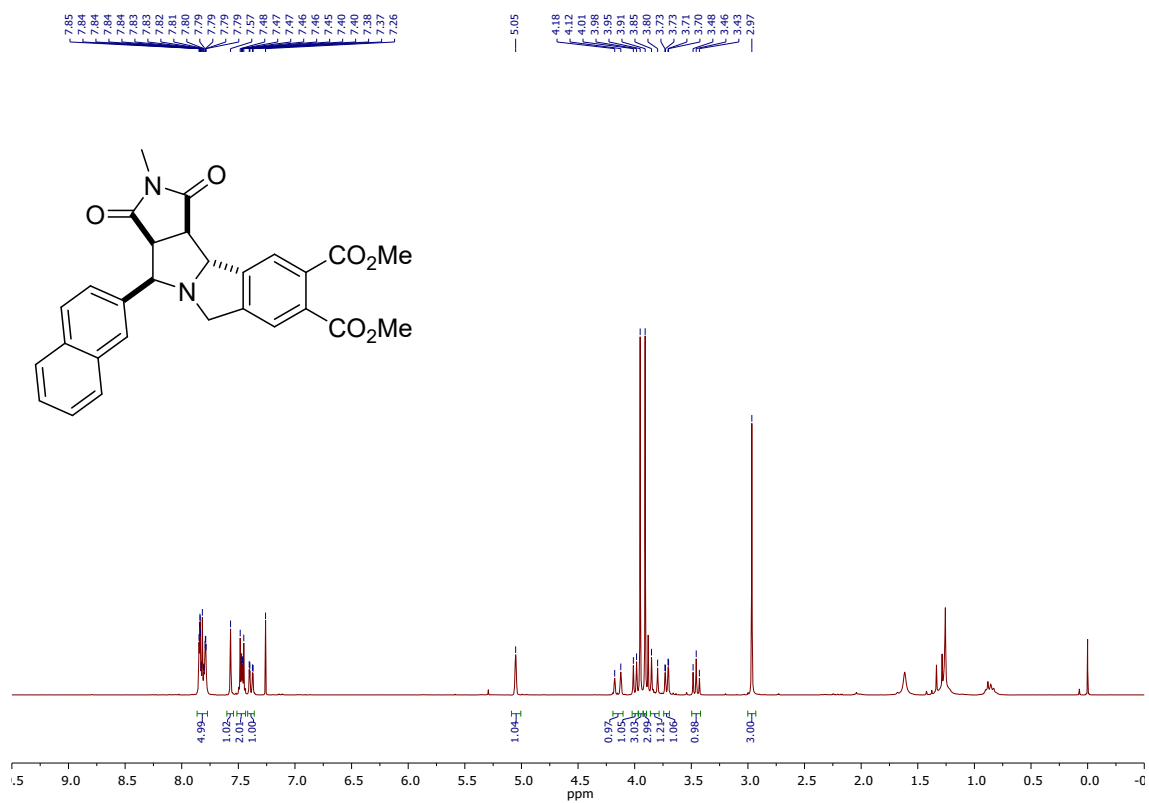
¹H NMR of 4ba



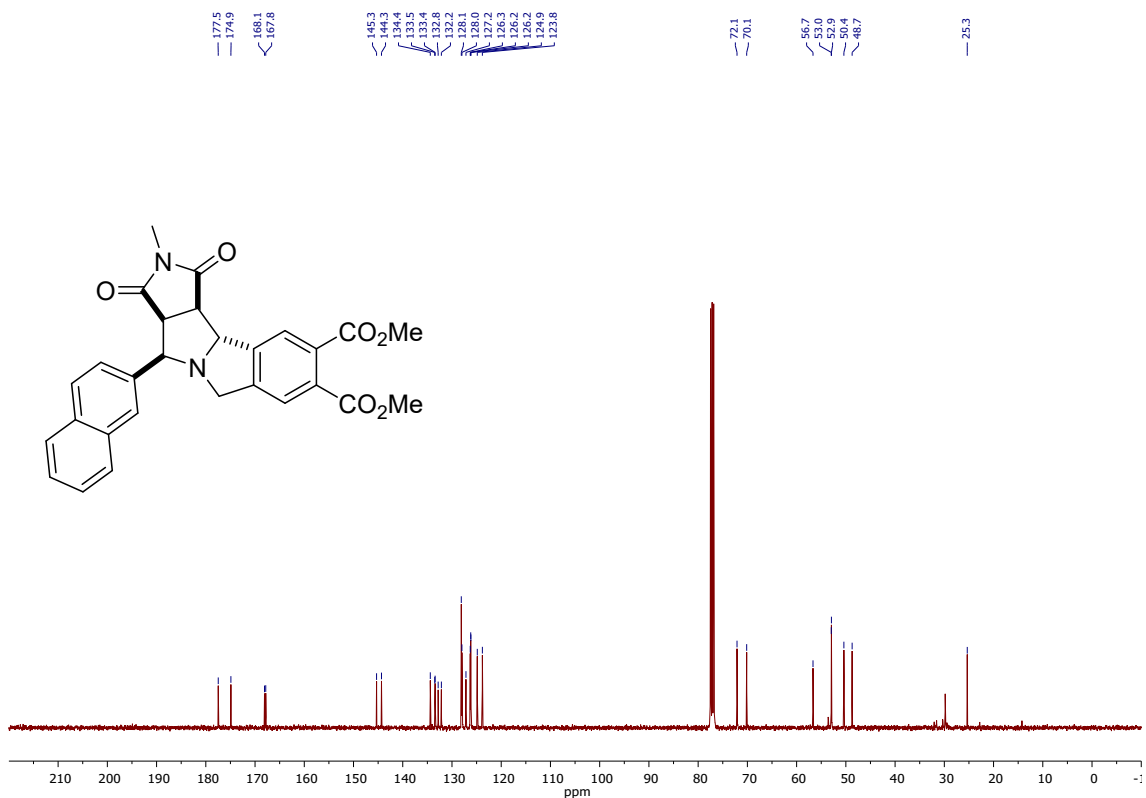
¹³C{¹H} NMR of 4ba



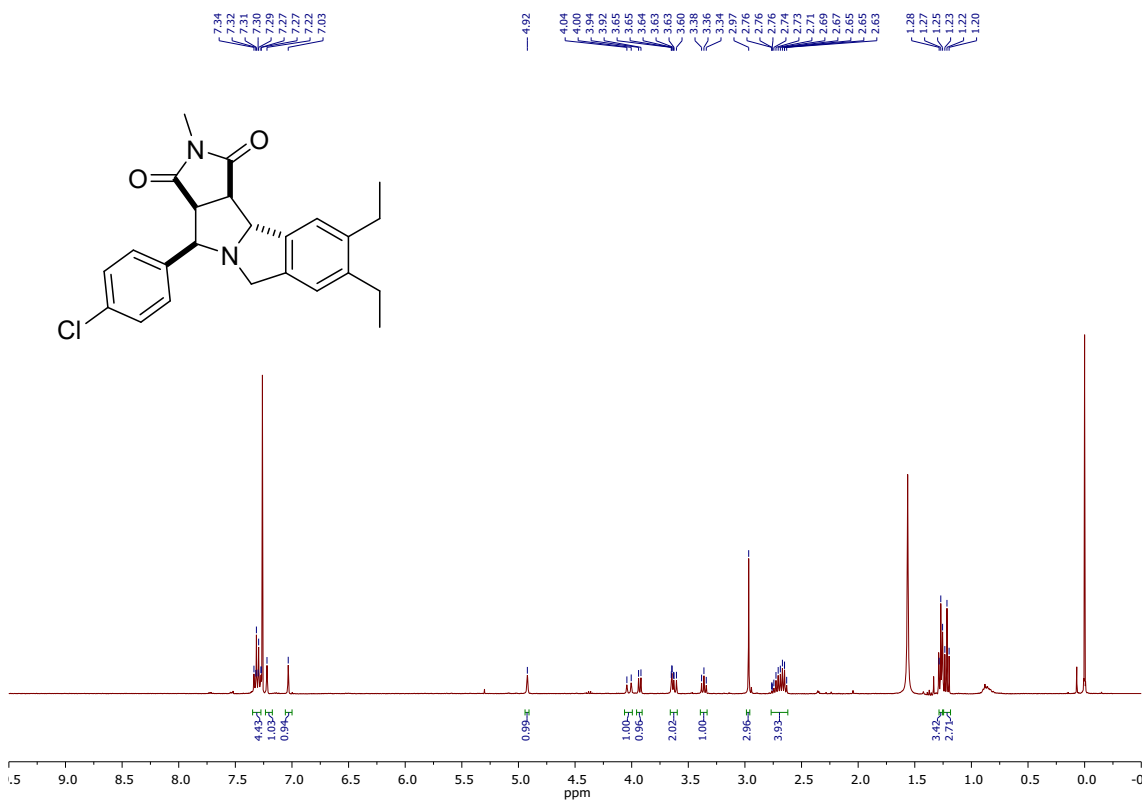
¹H NMR of 4bc



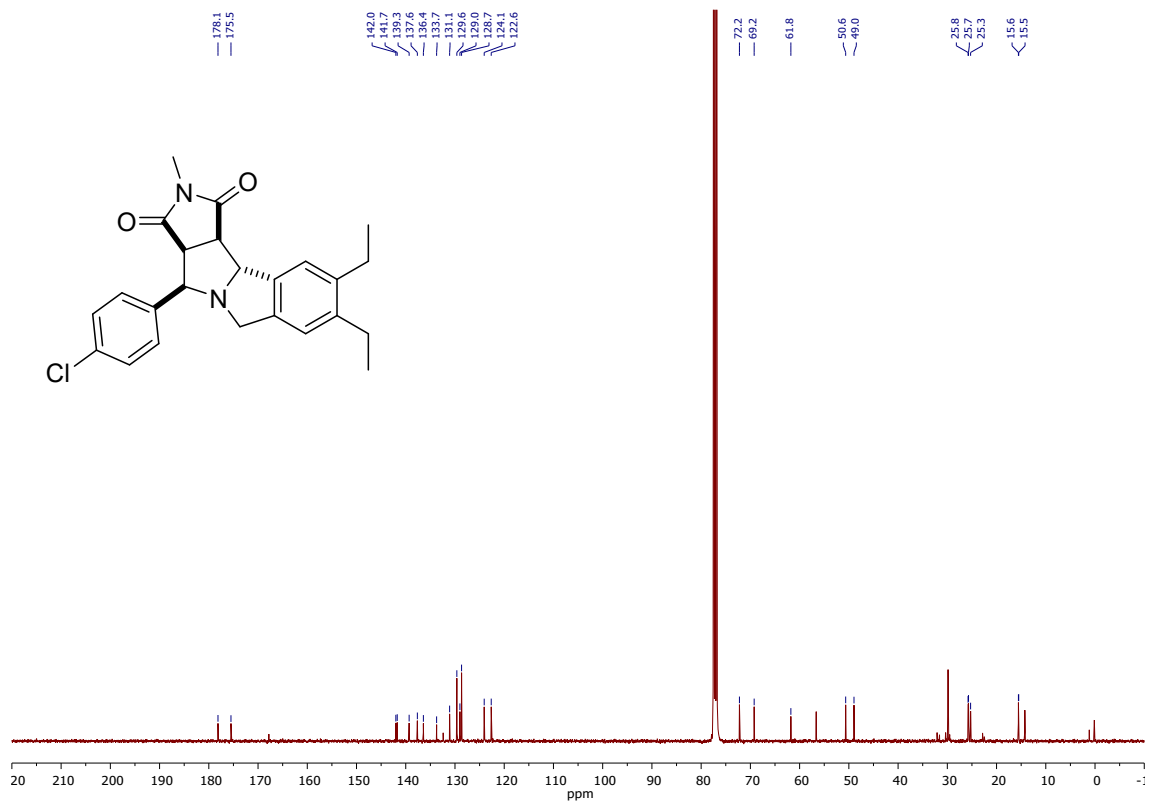
$^{13}\text{C}\{^1\text{H}\}$ NMR of **4bc**



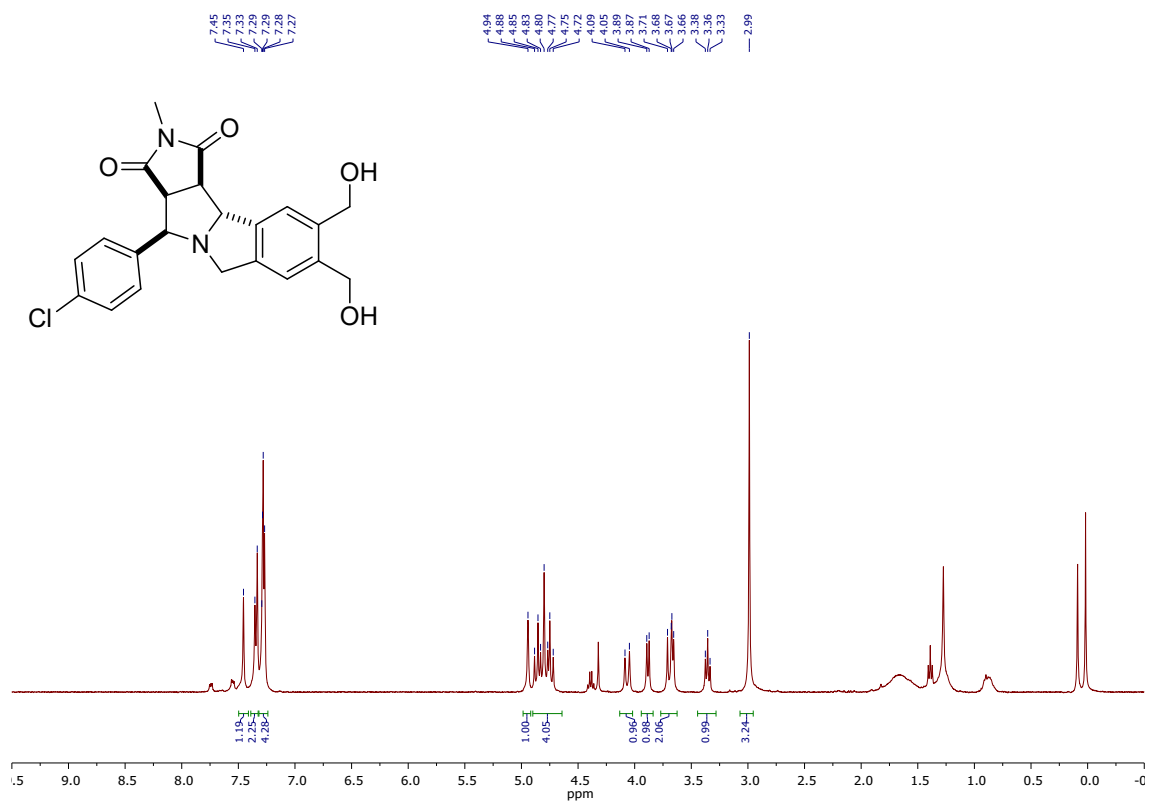
^1H NMR of **4da**



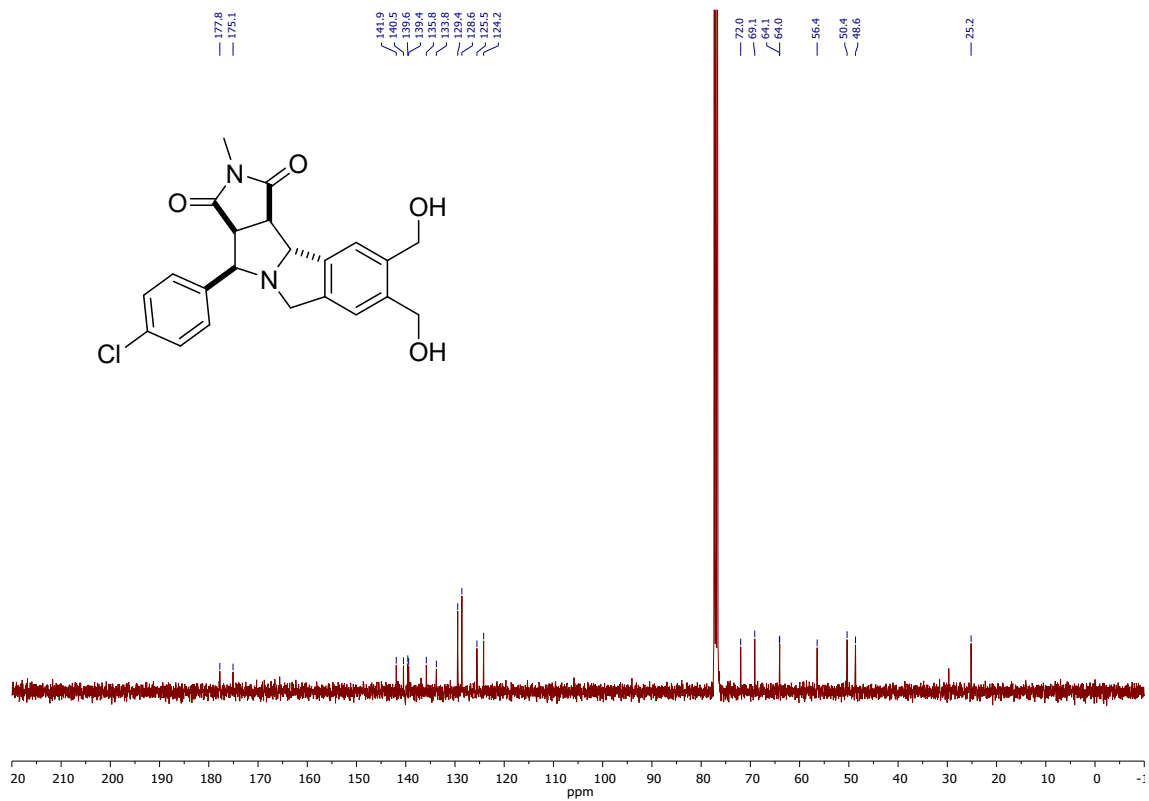
$^{13}\text{C}\{^1\text{H}\}$ NMR of **4da**



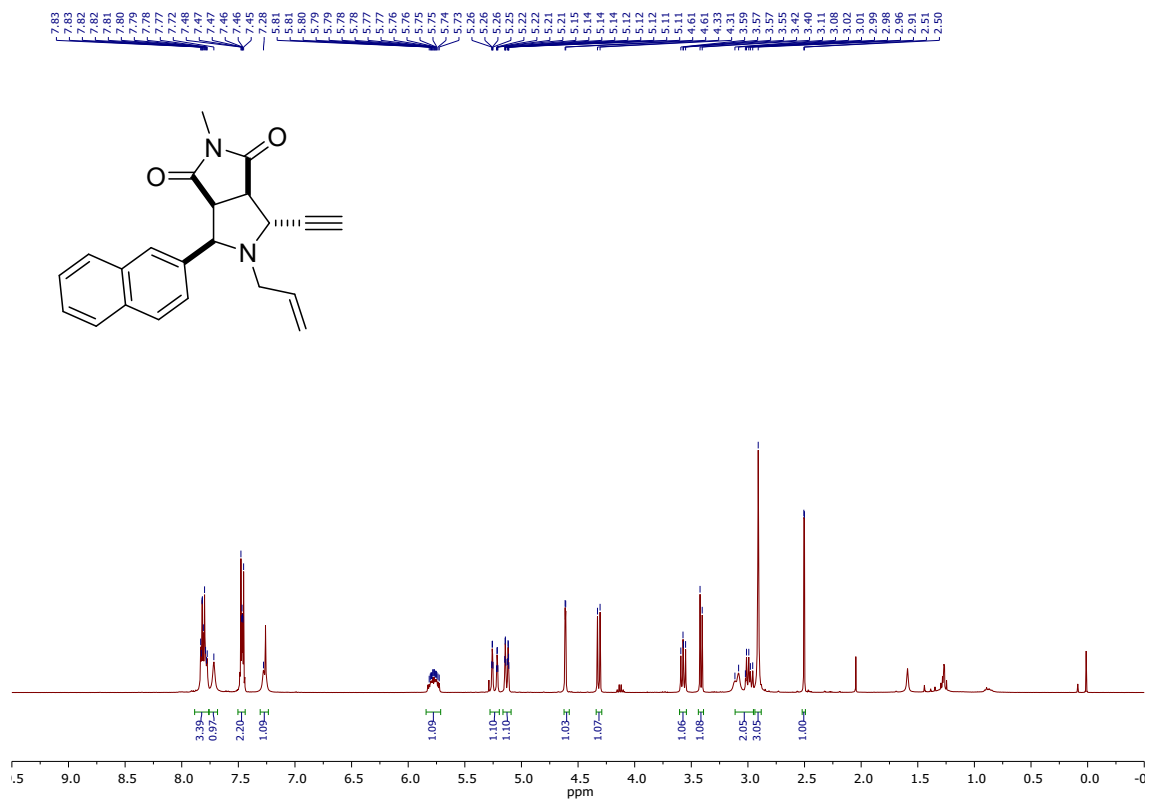
¹H NMR of 4db



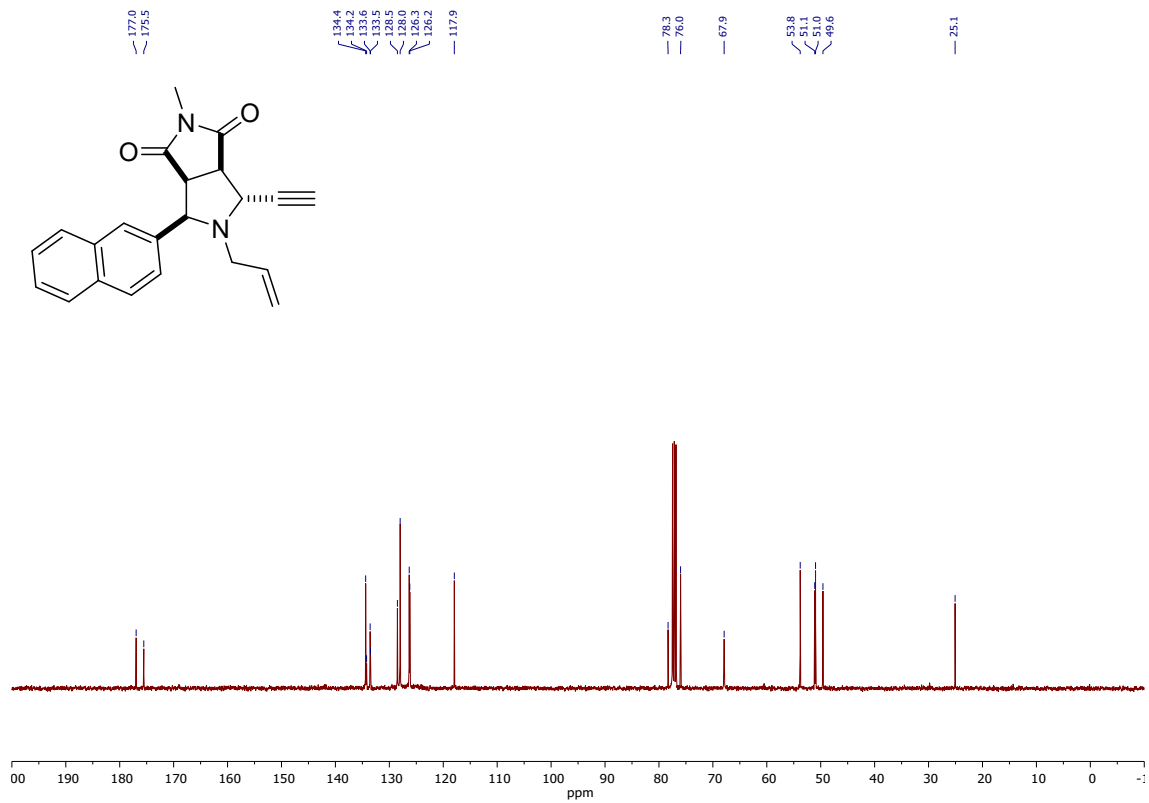
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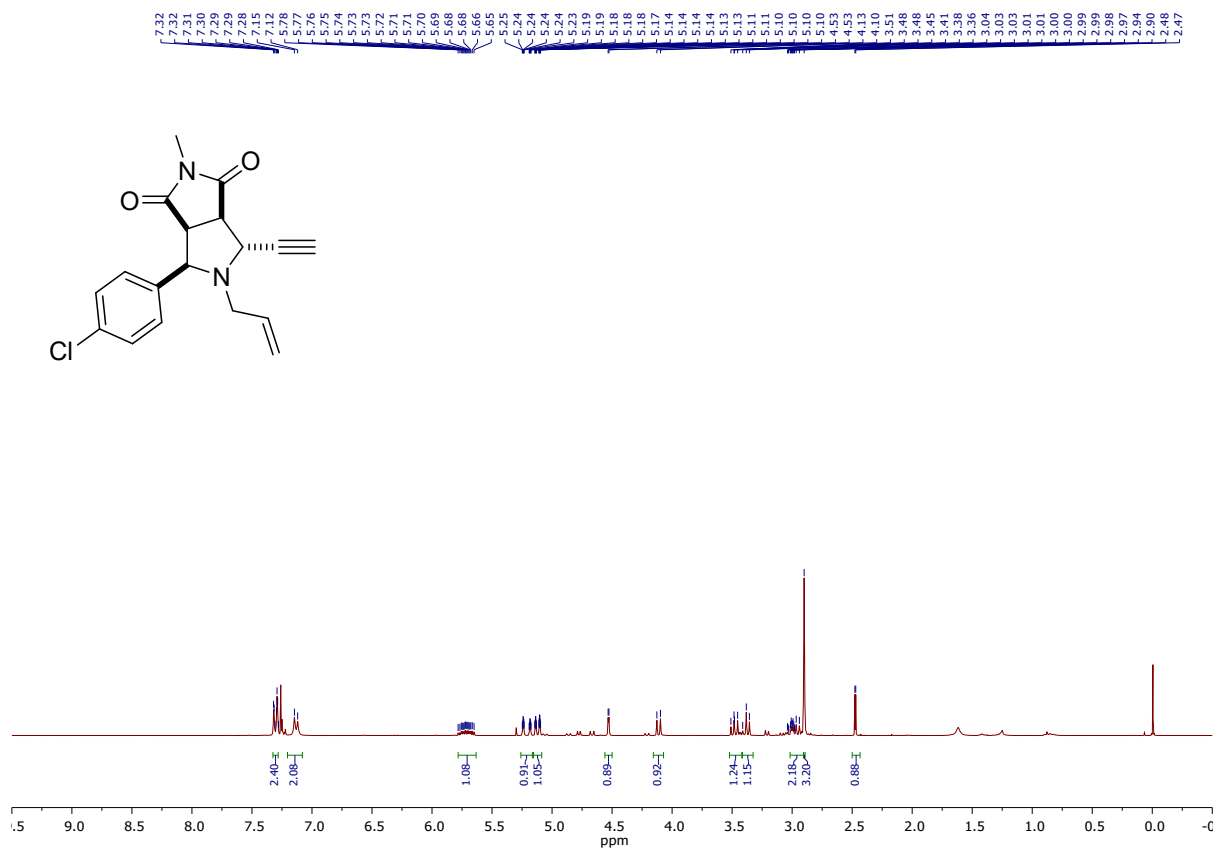
¹H NMR of 5ba



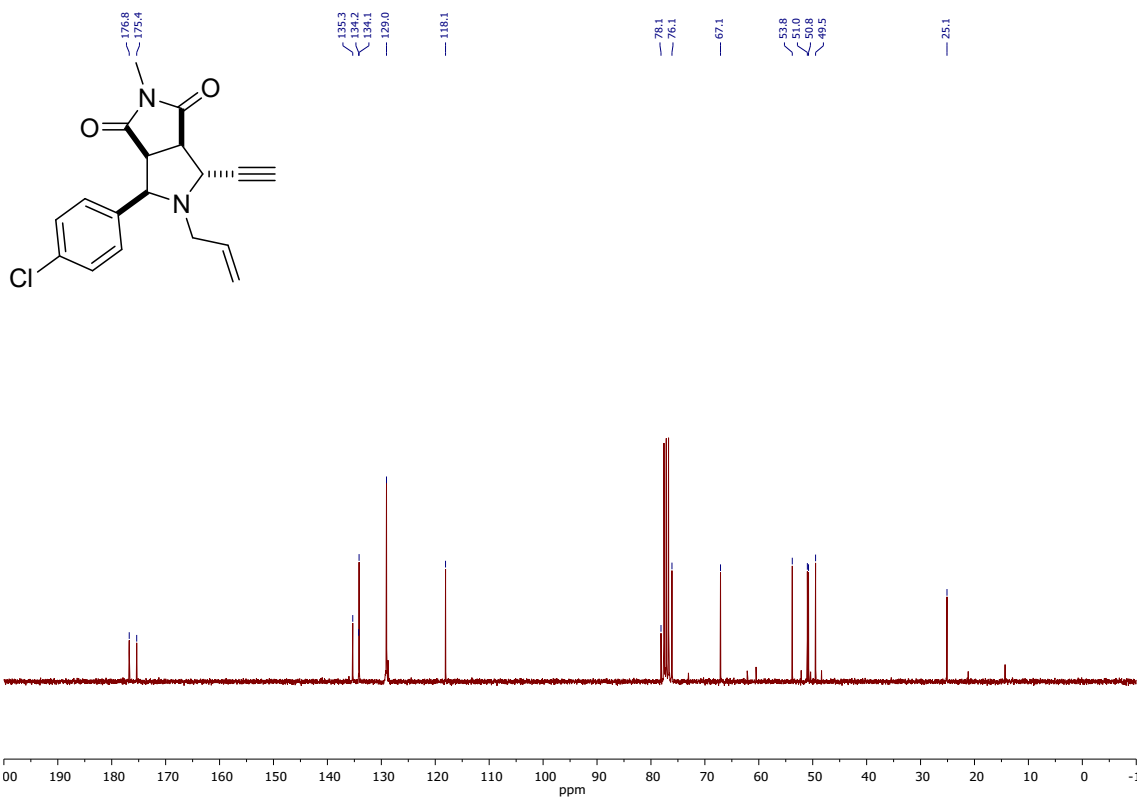
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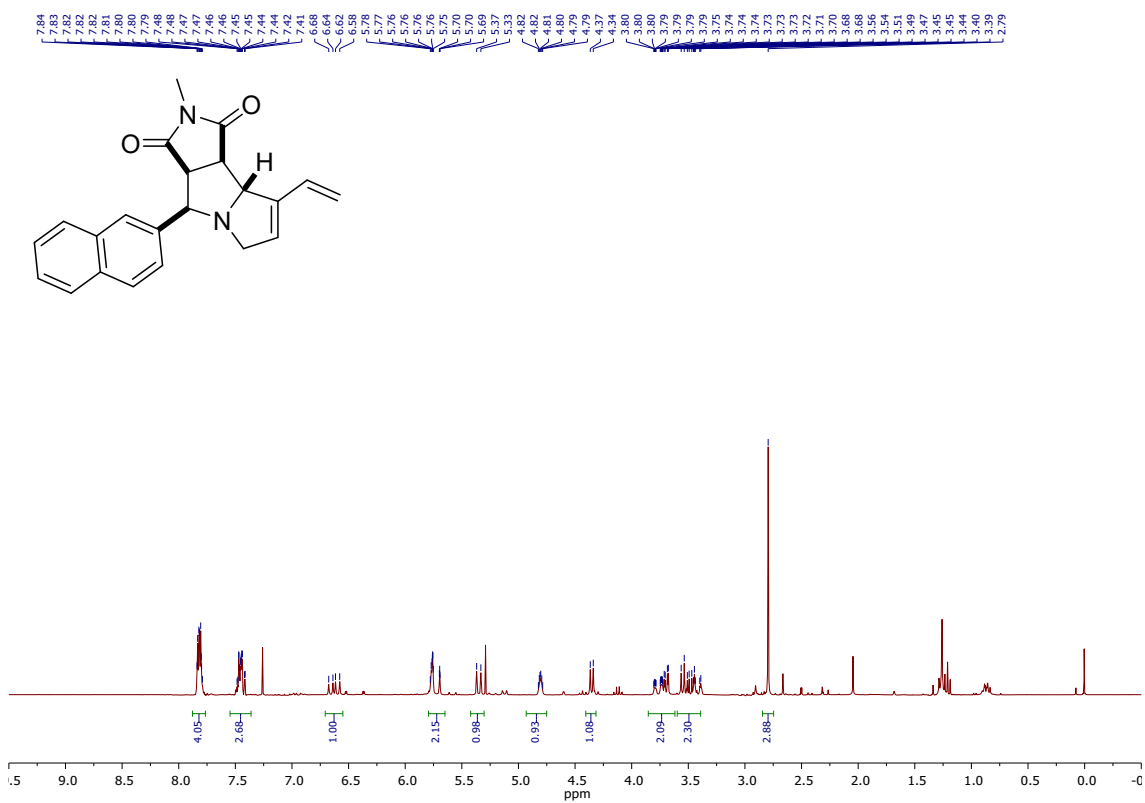
¹H NMR of 5da



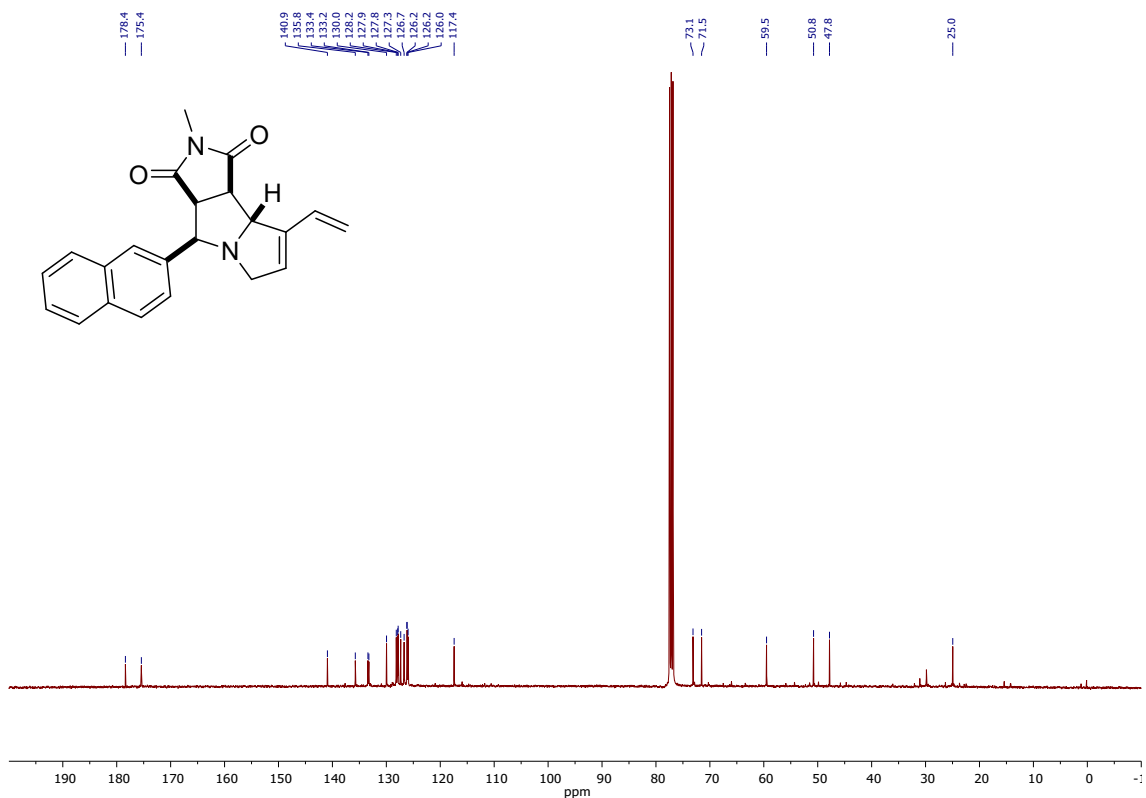
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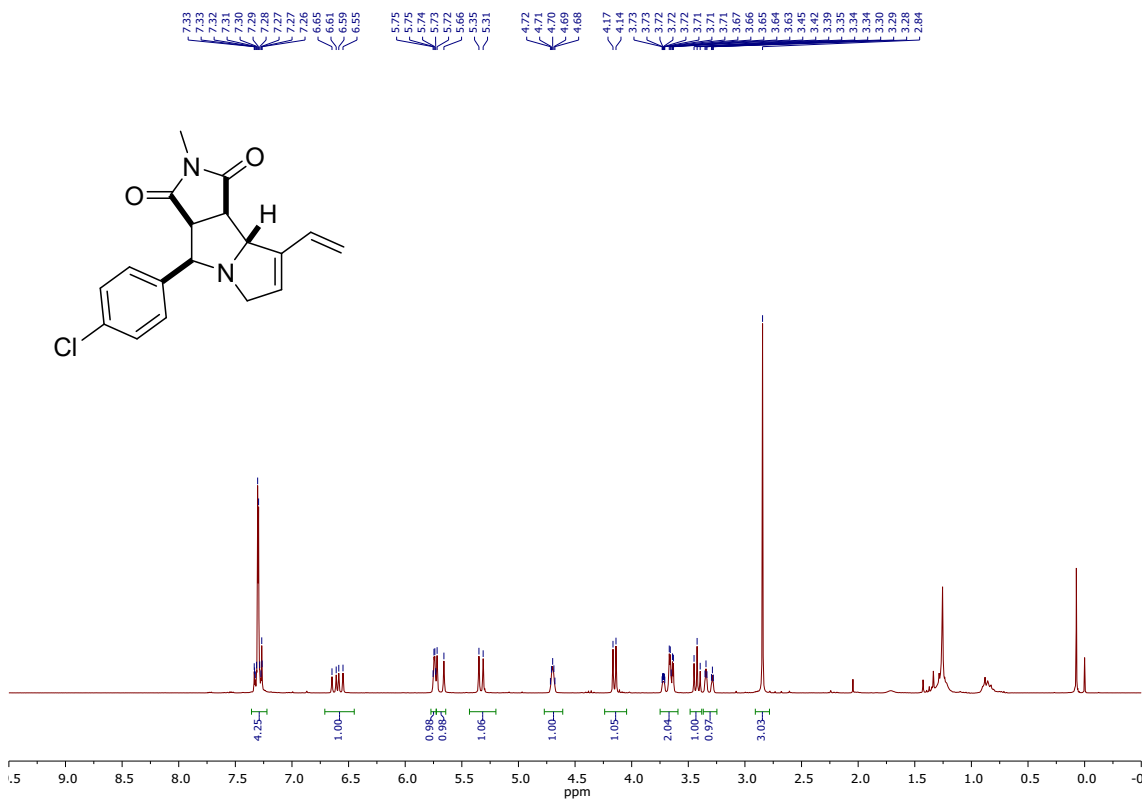
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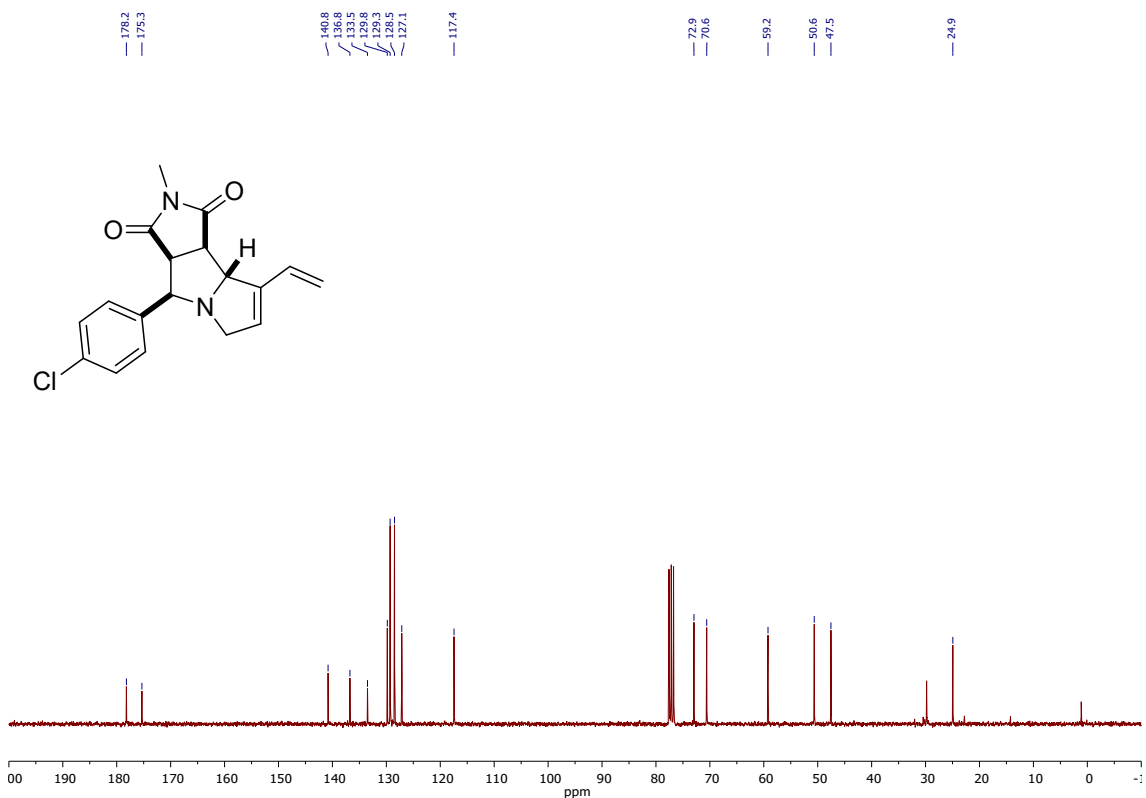
$^{13}\text{C}\{^1\text{H}\}$ NMR of **6da**



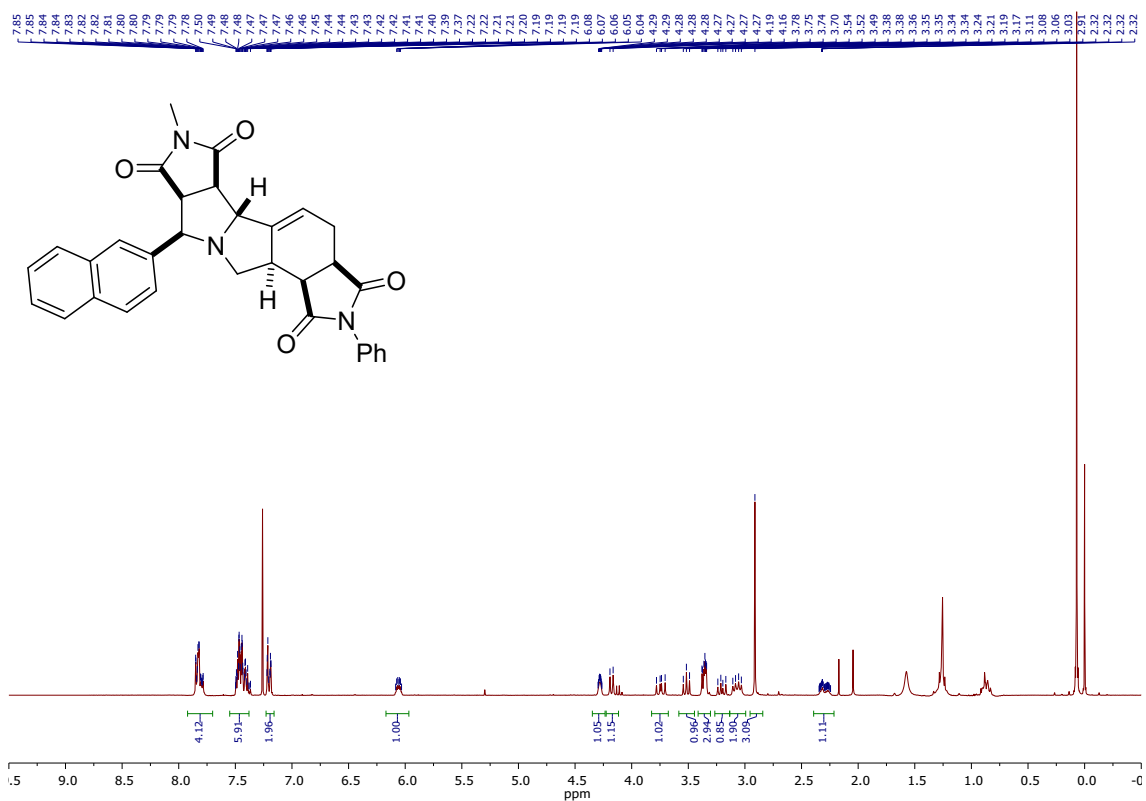
^1H NMR of **6db**



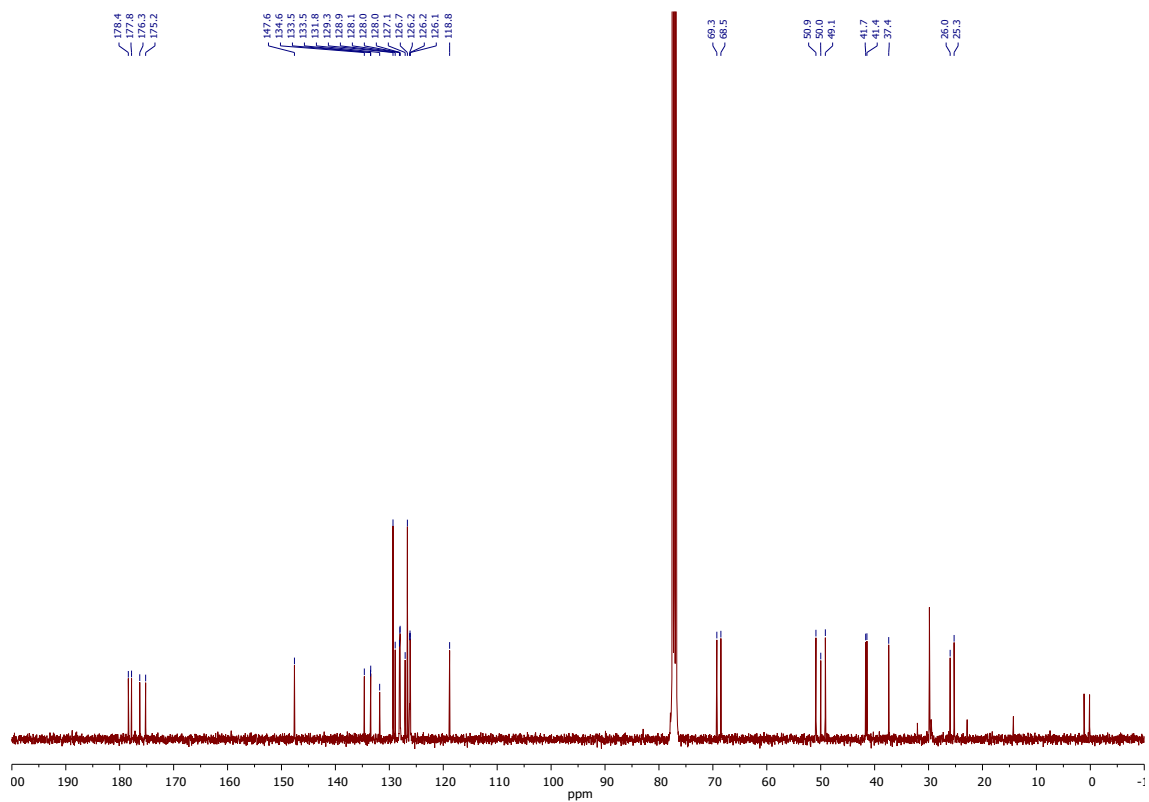
$^{13}\text{C}\{^1\text{H}\}$ NMR of **6db**



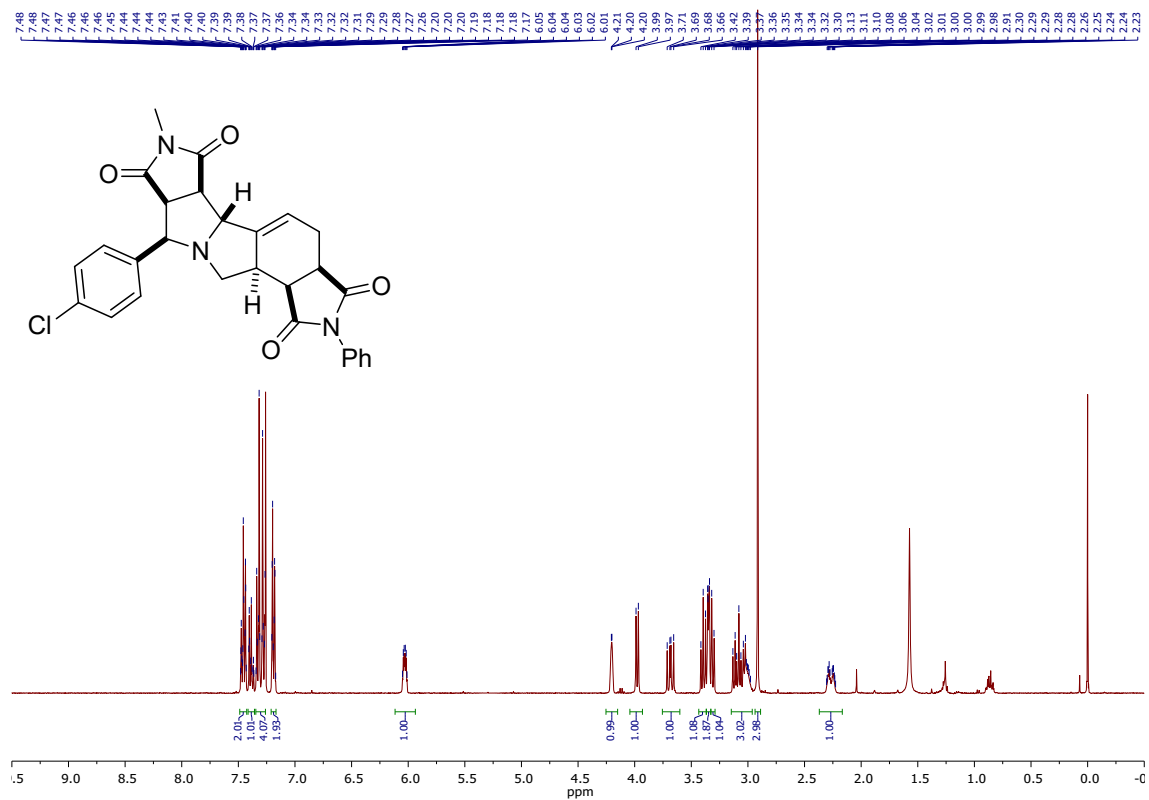
^1H NMR of **7ba**



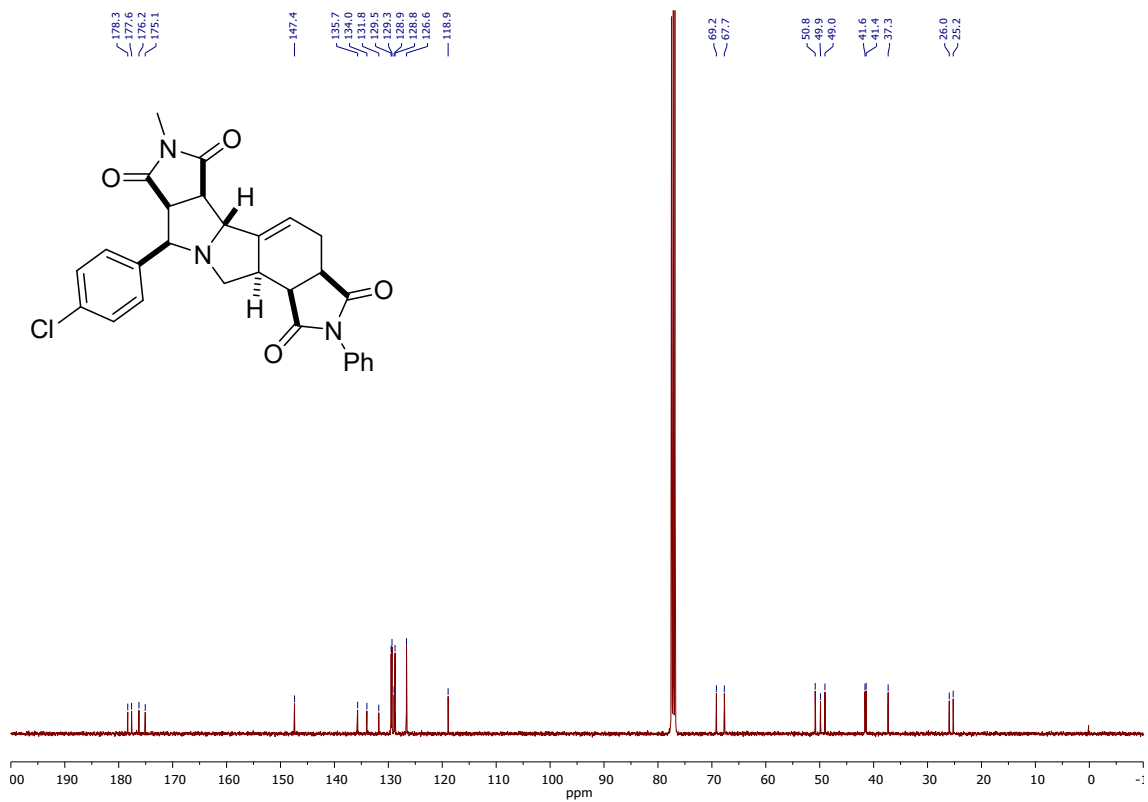
$^{13}\text{C}\{\text{H}\}$ NMR of **7ba**



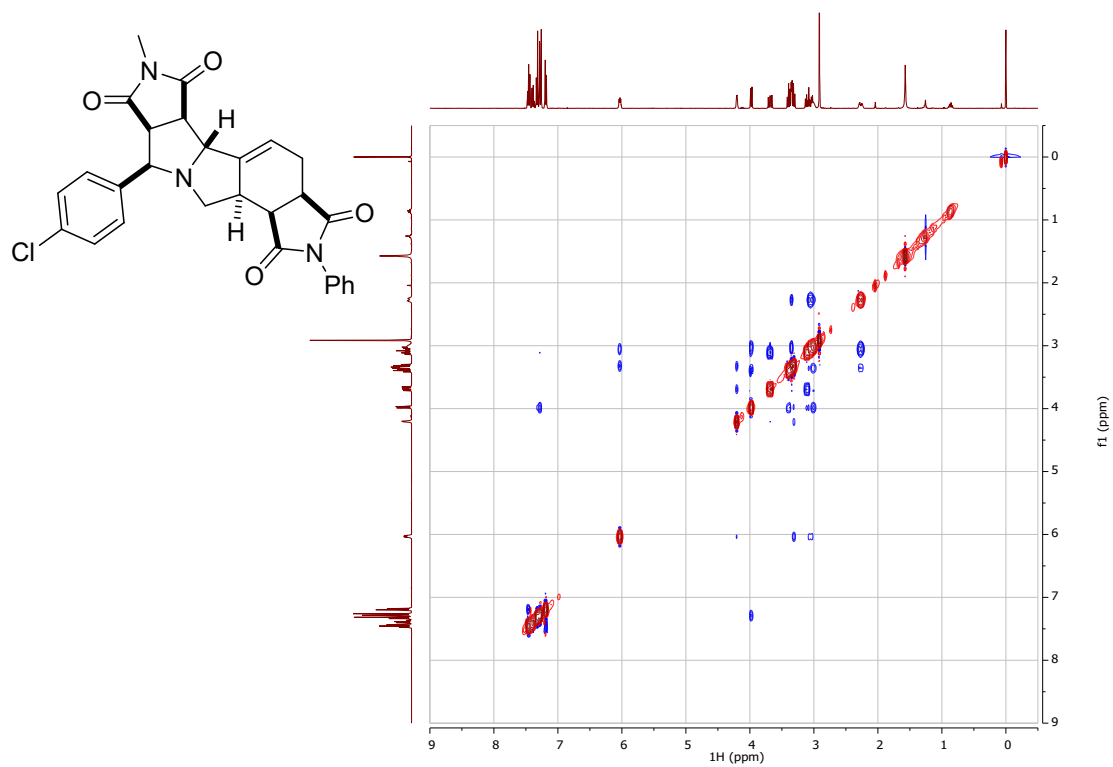
^1H NMR of **7da**



$^{13}\text{C}\{^1\text{H}\}$ NMR of 7da



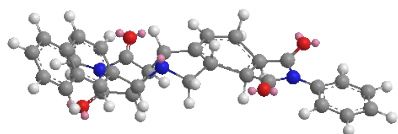
NOESY of 7da



2. DFT CALCULATIONS

DFT calculations for optimization of saddle points were performed in terms of ONIOM method implemented in Gaussian16 suite of programs. Atoms in high layer were represented in ball&stick. Transparent ball&stick atoms represent the ones included in the low layer. In the high-level layer, the electron correlation was taken into account by using the hybrid functional B3LYP3. In order to consider nonbonding interactions and dispersion forces, single-point calculations of the optimized ONIOM structures were carried out employing the Truhlar functional M06. All stationary points were characterized by harmonic analysis. Reactants, intermediates and cycloadducts have positive definite Hessian matrices.

Favoured TS (347.14 kcal·mol⁻¹) for **7ba**



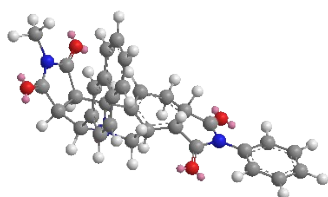
Cartesian coordinates (Å)

	X	Y	Z
C(1)	-2.287	0.133	-0.695
C(2)	-2.712	0.814	0.611
C(3)	-1.399	1.131	1.371
C(4)	-0.269	0.665	0.442
N(5)	-0.879	-0.225	-0.537
C(6)	-3.375	2.172	0.448
N(7)	-2.608	3.137	1.053
C(8)	-1.478	2.623	1.640
C(9)	-0.889	-1.636	-0.152
C(10)	-2.158	-2.205	-0.779
C(11)	-3.010	-1.170	-0.908
C(12)	-2.523	-3.943	-0.460
C(13)	-3.828	-4.129	-0.734
C(14)	-4.834	-2.579	-1.252
C(15)	-4.314	-1.333	-1.183
C(16)	-1.950	-5.174	-0.639
N(17)	-2.842	-6.093	-0.774
C(18)	-3.910	-5.447	-1.096
C(19)	-2.970	4.544	1.102
O(20)	-0.672	3.269	2.266
O(21)	-4.416	2.375	-0.127
C(22)	0.502	1.788	-0.244
C(23)	-0.086	2.650	-1.091
C(24)	0.605	3.640	-1.674
C(25)	1.916	3.799	-1.426
C(26)	2.527	2.947	-0.580

C(27)	1.815	1.960	-0.004
C(28)	-2.702	-7.369	-0.635
C(29)	-3.719	-8.256	-0.762
C(30)	-3.594	-9.586	-0.619
C(31)	-2.411	-10.125	-0.306
C(32)	-1.382	-9.292	-0.120
C(33)	-1.542	-7.967	-0.271
O(34)	-4.880	-5.866	-1.698
O(35)	-0.740	-5.293	-0.702
C(36)	3.839	3.101	-0.323
C(37)	4.539	4.090	-0.900
C(38)	3.929	4.936	-1.742
C(39)	2.621	4.790	-2.002
H(40)	-2.423	0.791	-1.583
H(41)	-3.379	0.172	1.232
H(42)	-1.376	0.595	2.349
H(43)	0.470	0.085	1.046
H(44)	0.052	-2.138	-0.477
H(45)	-0.977	-1.748	0.955
H(46)	-1.806	-2.351	-1.843
H(47)	-2.285	-3.993	0.648
H(48)	-4.361	-4.376	0.242
H(49)	-5.197	-2.723	-2.292
H(50)	-5.898	-2.565	-0.930
H(51)	-4.945	-0.438	-1.319
H(52)	-2.065	5.192	1.085
H(53)	-3.587	4.838	0.224
H(54)	-3.546	4.753	2.032
H(55)	-1.158	2.567	-1.320
H(56)	0.073	4.324	-2.359
H(57)	2.323	1.271	0.692
H(58)	-4.756	-7.966	-0.972
H(59)	-4.470	-10.247	-0.740
H(60)	-2.297	-11.213	-0.174
H(61)	-0.403	-9.708	0.177
H(62)	-0.619	-7.419	-0.041
H(63)	4.365	2.419	0.367
H(64)	5.614	4.208	-0.683
H(65)	4.501	5.750	-2.217
H(66)	2.138	5.498	-2.698
Lp(67)	-0.597	-0.162	-1.064
Lp(68)	-0.772	3.857	2.330
Lp(69)	-0.199	2.978	2.495

Lp(70)	-4.618	2.938	-0.152
Lp(71)	-4.697	1.903	-0.369
Lp(72)	-4.878	-6.431	-1.882
Lp(73)	-5.325	-5.480	-1.811
Lp(74)	-0.512	-5.829	-0.817
Lp(75)	-0.409	-4.798	-0.633

Unfavoured TS (356.56 kcal·mol⁻¹) for **7ba**



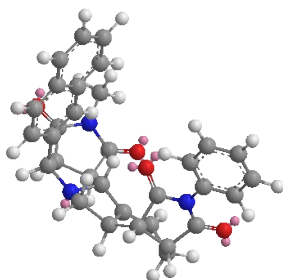
Cartesian coordinates (Å)

	X	Y	Z
C(1)	-1.761	-0.234	0.066
C(2)	-3.260	-0.409	-0.138
C(3)	-3.654	0.998	-0.711
C(4)	-2.398	1.903	-0.600
N(5)	-1.690	1.165	0.422
C(6)	-3.672	-1.367	-1.240
N(7)	-4.243	-0.667	-2.277
C(8)	-4.239	0.693	-2.075
C(9)	-0.309	1.365	0.806
C(10)	-0.024	0.056	1.559
C(11)	-0.900	-0.875	1.108
C(12)	1.185	-0.482	1.855
C(13)	1.280	-1.780	2.205
C(14)	0.192	-2.602	2.226
C(15)	-0.815	-2.177	1.427
C(16)	2.200	0.140	2.533
N(17)	3.009	-0.716	3.054
C(18)	2.328	-1.808	3.088
C(19)	-4.715	-1.291	-3.502
O(20)	-4.623	1.511	-2.875
O(21)	-3.501	-2.562	-1.227
C(22)	-1.531	2.190	-1.818
C(23)	-0.862	3.356	-1.880
C(24)	-0.080	3.666	-2.925
C(25)	0.059	2.810	-3.951
C(26)	-0.598	1.635	-3.912

C(27)	-1.376	1.344	-2.853
C(28)	4.218	-0.523	3.461
C(29)	5.008	-1.502	3.966
C(30)	6.269	-1.320	4.393
C(31)	6.844	-0.116	4.314
C(32)	6.128	0.878	3.779
C(33)	4.869	0.662	3.362
O(34)	2.492	-2.764	3.823
O(35)	2.230	1.352	2.630
C(36)	-0.463	0.769	-4.933
C(37)	0.316	1.067	-5.985
C(38)	0.969	2.237	-6.022
C(39)	0.840	3.105	-5.007
H(40)	-1.231	-0.431	-0.897
H(41)	-3.791	-0.641	0.813
H(42)	-4.489	1.411	-0.092
H(43)	-2.718	2.885	-0.170
H(44)	-0.199	2.280	1.432
H(45)	0.358	1.449	-0.083
H(46)	-0.381	0.220	2.617
H(47)	1.923	-2.355	1.463
H(49)	-0.186	-2.385	3.257
H(52)	-5.091	-2.322	-3.315
H(53)	-5.559	-0.719	-3.948
H(54)	-3.885	-1.340	-4.242
H(55)	-0.946	4.083	-1.055
H(56)	0.446	4.636	-2.923
H(57)	-1.891	0.374	-2.843
H(58)	4.696	-2.550	4.053
H(59)	6.851	-2.168	4.795
H(60)	7.881	0.044	4.650
H(61)	6.592	1.874	3.667
H(62)	4.433	1.561	2.908
H(63)	-0.989	-0.201	-4.928
H(64)	0.420	0.351	-6.817
H(65)	1.611	2.484	-6.884
H(66)	1.387	4.062	-5.057
Lp(67)	-2.013	1.233	0.926
Lp(68)	-4.836	1.312	-3.399
Lp(69)	-4.586	2.090	-2.722
Lp(70)	-3.681	-2.877	-1.704
Lp(71)	-3.236	-2.800	-0.744
Lp(72)	2.928	-2.740	4.227

Lp(73)	2.111	-3.225	3.770
Lp(74)	2.657	1.601	2.961
Lp(75)	1.798	1.664	2.356
H(77)	0.348	-3.699	2.234
H(78)	1.707	-0.241	0.876
H(79)	-1.435	-2.896	0.866

7ba (59.80 kcal·mol⁻¹)



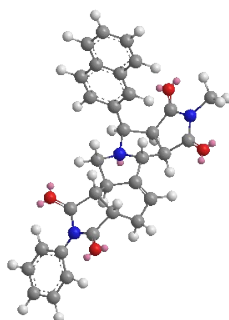
Cartesian coordinates (Å)

	X	Y	Z
C(1)	-0.292	-1.387	1.493
C(2)	-1.489	-2.035	2.176
C(3)	-1.909	-0.913	3.187
C(4)	-0.810	0.179	3.130
N(5)	0.271	-0.599	2.562
C(6)	-2.723	-2.218	1.313
N(7)	-3.716	-1.366	1.737
C(8)	-3.327	-0.563	2.782
C(9)	1.486	-0.019	2.026
C(10)	2.095	-1.248	1.301
C(11)	0.898	-2.096	0.953
C(12)	2.908	-1.068	0.019
C(13)	3.240	-2.416	-0.663
C(14)	2.400	-3.626	-0.192
C(15)	1.014	-3.217	0.238
C(16)	2.226	-0.417	-1.184
N(17)	2.771	-0.791	-2.276
C(18)	2.986	-2.041	-2.126
C(19)	-5.016	-1.265	1.092
O(20)	-4.009	0.298	3.284
O(21)	-2.817	-2.978	0.380
C(22)	-1.055	1.476	2.369
C(23)	-0.478	2.610	2.808
C(24)	-0.647	3.779	2.172

C(25)	-1.405	3.851	1.065
C(26)	-1.992	2.730	0.604
C(27)	-1.809	1.568	1.258
C(28)	2.963	-0.063	-3.319
C(29)	3.532	-0.523	-4.457
C(30)	3.738	0.239	-5.543
C(31)	3.397	1.534	-5.535
C(32)	2.870	2.043	-4.415
C(33)	2.674	1.260	-3.342
O(34)	2.955	-2.900	-2.982
O(35)	1.248	0.293	-1.091
C(36)	-2.750	2.790	-0.506
C(37)	-2.925	3.952	-1.154
C(38)	-2.339	5.067	-0.694
C(39)	-1.582	5.014	0.412
H(40)	-0.639	-0.732	0.661
H(41)	-1.218	-2.984	2.691
H(42)	-1.969	-1.359	4.211
H(43)	-0.536	0.445	4.181
H(44)	2.147	0.373	2.832
H(45)	1.268	0.817	1.330
H(46)	2.705	-1.820	2.044
H(47)	3.829	-0.474	0.231
H(48)	4.328	-2.654	-0.576
H(49)	2.888	-4.108	0.688
H(50)	2.340	-4.407	-0.984
H(51)	0.138	-3.830	-0.019
H(52)	-5.329	-2.238	0.651
H(53)	-5.807	-0.976	1.820
H(54)	-4.975	-0.501	0.284
H(55)	0.159	2.591	3.708
H(56)	-0.148	4.677	2.574
H(57)	-2.292	0.668	0.854
H(58)	3.889	-1.557	-4.570
H(59)	4.205	-0.191	-6.445
H(60)	3.572	2.170	-6.418
H(61)	2.614	3.115	-4.376
H(62)	2.273	1.796	-2.468
H(63)	-3.243	1.887	-0.906
H(64)	-3.547	3.991	-2.063
H(65)	-2.480	6.023	-1.224
H(66)	-1.108	5.944	0.773
Lp(67)	0.444	-0.982	2.993

Lp(68)	-4.561	0.382	3.065
Lp(69)	-3.772	0.614	3.735
Lp(70)	-3.336	-2.992	0.080
Lp(71)	-2.340	-3.317	0.247
Lp(72)	2.825	-2.740	-3.542
Lp(73)	3.063	-3.464	-2.808
Lp(74)	0.995	0.499	-1.594
Lp(75)	1.039	0.403	-0.543

Diast-7ba (60.13 kcal·mol⁻¹)



Cartesian coordinates (Å)

	X	Y	Z
C(1)	-1.437	-0.337	0.065
C(2)	-2.953	-0.284	0.207
C(3)	-3.264	1.148	-0.352
C(4)	-1.899	1.849	-0.578
N(5)	-1.073	1.041	0.293
C(6)	-3.738	-1.203	-0.709
N(7)	-4.387	-0.460	-1.667
C(8)	-4.176	0.892	-1.534
C(9)	0.375	1.055	0.290
C(10)	0.657	-0.139	1.240
C(11)	-0.497	-1.072	0.956
C(12)	1.973	-0.894	1.055
C(13)	1.948	-2.331	1.608
C(14)	0.628	-2.792	2.253
C(15)	-0.539	-2.321	1.426
C(16)	3.108	-0.319	1.891
N(17)	3.333	-1.012	2.942
C(18)	3.092	-2.223	2.609
C(19)	-5.228	-1.035	-2.705
O(20)	-4.646	1.737	-2.257
O(21)	-3.778	-2.406	-0.621
C(22)	-1.317	1.976	-1.980
C(23)	-0.549	3.042	-2.273

C(24)	-0.008	3.209	-3.489
C(25)	-0.219	2.305	-4.460
C(26)	-0.981	1.227	-4.191
C(27)	-1.513	1.079	-2.964
C(28)	3.784	-0.592	4.071
C(29)	3.997	-1.409	5.129
C(30)	4.461	-0.983	6.315
C(31)	4.719	0.315	6.513
C(32)	4.481	1.166	5.509
C(33)	4.016	0.715	4.332
O(34)	3.690	-3.220	2.957
O(35)	3.705	0.662	1.501
C(36)	-1.197	0.314	-5.156
C(37)	-0.663	0.468	-6.377
C(38)	0.095	1.542	-6.642
C(39)	0.316	2.456	-5.685
H(40)	-1.160	-0.652	-0.968
H(41)	-3.280	-0.400	1.265
H(42)	-3.869	1.703	0.407
H(43)	-1.967	2.877	-0.143
H(44)	0.790	2.016	0.672
H(45)	0.782	0.858	-0.728
H(46)	0.546	0.197	2.300
H(47)	2.270	-0.904	-0.020
H(48)	2.239	-3.045	0.800
H(49)	0.516	-2.374	3.280
H(50)	0.620	-3.904	2.339
H(51)	-1.386	-2.989	1.212
H(52)	-4.972	-2.100	-2.903
H(53)	-6.297	-0.976	-2.400
H(54)	-5.096	-0.492	-3.668
H(55)	-0.348	3.805	-1.501
H(56)	0.614	4.101	-3.674
H(57)	-2.121	0.186	-2.769
H(58)	3.784	-2.488	5.103
H(59)	4.618	-1.698	7.141
H(60)	5.090	0.676	7.486
H(61)	4.654	2.246	5.663
H(62)	3.820	1.514	3.602
H(63)	-1.818	-0.579	-4.964
H(64)	-0.846	-0.285	-7.161
H(65)	0.536	1.671	-7.645
H(66)	0.943	3.331	-5.925

Lp(67)	-1.241	1.179	0.855
Lp(68)	-4.999	1.557	-2.707
Lp(69)	-4.509	2.310	-2.141
Lp(70)	-4.108	-2.707	-1.021
Lp(71)	-3.464	-2.664	-0.179
Lp(72)	4.156	-3.158	3.327
Lp(73)	3.502	-3.744	2.732
Lp(74)	4.168	0.861	1.824
Lp(75)	3.520	0.906	0.985