Supporting Information

Novel Approach for the Synthesis of C_{60} Fullerenes Containing Strained 1,2-dimethylenebicyclo[2,2,0]hexane Fragments

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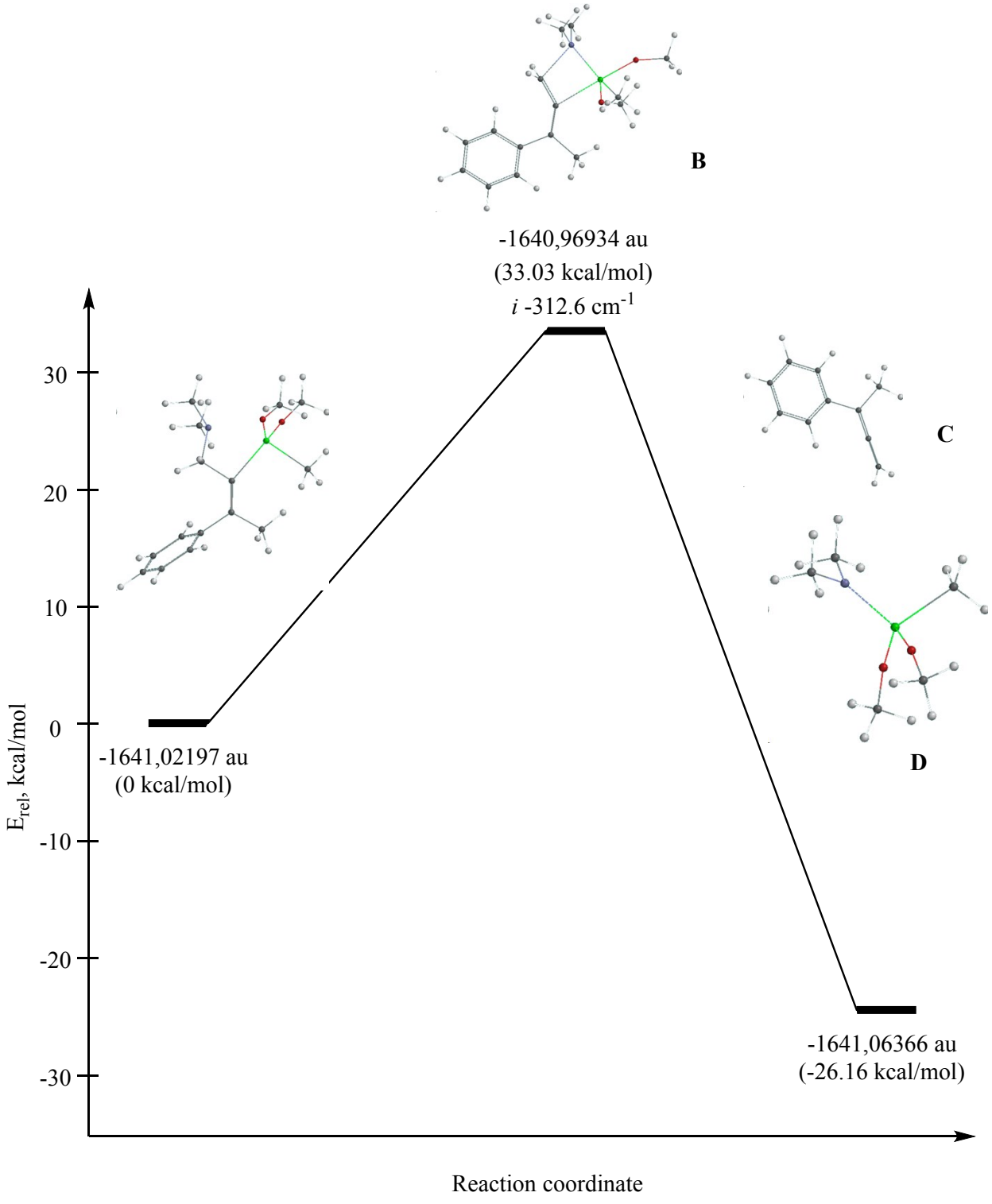

Figure S1. Reaction profile for the rearrangement stage on the example of *N,N*-dimethyl-3-phenylprop-2-yn-1-amine with dimethoxydimethyltitanium adduct (B3LYP/6-31G(d), 373.15 K).

Cartesian coordinates of optimized structures **A-D** and the number of imaginary frequencies:

N,N-Dimethyl-3-phenylprop-2-yn-1-amine with dimethoxydimethyltitanium adduct (**A**)

C	-0.273126	-0.183709	0.204910
C	-1.351831	-0.995610	0.241504
C	-0.330116	1.309089	-0.040060
N	0.858898	1.562819	-0.913136
Ti	1.875417	-0.330807	0.217119
C	2.029149	-1.925739	1.594753
C	-1.233799	-2.502543	0.333222
O	2.675498	0.885596	1.295246
O	2.676751	-1.053716	-1.216073
H	-1.696813	-2.880593	1.255043
H	-0.190459	-2.818406	0.314610
H	-1.754800	-2.994815	-0.498410
H	-1.255314	1.695531	-0.502339
H	-0.168860	1.875580	0.886300
C	1.411990	2.911888	-0.768771
C	0.541138	1.273923	-2.318611
C	3.677410	-1.616577	-2.014184
C	3.678785	1.116005	2.246189
C	-2.755476	-0.475041	0.195517
C	-5.404852	0.507294	0.120753
C	-3.693920	-0.983660	-0.720903
C	-3.184203	0.529393	1.080388
C	-4.491898	1.015049	1.045784
C	-4.998657	-0.494155	-0.763970
H	-3.394921	-1.760581	-1.419541
H	-2.486395	0.913646	1.819441

H	-4.798250	1.787012	1.747475
H	-5.700706	-0.896534	-1.490178
H	-6.424090	0.883619	0.092324
H	3.078399	-1.958775	1.909711
H	1.776718	-2.905808	1.174087
H	1.411269	-1.752212	2.483195
H	3.963938	-2.601788	-1.628858
H	4.569430	-0.980238	-2.038494
H	3.314191	-1.740871	-3.040751
H	3.939154	0.192643	2.776119
H	4.583069	1.510818	1.769104
H	3.334012	1.849314	2.984163
H	0.102818	0.272191	-2.393615
H	-0.172324	2.001973	-2.721266
H	1.456687	1.304536	-2.920316
H	1.706688	3.070685	0.274854
H	2.302830	3.009949	-1.399647
H	0.690642	3.681334	-1.066809

The number of imaginary frequencies = 0

Transition state (**B**)

C	0.559565	-0.152518	-0.063630
C	1.559325	0.740268	-0.084174
C	0.329324	-1.510194	0.030000
N	-1.719907	-1.870916	-0.080379
Ti	-1.796423	0.144906	-0.080483
C	-1.480106	1.228768	-1.890594
H	-1.792913	2.272927	-1.747324

H	-2.154601	0.788161	-2.641498
H	-0.460280	1.224220	-2.284416
C	1.282527	2.228469	-0.183283
O	-1.605210	0.987878	1.523922
O	-3.579572	0.422081	-0.317326
H	1.855298	2.785074	0.568839
H	0.224061	2.431867	-0.021326
H	1.559394	2.635757	-1.165286
H	0.501351	-2.175762	-0.819350
H	0.369963	-2.015414	0.997532
C	-2.106902	-2.659374	1.079275
H	-1.524625	-3.594225	1.147158
H	-3.171380	-2.931083	1.029419
H	-1.945785	-2.085959	1.997438
C	-1.931355	-2.570426	-1.340472
H	-1.617326	-1.943485	-2.182625
H	-2.994192	-2.814786	-1.477852
H	-1.355777	-3.510348	-1.384649
C	-4.612751	1.198100	-0.852269
H	-4.324678	1.614076	-1.828488
H	-4.863840	2.032970	-0.181778
H	-5.515383	0.586754	-0.988307
C	-2.485344	1.592019	2.439992
H	-2.297174	1.201301	3.449602
H	-3.534275	1.395377	2.176959
H	-2.325121	2.678766	2.461858
C	2.995888	0.330551	-0.023232
C	5.731355	-0.418569	0.049504

C	4.014534	1.227487	-0.401212
C	3.396516	-0.949494	0.403027
C	4.738191	-1.319031	0.443380
C	5.359014	0.857004	-0.373042
H	3.755337	2.226798	-0.733445
H	2.645825	-1.663796	0.726430
H	5.010140	-2.314278	0.786947
H	6.117395	1.572529	-0.681953
H	6.778815	-0.707001	0.076988

The number of imaginary frequencies = 1

Buta-2,3-dien-2-ylbenzene (**C**)

H	-3.577717	-1.808487	0.926092
C	-3.173506	-1.399739	0.000000
C	-2.254472	-0.471263	0.000000
H	-3.577717	-1.808487	-0.926092
C	-1.336860	0.475448	0.000000
C	-1.779142	1.928553	0.000000
H	-1.402110	2.457034	0.884586
H	-2.869218	1.998019	0.000000
H	-1.402110	2.457034	-0.884586
C	0.117483	0.156723	0.000000
C	2.877171	-0.442943	0.000000
C	1.080584	1.178892	0.000000
C	0.570797	-1.176011	0.000000
C	1.929214	-1.471395	0.000000
C	2.444861	0.881700	0.000000
H	0.770067	2.218767	0.000000

H	-0.157723	-1.981954	0.000000
H	2.252236	-2.509515	0.000000
H	3.168599	1.692917	0.000000
H	3.938917	-0.675121	0.000000

The number of imaginary frequencies = 0

(Dimethylamino)dimethoxy(methyl)titanium (**D**)

N	-1.639090	-0.024613	0.254645
Ti	0.187715	-0.001426	-0.262321
C	0.159022	0.024950	-2.369724
H	-0.337077	-0.869113	-2.770140
H	1.188452	0.049403	-2.755820
H	-0.370239	0.910595	-2.745843
O	0.988969	-1.536579	0.192135
O	0.955620	1.539834	0.223922
C	1.902547	-2.453132	0.721835
H	1.395783	-3.399081	0.955691
H	2.357311	-2.067178	1.644687
H	2.703007	-2.660729	-0.000945
C	1.822872	2.504292	0.744196
H	1.410452	2.930279	1.669230
H	1.961682	3.318353	0.020351
H	2.806806	2.070548	0.970284
C	-2.395449	-1.241957	0.499446
H	-3.253406	-1.326589	-0.187696
H	-2.792409	-1.268336	1.528573
H	-1.759117	-2.120911	0.359579
C	-2.423983	1.180502	0.468965

H	-3.285225	1.227431	-0.217827
H	-1.809458	2.070566	0.303625
H	-2.819422	1.224447	1.498048

The number of imaginary frequencies = 0

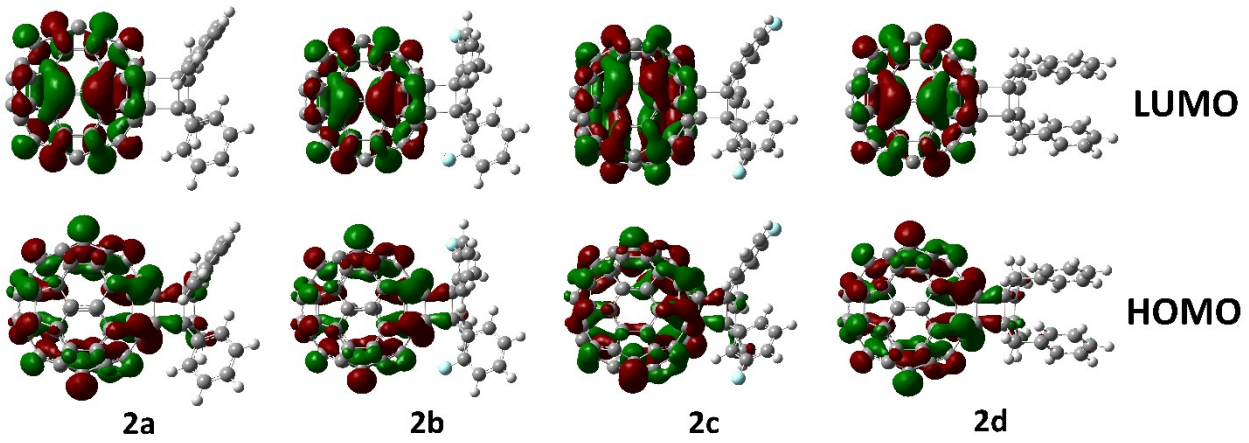

Figure S2. Frontier HOMO and LUMO of compounds **2a-d** calculated at the PBEPBE/6-311G(d,p) level of theory.

Cartesian coordinates

2a

6	-0.329526000	-3.128721000	-1.087956000
6	-1.606232000	-3.535755000	-0.520009000
6	-1.819891000	-3.445429000	0.860738000
6	-0.765199000	-2.945595000	1.730093000
6	0.461570000	-2.537279000	1.180733000
6	0.683334000	-2.629896000	-0.251772000
6	-2.652059000	-3.133761000	-1.446157000
6	-3.087165000	-2.948410000	1.370168000
6	-1.374342000	-2.146333000	2.767723000
6	1.146180000	-1.366198000	1.662607000
6	1.500769000	-1.513412000	-0.650712000
6	-0.583370000	-2.483279000	-2.355097000
6	0.549507000	-0.586928000	2.642126000
6	-0.726830000	-0.977800000	3.203646000
6	0.563590000	0.890881000	2.550122000
6	-1.501496000	0.224283000	3.458630000
6	-3.874511000	-2.652546000	-0.956217000
6	-2.809532000	-2.144207000	2.551011000
6	-0.706200000	1.371276000	3.054928000
6	-3.554466000	-0.981399000	2.796114000
6	-4.096018000	-2.557835000	0.478675000
6	2.042729000	-0.793231000	0.575924000
6	1.239023000	-0.882610000	-1.854504000
6	-4.509061000	-1.506447000	-1.584289000
6	0.187227000	-1.367242000	-2.721948000
6	-2.017271000	-2.482192000	-2.582309000
6	1.258805000	0.593152000	-1.948476000
6	-0.450193000	-0.222280000	-3.347582000
6	-2.631121000	-1.374114000	-3.185368000
6	-2.888879000	0.223920000	3.267556000
6	2.072009000	0.809624000	0.484603000

6	-4.867782000	-1.353751000	0.735816000
6	0.209088000	0.981277000	-2.870624000
6	-1.830772000	-0.225607000	-3.584246000
6	-3.897626000	-0.880021000	-2.680030000
6	-3.885331000	0.574413000	-2.773748000
6	-5.124265000	-0.703812000	-0.539341000
6	-4.600870000	-0.580762000	1.875238000
6	-4.588092000	0.873386000	1.781509000
6	-2.610495000	0.977636000	-3.336217000
6	-1.976355000	2.142111000	-2.878846000
6	-2.598756000	2.944994000	-1.836765000
6	-0.542966000	2.146070000	-2.650174000
6	1.176046000	1.530425000	1.482963000
6	-4.842384000	1.498781000	0.552217000
6	1.540790000	1.370658000	-0.835870000
6	0.726486000	2.534743000	-0.581685000
6	-5.111624000	0.695058000	-0.629283000
6	-3.534727000	1.370182000	2.645425000
6	-2.770557000	2.480402000	2.256707000
6	-4.484271000	1.346235000	-1.767636000
6	-3.828939000	2.552677000	-1.290639000
6	-0.277200000	2.942475000	-1.474619000
6	-1.545425000	3.442334000	-0.966725000
6	-4.050151000	2.646452000	0.144706000
6	0.506292000	2.635211000	0.850381000
6	-1.334442000	2.485340000	2.472102000
6	-3.035034000	3.130590000	0.981596000
6	-0.713394000	3.132546000	1.340222000
6	-1.759521000	3.534934000	0.413649000
6	3.650654000	0.797908000	0.747616000
6	3.991834000	0.765422000	2.246462000
6	4.311606000	1.743935000	3.105853000
1	4.589877000	1.524540000	4.139306000
1	4.322583000	2.789971000	2.792145000
6	3.639602000	-0.819154000	0.813609000
6	3.937164000	-0.704131000	2.311770000
6	4.008848000	-1.580334000	3.327610000
1	3.869195000	-2.653267000	3.187741000
1	4.184415000	-1.234010000	4.349246000
6	4.566356000	1.664864000	-0.073727000
6	6.369761000	3.360633000	-1.441817000
6	4.184652000	2.961183000	-0.466787000
6	5.881961000	1.246045000	-0.353937000
6	6.768983000	2.081372000	-1.038216000
6	5.076662000	3.799790000	-1.144777000
1	3.186356000	3.333212000	-0.233238000
1	6.215571000	0.258216000	-0.033017000
1	7.780627000	1.729210000	-1.253541000
1	4.754674000	4.801493000	-1.439235000
1	7.064506000	4.012398000	-1.976409000
6	4.457685000	-1.717488000	-0.073346000
6	5.960813000	-3.403040000	-1.776954000

6	4.515419000	-1.481381000	-1.463126000
6	5.184060000	-2.805476000	0.442549000
6	5.924147000	-3.642236000	-0.400358000
6	5.257220000	-2.313953000	-2.303930000
1	3.994822000	-0.622813000	-1.890255000
1	5.189119000	-2.992178000	1.516566000
1	6.478491000	-4.481876000	0.025705000
1	5.290325000	-2.105105000	-3.375698000
1	6.540278000	-4.054848000	-2.434764000

2b

6	-0.492716000	-3.241549000	-0.615830000
6	-1.767348000	-3.537430000	0.018375000
6	-1.960325000	-3.235258000	1.372261000
6	-0.886674000	-2.630252000	2.146864000
6	0.340751000	-2.331968000	1.533953000
6	0.533962000	-2.638016000	0.127902000
6	-2.816726000	-3.259275000	-0.948218000
6	-3.213065000	-2.645995000	1.814329000
6	-1.470260000	-1.674413000	3.060135000
6	1.059310000	-1.117517000	1.833765000
6	1.352843000	-1.604940000	-0.444390000
6	-0.749265000	-2.787428000	-1.963383000
6	0.480922000	-0.187335000	2.684939000
6	-0.797369000	-0.466816000	3.311009000
6	0.511333000	1.259000000	2.366991000
6	-1.551131000	0.772802000	3.386636000
6	-4.024706000	-2.688880000	-0.523381000
6	-2.908628000	-1.679372000	2.859303000
6	-0.743610000	1.831217000	2.807265000
6	-3.631888000	-0.479960000	2.931966000
6	-4.227518000	-2.377723000	0.883951000
6	1.931917000	-0.726735000	0.649476000
6	1.106967000	-1.162570000	-1.730450000
6	-4.647743000	-1.638153000	-1.310492000
6	0.035407000	-1.753989000	-2.502801000
6	-2.185007000	-2.795311000	-2.174958000
6	1.152858000	0.282709000	-2.041218000
6	-0.589550000	-0.703655000	-3.285907000
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6	-1.973127000	-0.718273000	-3.505490000
6	-4.039922000	-1.193531000	-2.493730000
6	-4.004907000	0.229907000	-2.804234000
6	-5.236627000	-0.677612000	-0.391595000
6	-4.683658000	-0.203974000	1.971770000
6	-4.648495000	1.219607000	1.661457000
6	-2.730550000	0.521475000	-3.433282000
6	-2.071441000	1.729396000	-3.161825000

6	-2.667457000	2.689383000	-2.244539000
6	-0.634451000	1.742335000	-2.950922000
6	1.116573000	1.721267000	1.208613000
6	-4.907179000	1.658356000	0.354754000
6	1.470010000	1.217200000	-1.064452000
6	0.669569000	2.416295000	-0.978916000
6	-5.202609000	0.691616000	-0.690199000
6	-3.575489000	1.821299000	2.430329000
6	-2.798684000	2.846078000	1.871118000
6	-4.577816000	1.153986000	-1.918804000
6	-3.897716000	2.406170000	-1.634202000
6	-0.340764000	2.701022000	-1.911146000
6	-1.595805000	3.292915000	-1.470843000
6	-4.102353000	2.718754000	-0.228239000
6	0.458483000	2.727572000	0.423212000
6	-1.360622000	2.855738000	2.069193000
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6	-0.744111000	3.314664000	0.846870000
6	-1.794037000	3.595895000	-0.118611000
6	3.558949000	0.814350000	0.634761000
6	3.841190000	0.829459000	2.153348000
6	3.898347000	1.838145000	3.033331000
1	4.115407000	1.658436000	4.088865000
1	3.727920000	2.871003000	2.722876000
6	3.544644000	-0.792165000	0.765210000
6	4.022787000	-0.630190000	2.211947000
6	4.535484000	-1.439727000	3.151772000
1	4.641157000	-2.512696000	3.004877000
1	4.871409000	-1.021056000	4.103970000
6	4.590164000	1.624233000	-0.113160000
6	6.628162000	3.188654000	-1.335571000
6	4.381762000	2.951792000	-0.511086000
6	5.899027000	1.127646000	-0.291875000
6	6.901149000	1.887631000	-0.898132000
6	5.357320000	3.729315000	-1.131742000
1	6.128930000	0.120535000	0.059311000
1	7.898101000	1.461405000	-1.025374000
1	5.105945000	4.749917000	-1.424777000
1	7.402653000	3.788163000	-1.818021000
6	4.145274000	-1.790951000	-0.189920000
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6	4.583027000	-1.451030000	-1.484570000
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6	4.635023000	-4.141509000	-0.740330000
6	5.066107000	-2.415411000	-2.374620000
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1	4.610409000	-5.183947000	-0.418966000
1	5.402317000	-2.110198000	-3.367332000
1	5.485394000	-4.519501000	-2.688571000
9	3.182559000	3.545452000	-0.249186000
9	3.620738000	-3.568352000	1.309422000

2c

6	-0.437195000	-2.988401000	-1.431551000
6	-1.710205000	-3.484309000	-0.930012000
6	-1.938049000	-3.561349000	0.449191000
6	-0.902067000	-3.145149000	1.382157000
6	0.320563000	-2.651017000	0.898304000
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2d

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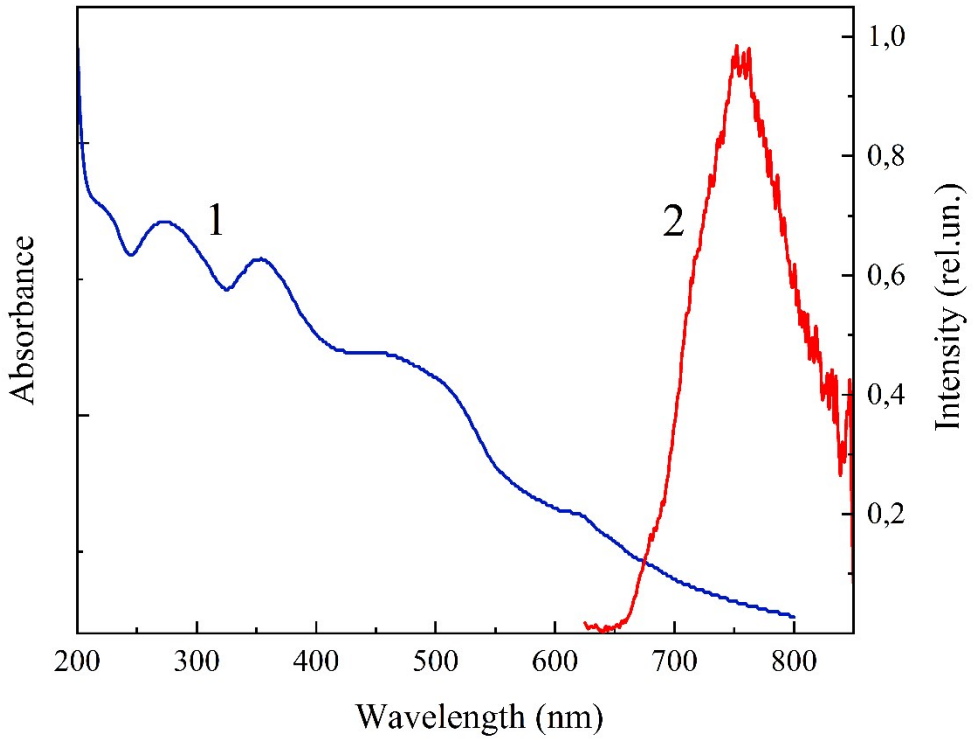


Figure S3. Absorption (1) and PL (2) spectra of C_{60} fullerene in film. $T = 298$ K.

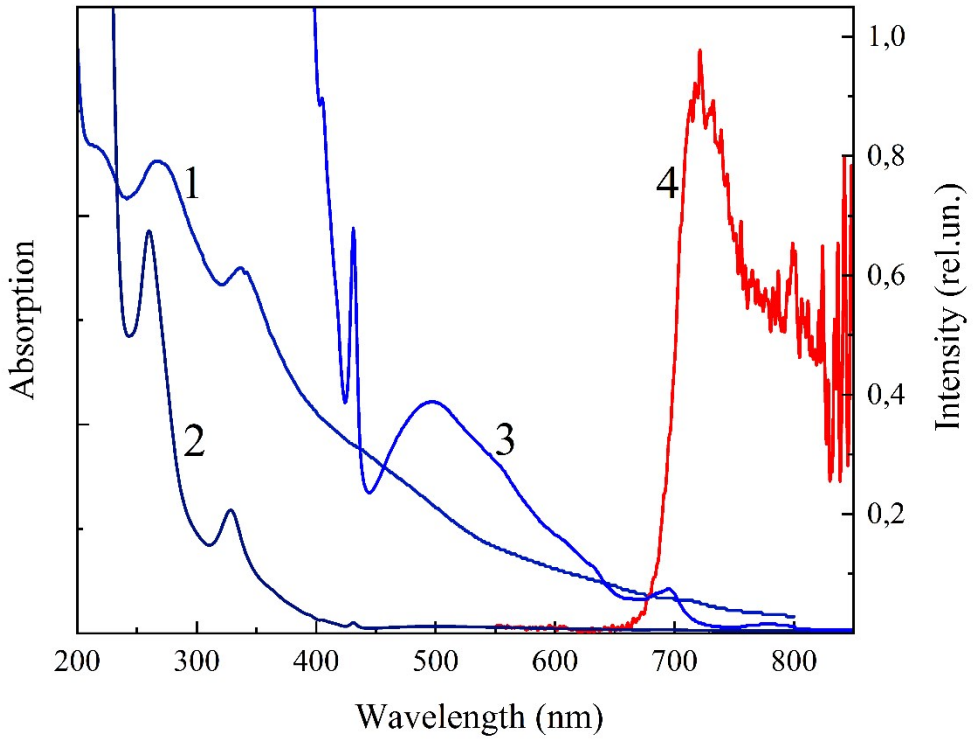


Figure S4. Absorption (1-3) and PL (4) spectra of **PCBM** in film (1, 4) and in $CHCl_3$ solution (2, 3). [**PCBM**] = 10^{-4} M (2, 3), l = 0.1 cm (2) and 1 cm (3). $T = 298$ K.

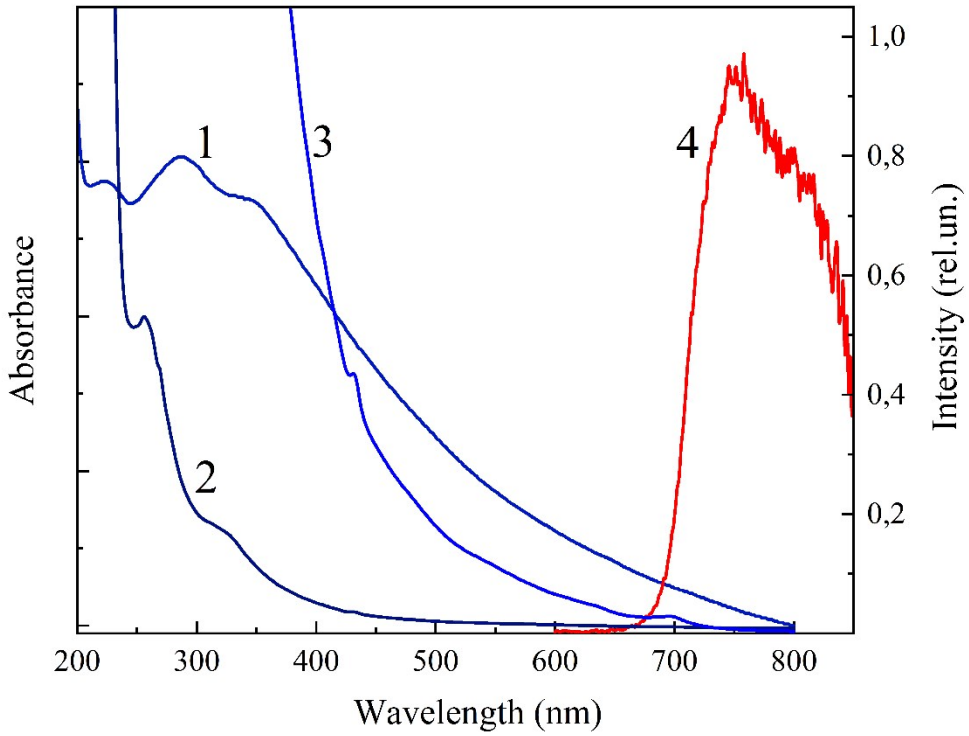


Figure S5. Absorption (1-3) and PL (4) spectra of **2a** in film (1, 4) and in $CHCl_3$ solution (2, 3). [**2a**] = 10^{-4} M (2, 3), l = 0.1 cm (2) and 1 cm (3). T = 298 K.

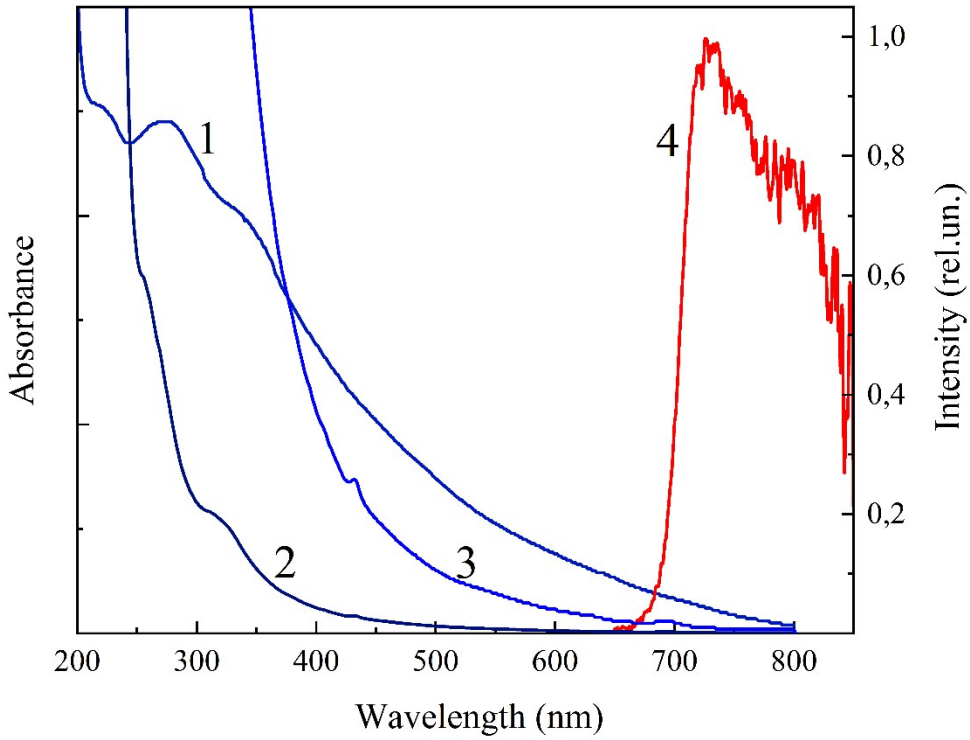


Figure S6. Absorption (1-3) and PL (4) spectra of **2b** in film (1, 4) and in $CHCl_3$ solution (2, 3). [**2b**] = 10^{-4} M (2, 3), l = 0.1 cm (2) and 1 cm (3). T = 298 K.

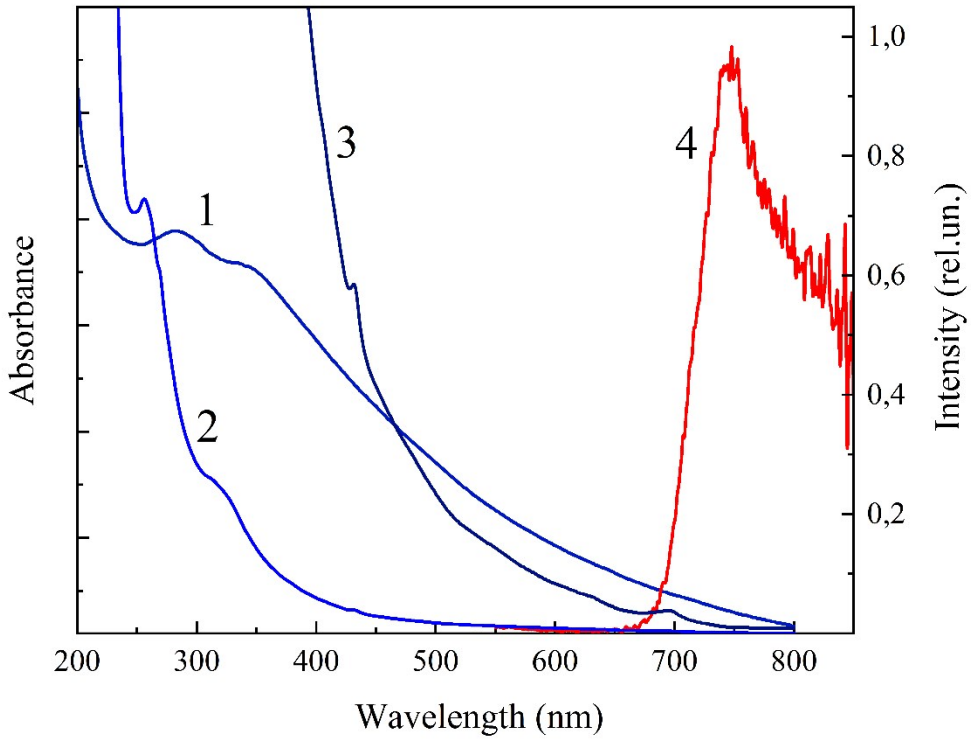


Figure S7. Absorption (1-3) and PL (4) spectra of **2c** in film (1, 4) and in $CHCl_3$ solution (2, 3). [**2c**] = 10^{-4} M (2, 3), l = 0.1 cm (2) and 1 cm (3). T = 298 K.

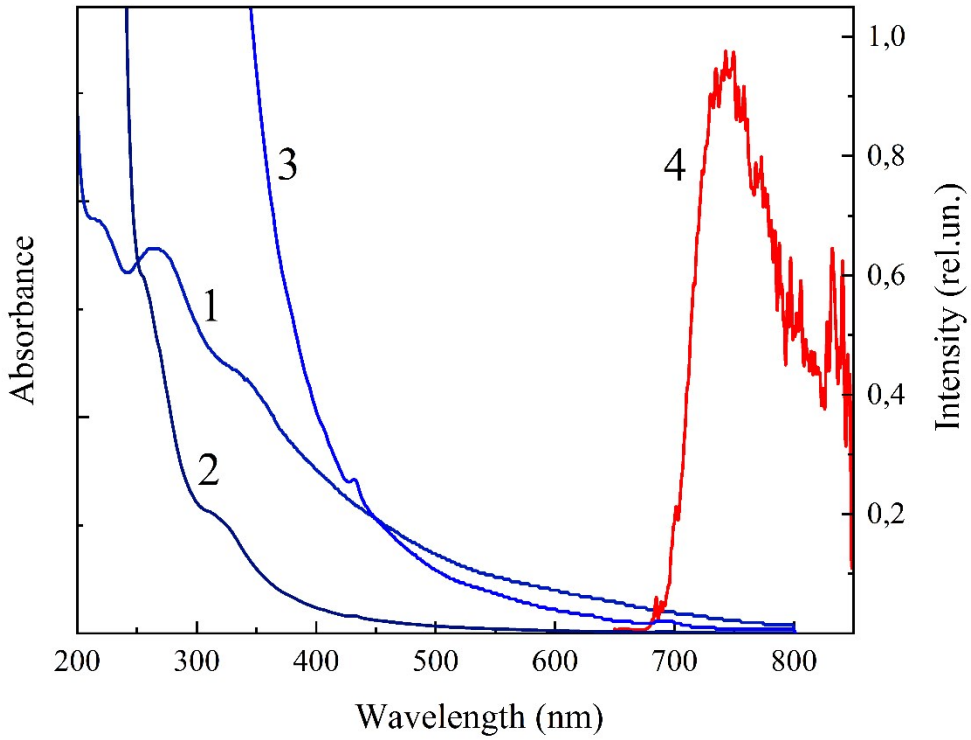


Figure S8. Absorption (1-3) and PL (4) spectra of **2d** in film (1, 4) and in $CHCl_3$ solution (2, 3). [**2d**] = 10^{-4} M (2, 3), l = 0.1 cm (2) and 1 cm (3). T = 298 K.

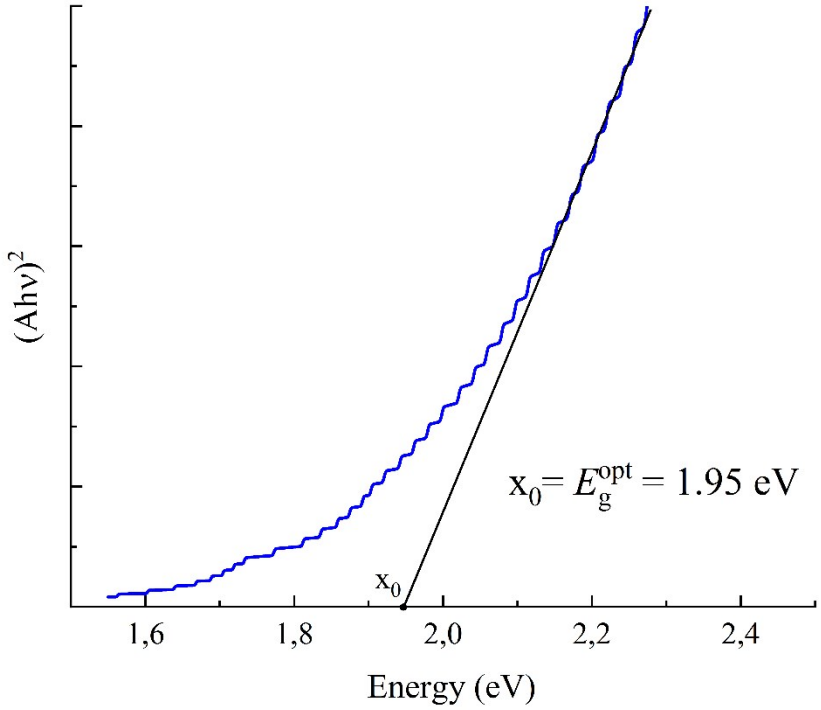


Figure S9. Evaluation of the optical energy gap E_g^{opt} by the graphical Tauc method from the absorption spectrum of PCBM film.

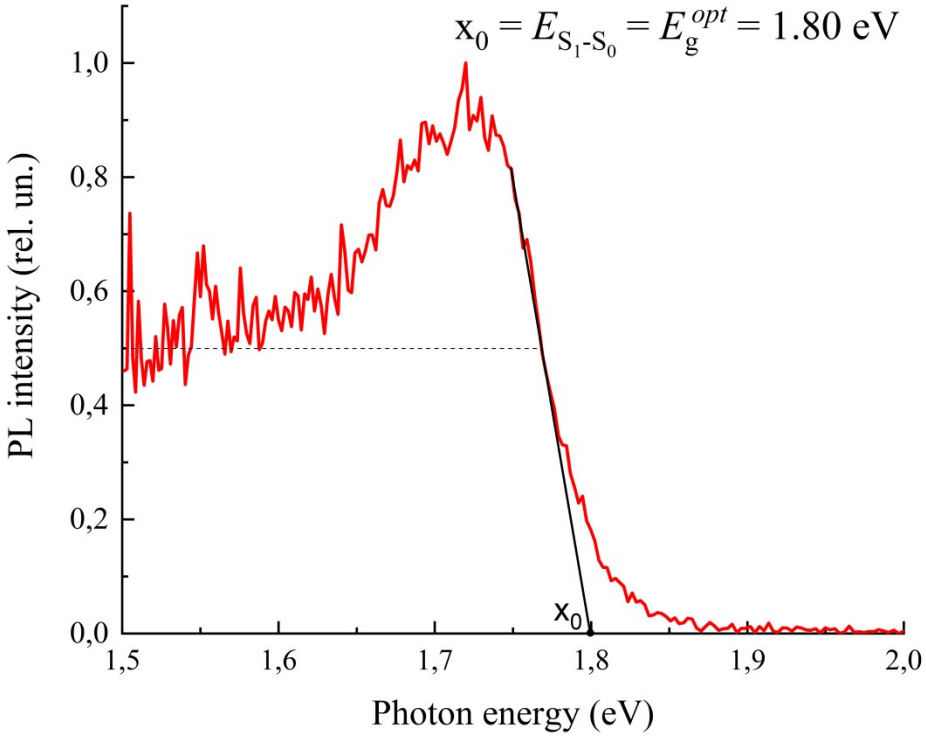


Figure S10. Evaluation of the optical energy gap E_g^{opt} by the tangent method from the PL spectrum of PCBM film.

2. Experimental

Measurements and materials

All reactions were performed under an argon atmosphere and in anhydrous solvent. The solvents and reagents were dried or refined according to the literature procedures. Commercially available [60]fullerene (99.5% pure, Sigma-Aldrich) was used. The reaction products were analyzied on a HPLC chromatograph Shimadzu SPD-20A (Japan) equipped with the UV detector at 313 or 340 nm. The mixtures were separated on a metal preparative column Cosmosil Buckyprep Waters (250×10 mm) at ~20 °C. Toluene was used as eluent, the flow rate was 3.0 mL•min^{-1}. The $^{1}H\{^{13}C\}$ NMR spectra were run on a Bruker Avance-500 spectrometer at 500.17 and 125.78 MHz, respectively. The mixture of $CDCl_3$ and CS_2 (1:5) was used as a solvent. The mass spectra were obtained on aUltraFlex III TOF/TOF (Bruker Daltonik GmbH, Germany) operating in a linear (TOF) and reflection (TOF/TOF) positive and negative ion modes. S_8 and DCTB (trans-2-[3-(4-tret-butylphenyl)-2-methyl-2-propenyliden]malononitrile) are used as a matrix. For the application on a metal target, the toluene solutions of the samples were used.

The photoluminescence (PL) and PL excitation spectra were recorded using a Horiba FluoroLog-3 spectrofluorimeter (model FL-3-22). All spectra were scaled by introducing the corrections for the Xe-lamp (450 W), detector (PMT Hamamatsu R928), and diffraction gratings using special software FluorEssence 3.5. The PL of films were recorded using a solid sample holder at an angle of 15 or 60 degrees to the exciting light.

As is known, the PL spectra of fullerenes and its derivatives usually contain one or several broad structureless bands with no vibronic structure. Therefore, we used the tangent method to calculate the energies of the radiative S_1 levels of the compounds. This method implies in making tangent to the left part of the PL spectrum curve in coordinates “PL intensity – photon energy (eV)”. The tangent is applied in the point attributed to the half of the maximal intensity. In this mode, the energy of the S_1 level, which is equal to the electronic transition energy $S_1 \rightarrow S_0$ and accordingly to the optical energy gap E_g^{opt}, corresponds to the intersection of the tangent with the abscissa axis.

UV-visible absorption spectra were recorded in the range 200–800 nm with Shimadzu UV-1800 spectrophotometer. The E_g^{opt} were estimated from the optical absorption edge in thin films and using known Tauc relation: $Ahv = (hv - E_g^{opt})^n$, were n = ½ for allowed direct, A – absorbance. The films were prepared by deposition of the substance on a quartz substrate followed by solvent $CHCl_3$ evaporation.

General procedure for the synthesis of 2,3-dimethylenebicyclo[2.2.0]hexane C_{60} derivatives.

A 50 mL glass reactor was charged with C_{60} (80 mg, 0.1112 mmol) in dry chlorobenzene (12 mL), aminomethylated alkyne (0.3336 mmol) and Ti(O*i*-Pr)$_4$ (0.08 mL, 0.278 mmol) under a dried argon atmosphere at room temperature. The resulting solution was heated to 80 ^{o}C (oil bath), and EtMgBr (1 M solution in diethyl ether, 1.112mmol) was added dropwise during 2—3 min. The reaction mixture stirred for 30 min and was quenched with an 8-10 % (aq.) solution of HCl. The layers were separated and the organic layer passed through a column with small amount of silica gel. The reaction products **2a-d**, and the starting fullerene C_{60} were separated by the HPLC, eluent was toluene. The samples were washed with hexane and Et_2O before NMR.

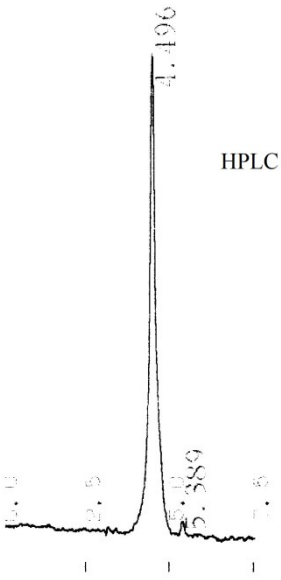
1',4'-Diphenyl-2',3'-Dimethylenebicyclo[2.2.0]hexano[5',6':1,9](C_{60}-I_h)[5,6]fullerene (2a). Brown powder (52 mg, 65 % yield). UV ($CHCl_3$) λ = 256, 316, 431, 695. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.51 (d, *J* = 7.0 Hz, 1H, CH (Ph)), 7.25-7.31 (m, 1H, CH (Ph)), 6.24 (s, 2H, CH_2), 5.69 (s, 2H, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$) *δ* = 154.4, 149.8, 147.7, 146.6, 146.3, 145.9, 145.8, 145.6, 145.5, 144.9, 143.2, 142.9, 142.4, 142.3, 141.9, 140.3, 139.1, 135.6, 130.0, 128.3, 127.5, 115.7, 71.0, 30.1. HRMS (MALDI TOF) $[M]^-$ calcd. for $C_{78}H_{14}$ 950.1095; Found 950.1101.

1',4'-Di(o-fluorophenyl)-2',3'--Dimethylenebicyclo[2.2.0]hexano[5',6':1,9](C_{60}-I_h)[5,6]fullerene (2b). Brown powder (41 mg, 51 % yield). UV ($CHCl_3$) λ = 255, 312, 432, 694. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.52 (t, *J* = 6.7 Hz, 1H, CH (Ph)), 7.28 (s, 1H, CH (Ph)), 7.05-7.13 (m, 1H, CH (Ph)), 6.31 (s, 2H, CH_2), 5.69 (s, 2H, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$) *δ* = 160.7, 158.7, 154.8, 147.8, 147.6, 146.6, 146.3, 145.9, 145.6, 145.5, 144.8, 143.2, 142.8, 142.4, 142.2, 141.8, 140.1, 137.4, 135.2, 131.3, 129.8, 126.9, 124.0, 116.1, 115.8, 115.6, 69.4, 30.0. HRMS (MALDI TOF) $[M]^-$ m/z = calcd. for $C_{78}H_{12}F_2$ 986.0907; Found 986.0903.

1',4'-Di(m-fluorophenyl)-2',3'-Dimethylenebicyclo[2.2.0]hexano[5',6':1,9](C_{60}-I_h)[5,6]fullerene (2c). Brown powder (46 mg, 57 % yield). UV ($CHCl_3$) λ = 256, 312, 432, 694. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.32-7.35 (m, 1H, CH (Ph)), 7.28 (s, 1H, CH (Ph)), 7.22 (d, *J* = 9.4 Hz, 1H, CH (Ph)), 7.00 (s (b), 1H, CH (Ph)), 6.29 (s, 2H, CH_2), 5.70 (s, 2H, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 163.6, 161.6, 154.1, 149.2, 147.8, 146.6, 146.4, 145.8, 145.7, 145.6, 144.8, 143.2, 142.9, 142.4, 142.3, 141.9, 140.9, 140.8, 140.3, 139.8, 135.5, 130.0, 129.9, 125.7, 116.9, 116.8, 116.1, 114.8, 114.6, 70.8, 30.0. HRMS (MALDI TOF) $[M]^-$ m/z = calcd. for $C_{78}H_{12}F_2$ 986.0907; Found 986.0910.

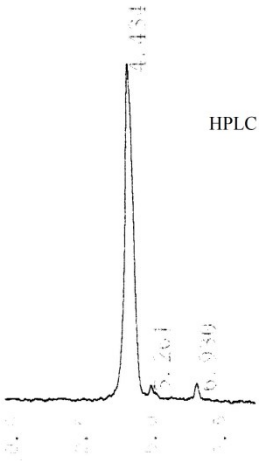
1',4'-Dibenzyl-2',3'-Dimethylenebicyclo[2.2.0]hexano[5',6':1,9](C_{60}-I_h)[5,6]fullerene (2d). Brown powder (54 mg, 68 % yield). UV ($CHCl_3$) λ = 256, 311, 433, 696. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.46 (d, *J* = 7.3 Hz, 1H, CH (Ph)), 7.25-7.28 (m, 1H, CH (Ph)), 7.15-7.18 (m, 1H, CH (Ph)), 5.70 (s, 2H, CH_2), 6.05 (s, 2H, CH_2), 4.35 (s, 2H, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 154.1, 149.2, 147.6, 146.5, 146.2, 145.8, 145.6, 145.4, 144.7, 143.0, 142.7, 142.3, 141.9, 141.7, 139.9, 138.5, 137.7, 135.5, 130.0, 129.3, 128.6, 126.7, 112.5, 70.2, 38.3, 30.0. HRMS (MALDI TOF) $[M]^-$ m/z = calcd. for $C_{80}H_{18}$ 978.1408; Found 978.1399.

3. Copies of MALDI, ^{1}H, ^{13}C, HSQC, HMBC spectra



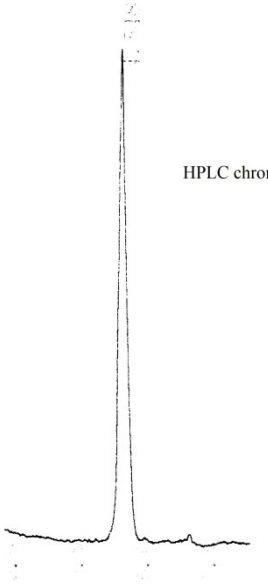
HPLC chromatogramma of **2a**

PKNO	TIME	AREA	HEIGHT	CONC
1	4.496	373950	26107	98.7095
2	5.389	4889	738	1.2905
	TOTAL	378839	26845	100



HPLC chromatogramma of **2b**

CH	PKNO	TIME	AREA	HEIGHT	CONC
1	1	4.434	452352	21646	97.156
	2	5.261	3942	596	0.8466
	3	6.93	9300	986	1.9974
	TOTAL		465593	23228	100

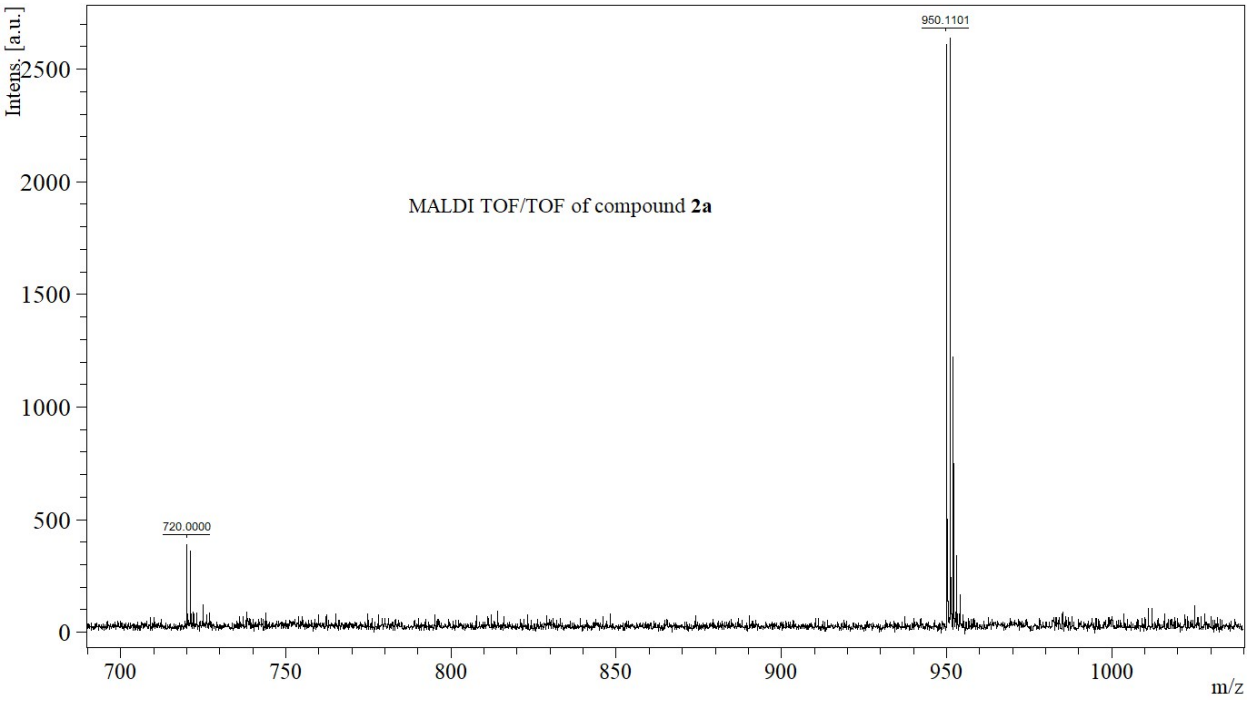


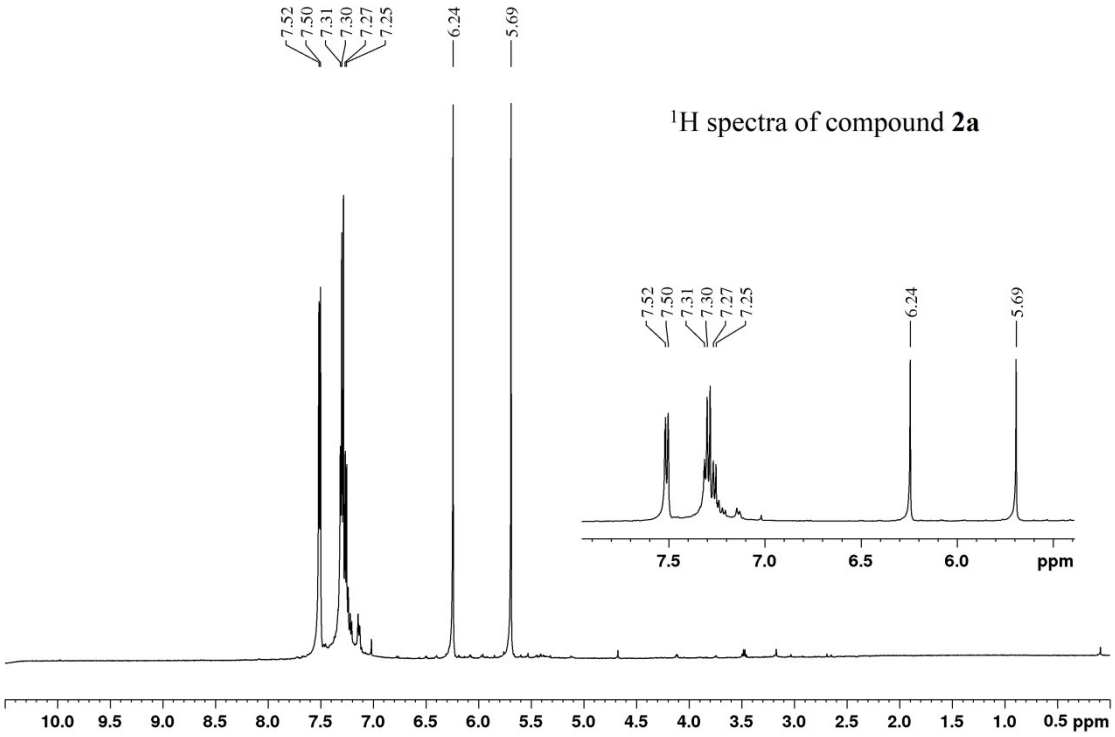
HPLC chromagramma of **2c**

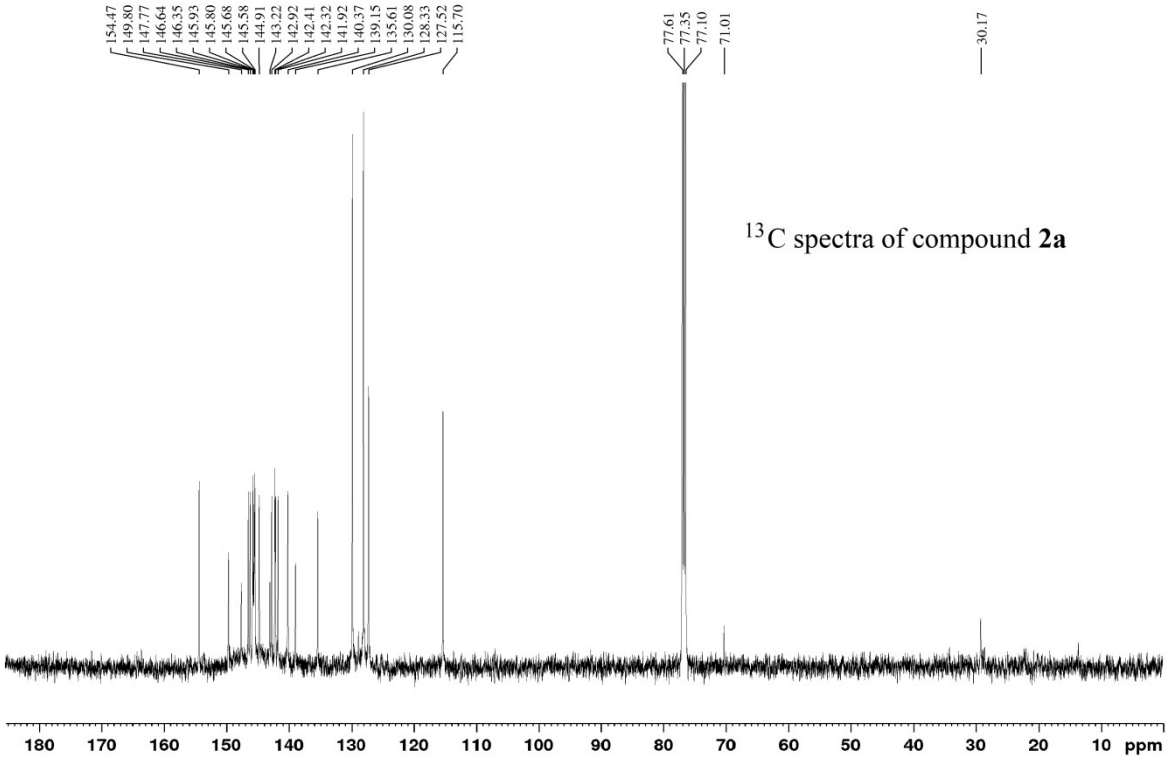
CH	PKNO	TIME	AREA	HEIGHT		IDNO	CONC
1	1	4.548	698378	53843			100
		TOTAL	698378	53843			100

HPLC chromatogramma of **2d**

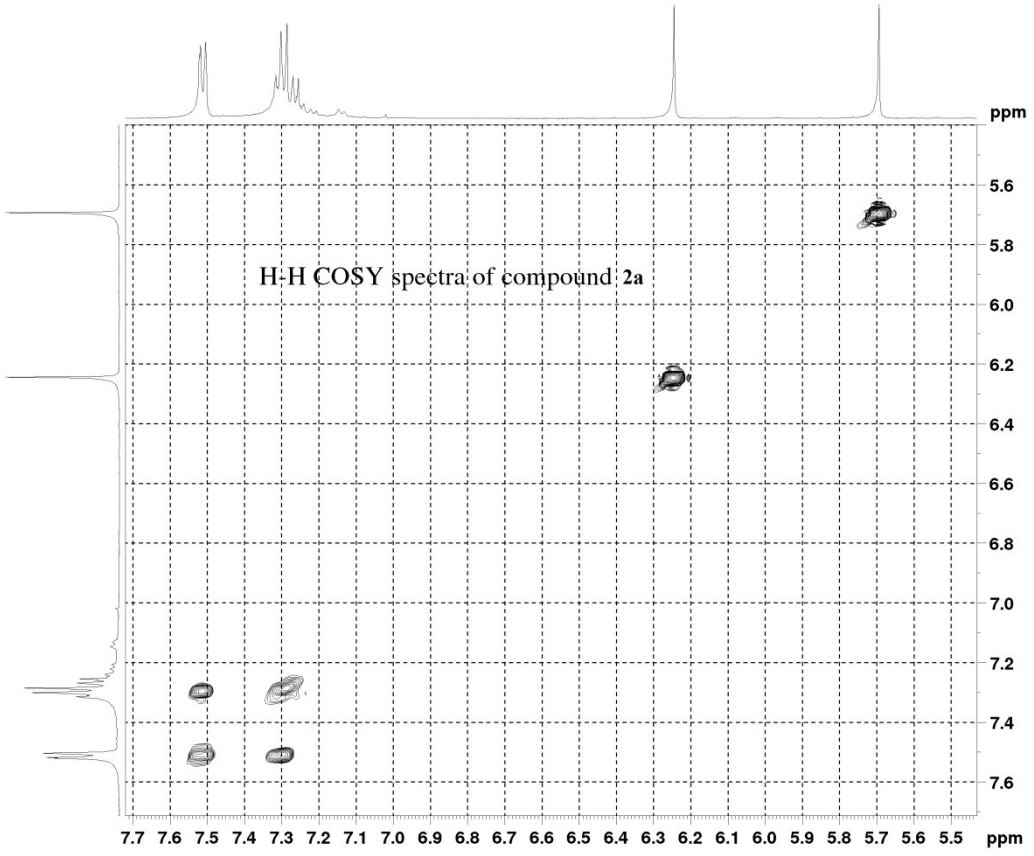
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC
1	1	3.867	11183	1255			0.7425
	2	4.153	9952	1328	V		0.6608
	3	4.508	1480301	105927	V		98.284
	4	5.416	4710	717			0.3127
		TOTAL	1506146	109227			100


Intens. [a.u.]
2500
2000
1500
1000
500
0
950.1101
720.0000
MALDI TOF/TOF of compound 2a
700
750
800
850
900
950
1000
m/z

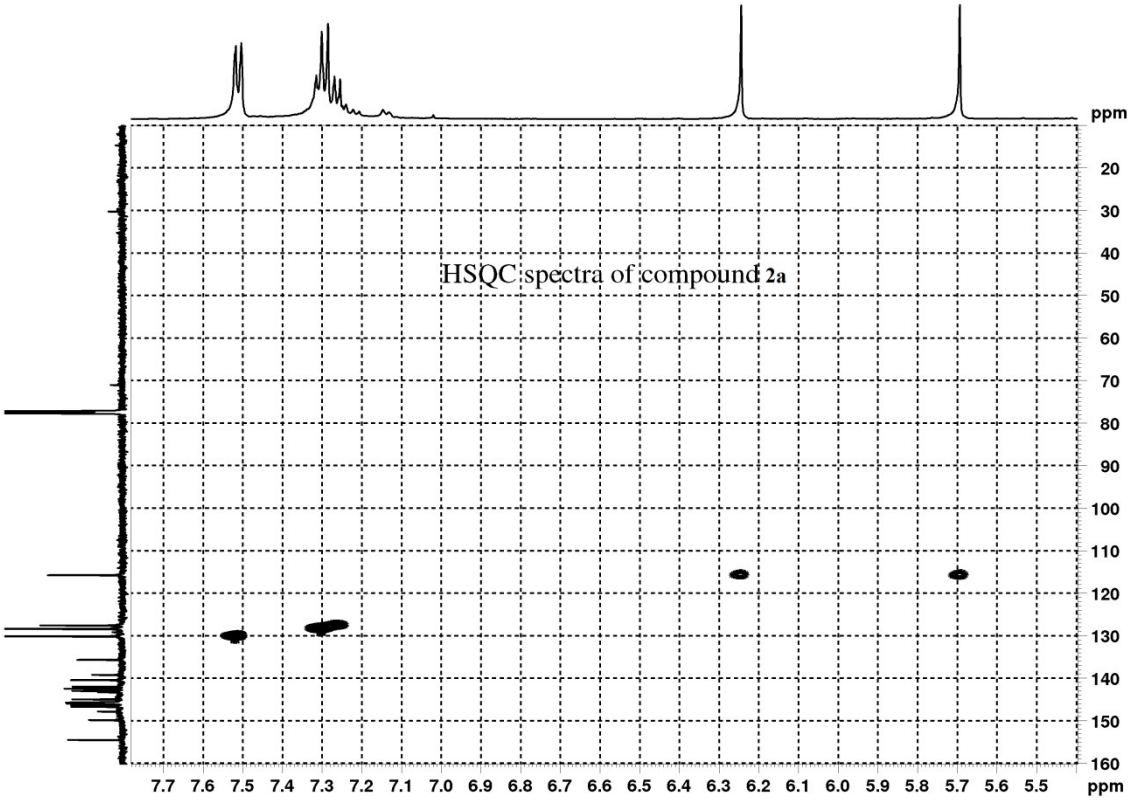

7.52
7.50
7.31
7.30
7.27
7.25
6.24
5.69
1H spectra of compound 2a
7.5
7.0
6.5
6.0
ppm
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5 ppm



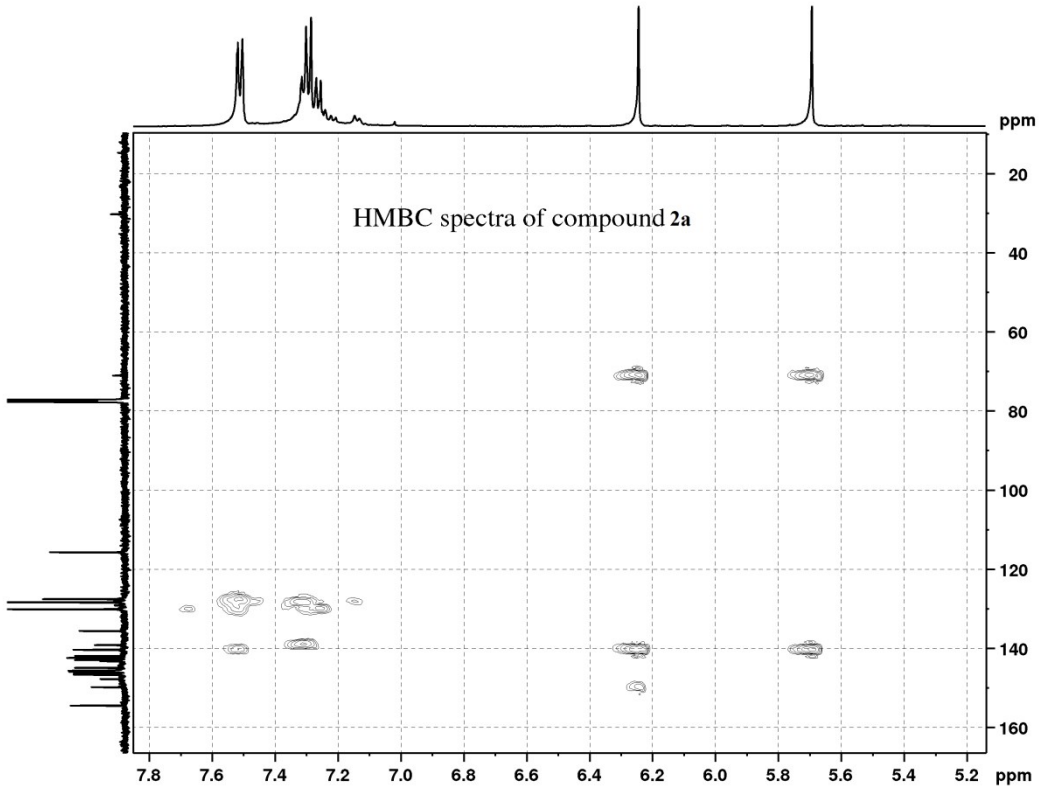
^{13}C spectra of compound **2a**



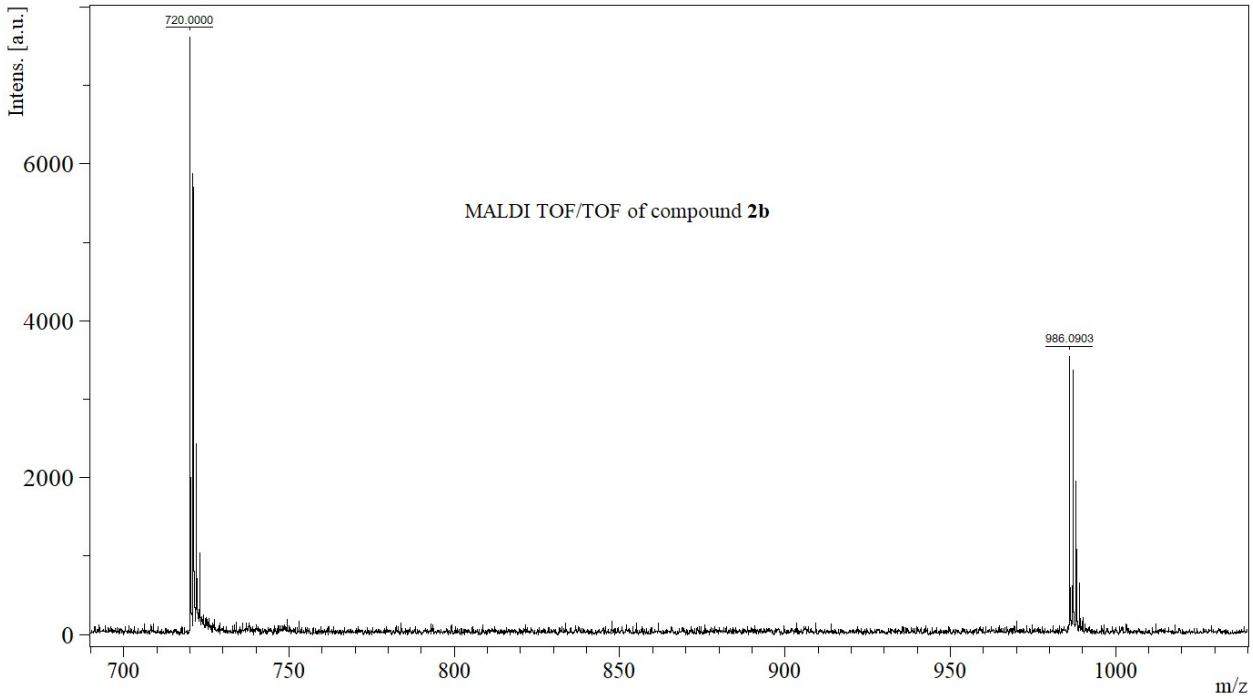
H-H COSY spectra of compound **2a**



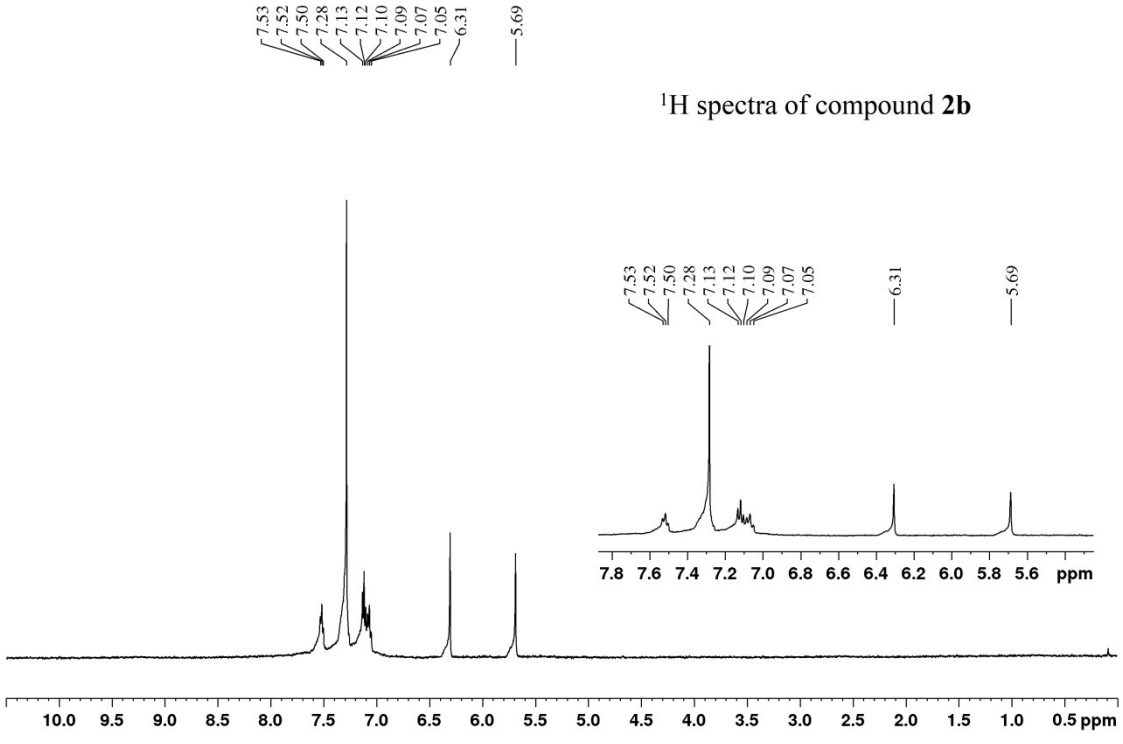
HSQC spectra of compound **2a**



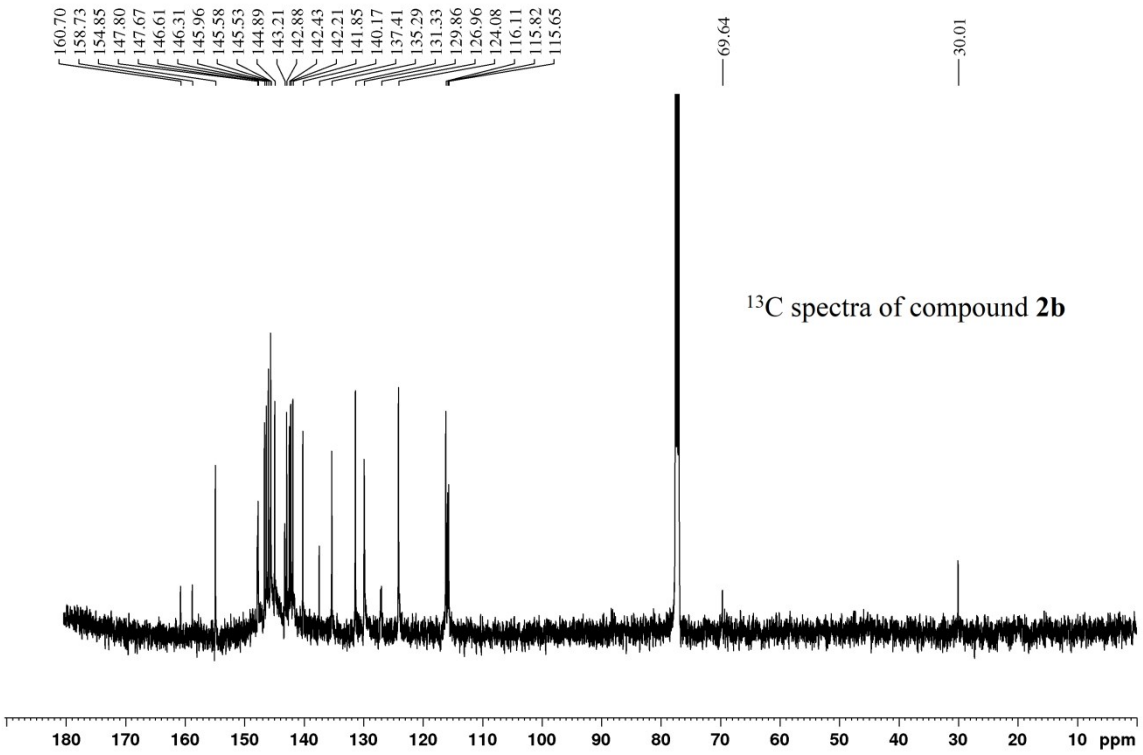
HMBC spectra of compound **2a**



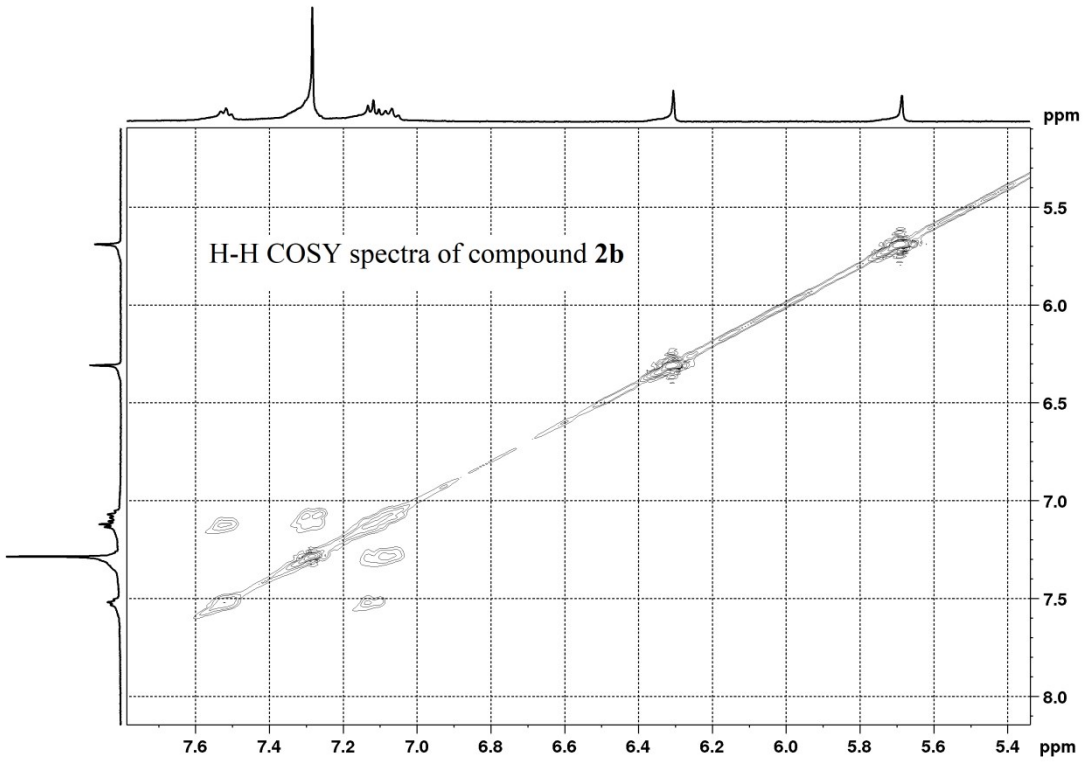
MALDI TOF/TOF of compound **2b**



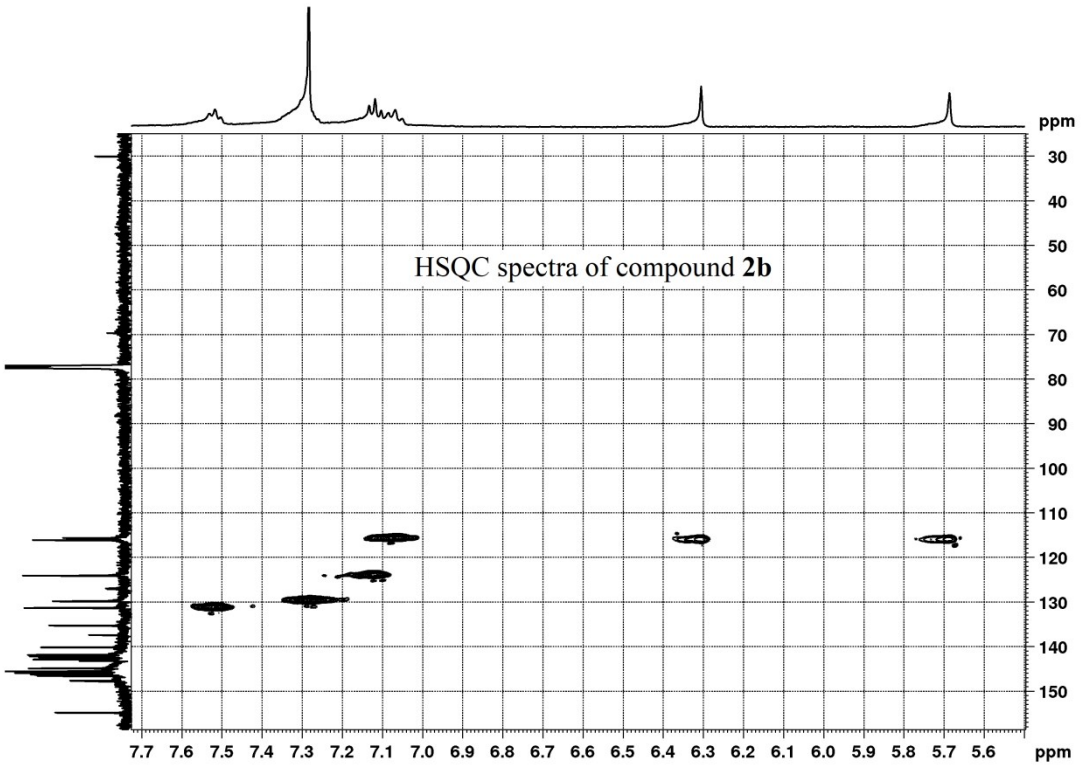
^{1}H spectra of compound **2b**

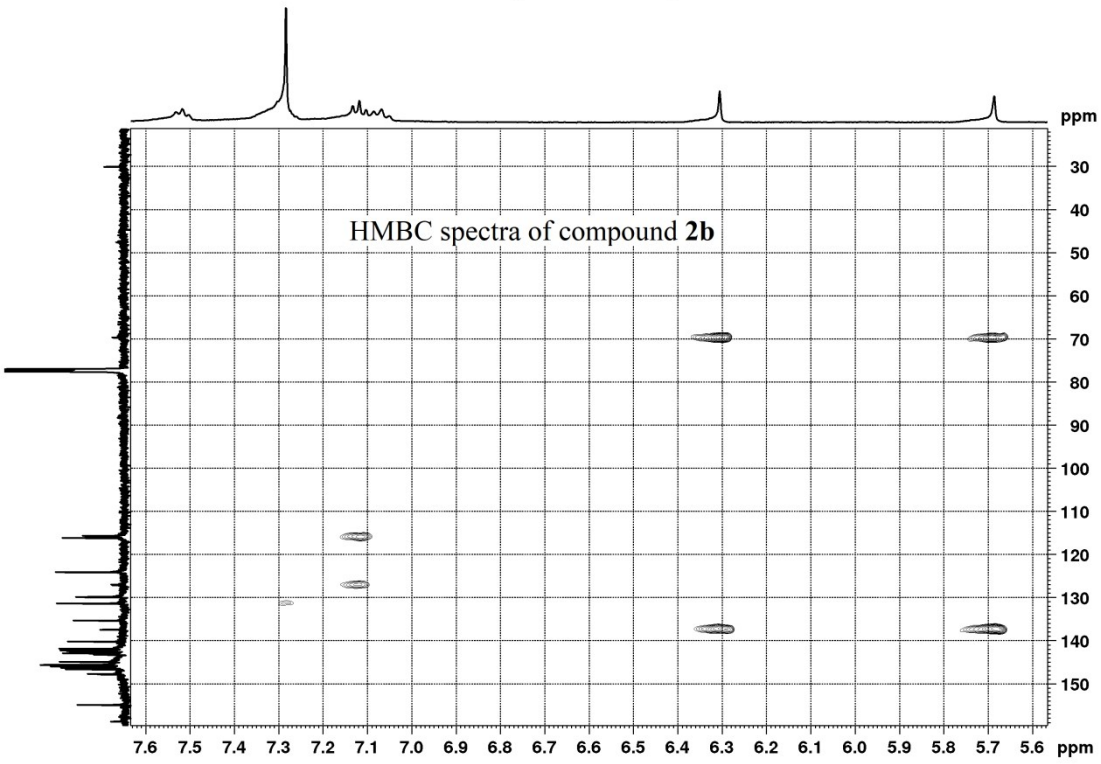


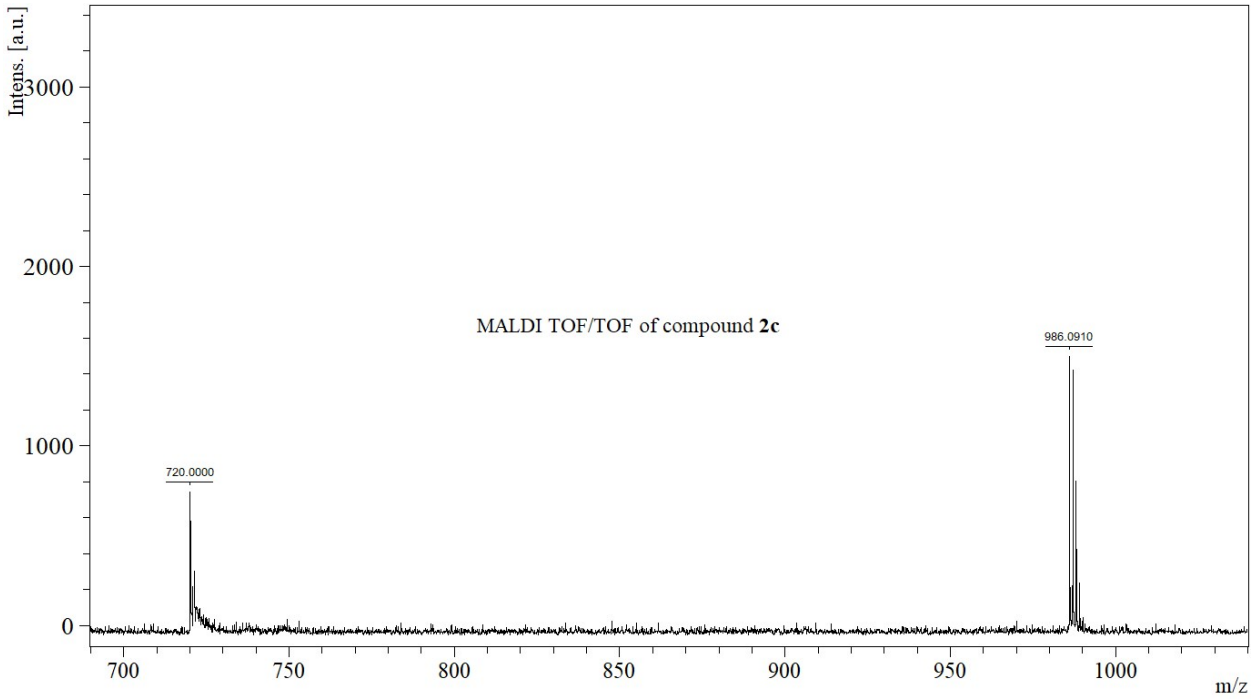
^{13}C spectra of compound **2b**

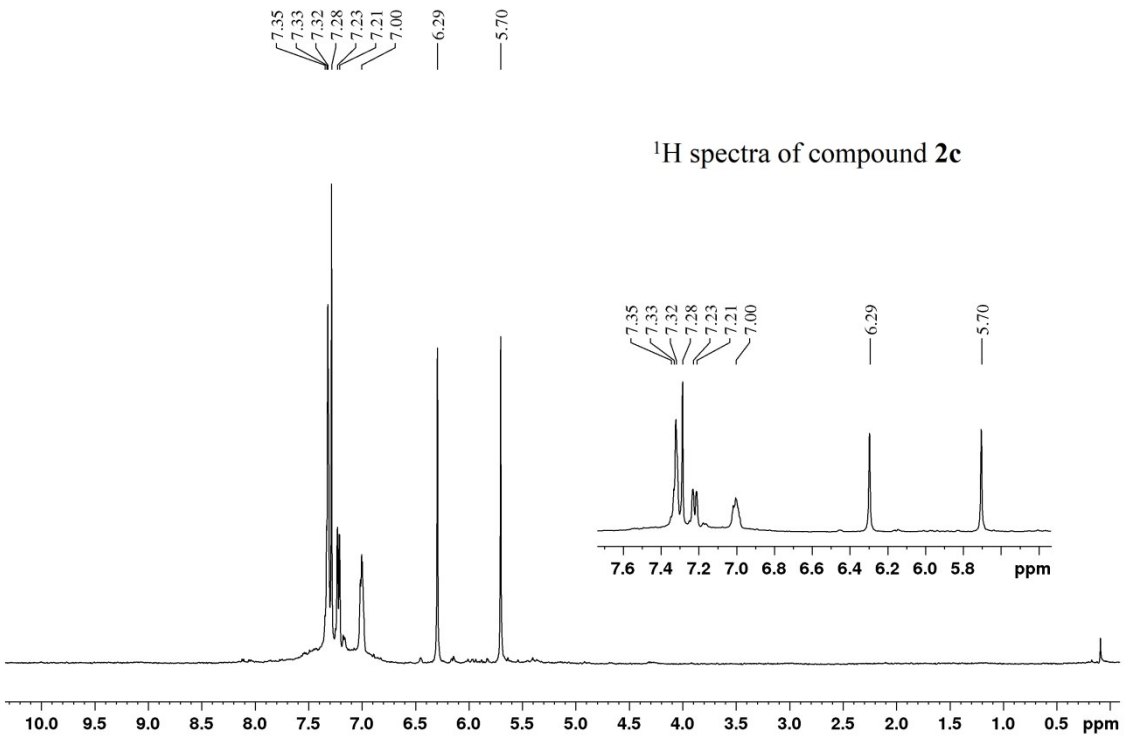


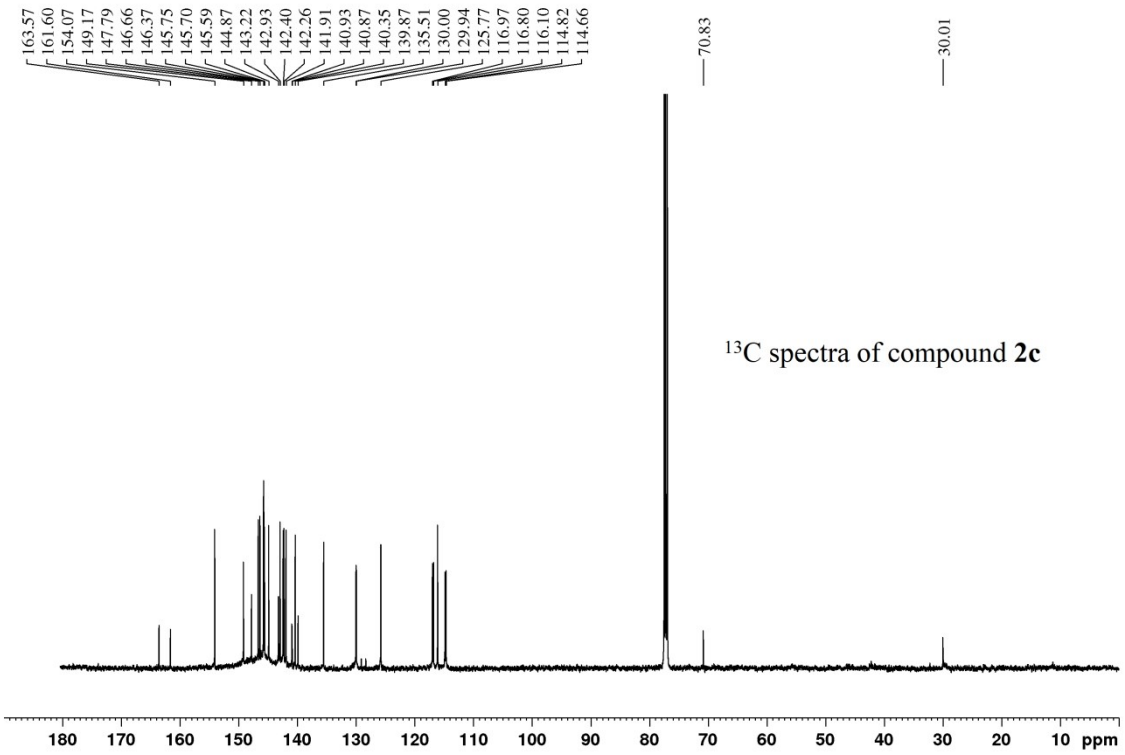
H-H COSY spectra of compound **2b**


HSQC spectra of compound **2b**
ppm
30
40
50
60
70
80
90
100
110
120
130
140
150
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6
ppm

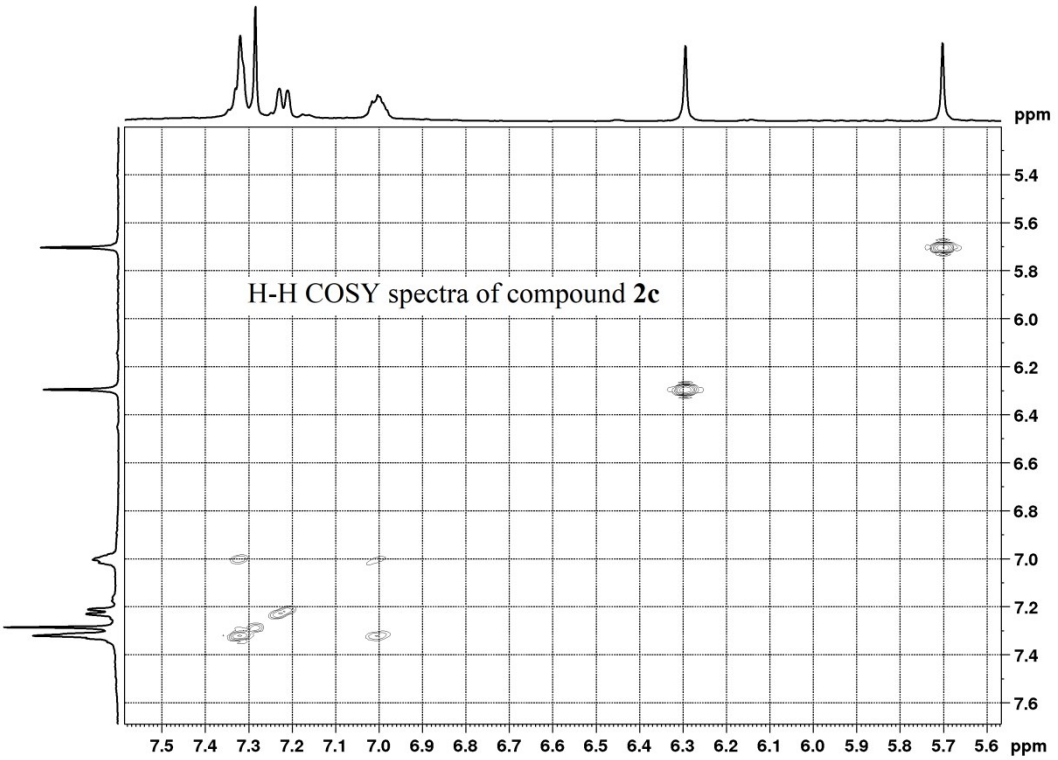

HMBC spectra of compound **2b**
ppm
30
40
50
60
70
80
90
100
110
120
130
140
150
7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6
ppm


Intens. [a.u.]
3000
2000
1000
0
MALDI TOF/TOF of compound 2c
720.0000
986.0910
700
750
800
850
900
950
1000
m/z

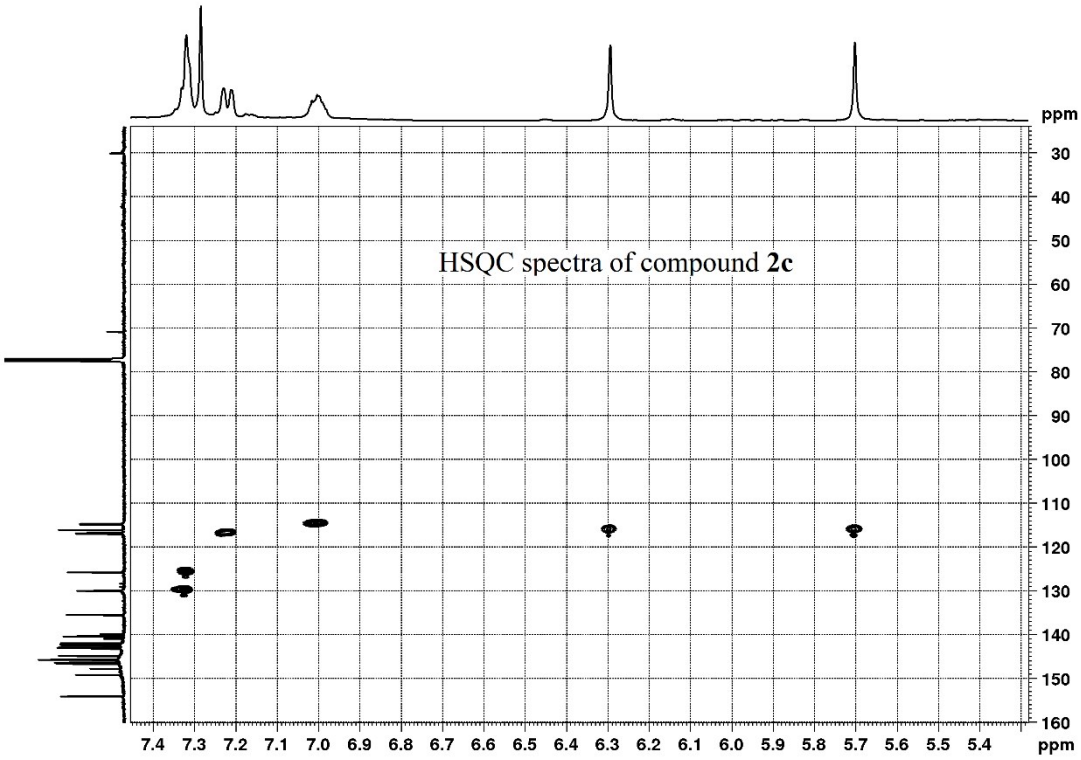

7.35
7.33
7.32
7.28
7.23
7.21
7.00
6.29
5.70
1H spectra of compound 2c
7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 ppm
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

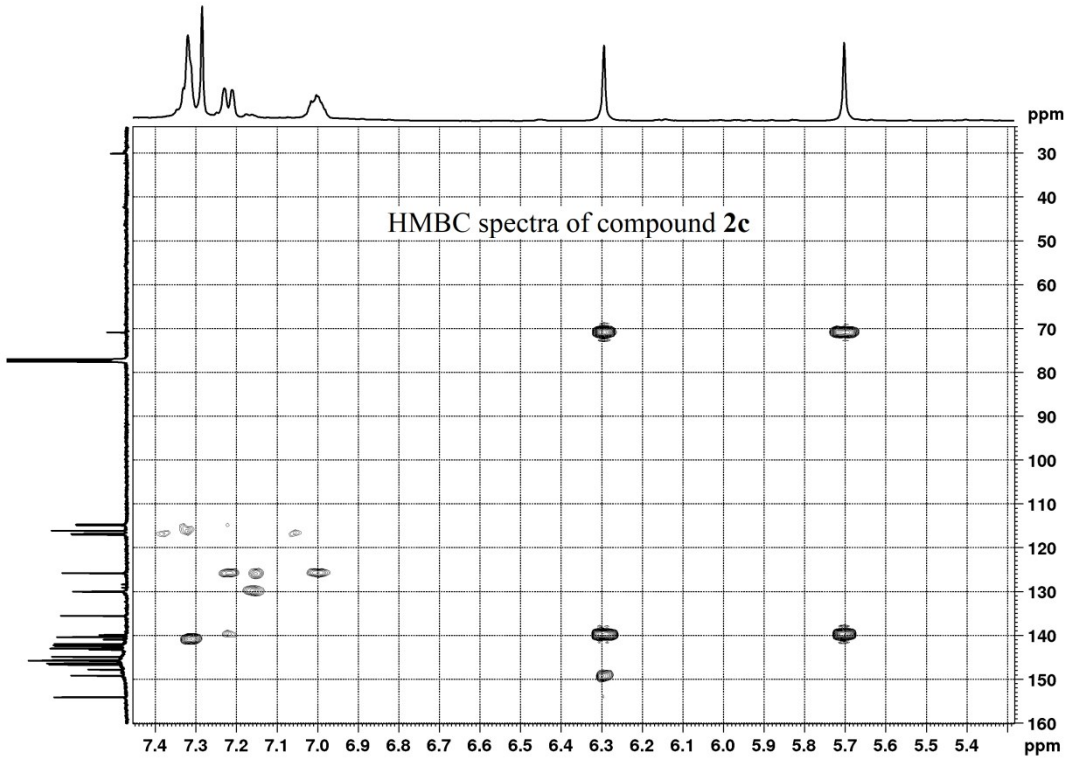


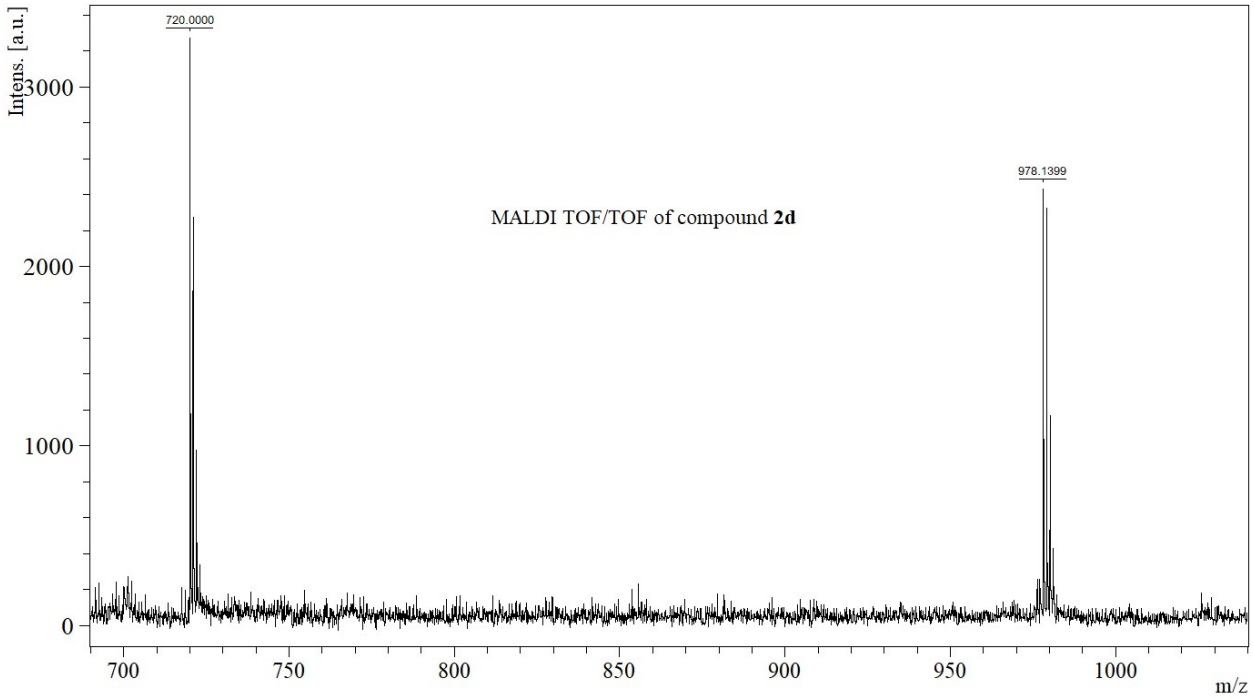
^{13}C spectra of compound **2c**



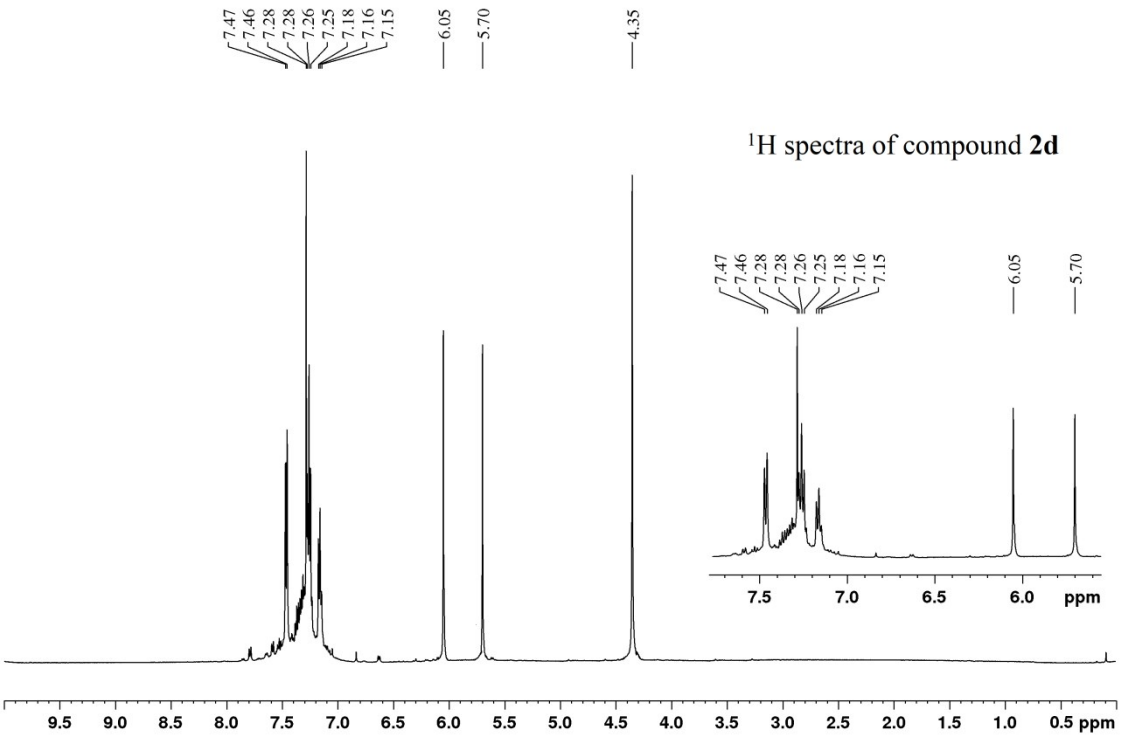
H-H COSY spectra of compound **2c**


HSQC spectra of compound **2c**
ppm
30
40
50
60
70
80
90
100
110
120
130
140
150
160
7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4
ppm

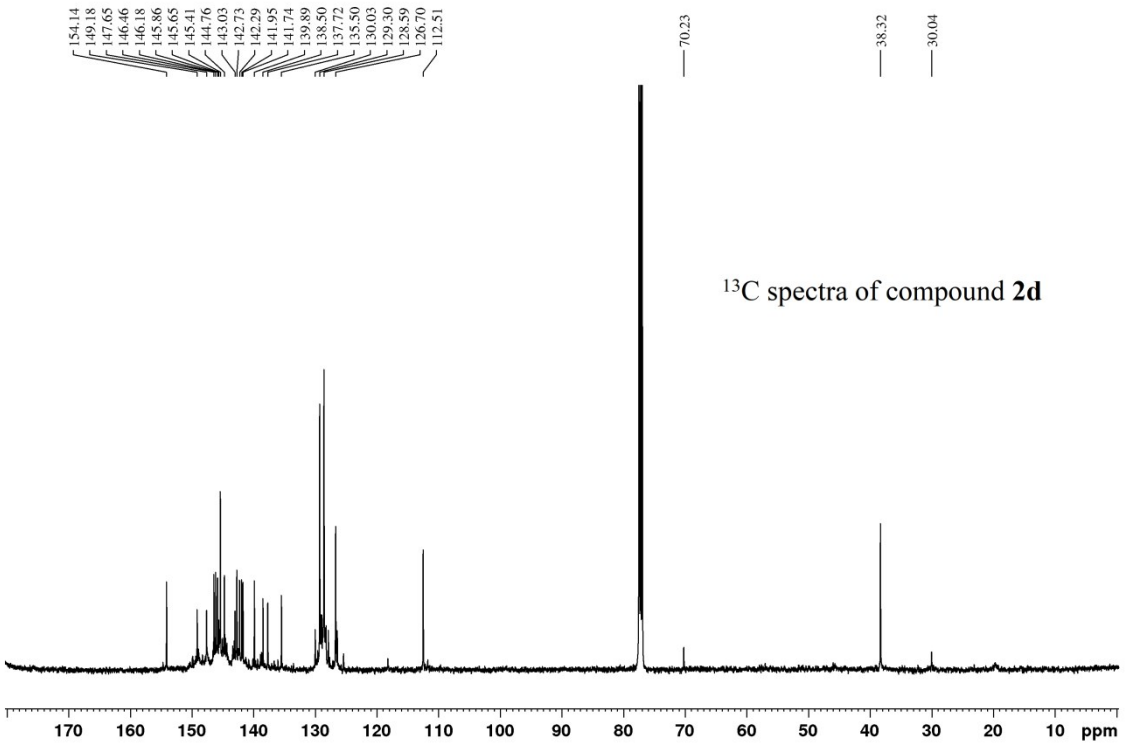

HMBC spectra of compound **2c**
ppm
30
40
50
60
70
80
90
100
110
120
130
140
150
160
7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4
ppm



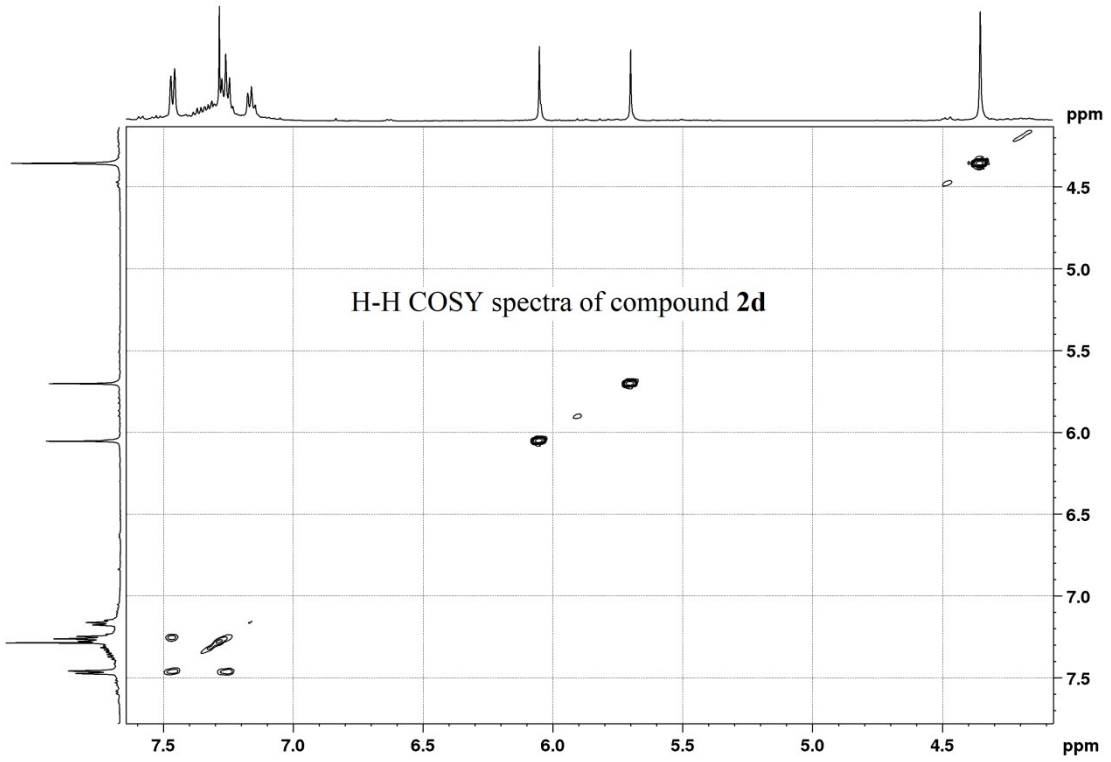
MALDI TOF/TOF of compound **2d**



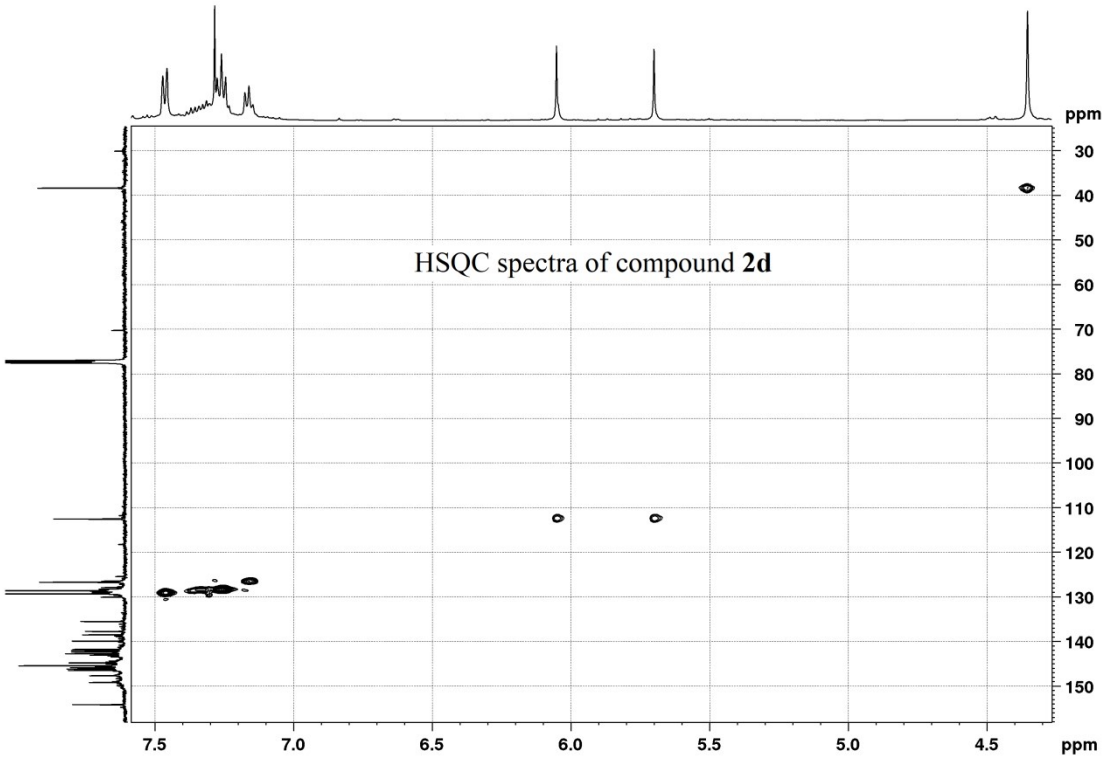
^{1}H spectra of compound **2d**

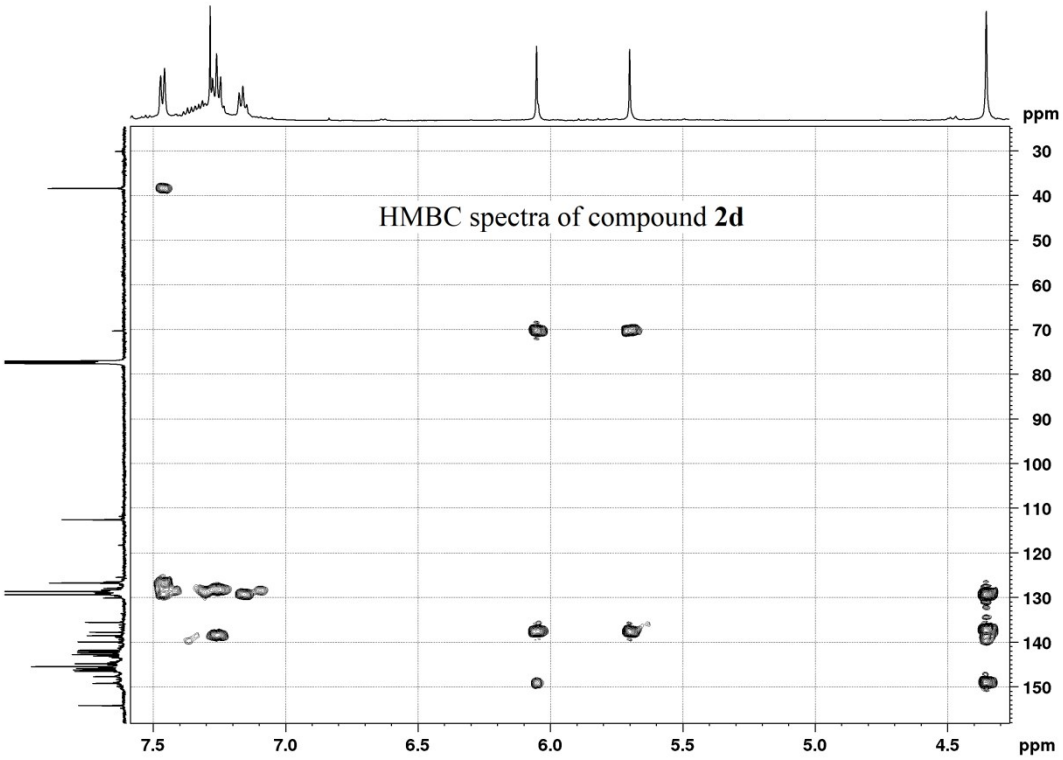


^{13}C spectra of compound **2d**



H-H COSY spectra of compound **2d**


HSQC spectra of compound **2d**
ppm
30
40
50
60
70
80
90
100
110
120
130
140
150
7.5
7.0
6.5
6.0
5.5
5.0
4.5
ppm


HMBC spectra of compound **2d**
ppm
30
40
50
60
70
80
90
100
110
120
130
140
150
7.5
7.0
6.5
6.0
5.5
5.0
4.5
ppm