Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Stokes Shift/emission efficiency trade–off in Donor-Acceptor perylene monoimides for Luminescent Solar Concentrators.

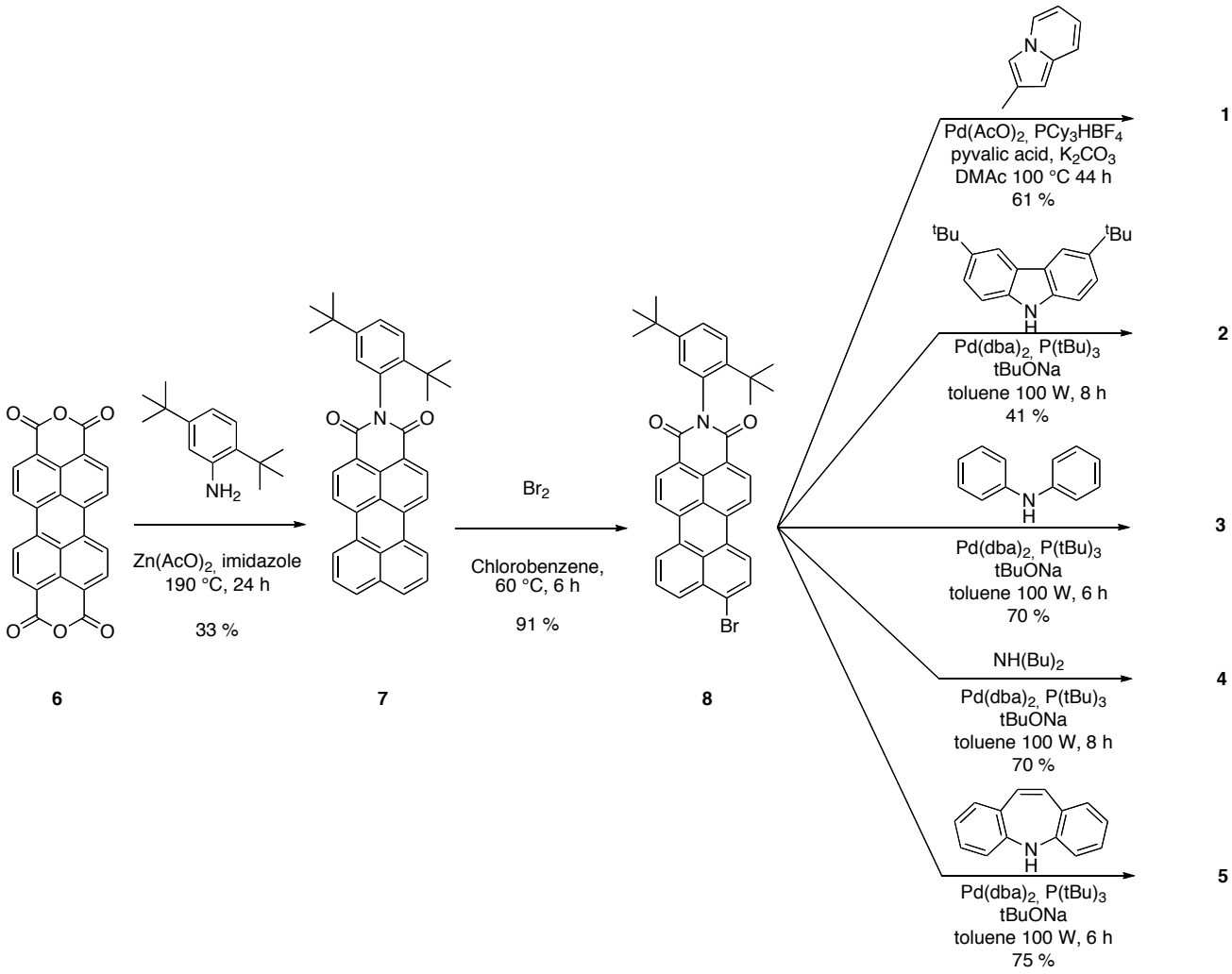
Riccardo Turrisi, Alessandro Sanguineti, Mauro Sassi, Brett Savoie, Atsuro Takai, Giorgio E. Patriarca, Matteo M. Salamone, Riccardo Ruffo, Gianfranco Vaccaro, Francesco Meinardi, Mark Ratner, Antonio Facchetti, Tobin J. Marks and Luca Beverina*

Supporting Information

1. Synthesis of all new compounds

Derivatives **7**[1], **8**[2] and **5**[3] were prepared according to the reported literature procedures, all other chemicals and solvents where purchased from Sigma Aldrich and Alfa Chemicals and sed directly as received unless otherwise explicitly stated in the corresponding preparation. NMR spectra were recorded on a Bruker AMX Avance 500 MHz instrument. Microwave enhanced reactions were performed in a CEM Discover Instrument working under Dynamic conditions. Melting points are uncorrected.

Perylen monoimides **2-4** were prepared according to a standard Buckwald-Hartwig amination protocol, whereas derivative **1** was prepared by direct arylation of bromide **8** with 2-methylindolizine.



Scheme S1.

General procedure for the synthesis of perylene monoimides according to B-H arylation. 9-Bromo-*N*-(2,5-Di-*tert*-butylphenyl)perylene-3,4-dicarboximide **8** (600 mg, 1.019 mmol), sodium tert-butoxide (141 mg, 1.470 mg) and the corresponding amine (1.0 eq), are loaded in a 100 mL two-neck round bottom flask equipped with a condenser under N_2 atmosphere. The mixture is suspended in anhydrous toluene (30 mL) and degassed with few vacuum/N_2 cycles. In a 25 mL two-neck round bottom flask, the catalyst is prepared: $Pd(dba)_2$ (30 mg, 0.051 mmol) is suspended in anhydrous toluene (5 mL) and $P(^tBu)_3$ (solution 1M in toluene) (0.12 mL, 0.102 mmol) is added. The mixture is left under stirring 15 min and then it is transferred into the reaction flask by standard cannula technique. The final reaction mixture is reacted under microwave irradiation in N_2 atmosphere. After the reported reaction time, the solvent is removed from the mixture and the crude solid is purified by column chromatography.

Derivative **2**. Bromide **8** (600 mg, 1.019 mmol), 3,6-di-*tert*-butylcarbazole (313 mg, 1.120 mmol) and sodium tert-butoxide (141 mg, 1.470 mg) are allowed to react under microwave irradiation (100 W, 8 h) under N_2 atmosphere. Solvent is removed and the dark crude solid is purified by column chromatography (silica, toluene/CH_2Cl_2 1:8) to give the title compound as a red solid (330 mg, 0.419 mmol, 41%). m.p. > 350 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ[ppm]: 8.72 (d, 1H, J=7.9), 8.71 (d, 1H, J=7.8), 8.64 (d, 1H, J=8.2), 8.57 (d, 1H, J=8.4), 8.55-8.53 (m, 1H), 8.23 (d, 2H, J=1.7), 7.77 (d, 1H, J=8.0), 7.61 (d, 1H, J=8.6), 7.61-7.51 (m, 3H), 7.47 (dd, 1H, J=8.5, J=2.2), 7.45-7.42 (m, 2H), 7.05-7.02 (m, 3H), 1.49 (s, 18H), 1.34 (s, 9H), 1.33 (s, 9H); ^{13}C NMR (125.7 MHz, Chloroform-*d*) δ[ppm]: 165.8, 150.9, 144.7, 144.1, 141.3, 138.2, 138.1, 137.8, 133.9, 132.9, 132.8, 132.7, 131.2, 130.8, 130.4, 130.3, 129.6, 128.7, 128.6, 128.3, 127.9, 127.8, 127.0, 125.3, 124.8, 124.7, 124.5, 122.6, 121.6, 121.5, 117.3, 110.4, 36.4, 35.7, 35.1, 32.9, 32.6, 32.1. Anal. Calcd for $C_{56}H_{54}N_2O_2$: C, 85.46; H, 6.92; N, 3.56. Found: C, 85.57; H, 6.83; N, 3.64.

Derivative **3**. Bromide **8** (600 mg, 1.019 mmol), diphenylamine (203 mg, 1.020 mmol) and sodium tert-butoxide (141 mg, 1.470 mg) are allowed to react under microwave irradiation (100 W, 6 h) under a N_2 atmosphere. The solvent is removed and the crude purple solid residue is purified by column chromatography (silica, toluene/AcOEt 9:1) to give the title compound as a violet solid (480 mg, 0.710 mmol, 70%). m.p. 300 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ[ppm]: 8.66 (d, 1H, J=8.0), 8.65 (d, 1H, J=8.0), 8.48 (d, 2H, J=7.7), 8.45 (d, 1H, J=7.9), 8.39 (d, 1H, J=8.2), 8.05 (d, 1H, J=8.4), 7.59 (d, 1H, J=8.6), 7.49 (t, 1H, J=8.0), 7.45 (dd, 1H, J=8.6, J=2.2), 7.41 (d, 1H, J=8.1), 7.28-7.25 (m, 4H), 7.10 (d, 4H, J=7.7), 7.05-7.02 (m, 3H), 1.33 (s, 9H), 1.31 (s, 9H); ^{13}C NMR (125.7 MHz, Chloroform-*d*) δ[ppm]:165.9, 150.8, 149.2, 147.9, 144.7, 138.4, 138.3, 134.0, 132.9, 132.8, 132.2, 131.2, 130.7, 130.3, 129.7, 128.7, 128.5, 128.3, 128.0, 127.6, 127.5, 127.0, 125.6,

125.0, 123.8, 123.7, 122.2, 121.7, 121.1, 120.8, 36.4, 35.1, 32.6, 32.1. Anal. Calcd for $C_{48}H_{40}N_2O_2$: C, 85.18; H, 5.96; N, 4.14. Found: C, 85.24; H, 5.91; N, 4.09.

Derivative **4**. Bromide **8** (600 mg, 1.019 mmol), dibutylamine (132 mg, 1.021 mmol) and sodium tert-butoxide (141 mg, 1.470 mg) are allowed to react under microwave irradiation (100 W, 8 h) under N_2 atmosphere. Solvent is removed and the dark-purple solid residue is purified by column chromatography (silica, AcOEt/ETP 2:8) to give the title compound as a purple solid (300 mg, 0.471 mmol, 46%). M.p. = 155 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ[ppm]: 8.64 (d, 1H, J=8.1), 8.62 (d, 1H, J=8.2), 8.50 (d, 1H, J=7.4), 8.42 (t, 2H, J=8.9), 8.34 (t, 2H, J=8.6), 7.63 (t, 1H, J=7.9), 7.59 (d, 1H, J=9.0), 7.44 (dd, 1H, J=8.6, J=2.2), 7.6 (d, 1H, J=8.1), 7.02 (d, 1H, J=2.2) 3.30 (t, 4H, J=7.4), 1.61-1.55 (m, 4H), 1.33 (s, 9H), 1.30 (s, 9H), 0.89 (t, 6H, J=7.3); ^{13}C NMR (125.7 MHz, Chloroform-*d*) δ[ppm]: 166.0, 165.9, 153.3, 150.8, 144.7, 139.1, 138.9, 134.2, 132.9, 132.7, 131.4, 131.3, 130.4, 130.3, 129.5, 128.8, 128.5, 127.5, 126.9, 126.8, 125.4, 125.0, 124.1, 121.8, 120.6, 120.5, 119.7, 119.2, 54.5, 36.4, 35.1, 32.6, 32.1, 30.2, 21.3, 14.8. Anal. Calcd for $C_{44}H_{48}N_2O_2$: C, 82.98; H, 4.40; N, 7.60. Found: C, 82.72; H, 4.23; N, 7.67.

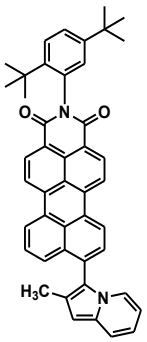
Derivative **1**. Bromide **8** (600 mg, 1.019 mmol), $Pd(AcO)_2$ (3.00 mg, 13.36 μmol), pivalic acid (33 mg, 0.323 mmol), K_2CO_3 (211 mg, 1.529 mmol), tricyclohexylphosphine tetrafluoroborate (7.80 mg, 21.18 μmol) and 2-methylindolizine (147 mg, 1.121 mmol) are loaded in a screw-capped tube under Argon atmosphere. The mixture is suspended in anhydrous DMAc (3.5 mL) and then stirred at 100 °C for 44 h. The mixture is poured into water (100 mL) to give a solid precipitate that is isolated by filtration and purified by column chromatography (silica, CH_2Cl_2/Toluene 10:1) to give the title compound as a purple solid (400 mg, 0.626 mmol, 61%). M.p. = 230 °C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ[ppm]: 8.70 (d, 1H, J=7.9), 8.69 (d, 1H, J=7.9), 8.61 (d, 1H, J=7.8), 8.54-8.51 (m, 3H), 7.73 (d, 1H, J=7.7), 7.61-7.50 (m, 4H), 7.46 (dd, 1H, J= 8.6 J=2.1), 7.42 (d, 1H, J=9.0), 7.04 (bs, 1H), 6.72 (t, 1H, J=7.7), 6.54 (bs, 1H), 6.40-6.36 (m, 1H), 2.27-22.5 (m, 3H), 1.34 (s, 9H), 1.32 (s, 9H); ^{13}C NMR (125.7 MHz, Chloroform-*d*) δ[ppm]: 165.8, 150.9, 144.6, 138.4, 138.2, 134.4, 134.0, 133.9, 133.4, 132.9, 131.5, 131.4, 131.2, 130.7, 130.2, 130.1, 130.0, 128.7, 128.4, 127.8, 127.0, 126.1, 124.9, 124.6, 124.0, 122.3, 121.3, 121.2, 120.6, 119.3, 118.2, 110.9, 101.8, 36.4, 35.1, 32.6, 32.1, 13.3. Anal. Calcd for $C_{45}H_{38}N_2O_2$: C, 84.61; H, 6.00; N, 4.39. Found: C, 84.47; H, 5.99; N, 4.56.

2. Copy of the NMR spectra and Table S1.

2.1. Table S1. ^{1}H and ^{13}C NMR chemical shifts for selected position of derivatives 1-5.

	Perylene ring position and nucleus								
Derivative	**5 ^{1}H**	**5 ^{13}C**	**6 ^{1}H**	**6 ^{13}C**	**7 ^{1}H**	**7 ^{13}C**	**8 ^{1}H**	**8 ^{13}C**	**6b ^{13}C**
1	8.69	132.90	8.52	121.32	8.61	124.62	7.73	131.48	130.26
2	8.72	132.90	8.54	121.57	8.64	124.82	7.77	128.34	130.40
3	8.65	132.82	8.39	121.73	8.45	125.57	7.41	128.26	127.64
4	8.60	132.92	8.30	119.64	8.38	125.44	7.25	119.19	124.10
5	8.55	132.97	8.29	120.41	8.29	124.92	7.28	127.21	123.81

2.2. Derivative **1**.



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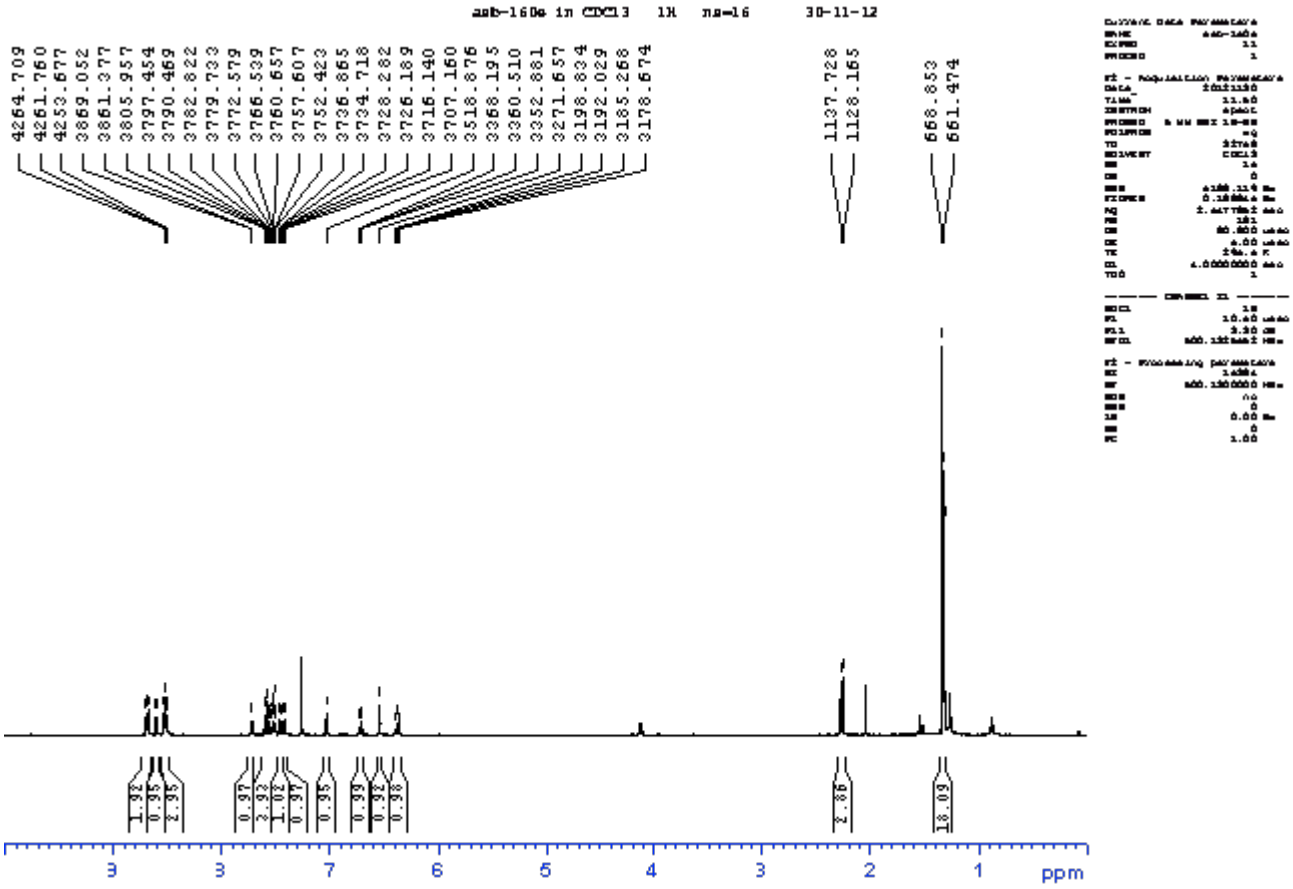

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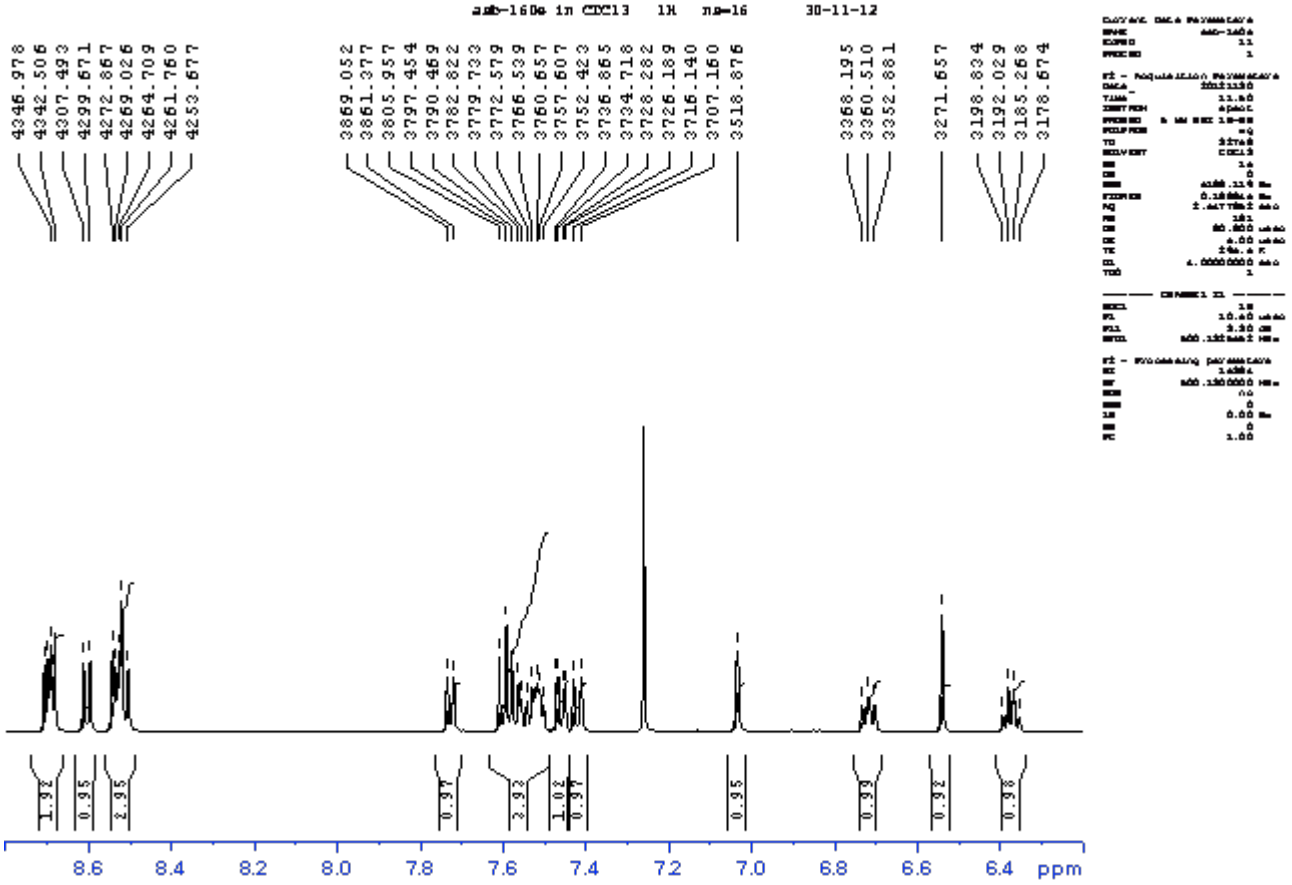
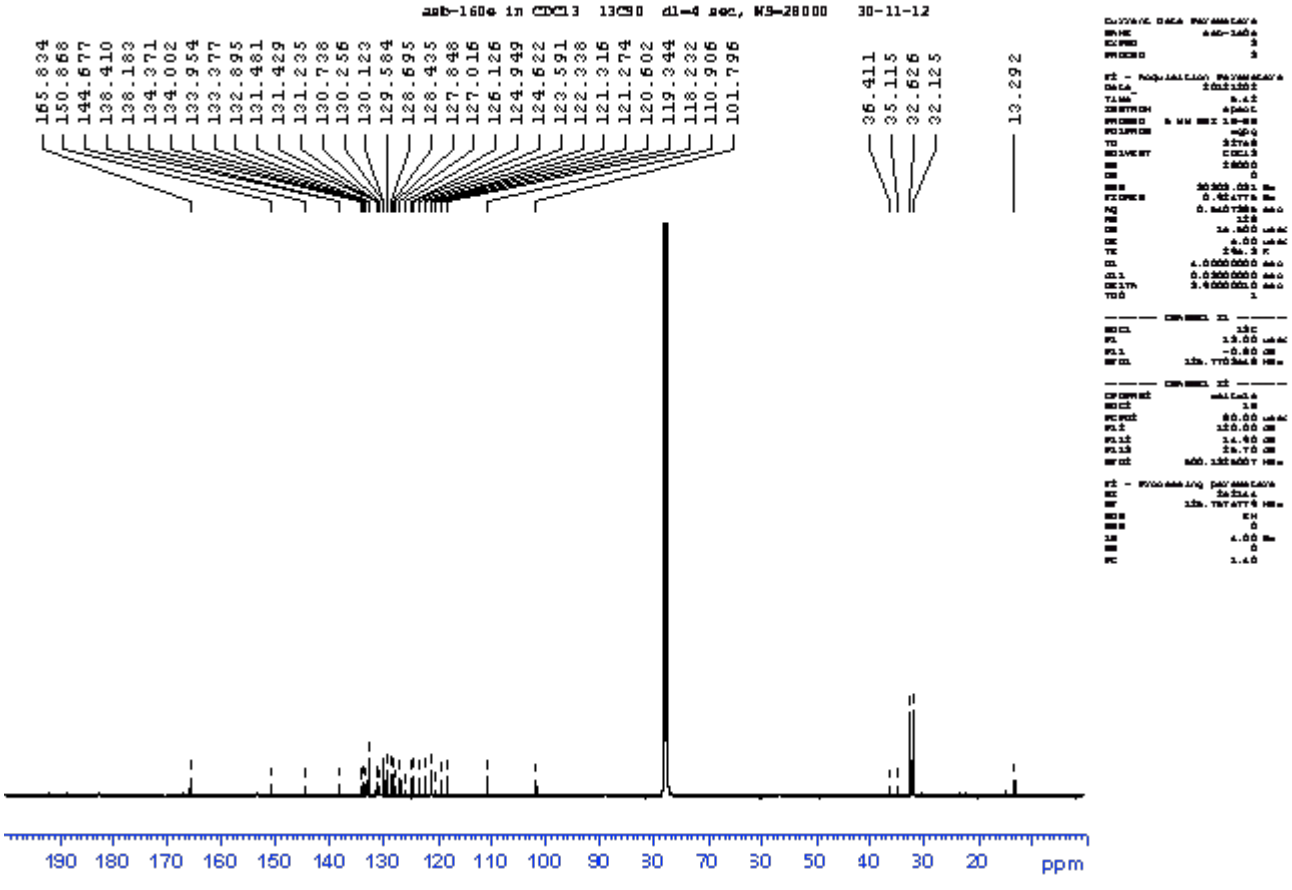


^{13}C full spectral range



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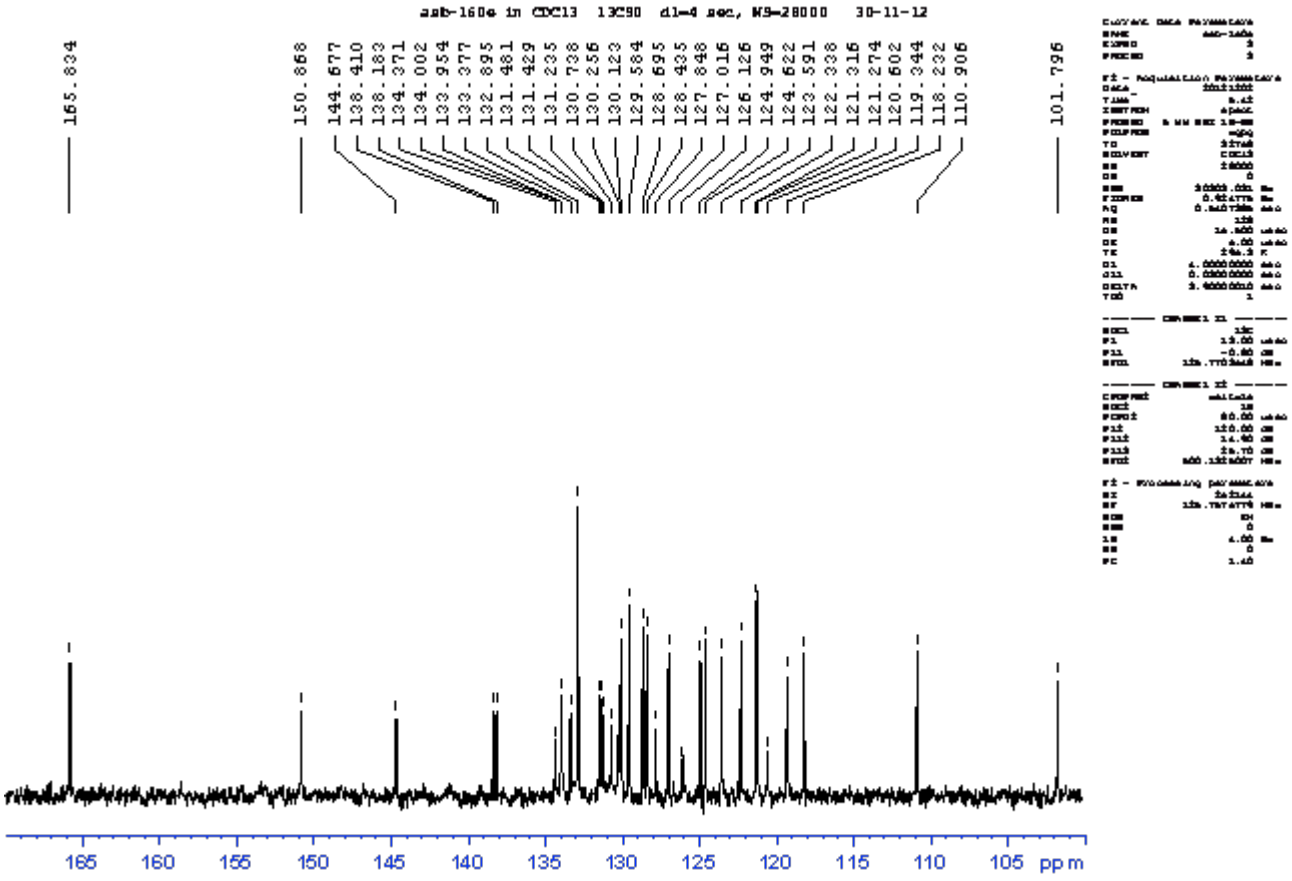

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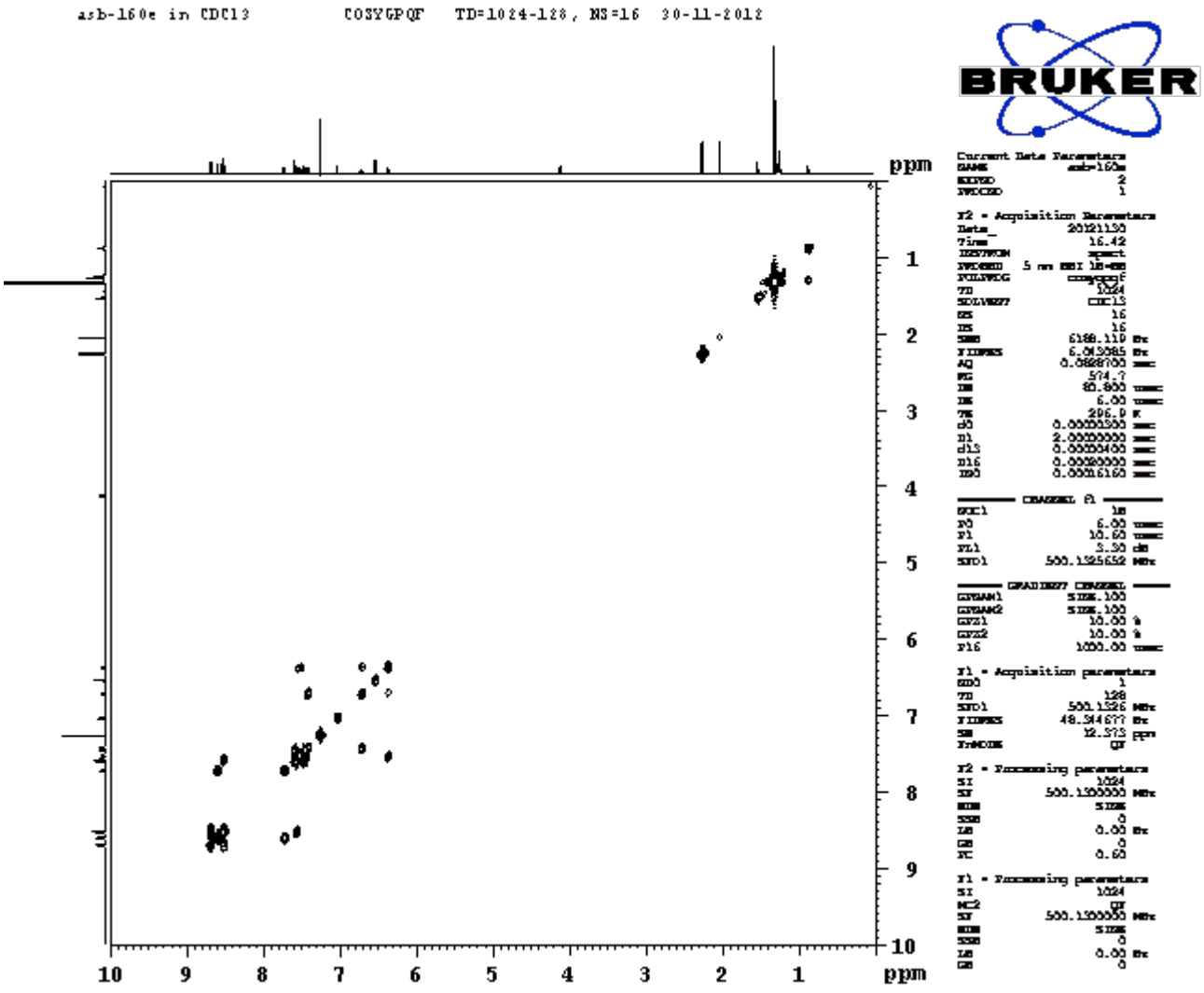

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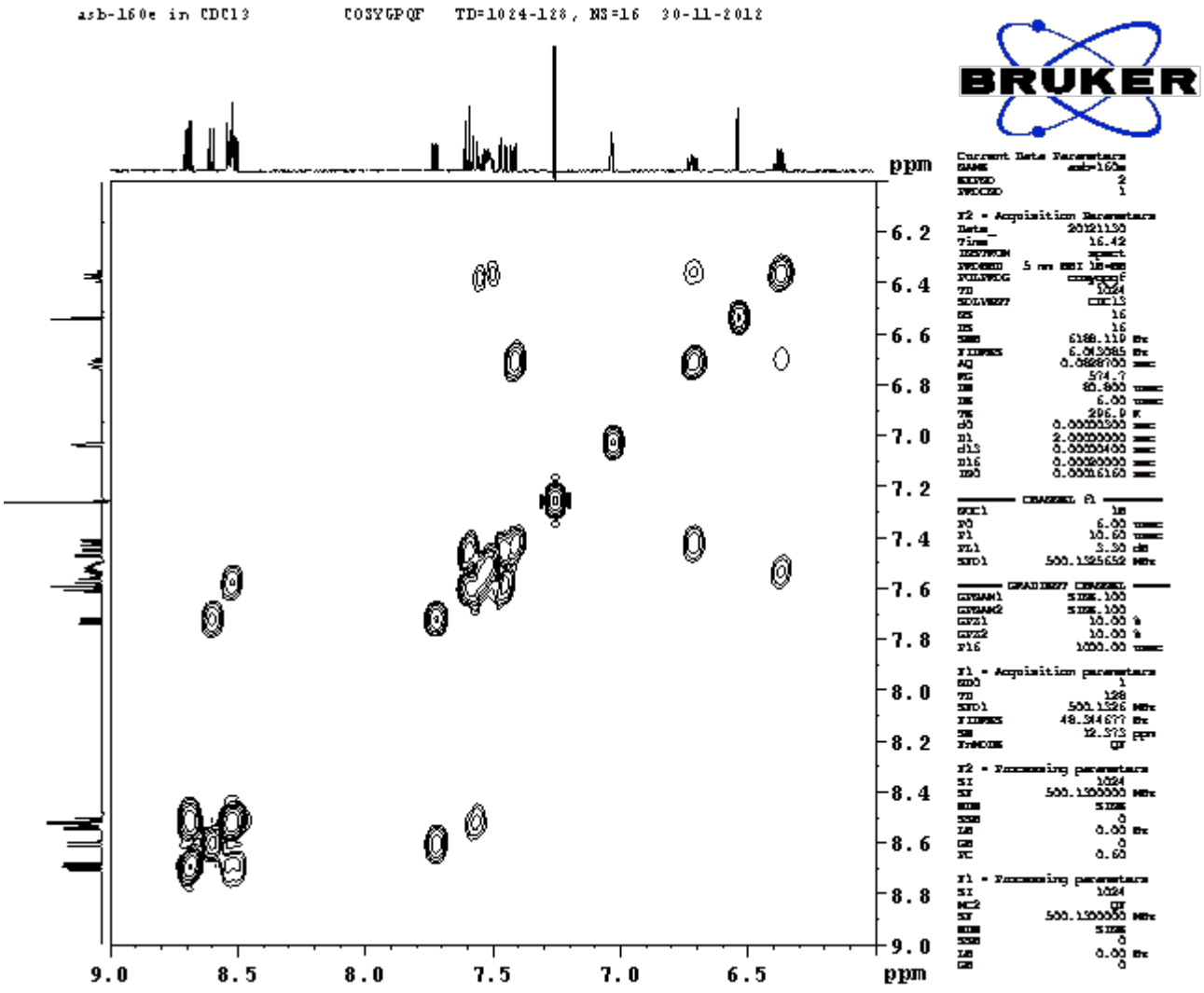
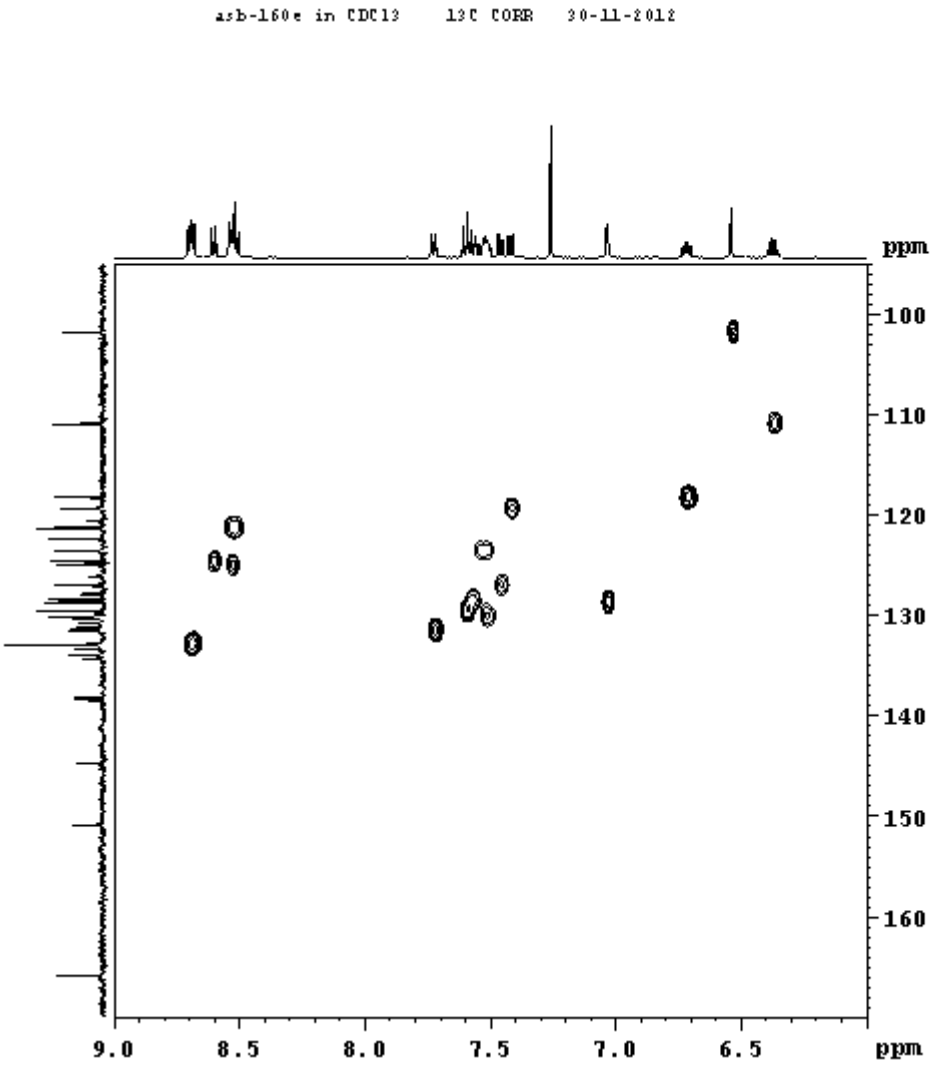
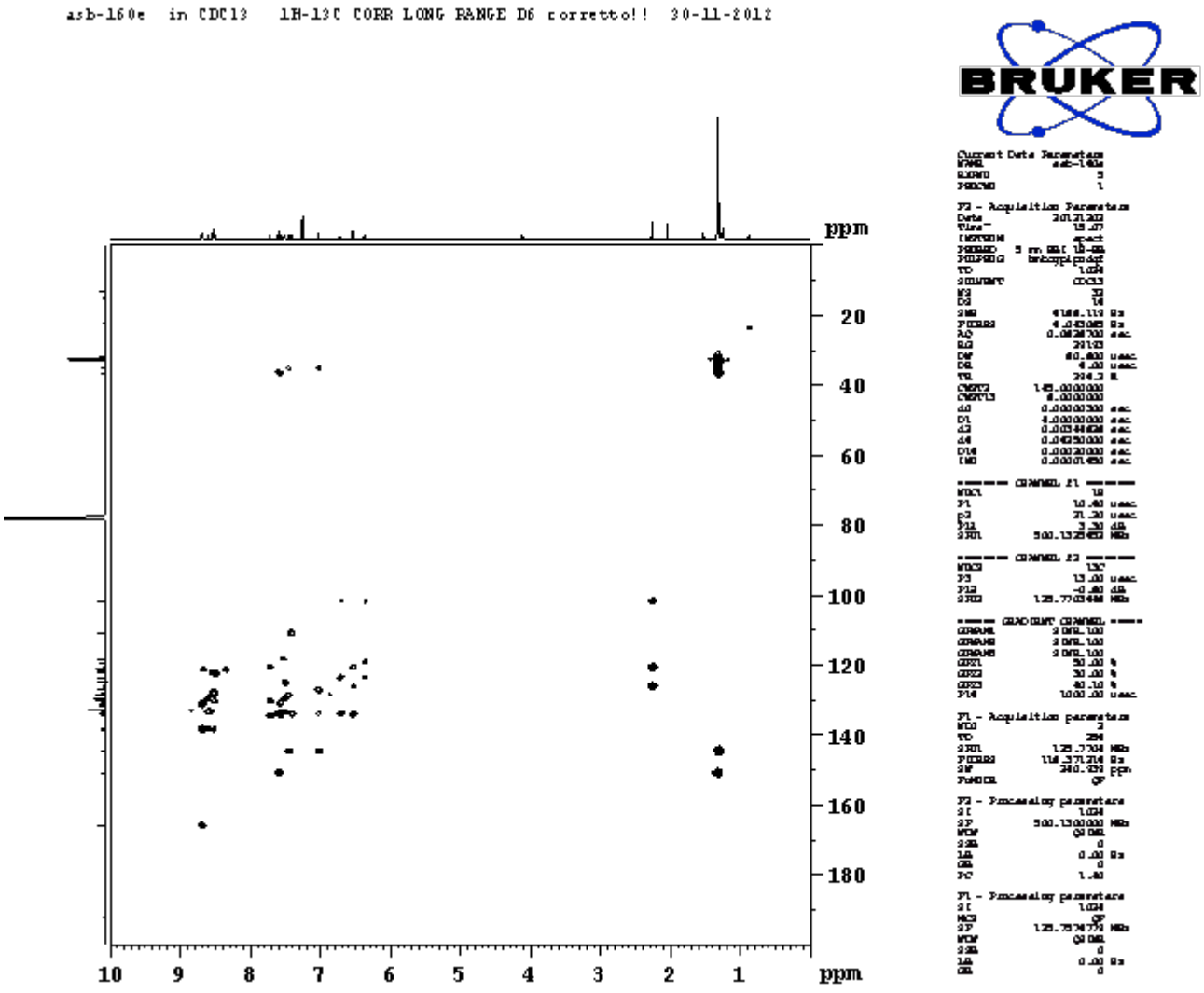


^{1}H ^{13}C HETCOR full spectral range



^{1}H ^{13}C HETCOR long range coupling - full spectral range



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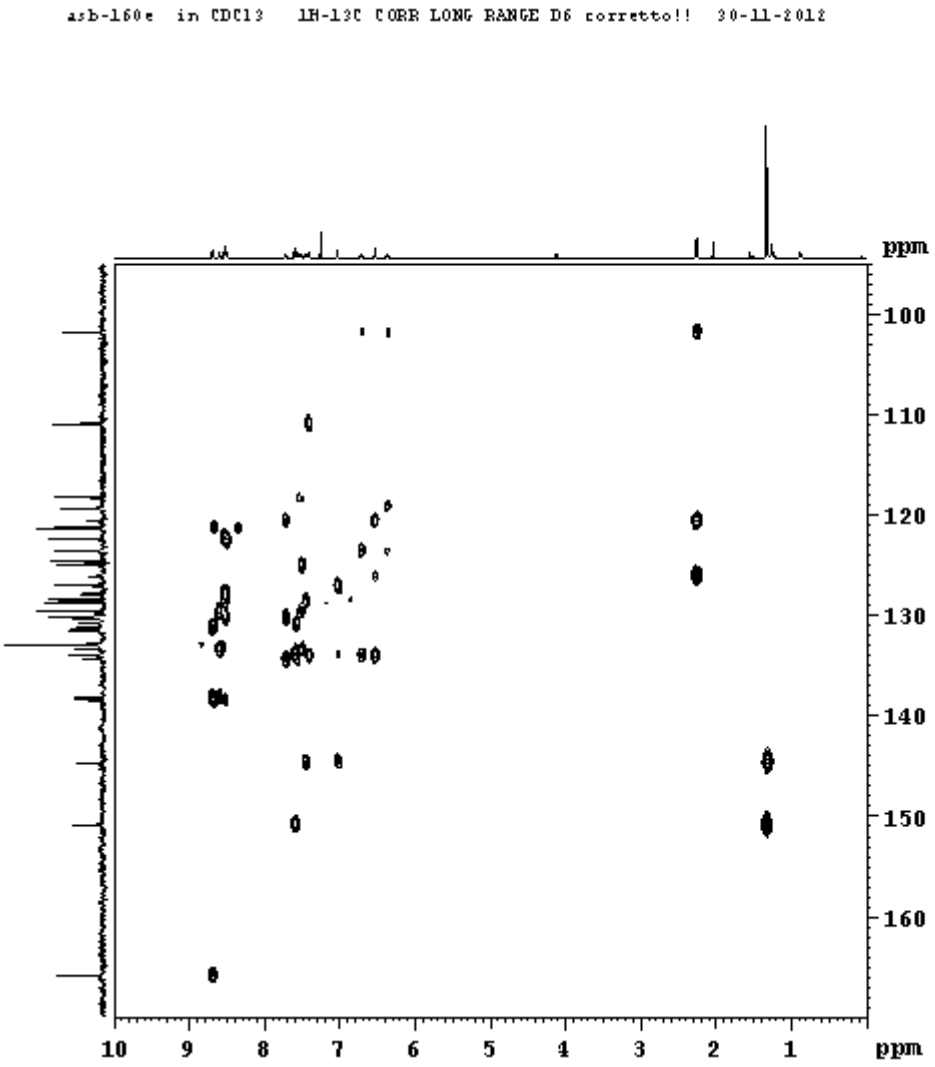

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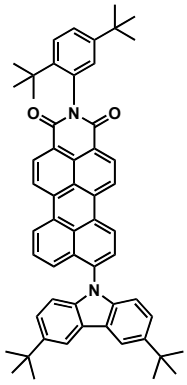

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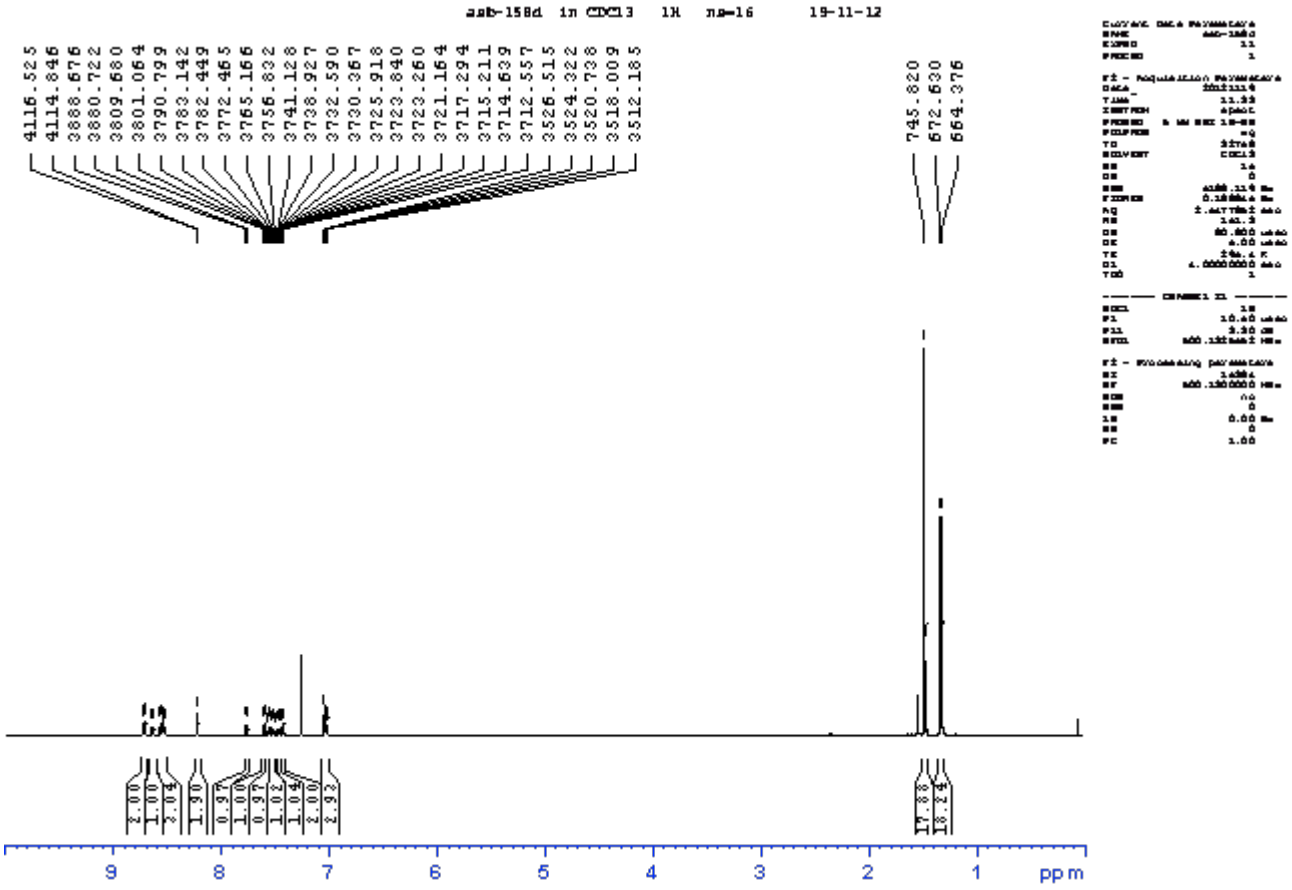

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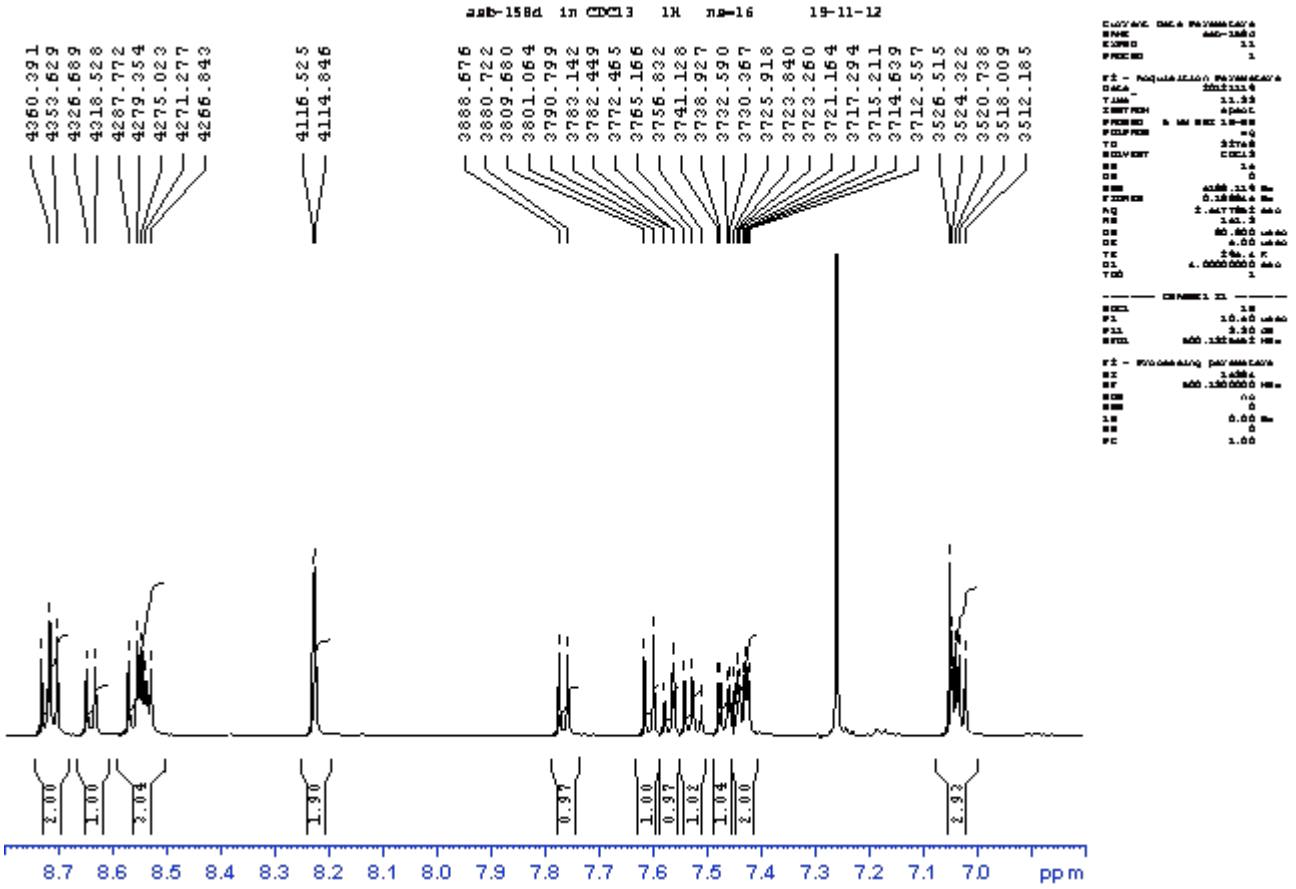

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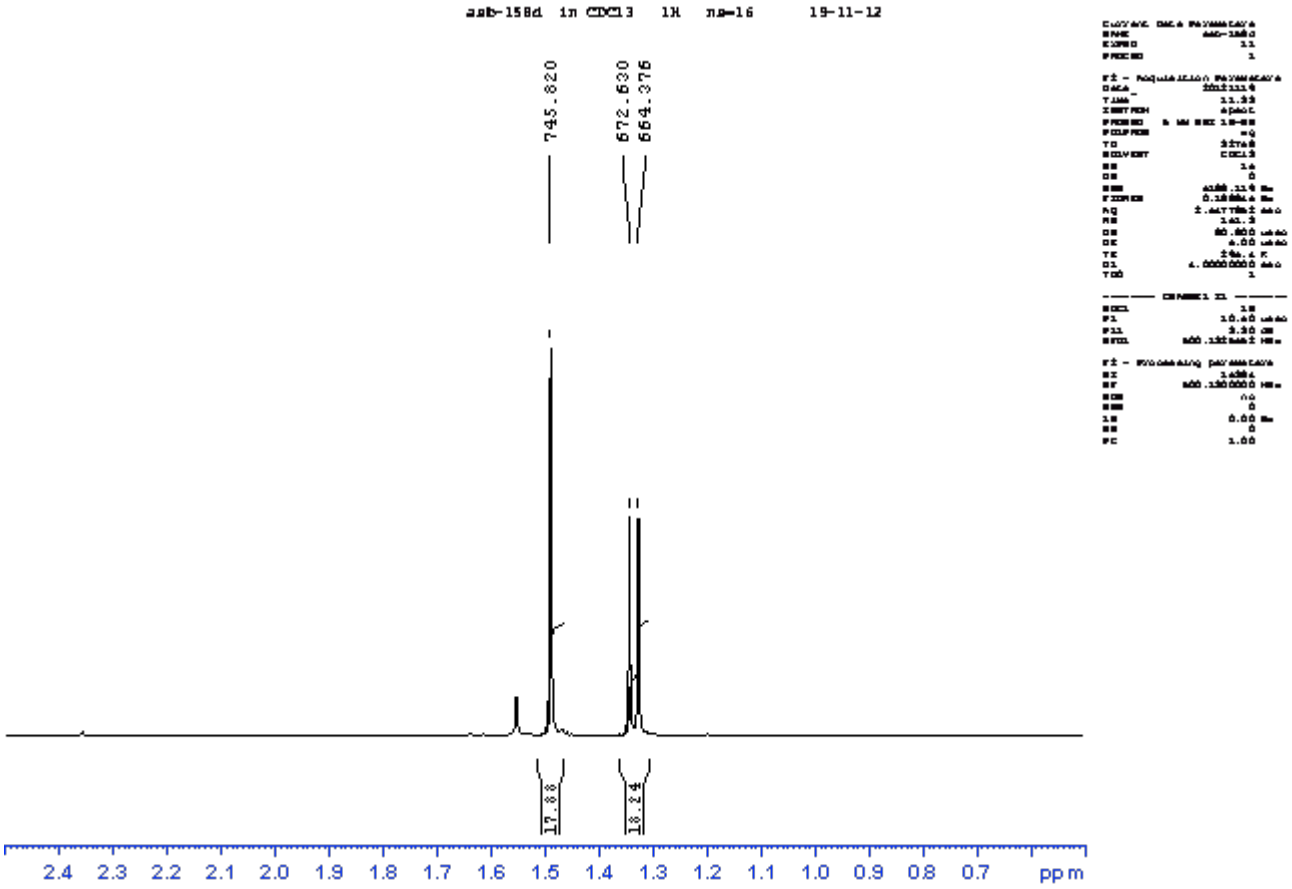

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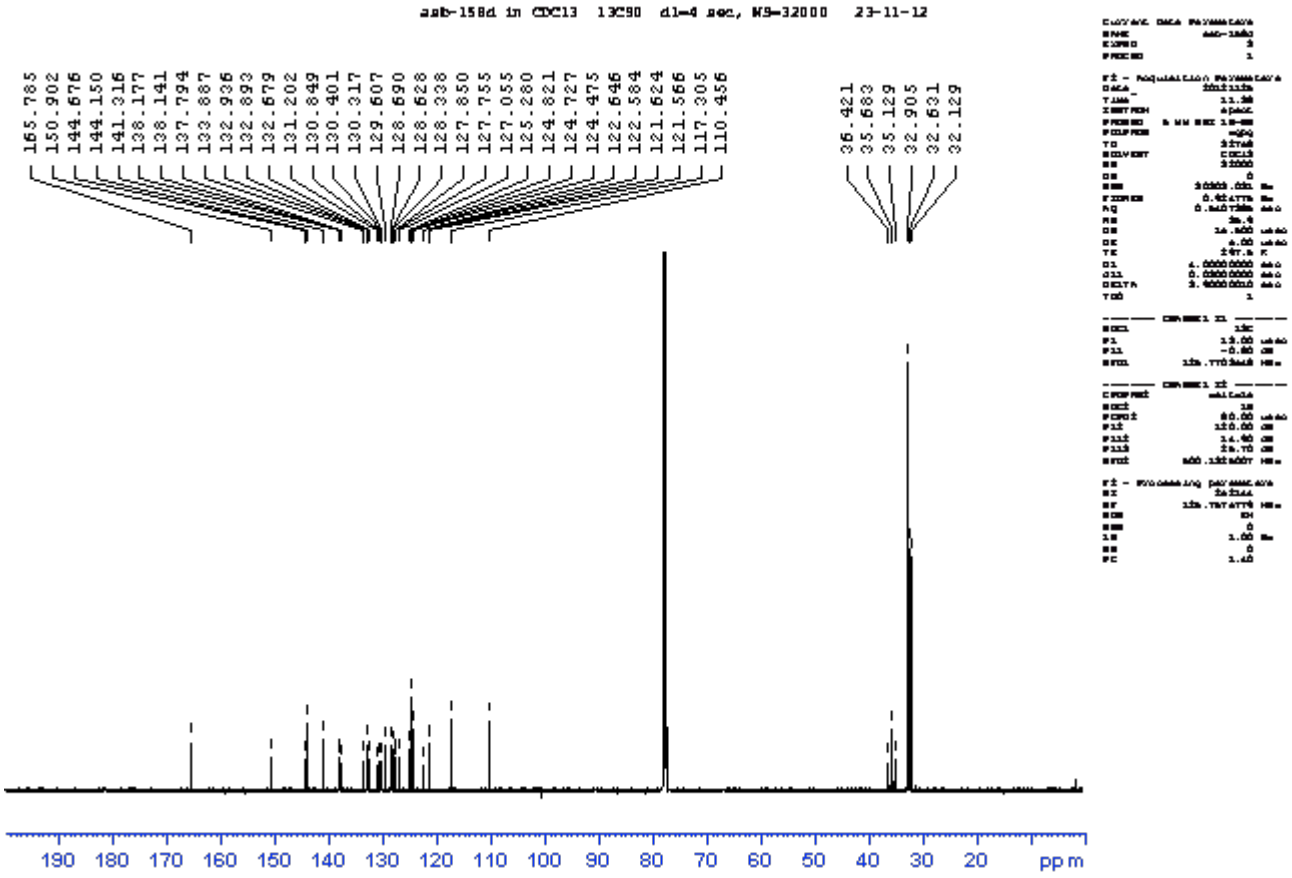

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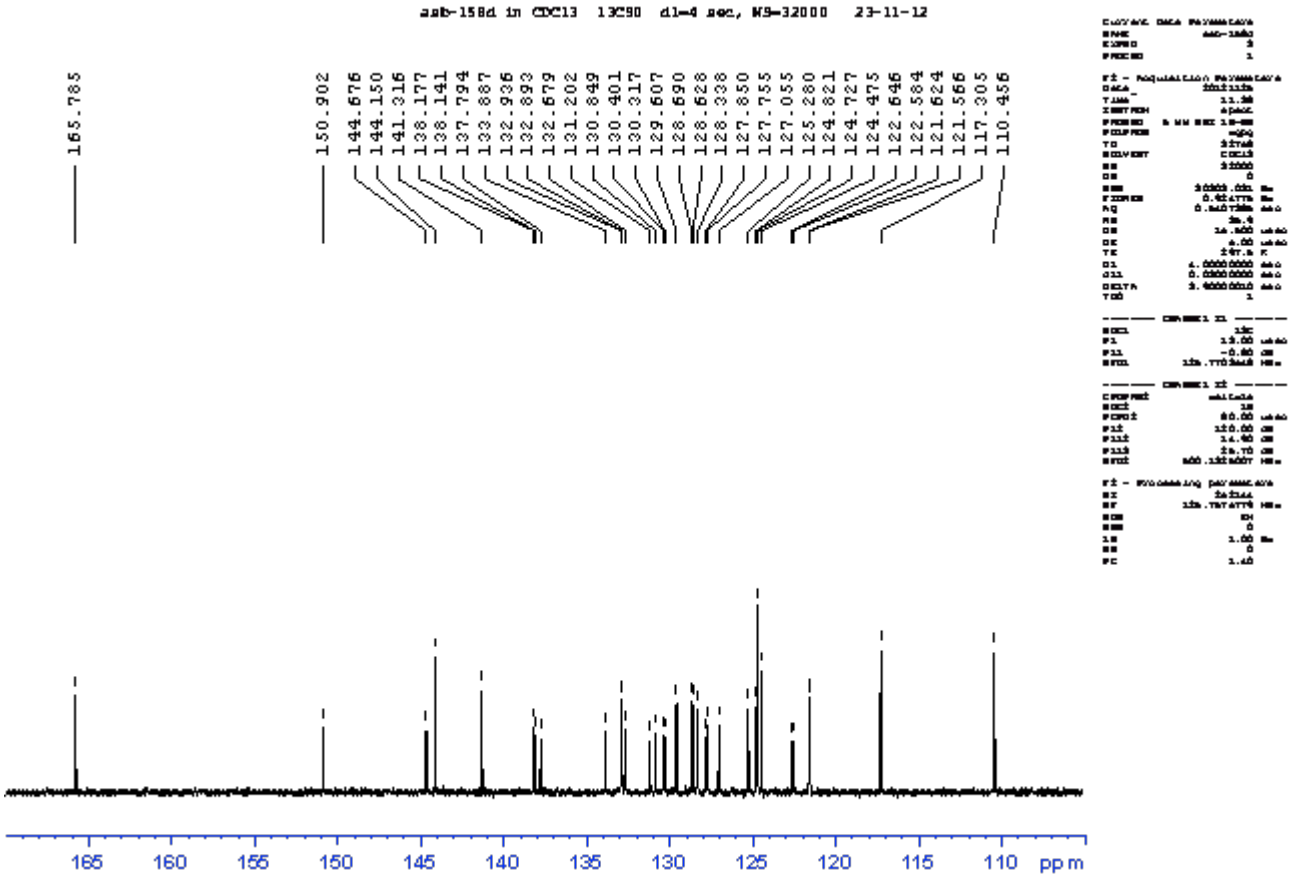

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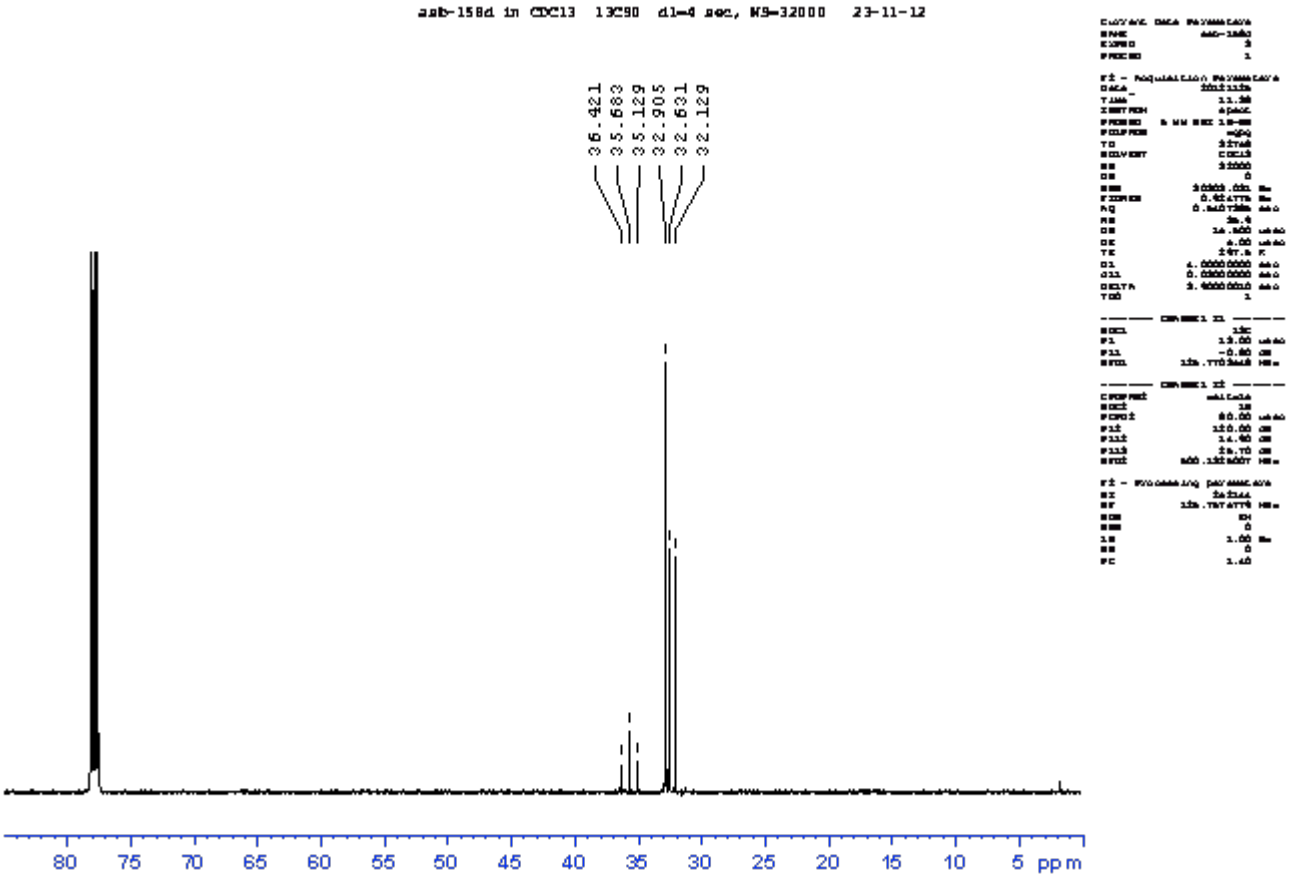

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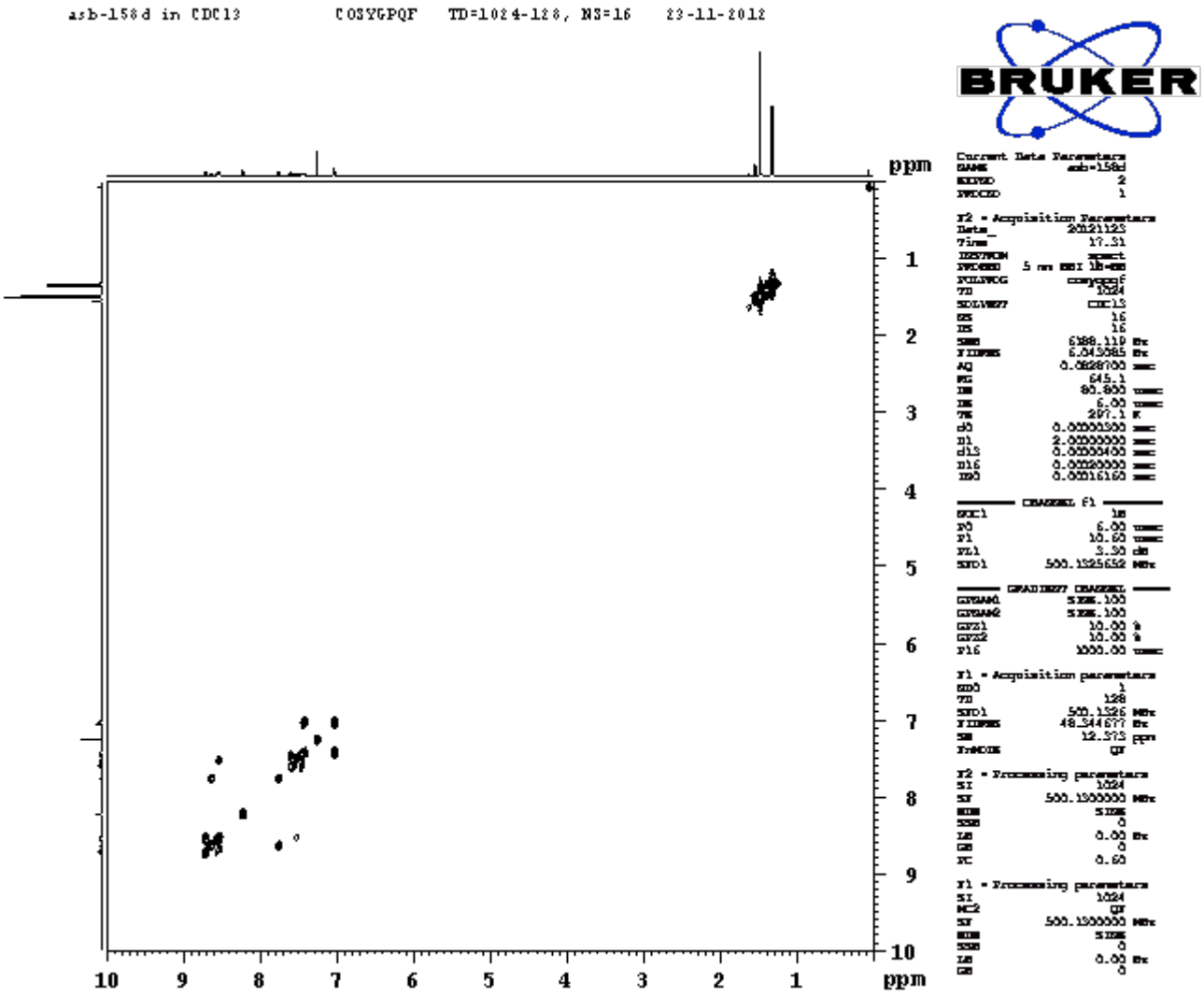

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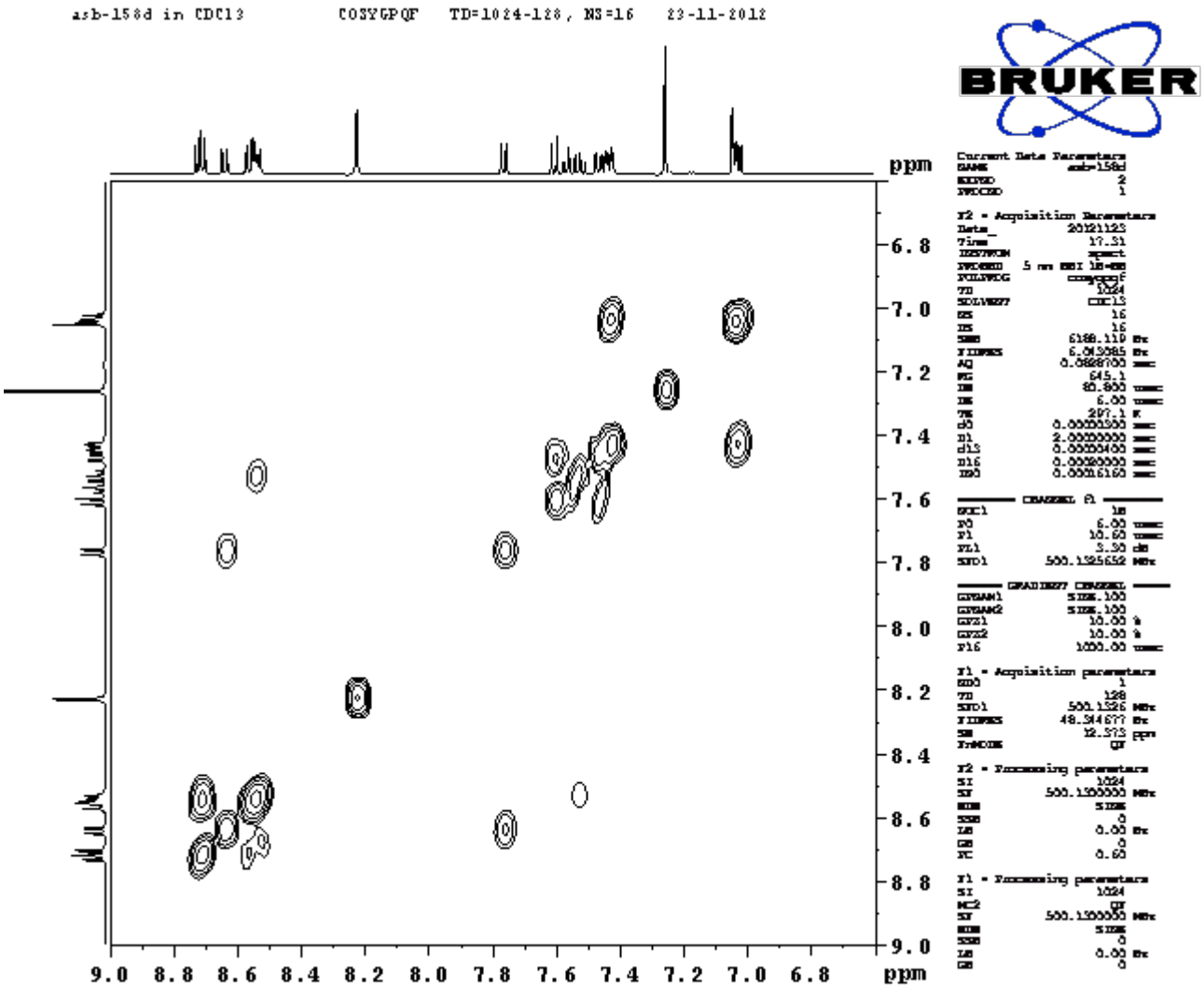

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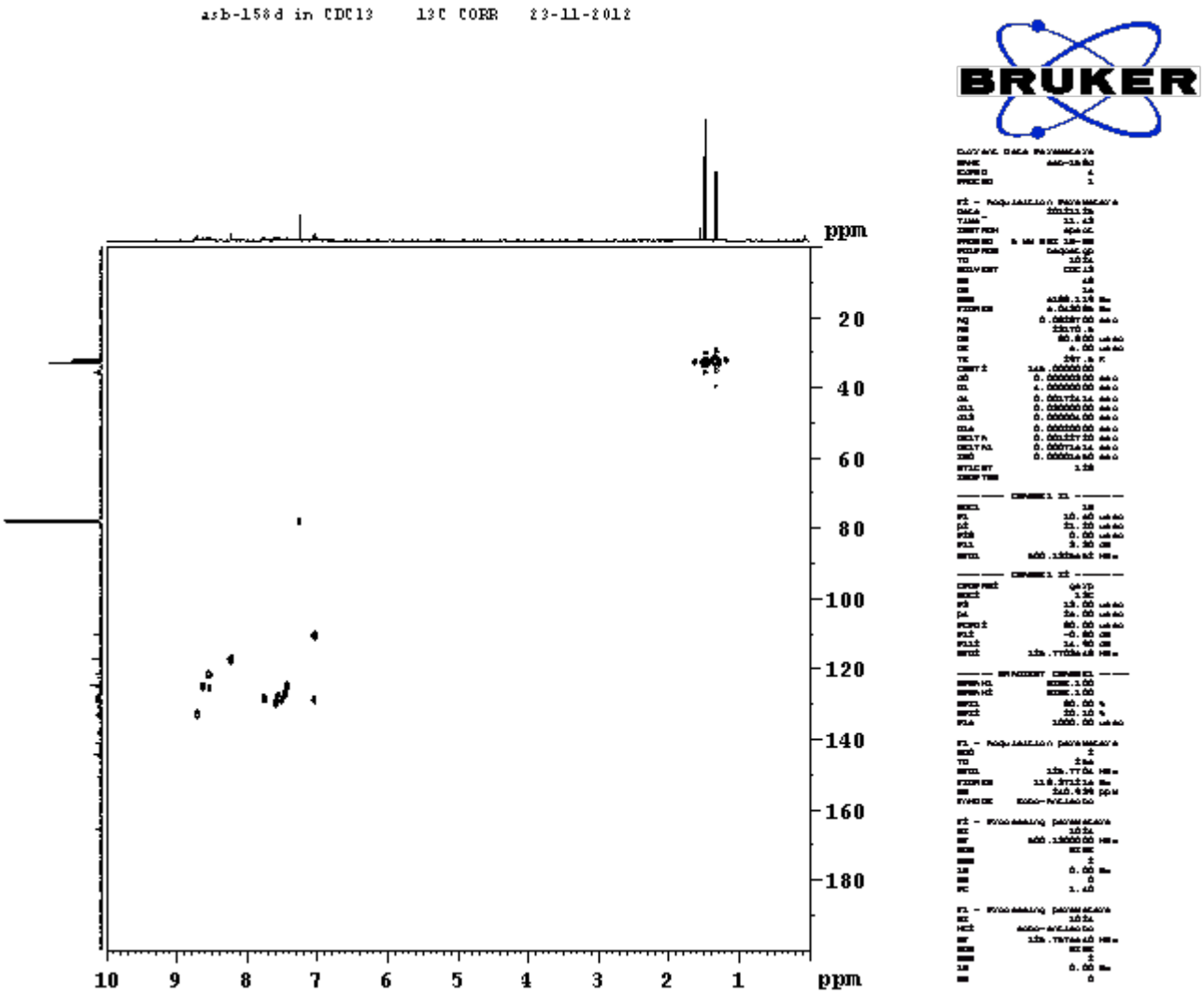

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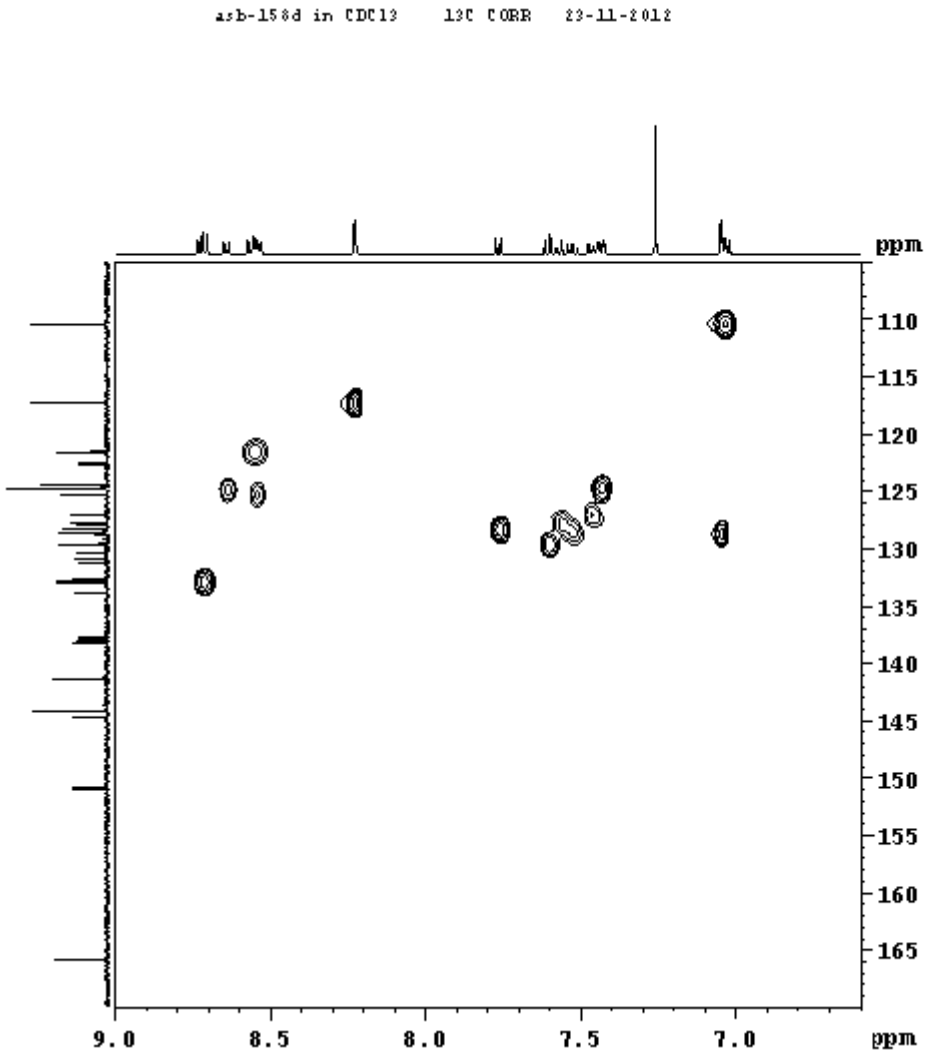
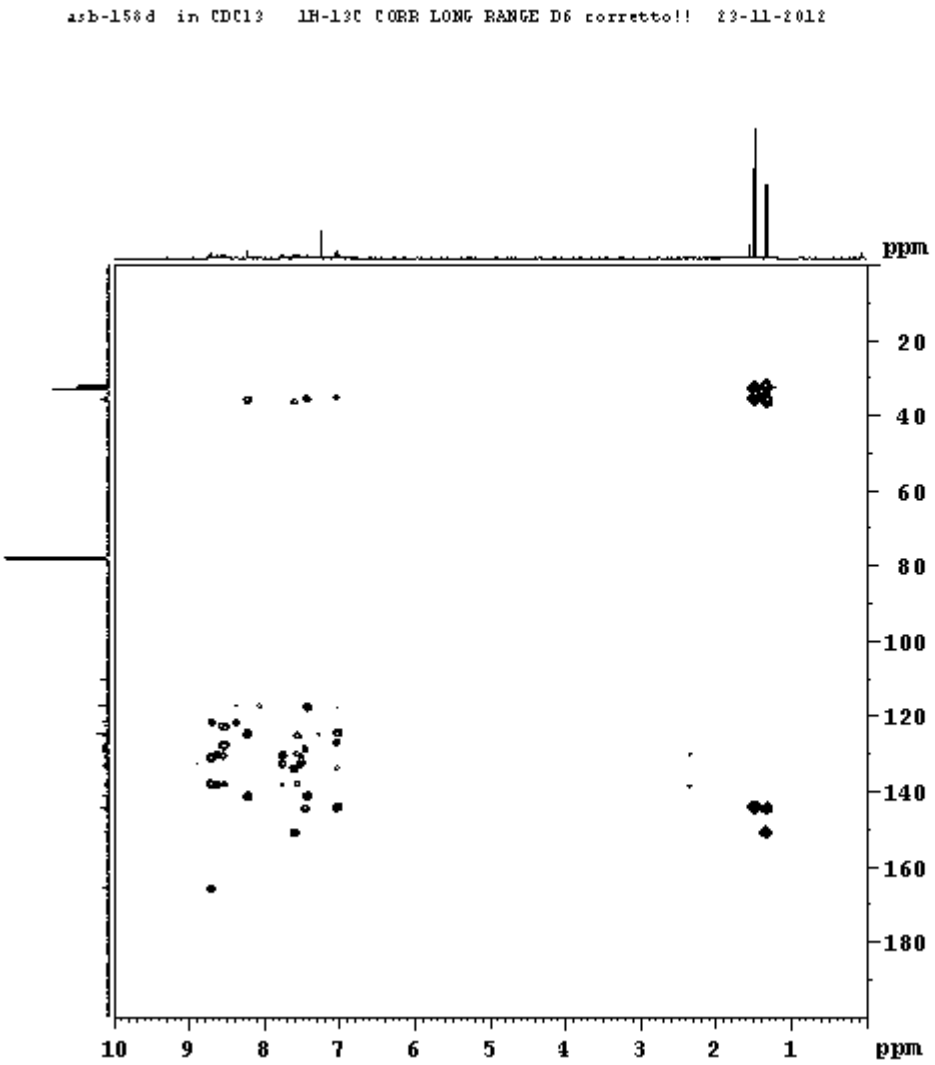
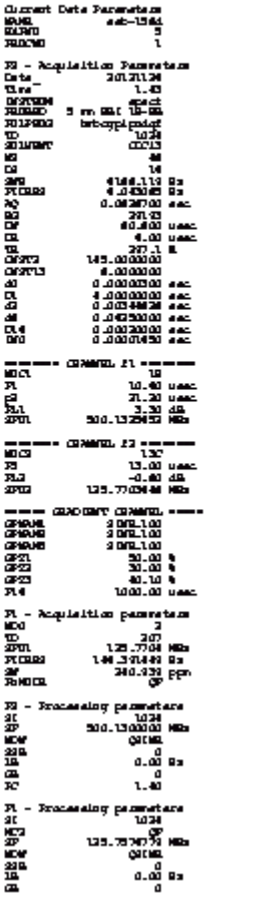


^{1}H ^{13}C HETCOR long range coupling - full spectral range





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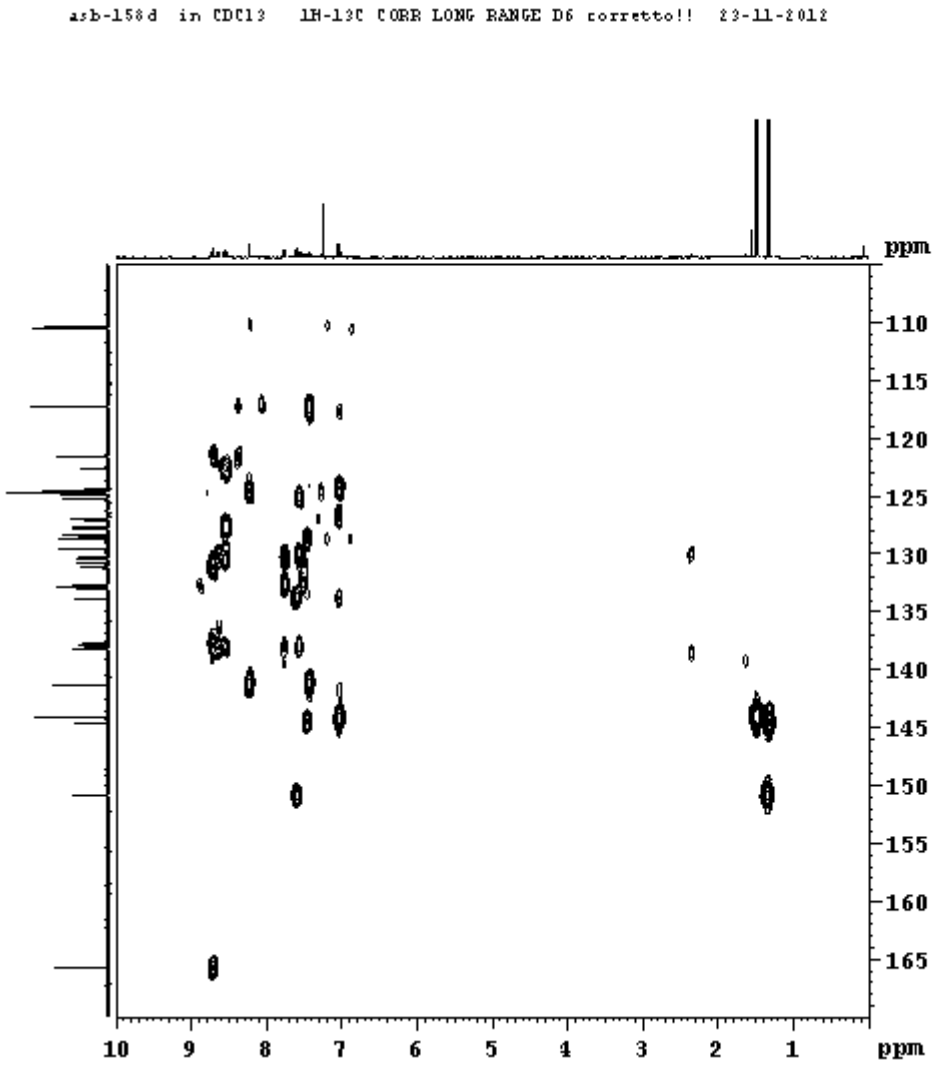

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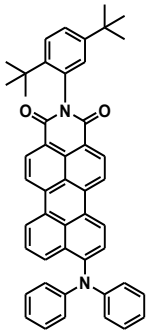
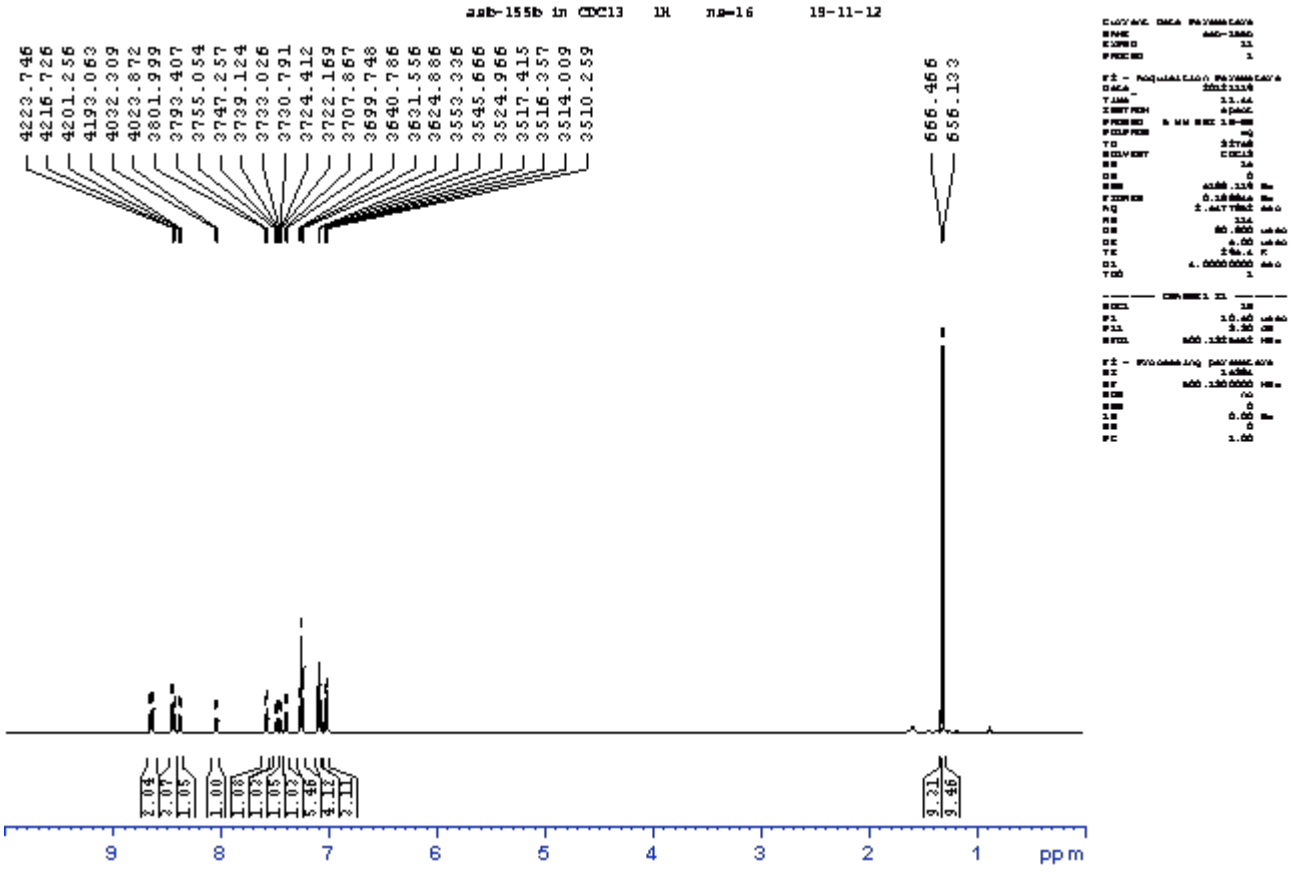
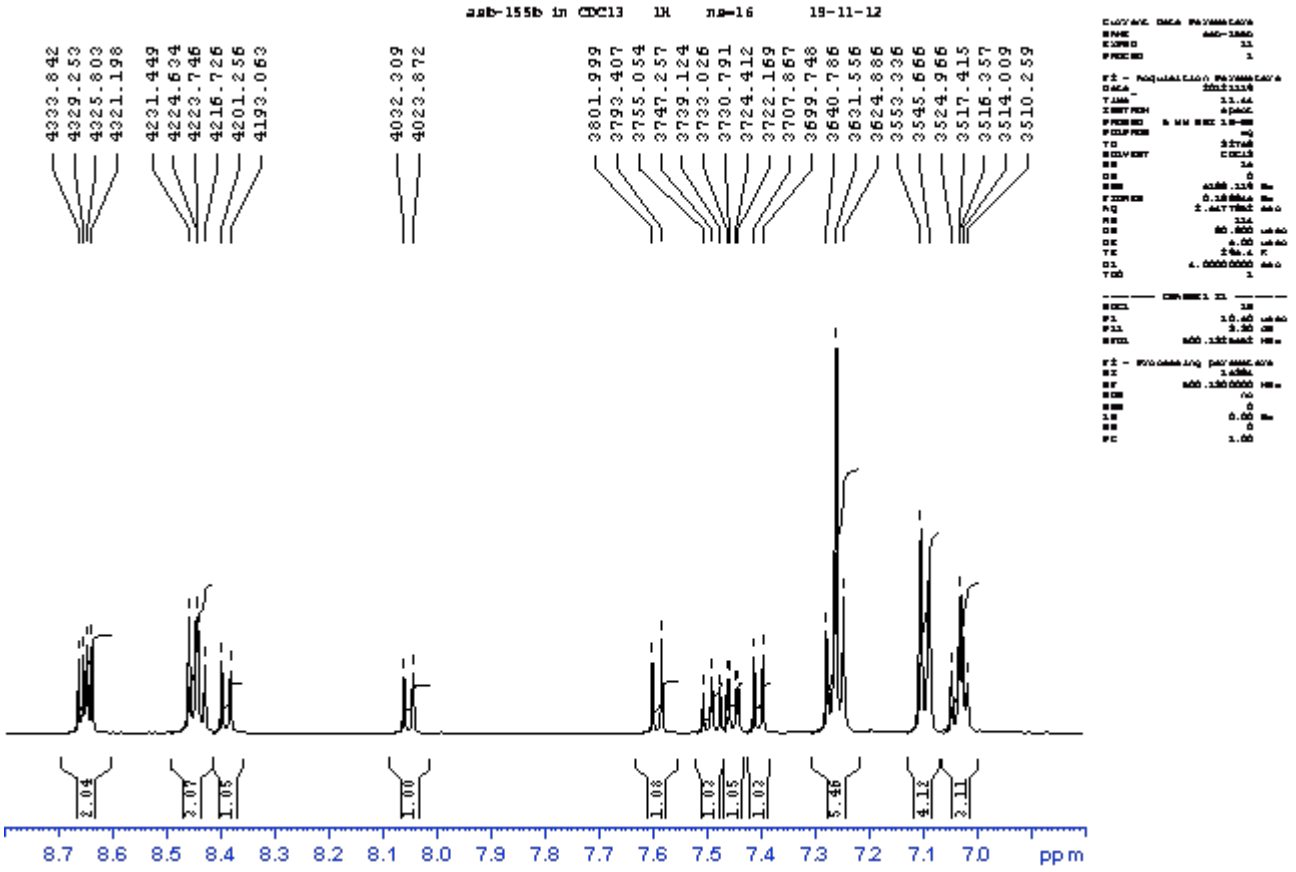


3

^{1}H full range



Aromatic region



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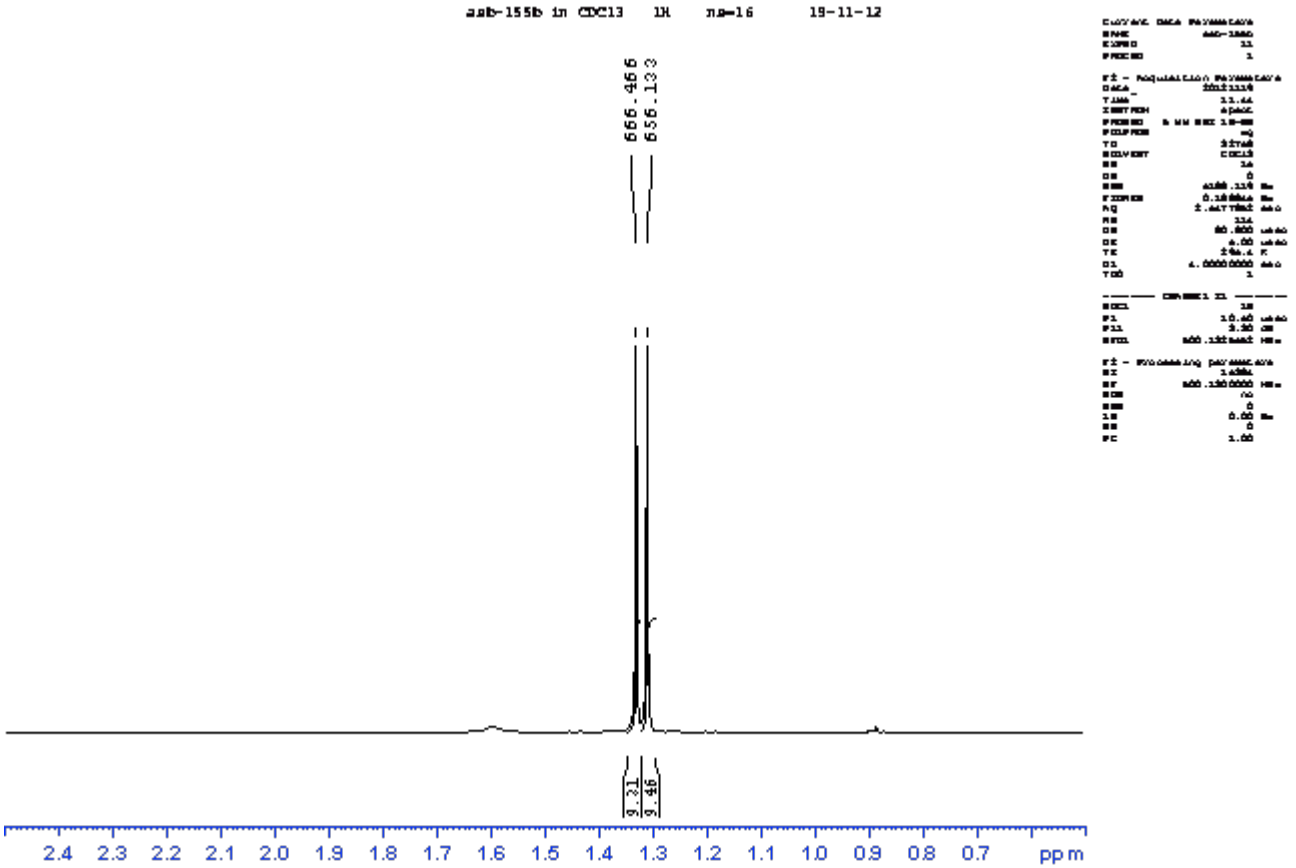
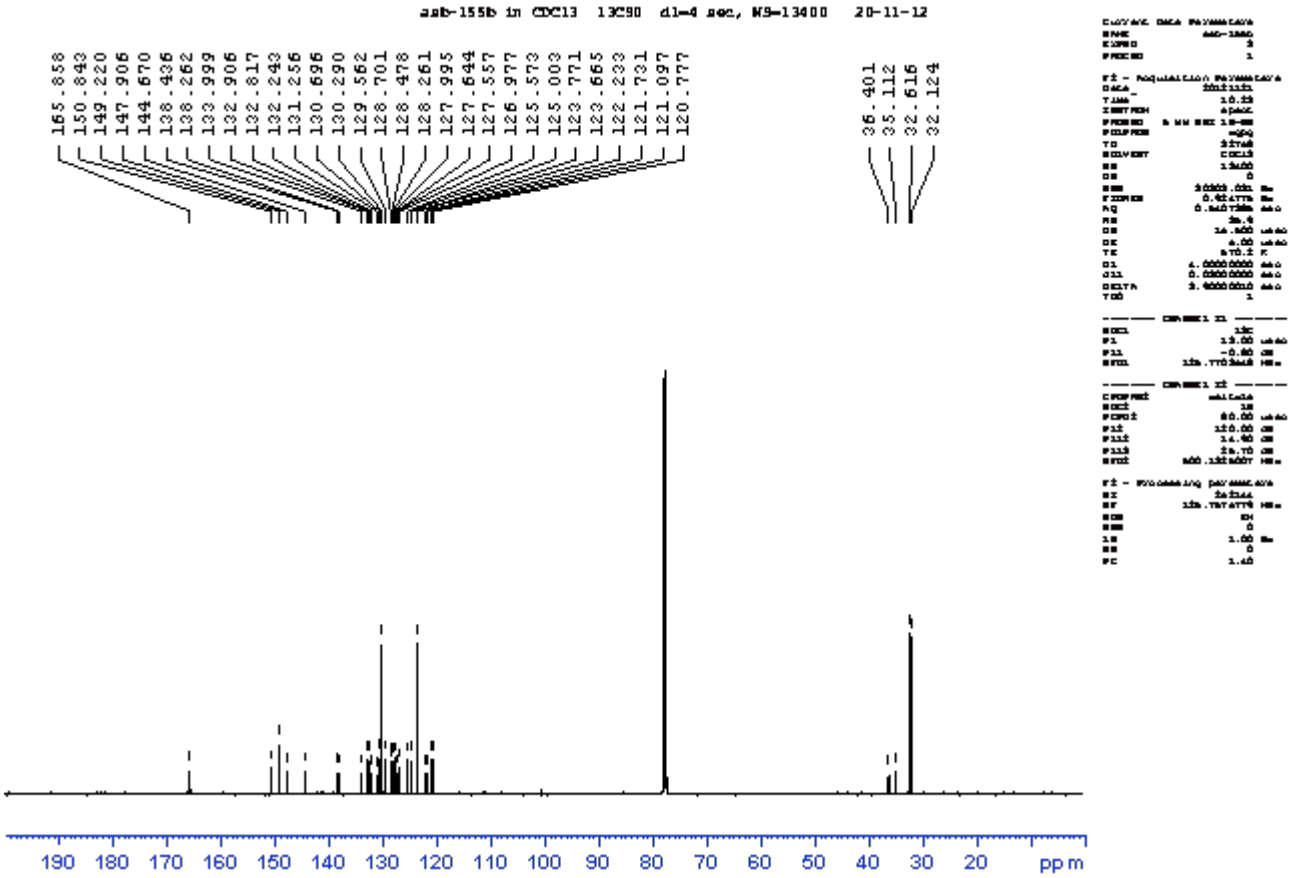


^{13}C Full spectral range



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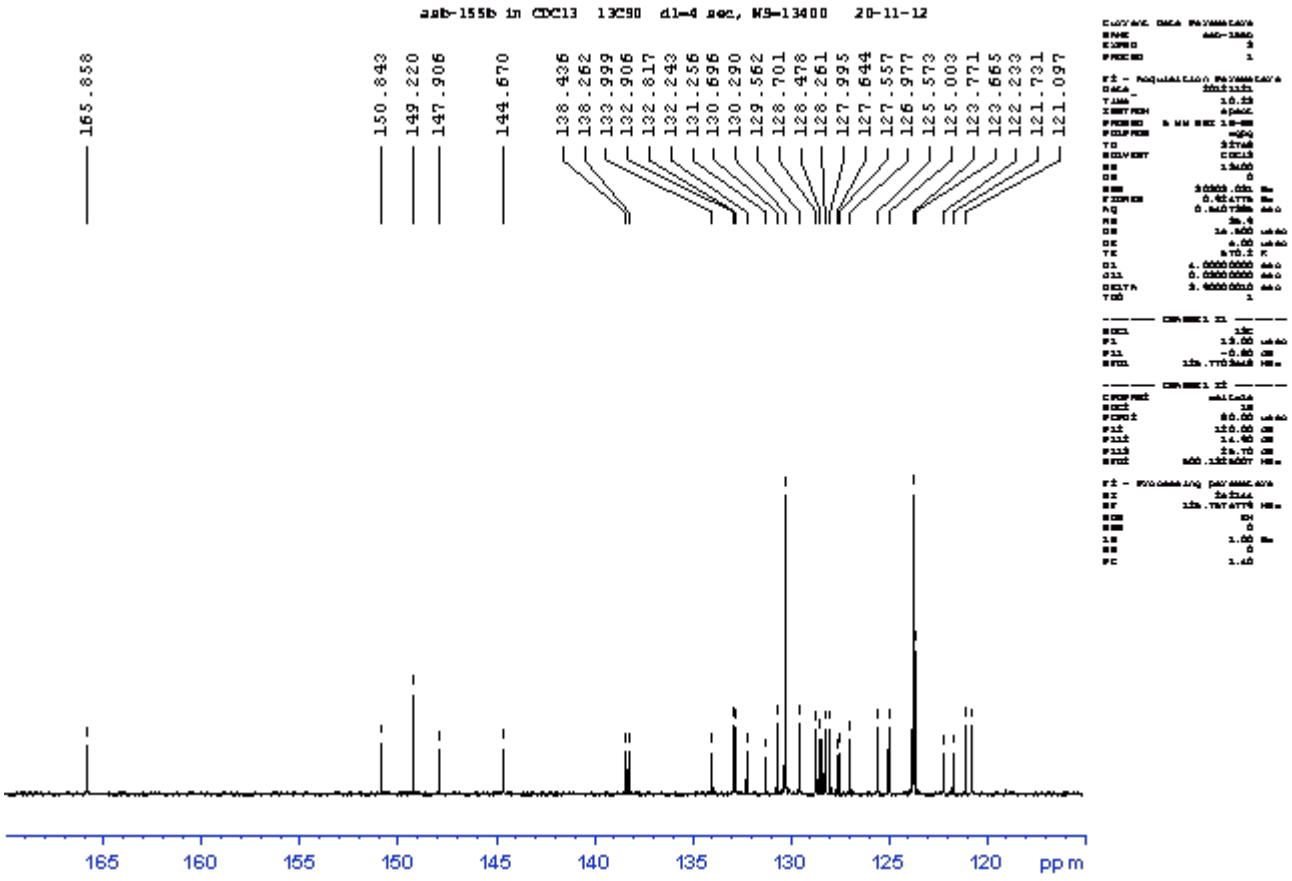

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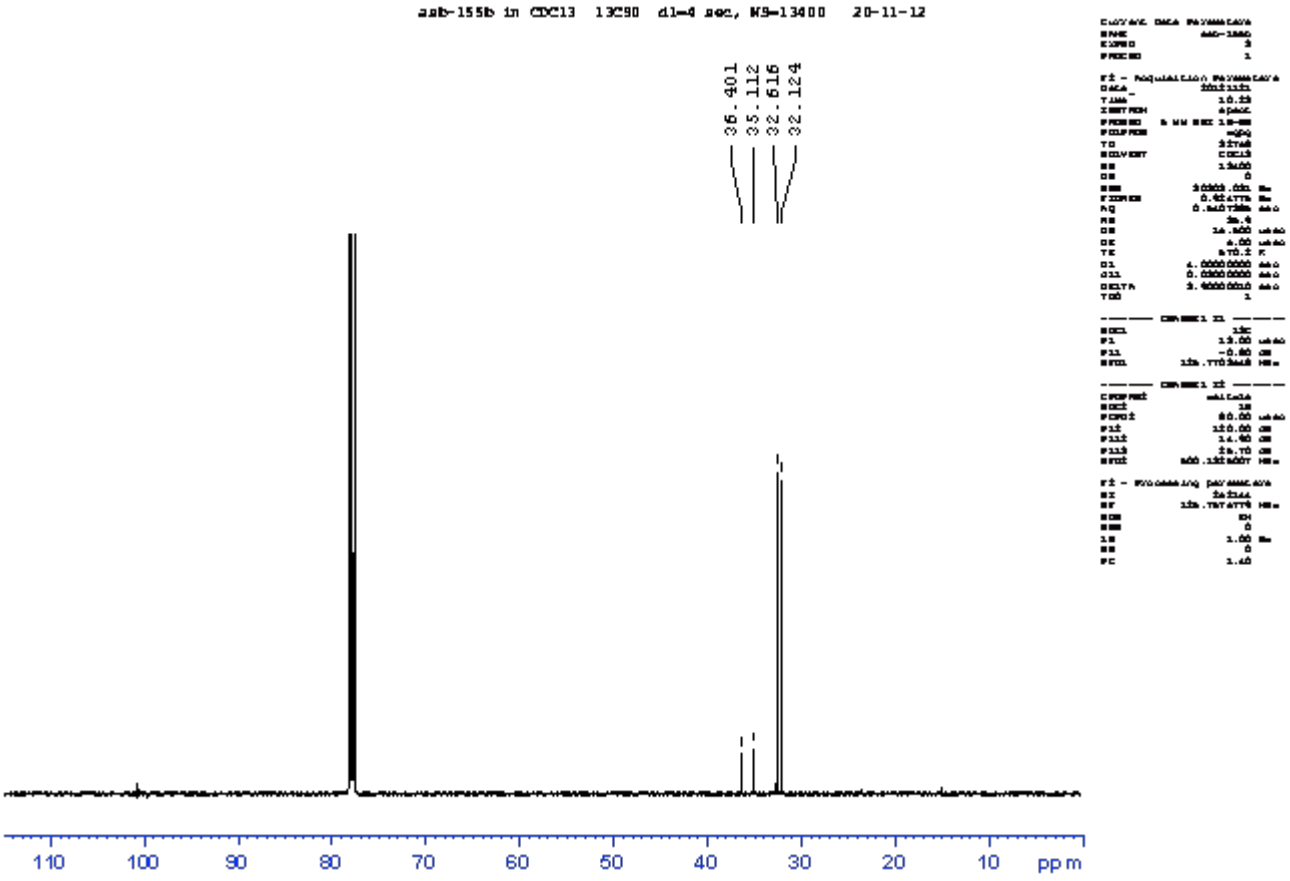
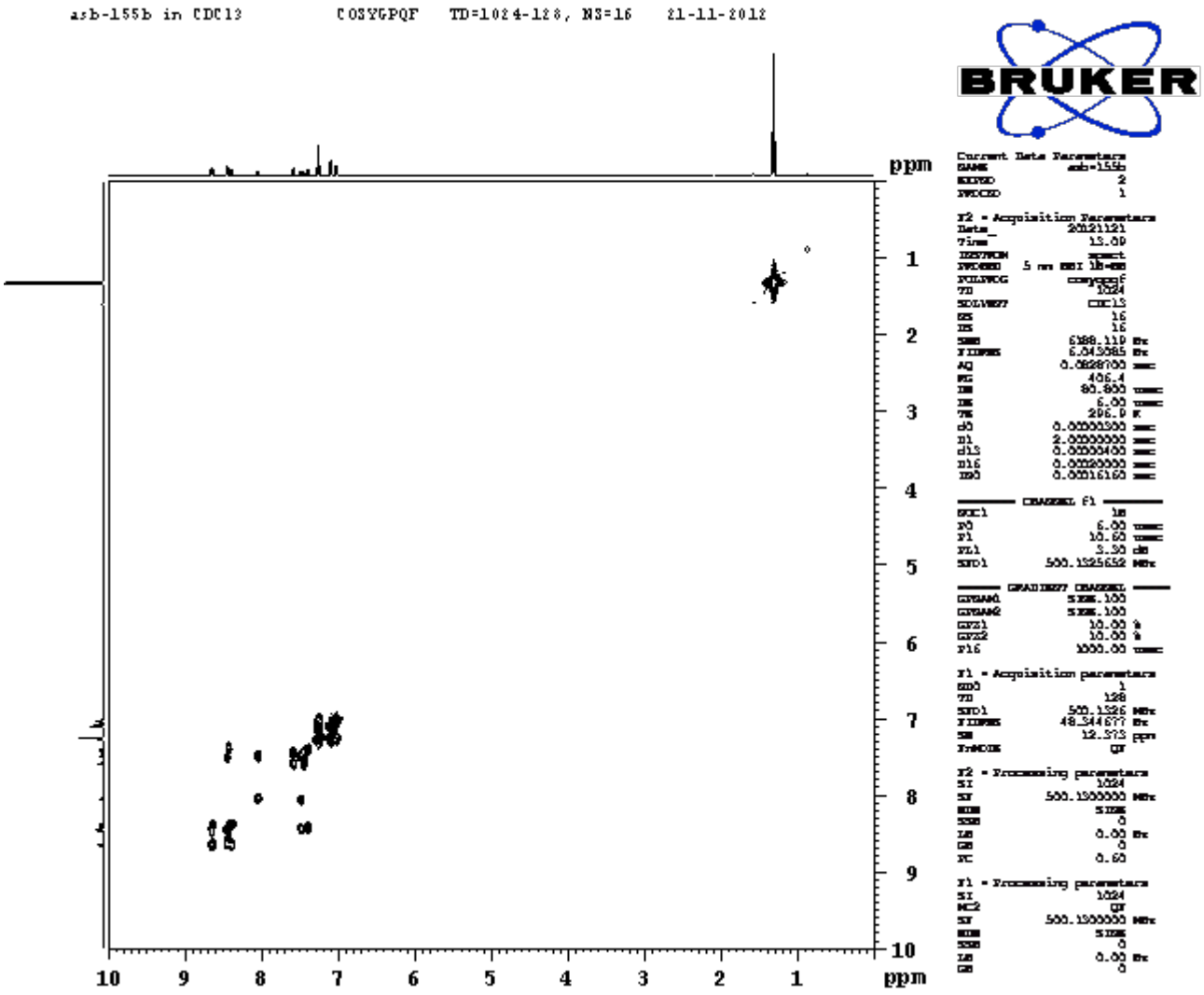
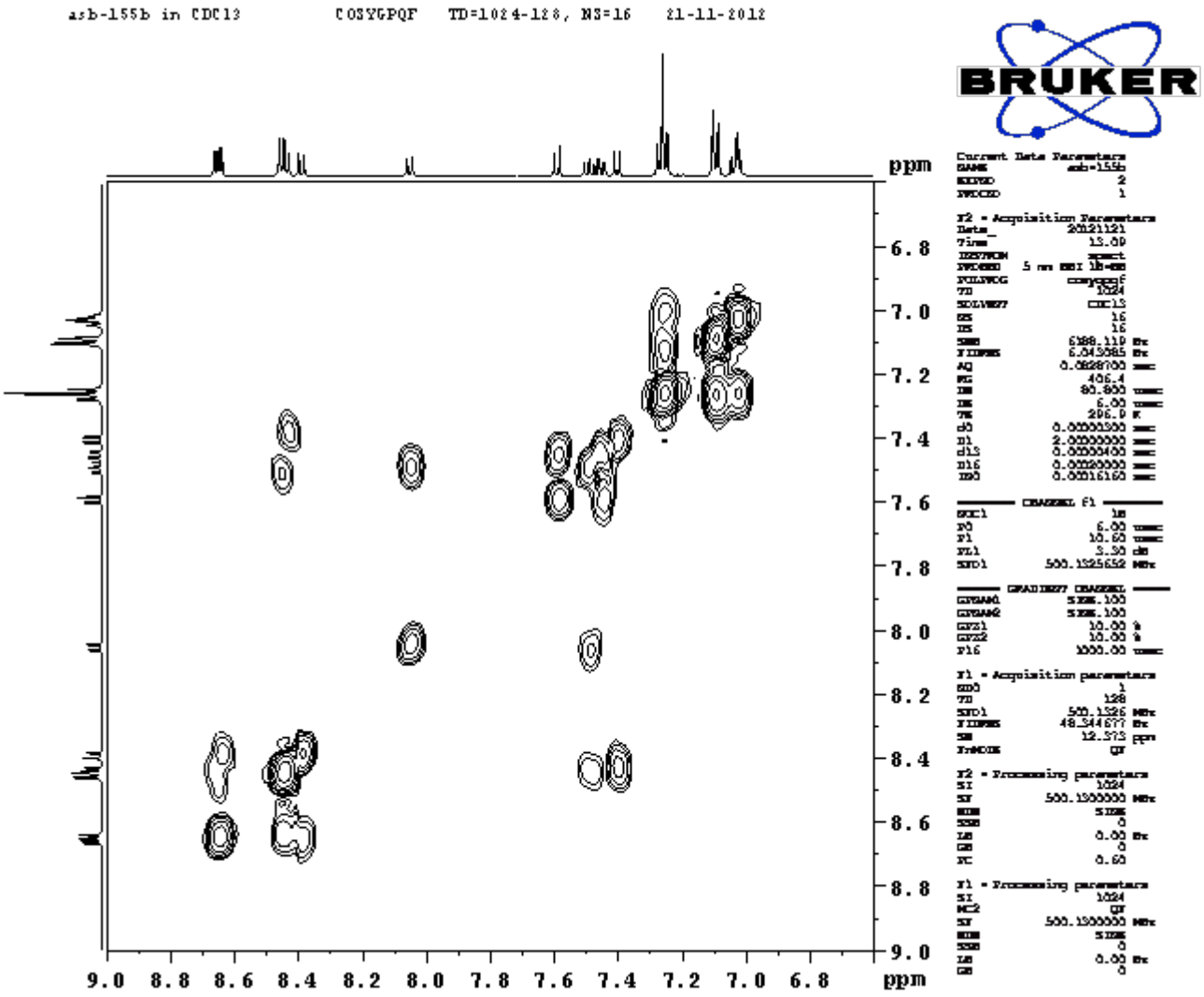


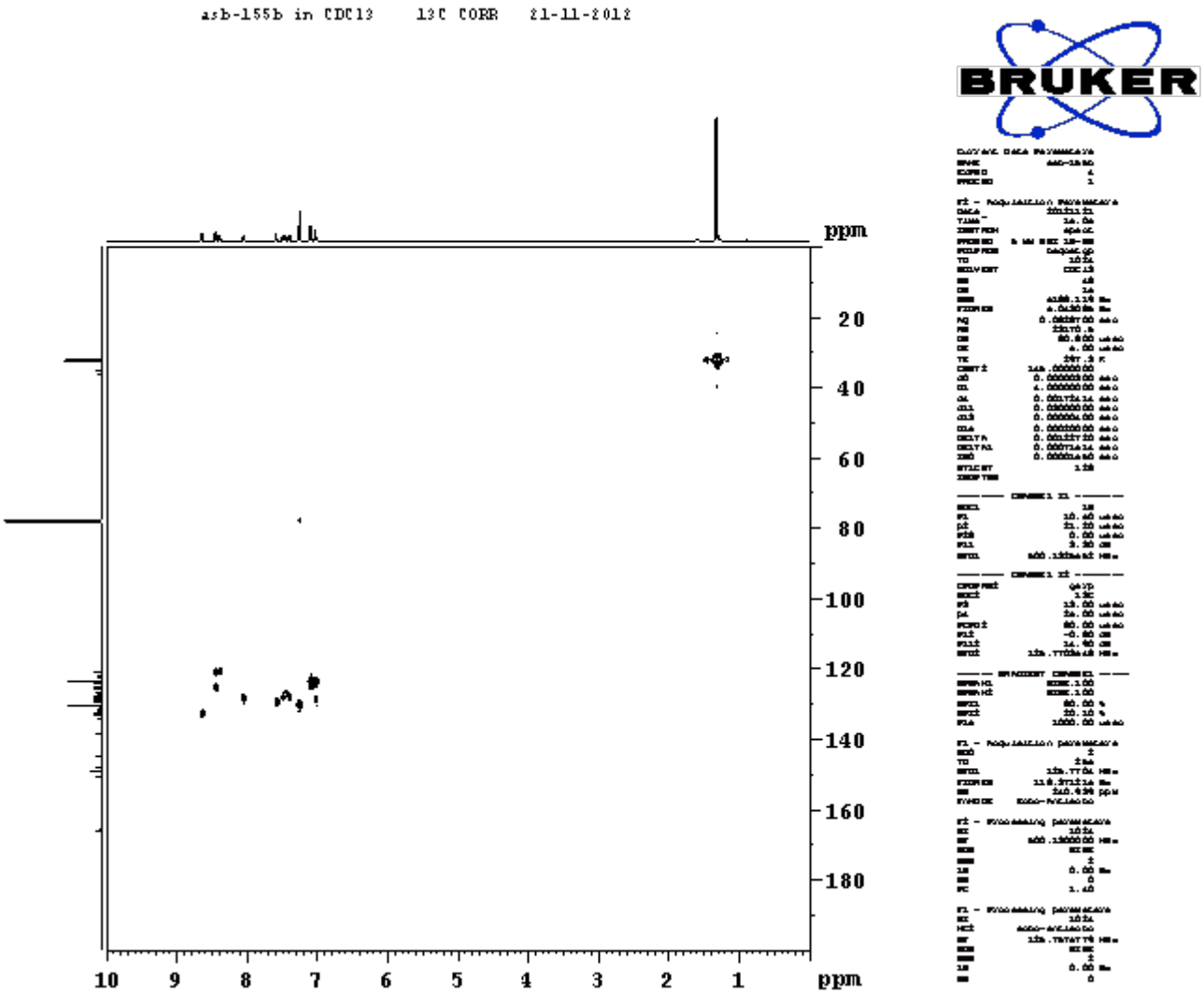
^{1}H COSY full spectral range



aromatic region



^{1}H ^{13}C HETCOR full spectral range



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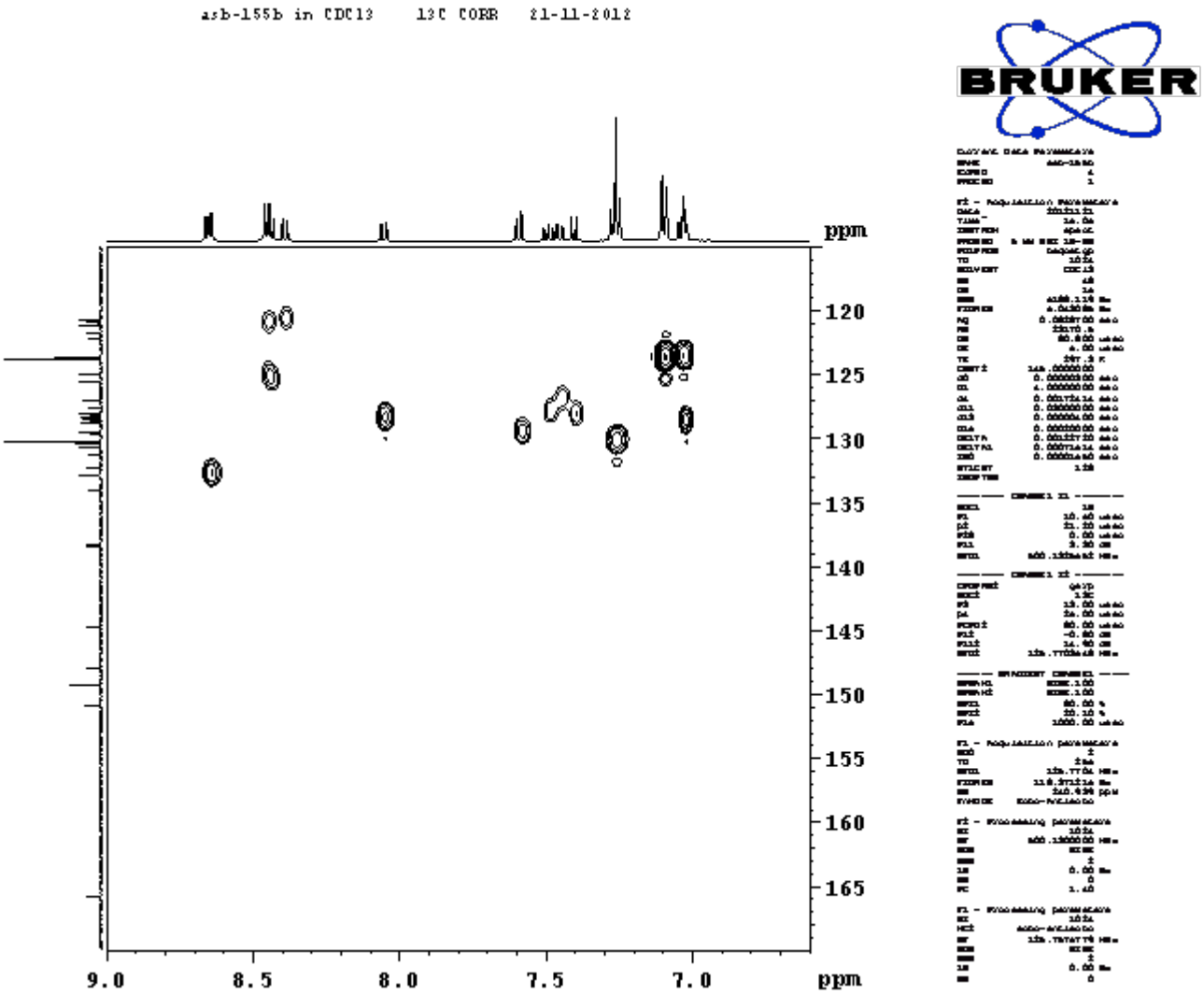
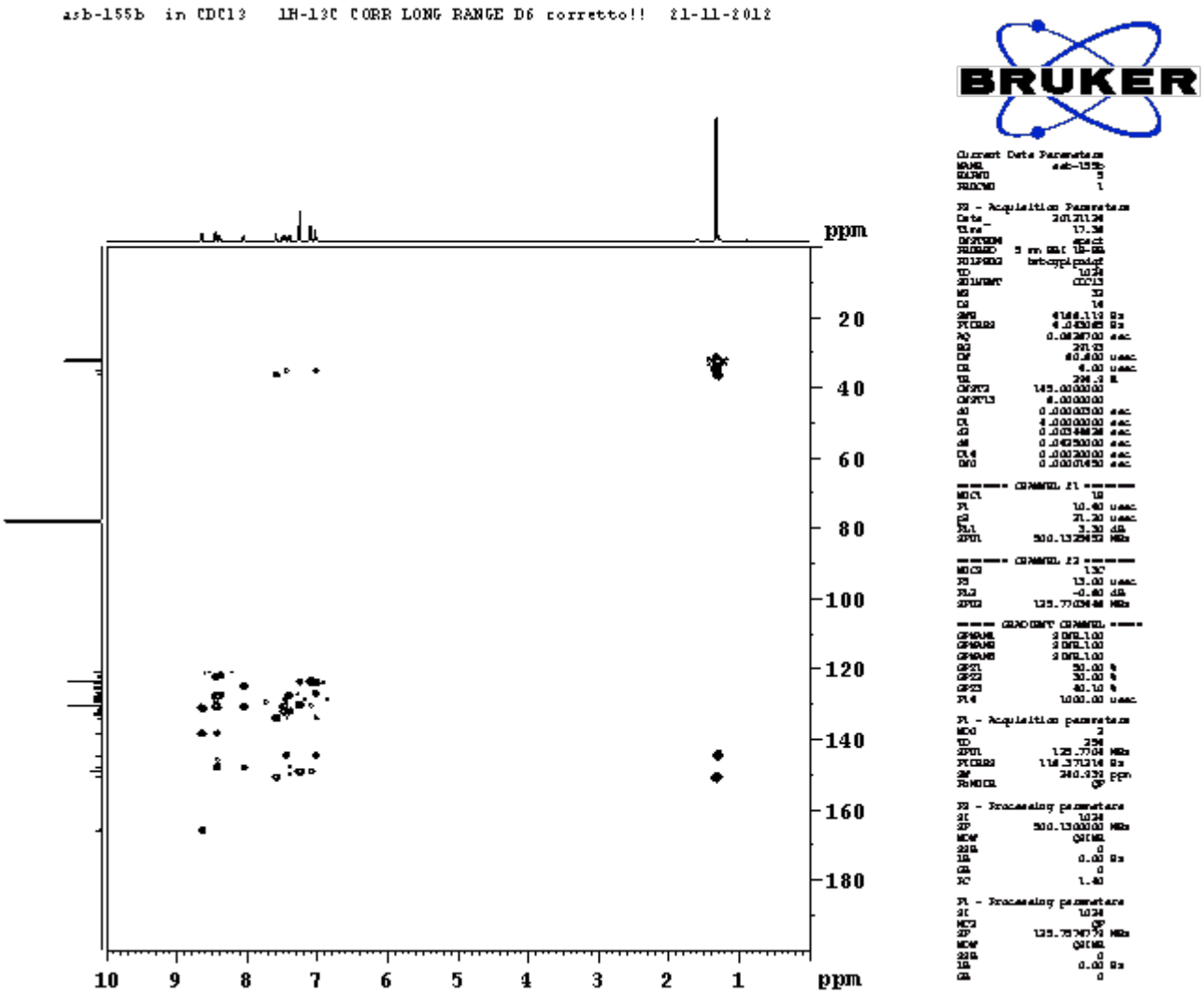
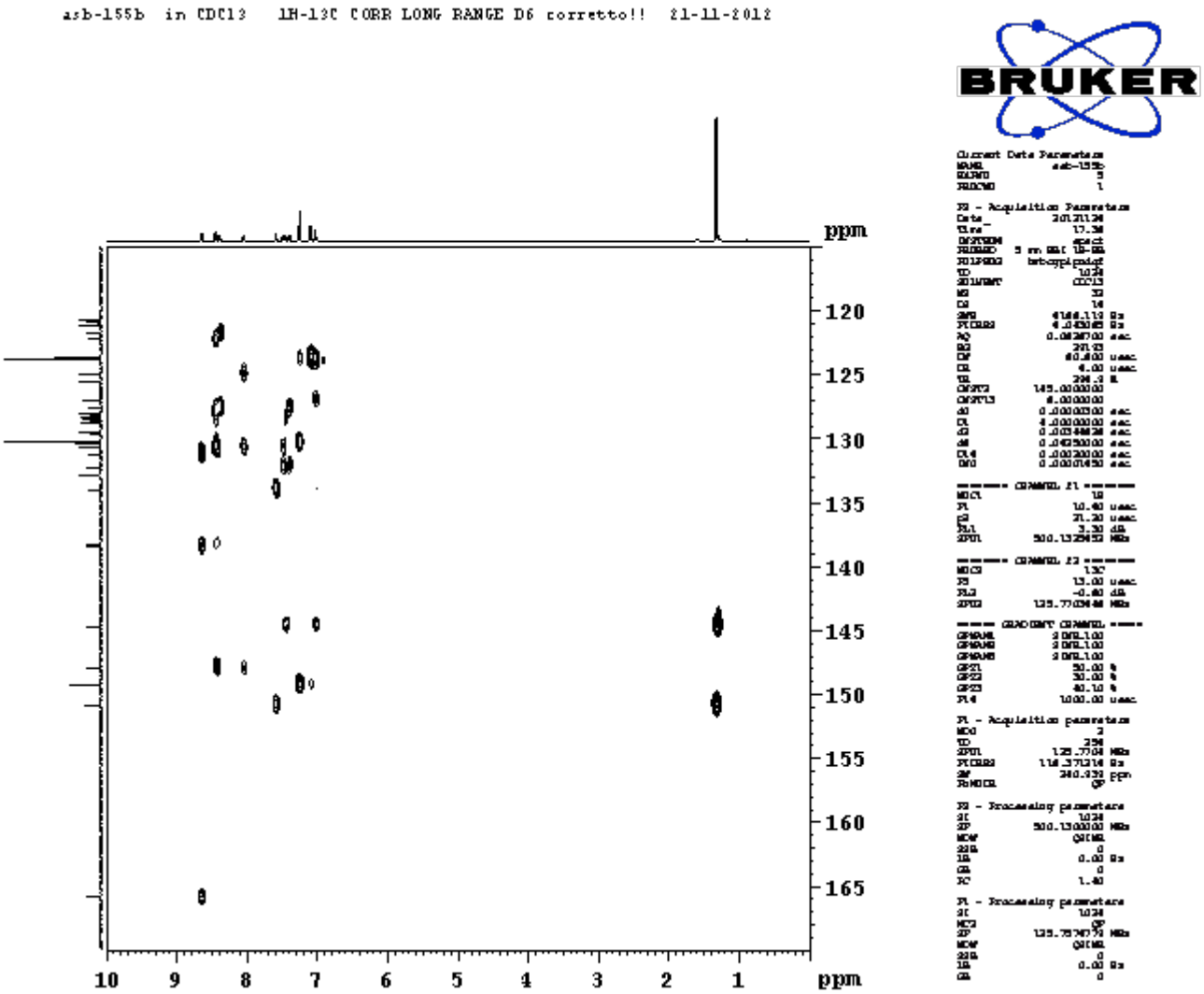


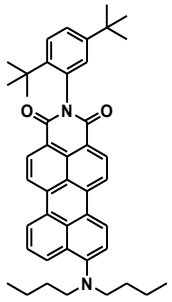
^{1}H ^{13}C HETCOR long range coupling - full spectral range



Aromatic expansion

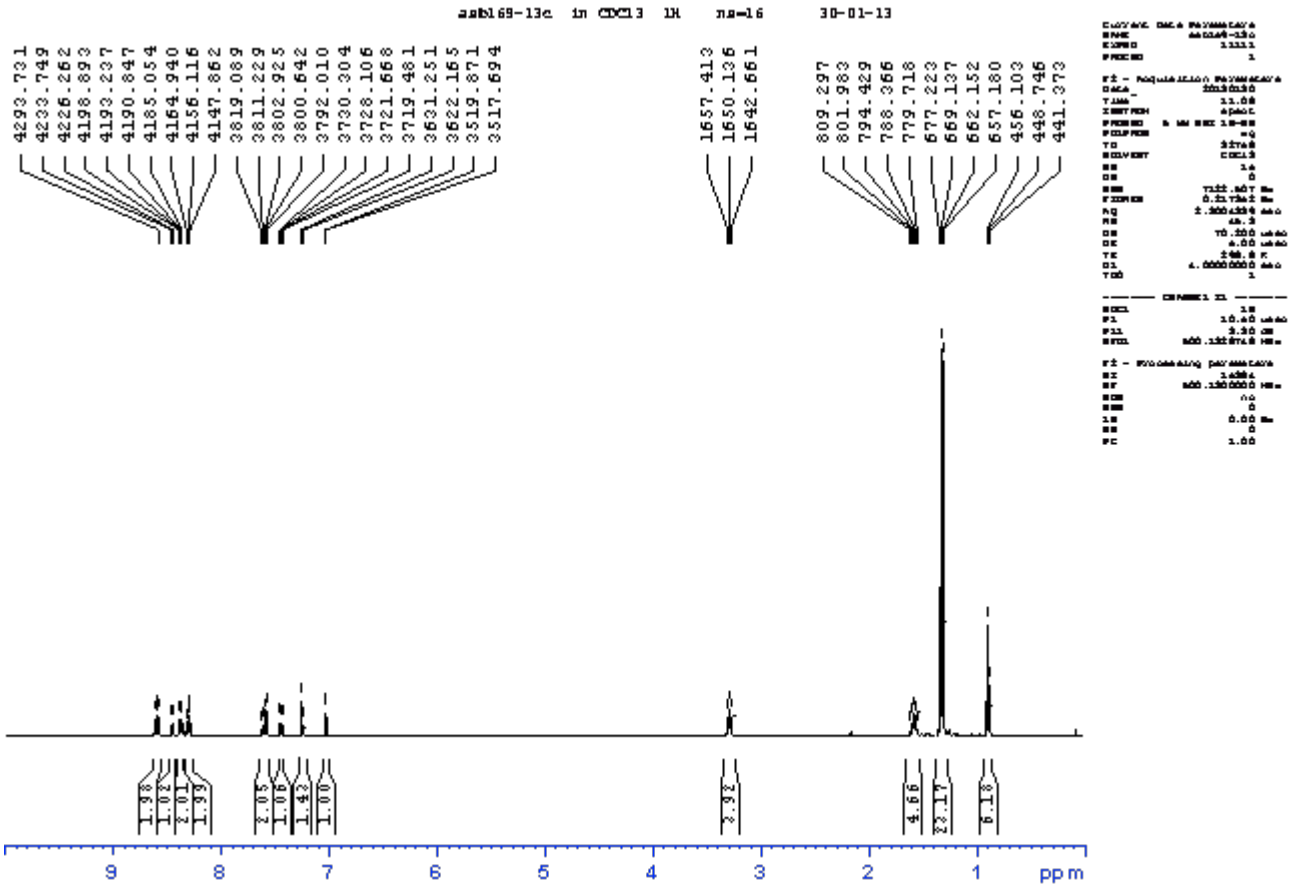


2.5. Derivative **4**.



4

^{1}H full spectral range.



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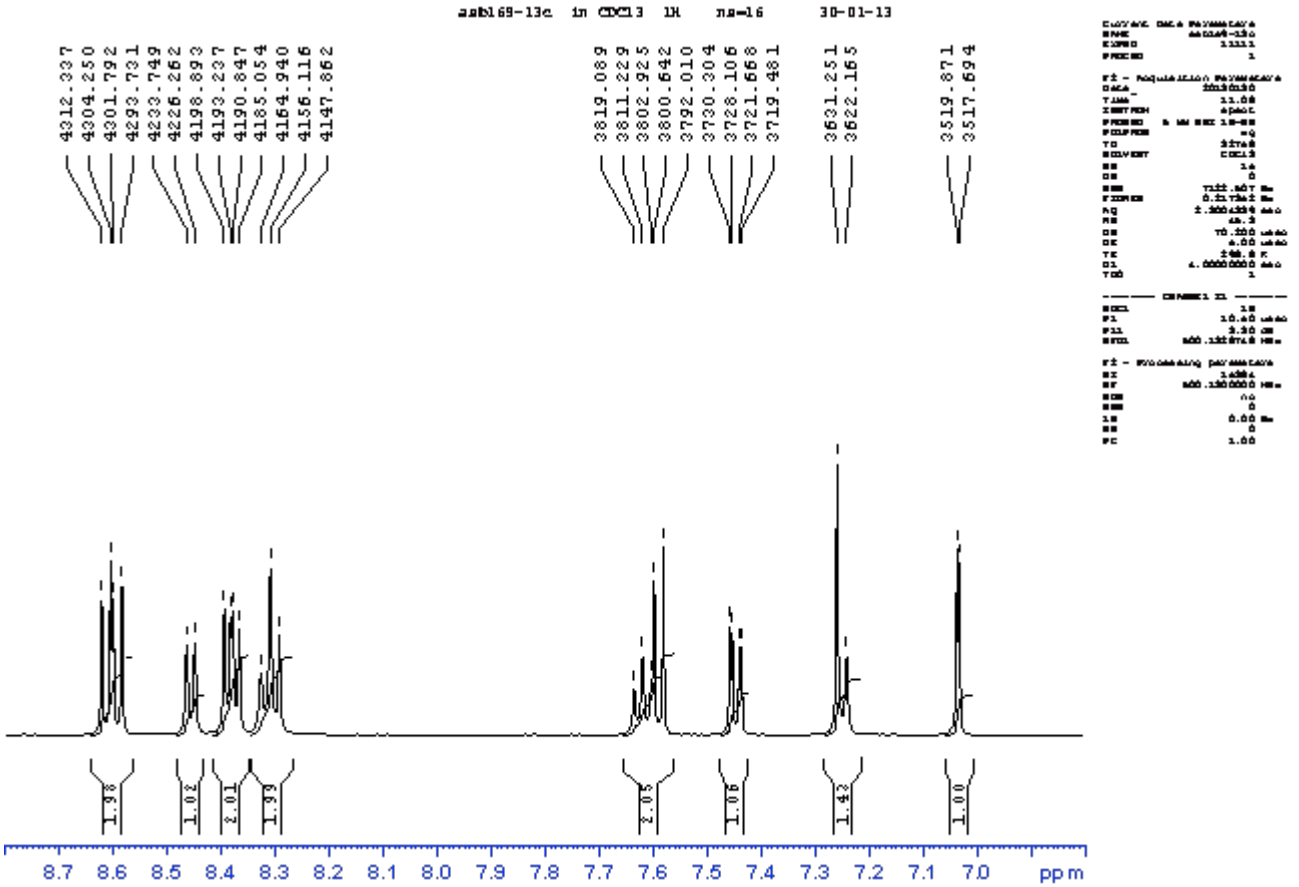
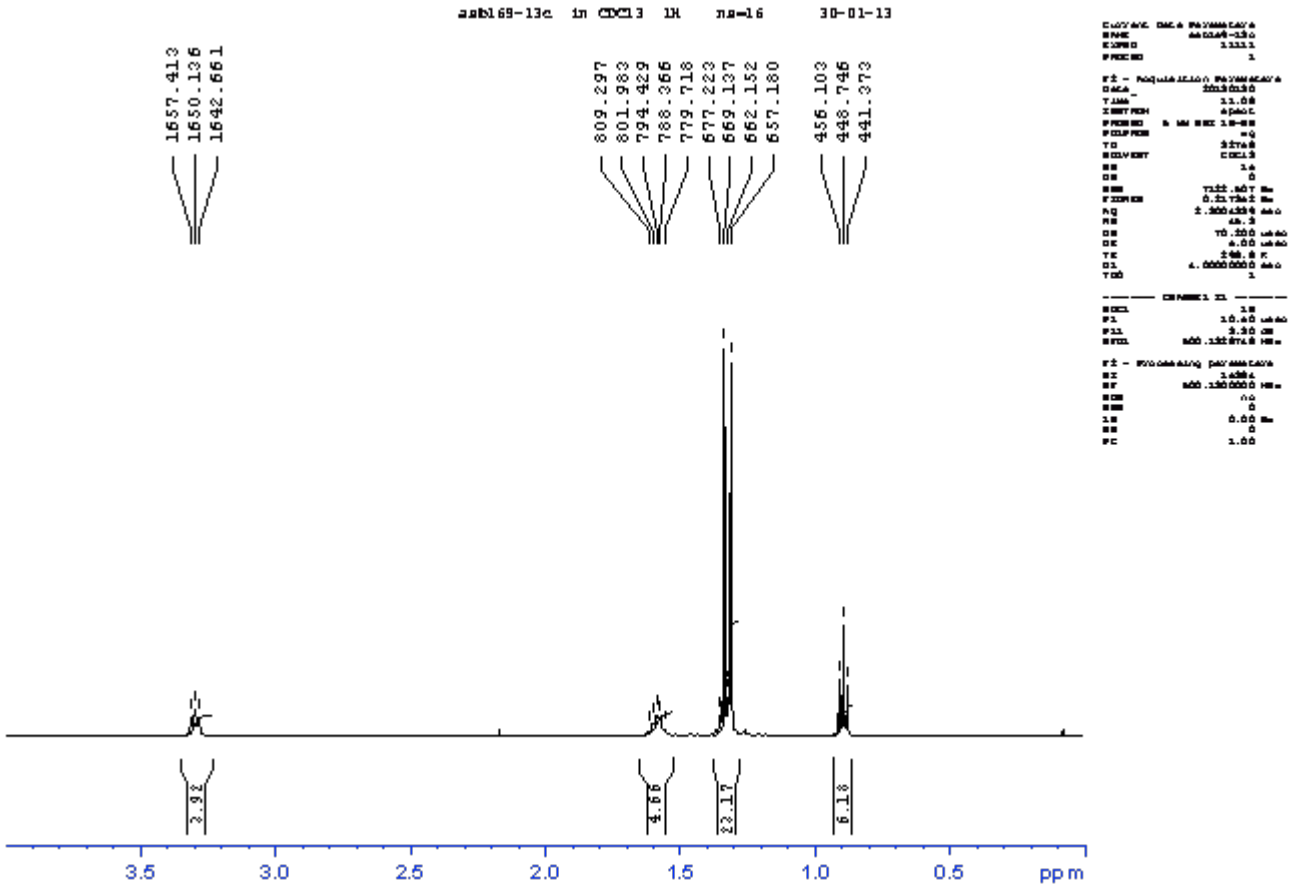
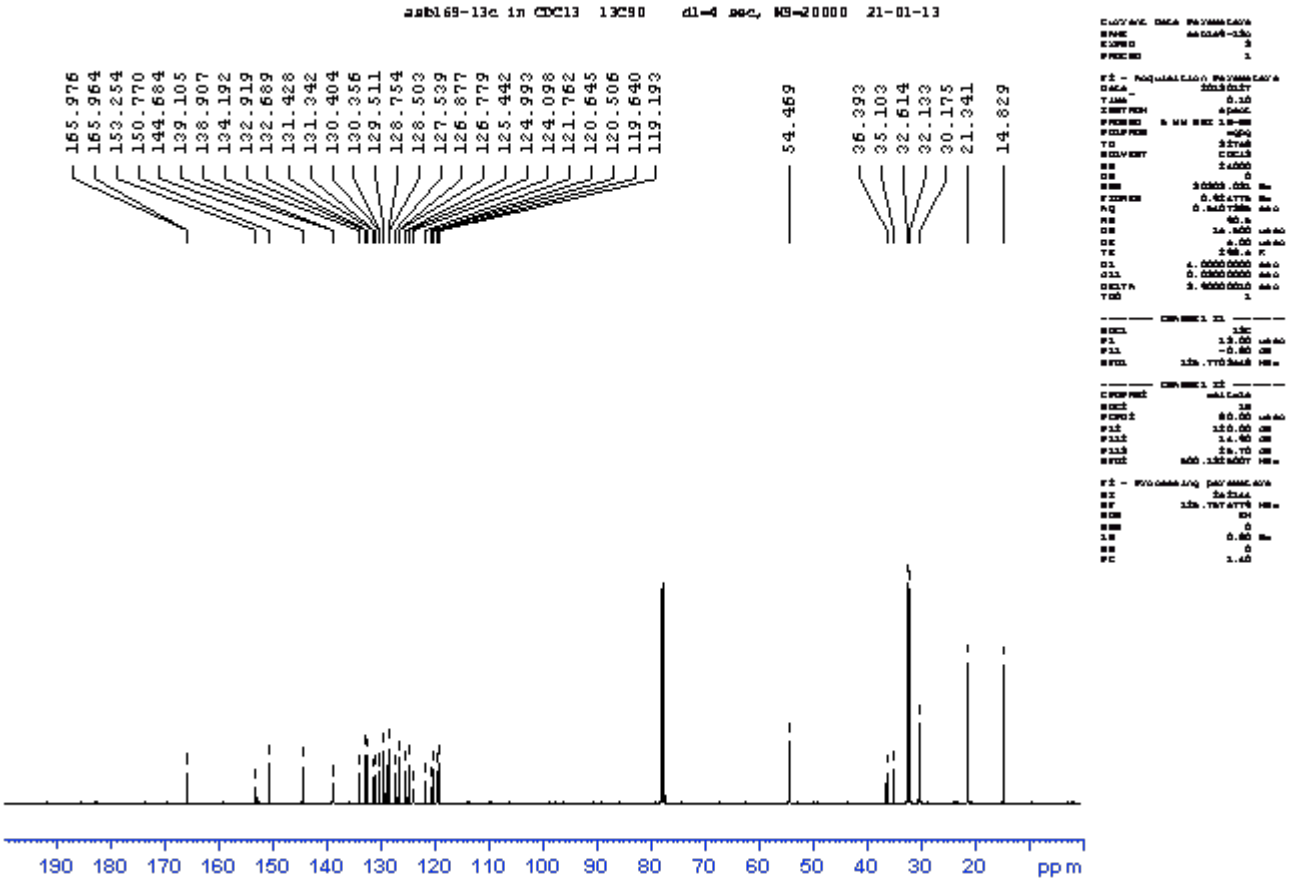


Alifatic region



^{13}C full spectral range



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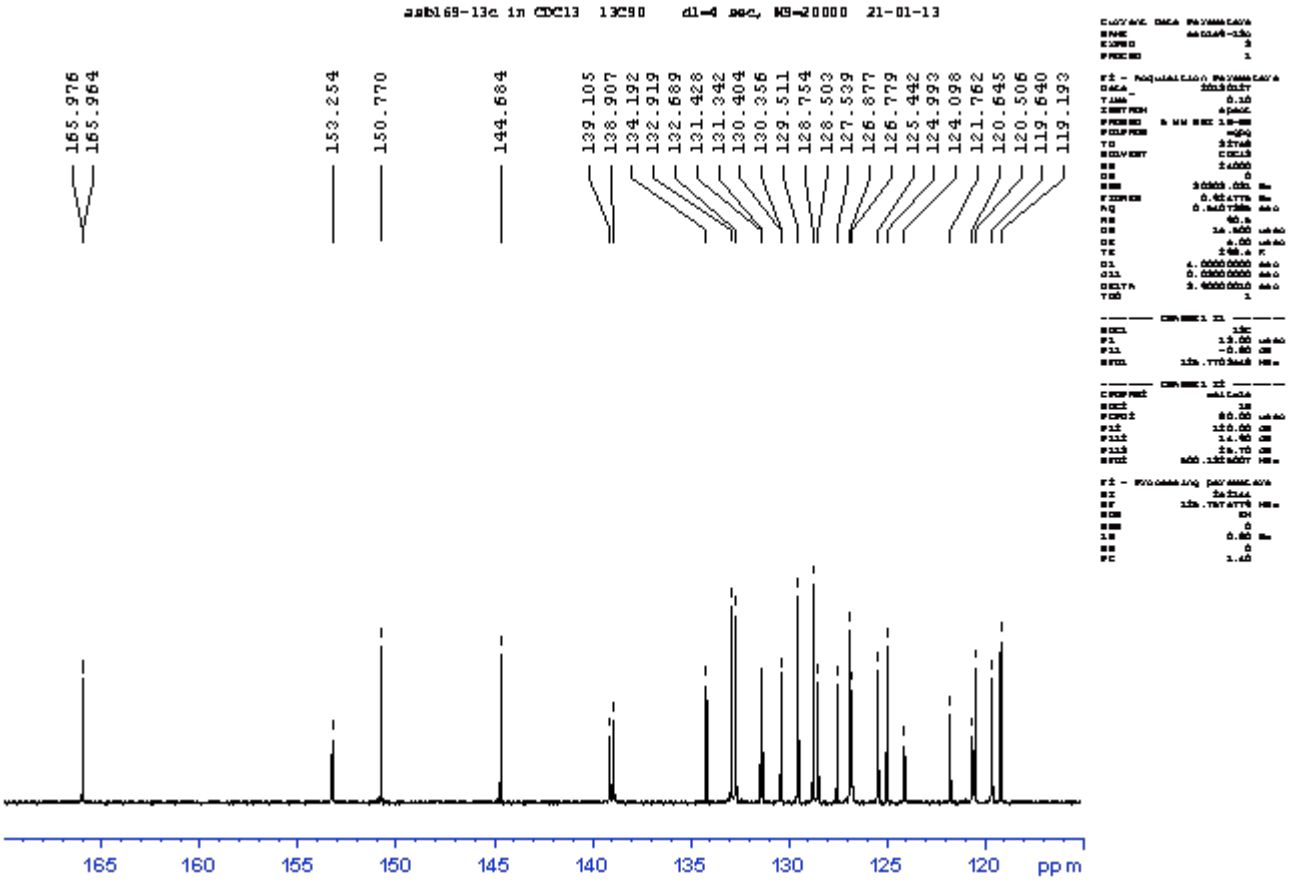

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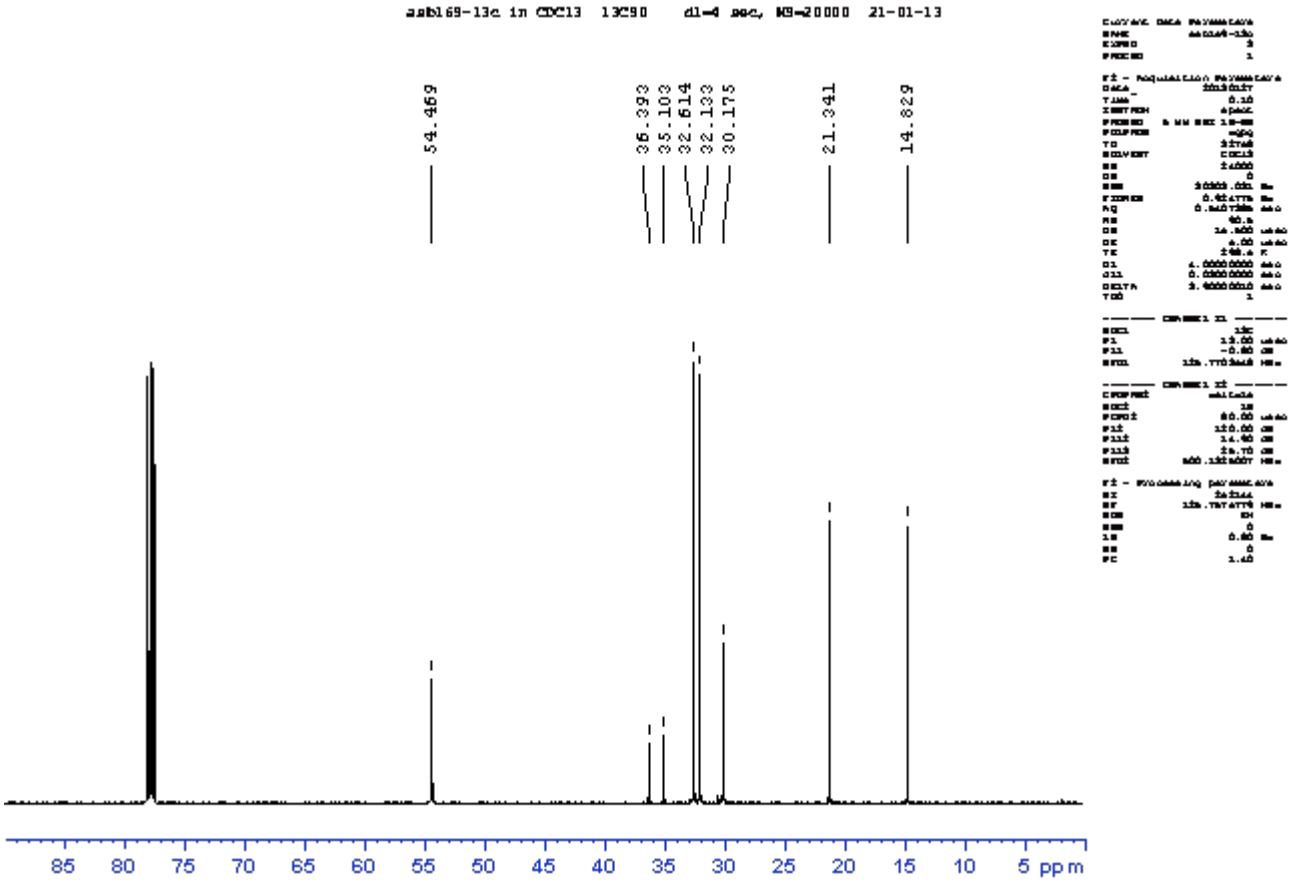
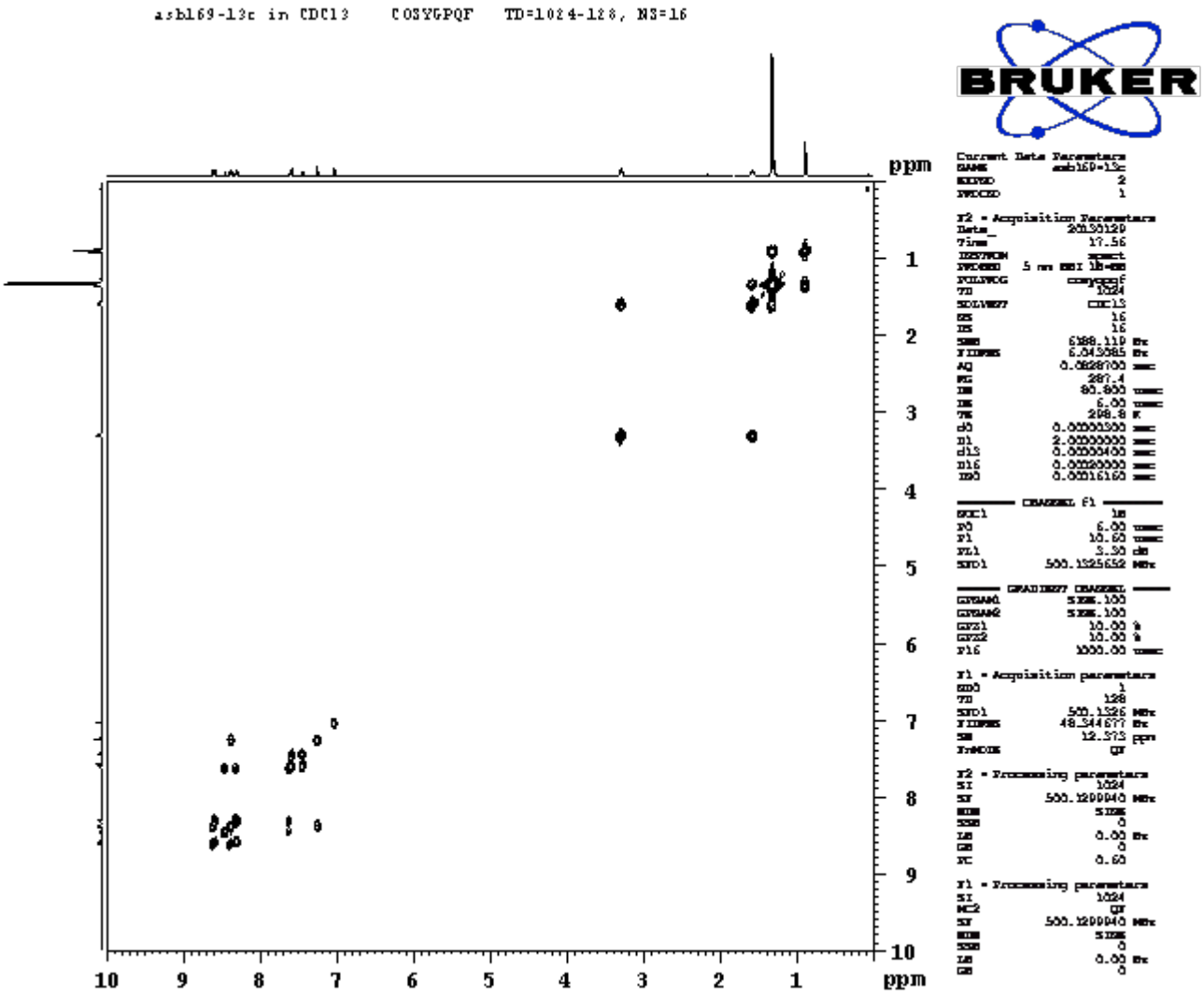


^{1}H COSY full spectral range



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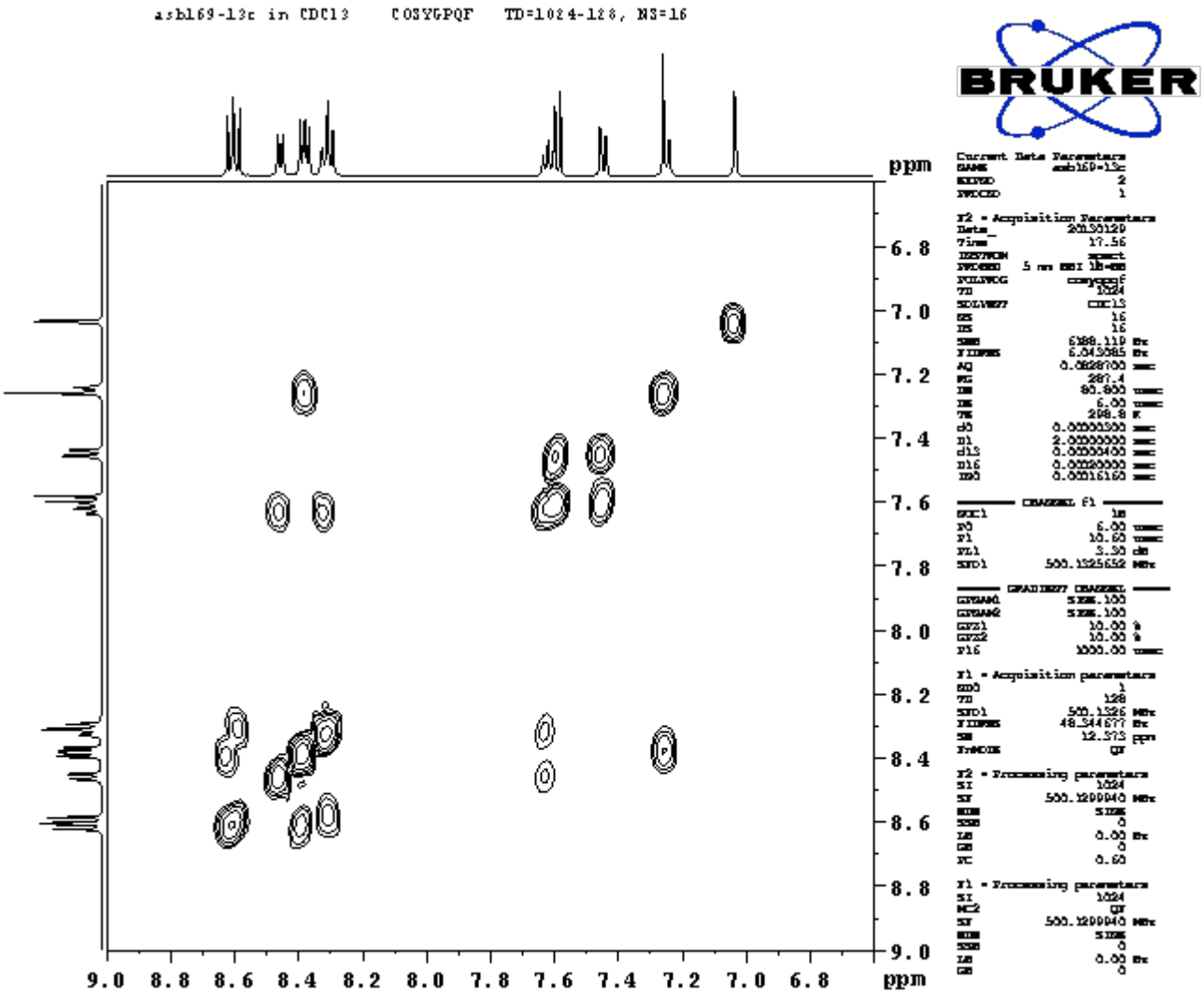
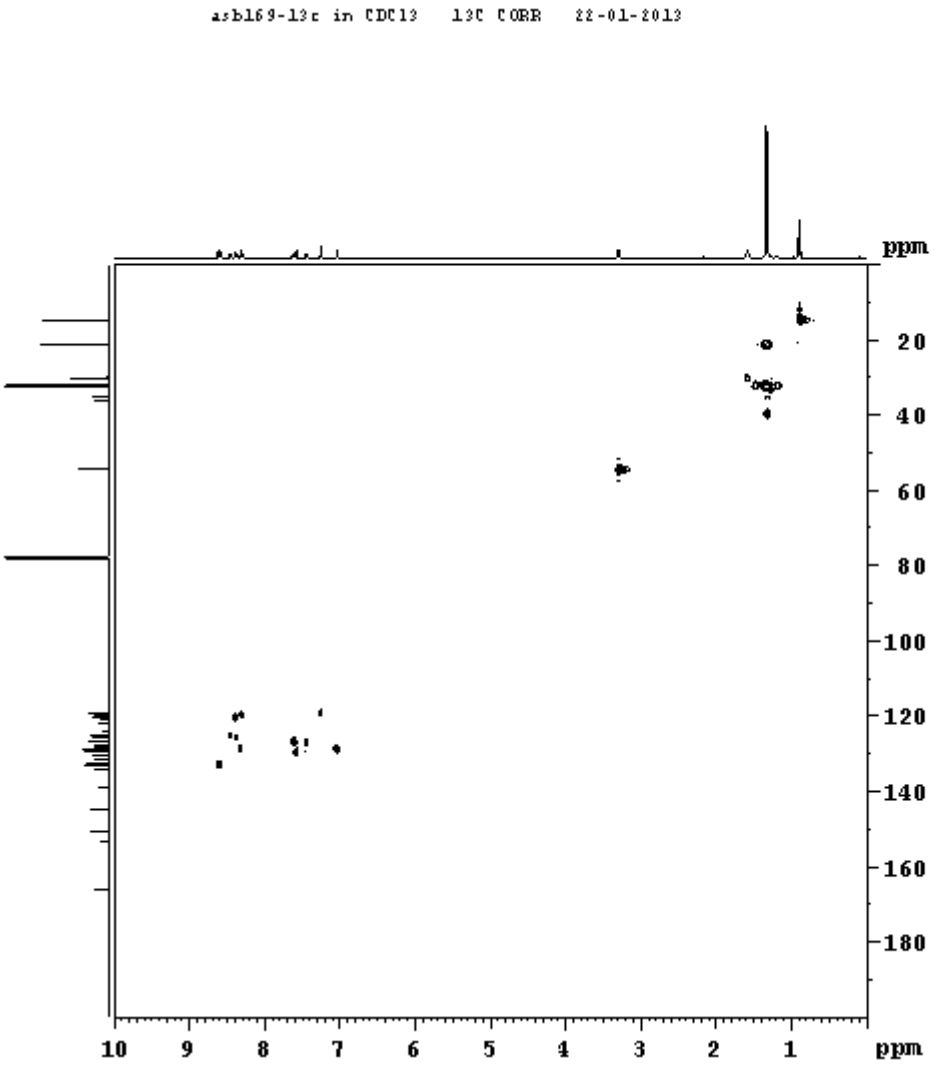


^{1}H ^{13}C HETCOR full spectral range



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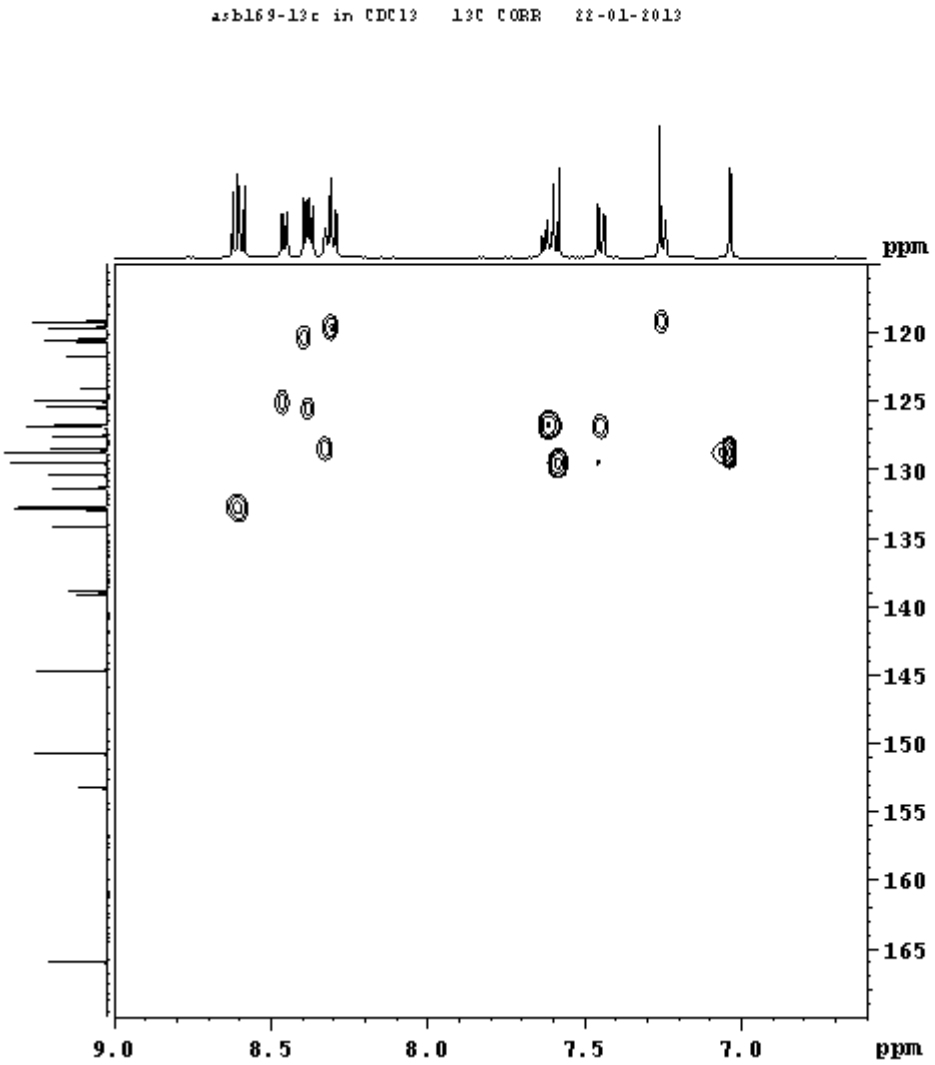
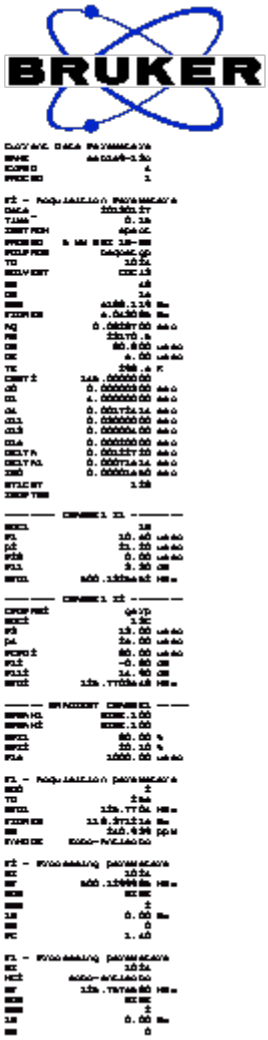
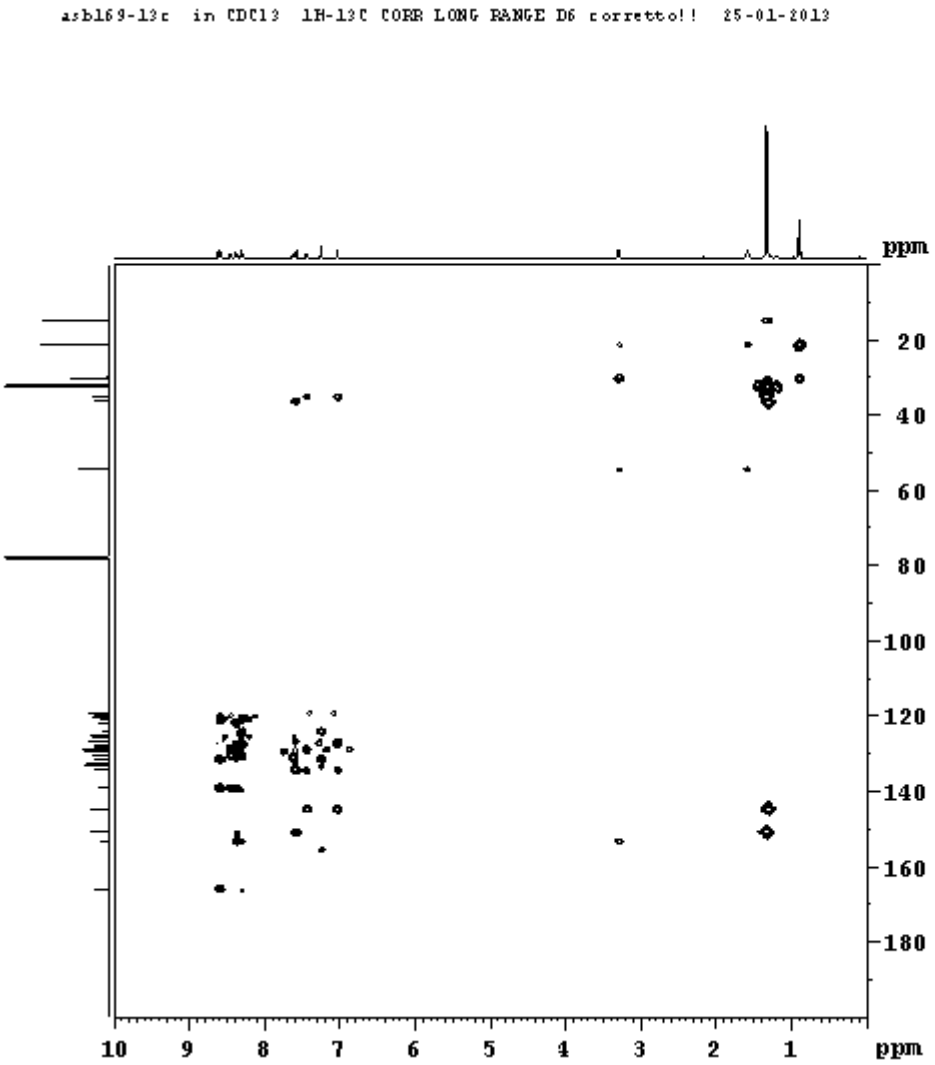




^{1}H ^{13}C HETCOR long range coupling - full spectral range



Current Data Parameters

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EXPNO	5
PROCNO	1

F2 - Acquisition Parameters

Date_	20130127
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PULPROG	hmbcgplpndqf
TD	1024
SOLVENT	CDCl3
NS	48
DS	16
SWH	4166.113 Hz
FIDRES	4.070423 Hz
AQ	0.0983008 sec
RG	14544
DW	60.000 usec
DE	6.00 usec
TE	298.4 K
CNST2	145.0000000
CNST13	8.0000000
d0	0.00003000 sec
d2	0.00000000 sec
d3	0.00344828 sec
d6	0.06250000 sec
D14	0.00200000 sec
D20	0.00017450 sec

======== CHANNEL f1 ========

NUC1	1H
P1	10.40 usec
P2	21.20 usec
PL1	3.30 dB
SFO1	500.1325452 MHz

======== CHANNEL f2 ========

NUC2	13C
P3	13.00 usec
PL2	-0.40 dB
SFO2	125.7703448 MHz

====== GRADIENT CHANNEL =====

GPNAM1	SINE.100
GPNAM2	SINE.100
GPNAM3	SINE.100
GPZ1	50.00 %
GPZ2	30.00 %
GPZ3	40.10 %
P16	1000.00 usec

F1 - Acquisition parameters

NDO	2
TD	256
SFO1	125.7704 MHz
FIDRES	118.371214 Hz
SW	240.939 ppm
FnMODE	QF

F2 - Processing parameters

SI	1024
SF	500.1300000 MHz
WDW	QSINE
SSB	0
LB	0.00 Hz
GB	0
PC	1.40

F1 - Processing parameters

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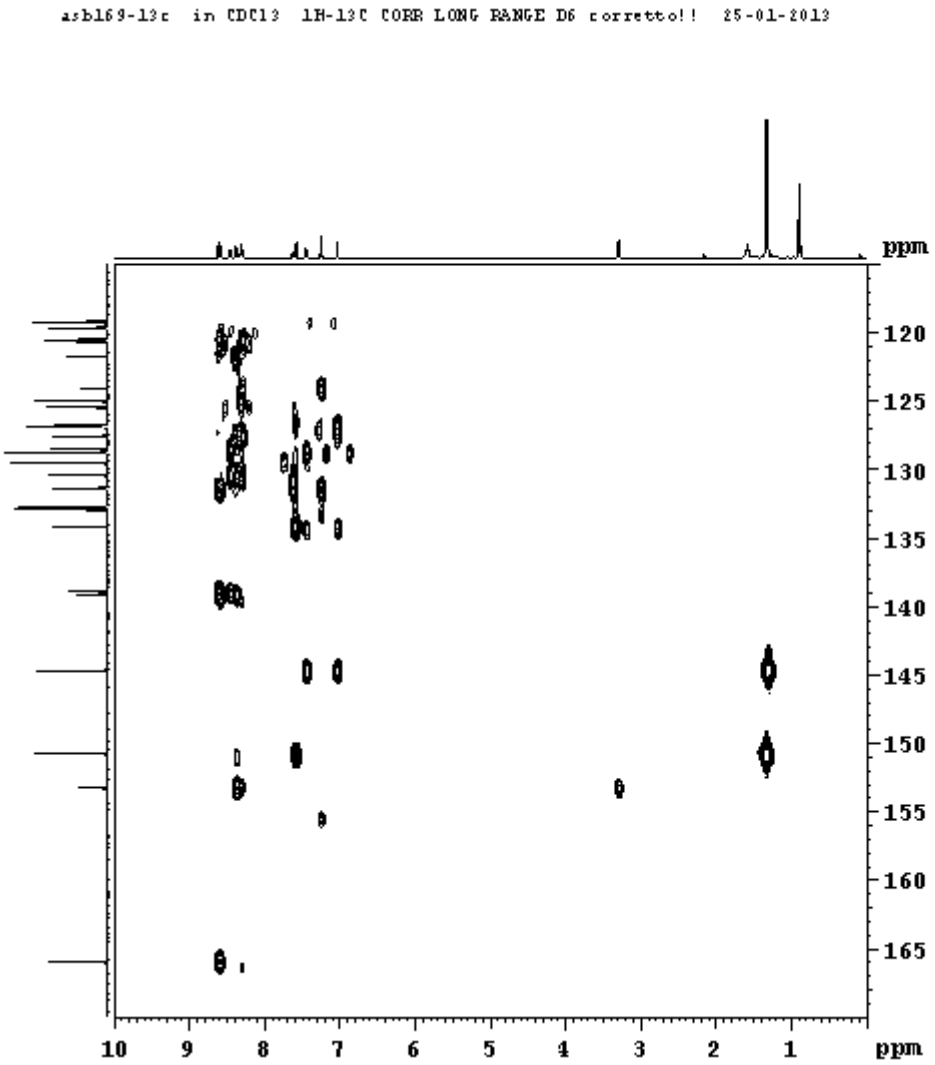
SSB	0
LB	0.00 Hz
GB	0

Aromatic region



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PROCNO 1

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SOLVENT CDCl3
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DS 16
SWH 6164.113 Hz
FIDRES 6.015248 Hz
AQ 0.0829700 sec
RG 14544
DW 40.600 usec
DE 6.00 usec
TE 298.4 K
CNST2 145.0000000
CNST13 8.0000000
d0 0.00003000 sec
D1 4.00000000 sec
d3 0.00344828 sec
d4 0.00172500 sec
D14 0.00012000 sec
D20 0.00017450 sec

======== CHANNEL f1 ========
NUC1 1H
P1 10.40 usec
P2 21.20 usec
PL1 3.30 dB
SFO1 500.1325452 MHz

======== CHANNEL f2 ========
NUC2 13C
P3 13.00 usec
PL2 -0.40 dB
SFO2 125.7703448 MHz

====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPNAM3 SINE.100
GPZ1 50.00 %
GPZ2 30.00 %
GPZ3 40.10 %
P16 1000.00 usec

F1 - Acquisition parameters
NUC0 1H
TD 256
SFO1 125.7704 MHz
FIDRES 118.371214 Hz
SW 240.939 ppm
FnMODE QF

F2 - Processing parameters
SI 1024
SF 500.1300000 MHz
WDW QSINE
SSB 0
LB 0.00 Hz
GB 0
PC 1.40

F1 - Processing parameters
SI 1024
MC2 QF
SF 125.7573580 MHz
WDW QSINE
SSB 0
LB 0.00 Hz
GB 0

3. Figure S1. Examples of absorption and emission spectra of D-A and TW compounds.

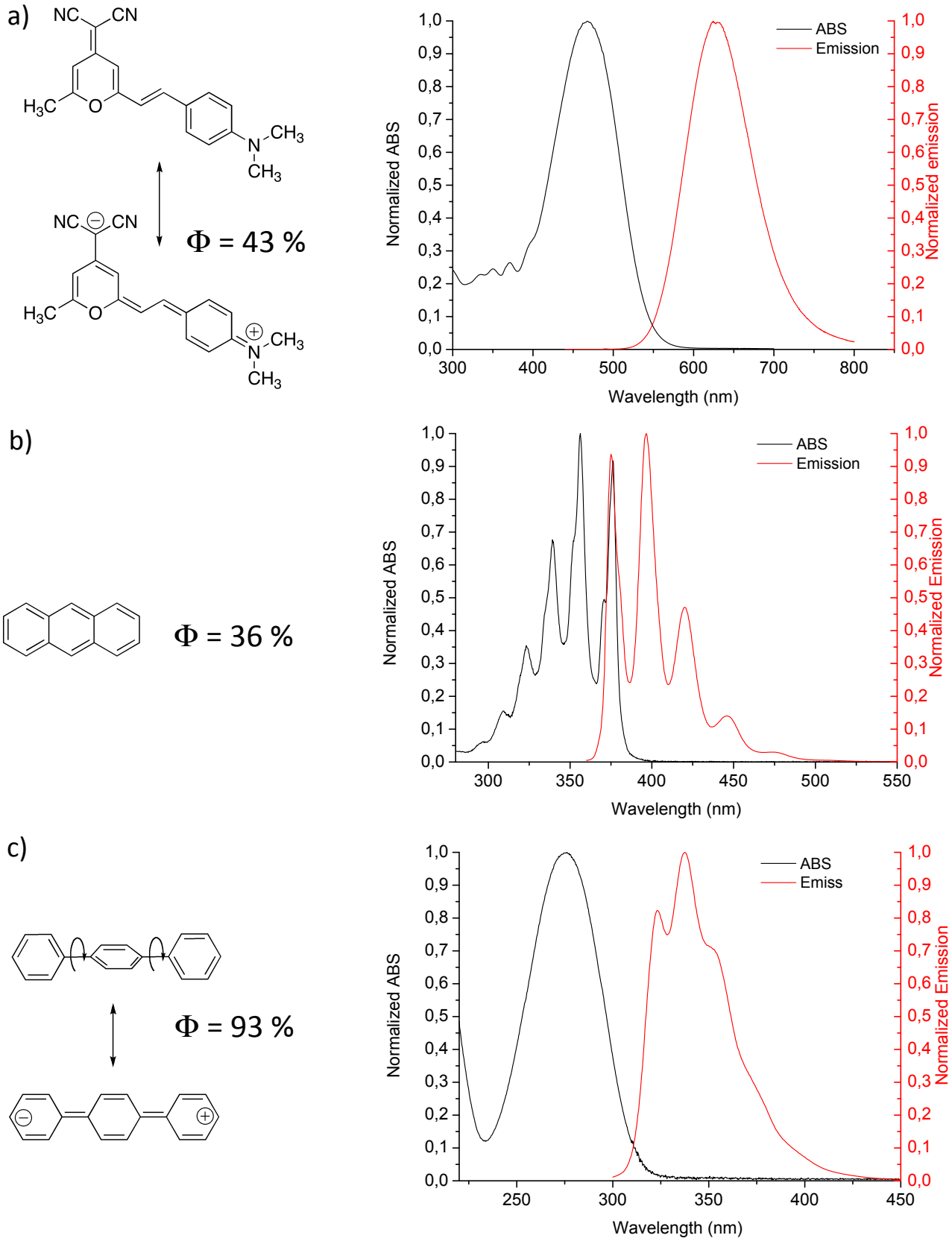

Figure S1. Comparison between the absorption (black curves), emission (red curves) and fluorescence quantum yields of representative molecules pertaining to: a) Donor-Acceptor compounds: the laser dye DCM (4-

(Dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran). Solvent MeOH. b) planar, rigid derivative: anthracene. Solvent cyclohexane. c) Twisted derivative: p-terphenyl. Solvent cyclohexane. (Source: http://omlc.org/spectra/).

4. CV plots for derivatives 1-5.

For the electrochemical characterization all perylene derivatives were dissolved (concentration in the order of 10^{-4} M) in the supporting electrolyte that was a 0.1 M solution of tetrabutylammonium perchlorate (Fluka, electrochemical grade, ≥99.0%) in a solution of anhydrous acetonitrile (Aldrich, 99.8%) and dichloromethane (Aldrich, 99.8%), 2:1 by volume. Cyclic Voltammetries at scan rate of 50 mV/s were carried out using a PARSTA2273 potentiostat in a single chamber three electrodes electrochemical cell in a glove box filled with Argon ($[O_2] \leq 1$ ppm). The working, counter and pseudo-reference electrodes were a Glassy Carbon (GC) pin (3mm diameter), a Pt flag, and a Ag/AgCl wire, respectively. The GC surface was polished with alumina 0.1 μm suspension, sonicated for 15 min. in deionized water and washed with 2-propanol before using. The Ag/AgCl pseudo-reference electrode was calibrated before and after each measurement using a 1 mM ferrocene solution in the electrolyte.

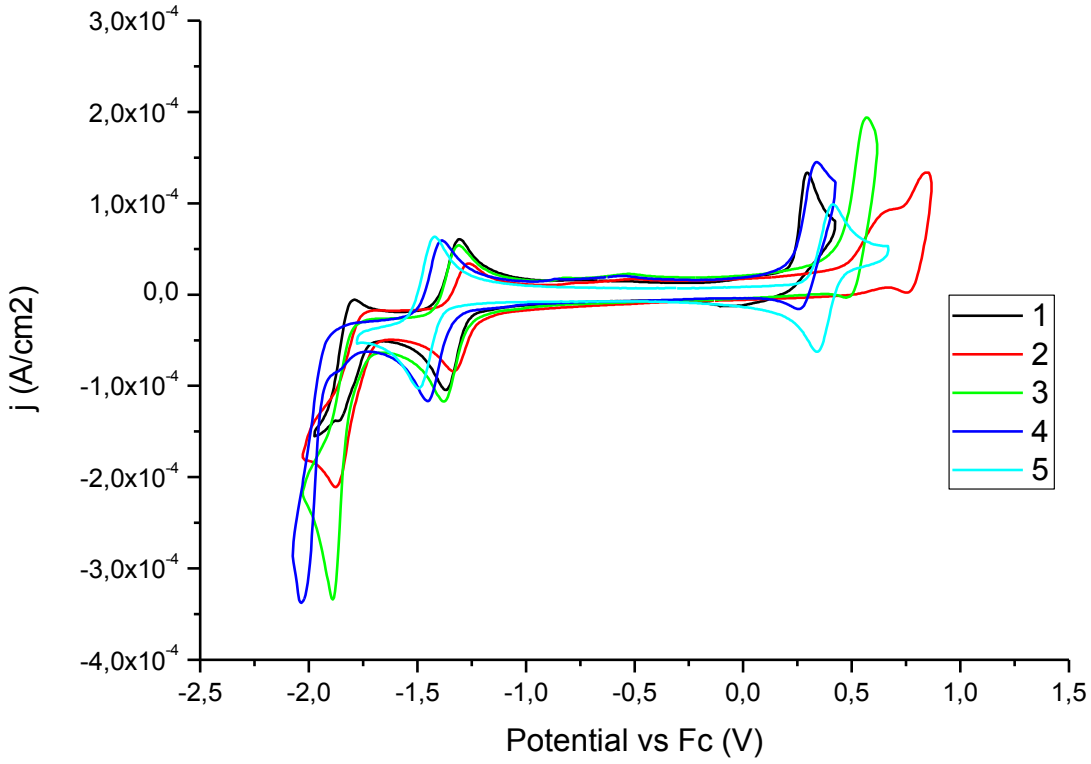

Figure S2. Cyclic voltammetry plots for derivatives **1**-**5** 10^{-4} M solution in acetonitrile with 0.1 M tetrabutylammonium *p*-toluenesulfonate as the supporting electrolyte.

5. Spectroelectrochemical characterization of derivatives 1-5.

For the spectroelectrochemical (SE) characterization all perylene derivatives were dissolved (concentration in the order of 10^{-4} M) in the supporting electrolyte that was a 0.1 M solution of tetrabutylammonium perchlorate (Fluka, electrochemical grade, ≥99.0%) in a solution of anhydrous acetonitrile (Aldrich, 99.8%) and dichloromethane (Aldrich, 99.8%), 2:1 by volume. Potentiostatic pulse were applied using a PARSTA2273 potentiostat with a single chamber three electrodes SE optical cuvette in a glove box filled with Nitrogen ([O_2, H_2O] ≤ 0.1 ppm). The working, counter and pseudo-reference electrodes were a gold mesh (1cm^2), a Pt wire and a Ag/AgCl wire, respectively. The Ag/AgCl pseudo-reference electrode was calibrated before and after each measurement using a 1 mM ferrocene solution in the electrolyte. Optical SE cuvette has an optical path of 1mm. Spectra are taken using an Als Co. SEC2000 spectrophotometer. All the spectra are taken after the applications of a potential bias for a time long enough, minimum 30s, to reach the optical equilibrium state for that applied potential.

5.1. Derivative 1.

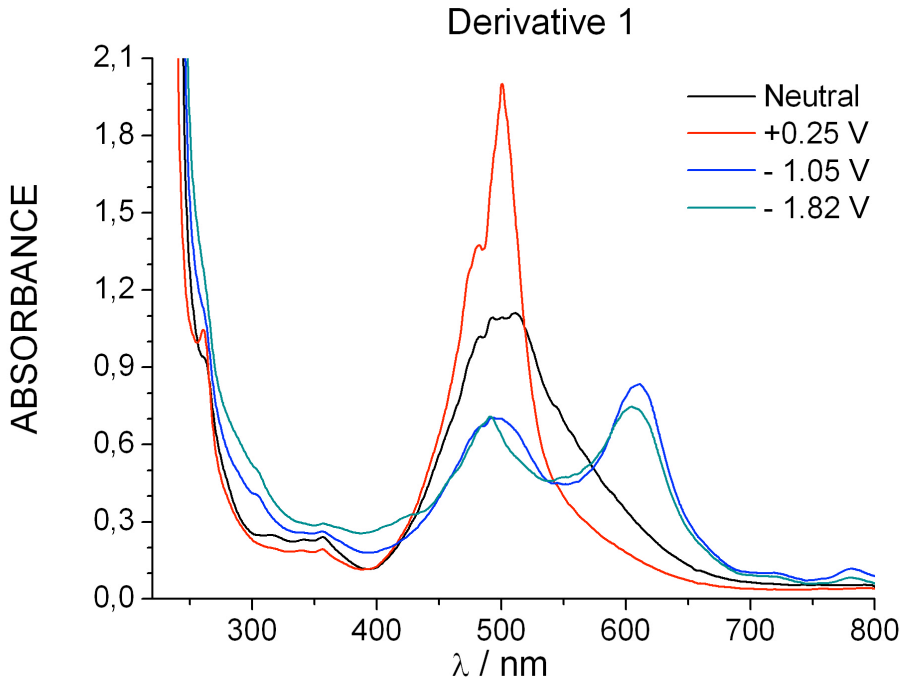

Figure S3. Spectroelectrochemical characterization of derivative **1** 10^{-4} M solution in acetonitrile with 0.1 M tetrabutylammonium p-toluenesulfonate as the supporting electrolyte.

5.2. Derivative 2

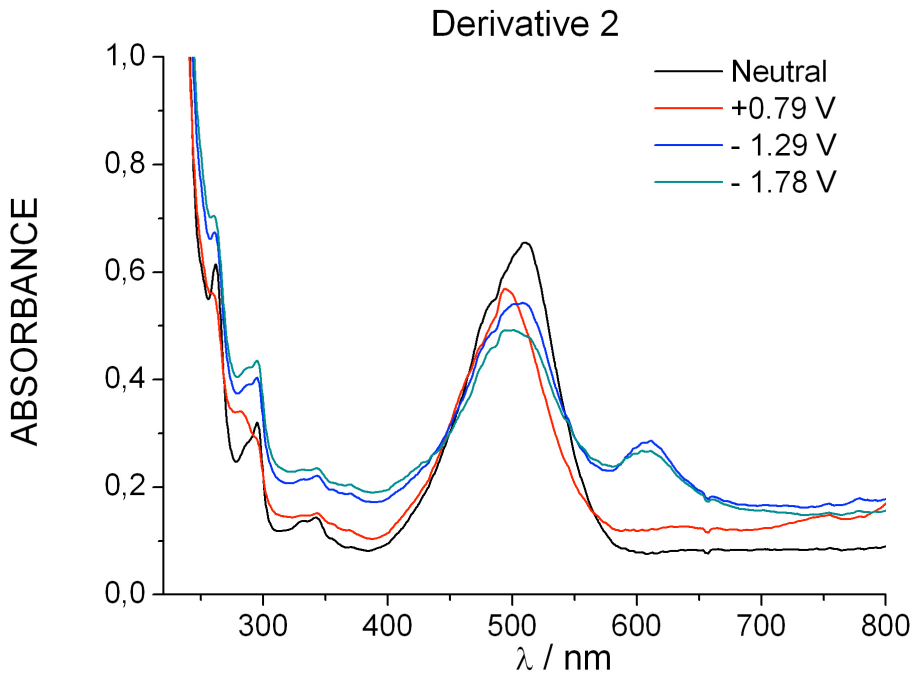

Figure S4. Spectroelectrochemical characterization of derivative **2** 10^{-4} M solution in acetonitrile with 0.1 M tetrabutylammonium *p*-toluenesulfonate as the supporting electrolyte.

5.3. Derivative 3

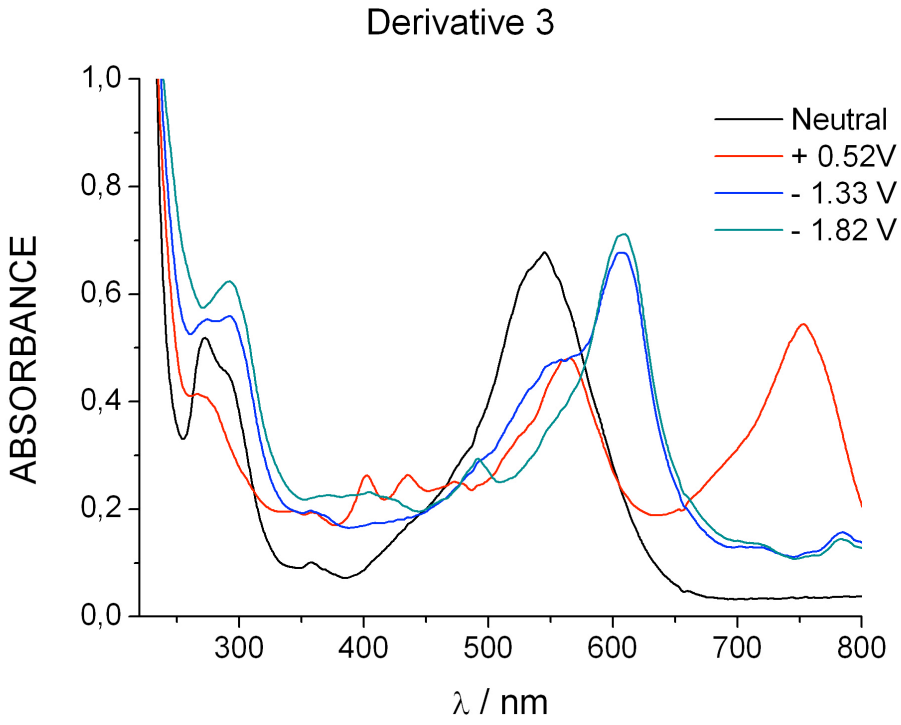

Figure S5. Spectroelectrochemical characterization of derivative **3** 10^{-4} M solution in acetonitrile with 0.1 M tetrabutylammonium *p*-toluenesulfonate as the supporting electrolyte.

5.4. Derivative 4

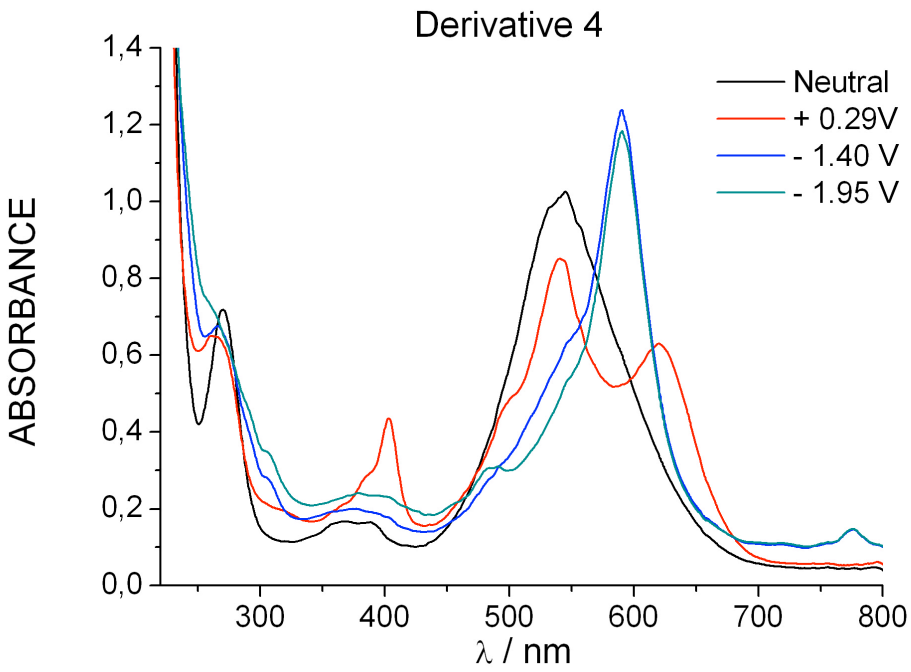

Figure S6. Spectroelectrochemical characterization of derivative **4** 10^{-4} M solution in acetonitrile with 0.1 M tetrabutylammonium *p*-toluenesulfonate as the supporting electrolyte.

5.5. Derivative 5

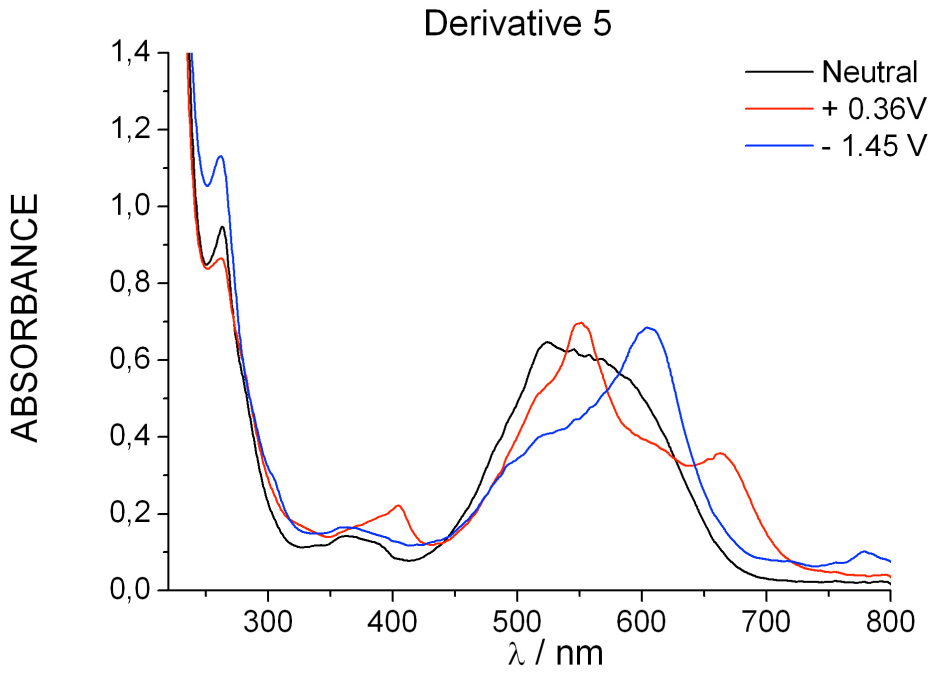

Figure S7. Spectroelectrochemical characterization of derivative **5** 10^{-4} M solution in acetonitrile with 0.1 M tetrabutylammonium *p*-toluenesulfonate as the supporting electrolyte.

6. Characterization of derivative 1 photostability in Chloroform solution.

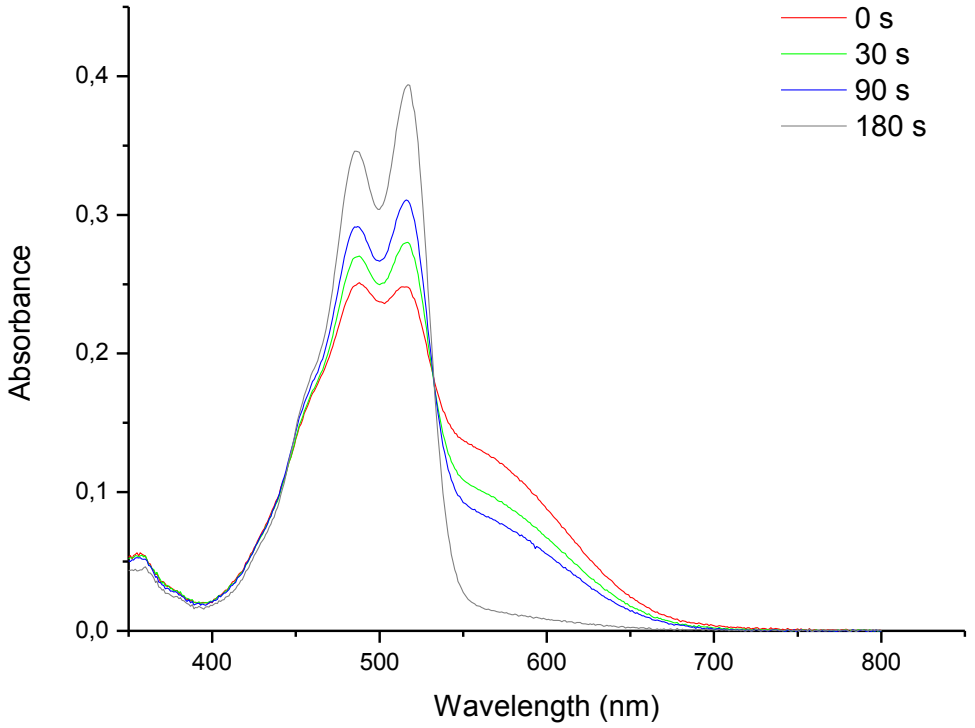

Figure S8. UV-Vis absorption spectra of an air equilibrated solution of derivative **1** in $CHCl_3$ as a function of the irradiation time under standard ambient diffused light.

7. General procedure for the LSC preparation.

In a typical procedure, 100 mg of AIBN were dissolved in 100 ml of freshly distilled MMA. The solution was placed in a beaker and slowly heated on a hot plate until the temperature of 80 °C was reached. This temperature was maintained for 5 minutes, during which time viscosity increased substantially. The solution was immediately transferred in an ice bath and cooled at 20°C. A solution of the appropriate perylen dye in freshly distilled MMA (60 ml) was added along with 15 mg of lauryl peroxide. The viscous syrup thus obtained was poured in a mould of 7 mm thickness and 100 cm^2 area and heated in a water bath at 56°C for 48 h. At the end of this thermal treatment the syrup turns into a solid slab that is further cured at 95°C for 24 h. After cooling, the slab can be easily separated by the glass mould and polished for optical measurements. Figure S8 shows an example of the setup we employed. In particular the slab shown contains derivative **4**.

Figure S9. Experimental setup for the cell cating of the PMMA based LSC.

8. Details of the computational investigation.

All DFT calculations were performed using the Q-Chem software suite.[4] Initial geometry optimizations were performed using the empirical EDF1 functional and 6-31G** basis set, followed by optimization at the hybrid level with B3LYP paired with a 6-31G** basis set. This protocol was followed for both neutral and cationic electronic configurations. The reported ground state dipole moments, HOMO and LUMO Kohn-Sham orbitals and eigenvalues were obtained from single-point B3LYP/6-31G** calculations on the optimized neutral geometries.

B3LYP paired with polarized gaussian basis sets have previously been used to describe the ground and excited state energetics and geometries of functionalized perelyene diimides.[5] For ground state geometries, this level of theory has been shown to be highly accurate.[6] Similarly for MO energies this level of theory shows accurate trends in energy shifts with functionalization when compared with calculations done with larger basis sets.[6]

9. Details on the UPS measurements.

Glass slides (2.5 cm x 1.5 cm) were subsequently cleaned by sonication at 50° C in soapy water, deionized water, isopropanol, ethanol and acetone, then treated in an ozone plasma (residual pressure 400-500 mmHg) for 10 minutes to remove organic residues. After each of the following cleaning and processing steps the slides were flushed with dry 200 nm dust-filtered nitrogen The substrates were then transferred in a nitrogen-filled glove box and 100 nm of silver (Silver slugs Premion 99.999% from Alfa-Aesar) were evaporated at a 0.2 Å/s rate. The various solutions (5 x 10-3 M in anhydrous DCM) were spun-cast at 1500 rpm for 30 seconds. The materials were glued to a sample holder with copper tape, transferred in Desivac and moved to the prechamber of a Thermo Scientific ESCALAB 250Xi. After overnight pumping the substrates were moved to the main chamber and UPS scans measured (base pressure 2 x 10-8 atm, using He-I emission line at 21.22 eV while under -9 V bias). The spectra were collected and processed using Thermo Scientific Avantage 5.35.

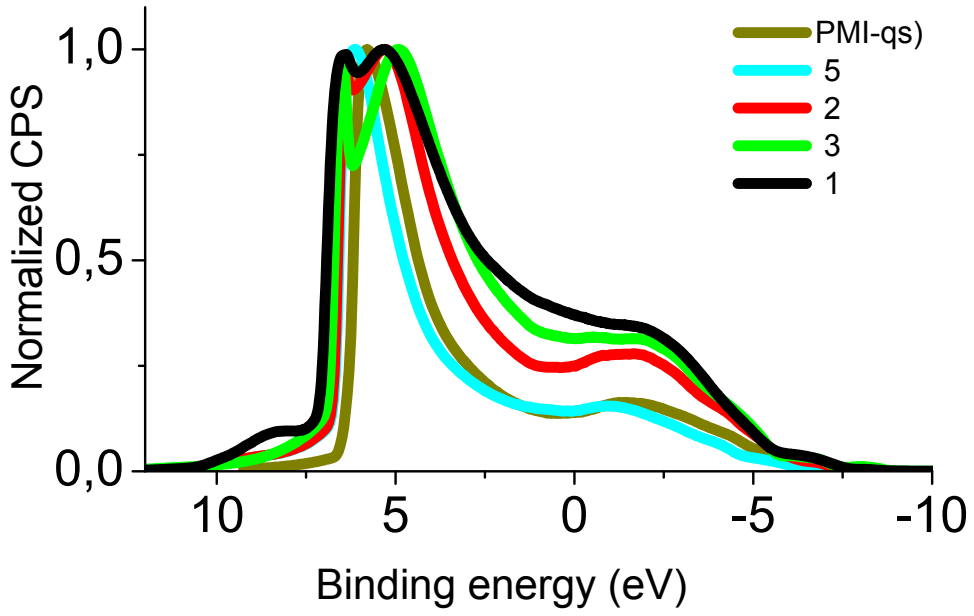

Figure S10. Full photoemission spectra of derivatives **PMI-qs**, **1**,**2**,**3** and **5**.

10. **Supplementary data on time resolved transient absorption characterization of 5.**

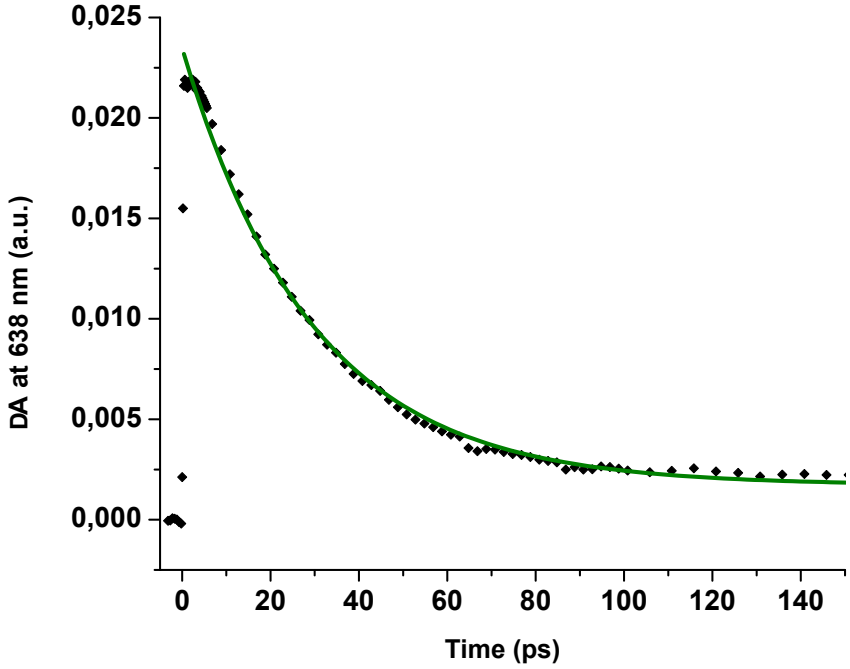

Figure S11. Time profiles of differential absorbance of a CH_2Cl_2 solution of **5** at 638 nm. The fitting curve corresponds to a first order decay.

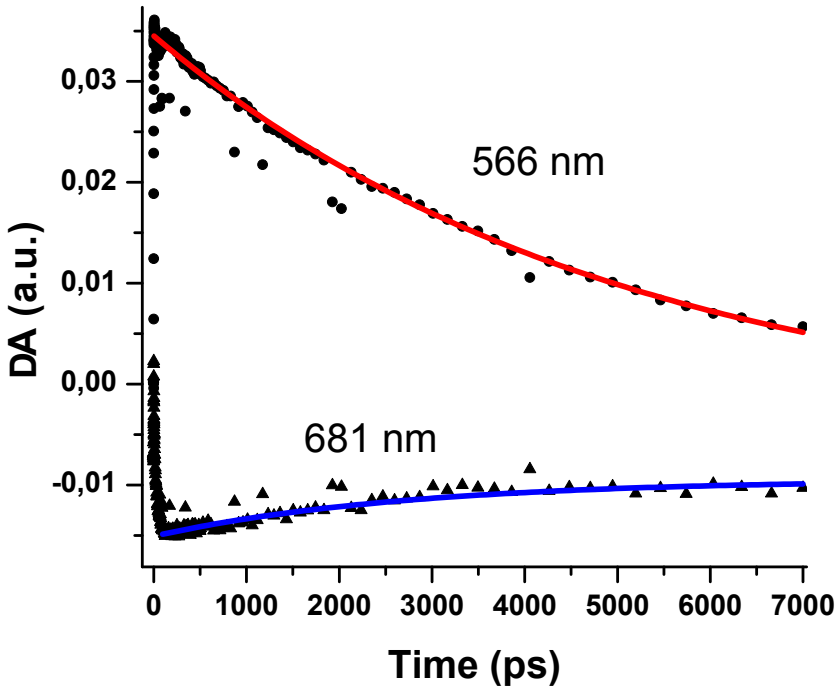

Figure S12. Time profiles of differential absorbance of a CH_2Cl_2 solution of **5** at 566 nm (red) and 681 nm (blue). The fitting curves correspond to a first order decay.

11. Figure S13.

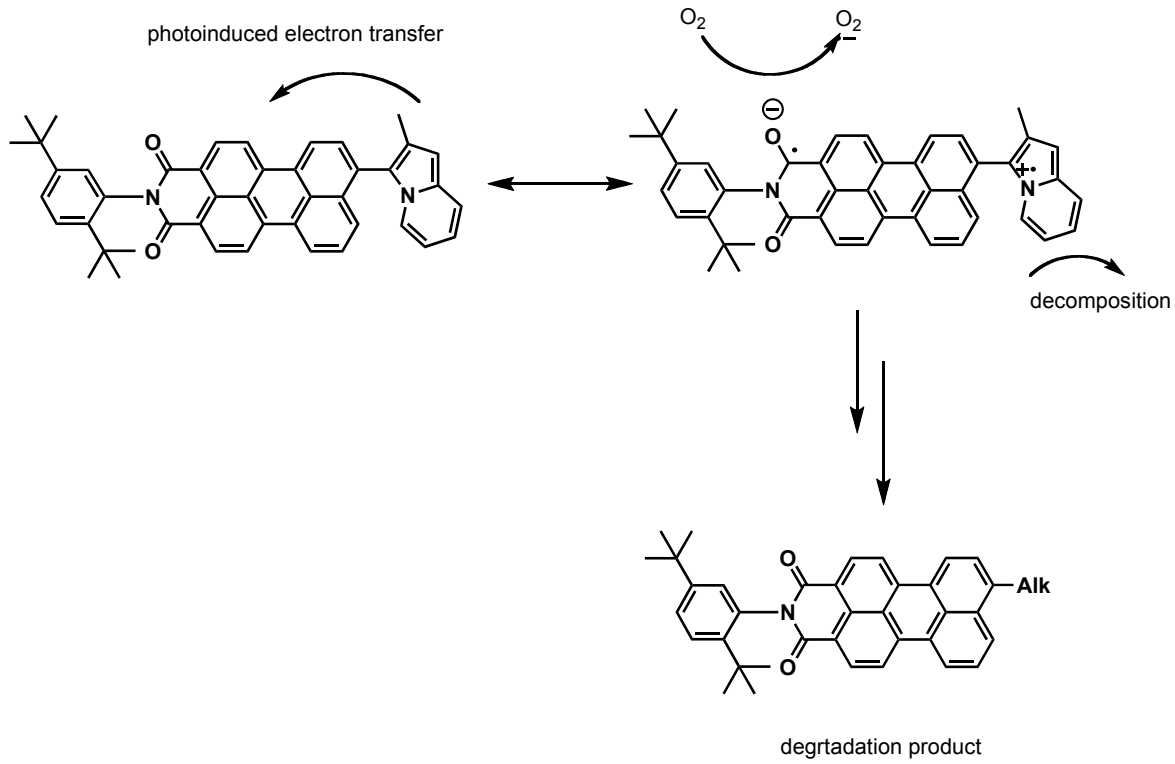

Figure S13. Tentative, unverified mechanism for the photochemical degradation of derivative **1**.

12. Details for the luminescence quantum yield measurements.

Absolute quantum yield measurements were conducted following the well-known procedure described by de Mello et al,[7] using a 405 nm (3.06 eV) pulsed diode laser with a repetition rate of 2 MHz (Edinburgh EPL405) and a Labsphere Spectraflect integrating sphere connected to a Hamamatsu mini-spectrometer through an optical fibre with a 600 nm core. The spectral response of the system (integrating sphere, optic fibre and spectrometer) was corrected by a calibrated tungsten halogen lamp (Ocean Optics LS-1-CAL).

13. References for the Supporting Information.

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