

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*

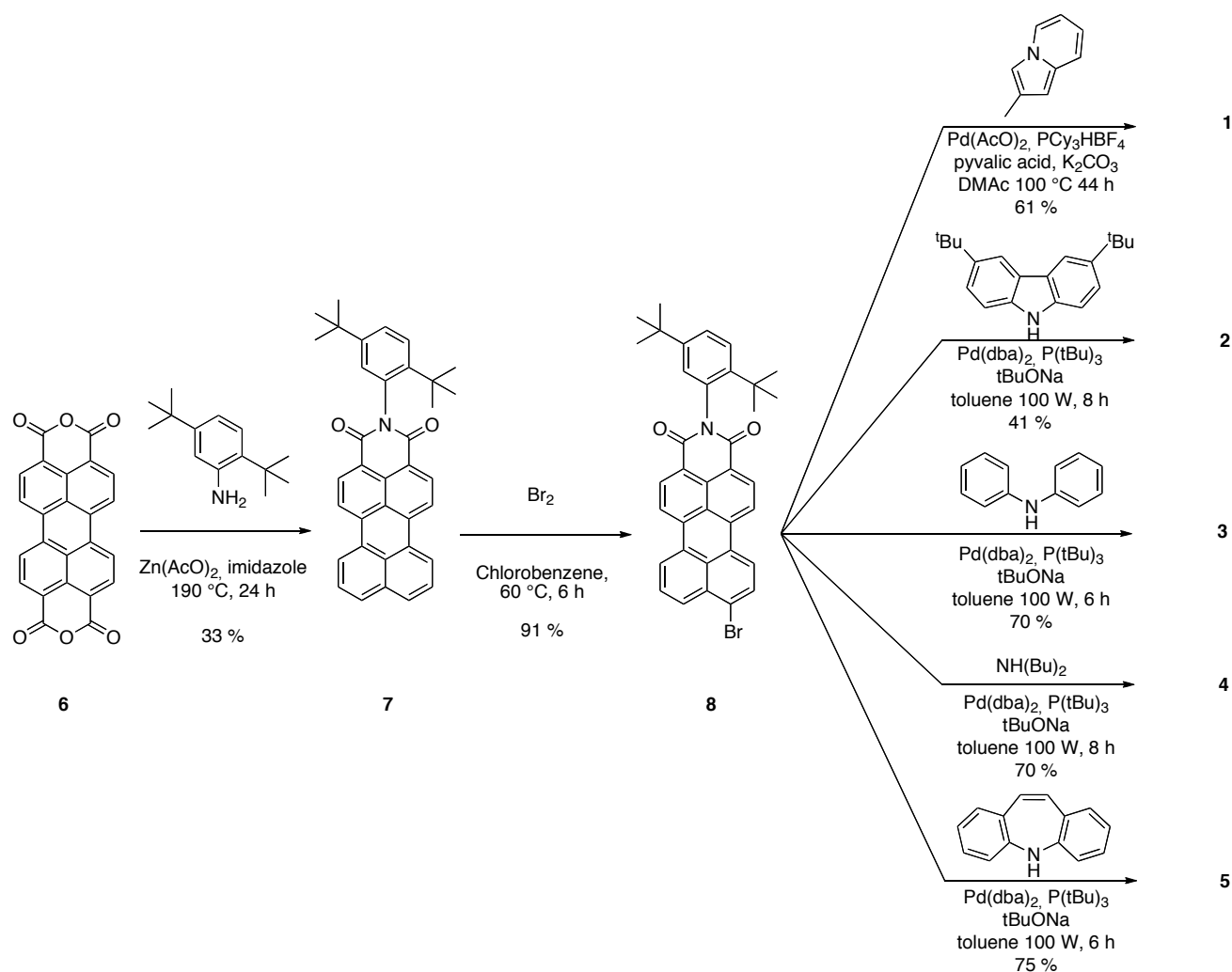
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1. Synthesis of all new compounds

Derivatives **7**¹, **8**² and **5**³ were prepared according to the reported literature procedures, all other chemicals and solvents were purchased from Sigma Aldrich and Alfa Chemicals and used 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 mmol) and the corresponding amine (1.0 eq), are loaded in a 100 mL two-neck round bottom flask equipped with a condenser under N₂ atmosphere. The mixture is suspended in anhydrous toluene (30 mL) and degassed with few vacuum/N₂ 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(^{*t*}Bu)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 N₂ 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 mmol) are allowed to react under microwave irradiation (100 W, 8 h) under N₂ atmosphere. Solvent is removed and the dark crude solid is purified by column chromatography (silica, toluene/CH₂Cl₂ 1:8) to give the title compound as a red solid (330 mg, 0.419 mmol, 41%). m.p. > 350 °C. ¹H 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); ¹³C 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 C₅₆H₅₄N₂O₂: 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 mmol) are allowed to react under microwave irradiation (100 W, 6 h) under a N₂ 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. ¹H 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); ¹³C 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 mmol) 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. 1H 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.

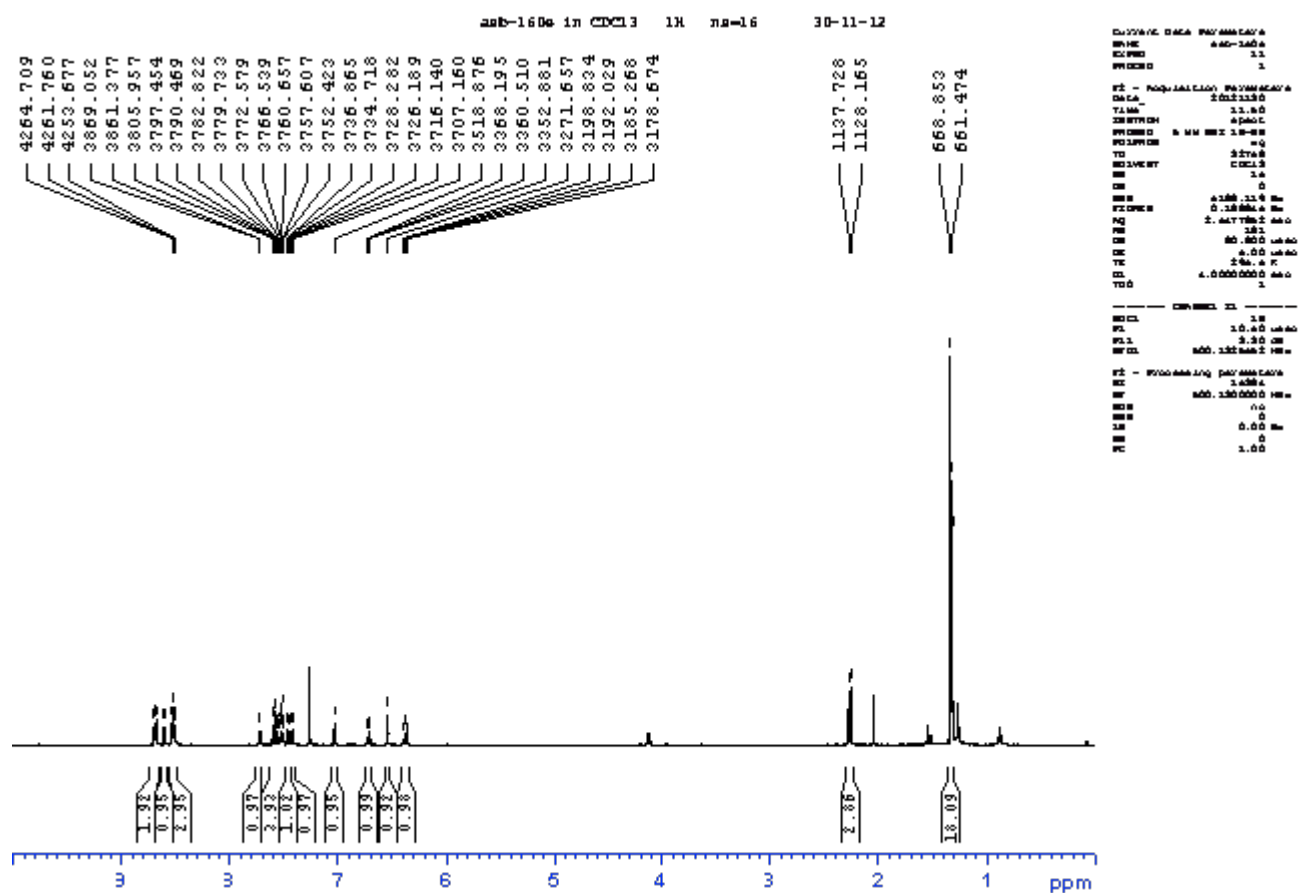
Derivative **1**. Bromide **8** (600 mg, 1.019 mmol), $Pd(AcO)_2$ (3.00 mg, 13.36 μ mol), pivalic acid (33 mg, 0.323 mmol), K_2CO_3 (211 mg, 1.529 mmol), tricyclohexylphosphine tetrafluoroborate (7.80 mg, 21.18 μ mol) and 2-methylindolizine (147 mg, 1.121 mmol) are loaded in a screw-capped tube under 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. 1H 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), 2.27-2.25 (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.

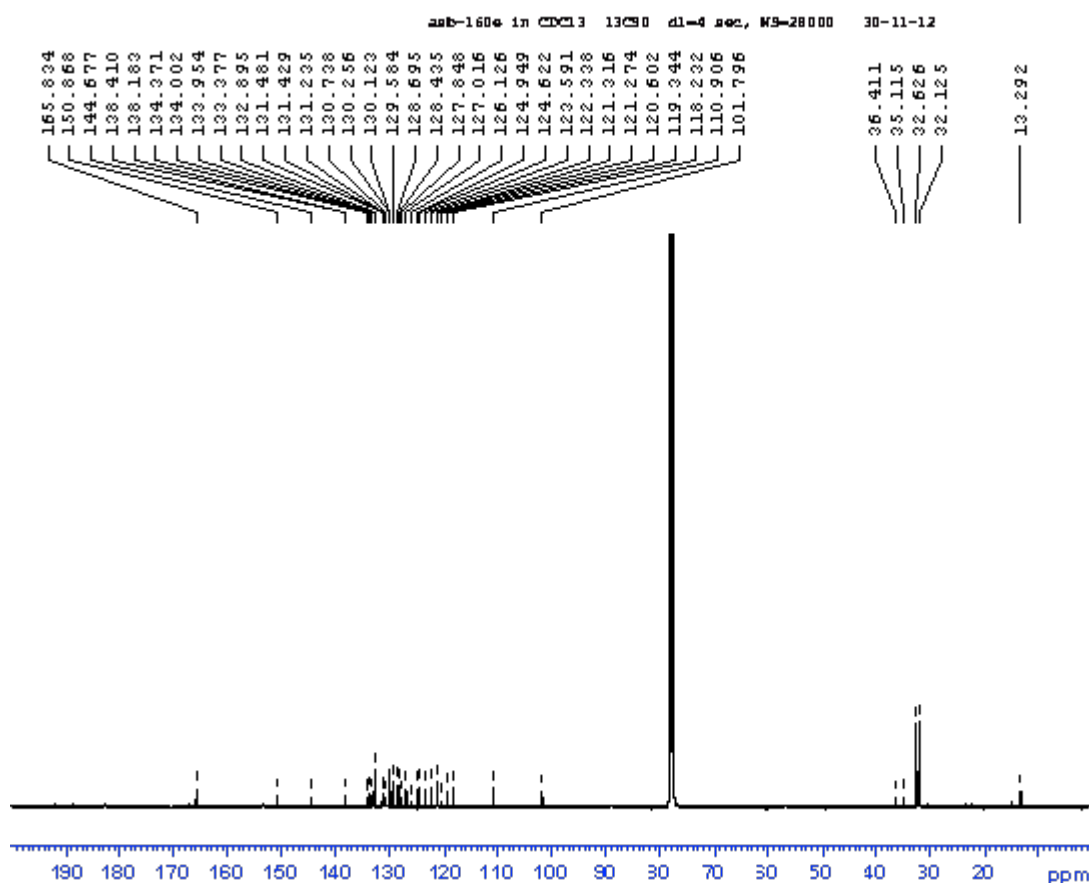
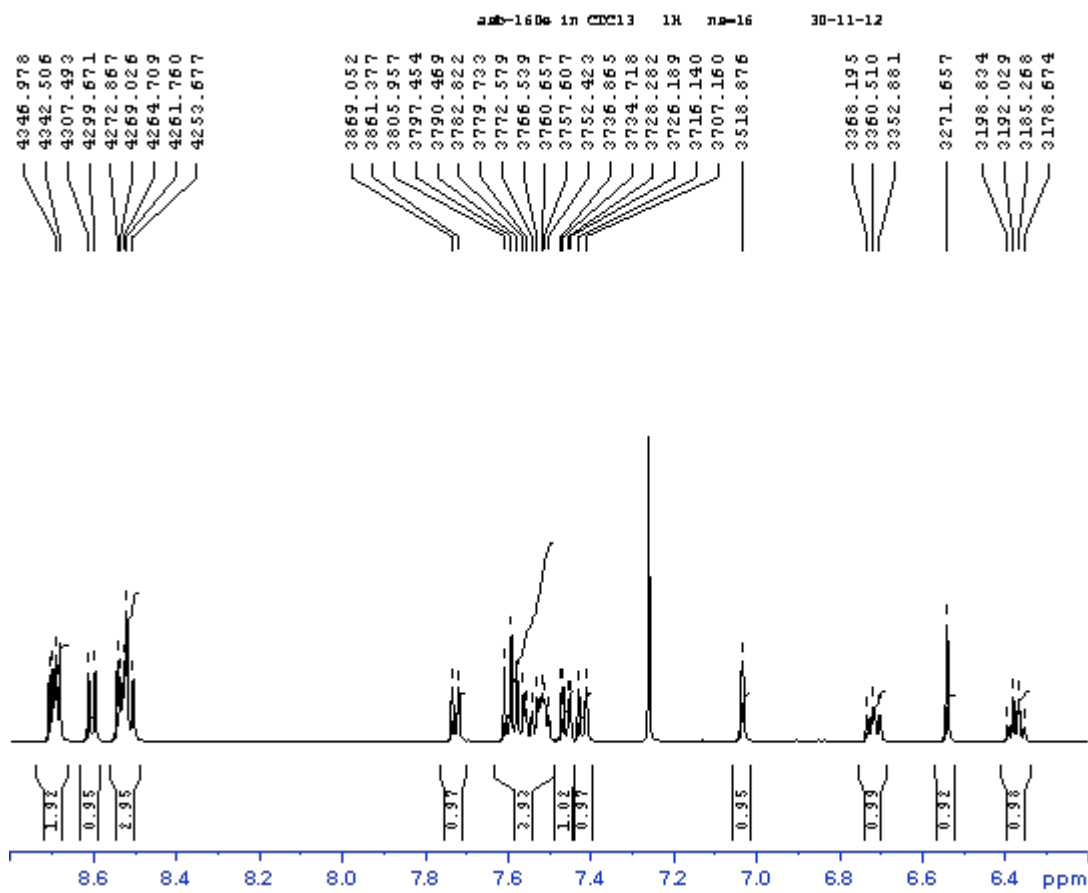
2. Copy of the NMR spectra and Table S1.

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

	Perylene ring position and nucleus								
Derivative	5 ^1H	5 ^{13}C	6 ^1H	6 ^{13}C	7 ^1H	7 ^{13}C	8 ^1H	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.

¹H full spectral range



165.834
 150.868
 144.677
 138.410
 138.182
 134.371
 134.002
 133.954
 133.377
 132.895
 131.481
 131.429
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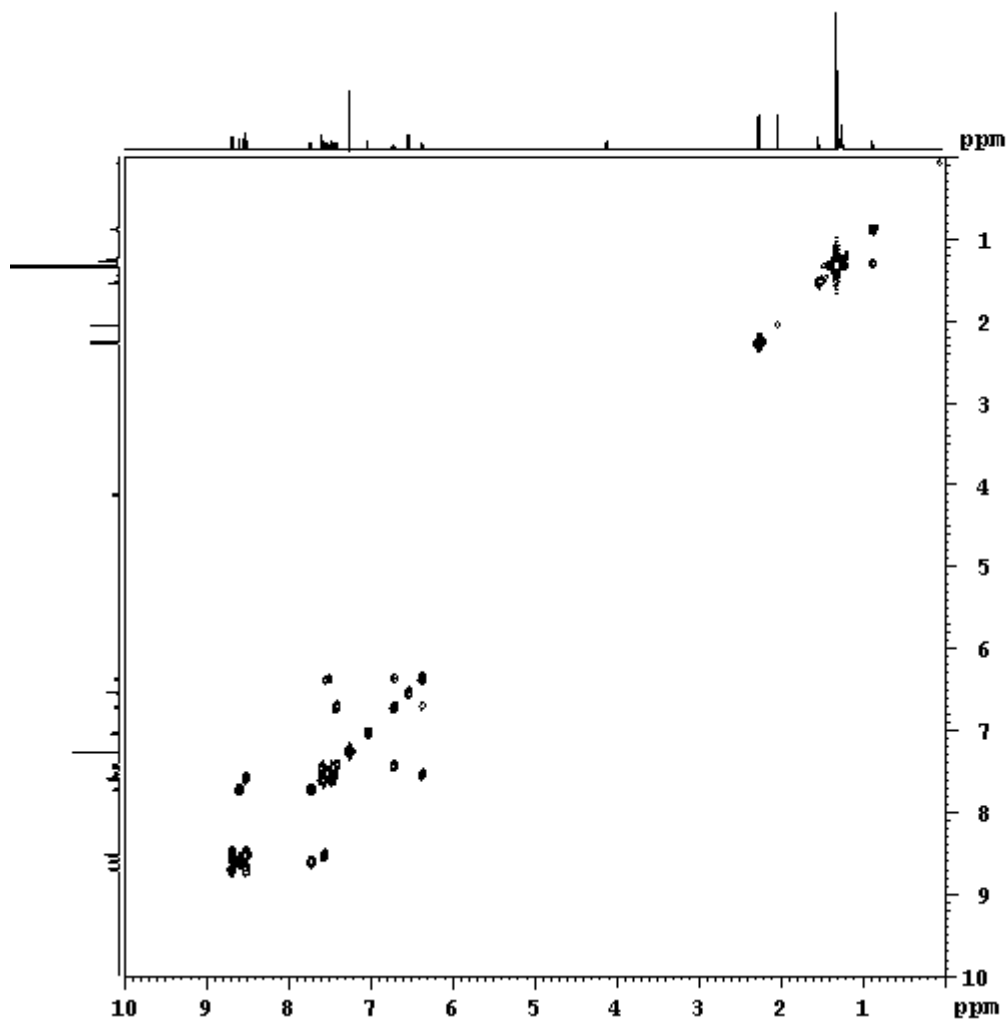
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¹H COSY full spectral range

asb-160e in CDCl₃

COSYGPQF

TD=1024-128, NS=16 20-11-2012



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PROCNO 1

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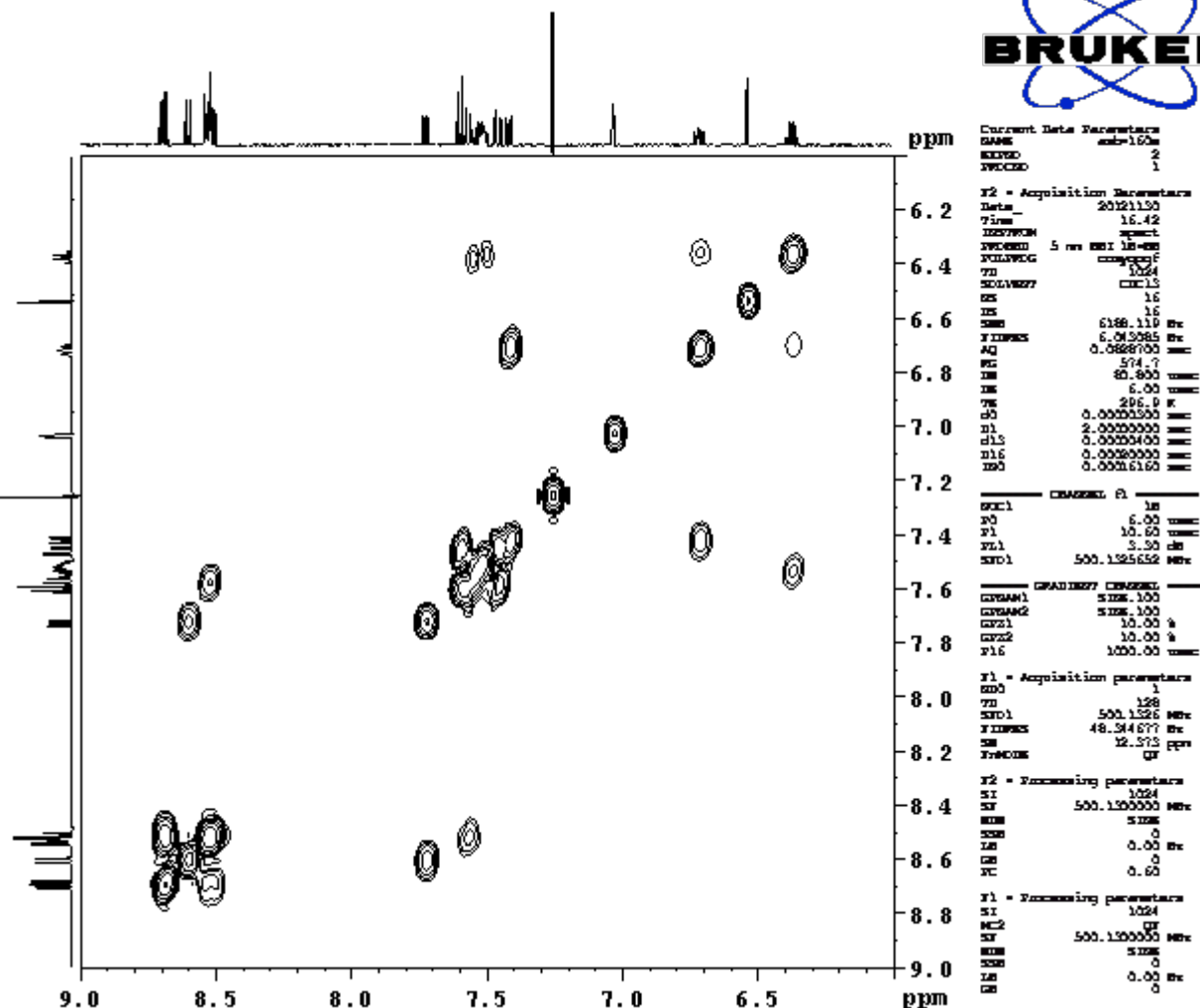
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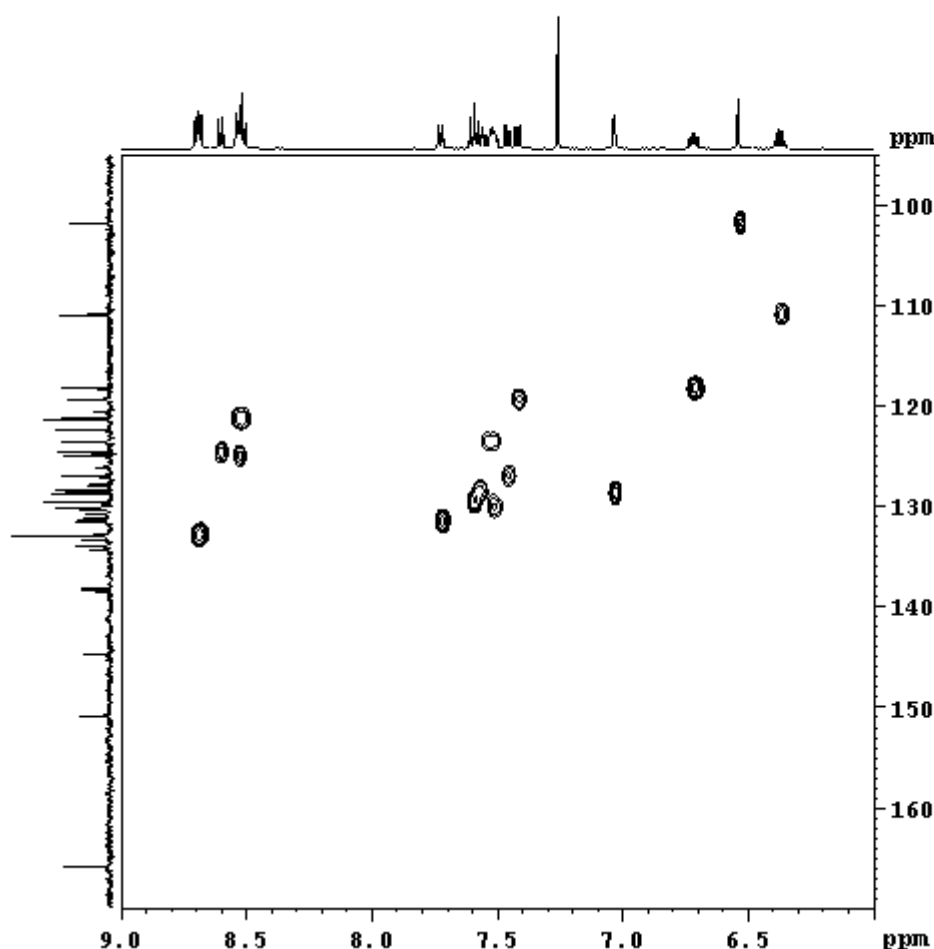
Aromatic region

asb-160e in CDCl₃

COSYGPQF TD=1024-128, NS=16 20-11-2012

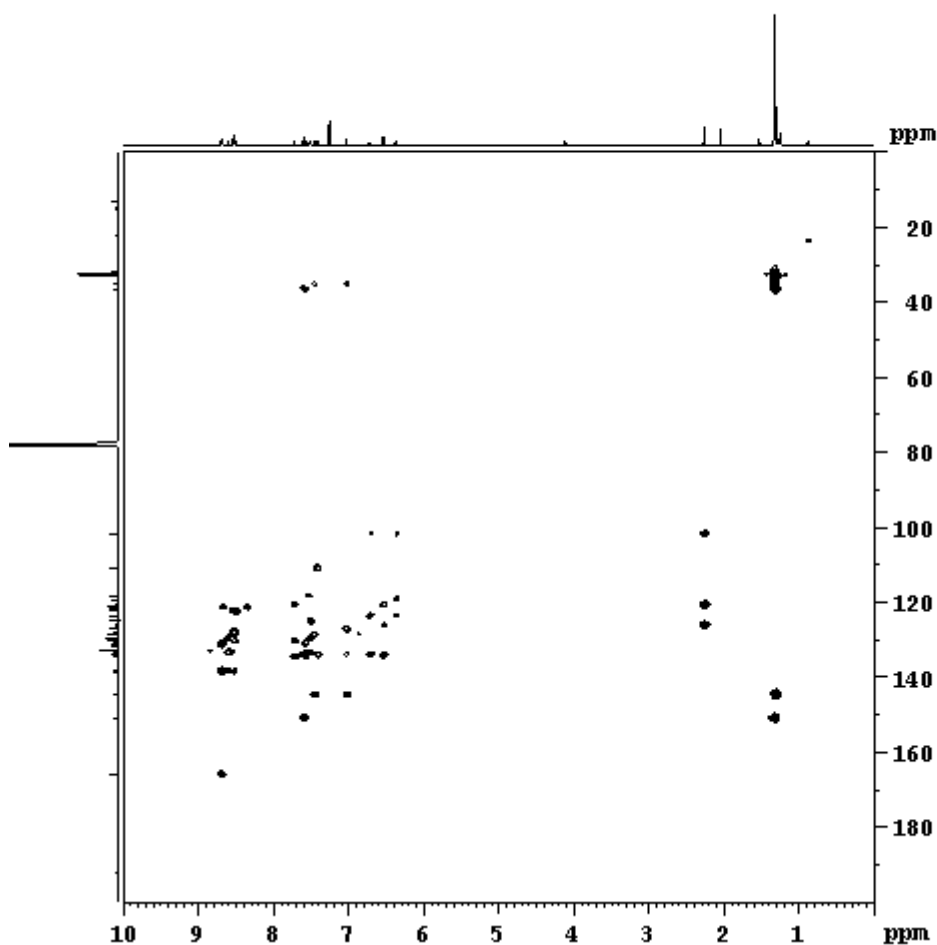


asb-160g in CDC13 13C CORR 30-11-2013

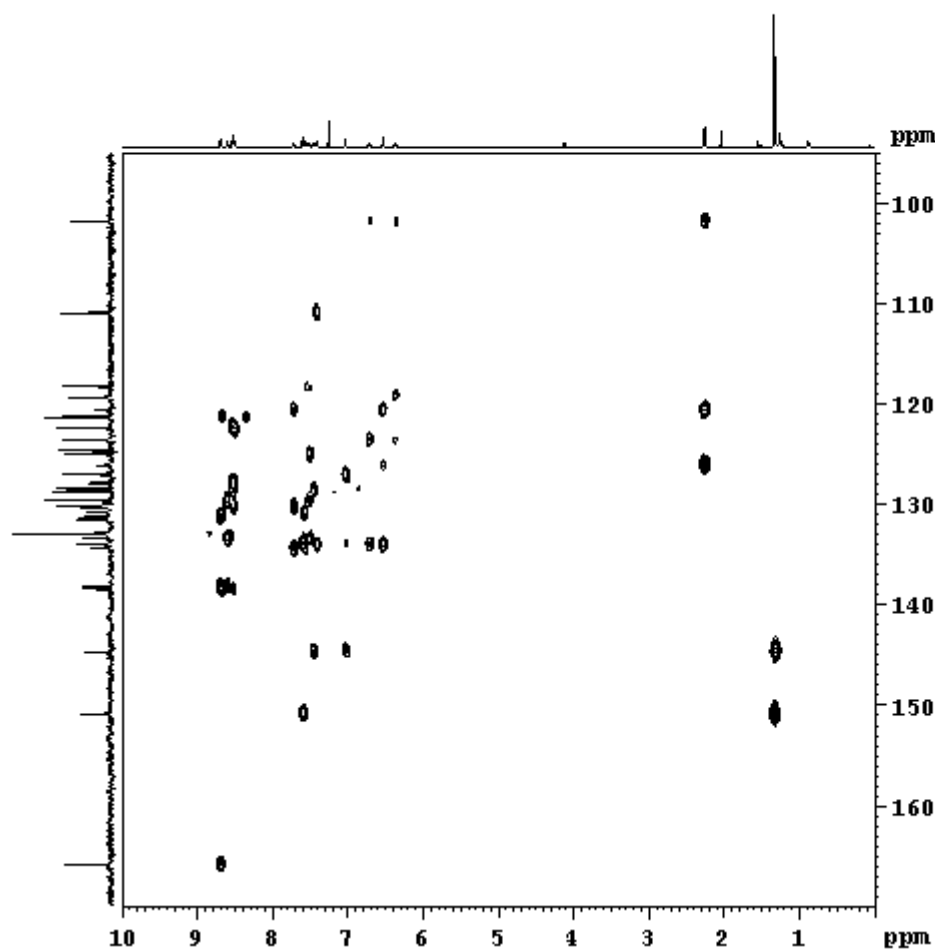
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$^1\text{H } ^{13}\text{C}$ HETCOR long range coupling - full spectral range

asb-160e in CDC13 1H-13C CORR LONG RANGE D6 corretto!! 30-11-2012

[illegible]

asb-160g in CDC13 1H-13C CORB LONG RANGE D6 corrected!! 30-11-2012

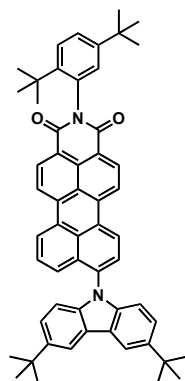


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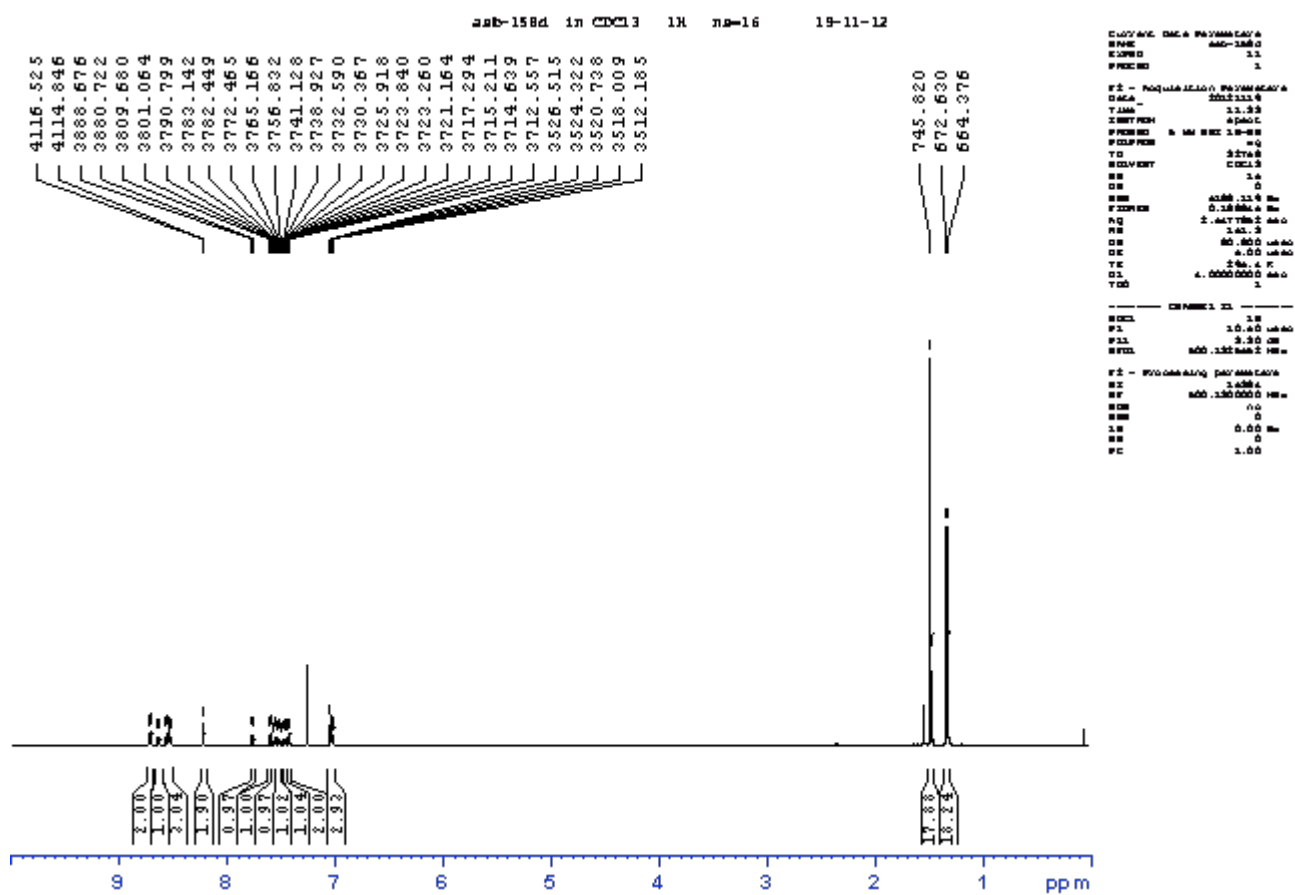
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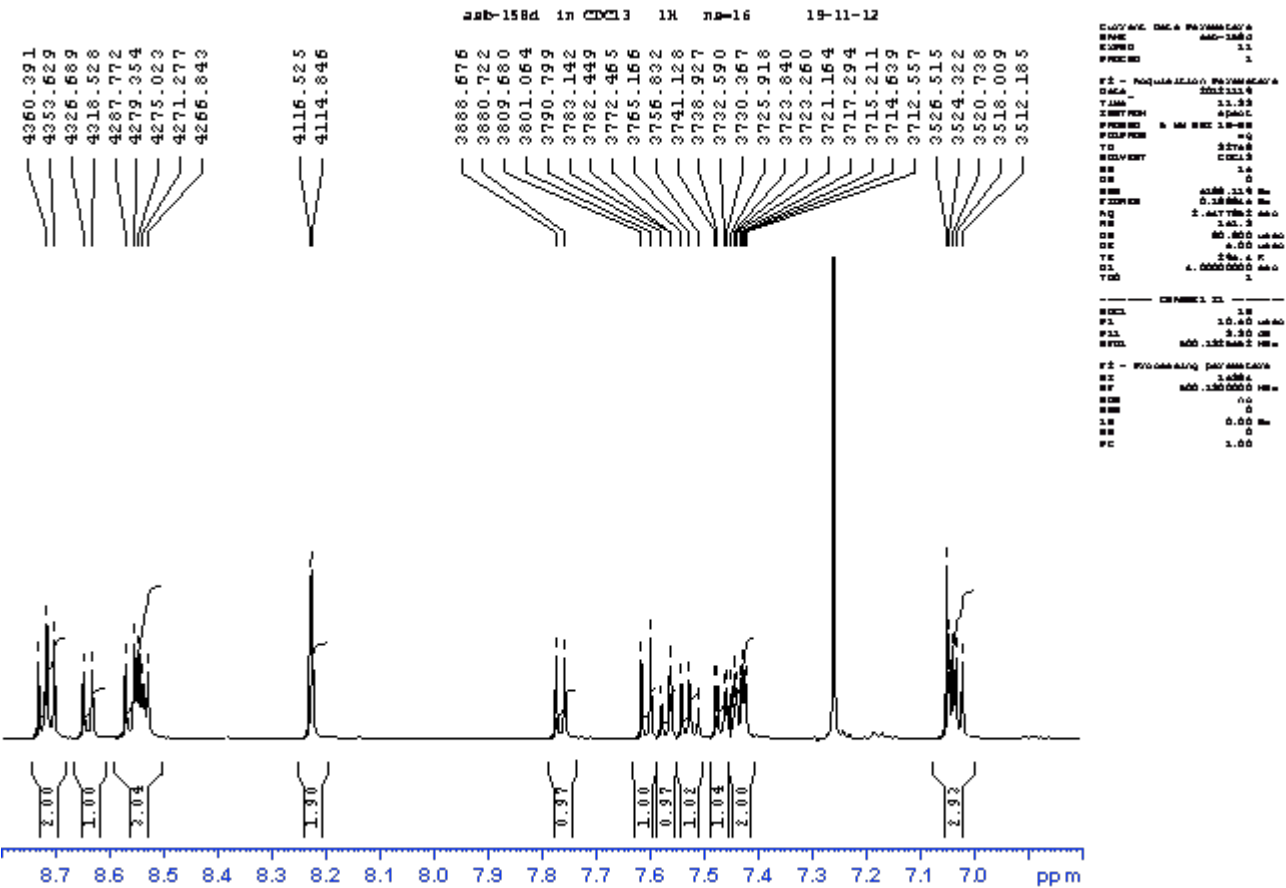
2.3. Derivative 2.



2

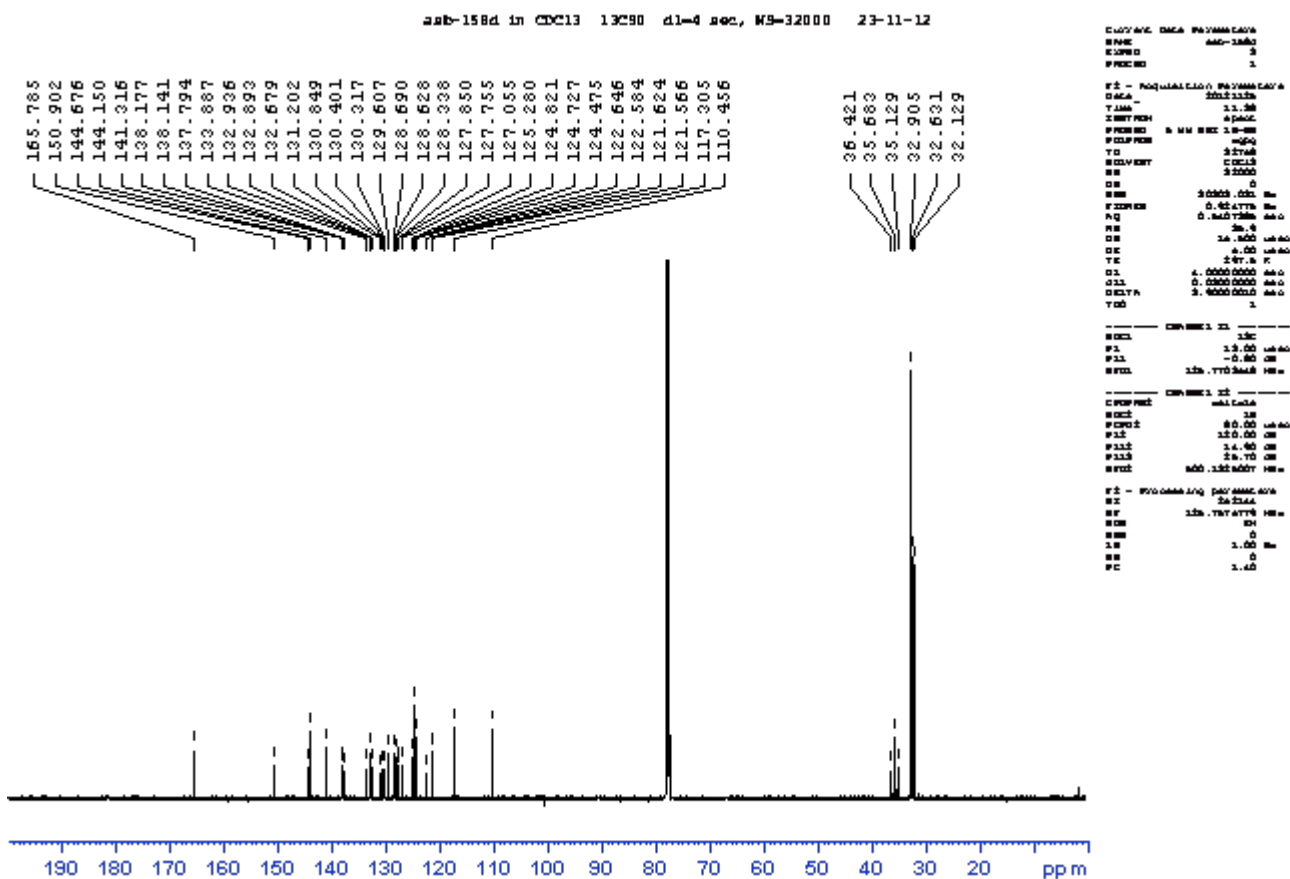
¹H full spectral range

Aromatic region



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[illegible]

¹³C full spectral range

¹³C NMR spectrum of compound 158d in CDCl₃. The spectrum shows peaks from 110 to 166 ppm. The following table lists the chemical shifts (ppm) for the observed peaks:

Chemical Shift (ppm)
165.785
150.902
144.676
144.150
141.316
138.177
138.141
137.794
133.887
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130.401
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128.338
127.850
127.755
127.055
125.280
124.821
124.727
124.475
122.646
122.584
121.624
121.566
117.305
110.456

[illegible]

sub-158d in CDCl₃ 13C90 d1=4 sec, W9=32000 23-11-12

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35.683
35.129
32.905
32.631
32.129

80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm

sub-158d in CDC13 13C90 dl-d noc, WS-32000 23-11-12

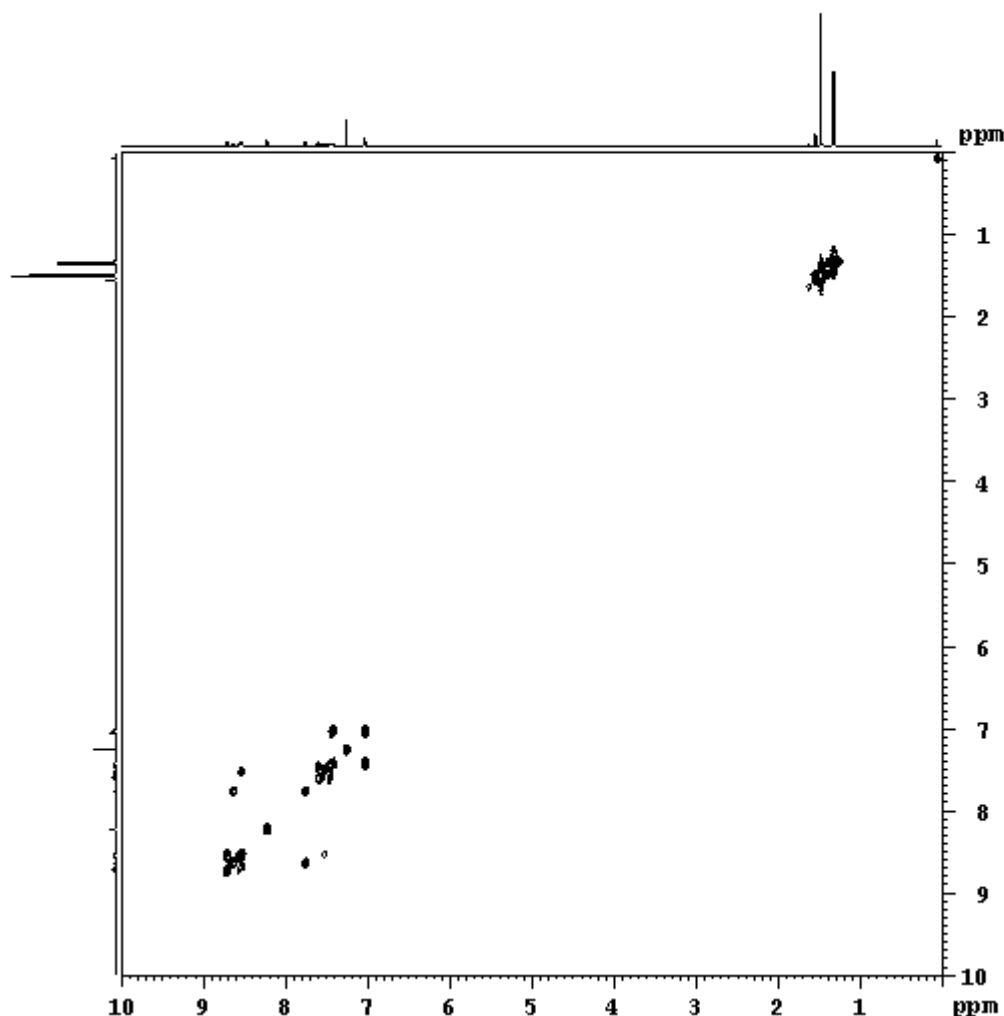
[illegible]

^1H COSY full spectral range

C O3 YGPQF

TD=1024-128, NS=16

23-11-2012



```
Current Data Parameters
NAME          sub=158d
NPTS          2
NPTS2         1
```

```

I2 = Acquisition Parameters
Date: 20211225
Time: 17.31
INSTRUM:
SPCNAME: 5 mm EMT 18-000
SOLARWG:
WD: 1024
SCALEWG: CH13
G2: 16
I2: 16
SPEX: 368.119 Str:
F2 (nm): 5.94368 Str:
AQ: 0.0828700
RG: 645.1
IR: 80.800
DE: 5.00
WE: 297.1 K
c0: 0.00000000
c1: 0.00000000
c2: 0.00000000
c3: 0.00000000
c4: 0.00000000
c5: 0.00000000
c6: 0.00000000
c7: 0.00000000

```

```
===== CHARGES: Fl =====
SPEC1          1m
FO              6.00  =====
FI             10.60  =====
FLI            9.90  dm
SFO1           500.1325652  MW
```

ITEM	QUANTITY	PRICE	TOTAL
ITEM1	100	10.00	1000.00
ITEM2	100	10.00	1000.00
ITEM3	100	10.00	1000.00
ITEM4	100	10.00	1000.00
ITEM5	100	10.00	1000.00
ITEM6	100	10.00	1000.00
ITEM7	100	10.00	1000.00
ITEM8	100	10.00	1000.00
ITEM9	100	10.00	1000.00
ITEM10	100	10.00	1000.00
ITEM11	100	10.00	1000.00
ITEM12	100	10.00	1000.00
ITEM13	100	10.00	1000.00
ITEM14	100	10.00	1000.00
ITEM15	100	10.00	1000.00
ITEM16	100	10.00	1000.00
ITEM17	100	10.00	1000.00
ITEM18	100	10.00	1000.00
ITEM19	100	10.00	1000.00
ITEM20	100	10.00	1000.00
ITEM21	100	10.00	1000.00
ITEM22	100	10.00	1000.00
ITEM23	100	10.00	1000.00
ITEM24	100	10.00	1000.00
ITEM25	100	10.00	1000.00
ITEM26	100	10.00	1000.00
ITEM27	100	10.00	1000.00
ITEM28	100	10.00	1000.00
ITEM29	100	10.00	1000.00
ITEM30	100	10.00	1000.00
ITEM31	100	10.00	1000.00
ITEM32	100	10.00	1000.00
ITEM33	100	10.00	1000.00
ITEM34	100	10.00	1000.00
ITEM35	100	10.00	1000.00
ITEM36	100	10.00	1000.00
ITEM37	100	10.00	1000.00
ITEM38	100	10.00	1000.00
ITEM39	100	10.00	1000.00
ITEM40	100	10.00	1000.00
ITEM41	100	10.00	1000.00
ITEM42	100	10.00	1000.00
ITEM43	100	10.00	1000.00
ITEM44	100	10.00	1000.00
ITEM45	100	10.00	1000.00
ITEM46	100	10.00	1000.00
ITEM47	100	10.00	1000.00
ITEM48	100	10.00	1000.00
ITEM49	100	10.00	1000.00
ITEM50	100	10.00	1000.00
ITEM51	100	10.00	1000.00
ITEM52	100	10.00	1000.00
ITEM53	100	10.00	1000.00
ITEM54	100	10.00	1000.00
ITEM55	100	10.00	1000.00
ITEM56	100	10.00	1000.00
ITEM57	100	10.00	1000.00
ITEM58	100	10.00	1000.00
ITEM59	100	10.00	1000.00
ITEM60	100	10.00	1000.00
ITEM61	100	10.00	1000.00
ITEM62	100	10.00	1000.00
ITEM63	100	10.00	1000.00
ITEM64	100	10.00	1000.00
ITEM65	100	10.00	1000.00
ITEM66	100	10.00	1000.00
ITEM67	100	10.00	1000.00
ITEM68	100	10.00	1000.00
ITEM69	100	10.00	1000.00
ITEM70	100	10.00	1000.00
ITEM71	100	10.00	1000.00
ITEM72	100	10.00	1000.00
ITEM73	100	10.00	1000.00
ITEM74	100	10.00	1000.00
ITEM75	100	10.00	1000.00
ITEM76	100	10.00	1000.00
ITEM77	100	10.00	1000.00
ITEM78	100	10.00	1000.00
ITEM79	100	10.00	1000.00
ITEM80	100	10.00	1000.00
ITEM81	100	10.00	1000.00
ITEM82	100	10.00	1000.00
ITEM83	100	10.00	1

```

F1 = Acquisition parameters
END      1
F2      128
SFO1     500.1326 MHz
FIDRES    48.544677 Hz
SR       12.573 ppm
FWDOM     0

```

```

F2 = Processing parameters
SI          1024
SY          500.13000000 Hz
S100        5.1200
S200         0
L0          0.00 Hz
L2          0
YC          0.60

```

```

R1 = Processing parameters
SI          1.024
MC2         GF
SF          500..1000000 MHz
SI         512KB
S2         0
Z0         0.00 Ohm
P0         0

```

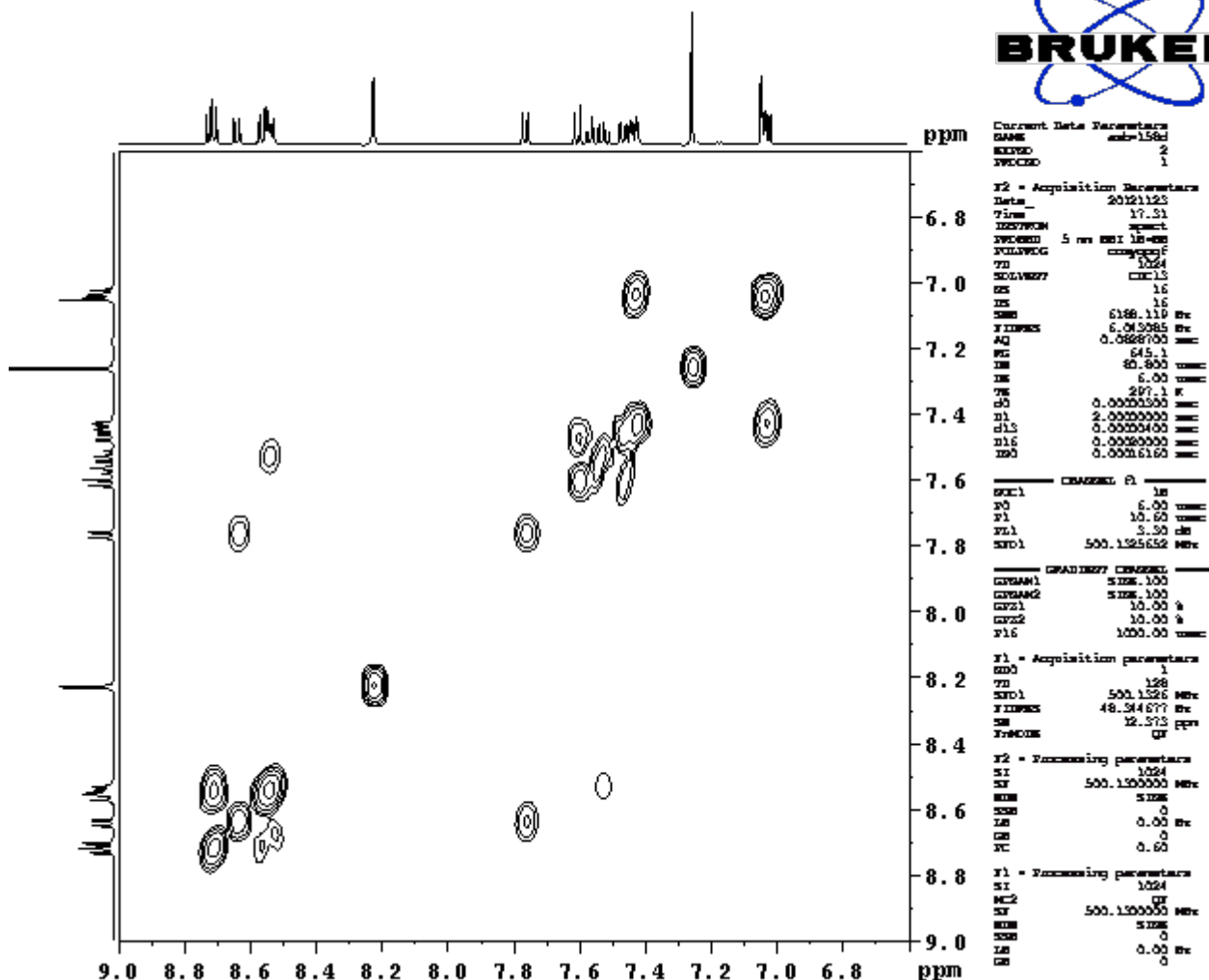
Aromatic region

asb-158d in CDCl₃

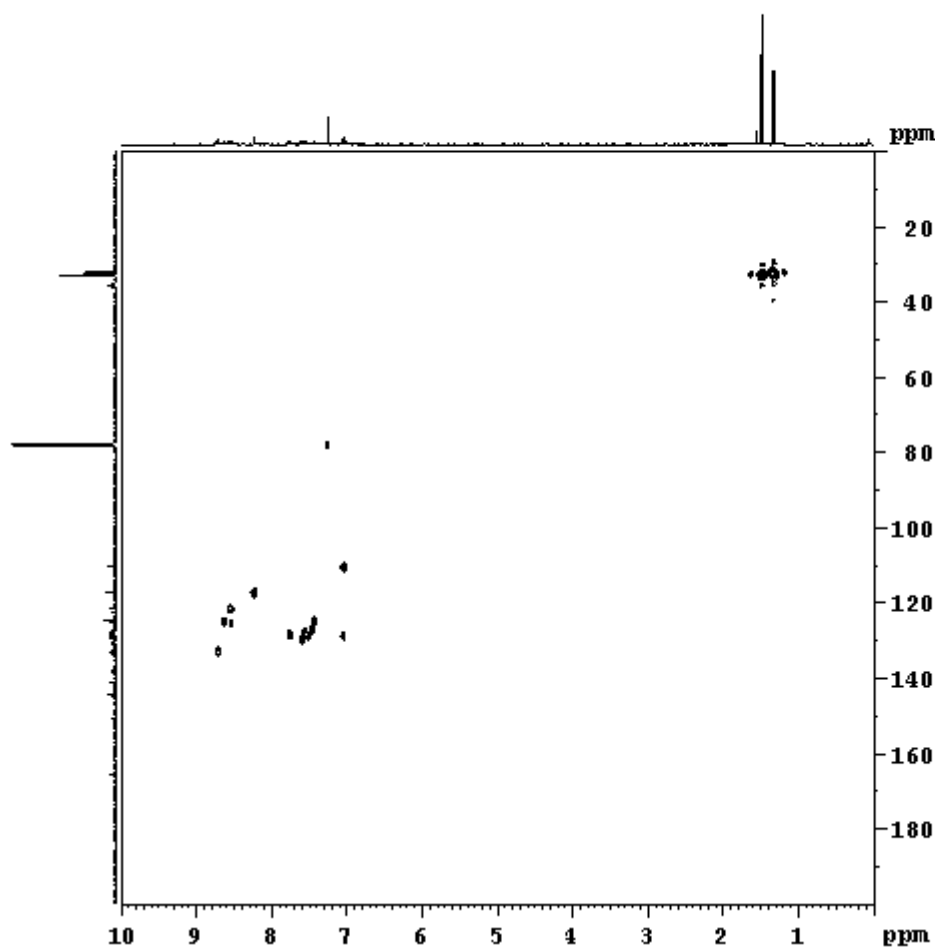
COSY6PQF

TD=1024-128, NS=16

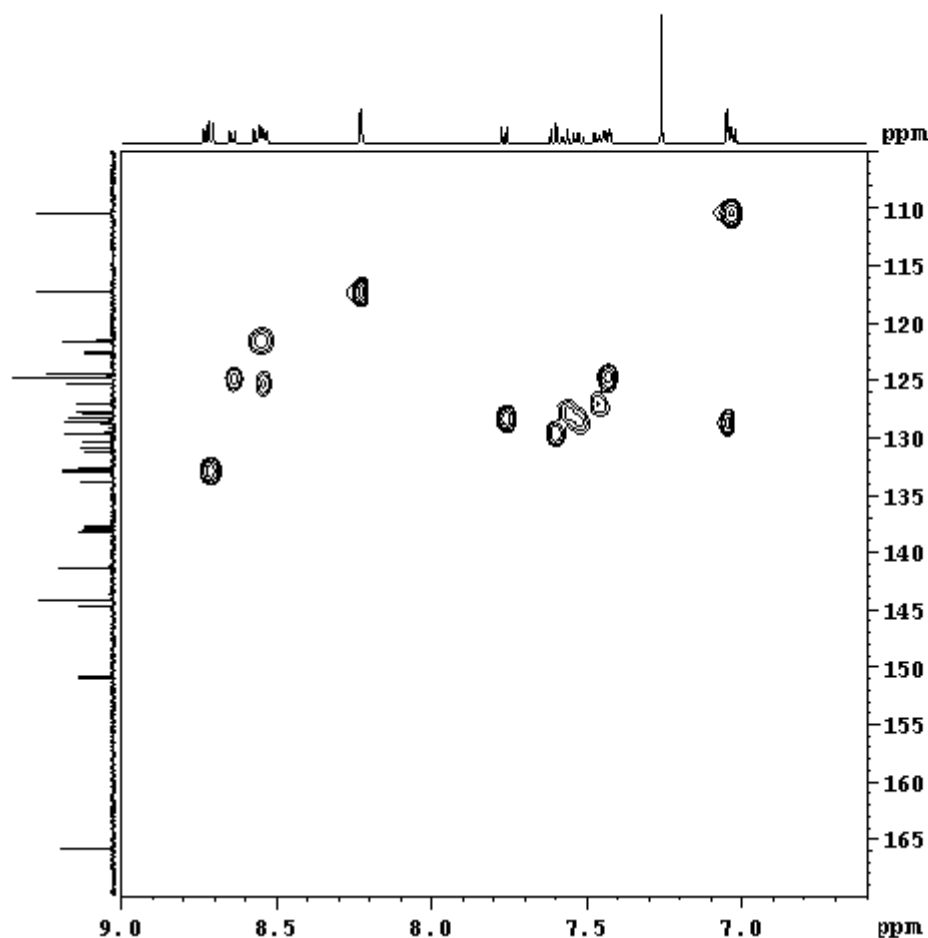
23-11-2012



asb-158d in CDC13 13C CORR 22-11-2012

[illegible]

asb-158d in CDC13 13C COBB 23-11-2012



COPY DATE	DATE	PAGE NUMBER
DATE		NO. OF PAGES
COPY NO.		4
PAGE NO.		3

[illegible]

COMPANEL 11		
REC 1	1.8	
FL	10.60	10000
LC	21.20	10000
PLD	0.00	10000
PL1	3.20	00
WTU 1	600.1333333	10000

CROSSING		F ₂	
3RD event		4607	
BC1 ±		1.5C	
F ₂		1.9.00	unobd
3d		2.6.00	unobd
PCW1 ±		80.00	unobd
F ₂ ±		-0.80	CM
F ₂ ±		2.4.00	CM
BC1 ±		1.5b, TT000.8	MM

SUFFICIENT COMPENSATION	
SPX P+CL	21.00
SPX P+CL	21.00
SPX 1	20.00
SPX 2	20.00
PLA	1000.00

```
FL - Acquisition parameters
END          +
FO           the
INFO1        1 file, 770k, 18m
FILE NAME    116, 3741k, 18m
IN           1st, 1994
PAGE COUNT   1000-1000, 1000
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[illegible]

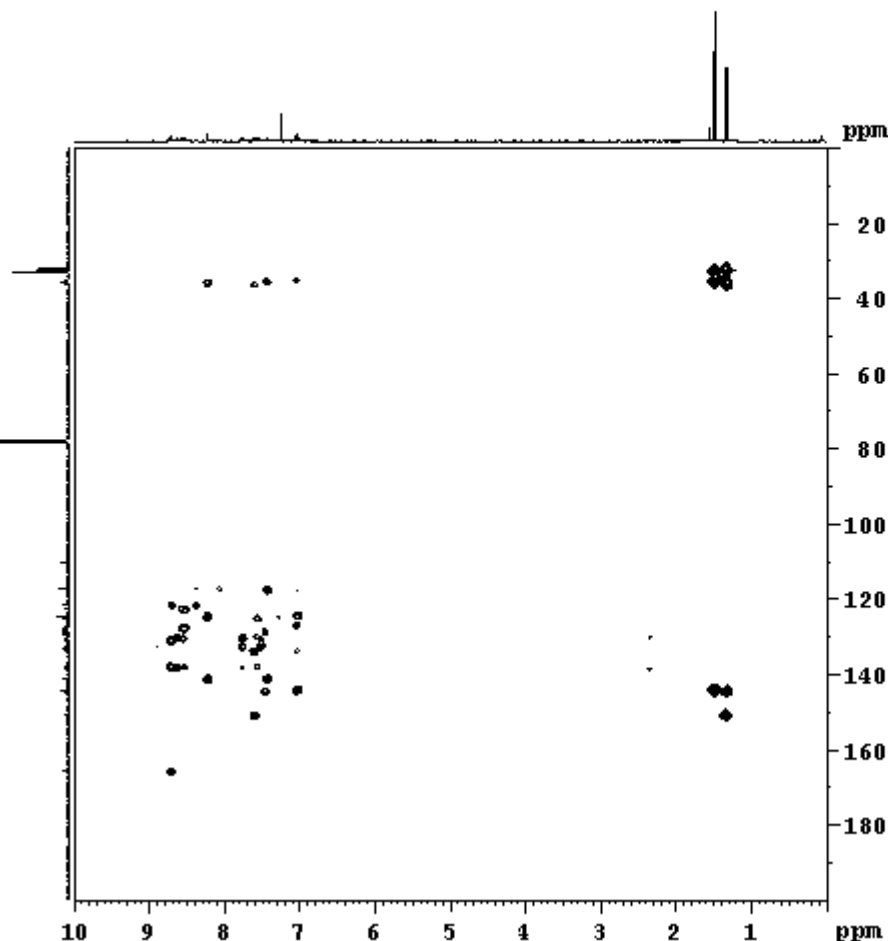
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F2 - W/COOLING p0000000000000000
KZ      1.000
CUT      0.000-0.000000
WF      1.000 TAYLOR HILL
KCN      0.000
KCM      0.000
LB      0.000

```

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

asb-158d in CDCl₃ 1H-13C CORR LONG RANGE D6 corretto!! 23-11-2012



Current Data Parameters
NAME asb-158d
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121124
Time 1.43
INSTRUM spect
PROBHD 5 mm BBO 1H-13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl₃
AQ 46
RG 320
DS 4
SWH 4166.112 Hz
FIDRES 0.000000 Hz
AQ 0.000000 sec
RG 271.25
CF 80.000 usec
CL 4.00 usec
CR 207.1
CPCP2 145.000000
CPCP13 8.000000
AS 0.000000 sec
CL 4.000000 sec
CS 0.000000 sec
CR 0.000000 sec
CL 4.000000 sec
CR 0.000000 sec
CL 4.000000 sec
CR 0.000000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 10.00 usec
PL 0
PL2 21.20 usec
PL3 3.30 dB
SFO1 200.1324600 MHz

===== CHANNEL f2 =====
NUC2 1H
P2 13.00 usec
PL2 -0.60 dB
SFO2 500.1360490 MHz

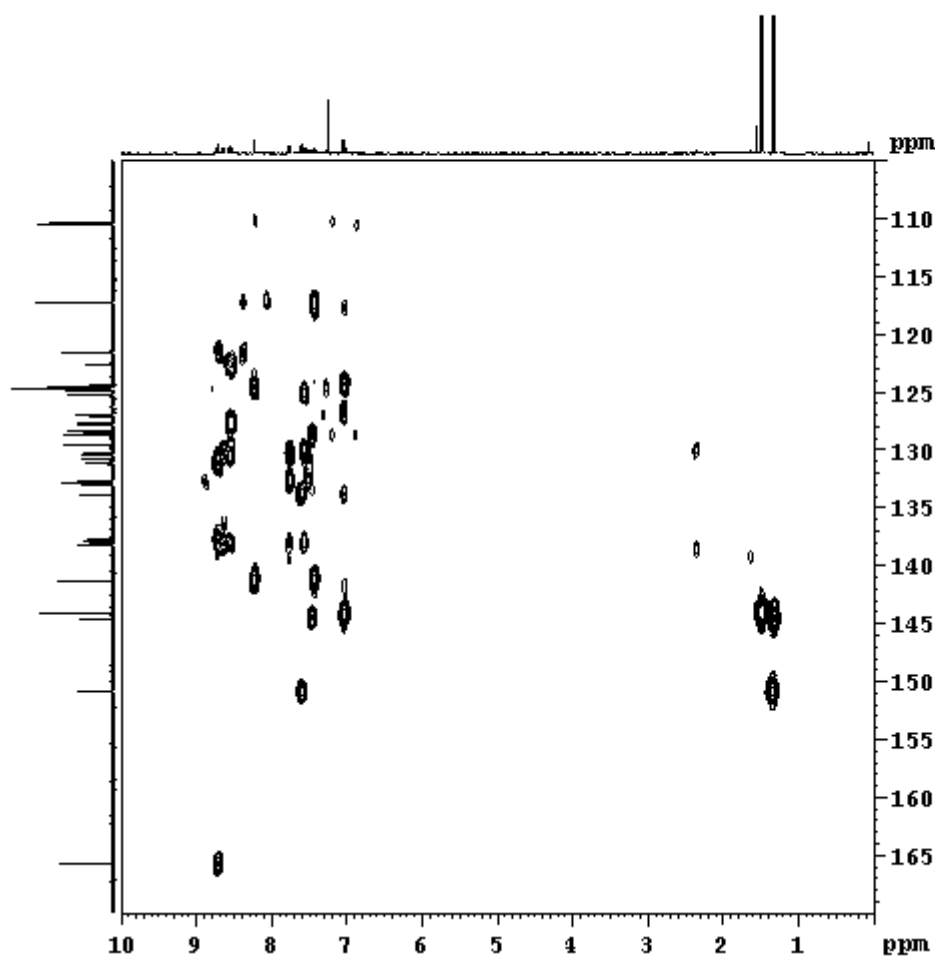
===== CHANNEL f3 =====
CPDPRG2 GPCPGMT
CPDPRG1 3 DFT.1.00
CPDPRG2 3 DFT.1.00
CPDPRG3 3 DFT.1.00
CPDPRG4 3 DFT.1.00
CPDPRG5 3 DFT.1.00
CPDPRG6 3 DFT.1.00
CPDPRG7 3 DFT.1.00
CPDPRG8 3 DFT.1.00
CPDPRG9 3 DFT.1.00
CPDPRG10 3 DFT.1.00
CPDPRG11 3 DFT.1.00
CPDPRG12 3 DFT.1.00
CPDPRG13 3 DFT.1.00
CPDPRG14 3 DFT.1.00
CPDPRG15 3 DFT.1.00
CPDPRG16 3 DFT.1.00
CPDPRG17 3 DFT.1.00
CPDPRG18 3 DFT.1.00
CPDPRG19 3 DFT.1.00
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CPDPRG61 3 DFT.1.00
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CPDPRG81 3 DFT.1.00
CPDPRG82 3 DFT.1.00
CPDPRG83 3 DFT.1.00
CPDPRG84 3 DFT.1.00
CPDPRG85 3 DFT.1.00
CPDPRG86 3 DFT.1.00
CPDPRG87 3 DFT.1.00
CPDPRG88 3 DFT.1.00
CPDPRG89 3 DFT.1.00
CPDPRG90 3 DFT.1.00
CPDPRG91 3 DFT.1.00
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CPDPRG93 3 DFT.1.00
CPDPRG94 3 DFT.1.00
CPDPRG95 3 DFT.1.00
CPDPRG96 3 DFT.1.00
CPDPRG97 3 DFT.1.00
CPDPRG98 3 DFT.1.00
CPDPRG99 3 DFT.1.00
CPDPRG100 3 DFT.1.00

F1 - Acquisition parameters
NUC1 13C
TD 65536
SFO1 200.1324600 MHz
PULPROG zgpg30
PL 0
PL2 21.20 usec
PL3 3.30 dB
SFO2 500.1360490 MHz

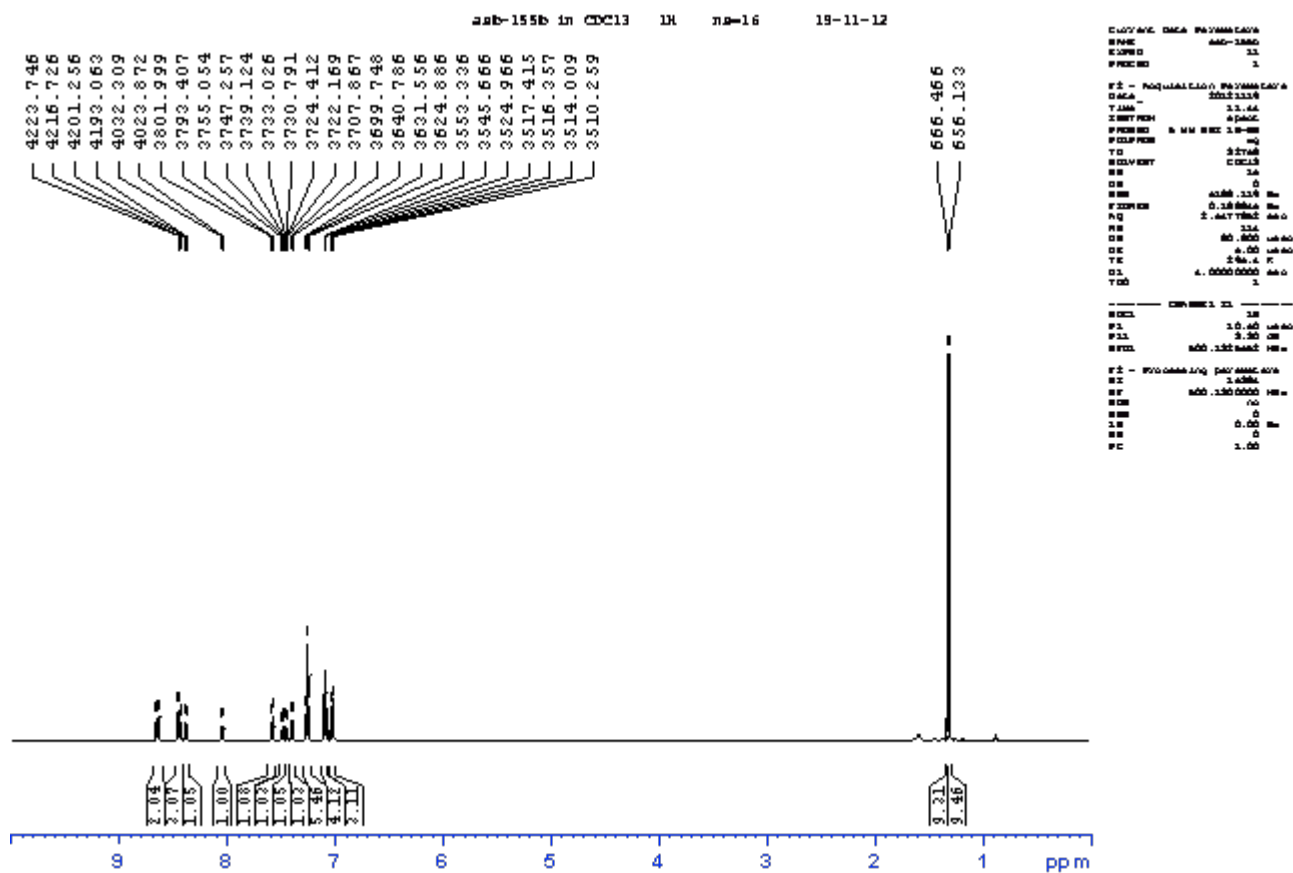
F2 - Processing parameters
SI 32768
SF 200.1324600 MHz
WDW EM
SSB 0
GB 0
PC 0
SC 1.40

F1 - Processing parameters
SI 32768
SF 200.1324600 MHz
WDW EM
SSB 0
GB 0
PC 0
SC 1.40

asb-158d in CDC13 1H-13C CORB LONG RANGE D6 corrected!! 23-11-2012

[illegible]

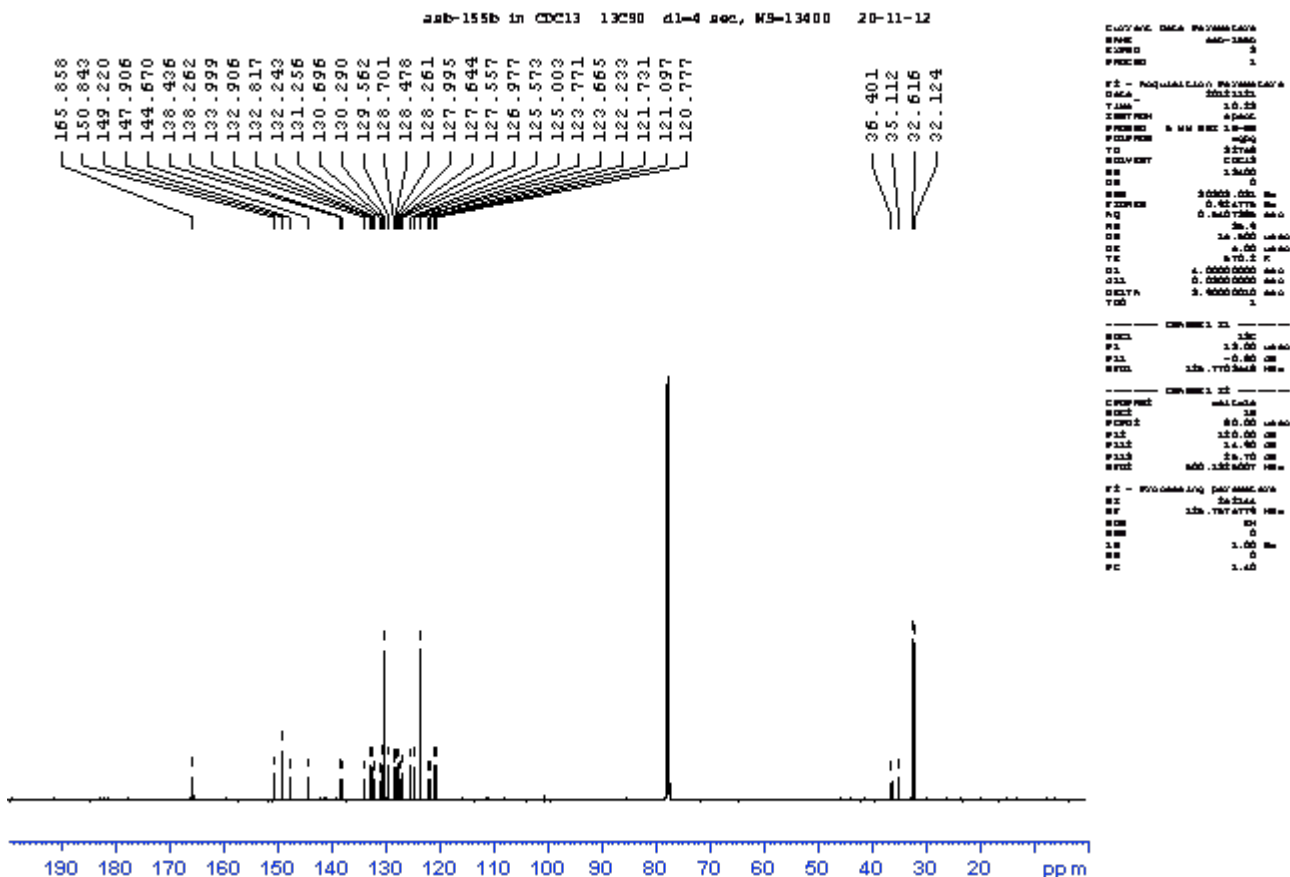
2.4. Derivative 3.

¹H full range

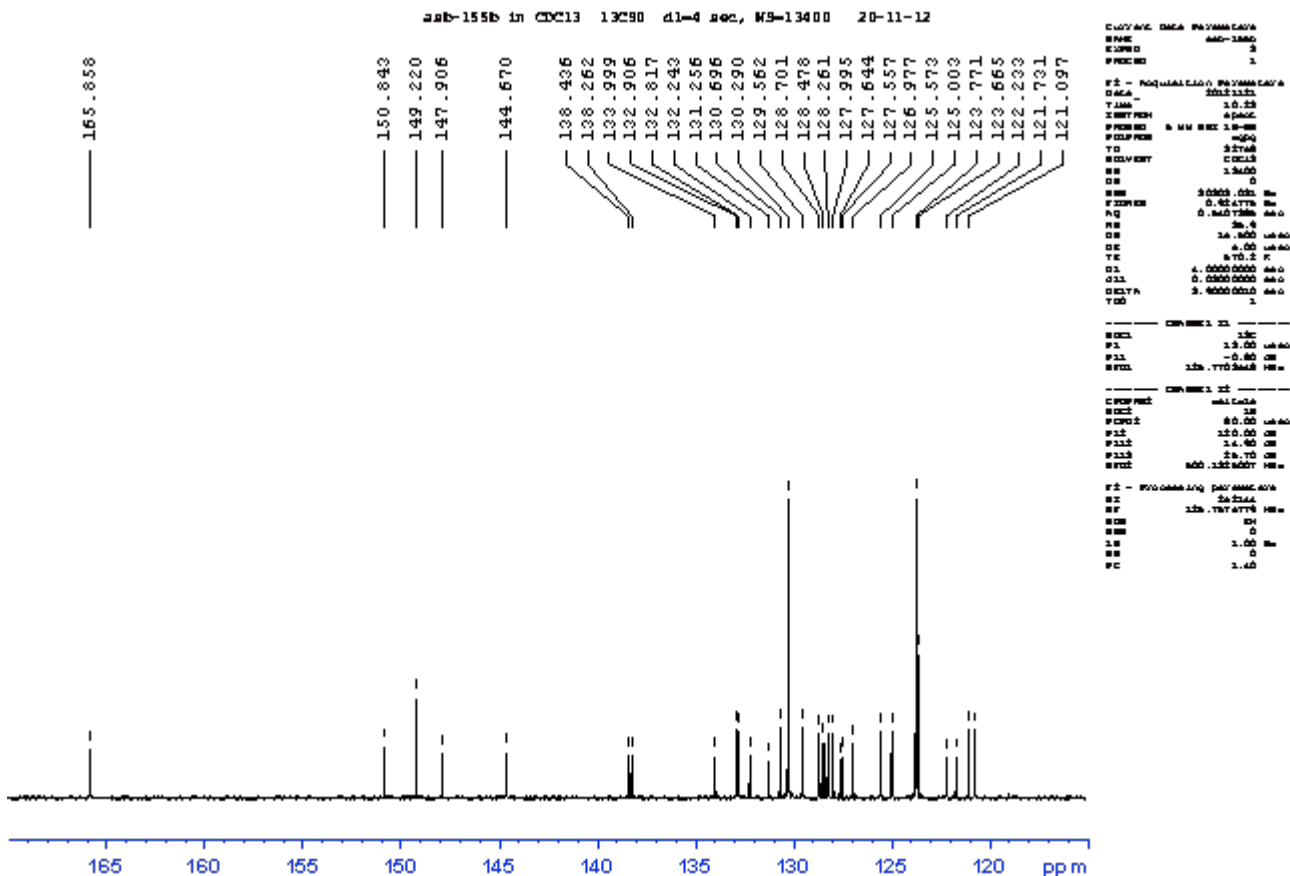
¹H NMR spectrum (400 MHz, CDCl₃) of compound 155b. The spectrum shows peaks in the aromatic region (6.8-7.7 ppm) and aliphatic region (1.0-2.6 ppm). Integration values are provided below the peaks.

Chemical Shift (ppm)	Integration
7.65, 7.62, 7.58, 7.55, 7.52, 7.48, 7.45, 7.42, 7.38, 7.35, 7.32, 7.28, 7.25, 7.22, 7.18, 7.15, 7.12, 7.08, 7.05, 7.02, 6.98, 6.95, 6.92, 6.88, 6.85, 6.82, 6.78, 6.75, 6.72, 6.68, 6.65, 6.62, 6.58, 6.55, 6.52, 6.48, 6.45, 6.42, 6.38, 6.35, 6.32, 6.28, 6.25, 6.22, 6.18, 6.15, 6.12, 6.08, 6.05, 6.02, 5.98, 5.95, 5.92, 5.88, 5.85, 5.82, 5.78, 5.75, 5.72, 5.68, 5.65, 5.62, 5.58, 5.55, 5.52, 5.48, 5.45, 5.42, 5.38, 5.35, 5.32, 5.28, 5.25, 5.22, 5.18, 5.15, 5.12, 5.08, 5.05, 5.02, 4.98, 4.95, 4.92, 4.88, 4.85, 4.82, 4.78, 4.75, 4.72, 4.68, 4.65, 4.62, 4.58, 4.55, 4.52, 4.48, 4.45, 4.42, 4.38, 4.35, 4.32, 4.28, 4.25, 4.22, 4.18, 4.15, 4.12, 4.08, 4.05, 4.02, 3.98, 3.95, 3.92, 3.88, 3.85, 3.82, 3.78, 3.75, 3.72, 3.68, 3.65, 3.62, 3.58, 3.55, 3.52, 3.48, 3.45, 3.42, 3.38, 3.35, 3.32, 3.28, 3.25, 3.22, 3.18, 3.15, 3.12, 3.08, 3.05, 3.02, 2.98, 2.95, 2.92, 2.88, 2.85, 2.82, 2.78, 2.75, 2.72, 2.68, 2.65, 2.62, 2.58, 2.55, 2.52, 2.48, 2.45, 2.42, 2.38, 2.35, 2.32, 2.28, 2.25, 2.22, 2.18, 2.15, 2.12, 2.08, 2.05, 2.02, 1.98, 1.95, 1.92, 1.88, 1.85, 1.82, 1.78, 1.75, 1.72, 1.68, 1.65, 1.62, 1.58, 1.55, 1.52, 1.48, 1.45, 1.42, 1.38, 1.35, 1.32, 1.28, 1.25, 1.22, 1.18, 1.15, 1.12, 1.08, 1.05, 1.02, 1.00, 0.98, 0.95, 0.92, 0.88, 0.85, 0.82, 0.78, 0.75, 0.72, 0.68, 0.65, 0.62, 0.58, 0.55, 0.52, 0.48, 0.45, 0.42, 0.38, 0.35, 0.32, 0.28, 0.25, 0.22, 0.18, 0.15, 0.12, 0.08, 0.05, 0.02, 0.00	7.65, 7.62, 7.58, 7.55, 7.52, 7.48, 7.45, 7.42, 7.38, 7.35, 7.32, 7.28, 7.25, 7.22, 7.18, 7.15, 7.12, 7.08, 7.05, 7.02, 6.98, 6.95, 6.92, 6.88, 6.85, 6.82, 6.78, 6.75, 6.72, 6.68, 6.65, 6.62, 6.58, 6.55, 6.52, 6.48, 6.45, 6.42, 6.38, 6.35, 6.32, 6.28, 6.25, 6.22, 6.18, 6.15, 6.12, 6.08, 6.05, 6.02, 5.98, 5.95, 5.92, 5.88, 5.85, 5.82, 5.78, 5.75, 5.72, 5.68, 5.65, 5.62, 5.58, 5.55, 5.52, 5.48, 5.45, 5.42, 5.38, 5.35, 5.32, 5.28, 5.25, 5.22, 5.18, 5.15, 5.12, 5.08, 5.05, 5.02, 4.98, 4.95, 4.92, 4.88, 4.85, 4.82, 4.78, 4.75, 4.72, 4.68, 4.65, 4.62, 4.58, 4.55, 4.52, 4.48, 4.45, 4.42, 4.38, 4.35, 4.32, 4.28, 4.25, 4.22, 4.18, 4.15, 4.12, 4.08, 4.05, 4.02, 3.98, 3.95, 3.92, 3.88, 3.85, 3.82, 3.78, 3.75, 3.72, 3.68, 3.65, 3.62, 3.58, 3.55, 3.52, 3.48, 3.45, 3.42, 3.38, 3.35, 3.32, 3.28, 3.25, 3.22, 3.18, 3.15, 3.12, 3.08, 3.05, 3.02, 2.98, 2.95, 2.92, 2.88, 2.85, 2.82, 2.78, 2.75, 2.72, 2.68, 2.65, 2.62, 2.58, 2.55, 2.52, 2.48, 2.45, 2.42, 2.38, 2.35, 2.32, 2.28, 2.25, 2.22, 2.18, 2.15, 2.12, 2.08, 2.05, 2.02, 1.98, 1.95, 1.92, 1.88, 1.85, 1.82, 1.78, 1.75, 1.72, 1.68, 1.65, 1.62, 1.58, 1.55, 1.52, 1.48, 1.45, 1.42, 1.38, 1.35, 1.32, 1.28, 1.25, 1.22, 1.18, 1.15, 1.12, 1.08, 1.05, 1.02, 1.00, 0.98, 0.95, 0.92, 0.88, 0.85, 0.82, 0.78, 0.75, 0.72, 0.68, 0.65, 0.62, 0.58, 0.55, 0.52, 0.48, 0.45, 0.42, 0.38, 0.35, 0.32, 0.28, 0.25, 0.22, 0.18, 0.15, 0.12, 0.08, 0.05, 0.02, 0.00
7.65, 7.62, 7.58, 7.55, 7.52, 7.48, 7.45, 7.42, 7.38, 7.35, 7.32, 7.28, 7.25, 7.22, 7.18, 7.15, 7.12, 7.08, 7.05, 7.02, 6.98, 6.95, 6.92, 6.88, 6.85, 6.82, 6.78, 6.75, 6.72, 6.68, 6.65, 6.62, 6.58, 6.55, 6.52, 6.48, 6.45, 6.42, 6.38, 6.35, 6.32, 6.28, 6.25, 6.22, 6.18, 6.15, 6.12, 6.08, 6.05, 6.02, 5.98, 5.95, 5.92, 5.88, 5.85, 5.82, 5.78, 5.75, 5.72, 5.68, 5.65, 5.62, 5.58, 5.55, 5.52, 5.48, 5.45, 5.42, 5.38, 5.35, 5.32, 5.28, 5.25, 5.22, 5.18, 5.15, 5.12, 5.08, 5.05, 5.02, 4.98, 4.95, 4.92, 4.88, 4.85, 4.82, 4.78, 4.75, 4.72, 4.68, 4.65, 4.62, 4.58, 4.55, 4.52, 4.48, 4.45, 4.42, 4.38, 4.35, 4.32, 4.28, 4.25, 4.22, 4.18, 4.15, 4.12, 4.08, 4.05, 4.02, 3.98, 3.95, 3.92, 3.88, 3.85, 3.82, 3.78, 3.75, 3.72, 3.68, 3.65, 3.62, 3.58, 3.55, 3.52, 3.48, 3.45, 3.42, 3.38, 3.35, 3.32, 3.28, 3.25, 3.22, 3.18, 3.15, 3.12, 3.08, 3.05, 3.02, 2.98, 2.95, 2.92, 2.88, 2.85, 2.82, 2.78, 2.75, 2.72, 2.68, 2.65, 2.62, 2.58, 2.55, 2.52, 2.48, 2.45, 2.42, 2.38, 2.35, 2.32, 2.28, 2.25, 2.22, 2.18, 2.15, 2.12, 2.08, 2.05, 2.02, 1.98, 1.95, 1.92, 1.88, 1.85, 1.82, 1.78, 1.75, 1.72, 1.68, 1.65, 1.62, 1.58, 1.55, 1.52, 1.48, 1.45, 1.42, 1.38, 1.35, 1.32, 1.28, 1.25, 1.22, 1.18, 1.15, 1.12, 1.08, 1.05, 1.02, 1.00, 0.98, 0.95, 0.92, 0.88, 0.85, 0.82, 0.78, 0.75, 0.72, 0.68, 0.65, 0.62, 0.58, 0.55, 0.52, 0.48, 0.45, 0.42, 0.38, 0.35, 0.32, 0.28, 0.25, 0.22, 0.18, 0.15, 0.12, 0.08, 0.05, 0.02, 0.00	

[illegible]

¹³C Full spectral range

Aromatic region



sub-155b in CDCl₃ 13C90 d1=4 sec, W9-13400 20-11-12

36.401
35.112
32.616
32.124

110 100 90 80 70 60 50 40 30 20 10 ppm

[illegible]

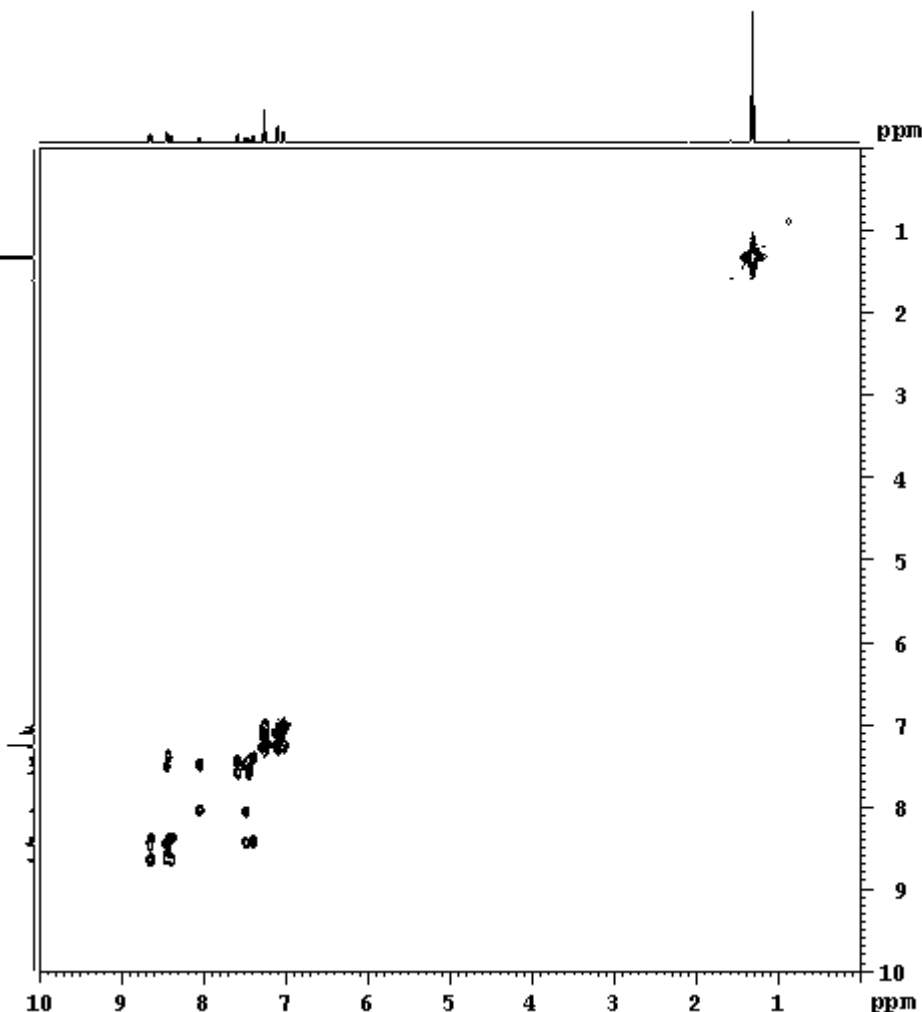
¹H COSY full spectral range

asb-155b in CDCl₃

COSY6PQF

TD=1024-128, NS=16

21-11-2012



Current Data Parameters
NAME asb-155b
KEYED 2
SWH00 1

F2 - Acquisition Parameters
Date_ 20121121
Time 15.00
INSTRUM spect
PROBHD 5 mm BBI 1H-400
PULPROG zgpg30
TD 1024
SOLVENT CDCl₃
NS 16
DS 16
SWH 6188.110 Hz
FIDRES 6.045085 Hz
AQ 0.0228700 sec
RG 406.4
IN 80.800 MHz
DE 6.00 MHz
TE 296.0 K
d0 0.0000000 sec
d1 2.0000000 sec
d15 0.0000000 sec
d16 0.0000000 sec
d20 0.0001610 sec

===== CHANNEL F1 =====
NUC1 1H
P0 6.00 MHz
P1 10.00 MHz
PL1 3.30 dB
SFO1 500.1325652 MHz

===== CHANNEL F2 =====
NUC2 13C
P0 10.00 MHz
P1 10.00 MHz
PL1 0.00 dB
SFO2 100.628150 MHz

F1 - Acquisition parameters
SFO 128
SFO1 500.13256 MHz
FIDRES 48.344677 Hz
SR 12.573 ppm
SWH00 0

F2 - Processing parameters
SI 1024
SF 500.1300000 MHz
WDW 0
SSB 0
LB 0.00 Hz
GB 0
MC 0.60

F1 - Processing parameters
SI 1024
SF 500.1300000 MHz
WDW 0
SSB 0
LB 0.00 Hz
GB 0

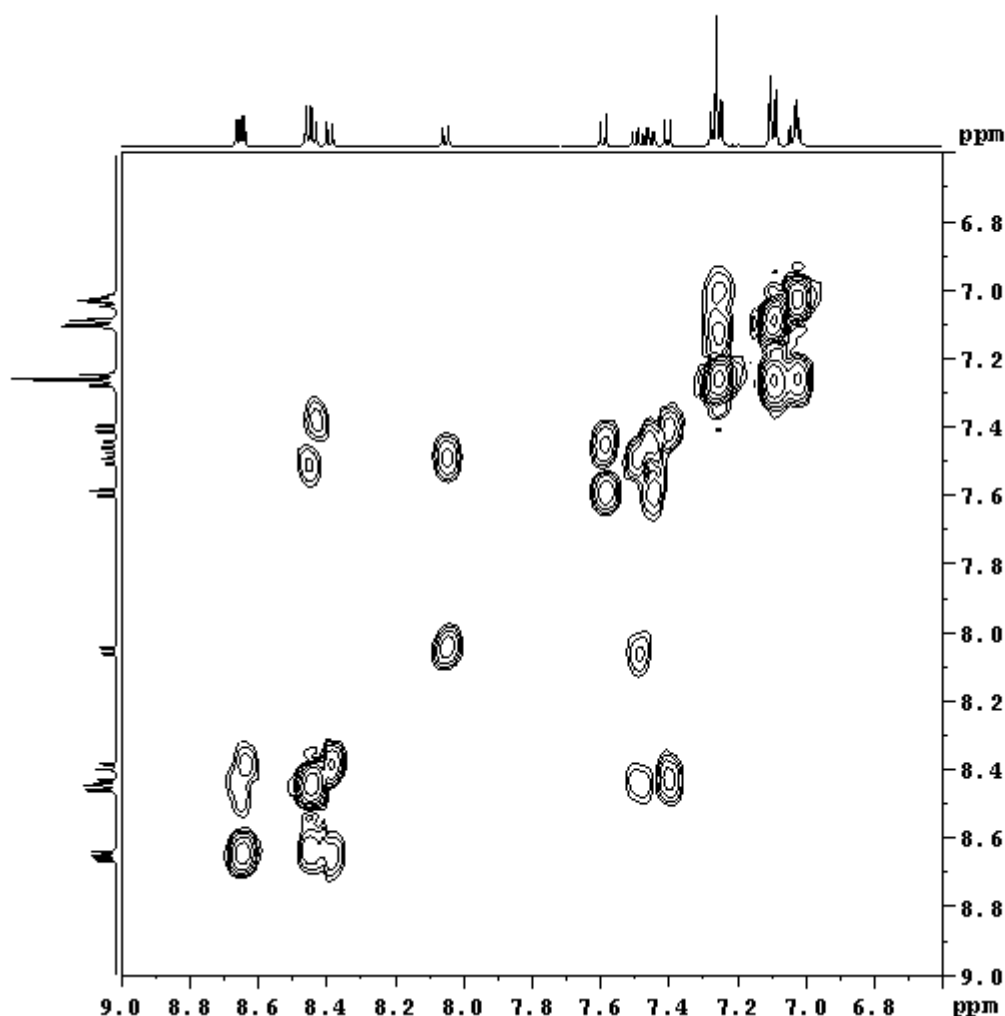
aromatic region

asb-155b in CDCl₃

COSY6PQF

TD=1024-128, NS=16

21-11-2012



Current Data Parameters
 NAME asb-155b
 KEYED 2
 SWHCD 1

F2 - Acquisition Parameters
 Date_ 20121121
 Time 15.00
 INSTRUM spect
 PROCNO 5 run 001 1b-000
 F2F1WVG cosygpgp
 F2 1024
 SOLVENT CDCl₃
 NS 16
 DS 16
 SFO 638.119 MHz
 FIDRES 6.045085 Hz
 AQ 0.0228700 sec
 RG 406.4
 IN 80.000 sec
 DE 6.00 sec
 TE 296.0 K
 d0 0.0000000 sec
 d1 2.0000000 sec
 d15 0.0000000 sec
 d16 0.0000000 sec
 d20 0.00016160 sec

CHARGE: F1
 GC1 1a
 P0 6.00 sec
 P1 10.00 sec
 PL1 3.30 dB
 SFO1 500.1325652 MHz

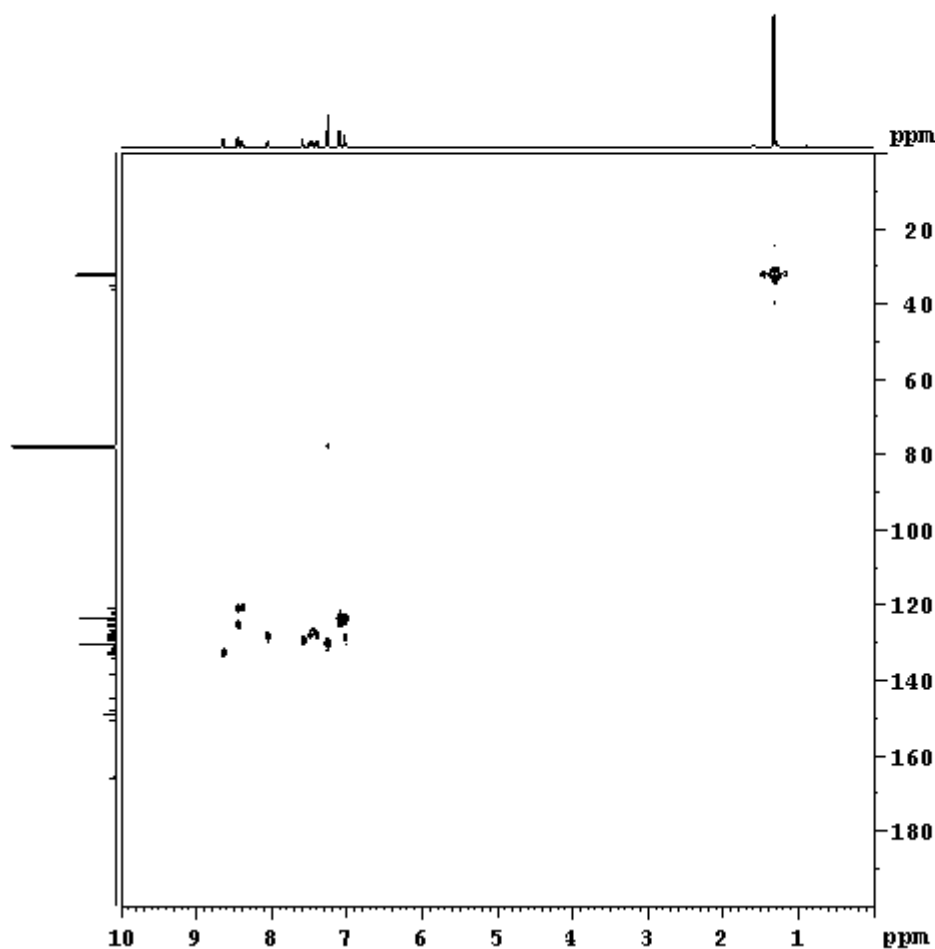
GRABBER GRABBER
 GRAB0 500.100
 GRAB2 500.100
 GRV1 10.00 s
 GRV2 10.00 s
 P16 1000.00 sec

F1 - Acquisition parameters
 FID 128
 F2 1024
 SFO1 500.1326 MHz
 FIDRES 48.344677 Hz
 IN 12.575 ppm
 FIDRES 0

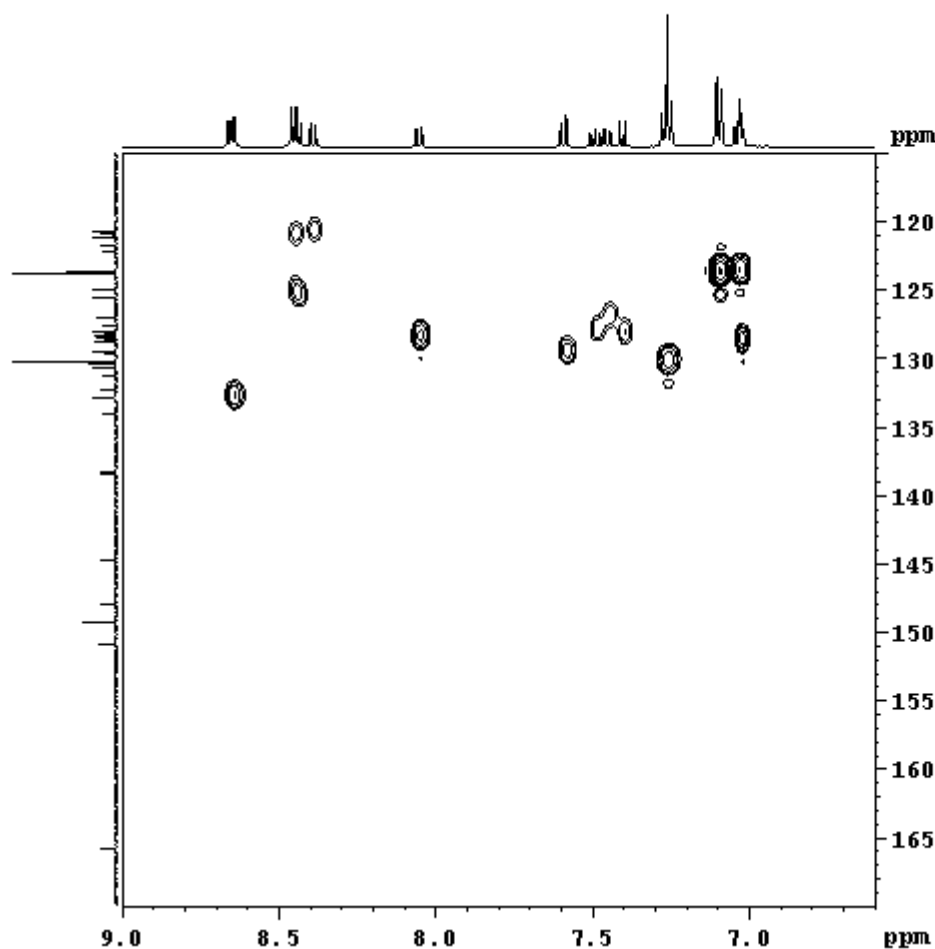
F2 - Processing parameters
 SI 1024
 SF 500.1300000 MHz
 RG 0
 SFO 0
 LB 0.00 Hz
 GB 0
 XC 0.60

F1 - Processing parameters
 SI 1024
 SF 500.1300000 MHz
 RG 0
 SFO 0
 LB 0.00 Hz
 GB 0

asb-155b in CDC13 13C COBB 21-11-2012

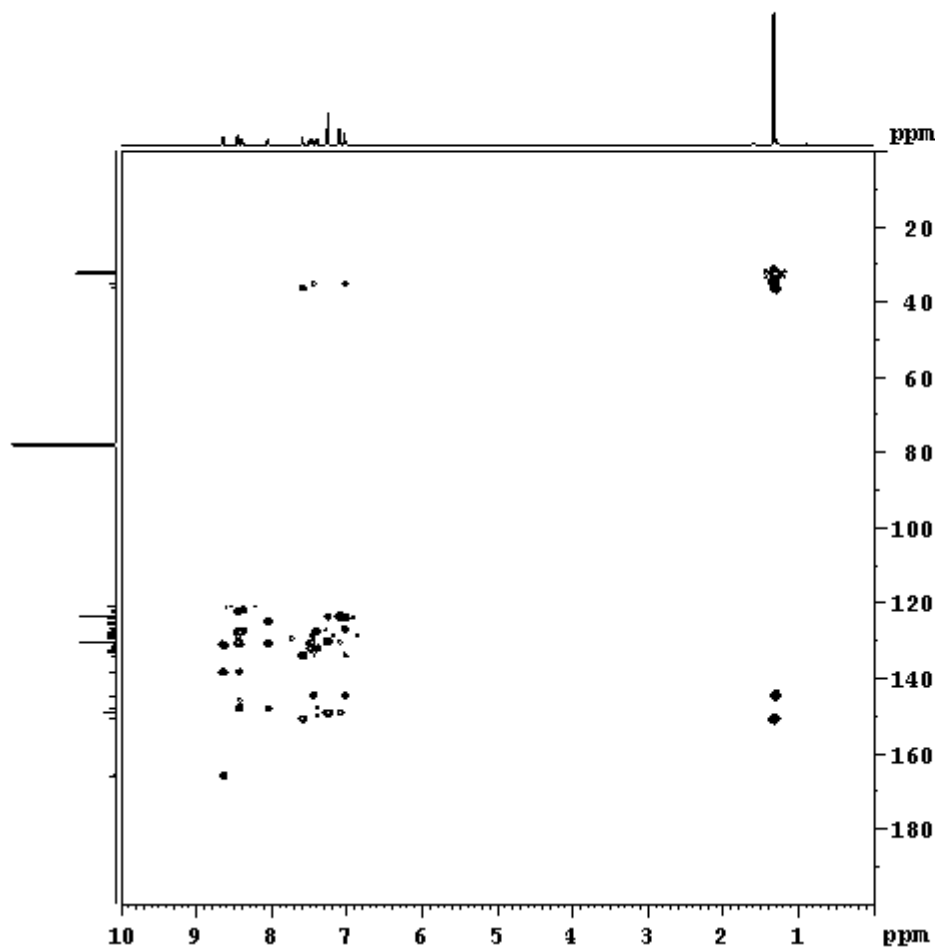
[illegible]

asb-155b in CDC13 13C CORR 21-11-2012

[illegible]

¹H ¹³C HETCOR long range coupling - full spectral range

asb-155b in CDC13 LH-13C CORR LONG RANGE D6 corretto!! 21-11-2012



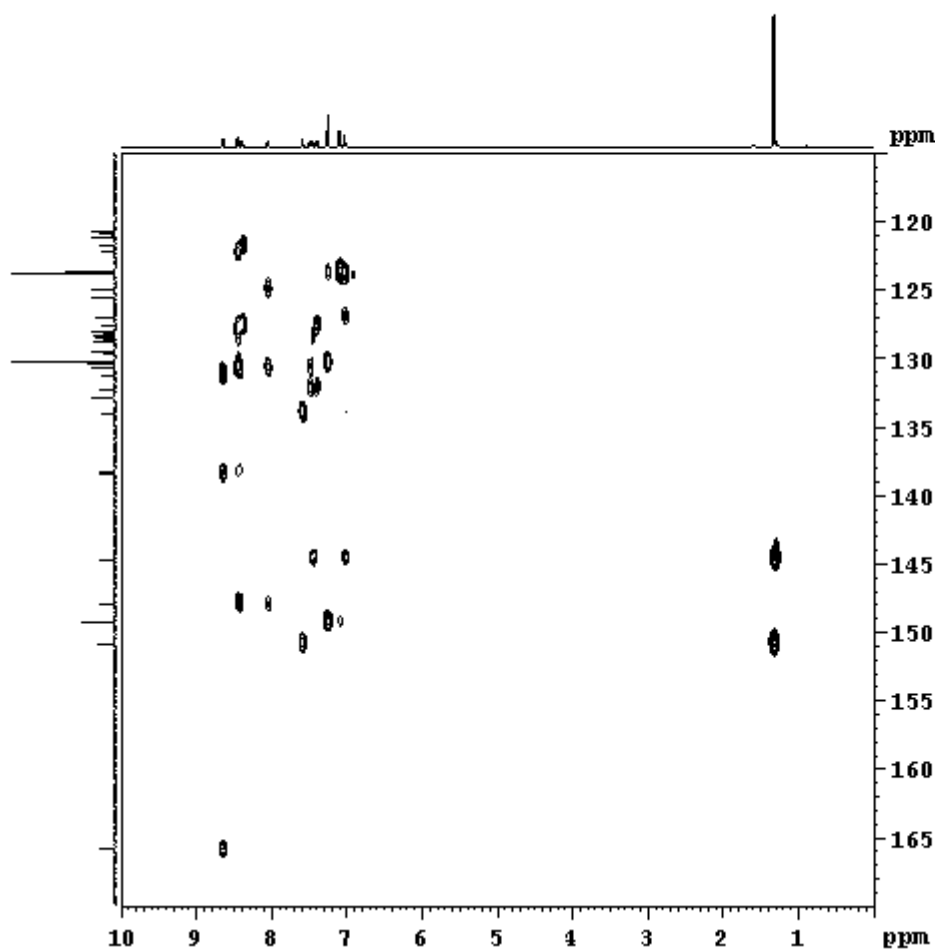
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Current Data Parameters
NAME          val=123.0
RANGE        1
SUBNAME      1

-- Acquisition Parameters
Date         20171124
Time         17.38
DETECTOR     acsc
PULPROG      5 sec flat 16-88
NOFREQ       hrfreqprod1
PC           10
SOLNAME      C0013
CO           32
CQ           1
SFR          4148.114 Hz
PCORR        0.430389 Hz
RG           0.0826703 sec
CPR          0.000000
CPC          0.000000
CPS          145.000000 Hz
CPCPR13      8.0000000
CPCPR14      8.0000000
CPCPR15      8.0000000
CPCPR16      8.0000000
CPCPR17      8.0000000
CPCPR18      8.0000000
CPCPR19      8.0000000
CPCPR20      8.0000000
CPCPR21      8.0000000
CPCPR22      8.0000000
CPCPR23      8.0000000
CPCPR24      8.0000000
CPCPR25      8.0000000
CPCPR26      8.0000000
CPCPR27      8.0000000
CPCPR28      8.0000000
CPCPR29      8.0000000
CPCPR30      8.0000000
CPCPR31      8.0000000
CPCPR32      8.0000000
CPCPR33      8.0000000
CPCPR34      8.0000000
CPCPR35      8.0000000
CPCPR36      8.0000000
CPCPR37      8.0000000
CPCPR38      8.0000000
CPCPR39      8.0000000
CPCPR40      8.0000000
CPCPR41      8.0000000
CPCPR42      8.0000000
CPCPR43      8.0000000
CPCPR44      8.0000000
CPCPR45      8.0000000
CPCPR46      8.0000000
CPCPR47      8.0000000
CPCPR48      8.0000000
CPCPR49      8.0000000
CPCPR50      8.0000000
CPCPR51      8.0000000
CPCPR52      8.0000000
CPCPR53      8.0000000
CPCPR54      8.0000000
CPCPR55      8.0000000
CPCPR56      8.0000000
CPCPR57      8.0000000
CPCPR58      8.0000000
CPCPR59      8.0000000
CPCPR60      8.0000000
CPCPR61      8.0000000
CPCPR62      8.0000000
CPCPR63      8.0000000
CPCPR64      8.0000000
CPCPR65      8.0000000
CPCPR66      8.0000000
CPCPR67      8.0000000
CPCPR68      8.0000000
CPCPR69      8.0000000
CPCPR70      8.0000000
CPCPR71      8.0000000
CPCPR72      8.0000000
CPCPR73      8.0000000
CPCPR74      8.0000000
CPCPR75      8.0000000
CPCPR76      8.0000000
CPCPR77      8.0000000
CPCPR78      8.0000000
CPCPR79      8.0000000
CPCPR80      8.0000000
CPCPR81      8.0000000
CPCPR82      8.0000000
CPCPR83      8.0000000
CPCPR84      8.0000000
CPCPR85      8.0000000
CPCPR86      8.0000000
CPCPR87      8.0000000
CPCPR88      8.0000000
CPCPR89      8.0000000
CPCPR90      8.0000000
CPCPR91      8.0000000
CPCPR92      8.0000000
CPCPR93      8.0000000
CPCPR94      8.0000000
CPCPR95      8.0000000
CPCPR96      8.0000000
CPCPR97      8.0000000
CPCPR98      8.0000000
CPCPR99      8.0000000
CPCPR100     8.0000000
CPCPR101     8.0000000
CPCPR102     8.0000000
CPCPR103     8.0000000
CPCPR104     8.0000000
CPCPR105     8.0000000
CPCPR106     8.0000000
CPCPR107     8.0000000
CPCPR108     8.0000000
CPCPR109     8.0000000
CPCPR110     8.0000000
CPCPR111     8.0000000
CPCPR112     8.0000000
CPCPR113     8.0000000
CPCPR114     8.0000000
CPCPR115     8.0000000
CPCPR116     8.0000000
CPCPR117     8.0000000
CPCPR118     8.0000000
CPCPR119     8.0000000
CPCPR120     8.0000000
CPCPR121     8.0000000
CPCPR122     8.0000000
CPCPR123     8.0000000
CPCPR124     8.0000000
CPCPR125     8.0000000
CPCPR126     8.0000000
CPCPR127     8.0000000
CPCPR128     8.0000000
CPCPR129     8.0000000
CPCPR130     8.0000000
CPCPR131     8.0000000
CPCPR132     8.0000000
CPCPR133     8.0000000
CPCPR134     8.0000000
CPCPR135     8.0000000
CPCPR136     8.0000000
CPCPR137     8.0000000
CPCPR138     8.0000000
CPCPR139     8.0000000
CPCPR140     8.0000000
CPCPR141     8.0000000
CPCPR142     8.0000000
CPCPR143     8.0000000
CPCPR144     8.0000000
CPCPR145     8.0000000
CPCPR146     8.0000000
CPCPR147     8.0000000
CPCPR148     8.0000000
CPCPR149     8.0000000
CPCPR150     8.0000000
CPCPR151     8.0000000
CPCPR152     8.0000000
CPCPR153     8.0000000
CPCPR154     8.0000000
CPCPR155     8.0000000
CPCPR156     8.0000000
CPCPR157     8.0000000
CPCPR158     8.0000000
CPCPR159     8.0000000
CPCPR160     8.0000000
CPCPR161     8.0000000
CPCPR162     8.0000000
CPCPR163     8.0000000
CPCPR164     8.0000000
CPCPR165     8.0000000
CPCPR166     8.0000000
CPCPR167     8.0000000
CPCPR168     8.0000000
CPCPR169     8.0000000
CPCPR170     8.0000000
CPCPR171     8.0000000
CPCPR172     8.0000000
CPCPR173     8.0000000
CPCPR174     8.0000000
CPCPR175     8.0000000
CPCPR176     8.0000000
CPCPR177     8.0000000
CPCPR178     8.0000000
CPCPR179     8.0000000
CPCPR180     8.0000000
CPCPR181     8.0000000
CPCPR182     8.0000000
CPCPR183     8.0000000
CPCPR184     8.0000000
CPCPR185     8.0000000
CPCPR186     8.0000000
CPCPR187     8.0000000
CPCPR188     8.0000000
CPCPR189     8.0000000
CPCPR190     8.0000000
CPCPR191     8.0000000
CPCPR192     8.0000000
CPCPR193     8.0000000
CPCPR194     8.0000000
CPCPR195     8.0000000
CPCPR196     8.0000000
CPCPR197     8.0000000
CPCPR198     8.0000000
CPCPR199     8.0000000
CPCPR200     8.0000000
CPCPR201     8.0000000
CPCPR202     8.0000000
CPCPR203     8.0000000
CPCPR204     8.0000000
CPCPR205     8.0000000
CPCPR206     8.0000000
CPCPR207     8.0000000
CPCPR208     8.0000000
CPCPR209     8.0000000
CPCPR210     8.0000000
CPCPR211     8.0000000
CPCPR212     8.0000000
CPCPR213     8.0000000
CPCPR214     8.0000000
CPCPR215     8.0000000
CPCPR216     8.0000000
CPCPR217     8.0000000
CPCPR218     8.0000000
CPCPR219     8.0000000
CPCPR220     8.0000000
CPCPR221     8.0000000
CPCPR222     8.0000000
CPCPR223     8.0000000
CPCPR224     8.0000000
CPCPR225     8.0000000
CPCPR226     8.0000000
CPCPR227     8.0000000
CPCPR228     8.0000000
CPCPR229     8.0000000
CPCPR230     8.0000000
CPCPR231     8.0000000
CPCPR232     8.0000000
CPCPR233     8.0000000
CPCPR23
```

Aromatic expansion

asb-155b in CDCl3 1H-13C CORR LONG RANGE D6 corretto!! 21-11-2012



```

Current Data Parameters
NAME      asb-155b
EXPNO     3
PROCNO    1

F2 - Acquisition Parameters
Date_     20121124
Time      17.38
INSTRUM   spect
PROBHD    5 mm BBO (1H-13
PULPROG   zgpg30
TD         65536
SOLVENT   cdcl3
NS         32
DS         4
SWH        4166.1110 Hz
FIDRES     0.000000 Hz
AQ         0.0026700 sec
RG         271.25
CF         80.000 U/s
CQ         0.00 U/s
CY         248.2 Hz
CZ         145.000000 Hz
DECT13     0.000000
d0         0.000000 sec
d1         0.000000 sec
d2         0.000000 sec
d3         0.000000 sec
d4         0.000000 sec
d5         0.000000 sec
d6         0.000000 sec

===== CHANNEL f1 =====
NUC1       13C
P1         10.00 U/s
PC         21.20 U/s
PS1        3.30 dB
SFO1       500.1324853 MHz

===== CHANNEL f2 =====
NUC2       13C
P2         13.00 U/s
PC         -0.80 dB
SFO2       125.7705488 MHz

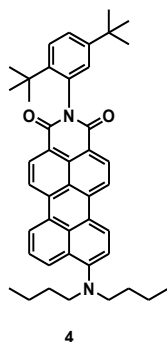
===== CHANNEL f3 =====
CPDPRG2    zgpg30
CPDPRG3    zgpg30
CPDPRG4    zgpg30
CPDPRG5    zgpg30
CPDPRG6    zgpg30
CPDPRG7    zgpg30
CPDPRG8    zgpg30
CPDPRG9    zgpg30
CPDPRG10   zgpg30
CPDPRG11   zgpg30
CPDPRG12   zgpg30
CPDPRG13   zgpg30
CPDPRG14   zgpg30
CPDPRG15   zgpg30
CPDPRG16   zgpg30
CPDPRG17   zgpg30
CPDPRG18   zgpg30
CPDPRG19   zgpg30
CPDPRG20   zgpg30
CPDPRG21   zgpg30
CPDPRG22   zgpg30
CPDPRG23   zgpg30
CPDPRG24   zgpg30
CPDPRG25   zgpg30
CPDPRG26   zgpg30
CPDPRG27   zgpg30
CPDPRG28   zgpg30
CPDPRG29   zgpg30
CPDPRG30   zgpg30
CPDPRG31   zgpg30
CPDPRG32   zgpg30
CPDPRG33   zgpg30
CPDPRG34   zgpg30
CPDPRG35   zgpg30
CPDPRG36   zgpg30
CPDPRG37   zgpg30
CPDPRG38   zgpg30
CPDPRG39   zgpg30
CPDPRG40   zgpg30
CPDPRG41   zgpg30
CPDPRG42   zgpg30
CPDPRG43   zgpg30
CPDPRG44   zgpg30
CPDPRG45   zgpg30
CPDPRG46   zgpg30
CPDPRG47   zgpg30
CPDPRG48   zgpg30
CPDPRG49   zgpg30
CPDPRG50   zgpg30
CPDPRG51   zgpg30
CPDPRG52   zgpg30
CPDPRG53   zgpg30
CPDPRG54   zgpg30
CPDPRG55   zgpg30
CPDPRG56   zgpg30
CPDPRG57   zgpg30
CPDPRG58   zgpg30
CPDPRG59   zgpg30
CPDPRG60   zgpg30
CPDPRG61   zgpg30
CPDPRG62   zgpg30
CPDPRG63   zgpg30
CPDPRG64   zgpg30
CPDPRG65   zgpg30
CPDPRG66   zgpg30
CPDPRG67   zgpg30
CPDPRG68   zgpg30
CPDPRG69   zgpg30
CPDPRG70   zgpg30
CPDPRG71   zgpg30
CPDPRG72   zgpg30
CPDPRG73   zgpg30
CPDPRG74   zgpg30
CPDPRG75   zgpg30
CPDPRG76   zgpg30
CPDPRG77   zgpg30
CPDPRG78   zgpg30
CPDPRG79   zgpg30
CPDPRG80   zgpg30
CPDPRG81   zgpg30
CPDPRG82   zgpg30
CPDPRG83   zgpg30
CPDPRG84   zgpg30
CPDPRG85   zgpg30
CPDPRG86   zgpg30
CPDPRG87   zgpg30
CPDPRG88   zgpg30
CPDPRG89   zgpg30
CPDPRG90   zgpg30
CPDPRG91   zgpg30
CPDPRG92   zgpg30
CPDPRG93   zgpg30
CPDPRG94   zgpg30
CPDPRG95   zgpg30
CPDPRG96   zgpg30
CPDPRG97   zgpg30
CPDPRG98   zgpg30
CPDPRG99   zgpg30
CPDPRG100  zgpg30

F1 - Acquisition parameters
NUC1       1H
P1         10.00 U/s
PC         21.20 U/s
PS1        3.30 dB
SFO1       500.1324853 MHz

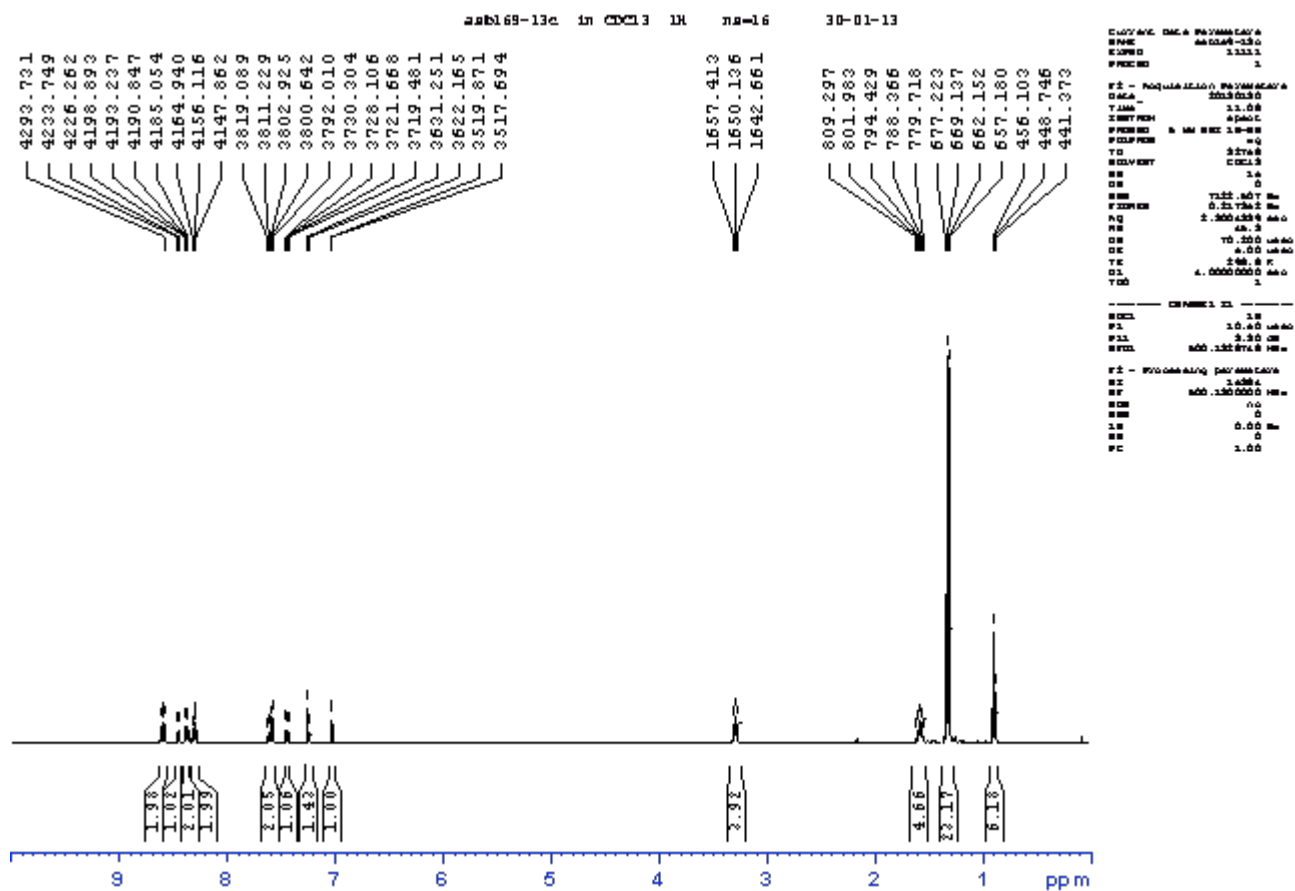
F2 - Processing parameters
SI         32768
SF         500.1324853 MHz
WDW         EM
SSB         0
GB          0.00 Hz
CB          0
SC          1.80

F3 - Processing parameters
SI         32768
SF         125.7705488 MHz
WDW         EM
SSB         0
GB          0.00 Hz
CB          0
SC          1.80
    
```

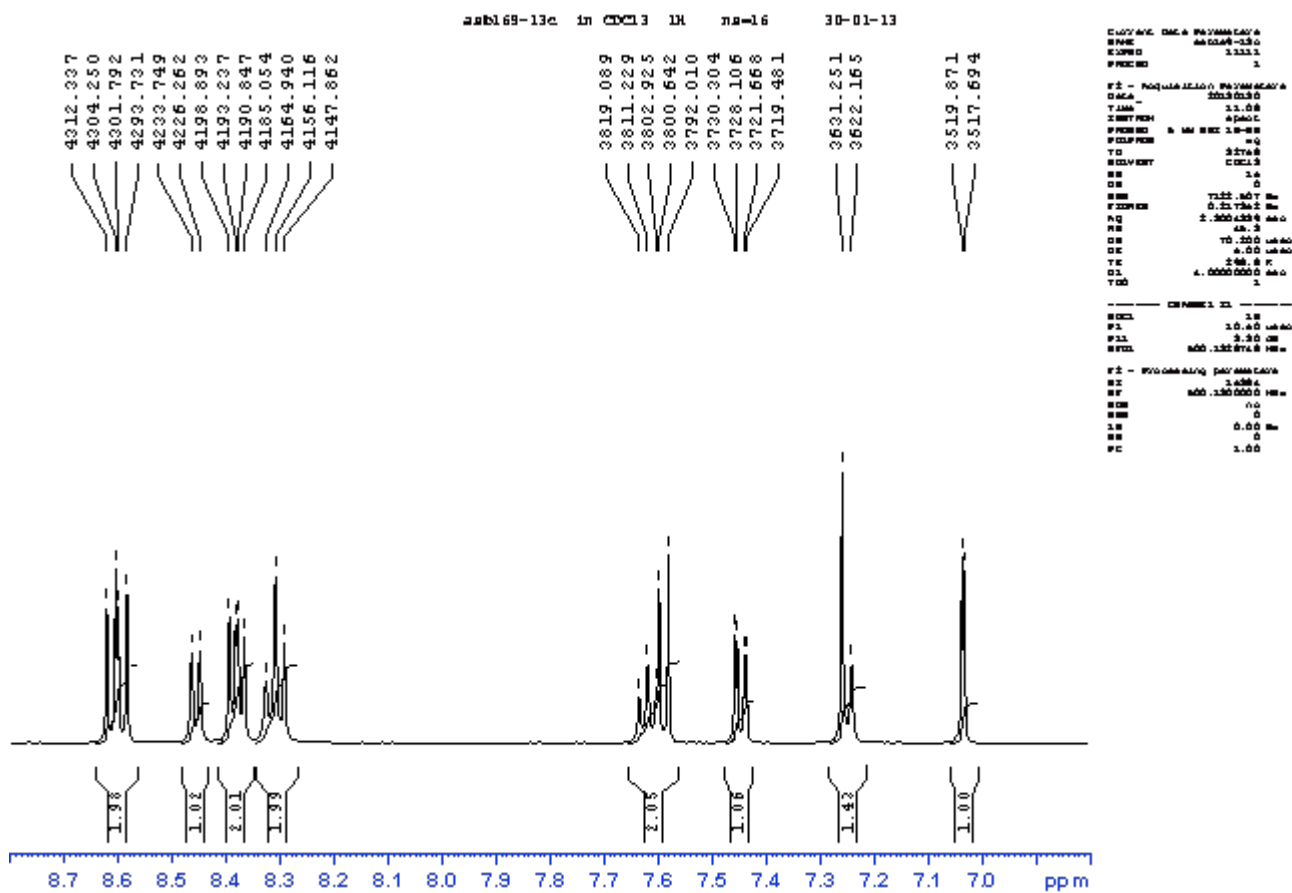
2.5. Derivative 4.



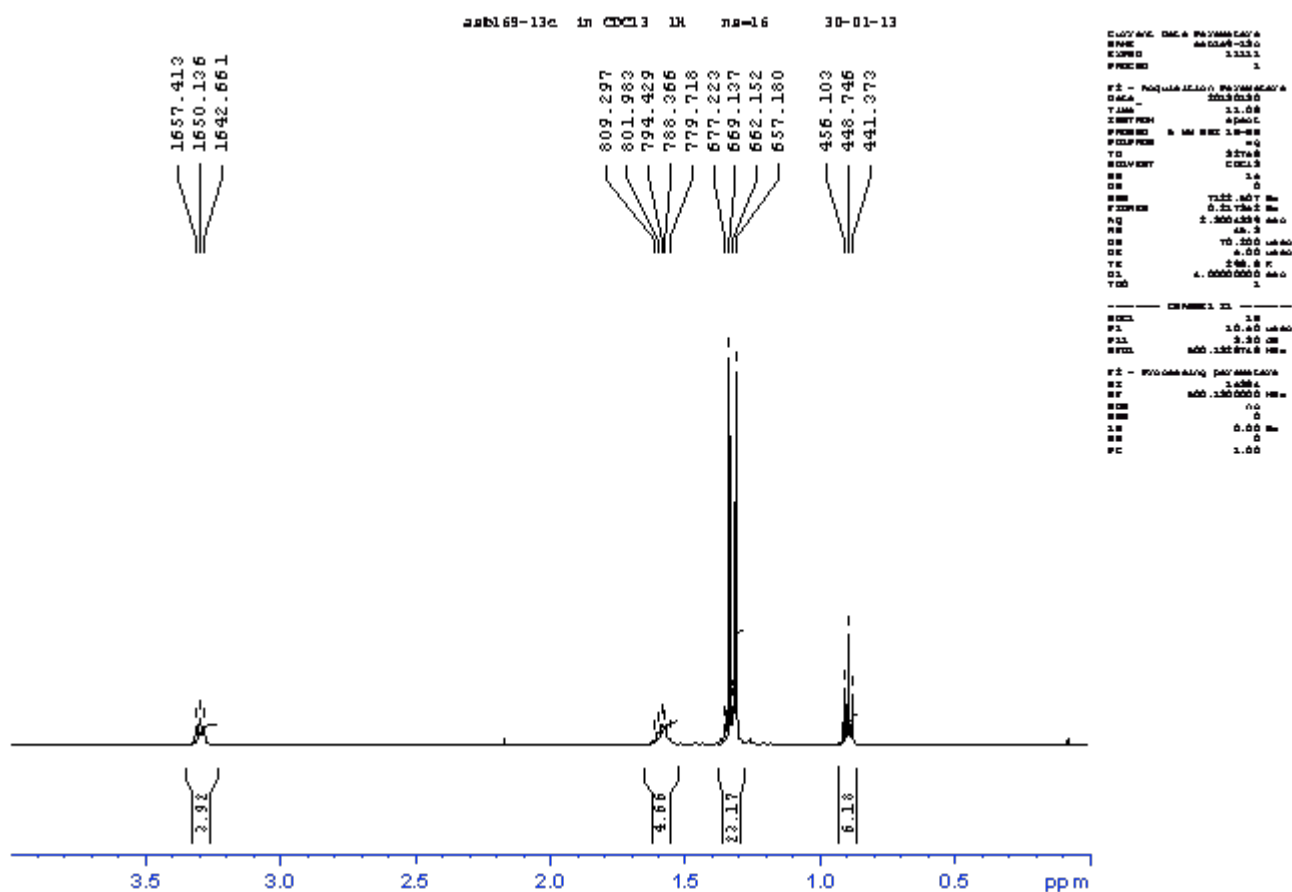
^1H full spectral range.

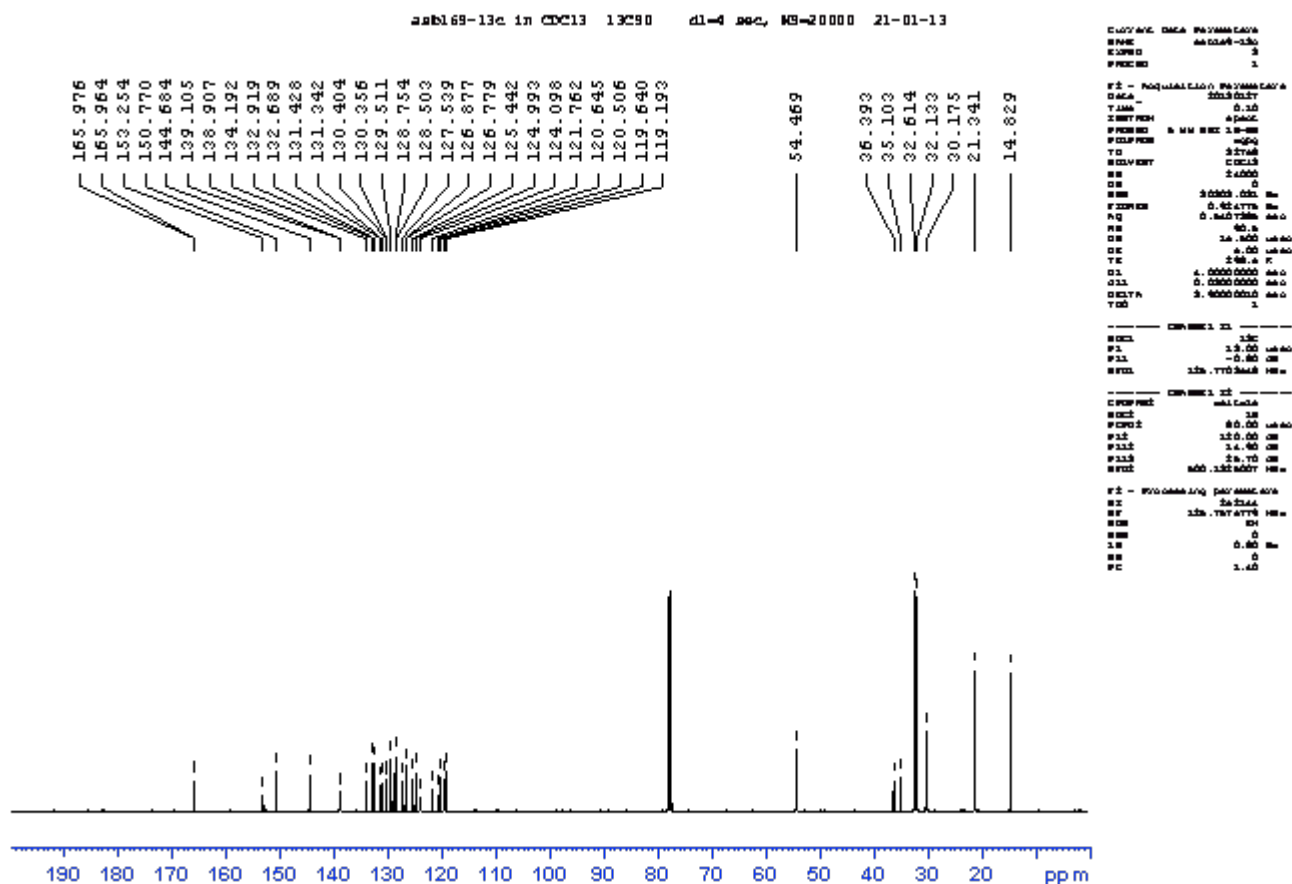


Aromatic region

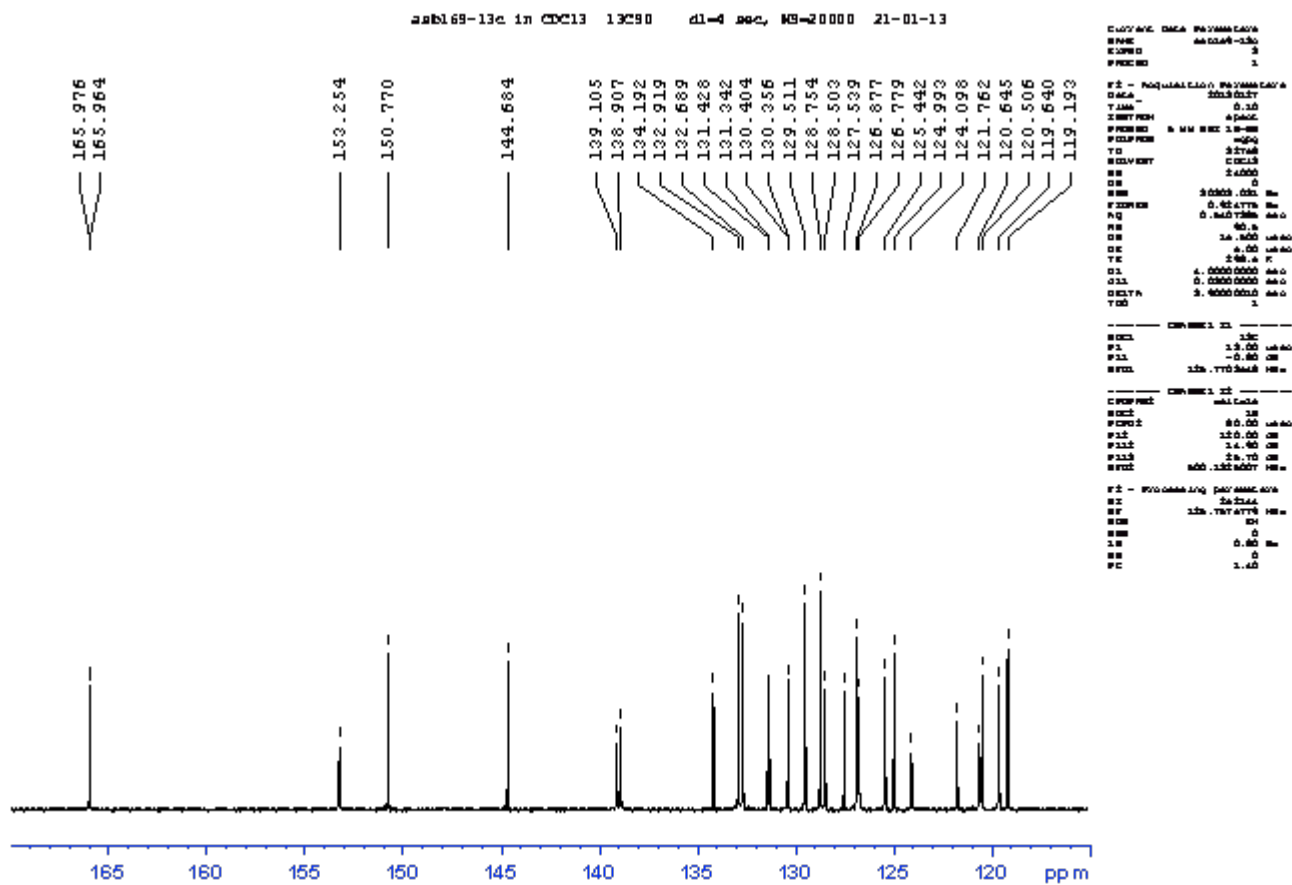


Alifatic region



¹³C full spectral range

Aromatic region



asbl69-13c in CDCl3 13C90 d1=4 sec, NS=20000 21-01-13

54.469

36.393

35.103

32.614

32.133

30.175

21.341

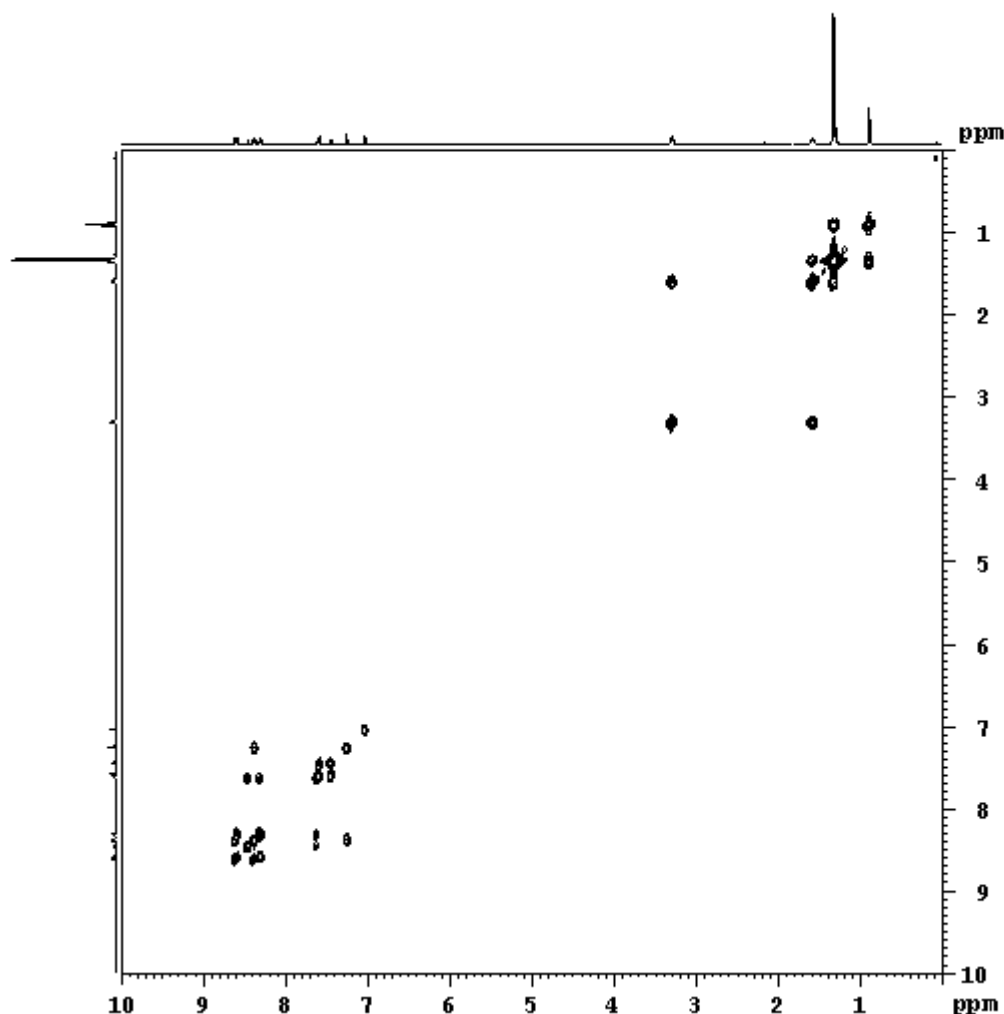
14.829

85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 ppm

[illegible]

¹H COSY full spectral range

ash169-13c in CDCl₃ COSY6PQF TD=1024-128, NS=16



Current Data Parameters
NAME ash169-13c
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150120
Time 17.56
INSTRUM spect
PROBHD 5 mm BBI 1H-400
PULPROG zgpg30
TD 1024
SOLVENT CDCl₃
NS 16
DS 16
SWH 6388.110 Hz
FIDRES 0.045085 Hz
AQ 0.0228700 sec
RG 287.4
IN 60.000 cm/s
DE 6.00 cm
TE 298.2 K
d0 0.0000000 sec
d1 2.0000000 sec
d15 0.0000000 sec
d16 0.0000000 sec
d20 0.0001610 sec

===== CHANNEL F1 =====
NUC1 1H
P1 6.00 cm
PL 10.00 cm
PC1 3.30 dB
SFO1 500.1325652 MHz

===== CHANNEL F2 =====
CPDPRG2 SSB 1.00
CROSS2 SSB 1.00
NUC2 13C
PC2 10.00 dB
PL2 10.00 dB
P15 1000.00 cm

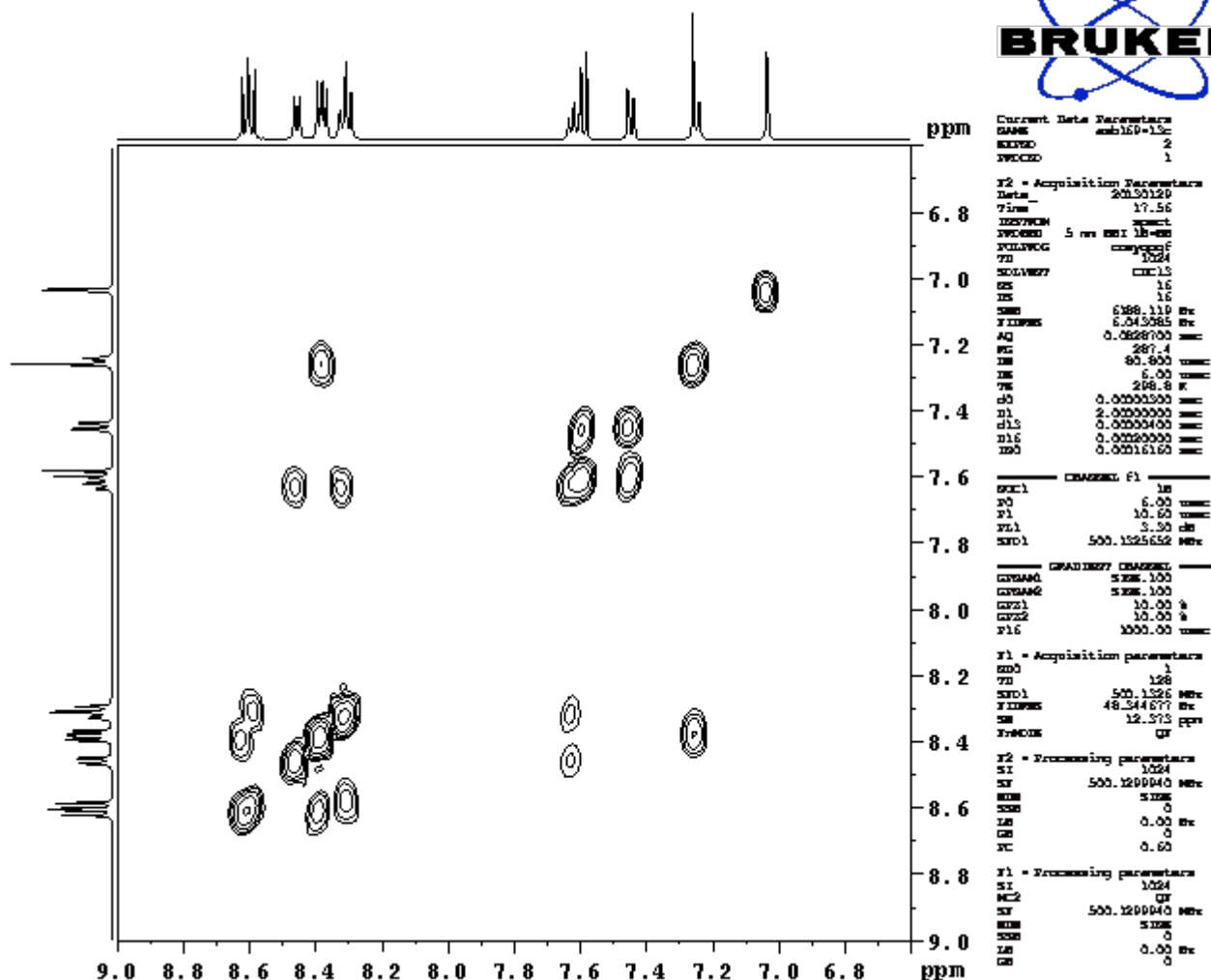
F1 - Acquisition parameters
EXPNO 1
TD 128
SFO1 500.1326 MHz
FIDRES 48.344677 Hz
SR 12.573 ppm
INSTRUM spect

F2 - Processing parameters
SI 1024
SF 500.1200040 MHz
WDW SSB
SSB 0
LB 0.00 Hz
GB 0
PC 0.60

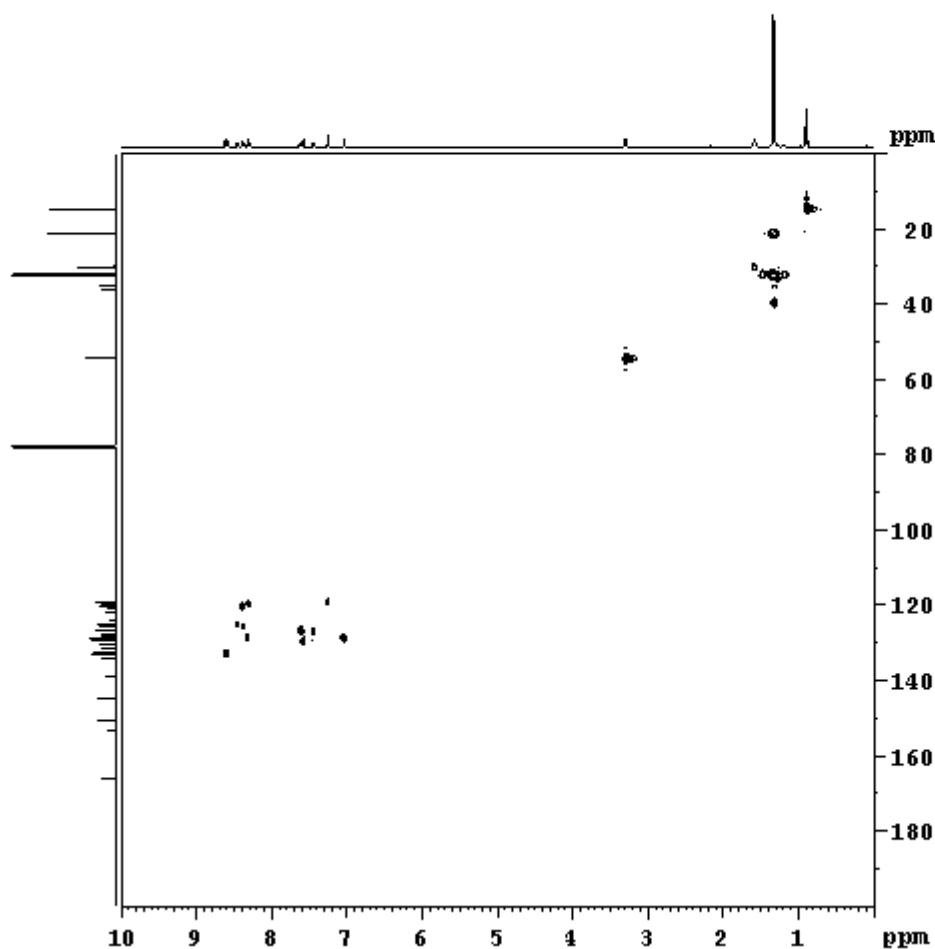
F1 - Processing parameters
SI 1024
PC2 0.00
SF 500.1200040 MHz
WDW SSB
SSB 0
LB 0.00 Hz
GB 0

Aromatic region

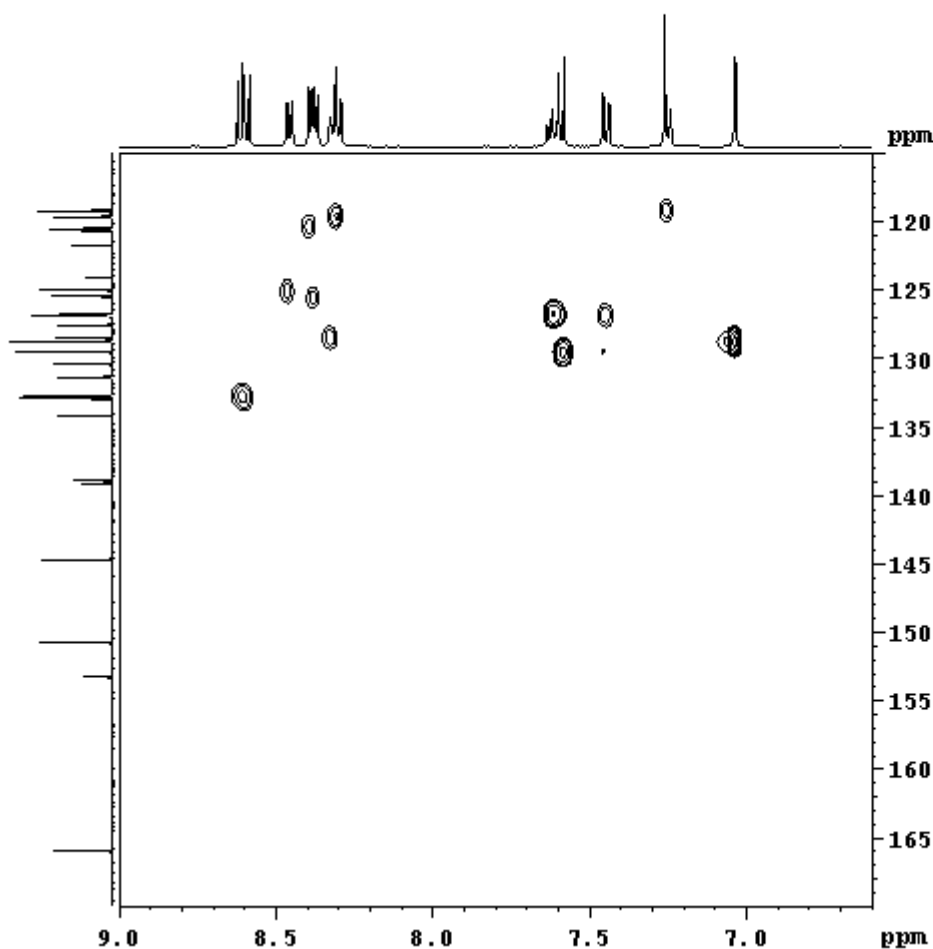
ash169-13c in CDCl3 COSY6PQF TD=1024-128, NS=16



asb169-13F in CDC13 13F CORR 22-01-2013

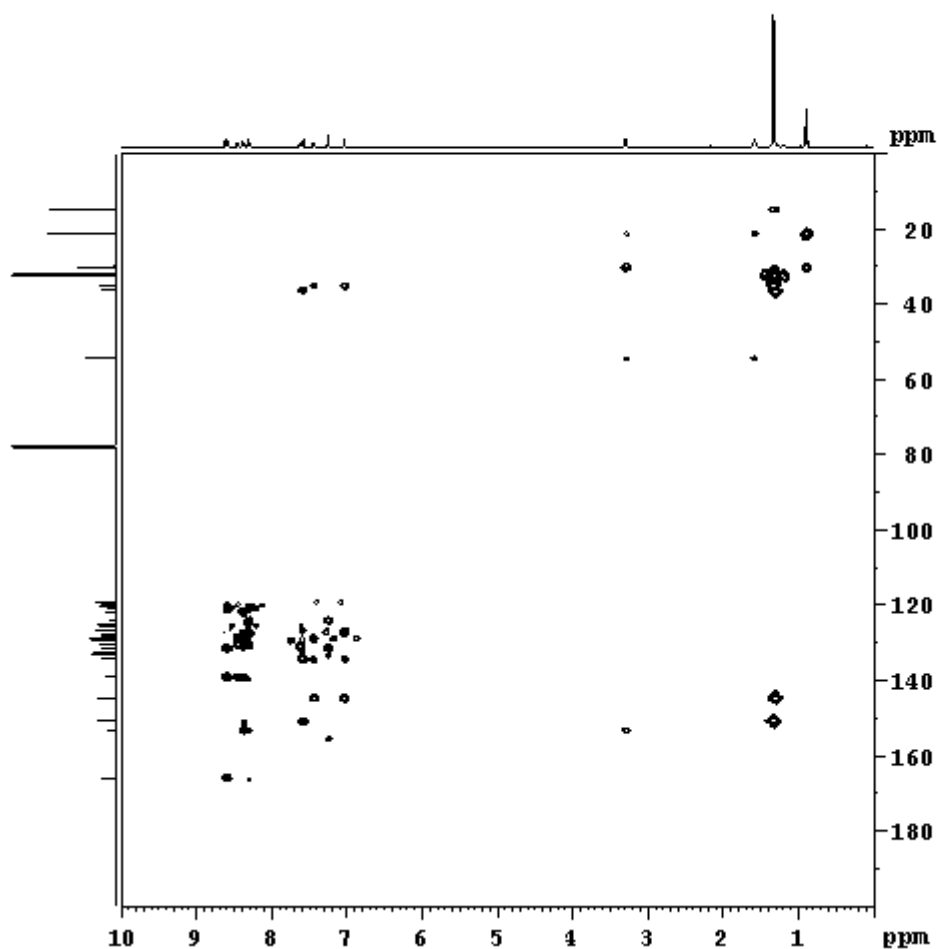
[illegible]

asb169-13C in CDC13 13C COBB 22-01-2013

[illegible]

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

asbl69-13c in CDCl3 1H-13C CORR LONG RANGE D6 corretto!! 25-01-2013



Current Data Parameters
NAME asbl69-13c
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130127
Time 14.14
INSTRUM spect
PROBHD 5 mm BBO 1H-13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 400
DS 4
SWH 4166.110 Hz
F2 4166.110 Hz
AQ 0.0826700 sec
RG 1024
CF 80.000 U/s
CQ 0.00 U/s
CY 238.4 Hz
CZ 145.000000 sec
DECT13 0.000000 sec
d0 0.000000 sec
d1 0.000000 sec
d2 0.000000 sec
d3 0.000000 sec
d4 0.000000 sec
d5 0.000000 sec
d6 0.000000 sec

===== CHANNEL f1 =====
NUC1 13
P1 10.00 U/s
PC 21.30 U/s
PL1 3.30 dB
SFO1 500.132485 MHz

===== CHANNEL f2 =====
NUC2 1H
P2 13.00 U/s
PC -0.80 dB
SFO2 125.759948 MHz

===== CHANNEL f3 =====
CPDPRG2 zgpg30
GPM1 300.00 Hz
GPM2 300.00 Hz
GPM3 300.00 Hz
GPM4 300.00 Hz
GPM5 300.00 Hz
GPM6 300.00 Hz
GPM7 300.00 Hz
GPM8 300.00 Hz
GPM9 300.00 Hz
GPM10 300.00 Hz
GPM11 300.00 Hz
GPM12 300.00 Hz
GPM13 300.00 Hz
GPM14 300.00 Hz
GPM15 300.00 Hz
GPM16 300.00 Hz
GPM17 300.00 Hz
GPM18 300.00 Hz
GPM19 300.00 Hz
GPM20 300.00 Hz
GPM21 300.00 Hz
GPM22 300.00 Hz
GPM23 300.00 Hz
GPM24 300.00 Hz
GPM25 300.00 Hz
GPM26 300.00 Hz
GPM27 300.00 Hz
GPM28 300.00 Hz
GPM29 300.00 Hz
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GPM31 300.00 Hz
GPM32 300.00 Hz
GPM33 300.00 Hz
GPM34 300.00 Hz
GPM35 300.00 Hz
GPM36 300.00 Hz
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GPM38 300.00 Hz
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GPM59 300.00 Hz
GPM60 300.00 Hz
GPM61 300.00 Hz
GPM62 300.00 Hz
GPM63 300.00 Hz
GPM64 300.00 Hz
GPM65 300.00 Hz
GPM66 300.00 Hz
GPM67 300.00 Hz
GPM68 300.00 Hz
GPM69 300.00 Hz
GPM70 300.00 Hz
GPM71 300.00 Hz
GPM72 300.00 Hz
GPM73 300.00 Hz
GPM74 300.00 Hz
GPM75 300.00 Hz
GPM76 300.00 Hz
GPM77 300.00 Hz
GPM78 300.00 Hz
GPM79 300.00 Hz
GPM80 300.00 Hz
GPM81 300.00 Hz
GPM82 300.00 Hz
GPM83 300.00 Hz
GPM84 300.00 Hz
GPM85 300.00 Hz
GPM86 300.00 Hz
GPM87 300.00 Hz
GPM88 300.00 Hz
GPM89 300.00 Hz
GPM90 300.00 Hz
GPM91 300.00 Hz
GPM92 300.00 Hz
GPM93 300.00 Hz
GPM94 300.00 Hz
GPM95 300.00 Hz
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GPM97 300.00 Hz
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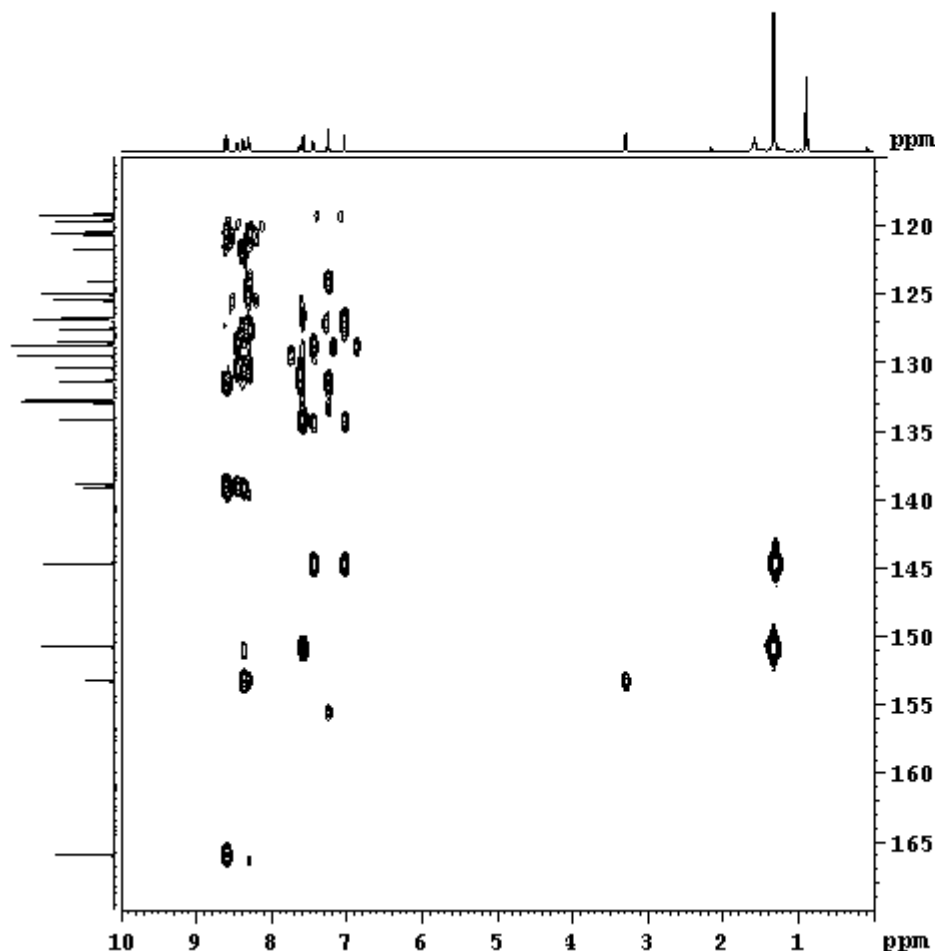
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PL1 3.30 dB
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WDW EM
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LB 0.00 Hz
GB 0
RC 1.40

F1 - Processing parameters
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SF 500.132485 MHz
WDW EM
SSB 0
LB 0.00 Hz
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RC 1.40

Aromatic region

asb169-13c in CDCl3 1H-13C CORR LONG RANGE D6 corretto!! 25-01-2013



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Current Data Parameters
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EXPNO     3
PROCNO    1

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

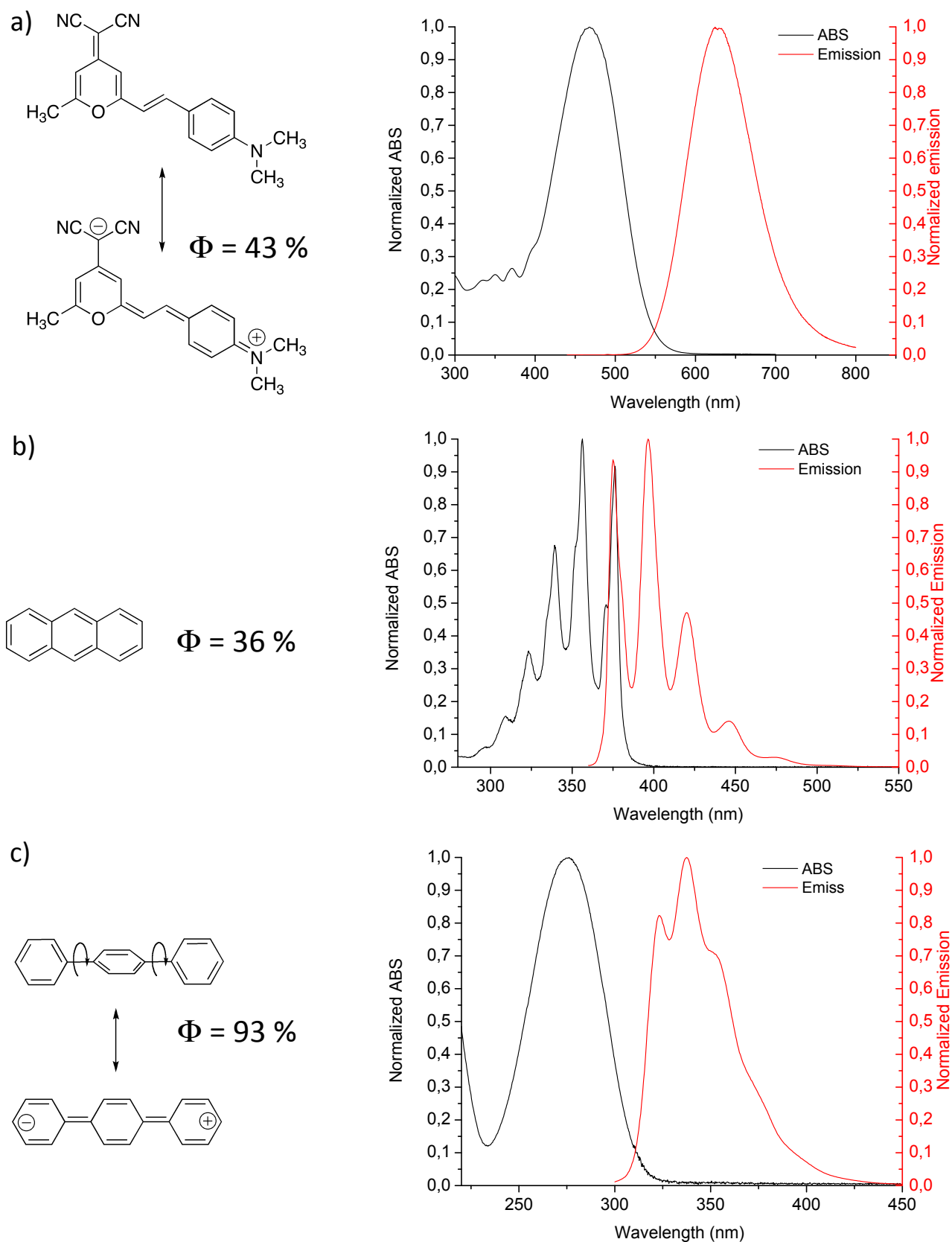


Figure S1. Comparison between the absorption (black curves), emission (red curves) and fluorescence quantum yields of representative molecules pertaining to: a) Donor-Acceptor compounds: the laser dye DCM (4-

(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, $\geq 99.0\%$) in a solution of anhydrous acetonitrile (Aldrich, 99.8%) and dichloromethane (Aldrich, 99.8%), 2:1 by volume. Cyclic Voltammeteries 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 μ m 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.

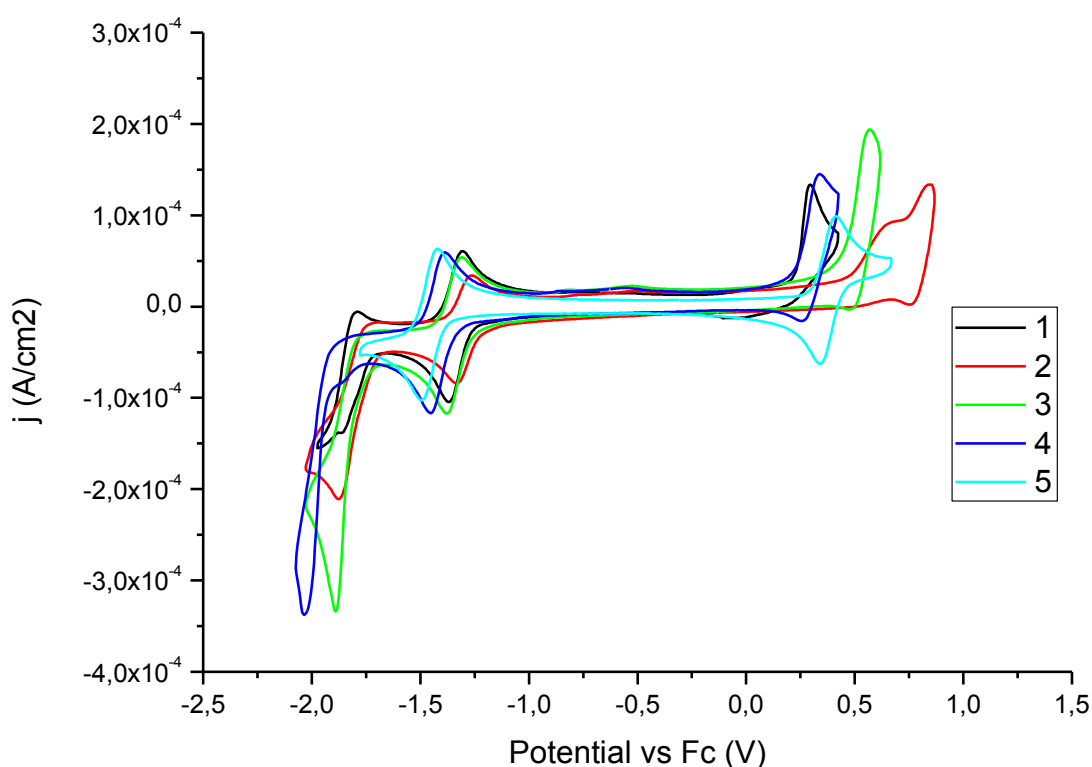


Figure S2. Cyclic voltammetry plots for derivatives **1-5** 10^{-4} M solution in acetonitrile with 0.1 M tetrabutylammonium *p*-toluenesulfonate as the supporting electrolyte.

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, $\geq 99.0\%$) 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 ($[O_2, H_2O] \leq 0.1$ 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.

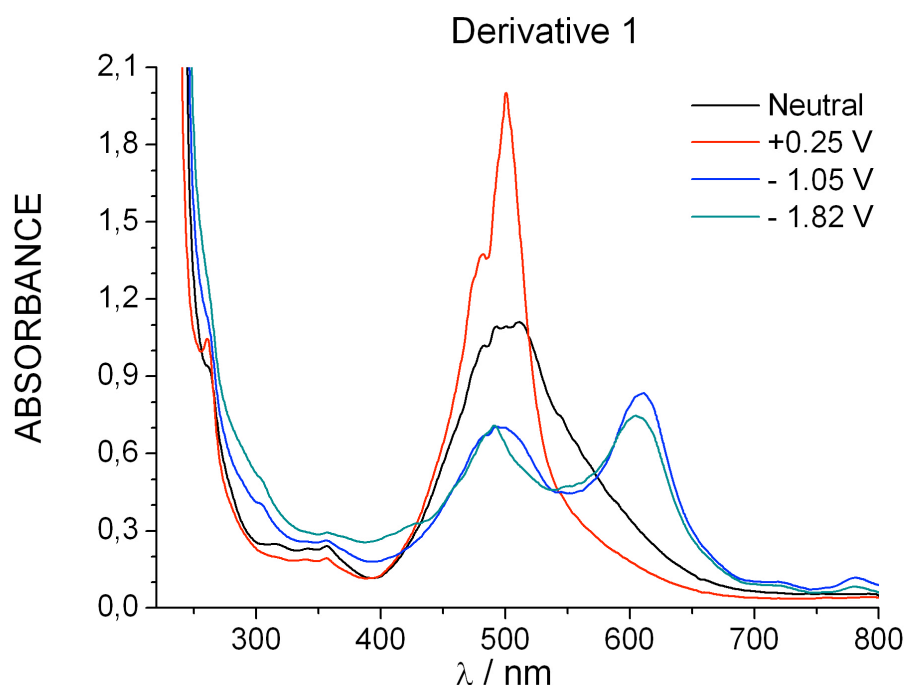


Figure S3. Spectroelectrochemical characterization of derivative 1 10^{-4} M solution in acetonitrile with 0.1 M tetrabutylammonium p-toluenesulfonate as the supporting electrolyte.

5.2. Derivative 2

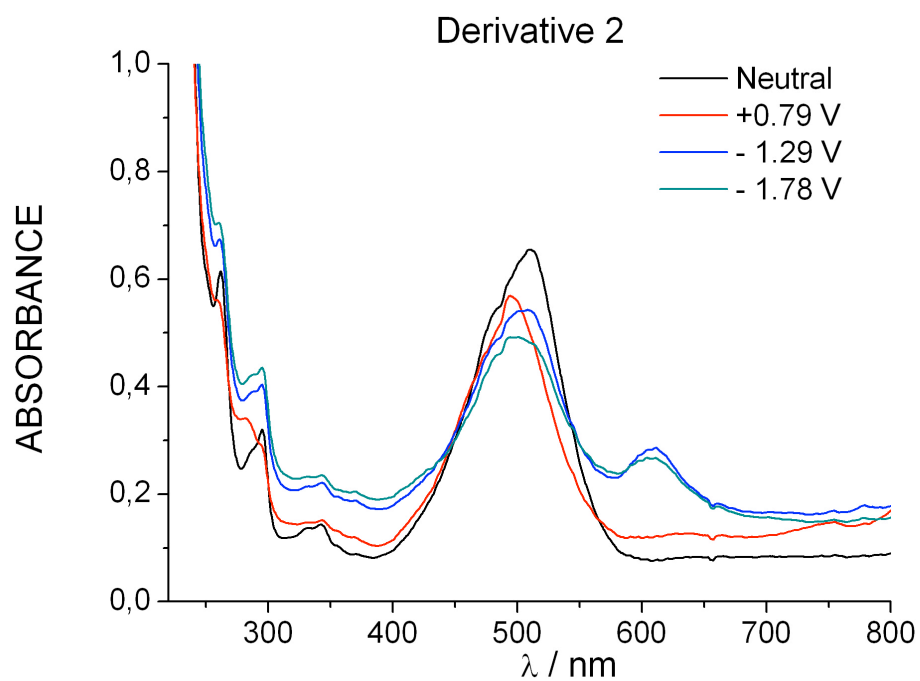


Figure S4. Spectroelectrochemical characterization of derivative **2** 10^{-4} M solution in acetonitrile with 0.1 M tetrabutylammonium *p*-toluenesulfonate as the supporting electrolyte.

5.3. Derivative 3

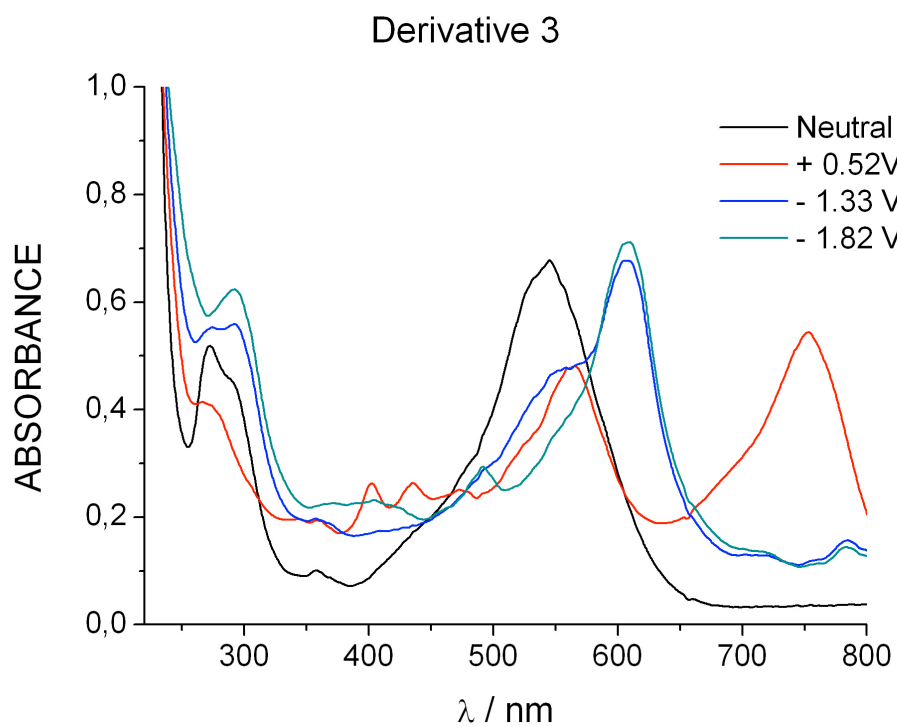


Figure S5. Spectroelectrochemical characterization of derivative **3** 10^{-4} M solution in acetonitrile with 0.1 M tetrabutylammonium *p*-toluenesulfonate as the supporting electrolyte.

5.4. Derivative 4

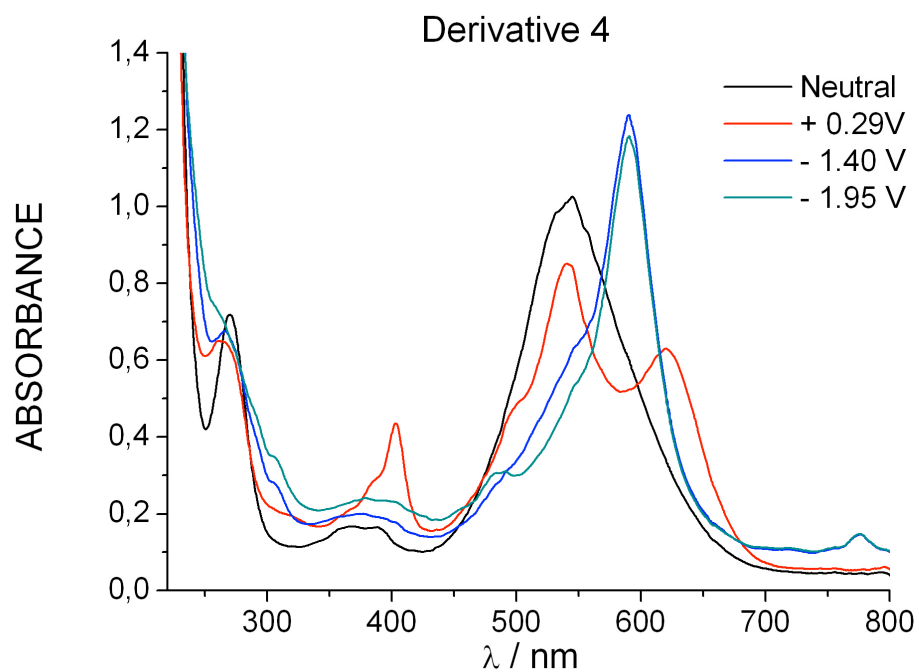


Figure S6. Spectroelectrochemical characterization of derivative **4** 10^{-4} M solution in acetonitrile with 0.1 M tetrabutylammonium *p*-toluenesulfonate as the supporting electrolyte.

5.5. Derivative 5

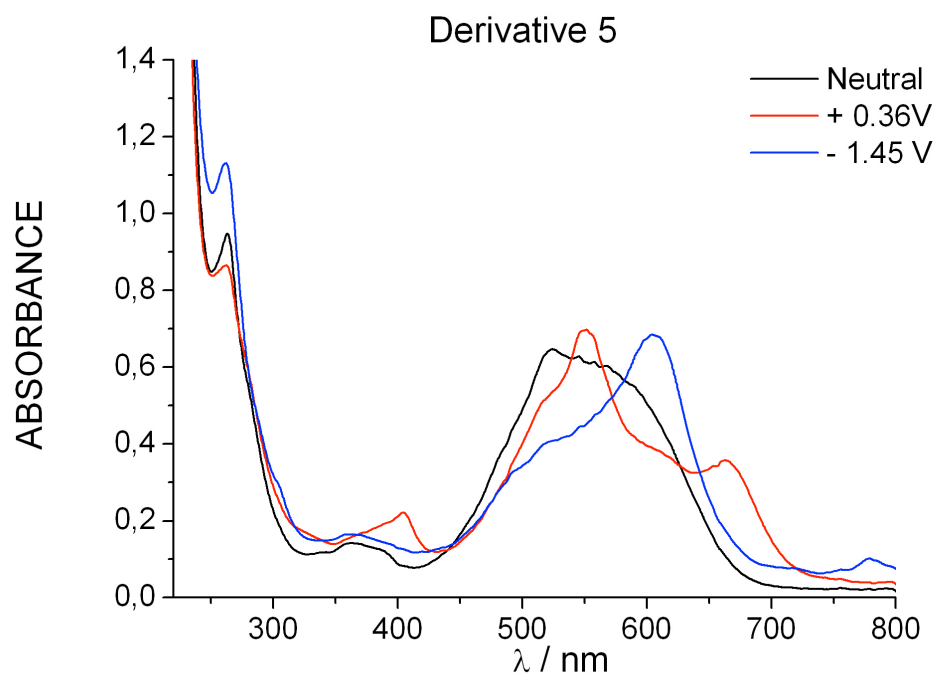


Figure S7. Spectroelectrochemical characterization of derivative **5** 10^{-4} M solution in acetonitrile with 0.1 M tetrabutylammonium *p*-toluenesulfonate as the supporting electrolyte.

6. Characterization of derivative **1** photostability in Chloroform solution.

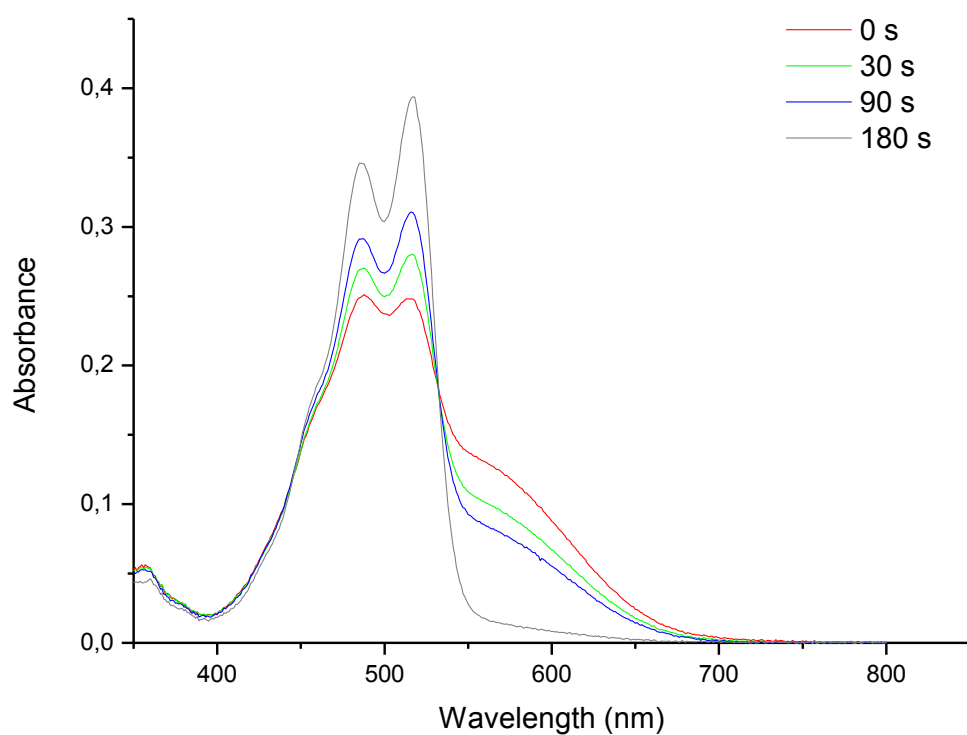


Figure S8. UV-Vis absorption spectra of an air equilibrated solution of derivative **1** in CHCl₃ as a function of the irradiation time under standard ambient diffused light.

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 cm² 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 (5×10^{-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 2×10^{-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 Advantage 5.35.

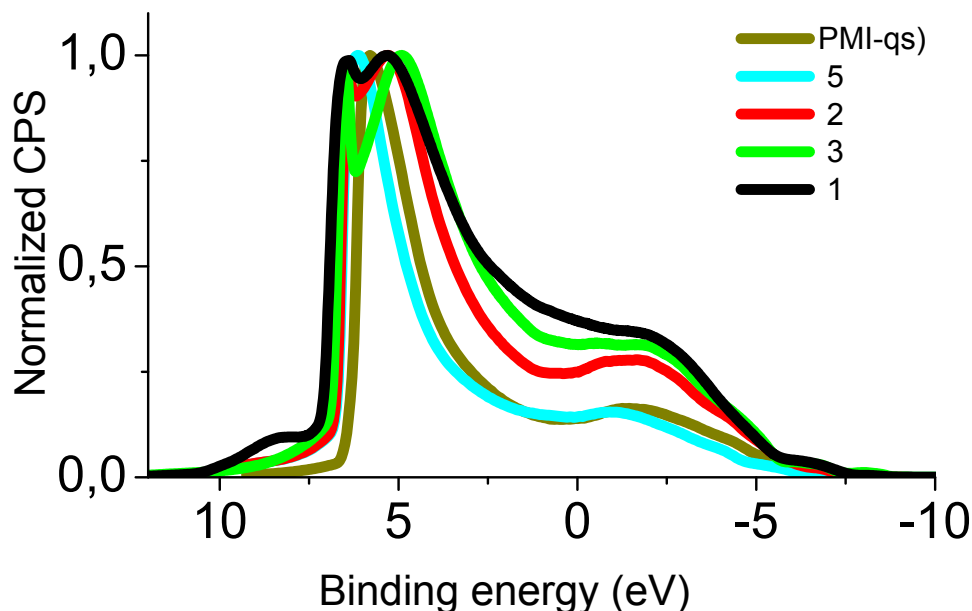


Figure S10. Full photoemission spectra of derivatives **PMI-qs**, **1,2,3** and **5**.

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

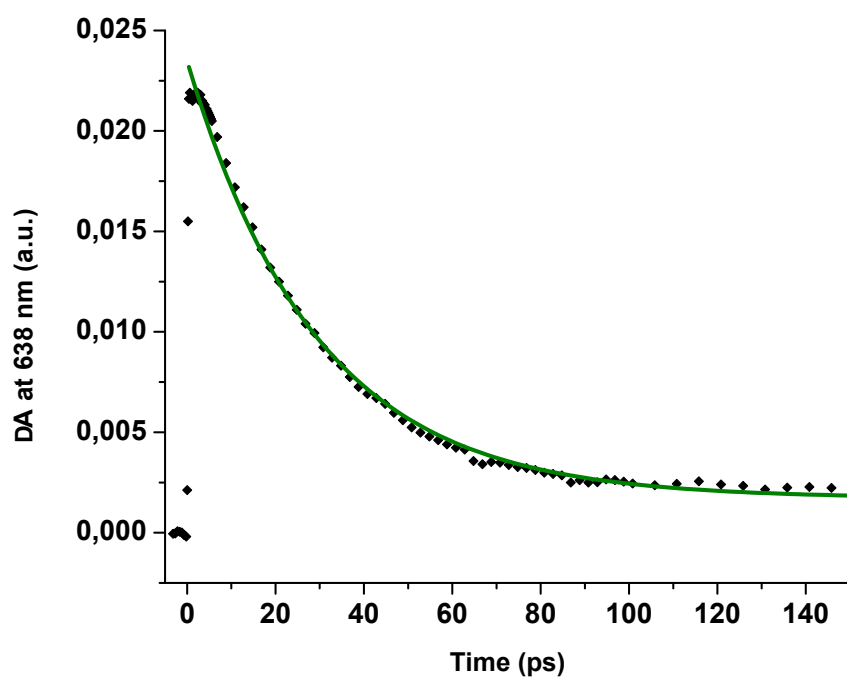


Figure S11. Time profiles of differential absorbance of a CH_2Cl_2 solution of **5** at 638 nm. The fitting curve corresponds to a first order decay.

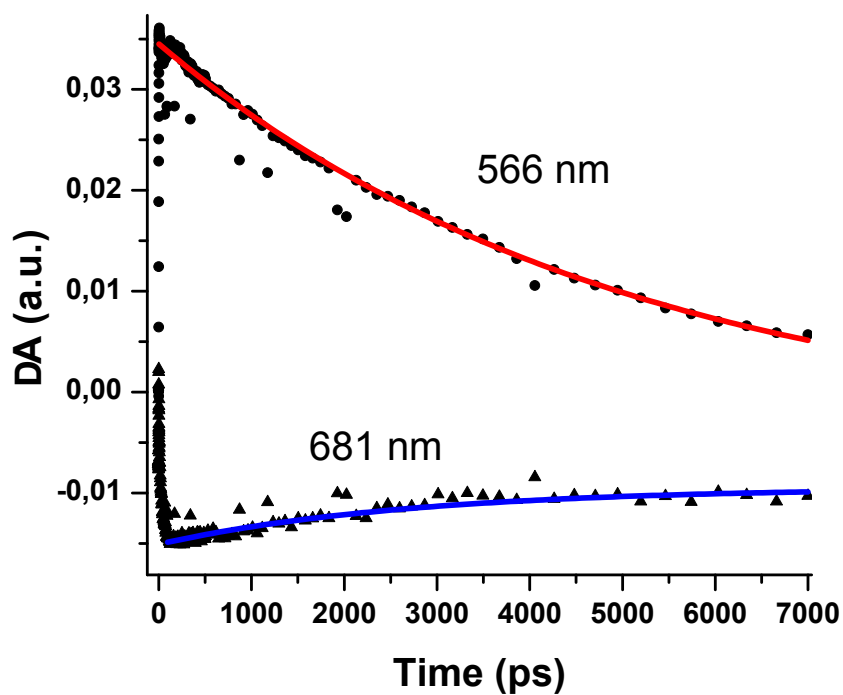


Figure S12. Time profiles of differential absorbance of a CH₂Cl₂ solution of **5** at 566 nm (red) and 681 nm (blue). The fitting curves correspond to a first order decay.

11. Figure S13.

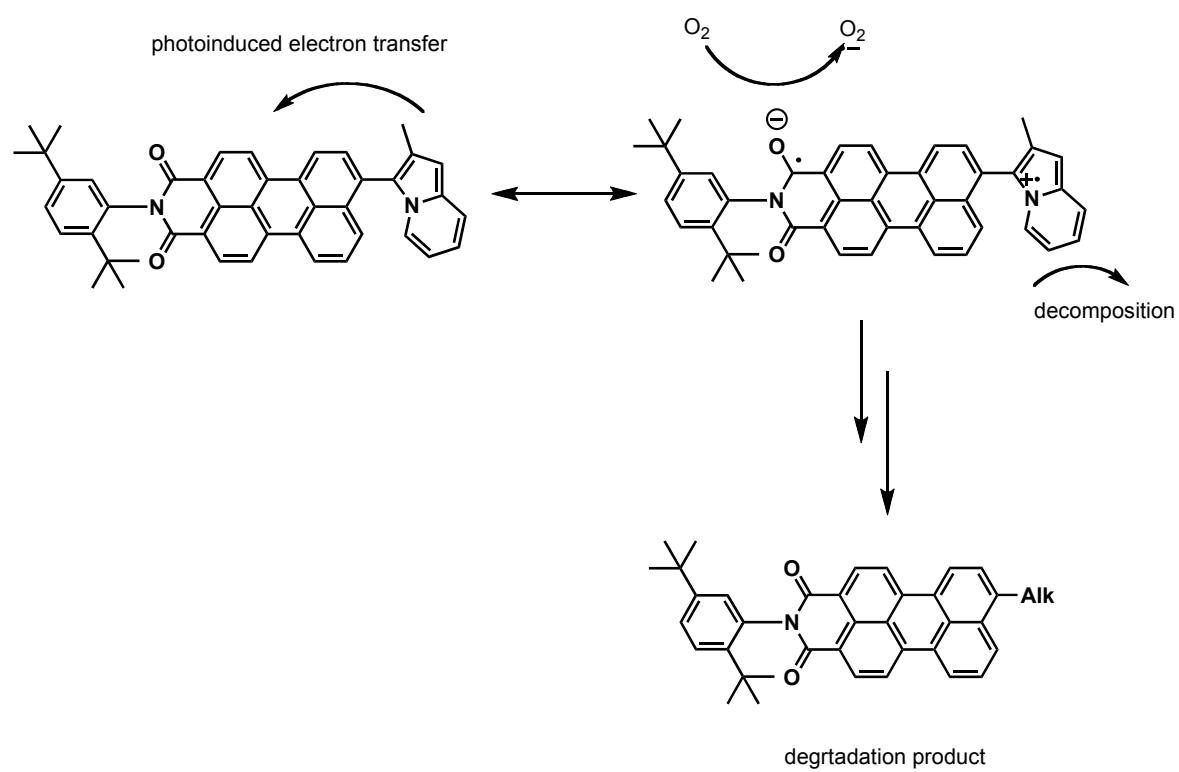


Figure S13. Tentative, unverified mechanism for the photochemical degradation of derivative **1**.

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 Spectraflex 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.

- ¹ H. Langhals, *Tetrahedron Letters*, 1995, **36**, 6423–6424.
- ² Y. Nagao et al. *Dyes and pigments*, 1991, **16**, 19–25.
- ³ A. Sanguineti et al. *Chem. Commun.*, 2013, **49**, 1618–1620
- ⁴ Shao et al. *Phys. Chem. Chem. Phys.* 2006, **8**, 3172-3191.
- ⁵ Clark et al. *J. Am. Chem. Soc.* 2007, **129**, 7586-7595.
- ⁶ Delgado et al. *J. Am. Chem. Soc.* 2010, **132**, 3375-3387.
- ⁷ J. C. deMello, H. F. Wittmann, R. H. Friend, *Adv. Mater.* 1997, 9, 230.