Electronic Supplementary Information

Stepwise π-Extension of meso-Alkylidenyl Porphyrins through Sequential 1,3-Dipolar Cycloaddition and Redox Reactions

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General

Proton NMR spectra (300 MHz, Bruker AvanceTM and 400 MHz, Bruker DPX-400) were recorded using TMS as the internal standard. High resolution mass spectra were obtained on an Voyager-DE STR MALDITOF mass spectrometer. Column chromatography was performed over silica gel (Merck, 230-400 mesh). Pyrrole was distilled at atmospheric pressure from CaH2. All other reagents were obtained from Aldrich and used as received unless noted otherwise.

Figure S1. ^{1}H NMR spectrum of compound (**2**) in $CDCl_3$.

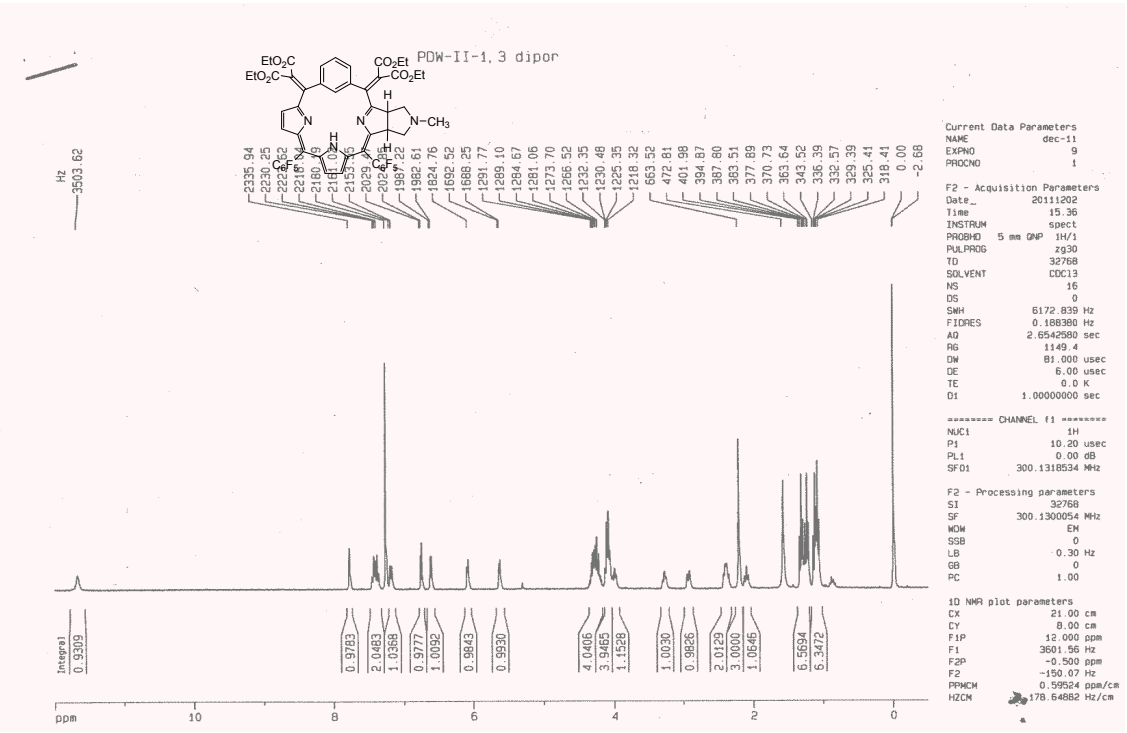


Figure S2. ^{13}C NMR spectrum of compound (**2**) in $CDCl_3$.

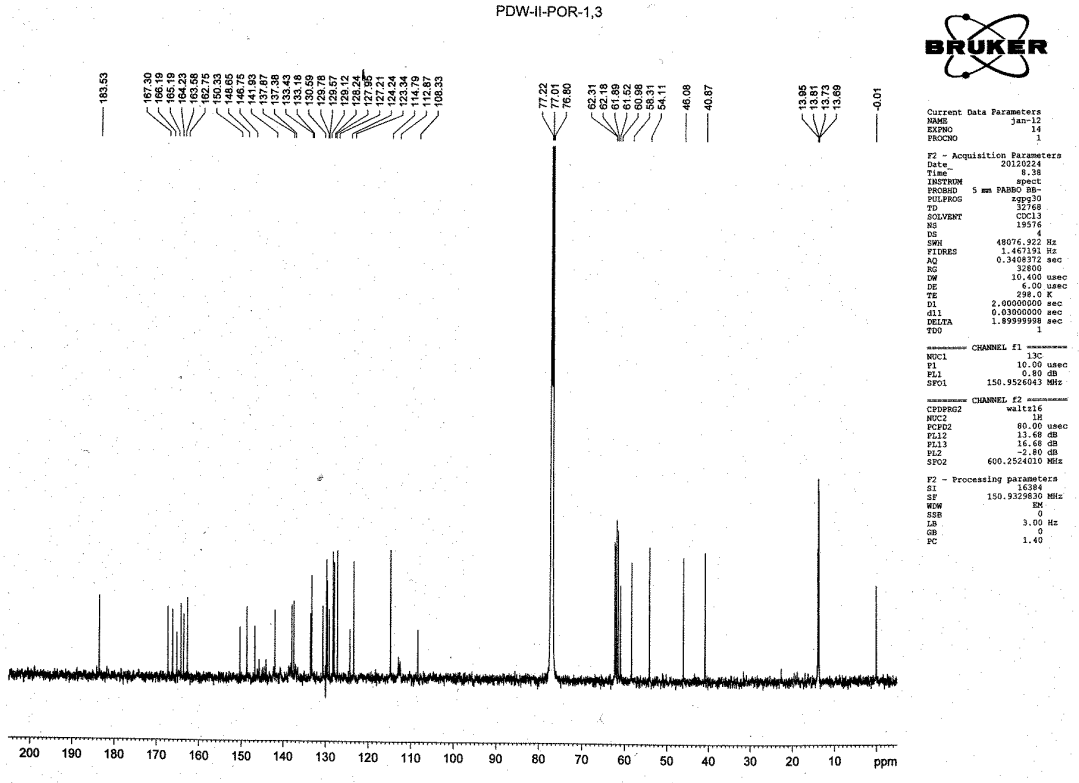


Figure S3. MALDI-TOF mass spectrum of compound (**2**).

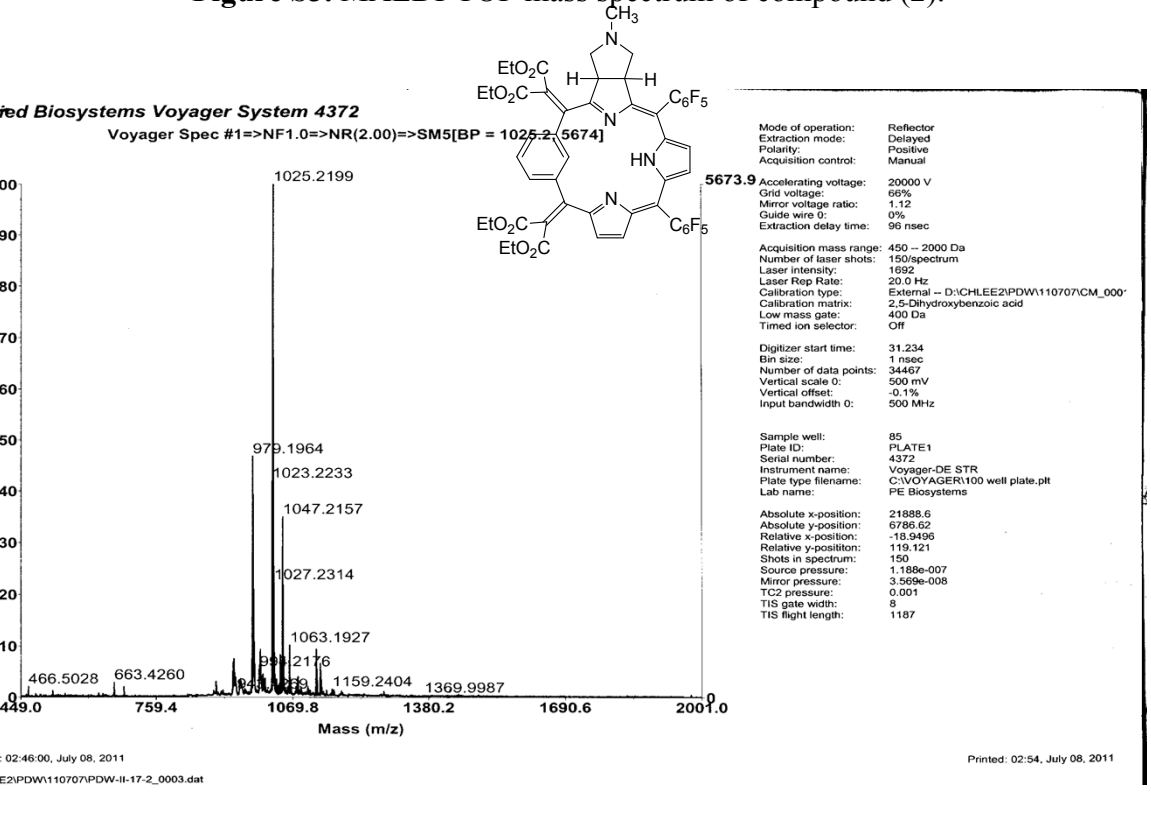


Figure S4. ^{1}H NMR spectrum of compound (**3**) in CD_2Cl_2.

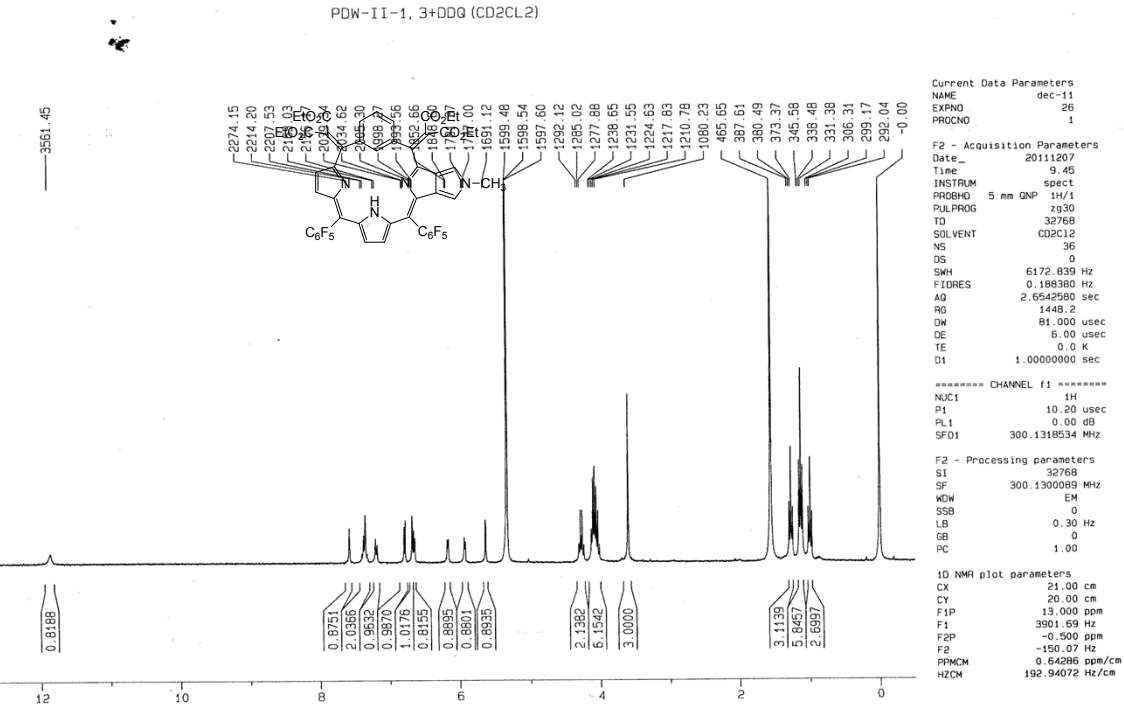


Figure S5. MALDI-TOF mass spectrum of compound (**3**)

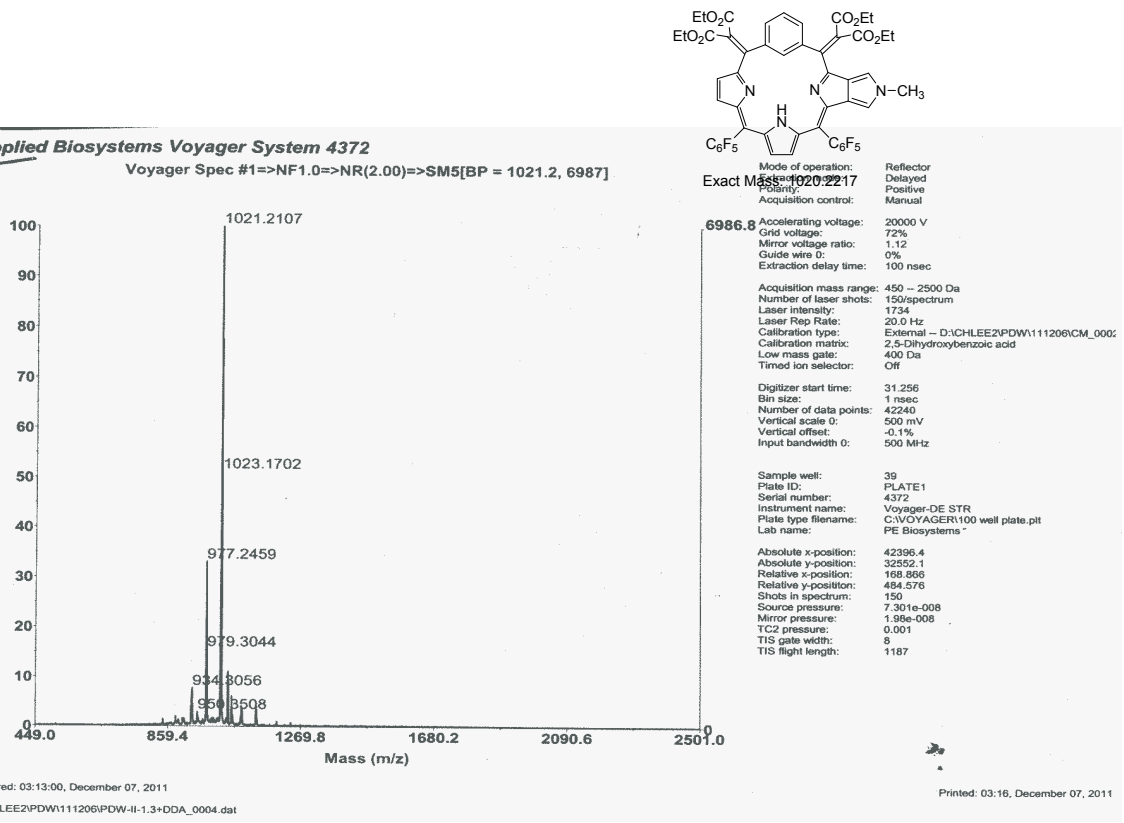
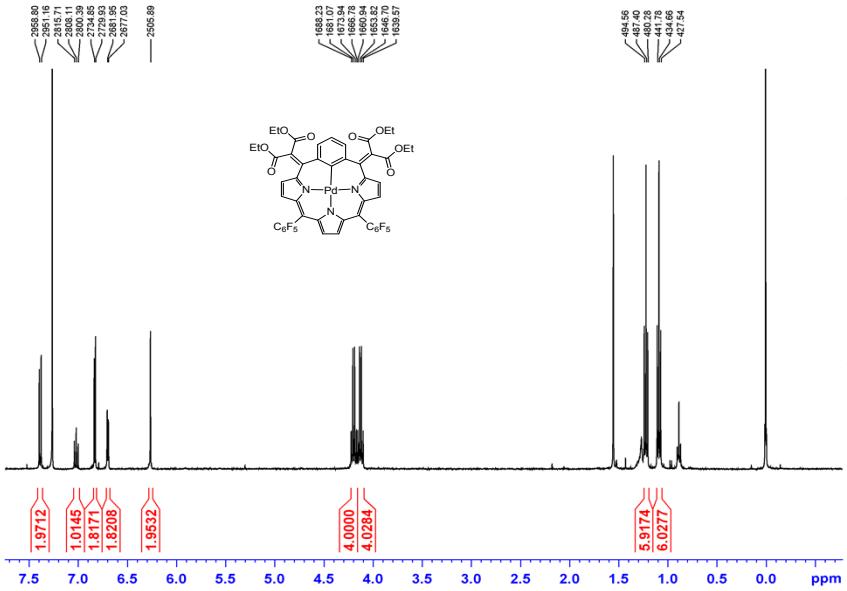


Figure S6. ^{1}H NMR spectrum of compound (**4**) in $CDCl_3$

PDW-II-102-PD-1

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TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               8223.685 Hz
FIDRES           0.125483 Hz
AQ               3.9845889 sec
RG                  186.53
DW                 60.800 usec
DE                  6.50 usec
TE                 295.9 K
D1              1.00000000 sec
TD0                     1

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SFO1         400.1324710 MHz

F2 - Processing parameters
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LB                   0.30 Hz
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PC                   1.00
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Figure S7. ^{13}C NMR spectrum of compound (**4**) in $CDCl_3$

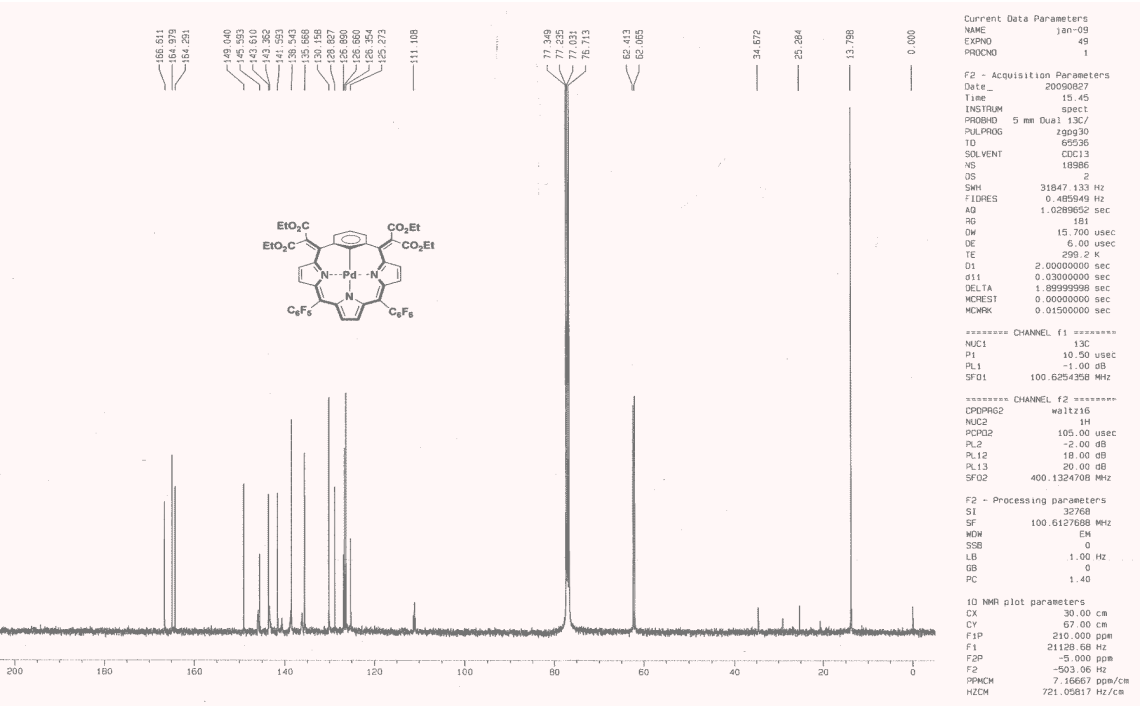
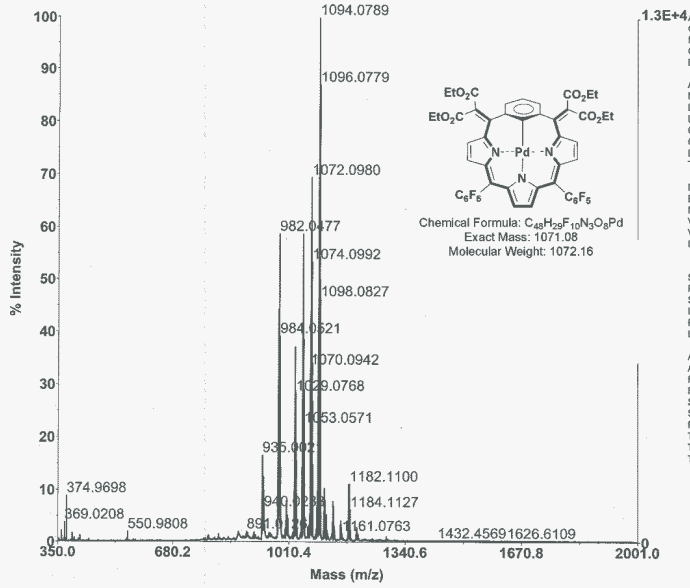


Figure S8. MALDI-TOF mass spectrum of compound **(4).**

Applied Biosystems Voyager System 4372

Voyager Spec #1=>NF1.0=>NR(2.00)[BP = 1094.1, 12717]



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Molecular Weight: 1072.16

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Grid voltage:	64%
Mirror voltage ratio:	1.12
Guide wire 0:	0.02%
Extraction delay time:	91 nsec
Acquisition mass range:	300 – 2000 Da
Number of laser shots:	200/spectrum
Laser intensity:	1668
Laser Rep Rate:	20.0 Hz
Calibration type:	External -- D:\CHLEE2\J...
Calibration matrix:	2,5-Dihydroxybenzoic acid
Low mass gate:	200 Da
Timed ion selector:	Off
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Bin size:	1 nsec
Number of data points:	40164
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Vertical offset:	0%
Input bandwidth 0:	500 MHz
Sample well:	45
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Serial number:	4372
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Plate type filename:	C:\VOYAGER\100 well plate.plt
Lab name:	PE Biosystems
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Absolute y-position:	26995.6
Relative x-position:	-553.587
Relative y-position:	8.05372
Shots in spectrum:	200
Source pressure:	1.22e-007
Mirror pressure:	5.022e-008
TC2 pressure:	0.001
TIS gate width:	8
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Printed: 04:56, August 27, 2009

Figure S9. ^{1}H NMR spectrum of compound **(5)** in $CDCl_3$

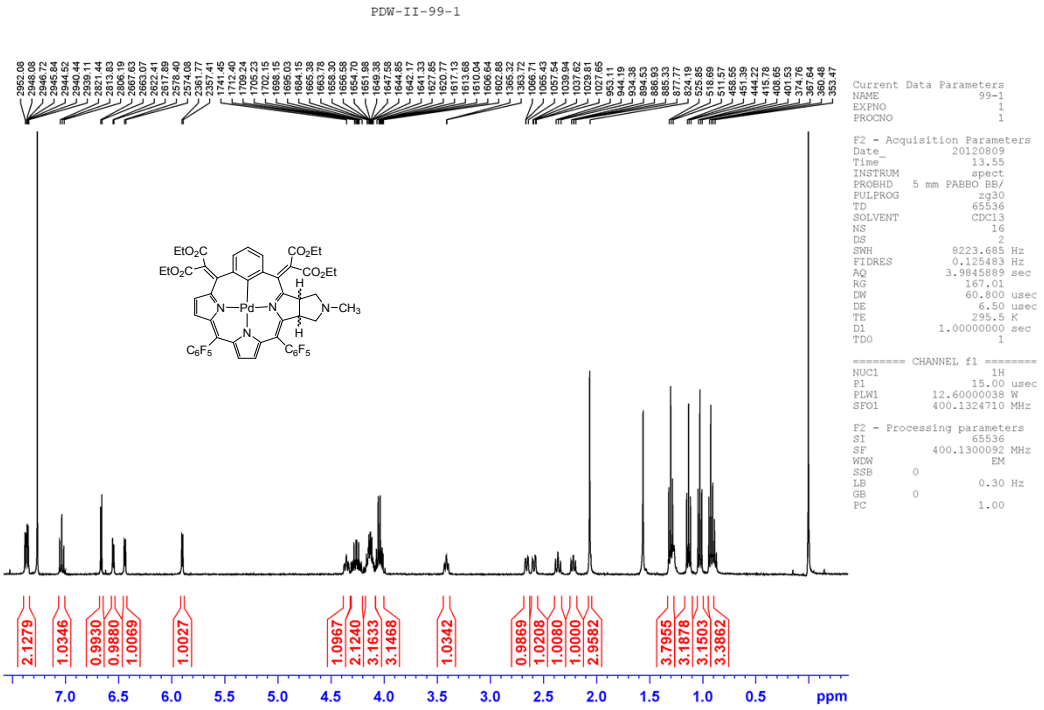


Figure S10. ^{13}C NMR spectrum of compound **(5)** in $CDCl_3$

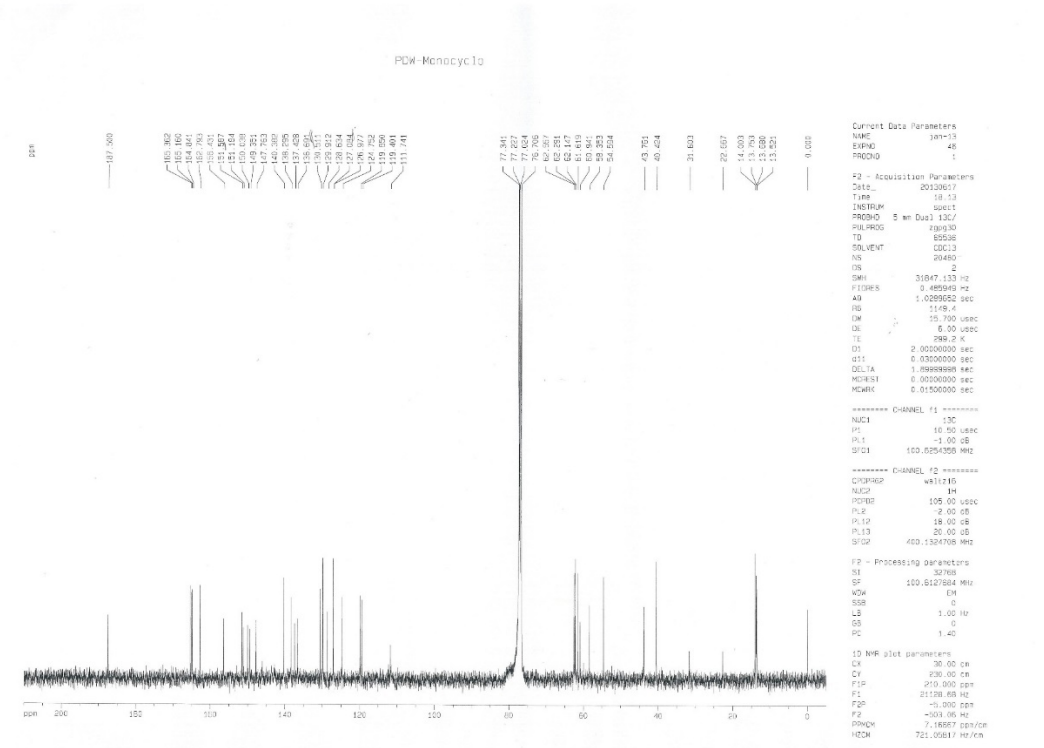


Figure S11. MALDI-TOF mass spectrum of compound **(5)**

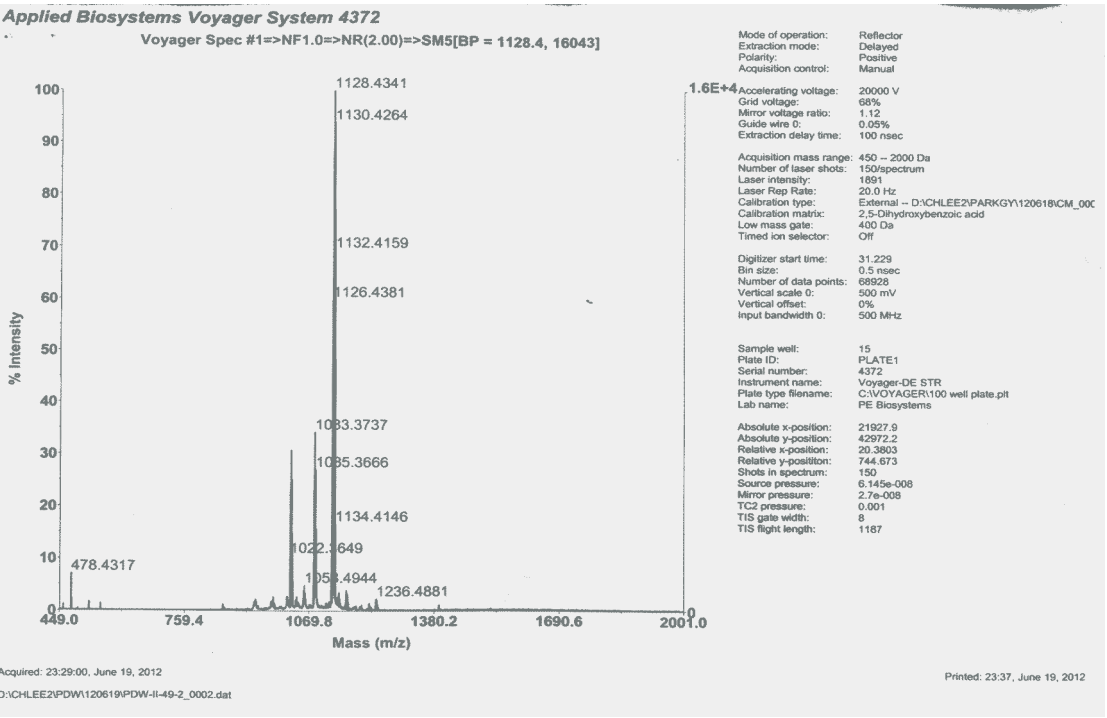
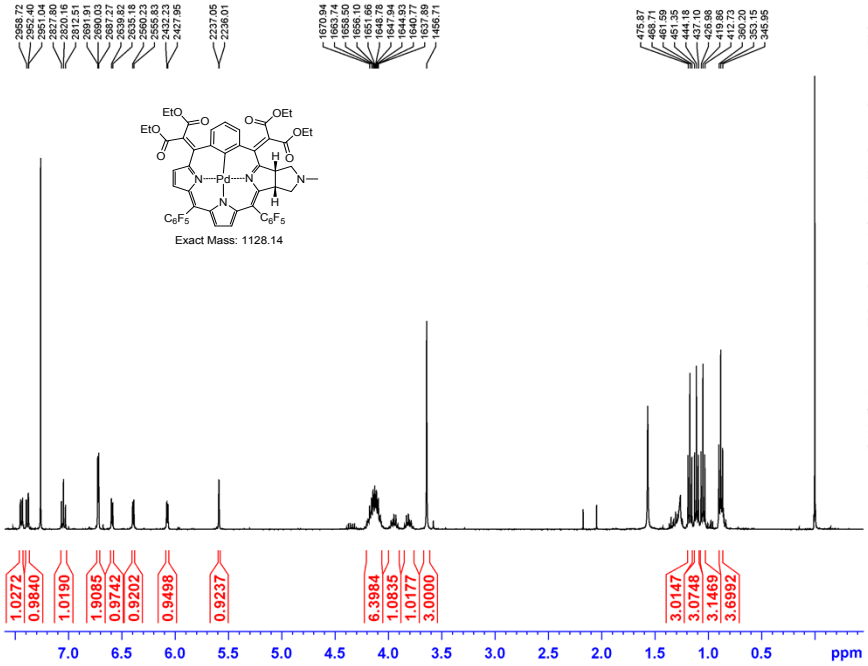


Figure S12. ^{1}H NMR spectrum of compound **(6)** in $CDCl_3$

PDW-II-103

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PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
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DS                         2
SWH                 8223.685 Hz
FIDRES              0.125483 Hz
AQ                  3.9845889 sec
RG                     140.47
DW                     60.800 usec
DE                      6.50 usec
TE                     296.2 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                       1H
P1                      15.00 usec
PLW1             12.60000038 W
SFO1             400.1324710 MHz

F2 - Processing parameters
SI                     65536
SF               400.1300091 MHz
WDW                       EM
SSB       0
LB                      0.30 Hz
GB        0
PC                      1.00
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Figure S13. MALDI-TOF mass spectrum of compound **(6)**

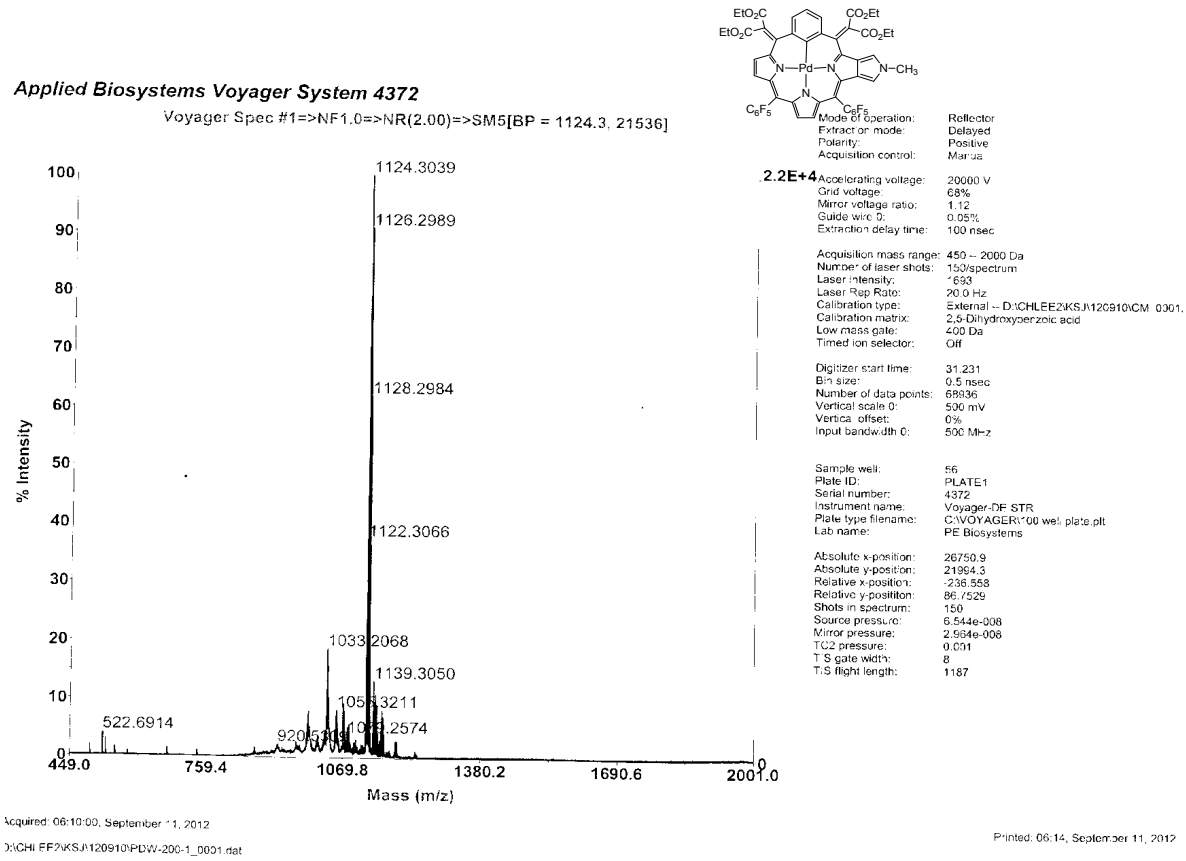


Figure S14. ^{1}H NMR spectrum of compound **(7)** in $CDCl_3$.

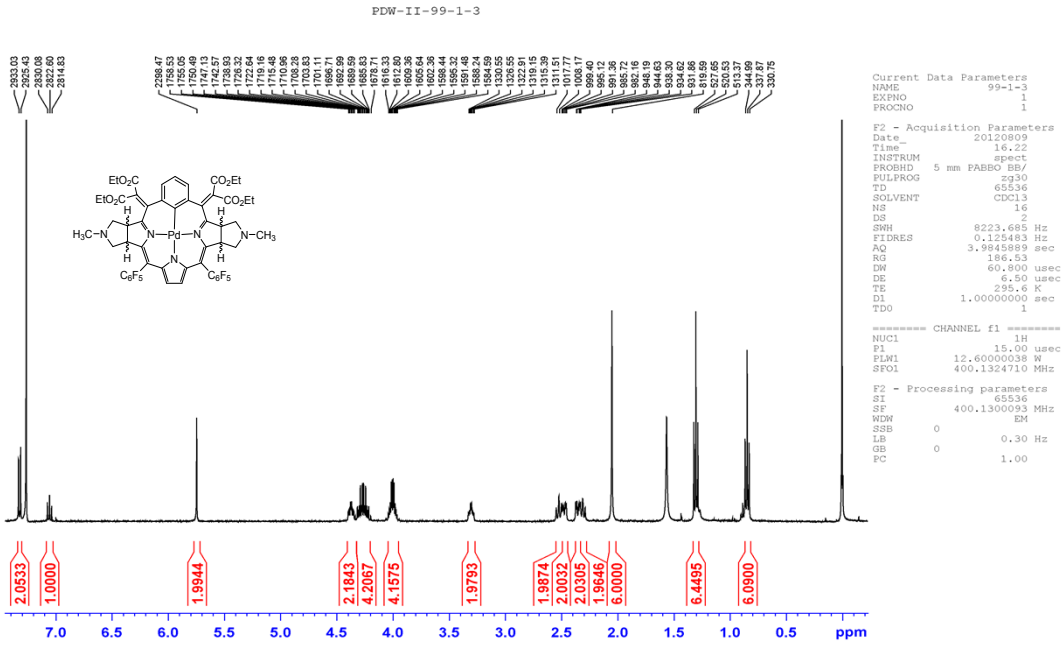


Figure S15. ^{13}C NMR spectrum of of compound **(7)** in $CDCl_3$

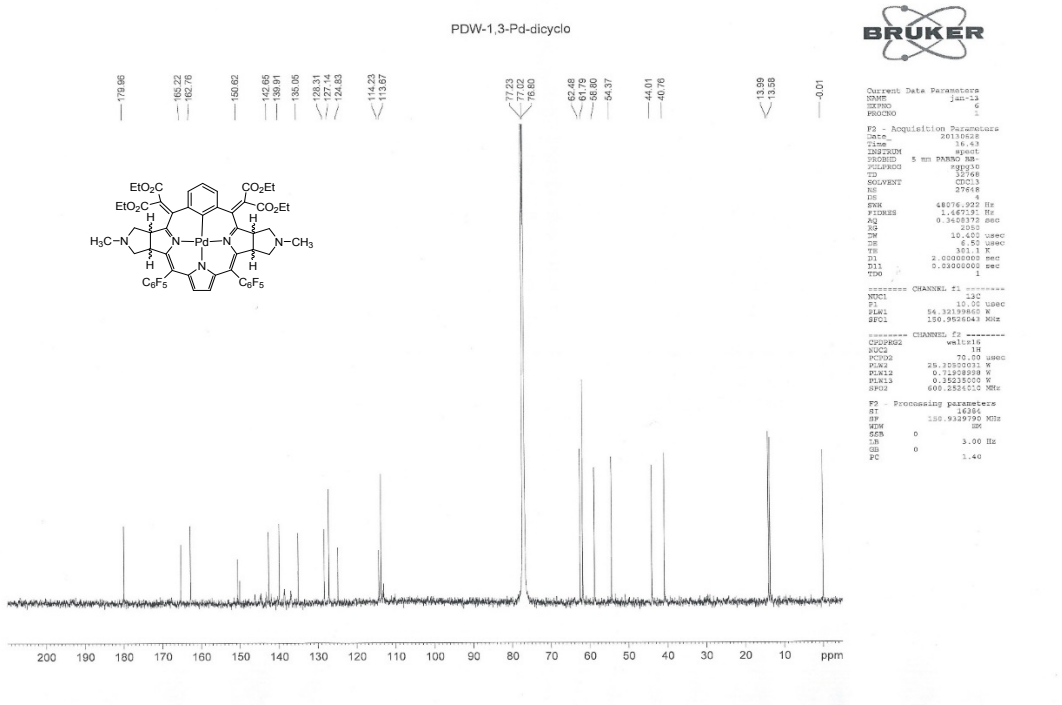


Figure S16. MALDI-TOF mass spectrum of compound **(7)**.

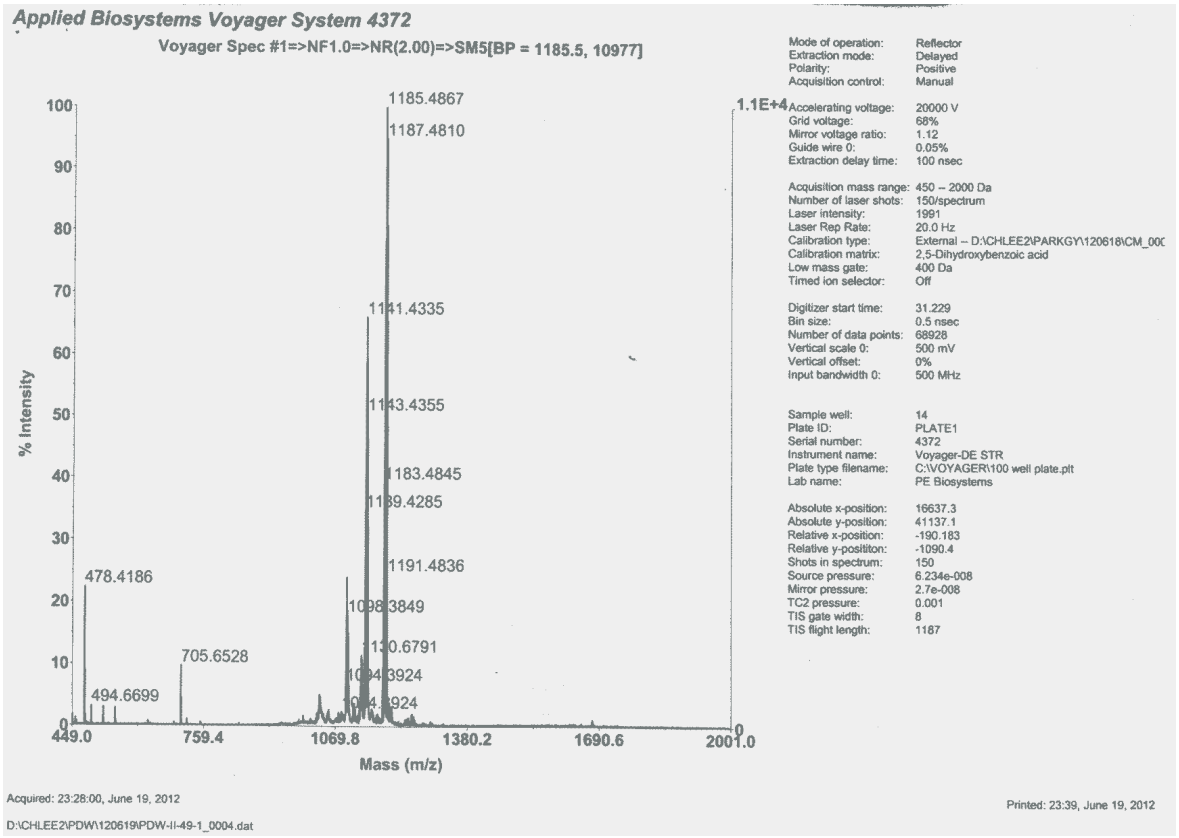


Figure S17. ^{1}H NMR spectrum of compound (**9**) in $CDCl_3$.

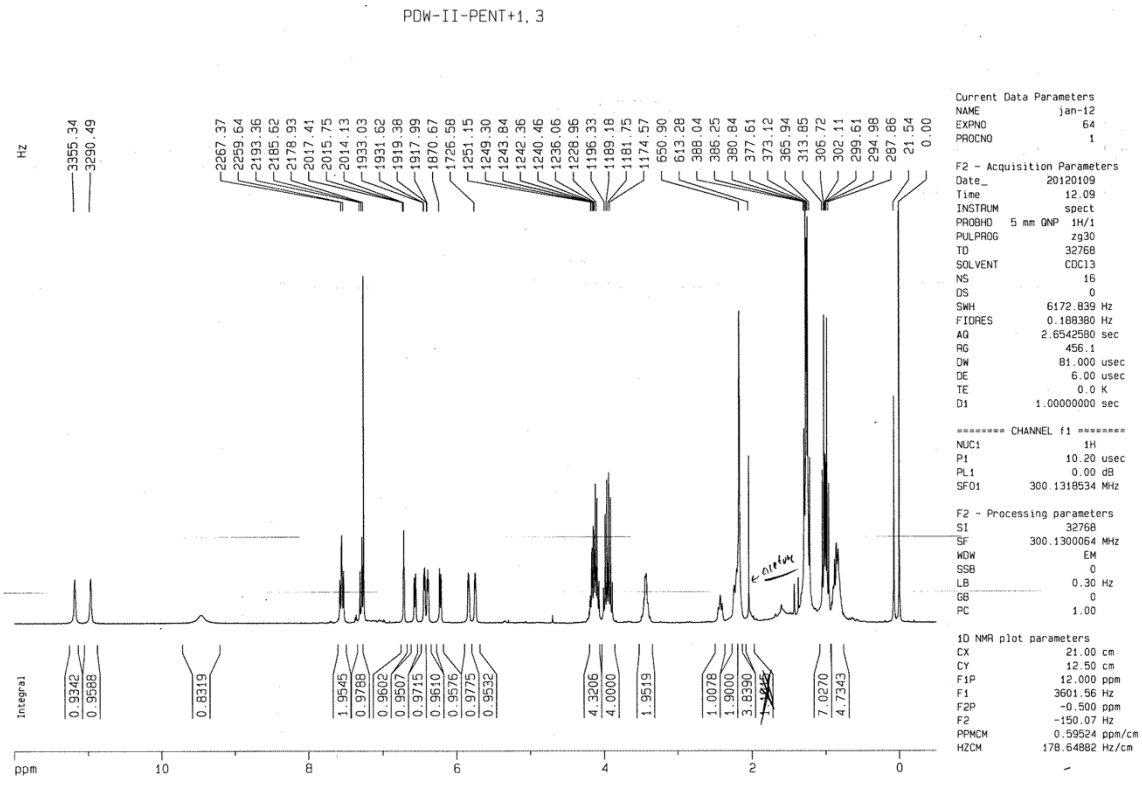


Figure S18. ^{13}C NMR spectrum of compound (**9**) in $CDCl_3$.

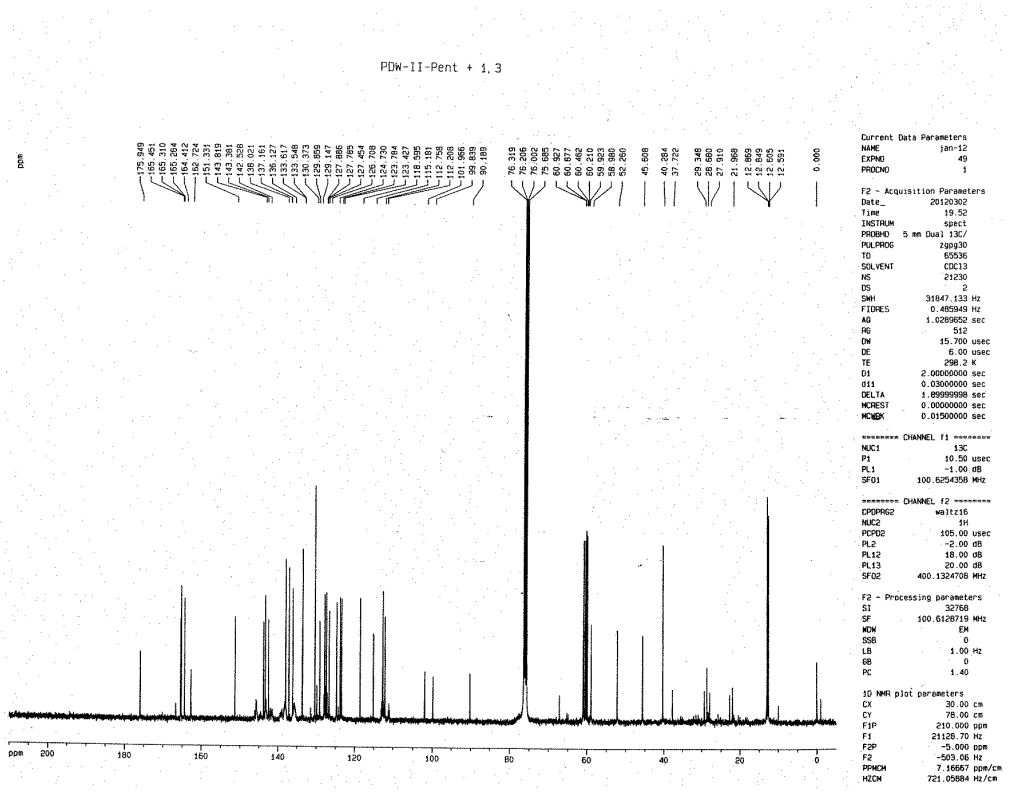


Figure S19. MALDI-TOF Mass spectrum of compound (**9**).

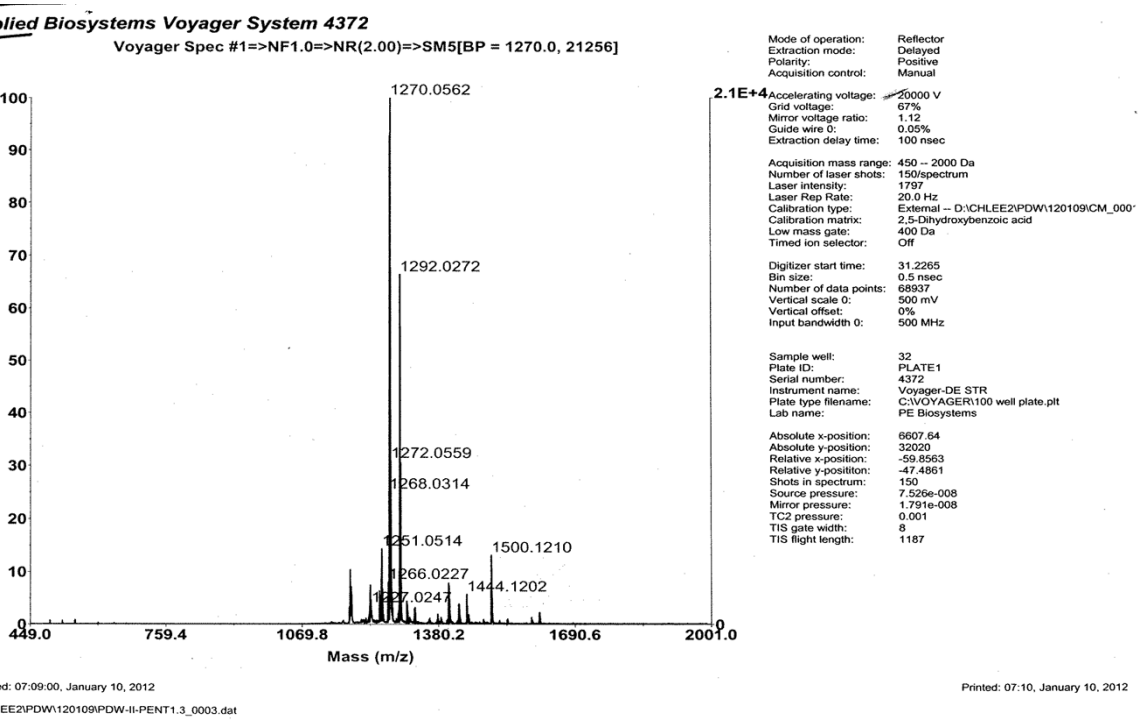
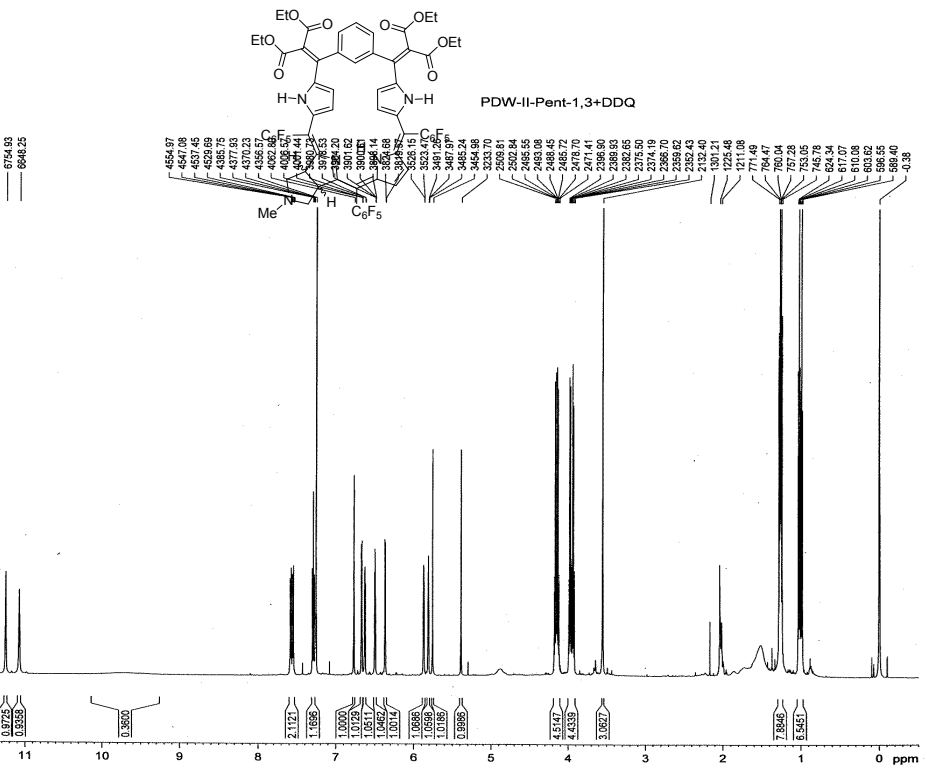


Figure S20. ^{1}H NMR spectrum of spectrum of compound (**10**) in $CDCl_3$.



BRUKER

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PROCNO                     1

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FIDRES            0.376450 Hz
AQ                1.3282462 sec
RG                      456
DW                 40.533 usec
DE                  6.00 usec
TE                 300.5 K
D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    1H
P1                 12.00 usec
PL1                -2.80 dB
SFO1          600.2537068 MHz

F2 - Processing parameters
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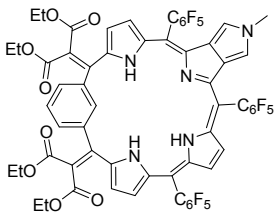

Figure S21. ^{13}C NMR spectrum of spectrum of compound (**10**) in $CDCl_3$.

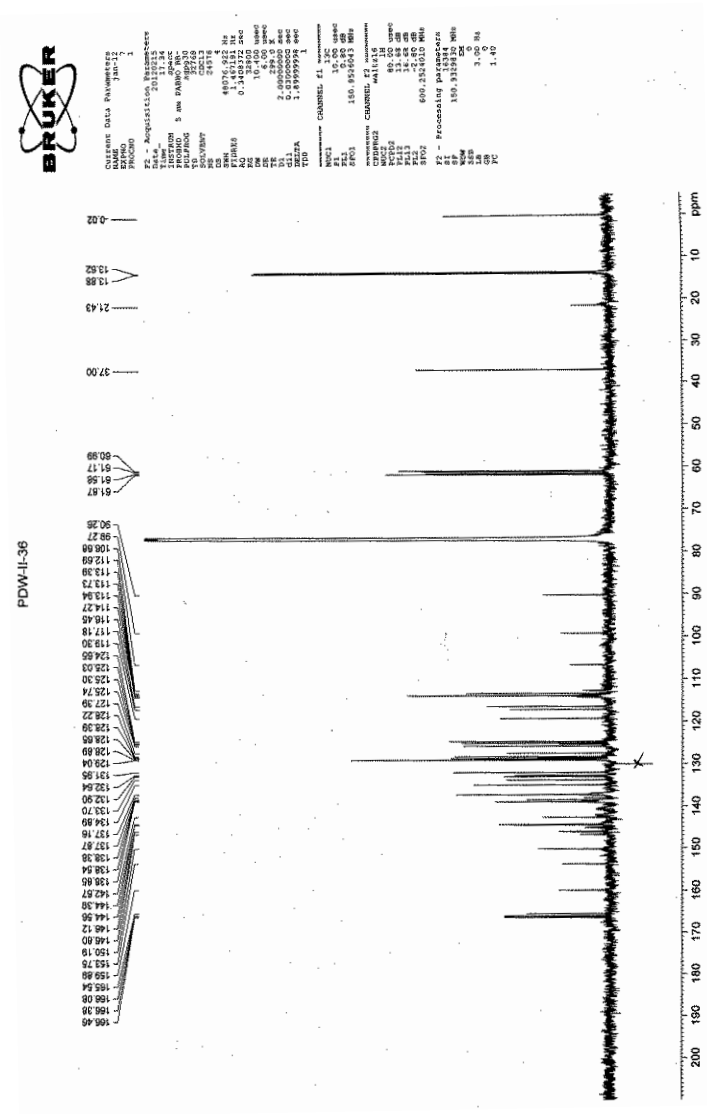

Figure S22. MALDI-TOF Mass spectrum of compound (**10**).

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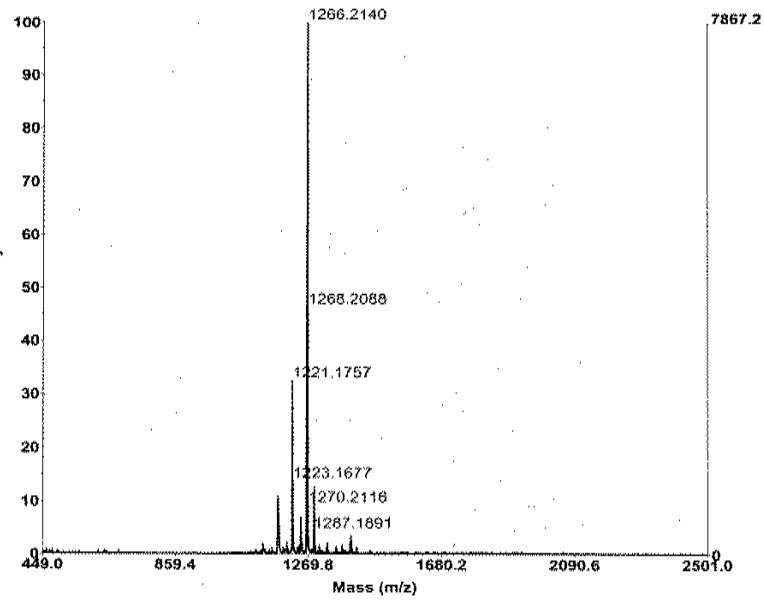
Voyager Spec #1=>NF1.0=>NR(2.00)=>SM5(BP = 1266.2, 7867]



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Grid voltage:	68%
Mirror voltage ratio:	1.12
Guide wire 0:	0.05%
Extraction delay time:	95 nsec
Acquisition mass range:	450 – 2500 Da
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Laser intensity:	1841
Laser Rep Rate:	20.0 Hz
Calibration type:	External – D:\CHLEE2\PDW\120221\CM_000
Calibration matrix:	2,5-Dihydroxybenzoic acid
Low mass gate:	400 Da
Timed ion selector:	Off
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Bin size:	0.5 nsec
Number of data points:	84410
Vertical scale 0:	500 mV
Vertical offset:	0%
Input bandwidth 0:	500 MHz
Sample well:	75
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Serial number:	4372
Instrument name:	Voyager-DE STR
Plate type filename:	C:\VOYAGER\100 well plate.plt
Lab name:	PE Biosystems
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Absolute y-position:	11504.6
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Relative y-position:	-153.002
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Mirror pressure:	1.943e-008
TC2 pressure:	0.001
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Printed: 07:16, February 22, 2012

Figure S23. ^{1}H NMR spectrum of compound (**12**) in $CDCl_3$.

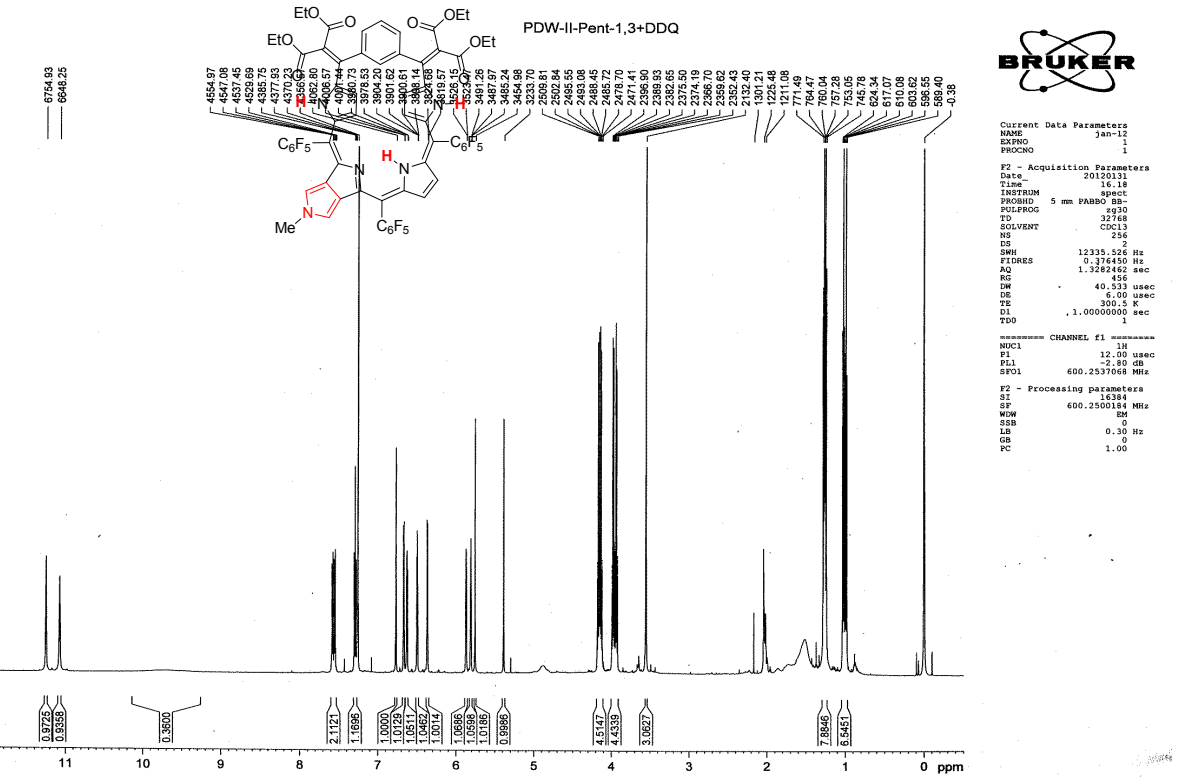
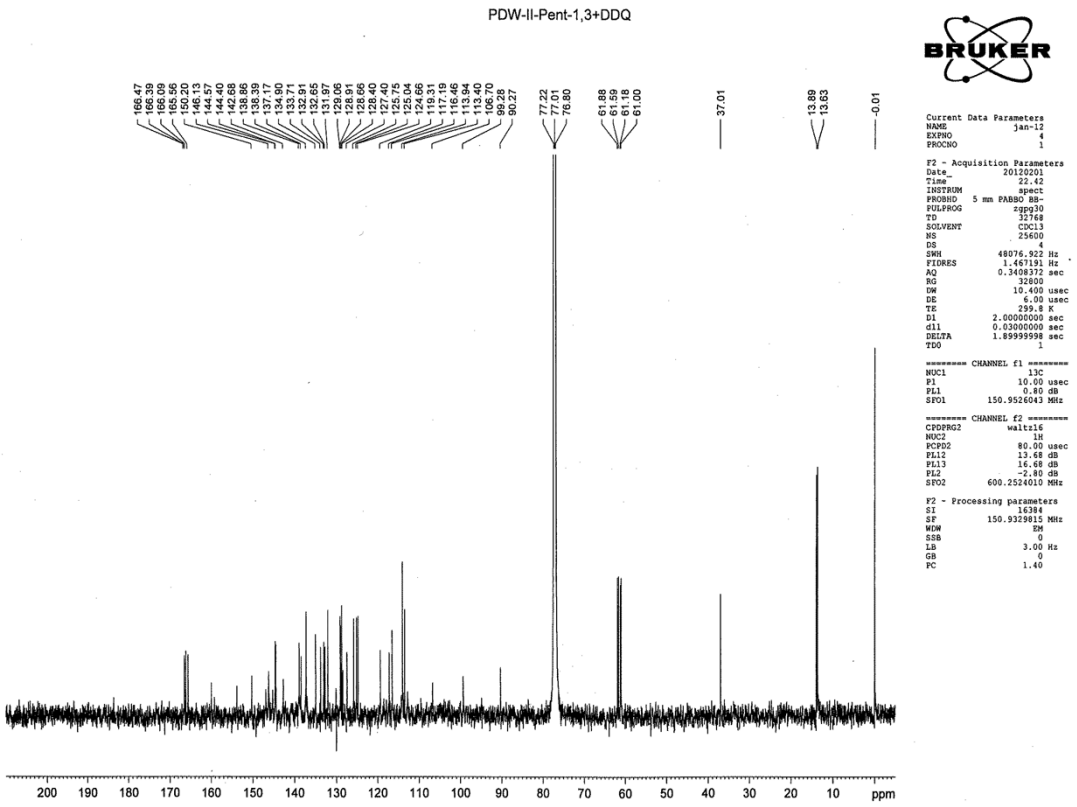


Figure S24. ^{13}C NMR spectrum of compound (**12**) in $CDCl_3$.

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AQ                  0.3408372 sec
RG                      32000
DW                     10.400 usec
DE                      6.00 usec
TE                     299.8 K
D1                 2.00000000 sec
d11                0.03000000 sec
DELTA              1.89999998 sec
TD0                        1

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P1                     10.00 usec
PL1                     0.80 dB
SFO1            150.9526043 MHz

======== CHANNEL f2 ========
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PCPD2                  80.00 usec
PL12                   13.68 dB
PL13                   16.68 dB
PL2                    -2.80 dB
SFO2            600.2524010 MHz

F2 - Processing parameters
SI                        16384
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WDW                       EM
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GB                         0
PC                      1.40
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Figure S25. MALDI-TOF Mass spectrum of compound (**12**) in $CDCl_3$.

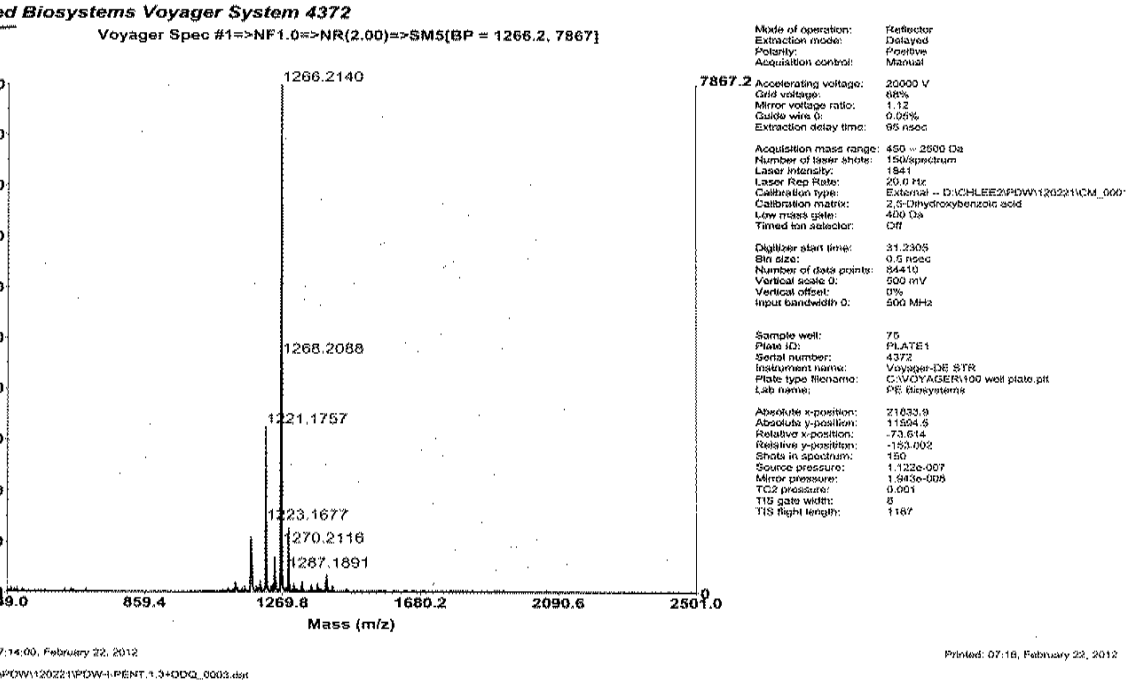


Figure S26. ^{1}H NMR spectrum of compound (**13**) in $CDCl_3$.

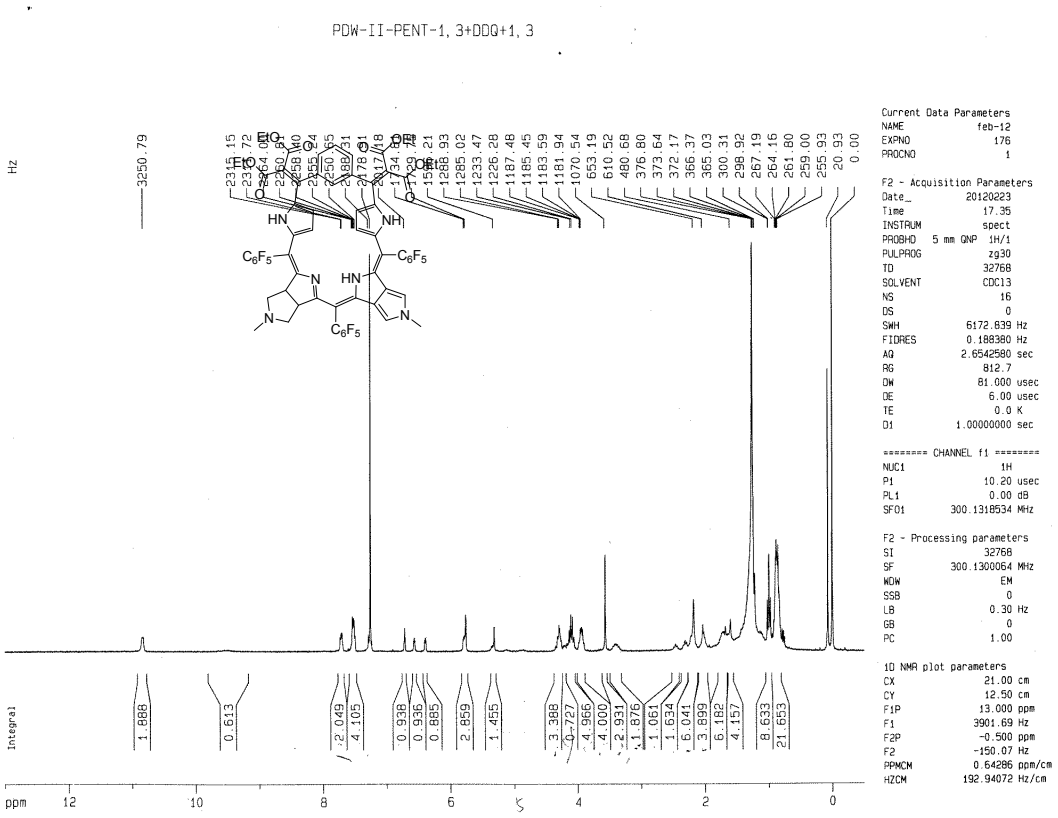


Figure S27. MALDI-TOF Mass spectrum of compound (**13**).

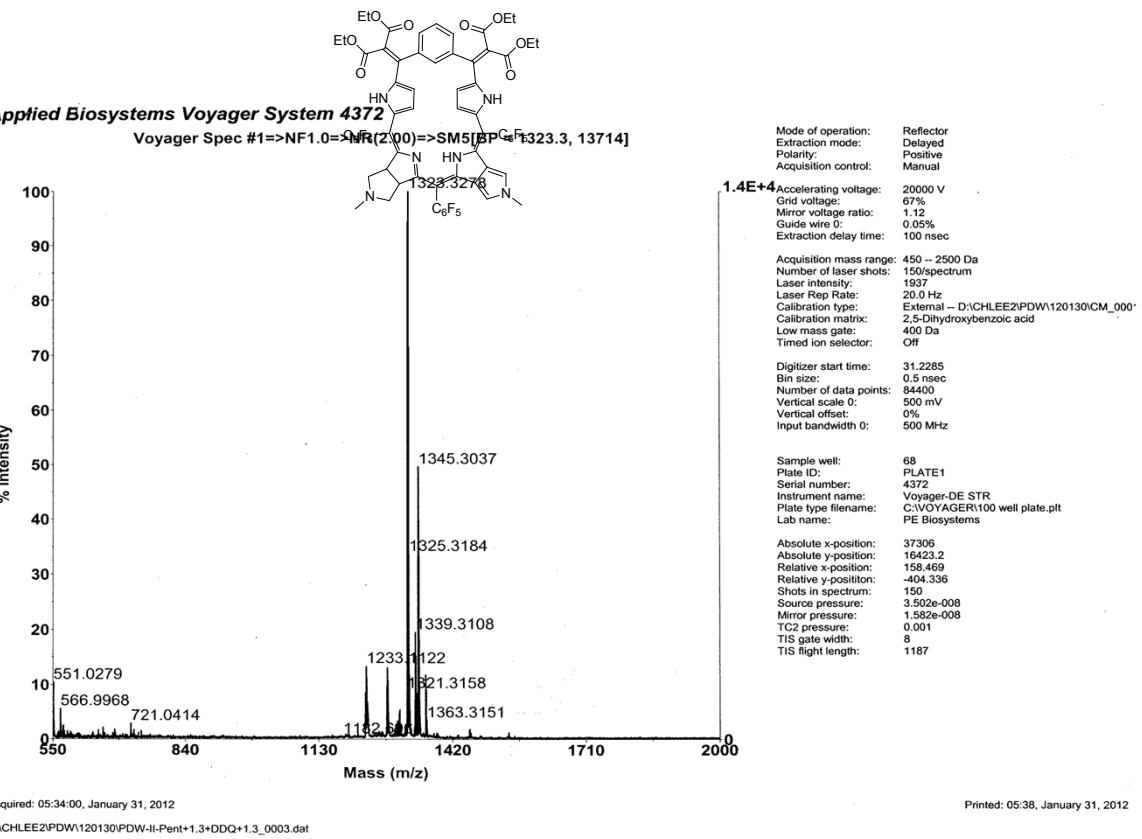
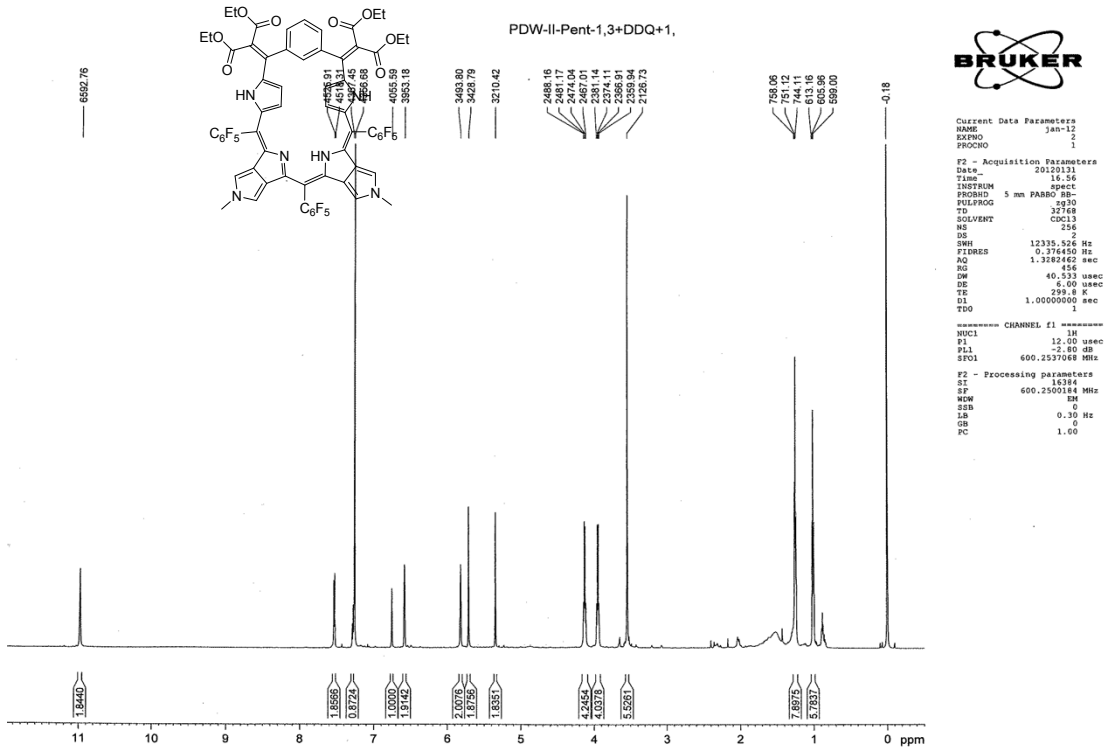


Figure S28. ^{1}H NMR spectrum of 6,26-Bis(diethoxycarbonylmethylidene)-11,16,21-di(pentafluorophenyl)-12,13[c]-(*N*-methylpyrrloe)-18,19[c]-(*N*-methylpyrrole)-(m-benzi)pentaphyrin (**14**) in $CDCl_3$.



BRUKER

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PROCNO                     1

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TD                    32768
SOLVENT               CDCl3
NS                      256
DS                        2
SWH               12335.526 Hz
FIDRES             0.376450 Hz
AQ                 1.3282462 sec
RG                      456
DW                   40.533 usec
DE                    6.00 usec
TE                   299.8 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                    12.00 usec
PL1                   -2.80 dB
SFO1             600.2537068 MHz

F2 - Processing parameters
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SF               600.2500184 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
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Figure S29. ^{13}C NMR spectrum of 6,26-Bis(diethoxycarbonylmethylidene)-11,16,21-di(pentafluorophenyl)-12,13[c]-(*N*-methylpyrrloe)-18,19[c]-(*N*-methylpyrrole)-(*m*-benzi)pentaphyrin (**14**) in $CDCl_3$.

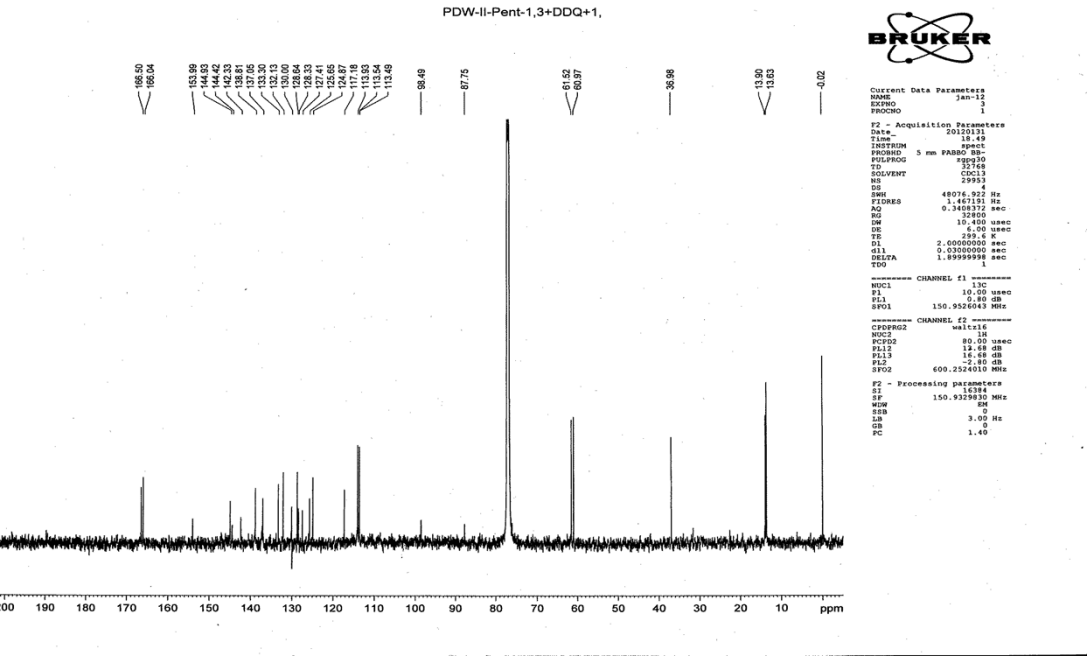

Figure S30. MALDI-TOF Mass of 6,26-Bis(diethoxycarbonylmethylidene)-11,16,21-di(pentafluorophenyl)-12,13[c]-(*N*-methylpyrrloe)-18,19[c]-(*N*-methylpyrrole)-(*m*-benzi)pentaphyrin (**14**).

Biosystems Voyager System 4372

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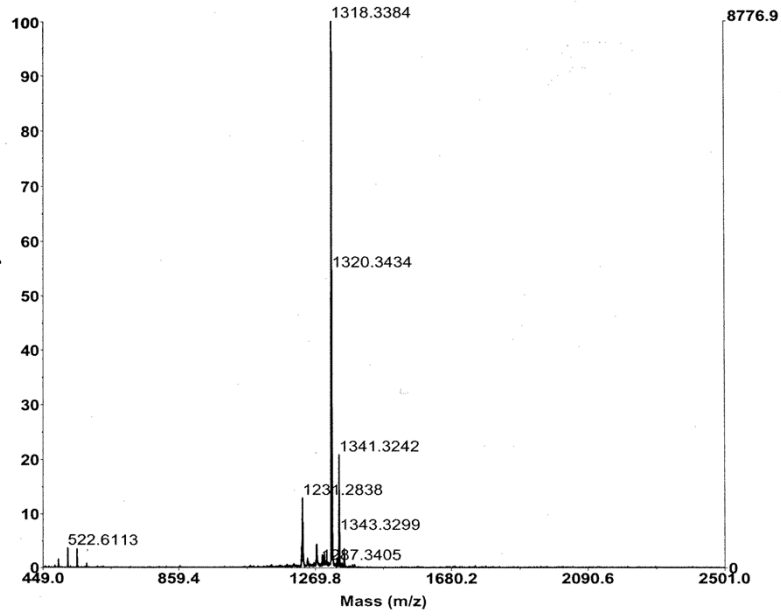

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Grid voltage:	67%
Mirror voltage ratio:	1.12
Guide wire 0:	0.05%
Extraction delay time:	100 nsec
Acquisition mass range:	450 -- 2500 Da
Number of laser shots:	150/spectrum
Laser intensity:	1663
Laser Rep Rate:	20.0 Hz
Calibration type:	External -- D:\CHLEE2\PDW\120131\CM_000
Calibration matrix:	2,5-Dihydroxybenzoic acid
Low mass gate:	400 Da
Timed ion selector:	Off
Digitizer start time:	31.2275
Bin size:	0.5 nsec
Number of data points:	84403
Vertical scale 0:	500 mV
Vertical offset:	0%
Input bandwidth 0:	500 MHz
Sample well:	74
Plate ID:	PLATE1
Serial number:	4372
Instrument name:	Voyager-DE STR
Plate type filename:	C:\VOYAGER\100 well plate.plt
Lab name:	PE Biosystems
Absolute x-position:	16505.7
Absolute y-position:	11322
Relative x-position:	-321.81
Relative y-posititon:	-425.507
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Source pressure:	1.075e-007
Mirror pressure:	1.855e-008
TC2 pressure:	0.001
TIS gate width:	8
TIS flight length:	1187

ired: 07:34:00, February 01, 2012

HLEE2\PDW\120131\PDW-II-PENT1.3+DDQ+1.3+DDQ_0001.dat

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