Electronic Supplementary Material (ESI) for New Journal of Chemistry.
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Supplementary Information for:

Synthesis and Photophysical Characteristics of 2,3,12,13-Tetraalkylbacteriochlorins

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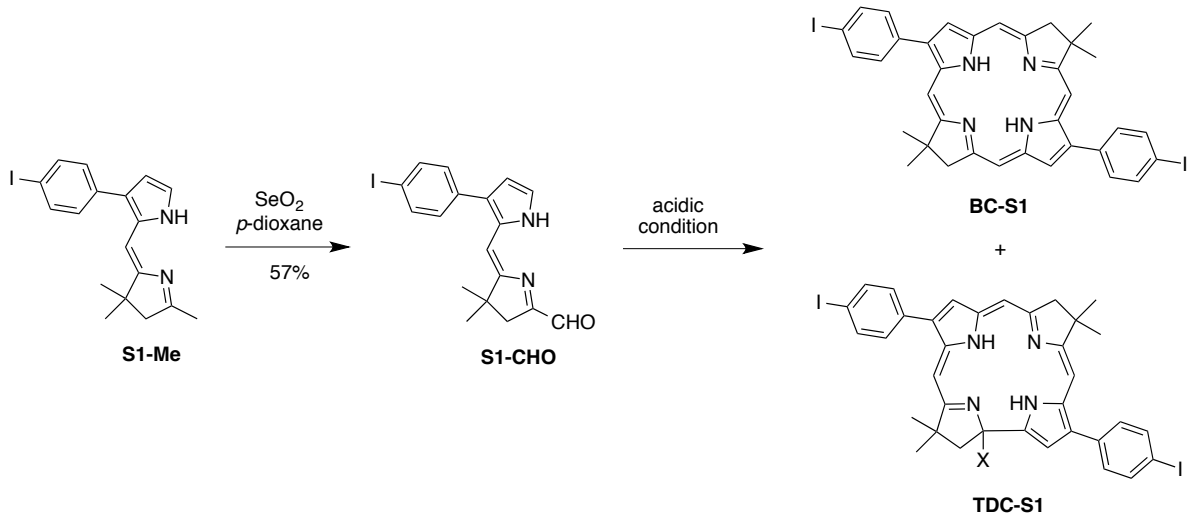
David F. Bocian,* Dewey Holten,* and Jonathan S. Lindsey*

Table of Contents

1. Acid catalysis survey of the self-condensation of a dihydrodipyrrin-carboxaldehyde



Scheme S1. Self-condensation of dihydrodipyrrin-carboxaldehyde **S1-CHO**.

1.1. Preparation of dihydrodipyrrin-carboxaldehyde S1-CHO.

1-Formyl-2,3-dihydro-3,3-dimethyl-7-(4-iodophenyl)dipyrrin (S1-CHO). A solution of **S1-Me**[S1] (50 mg, 0.13 mmol) in 1,4-dioxane (2.6 mL) was treated with SeO_2 (21 mg, 0.19 mmol) at room temperature. The reaction mixture was stirred at room temperature and monitored via UV-Vis spectroscopy. After completion (in this case 2 h), the reaction mixture was treated with saturated aqueous $NaHCO_3$ solution and extracted with ethyl acetate. The organic extract was washed (brine), dried (Na_2SO_4), concentrated, and chromatographed [silica, hexanes/ethyl acetate (3:1)] to afford a red solid (30 mg, 57%): ^{1}H NMR δ 1.23 (s, 6H), 2.73 (s, 2H), 6.30 (s, 1H), 6.33 (m, 1H), 7.01 (m, 1H), 7.18 (d, J = 5.1 Hz, 2H), 7.75 (d, J = 5.1 Hz, 2H), 10.00 (s, 1H), 10.81 (br, 1H); ^{13}C NMR δ 29.4, 41.3, 46.2, 91.9, 110.0, 112.5, 122.2, 127.3, 130.8, 136.0, 137.9, 161.3, 169.4, 190.2 (14 out of 15 distinct carbons were found); ESI-MS obsd 405.0465, calcd 405.0458 [$(M + H)^+$, M = $C_{18}H_{17}N_2OI$].

1.2. Survey of acidic conditions. The reactions of **S1-CHO** in the presence of different acids were examined. Each reaction was carried out (1.0 mL scale) with 10 mM dihydrodipyrrin-carboxaldehyde **S1-CHO** and the indicated amount of acid in CH_2Cl_2 at room temperature in a microreaction vial. Each reaction was monitored by UV-Vis absorption spectroscopy. Once the starting material was consumed and the absorption spectrum no longer changed, the reaction mixture was quenched by the addition of saturated aqueous $NaHCO_3$ solution. The mixture was extracted with CH_2Cl_2. The organic extract was washed, dried and concentrated to give the crude product. The resulting **BC-S1** and **TDC-S1** were checked via absorption spectroscopy and MALDI-MS. The relative yield of each component was determined by absorption spectroscopy.

For most reactions (Entries 2, 3-7, and 9), the absorption spectrum of each crude product showed a typical tetradehydrocorrin absorption pattern. Also, the MALDI-MS analysis of reaction mixture showed a major peak at *m/z* = 762.9, consistent with a tetradehydrocorrin wherein X = H (likely a product rather than precursor ion on the basis of consideration of the reaction of **S1-CHO**). If not a product ion, such a composition would be expected to tautomerize to give the tetradehydrocorrole. Regardless, the resulting putative **TDC-S1** was unstable on silica column chromatography and was not isolated; hence, the assignment remains unproven.

Table S1. Survey conditions for self-condensation of **S1-CHO**. [a]

entry	acid	[acid], (mM)	time	BC-S1	TDC-S1
1	-[b]	-	48 h	-[c]	-[c]
2	$TsOH{\cdot}H_2O$ in CH_3OH	10	16 h	<1%[d]	major[e]
3	TFA	10	1 h	-[c]	-[c]
4	$ZnCl_2$	10	16 h	-[c]	major[f]
5	$In(OTf)_3$	10	1 h	<1%[d]	major[e]
6	$In(OTf)_3$	50	10 min	<1%[d]	major[e]
7	$Sc(OTf)_3$	10	1 h	<1%[d]	major[e]
8	$Zn(OTf)_2$	10	90 min	-[c]	trace
9	$ZnBr_2$	50	30 min	<1%	major[f]

[a]All reactions were carried out (1.0 mL scale) with 10 mM **S1-CHO** and the indicated amount of acid in CH_2Cl_2 at room temperature. Each reaction was monitored by UV-Vis absorption spectroscopy. Products were detected with MALDI-MS. [b]No acid was added. [c]Not detected. [d]**BC-S1** was isolated by chromatography [silica, hexanes/CH_2Cl_2 (1:1)], characterized by UV-Vis absorption spectroscopy and MALDI-MS. [e]Observed by MALDI-MS and UV-Vis absorption spectroscopy but was not isolated. M = H, H. [f]Observed by MALDI-MS and UV-Vis absorption spectroscopy but was not be isolated. M = Zn.

Reference.

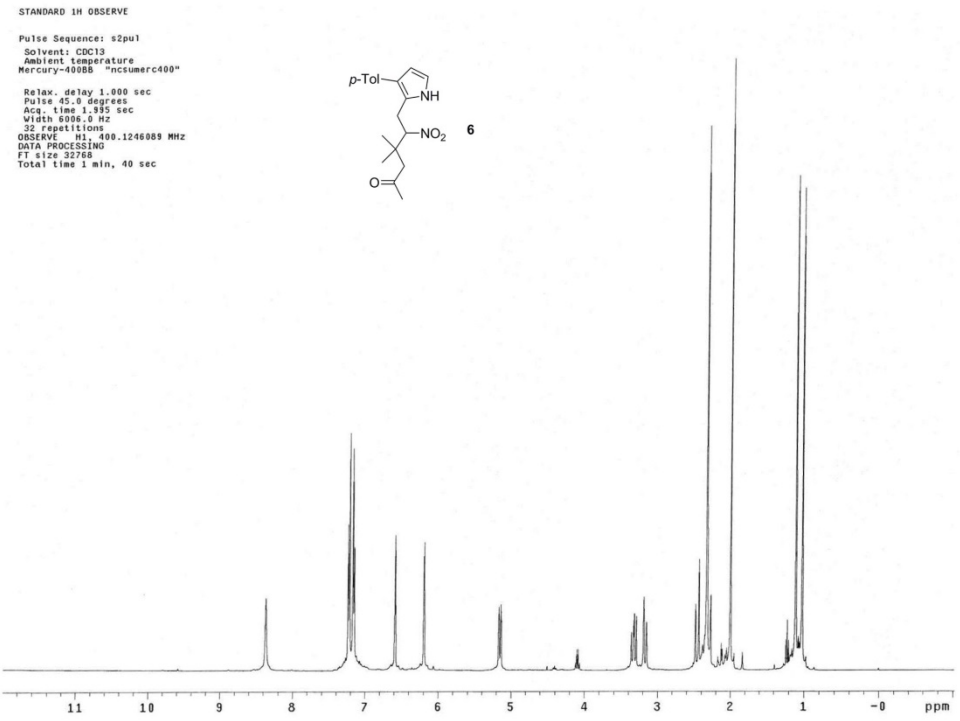
(S1) Balasubramanian, T.; Strachan, J.-P.; Boyle, P. D.; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 7919–7929.

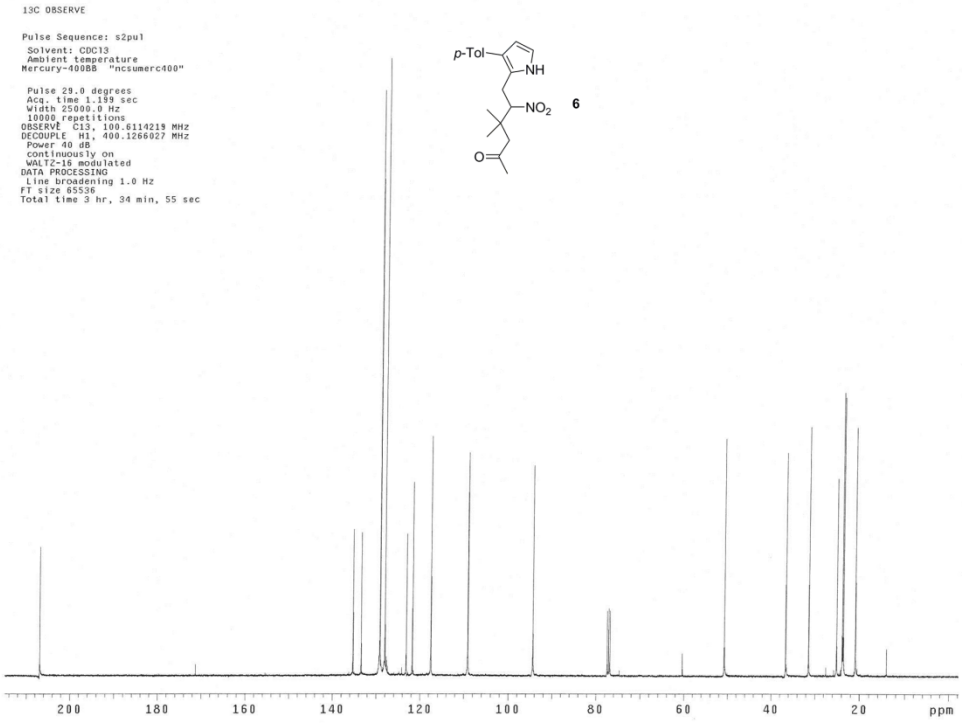
2. X-ray structural data for BC-MM

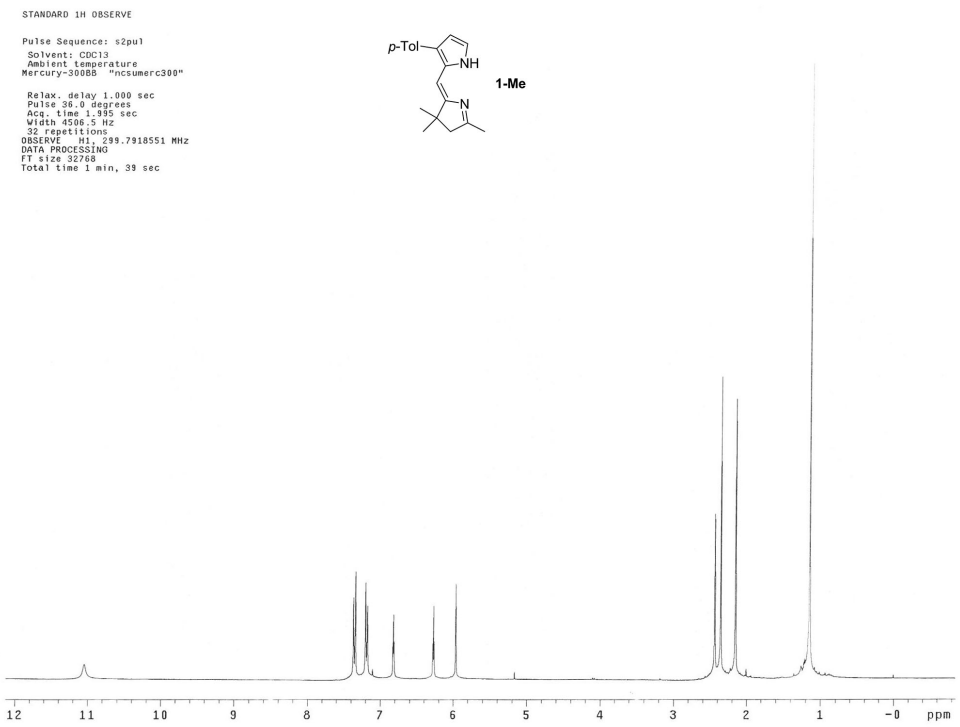
Table S2. Summary of Crystal Data for BC-MM

CCDC registry	
Formula	$C_{28}H_{34}N_4$
Formula Weight (g/mol)	426.59
Crystal Dimensions (mm)	0.136 × 0.241 × 0.483
Crystal System	Monoclinic
Space Group	$P2_{1/c}$
Temperature, K	100(2)
a, Å	7.6659(13)
b, Å	15.982(3)
c, Å	9.5235(15)
α, deg	90
β, deg	92.263(8)
γ, deg	90
V, Å^3	1165.9(3)
Number of reflections to determine final unit cell	158
Min and Max 2θ for cell determination (deg)	7.262, 59.29
Z	2
F (000)	460
ρ (g/cm)	1.215
λ, Å, (MoKα)	0.71073
μ, (mm^{-1})	0.072
Max 2θ for data collection (deg)	2.49, 31.20
Measured fraction of data	0.996
Number of reflections measured	25895
Unique reflections measured	3766
R_{merge}	3.83%
Number of parameters in least-squares	153
R_1	0.0436
wR_2	0.1184
R_1(all data)	0.0547
wR_2 (all data)	0.1251

3. Spectral data.



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Acq. time 1.995 sec
Width 4506.5 Hz
32 repetitions
OBSERVE H1, 299.7918551 MHz
DATA PROCESSING
FT size 32768
Total time 1 min, 39 sec
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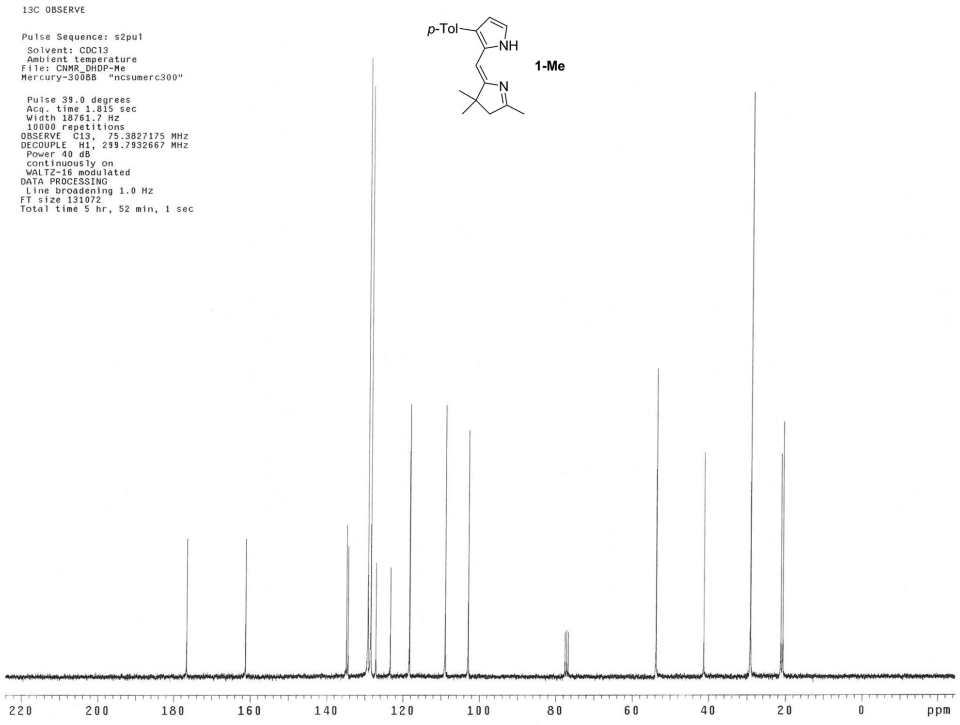
N
1-Me
12
11
10
9
8
7
6
5
4
3
2
1
-0
ppm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Acq. time 1.815 sec
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10000 repetitions
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DECOUPLE H1, 299.7932667 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 5 hr, 52 min, 1 sec
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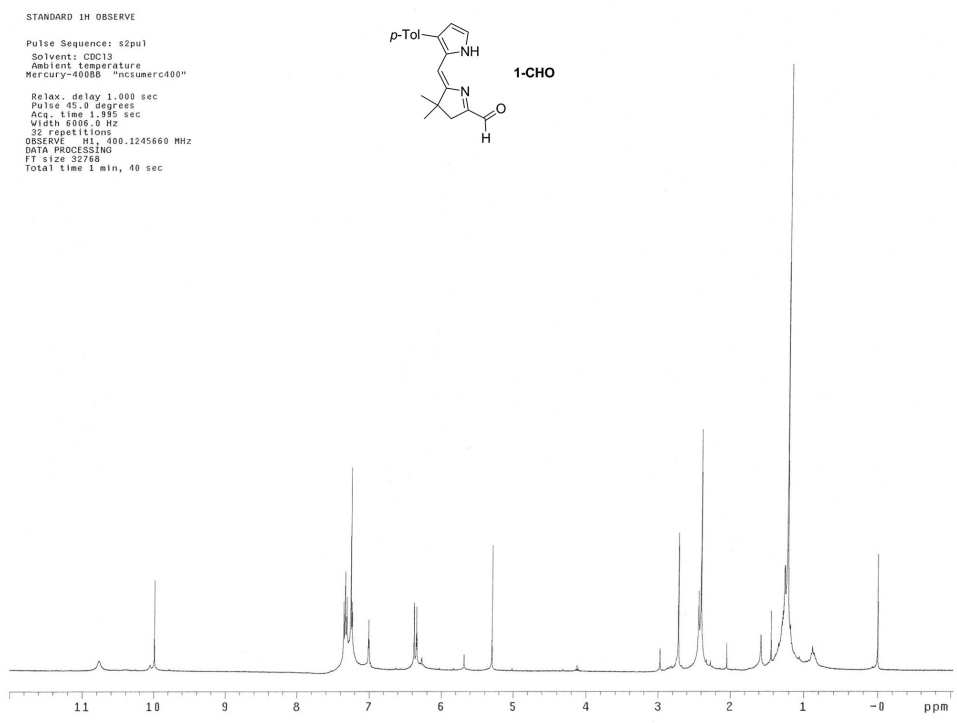
NH
N
1-Me
220
200
180
160
140
120
100
80
60
40
20
0
ppm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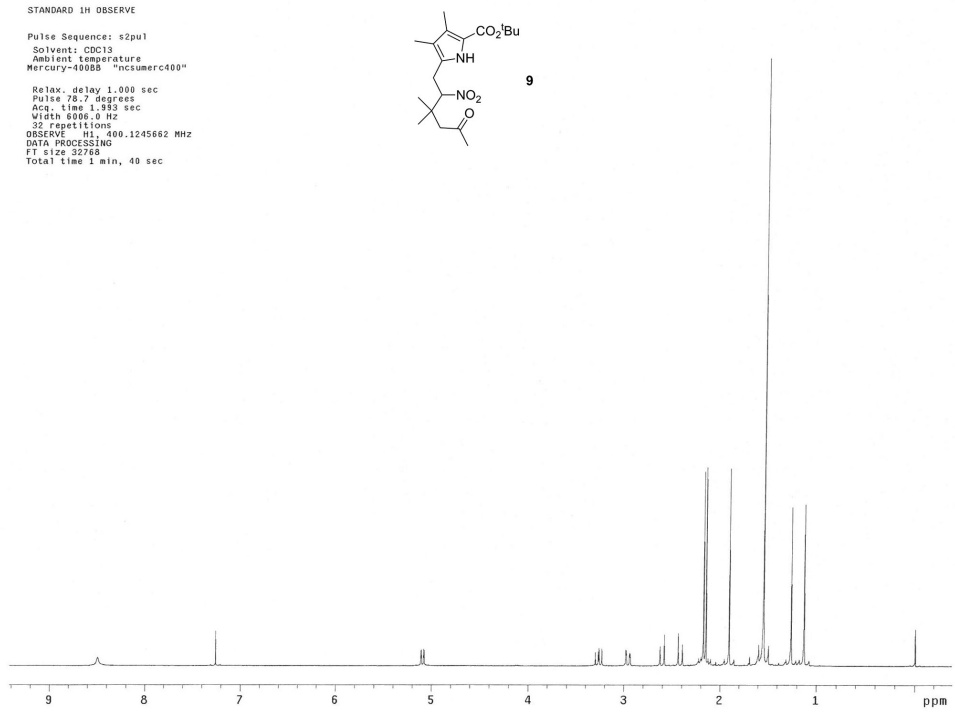
Pulse 45.0 degrees
Acq. time 1.995 sec
Width 6006.0 Hz
32 repetitions
OBSERVE H1, 400.1245660 MHz
DATA PROCESSING
FT size 32768
Total time 1 min, 40 sec
p-Tol
NH
N
O
H
1-CHO
11
10
9
8
7
6
5
4
3
2
1
-0
ppm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Ambient temperature
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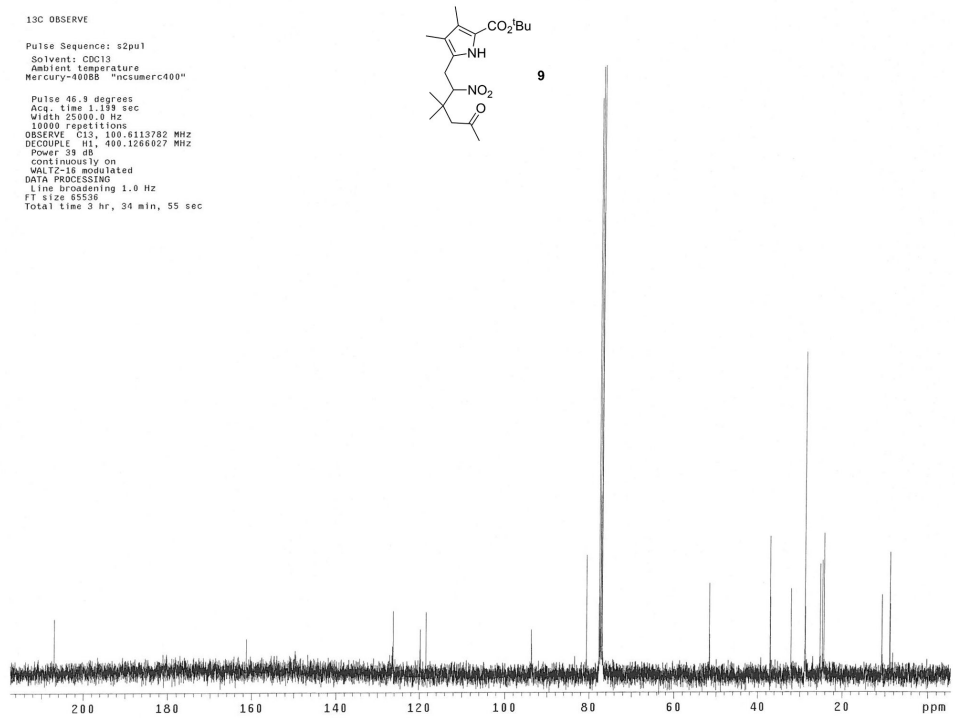
Relax. delay 1.000 sec
Pulse 78.7 degrees
Acq. time 1.993 sec
Width 6006.0 Hz
32 repetitions
OBSERVE H1, 400.1245662 MHz
DATA PROCESSING
FT size 32768
Total time 1 min, 40 sec
CO2tBu
NH
NO2
O
9
9
8
7
6
5
4
3
2
1
ppm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Width 25000.0 Hz
10000 repetitions
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DECOUPLE H1, 400.1266027 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 3 hr, 34 min, 55 sec
CO2tBu
NH
NO2
O
9
200
180
160
140
120
100
80
60
40
20
ppm

STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300BB "ncsumerc638"

Relax. delay 1.000 sec
Pulse 50.4 degrees
Acq. time 1.995 sec
Width 4506.5 Hz
16 repetitions
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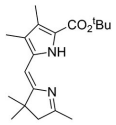
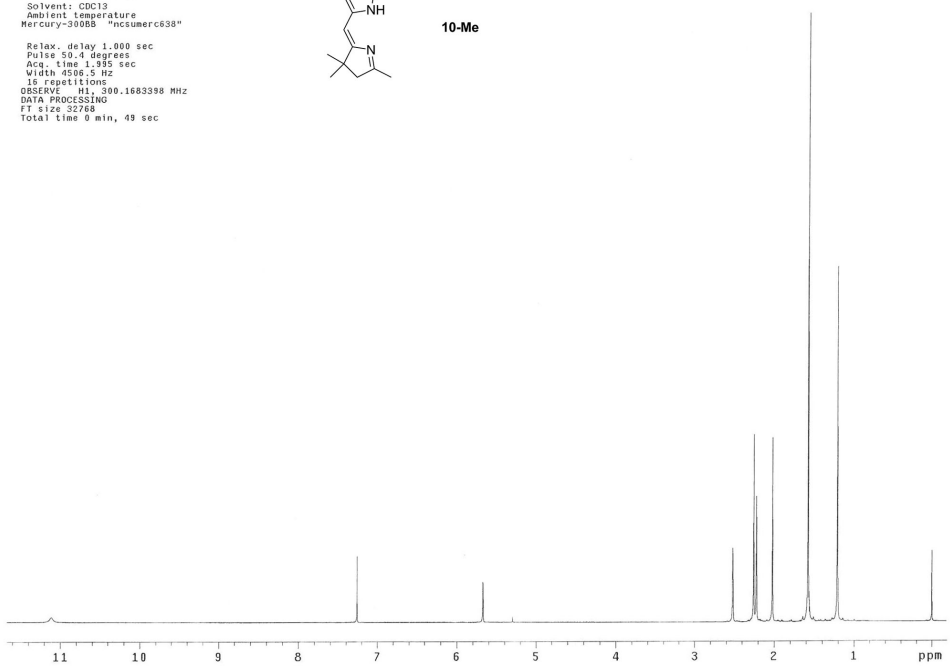
DATA PROCESSING
FT size 32768
Total time 0 min, 49 sec



10-Me



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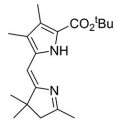
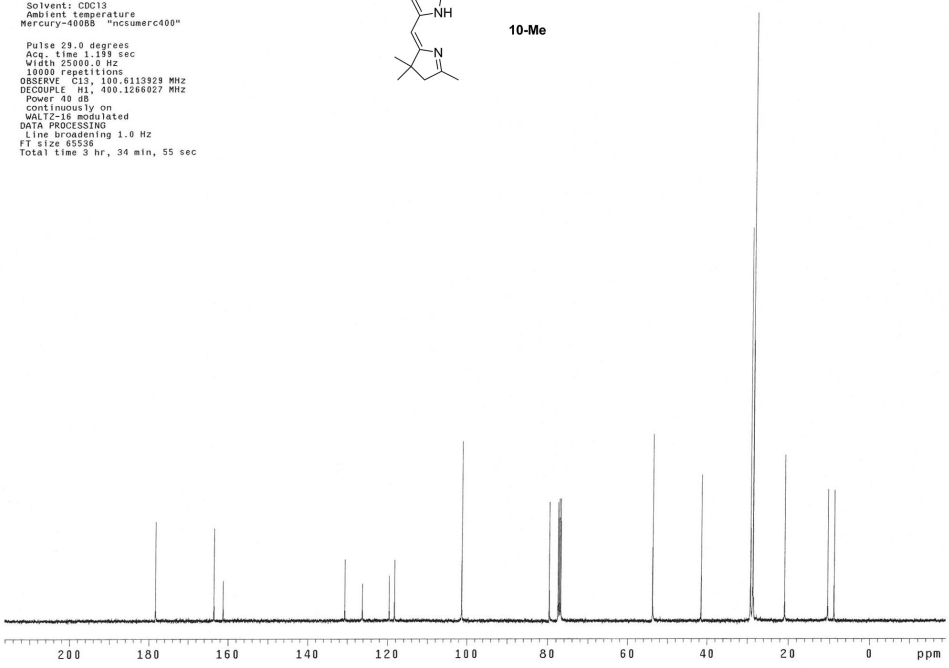
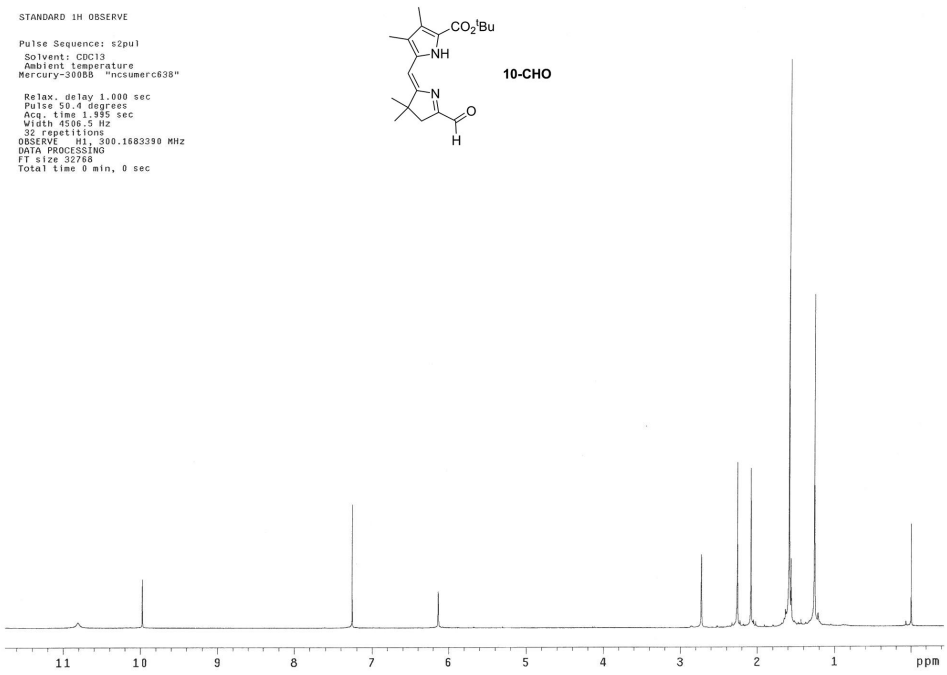
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "ncsumerc400"

Pulse 29.0 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
10000 repetitions
OBSERVE C13, 100.6113929 MHz
DECOUPLE H1, 400.1266027 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 3 hr, 34 min, 55 sec



10-Me

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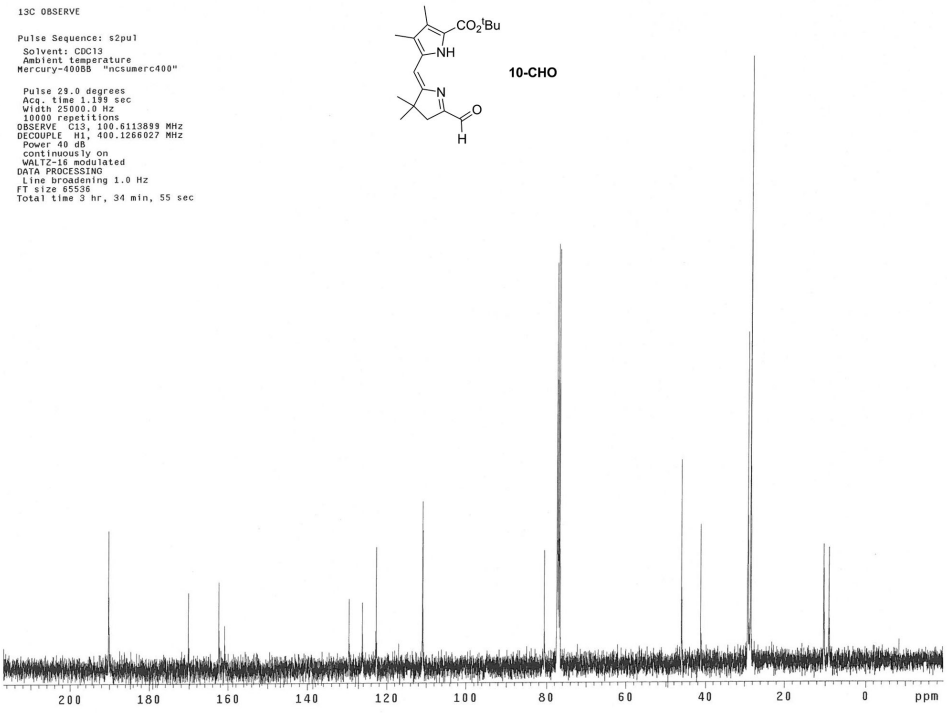
Solvent: CDCl3
Ambient temperature
Mercury-300BB "ncsumerc638"
Relax. delay 1.000 sec
Pulse 50.4 degrees
Acq. time 1.995 sec
Width 4506.5 Hz
32 repetitions
OBSERVE H1, 300.1683390 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 0 sec
CO2tBu
NH
N
O
H
10-CHO
11
10
9
8
7
6
5
4
3
2
1
ppm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Solvent: CDCl3
Ambient temperature
Mercury-400BB "ncsumerc400"
Pulse 29.0 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
10000 repetitions
OBSERVE C13, 100.6113889 MHz
DECOUPLE H1, 400.1266027 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 3 hr, 34 min, 55 sec
CO2tBu
NH
N
O
H
10-CHO
200
180
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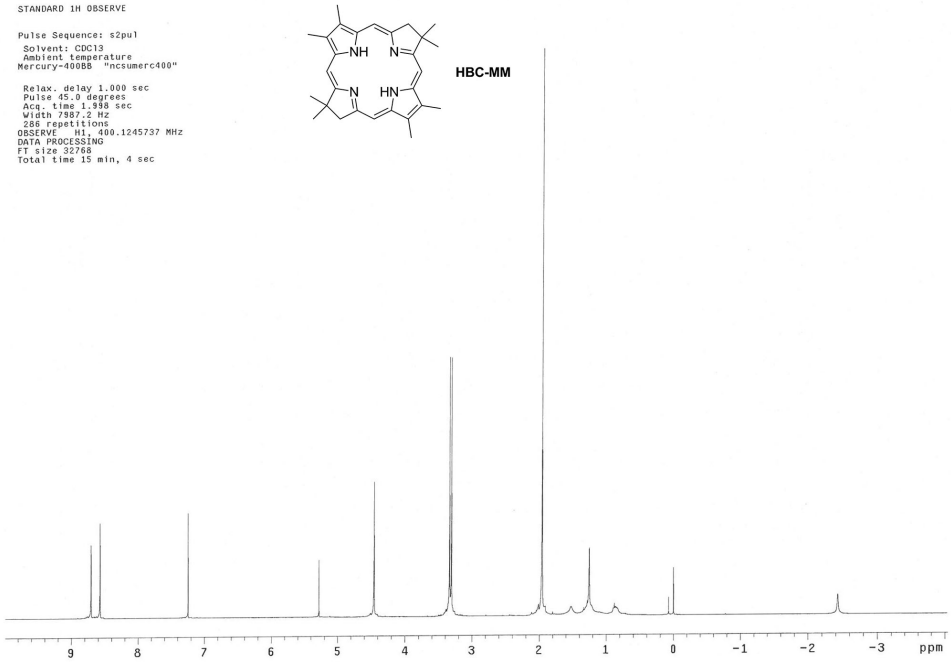
140
120
100
80
60
40
20
0
ppm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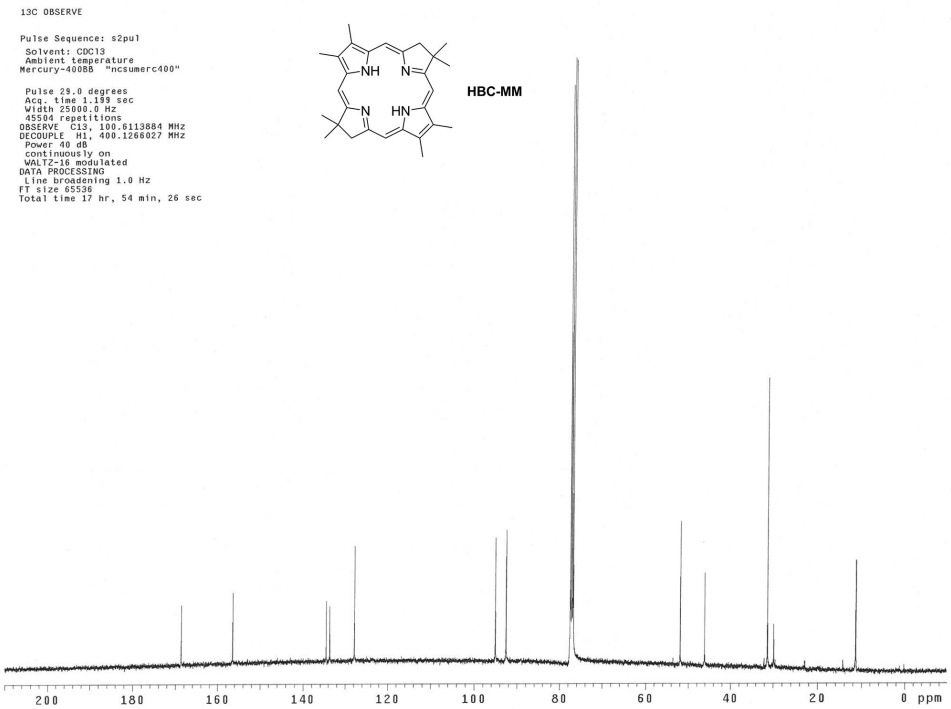
Ambient temperature
Mercury-400BB "ncsumerc400"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.998 sec
Width 7987.2 Hz
286 repetitions
OBSERVE H1, 400.1245737 MHz
DATA PROCESSING
FT size 32768
Total time 15 min, 4 sec
NH
N
N
HN
HBC-MM
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
ppm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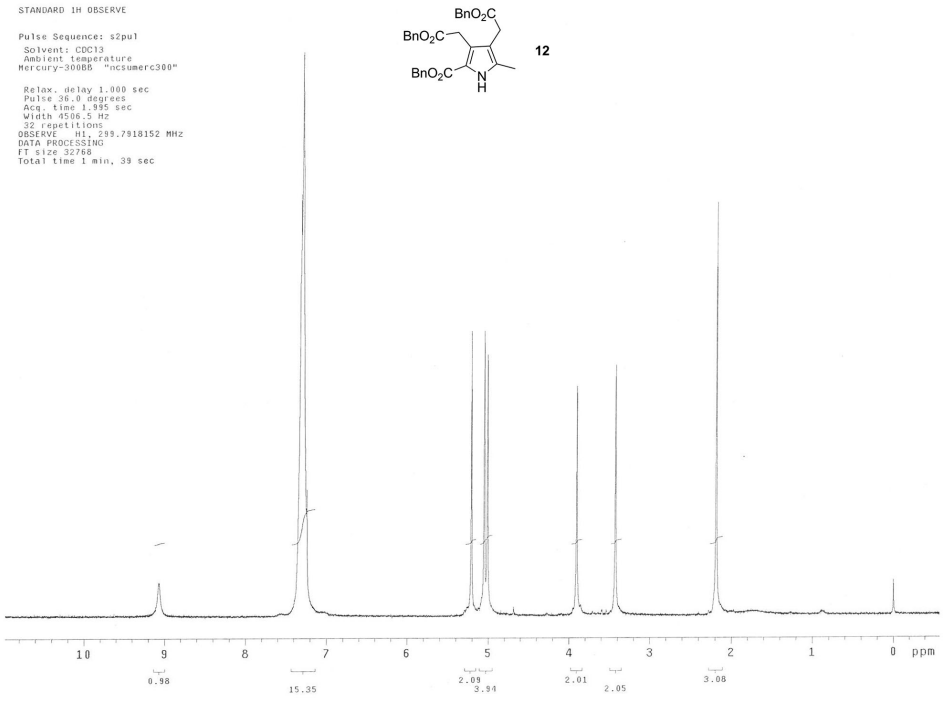
Solvent: CDCl3
Ambient temperature
Mercury-400BB "ncsumerc400"
Pulse 29.0 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
45504 repetitions
OBSERVE C13, 100.6113884 MHz
DECOUPLE H1, 400.1266027 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 17 hr, 54 min, 26 sec
NH
N
N
HN
HBC-MM
200
180
160
140
120
100
80
60
40
20
0 ppm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Ambient temperature
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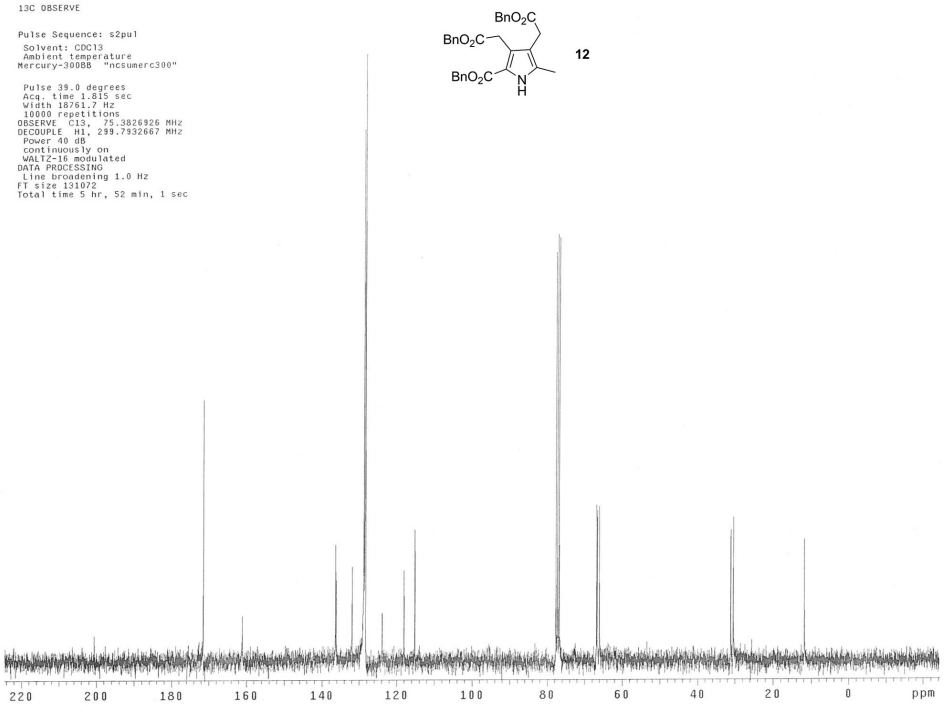
Pulse 36.0 degrees
Acq. time 1.995 sec
Width 4506.5 Hz
32 repetitions
OBSERVE H1, 299.7918152 MHz
DATA PROCESSING
FT size 32768
Total time 1 min, 39 sec
BnO2C
BnO2C
BnO2C
N
H
12
10
9
8
7
6
5
4
3
2
1
0
ppm
0.98
15.35
2.09
3.94
2.01
2.05
3.08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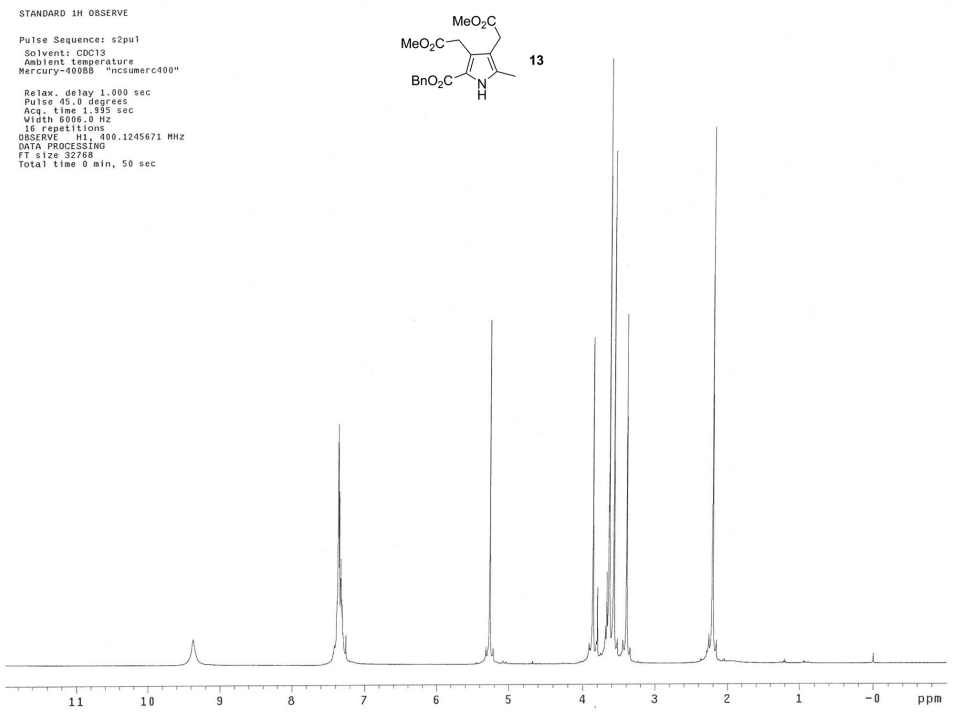
Solvent: CDCl3
Ambient temperature
Mercury-300BB "ncsumerc300"
Pulse 39.0 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
10000 repetitions
OBSERVE C13, 75.3826926 MHz
DECOUPLE H1, 299.7932667 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 5 hr, 52 min, 1 sec
BnO2C
BnO2C
BnO2C
N
H
12
220
200
180
160
140
120
100
80
60
40
20
0
ppm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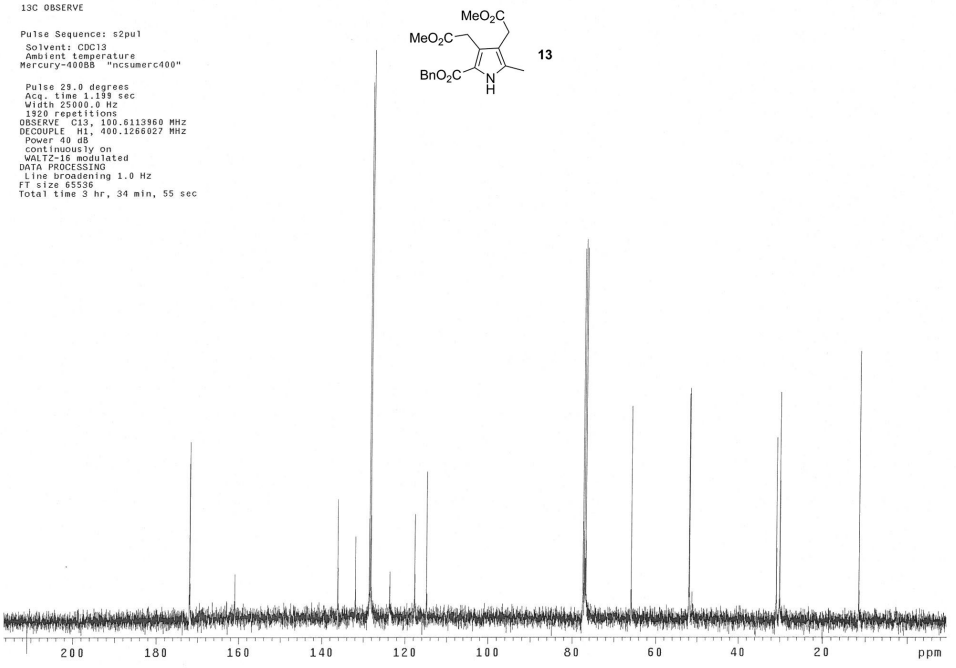
Solvent: CDCl3
Ambient temperature
Mercury-400BB "ncsumerc400"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.995 sec
Width 6006.0 Hz
16 repetitions
OBSERVE H1, 400.1245671 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 50 sec
MeO2C
MeO2C
BnO2C
N
H
13
11
10
9
8
7
6
5
4
3
2
1
-0
ppm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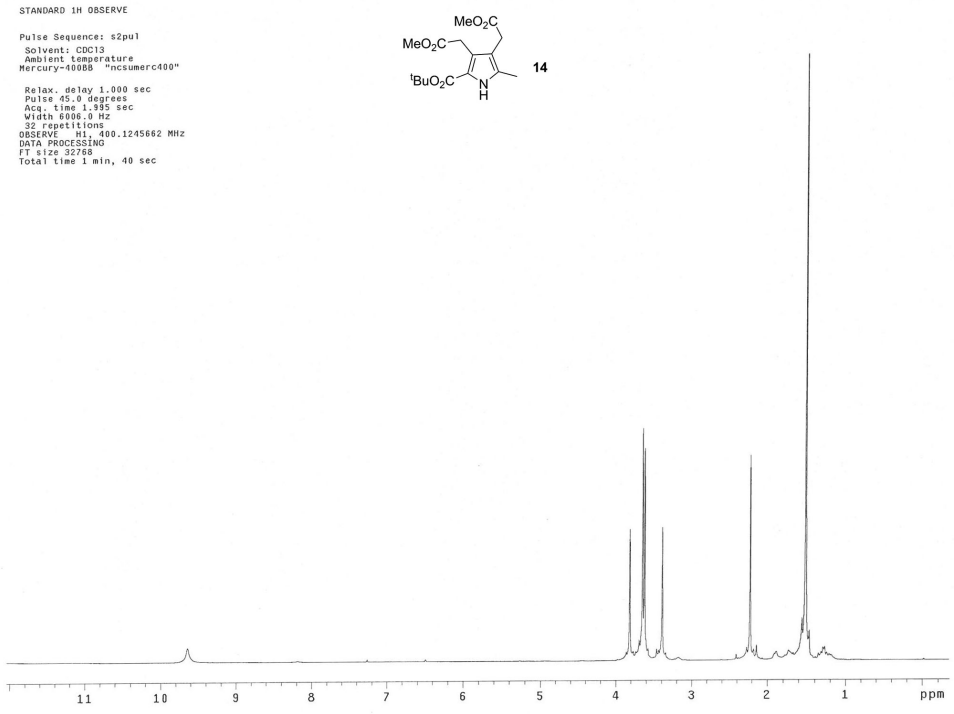
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "ncsumerc400"
Pulse 29.0 degrees
Acq. time 1.193 sec
Width 25000.0 Hz
1920 repetitions
OBSERVE C13, 100.6113960 MHz
DECOUPLE H1, 400.1266027 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 3 hr, 34 min, 55 sec
MeO2C
MeO2C
BnO2C
N
H
13
200
180
160
140
120
100
80
60
40
20
ppm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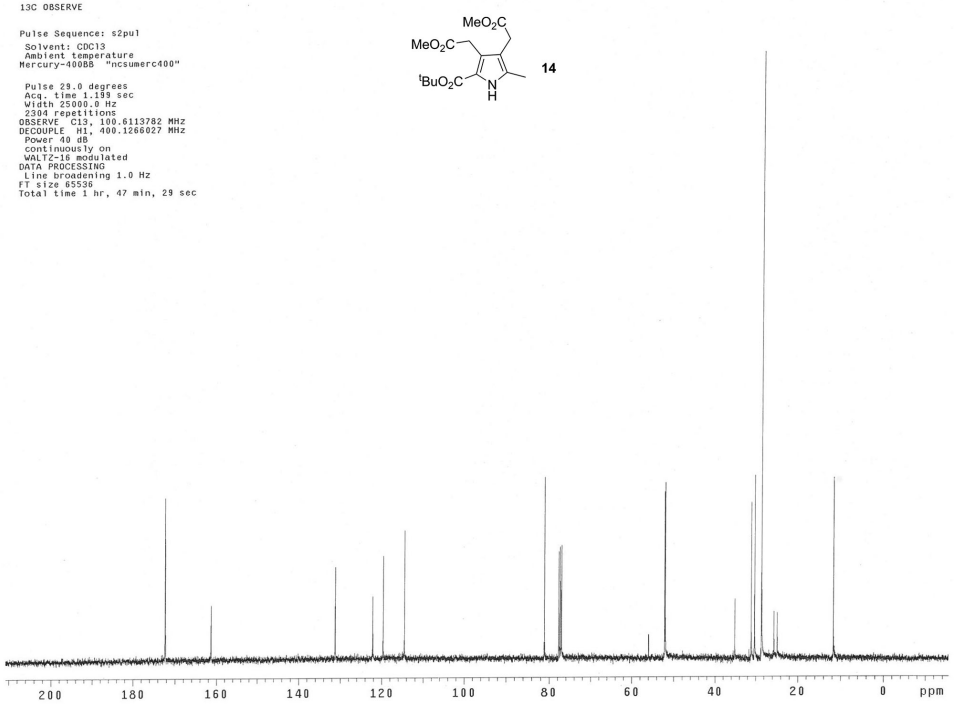
Acq. time 1.995 sec
Width 6006.0 Hz
32 repetitions
OBSERVE H1, 400.1245662 MHz
DATA PROCESSING
FT size 32768
Total time 1 min, 40 sec
MeO2C
MeO2C
tBuO2C
N
H
14
11
10
9
8
7
6
5
4
3
2
1
ppm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Solvent: CDCl3
Ambient temperature
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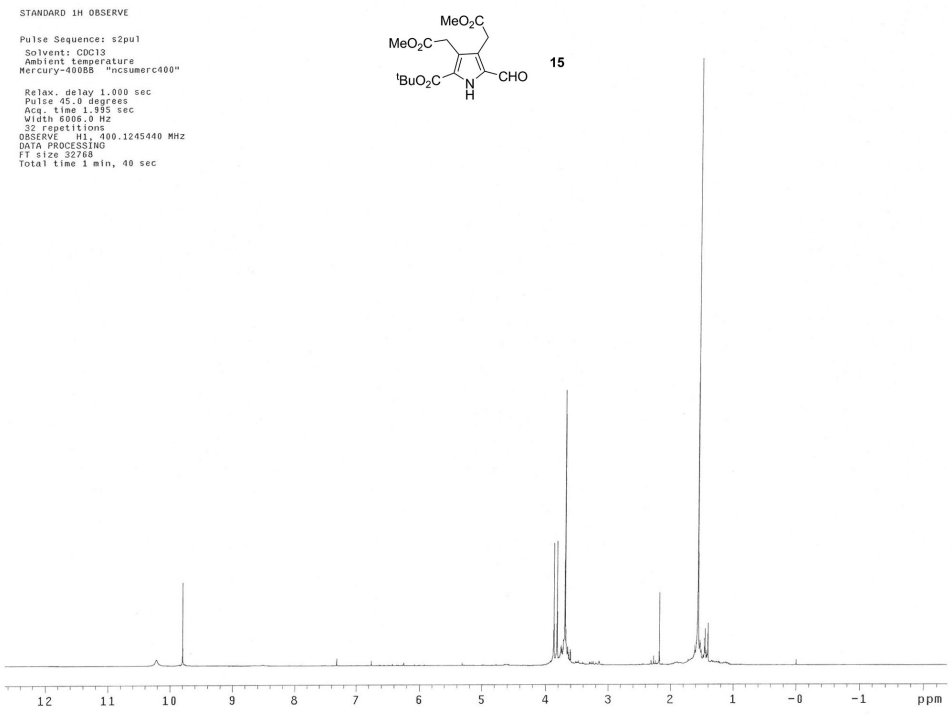
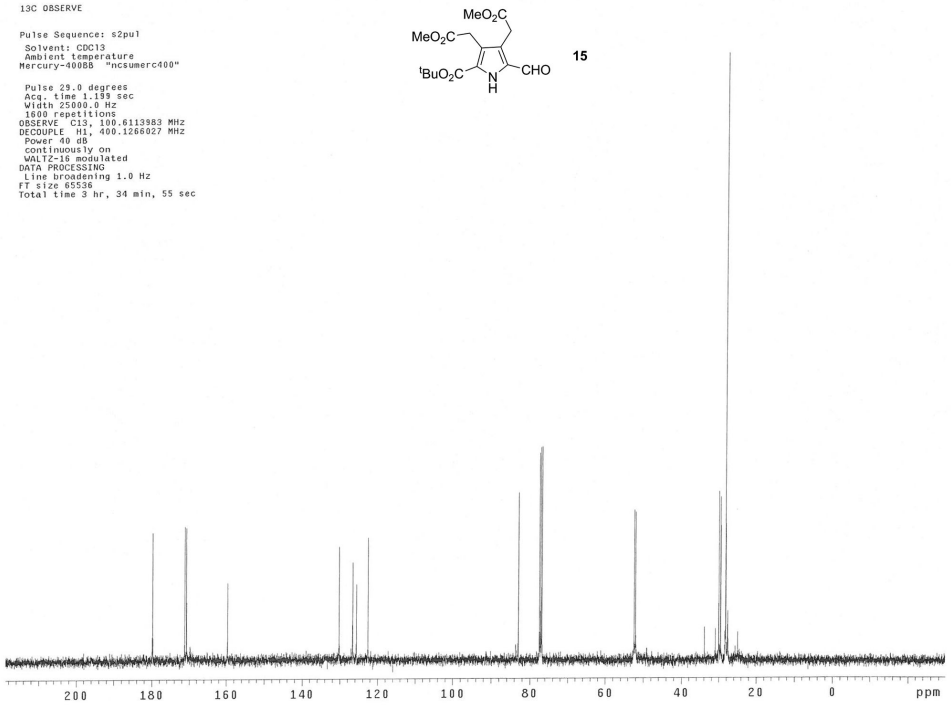
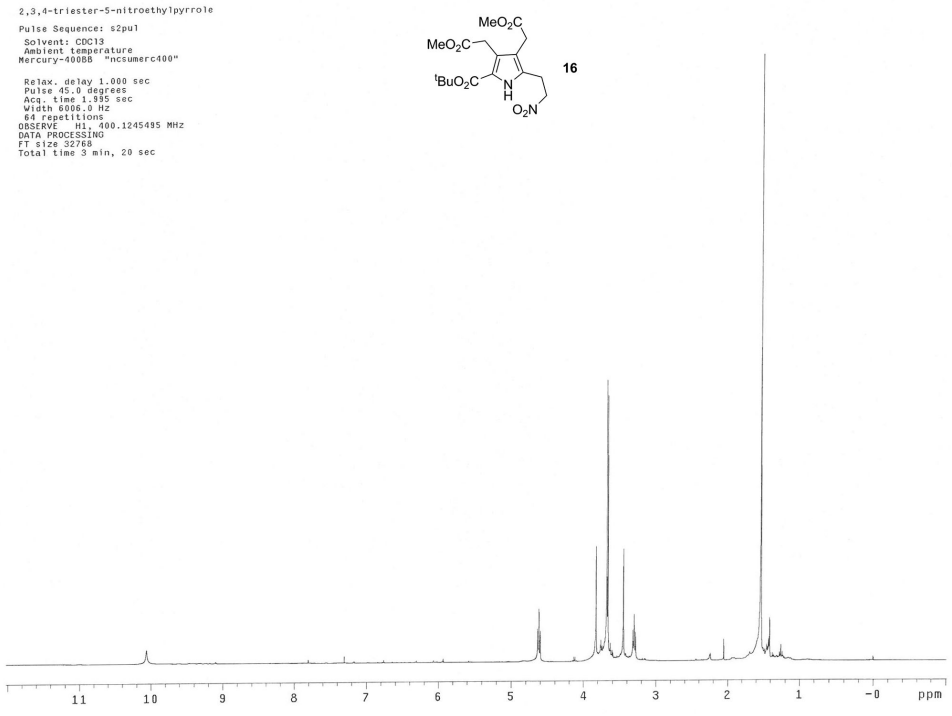
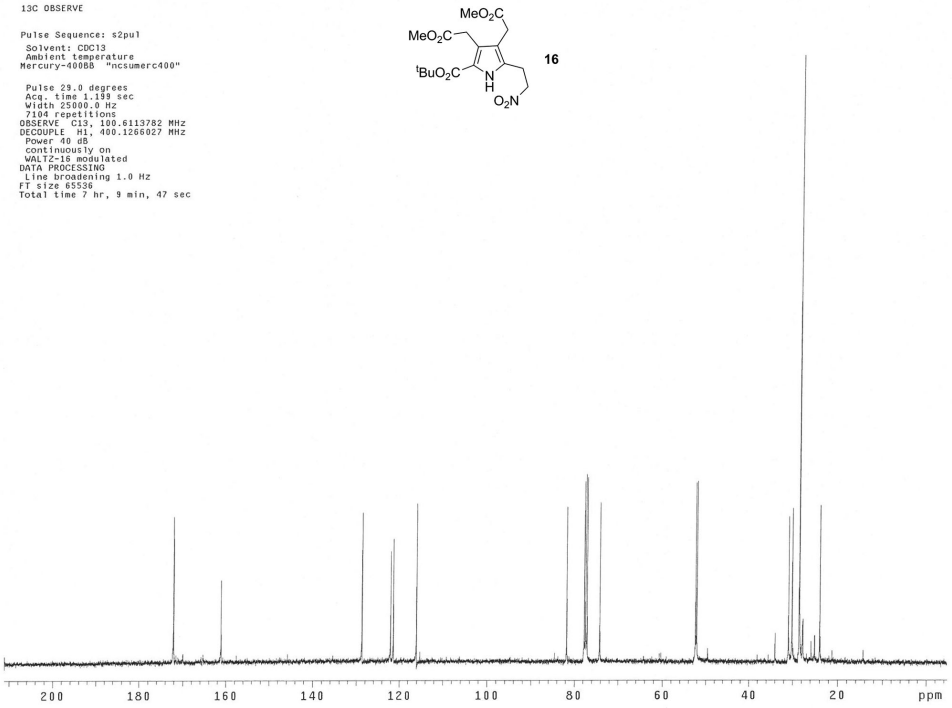
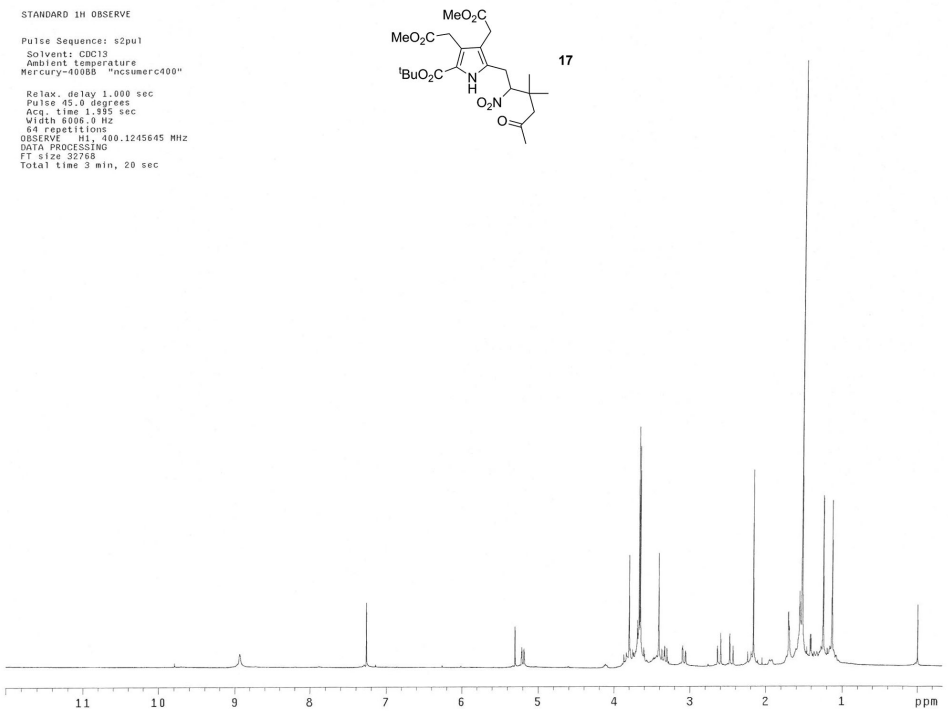
Acq. time 1.199 sec
Width 25000.0 Hz
2304 repetitions
OBSERVE C13, 100.6113782 MHz
DECOUPLE H1, 400.1266027 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 1 hr, 47 min, 29 sec
MeO2C
MeO2C
tBuO2C
N
H
14
200
180
160
140
120
100
80
60
40
20
0
ppm

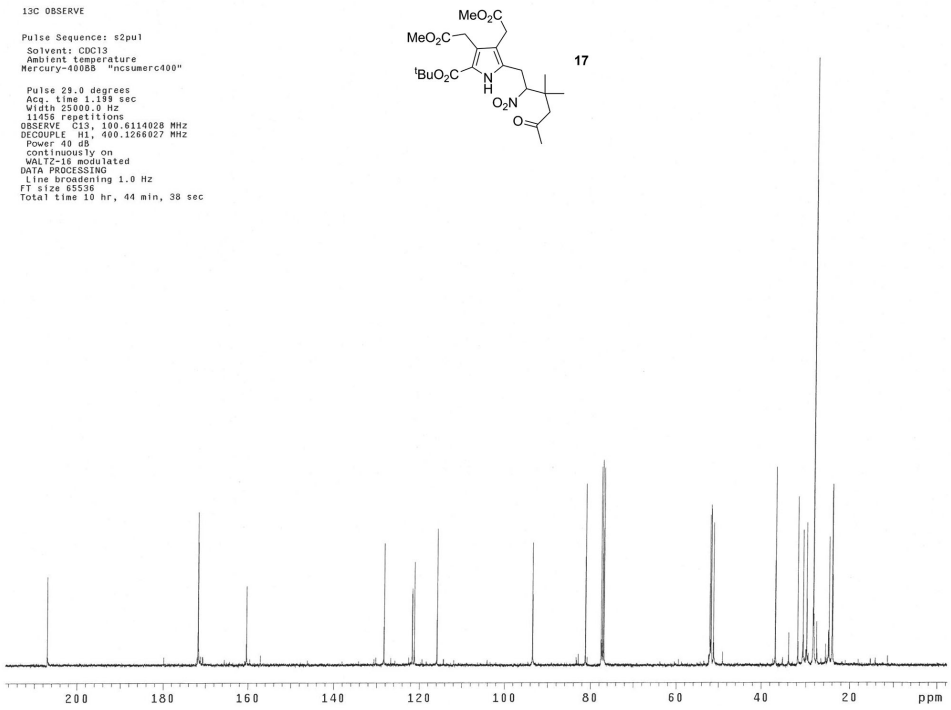

STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "ncsumerc400"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.995 sec
Width 6006.0 Hz
32 repetitions
OBSERVE H1, 400.1245440 MHz
DATA PROCESSING
FT size 32768
Total time 1 min, 40 sec
MeO2C
MeO2C
tBuO2C
N
H
CHO
15
12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm

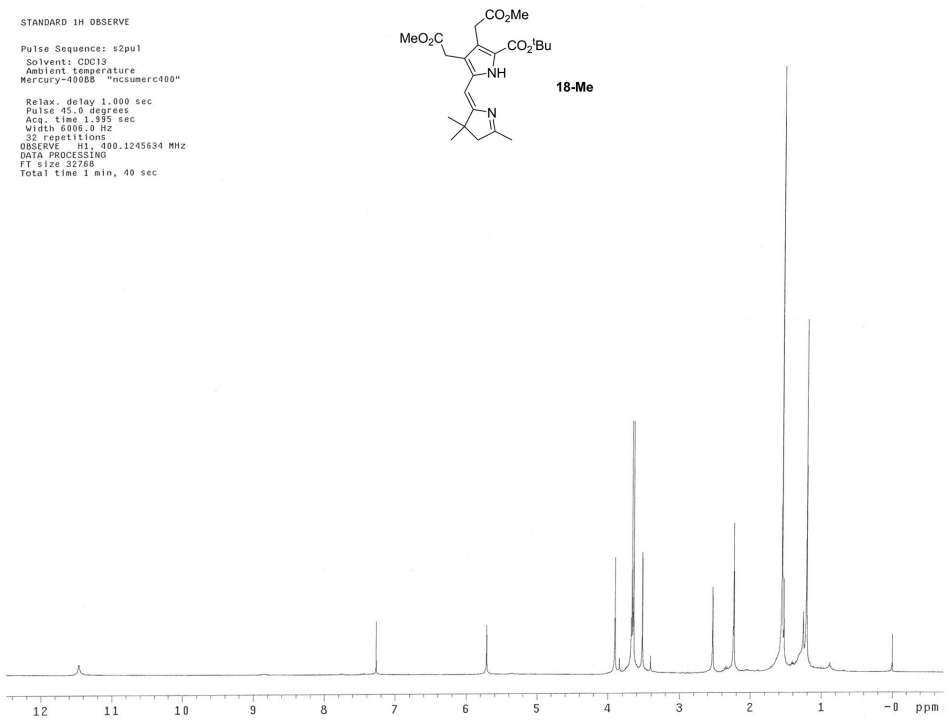

13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "ncsumerc400"
Pulse 29.0 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
1600 repetitions
OBSERVE C13, 100.6113983 MHz
DECOUPLE H1, 400.1266027 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 3 hr, 34 min, 55 sec
MeO2C
MeO2C
tBuO2C
N
H
CHO
15
200
180
160
140
120
100
80
60
40
20
0
ppm

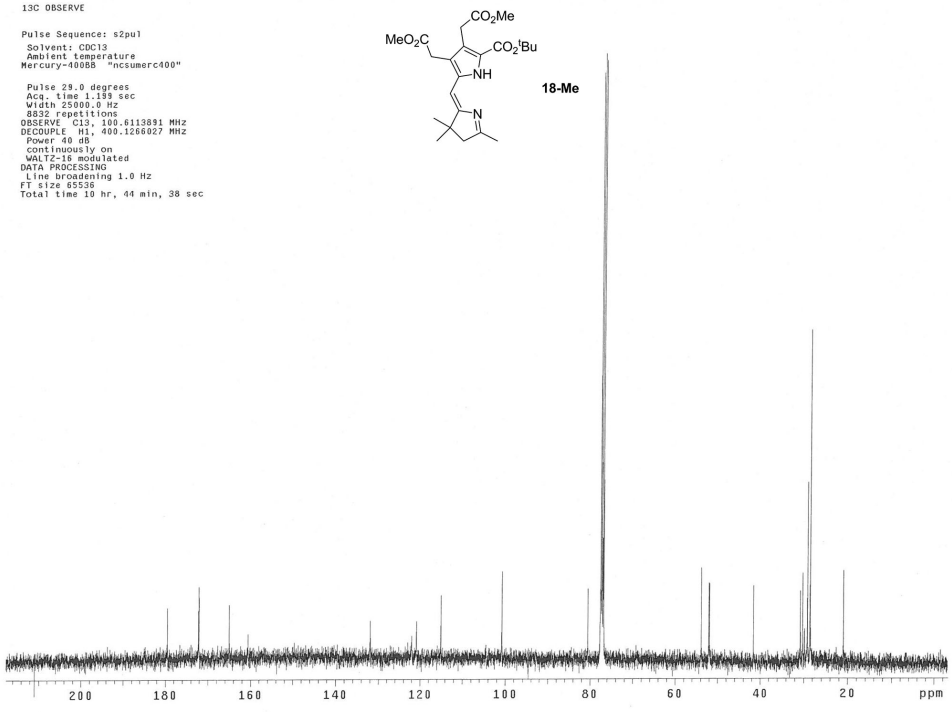

2,3,4-triester-5-nitroethylpyrrole
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "ncsumerc400"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.995 sec
Width 6006.0 Hz
64 repetitions
OBSERVE H1, 400.1245495 MHz
DATA PROCESSING
FT size 32768
Total time 3 min, 20 sec
MeO2C
MeO2C
tBuO2C
N
H
O2N
16
11
10
9
8
7
6
5
4
3
2
1
-0
ppm

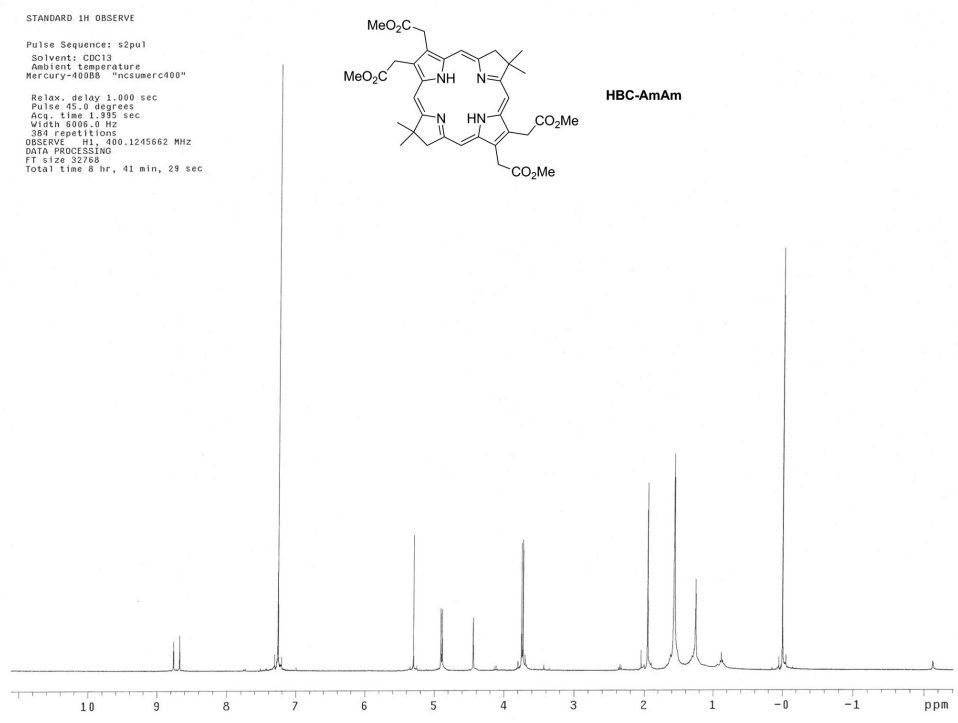

13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "ncsumerc400"
Pulse 29.0 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
7104 repetitions
OBSERVE C13, 100.6113782 MHz
DECOUPLE H1, 400.1266027 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 7 hr, 9 min, 47 sec
MeO2C
MeO2C
tBuO2C
N
H
O2N
16
200
180
160
140
120
100
80
60
40
20
ppm

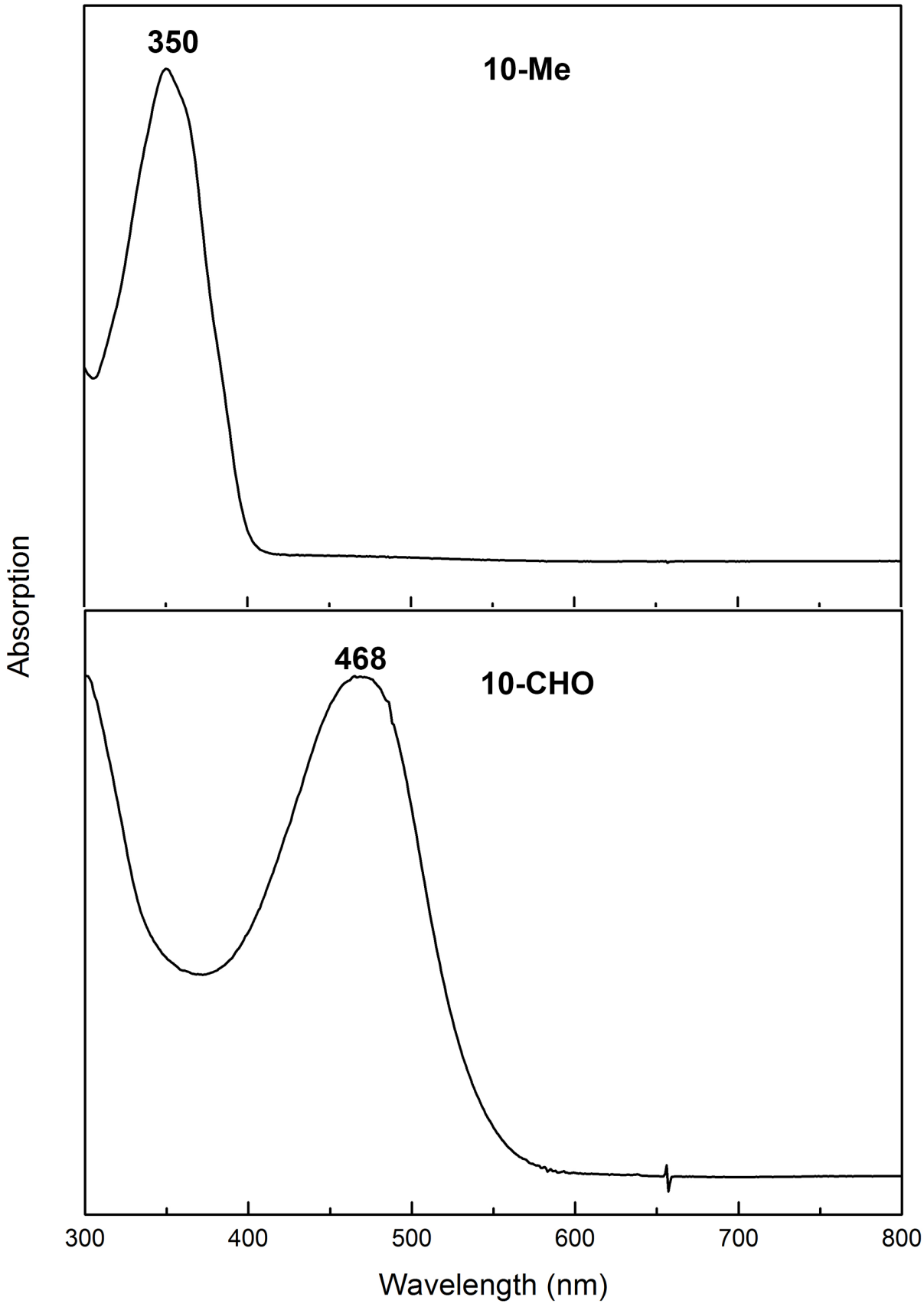

STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "ncsumerc400"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.995 sec
Width 6006.0 Hz
64 repetitions
OBSERVE H1, 400.1245645 MHz
DATA PROCESSING
FT size 32768
Total time 3 min, 20 sec
MeO2C
MeO2C
tBuO2C
N
H
O2N
O
17
11
10
9
8
7
6
5
4
3
2
1
ppm


13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "ncsumerc400"
Pulse 29.0 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
11456 repetitions
OBSERVE C13, 100.6114028 MHz
DECOUPLE H1, 400.1266027 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 10 hr, 44 min, 38 sec
MeO2C
MeO2C
tBuO2C
N
H
O2N
O
17
200
180
160
140
120
100
80
60
40
20
ppm


STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "ncsumerc400"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.995 sec
Width 6006.0 Hz
32 repetitions
OBSERVE H1, 400.1245634 MHz
DATA PROCESSING
FT size 32768
Total time 1 min, 40 sec
CO2Me
MeO2C
CO2tBu
NH
N
18-Me
12
11
10
9
8
7
6
5
4
3
2
1
-0
ppm


13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "ncsumerc400"
Pulse 29.0 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
8832 repetitions
OBSERVE C13, 100.6113891 MHz
DECOUPLE H1, 400.1268027 MHz
Power 40 dB
continuously On
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 10 hr, 44 min, 38 sec
CO2Me
MeO2C
CO2tBu
NH
N
18-Me
200
180
160
140
120
100
80
60
40
20
ppm


STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "ncsumerc400"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.995 sec
Width 6006.0 Hz
384 repetitions
OBSERVE H1, 400.1245662 MHz
DATA PROCESSING
FT size 32768
Total time 8 hr, 41 min, 29 sec
MeO2C
MeO2C
NH
N
N
HN
CO2Me
CO2Me
HBC-AmAm
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm


350
10-Me
468
10-CHO
Absorption
300
400
500
600
700
800
Wavelength (nm)