SUPPORTING INFORMATION

for

New azaborine–thiophene heteroacenes

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Experimental Part

Materials and Methods

All reactions were carried under dry nitrogen or argon atmosphere (specified in procedure). The reagents *n*-butyllithium (2.0 M in hexanes), tributyltin chloride, palladium (II) chloride (Alfa Aesar), tin (II) chloride, glyoxal, phenyl dichloroborane, triethylamine were obtained commercially and used as received. Fuming nitric acid was prepared in the laboratory. All solvents were of at least reagent grade and dried if necessary.

^{1}H NMR and ^{13}C NMR spectra were run on a Varian Mercury 300 or 400 MHz NMR spectrometer. Low-resolution mass spectra (70 eV, EI and ESI were run on a Kratos 7525 RFA or Finnigan LCQ DUO mass spectrometer. UV-vis spectra were measured with a Varian Cary 5000 spectrometer in 1 cm cuvettes (in CH_2Cl_2 solutions). Fluorescence spectra were measured with a Varian Eclipse spectrofluorometer, in 1 cm cuvettes (in CH_2Cl_2 solutions). Quantum yield was determined relative to 9,10-diphenylanthracene (Φ_{PL} = 90%).

Electrochemical Measurements: All electrochemical measurements were performed at room temperature in a three-electrode cell using a CHI-770 Electrochemical Workstation. Electrochemical investigations were conducted in anhydrous CH_2Cl_2 with a Pt disk (d=1.6 mm) as the working electrode, platinum wire as the auxiliary electrode and Ag/AgCl reference electrode. Bu_4ClO_4 (0.1 M) was used as a supporting electrolyte. The electrolyte solution was purged with Ar gas before and between electrochemical measurements. The redox potential of Fc/Fc^+ couple in our conditions occurred at 0.50 V *vs.* Ag/AgCl.

X-ray Measurements. Needles of **1a** and **1b** was mounted on a nylon loop with paratone. X-ray data were collected at 100 K using omega scans with a Bruker APEX I CCD detector on a D8 3-circle goniometer and Mo KR (λ) 0.71073 Å) radiation. The data were scanned using Bruker's SMART program and integrated using Bruker's SAINT software.[1] The structure was solved by direct methods using SHELXS-97[2] and refined by a least-squares methods on F_2 using SHELXL-97 incorporated in the SHELXTL[433] suite of programs.

Description of Density Functional Theory Calculations (DFT). All calculations were performed on neutral closed shell molecules with density functional theory at B3LYP/6-311G(d,p) level implemented in GAUSSIAN 03W.[4] Default convergence criteria and no symmetry constrains were used. Reorganization energy λ was calculated as the difference between the total energy of radical cation in the optimized geometry and in the geometry of a neutral molecule (λ_+) plus the difference between the total energy of a neutral molecule in the optimized geometry and in the geometry of a radical cation (λ_0).

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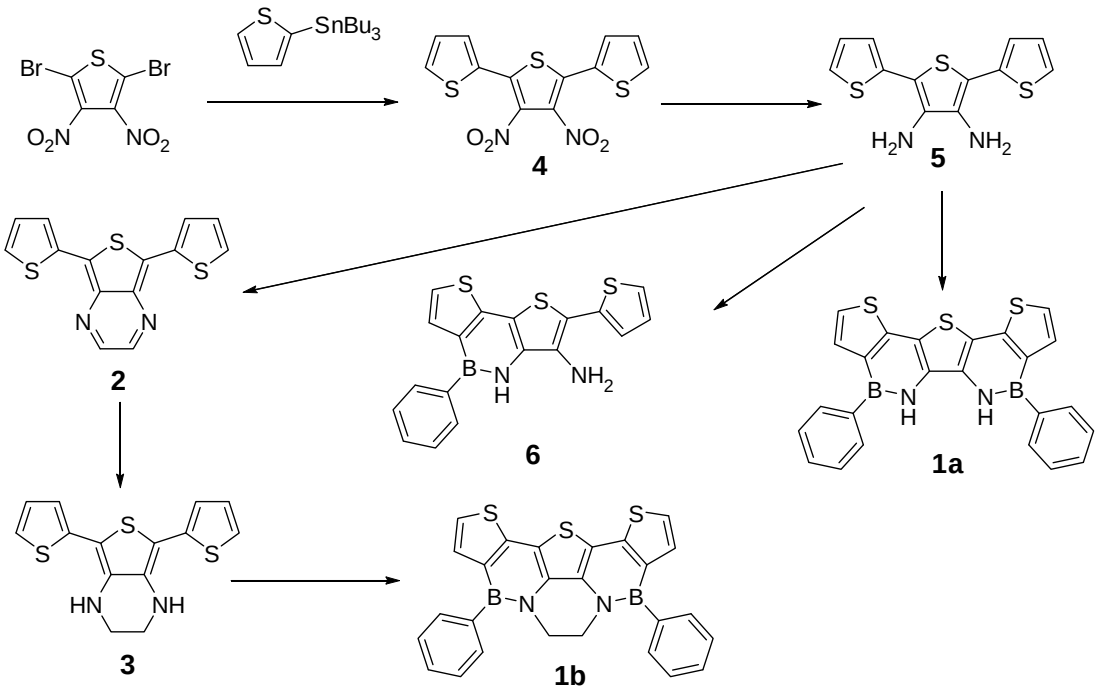
[1] Bruker (2006). SAINT Release 7.34A. Integration Software for Single Crystal Data. Bruker AXS Inc., Madison, USA.

[2] Sheldrick, G. M. (1997). SHELXS97. Program for Crystal Structure solution. University of G□ottingen, Germany.

[3] Bruker (1997). SHELXTL (1997). Release 5.10; The Complete Software Package for Single Crystal Structure Determination. Bruker AXS Inc., Madison, USA.

[4] Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.



2,5-Bis(2-thienyl)-3,4-dinitrothiophene (4). This was synthesized by Stille coupling of 2,5-dibromo-3,4-dinitrothiophene[5] with tributyl-2-thienylstannane as described previously.[6] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.61 (dd, J = 5.2, 1.2 Hz, 2H), 7.55 (dd, J = 4.0, 1.2 Hz, 2H), 7.18 (dd, J = 5.2, 4.0 Hz, 2H).

2,5-Bis(2-thienyl)-3,4-diaminothiophene (5). This was synthesized by modified published procedure[7] with an improved yield. To a solution of 2,5-bis(2-thienyl)-3,4-dinitrothiophene (5.0 g, 14.8 mmol) in ethanol (200 mL) and concentrated HCl (100 mL) under argon was added $SnCl_2 \times 2H_2O$ (60 g, 267 mmol). The reaction mixture was refluxed for 15 h. Then, the mixture was poured into aqueous KOH (25 %) to basify the solution. The solution was filtered and the product was extracted with toluene (3×150 mL). The organic phase was dried over $MgSO_4$ and the solvent was evaporated. The product was purified by chromatography on silica gel to give the desired product as a yellow powder (3.12 g, 76 %), ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 7.27 (dd, J = 4.5, 1.5 Hz, 2H), 7.09 (m, 4H), 3.74 (s, 4H).

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[5] D. D. Kenning, K. A. Mitchell, T. R. Calhoun, M. R. Funfar, D. J. Sattler, S. C. Rasmussen *J. Org. Chem.* **2002**, *67*, 9073
[6] Y. Xia, J. Luo, X. Deng, X. Li, X. Zhu, W. Yang, Y. Cao, *Macromol. Chem. Phys.*, **2006**, *207*, 511
[7] C. Kitamura, S. Tanaka, Y. Yamashita, *Chem. Mater.*, **1996**, *8*, 570

5,7-bis(2-thienyl)thieno[3,4-*b*]pyrazine (2). This was synthesized according to procedure.[7] To a solution of **5** (1.026 g, 3.70 mmol) in ethanol (20 mL) under argon was added glyoxal (40 % in water) (0.29 mL, 1.98 mmol) and Na_2CO_3 (3.92 g, 37.0 mmol). The reaction mixture was refluxed for 2h, the reaction turned purple. Then, water was added (50 mL) and the product was extracted by 3 × 50 mL of diethyl ether. The organic phase was dried over $MgSO_4$ and the solvent was evaporated. The product was purified by chromatography on silica gel to give product pyrazine **2** as a purple powder (1.10 g, 99 %). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.54 (s, 2H), 7.65 (dd, J = 4.0 Hz, J = 1.2 Hz, 2H), 7.42 (dd, J = 5.2 Hz, J = 1.2 Hz, 2H), 7.14 (dd, ^3J = 5.2 Hz, ^3J = 4.0 Hz, 2H).

Ethylenediaminoterthiophene (3) To a solution of **2** (0.38 g, 1.26 mmol) in ethanol (10 mL) under argon was added $NaBH_4$ (2.4 g, 63 mmol). The reaction mixture was refluxed for 1h, the solution turned orange. Then water was added (20 mL) and the product was extracted by 3 x 50 mL of ethyl acetate. The organic phase was dried over $MgSO_4$ and the solvent was evaporated. Quick filtration through a silica gel plug gave intermediate **3** as yellow powder (0.39 g, 99 %) which was of sufficient purity for further reaction (>95% by NMR). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 7.21 (m, 2H), 7.06 (m, 4H), 4.30 (br. s, 2H), 3.42 (s, 4H). We note that the product should be isolated/purified rapidly and stored under nitrogen as prolonged exposure to air leads to oxidation.

Azaborine (1a). To a solution of 2,5-bis(2-thienyl)-3,4-diaminothiophene **5** (1.00 g, 3.60 mmol) in chlorobenzene (50 mL) under argon was added phenyldichloroborane (1.71 g, 10.8 mmol) and triethylamine (2 mL, 14 mmol). The reaction mixture was refluxed for 48h. Then the solvent was evaporated and the product was purified by chromatography on silica gel to give product **1a** as yellow powder (1.40 g, 86 %), m.p. 216 °C . ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 8.37 (br. s, 2H), 7.91 (m, 4H), 7.77 (d, ^3J = 5.0 Hz, 2H), 7.53 (m, 6H), 7.36 (d, ^3J = 5.0 Hz, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$, ppm): 148.6, 133.4, 131.9, 130.2, 129.5, 128.6, 123.4, 117.0.[8] MS (ESI) m/z = 449.52 (100 %) $[M–H]^-$. $C_{24}H_{16}S_3B_2N_2$: Calcd. C 64.03, H 3.58, N 6.22; Found C 64.12, H 3.72, N 6.20.

Azaborine (1b). To a solution of ethylenediaminoterthiophene **3** (0.392 g, 1.29 mmol) in chlorobenzene (50 mL) under argon was added phenyldichloroborane (0.43 mL, 3.22 mmol) and triethylamine (0.6 mL, 3.9 mmol). The reaction mixture refluxed overnight, then the solvent was evaporated in vacuo and the product was purified by chromatography on silica gel to give product **1b** as yellow powder (0.33 g, 54 %), m.p. 224-226 °C. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 7.66 (m, 4H),

[8] ^{13}C NMR signal for the carbon attached to boron is not observed due to coupling with adjacent ^{11}B.

7.48 (m, 8H), 7.27 (d, J = 5.1 Hz, 2H), 4.31 (s, 4H). ^{13}C NMR (125.8 MHz, $CDCl_3$, ppm): 146.7, 139.8 (br), 138.4 (br), 133.7, 132.7, 131.0, 128.4, 128.1, 122.7, 116.2, 46.2. MS (ESI) m/z = 476.0 $[M]^+$. $C_{26}H_{18}S_3B_2N_2$: Calcd. C 65.57, H 3.81, N 5.88, S 20.20; Found C 65.11, H 3.74, N 5.95, S 19.91. The reaction was repeated with 0.75 g of **3** without heating (stirring overnight); the purification as above gave the same product **1b** (0.51 g, 42%).

Azaborine (6). To a solution of 2,5-bis(2-thienyl)-3,4-diaminothiophene **4** (106 mg, 0.381 mmol) in chlorobenzene (50 mL) under argon was added phenyldichloroborane (60 μL, 0.45 mmol). The reaction mixture was refluxed for 2 h and the solvent was evaporated. Excess of triethylamine (3 drops) was added and the product was purified by chromatography on silica gel (EtOAc/hexane) to give product **6** as a yellow-brownish solid which rapidly decomposes on storage (45 mg, 32 %). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.01 (br. s, 1H, NH), 7.88 (dd, J = 7.6 Hz, 2H, *o*-H), 7.75 (d, J = 5.2 Hz, 1H, *th*-H), 7.50 (m, 3H, *m-,p*-H), 7.35 (d, J = 4.8 Hz, 1H, *th*-H), 7.31 (d, J = 5.2 Hz, 1H, *th*-H), 7.21 (d, J = 3.6 Hz, 1H, *th*-H), 7.13 (dd, J = 4.8 and 3.6 Hz, 1H, *th*-H), 3.5 (br, 2H, NH_2). MS (EI) m/z = 364 $[M^+]$.

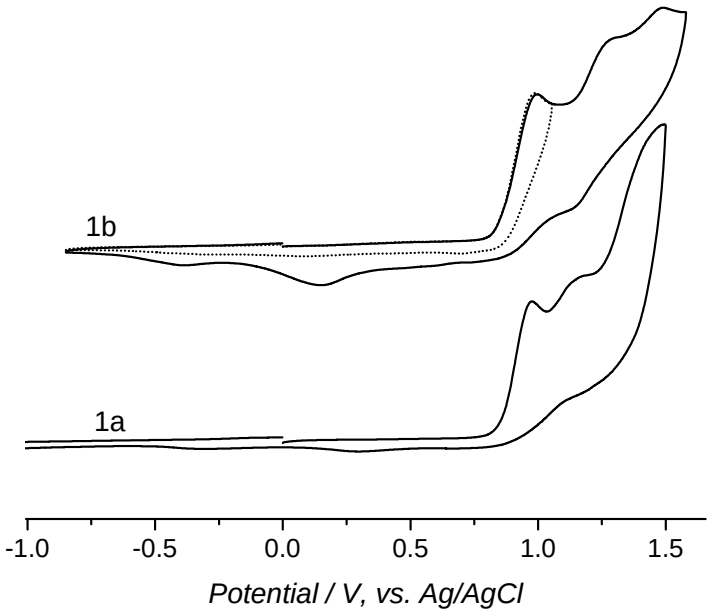


Fig. S1. CVs of **1a** (bottom curve) and **1b** (top curves) in 0.1 M Bu_4NClO_4/CH_2Cl_2, scan rate 0.1 V s^{-1}.

Fluoride titration experiments

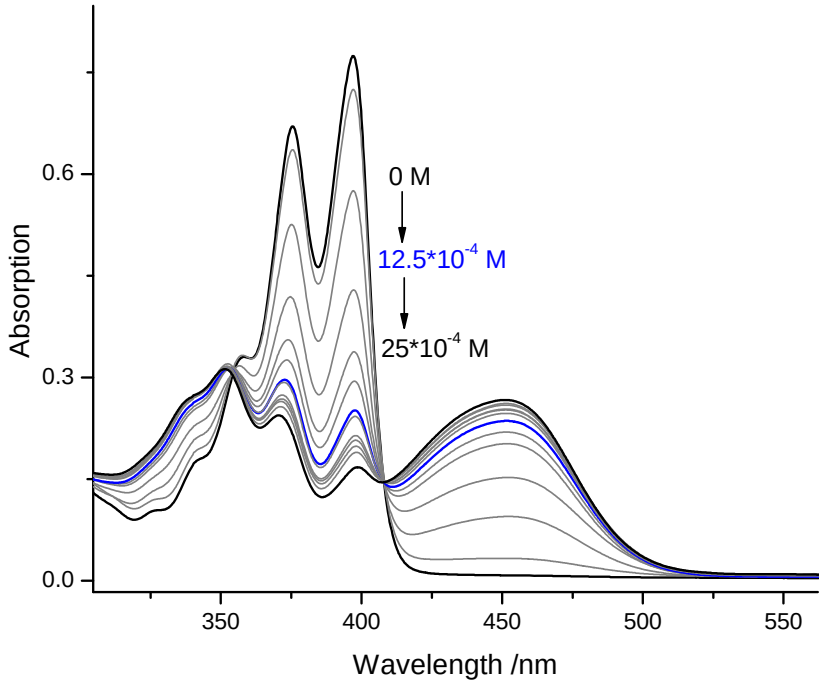


Fig. S2. UV-Vis of titration of **1b** (3.1×10^{-5} M, 2mL) with TBAF in DCM (see also Table S1).

Table S1. UV-Vis titration of **1b** (3.1×10^{-5} M, 2mL) with TBAF in DCM. Extinction coefficients are: **1b**: $\varepsilon_{397nm} = 33{,}500\ cm^{-1}\ M^{-1}$; $\varepsilon_{453nm} = 0$; **1b:F$^-$**: $\varepsilon_{397nm} = 13{,}300\ cm^{-1}\ M^{-1}$; $\varepsilon_{453nm} = 4{,}000$

$[TBAF]_0$	Abs_{397}	Abs_{453}
0	0.7742	0.00776
0.000125	0.72405	0.03256
0.00025	0.5752	0.09388
0.0005	0.4288	0.1523
0.00075	0.337	0.2018
Abs0.001	0.29443	0.2189
0.00125	0.2512	0.2356
0.0015	0.242	0.2466
0.00175	0.214	0.2532
0.002	0.207	
0.00225	0.1975	0.259
0.0025	0.1893	

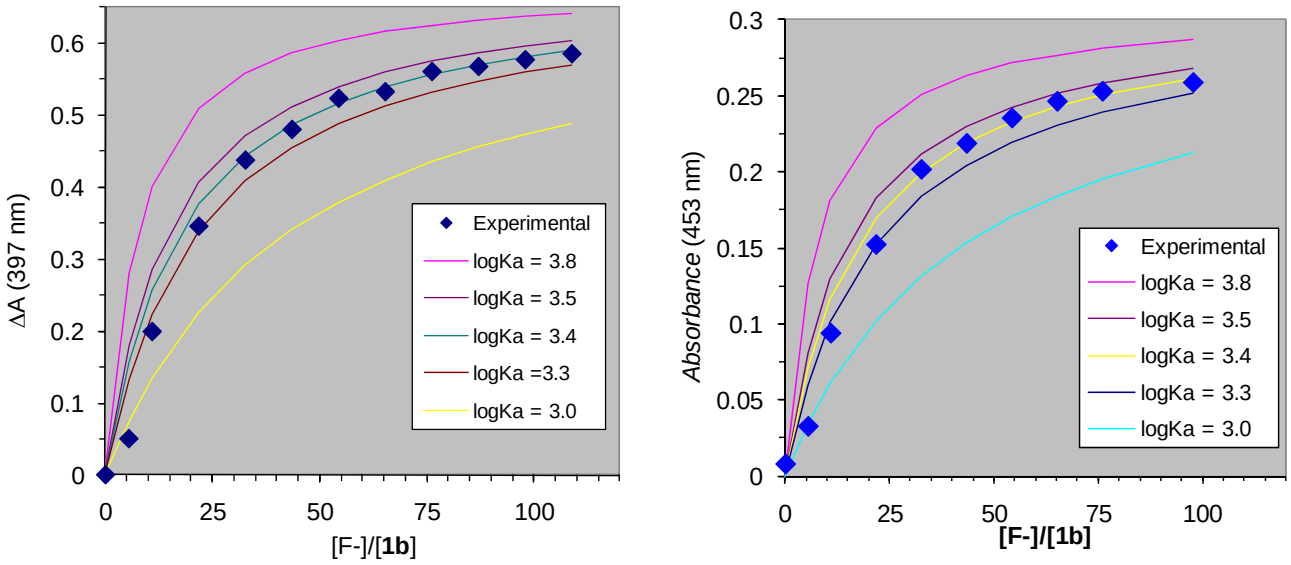
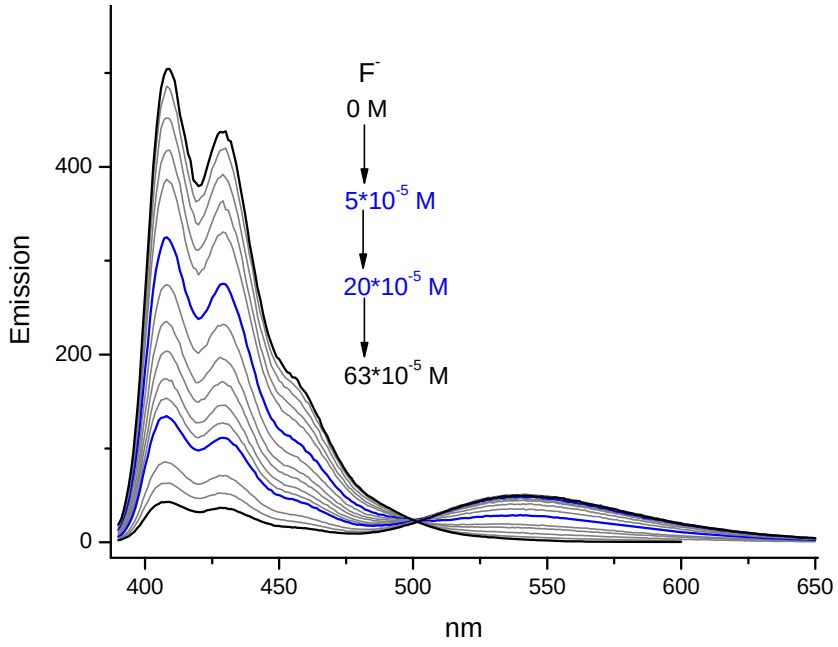


Fig. S3. Binding isotherms for **1b:F**$^{-}$ based on UV-Vis titration (Fig. S2, Table S1) measured by depletion of the **1b** absorption (397 nm, left) and appearance of the **1b:F**$^{-}$ absorption (453 nm, right).



Fig, S4.Fluorescence titration of **1b** (0.85×10^{-5} M, 2mL) with TBAF in DCM.

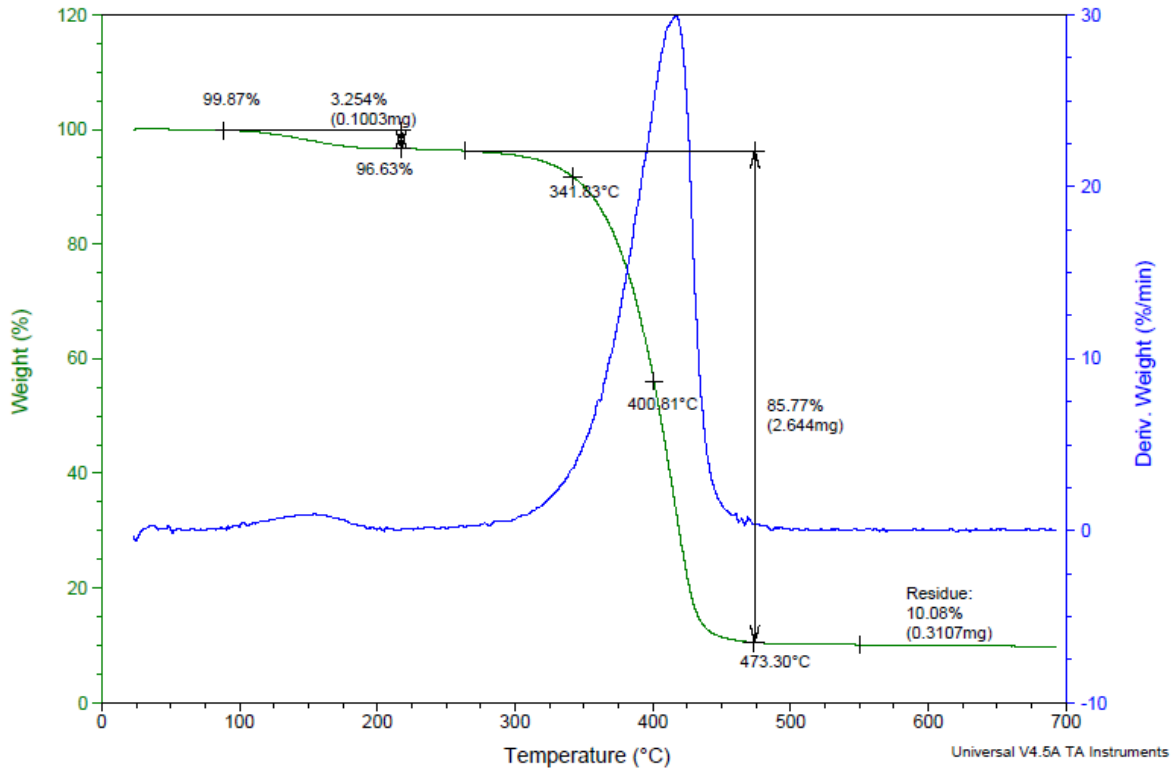


Fig. S5. Thermogravimetric analysis of azaborine **1a**. 3% mass loss at 100–150 ºC is due to specifically bound molecule of water (hydrogen bonding to two N-H fragments; see X-ray data for **1a**). T_{dec} ~ 300ºC (based on 5% mass loss).

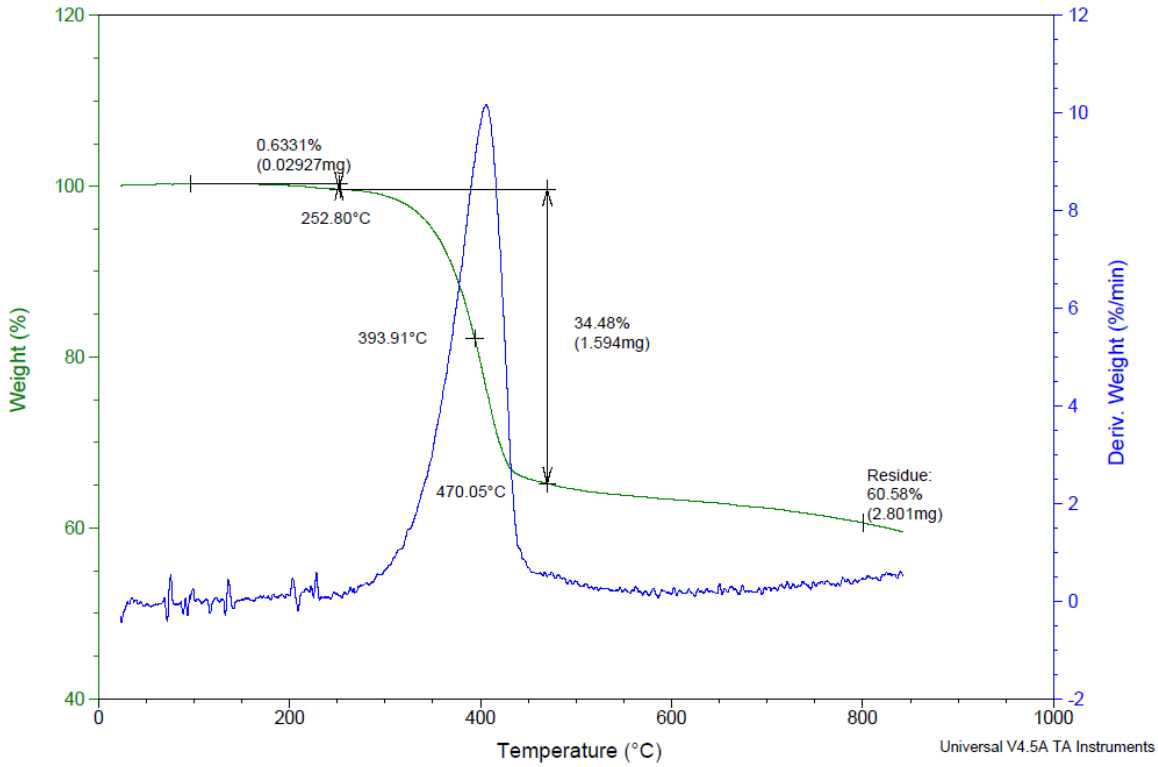


Fig. S6. Thermogravimetric analysis of azaborine **1b**. T_{dec} ~ 300ºC (based on 5% mass loss).

ML375-1

OK

STANDARD 1H OBSERVE

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Ambient temperature
Mercury-300 "m300"

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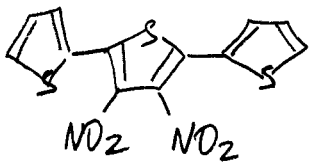

Compound 4

ML 377-1

STANDARD 1H OBSERVE

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Mercury-300 "m300"

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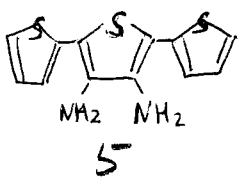

5

Compound 5

ML396-3

400 MHz

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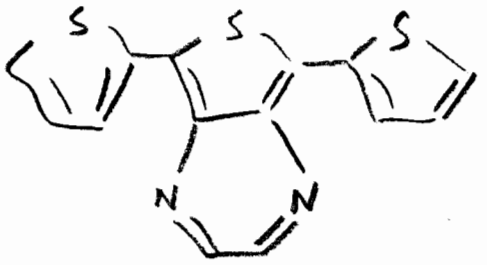

2

Compound 2

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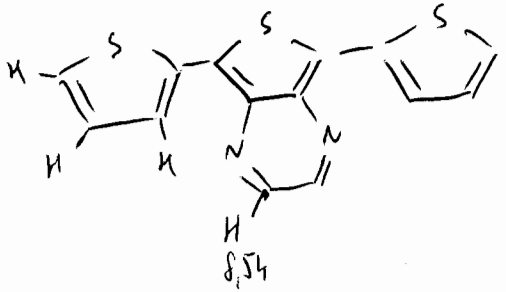

δ 8,54

$^4J = 1,2$
$^3J = 5,2$
7,42

$^3J = 4Hz$ 7,65
$^4J = 1,9Hz$

7,14
$^3J = 5,2$
$^3J = 4,2$

8.535
7.653
7.650
7.643
7.640
7.427
7.424
7.414
7.411
7.263
7.148
7.139
7.135
7.126

Compound 2

8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 ppm

25.51 23.73 24.06 26.70

STANDARD 1H OBSERVE

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Solvent: CDCl3
Ambient temperature
Mercury-300 "m300"

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Acq. time 1.995 sec
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12 repetitions
OBSERVE H1, 300.0549900 MHz
DATA PROCESSING
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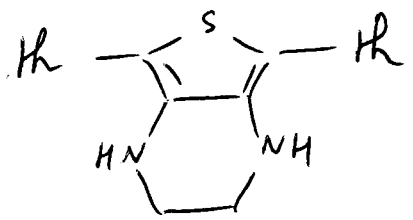
Total time 0 min, 0 sec

3

TL 419-B



Compound 3

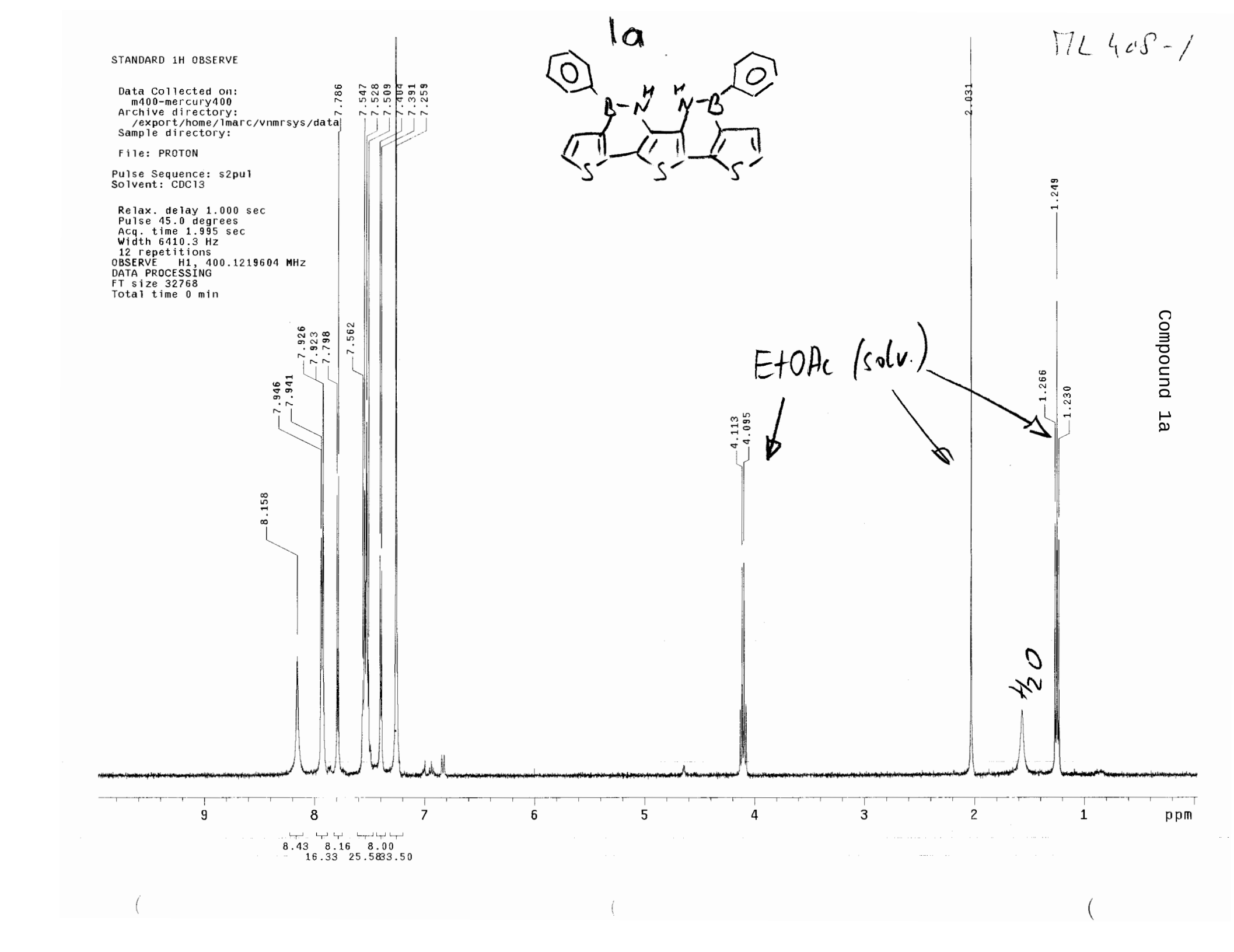
7.196
7.066
7.058
7.054
7.217
7.209
7.205
3.421

7,06
7,21
4,30

2H
4H
2H
4H

9 8 7 6 5 4 3 2 1 ppm

16.61
32.85
16.13
34.42


1a
ML 405-1
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12 repetitions
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DATA PROCESSING
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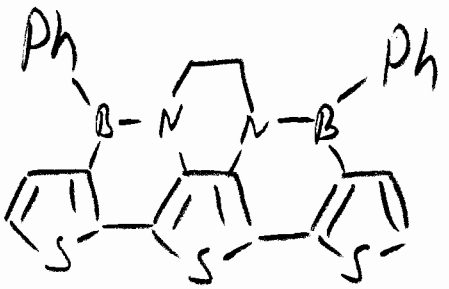
7.528
7.509
7.404
7.391
7.259
7.926
7.923
7.798
7.562
7.946
7.941
8.158
4.113
4.095
2.031
1.249
1.266
1.230
EtOAc (solv.)
H2O
Compound 1a
9
8
7
6
5
4
3
2
1
ppm
8.43
8.16
8.00
16.33
25.58
33.50

16- $CDCl_3$ - 400 MHz



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Sample directory:

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Solvent: CDCl3

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Pulse 45.0 degrees
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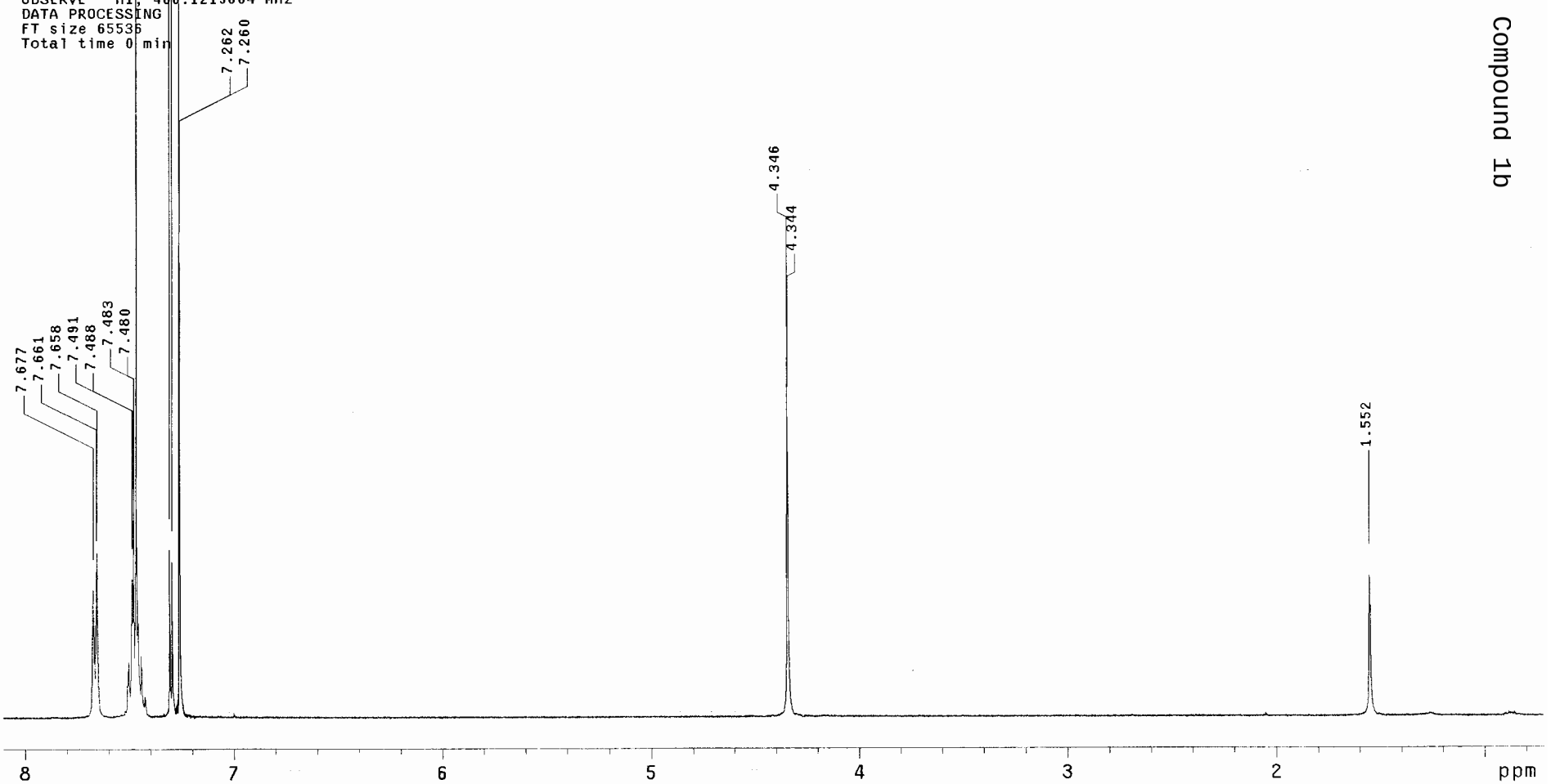
Total time 0 min

Compound 1b



STANDARD 1H OBSERVE

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Sample directory:

File: PROTON

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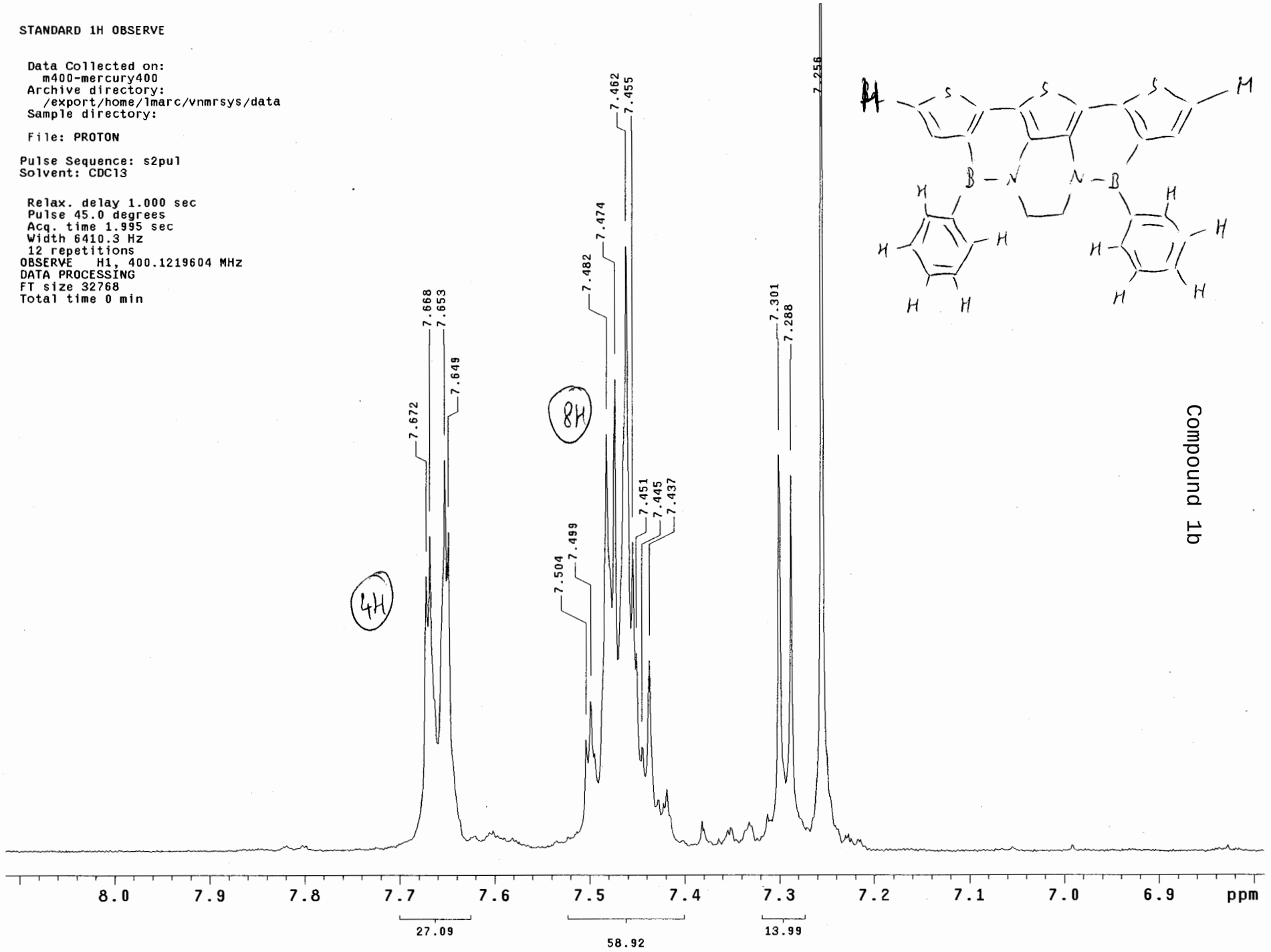
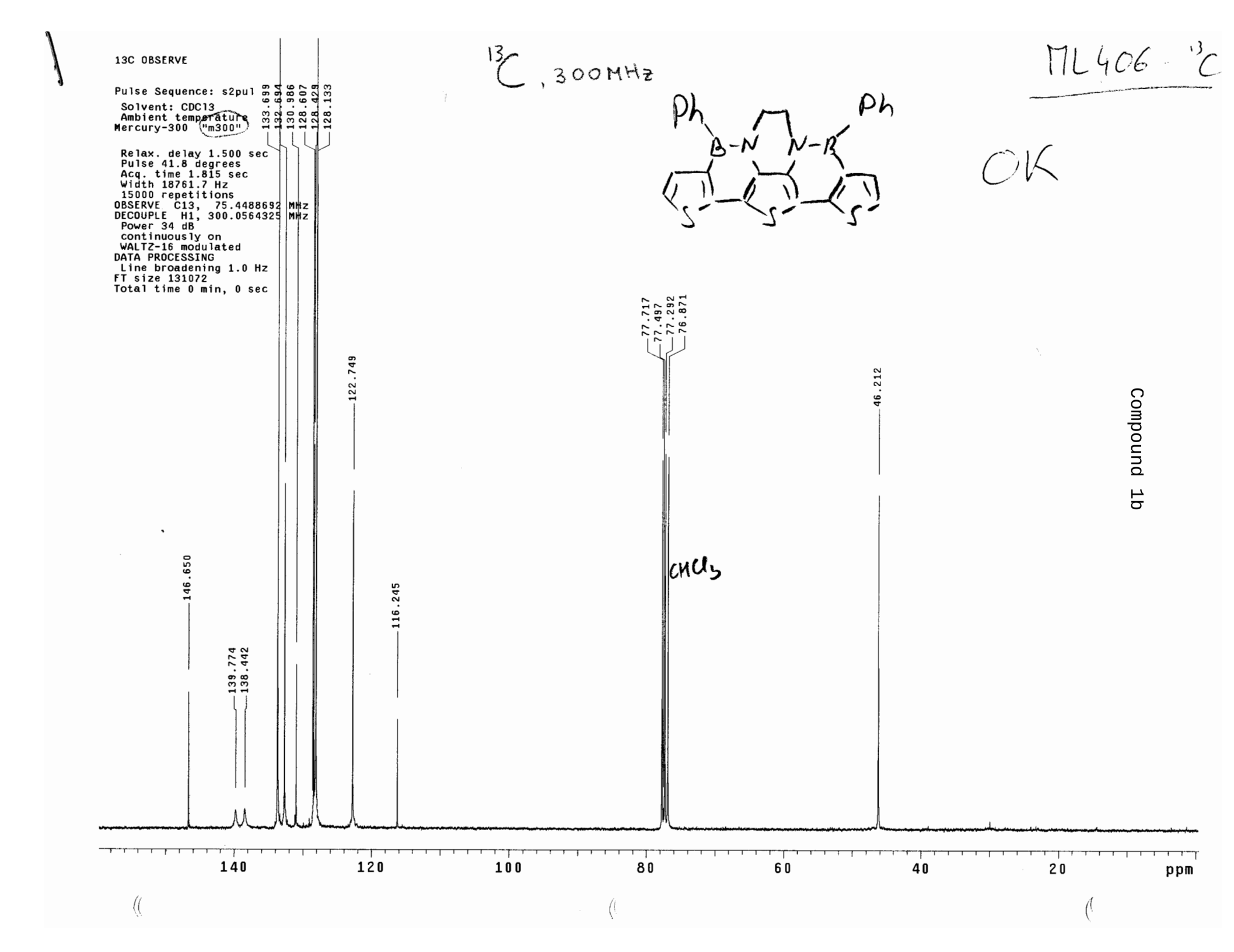
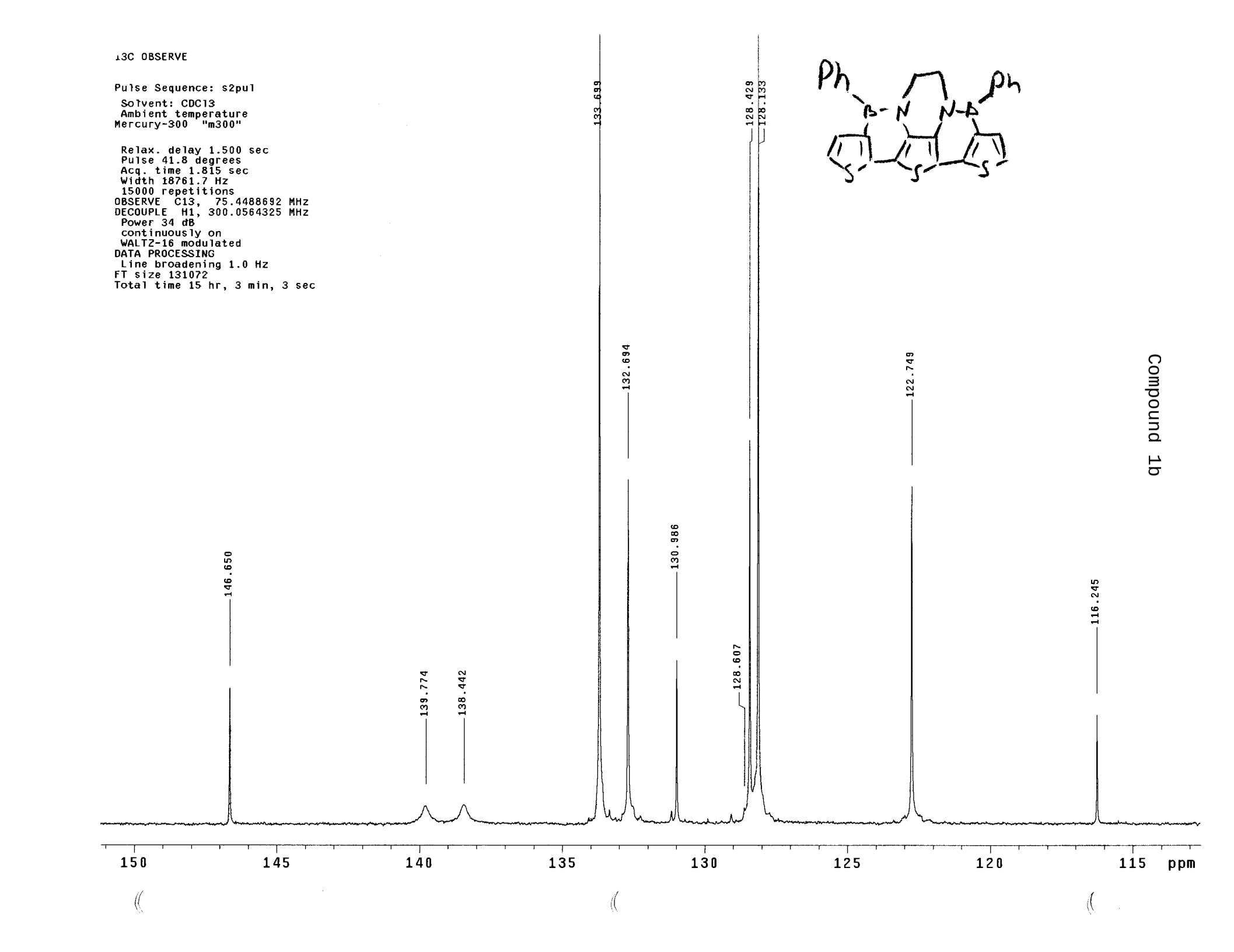
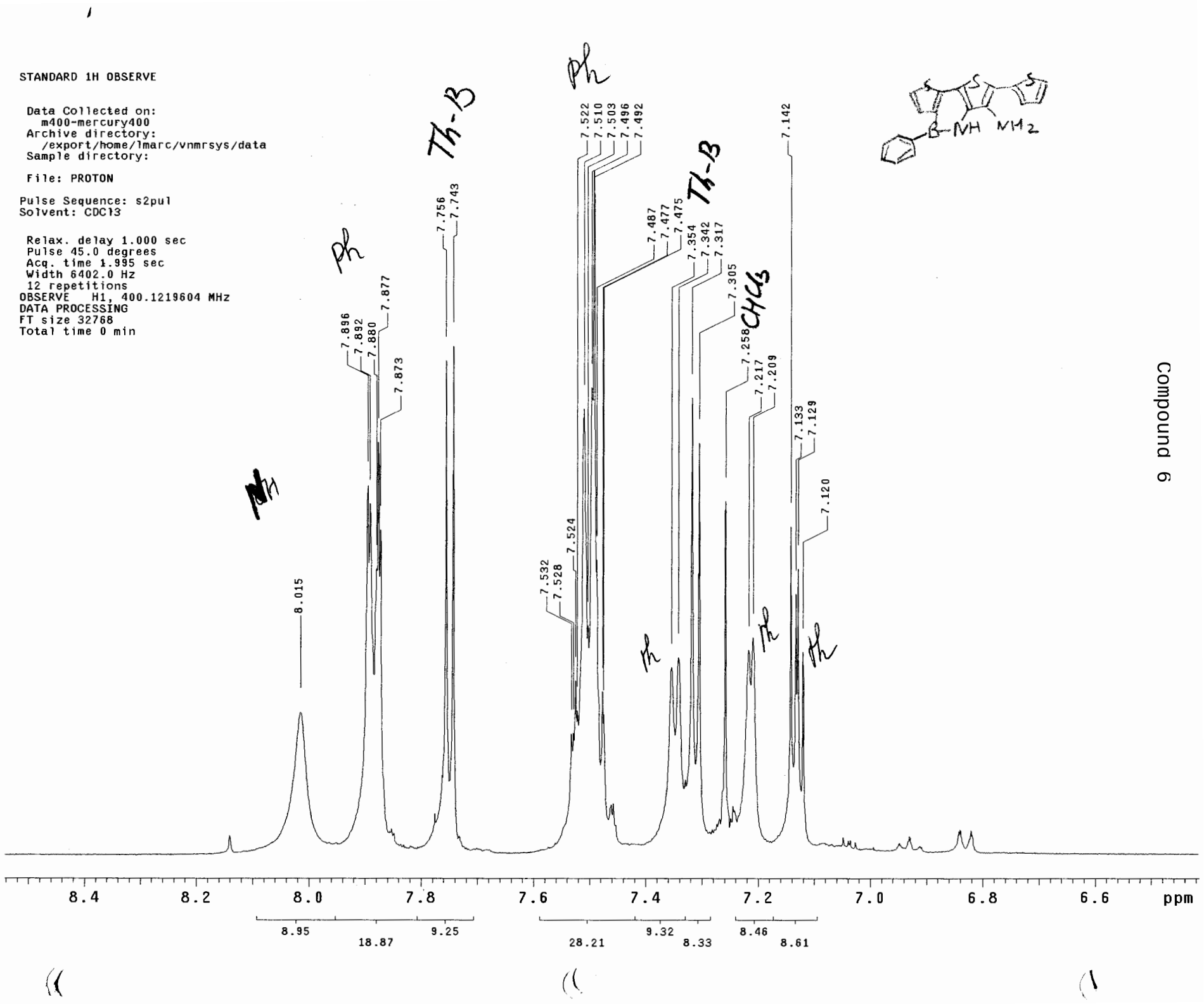


Compound 1b

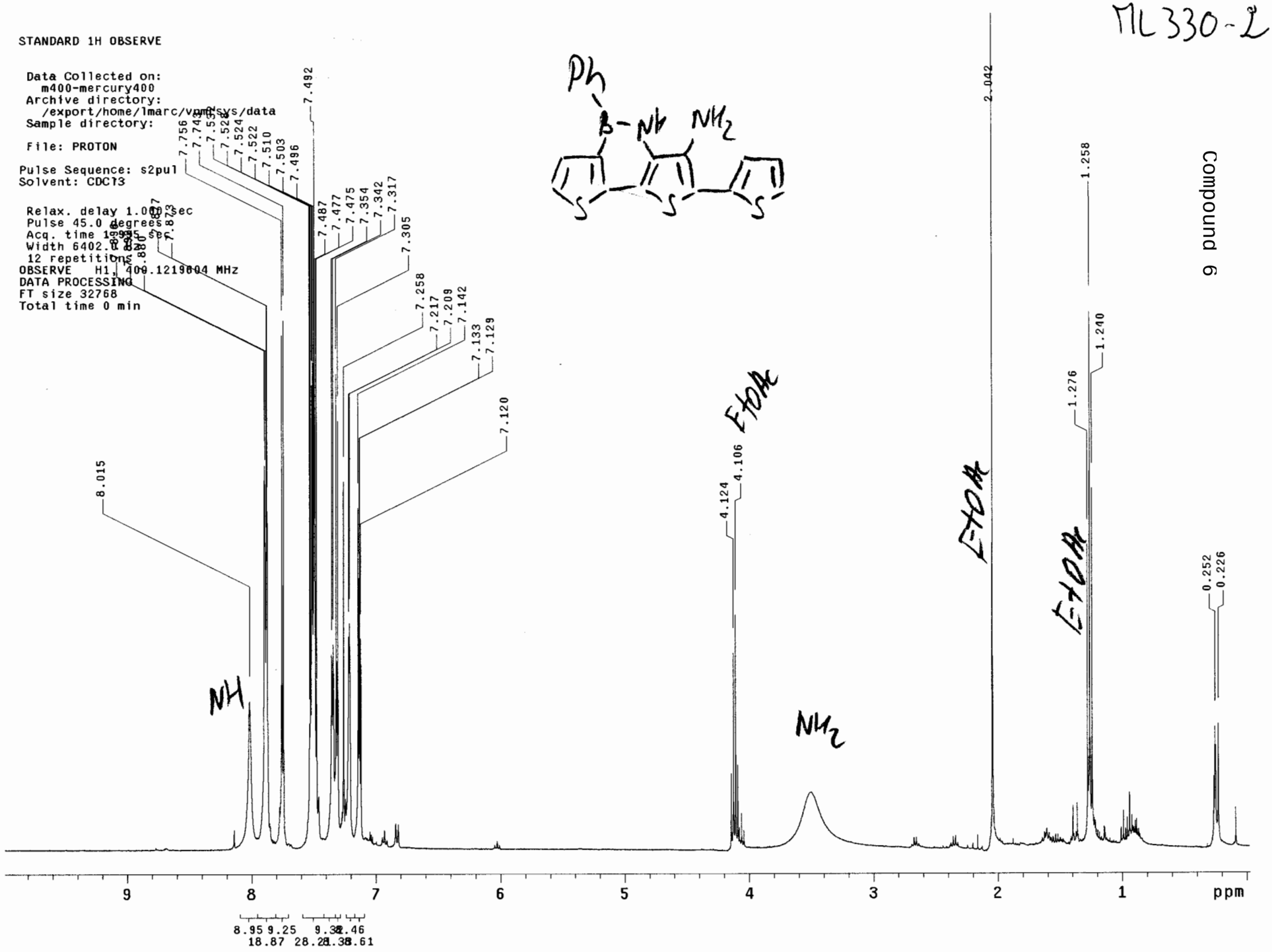

13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300 "m300"
Relax. delay 1.500 sec
Pulse 41.8 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
15000 repetitions
OBSERVE C13, 75.4488692 MHz
DECOUPLE H1, 300.0564325 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 0 min, 0 sec
13C, 300MHz
ML406 - 13C
OK
Ph
Ph
B-N
N-R
S
S
S
133.699
132.694
130.986
128.607
128.429
128.133
122.749
77.717
77.497
77.292
76.871
46.212
146.650
139.774
138.442
116.245
CHCl3
Compound 1b
140
120
100
80
60
40
20
ppm


13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300 "m300"
Relax. delay 1.500 sec
Pulse 41.8 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
15000 repetitions
OBSERVE C13, 75.4488692 MHz
DECOUPLE H1, 300.0564325 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 15 hr, 3 min, 3 sec
Ph
B
N
N
B
Ph
S
S
S
146.650
139.774
138.442
133.699
132.694
130.986
128.607
128.429
128.133
122.749
116.245
150
145
140
135
130
125
120
115
ppm
Compound 1b


STANDARD 1H OBSERVE
Data Collected on:
m400-mercury400
Archive directory:
/export/home/lmarc/vnmrsys/data
Sample directory:
File: PROTON
Pulse Sequence: s2pul
Solvent: CDCl3
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.995 sec
Width 6402.0 Hz
12 repetitions
OBSERVE H1, 400.1219604 MHz
DATA PROCESSING
FT size 32768
Total time 0 min
Th-B
Ph
Ph
Th-B
Th
Ph
Ph
CH3
NH
NH2
8.015
7.896
7.892
7.880
7.877
7.873
7.756
7.743
7.532
7.528
7.524
7.522
7.510
7.503
7.496
7.492
7.487
7.477
7.475
7.354
7.342
7.317
7.305
7.258
7.217
7.209
7.142
7.133
7.129
7.120
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
ppm
8.95
18.87
9.25
28.21
9.32
8.33
8.46
8.61

Compound 6

ML330-2



Compound 6