

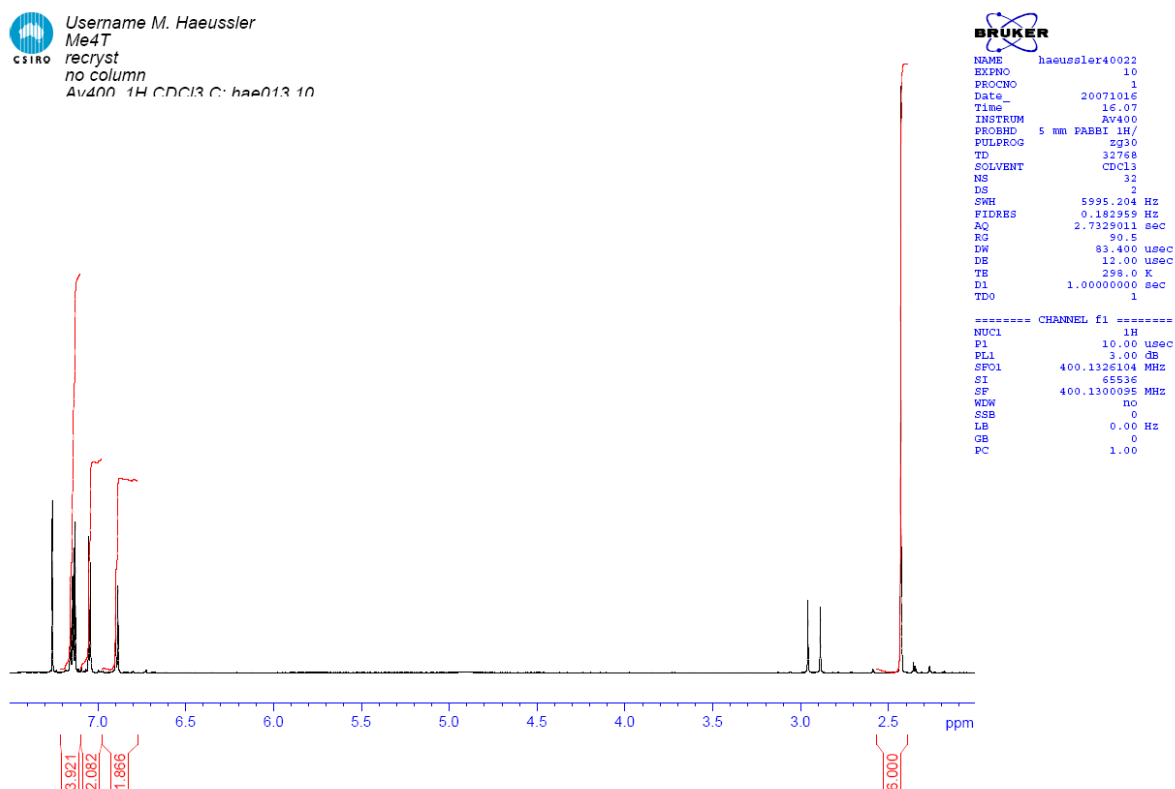
Block copolymers containing organic semiconductor segments by RAFT polymerization

Ming Chen, Matthias Häussler, Graeme Moad, Ezio Rizzardo

Supplementary Material (NMR Spectra)

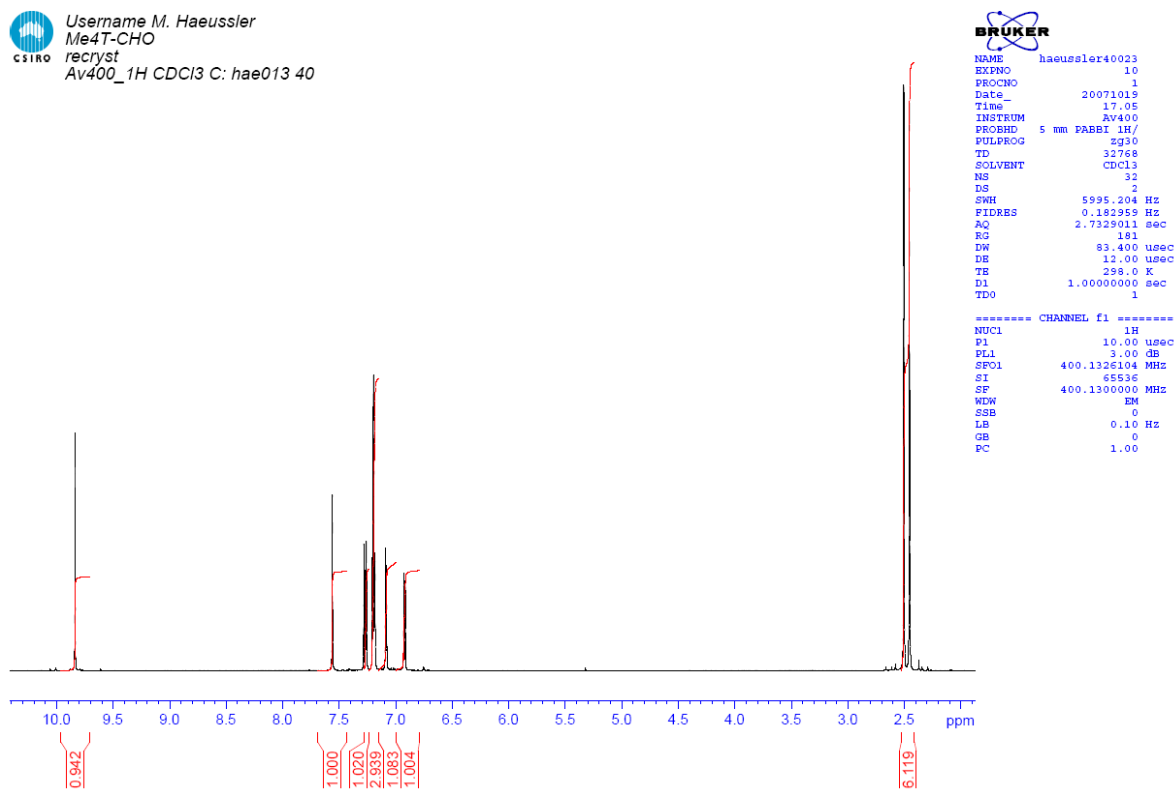
5

^1H NMR (CDCl_3): δ 7.15 (d, $J = 5.2$ Hz, 2H, 5,5'''-H), 7.13 (d, $J = 3.8$ Hz, 2H, 3',4''-H), 7.05 (d, 2H, $J = 3.8$ Hz, 4',3''-H), 6.89 (d, $J = 5.2$ Hz, 2 H, 4,4'''-H), 2.43 (s, 6H, $-\text{CH}_3$). Signals at ca. 2.8 and 3.0 ppm are due to *N,N*-dimethylformamide (DMF).



6

^1H NMR (CDCl_3): δ 9.81 (s, 1H, -CHO), 7.54 (s, 1H, 3-H), 7.24 (d, $J = 3.8$ Hz, 1H, 3'-H), 7.17 (m, 3H, 4', 4'', 5'''-H), 7.06 (d, $J = 3.9$ Hz, 1H, 3''-H), 6.90 (d, 1H, $J = 5.1$ Hz, 4'''-H), 2.48 (s, 3H, 4- CH_3), 2.43 (s, 3H, 3'''- CH_3).



7

^1H NMR (CDCl_3): δ 7.15 (d, $J = 5.2$ Hz, 1H, $5'''$ -H), 7.13 (dd, $J = 3.8$ Hz, 2H, $3', 4''$ -H), 7.05 (d, 1H, $J = 3.8$ Hz, $4'$ -H), 7.02 (d, 1H, $J = 3.8$ Hz, $3''$ -H), 6.89 (d, $J = 5.2$ Hz, 1H, $4'''$ -H), 6.81 (s, 1H, 3-H), 4.77 (s, 2H, $-\text{OCH}_2$), 2.43 (s, 3H, $3'''$ - CH_3), 2.38 (s, 3H, 4- CH_3)

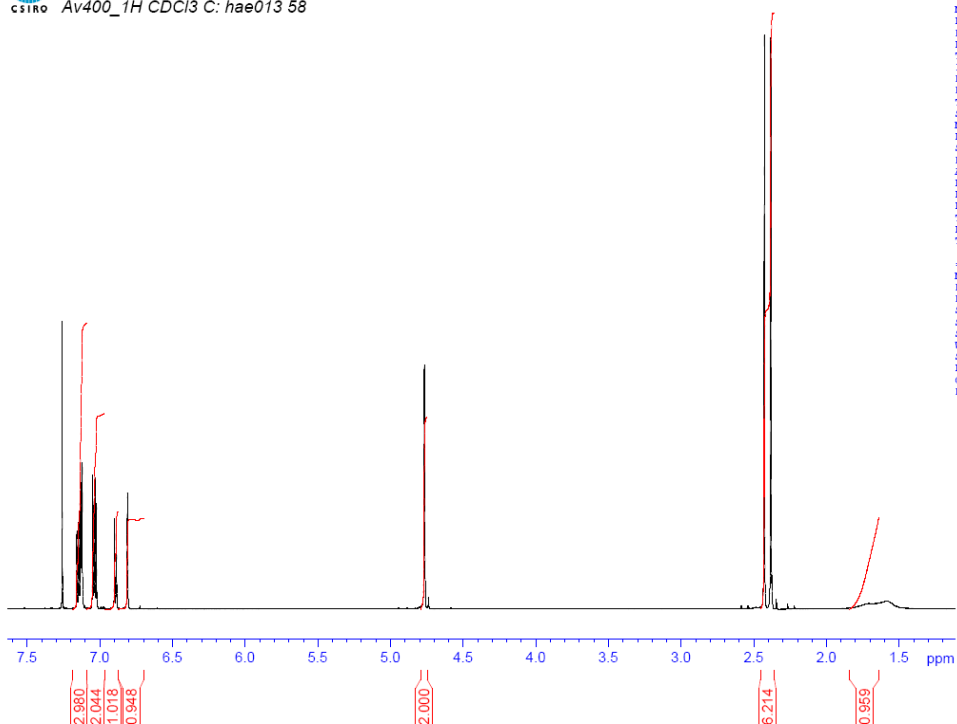


Username M. Haeussler
Me4T-CH₂OH
Av400_1H CDCl₃ C: hae013 58



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EXPNO     10
PROCNO    1
Date_     20071003
Time      13.27
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DS         2
SNR        5995.204 Hz
FIDRES     0.182959 Hz
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TDO        1

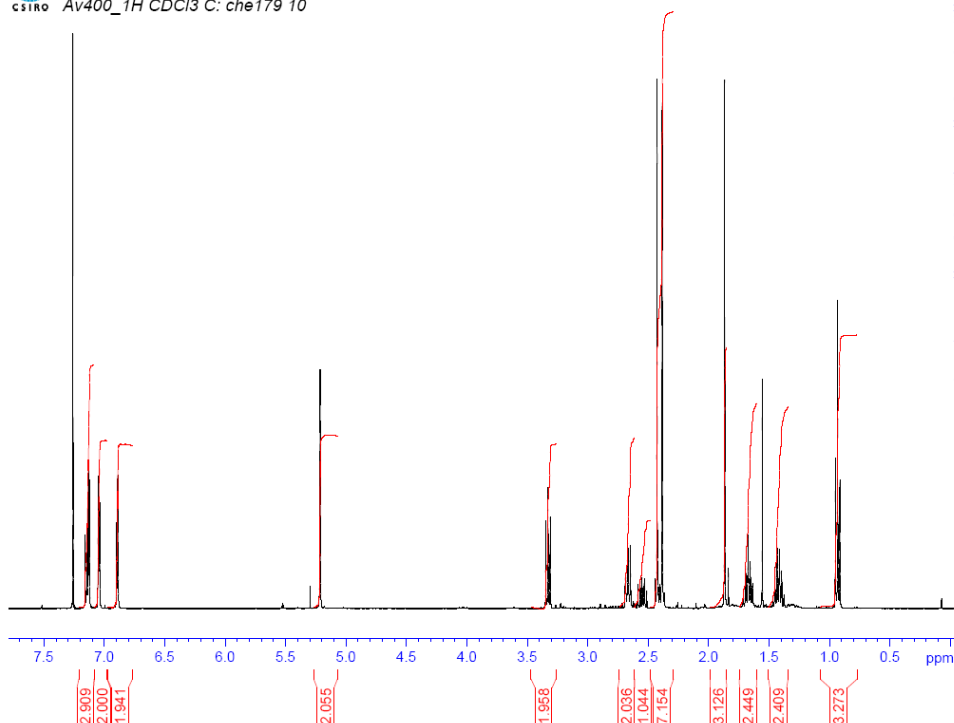
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PC         1.00
```



8

^1H NMR (CDCl_3): δ 7.15 (d, $J = 5.2$ Hz, 1H, $5''''\text{-H}$), 7.13 (dd, $J = 3.8$ Hz, 2H, $3',4'''\text{-H}$), 7.05 (dd, 2H, $J = 3.8$ Hz, $4',3'''\text{-H}$), 6.89 (d, $J = 5.2$ Hz, 1H, $4'''\text{-H}$), 6.88 (s, 1H, 3-H), 5.22 (s, 2H, $-\text{OCH}_2$), 3.33 (t, 2H, $J = 7.5$ Hz, $-\text{SCH}_2$), 2.67 (m, 2H, $\text{C}(\text{O})\text{CH}_2$), 2.56 (m, 1H, CH_2CMeCN), 2.43 (s, 3H, $3'''\text{-CH}_3$), 2.41 (m, 1H, CH_2CMeCN), 2.38 (s, 3H, 4- CH_3), 1.87 (s, 3H, $\text{C}(\text{CN})\text{CH}_3$), 1.68 (m, 2H, SCH_2CH_2), 1.43 (m, 2H, $\text{SCH}_2\text{CH}_2\text{CH}_2$), 0.93 (t, 3H, $J = 7.5$ Hz, $\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$).

Username M. Chen
Me4T-RAFT ester
Av400_1H CDCl_3 C: che179 10



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NAME          chan0303
EXPNO         10
PROCNO        1
Date_         20071026
Time          15.58
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PULPROG       zg30
TD            32768
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SWH           5995.204 Hz
FIDRES       0.182959 Hz
AQ           2.7329011 sec
RG           90.5
DW           83.400 usec
DE           12.00 usec
TE           298.0 K
D1           1.00000000 sec
TD0           1

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PL1           3.00 dB
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SI           65536
SP           400.1300095 MHz
WDW           no
SSB           0
LB           0.00 Hz
GB           0
PC           1.00
    
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^1H NMR (CDCl_3): δ 7.89 (d, $3J = 3.6$ Hz, 2H; CH), 7.76 (s, 2H; CH), 6.85 (dd, $3J = 3.6$ Hz, $4J = 1.1$ Hz, 2H; CH), 2.58 (s, 6H; CH_3).

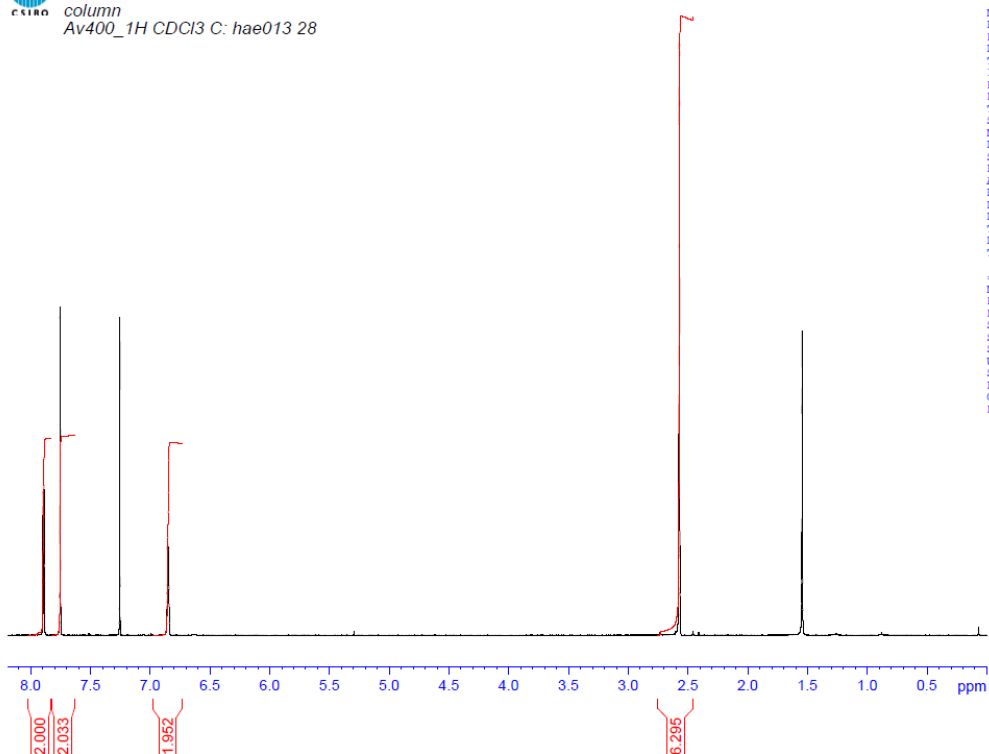


Username M. Haeussler
MeTBTMe
column
Av400_1H CDCl_3 C: hae013 28



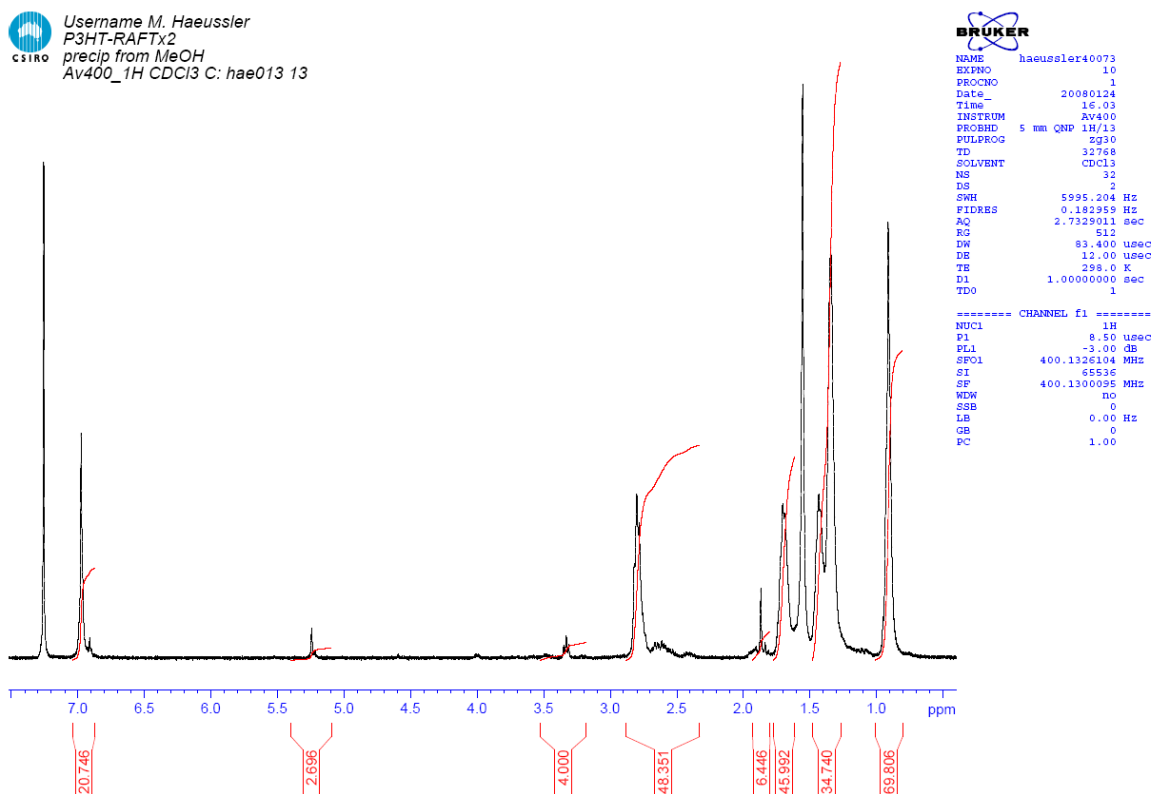
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PROCNO 1
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FIDRES 0.182959 Hz
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D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
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SI 65536
SF 400.1300095 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00



17

^1H NMR (CDCl_3): δ 6.89 (s, Tp-H), 5.25 (s, $-\text{OCH}_2$), 3.33 (t, $-\text{SCH}_2$), 2.79 (Tp $\text{CH}_2\text{C}_5\text{H}_{11}$), 2.67 (m, $\text{C}(\text{O})\text{CH}_2$), 2.56 (m, CH_2CMeCN), 2.41 (m, CH_2CMeCN), 1.87 (s, $\text{C}(\text{CN})\text{CH}_3$), 1.70 (m, Tp $\text{CH}_2\text{CH}_2\text{C}_4\text{H}_9$ and SCH_2CH_2), 1.43 (m, Tp $\text{C}_2\text{H}_4\text{C}_3\text{H}_6\text{CH}_3$ and $\text{SC}_2\text{H}_4\text{CH}_2$), 0.93 (m, Tp- $\text{C}_5\text{H}_{11}\text{-CH}_3$ and $\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$) (Tp = thiophene).



20

^1H NMR (CDCl_3): δ 6.74 (d, 1H, J = 3.5 Hz, 3 Tp-H), 6.72 (dd, 1H, J = 17.1 and 10.8 Hz, Tp-CH=), 6.60 (d, 1H, J = 2.5 Hz, 2 Tp-H), 5.43 (d, 1H, J = 17.3 Hz, =CHH), 5.04 (d, 1H, J = 10.8 Hz, =CHH), 2.45 (s, 3H, CH_3) (Tp = thiophene).

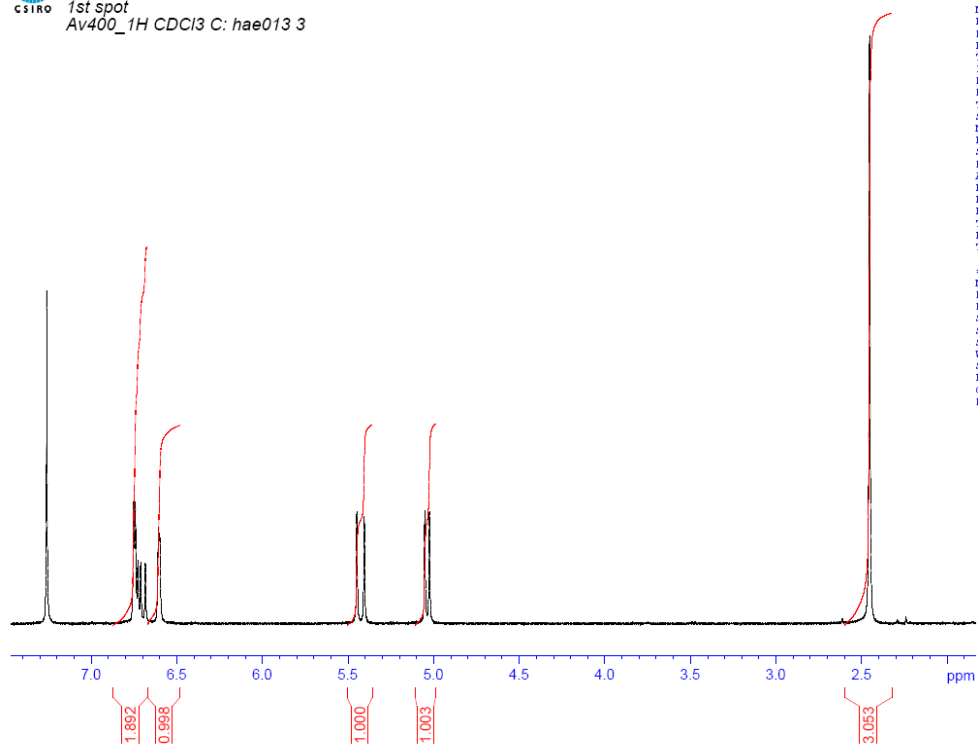


Username M. Haeussler
MeTpVin
1st spot
Av400_1H CDCl3 C: hae013 3



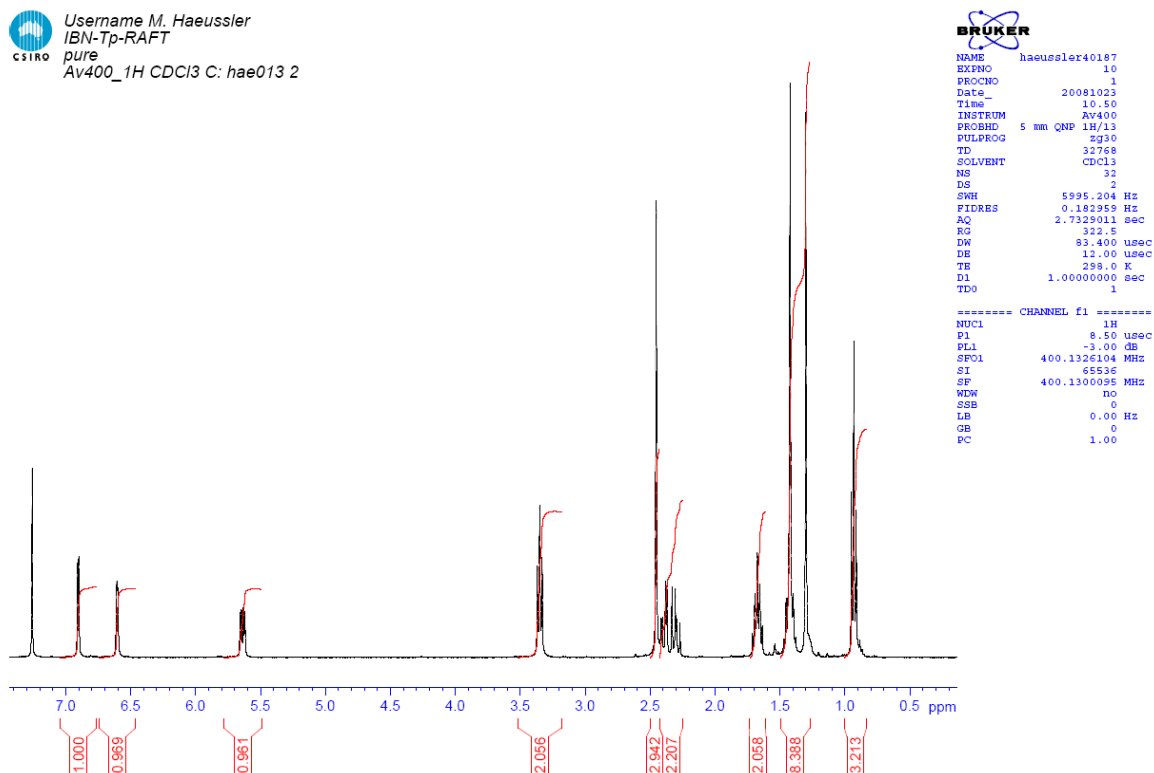
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FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 1024
DW 83.400 usec
DE 12.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1

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GB 0
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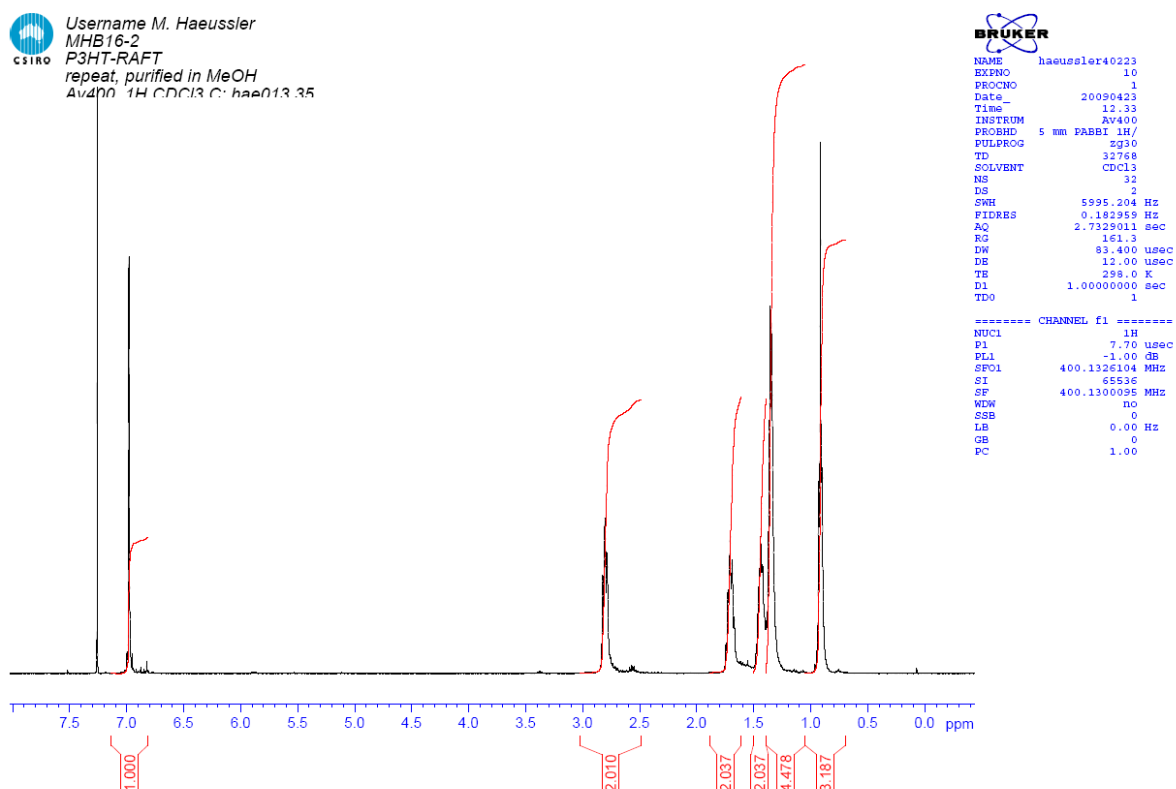
21

^1H NMR (CDCl_3): δ 6.91 (d, 1H, $J = 3.4$ Hz, 4 Tp-H), 6.60 (d, 1H, 3.4 Hz, 3 Tp-H), 5.64 (dd, 1H, $J = 10.4$ and 4.3 Hz, Tp-CHCH $_2$), 3.35 (t, 2H, $J = 7.35$, S-CH $_2$), 2.45 (s, 3H, Tp-CH $_3$), 2.33 (m, 2H, Tp-CHCH $_2$), 1.67 (m, 2H, S-CH $_2$ CH $_2$), 1.42 (s, 6H, C(CN)(CH $_3$) $_2$), 1.30 (s, 2H, CH $_2$ CH $_3$), 0.93 (t, 3H, $J = 7.3$ Hz, CH $_2$ CH $_3$) (Tp = thiophene).



24

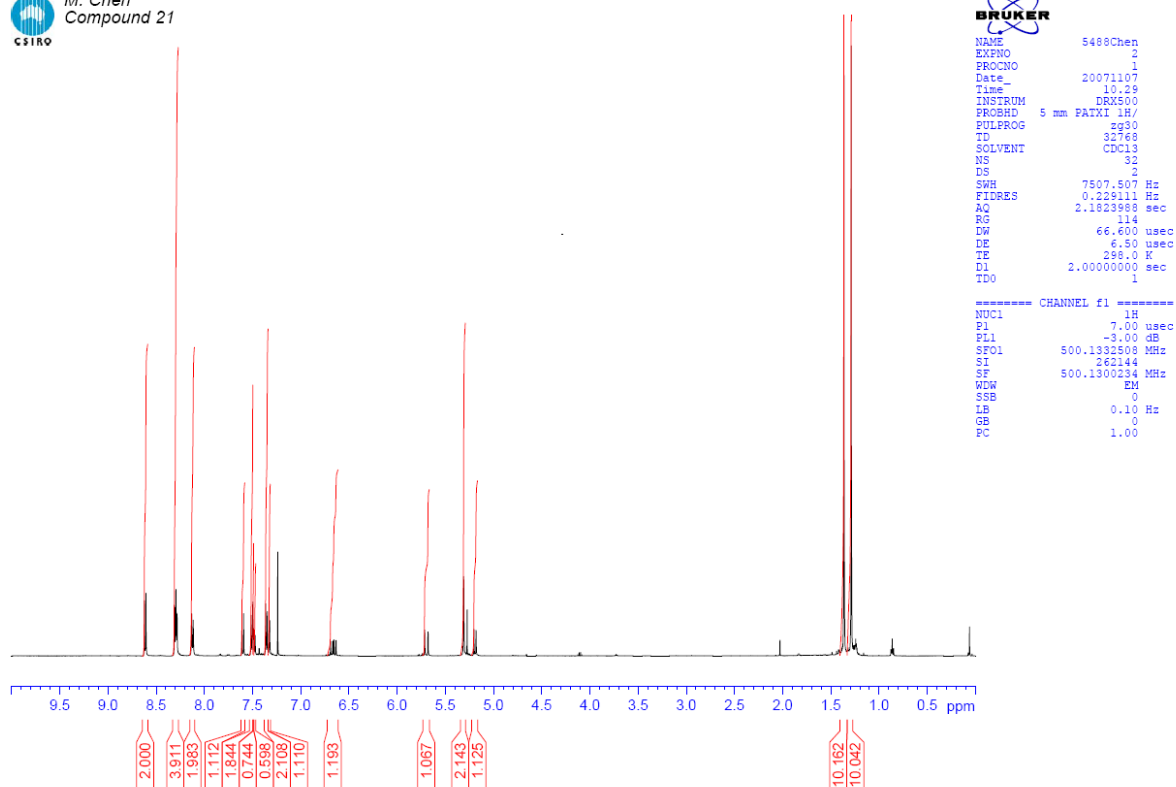
^1H NMR (CDCl_3): δ 6.98 (s, Tp-H), 5.88 (m, Tp-CH-S), 3.38 (m, S- $\text{CH}_2\text{C}_3\text{H}_7$), 2.8 (t, Tp- CH_2), 2.55 (t, Br-Tp- CH_2), 1.71 (m, Tp- CH_2CH_2), 1.44 and 1.35 (m, CH_2 of hexyl and butyl groups), 0.94 (m, CH_3 of hexyl and butyl groups) (Tp = thiophene). Expansions of this NMR are shown in Figure 1 of paper.



29

^1H NMR (CDCl_3): δ 8.61 (d, 2H, $J = 8.0$ Hz, perylene-H), 8.30 (dd, 4H, $J = 8.0, 5.3$ Hz, perylene -H), 8.12 (d, 2H, $J = 8.2$ Hz, perylene -H), 7.60 (d, 1H, $J = 8.7$ Hz, Ph-H), 7.47-7.53 (m, 3H, Ph-H), 7.36 (d, 2H, $J = 8.2$, Ph-H), 7.33 (d, 1H, $J = 2.3$ Hz, Ph-H), 6.73 (dd, 1H, $J = 17.6$ and 10.9 Hz, =CHH), 5.76 (d, 1H, $J = 17.6$ Hz, =CHH), 5.31 (s, 2H, St- $\text{CH}_2\text{-N-}$), 5.25 (d, 1H, $J = 10.9$ Hz, $\text{CH}=\text{CH}_2$), 1.36 (s, 9H, $-\text{C}(\text{CH}_3)_3$), 1.29 (s, 9H, $-\text{C}(\text{CH}_3)_3$).

M. Chen
Compound 21



30

^1H NMR (CDCl_3): δ 8.67 (b, 2H, perylene-H), 8.46 (b, 4H, perylene-H), 8.33(b, 2H, perylene-H), 7.20 (b, 1H, Ph-H), 5.42 (m, 1H, -S-CH(Ph)-CH₂-), 5.35 (s, 2H, Ph-CH₂-N-), 3.26 (t, 2H, J=7.45 Hz, -CH₂-CH₂-S-), 2.34 (m, 2H, -CH(Ph)-CH₂-C-), 1.36 (s, 9H, -C(CH₃)₃), 1.34 (s, 6H, -C(CN)(CH₃)₂), 1.29 (s, 9H, -C(CH₃)₃), 0.86 (t, 3H, J=7.3 Hz, -CH₂CH₃).

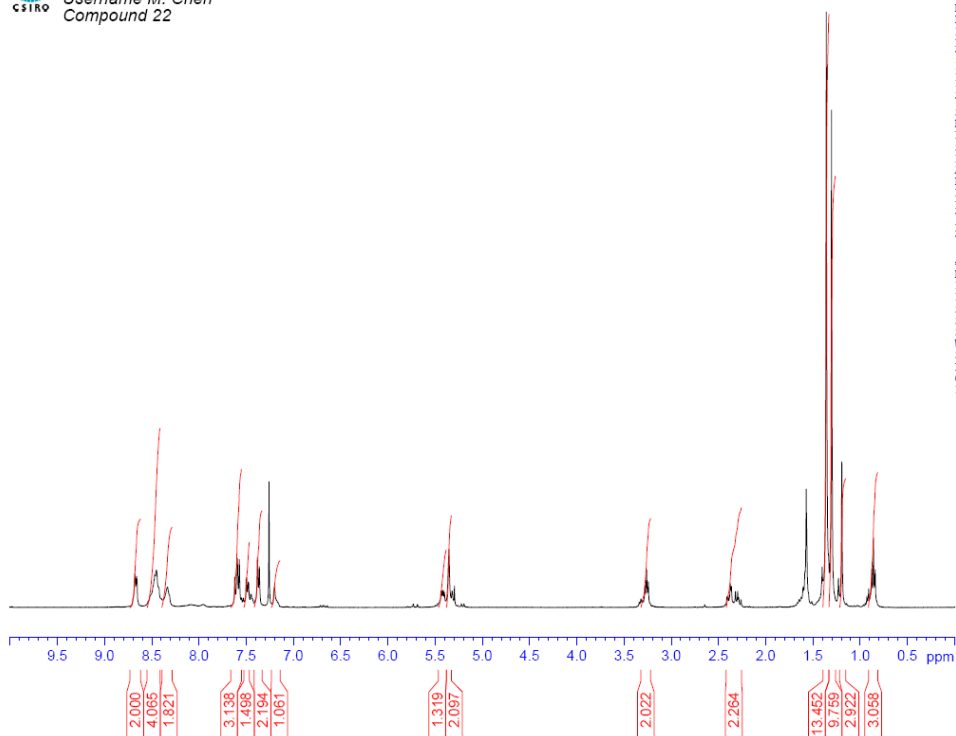


Username M. Chen
Compound 22



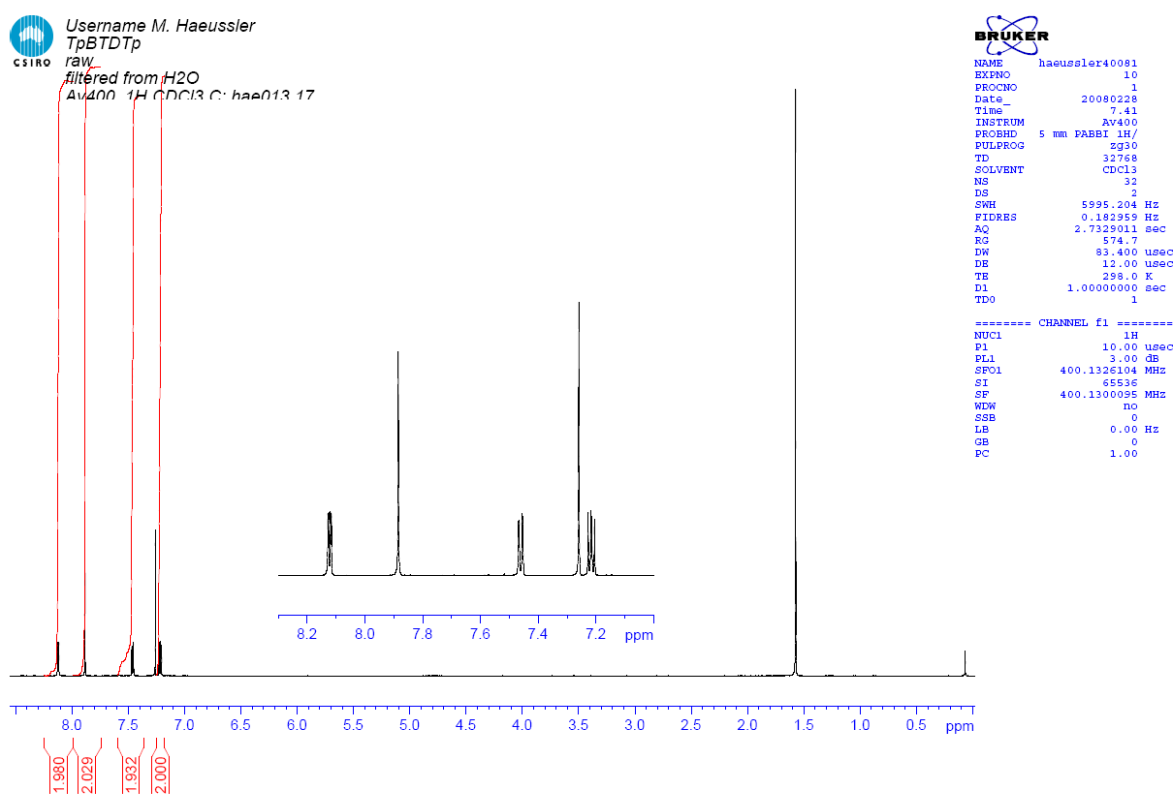
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PROCNO    1
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FIDRES     0.182959 Hz
AQ         2.7329011 sec
RG         328.1
DW         83.400 usec
DE         12.00 usec
TE         298.0 K
D1         1.00000000 sec
TD0        1

===== CHANNEL f1 =====
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PL1        -3.00 dB
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SF         400.1300095 MHz
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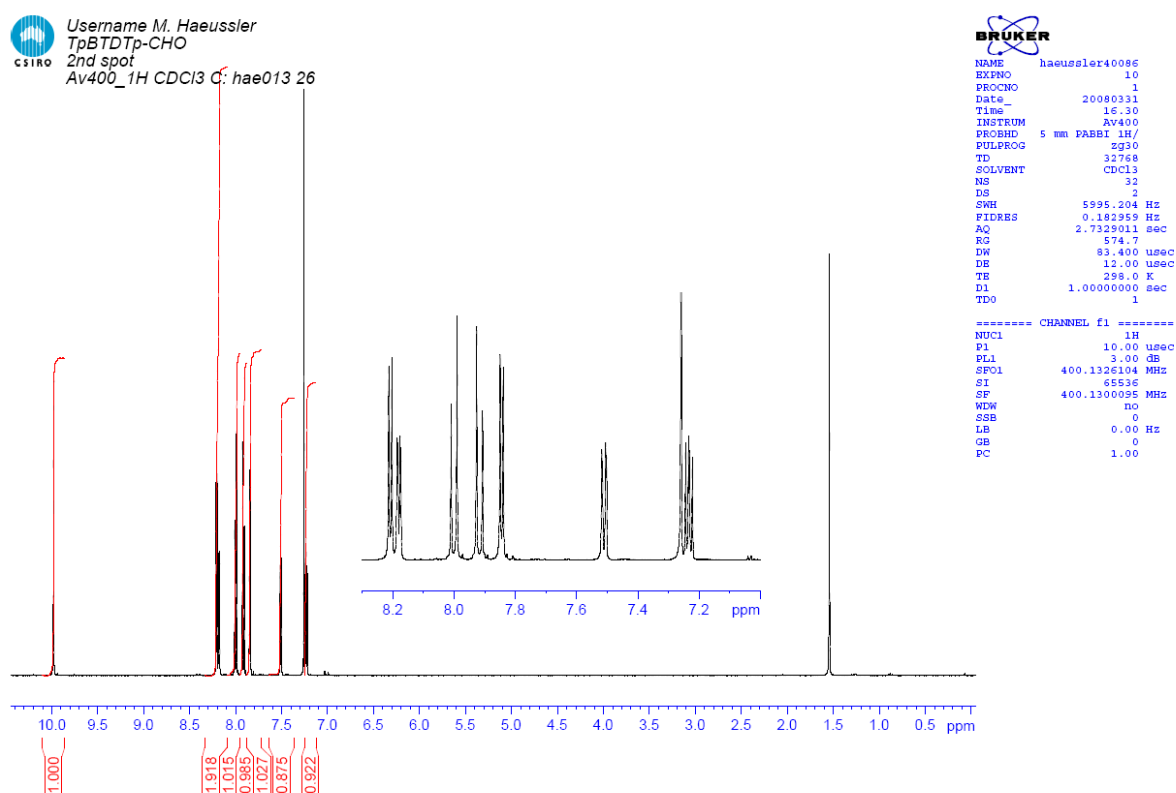
11

^1H NMR (CDCl_3): δ 8.12 (d, 2H, $J = 3.8$ Hz, 3,3' Tp-H), 7.88 (s, 2H, 5,6 B-H), 7.46 (d, 2H, $J = 5.1$ Hz, 5,5' Tp-H), 7.21 (dd, 2H, $J = 5.1, 3.8$ Hz, 4,4' Tp-H) (Tp = thiophene).



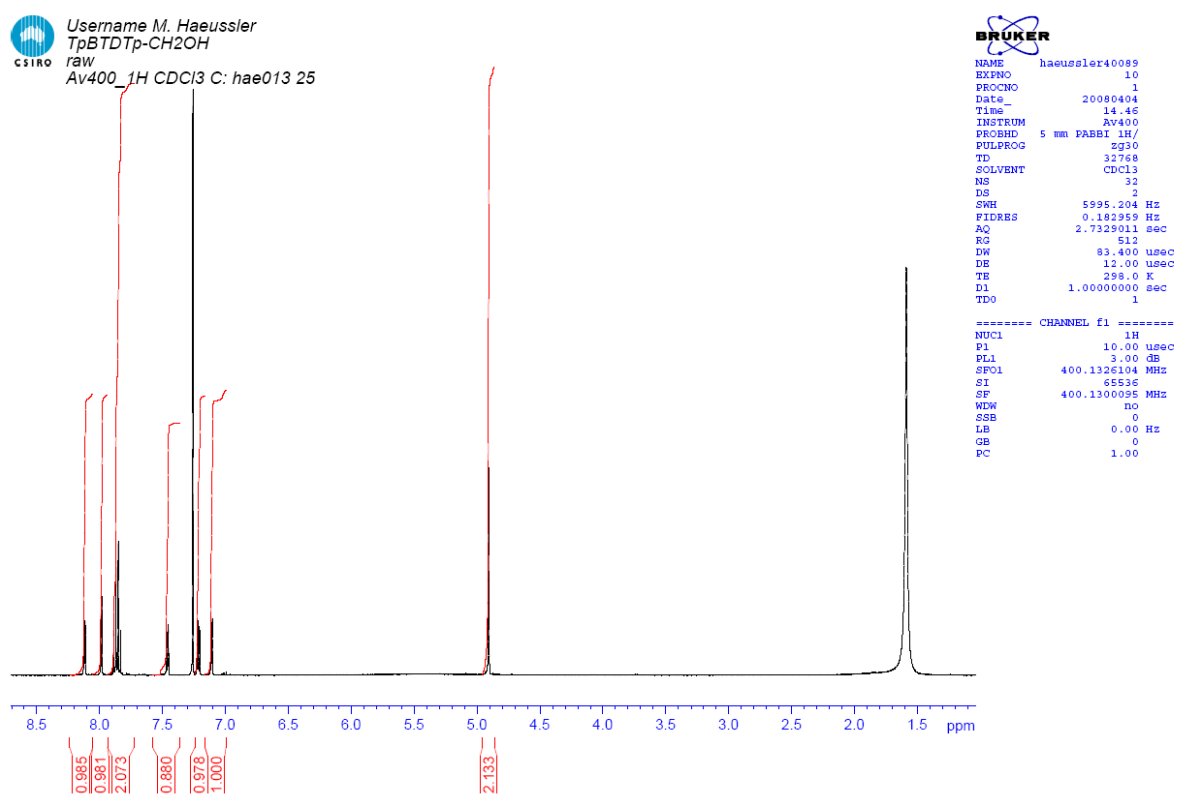
S1

^1H NMR (CDCl_3): δ 9.98 (s, 1H, -CHO), 8.21 (d, 1H, $J = 4.1$ Hz, 4 Tp-H), 8.18 (d, 1H, $J = 3.8$ Hz, 3' Tp-H), 8.0 (d, 1H, $J = 7.7$ Hz, 5 B-H), 7.92 (d, 1H, $J = 7.7$ Hz, 6 B-H), 7.85 (d, 1H, $J = 4.1$ Hz, 3 Tp-H), 7.51 (d, 1H, $J = 5.1$ Hz, 5' Tp-H), 7.23 (dd, 1H, $J = 5.1$ and 3.8 Hz, 4' Tp-H) (Tp = thiophene, B = benzothiadiazole).



S2

^1H NMR (CDCl_3): δ 8.12 (d, 1H, $J = 3.8$ Hz, 4 Tp-H), 7.98 (d, 1H, $J = 3.8$ Hz, 3' Tp-H), 7.88 (d, 1H, $J = 7.6$ Hz, 5 B-H), 7.84 (d, 1H, $J = 7.6$ Hz, 6 B-H), 7.46 (d, 1H, $J = 5.2$ Hz, 5' Tp-H), 7.21 (dd, 1H, $J = 5.1, 3.8$ Hz, 4' Tp-H), 7.11 (d, 1H, $J = 3.8$ Hz, 3 Tp-H), 4.91 (s, 2H, $-\text{OCH}_2$) (Tp = thiophene, B = benzothiadiazole).



32

^1H NMR (CDCl_3): δ 8.12 (d, 1H, $J=3.5$ Hz, 4 Tp-H), 7.98 (d, 1H, $J=3.8$ Hz, 3' Tp-H), 7.88 (d, 1H, $J=7.6$ Hz, 5 B-H), 7.84 (d, 1H, $J=7.6$ Hz, 6 B-H), 7.46 (d, 1H, $J=5.2$ Hz, 5' Tp-H), 7.42 (d, 2H, $J=8.1$, 3 Ph-H), 7.42 (d, 2H, $J=8.1$ Hz, 2 Ph-H), 7.22 (dd, 1H, $J=5.2$, 3.8 Hz, 4' Tp-H), 7.10 (d, 1H, $J=3.5$ Hz, 3 Tp-H), 6.73 (dd, 1H, $J=17.6$ and 10.9 Hz, =CHH), 5.76 (d, 1H, $J=17.6$ Hz, =CHH), 5.25 (d, 1H, $J=10.9$ Hz, $\text{CH}=\text{CH}_2$), 4.77 (s, 2H, $-\text{OCH}_2\text{Tp}$), 4.62 (s, 2H, $-\text{OCH}_2\text{Ph}$) (Tp = thiophene, B= benzothiadiazole).

