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Supporting Information

Engineering the band gap and energy level of conjugated polymers by using a second acceptor unit

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Fabrication and Characterization of Organic Field-Effect Transistors (OFETs)

Top-contact/bottom-gate (TC/BG) OTFT devices were fabricated using n^+-Si/SiO_2 substrates where n^+-Si and SiO_2 were used as the gate electrode and gate dielectric, respectively. The substrates were subjected to cleaning using ultrasonication in acetone, a cleaning agent, deionized water (twice), and *iso*-propanol. The cleaned substrates were dried under vacuum at 80 ^oC. The substrates were then treated with plasma for 15 min and transfer into a glove box. The substrates were modified with OTS according to the literature reported by Bao and coworkers. Polymer or polymer/$PC_{71}BM$ films were casted or spin-coated on the OTS-modified Si/SiO_2 substrate from ODCB or TCB and 2 vol % DIO with the polymer concentration of 10 mg/mL, optionally followed by thermal annealing at 160 ^oC for 30 min under nitrogen. After polymer thin film deposition, about 25 nm thick gold was deposited as source and drain contacts using a shadow mask. The OTFT devices had a channel length (L) of 50 μm and a channel width (W) of 2.5 mm. *J-V* characteristics were obtained using an Agilent B2902A Source Meter with a Micromanipulator 6150 probe station in a clean and shielded box at room temperature in air.

Fabrication and characterization of BHJ polymer solar cells

All the polymer solar cell devices were fabricated with the device configuration of glass/ITO/PEDOT:PSS/polymer:$PC_{71}BM$/LiF/Al. The conductivity of ITO is 15 Ω/□, and PEDOT:PSS is Baytron Al 4083 from H.C. Starck. ITO-coated glass substrates were ultrasonically cleaned sequentially in detergent, water, acetone, and *iso*-propanol. The substrates were covered by a 30 nm layer of PEDOT: PSS by spin coating. After annealing in air at 140 °C for 10 min, the samples were cooled to room temperature. The substrates were then transferred into a nitrogen-filled glove box. The polymers and $PC_{71}BM$ were dissolved at a 1:2 weight ratio in DCB with 2% (v/v) of DIO. The solutions were then heated at 90 °C and stirred overnight. The photoactive layer was then spin coated onto the PEDOT:PSS layer at 1500-2000 rmp. The top electrode was thermally evaporated, with a 0.6 nm LiF layer, followed by 80 nm of aluminum at a pressure of 10^{-6} Torr through a shadow mask. Six cells were fabricated on one substrate and the effective area of every cell is 4 mm^2. The measurement of devices was conducted in the glove box. Current−voltage characteristics were recorded using a Keithley 2400 Source Meter under AM 1.5 illumination with an intensity of 100 mW/cm^2 from a solar simulator (Model SS-50A, photo Emission Tech., Inc.). The $J-V$ curves were recorded at the temperature of about 20 °C. The external quantum efficiency (EQE) spectra were characterized using a Keithley 485 picoammeter under illumination of monochromatic light through the ITO side of devices.

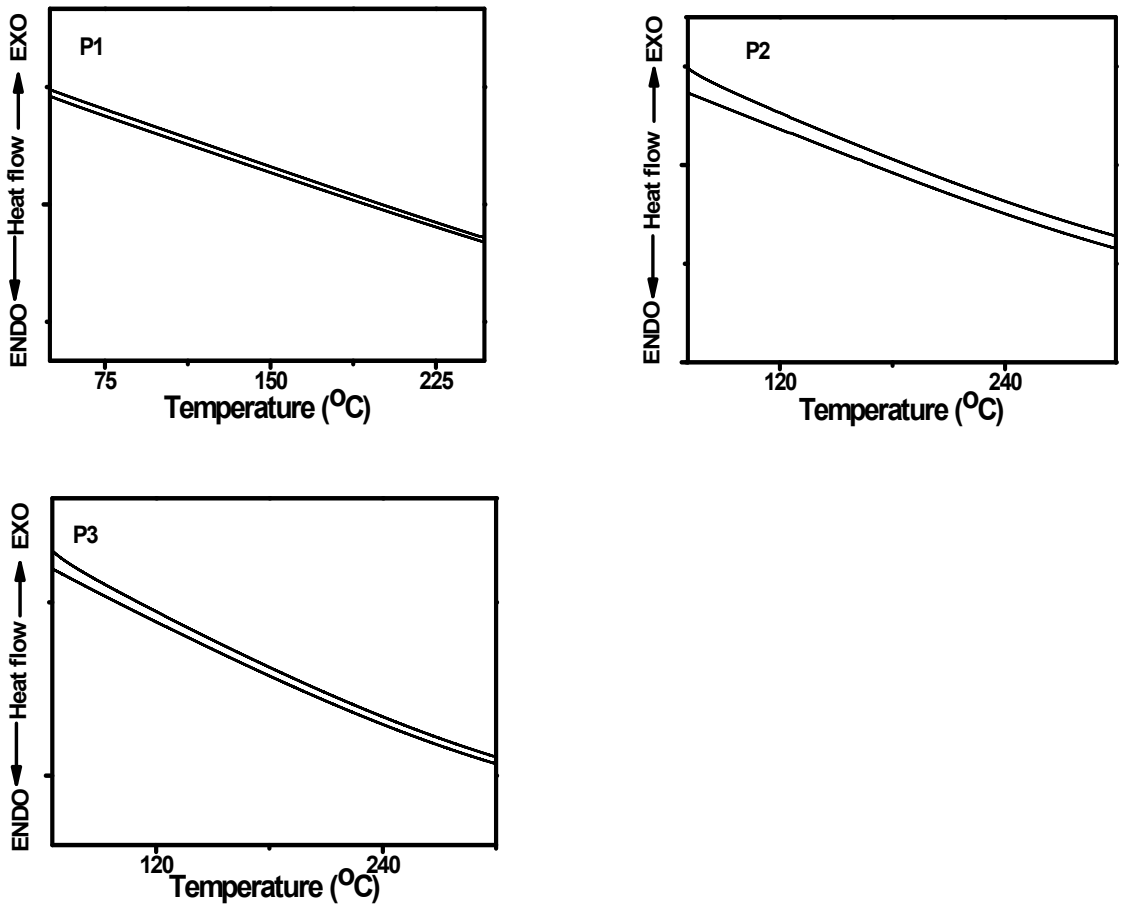

Figure S1. DSC curve of **P1-3** with a scanning rate of 10 °C/min.

Table S1. Summary of XRD data of powdery samples (**P1-3**)

Sample	2 θ (°)					*d*-spacing (Å)				
P1	4.31	8.54	12.16	19.54	25.47	20.45	10.35	7.27	4.54	3.49
P2	4.25	8.22	12.23	19.68	23.60	20.75	10.75	6.65	4.50	3.61
P3	4.39	8.65	12.66	19.61	25.62	20.11	10.22	6.99	4.52	3.47

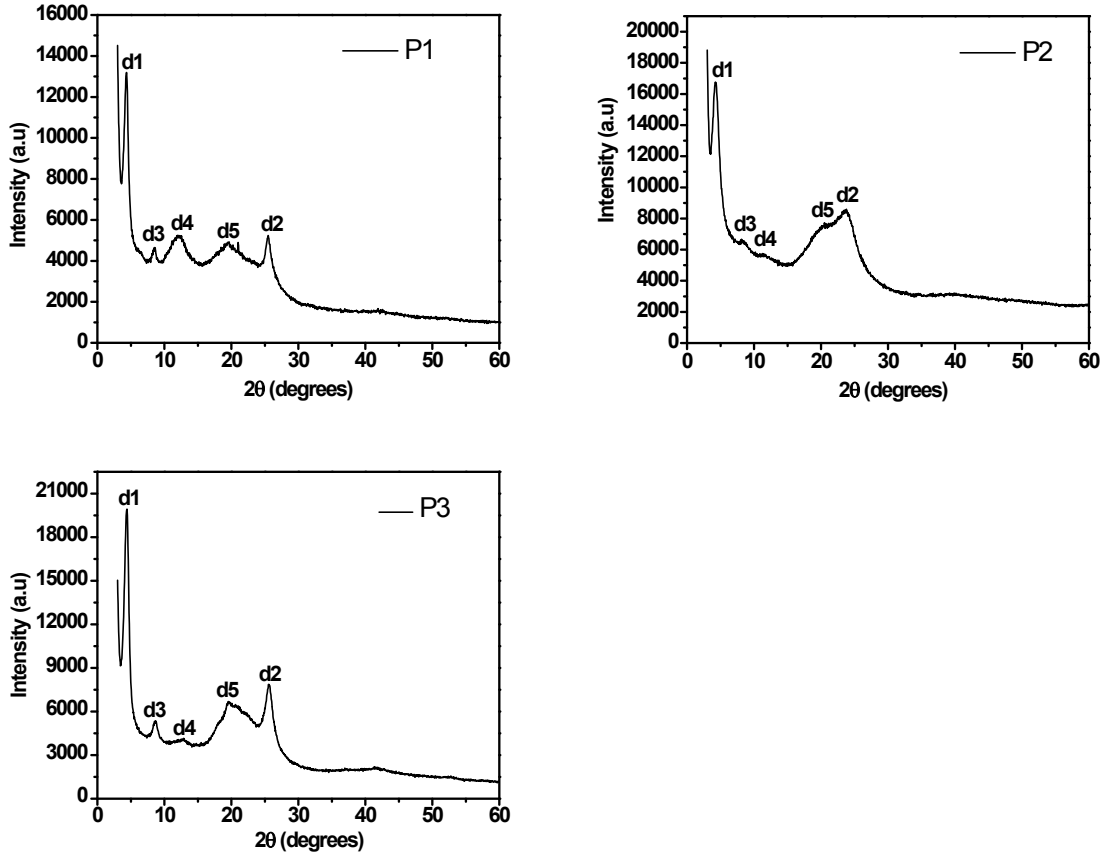

Figure S2. X-ray diffraction patterns of powdery **P1-3** samples.

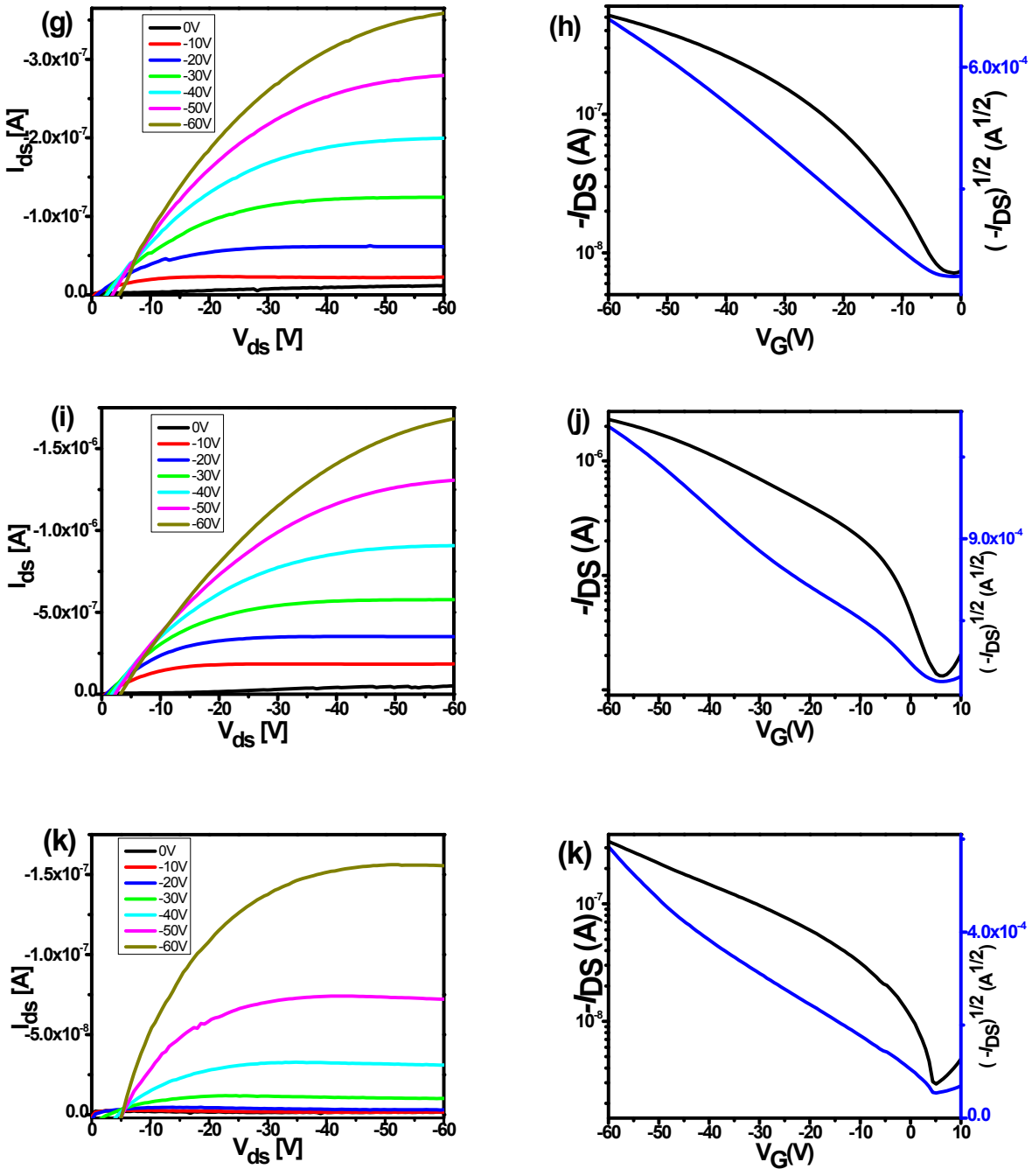

Figure S3. Output and transfer characteristics of **P1** (g, h), **P2** (i, j), and **P3** (k, l) devices of the spin-coated film of the blend of **P1-3**:$PC_{71}BM$ in DCB with 2% DIO (by volume) transistors based on OTS-modified Si/SiO_2 substrate. Hole mobilities are 7.00 × 10^{-4}, 2.37 × 10^{-3}, and 2.90 × 10^{-4} $cm^2V^{-1}s^{-1}$ for **P1**, **P2**, and **P3**, respectively.

Table S2. OFET Device Performances of polymers **P1**, **P2**, and **P3**.

	μ ($cm^2V^{-1}s^{-1}$) [a]	$I_{on/off}$	time (min)	annealing temperature (^oC)
P1	6.06×10^{-4} (4.95×10^{-4})	$>10^3$	30	160
P1:$PC_{71}BM$	7.00×10^{-4} (5.75×10^{-4})	$\sim10^2$	30	160
P2	1.28×10^{-3} (1.24×10^{-3})	$>10^3$	30	160
P2:$PC_{71}BM$	2.37×10^{-3} (1.34×10^{-3})	$>10^2$	30	160
P3	1.94×10^{-4} (1.37×10^{-4})	$>10^3$	30	160
P3:$PC_{71}BM$	2.90×10^{-4} (2.52×10^{-4})	$>10^2$	30	160

[a] Maximum value of hole mobilities after annealing at 160 ^{o}C for 30 min and average mobilities are shown in parentheses for more than 3 or 3 devices are tested for each polymer with or without $PC_{71}BM$.

Table S3. OPV Performances of **P1**

active layer	solvent	J_{sc} (mAcm^{-2})	V_{oc} (V)	*FF*	PCE (%)
P1:$PC_{71}BM$ (1:1)	DCB	5.85	0.77	0.40	1.80
	DCB	5.69	0.77	0.39	1.71
	DCB	5.61	0.75	0.39	1.66
P1:$PC_{71}BM$ (1:1)	DCB	5.59	0.76	0.40	1.70
	DCB	4.89	0.72	0.40	1.44
	DCB	5.51	0.72	0.39	1.53
P1:$PC_{71}BM$ (1:1)	DCB	5.77	0.75	0.40	1.73
	DCB	5.39	0.74	0.40	1.59
P1:$PC_{71}BM$ (1:2)	DCB	7.58	0.79	0.44	2.62
		7.52	0.78	0.42	2.50
P1:$PC_{71}BM$ (1:2)	DCB	7.40	0.78	0.44	2.59
		7.75	0.79	0.44	2.74
P1:$PC_{71}BM$ (1:2)	DCB	7.64	0.79	0.45	2.71
		7.61	0.78	0.45	2.70
		7.89	0.78	0.45	2.75
P1:$PC_{71}BM$ (1:2)	DCB+ 2% DIO	5.36	0.77	0.48	1.99
		5.05	0.76	0.48	1.85
P1:$PC_{71}BM$ (1:2)	DCB+ 2% DIO	5.03	0.76	0.51	1.97
		5.12	0.75	0.51	1.96
P1:$PC_{71}BM$ (1:2)	DCB+ 2% DIO	4.79	0.76	0.50	1.83
		4.76	0.75	0.50	1.80

Table S4. OPV Performances of **P2**

active layer	solvent	J_{sc} (mAcm^{-2})	V_{oc} (V)	*FF*	PCE (%)
P2:$PC_{71}BM$ (1:1)	DCB	5.33	0.84	0.36	1.63
		5.44	0.82	0.37	1.63
		5.46	0.80	0.37	1.63
P2:$PC_{71}BM$ (1:1)	DCB	5.43	0.85	0.38	1.75
		5.36	0.84	0.38	1.69
P2:$PC_{71}BM$ (1:1)	DCB	5.48	0.80	0.38	1.66
		5.38	0.78	0.38	1.62
P2:$PC_{71}BM$ (1:2)	DCB	5.79	0.83	0.47	2.25
		5.64	0.82	0.47	2.18
		5.66	0.80	0.46	2.07
P2:$PC_{71}BM$ (1:2)	DCB	5.82	0.82	0.46	2.21
		5.56	0.81	0.47	2.13
		5.49	0.81	0.46	2.05
		5.55	0.80	0.46	2.04
P2:$PC_{71}BM$ (1:2)	DCB+ 2% DIO	6.70	0.84	0.54	3.01
		7.57	0.85	0.53	3.41
		7.02	0.84	0.54	3.18
P2:$PC_{71}BM$ (1:2)	DCB+ 2% DIO	6.60	0.84	0.54	3.02
		7.33	0.85	0.54	3.38
P2:$PC_{71}BM$ (1:2)	DCB+ 2% DIO	6.41	0.84	0.52	2.83
		7.13	0.83	0.51	3.06

Table S5. OPV Performances of **P3**

active layer	solvent	J_{sc} (mAcm^{-2})	V_{oc} (V)	*FF*	PCE (%)
P3:$PC_{71}BM$ (1:1)	DCB	3.87	0.90	0.37	1.30
		4.10	0.87	0.42	1.48
		4.18	0.89	0.38	1.42
P3:$PC_{71}BM$ (1:1)	DCB	4.03	0.88	0.39	1.39
		4.06	0.87	0.40	1.40
		4.07	0.86	0.39	1.37
P3:$PC_{71}BM$ (1:1)	DCB	4.04	0.89	0.38	1.37
		4.01	0.90	0.38	1.38
		3.83	0.89	0.37	1.26
P3:$PC_{71}BM$ (1:2)	DCB	7.07	0.93	0.42	2.75
		7.09	0.90	0.43	2.75
		7.06	0.90	0.42	2.69
P3:$PC_{71}BM$ (1:2)	DCB	6.76	0.83	0.43	2.39
		7.18	0.89	0.42	2.68
		7.07	0.86	0.42	2.57
P3:$PC_{71}BM$ (1:2)	DCB	7.02	0.92	0.43	2.79
		6.96	0.94	0.41	2.70
		6.80	0.84	0.40	2.53
P3:$PC_{71}BM$ (1:2)	DCB+ 2% DIO	2.99	0.82	0.53	1.29
		2.89	0.80	0.52	1.21
P3:$PC_{71}BM$ (1:2)	DCB+ 2% DIO	3.63	0.76	0.53	1.47
		3.63	0.75	0.54	1.49
P3:$PC_{71}BM$ (1:2)	DCB+ 2% DIO	3.58	0.78	0.54	1.50
		3.50	0.76	0.54	1.45
P3:$PC_{71}BM$ (1:2)	DCB+ 2% DIO	3.33	0.80	0.53	1.43
		3.27	0.79	0.54	1.39

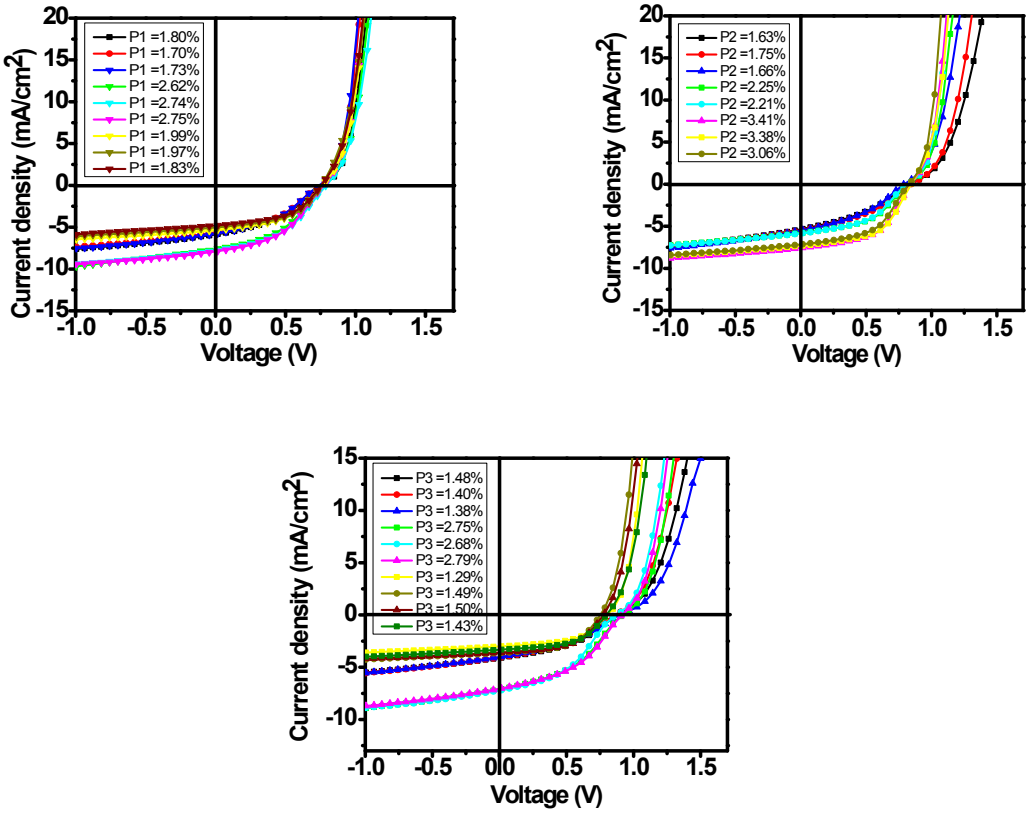

Figure S4. Graphical representation of photovoltaic performance of **P1-3**.

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DE 6.50 usec
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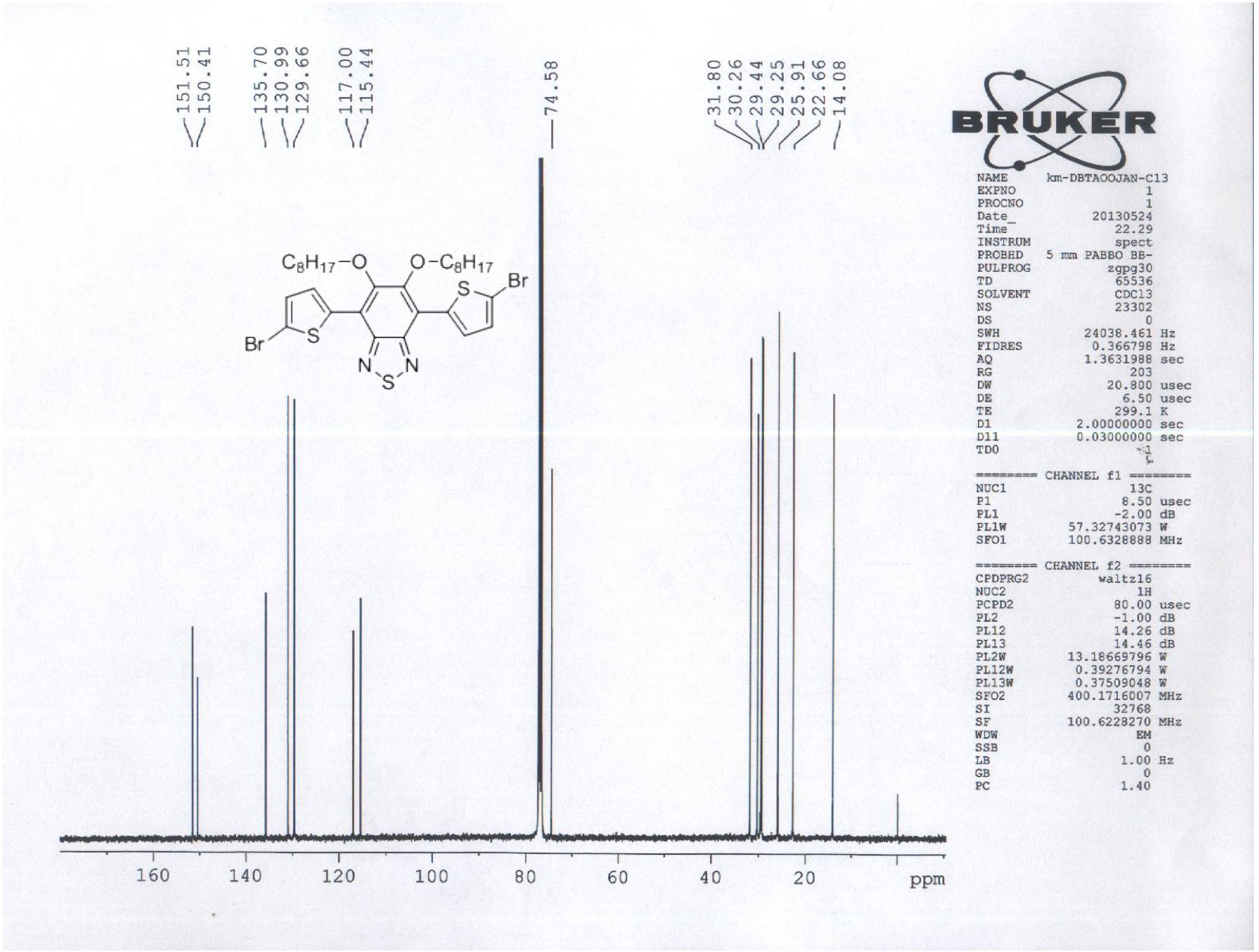
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Br
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N
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N
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60
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PL1 -2.00 dB
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NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.26 dB
PL13 14.46 dB
PL2W 13.18669796 W
PL12W 0.39276794 W
PL13W 0.37509048 W
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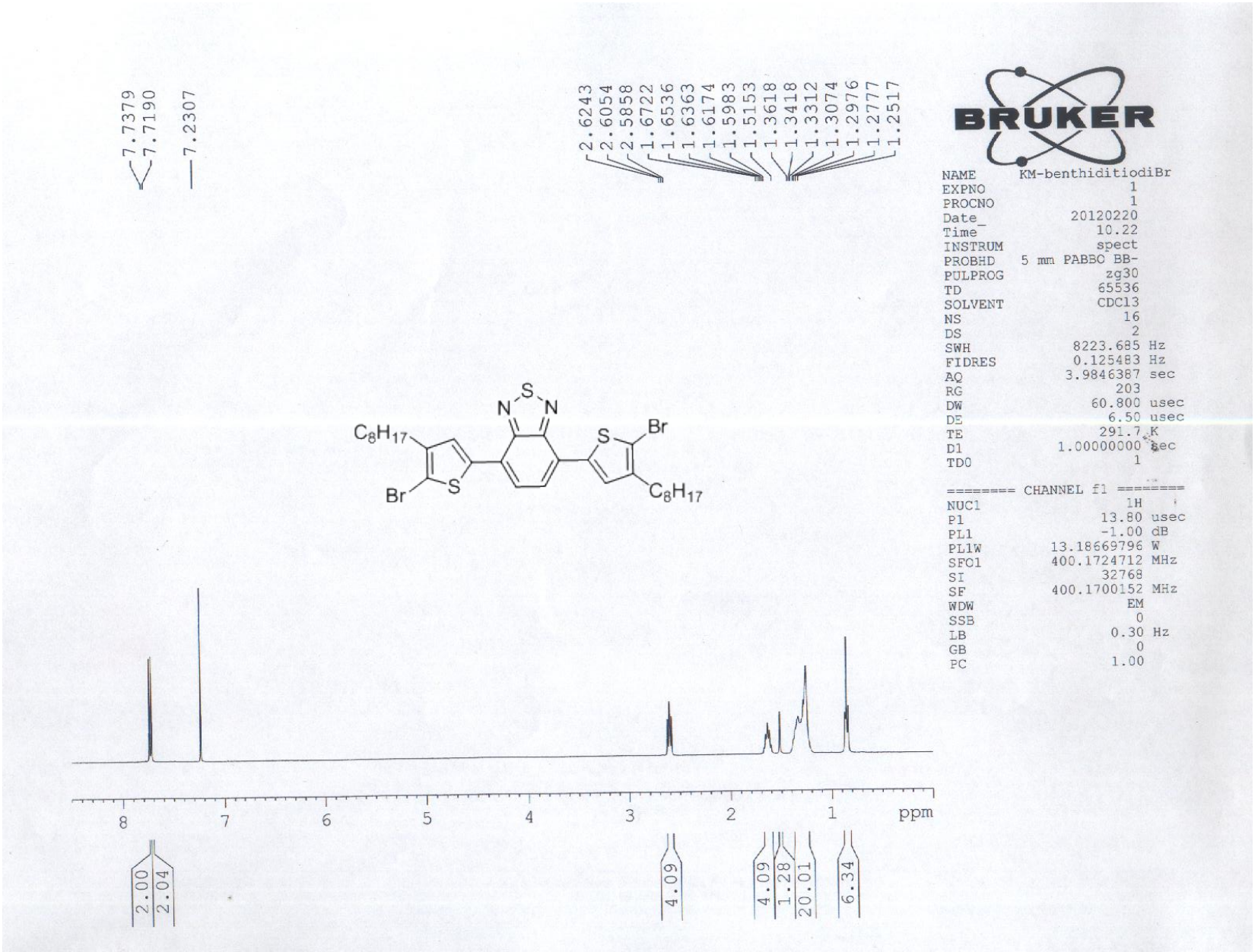
SSB 0
LB 1.00 Hz
GB 0
PC 1.40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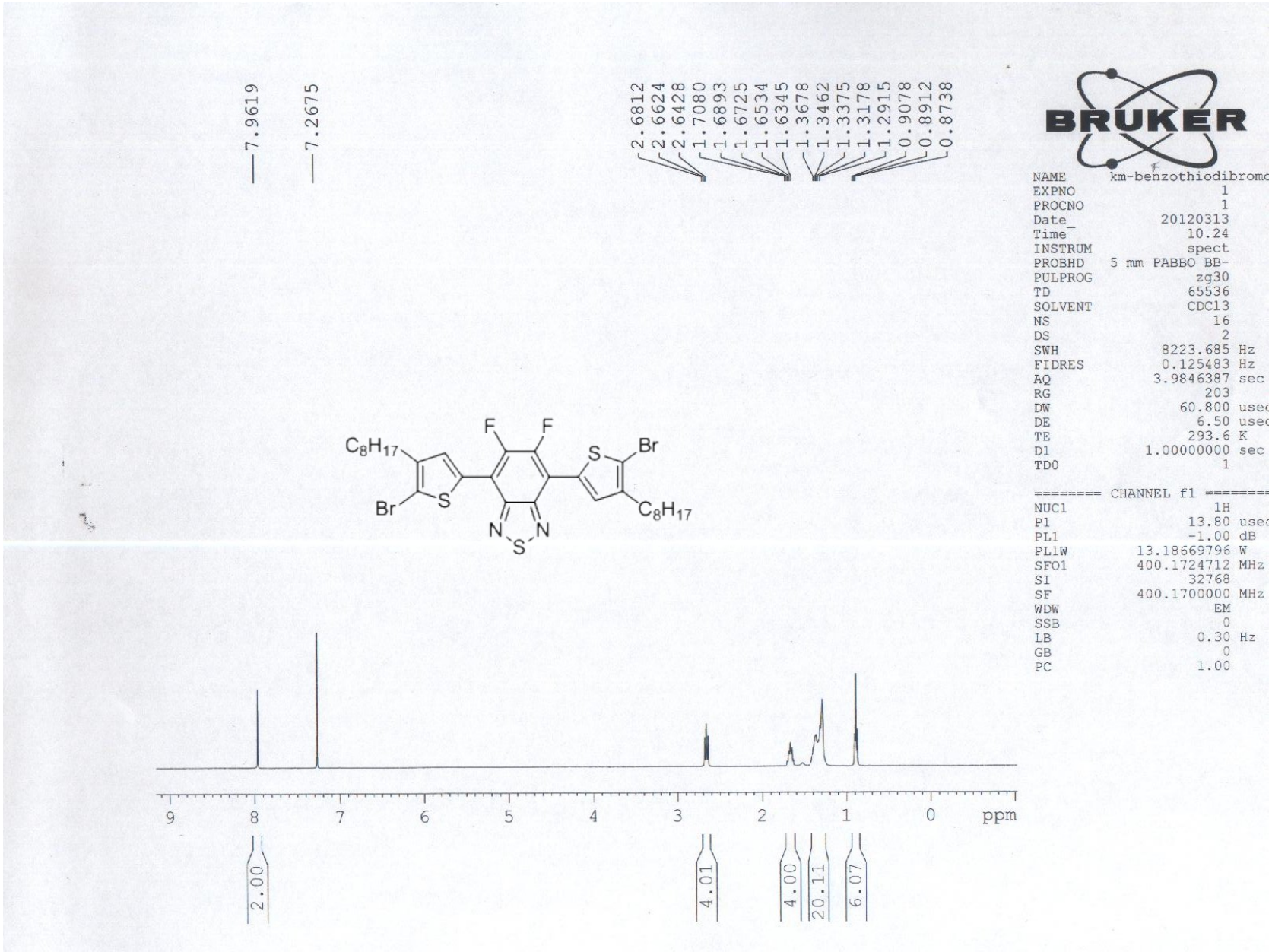
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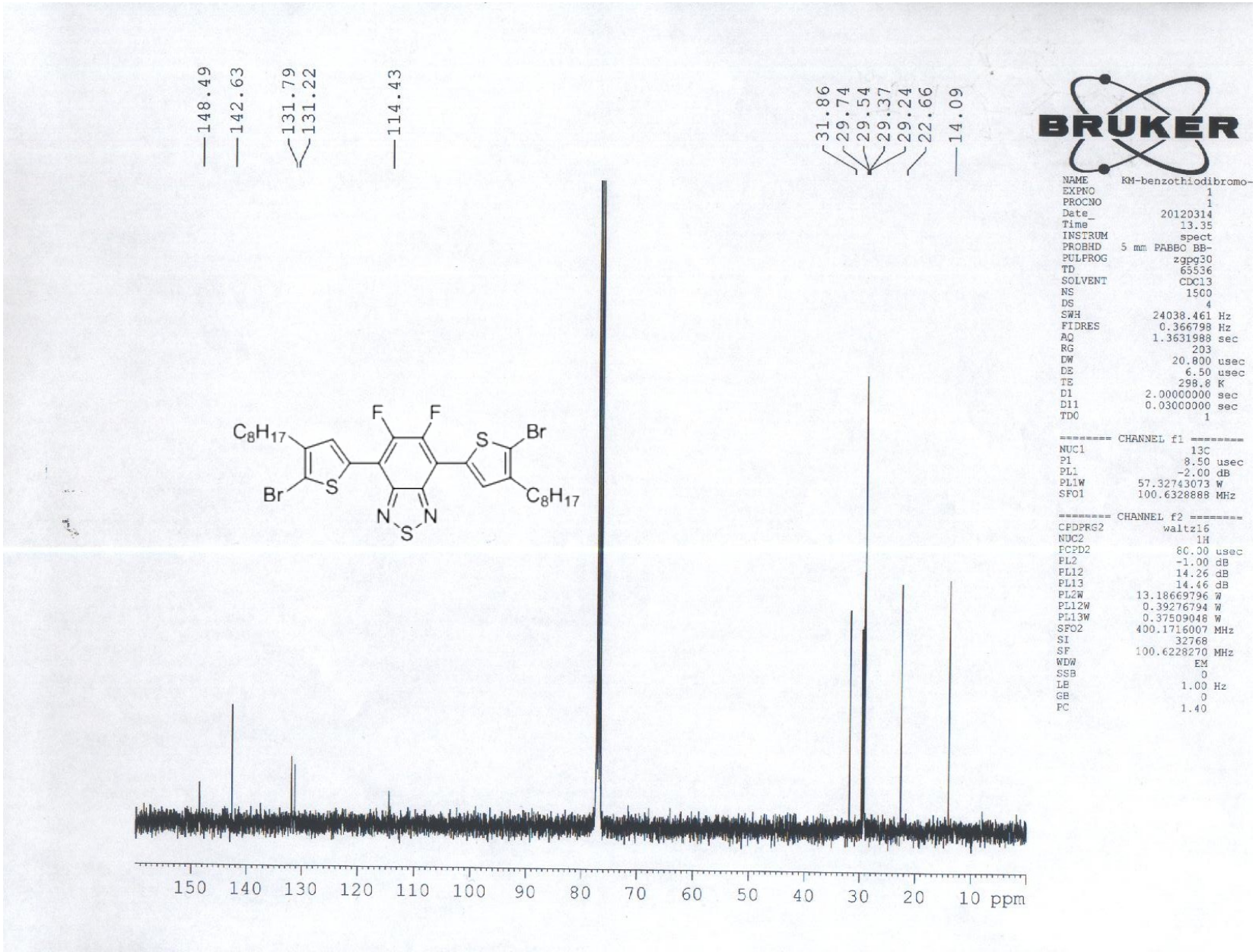

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P1	8.50 usec
PL1	-2.00 dB
PL1W	57.32743073 W
SFO1	100.6328888 MHz
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CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-1.00 dB
PL12	14.26 dB
PL13	14.46 dB
PL2W	13.18669796 W
PL12W	0.39276794 W
PL13W	0.37509048 W
SFO2	400.1716007 MHz
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RG 203
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DE 6.50 usec
TE 297.7 K
D1 1.00000000 sec
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======== CHANNEL f1 ========
NUC1 1H
P1 13.80 usec
PL1 -1.00 dB
PL1W 13.18669796 W
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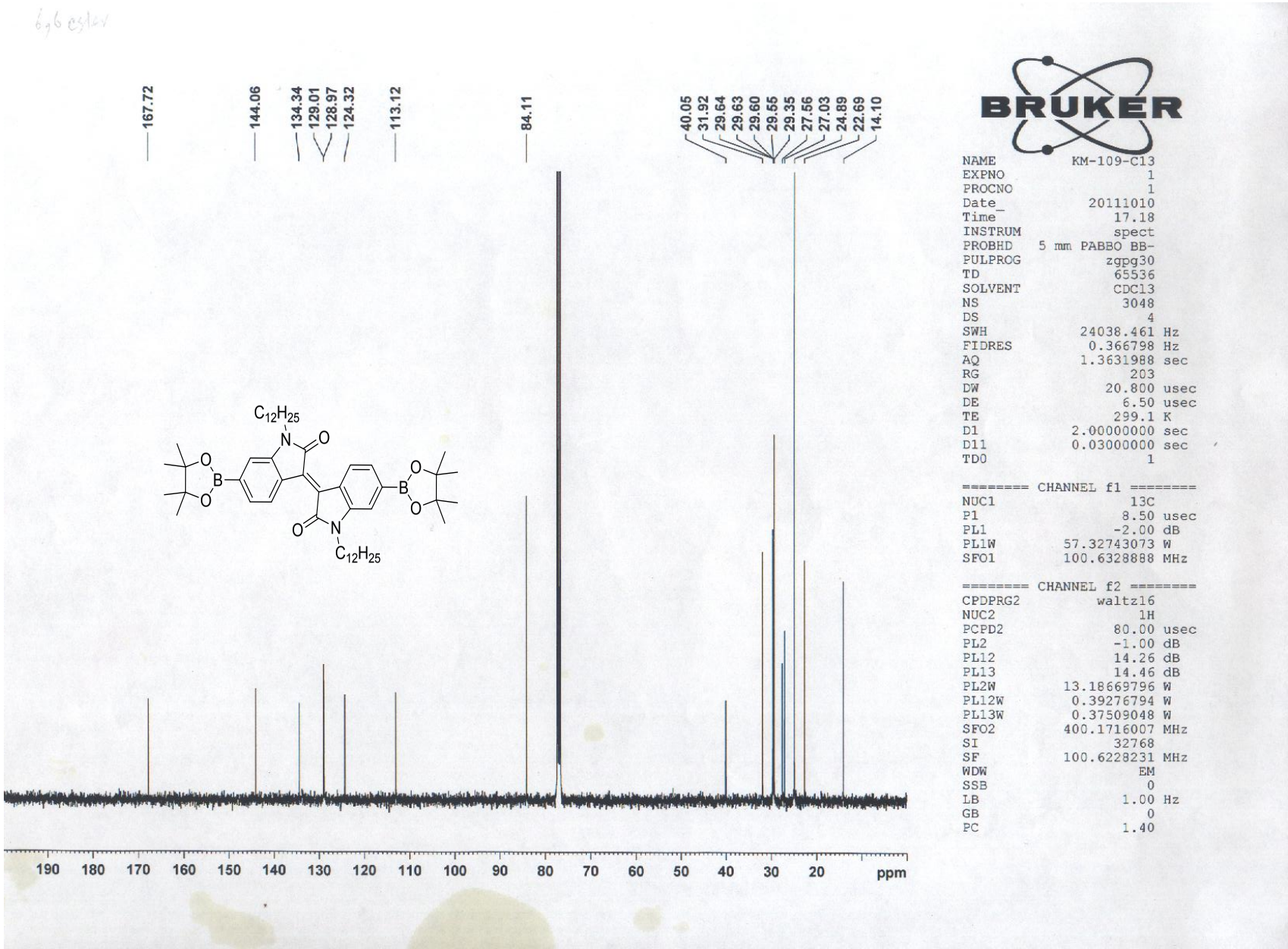

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NS	3048
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FIDRES	0.366798 Hz
AQ	1.3631988 sec
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DW	20.800 usec
DE	6.50 usec
TE	299.1 K
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D11	0.03000000 sec
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NUC1	13C
P1	8.50 usec
PL1	-2.00 dB
PL1W	57.32743073 W
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NUC2	1H
PCPD2	80.00 usec
PL2	-1.00 dB
PL12	14.26 dB
PL13	14.46 dB
PL2W	13.18669796 W
PL12W	0.39276794 W
PL13W	0.37509048 W
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SI	32768
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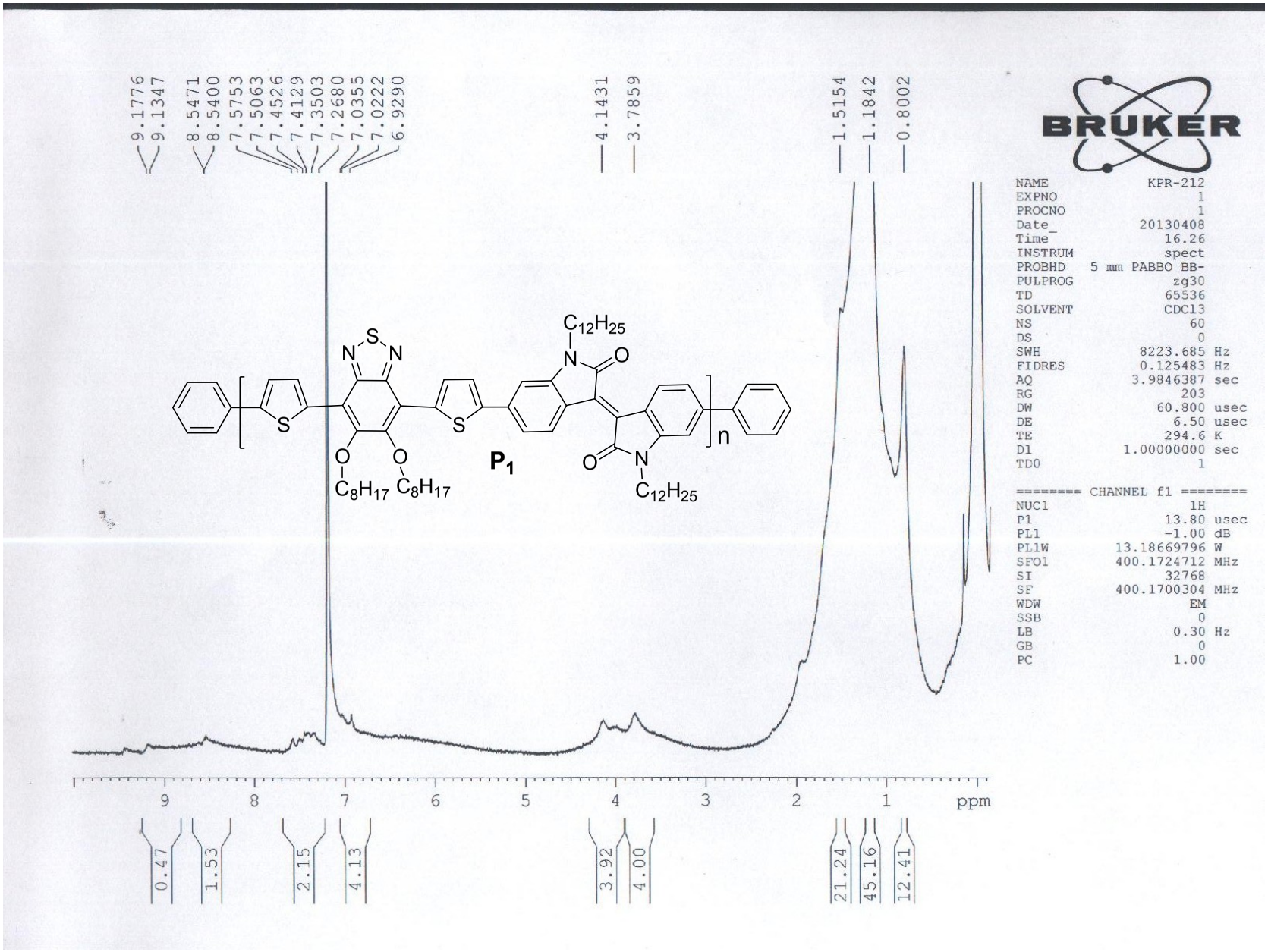
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40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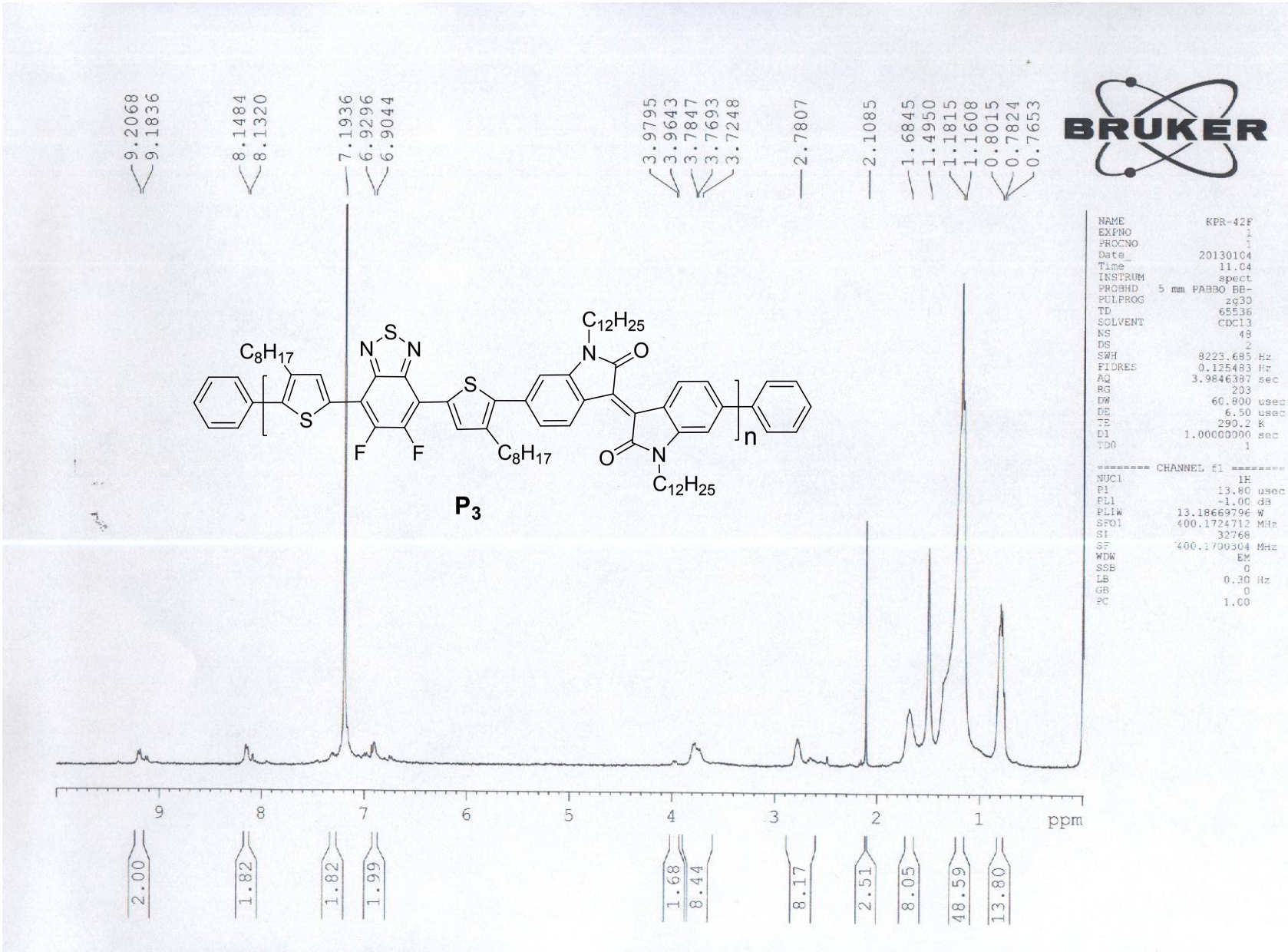
7.0355
7.0222
6.9290
4.1431
3.7859
1.5154
1.1842
0.8002
P1
n
ppm
0.47
1.53
2.15
4.13
3.92
4.00
21.24
45.16
12.41
BRUKER
NAME KPR-212
EXPNO 1
PROCNO 1
Date_ 20130408
Time 16.26
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 60
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 203
DW 60.800 usec
DE 6.50 usec
TE 294.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.80 usec
PL1 -1.00 dB
PL1W 13.18669796 W
SFO1 400.1724712 MHz
SI 32768
SF 400.1700304 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

BRUKER
NAME KPR-3
EXPNO 1
PROCNO 1
Date_ 20130109
Time 14.41
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 60
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 203
DW 60.800 usec
DE 6.50 usec
TE 293.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.80 usec
PL1 -1.00 dB
PL1W 13.18669796 W
SFO1 400.1724712 MHz
SI 32768
SF 400.1700307 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.4414
9.2023
9.1836
8.0101
7.9930
7.9384
7.8316
7.8147
7.4506
6.9279
6.9074
3.7828
2.7716
2.6856
2.6545
2.6340
2.6161
1.6881
1.4527
1.2051
1.1831
1.1675
0.8019
0.7869
1.69
3.43
1.92
1.86
7.66
4.40
24.52
37.77
12.02
ppm
P2
n


9.2068
9.1836
8.1484
8.1320
7.1936
6.9296
6.9044
3.9795
3.9643
3.7847
3.7693
3.7248
2.7807
2.1085
1.6845
1.4950
1.1815
1.1608
0.8015
0.7824
0.7653
BRUKER
NAME KPR-42F
EXPNO 1
PROCNO 1
Date_ 20130104
Time 11.04
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 48
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 203
DW 60.800 usec
DE 6.50 usec
TE 290.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.80 usec
PL1 -1.00 dB
PL1W 13.18669796 W
SFO1 400.1724712 MHz
SI 32768
SF 400.1700304 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
C8H17
S
N
S
N
F
F
S
C8H17
C12H25
N
O
O
N
C12H25
n
P3
9
8
7
6
5
4
3
2
1
ppm
2.00
1.82
1.82
1.99
1.68
8.44
8.17
2.51
8.05
48.59
13.80