Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information for

Tetrathienyl-functionalized red- and NIR-absorbing BODIPY dyes appending various peripheral substituents

Ping Liu,[a,b] Feng Gao,[a] Lina Zhou,[a] Yu Chen,[b] and Zhijian Chen*[a]

[a]*School of Chemical Engineering and Technology, Collaborative Innovation Center of Chemical Science and Engineering, Tianjin University, Tianjin 300072, China.*
[b]*Department of Chemistry, School of Sciences, Tianjin University, Tianjin 300072, China.*
zjchen@tju.edu.cn

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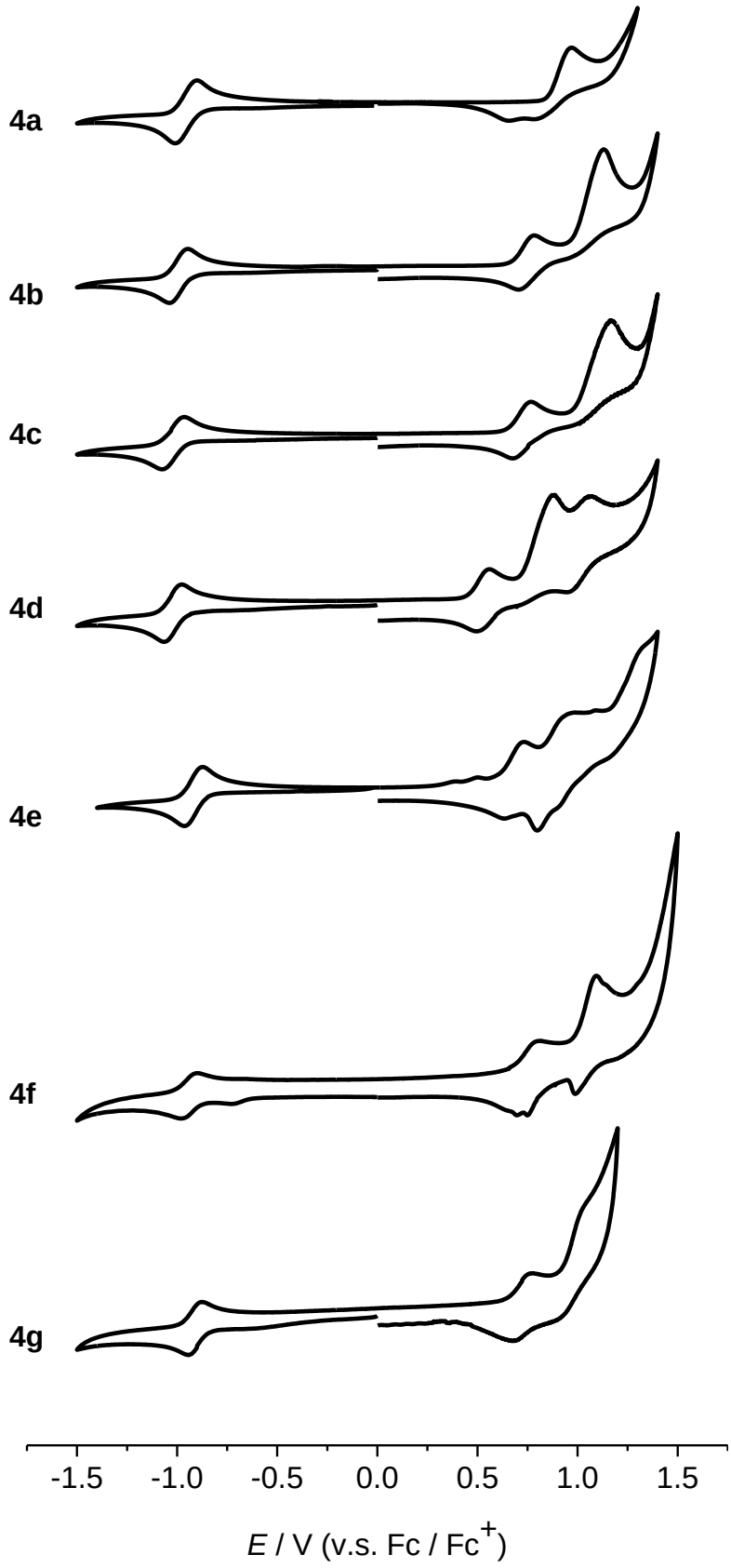


Figure S1 Cyclic Voltammograms of BODIPYs **4a-g** in dry dichloromethane (10^{-3} M). The scan rate is 100 mV s^{-1} and the supporting electrolyte is NBu_4PF_6 (0.1 M).

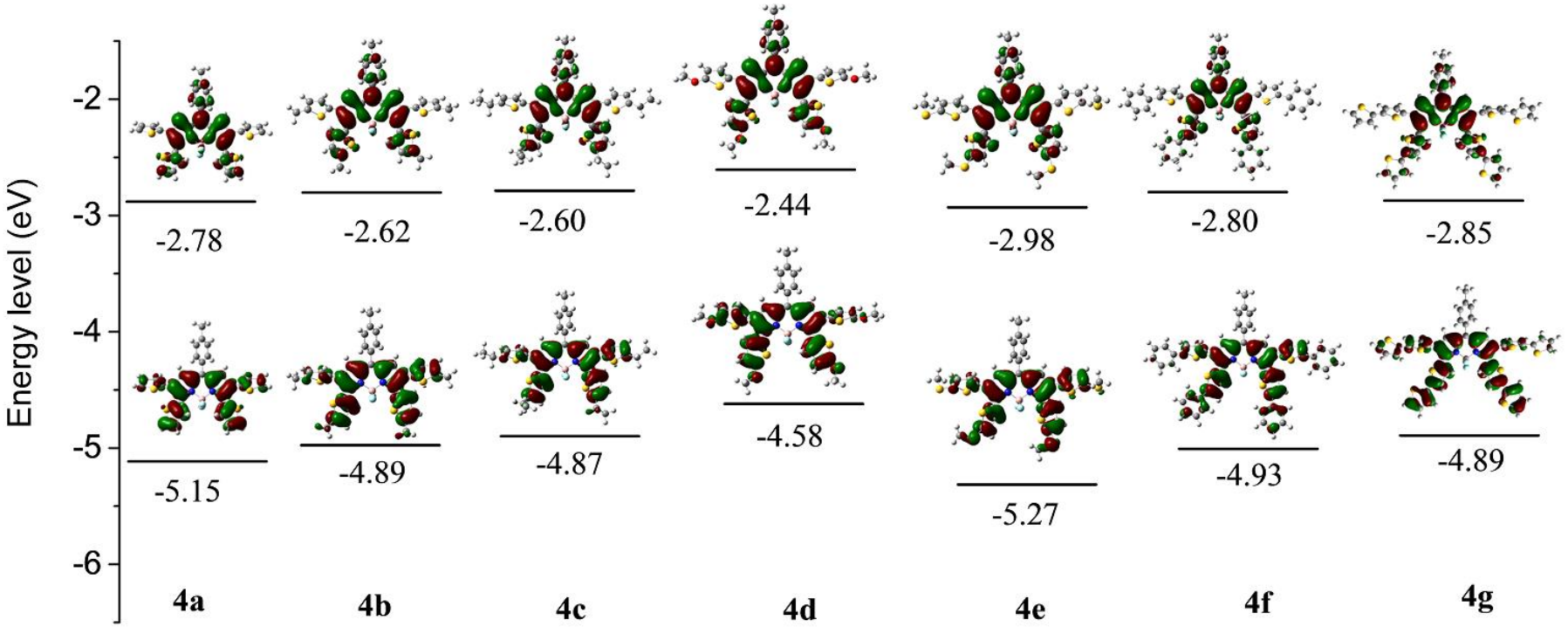


Figure S2 The calculated HOMOs and LUMOs of dyes **4a**-**g** (for **4c**, four ethyl groups were used instead of the hexyl groups).

Table **S1** DFT calculated energy level[a]

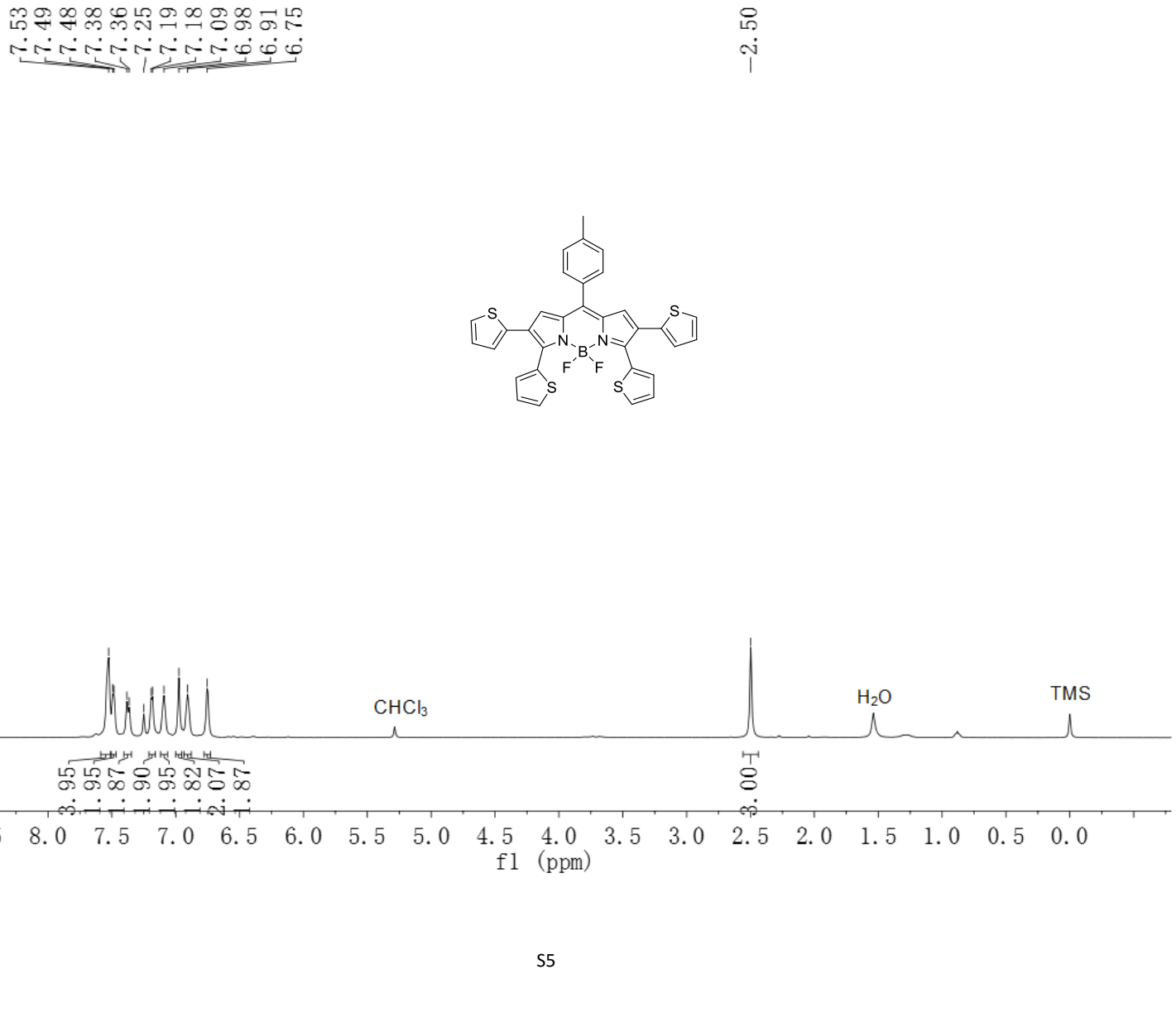
	HOMO / eV	LUMO / eV	ΔE^b / eV
4a	-5.15	-2.78	2.37
4b	-4.89	-2.62	2.27
4c	-4.87	-2.60	2.27
4d	-4.58	-2.44	2.14
4e	-5.27	-2.98	2.29
4f	-4.93	-2.80	2.13
4g	-4.89	-2.85	2.04

[a]B3LYP/6-31G(d) basis set was used. The calculations were performed with the GAUSSIAN 03 program. [b]ΔE = LUMO – HOMO.

Table **S2** fluorescence quantum yields of dyes **4a-c**, **4f** in different solvents

	n-Hexane	Toluene	DCM	THF	CH_3CN
4a	0.39	0.18	0.16	0.082	0.025
4b	0.19	0.11	0.037	0.040	0.008
4c	0.25	0.12	0.045	0.044	0.009
4f	0.17	0.10	0.019	0.017	0.010

Using zinc phthalocyanine (Φ = 0.30 in 1-chloronaphthalene) as standard.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2.50
S
N
B
F
F
CHCl3
H2O
TMS
3.95
1.95
1.87
1.90
1.95
1.82
2.07
1.87
3.00
0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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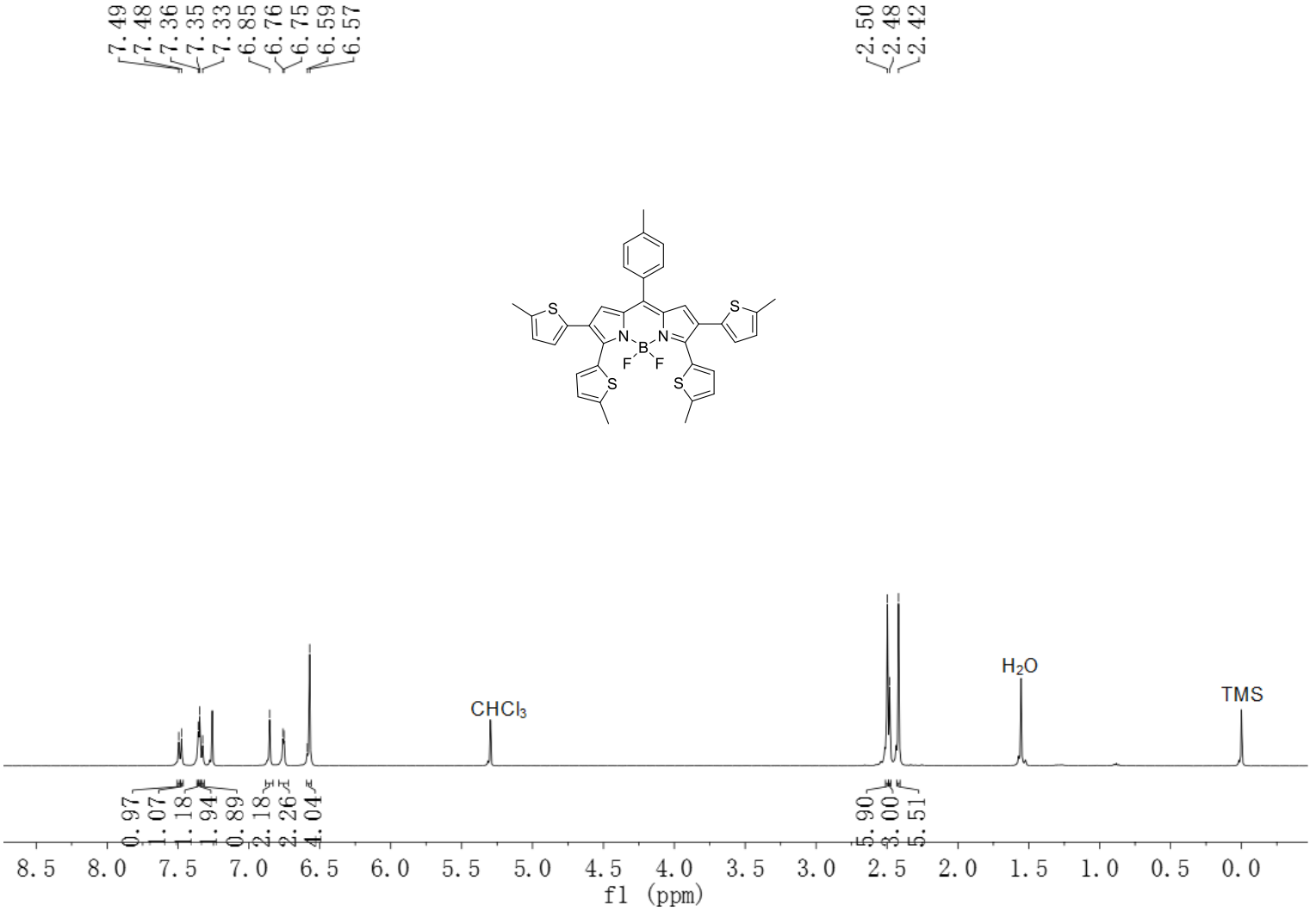
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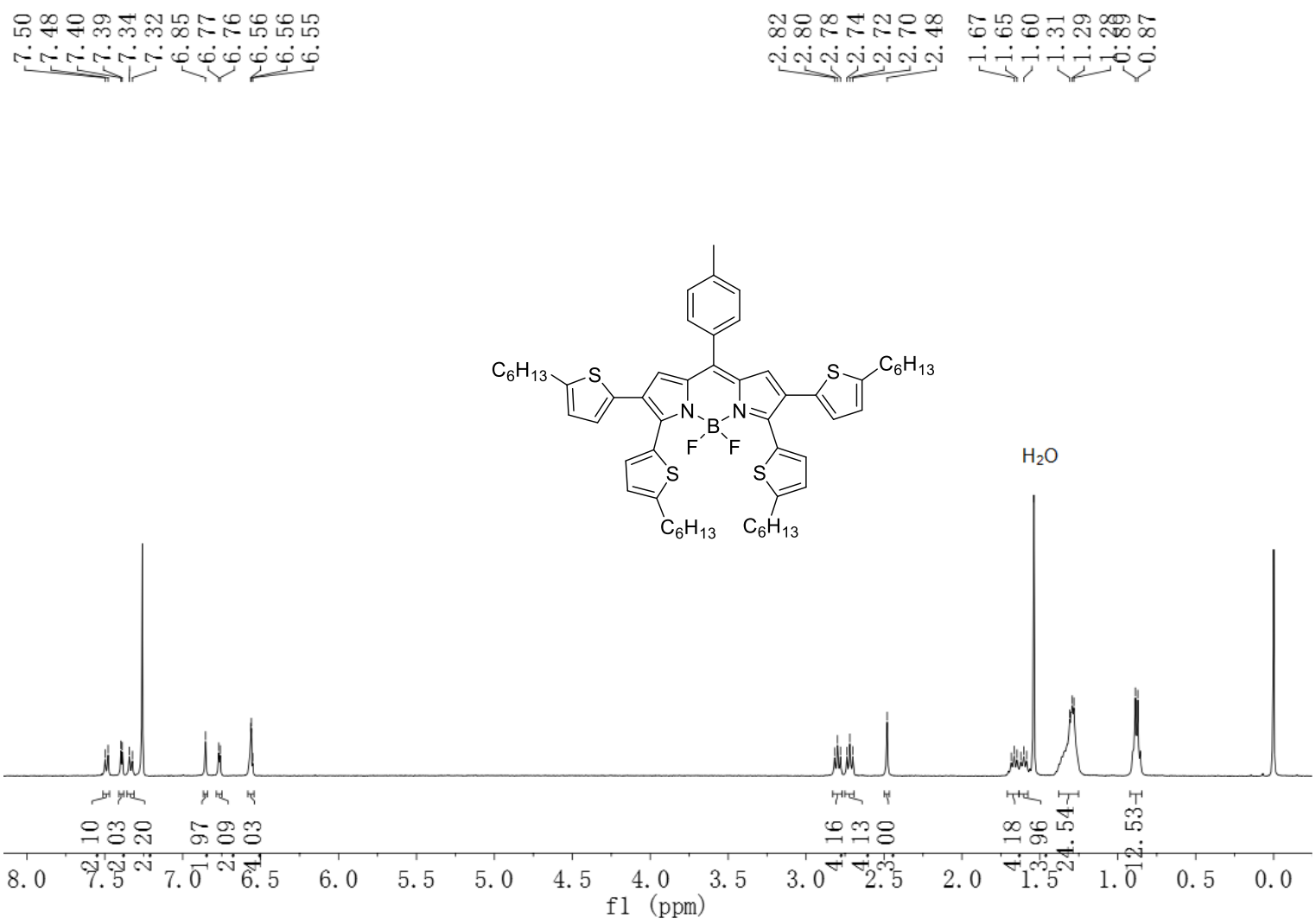
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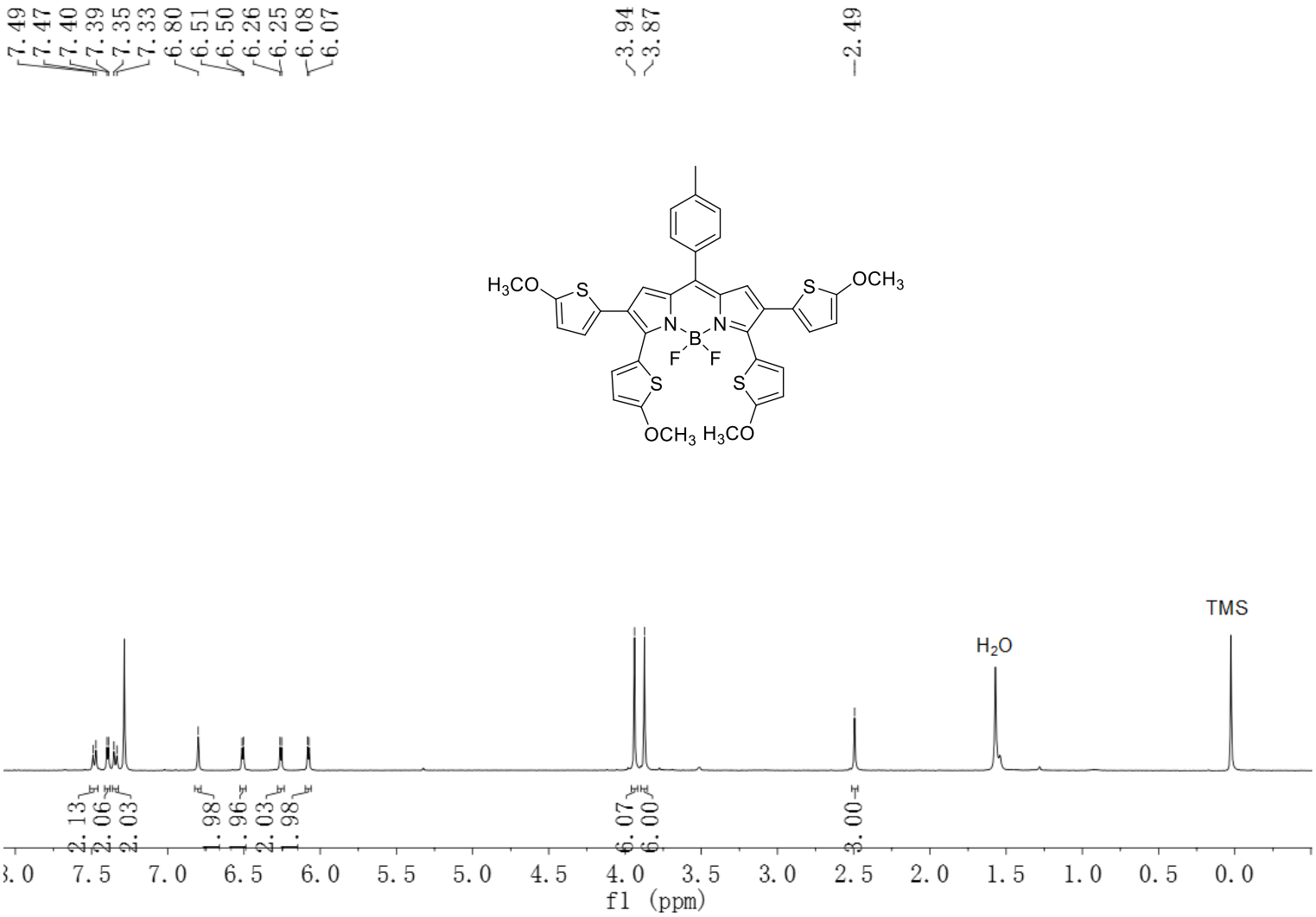
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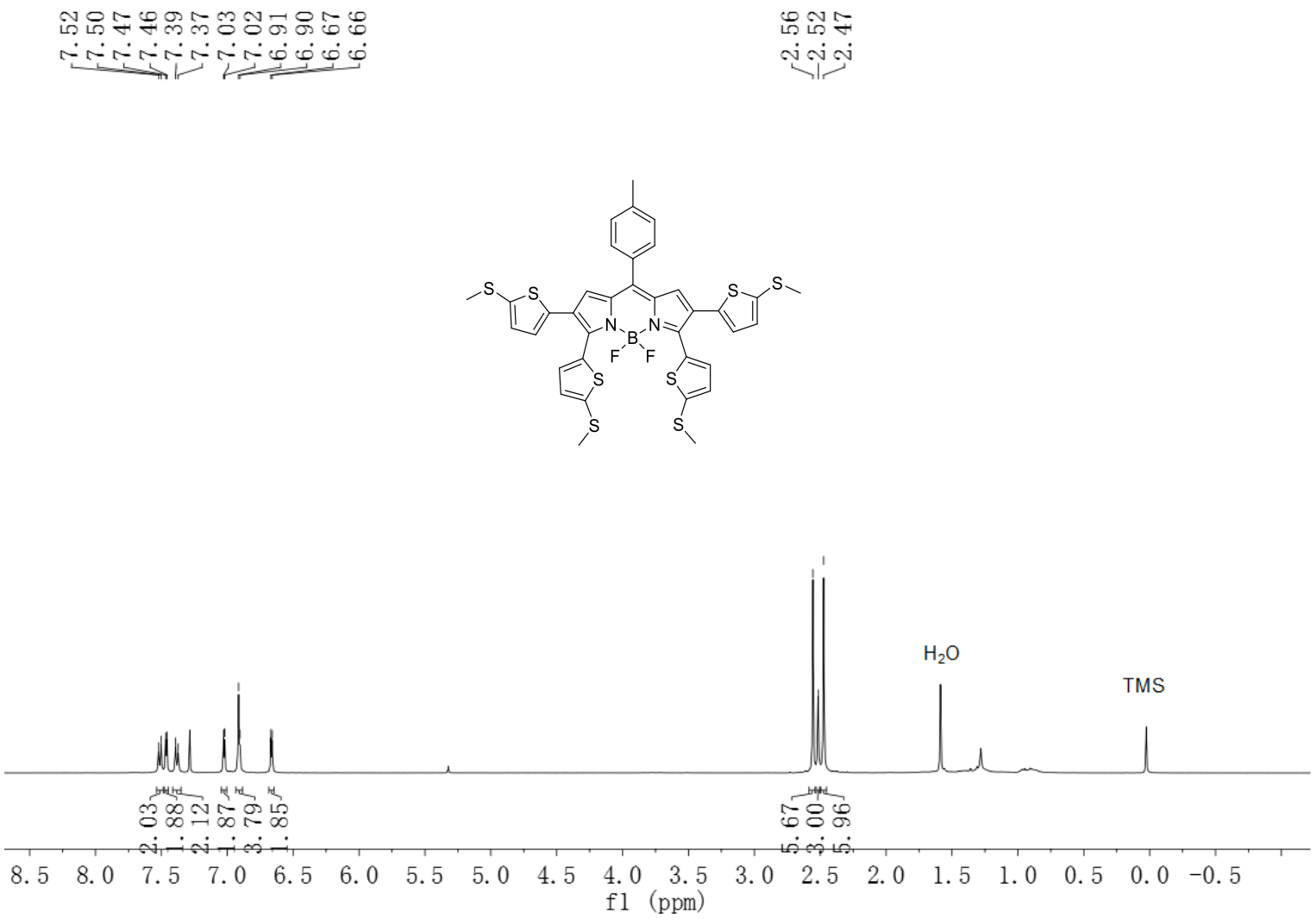
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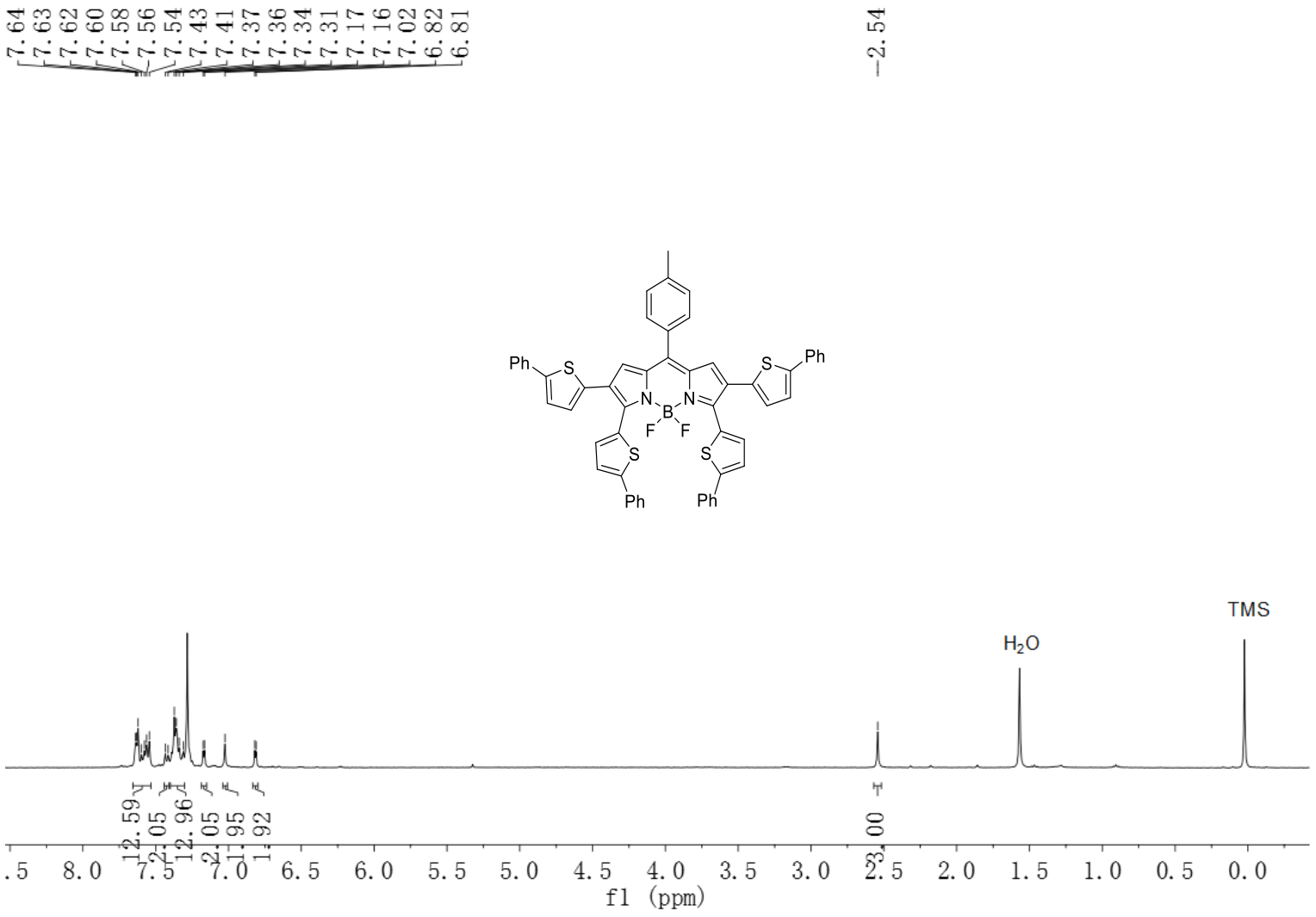
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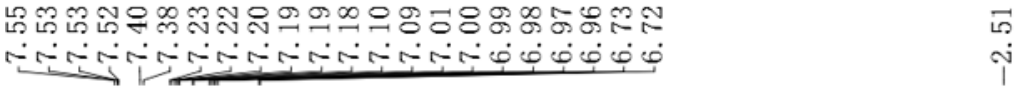
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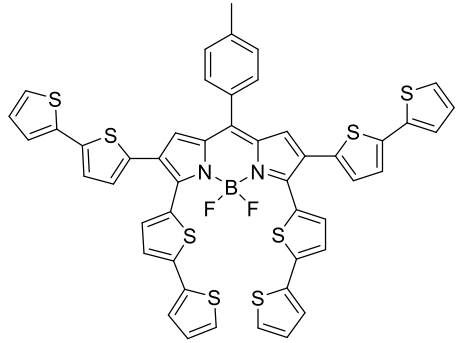
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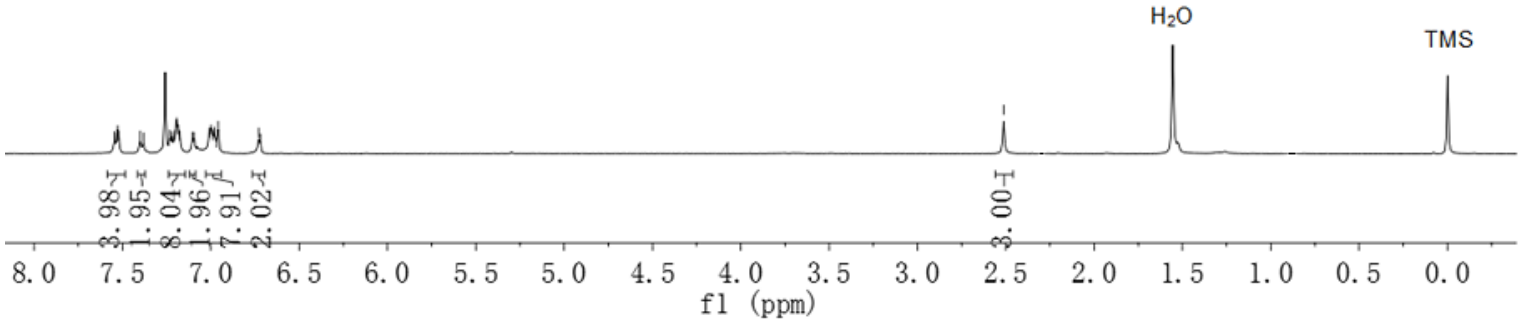
S
S
S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TMS
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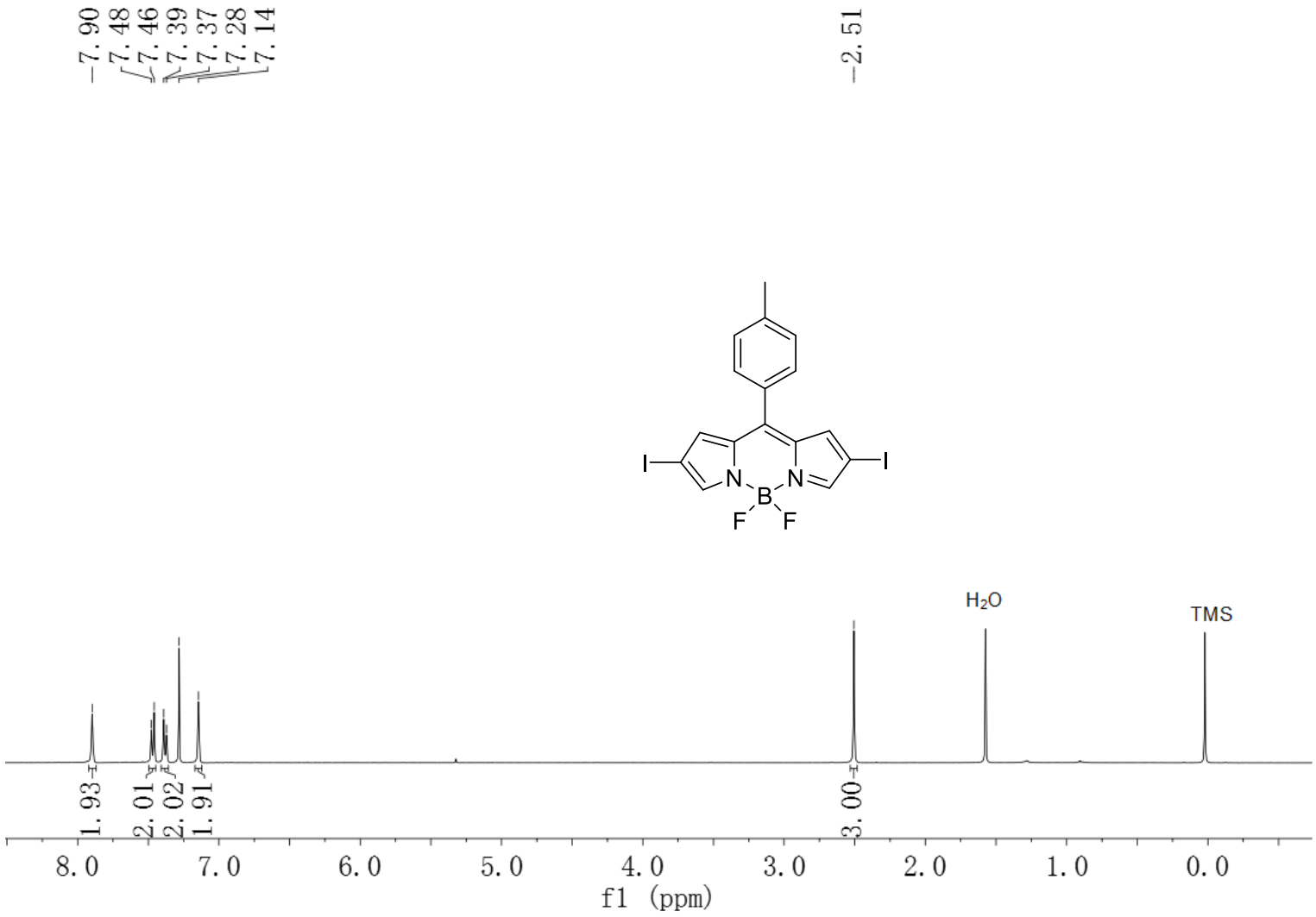
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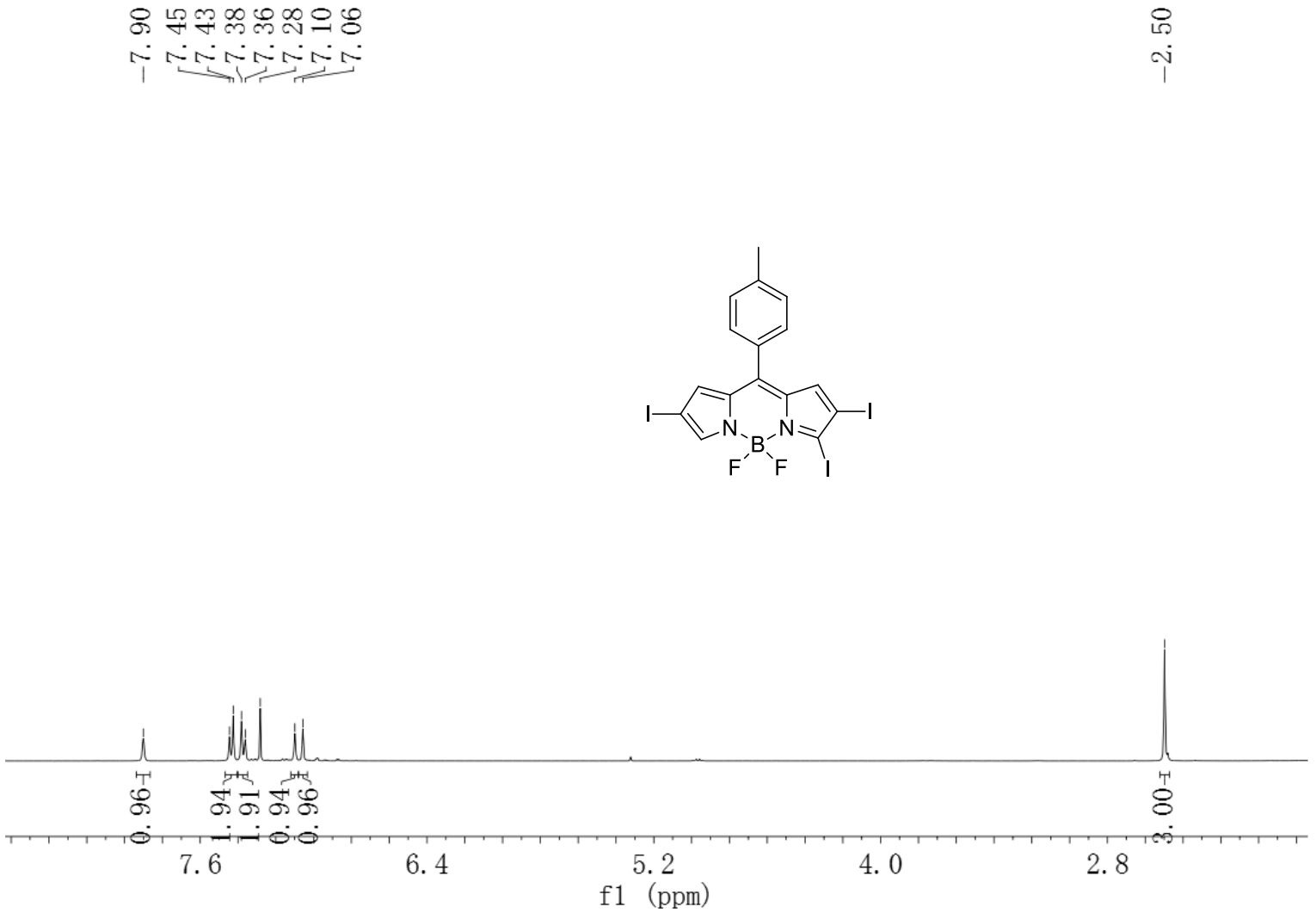
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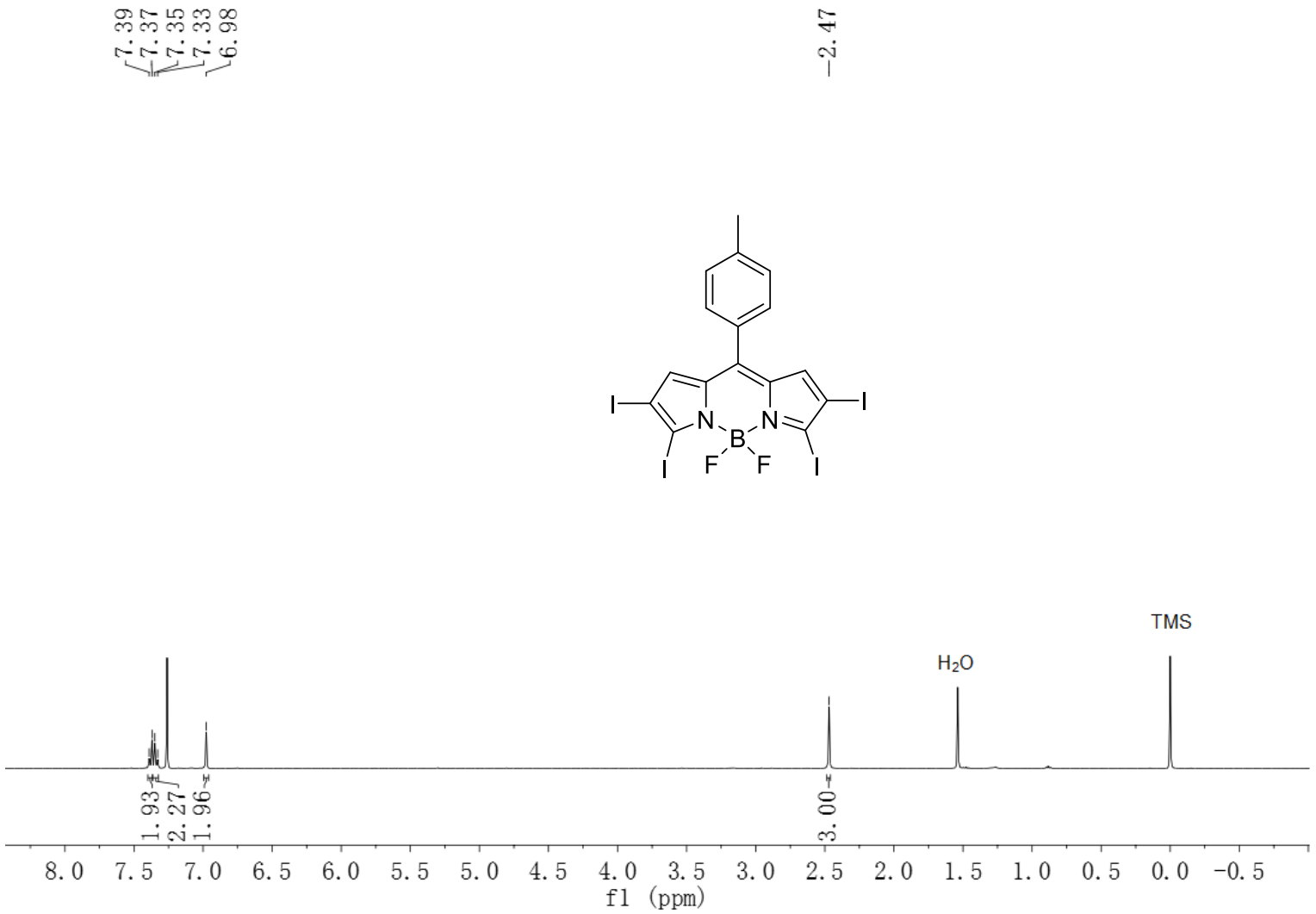
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H2O
1.93
2.27
1.96
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
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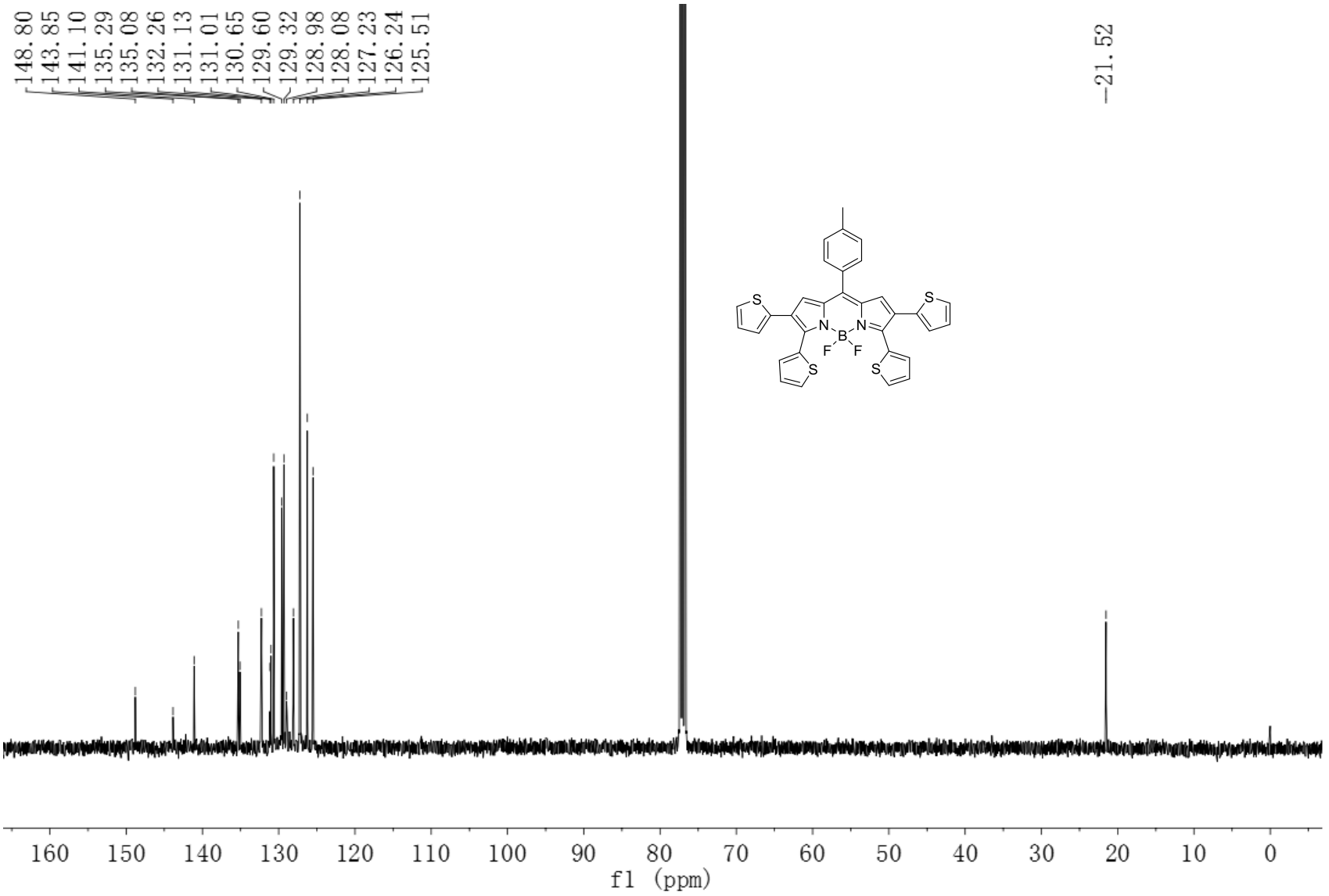
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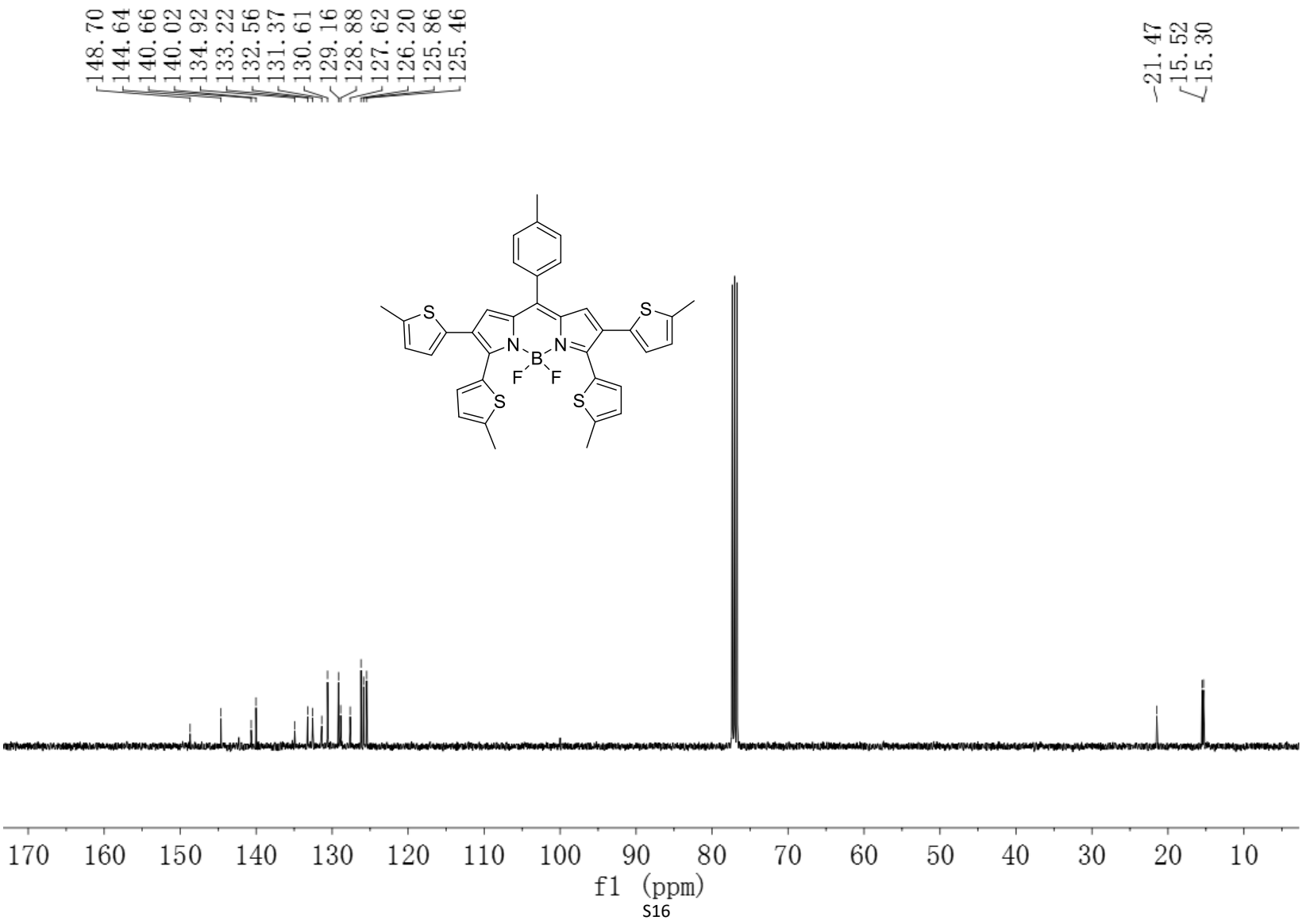
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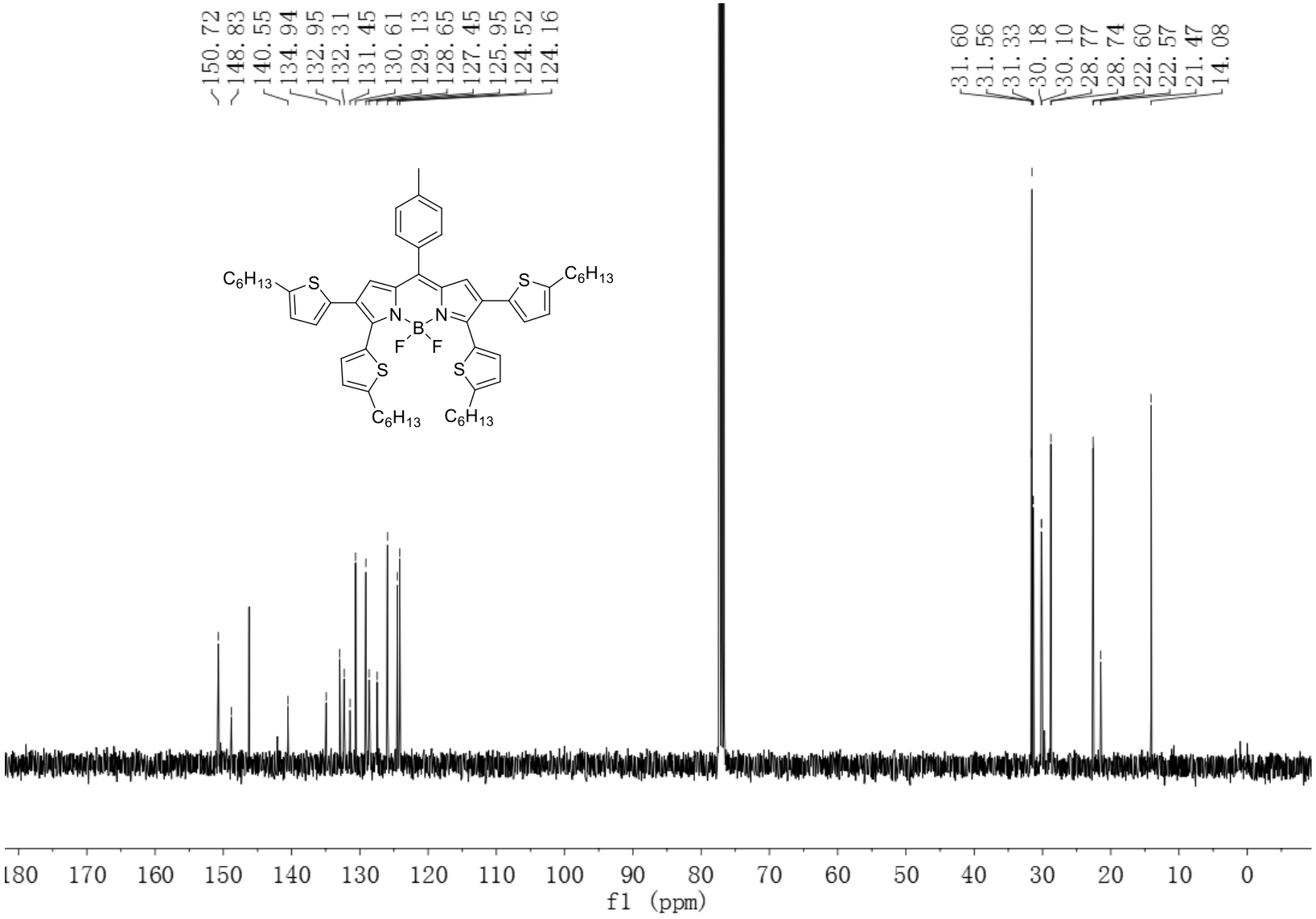
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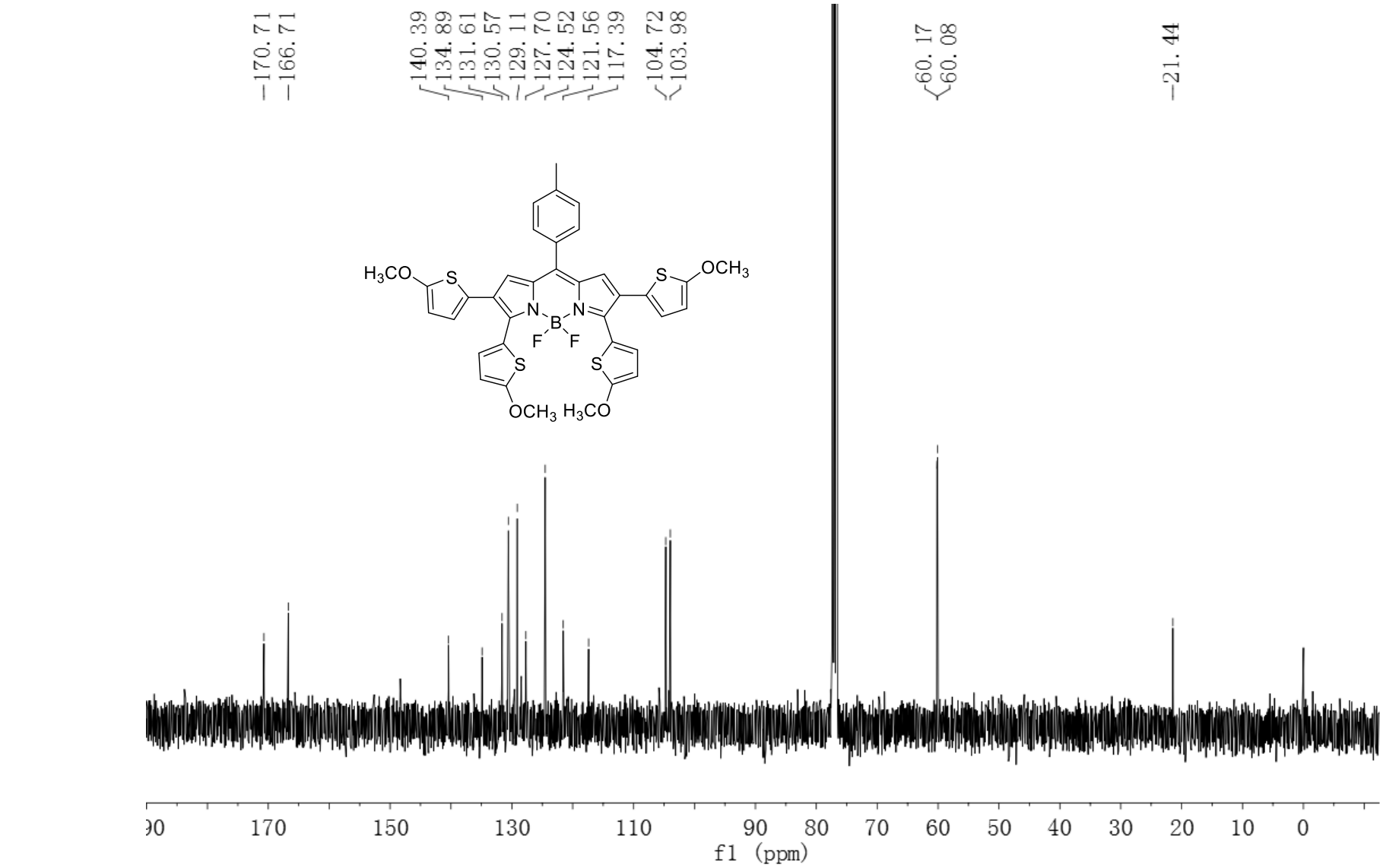
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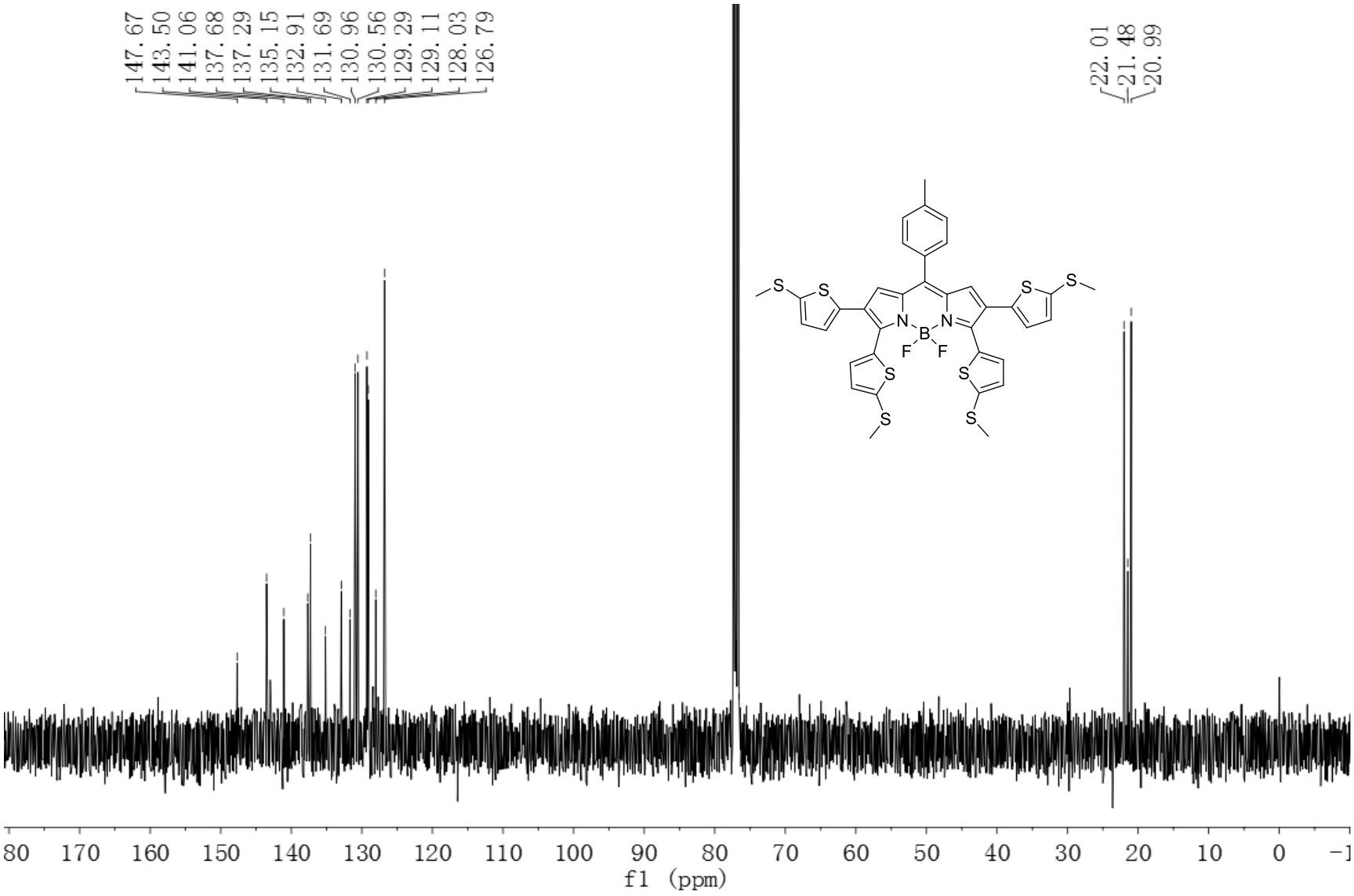
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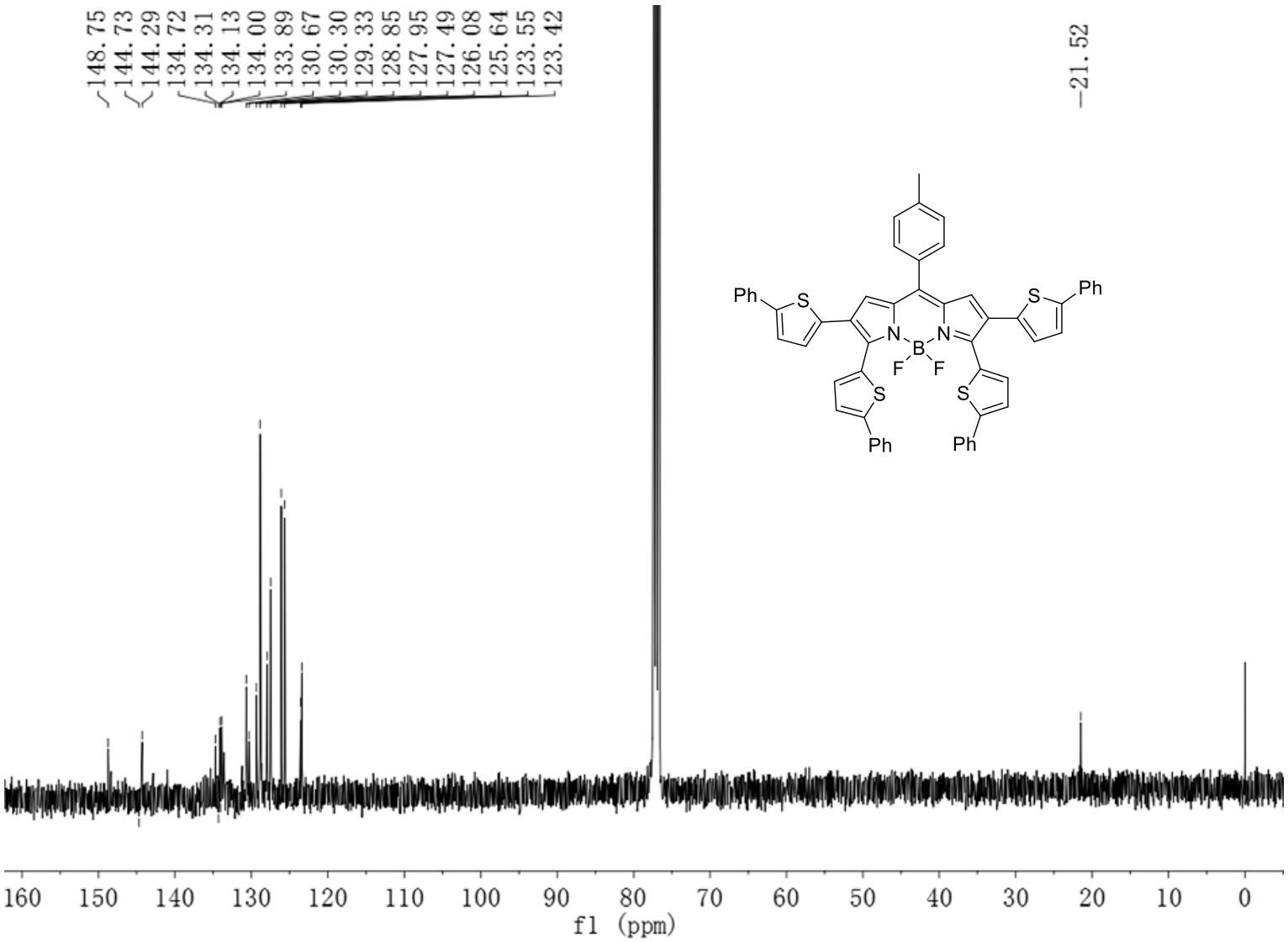
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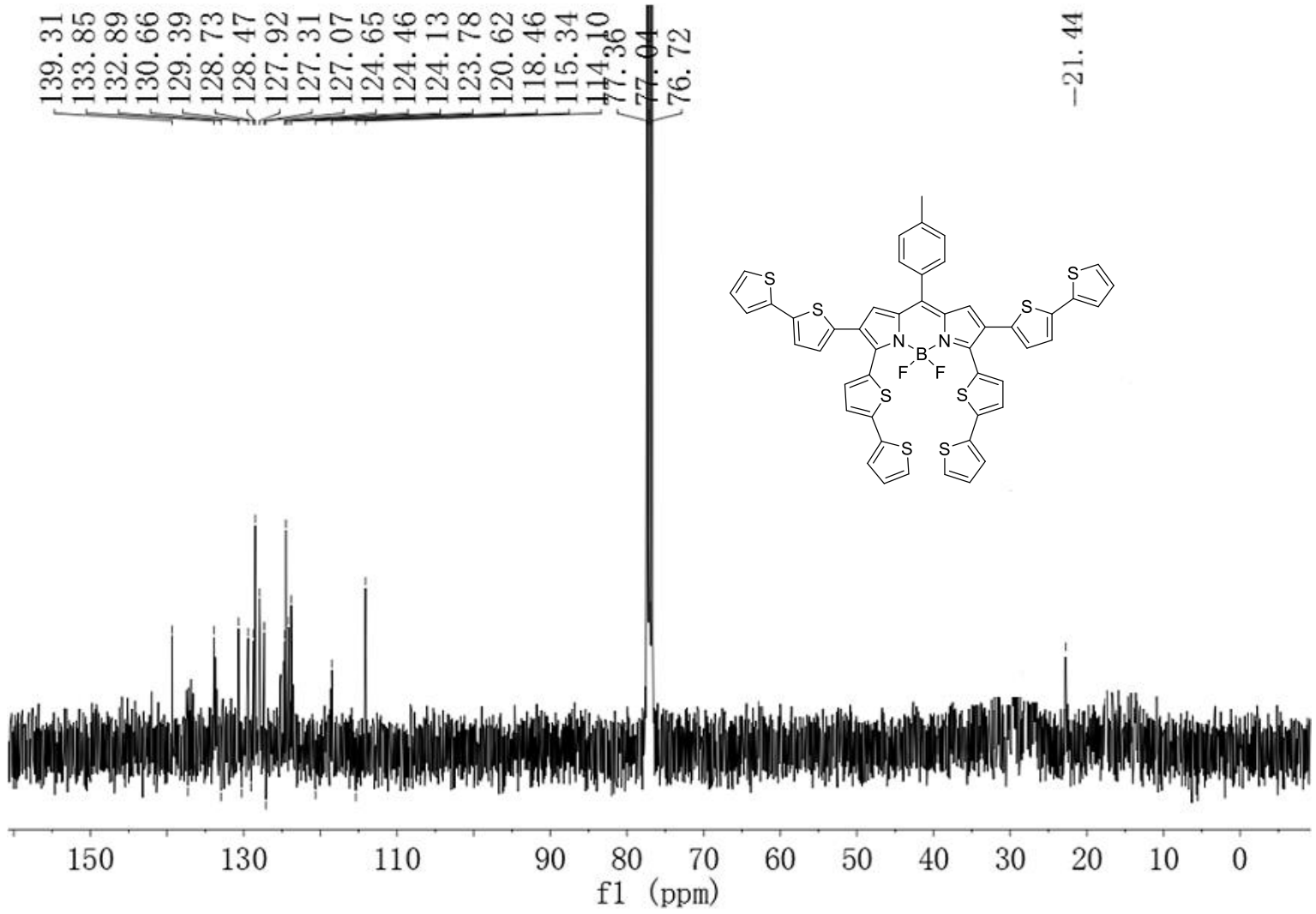
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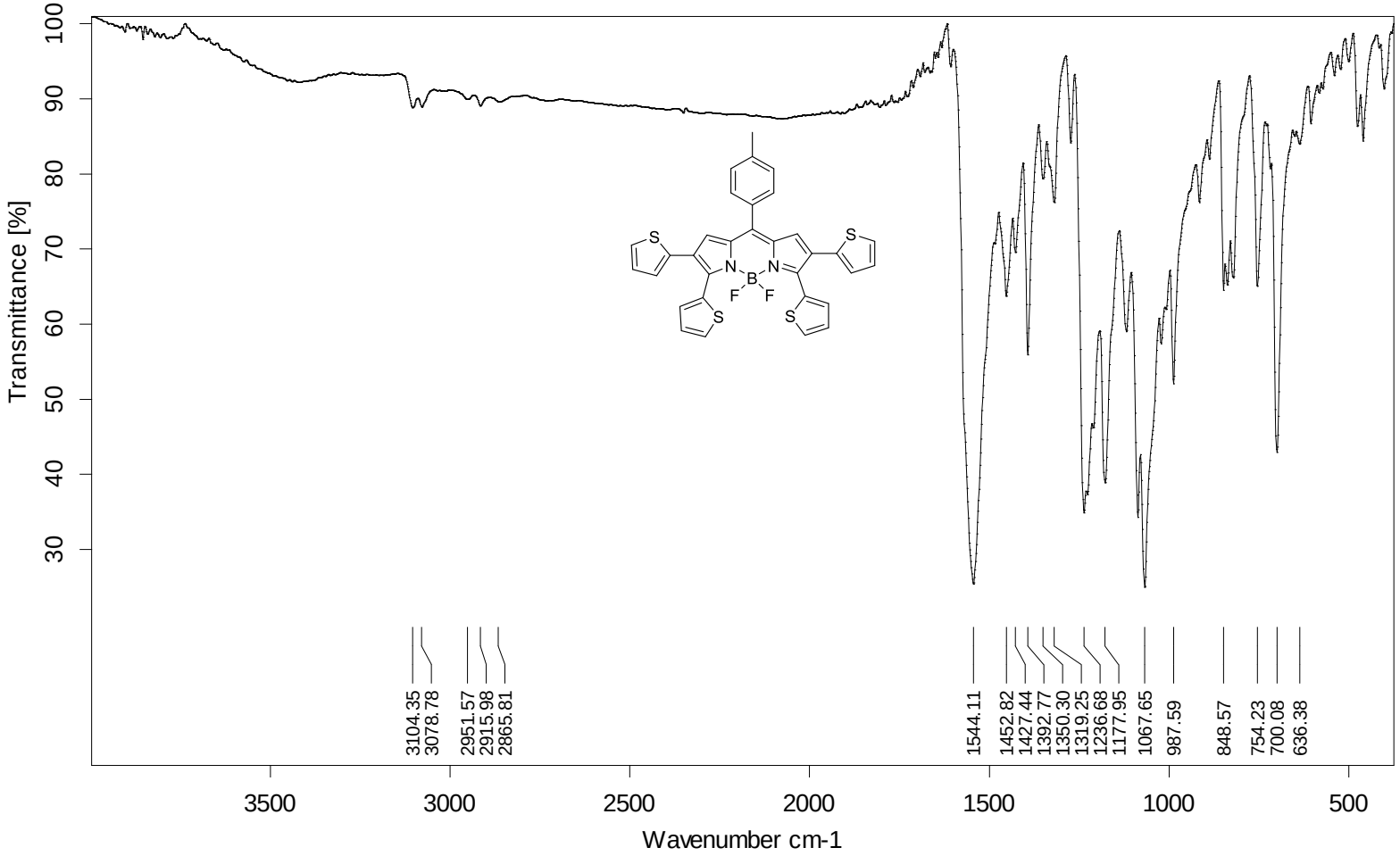
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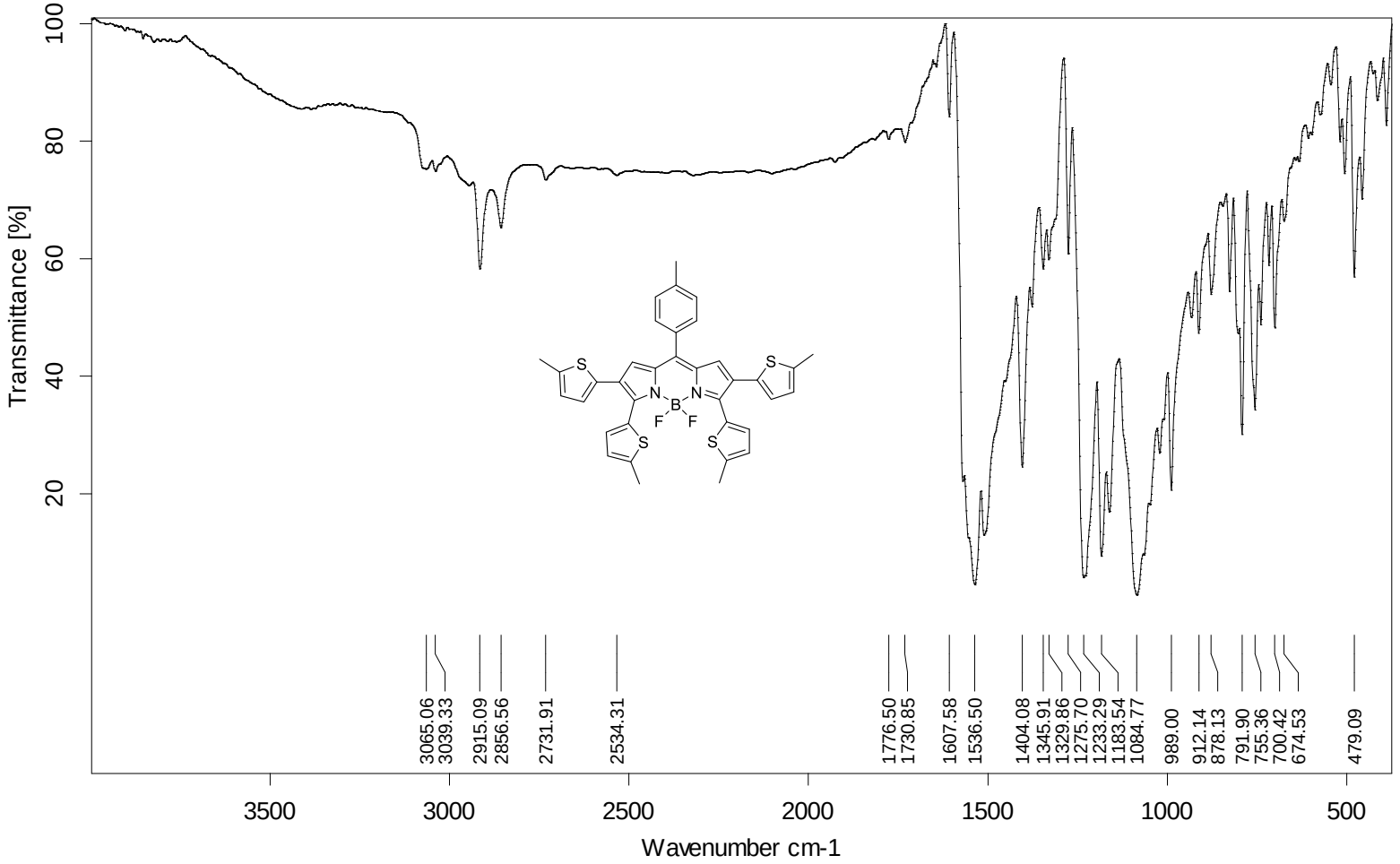
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Wavenumber cm-1
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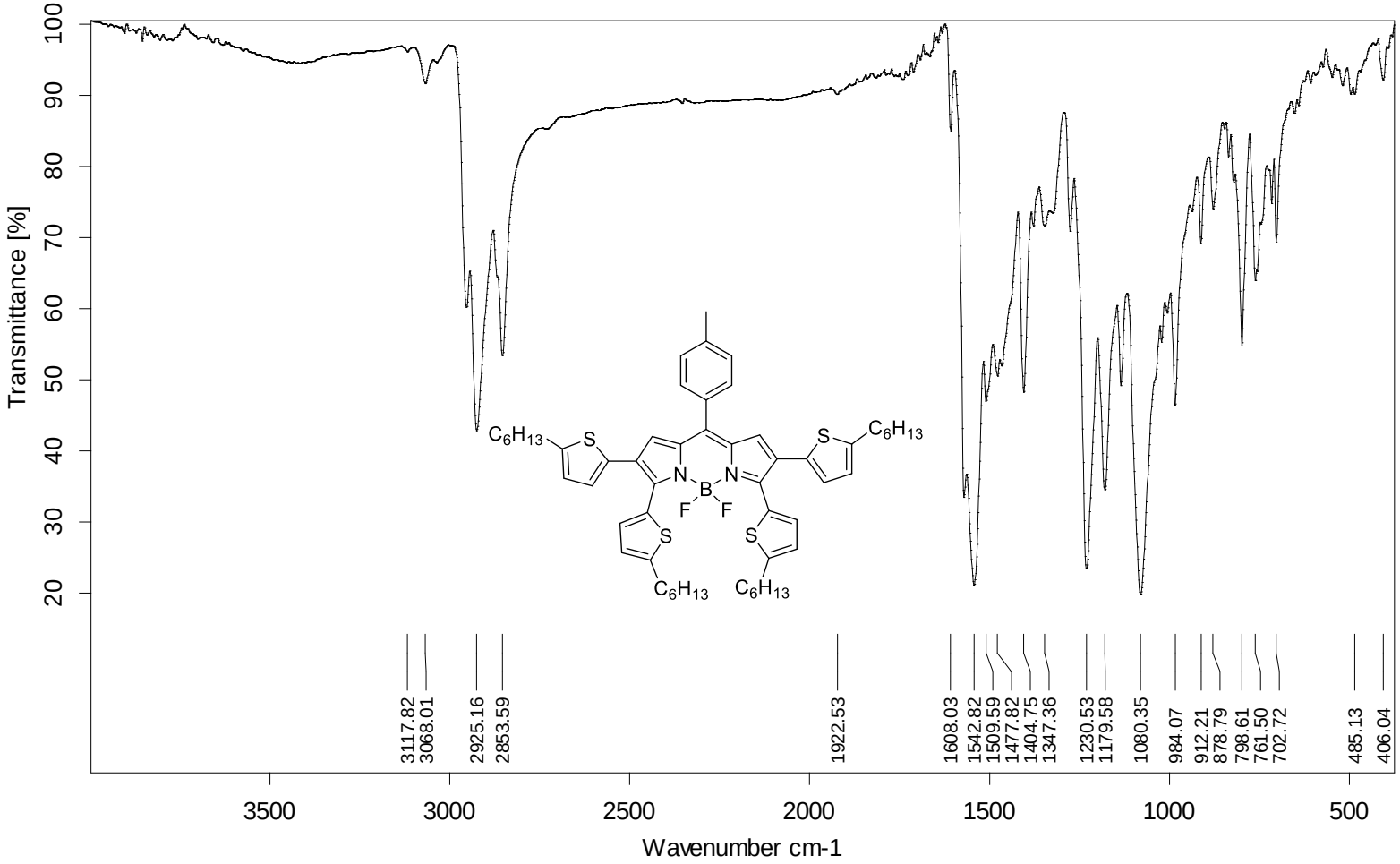
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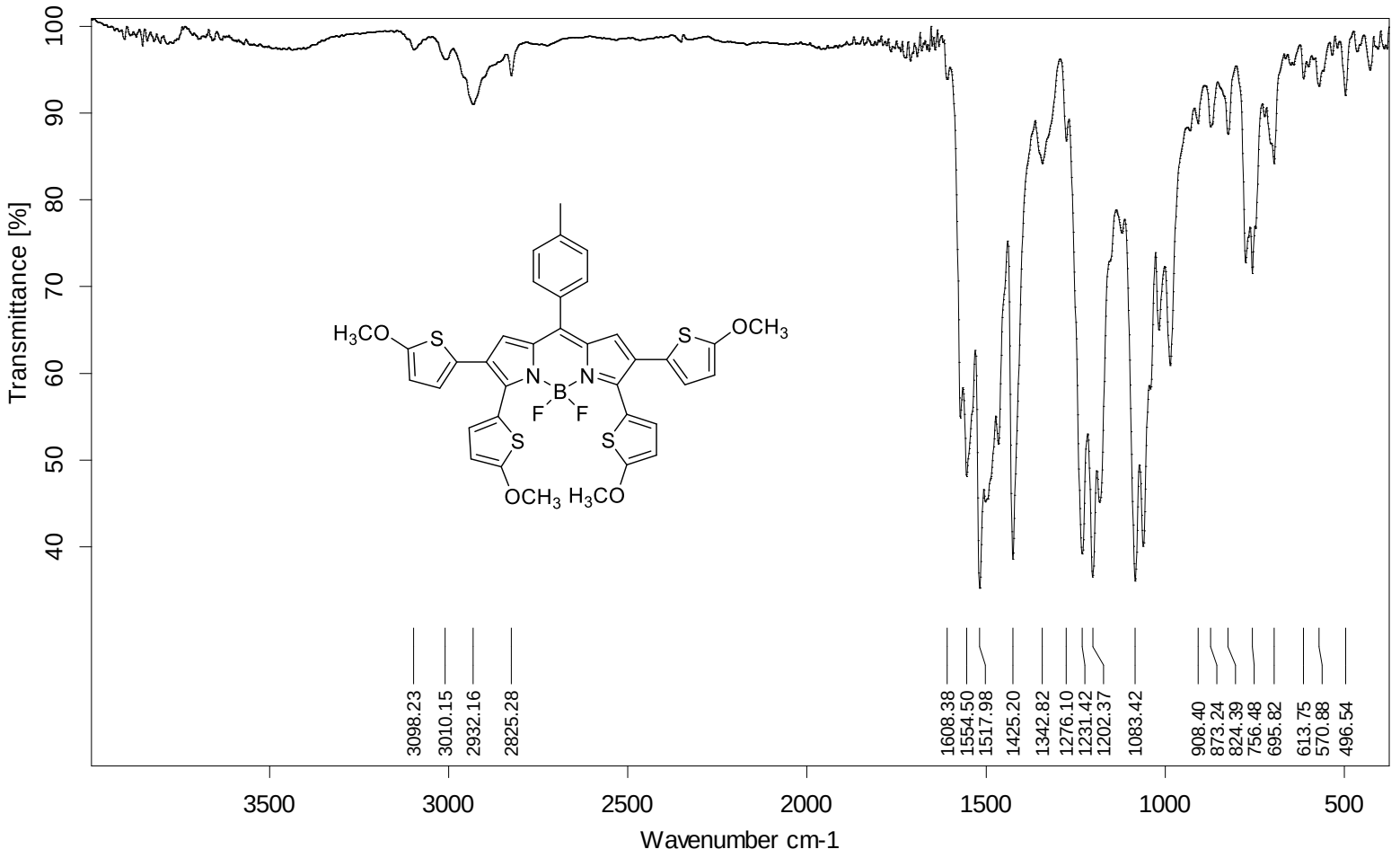
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1000
500
Wavenumber cm-1
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1517.98
1425.20
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1276.10
1231.42
1202.37
1083.42
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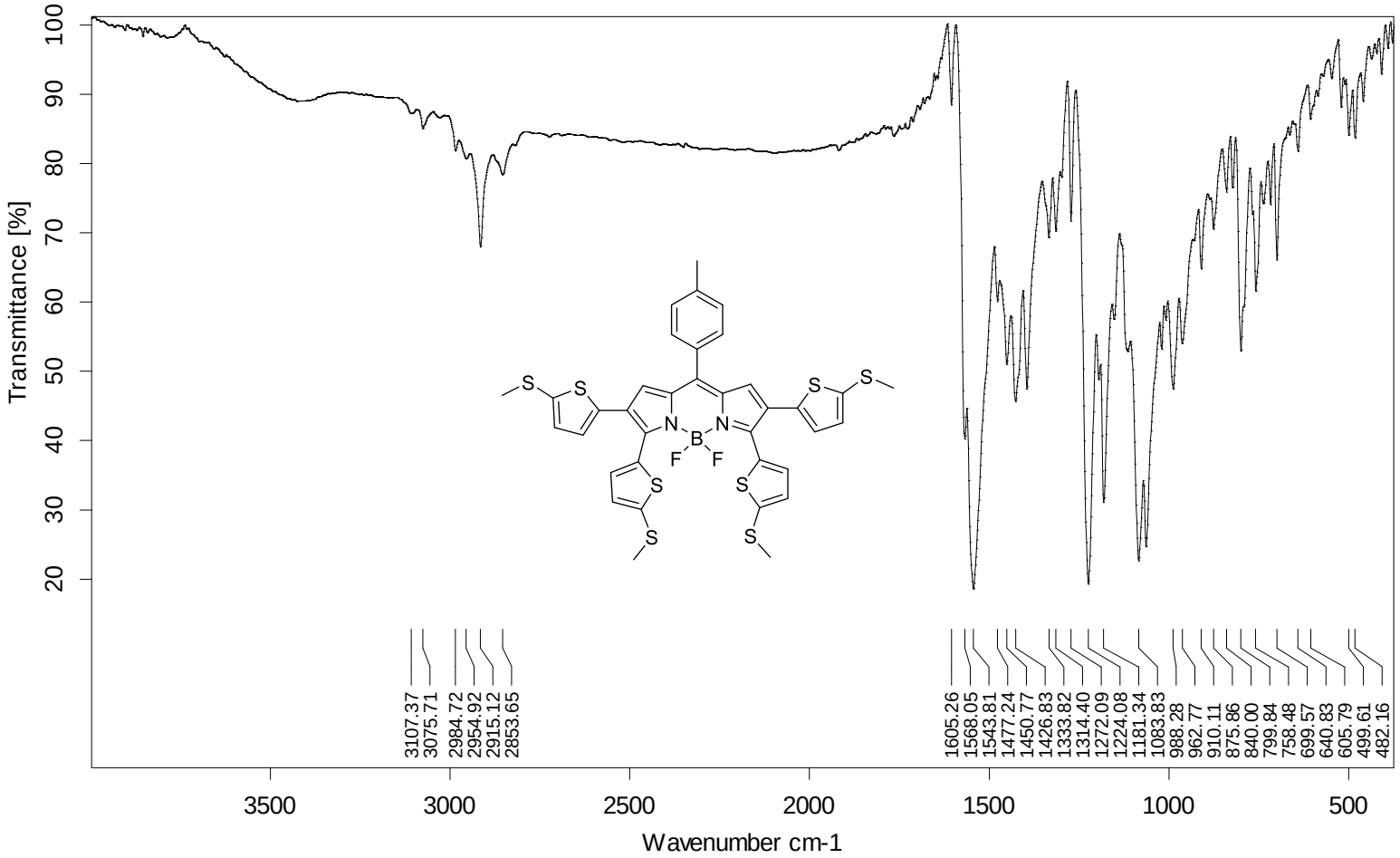
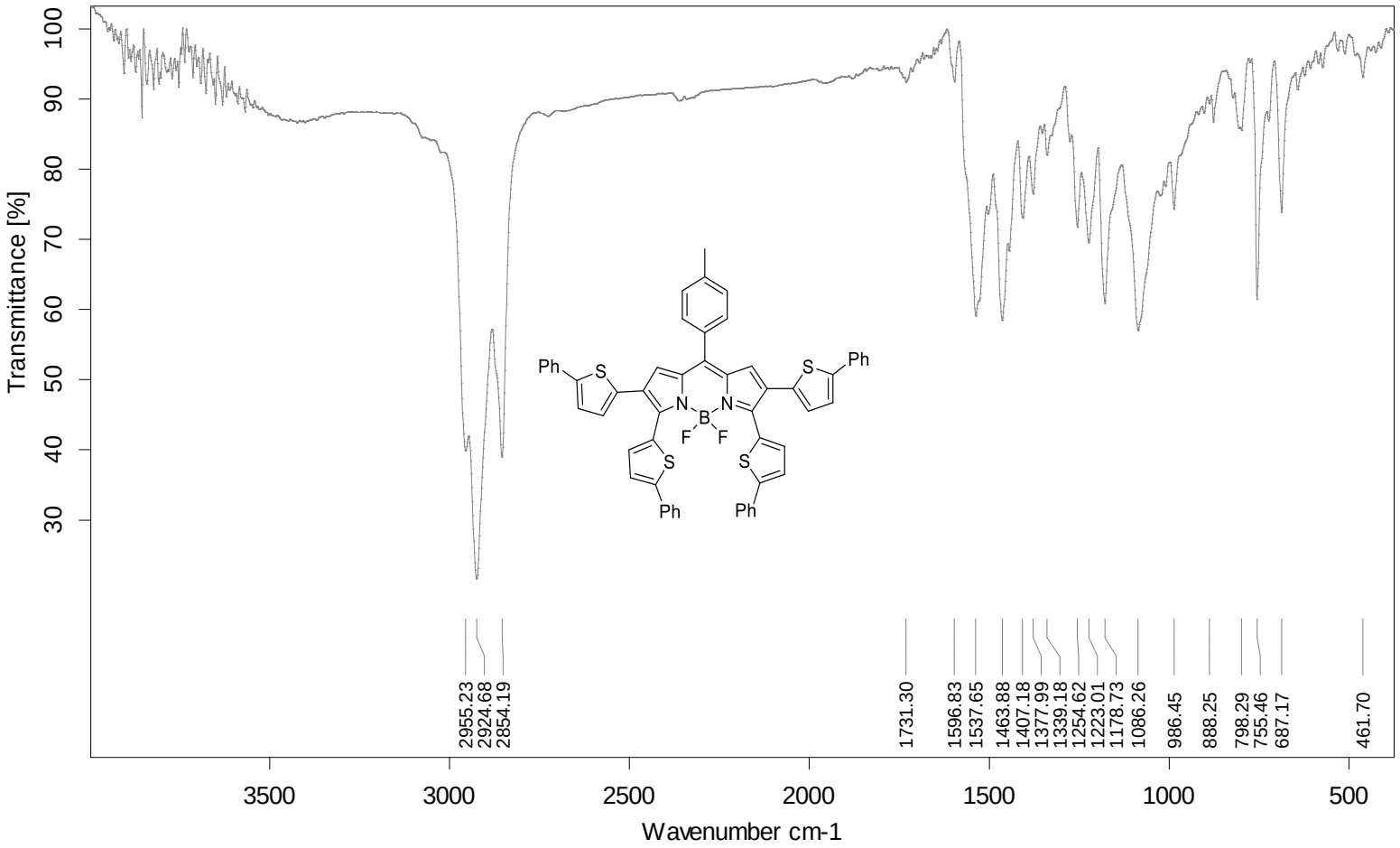
OCH3 H3CO


Transmittance [%]
100
90
80
70
60
50
40
30
20
3107.37
3075.71
2984.72
2954.92
2915.12
2853.65
1605.26
1568.05
1543.81
1477.24
1450.77
1426.83
1333.82
1314.40
1272.09
1224.08
1181.34
1083.83
988.28
962.77
910.11
875.86
840.00
799.84
758.48
699.57
640.83
605.79
499.61
482.16
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
S
S
S
S
N
B
N
F
F
S
S
S
S
S
S


Transmittance [%]
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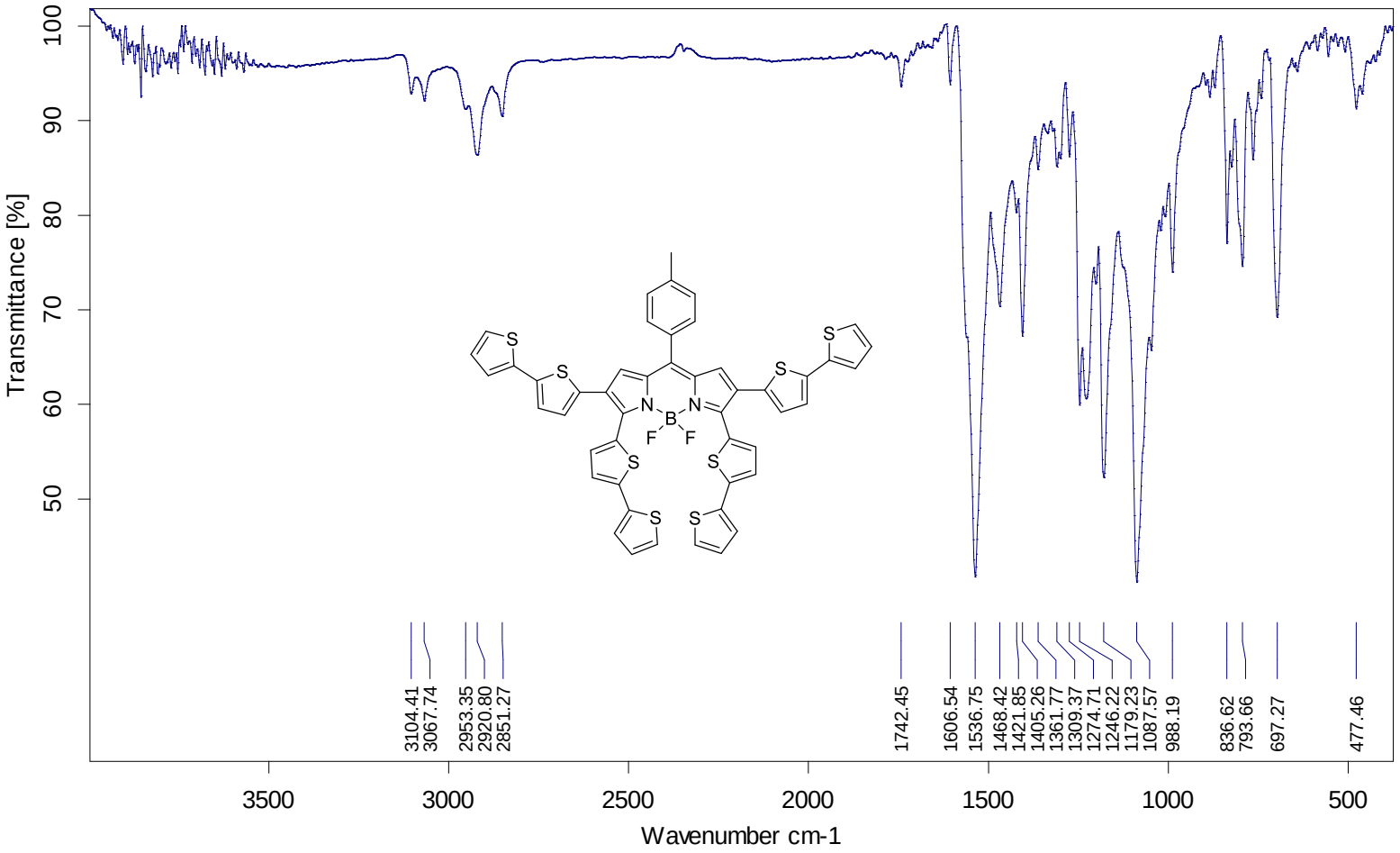
70
60
50
40
30
2955.23
2924.68
2854.19
1731.30
1596.83
1537.65
1463.88
1407.18
1377.99
1339.18
1254.62
1223.01
1178.73
1086.26
986.45
888.25
798.29
755.46
687.17
461.70
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
Ph
S
N
B
F
F
S
Ph
S
Ph
S
Ph


Transmittance [%]
100
90
80
70
60
50
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
3104.41
3067.74
2953.35
2920.80
2851.27
1742.45
1606.54
1536.75
1468.42
1421.85
1405.26
1361.77
1309.37
1274.71
1246.22
1179.23
1087.57
988.19
836.62
793.66
697.27
477.46
S
N
B
F