Supplementary information

Synthesis of 2,5-bis(9H-fluoren-9-ylidene)-2,5-dihydrothiophene derivatives and systematic study of the substituent effect

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* Corresponding author. *E-mail address*: jh@zstu.edu.cn (H. Jiang).

Contents

1. TG curves of **B1-B9**

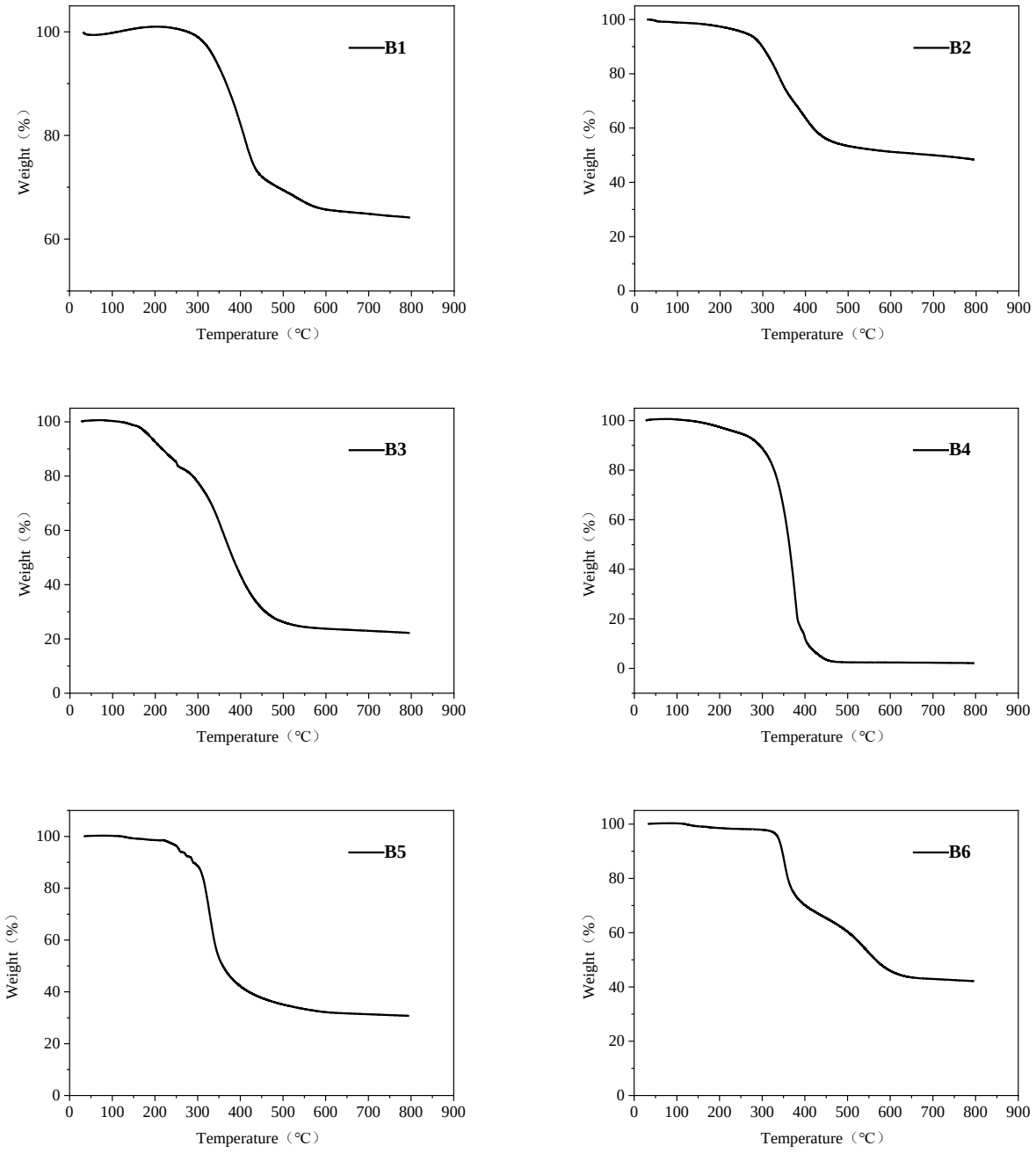


Fig. S1 TG curves of **B1-B9**

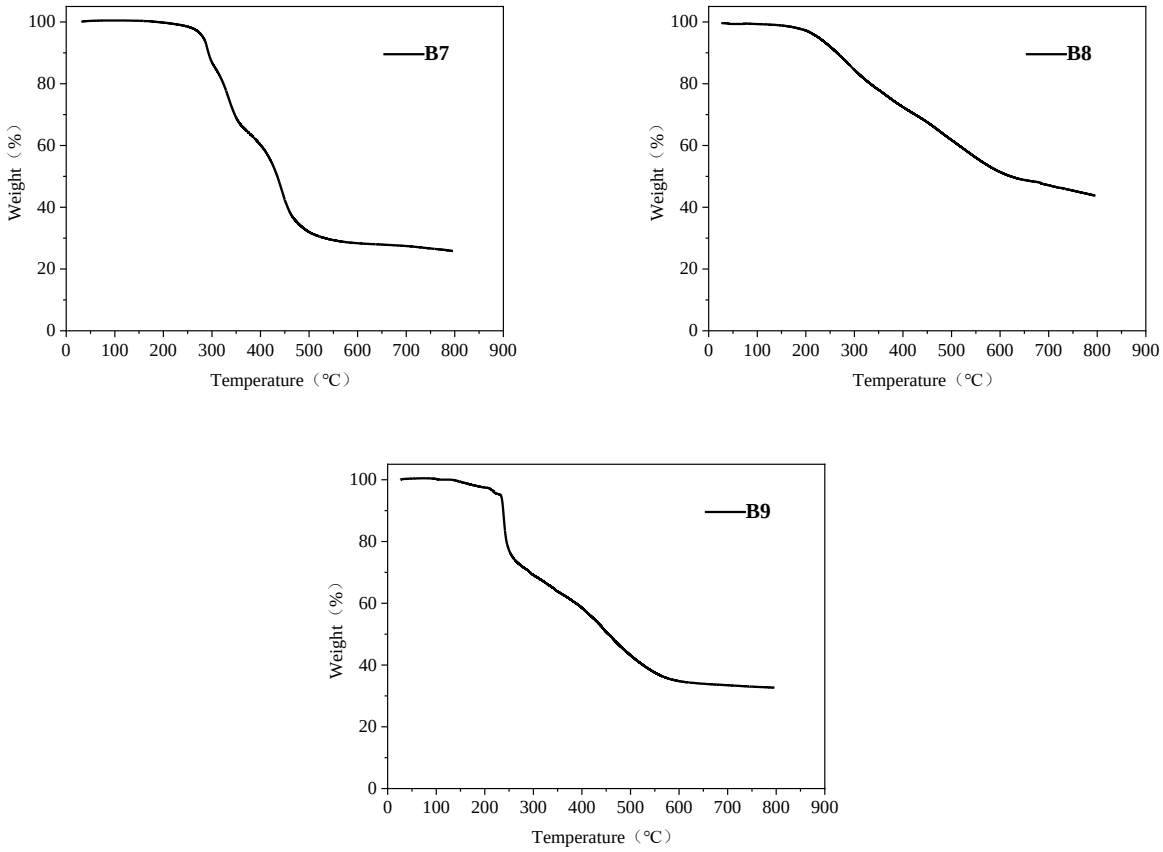


Fig. S1 TG curves of **B1-B9** (continued)

2. Color of **ThBF** derivatives

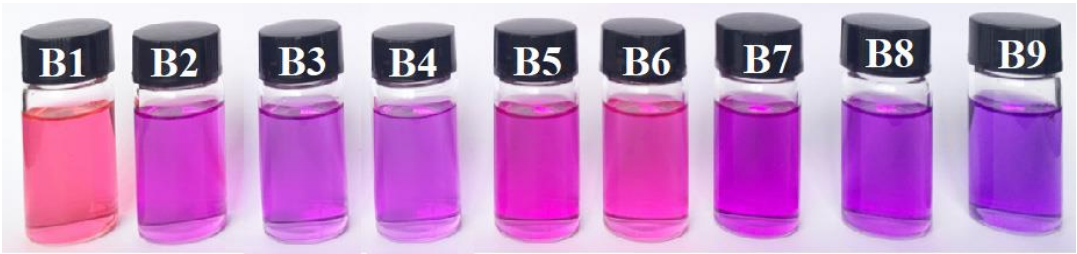
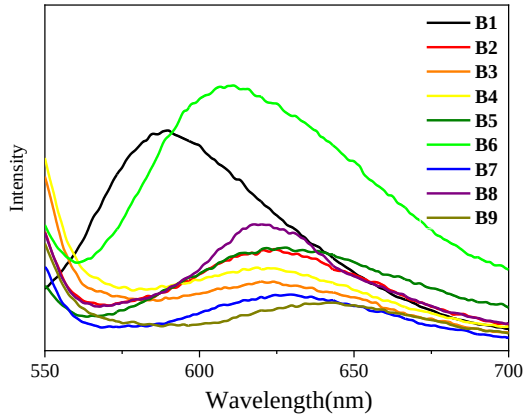
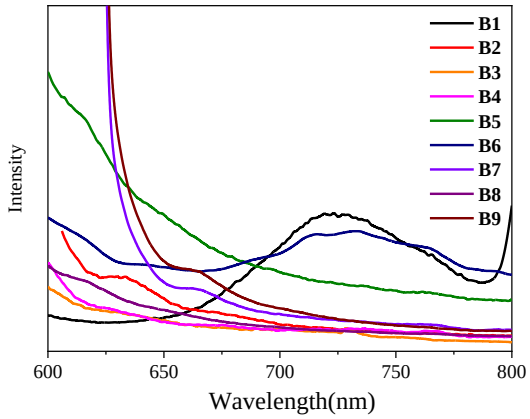


Fig. S2 Photographs of solution of **ThBF**s in dichloromethane (2×10^{-5} mol/L)

3. Fluorescence spectra of **B1**-**B9**



(a) in toluene solution (10^{-5} mol/L)



(b) as powder

Fig. S3 Fluorescence spectra of **B1**-**B9**

The intensities were tested at the excitation wavelength of 470 nm. The maximum emission wavelengths (λ_{max}/nm) in toluene solution were 590 (**B1**), 624 (**B2**), 620 (**B3**), 622 (**B4**), 628 (**B5**), 611(**B6**), 630 (**B7**), 620 (**B8**), and 643 (**B9**). Only **B1** (λ_{max}: 725 nm) and **B5** (λ_{max}: 730 nm) exhibited weak photoluminescence as powder.

4. CV curves of **B1-B9**

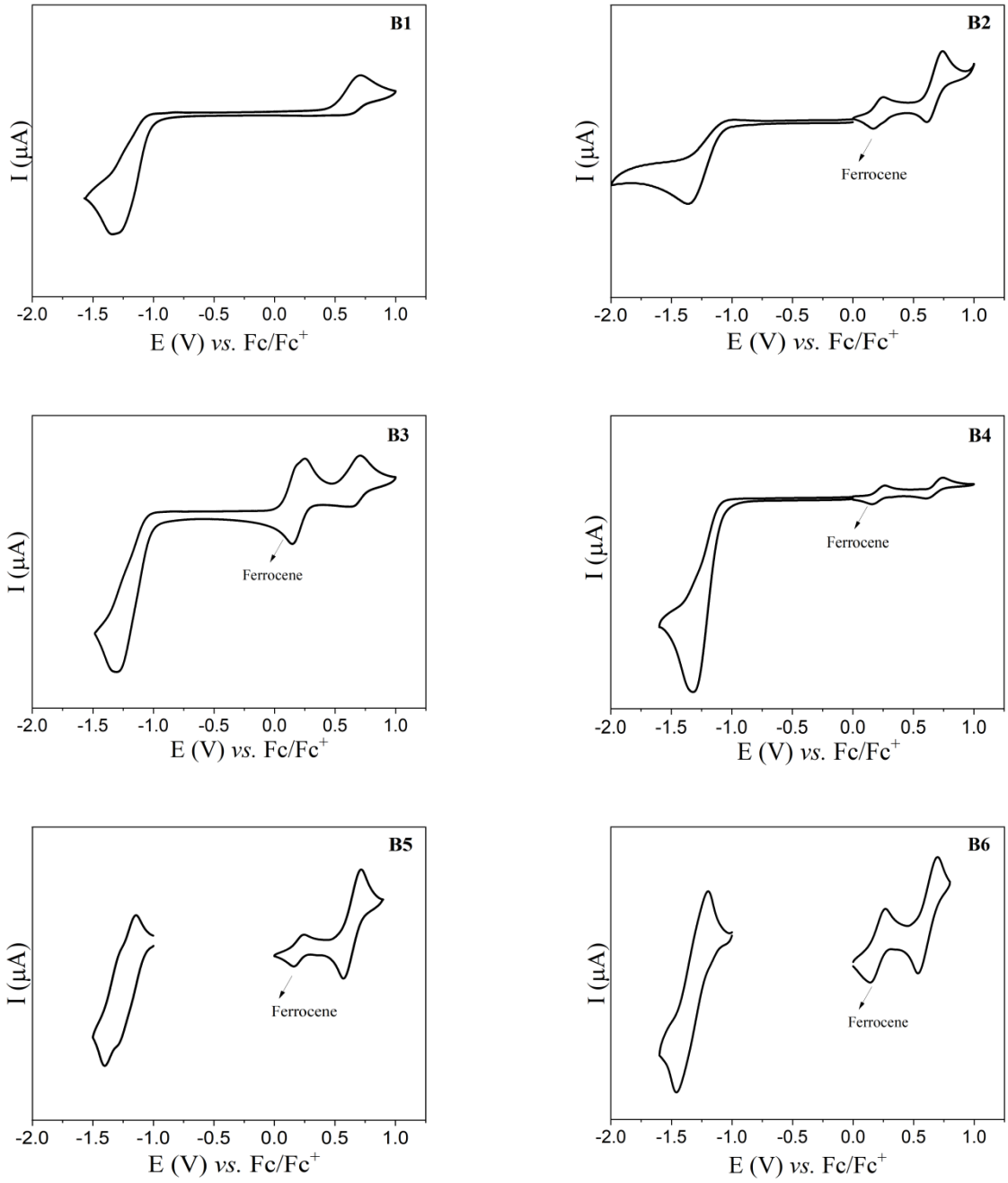


Fig. S4 CV curves of **B1-B9**

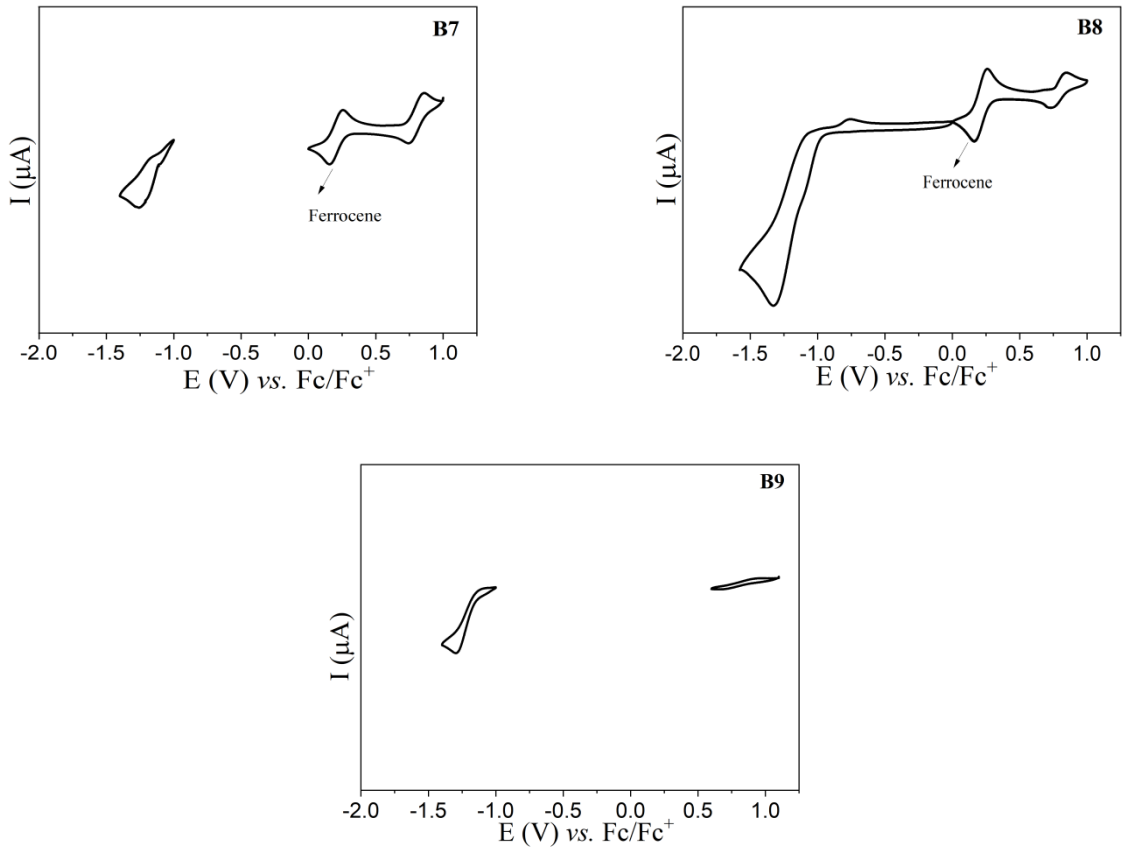


Fig. S4 CV curves of **B1-B9** (continued)

5. Calculated molecular structures of **B1-B9**

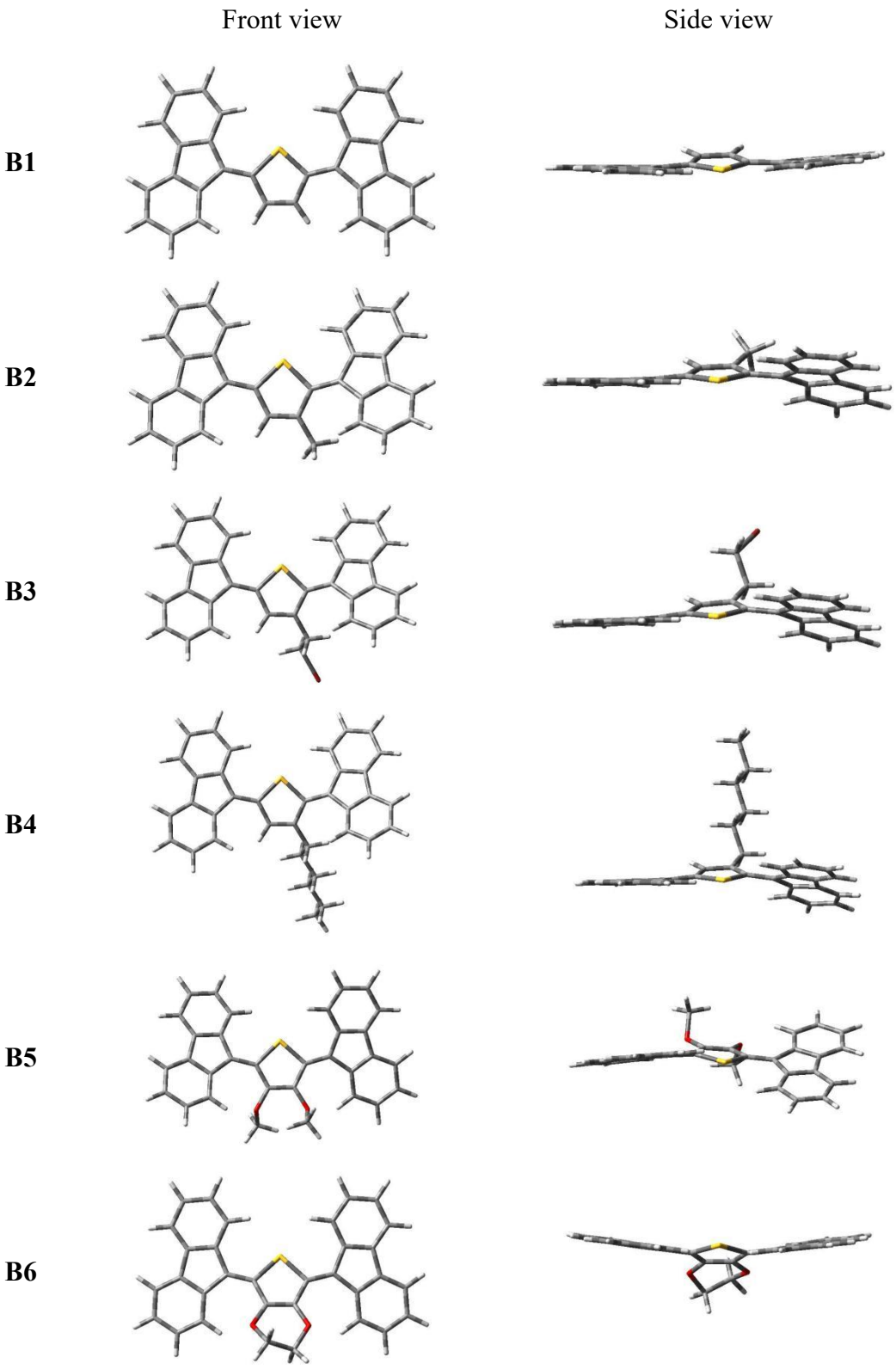


Fig. S5 Calculated molecular structures of **B1-B9**

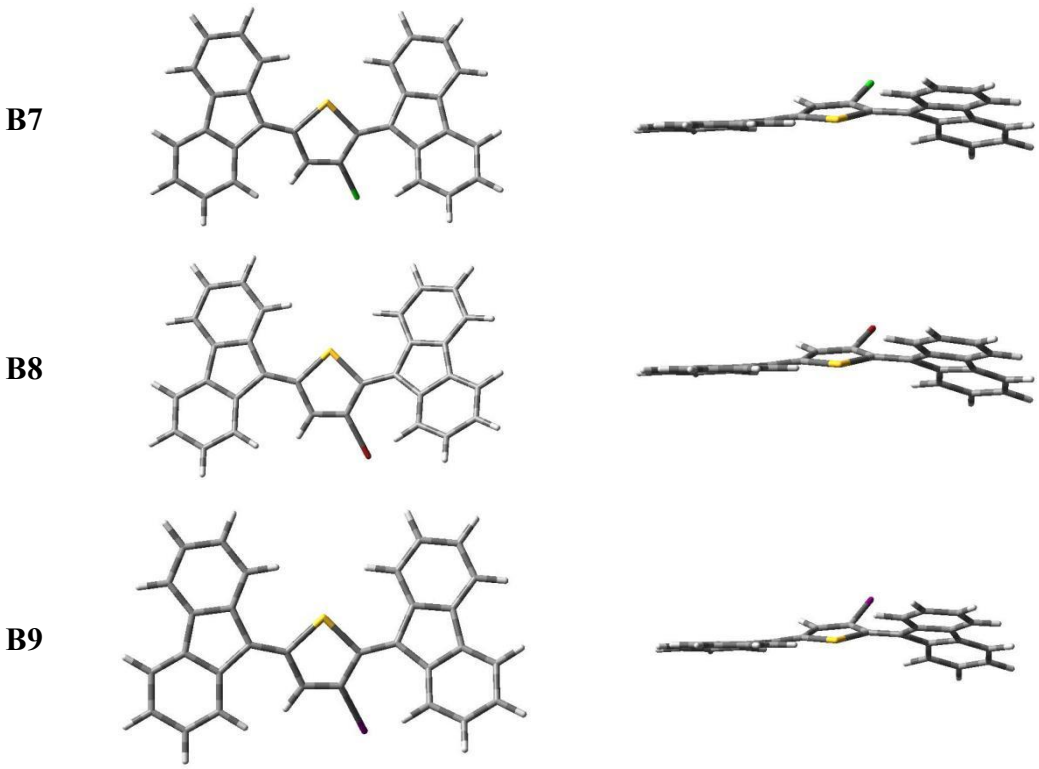
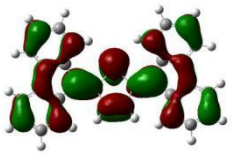
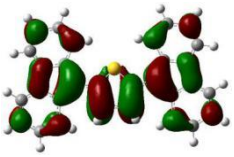
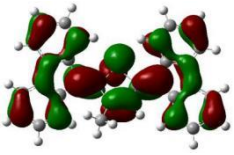
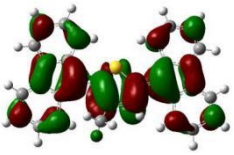
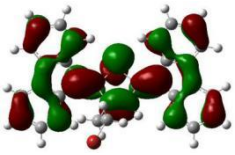
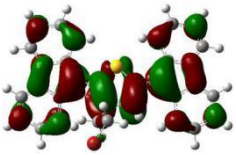
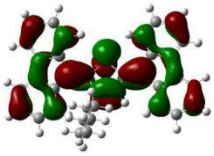
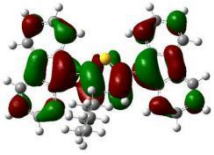
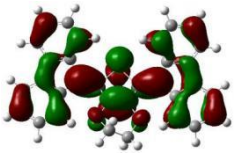
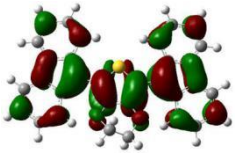
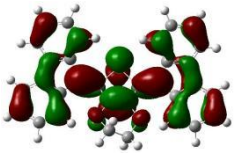
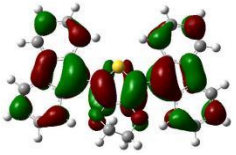
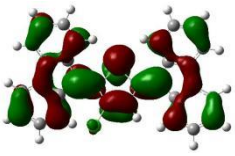
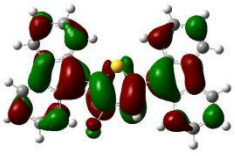


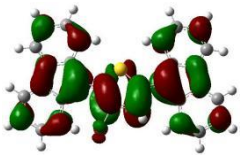
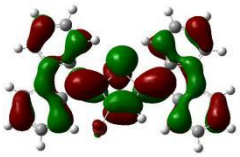
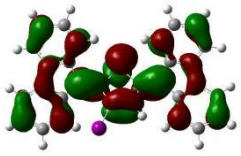
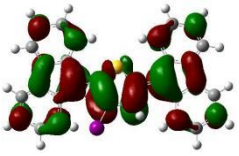
Fig. S5 Calculated molecular structures of **B1**-**B9** (continued)

6. HOMO/LUMO energy diagrams of **B1**-**B9**

Tab. S1 HOMO/LUMO energy diagrams of **B1**-**B9**

	HOMO	LUMO	Gap
B1			2.33
	-5.3228 eV	-2.9939 eV	
B2			2.22
	-5.2553 eV	-3.0385 eV	
B3			2.19
	-5.3879 eV	-3.1958 eV	
B4			2.21
	-5.2246 eV	-3.0195 eV	
B5			2.29
	-5.1522 eV	-2.8592 eV	
B6			2.21
	-5.199 eV	-2.985 eV	
B7			2.20
	-5.440 eV	-3.244 eV	

Tab. S1 HOMO/LUMO energy diagrams of **B1**-**B9** (continued)

	HOMO	LUMO	Gap
B8			2.19
	-5.420 eV	-3.226 eV	
B9			2.27
	-5.398 eV	-3.005 eV	

The above optimized structure and the HOMO/LUMO energy diagrams were calculated by Gaussian 09.[a] And The biradical characters and the energies of the singlet $E(S_1)$ and triplet $E(T_1)$ excited states were calculated by Gaussian 16.[b]

[a] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, 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, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

[b] Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2019.

7. Calculated biradical character of **B1**-**B9**

The biradical character (y) was calculated by using the spin-unrestricted Hartree−Fock method at the UHF/6-311G(d) level. The y value was calculated using the occupation number of the lowest unoccupied natural orbital (LUNO) and the highest unoccupied natural orbital (HONO) of **B1**-**B9**, which was expressed as:

$$y = 1 - \frac{2T}{1+T^2}$$

where

$$T = \frac{n_{\mathrm{HONO}} - n_{\mathrm{LUNO}}}{2}$$

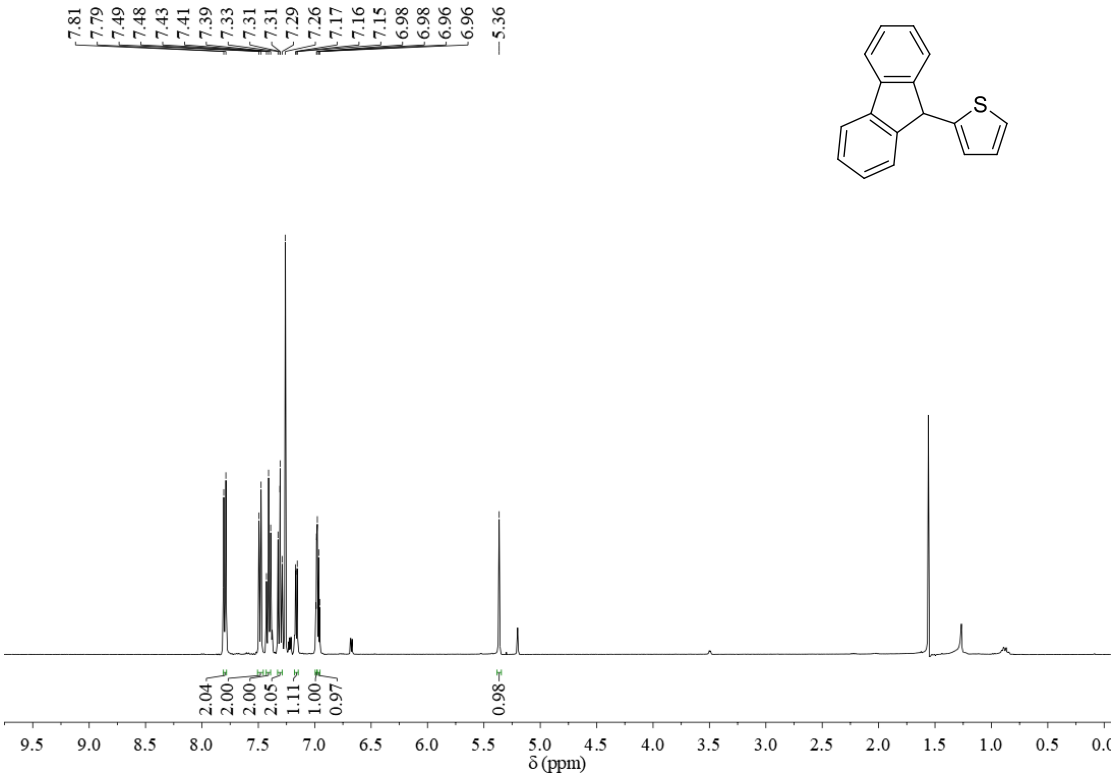
The detailed n_{HONO}, n_{LUNO}, T and y values of **B1**-**B9** were listed in Tab. S2.

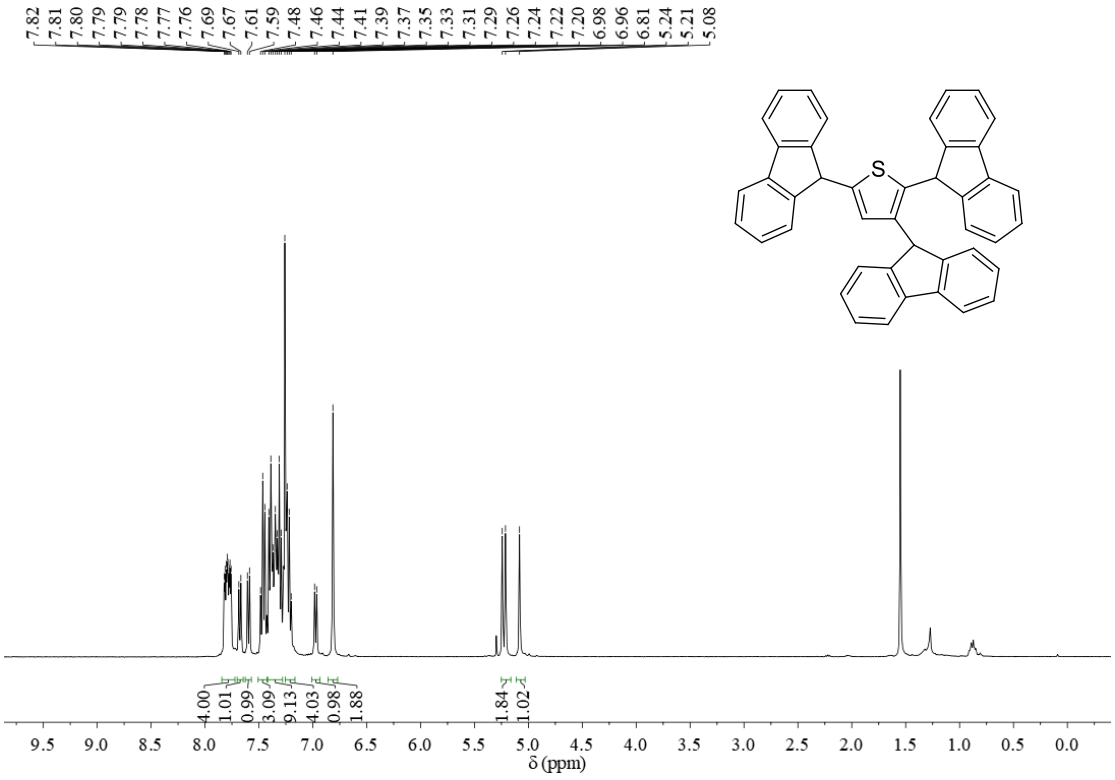
Tab. S2 The n_{HONO}, n_{LUNO}, T and y values of **B1**-**B9**

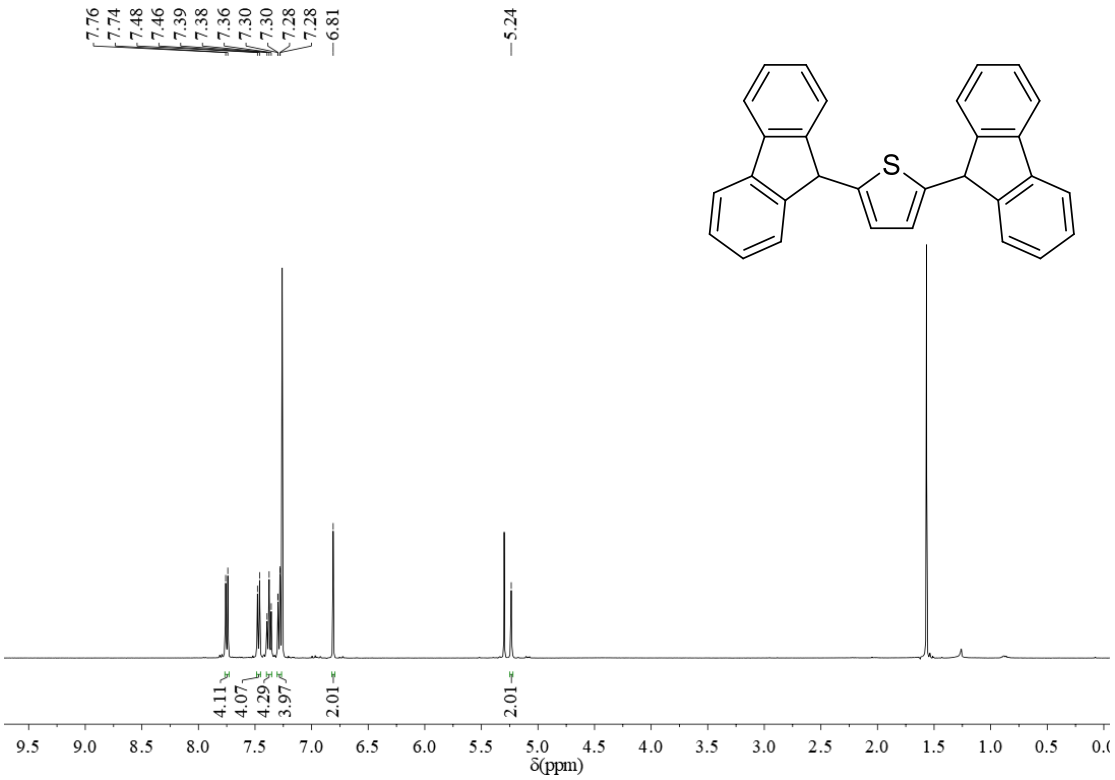
	n_{HONO}	n_{LUNO}	T	y
B1	1.43023	0.56977	0.43023	0.27400
B2	1.38825	0.61175	0.38825	0.325216
B3	1.39108	0.60892	0.39108	0.321597
B4	1.38523	0.61477	0.38523	0.329103
B5	1.99993	0.00007	0.99993	2.45×10^{-9}
B6	2	0	1	0
B7	1.42309	0.57691	0.42309	0.282293
B8	1.42173	0.57827	0.42173	0.283902
B9	1.37644	0.62356	0.37644	0.34060

Reference: S. Intorp, M. Hodecker, M. Müller, O. Tverskoy, M. Rosenkranz, E. Dmitrieva, A. Popov, F. Rominger, J. Freudenberg, A. Dreuw and U. Bunz, *Angew. Chem. Int. Ed.*, 2020, **59**, 12396-12401.

8. ^{1}H NMR and ^{13}C NMR spectra of **ThBF**s and corresponding intermediates



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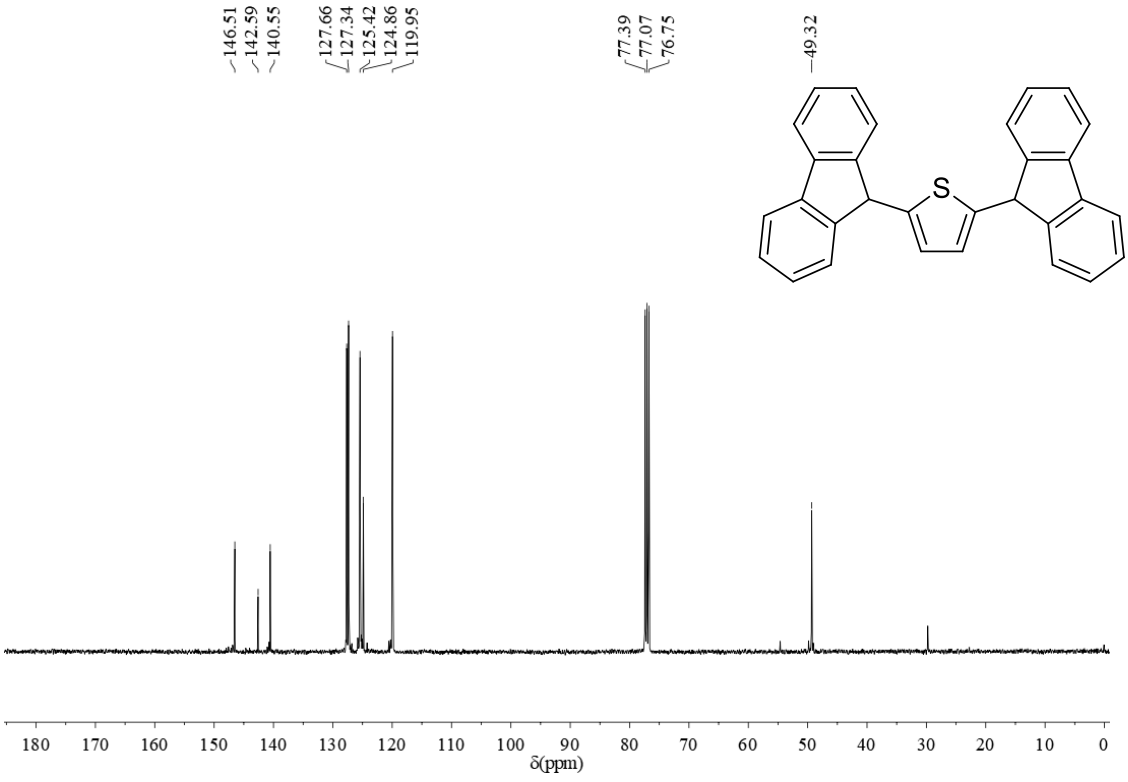
7.48
7.46
7.39
7.38
7.36
7.30
7.30
7.28
7.28
6.81
5.24
S
4.11
4.07
4.29
3.97
2.01
2.01
δ(ppm)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142.59
140.55
127.66
127.34
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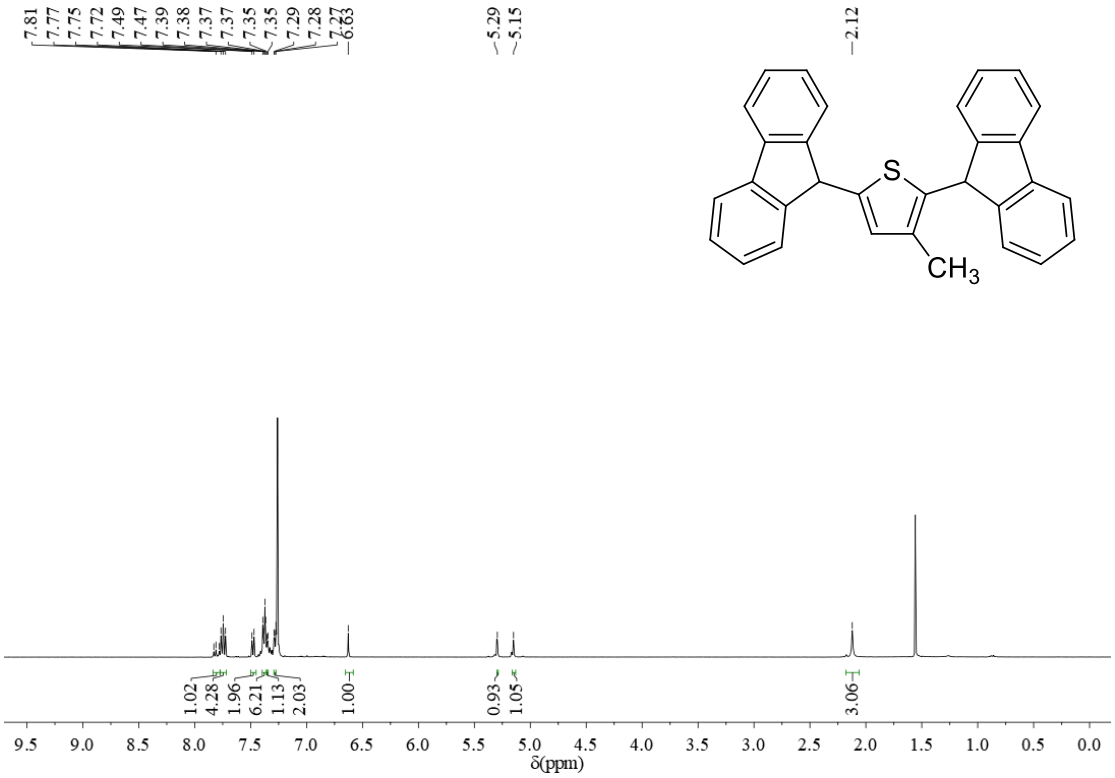
124.86
119.95
77.39
77.07
76.75
49.32
S
δ(ppm)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7.38
7.37
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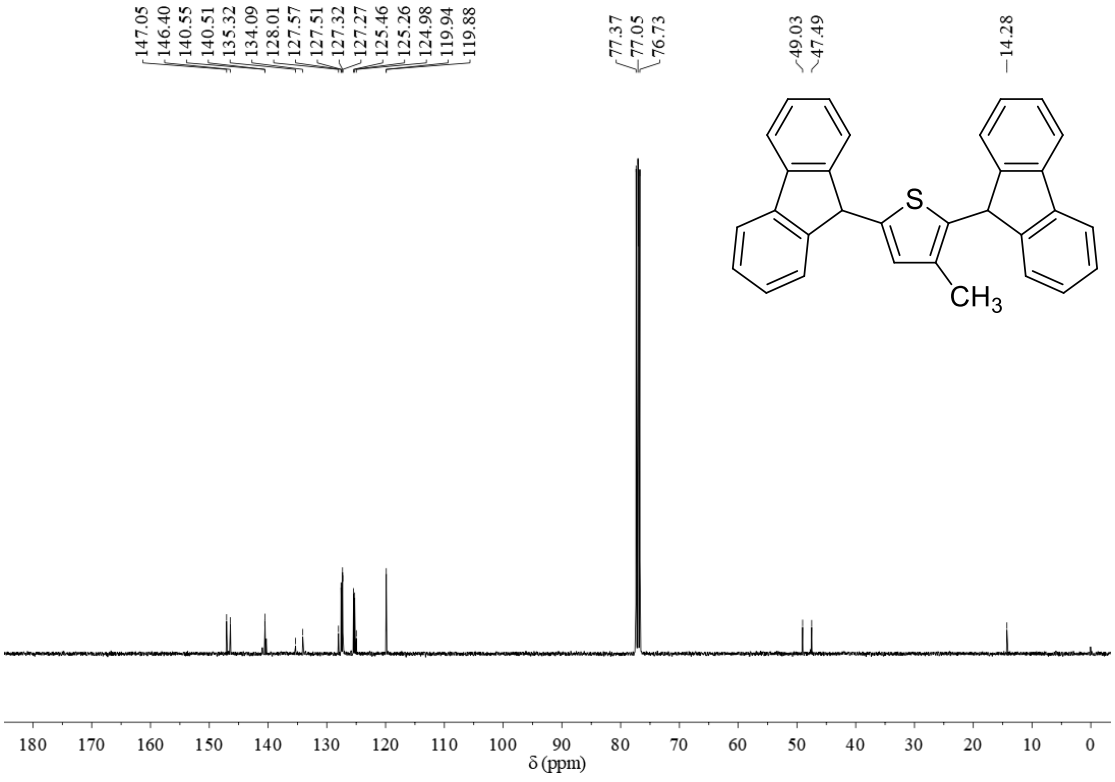
7.35
7.29
7.28
7.27
6.63
5.29
5.15
2.12
S
CH3
1.02
4.28
1.96
6.21
1.13
2.03
1.00
0.93
1.05
3.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ(ppm)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119.94
119.88
77.37
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S
CH3
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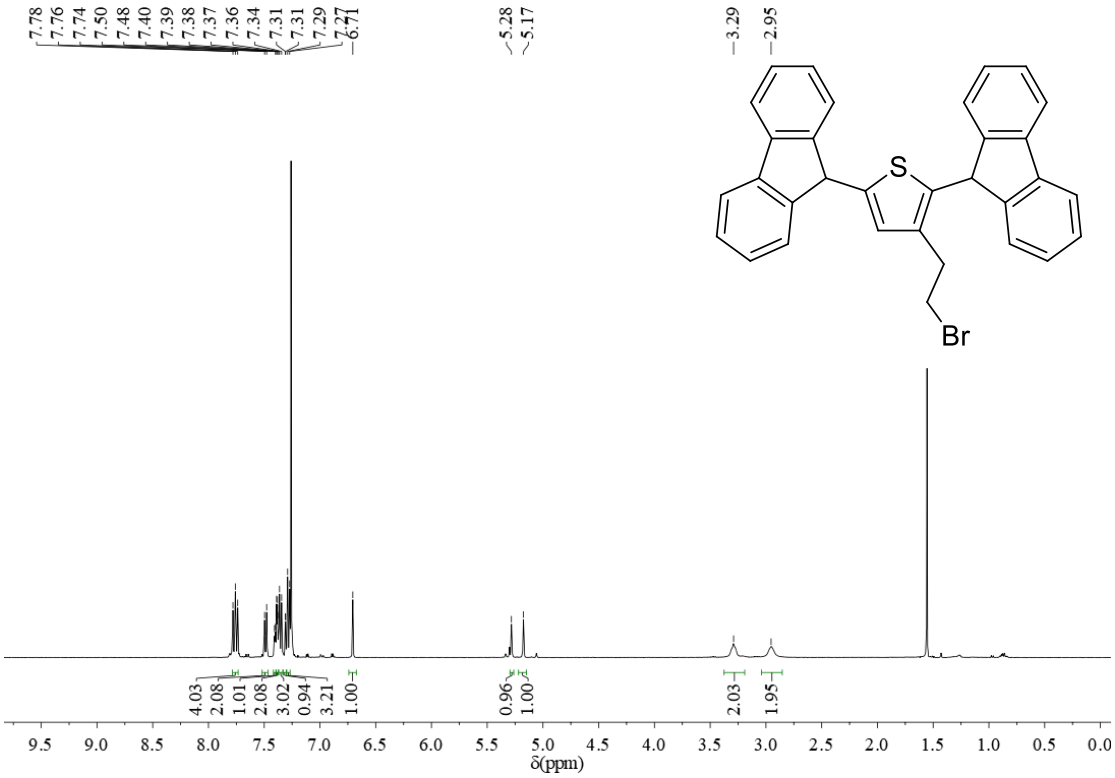
δ (ppm)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2.03
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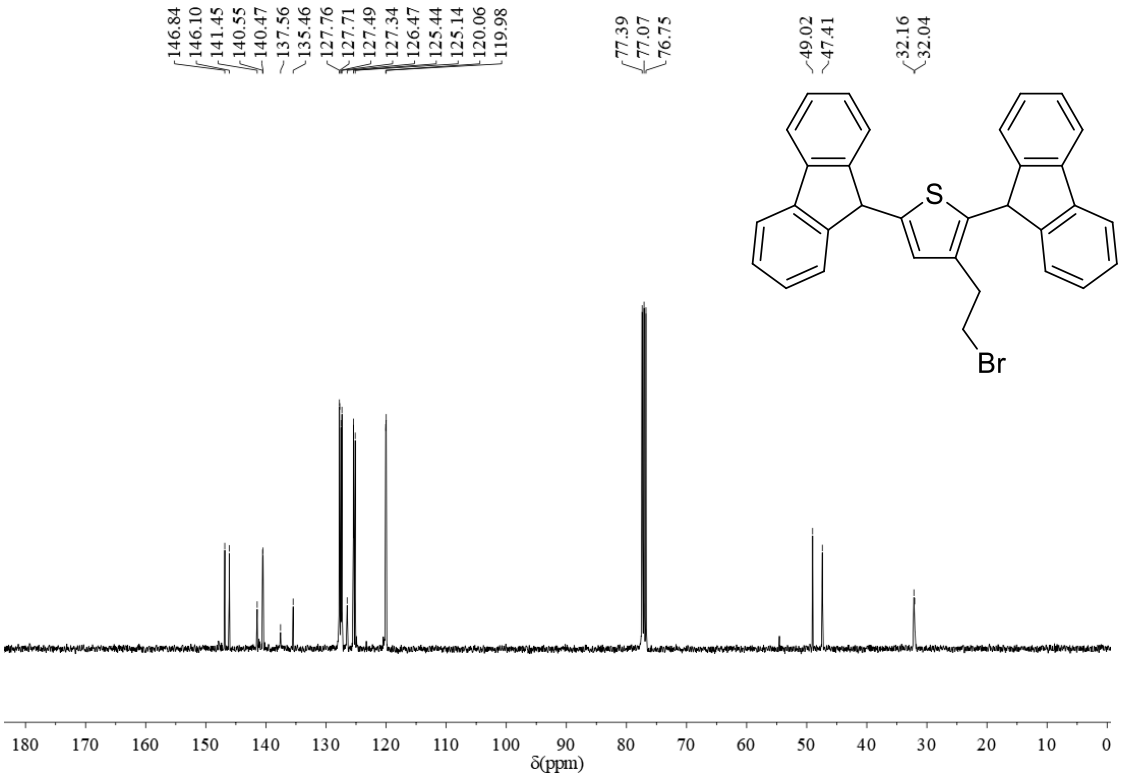
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77.39
77.07
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32.16
32.04
S
Br
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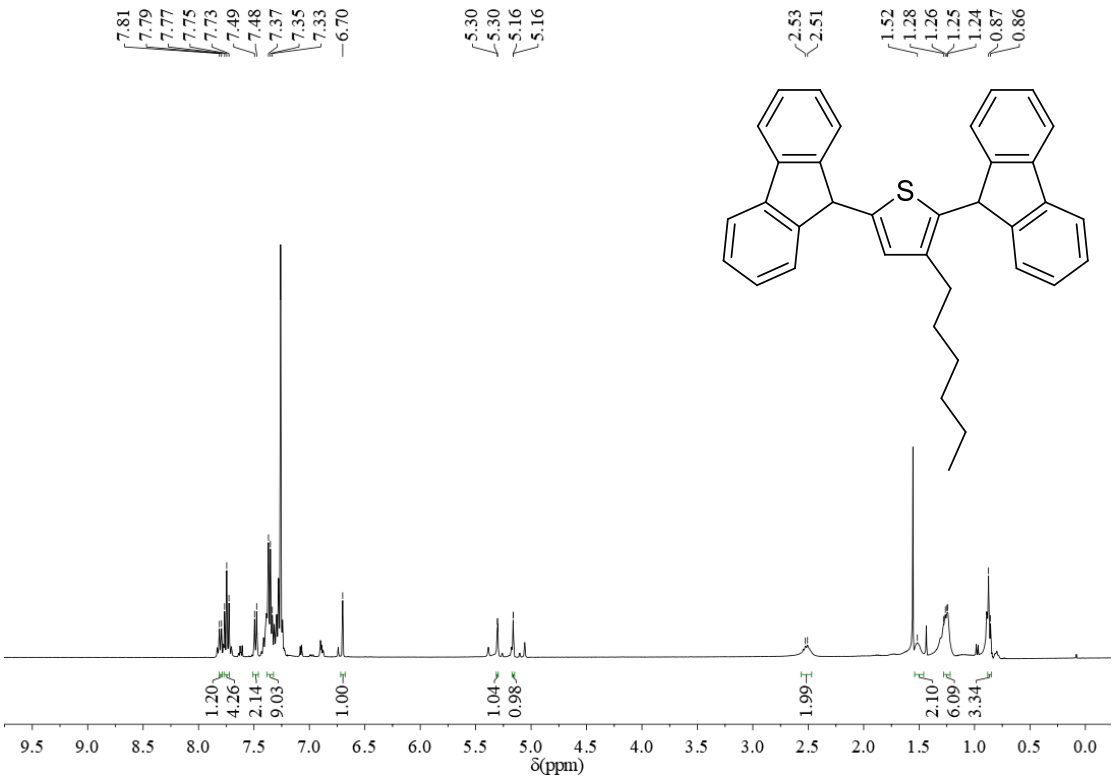
δ(ppm)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7.79
7.77
7.75
7.73
7.49
7.48
7.37
7.35
7.33
6.70
5.30
5.30
5.16
5.16
2.53
2.51
1.52
1.28
1.26
1.25
1.24
0.87
0.86
S
1.20
4.26
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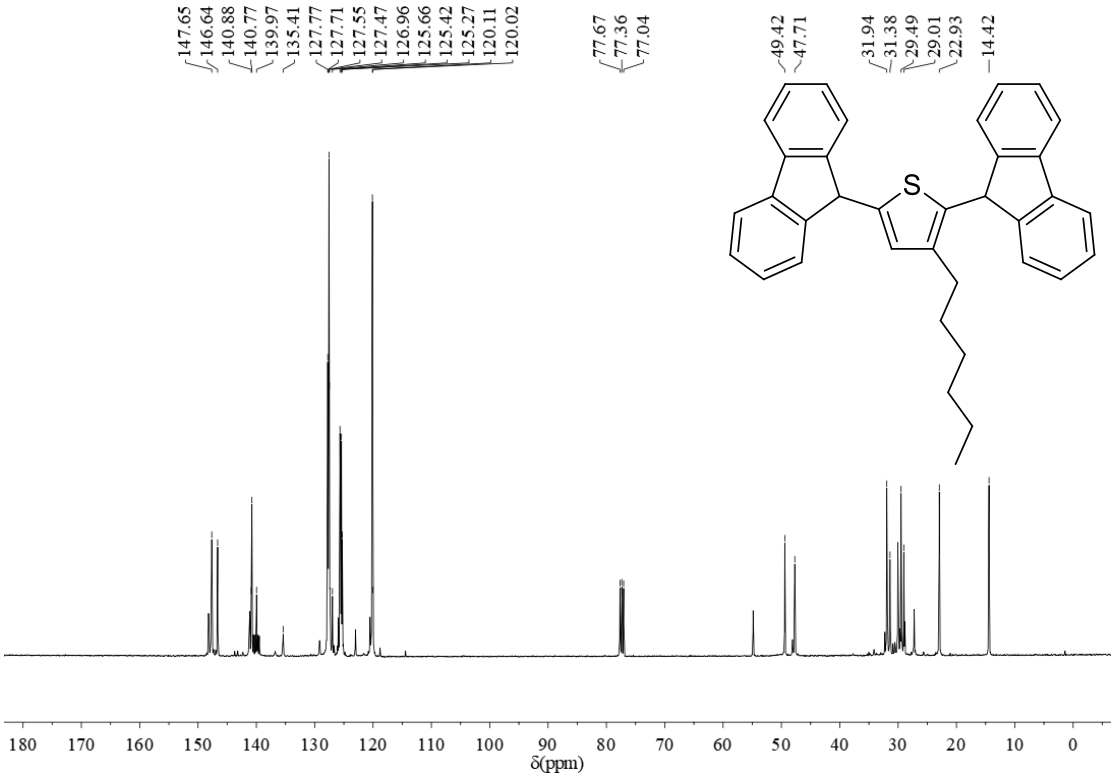
9.03
1.00
1.04
0.98
1.99
2.10
6.09
3.34
δ(ppm)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127.71
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127.47
126.96
125.66
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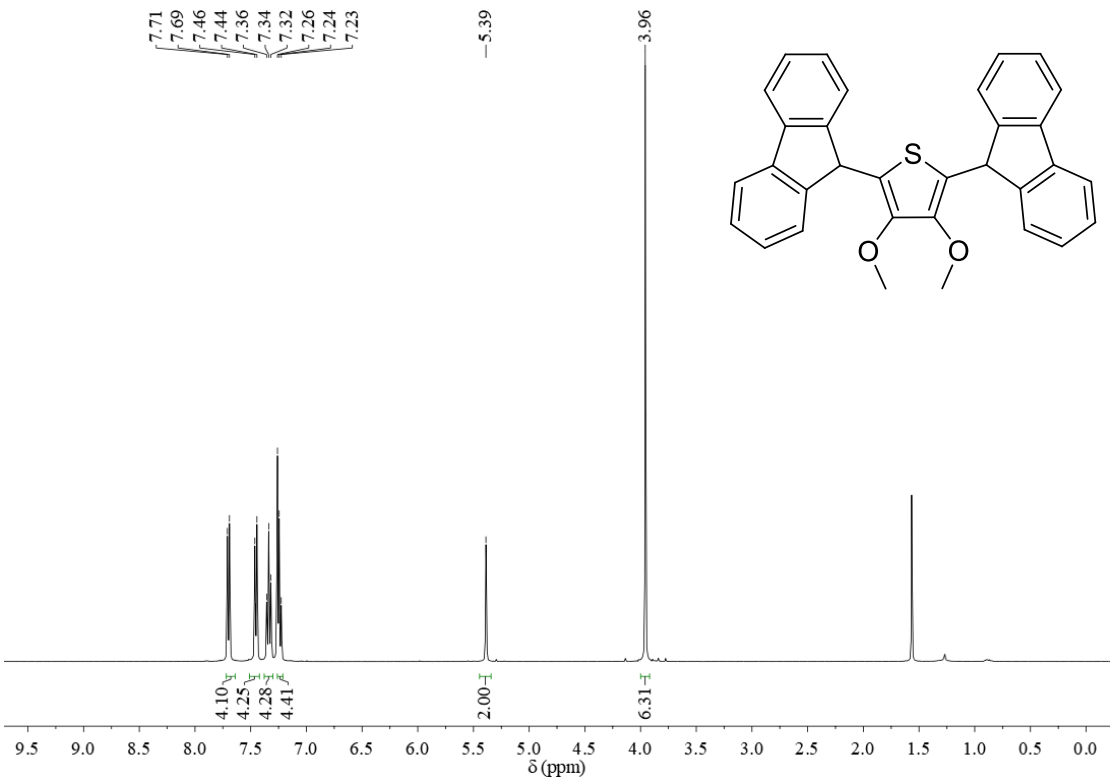
125.27
120.11
120.02
77.67
77.36
77.04
49.42
47.71
31.94
31.38
29.49
29.01
22.93
14.42
S
δ(ppm)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7.69
7.46
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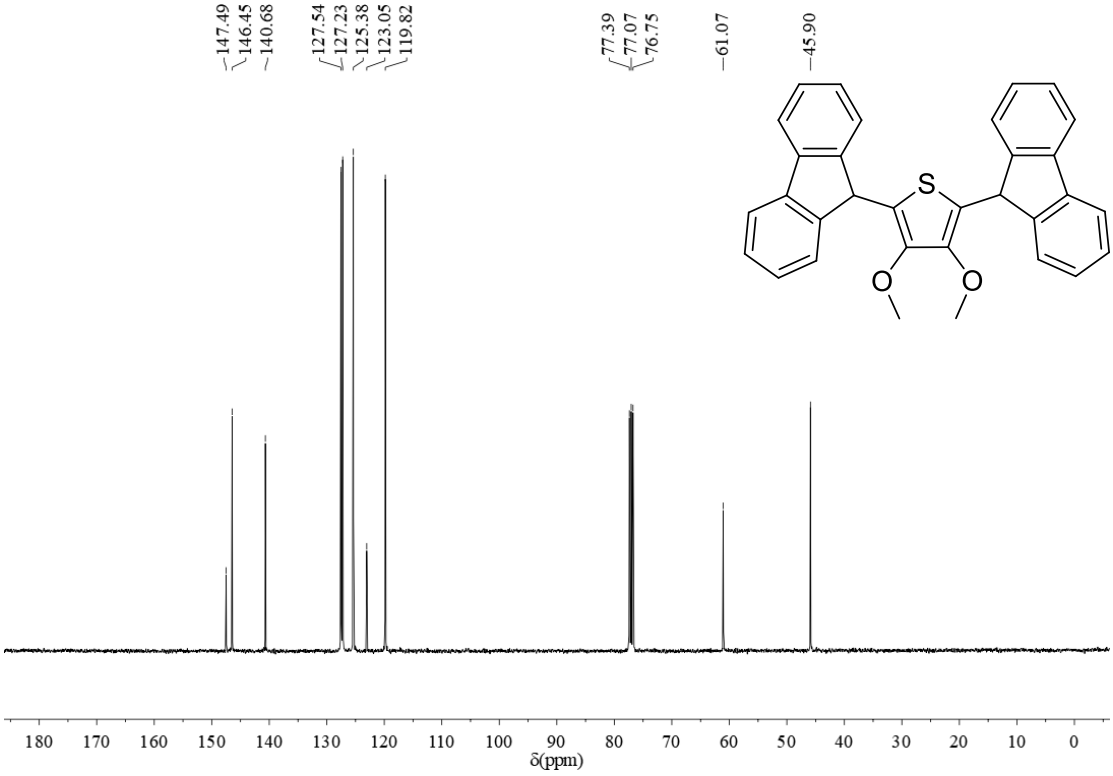
7.36
7.34
7.32
7.26
7.24
7.23
5.39
3.96
S
O
O
4.10
4.25
4.28
4.41
2.00
6.31
δ (ppm)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146.45
140.68
127.54
127.23
125.38
123.05
119.82
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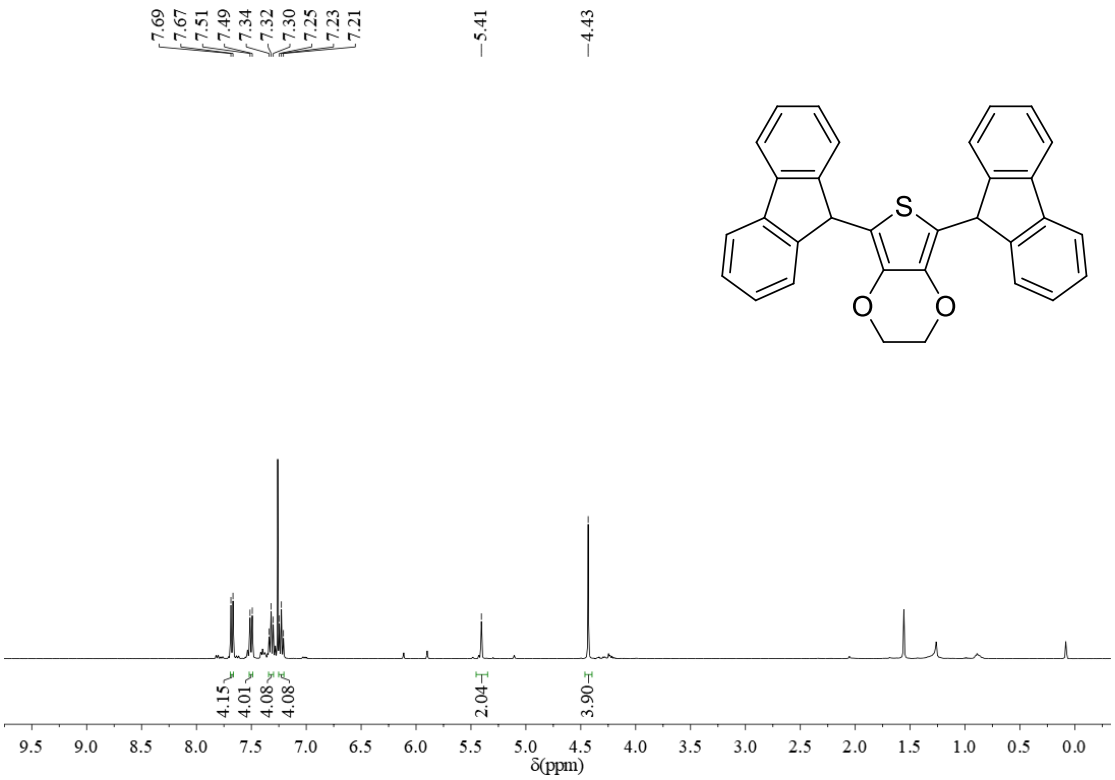
77.07
76.75
61.07
45.90
S
O
O
δ(ppm)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7.32
7.30
7.25
7.23
7.21
5.41
4.43
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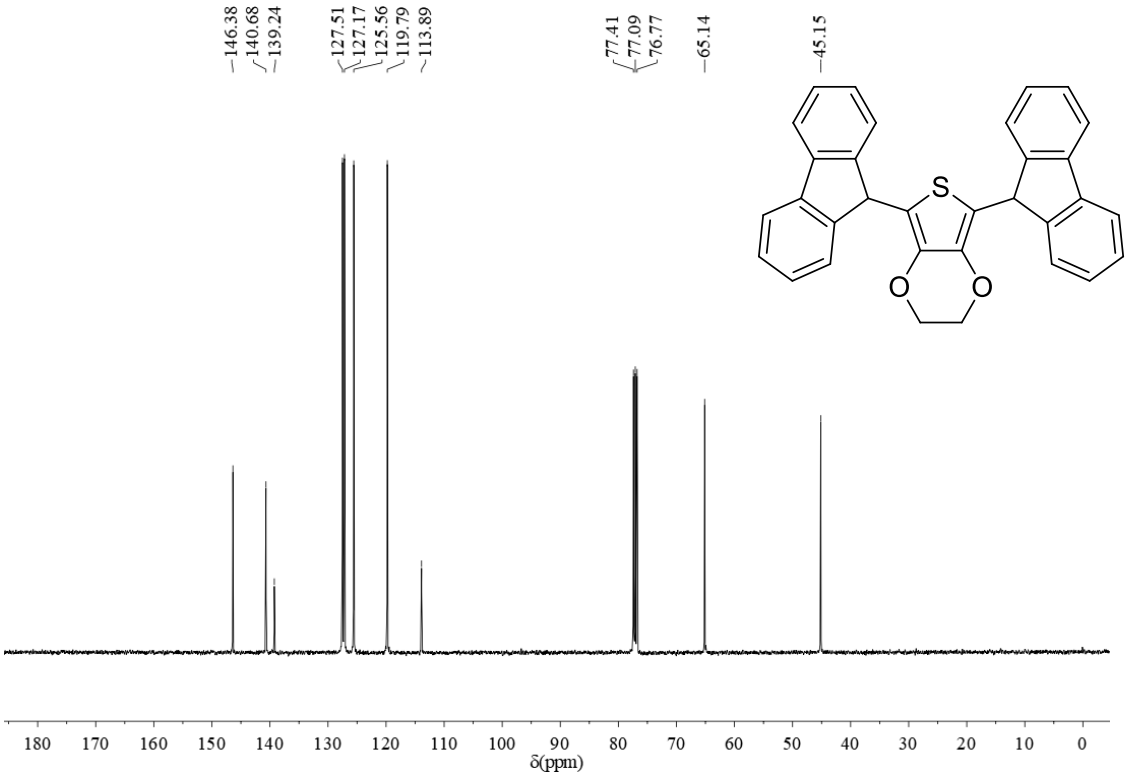
4.08
4.08
2.04
3.90
δ(ppm)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140.68
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127.51
127.17
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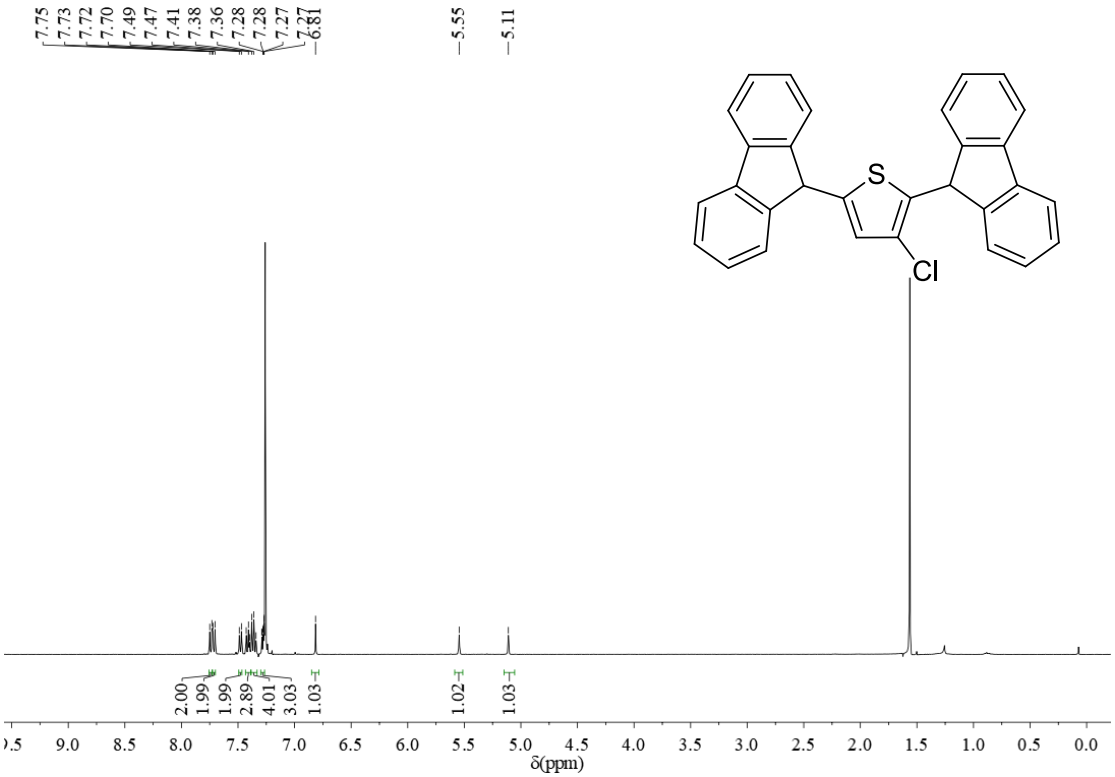
119.79
113.89
77.41
77.09
76.77
65.14
45.15
S
O
O
δ(ppm)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7.73
7.72
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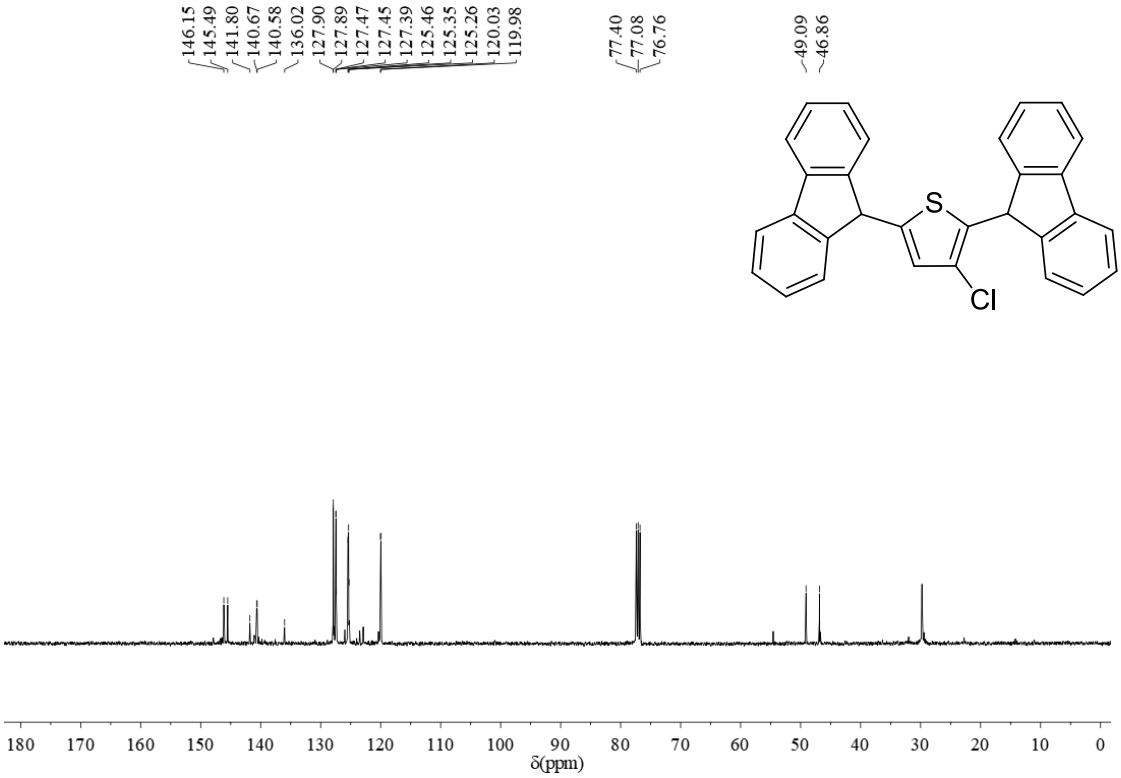
7.49
7.47
7.41
7.38
7.36
7.28
7.28
7.27
6.81
5.55
5.11
S
Cl
2.00
1.99
1.99
2.89
4.01
3.03
1.03
1.02
1.03
δ(ppm)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145.49
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140.58
136.02
127.90
127.89
127.47
127.45
127.39
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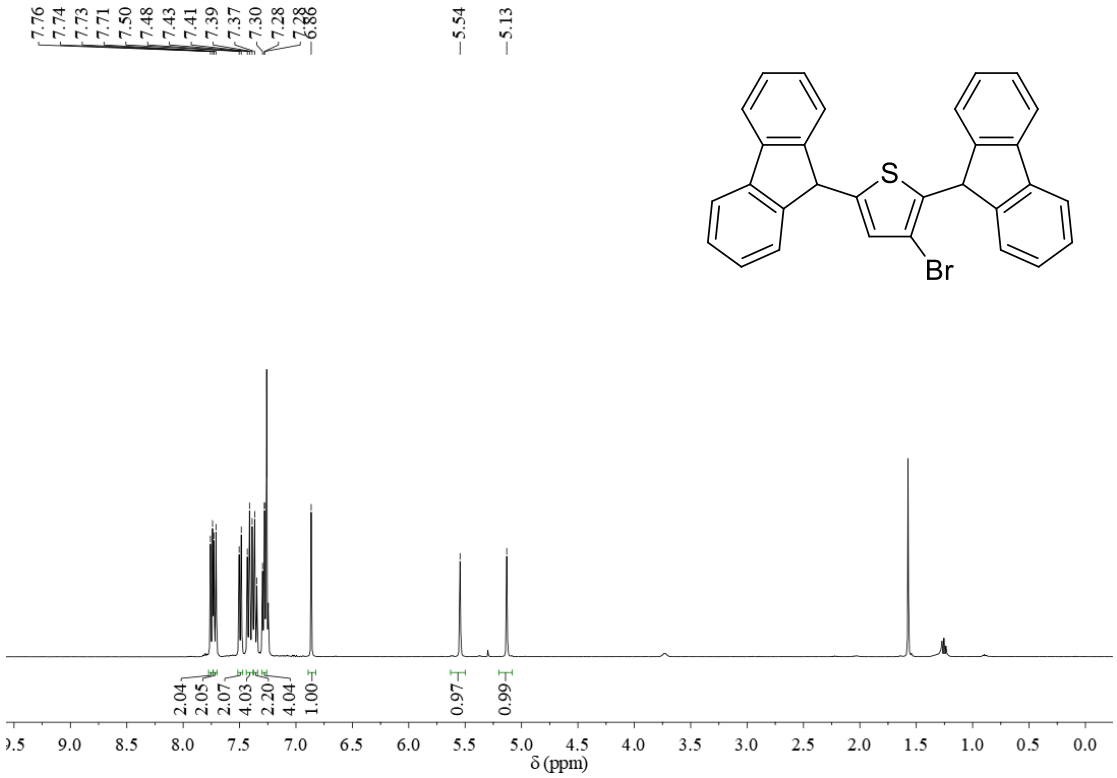
125.26
120.03
119.98
77.40
77.08
76.76
49.09
46.86
S
Cl
δ(ppm)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7.74
7.73
7.71
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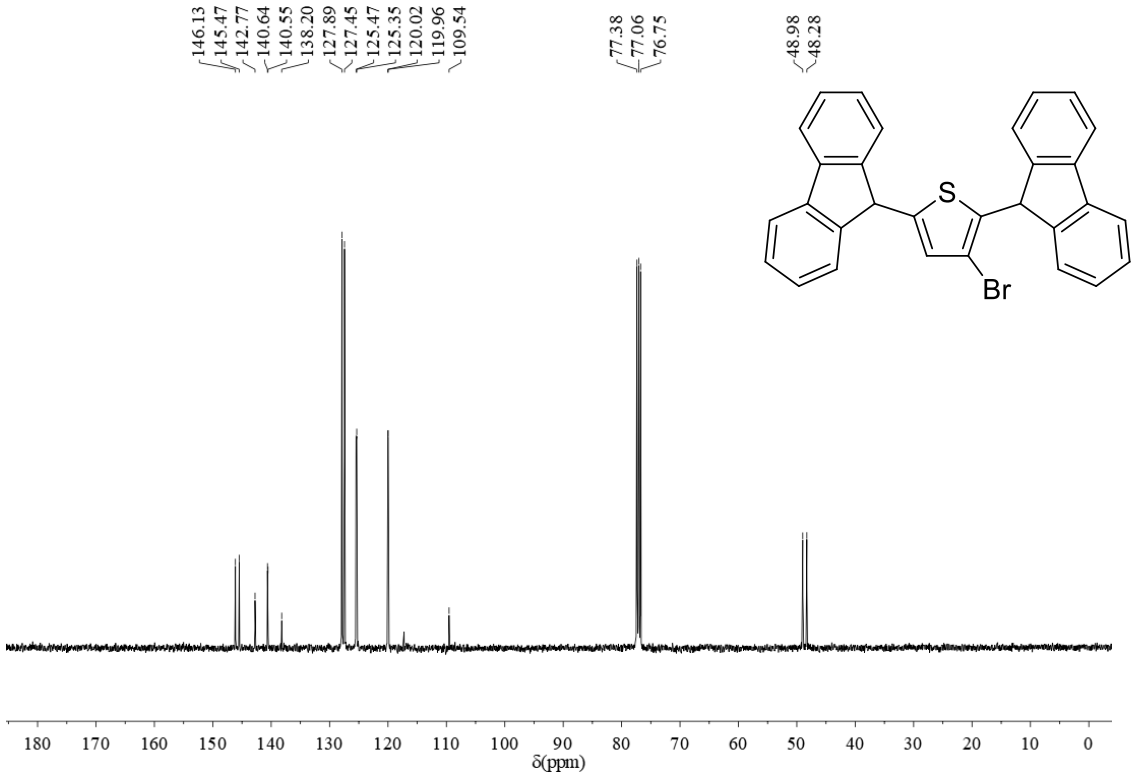
7.48
7.43
7.41
7.39
7.37
7.30
7.28
6.86
5.54
5.13
S
Br
2.04
2.05
2.07
4.03
2.20
4.04
1.00
0.97
0.99
δ (ppm)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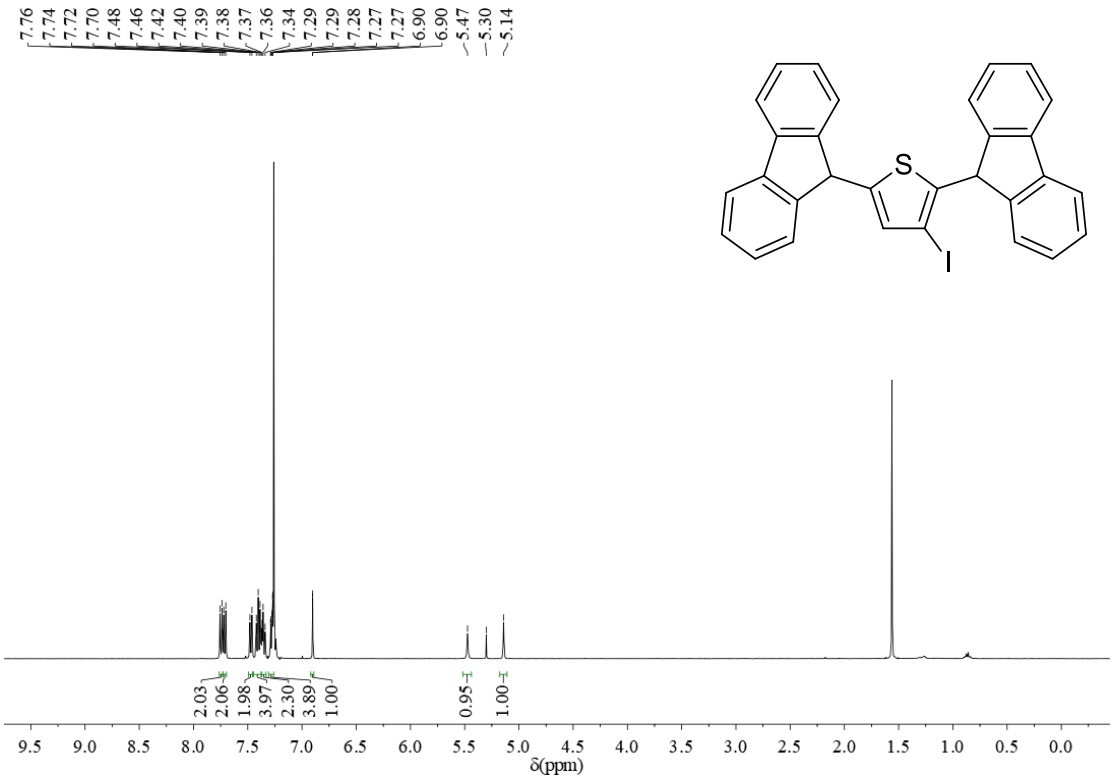
142.77
140.64
140.55
138.20
127.89
127.45
125.47
125.35
120.02
119.96
109.54
77.38
77.06
76.75
48.98
48.28
S
Br
δ(ppm)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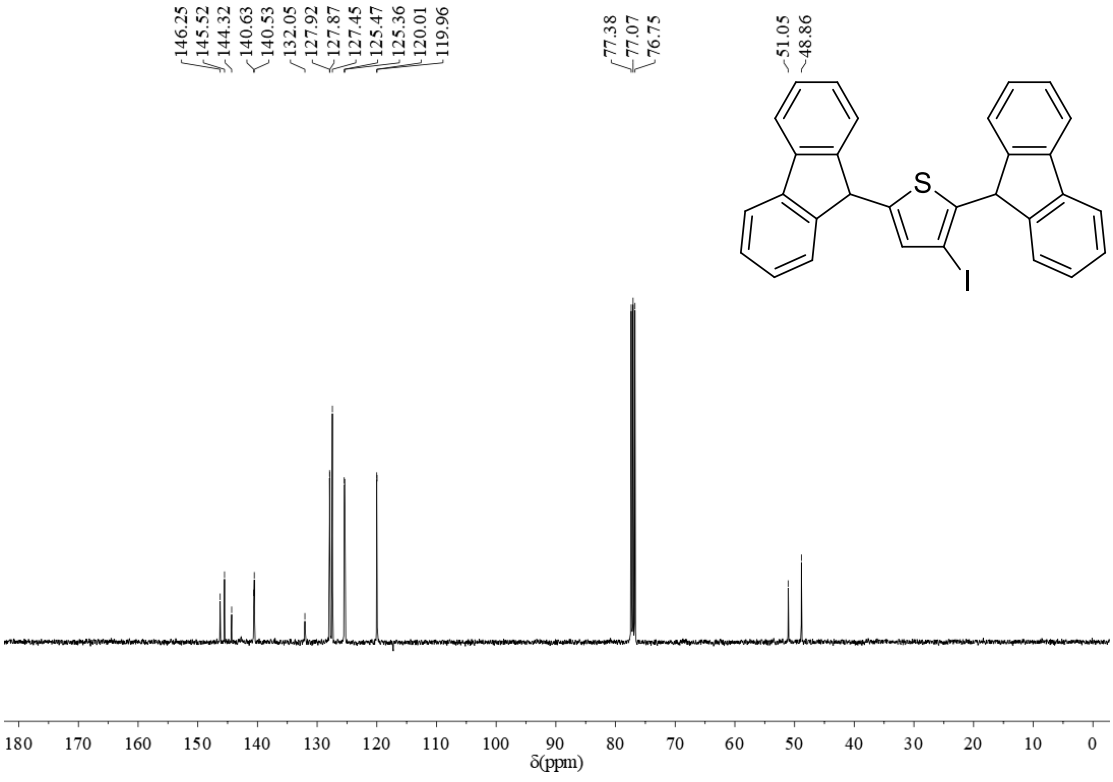
7.74
7.72
7.70
7.48
7.46
7.42
7.40
7.39
7.38
7.37
7.36
7.34
7.29
7.29
7.28
7.27
7.27
6.90
6.90
5.47
5.30
5.14
S
I
2.03
2.06
1.98
3.97
2.30
3.89
1.00
0.95
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ(ppm)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145.52
144.32
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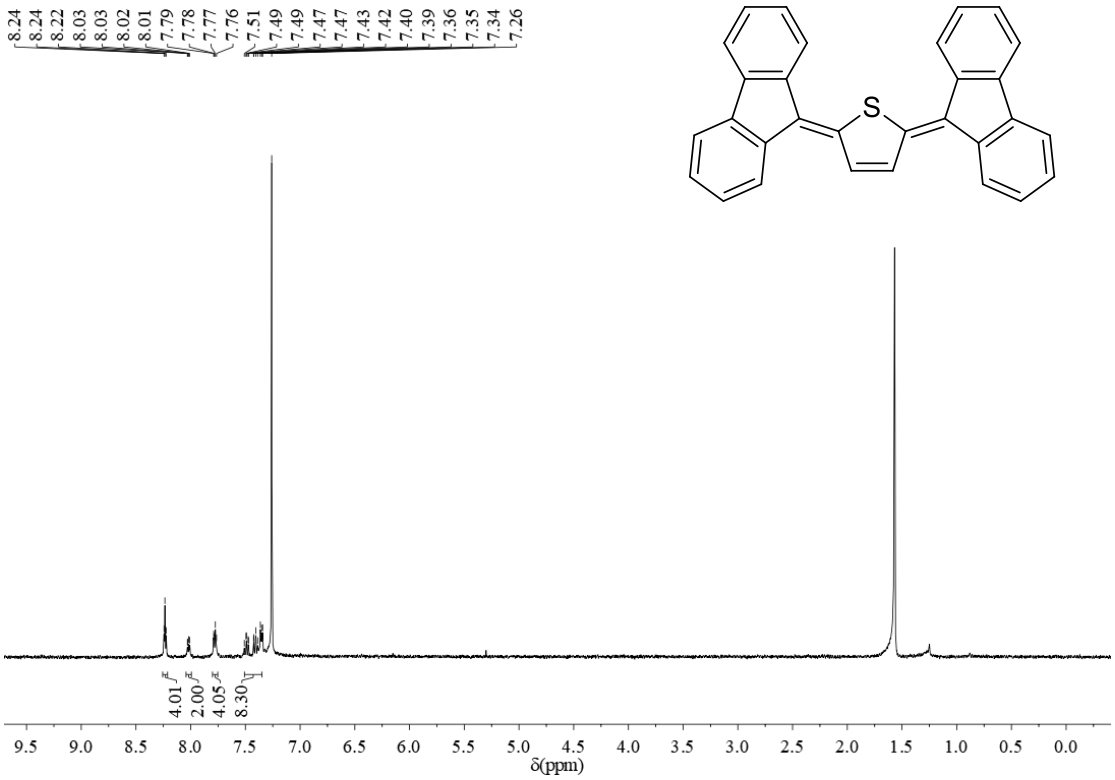
140.53
132.05
127.92
127.87
127.45
125.47
125.36
120.01
119.96
77.38
77.07
76.75
51.05
48.86
S
I
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ(ppm)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8.03
8.02
8.01
7.79
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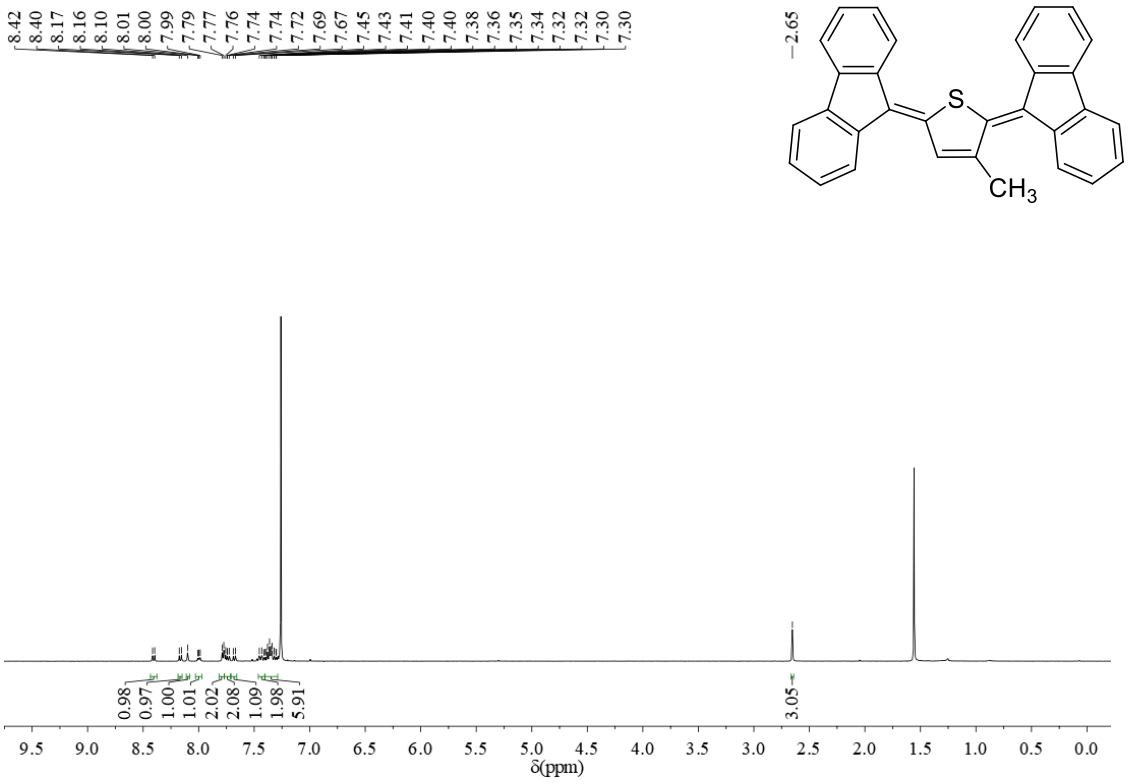
7.77
7.76
7.51
7.49
7.49
7.47
7.47
7.43
7.42
7.40
7.39
7.36
7.35
7.34
7.26
S
4.01
2.00
4.05
8.30
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ(ppm)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7.76
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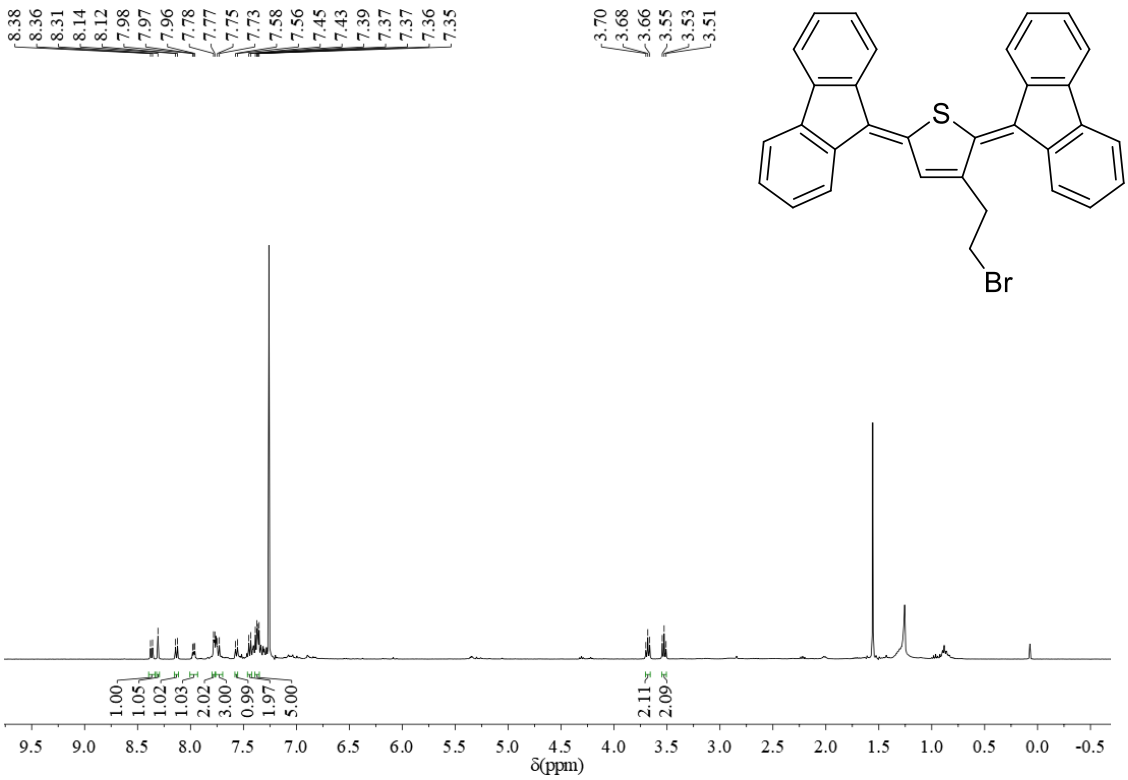
7.67
7.45
7.43
7.41
7.40
7.40
7.38
7.36
7.35
7.34
7.32
7.32
7.30
7.30
2.65
S
CH3
0.98
0.97
1.00
1.01
2.02
2.08
1.09
1.98
5.91
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ(ppm)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8.36
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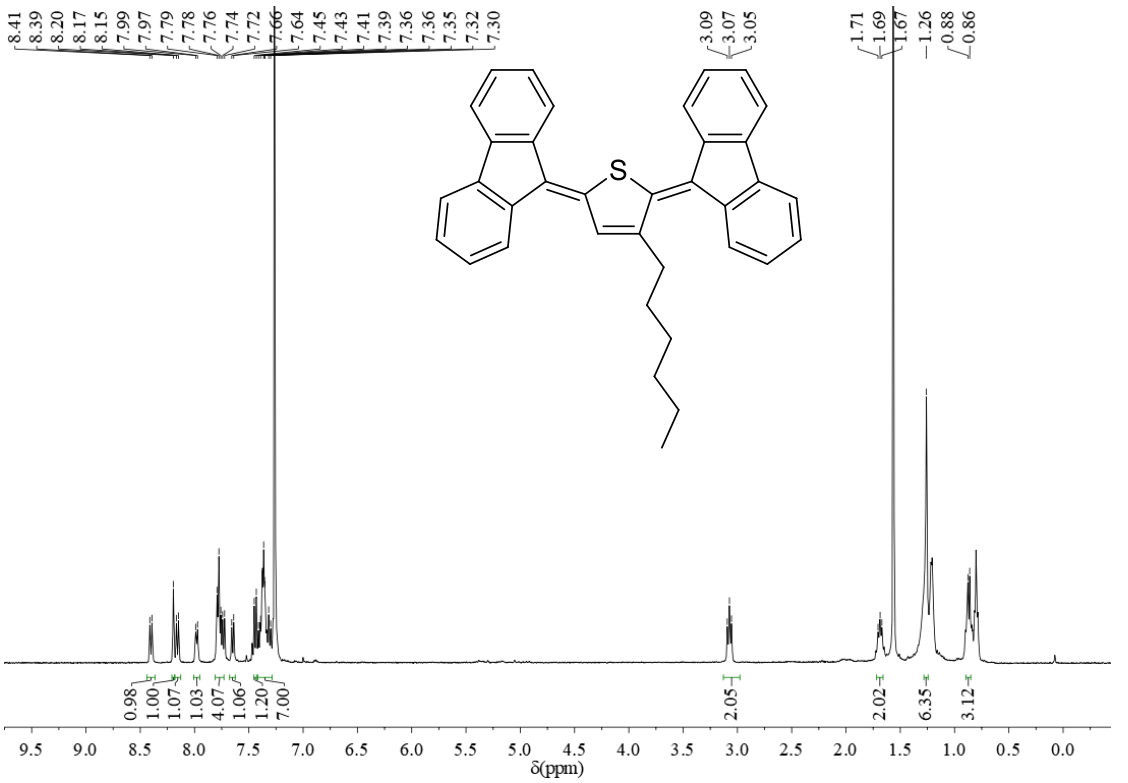
7.97
7.96
7.78
7.77
7.75
7.73
7.58
7.56
7.45
7.43
7.39
7.37
7.37
7.36
7.35
3.70
3.68
3.66
3.55
3.53
3.51
S
Br
1.00
1.05
1.02
1.03
2.02
3.00
0.99
1.97
5.00
2.11
2.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
δ(ppm)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8.17
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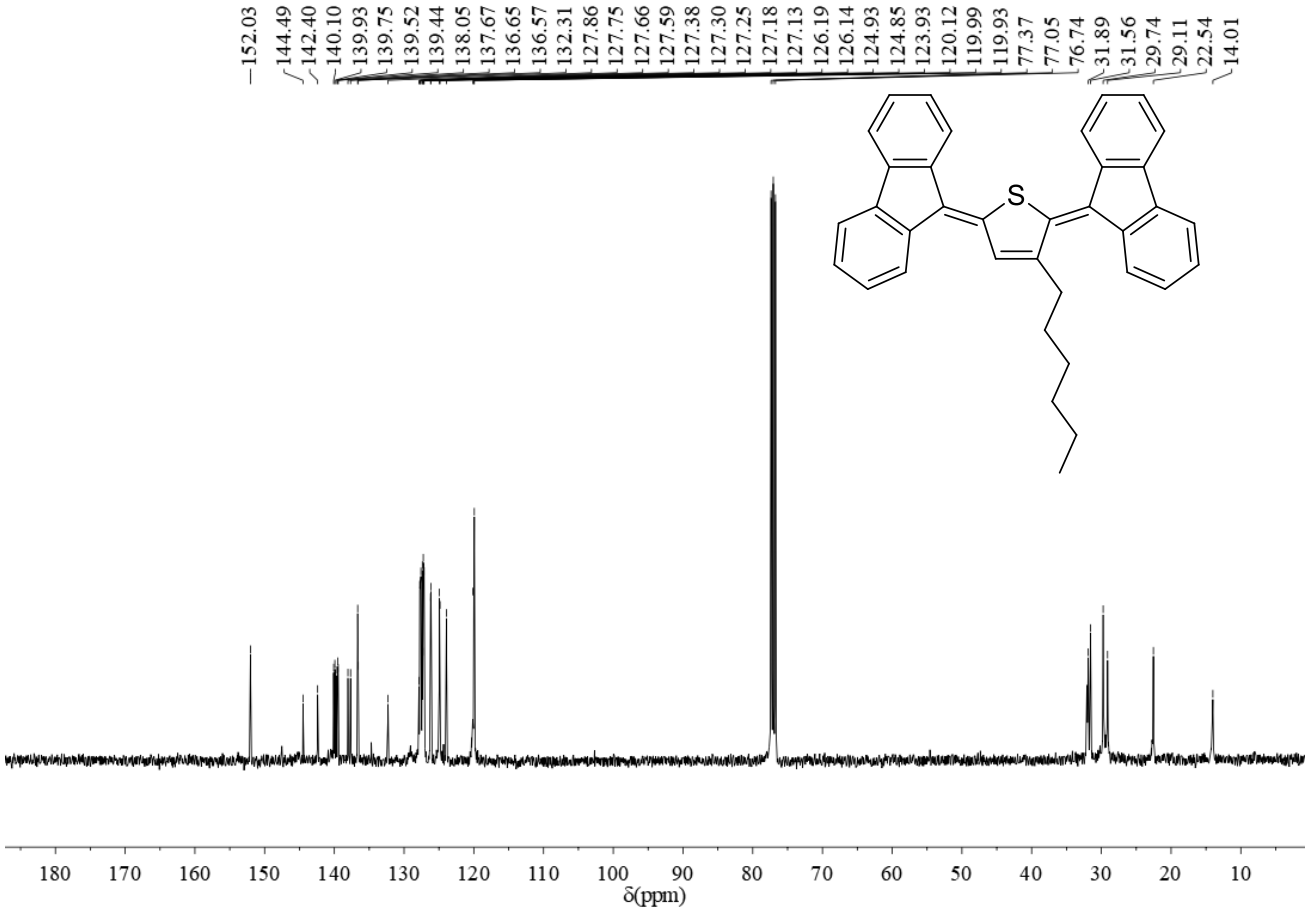
7.99
7.97
7.79
7.78
7.76
7.74
7.72
7.66
7.64
7.45
7.43
7.41
7.39
7.36
7.36
7.35
7.32
7.30
3.09
3.07
3.05
1.71
1.69
1.67
1.26
0.88
0.86
S
0.98
1.00
1.07
1.03
4.07
1.06
1.20
7.00
2.05
2.02
6.35
3.12
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ(ppm)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136.65
136.57
132.31
127.86
127.75
127.66
127.59
127.38
127.30
127.25
127.18
127.13
126.19
126.14
124.93
124.85
123.93
120.12
119.99
119.93
77.37
77.05
76.74
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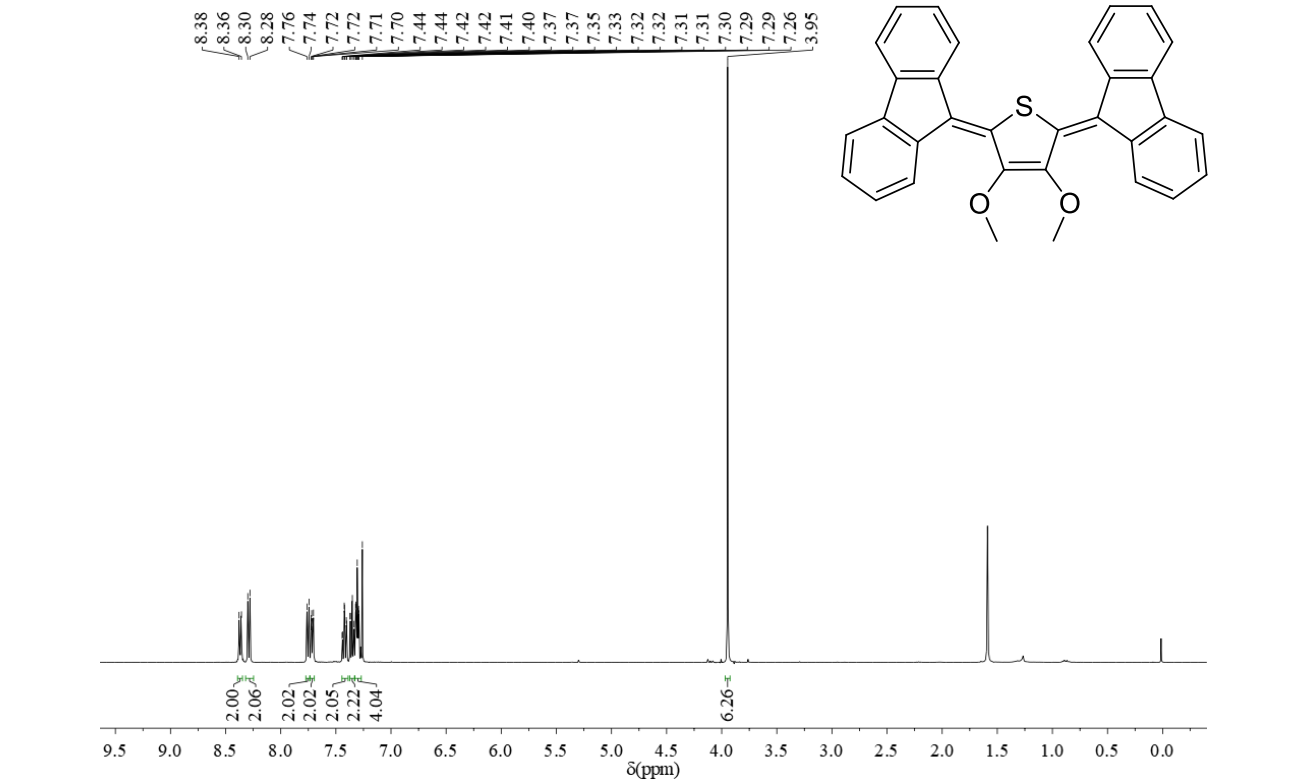
31.56
29.74
29.11
22.54
14.01
S
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
δ(ppm)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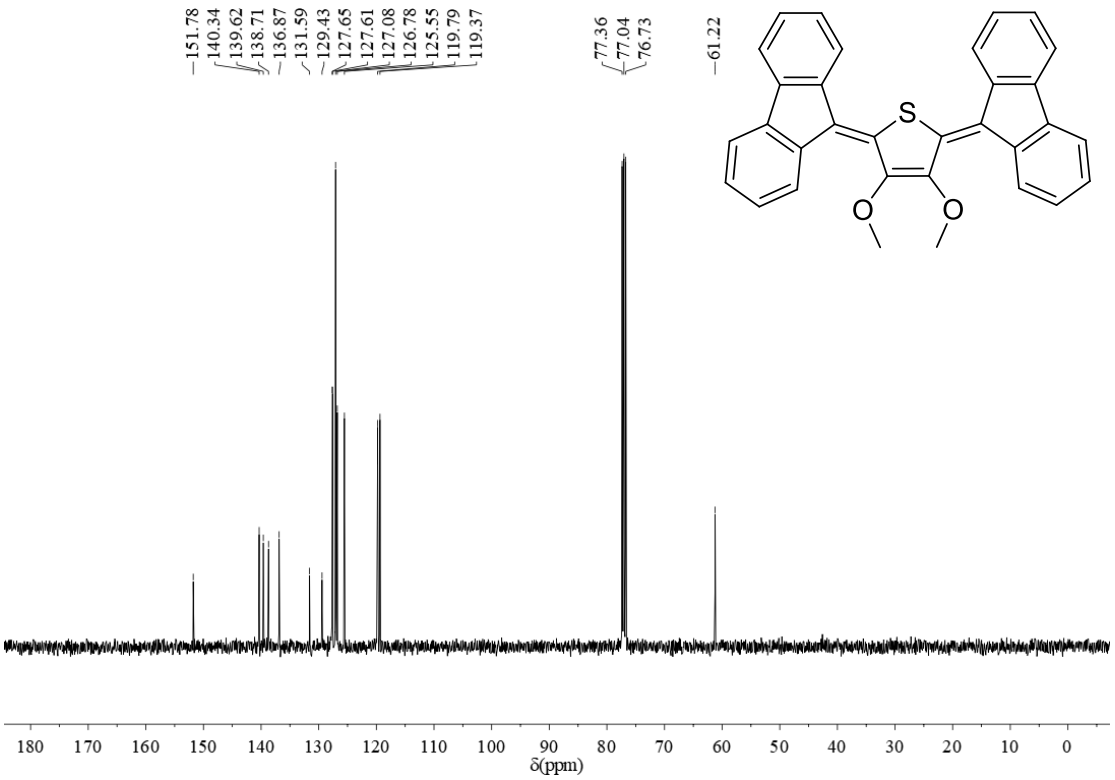
7.71
7.70
7.44
7.44
7.42
7.42
7.41
7.40
7.37
7.37
7.35
7.33
7.32
7.32
7.31
7.31
7.30
7.29
7.29
7.26
3.95
S
O
O
2.00
2.06
2.02
2.02
2.05
2.22
4.04
6.26
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ(ppm)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125.55
119.79
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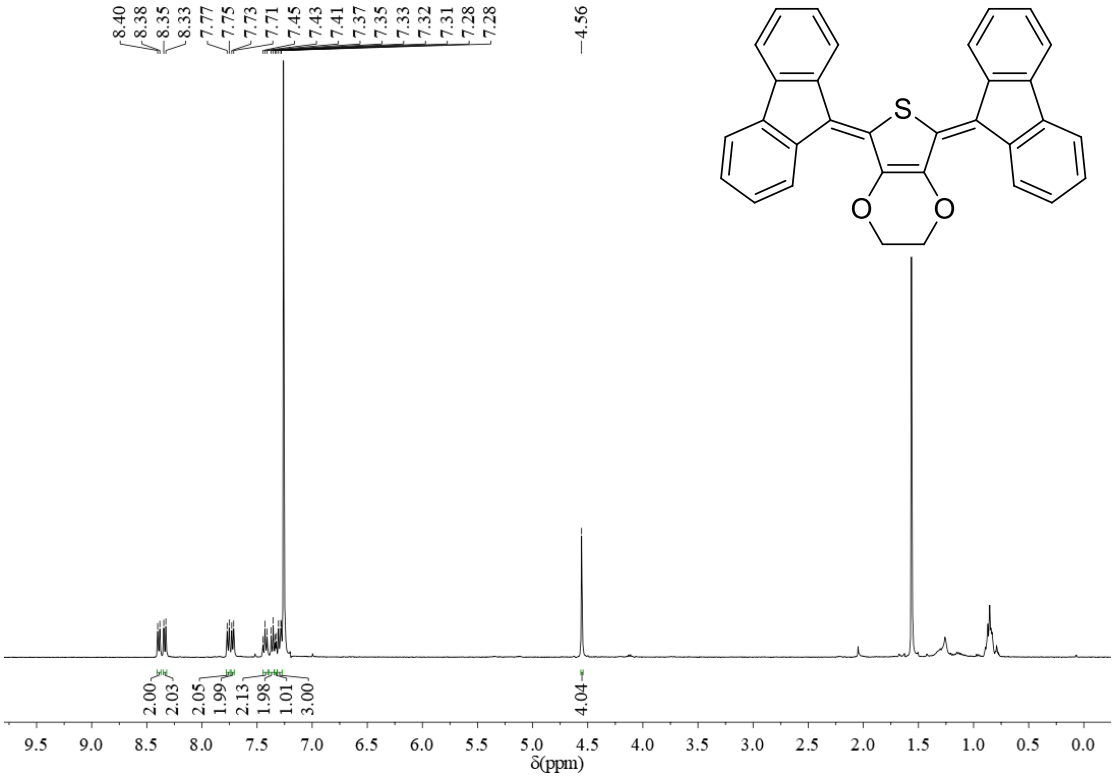
77.36
77.04
76.73
61.22
S
O
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ(ppm)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7.41
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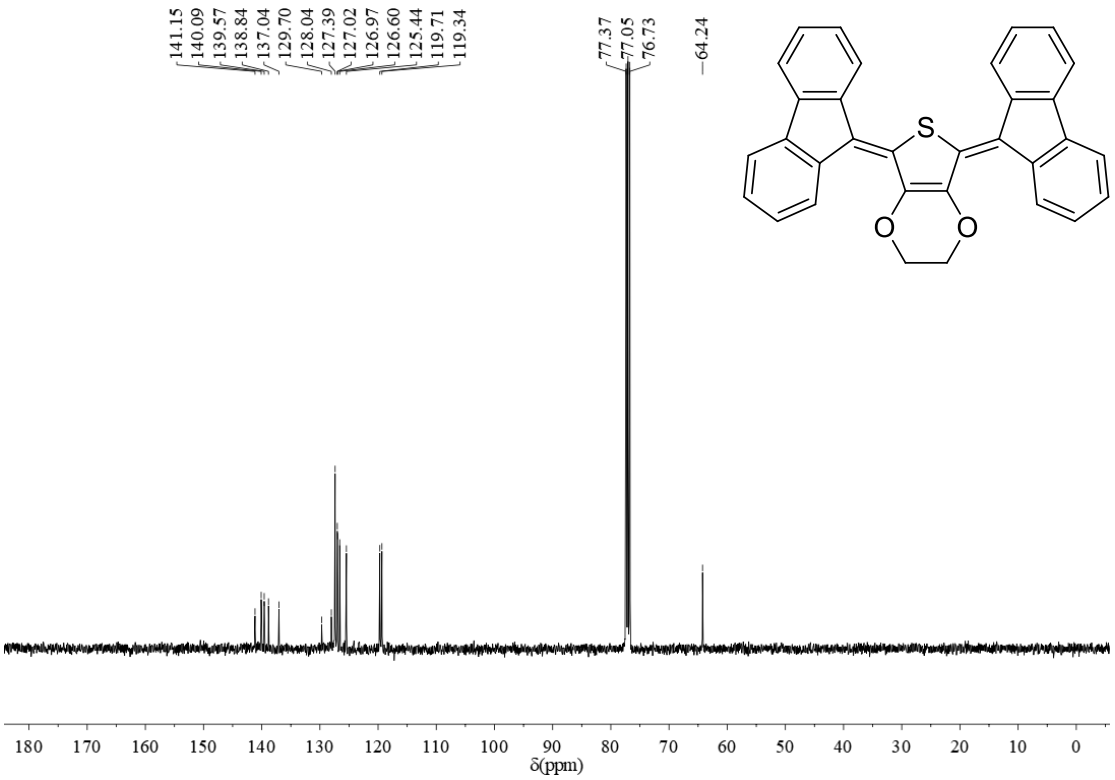
7.35
7.33
7.32
7.31
7.28
7.28
4.56
S
O
O
2.00
2.03
2.05
1.99
2.13
1.98
1.01
3.00
4.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ(ppm)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128.04
127.39
127.02
126.97
126.60
125.44
119.71
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77.37
77.05
76.73
64.24
S
O
O
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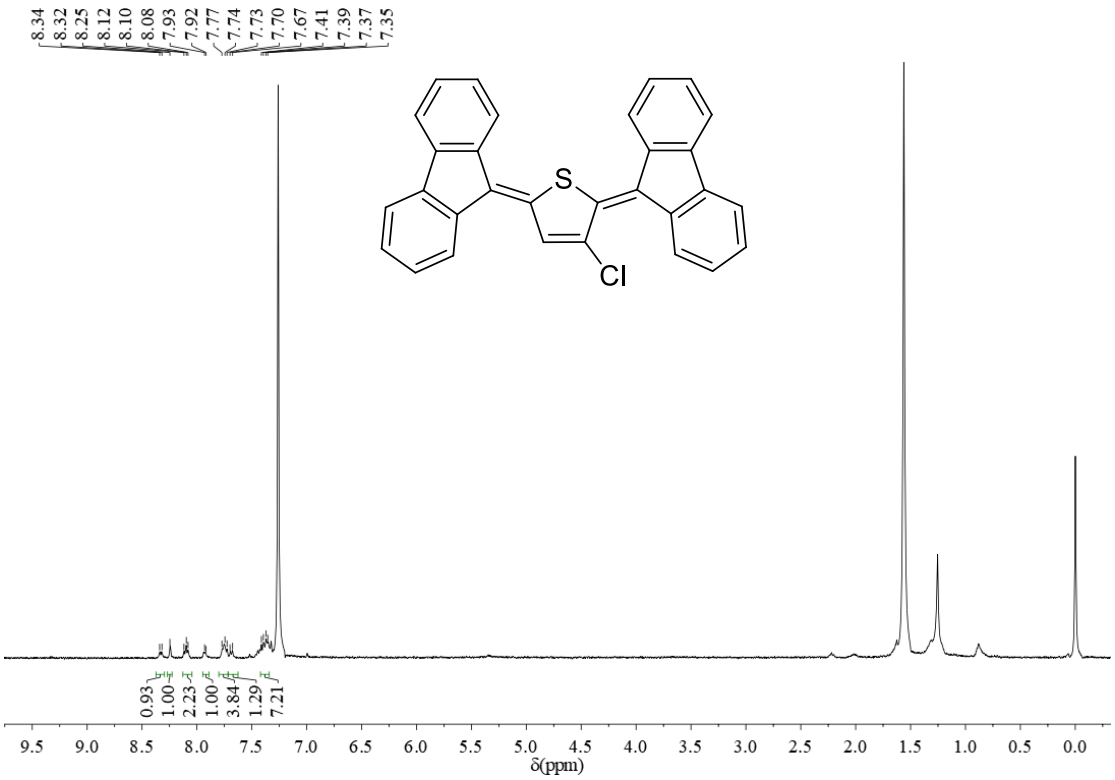
δ(ppm)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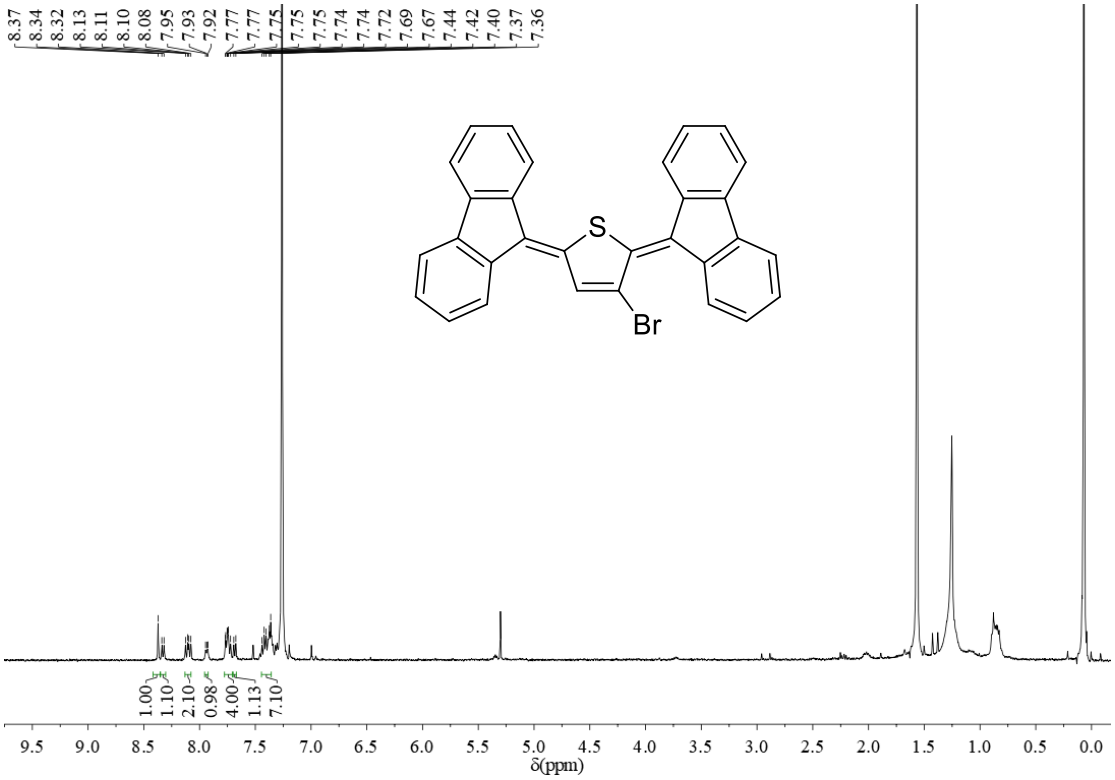
7.92
7.77
7.74
7.73
7.70
7.67
7.41
7.39
7.37
7.35
S
Cl
0.93
1.00
2.23
1.00
3.84
1.29
7.21
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ(ppm)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8.08
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7.92
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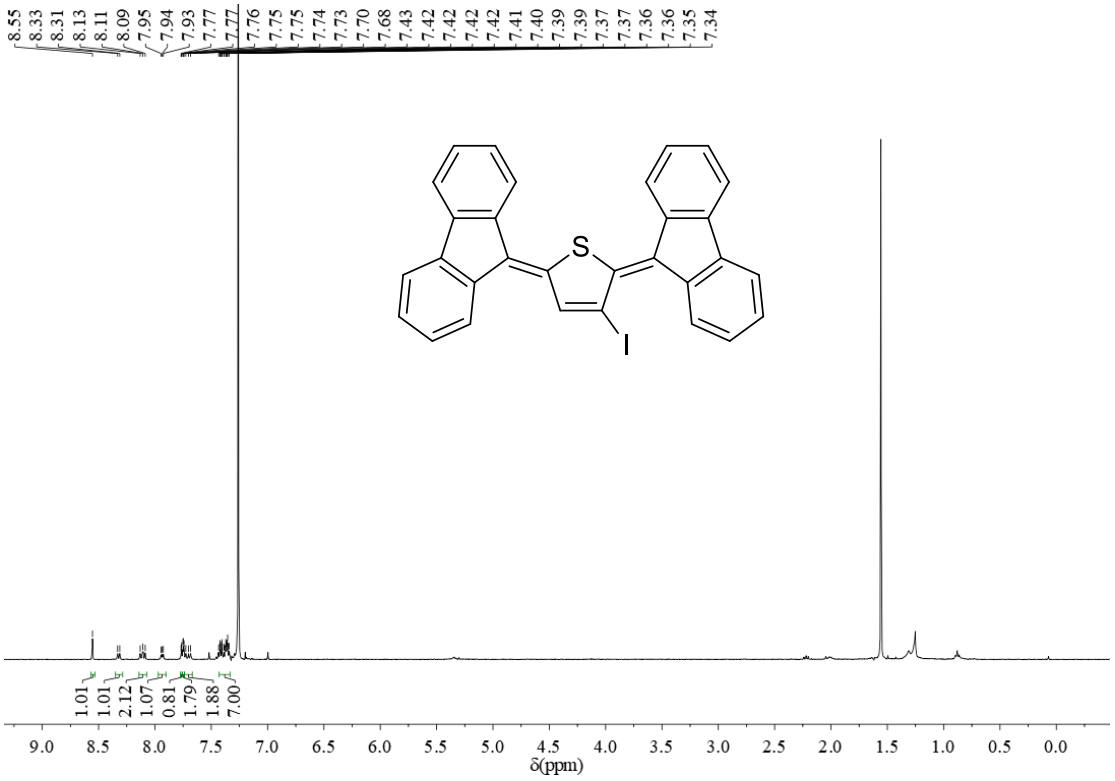
7.75
7.75
7.74
7.74
7.72
7.69
7.67
7.44
7.42
7.40
7.37
7.36
S
Br
1.00
1.10
2.10
0.98
4.00
1.13
7.10
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ(ppm)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7.77
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7.39
7.37
7.37
7.36
7.36
7.35
7.34
S
I
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1.01
2.12
1.07
0.81
1.79
1.88
7.00
9.0 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
δ(ppm)