Supporting Information for

Tetraphenylethylene- and fluorene-functionalized near-infrared aza-BODIPY dyes for living cell imaging

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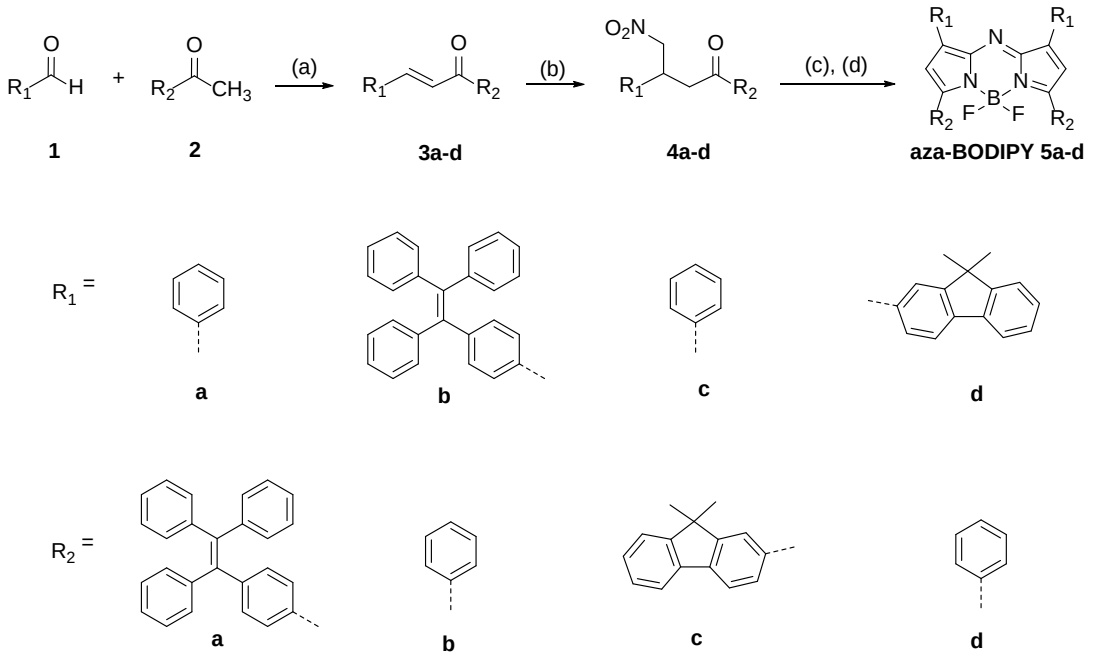


Scheme S1. The synthesis of aza-BODIPYs **5a-d**. (a) KOH, ethanol, H_2O, rt, 24h; (b) CH_3NO_2, ethanol, diethylamine, 80 ^oC reflux, 6-12h; (c) ammonium acetate, 120 ^oC reflux, 12h; (d) $BF_3 \bullet OEt_2$, DIEA, dry CH_2Cl_2, r.t., 12h.

(E)-1-(4-(1,2,2-triphenylvinyl)phenyl)-3-phenylprop-2-en-1-one (3a)

1-(4-(1, 2, 2-triphenylvinyl) phenyl) ethanone (7.0 g, 18.70 mmol) was dissolved in ethanol (80 ml), and 2M KOH (100 ml) was added to the solution through a dropping funnel. Benzaldehyde (2.98 g, 28.5 mmol) in ethanol (20ml) was slowly added dropwise to the reaction system and stirred at room temperature for 24 h. The reaction mixture was filtered and washed with water until neutral, then the resulting solid was recrystallized from ethanol to give pale yellow crystals (8.47 g, 98%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.81 (dd, J = 11.9, 3.6 Hz, 3H), 7.64 (dd, J = 6.4, 2.7 Hz, 2H), 7.51 (d, J = 15.7 Hz, 1H), 7.47 – 7.38 (m, 3H), 7.25 – 6.94 (m, 17H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ = 189.77, 148.88, 144.44, 143.28, 143.22, 143.12, 142.64, 139.98, 135.99, 135.00, 131.64, 131.36, 131.31, 130.50, 128.98, 128.46, 128.04, 127.95, 127.91, 127.76, 126.97, 126.81, 121.98; HRMS (ESI): calculated for $C_{35}H_{26}O$, $[M + Na]^+$ = 485.1876 m/z, found 485.1871 m/z.

(E)-3-(4-(1,2,2-triphenylvinyl)phenyl)-1-phenylprop-2-en-1-one(3b)

Following the above-described procedure of **3a**, using 4-(1,2,2-triphenylvinyl) benzaldehyde (8.0 g, 22.21 mmol) and acetophenone (4.0 g, 33.32mmol) as starting materials, **3b** (10.06 g, 98%) was recrystallized as orange-yellow crystal. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.04 – 7.97 (m, 2H), 7.73 (d, J = 15.7 Hz, 1H), 7.60 (t, J = 7.4 Hz, 1H), 7.50 (dd, J = 14.4, 7.2 Hz, 3H), 7.45 – 7.37 (m, 2H), 7.19 – 7.01 (m, 17H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ = 190.51, 146.54, 144.63, 143.44, 143.31, 132.74, 132.00, 131.41, 131.38, 131.34, 128.64, 128.51, 127.96, 127.92, 127.87, 127.74, 126.86, 126.75, 121.65; HRMS (ESI): calculated for $C_{35}H_{26}O$, $[M + Na]^+$ = 485.1876 m/z, found 485.1873 m/z.

(E)-1-(9,9-dimethyl-9H-fluoren-2-yl)-3-phenylprop-2-en-1-one(3c)

A mixture of 1-(9, 9-dimethyl-9H-fluoren-2-yl) ethanone (4.73g, 20mmol), benzaldehyde (2.55 g, 24mmol,) and NaOH (1.6g, 40mmol) in 100ml MeOH/ $CHCl_3$ (9:1) were heated under reflux for 12h. The resulting solution was neutralized with dilute HCl and extracted with CH_2Cl_2 (50ml×3). The combined organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated to dryness. The crude product was then purified by column chromatography on silica gel (n-hexane: CH_2Cl_2= 4:1) to afford pale yellow solid **3c** (5.45 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.13 (s, 1H), 8.06 (d, J = 7.9 Hz, 1H), 7.85 (dd, J = 15.9, 11.9 Hz, 3H), 7.66 (dd, J = 22.0, 10.5 Hz, 3H), 7.44 (dd, J = 19.8, 14.5 Hz, 6H), 1.56 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ =190.15, 154.88, 154.03, 144.48, 144.04, 137.99, 137.16, 135.10, 130.50, 129.01, 128.64 , 128.50, 128.28, 127.30, 122.90, 122.37, 121.03, 119.89, 47.1 , 27.04 ; HRMS (ESI): calculated for $C_{24}H_{20}O$, $[M + Na]^+$ = 347.1406 m/z, found 347.1401 m/z.

(E)-3-(9,9-dimethyl-9H-fluoren-2-yl)-1-phenylprop-2-en-1-one(3d)

Following the above-described procedure of **3a**, using 9, 9-Dimethyl-9H-fluorene-2-carbaldehyde (3.95 g, 17.77 mmol) and acetophenone (2.56 g, 21.32mmol) as starting materials, **3d** (5.19 g, 98%) was recrystallized as orange-yellow crystal. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.06 (d, J = 7.1 Hz, 2H), 7.91 (d, J = 15.7 Hz, 1H), 7.73 (d, J = 14.6 Hz, 3H), 7.59 (t, J = 24.9 Hz, 5H), 7.45 (s, 1H), 7.36 (d, J = 8.7 Hz, 2H), 1.53 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ = 190.67, 154.32, 145.48, 142.07, 138.47, 138.32, 133.95, 132.72, 128.66, 128.56, 128.31, 128.18, 127.26, 122.79, 122.47, 121.30, 120.58, 120.49, 46.93, 27.13; HRMS (ESI): calculated for $C_{24}H_{20}O$, $[M + Na]^+$ = 347.1406 m/z, found 347.1406 m/z.

1-(4-(1,2,2-triphenylvinyl)phenyl)-4-nitro-3-phenylbutan-1-one(4a)

3a (6.0 g, 12.98 mmol), nitromethane (11.88 g, 194.7 mmol) and diethylamine (14.24 g, 194.7 mmol) were dissolved in 100 ml ethanol then refluxed for 12 h and monitored by TLC. After the reaction was completed, the reaction system was cooled to room temperature and the solvent was removed by rotary evaporation. The product was dissolved in ethyl acetate (50ml), then washed with water (50ml×3). The resulting organic layer was washed with brine and dried over anhydrous magnesium sulfate. After removing the solvents by evaporation, the resulting crude mixture was separated by column chromatography (petroleum ether: CH_2Cl_2 = 2: 1) to afford a yellow oily liquid **4a** (4.89g, 72%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ = 7.64 (d, J = 8.4 Hz, 2H), 7.36 – 7.21 (m, 5H), 7.11 (s, 11H), 7.00 (d, J = 9.5 Hz, 6H), 4.81 (dd, J = 12.5, 6.6 Hz, 1H), 4.66 (dd, J = 12.5, 8.1 Hz, 1H), 4.25 – 4.08 (m, 1H), 3.36 (t, J = 6.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ = 196.36, 149.63, 143.12, 143.07, 142.96, 142.86, 139.70, 139.25, 134.09, 131.68, 131.30, 131.26, 129.07, 127.96, 127.94, 127.86, 127.77, 127.51, 127.04, 126.89, 129.86, 79.45, 41.52, 39.27 ; HRMS (ESI): calculated for $C_{36}H_{29}NO$, $[M + Na]^+$ = 546.2040 m/z, found 546.2039 m/z.

3-(4-(1,2,2-triphenylvinyl)phenyl)-4-nitro-1-phenyl-butan-1-one(4b)

Following the above-described procedure of **4a,** using **3b** (8.0 g, 17.31mol) as starting material. **4b** (5.71 g, 63%) was isolated as yellow oily liquid (CH_2Cl_2: petroleum ether= 1: 2). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.90 (d, J = 7.7 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.7 Hz, 2H), 7.09 (s, 8H), 6.97 (d, J = 12.7 Hz, 11H), 4.77 (dd, J = 12.3, 6.6 Hz, 1H), 4.64 – 4.56 (m, 1H), 4.18 – 4.07 (m, 1H), 3.46 – 3.31 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ = 197.01, 143.56, 143.42, 143.41, 143.38, 141.46, 140.20, 137.12, 136.53, 133.56, 131.92, 131.33, 131.31, 128.77, 128.06, 127.73, 127.68, 126.80, 126.57, 126.53, 79.64, 41.38, 39.06; HRMS (ESI): calculated for $C_{36}H_{29}NO$, $[M + Na]^+$ = 546.2040 m/z, found 546.2043 m/z.

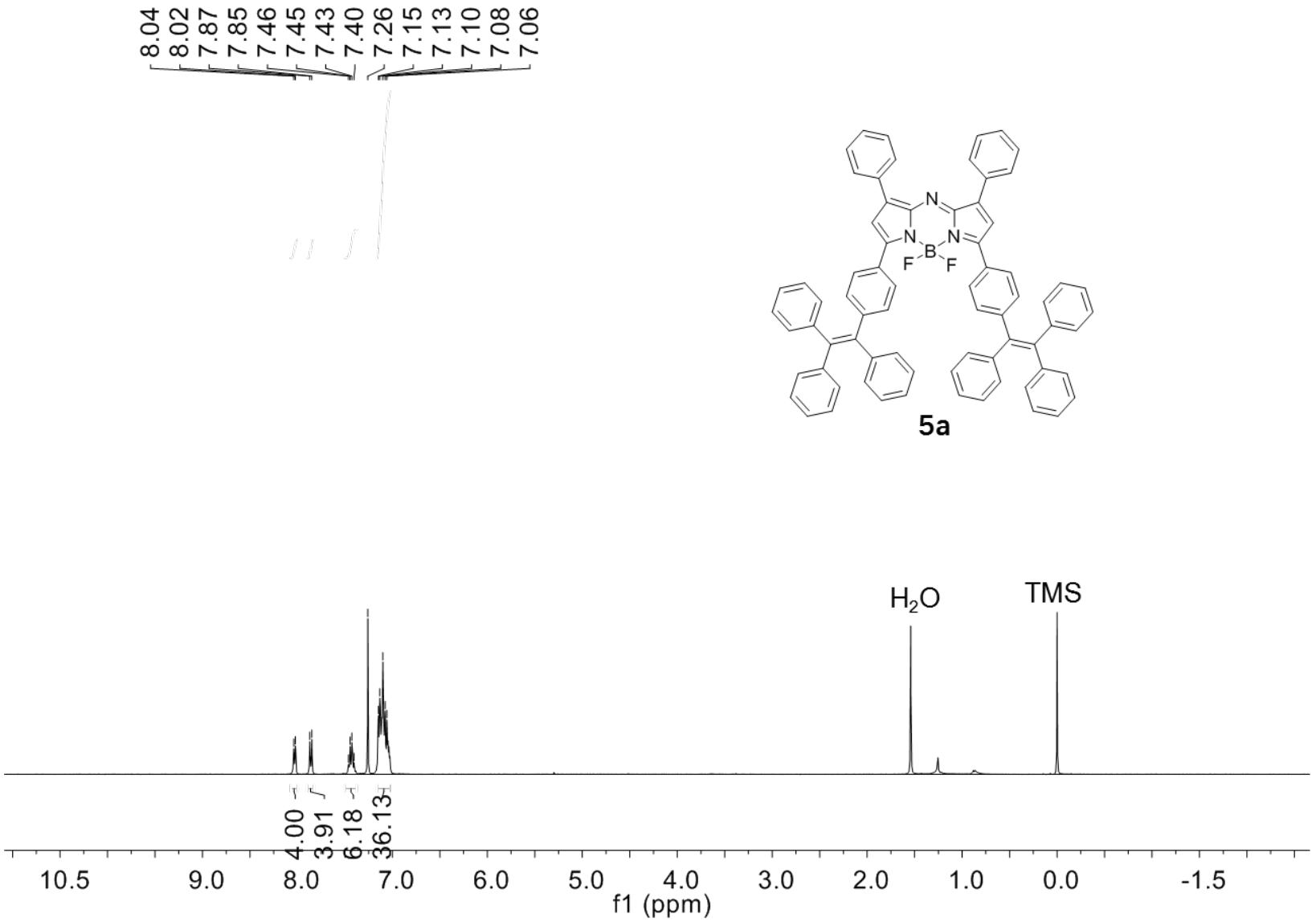
1-(9,9-dimethyl-9H-fluoren-2-yl)-4-nitro-3-phenylbutan-1-one(4c)

Following the above-described procedure of **4a,** using **3c** (4.16g, 12.82mol) as starting materials. **4c** (3.36 g, 68%) was isolated as yellow oily liquid (CH_2Cl_2: petroleum ether= 1: 2). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.99 (s, 1H), 7.95 – 7.90 (m, 1H), 7.76 (d, J = 7.8 Hz, 2H), 7.47 (d, J = 6.2 Hz, 1H), 7.34 (ddd, J = 23.7, 13.6, 8.6 Hz, 7H), 4.87 (dt, J = 31.2, 15.6 Hz, 1H), 4.78 – 4.65 (m, 1H), 4.33 – 4.22 (m, 1H), 3.60 – 3.42 (m, 2H), 1.50 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ = 196.60, 169.90, 154.88, 154.02, 144.67, 139.34, 137.71, 135.26, 129.11, 128.85, 127.89,

127.83, 127.56, 127.35, 122.91, 122.30, 121.12, 119.96, 79.62, 47.09, 41.75, 39.50, 26.95; HRMS (ESI): calculated for $C_{36}H_{29}NO$, $[M + Na]^+$ = 408.1570 m/z, found 408.1572 m/z.

3-(9,9-dimethyl-9H-fluoren-2-yl)-4-nitro-1-phenylbutan-1-one(4d)

Following the above-described procedure of **4a**, using **3d** (3.24g, 10.00mol) as starting materials. **4d** (1.4 g, 36%) was isolated as colourless oily liquid (CH_2Cl_2: petroleum ether= 1: 2). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.97 (d, J = 7.9 Hz, 2H), 7.71 (d, J = 7.7 Hz, 2H), 7.59 (t, J = 7.1 Hz, 1H), 7.48 (t, J = 7.6 Hz, 3H), 7.41 – 7.25 (m, 4H), 4.94 (dd, J = 12.3, 6.6 Hz, 1H), 4.85 – 4.75 (m, 1H), 4.42 – 4.32 (m, 1H), 3.55 (s, 2H), 1.51 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ = 197.17, 154.45, 153.70, 139.06, 138.57, 138.19, 136.53, 133.57, 128.77, 128.09, 127.47, 127.0, 126.11, 122.64, 121.92, 120.53, 120.09, 79.46, 46.91, 41.85, 39.74, 27.14, 27.10; HRMS (ESI): calculated for $C_{36}H_{29}NO$, $[M + Na]^+$ = 408.1570 m/z, found 408.1572 m/z.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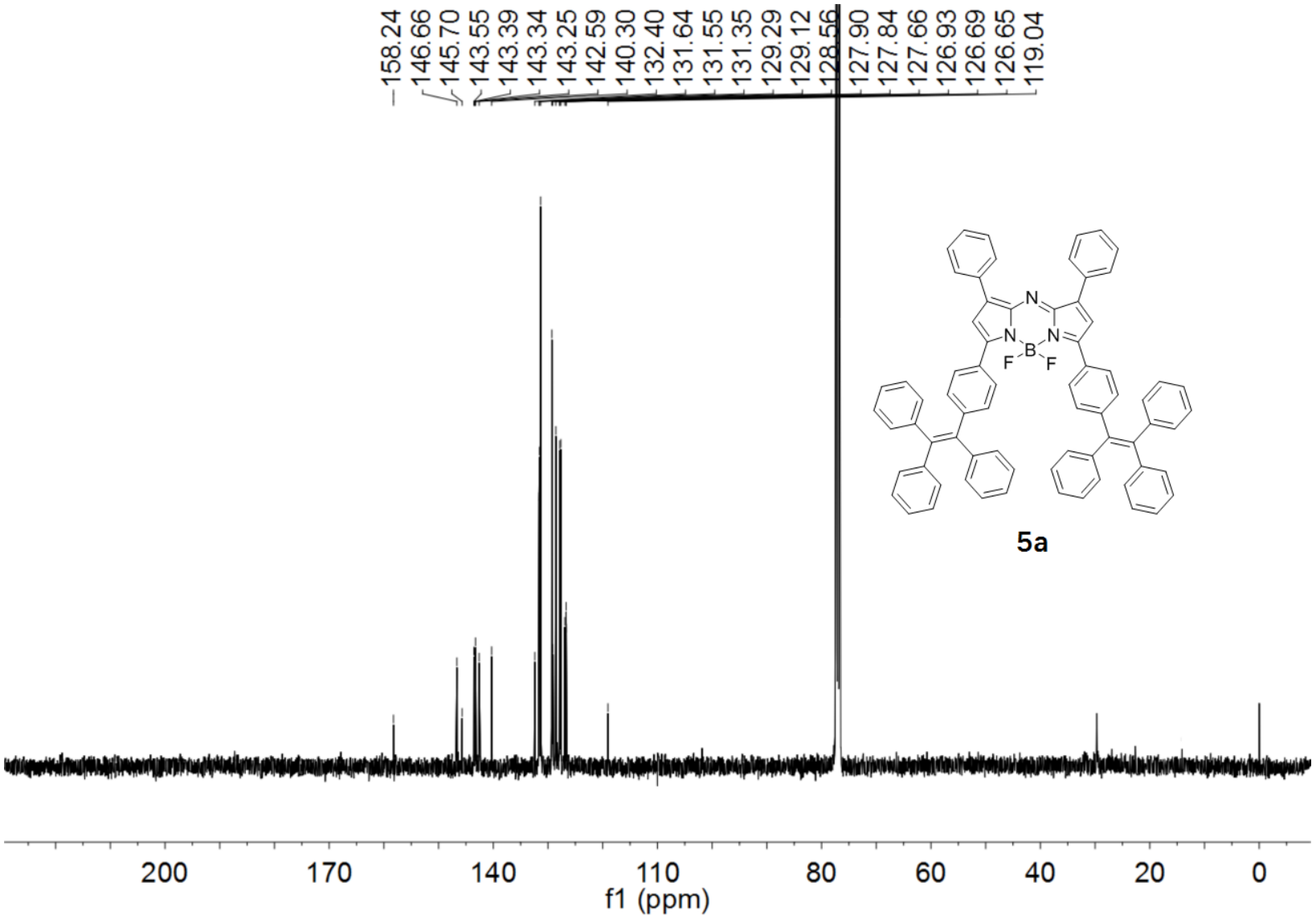
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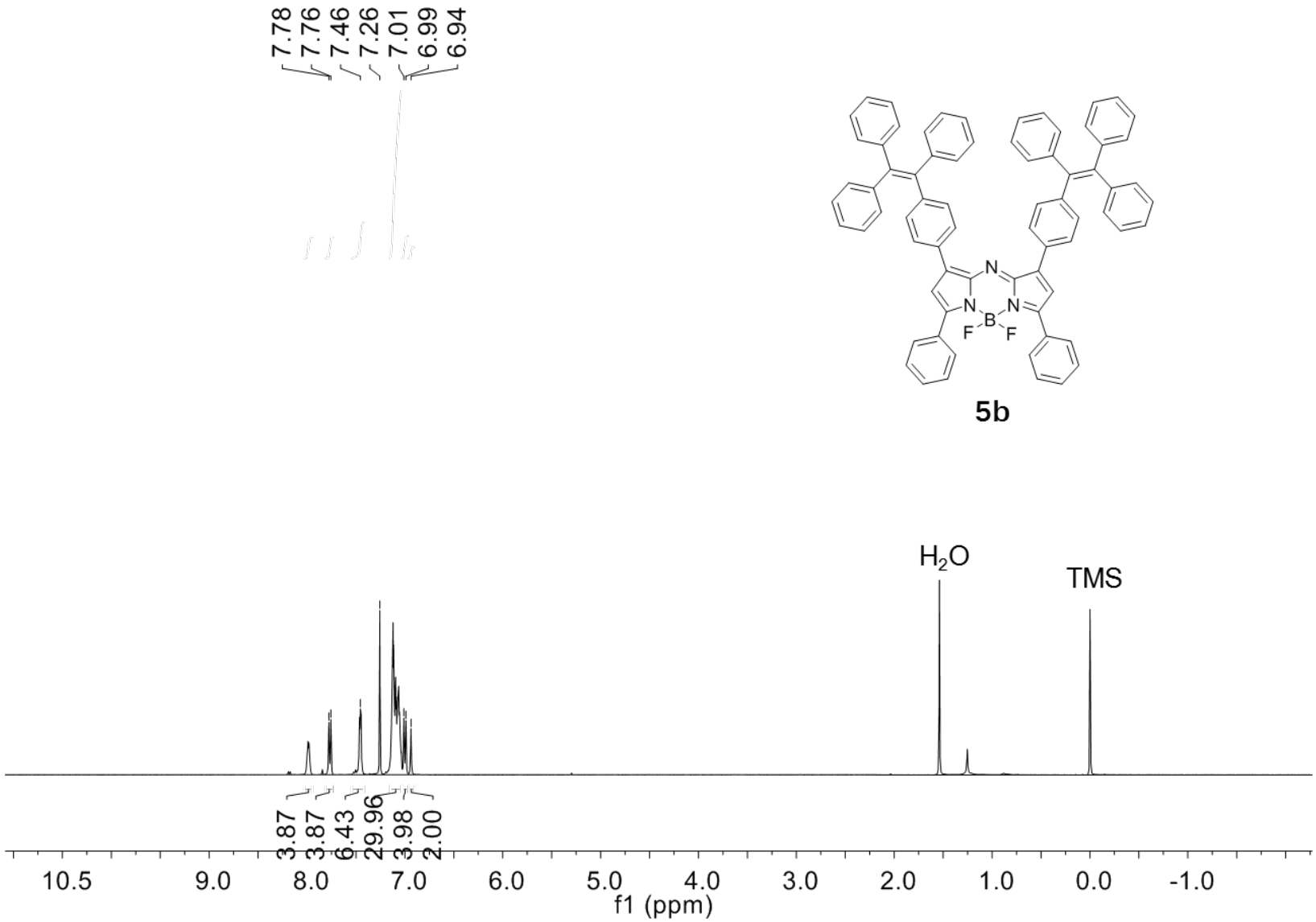
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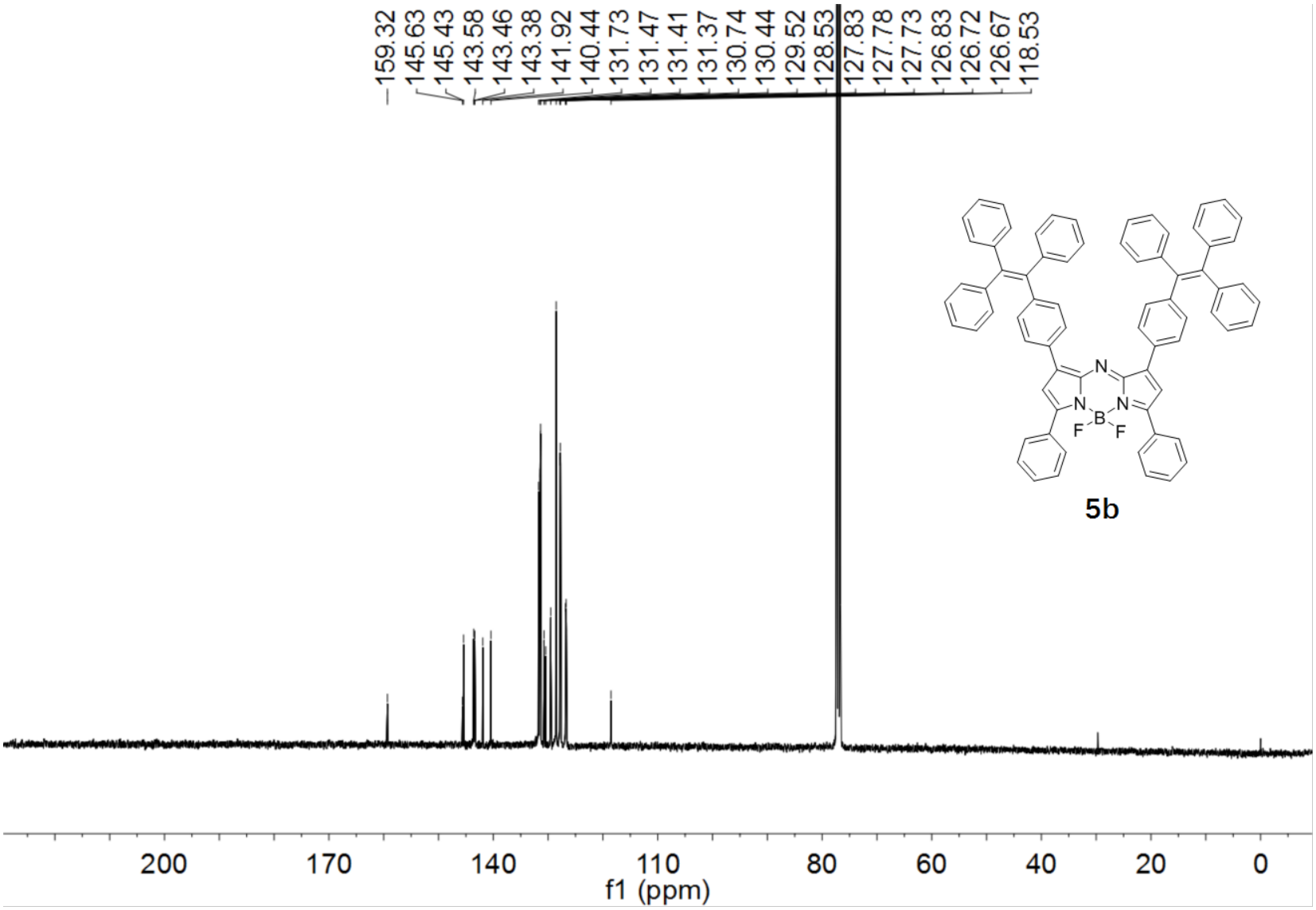
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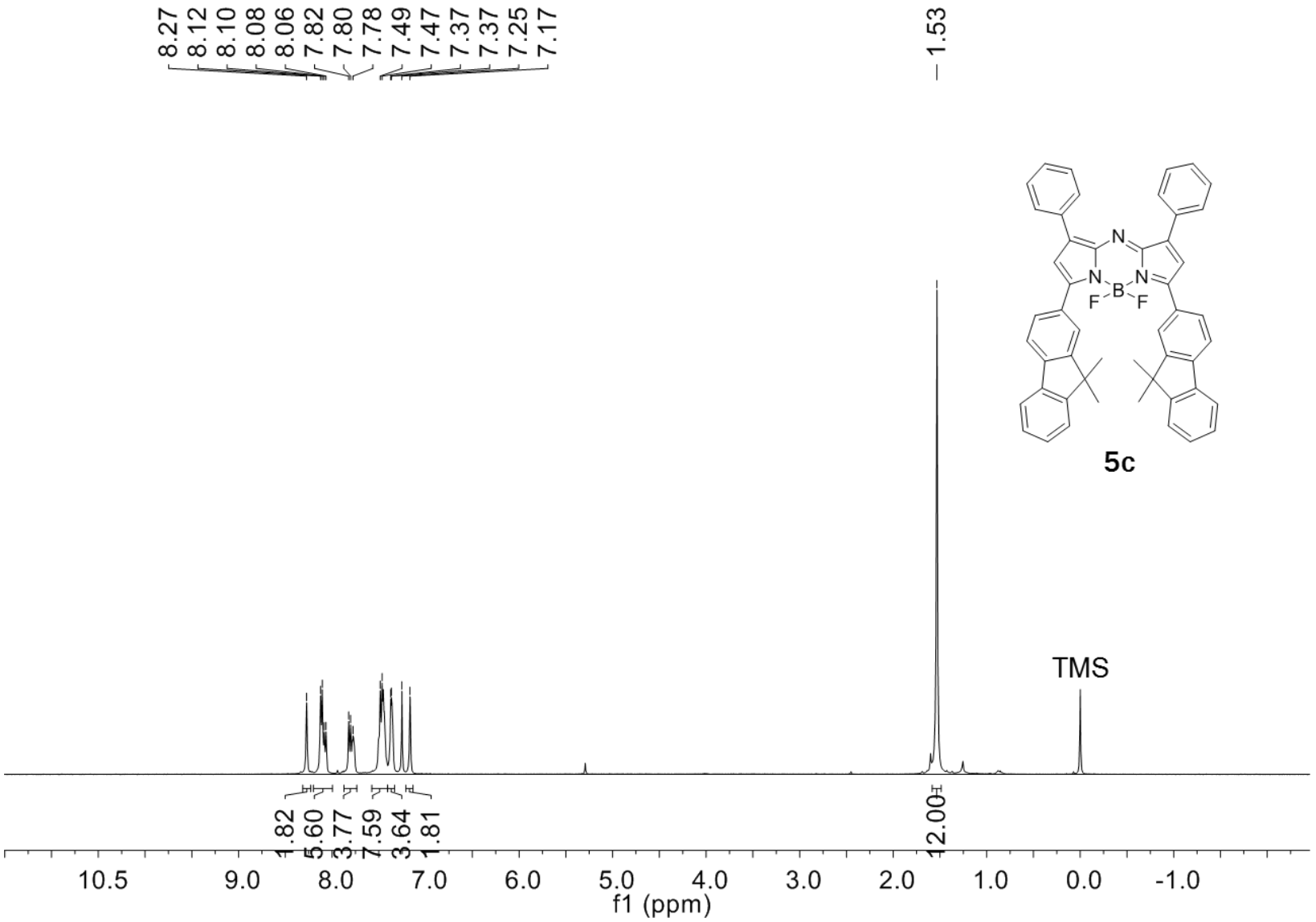
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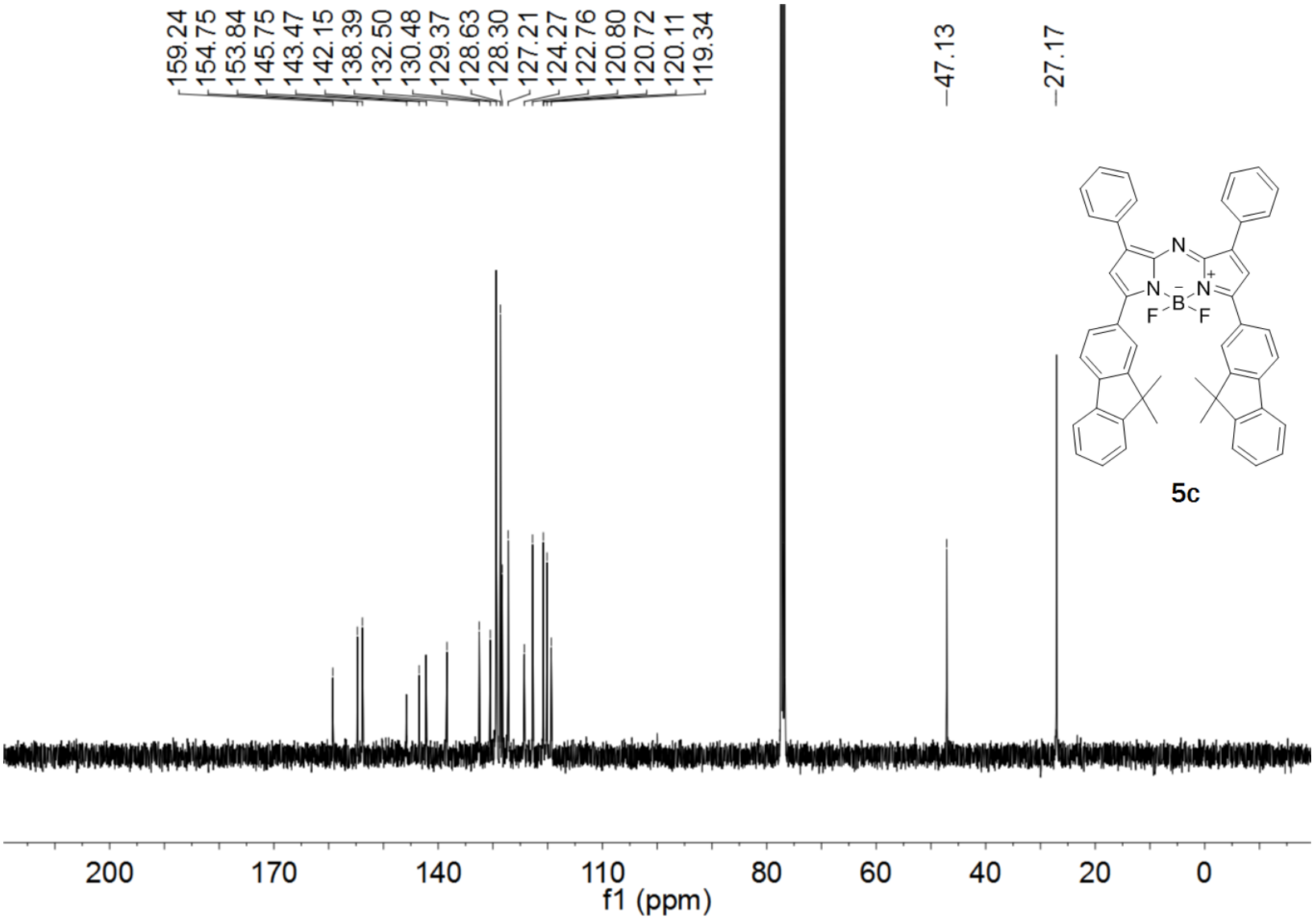
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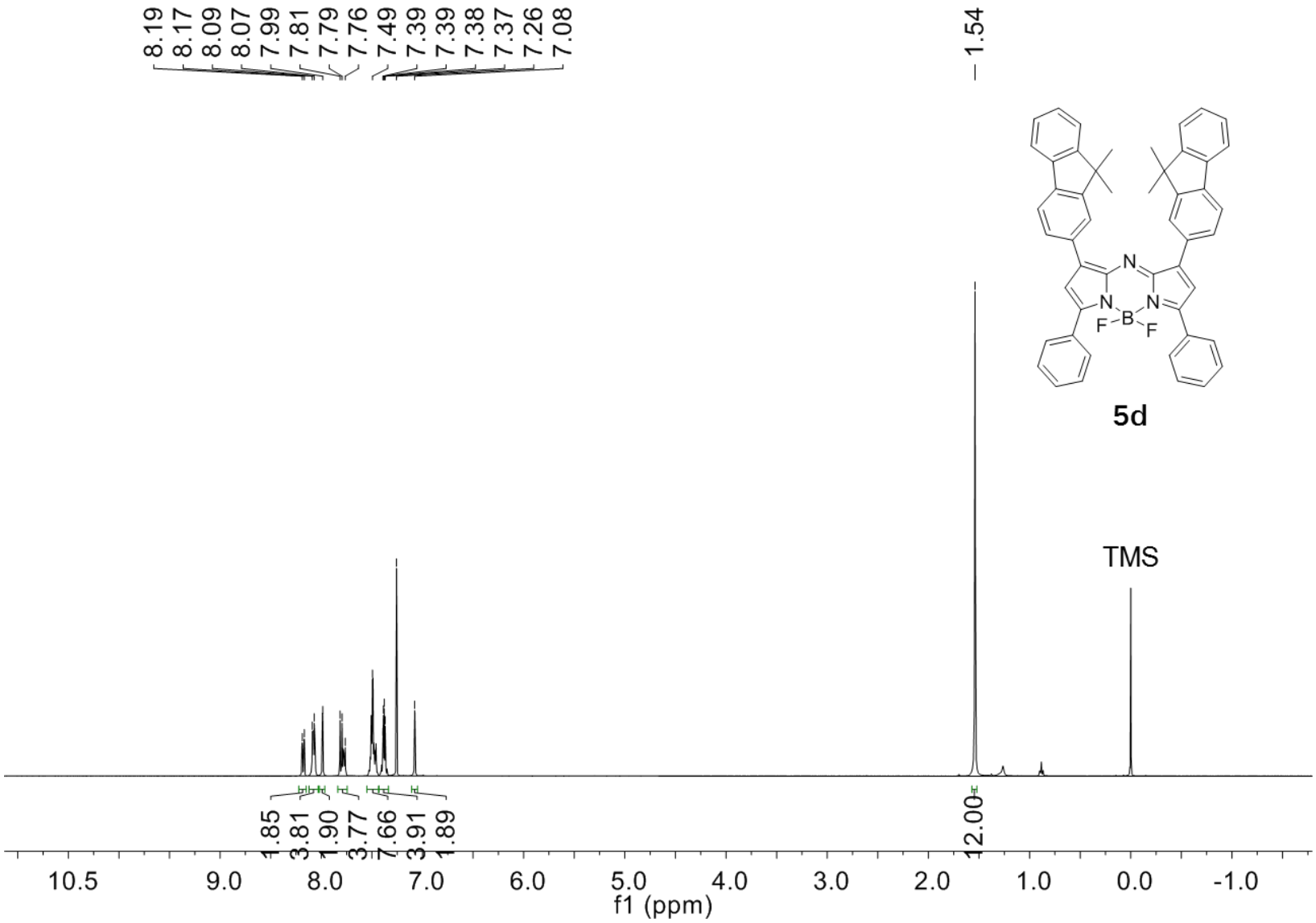
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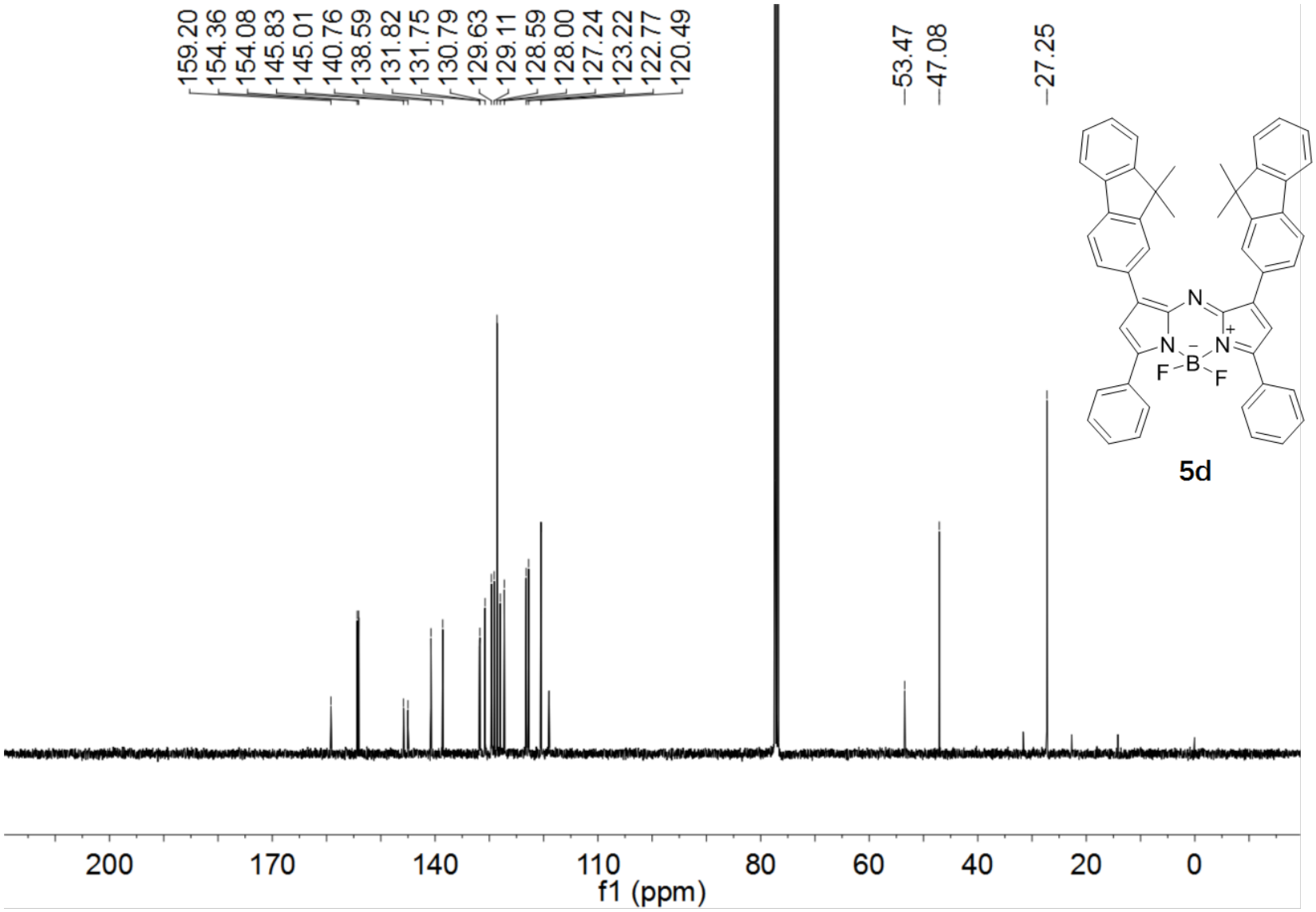
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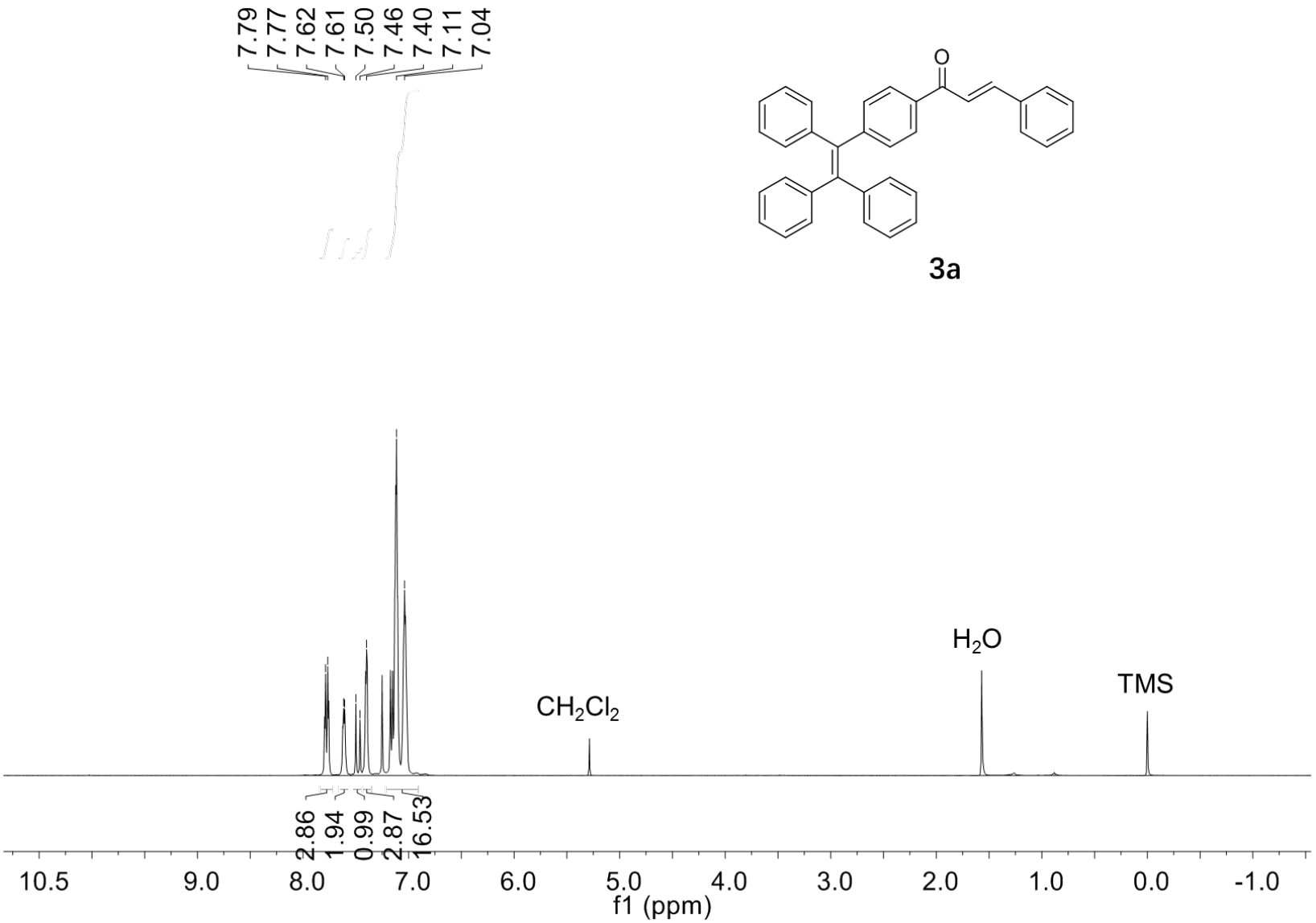
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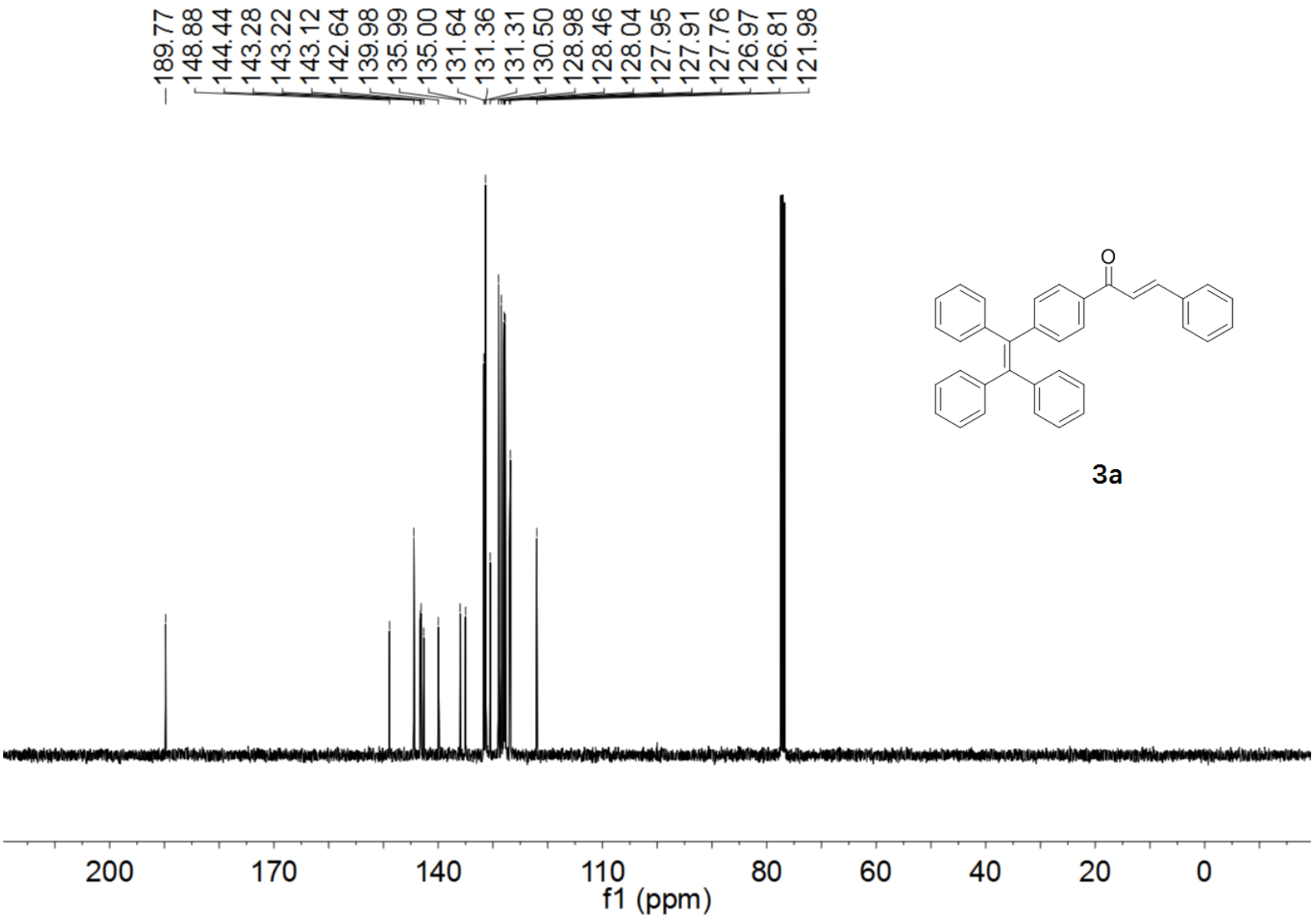
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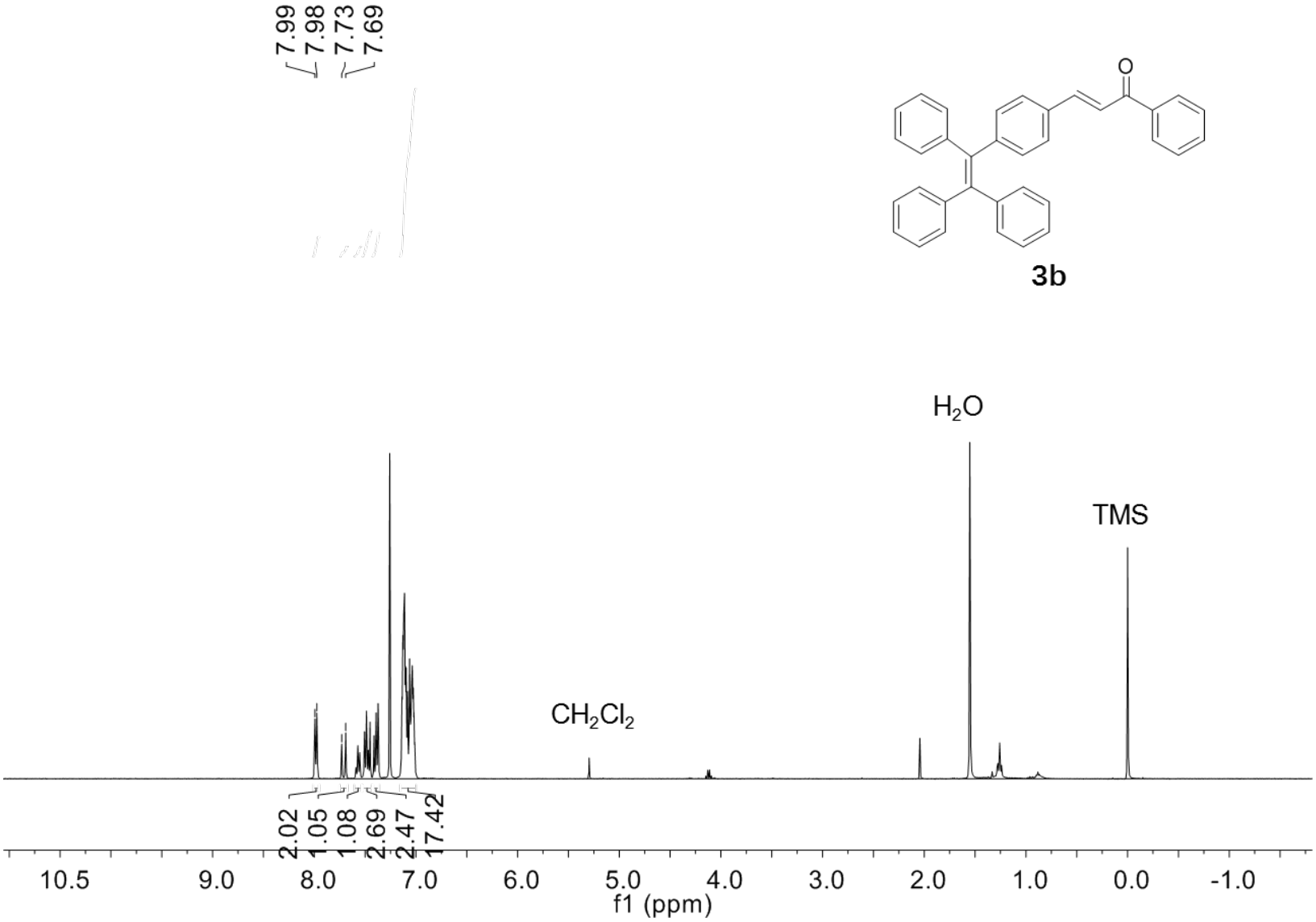
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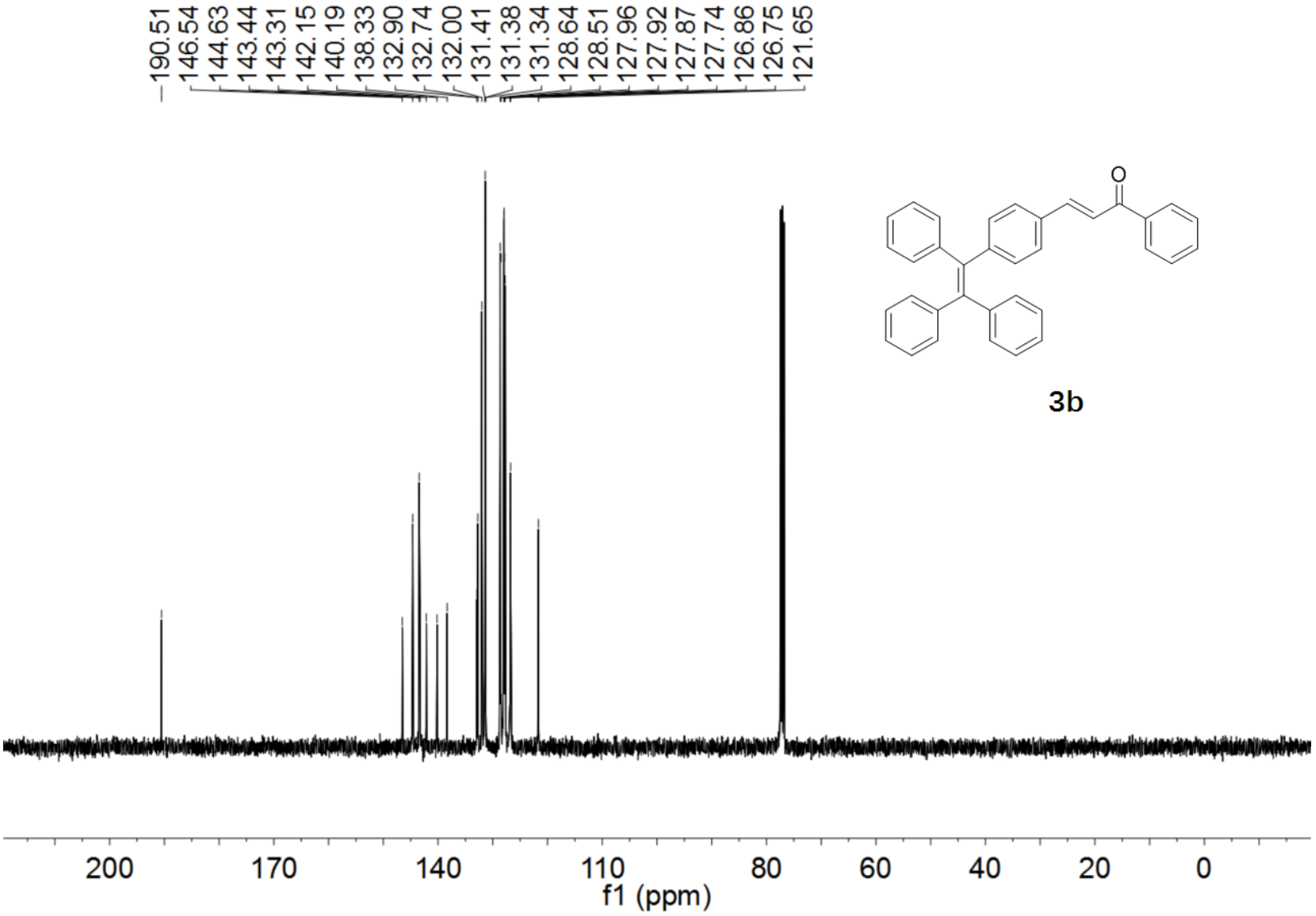
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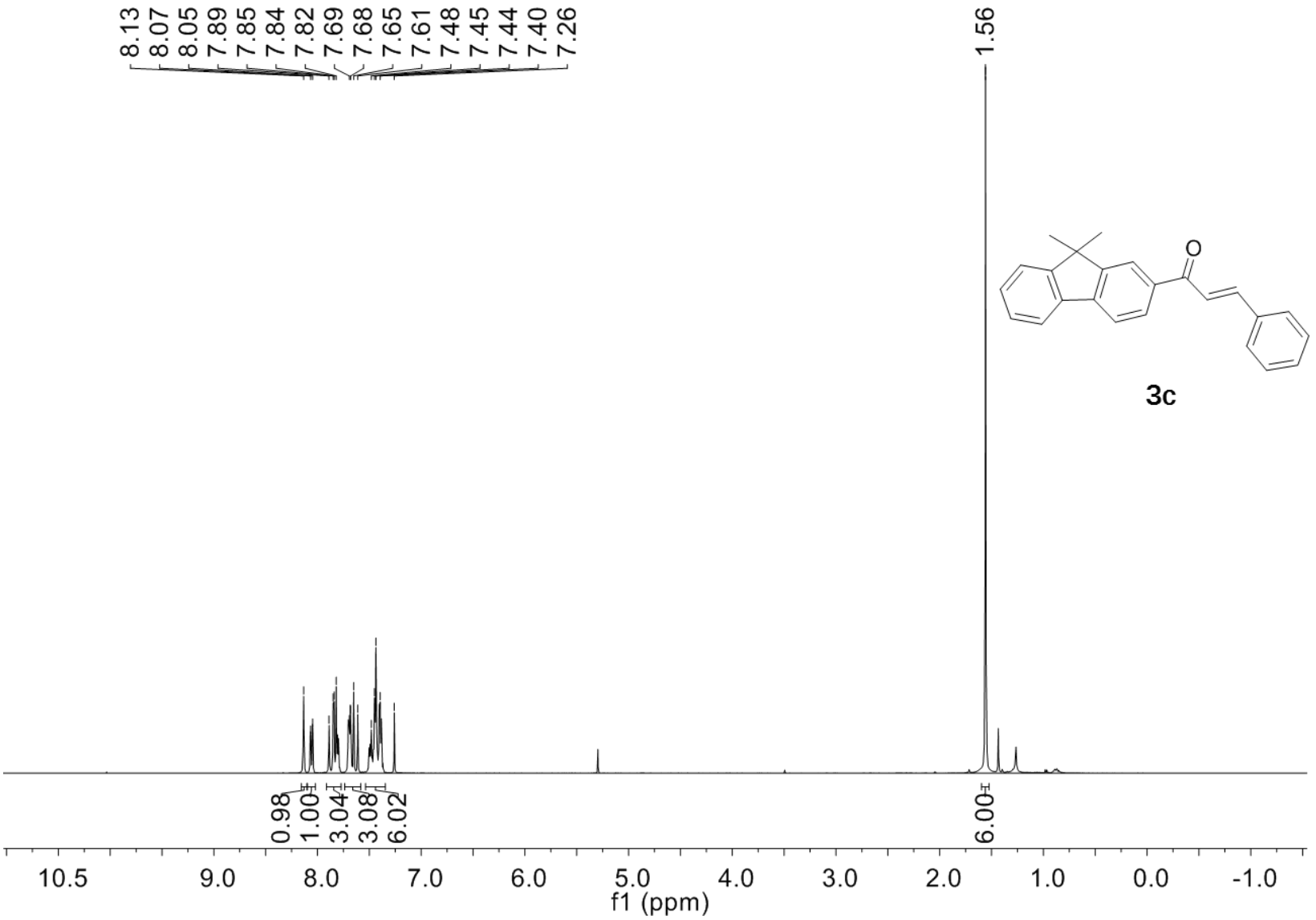
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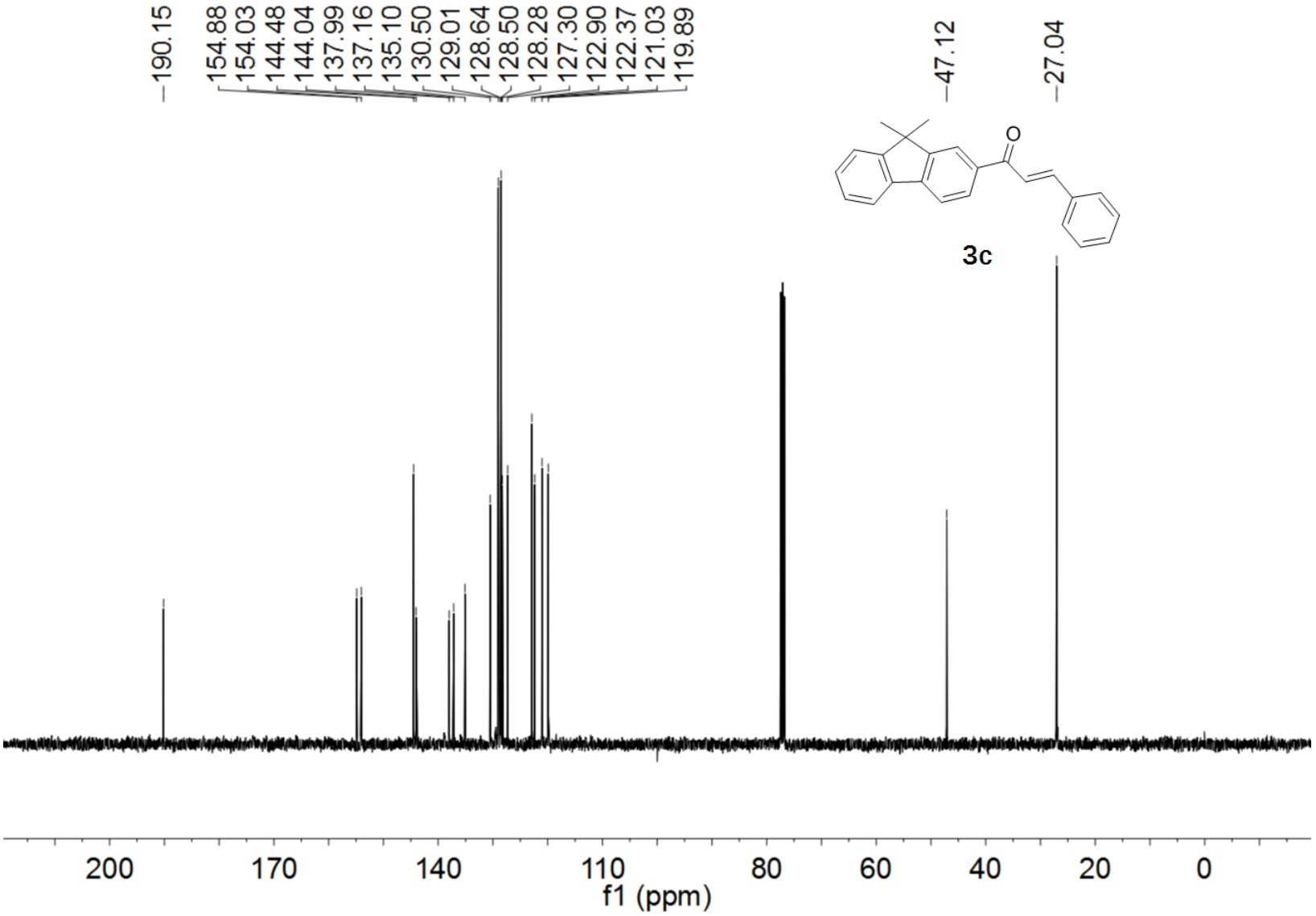
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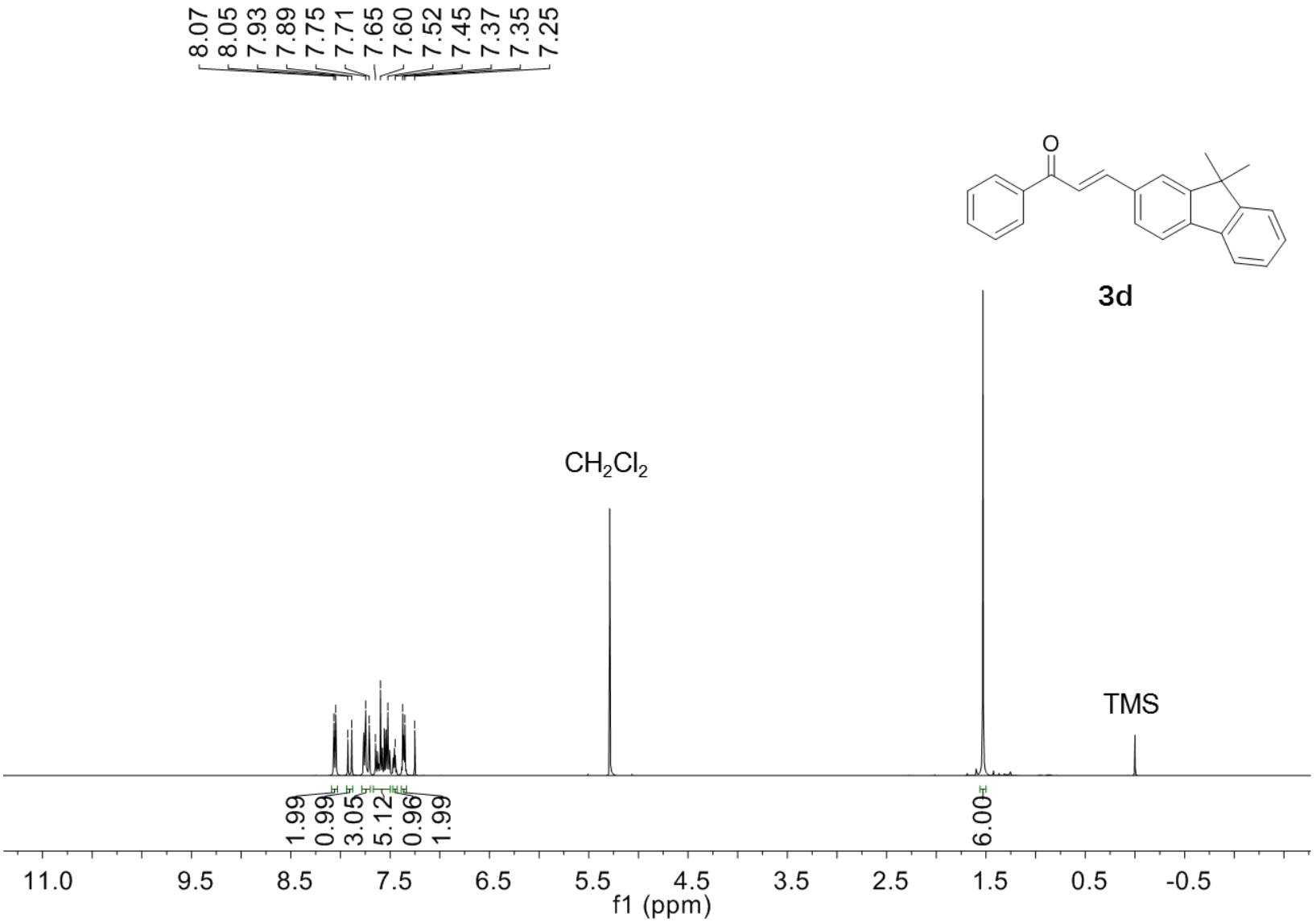
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7.75
7.71
7.65
7.60
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7.45
7.37
7.35
7.25
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CH2Cl2
TMS
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0.96
1.99
6.00
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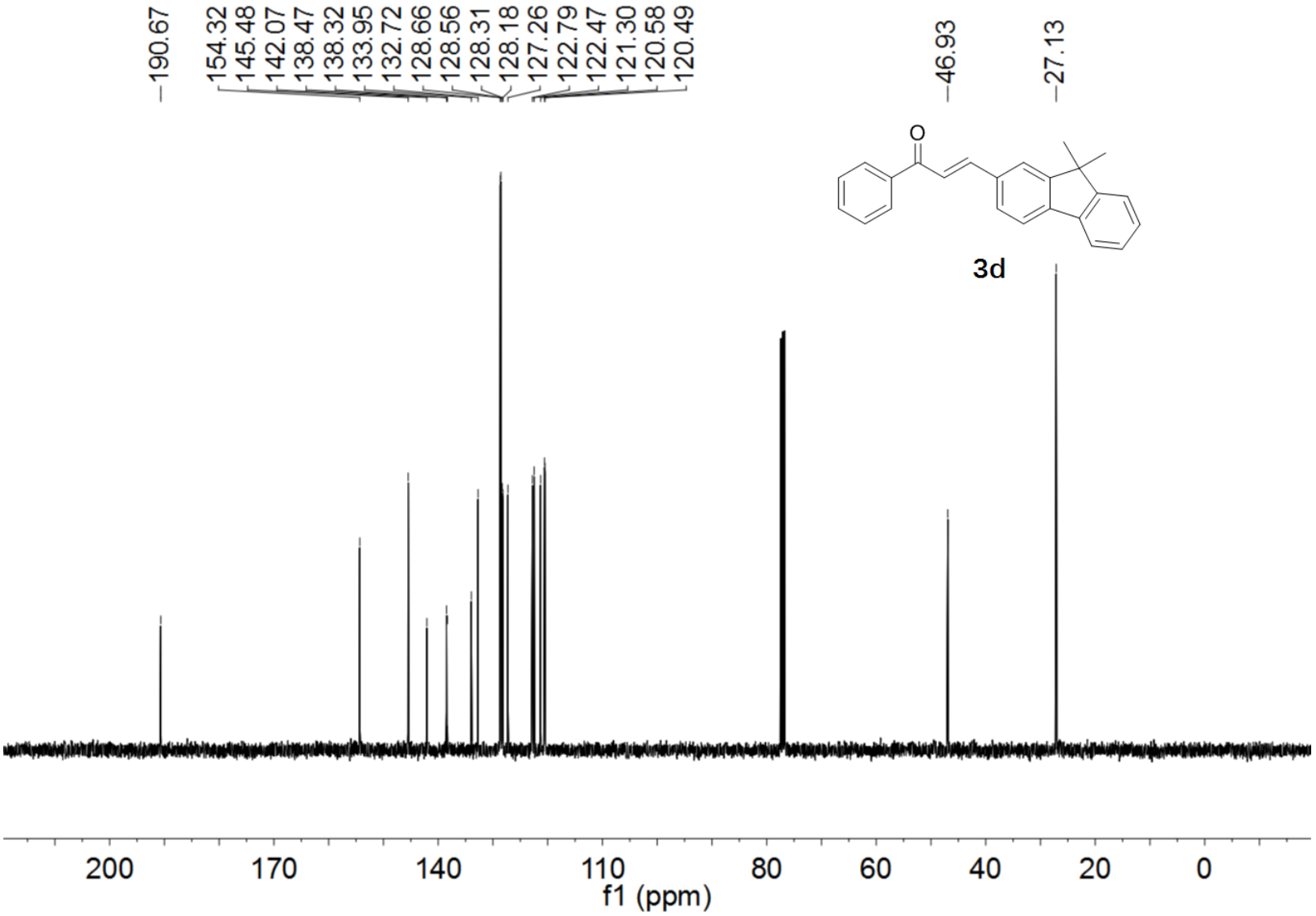
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122.47
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20
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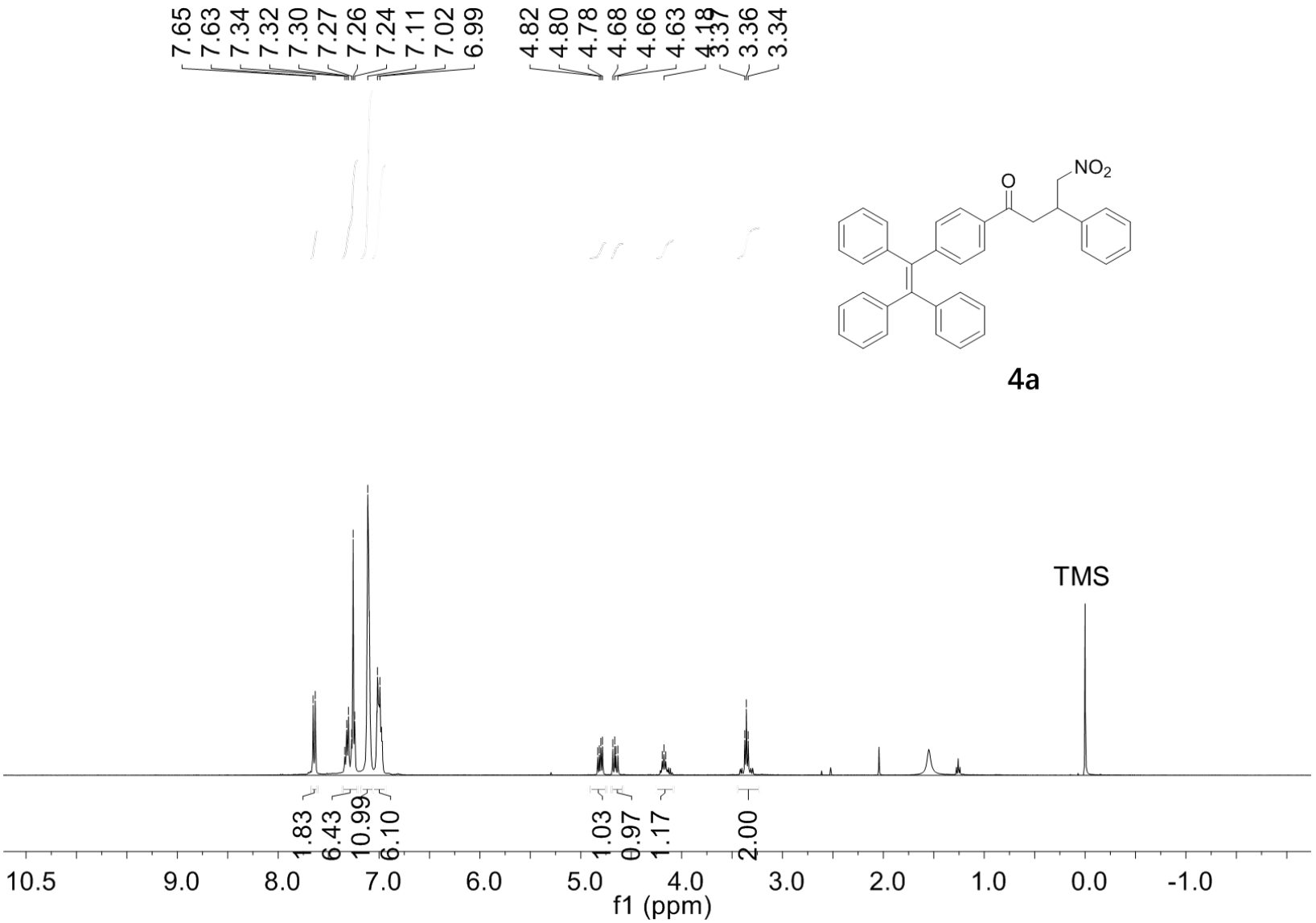
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4.18
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3.36
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0.97
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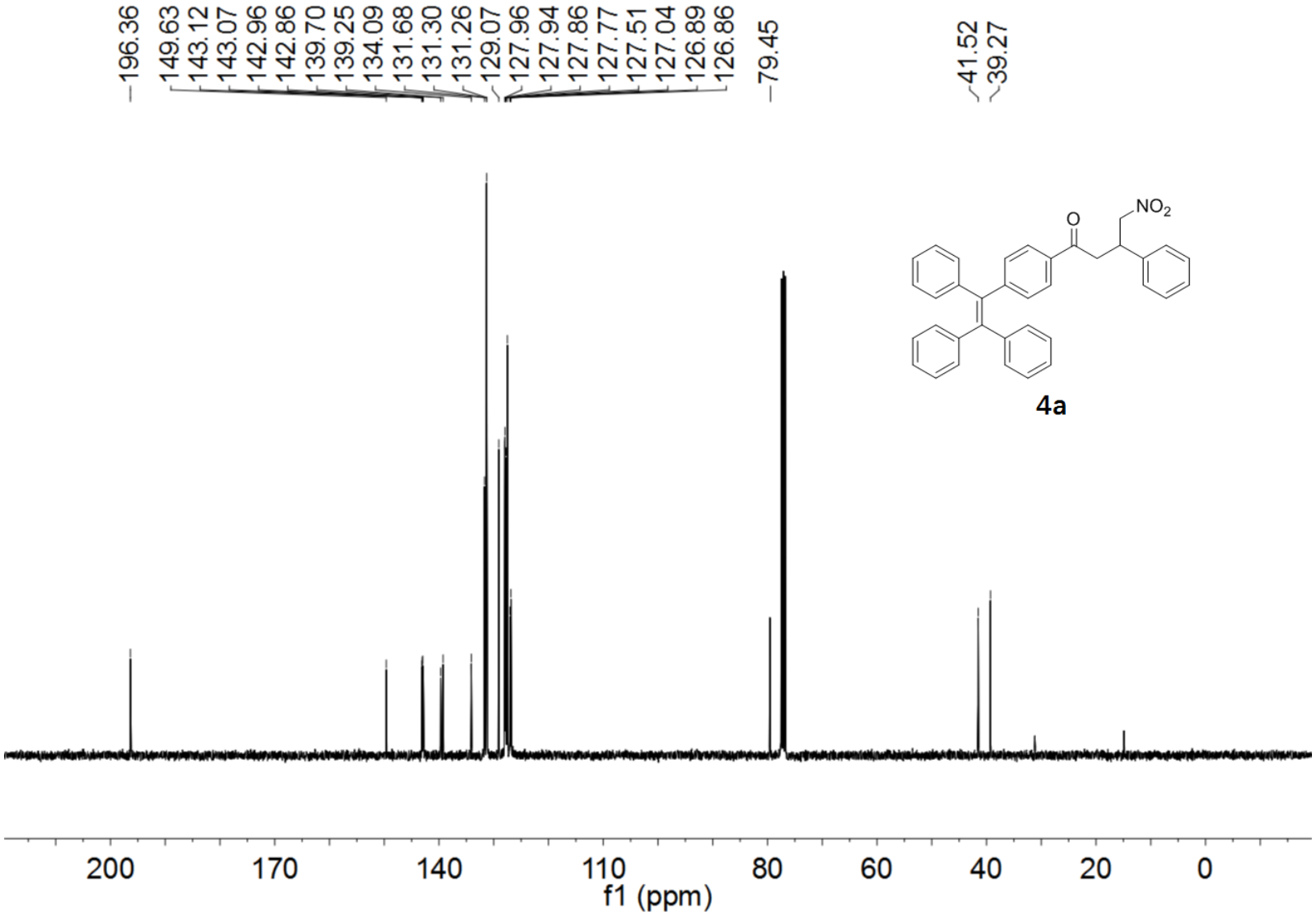
f1 (ppm)

4a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126.86
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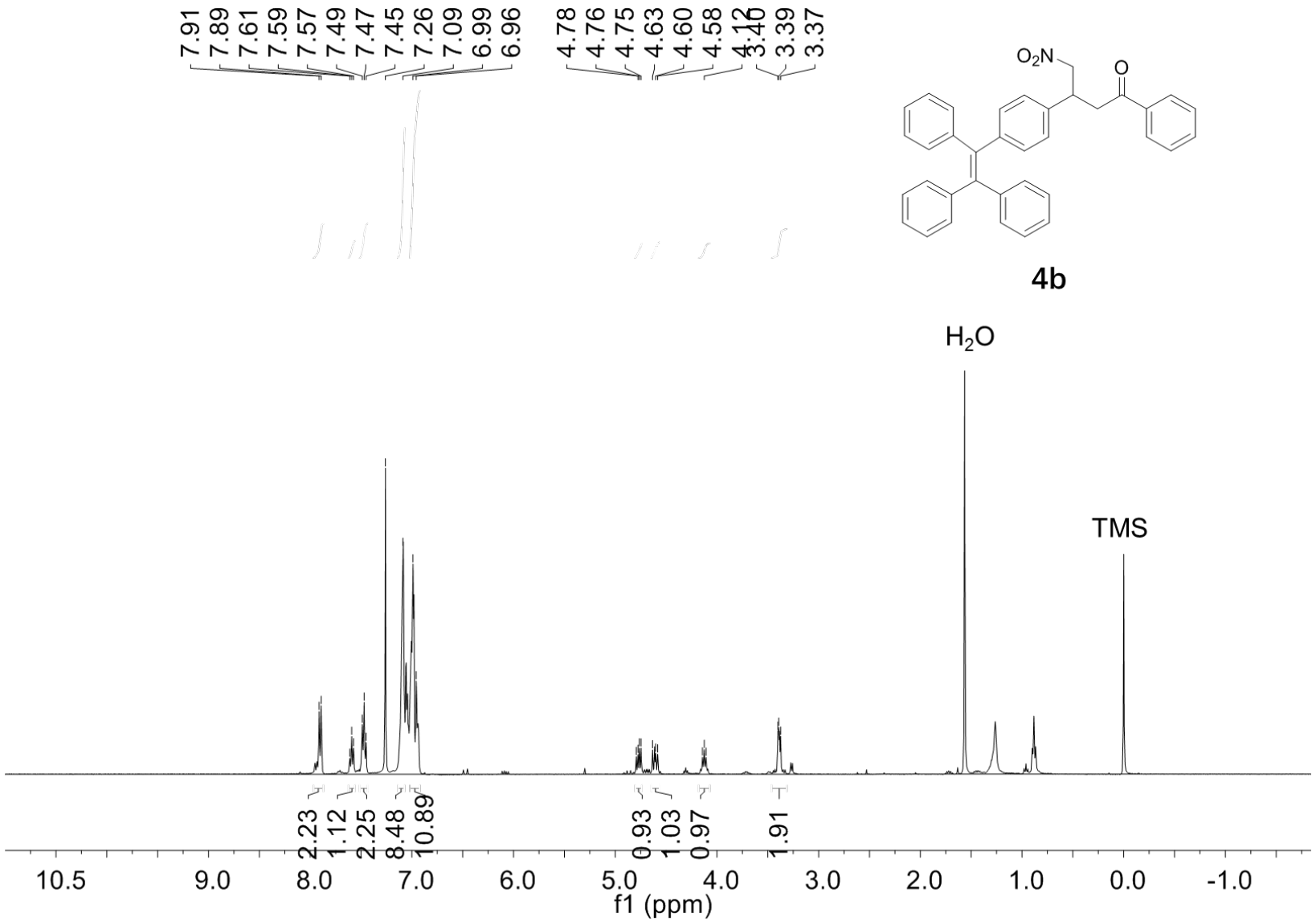
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4.76
4.75
4.63
4.60
4.58
4.12
3.40
3.39
3.37
O2N
O
4b
H2O
TMS
2.23
1.12
2.25
8.48
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0.93
1.03
0.97
1.91
10.5
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4.0
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1.0
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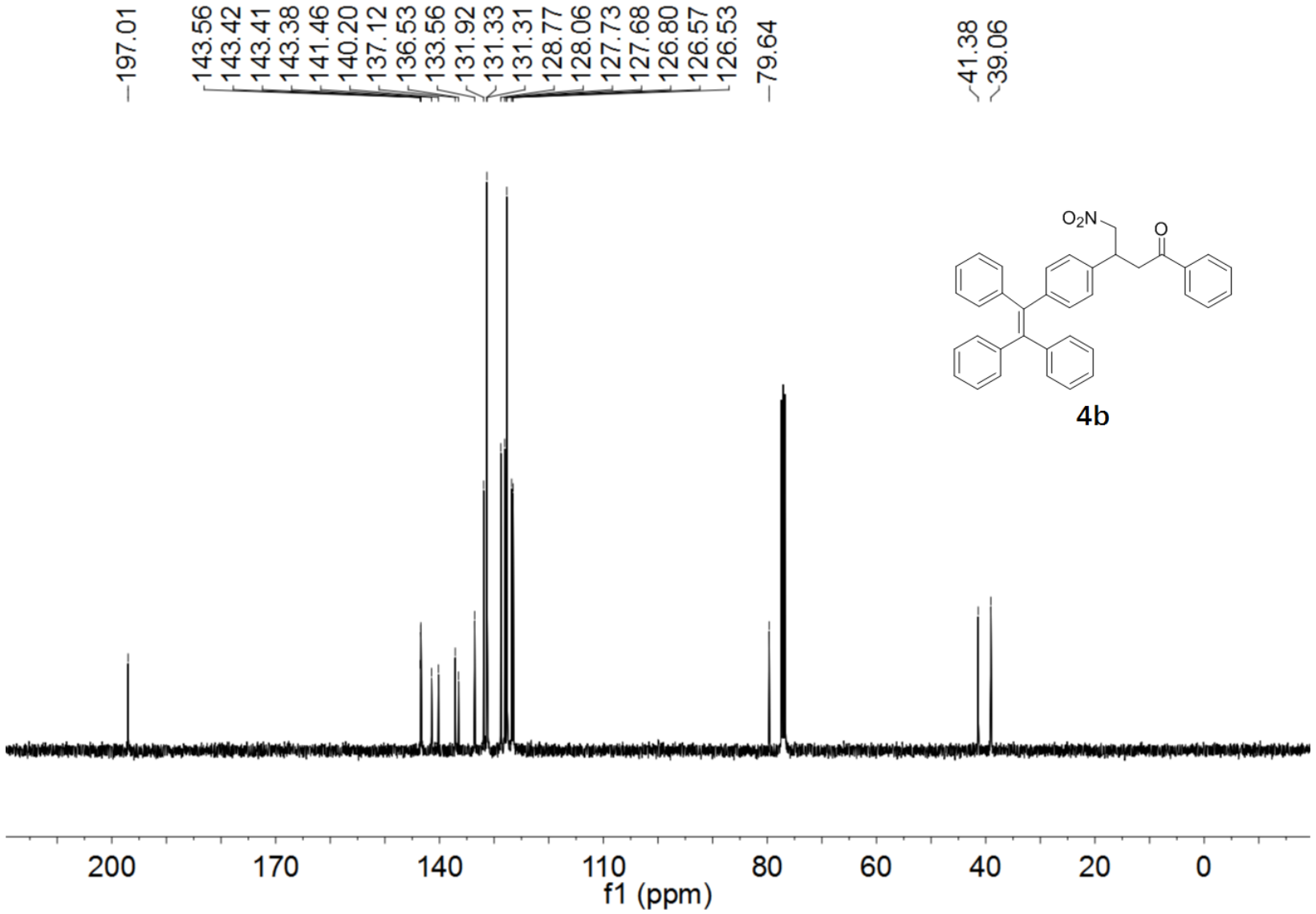
f1 (ppm)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126.80
126.57
126.53
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O
4b
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110
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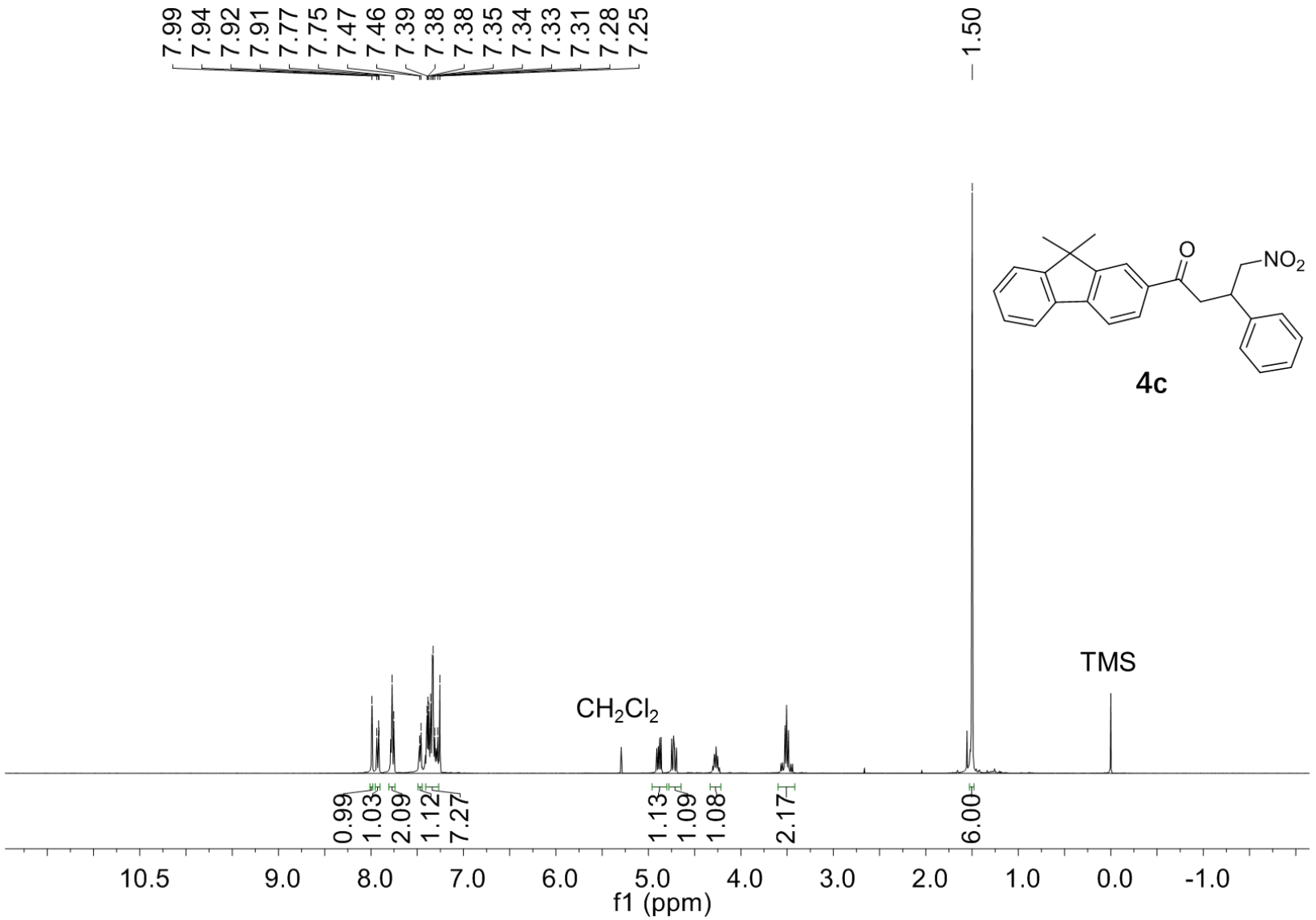
f1 (ppm)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7.38
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7.34
7.33
7.31
7.28
7.25
1.50
O
NO2
4c
TMS
CH2Cl2
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1.03
2.09
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7.27
1.13
1.09
1.08
2.17
6.00
10.5
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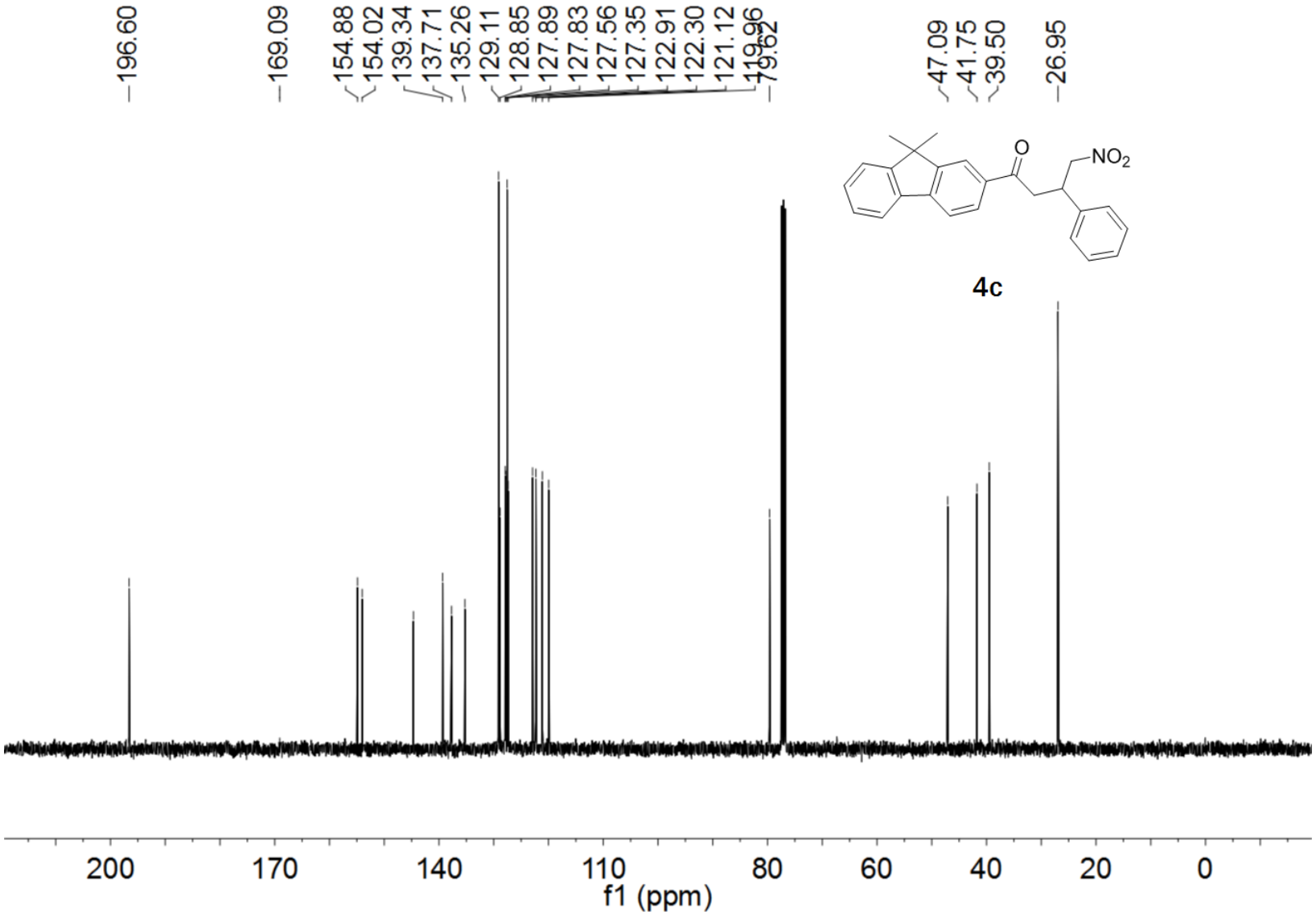
f1 (ppm)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127.56
127.35
122.91
122.30
121.12
119.96
79.62
47.09
41.75
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26.95
O
NO2
4c
200
170
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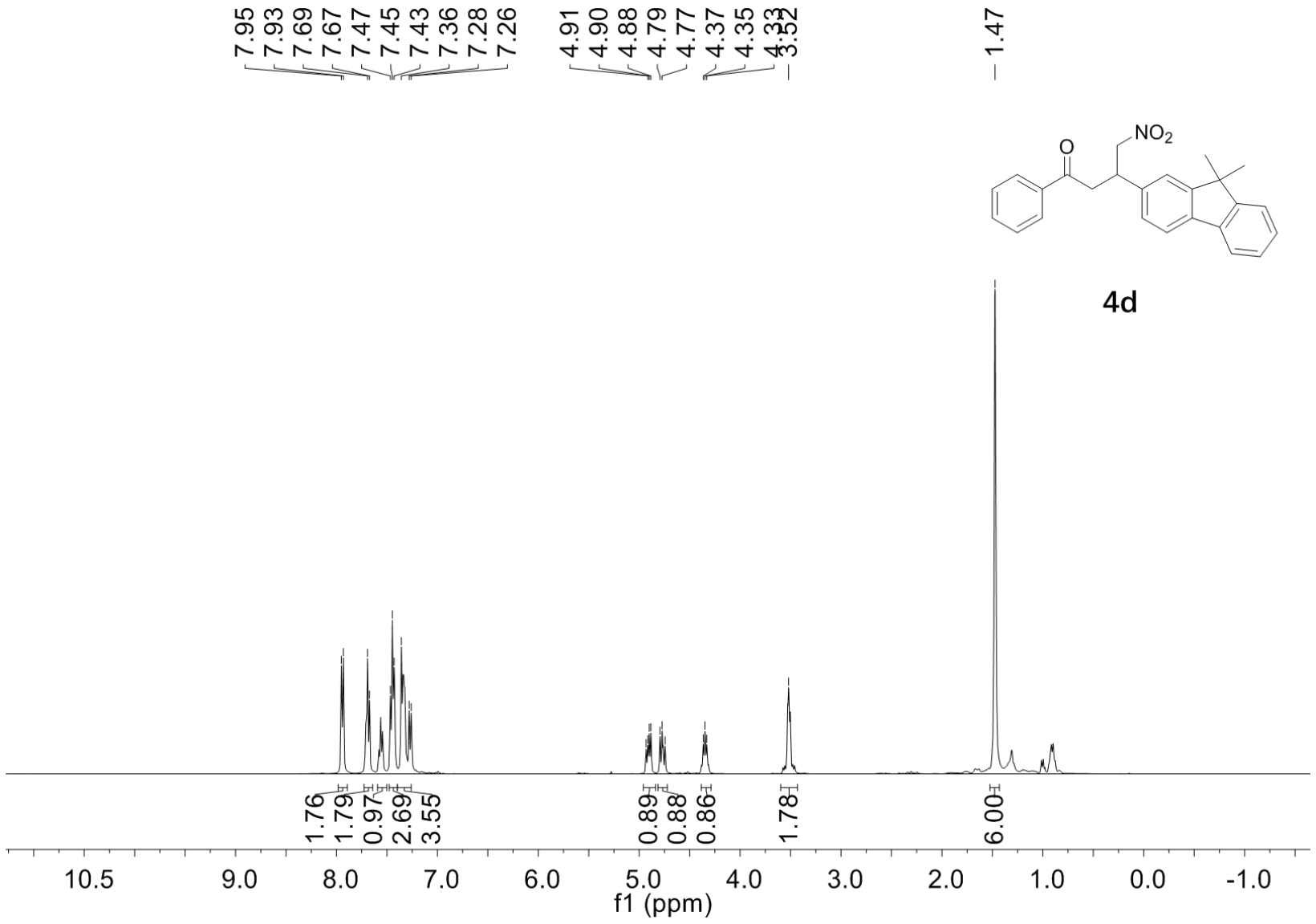
110
80
60
40
20
0
f1 (ppm)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7.28
7.26
4.91
4.90
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4.79
4.77
4.37
4.35
4.33
3.52
1.47
NO2
O
4d
1.76
1.79
0.97
2.69
3.55
0.89
0.88
0.86
1.78
6.00
10.5
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7.0
6.0
5.0
4.0
3.0
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1.0
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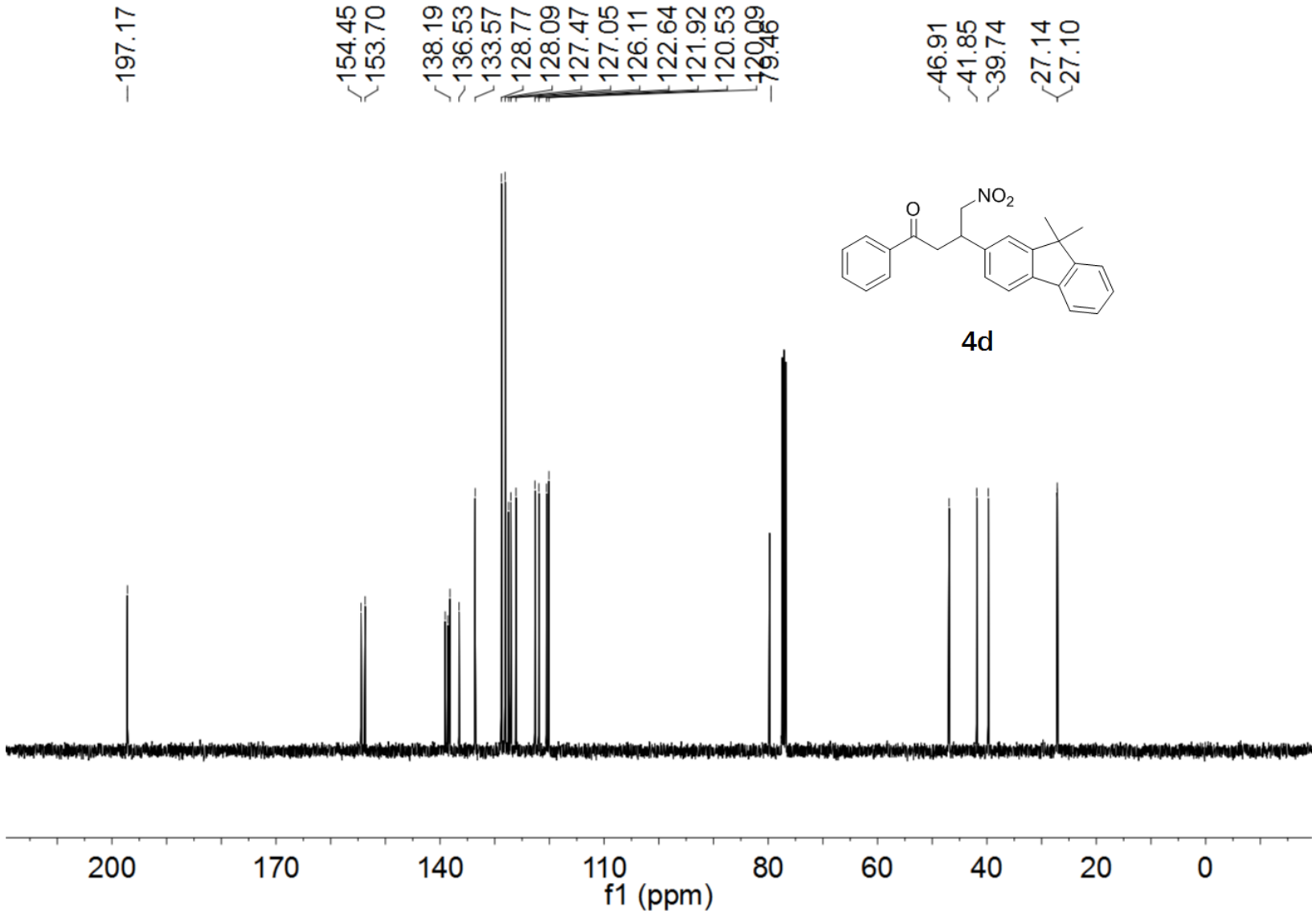
-1.0
f1 (ppm)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153.70
138.19
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133.57
128.77
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127.47
127.05
126.11
122.64
121.92
120.53
120.09
79.46
46.91
41.85
39.74
27.14
27.10
O
NO2
4d
200
170
140
110
80
60
40
20
0
f1 (ppm)

Table S1 DFT calculated energy levels[a]

	HOMO / eV	LUMO / eV	ΔE[b] / eV
5a	-5.05	-3.09	1.96
5b	-5.13	-3.10	2.03
5c	-5.12	-3.09	2.02
5d	-5.22	-3.10	2.12

[a] The geometries of the dyes **5a-d** were optimized with Gauss View 5.0 and the 3D molecular configuration were obtained. Furthermore, the quantum chemical calculation was performed with Gaussian 03 quantum chemistry package and the energy levels were calculated with density functional theory (DFT) at the B3LYP/6-31G(d) level. [b] ΔE = LUMO – HOMO.

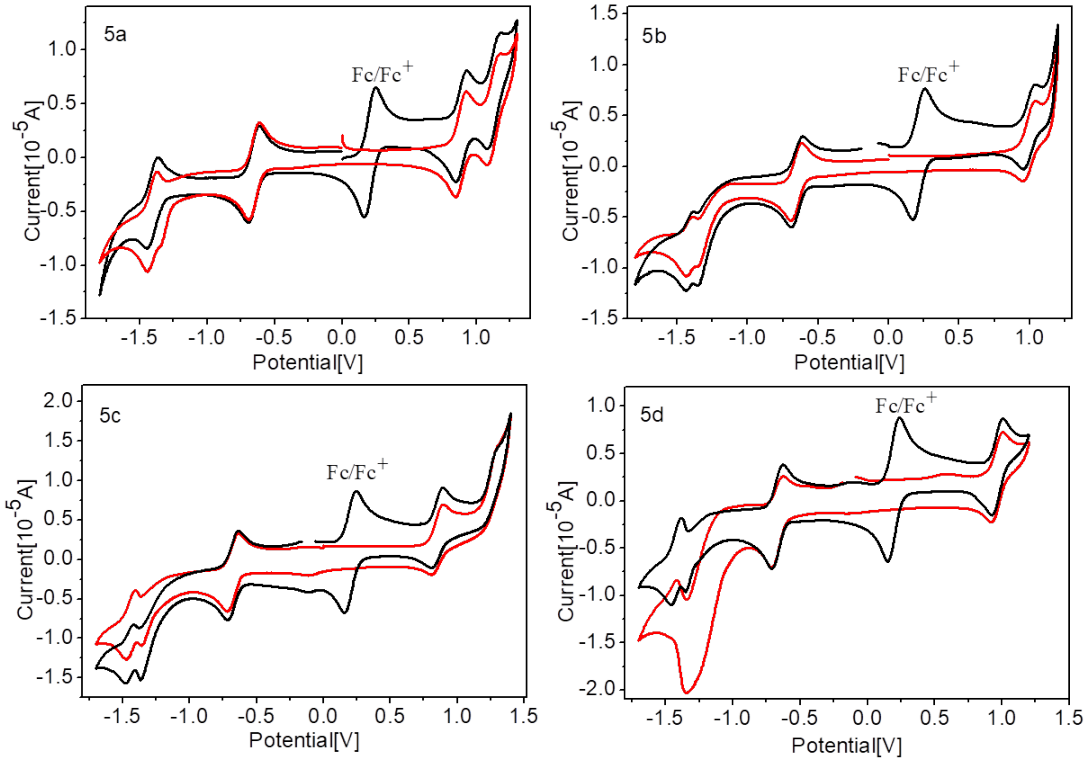

Figure S1 Cyclic voltammograms of aza-BODIPYs **5a-d** in dry dichloromethane (5×10^{-3} M). The scan rate is 50 mV s^{-1} and the supporting electrolyte is NBu_4PF_6 (0.1 M).

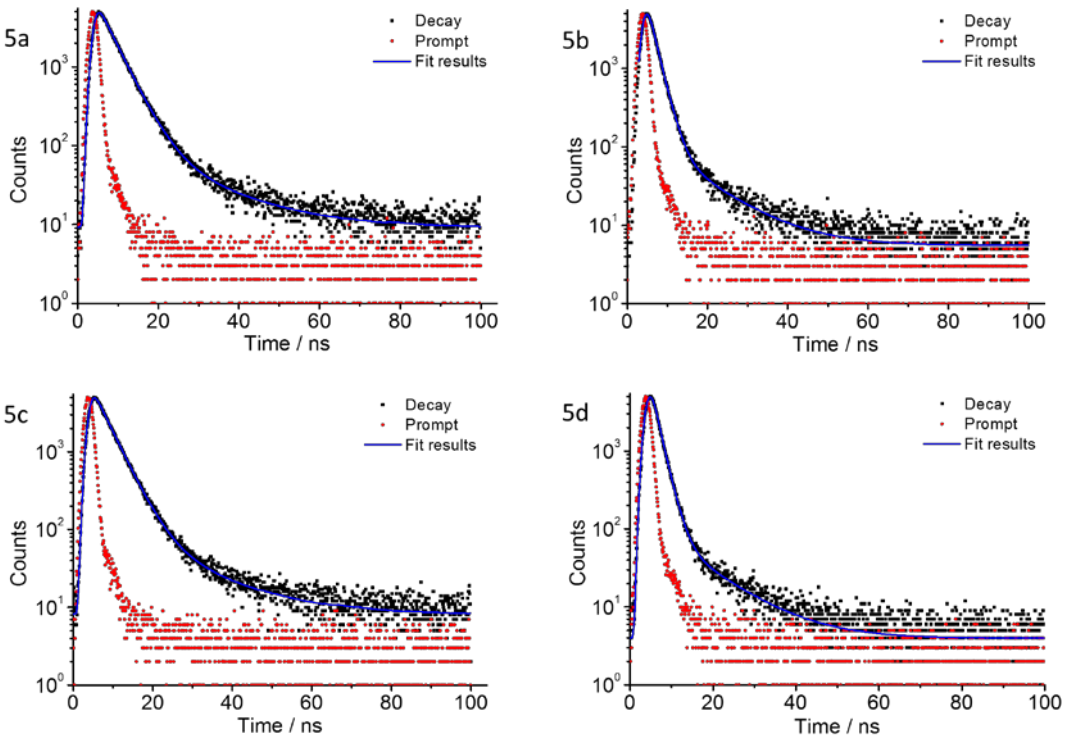

Figure S2 Fluorescence decay curve of aza-BODIPY **5a-d** in toluene (λ_{ex} = 564 nm).

Table S2 The measured fluorescence lifetimes for aza-BODIPY **5a-d**.

dye	τ_1/ns	τ_2/ns	τ/ns	χ^2
5a	3.89(92.73%)	15.67(7.27%)	4.75	1.163
5b	1.82(93.06%)	11.23(6.94%)	2.47	1.156
5c	3.83(93.44%)	15.30(6.56%)	4.58	1.097
5d	1.62(94.00%)	10.78(6.00%)	2.17	1.206