Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

Electronic Supplementary Information

Photochromism and fluorescent properties of bisbenzothienylethene and S,S,S',S'-tetraoxide derivatives with dual conjugated fluorescent groups on their side chains

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Contents

1. Experimental details

Apparatus. ^{1}H-NMR spectra were recorded on a Bruker DRX300 (300 MHz). ^{1}H-NMR chemical shifts in $CDCl_3$ were determined using tetrametylsilane (TMS) as an internal standard. MALDI-TOF-Mass spectra were recorded on a Shimadzu AXIMA-CFR. Electron impact mass spectra were measured with JEOL JMS-AX-600. Infrared absorption spectra were recorded with JASCO FT-IR-4100. Melting points were measured with Yazawa BY-2.

Chemical reactions were carried out under a dry N_2 atmosphere. All solvents including dry tetrahydrofuran (THF) were purchased and used as received. Flash column chromatography was carried out on 230-400 mesh silica gel using ethyl acetate and hexane as the eluent unless otherwise described. Analytical thin-layer chromatography was performed on the pre-coated 0.25 mm thick silica gel TLC plates.

A microwave heating apparatus (Boitage 11560) was used for the synthesis of **3o**.

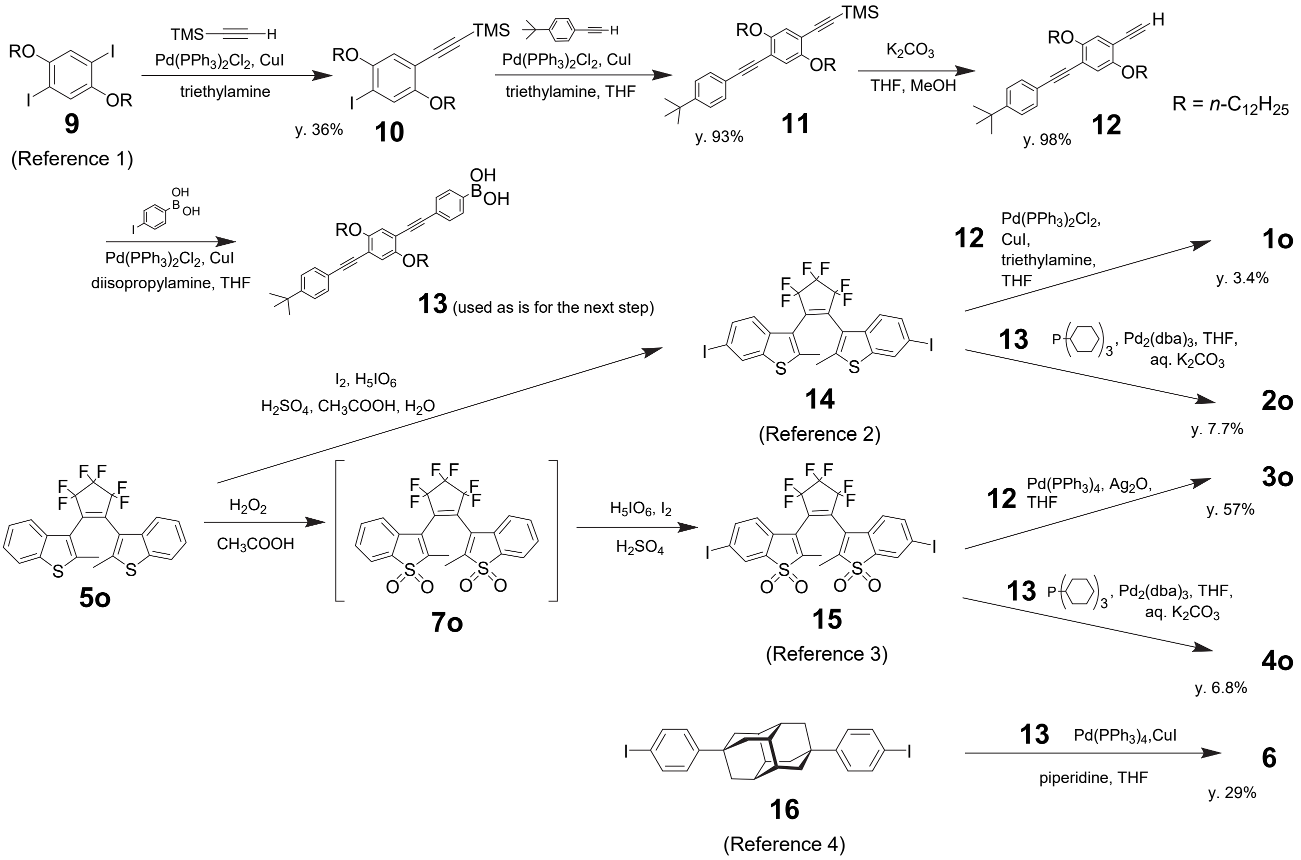
Optical measurements. Absorption spectra were recorded on a JASCO V-550. Fluorescence spectra were recorded on a JASCO FP-6500 spectrophotometer. Fluorescence quantum yields of **1** were determined using JASCO FP-6500 or FP-8500 spectrophotometers.

Photochemical reactions were carried out in a 10 mm length quarts cell. Photoirradiation with 313-nm light was carried out using a 500-W ultra-high-pressure mercury lamp (USHIO USH-500D or UI501HQ), separated by filters (a 5 cm water filter, a UV-31 glass filter, a UV-D33S glass filter, a 5 cm aqueous $NiSO_4$ filter, a 1 cm aqueous K_2CrO_4 filter and a 1 cm aqueous potassium hydrogenphthalate filter). Photoirradiation with 506-nm light was carried out using a 500-W Xenon lamp (USHIO UXL-500D-0), separated by filters (a 5 cm water filter, a Pyrex glass filter, a Y-47 glass filter and a KL-50 interference glass filter). Photoirradiation with 578-nm light was carried out using a 500-W Xenon lamp (USHIO UXL-500D-0), separated by filters (a 5 cm water filter, an O-54 glass filter and a KL-56 interference glass filter). Irradiation with >490-nm light was carried out using a 500-W Xenon lamp (USHIO UXL-500D-0), separated by filters (a 5 cm water filter, a Pyrex glass filter and a Y-49 glass filter). Irradiation with >540-nm light was carried out using a 500-W Xenon lamp (USHIO UXL-500D-0), separated by filters (a 5 cm water filter, a Pyrex glass filter and an O-54 glass filter).

Computational details. DFT geometry optimization and TD DFT calculations for absorption spectra were carried out with Spartan’16 (Wavefunction Inc.) at B3LYP/6-31G* level.

2. Synthesis procedure of 1o, 2o, 3o, 4o and 6.

Synthesis of **1o**, **2o**, **3o**, **4o** and **6** were carried out according to the following scheme.



Synthesis of 1,4-bis(dodecyloxy)-2-iodo-5-trimethylsilylethynylbenzene (10)

To a solution of **9** [1] (1.01 g, 1.44 mmol), $Pd(PPh_3)_2Cl_2$ (19.4 mg, 0.028 mmol, 0.019 eq), CuI (13.9 mg, 0.073 mmol, 0.051 eq) and triethylamine (25 ml) in a two-necked flask was added dropwise trimethylsilylacetylene (152 μL, 1.08 mmol, 0.75 eq), and the resulting solution was stirred at room temperature for overnight. The solvent was removed in vacuo, and 3 mol dm^{-3} aq. hydrochloric acid and $CHCl_3$ were added. The organic materials were extracted with $CHCl_3$, and the combined organic layer was washed with brine. The organic layer was dried over anhydrous Na_2SO_4, the drying agent filtered off, and the solvent evaporated. The organic material thus obtained was further purified with the silica gel column chromatography (hexane/ $CHCl_3$ as the eluent) to give brownish powdery **10** (346 mg, 36%) together with the starting **9** (527 mg, 52%).

^1H NMR (300 MHz, $CDCl_3$, TMS): δ/ppm = 0.25 (9H, s), 0.88 (6H, t, *J*/Hz =7.2), 1.26 (32H, m), 1.49 (4H, m), 1.79 (4H, m), 3.93 (4H, m), 6.83 (1H, s), 7.25 (1H, s).

LRMS (EI, 70eV) m/z (rel intensity/%) = 668 (M^+, 100).

IR (neat) ν/cm^{-1} = 2957, 2920, 2848, 2160, 1485, 1467, 1372, 1250, 1213, 1162, 1032, 1002, 857, 841, 759, 722, 664, 640, 506, 490, 449, 439, 414.

Mp 38.0-40.9 °C.

Synthesis of 1,4-bis(dodecyloxy)-2-(4'-*teert*-butylphenylethynyl)-5-trimethylsilylethynylbenzene (11)

To a mixture of **10** (663 mg, 0.99 mmol), 4-*tert*-butylphenylacetylene (208 mg, 1.31 mmol, 1.3 eq), $Pd(PPh_3)_2Cl_2$ (25.9 mg, 0.037 mmol, 0.04 eq) and CuI (8.1 mg, 0.043 mmol, 0.04 eq) in THF (10 mL) was added triethylamine (5 ml) in a two-necked flask, and the resulting solution was stirred at room temperature for overnight. The solvent was removed in vacuo, and 3 mol dm^{-3} aq. hydrochloric acid and CH_2Cl_2 were added. The organic materials were extracted with CH_2Cl_2, and the combined organic layer was washed with brine. The organic layer was dried over anhydrous Na_2SO_4, the drying agent filtered off, and the solvent evaporated. The organic material thus obtained was further purified with the silica gel column chromatography to give brownish powdery **11** (646 mg, 93%).

^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ/ppm = 0.26 (9H, s), 0.88 (6H, m), 1.1-1.4 (41H, m), 1.52 (4H, m), 1.81 (4H, m), 3.98 (4H, m), 6.93 (1H, s), 6.95 (1H, s), 7.35 (2H, d, *J*/Hz = 8.7), 7.45 (2H, d, *J*/Hz = 8.7).

LRMS (EI, 70eV) m/z (rel intensity %) = 699 (M^+, 100).

IR (neat) ν/cm^{-1} = 2921, 2849, 2155, 1517, 1496, 1469, 1410, 1388, 1272, 1250, 1217, 1116, 1033, 891, 842, 759, 722, 639, 559, 537, 483, 405.

Mp 45.0-48.9 °C.

Synthesis of 1,4-bis(dodecyloxy)-2-(4'-*tert*-butylphenyleneethynyl)-5-ethynylbenzene (12)

To a mixture of **11** (629 mg, 0.90 mmol) and K_2CO_3 (187 mg, 1.35 mmol, 1.5 eq) was added THF (13 mL) and CH_3OH (13 mL) and the resulting mixture was stirred at room temperature for overnight. To the solution was added hexane and sat. aq. NH_4Cl, and the organic material was extracted with hexane three times. The combined organic layer was dried over anhydrous Na_2SO_4, the drying agent filtered off, and the solvent evaporated. The organic material thus obtained was further purified with the silica gel column chromatography to give brownish powdery **12** (554 mg, 98%).

^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ/ppm = 0.88 (6H, m), 1.2-1.4 (41H, m), 1.52 (4H, m), 1.82 (4H, m), 3.33 (1H, s), 3.99 (4H, m), 6.97 (1H, s), 6.98 (1H, s), 7.36 (2H, d, *J*/Hz = 8.7), 7.46 (2H, d, *J*/Hz = 8.7).

LRMS (EI, 70eV) m/z (rel intensity %) = 626 (M^+, 100).

IR (neat) ν/cm^{-1} = 3290, 2920, 2850, 2362, 1518, 1496, 1466, 1410, 1391, 1276, 1219, 1031, 1007, 876, 861, 830, 793, 723, 677, 655, 633, 559, 481, 458, 418, 404.

Mp 43.1-48.0 °C.

Synthesis of 1,4-bis(dodecyloxy)-2-(4'-*tert*-butylphenyleneethynyl)-5-(4"-phenylene)boronic acid (13)

To a solution of **12** (150 mg, 0.24 mmol), 4-iodophenylboronic acid (72 mg, 0.29 mmol, 1.2 eq), $Pd(PPh_3)_4$ (14.5 mg, 0.013 mmol, 0.05 eq), CuI (3.3 mg, 0.017 mmol, 0.07 eq) in THF (5 mL) was added diisopropylamine (5 mL) in a two-necked flask, and the resulting solution was stirred at room temperature for overnight. The solid material formed was filtered off, and the solvent was removed in vacuo. The organic material was extracted from the solid material obtained by CH_2Cl_2 several times, and the solvent of the combined organic layer was evaporated to give an orange powder. It was used for the next reactions without further purification.

Synthesis of 1o

To a mixture of **14** [2] (50.2 mg, 0.070 mmol), **12** (96 mg, 0.15 mmol, 2.2 eq), $Pd(PPh_3)_2Cl_2$ (11.8 mg, 0.017 mmol, 0.24 eq) and CuI (11.1 mg, 0.058 mmol, 0.84 eq) in THF (6 mL) was added triethylamine (5 ml) in a two-necked flask, and the resulting solution was stirred at room temperature for 1.5 h. To the solution was added 3 mol dm^{-3} aq. hydrochloric acid and CH_2Cl_2. The organic materials were extracted with CH_2Cl_2 several times, and the combined organic layer was washed with brine. The organic layer was dried over anhydrous Na_2SO_4, the drying agent filtered off, and the solvent evaporated. The organic material thus obtained was further purified with the silica gel column chromatography to give **11** as a yellow oil (4.1 mg, 3.4%).

^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ/ppm = 0.86 (12H, m), 1.2-1.4 (82H, m), 1.4-1.6 (8H, m), 1.85 (8H, m), 2.21, 2.49 (6H, s), 4.03 (8H, m), 6.97-7.01 (4H, m), 7.3-7.9 (14H, Aromatic protons).

MALDI-TOF MS (Reflectron mode) m/z = 1717 (M^+).

IR (neat) ν/cm^{-1} = 2923, 2853, 1496, 1464, 1414, 1381, 1340, 1269, 1215, 1147, 1113, 1046, 997, 964, 861, 833, 758, 735, 701, 560, 526, 489, 476, 463, 443, 426.

Synthesis of 2o

To a solution of **14** (50.3 mg, 0.070 mmol) and **12** (133 mg, 0.18 mmol, 2.6 eq) in THF (7 mL) in a two-necked flask was added aq. sat. K_2CO_3 (7 mL), $Pd_2(dba)_3$ (15.9 mg, 0.017 mmol, 0.25 eq) and tricyclohexylphosphine (2.1 mg, 0.0075 mmol, 0.11 eq), and the resulting solution was stirred at room temperature for overnight. To the solution was added 1 mol dm^{-3} aq. hydrochloric acid and $CHCl_3$. The organic materials were extracted with $CHCl_3$ several times, and the combined organic layer was washed with brine. The organic layer was dried over anhydrous Na_2SO_4, the drying agent filtered off, and the solvent evaporated. The organic material thus obtained was further purified with the silica gel column chromatography to give **2o** as a yellow oil (10.0 mg, 7.7%).

^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ/ppm = 0.86 (12H, m), 1.2-1.4 (82H, m), 1.4-1.6 (8H, m), 1.85 (8H, m), 2.26, 2.54 (6H, s), 4.04 (8H, m), 7.01, 7.03 (4H, s), 7.3-8.0 (22H, Aromatic protons).

MALDI-TOF MS (Reflectron mode) m/z = 1869 (M^+).

IR (neat) ν/cm^{-1} = 2921, 2852, 1518, 1494, 1465, 1414, 1380, 1339, 1269, 1214, 1193, 1146, 1112, 1091, 1047, 1030, 993, 966, 834, 815, 758, 721, 561, 529, 476, 457, 447, 439, 418.

Synthesis of 3o

A solution of **15** [3] (50.5 mg, 0.064 mmol), **13** (82.3 mg, 0.13 mmol, 2.0 eq), $Pd(PPh_3)_4$ (6.0 mg, 0.0052 mmol, 0.081 eq) and Ag_2O (24.9 mg, 0.11 mmol, 1.7 eq) in THF (6 mL) in a vial for the microwave heating apparatus was heated at 80 °C for 15 min. Insoluble materials were filtered off through Celite, and the solvent of the filtrate was removed in vacuo. The organic material thus obtained was further purified with the silica gel column chromatography to give **3o** as a brown amorphous solid (64.8 mg, 56.5%).

^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ/ppm = 0.87 (12H, t, *J*/Hz = 7.2), 1.2-1.4 (82H, m), 1.4-1.6 (8H, m), 1.84

(8H, m), 2.06, 2.22 (6H, s), 4.02 (8H, m), 6.9-7.2 (6H, m), 7.3-7.9 (12H, Aromatic protons).
MALDI-TOF MS (Reflectron mode) m/z = 1781 (M^+).
IR (neat) ν/cm^{-1} = 2921, 2852, 1496, 1467, 1416, 1321, 1276, 1216, 1173, 1153, 1132, 1115, 1042, 1018, 952, 834, 722, 571, 495, 478, 462, 431, 421.

Synthesis of 4o.
To a solution of **15** (30.3 mg, 0.039 mmol) and **13** (73 mg, 0.098 mmol, 2.5 eq) in THF (5 mL) in a two-necked flask was added aq. sat. K_2CO_3 (5 mL), $Pd_2(dba)_3$ (7.8 mg, 0.0085 mmol, 0.22 eq) and tricyclohexylphosphine (1.2 mg, 0.0043 mmol, 0.11 eq), and the resulting solution was stirred at room temperature for 2 h 40 min. To the solution was added 0.5 mol dm^{-3} aq. hydrochloric acid and $CHCl_3$. The organic materials were extracted with $CHCl_3$ several times, and the combined organic layer was washed with brine. The organic layer was dried over anhydrous Na_2SO_4, the drying agent filtered off, and the solvent evaporated. The organic material thus obtained was further purified with the silica gel column chromatography to give **4o** as an orange oil (5.1 mg, 6.8%).
^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ/ppm = 0.86 (12H, m), 1.2-1.4 (82H, m), 1.4-1.6 (8H, m), 1.85 (8H, m), 2.11, 2.25 (6H, s), 4.03 (8H, m), 7.03 (4H, m), 7.2~8.0 (22H, Aromatic protons).
MALDI-TOF MS (Reflectron mode) m/z = 1933 (M^+).
IR (neat) ν/cm^{-1} = 2923, 2852, 1519, 1495, 1469, 1415, 1318, 1277, 1216, 1173, 1153, 1129, 1113, 1060, 1043, 1015, 957, 833, 721, 687, 562, 489, 478, 468, 448.

Synthesis of 6.
To a mixture of 4,9-bis(4-iodophenyl)diamantane **16** [4] (98.4 mg, 0.166 mmol), $Pd(PPh_3)_4$ (21.9 mg, 0.019 mmol, 0.11 eq) and CuI (6.4 mg, 0.034 mmol, 0.20 eq) in a three-necked flask was added piperidine (10 mL), and the resulting mixture was heated up to 60 °C. When THF (5 mL) was added to the mixture, the content became a clear solution. To it was added a solution of **13** (209 mg, 0.333 mmol, 2.0 eq) in piperidine (6 mL) dropwise. After the solution was heated at 60-70 °C for 4 h, it was stirred for overnight at room temperature. After the solvent was removed from the reaction flask in vacuo, 3 mol dm^{-3} aq. hydrochloric acid and CH_2Cl_2 was added and the organic materials were extracted with CH_2Cl_2 several times. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, the drying agent filtered off, and the solvent evaporated. The organic material thus obtained was further purified with the silica gel column chromatography (hexane/ $CHCl_3$ as the eluent) to give **6** as a yellow powder (75.4 mg, 29%).
^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ/ppm = 0.88 (12H, t, *J*/Hz = 7.2), 1.2-1.4 (82H, m), 1.5-1.6 (8H, m), 1.85 (8H, m), 1.98 (18H), 4.03 (8H, t, *J*/Hz =6.4), 7.01 (4H, s), 7.36 (4H, d, *J*/Hz = 8.3), 7.39 (4H, d, *J*/Hz = 8.7), 7.48 (4H, d, *J*/Hz = 9.8), 7.50 (4H, d, *J*/Hz = 9.8).
MALDI-TOF MS (Reflectron mode) m/z = 1592 (M^+).
IR (neat) ν/cm^{-1} = 2919, 2849, 1516, 1492, 1466, 1415, 1377, 1267, 1212, 1017, 867, 833, 797, 722, 706, 665, 560, 465.
Mp 134.0-137.0 °C

References

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[2] K. Matsuda, M. Irie, *Chem. Eur. J.*, 2001, **7**, 3466-3473.

[3] Y.-C. Jeong, S. I. Yang, E. Kim, K.-H. Ahn, *Tetrahedron*, 2006, **62**, 5855-5861.

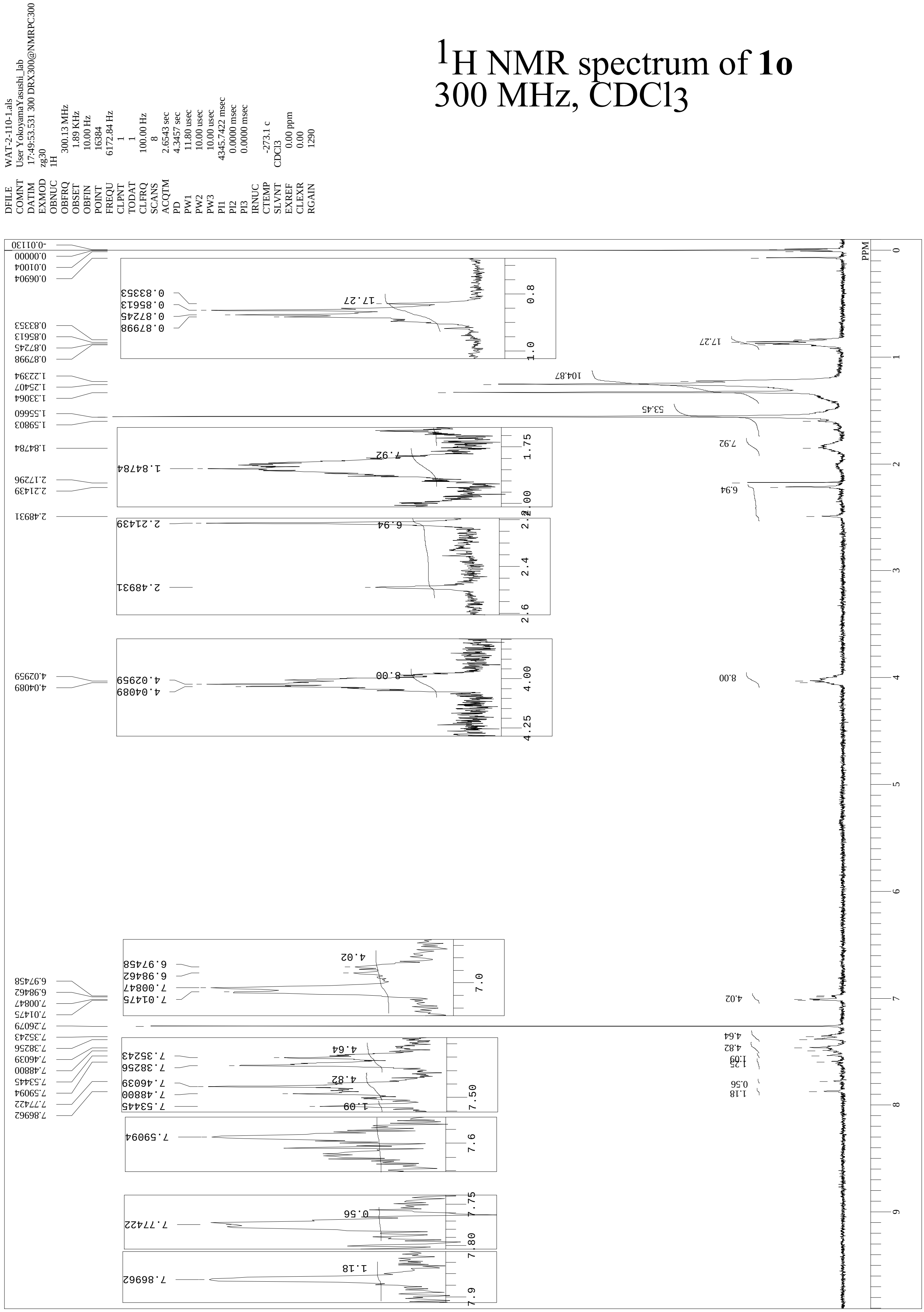
[4] T. Gushiken, S. Ujiie, T. Ubukata, Y. Yokoyama, *Bull. Chem. Soc. Jpn.*, 2011, **84**, 269-282.

3. ^{1}H NMR spectra

300 MHz in $CDCl_3$ with TMS as the internal standard

^{1}H NMR spectrum of **1o**

300 MHz, $CDCl_3$



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^{1}H NMR spectrum of **2o**
300 MHz, $CDCl_3$

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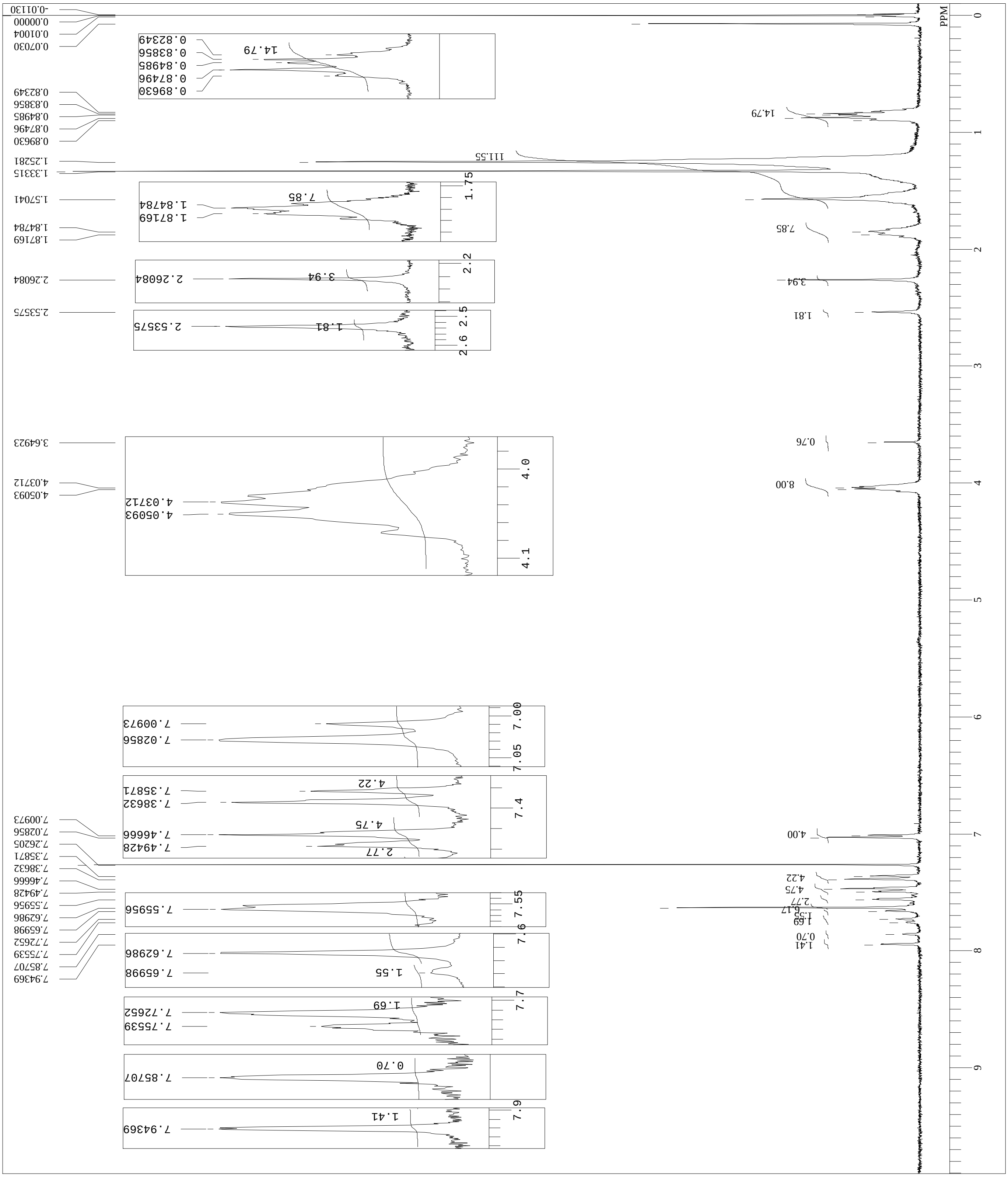

^{1}H NMR spectrum of **3o**
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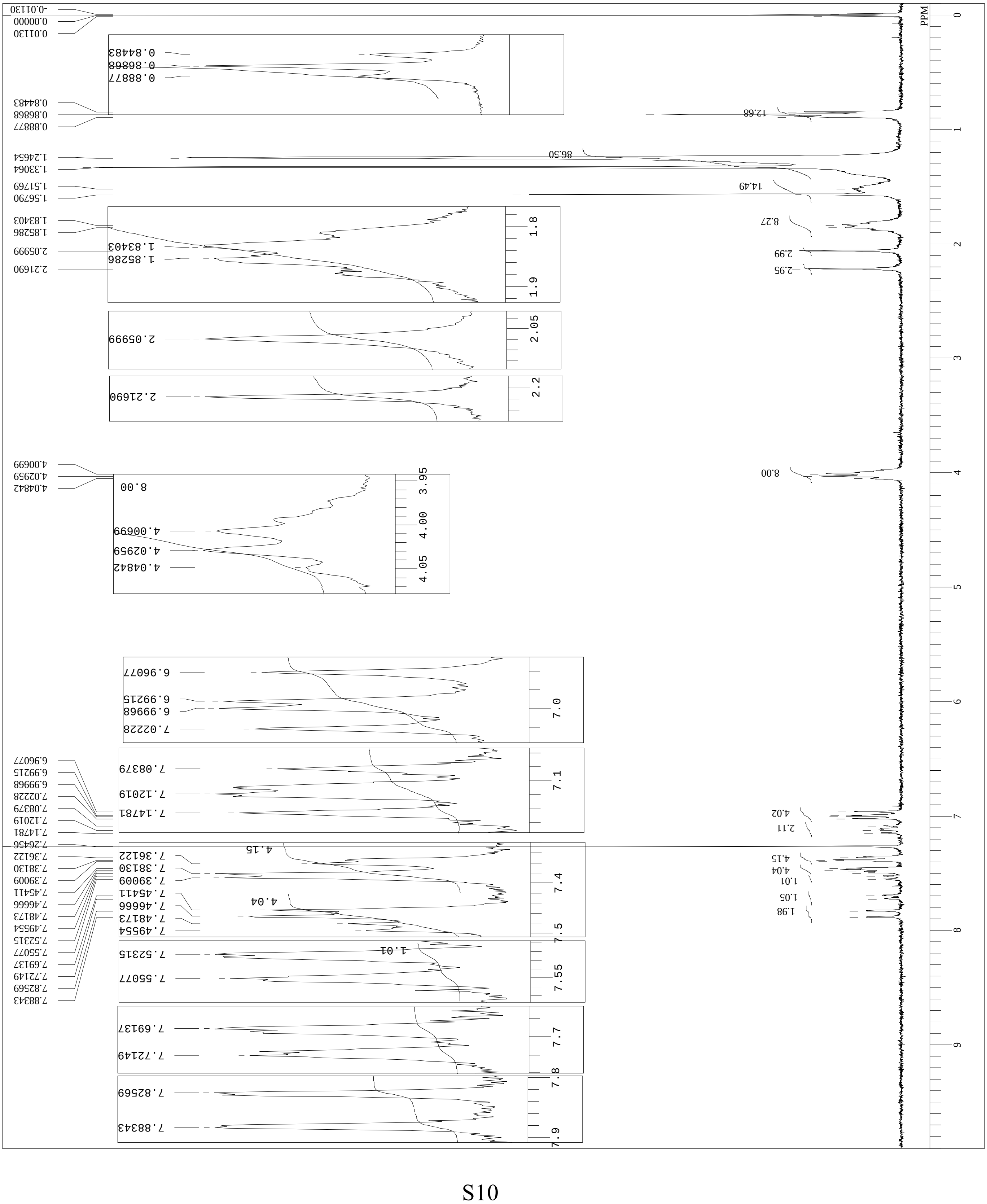

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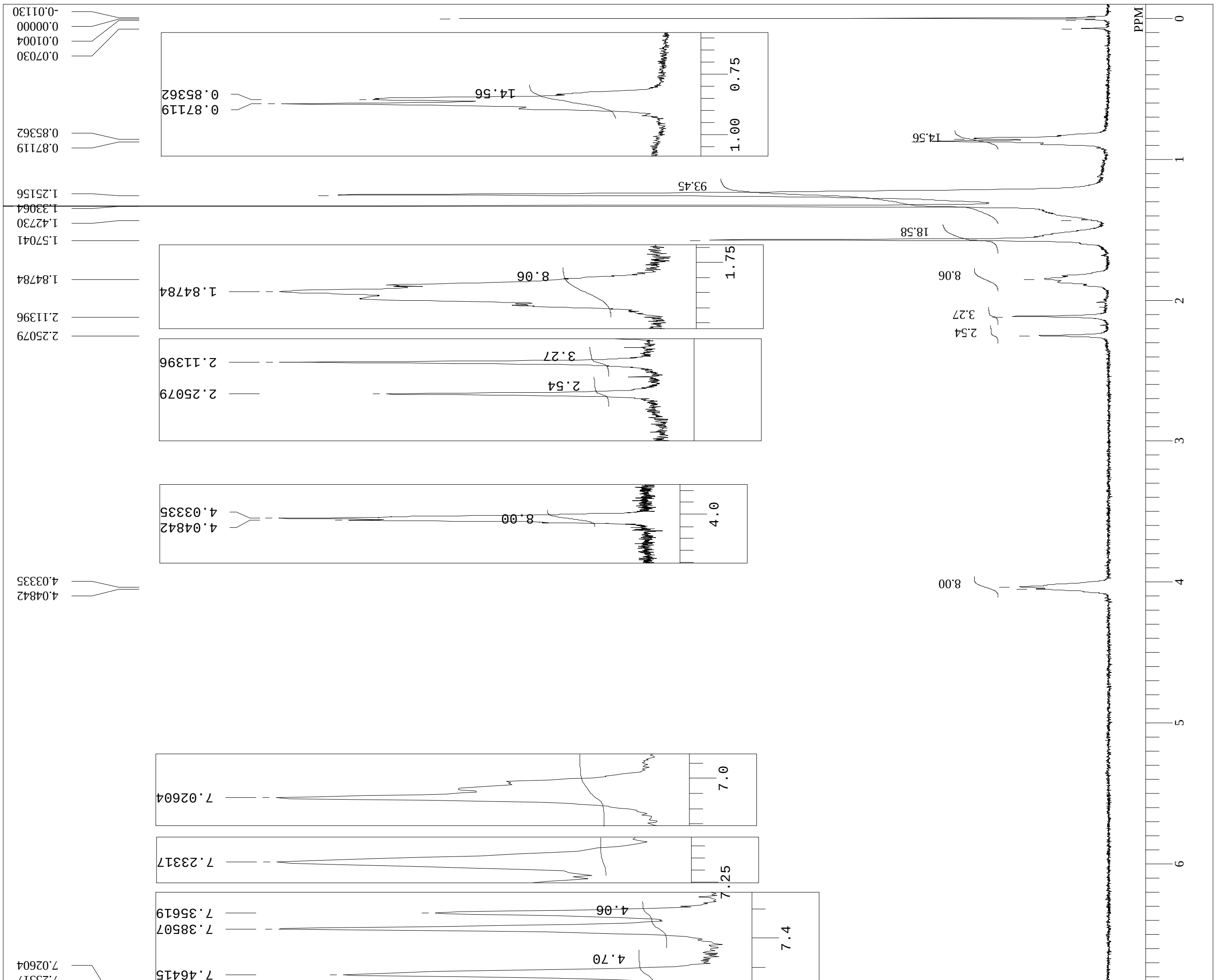
^{1}H NMR spectrum of **4o**
300 MHz, $CDCl_3$



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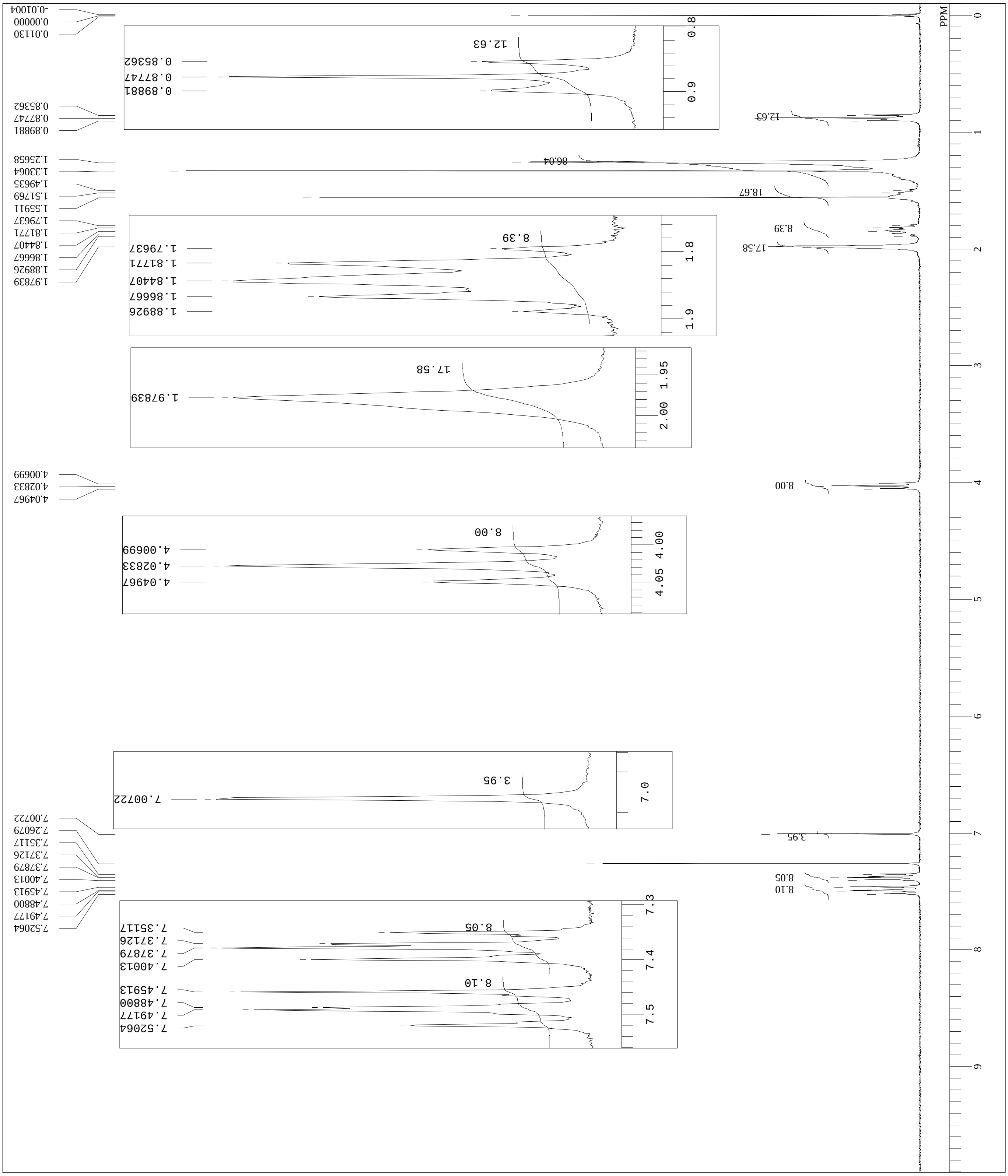
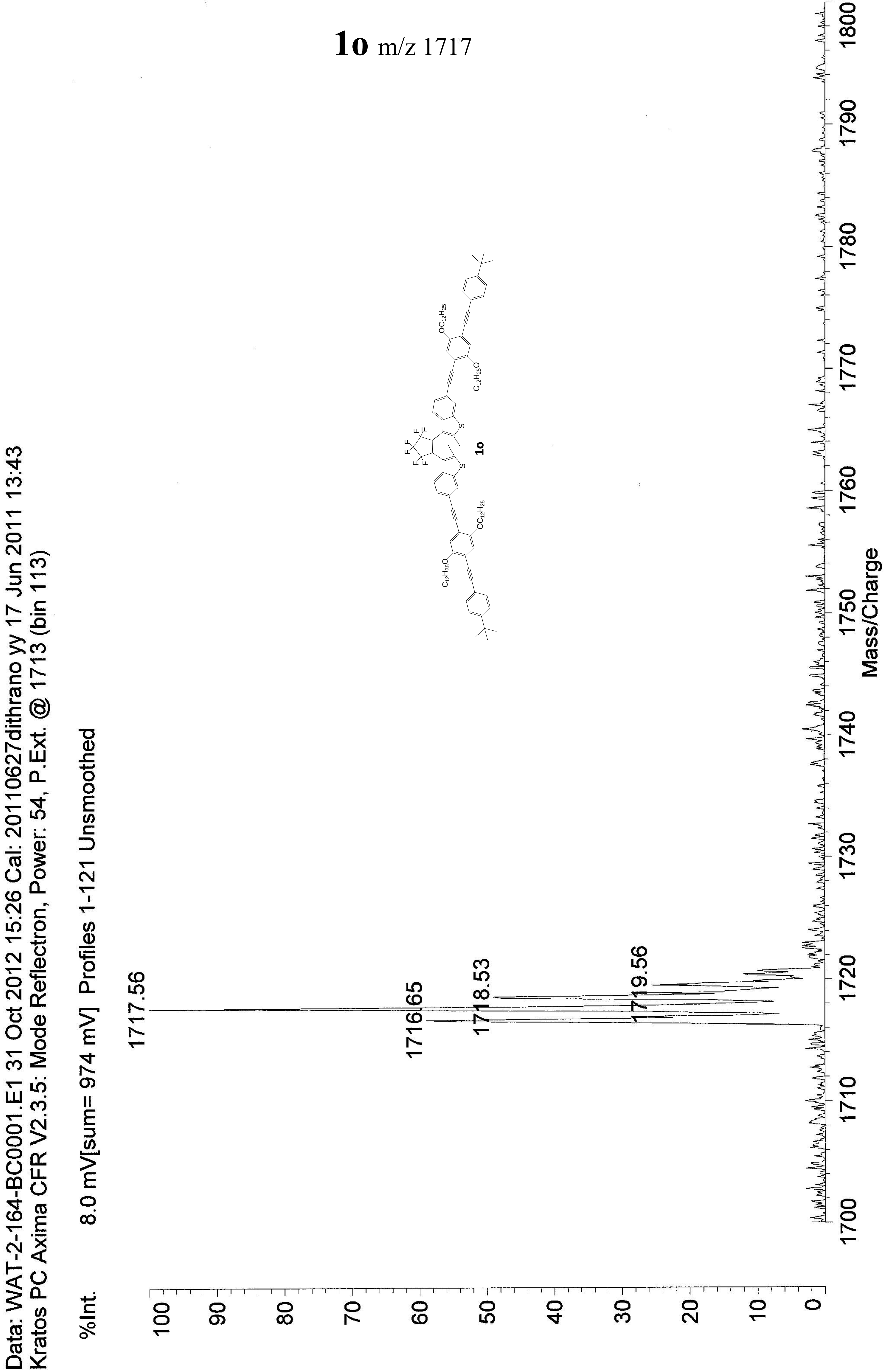
^{1}H NMR spectrum of **6**
300 MHz, $CDCl_3$



4. MALDI-TOF mass spectra



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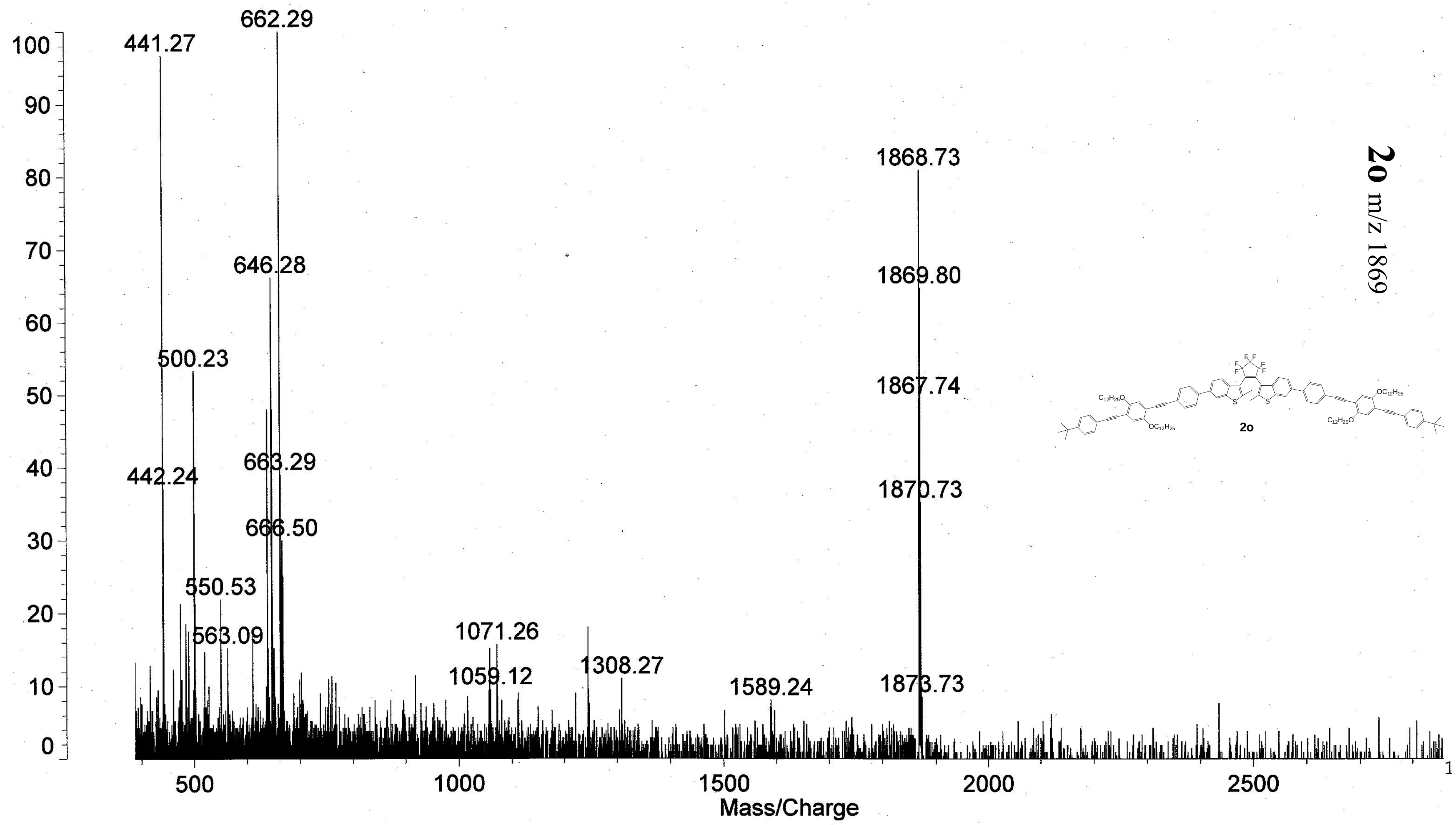

2o m/z 1869

3o m/z 1781

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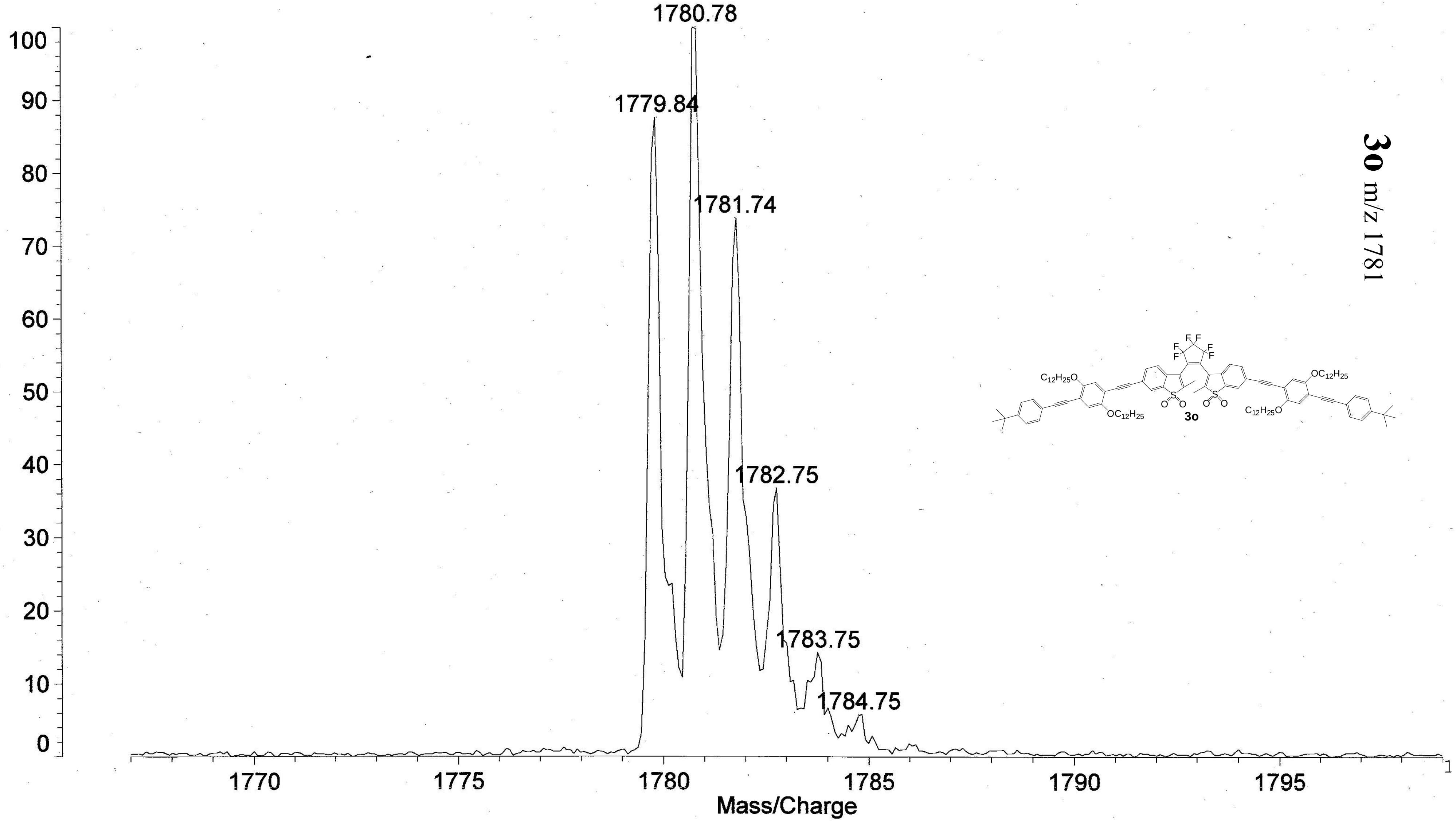

4o m/z 1933

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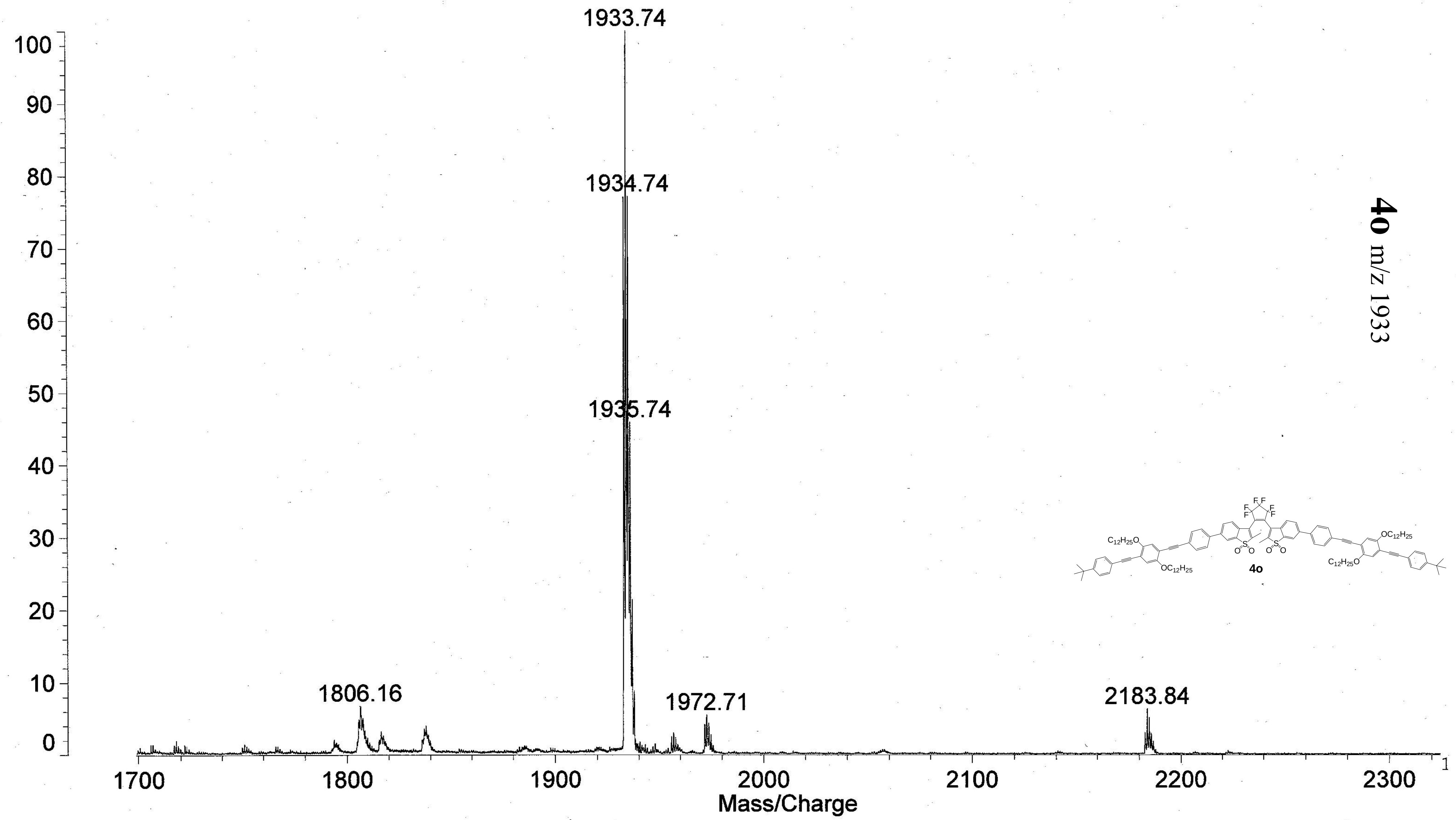
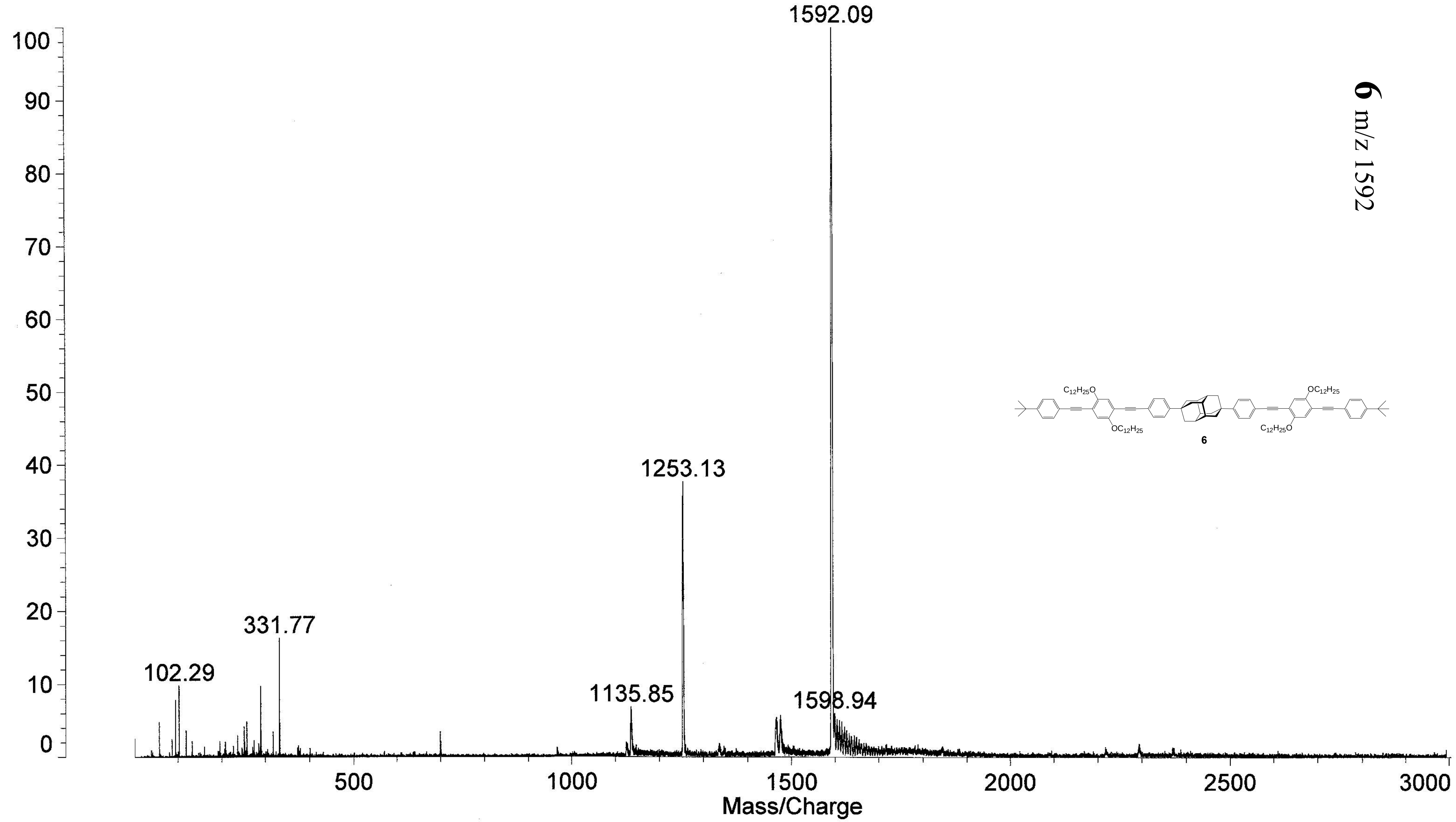
%Int. 557 mV[sum= 111317 mV] Profiles 1-200 Unsmoothed



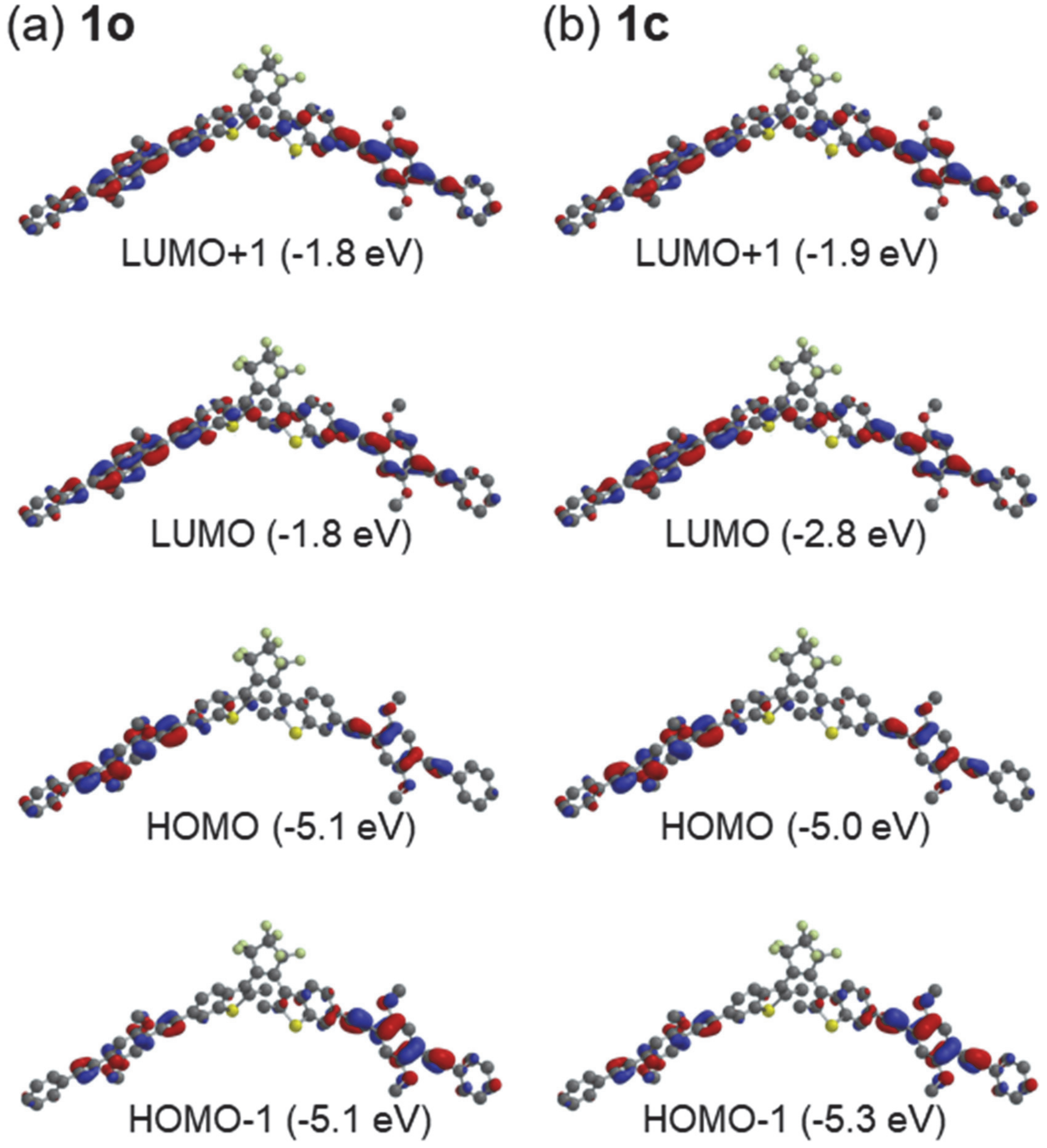
Data: WAT-2-148-Dia.0001.C22 15 Oct 2012 17:06 Cal: 111214_clfilm_PTIO 14 Dec 2011 16:25
Kratos PC Axima CFR V2.3.5: Mode Reflectron, Power: 62, P.Ext. @ 164 (bin 52)

%Int. 216 mV[sum= 10792 mV] Profiles 1-50 Unsmoothed

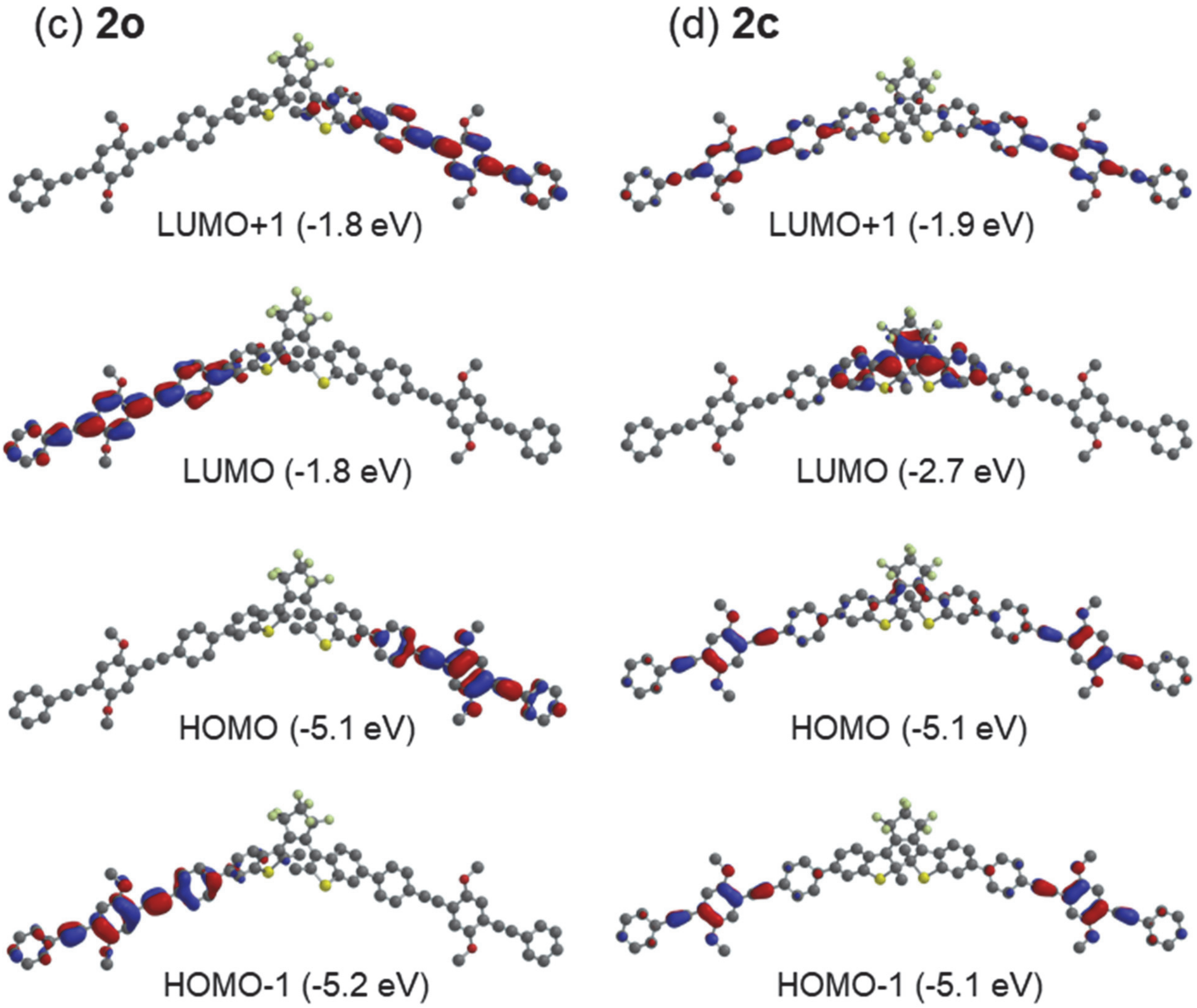


6 m/z 1592

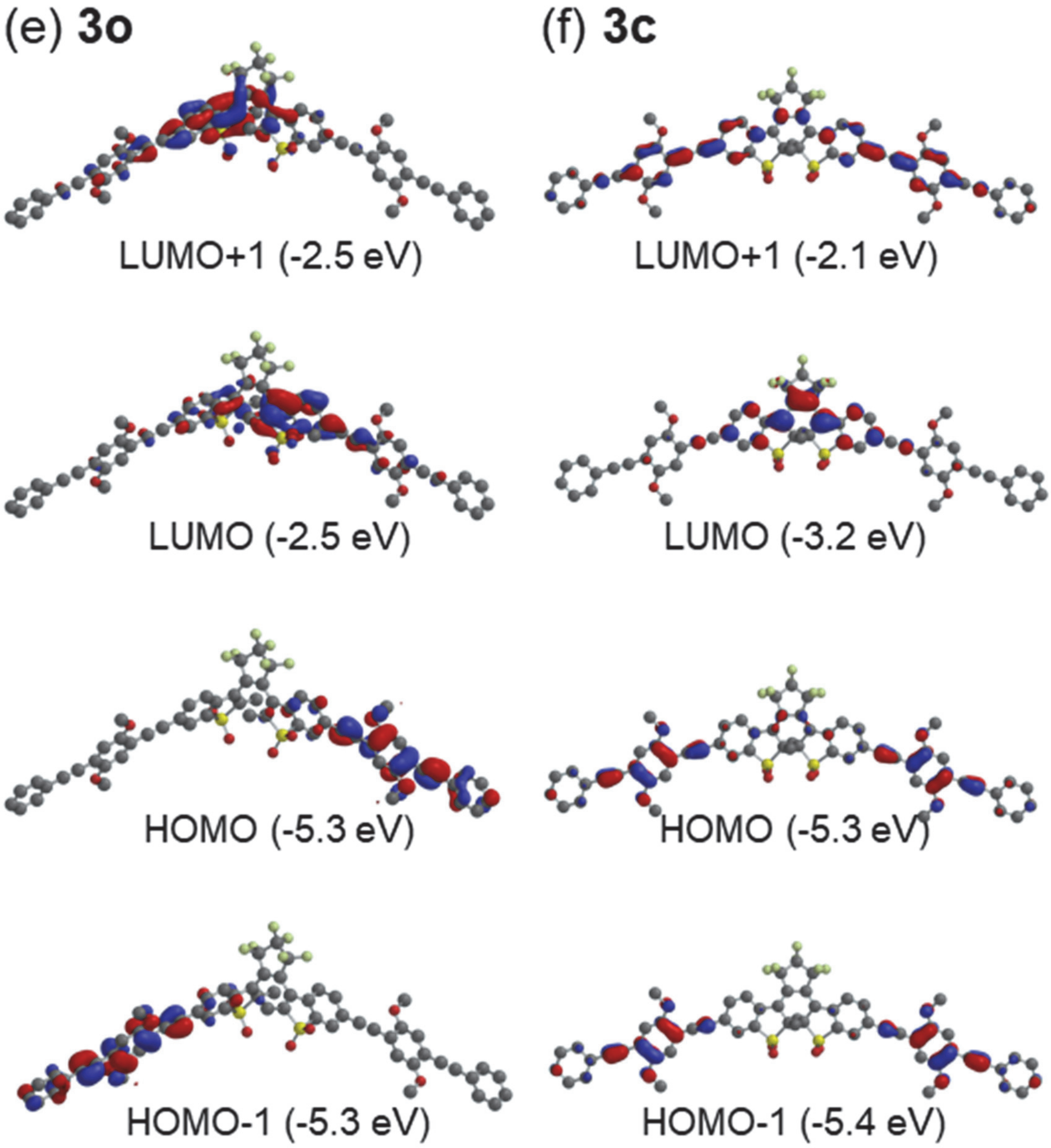
5. Frontier orbitals of DFT-optimized structures of 1o/1c, 2o/2c, 3o/3c and 4o/4c



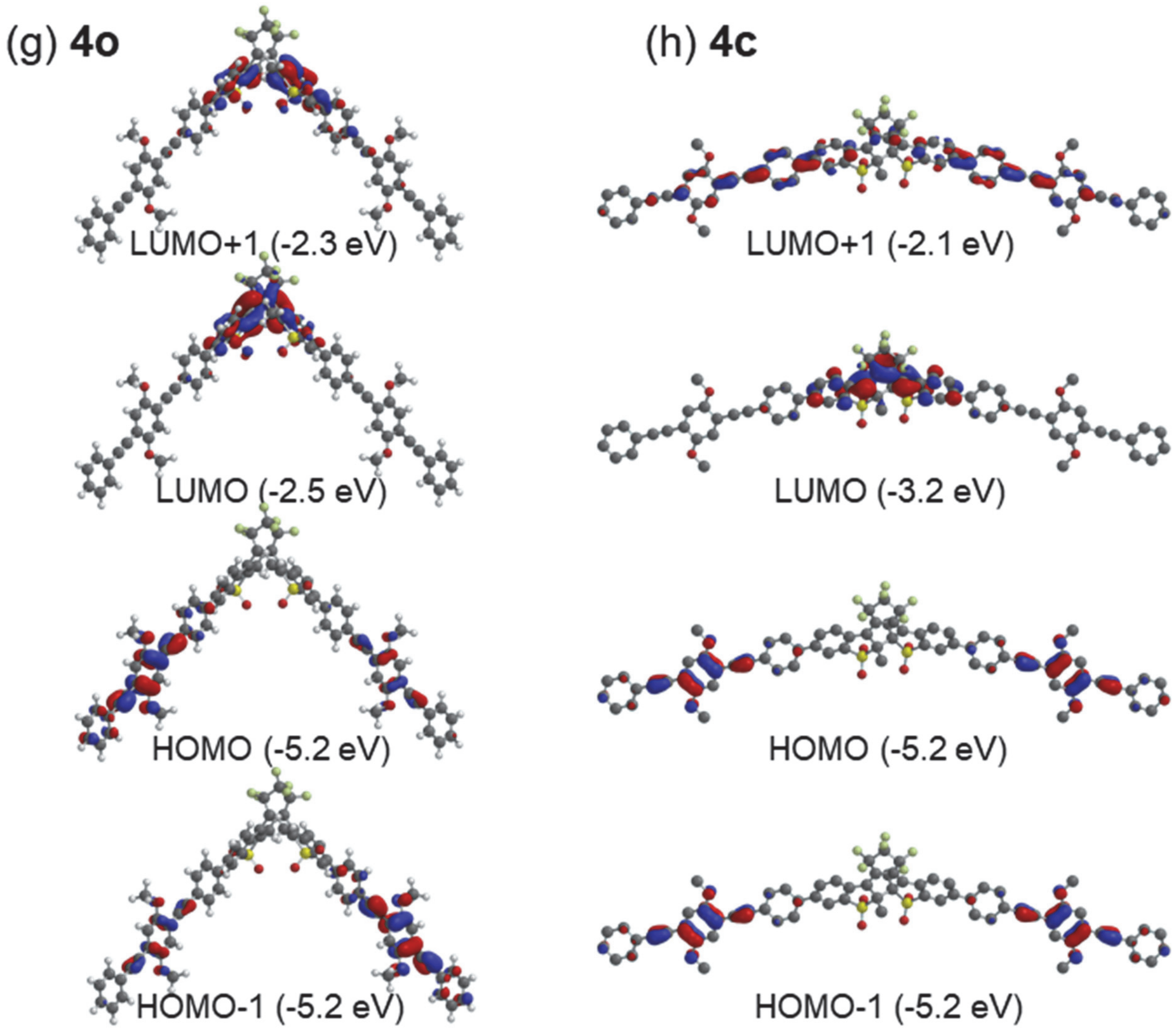
ESI-Fig. 1. Frontier orbitals of (a) **1o** and (b) **1c**



ESI-Fig. 1 (continued). Frontier orbitals of (c) **2o** and (d) **2c**

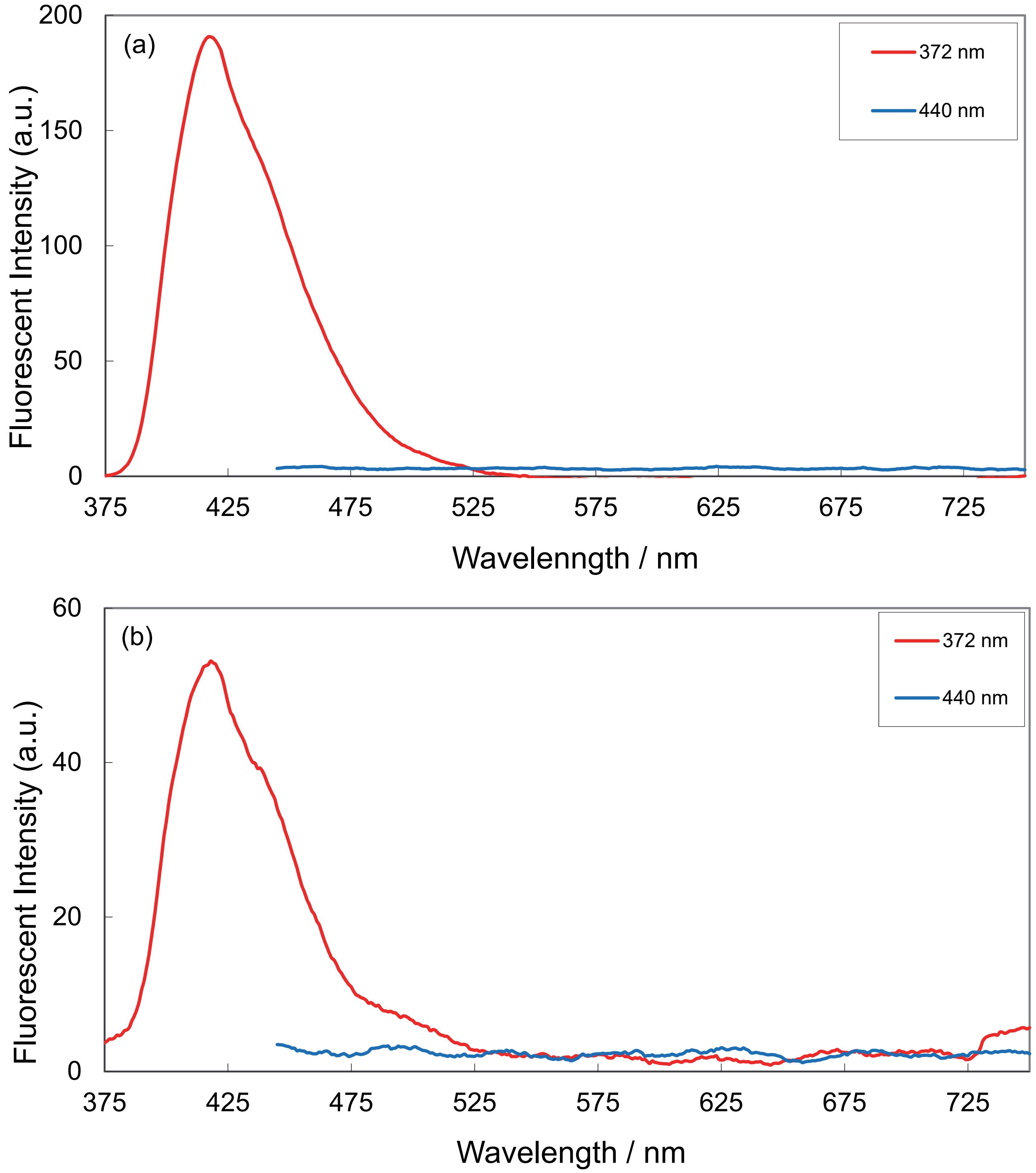

(e) **3o** (f) **3c**

ESI-Fig. 1 (continued). Frontier orbitals of (e) **3o** and (f) **3c**



ESI-Fig. 1 (continued). Frontier orbitals of (g) **4o** and (h) **4c**

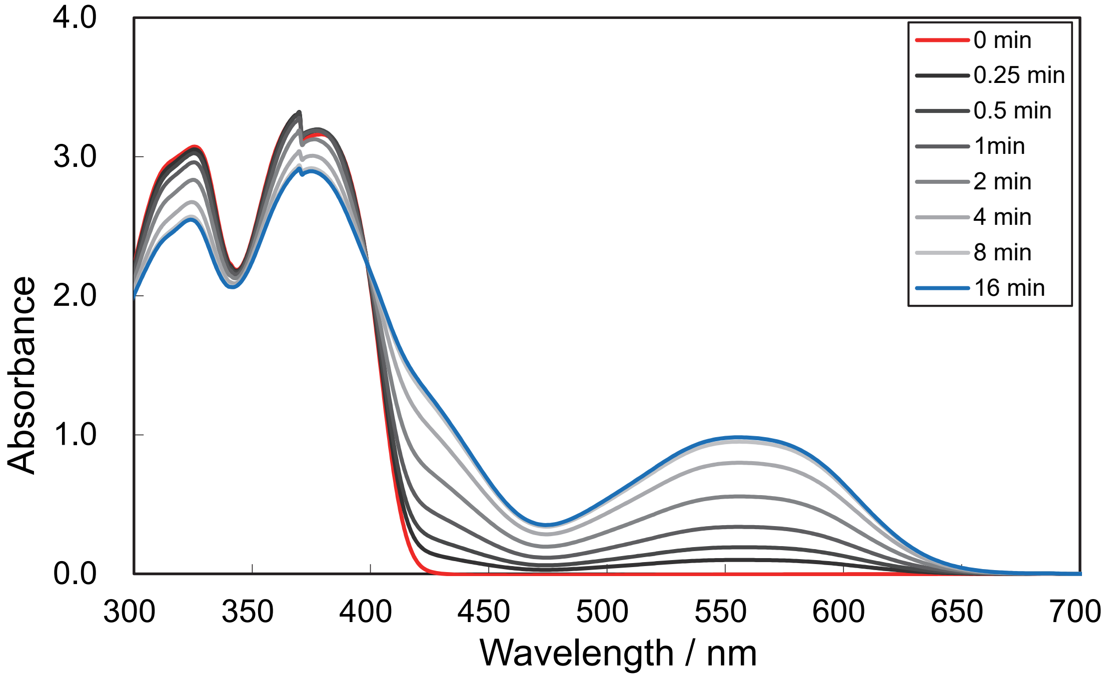
6. Fluorescence spectra of 1o and its photostationary state of 313-nm light irradiation



ESI-Fig. 2. Fluorescence spectra of (a) **1o** and (b) its photostationary state of 313-nm light irradiation.

Concentration: 1.15 x 10^{-6} mol dm^{-3} in toluene. Excitation: 372 nm (red) and 440 nm (blue).

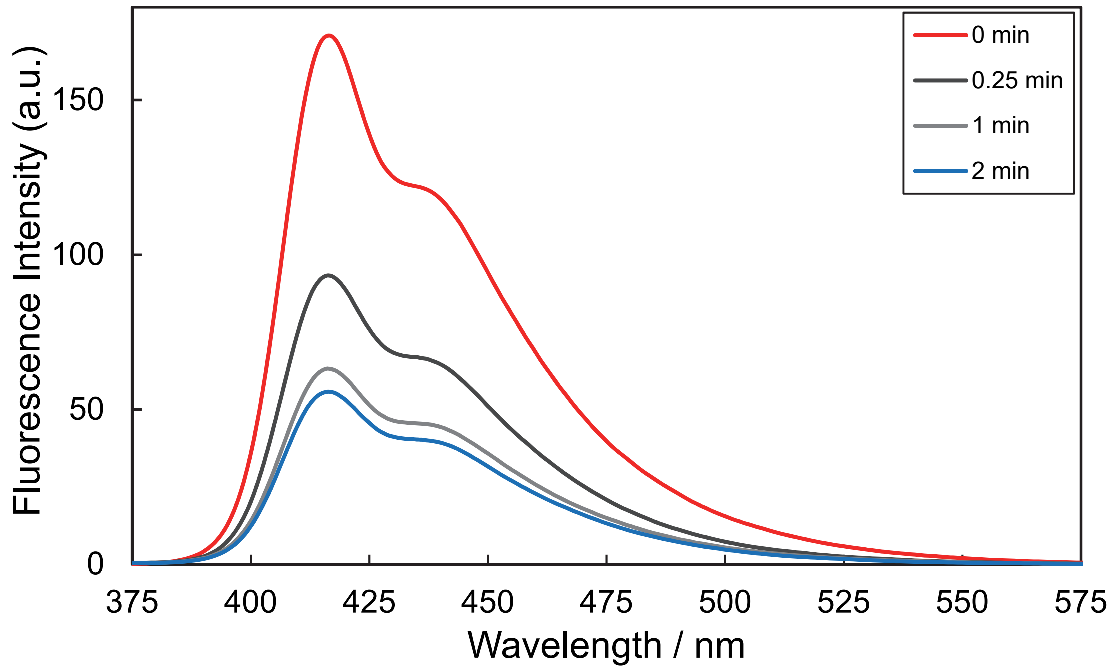
7. Absorption spectral change of 2o by 313-nm light irradiation in toluene



ESI-Fig. 3. Absorption spectral change of **2o** by UV irradiation in toluene.

Concentration: 4.14 x 10^{-5} mol dm^{-3}. Irradiation: 313 nm, 0.29 mW cm^{-2}.

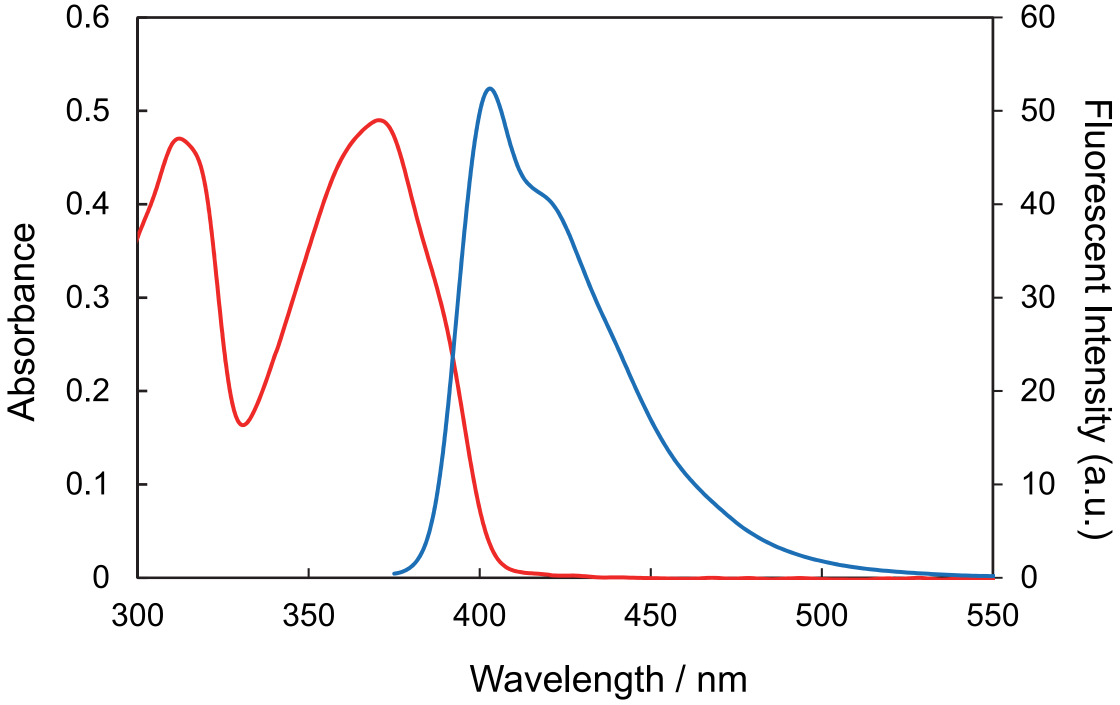
8. Fluorescence spectral change of 2o by 313-nm light irradiation in toluene



ESI-Fig. 4. Fluorescence spectral change of **2o** by UV irradiation in toluene.

Concentration: 1.66 x 10^{-6} mol dm^{-3}. Irradiation: 313 nm, 0.29 mW cm^{-2}. Excitation: 372 nm.

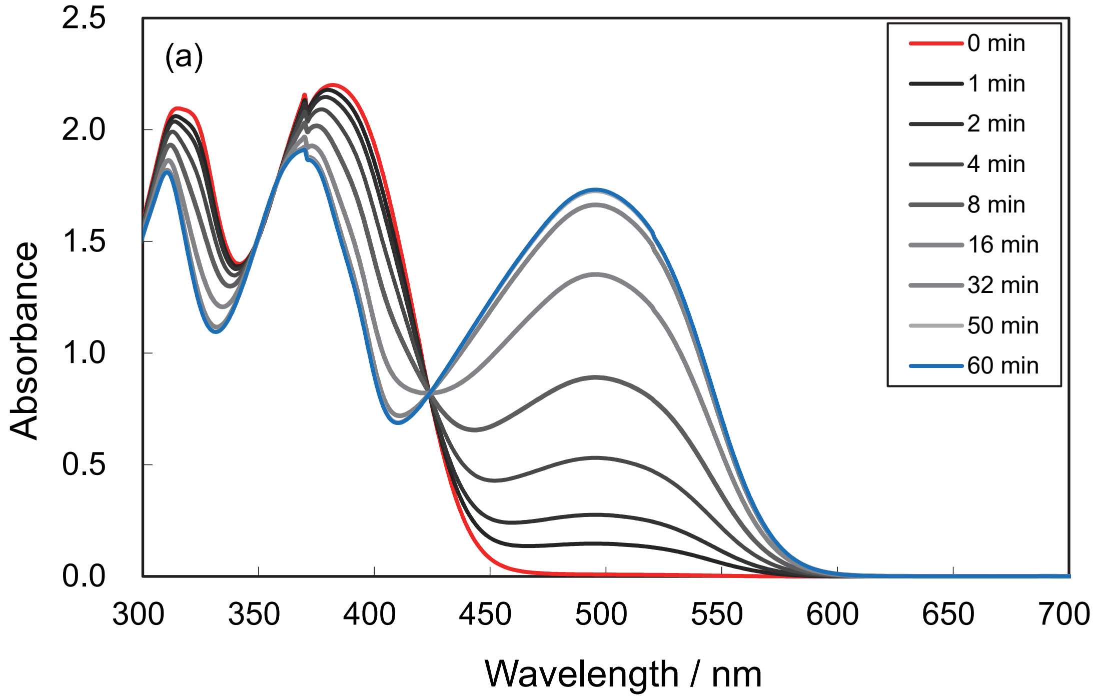
9. Absorption and fluorescence spectra of model compound 6 in toluene

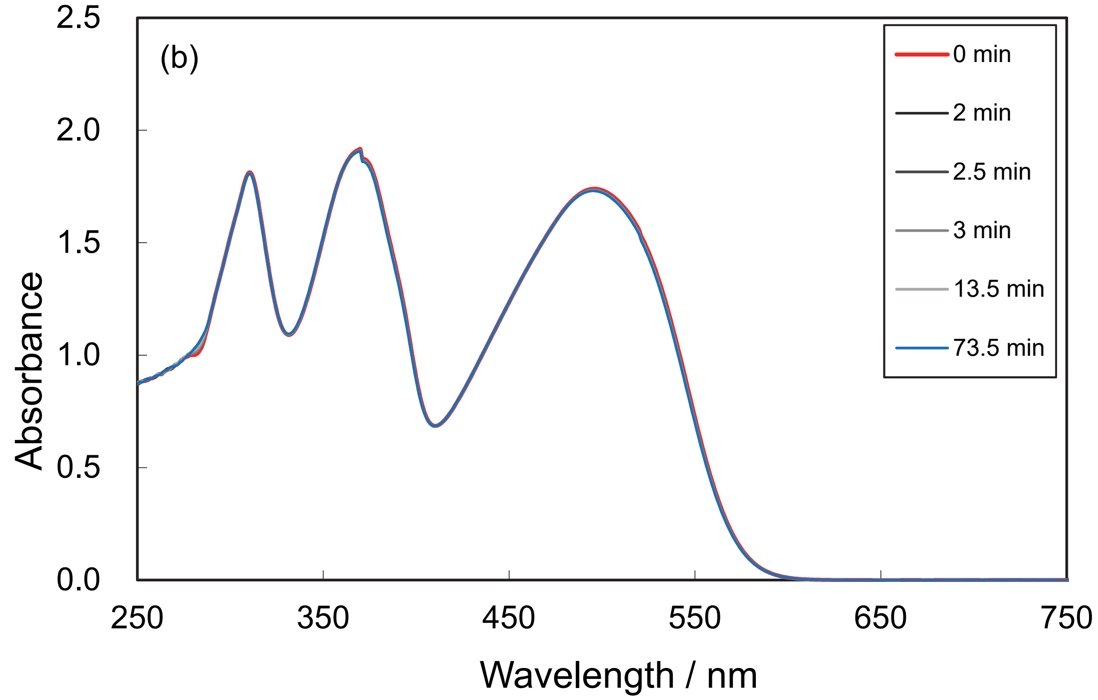


ESI-Fig. 5. Absorption spectrum and fluorescence spectrum of **6** in toluene.

Red: Absorption spectrum. Blue: Fluorescence spectrum excited by 372-nm light. Concentration: 6.16 x 10^{-6} mol dm^{-3}.

10. Absorption spectral change of 4o by UV and visible light irradiation in toluene

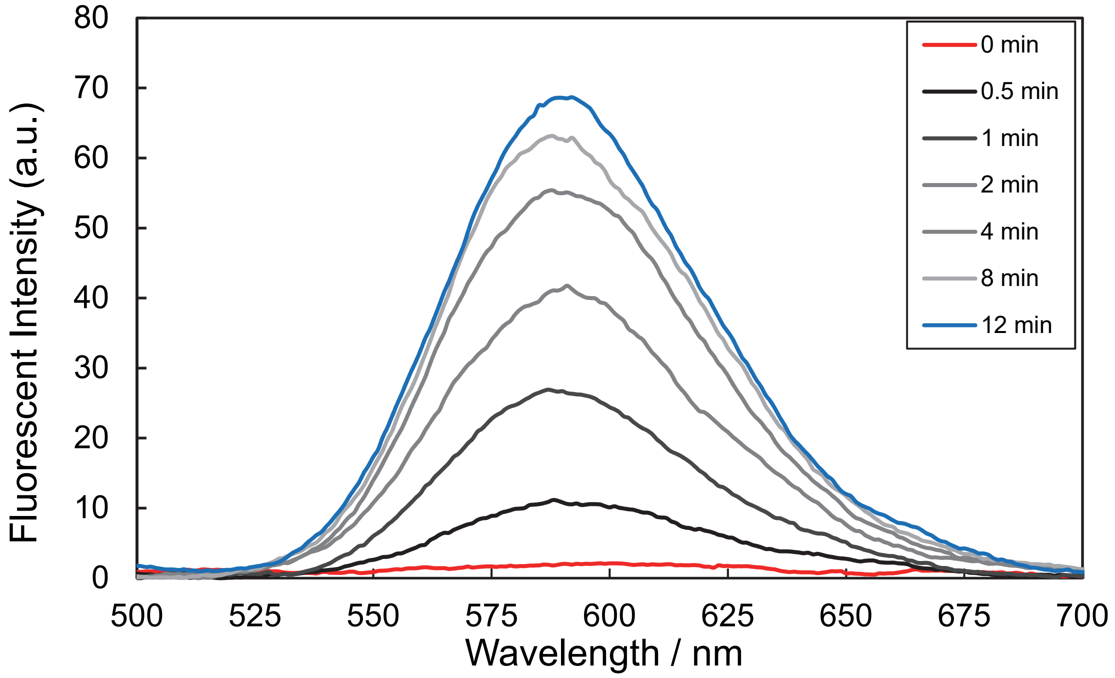




ESI-Fig. 6. Absorption spectral change of **4o** by UV and vis light irradiation in toluene.

Concentration: 3.00 x 10^{-5} mol dm^{-3}. (a) Irradiation: 313 nm, 0.31 mW cm^{-2}. (b) 506 nm to the resultant solution of (a), 3.0 mW cm^{-2}, 0 – 2 min; >490 nm, 50 mW cm^{-2}, 2 – 2.5 min; >490 nm, 100 mW cm^{-2}, 2.5 – 3 min: >490 nm, 800 mW cm^{-2}, 3 – 73.5 min.

11. Fluorescence spectral change of 4o by 313-nm light irradiation in toluene



ESI-Fig. 7. Spectral fluorescence change of **4o** by UV irradiation in toluene.

Concentration: 1.20 x 10^{-6} mol dm^{-3}. Irradiation: 313 nm, 0.30 mW cm^{-2}. Excitation: 495 nm.

12. Absorption spectral properties obtained by TD DFT calculations of 1o

ESI-Table 1. Absorption spectral properties obtained by TD DFT calculations of **1o**[a]

λ_{max}/nm	Strength	MO Component	
394	0.083	HOMO-1 to LUMO+2	59%
		HOMO to LUMO	25%
397	0.004	HOMO to LUMO+2	58%
		HOMO-1 to LUMO	24%
		HOMO to LUMO+1	11%
401	0.187	HOMO to LUMO	32%
		HOMO-1 to LUMO+1	26%
		HOMO to LUMO+1	19%
402	1.230	HOMO to LUMO+1	63%
		HOMO to LUMO	18%
405	2.711	HOMO-1 to LUMO	60%
		HOMO to LUMO+2	18%
		HOMO to LUMO	10%

a HOMO-1: -5.1 eV; HOMO: -5.1 eV; LUMO: -1.8 eV; LUMO+1; -1.8 eV.

13. Absorption spectral properties obtained by TD DFT calculations of 2o

ESI-Table 2. Absorption spectral properties obtained by TD DFT calculations of **2o**[a]

λ_{max}/nm	Strength	MO Component	
373	0.009	HOMO-1 to LUMO+2	74%
		HOMO-1 to LUMO+1	17%
379	0.002	HOMO-1 to LUMO+1	82%
388	0.161	HOMO to LUMO+2	79%
391	1.449	HOMO-1 to LUMO	72%
401	0.013	HOMO to LUMO	98%

a HOMO-1: -5.2 eV; HOMO: -5.1 eV; LUMO: -1.8 eV; LUMO+1; -1.8 eV.