Electric Supporting Information

A benzofuran[*b*]-fused BODIPY as an efficient sensitizer for photocatalytic hydrogen production

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Table of contents

Synthesis of 1 and 2

Ethyl 3-(4-bromophenyl)-5-phenyl-1*H*-pyrrole-2-carboxylate (5): To a solution of **3** (17.7 g, 61.6 mmol) in EtOH (300 mL) was added ethyl nitroacetate **4** (6.8 mL, 61.6 mmol) and Et_3N (0.85 mL, 6.16 mmol). The resultant mixture was refluxed overnight. After the reaction, it was extracted EtOAc and water. The organic layer was dried with Na_2SO_4 and was evaporated. The residue was chromatographed on silica gel (Wakogel C-300) using benzene and hexane (3:1 v/v) to give 25.4 g of Michael adduct (FAB-MS：*m/z* = 420 $[M+H]^+$, 422$[M+2+H]^+$) quantitatively, being then dissolved in dry EtOH (180 mL). To the solution was added formamidine sulfinic acid (22.9 g, 212 mmol). The resultant mixture was refluxed overnight. Atter the reaction, resultant solid was filtered off and washed with water. In this way, 5.2 g of **5** was obtained in 23% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm), 1.28 (3H, t, J = 7.08 Hz), 4.29 (2H, q, J = 7.11 Hz_e), 6.59 (1H, d, J = 3.10 Hz), 7.34 (1H, tt, J = 7.42, 1.38 Hz), 7.44 (2H, tt, J = 7.72, 1.60 Hz), 7.48 (2H, dt, J = 8.70, 2.04 Hz), 7.51 (2H, dt, J = 8.65, 2.02 Hz), 7.57–7.60 (2H, m), 9.30 (1H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) ; 160.9, 135.5, 134.0, 132.2, 131.2, 130.9, 130.8, 129.2, 129.2, 128.8, 121.2, 118.6, 109.7, 60.5, 14.3. HRMS (APCI): calcd for $C_{19}H_{16}BrNO_2$, 370.0437, 344.0418, found 370.0431 $[M + H]^+$, 372.0412 $[M+H+2]^+$.

3-(4-Bromophenyl)-5-phenyl-1*H*-pyrrole-2-carboxylic acid (6): To a solution of **5** (5.18 g, 14.0 mmol) in EtOH (370 mL) was added 2M NaOH aqueous solution (95 mL). The resultant solution was refluxed for 2 h. After the reaction, adding 35% HCl aqueous solution caused solidification that was filtered off and washed with water. 3.2 g of **6** was obtained in 68% yield.

^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm), 6.76 (1H, d, J = 2.70 Hz), 7.28 (1H, tt, J = 7.40, 1.34 Hz), 7.39 (2H, tt, J = 7.72, 1.53 Hz), 7.52 (2H, dt, J = 8.85, 2.00 Hz), 7.55 (2H, dt, J = 8.75, 1.98 Hz), 7.80–7.90 (2H, m), 11.9 (1H, s), 12.5 (1H, s). ^{13}C NMR (126 MHz, DMSO-d_6) δ (ppm) , 161.8, 135.3, 134.7, 131.4, 131.0, 130.6, 130.4, 128.6, 127.3, 125.3, 119.8, 119.3, 109.6. HRMS (APCI): calcd. for $C_{17}H_{12}BrNO_2$, 342.0124, 344.0104. found 342.0117 $[M + H]^+$, 344.0095 $[M +H+2]^+$

3-(4-Bromophenyl)-5-phenyl-1*H*-pyrrole-2-carbaldehyde (7): Compound **6** (7.5 g, 21.9 mmol) was dissolved in CF_3COOH (180 mL) under N_2 atmosphere and resultant solution was stirred at 50 °C for 30 min. After adding trimethyl orthoformate (40 mL, 766 mmol) into the solution, the mixture was stirred at 50 °C over night. And then the reaction solution was neutralized with $NaHCO_3$ aqueous solution and extracted with dichloromethane. The organic phase was dried with Na_2SO_4 and evaporated. The residue was chromatographed on silica gel (Wakogel C-300) using dichloromethane as eluent to give 4.17 g of **7** in 57% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 6.70 (1H, d, J = 2.80 Hz), 7.38–7.43 (3H, m), 7.47 (2H, tt, J = 7.58, 1.62 Hz), 7.60 (2H, dt, J = 8.40, 2.19Hz), 7.62–7.64 (2H, m), 9.50 (1H, br), 9.61 (1H, s). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 178.9, 139.0, 136.8, 132.4, 132.0, 130.6, 130.6, 130.2, 129.3, 129.1, 129.0, 125.3, 122.3, 108.9. HRMS (APCI): calcd. for $C_{17}H_{12}BrNO$, 326.0175, 328.0155. found 326.0169 $[M + H]^+$, 328.0152 $[M+H+2]^+$.

Difluoroboron chlated 2-(*Z*)-((3-(4-bromophenyl)-5-phenyl-1*H*-pyrrol-2-yl)methylele)-1*H*-benzofuro[3,2-*b*] pyrrole (9): After a solution of 1*H*-benzofuro[3,2-*b*]pyrrole-2-carboxylic acid **8** (1.10 g, 5.47 mmol) was stirred at 50 °C for 40 min, **7** (1.80 g, 5.52 mmol) and $POCl_3$ (30 mL, 329 mmol) was added to the solution and resultant

mixture was stirred for 3 h. After quenching the reaction by adding saturated $NaHCO_3$ aqueous solution, the resultant solution was partitioned between water and dichloromethane. The organic phase was dried with Na_2SO_4 aqueous solution and was evaporated to give solid that was then dissolved in dry dichloromethane (240 mL). To the solution were added Et_3N (8.2 mL, 59 mmol) and $BF_3 \cdot Et_2O$ (11 mL, 88 mmol) under N_2 atmosphere. The mixture was stirred for 6 h. After quenching the reaction by adding saturated $NaHCO_3$ aqueous solution, the resultant solution was extracted with dichloromethane and water. The organic phase was dried with Na_2SO_4 aqueous solution and then evaporated. The residue was washed with water and chromatographed on silica gel (Wakogel C-300) using dichloromethane and hexane (2:3 v/v) as eluent to give 1.20 g of **9** in 42% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 6.62 (1H, s), 6.73 (1H, s), 7.29–7.32 (2H, m), 7.41–7.44 (3H, m), 7.47 (1H, ddd, J = 7.75, 7.12, 1.32 Hz), 7.50−7.55 (3H, m), 7.65 (2H, dt, J = 9.05, 2.18 Hz), 8.01–8.04 (2H, m), 8.08 (1H, d, J = 7.55 Hz, H_a). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 164.8, 158.3, 132.3, 132.2, 132.1, 130.7, 130.4, 130.4, 130.0, 129.5, 128.4, 128.2, 124.3, 124.2, 123.3, 116.8, 112.8, 103.6. HRMS (APCI): calcd for $C_{27}H_{16}BBrF_2N_2O$, 512.0506, 514.0484. found 512.0531 $[M]^+$, 514.0525 $[M+2]^+$.

Difluoroboron chlated 2-(*Z*)-((3-(4-formylphenyl)-5-phenyl-1*H*-pyrrol-2-yl)methylene)-1*H*-benzofuro[3,2-*b*] pyrrole (11): To a solution of **9** (1.2 g, 2.3 mmol) and 2-(4,4,5,5-tetramethy-1,3,2-dioxaborolan-2-yl)-3-hexylthiophene-5-carbaldehyde **10** (1.9 g, 5.8 mmol) in dry THF (80 mL) were added 2.0 M K_2CO_3 aqueous solution (23 mL). The resultant solution was degassed by three freeze–pump–thaw cycles, then $Pd(PPh_3)_4$ (0.78 g, 0.67 mmol) was added to it. The mixture was refluxed overnight and then cooled to room temperature. After removing Pd, it was extracted with CH_2Cl_2 and water. The organic phase was dried with Na_2SO_4 and then evaporated. The residue was chromatographed on silica gel (Wakogel C-300) using benzene and hexane (4:1 v/v) as eluent to give 0.68 g of **11** in 47% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 0.88 (3H, t, J = 6.92 Hz), 1.24−1.31 (4H, m), 1.68 (2H, quint, J = 7.66 Hz), 2.75 (2H, t, J = 7.85 Hz), 6.64 (1H, s), 6.79 (1H, s), 7.31 (1H, ddd, J = 7.42, 6.95, 1.05 Hz), 7.42 (1H, s), 7.43 (1H, d, J = 8.00 Hz), 7.47 (1H, ddd, J = 7.75, 7.12, 1.30 Hz), 7.52−7.57 (3H, m), 7.61 (2H, dd, J = 6.38, 2.10 Hz), 7.65 (2H, dd, J = 8.35 Hz), 7.70 (1H, s), 8.04–8.06 (2H, m), 8.09 (1H, d, J = 7.65 Hz), 9.90 (1H, s). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm), 182.9, 165.1, 147.5, 144.5, 143.5, 141.7, 140.8, 138.6, 137.5, 137.4, 134.1, 133.7, 132.2, 130.7, 130.0, 129.8, 129.5, 129.5, 129.5, 129.3, 128.5, 128.4, 124.3, 124.2, 118.6, 116.8, 112.8, 103.6, 30.8, 30.5, 29.1, 28.9, 28.9, 28.7, 22.6, 22.5, 14.1, 14.0. HRMS (APCI): calcd for $C_{38}H_{31}BF_2N_2O_2S$, 629.2247, found 629.2285 $[M+H]^+$.

Difluoroboron chlated 2-(*Z*)-((3-(1-(3-hexyl-5-(2-carboxy-2-cyanovinyl)thiophen))-2-yl)-phenyl-4-yl)-5-phenyl-1*H*-pyrrol-2-yl)methylene)-1*H*-benzofuro[3,2-*b*]pyrrole 1 ; Under N_2 condition, a solution of **10** (1.09 g, 1.74 mmol), 2-cyanoaceteic acid (0.355 g, 4.17 mmol) and ammonium acetate (0.383 g, 4.97 mmol) in acetic acid (100 mL) was refluxed for 2 h. After quenching with water, the solution was extracted with CH_2Cl_2. The organic layer was washed with water, dried with Na_2SO_4 and evaporated. The residue was chromatographed on silica gel (Wakogel C-300) using a gradient of AcOH (0–0.5% v/v) in CH_2Cl_2 as an eluent. Obtained solid was reprecipitated with THF/MeOH. In this way, 0.467 g of **1** was obtained with 39% yield.

^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 0.84 (3H, t, J = 6.80 Hz), 1.23−1.33 (6H, m), 1.63 (2H, quint, J = 7.54 Hz), 2.76 (2H, t, J = 7.70 Hz), 7.19 (1H, s), 7.23 (1H, s), 7.45 (1H, t, J = 7.78 Hz), 7.55−7.63 (4H, m), 7.70 (1H, d,

J = 8.35 Hz), 7.73 (2H, dd, J = 6.45, 1.80 Hz), 7.87–7.89 (2H, m), 8.02 (2H, s), 8.08 (2H,dt, J =6.55, 1.72 Hz), 8.49 (1H, s), 13.8 (1H, s). ^{13}C NMR (126 MHz, THF-d_8) δ (ppm) 166.0, 163.9, 159.6, 155.4, 147.9, 146.6, 141.6, 141.2, 135.7, 134.9, 134.8, 133.4, 131.3, 130.6, 130.6, 130.6, 130.6, 130.5, 130.4, 130.4, 130.3, 129.0, 124.9, 124.7, 119.6, 117.9, 116.4, 113.5, 104.6, 100.4, 32.6, 31.5, 30.0, 29.3, 23.5, 14.4. HRMS (ESI-MS)：calcd for $C_{41}H_{32}BF_2N_3O_3S$, 695.2238, found 695.2244 $[M]^+$; Elemental analysis: Calc. For $C_{41}H_{32}BF_2N_3O_3S \cdot 1.2\ H_2O$: C, 68.66; H, 4.83; N, 5.86, Found: C, 68.64; H, 4.50; N, 5.91

Difluoroboron chlated (E)-2-cyano-3-(Z)-2-(3,5-dimethyl-1H-pyrrol-2-yl)ethylidene)-3,5-dimethyl-2H-pyrrol-4-yl)acrylic acid 2; Under N_2 condition, a solution of **12** (0.931 g, 3.37 mmol), 2-cyanoaceteic acid (0.714 g, 8.40 mmol) and ammonium acetate (0.843 g, 10.9 mmol) in acetic acid (180 mL) was refluxed for 2 h. After quenching with water, the solution was separated between CH_2Cl_2 and 1M HCl aqueous solution. The organic layer was dried with Na_2SO_4 and evaporated. The residue was washed with CH_2Cl_2, solved in THF and chromatographed on silica gel (Wakogel C-300) using a gradient of AcOH (0–0.8% v/v) in CH_2Cl_2 as an eluent. 0.351 g of **2** was obtained with 34% yield after washing with THF.

^{1}H NMR (500 MHz, THF-d_8): δ (ppm) 2.32 (1H, s) , 2.42 (1H, s), 2.53 (1H, s), 2.57 (1H, s), 6.27 (1H, s), 7.59 (1H, s), 8.21 (1H, s), 11.9 (1H, s).^{13}C NMR (126 MHz, DMSO-d_6) δ (ppm) 163.2, 161.9, 153.2, 148.1, 146.0, 138.7, 135.5, 131.7, 123.3, 122.0, 121.6, 116.4, 104.9, 14.6, 13.9, 11.5, 11.1. HRMS (APCI)：calcd. For $C_{17}H_{16}BF_2N_3O_2$, 343.1301, found 343.1298 $[M]^+$. Elemental analysis: calcd. For $C_{17}H_{16}BF_2N_3O_2$: C, 59.51; H, 4.70; N, 12.25, Found: C, 59.46; H, 4.83; N, 12.22

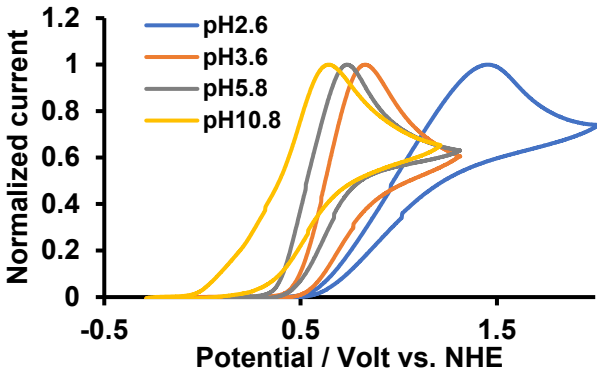

Fig. S1. Cyclic voltammogram of ascorbic acid in several pH containing phosphate buffer solution as an electrolyte.

Table S1. Theoretical data for compound 1. (Calculated by B3LYP/6-31G(d,p) level using Gaussian 16W).

$\lambda_{(calcd.)}$ / nm	Calculated assignment [a]				f (Calcd.)
534.14	HOMO	→	LUMO	(87.2%)	0.6091
	HOMO	→	LUMO+1	(12.2%)	
483.22	HOMO	→	LUMO+1	(81.4%)	0.3075
	HOMO	→	LUMO	(10.0%)	
	HOMO−1	→	LUMO	(7.2%)	
459.47	HOMO−1	→	LUMO	(79.0%)	0.2418
	HOMO−2	→	LUMO	(12.0%)	
	HOMO	→	LUMO+1	(3.5%)	
433.75	HOMO−2	→	LUMO	(82.7%)	0.1416
	HOMO−1	→	LUMO	(9.2%)	
386.57	HOMO−1	→	LUMO+1	(88.0%)	0.6734
	HOMO−5	→	LUMO	(3.1%)	

[a] Data given in parentheses are 2 × (CI coefficient)^2 × 100%

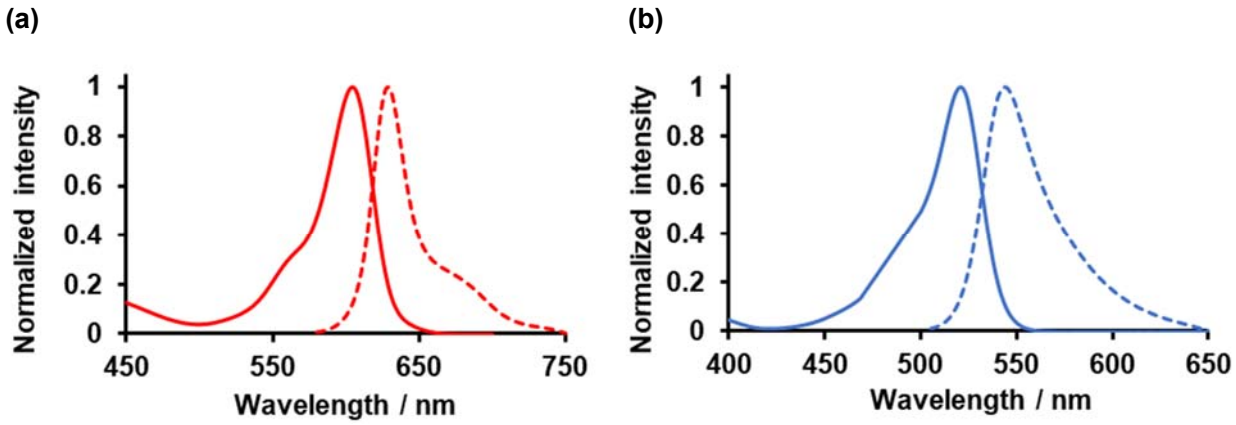

Fig. S2. Normalized absorption (blue solid line) and fluorescence (dashed line) spectra of **1** (a) and **2** (b) in THF.

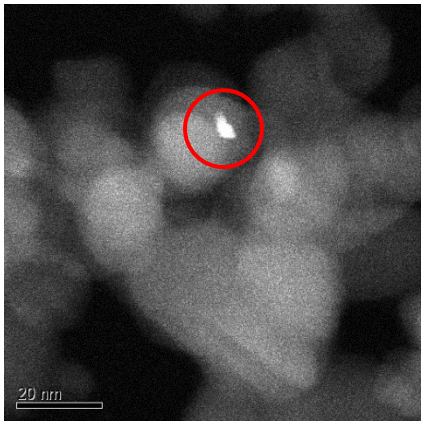

Fig. S3. High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images of P25/Pt.

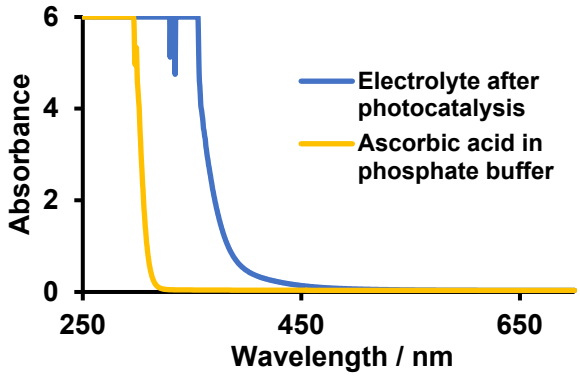

Fig. S4. UV-vis absorption spectrum of electrolyte (blue solid line) after 30 h photocatalysis using P25/Pt/**1** and ascorbic acid in phosphate buffer solution (orange dashed line).

Fig. S5. Photographs of P25/Pt/**1** before (left) and after (right) 30 h of photoirradiation.

Fig. S6. Photographs of P25/Pt/**2** before (left) and after (right) 10 h of photoirradiation.

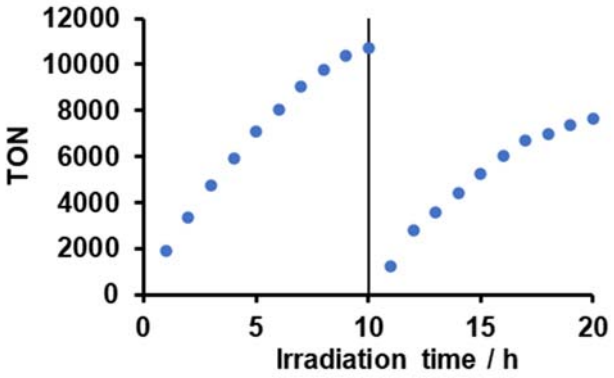

Fig. S7. Cycling test of H_2 evaluation for P25/Pt/**1** (6.0 mg) in the presence of ascorbic acid in phosphate buffer (pH 7.0) under 100 mW cm^{-2} light irradiation ($\lambda > 400$ nm).

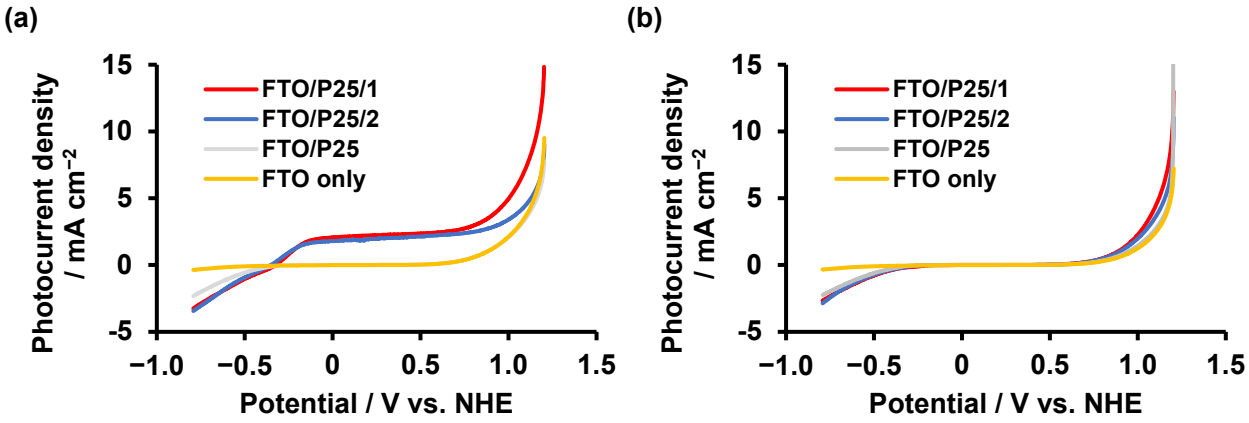

Fig. S8. Liner sweep voltammetry of FTO/P25/**1** and FTO/P25/**2** with photoirradiation (a) and under dark conditions (b). Scan rate = 0.05 V s^{-1}.

Table S2. Photoluminescence decay profiles of **1** in the presence and absence of ascorbic acid in MeOH.

	τ_1 / ns	A_1 /%	τ_2 / ns	A_2 /%	$<\tau>^a$
1 plus AA	0.082	34.9	2.15	65.1	2.11
1	0.10	37.6	4.99	62.4	4.93

[a]The $<\tau>$ values of were determined with $<\tau> = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$.

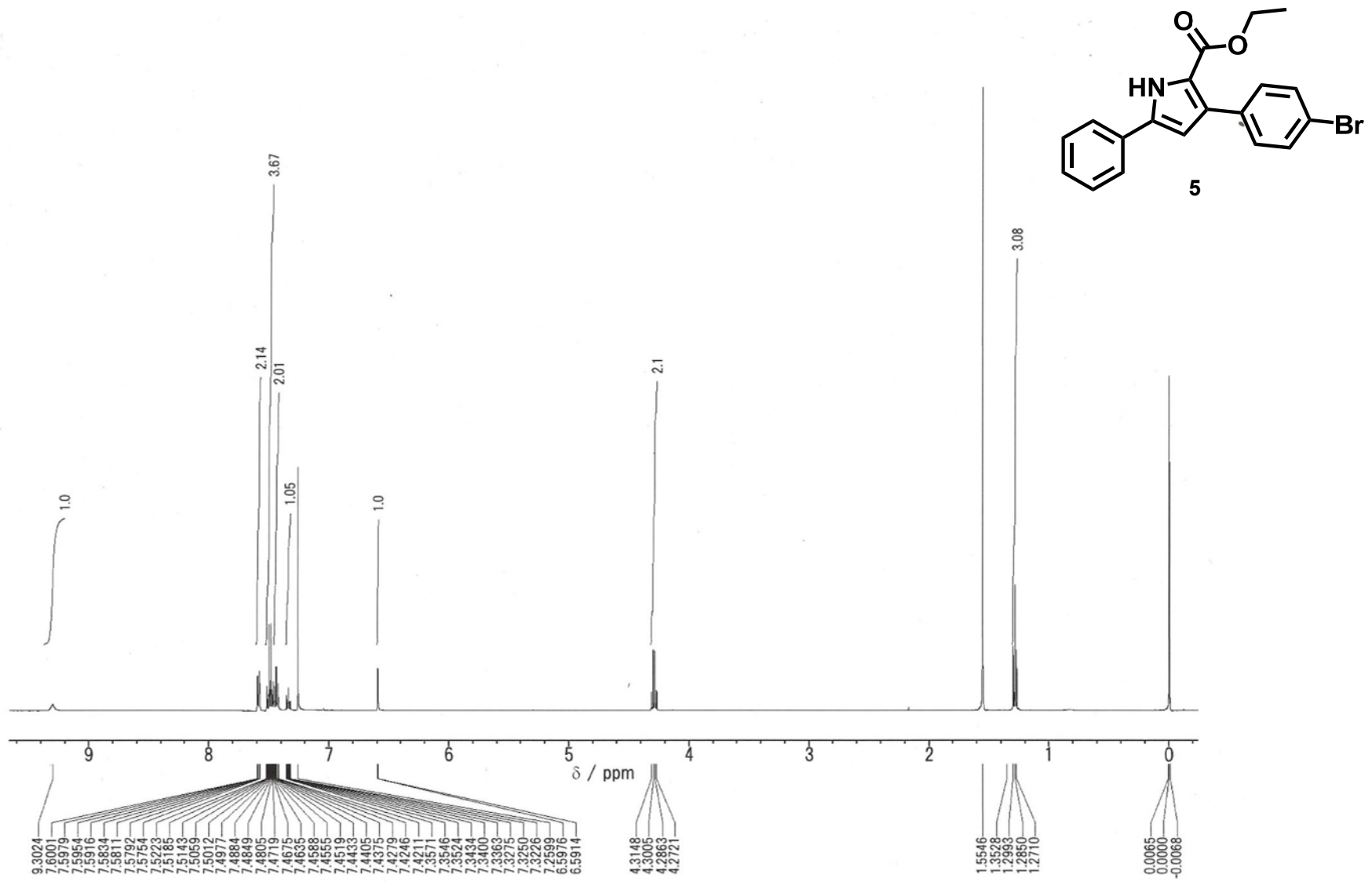

Fig. S9. ^{1}H NMR spectrum of **5** (500 MHz) in $CDCl_3$.

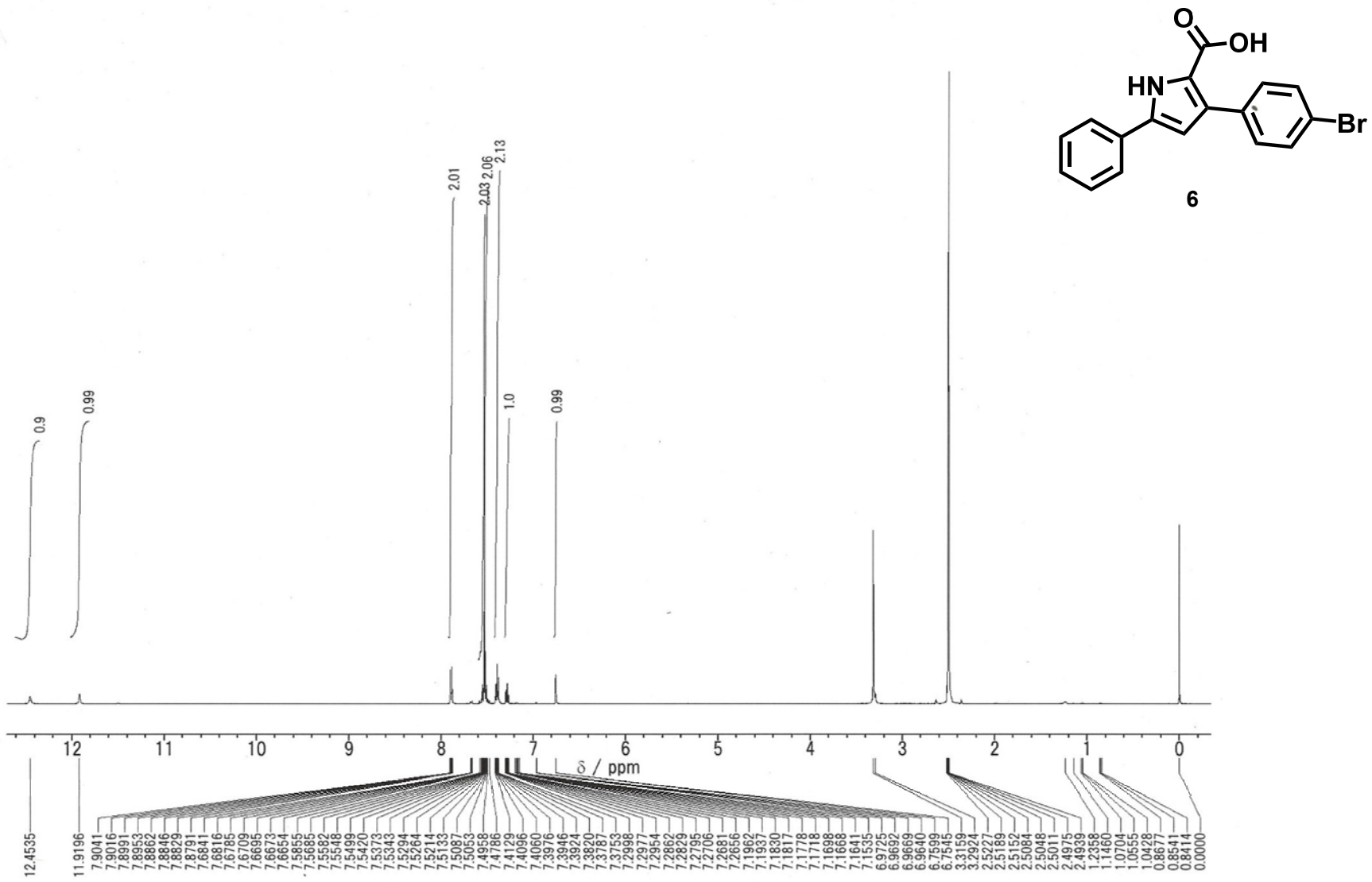

Fig. S10. [1]H NMR spectrum of **6** (500 MHz) in DMSO-d_6.

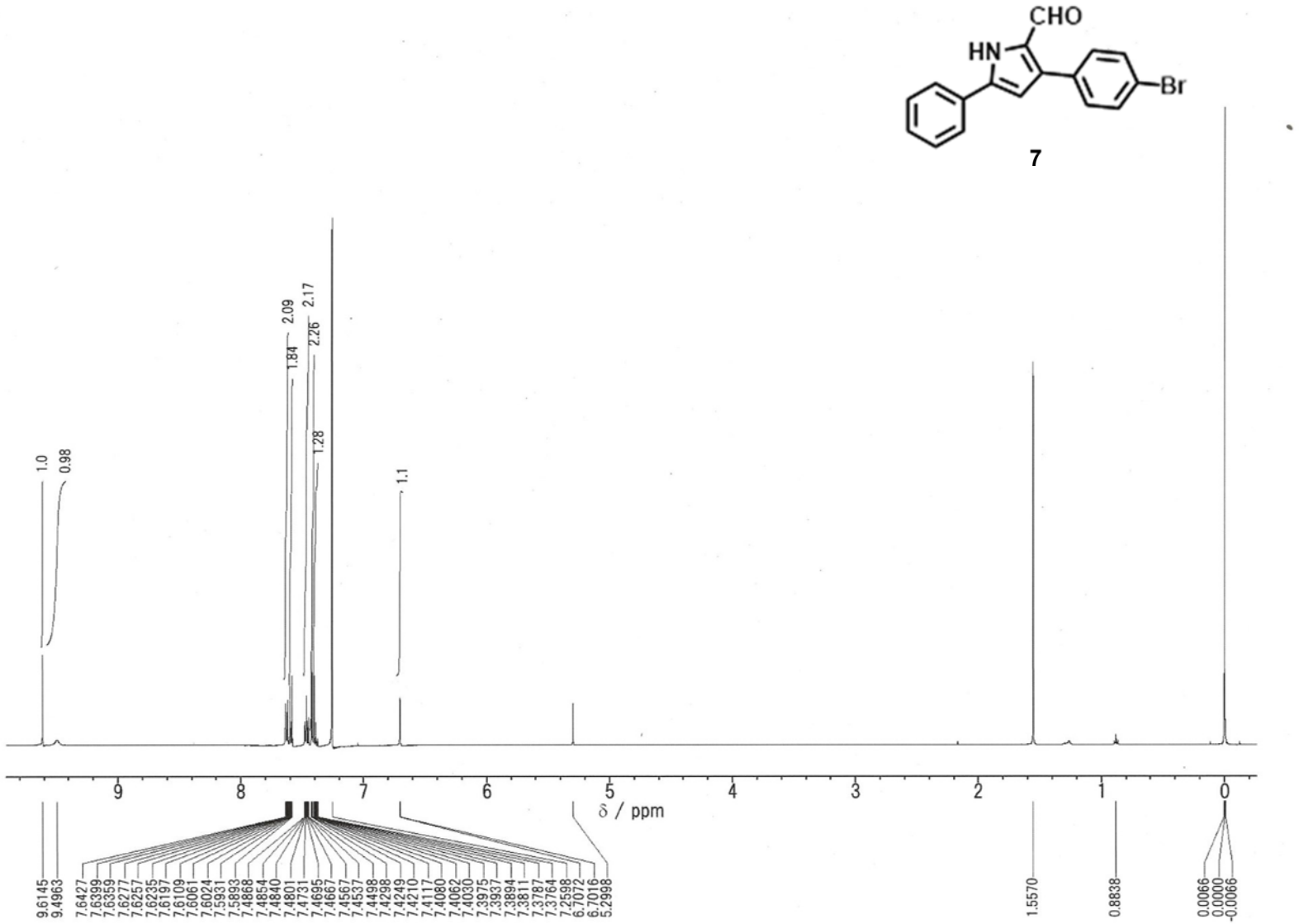

Fig. S11. ^{1}H NMR spectrum of **7** (500 MHz) in $CDCl_3$.

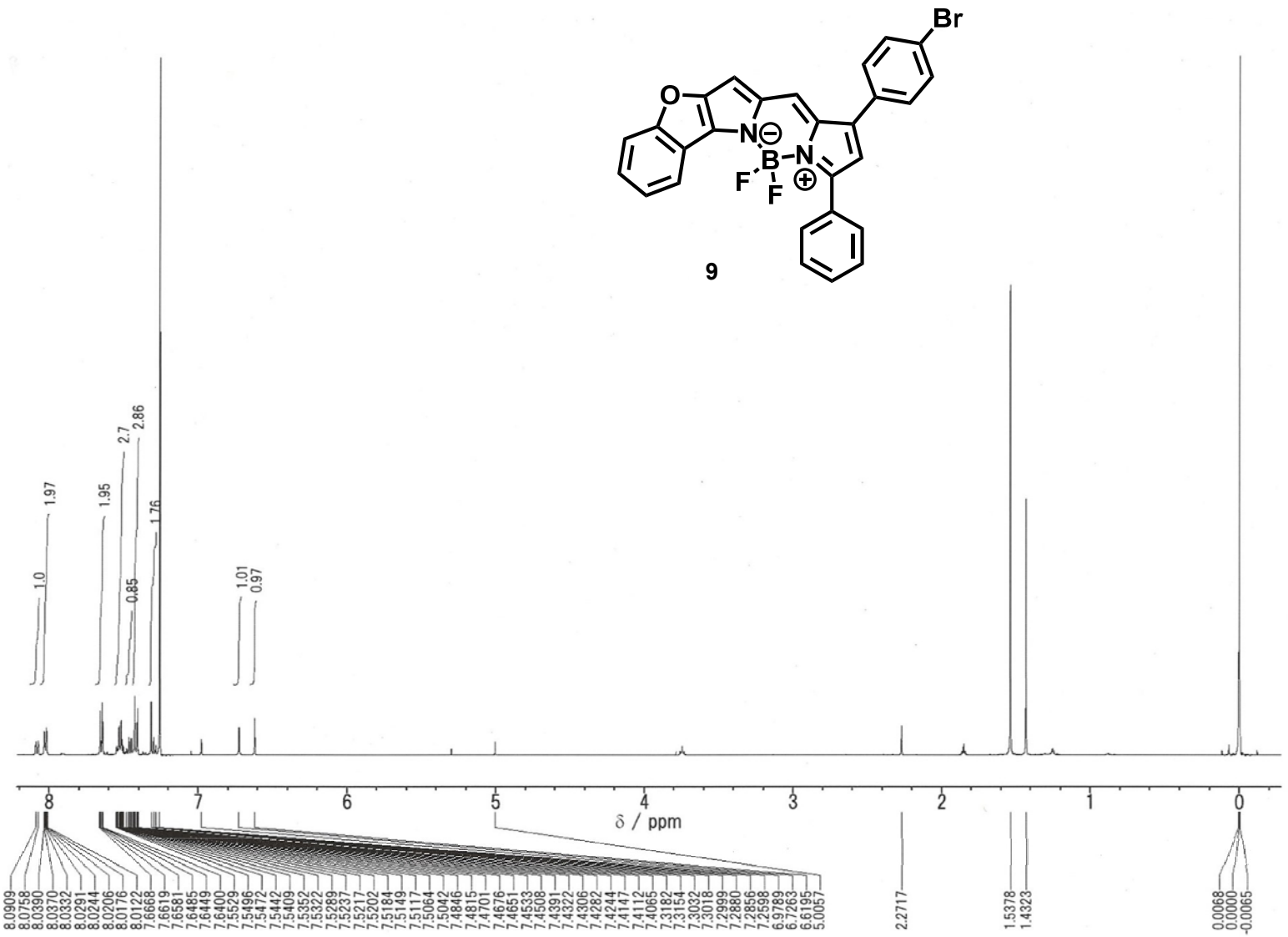

Fig. S12. ^{1}H NMR spectrum of **9** (500 MHz) in $CDCl_3$.

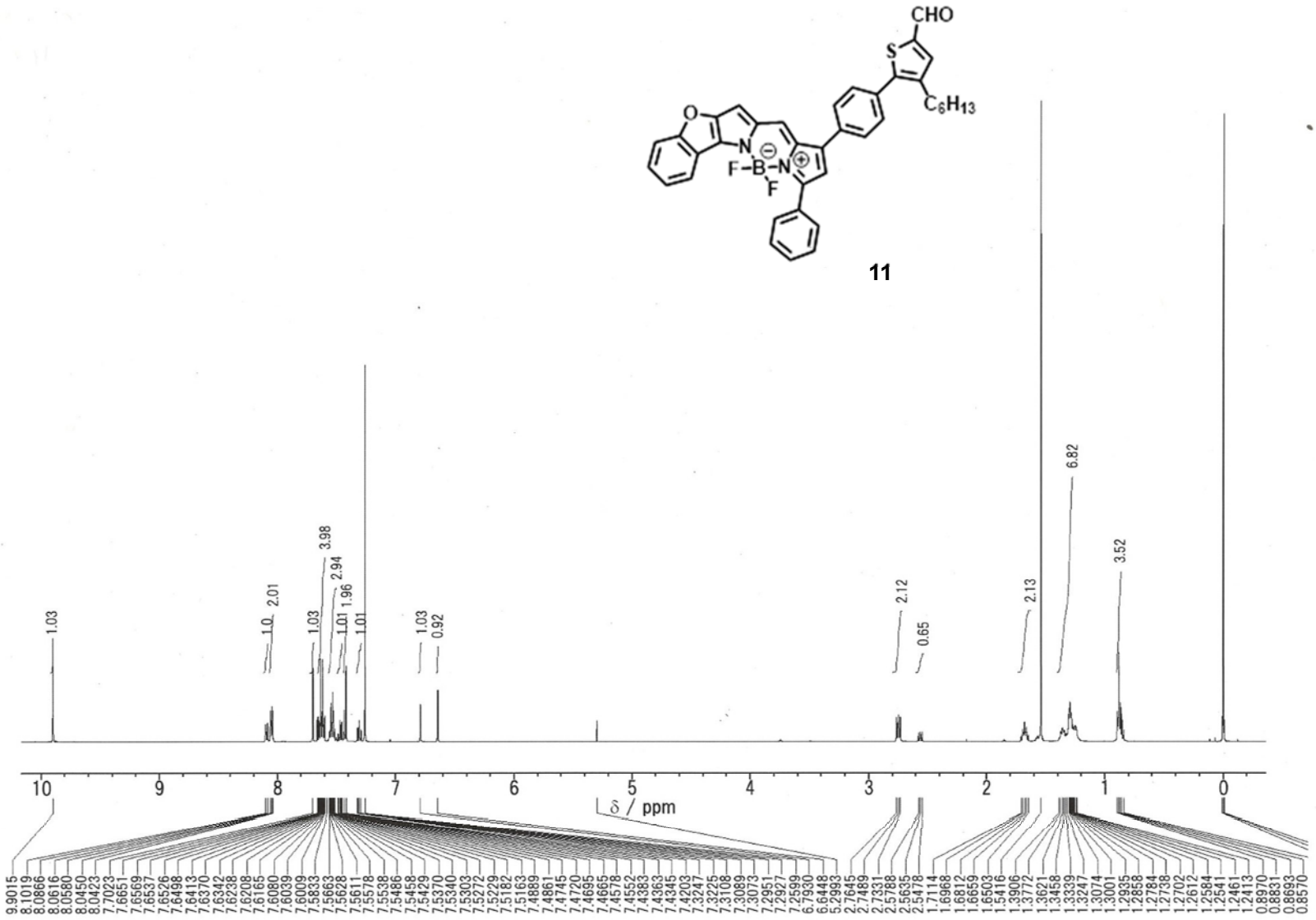

Fig. S13. ^{1}H NMR spectrum of **11** (500 MHz) in $CDCl_3$.

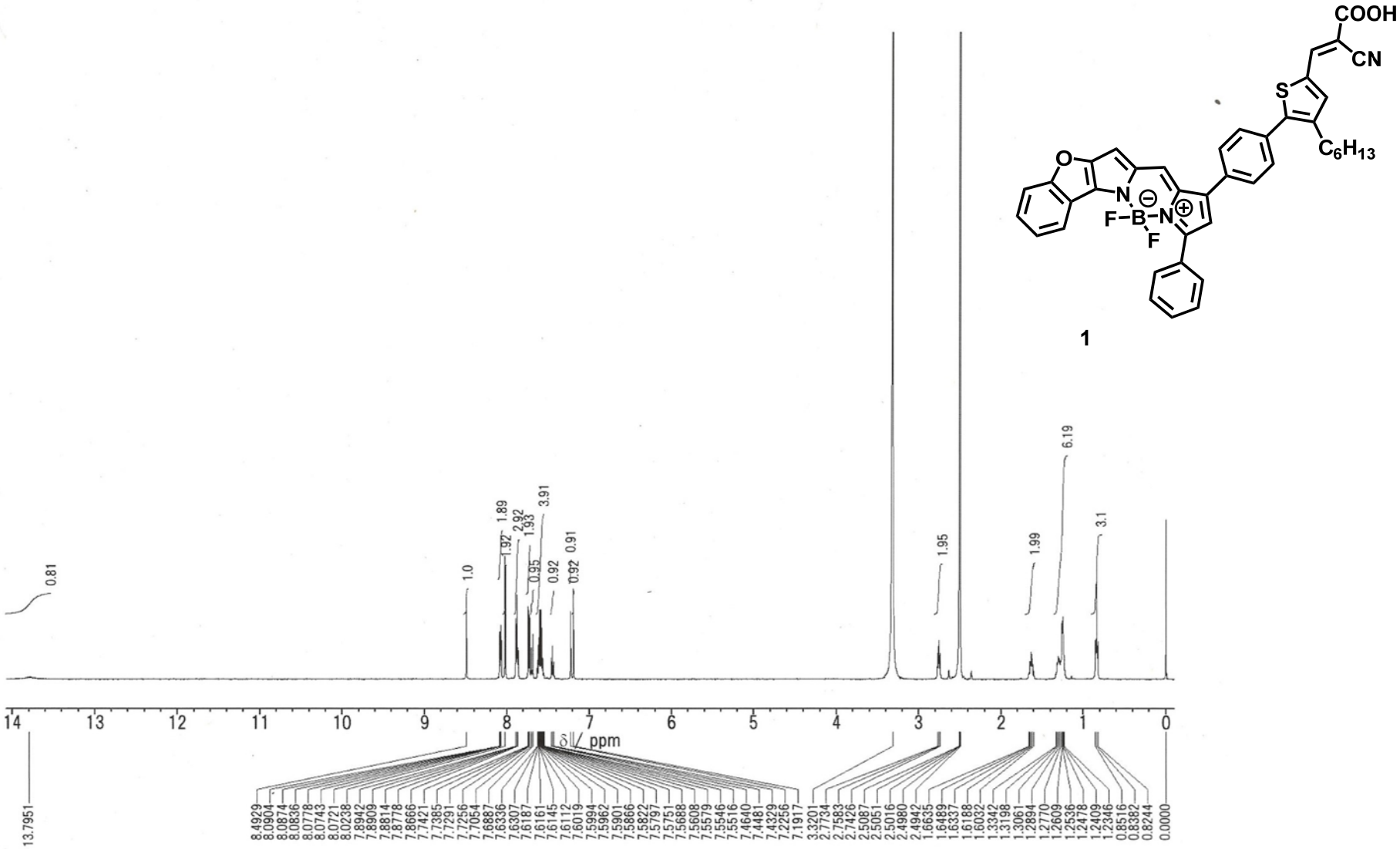

Fig. S14. ^{1}H NMR spectrum of **1** (500 MHz) in DMSO-d_6.

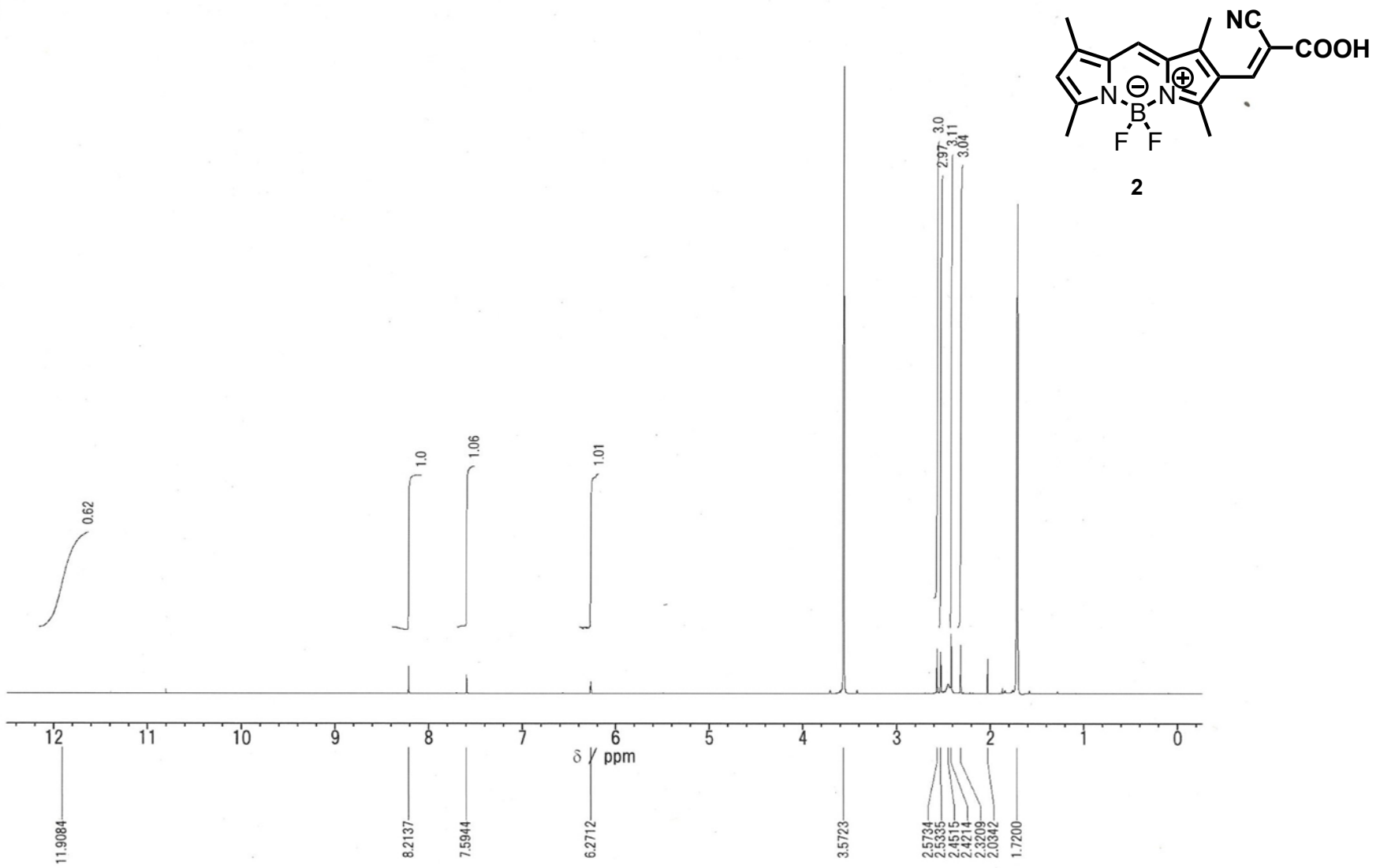

Fig. S15. ^{1}H NMR spectrum of **2** (500 MHz) in THF-d_8.

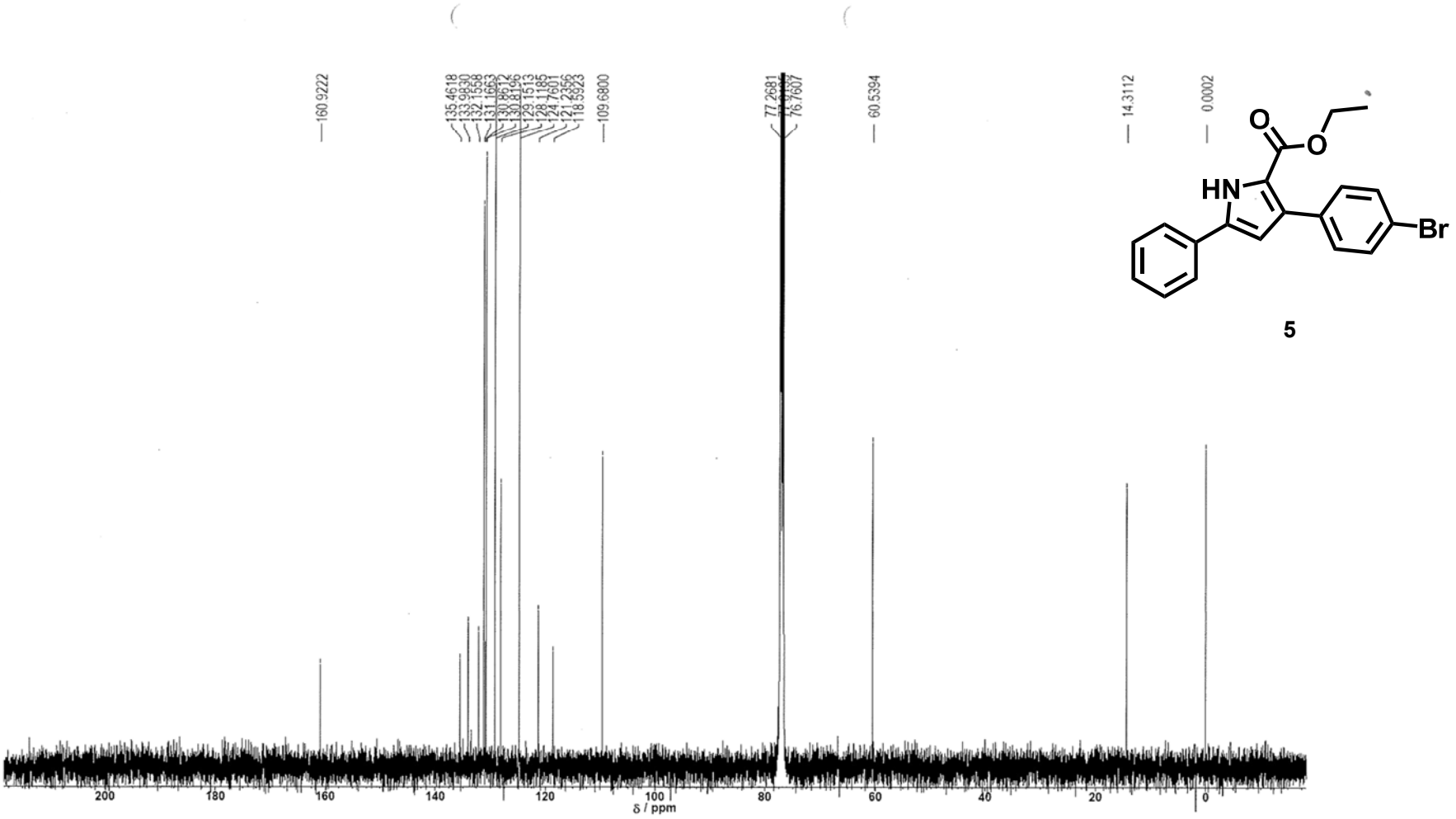

Fig. S16. ^{13}C NMR spectrum of **5** (500 MHz) in $CDCl_3$.

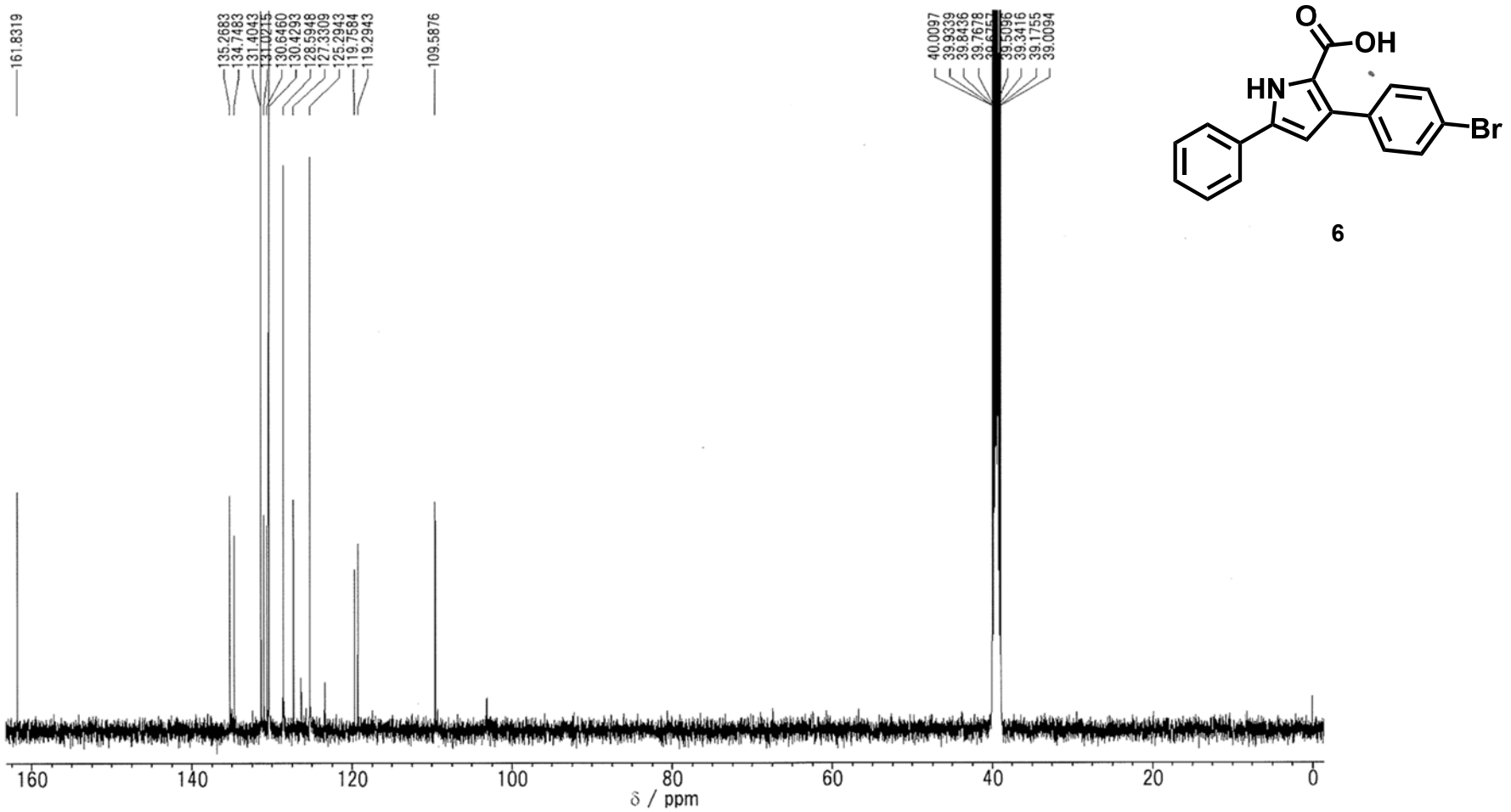

Fig. S17. ^{13}C NMR spectrum of **6** (500 MHz) in DMSO-d_6.

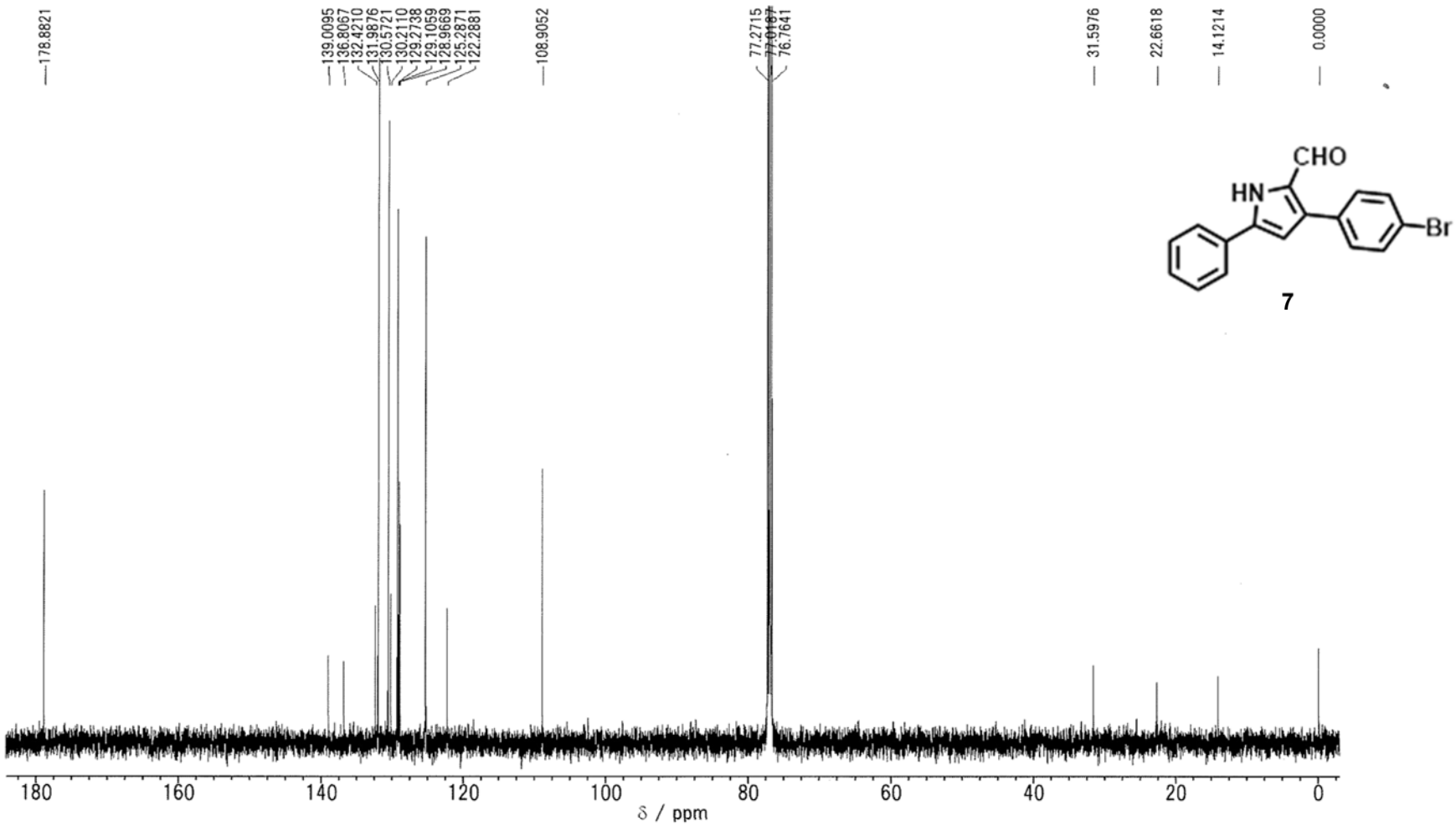

Fig. S18. ^{13}C NMR spectrum of **7** (500 MHz) in $CDCl_3$.

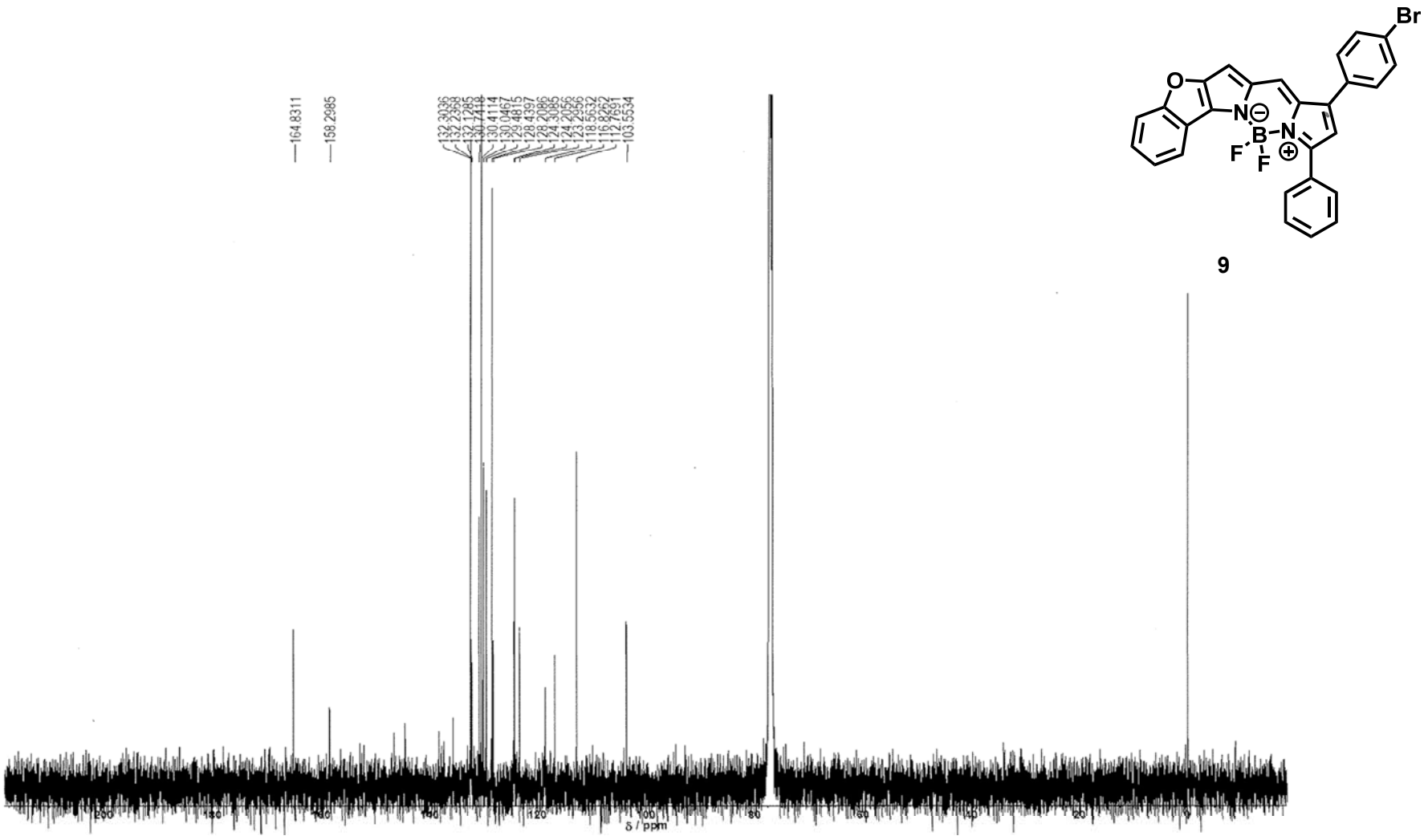

Fig. S19. ^{13}C NMR spectrum of **9** (500 MHz) in $CDCl_3$.

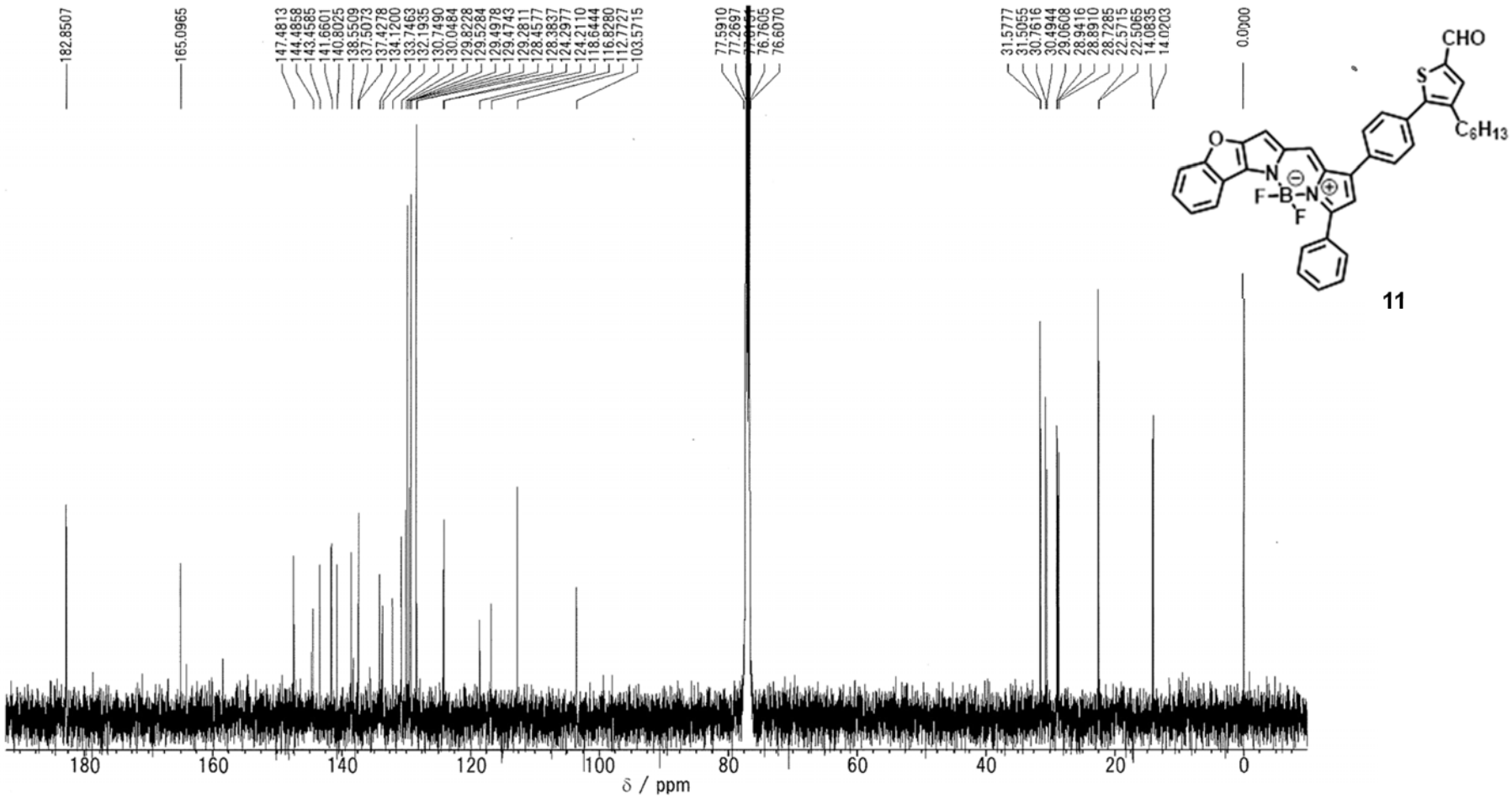

Fig. S20. ^{13}C NMR spectrum of **11** (500 MHz) in $CDCl_3$.

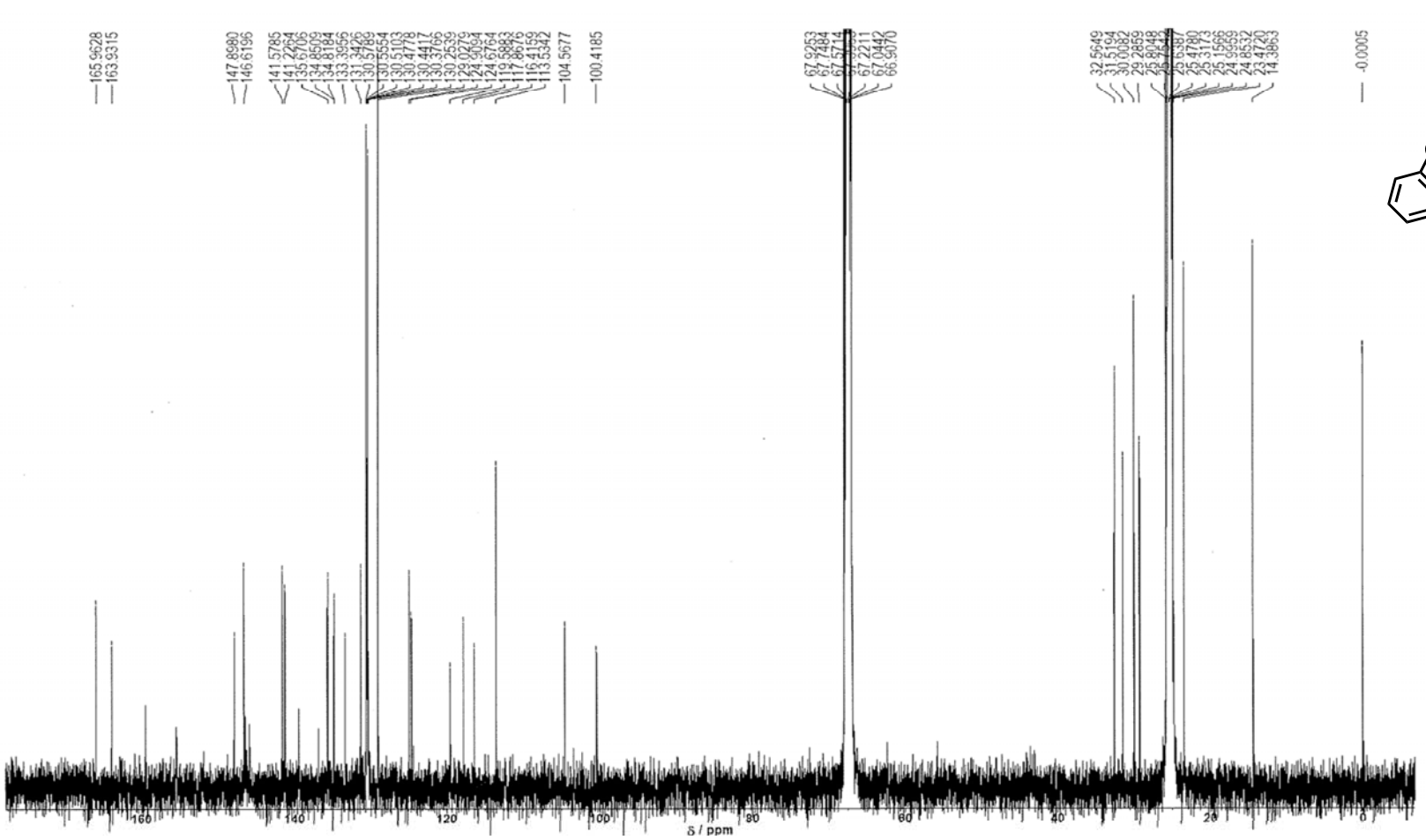

Fig. S21. ^{13}C NMR spectrum of **1** (500 MHz) in THF-d_8.

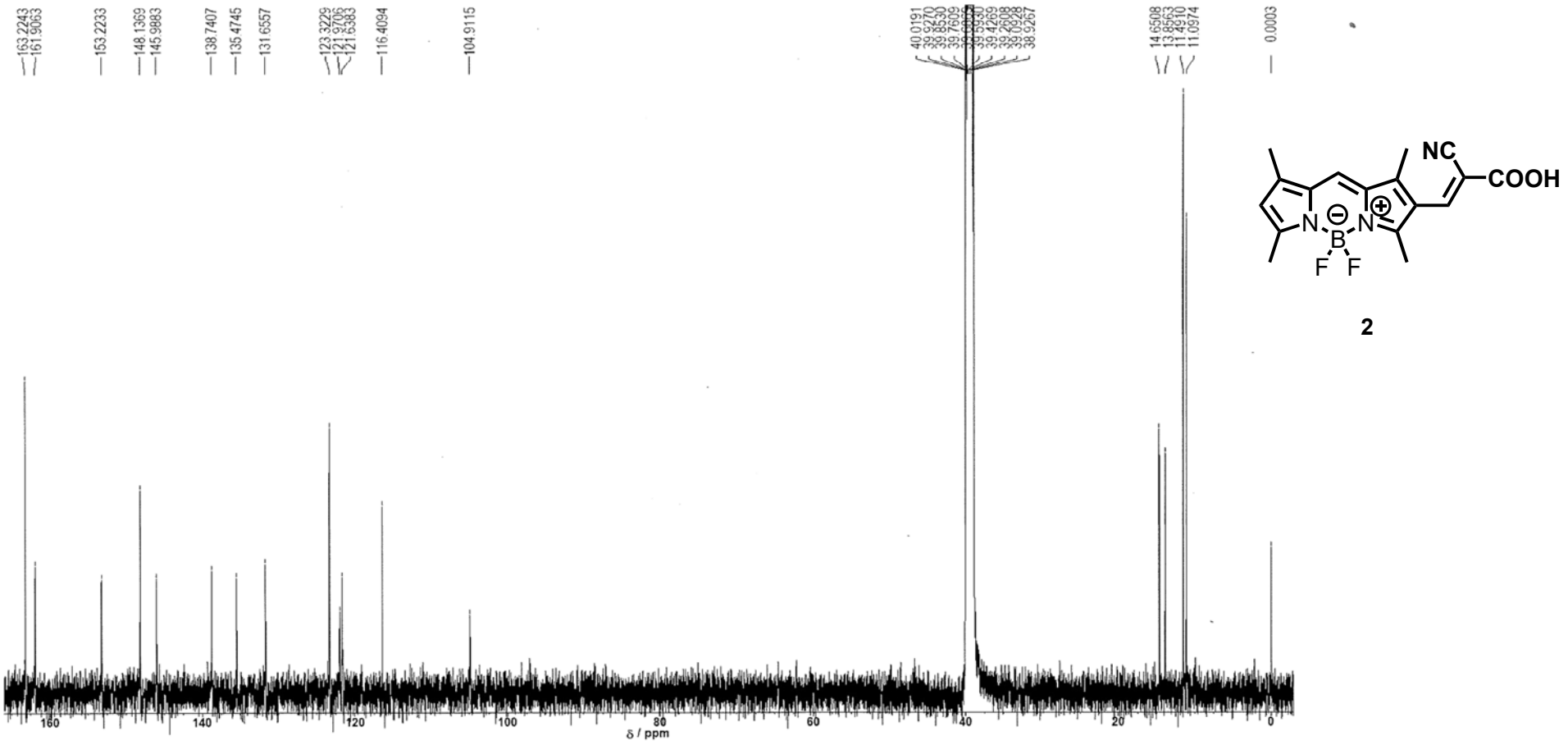

Fig. S22. ^{13}C NMR spectrum of **2** (500 MHz) in DMSO-d_6.

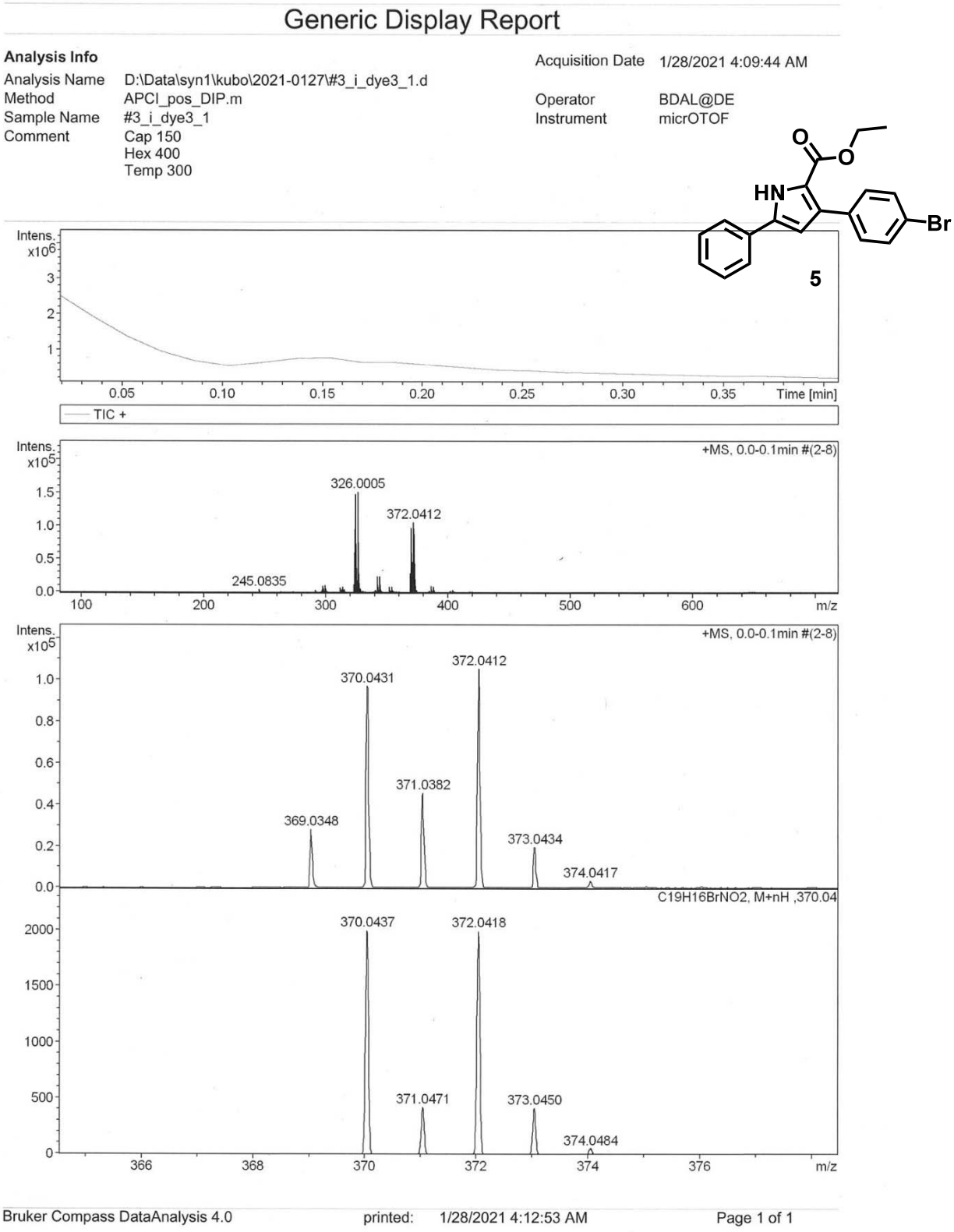

Fig. S23. High resolution of APCI mass spectrum (positive mode) of **5**.

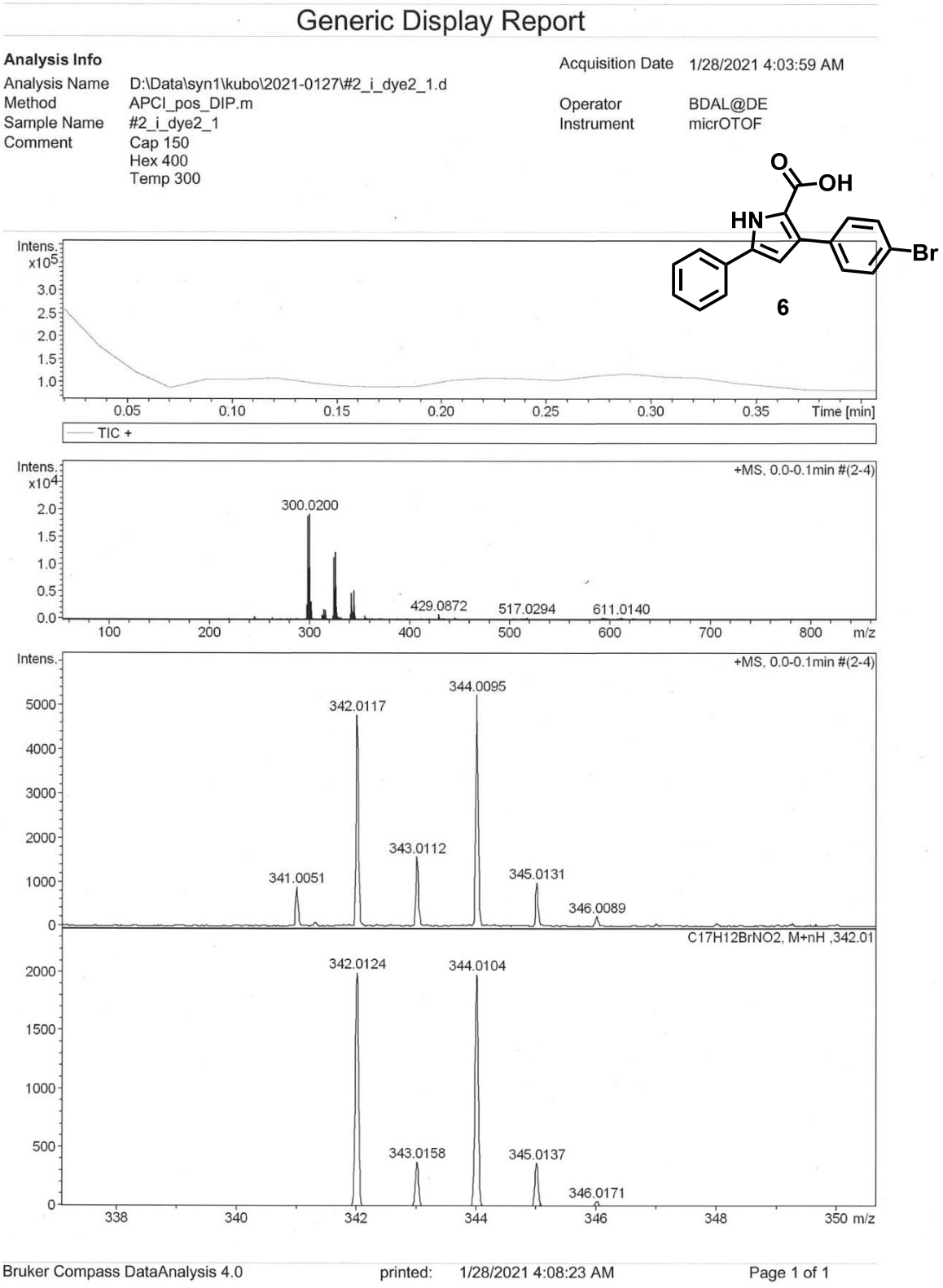

Fig. S24. High resolution of APCI mass spectrum (positive mode) of **6**.

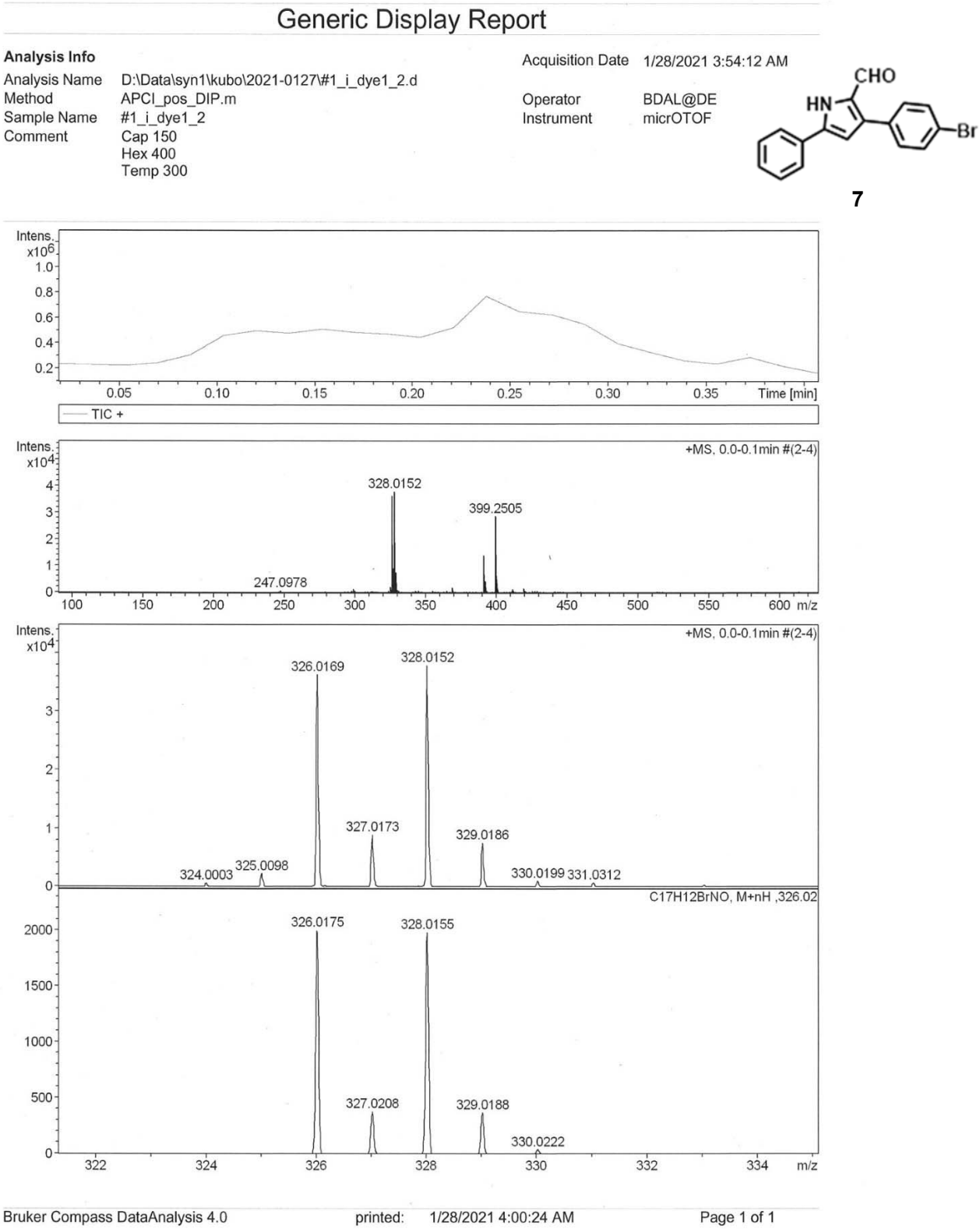

Fig. S25. High resolution of APCI mass spectrum (positive mode) of **7**.

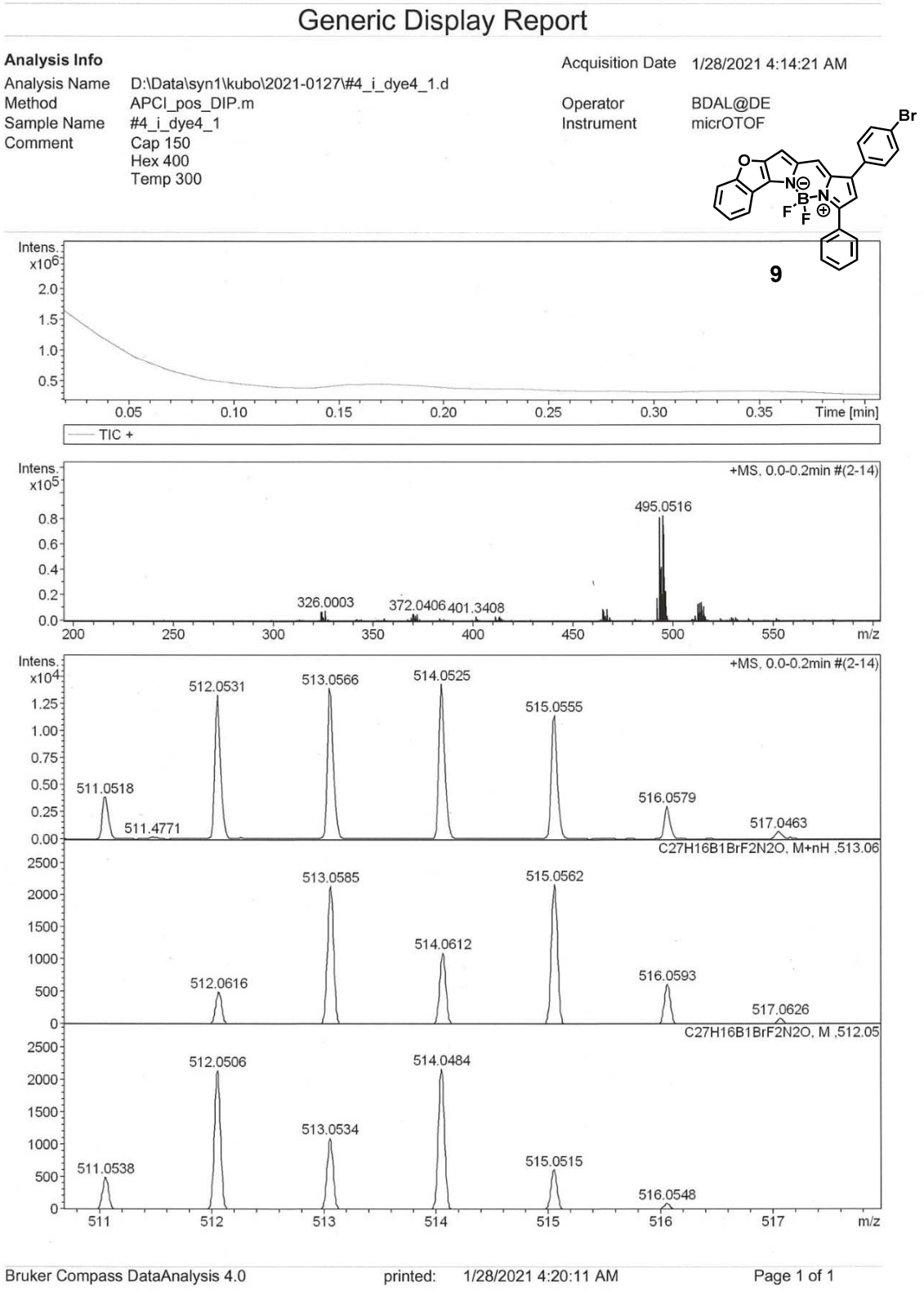

Fig. S26. High resolution of APCI mass spectrum (positive mode) of **9**.

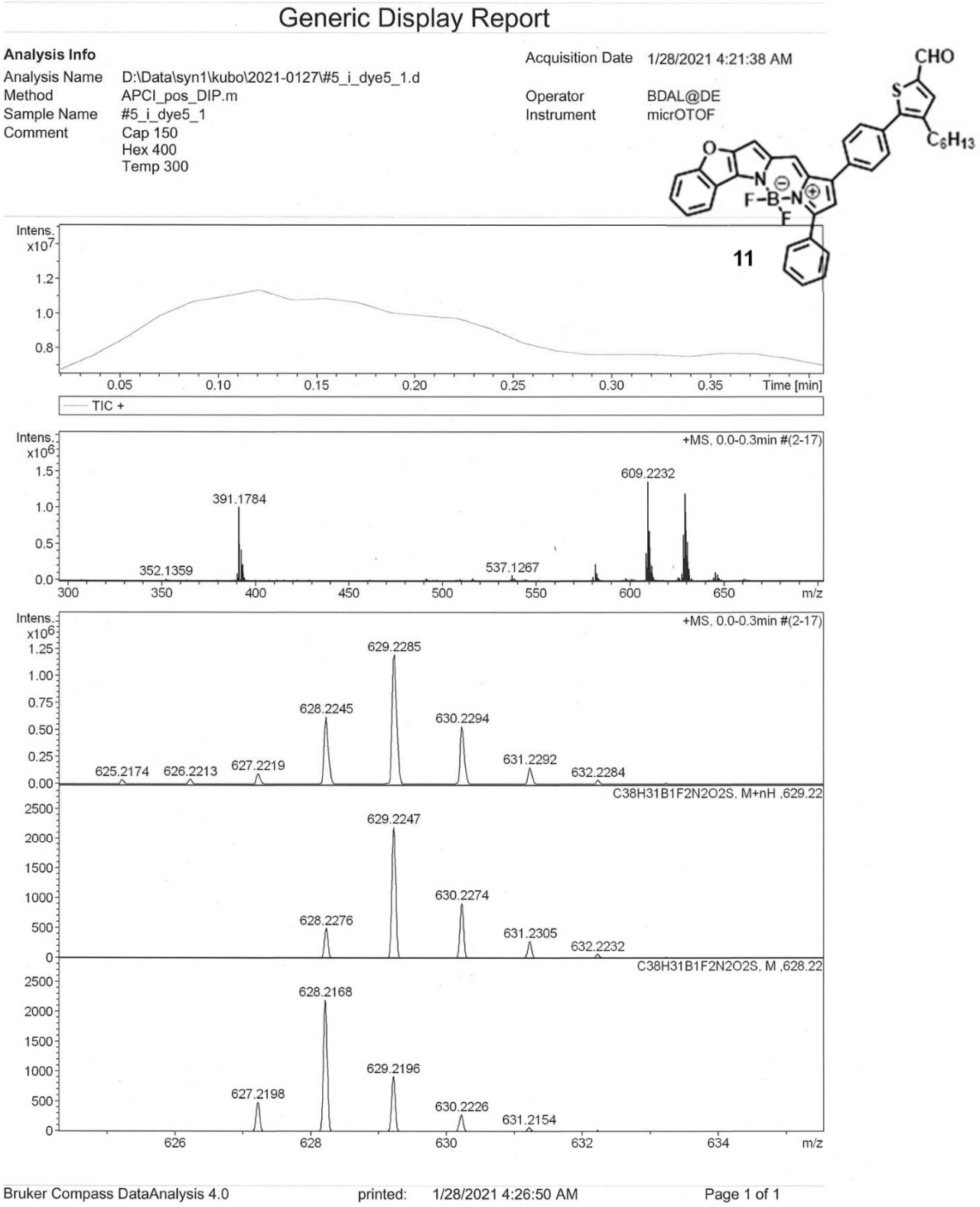

Fig. S27. High resolution of APCI mass spectrum (positive mode) of **11**.

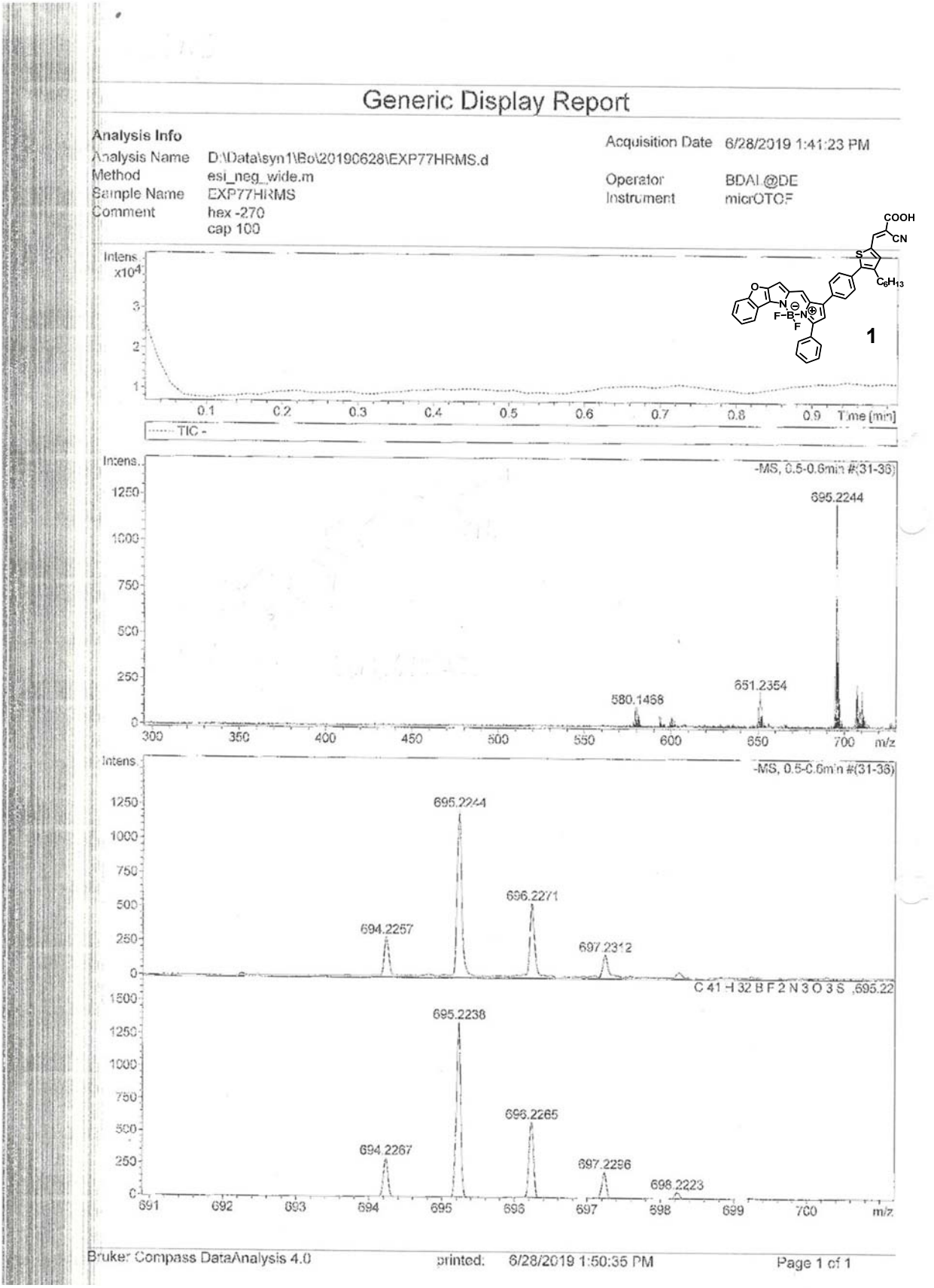

Fig. S28. High resolution of APCI mass spectrum (negative mode) of **1**.

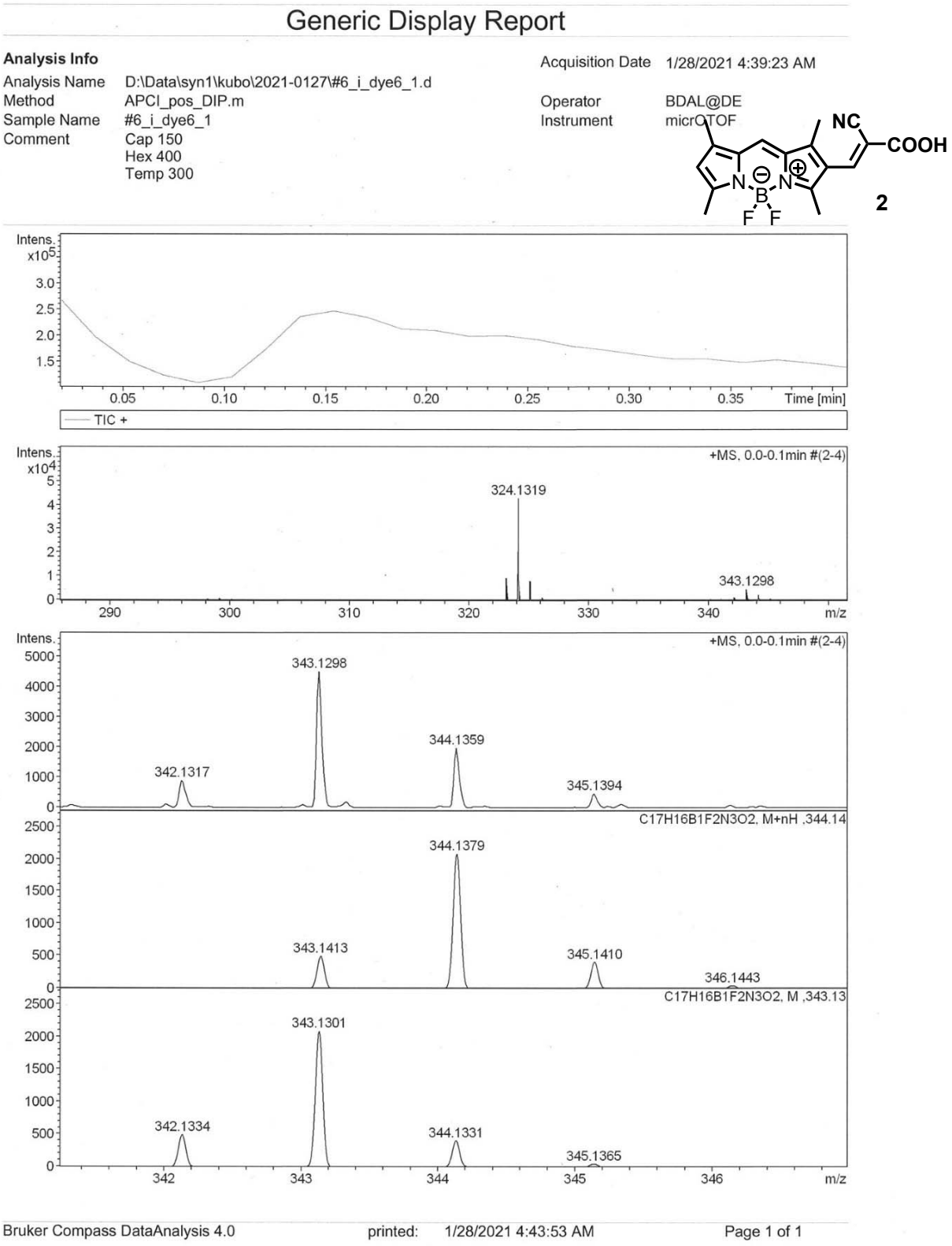

Fig. S29. High resolution of APCI mass spectrum (positive mode) of **2**.