# Electronic Supporting Information

# Facile "one pot" route to the novel benzazulene–type dye class: asymmetric, derivatizable, 5–7–6 fused ring puckered half BODIPY design

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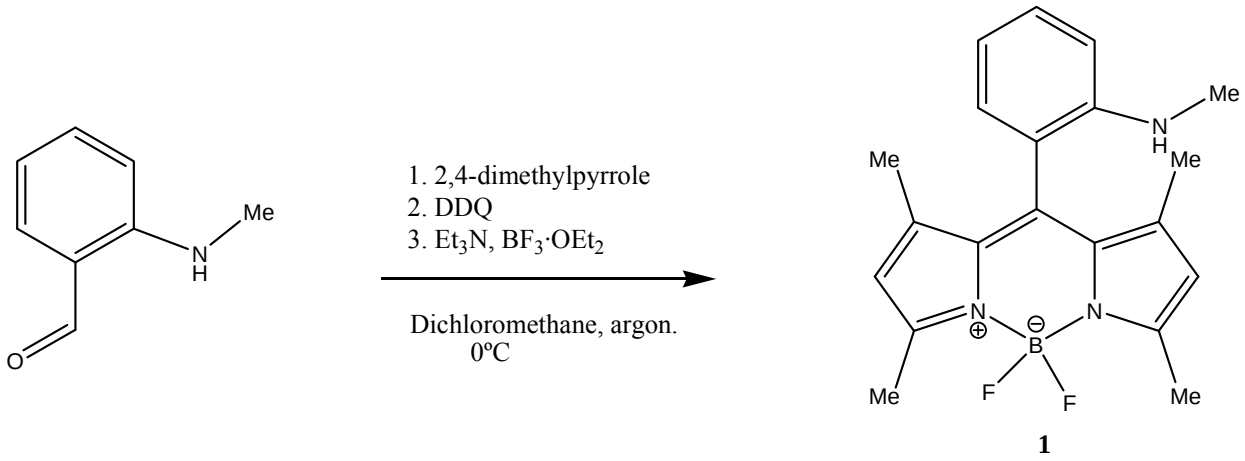
## Experimental Section

**General Remarks.** All reagents used herein were used as received from the suppliers (Aldrich, Acros, and Junsei companies). Melting points were taken on an electro–thermal melting point apparatus and are reported uncorrected. Synthetic details for the preparation of the dipyrromethanes and for the BODIPY systems follow literature methods. $^{1}H$ and $^{13}C$ NMR spectra were acquired using a Bruker Avance 400 MHz spectrometer. TMS was used as an internal standard. $^{1}H$ and $^{13}C$ NMR spectral signals were calibrated internally by the respective protio impurity or carbon resonance of the NMR spectroscopic solvent *e.g.*, $CDCl_3$ ($^{1}H$: δ 7.24; $^{13}C$: δ 77.0). High resolution matrix–assisted laser desorption/ionization (MALDI) mass spectrometry was performed on a VG AUTOSPEC ULTIMA by the research support staff at KAIST. This instrument possesses a trisector double focusing magnetic sector analyzer and was operated at a resolution of 80,000. Absorption spectra were measured using a JASCO V–530 UV/Vis spectrophotometer. Fluorescence measurements were carried out with a Shimadzu RF–5301pc spectrofluorophotometer.

**Experimental procedure for compound (1):**

In a round bottom flask, 2–methylaminobenzaldehyde (300 mg, 2.20 mmol) was taken in dichloromethane at 0 ºC under argon and treated with 2,4–dimethylpyrrole (0.42 mL, 4.4 mmol) and 2 drops of trifluoroacetic acid and allowed to stir for ~1.0 h, followed by addition of 2,3–dichloro–5,6–dicyanobenzoquinone( DDQ) (499 mg, 2.20 mmol). At the same temperature after additional stirring for ~1.0 h, triethylamine (3.0 mL, 0.022 mol) was added, followed by $BF_3{\cdot}OEt_2$ (2.7 mL, 0.022 mol); stirring continued overnight. The reaction mixture was passed through a silica pad, followed by PTLC purification of the residue after rotary evaporation of the filtrate to give required BODIPY as red solid (80 mg, 10.2 %).

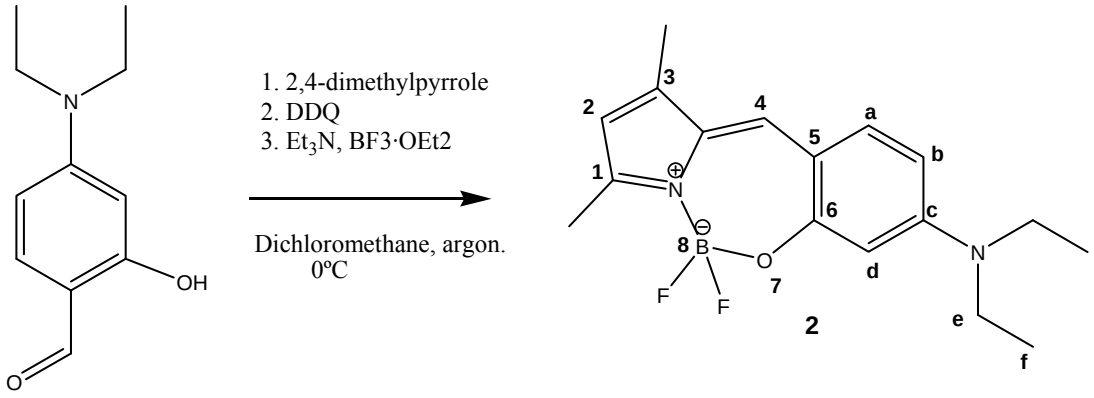



**1**

Scheme **1**: synthesis of compound **1.**

**Experimental procedure for synthesis of novel compound 2 (and analogues)**:

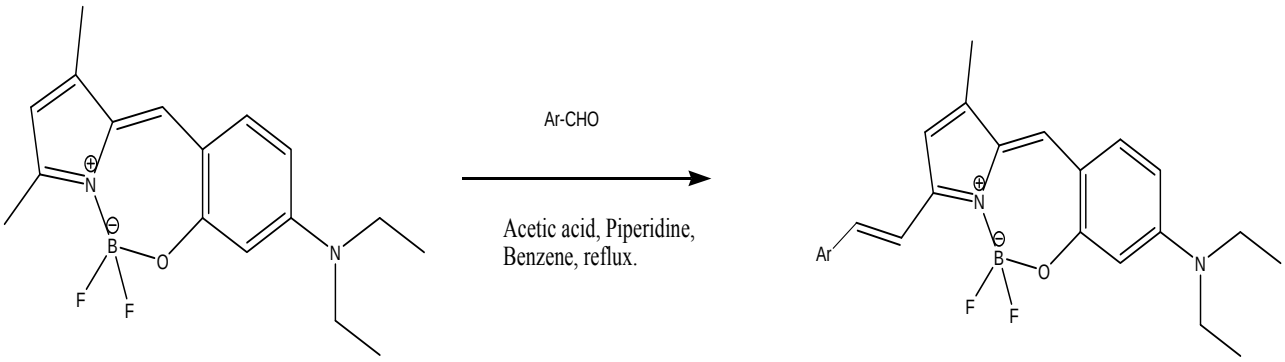
A round bottom flask evacuated with argon, was charged with 4–diethylaminosalicylaldehyde (500 mg, 2.58 mmol), followed by the addition of 2,4–dimethylpyrrole (0.50 mL, 5.17mmol) and 2 drops of trifluoroacetic acid in dichloromethane (*ca*. 30 mL) at 0 ºC. This mixture was allowed to stir for ~1.0 h. To the reaction mixture, with the temperature maintained at 0 ºC, 2,3–dichloro–5,6–dicyanobenzoquinone (DDQ) (587 mg, 2.58 mmol) was added; the reaction mixture was stirred for another ~1.0 h. Lastly, at the same temperature, triethylamine (3.6 mL, 0.0258 mol) was added and $BF_3{\cdot}OEt_2$ (3.2 mL, 0.0258 mol); the reaction mixture was allowed to stir overnight. Ultimately, the reaction mixture was passed through a silica pad and the residue further purified by PTLC after rotary evaporation to obtain the required compound as a (yellow fluorescent) red solid (350 mg, 43%). [*Note*: Analogous syntheses were made for compounds deriving from these salicylaldehyde starting materials: 5–methoxysalicylaldehyde, 5–bromosalicylaldehyde, 4–methoxysalicylaldehyde, and 2–hydroxy–1–naphthaldehyde.]




Scheme **2**: Synthesis of compound **2.**

**Experimental procedure for synthesis of compounds (2 a–b):**

In a round bottom flask, compound **2** (100 mg, 0.314 mmol) was taken in benzene (*ca*. 30 mL); this mixture was treated with 2–thiophenecarboxaldehyde (0.05 mL, 0.062 mmol), glacial acetic acid (0.5 mL) and piperidine (0.5 mL). The reaction mixture was refluxed to dryness. Water was added and organic layer was separated and washed with water (2 times). The organic solvent was isolated, reduced in volume by rotary evaporation, and purified by column chromatography, followed by PTLC purification as well to give the product as a blue solid (27 mg, 20.8 %).




Scheme **3**: Synthesis of compound **2a – b.**

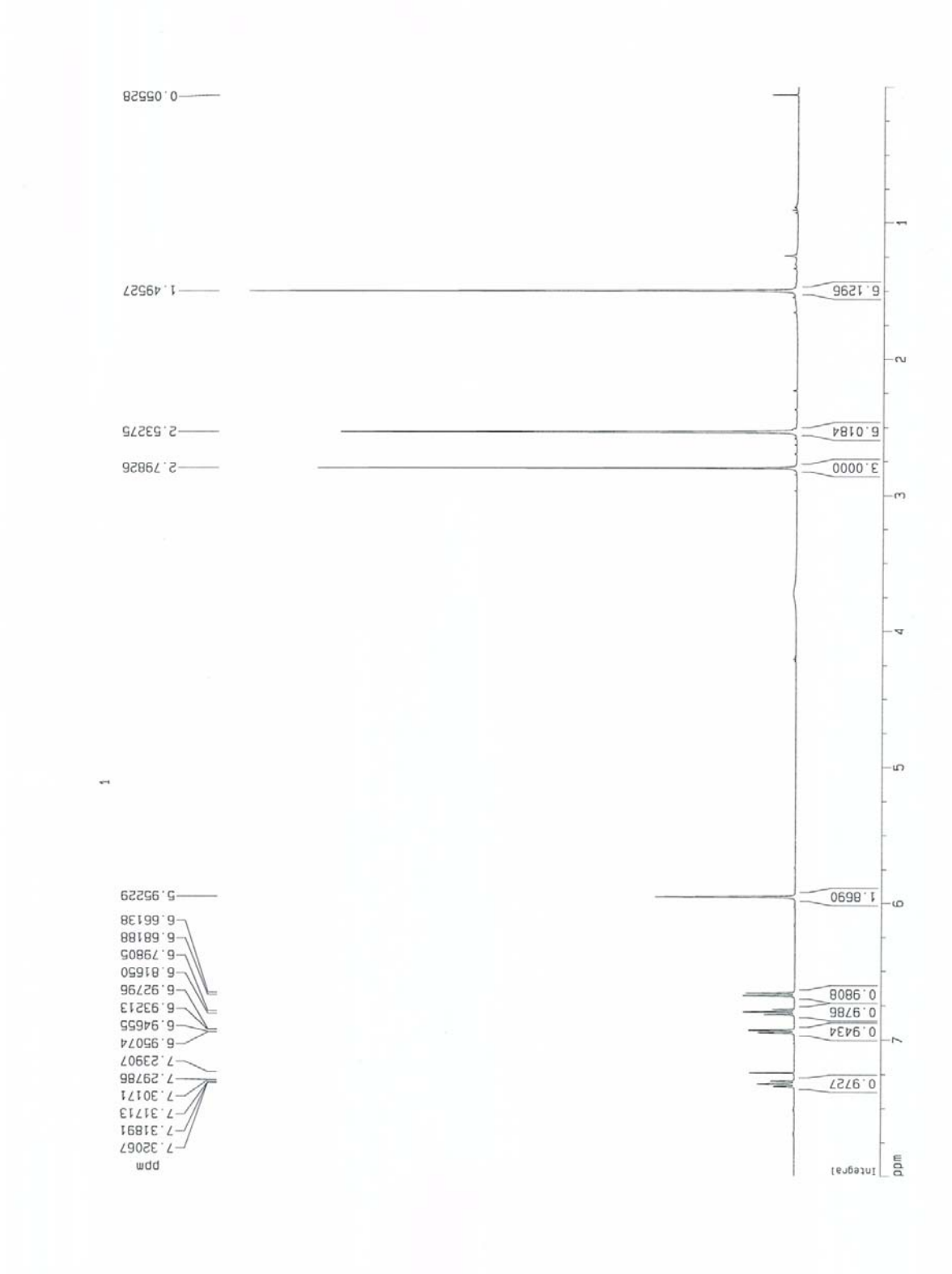



**Fig. S1**: $^{1}$H NMR spectrum of compound **1.**

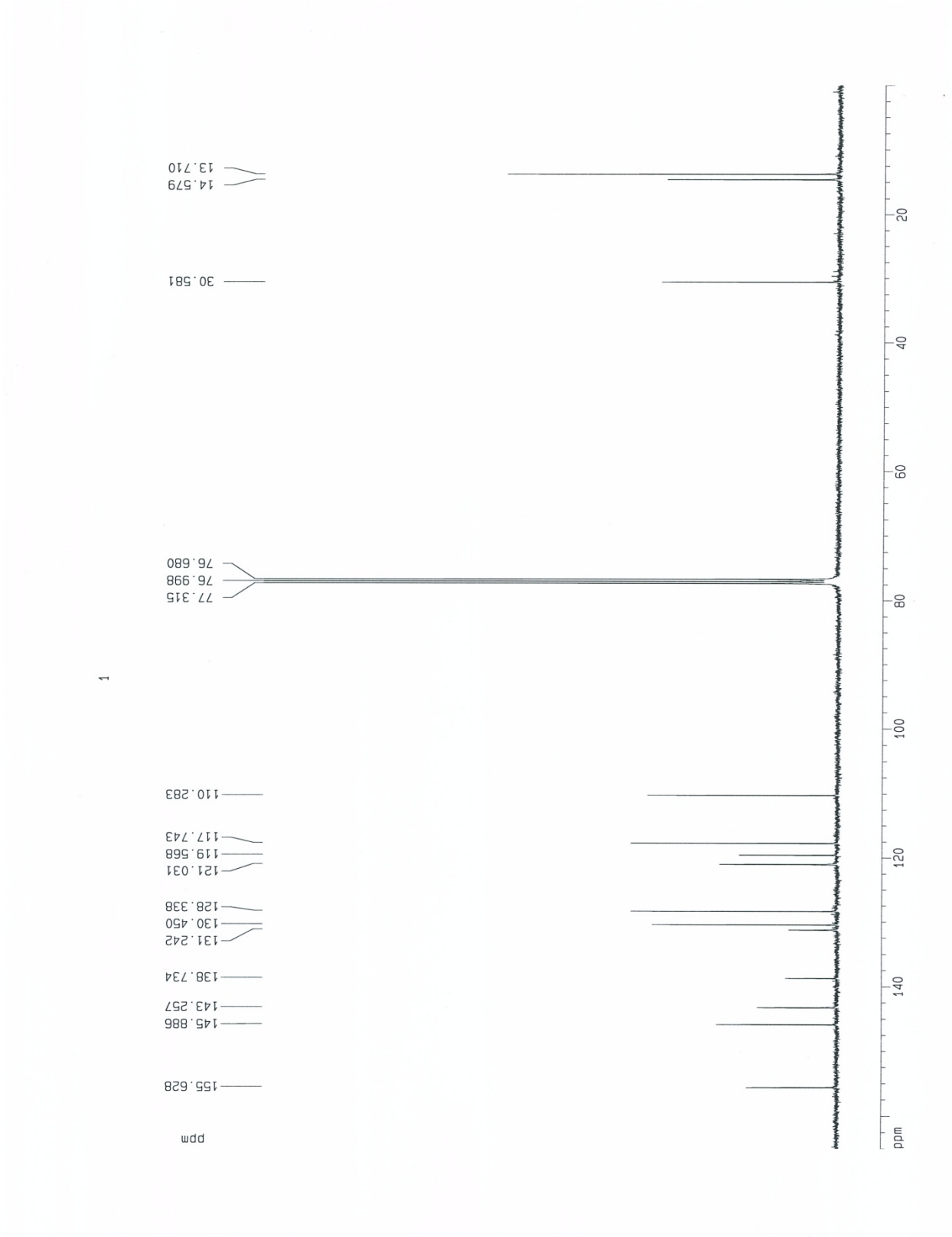



**Fig. S2:** $^{13}$C NMR spectrum of compound **1.**

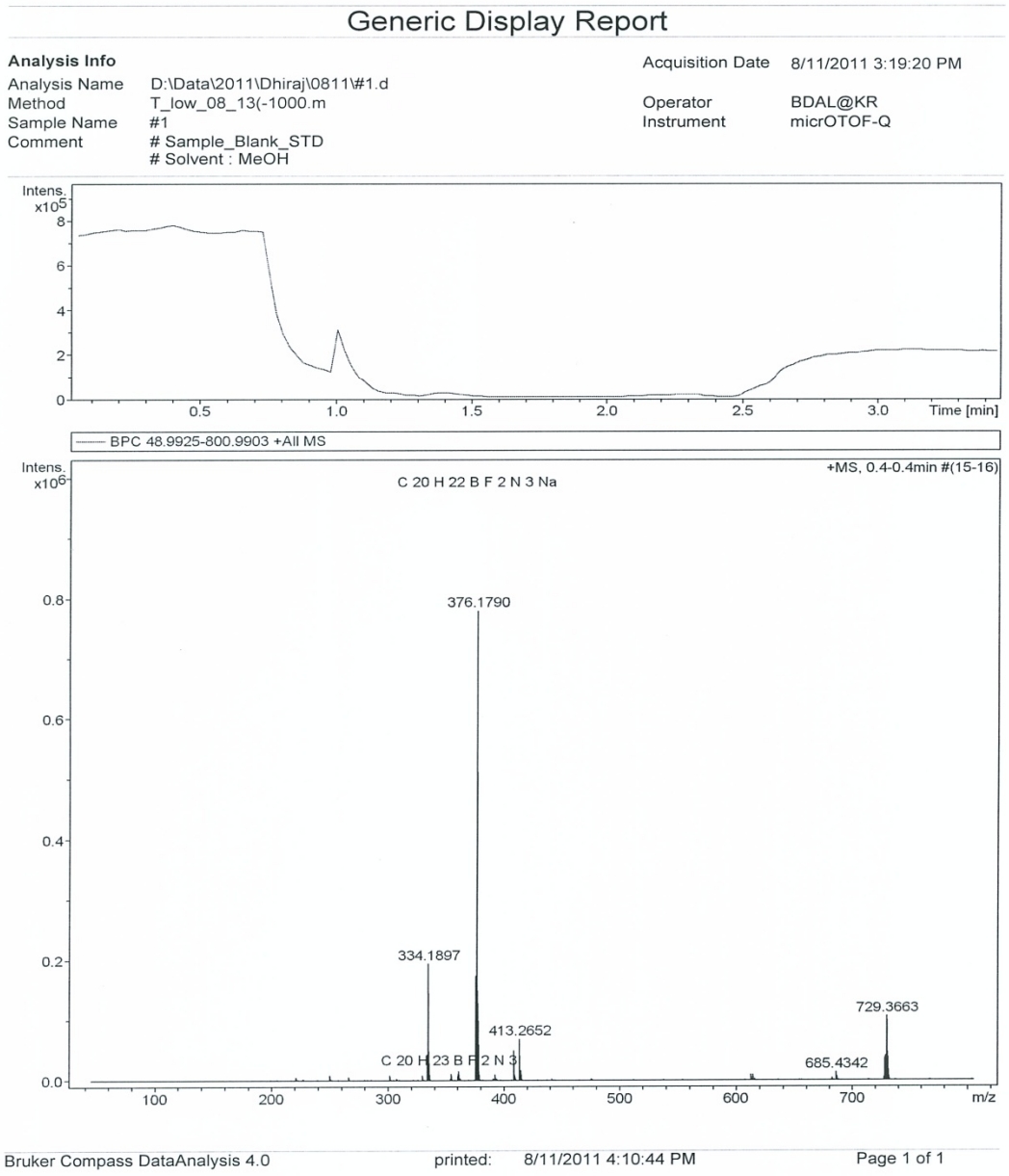



**Fig. S3:** ESI MASS spectrum of compound **1.**

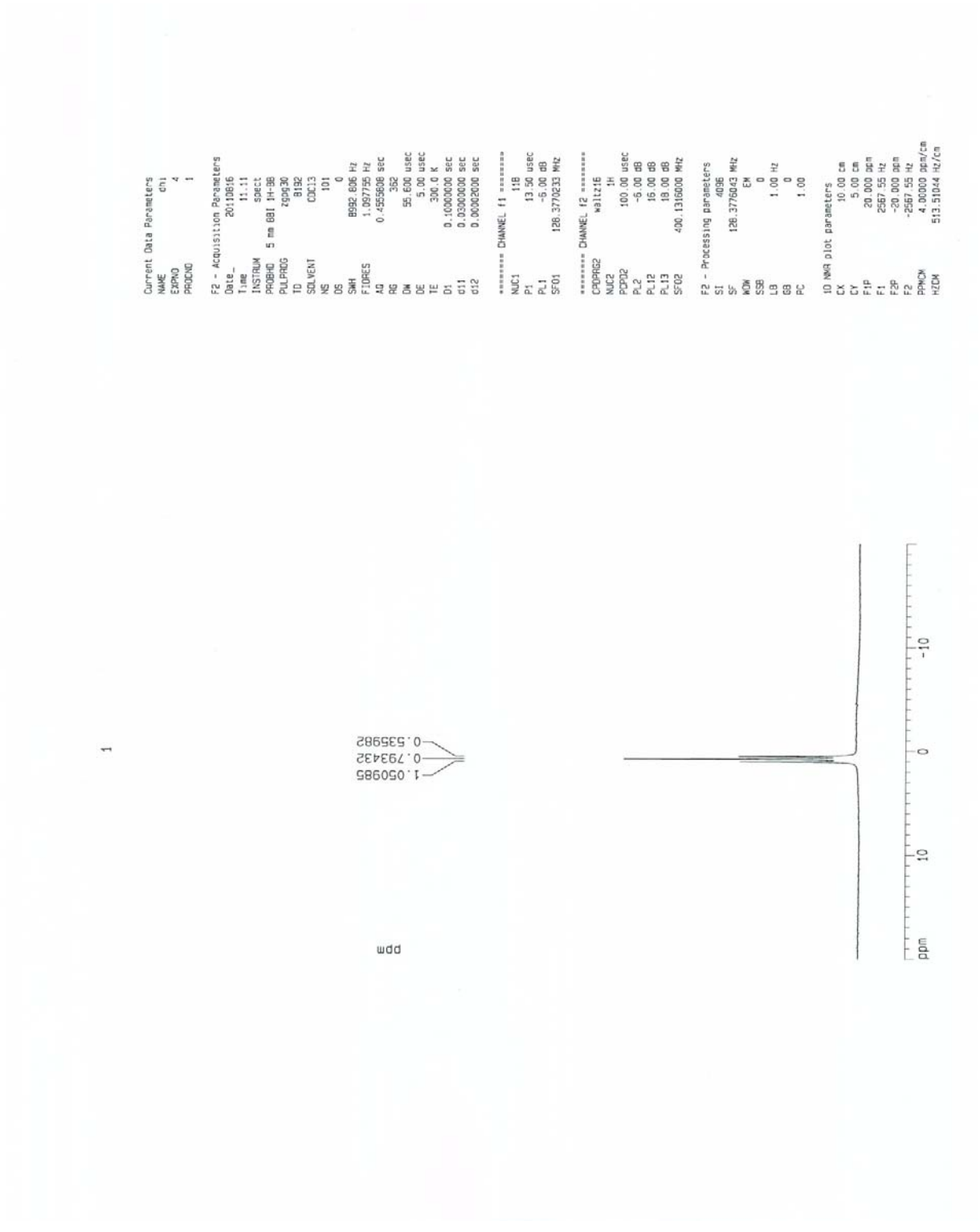



**Fig. S4 :** $^{11}$B NMR spectrum of compound **1**.

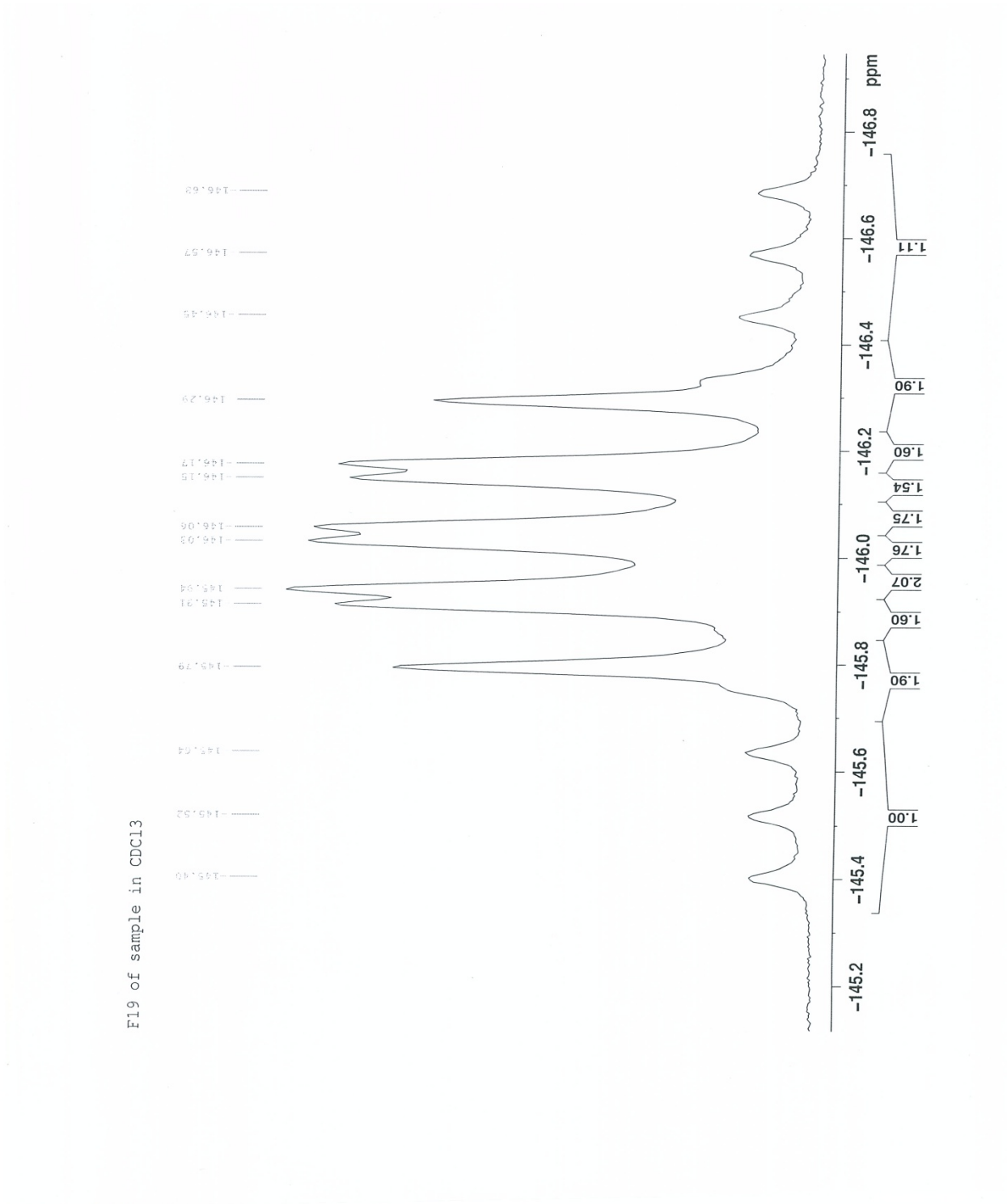



**Fig. S5:** $^{19}$F NMR spectrum of compound **1**.

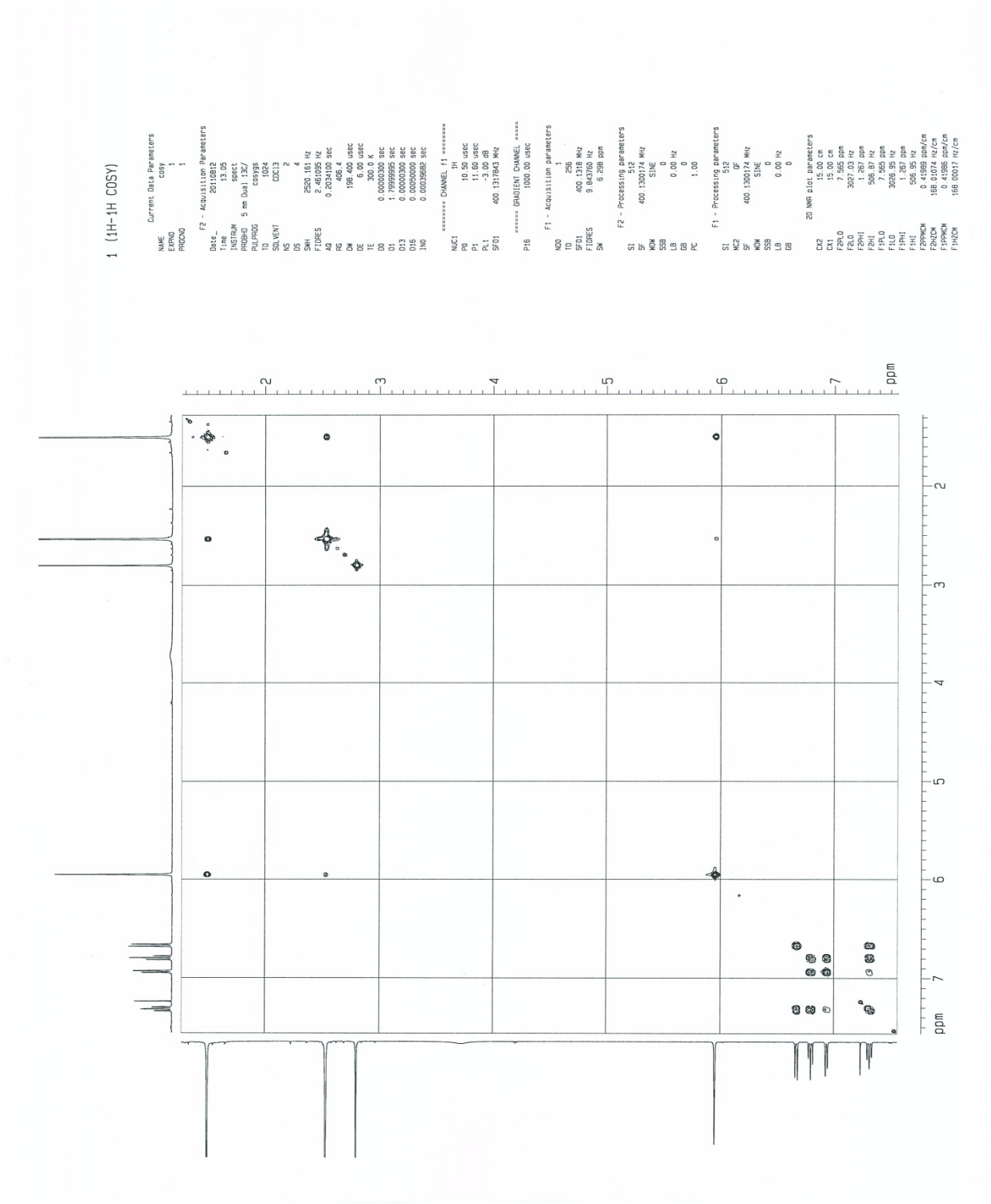



**Fig. S6**: $^{1}H–^{1}H$ COSY NMR spectrum of compound **1.**

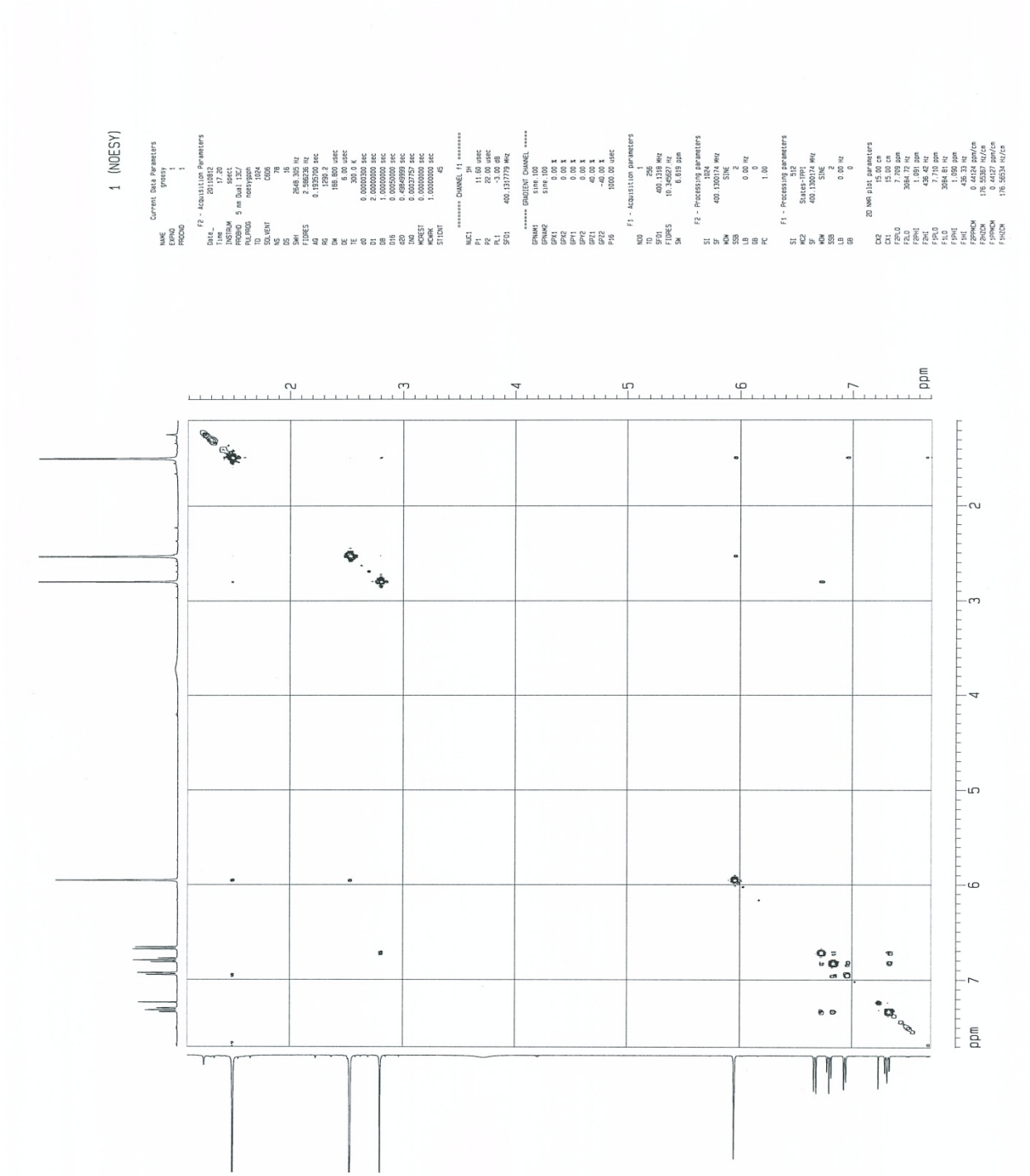



**Fig. S7**: $^{1}$H–$^{1}$H NOESY NMR spectrum of compound **1**.

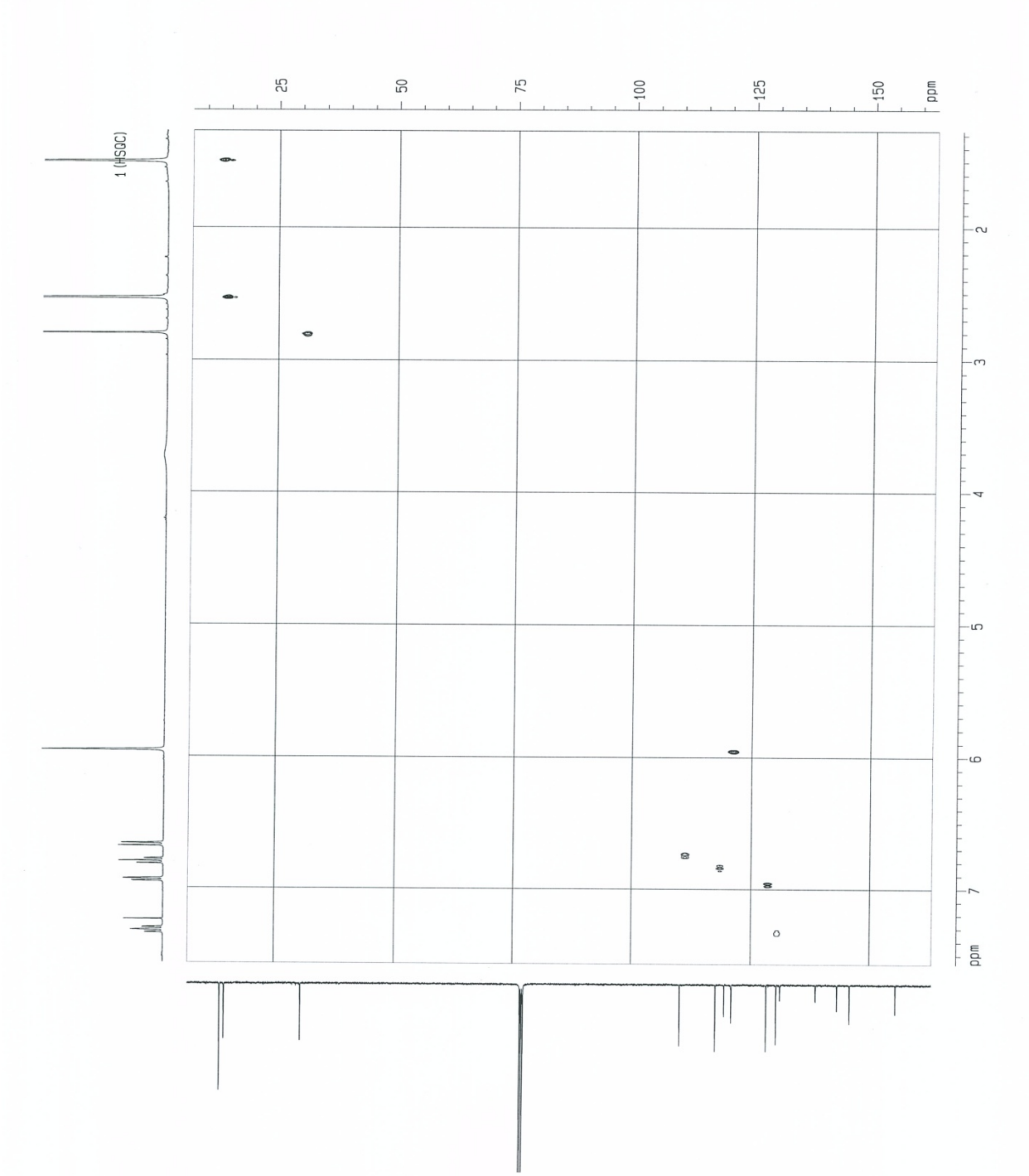



**Fig. S8**: $^{1}H$–$^{1}H$ HSQC NMR spectrum of compound **1.**

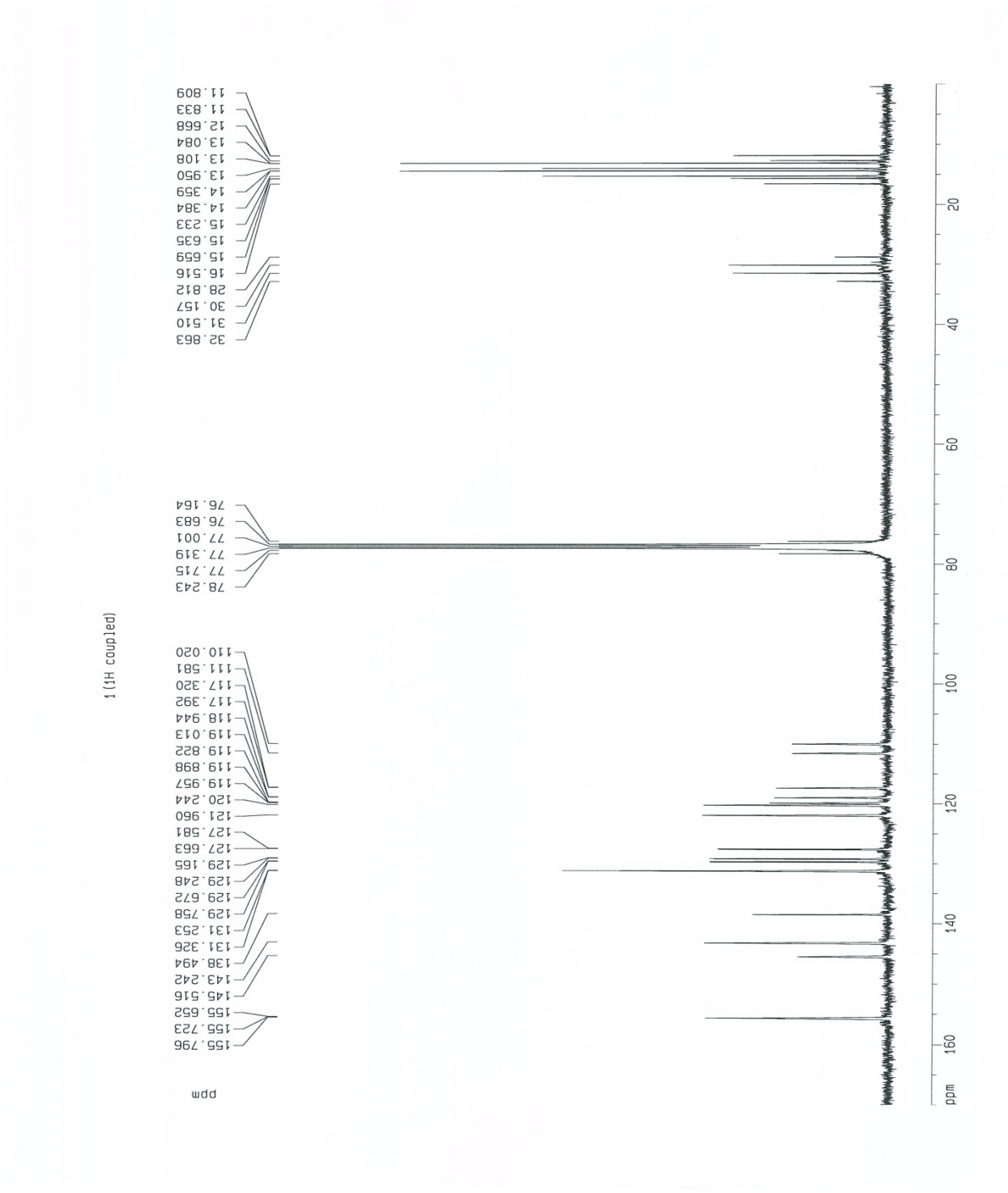
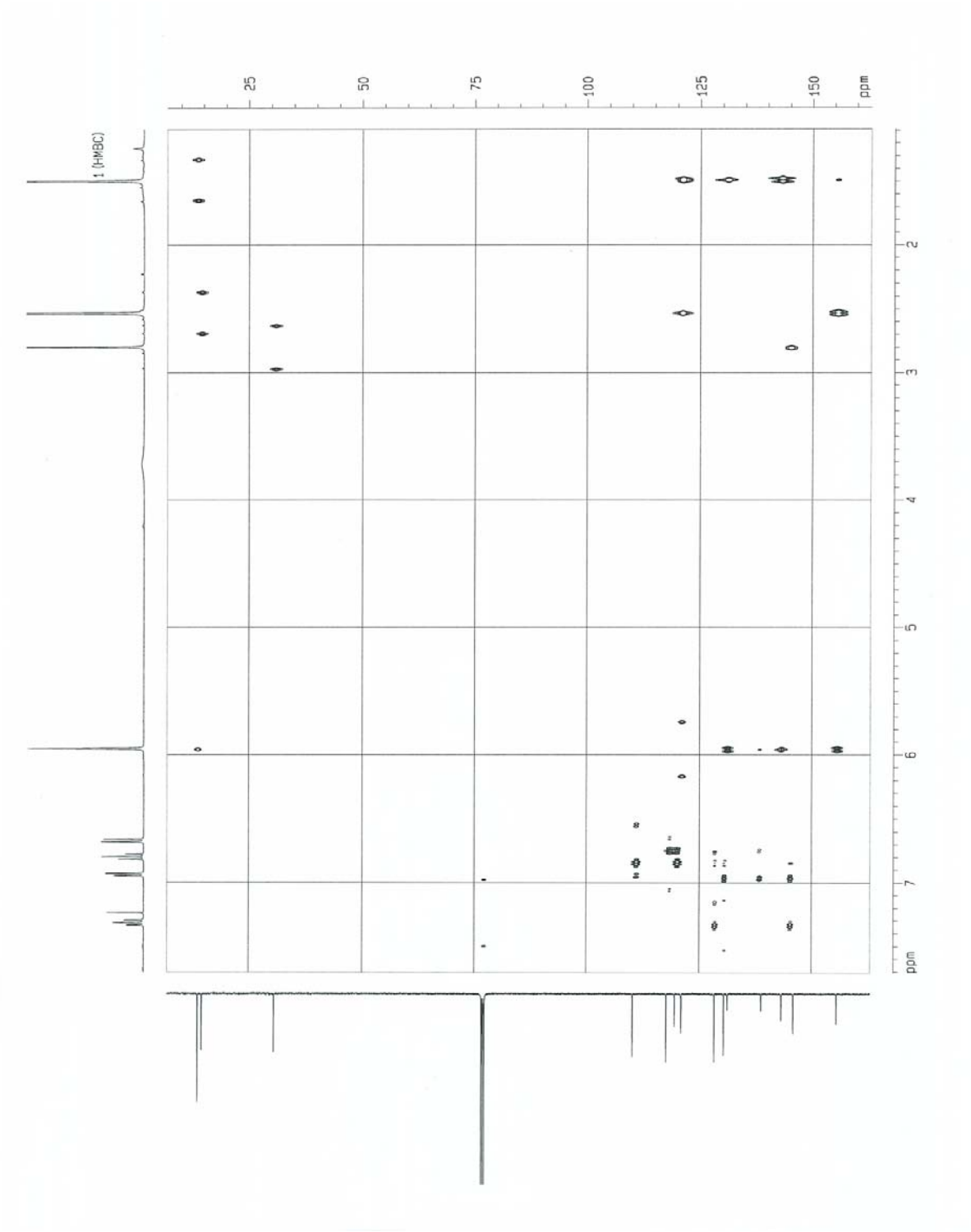



**Fig. S9**: $^{1}$H–coupled NMR spectrum of compound.




**1**

**Fig. S10**: $^{1}H$–$^{1}H$ HMBC NMR spectrum of compound **1**.

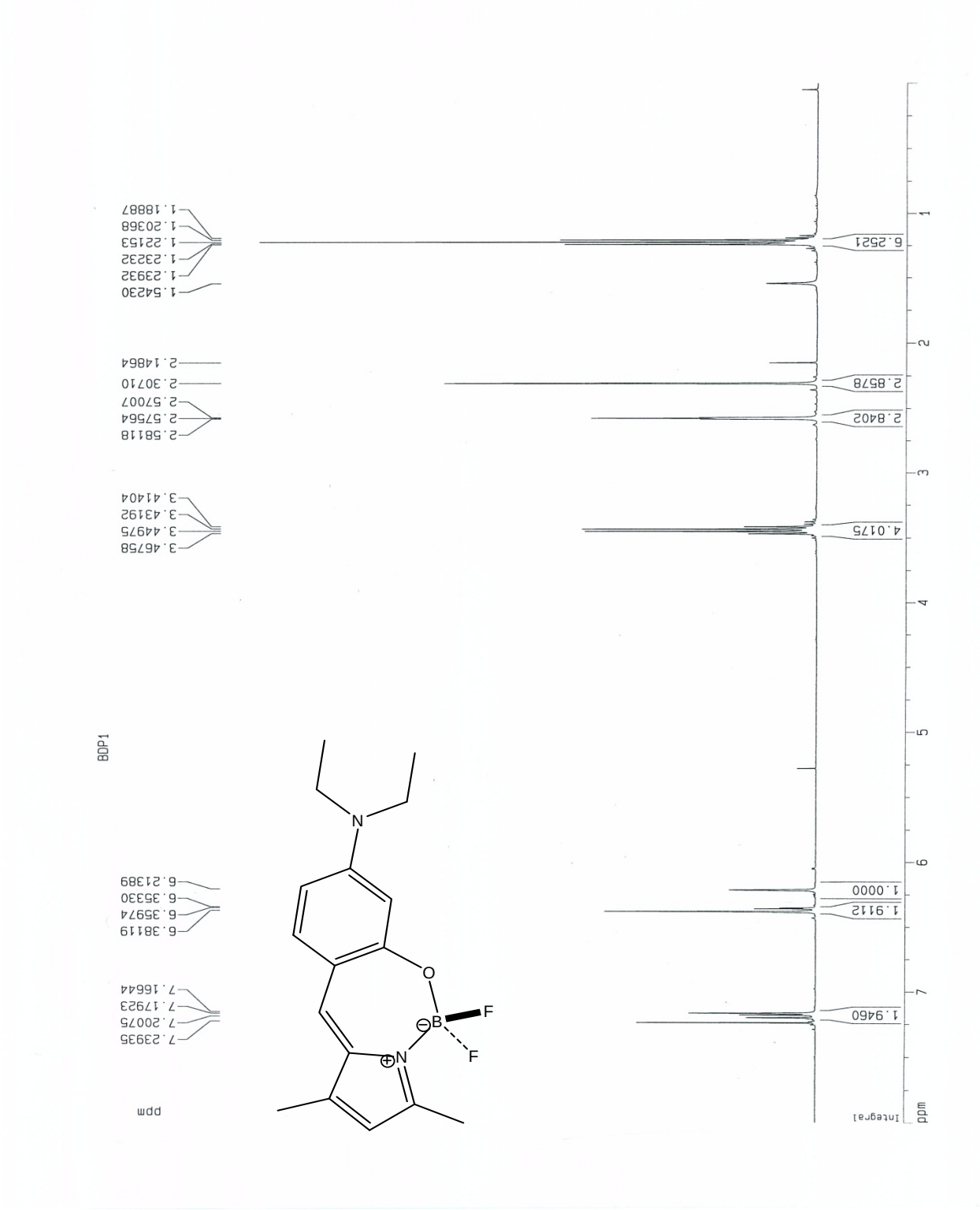



**Fig. S11**: $^{1}$H NMR spectrum of compound **2**.

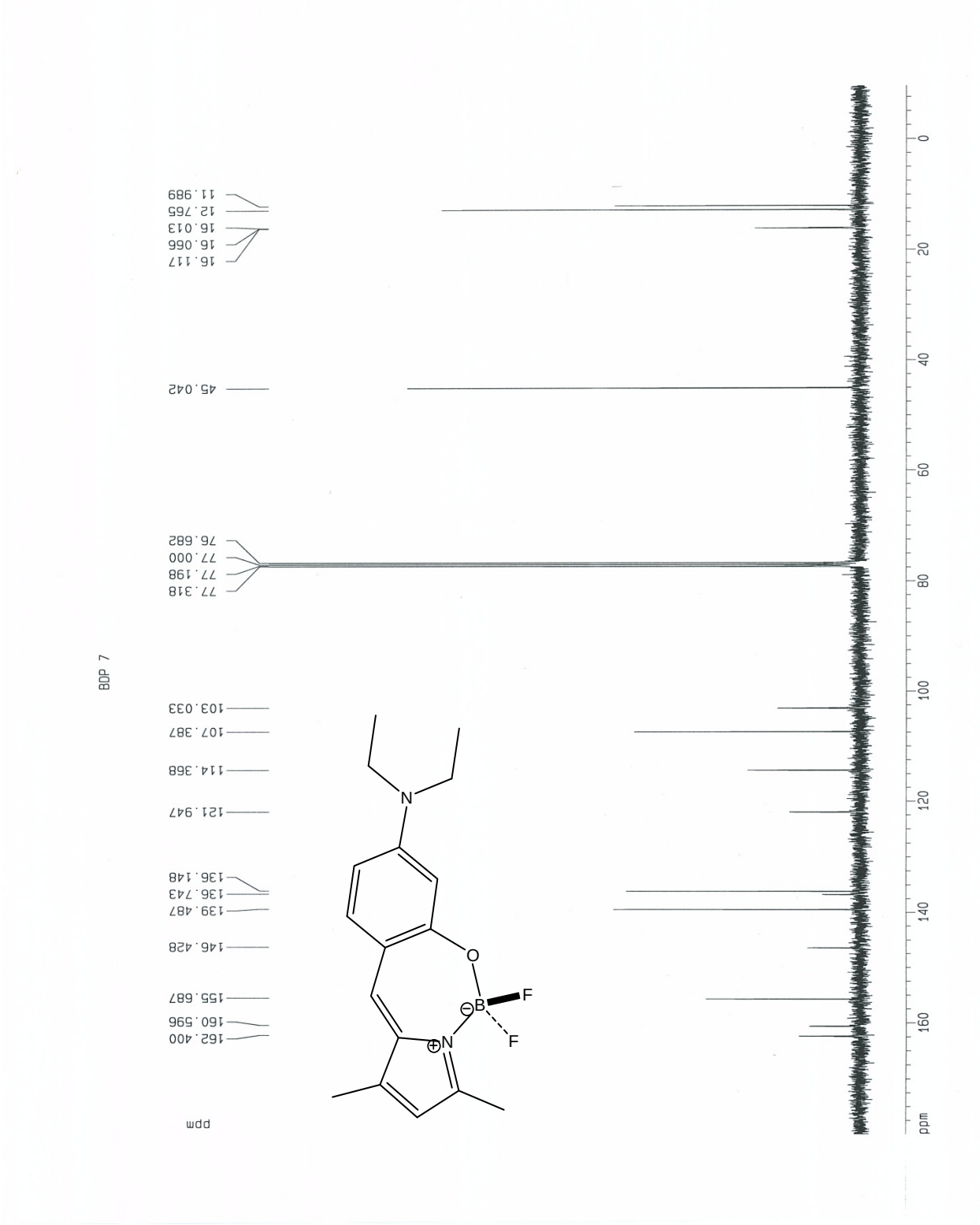



**Fig.S12**: $^{13}$C NMR spectrum of compound **2**.

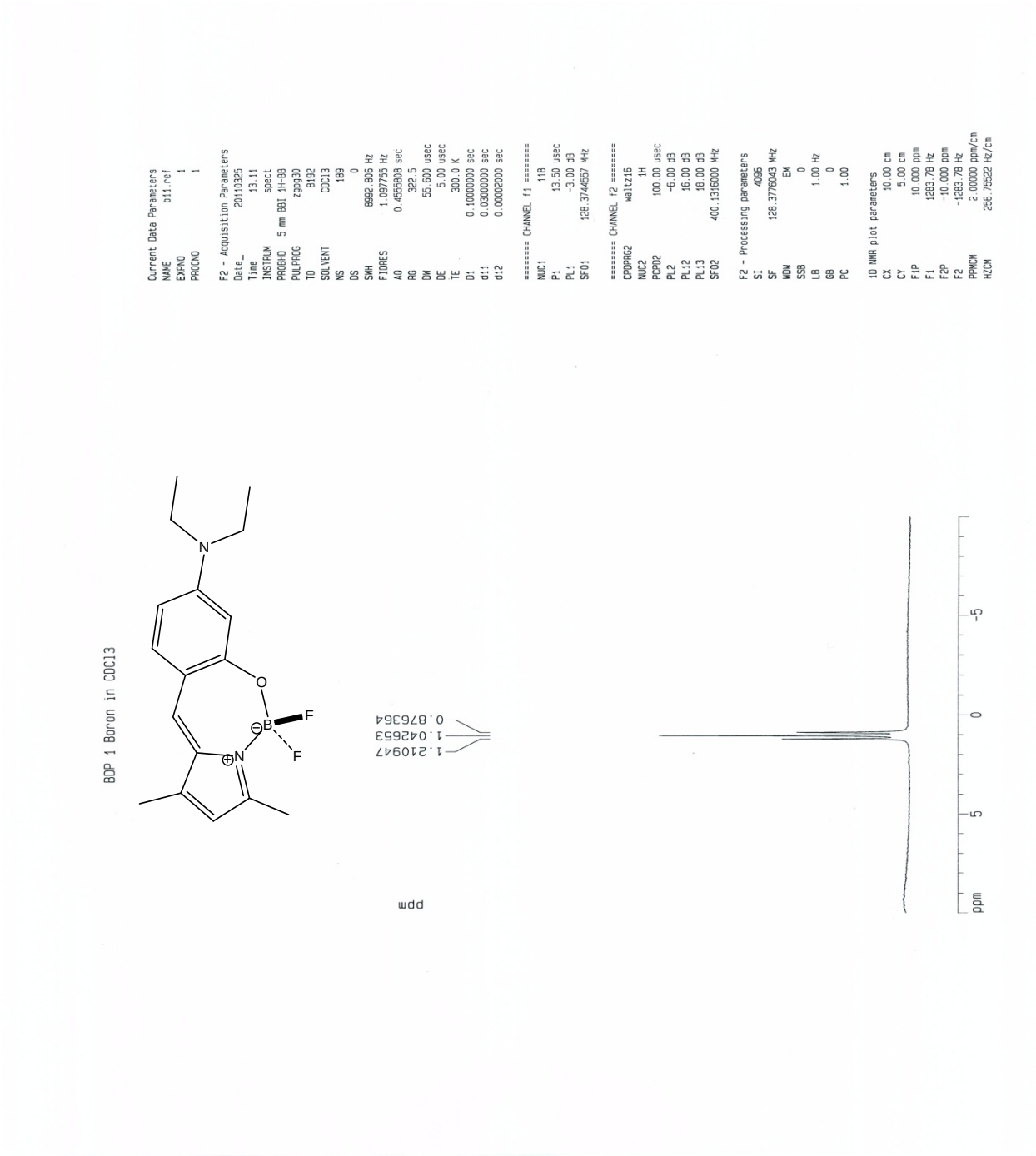



**Fig.S13**: $^{11}$B NMR spectrum of compound **2**.

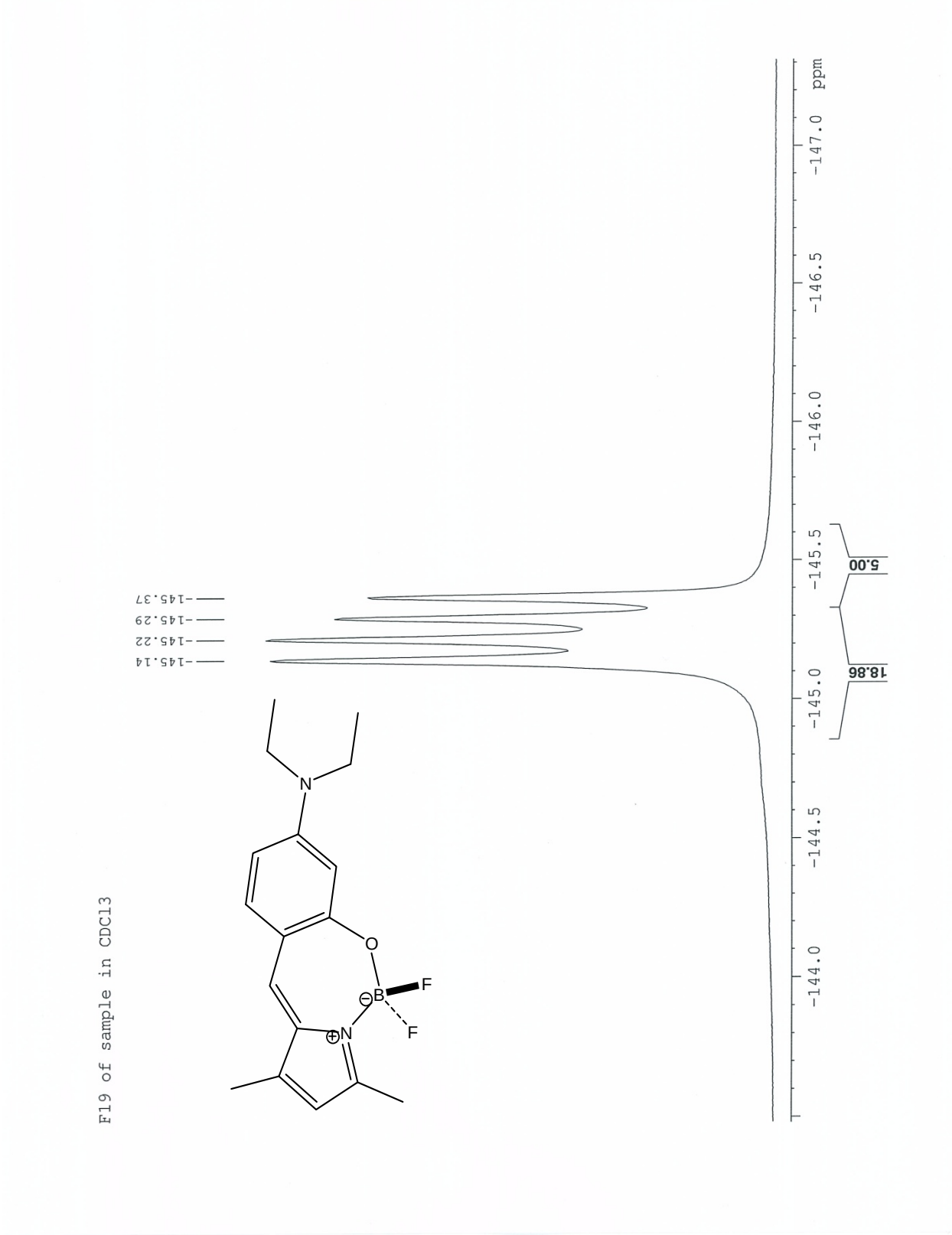



**Fig.S14**: $^{19}$F NMR spectrum of compound **2**.

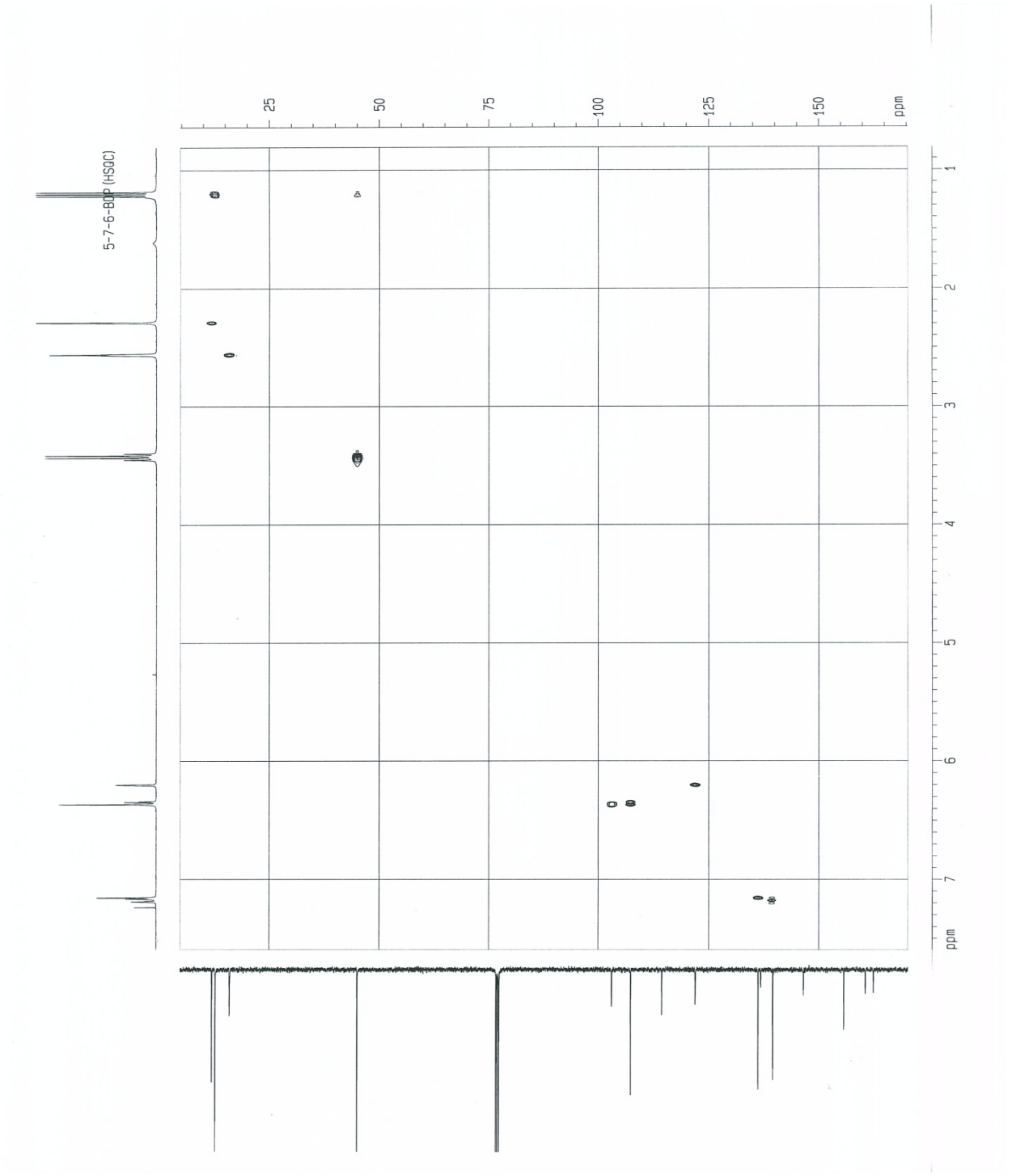



**Fig S15**: $^{1}H$–$^{13}C$ HSQC NMR spectrum of compound **2**.

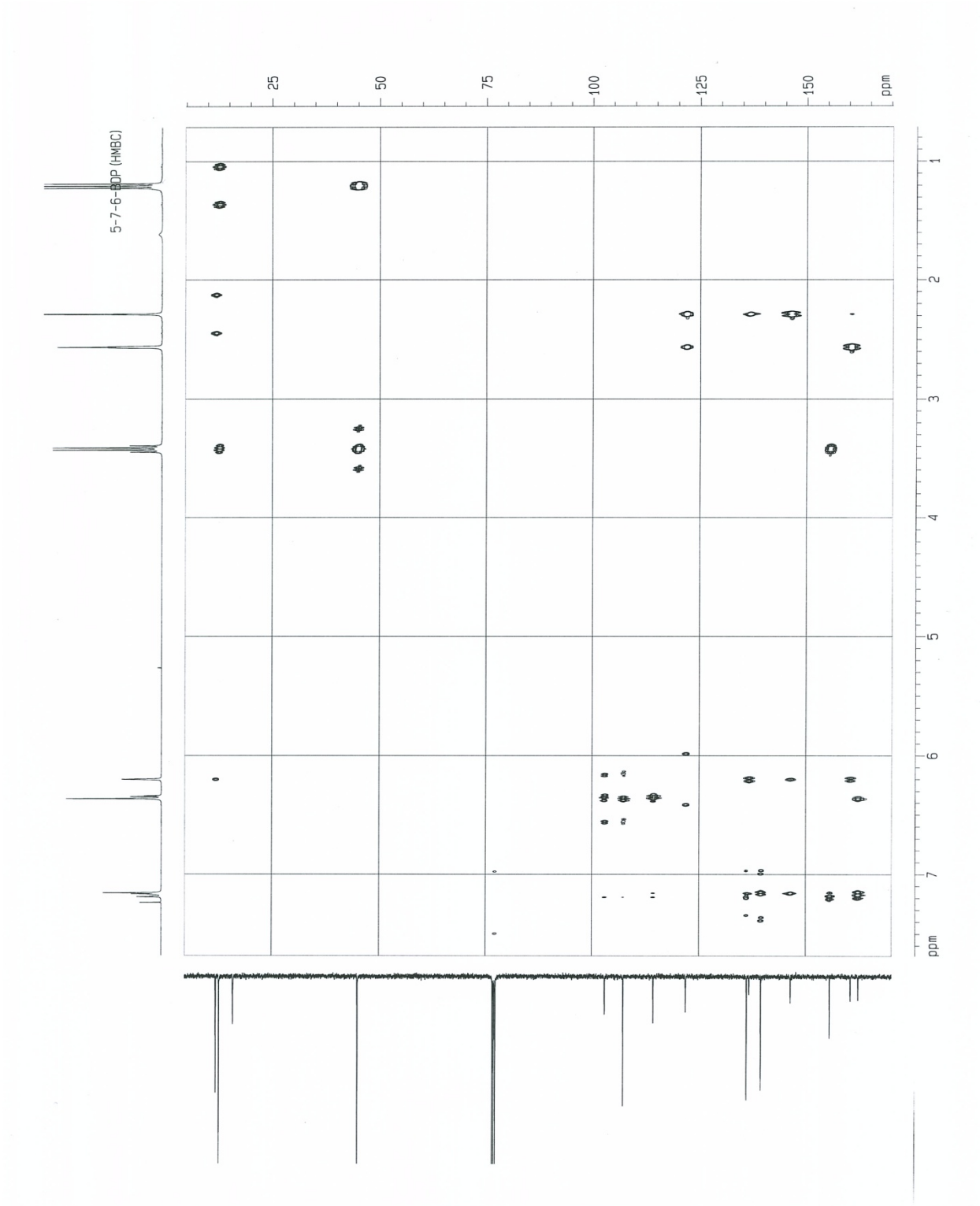



**Fig. S16**: $^{1}H–^{13}C$ HMBC NMR spectrum of compound **2**.

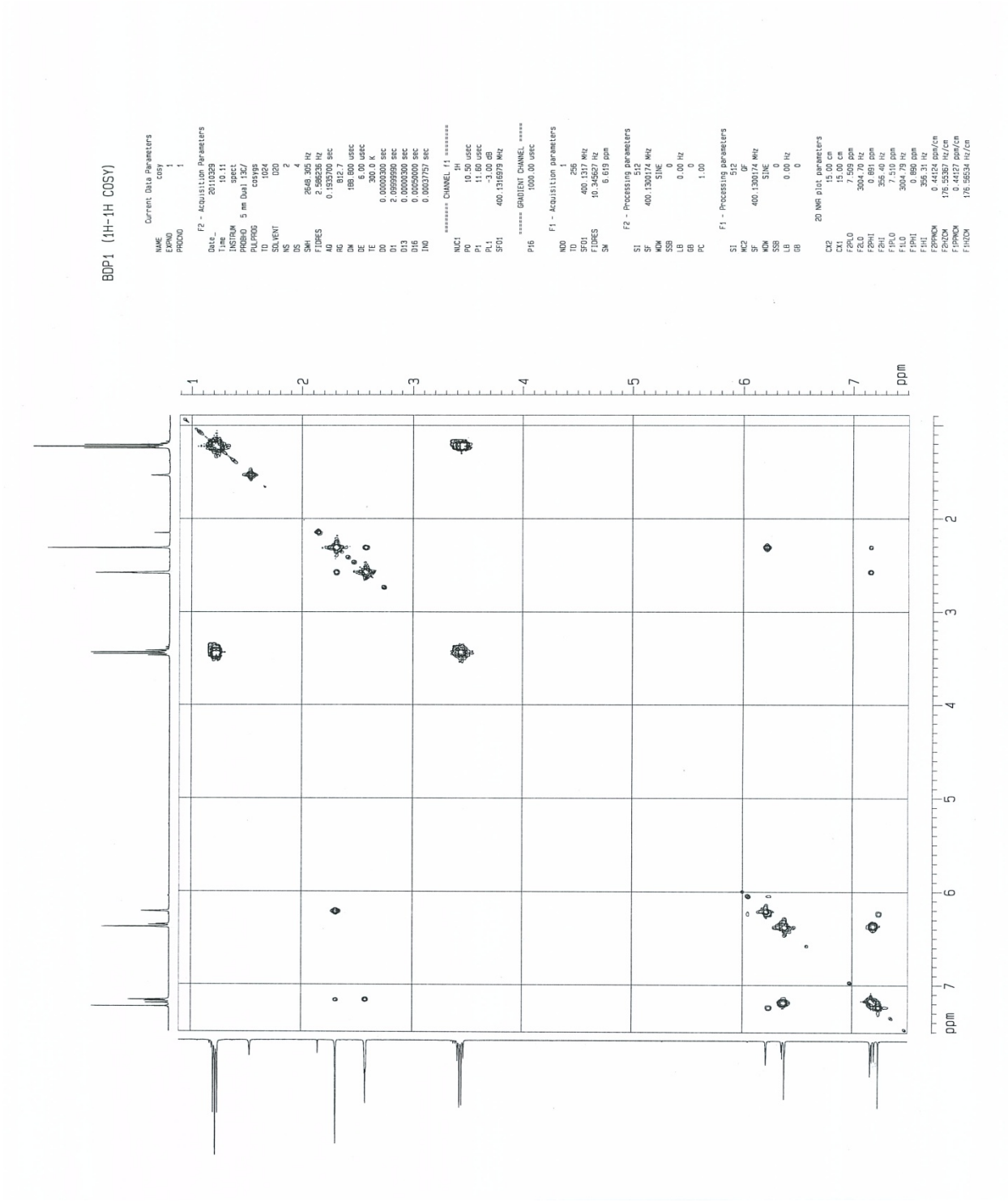



**Fig S17**: $^{1}$H–$^{1}$H COSY NMR spectrum of compound **2**.

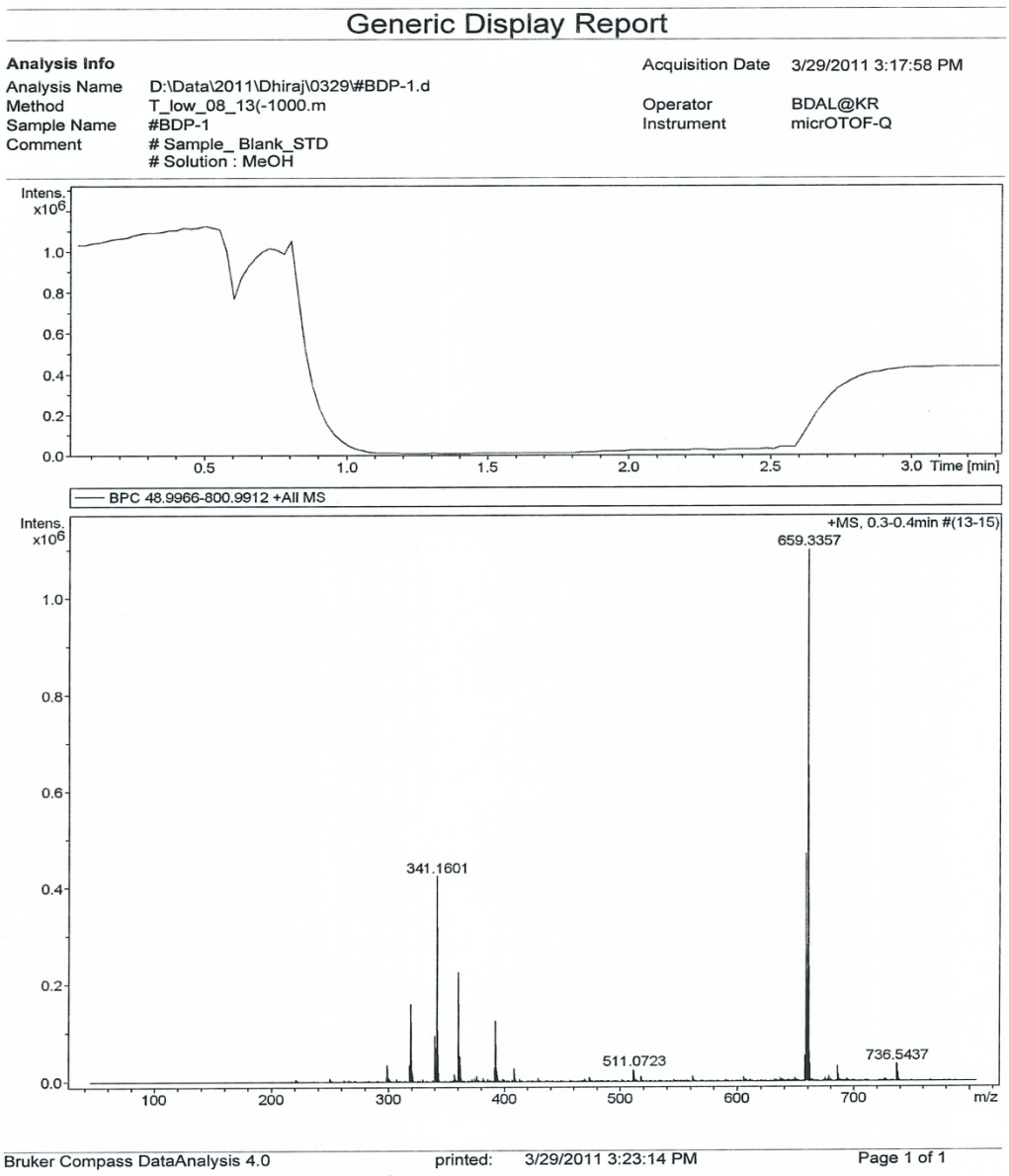



**Fig. S18**: ESI mass spectrum of compound **2**.

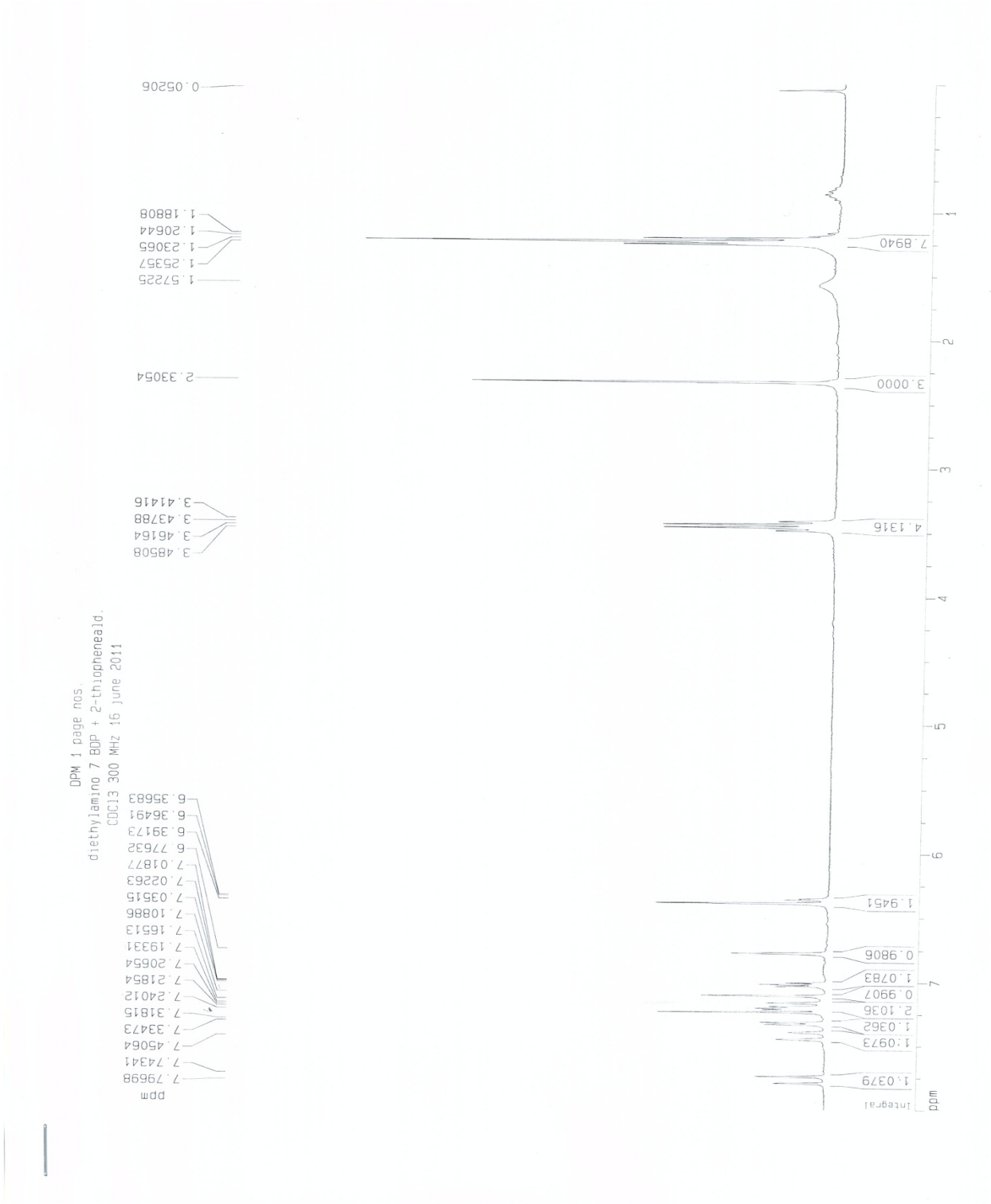



**Fig. S19:** $^{1}$H NMR spectrum of compound **2a.**

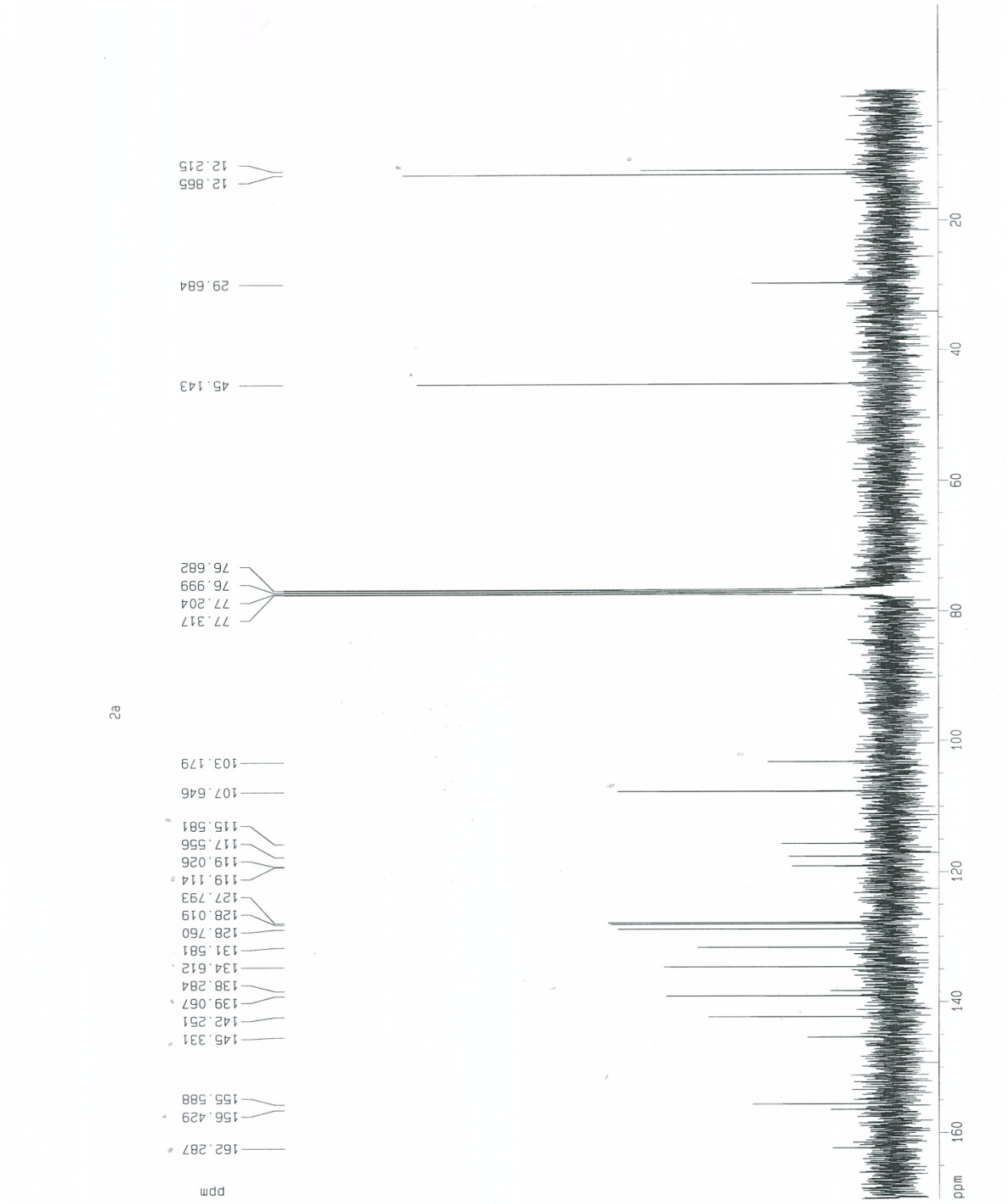



**Fig. S20:** $^{13}$C NMR spectrum of compound **2a**.

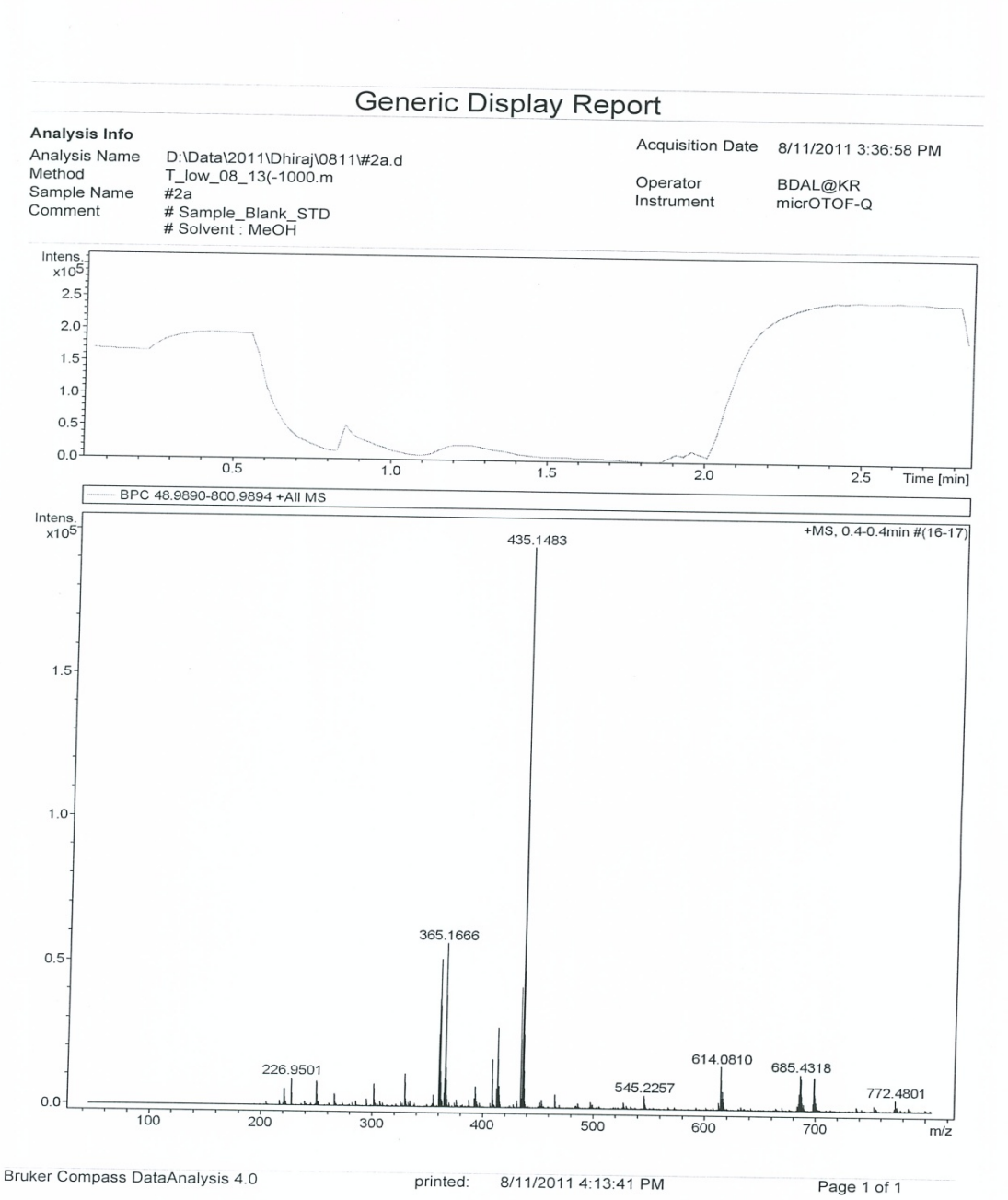



**Fig. S21:** ESI mass spectrum of compound **2a**.

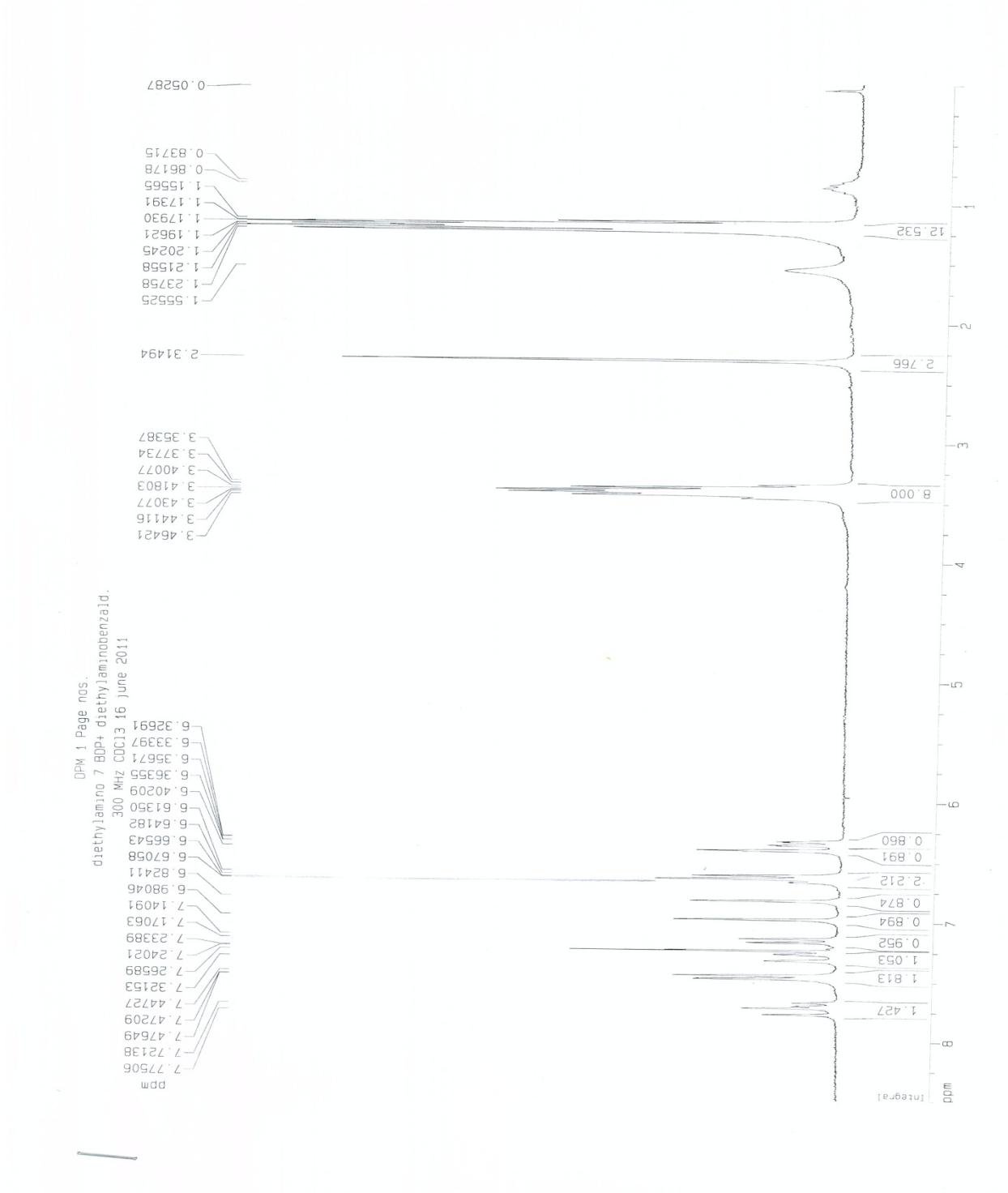



**Fig. S22:** $^{1}$H NMR spectrum of compound **2b**.

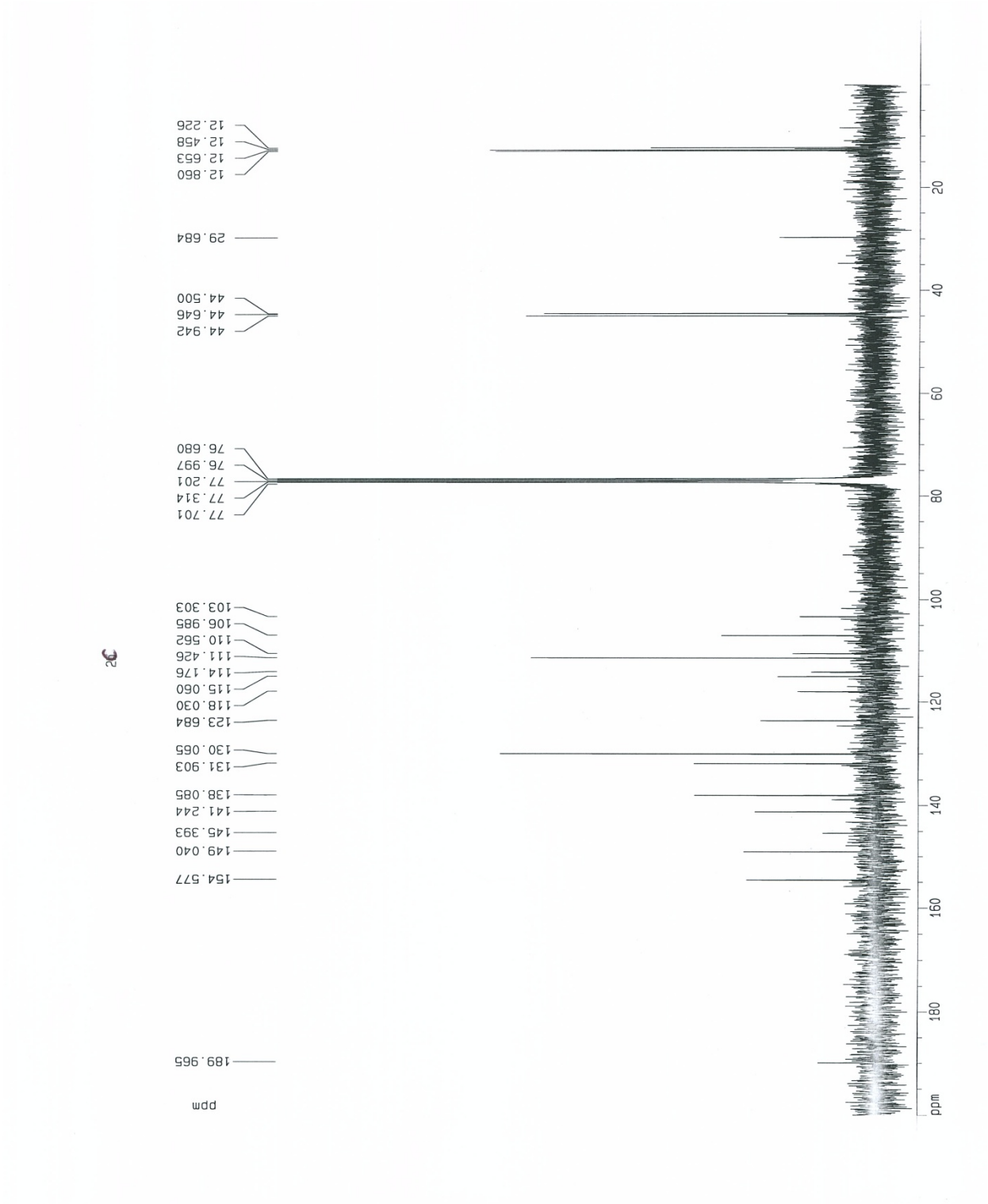



**Fig. S23:** $^{13}$C NMR spectrum of compound **2b**.

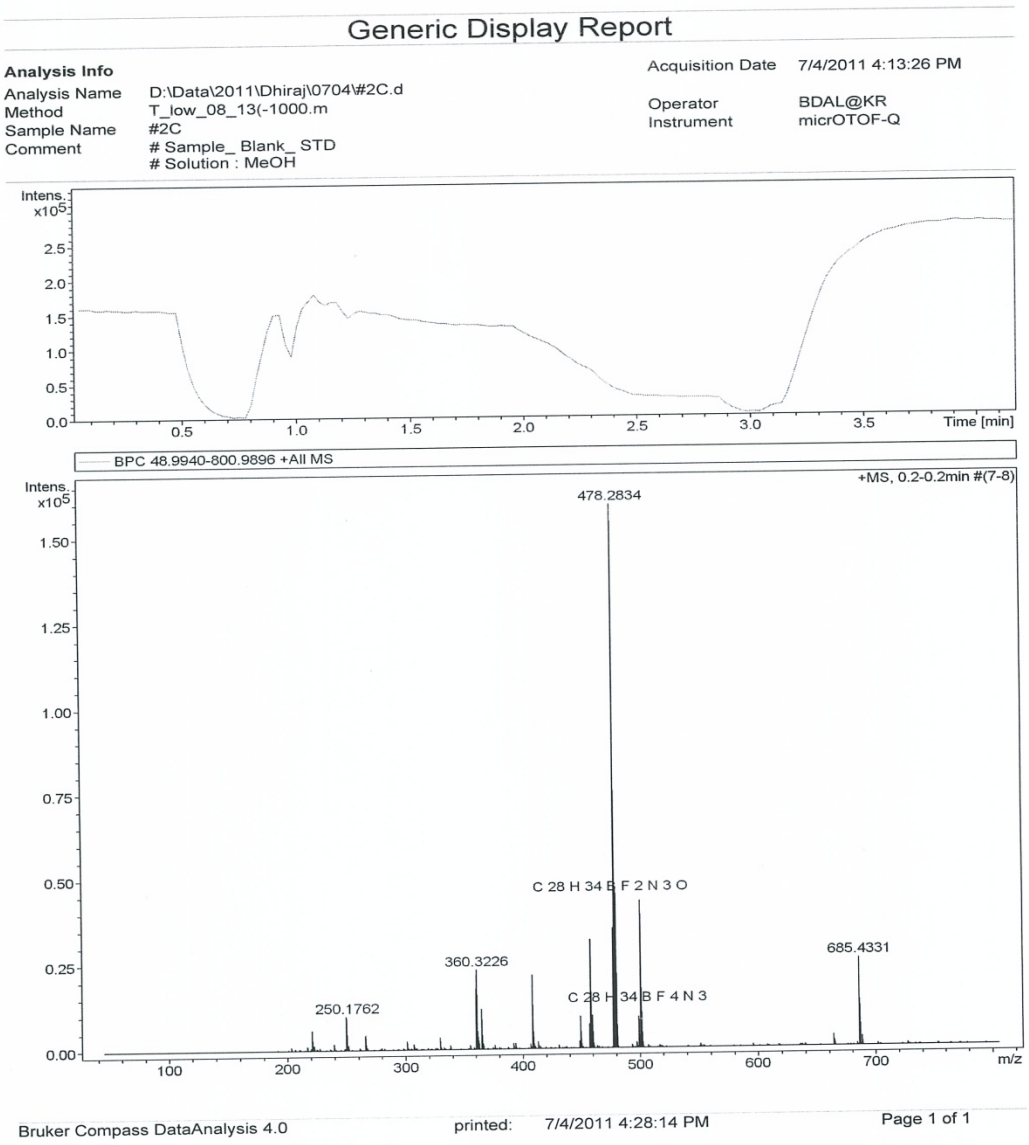



**Fig. S24:** ESI mass spectrum for compound **2b.**

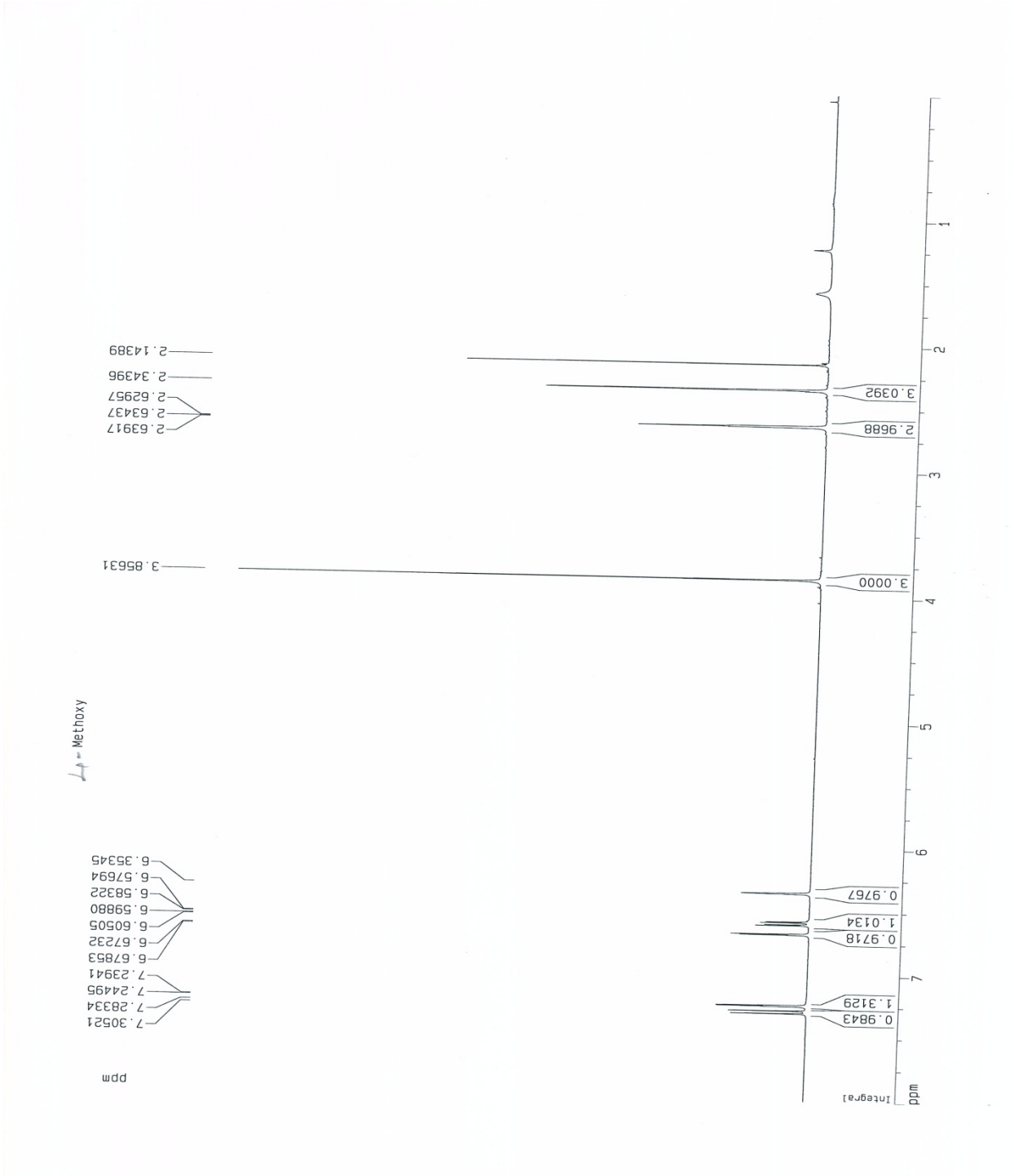



**Fig. S25**: $^{1}$H NMR spectrum of pure "half–BODIPY" product from reaction of 2,4–dimethylpyrrole and 4–methoxysalicylaldehyde.

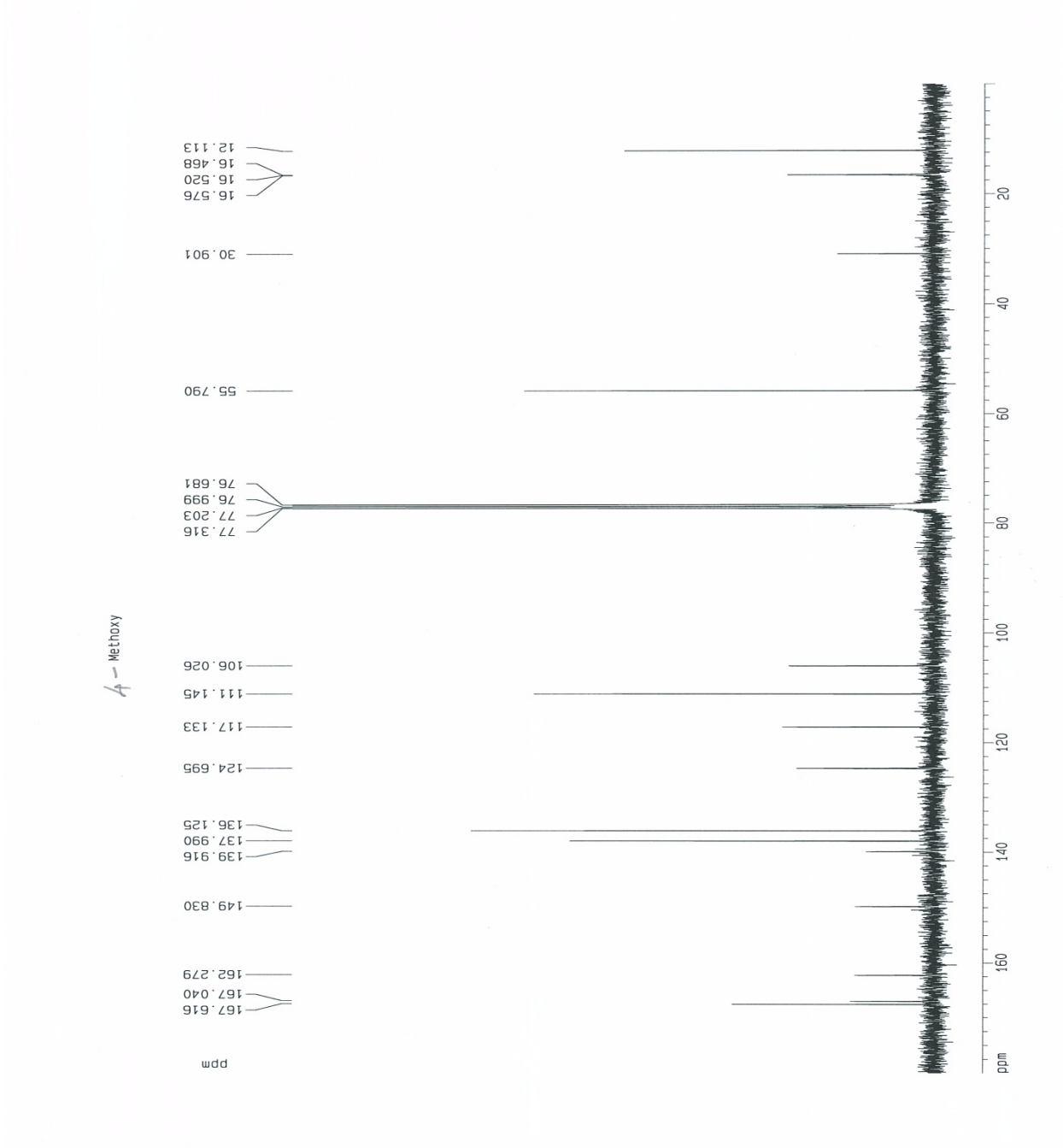



**Fig. S26**: $^{13}$C NMR spectrum of pure "half– BODIPY" product from the reaction of 2,4–dimethylpyrrole and 4–methoxysalicylaldehyde.

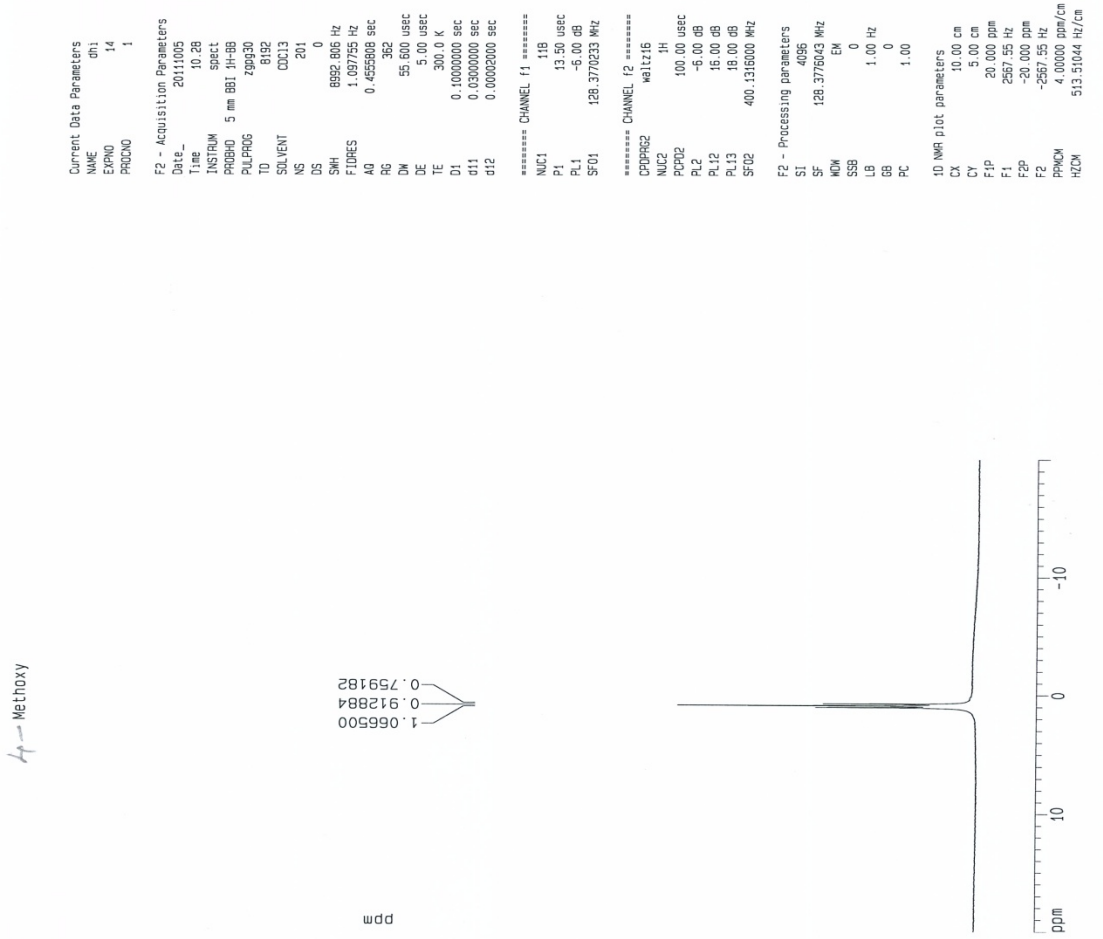



**Fig. S27**: $^{11}$B NMR spectrum of pure "half– BODIPY" product from the reaction of 2,4–dimethylpyrrole and 4–methoxysalicylaldehyde.

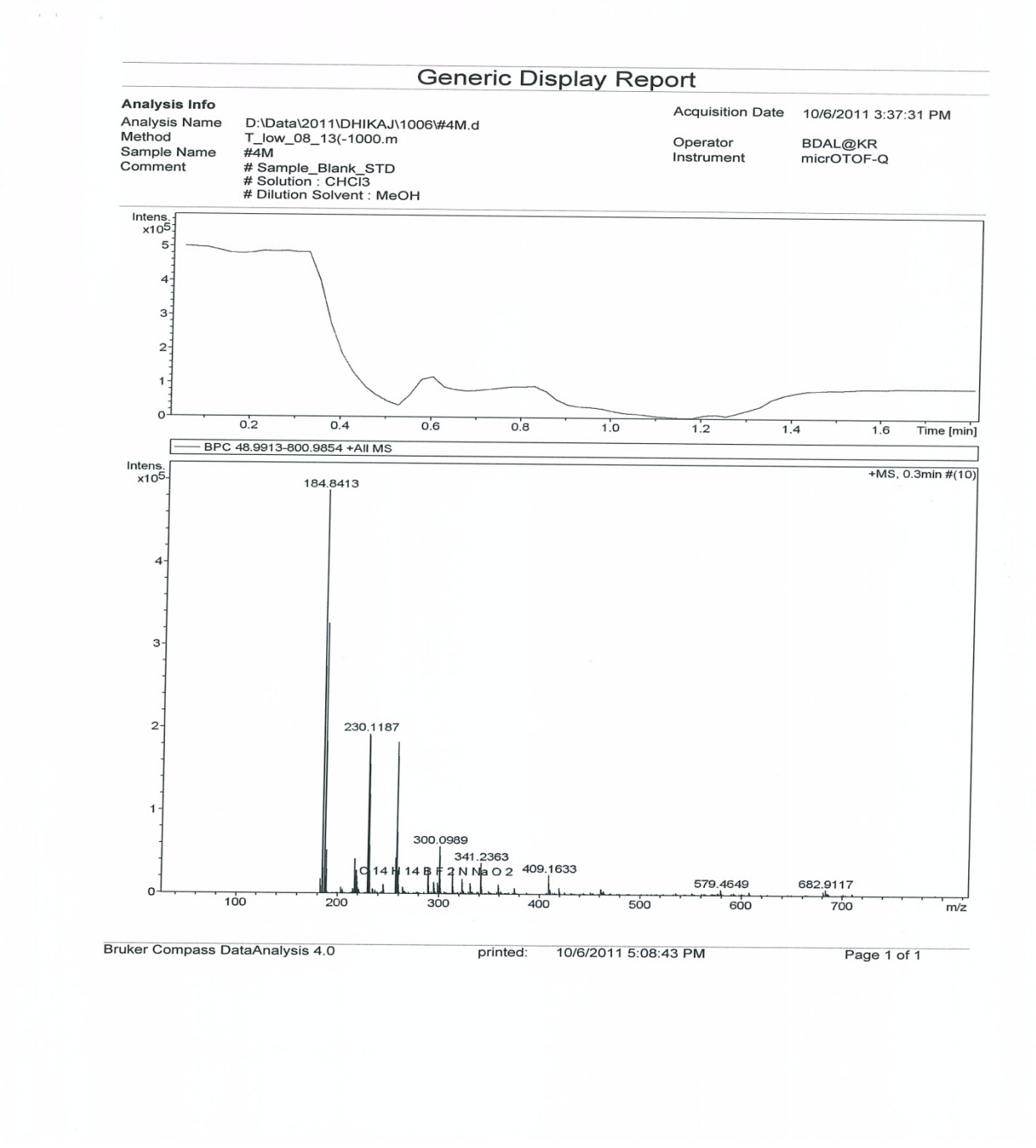



**Fig. S28**: ESI mass spectrum of pure "half–BODIPY" product from the reaction of 2,4–dimethylpyrrole and 4–methoxysalicylaldehyde.

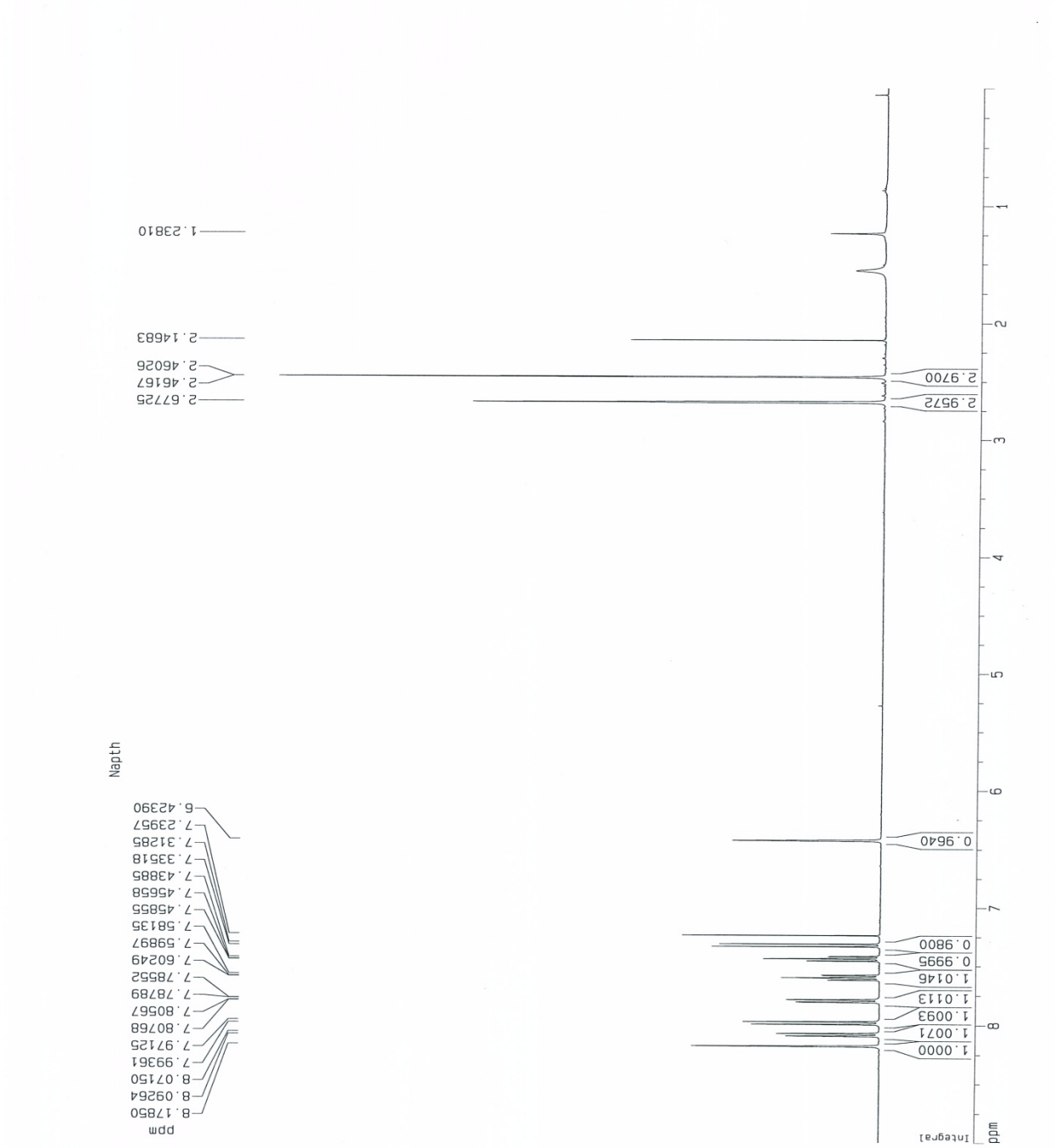



**Fig. S29**: $^{1}$H NMR spectrum of pure "half–BODIPY" product from the reaction of 2,4–dimethylpyrrole with 2–hydroxy–1–naphthaldehyde.

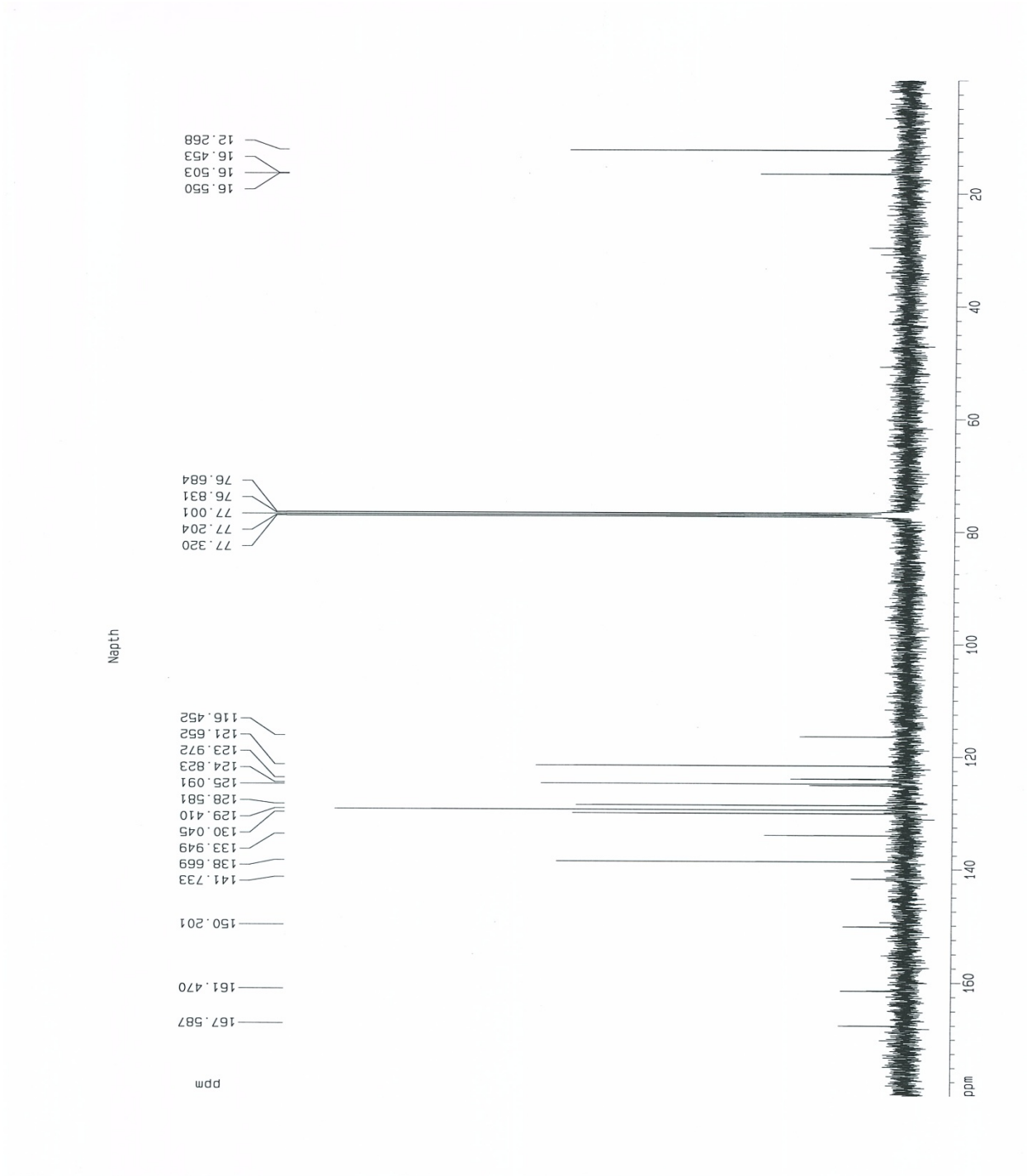



**Fig. S30**: $^{13}$C NMR spectrum of pure "half–BODIPY" product from the reaction of 2,4–dimethylpyrrole with 2–hydroxy–1–naphthaldehyde.

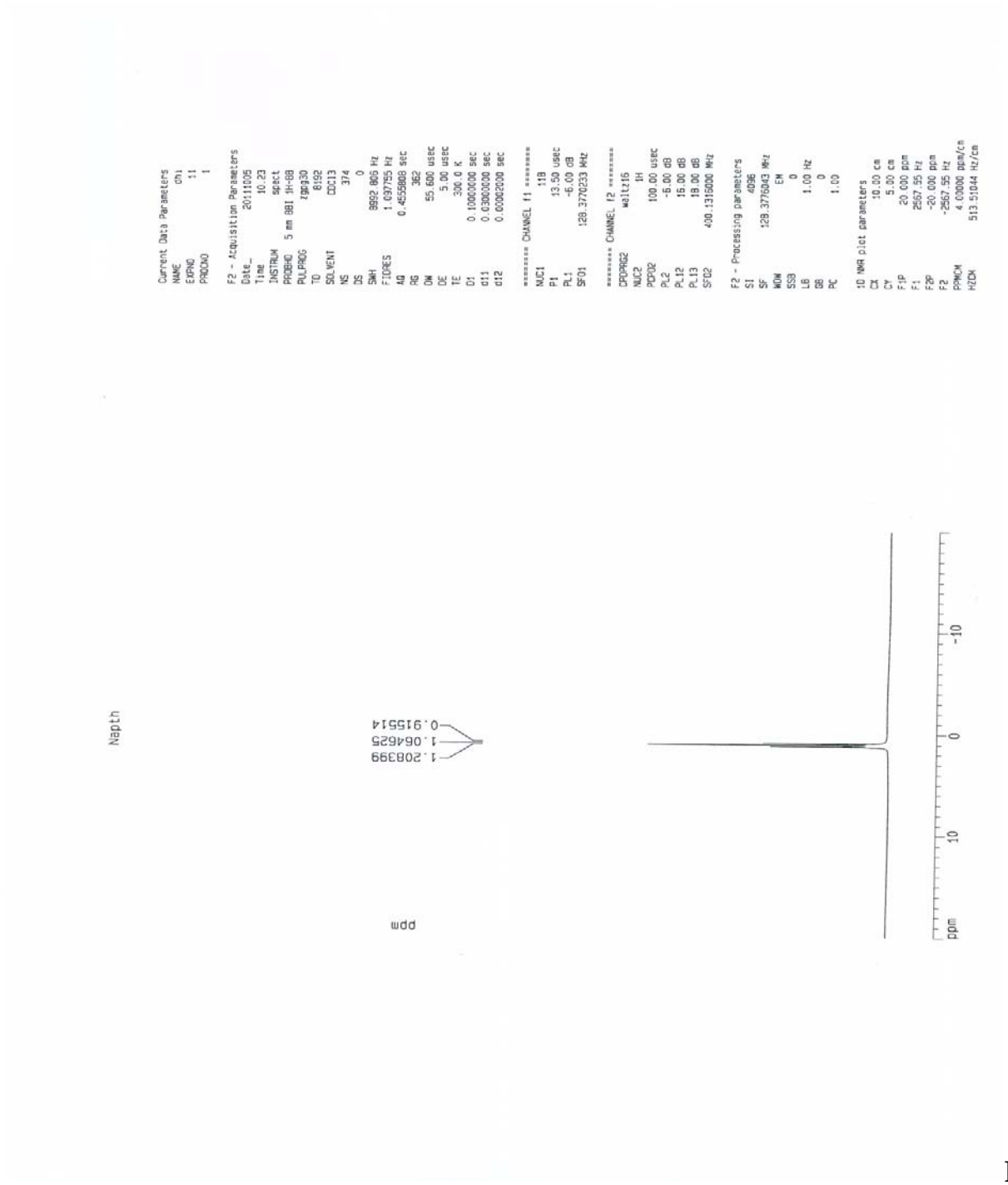



**Fig. S31**: $^{11}$B NMR spectrum of pure "half–BODIPY" product from reaction of 2,4–dimethylpyrrole and 2–hydroxy–1–naphthaldehyde.

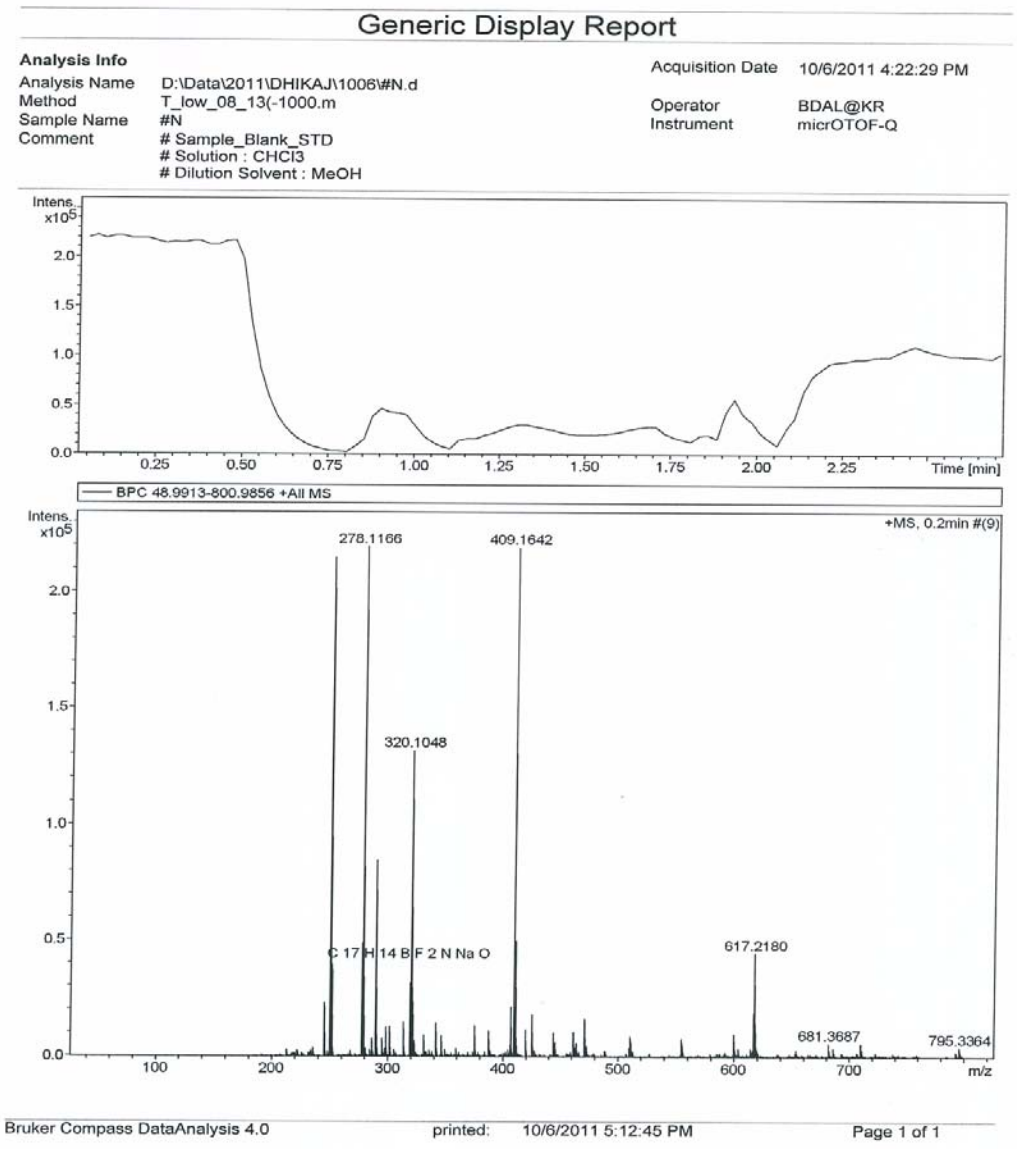



**Fig. S32**: ESI mass spectrum of pure "half–BODIPY" product from the reaction of 2,4–dimethylpyrrole with 2–hydroxy–1–naphthaldehyde.

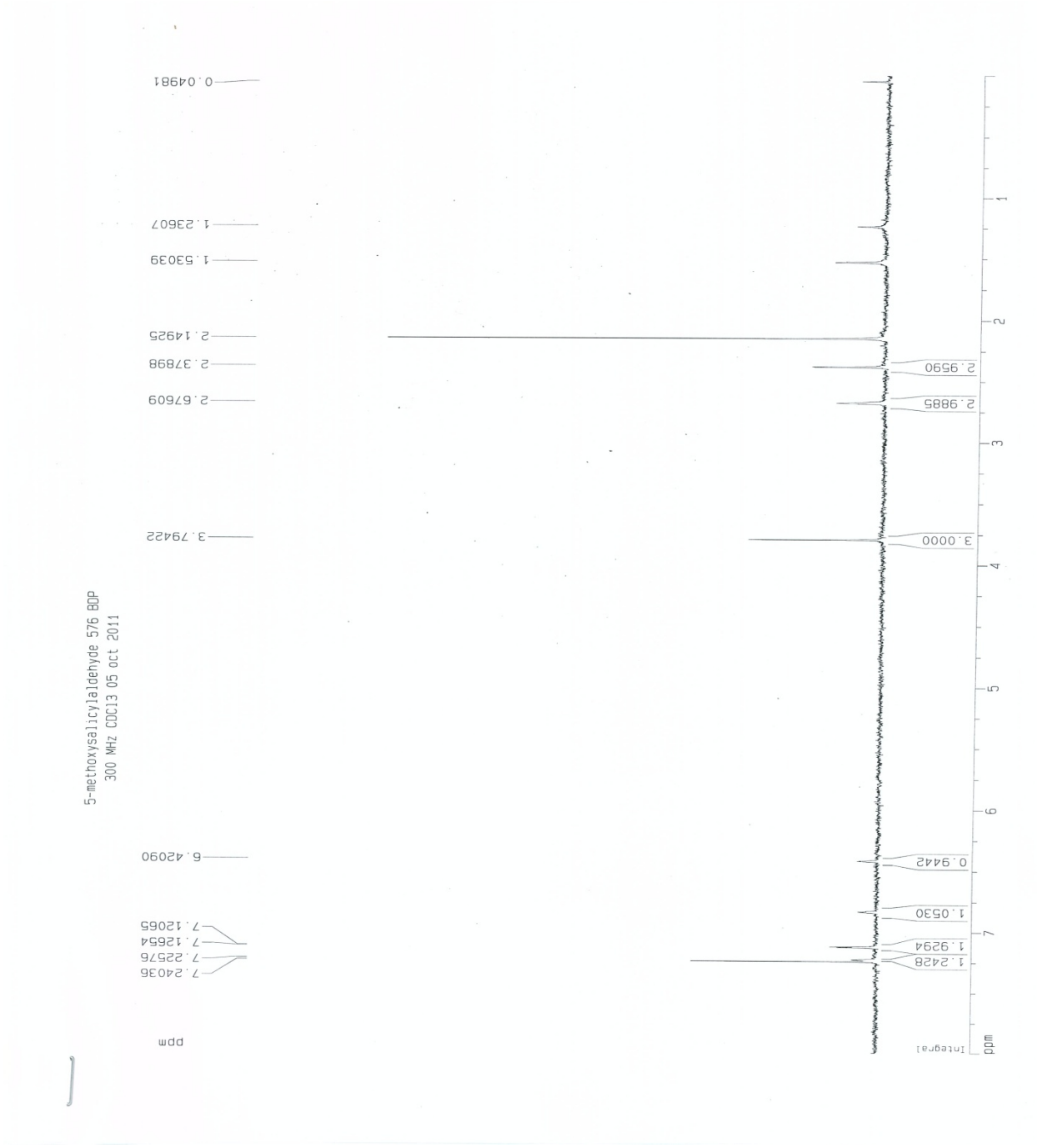



**Fig. S33**: $^{1}$H NMR spectrum of pure "half–BODIPY" product from reaction of 2,4–dimethylpyrrole with 5–methoxysalicylaldehyde.

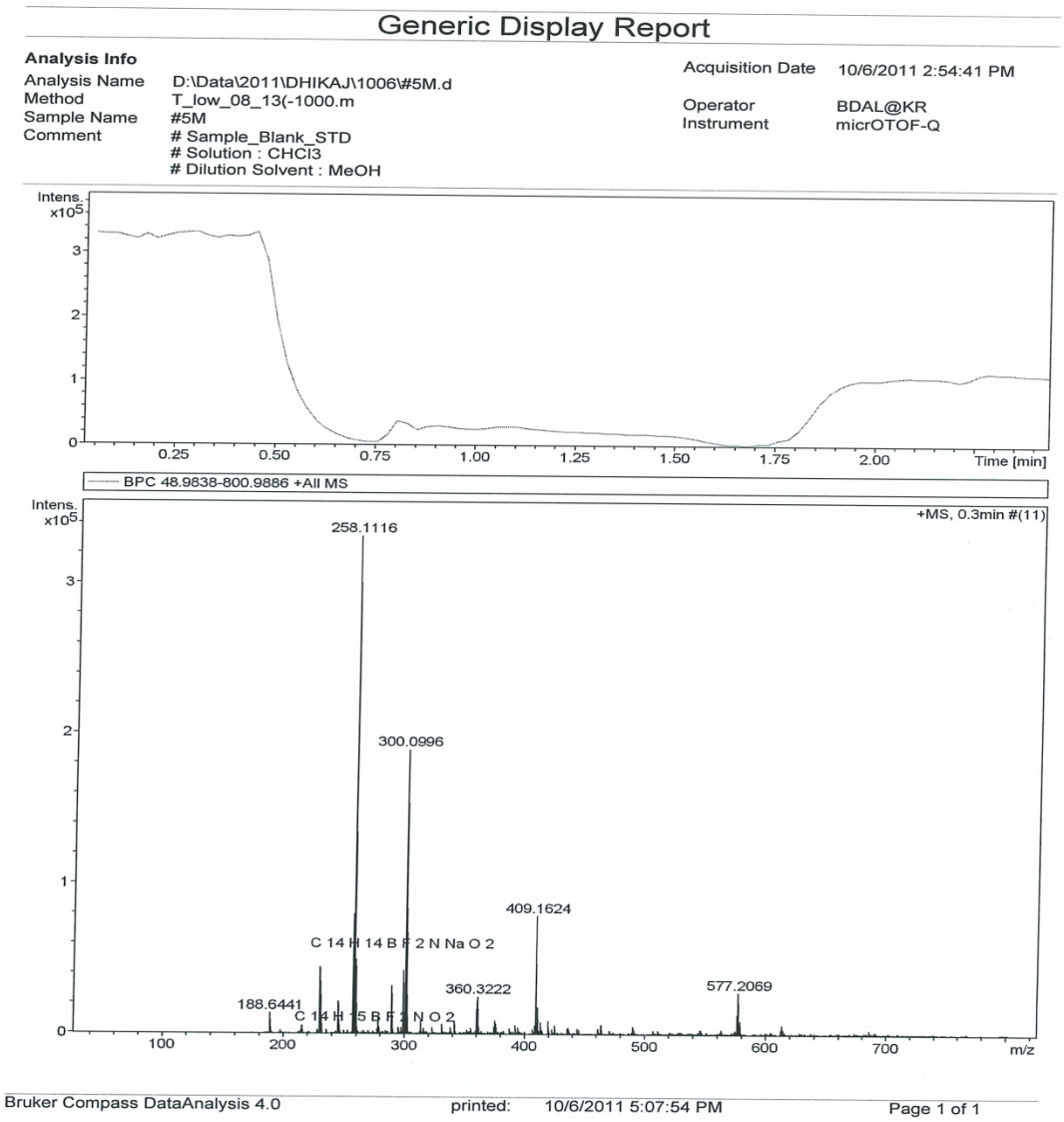



**Fig. S34**: ESI mass spectrum of pure "half–BODIPY" product from reaction of 2,4–dimethylpyrrole with 5–methoxysalicylaldehyde.

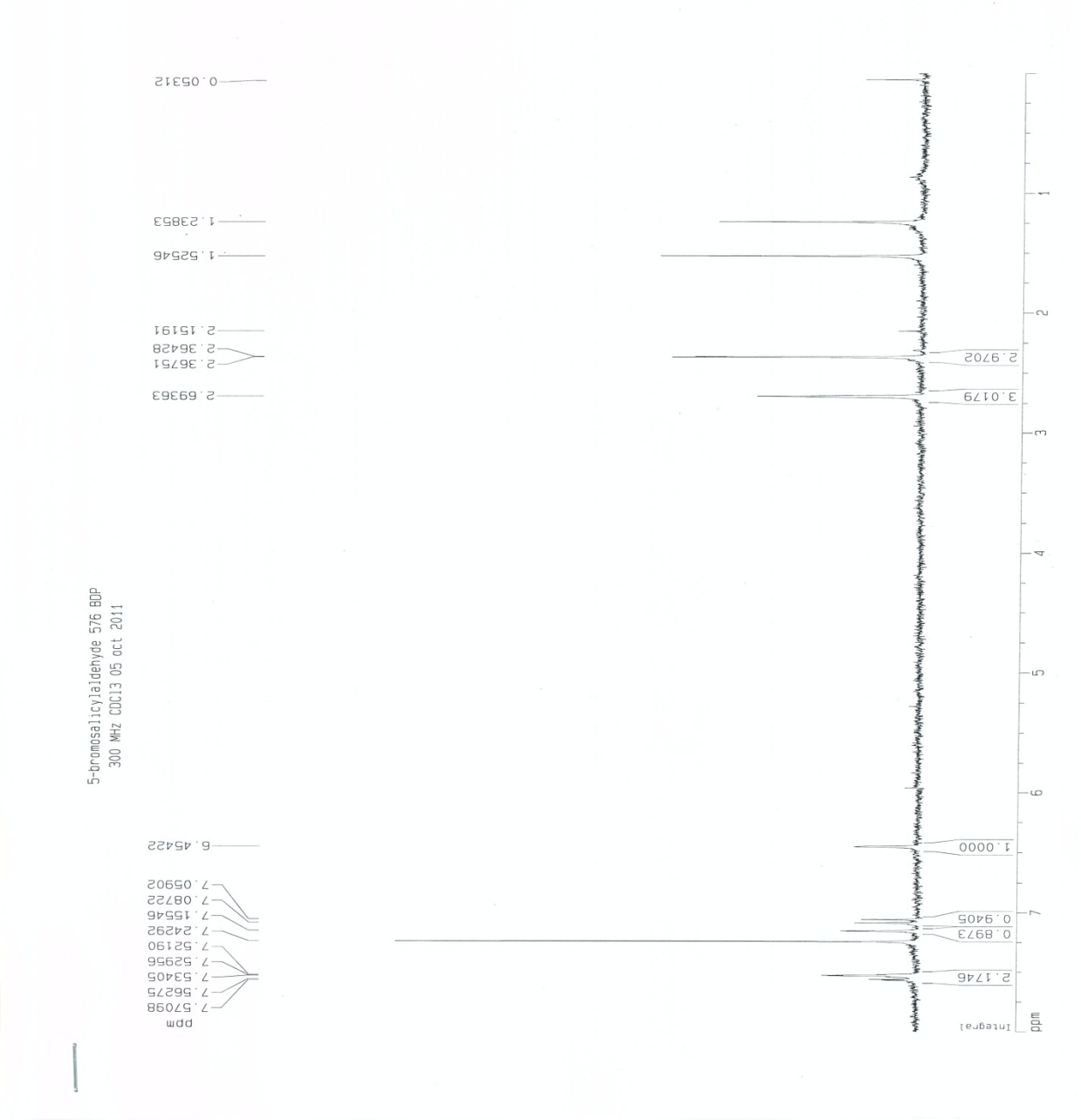



**Fig. S35**: $^{1}$H NMR spectrum of pure "half–BODIPY" product from reaction of 2,4–dimethylpyrrole and 5–bromosalicylaldehyde.

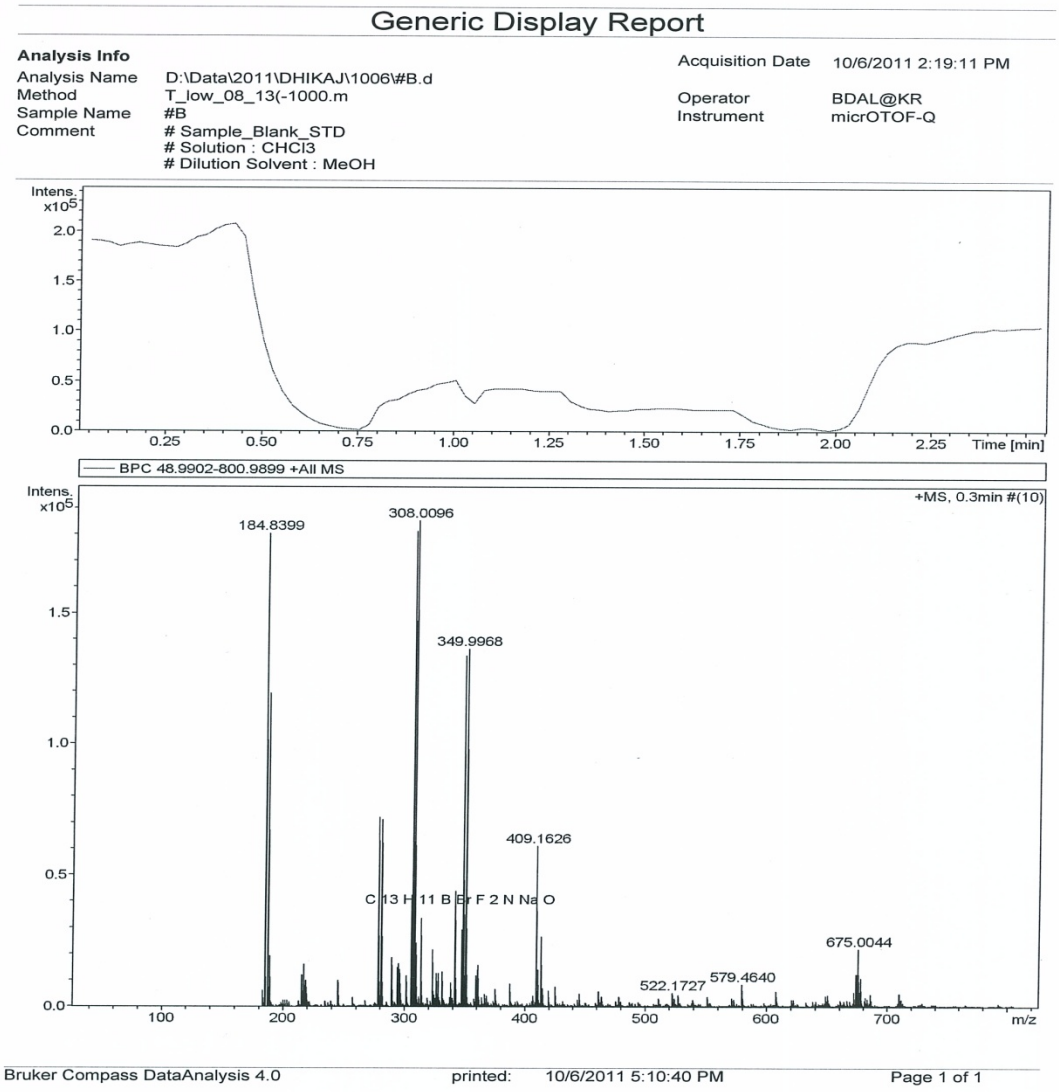



**Fig. S36**: ESI mass spectrum of pure "half–BODIPY" product from the reaction of 2,4–dimethylpyrrole and 5–bromosalicylaldehyde.

**Spectroscopic Data for "half– BODIPY" product from reaction of 2,4–dimethylpyrrole with 2–hydroxynaphthaldehyde:** **$^{1}$H NMR** (400 MHz, $CDCl_3$, δ 7.24): δ = 8.18 (s, 1H), 8.08 (d, 1H, $^{3}J_{H–H}$ = 8.5 Hz), 7.98 (d, 1H, $^{3}J_{H–H}$ = 8.9 Hz), 7.80 (d, 1H, $^{3}J_{H–H}$ = 8.0 Hz), 7.60 (t, 1H, $^{3}J_{H–H}$ = 7.0 Hz), 7.44 (t, 1H, $^{3}J_{H–H}$ = 7.1 Hz), 7.32 (d, 1H, $^{3}J_{H–H}$ = 8.9 Hz), 6.42 (s, 1H), 2.68 (s, 3H), 2.46 (s, 3H). **$^{13}$C–NMR** (100 MHz, $CDCl_3$, δ = 77.0): δ =167.6, 161.5, 150.2, 141.7, 138.7, 133.9, 130.0, 129.4, 128.6, 125.1, 124.8, 124.0, 121.7, 116.5, 16.5, 12.3. **$^{11}$B–NMR** ($CDCl_3$, $BF_3{\cdot}OEt_2$, δ 0.00): δ 1.06 (t, $^{1}J_{B–F}$= 18.8 Hz). **MS**: Calculated for $C_{17}H_{14}BF_2NO$, M = 297.10; found M = 320.10 ($M + Na^+$).

**Spectroscopic Data for "half– BODIPY" product from reaction of 2,4–dimethylpyrrole with 4–methoxysalicylaldehyde:**4–METHOXY: **$^{1}$H NMR** (400 MHz, $CDCl_3$, δ 7.24): δ = 7.29 (d, 1H, $^{3}J_{H–H}$ = 8.7 Hz), 7.24 (s, 1H), 6.68 (s, 1H), 6.59 (d, 1H, $^{3}J_{H–H}$ = 8.7 Hz), 6.35 (s, 1H), 3.86 (s, 3H), 2.63 (s, 3H), 2.34 (s, 3H). **$^{13}$C–NMR** (100 MHz, $CDCl_3$, δ = 77.0): δ =167.6, 167.0, 162.2, 149.8, 139.9, 138.0, 136.1, 124.7, 117.1, 111.1, 106.0, 55.8, 30.9, 16.5, 12.1. **$^{11}$B–NMR** ($CDCl_3$, $BF_3{\cdot}OEt_2$, δ 0.00): δ 0.91 (t, $^{1}J_{B–F}$= 19.7 Hz). **MS**: Calculated for $C_{14}H_{14}BF_2NO_2$, M = 277.07; found M = 300.10 ($M + Na^+$).

**Spectroscopic Data for "half– BODIPY" product from reaction of 2,4–dimethylpyrrole with 5–methoxysalicylaldehyde:**5–METHOXY: **$^{1}$H NMR** (300 MHz, $CDCl_3$, δ 7.24): δ = 7.23 (s, 1H), 7.13 (s, 1H), 7.12 (s, 1H), 6.80 (s, 1H), 6.42 (s, 1H), 3.79 (s, 3H), 2.68

(s, 3H), 2.38 (s, 3H). **MS**: Calculated for $C_{14}H_{14}BF_2NO_2$, M = 277.07; found M = 300.10 (M + $Na^+$).

**Spectroscopic Data for "half– BODIPY" product from reaction of 2,4–dimethylpyrrole with 5–bromosalicylaldehyde:** 5–BROMO: **$^1$H NMR** (400 MHz, $CDCl_3$, δ 7.24): δ = 7.53 (m, 2H), 7.16 (s, 1H), 7.07 (d, 1H, $^3J_{H–H}$ = 8.5 Hz), 6.45 (s, 1H), 2.69 (s, 3H), 2.37 (s, 3H). **MS**: Calculated for $C_{13}H_{11}BBrF_2NO$, M = 325.94; found M = 350.00 (M + $Na^+$ + $H^+$)

**Table 1.** Crystal data and structure refinement for **1** (CCDC # 831215).

| | |
|---|---|
| Identification code | 1 |
| Empirical formula | $C_{20}$ $H_{22}$ B $F_2$ $N_3$ |
| Formula weight | 353.22 |
| Temperature | 296(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Orthorhombic |
| Space group | Pbca |
| Unit cell dimensions | a = 12.7459(15) Å = 90°. |
| | b = 12.7700(13) Å = 90°. |
| | c = 23.352(3) Å = 90°. |
| Volume | 3800.9(7) $Å^3$ |
| Z | 8 |
| Density (calculated) | 1.235 $Mg/m^3$ |
| Absorption coefficient | 0.087 $mm^{-1}$ |
| F(000) | 1488 |
| Crystal size | 0.3 x 0.15 x 0.1 mm |
| Theta range for data collection | 1.74 to 24.80°. |
| Index ranges | –14<=h<=14, –14<=k<=15, –27<=l<=27 |
| Reflections collected | 22184 |
| Independent reflections | 3254 [R(int) = 0.1506] |
| Completeness to theta = 24.80° | 99.4 % |
| Refinement method | Full–matrix least–squares on $F^2$ |
| Data / restraints / parameters | 3254 / 0 / 245 |
| Goodness–of–fit on $F^2$ | 1.014 |
| Final R indices [I>2 sigma(I)] | R1 = 0.0643, wR2 = 0.1337 |
| R indices (all data) | R1 = 0.1527, wR2 = 0.1860 |
| Extinction coefficient | 0.0193(17) |
| Largest diff. peak and hole | 0.461 and –0.420 $e/Å^{-3}$ |

**Table 2.** Crystal data structure refinement for **2** (CCDC # 822264).

| | | |
|---|---|---|
| Identification code | 2 | |
| Empirical formula | $C_{17}H_{21}BF_2N_2O$ | |
| Formula weight | 318.17 | |
| Temperature | 296(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/c | |
| Unit cell dimensions | a = 9.0254(19) Å | = 90°. |
| | b = 11.308(2) Å | = 93.845(6)°. |
| | c = 16.035(4) Å | = 90°. |
| Volume | 1632.9(6) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.294 $Mg/m^3$ | |
| Absorption coefficient | 0.096 $mm^{-1}$ | |
| F(000) | 672 | |
| Crystal size | 0.4 x 0.3 x 0.2 mm | |
| Theta range for data collection | 2.21 to 24.30°. | |
| Index ranges | –10<=h<=10, –13<=k<=13, –18<=l<=18 | |
| Reflections collected | 17948 | |
| Independent reflections | 2652 [R(int) = 0.0423] | |
| Completeness to theta = 24.30° | 99.6 % | |
| Refinement method | Full–matrix least–squares on $F^2$ | |
| Data / restraints / parameters | 2652 / 0 / 212 | |
| Goodness–of–fit on $F^2$ | 1.029 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0608, wR2 = 0.1632 | |
| R indices (all data) | R1 = 0.0815, wR2 = 0.1790 | |
| Extinction coefficient | 0.000(2) | |
| Largest diff. peak and hole | 0.688 and –0.213 $e/Å^{-3}$ | |

**Table 3.** Crystal data and structure refinement for **2a** (CCDC # 830331).

| | | |
|---|---|---|
| Identification code | 2a | |
| Empirical formula | $C_{22}H_{23}BF_2N_2OS$ | |
| Formula weight | 412.29 | |
| Temperature | 296(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | C2/c | |
| Unit cell dimensions | a = 20.366(9) Å | = 90°. |
| | b = 7.556(3) Å | = 106.43(3)°. |
| | c = 27.882(12) Å | = 90°. |
| Volume | 4115(3) $Å^3$ | |
| Z | 8 | |
| Density (calculated) | 1.331 $Mg/m^3$ | |
| Absorption coefficient | 0.191 $mm^{-1}$ | |
| F(000) | 1728 | |
| Crystal size | 0.25 x 0.22 x 0.12 $mm^3$ | |
| Theta range for data collection | 2.09 to 28.36°. | |
| Index ranges | –21<=h<=27, –10<=k<=9, –35<=l<=37 | |
| Reflections collected | 15529 | |
| Independent reflections | 5067 [R(int) = 0.1113] | |
| Completeness to theta = 28.36° | 98.4 % | |
| Max. and min. transmission | 0.9775 and 0.9539 | |
| Refinement method | Full–matrix least–squares on $F^2$ | |
| Data / restraints / parameters | 5067 / 0 / 265 | |
| Goodness–of–fit on $F^2$ | 1.016 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0802, wR2 = 0.1734 | |
| R indices (all data) | R1 = 0.2109, wR2 = 0.2139 | |
| Extinction coefficient | 0.0046(7) | |
| Largest diff. peak and hole | 0.332 and –0.446 $e/Å^{-3}$ | |

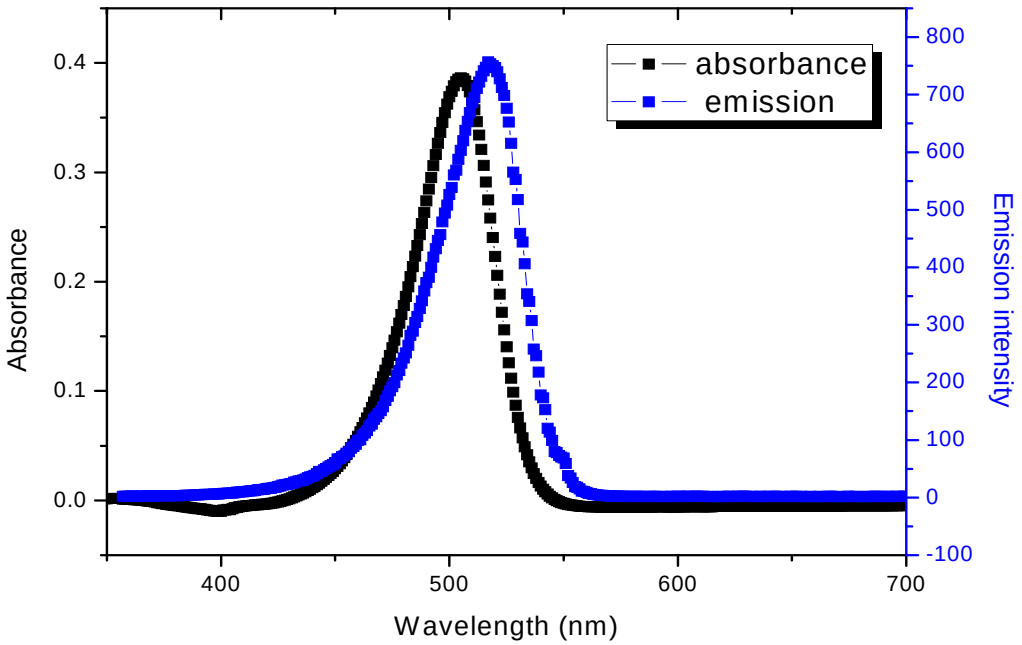



**Fig. S37:** Absoption and emission spectrum of compound **2** in acetonitrile**.**

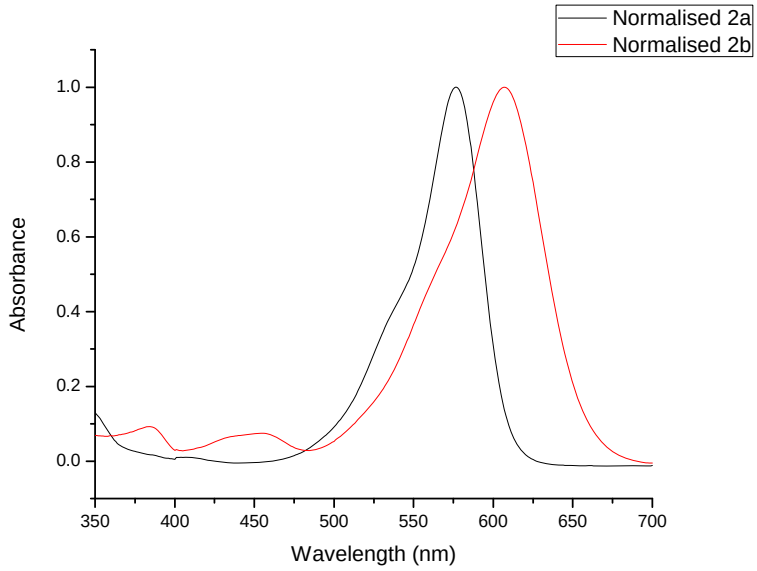



**Fig. S38: Absorption spectrum of compound 2a and 2b in acetonitrile.**

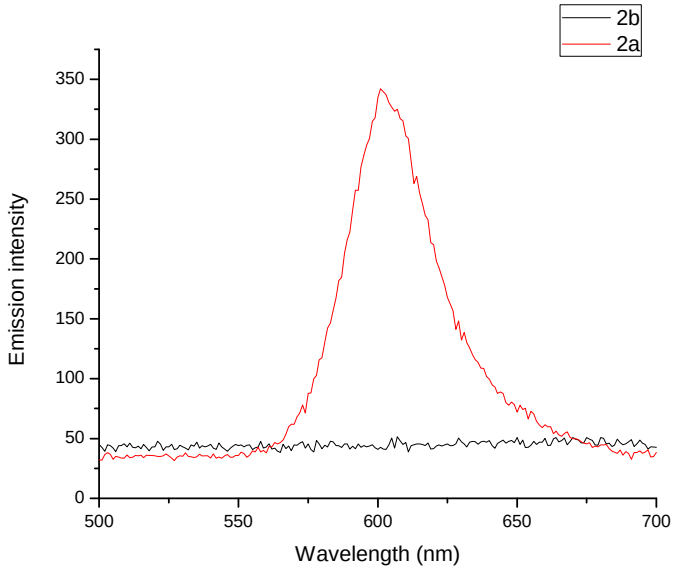



**Fig. S39: Emission spectrum of compound 2a and 2b in acetonitrile.**

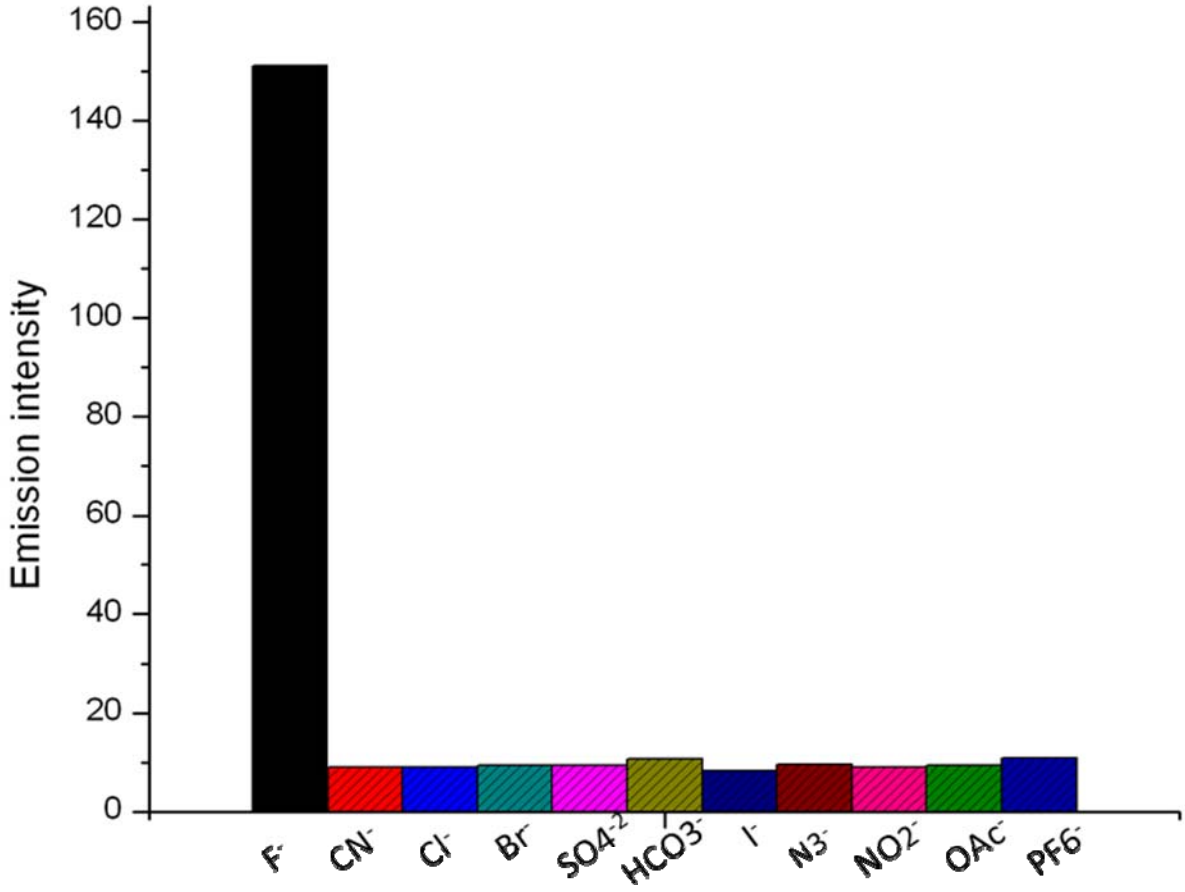



**Fig. S40:** Comparison of different anions with fluoride anion for compound **1** ( $5 \times 10^{-5}$ ).

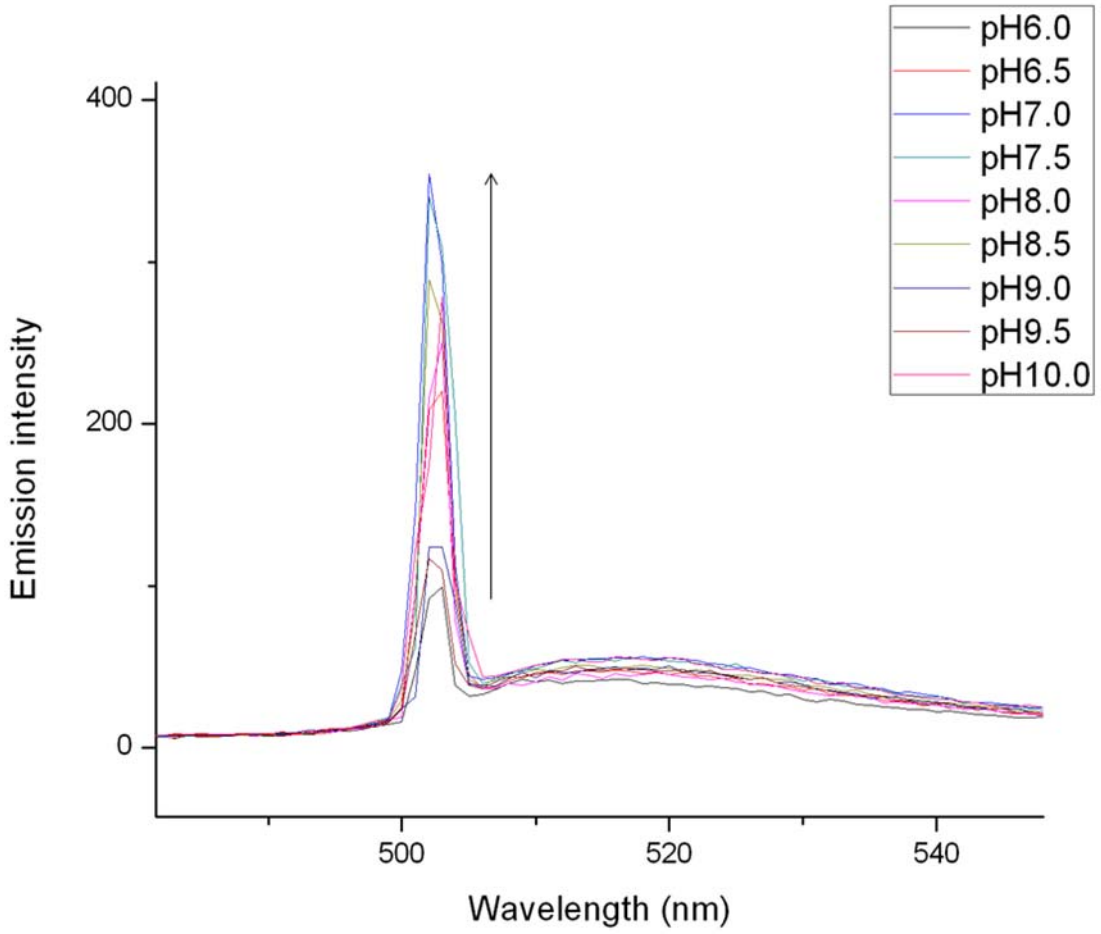



**Fig. S 41:** pH titration data for compound 1 against buffer solutions at different pH's.

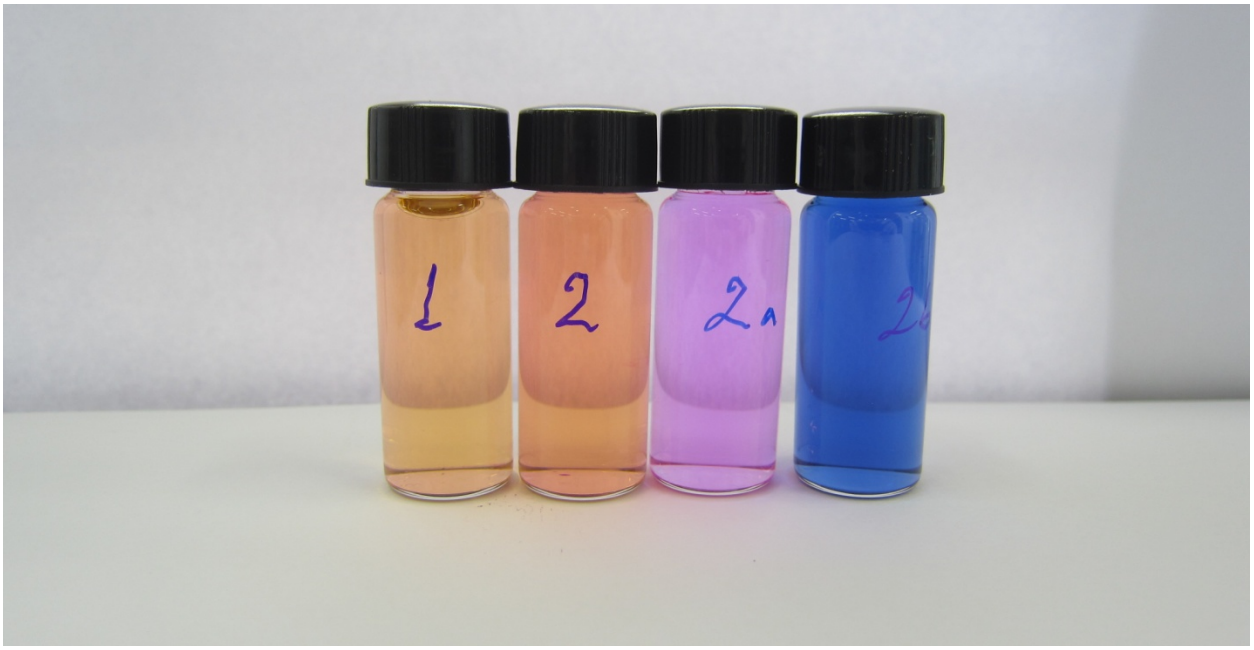



**Fig S42:** Appearance of compounds **1, 2, 2a, 2b** (from left to right) under white light.


**Fig S43:** Appearance of compounds **1, 2, 2a, 2b** (from left to right) under UV lamp (365nm).

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