

## Supporting Information

### Thermo- and Photostable Symmetrical Benzo[*cd*]indolenyl-Substituted Heptamethine Cyanine Dyes Carrying a Tetrakis(pentafluorophenyl)borate that Absorb Only Near-Infrared Light over 1000 nm

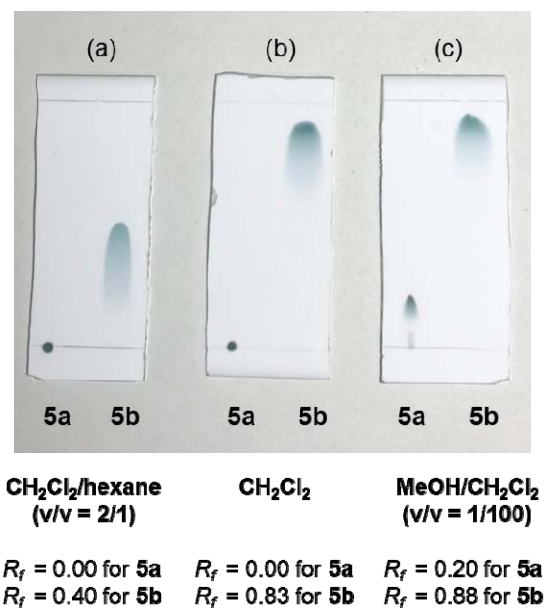
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<sup>2</sup> Division of Instrumental Analysis, Life Science Research Center, Gifu University, 1-1 Yanagido, Gifu 501-1193, Japan.

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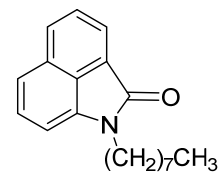
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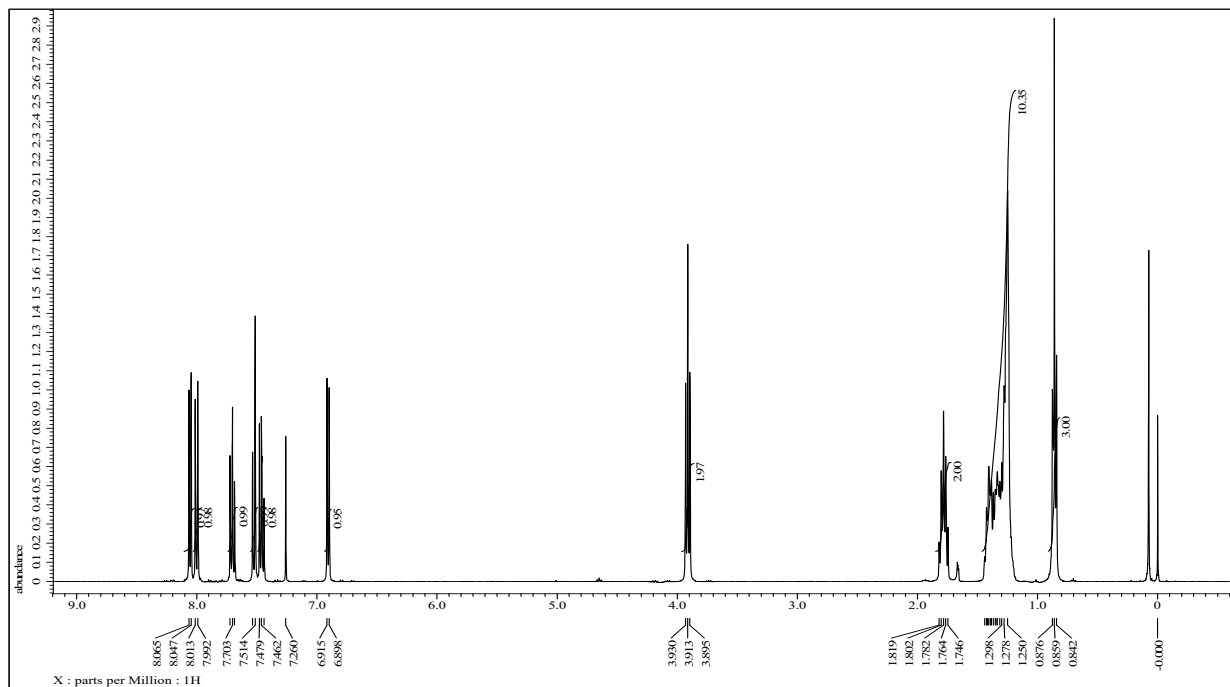
**Figure S1.** TLC plates of the prepared symmetrical benzo[*cd*]indolenyl-substituted heptamethine cyanine dyes **5a**,**b** using  $\text{CH}_2\text{Cl}_2/\text{hexane}$  (a),  $\text{CH}_2\text{Cl}_2$  (b), and  $\text{MeOH}/\text{CH}_2\text{Cl}_2$  (c).

The obtained symmetrical benzo[*cd*]indolenyl-substituted heptamethine cyanine dye **5a** carrying the  $\text{ClO}_4^-$  anion is highly polar. As a result, the  $R_f$  value of **5a** carrying the  $\text{ClO}_4^-$  anion is 0.20, using much polar solvents, such as methanol/ $\text{CH}_2\text{Cl}_2$  (v/v = 1/100) as an eluent on a TLC plate, as shown in Figure S3(c). Interestingly, the  $R_f$  value (0.88) of the corresponding heptamethine cyanine dye **5b** carrying the  $(\text{C}_6\text{F}_5)_4\text{B}^-$  anion is much greater than that of the dye **5a**, using the same mixed solvents, as shown in Figure 3(c). As shown in Figures 3(a),(b), even the use of less polar solvents, such as  $\text{CH}_2\text{Cl}_2/\text{hexane}$  (v/v = 2/1) or  $\text{CH}_2\text{Cl}_2$ , as eluents on TLC plates resulted in moderate to high  $R_f$  values (0.40 and 0.83) for the dye **5b**, although the  $R_f$  values for the dye **5a** carrying the  $\text{ClO}_4^-$  anion are zero under the same conditions.

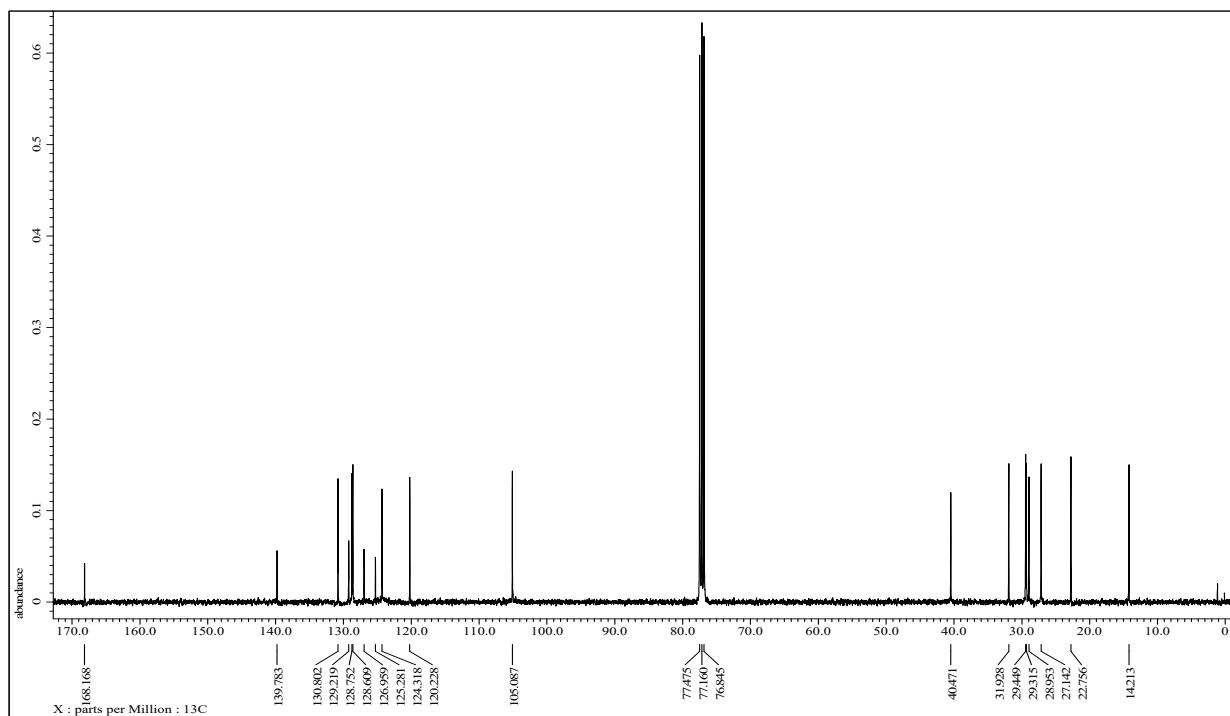
# 1-Octylbenzo[cd]indol-2(1H)-one (2)



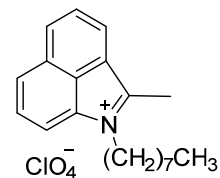
## <sup>1</sup>H NMR



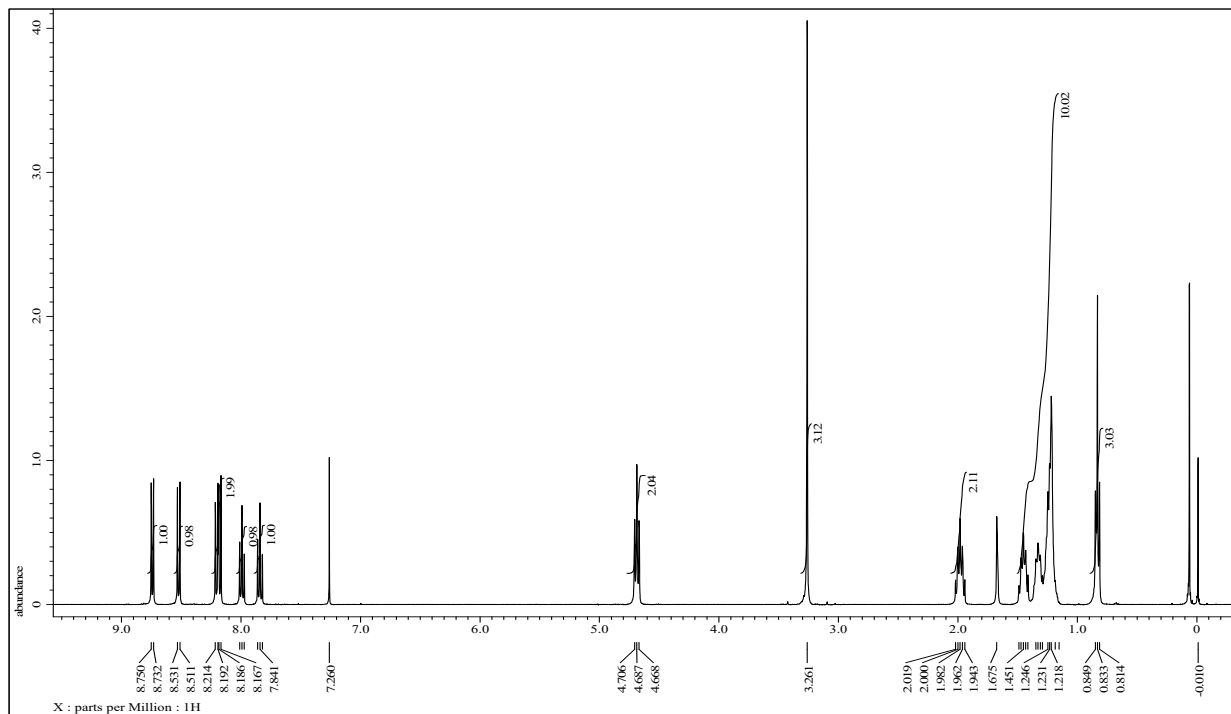
## <sup>13</sup>C NMR



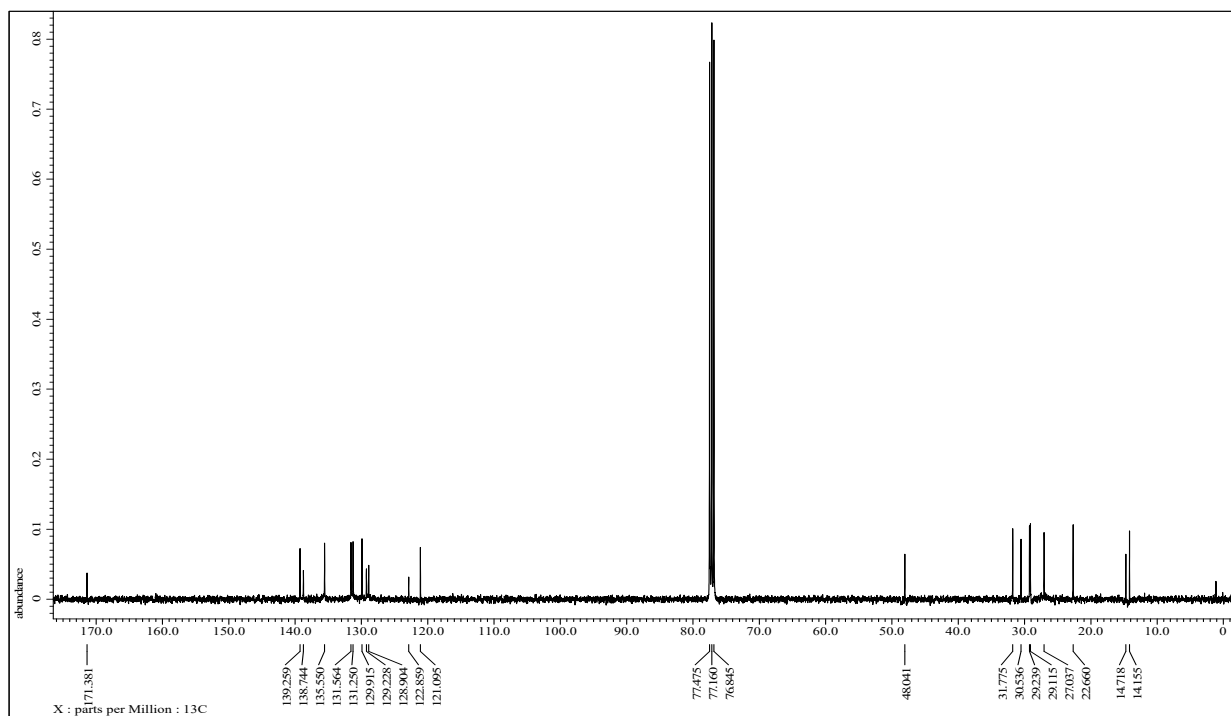
## 2-Methyl-1-octylbenzo[cd]indol-1-ium perchlorate (3)



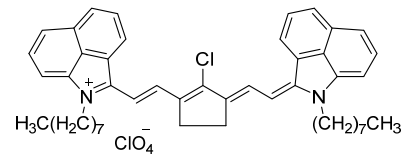
### $^1\text{H}$ NMR



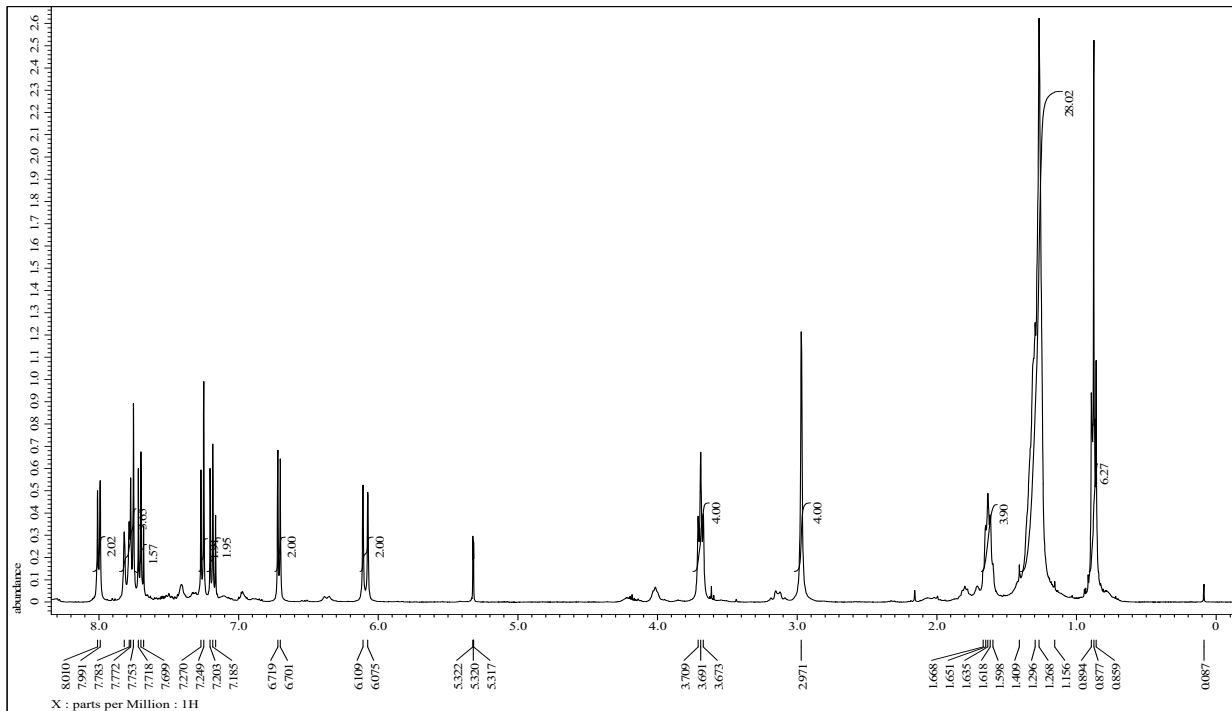
### $^{13}\text{C}$ NMR



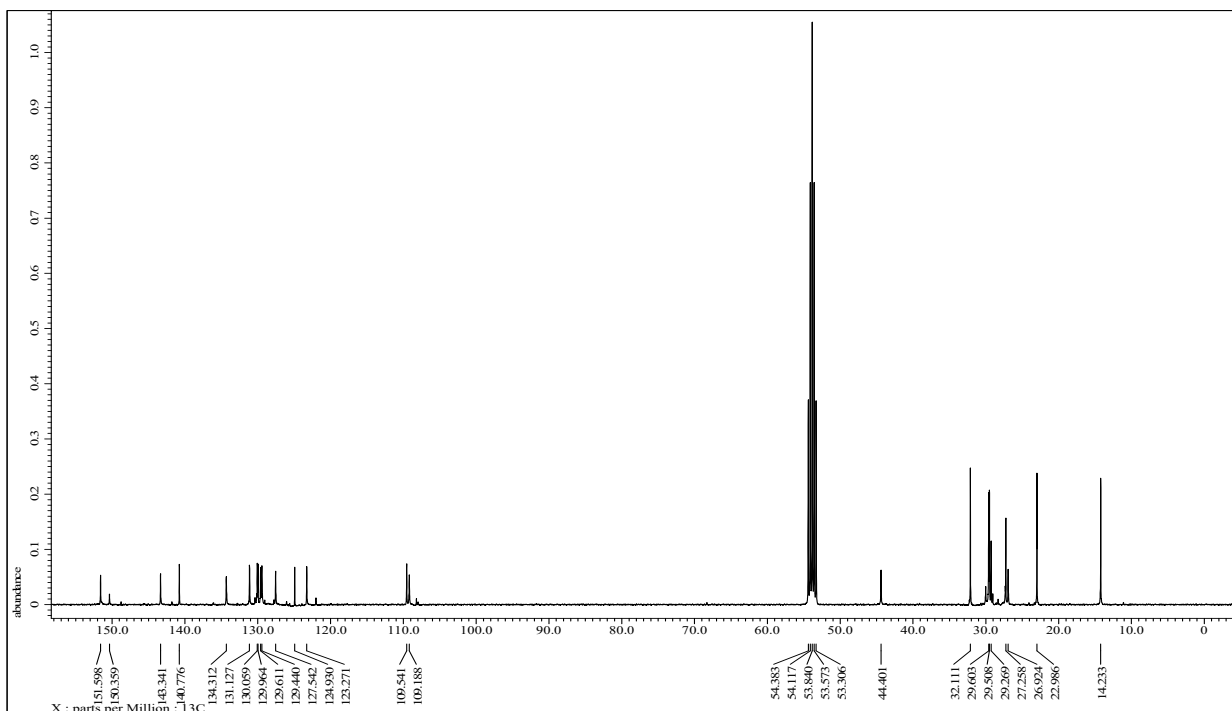
**2-((*E*)-2-((*E*)-2-Chloro-3-((*E*)-2-(1-octylbenzo[*cd*]indol-2(*1H*)-ylidene)ethylidene)cyclopent-1-en-1-yl)vinyl)-1-octylbenzo[*cd*]indol-1-ium perchlorate (5a)**



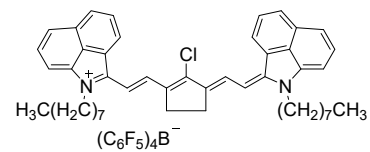
**$^1\text{H}$  NMR**



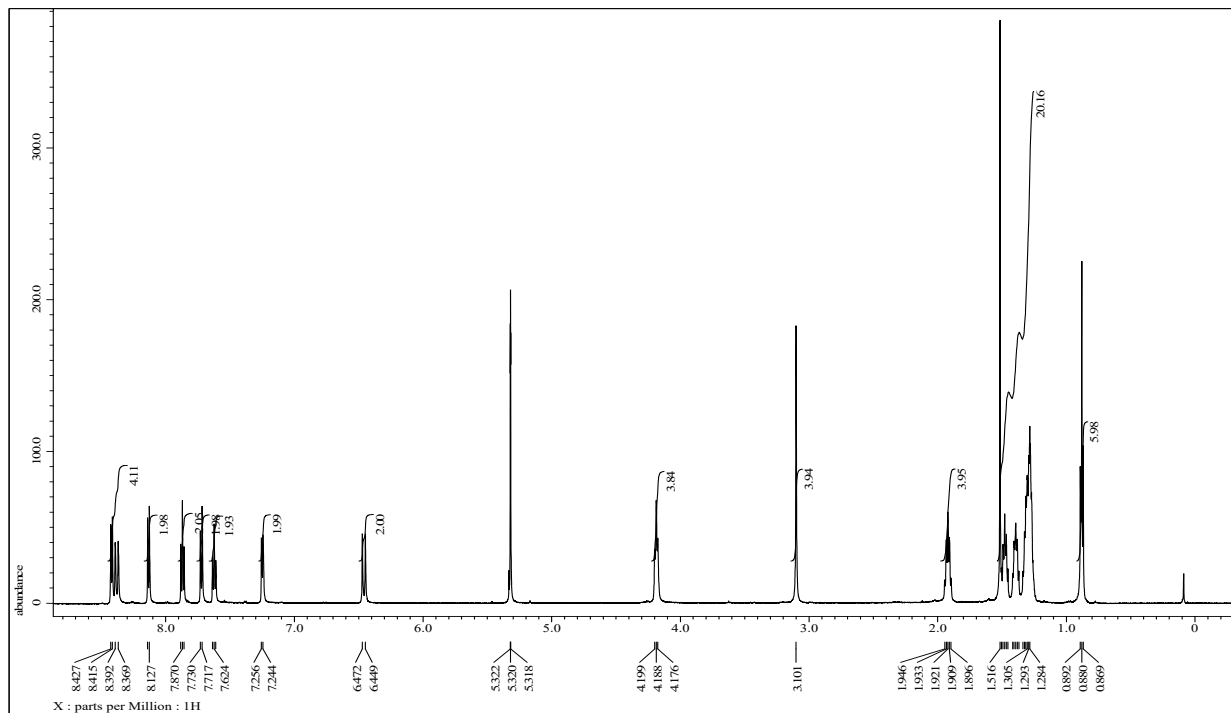
**$^{13}\text{C}$  NMR**



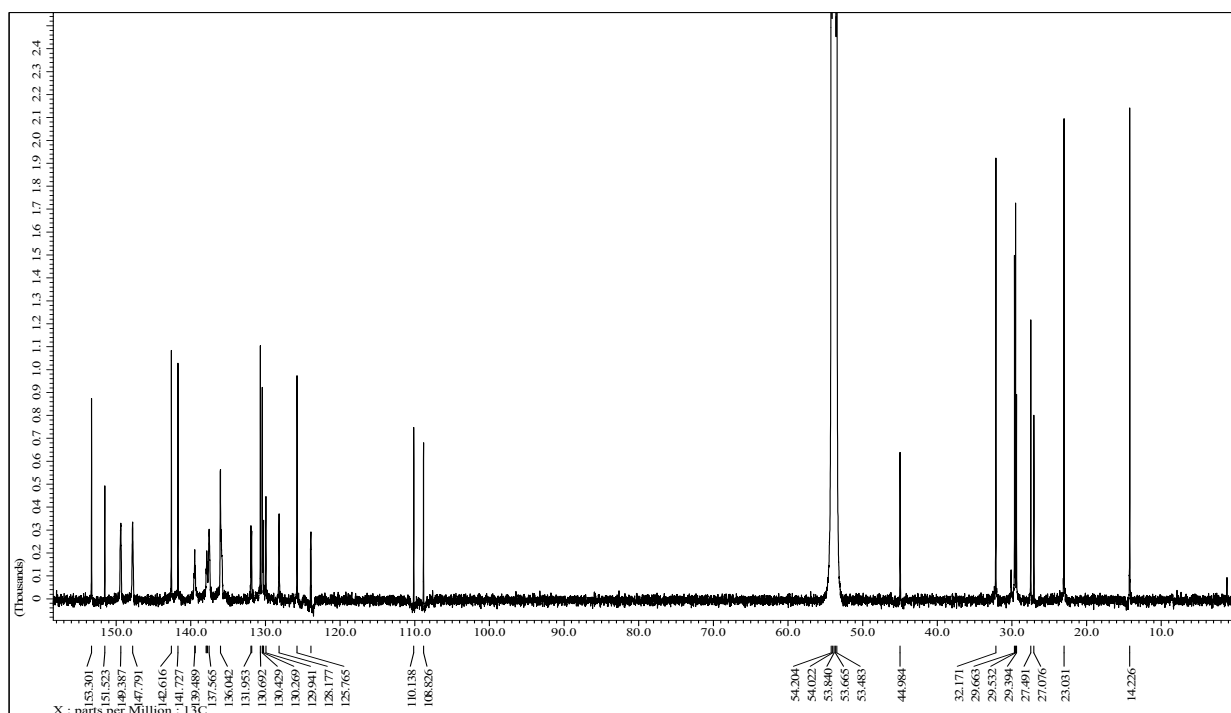
2-((*E*)-2-((*E*)-2-Chloro-3-((*E*)-2-(1-octylbenzo[*cd*]indol-2(*1H*)-ylidene)ethylidene)cyclopent-1-en-1-yl)vinyl)-1-octylbenzo[*cd*]indol-1-ium tetrakis(perfluorophenyl)borate (**5b**)



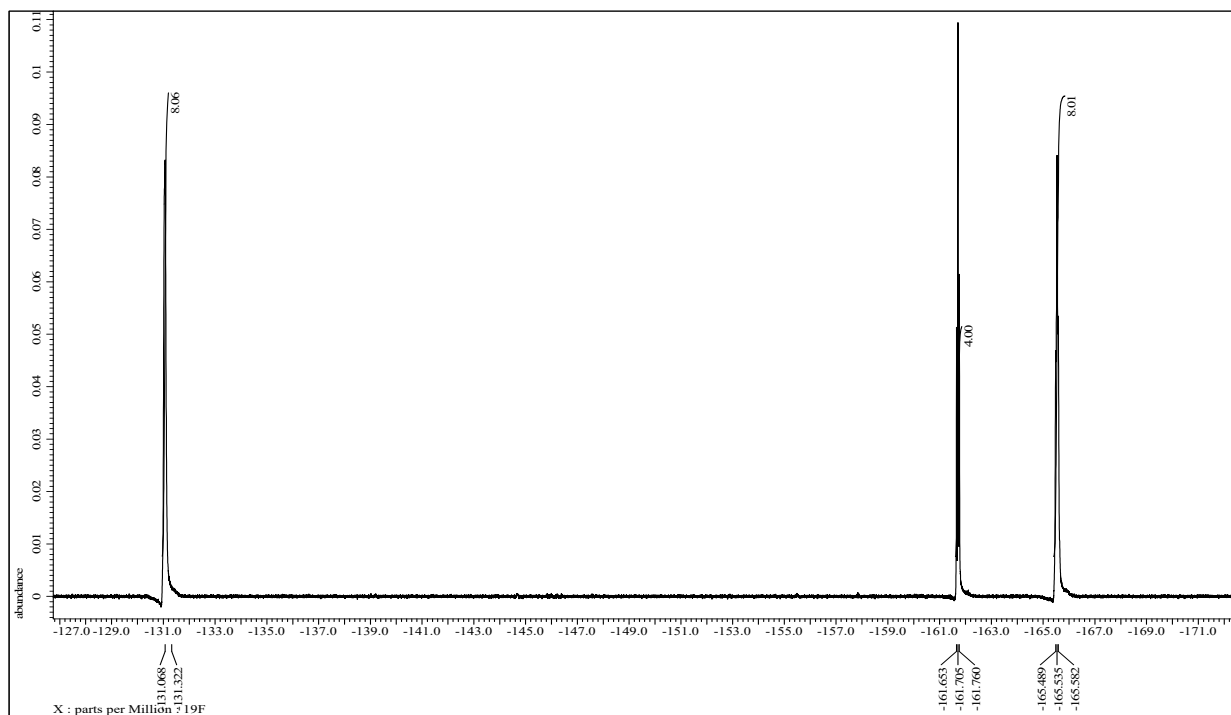
<sup>1</sup>H NMR



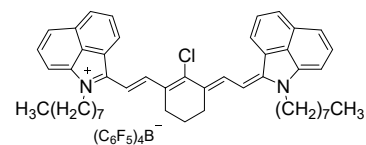
<sup>13</sup>C NMR



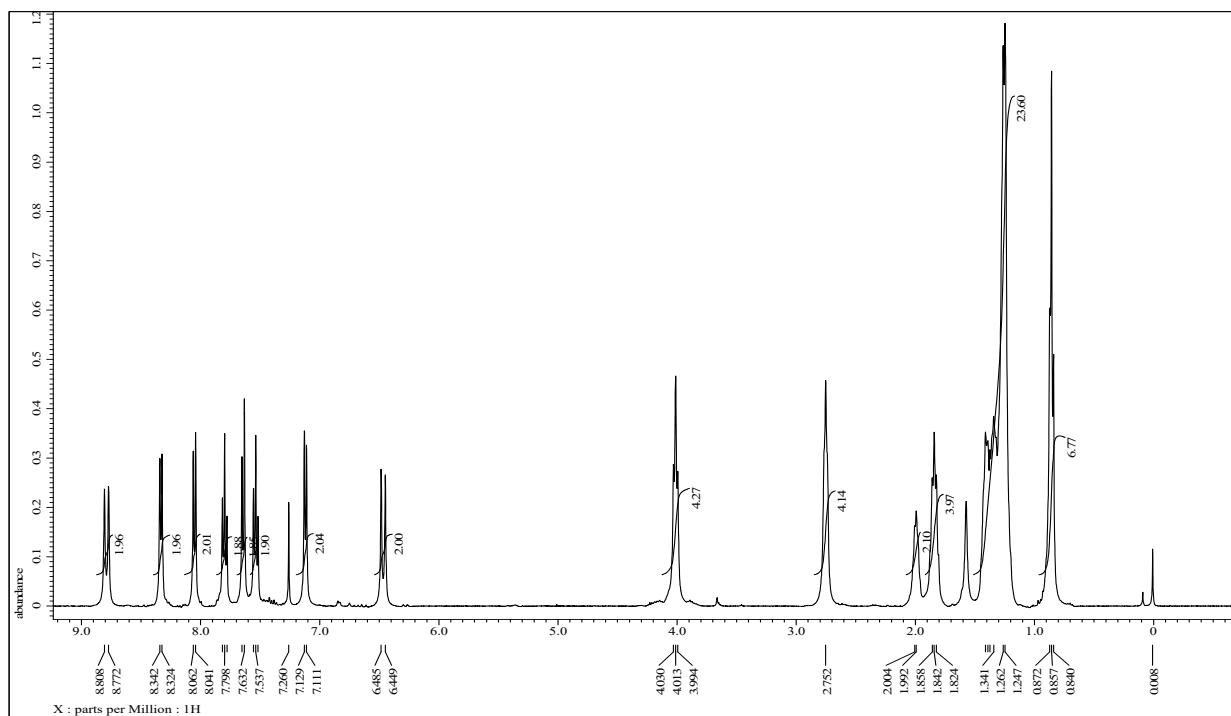
# <sup>19</sup>F NMR



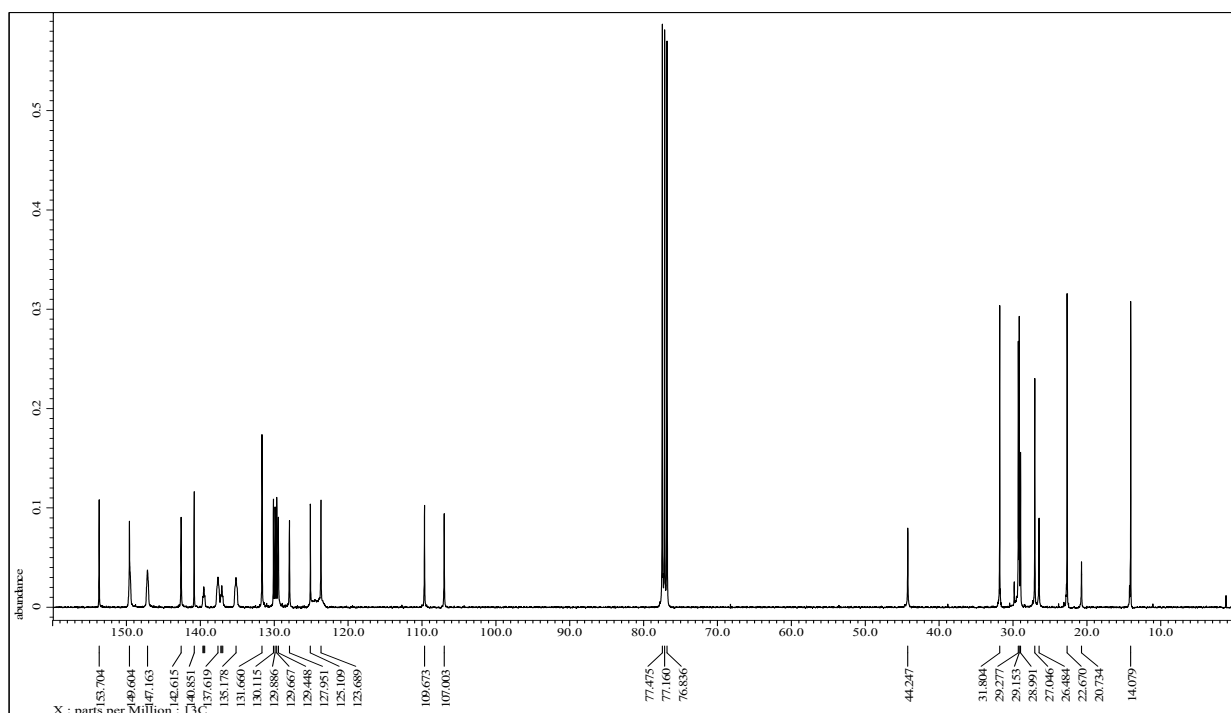
2-((*E*)-2-((*E*)-2-Chloro-3-((*E*)-2-(1-octylbenzo[*cd*]indol-2(*H*)-ylidene)ethylidene)cyclohex-1-en-1-yl)vinyl)-1-octylbenzo[*cd*]indol-1-ium tetrakis(perfluorophenyl)borate (6)



$^1\text{H}$  NMR

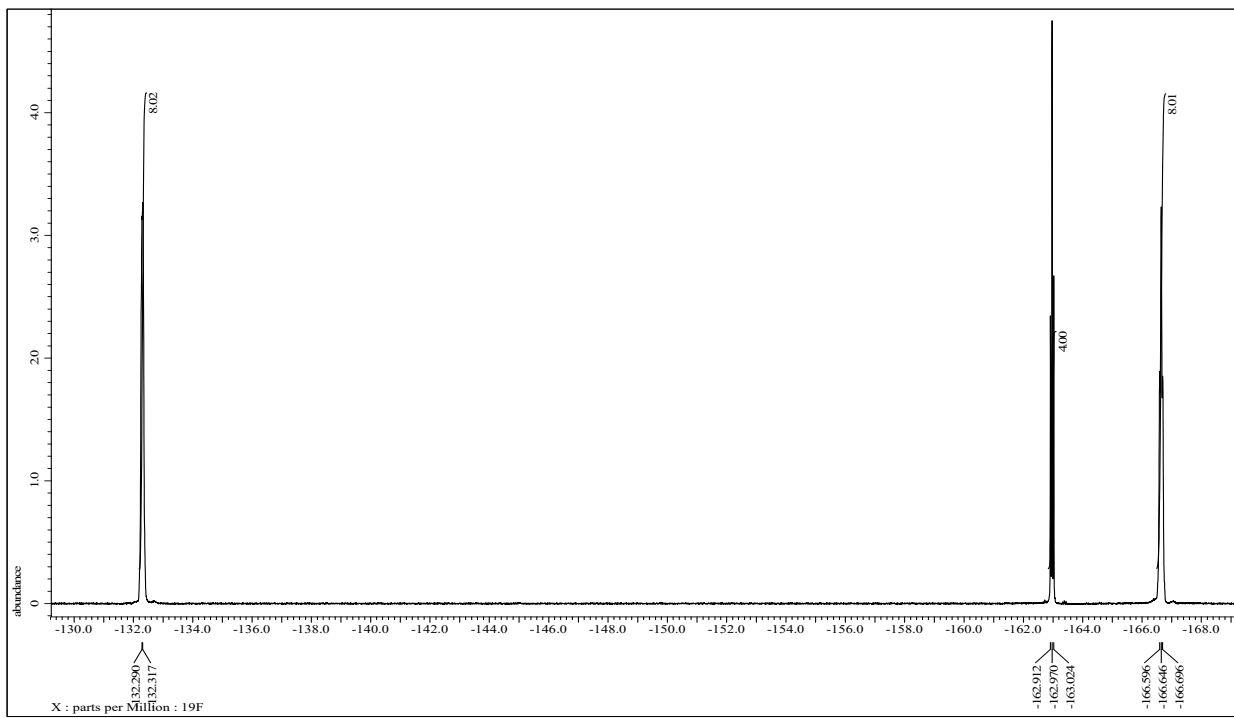


$^{13}\text{C}$  NMR

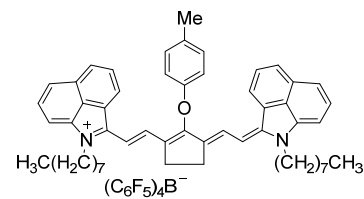




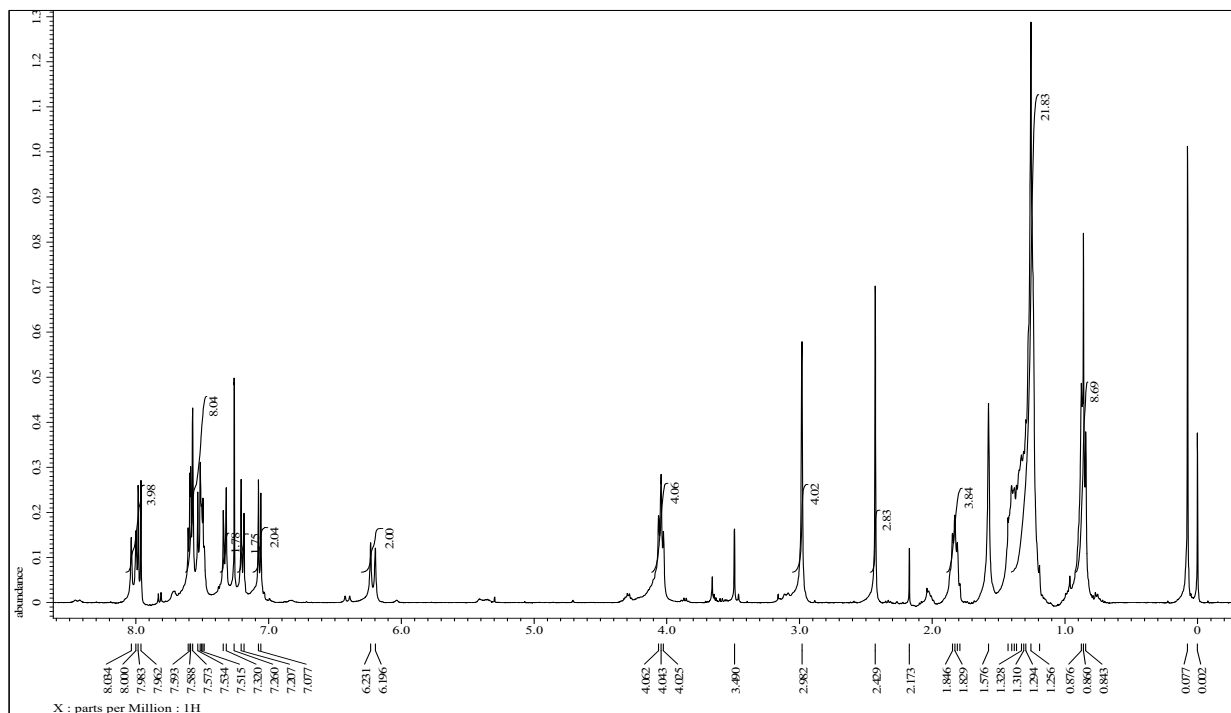
# <sup>19</sup>F NMR



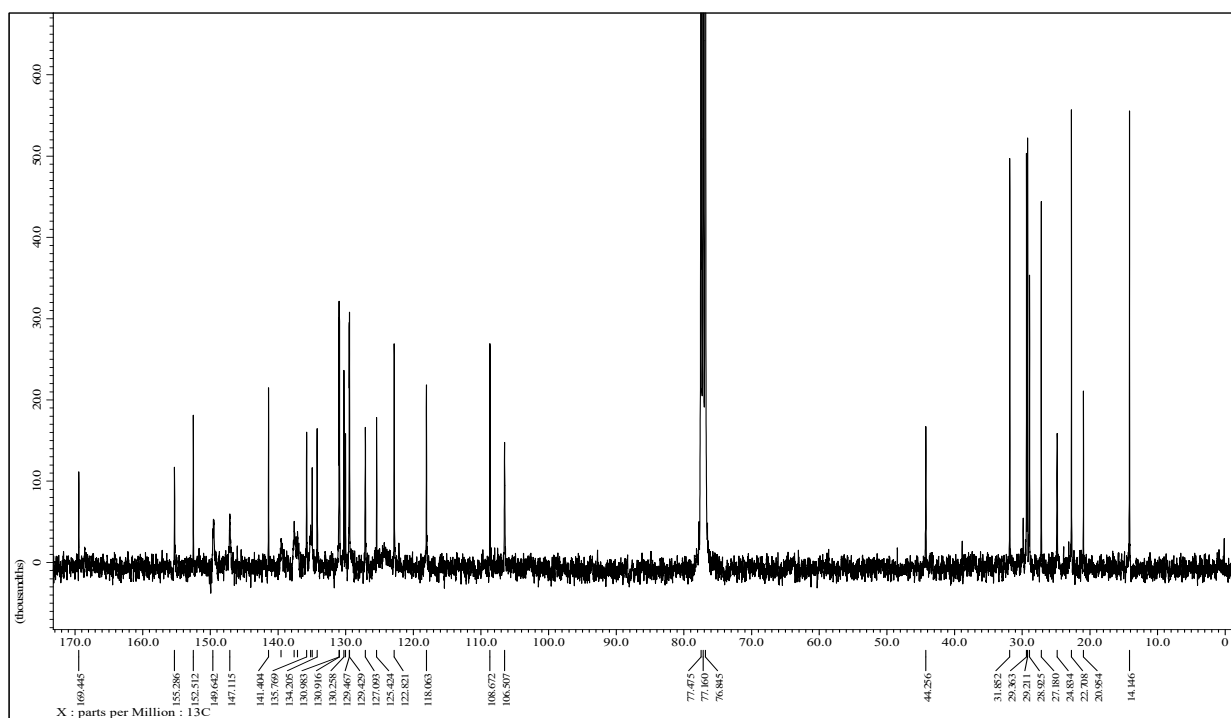
**1-Octyl-2-((E)-2-((E)-3-((E)-2-(1-octylbenzo[cd]indol-2(1H)-ylidene)ethylidene)-2-(p-tolyloxy)cyclopent-1-en-1-yl)vinyl)benzo[cd]indol-1-ium tetrakis(perfluorophenyl)borate (5c)**



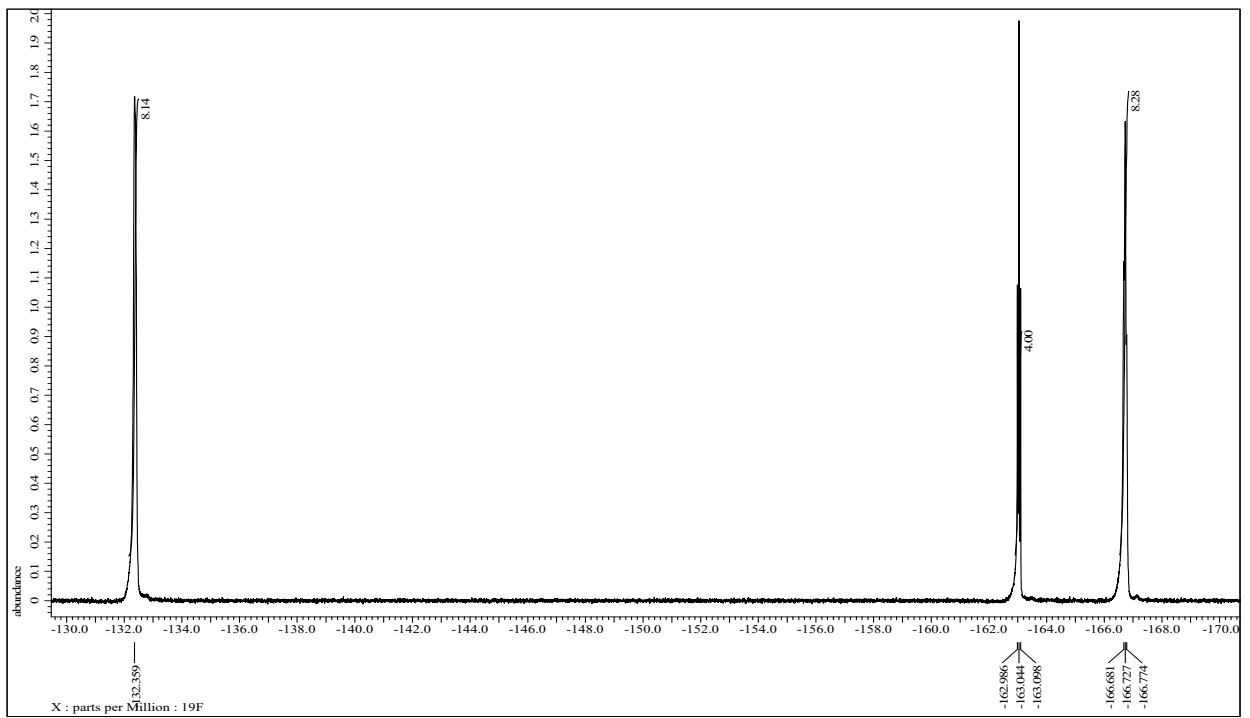
**$^1H$  NMR**



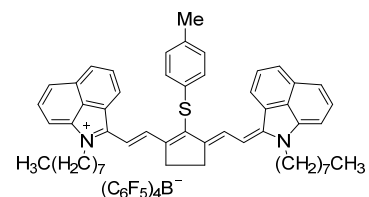
**$^{13}C$  NMR**



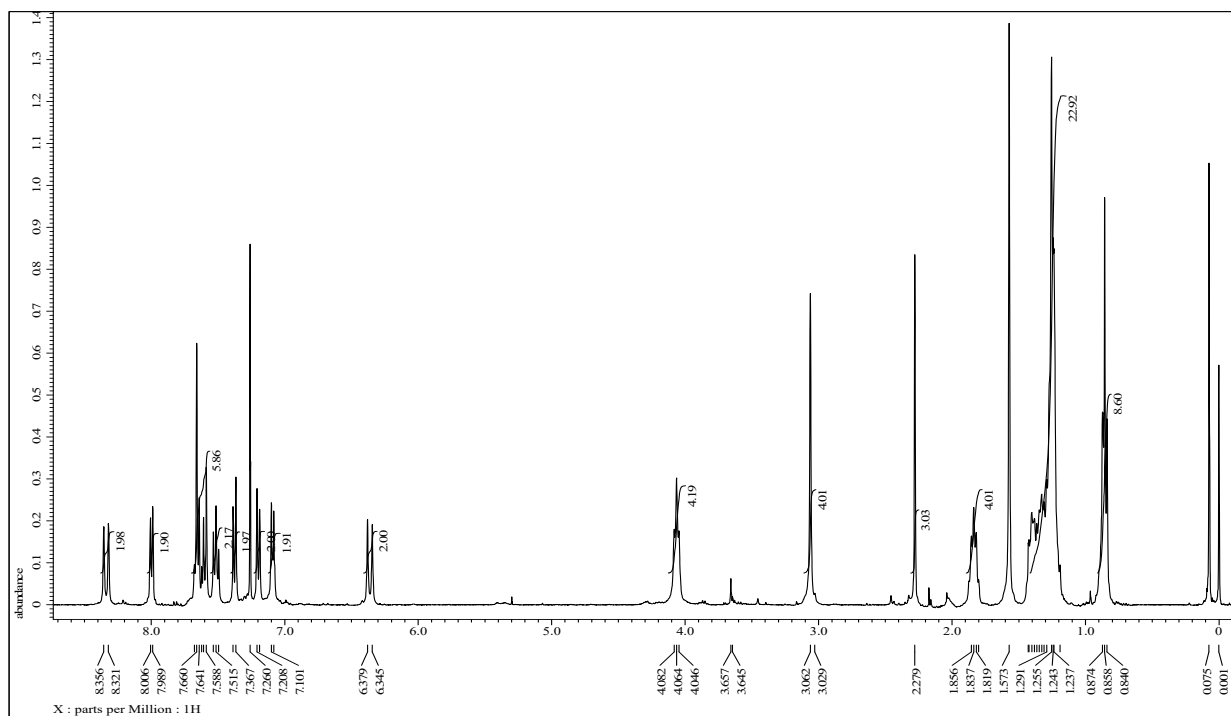
# <sup>19</sup>F NMR



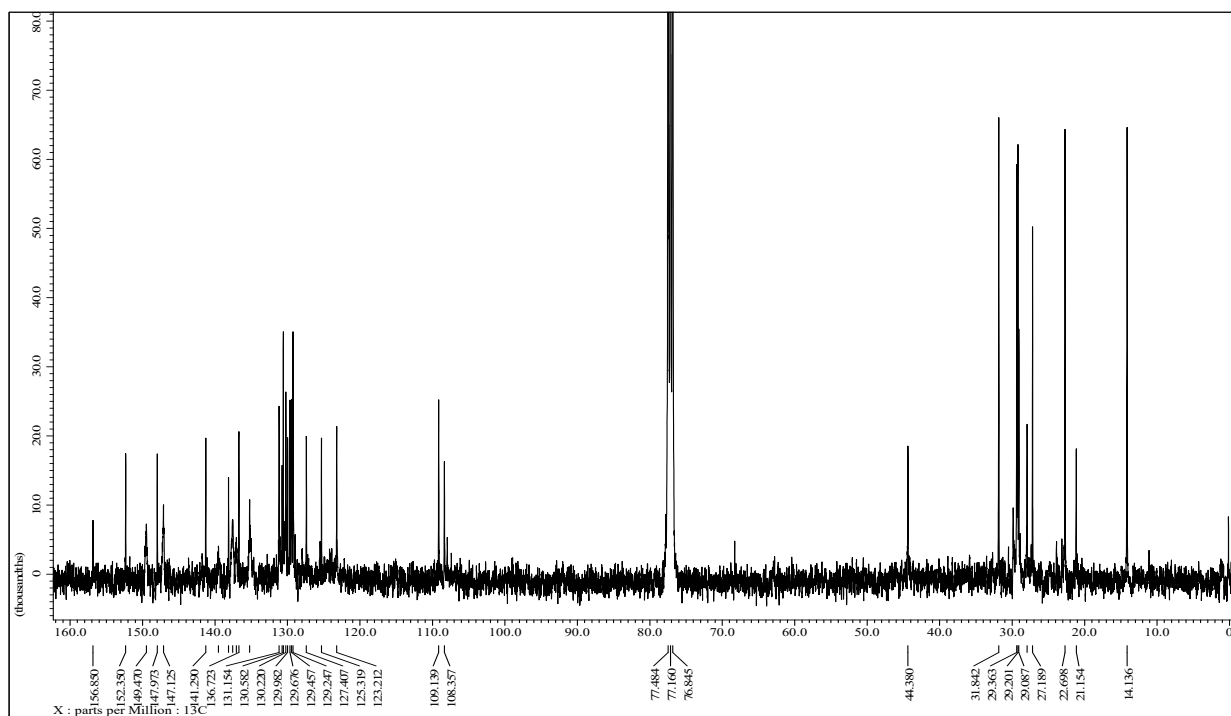
**1-Octyl-2-((E)-2-((E)-3-((E)-2-(1-octylbenzo[cd]indol-2(1H)-ylidene)ethylidene)-2-(p-tolylthio)cyclopent-1-en-1-yl)vinyl)benzo[cd]indol-1-ium tetrakis(perfluorophenyl)borate (5d)**



**<sup>1</sup>H NMR**



**<sup>13</sup>C NMR**



**<sup>19</sup>F NMR**

