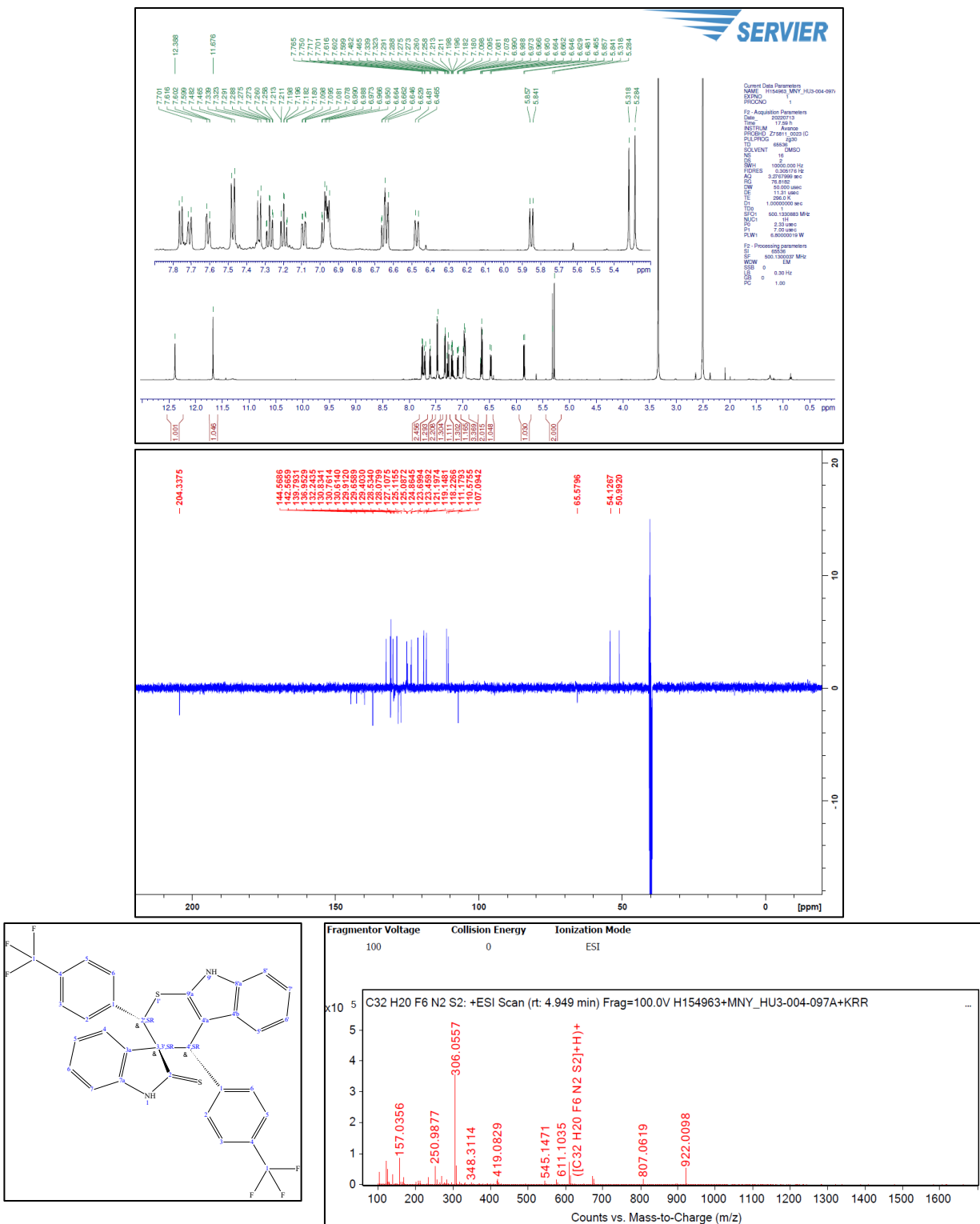


**NEW REACTIONS OF THIO-OXINDOLES AND ARYL  
ALDEHIDES: MICROWAVE-INDUCED ONE STEP SYNTHESIS  
OF STRUCTURALLY DIVERSE THIOPYRANO-DIINDOLES**

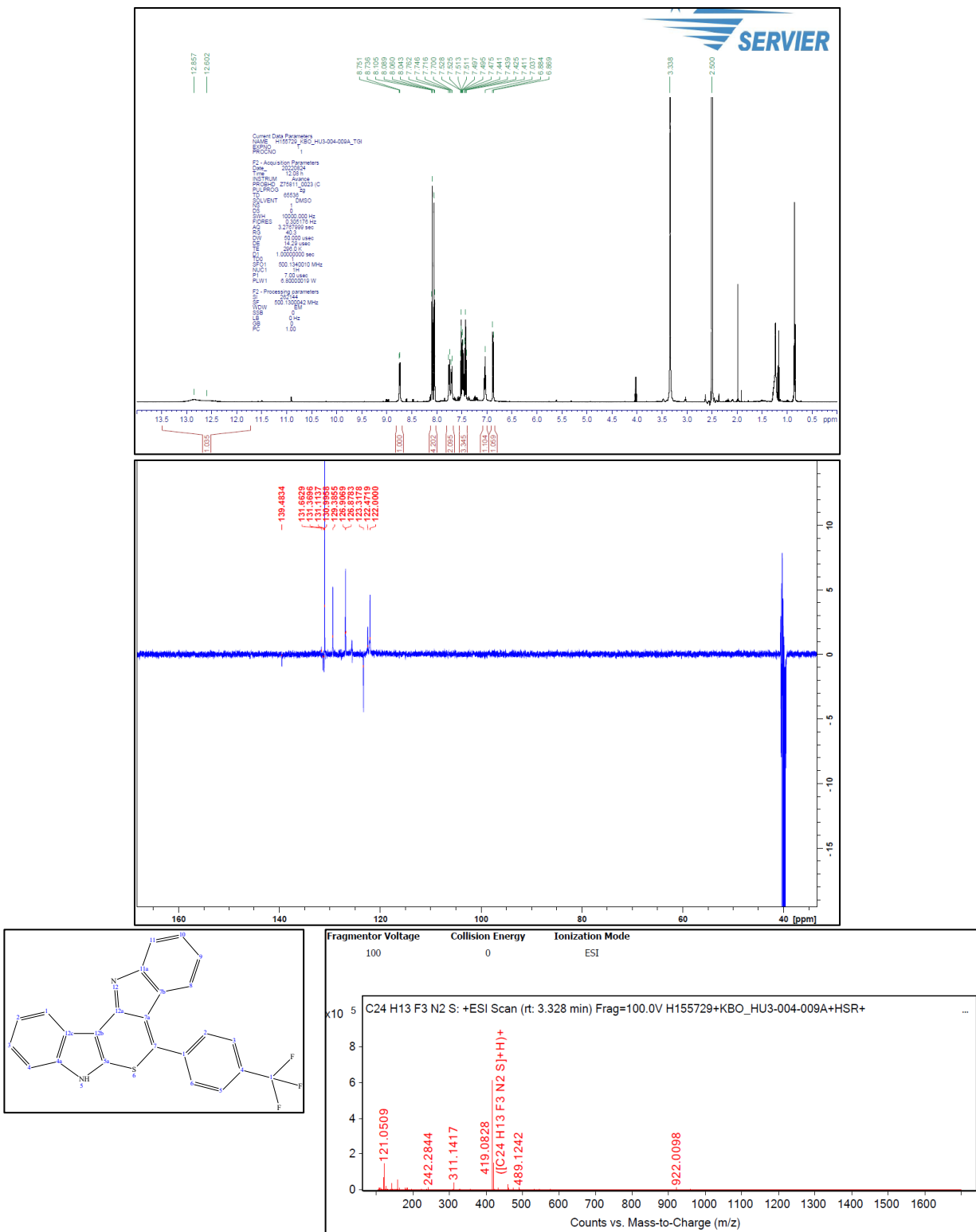
**Krisztián Biró, János Tatai and Miklós Nyerges**

Servier Research Institute of Medicinal Chemistry, 7, Záhony street, 1031 Budapest, HUNGARY

**Supporting Information**

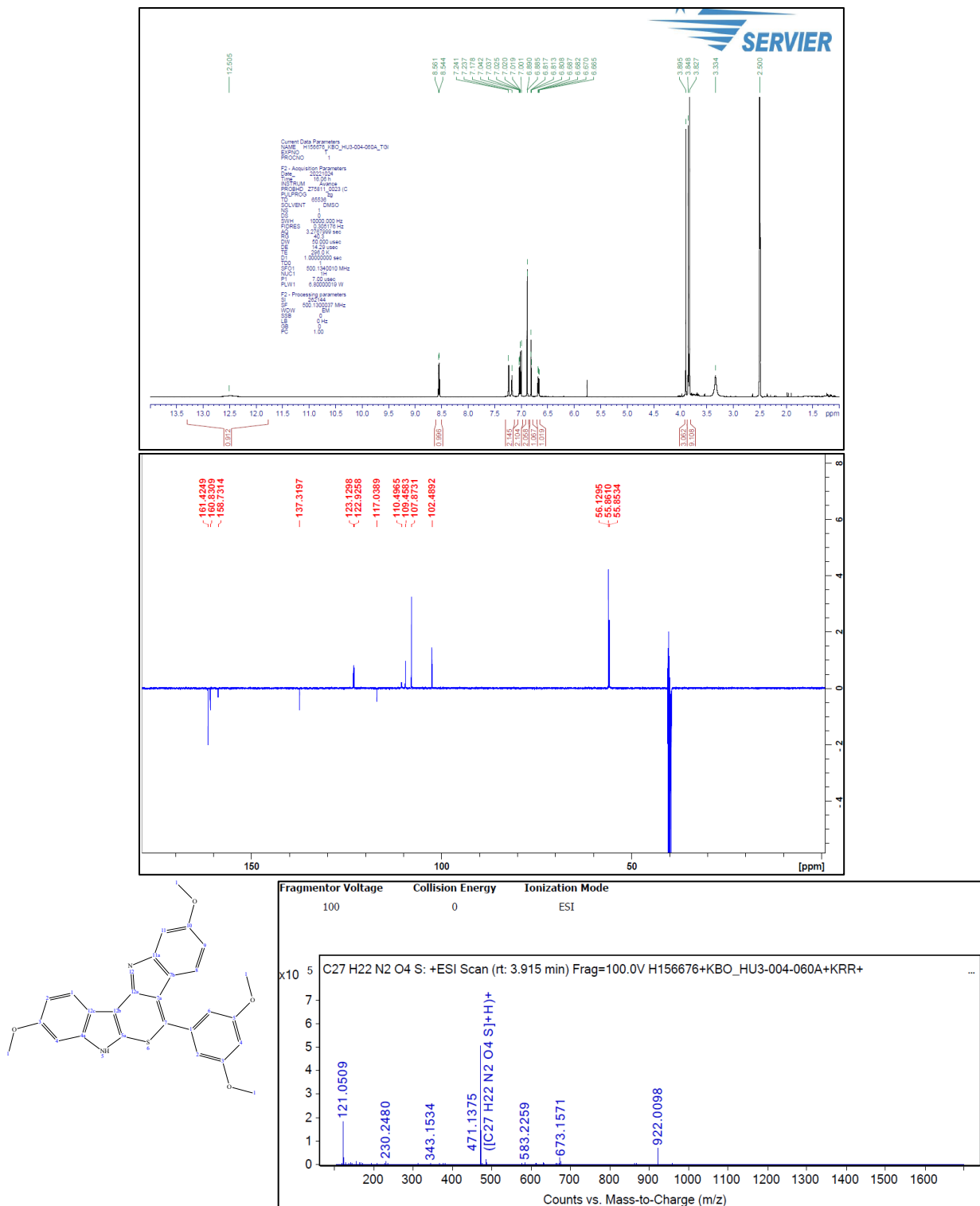


**Figure S1.** <sup>1</sup>H-NMR and <sup>13</sup>C-NMR and HRMS spectrum of **6a** (2',4'-bis[4-trifluoromethyl]phenyl)-4',9'-dihydro-2*H*-spiro[indole-3,3'-thiopyrano[2,3-*b*]indole]-2(1*H*)-thione

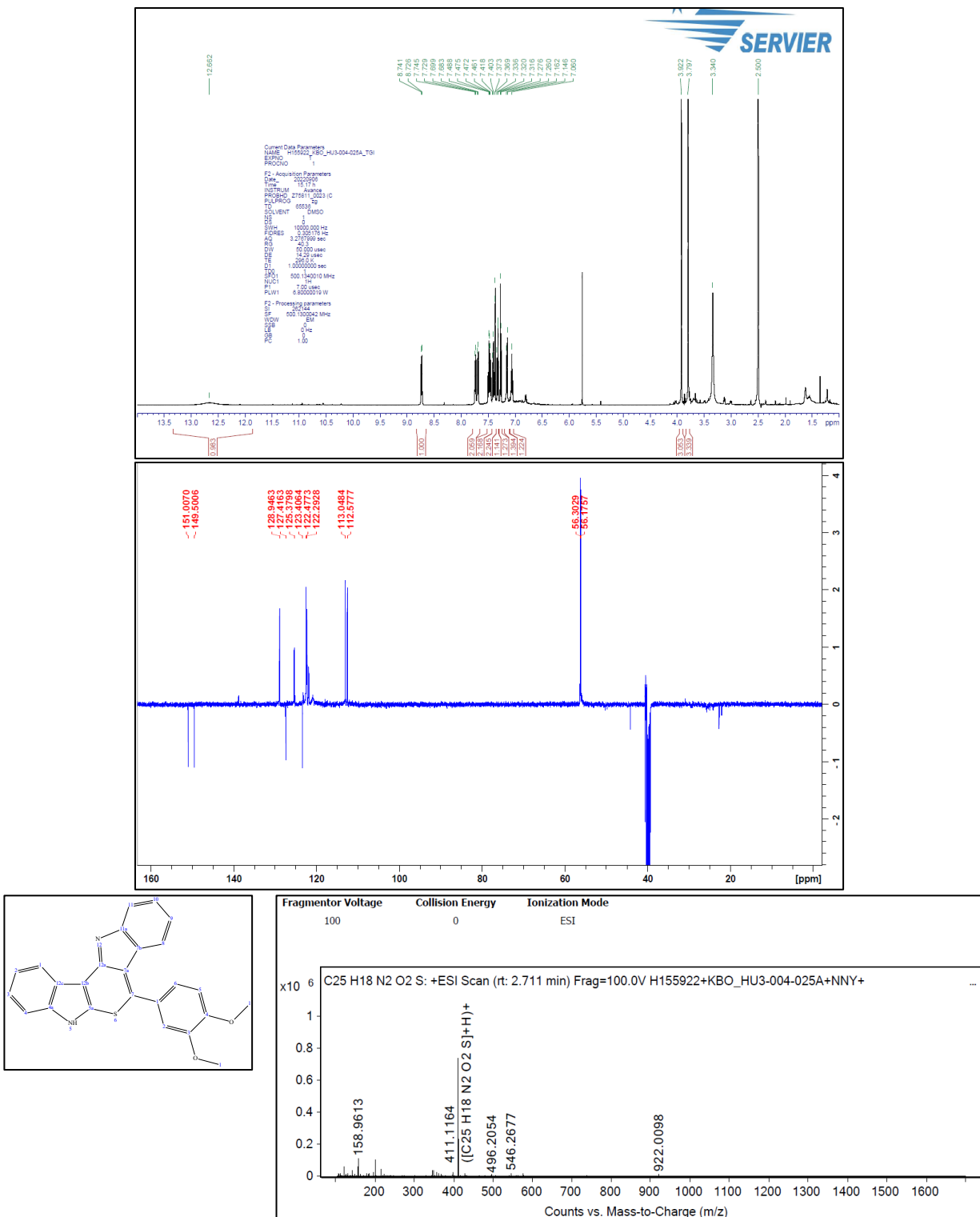


**Figure S2. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR and HRMS spectrum of **9a** (7-[4-(trifluoromethyl)phenyl]-5*H*-thiopyrano[2,3-*b*:4,5-*b'*]diindole)**

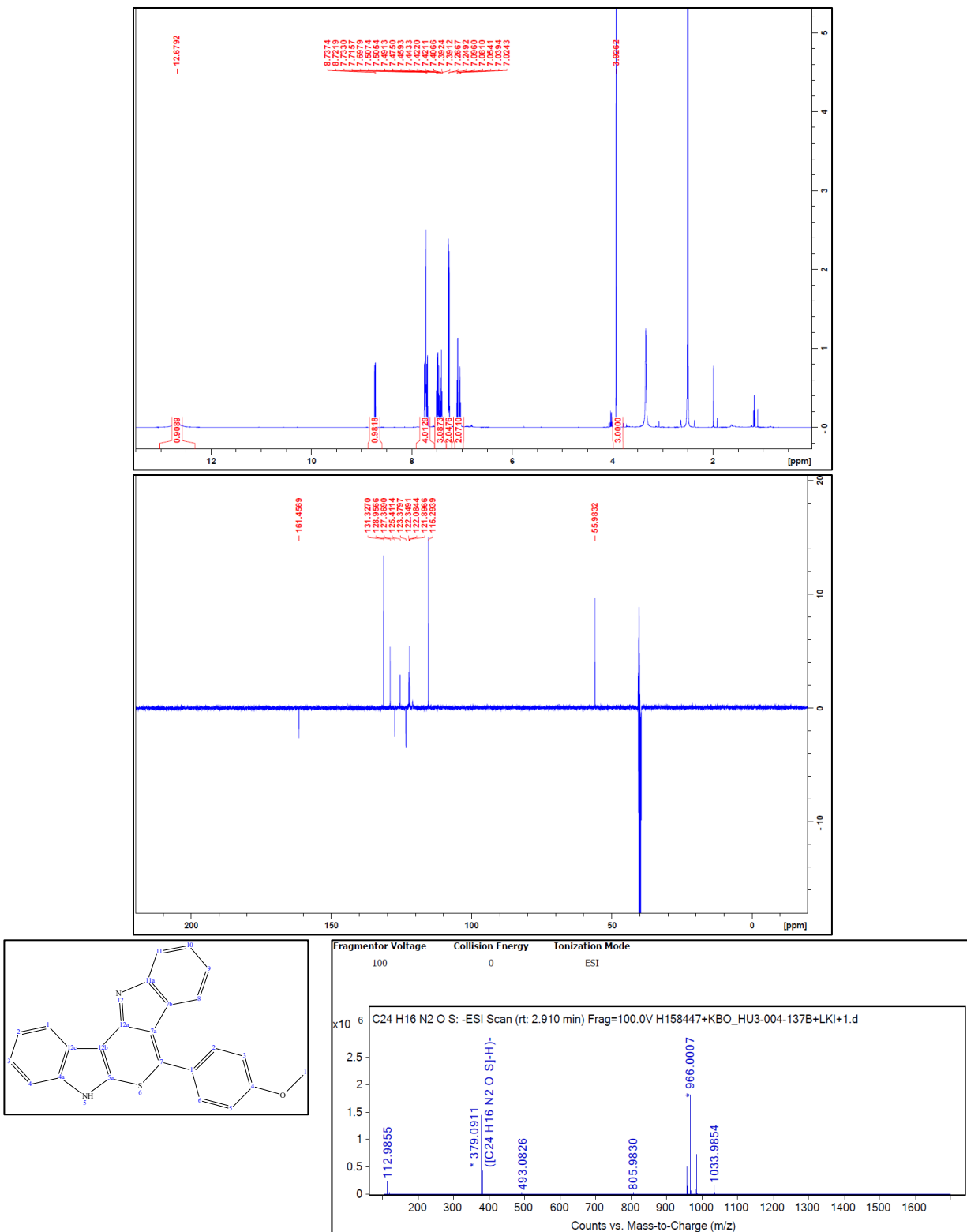




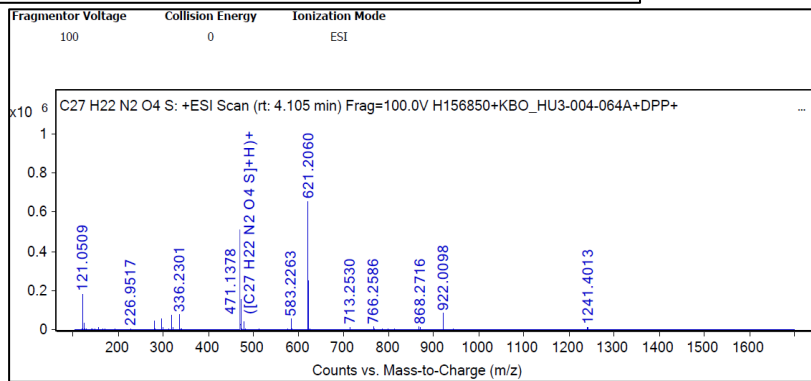
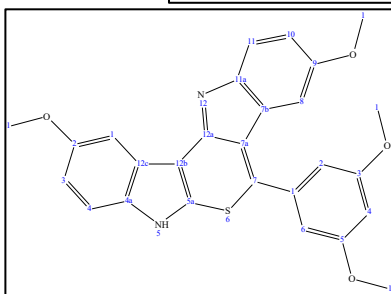
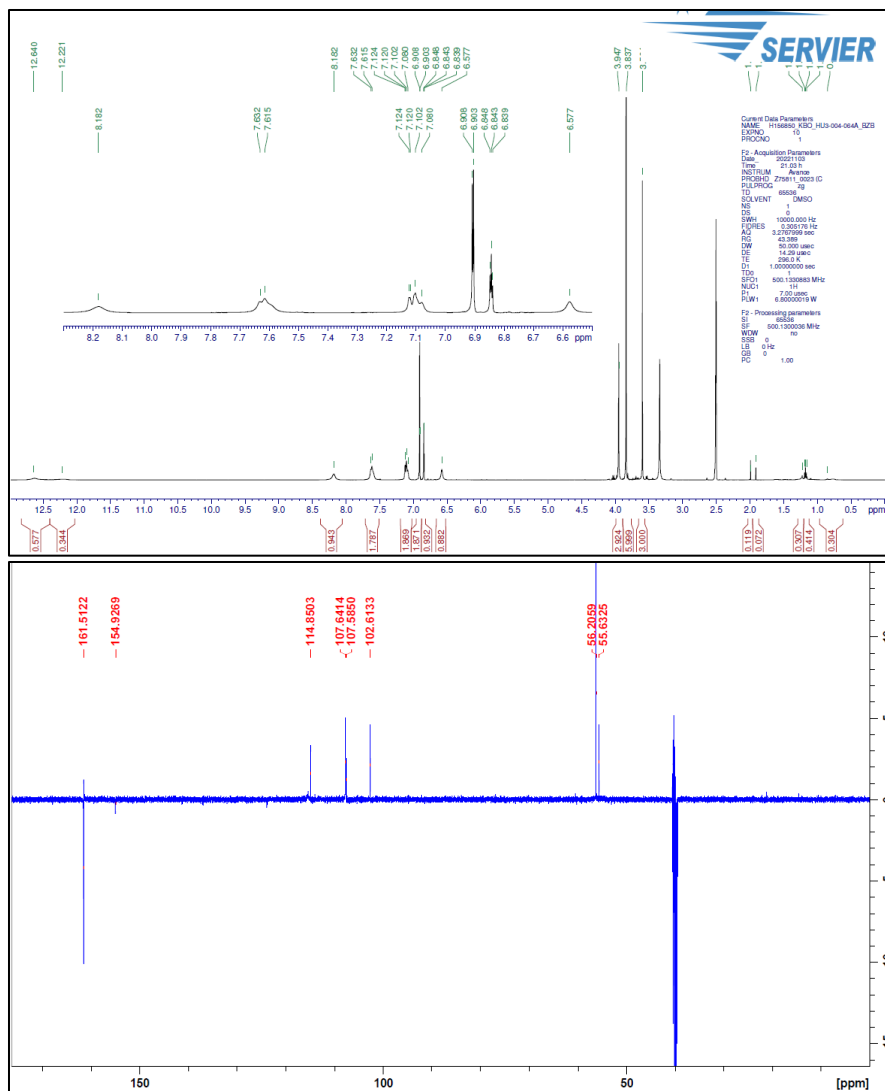
**Figure S4. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR and HRMS spectrum of **9c** 7-(3,5-dimethoxyphenyl)-3,10-dimethoxy-5H-thiopyrano[2,3-*b*:4,5-*b'*]diindole**



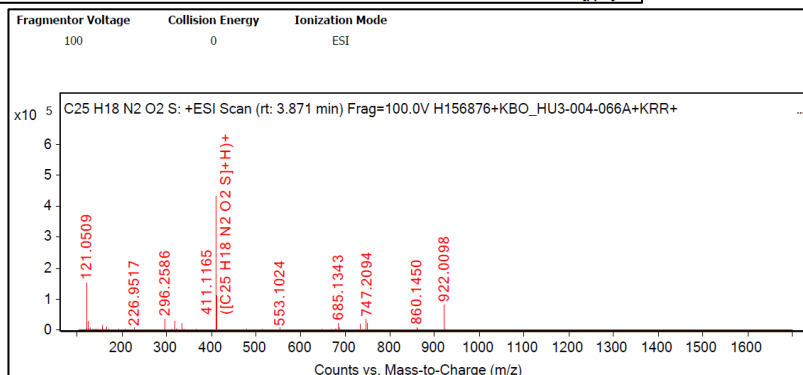
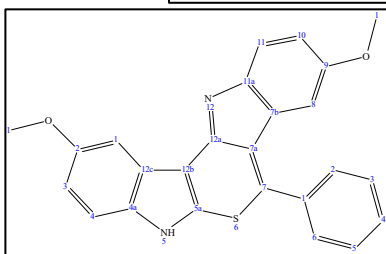
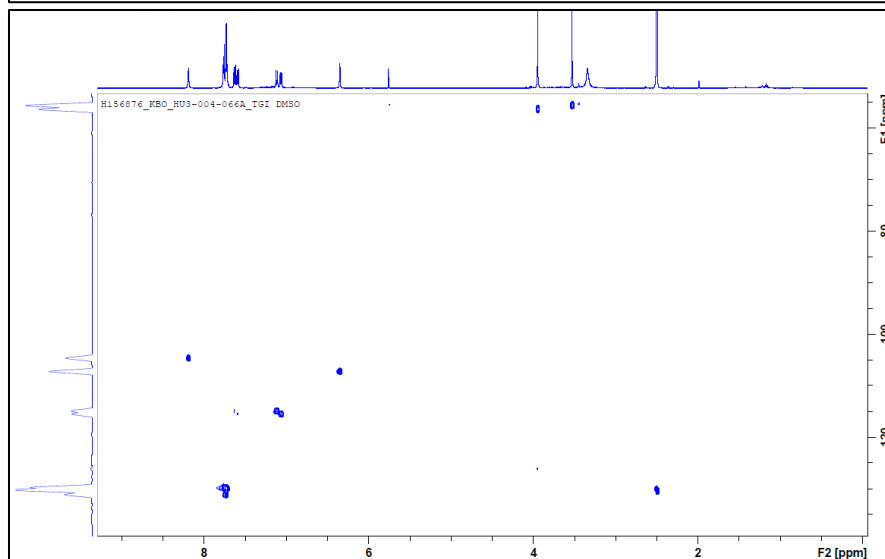
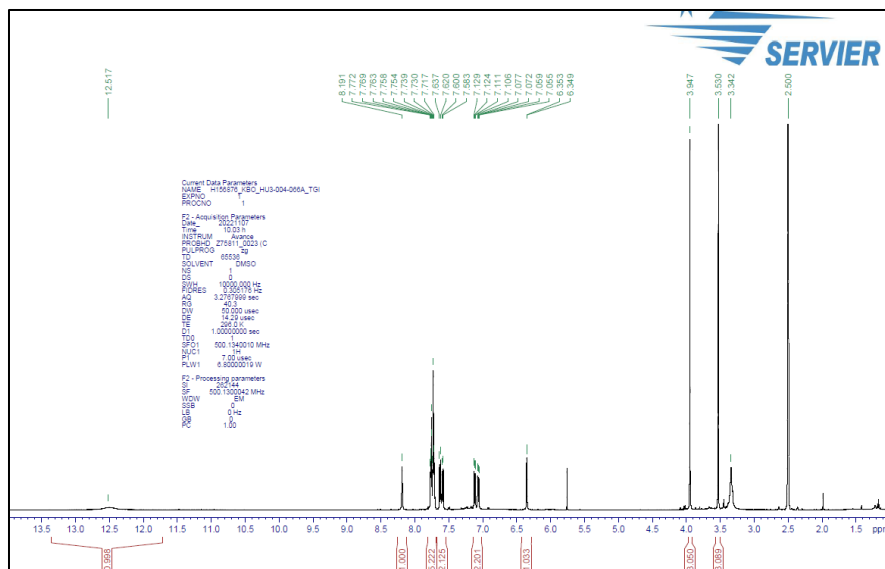
**Figure S5.** <sup>1</sup>H-NMR and <sup>13</sup>C-NMR and HRMS spectrum of **9d** 7-(3,4-dimethoxyphenyl)-5H-thiopyrano[2,3-b:4,5-b']diindole



**Figure S6.**  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR and HRMS spectrum of **9e** 7-(4-methoxyphenyl)-5*H*-thiopyrano[2,3-*b*:4,5-*b'*]diindole



**Figure S7.**  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  and HRMS spectrum of **9f** 7-(3,5-dimethoxyphenyl)-2,9-dimethoxy-5H-thiopyrano[2,3-*b*:4,5-*b'*]diindole



**Figure S8.**  $^1\text{H}$ -NMR and HSQC and HRMS spectrum of **9g** 2,9-dimethoxy-7-phenyl-5*H*-thiopyrano[2,3-*b*:4,5-*b'*]diindole

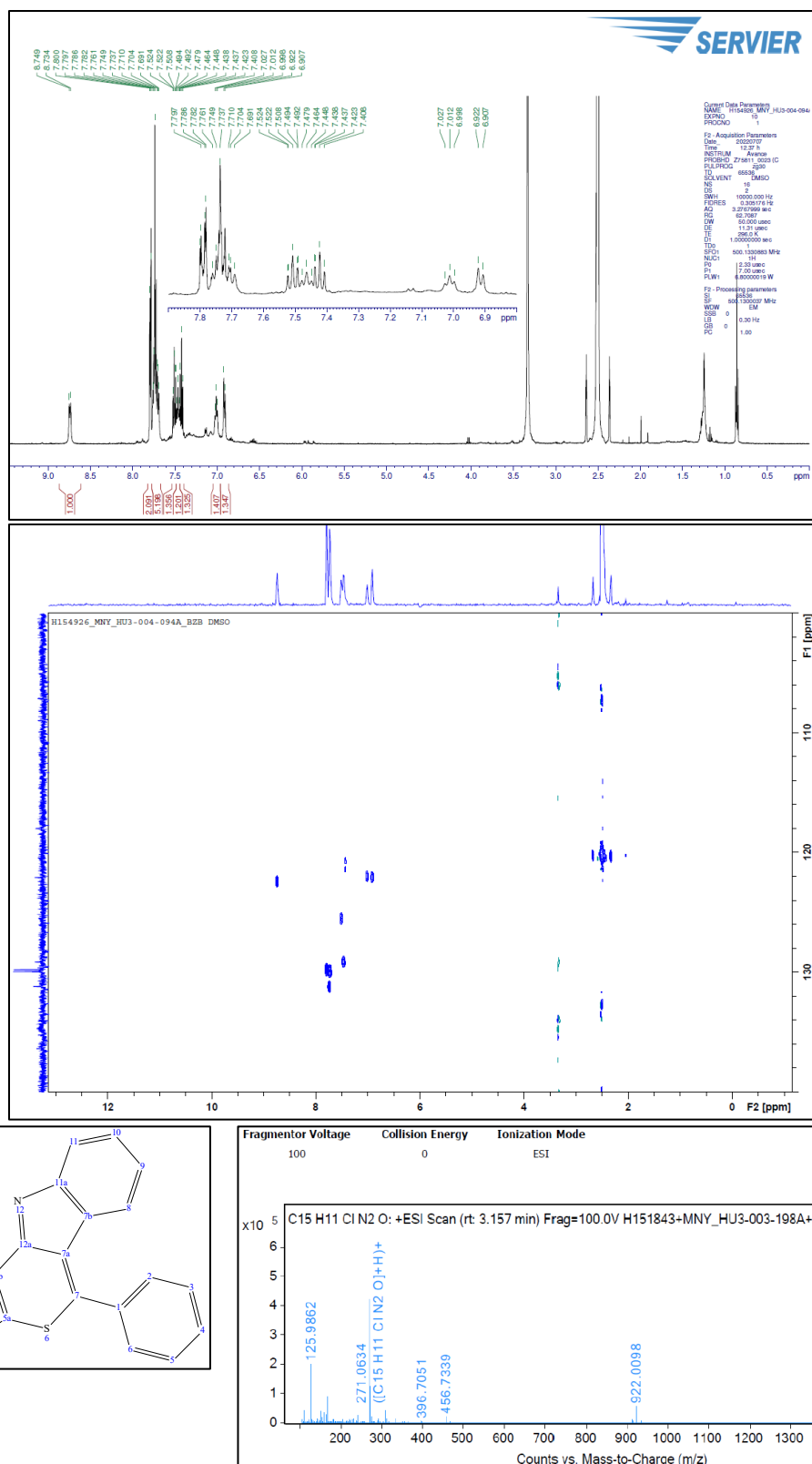
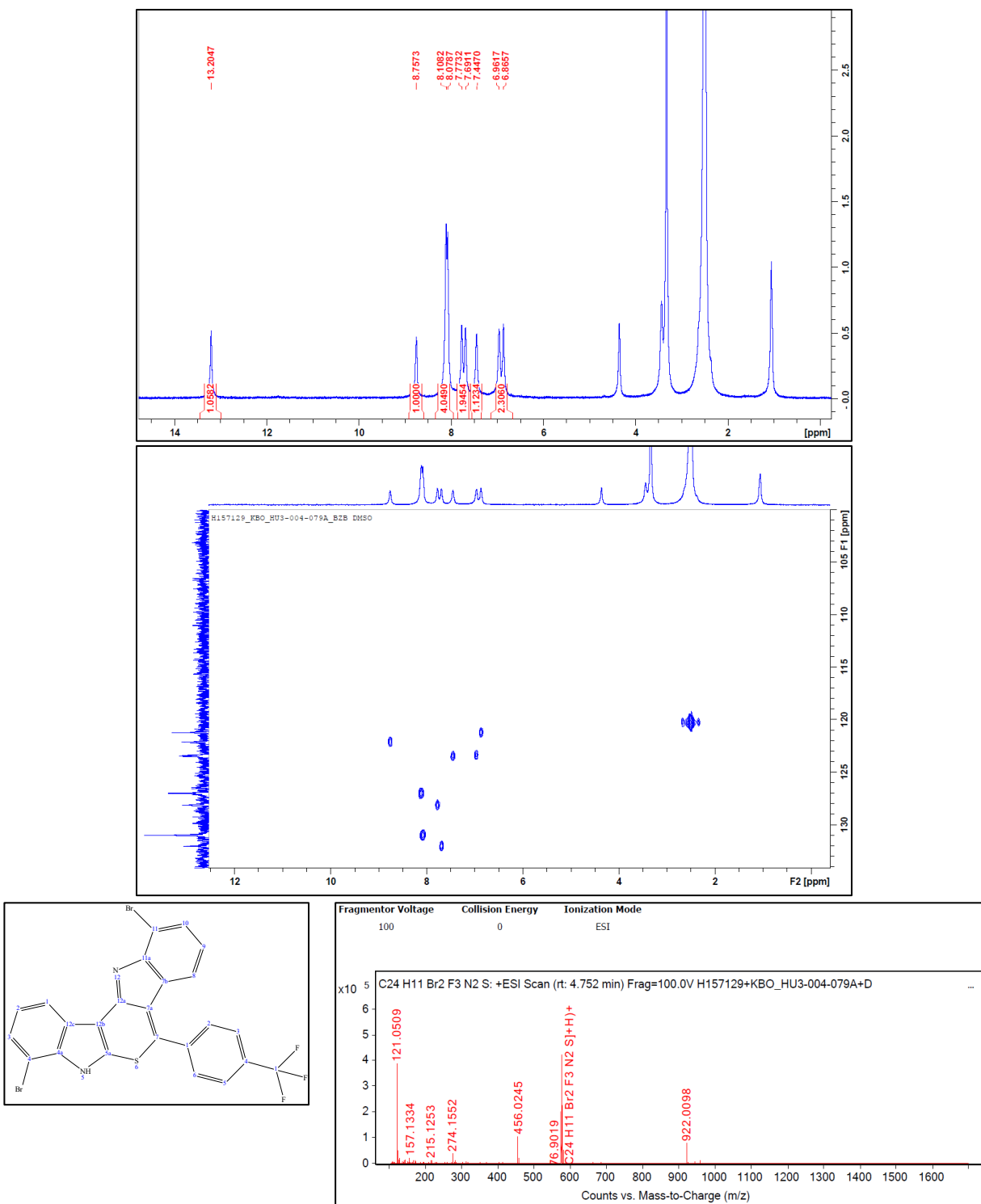
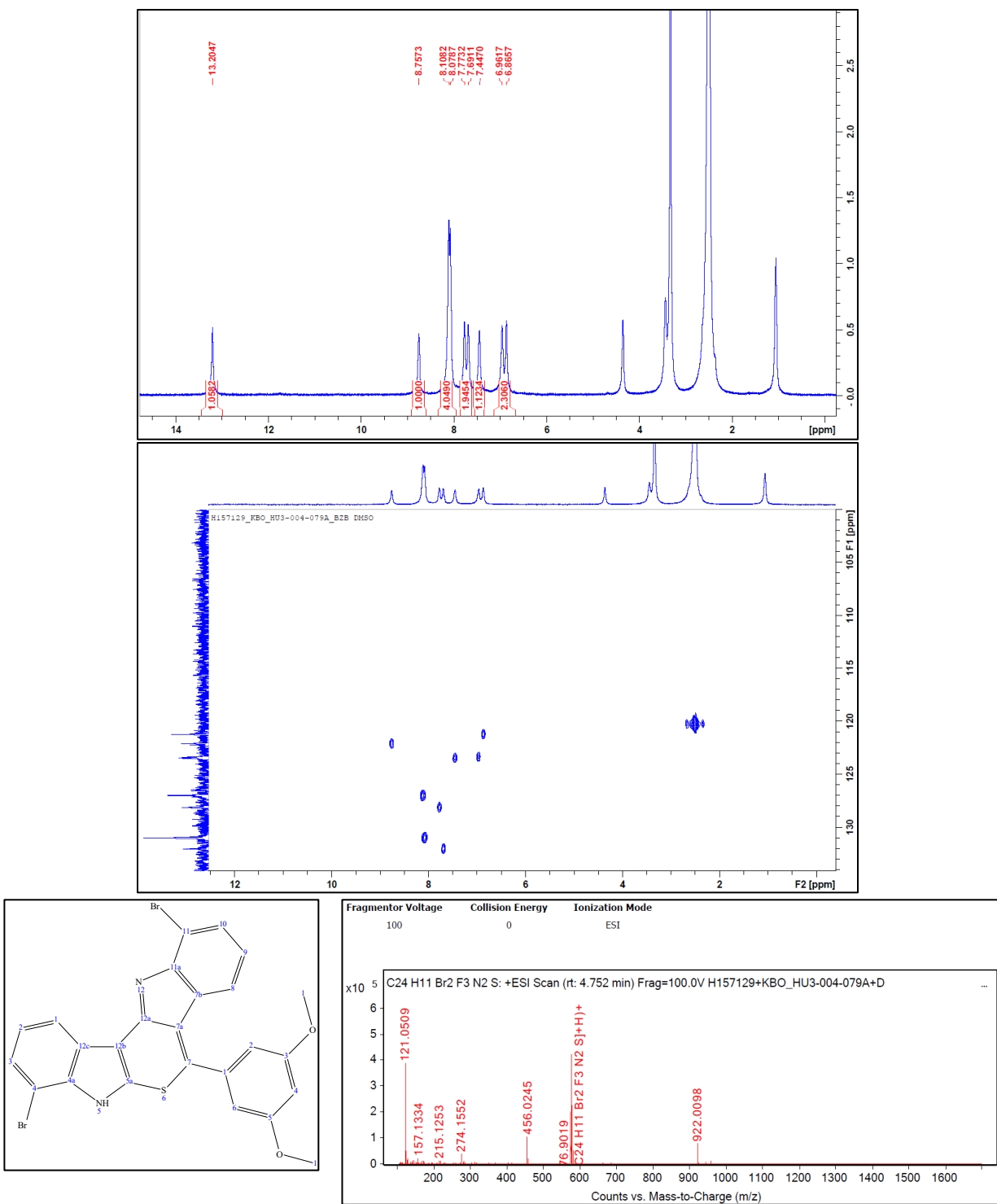
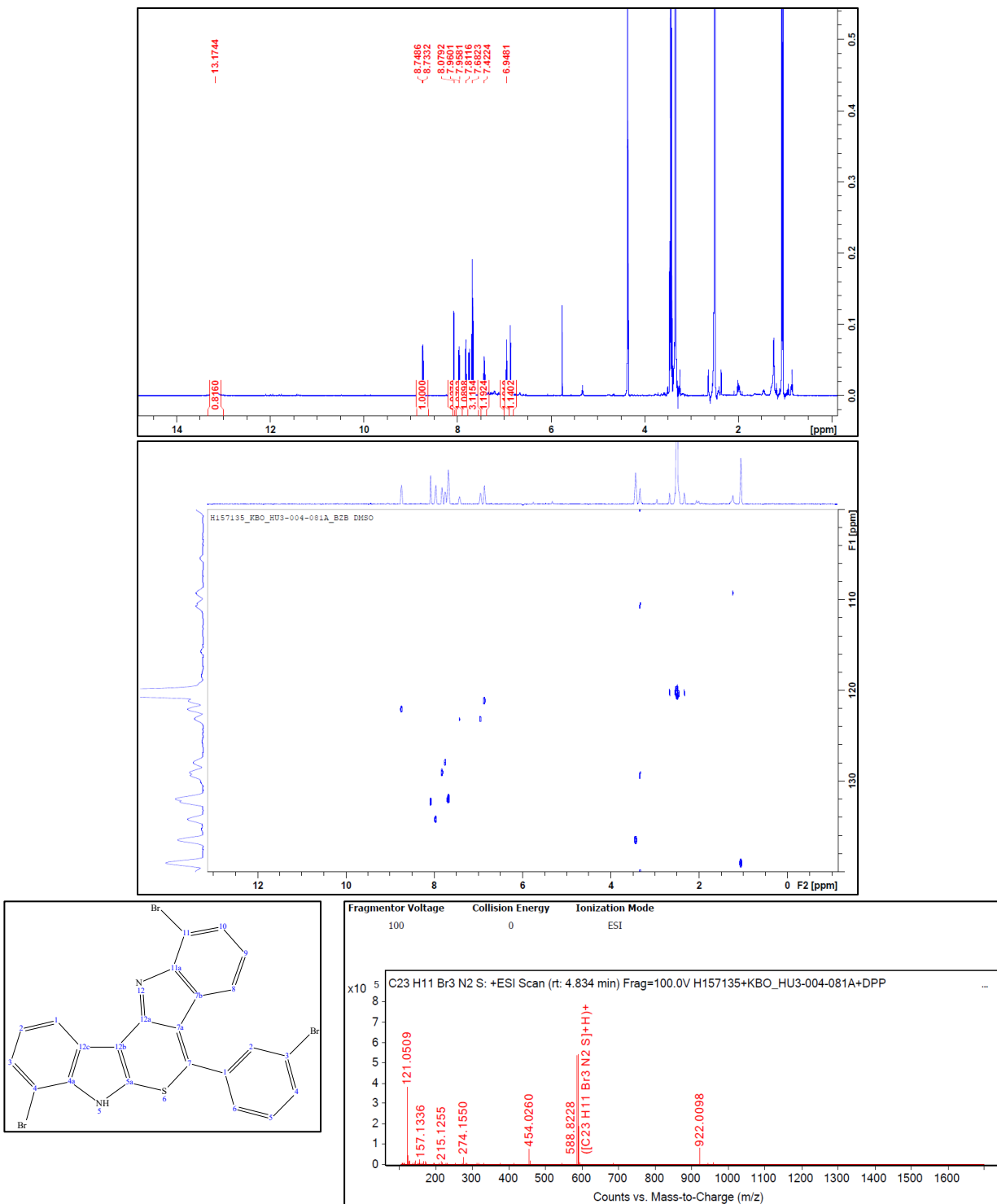


Figure S9. <sup>1</sup>H-NMR and HSQC and HRMS spectrum of **9h** 7-phenyl-5*H*-thiopyrano[2,3-*b*:4,5-*b'*]diindole

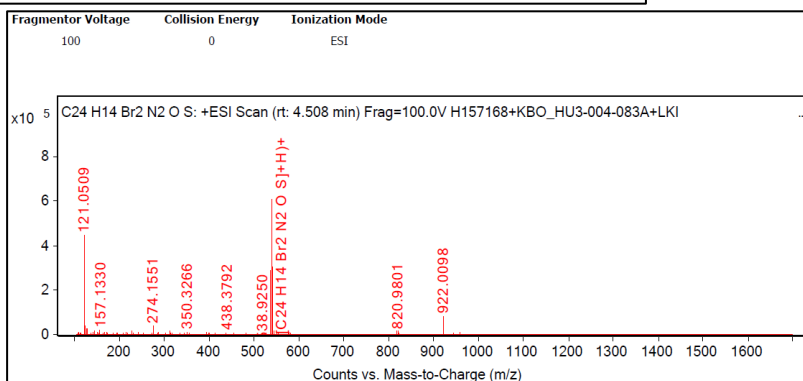
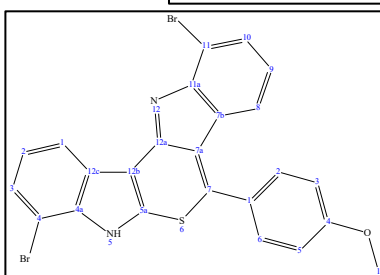
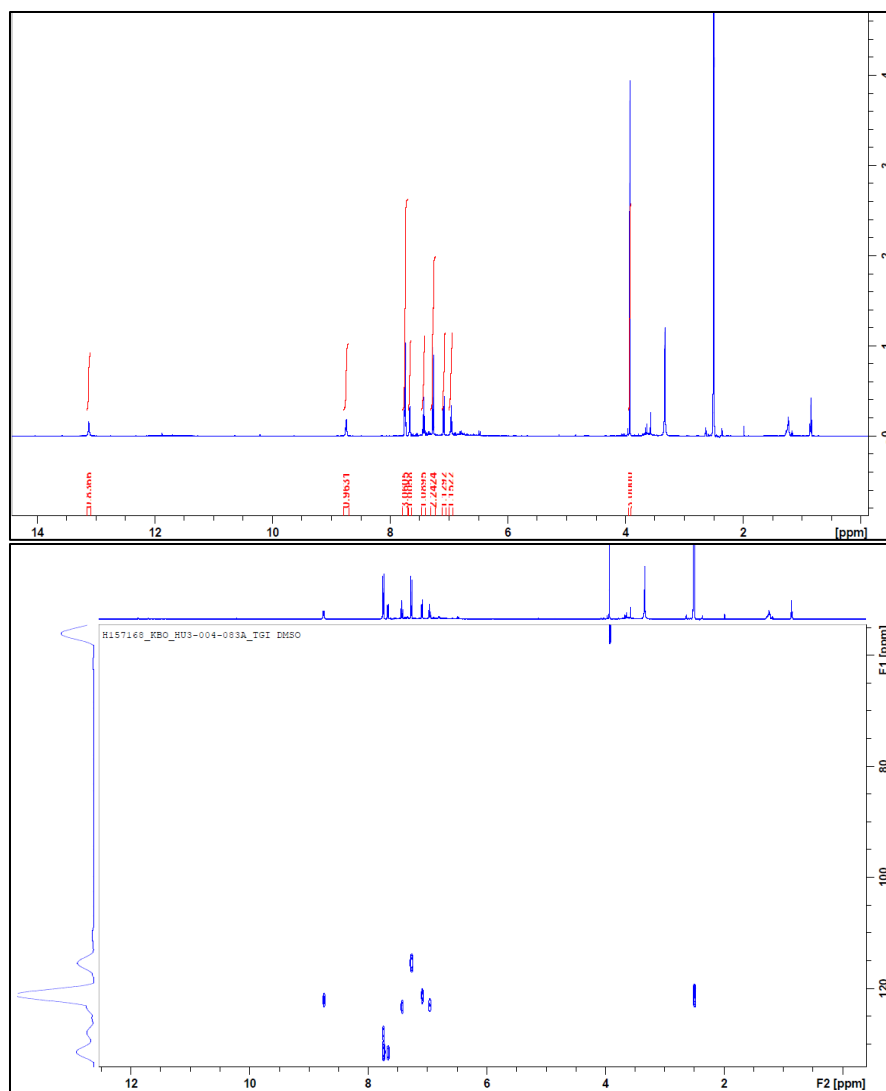




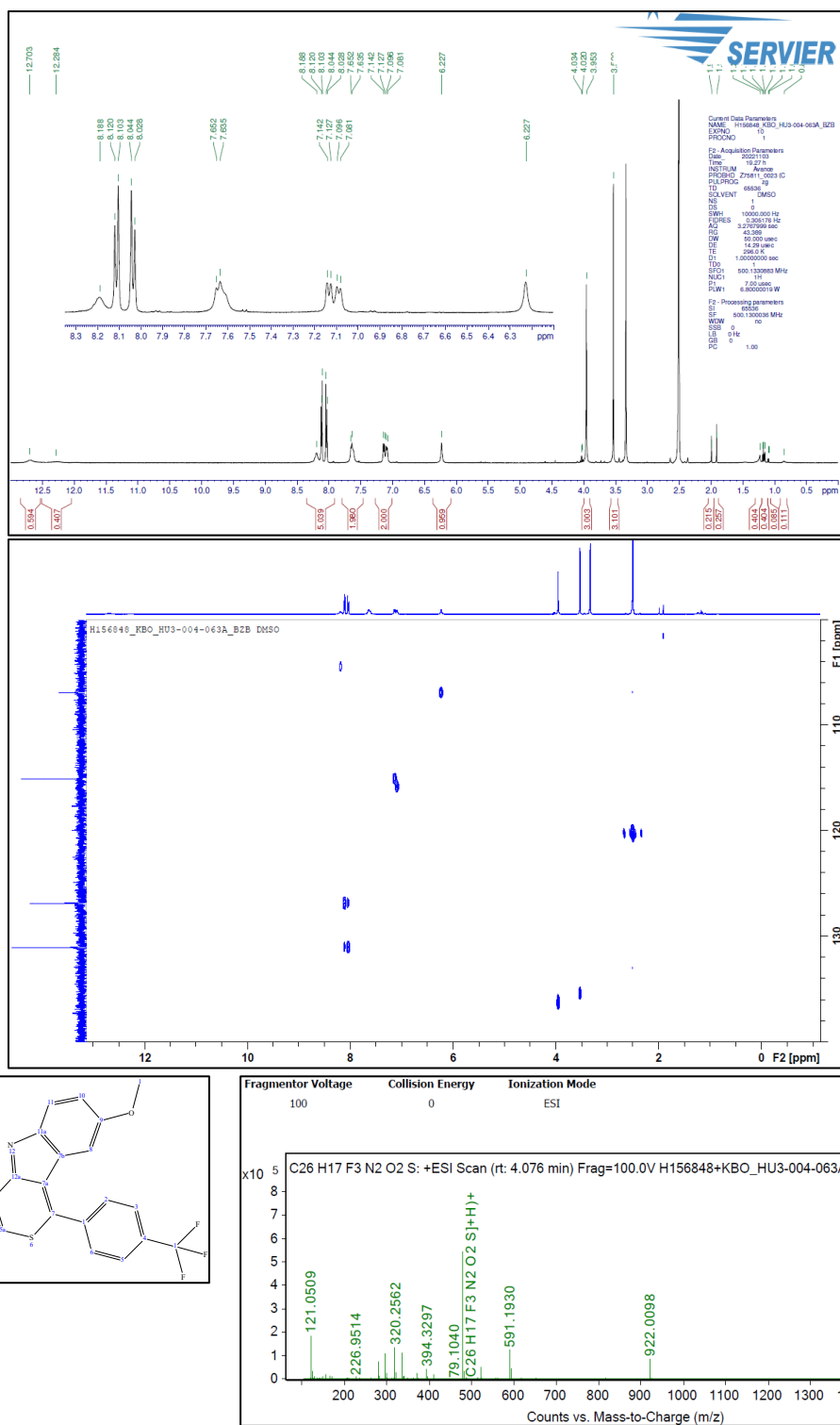
**Figure S11.**  $^1\text{H-NMR}$  and HSQC and HRMS spectrum of **9j** 4,11-dibromo-7-(3,5-dimethoxyphenyl)-5*H*-thiopyrano[2,3-*b*:4,5-*b'*]diindole



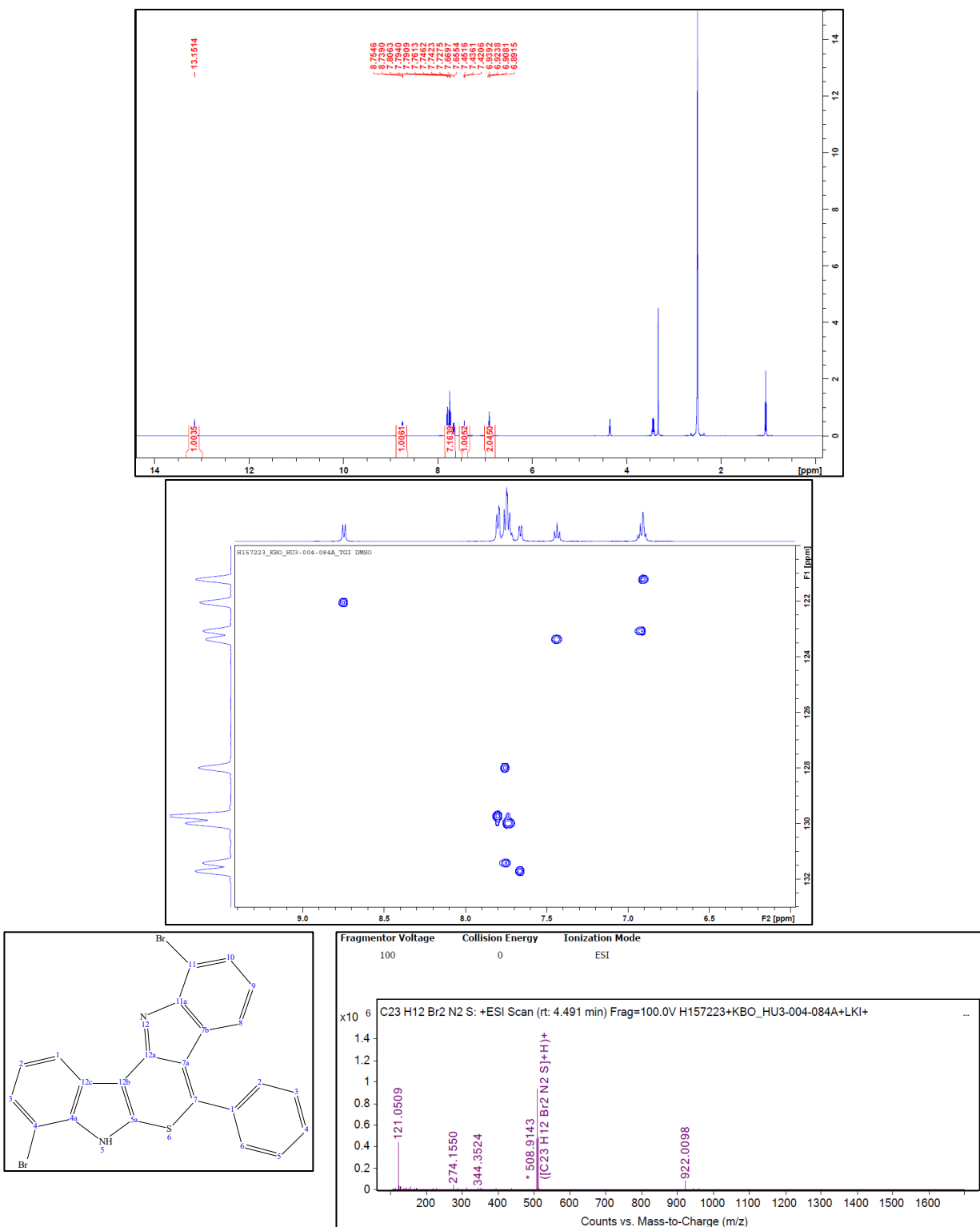
**Figure S12.**  $^1\text{H-NMR}$  and HSQC and HRMS spectrum of **9k** 4,11-dibromo-7-(3-bromophenyl)-5H-thiopyrano[2,3-*b*:4,5-*b'*]diindole



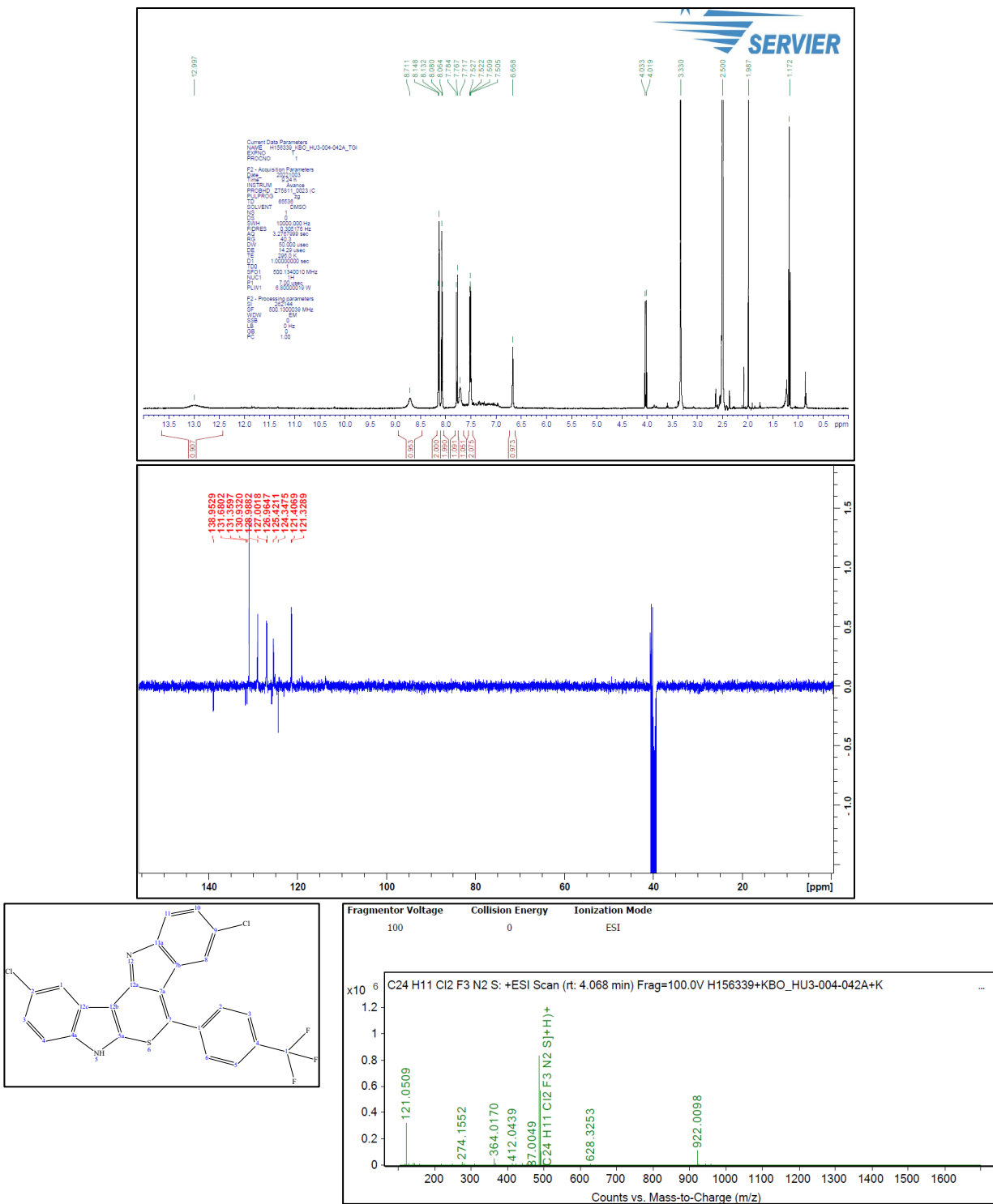
**Figure S13.** <sup>1</sup>H-NMR and HSQC and HRMS spectrum of **91** 4,11-dibromo-7-(4-methoxyphenyl)-5H-thiopyrano[2,3-*b*:4,5-*b'*]diindole



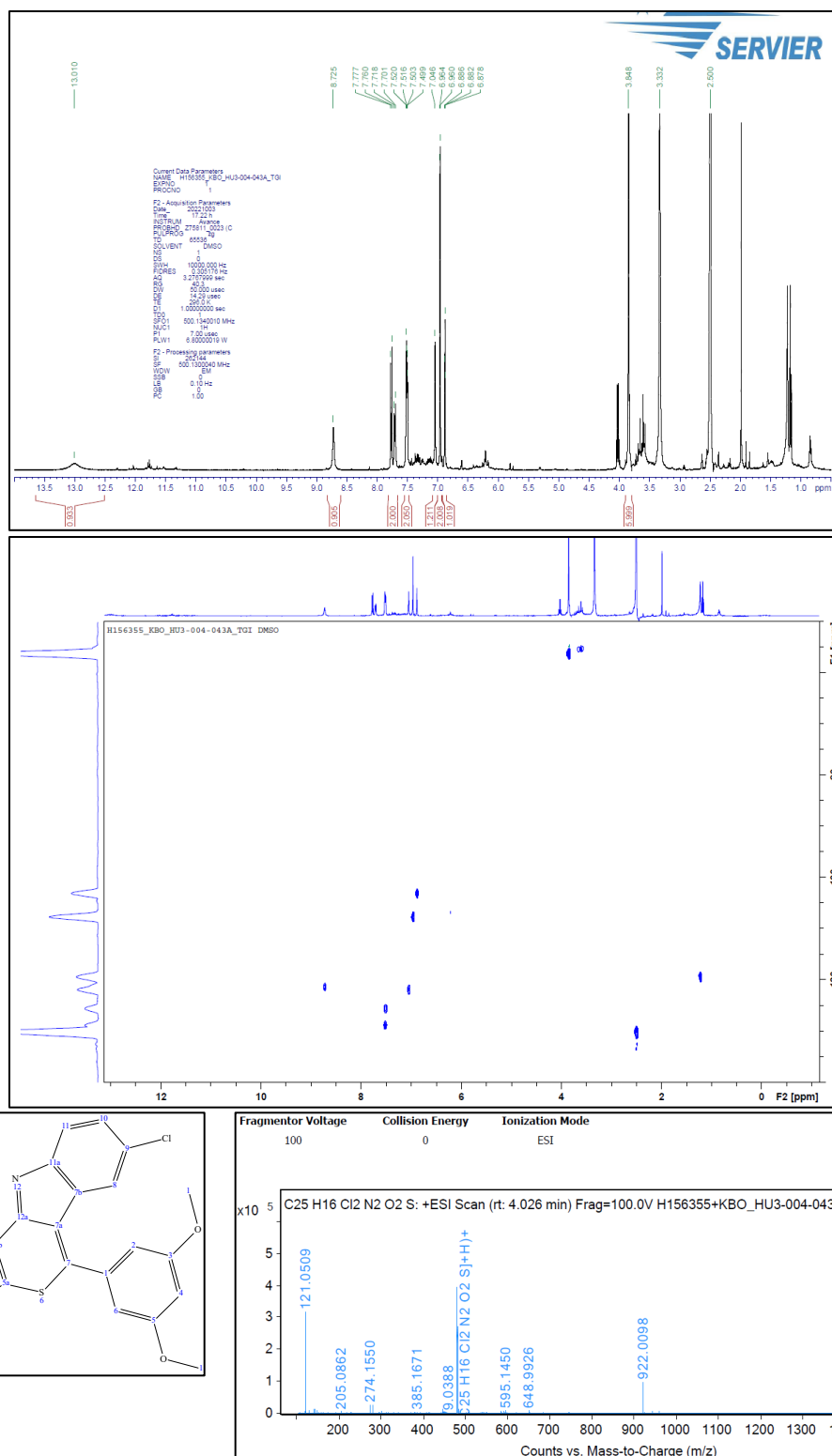
**Figure S14.** <sup>1</sup>H-NMR and HSQC and HRMS spectrum of **9m** 2,9-dimethoxy-7-[4-(trifluoromethyl)phenyl]-5H-thiopyrano[2,3-*b*:4,5-*b'*]diindole



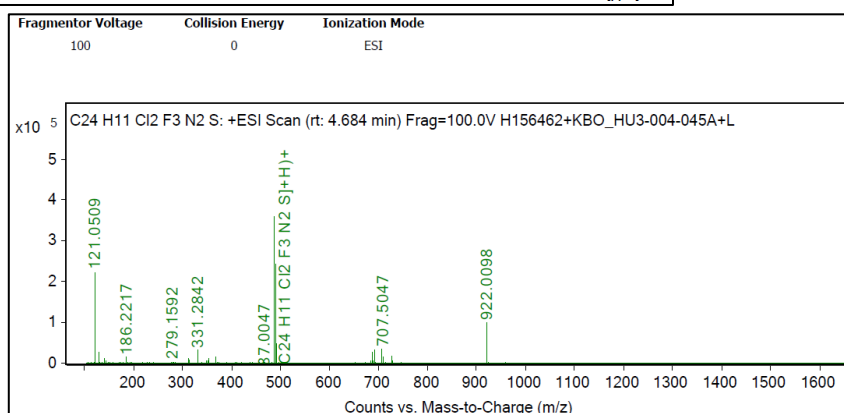
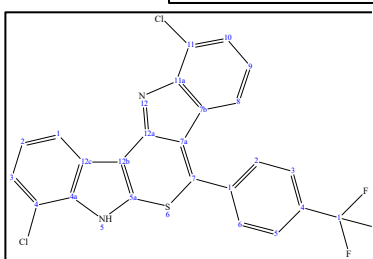
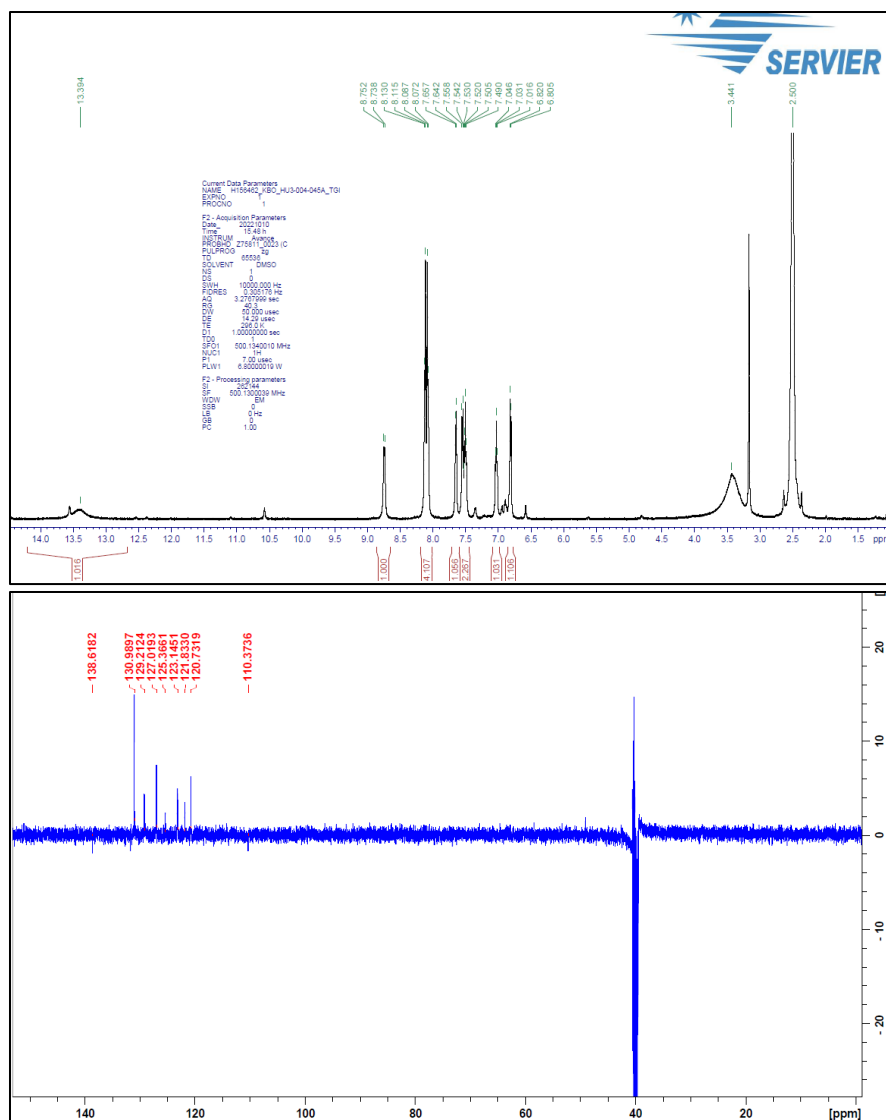
**Figure S15.** <sup>1</sup>H-NMR and HSQC and HRMS spectrum of **9n** 4,11-dibromo-7-phenyl-5*H*-thiopyrano[2,3-*b*:4,5-*b'*]diindole



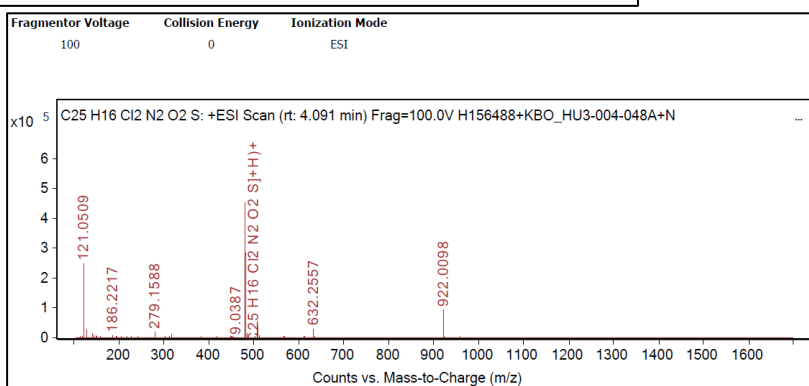
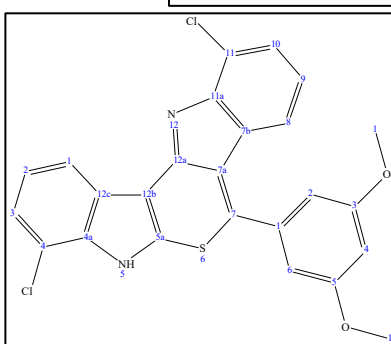
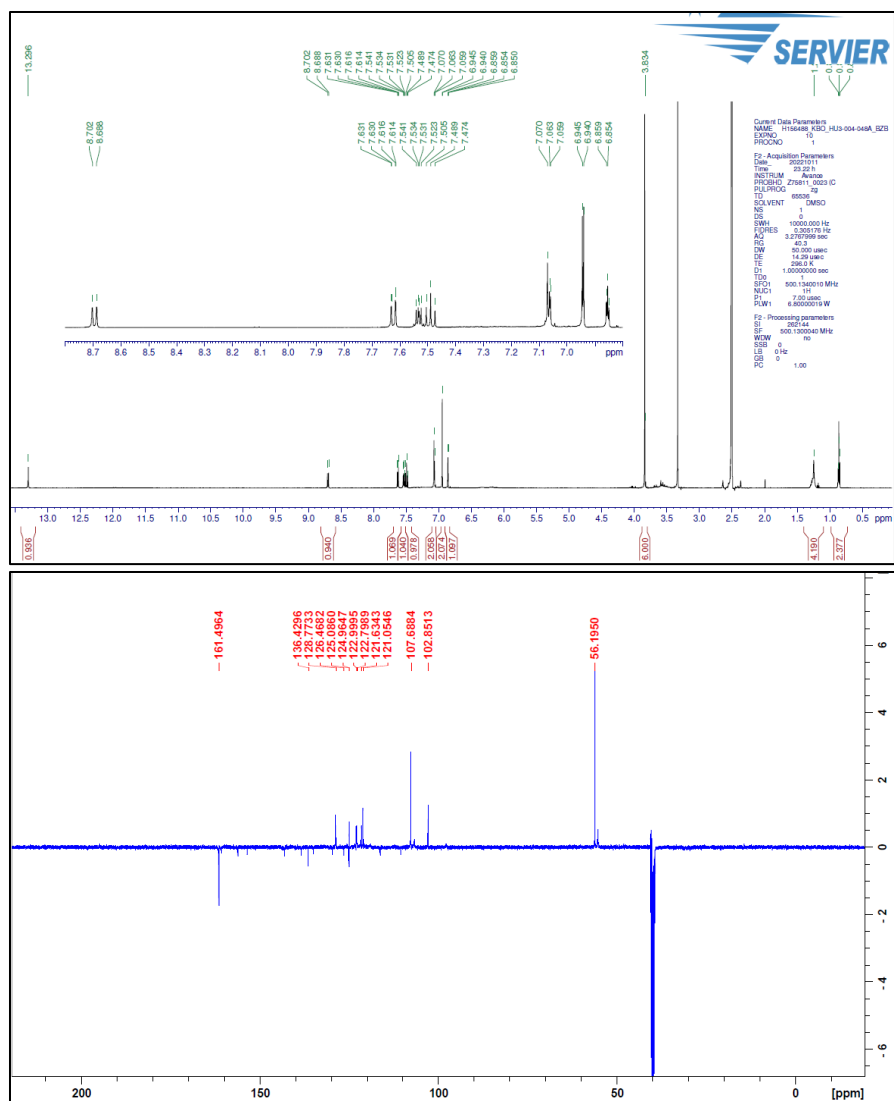
**Figure S16.** <sup>1</sup>H-NMR and <sup>13</sup>C-NMR and HRMS spectrum of **9o** 2,9-dichloro-7-[4-(trifluoromethyl)phenyl]-5H-thiopyrano[2,3-*b*:4,5-*b'*]diindole



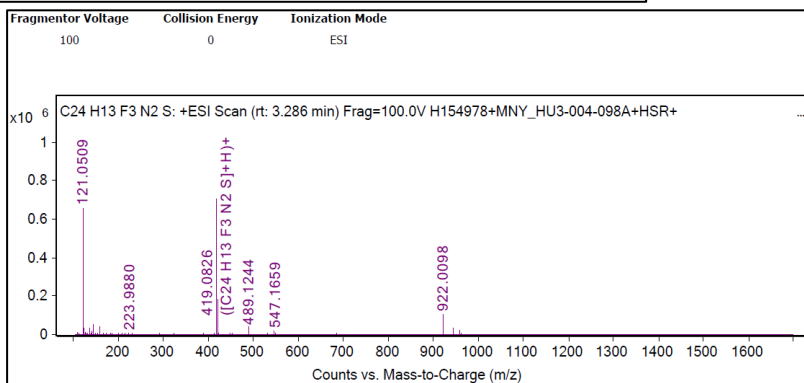
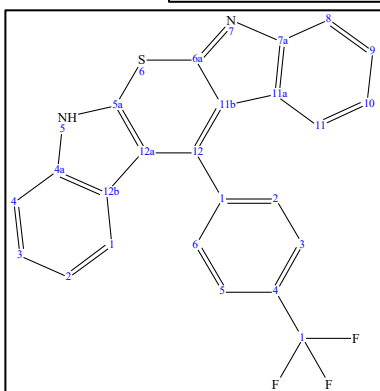
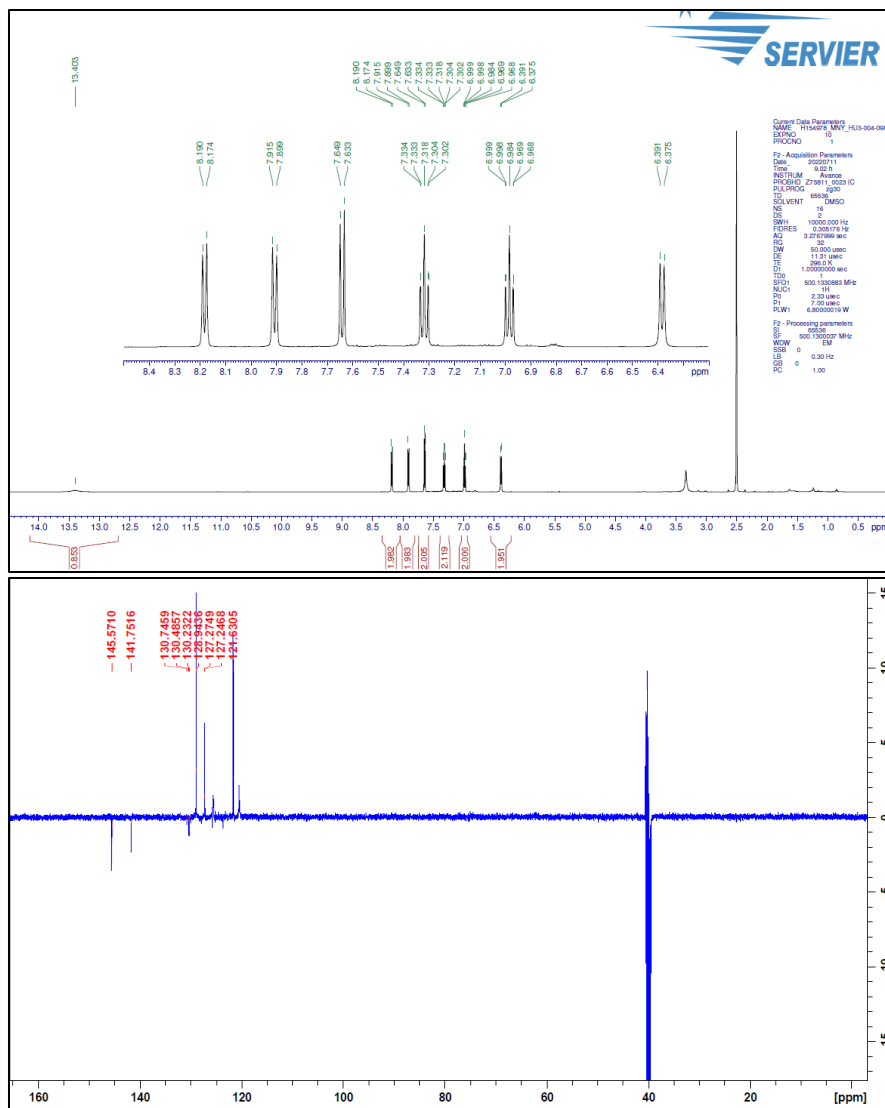
**Figure S17.** <sup>1</sup>H-NMR and HSQC and HRMS spectrum of **9p** 2,9-dichloro-7-(3,5-dimethoxyphenyl)-5*H*-thiopyrano[2,3-*b*:4,5-*b'*]diindole



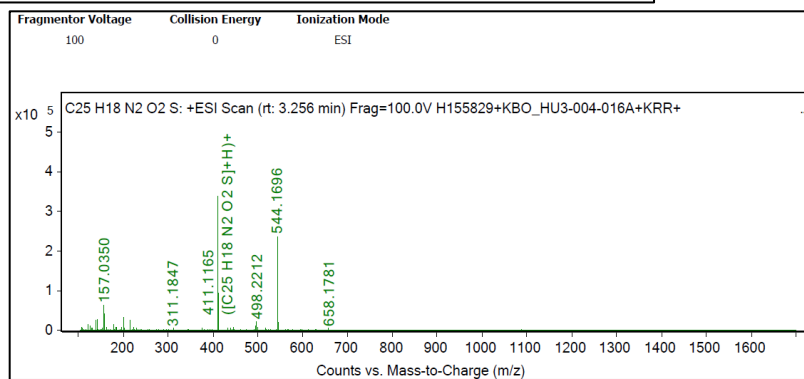
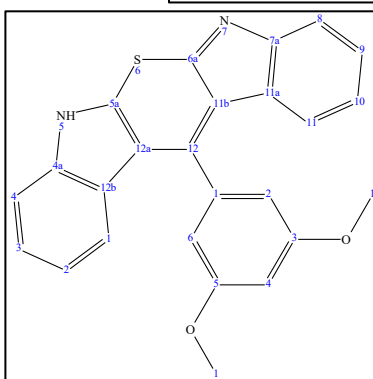
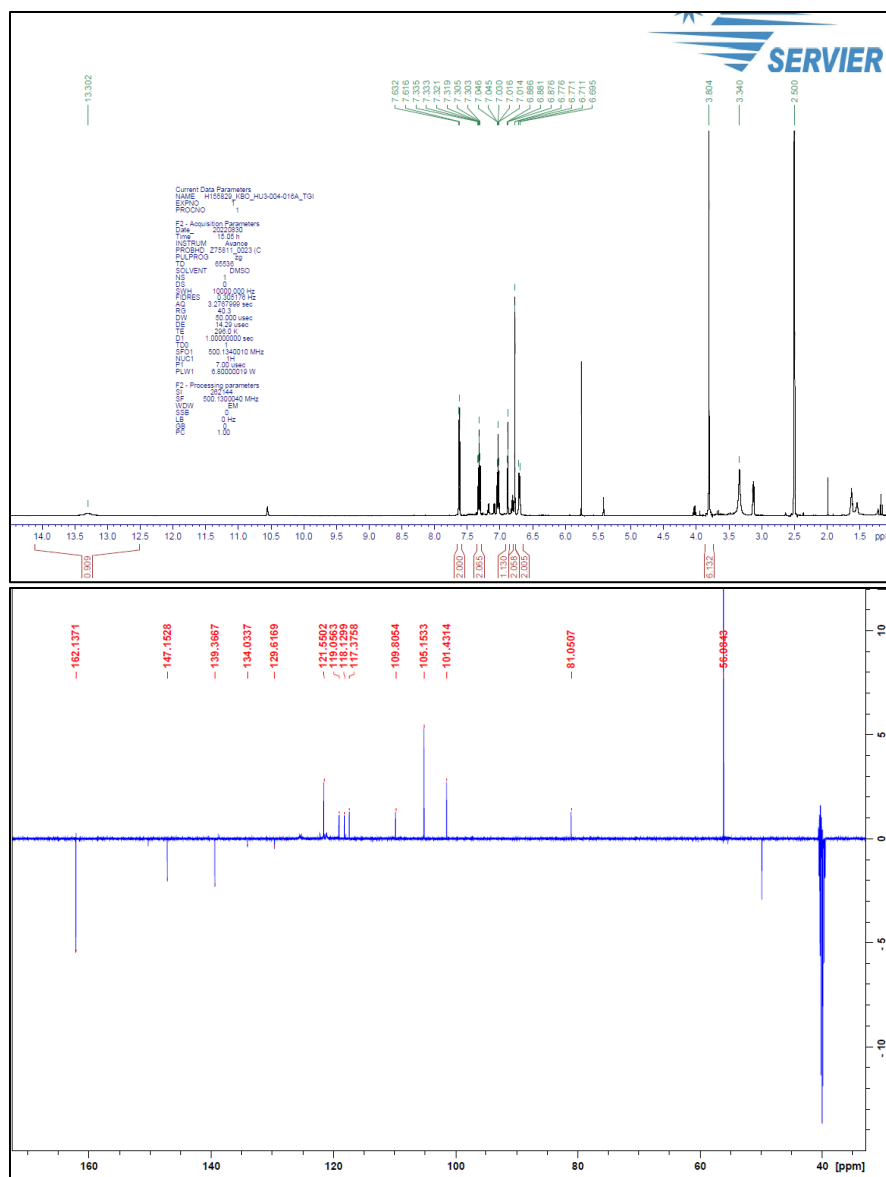
**Figure S18.** <sup>1</sup>H-NMR and <sup>13</sup>C-NMR and HRMS spectrum of **9q** 4,11-dichloro-7-[4-(trifluoromethyl)phenyl]-5H-thiopyrano[2,3-*b*:4,5-*b'*]diindole



**Figure S19.** <sup>1</sup>H-NMR and <sup>13</sup>C-NMR and HRMS spectrum of **9r** 4,11-dichloro-7-(3,5-dimethoxyphenyl)-5H-thiopyrano[2,3-*b*:4,5-*b'*]diindole

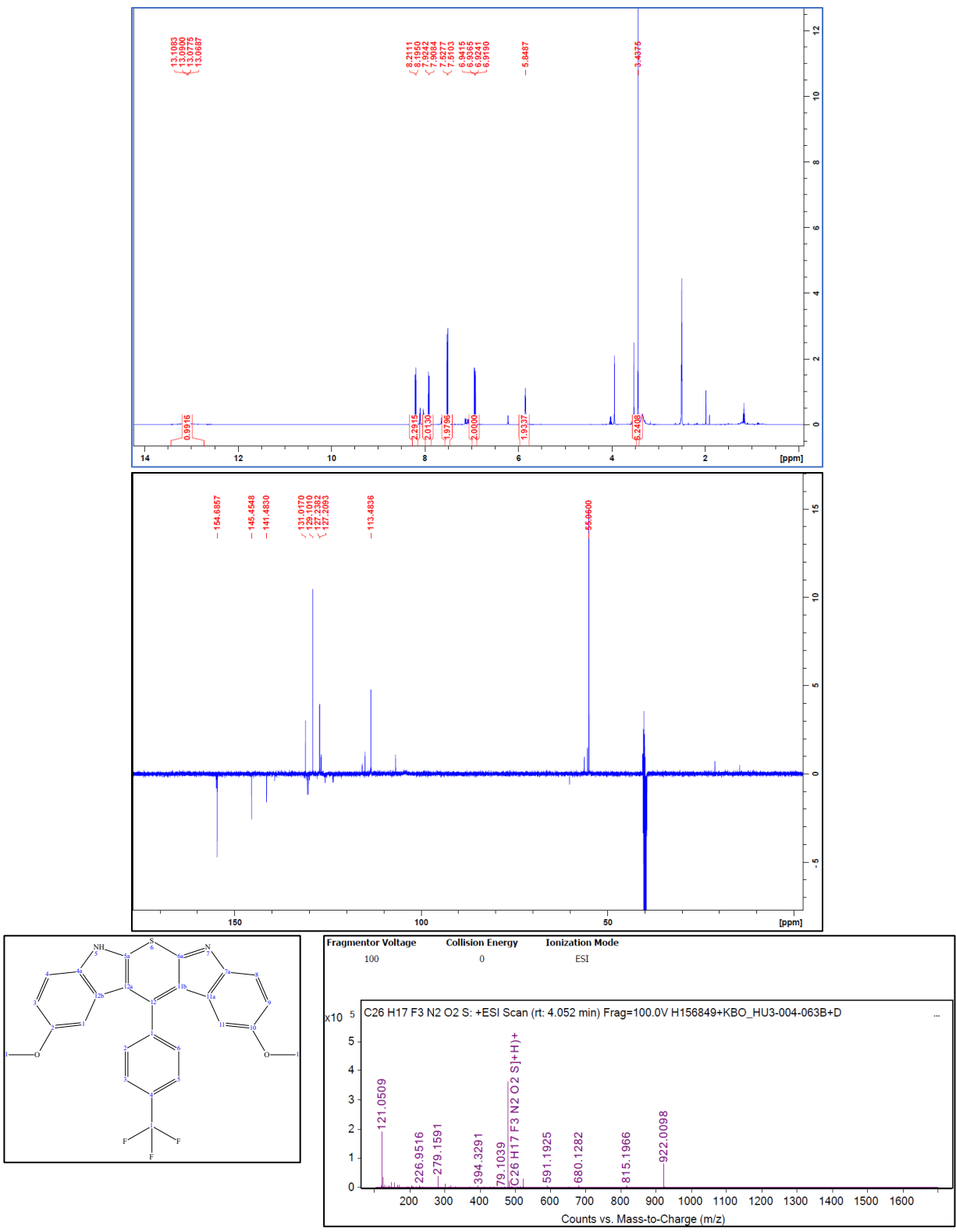


**Figure S20.**  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR and HRMS spectrum of **10a** 12-[4-(trifluoromethyl)phenyl]-5H-thiopyrano[2,3-*b*:6,5-*b'*]diindole

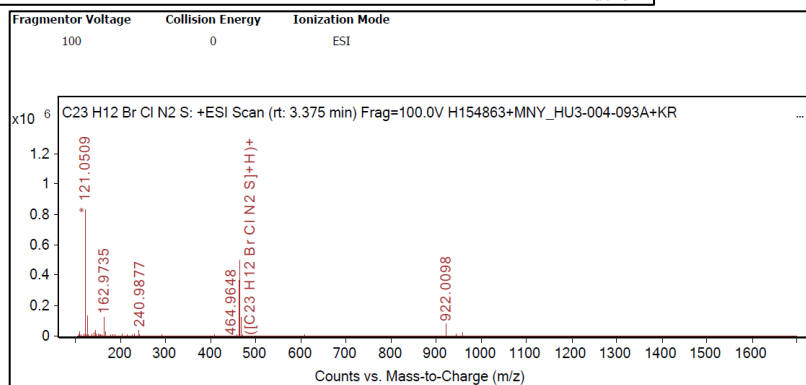
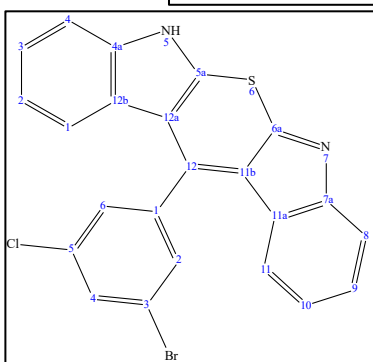
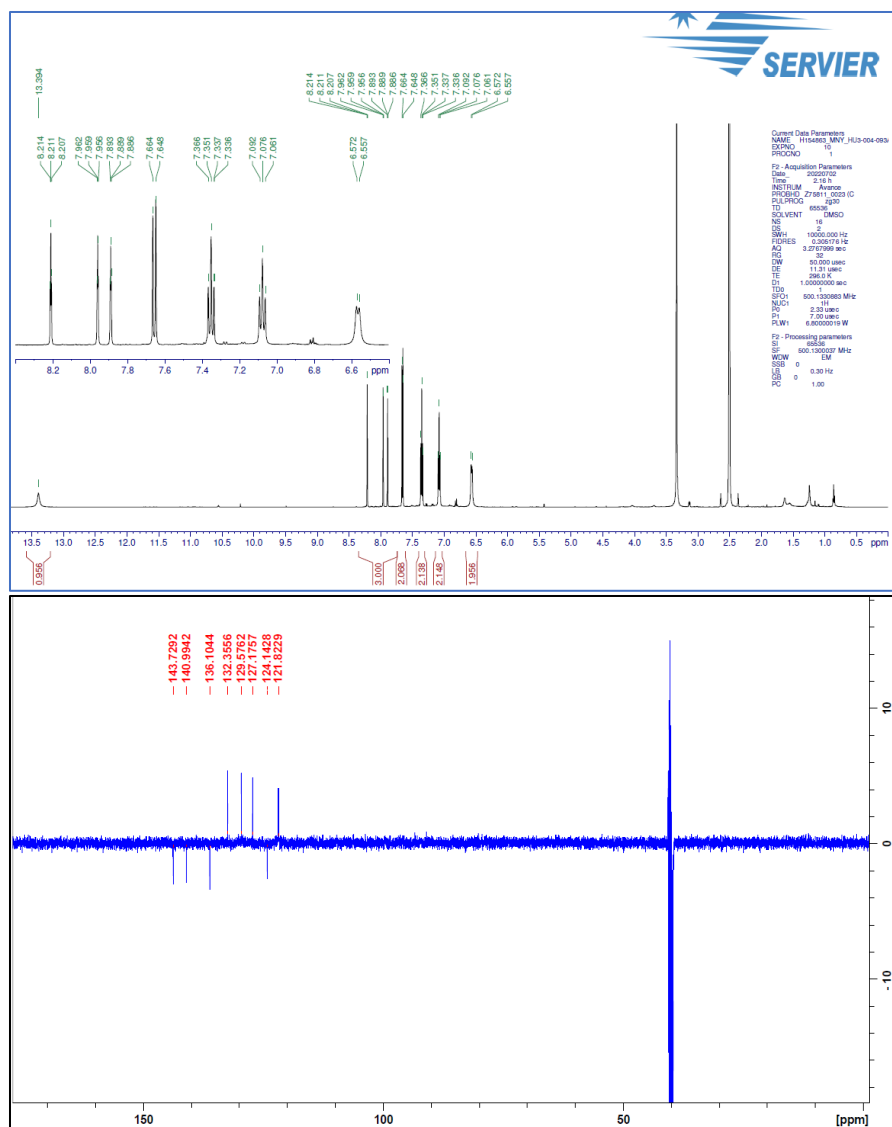


**Figure S21.**  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR and HRMS spectrum of **10b** 12-(3,5-dimethoxyphenyl)-5H-thiopyrano[2,3-b:6,5-b']diindole



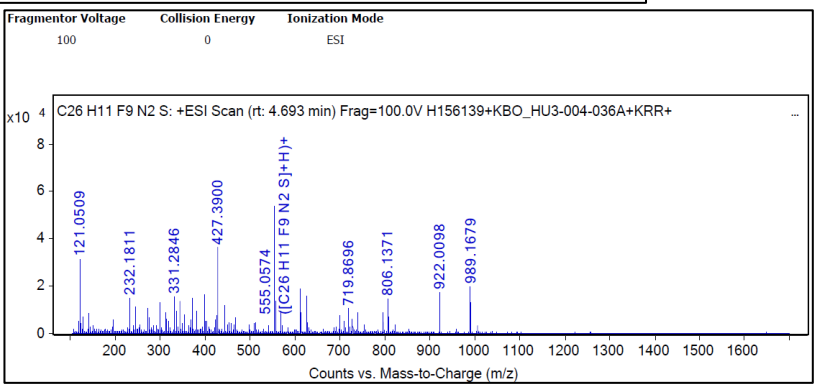
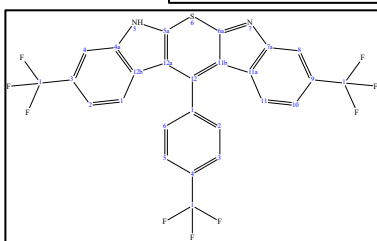
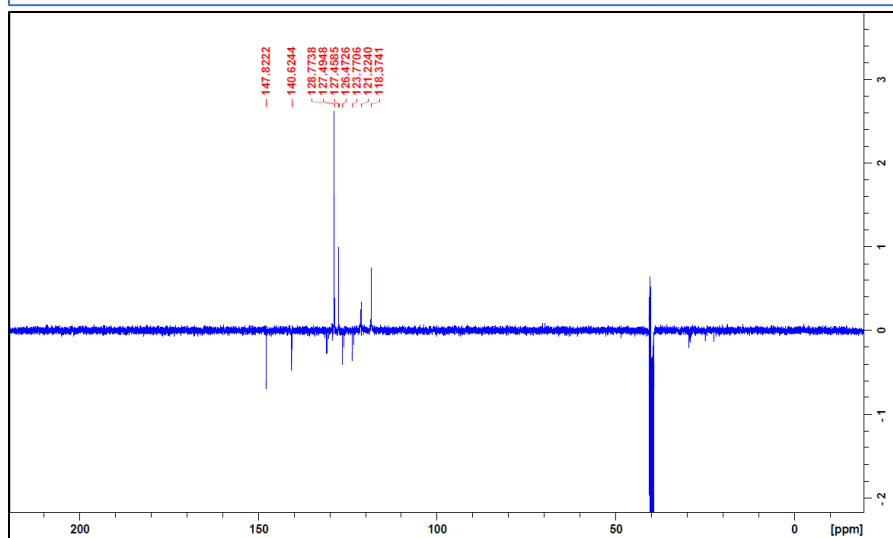
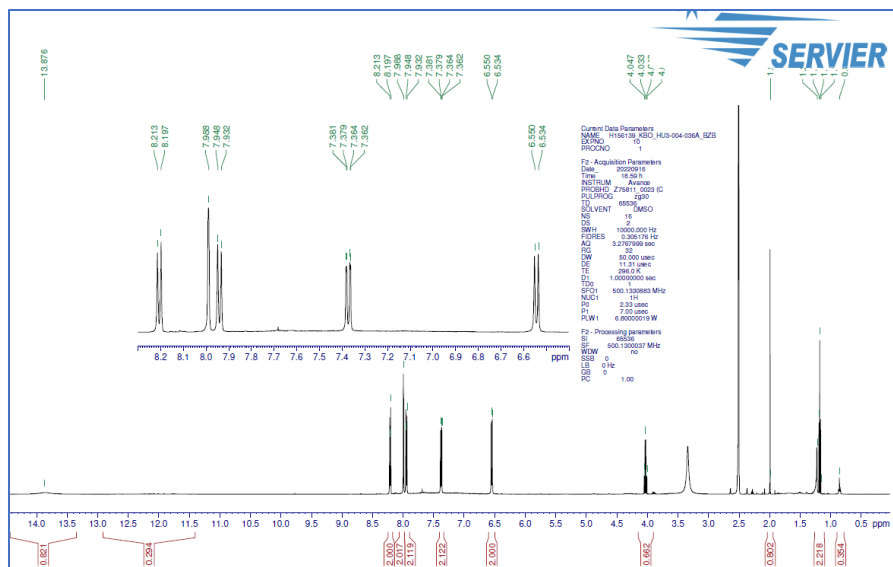


**Figure S23.** <sup>1</sup>H-NMR and <sup>13</sup>C-NMR and HRMS spectrum of **10d** 2,10-dimethoxy-12-[4-(trifluoromethyl)phenyl]-5H-thiopyrano[2,3-b:6,5-b']diindole

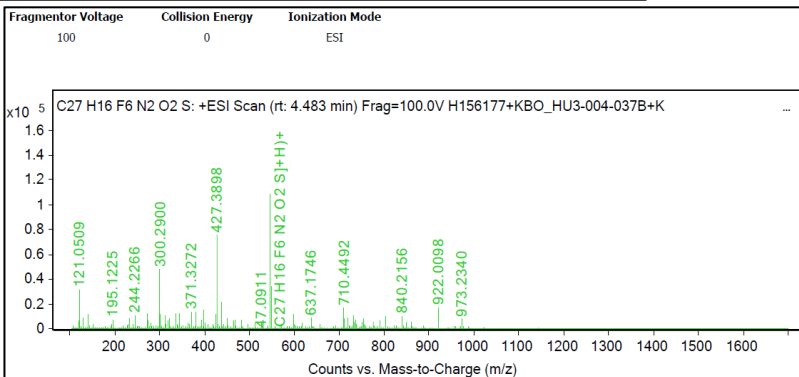
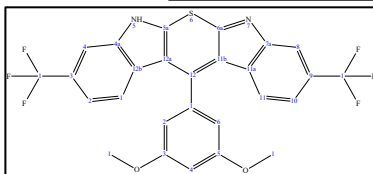
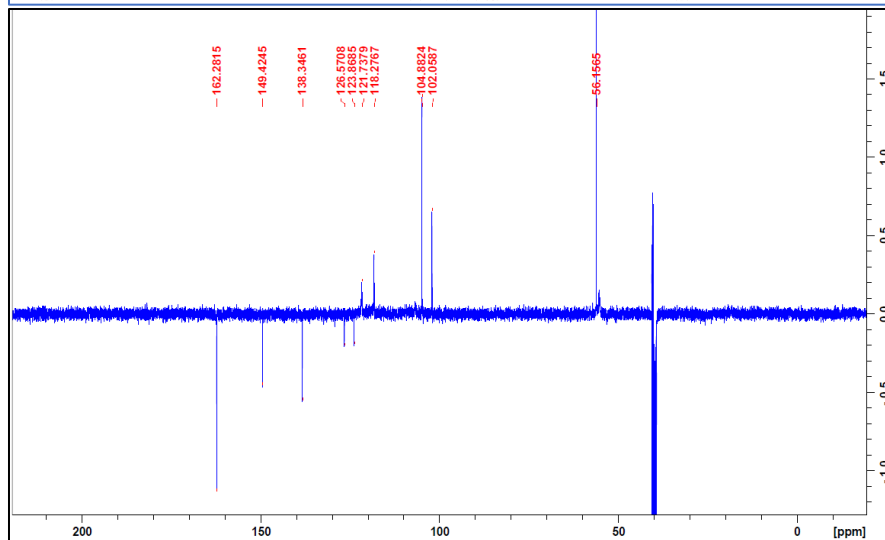
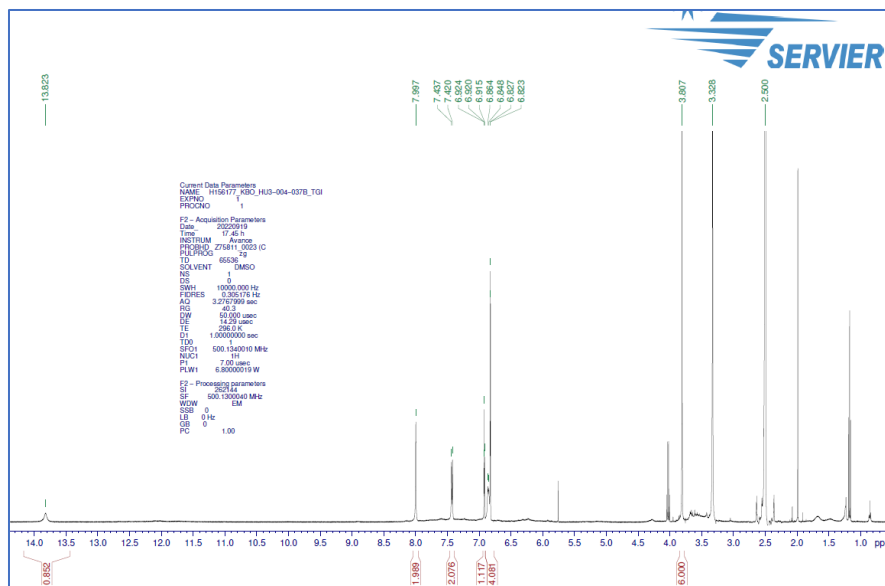


**Figure S24.**  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR and HRMS spectrum of **10e** 12-(3-bromo-5-chlorophenyl)-5H-thiopyrano[2,3-b:6,5-b']diindole

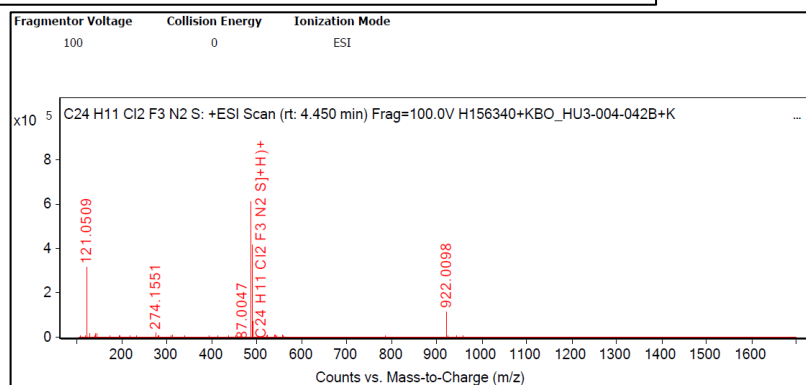
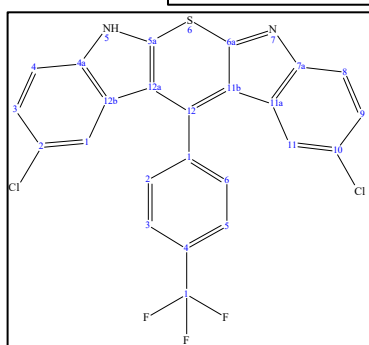
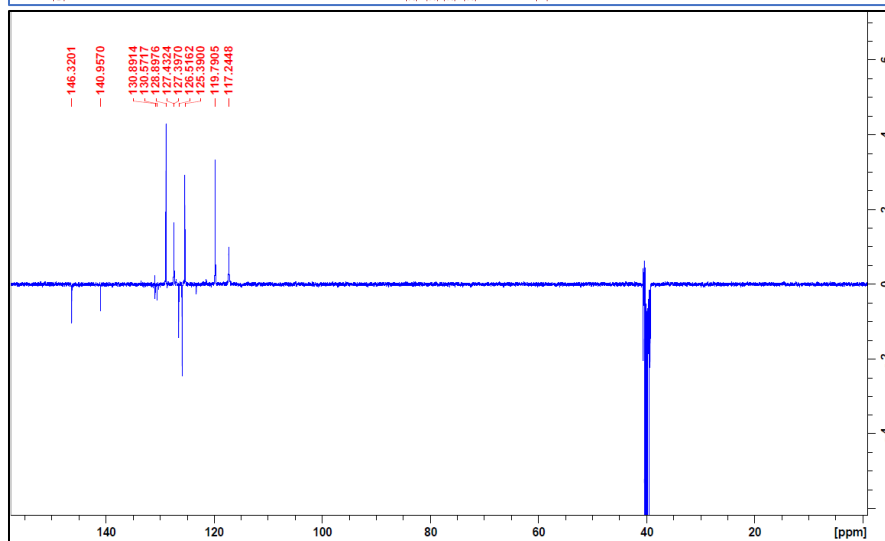
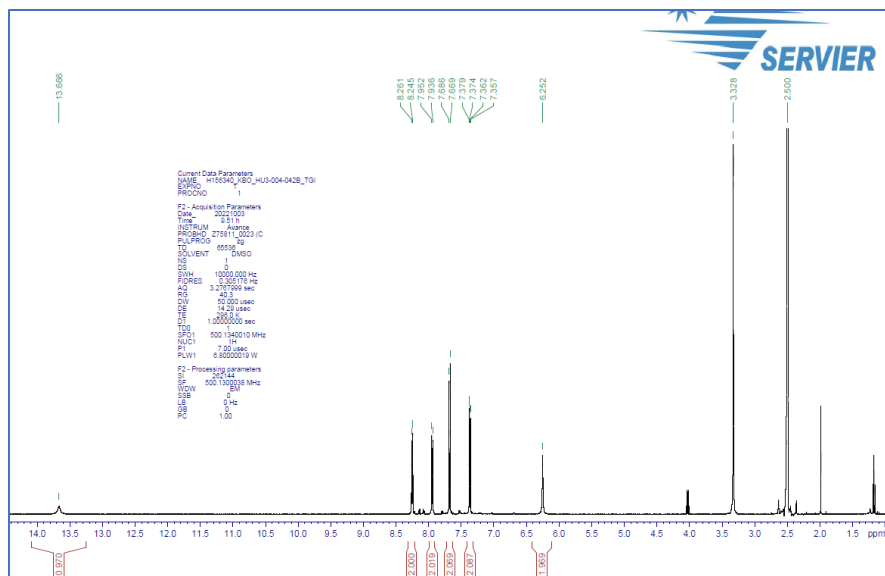




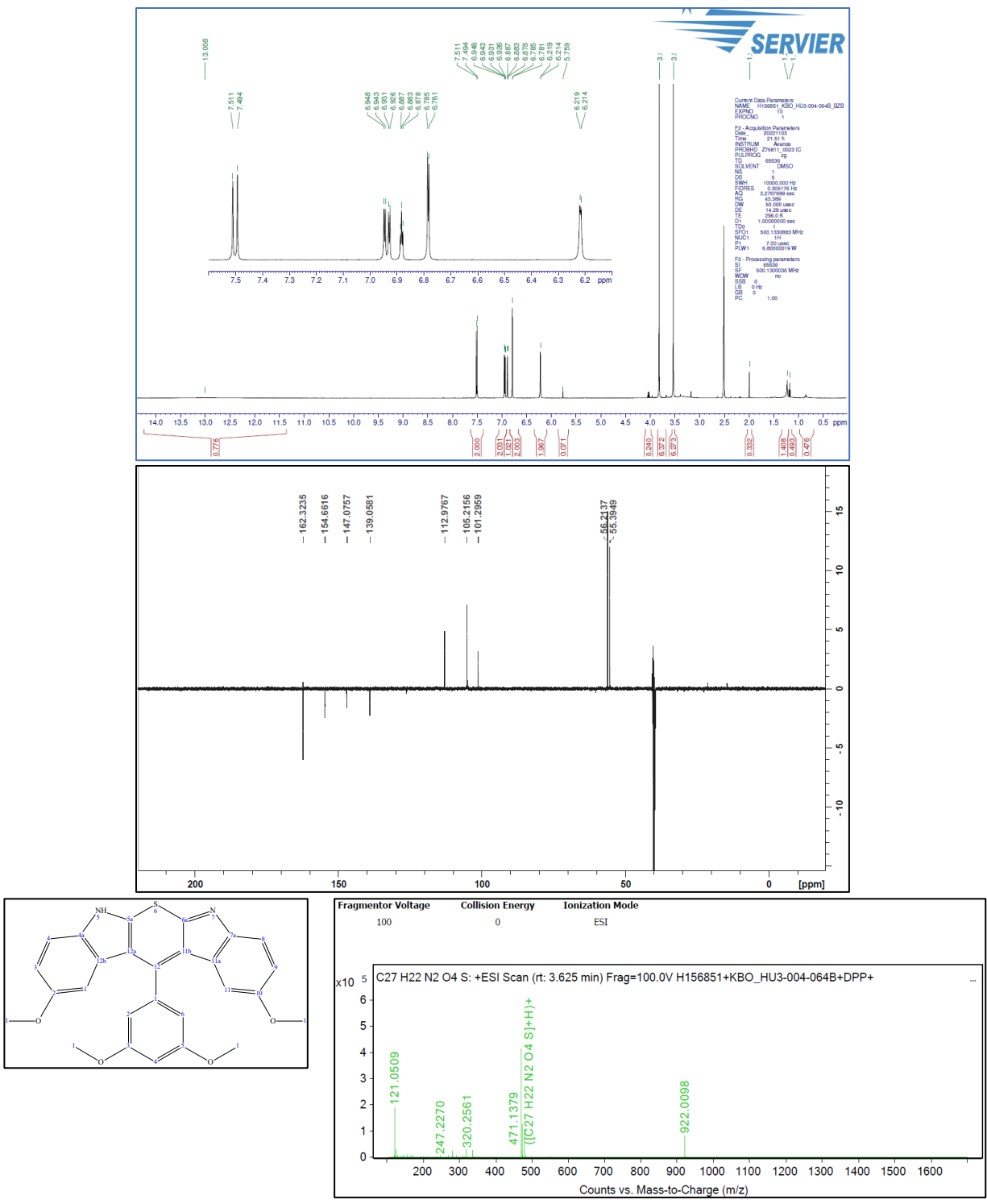
**Figure S26.**  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR and HRMS spectrum of **10g** 3,9-bis(trifluoromethyl)-12-[4-(trifluoromethyl)phenyl]-5H-thiopyrano[2,3-b:6,5-b']diindole



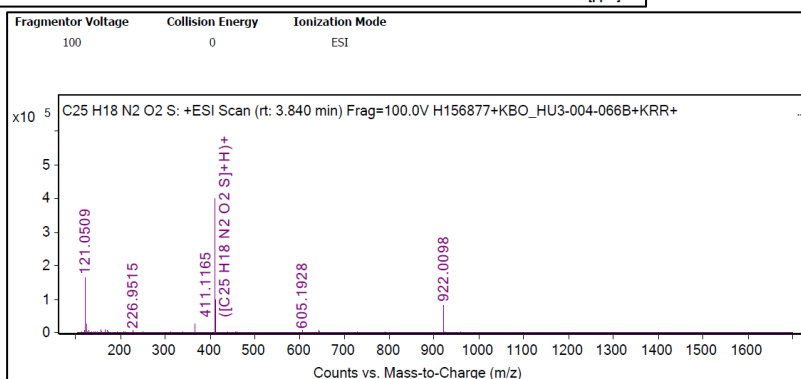
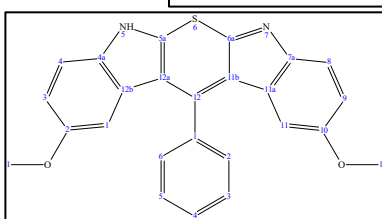
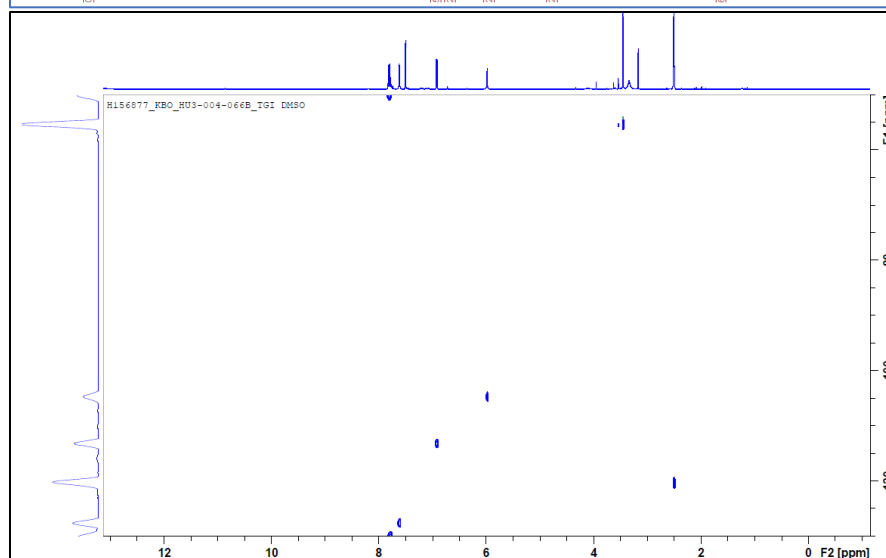
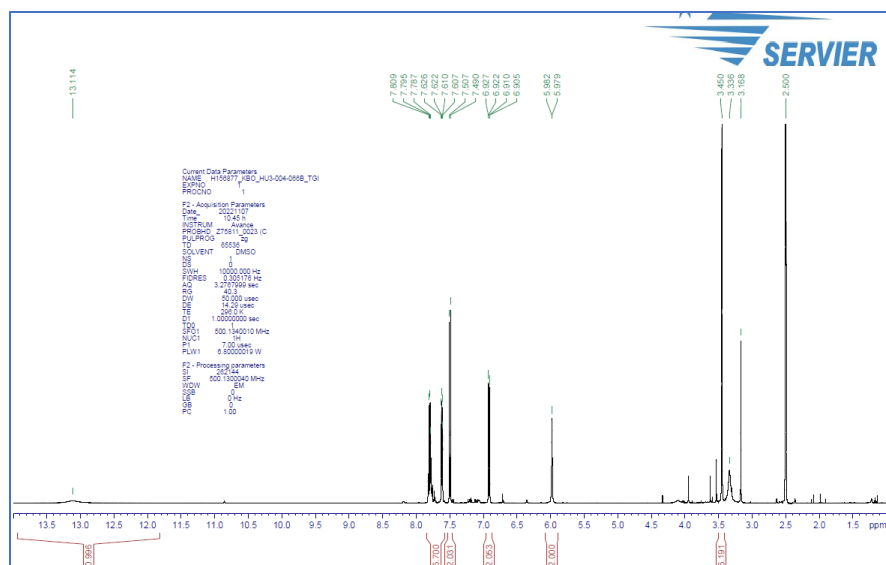
**Figure S27.** <sup>1</sup>H-NMR and <sup>13</sup>C-NMR and HRMS spectrum of **10h** 12-(3,5-dimethoxyphenyl)-3,9-bis(trifluoromethyl)-5H-thiopyrano[2,3-*b*:6,5-*b'*]diindole



**Figure S28.**  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  and HRMS spectrum of **10i** 2,10-dichloro-12-[4-(trifluoromethyl)phenyl]-5H-thiopyrano[2,3-*b*:6,5-*b'*]diindole



**Figure S29.** <sup>1</sup>H-NMR and <sup>13</sup>C-NMR and HRMS spectrum of **10j** 12-(3,5-dimethoxyphenyl)-2,10-dimethoxy-5H-thiopyrano[2,3-*b*:6,5-*b'*]diindole



**Figure S30.**  $^1\text{H-NMR}$  and HSQC and HRMS spectrum of **10k** 2,10-dimethoxy-12-phenyl-5H-thiopyrano[2,3-b:6,5-b']diindole

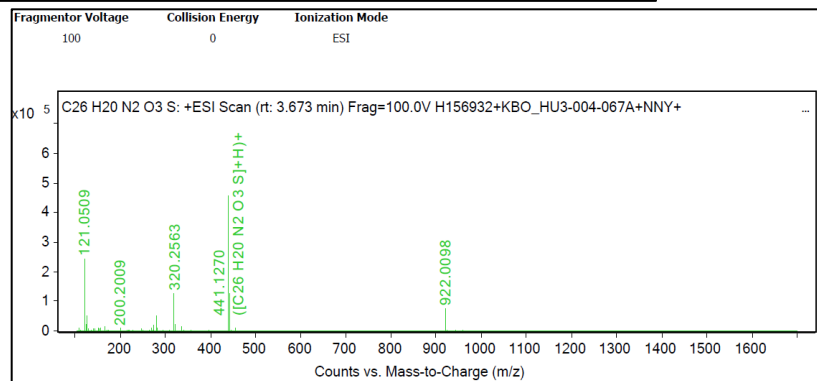
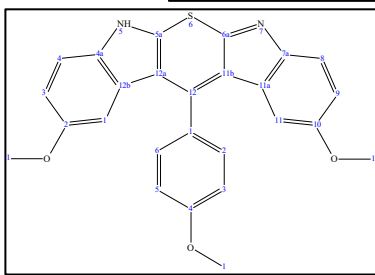
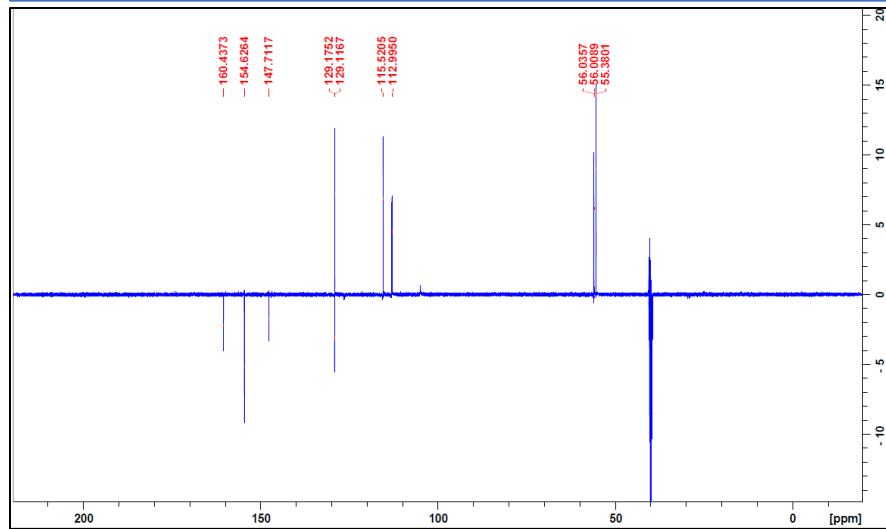
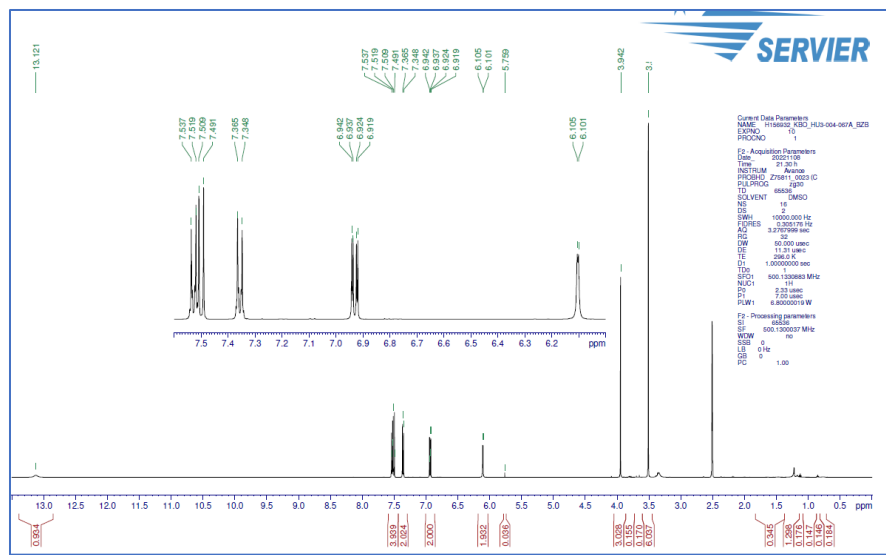
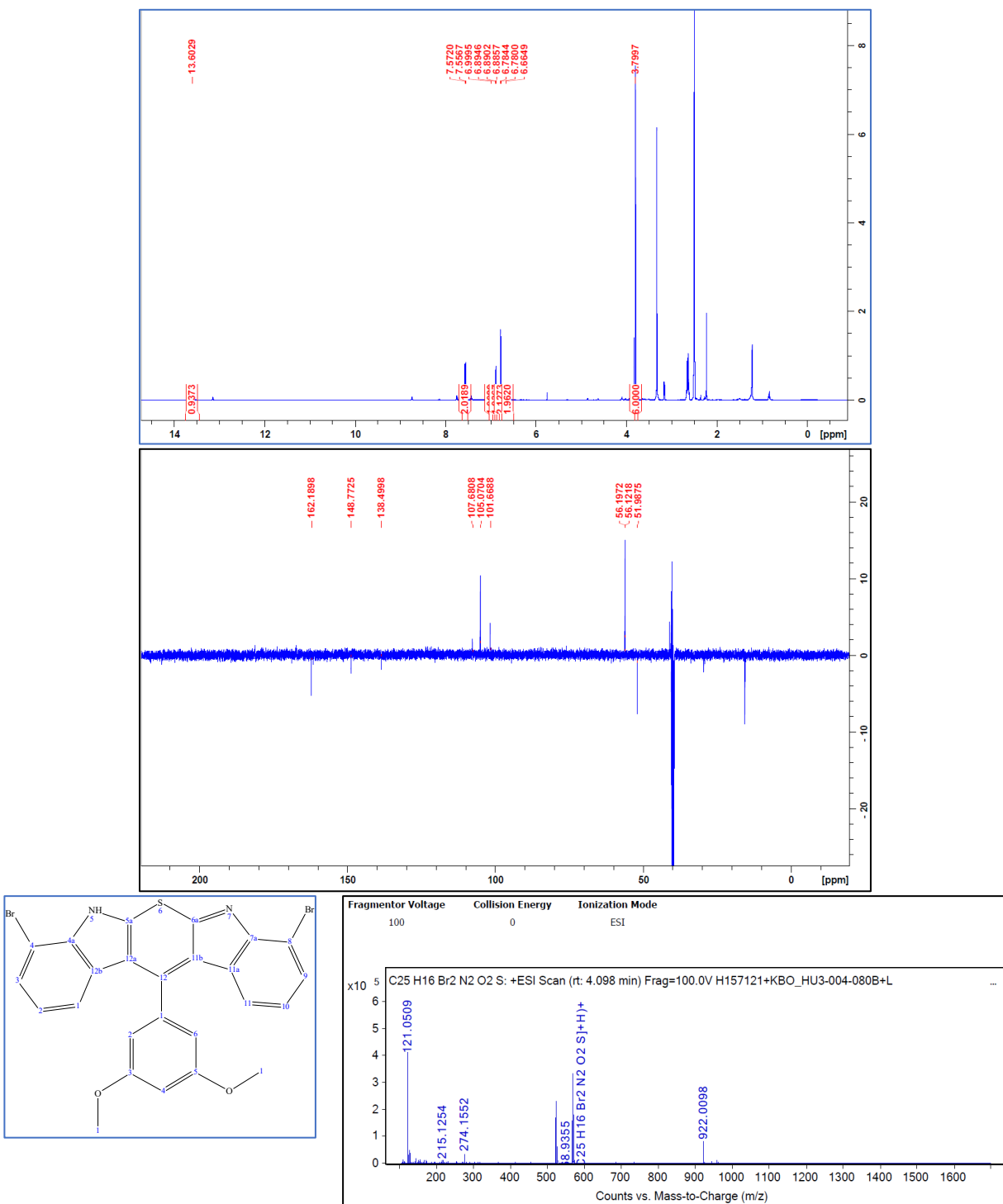
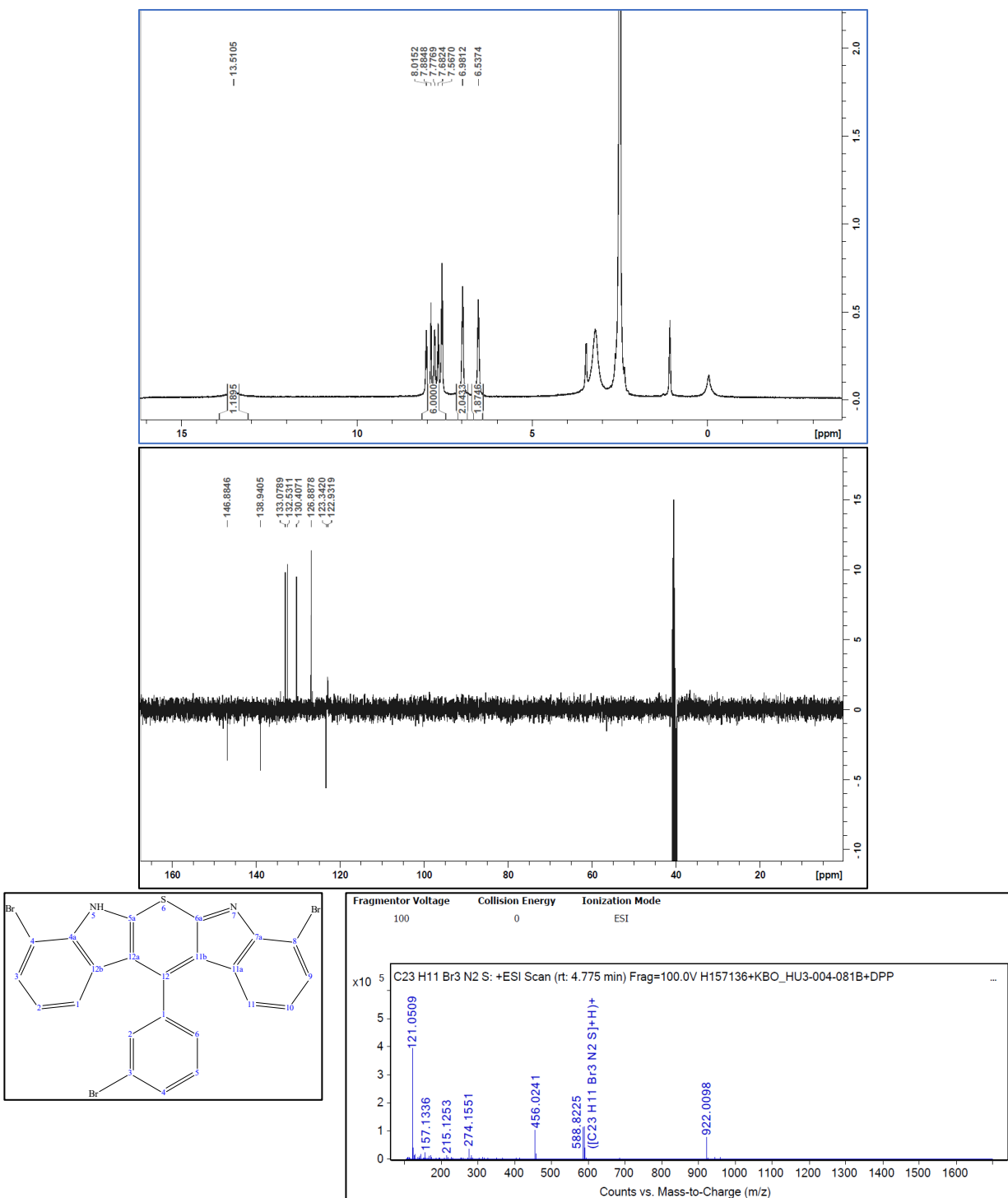
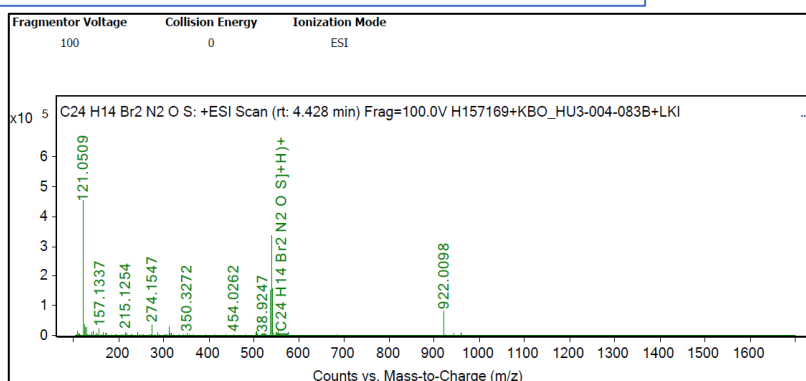
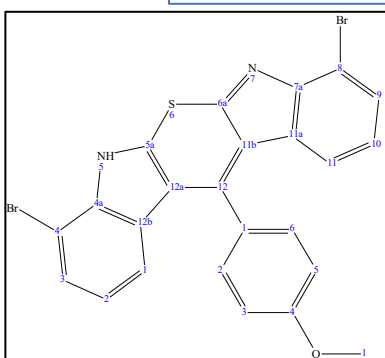
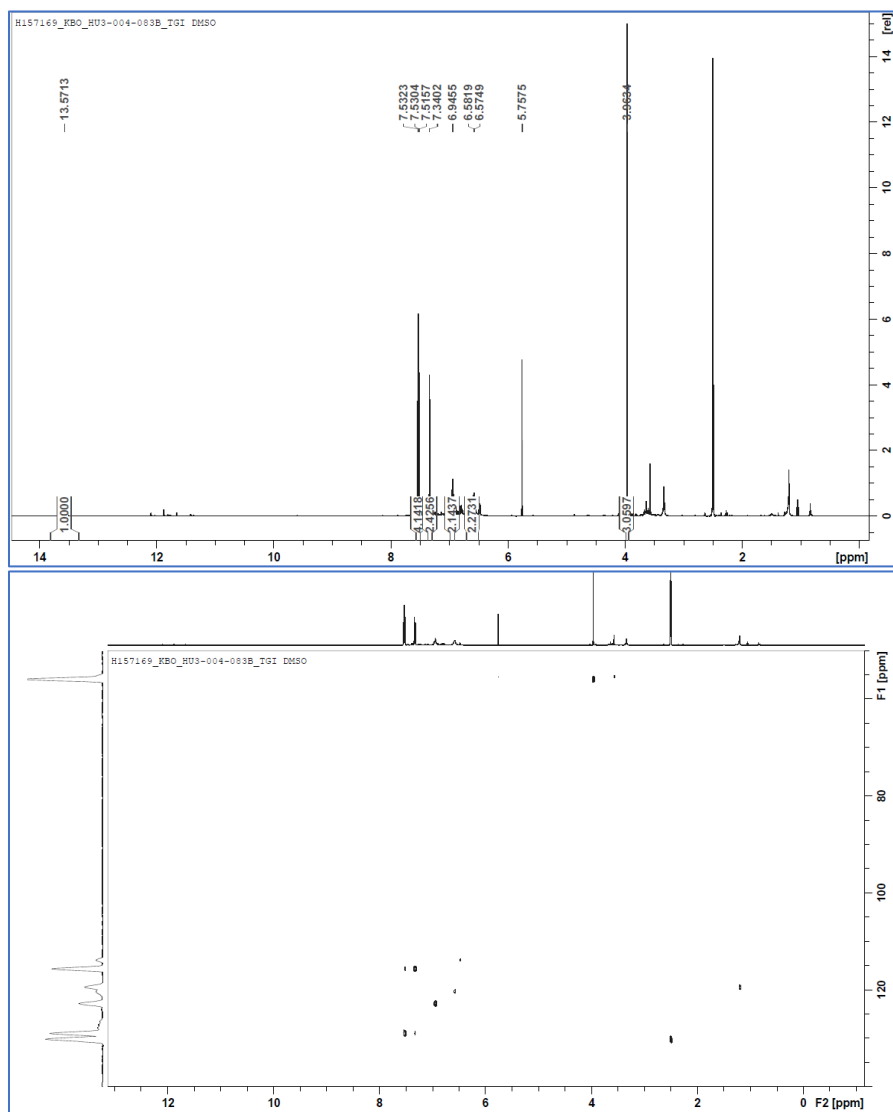


Figure S31. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR and HRMS spectrum of **101** 2,10-dimethoxy-12-(4-methoxyphenyl)-5H-thiopyrano[2,3-*b*:6,5-*b'*]diindole

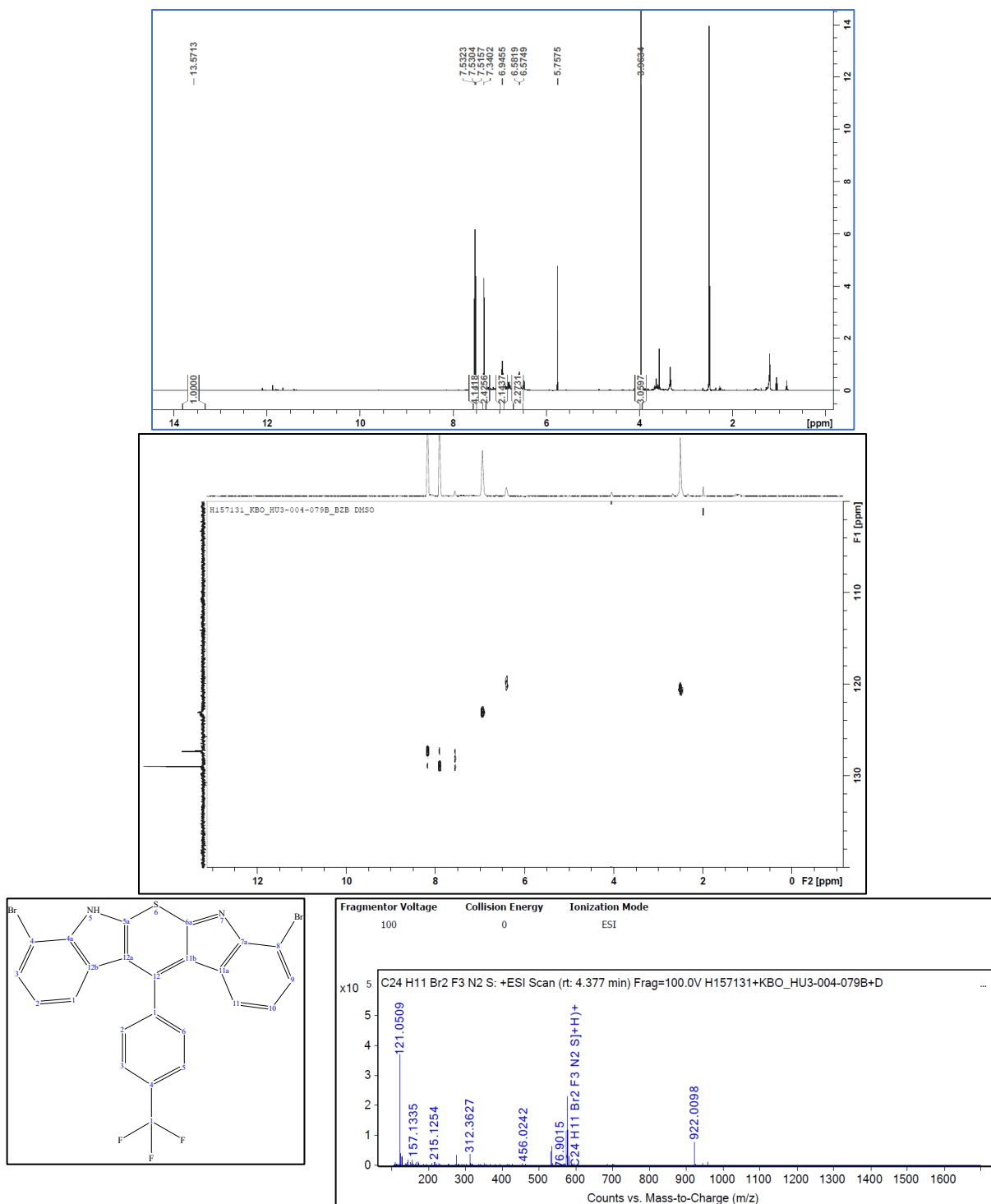


**Figure S32.** <sup>1</sup>H-NMR and <sup>13</sup>C-NMR and HRMS spectrum of **10m** 4,8-dibromo-12-(3,5-dimethoxyphenyl)-5H-thiopyrano[2,3-*b*:6,5-*b'*]diindole

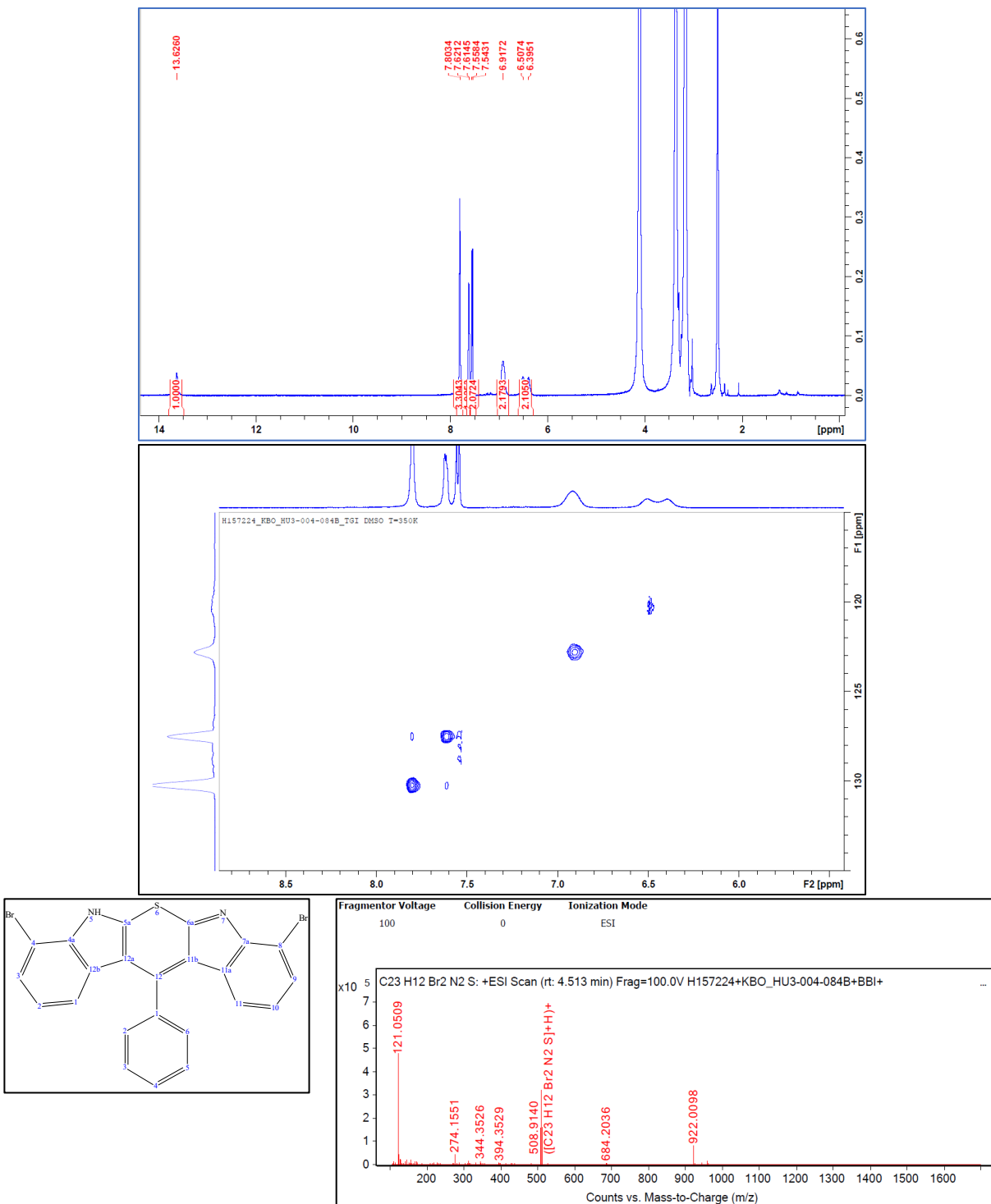




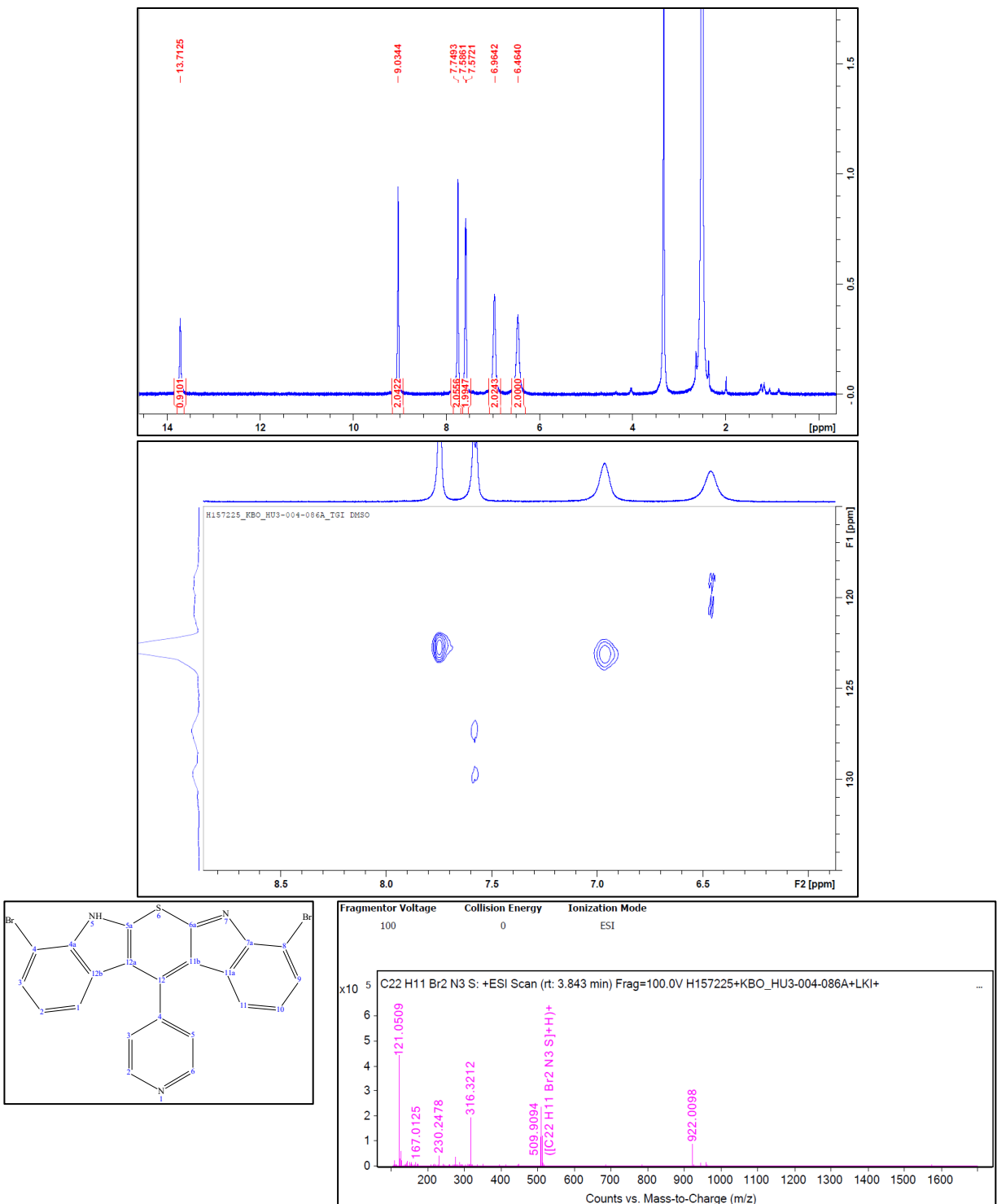
**Figure S34.**  $^1\text{H}$ -NMR and HSQC and HRMS spectrum of **10o** 4,8-dibromo-12-(4-methoxyphenyl)-5H-thiopyrano[2,3-*b*:6,5-*b'*]diindole



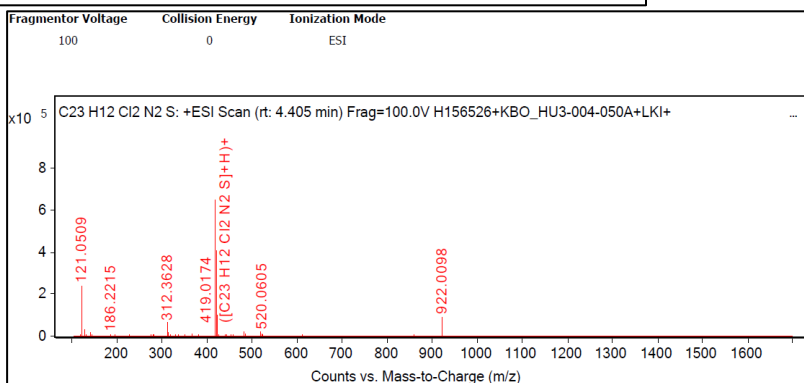
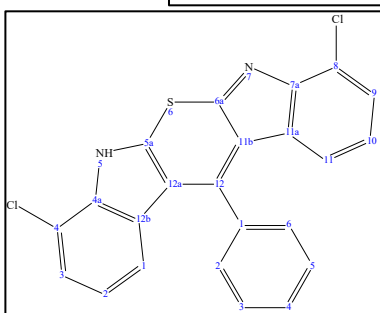
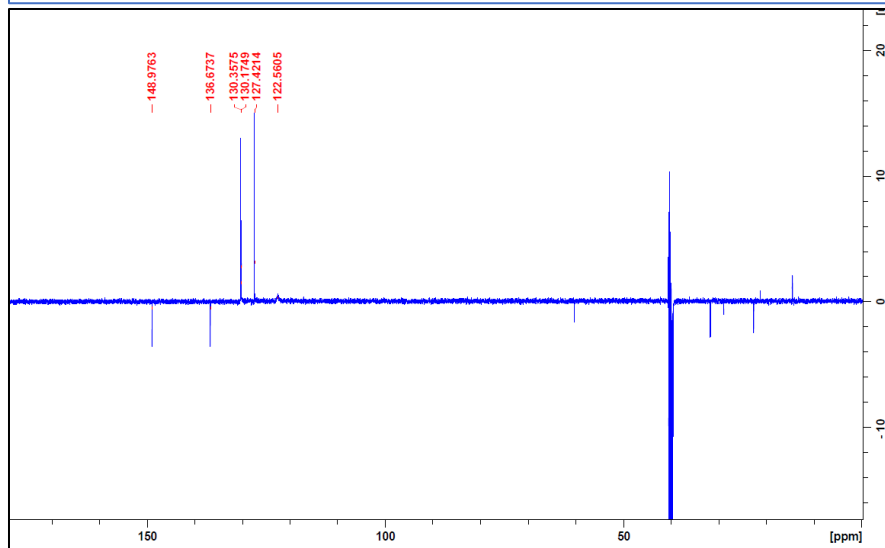
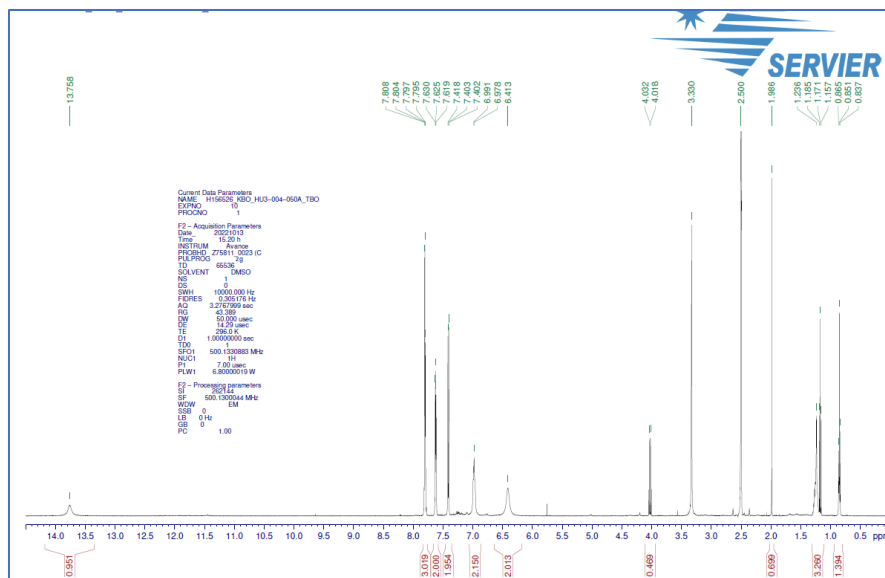
**Figure S35.** <sup>1</sup>H-NMR and HSQC and HRMS spectrum of **10p** 4,8-dibromo-12-[4-(trifluoromethyl)phenyl]-5*H*-thiopyrano[2,3-*b*:6,5-*b'*]diindole



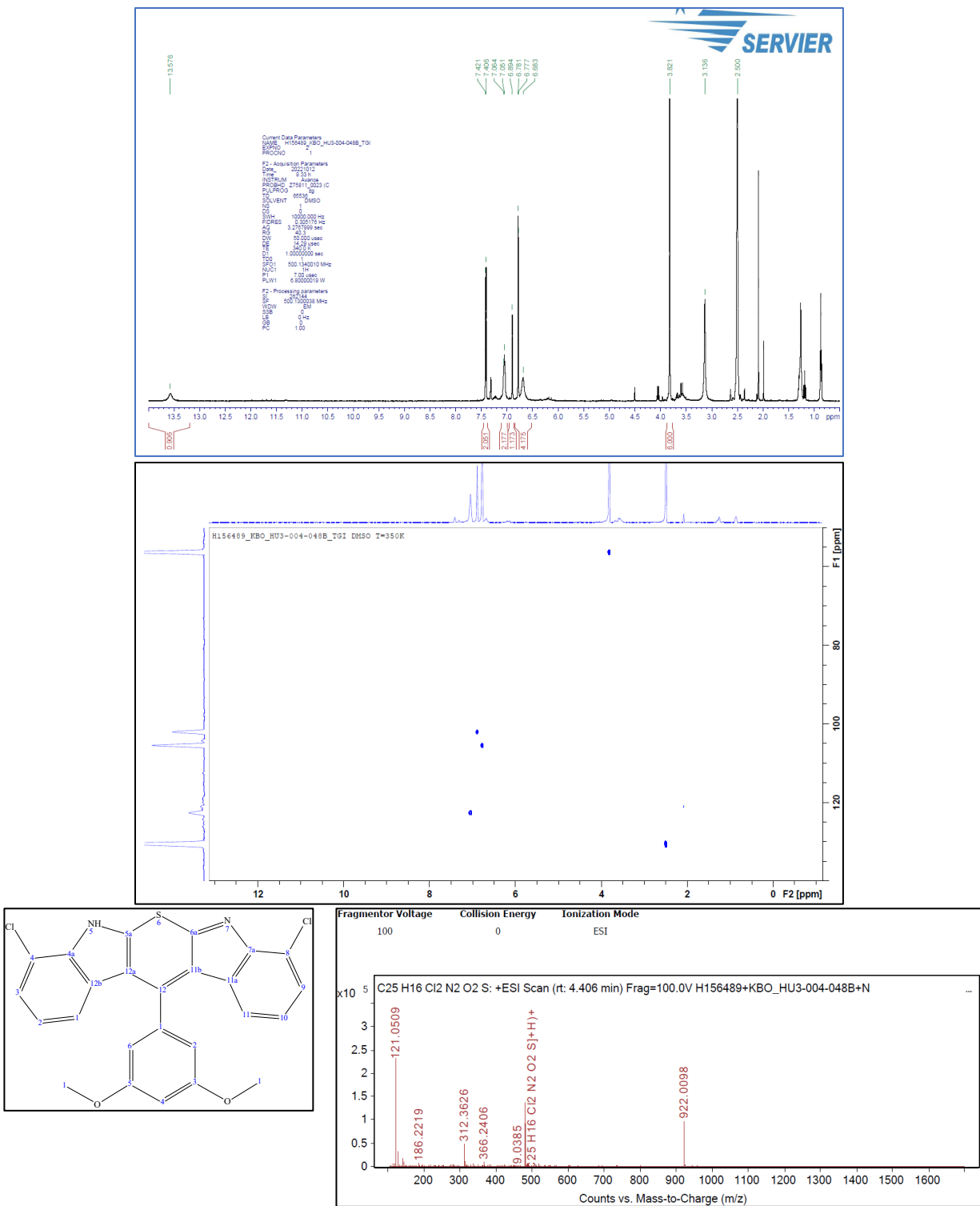
**Figure S36.** <sup>1</sup>H-NMR and HSQC and HRMS spectrum of **10q** 4,8-dibromo-12-phenyl-5*H*-thiopyrano[2,3-*b*:6,5-*b'*]diindole



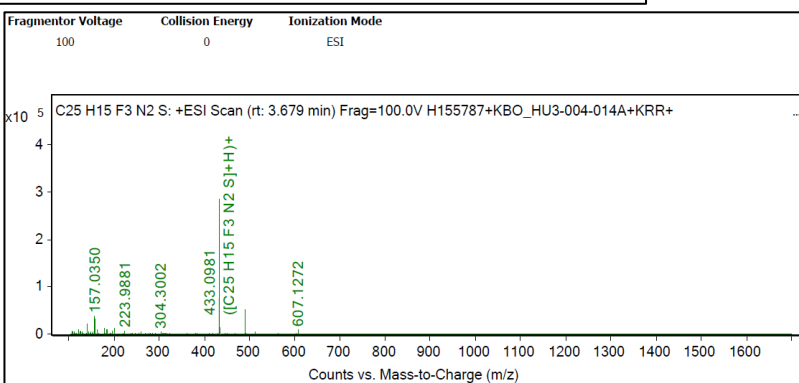
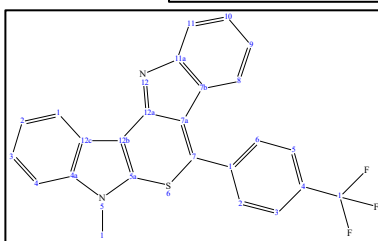
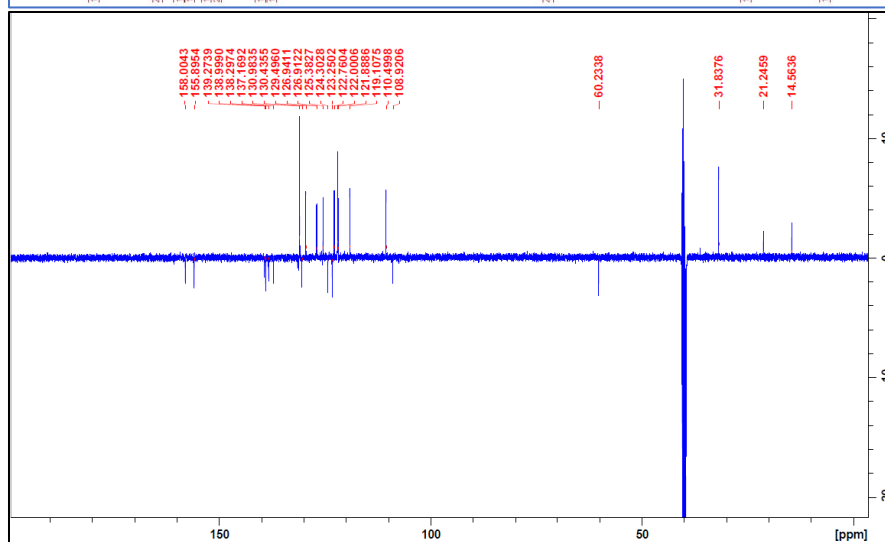
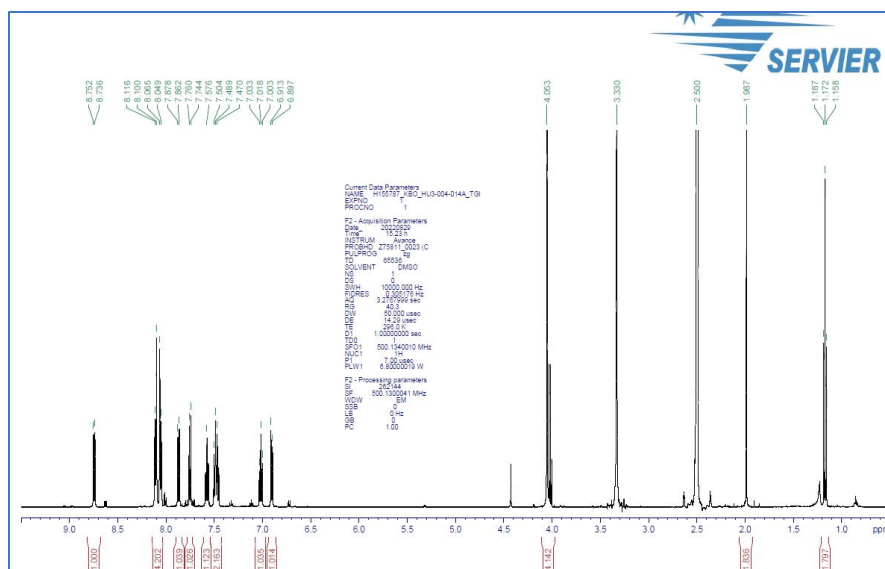
**Figure S37.** <sup>1</sup>H-NMR and HSQC and HRMS spectrum of **10r** 4,8-dibromo-12-(pyridin-4-yl)-5H-thiopyrano[2,3-b:6,5-b']diindole



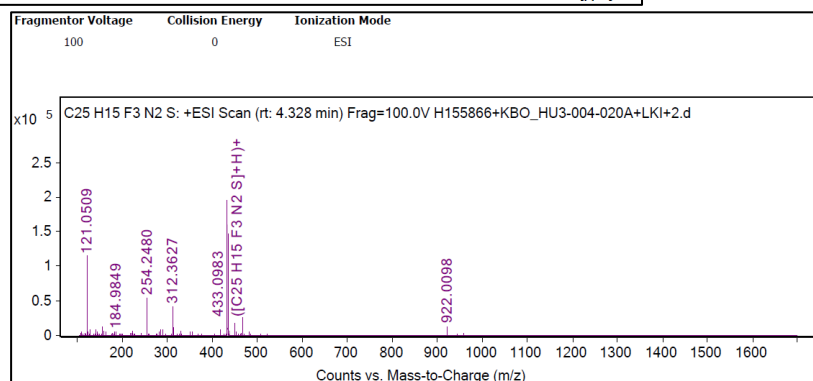
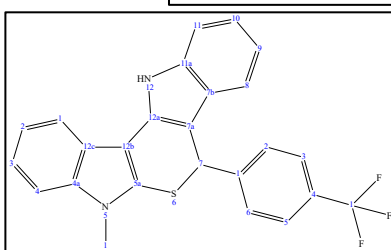
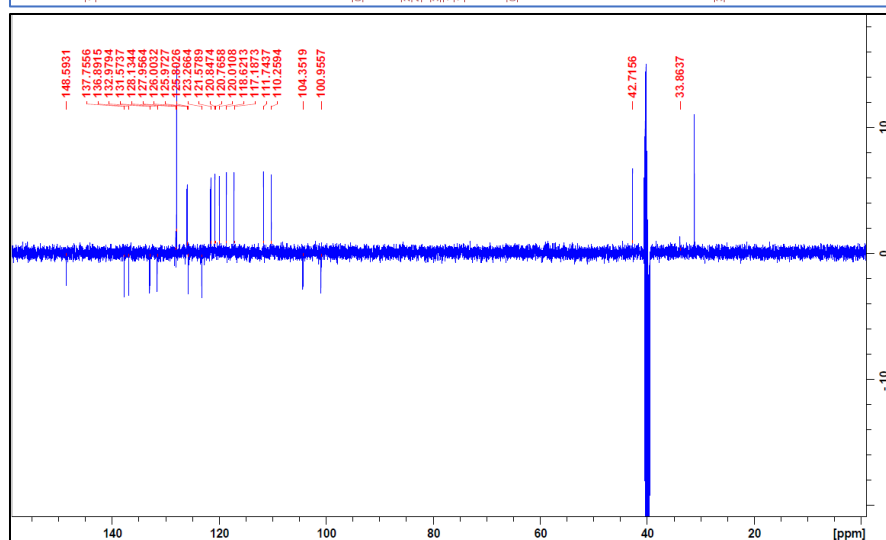
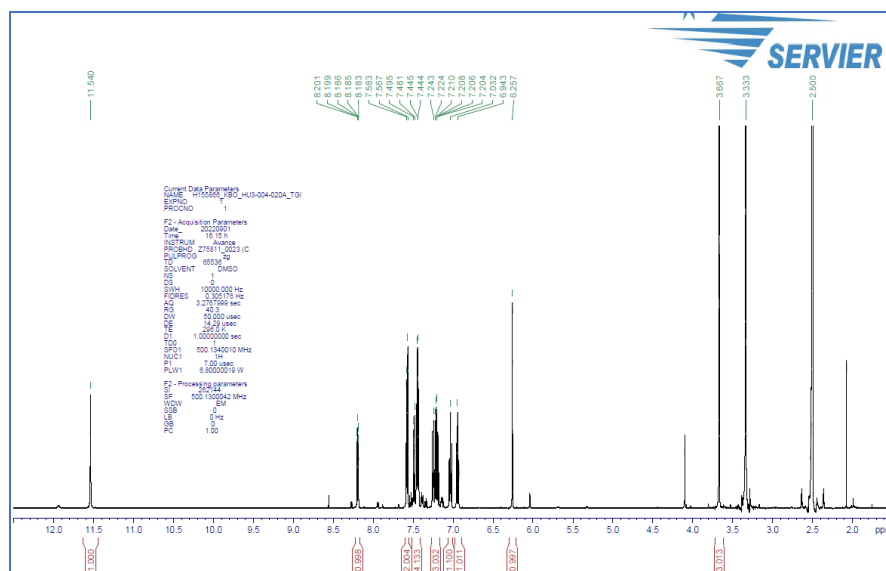
**Figure S38.**  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR and HRMS spectrum of **10s** 4,8-dichloro-12-phenyl-5H-thiopyrano[2,3-b:6,5-b']diindole



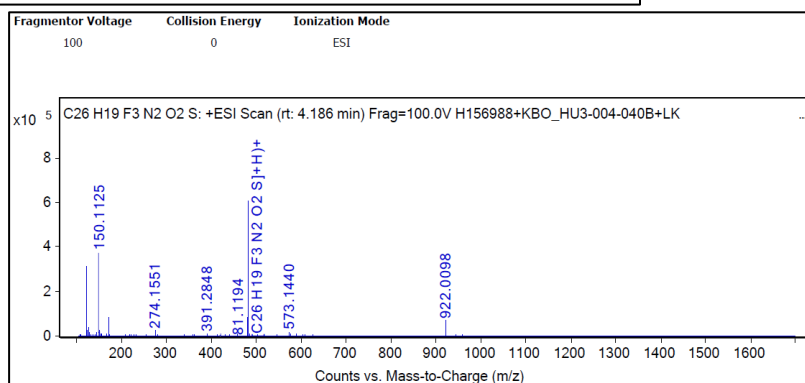
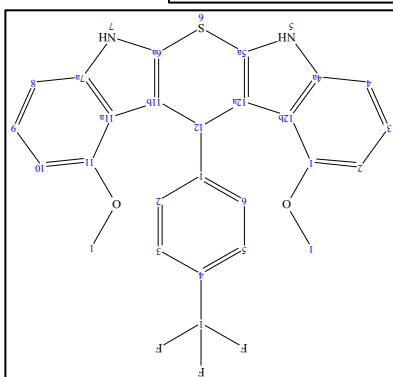
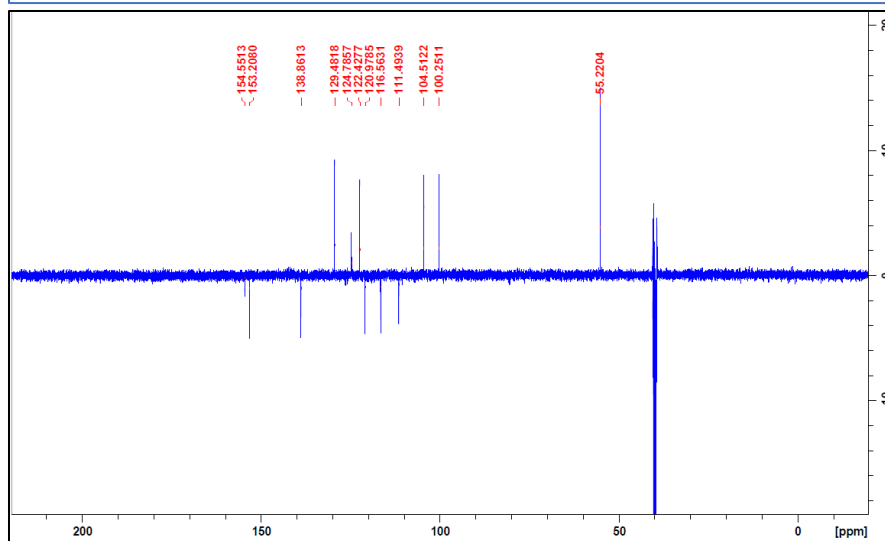
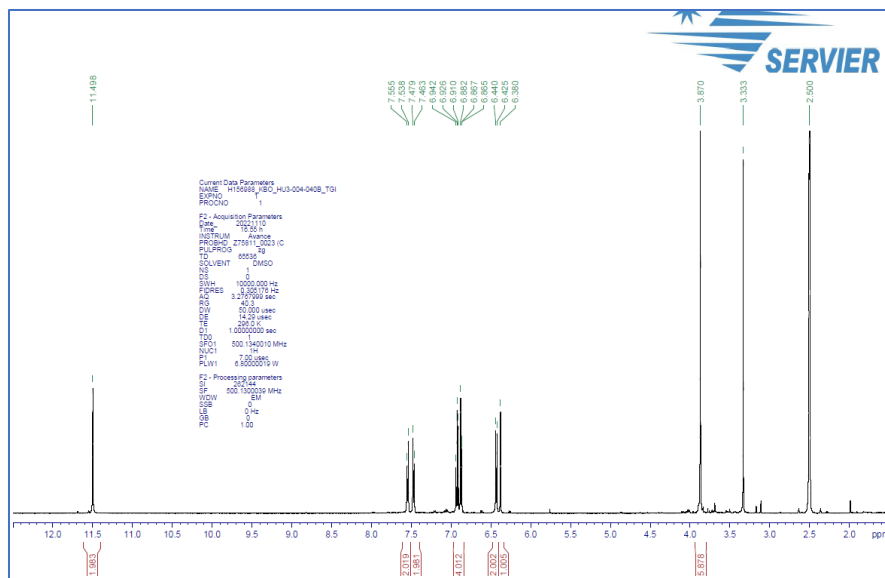
**Figure S39.**  $^1\text{H-NMR}$  and HSQC and HRMS spectrum of **10t** 4,8-dichloro-12-(3,5-dimethoxyphenyl)-5H-thiopyrano[2,3-*b*:6,5-*b'*]diindole



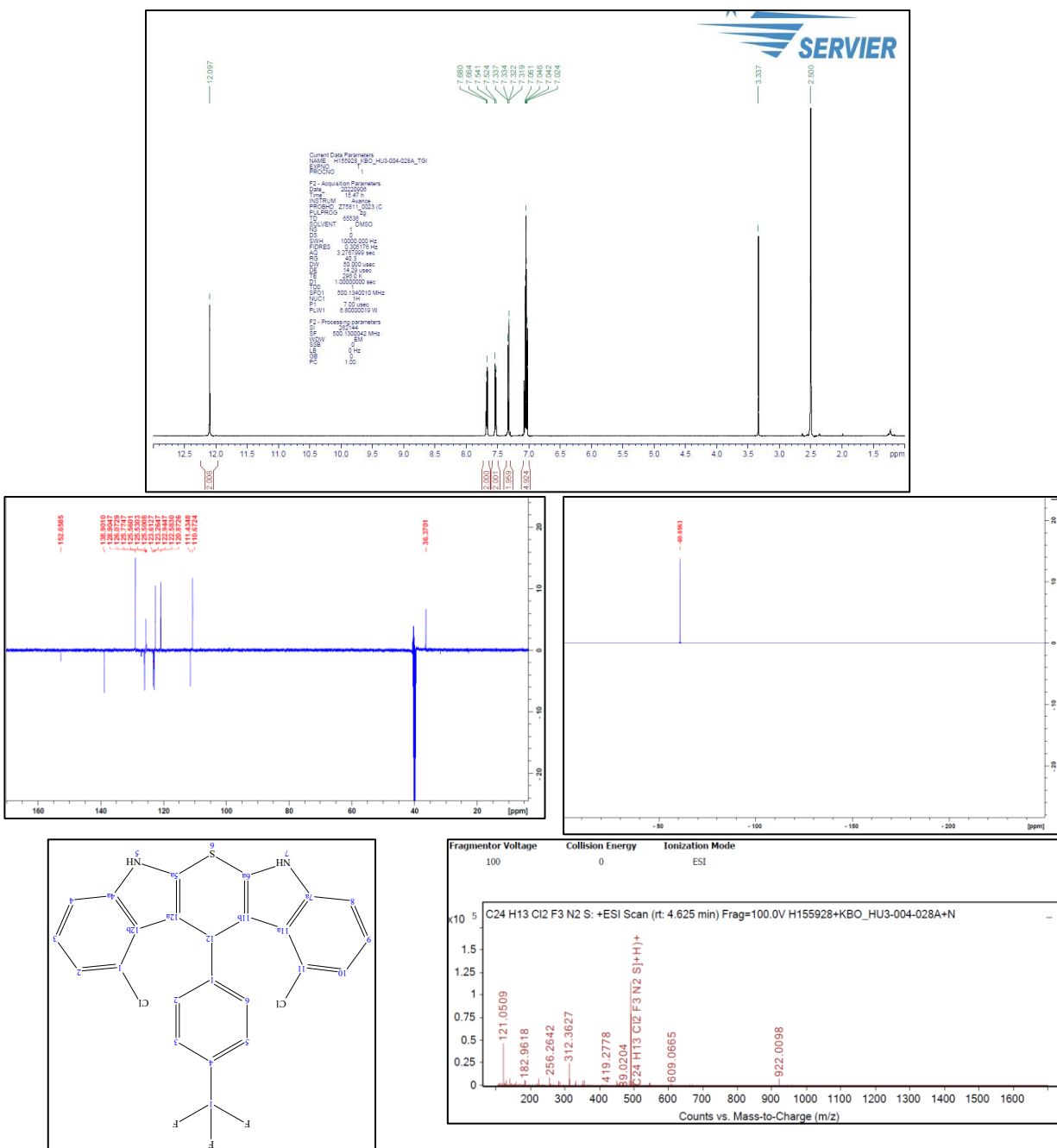
**Figure S40.**  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR and HRMS spectrum of **11** 5-methyl-7-[4-(trifluoromethyl)phenyl]-5H-thiopyrano[2,3-*b*:4,5-*b'*]-diindole



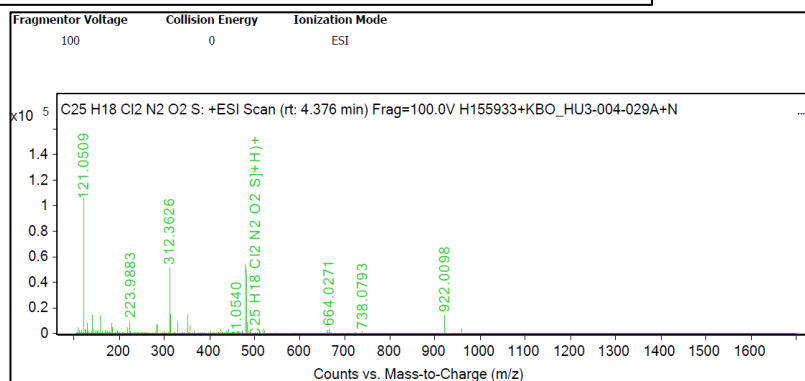
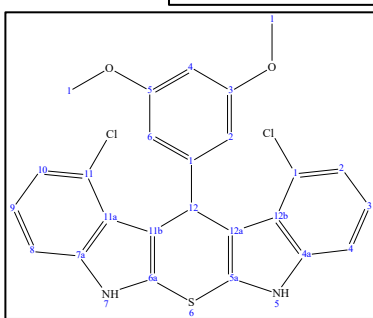
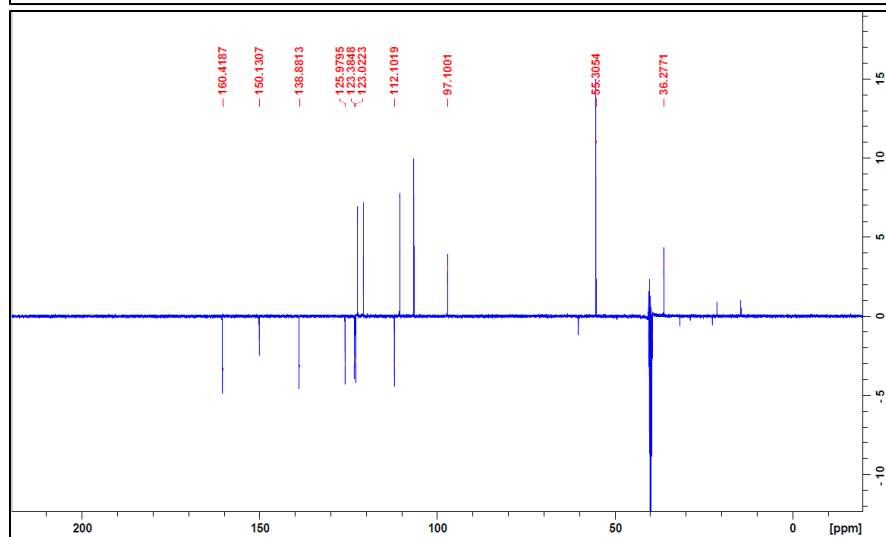
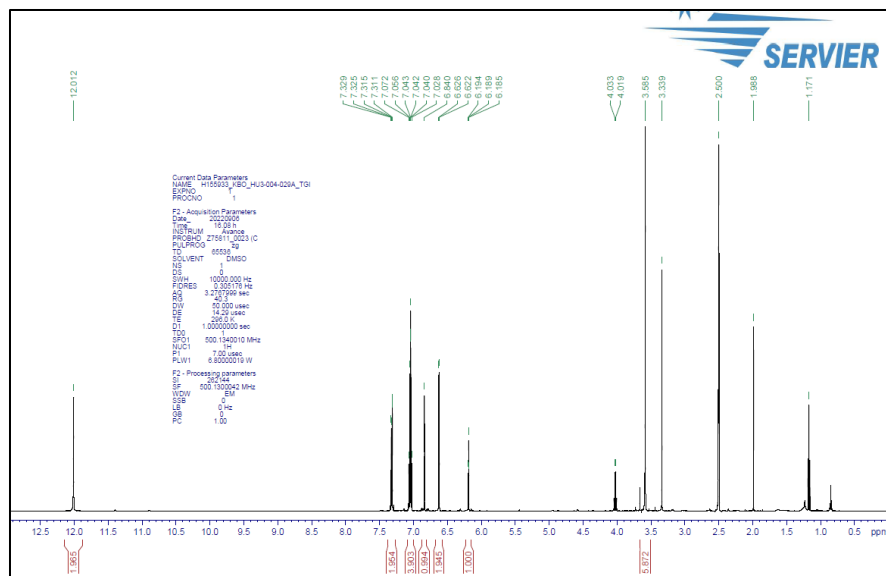
**Figure S41.** <sup>1</sup>H-NMR and <sup>13</sup>C-NMR and HRMS spectrum of **12** 5-methyl-7-[4-(trifluoromethyl)phenyl]-7,12-dihydro-5H-thiopyrano[2,3-b:4,5-b']diindole



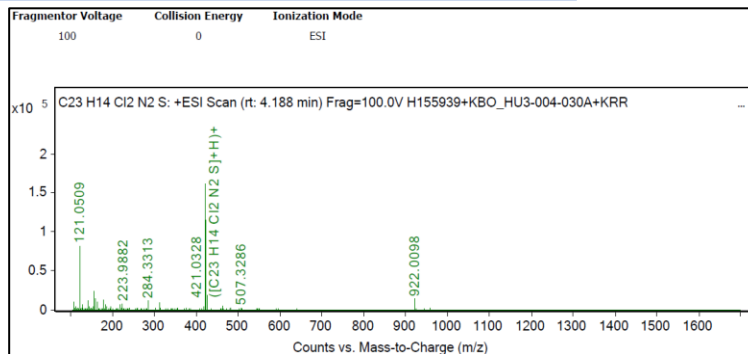
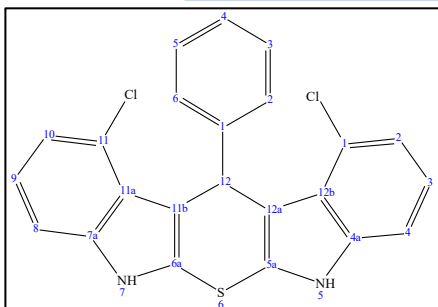
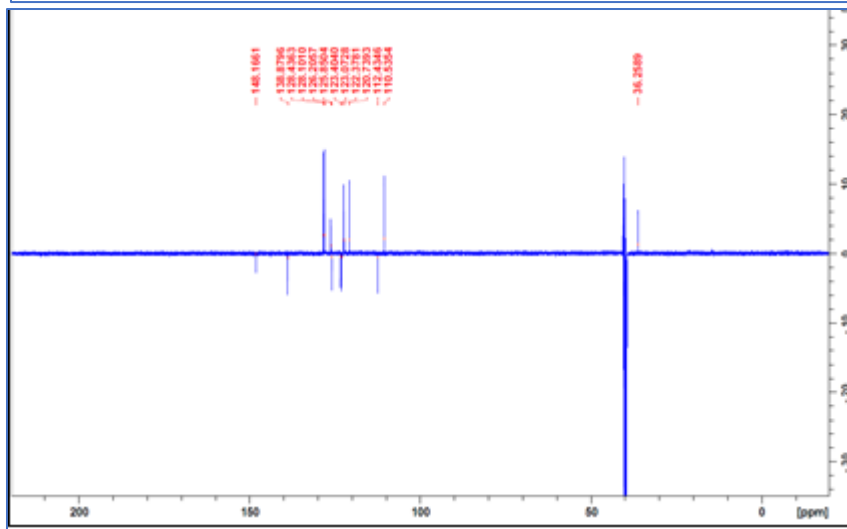
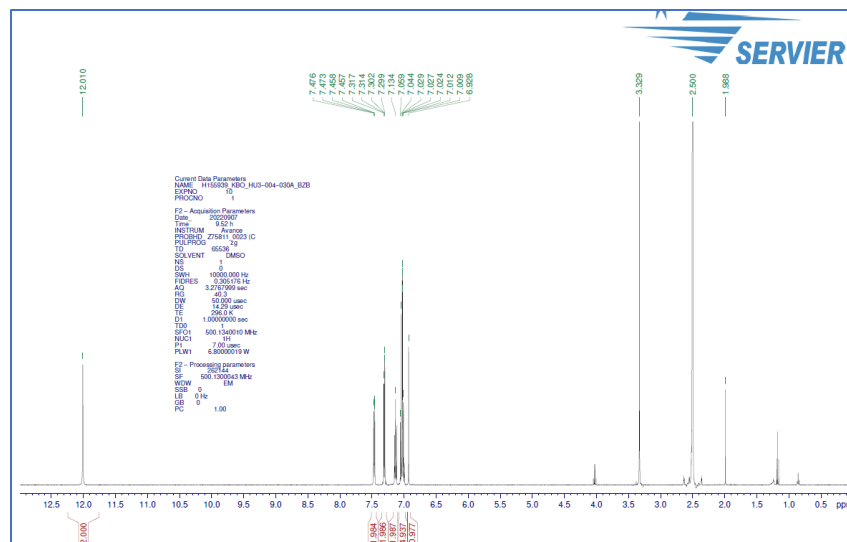
**Figure S42.**  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR and HRMS spectrum of **13a** 1,11-dimethoxy-12-[4-(trifluoromethyl)phenyl]-7,12-dihydro-5H-thiopyrano[2,3-b:6,5-b']diindole



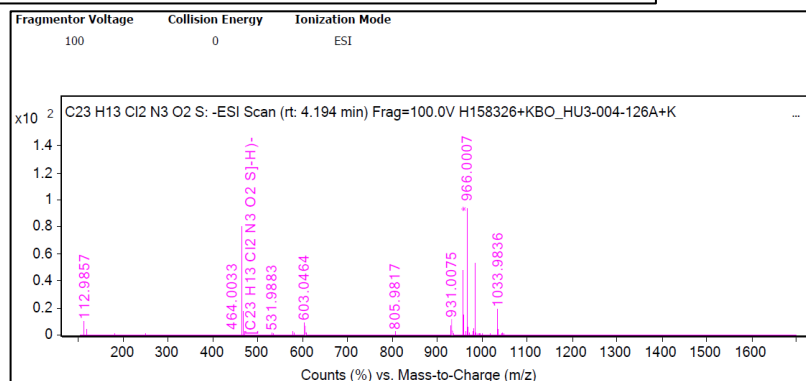
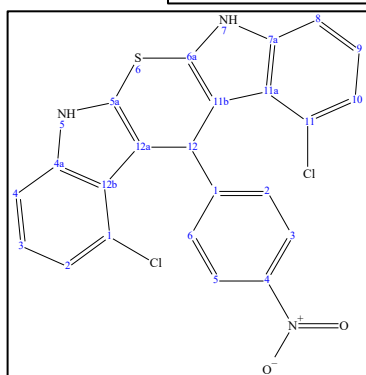
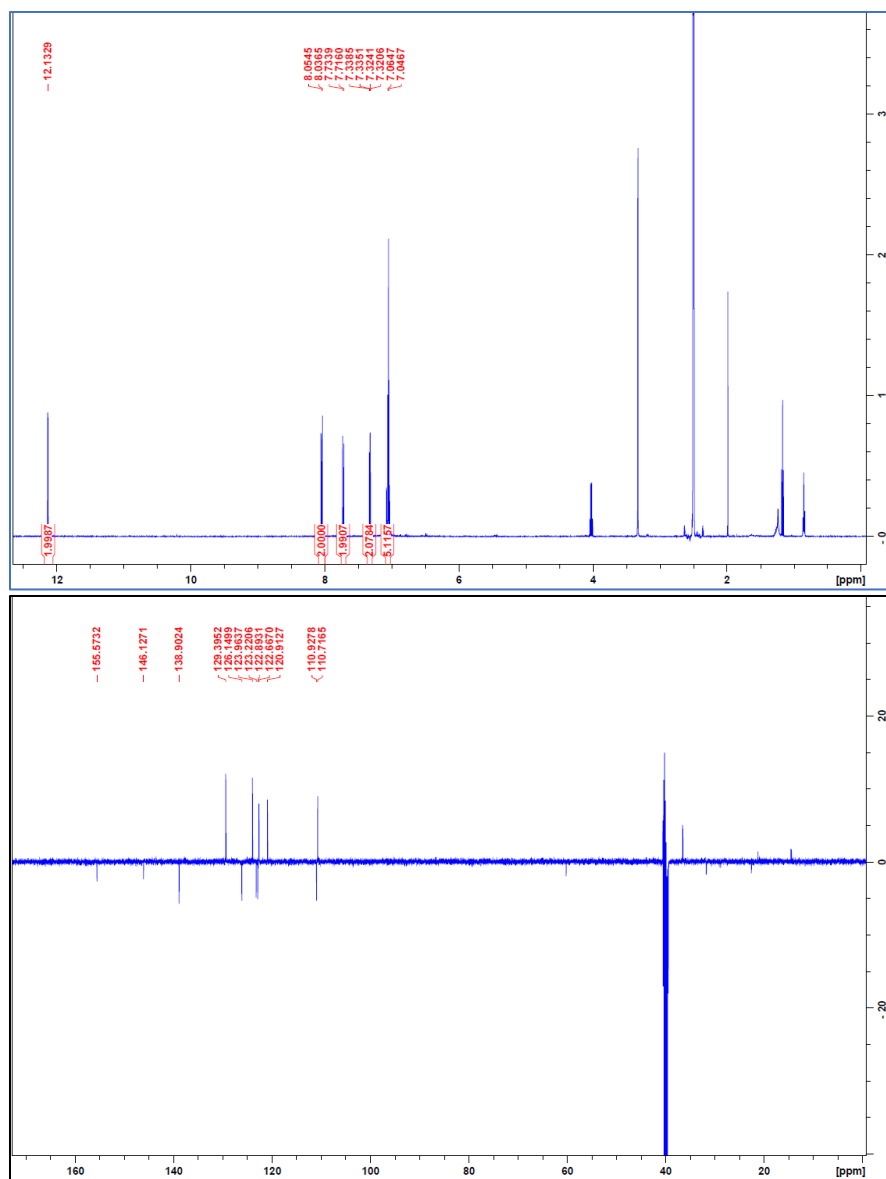
**Figure S43.**  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR and  $^{19}\text{F}$  and HRMS spectrum of **13b** 1,1-dichloro-12-[4-(trifluoromethyl)phenyl]-7,12-dihydro-5*H*-thiopyrano[2,3-*b*:6,5-*b'*]diindole



**Figure S44.**  $^1\text{H}$ -NMR and HSQC and HRMS spectrum of **13c** 1,11-dichloro-12-(3,5-dimethoxyphenyl)-7,12-dihydro-5H-thiopyrano[2,3-b:6,5-b']diindole

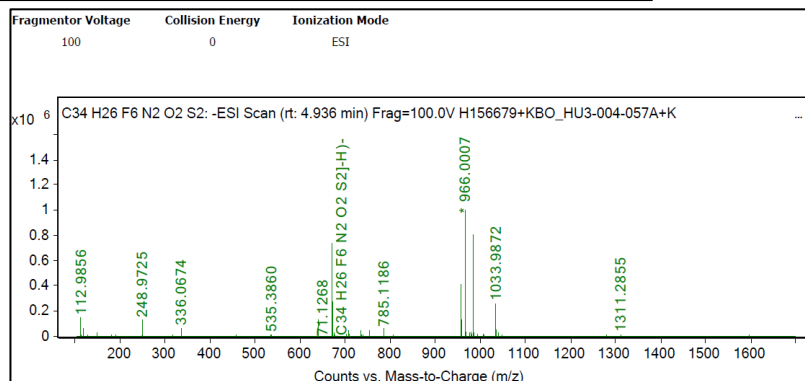
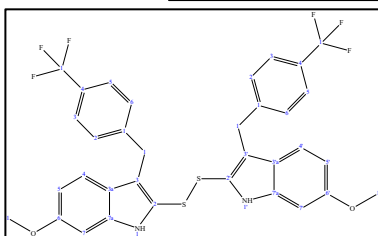
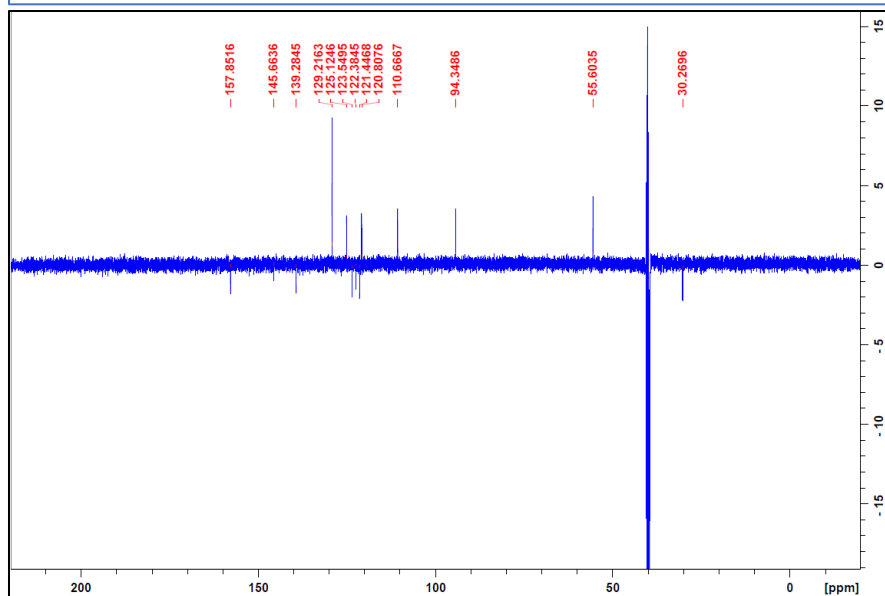
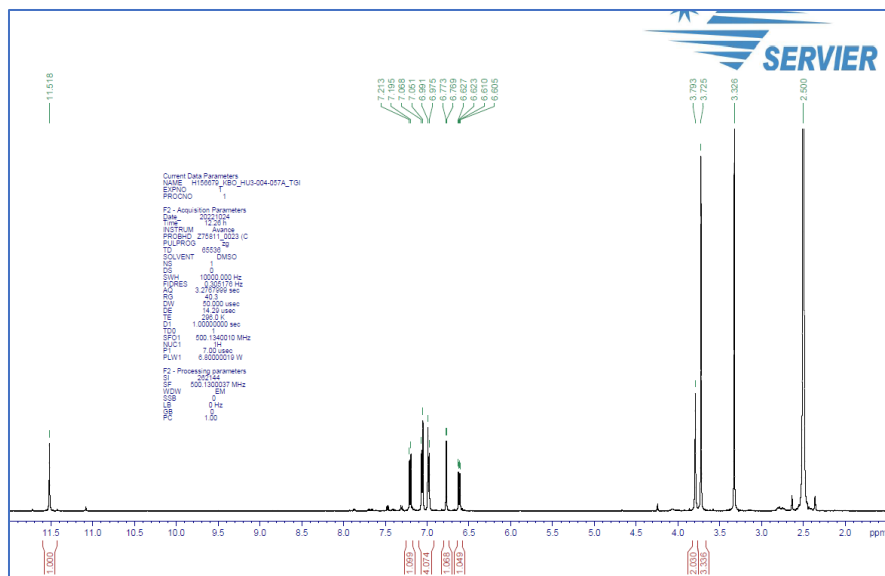


**Figure S45.**  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR and HRMS spectrum of **13d** 1,1-dichloro-12-phenyl-7,12-dihydro-5H-thiopyrano[2,3-*b*:6,5-*b'*]diindole

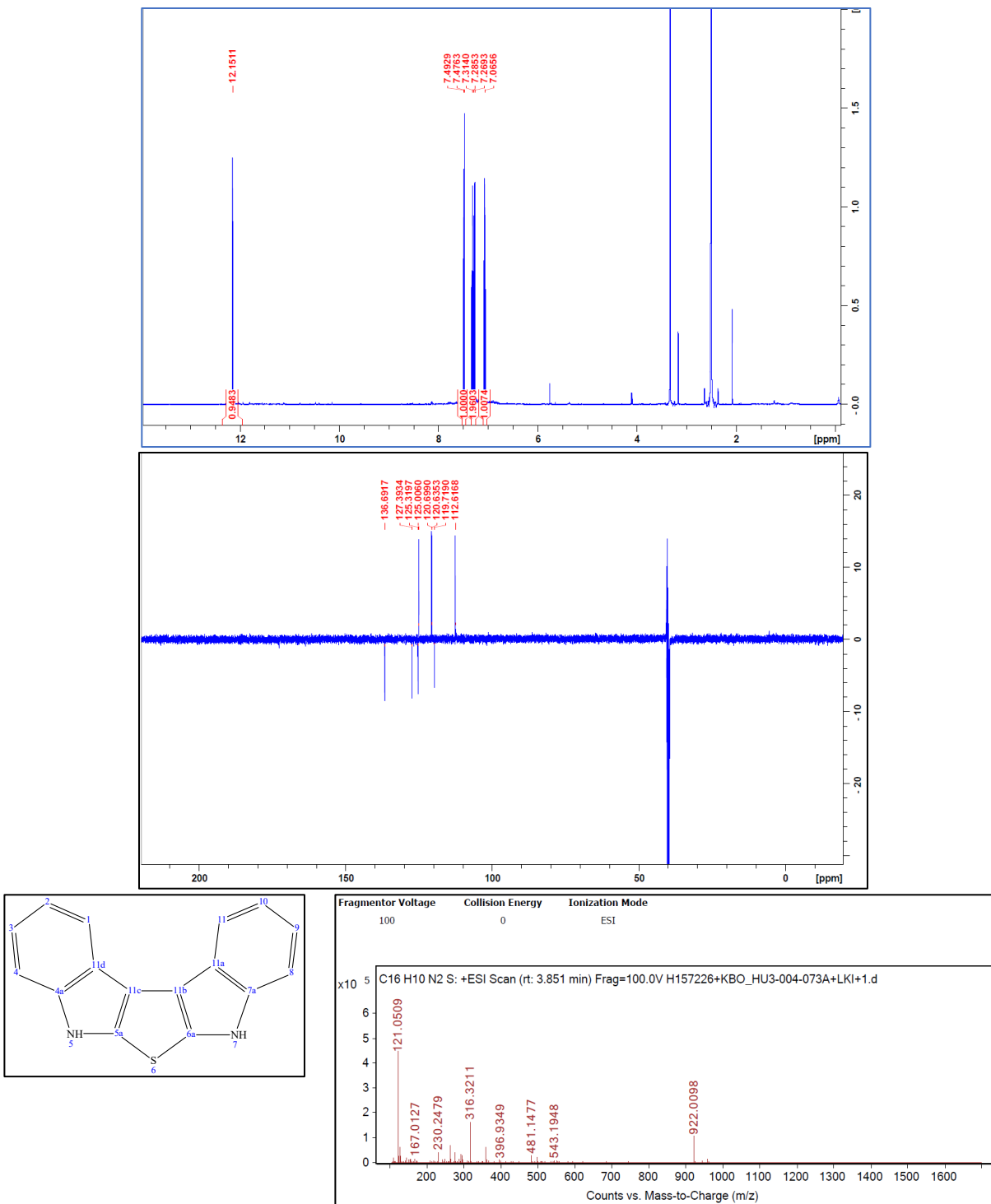


**Figure S46.** <sup>1</sup>H-NMR and <sup>13</sup>C-NMR and HRMS spectrum of **13e** 1,1-dichloro-12-(4-nitrophenyl)-7,12-dihydro-5H-thiopyrano[2,3-*b*:6,5-*b'*]indole

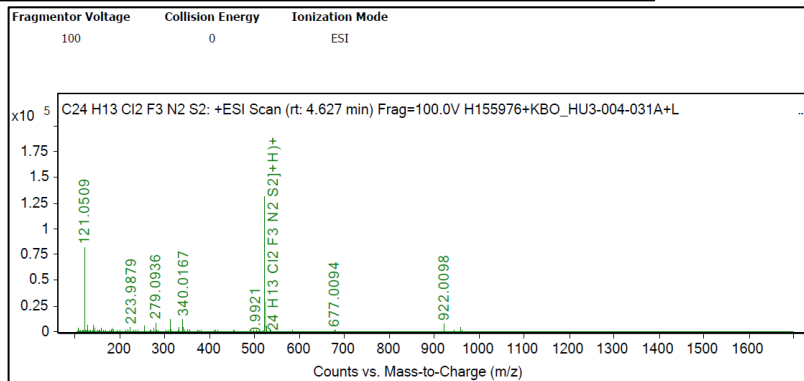
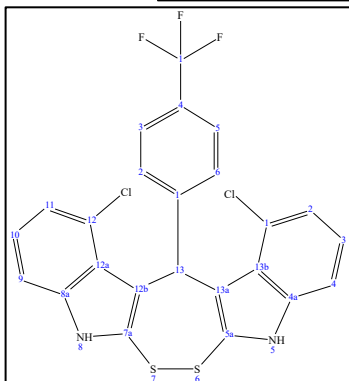
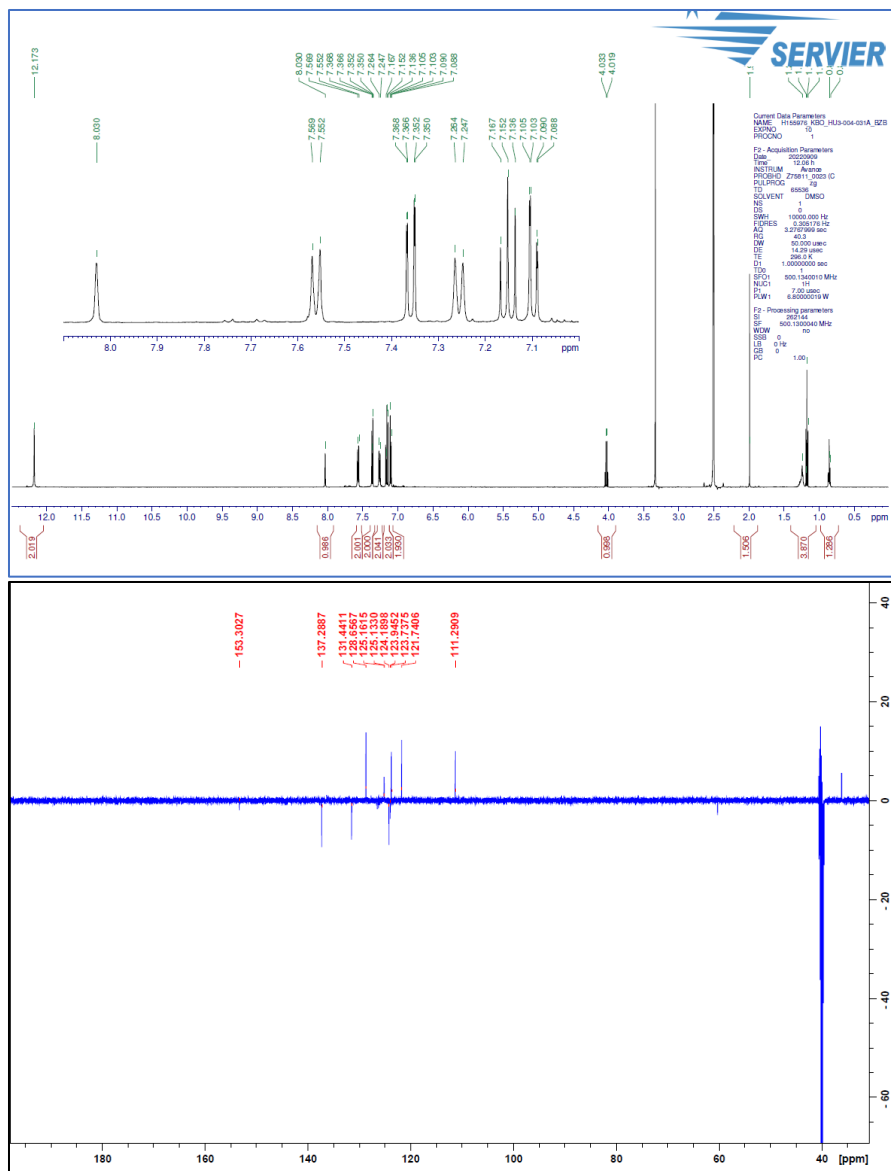




**Figure S48.**  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR and HRMS spectrum of **15** 2,2'-disulfaneylbis(6-methoxy-3-((trifluoromethyl)phenyl)methyl)-1*H*-indole)



**Figure S49.** <sup>1</sup>H-NMR and <sup>13</sup>C-NMR and HRMS spectrum of **17** 5,7-dihydrothieno[2,3-*b*:5,4-*b'*]diindole



**Figure S50.**  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR and HRMS spectrum of **19** 1,12-dichloro-13-[4-(trifluoromethyl)phenyl]-8,13-dihydro-5H-[1,2]dithiepine[3,4-*b*:7,6-*b'*]diindole