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Supporting Information

Whole-rainbow-color Organic Solid Fluorophores from Subtle Modification of Thiazolo[5,4-b]thieno[3,2-e]pyridines (TTPs)

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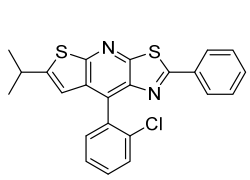
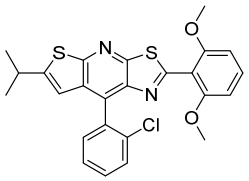
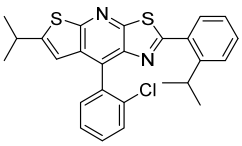
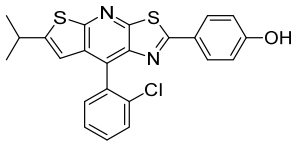
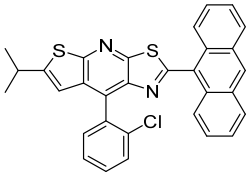
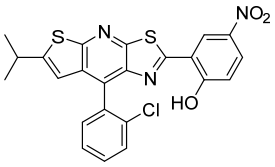
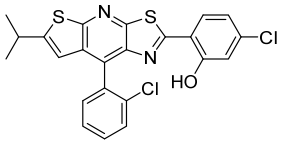
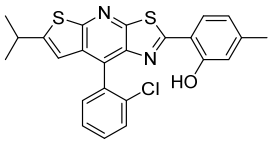
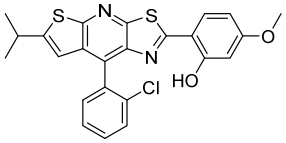
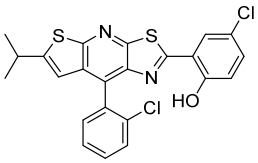
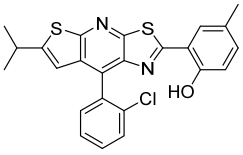
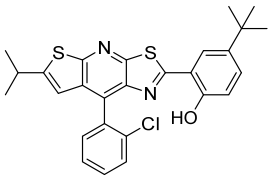
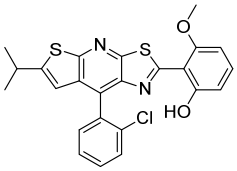
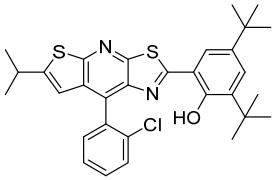
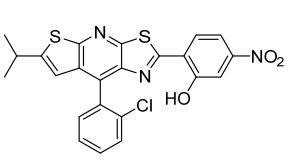
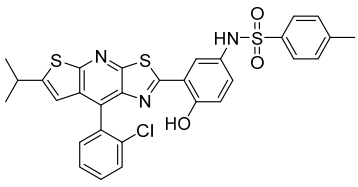
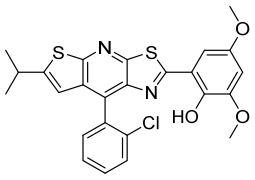
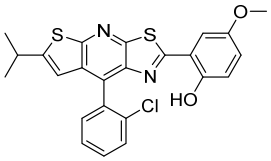
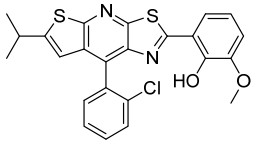
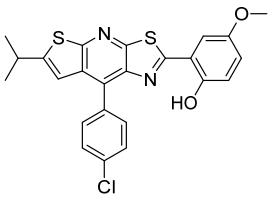
Experimental Procedures

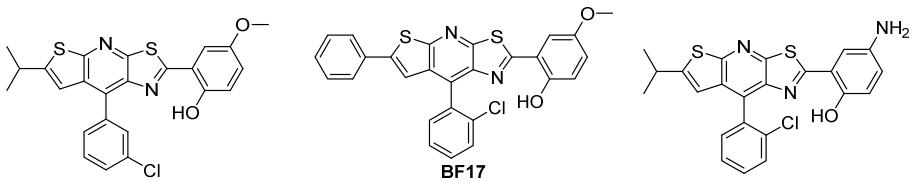
All starting materials and reagents were purchased from commercial suppliers and used directly without further purification. All solvents for UV and FL analyses were spectroscopic grade. Flash column chromatography was performed on silica gel (200-300 mesh). Thin-layer chromatography (TLC) was performed on precoated silica gel F-254 plates (0.25 mm, E. Merck). ^{1}H NMR and ^{13}C NMR spectra were recorded at r.t. on a Bruker AVANCE III 400 instrument with TMS as an internal reference. EI mass spectra were recorded on the Thermo DSQ mass spectrometer. HRMS were performed on a Thermo MAT95XP mass spectrometer. IR spectra were recorded on a Thermo Nicolet Avatar 330 FT-IR or a Bruker EQUINOX 55 FT-IR. Melting Point (m.p.) values were determined on a WRS-1B digital m.p. apparatus and were not calibrated.

The single crystals were grown from tetrahydrofuran and ethanol (**BF3**, **BF9** and **BF10**), or chloroform and hexane (**AF1**, **BF1, BF2, BF6, BF7** and **BF14**), or chloroform (**BF15**, **BF16** and **BF18**). Single-crystal X-ray diffraction data were collected at 293(2) K on an Oxford Germini S Ultra diffractometer or an Agilent SuperNova, Dual, Cu at zero, AtlasS2 diffractometer, with Cu-Kα radiation (λ=1.54178 Å).

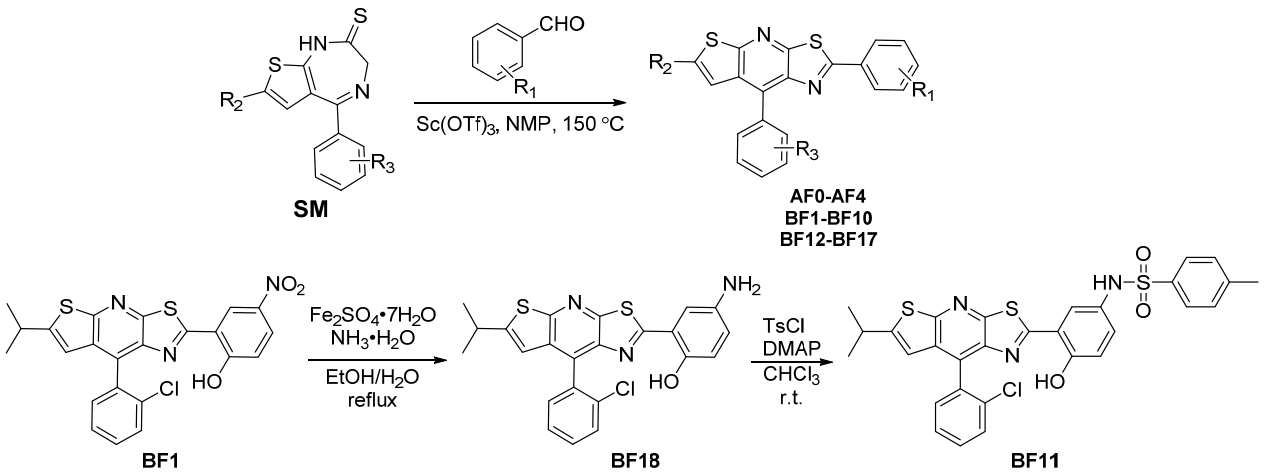
The UV spectra were obtained using a spectrometer (UV-3600 or UV-2700) from Shimadzu. The FL spectra and fluorescence lifetime were obtained using a spectrometer (FLS980) from Edinburgh Instruments. The absolute photoluminescence quantum yields were measured using Hamamatsu C9920-02G.

Table S1. Chemical structures of the target compounds.

 **AF0**	 **AF1**	 **AF2**	 **AF3**
 **AF4**	 **BF1**	 **BF2**	 **BF3**
 **BF4**	 **BF5**	 **BF6**	 **BF7**
 **BF8**	 **BF9**	 **BF10**	 **BF11**
 **BF12**	 **BF13**	 **BF14**	 **BF15**



Scheme S1. Synthesis of the target compounds.



The synthesis of the thiazolo[5,4-b]thieno[3,2-e]pyridines (TTPs) was outlined in Scheme S1. Compound **SM**, a key intermediate, was synthesized from the commercially available starting materials according to our previously reported protocol.[1, 2]

5-(3-chlorophenyl)-7-isopropyl-1,3-dihydro-2*H*-thieno[2,3-e][1,4]diazepine-2-thione (**SM1**)

Yellow solids (total yields: 35%); m.p.: 168-170 °C; MS (EI): m/z (%) = 333 (100) M^+, 319 (20), 125 (25). HRMS–EI: m/z M^+ calcd for $C_{16}H_{15}N_2ClS_2$: 334.0360; found: 334.0354. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (s, 1H, Ar*H*), 7.51 – 7.38 (m, 2H, Ar*H*), 7.36 – 7.27 (m, 1H, Ar*H*), 6.50 (s, 1H, Ar*H*), 4.84 (s, 2H, CH_2), 3.06 (hept, *J* = 7.0 Hz, 1H, C*H*), 1.28 (d, *J* = 6.8 Hz, 6H, 2CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.7, 166.1, 146.5, 139.8, 134.4, 130.6, 129.5, 129.4, 127.7, 121.3, 100.0, 64.4, 29.9, 24.3. IR (KBr): 3433, 3130, 2961, 2926, 2867, 1898, 1596, 1563, 1523, 1485, 1414, 1343, 1312, 1286, 1239, 1099, 1054, 990, 896, 876, 859, 835, 814, 787, 740, 712, 692, 660, 601 cm^{-1}

5-(4-chlorophenyl)-7-isopropyl-1,3-dihydro-2*H*-thieno[2,3-e][1,4]diazepine-2-thione (**SM2**)

Yellow solids (total yields: 32%); m.p.: 209-211 °C; MS (EI): m/z (%) = 333 (100) M^+, 149 (52), 69 (62), 55 (100). HRMS–EI: m/z M^+ calcd for $C_{16}H_{15}N_2ClS_2$: 334.0360; found: 334.0353. ^{1}H NMR (400 MHz, Chloroform-*d* and DMSO-d_6) δ 7.58 (d, *J* = 8.1 Hz, 2H, Ar*H*), 7.42 (d, *J* = 8.1 Hz, 2H, Ar*H*), 6.51 (s, 1H, Ar*H*), 4.69 (s, 2H CH_2), 3.13 – 3.05 (m, 1H, C*H*), 1.30 (d, *J* = 6.8 Hz, 6H, 2CH_3). ^{13}C NMR (101 MHz, $CDCl_3$ and DMSO-d_6) δ 200.5, 170.0, 150.2, 141.5, 141.0, 135.6, 133.3, 131.6, 125.9, 70.0, 34.5, 29.1. IR (KBr): 3432, 3122, 3096, 3034, 2964, 2952, 2832, 1591, 1556, 1518, 1480, 1399, 1350, 1312, 1287, 1234, 1187, 1166, 1090, 1051, 1030, 1014, 992, 847, 834, 806, 770, 740, 720, 618 cm^{-1}

General Procedure for synthesis of **AF1**, **AF2**, **AF4, BF1**-**BF10** and **BF12**-**BF17**: A 10 mL of vial was added with **SM** (0.3 mmol), $Sc(OTf)_3$ (1.5 mg, 0.003 mmol), corresponding aldehyde (0.6 mmol), NMP (2.0 mL) and sealed. The reaction was stirred in an oil bath preheated to 150 °C for 12 h. After cooled to room temperature, the reaction mixture was dilute with 120 mL EtOAc. The organic phase was washed with saturated aqueous NH_4Cl (30 mL × 3), water and brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by flash c.c. on silica gel to afford desired compound. [1]

8-(2-chlorophenyl)-2-(2,6-dimethoxyphenyl)-6-isopropylthiazolo[5,4-b]thieno[3,2-e]pyridine (**AF1**)

White solids (84 mg, 58%); m.p.: 121-122 °C; MS (EI): m/z (%) = 480 (46) M^+, 445 (100). HRMS–EI: m/z M^+ calcd for $C_{25}H_{21}O_2N_2ClS_2$: 480.0727; found: 480.0724. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.52 (m, 2H, Ar*H*), 7.47 – 7.33 (m, 3H, Ar*H*), 6.73 (s, 1H, Ar*H*), 6.63 (d, *J* = 8.5 Hz, 2H, Ar*H*), 3.80 (s, 6H, 2OCH_3), 3.24 (hept, *J* = 6.9 Hz, 1H, C*H*), 1.41 (d, *J* = 6.9 Hz, 6H, 2CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 158.9, 158.9, 157.0, 154.0, 142.1, 134.8, 134.3, 133.7, 132.0, 131.8, 131.0, 130.0, 129.8, 126.6, 115.4, 112.6, 104.4, 56.2, 31.3, 24.1, 24.0. IR (KBr): 3448, 2951, 1596, 1547, 1513, 1474, 1432, 1381, 1340, 1302, 1259, 1215, 1180, 1114, 1064, 1034, 952, 782, 737, 701 cm^{-1}

8-(2-chlorophenyl)-6-isopropyl-2-(2-isopropylphenyl)thiazolo[5,4-b]thieno[3,2-e]pyridine (**AF2)**

Pale yellow solids (45 mg, 32%); m.p.: 56-58 °C; MS (EI): m/z (%) = 462 (100) M^+, 447 (57), 429 (89), 144 (78). HRMS–EI: m/z M^+ calcd for $C_{26}H_{23}N_2ClS_2$: 462.0986; found: 462.0980. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.58 (m, 2H, Ar*H*), 7.55 – 7.40 (m, 5H, Ar*H*), 7.33 – 7.24 (m, 2H, Ar*H*), 6.80 (s, 1H, Ar*H*), 3.79 (hept, *J* = 6.8 Hz, 1H, C*H*), 3.27 (hept, *J* = 6.8 Hz, 1H, C*H*), 1.43 (d, *J* = 6.9 Hz, 6H, 2CH_3), 1.20 (dd, *J* = 9.4, 6.9 Hz, 6H, 2CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 159.3, 155.9, 154.6, 148.5, 143.0, 134.7, 134.6, 133.6, 132.3, 131.7, 131.3, 130.9, 130.5, 129.9, 129.8, 126.6, 125.8, 115.2, 31.3, 29.4, 24.1, 24.0, 24.0. IR (KBr): 3434, 3060, 3020,

2962, 2926, 2866, 1598, 1553, 1517, 1468, 1436, 1382, 1362, 1340, 1278, 1228, 1211, 1198, 1130, 1083, 1050, 1034, 956, 889, 870, 729, 801, 780, 754, 700, 679, 629, 593 cm^{-1}

2-(anthracen-9-yl)-8-(2-chlorophenyl)-6-isopropylthiazolo[5,4-b]thieno[3,2-e]pyridine (**AF4**)

Yellow solids (93 mg, 60%); m.p.: 194-196 °C; MS (EI): m/z (%) = 520 (100) M^+, 485 (60), 203 (32). HRMS–EI: m/z M^+ calcd for $C_{31}H_{21}N_2ClS_2$: 520.0829; found: 520.0826. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.60 (s, 1H, Ar*H*), 8.11 – 7.93 (m, 4H, Ar*H*), 7.63 – 7.36 (m, 8H, Ar*H*), 6.84 (s, 1H, Ar*H*), 3.37 – 3.24 (m, 1H, C*H*), 1.46 (d, *J* = 6.8 Hz, 6H, 2CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 159.8, 156.8, 155.0, 142.7, 135.1, 134.6, 133.6, 131.6, 131.6, 131.0, 130.7, 130.1, 130.1, 129.9, 128.5, 127.3, 126.9, 126.8, 125.5, 125.5, 115.3, 31.4, 24.2, 24.1. IR (KBr): 3445, 3057, 2956, 5927, 2868, 1552, 1514, 1468, 1439, 1405, 1384, 1366, 1331, 1301, 1278, 1214, 1179, 1159, 1125, 1096, 1064, 1048, 1017, 906, 891, 870, 842, 822, 800, 780, 749, 729, 698, 646, 626, 595, 531, 603 cm^{-1}

2-(8-(2-chlorophenyl)-6-isopropylthiazolo[5,4-b]thieno[3,2-e]pyridin-2-yl)-4-nitrophenol (**BF1**)

Yellow solids (50 mg, 35%), m.p.: 206-208 °C; MS (EI): m/z (%) = 481 (65) M^+, 466 (100), 446 (58). HRMS–EI: m/z M^+ calcd for $C_{23}H_{16}O_3N_3ClS_2$: 481.0316; found: 481.0312. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 13.09 (s, 1H, O*H*), 8.65 (d, *J* = 2.7 Hz, 1H, Ar*H*), 8.27 (dd, *J* = 9.2, 2.7 Hz, 1H, Ar*H*), 7.70 (d, *J* = 7.6 Hz, 1H, Ar*H*), 7.62 – 7.49 (m, 3H, Ar*H*), 7.12 (d, *J* = 9.1 Hz, 1H, Ar*H*), 3.34 – 3.22 (m, 1H, C*H*), 1.43 (d, *J* = 6.8 Hz, 6H, 2CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 163.1, 160.5, 156.0, 152.5, 140.1, 133.5, 133.3, 133.0, 131.7, 131.3, 130.6, 130.1, 127.8, 127.0, 124.5, 118.6, 116.5, 115.0, 31.2, 23.9, 23.9. IR (KBr): 3089, 2964, 1630, 1584, 1528, 1475, 1386, 1284, 1254, 1210, 1103, 1050, 989, 885, 828, 803, 744, 701, 637 cm^{-1}.

5-chloro-2-(8-(2-chlorophenyl)-6-isopropylthiazolo[5,4-b]thieno[3,2-e]pyridin-2-yl)phenol (**BF2**)

Pale yellow solids (55 mg, 35%), m.p.: 203-204 °C; MS (EI): m/z (%) = 470 (42) M^+, 455 (58), 210 (100). HRMS–EI: m/z M^+ calcd for $C_{23}H_{16}ON_2ClS_2$: 470.0076; found: 470.0079. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.66 (m, 1H, Ar*H*), 7.62 (d, *J* = 8.4 Hz, 1H, Ar*H*), 7.58 – 7.47 (m, 3H, Ar*H*), 7.03 (s, 1H, Ar*H*), 6.96 (d, *J* = 8.4 Hz, 1H, Ar*H*), 6.80 (s, 1H, Ar*H*), 3.34 – 3.21 (m, 1H, C*H*), 1.43 (d, *J* = 6.7 Hz, 6H, 2CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 159.9, 158.9, 155.6, 152.7, 140.6, 138.7, 133.8, 133.3, 133.2, 131.6, 131.4, 130.5, 130.3, 129.3, 127.0, 120.2, 118.0, 115.5, 115.2, 31.4, 24.0, 24.0. IR (KBr): 3425, 3057, 2964, 2928, 2870, 1619, 1575, 1546, 1518, 1472, 1370, 1318, 1281, 1248, 1212, 1078, 1050, 1034, 966, 855, 830, 790, 759, 738, 712, 697, 626, 614, 595, 483 cm^{-1}.

2-(8-(2-chlorophenyl)-6-isopropylthiazolo[5,4-b]thieno[3,2-e]pyridin-2-yl)-5-methylphenol (**BF3**)

Pale yellow solids (50mg, 37%); m.p.: 197-199 °C; MS (EI): m/z (%) = 450 (100) M^+, 435 (93), 415 (65). HRMS–EI: m/z M^+ calcd for $C_{24}H_{19}ON_2ClS_2$: 450.0622; found: 450.0624. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 – 7.65 (m, 1H, Ar*H*), 7.59 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.56 – 7.45 (m, 3H, Ar*H*), 6.86 – 6.77 (m, 3H, Ar*H*), 3.33 – 3.20 (m, 1H, C*H*), 2.38 (s, 3H, CH_3), 1.42 (d, *J* = 6.8 Hz, 6H, 2CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 159.3, 158.1, 155.2, 153.0, 144.4, 140.9, 134.0, 133.3, 132.9, 131.5, 131.4, 130.4, 130.2, 128.4, 126.9, 120.9, 118.1, 115.2, 114.4, 31.3, 24.1, 24.0, 21.8. IR (KBr): 3426. 3022. 2964. 2928. 2870, 1630, 1578, 1550, 1516, 1475, 1380, 1310, 1281, 1250, 1224, 1210, 1163, 1139, 1068, 1051, 1035, 973, 927, 869, 839, 799, 751, 733, 706, 629, 594, 573, 507, 465, 443 cm^{-1}

2-(8-(2-chlorophenyl)-6-isopropylthiazolo[5,4-b]thieno[3,2-e]pyridin-2-yl)-5-methoxyphenol (**BF4**)

Pale yellow solids (40 mg, 29%); m.p.: 175-176 °C; MS (EI): m/z (%) = 466 (100) M^+, 451 (82), 431 (52). HRMS–EI: m/z M^+ calcd for $C_{24}H_{19}O_2N_2ClS_2$: 466.0571; found: 466.0573. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.63 (m, 1H, Ar*H*), 7.58 – 7.46 (m, 4H, Ar*H*), 6.79 (s, 1H, Ar*H*), 6.57 – 6.46 (m, 2H, Ar*H*), 3.83 (s, 3H, OCH_3), 3.33 – 3.16 (m, 1H, C*H*), 1.41 (d, *J* = 6.9 Hz, 6H, 2CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 163.8, 160.3, 158.9, 155.1, 152.9, 140.9, 134.1, 133.3, 132.4, 131.5, 131.3, 130.3, 130.2, 129.9, 126.9, 115.2, 110.5, 107.7, 101.4, 55.5, 31.3, 24.1, 24.0. IR (KBr): 3397, 2964, 1720, 1632, 1523, 1478, 1380, 1342, 1281, 1253, 1207, 1167, 1145, 1070, 1051, 1033, 971, 943, 860, 826, 800, 754, 737, 707, 645, 628, 590, 564, 462 cm^{-1}.

4-chloro-2-(8-(2-chlorophenyl)-6-isopropylthiazolo[5,4-b]thieno[3,2-e]pyridin-2-yl)phenol (**BF5**)

Pale yellow solids (50 mg, 35%); m.p.: 172-173 °C; MS (EI): m/z (%) = 470 (100) M^+, 455 (90), 435 (58). HRMS–EI: m/z M^+ calcd for $C_{23}H_{16}ON_2Cl_2S_2$: 470.0076; found: 470.0073. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 – 7.64 (m, 2H, Ar*H*), 7.58 – 7.45 (m, 3H, Ar*H*), 7.36 – 7.28 (m, 1H, Ar*H*), 7.01 – 6.94 (m, 1H, Ar*H*), 6.81 (s, 1H, Ar*H*), 3.34 – 3.20 (m, 1H, C*H*), 1.43 (d, *J* = 6.6 Hz, 6H, 2CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 160.1, 156.8, 155.7, 152.8, 140.7, 133.8, 133.4, 133.3, 132.9, 131.6, 131.4, 130.5, 130.3, 127.6, 127.0, 124.3, 119.5, 117.7, 115.2, 31.4, 24.1, 24.0. IR (KBr): 3440 , 3058, 2960, 2926, 2866, 1619, 1575, 1545, 1517, 1467, 1370, 1337, 1311, 1275, 1247, 1207, 1181, 1128, 1094, 1067, 1045, 1001, 979, 829, 839, 820, 802, 775, 748, 699, 643, 623, 592, 550, 530, 450 cm^{-1}

2-(8-(2-chlorophenyl)-6-isopropylthiazolo[5,4-b]thieno[3,2-e]pyridin-2-yl)-4-methylphenol (**BF6**)

Pale yellow solids (40mg, 30%); m.p.: 193-194 °C; MS (EI): m/z (%) = 450 (100) M^+, 435 (75), 415 (52). HRMS–EI: m/z M^+ calcd for $C_{24}H_{19}ON_2ClS_2$: 450.0622; found: 450.0625. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.62 (m, 1H, Ar*H*), 7.57 – 7.46 (m, 4H, Ar*H*), 7.20 (d, *J* = 8.4 Hz, 1H, Ar*H*), 6.93 (d, *J* = 8.4 Hz, 1H, Ar*H*), 6.80 (s, 1H, Ar*H*), 3.34 – 3.18 (m, 1H, C*H*), 2.38 (s, 3H, CH_3), 1.42 (d, *J* = 6.8 Hz, 6H, 2CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 159.5, 156.1, 155.3, 153.1, 141.0, 134.2, 134.0, 133.3, 133.0, 131.5, 131.5, 130.4, 130.2, 128.9, 128.5, 126.9, 117.7, 116.4, 115.2, 31.4, 24.1, 24.0, 20.5. IR (KBr): 3447, 2930, 2924, 2873, 1626, 1591, 1550, 1522, 1500, 1471, 1425, 1382, 1315, 1284, 1253, 1219, 1182, 1134, 1118, 1093, 1069, 1050, 1062, 979, 984, 873, 824, 803, 770, 755, 737, 702, 626, 594, 538, 455 cm^{-1}

4-(tert-butyl)-2-(8-(2-chlorophenyl)-6-isopropylthiazolo[5,4-b]thieno[3,2-e]pyridin-2-yl)phenol (**BF7**)

Yellow solids (45mg, 30%); m.p.: 161-162 °C; MS (EI): m/z (%) = 492 (32) M^+, 477 (100). HRMS–EI: m/z M^+ calcd for $C_{27}H_{25}ON_2ClS_2$: 492.1091; found: 492.1089. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.64 (m, 2H, Ar*H*), 7.56 – 7.48 (m, 3H, Ar*H*), 7.47 – 7.42 (m, 1H, Ar*H*), 6.98 (d, *J* = 8.7 Hz, 1H, Ar*H*), 6.81 (s, 1H, Ar*H*), 3.32 – 3.22 (m, 1H, C*H*), 1.42 (d, *J* = 6.8 Hz, 6H, 2CH_3), 1.39 (s, 9H, 3CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 159.5, 156.0, 155.3, 153.0, 142.5, 141.0, 134.0, 133.3, 133.0, 131.5, 130.9, 130.4, 130.2, 126.9, 124.7, 117.6, 116.0, 115.2, 34.2, 31.4, 31.4, 24.1, 24.0. IR (KBr): 3057, 2956, 2868, 1624, 1588, 1550, 1500, 1468, 1438, 1381, 1363, 1316, 1282, 1260, 1211, 1193, 1116, 1052, 1038, 1026, 986, 872, 826, 802, 754, 738, 700, 649, 628, 594, 570, 505, 447 cm^{-1}

2-(8-(2-chlorophenyl)-6-isopropylthiazolo[5,4-b]thieno[3,2-e]pyridin-2-yl)-3-methoxyphenol (**BF8**)

Yelllow solids (45 mg, 32%), m.p.: 250-251 °C; MS (EI): m/z (%) = 466 (100) M^+, 431 (55). HRMS–EI: m/z M^+ calcd for $C_{24}H_{16}O_2N_2ClS_2$: 466.0571; found: 466.0567. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 – 7.65 (m, 1H, Ar*H*), 7.60 – 7.46 (m, 3H, Ar*H*), 7.32 – 7.26 (m, 1H, Ar*H*), 6.81 (s, 1H, Ar*H*), 6.71 – 6.64 (m, 1H, Ar*H*), 6.56 – 6.49 (m, 1H, Ar*H*), 4.08 (s, 3H, OCH_3), 3.32 – 3.21 (m, 1H, C*H*), 1.42 (d, *J* = 6.8 Hz, 6H, 2CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6, 160.5, 159.4, 158.2, 154.9, 153.9, 138.2, 134.1, 133.3, 133.0, 132.2, 131.5, 131.2, 130.4, 130.2, 127.0, 115.1, 110.6, 107.4, 101.1, 55.9, 31.4, 24.1, 24.0. IR (KBr): 3055, 3004, 2968, 2930, 2869, 2836, 2736, 1623, 1588, 1565, 1520, 1497, 1427, 1382, 1367, 1322, 1283, 1245, 1212, 1183, 1129, 1092, 1069, 1051, 1033, 973, 938, 875, 844, 824, 807, 780, 766, 739, 736, 697, 628, 592, 527, 451 cm^{-1}.

2,4-di-tert-butyl-6-(8-(2-chlorophenyl)-6-isopropylthiazolo[5,4-b]thieno[3,2-e]pyridin-2-yl)phenol (**BF9**)

Yellow solids (45 mg, 40%); m.p.234-235 °C; MS (EI): m/z (%) = 548 (78) M^+, 533 (100), 505 (38). HRMS–EI: m/z M^+ calcd for $C_{31}H_{33}ON_2ClS_2$: 548.1721; found: 548.1717. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.28 (s, 1H, O*H*), 7.74 – 7.65 (m, 1H, Ar*H*), 7.60 – 7.44 (m, 5H, Ar*H*), 6.79 (s, 1H, Ar*H*), 3.33 – 3.20 (m, 1H, C*H*), 1.49 – 1.36 (m, 24H, 8CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 159.2, 155.4, 155.0, 153.3, 141.2, 141.1, 137.7, 134.1, 133.3, 132.9, 131.6, 131.4, 130.3, 130.2, 128.2, 126.9, 123.0, 115.9, 115.3, 35.3, 34.3, 31.4, 31.3, 29.5, 24.1, 24.0. IR (KBr): 3431, 2958, 2868, 1612, 1549, 1466, 1391, 1361, 1315, 1280, 1249, 1203, 1178, 2053, 867, 824, 756, 703 cm^{-1}.

2-(8-(2-chlorophenyl)-6-isopropylthiazolo[5,4-b]thieno[3,2-e]pyridin-2-yl)-5-nitrophenol (**BF10**)

Yellow solids (50 mg, 35%), m.p.: 247-248 °C; MS (EI): m/z (%) = 481 (75) M^+, 466 (100), 178 (82). HRMS–EI: m/z M^+ calcd for $C_{23}H_{16}O_3N_3ClS_2$: 481.0316; found: 481.0319. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 12.45 (s, 1H, O*H*), 7.85 – 7.75 (m, 3H, Ar*H*), 7.70 (d, *J* = 7.6 Hz, 1H, Ar*H*), 7.61 – 7.49 (m, 3H, Ar*H*), 6.83 (s, 1H, Ar*H*), 3.33 – 3.22 (m, 1H, C*H*), 1.43 (d, *J* = 6.8 Hz, 6H, 2CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 160.9, 158.6, 156.3, 152.7, 150.0, 140.5, 133.9, 133.5, 133.2, 131.9, 131.4, 130.7, 130.3, 129.1, 127.1, 121.6, 115.1, 114.2, 113.3, 31.4, 24.0, 24.0. IR (KBr): 3062, 2966, 2930, 2870, 1617, 1524, 1471, 1386, 1346, 1283, 1258, 1214, 1182, 1136, 1075, 1050, 1035, 975, 931, 877, 846, 812, 781, 755, 736, 711, 625, 595, 499, 449 cm^{-1}.

2-(8-(2-chlorophenyl)-6-isopropylthiazolo[5,4-b]thieno[3,2-e]pyridin-2-yl)-4,6-dimethoxyphenol (**BF12**)

Yellow solids (45mg, 30%); m.p.: 190-191 °C; MS (EI): m/z (%) = 496 (88) M^+, 481 (78), 139 (82), 55 (100). HRMS–EI: m/z M^+ calcd for $C_{25}H_{21}O_3N_2ClS_2$: 496.0677; found: 496.0675. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.61 (m, 1H, Ar*H*), 7.52 – 7.44 (m, 3H, Ar*H*), 6.79 (s, 1H, Ar*H*), 6.73 – 6.70 (m, 1H, Ar*H*), 6.66 – 6.63 (m, 1H, Ar*H*), 3.91 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 3.31 – 3.22 (m, 1H, C*H*), 1.42 (d, *J* = 6.8 Hz, 6H, 2CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 159.6, 155.3, 153.0, 152.5, 149.8, 143.3, 140.9, 133.8, 133.2, 131.6, 131.3, 130.4, 130.3, 127.0, 115.5, 115.2, 104.0, 100.9, 56.1, 55.9, 31.3, 24.1, 24.0. IR (KBr): 3433, 2956, 1619, 1550, 1051, 1461, 1417, 1344, 1315, 1277, 1203, 1163, 1128, 1105, 1057, 1020, 830, 758, 480 cm^{-1}

2-(8-(2-chlorophenyl)-6-isopropylthiazolo[5,4-b]thieno[3,2-e]pyridin-2-yl)-4-methoxyphenol (**BF13**)

Yellow solids (70 mg, 50%), m.p.: 171-173 °C; MS (EI): m/z (%) = 466 (54) M^+, 451 (100). HRMS–EI: m/z M^+ calcd for $C_{24}H_{19}O_2N_2ClS_2$: 466.0571; found: 466.0569. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 7.4 Hz, 1H, Ar*H*), 7.56 – 7.46 (m, 3H, Ar*H*), 7.16 – 7.12 (m, 1H, Ar*H*), 7.02 – 6.93 (m, 2H, Ar*H*), 6.80 (s, 1H, Ar*H*), 3.85 (s, 3H, OCH_3), 3.31 – 3.20 (m, 1H, C*H*), 1.41 (d, *J* = 6.8 Hz, 6H, 2CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 159.6, 155.4, 153.0, 152.5, 141.0, 133.9, 133.3, 133.1, 131.5, 131.5, 130.4, 130.2, 126.9, 120.6, 118.8, 116.4, 115.2, 111.7, 56.0, 31.3, 24.1, 24.0. IR (KBr): 3057, 2957, 2834, 1596, 1566, 1546, 1517, 1497, 1467, 1439, 1385, 1337, 1316, 1277, 1284, 1209, 1176, 1132, 1039, 1004, 989, 877, 842, 824, 803, 788, 774, 737, 700, 677, 628, 592, 546, 452 cm^{-1}.

2-(8-(2-chlorophenyl)-6-isopropylthiazolo[5,4-b]thieno[3,2-e]pyridin-2-yl)-6-methoxyphenol (**BF14**)

Yelllow solids (35 mg, 25%), m.p.: 198-199 °C; MS (EI): m/z (%) = 466 (78) M^+, 55 (100). HRMS–EI: m/z M^+ calcd for $C_{24}H_{19}O_2N_2ClS_2$: 466.0571; found: 466.0568. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.61 (m, 1H, Ar*H*), 7.53 – 7.44 (m, 3H, Ar*H*), 7.36 – 7.31 (m, 1H, Ar*H*), 7.02 – 6.91 (m, 2H, Ar*H*), 6.79 (s, 1H, Ar*H*), 3.94 (s, 3H, OCH_3), 3.31 – 3.22 (m, 1H, C*H*), 1.42 (d, *J* = 6.9 Hz, 6H, 2CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 159.7, 155.4, 153.0, 148.9, 148.4, 140.8, 133.8, 133.2, 133.2, 131.5, 131.3, 130.4, 130.3, 127.0, 120.0, 119.3, 116.7, 115.2, 114.0, 56.1, 31.4, 24.1, 24.0. IR (KBr): 2963, 2930, 2867, 2833, 1622, 1587, 1550, 1523, 1502, 1456, 1428, 1338, 1313, 1282, 1250, 1185, 1122, 1093, 1068, 1048, 1005, 876, 834, 815, 798, 755, 732, 707, 628, 592, 445 cm^{-1}.

2-(8-(4-chlorophenyl)-6-isopropylthiazolo[5,4-b]thieno[3,2-e]pyridin-2-yl)-4-methoxyphenol (**BF15**)

Yelllow solids (56 mg, 40%), m.p.: 206-207 °C; MS (EI): m/z (%) = 466 (60) M^+, 451 (100). HRMS–EI: m/z M^+ calcd for $C_{24}H_{19}O_2N_2ClS_2$: 466.0571; found: 466.0570. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 – 7.70 (m, 2H, Ar*H*), 7.64 – 7.59 (m, 2H, Ar*H*), 7.15 (s, 1H, Ar*H*), 7.09 – 6.97 (m, 3H, Ar*H*), 3.88 (s, 3H, OCH_3), 3.34 – 3.23 (m, 1H, C*H*), 1.43 (d, *J* = 6.8 Hz, 6H, 2CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 160.1, 155.5, 153.4, 152.6, 152.4, 140.3, 135.3, 134.4, 133.4, 131.1, 130.6, 129.1, 120.6, 118.8, 116.3, 114.8, 111.7, 56.0, 31.4, 24.0. IR (KBr): 3424, 3059, 2961, 2832, 1590, 1542, 1488, 1387, 1365, 1318, 1279, 1220, 1197, 1175, 1085, 1045, 1013, 987, 873, 852, 836, 819, 796, 767, 734, 698, 632, 614, 597, 549, 516, 492, 473 cm^{-1}.

2-(8-(3-chlorophenyl)-6-isopropylthiazolo[5,4-b]thieno[3,2-e]pyridin-2-yl)-4-methoxyphenol (**BF16**)

Yellow solids (56mg, 40%), m.p.: 177-179 °C; MS (EI): m/z (%) = 466 (63) M^+, 451 (100), 365 (36). HRMS–EI: m/z M^+ calcd for $C_{24}H_{19}O_2N_2ClS_2$: 466.0571; found: 466.0570. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 11.76 (s, 1H, O*H*), 7.76 (s, 1H, Ar*H*), 7.69 – 7.64 (m, 1H, Ar*H*), 7.61 – 7.51 (m, 2H, Ar*H*), 7.15 (s, 1H, Ar*H*), 7.08 (s, 1H, Ar*H*), 7.05 – 6.97 (m, 2H, Ar*H*), 3.88 (s, 3H, OCH_3), 3.36 – 3.20 (m, 1H, C*H*), 1.44 (d, *J* = 6.9 Hz, 6H, 2CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 160.1, 155.7, 153.4, 152.5, 152.5, 140.4, 136.8, 134.7, 134.0, 130.6, 130.0, 129.7, 129.2, 128.0, 120.6, 118.9, 116.3, 114.7, 111.7, 56.0, 31.4, 24.1. IR (KBr): 3424, 2965, 2835, 1594, 1545, 1495, 1472, 1387, 1367, 1332, 1313, 1280, 1218, 1179, 1111, 1079, 1039, 988, 884, 864, 838, 789, 766, 731, 707, 690, 675, 634, 597, 556 cm^{-1}.

2-(8-(2-chlorophenyl)-6-phenylthiazolo[5,4-b]thieno[3,2-e]pyridin-2-yl)-4-methoxyphenol (**BF17**)

Yellow solids (8 mg, 5%); m.p.: 260-262 °C; MS (EI): m/z (%) = 500 (68) M^+, 485 (100), 393 (30). HRMS–EI: m/z M^+ calcd for $C_{27}H_{17}O_2N_2ClS_2$: 500.0414; found: 500.0419. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 – 7.68 (m, 3H, Ar*H*), 7.62 – 7.51 (m, 3H, Ar*H*), 7.49 – 7.39 (m, 3H, Ar*H*), 7.33 (s, 1H, Ar*H*), 7.17 (s, 1H, Ar*H*), 7.07 – 6.94 (m, 2H, Ar*H*), 3.88 (s, 3H, OCH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7, 159.8, 153.9, 152.6, 145.1, 141.4, 133.8, 133.7, 133.5, 133.3, 132.4, 131.5, 130.6, 130.3, 129.2, 129.1, 127.0, 126.6,

120.9, 118.9, 116.3, 116.1, 111.7, 56.1. IR (KBr): 3452, 2925, 1797, 1632, 1586, 1542, 1499, 1466, 1381, 1334, 1281, 1193, 1044, 985, 877, 832, 808, 784, 748, 703, 634, 579 cm^{-1}

4-amino-2-(8-(2-chlorophenyl)-6-isopropylthiazolo[5,4-b]thieno[3,2-e]pyridin-2-yl)phenol (**BF18**)

A solution of **BF1** (145 mg 0.3 mmol) and EtOH/H_2O (1/1, 30mL) was heated to reflux under nitrogen atmosphere, and a saturated iron sulfate heptahydrate solution (1.7 g, 6 mmol) were added followed by the addition of aqueous ammonia (1.5 mL). The resulting mixture was kept at reflux until completation of the reaction.The mixture was cooled to room temperature and extracted with CH_2Cl_2 and water. The organic solvent was washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by flash c.c. on silica gel to afford desired compound as yellow solids (60 mg, 44%), m.p.: 255-256 °C; MS (EI): m/z (%) = 451 (100) M^+, 436 (35), 218 (45), 207 (50). HRMS–EI: m/z M^+ calcd for $C_{23}H_{18}ON_3ClS_2$: 451.0574; found: 451.0570. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 11.55 (s, 1H, O*H*), 7.68 – 7.63 (m, 1H, Ar*H*), 7.54 – 7.45 (m, 3H, Ar*H*), 7.06 (s, 1H, Ar*H*), 6.89 – 6.77 (m, 3H, Ar*H*), 3.50 – 3.19 (m, 1H, C*H*), 1.41 (d, *J* = 6.8 Hz, 6H, 2CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 159.5, 155.3, 153.1, 151.8, 141.1, 138.1, 133.9, 133.3, 133.1, 131.5, 130.4, 130.2, 126.9, 122.2, 118.7, 116.6, 115.2, 114.0, 31.3, 24.1, 24.0. IR (KBr): 3428, 3338, 2964, 1635, 1592, 1548, 1499, 1471, 1285, 1259, 1200, 1051, 884, 831, 754, 736, 705, 630, 546 cm^{-1}.

N-(3-(8-(2-chlorophenyl)-6-isopropylthiazolo[5,4-b]thieno[3,2-e]pyridin-2-yl)-4-hydroxyphenyl)-4-methylbenzenesulfonamide (**BF11**)

To a 25 mL three neck round flask was added **BF18** (90 mg, 0.2 mmol), p-tosyl chloride (42 mg, 0.22 mmol), 4-dimethylaminopyridine (26 mg, 0.22 mmol), dichloromethane and a magnetic stir bar under nitrogen atmosphere. The reaction mixture was stirred at r.t. over night. After completation of the reaction, the mixture was quenched with water and 30 mL CH_2Cl_2 was added. The organic solvent was washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by flash c.c. on silica gel to afford desired compound as yellow solids (36 mg, 30%). m.p.: 131-133 °C; MS (EI): m/z (%) = 605 (6) M^+, 450 (92), 91 (100). HRMS–EI: m/z M^+ calcd for $C_{30}H_{24}O_3N_3ClS_3$: 605.0663; found: 605.0665. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 12.02 (s, 1H, O*H*), 7.71 – 7.63 (m, 3H, Ar*H*), 7.54 – 7.46 (m, 3H, Ar*H*), 7.39 – 7.35 (m, 1H, Ar*H*), 7.29 – 7.27 (m, 1H, Ar*H*), 7.12 – 7.06 (m, 1H, Ar*H*), 6.97 – 6.87 (m, 2H, Ar*H*), 6.79 (s, 1H, Ar*H*), 3.25 (hept, *J* = 6.9 Hz, 1H, C*H*), 2.40 (s, 3H, CH_3), 1.41 (d, *J* = 6.8 Hz, 6H, 2CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 160.0, 156.6, 155.7, 152.9, 144.1, 140.7, 135.8, 133.8, 133.3, 133.2, 131.6, 131.4, 130.5, 130.2, 129.7, 129.6, 128.1, 127.5, 127.0, 123.9, 118.8, 116.8, 115.1, 31.4, 24.1, 24.0, 21.6. IR (KBr): 3432, 3269, 2964, 2925, 1655, 1632, 1594, 1547, 1494, 1467, 1442, 1383, 1330, 1282, 1214, 1186, 1160, 1092, 1052, 1001, 810, 755, 705, 667, 540 cm^{-1}

Results and Discussion

Table S2. Optical properties of the compounds in the solid state.

	λ_{abs} [a] [nm]	λ_{em} [nm]	Δ_{ss} [cm^{-1}]	Φ_F [b] [%]	τ [ns]	x,y(CIE 1931)	k_r [c] [10^8 s^{-1}]	k_{nr} [d] [10^8 s^{-1}]
AF0	370	415, 530	2930,8159	2	0.58, 4.28	0.28, 0.33	0.3448, 0.0467	16.90, 2.290
AF1	367	403	2434	1	0.24	0.22, 0.18	0.4167	41.25
AF2	373	410	2419	3	0.37	0.23, 0.22	0.8108	26.22
AF3	395	452	3192	1	0.46	0.19, 0.21	0.2174	21.52
AF4	370	475	5974	5	0.52	0.20, 0.31	0.9615	18.27
BF1	356	525	9042	42	3.59	0.33, 0.62	1.170	1.616
BF2	393	530	6577	55	4.63	0.36, 0.60	1.188	0.9719
BF3	400	532	6203	60	4.50	0.39, 0.59	1.333	0.8889
BF4	395	536	6659	10	3.97	0.37, 0.57	0.2519	2.267
BF5	400	550	6818	63	5.61	0.44, 0.54	1.123	0.6595
BF6	400	550	6818	60	4.19	0.45, 0.54	1.432	0.9547
BF7	402	555	6858	62	3.89	0.44, 0.55	1.594	0.9769
BF8	400	560	7143	38	5.47	0.47, 0.52	0.6947	1.133
BF9	400	563	7238	44	3.77	0.49, 0.50	1.167	1.485
BF10	400	575	7609	35	4.22	0.54, 0.46	0.8294	1.540
BF11	415	580	6855	32	3.20	0.51, 0.48	1.000	2.125
BF12	405	593	7828	15	3.33	0.58, 0.42	0.4505	2.553
BF13	385	565/600	8275/9307	50	6.2, 6.22	0.51, 0.49	0.8065, 0.8039	0.8065, 0.8039
BF14	400	550/590	6818/8050	32	3.21, 3.28	0.49, 0.51	0.9969, 0.9756	2.118, 2.073
BF15	405	613	8378	20	4.66	0.56, 0.43	0.4292	1.717
BF16	405	618	8510	21	3.56	0.58, 0.42	0.5899	2.219
BF17	406	625	8630	15	2.13	0.64, 0.35	0.7042	3.991
BF18	467	655	6146	5	0.91	0.63, 0.37	0.5495	10.44

[a] Longest wavelength absorption maximum. [b] Absolute fluorescence quantum yield. [c] $k_r = \Phi_F/\tau$ [d] $\Phi_F = k_r/(k_{nr} * k_r)$

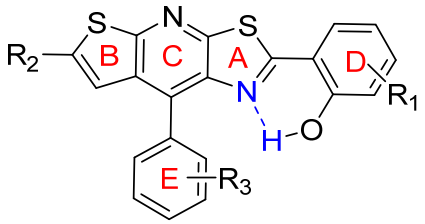
Table S3. Optical properties of the compounds in solution.

	solvent	λ_{abs} [a] [nm]	λ_{em} [nm]	Δ_{ss} [cm^{-1}]	Φ_F [b] [%]	τ [ns]	k_r [c] [10^8 s^{-1}]	k_{nr} [d] [10^8 s^{-1}]
AF0	benzene	340	395	4095	9	0.69	1.304	13.19
	THF	338	400	4586	7	0.59	1.186	15.76
AF1	benzene	323	390	5319	3	0.06	5.000	16.17
	THF	331	393	4766	3	0.05	6.000	194.0
AF2	benzene	331	395	4895	5	0.39	1.282	24.36
	THF	329	398	5269	6	0.38	1.579	24.74
AF3	benzene	360	387	1938	10	0.28	3.571	32.14
	THF	361	392	2190	12	0.18	6.667	48.89
AF4	benzene	390	542	7191	72	3.6	2.000	0.7778
	THF	390	545	7292	85	3.56	2.388	0.4213
BF1	benzene	372	520	7651	56	2.42	2.314	1.818
	THF	367	528	8308	26	2.00	1.300	3.700
	DMF	451	495	3234	0	0.79	0.000	-
	DMSO	455	505	1776	1	2.70	0.037	3.667
BF2	benzene	375	530	7799	12	0.65	1.846	13.54
	THF	372	396/525	1629/7834	3	0.5, 0.28	0.600, 1.071	19.40, 34.64
BF3	benzene	374	545	8389	4	0.21	1.905	45.71
	THF	372	395/545	1565/8533	2	0.15, 0.05	1.333, 4.000	65.33, 196.0
BF4	benzene	378	525	7404	2	0.08	2.500	122.5
	THF	377	406/525	1895/7478	1	0.12, 0.01	0.8333, 10.00	82.50, 990.0
BF5	benzene	379	555	8367	8	0.45	1.778	20.44
	THF	375	399/555	1604/8649	2	0.20, n.d.[e]	1.000	49.00
BF6	benzene	377	570	8981	4	0.19	2.105	50.53
	THF	375	399/575	1604/9275	2	0.17, 0.04	1.176, 5.000	57.65, 240.5
BF7	benzene	376	565	8897	4	0.39	1.026	24.62
	THF	374	400/575	1738/9347	2	0.21, 0.02	0.9524, 10.00	46.67, 490.0
BF8	benzene	369	550	8918	21	2.17	0.9677	3.641
	THF	368	560	9317	7	0.83	0.8434	11.20
BF9	benzene	379	582	9203	7	0.16	4.375	58.13
	THF	377	583	9372	0	0.02	0.000	-
BF10	benzene	405	565	6992	31	3.74	0.8289	1.845
	THF	401	565	7238	24	3.66	0.6557	2.077
	DMF	517	750	6009	1	n.d. [e]	-	-
	DMSO	383	620	9981	2	0.62	0.3226	15.81

	solvent	λ_{abs} [a] [nm]	λ_{em} [nm]	Δ_{ss} [cm^{-1}]	Φ_F [b] [%]	τ [ns]	k_r [c] [10^8 s^{-1}]	k_{nr} [d] [10^8 s^{-1}]
BF11	benzene	376	585	9502	8	0.37	2.162	24.86
	THF	374	430/590	3482/9789	5	1.01, 0.08	0.4950, 6.250	9.406, 118.8
BF12	benzene	386	425/622	2377/9830	4	1.0, n.d. [e]	0.400	9.600
	THF	380	450	4094	9	1.12	0.8036	8.125
BF13	benzene	383	605	9581	6	0.18	3.333	52.22
	THF	380	426/605	2842/9787	13	0.72, 0.13	1.806, 10.00	12.08, 66.92
BF14	benzene	357	401/593	3074/11148	1	n.d.[e], 0.29	0.3448	34.14
	THF	361	396	2448	5	0.22	2.273	43.18
BF15	benzene	383	609	9689	4	0.12	3.333	80.00
	THF	380	434/600	3274/9649	3	0.78, 0.13	0.3846, 2.308	12.44, 74.62
BF16	benzene	385	610	9580	4	0.17	2.353	56.47
	THF	381	440/610	3519/9853	4	0.73, 0.12	0.5479, 3.333	13.15, 80.00
BF17	benzene	394	611	9014	2	0.27	0.7407	36.30
	THF	389	440/610	2980/9313	5	0.61, 0.10	0.8197, 5.000	15.57, 95.00
BF18	benzene	406	517/653	5288/9316	1	3.5, 0.23	0.02857, 0.4348	2.829, 43.04
	THF	414	544	5772	2	4.08	0.04902	2.402

[a] Longest wavelength absorption maximum. [b] Absolute fluorescence quantum yield. [c] $k_r = \Phi_F/\tau$ [d] $\Phi_F = k_r/(k_{nr} * k_r)$ [e] Below the detection limit.

Table S4. Molecular interactions and the dihedral angles of the compounds in the single crystals. .



	dihedral angle (°)					Intramolecular H-bond (Å)	π-π interaction (Å)			
	A-C	B-C	A-B	C-E	A-D					
AF1	4.706	2.852	7.449	54.417	55.031	-	B-E' 3.794	C-E' 3.645		
BF1	0.718	0.689	0.381	58.144 58.596	1.682	1.89	A-A' 3.738	B-D' 3.989	C-D' 3.897	E-E' 3.954
BF2	1.056	0.440	1.096	58.837	1.409	1.89	A-A' 3.840	A-C' 3.781	B-D' 3.891	C-D' 3.934
BF3	3.349	0.875	3.961	62.623	7.414	1.90	A-B' 3.820	A-C' 3.644	C-C' 3.750	D-D' 3.914
BF6	1.615	0.801	2.409	68.103	1.654	1.87	A-B' 3.821	A-C' 3.674	C-C' 3.765	
BF7	1.774	2.493	3.639	61.103	5.079	1.90	A-B' 3.736	A-C' 3.692	B-C' 3.610	
BF9	0.699	0.769	1.389	78.133 83.990	6.318	1.86	A-B' 3.898			
BF10	0.316	2.316	2.596	62.150 61.938	3.229	1.89	A-A' 3.863			
BF14	0.935	1.317	1.275	68.679	2.268	1.90	-			
BF15	1.244	1.258	2.425	48.644 46.728	5.129	1.93	A-B' 3.851	A-C' 3.805	B-C' 3.811	A-D' 3.875
BF16	1.912	0.919	2.663	46.368	4.944	1.97	C-D' 3.704	D-D' 3.589		
BF18	1.861	0.688	2.549	67.684	2.468	1.89	A-B' 3.880	A-C' 3.688	C-C' 3.827	

Table S5. Crystal data and structure refinement for the single crystals. (**AF1**, **BF1**, **BF2**, **BF3**, **BF6**, **BF7**)

compounds	**AF1**	**BF1**	**BF2**	**BF3**	**BF6**	**BF7**
formula	C25H21ClN2O2S2	C25H22ClN3O4S2	C23H16Cl2N2OS2	C24H19ClN2OS2	C24H19ClN2OS2	C27H25ClN2OS2
fw	481.01	528.02	471.40	450.98	450.98	493.06
crystal system	Orthorhombic	Triclinic	Triclinic	Triclinic	Orthorhombic	Monoclinic
T (K)	293 (2)	293 (2)	293 (2)	293 (2)	293(2)	293(2)
space group	P2(1)2(1)2(1)	P-1	P-1	P-1	Pbca	P2(1)/c
a / Å	7.71230(10)	7.5032(4)	7.7588(3)	8.0688(2)	9.29150(10)	7.32260(10)
b / Å	14.4156(2)	12.2427(9)	10.6540(5)	11.8414(2)	19.1222(3)	11.19770(10)
c / Å	20.6891(3)90	14.1014(11)	14.3833(8)	12.8095(2)	24.9136(4)	31.2881(5)
α / °	90	88.124(6)	111.453(5)	115.263(2)	90	90
β / °	90	76.840(5)	96.496(4)	105.748(2)	90	96.368(2)
γ / °	90	82.587(5)	93.193(4)	95.196(2)	90	90
V/Å^3, Z	2300.16(5), 4	1250.78(15), 2	1093.40(10), 2	1034.91(4), 2	4426.50(11), 8	2549.68(6), 4
F (000)	1000	548	484	468	1872	1032
crystal size / mm^3	0.4 x 0.2 x 0.1	0.2 x 0.1 x 0.1	0.4 x 0.2 x 0.2	0.4 x 0.2 x 0.1	0.6 x 0.4 x 0.1	0.55 x 0.35 x 0.25
reflections collected / unique [R_{int}]	5338 / 3201 [R(int) = 0.0320]	6848 / 3902 [R(int) = 0.0284]	7036 / 3434 [R(int) = 0.0190]	19503 / 4104 [R(int) = 0.0301]	10737 / 3511 [R(int) = 0.0228]	18938 / 4977 [R(int) = 0.0244]
data / restraints /parameter	3201 / 0 / 294	3902 / 7 / 289	3434 / 0 / 274	4104 / 0 / 275	3511 / 0 / 275	4977 / 0 / 304
D_c / mg·m^{-3}	1.389	1.402	1.432	1.447	1.353	1.284
μ / mm^{-1}	3.373	3.226	4.600	3.672	3.434	3.024
goodness-of-fit on F^2	1.055	1.038	1.035	1.042	1.043	1.044
R_1,[a] wR_2[b] [I≥2σ(I)]	R1 = 0.0324, wR2 = 0.0795	R1 = 0.0589 wR2 = 0.1512	R1 = 0.0456 wR2 = 0.1269	R1 = 0.0295 wR2 = 0.0797	R1 = 0.0366 wR2 = 0.1009	R1 = 0.0455 wR2 = 0.1230
R_1,[a] wR_2[b] (all data)	R1 = 0.0339 wR2 = 0.0811	R1 = 0.0785 wR2 = 0.1681	R1 = 0.0482 wR2 = 0.1303	R1 = 0.0300 wR2 = 0.0802	R1 = 0.0393 wR2 = 0.1037	R1 = 0.0500 wR2 = 0.1265

[a] $R_1 = \Sigma \, || F_o | - | F_c || / \Sigma \, | F_o |$. [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma w(F_o^2)^2]^{1/2}$, where $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$ and $P = (F_o^2 + 2F_c^2)/3$.

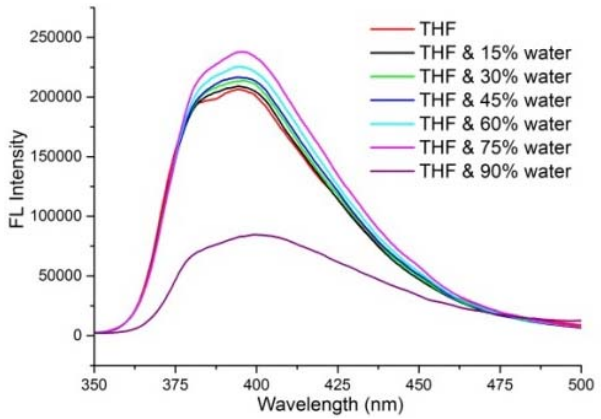
Table S6. Crystal data and structure refinement for the single crystals. (**BF9**, **BF10**, **BF14**, **BF15**, **BF16**, **BF18**)

compounds	**BF9**	**BF10**	**BF14**	**BF15**	**BF16**	**BF18**
formula	C31H33ClN2OS2	C23H16ClN3O3S2	C24H19ClN2O2S2	C24H19ClN2O2S2	C24H19ClN2O2S2	C23H18ClN3OS2
fw	549.16	481.96	466.98	466.98	466.98	451.97
crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Triclinic	Orthorhombic
T (K)	293 (2)	293 (2)	293 (2)	293 (2)	293(2)	293(2)
space group	P2(1)/c	P2(1)/c	Pbca	P2(1)/n	P-1	Pbca
a / Å	25.724(5)	12.8419(4)	20.1226(5)	18.2963(13)	7.6464(3)	9.2883(2)
b / Å	10.867(2)	9.1338(4)	9.5608(4)	4.8690(3)	9.8781(6)	19.0608(3)
c / Å	10.591(2)	19.5081(8)	22.8331(8)	25.311(2)	14.4376(11)	24.5265(5)
α / °	90	90	90	25.311(2)	91.312(6)	90
β / °	100.70(3)	104.550	90	98.904(7)	96.272(5)	90
γ / °	100.70(3)	90	90	90	94.020(4)	90
V/Å^3, Z	2909.1(10), 4	2214.82(15), 4	4392.8(3), 8	2227.7(3), 4	1080.79(11), 2	4342.23(15), 8
F (000)	1160	992	1936	968	484	1872
crystal size / mm^3	0.43 x 0.31 x 0.16	0.40 x 0.25 x 0.10	0.40 x 0.40 x 0.20	0.40 x 0.10 x 0.01	1.00 x 0.50 x 0.20	0.40 x 0.30 x 0.10
reflections collected / unique [R_{int}]	18021 / 5700 [R(int) = 0.0490]	8949 / 3512 [R(int) = 0.0270]	12915 / 3471 [R(int) = 0.0314]	7903 / 3534 [R(int) = 0.0465]	6878 / 3406 [R(int) = 0.0351]	11981 / 3459 R(int) = 0.0305]
data / restraints /parameter	5700 / 19 / 311	3512 / 9 / 258	3471 / 0 / 284	3534 / 6 / 279	3406 / 0 / 285	3459 / 6 / 274
D_c / mg·m^{-3}	1.254	1.445	1.412	1.392	1.435	1.383
μ / mm^{-1}	0.301	3.556	3.516	3.466	3.572	3.516
goodness-of-fit on F^2	1.026	1.047	1.021	1.029	1.199	1.063
R_1,[a] wR_2[b] [I≥2σ(I)]	R1 = 0.0861 wR2 = 0.2341	R1 = 0.0686 wR2 = 0.1990	R1 = 0.0566 wR2 = 0.1640	R1 = 0.0572 wR2 = 0.1454	R1 = 0.1041 wR2 = 0.3465	R1 = 0.0547 wR2 = 0.1614
R_1,[a] wR_2[b] (all data)	R1 = 0.1022 wR2 = 0.2521	R1 = 0.0760 wR2 = 0.2082	R1 = 0.0617 wR2 = 0.1705	R1 = 0.0884 wR2 = 0.1730	R1 = 0.1075 wR2 = 0.3475	R1 = 0.0606 wR2 = 0.1691

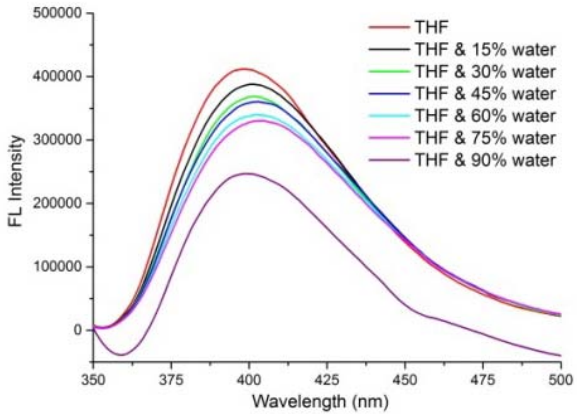
[a] $R_1 = \Sigma \,||F_o| - |F_c||/\Sigma\,|F_o|$. [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$, where $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$ and $P = (F_o^2 + 2F_c^2)/3$.

CCDC 1527732 (**AF1**), CCDC 1527733 (**BF1**), CCDC 1527734 (**BF2**), CCDC 1527735 (**BF3**), CCDC 1527736 (**BF6**), CCDC 1527737 (**BF7**), CCDC 1527738 (**BF9**), CCDC 1527739 (**BF10**), CCDC 1527740 (**BF14**), CCDC 1527741 (**BF16**), CCDC 1527742 (**BF15**) and CCDC 1527743 (**BF18**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center.

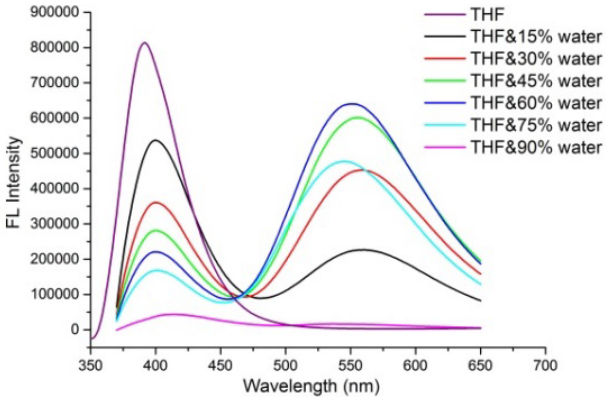
Figure S1. PL spectra of compounds in THF and THF/water mixtures with different water fractions.



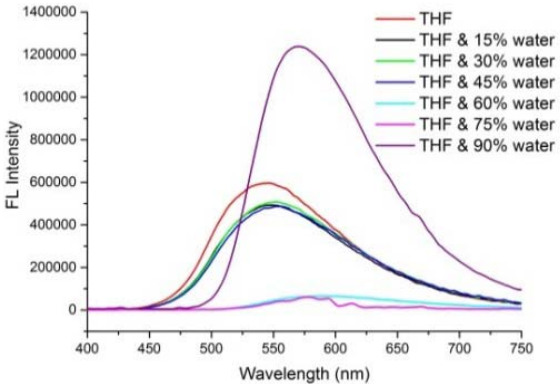
AF1



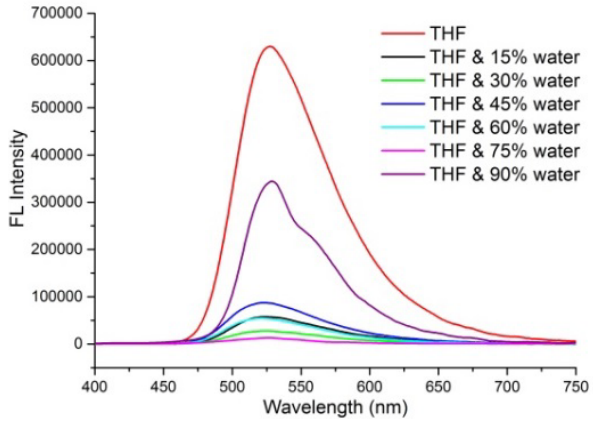
AF2



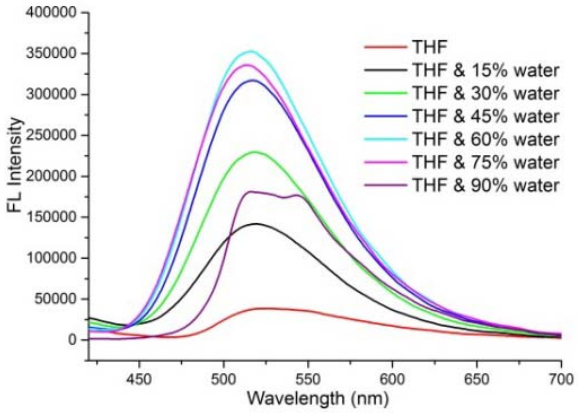
AF3



AF4



BF1



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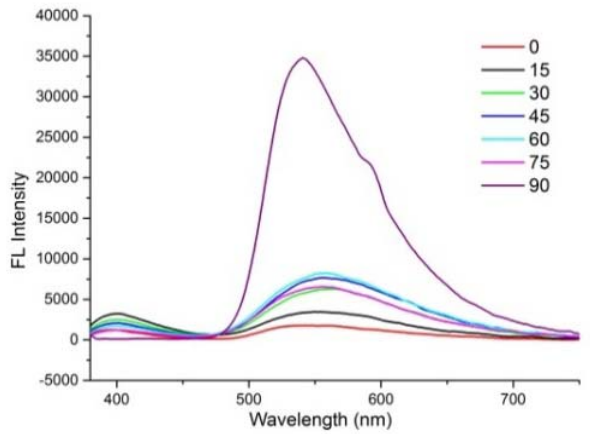
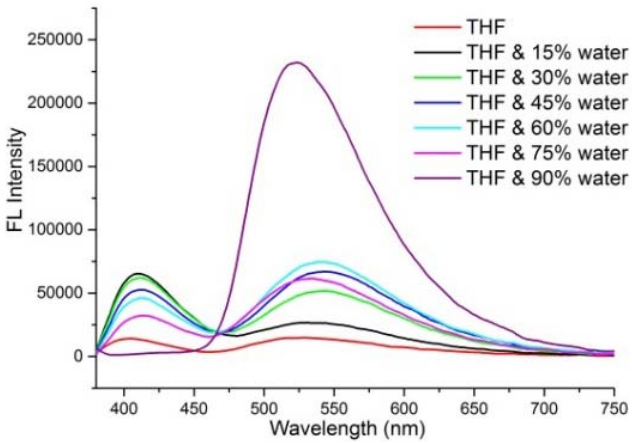
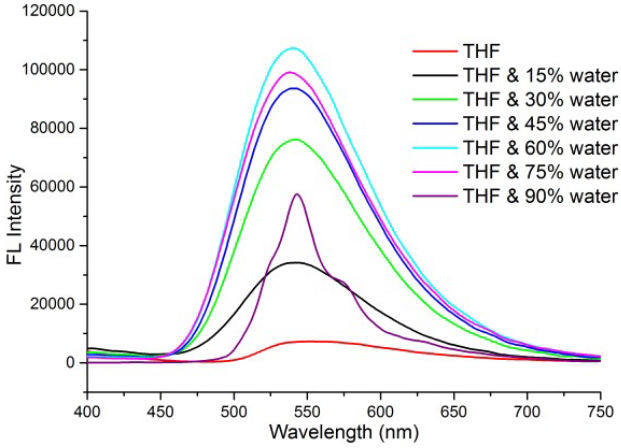


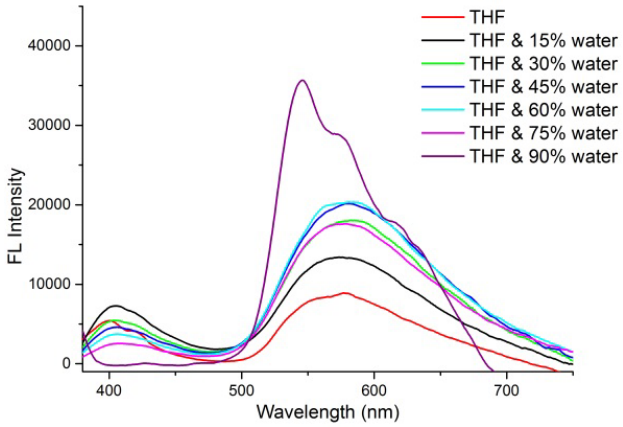
BF3



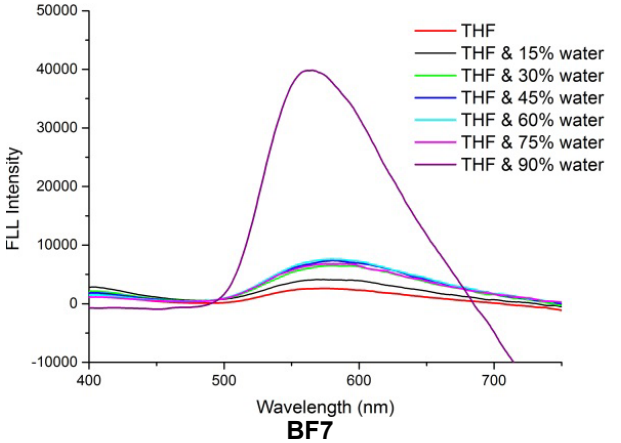
BF4



BF5



BF6



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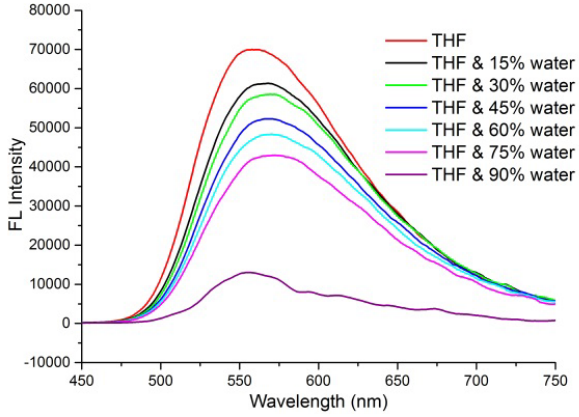
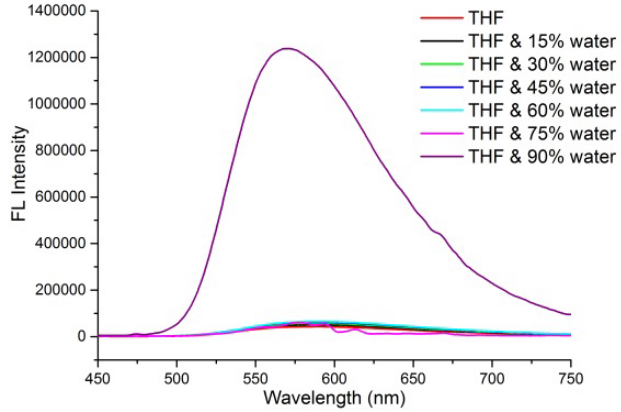


BF8



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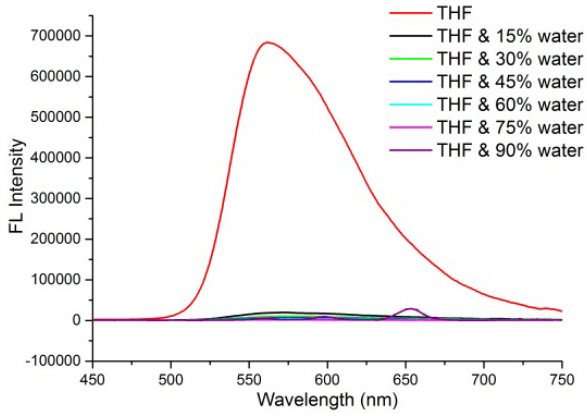
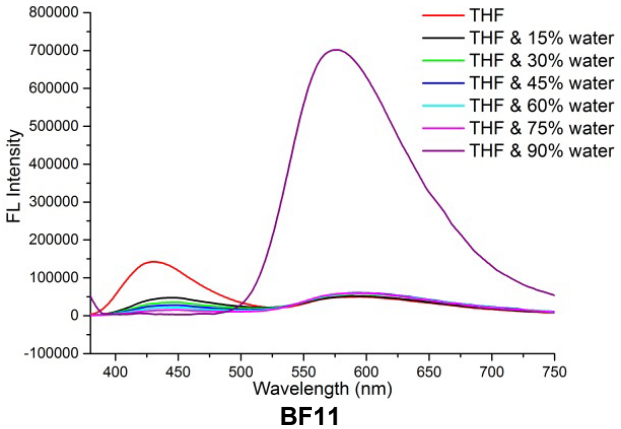
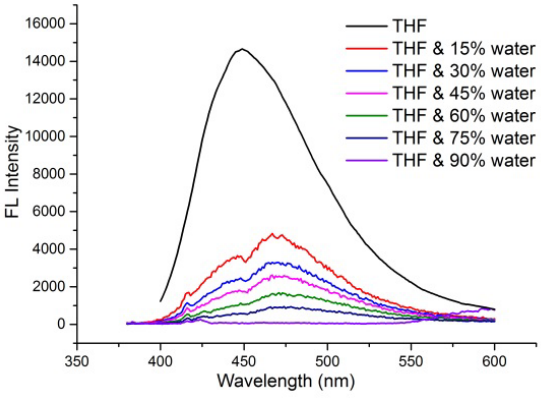


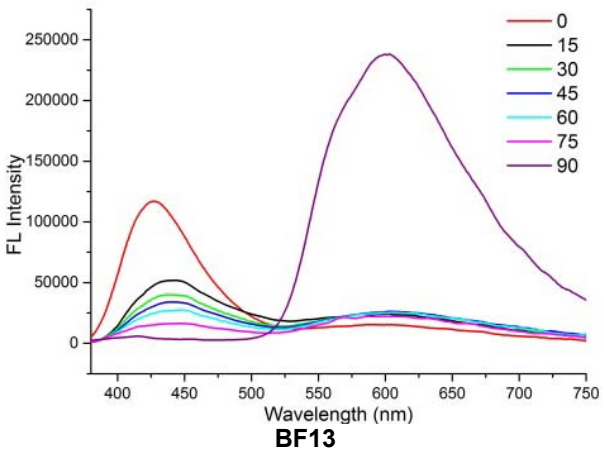
BF10



BF11



BF12



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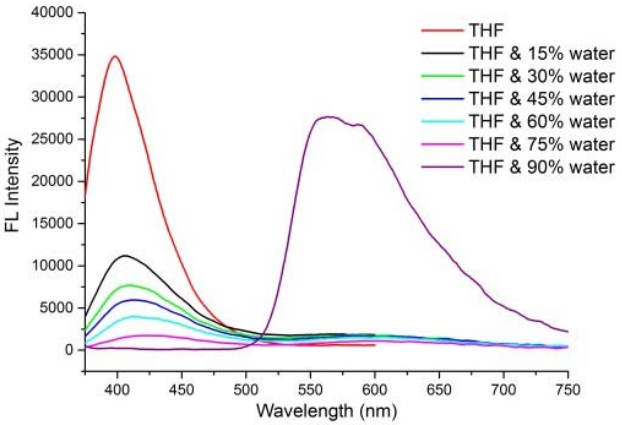

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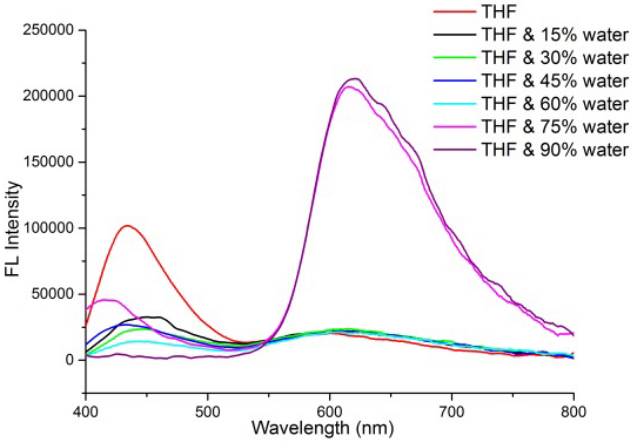

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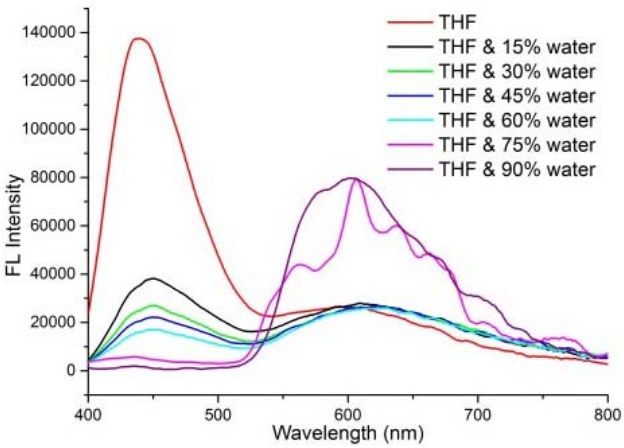

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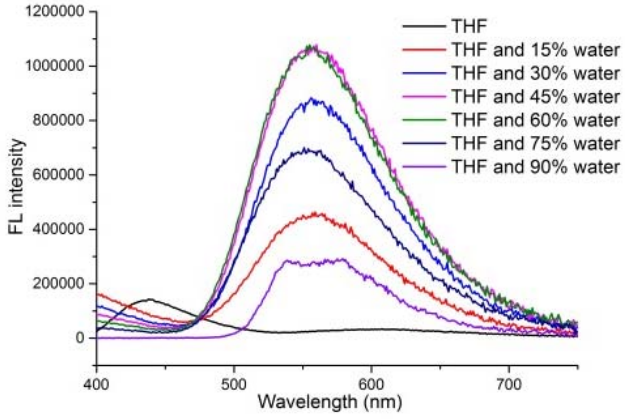

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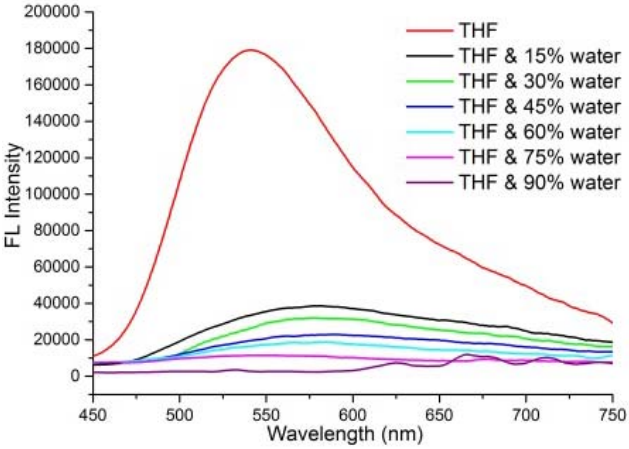
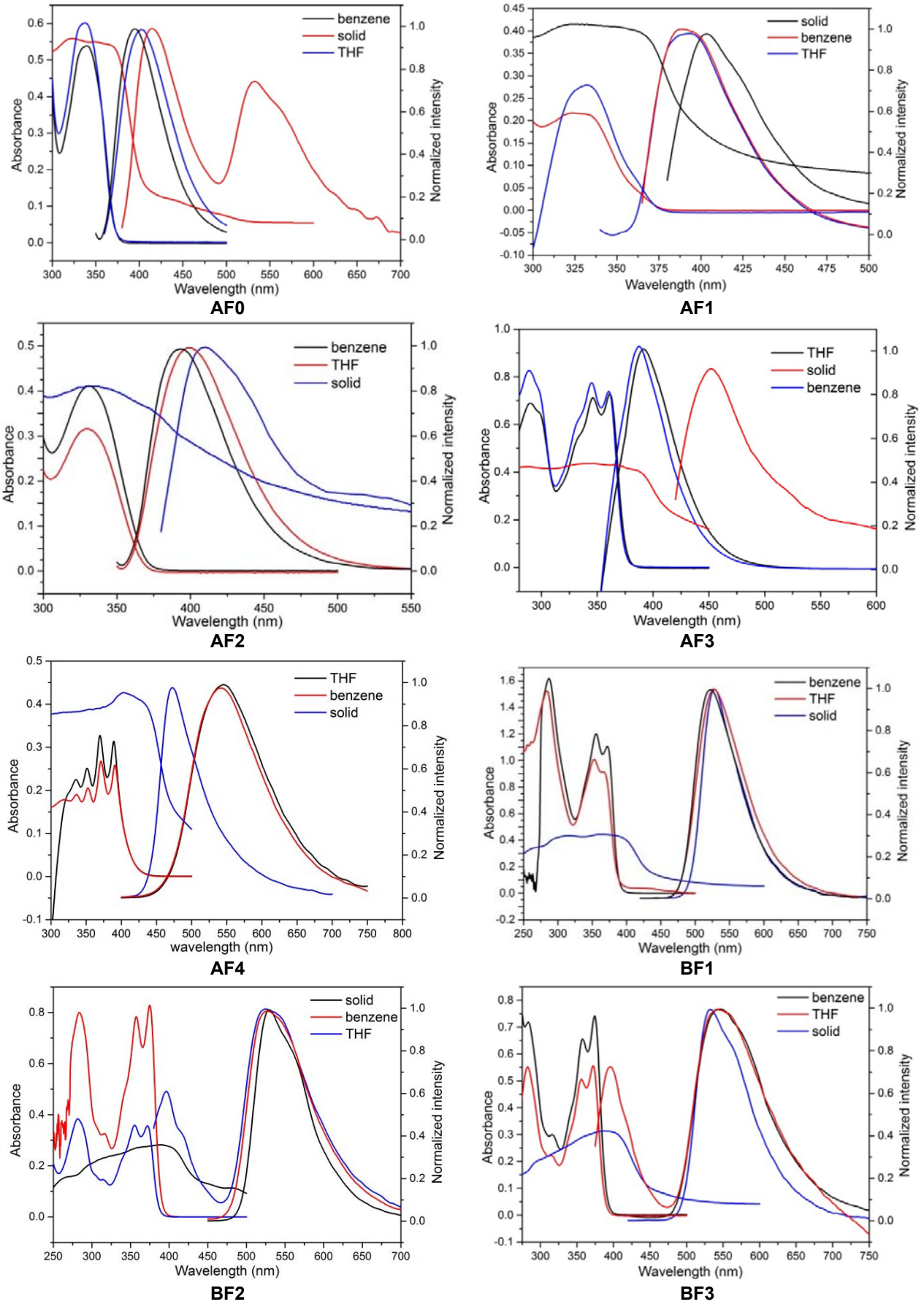
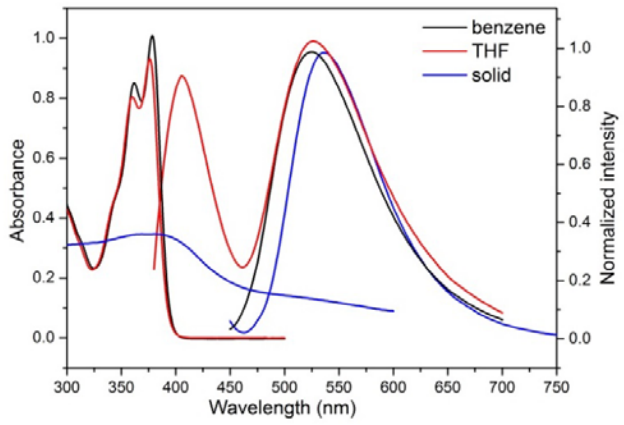


BF18

Figure S2. UV absorption spectra and PL emission spectra of the target compounds.





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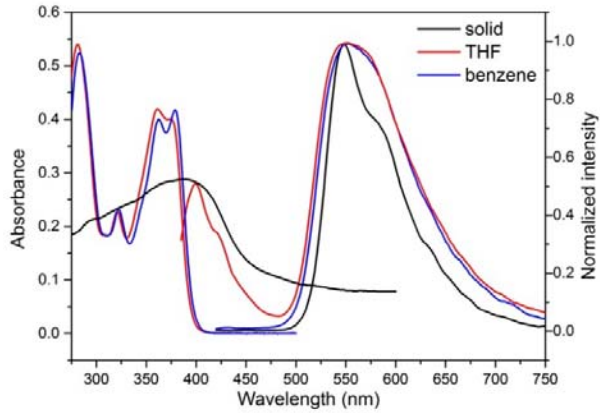

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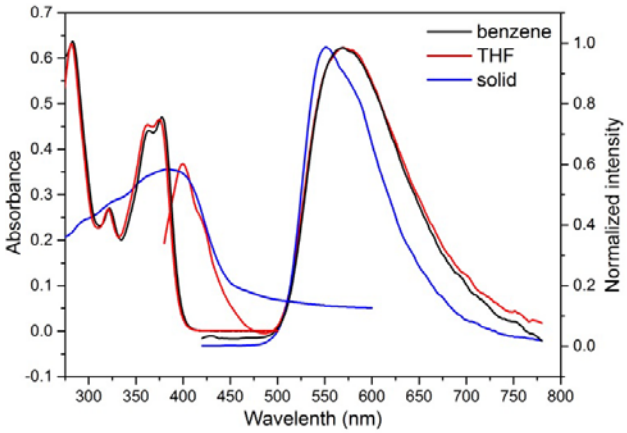

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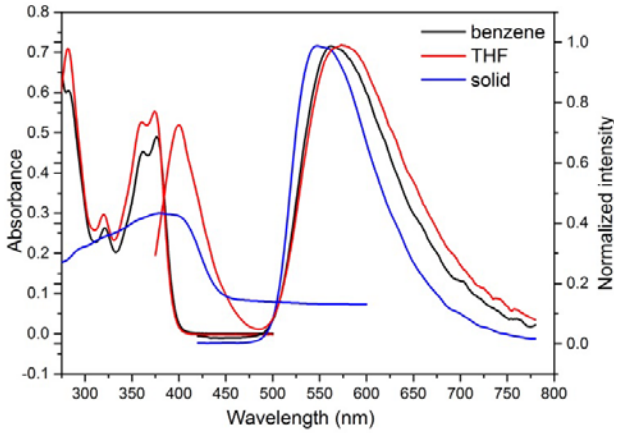

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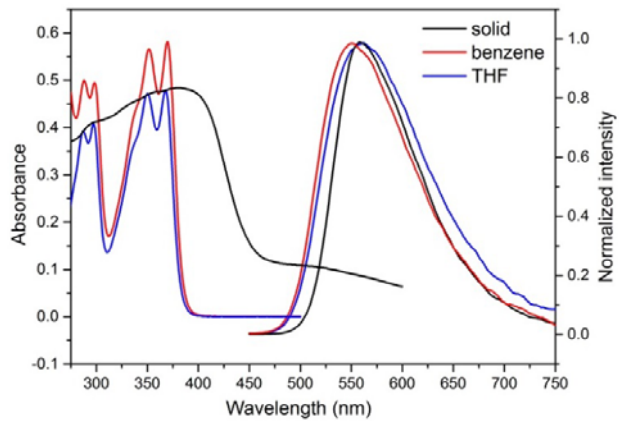

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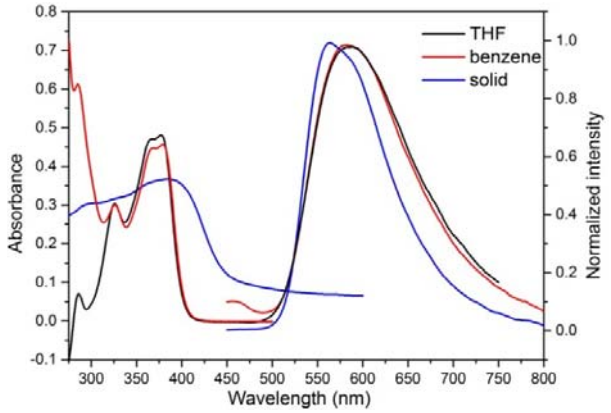

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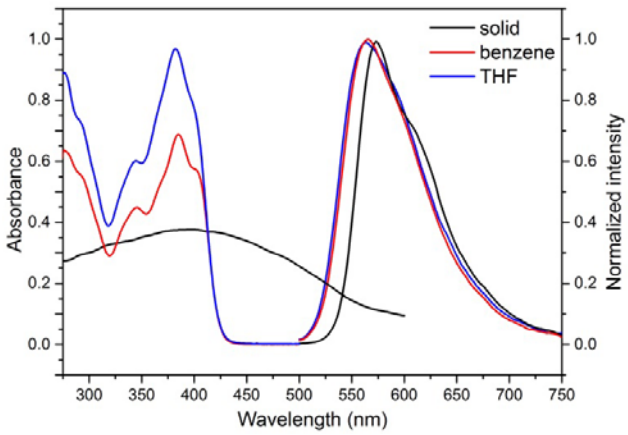

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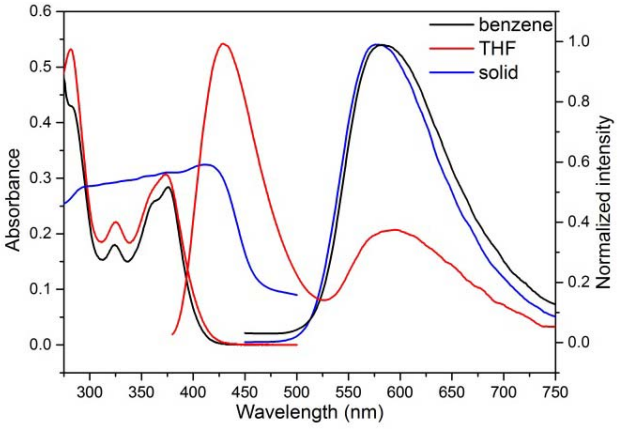

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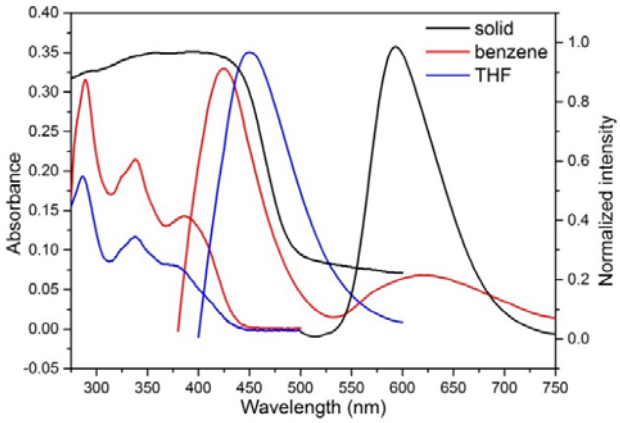

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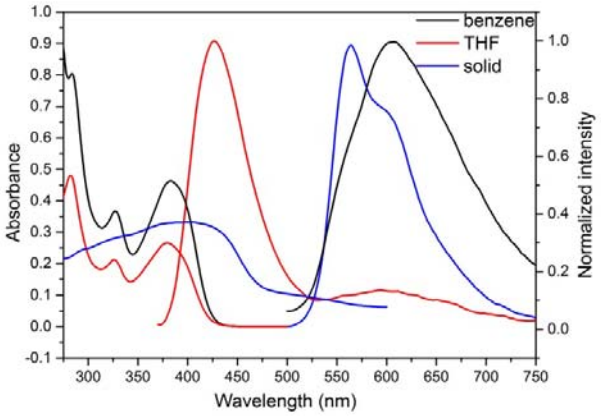

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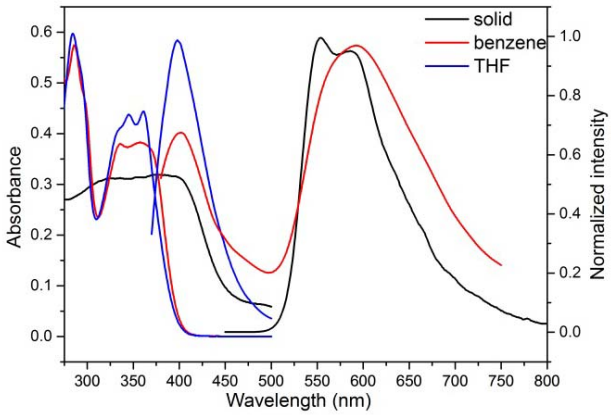

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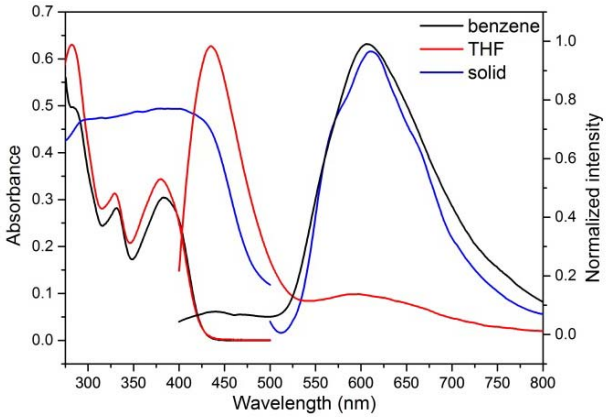

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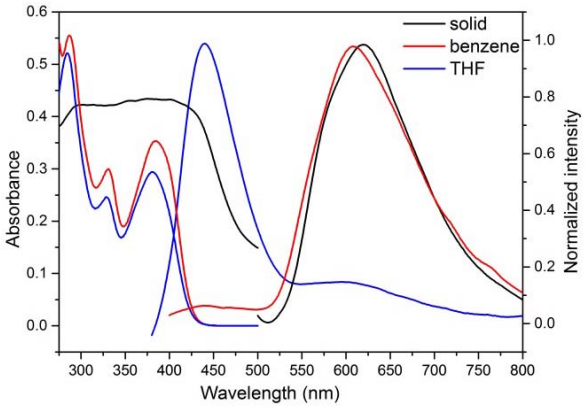

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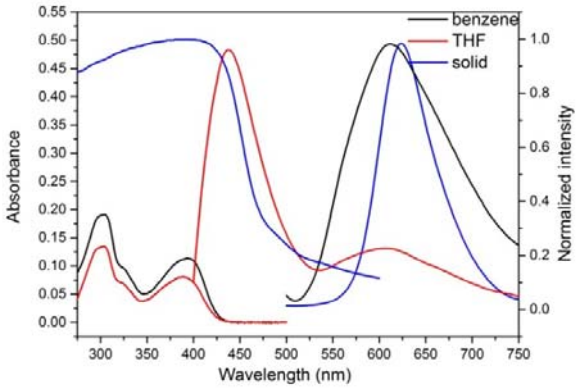

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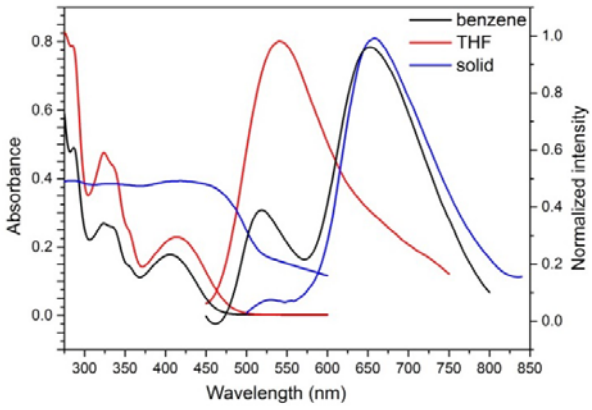


BF18

Figure S3. UV absorption spectra in the solid state.

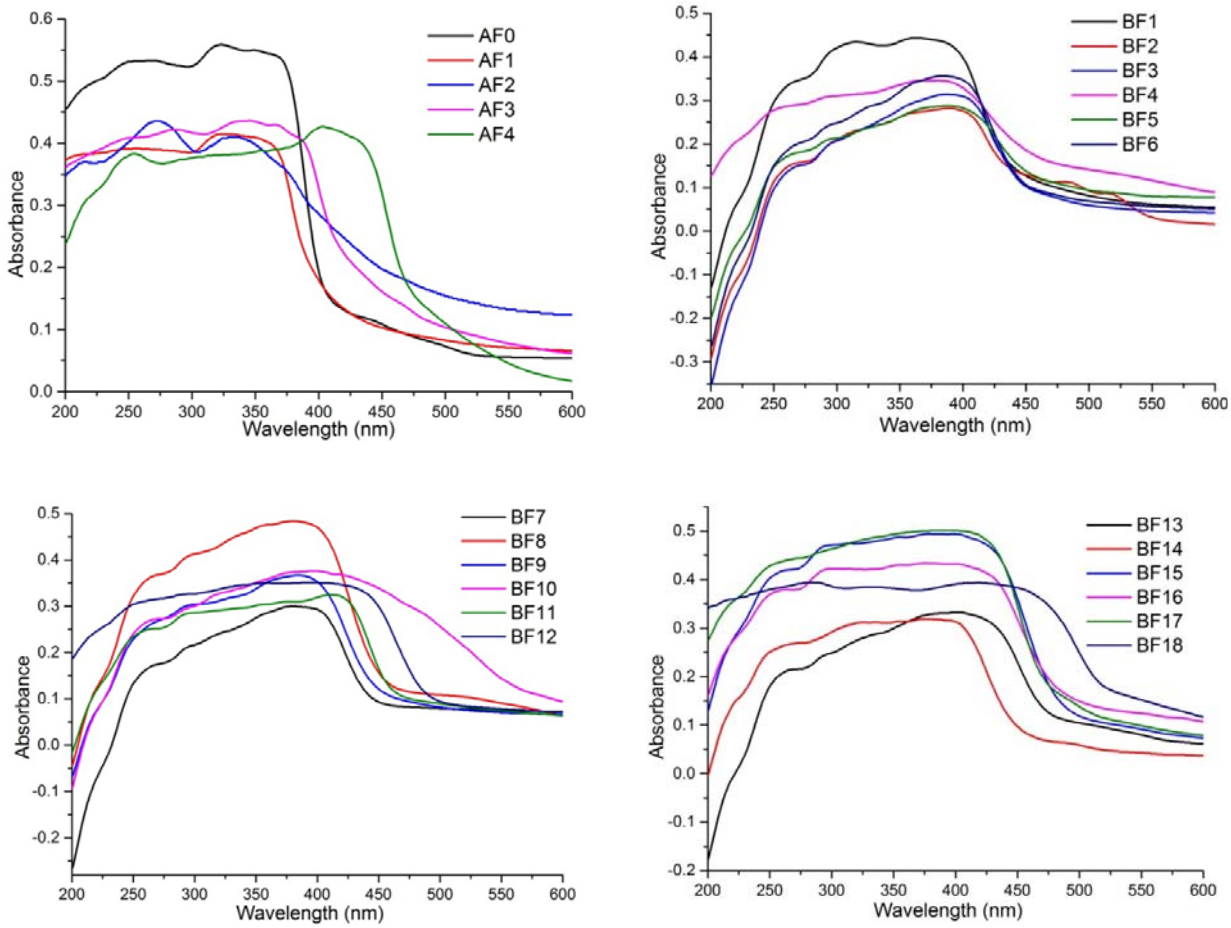
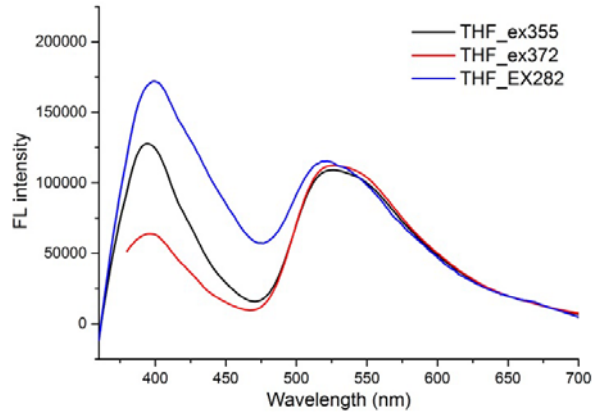


Figure S4. PL emission spectra under different excitation wavelengths of the compounds which exhibiting dual emission peaks in solution.



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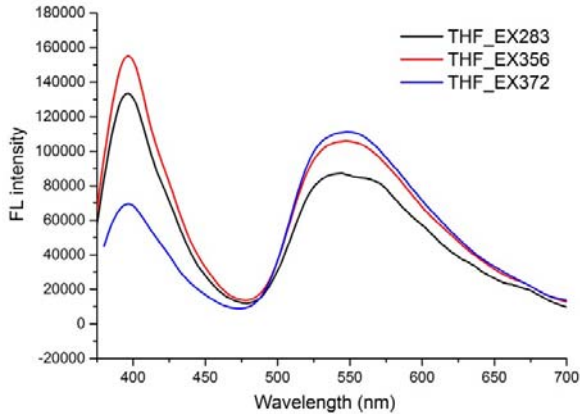

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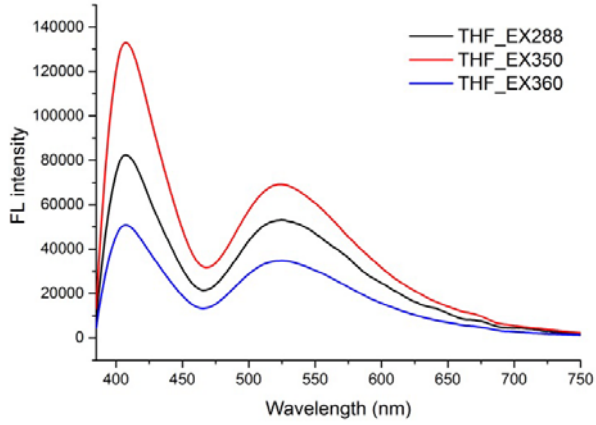

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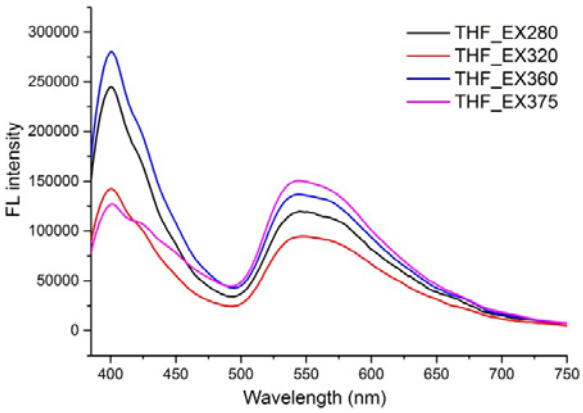

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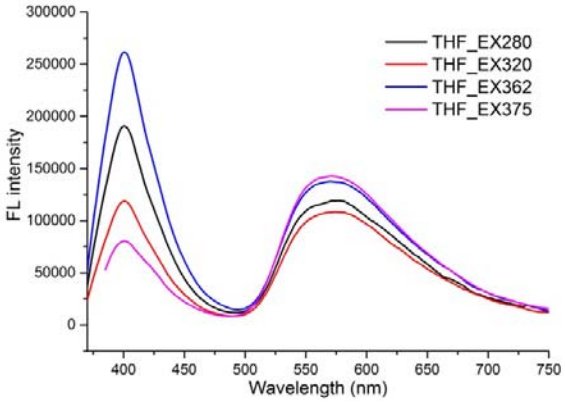

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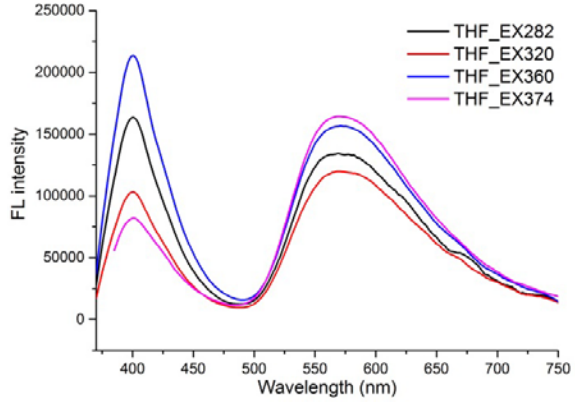

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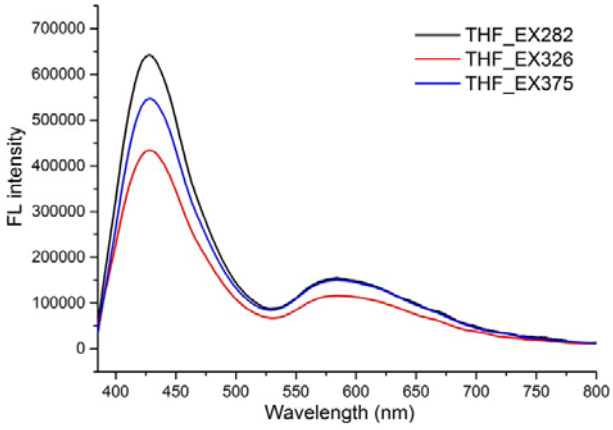

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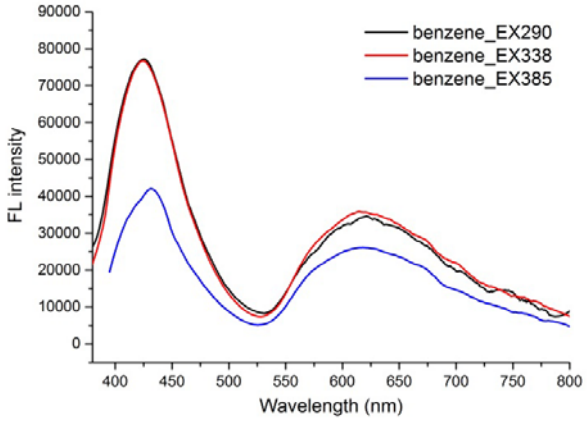

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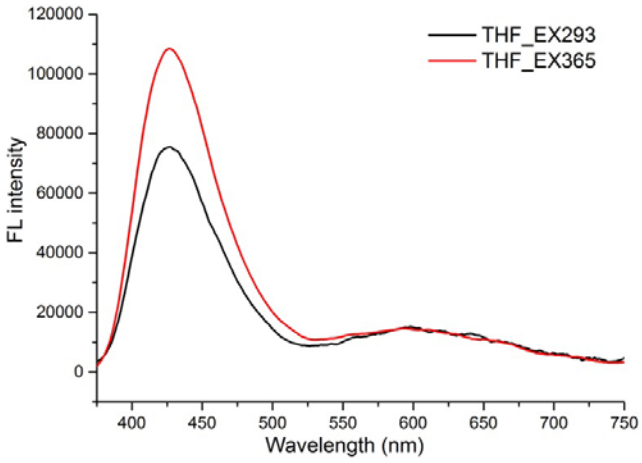

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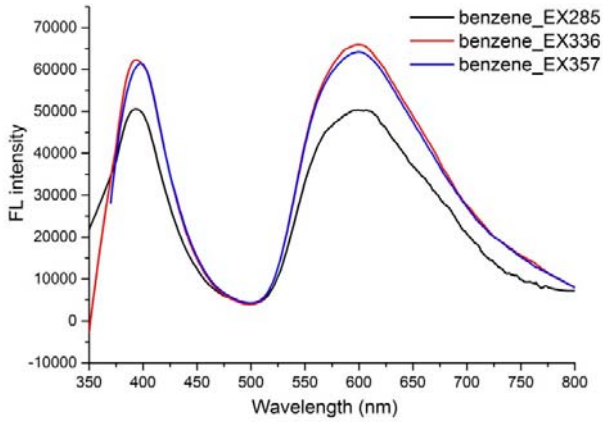

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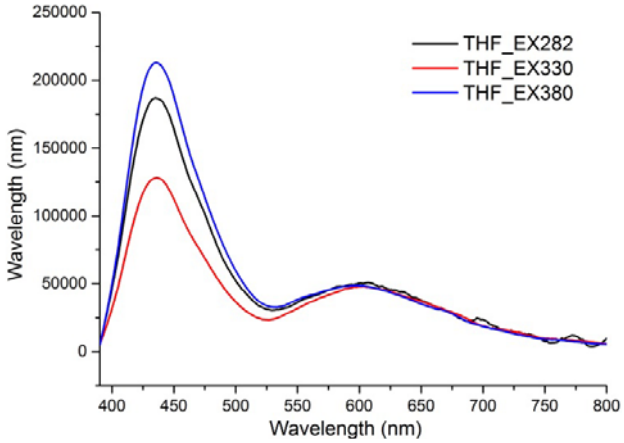

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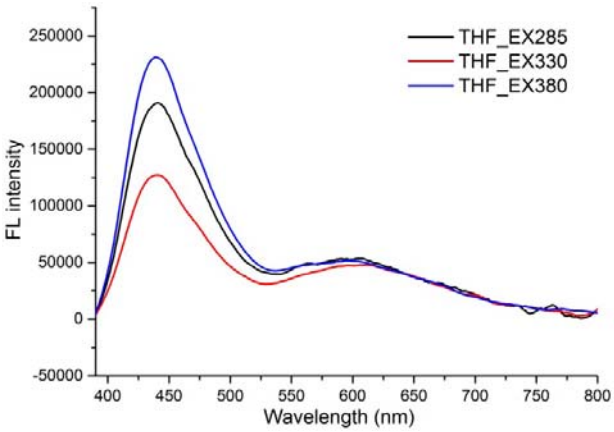

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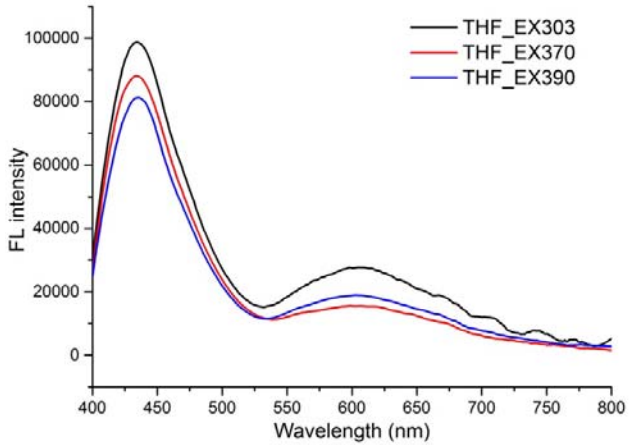

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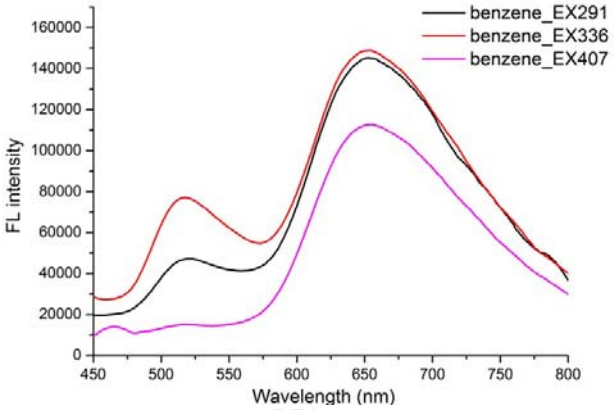
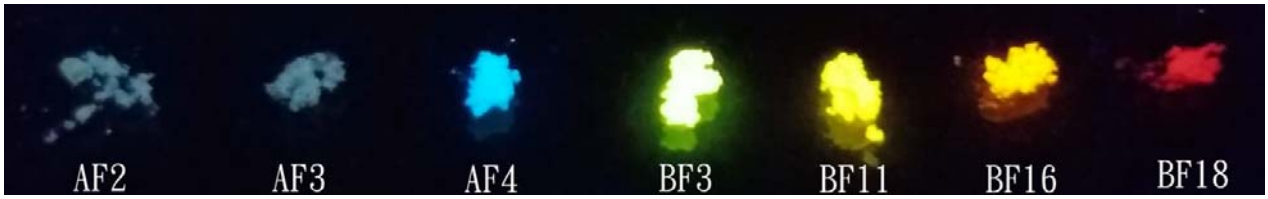
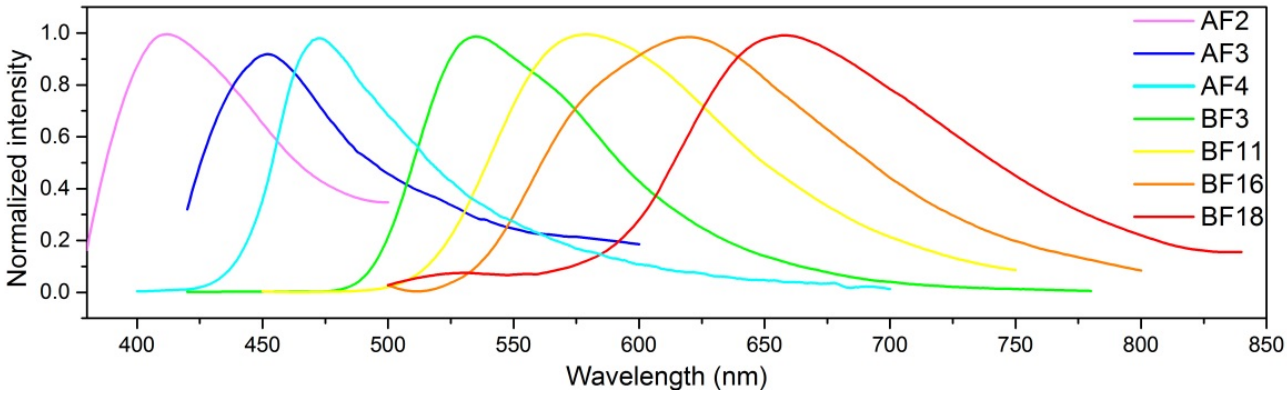


BF18

Figure S5. Photographs taken under irradiation with 365 nm UV light (rainbow colours), normalized PL spectra in the solid state and PL spectra plotted on a CIE 1931 chromaticity diagram.





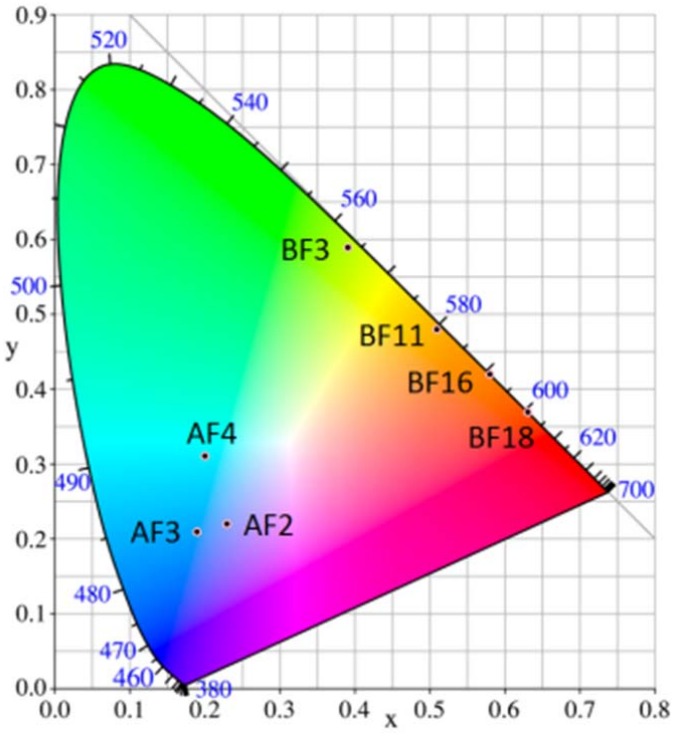


Figure S6. Molecular interaction of **AF1** in single crystals.

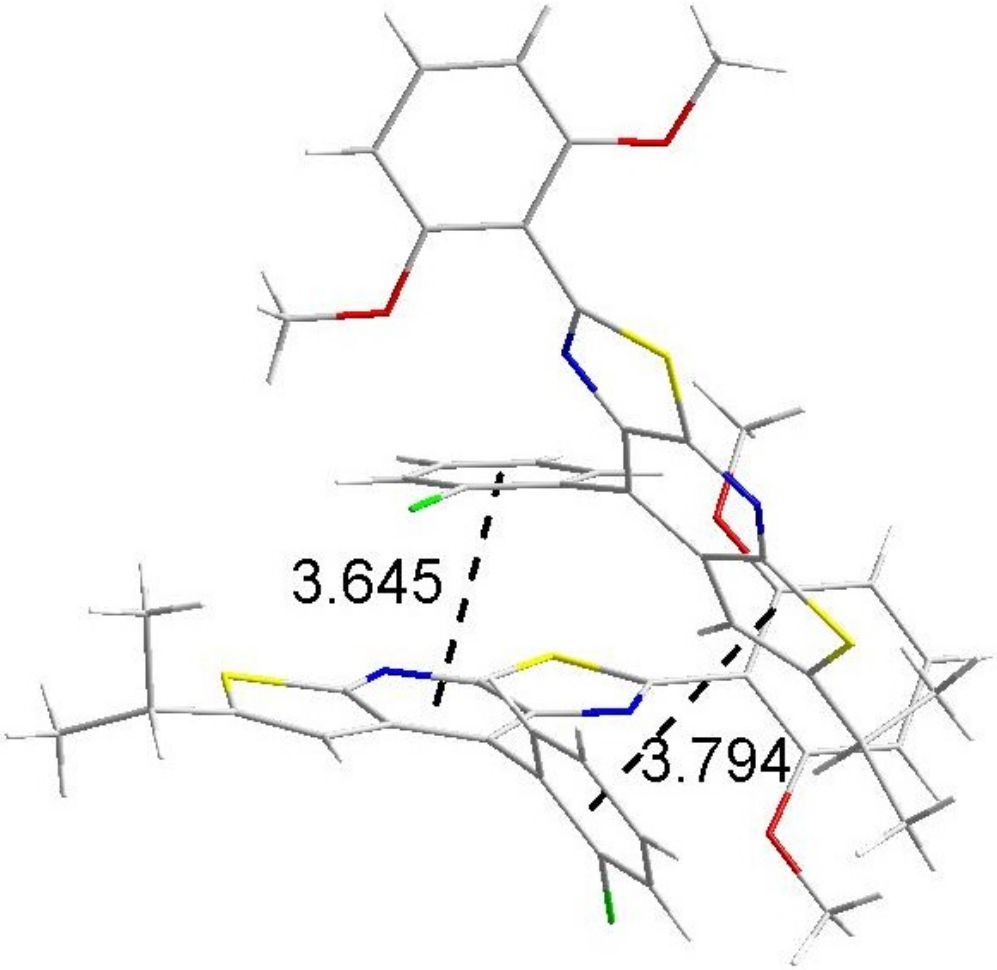


Figure S7. Molecular interaction of **BF1** in single crystals.

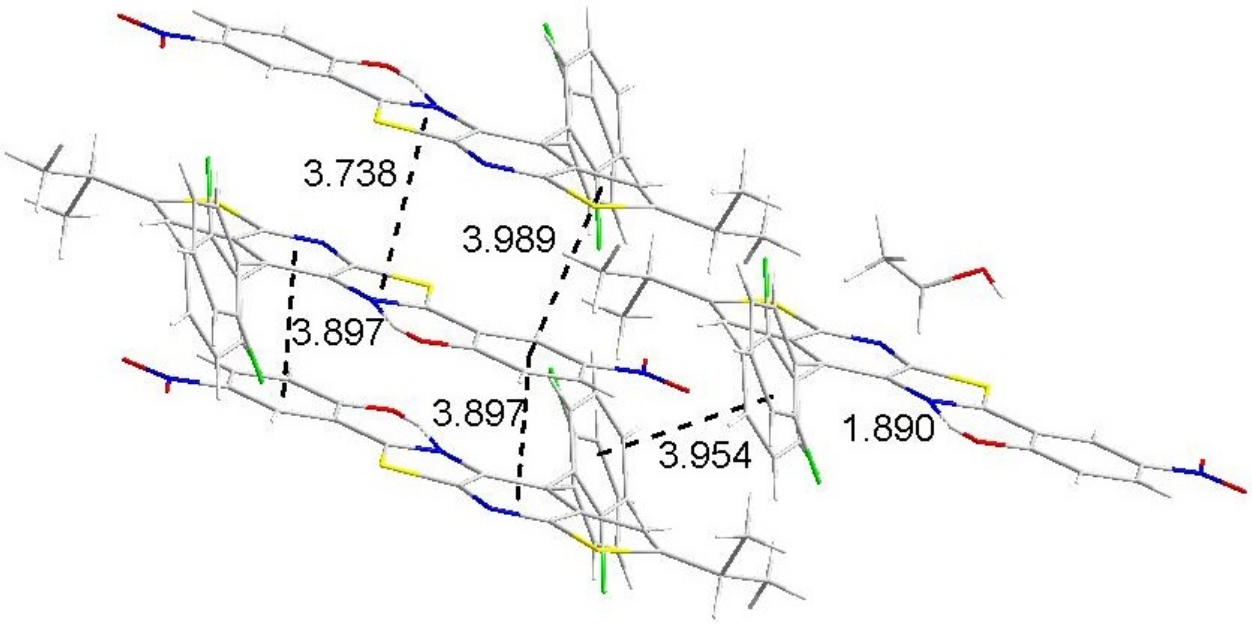


Figure S8. Molecular interaction of **BF2** in single crystals.

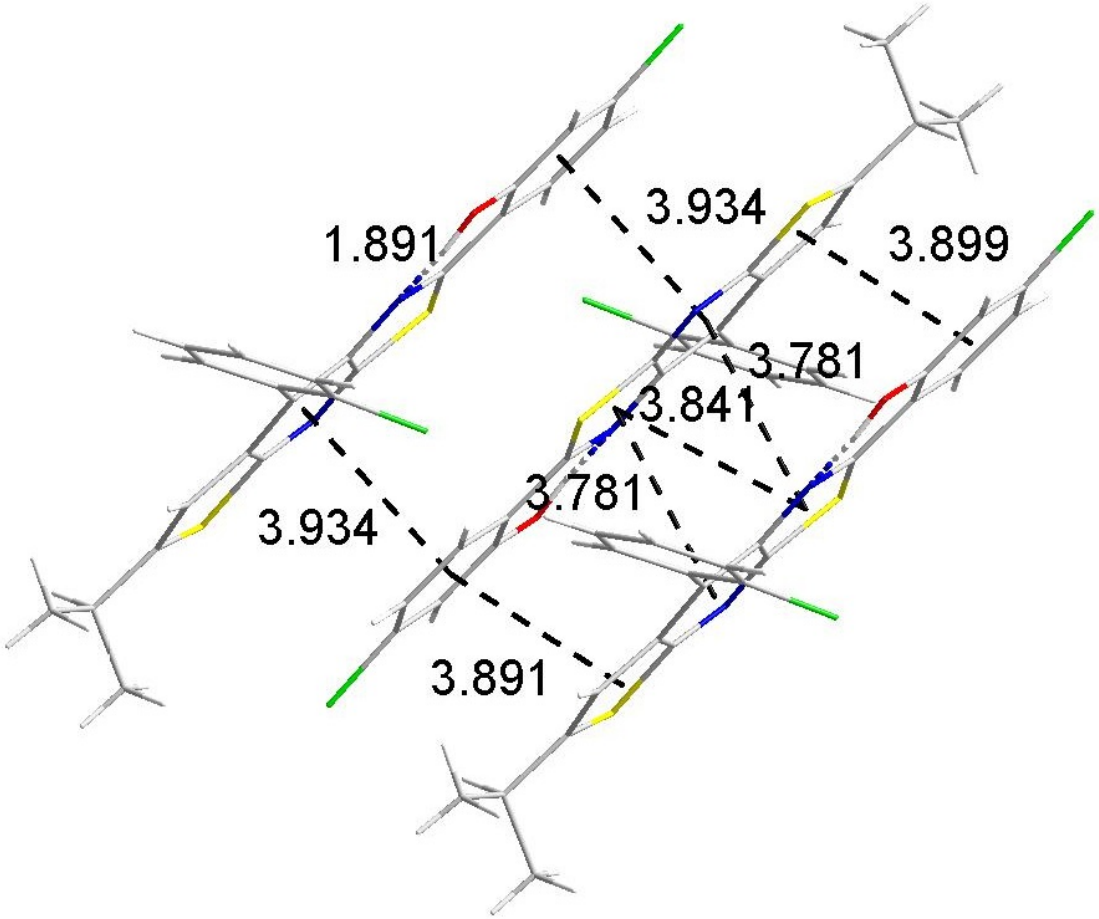


Figure S9. Molecular interaction of **BF3** in single crystals.

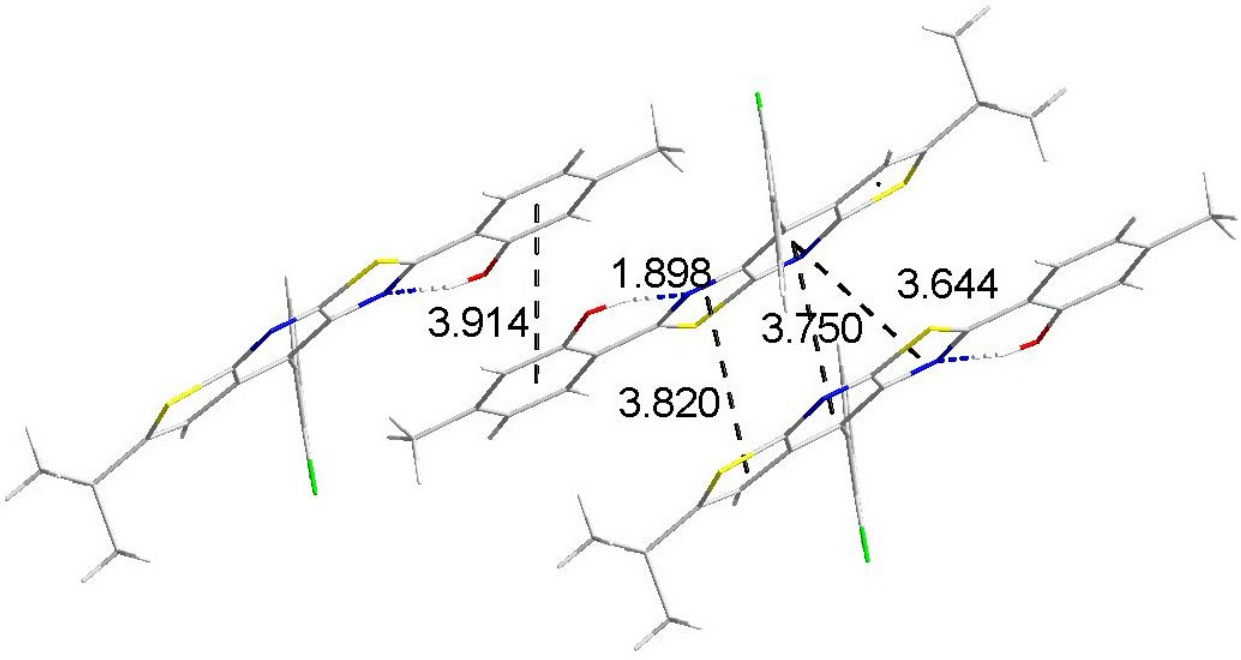


Figure S10. Molecular interaction of **BF6** in single crystals.

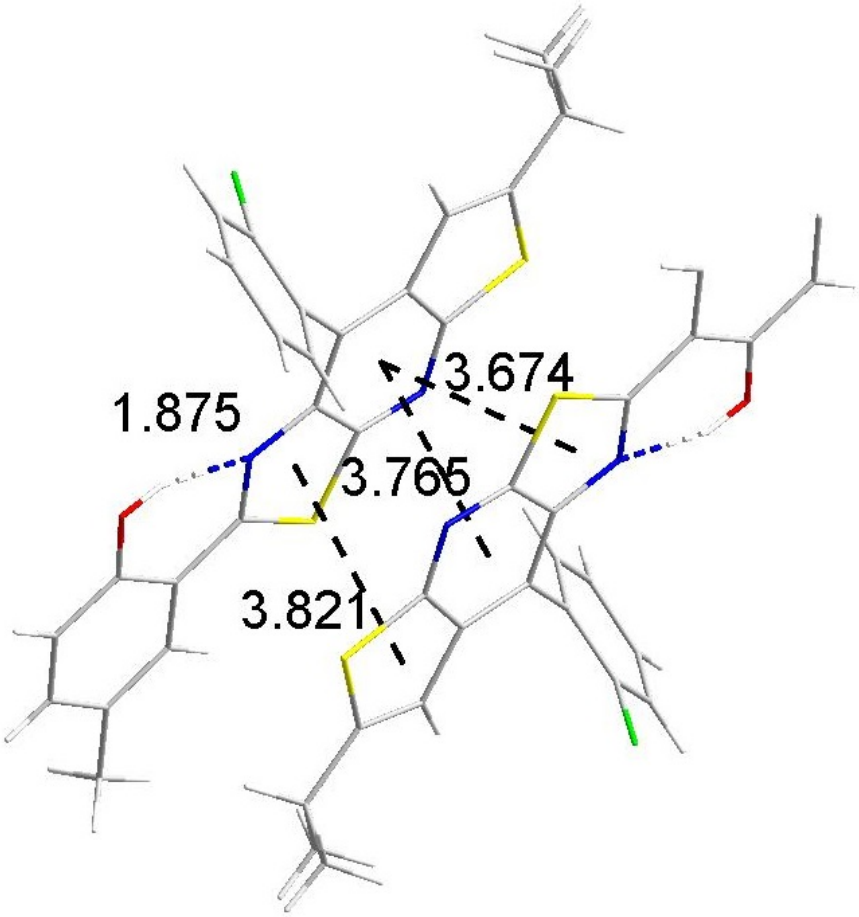


Figure S11. Molecular interaction of **BF7** in single crystals.

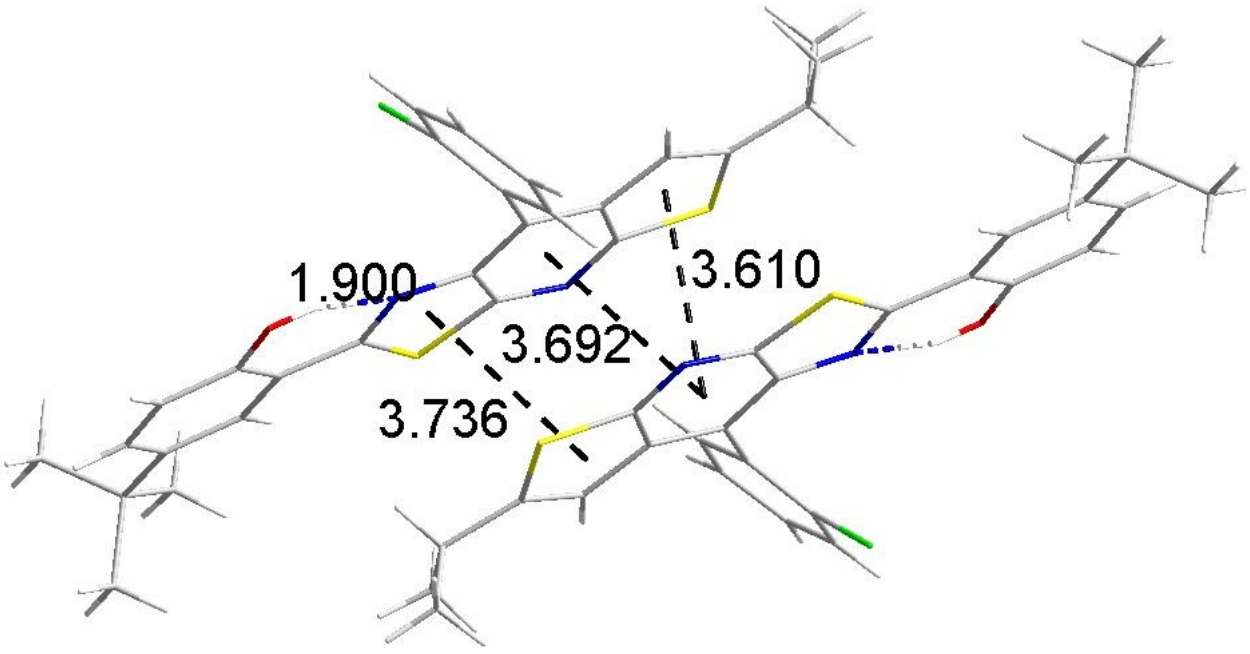


Figure S12. Molecular interaction of **BF9** in single crystals.

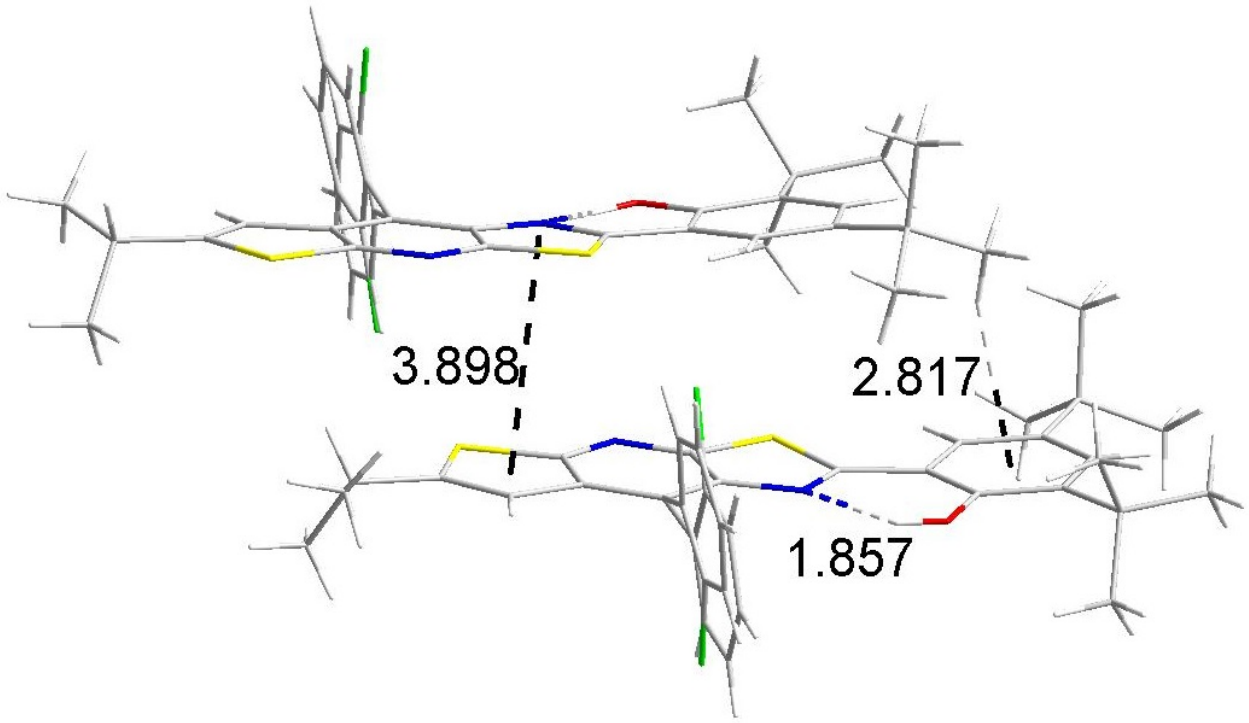


Figure S13. Molecular interaction of **BF10** in single crystals.

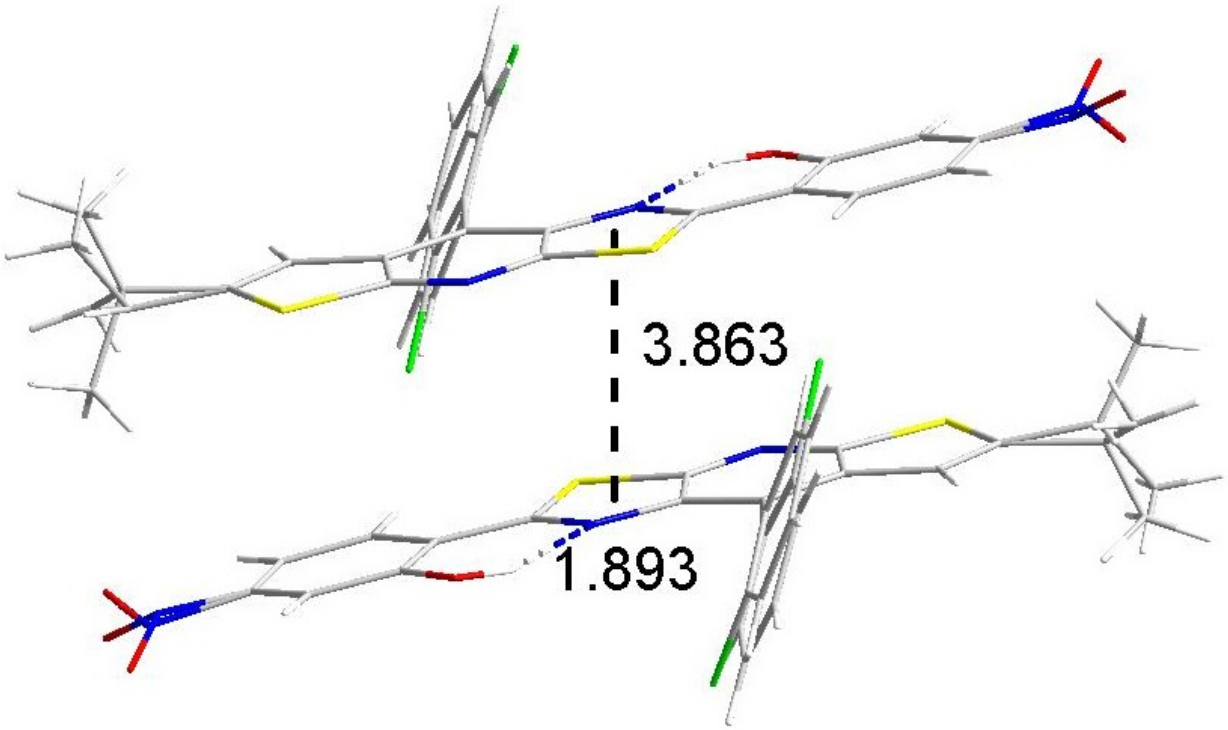


Figure S14. Molecular interaction of **BF14** in single crystals.

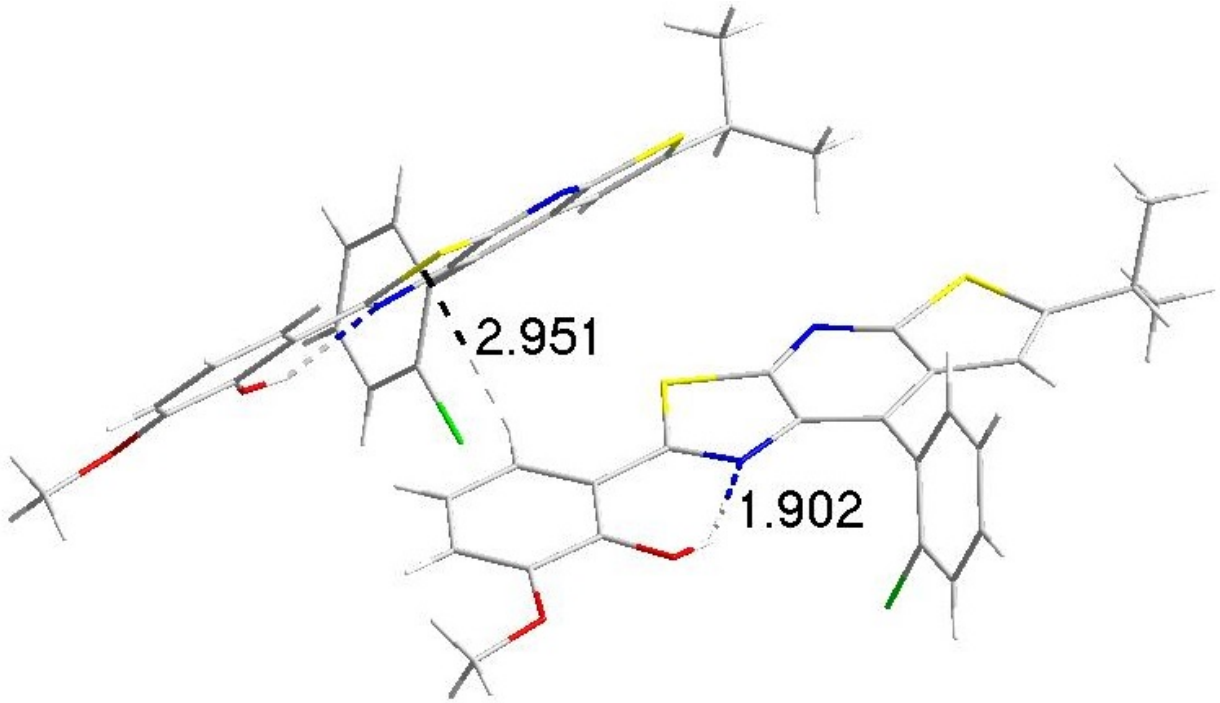


Figure S15. Molecular interaction of **BF15** in single crystals.

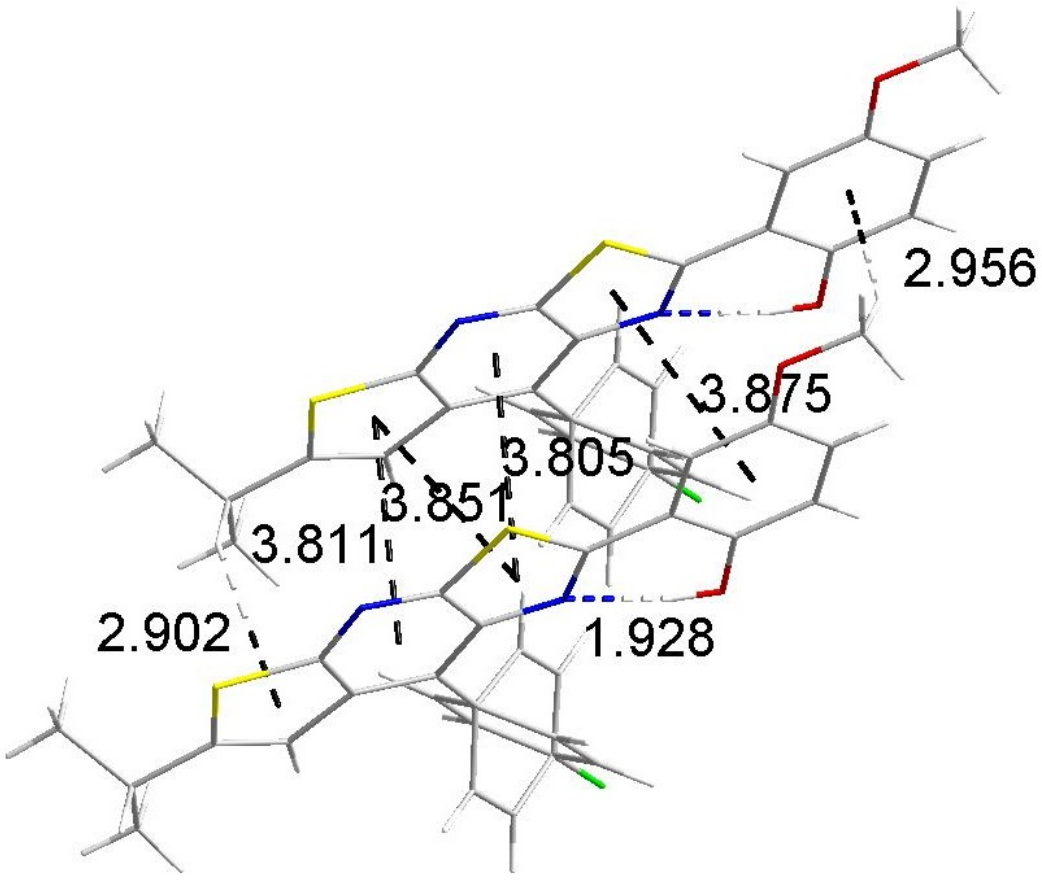


Figure S16. Molecular interaction of **BF16** in single crystals.

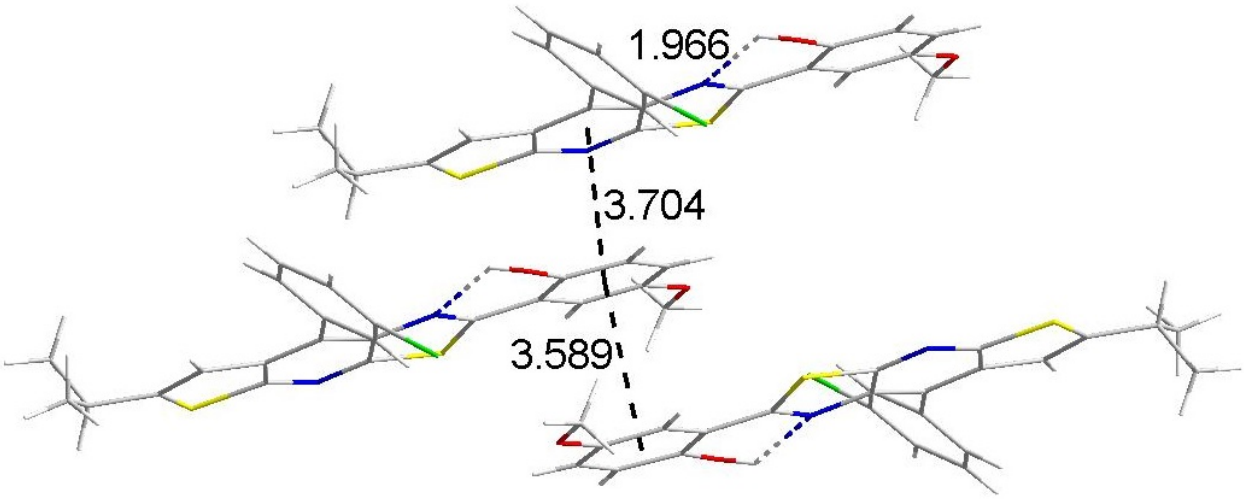
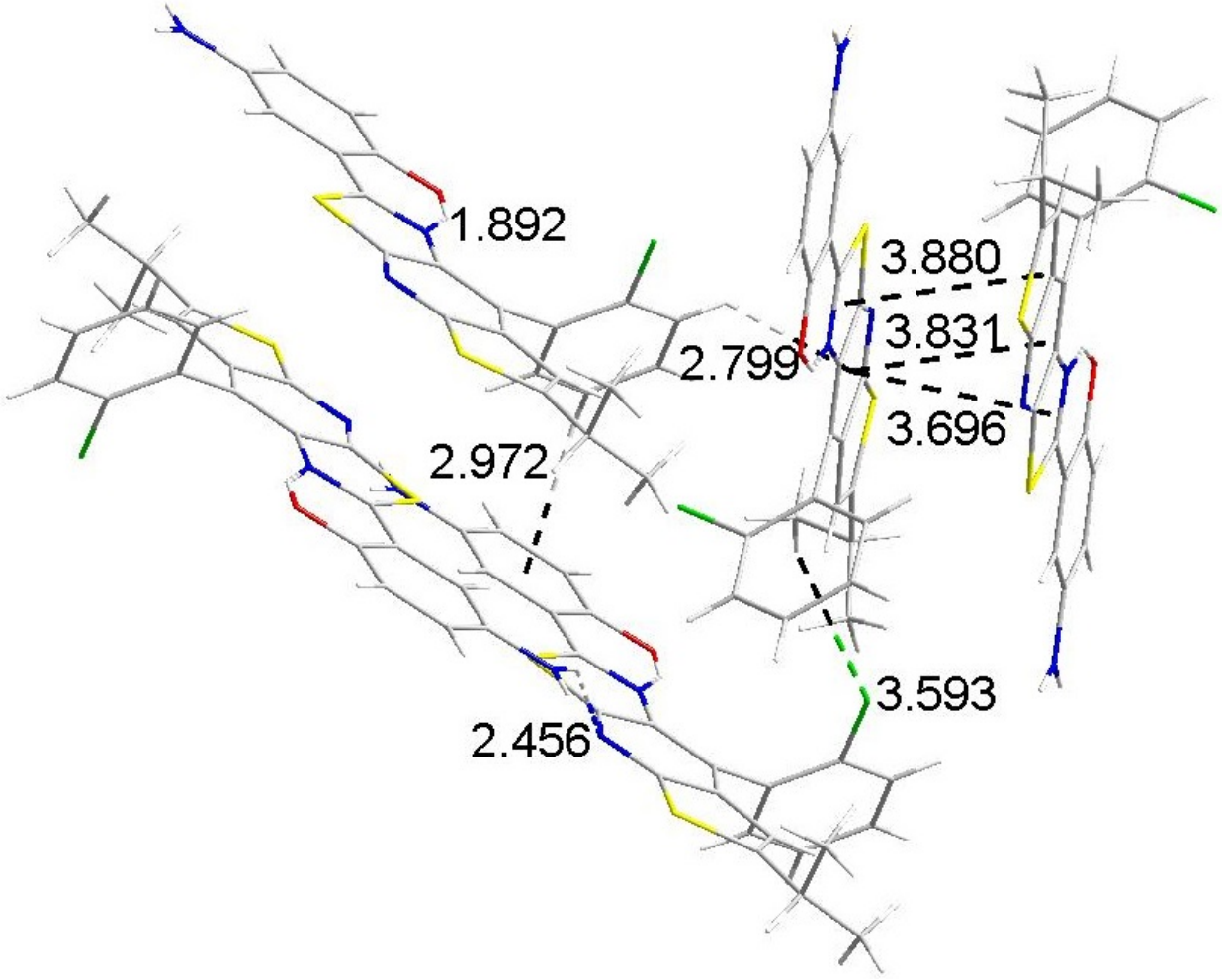
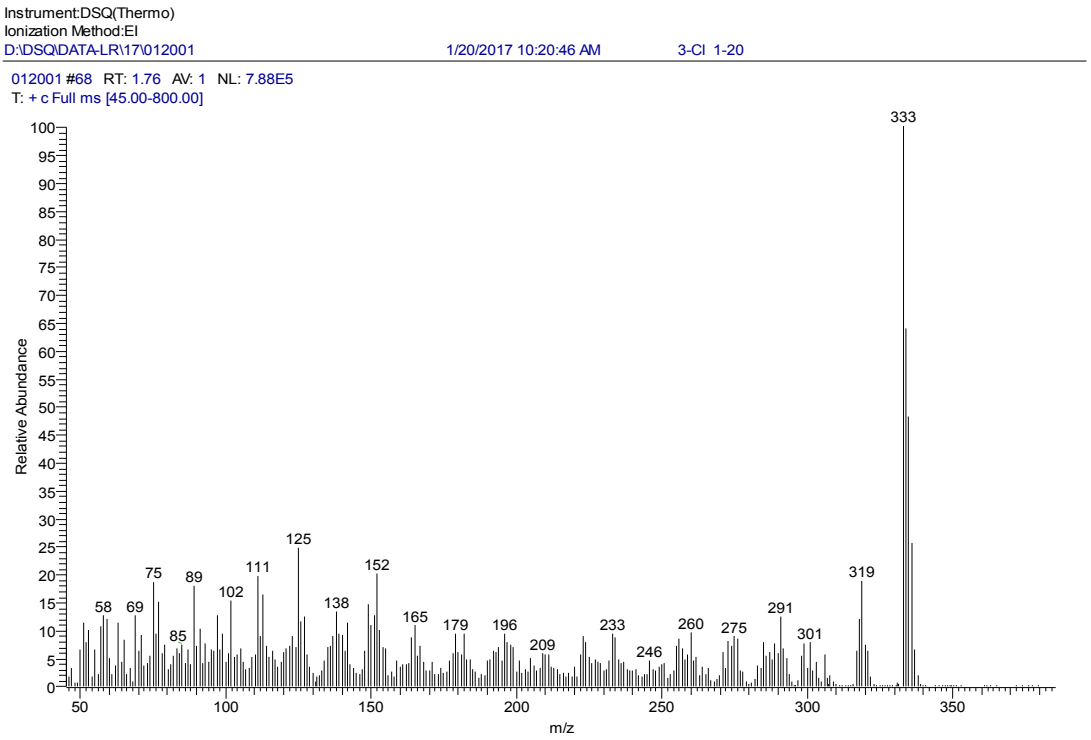


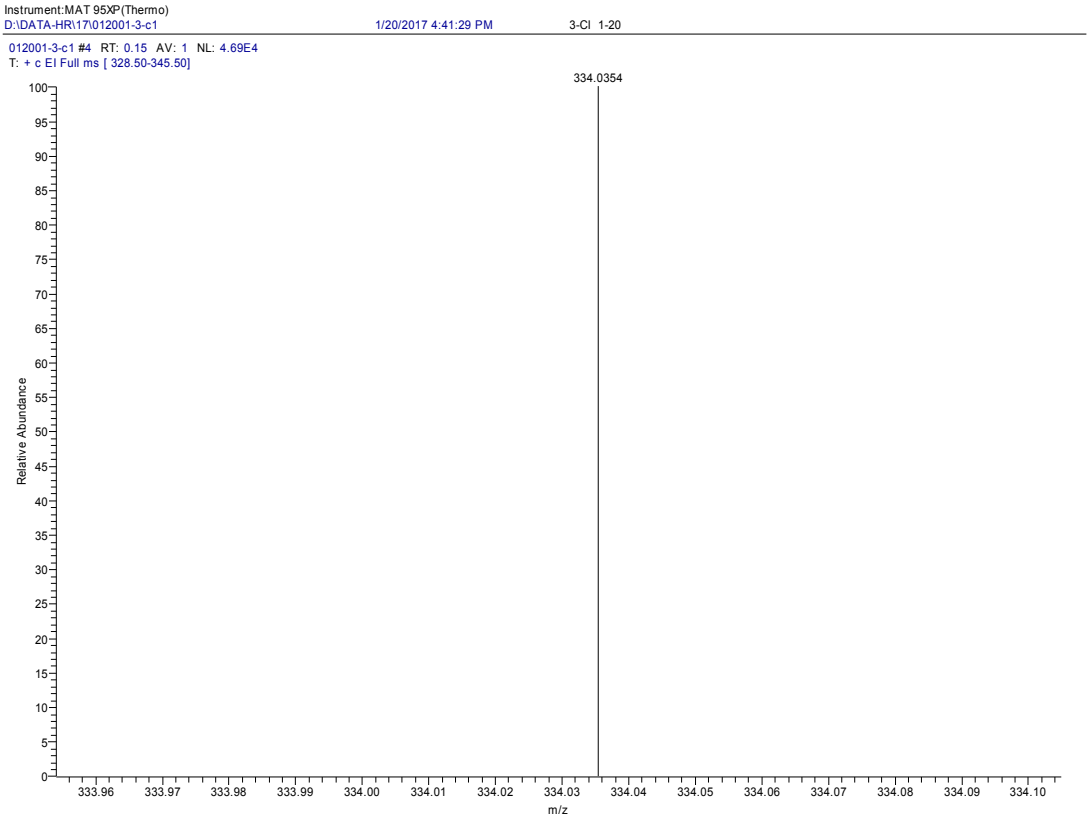
Figure S17. Molecular interaction of **BF18** in single crystals.

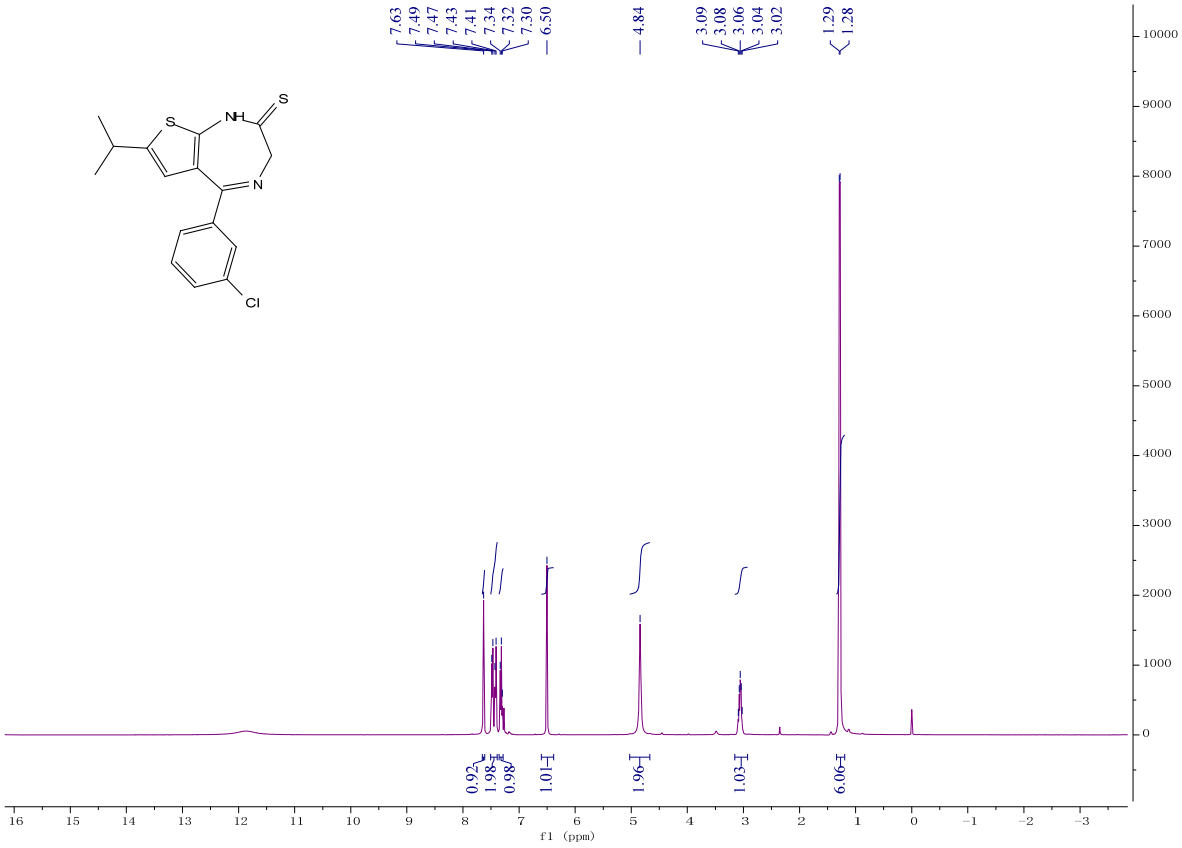


MS and NMR spectra of the new compounds

SM1



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3.04
3.02
1.29
1.28
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N
Cl
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1.96
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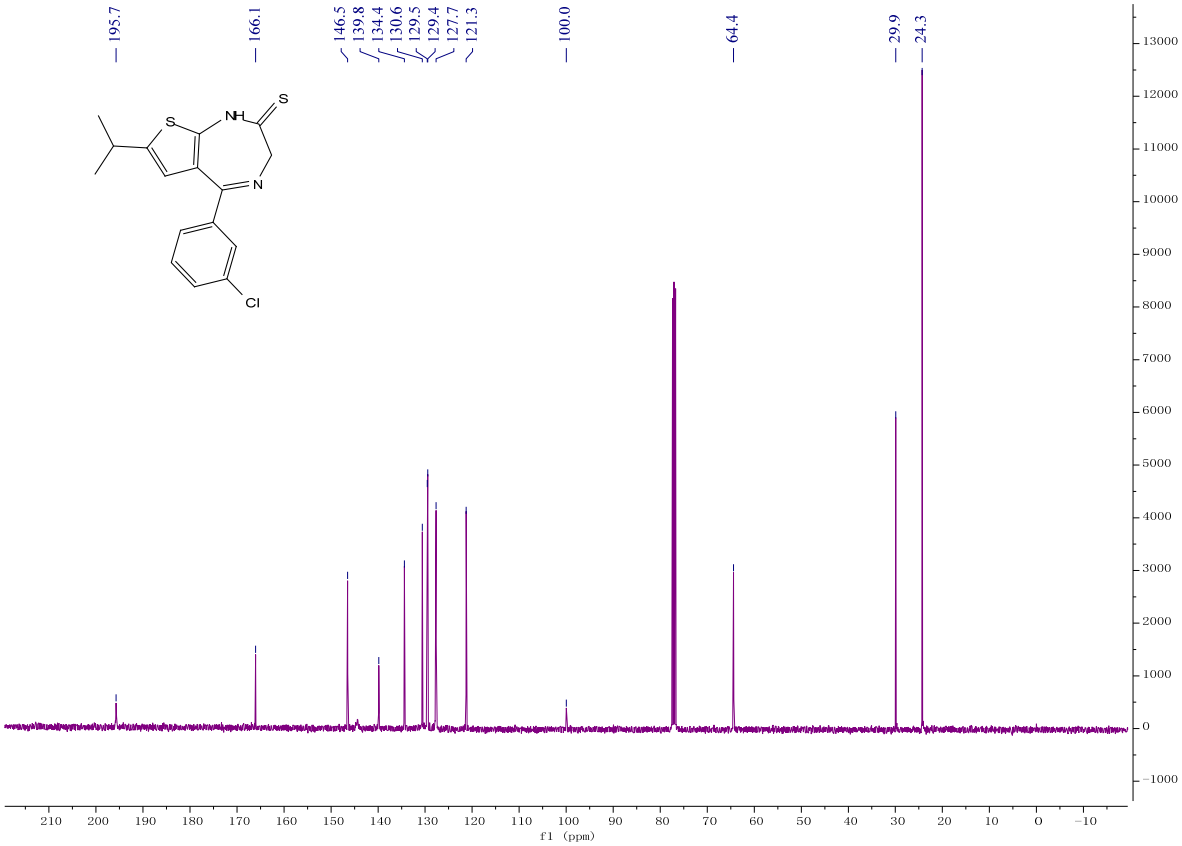
6.06
f1 (ppm)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134.4
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100.0
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29.9
24.3
S
NH
S
N
Cl
f1 (ppm)

SM2

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Ionization Method:EI
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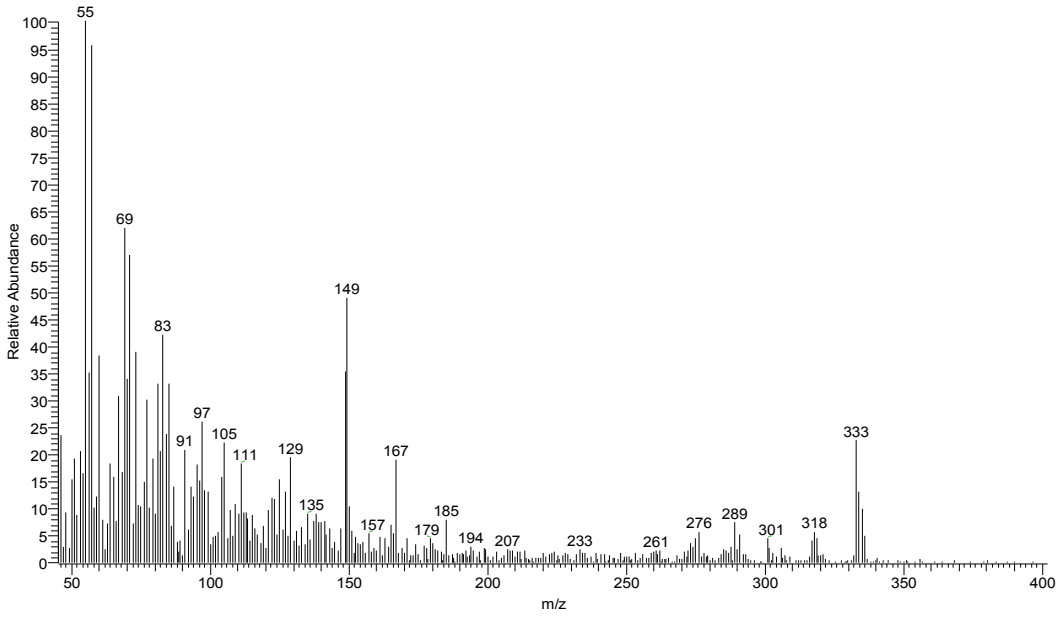
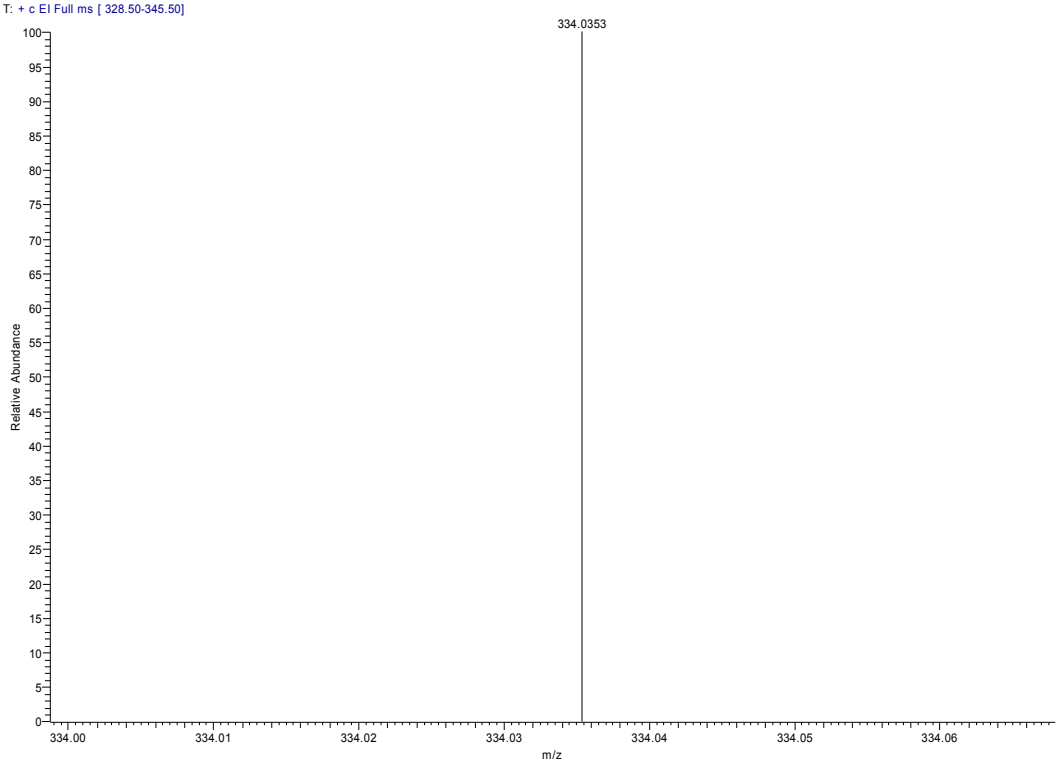
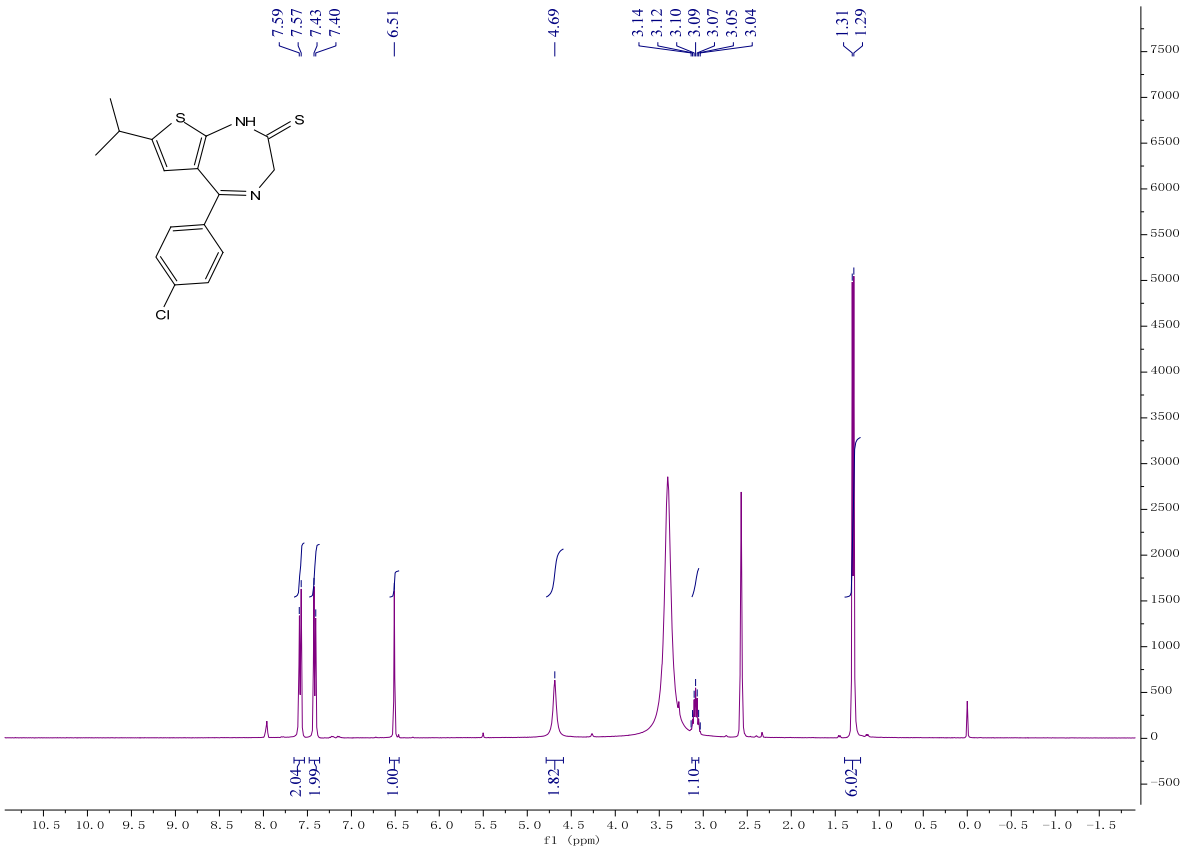
011904 #130 RT: 2.48 AV: 1 NL: 7.90E4
T: + c Full ms [45.00-600.00]

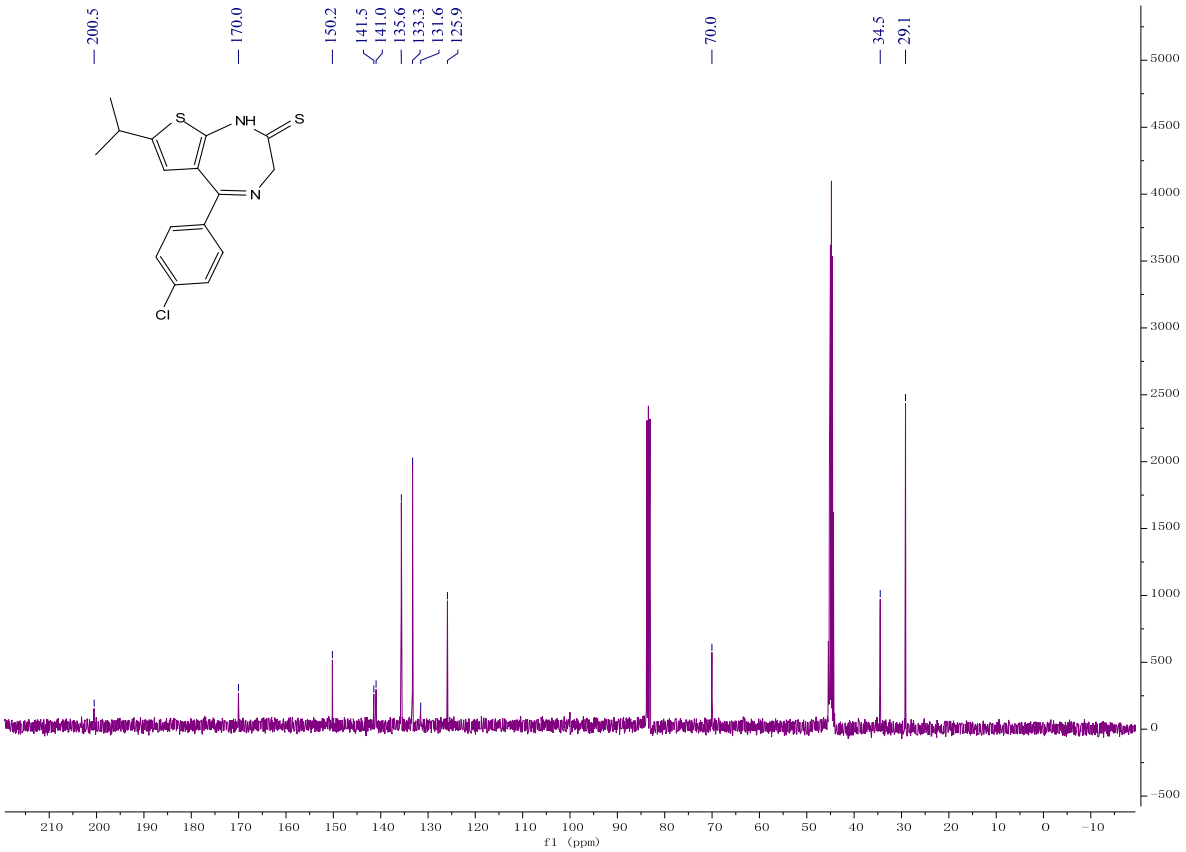


Instrument:MAT 95XP(Thermo)
D:\DATA-HR\17\011902-4-c3 1/20/2017 10:36:28 AM 4-Cl

011902-4-c3 #14 RT: 0.55 AV: 1 NL: 2.03E5
T: + c EI Full ms [328.50-345.50]



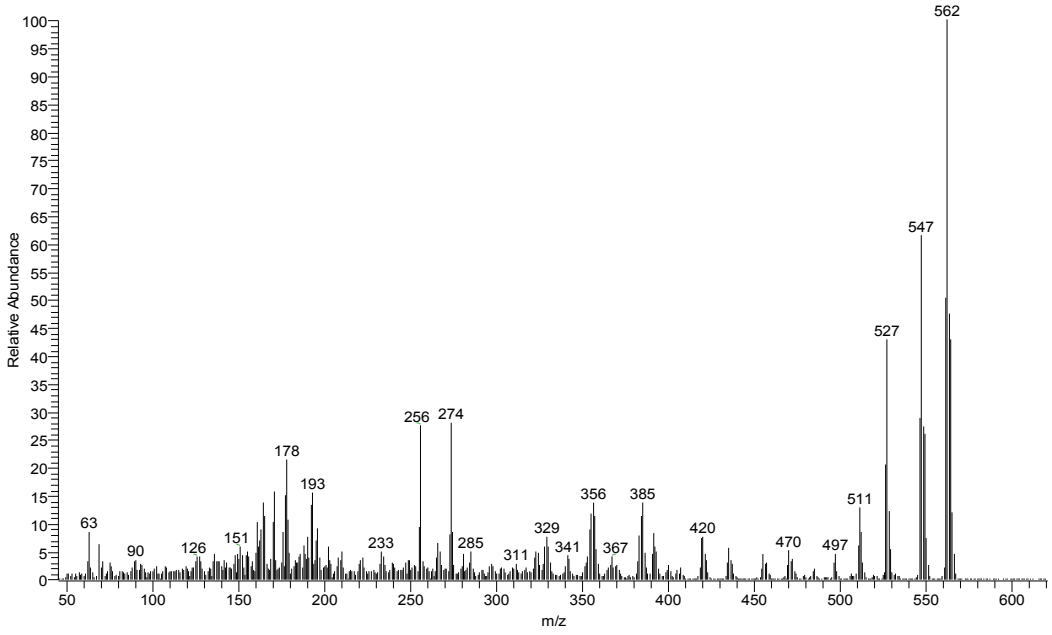

7.59
7.57
7.43
7.40
6.51
4.69
3.14
3.12
3.10
3.09
3.07
3.05
3.04
1.31
1.29
S
NH
S
N
Cl
2.04
1.99
1.00
1.82
1.10
6.02
f1 (ppm)


200.5
170.0
150.2
141.5
141.0
135.6
133.3
131.6
125.9
70.0
34.5
29.1
S
NH
S
N
Cl
f1 (ppm)

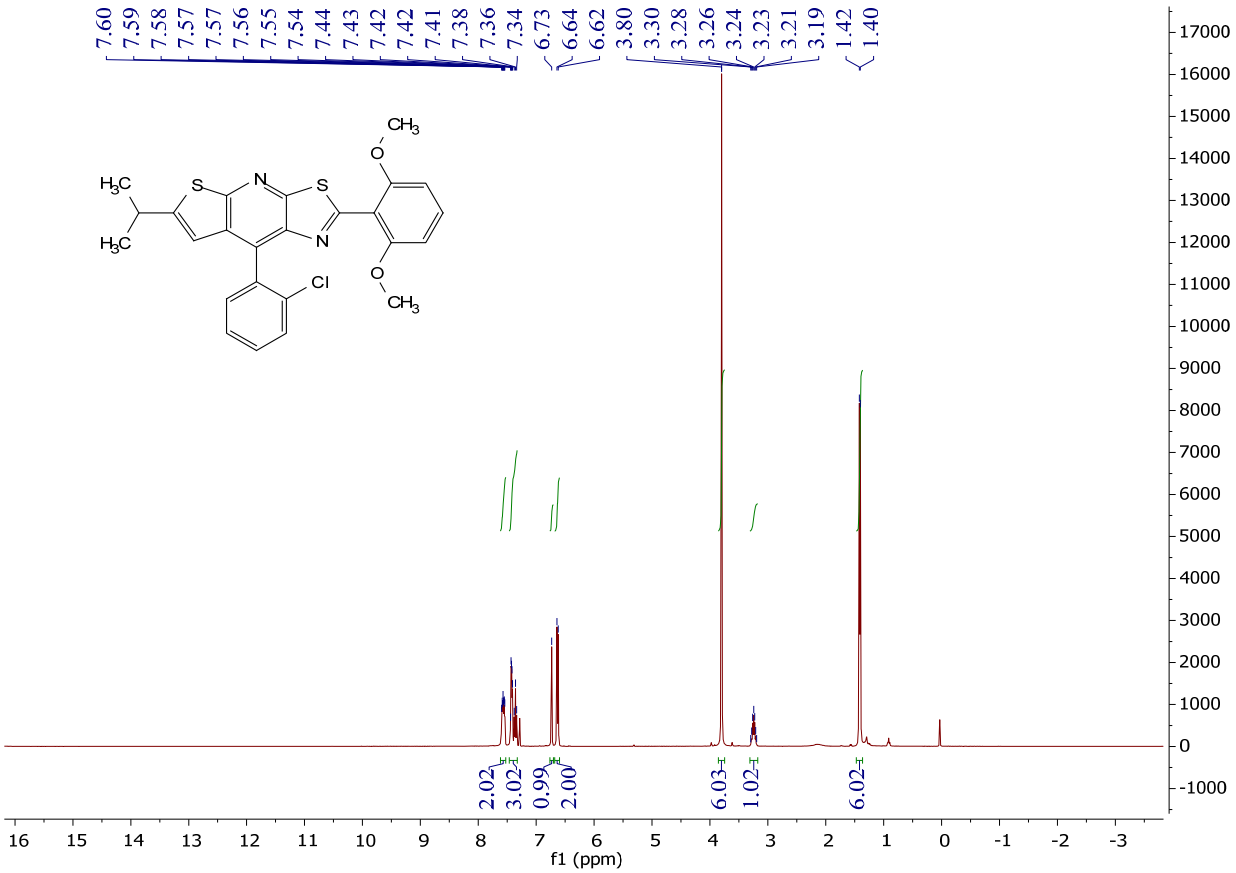
AF1

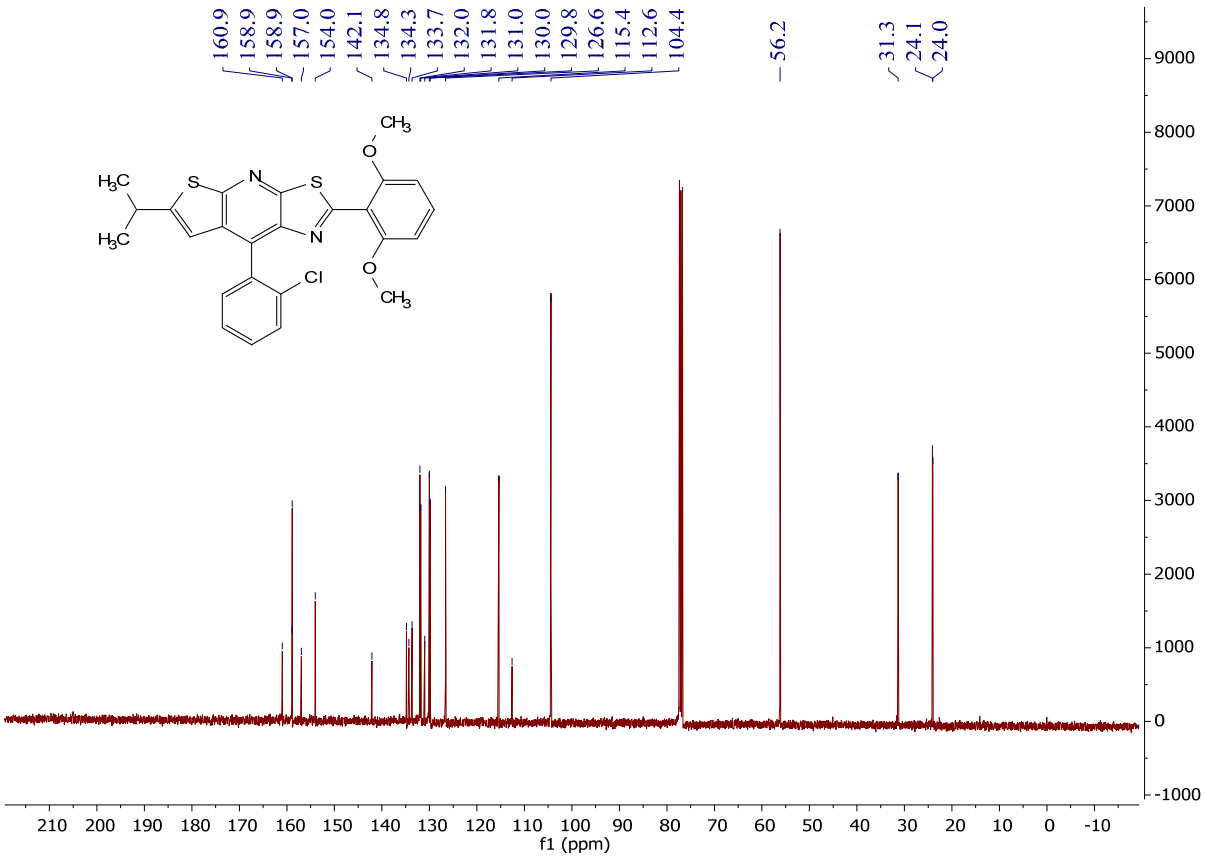
Instrument:DSQ(Thermo)
Ionization Method:EI
D:\DSQ\DATA-LR\15\072002 7/20/2015 5:05:32 PM F8

072002 #98 RT: 2.52 AV: 1 NL: 9.75E6
T: + c Full ms [45.00-800.00]



Mass	Relative Intensity	Theoretical Mass	Delta [ppm]	Delta [mmu]	RDB	Composition
480.0724	100.0	480.0727	-0.7	-0.3	16.0	C_{25} H_{21} O_7 N_2 Cl_1 S_1

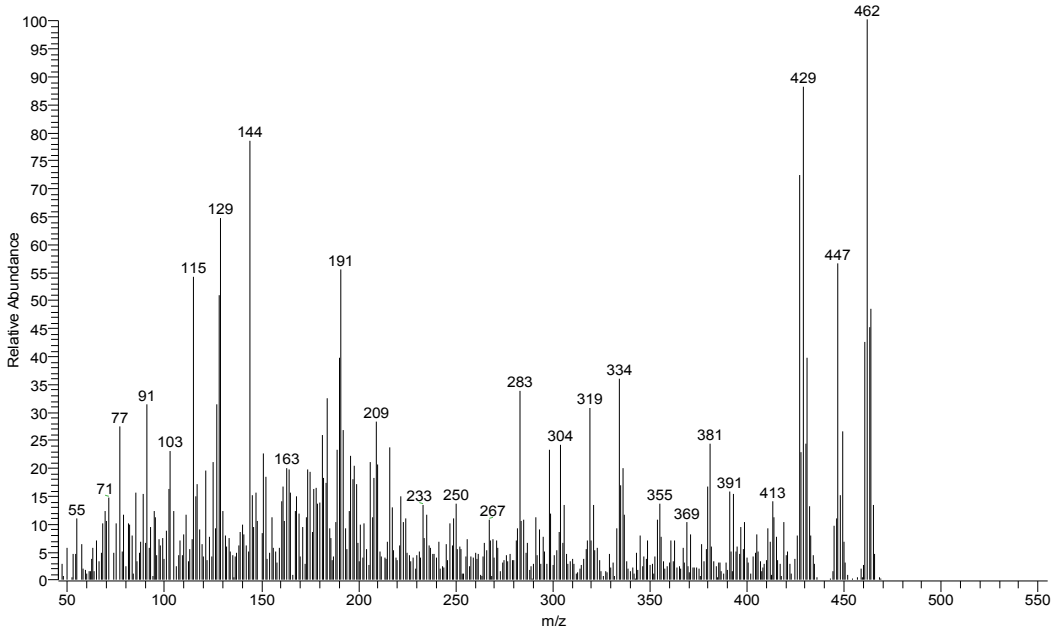

7.60
7.59
7.58
7.57
7.57
7.56
7.55
7.54
7.44
7.43
7.42
7.42
7.41
7.38
7.36
7.34
6.73
6.64
6.62
3.80
3.30
3.28
3.26
3.24
3.23
3.21
3.19
1.42
1.40
2.02
3.02
0.99
2.00
6.03
1.02
6.02
f1 (ppm)


160.9
158.9
158.9
157.0
154.0
142.1
134.8
134.3
133.7
132.0
131.8
131.0
130.0
129.8
126.6
115.4
112.6
104.4
56.2
31.3
24.1
24.0
f1 (ppm)

AF2

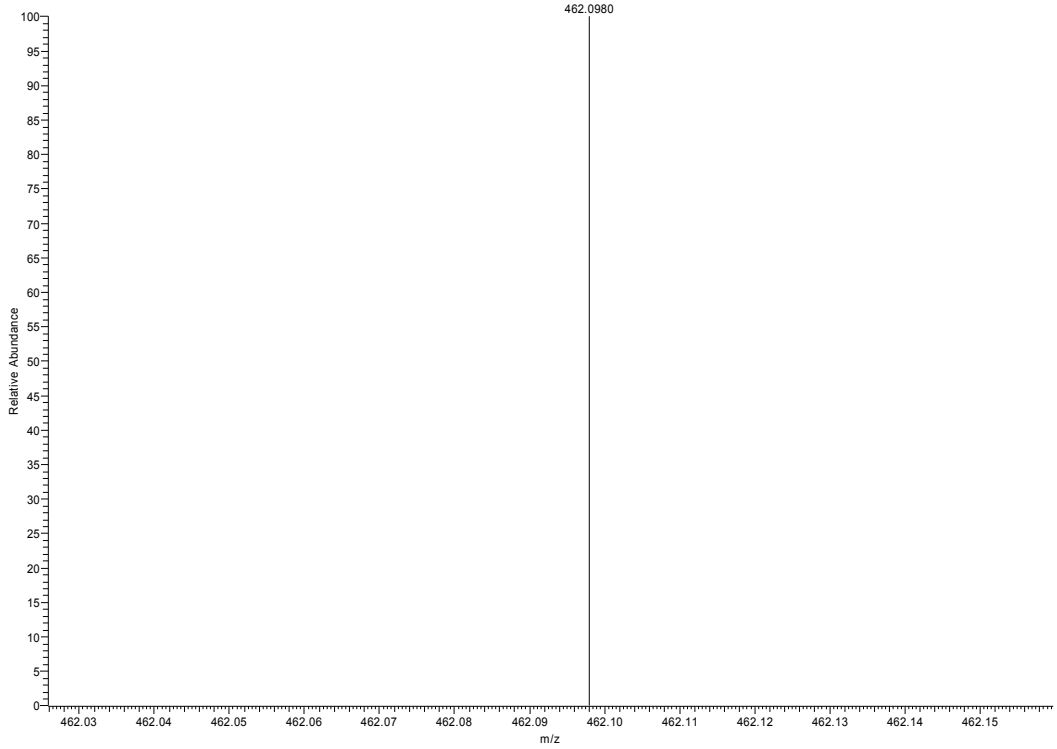
Instrument:DSQ(Thermo)
Ionization Method:EI
D:\DSQ\DATA-LR\17\010909 1/9/2017 4:18:32 PM F57

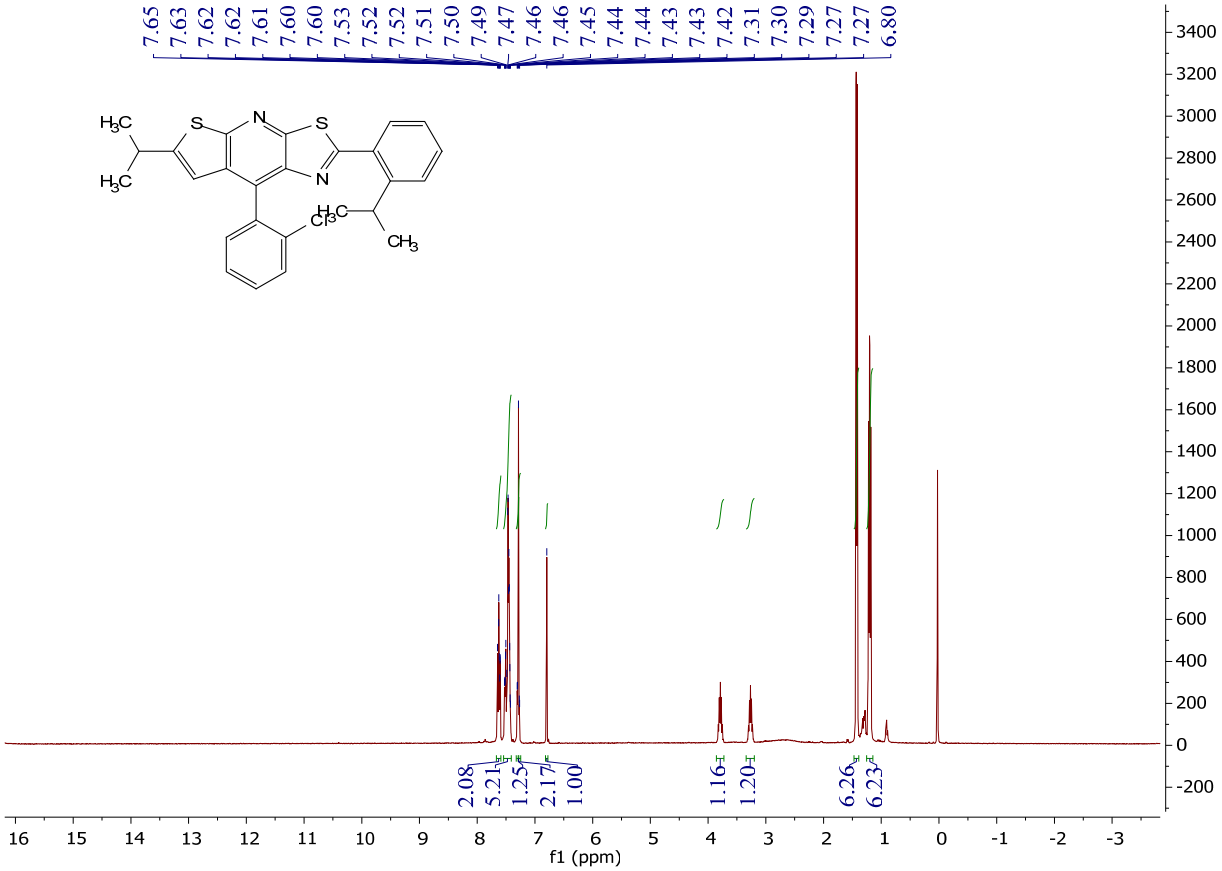
010909 #35 RT: 0.91 AV: 1 SB: 1 0.07 NL: 4.76E4
T: + c Full ms [45.00-800.00]

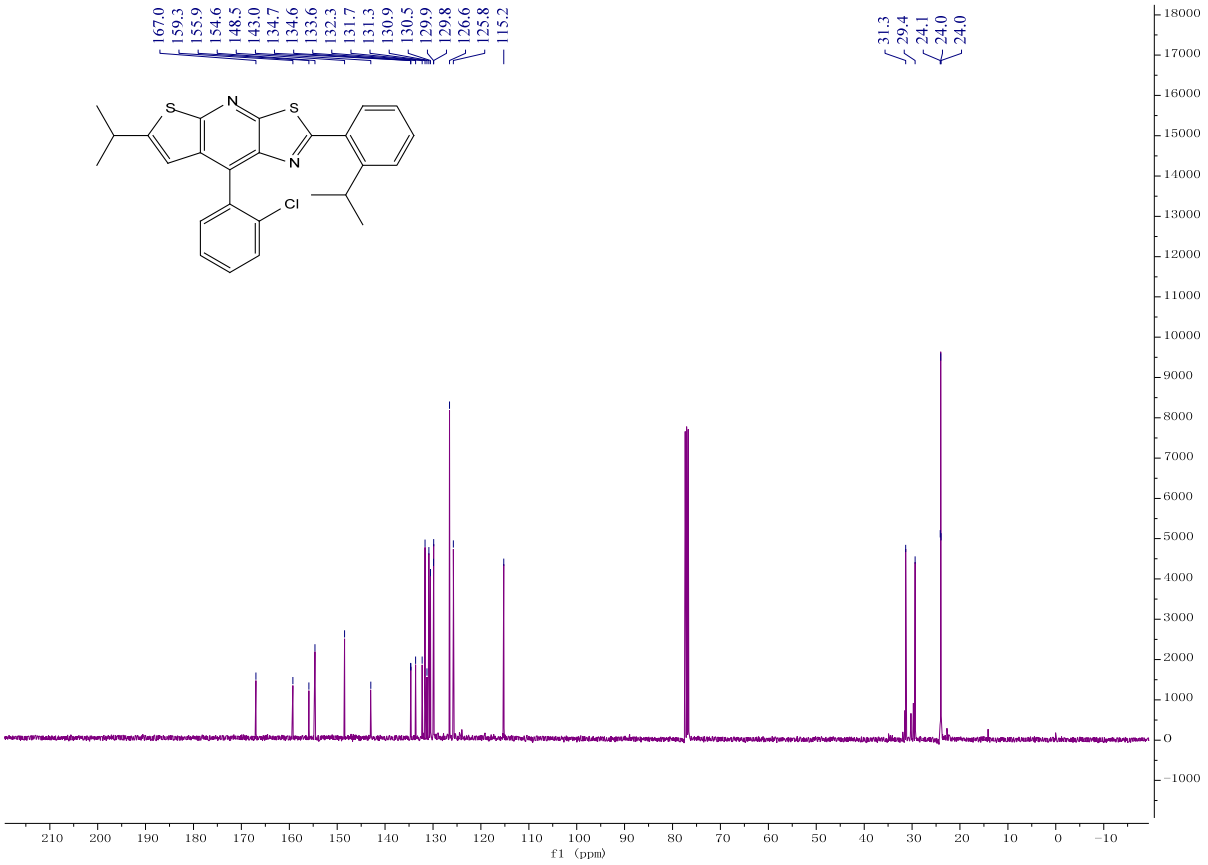


Instrument:MAT 95XP(Thermo)
D:\DATA-HR\17\011006-f57-c3 1/10/2017 5:19:25 PM F57

011006-f57-c3 #7 RT: 0.28 AV: 1 NL: 6.06E4
T: + c EI Full ms [452.50-469.50]



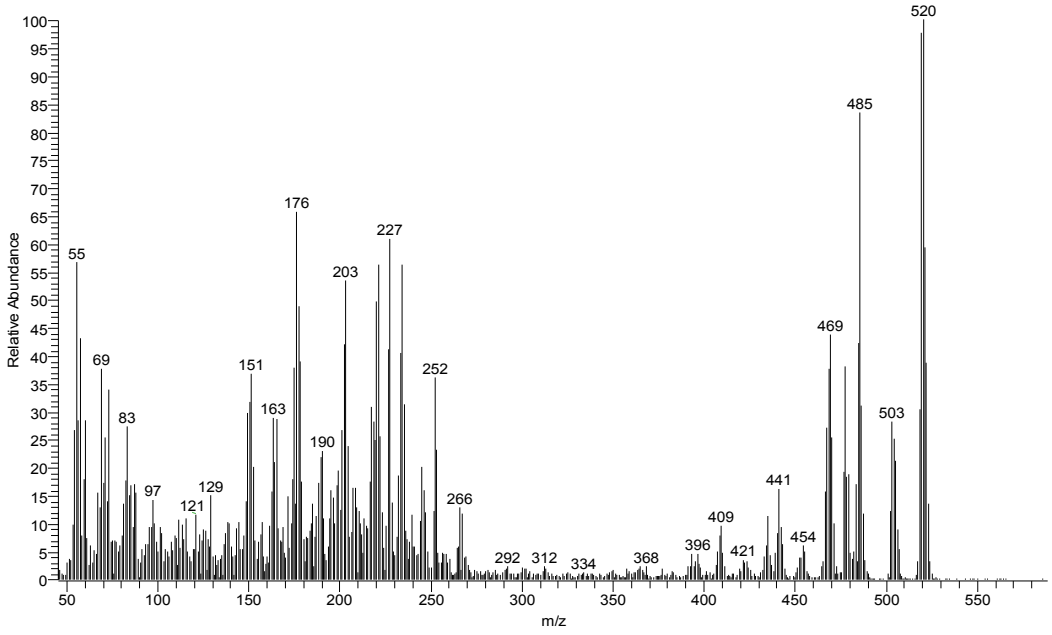

7.65
7.63
7.62
7.62
7.61
7.60
7.60
7.53
7.52
7.52
7.51
7.50
7.49
7.47
7.46
7.46
7.45
7.44
7.44
7.43
7.43
7.42
7.31
7.30
7.29
7.27
7.27
6.80
2.08
5.21
1.25
2.17
1.00
1.16
1.20
6.26
6.23
f1 (ppm)


167.0
159.3
155.9
154.6
148.5
143.0
134.7
134.6
133.6
132.3
131.7
131.3
130.9
130.5
129.9
129.8
126.6
125.8
115.2
31.3
29.4
24.1
24.0
24.0
f1 (ppm)

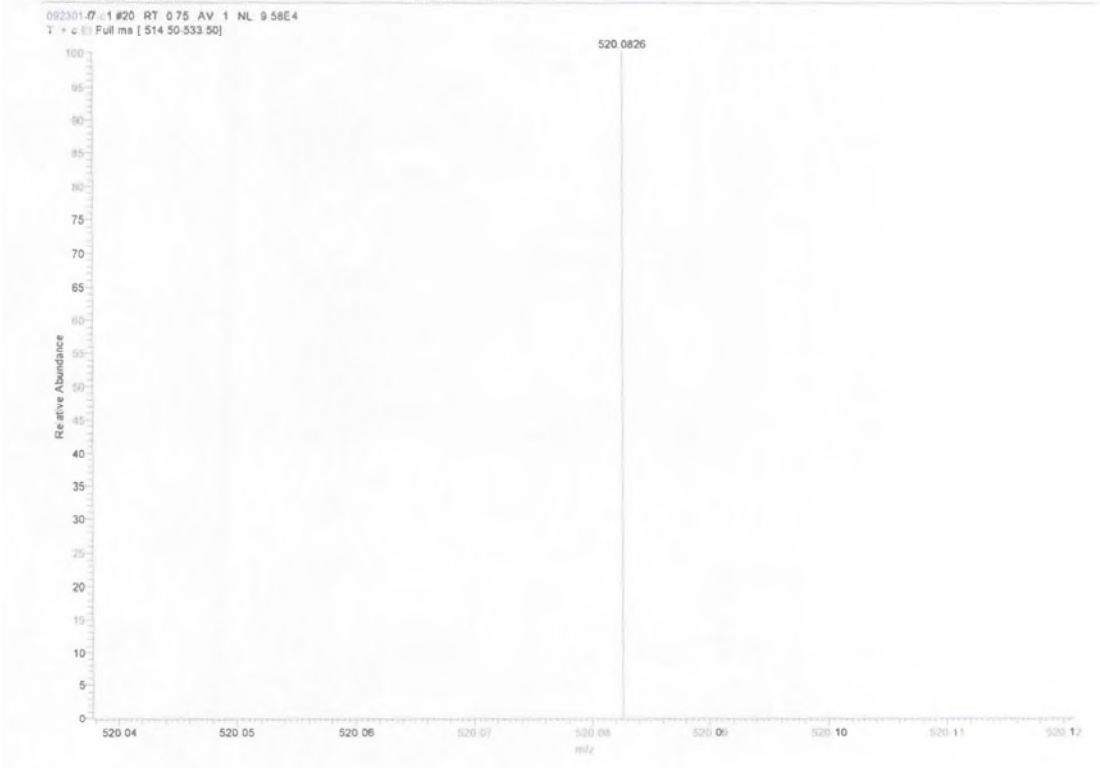
AF4

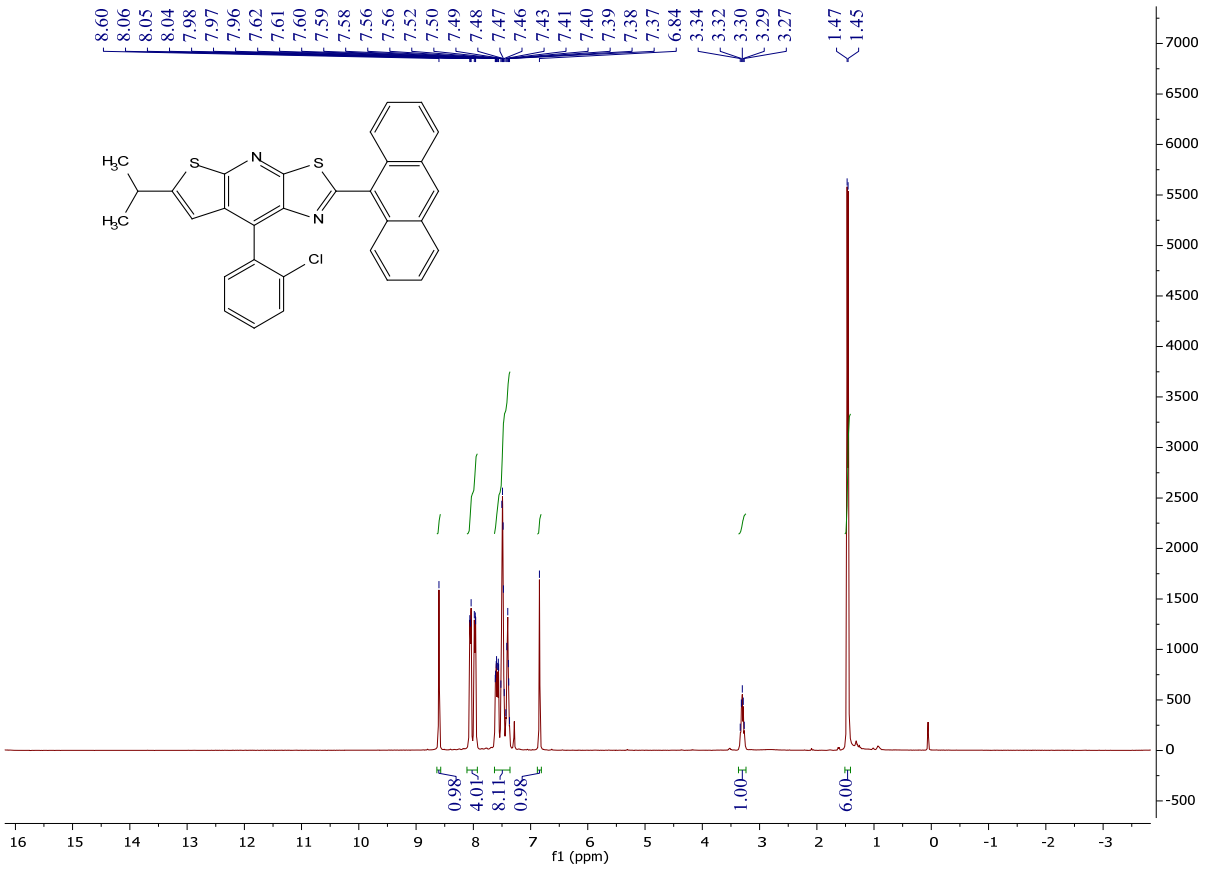
Instrument:DSQ(Thermo)
Ionization Method:EI
D:\DSQ\DATA-LR\15\072003 7/20/2015 5:20:17 PM F7

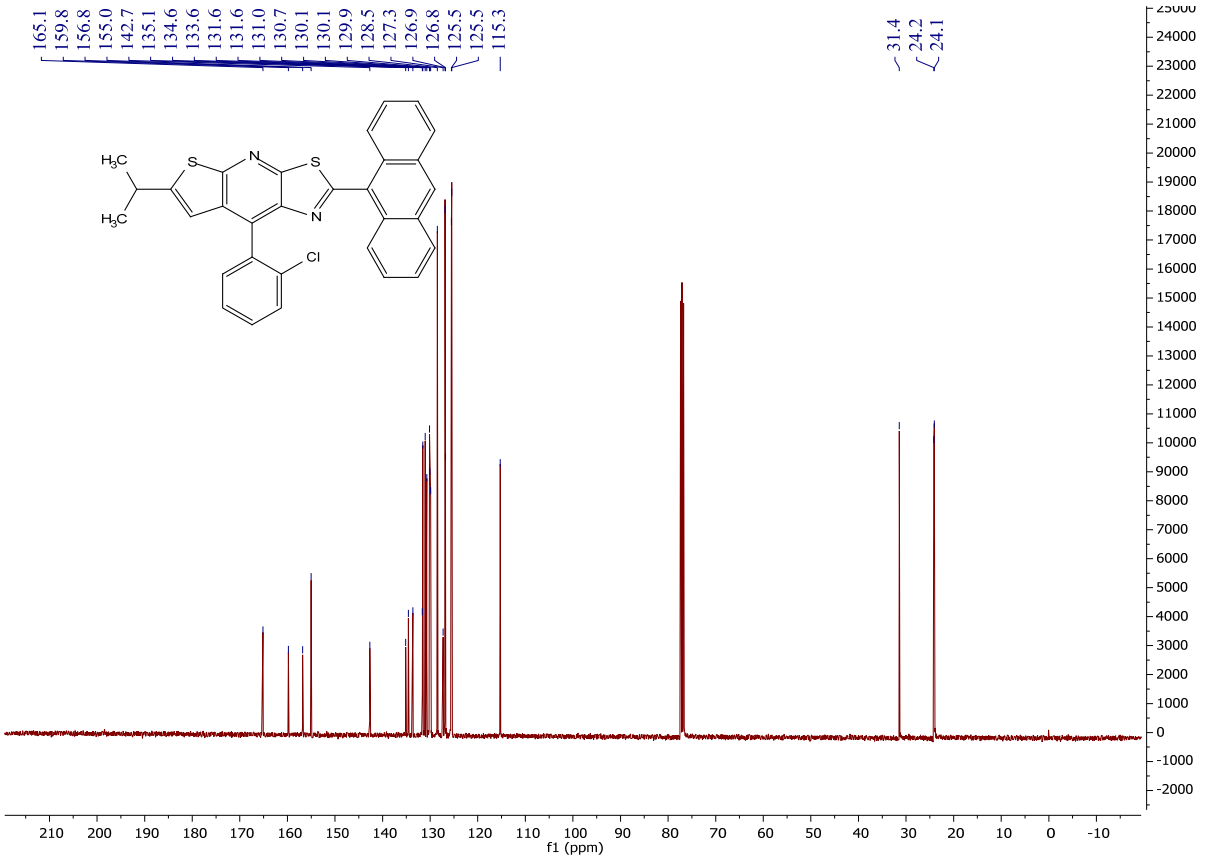
072003 #107 RT: 2.75 AV: 1 NL: 3.10E5
T: + c Full ms [45.00-800.00]



Mass	Relative Intensity	Theoretical Mass	Delta [ppm]	Delta [mmu]	RDB	Composition
520.0826	100.0	520.0829	-0.6	-0.3	22.0	C_{31} H_{21} N_3 Cl_1 S_2



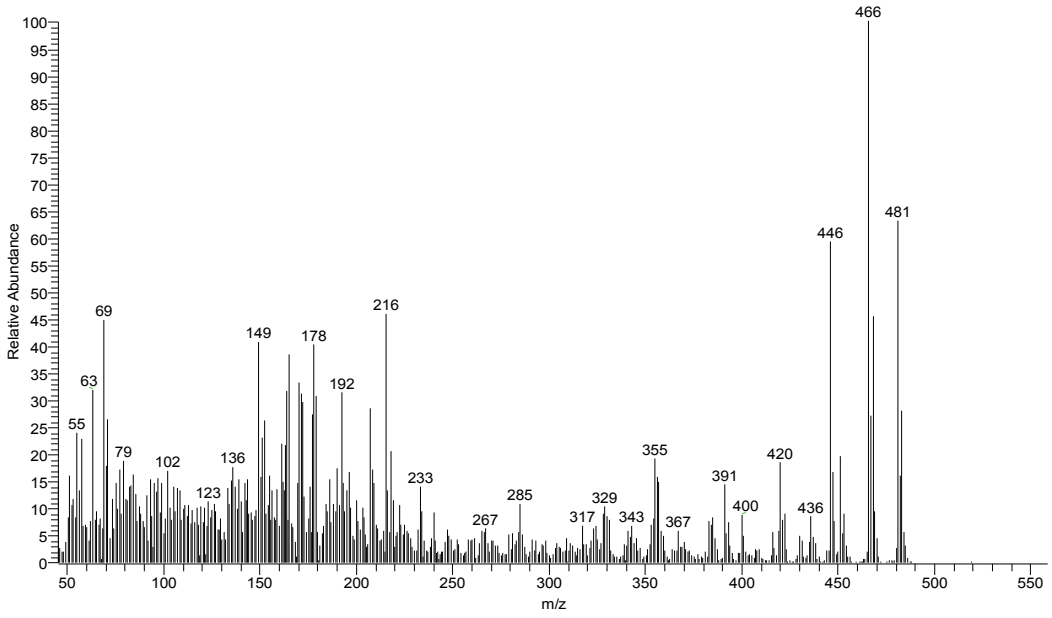

8.60
8.06
8.05
8.04
7.98
7.97
7.96
7.62
7.61
7.60
7.59
7.58
7.56
7.56
7.52
7.50
7.49
7.48
7.47
7.46
7.43
7.41
7.40
7.39
7.38
7.37
6.84
3.34
3.32
3.30
3.29
3.27
1.47
1.45
H3C
H3C
S
N
S
N
Cl
0.98
4.01
8.11
0.98
1.00
6.00
f1 (ppm)


165.1
159.8
156.8
155.0
142.7
135.1
134.6
133.6
131.6
131.6
131.0
130.7
130.1
130.1
129.9
128.5
127.3
126.9
126.8
125.5
125.5
115.3
31.4
24.2
24.1
H3C
H3C
S
N
S
N
Cl
f1 (ppm)

BF1

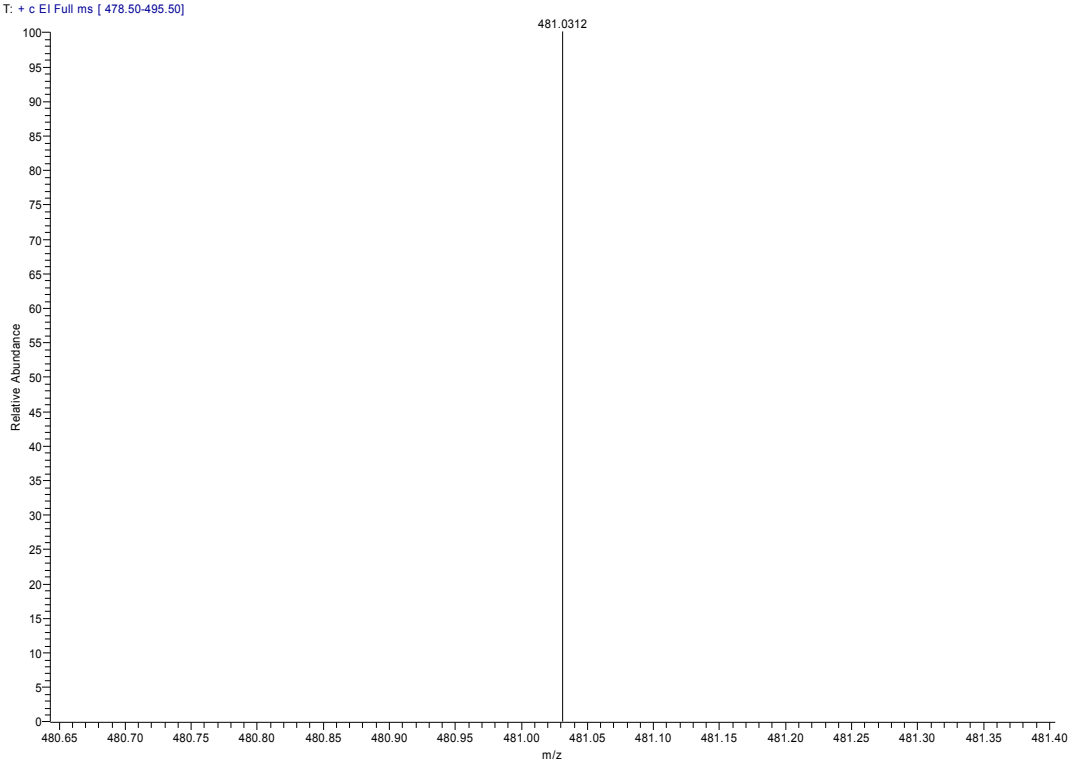
Instrument:DSQ(Thermo)
Ionization Method:EI
D:\DSQ\DATA-LR\16\060717 6/7/2016 4:51:26 PM F36

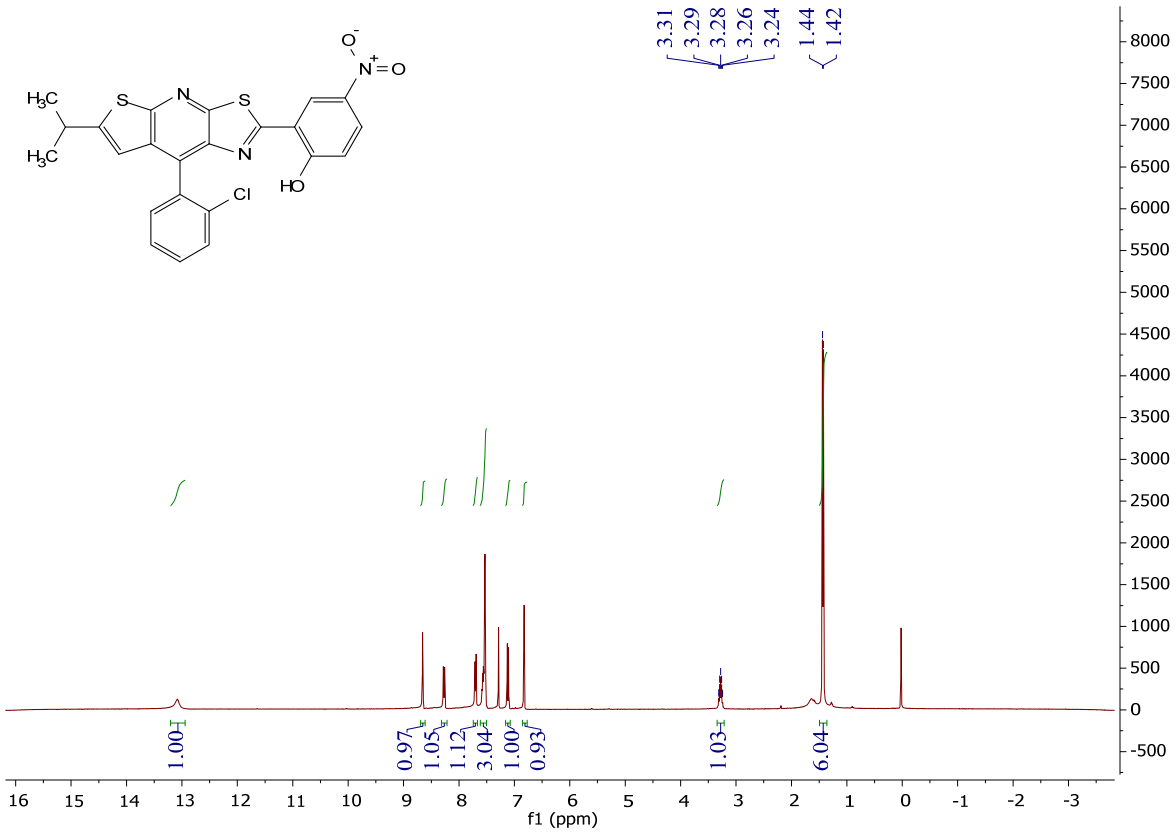
060717 #66 RT: 1.70 AV: 1 NL: 1.59E5
T: + c Full ms [45.00-800.00]

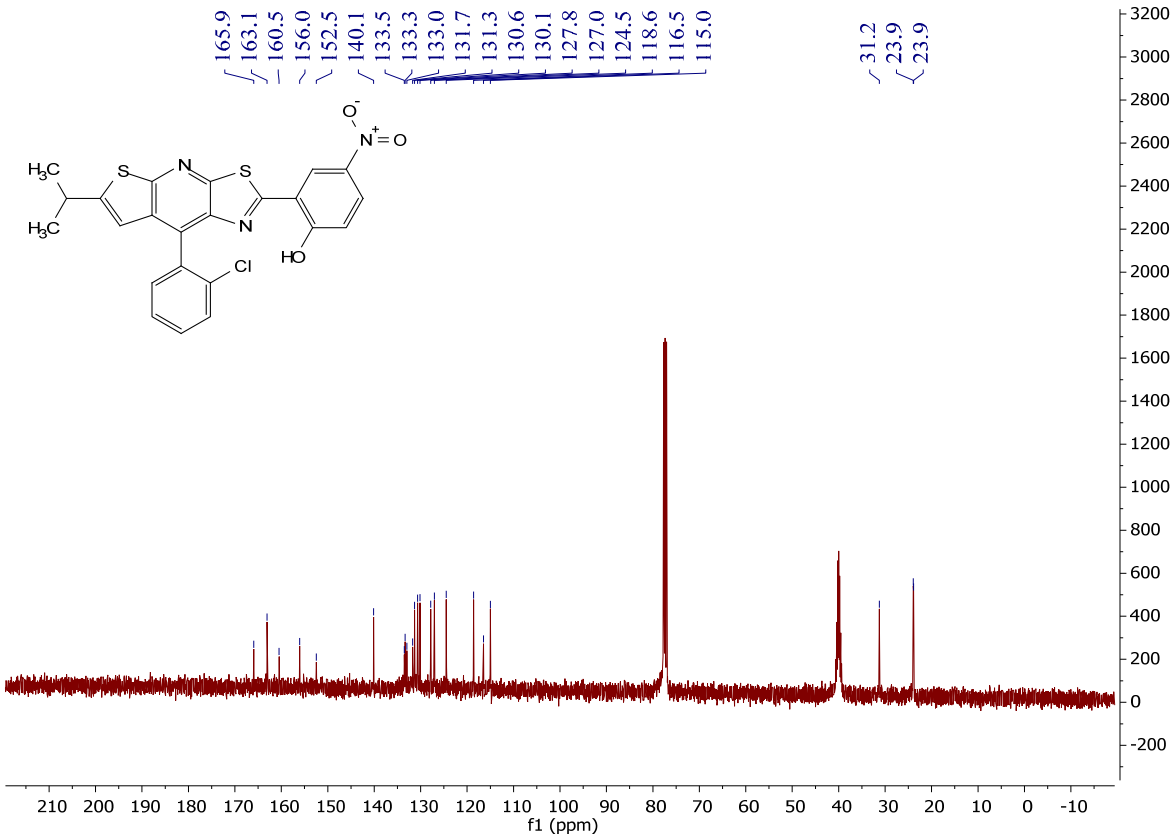


Instrument:MAT 95XP(Thermo)
D:\DATA-HR\16\062002-f36-c1 6/20/2016 4:23:55 PM F36

062002-f36-c1 #12 RT: 0.48 AV: 1 NL: 6.97E4
T: + c EI Full ms [478.50-495.50]



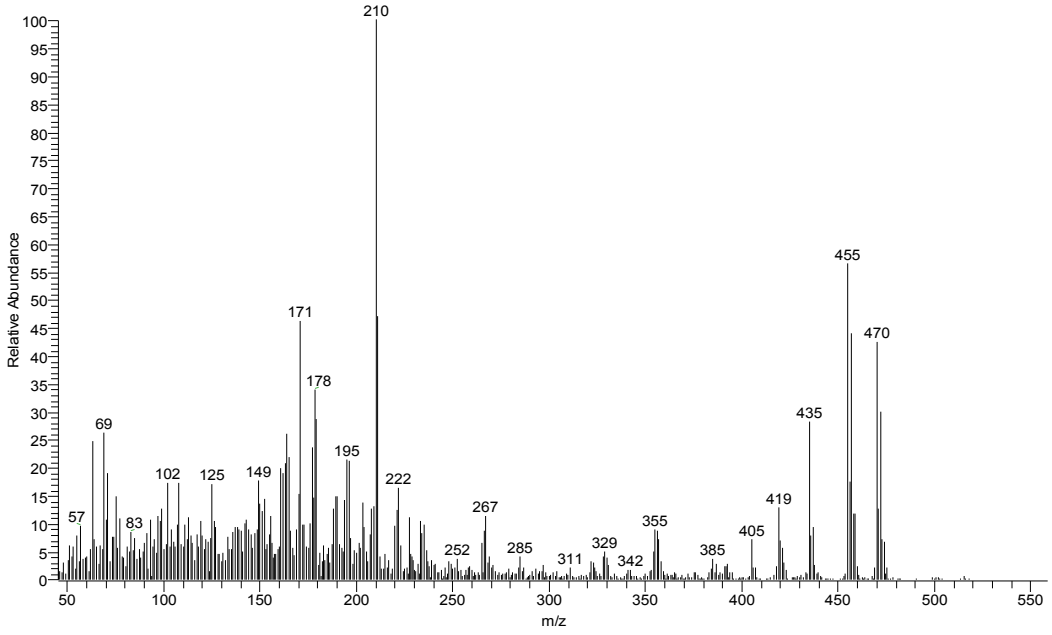

3.31
3.29
3.28
3.26
3.24
1.44
1.42
1.00
0.97
1.05
1.12
3.04
1.00
0.93
1.03
6.04
f1 (ppm)


165.9
163.1
160.5
156.0
152.5
140.1
133.5
133.3
133.0
131.7
131.3
130.6
130.1
127.8
127.0
124.5
118.6
116.5
115.0
31.2
23.9
23.9
f1 (ppm)

BF2

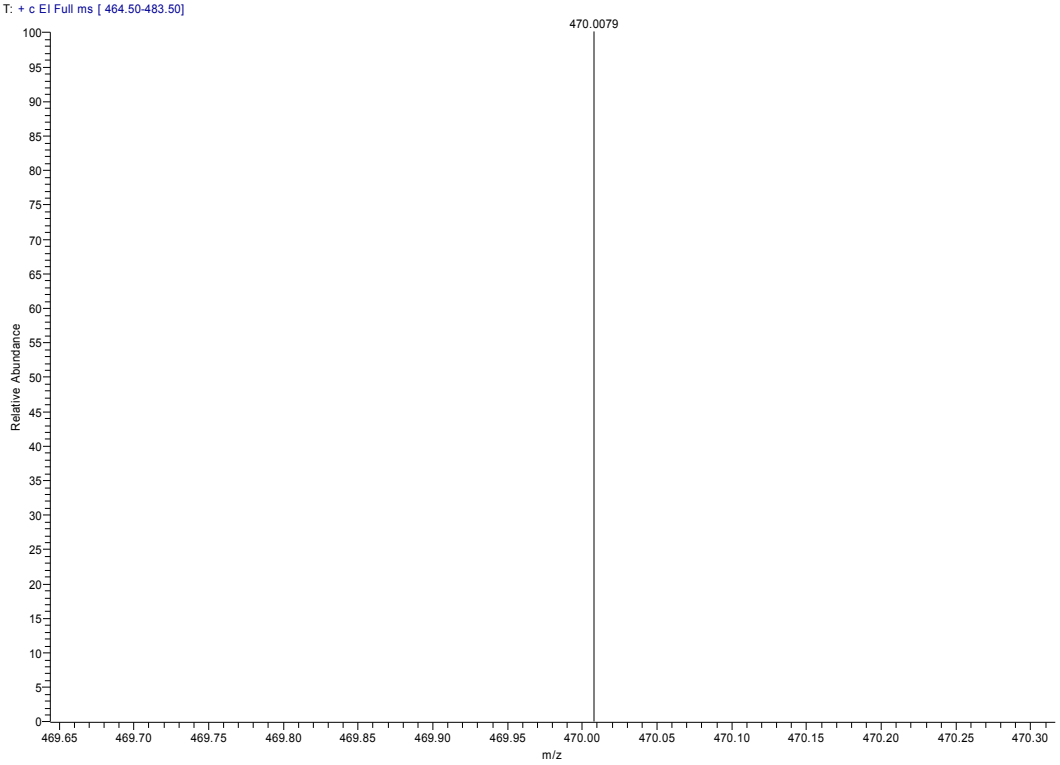
Instrument:DSQ(Thermo)
Ionization Method:EI
D:\DSQ\DATA-LR\16\062302 6/23/2016 4:31:51 PM F42

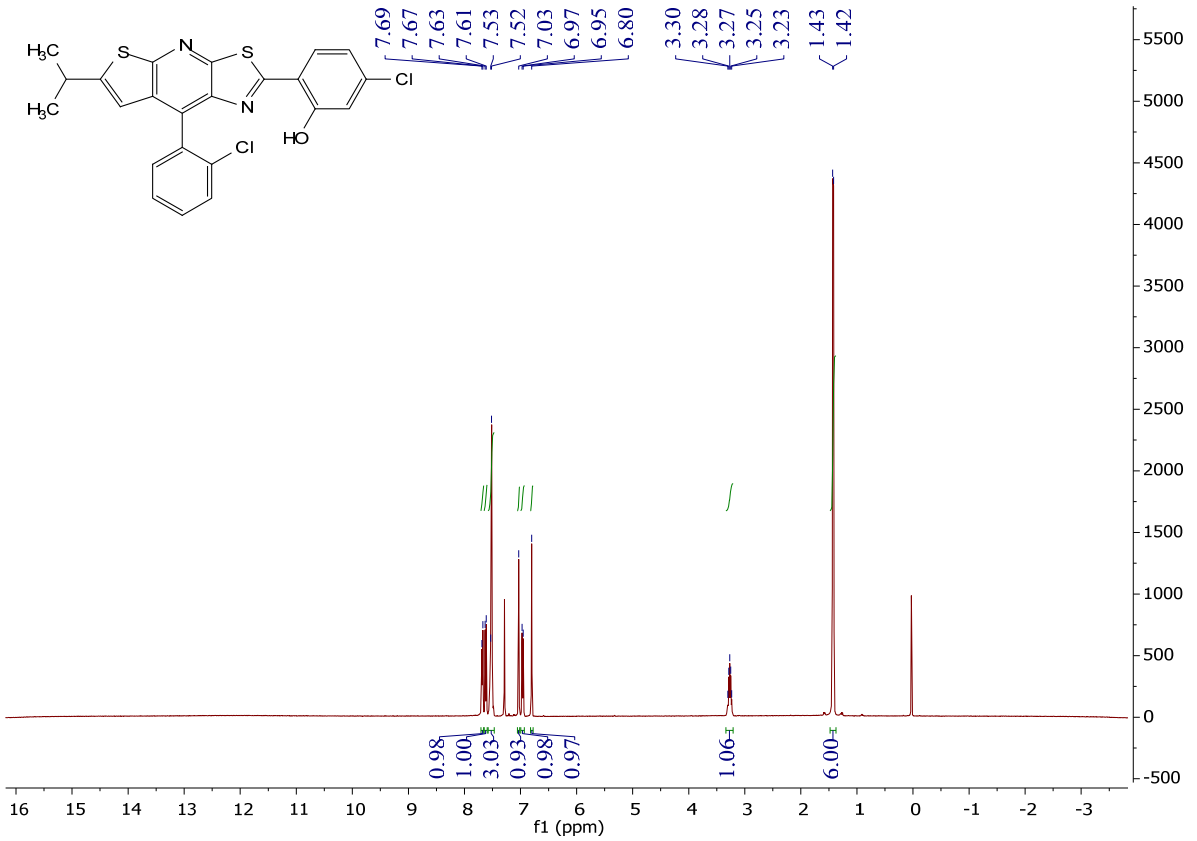
062302 #56 RT: 1.45 AV: 1 NL: 1.81E5
T: + c Full ms [45.00-800.00]

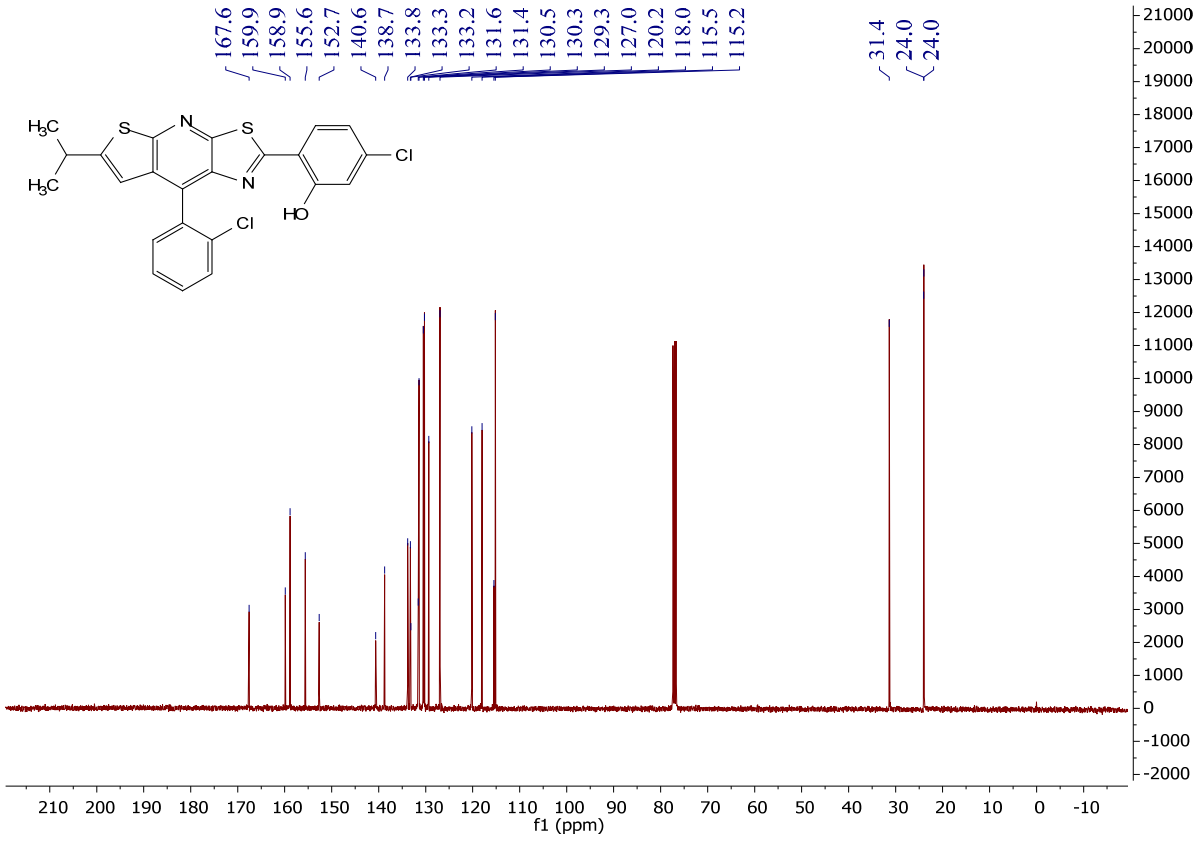


Instrument:MAT 95XP(Thermo)
D:\DATA-HR\16\062402-f42-c1 6/24/2016 11:53:59 AM F42

062402-f42-c1 #15 RT: 0.58 AV: 1 NL: 2.19E5
T: + c EI Full ms [464.50-483.50]



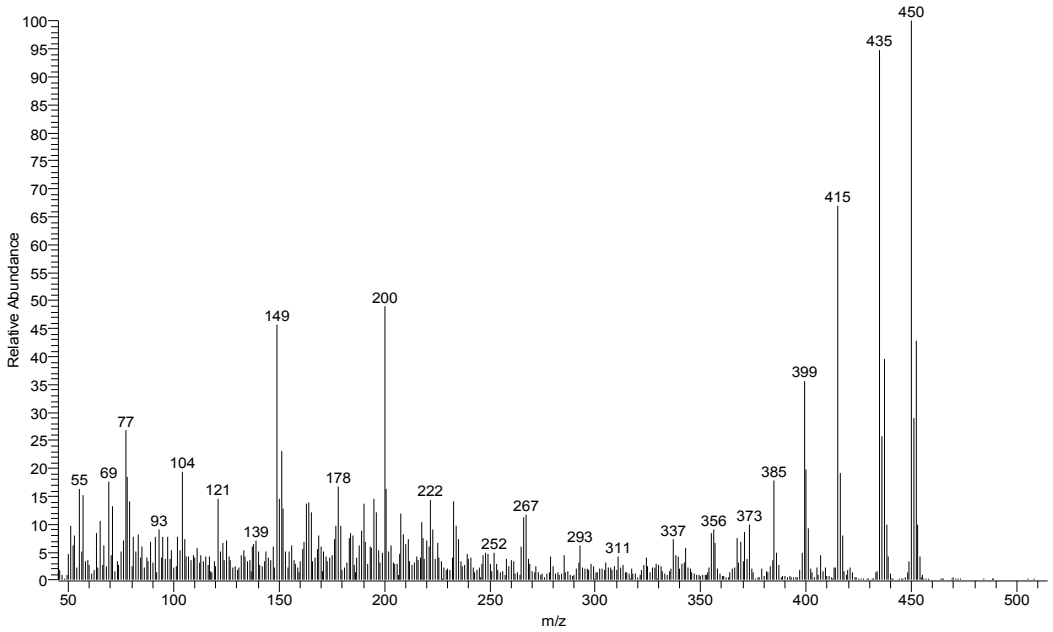

7.69
7.67
7.63
7.61
7.53
7.52
7.03
6.97
6.95
6.80
3.30
3.28
3.27
3.25
3.23
1.43
1.42
0.98
1.00
3.03
0.93
0.98
0.97
1.06
6.00
f1 (ppm)


167.6
159.9
158.9
155.6
152.7
140.6
138.7
133.8
133.3
133.2
131.6
131.4
130.5
130.3
129.3
127.0
120.2
118.0
115.5
115.2
31.4
24.0
24.0
f1 (ppm)

BF3

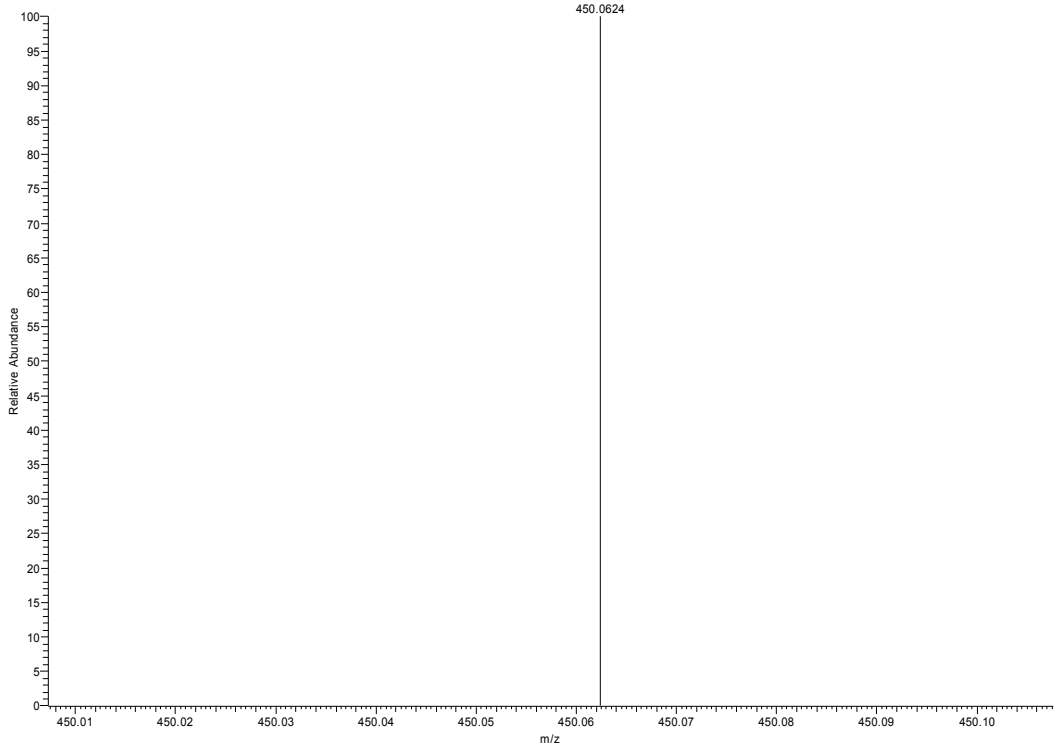
Instrument:DSQ(Thermo)
Ionization Method:EI
D:\DSQ\DATA-LR\16\102403 10/24/2016 11:59:14 AM F68

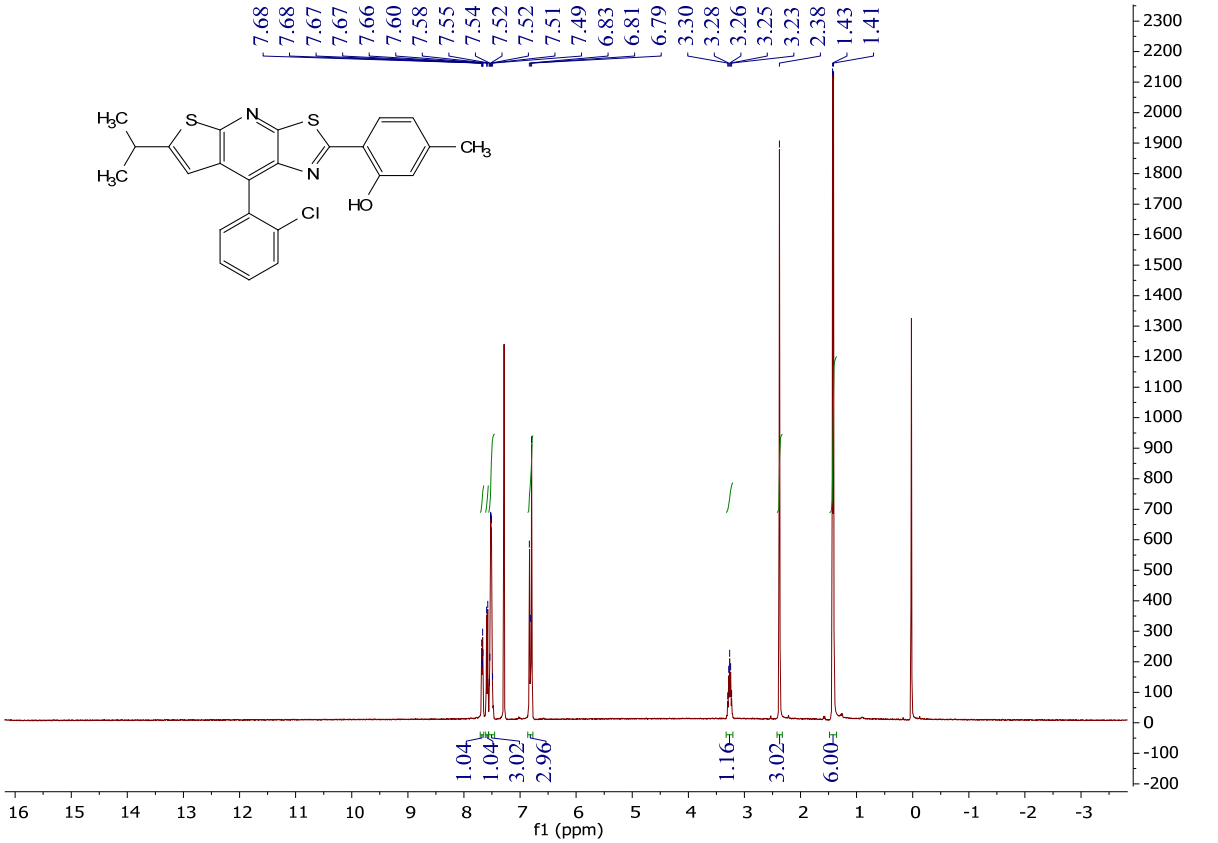
102403 #62 RT: 1.60 AV: 1 NL: 3.08E5
T: + c Full ms [45.00-800.00]

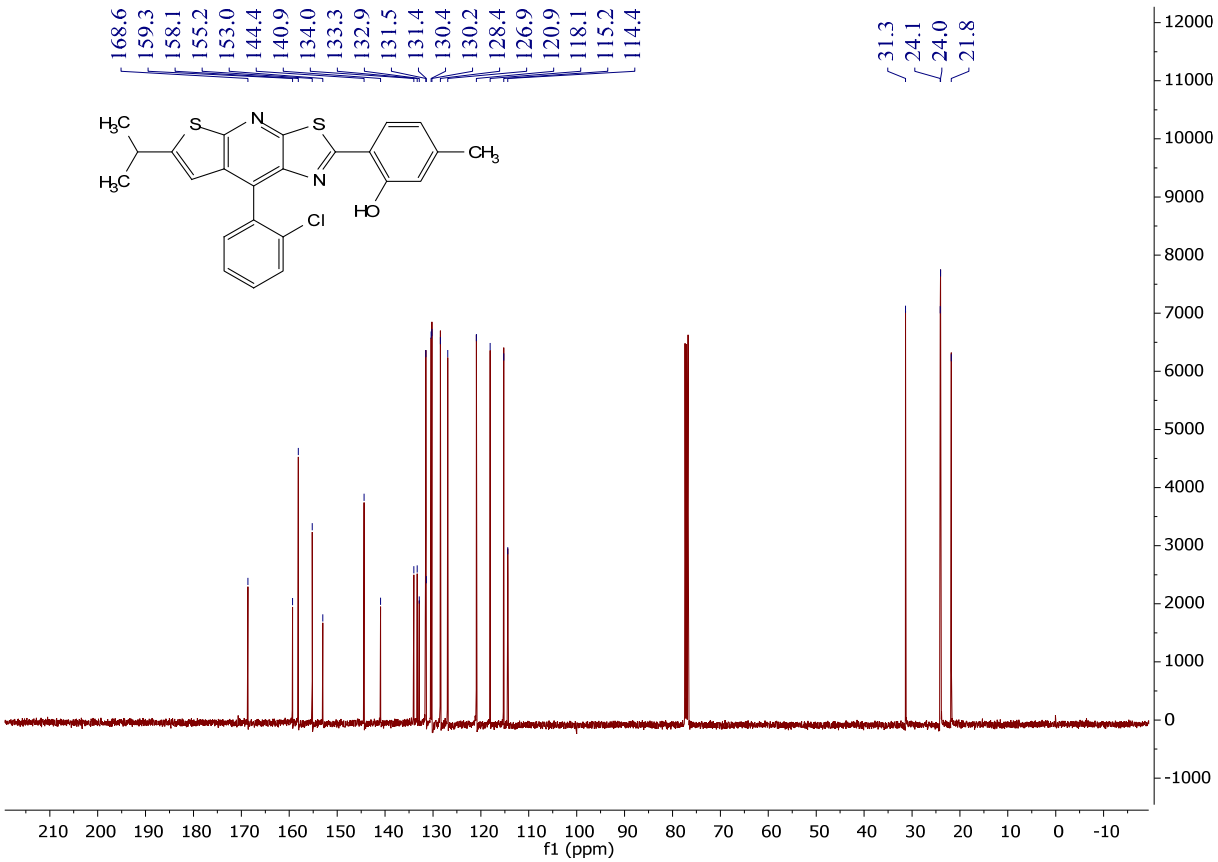


Instrument:MAT 95XP(Thermo)
D:\DATA-HR\16\102703-f68-c3 10/27/2016 9:47:28 AM F68

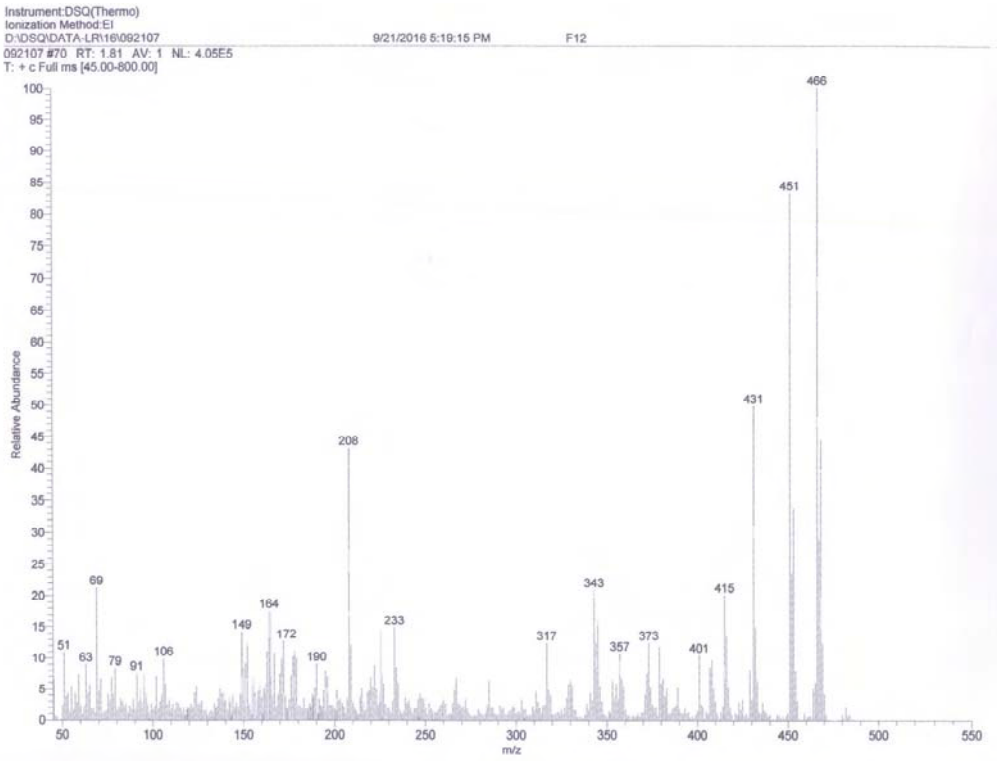
102703-f68-c3 #14 RT: 0.52 AV: 1 NL: 1.84E5
T: + c EI Full ms [440.50-457.50]



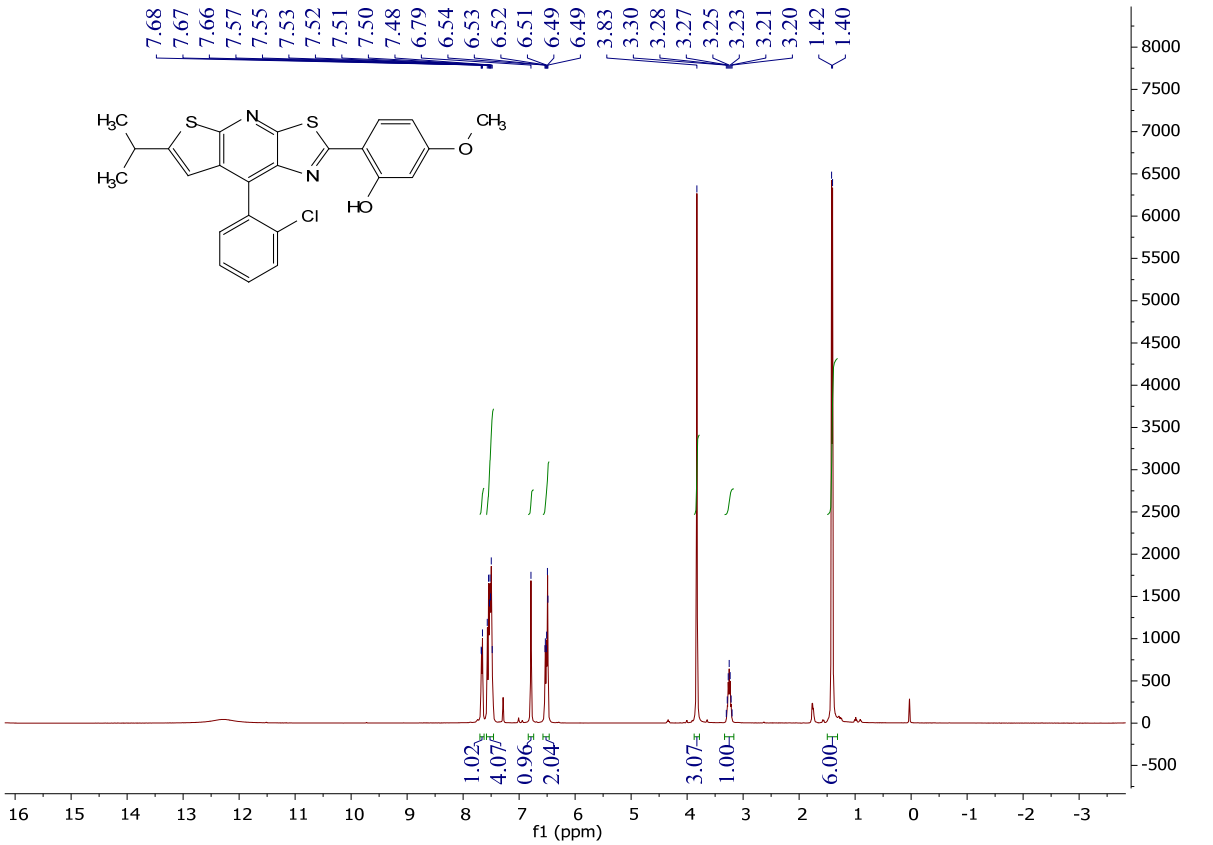

7.68
7.68
7.67
7.67
7.66
7.60
7.58
7.55
7.54
7.52
7.52
7.51
7.49
6.83
6.81
6.79
3.30
3.28
3.26
3.25
3.23
2.38
1.43
1.41
1.04
1.04
3.02
2.96
1.16
3.02
6.00
f1 (ppm)

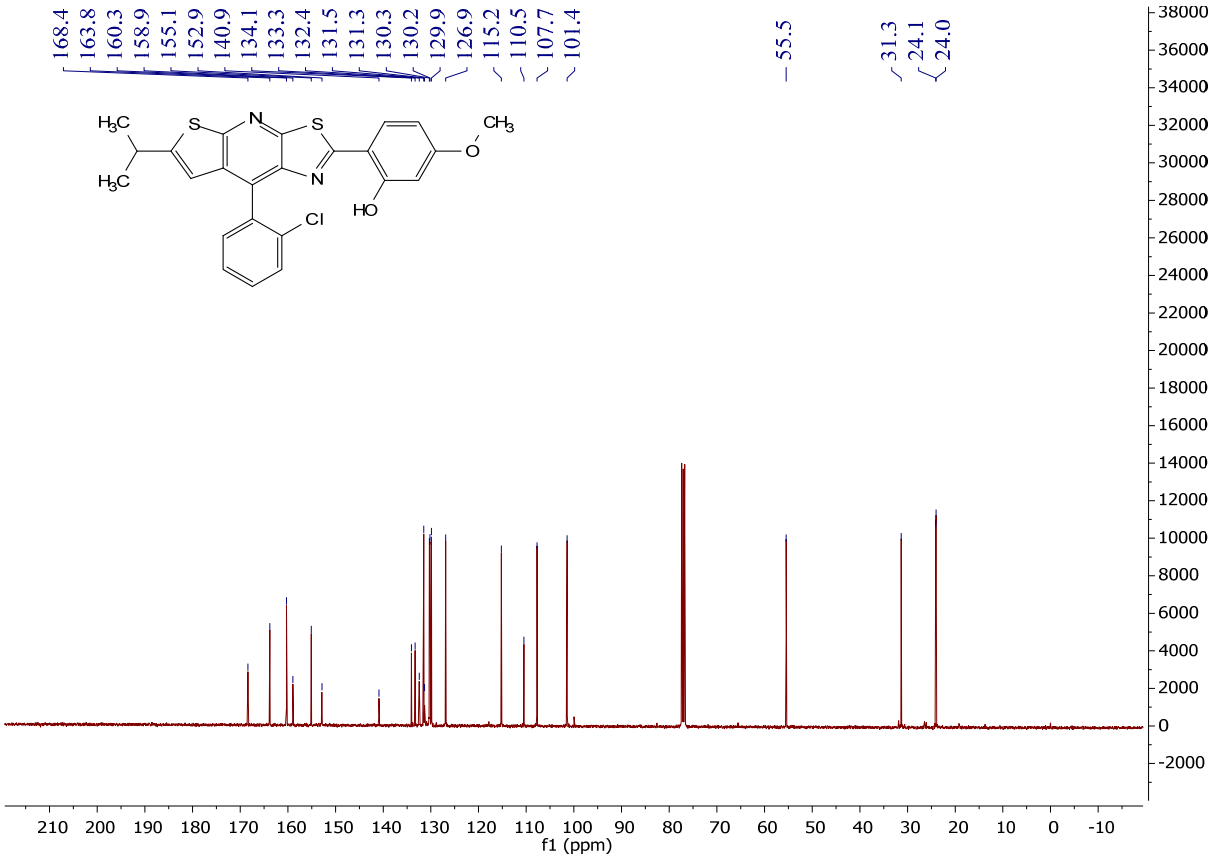

168.6
159.3
158.1
155.2
153.0
144.4
140.9
134.0
133.3
132.9
131.5
131.4
130.4
130.2
128.4
126.9
120.9
118.1
115.2
114.4
31.3
24.1
24.0
21.8
f1 (ppm)

BF4



Mass	Relative Intensity	Theoretical Mass	Delta [ppm]	Delta [mmu]	RDB	Composition
466.0573	100.0	466.0571	0.5	0.2	16.0	$C_{34}H_{19}O_7N_3Cl_1S_2$

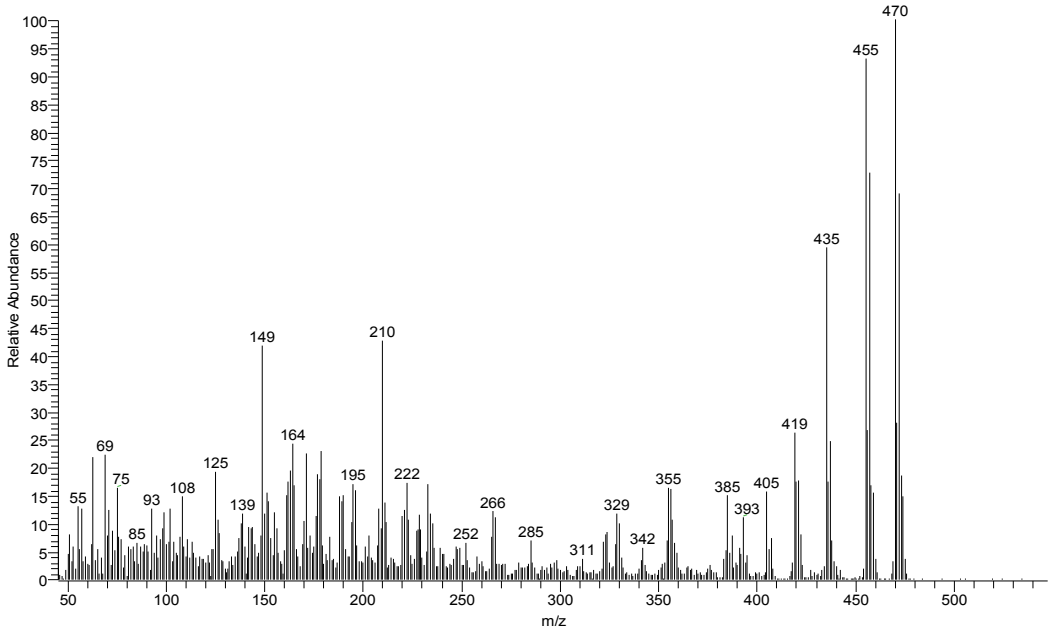

7.68
7.67
7.66
7.57
7.55
7.53
7.52
7.51
7.50
7.48
6.79
6.54
6.53
6.52
6.51
6.49
6.49
3.83
3.30
3.28
3.27
3.25
3.23
3.21
3.20
1.42
1.40
1.02
4.07
0.96
2.04
3.07
1.00
6.00
f1 (ppm)


168.4
163.8
160.3
158.9
155.1
152.9
140.9
134.1
133.3
132.4
131.5
131.3
130.3
130.2
129.9
126.9
115.2
110.5
107.7
101.4
55.5
31.3
24.1
24.0
f1 (ppm)

BF5

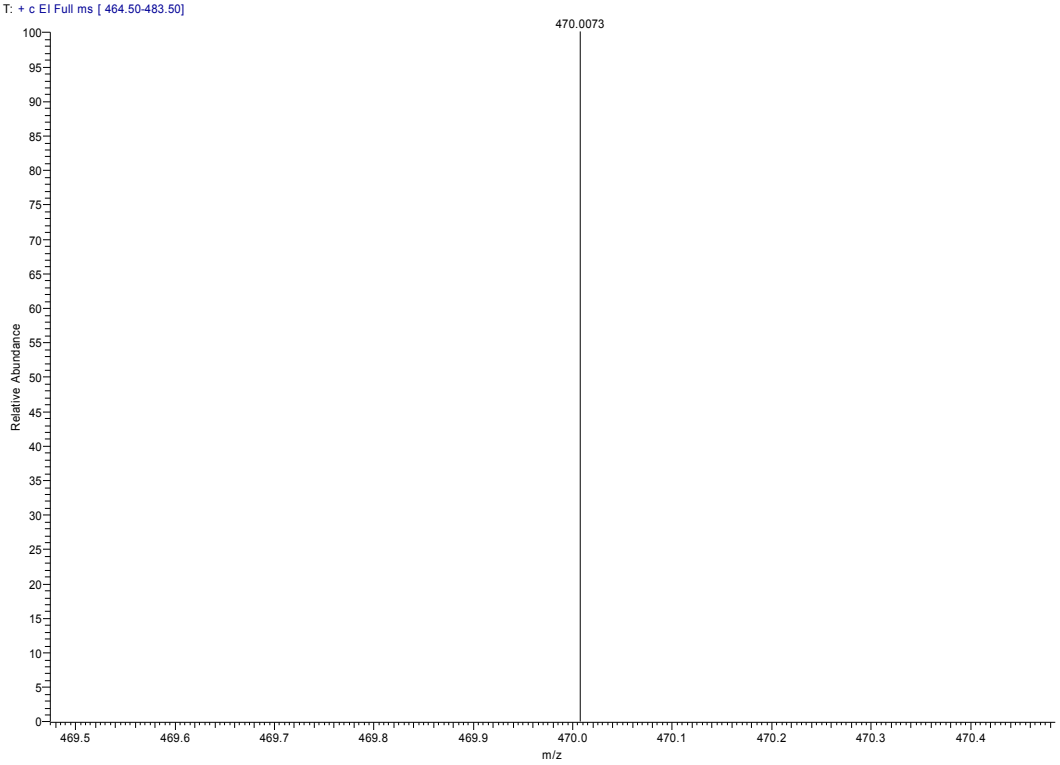
Instrument:DSQ(Thermo)
Ionization Method:EI
D:\DSQ\DATA-LR\16\102402 10/24/2016 11:54:37 AM F66

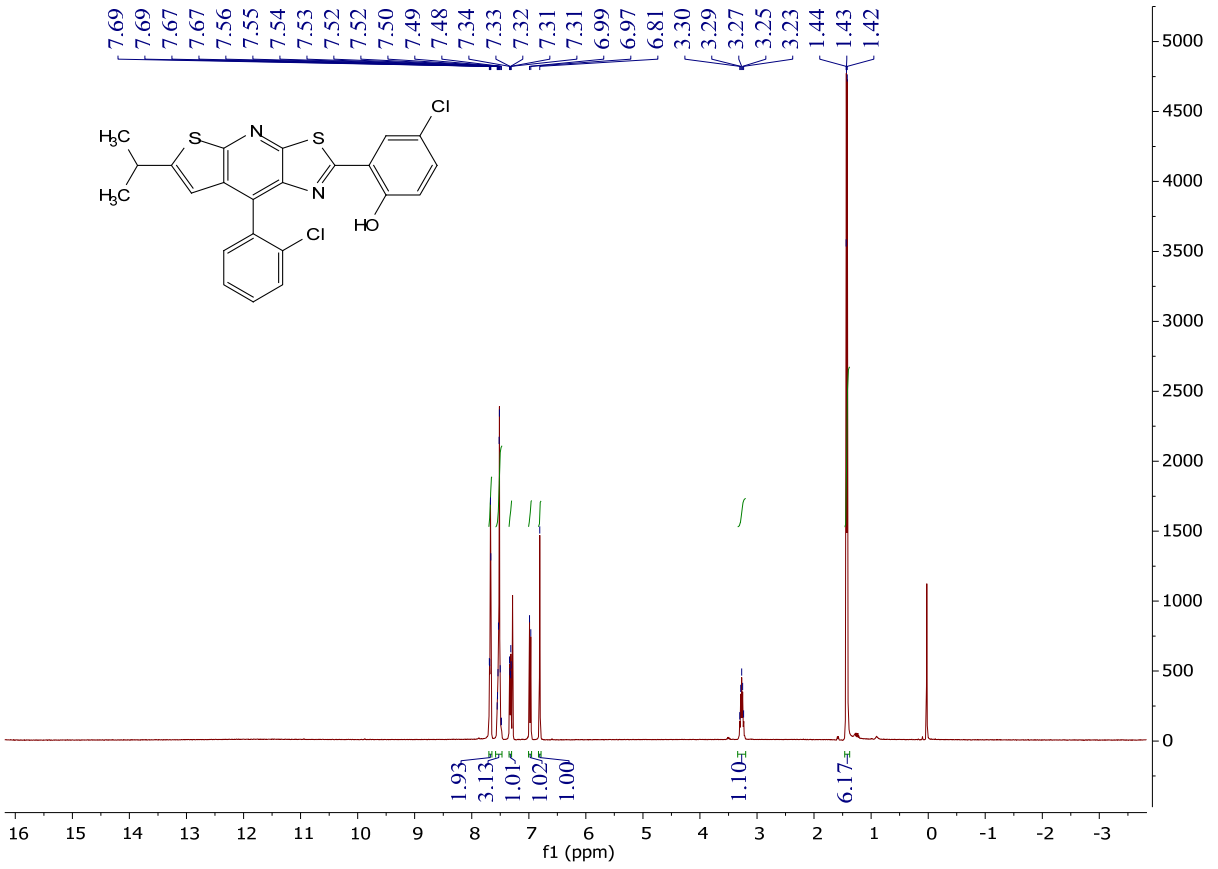
102402 #63 RT: 1.63 AV: 1 NL: 3.71E5
T: + c Full ms [45.00-800.00]

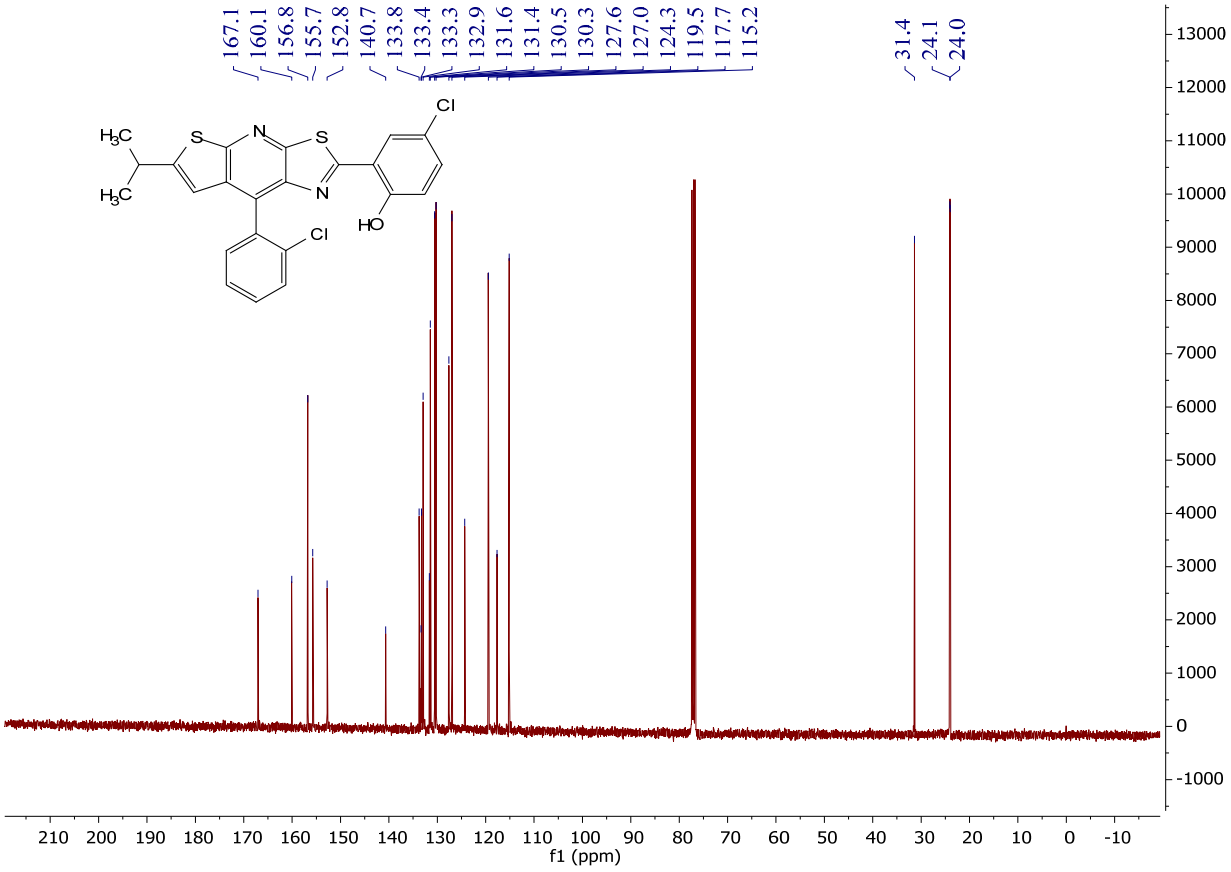


Instrument:MAT 95XP(Thermo)
D:\DATA-HR\16\102701-f66-c1 10/27/2016 9:19:15 AM F66

102701-f66-c1 #12 RT: 0.46 AV: 1 NL: 1.17E5
T: + c EI Full ms [464.50-483.50]



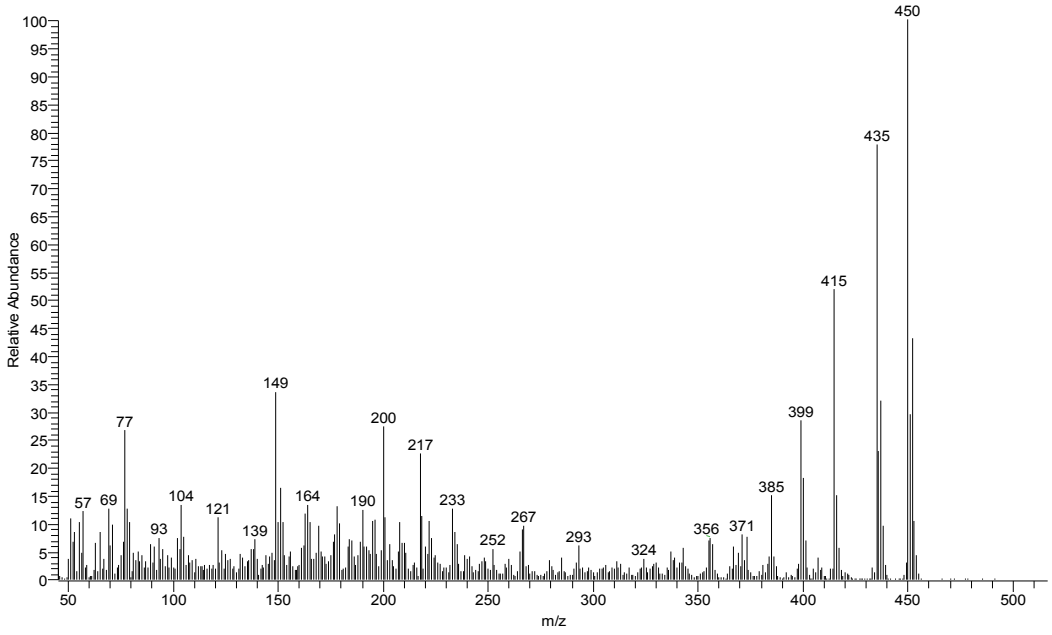

7.69
7.69
7.67
7.67
7.56
7.55
7.54
7.53
7.52
7.52
7.50
7.49
7.48
7.34
7.33
7.32
7.31
7.31
6.99
6.97
6.81
3.30
3.29
3.27
3.25
3.23
1.44
1.43
1.42
Cl
H3C
S
N
S
H3C
N
HO
Cl
1.93
3.13
1.01
1.02
1.00
1.10
6.17
f1 (ppm)


167.1
160.1
156.8
155.7
152.8
140.7
133.8
133.4
133.3
132.9
131.6
131.4
130.5
130.3
127.6
127.0
124.3
119.5
117.7
115.2
31.4
24.1
24.0
Cl
H3C
S
N
S
H3C
N
HO
Cl
f1 (ppm)

BF6

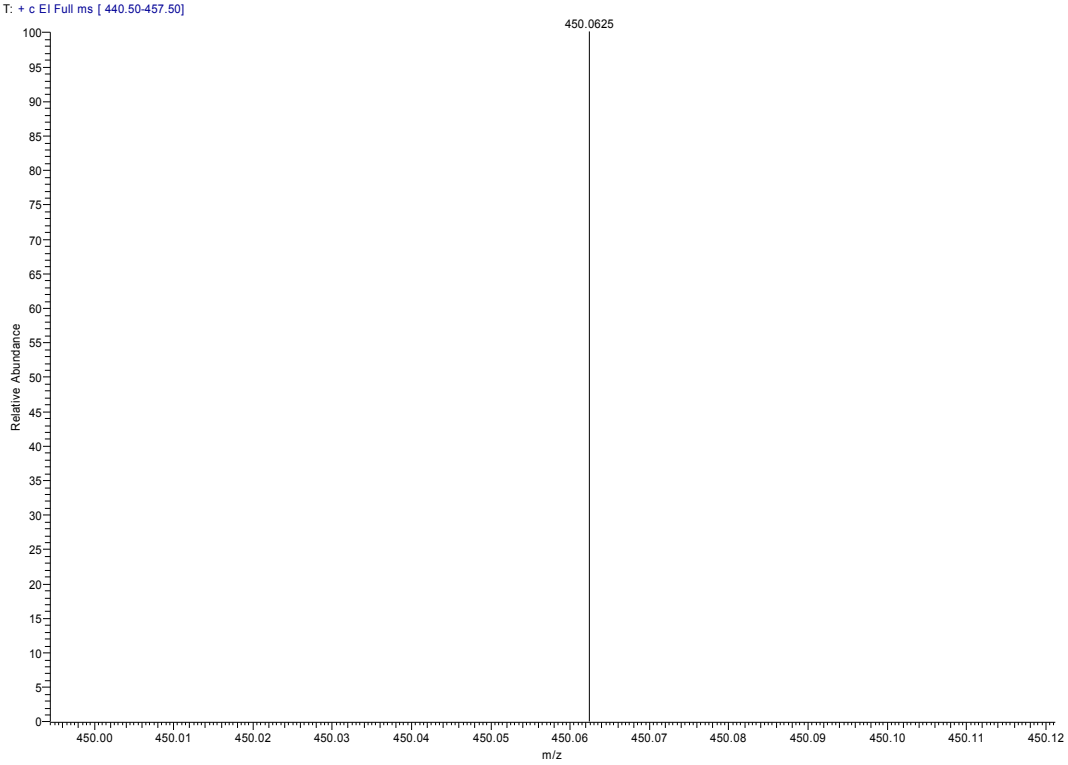
Instrument:DSQ(Thermo)
Ionization Method:EI
D:\DSQ\DATA-LR\16\102401 10/24/2016 11:49:18 AM F67

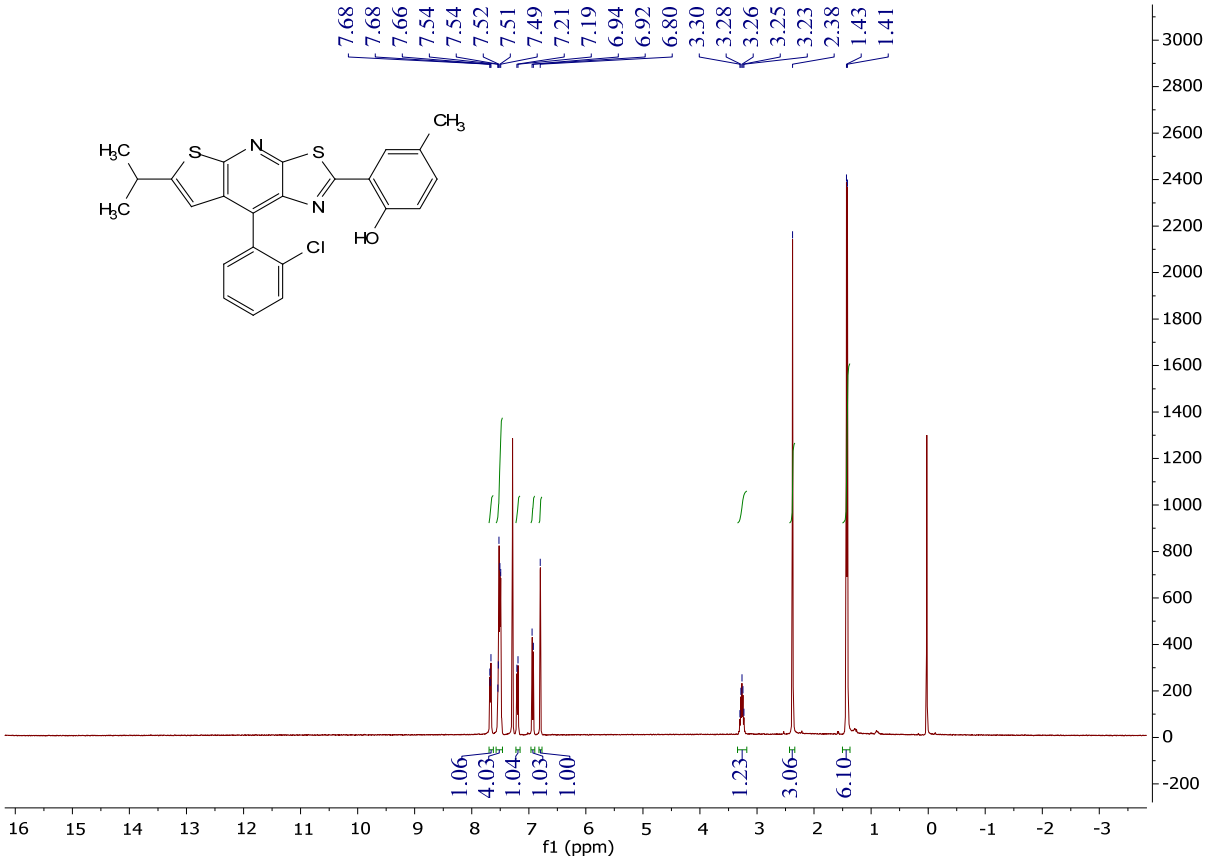
102401 #62 RT: 1.60 AV: 1 NL: 4.12E5
T: + c Full ms [45.00-800.00]

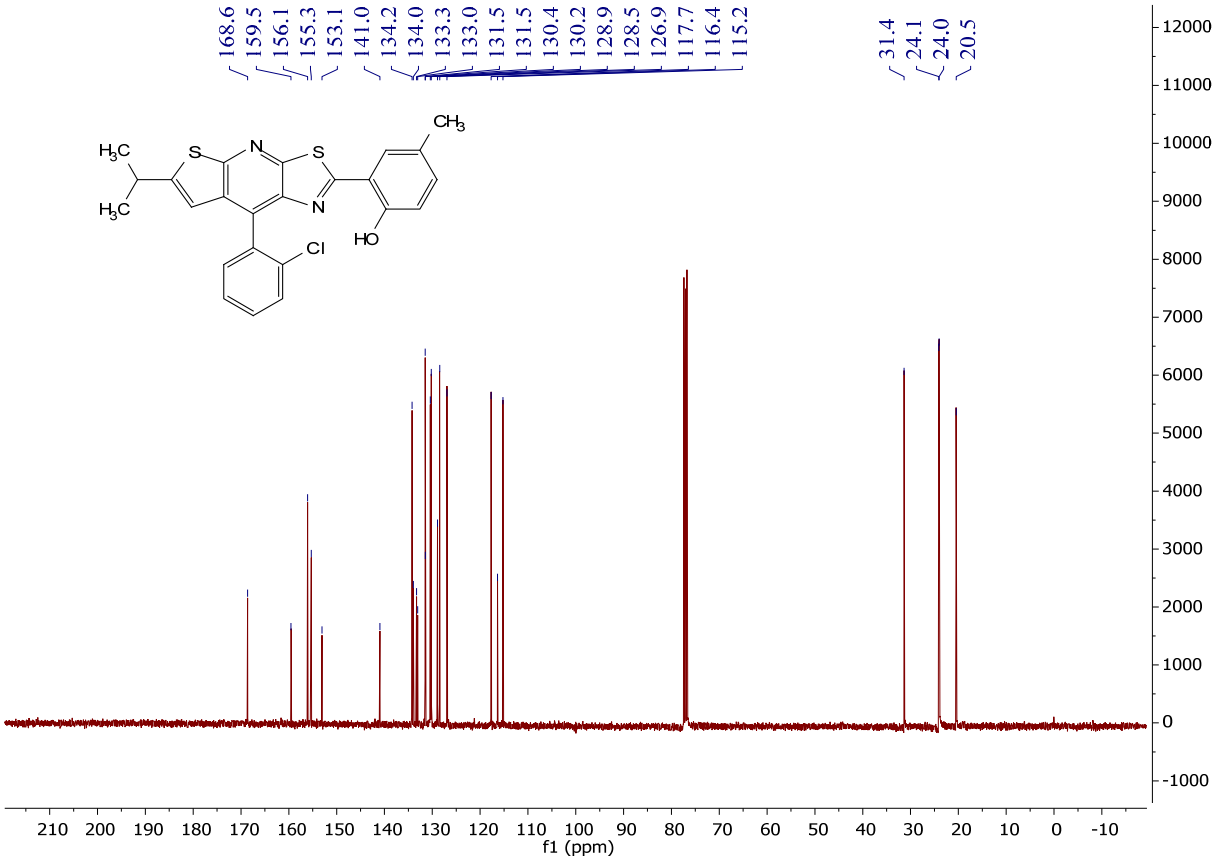


Instrument:MAT 95XP(Thermo)
D:\DATA-HR\16\102702-f67-c1 10/27/2016 9:40:52 AM F67

102702-f67-c1 #9 RT: 0.34 AV: 1 NL: 4.22E4
T: + c EI Full ms [440.50-457.50]



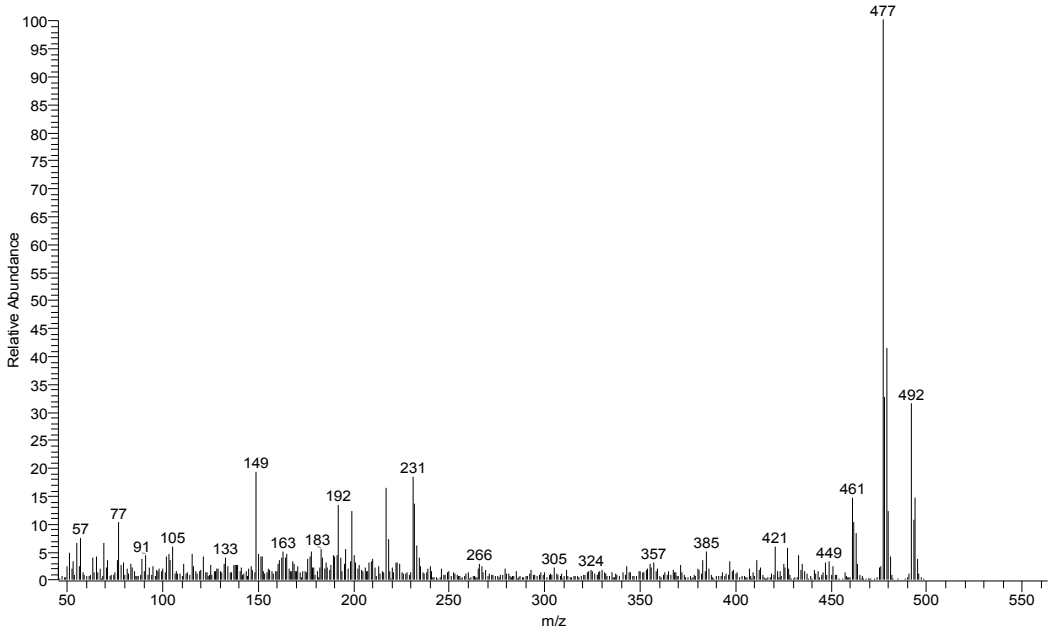

7.68
7.68
7.66
7.54
7.54
7.52
7.51
7.49
7.21
7.19
6.94
6.92
6.80
3.30
3.28
3.26
3.25
3.23
2.38
1.43
1.41
CH3
H3C
S
N
S
H3C
N
HO
Cl
1.06
4.03
1.04
1.03
1.00
1.23
3.06
6.10
f1 (ppm)


168.6
159.5
156.1
155.3
153.1
141.0
134.2
134.0
133.3
133.0
131.5
131.5
130.4
130.2
128.9
128.5
126.9
117.7
116.4
115.2
31.4
24.1
24.0
20.5
CH3
H3C
S
N
S
H3C
N
HO
Cl
f1 (ppm)

BF7

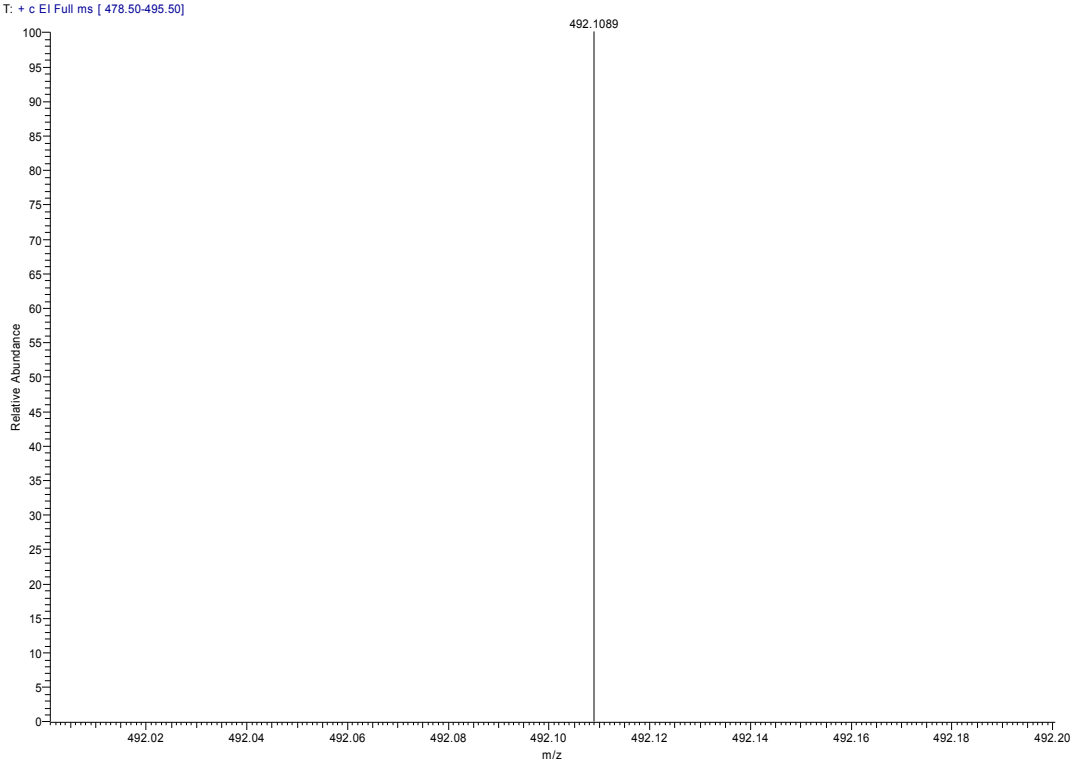
Instrument:DSQ(Thermo)
Ionization Method:EI
D:\DSQ\DATA-LR\16\102802 10/28/2016 11:01:40 AM F69

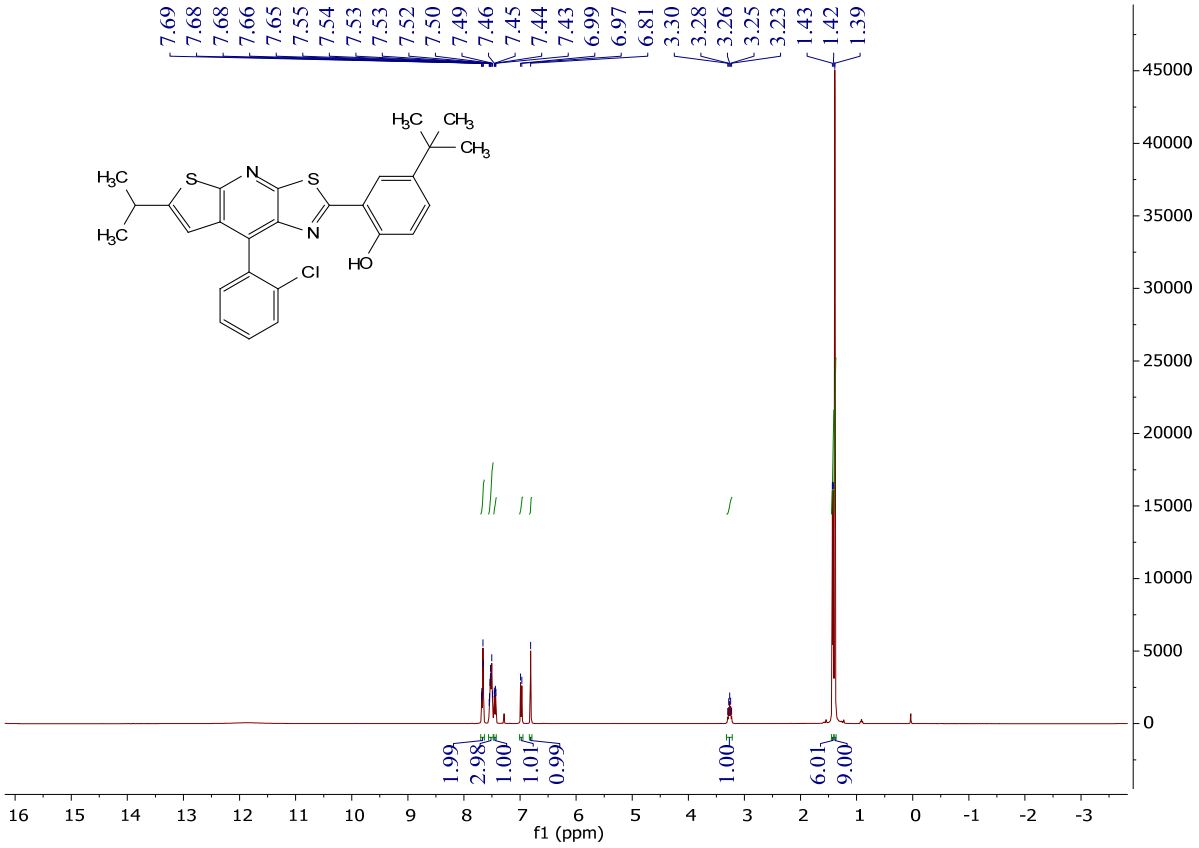
102802 #54 RT: 1.40 AV: 1 NL: 1.92E5
T: + c Full ms [45.00-800.00]

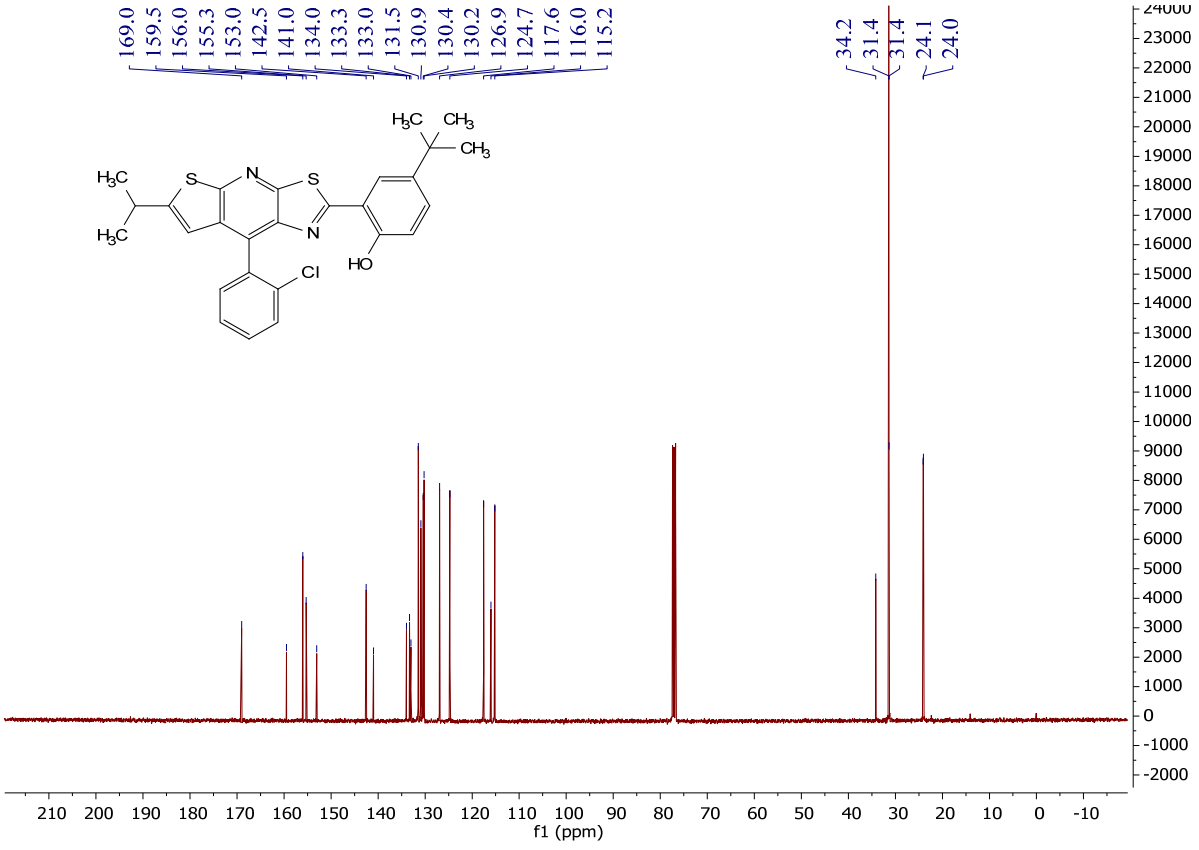


Instrument:MAT 95XP(Thermo)
D:\DATA-HR\16\102801-f69-c2 10/28/2016 4:41:48 PM F69

102801-f69-c2 #7 RT: 0.29 AV: 1 NL: 5.16E4
T: + c EI Full ms [478.50-495.50]



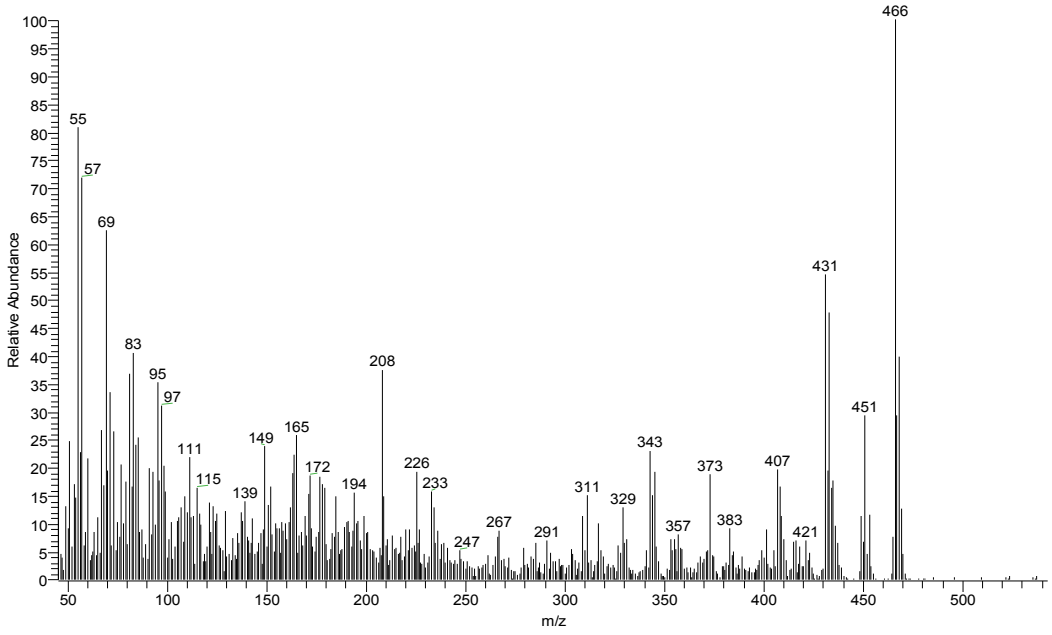

7.69
7.68
7.68
7.66
7.65
7.55
7.54
7.53
7.53
7.52
7.50
7.49
7.46
7.45
7.44
7.43
6.99
6.97
6.81
3.30
3.28
3.26
3.25
3.23
1.43
1.42
1.39
H3C
CH3
CH3
H3C
S
N
S
N
H3C
Cl
HO
1.99
2.98
1.00
1.01
0.99
1.00
6.01
9.00
f1 (ppm)


169.0
159.5
156.0
155.3
153.0
142.5
141.0
134.0
133.3
133.0
131.5
130.9
130.4
130.2
126.9
124.7
117.6
116.0
115.2
34.2
31.4
31.4
24.1
24.0
H3C
CH3
CH3
H3C
S
N
S
N
H3C
Cl
HO
f1 (ppm)

BF8

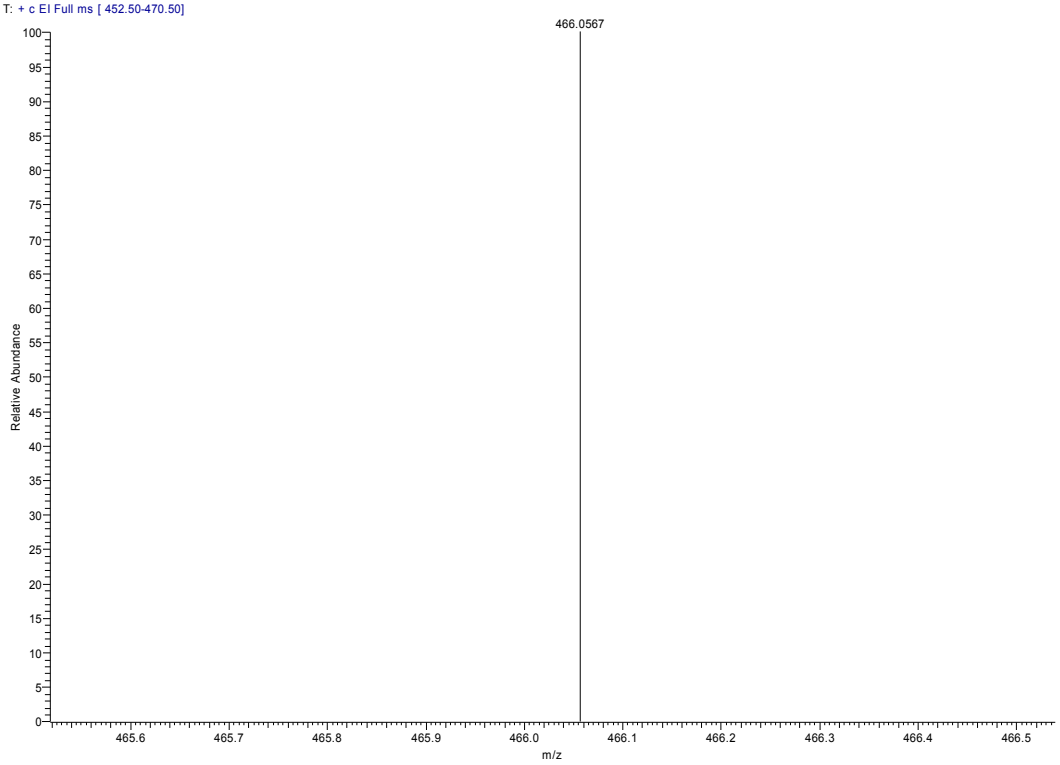
Instrument:DSQ(Thermo)
Ionization Method:EI
D:\DSQ\DATA-LR\16\092908 9/29/2016 4:15:32 PM F62

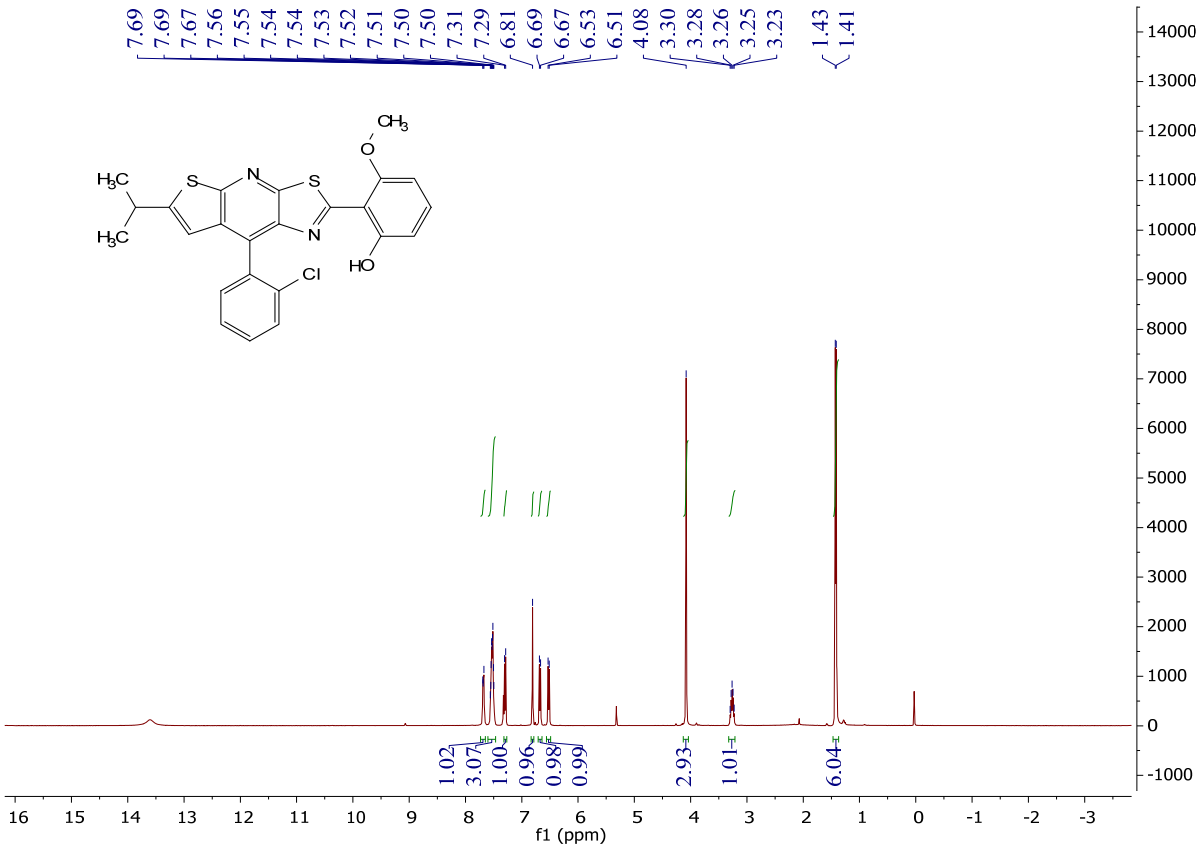
092908 #68 RT: 1.76 AV: 1 NL: 8.45E4
T: + c Full ms [45.00-800.00]

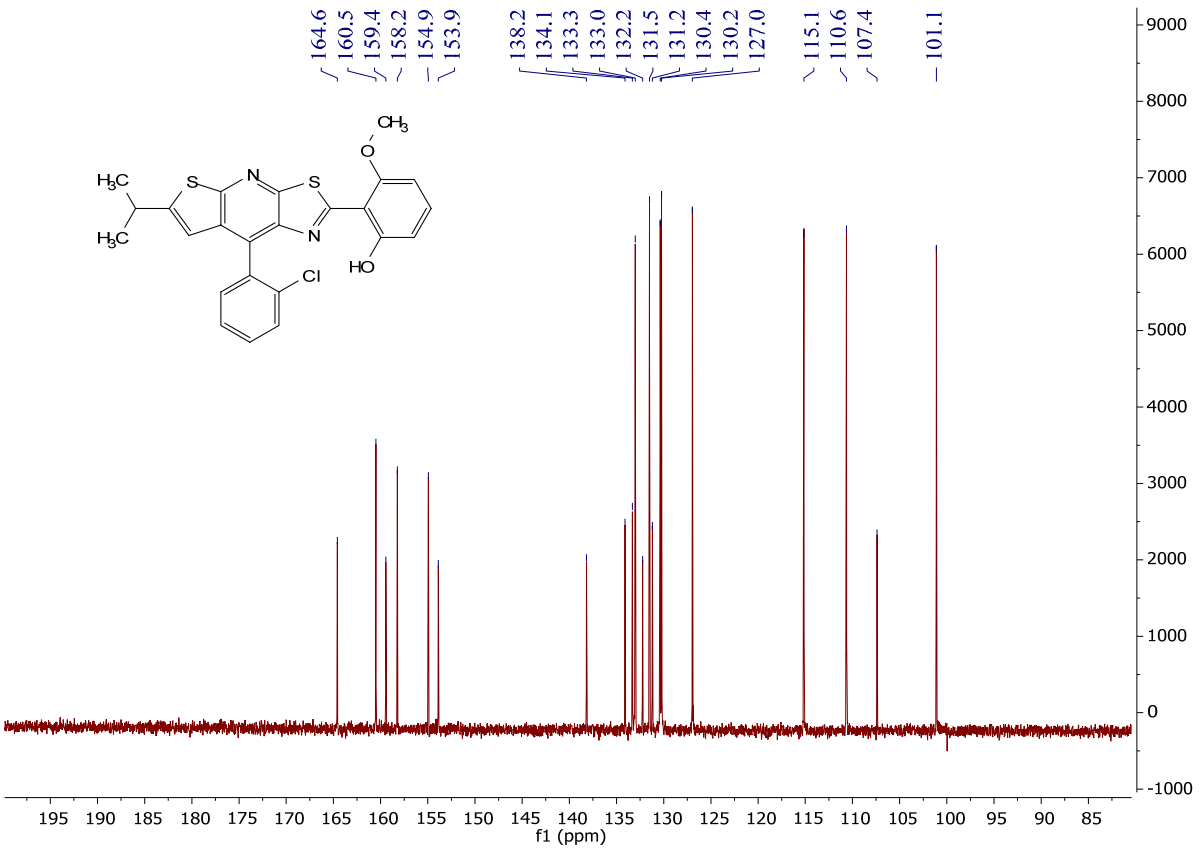


Instrument:MAT 95XP(Thermo)
D:\DATA-HR\16\093003-f62-c2 9/30/2016 10:52:42 AM F62

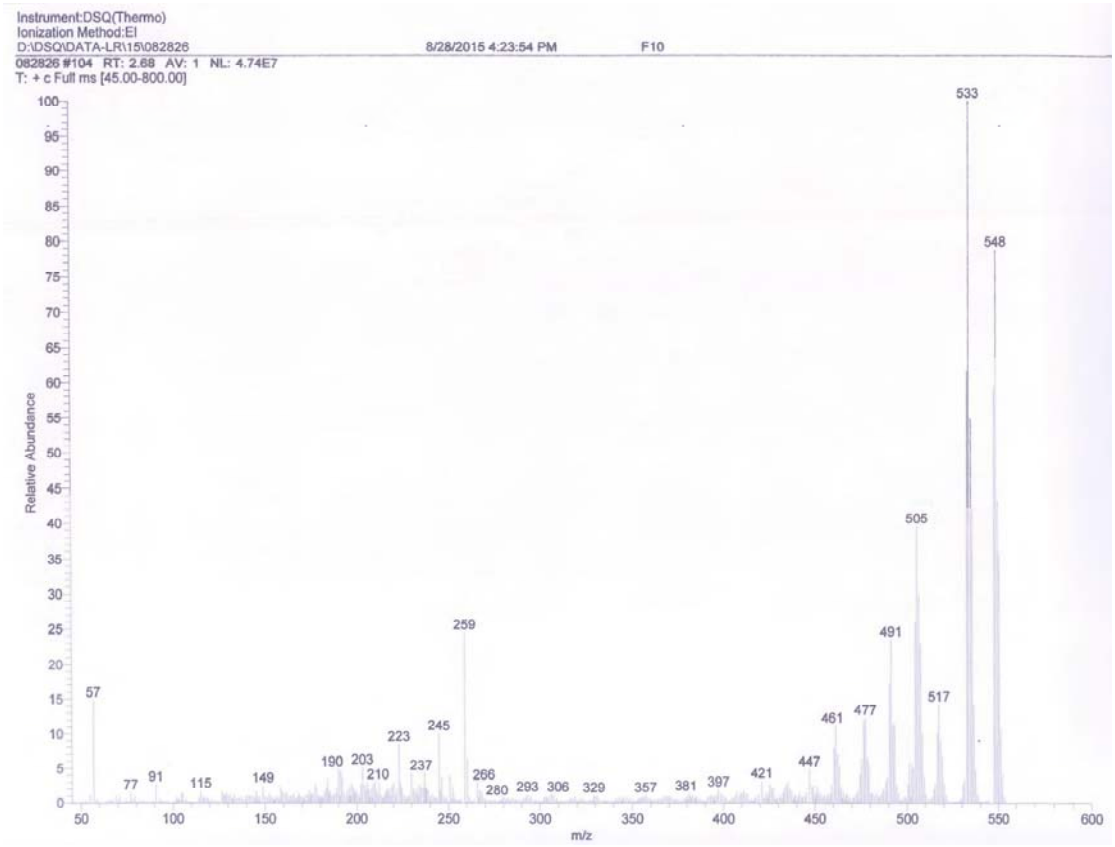
093003-f62-c2 #10 RT: 0.40 AV: 1 NL: 5.79E4
T: + c EI Full ms [452.50-470.50]

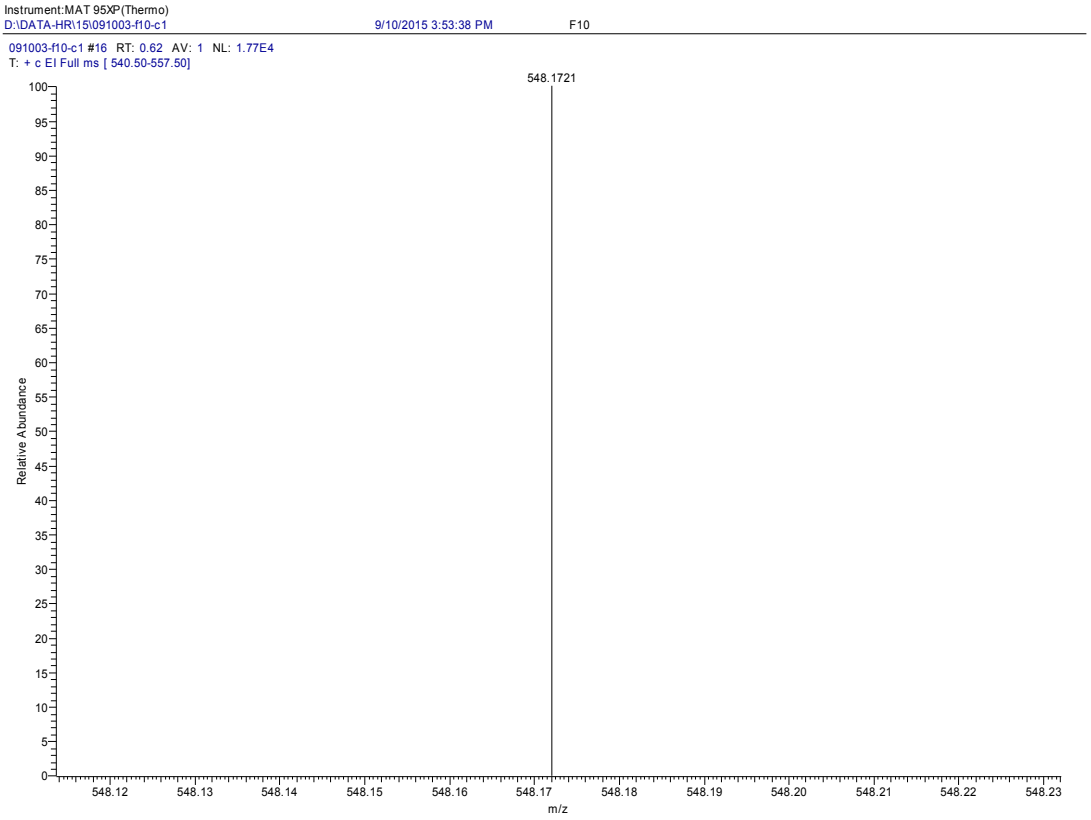


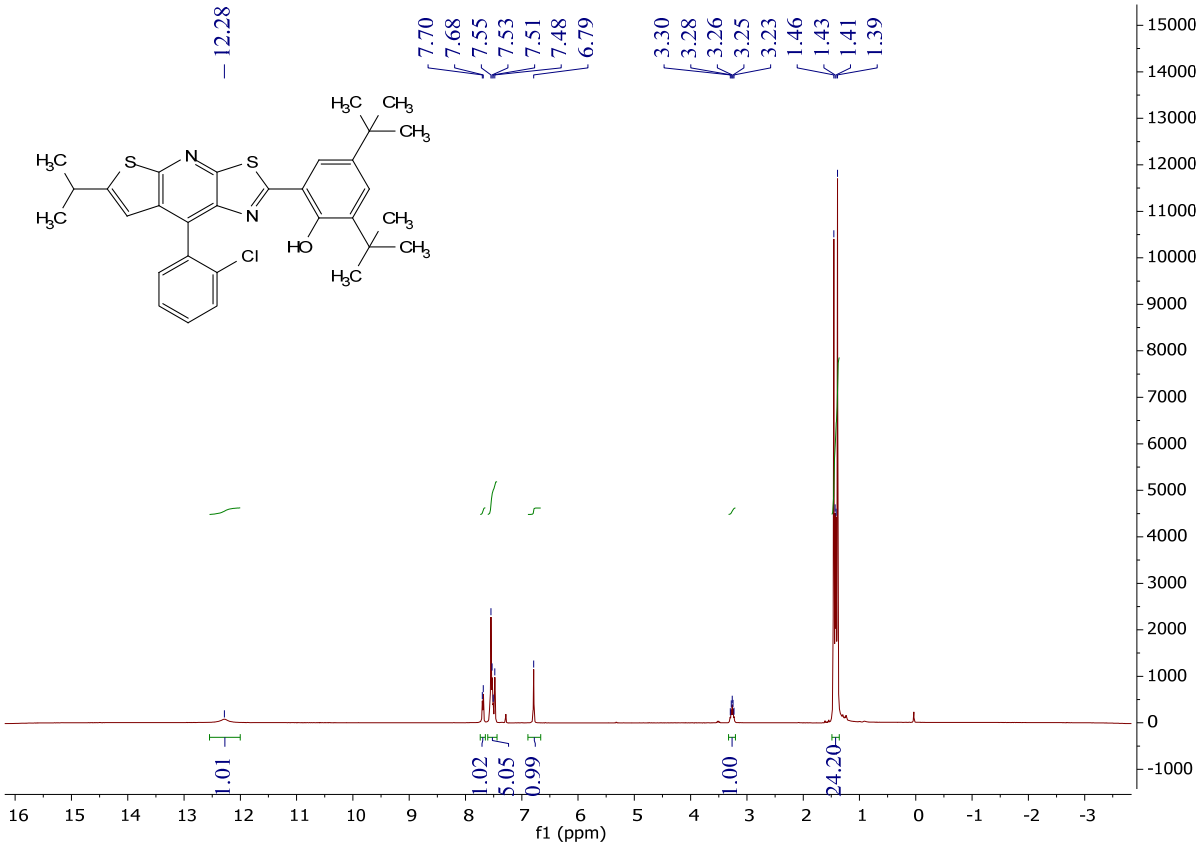

7.69
7.69
7.67
7.56
7.55
7.54
7.54
7.53
7.52
7.51
7.50
7.50
7.31
7.29
6.81
6.69
6.67
6.53
6.51
4.08
3.30
3.28
3.26
3.25
3.23
1.43
1.41
1.02
3.07
1.00
0.96
0.98
0.99
2.93
1.01
6.04
f1 (ppm)

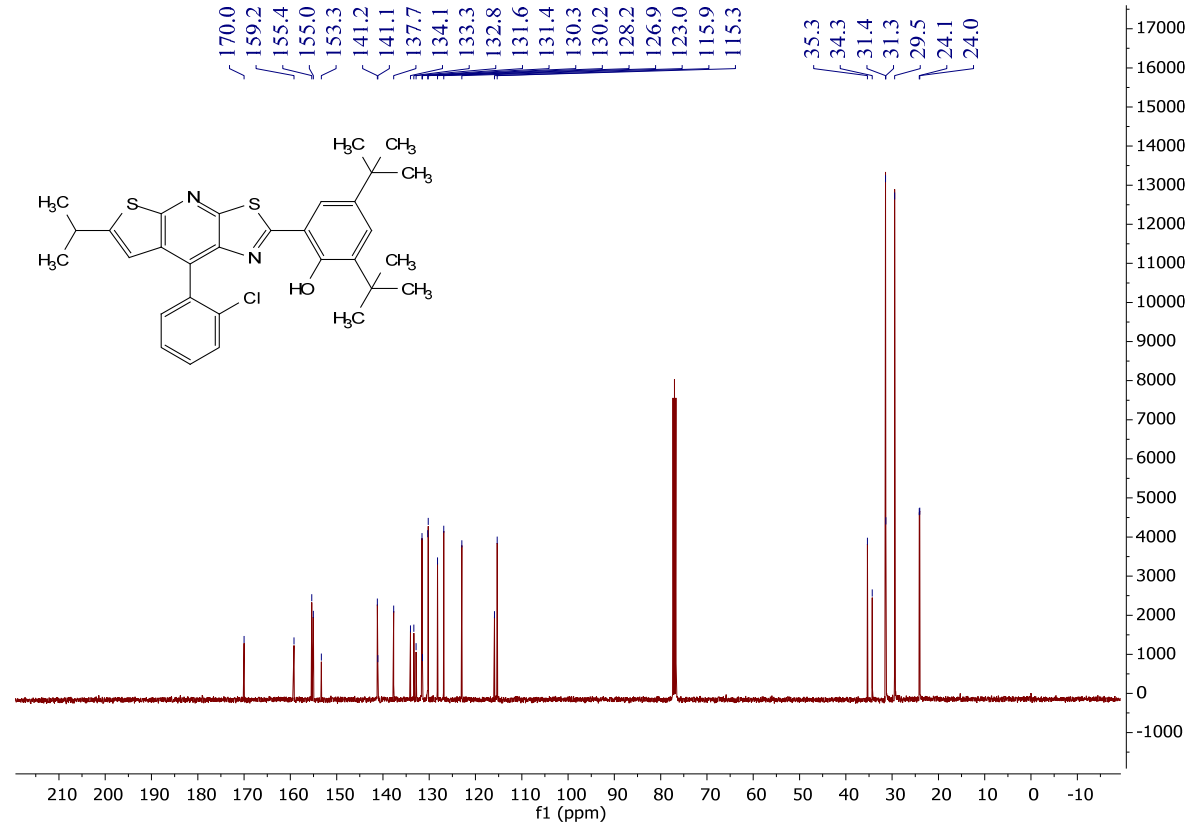

164.6
160.5
159.4
158.2
154.9
153.9
138.2
134.1
133.3
133.0
132.2
131.5
131.2
130.4
130.2
127.0
115.1
110.6
107.4
101.1
f1 (ppm)

BF9


Instrument:DSQ(Thermo)
Ionization Method:EI
D:\DSQ\DATA-LR\15\082826
8/28/2015 4:23:54 PM
F10
082826 #104 RT: 2.68 AV: 1 NL: 4.74E7
T: + c Full ms [45.00-800.00]
Relative Abundance
m/z
533
548
505
259
491
517
57
461
477
223
245
447
190
203
210
237
266
77
91
115
149
280
293
306
329
357
381
397
421


Instrument:MAT 95XP(Thermo)
D:\DATA-HR\15\091003-f10-c1
9/10/2015 3:53:38 PM
F10
091003-f10-c1 #16 RT: 0.62 AV: 1 NL: 1.77E4
T: + c EI Full ms [540.50-557.50]
548.1721
Relative Abundance
m/z

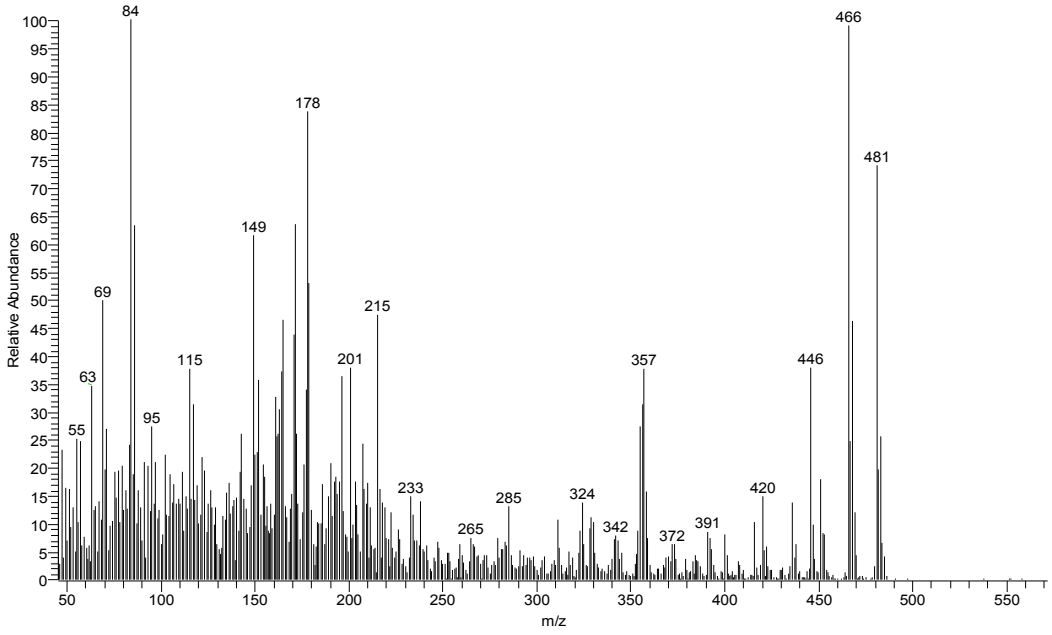

12.28
7.70
7.68
7.55
7.53
7.51
7.48
6.79
3.30
3.28
3.26
3.25
3.23
1.46
1.43
1.41
1.39
1.01
1.02
5.05
0.99
1.00
24.20
f1 (ppm)


170.0
159.2
155.4
155.0
153.3
141.2
141.1
137.7
134.1
133.3
132.8
131.6
131.4
130.3
130.2
128.2
126.9
123.0
115.9
115.3
35.3
34.3
31.4
31.3
29.5
24.1
24.0
f1 (ppm)

BF10

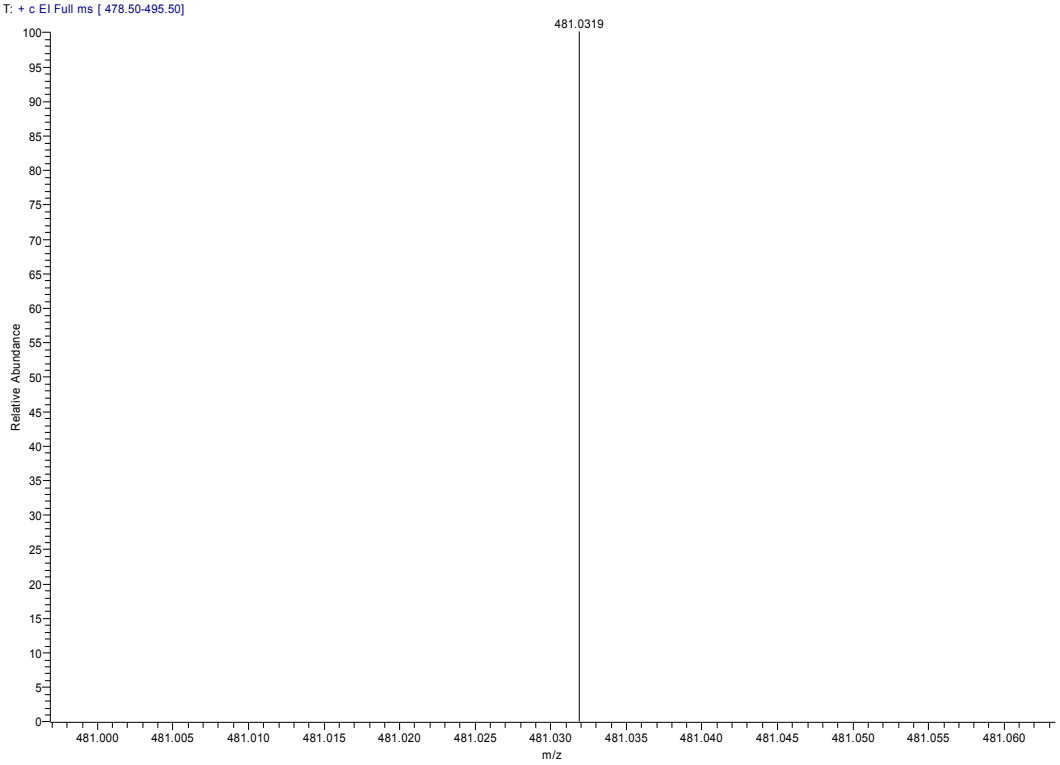
Instrument:DSQ(Thermo)
Ionization Method:EI
D:\DSQ\DATA-LR\16\062303 6/23/2016 4:38:07 PM F43

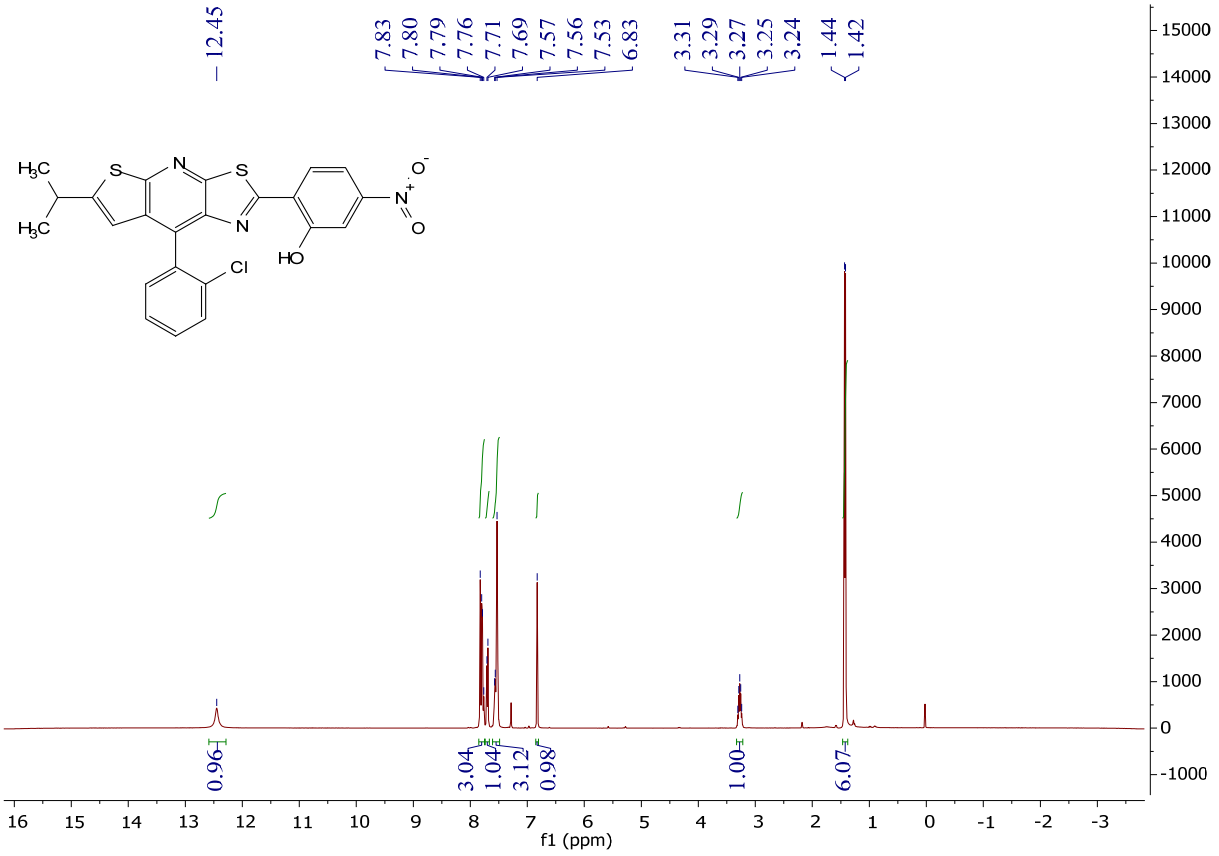
062303 #69 RT: 1.78 AV: 1 NL: 1.08E5
T: + c Full ms [45.00-800.00]

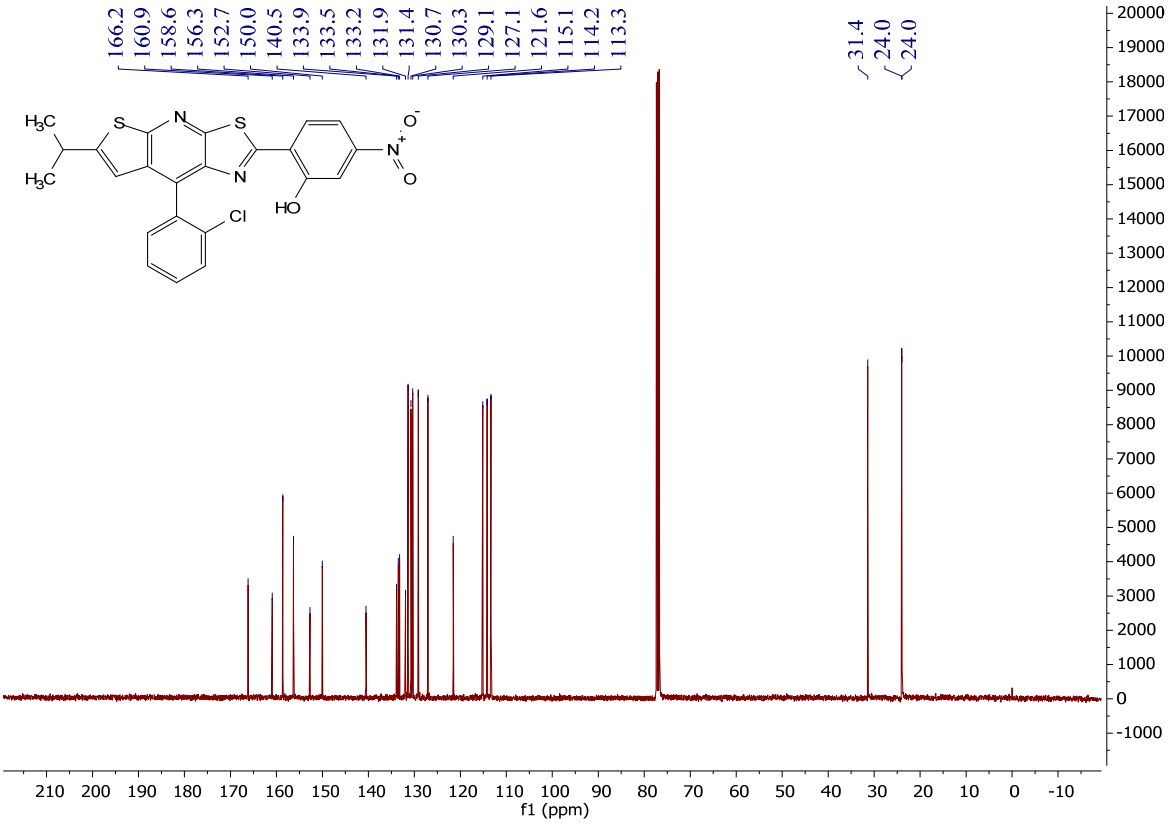


Instrument:MAT 95XP(Thermo)
D:\DATA-HR\16\062401-f43-c1 6/24/2016 10:28:35 AM F43

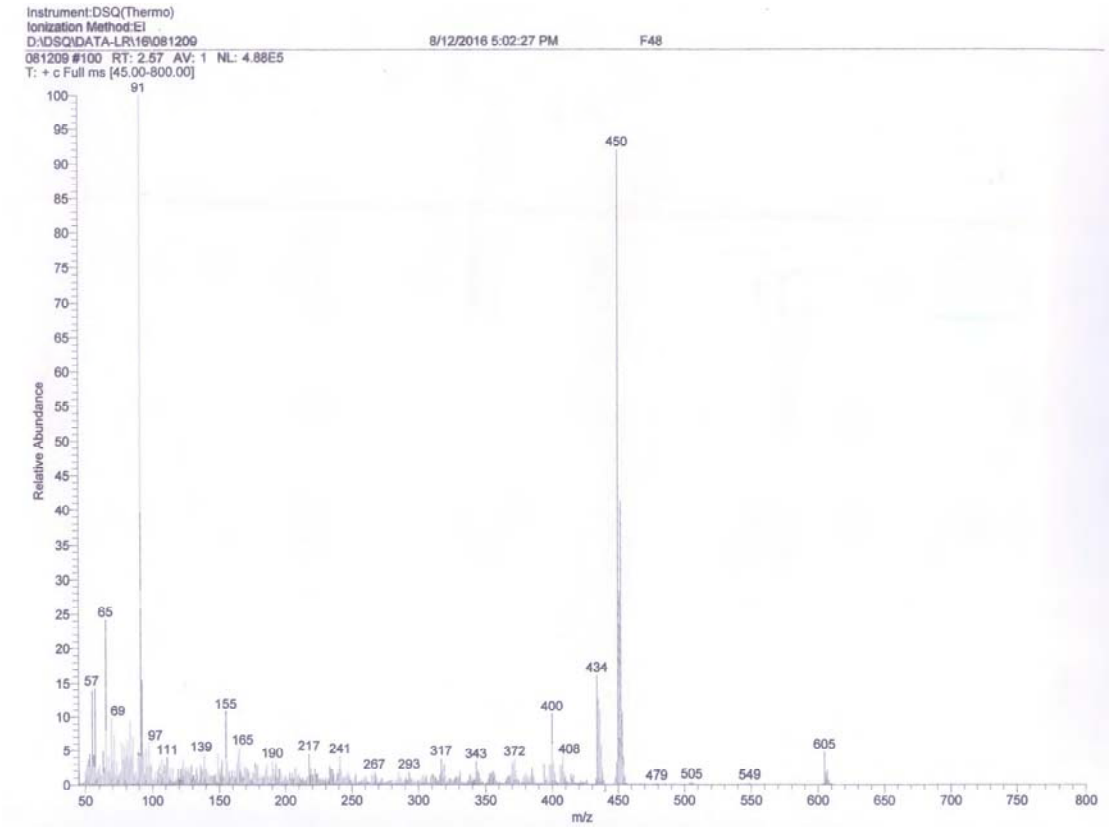
062401-f43-c1 #20 RT: 0.74 AV: 1 NL: 6.61E4
T: + c EI Full ms [478.50-495.50]

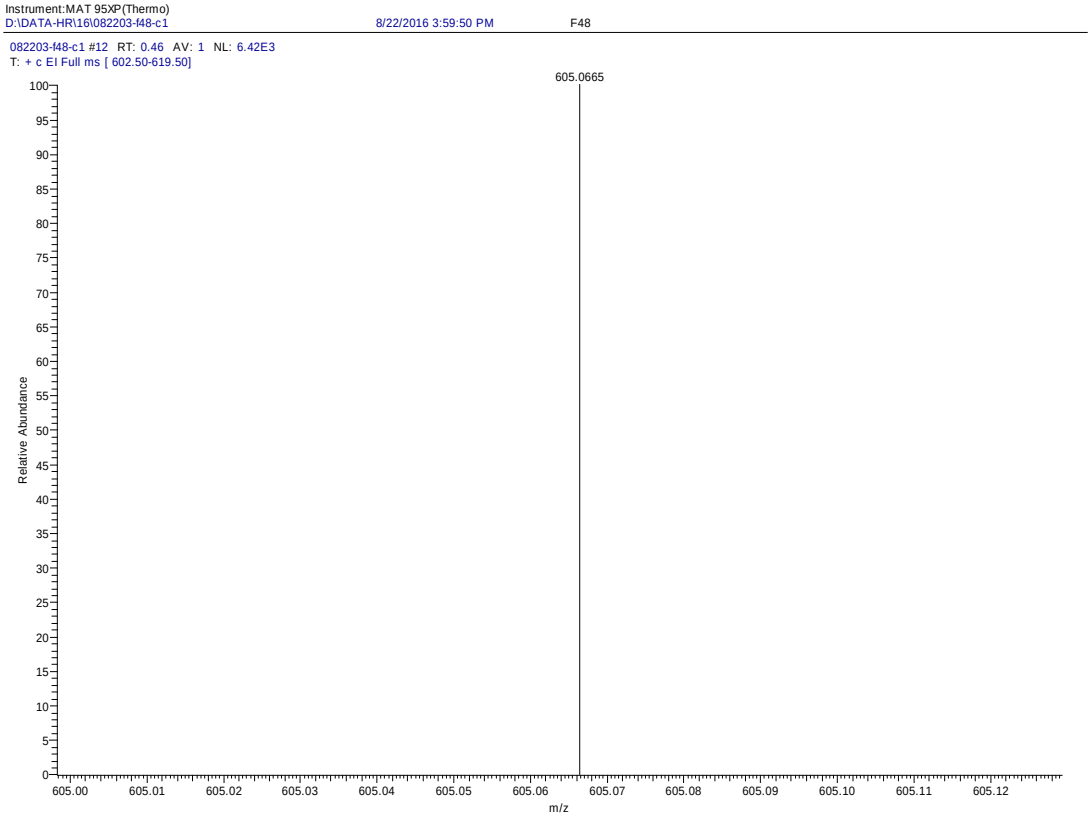


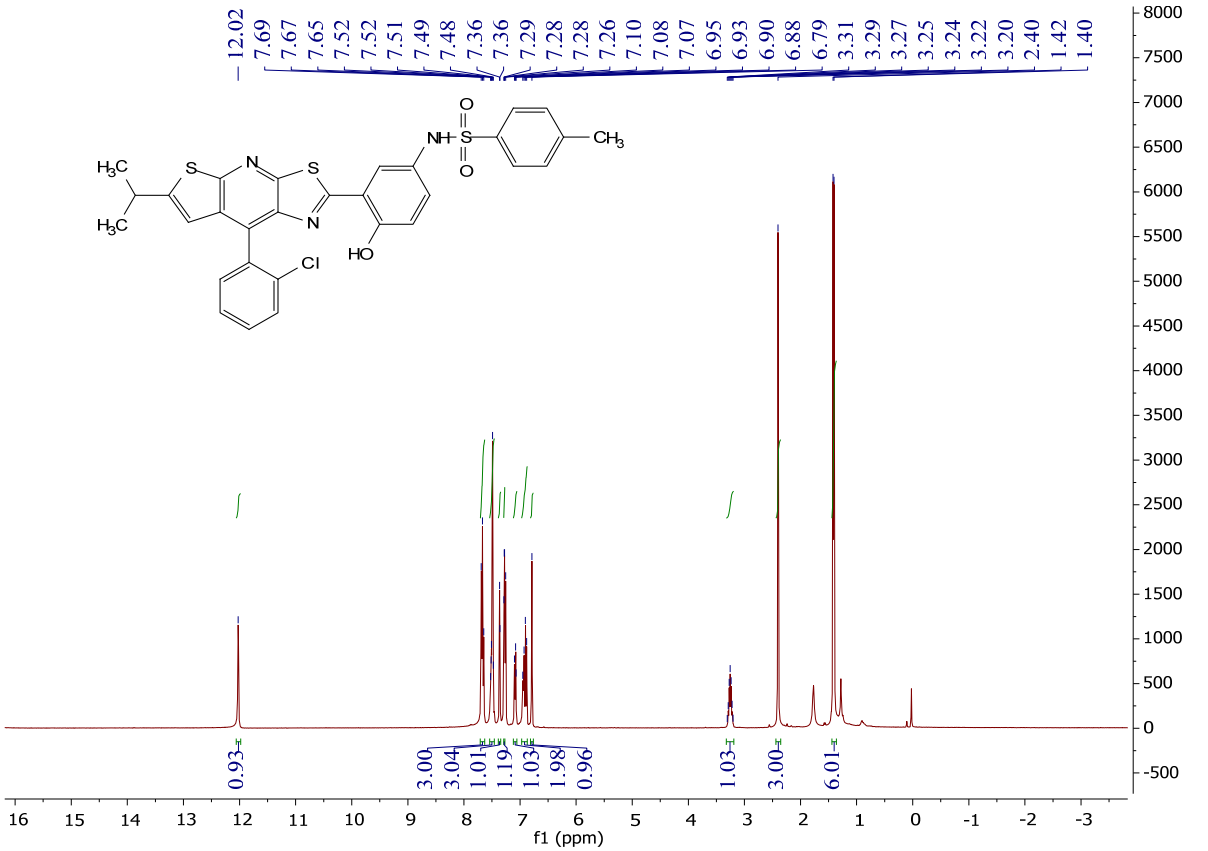

12.45
7.83
7.80
7.79
7.76
7.71
7.69
7.57
7.56
7.53
6.83
3.31
3.29
3.27
3.25
3.24
1.44
1.42
0.96
3.04
1.04
3.12
0.98
1.00
6.07
f1 (ppm)

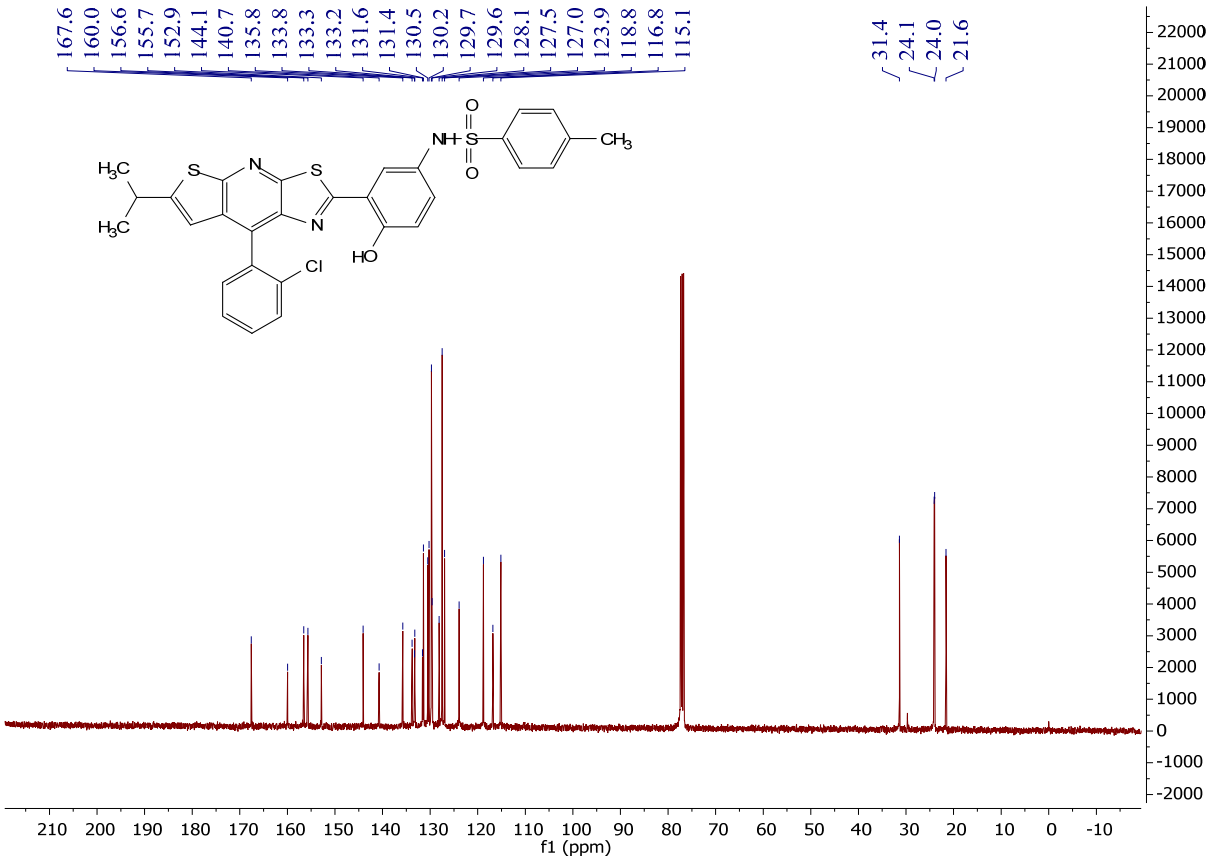

166.2
160.9
158.6
156.3
152.7
150.0
140.5
133.9
133.5
133.2
131.9
131.4
130.7
130.3
129.1
127.1
121.6
115.1
114.2
113.3
31.4
24.0
24.0
f1 (ppm)

BF11


Instrument:DSQ(Thermo)
Ionization Method:EI
D:\DSQ\DATA-LR\16\081209
8/12/2016 5:02:27 PM
F48
081209 #100 RT: 2.57 AV: 1 NL: 4.88E5
T: + c Full ms [45.00-800.00]
Relative Abundance
m/z
91
450
65
57
69
97
111
139
155
165
190
217
241
267
293
317
343
372
400
408
434
479
505
549
605


Instrument:MAT 95XP(Thermo)
D:\DATA-HR\16\082203-f48-c1
8/22/2016 3:59:50 PM
F48
082203-f48-c1 #12 RT: 0.46 AV: 1 NL: 6.42E3
T: + c EI Full ms [602.50-619.50]
605.0665
Relative Abundance
m/z

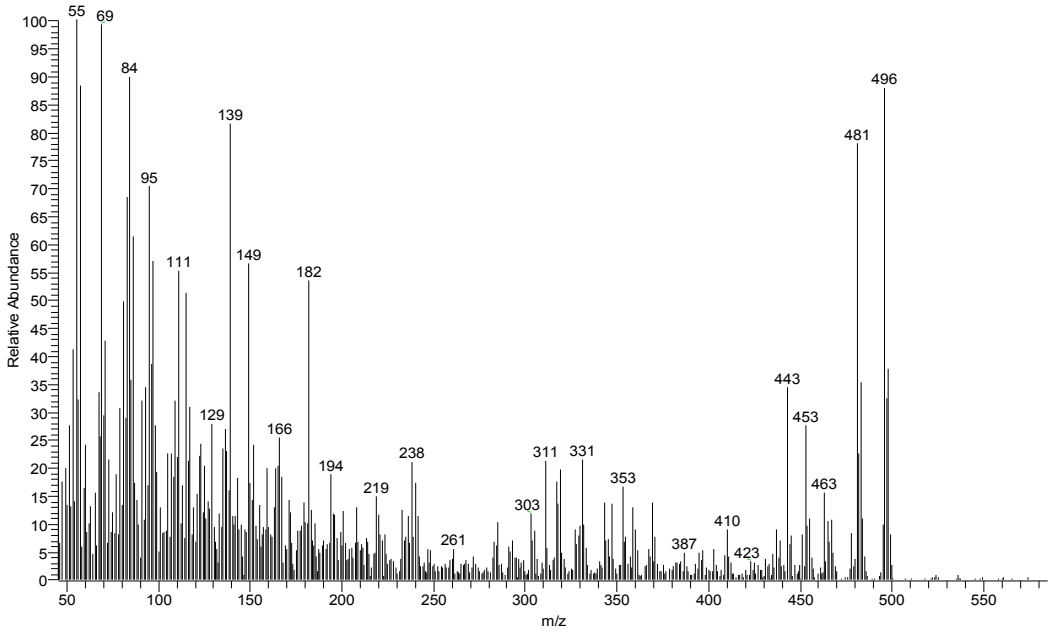

12.02
7.69
7.67
7.65
7.52
7.52
7.51
7.49
7.48
7.36
7.36
7.29
7.28
7.28
7.26
7.10
7.08
7.07
6.95
6.93
6.90
6.88
6.79
3.31
3.29
3.27
3.25
3.24
3.22
3.20
2.40
1.42
1.40
0.93
3.00
3.04
1.01
1.19
1.03
1.98
0.96
1.03
3.00
6.01
f1 (ppm)


167.6
160.0
156.6
155.7
152.9
144.1
140.7
135.8
133.8
133.3
133.2
131.6
131.4
130.5
130.2
129.7
129.6
128.1
127.5
127.0
123.9
118.8
116.8
115.1
31.4
24.1
24.0
21.6
f1 (ppm)

BF12

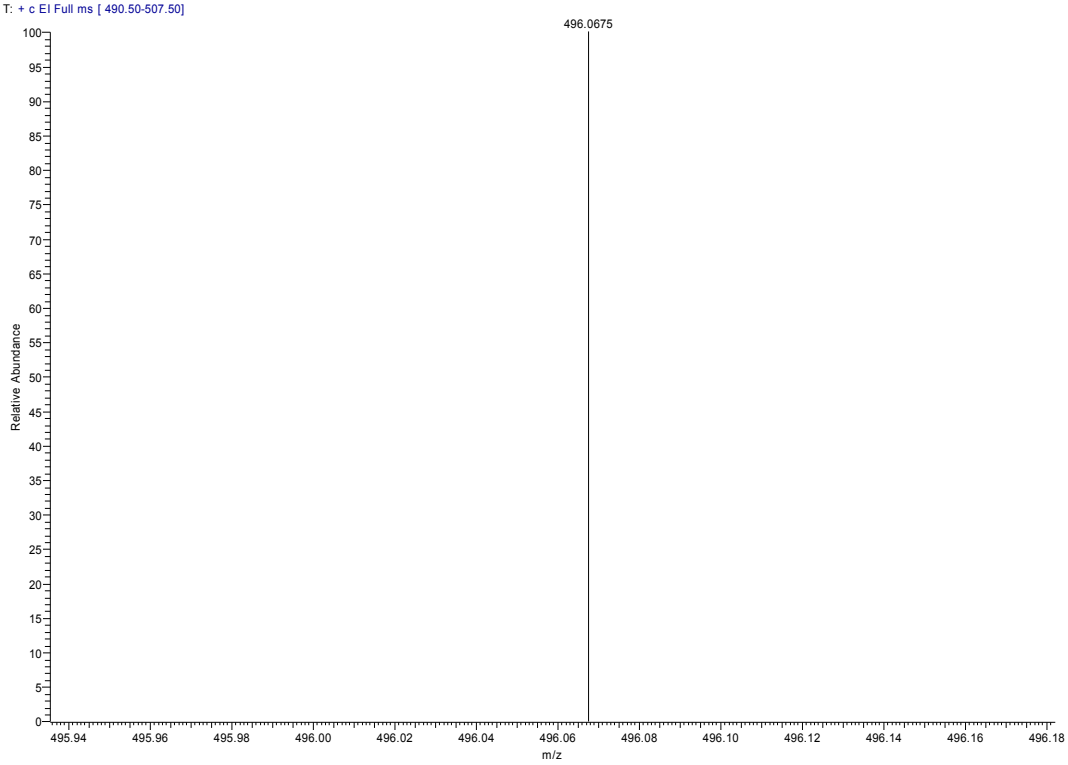
Instrument:DSQ(Thermo)
Ionization Method:EI
D:\DSQ\DATA-LR\16\111805 11/18/2016 12:01:01 PM F70

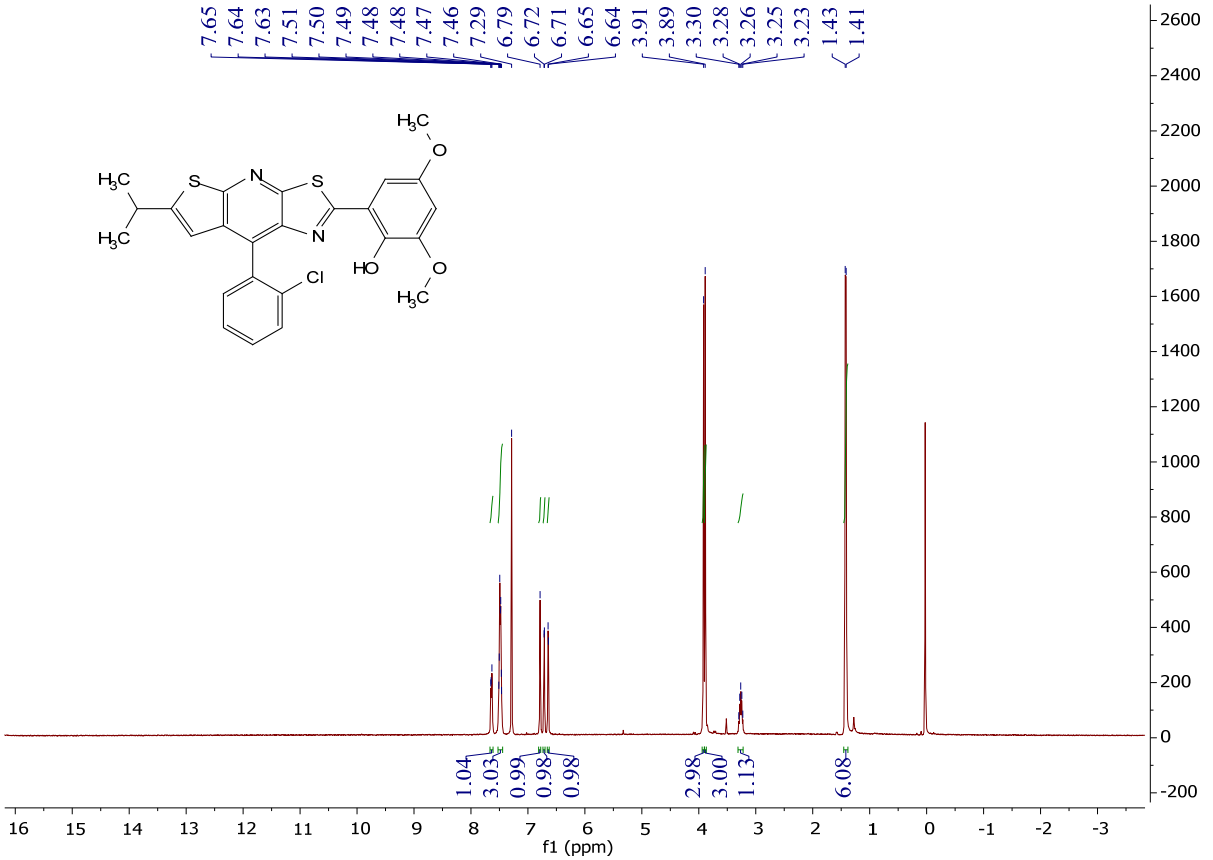
111805 #68 RT: 1.76 AV: 1 NL: 5.84E4
T: + c Full ms [45.00-800.00]

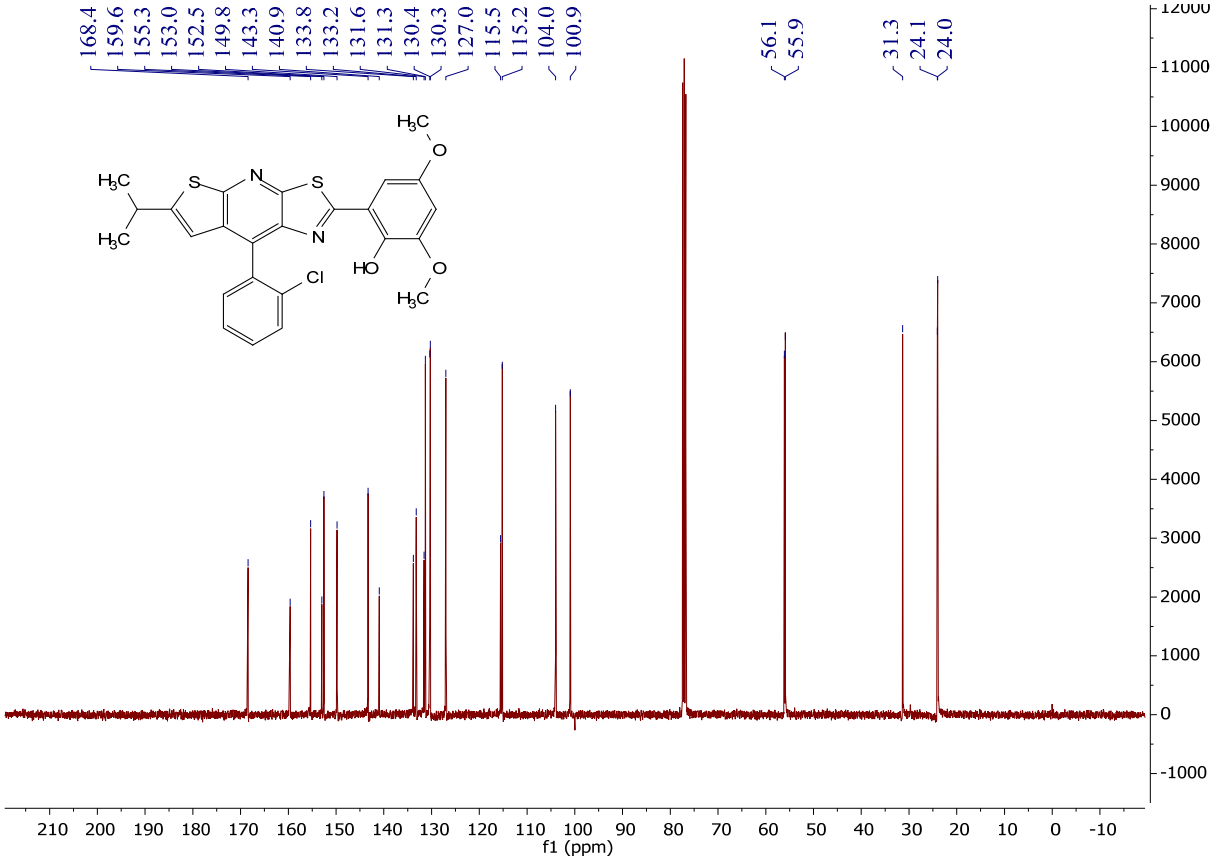


Instrument:MAT 95XP(Thermo)
D:\DATA-HR\16\112102-f70-c1 11/21/2016 5:10:12 PM F70

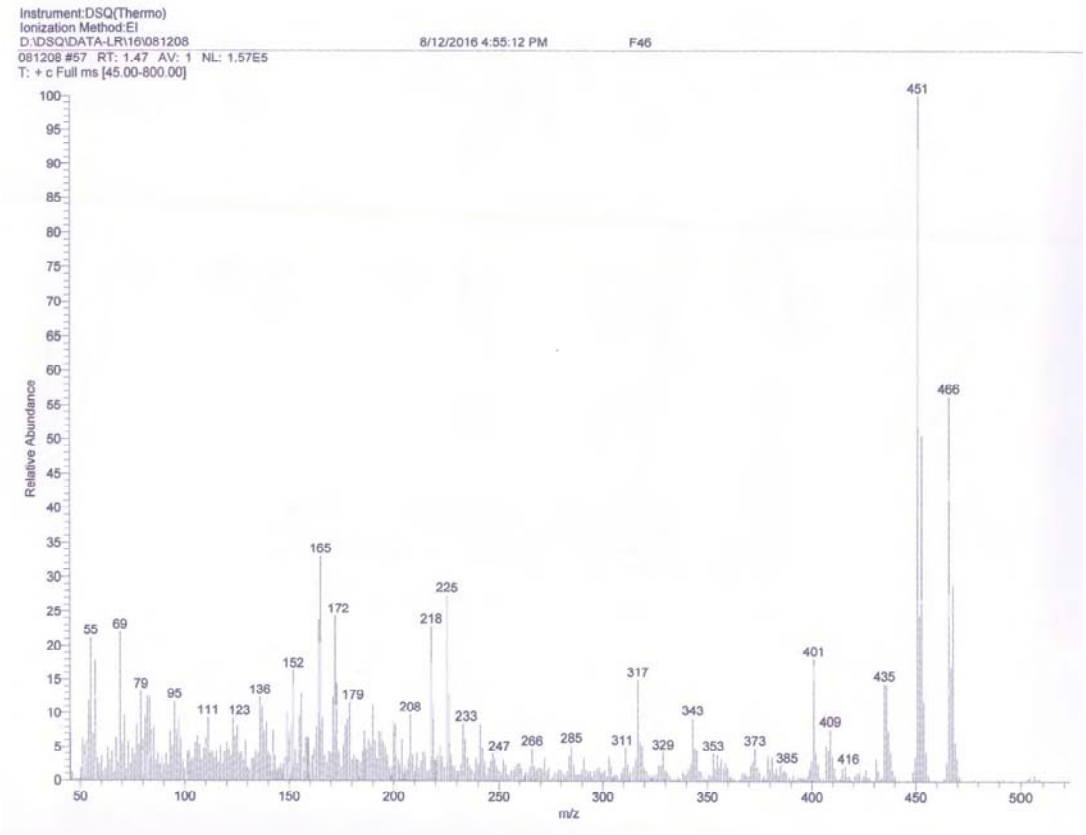
112102-f70-c1 #13 RT: 0.49 AV: 1 NL: 5.05E4
T: + c EI Full ms [490.50-507.50]

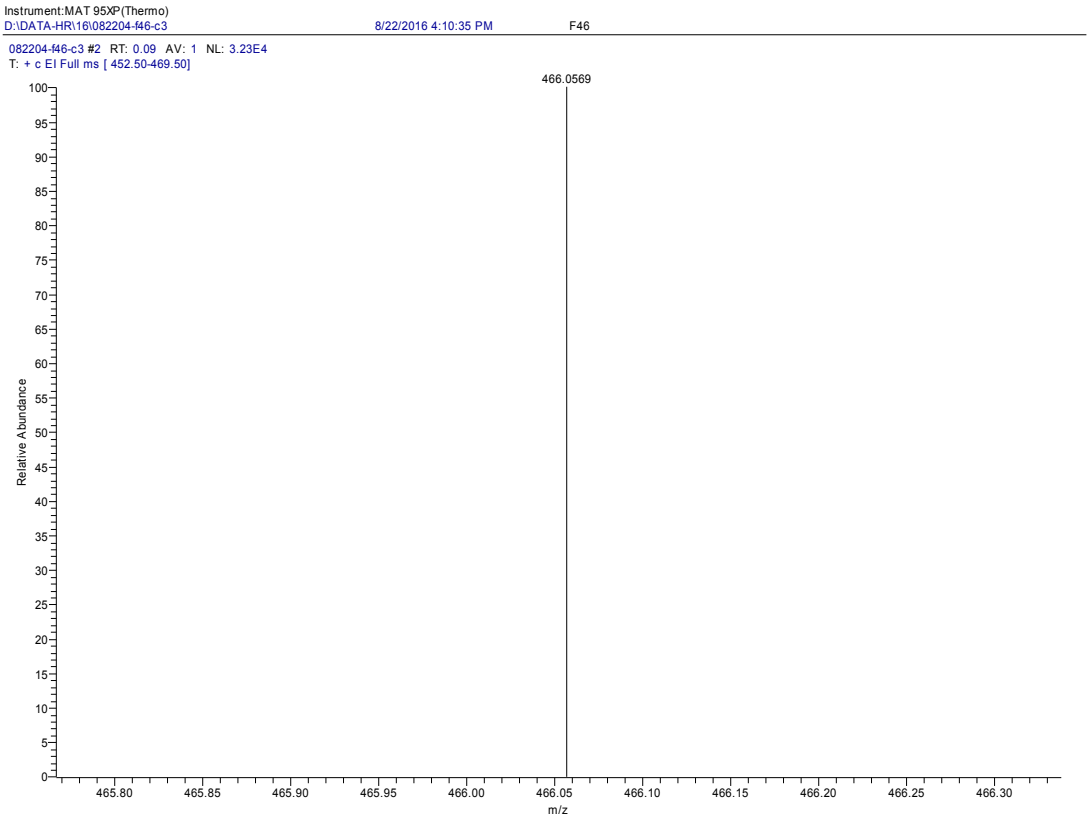


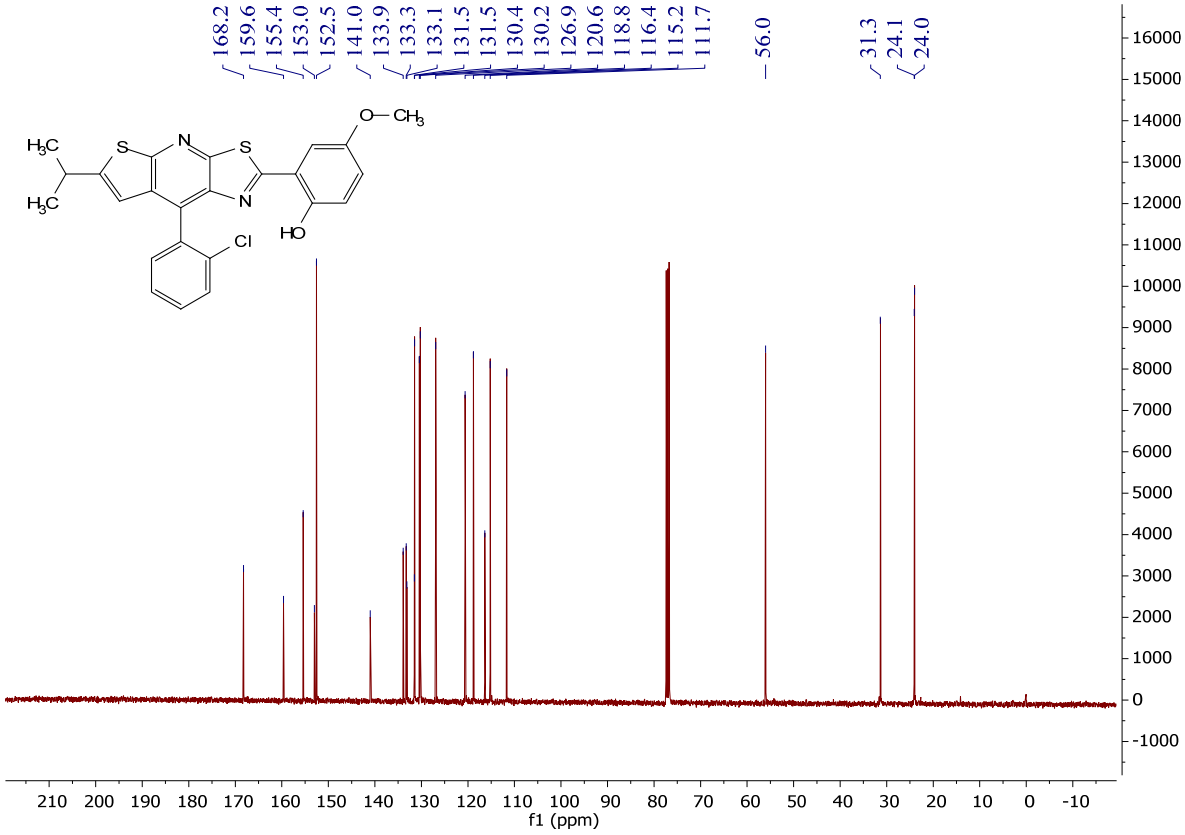

7.65
7.64
7.63
7.51
7.50
7.49
7.48
7.48
7.47
7.46
7.29
6.79
6.72
6.71
6.65
6.64
3.91
3.89
3.30
3.28
3.26
3.25
3.23
1.43
1.41
1.04
3.03
0.99
0.98
0.98
2.98
3.00
1.13
6.08
f1 (ppm)

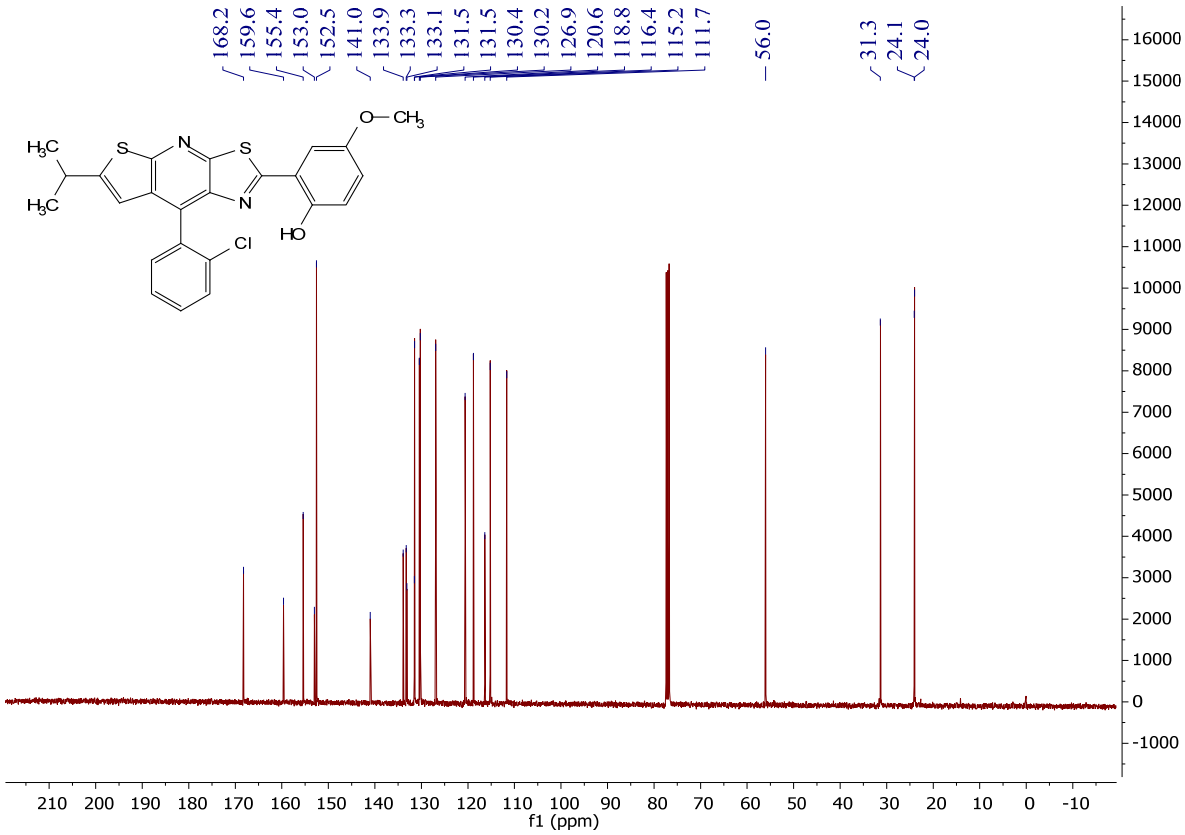

168.4
159.6
155.3
153.0
152.5
149.8
143.3
140.9
133.8
133.2
131.6
131.3
130.4
130.3
127.0
115.5
115.2
104.0
100.9
56.1
55.9
31.3
24.1
24.0
f1 (ppm)

BF13


Instrument:DSQ(Thermo)
Ionization Method:EI
D:\DSQ\DATA-LR\16\081208
8/12/2016 4:55:12 PM
F46
081208 #57 RT: 1.47 AV: 1 NL: 1.57E5
T: + c Full ms [45.00-800.00]
Relative Abundance
m/z
451
466
165
225
172
218
55
69
79
95
111
123
136
152
179
208
233
247
266
285
311
317
329
343
353
373
385
401
409
416
435


Instrument:MAT 95XP(Thermo)
D:\DATA-HR\16\082204-f46-c3
8/22/2016 4:10:35 PM
F46
082204-f46-c3 #2 RT: 0.09 AV: 1 NL: 3.23E4
T: + c EI Full ms [452.50-469.50]
Relative Abundance
m/z
466.0569

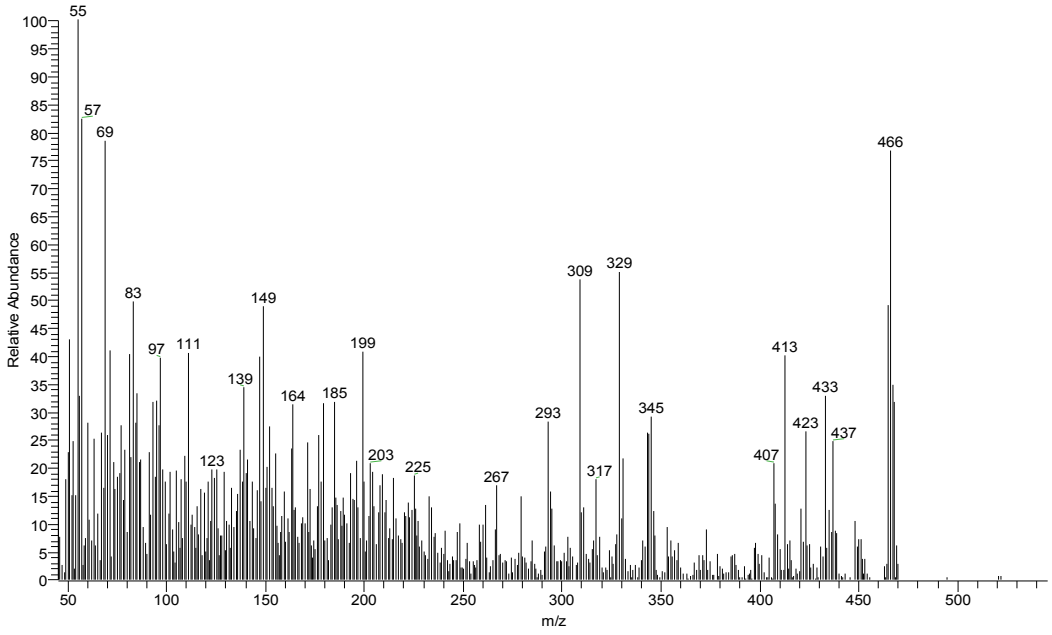

168.2
159.6
155.4
153.0
152.5
141.0
133.9
133.3
133.1
131.5
131.5
130.4
130.2
126.9
120.6
118.8
116.4
115.2
111.7
56.0
31.3
24.1
24.0
O—CH3
H3C
H3C
S
N
S
N
HO
Cl
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


168.2
159.6
155.4
153.0
152.5
141.0
133.9
133.3
133.1
131.5
131.5
130.4
130.2
126.9
120.6
118.8
116.4
115.2
111.7
56.0
31.3
24.1
24.0
O—CH3
H3C
H3C
S
N
S
N
HO
Cl
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

BF14

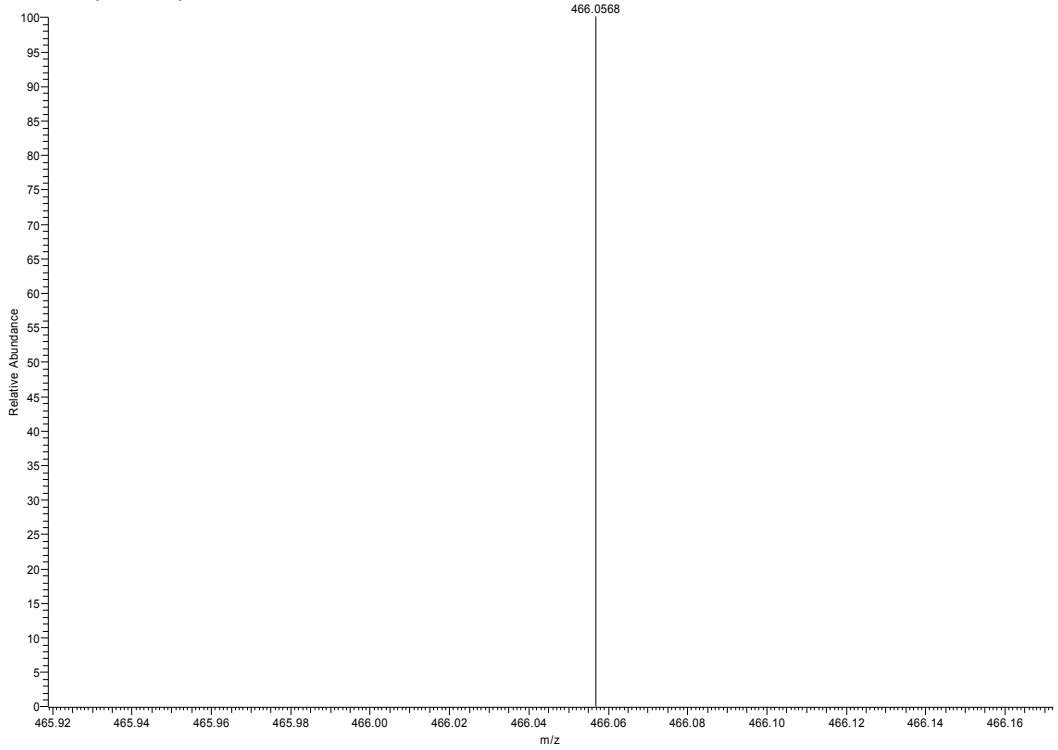
Instrument:DSQ(Thermo)
Ionization Method:EI
D:\DSQ\DATA-LR\16\092906 9/29/2016 4:03:50 PM F61

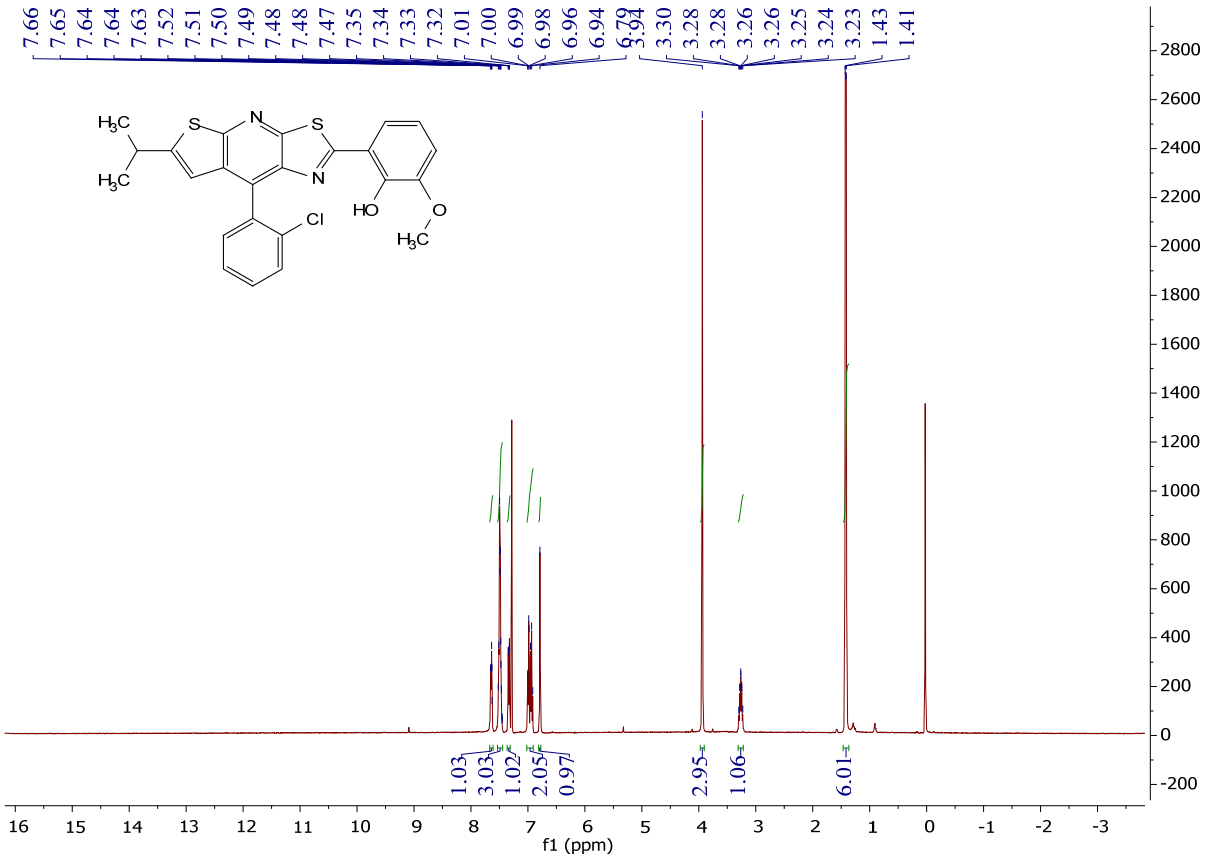
092906 #76 RT: 1.96 AV: 1 NL: 3.33E4
T: + c Full ms [45.00-800.00]

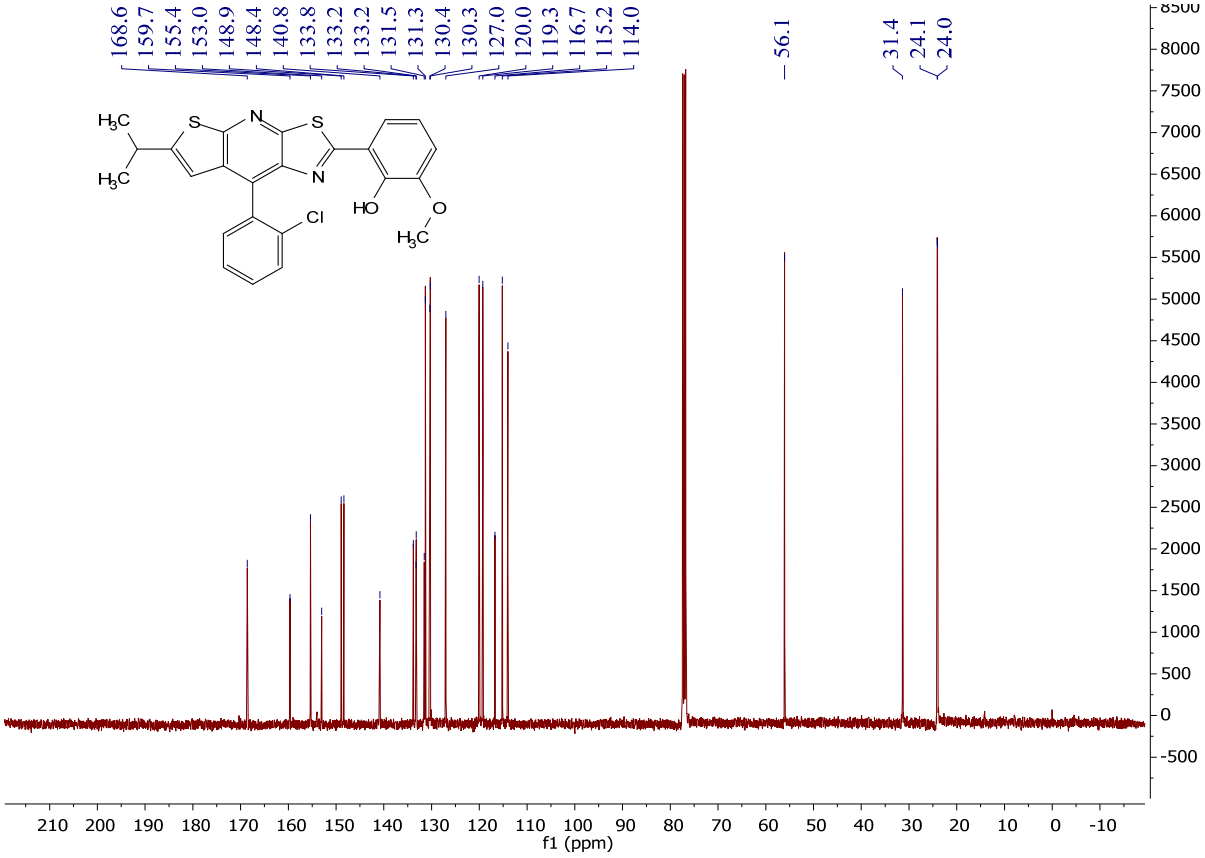


Instrument:MAT 95XP(Thermo)
D:\DATA-HR\16\093004-f61-c1 9/30/2016 10:58:00 AM F61

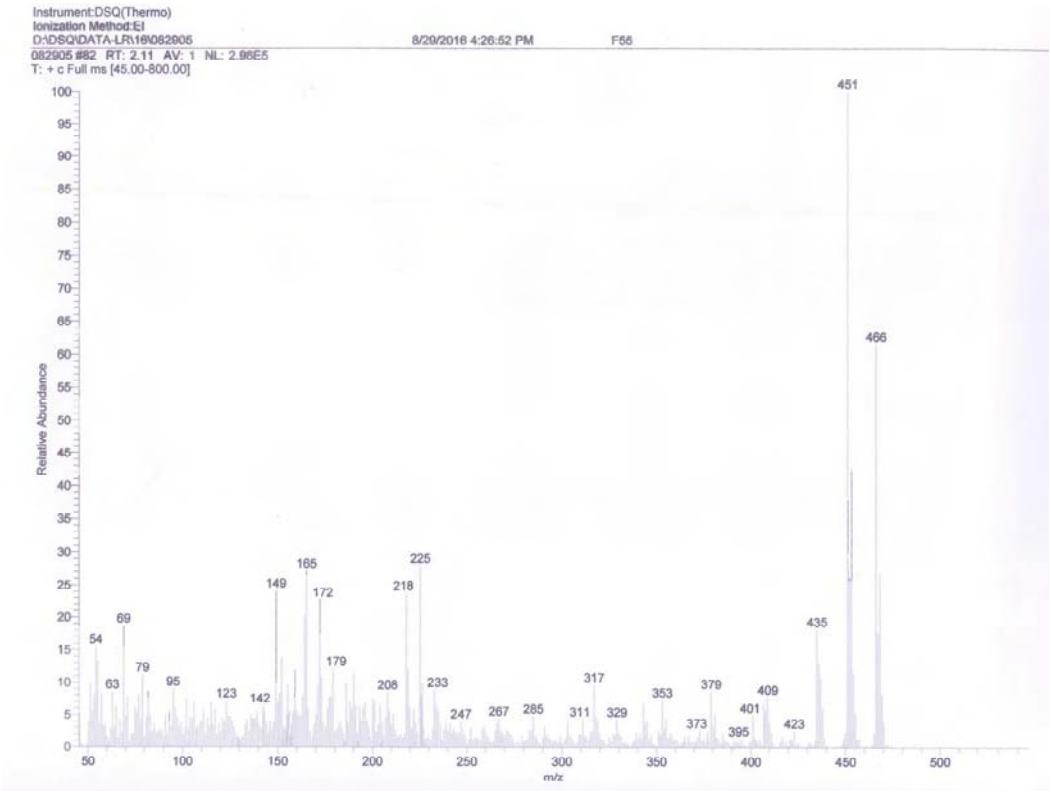
093004-f61-c1 #4 RT: 0.16 AV: 1 NL: 1.47E4
T: + c EI Full ms [452.50-470.50]

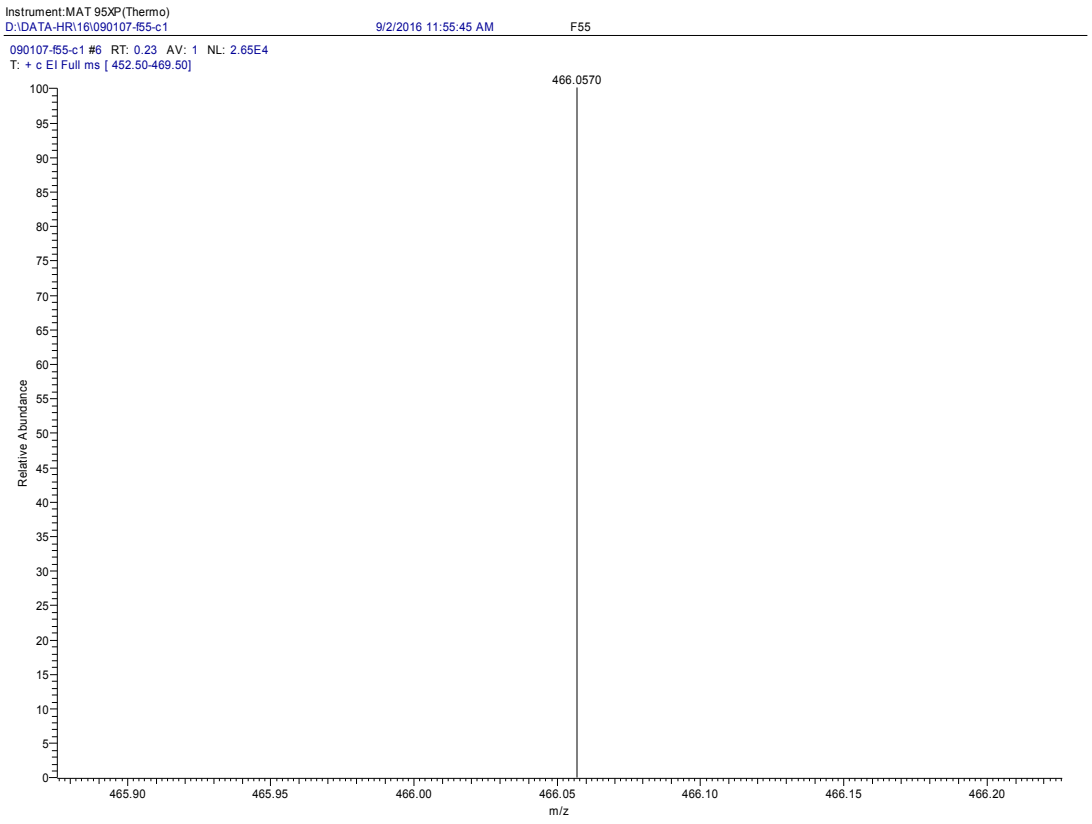


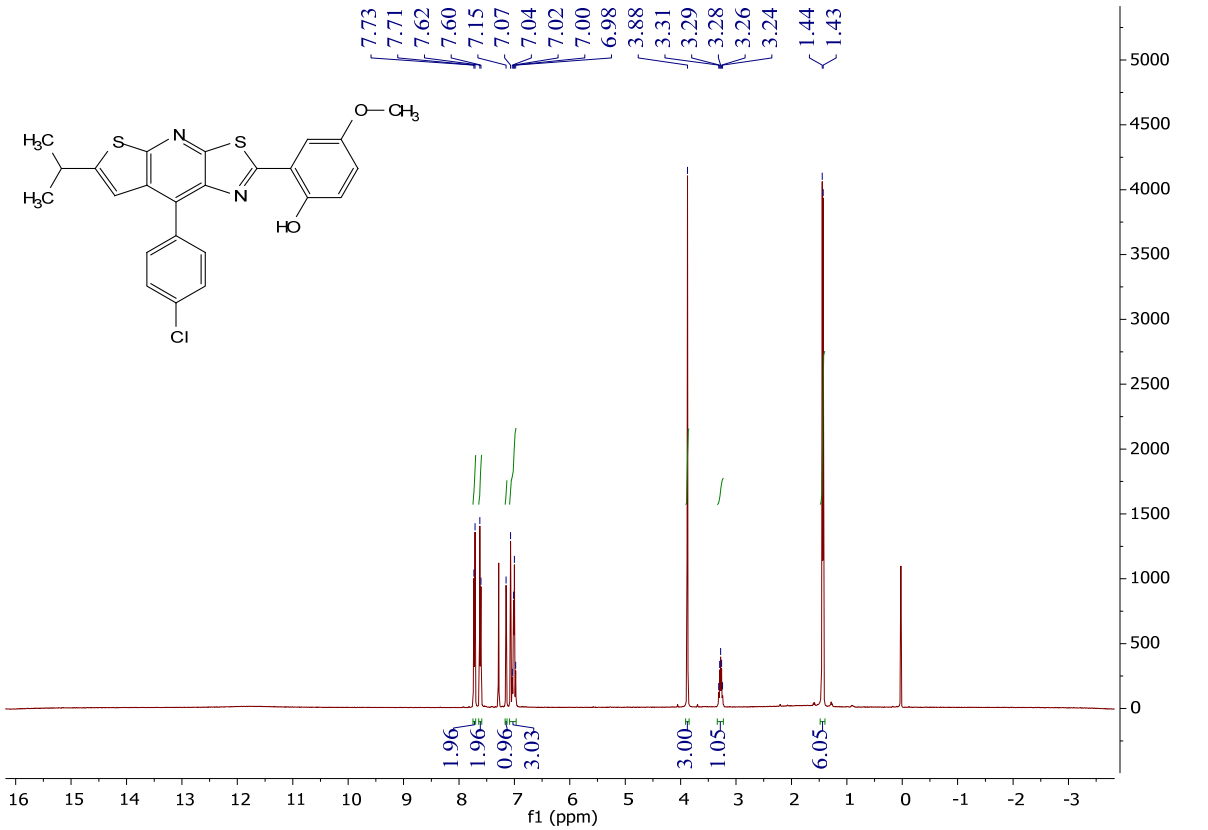

7.66
7.65
7.64
7.64
7.63
7.52
7.51
7.50
7.49
7.48
7.48
7.47
7.35
7.34
7.33
7.32
7.01
7.00
6.99
6.98
6.96
6.94
6.79
3.94
3.30
3.28
3.28
3.26
3.26
3.25
3.24
3.23
1.43
1.41
1.03
3.03
1.02
2.05
0.97
2.95
1.06
6.01
f1 (ppm)

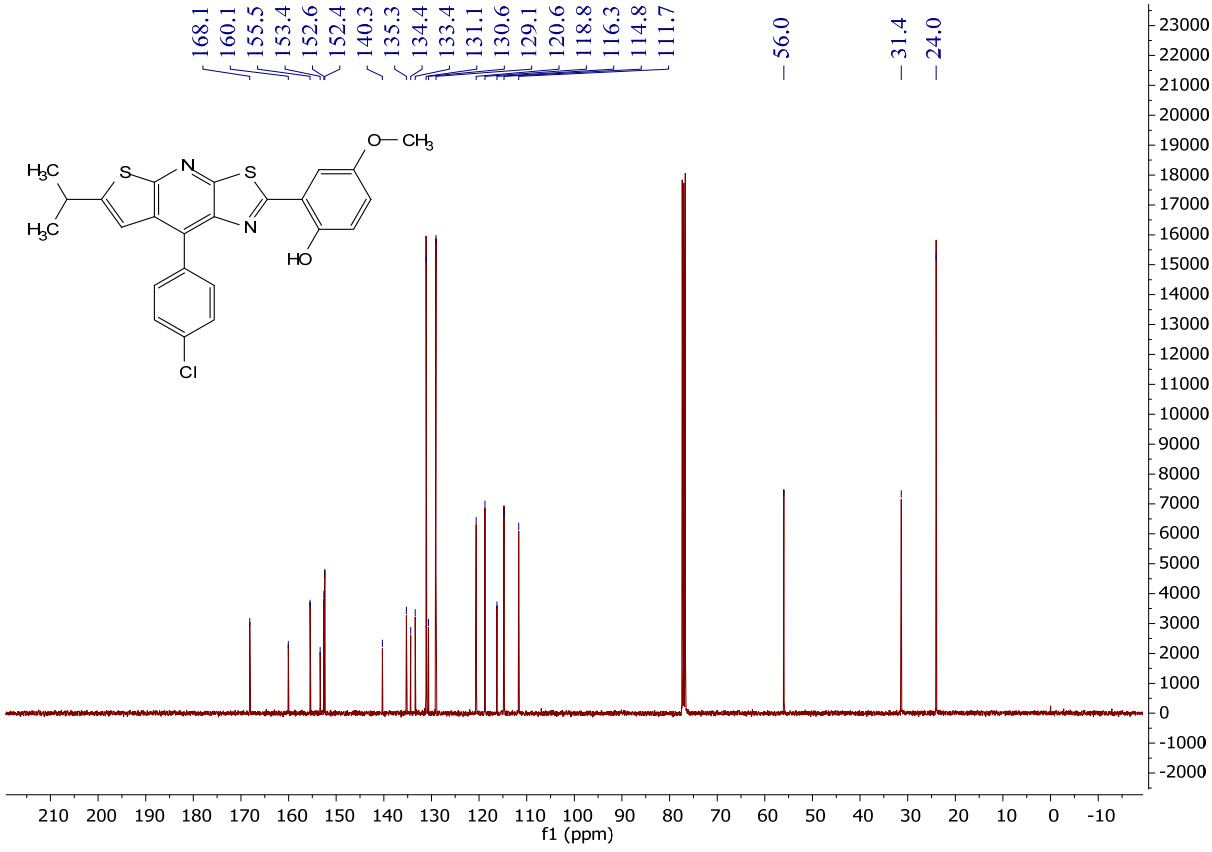

168.6
159.7
155.4
153.0
148.9
148.4
140.8
133.8
133.2
133.2
131.5
131.3
130.4
130.3
127.0
120.0
119.3
116.7
115.2
114.0
56.1
31.4
24.1
24.0
f1 (ppm)

BF15

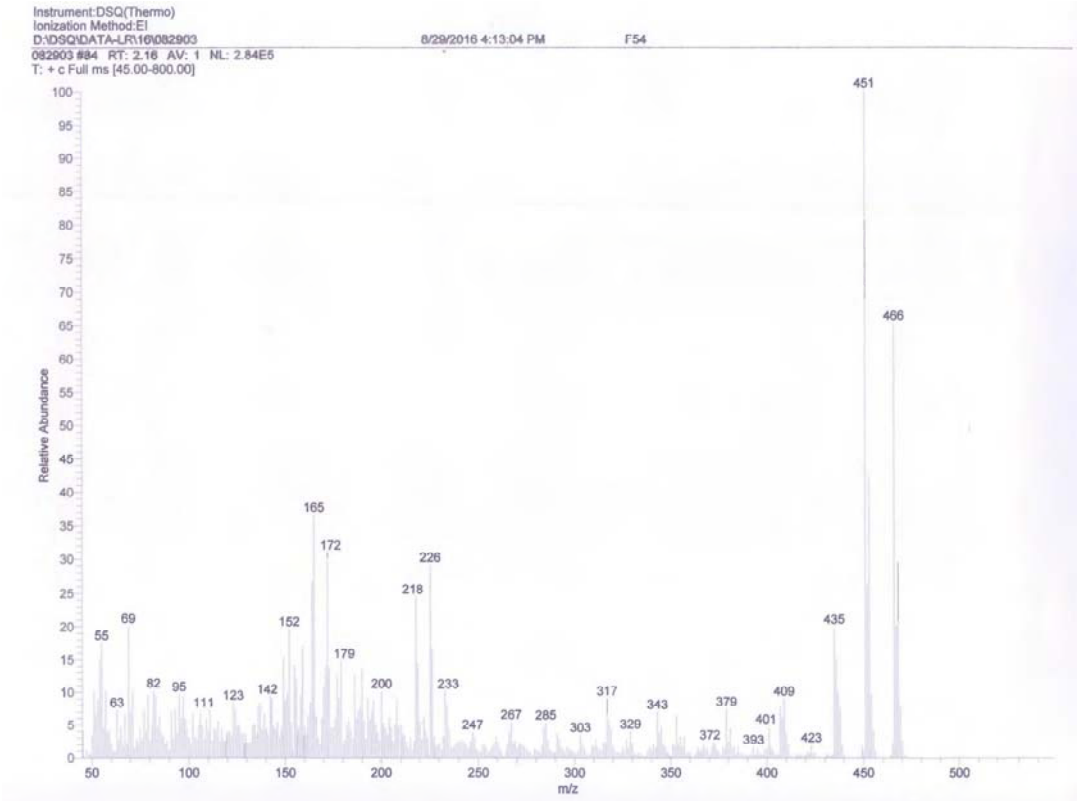

Instrument:DSQ(Thermo)
Ionization Method:EI
D:\DSQ\DATA-LR\16\082905
8/29/2016 4:26:52 PM
F55
082905 #82 RT: 2.11 AV: 1 NL: 2.96E5
T: + c Full ms [45.00-800.00]
Relative Abundance
m/z
451
466
225
165
149
172
218
69
54
435
179
79
63
95
123
142
208
233
317
247
267
285
311
329
353
373
379
395
401
409
423

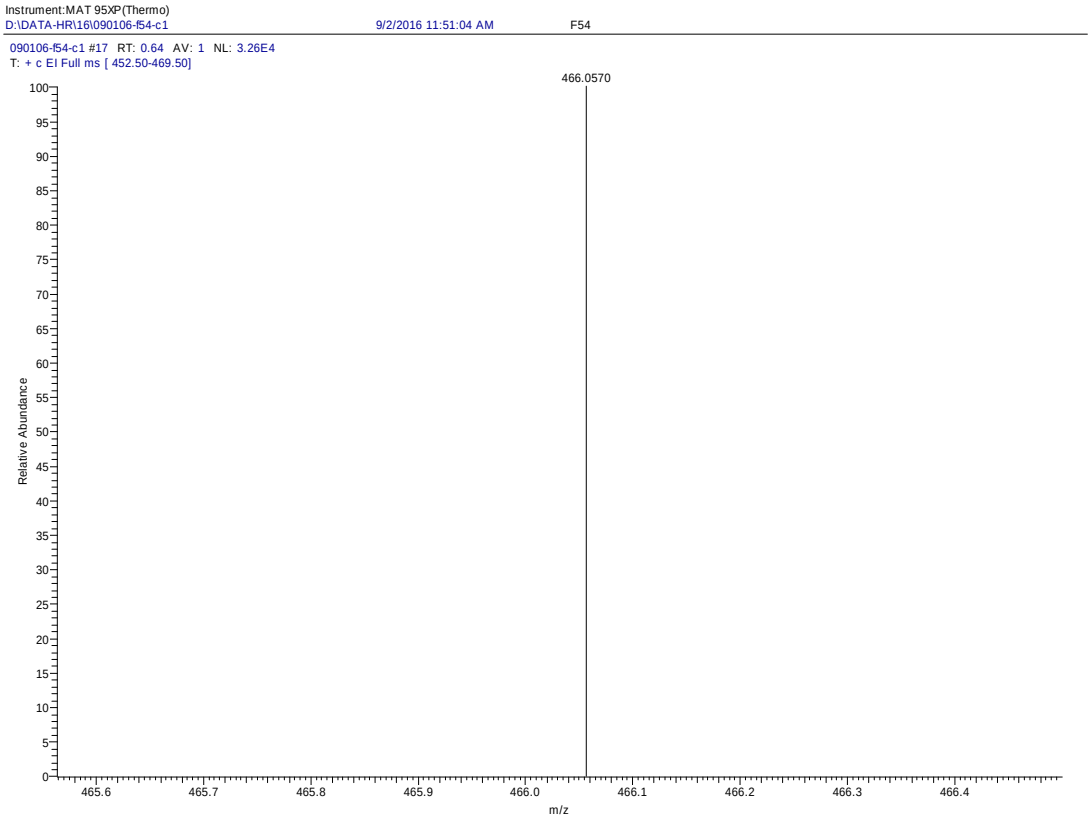

Instrument:MAT 95XP(Thermo)
D:\DATA-HR\16\090107-f55-c1
9/2/2016 11:55:45 AM
F55
090107-f55-c1 #6 RT: 0.23 AV: 1 NL: 2.65E4
T: + c EI Full ms [452.50-469.50]
466.0570
Relative Abundance
m/z

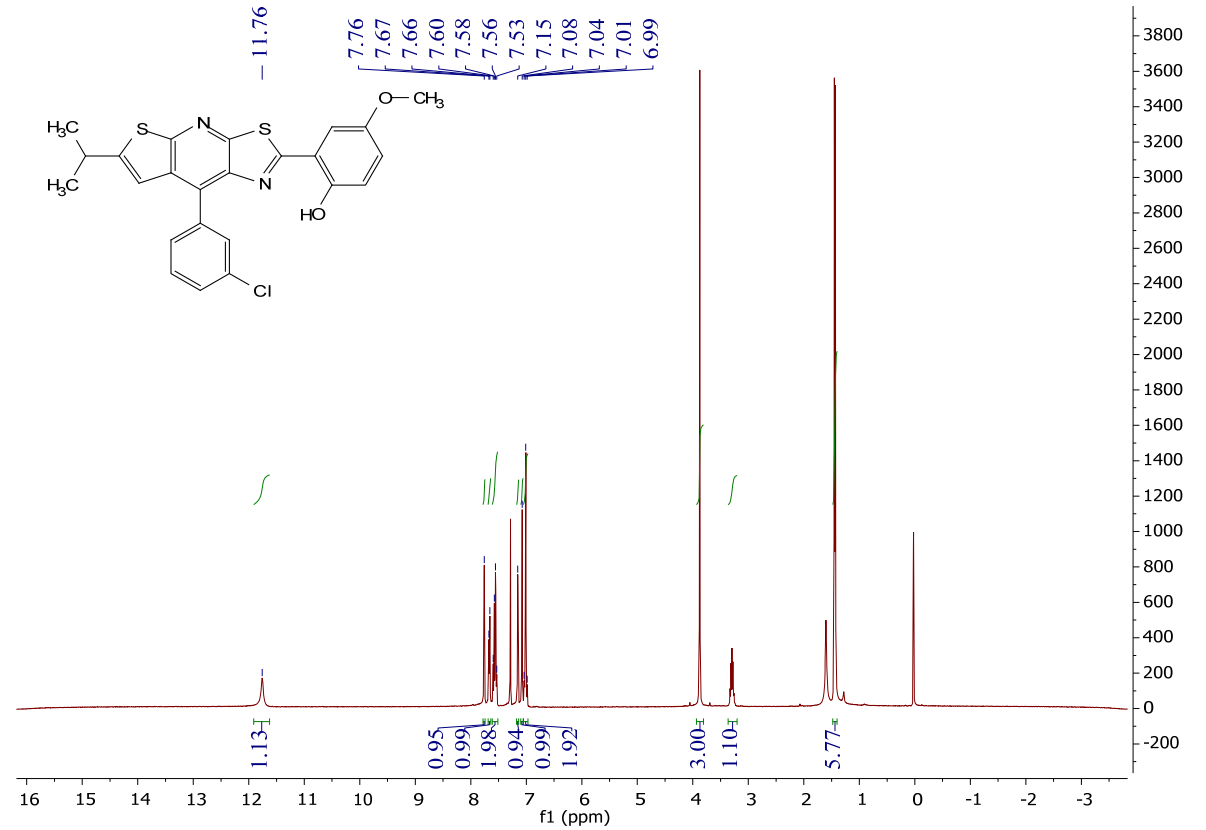

7.73
7.71
7.62
7.60
7.15
7.07
7.04
7.02
7.00
6.98
3.88
3.31
3.29
3.28
3.26
3.24
1.44
1.43
O—CH3
H3C
H3C
S
N
S
N
HO
Cl
1.96
1.96
0.96
3.03
3.00
1.05
6.05
f1 (ppm)

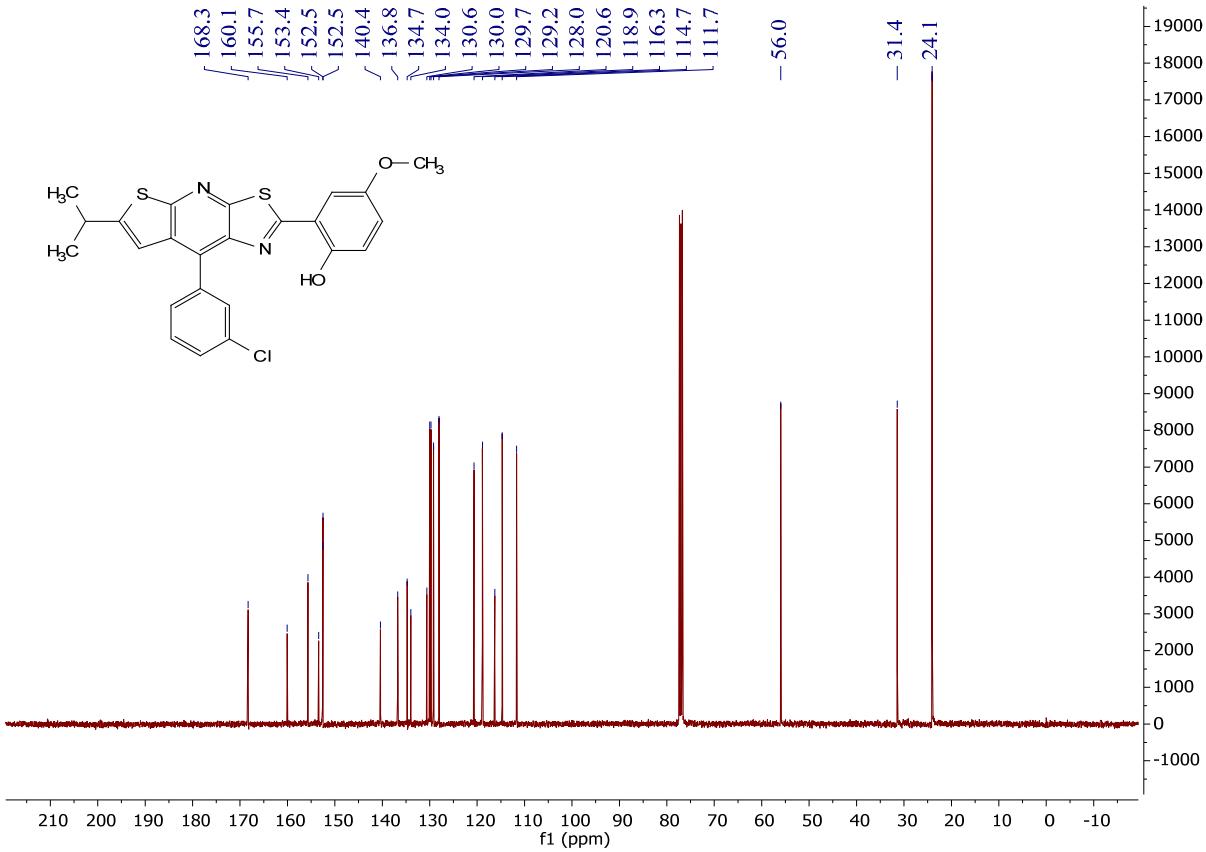

168.1
160.1
155.5
153.4
152.6
152.4
140.3
135.3
134.4
133.4
131.1
130.6
129.1
120.6
118.8
116.3
114.8
111.7
56.0
31.4
24.0
O—CH3
H3C
H3C
S
N
S
N
HO
Cl
f1 (ppm)

BF16

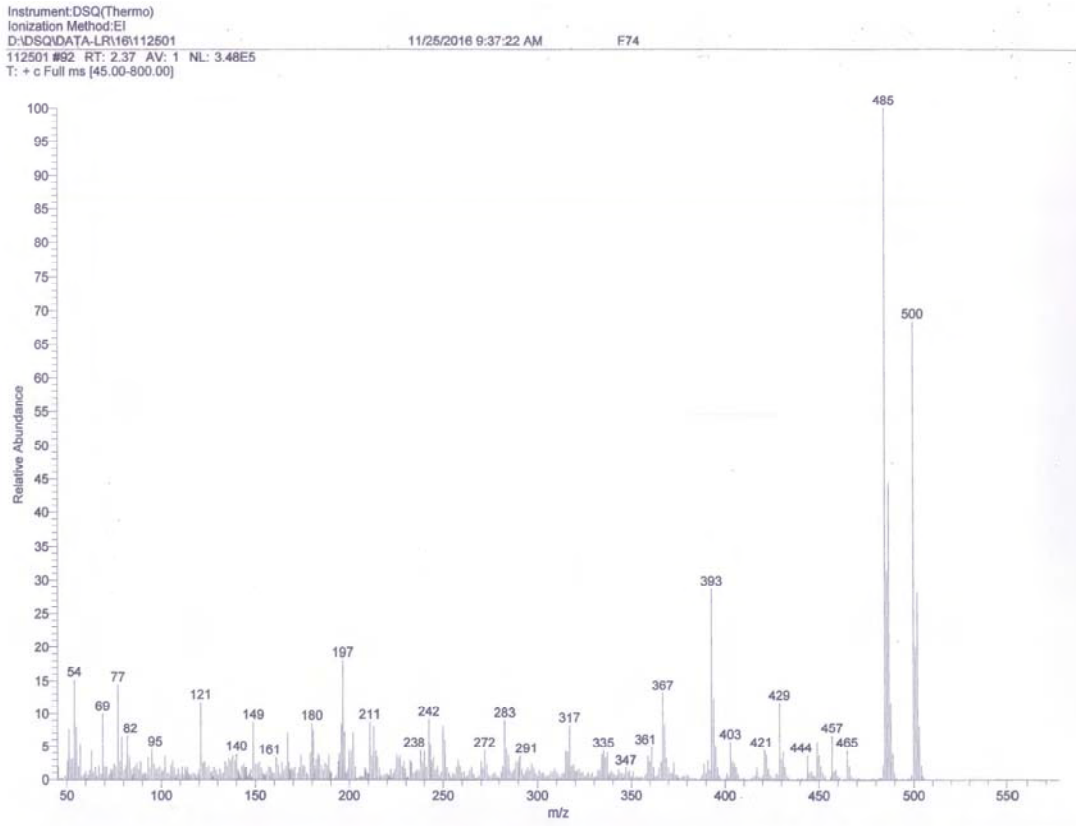

Instrument:DSQ(Thermo)
Ionization Method:EI
D:\DSQ\DATA-LR\16\082903
8/29/2016 4:13:04 PM
F54
082903 #84 RT: 2.16 AV: 1 NL: 2.84E5
T: + c Full ms [45.00-800.00]
Relative Abundance
m/z
451
466
165
172
226
218
435
69
55
152
179
200
233
317
63
82
95
111
123
142
247
267
285
303
329
343
372
379
393
401
409
423

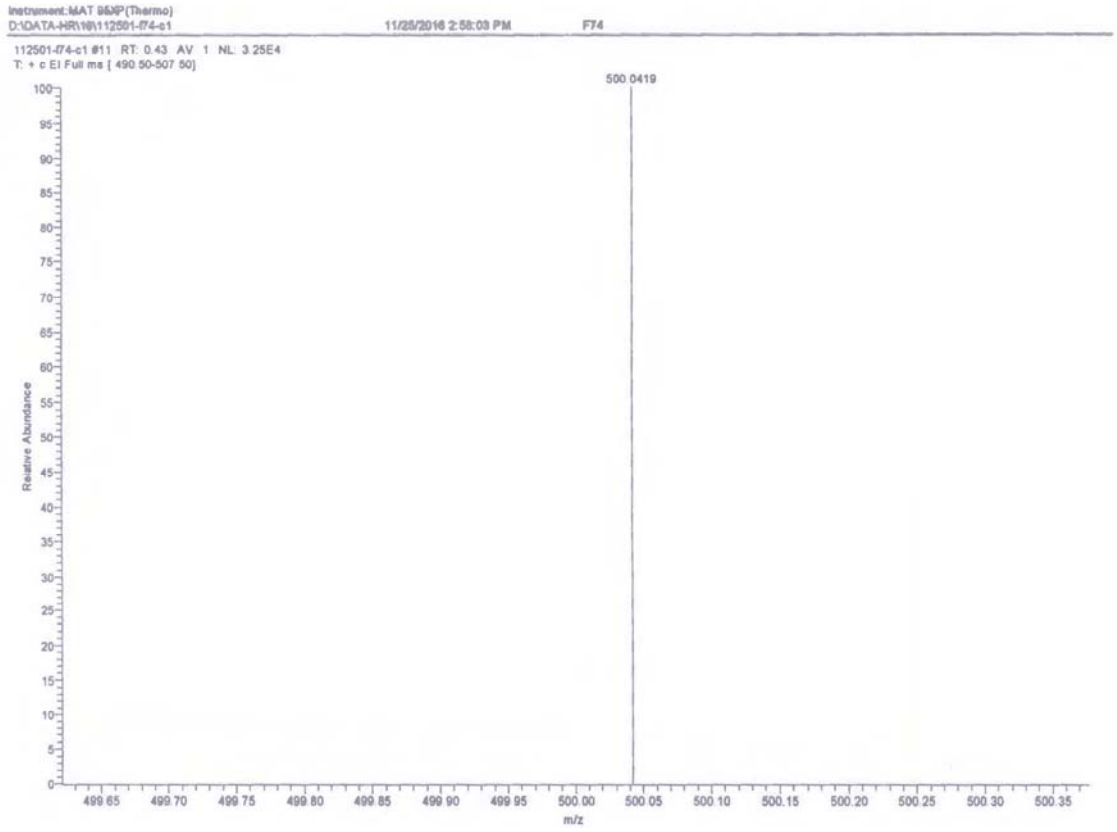

Instrument:MAT 95XP(Thermo)
D:\DATA-HR\16\090106-f54-c1
9/2/2016 11:51:04 AM
F54
090106-f54-c1 #17 RT: 0.64 AV: 1 NL: 3.26E4
T: + c EI Full ms [452.50-469.50]
466.0570
Relative Abundance
m/z

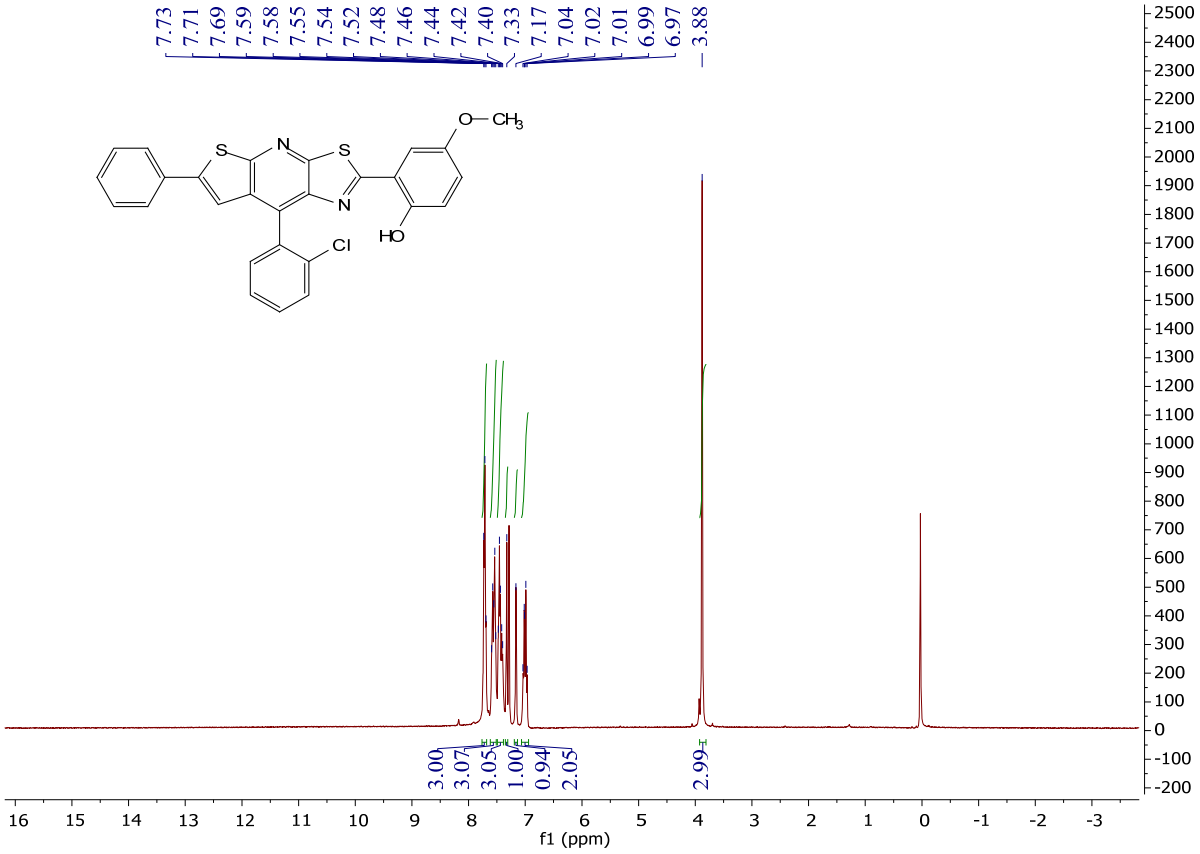

11.76
7.76
7.67
7.66
7.60
7.58
7.56
7.53
7.15
7.08
7.04
7.01
6.99
1.13
0.95
0.99
1.98
0.94
0.99
1.92
3.00
1.10
5.77
f1 (ppm)

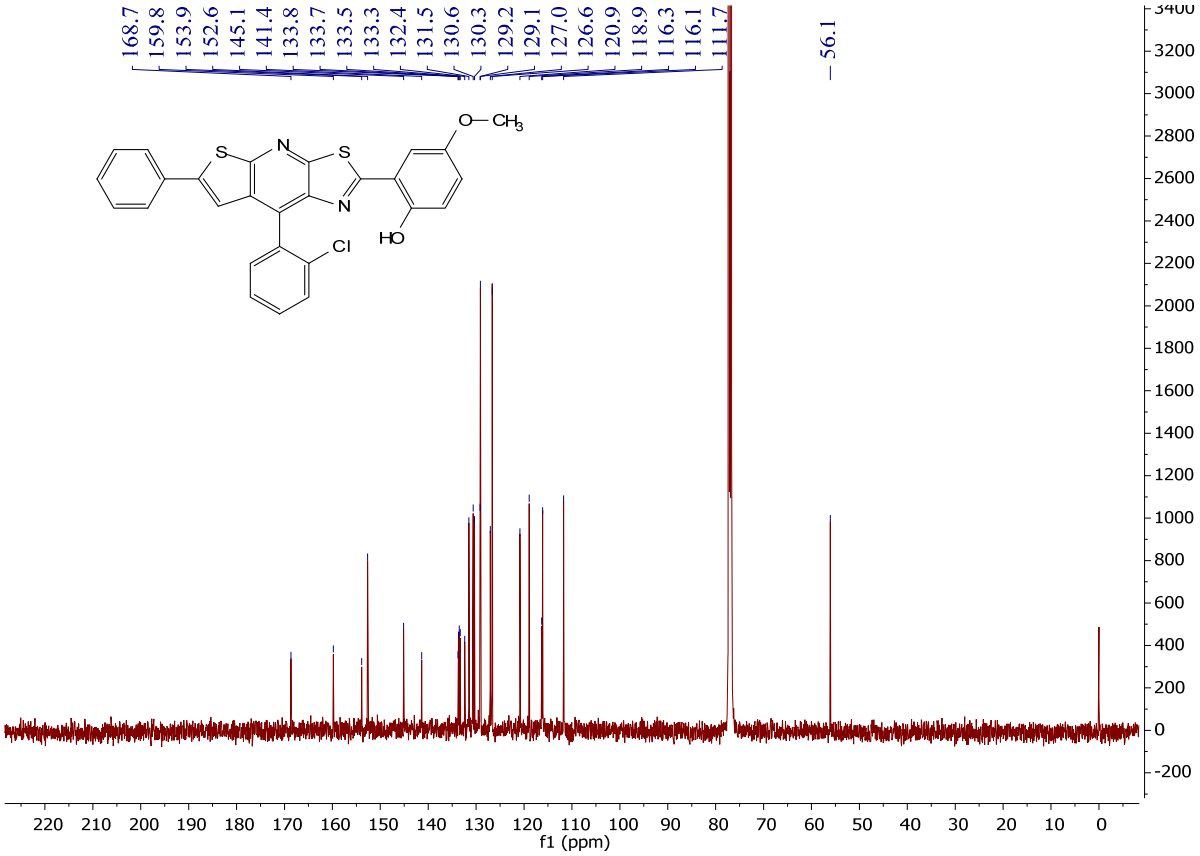

168.3
160.1
155.7
153.4
152.5
152.5
140.4
136.8
134.7
134.0
130.6
130.0
129.7
129.2
128.0
120.6
118.9
116.3
114.7
111.7
56.0
31.4
24.1
f1 (ppm)

BF17


Instrument:DSQ(Thermo)
Ionization Method:EI
D:\DSQ\DATA-LR\16\112501
11/25/2016 9:37:22 AM
F74
112501 #92 RT: 2.37 AV: 1 NL: 3.48E5
T: + c Full ms [45.00-800.00]
Relative Abundance
m/z
485
500
393
197
54
77
69
82
95
121
140
149
161
180
211
238
242
272
283
291
317
335
347
361
367
403
421
429
444
457
465


Instrument:MAT 95XP (Thermo)
D:\DATA-HR\16\112501-f74-c1
11/25/2016 2:58:03 PM
F74
112501-f74-c1 #11 RT: 0.43 AV: 1 NL: 3.25E4
T: + c EI Full ms [490.50-507.50]
500.0419
Relative Abundance
m/z

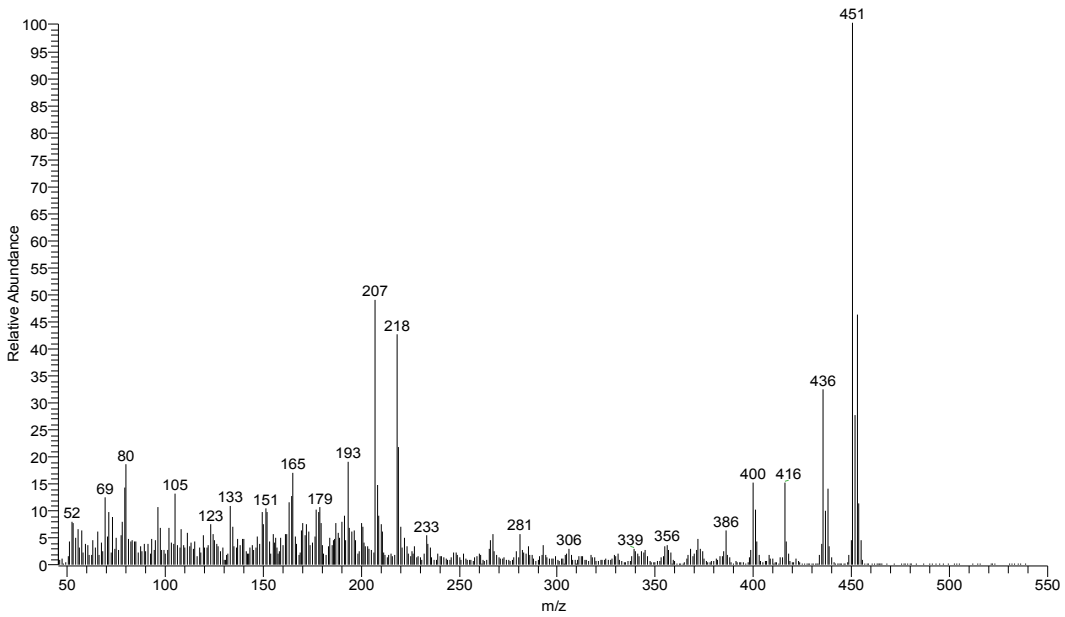

7.73
7.71
7.69
7.59
7.58
7.55
7.54
7.52
7.48
7.46
7.44
7.42
7.40
7.33
7.17
7.04
7.02
7.01
6.99
6.97
3.88
O—CH3
S
N
S
N
HO
Cl
3.00
3.07
3.05
1.00
0.94
2.05
2.99
f1 (ppm)


168.7
159.8
153.9
152.6
145.1
141.4
133.8
133.7
133.5
133.3
132.4
131.5
130.6
130.3
129.2
129.1
127.0
126.6
120.9
118.9
116.3
116.1
111.7
56.1
O—CH3
S
N
S
N
HO
Cl
f1 (ppm)

BF18

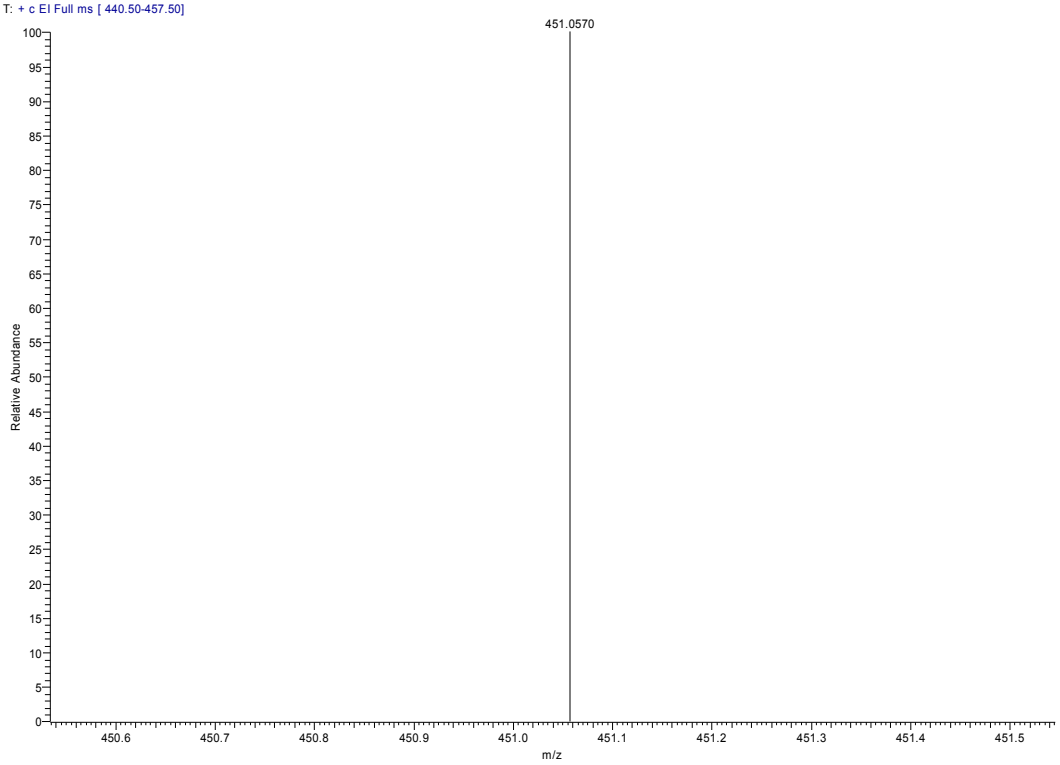
Instrument:DSQ(Thermo)
Ionization Method:EI
D:\DSQ\DATA-LR\16\061404 6/14/2016 11:14:03 AM F38

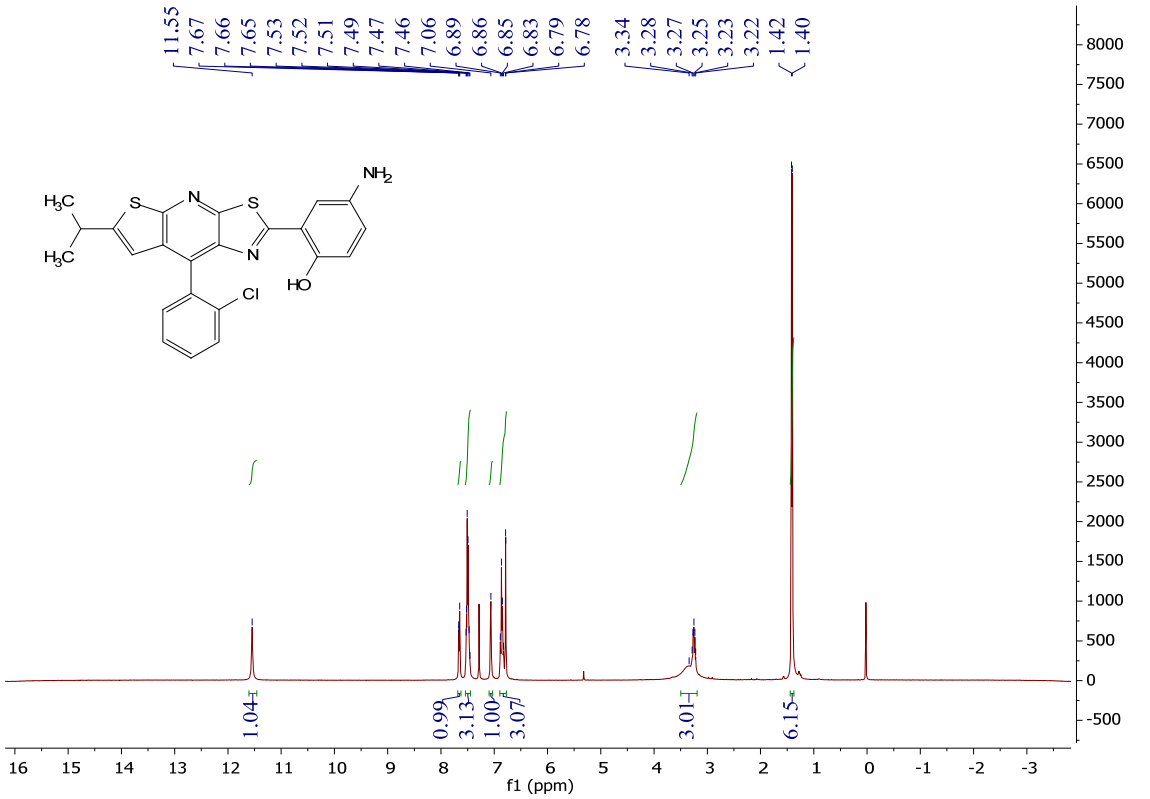
061404 #102 RT: 2.63 AV: 1 NL: 1.73E6
T: + c Full ms [45.00-800.00]

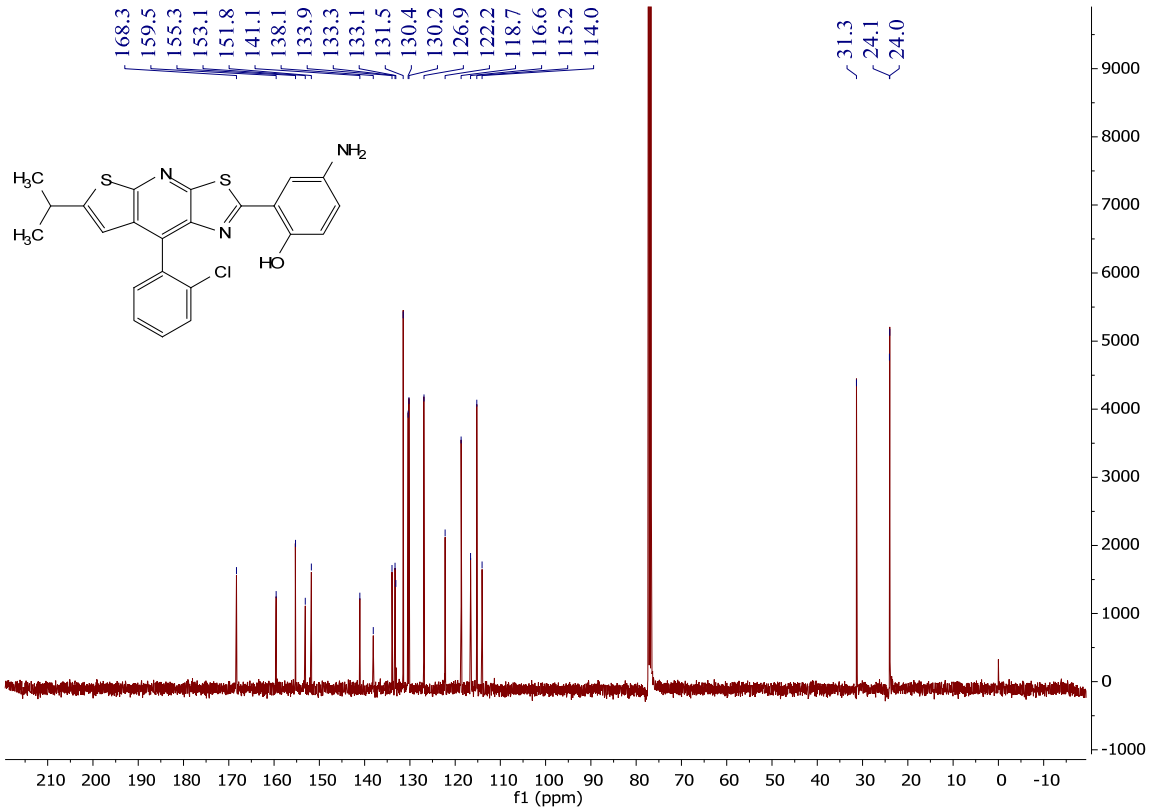


Instrument:MAT 95XP(Thermo)
D:\DATA-HR\16\062003-f38-c1 6/20/2016 4:29:09 PM F38

062003-f38-c1 #10 RT: 0.38 AV: 1 NL: 3.22E4
T: + c EI Full ms [440.50-457.50]




11.55
7.67
7.66
7.65
7.53
7.52
7.51
7.49
7.47
7.46
7.06
6.89
6.86
6.85
6.83
6.79
6.78
3.34
3.28
3.27
3.25
3.23
3.22
1.42
1.40
NH2
H3C
H3C
S
N
S
N
HO
Cl
1.04
0.99
3.13
1.00
3.07
3.01
6.15
f1 (ppm)


168.3
159.5
155.3
153.1
151.8
141.1
138.1
133.9
133.3
133.1
131.5
130.4
130.2
126.9
122.2
118.7
116.6
115.2
114.0
31.3
24.1
24.0
NH2
H3C
H3C
S
N
S
N
HO
Cl
f1 (ppm)

References

1. L. Huang, R. Yu, L. Leng, F. Gong, X. Zhu and Y. Wan, *Synthesis*, 2014, **46**, 2317-2326.
2. M. Huang, R. Yu, K. Xu, S. Ye, S. Kuang, X. Zhu and Y. Wan, *Chem. Sci.*, 2016, **7**, 4485-4491.