N-S Bond Cleavage of Tosyl Hydrazones by Dual Reactive Arynes: Synthesis of Diaryl Sulfones, Spiro[indazole-3,3'-indolin]-2'-one, and N-Phenyl benzenesulfonohydrazides

Suresh Snoxma Smile and Ponnusamy Shanmugam*

Organic and Bioorganic Chemistry Division, Central Leather Research Institute, Adyar, Chennai-600020, India

1. General remarks

All the reactions were carried out in oven-dried glassware. Unless otherwise specified, all reactions were carried out under an atmosphere of argon. Commercial dry CH_3CN was stored under nitrogen over 4 Å molecular sieves. The symmetrical and unsymmetrical and hetaryne precursors were purchased from Sigma-Aldrich and used as received, without any further purification. Anhydrous CsF was dried and stored under a nitrogen atmosphere. Progress of reactions was monitored by Thin Layer Chromatography (TLC) using Merck pre-coated TLC plates (Merck 60 F254) and compounds were visualized with a UV light at 254 nm. Further visualization was achieved by staining with iodine. Purification of crude compounds were done by column chromatography using Silica gel (Mesh size 100-200).The NMR spectra were recorded on a Bruker-400 MHz NMR spectrometer (400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR) with $CDCl_3$ or DMSO-d6 as the solvent and TMS as an internal reference. Integrals are in

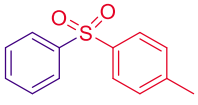
accordance with assignments; Coupling constants (*J*) were reported in Hertz (Hz). All the reported ^{13}C spectra are proton-decoupled. Multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplets), dd (doublet of doublet), brs (broad singlet). The FTIR spectra were recorded on a Perkin-Elmer RX-IFT-IR by KBr Pellet technique and absorbencies are reported in cm^{-1}. The HRMS analyses were done on a Q-T Micro mass spectrometer. Yields refer to quantities obtained after chromatography.

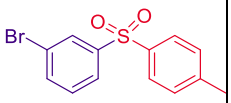
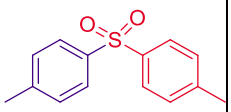
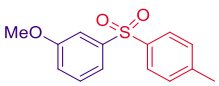
2. Experimental Details

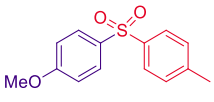
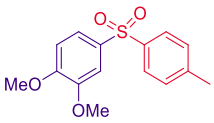
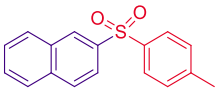
General experimental procedure for the preparation of compounds 3, 4, and 5

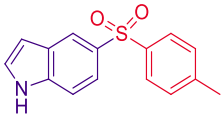
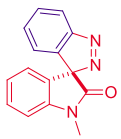
In a reaction tube charged with 4-methyl-N-methyl isatin-benzenesulfonohydrazide 1 (50 mg, 1.8 mmoles), dry acetonitrile (2 mL) under Ar atmosphere was added benzyne precursor 2-(trimethylsilyl) phenyl trifluoro methane sulfonate (3 equivalents, 0.100 mL) followed by 3 equivalents of CsF as fluoride source. The entire setup was kept in a preheated oil bat at 60˚C. The progress of the reaction was monitored by TLC. After completion of the reaction (ca. 10 min.), the solvent was removed in vacuo. The resulted crude mixture was purified through a silica gel column chromatography using a gradient elution using hexane-EtOAc (up to 20%) to obtain pure compounds 3, 4, and 5 in excellent combined yield.

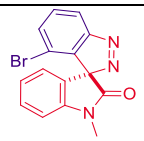
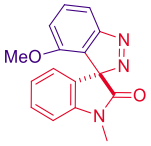
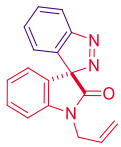
3. Spectroscopic data of synthesized compounds

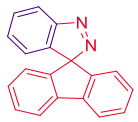
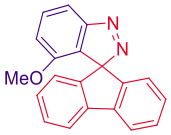
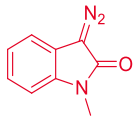
<table>
<tr><td colspan="2">1-Methyl-4-(phenylsulfonyl)benzene(3a)</td></tr>
<tr><td> 
3a</td><td>Nature: White powder; 19mg, yield:51%;
R_f (25% EtOAc-Hexane):0.40
FTIR (KBr) ν_{max}: 3090, 3059, 2980, 2869, 1657, 1593, 1448, 1401,1307, 1297, 1156, 1107, 998 cm^{-1};
^{1}H NMR ($CDCl_3$/TMS, 400 MHz,):δ 7.95 – 7.91 (m, 2H), 7.86 – 7.80 (m, 2H), 7.56 – 7.46 (m, 3H), 7.32 –7.27 (m, 2H), 2.39 (s, 3H)
^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 144.2, 142.0, 138.7, 133.0, 129.9, 129.2(2C), 127.7(2C), 127.5(2C), 21.6;
HRMS-ESI: Calcd. for $C_{13}H_{13}O_2S[M+H]^+$m/z: 233.0636; Found 233.0641.</td></tr>
<tr><td colspan="2">1-Bromo-3-tosylbenzene(3b)</td></tr>
</table>

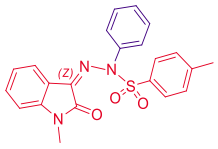
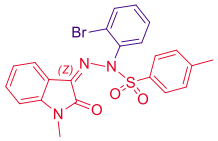
 **3b**	**Nature:** Colourless liquid;26mg, yield: 46%; **R_f** (25% EtOAc-Hexane):0.40; **FTIR** (KBr) ν_{max}: 3079, 3039, 2981, 2927, 1929, 1894,1702, 1662, 1592, 1492, 1321, 1293, 1119, 1016, 958, 914 cm^{-1}; **^{1}H NMR** ($CDCl_3$/TMS, 400 MHz,):δ8.06 (t, *J* = 1.8 Hz, 1H), 7.88 – 7.80 (m, 3H), 7.68 – 7.64 (m, 1H), 7.39 – 7.29 (m, 3H), 2.41 (s, 3H); **^{13}C NMR** ($CDCl_3$/TMS, 100 MHz): δ 144.7, 143.9, 1379, 136.1, 130.8, 130.4(2C), 130.1, 127.9(2C), 126.1, 123.2, 21.6; **HRMS-ESI**: Calcd. for $C_{13}H_{12}BrO_2S$ $[M+H]^+$*m/z*: 312.9771; Found 312.9741.
4-Methyl-1-tosylbenzene (**3c**)	
 **3c**	**Nature:** White powder; 21mg, yield: 40%; **R_f** (25% EtOAc-Hexane):0.40; **FTIR** (KBr) ν_{max}: 3300, 3043, 2954, 2924, 1596, 1493, 1451, 1379, 1320, 1152, 1103, 1073cm^{-1}; **^{1}H NMR** ($CDCl_3$/TMS, 400 MHz,):δ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.79 (m, 3H), 7.73 (ddd, *J* = 6.3, 1.7, 0.6 Hz, 1H), 7.36 (ddd, *J* = 4.6, 2.9, 1.1 Hz, 1H), 7.30 – 7.25 (m, 3H), 2.38 (d, *J* = 3.4 Hz, 6H); **^{13}C NMR** ($CDCl_3$/TMS, 100 MHz): δ 144.1, 143.9, 141.8, 139.5, 139.1 138.8, 133.8, 129.9, 129.1, 127.8, 127.6, 124.7, 21.6, 21.5; **HRMS-ESI**: Calcd. for $C_{14}H_{15}O_2S[M+H]^+$*m/z*: 247.0793; Found 247.0782.
3-Methoxy-1-tosylbenzene (**3d**)	
 **3d**	**Nature:** White powder: 23mg, yield: 41%; **R_f** (25% EtOAc-Hexane):0.40; **FTIR** (KBr) ν_{max}: 3450, 3044, 2975, 2923, 2108, 1919, 1682, 1596, 1495, 1456, 1319, 1298, 1182, 1107, 1021 cm^{-1}; **^{1}H NMR** ($CDCl_3$/TMS, 400 MHz,):δ7.88 – 7.83 (m, 2H), 7.82 – 7.77 (m, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 6.97 – 6.92 (m, 2H), 3.83 (s, 3H), 2.38 (s, 3H); **^{13}C NMR** ($CDCl_3$/TMS, 100 MHz): δ 163.2, 143.7, 139.5, 133.6, 129.8(2C), 129.7(2C), 127.4(2C), 114.5(2C), 55.6, 21.5; **HRMS-ESI**: Calcd. for $C_{14}H_{15}O_3S[M+H]^+$*m/z*: 263.0742; Found 263.0732.

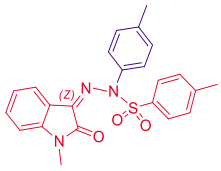
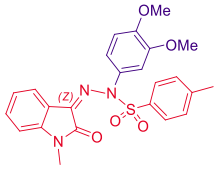
4-Methoxy-1-tosylbenzene (**3e**)	
 **3e**	**Nature:** White powder: 25mg, yield:45%; **R_f** (25% EtOAc-Hexane):0.40; **FTIR** (KBr) ν_{max}: 3450, 3096, 2575, 2108, 2095, 1919, 1682, 1596, 1495, 1319, 1182, 1107, 1071, 1021 cm^{-1}; **^{1}H NMR** ($CDCl_3$/TMS, 400 MHz,):δ7.88 – 7.83 (m, 2H), 7.82 – 7.77 (m, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 6.97 – 6.92 (m, 2H), 3.83 (s, 3H), 2.38 (s, 3H); **^{13}C NMR** ($CDCl_3$/TMS, 100 MHz):δ163.2, 143.7, 139.5, 133.6, 129.8(2C), 129.7(2C), 127.4(2C), 114.5(2C), 55.6, 21.5; **HRMS-ESI**: Calcd. for $C_{14}H_{15}O_3S[M+H]^+$*m/z*: 263.0742; Found 263.0732.
4,5-Dimethoxy-1-tosylbenzene (**3f**)	
 **3f**	**Nature: White solid**: 22mg, yield:35%; **R_f** (25% EtOAc-Hexane):0.40; **FTIR** (KBr) ν_{max}: 3445, 3084, 3053, 2848, 1592, 1508, 1470, 1456, 1313, 1297, 1185, 1103, 1079, 1021 cm^{-1}; **^{1}H NMR** ($CDCl_3$/TMS, 400 MHz,):δ7.83 – 7.79 (m, 2H), 7.55 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.38 (d, *J* = 2.1 Hz, 1H), 7.30 – 7.26 (m, 2H), 6.92 (d, *J* = 8.5 Hz, 1H), 3.91 (d, *J* = 2.8 Hz, 6H), 2.39 (s, 3H); **^{13}C NMR** ($CDCl_3$/TMS, 100 MHz): δ 152.9, 149.2, 143.8, 139.3, 133.5, 129.9(2C), 127.3(2C), 121.7(2C), 110.8, 109.8, 56.2, 56.1, 21.5; **HRMS-ESI**: Calcd. for $C_{15}H_{16}O_4SNa$ $[M+Na]^+$*m/z*: 315.0667; Found 315.0656.
2-Tosylnaphthalene **(3g)**	
 **3g**	**Nature:** White powder: 29mg, yield:48%; **R_f** (25% EtOAc-Hexane):0.40; **FTIR** (KBr) ν_{max}: 3064, 2958, 2852, 1595, 1506, 1495, 1457, 1347, 1317, 1305, 1155, 1093 cm^{-1}; **^{1}H NMR** ($CDCl_3$/TMS, 400 MHz,):δ8.59 – 8.53 (m, 1H), 7.99 – 7.94 (m, 1H), 7.94 – 7.88 (m, 2H), 7.88 – 7.82 (m, 3H), 7.66 – 7.56 (m, 2H), 7.29 (dd, *J* = 8.5, 0.6 Hz, 2H), 2.38 (s, 3H); **^{13}C NMR** ($CDCl_3$/TMS, 100 MHz): δ 144.2, 138.8, 138.7, 134.9, 132.3,

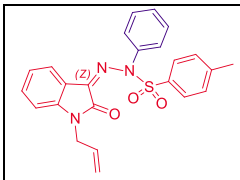
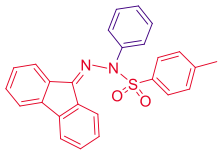
	129.9(2C), 129.5, 129.4, 129.1(2C), 128.9, 127.9, 127.8, 127.6, 122.6, 21.6 ; **HRMS-ESI**: Calcd. for $C_{17}H_{14}O_2SNa$ $[M+Na]^+$*m/z*: 305.0612; Found 305.0603.
6-Tosyl-1H-indole (**3h**)	
 **3h**	**Nature:** Yellow powder: 25mg, yield:43%; **R_f** (25% EtOAc-Hexane):0.40; **FTIR** (KBr) ν_{max}: 3316, 2958, 2921, 1597, 1496, 1349, 1327, 1279, 1146, 1053, 1019, 972, 917cm^{-1}; **^{1}H NMR** ($CDCl_3$/TMS, 400 MHz,):δ 8.71 (s, 1H), 8.22 (d, *J* = 1.6 Hz, 1H), 7.80 (dd, *J* = 7.5, 4.5 Hz, 1H), 7.76 (t, *J* = 6.1 Hz, 2H), 7.60 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.34 (d, *J* = 8.6 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.19 – 7.13 (m, 3H), 6.57 – 6.53 (m, 1H), 2.28 (s, 3H); **^{13}C NMR** ($CDCl_3$/TMS, 100 MHz): δ 143.4, 139.9, 137.9, 132.7, 129.6, 127.5, 127.3,126.8, 121.7,121.2, 120.8, 118.9, 104.0, 102.1, 21.5; **HRMS-ESI**: Calcd. for $C_{15}H_{14}NO_2S[M+H]^+$*m/z*: 272.0745; Found 272.0733.
1'-Methylspiro[indazole-3,3'-indolin]-2'-one **(4a)**	
 **4a**	**Nature:** White Solid: 12mg, yield:32%; **R_f** (25% EtOAc-Hexane):0.40; **FTIR** (KBr) ν_{max}: 3087, 3071, 2941, 2889, 1723, 1610, 1493, 1424, 1366, 1303, 1252, 1125, 1085, 1062, 996, 930cm^{-1}; **^{1}H NMR** ($CDCl_3$/TMS, 400 MHz,):δ8.23 (d, *J* = 7.9 Hz, 1H), 7.61 (td, *J* = 7.8, 1.0 Hz, 1H), 7.47 (dtd, *J* = 21.7, 7.6, 1.0 Hz, 2H), 7.34 (d, *J* = 7.5 Hz, 1H), 7.02 (ddd, *J* = 11.5, 8.4, 4.4 Hz, 2H), 6.58 – 6.49 (m, 1H), 3.37 (s, 3H); **^{13}C NMR** ($CDCl_3$/TMS, 100 MHz): δ 167.1, 160.2, 145.9, 137.9, 130.9, 130.8, 130.1, 124.2, 123.5, 122.6, 122.0, 121.6, 109.2, 99.5, 27.4; **HRMS-ESI**: Calcd. for $C_{15}H_{12}N_3O[M+H]^+$*m/z*: 250.0980; Found 250.0991.
4-Bromo-1'-methylspiro[indazole-3,3'-indolin]-2'-one **(4b)**	
	Nature: White Solid:16mg, yield:27%; **R_f** (25% EtOAc-Hexane):0.40; **FTIR** (KBr) ν_{max}: 3451, 2922, 1722, 1611, 1583, 1492, 1449, 1363, 1344, 1255, 1126, 1019, 950 cm^{-1};

 **4b**	**^{1}H NMR** ($CDCl_3$/TMS, 400 MHz,):δ8.18 (dd, *J* = 7.8, 0.6 Hz, 1H), 7.60 (dd, *J* = 7.9, 0.6 Hz, 1H), 7.53 – 7.44 (m, 2H), 7.08 – 6.99 (m, 2H), 6.57 (dd, *J* = 7.4, 0.6 Hz, 1H), 3.42 (s, 3H); **^{13}C NMR** ($CDCl_3$/TMS, 100 MHz): δ 165.2, 160.2, 146.3, 138.5, 133.9, 131.9, 131.0, 124.1, 123.5, 120.9, 118.8, 117.5, 109.3, 101.1, 27.5; **HRMS-ESI**: Calcd. for $C_{15}H_{11}BrN_3O[M+H]^+$*m/z*: 250.0980; Found 250.0991.
4-Methoxy-1'-methylspiro[indazole-3,3'-indolin]-2'-one **(4c)**	
 **4c**	**Nature:** White Solid: 16mg, yield:27%; **R_f** (25% EtOAc-Hexane):0.40; **FTIR** (KBr) ν_{max}: 3093, 3064, 3013, 2946, 1721, 1613, 1491, 1329, 1292, 1173, 1127, 1025, 992, 936 cm^{-1}; **^{1}H NMR** ($CDCl_3$/TMS, 400 MHz,):δ7.73 (d, *J* = 2.2 Hz, 1H), 7.44 (td, *J* = 7.8, 1.2 Hz, 1H), 7.21 (d, *J* = 8.2 Hz, 1H), 7.07 – 6.99 (m, 3H), 6.60 – 6.55 (m, 1H), 3.94 (s, 3H), 3.37 (s, 3H); **^{13}C NMR** ($CDCl_3$/TMS, 100 MHz): δ 167.4, 161.9, 161.6, 145.9, 130.7, 129.7, 124.3, 123.4, 122.9, 121.8, 118.3, 109.1(2C), 106.1, 55.9, 27.4; **HRMS-ESI**: Calcd. for $C_{16}H_{14}N_3O_2[M+H]^+$*m/z*: 280.1086; Found 280.1080.
1'-Allylspiro[indazole-3,3'-indolin]-2'-one **(4d)**	
 **4d**	**Nature:** White Solid: 14mg, yield:26%; **R_f** (25% EtOAc-Hexane):0.40; **FTIR** (KBr) ν_{max}: 3084, 3065, 3036, 2979, 1594, 1494, 1448, 1308, 1295, 1156, 1071, 1018, 998 cm^{-1}; **^{1}H NMR** ($CDCl_3$/TMS, 400 MHz,):δ 8.17 (d, *J* = 7.9 Hz, 1H), 7.55 (td, *J* = 7.8, 1.0 Hz, 1H), 7.43 (td, *J* = 7.5, 0.9 Hz, 1H), 7.33 (td, *J* = 7.8, 1.2 Hz, 1H), 7.27 (d, *J* = 7.4 Hz, 1H), 6.94 (ddd, *J* = 11.0, 8.4, 4.4 Hz, 2H), 6.49 (dd, *J* = 7.4, 0.6 Hz, 1H), 5.87 (ddt, *J* = 17.1, 10.4, 5.2 Hz, 1H), 5.29 (ddd, *J* = 13.7, 11.2, 0.8 Hz, 2H), 4.41 (ddd, *J* = 5.4, 4.0, 1.7 Hz, 2H); **^{13}C NMR** ($CDCl_3$/TMS, 100 MHz): δ 166.8, 160.2, 145.2, 138.1, 13.0, 130.7, 130.6, 130.0, 124.3, 123.5, 122.5, 122.1, 121.7, 118.2, 110.1, 99.4, 43.4; **MS-ESI**: Calcd. for $C_{17}H_{14}N_3O[M+H]^+$*m/z*: 276.11; Found 276.21.
Spiro[fluorene-9,3'-indazole] **(4e)**	

 **4e**	**Nature:** White **Solid**: 20mg, yield: 37%; **R_f** (25% EtOAc-Hexane):0.40; **FTIR** (KBr) ν_{max}: 3057, 3022, 2851, 1596, 1460,1285, 1263, 1175, 1152, 1087, 953, 932, 873cm^{-1}; **^{1}H NMR** ($CDCl_3$/TMS, 400 MHz,):δ 8.17 (d, *J* = 7.9 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 2H), 7.50 (td, *J* = 7.9, 1.0 Hz, 1H), 7.35 (dtd, *J* = 8.3, 7.5, 0.9 Hz, 3H), 7.09 (td, *J* = 7.5, 1.0 Hz, 2H), 7.03 (d, *J* = 7.4 Hz, 1H), 6.48 (d, *J* = 7.6 Hz, 2H); **^{13}C NMR** ($CDCl_3$/TMS, 100 MHz): δ 159.2, 143.4, 140.6, 138.1, 130.7, 129.6, 129.4, 128.2, 123.8, 122.6, 121.4, 120.7, 103.2; **HRMS-ESI**: Calcd. for $C_{19}H_{13}N_2[M+H]^+$*m/z*: 269.1079; Found 269.1074.
4'-Methoxyspiro[fluorene-9,3'-indazole] **(4f)**	
 **4f**	**Nature:** White Solid: 23mg, yield:38%; **R_f** (25% EtOAc-Hexane):0.40; **FTIR** (KBr) ν_{max}: 3050, 2925, 2853, 1606, 1495, 1467, 1276, 1213, 1077, 993, 946, 860, 844 cm^{-1}; **^{1}H NMR** ($CDCl_3$/TMS, 400 MHz,):δ7.77 (d, *J* = 7.7 Hz, 3H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.35 (td, *J* = 7.5, 1.0 Hz, 2H), 7.08 (td, *J* = 7.5, 1.0 Hz, 2H), 6.82 (d, *J* = 8.1 Hz, 1H), 6.51 (d, *J* = 7.6 Hz, 2H), 3.35 (s, 3H); **^{13}C NMR** ($CDCl_3$/TMS, 100 MHz): δ 161.1, 155.4, 143.5, 136.9, 131.5, 129.3(2C), 127.8(2C), 126.9, 123.3(2C), 120.6, 113.6, 113.2, 102.7, 55.9; **HRMS-ESI**: Calcd. for $C_{20}H_{15}N_2O[M+H]^+$*m/z*: 299.1184; Found 299.1194.
*3-Diazo-1-methylindolin-2-one***(4g)**	
 **4g**	**Nature:** Orange Crystal: 11mg, yield:29%; **R_f** (25% EtOAc-Hexane):0.40; **FTIR** (KBr) ν_{max}: 2954, 2853, 2109, 2097, 1687, 1671, 1468, 1420, 1371, 1314, 1123, 1096, 1019 cm^{-1}; **^{1}H NMR** ($CDCl_3$/TMS, 400 MHz,):δ 7.20 (ddt, *J* = 8.2, 3.0, 1.2 Hz, 2H), 7.12 – 7.07 (m, 1H), 6.94 – 6.90 (m, 1H), 3.33 (s, 3H); **^{13}C NMR** ($CDCl_3$/TMS, 100 MHz): δ 166.9, 134.5, 125.5(2C), 122.1, 118.2, 116.7, 108.6, 26.8;

	HRMS-ESI: Calcd. for $C_9H_8N_3O$ $[M+H]^+$*m/z*: 174.0667; Found 174.0675.
(E)-4-Methyl-N'-(1-methyl-2-oxoindolin-3-ylidene)-N-phenylbenzenesulfonohydrazide **(5a)**	
 **5a**	**Nature:** Yellow solid:9mg, yield:13%; **R_f** (25% EtOAc-Hexane):0.40; **FTIR** (KBr) ν_{max}: 2923, 2852, 1734, 1606, 1486, 1372, 1358, 1186, 1170, 1088, 973, 888 cm^{-1}; **^{1}H NMR** ($CDCl_3$/TMS, 400 MHz,):δ7.60 (d, *J* = 8.3 Hz, 2H), 7.30 (td, *J* = 7.8, 1.1 Hz, 1H), 7.25 – 7.22 (m, 5H), 7.17 (dd, *J* = 7.4, 2.5 Hz, 2H), 6.83 (t, *J* = 7.7 Hz, 1H), 6.73 (d, *J* = 7.9 Hz, 1H), 3.21 (s, 3H), 2.40 (s, 3H); **^{13}C NMR** ($CDCl_3$/TMS, 100 MHz): δ 144.8, 133.8, 129.9(2C), 129.1, 128.9(2C), 128.5(2C), 128.0(2C), 125.8(2C), 122.8, 108.8, 26.9, 21.7; **HRMS-ESI**: Calcd. for $C_{22}H_{19}N_3O_3SNa$ $[M+Na]^+$*m/z*: 428.1045; Found 428.1043.
(E)-N-(2-Bromophenyl)-4-methyl-N'-(1-methyl-2-oxoindolin-3-ylidene)benzenesulfonohydrazide **(5b)**	
 **5b**	**Nature:** Orange solid: 16mg, yield:18%; **R_f** (25% EtOAc-Hexane):0.40; **FTIR** (KBr) ν_{max}: 3449, 3090, 3064, 2928, 1736, 1610, 1570, 1418, 1369, 1171, 1105, 1067, 966, 922, 884, 815cm^{-1}; **^{1}H NMR** ($CDCl_3$/TMS, 400 MHz,):δ 7.60 (dd, *J* = 7.7, 0.7 Hz, 1H), 7.57 – 7.53 (m, 2H), 7.40 – 7.34 (m, 2H), 7.32 (t, *J* = 1.9 Hz, 1H), 7.27 – 7.25 (m, 2H), 7.22 (ddd, *J* = 8.2, 2.1, 1.1 Hz, 1H), 7.12 (t, *J* = 8.0 Hz, 1H), 6.95 (td, *J* = 7.7, 0.9 Hz, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 3.22 (s, 3H), 2.42 (s, 3H); **^{13}C NMR** ($CDCl_3$/TMS, 100 MHz): δ 162.9, 154.8, 147.1, 145.2, 143.0, 134.6, 130.9, 130.3, 129.9, 129.8(2C), 129.3(2C), 128.9, 128.2, 124.2, 123.1, 122.1, 115.1, 108.9, 26.2, 21.7; **HRMS-ESI**: Calcd. for $C_{22}H_{18}BrN_3O_3SNa$ $[M+Na]^+$*m/z*: 506.0150;Found 506.0148.
(E)-4-Methyl-N'-(1-methyl-2-oxoindolin-3-ylidene)-N-(p-tolyl)benzenesulfonohydrazide **(5c)**	
	Nature: Yellow solid: 10mg, yield:11%; **R_f** (25% EtOAc-Hexane):0.40;

 **5c**	**FTIR** (KBr) ν_{max}: 3059, 2920, 2851, 1719, 1635, 1490, 1345, 1270, 1123, 1017, 986, 932, 883, 816cm^{-1}; **^{1}H NMR** ($CDCl_3$/TMS, 400 MHz,): δ 8.09 (d, *J* = 8.1 Hz, 1H), 8.05 – 8.02 (m, 1H), 7.47 – 7.38 (m, 3H), 7.33 – 7.29 (m, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.15 – 7.13 (m, 1H), 7.06 – 6.98 (m, 4H), 6.59 – 6.53 (m, 2H), 3.38 (d, *J* = 1.3 Hz, 6H), 2.54 (s, 3H); **^{13}C NMR** ($CDCl_3$/TMS, 100 MHz): δ 167.4, 160.9, 158.6, 145.9, 141.9, 140.6, 138.4, 135.1, 130.7(2C), 124.2, 124.1, 123.4, 123.2(2C), 122.3, 122.2, 121.6, 109.1(2C), 27.3, 21.6, 21.5; **MS-ESI**: Calcd. for $C_{22}H_{22}N_3O_3S[M+H]^+$*m/z*: 420.13; Found 420.05.
(E)-N-(3,4-Dimethoxyphenyl)-4-methyl-N'-(1-methyl-2-oxoindolin-3ylidene)benzene sulfonohydrazide **(5d)**	
 **5d**	**Nature:** Yellow solid: 12mg, yield:12%; **R_f** (25% EtOAc-Hexane):0.40; **FTIR** (KBr) ν_{max}: 2955, 2853, 1738, 1610, 1511, 1469, 1369, 1264, 1170, 1023, 941, 868, 815 cm^{-1}; **^{1}H NMR** ($CDCl_3$/TMS, 400 MHz,):δ7.65 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.28 (m, 2H), 7.25 (s, 1H), 6.85 (t, *J* = 7.8 Hz, 1H), 6.76 – 6.67 (m, 3H), 6.62 (d, *J* = 2.3 Hz, 1H), 3.84 (s, 3H), 3.66 (s, 3H), 3.21 (s, 3H), 2.41 (s, 3H); **^{13}C NMR** ($CDCl_3$/TMS, 100 MHz): δ 163.3, 148.8, 146.7, 144.7, 134.6, 133.7, 130.9(2C), 130.0(2C), 129.1, 128.6, 122.8, 118.8, 115.1, 110.3(2C), 109.6(2C), 108.6, 56.1, 55.9, 26.2, 21.6; **HRMS-ESI**: Calcd. for $C_{24}H_{23}N_3O_5SNa$ $[M+Na]^+$*m/z*: 488.1256; Found 488.1253.
(E)-N'-(1-Allyl-2-oxoindolin-3-ylidene)-4-methyl-N-phenylbenzenesulfonohydrazide **(5e)**	
	Nature: Yellow Solid: 11mg, yield: 13%; **R_f** (25% EtOAc-Hexane):0.40; **FTIR** (KBr) ν_{max}: 2959, 2924, 2853, 1731, 1607, 1469, 1362, 1172, 1089, 1022, 884cm^{-1}; **^{1}H NMR** ($CDCl_3$/TMS, 400 MHz,):δ 7.55 – 7.52 (m, 2H), 7.19 – 7.15 (m, 6H), 7.13 – 7.09 (m, 2H), 6.74 (td, *J* = 7.7, 1.0 Hz, 1H), 6.67 (d, *J* = 7.7 Hz,

 **5e**	1H), 5.79 – 5.68 (m, 1H), 5.22 – 5.14 (m, 2H), 4.27 (dt, *J* = 5.4, 1.6 Hz, 2H), 2.34 (s, 3H); **^{13}C NMR** ($CDCl_3$/TMS, 100 MHz): δ 146.1, 144.8, 141.8, 133.7, 130.9, 130.8(2C), 129.9(2C), 129.1(2C), 128.9(2C), 128.6(2C), 128.1, 125.8(2C), 122.7, 118.3, 115.1, 109.5, 42.5, 21.7; **MS-ESI**: Calcd. for $C_{24}H_{22}N_3O_3S[M+H]^+$*m/z*: 432.13; Found 432.21.
N'-(9H-Fluoren-9-ylidene)-4-methyl-N-phenylbenzenesulfonohydrazide **(5f)**	
 **5f**	**Nature:** Yellow solid: 10mg, yield: 12%; **R_f** (25% EtOAc-Hexane):0.40; FTIR (KBr) ν_{max}: 3331, 2953, 1715, 1609, 1489, 1355, 1215, 1187, 1090, 982, 916, 883, 814cm^{-1}; **^{1}H NMR** ($CDCl_3$/TMS, 400 MHz,):δ 8.18 (d, *J* = 7.7 Hz, 1H), 7.76 (dd, *J* = 7.9, 3.9 Hz, 1H), 7.47 – 7.42 (m, 4H), 7.34 (td, *J* = 7.5, 1.0 Hz, 1H), 7.28 (td, *J* = 7.5, 0.9 Hz, 1H), 7.22 (ddd, *J* = 8.4, 3.5, 1.7 Hz, 3H), 7.16 (dd, *J* = 8.4, 4.5 Hz, 3H), 7.14 – 7.07 (m, 3H), 2.36 (s, 3H); **^{13}C NMR** ($CDCl_3$/TMS, 100 MHz): δ 166.8, 144.3, 413.2, 143.1, 141.8, 136.6, 132.5, 133.0, 130.9, 130.1, 129.9, 129.8(2C), 128.7, 128.5(2C), 128.2(2C), 127.0(2C), 124.9, 123.2(2C), 119.9, 119.8, 21.7; **HRMS-ESI**: Calcd. for $C_{26}H_{20}N_2O_2SNa$ $[M+Na]^+$*m/z*:447.1143; Found 447.1143.

4. Copies of NMR and HRMS Spectra

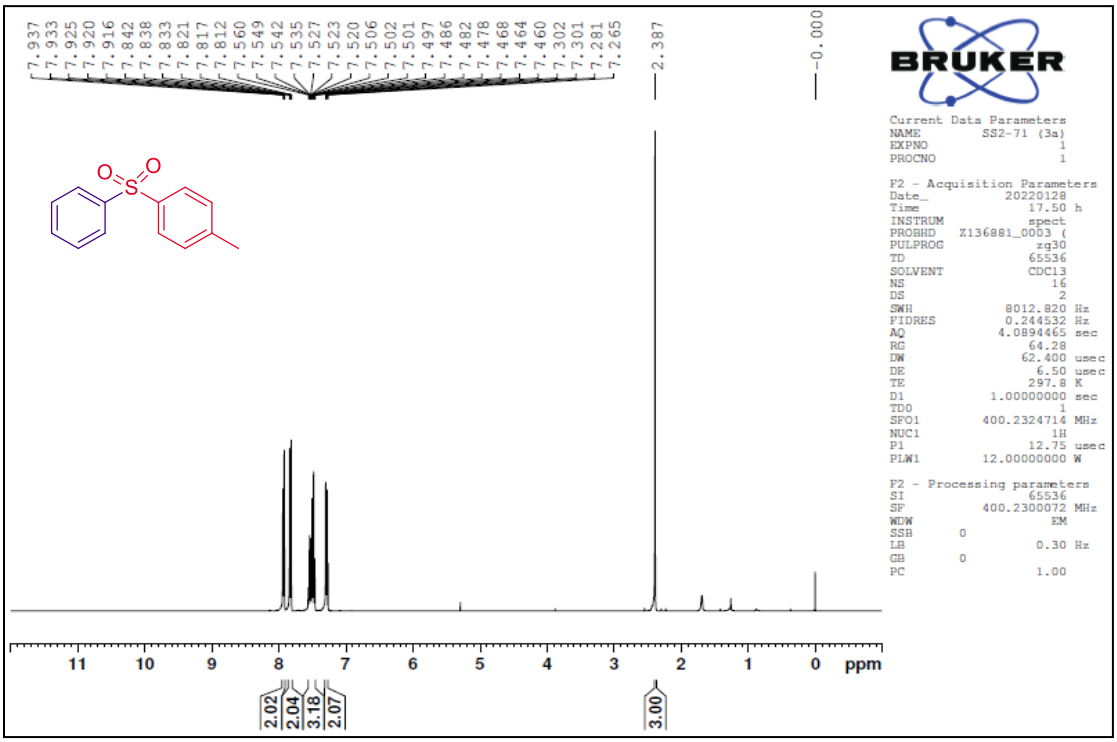


Figure1.[1]H NMR spectrum of compound **3a**

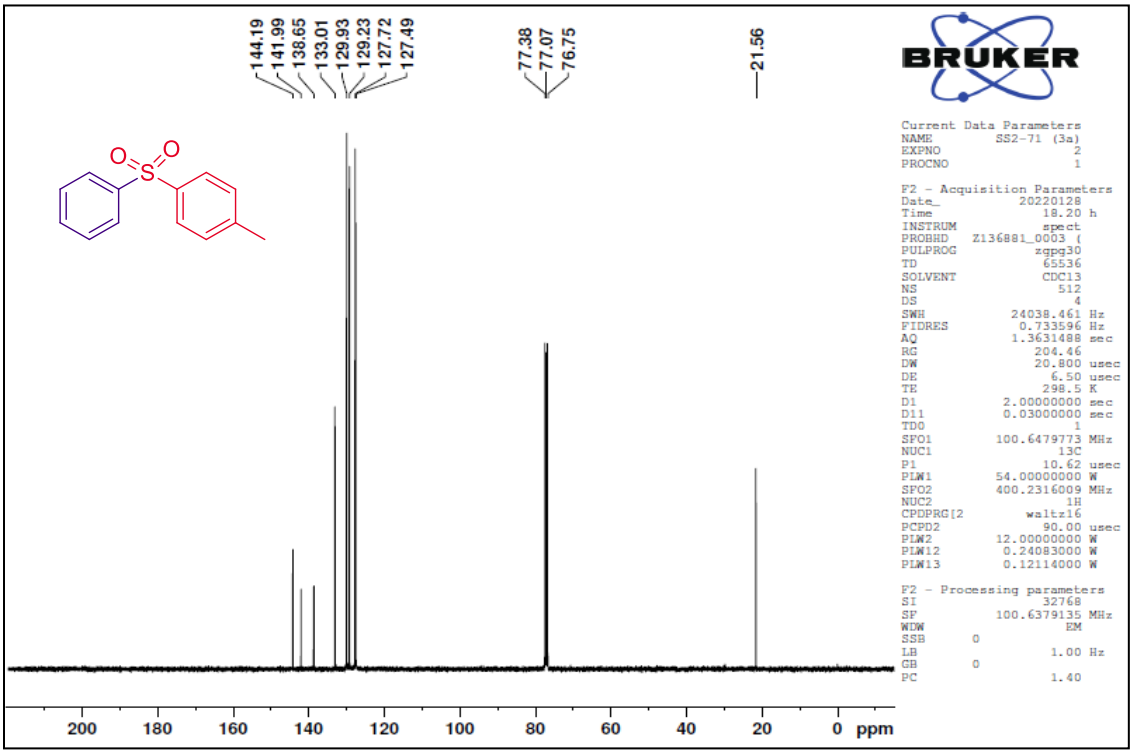


Figure 2.[13]C NMR spectrum of compound **3a**

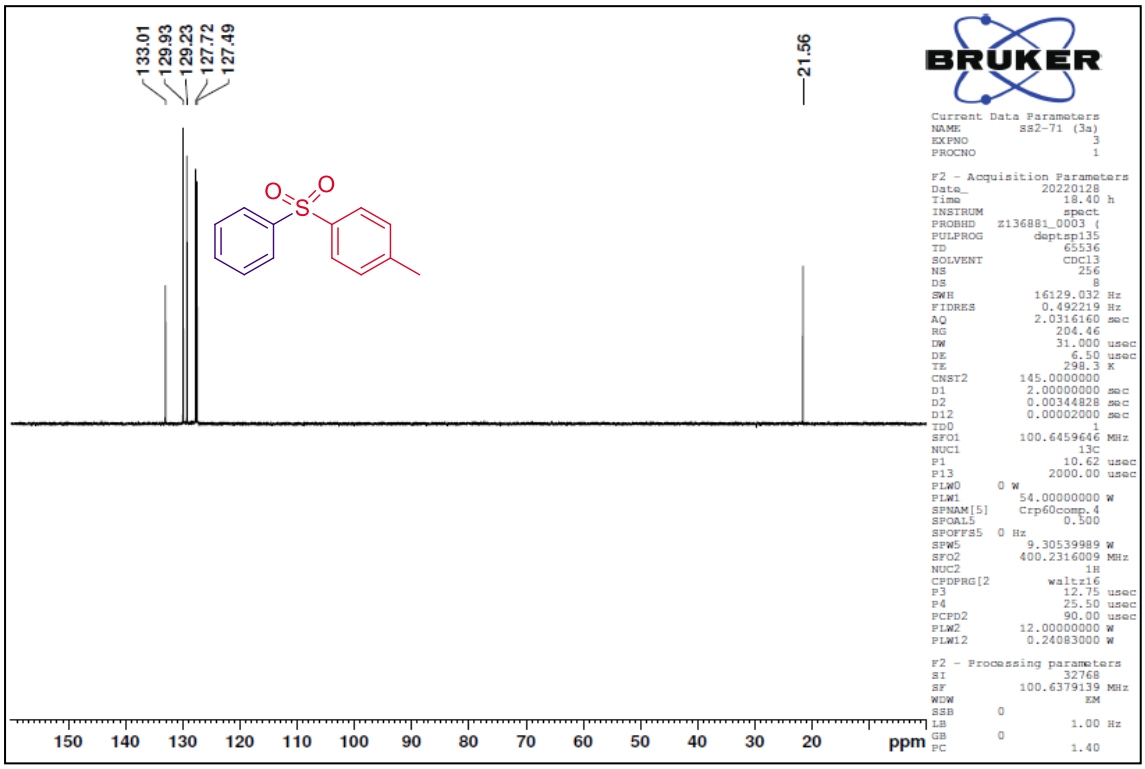


Figure 3.DEPT135 NMR spectrum of compound **3a**

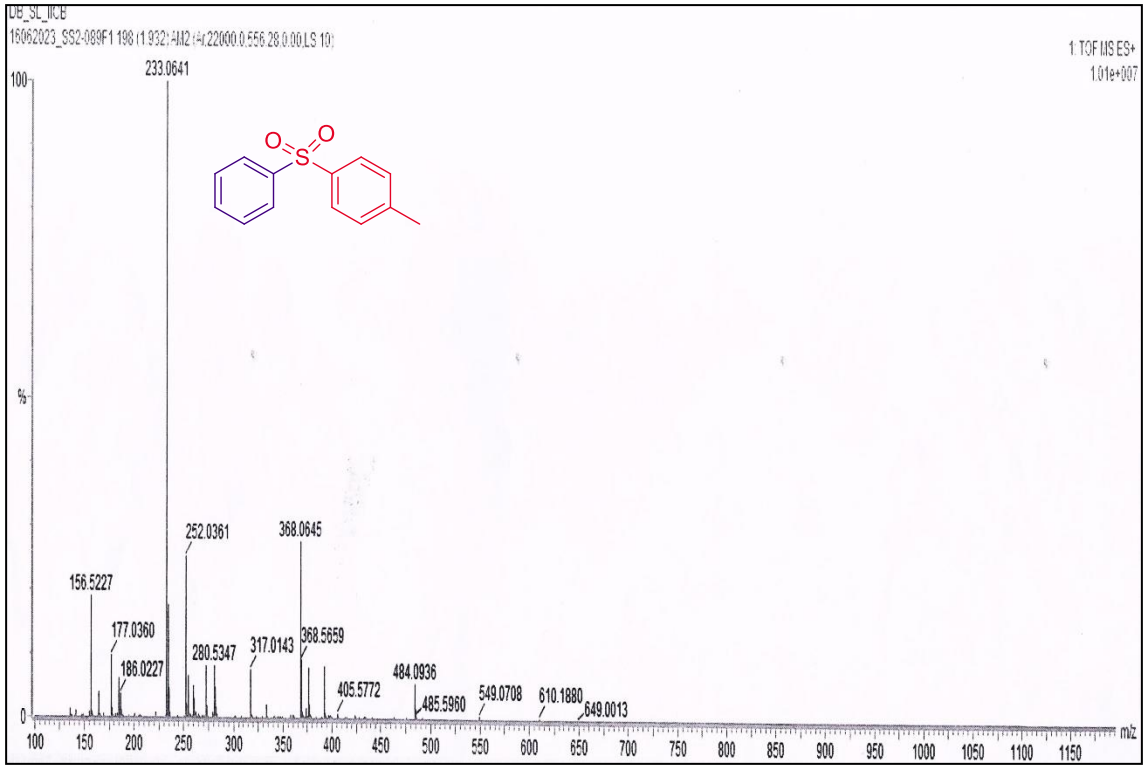


Figure 4.HRMS spectrum of compound **3a**

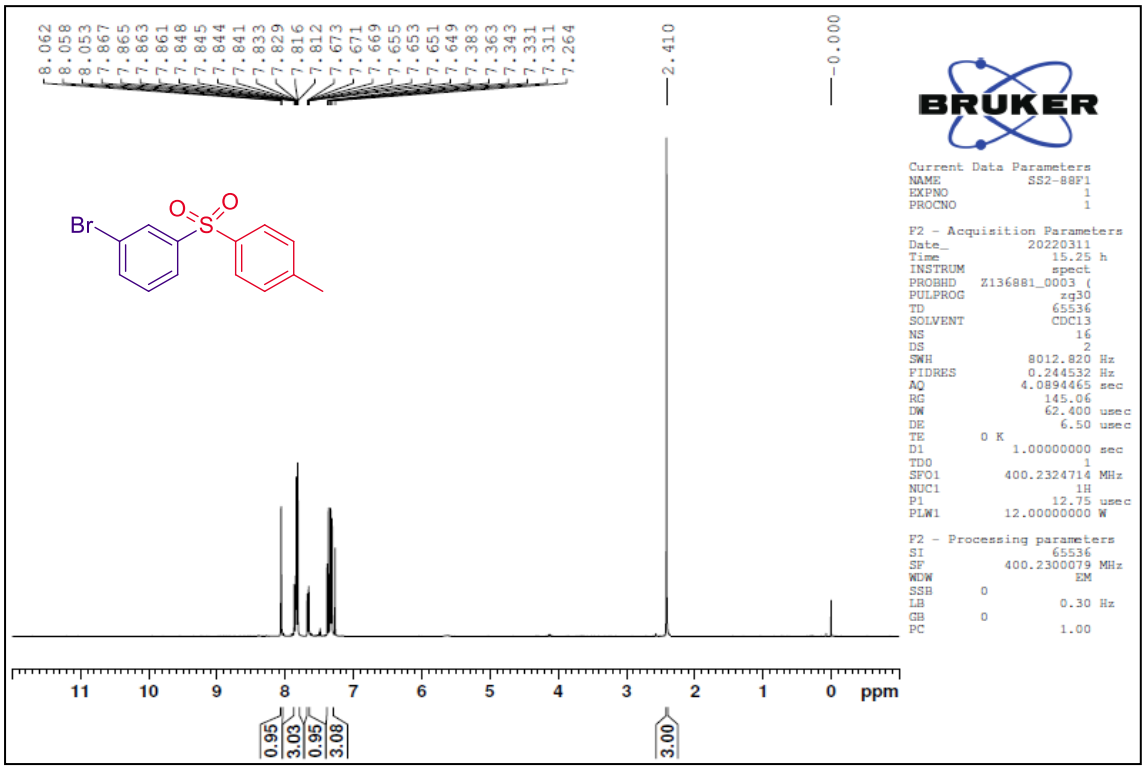


Figure 5. ^{1}H NMR spectrum of compound **3b**

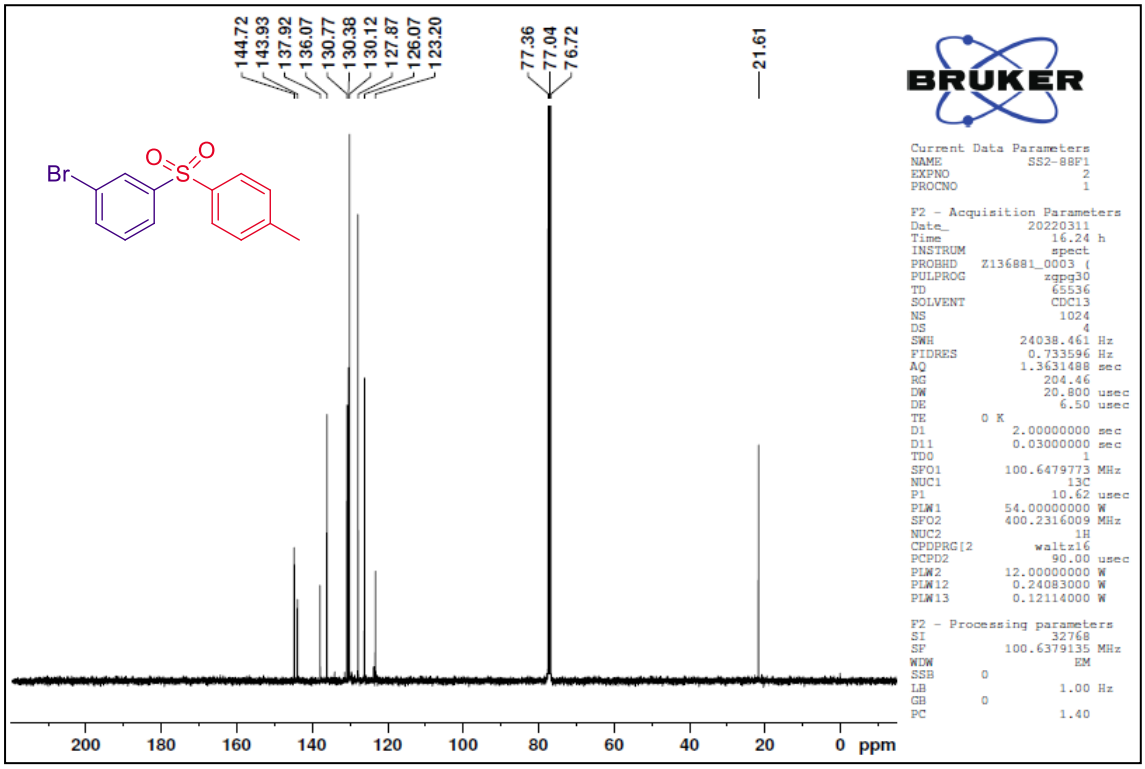


Figure 6. ^{13}C NMR spectrum of compound **3b**

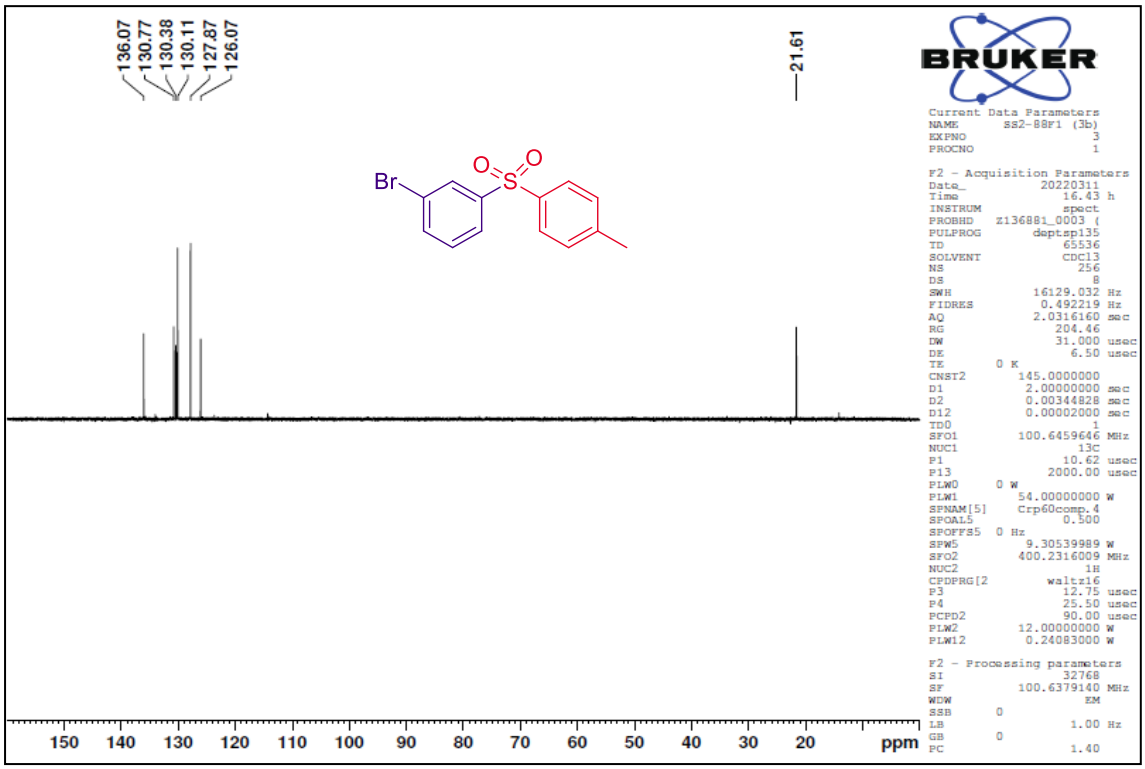


Figure 7.DEPT135 NMR spectrum of compound **3b**

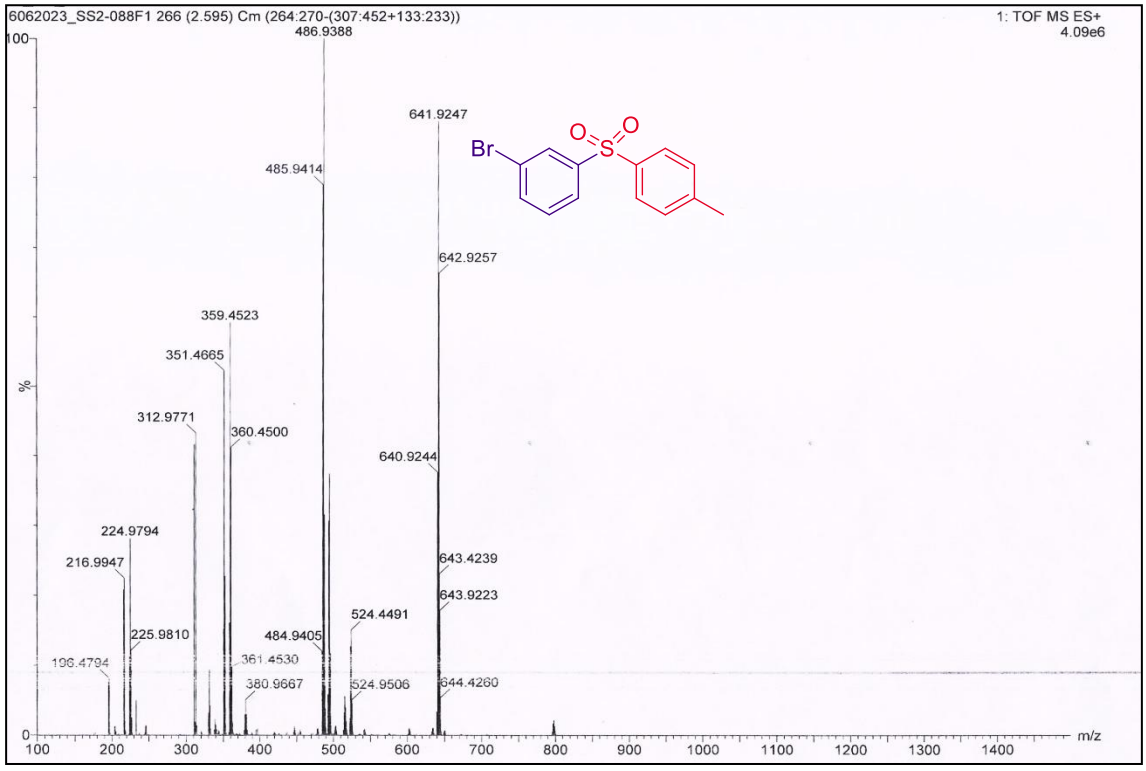


Figure 8.HRMS spectrum of compound **3b**

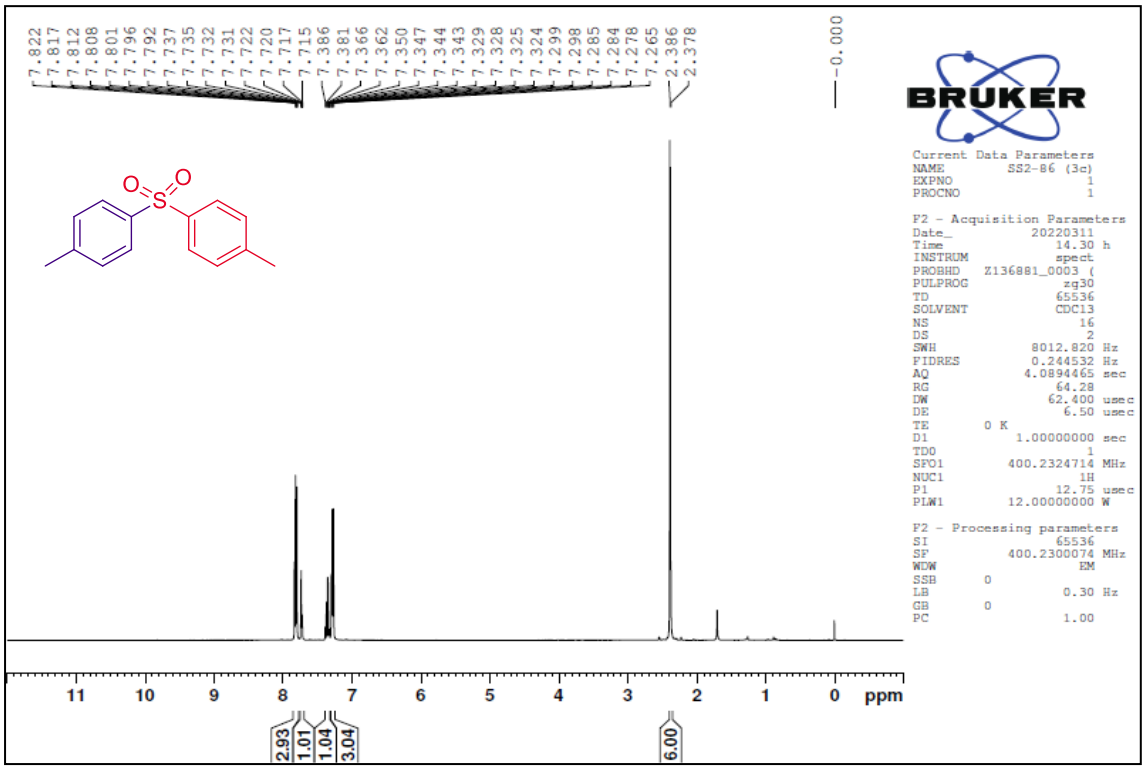


Figure 9. ^{1}H NMR spectrum of compound **3c**

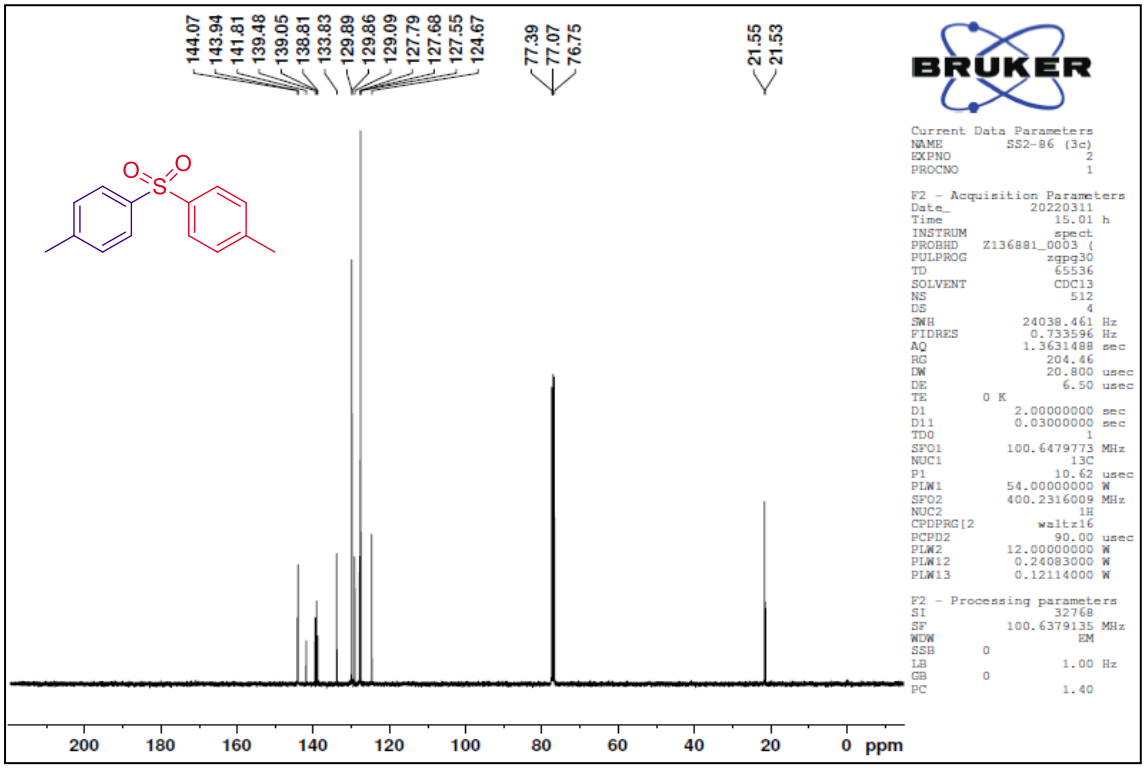


Figure 10. ^{13}C NMR spectrum of compound **3c**

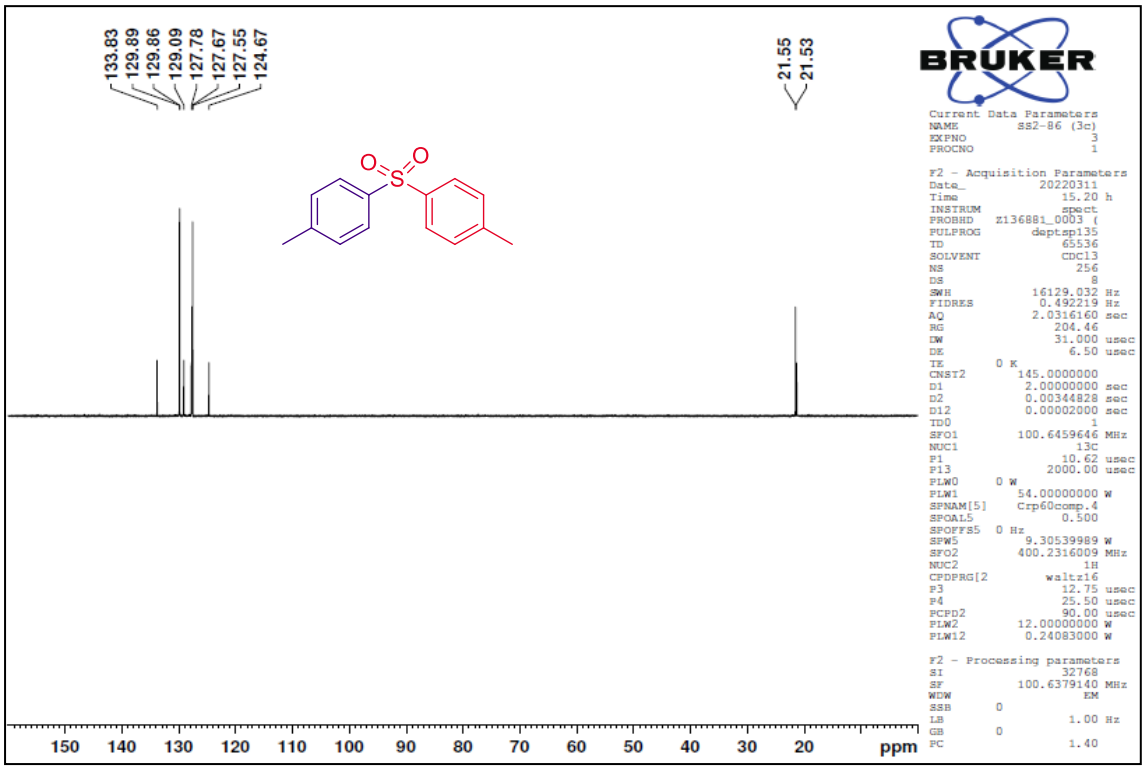


Figure 11.DEPT135 NMR spectrum of compound **3c**

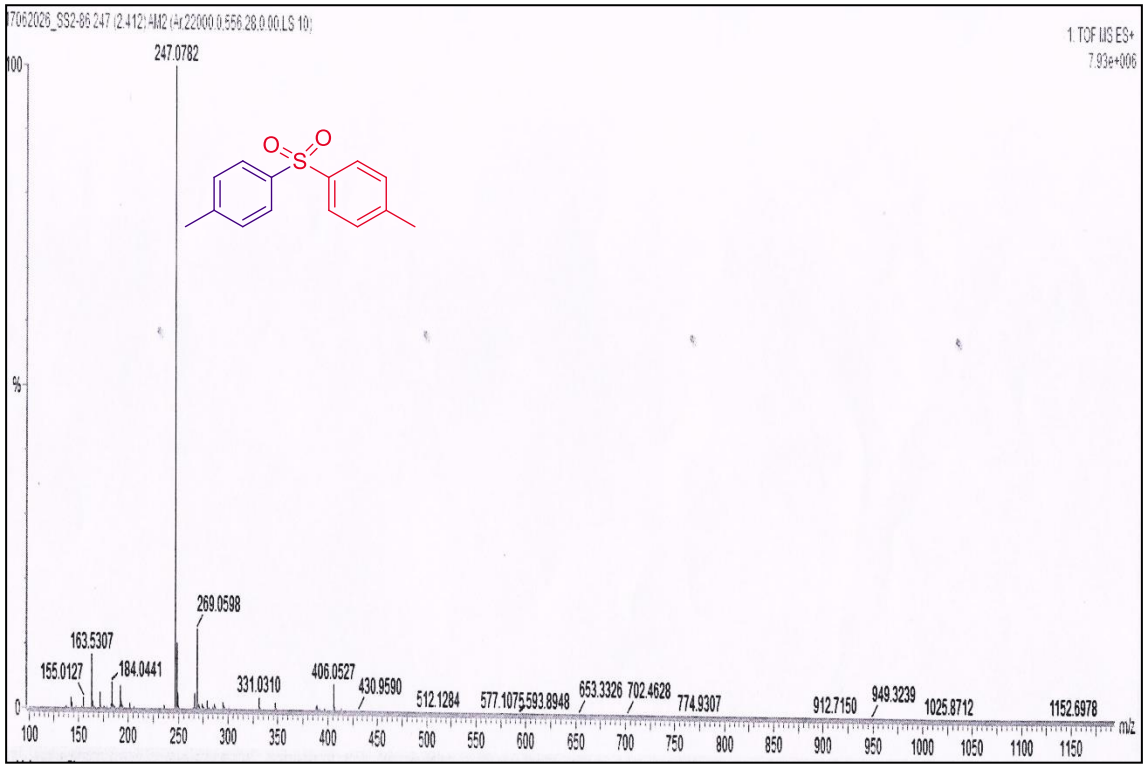


Figure 12. HRMS spectrum of compound **3c**

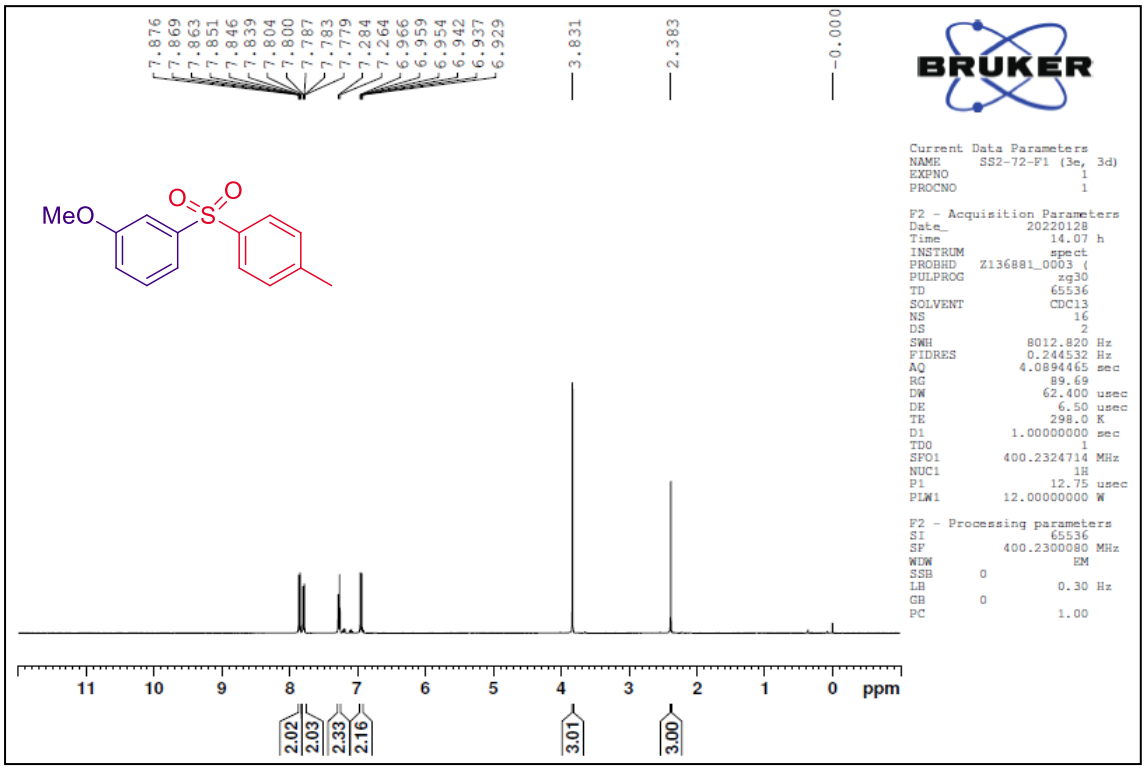


Figure 13. ^{1}H NMR spectrum of compound **3d**

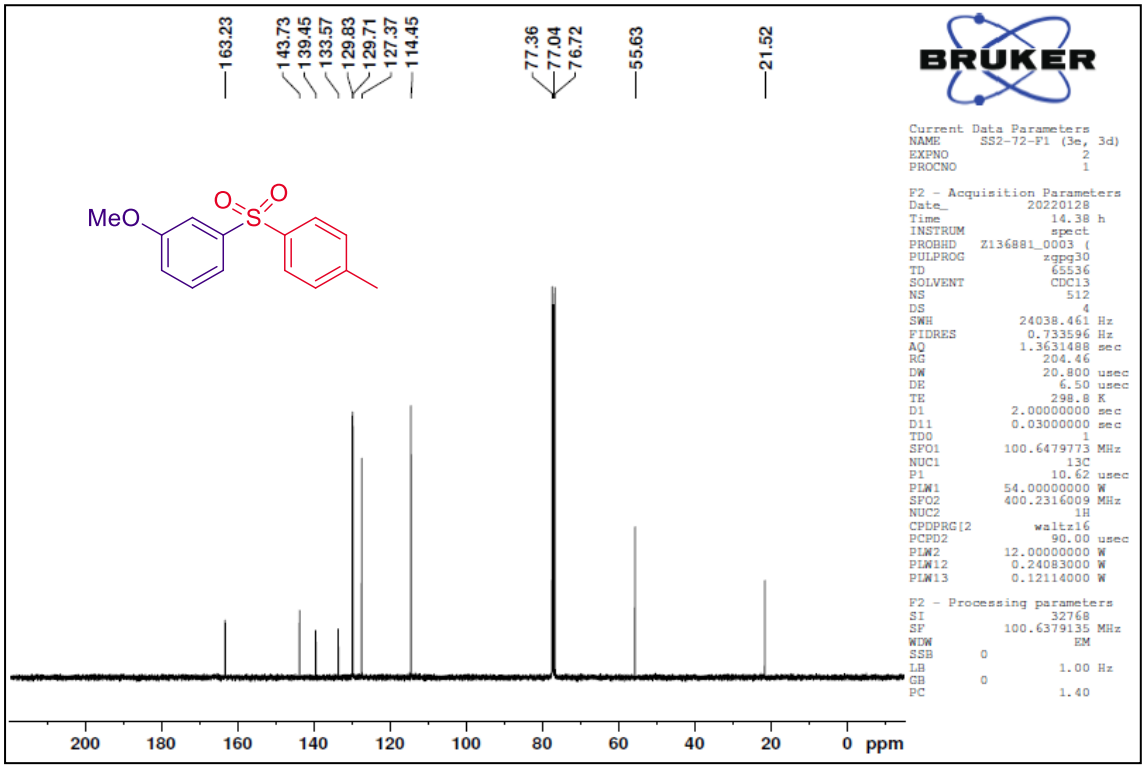


Figure 14. ^{13}C NMR spectrum of compound **3d**

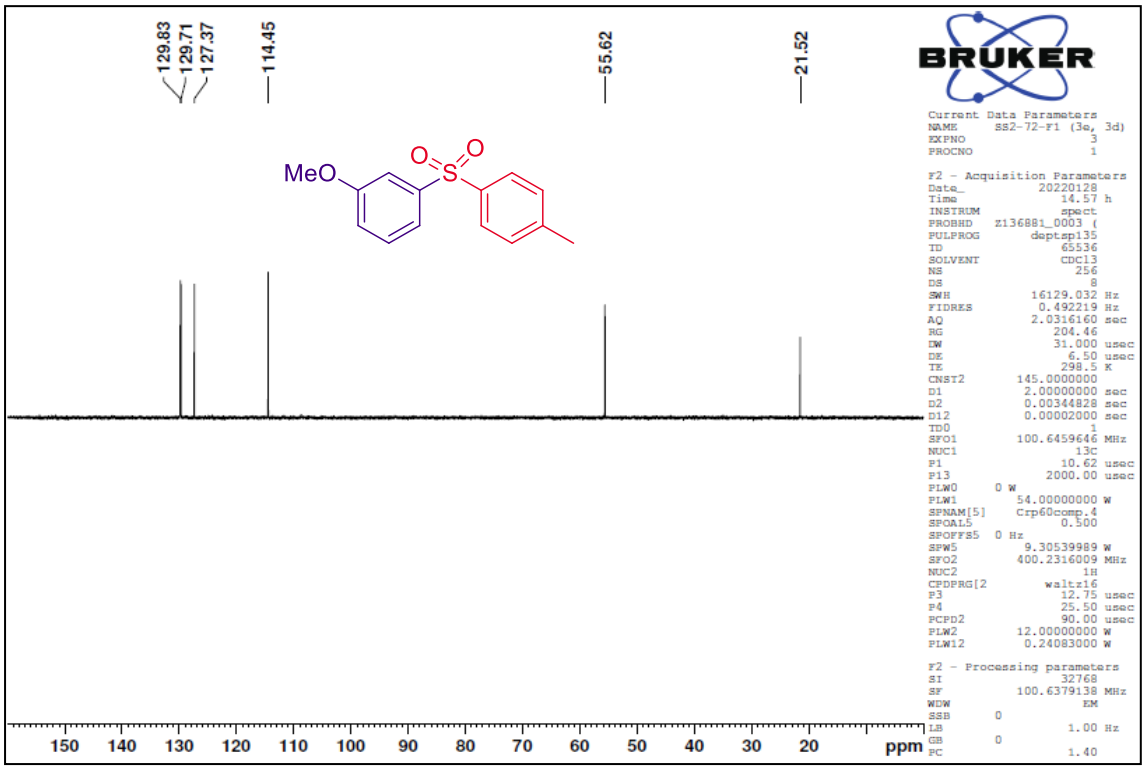


Figure 15.DEPT135 NMR spectrum of compound **3d**

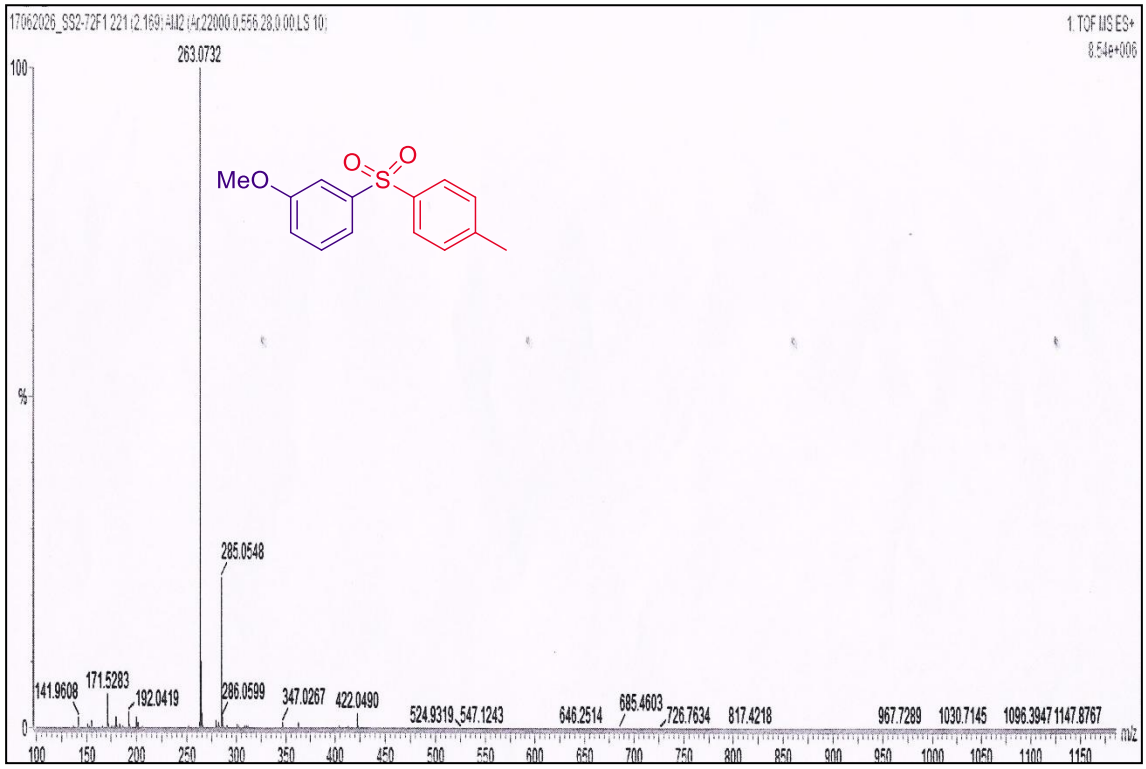


Figure 16.HRMS spectrum of compound **3d**

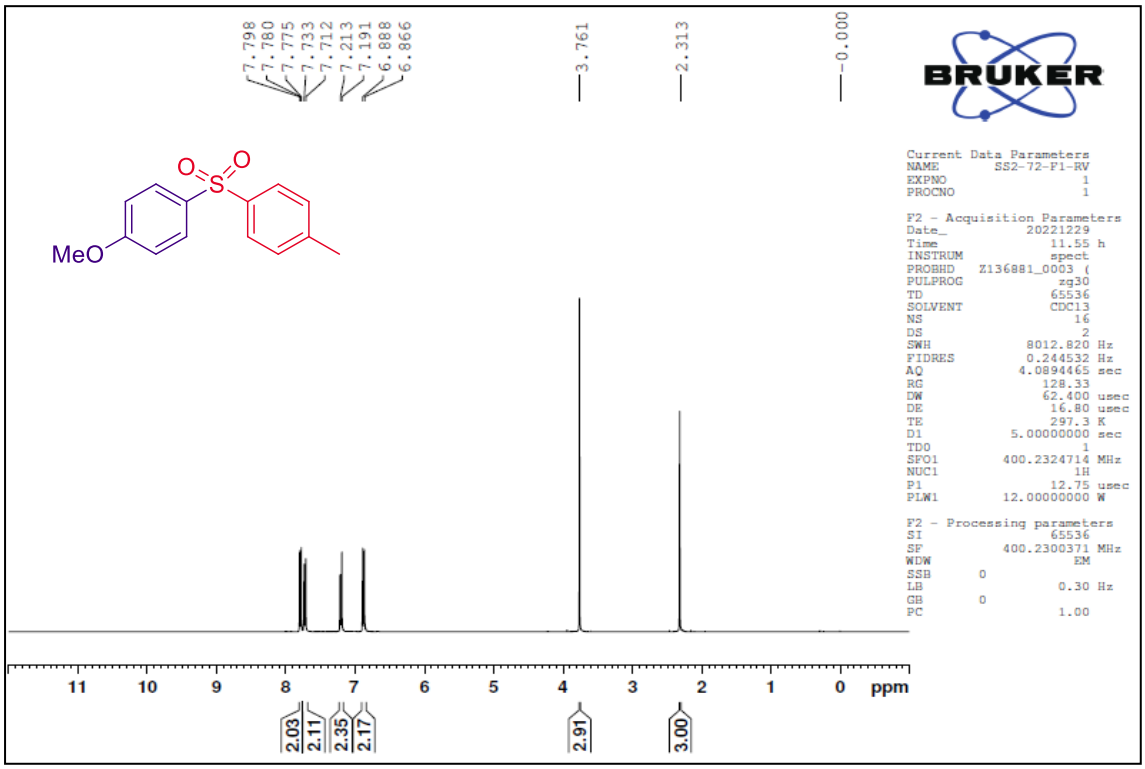


Figure 17. ^{1}H NMR spectrum of compound **3e**

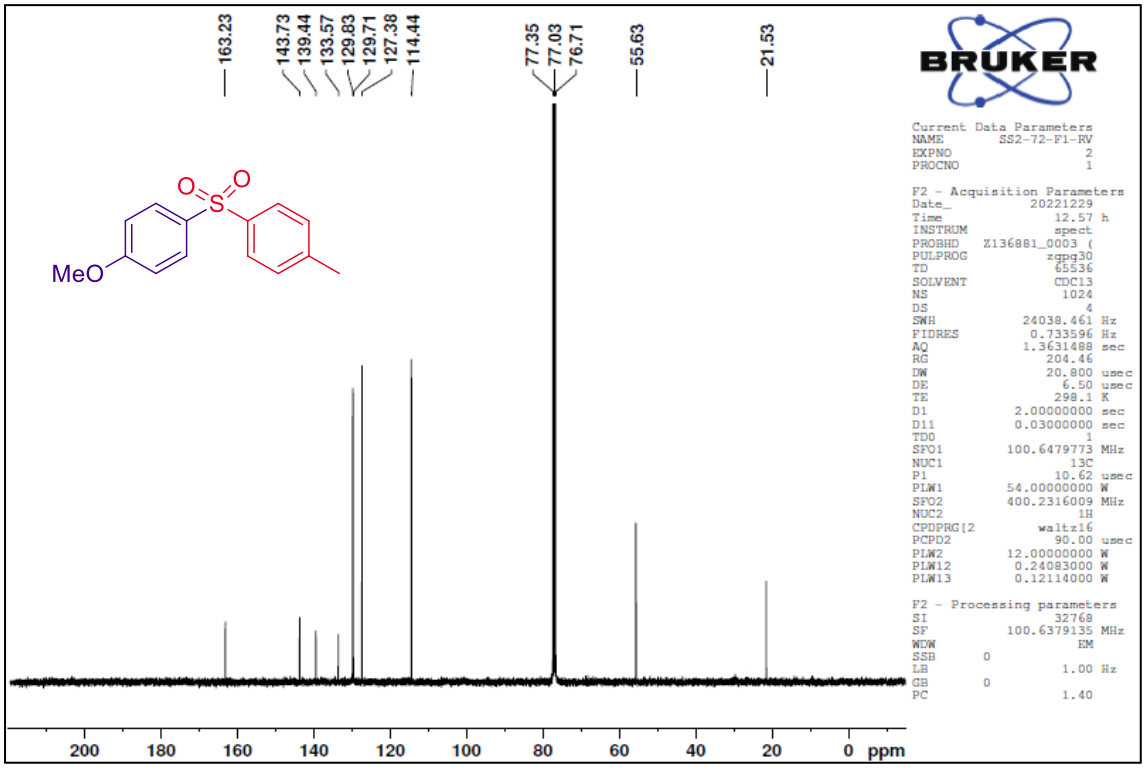


Figure 18. ^{13}C NMR spectrum of compound **3e**

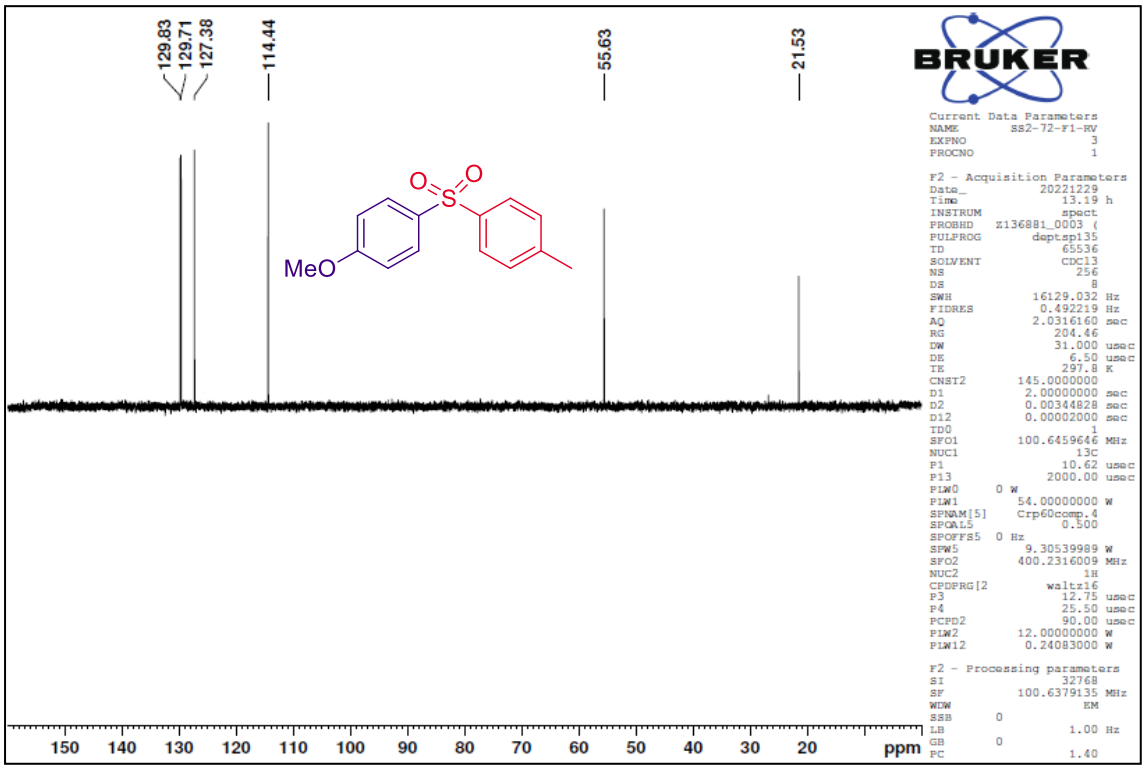


Figure 19.DEPT-135 NMR spectrum of compound **3e**

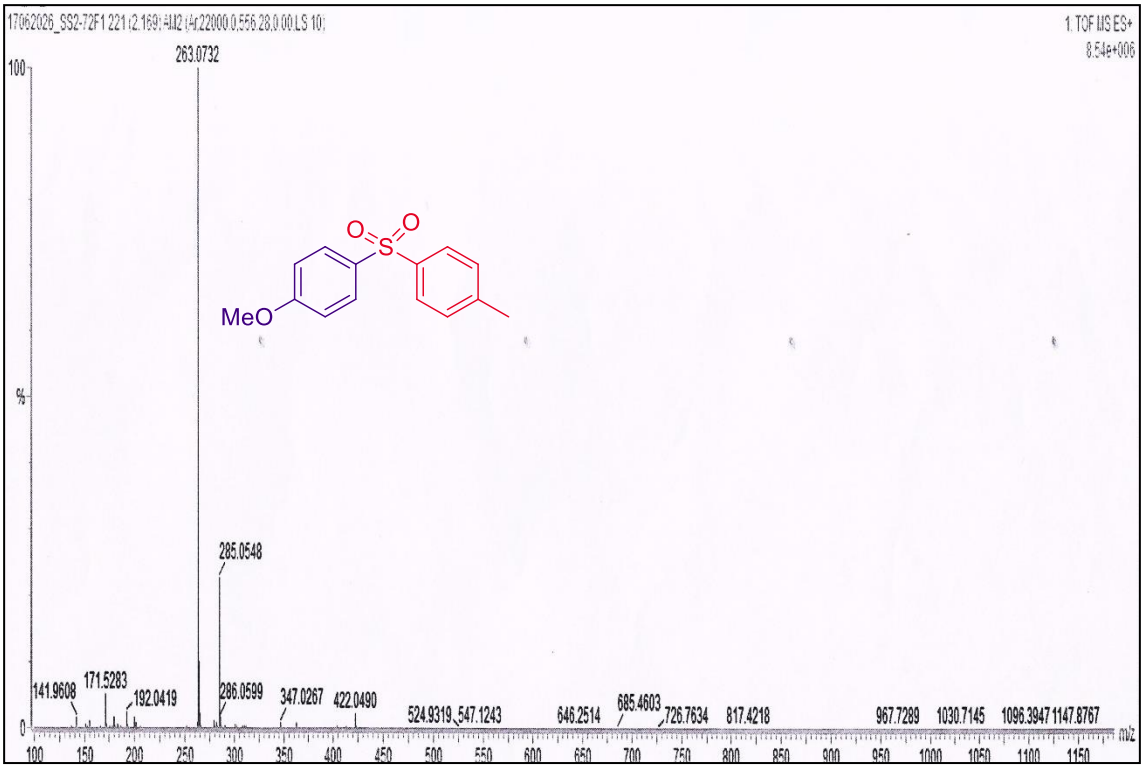


Figure 20.HRMS spectrum of compound **3e**

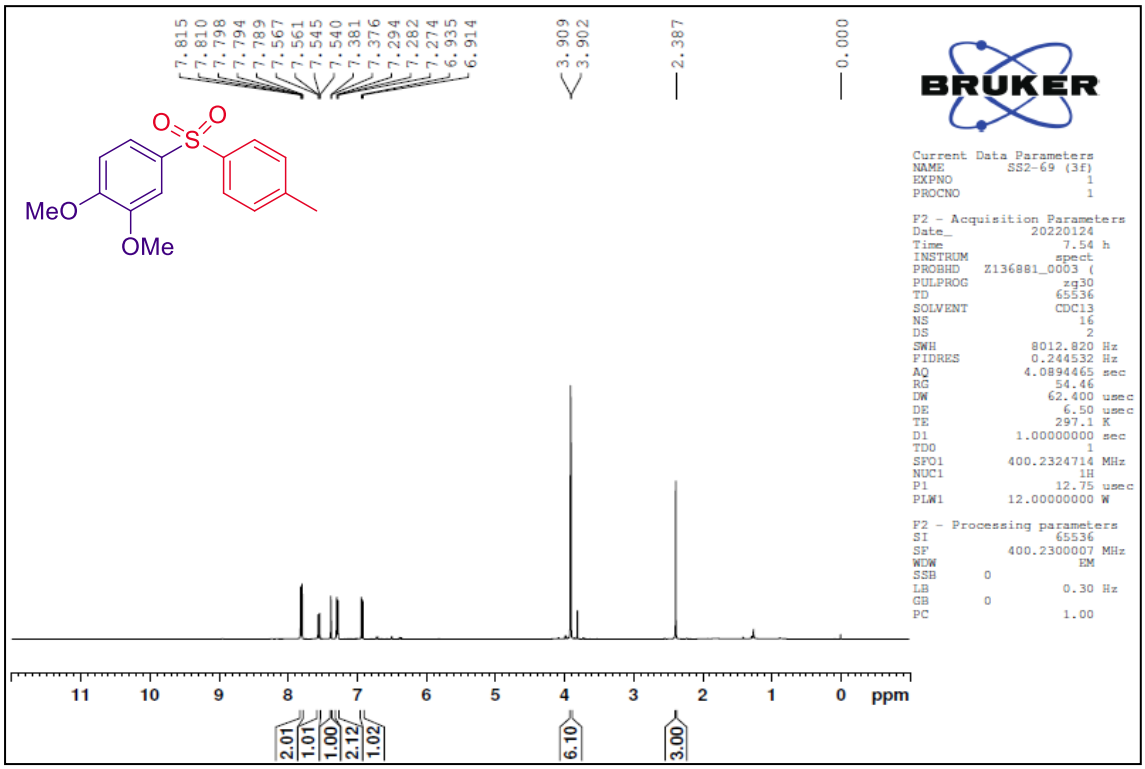


Figure 21. ^{1}H NMR spectrum of compound **3f**

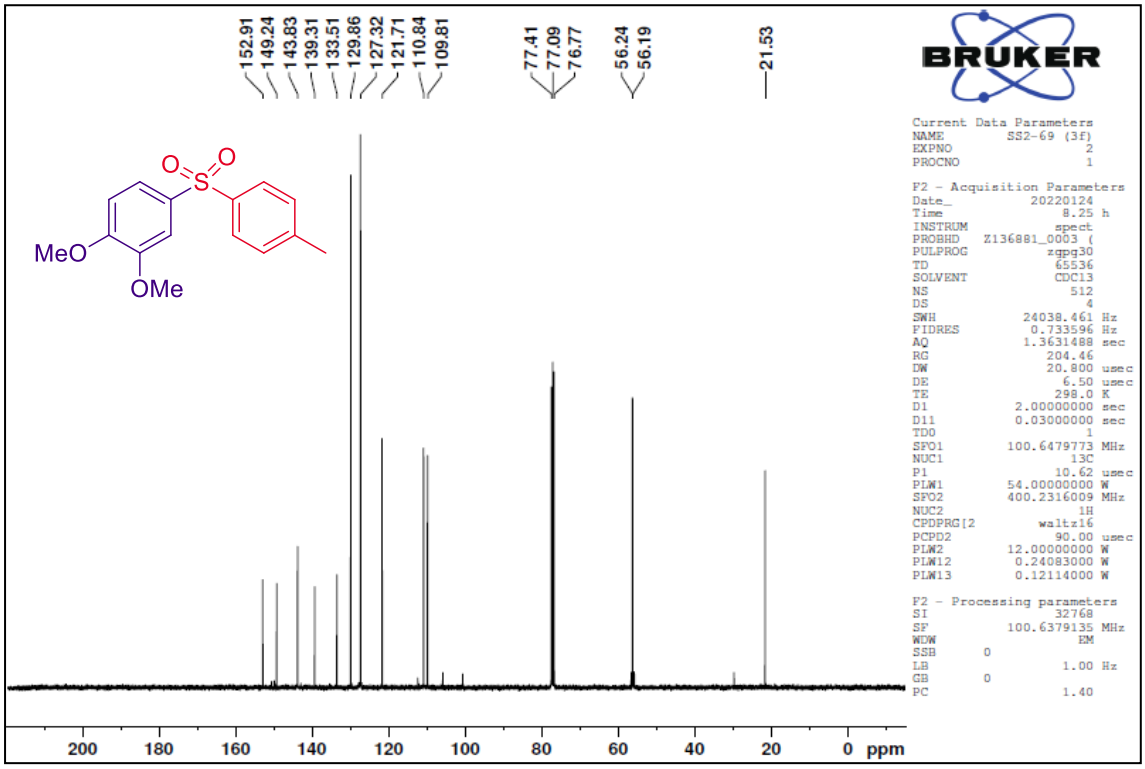


Figure 22. ^{13}C NMR spectrum of compound **3f**

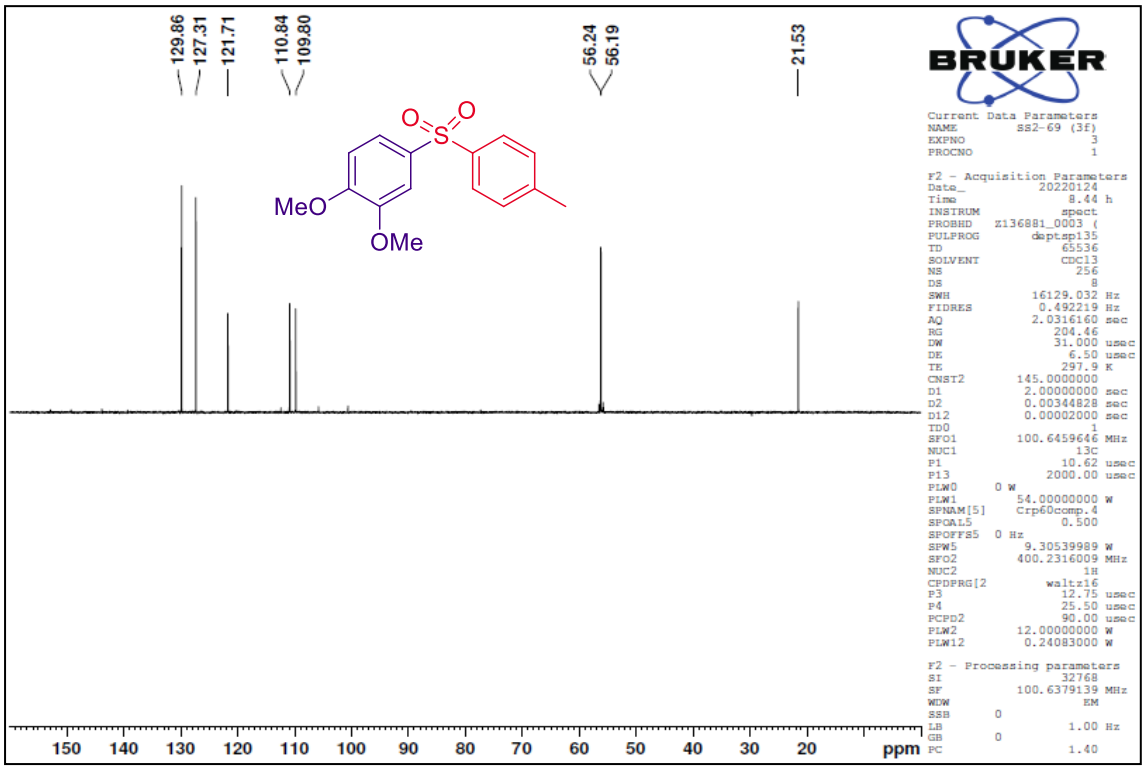


Figure 23.DEPT135 NMR spectrum of compound **3f**

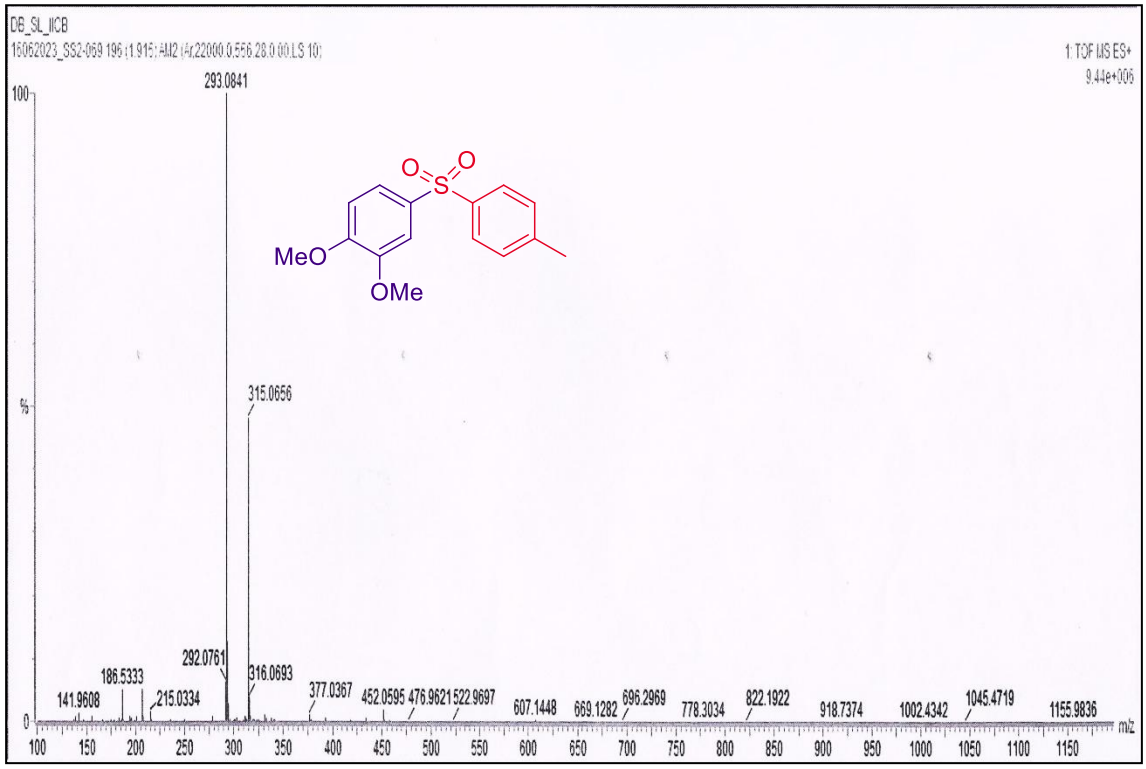


Figure 24.HRMS spectrum of compound **3f**

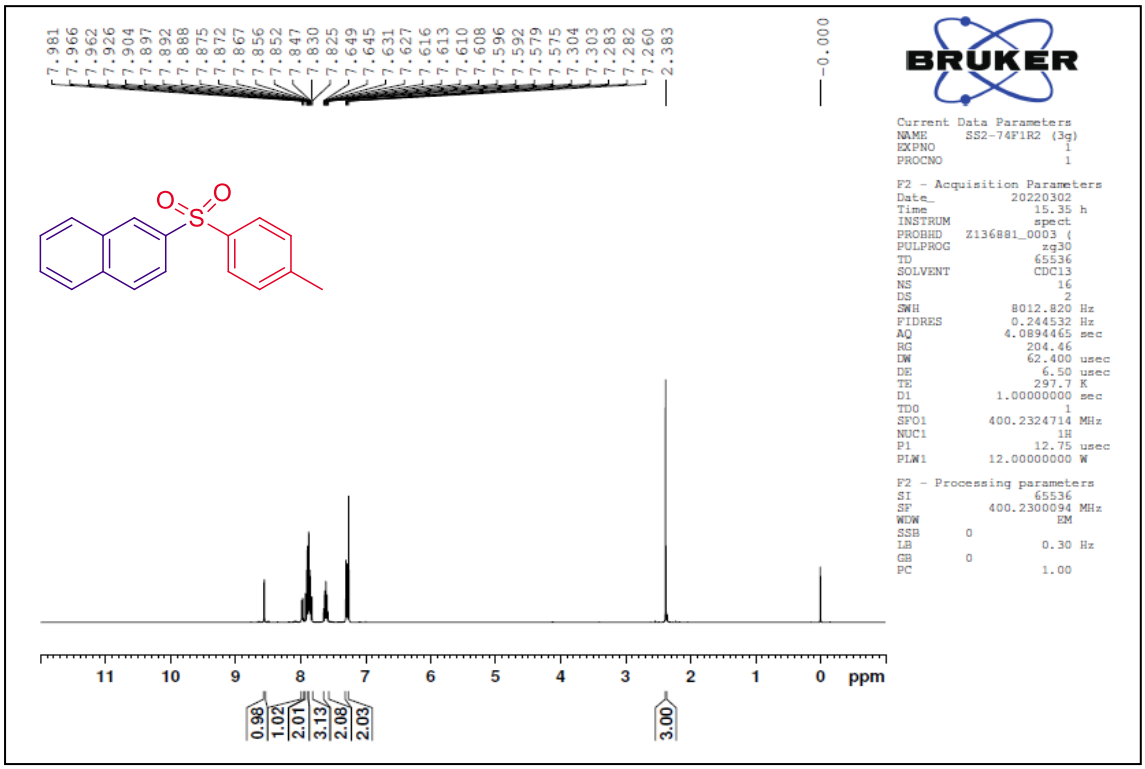


Figure 25. ^{1}H NMR spectrum of compound **3g**

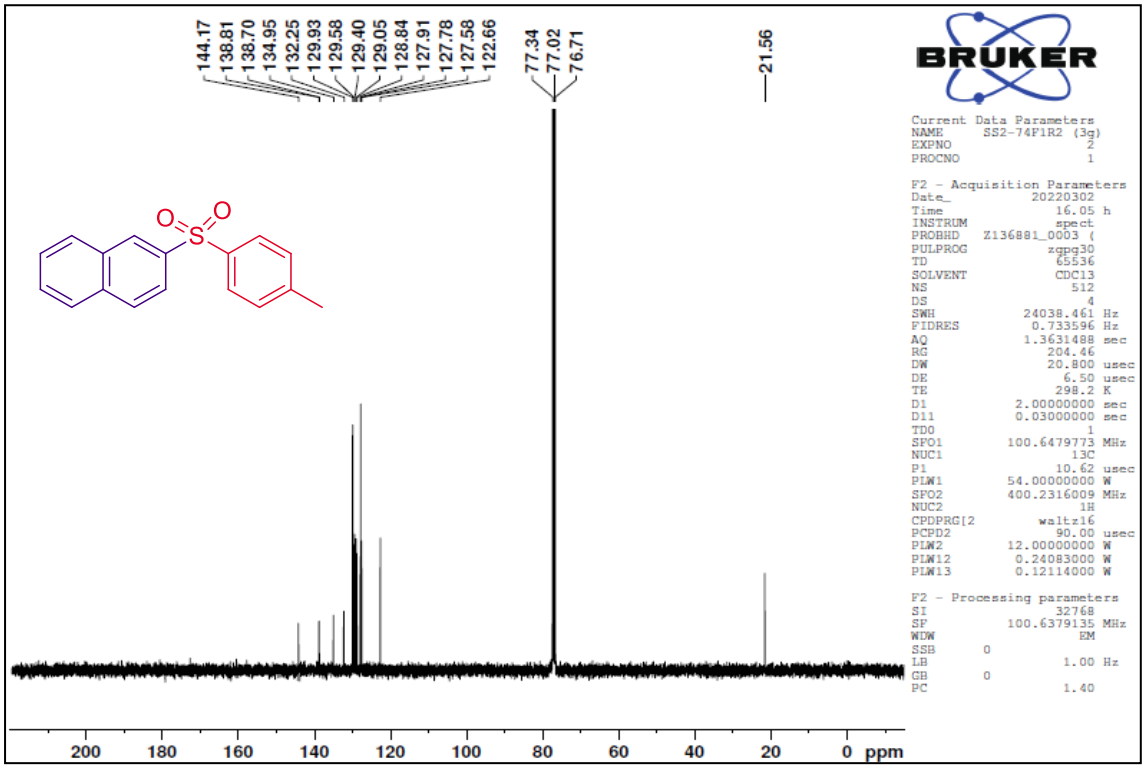


Figure 26. ^{13}C NMR spectrum of compound **3g**

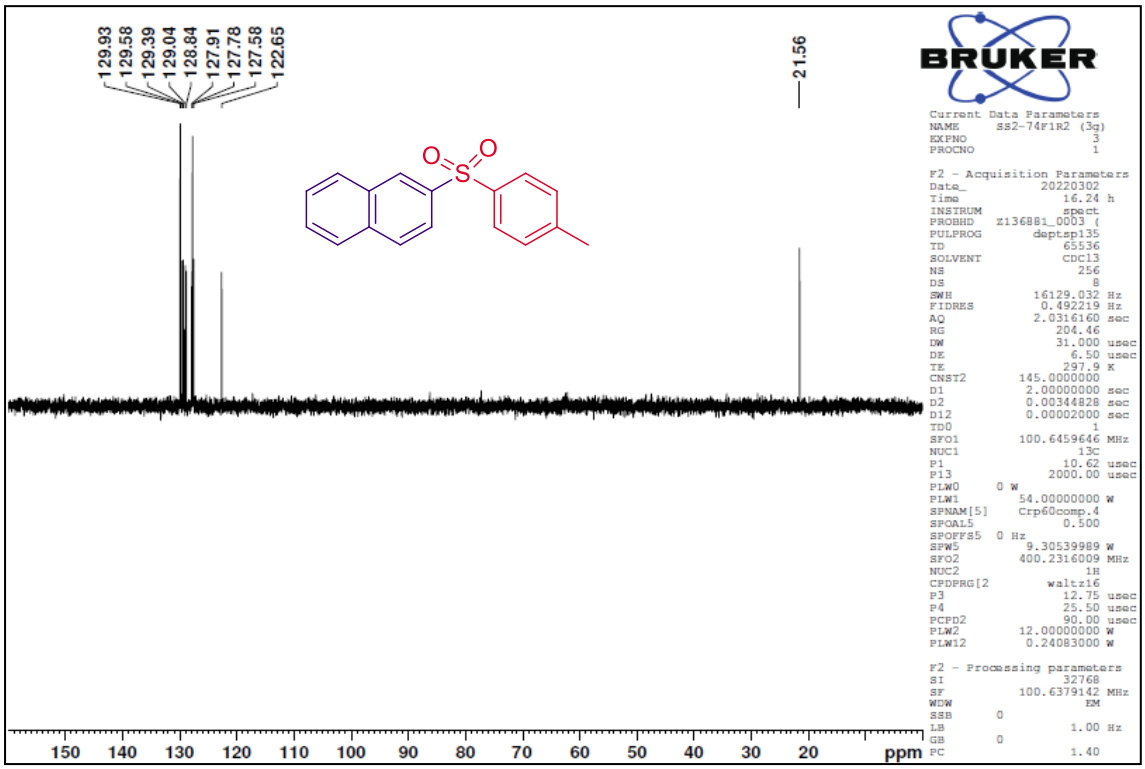


Figure 27.DEPT135 NMR spectrum of compound **3g**

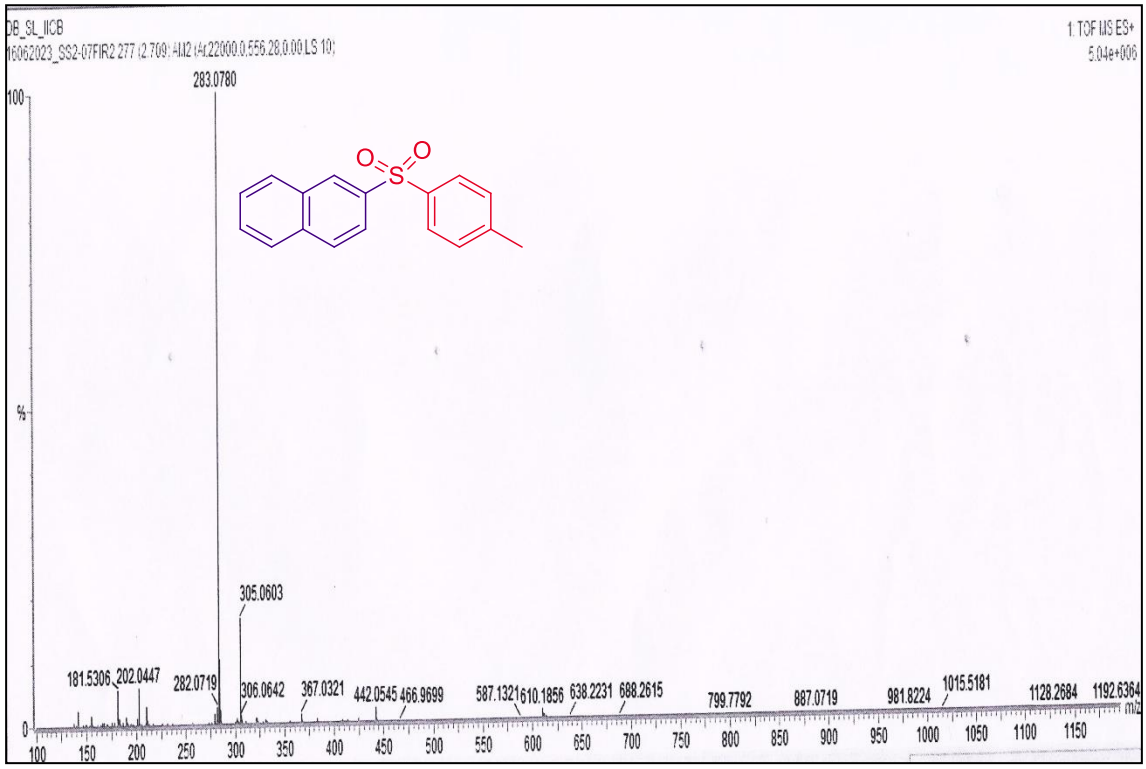


Figure 28.HRMS spectrum of compound **3g**

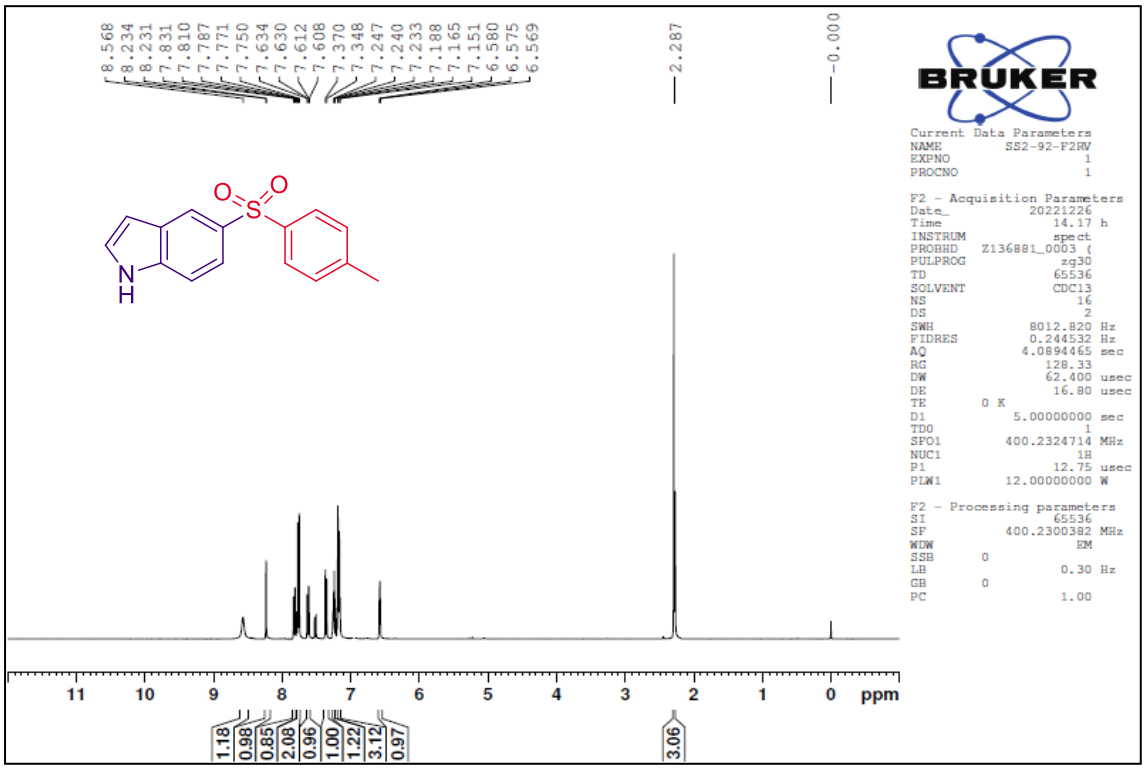


Figure 29. ^{1}H NMR spectrum of compound **3h**

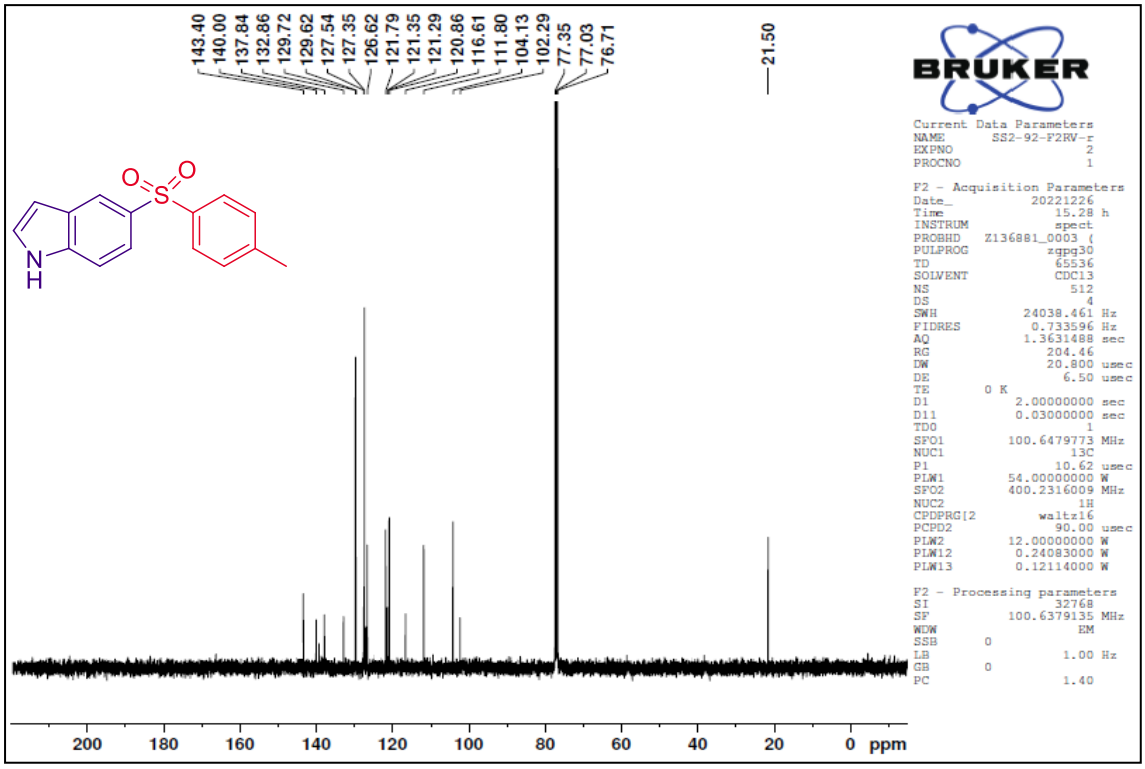


Figure 30. ^{13}C NMR spectrum of compound **3h**

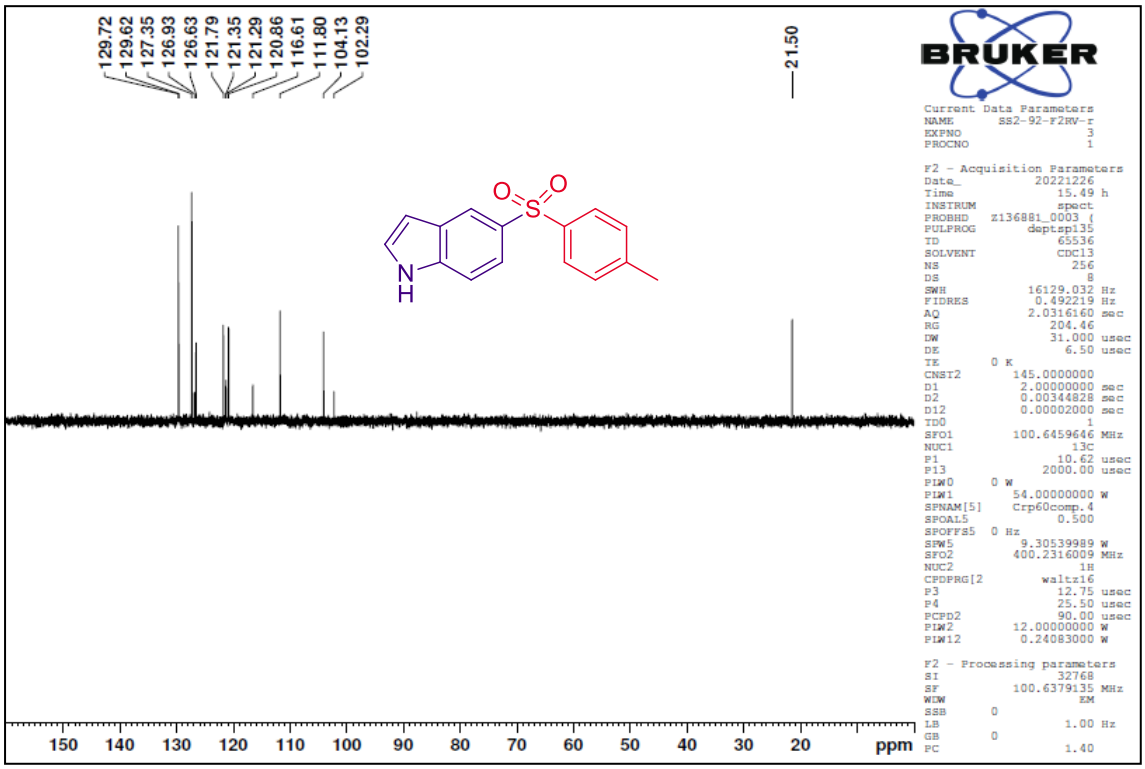


Figure 31.DEPT135 NMR spectrum of compound **3h**

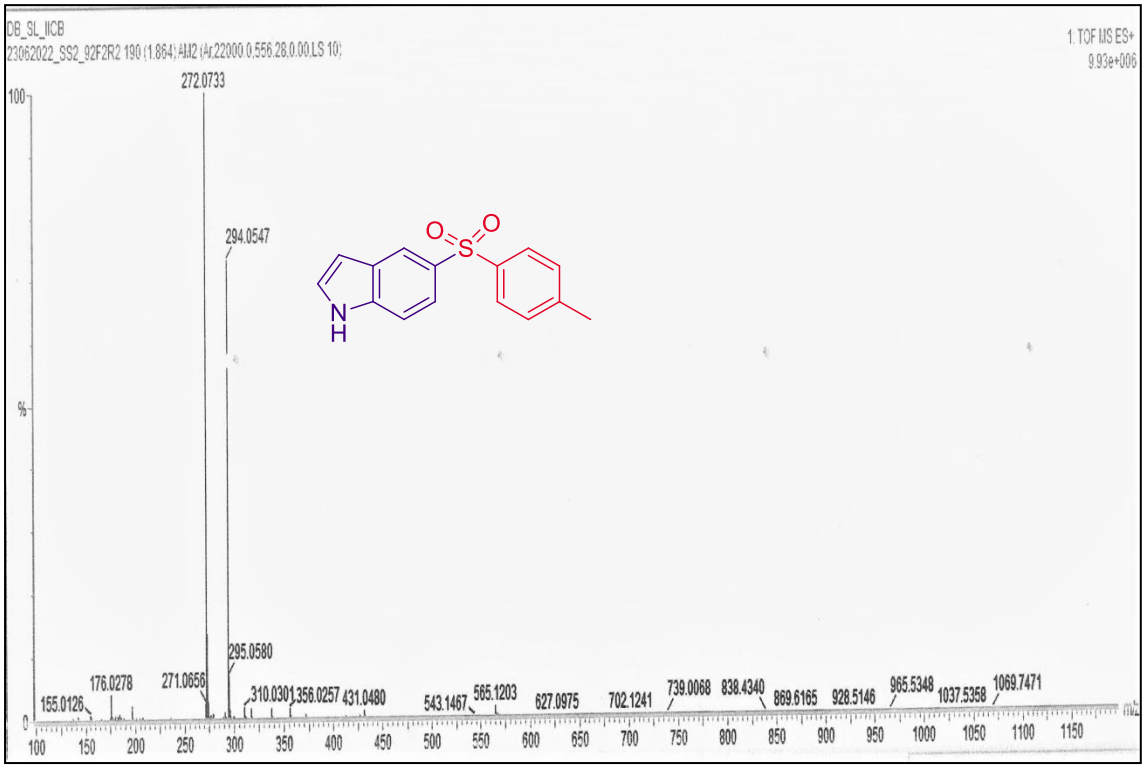


Figure 32.HRMS spectrum of compound **3h**

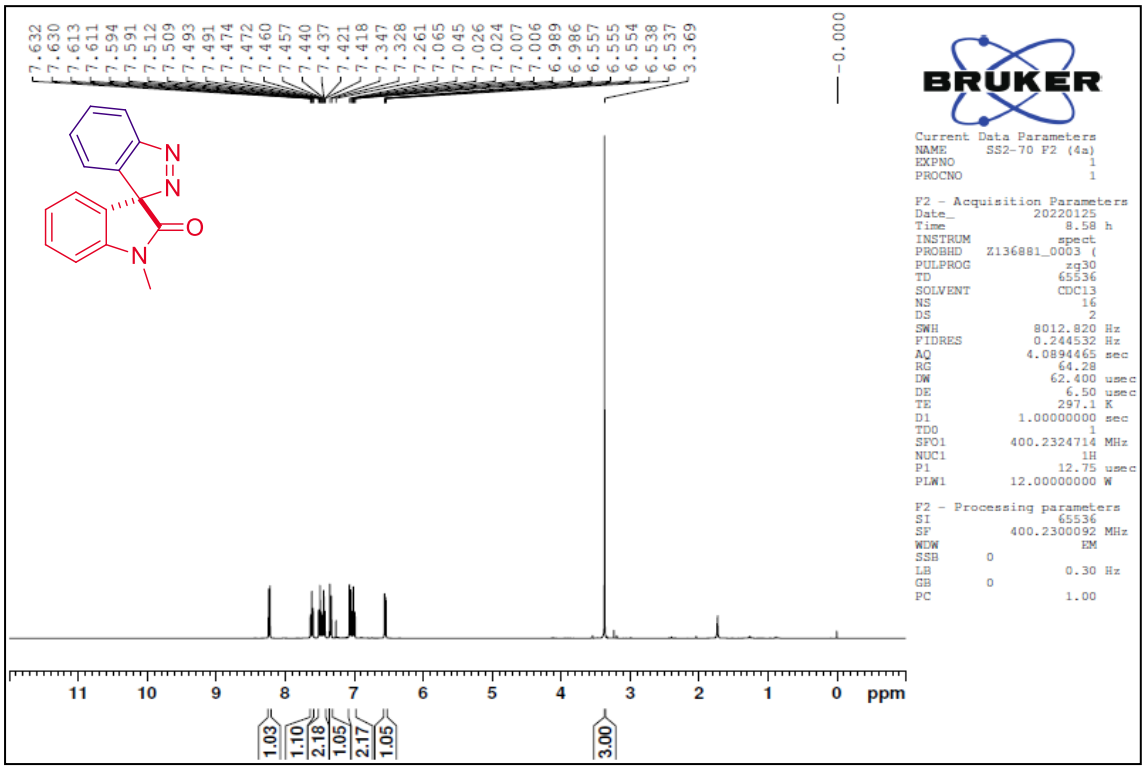


Figure 33. ^{1}H NMR spectrum of compound **4a**

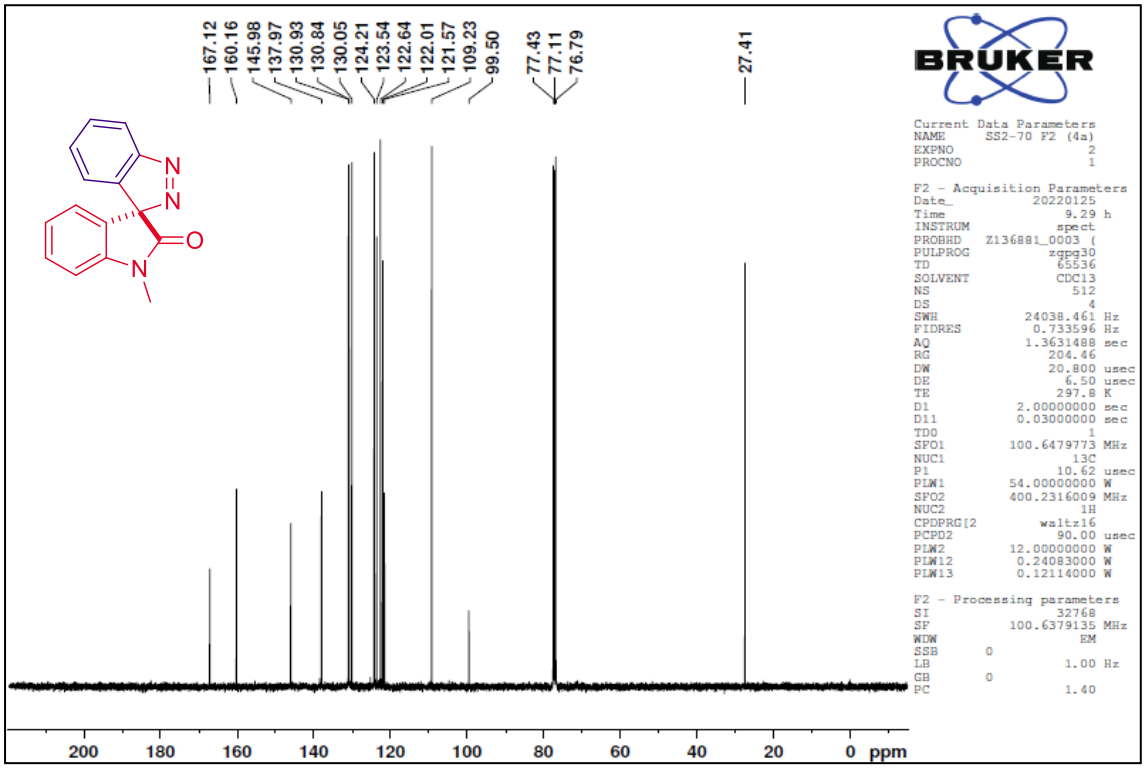


Figure 34. ^{13}C NMR spectrum of compound **4a**

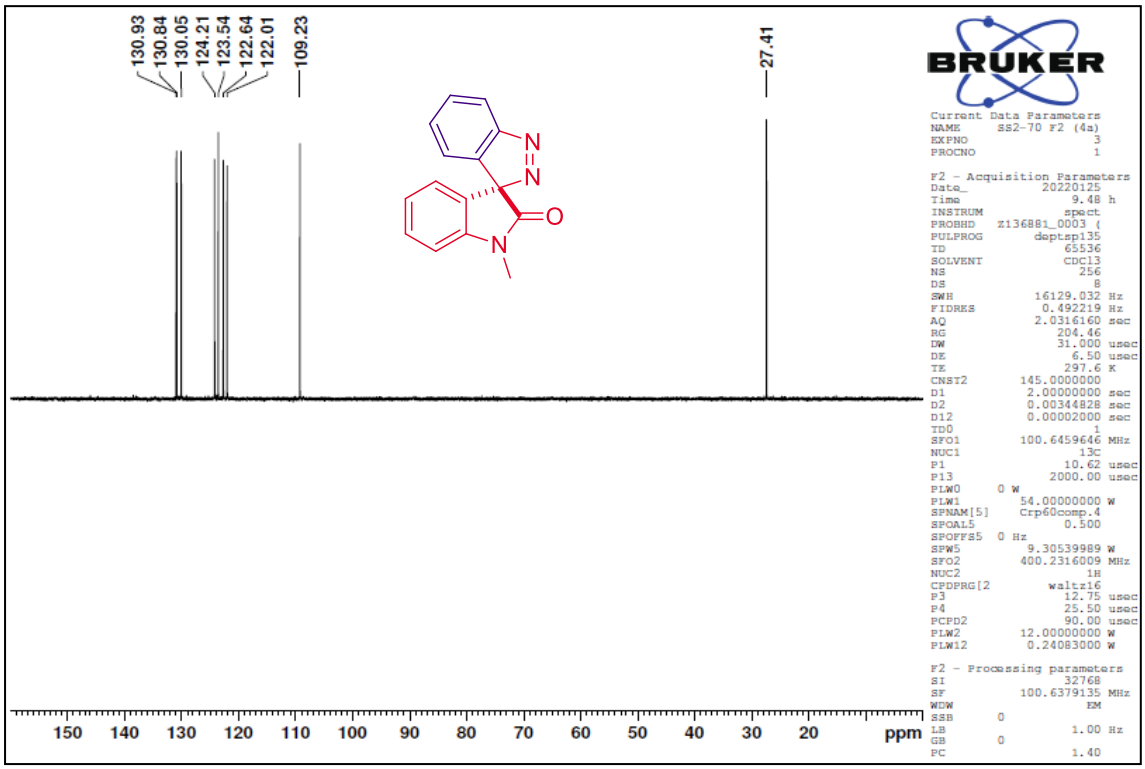


Figure 35.DEPT135 NMR spectrum of compound **4a**

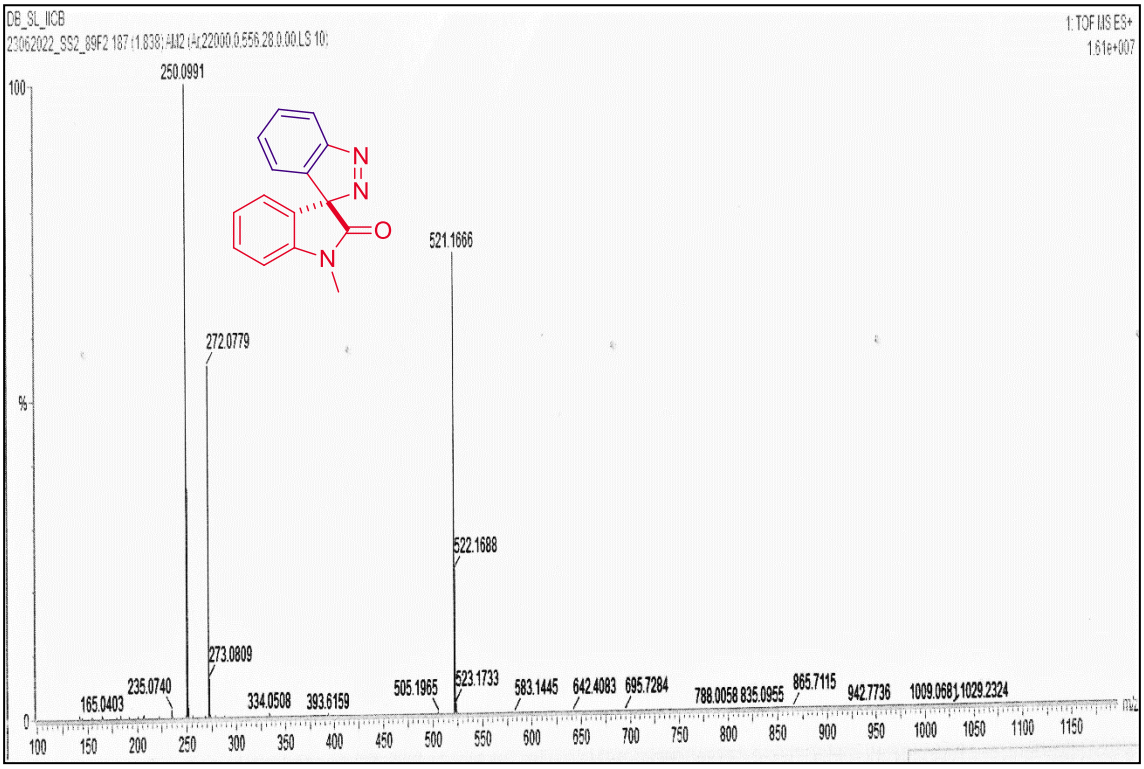


Figure 36.HRMS spectrum of compound **4a**

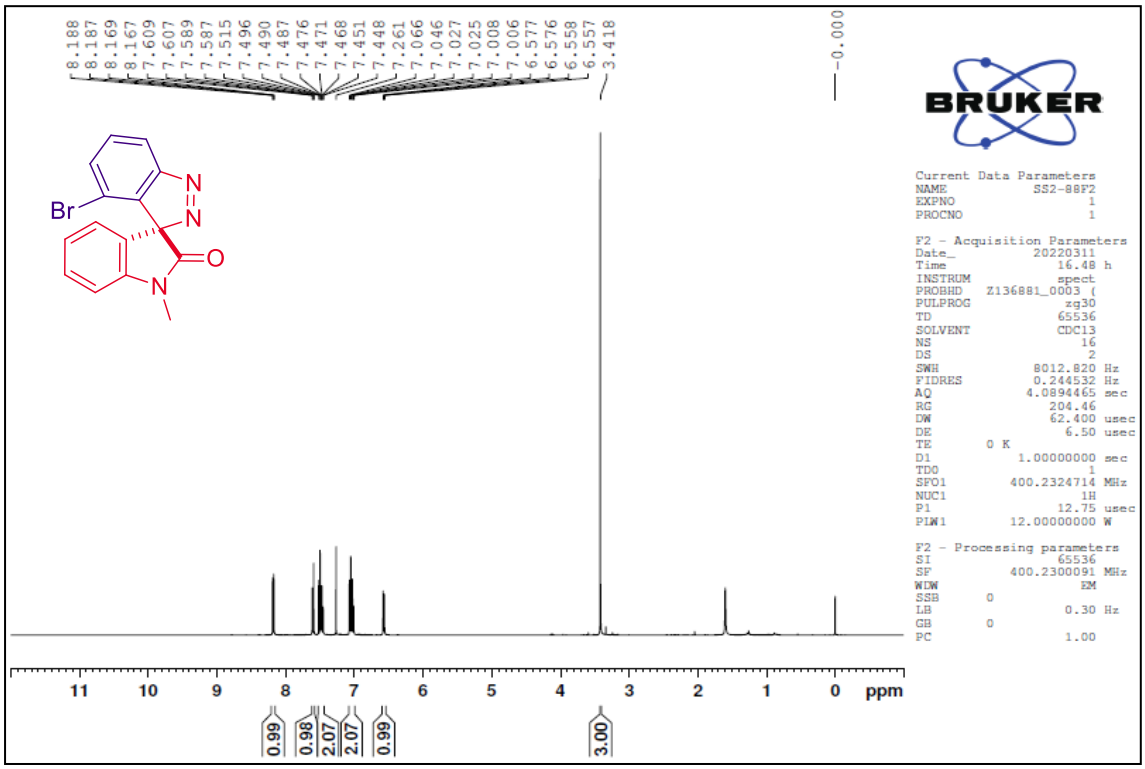


Figure 37. ^{1}H NMR spectrum of compound **4b**

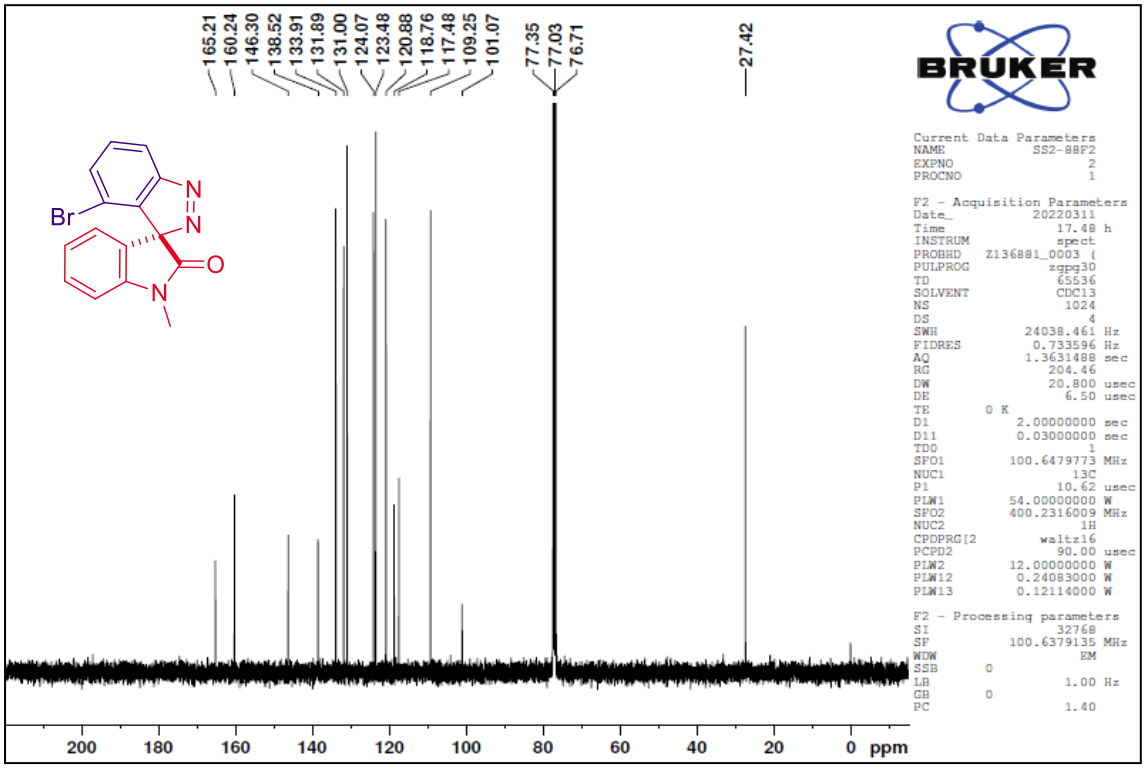


Figure 38. ^{13}C NMR spectrum of compound **4b**

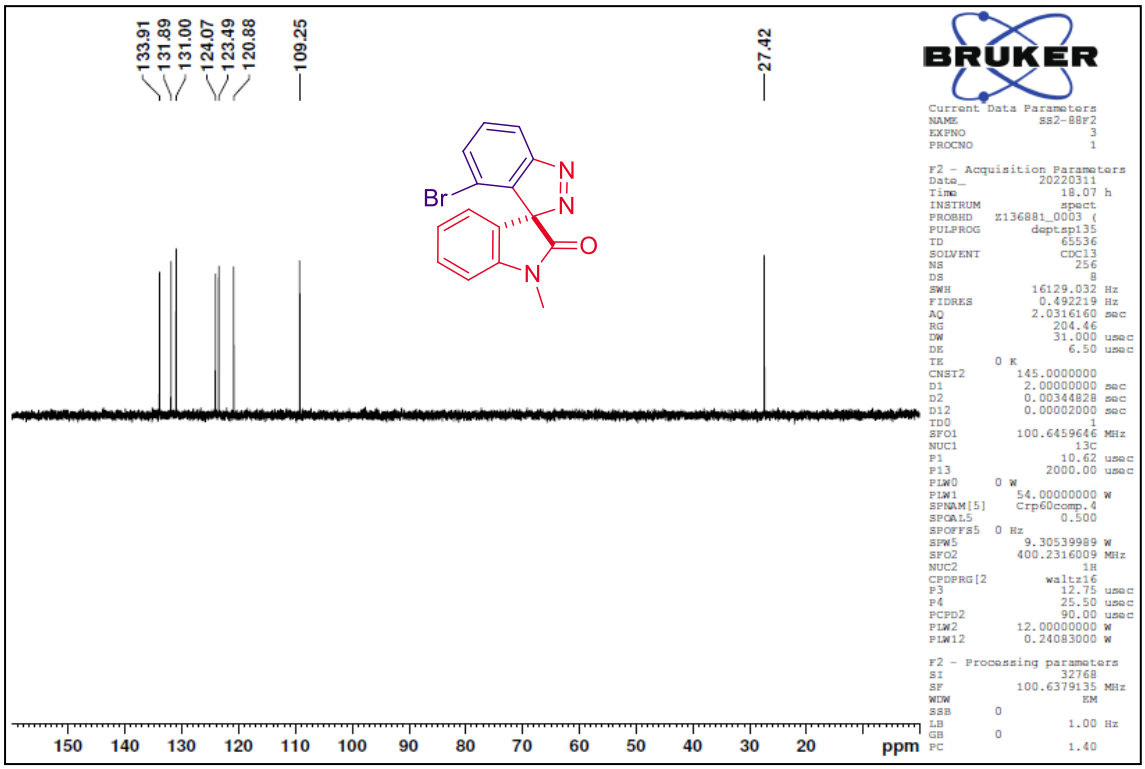


Figure 39.DEPT-135 NMR spectrum of compound **4b**

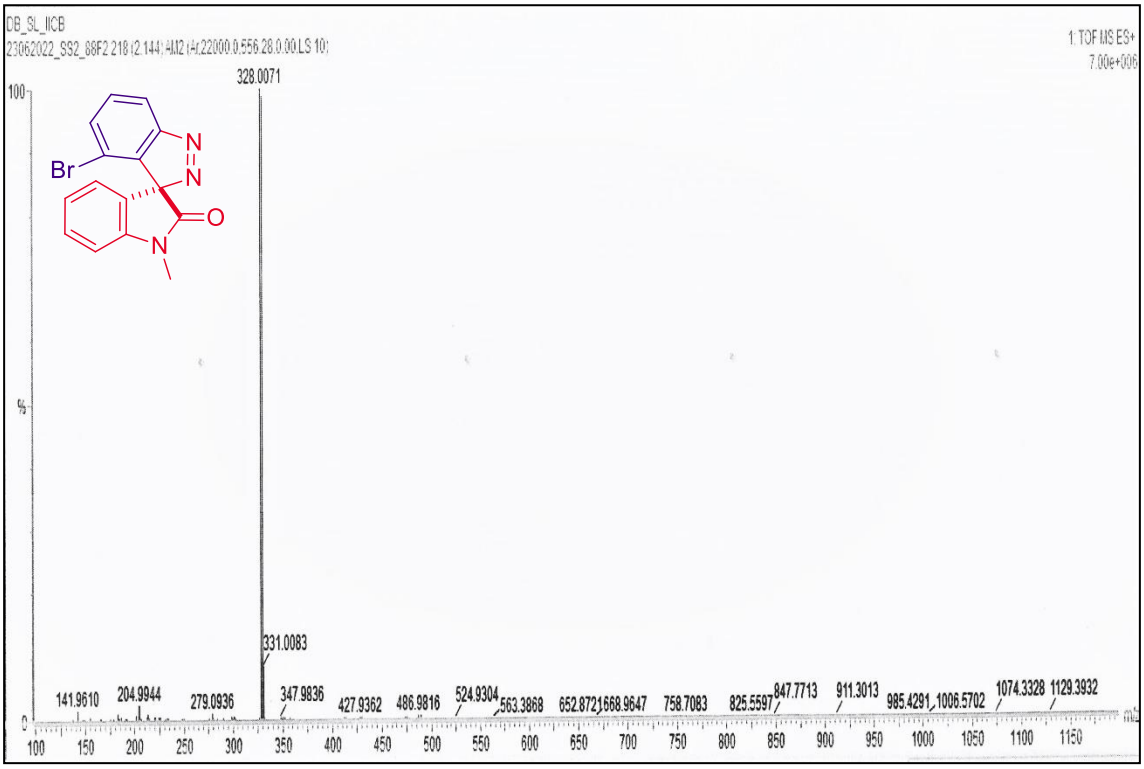


Figure 40.HRMS spectrum of compound **4b**

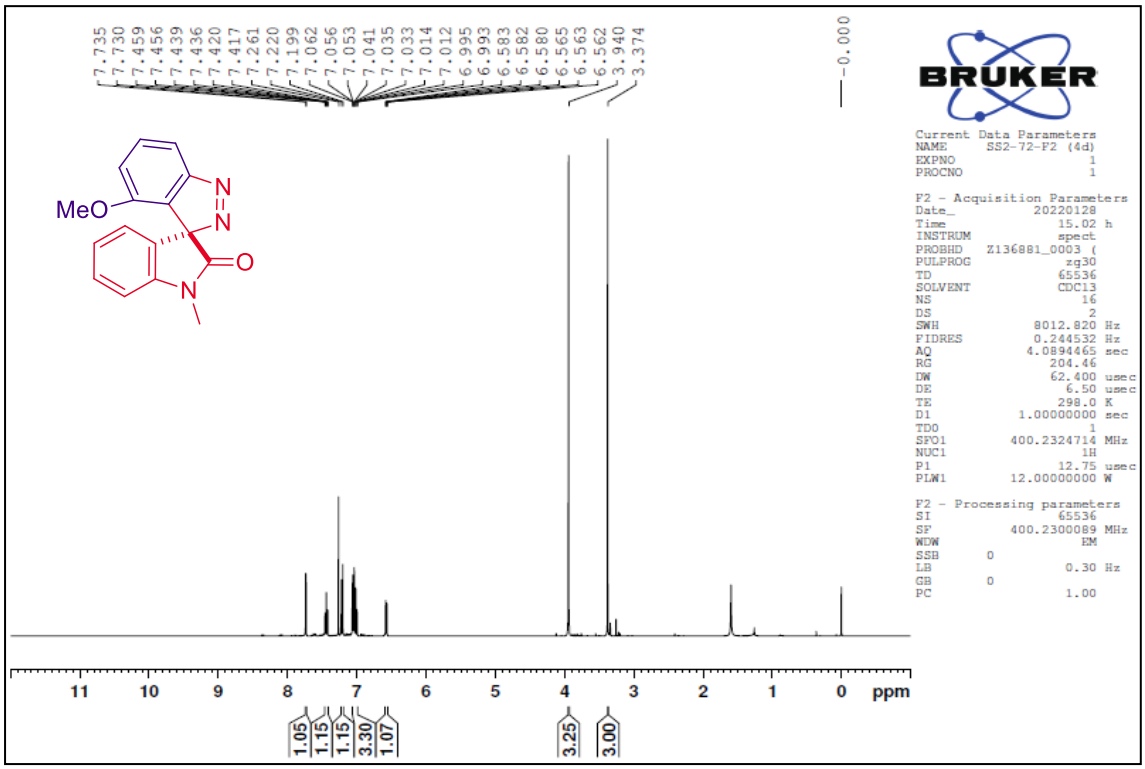


Figure 41. ^{1}H NMR spectrum of compound **4c**

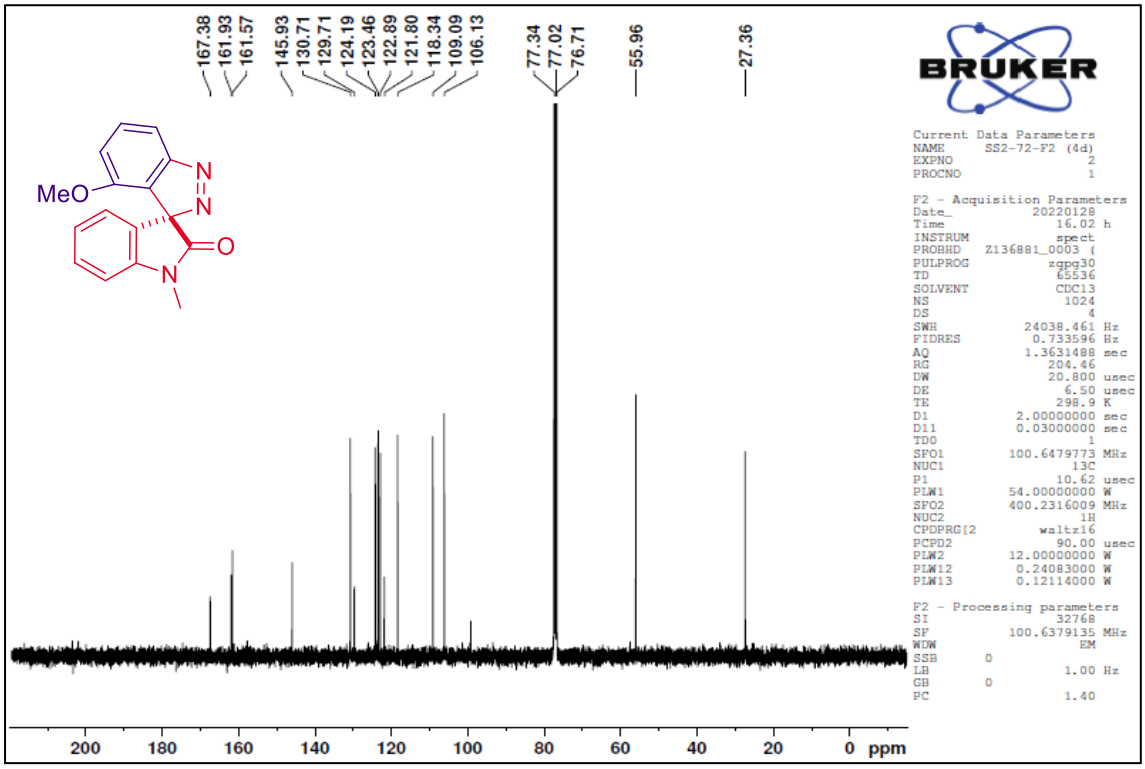


Figure 42. ^{13}C NMR spectrum of compound **4c**

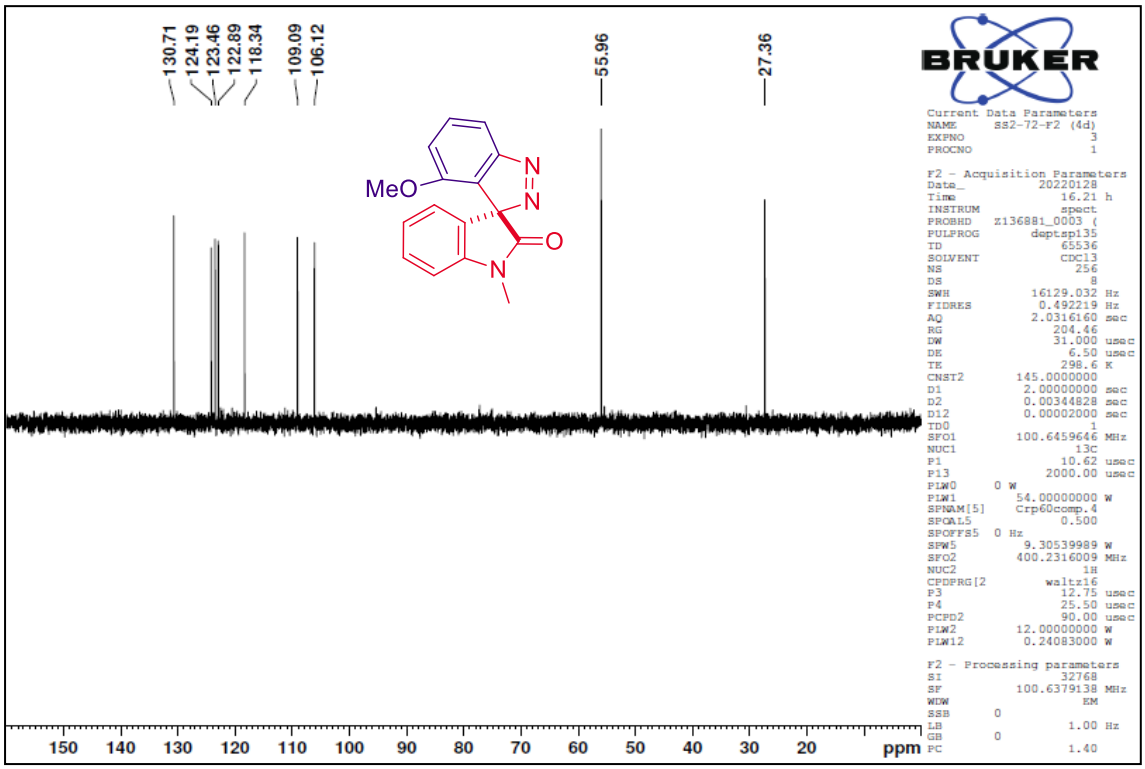


Figure 43.DEPT135 NMR spectrum of compound **4c**

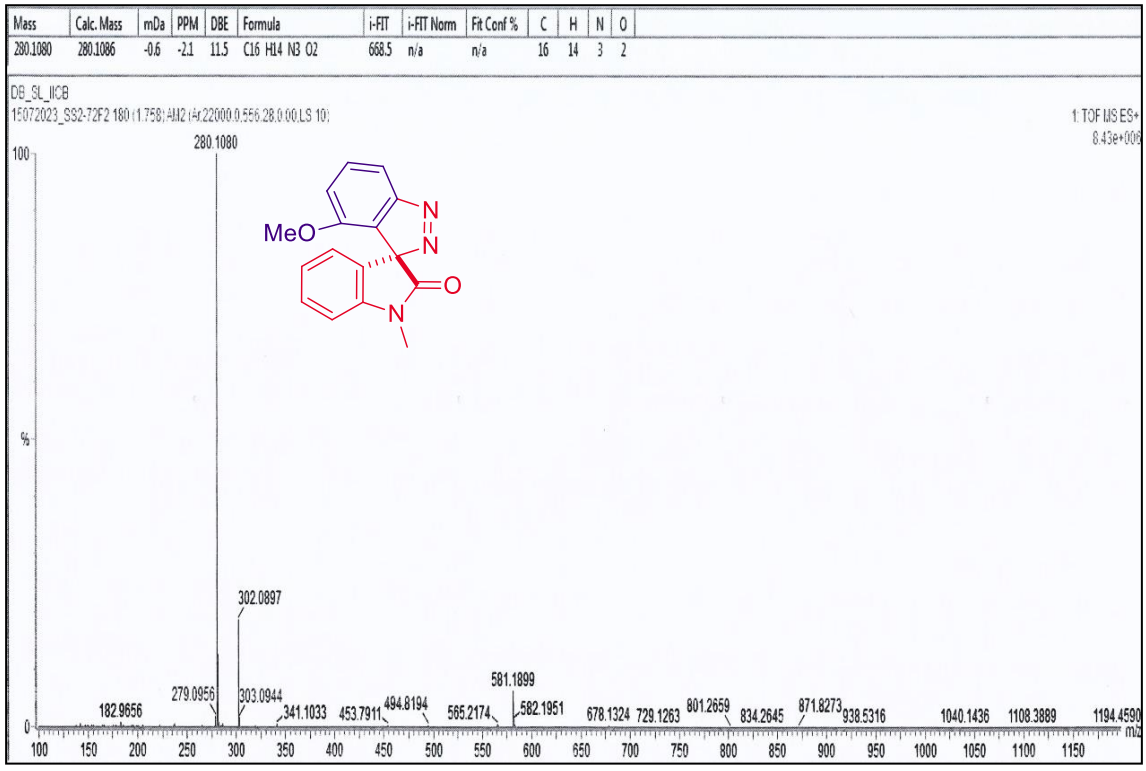


Figure 44.HRMS spectrum of compound **4c**

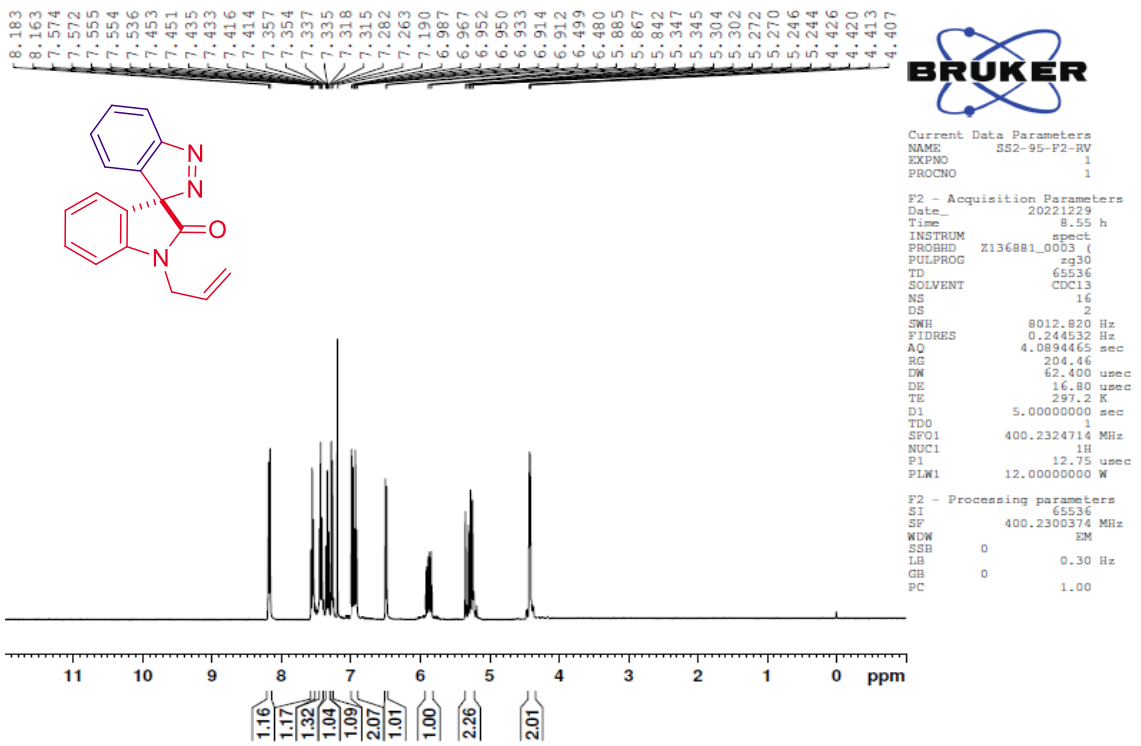


Figure 45. ^{1}H NMR spectrum of compound **4d**

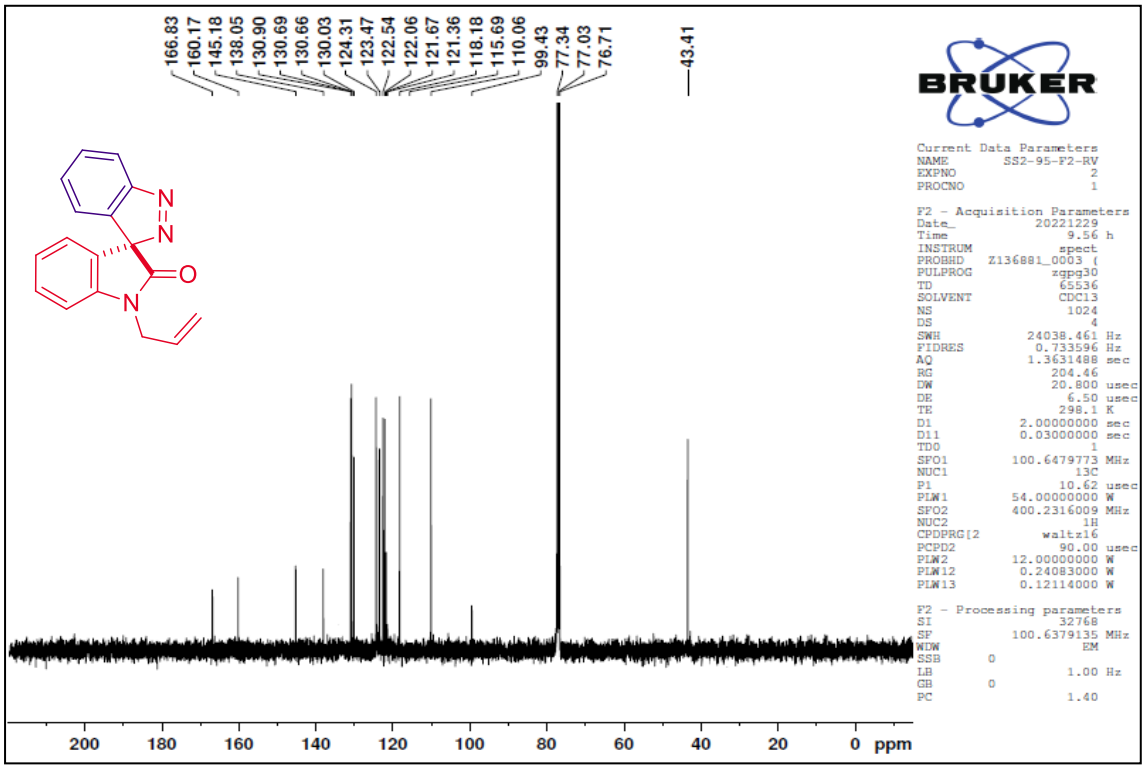


Figure 46. ^{13}C NMR spectrum of compound **4d**

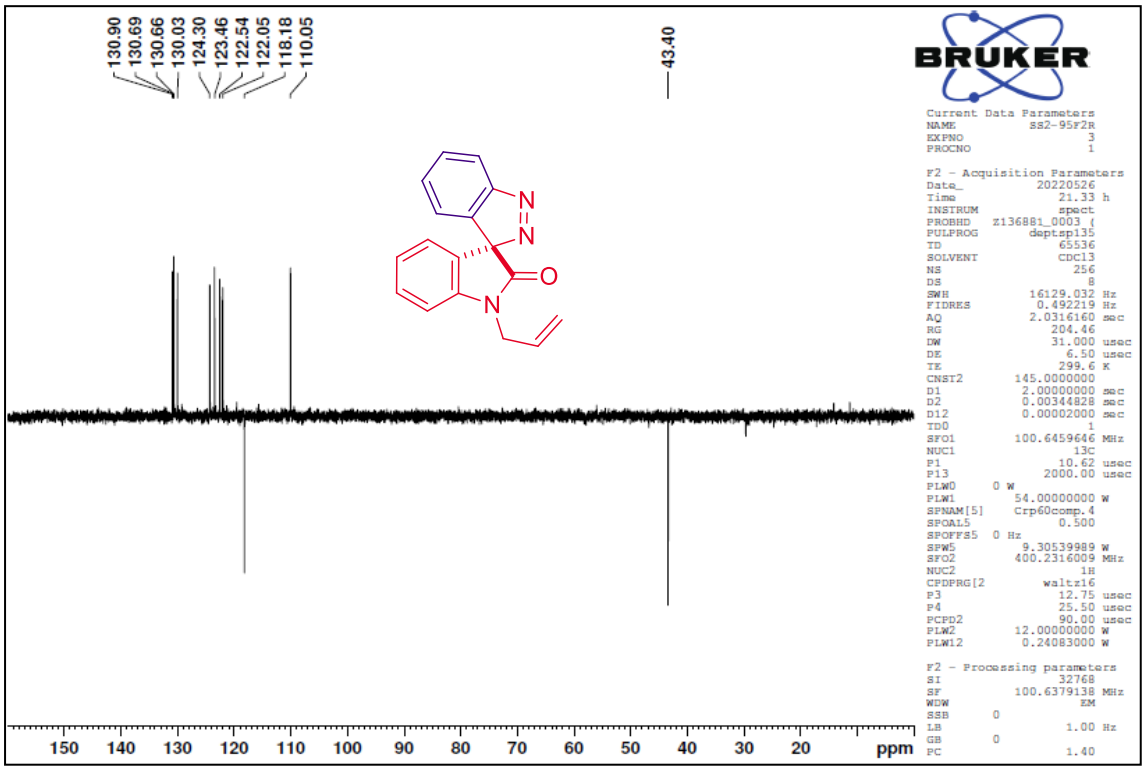


Figure 47.DEPT135 NMR spectrum of compound **4d**

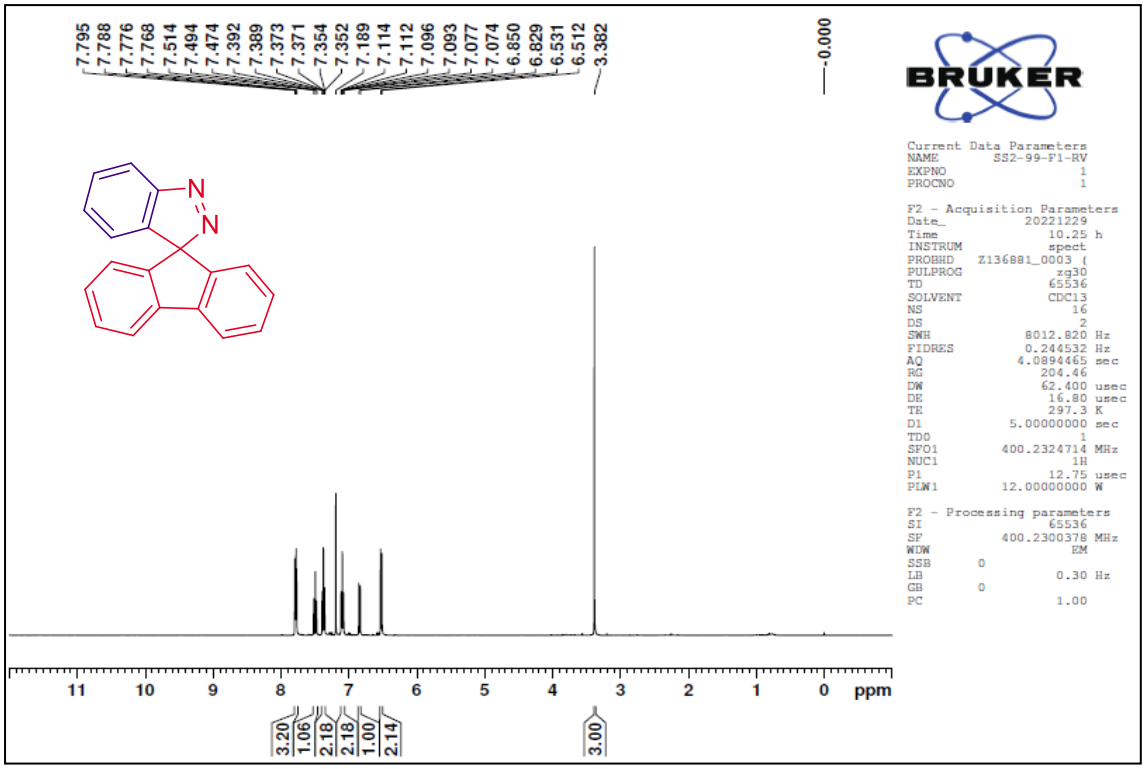


Figure 49.^{1}H NMR spectrum of compound **4e**

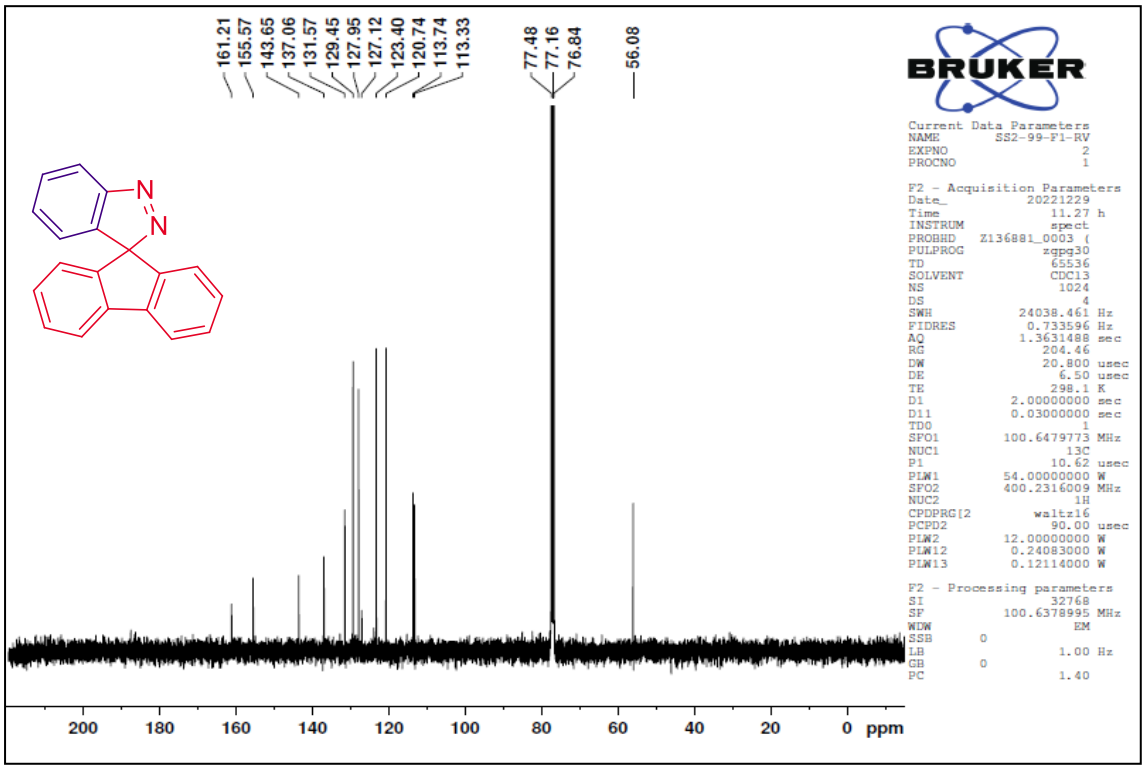


Figure 50. ^{13}C NMR spectrum of compound **4e**

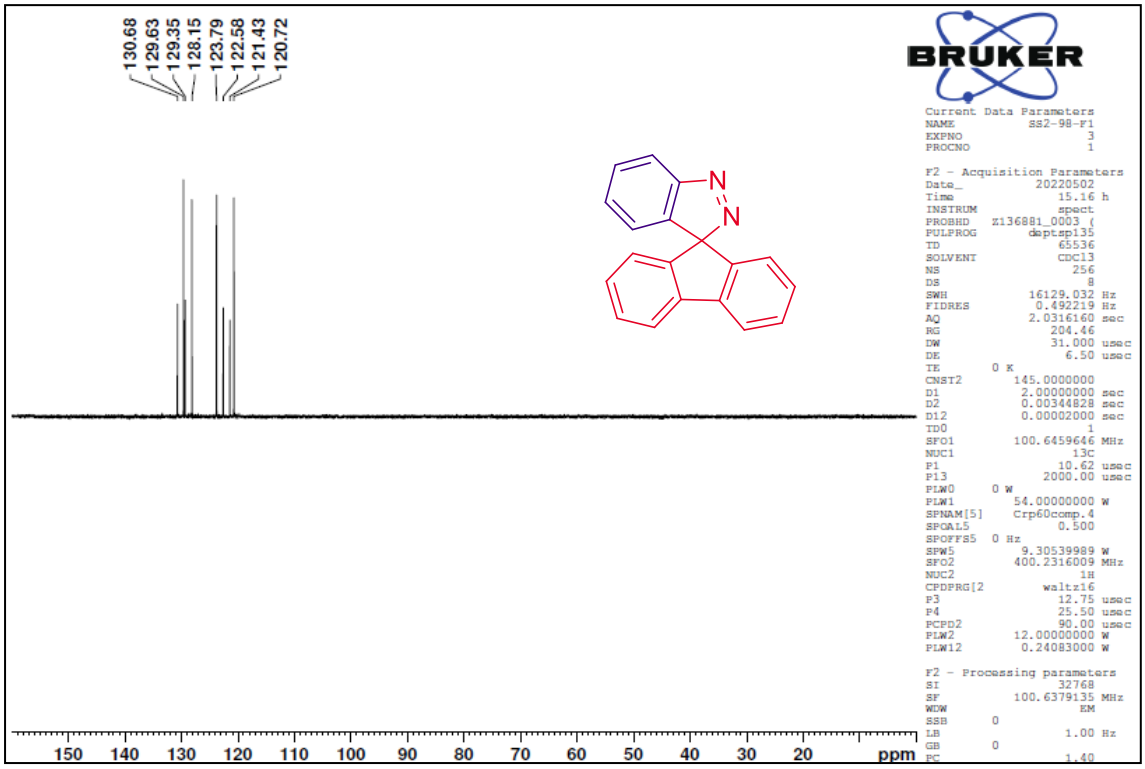


Figure 51.DEPT135 NMR spectrum of compound **4e**

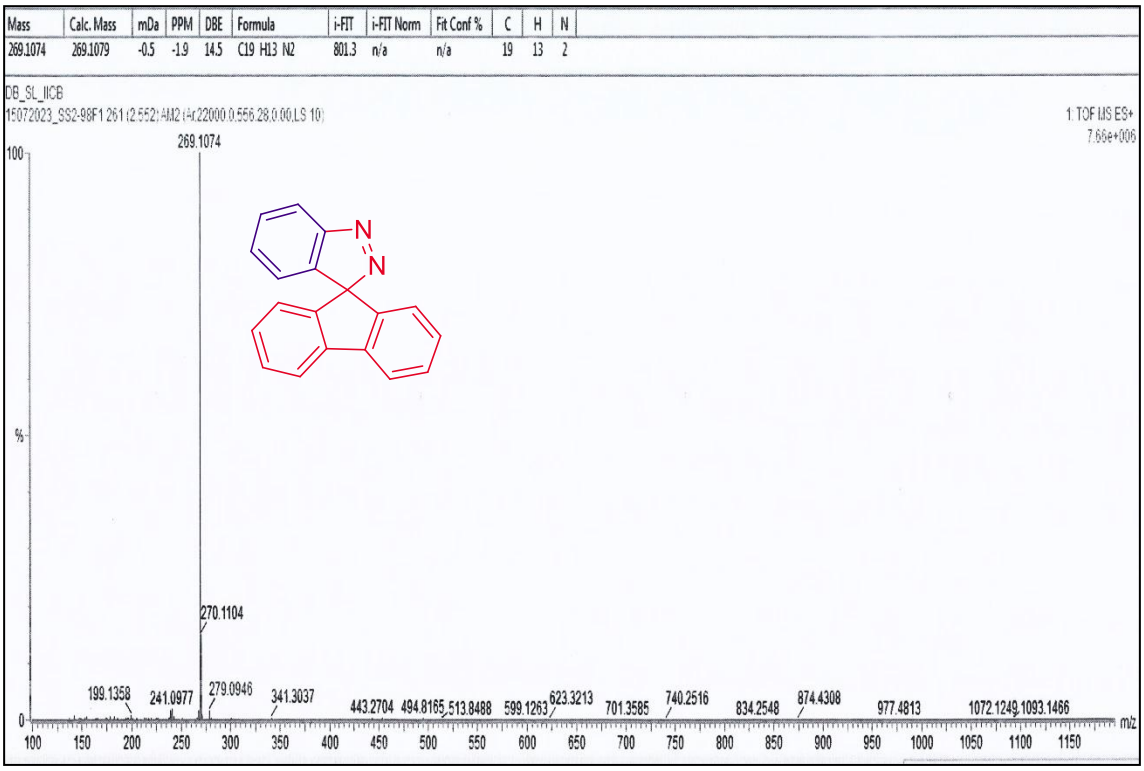


Figure 52.HRMS spectrum of compound **4e**

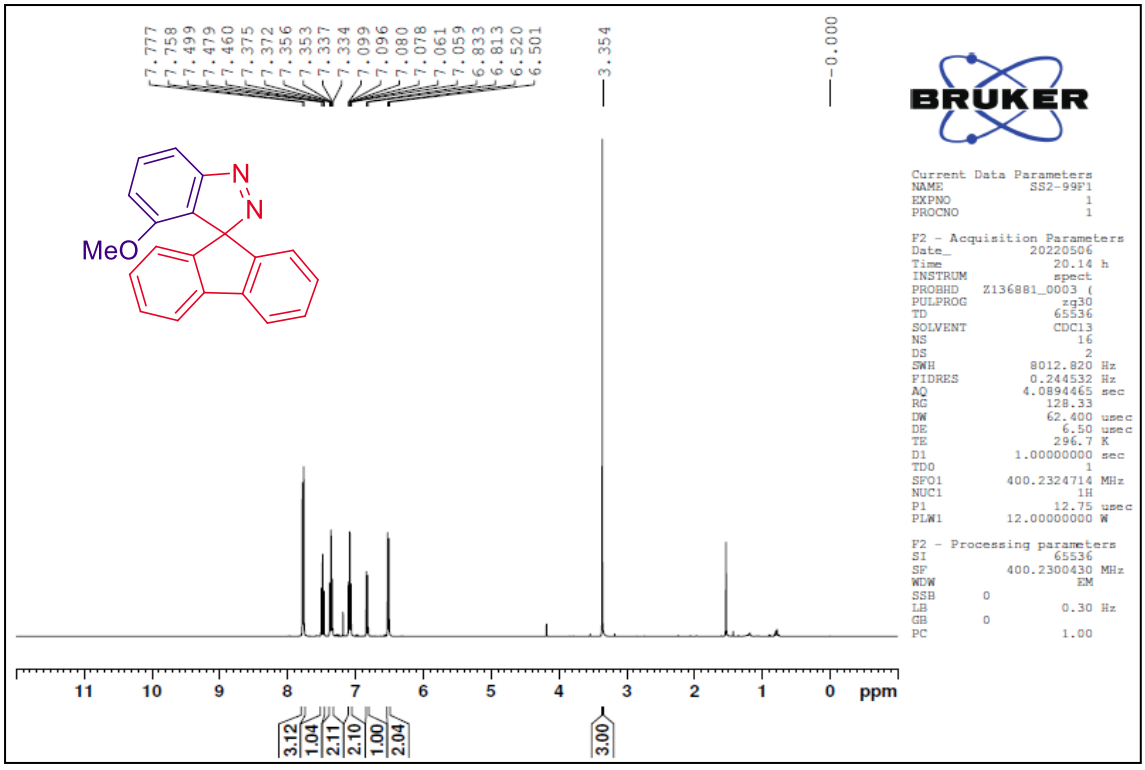


Figure 53.^{1}H NMR spectrum of compound **4f**

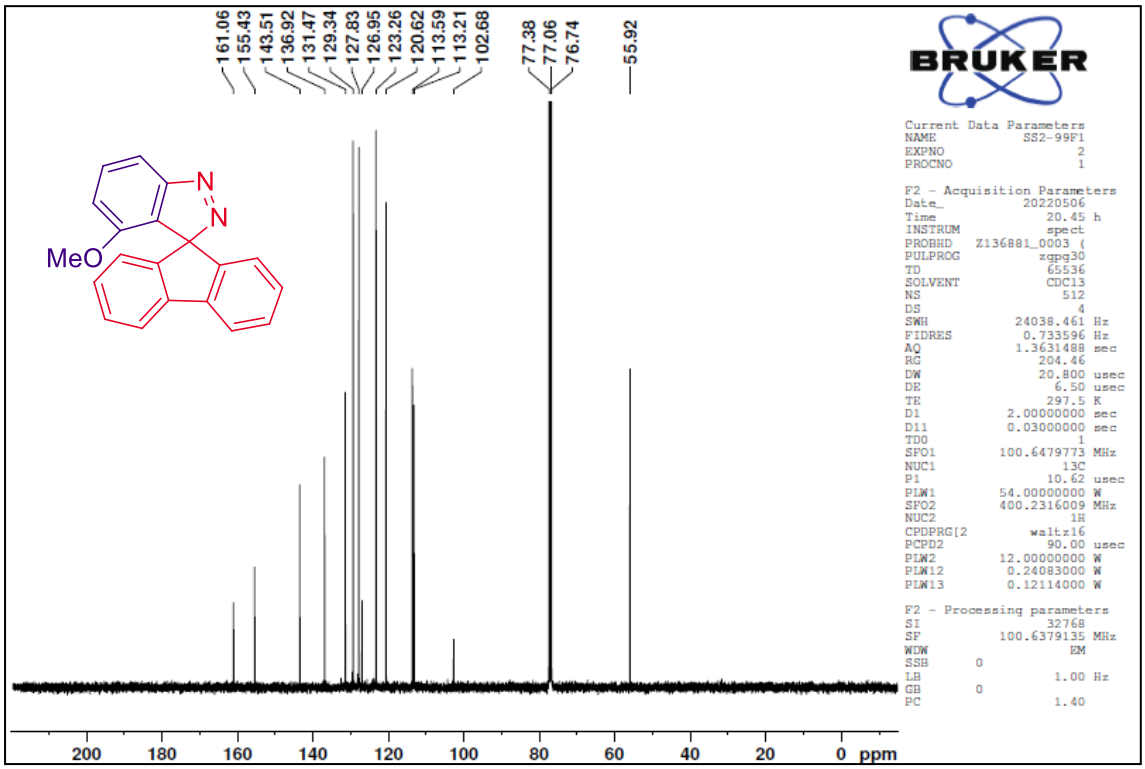


Figure 54. ^{13}C NMR spectrum of compound **4f**

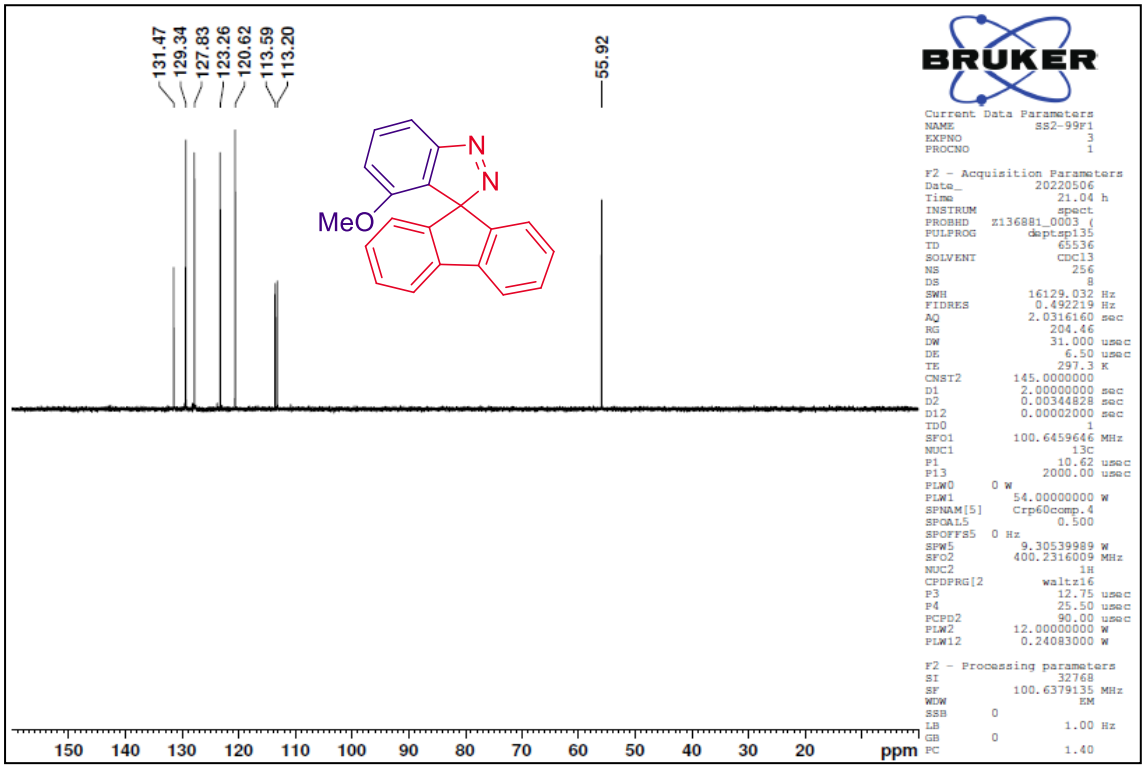


Figure 55. DEPT135 NMR spectrum of compound **4f**

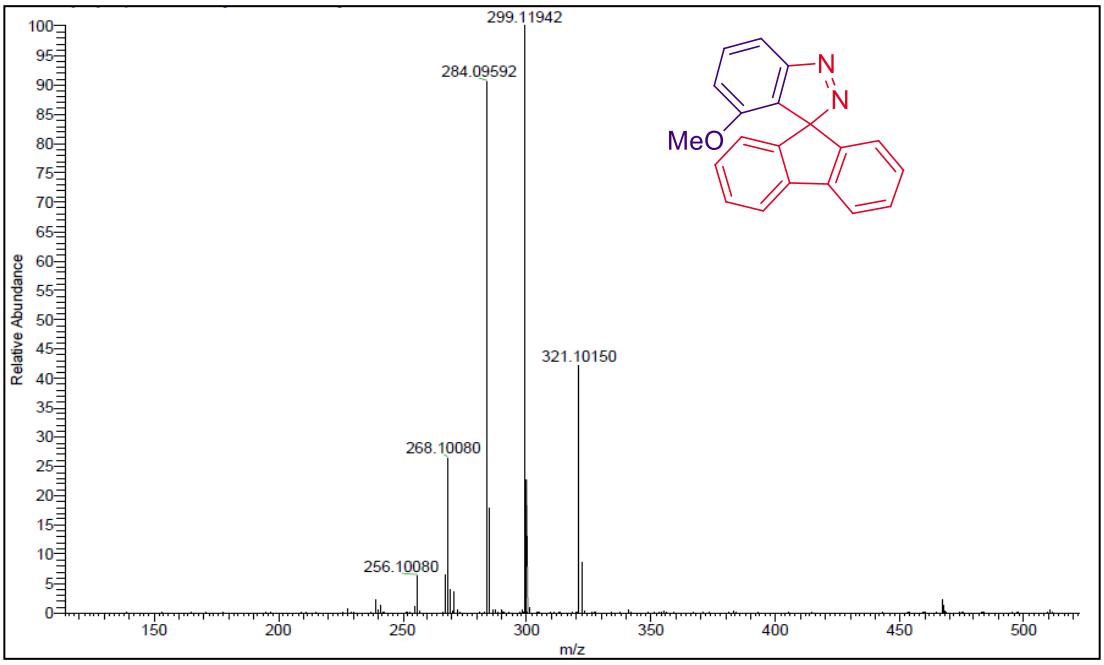


Figure 56.HRMS spectrum of compound **4f**

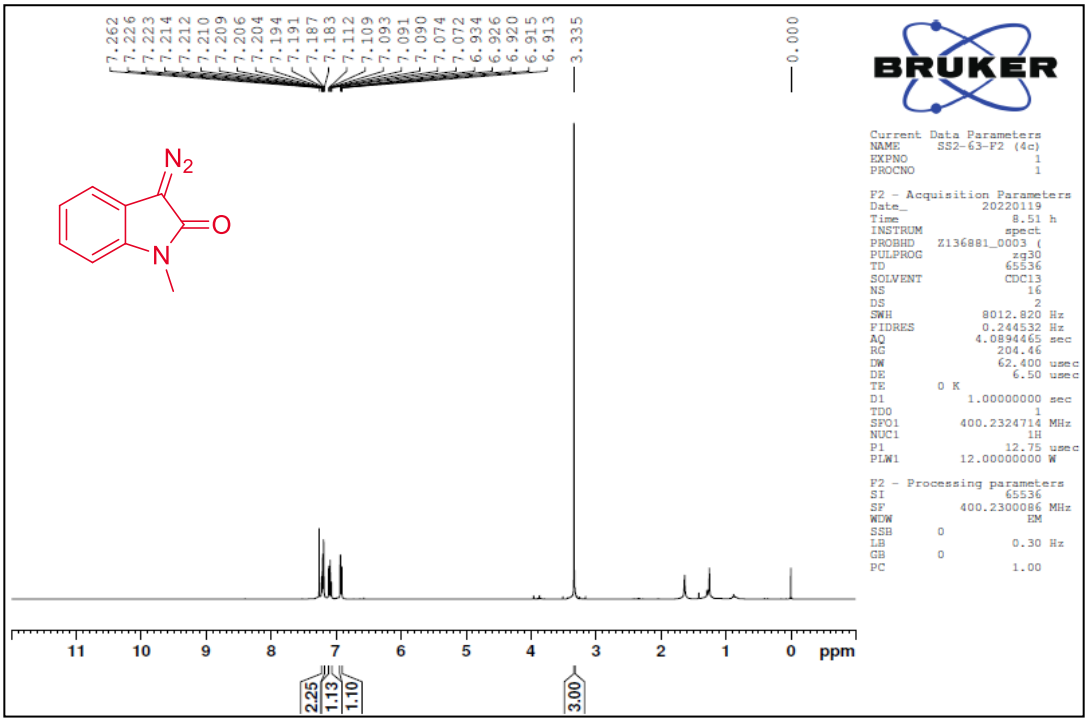


Figure 57.^{1}H NMR spectrum of compound **4g**

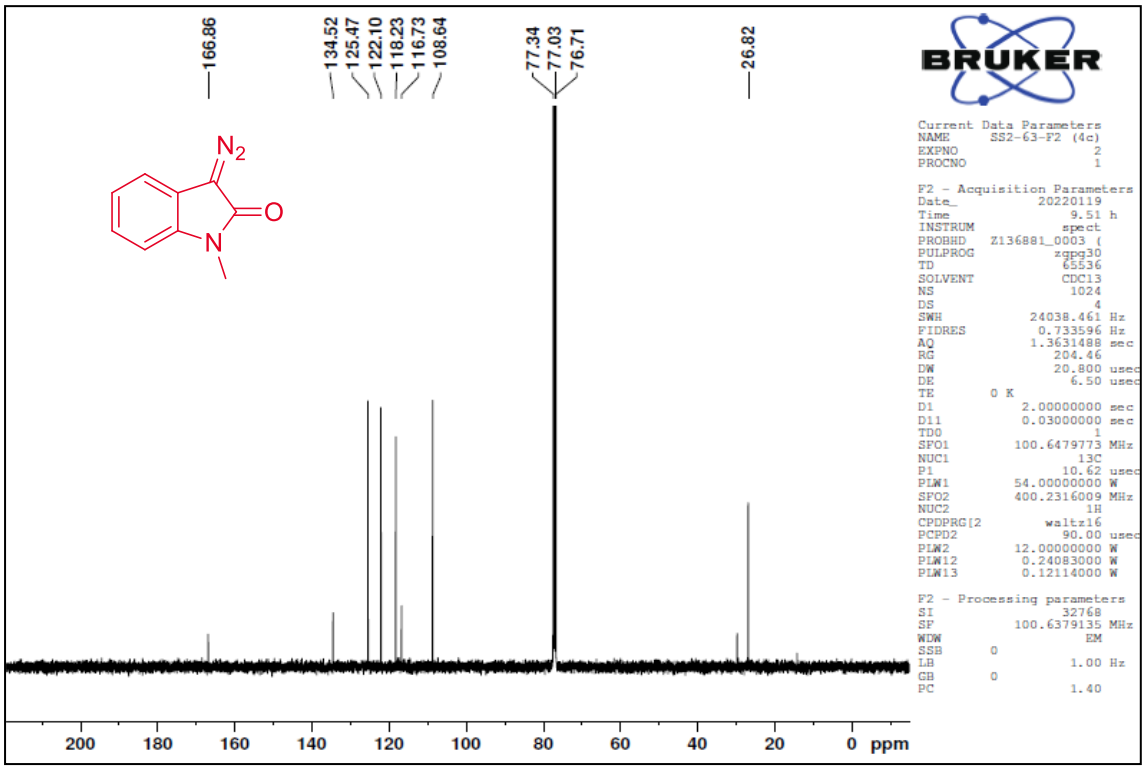


Figure 58. ^{13}C NMR spectrum of compound **4g**

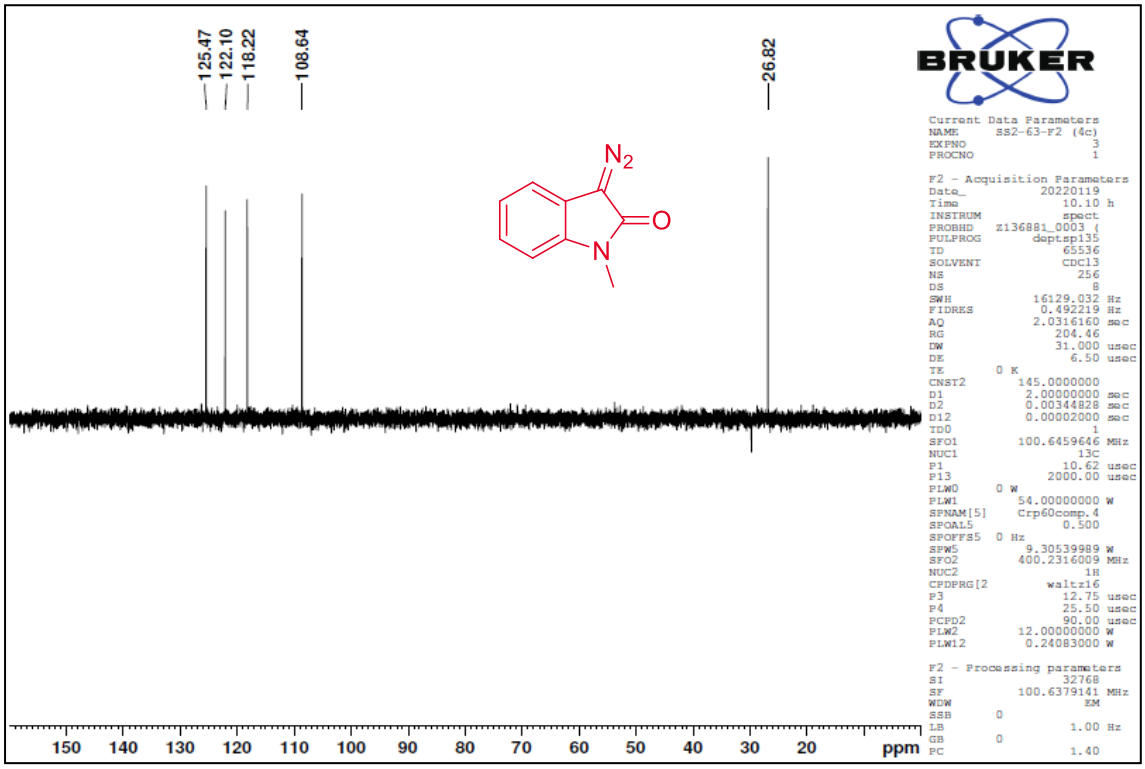


Figure 59.DEPT135 NMR spectrum of compound **4g**

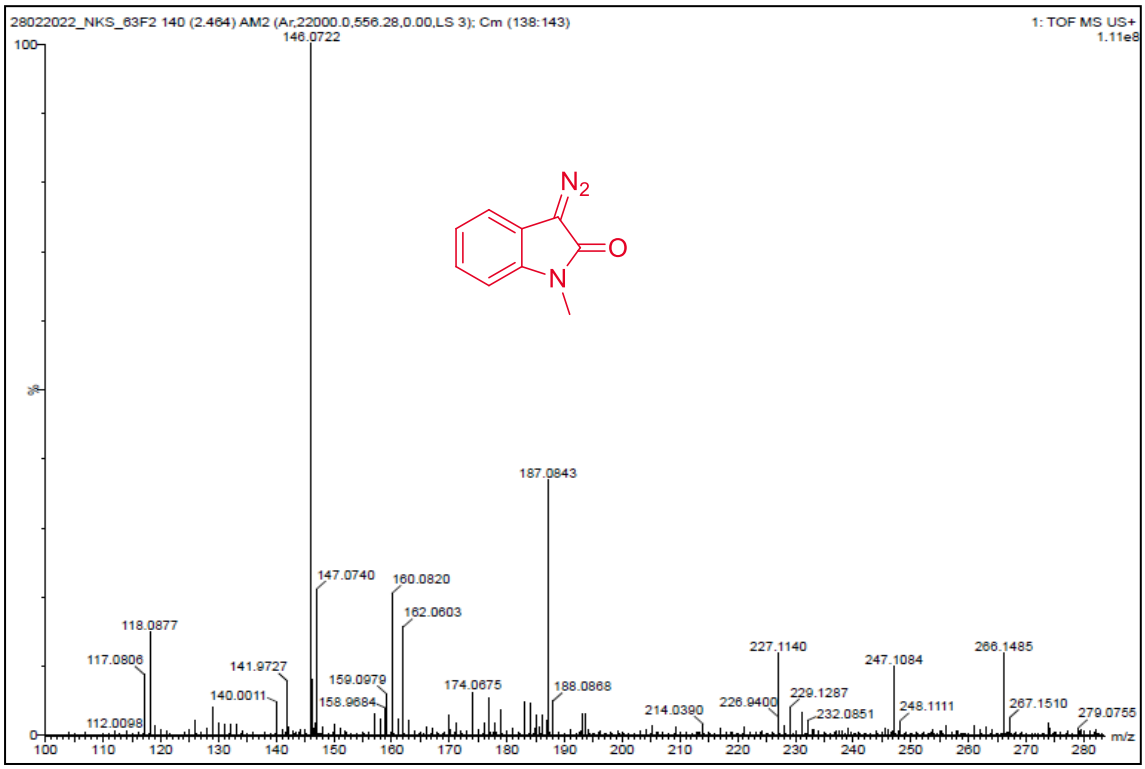


Figure 60.HRMS spectrum of compound **4g**

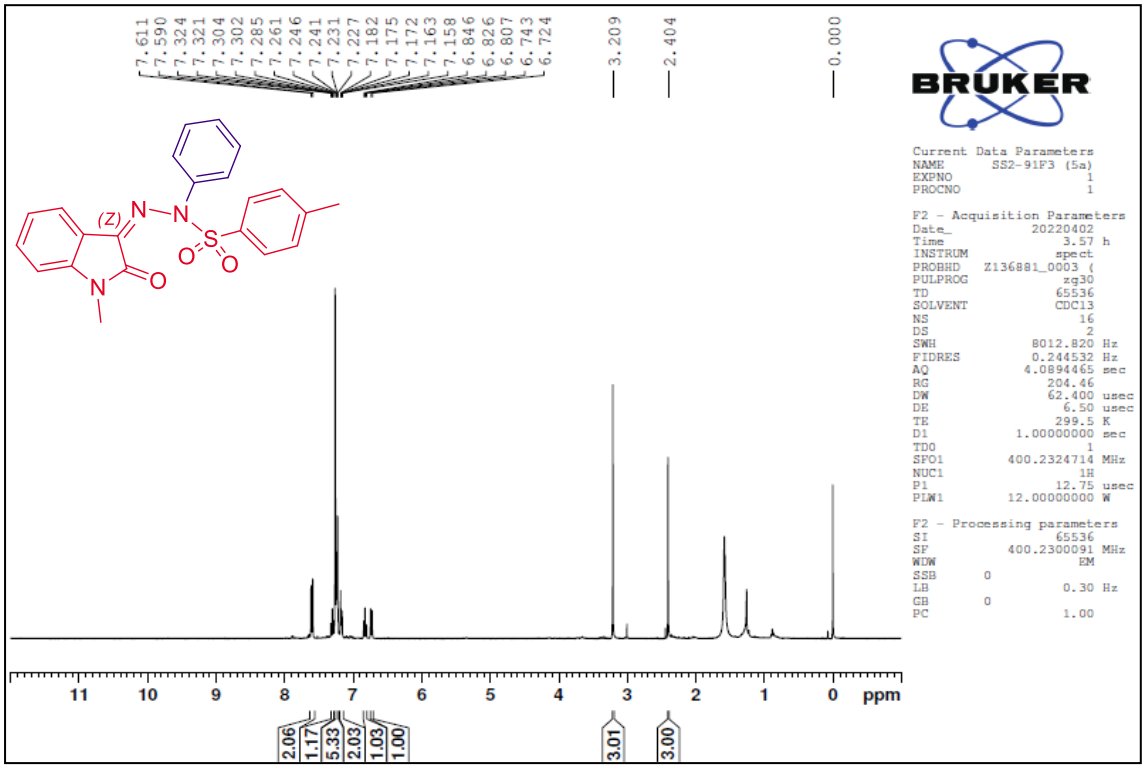


Figure 61.^{1}H NMR spectrum of compound **5a**

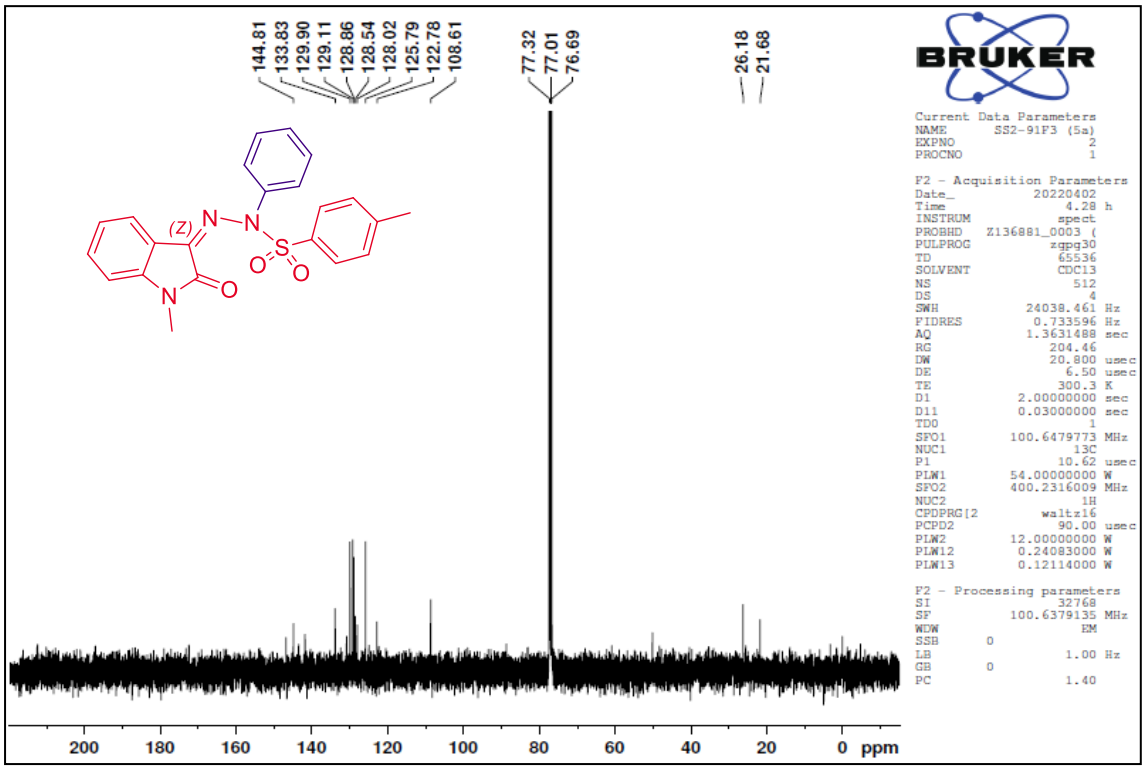


Figure 62. ^{13}C NMR spectrum of compound **5a**

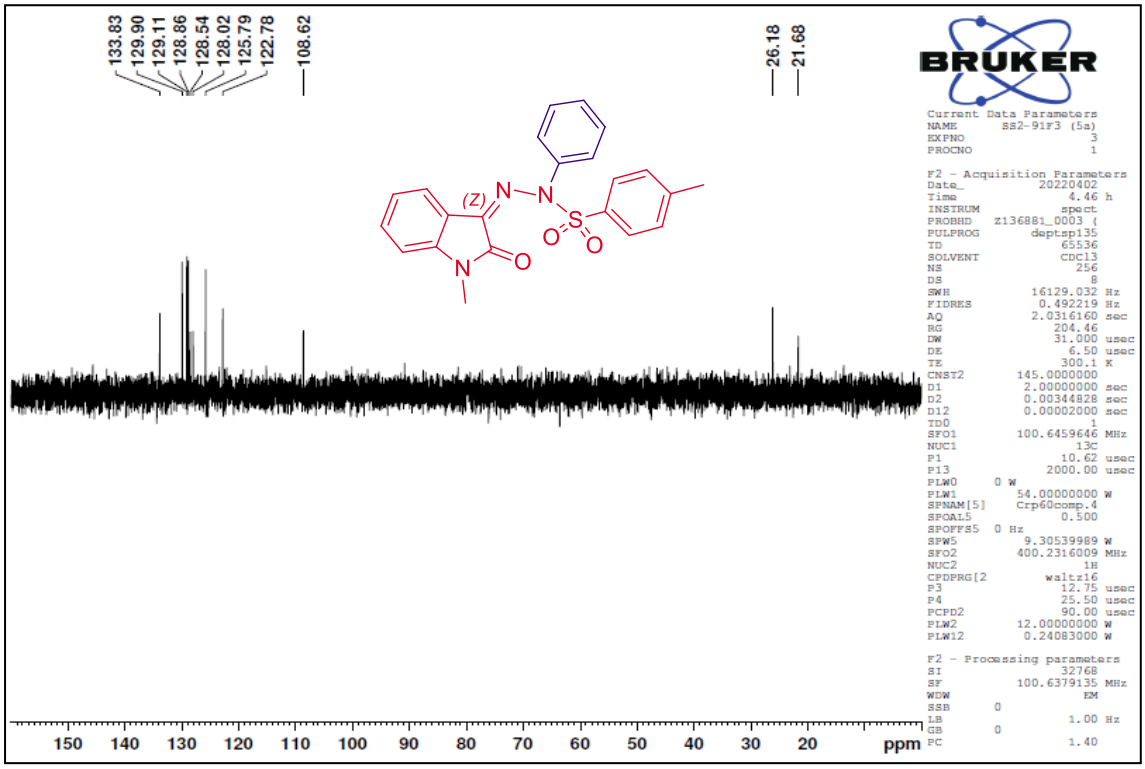


Figure 63.DEPT135 NMR spectrum of compound **5a**

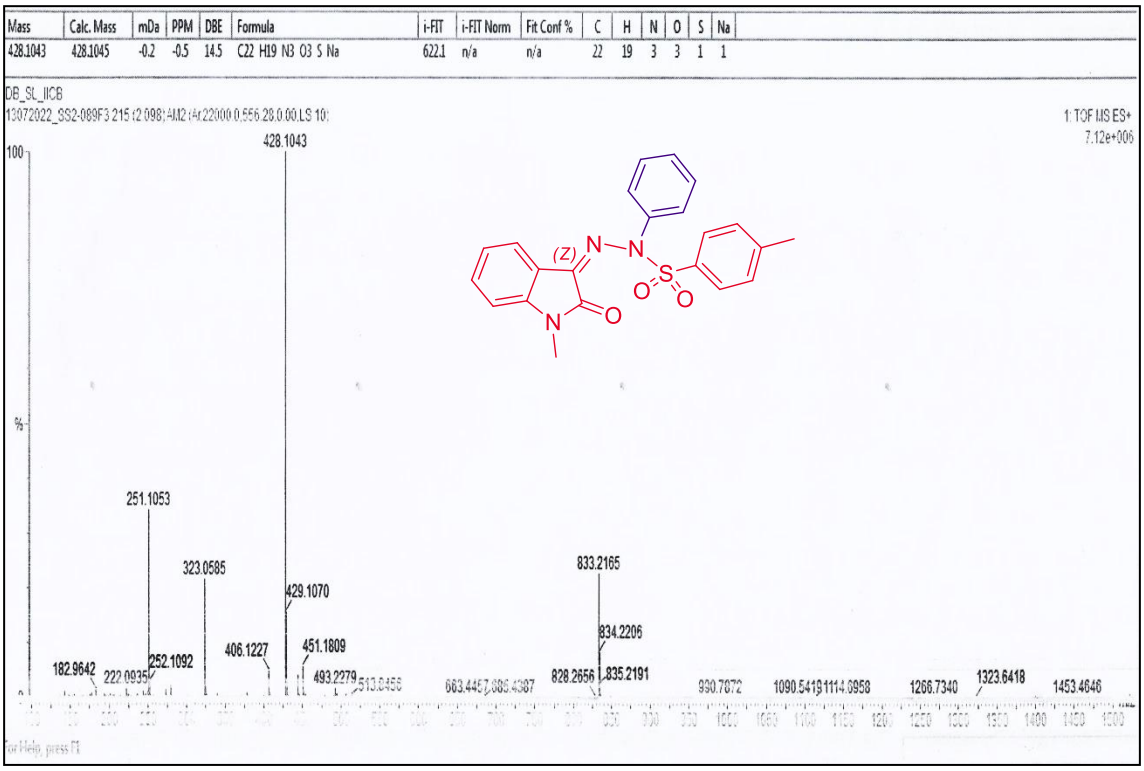


Figure 64.HRMS spectrum of compound **5a**

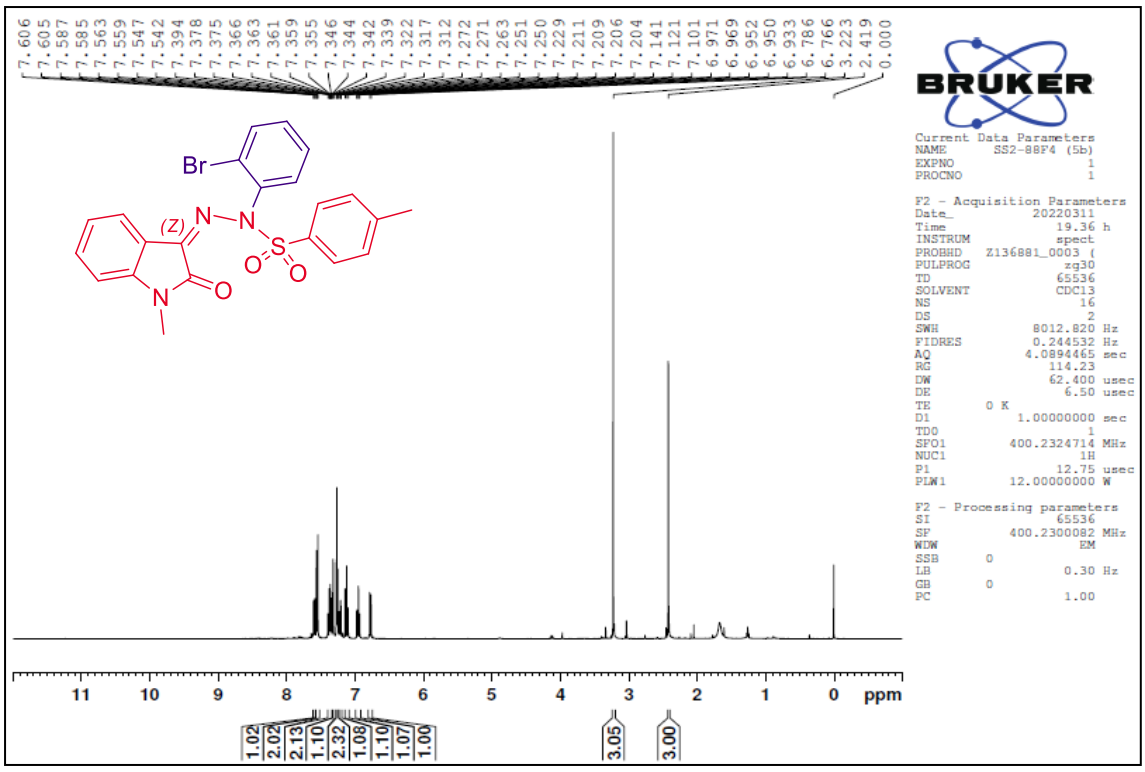


Figure 65.^{1}H NMR spectrum of compound **5b**

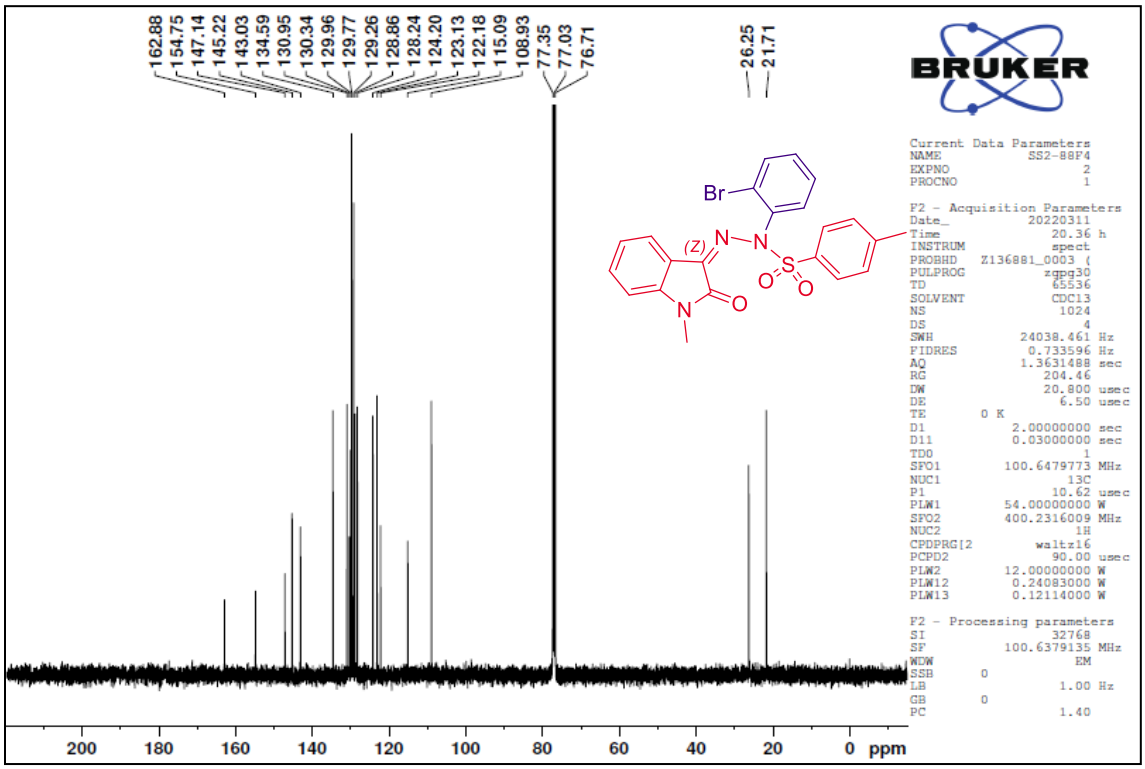


Figure 66. ^{13}C NMR spectrum of compound **5b**

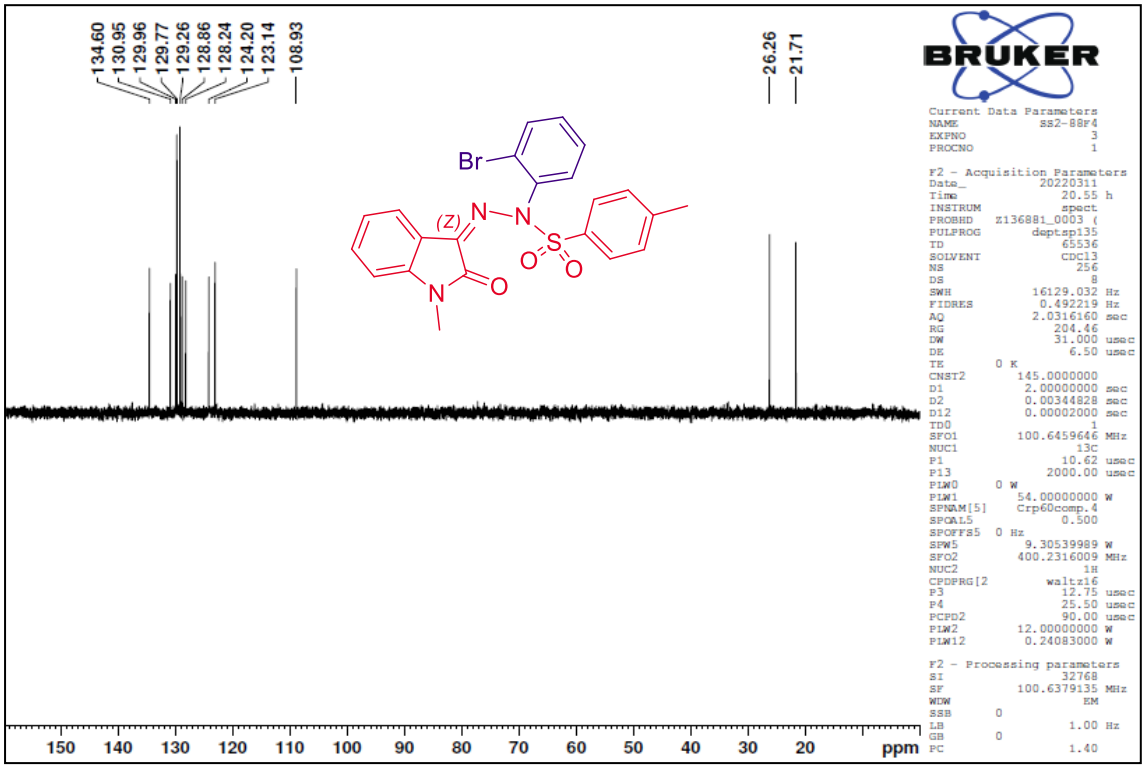


Figure 67.DEPT135 NMR spectrum of compound **5b**

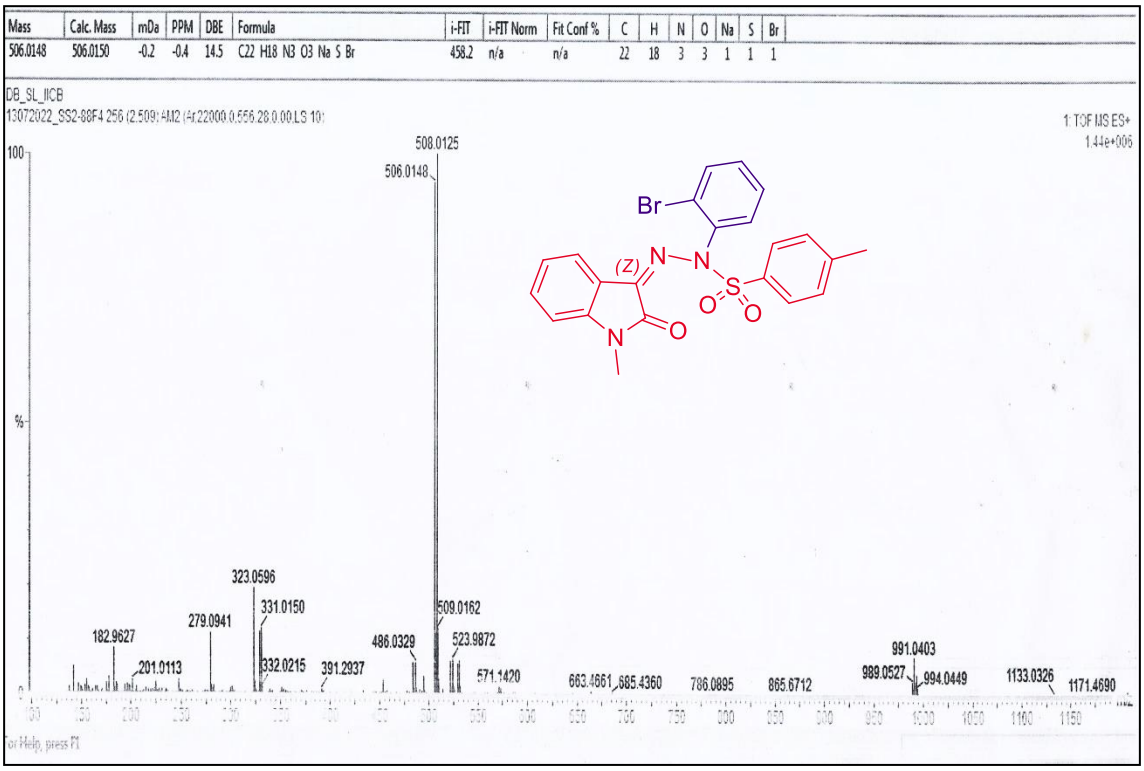


Figure 68.HRMS spectrum of compound **5b**

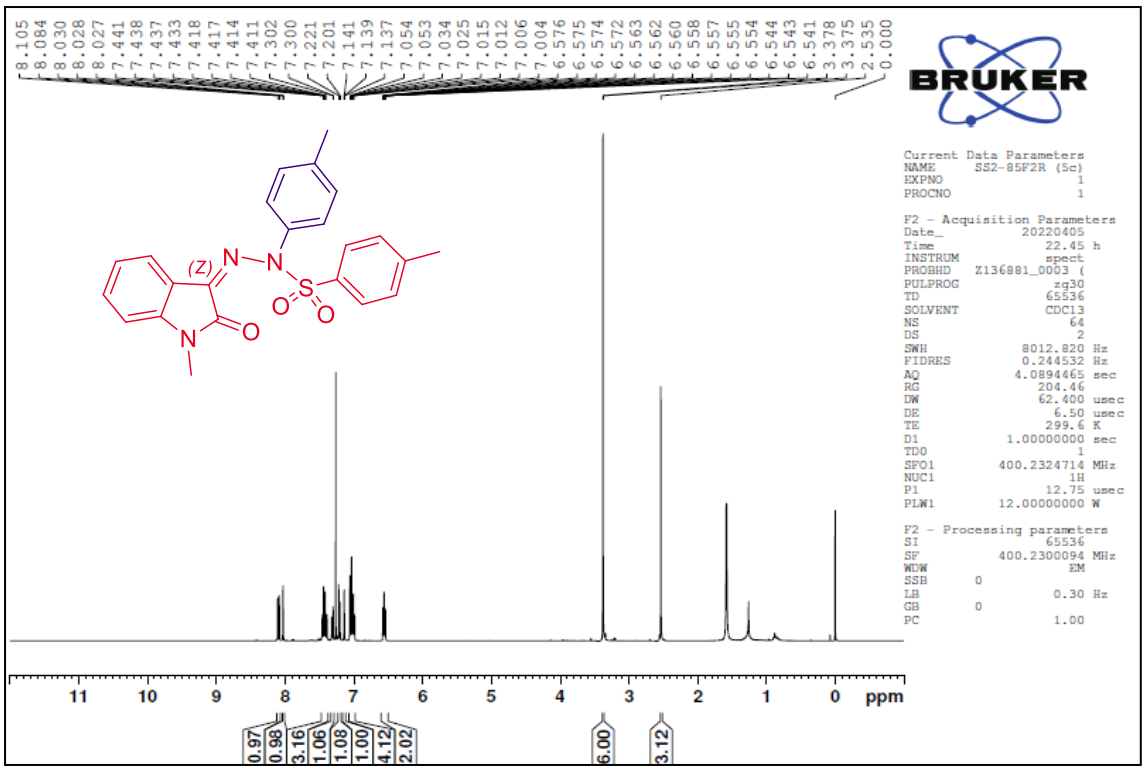


Figure 69.[1]H NMR spectrum of compound **5c**

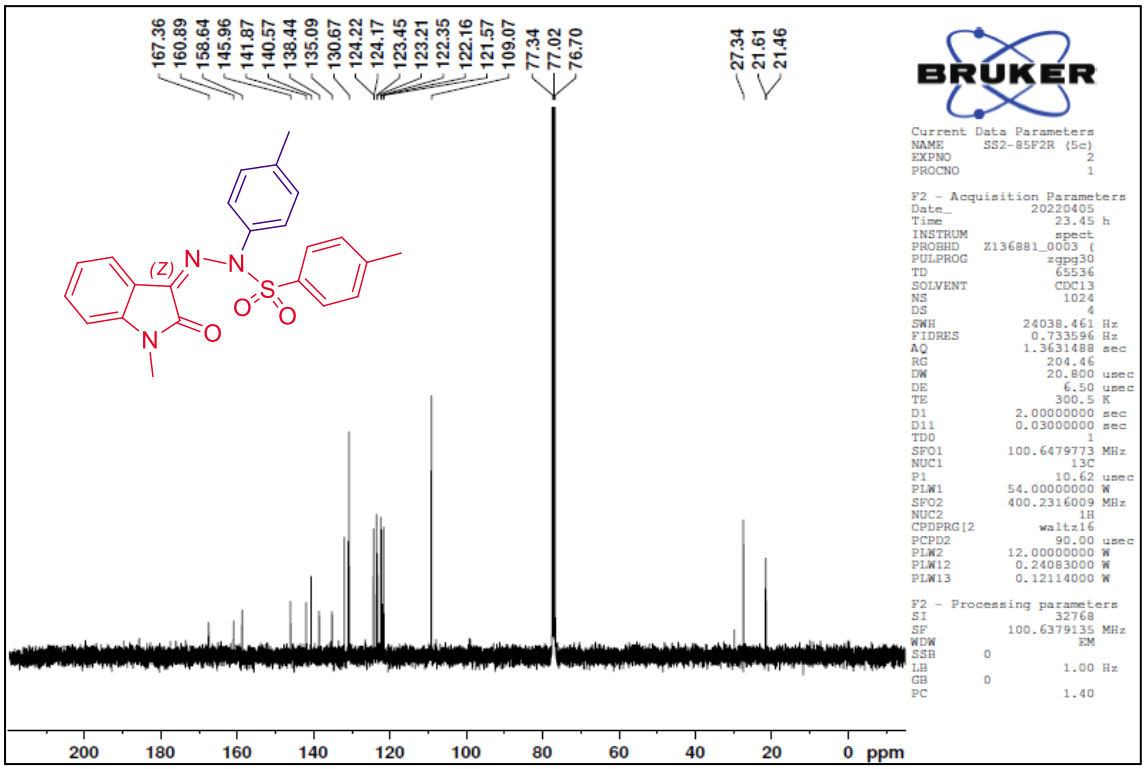


Figure 70.^{13}C NMR spectrum of compound **5c**

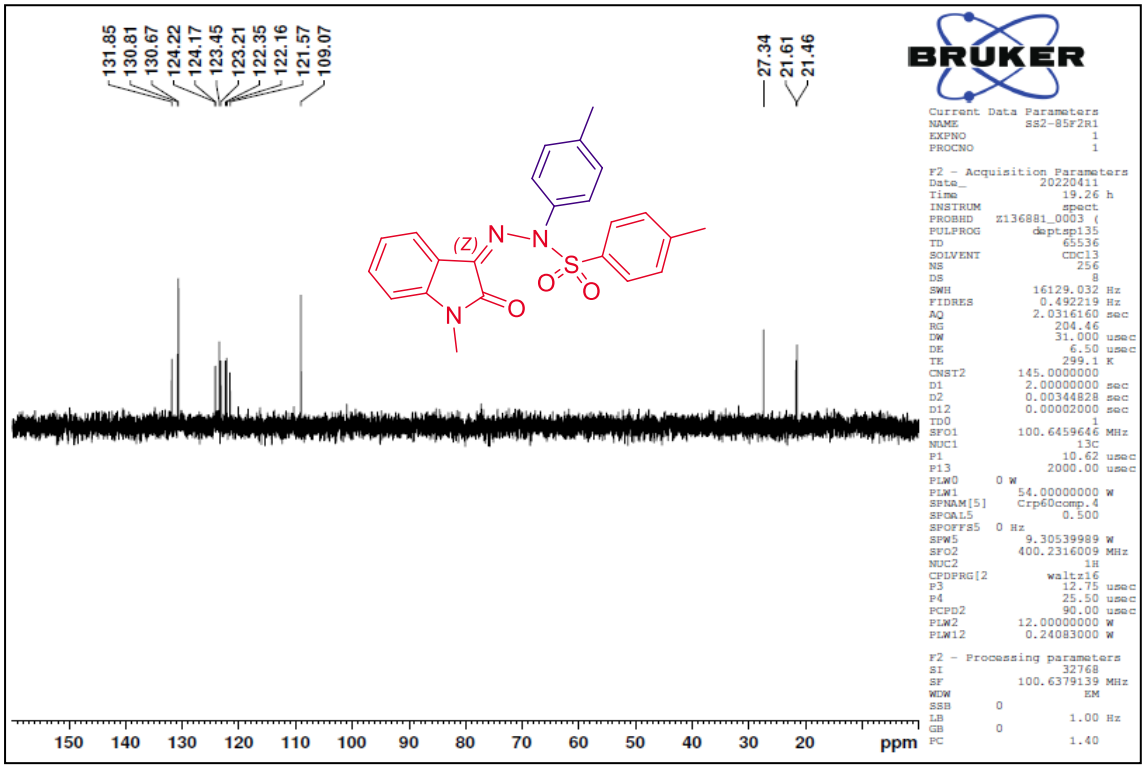


Figure 71.DEPT135 NMR spectrum of compound **5c**

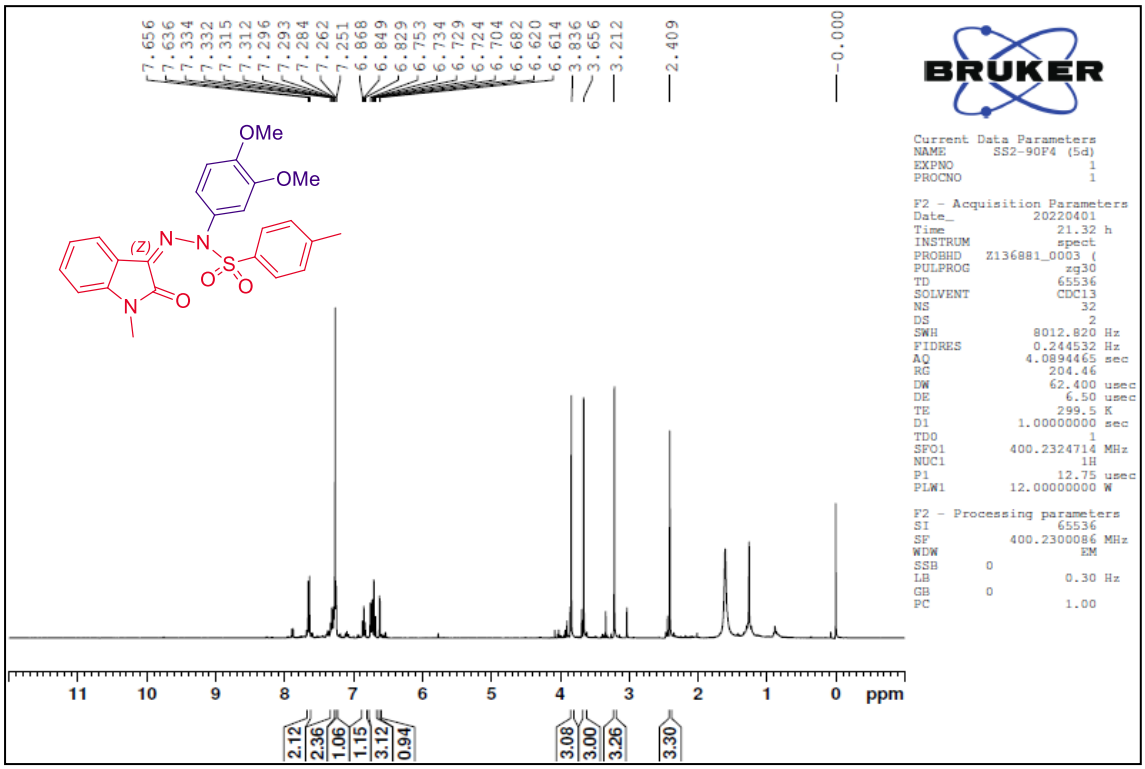


Figure 73. ^{1}H NMR spectrum of compound **5d**

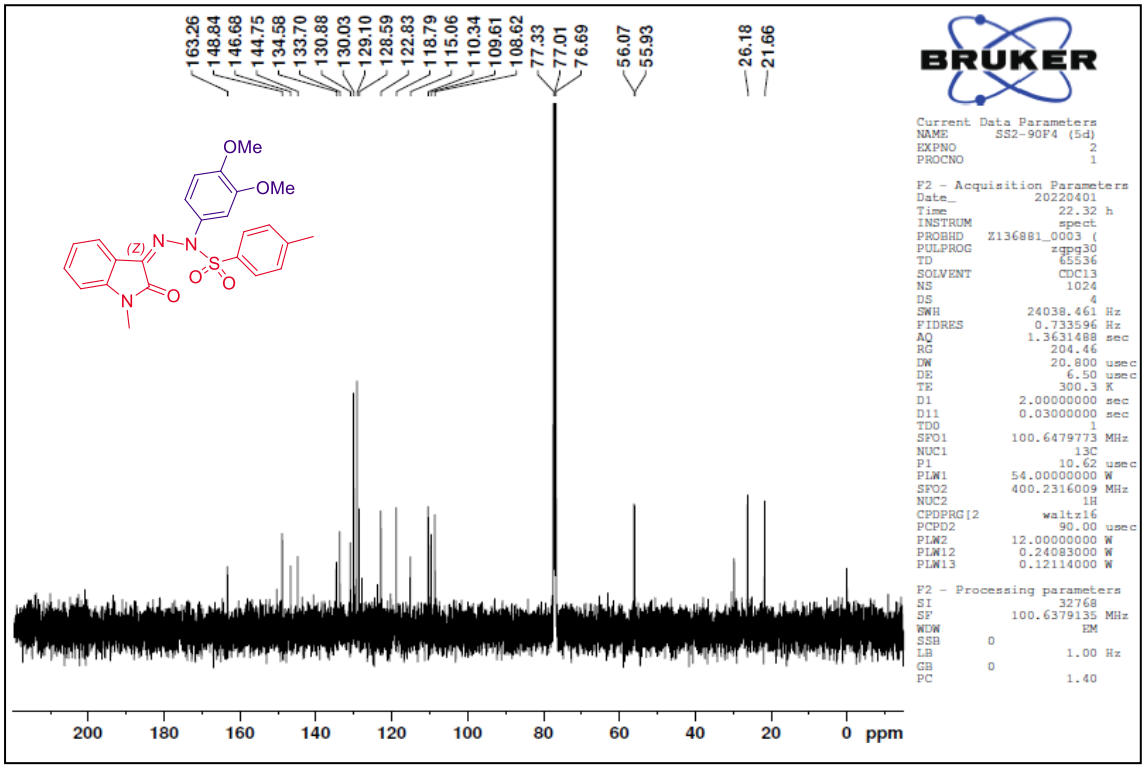


Figure 74. ^{13}C NMR spectrum of compound **5d**

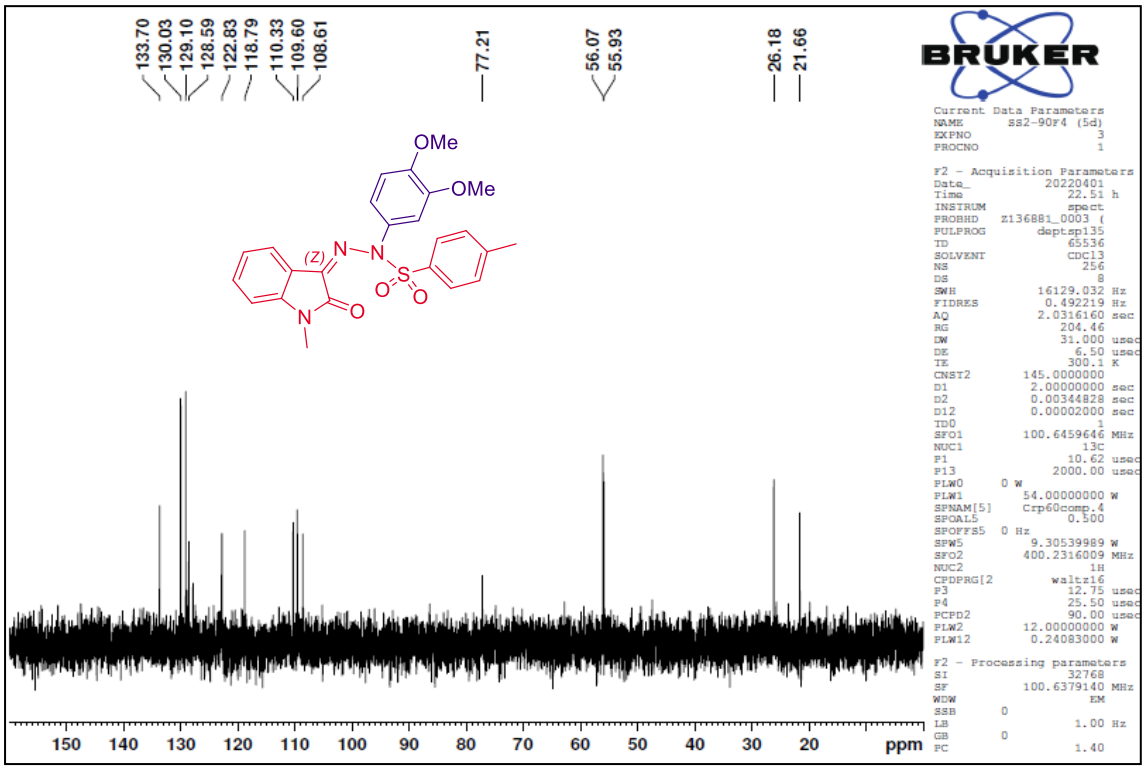


Figure 75.DEPT135 NMR spectrum of compound **5d**

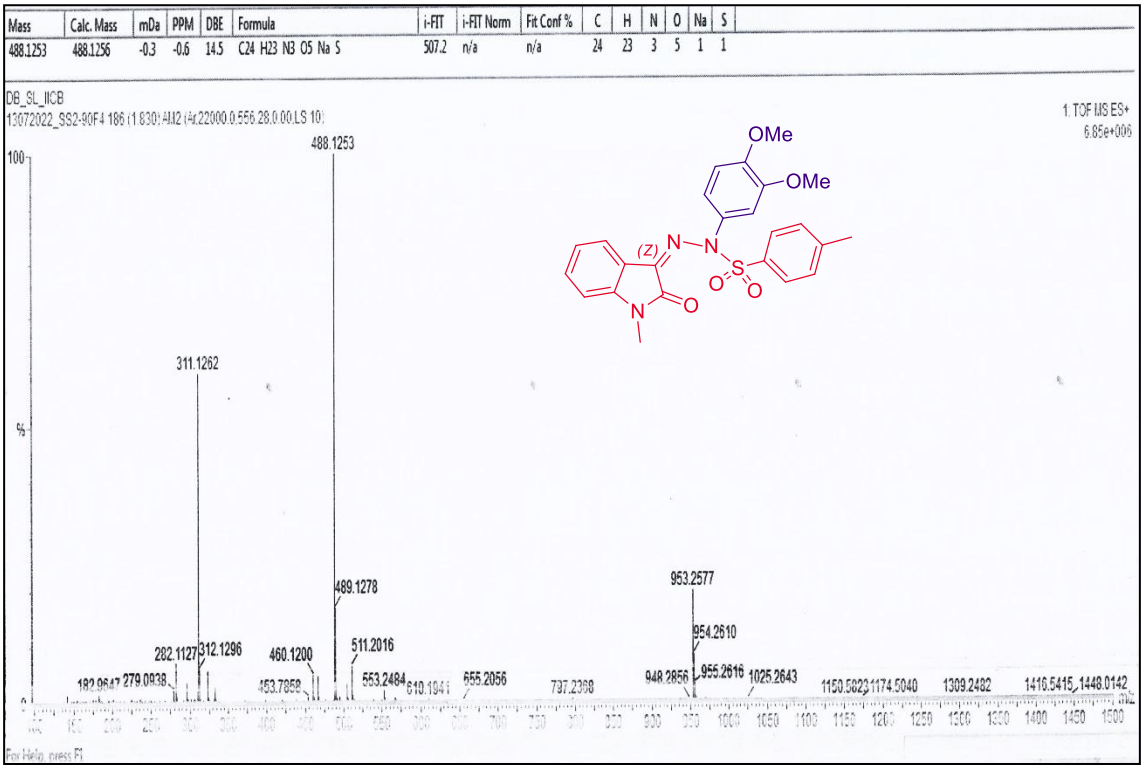


Figure 76.HRMS spectrum of compound **5d**

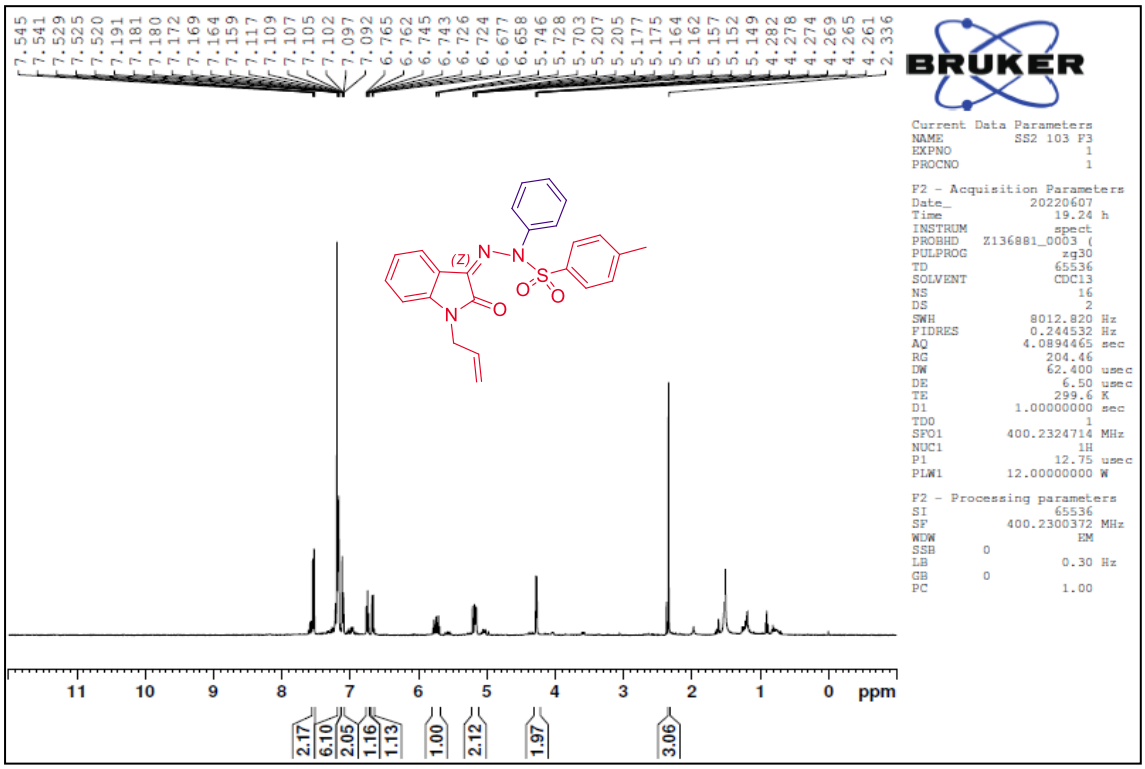


Figure 77. ^{1}H NMR spectrum of compound **5e**

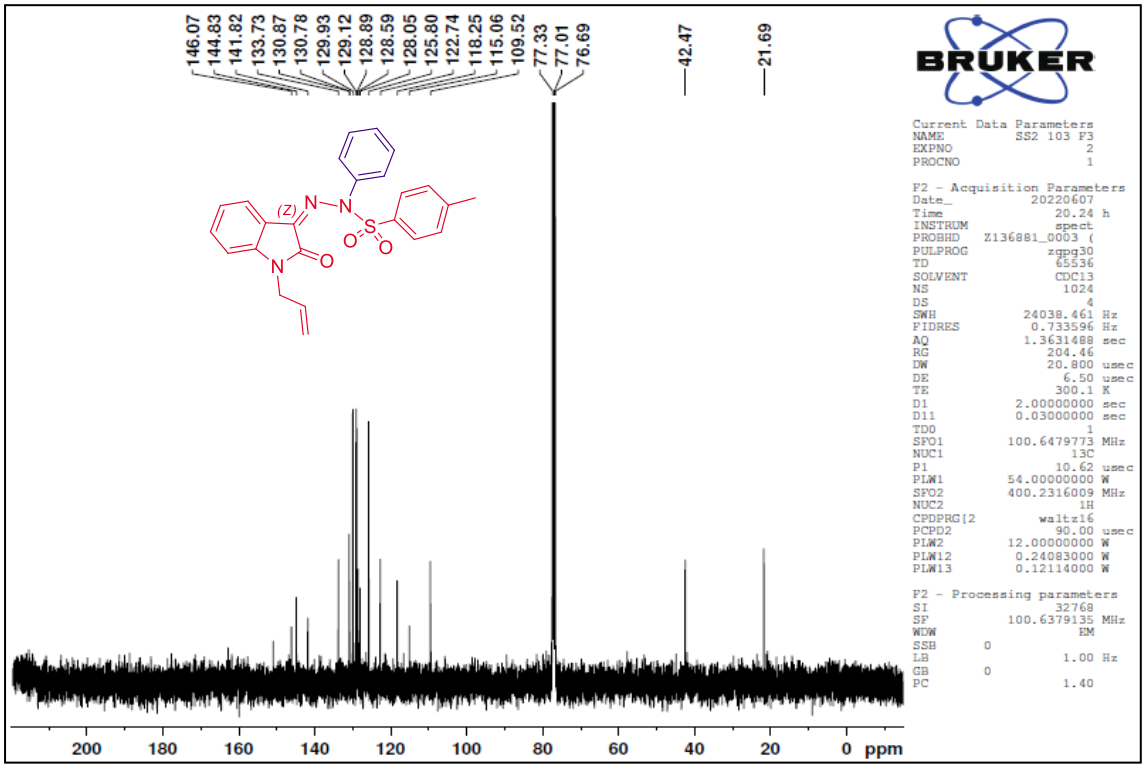


Figure 78. ^{13}C NMR spectrum of compound **5e**

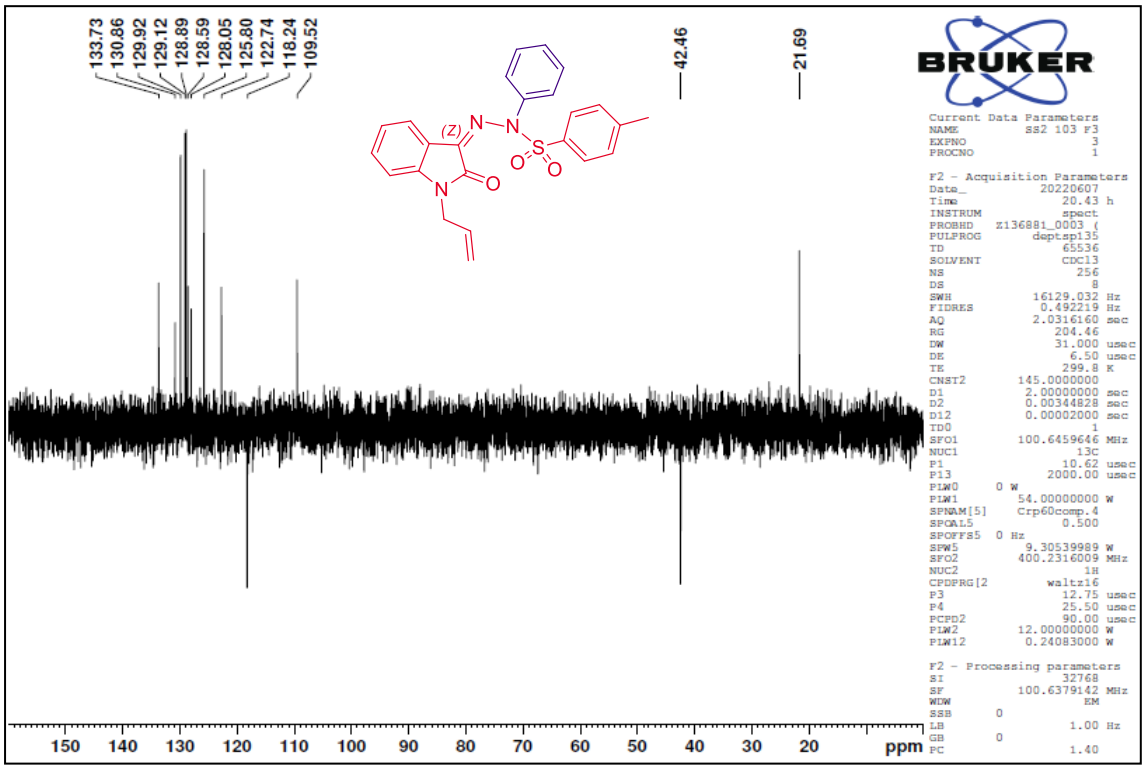


Figure 79.DEPT135 NMR spectrum of compound **5e**

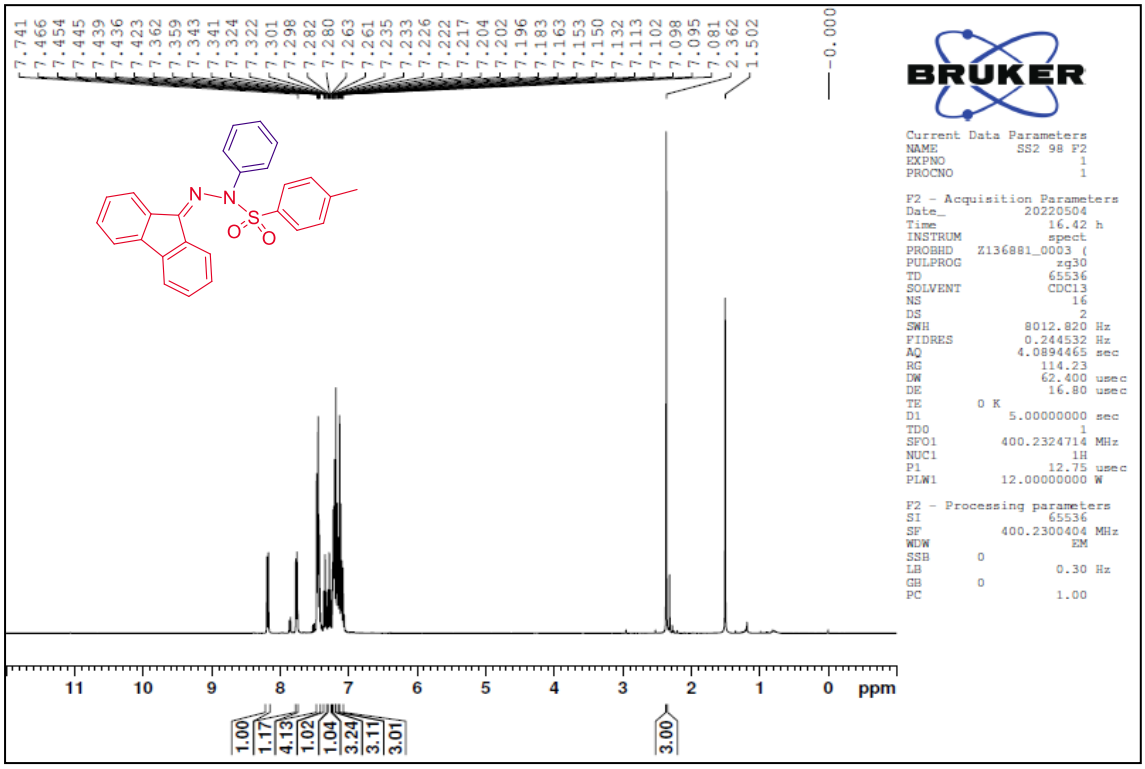


Figure 81.^{1}H NMR spectrum of compound**5f**

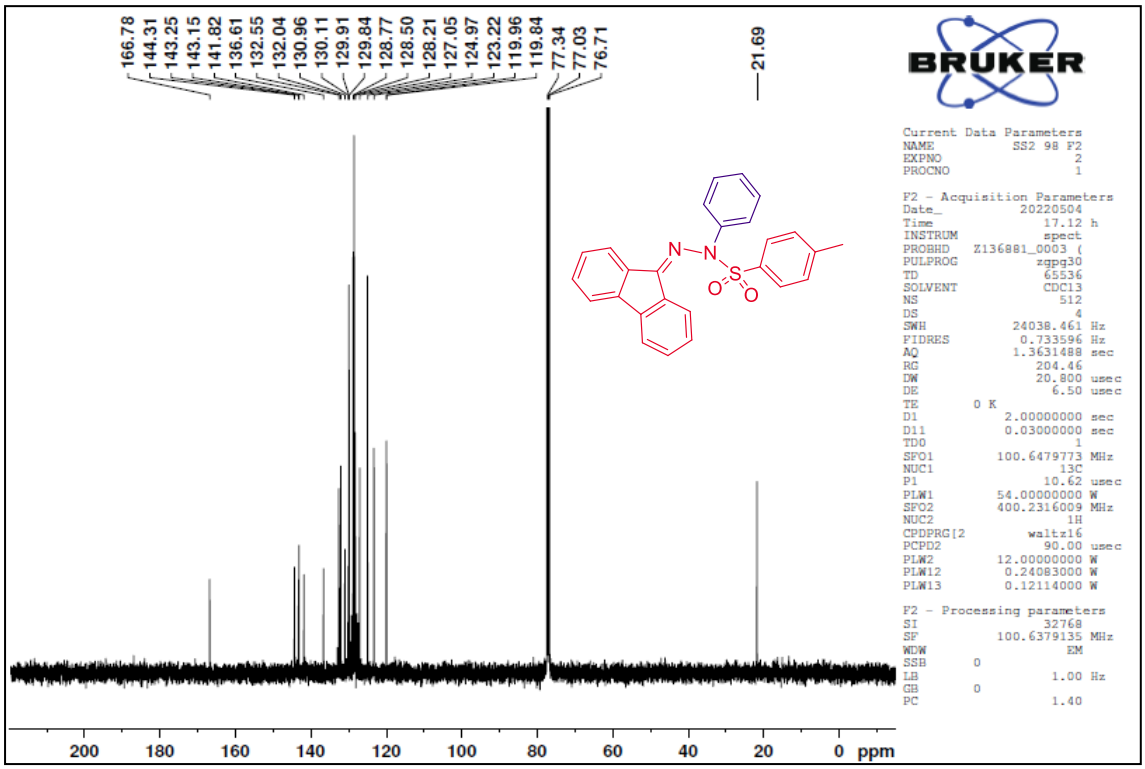


Figure 82. ^{13}C NMR spectrum of compound **5f**

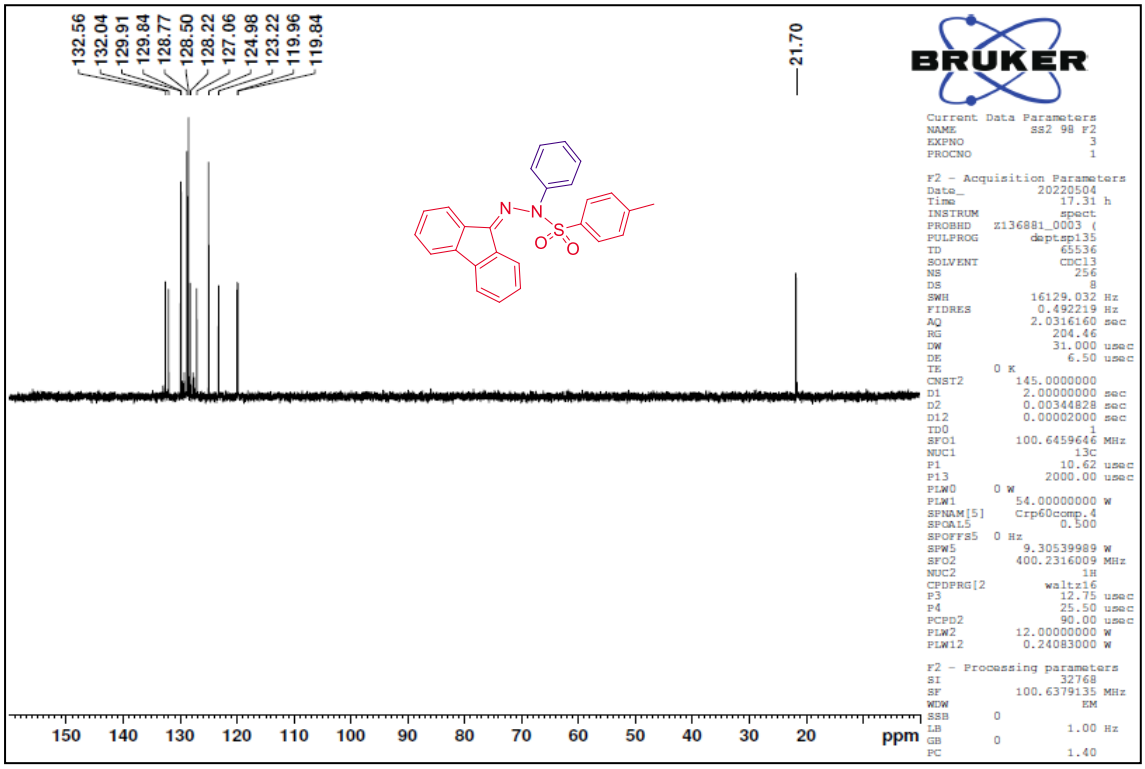


Figure 83. DEPT135 NMR spectrum of compound **5f**

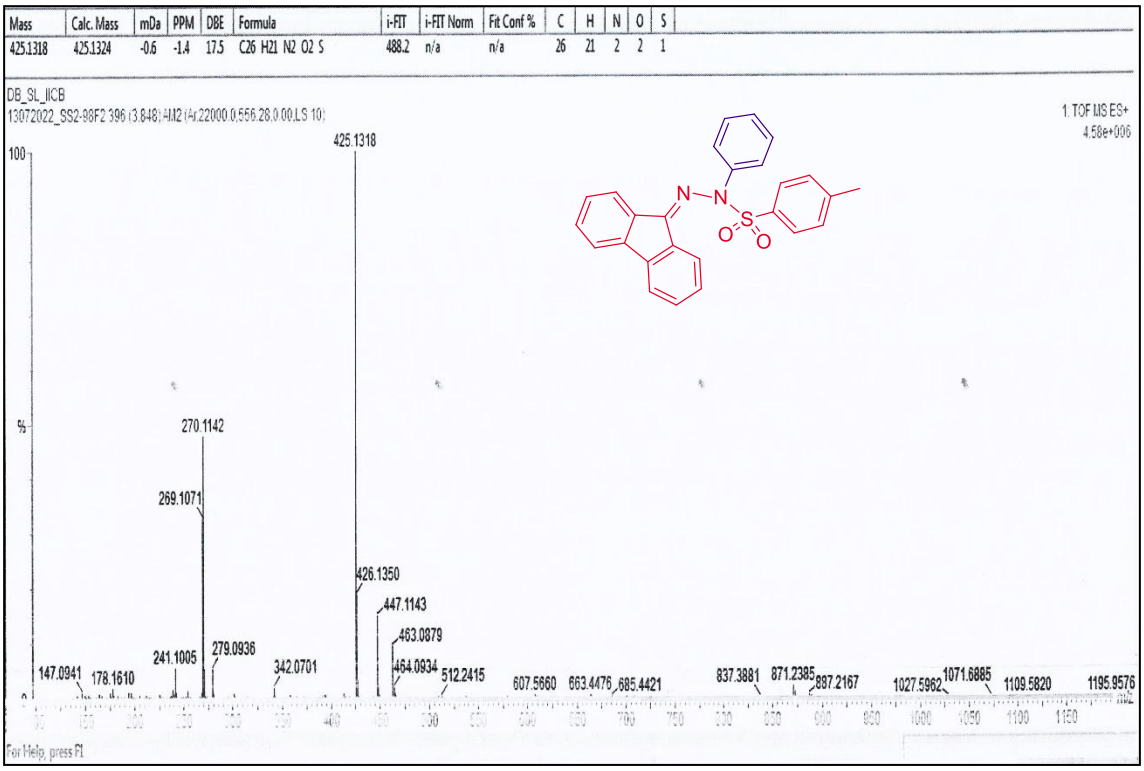
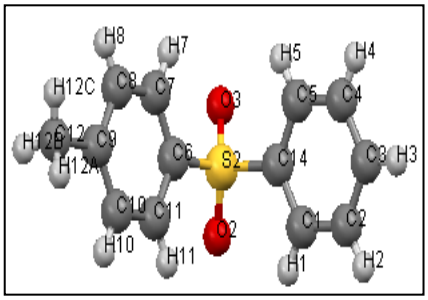


Figure 84.HRMS spectrum of compound **5f**

5.1 Crystallographic data of compound 3a



ORTEP diagram of compounds **3a** (CCDC-2179829)

Table 1. Sample and crystal data for 3a.

Identification code	3a	
Chemical formula	$C_{13}H_{12}O_2S$	
Formula weight	232.29 g/mol	
Temperature	300(2) K	
Wavelength	0.71073 Å	
Crystal size	0.050 x 0.140 x 0.180 mm	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 13.0543(13) Å	α = 90°
	b = 7.8336(8) Å	β = 95.968(3)°
	c = 11.5876(12) Å	γ = 90°
Volume	1178.6(2) $Å^3$	
Z	4	
Density (calculated)	1.309 g/cm^3	
Absorption coefficient	0.256 mm^{-1}	
F(000)	488	

Table 2. Data collection and structure refinement for 3a.

Theta range for data collection	3.04 to 28.36°	
Index ranges	-17<=h<=17, -10<=k<=10, -15<=l<=15	
Reflections collected	26064	
Independent reflections	2939 [R(int) = 0.0500]	
Max. and min. transmission	0.7457 and 0.6516	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	2939 / 0 / 146	
Goodness-of-fit on F^2	1.039	
Final R indices	1916 data; $I>2\sigma(I)$	R1 = 0.0524, wR2 = 0.0991
	all data	R1 = 0.0918, wR2 = 0.1198
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0293P)^2+0.7008P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.260 and -0.299 eÅ^{-3}	
R.M.S. deviation from mean	0.038 eÅ^{-3}	

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for 3a.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
S2	0.27013(4)	0.33249(8)	0.68056(5)	0.0618(2)
O2	0.26997(14)	0.3924(3)	0.79781(14)	0.0882(6)
O3	0.22698(13)	0.1681(2)	0.6495(2)	0.0929(7)

	x/a	y/b	z/c	U(eq)
C1	0.47206(17)	0.4222(3)	0.71525(19)	0.0569(6)
C2	0.57291(18)	0.4185(3)	0.6904(2)	0.0663(6)
C3	0.59901(18)	0.3292(3)	0.5966(2)	0.0640(6)
C4	0.5255(2)	0.2432(3)	0.5269(2)	0.0683(7)
C5	0.42445(18)	0.2435(3)	0.55074(19)	0.0604(6)
C6	0.20643(15)	0.4849(3)	0.58732(18)	0.0490(5)
C7	0.15909(18)	0.4370(3)	0.4805(2)	0.0654(6)
C8	0.10905(19)	0.5589(4)	0.4093(2)	0.0726(7)
C9	0.10575(16)	0.7271(3)	0.4420(2)	0.0617(6)
C10	0.15569(18)	0.7731(3)	0.5483(2)	0.0651(6)
C11	0.20576(17)	0.6536(3)	0.62077(19)	0.0587(6)
C12	0.0487(2)	0.8585(4)	0.3647(3)	0.0944(10)
C14	0.39851(15)	0.3330(2)	0.64603(17)	0.0450(5)

Table 4. Bond lengths (Å) for 3a.

S2-O3	1.4361(19)	S2-O2	1.4376(19)
S2-C6	1.760(2)	S2-C14	1.763(2)
C1-C14	1.376(3)	C1-C2	1.377(3)
C2-C3	1.365(3)	C3-C4	1.366(3)
C4-C5	1.376(3)	C5-C14	1.380(3)
C6-C7	1.377(3)	C6-C11	1.378(3)
C7-C8	1.381(3)	C8-C9	1.373(4)
C9-C10	1.380(3)	C9-C12	1.509(3)
C10-C11	1.376(3)		

Table 5. Bond angles (°) for 3a.

O3-S2-O2	119.36(13)	O3-S2-C6	107.84(11)
O2-S2-C6	108.16(11)	O3-S2-C14	107.62(11)
O2-S2-C14	107.98(10)	C6-S2-C14	105.00(9)
C14-C1-C2	119.5(2)	C3-C2-C1	120.0(2)
C2-C3-C4	120.4(2)	C3-C4-C5	120.7(2)
C4-C5-C14	118.8(2)	C7-C6-C11	119.9(2)
C7-C6-S2	120.43(18)	C11-C6-S2	119.64(17)
C6-C7-C8	119.3(2)	C9-C8-C7	121.7(2)
C8-C9-C10	118.1(2)	C8-C9-C12	121.3(3)
C10-C9-C12	120.6(3)	C11-C10-C9	121.1(2)
C10-C11-C6	119.8(2)	C1-C14-C5	120.7(2)
C1-C14-S2	119.41(16)	C5-C14-S2	119.91(16)

Table 6. Anisotropic atomic displacement parameters (Å^2) for 3a.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S2	0.0514(3)	0.0653(4)	0.0694(4)	0.0198(3)	0.0100(3)	0.0037(3)
O2	0.0790(12)	0.1337(17)	0.0552(10)	0.0260(11)	0.0221(9)	0.0295(12)
O3	0.0608(10)	0.0601(11)	0.1563(19)	0.0330(12)	0.0045(11)	-0.0117(9)
C1	0.0625(14)	0.0525(13)	0.0549(13)	-0.0083(10)	0.0015(10)	0.0043(11)
C2	0.0577(14)	0.0582(15)	0.0810(17)	-0.0028(13)	-0.0026(12)	-0.0066(11)
C3	0.0526(13)	0.0678(16)	0.0734(16)	0.0161(13)	0.0154(11)	0.0029(12)
C4	0.0763(17)	0.0788(18)	0.0519(14)	-0.0026(12)	0.0161(12)	0.0140(14)
C5	0.0648(14)	0.0621(15)	0.0521(13)	-0.0067(11)	-0.0044(11)	0.0015(11)
C6	0.0417(10)	0.0532(13)	0.0522(12)	0.0017(10)	0.0055(9)	0.0015(9)
C7	0.0648(14)	0.0575(14)	0.0717(16)	-0.0080(12)	-0.0036(12)	-0.0031(12)
C8	0.0624(15)	0.089(2)	0.0626(15)	-0.0014(14)	-0.0110(12)	-0.0014(14)
C9	0.0420(11)	0.0789(17)	0.0657(15)	0.0175(13)	0.0120(10)	0.0099(11)

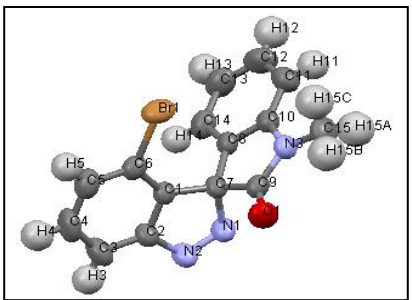
	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C10	0.0649(14)	0.0536(14)	0.0781(17)	-0.0009(12)	0.0138(12)	0.0118(12)
C11	0.0582(13)	0.0645(15)	0.0529(13)	-0.0080(11)	0.0027(10)	0.0056(11)
C12	0.0670(16)	0.118(3)	0.100(2)	0.0490(19)	0.0189(15)	0.0313(17)
C14	0.0486(11)	0.0417(11)	0.0443(11)	0.0061(9)	0.0029(8)	0.0027(9)

Table 7. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for 3a.

	x/a	y/b	z/c	U(eq)
H1	0.4538	0.4845	0.7783	0.068000
H2	0.6233	0.4768	0.7375	0.080000
H3	0.6672	0.3268	0.5801	0.077000
H4	0.5440	0.1839	0.4627	0.082000
H5	0.3745	0.1844	0.5035	0.072000
H7	0.1608	0.3238	0.4565	0.078000
H8	0.0767	0.5262	0.3374	0.087000
H10	0.1555	0.8868	0.5714	0.078000
H11	0.2391	0.6867	0.6921	0.070000
H12A	0.0864	0.9639	0.3696	0.142000
H12B	-0.0184	0.8767	0.3895	0.142000
H12C	0.0417	0.8185	0.2860	0.142000

Symmetry transformations used to generate equivalent atoms:

5.2 Crystallographic data of



compound 4b

ORTEP diagram of compounds **4b** (CCDC-2179825)

Table 1. Sample and crystal data for 4b.

Identification code	4b	
Chemical formula	$C_{15}H_{10}BrN_3O$	
Formula weight	328.17 g/mol	
Temperature	300(2) K	
Wavelength	0.71073 Å	
Crystal size	0.070 x 0.110 x 0.150 mm	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 12.2098(8) Å	α = 90°
	b = 8.7386(6) Å	β = 108.433(2)°
	c = 13.4142(9) Å	γ = 90°
Volume	1357.82(16) $Å^3$	
Z	4	
Density (calculated)	1.605 g/cm^3	
Absorption coefficient	3.025 mm^{-1}	
F(000)	656	

Table 2. Data collection and structure refinement for 4b.

Theta range for data collection	1.97 to 27.12°
Index ranges	-15<=h<=14, -11<=k<=11, -14<=l<=17
Reflections collected	23806
Independent reflections	2977 [R(int) = 0.0518]

Max. and min. transmission	0.8160 and 0.6600	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	2977 / 0 / 182	
Goodness-of-fit on F^2	1.021	
Δ/σ_{max}	0.001	
Final R indices	2025 data; $I>2\sigma(I)$	R1 = 0.0453, wR2 = 0.1039
	all data	R1 = 0.0810, wR2 = 0.1172
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0591P)^2+0.4927P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.651 and -0.441 eÅ^{-3}	
R.M.S. deviation from mean	0.071 eÅ^{-3}	

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for 4b.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
Br1	0.71105(3)	0.51711(4)	0.41938(3)	0.06601(19)
O1	0.6294(2)	0.2080(3)	0.1790(2)	0.0694(7)
N1	0.3833(2)	0.2922(3)	0.1584(2)	0.0547(7)
N2	0.3503(2)	0.2141(3)	0.2224(2)	0.0568(7)
N3	0.6232(2)	0.4610(3)	0.1321(2)	0.0515(7)
C1	0.5107(2)	0.3401(3)	0.3273(2)	0.0411(7)
C2	0.4244(3)	0.2369(3)	0.3271(2)	0.0484(8)
C3	0.4163(3)	0.1734(4)	0.4183(3)	0.0649(10)
C4	0.4993(3)	0.2153(6)	0.5109(3)	0.0712(12)

	x/a	y/b	z/c	U(eq)
C5	0.5878(3)	0.3159(4)	0.5121(3)	0.0626(9)
C6	0.5923(3)	0.3793(3)	0.4196(2)	0.0464(7)
C7	0.4899(2)	0.3838(4)	0.2155(2)	0.0436(7)
C8	0.4760(3)	0.5508(4)	0.1872(2)	0.0428(7)
C9	0.5901(3)	0.3347(4)	0.1738(2)	0.0487(8)
C10	0.5568(3)	0.5904(4)	0.1397(2)	0.0477(8)
C11	0.5662(3)	0.7381(4)	0.1079(3)	0.0643(10)
C12	0.4918(4)	0.8459(4)	0.1265(3)	0.0787(12)
C13	0.4116(4)	0.8071(4)	0.1737(3)	0.0704(11)
C14	0.4026(3)	0.6586(4)	0.2048(3)	0.0568(9)
C15	0.7229(4)	0.4646(5)	0.0961(3)	0.0736(11)

Table 4. Bond lengths (Å) for 4b.

Br1-C6	1.886(3)	O1-C9	1.199(4)
N1-N2	1.259(3)	N1-C7	1.513(4)
N2-C2	1.423(4)	N3-C9	1.356(4)
N3-C10	1.413(4)	N3-C15	1.445(4)
C1-C6	1.365(4)	C1-C2	1.387(4)
C1-C7	1.489(4)	C2-C3	1.375(4)
C3-C4	1.381(5)	C4-C5	1.389(5)
C5-C6	1.376(4)	C7-C8	1.504(4)

C7-C9	1.558(4)	C8-C14	1.371(4)
C8-C10	1.378(4)	C10-C11	1.375(5)
C11-C12	1.385(6)	C12-C13	1.366(6)
C13-C14	1.378(5)		

Table 5. Bond angles (°) for 4b.

N2-N1-C7	110.5(2)	N1-N2-C2	110.9(2)
C9-N3-C10	111.7(3)	C9-N3-C15	123.2(3)
C10-N3-C15	124.7(3)	C6-C1-C2	120.1(3)
C6-C1-C7	133.8(3)	C2-C1-C7	106.1(3)
C3-C2-C1	121.9(3)	C3-C2-N2	128.3(3)
C1-C2-N2	109.8(3)	C2-C3-C4	117.0(3)
C3-C4-C5	121.7(3)	C6-C5-C4	119.8(3)
C1-C6-C5	119.4(3)	C1-C6-Br1	120.0(2)
C5-C6-Br1	120.6(3)	C1-C7-C8	118.2(2)
C1-C7-N1	102.7(2)	C8-C7-N1	112.1(2)
C1-C7-C9	112.8(3)	C8-C7-C9	102.4(2)
N1-C7-C9	108.6(2)	C14-C8-C10	120.7(3)
C14-C8-C7	130.6(3)	C10-C8-C7	108.7(3)
O1-C9-N3	127.6(3)	O1-C9-C7	125.3(3)
N3-C9-C7	107.1(3)	C11-C10-C8	121.4(3)
C11-C10-N3	128.5(3)	C8-C10-N3	110.1(3)
C10-C11-C12	117.3(4)	C13-C12-C11	121.4(4)
C12-C13-C14	120.8(4)	C8-C14-C13	118.4(3)

Table 6. Anisotropic atomic displacement parameters ($Å^2$) for4b.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

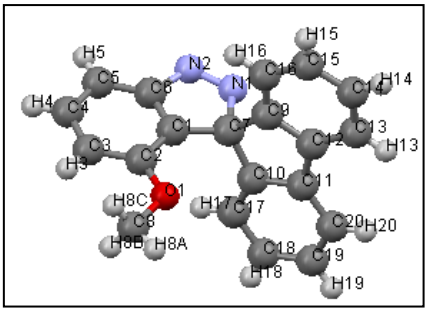
	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	0.0444(2)	0.0652(3)	0.0784(3)	-0.01519(17)	0.0050(2)	-0.00667(15)
O1	0.0804(18)	0.0526(15)	0.0871(19)	-0.0042(13)	0.0434(15)	0.0084(13)
N1	0.0492(16)	0.0686(18)	0.0424(16)	-0.0030(14)	0.0091(13)	-0.0145(14)
N2	0.0498(16)	0.0680(18)	0.0502(18)	0.0028(14)	0.0123(14)	-0.0160(14)
N3	0.0501(17)	0.0585(17)	0.0544(17)	-0.0051(13)	0.0287(14)	-0.0071(13)
C1	0.0379(16)	0.0478(17)	0.0384(17)	0.0011(13)	0.0130(14)	0.0031(13)
C2	0.0416(17)	0.0559(19)	0.048(2)	0.0049(15)	0.0150(15)	-0.0022(14)
C3	0.059(2)	0.077(3)	0.061(2)	0.0225(19)	0.022(2)	-0.0030(18)
C4	0.078(3)	0.093(3)	0.046(2)	0.0244(19)	0.025(2)	0.019(2)
C5	0.062(2)	0.078(2)	0.044(2)	0.0032(18)	0.0112(18)	0.016(2)
C6	0.0404(17)	0.0508(17)	0.0448(19)	-0.0034(15)	0.0089(15)	0.0093(14)
C7	0.0395(17)	0.0524(18)	0.0404(18)	-0.0008(14)	0.0148(14)	-0.0064(13)
C8	0.0441(18)	0.0505(17)	0.0320(16)	0.0004(13)	0.0096(14)	0.0000(14)
C9	0.0476(19)	0.056(2)	0.0445(19)	-0.0090(15)	0.0174(15)	-0.0041(16)
C10	0.0501(19)	0.0516(19)	0.0396(18)	-0.0011(14)	0.0116(15)	-0.0053(15)
C11	0.071(2)	0.062(2)	0.061(2)	0.0097(18)	0.021(2)	-0.0090(19)
C12	0.101(3)	0.050(2)	0.071(3)	0.0100(19)	0.007(2)	0.000(2)
C13	0.082(3)	0.062(2)	0.060(2)	0.0029(19)	0.012(2)	0.023(2)
C14	0.052(2)	0.071(2)	0.0433(19)	0.0014(16)	0.0092(16)	0.0128(17)
C15	0.066(3)	0.089(3)	0.080(3)	-0.005(2)	0.045(2)	-0.005(2)

Table 7. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for 4b.

	x/a	y/b	z/c	U(eq)
H3	0.3576	0.1052	0.4176	0.078000
H4	0.4958	0.1751	0.5740	0.085000
H5	0.6438	0.3404	0.5752	0.075000
H11	0.6202	0.7645	0.0751	0.077000
H12	0.4966	0.9470	0.1065	0.094000
H13	0.3625	0.8817	0.1849	0.085000
H14	0.3481	0.6322	0.2370	0.068000
H15A	0.6993	0.4926	0.0231	0.110000
H15B	0.7583	0.3653	0.1048	0.110000
H15C	0.7773	0.5384	0.1363	0.110000

Symmetry transformations used to generate equivalent atoms:

5.3 Crystallographic data of compound 4f



ORTEP diagram of compounds **4f** (CCDC-2179832)

Table 1. Sample and crystal data for 4f.

Identification code	4f	
Chemical formula	$C_{20}H_{14}N_2O$	
Formula weight	298.33 g/mol	
Temperature	300(2) K	
Wavelength	0.71073 Å	
Crystal size	0.100 x 0.190 x 0.230 mm	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 8.7215(4) Å	α = 90°
	b = 8.0965(4) Å	β = 98.010(2)°
	c = 21.5872(11) Å	γ = 90°
Volume	1509.48(13) $Å^3$	
Z	4	
Density (calculated)	1.313 g/cm^3	
Absorption coefficient	0.082 mm^{-1}	
F(000)	624	

Table 2. Data collection and structure refinement for 4f.

Theta range for data collection	1.91 to 28.20°	
Index ranges	-11<=h<=11, -10<=k<=8, -28<=l<=28	
Reflections collected	19671	
Independent reflections	3694 [R(int) = 0.0432]	
Max. and min. transmission	0.9920 and 0.9810	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	3694 / 0 / 209	
Goodness-of-fit on F^2	1.031	
Final R indices	2342 data; $I>2\sigma(I)$	R1 = 0.0495, wR2 = 0.1136
	all data	R1 = 0.0914, wR2 = 0.1405
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0585P)^2+0.3359P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.163 and -0.159 eÅ^{-3}	
R.M.S. deviation from mean	0.037 eÅ^{-3}	

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for 4f.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
O1	0.45954(13)	0.49932(13)	0.36249(6)	0.0536(3)
N1	0.65524(15)	0.99881(16)	0.39988(6)	0.0478(4)
N2	0.75385(16)	0.94521(18)	0.44315(7)	0.0519(4)
C1	0.61821(17)	0.71315(19)	0.40625(7)	0.0395(4)

	x/a	y/b	z/c	U(eq)
C2	0.57753(18)	0.54790(19)	0.40609(7)	0.0424(4)
C3	0.6611(2)	0.4446(2)	0.45008(8)	0.0546(5)
C4	0.7797(2)	0.5063(2)	0.49311(9)	0.0635(5)
C5	0.8206(2)	0.6701(2)	0.49437(8)	0.0608(5)
C6	0.73663(18)	0.7701(2)	0.45011(7)	0.0457(4)
C7	0.55520(17)	0.85754(18)	0.36848(7)	0.0401(4)
C8	0.4154(2)	0.3293(2)	0.36201(11)	0.0676(6)
C9	0.57317(18)	0.87072(18)	0.29948(7)	0.0418(4)
C10	0.38610(17)	0.90346(18)	0.36767(7)	0.0397(4)
C11	0.32315(18)	0.95793(19)	0.30806(7)	0.0425(4)
C12	0.44122(18)	0.94345(19)	0.26636(7)	0.0433(4)
C13	0.4395(2)	0.9869(2)	0.20388(8)	0.0562(5)
C14	0.5670(2)	0.9500(3)	0.17508(9)	0.0688(6)
C15	0.6935(2)	0.8718(3)	0.20733(10)	0.0706(6)
C16	0.7002(2)	0.8334(2)	0.27056(9)	0.0562(5)
C17	0.2992(2)	0.9004(2)	0.41606(8)	0.0503(4)
C18	0.1461(2)	0.9515(2)	0.40466(9)	0.0589(5)
C19	0.0831(2)	0.0054(2)	0.34611(10)	0.0588(5)
C20	0.1698(2)	0.0100(2)	0.29737(9)	0.0529(5)

Table 4. Bond lengths (Å) for 4f.

O1-C2	1.3526(19)	O1-C8	1.429(2)
N1-N2	1.2556(18)	N1-C7	1.5377(19)
N2-C6	1.436(2)	C1-C6	1.380(2)
C1-C2	1.384(2)	C1-C7	1.486(2)
C2-C3	1.393(2)	C3-C4	1.384(3)
C4-C5	1.373(3)	C5-C6	1.382(2)

C7-C10	1.519(2)	C7-C9	1.523(2)
C9-C16	1.379(2)	C9-C12	1.397(2)
C10-C17	1.374(2)	C10-C11	1.398(2)
C11-C20	1.390(2)	C11-C12	1.464(2)
C12-C13	1.392(2)	C13-C14	1.380(3)
C14-C15	1.375(3)	C15-C16	1.393(3)
C17-C18	1.387(2)	C18-C19	1.377(3)
C19-C20	1.379(3)		

Table 5. Bond angles (°) for 4f.

C2-O1-C8	117.60(13)	N2-N1-C7	111.02(12)
N1-N2-C6	110.38(13)	C6-C1-C2	119.48(14)
C6-C1-C7	107.32(14)	C2-C1-C7	133.15(14)
O1-C2-C1	116.92(13)	O1-C2-C3	125.09(15)
C1-C2-C3	117.99(15)	C4-C3-C2	120.79(17)
C5-C4-C3	122.02(16)	C4-C5-C6	116.17(17)
C1-C6-C5	123.54(16)	C1-C6-N2	109.73(13)
C5-C6-N2	126.70(15)	C1-C7-C10	118.89(13)
C1-C7-C9	120.74(13)	C10-C7-C9	101.75(12)
C1-C7-N1	101.51(11)	C10-C7-N1	108.27(12)
C9-C7-N1	104.45(12)	C16-C9-C12	121.13(16)
C16-C9-C7	128.77(15)	C12-C9-C7	109.89(14)
C17-C10-C11	121.19(15)	C17-C10-C7	128.67(14)
C11-C10-C7	110.12(14)	C20-C11-C10	119.57(16)
C20-C11-C12	131.69(15)	C10-C11-C12	108.72(13)
C13-C12-C9	119.94(16)	C13-C12-C11	131.45(15)
C9-C12-C11	108.60(13)	C14-C13-C12	118.76(17)
C15-C14-C13	120.80(18)	C14-C15-C16	121.31(19)
C9-C16-C15	117.94(18)	C10-C17-C18	118.67(16)

C19-C18-C17	120.55(18)	C18-C19-C20	121.18(17)
C19-C20-C11	118.84(17)		

Table 6. Anisotropic atomic displacement parameters (Å^2) for 4f.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	0.0552(7)	0.0315(6)	0.0700(8)	0.0039(5)	-0.0062(6)	-0.0034(5)
N1	0.0488(8)	0.0386(8)	0.0538(8)	-0.0028(6)	-0.0008(7)	-0.0014(6)
N2	0.0507(8)	0.0479(9)	0.0544(9)	-0.0057(7)	-0.0026(7)	-0.0004(7)
C1	0.0405(8)	0.0363(9)	0.0411(8)	0.0018(6)	0.0041(6)	0.0042(7)
C2	0.0443(9)	0.0358(9)	0.0476(9)	0.0030(7)	0.0085(7)	0.0050(7)
C3	0.0629(11)	0.0407(10)	0.0603(11)	0.0126(8)	0.0083(9)	0.0085(8)
C4	0.0697(12)	0.0602(13)	0.0571(11)	0.0161(9)	-0.0038(9)	0.0178(10)
C5	0.0601(11)	0.0637(13)	0.0533(10)	0.0018(9)	-0.0107(8)	0.0111(9)
C6	0.0461(9)	0.0440(10)	0.0458(9)	-0.0015(7)	0.0021(7)	0.0053(7)
C7	0.0418(8)	0.0306(8)	0.0463(9)	0.0017(6)	0.0007(7)	-0.0003(6)
C8	0.0592(11)	0.0342(10)	0.1073(16)	0.0053(10)	0.0038(11)	-0.0059(8)
C9	0.0455(9)	0.0311(8)	0.0486(9)	0.0019(7)	0.0057(7)	-0.0052(7)
C10	0.0431(8)	0.0287(8)	0.0463(9)	-0.0008(6)	0.0022(7)	0.0003(6)
C11	0.0449(9)	0.0320(8)	0.0484(9)	-0.0011(7)	-0.0015(7)	-0.0035(7)
C12	0.0491(9)	0.0346(8)	0.0442(9)	0.0008(7)	-0.0001(7)	-0.0069(7)
C13	0.0584(11)	0.0582(12)	0.0489(10)	0.0084(8)	-0.0032(9)	-0.0119(9)
C14	0.0756(14)	0.0804(15)	0.0512(11)	0.0083(10)	0.0116(10)	-0.0193(11)
C15	0.0696(13)	0.0796(15)	0.0683(13)	0.0019(11)	0.0295(11)	-0.0089(11)
C16	0.0502(10)	0.0523(11)	0.0672(12)	0.0049(9)	0.0125(9)	-0.0027(8)
C17	0.0541(10)	0.0466(10)	0.0503(10)	0.0009(8)	0.0076(8)	0.0027(8)
C18	0.0526(11)	0.0578(12)	0.0686(12)	-0.0082(9)	0.0168(9)	-0.0004(9)
C19	0.0417(9)	0.0550(12)	0.0779(13)	-0.0108(10)	0.0024(9)	0.0041(8)

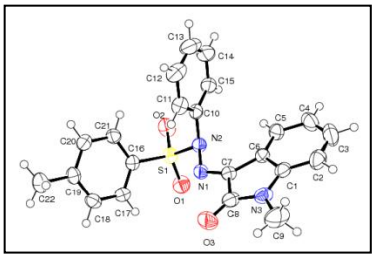
	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C20	0.0483(9)	0.0454(10)	0.0607(11)	-0.0008(8)	-0.0081(8)	0.0013(8)

Table 7. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for 4f.

	x/a	y/b	z/c	U(eq)
H3	0.6369	0.3327	0.4505	0.066000
H4	0.8333	0.4346	0.5221	0.076000
H5	0.9003	0.7114	0.5233	0.073000
H8A	0.3365	0.3090	0.3272	0.101000
H8B	0.3760	0.3033	0.4002	0.101000
H8C	0.5039	0.2614	0.3583	0.101000
H13	0.3540	1.0398	0.1819	0.067000
H14	0.5673	0.9784	0.1334	0.083000
H15	0.7764	0.8439	0.1865	0.085000
H16	0.7876	0.7842	0.2926	0.067000
H17	0.3422	0.8649	0.4557	0.060000
H18	0.0854	0.9492	0.4368	0.071000
H19	-0.0198	1.0393	0.3393	0.071000
H20	0.1265	1.0472	0.2581	0.064000

Symmetry transformations used to generate equivalent atoms:

5.4 Crystallographic data of compound 5a



ORTEP diagram of compounds **5a** (CCDC-2179553)

Table 1. Crystal data and structure refinement for 5a.

Identification code	5a	
Empirical formula	C22 H19 N3 O3 S	
Formula weight	405.46	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.1555(6) Å	α= 103.303(2)°.
	b = 10.4074(7) Å	β= 99.290(2)°.
	c = 11.9079(7) Å	γ = 112.822(2)°.
Volume	977.20(11) $Å^3$	
Z	2	
Density (calculated)	1.378 Mg/m^3	
Absorption coefficient	0.195 mm^{-1}	
F(000)	424	
Crystal size	0.238 x 0.117 x 0.052 mm^3	
Theta range for data collection	3.128 to 26.484°.	
Index ranges	-11<=h<=11, -13<=k<=13, -14<=l<=14	
Reflections collected	30992	
Independent reflections	4015 [R(int) = 0.1050]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.986 and 0.943	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4015 / 0 / 264	
Goodness-of-fit on F^2	1.027	
Final R indices [I>2sigma(I)]	R1 = 0.0511, wR2 = 0.1096	

R indices (all data)	R1 = 0.0846, wR2 = 0.1251
Extinction coefficient	n/a
Largest diff. peak and hole	0.246 and -0.358 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3)for **5a**.
U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	1200(3)	57(3)	1504(2)	41(1)
C(2)	1144(4)	-1265(3)	878(3)	57(1)
C(3)	2039(4)	-1240(3)	45(3)	65(1)
C(4)	2945(4)	41(3)	-169(2)	57(1)
C(5)	3008(3)	1373(3)	462(2)	43(1)
C(6)	2146(3)	1380(2)	1319(2)	35(1)
C(7)	1850(3)	2519(3)	2086(2)	34(1)
C(8)	638(3)	1745(3)	2724(2)	42(1)
C(9)	-714(4)	-810(4)	2781(3)	72(1)
C(10)	5227(3)	4704(2)	2334(2)	35(1)
C(11)	5682(3)	4747(3)	3515(2)	43(1)
C(12)	7218(4)	4849(3)	3989(3)	57(1)
C(13)	8265(4)	4854(3)	3269(3)	65(1)
C(14)	7814(4)	4820(3)	2102(3)	60(1)
C(15)	6291(3)	4751(3)	1625(2)	46(1)
C(16)	3862(3)	7197(2)	3324(2)	33(1)
C(17)	2497(3)	7217(3)	3664(2)	39(1)
C(18)	2663(3)	7878(3)	4855(2)	41(1)
C(19)	4167(3)	8509(3)	5718(2)	38(1)
C(20)	5532(3)	8499(3)	5348(2)	41(1)
C(21)	5399(3)	7862(3)	4162(2)	39(1)
C(22)	4308(4)	9142(3)	7020(2)	53(1)
N(1)	2351(2)	3906(2)	2327(2)	37(1)
N(2)	3627(2)	4622(2)	1822(2)	35(1)
N(3)	367(3)	306(2)	2363(2)	45(1)
O(1)	2015(2)	5881(2)	1111(2)	53(1)

O(2)	5049(2)	7011(2)	1471(2)	51(1)
O(3)	72(3)	2284(2)	3441(2)	64(1)
S(1)	3620(1)	6258(1)	1825(1)	38(1)

Table 3. Bond lengths [Å] and angles [°] for **5a**.

C(1)-C(2)	1.383(4)
C(1)-C(6)	1.404(3)
C(1)-N(3)	1.406(3)
C(2)-C(3)	1.383(4)
C(2)-H(2)	0.9300
C(3)-C(4)	1.378(5)
C(3)-H(3)	0.9300
C(4)-C(5)	1.391(4)
C(4)-H(4)	0.9300
C(5)-C(6)	1.388(3)
C(5)-H(5)	0.9300
C(6)-C(7)	1.464(3)
C(7)-N(1)	1.277(3)
C(7)-C(8)	1.523(3)
C(8)-O(3)	1.208(3)
C(8)-N(3)	1.368(3)
C(9)-N(3)	1.453(3)
C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600
C(10)-C(15)	1.383(3)
C(10)-C(11)	1.386(3)
C(10)-N(2)	1.454(3)
C(11)-C(12)	1.381(4)
C(11)-H(11)	0.9300
C(12)-C(13)	1.384(4)
C(12)-H(12)	0.9300
C(13)-C(14)	1.372(5)
C(13)-H(13)	0.9300
C(14)-C(15)	1.386(4)

C(14)-H(14)	0.9300
C(15)-H(15)	0.9300
C(16)-C(17)	1.381(3)
C(16)-C(21)	1.388(3)
C(16)-S(1)	1.758(2)
C(17)-C(18)	1.381(3)
C(17)-H(17)	0.9300
C(18)-C(19)	1.383(3)
C(18)-H(18)	0.9300
C(19)-C(20)	1.393(3)
C(19)-C(22)	1.501(3)
C(20)-C(21)	1.379(3)
C(20)-H(20)	0.9300
C(21)-H(21)	0.9300
C(22)-H(22A)	0.9600
C(22)-H(22B)	0.9600
C(22)-H(22C)	0.9600
N(1)-N(2)	1.428(3)
N(2)-S(1)	1.705(2)
O(1)-S(1)	1.4260(19)
O(2)-S(1)	1.4272(18)

C(2)-C(1)-C(6)	121.5(3)
C(2)-C(1)-N(3)	128.0(3)
C(6)-C(1)-N(3)	110.4(2)
C(1)-C(2)-C(3)	117.4(3)
C(1)-C(2)-H(2)	121.3
C(3)-C(2)-H(2)	121.3
C(4)-C(3)-C(2)	121.9(3)
C(4)-C(3)-H(3)	119.1
C(2)-C(3)-H(3)	119.1
C(3)-C(4)-C(5)	120.9(3)
C(3)-C(4)-H(4)	119.6
C(5)-C(4)-H(4)	119.6
C(6)-C(5)-C(4)	118.3(3)
C(6)-C(5)-H(5)	120.9

C(4)-C(5)-H(5)	120.9
C(5)-C(6)-C(1)	120.0(2)
C(5)-C(6)-C(7)	133.5(2)
C(1)-C(6)-C(7)	106.3(2)
N(1)-C(7)-C(6)	136.4(2)
N(1)-C(7)-C(8)	117.3(2)
C(6)-C(7)-C(8)	106.2(2)
O(3)-C(8)-N(3)	126.3(2)
O(3)-C(8)-C(7)	127.8(2)
N(3)-C(8)-C(7)	105.8(2)
N(3)-C(9)-H(9A)	109.5
N(3)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
N(3)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(15)-C(10)-C(11)	120.6(2)
C(15)-C(10)-N(2)	118.8(2)
C(11)-C(10)-N(2)	120.6(2)
C(12)-C(11)-C(10)	119.6(3)
C(12)-C(11)-H(11)	120.2
C(10)-C(11)-H(11)	120.2
C(11)-C(12)-C(13)	119.8(3)
C(11)-C(12)-H(12)	120.1
C(13)-C(12)-H(12)	120.1
C(14)-C(13)-C(12)	120.4(3)
C(14)-C(13)-H(13)	119.8
C(12)-C(13)-H(13)	119.8
C(13)-C(14)-C(15)	120.2(3)
C(13)-C(14)-H(14)	119.9
C(15)-C(14)-H(14)	119.9
C(10)-C(15)-C(14)	119.3(3)
C(10)-C(15)-H(15)	120.4
C(14)-C(15)-H(15)	120.4
C(17)-C(16)-C(21)	120.6(2)
C(17)-C(16)-S(1)	119.22(18)

C(21)-C(16)-S(1)	120.17(18)
C(16)-C(17)-C(18)	119.4(2)
C(16)-C(17)-H(17)	120.3
C(18)-C(17)-H(17)	120.3
C(17)-C(18)-C(19)	121.4(2)
C(17)-C(18)-H(18)	119.3
C(19)-C(18)-H(18)	119.3
C(18)-C(19)-C(20)	118.1(2)
C(18)-C(19)-C(22)	120.7(2)
C(20)-C(19)-C(22)	121.1(2)
C(21)-C(20)-C(19)	121.5(2)
C(21)-C(20)-H(20)	119.3
C(19)-C(20)-H(20)	119.3
C(20)-C(21)-C(16)	119.0(2)
C(20)-C(21)-H(21)	120.5
C(16)-C(21)-H(21)	120.5
C(19)-C(22)-H(22A)	109.5
C(19)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(19)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(7)-N(1)-N(2)	115.73(18)
N(1)-N(2)-C(10)	115.12(18)
N(1)-N(2)-S(1)	107.26(14)
C(10)-N(2)-S(1)	115.54(15)
C(8)-N(3)-C(1)	111.1(2)
C(8)-N(3)-C(9)	123.3(2)
C(1)-N(3)-C(9)	125.6(2)
O(1)-S(1)-O(2)	120.47(12)
O(1)-S(1)-N(2)	105.31(11)
O(2)-S(1)-N(2)	104.90(10)
O(1)-S(1)-C(16)	109.31(11)
O(2)-S(1)-C(16)	109.77(11)
N(2)-S(1)-C(16)	106.00(10)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for**5a**. The anisotropic Displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	31(1)	37(1)	47(1)	10(1)	1(1)	13(1)
C(2)	54(2)	34(2)	70(2)	9(1)	0(2)	19(1)
C(3)	82(2)	51(2)	56(2)	-3(2)	6(2)	40(2)
C(4)	63(2)	67(2)	43(2)	3(1)	12(1)	40(2)
C(5)	44(2)	45(2)	35(1)	6(1)	7(1)	20(1)
C(6)	32(1)	34(1)	34(1)	7(1)	5(1)	14(1)
C(7)	31(1)	34(1)	34(1)	9(1)	9(1)	13(1)
C(8)	31(1)	43(2)	46(1)	12(1)	10(1)	11(1)
C(9)	57(2)	58(2)	101(3)	46(2)	30(2)	14(2)
C(10)	36(1)	29(1)	37(1)	8(1)	10(1)	12(1)
C(11)	48(2)	40(1)	40(1)	15(1)	11(1)	16(1)
C(12)	51(2)	47(2)	63(2)	25(1)	-1(2)	13(1)
C(13)	35(2)	49(2)	100(3)	27(2)	3(2)	13(1)
C(14)	40(2)	49(2)	81(2)	14(2)	22(2)	14(1)
C(15)	39(2)	45(2)	45(1)	7(1)	15(1)	14(1)
C(16)	39(1)	29(1)	33(1)	13(1)	11(1)	14(1)
C(17)	33(1)	40(1)	41(1)	14(1)	9(1)	15(1)
C(18)	41(2)	44(1)	46(1)	16(1)	20(1)	21(1)
C(19)	47(2)	32(1)	37(1)	12(1)	14(1)	18(1)
C(20)	38(1)	37(1)	40(1)	10(1)	5(1)	14(1)
C(21)	37(1)	36(1)	43(1)	12(1)	15(1)	15(1)
C(22)	67(2)	49(2)	41(1)	10(1)	19(1)	26(2)
N(1)	36(1)	34(1)	39(1)	9(1)	16(1)	13(1)
N(2)	36(1)	33(1)	34(1)	11(1)	13(1)	13(1)
N(3)	37(1)	40(1)	58(1)	21(1)	15(1)	12(1)
O(1)	59(1)	60(1)	40(1)	13(1)	2(1)	32(1)
O(2)	65(1)	48(1)	48(1)	26(1)	33(1)	22(1)
O(3)	59(1)	63(1)	72(1)	18(1)	42(1)	22(1)
S(1)	48(1)	39(1)	31(1)	14(1)	13(1)	19(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **5a**.

	x	y	z	U(eq)
H(2)	528	-2137	1011	68
H(3)	2029	-2114	-382	78
H(4)	3521	15	-742	69
H(5)	3612	2237	313	52
H(9A)	-1085	-354	3396	107
H(9B)	-123	-1291	3103	107
H(9C)	-1649	-1522	2122	107
H(11)	4958	4708	3985	52
H(12)	7548	4914	4789	69
H(13)	9280	4880	3578	78
H(14)	8534	4842	1629	72
H(15)	5989	4738	837	55
H(17)	1474	6788	3097	46
H(18)	1745	7899	5082	50
H(20)	6556	8933	5914	49
H(21)	6324	7877	3927	46
H(22A)	3520	9532	7084	79
H(22B)	5401	9915	7419	79
H(22C)	4091	8383	7388	79

Table 6. Torsion angles [°] for **5a**.

C(6)-C(1)-C(2)-C(3)	-0.9(4)
N(3)-C(1)-C(2)-C(3)	178.0(3)
C(1)-C(2)-C(3)-C(4)	-0.6(4)
C(2)-C(3)-C(4)-C(5)	0.8(5)
C(3)-C(4)-C(5)-C(6)	0.5(4)
C(4)-C(5)-C(6)-C(1)	-1.9(4)
C(4)-C(5)-C(6)-C(7)	-175.8(3)
C(2)-C(1)-C(6)-C(5)	2.2(4)
N(3)-C(1)-C(6)-C(5)	-176.9(2)
C(2)-C(1)-C(6)-C(7)	177.6(2)
N(3)-C(1)-C(6)-C(7)	-1.6(3)
C(5)-C(6)-C(7)-N(1)	-6.7(5)
C(1)-C(6)-C(7)-N(1)	178.8(3)
C(5)-C(6)-C(7)-C(8)	173.9(3)
C(1)-C(6)-C(7)-C(8)	-0.6(3)
N(1)-C(7)-C(8)-O(3)	0.3(4)
C(6)-C(7)-C(8)-O(3)	179.9(3)
N(1)-C(7)-C(8)-N(3)	-177.0(2)
C(6)-C(7)-C(8)-N(3)	2.5(3)
C(15)-C(10)-C(11)-C(12)	0.4(4)
N(2)-C(10)-C(11)-C(12)	-178.9(2)
C(10)-C(11)-C(12)-C(13)	-2.3(4)
C(11)-C(12)-C(13)-C(14)	2.7(4)
C(12)-C(13)-C(14)-C(15)	-1.2(4)
C(11)-C(10)-C(15)-C(14)	1.0(4)
N(2)-C(10)-C(15)-C(14)	-179.6(2)
C(13)-C(14)-C(15)-C(10)	-0.6(4)
C(21)-C(16)-C(17)-C(18)	-1.4(4)
S(1)-C(16)-C(17)-C(18)	176.21(19)
C(16)-C(17)-C(18)-C(19)	-0.7(4)
C(17)-C(18)-C(19)-C(20)	1.8(4)
C(17)-C(18)-C(19)-C(22)	-176.2(2)
C(18)-C(19)-C(20)-C(21)	-1.0(4)
C(22)-C(19)-C(20)-C(21)	177.1(2)

C(19)-C(20)-C(21)-C(16)	-1.0(4)
C(17)-C(16)-C(21)-C(20)	2.1(4)
S(1)-C(16)-C(21)-C(20)	-175.39(19)
C(6)-C(7)-N(1)-N(2)	-6.3(4)
C(8)-C(7)-N(1)-N(2)	172.97(19)
C(7)-N(1)-N(2)-C(10)	-69.5(2)
C(7)-N(1)-N(2)-S(1)	160.37(17)
C(15)-C(10)-N(2)-N(1)	151.8(2)
C(11)-C(10)-N(2)-N(1)	-28.8(3)
C(15)-C(10)-N(2)-S(1)	-82.2(2)
C(11)-C(10)-N(2)-S(1)	97.1(2)
O(3)-C(8)-N(3)-C(1)	179.1(3)
C(7)-C(8)-N(3)-C(1)	-3.5(3)
O(3)-C(8)-N(3)-C(9)	1.9(4)
C(7)-C(8)-N(3)-C(9)	179.4(2)
C(2)-C(1)-N(3)-C(8)	-175.7(3)
C(6)-C(1)-N(3)-C(8)	3.4(3)
C(2)-C(1)-N(3)-C(9)	1.4(4)
C(6)-C(1)-N(3)-C(9)	-179.6(3)
N(1)-N(2)-S(1)-O(1)	-59.66(16)
C(10)-N(2)-S(1)-O(1)	170.47(16)
N(1)-N(2)-S(1)-O(2)	172.26(14)
C(10)-N(2)-S(1)-O(2)	42.39(18)
N(1)-N(2)-S(1)-C(16)	56.13(16)
C(10)-N(2)-S(1)-C(16)	-73.74(17)
C(17)-C(16)-S(1)-O(1)	11.5(2)
C(21)-C(16)-S(1)-O(1)	-170.91(19)
C(17)-C(16)-S(1)-O(2)	145.69(19)
C(21)-C(16)-S(1)-O(2)	-36.7(2)
C(17)-C(16)-S(1)-N(2)	-101.5(2)
C(21)-C(16)-S(1)-N(2)	76.0(2)

Symmetry transformations used to generate equivalent atoms: