Electronic Supplementary Material (ESI) for ChemComm.

A Diversity Oriented Clicking Strategy: The Stereoselective Synthesis of Highly-Functionalised Olefins from 2-Substituted-Alkynyl-1-Sulfonyl Fluorides

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General Methods

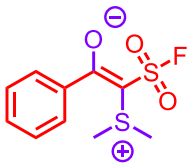
The petroleum ether used refers to the fraction with 40-60 °C boiling point. Commercial solvents and reagents were used as supplied. Unless otherwise stated, all reactions were monitored by TLC on Polygram® SIL/G_{25} plates and visualized using UV light and stained using basic $KMnO_4$. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on either a Bruker Ascend™ 400 (400 MHz) or a Ultrashield™ 500 PLUS (500 MHz) instrument as dilute solutions in the stipulated solvent. All chemical shifts (δ) are reported in parts per million (ppm) with ^{1}H and ^{13}C NMR referenced to solvent signals [^{1}H NMR: $CDCl_3$ (7.27), DMSO-d_6 (2.50); ^{13}C NMR: $CDCl_3$ (77.16), DMSO-d_6 (39.52)]. Coupling constants (*J*) are reported in Hertz (Hz) and recorded after averaging. The multiplicity of the ^{1}H NMR signals are designated by one of the following abbreviations: s=singlet, d=doublet, t=triplet, q=quartet, hept=heptet, m=multiplet, br=broad signal. HRMS were obtained using an Agilent 6530 accurate-mass Q-TOF LC/MS in electrospray ionization (ESI) mode Flash column chromatography was performed using a Biotage® Isolera™ on Biotage® KP-Sil SNAP cartridges. Melting points data were collected using a Gallenkamp melting point apparatus.

Synthesis and Experimental Data for Compounds 8a-8l

General Procedure A

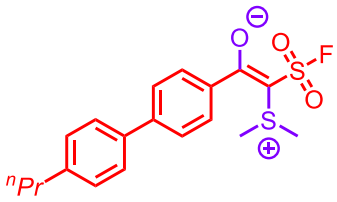
A solution of the required SASF **7** was stirred in DMSO (4.00 mL/mmol) at room temperature for 30 min. The reaction mixture was then extracted into EtOAc washed with brine (x2) and H_2O (x2). The organic layer was dried over anhydrous $MgSO_4$, filtered under vacuum and the solvent was removed under reduced pressure to obtain the analytically pure product.

(*Z*)-2-(Dimethylsulfonio)-2-(fluorosulfonyl)-1-phenylethen-1-olate (8a)[1]



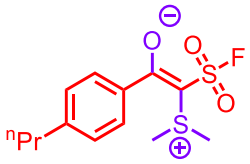
Following general procedure A (0.25 mmol), the title compound was isolated as a colourless solid (63 mg, 95%). **m.p.** 102-103 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 2H), 7.50 – 7.46 (m, 1H), 7.43 – 7.39 (m, 2H), 3.11 (s, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 188.2, 140.1, 131.2, 128.1, 127.6, 73.4 (d, *J* = 29.7 Hz), 28.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 78.0; **HRMS** (ESI^+): calculated for $C_{10}H_{12}FO_3S_2$ [$M+H^+$]: m/z = 263.0206, m/z found 263.0204; **IR** ν_{max} (ATR)/cm^{-1}: 3024, 2941, 2853, 1597, 1574, 1368, 1292, 1180, 989, 847.

(*Z*)-2-(Dimethylsulfonio)-2-(fluorosulfonyl)-1-(4'-propyl-[1,1'-biphenyl]-4-yl)ethen-1-olate (8b)



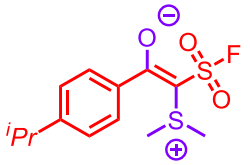
Following general procedure A (0.25 mmol), the title compound was isolated as a colourless solid (87 mg, 92%). **m.p.** 170-172 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (appt. d, *J* = 8.6 Hz, 2H), 7.63 (appt. d, *J* = 8.6 Hz, 2H), 7.55 (appt. d, *J* = 8.2 Hz, 2H), 7.28 – 4.91 (m, 4H), 3.15 (s, 6H), 2.68 – 2.60 (m, 2H), 1.74 – 1.62 (m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 187.8, 144.0, 142.6, 138.5, 137.8, 129.1, 128.4, 127.2, 126.6, 73.2 (d, *J* = 30.1 Hz), 37.8, 28.3, 24.6, 14.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 78.1; **HRMS** (ESI^+): calculated for $C_{19}H_{22}FO_3S_2$ [$M+H^+$]: m/z = 381.0989, m/z found 389.0986; **IR** ν_{max} (ATR)/cm^{-1}: 3042, 2953, 1926, 2870, 1605, 1422, 1393, 1300, 978.

(*Z*)-2-(Dimethylsulfonio)-2-(fluorosulfonyl)-1-(4-propylphenyl)ethen-1-olate (8c)



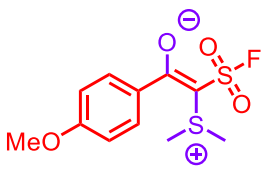
Following general procedure A (0.25 mmol), the title compound was isolated as a yellow solid (76 mg, >99%). **m.p.** 90-92 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (appt. d, *J* = 8.2 Hz, 2H), 7.22 (appt. d, *J* = 8.3 Hz, 2H), 3.12 (s, 6H), 2.68 – 2.57 (m, 2H), 1.72 – 1.60 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 188.1, 146.3, 137.5, 128.2, 127.8, 73.0 (d, *J* = 29.5 Hz), 38.1, 28.3 (d, *J* = 1.3 Hz), 24.3, 13.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 78.0; **HRMS** (ESI^+): calculated for $C_{13}H_{18}FO_3S_2$ $[M+H^+]$: m/z = 305.0676, m/z found 305.0676; **IR** ν_{max} (ATR)/cm^{-1}: 3044, 2953, 1928, 2868, 1589, 1560, 1422, 1375, 1292, 1231, 976.

(*Z*)-2-(Dimethylsulfonio)-2-(fluorosulfonyl)-1-(4-isopropylphenyl)ethen-1-olate (8d)



Following general procedure A (0.10 mmol), the title compound was isolated as a colourless solid (29 mg, 97%). **m.p.** 110-111 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (appt. d, *J* = 8.2 Hz, 1H), 7.26 (appt. d, *J* = 8.2 Hz, 2H), 3.11 (s, 6H), 2.95 (hept., *J* = 13.9 Hz, 1H), 1.27 (d, *J* = 6.9 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 188.0, 152.4, 137.6, 128.0, 126.2, 73.0 (d, *J* = 29.6 Hz), 34.2, 28.3, 23.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 77.9; **HRMS** (ESI^+): calculated for $C_{13}H_{18}FO_3S_2$ $[M+H^+]$: m/z = 305.0676, m/z found 305.0675; **IR** ν_{max} (ATR)/cm^{-1}: 3021, 2957, 1587, 1558, 1371, 1179, 1047, 829.

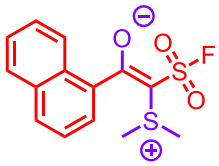
(*Z*)-2-(Dimethylsulfonio)-2-(fluorosulfonyl)-1-(4-methoxyphenyl)ethen-1-olate (8e)



Following general procedure A (0.25 mmol), the title compound was isolated as a yellow solid (71 mg, 97%). **m.p.** 127-128 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (appt. d, *J* = 8.8 Hz, 2H), 6.91 (appt. d, *J* = 8.8

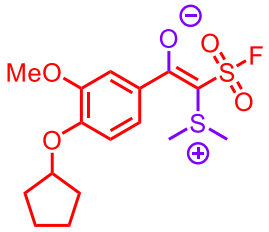
Hz, 2H), 3.84 (s, 3H), 3.07 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 187.1, 162.2, 132.3, 130.0, 113.4, 72.6 (d, *J* = 30.4 Hz), 55.4, 28.3 (d, *J* = 1.4 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ 78.3; **HRMS** (ESI^+): calculated for $C_{11}H_{14}FO_4S_2$ [$M+H^+$]: m/z = 293.0312, m/z found 293.0318; **IR** ν_{max} (ATR)/cm^{-1}: 2959, 1659, 1599, 1574, 1429, 1292, 1258, 1217, 1040, 810, 791.

(*Z*)-2-(Dimethylsulfonio)-2-(fluorosulfonyl)-1-(naphthalen-1-yl)ethen-1-olate (8f)



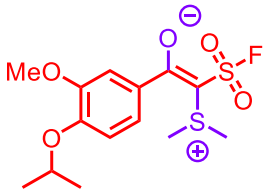
Following general procedure A (0.10 mmol), the title compound was isolated as a yellow solid (23 mg, 74%). **m.p.** 103-105 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 – 7.77 (m, 3H), 7.57 – 7.36 (m, 4H), 3.14 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 188.3, 138.2, 133.7, 130.2, 130.0, 128.6, 127.0, 126.4, 124.9, 124.8, 124.4, 75.9(d, *J* = 24.7 Hz), 28.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 76.2; **HRMS** (ESI^+): calculated for $C_{14}H_{14}FO_3S_2$ [$M+H^+$]: m/z = 313.0363, m/z found 313.0363; **IR** ν_{max} (ATR)/cm^{-1}: 3053, 2930, 1601, 1574, 1392, 1373, 1296, 1258, 1184, 1055, 1036, 978.

(*Z*)-1-(4-(Cyclopentyloxy)-3-methoxyphenyl)-2-(dimethylsulfonio)-2-(fluorosulfonyl)ethen-1-olate (8g)



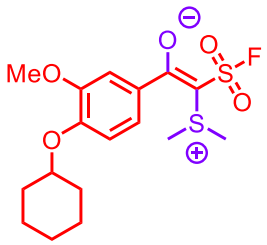
Following general procedure A (0.25 mmol), the title compound was isolated as a yellow solid (88 mg, 94%). **m.p.** 208-209 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 1H), 7.20 (d, *J* = 1.9 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 4.88 – 4.75 (m, 1H), 3.87 (s, 3H), 3.09 (s, 6H), 2.02 – 1.75 (m, 6H), 1.68 – 1.54 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 187.1, 151.0, 149.3, 131.8, 121.9, 112.9, 111.9, 80.5, 72.4 (d, *J* = 31.0 Hz), 56.1, 33.0, 28.4, 24.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 78.2; **HRMS** (ESI^+): calculated for $C_{16}H_{22}FO_5S_2$ [$M+H^+$]: m/z = 377.0887, m/z found 377.0884; **IR** ν_{max} (ATR)/cm^{-1}: 3019, 2957, 1651, 1591, 1508, 1423, 1202, 1173, 1043, 789.

(*Z*)-2-(Dimethylsulfonio)-2-(fluorosulfonyl)-1-(4-isopropoxy-3-methoxyphenyl)ethen-1-olate (8h)



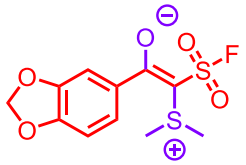
Following general procedure A (0.25 mmol), the title compound was isolated as a light brown solid (79 mg, 90%). **m.p.** 148 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 1H), 7.21 (d, *J* = 2.0 Hz, 1H), 6.89 – 6.85 (m, 1H), 4.61 (hept, *J* = 6.1 Hz, 1H), 3.88 (s, 3H), 3.09 (s, 6H), 1.39 (d, *J* = 6.1 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 187.1, 150.5, 149.6, 132.1, 121.9, 113.3, 111.9, 72.5 (d, *J* = 31.0 Hz), 71.3, 56.1, 28.3, 22.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 78.2; **HRMS** (ESI^+): calculated for $C_{14}H_{19}FO_5S_2$ [M+H^+]: m/z = 351.0731, m/z found 351.0731; **IR** ν_{max} (ATR)/cm^{-1}: 2976 1603, 1416, 1366, 1273, 1184, 928, 868.

(*Z*)-1-(4-(Cyclopentyloxy)-3-methoxyphenyl)-2-(dimethylsulfonio)-2-(fluorosulfonyl)ethen-1-olate (8i)



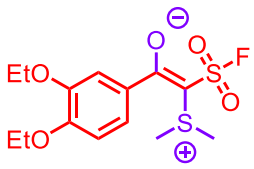
Following general procedure A (0.25 mmol), the title compound was isolated as a colourless solid (80 mg, 82%). **m.p.** 160-161 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 – 7.23 (m, 1H), 7.21 (d, *J* = 2.0 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 4.33 – 4.23 (m, 1H), 3.88 (s, 3H), 3.09 (s, 6H), 2.10 – 2.01 (m, 2H), 1.87 – 1.78 (m, 2H), 1.64 – 1.52 (m, 3H), 1.41 – 1.24 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 187.1, 150.5, 149.7, 132.1, 121.8, 113.6, 112.1, 77.1, 72.4 (d, *J* = 31.0 Hz), 56.1, 32.0, 28.4, 25.7, 24.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 78.2; **HRMS** (ESI^+): calculated for $C_{17}H_{24}FO_5S_2$ [M+H^+]: m/z = 391.1044, m/z found 391.1046; **IR** ν_{max} (ATR)/cm^{-1}: 3022, 2941, 1566, 1510, 1371, 1227 1184, 874.

(*Z*)-1-(Benzo[*d*][1,3]dioxol-5-yl)-2-(dimethylsulfonio)-2-(fluorosulfonyl)ethen-1-olate (8j)



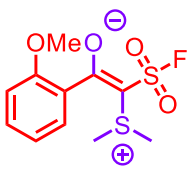
Following general procedure A (0.25 mmol), the title compound was isolated as a yellow solid (70 mg, 97%). **m.p.** 176-177 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.10 (d, *J* = 1.7 Hz, 1H), 6.82 (d, *J* = 8.1 Hz, 1H), 6.02 (s, 2H), 3.10 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.9, 150.4, 147.6, 134.0, 123.3, 108.5, 107.8, 101.7, 72.7 (d, *J* = 31.3 Hz), 28.3 (d, *J* = 1.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ 78.2; **HRMS** (ESI$^+$): calculated for $C_{11}H_{12}FO_5S_2$ [M+H$^+$]: m/z = 307.0105, m/z found 307.0108; **IR** ν_{max} (ATR)/cm^{-1}: 3036, 2947, 2839, 1607, 1568, 1508, 1369, 1304, 1180, 1024, 991, 841.

(*Z*)-1-(3,4-Diethoxyphenyl)-2-(dimethylsulfonio)-2-(fluorosulfonyl)ethen-1-olate (8k)



Following general procedure A (0.10 mmol), the title compound was isolated as a colourless solid (33 mg, 94%). **m.p.** 98-99 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 – 7.24 (m, 1H), 7.21 (d, *J* = 2.0 Hz, 1H), 6.86 (d, *J* = 8.3 Hz, 1H), 4.13 (appt. qd, *J* = 7.0, 2.5 Hz, 4H), 3.08 (s, 6H), 1.46 (appt. td, *J* = 7.0, 5.5 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 187.2, 151.8, 148.0, 132.1, 121.9, 113.3 (d, *J* = 6.0 Hz), 111.7, 72.4 (d, *J* = 31.0 Hz), 64.6, 64.5, 28.4, 28.3, 14.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 78.2; **HRMS** (ESI$^+$): calculated for $C_{14}H_{20}FO_5S_2$ [M+H$^+$]: m/z = 351.0731, m/z found 351.0732; **IR** ν_{max} (ATR)/cm^{-1}: 2984, 1593, 1570, 1510, 1397, 1369, 1327, 1173, 1042, 964.

(*Z*)-2-(Dimethylsulfonio)-2-(fluorosulfonyl)-1-(2-methoxyphenyl)ethen-1-olate (8l)



Following general procedure A (0.25 mmol, heated at 80 °C), the title compound was isolated as a colourless solid (58 mg, 79%). **m.p.** 158-159 °C;**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.33 (m, 1H), 7.29 –

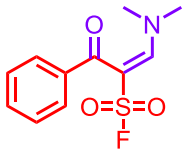
7.25 (m, 1H), 6.99 (appt. t, *J* = 7.3 Hz, 1H), 6.91 (d, *J* = 8.3 Hz, 1H), 3.83 (s, 3H), 3.09 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.1, 131.1, 130.2, 128.3, 120.8, 111.1, 74.9 (d, *J* = 23.0 Hz), 55.8, 28.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 74.0; **HRMS** (ESI^+): calculated for $C_{11}H_{14}FO_4S_2$ [$M+H^+$]: m/z = 293.0312, m/z found 293.0312; **IR** ν_{max} (ATR)/cm^{-1}: 2924, 1599, 1487, 1462, 1377, 1310, 1244, 1180.

Synthesis and Experimental Data for Compounds 9a-9j

General Procedure B

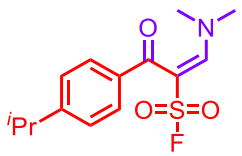
A solution of the required SASF **7** was stirred in anhydrous DMF (2.00 mL/mmol) at 80 °C for 2.5 h. The reaction mixture was then cooled to room temperature and extracted into EtOAc washed with brine (x2) and H_2O (x2). The organic layer was dried over anhydrous $MgSO_4$, filtered under vacuum and the solvent was removed under reduced pressure to obtain the analytically pure product.

(*E*)-1-(Dimethylamino)-3-oxo-3-phenylprop-1-ene-2-sulfonyl fluoride (9a)



Following general procedure B (0.10 mmol), the title compound was isolated as a low melting orange solid (24 mg, 92%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.85 (appt. d, *J* = 7.2 Hz, 2H), 7.60 – 7.55 (m, 1H), 7.47 (appt. t, *J* = 7.6 Hz, 2H), 3.32 (s, 3H), 2.71 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 188.1, 157.3, 139.5, 133.3, 129.2, 128.7, 100.1 (d, *J* = 22.3 Hz), 48.1, 42.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 73.4; **HRMS** (ESI^+): calculated for $C_{11}H_{12}FNO_3SNa$ [$M+Na^+$]: m/z = 280.0414, m/z found 280.0417; **IR** ν_{max} (ATR)/cm^{-1}: 1647, 1641, 1618, 1379, 1184.

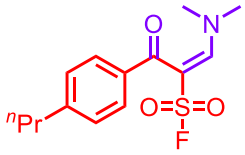
(*E*)-1-(Dimethylamino)-3-(4-isopropylphenyl)-3-oxoprop-1-ene-2-sulfonyl fluoride (9b)



Following general procedure B (0.25 mmol), the title compound was isolated as a yellow oil (71 mg, 95%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.80 (appt. d, *J* = 8.3 Hz, 2H), 7.32 (appt. d, *J* = 8.2 Hz, 2H), 3.28 (s, 3H), 3.02 – 2.91 (m, 1H), 2.66 (s, 3H), 1.27 (d, *J* = 6.9 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ

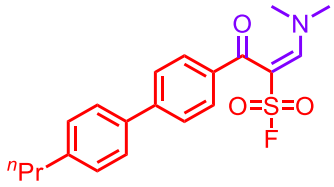
187.8, 156.7, 155.0, 137.1, 129.6, 126.9, 99.7 (d, *J* = 21.6 Hz), 47.9, 42.1, 34.4, 23.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 73.0; **HRMS** (ESI^+): calculated for $C_{14}H_{19}FNO_3S$ $[M+H^+]$: m/z = 300.1064, m/z found 300.1063; **IR** ν_{max} (ATR)/cm^{-1}: 2963, 2932, 1667, 1643, 1435, 1416, 1385, 1337, 1254, 1132, 1057, 957, 837.

(*E*)-1-(Dimethylamino)-3-oxo-3-(4-propylphenyl)prop-1-ene-2-sulfonyl fluoride (9c)



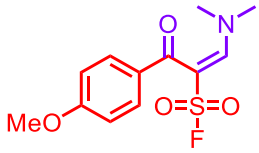
Following general procedure B (0.25 mmol), the title compound was isolated as a yellow oil (69 mg, 92%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 3H), 3.28 (s, 3H), 2.71 – 2.60 (m, 5H), 1.74 – 1.59 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 187.8, 156.8, 149.0, 137.1, 129.5, 128.9, 99.8 (d, *J* = 21.7 Hz), 47.9, 42.2, 38.2, 24.2, 13.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 73.0; **HRMS** (ESI^+): calculated for $C_{14}H_{19}FNO_3S$ $[M+H^+]$: m/z = 300.1064, m/z found 300.1061; **IR** ν_{max} (ATR)/cm^{-1}: 2961, 2934, 1651, 1626, 1435, 1385, 1254, 1184, 1134, 957, 912, 840.

(*E*)-1-(Dimethylamino)-3-(4'-isopropyl-[1,1'-biphenyl]-4-yl)-3-oxoprop-1-ene-2-sulfonyl fluoride (9d)



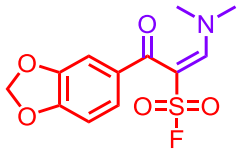
Following general procedure B (0.25 mmol), the title compound was isolated as a colourless solid (75 mg, 80%). **m.p.** 100-102 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 – 7.90 (m, 3H), 7.69 (appt. d, *J* = 8.6 Hz, 2H), 7.56 (appt. d, *J* = 8.2 Hz, 2H), 7.29 (appt. d, *J* = 8.3 Hz, 2H), 3.31 (s, 3H), 2.72 (s, 3H), 2.69 – 2.60 (m, 2H), 1.76 – 1.64 (m, 2H), 0.99 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 187.6, 157.0, 146.1, 143.2, 137.8, 137.2, 129.9, 129.2, 127.2, 127.1, 99.9 (d, *J* = 22.0 Hz), 48.0, 42.3, 37.8, 24.6, 14.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 73.3; **HRMS** (ESI^+): calculated for $C_{20}H_{23}FNO_3S$ $[M+H^+]$: m/z = 376.1377, m/z found 376.1380; **IR** ν_{max} (ATR)/cm^{-1}: 3024, 2953, 2928, 1651, 1609, 1440, 1418, 1173, 964, 835.

(*E*)-1-(Dimethylamino)-3-(4-methoxyphenyl)-3-oxoprop-1-ene-2-sulfonyl fluoride (9e)



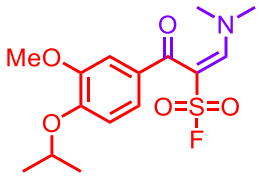
Following general procedure B (0.25 mmol), the title compound was isolated as an orange solid (63 mg, 88%). **m.p.** 126-127 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (appt. d, *J* = 8.9 Hz, 2H), 7.82 (s, 1H), 6.95 (appt. d, *J* = 8.9 Hz, 2H), 3.87 (s, 3H), 3.27 (s, 3H), 2.67 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 186.8, 164.0, 156.3, 132.1, 131.9, 114.0, 99.5 (d, *J* = 21.3 Hz), 55.7, 47.8, 41.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 72.9; **HRMS** (ESI^+): calculated for $C_{12}H_{15}FNO_4S$ [M+H$^+$]: m/z = 288.0700, m/z found 288.0701; **IR** ν_{max} (ATR)/cm^{-1}: 2972, 2943, 2833, 1643, 1622, 1599, 1531, 1254, 1171, 1022, 908, 839.

(*E*)-3-(Benzo[*d*][1,3]dioxol-5-yl)-1-(dimethylamino)-3-oxoprop-1-ene-2-sulfonyl fluoride (9f)



Following general procedure B (0.25 mmol), the title compound was isolated as an orange oil (71 mg, 95%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.49 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.36 (d, *J* = 1.7 Hz, 1H), 6.86 (d, *J* = 8.1 Hz, 1H), 6.06 (s, 2H), 3.30 (s, 3H), 2.72 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 186.4, 156.4, 152.4, 148.4, 134.0, 126.4, 108.9, 108.1, 102.2, 99.4 (d, *J* = 21.7 Hz), 47.9, 41.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 73.0; **HRMS** (ESI^+): calculated for $C_{12}H_{13}FNO_5S$ [M+H$^+$]: m/z = 302.0493, m/z found 302.0494; **IR** ν_{max} (ATR)/cm^{-1}: 3057, 2986, 2934, 1620, 1441m 1381, 1260, 1184, 1040.

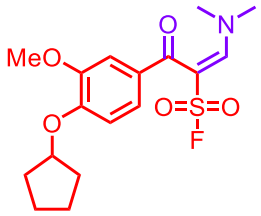
(*E*)-1-(Dimethylamino)-3-(4-isopropoxy-3-methoxyphenyl)-3-oxoprop-1-ene-2-sulfonyl fluoride (9g)



Following general procedure B (0.25 mmol), the title compound was isolated as a yellow solid (68 mg, 79%). **m.p.** 108 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.49 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.45 (d, *J* = 2.0 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 4.66 (hept, *J* = 6.1 Hz, 1H), 3.90 (s, 3H), 3.28 (s, 3H), 2.69 (s, 3H), 1.41 (d, *J* = 6.1 Hz, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 186.8, 156.2, 152.6, 150.1, 131.8, 124.8, 112.7,

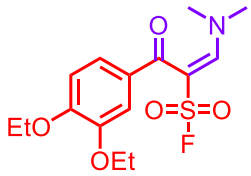
111.9, 99.4 (d, *J* = 21.5 Hz), 71.5, 56.2, 47.8, 41.8, 22.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 73.0; **HRMS** (ESI^+): calculated for $C_{15}H_{21}FNO_5S$ [$M+H^+$]: m/z = 346.1119, m/z found 346.1120; **IR** ν_{max} (ATR)/cm^{-1}: 2976, 2953, 2934, 1616, 1591, 1454, 1421, 1377, 1265, 1180, 1034, 939, 820.

(*E*)-3-(4-(Cyclopentyloxy)-3-methoxyphenyl)-1-(dimethylamino)-3-oxoprop-1-ene-2-sulfonyl fluoride (9h)



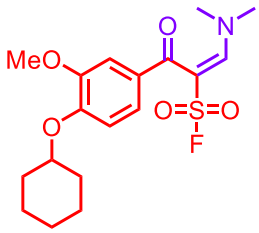
Following general procedure B (0.25 mmol), the title compound was isolated after purification by flash column chromatography (0-55% EtOAc in petroleum ether) as a yellow solid (64 mg, 69%). **m.p.** 98-99 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.49 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.43 (d, *J* = 2.0 Hz, 1H), 6.88 (d, *J* = 8.5 Hz, 1H), 4.88 – 4.81 (m, 1H), 3.89 (s, 3H), 3.27 (s, 3H), 2.67 (s, 3H), 2.07 – 1.76 (m, 6H), 1.70 – 1.55 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 186.8, 156.0, 153.0, 149.9, 131.6, 124.8, 112.7, 111.7, 99.2 (d, *J* = 21.1 Hz), 80.8, 56.2, 47.8, 41.7, 33.0, 24.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 72.9; **HRMS** (ESI^+): calculated for $C_{17}H_{23}FNO_5S$ [$M+H^+$]: m/z = 372.1275, m/z found 372.1278; **IR** ν_{max} (ATR)/cm^{-1}: 2972, 2940, 1620, 1591, 1506, 1418, 1263, 1182, 1074, 974, 874, 824.

(*E*)-3-(3,4-Diethoxyphenyl)-1-(dimethylamino)-3-oxoprop-1-ene-2-sulfonyl fluoride (9i)



Following general procedure B (0.25 mmol), the title compound was isolated as an orange solid (82 mg, 95%). **m.p.** 137-138 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.48 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.43 (d, *J* = 2.0 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 4.15 (appt. dq, *J* = 9.6, 7.0 Hz, 4H), 3.26 (s, 3H), 2.66 (s, 3H), 1.50 – 1.43 (m, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 186.8, 156.1, 153.7, 148.7, 131.9, 124.7, 113.1, 111.5, 99.3 (d, *J* = 21.1 Hz), 64.7, 64.7, 47.8, 41.7, 14.8, 14.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 72.8; **HRMS** (ESI^+): calculated for $C_{15}H_{21}FNO_5S$ [$M+H^+$]: m/z = 346.1119, m/z found 346.1117; **IR** ν_{max} (ATR)/cm^{-1}: 2978, 2932, 1645, 1612, 1593, 1396, 1263, 1175, 1042, 841.

(*E*)-3-(4-(Cyclohexyloxy)-3-methoxyphenyl)-1-(dimethylamino)-3-oxoprop-1-ene-2-sulfonyl fluoride (9j)



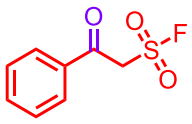
Following general procedure B (0.25 mmol), the title compound was isolated as a yellow solid (85 mg, 89%). **m.p.** 51-52 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.49 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.46 (d, *J* = 2.0 Hz, 1H), 6.91 (d, *J* = 8.5 Hz, 1H), 4.39 – 4.30 (m, 1H), 3.91 (s, 3H), 3.29 (s, 3H), 2.70 (s, 3H), 2.11 – 2.01 (m, 2H), 1.90 – 1.80 (m, 2H), 1.67 – 1.54 (m, 3H), 1.44 – 1.27 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 186.7, 156.1, 152.5, 150.2, 131.8, 124.8, 113.0, 112.0, 99.4 (d, *J* = 21.3 Hz), 77.1, 56.2, 47.8, 41.7, 31.9, 25.6, 24.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 72.9; **HRMS** (ESI^+): calculated for $C_{18}H_{25}FNO_5S$ [$M+H^+$]: m/z = 386.1432, m/z found 386.1434; **IR** ν_{max} (ATR)/cm^{-1}: 2936, 2857, 1651, 1620, 1506, 1450, 1377, 1267, 1126, 1032, 957.

Synthesis and Experimental Data for Compounds 14a-14f

General Procedure C

A solution of the required DMSO adduct **8** (0.10 mmol) and 10% Pd/C (3.00 mg, 30 mol%) in EtOAc (0.2M) under a H_2 atmosphere was stirred at 40 °C for 16 h. The reaction mixture was cooled to room temperature, diluted with EtOAC, filtered through Celite®, and washed with brine (x2) and H_2O (x2). The organic layer was dried over anhydrous $MgSO_4$, filtered under vacuum and the solvent was removed under reduced pressure to obtain the analytically pure product.

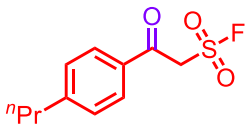
2-Oxo-2-phenylethane-1-sulfonyl fluoride (14a)[2.3]



Following general procedure C, the title compound was isolated as a colourless solid (20 mg, >99%). **m.p.** 83.9-84.5-111 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 – 7.93 (m, 2H), 7.74 – 7.68 (m, 1H), 7.60 – 7.53 (m, 2H), 5.01 (d, *J* = 2.3 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 184.8, 135.4, 134.6 (d, *J* = 2.8 Hz), 129.4,

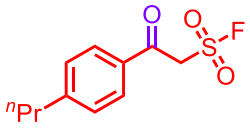
129.0, 57.6 (d, *J* = 15.9 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ 62.9; **HRMS** (ESI^+): calculated for $C_8H_7FO_3SNa$ [$M+Na^+$]: m/z = 224.9992, m/z found 224.9991.

2-Oxo-2-(4-propylphenyl)ethane-1-sulfonyl fluoride (14b)



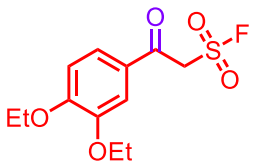
Following general procedure C, the title compound was isolated as a colourless solid (24 mg, >99%). **m.p.** 82.5-84.4 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.88 (appt. d, *J* = 8.4 Hz, 2H), 7.35 (appt. d, *J* = 8.4 Hz, 2H), 4.98 (d, *J* = 2.3 Hz, 2H), 2.73 – 2.65 (m, 2H), 1.74 – 1.64 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 184.3, 151.4, 132.4 (d, *J* = 2.9 Hz), 129.5, 129.2, 57.5 (d, *J* = 15.6 Hz), 38.3, 24.2, 13.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 62.8; **HRMS** (ESI^+): calculated for $C_{11}H_{13}FO_3SNa$ [$M+Na^+$]: m/z = 267.0462, m/z found 267.0467; **IR** ν_{max} (ATR)/cm^{-1}: 2961, 2932, 1694, 1605, 1416, 1327, 1213, 988.

2-(4-Isopropylphenyl)-2-oxoethane-1-sulfonyl fluoride (14c)



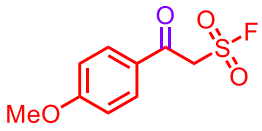
Following general procedure C, the title compound was isolated as a yellow solid (23 mg, 96%). **m.p.** 84.6-86.3 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (appt. d, *J* = 8.5 Hz, 2H), 7.40 (appt. d, *J* = 8.3 Hz, 2H), 4.97 (d, *J* = 2.3 Hz, 2H), 3.01 (hept, *J* = 6.9 Hz, 1H), 1.29 (d, *J* = 6.9 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 184.3, 157.4, 132.5 (d, *J* = 2.8 Hz), 129.4, 127.6, 57.5 (d, *J* = 15.7 Hz), 34.6, 23.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 62.8; **HRMS** (ESI^+): calculated for $C_{11}H_{13}FO_3SNa$ [$M+Na^+$]: m/z = 267.0462, m/z found 267.0464; **IR** ν_{max} (ATR)/cm^{-1}: 2965, 2253, 1688, 1605, 1420, 1206, 1188.

2-(3,4-Diethoxyphenyl)-2-oxoethane-1-sulfonyl fluoride (14d)



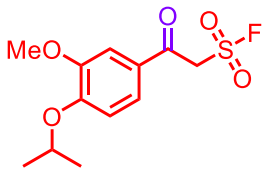
Following general procedure C, the title compound was isolated as a yellow solid (24 mg, 83%). **m.p.** 134.8-136.6 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 2.1 Hz, 1H), 7.49 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 4.94 (d, *J* = 2.3 Hz, 2H), 4.21 (q, *J* = 7.2 Hz, 2H), 4.16 (q, *J* = 7.2 Hz, 2H), 1.50 (appt. dt, *J* = 13.8, 7.0 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 182.8, 155.1, 149.1, 127.4 (d, *J* = 2.8 Hz), 124.2, 112.2, 111.4, 64.8, 64.8, 57.2 (d, *J* = 15.4 Hz), 14.6, 14.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 62.5; **HRMS** (ESI^+): calculated for $C_{12}H_{15}FO_5SNa$ [$M+Na^+$]: m/z = 313.0516, m/z found 313.0516; **IR** ν_{max} (ATR)/cm^{-1}: 2253, 1678, 1593, 1514, 1429, 1273, 1152, 1038.

2-(4-Methoxyphenyl)-2-oxoethane-1-sulfonyl fluoride (14e)



Following general procedure C, the title compound was isolated as a yellow solid (23 mg, >99%). **m.p.** 78.6-81.0 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.94 (appt. d, *J* = 9.0 Hz, 2H), 7.01 (appt. d, *J* = 9.0 Hz, 2H), 4.94 (d, *J* = 2.4 Hz, 2H), 3.92 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 182.9, 165.4, 131.7, 127.7 (d, *J* = 2.8 Hz), 114.7, 57.4 (d, *J* = 15.5 Hz), 55.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 62.6; **HRMS** (ESI^+): calculated for $C_9H_9FO_4SNa$ [$M+Na^+$]: m/z = 255.0098, m/z found 255.0100; **IR** ν_{max} (ATR)/cm^{-1}: 2253, 1682, 1682, 1601, 1422, 1269, 1173.

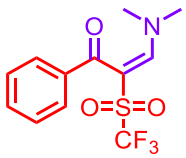
2-(4-Isopropoxy-3-methoxyphenyl)-2-oxoethane-1-sulfonyl fluoride (14f)



Following general procedure C (0.10 mmol), the title compound was isolated as a yellow oil (28 mg, 97%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 2.1 Hz, 1H), 7.50 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.93 (d, *J* = 8.6 Hz, 1H), 4.95 (d, *J* = 2.3 Hz, 2H), 4.71 (hept, *J* = 6.0 Hz, 1H), 3.92 (s, 3H), 1.44 (d, *J* = 6.1 Hz, 6H); **^{13}C NMR**

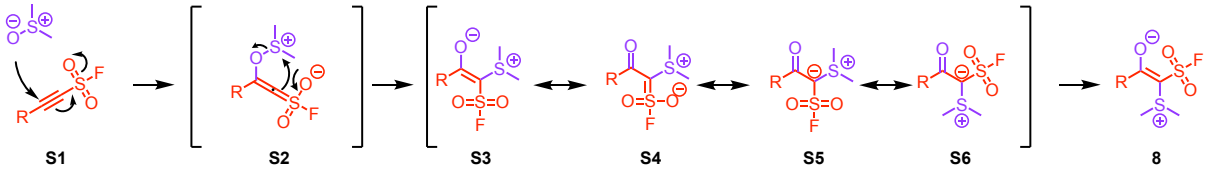
(101 MHz, $CDCl_3$) δ 182.9, 154.1, 150.5, 127.3 (d, *J* = 2.7 Hz), 124.4, 112.6, 111.2, 71.8, 57.3 (d, *J* = 15.4 Hz), 56.3, 22.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ 62.5; **HRMS** (ESI^+): calculated for $C_{12}H_{15}FO_5SNa$ [M+Na^+]: m/z = 313.0516, m/z found 313.0513; **IR** ν_{max} (ATR)/cm^{-1}: 2253, 1678, 1593, 1512, 1422, 1277, 1153, 1107.

(*E*)-3-(Dimethylamino)-1-phenyl-2-((trifluoromethyl)sulfonyl)prop-2-en-1-one (9a-CF_3)[1]



(*E*)-3-(Dimethylamino)-1-phenyl-2-((trifluoromethyl)sulfonyl)prop-2-en-1-one was synthesised according to the procedure by Hanack and Wilhelm.[1] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (appt. d, *J* = 7.8 Hz, 2H), 7.76 (s, 1H), 7.59 (appt. t, *J* = 7.3 Hz, 1H), 7.47 (appt. t, *J* = 7.5 Hz, 2H), 3.30 (s, 3H), 2.65 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 188.9, 158.2, 139.5, 133.6, 129.9, 128.6, 120.6 (q, *J* = 326.1 Hz), 97.4, 48.1, 41.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -78.1; **IR** ν_{max} (ATR)/cm^{-1}: 2981, 2933, 1697, 1595, 1580, 1452, 1331, 980, 985, 802.

Plausible Reaction Mechanism for the Reaction of DMSO with SASFs



Scheme S1. Plausible reaction mechanism for DMSO incorporation to SASFs.

First, nucleophilic addition of the oxygen atom of DMSO to the highly activated SASF triple bond occurs, pushing electron density onto the oxygen atom of the sulfonyl fluoride group to give intermediate **S2**. The oxygen atom then pushes electron density back through attacking the sulfur atom of DMSO and cleaving the S-O bond to give **S3**. It is then proposed that during tautomerisation of **S3**, tautomer **S5** can undergo free rotation of the C-C bond in order to give the least sterically hindered configuration and finally give the isomerised product **8**."

2D NMR Spectra for Compounds 9a-CF3 and 9a

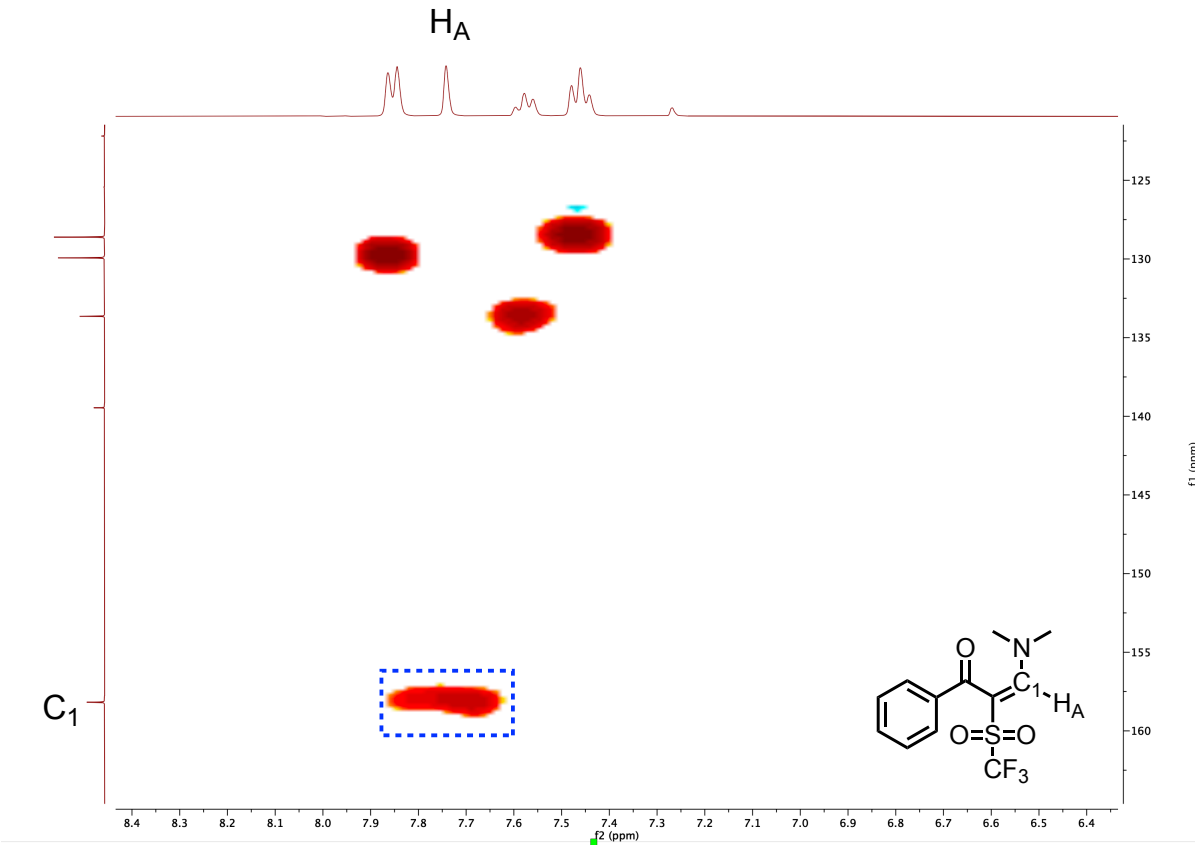


Figure S1. HSQC spectra of **9a-CF_3** ($CDCl_3$) showing the correlation between H_A and C_1 (blue).

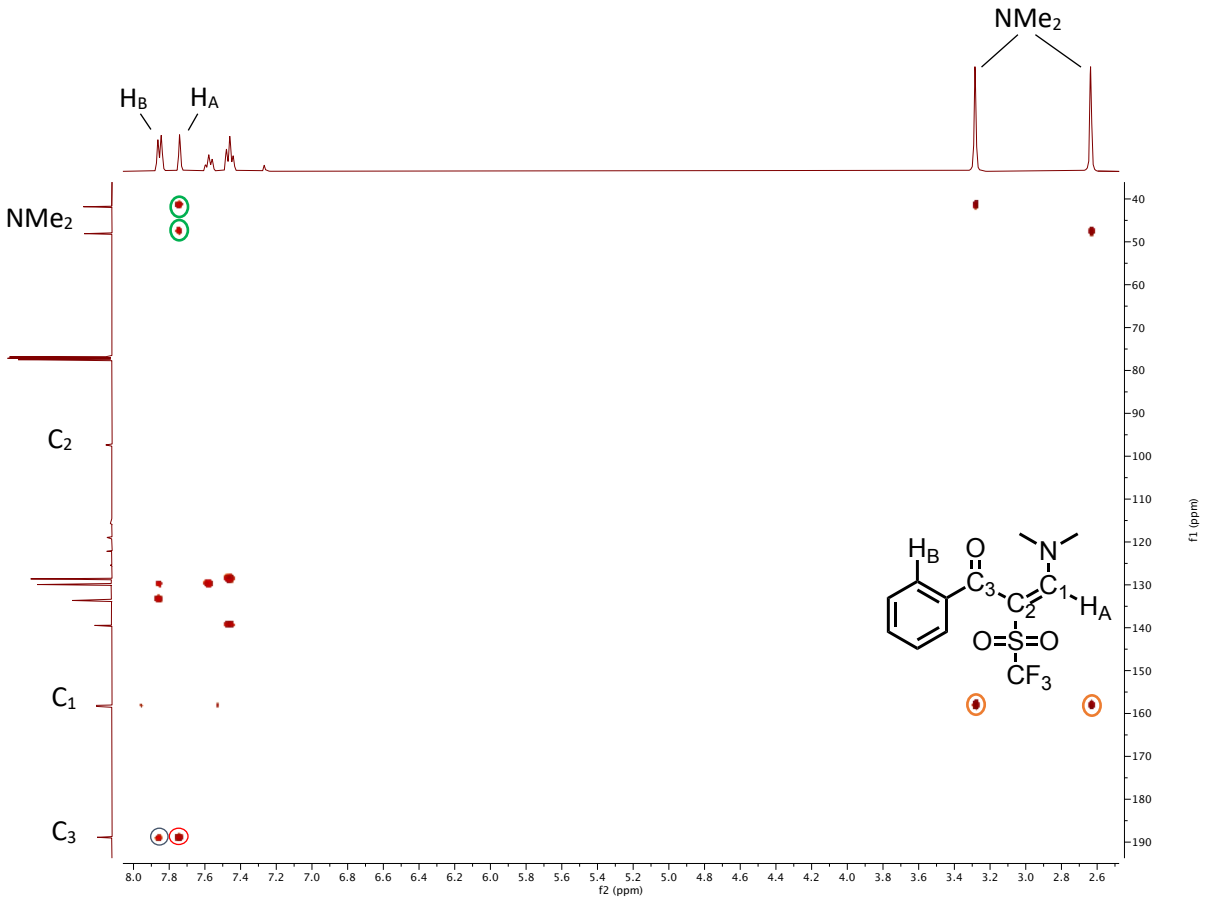


Figure S2. HMBC spectra of **9a-CF_3** ($CDCl_3$) showing the correlation between H_A and NMe_2 (green), H_A and C_3 (red), H_B and C_3 (blue) and NMe_2 and C_1 (orange).

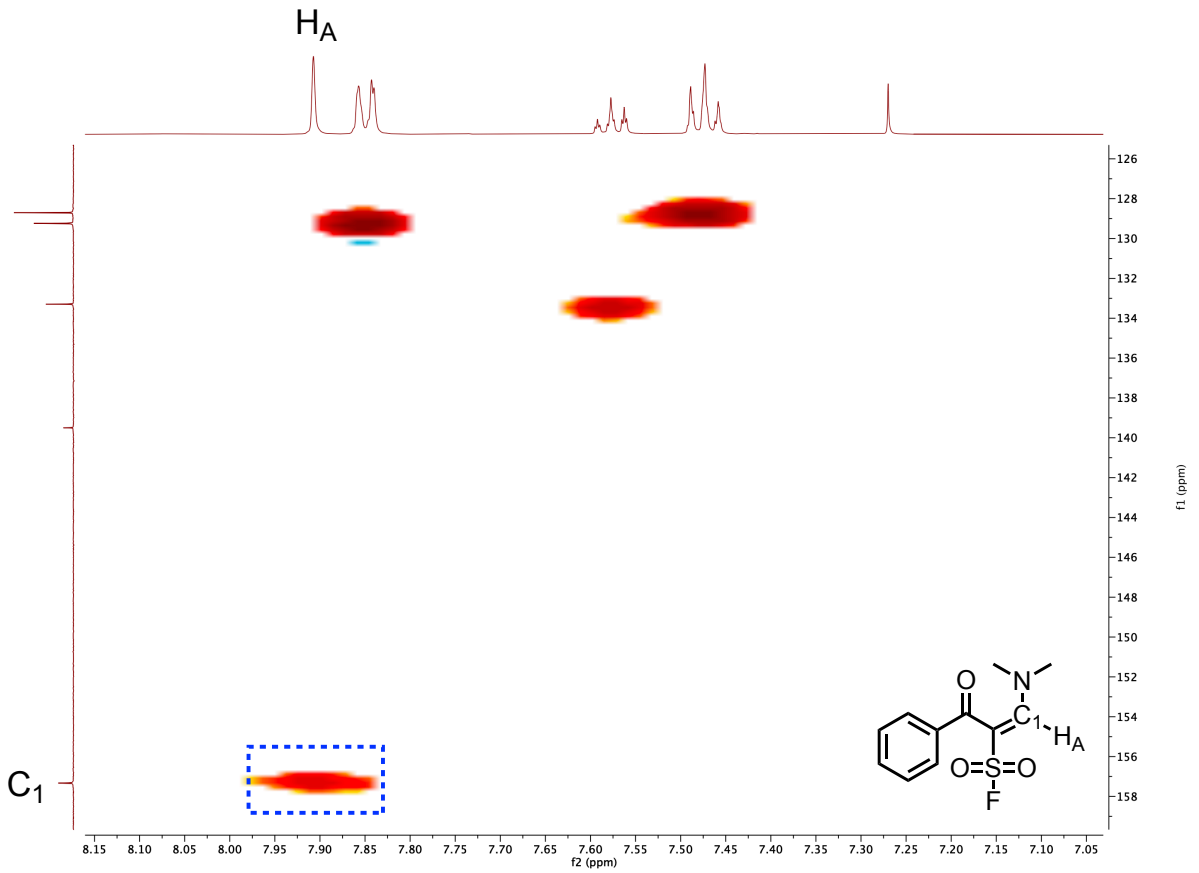


Figure S3. HSQC spectra of **9a** ($CDCl_3$) showing the correlation between H_A and C_1 (blue).

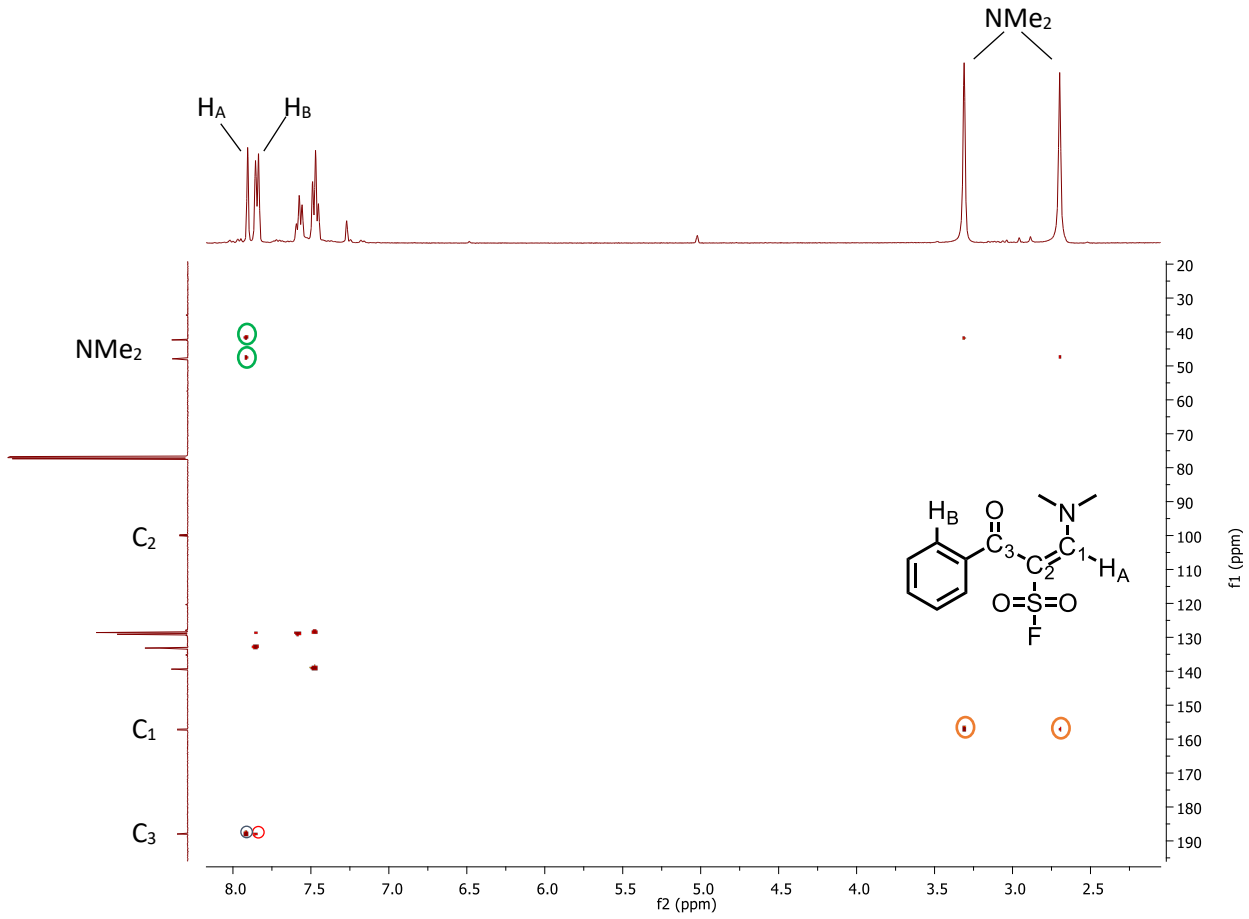
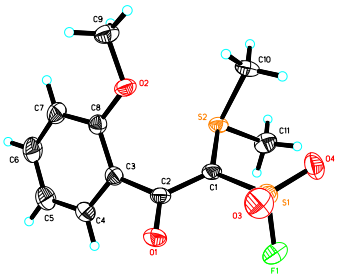


Figure S4. HMBC spectra of **9a** ($CDCl_3$) showing the correlation between H_A and NMe_2 (green), H_A and C_3 (blue), H_B and C_3 (red) and NMe_2 and C_1 (orange).

X-ray Crystallography Data

Method: All crystals were grown by slow diffusion ($CHCl_3$/petroleum ether).

X-ray data of structure 8l (CCDC2120509)



Datablock: mo_d8v19482_0m

Bond precision: C-C = 0.0047 A Wavelength=0.71073

Cell: a=9.4459(3) b=12.5540(5) c=13.0923(5)
alpha=114.362(1) beta=102.263(1) gamma=96.976(1)

Temperature: 293 K

	Calculated	Reported
Volume	1343.37(9)	1343.37(9)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C11 H13 F O4 S2	?
Sum formula	C11 H13 F O4 S2	C11 H13 F O4 S2
Mr	292.33	292.33
Dx,g cm-3	1.445	1.445
Z	4	4
Mu (mm-1)	0.411	0.411
F000	608.0	608.0
F000'	609.33	
h,k,lmax	11,15,15	11,15,15
Nref	4997	4987
Tmin,Tmax	0.944,0.972	0.562,0.746
Tmin'	0.944	

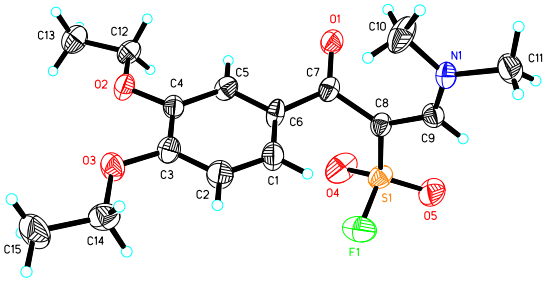
Correction method= # Reported T Limits: Tmin=0.562
Tmax=0.746 AbsCorr = MULTI-SCAN

Data completeness= 0.998 Theta(max)= 25.496

R(reflections)= 0.0466(3871) wR2(reflections)= 0.1115(4987)

S = 1.062 Npar= 331

X-ray data of structure 9i (CCDC2120512)



Datablock: mo_d8v20433_0m

Bond precision: C-C = 0.0134 A Wavelength=0.71073

Cell: a=8.4205(19) b=19.723(5) c=10.592(2)
alpha=90 beta=107.954(6) gamma=90

Temperature: 293 K

	Calculated	Reported
Volume	1673.4(7)	1673.4(7)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C15 H20 F N O5 S	?
Sum formula	C15 H20 F N O5 S	C15 H20 F N O5 S
Mr	345.38	345.38
Dx,g cm-3	1.371	1.371
Z	4	4
Mu (mm-1)	0.227	0.227
F000	728.0	728.0
F000'	728.91	
h,k,lmax	10,23,12	10,23,12
Nref	2943	2942
Tmin,Tmax	0.973,0.989	0.613,0.746
Tmin'	0.964	

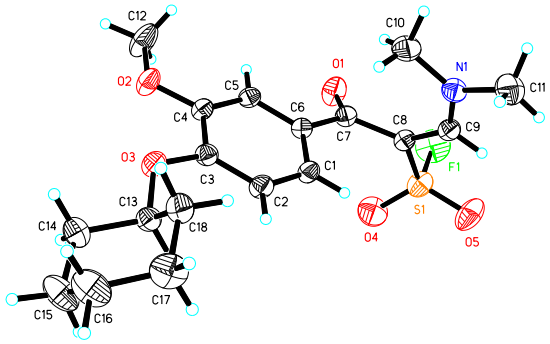
Correction method= # Reported T Limits: Tmin=0.613
Tmax=0.746 AbsCorr = MULTI-SCAN

Data completeness= 1.000 Theta(max)= 24.997

R(reflections)= 0.1343(1963) wR2(reflections)= 0.4419(2942)

S = 1.676 Npar= 213

X-ray data of structure 9j (CCDC2120511)



Datablock: d8v20436

Bond precision: C-C = 0.0043 A Wavelength=0.71073

Cell: a=12.521(11) b=13.867(12) c=11.473(8)
alpha=90 beta=100.55(2) gamma=90

Temperature: 293 K

	Calculated	Reported
Volume	1958(3)	1958(3)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C18 H24 F N O5 S	?
Sum formula	C18 H24 F N O5 S	C18 H24 F N O5 S
Mr	385.44	385.44
Dx,g cm-3	1.308	1.307
Z	4	4
Mu (mm-1)	0.202	0.202
F000	816.0	816.0
F000'	816.94	
h,k,lmax	15,16,13	15,16,13
Nref	3638	3635
Tmin,Tmax	0.981,0.992	0.485,0.746
Tmin'	0.976	

Correction method= # Reported T Limits: Tmin=0.485
Tmax=0.746 AbsCorr = MULTI-SCAN

Data completeness= 0.999 Theta(max)= 25.495

R(reflections)= 0.0531(2279) wR2(reflections)= 0.1457(3635)

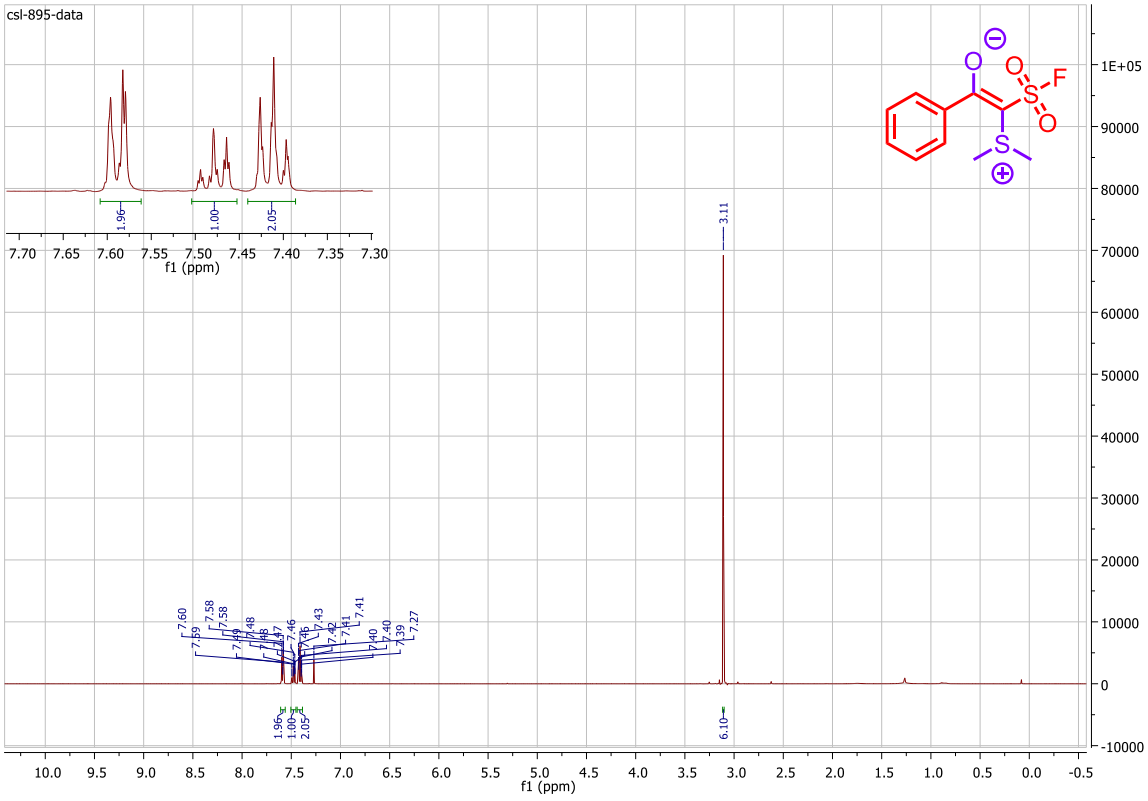
S = 1.056 Npar= 238

References

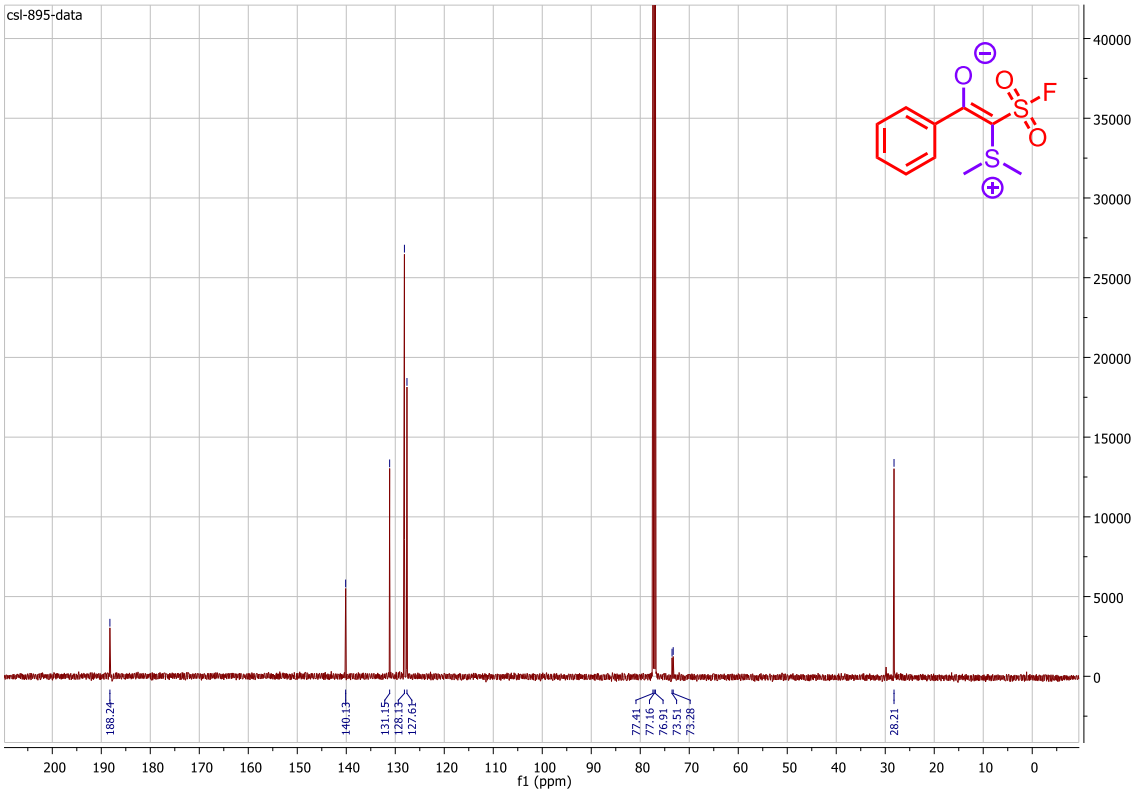
1 M. Hanack and B. Wilhelm, *Angew. Chem., Int. Ed.,* 1989, **28**, 1057–1059.
2 T. Henkel, T. Krügerke and K. Seppelt, *Angew. Chem., Int. Ed*., 1990, **29**, 1128–1129.
3 D. Chen, X. Nie, Q. Feng, Y. Zhang, Y. Wang, Q. Wang, L. Huang, S. Huang and S. Liao, *Angew. Chem., Int. Ed.*, 2021, **60**, 27271–27276.

^{1}H, ^{13}C and ^{19}F NMR spectra

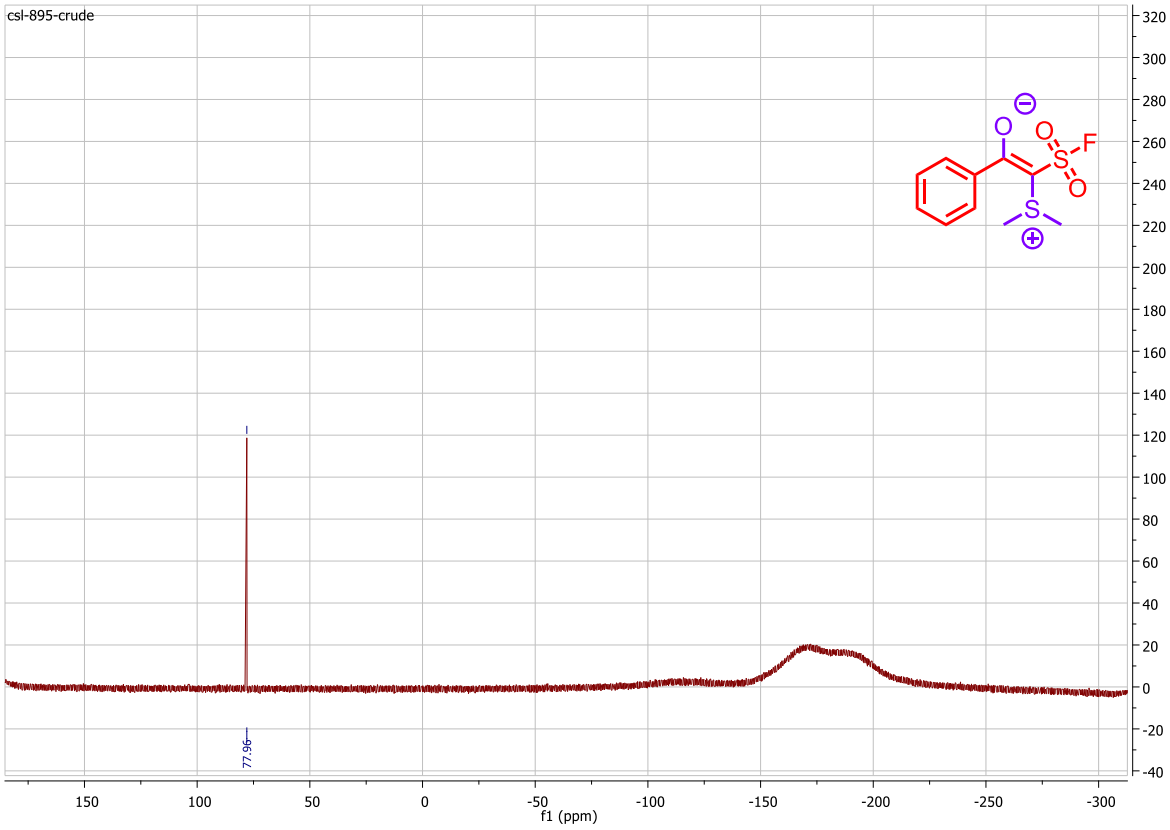
^{1}H NMR **8a**:



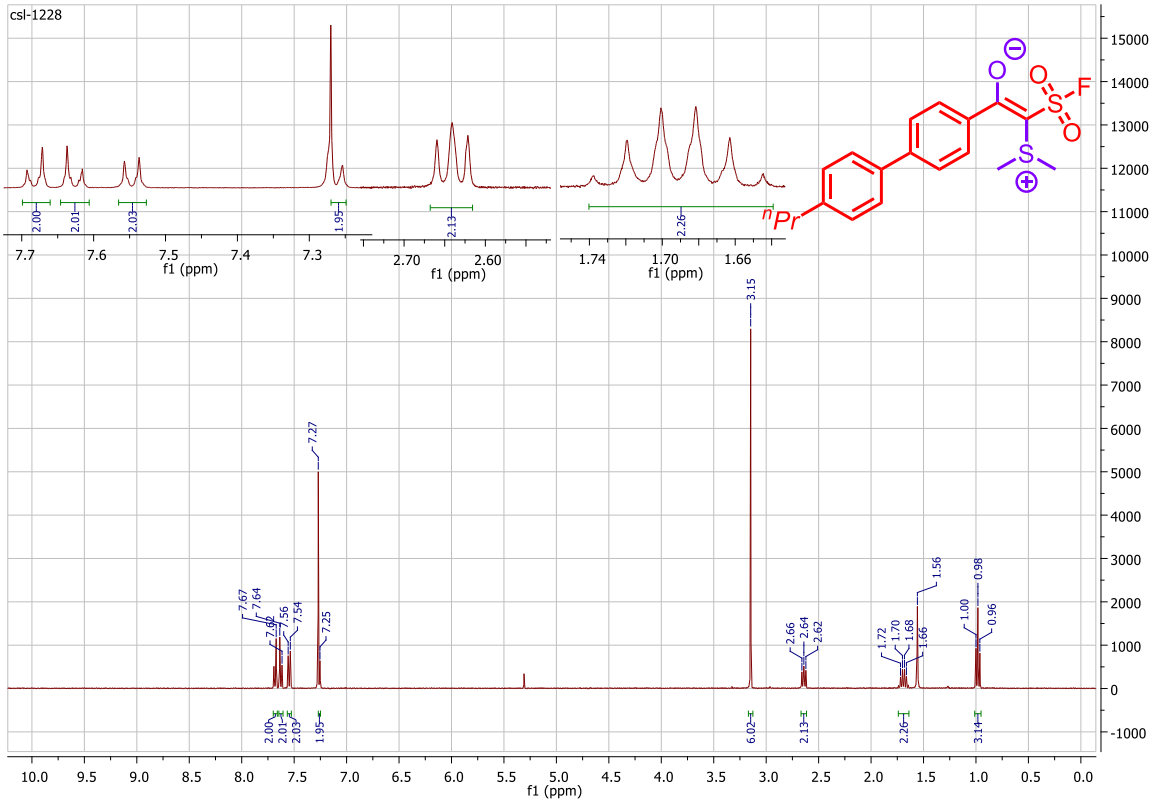
^{13}C NMR **8a**:



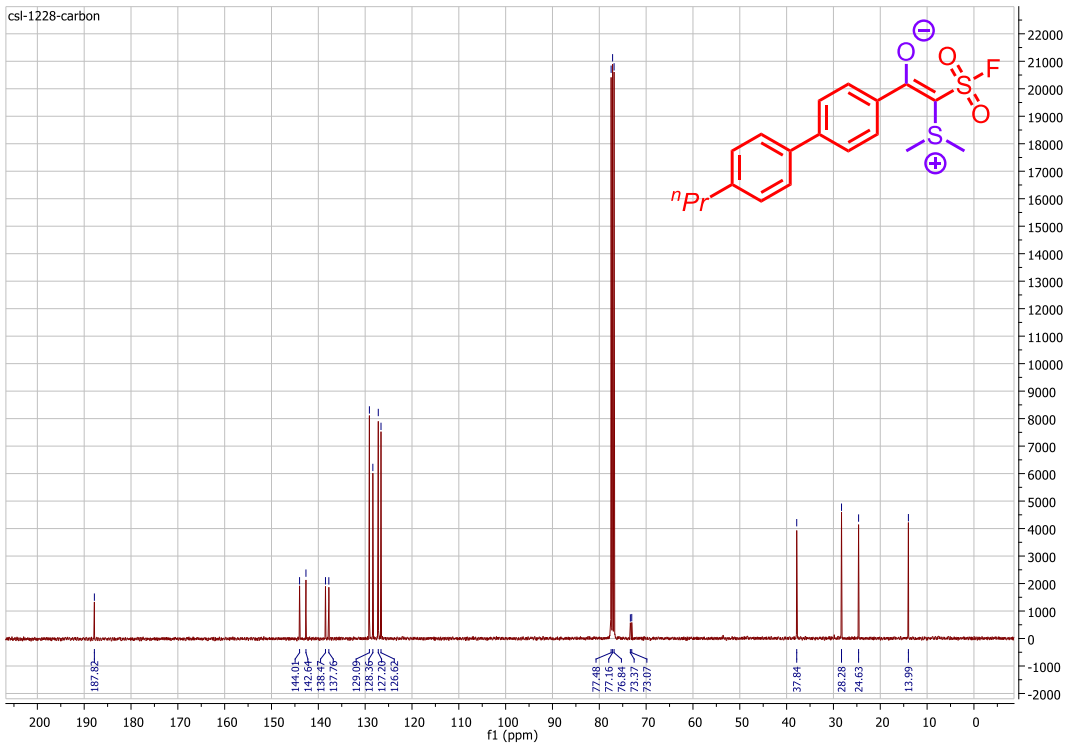
^{9}F NMR **8a**:


csl-895-crude
77.96
150
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
O
O
S
F
O
S

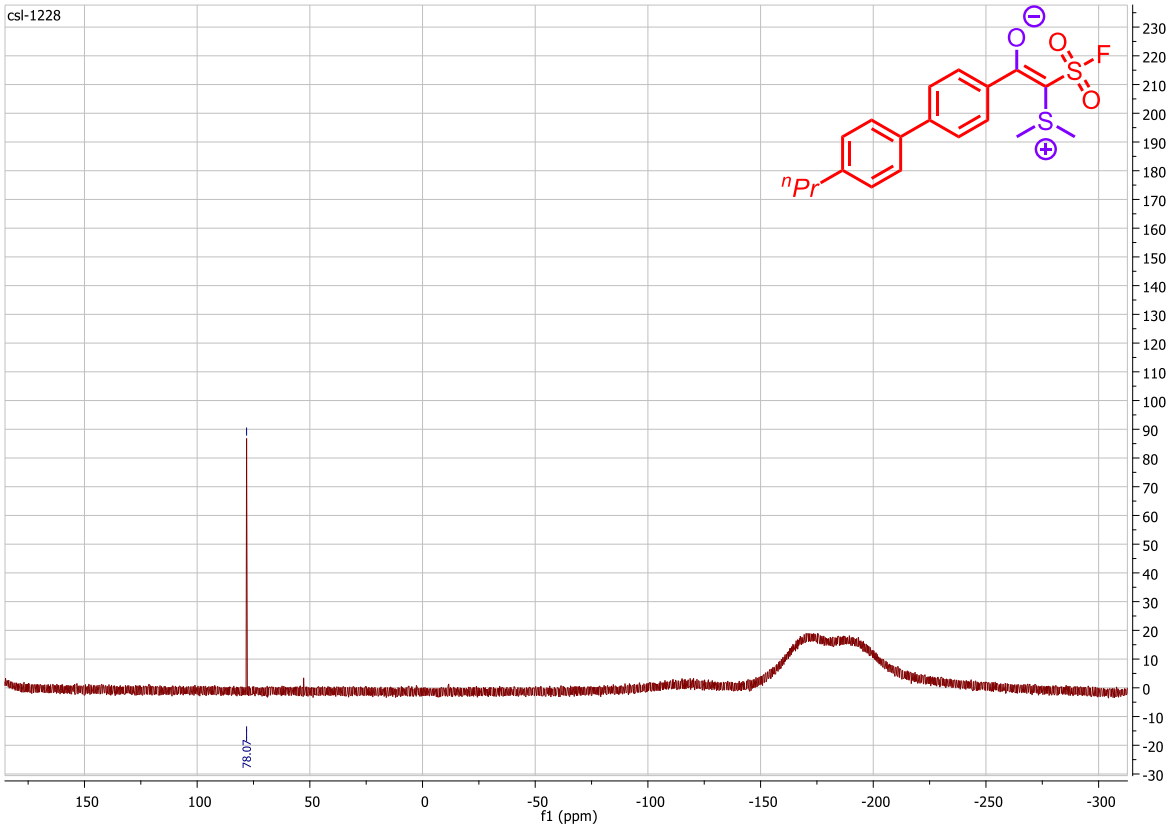
^{1}H NMR **8b**:



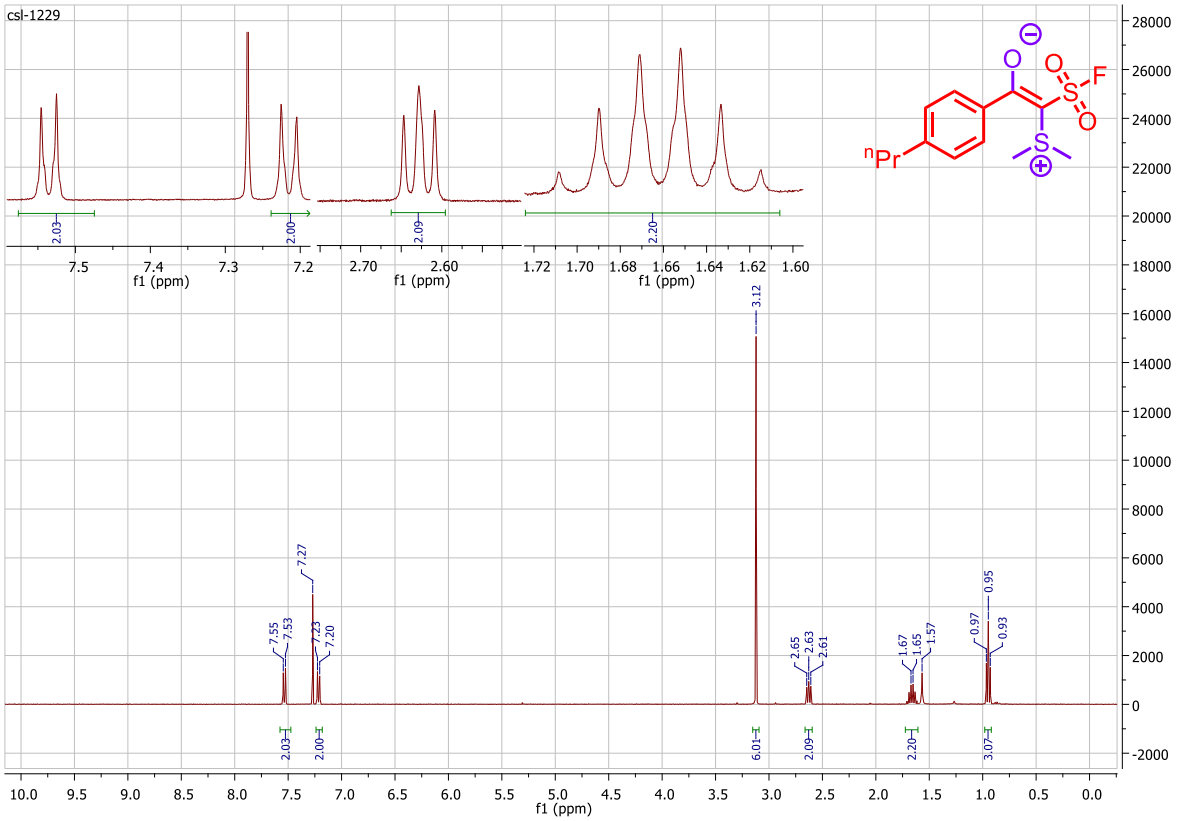
^{13}C NMR **8b**:



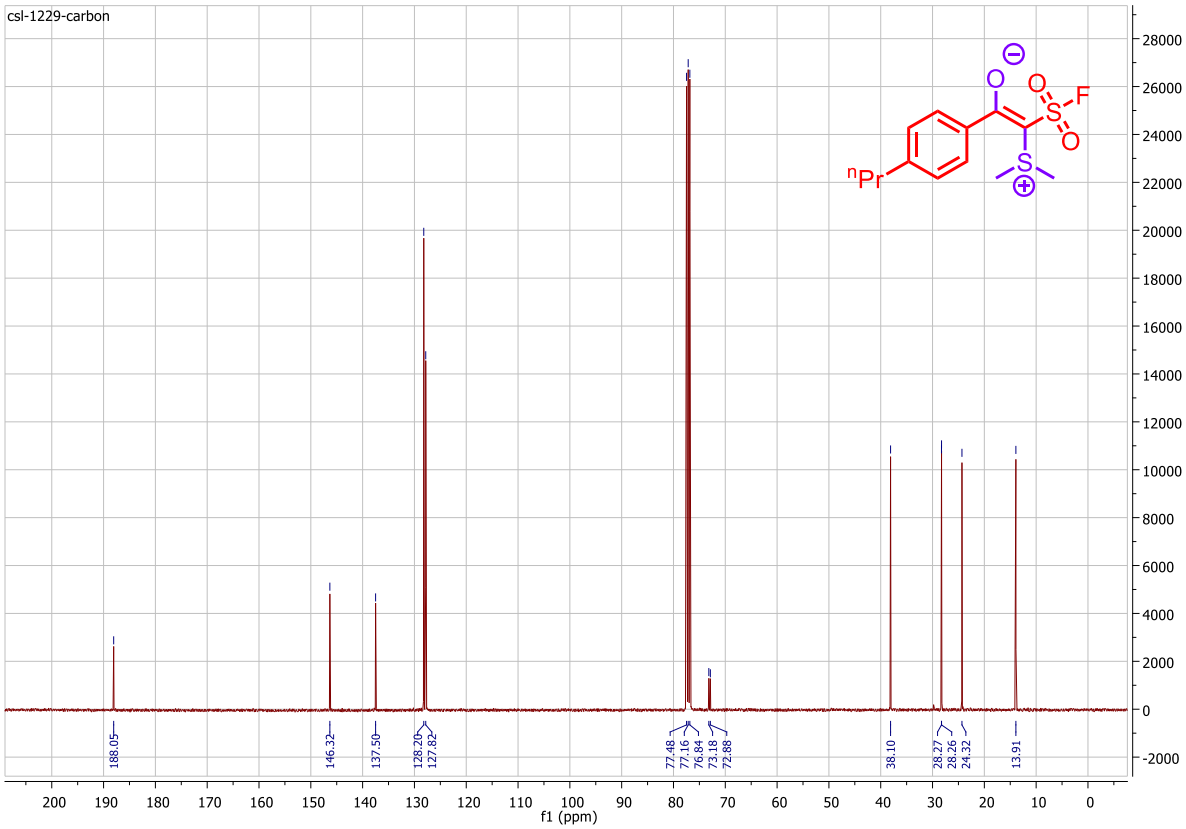
^{19}F NMR **8b**:


csl-1228
78.07
150
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
O
O
S
F
O
S
nPr

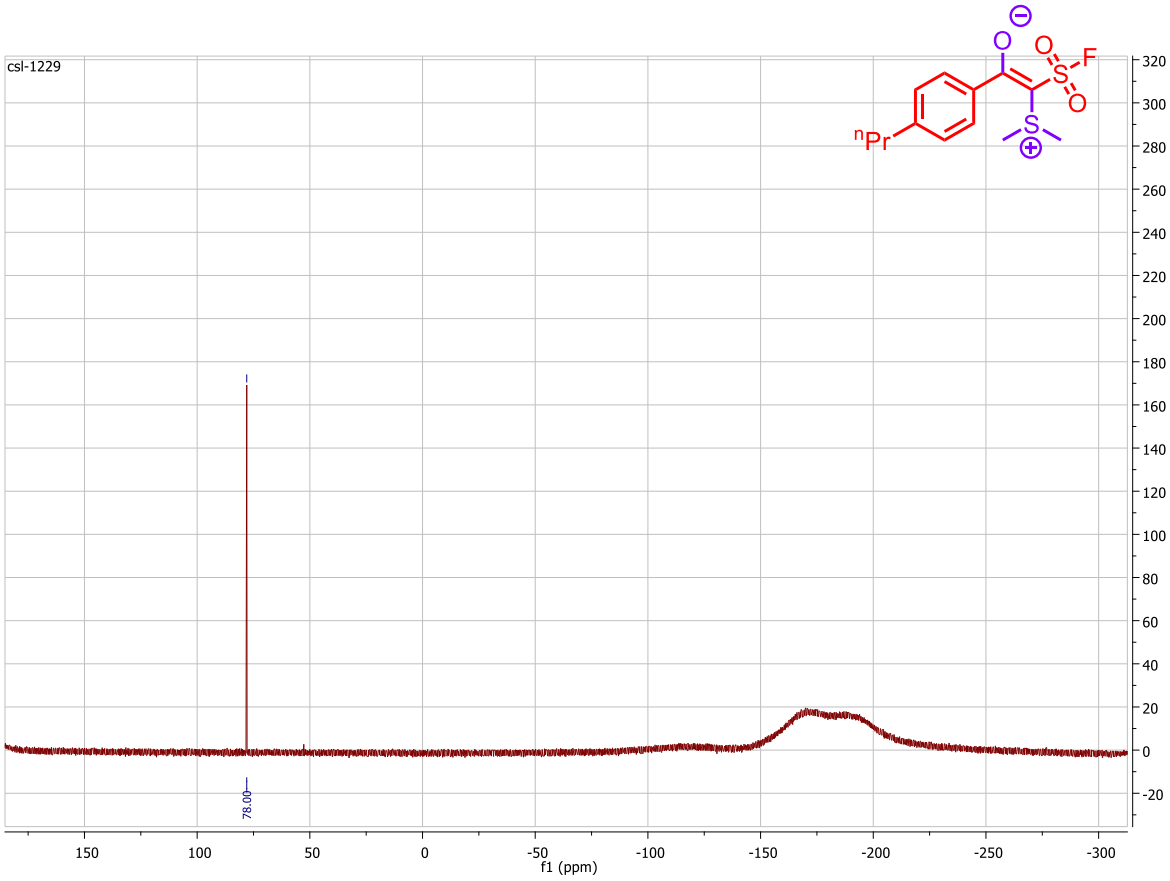
^{1}H NMR **8c**:



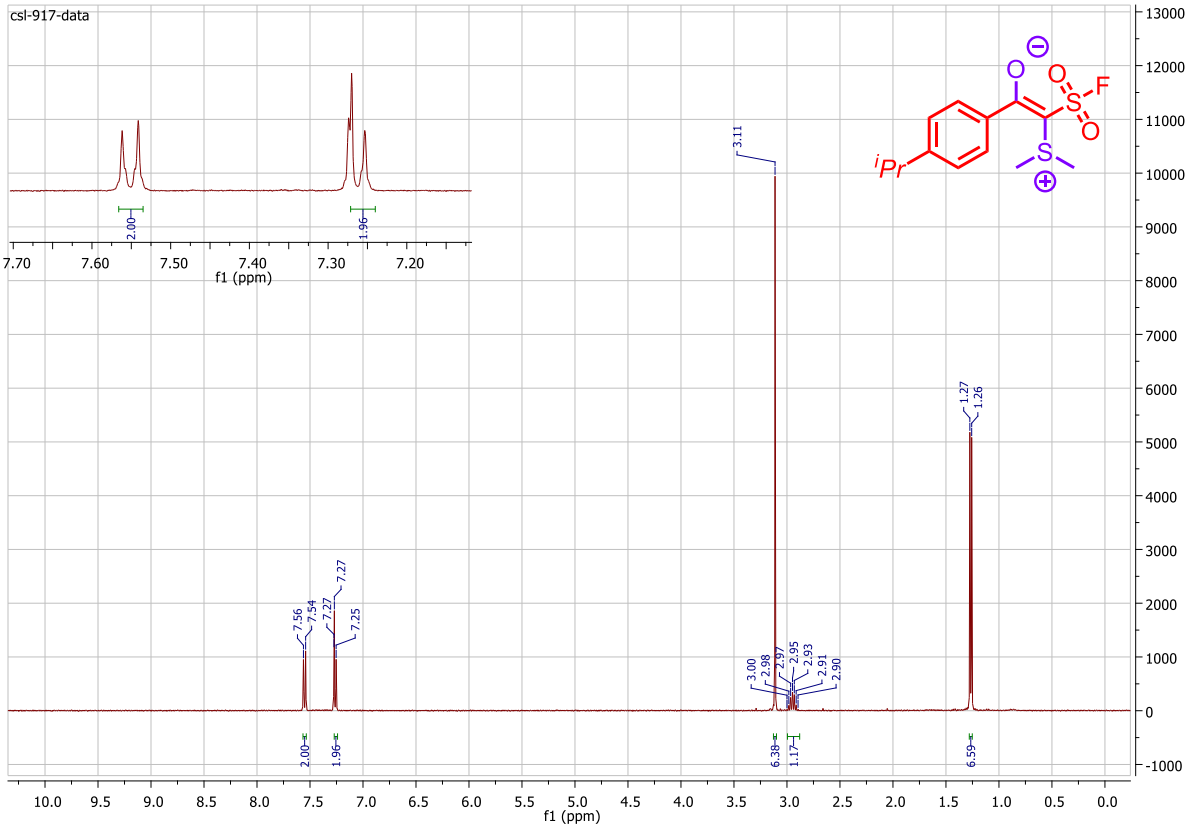
^{13}C NMR **8c**:



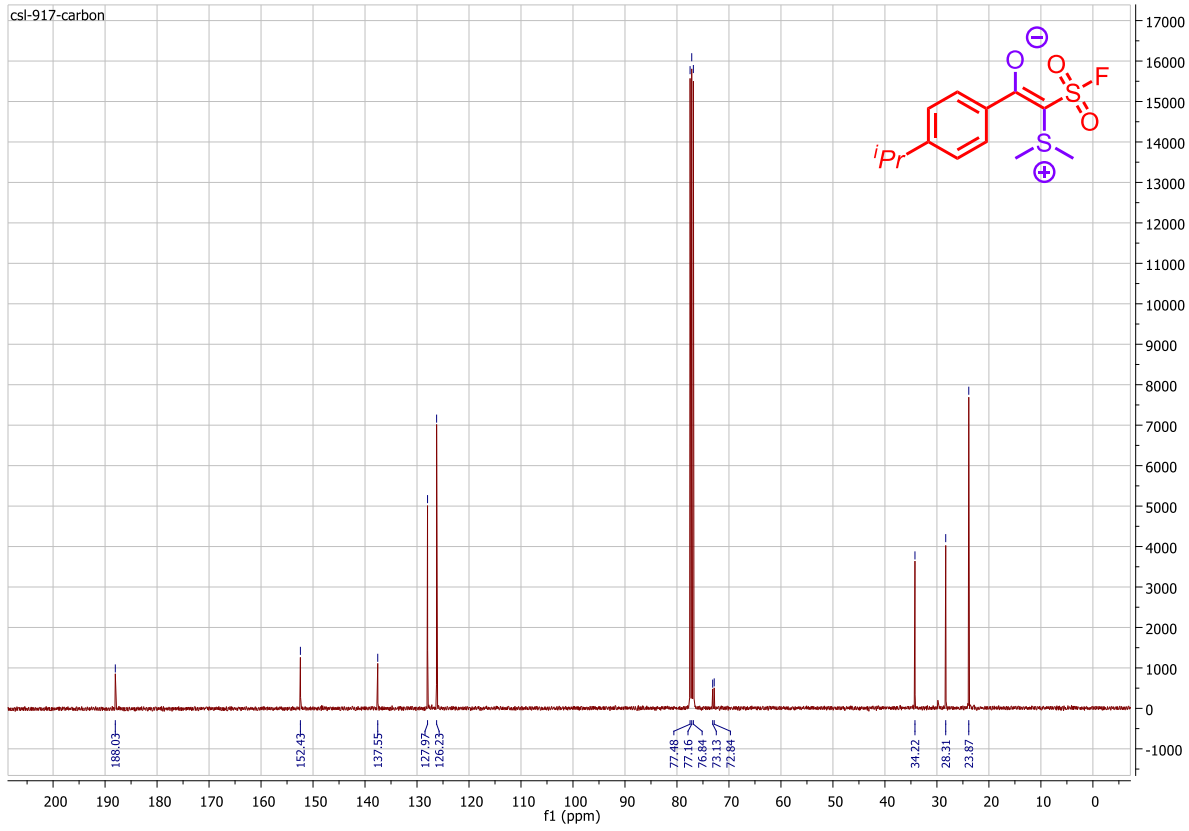
^{19}F NMR: **8c**:


csl-1229
78.00
150
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20

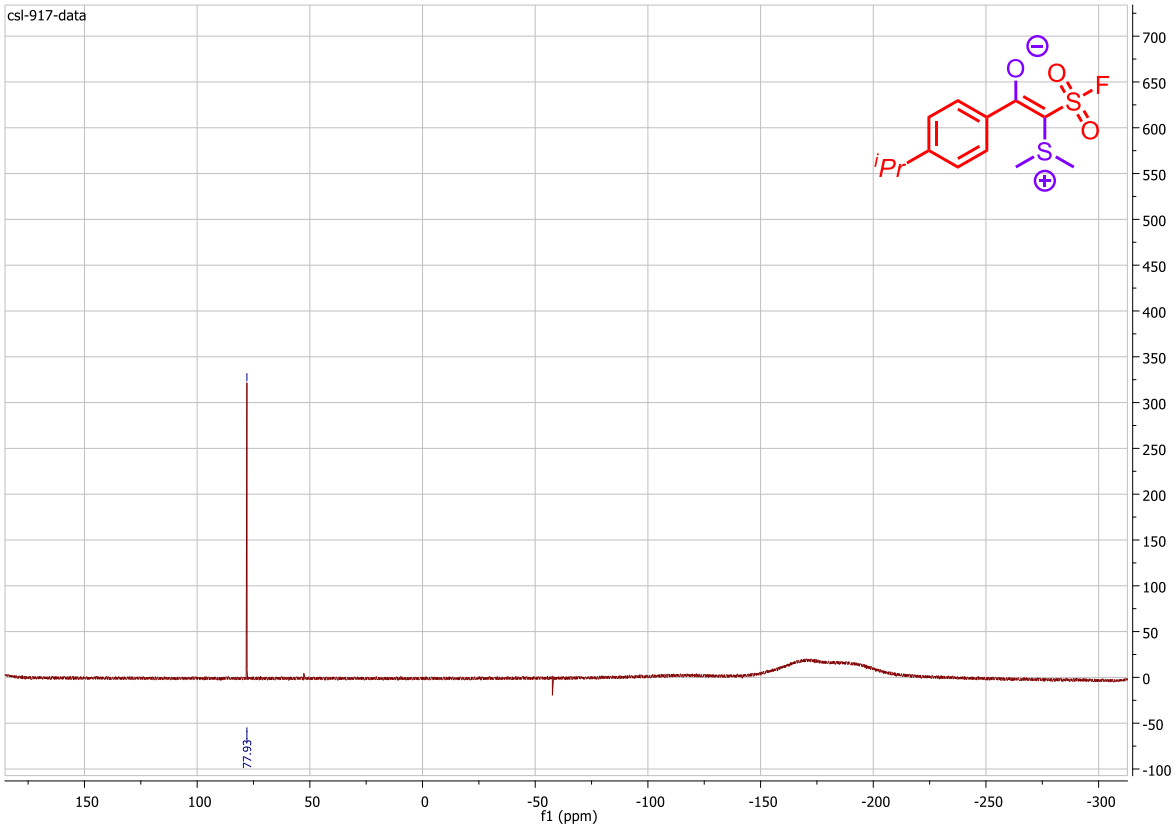
^{1}H NMR **8d**:



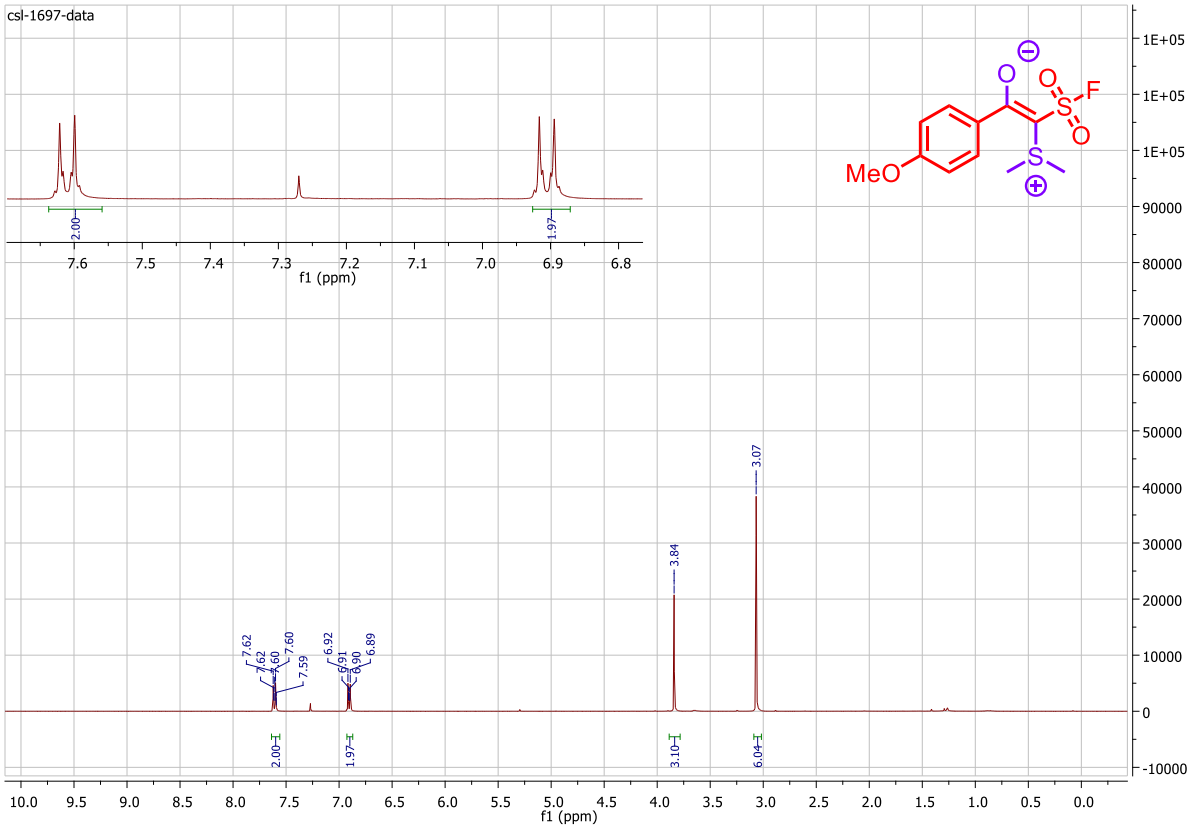
^{13}C NMR **8d**:



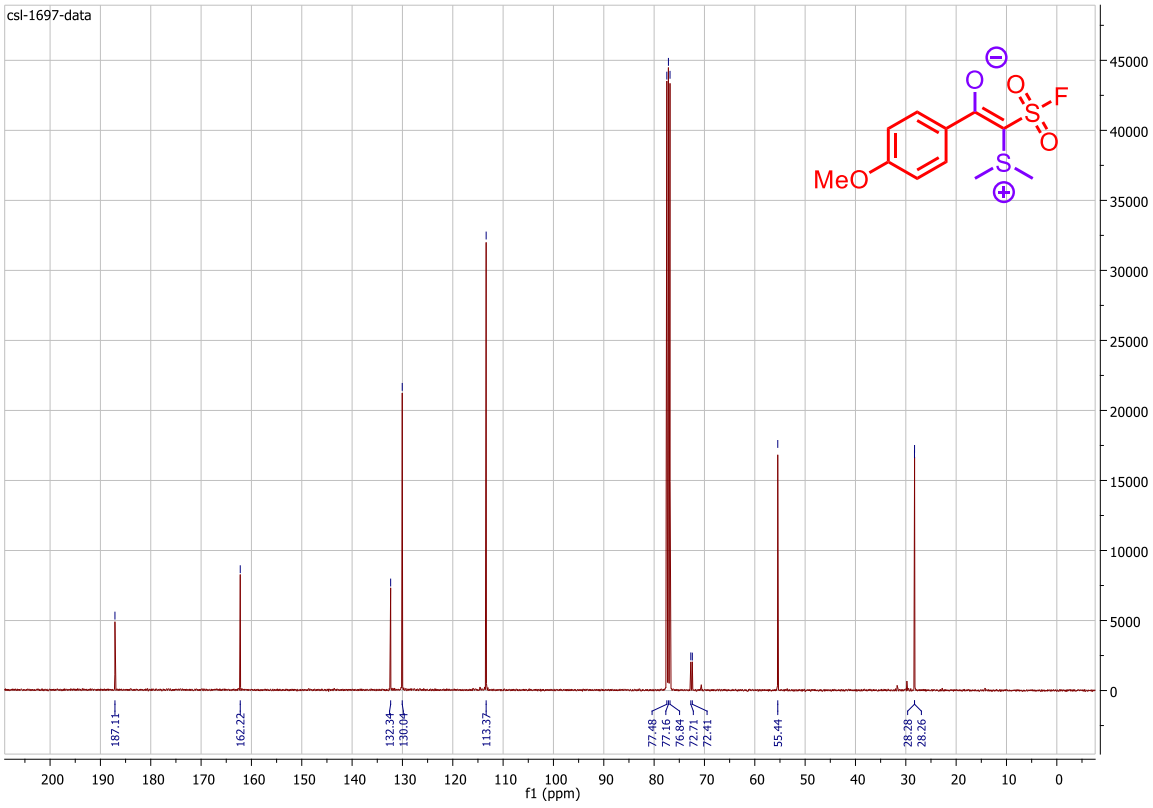
^{19}F NMR **8d**:


csl-917-data
77.93
150
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
-100
O
O
S
F
O
S
iPr

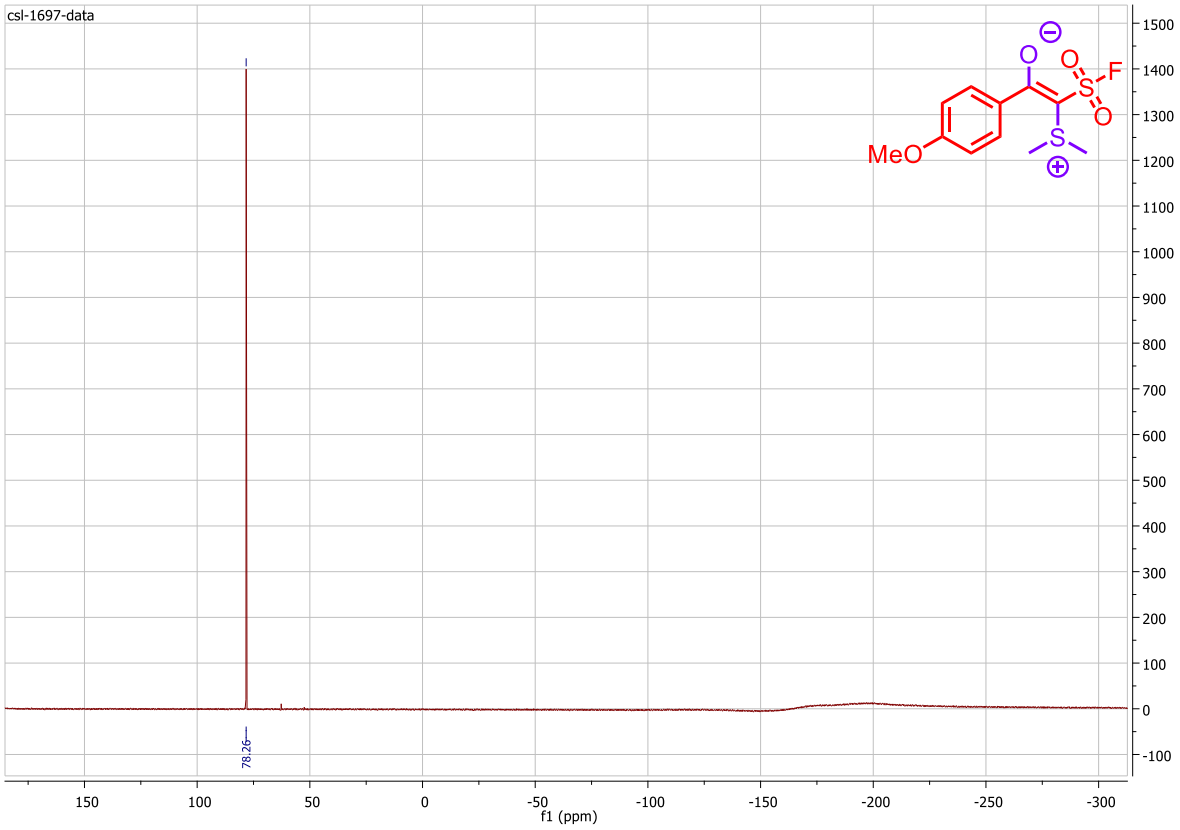
^{1}H NMR **8e**:



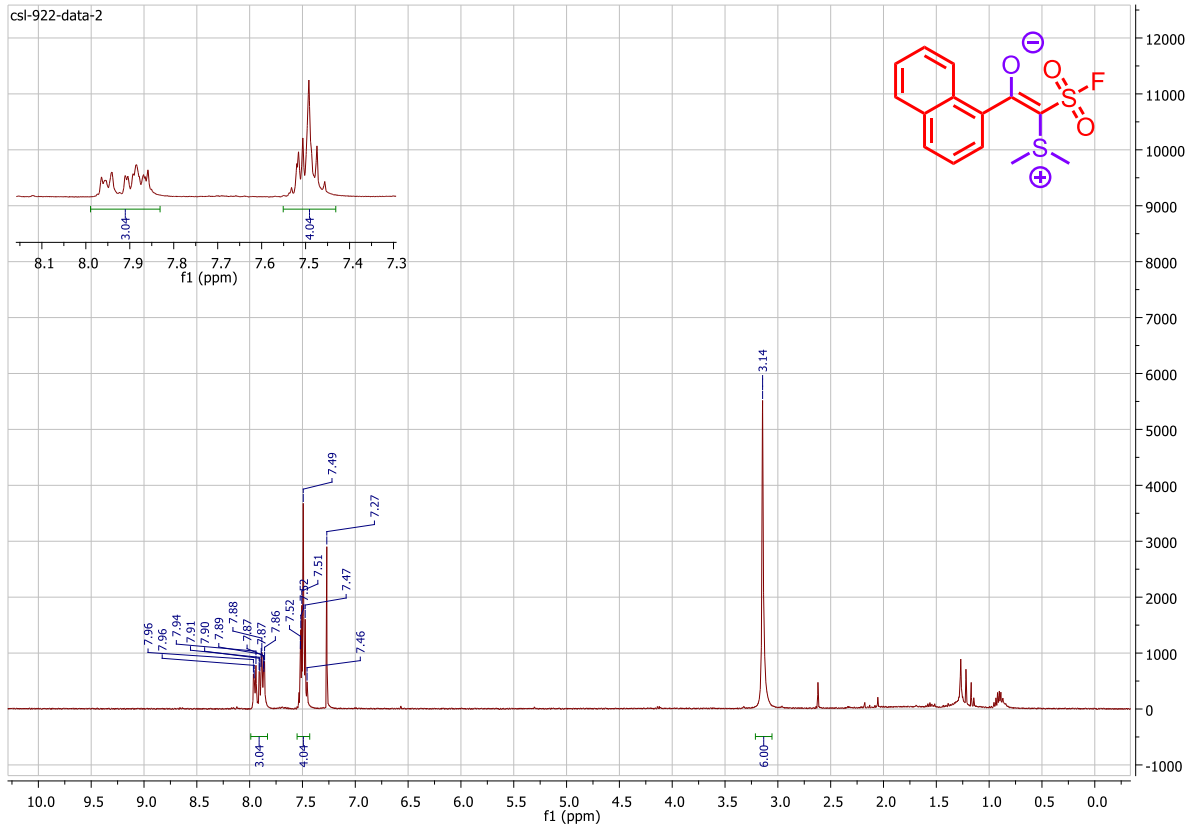
^{13}C NMR **8e**:



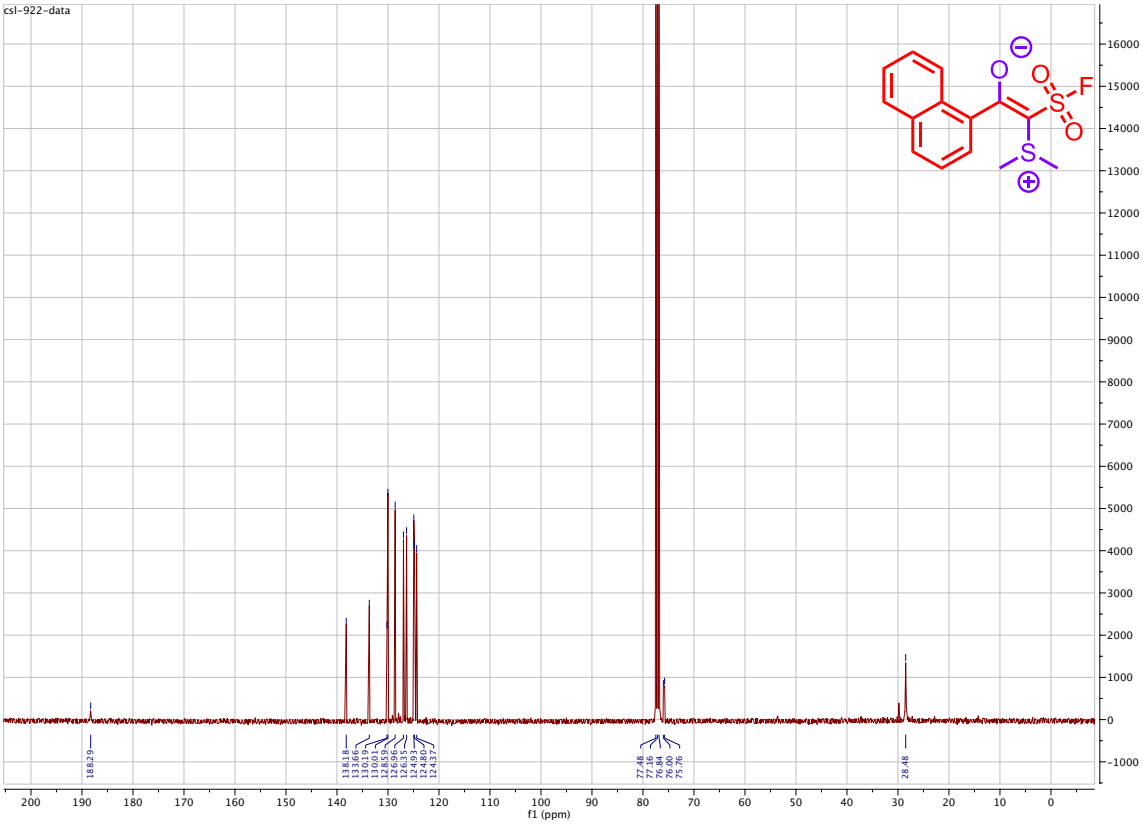
^{19}F NMR **8e**:


csl-1697-data
78.26
150
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
MeO
O
O
S
F
O
S

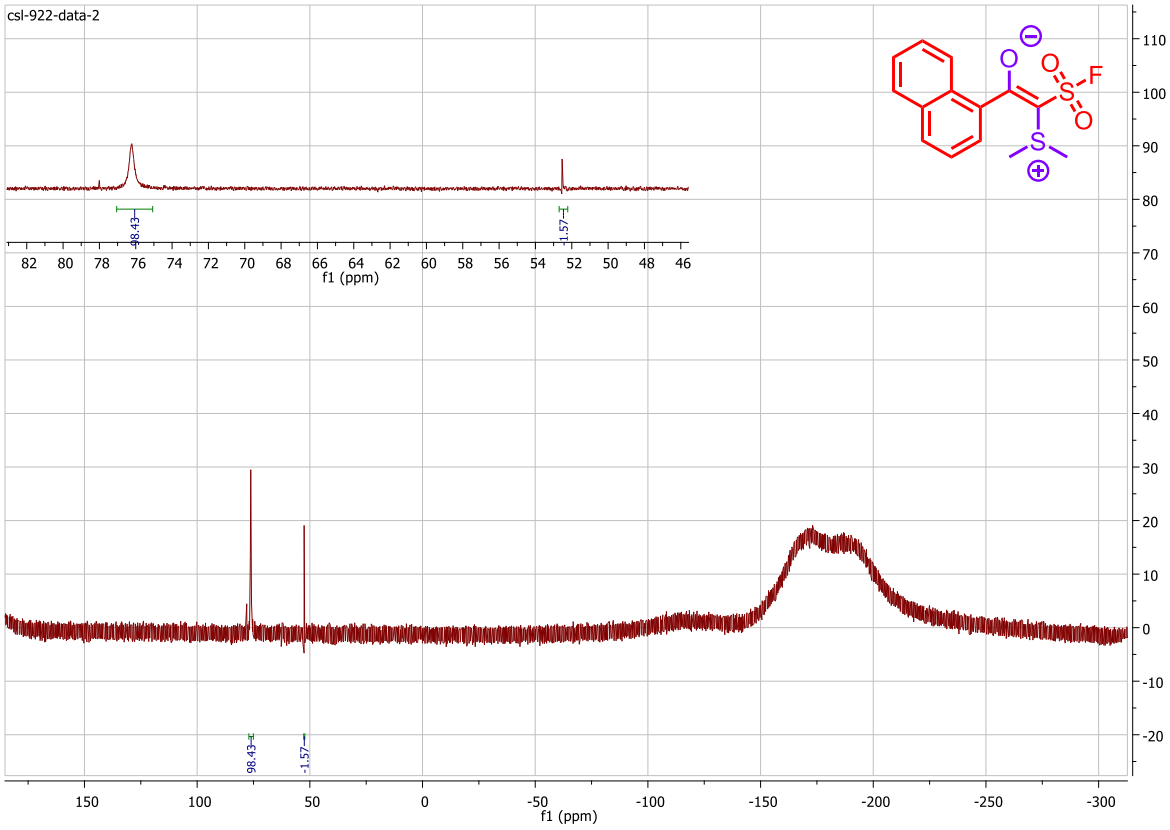
^{1}H NMR **8f**:



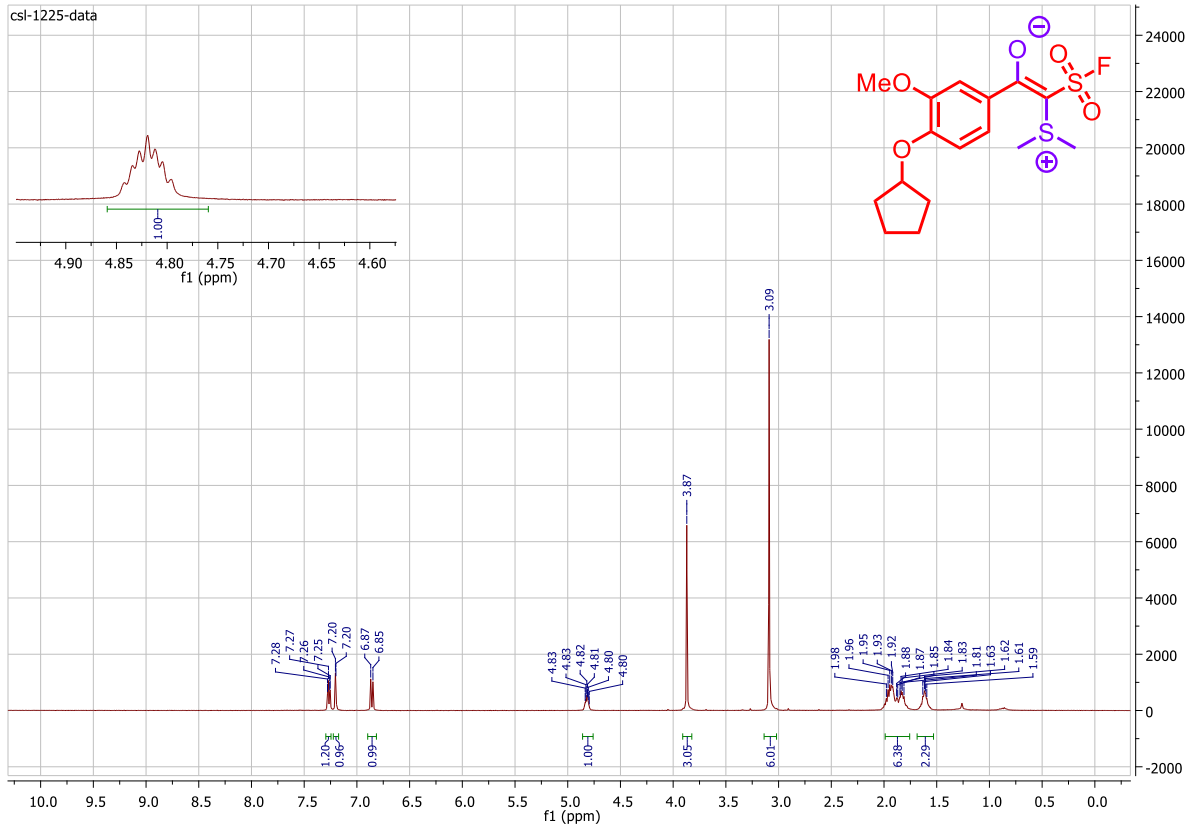
^{13}C NMR **8f**:



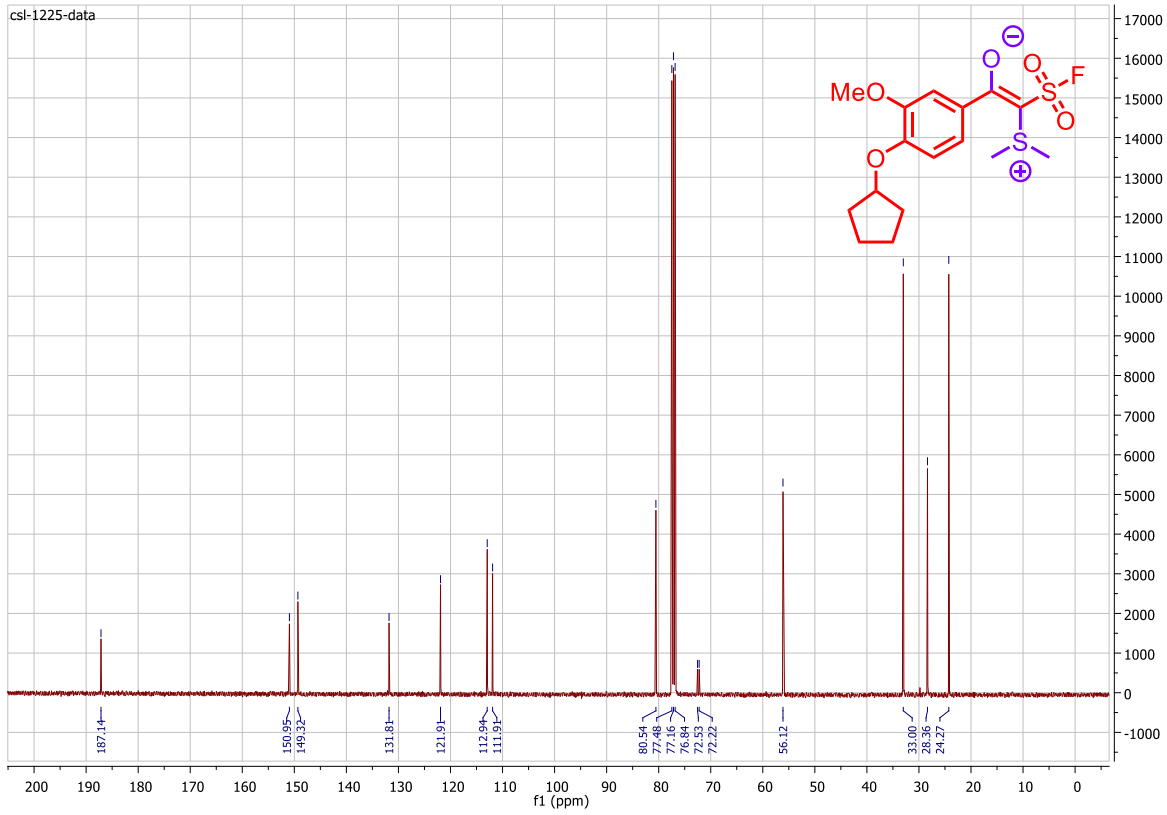
^{19}F NMR **8f**:



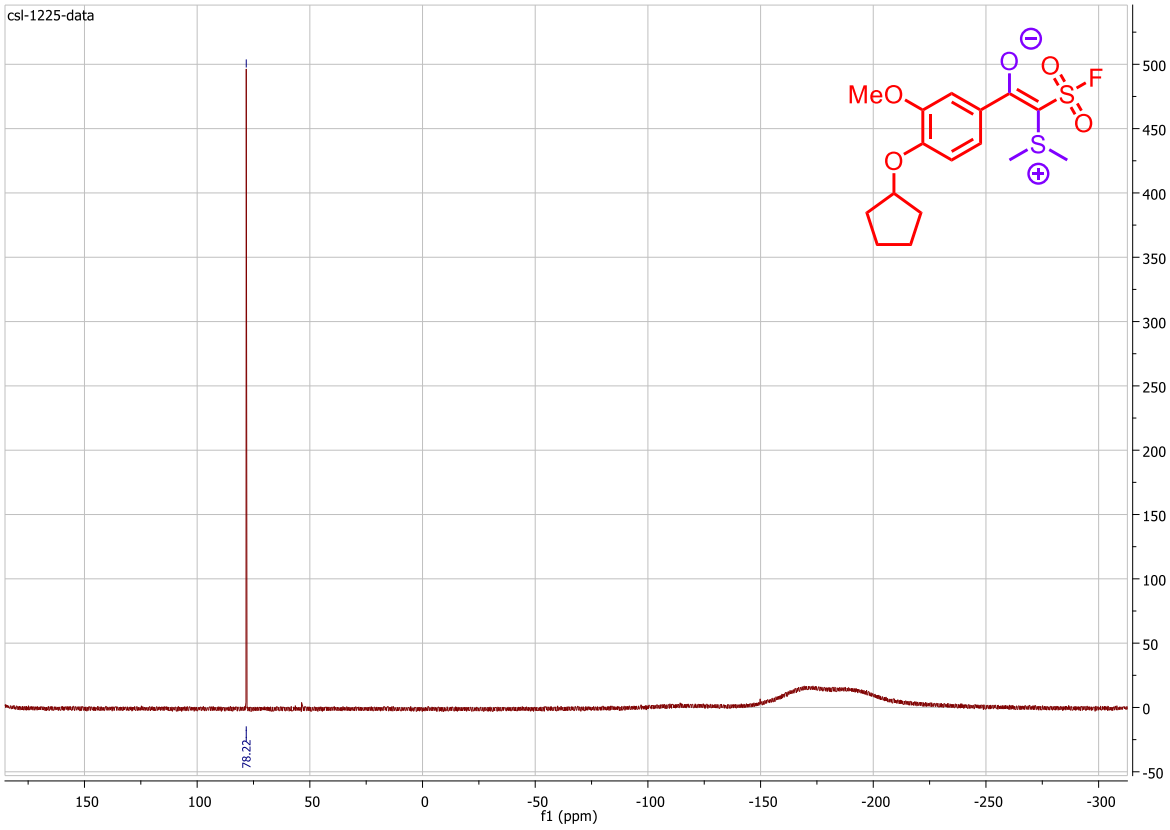
^{1}H NMR **8g**:



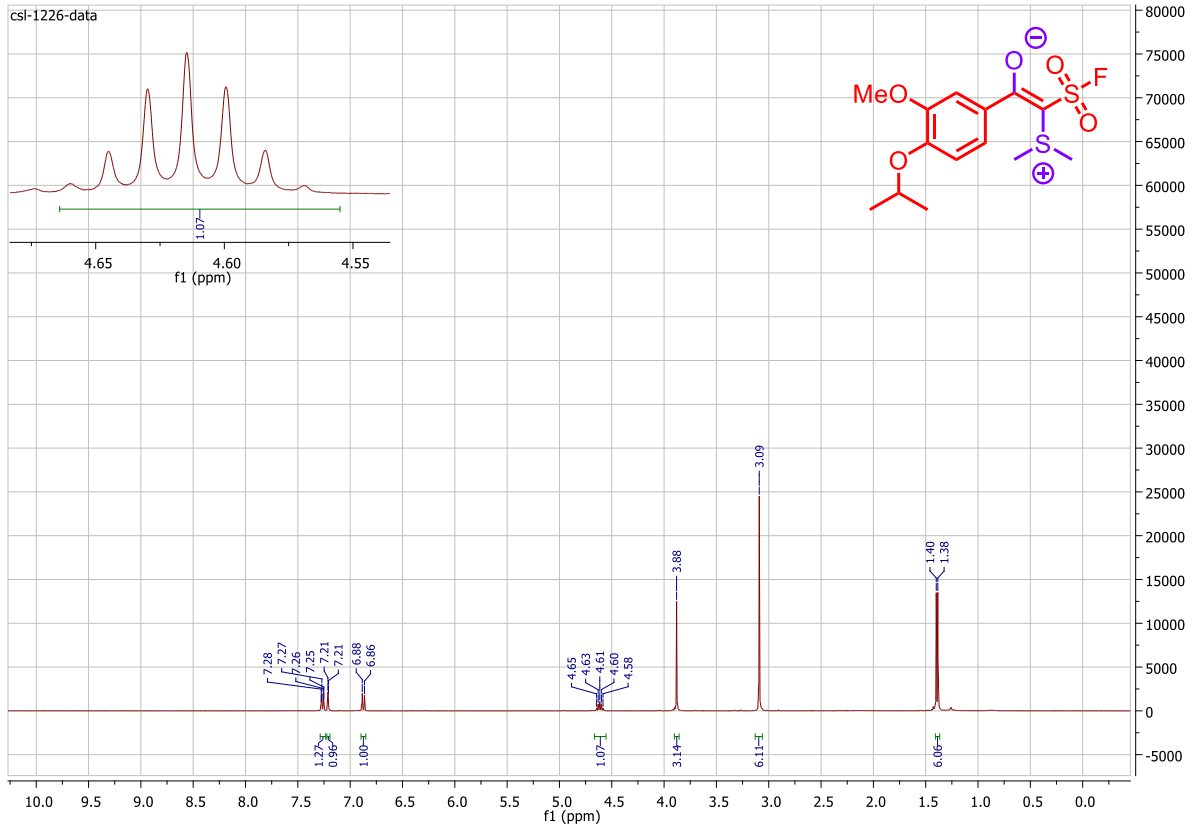
^{13}C NMR **8g**:



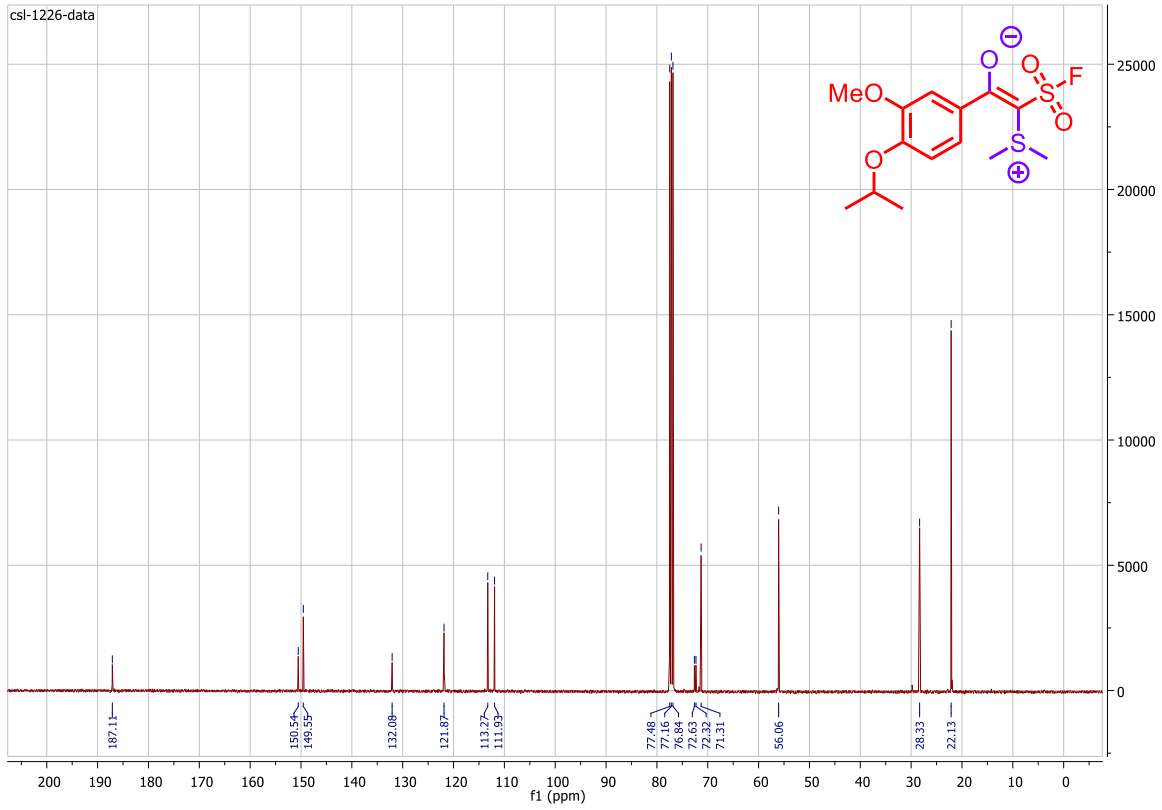
^{19}F NMR **8g**:


csl-1225-data
MeO
O
O
S
F
O
S
O
78.22
150
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)
500
450
400
350
300
250
200
150
100
50
0
-50

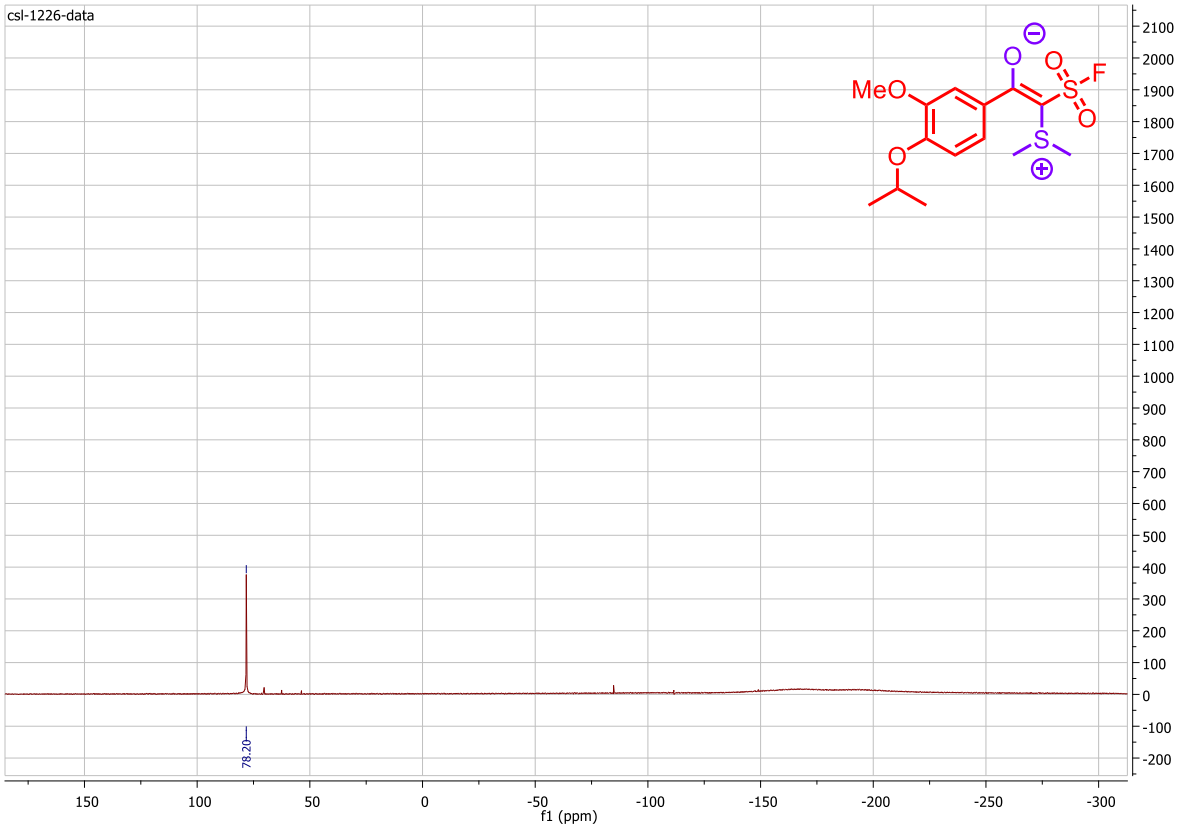
^{1}H NMR **8h**:



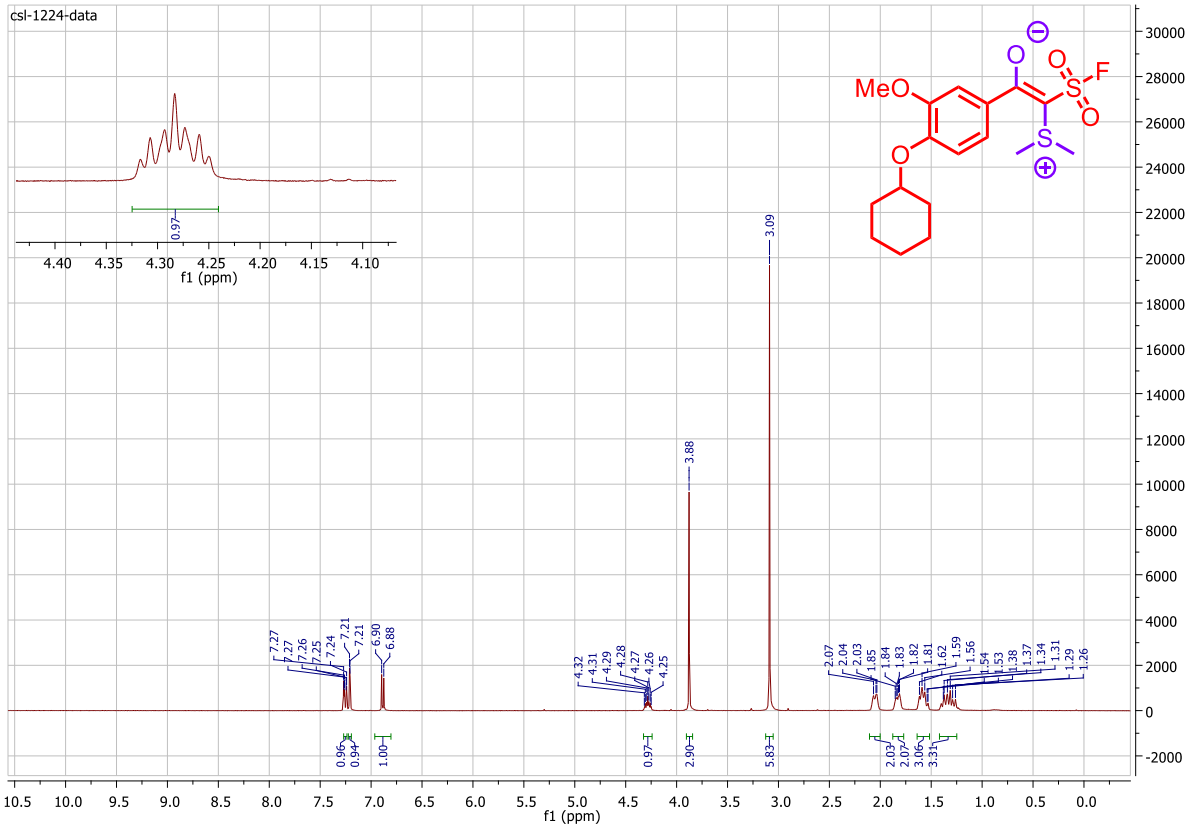
^{13}C NMR **8h**:



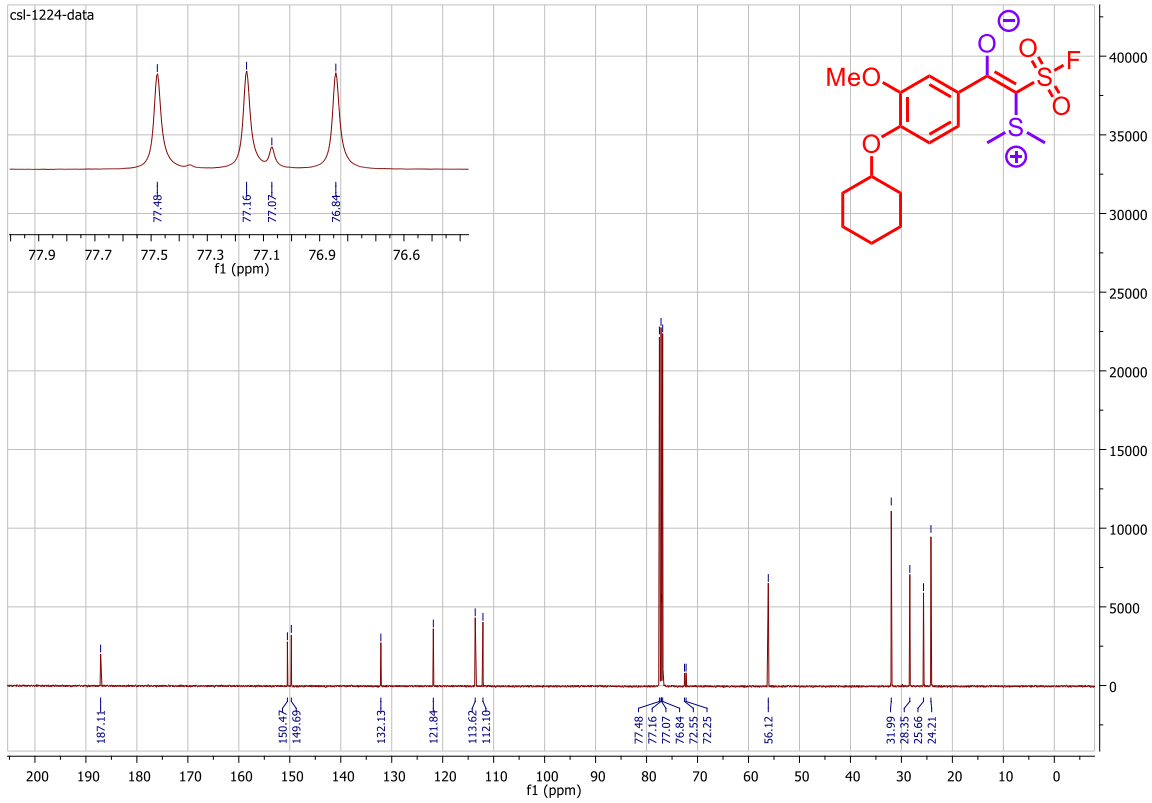
^{19}F NMR **8h**:


csl-1226-data
MeO
O
O
S
F
O
S
O
78.20
150
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200

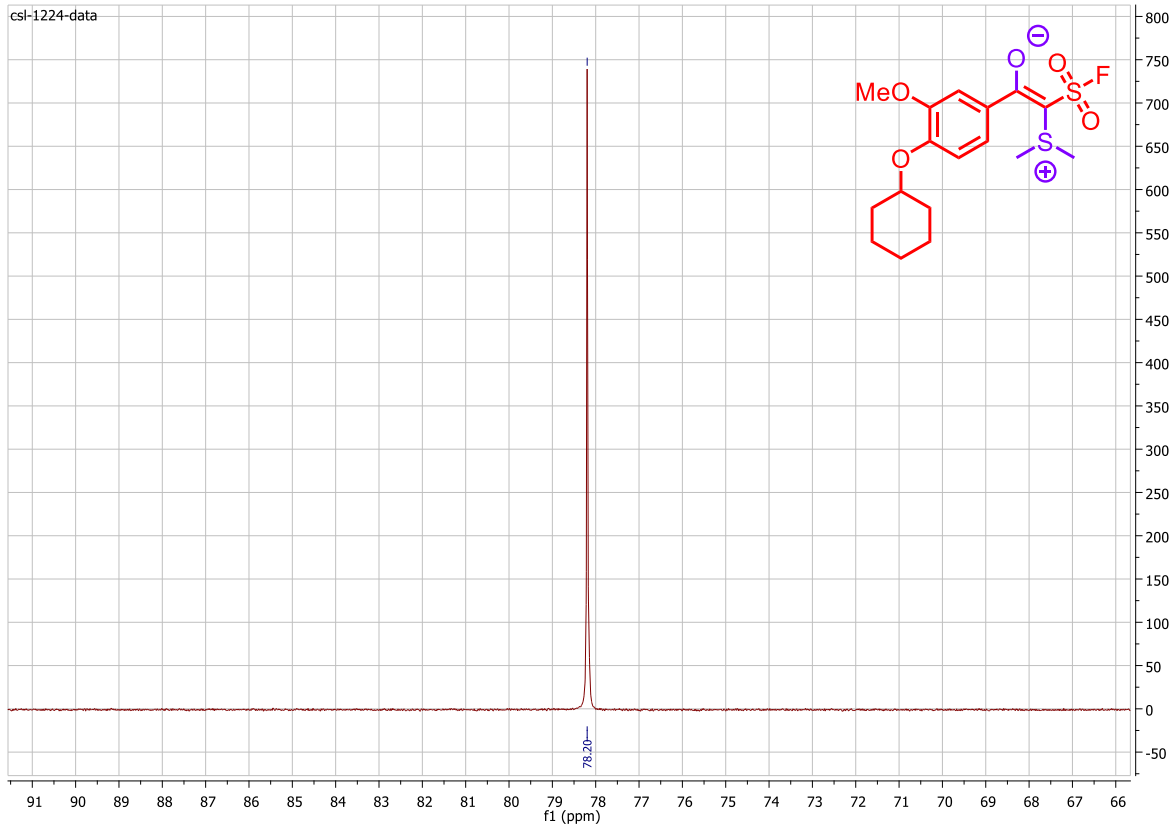
^{1}H NMR **8i**:



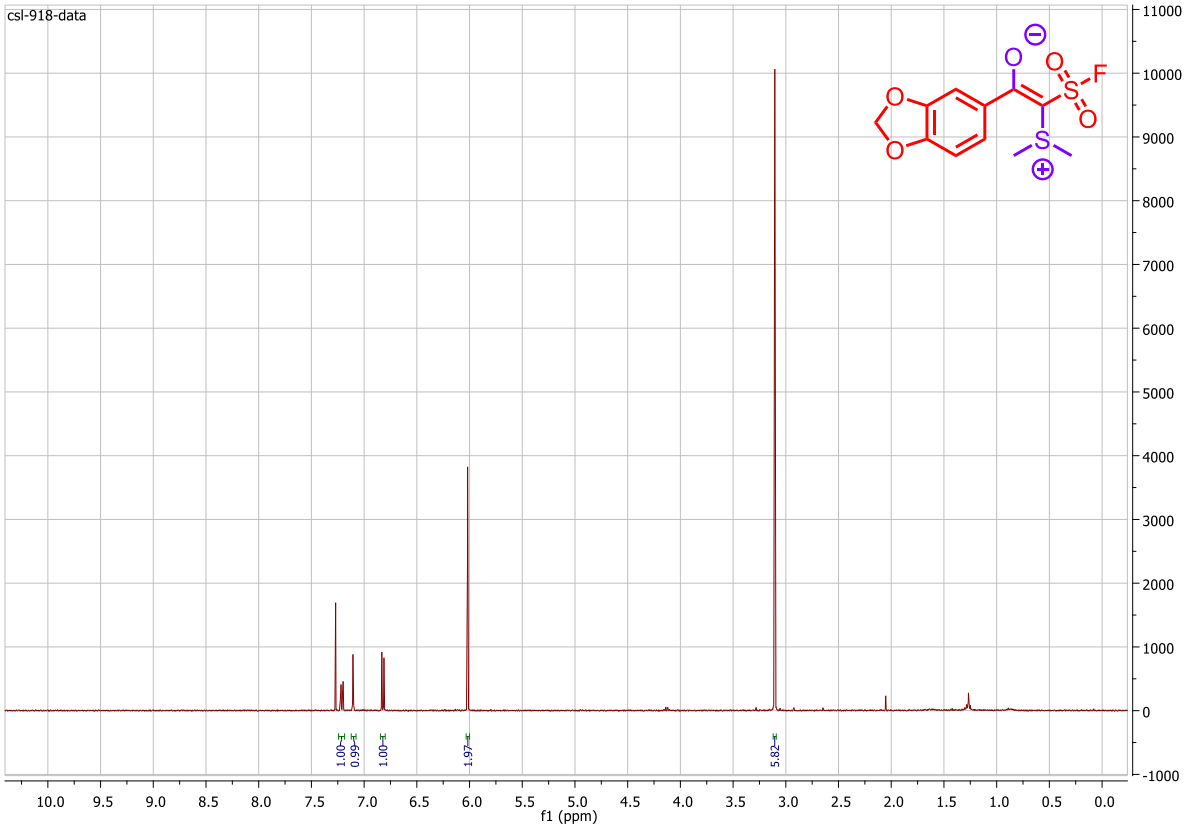
^{13}C NMR **8i**:



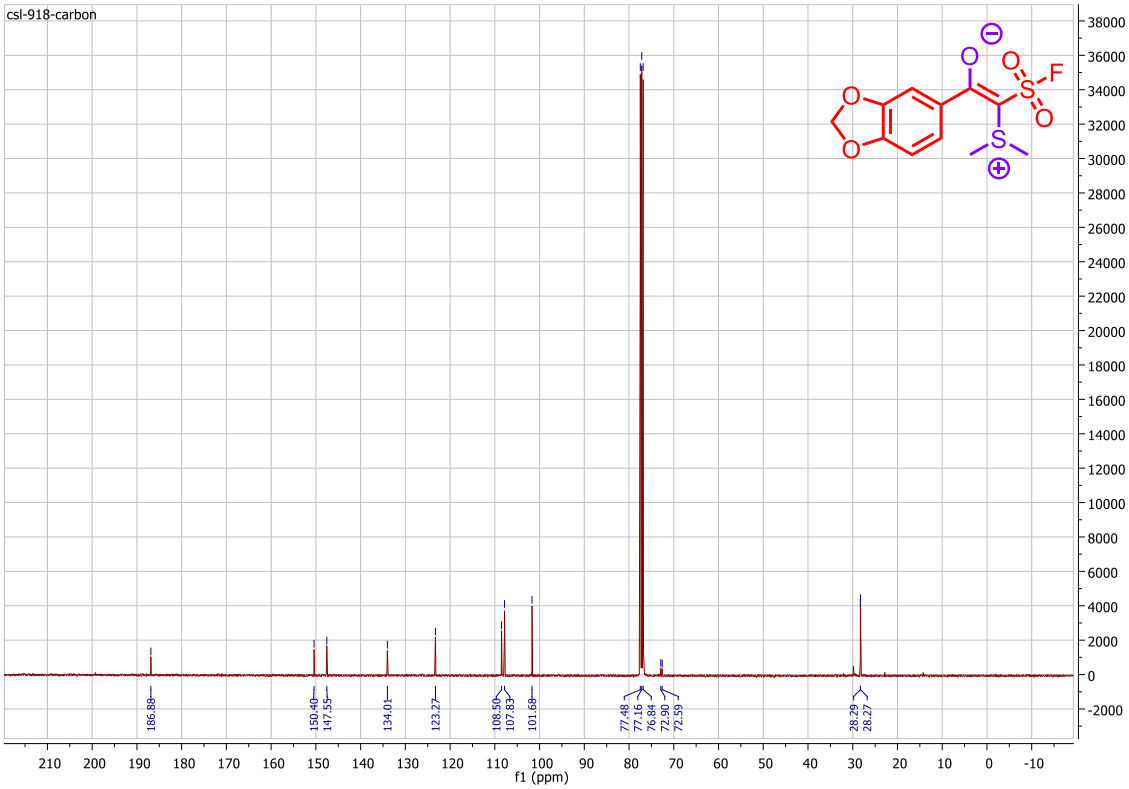
^{19}F NMR **8i**:


csl-1224-data
MeO
O
O
O
S
F
O
S
78.20
91 90 89 88 87 86 85 84 83 82 81 80 79 78 77 76 75 74 73 72 71 70 69 68 67 66
f1 (ppm)
800 750 700 650 600 550 500 450 400 350 300 250 200 150 100 50 0 -50

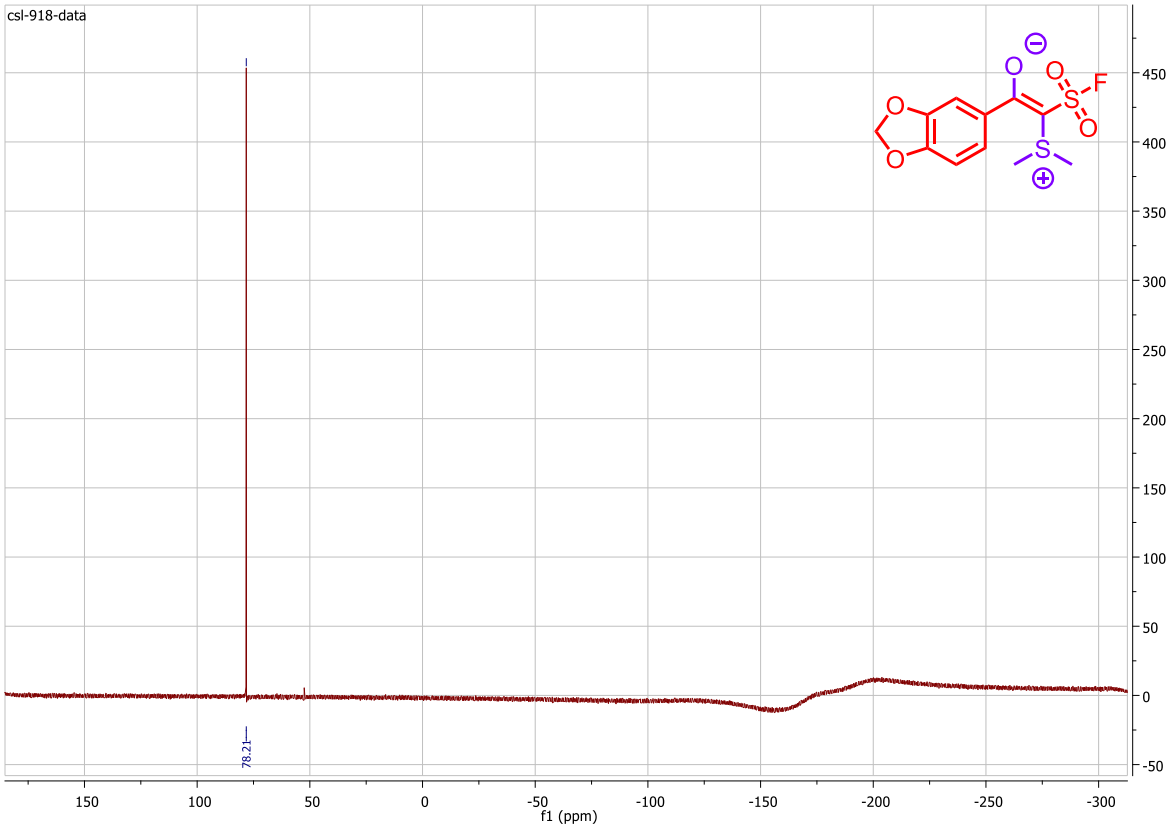
^{1}H NMR **8j**:



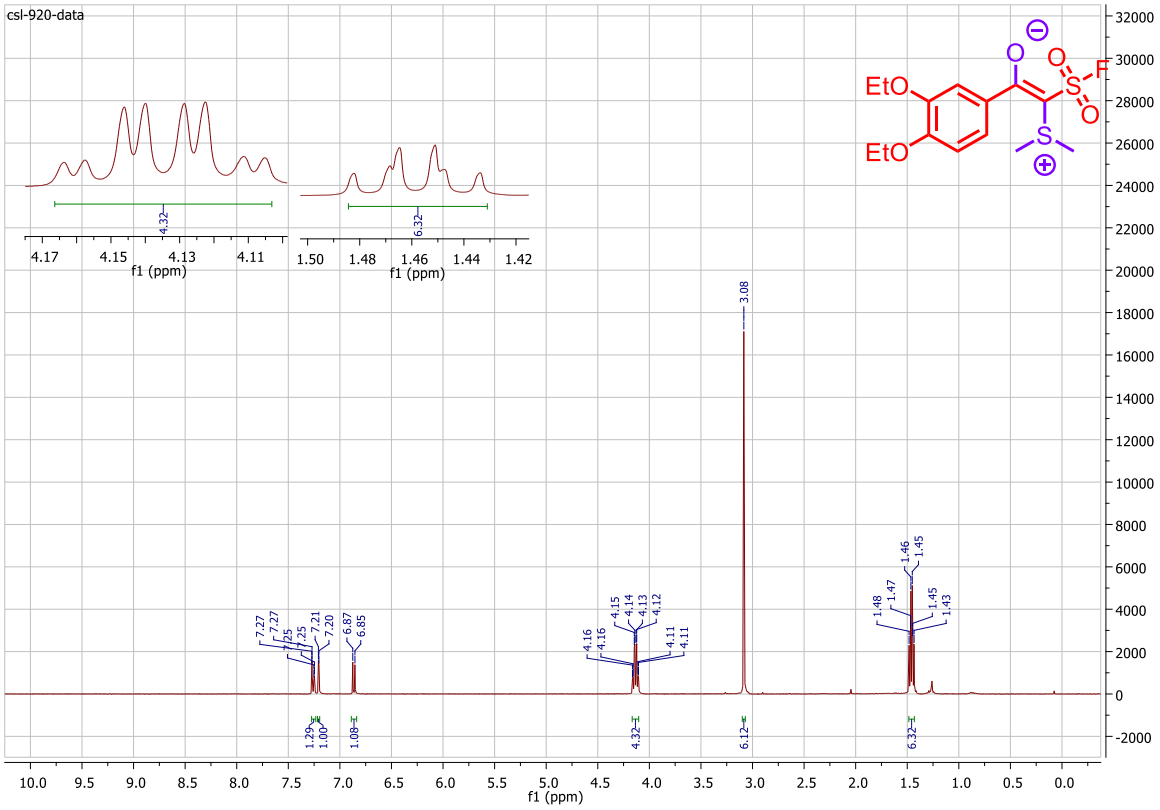
^{13}C NMR **8j**:



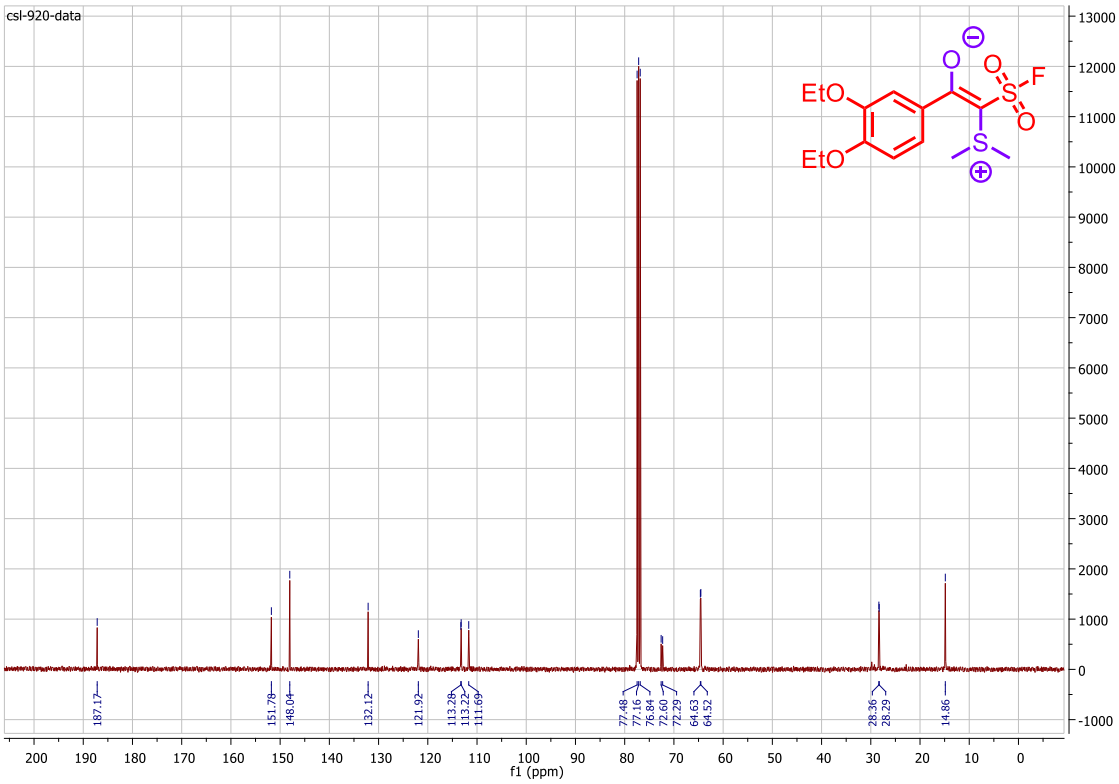
^{19}F NMR **8j**:


csl-918-data
78.21
150
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)
450
400
350
300
250
200
150
100
50
0
-50

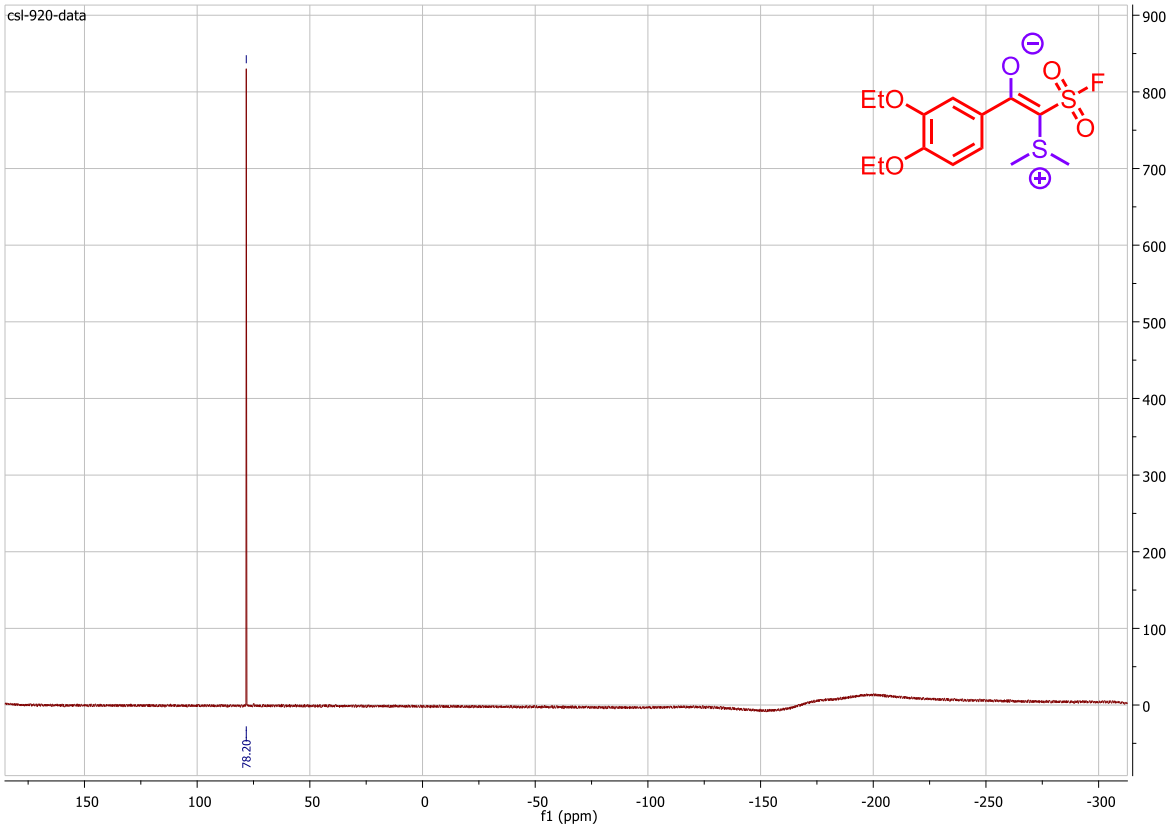
^{1}H NMR **8k**:



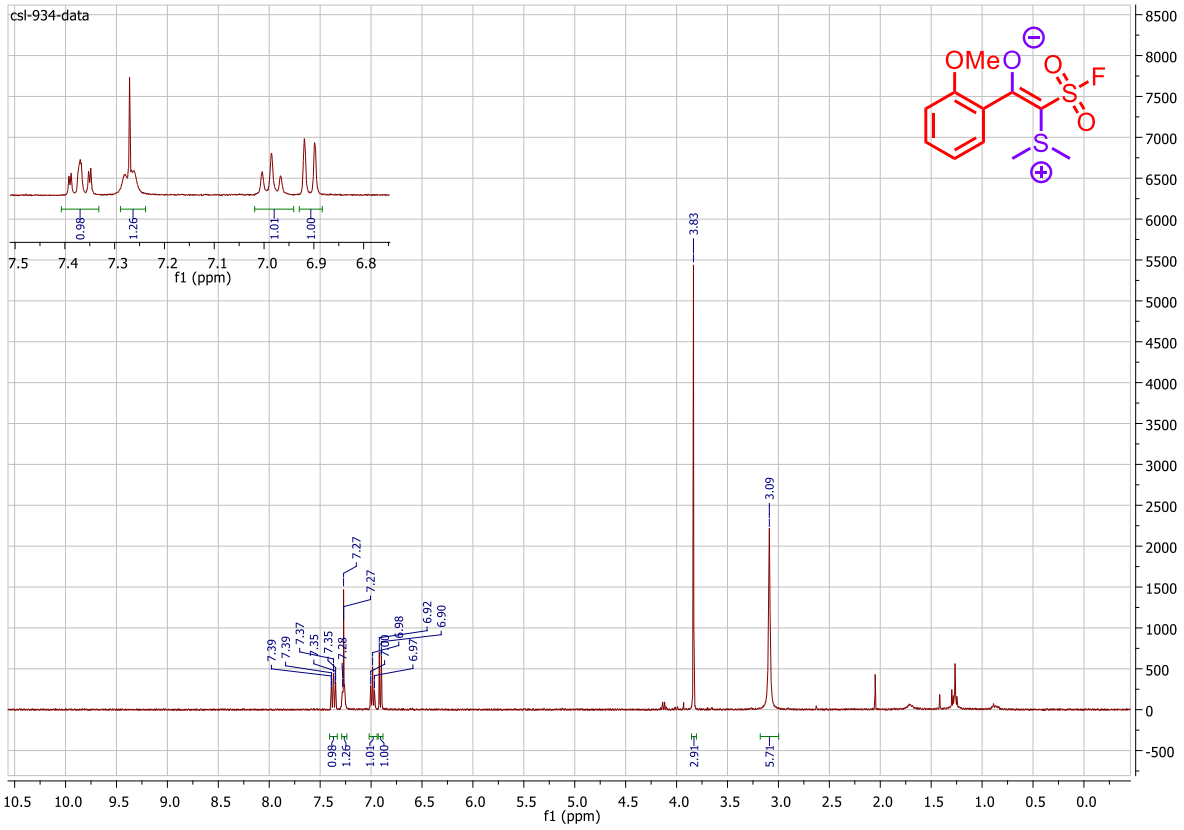
^{13}C NMR **8k**:



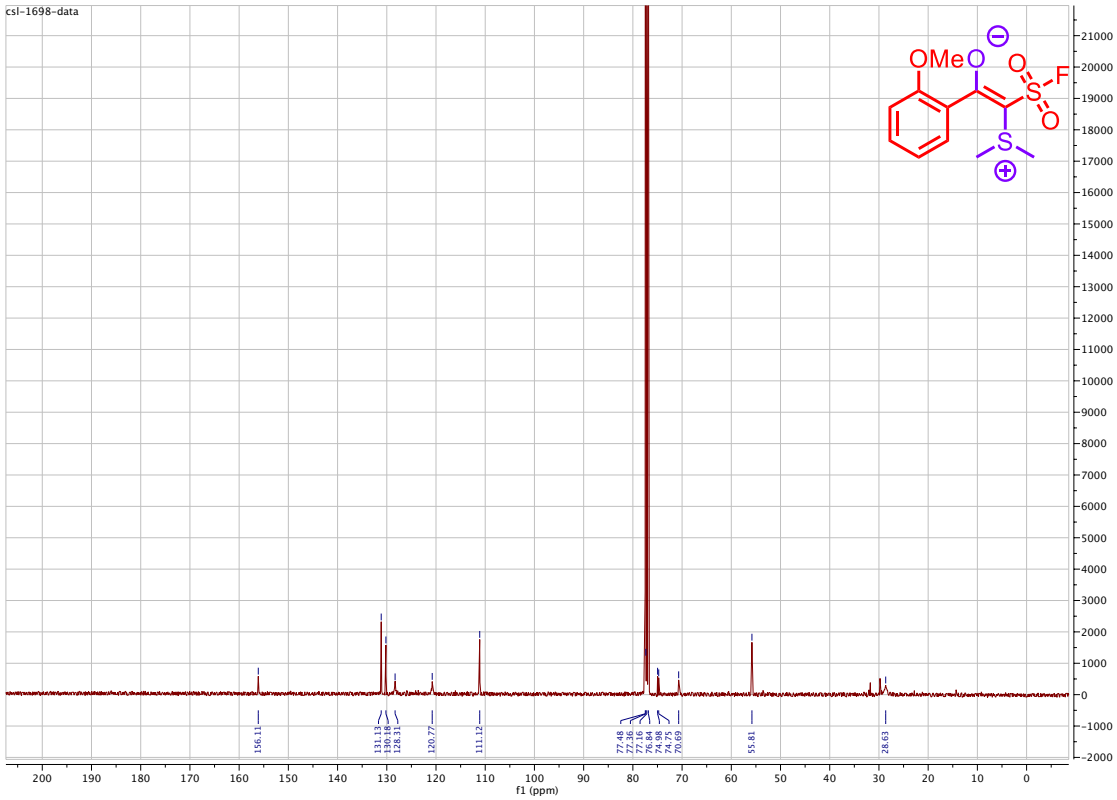
^{19}F NMR **8k**:


csl-920-data
EtO
EtO
O
O
S
F
O
S
78.20
150
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)
900
800
700
600
500
400
300
200
100
0

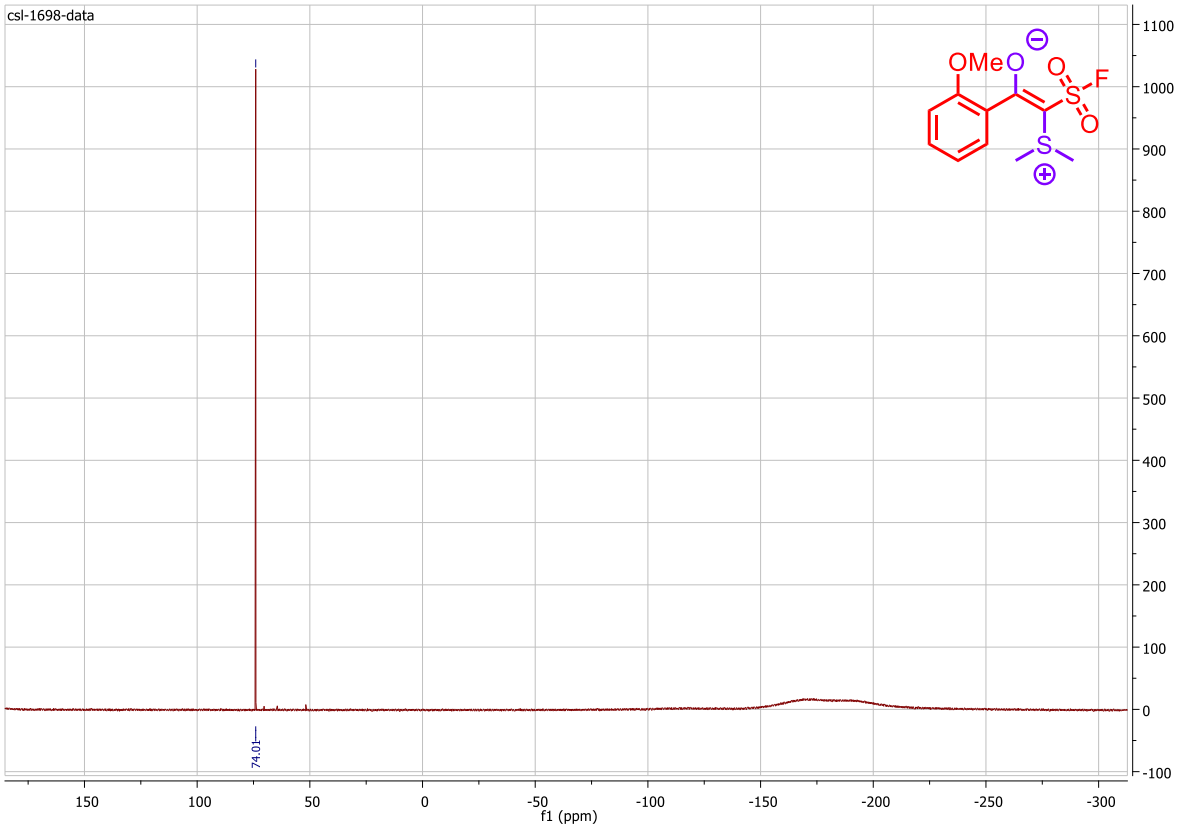
^{1}H NMR **8l**:



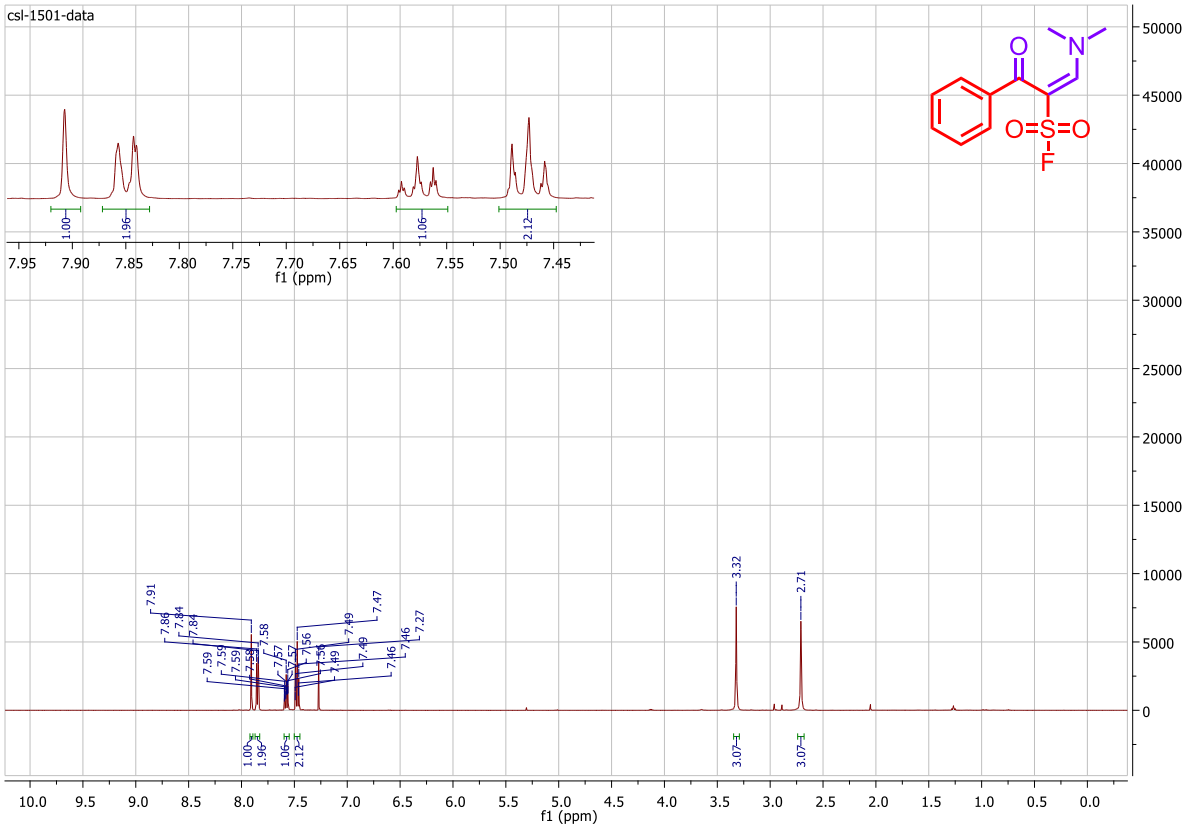
^{13}C NMR **8l**:



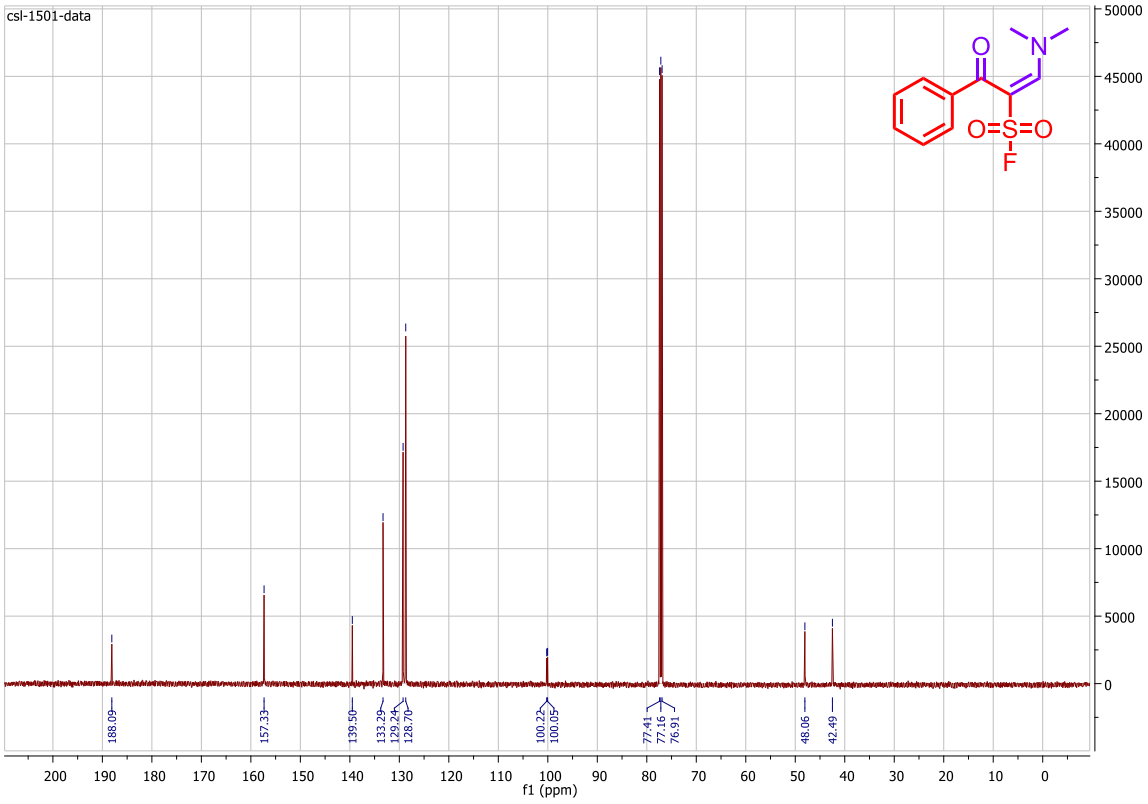
^{19}F NMR **8l**:


csl-1698-data
OMe
O
O
S
F
O
S
74.01
150
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

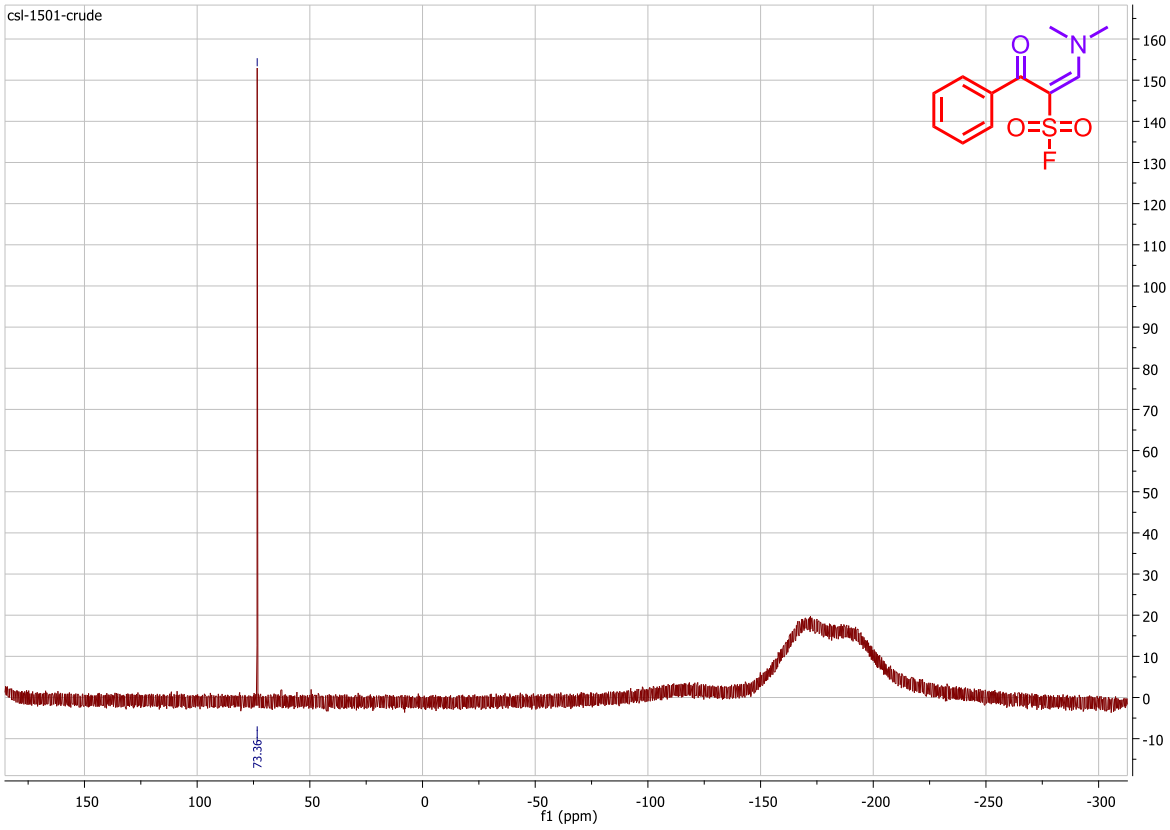
^{1}H NMR **9a**:



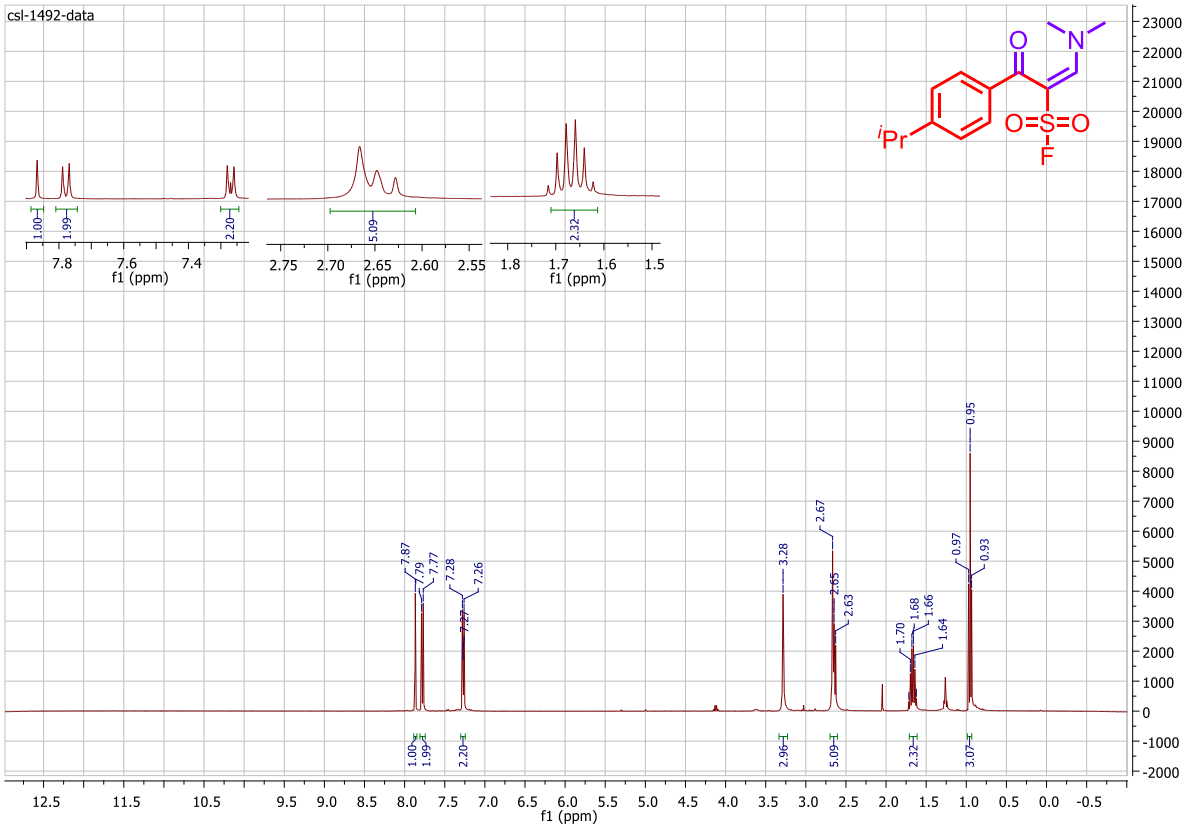
^{13}C NMR **9a**:



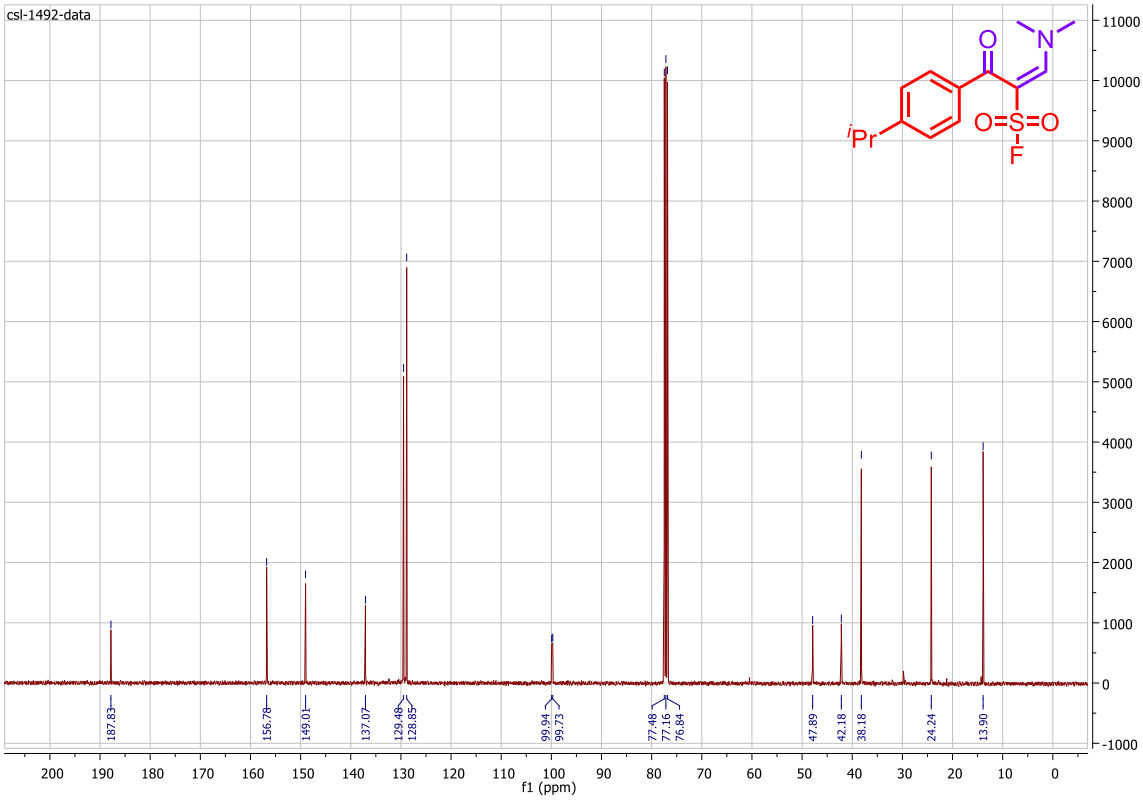
^{19}F NMR **9a**:


csl-1501-crude
73.36
150
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
O
N
O=S=O
F

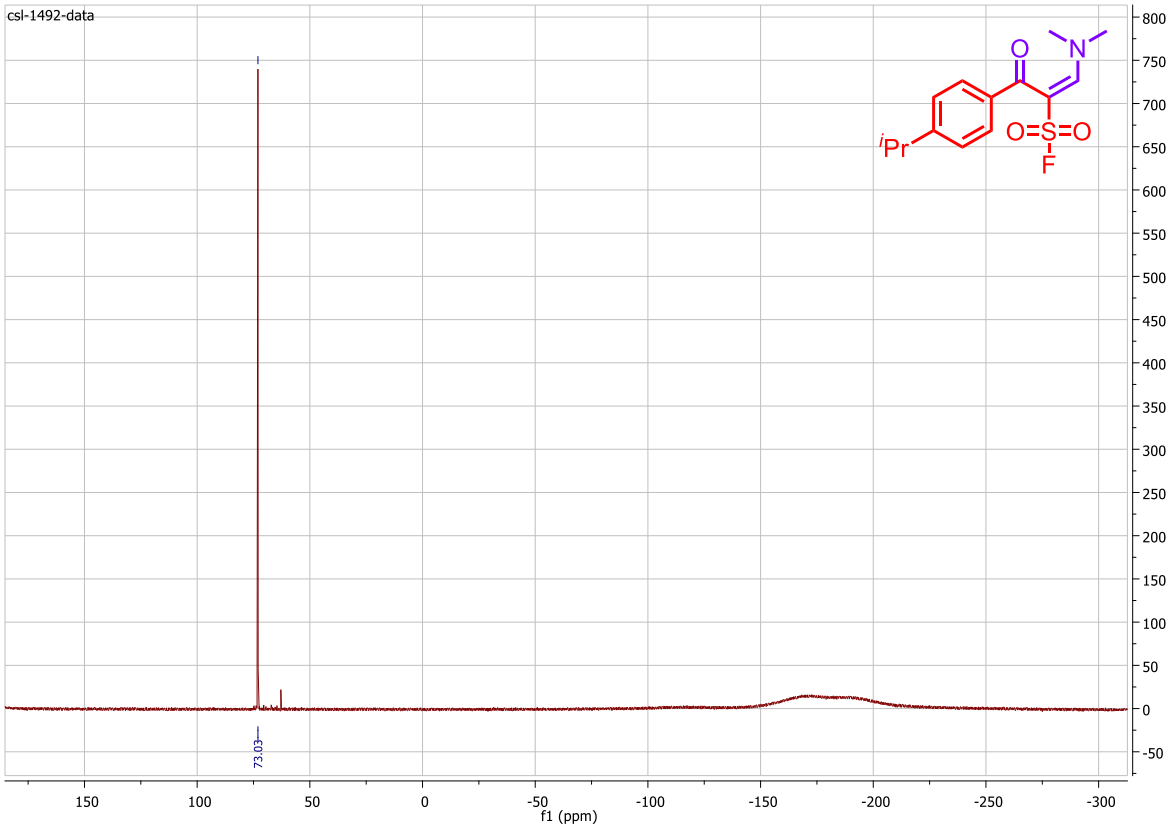
^{1}H NMR **9b**:



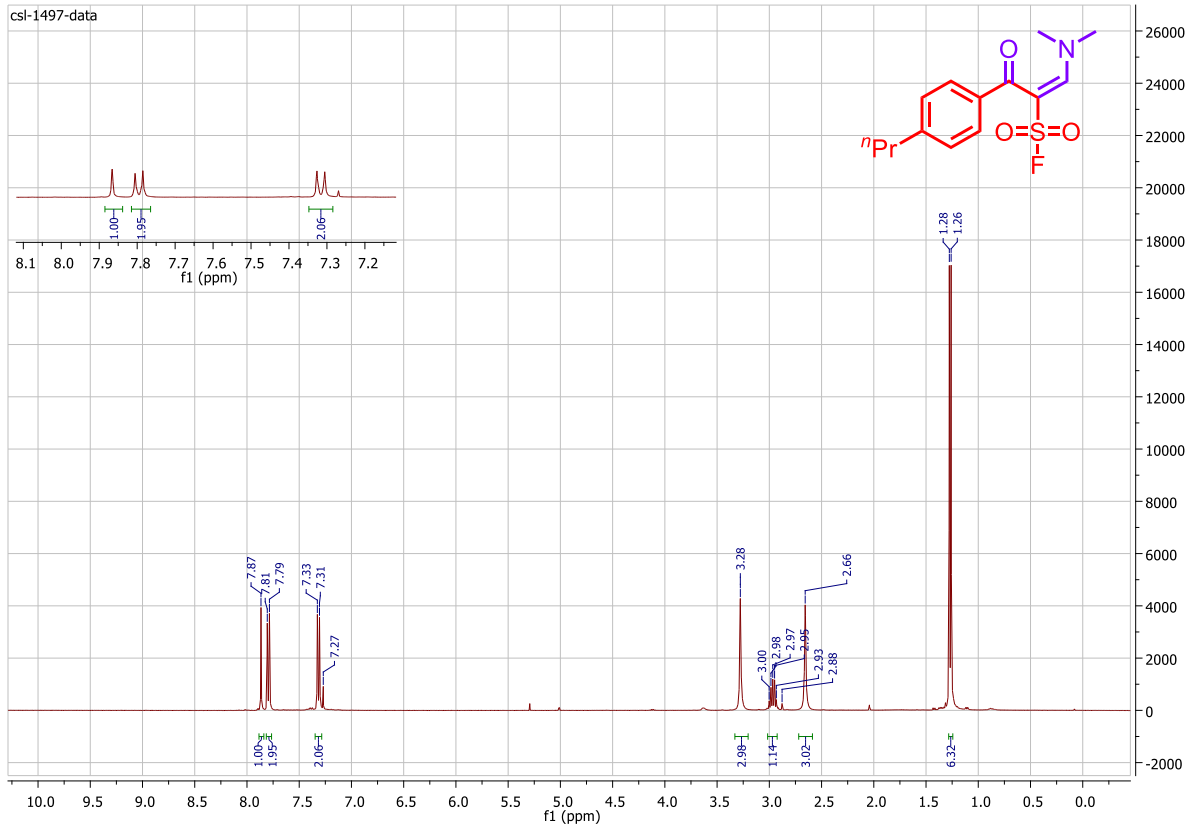
^{13}C NMR **9b**:



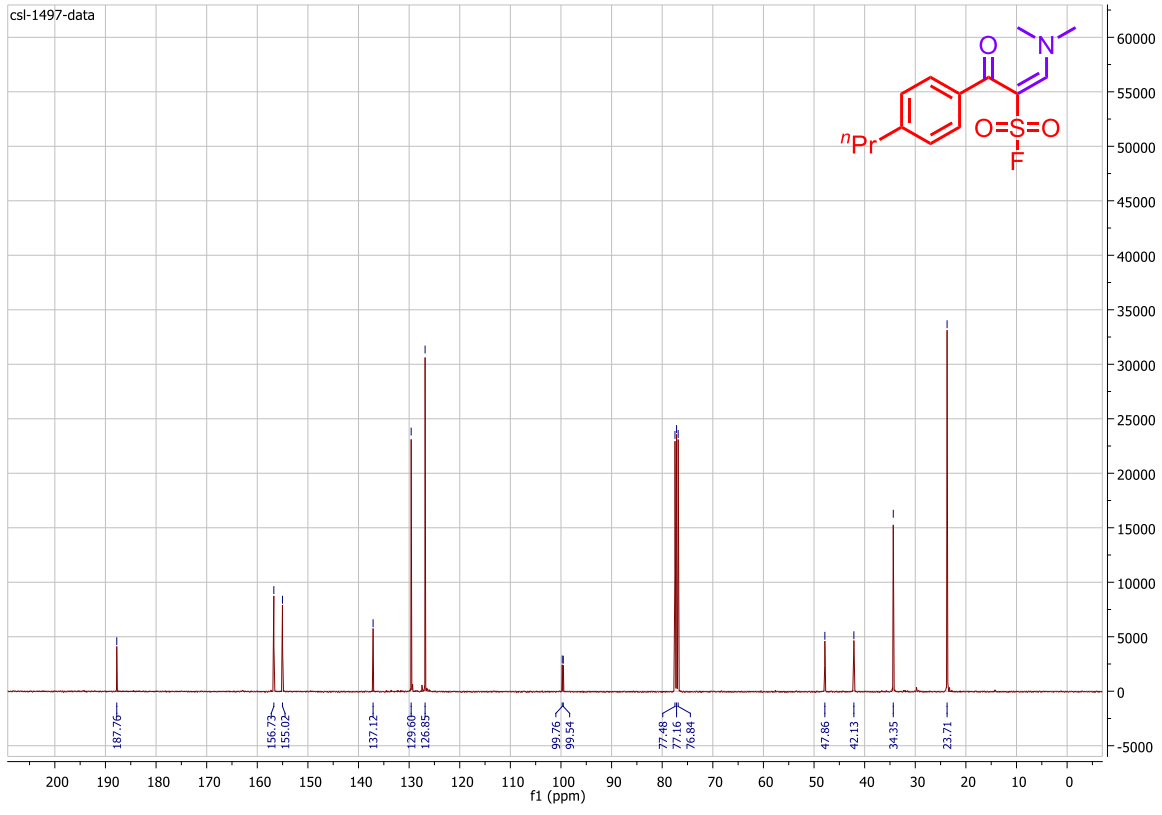
^{19}F NMR **9b**:


csl-1492-data
O
N
O=S=O
F
iPr
73.03
150
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50

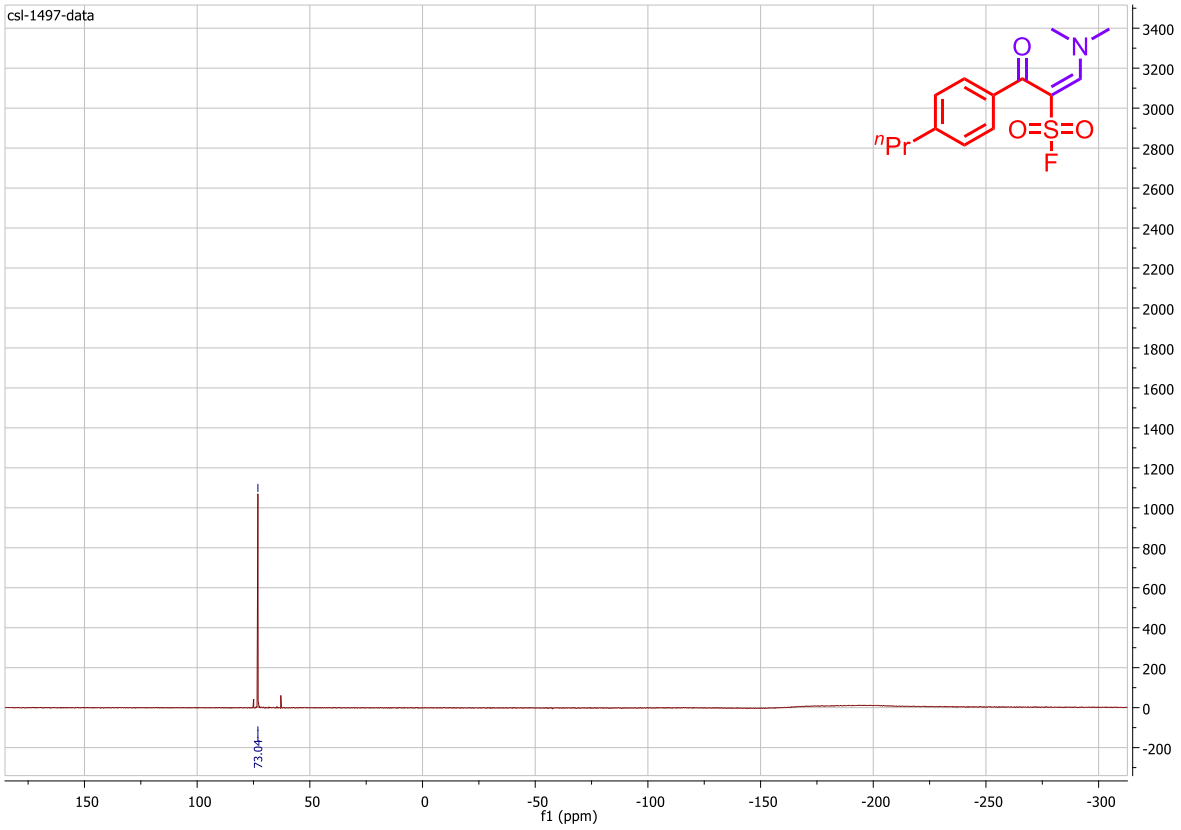
^{1}H NMR **9c**:



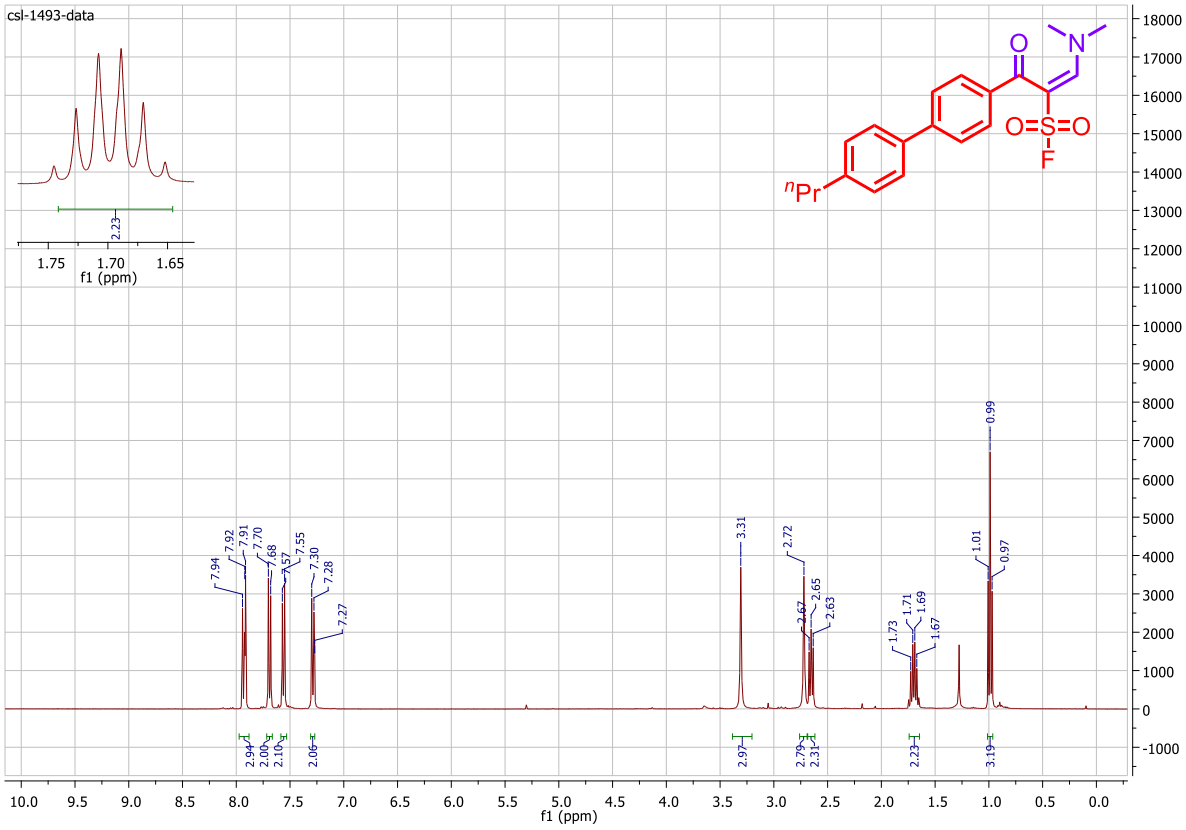
^{13}C NMR **9c**:



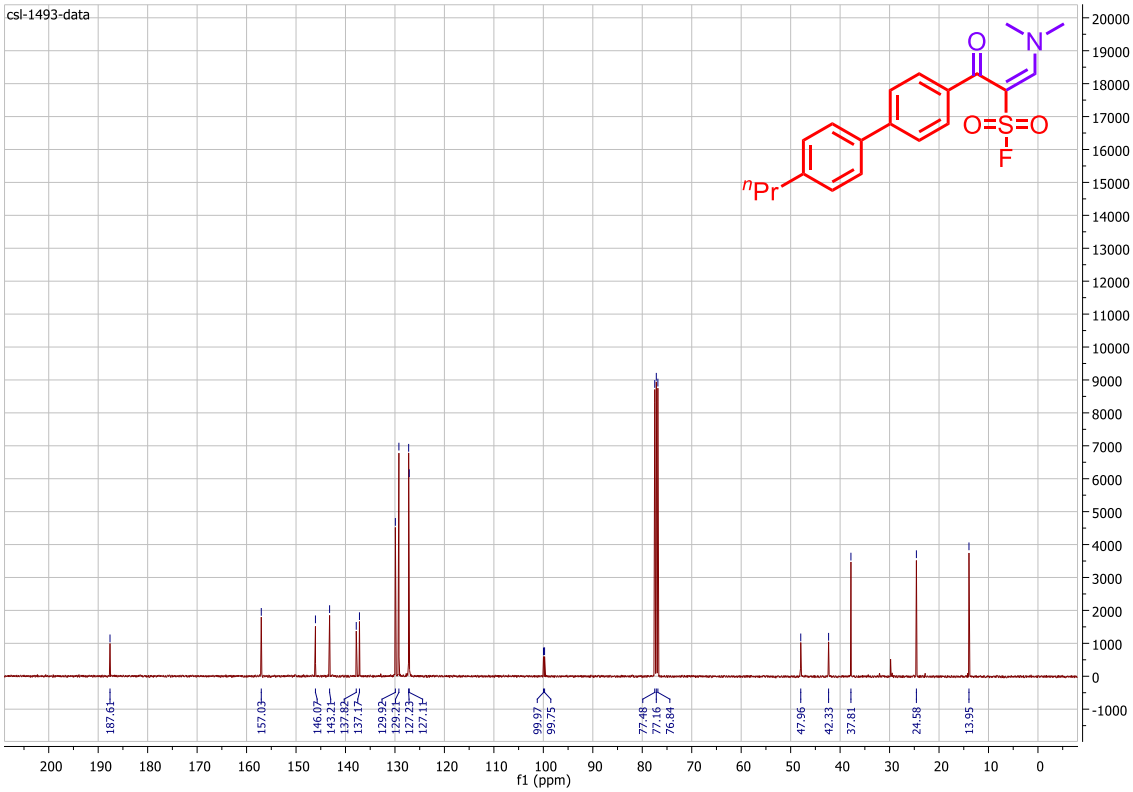
^{19}F NMR **9c**:


csl-1497-data
O
N
O=S=O
F
nPr
73.04
150
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

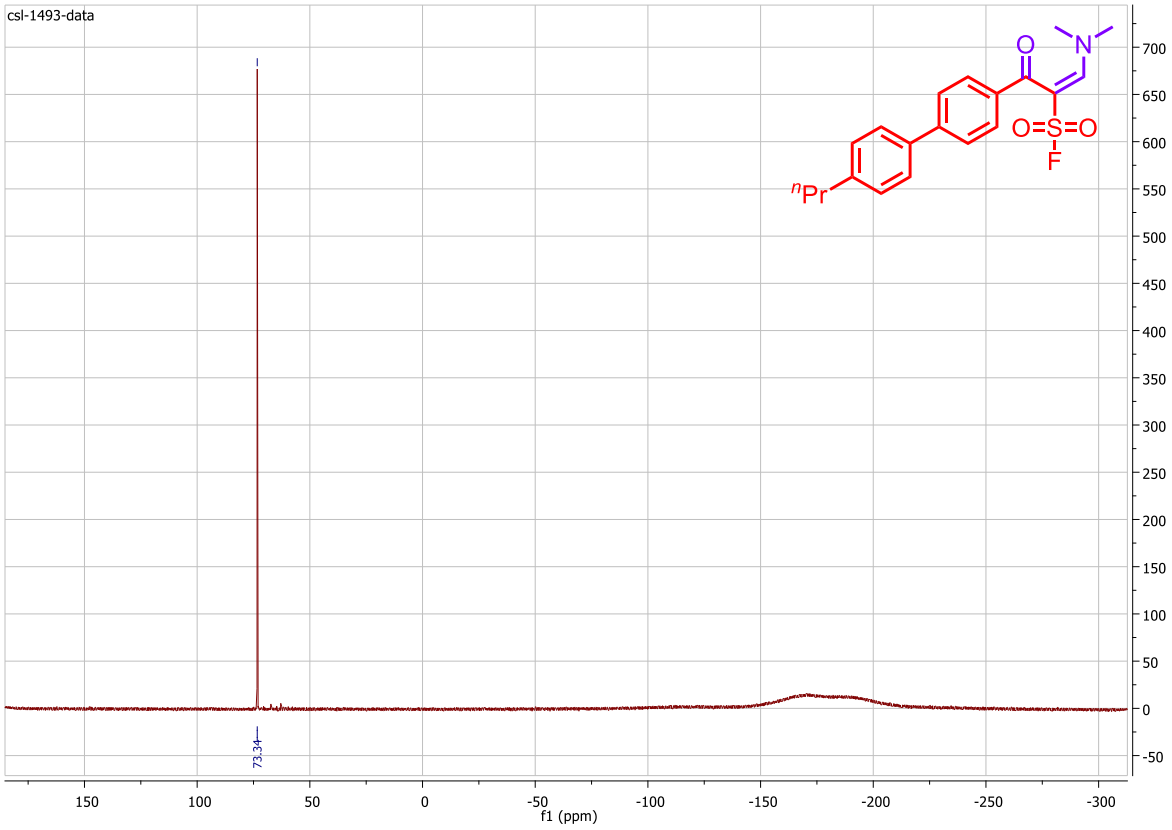
^{1}H NMR **9d**:



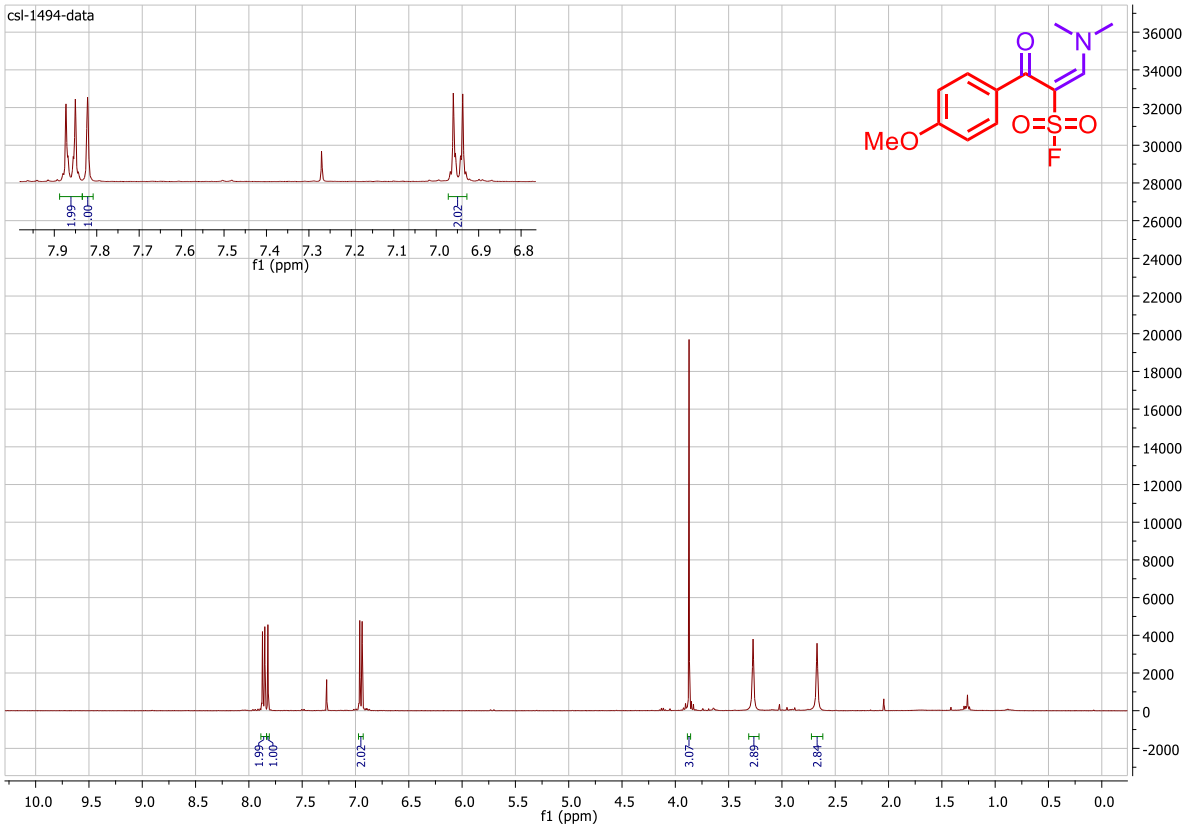
^{13}C NMR **9d**:



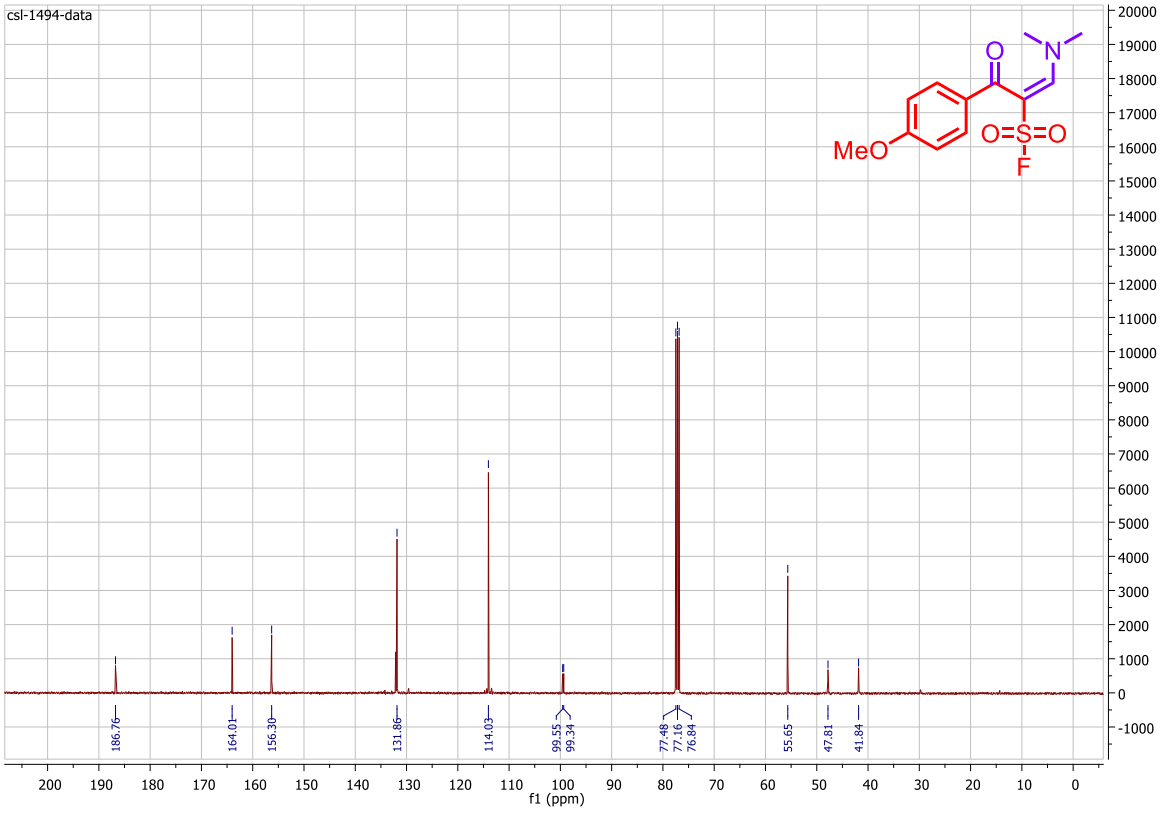
^{19}F NMR **9d**:


csl-1493-data
O
N
O=S=O
F
nPr
73.34
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
150
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)

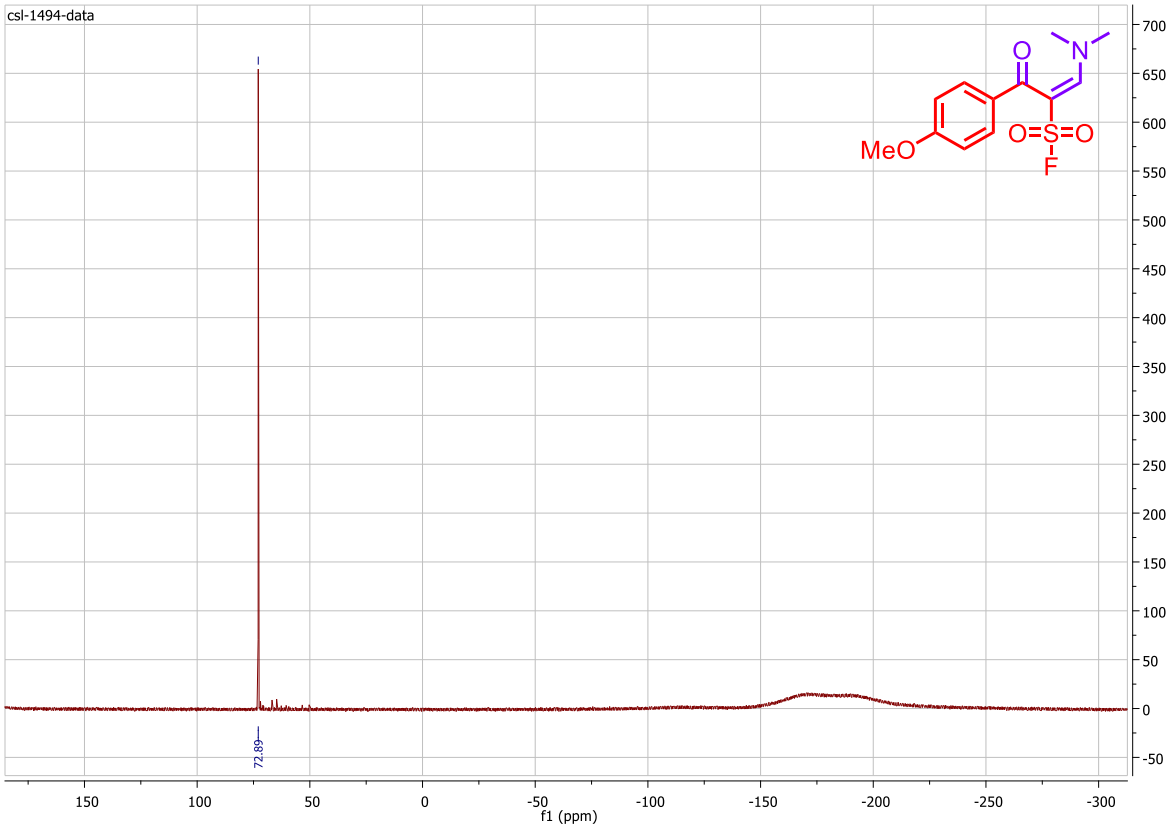
^{1}H NMR **9e**:



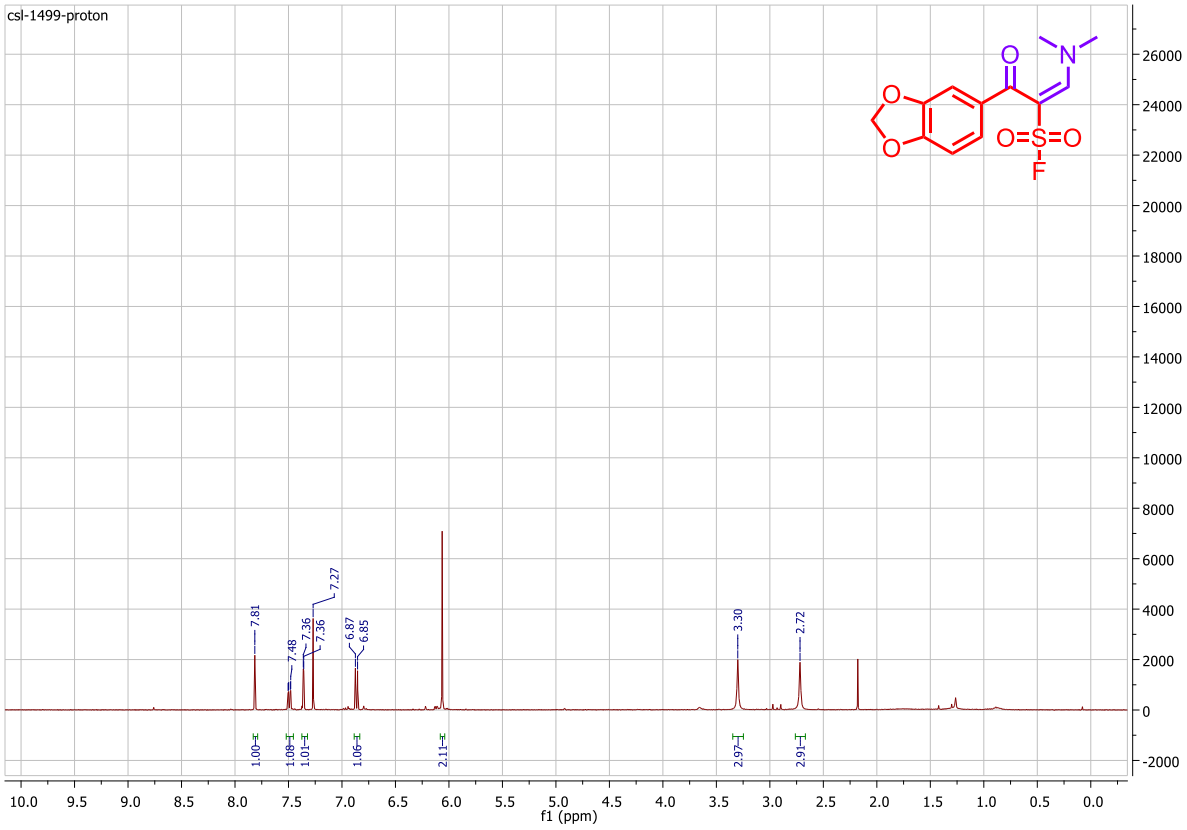
^{13}C NMR **9e**:



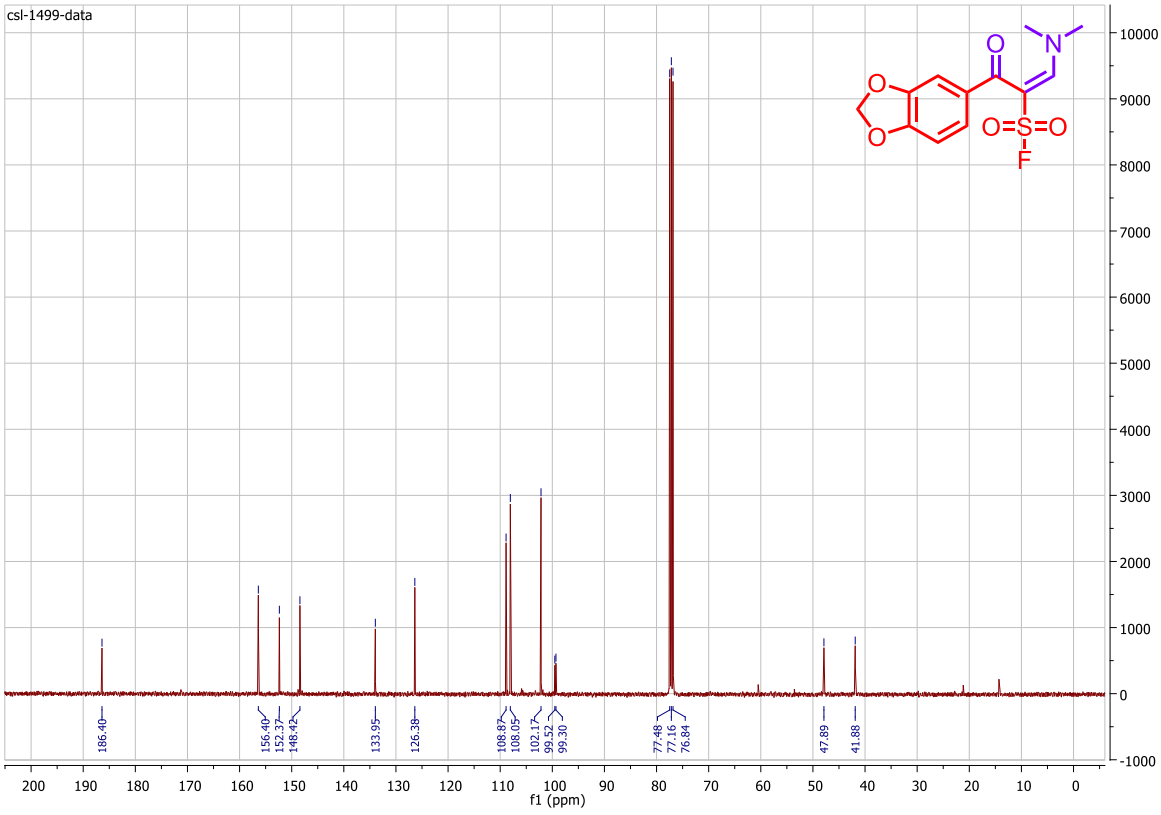
^{19}F NMR **9e**:


csl-1494-data
72.89
150
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
O
N
MeO
O=S=O
F

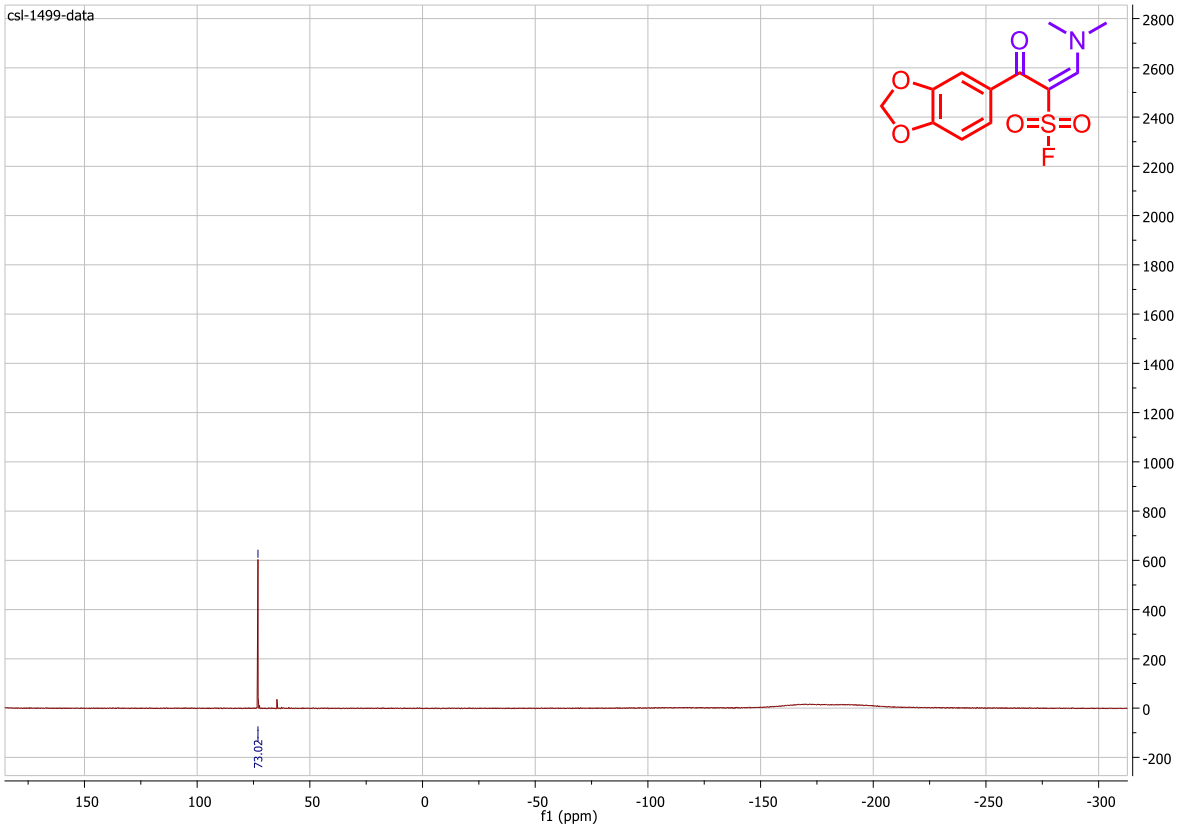
^{1}H NMR **9f**:



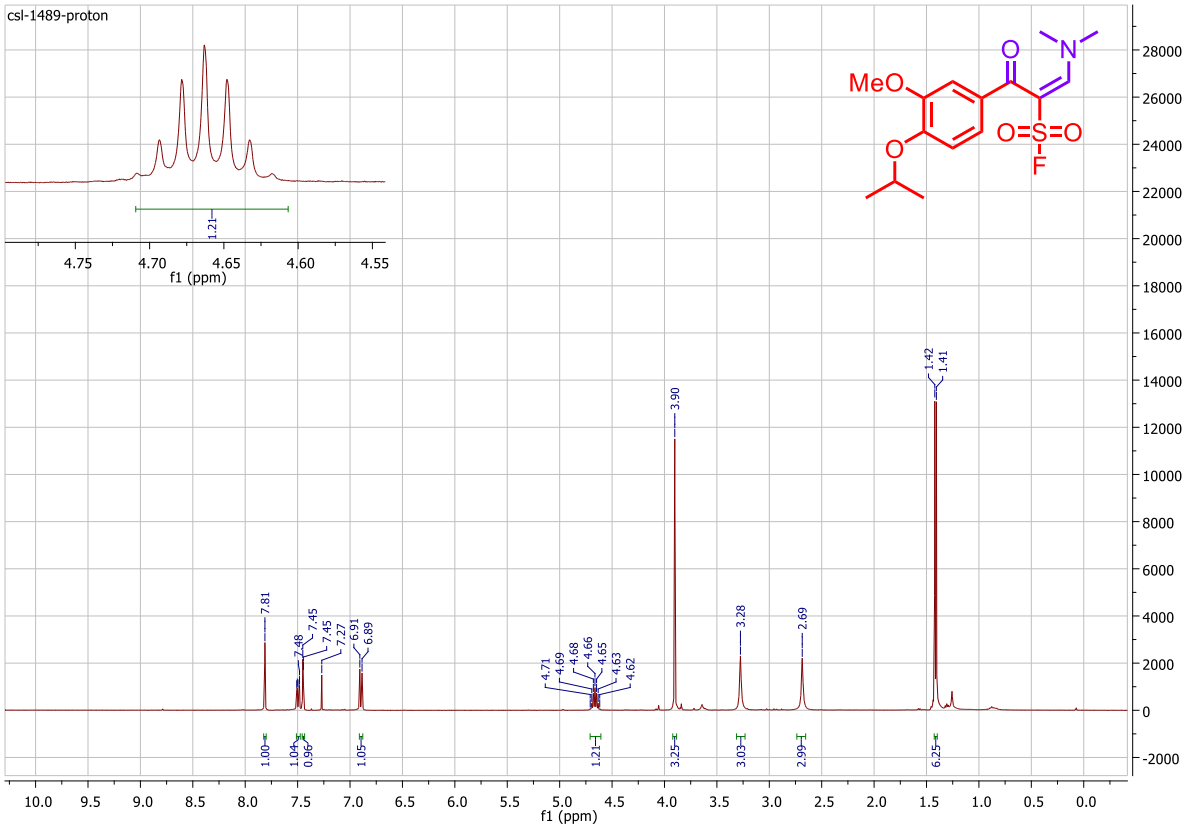
^{13}C NMR **9f**:



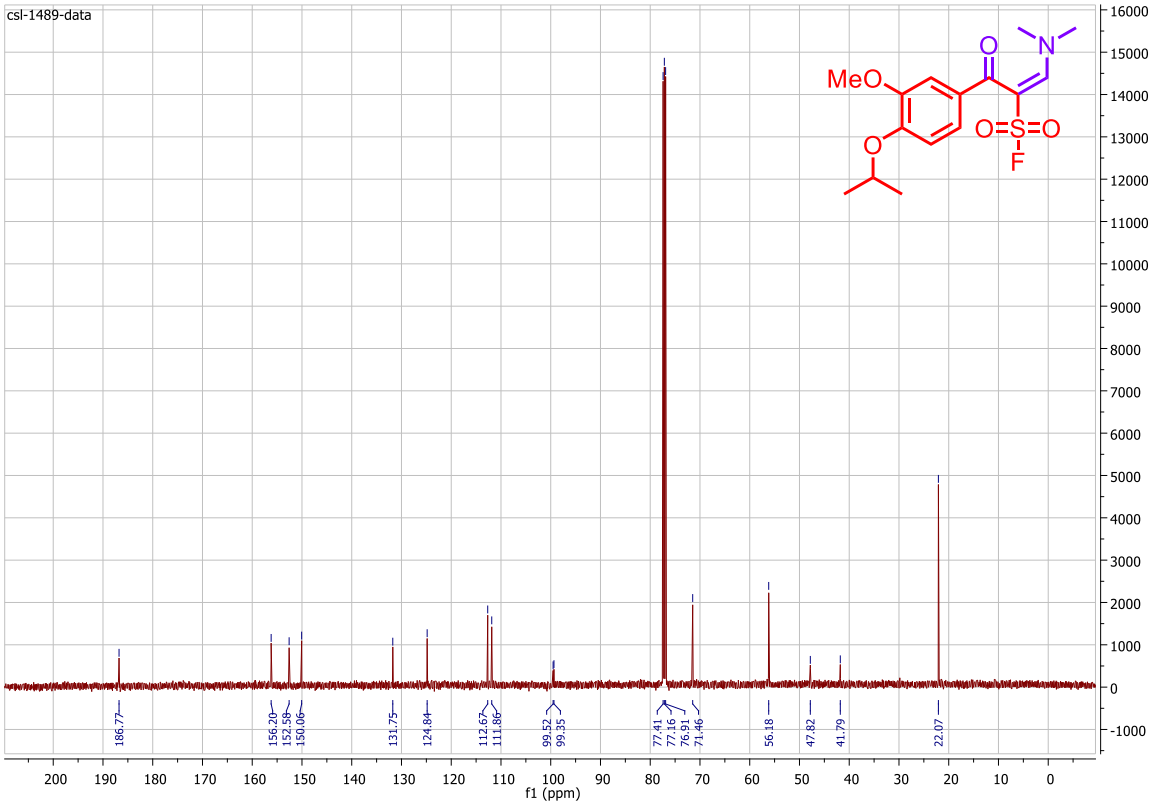
^{19}F NMR **9f**:


csl-1499-data
O
N
O
O
O=S=O
F
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
73.02
150
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)

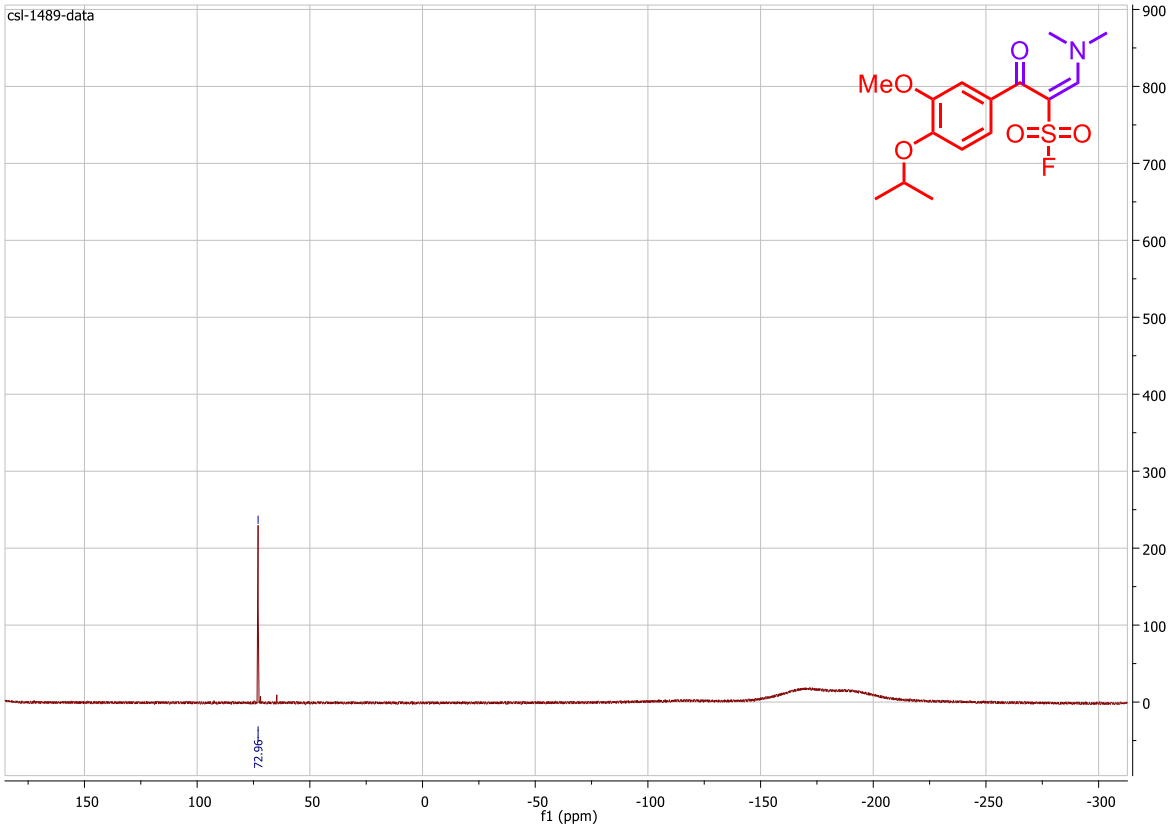
^{1}H NMR **9g**:



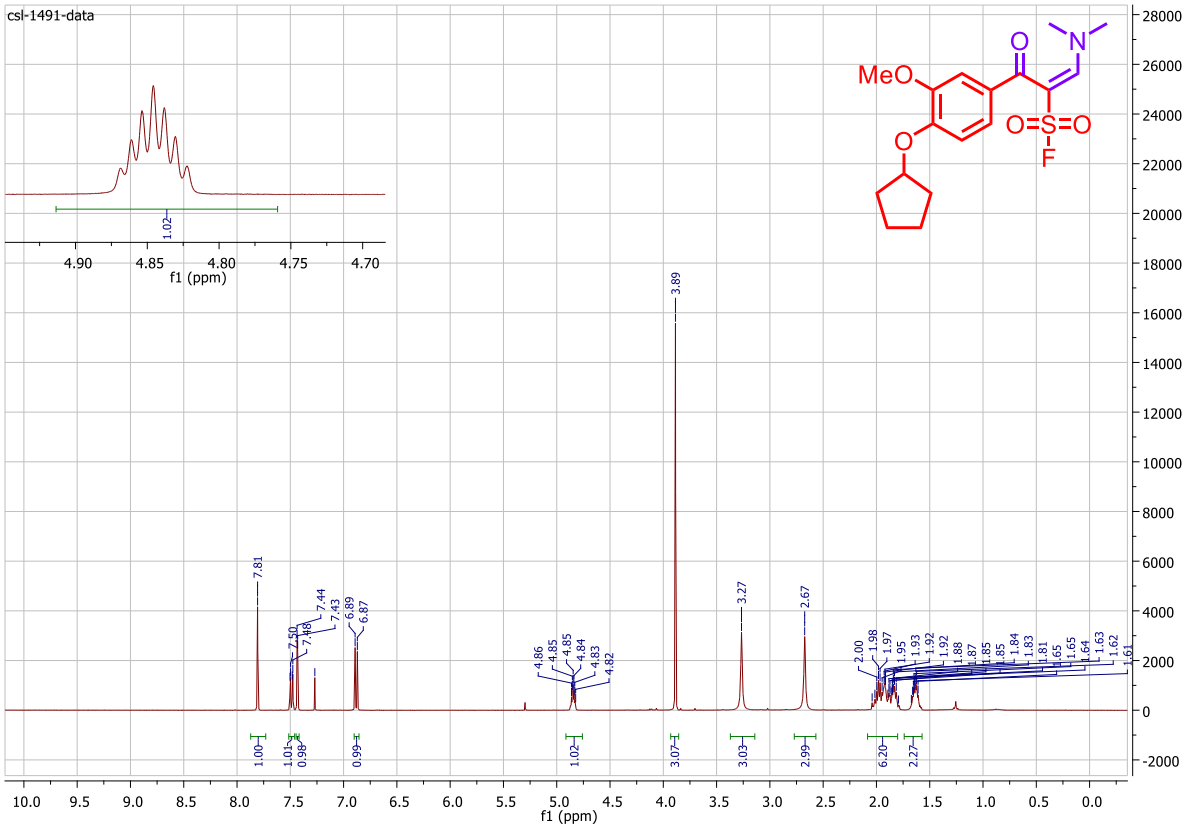
^{13}C NMR **9g**:



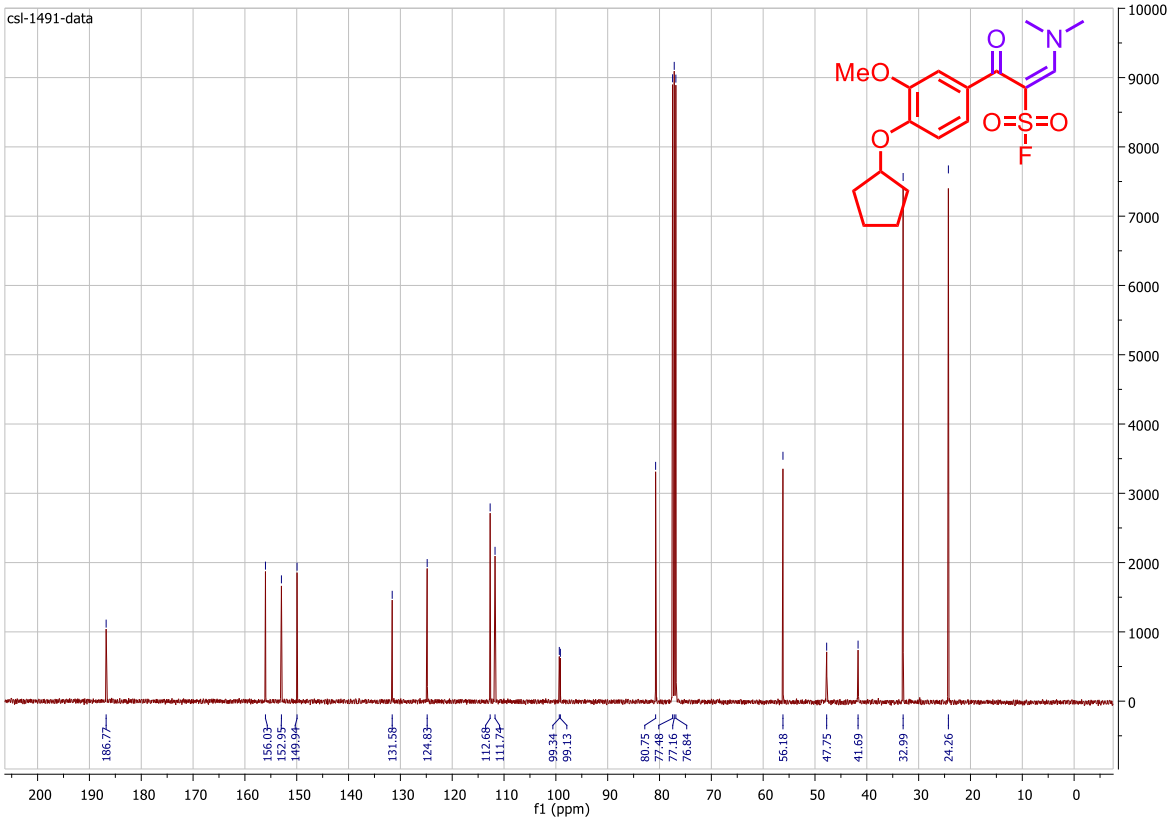
^{19}F NMR **9g**:


csl-1489-data
MeO
O
N
O=S=O
F
72.96
150
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)
900
800
700
600
500
400
300
200
100
0

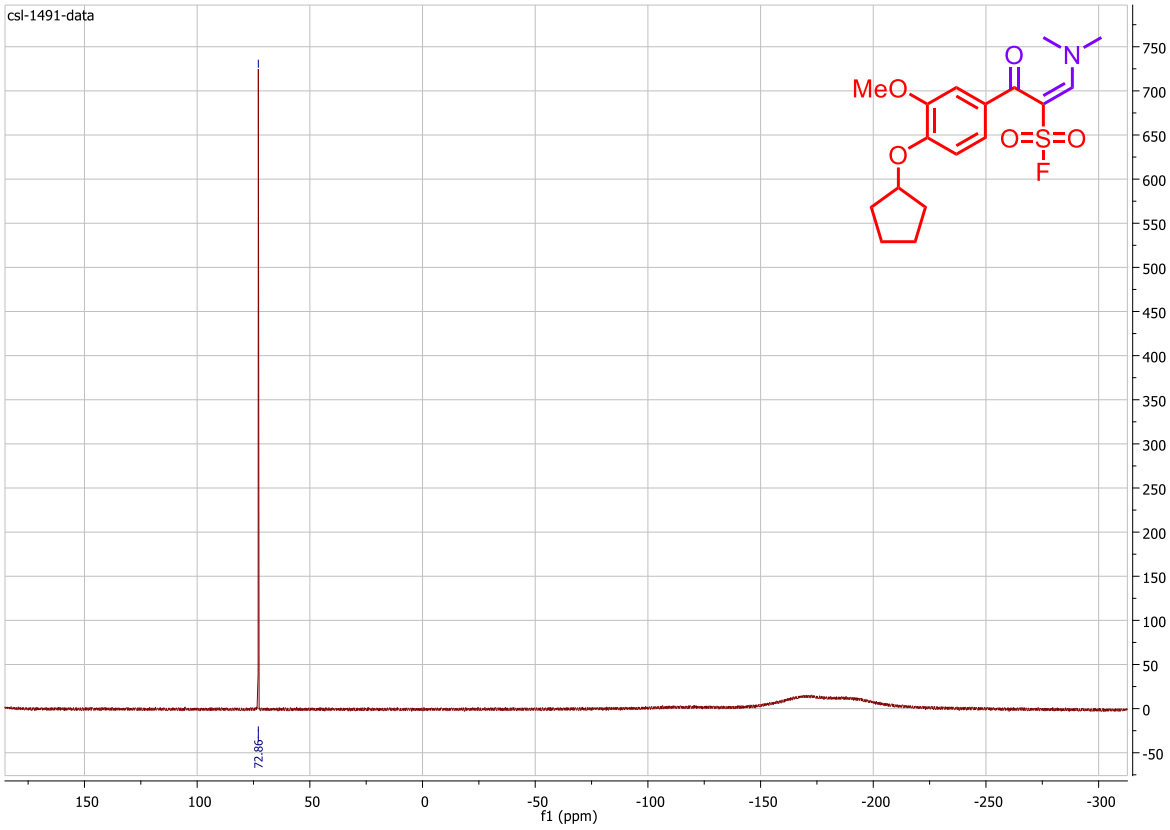
^{1}H NMR **9h**:



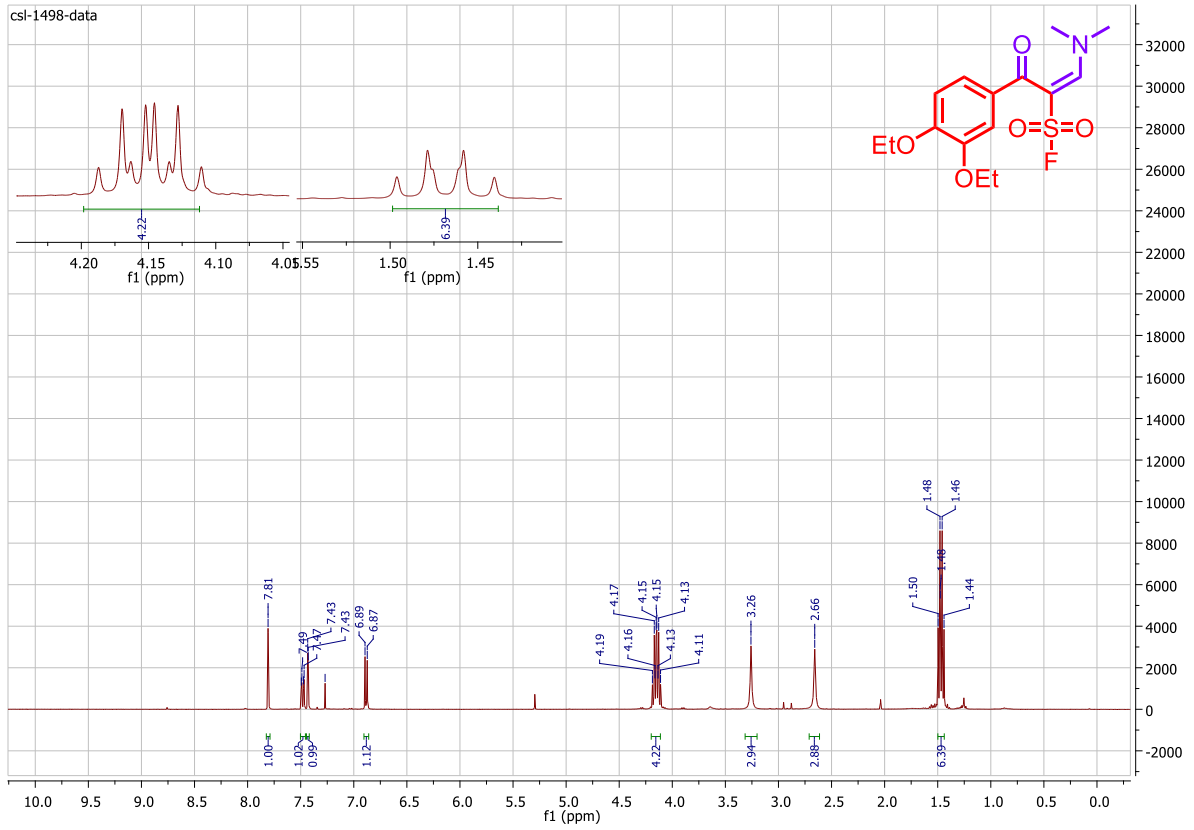
^{13}C NMR **9h**:



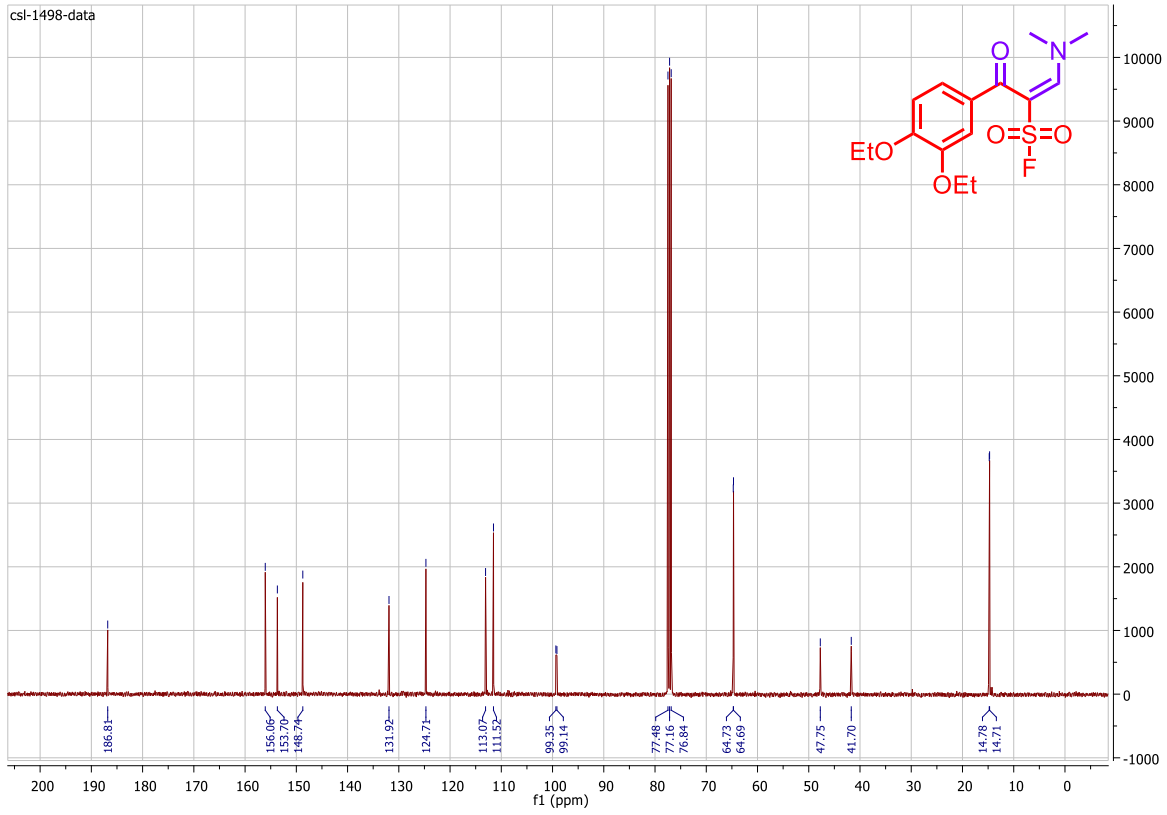
^{19}F NMR **9h**:


csl-1491-data
MeO
O
N
O=S=O
F
72.86
150
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50

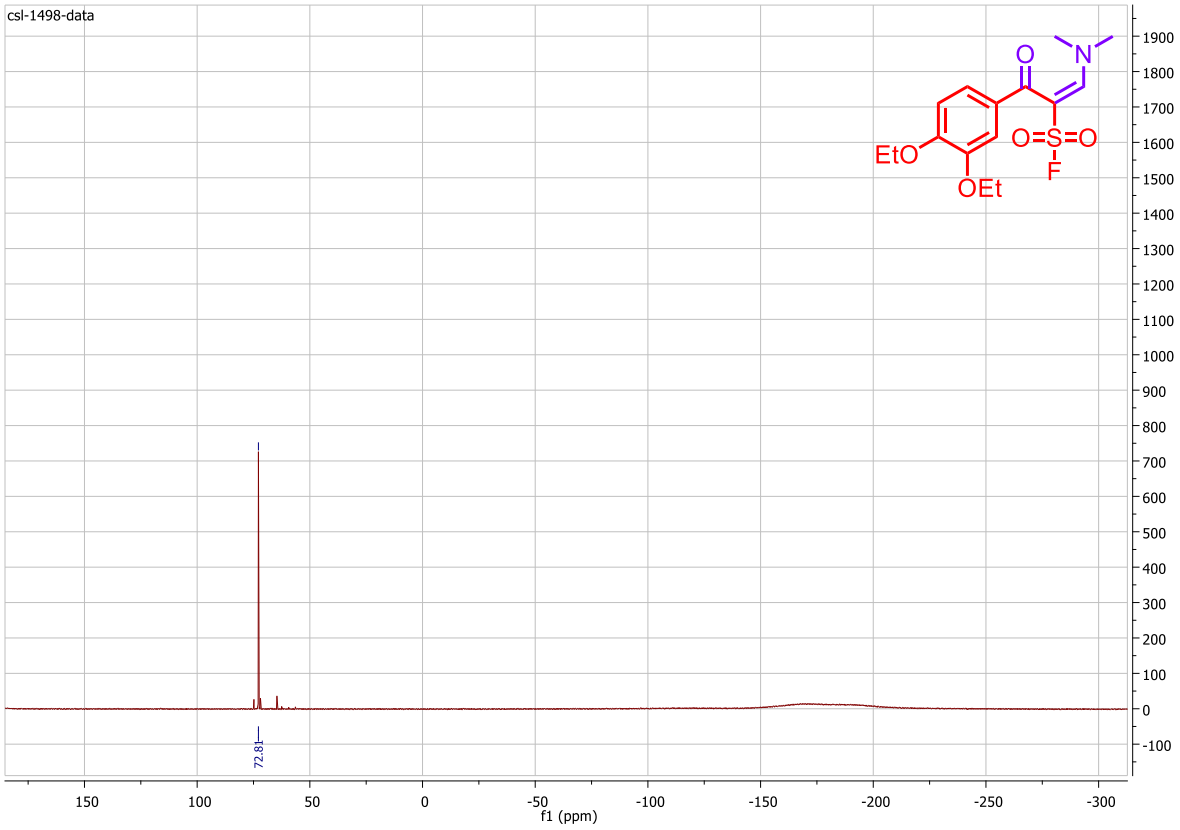
^{1}H NMR **9i**:



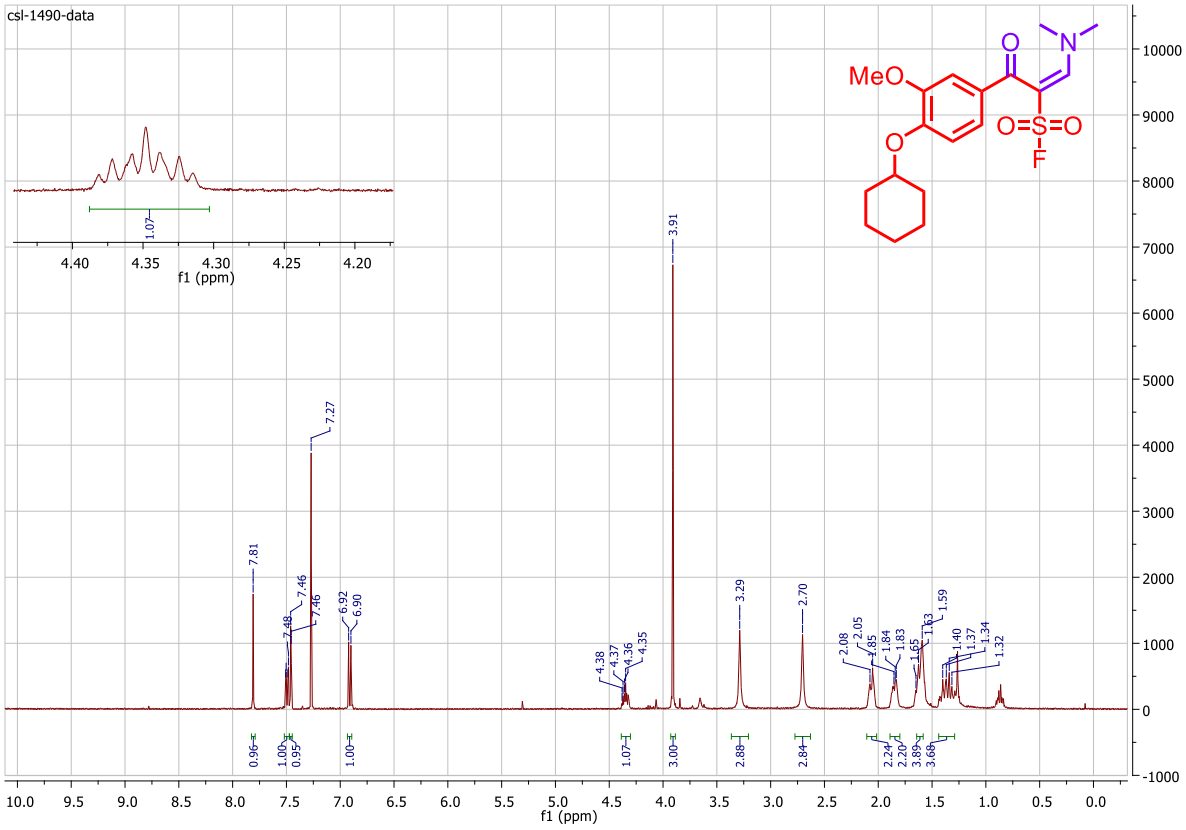
^{13}C NMR **9i**:



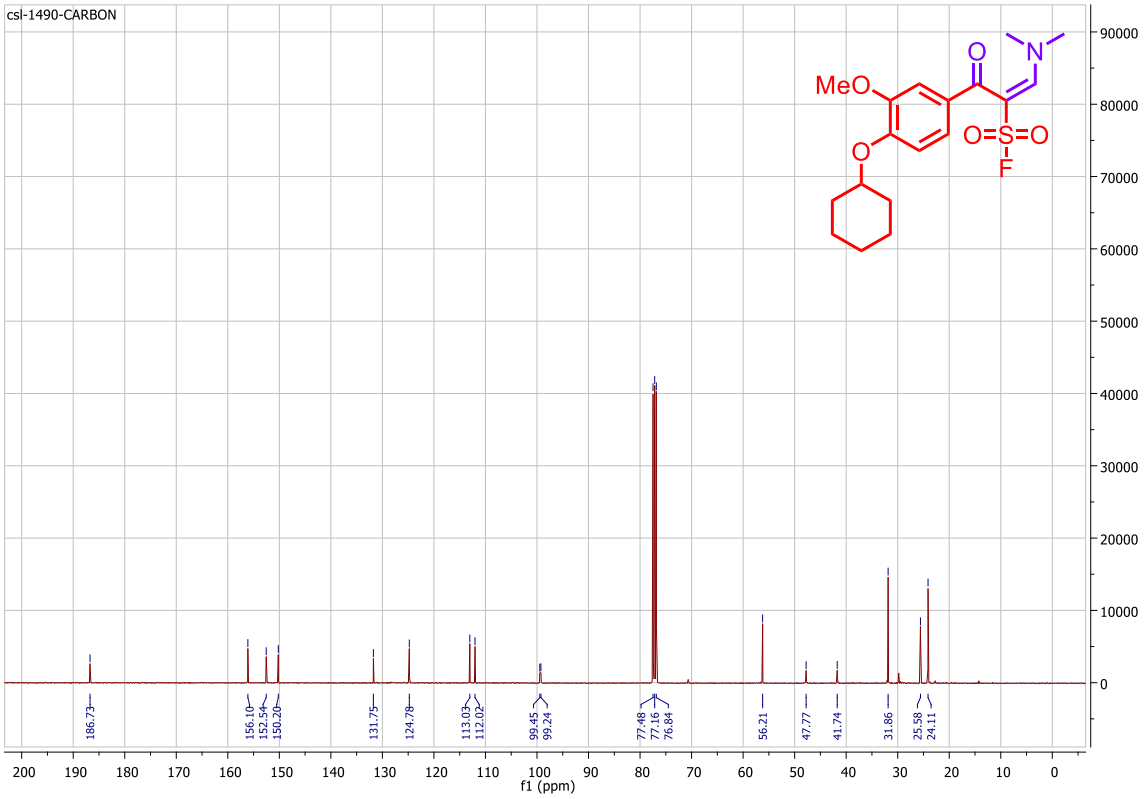
^{19}F NMR **9i**:


csl-1498-data
O
N
EtO
O=S=O
F
OEt
72.81
150
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

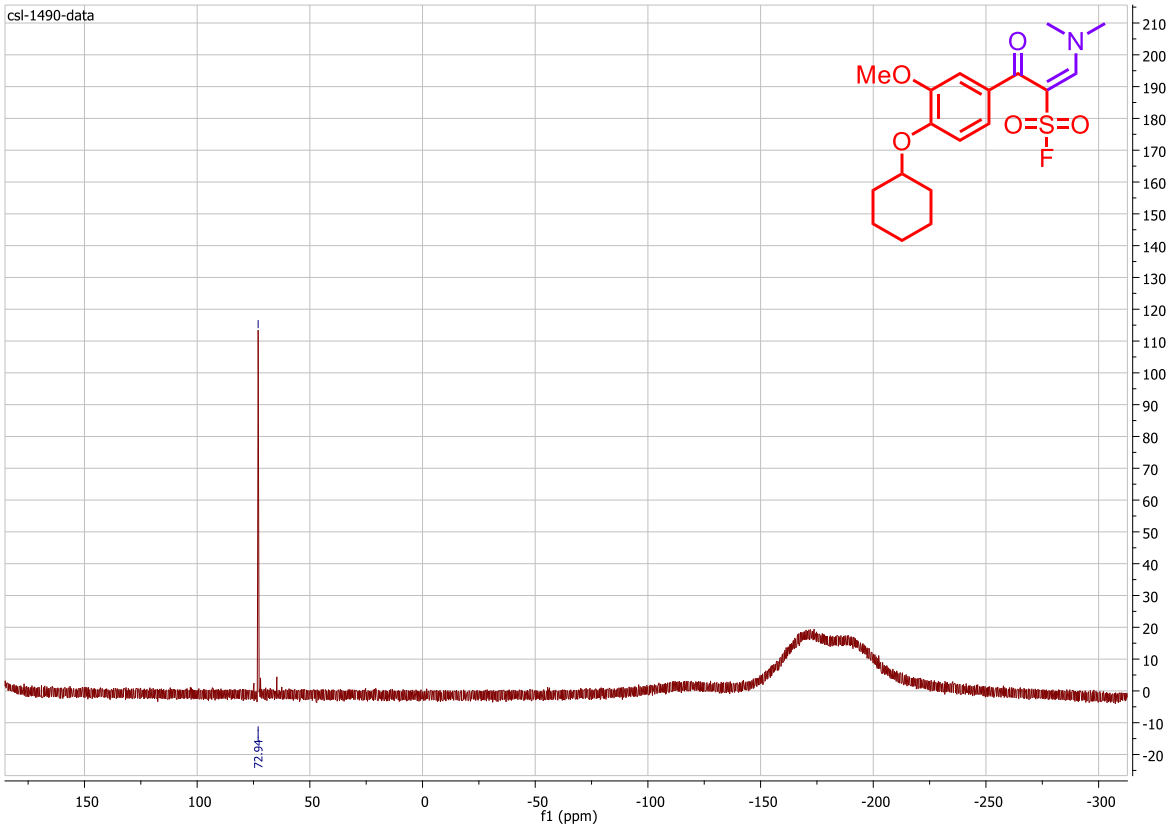
^{1}H NMR **9j**:



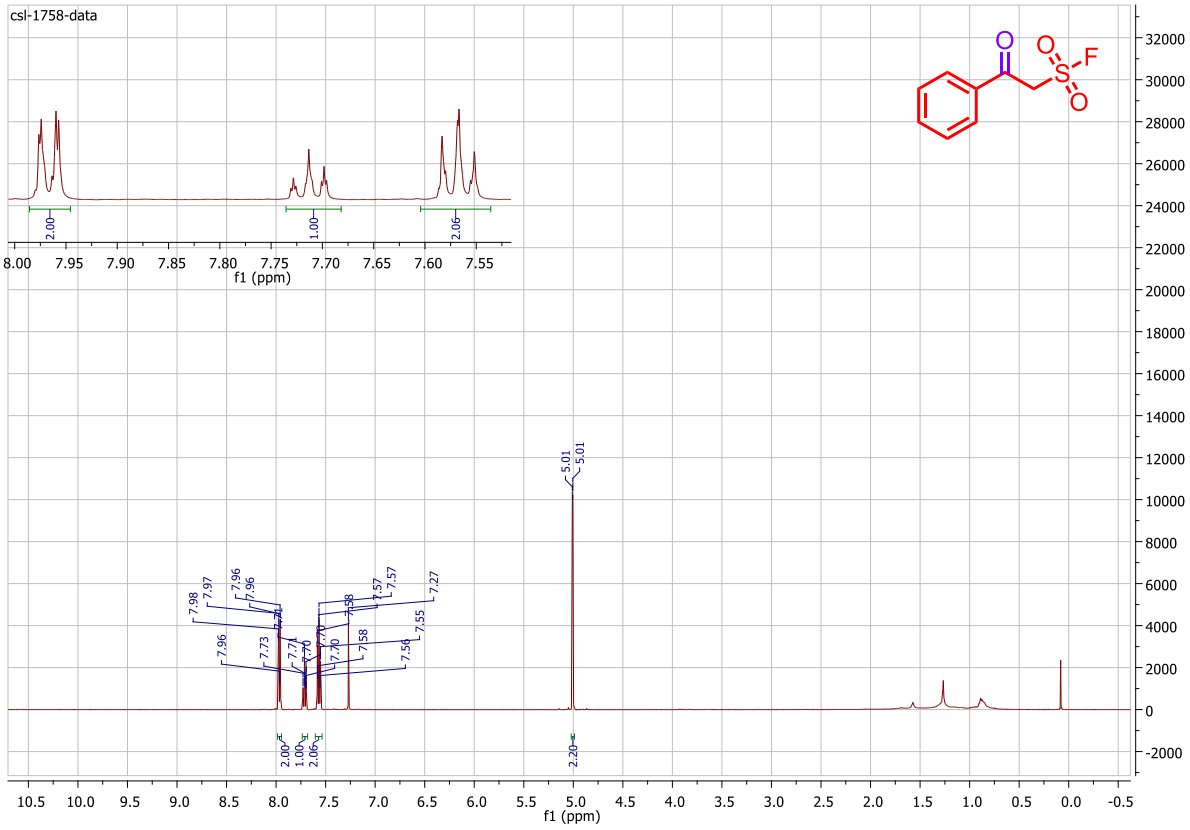
^{13}C NMR **9j**:



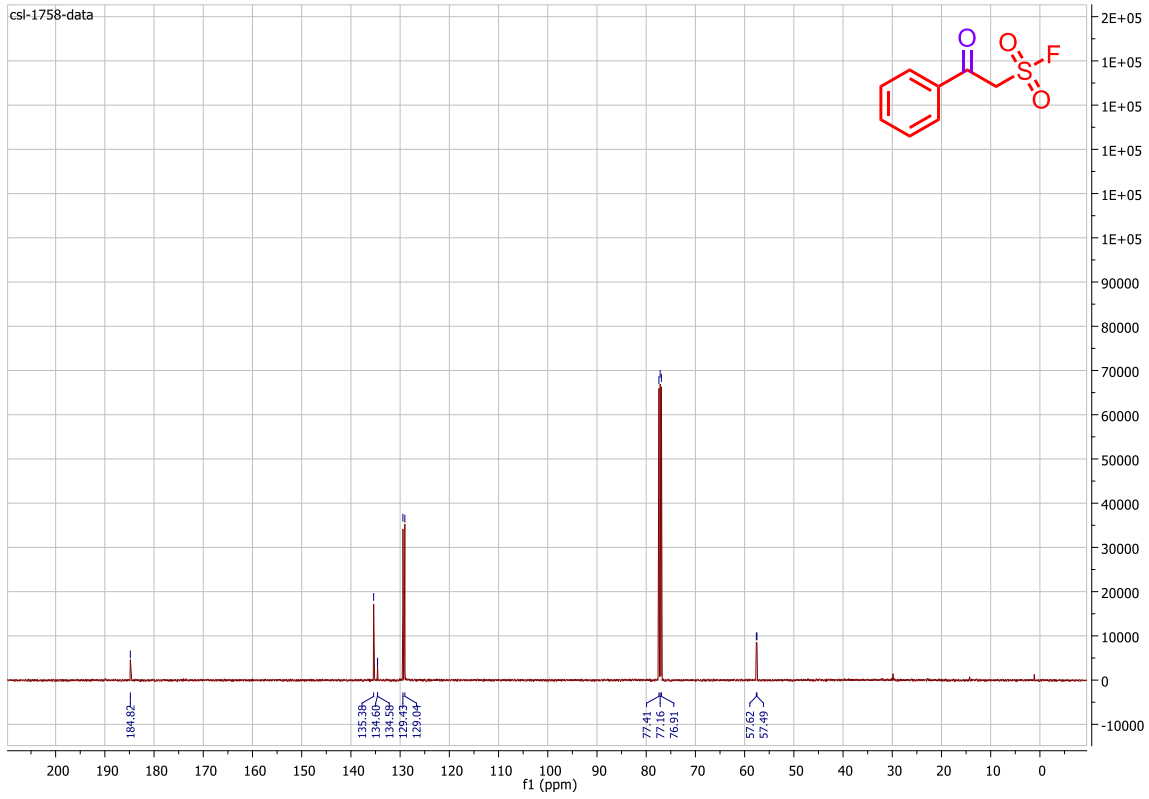
^{19}F NMR **9j**:


csl-1490-data
MeO
O
N
O=S=O
F
72.94
150
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20

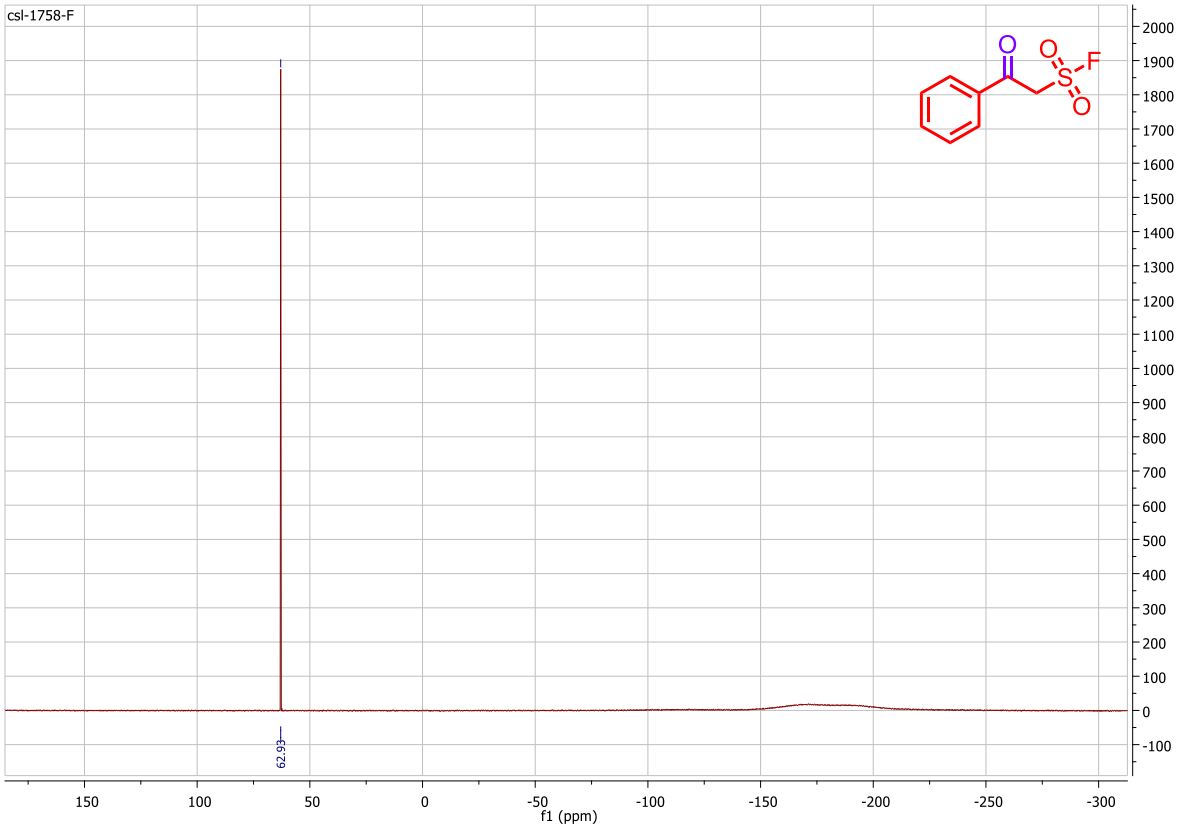
^{1}H NMR **14a**:



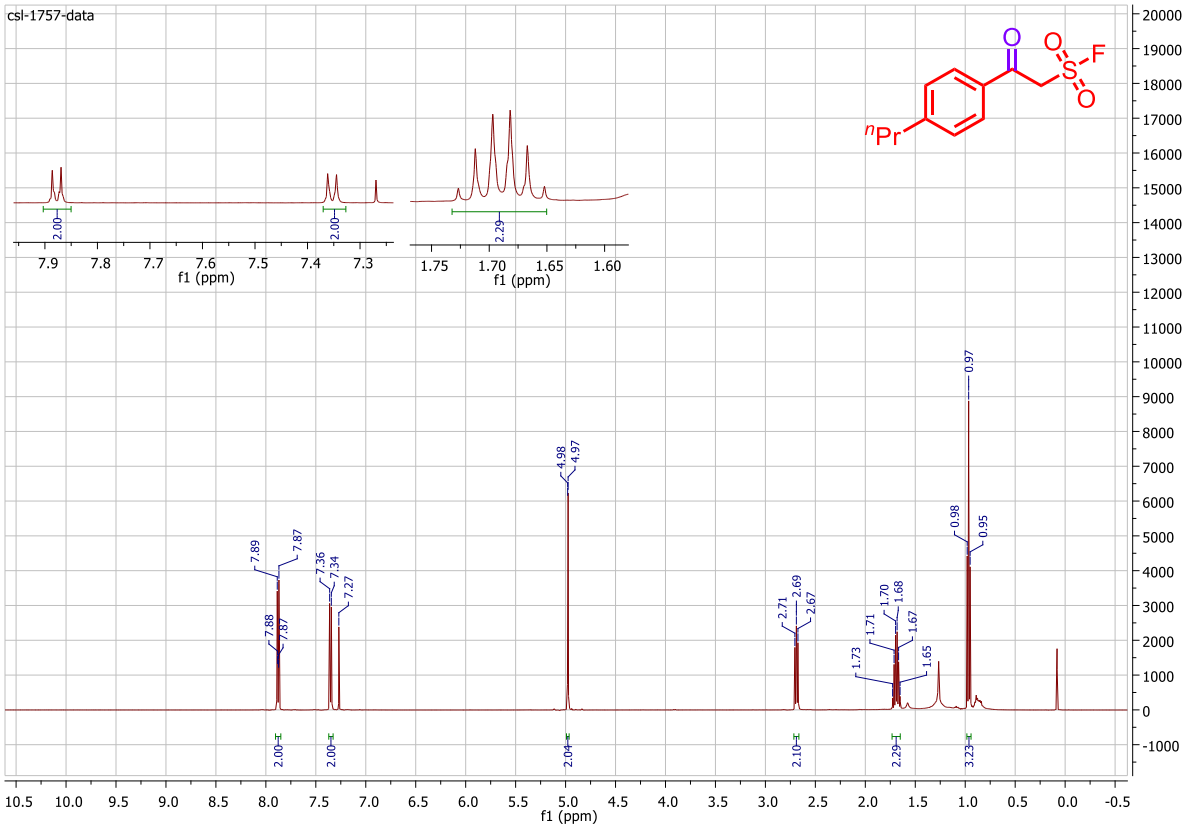
^{13}C NMR **14a**:



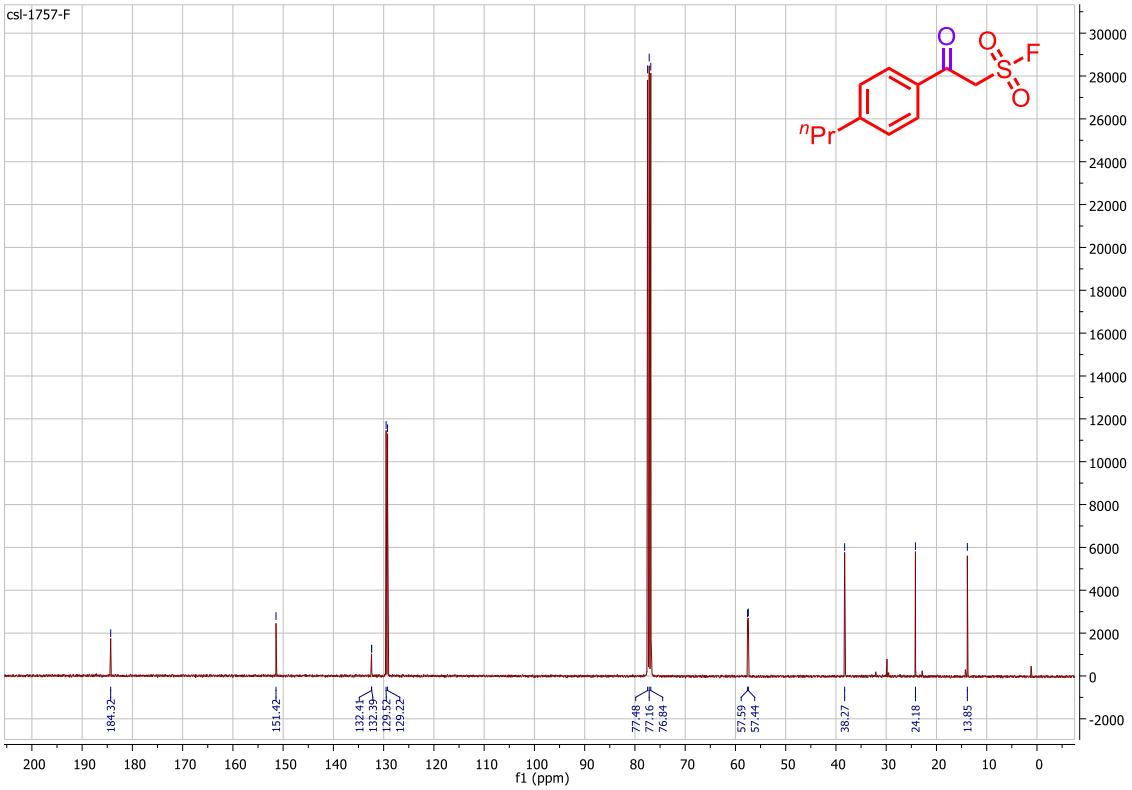
^{19}F NMR **14a**:


csl-1758-F
62.93
150
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
O
O
S
F
O

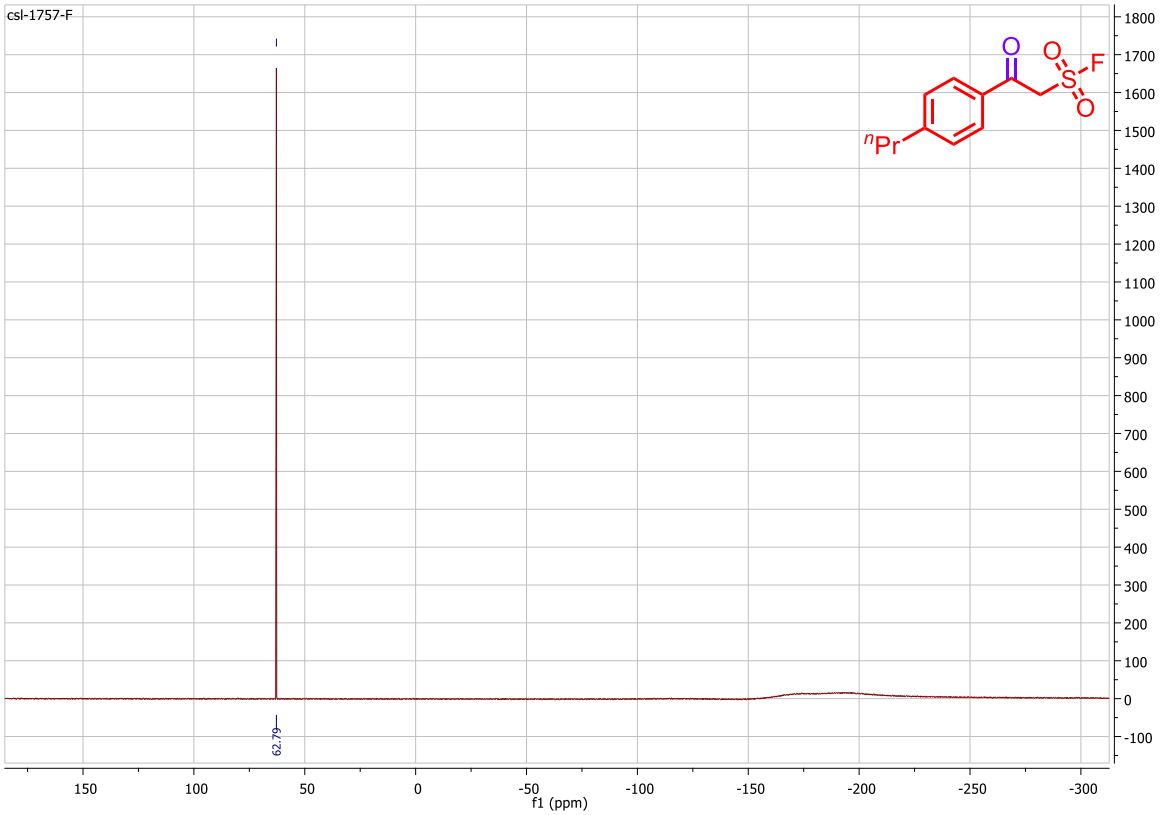
^{1}H NMR **14b**:



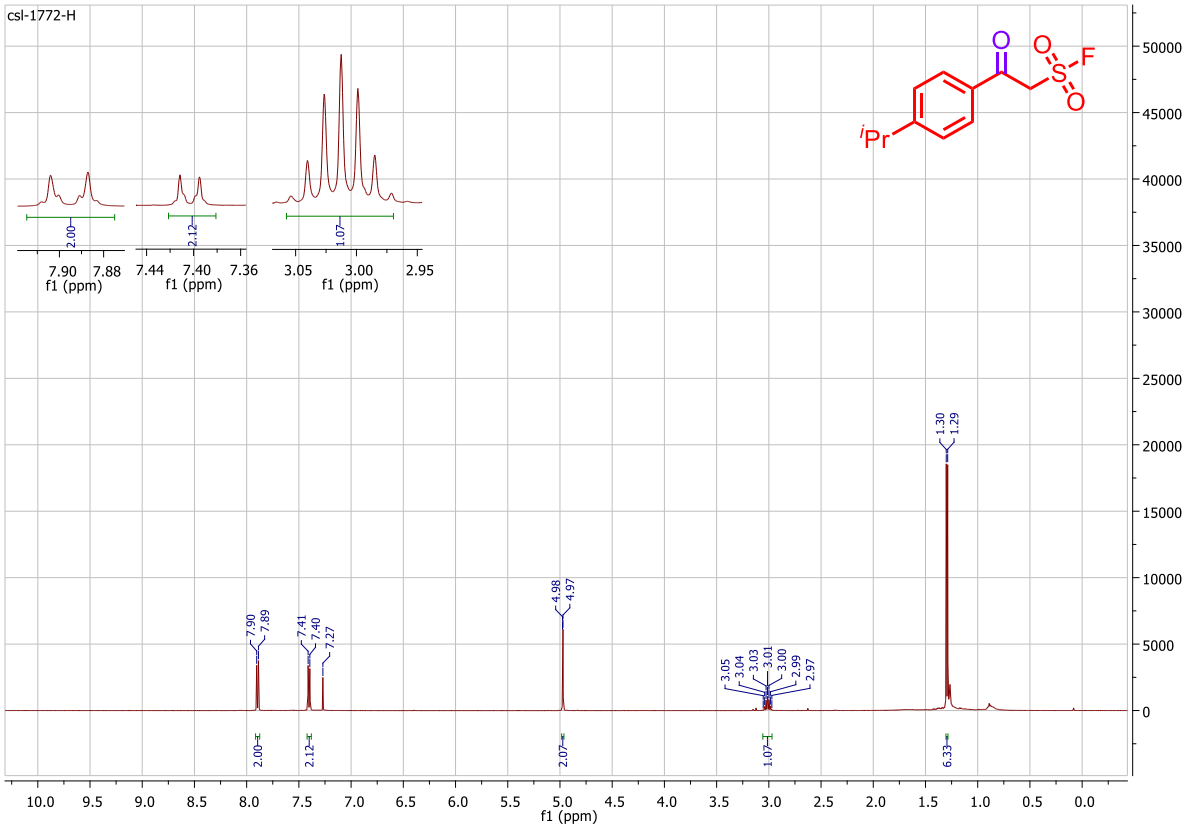
^{13}C NMR **14b**:



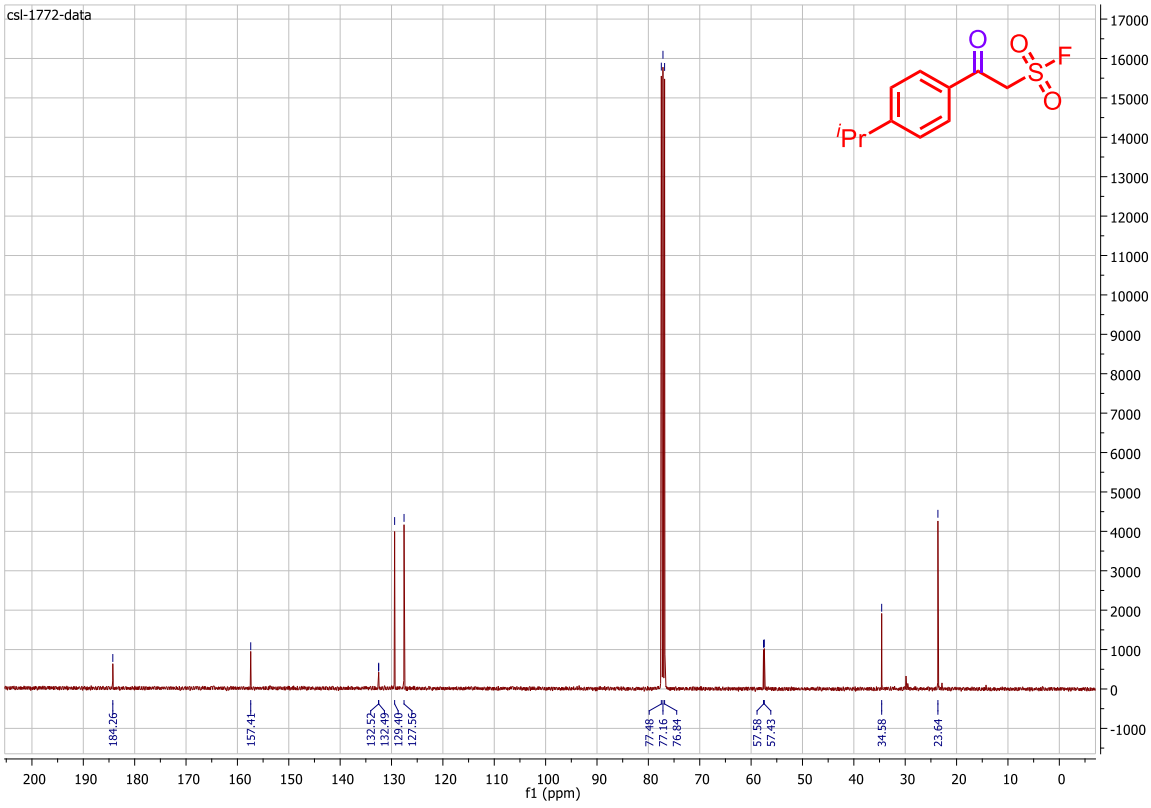
^{19}F NMR **14b**:


csl-1757-F
62.79
150
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
O
O
S
F
O
nPr

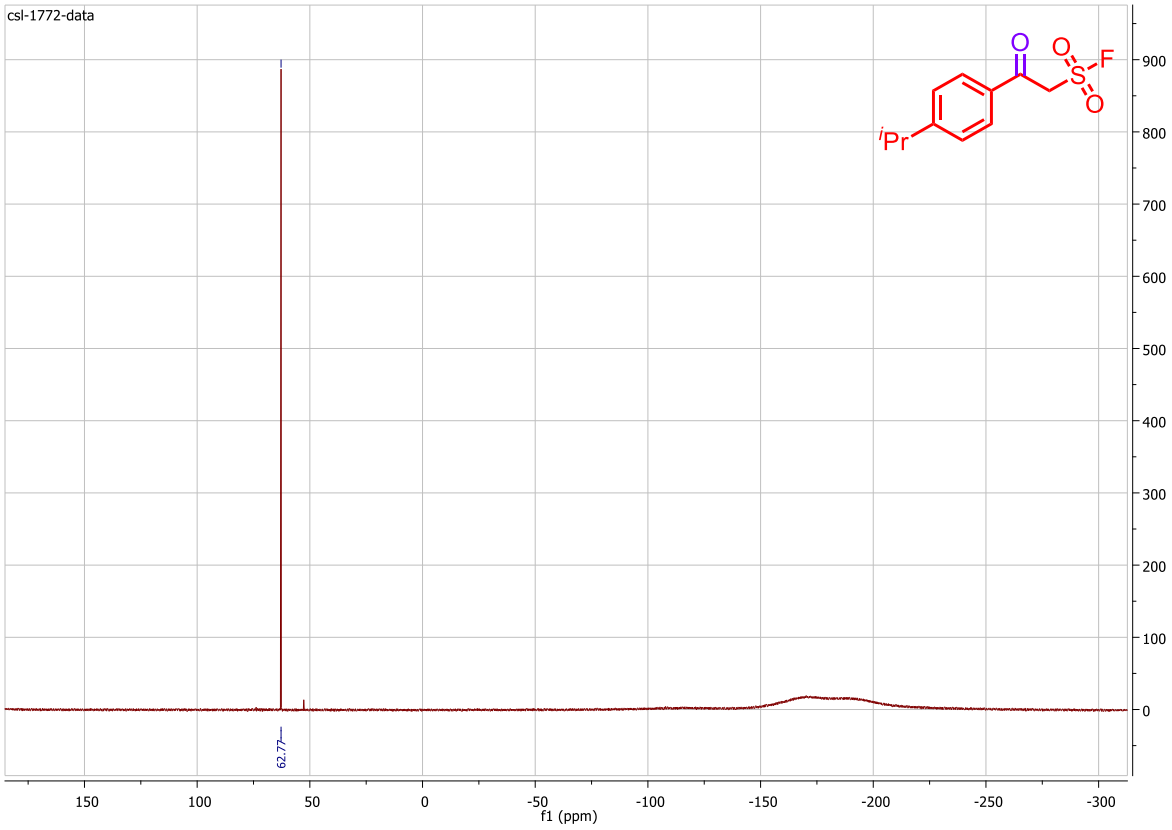
^{1}H NMR **14c**:



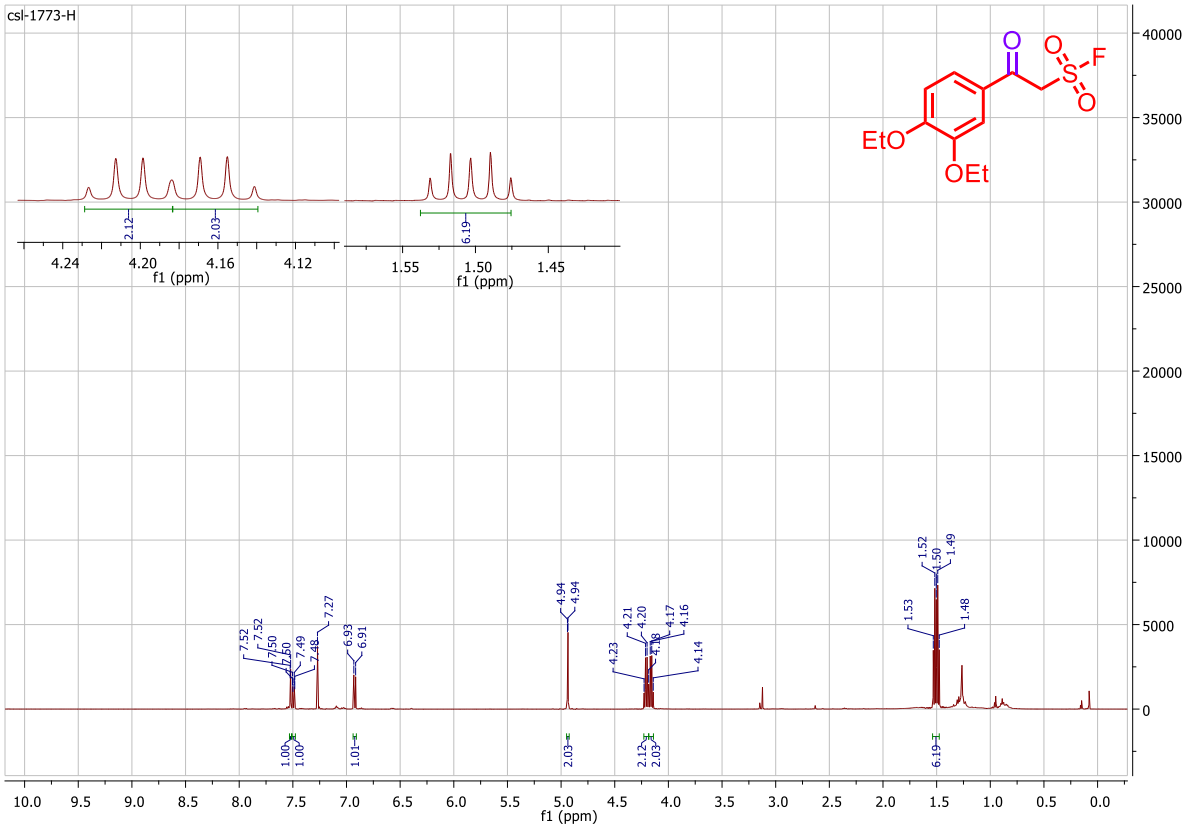
^{13}C NMR **14c**:



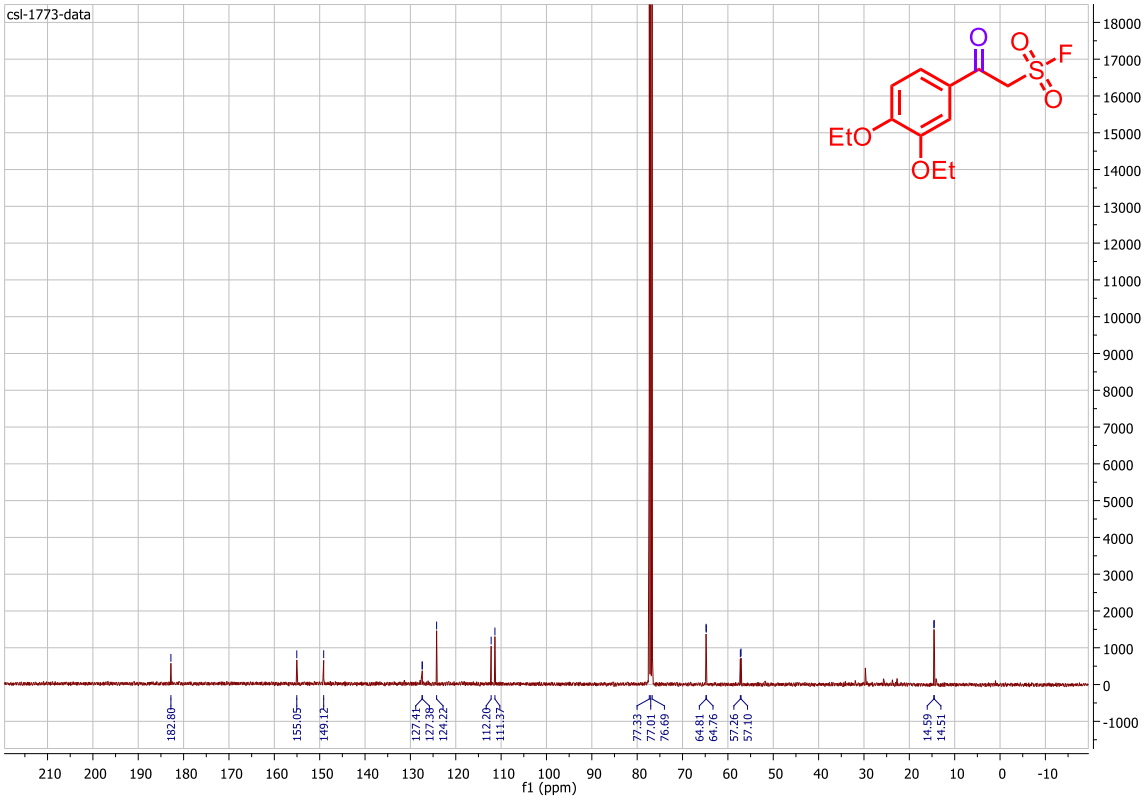
^{19}F NMR **14c**:


csl-1772-data
62.77
150
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)
900
800
700
600
500
400
300
200
100
0
O
O
S
F
O
iPr

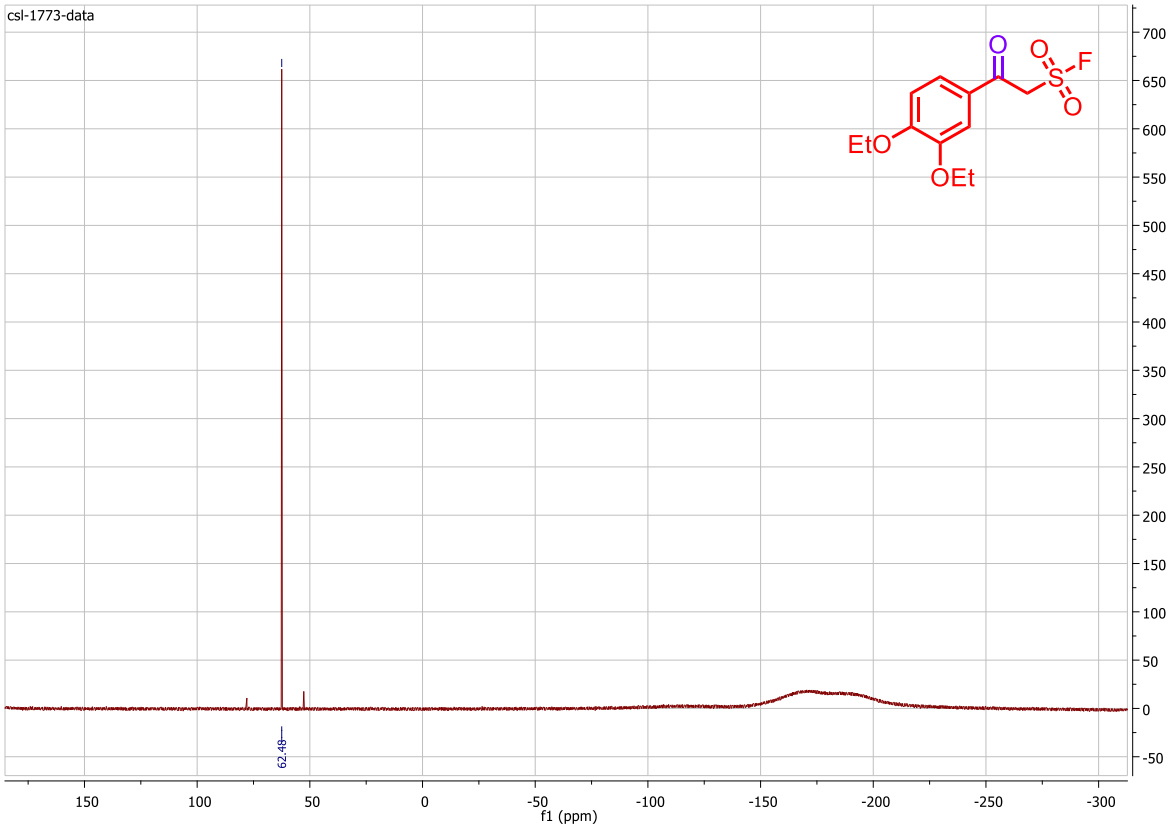
^{1}H NMR **14d**:



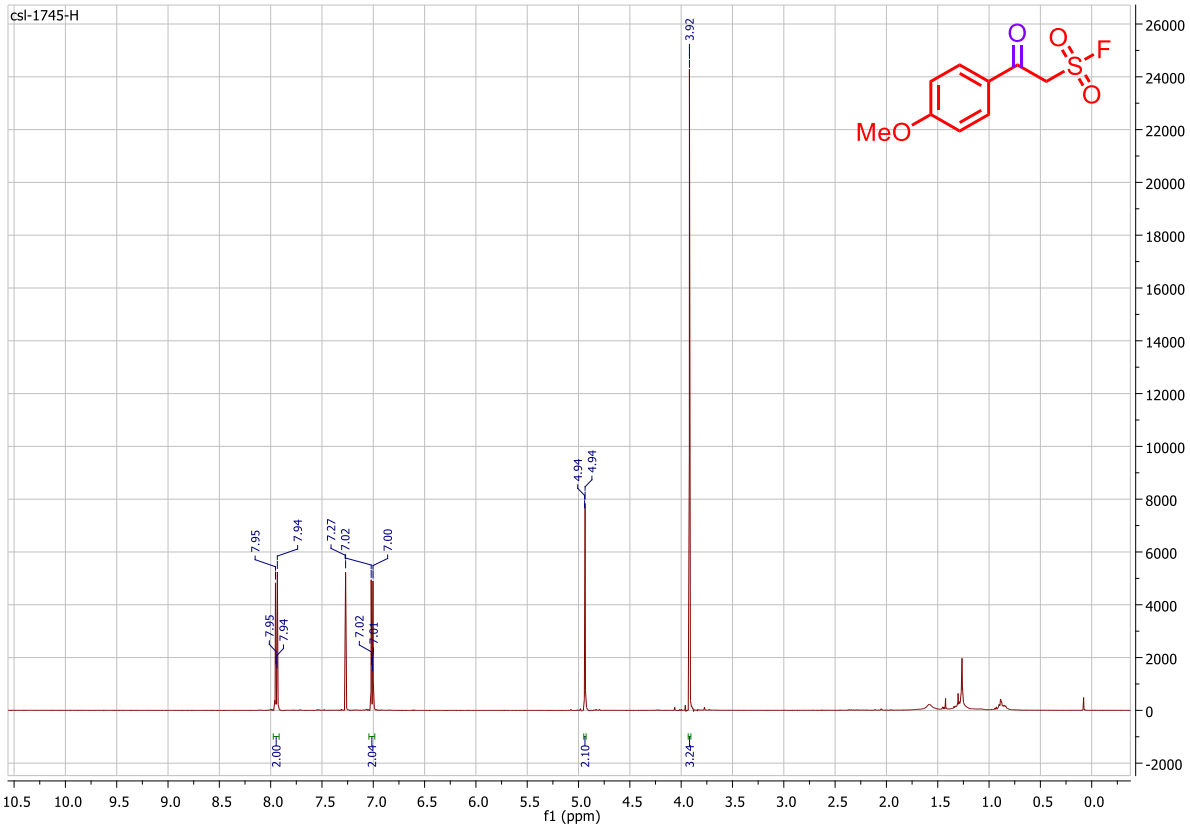
^{13}C NMR **14d**:



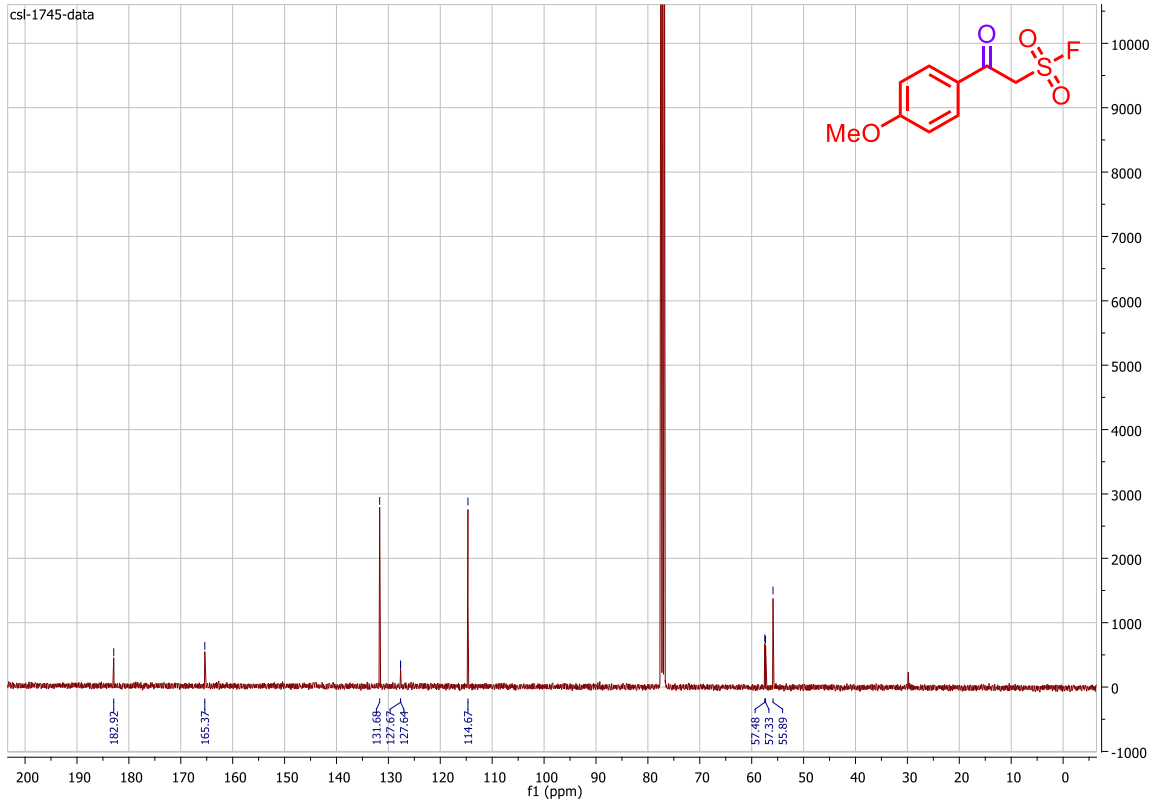
^{19}F NMR **14d**:


csl-1773-data
O
O
S
F
O
EtO
OEt
62.49
150
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50

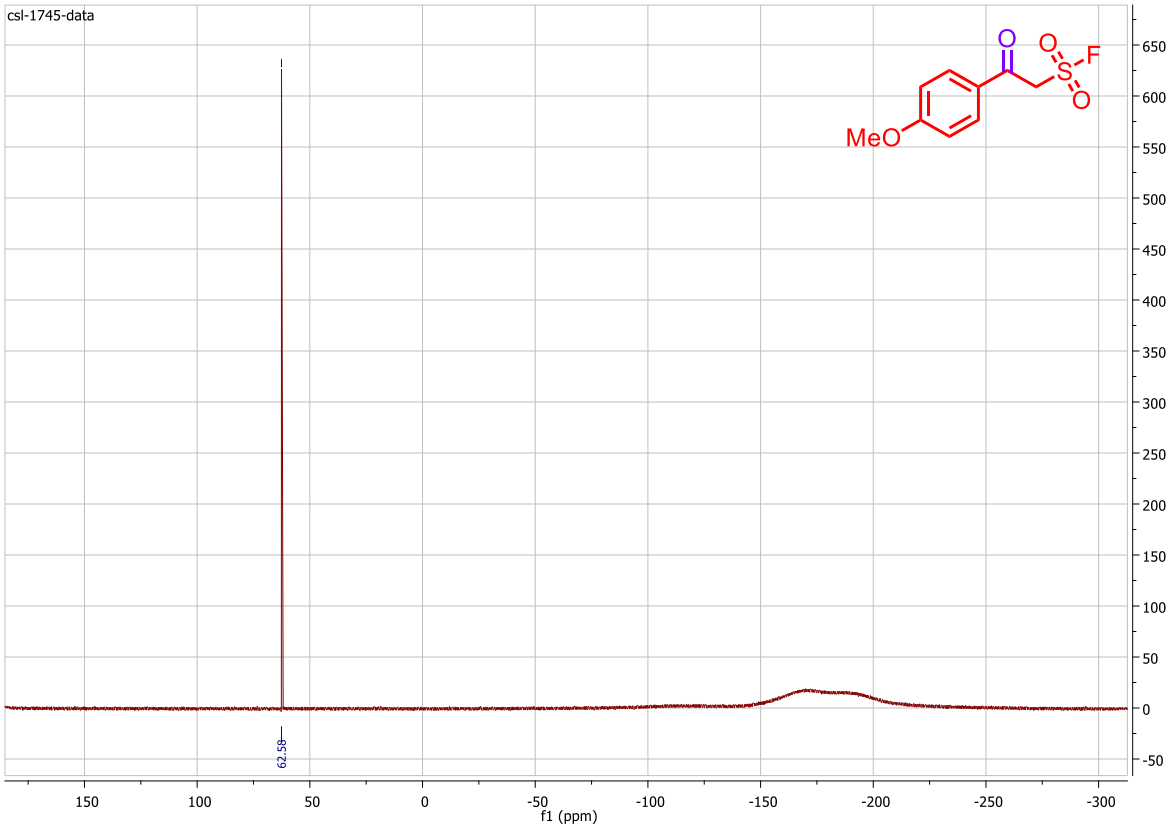
^{1}H NMR **14e**:



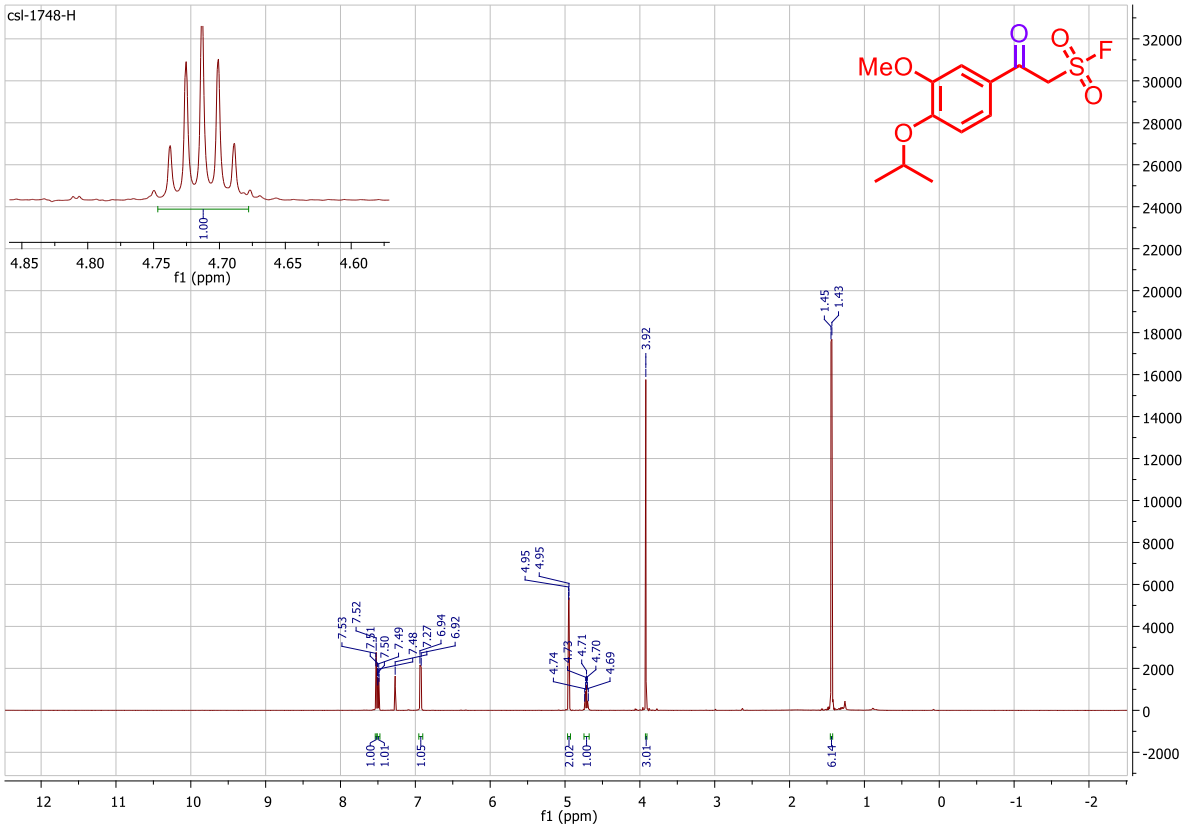
^{13}C NMR **14e**:



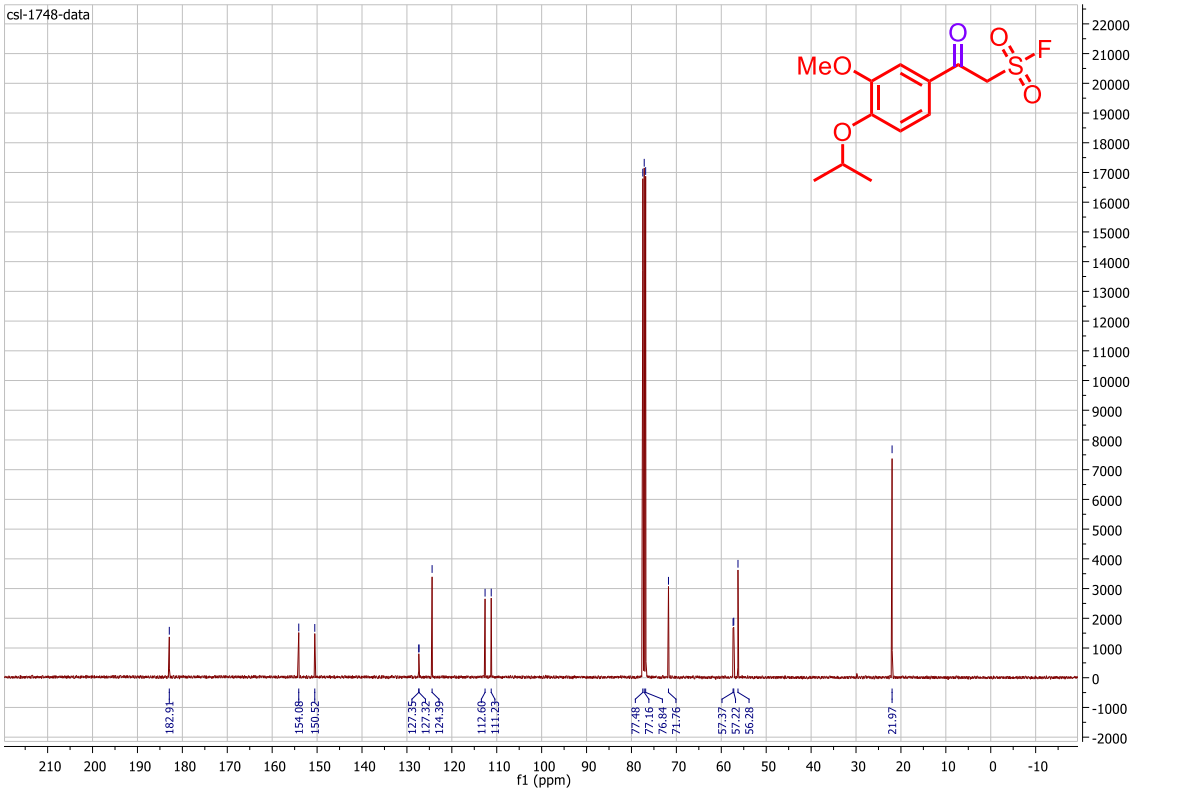
^{19}F NMR **14e**:


csl-1745-data
O
O
S
F
O
MeO
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
62.59
150
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)

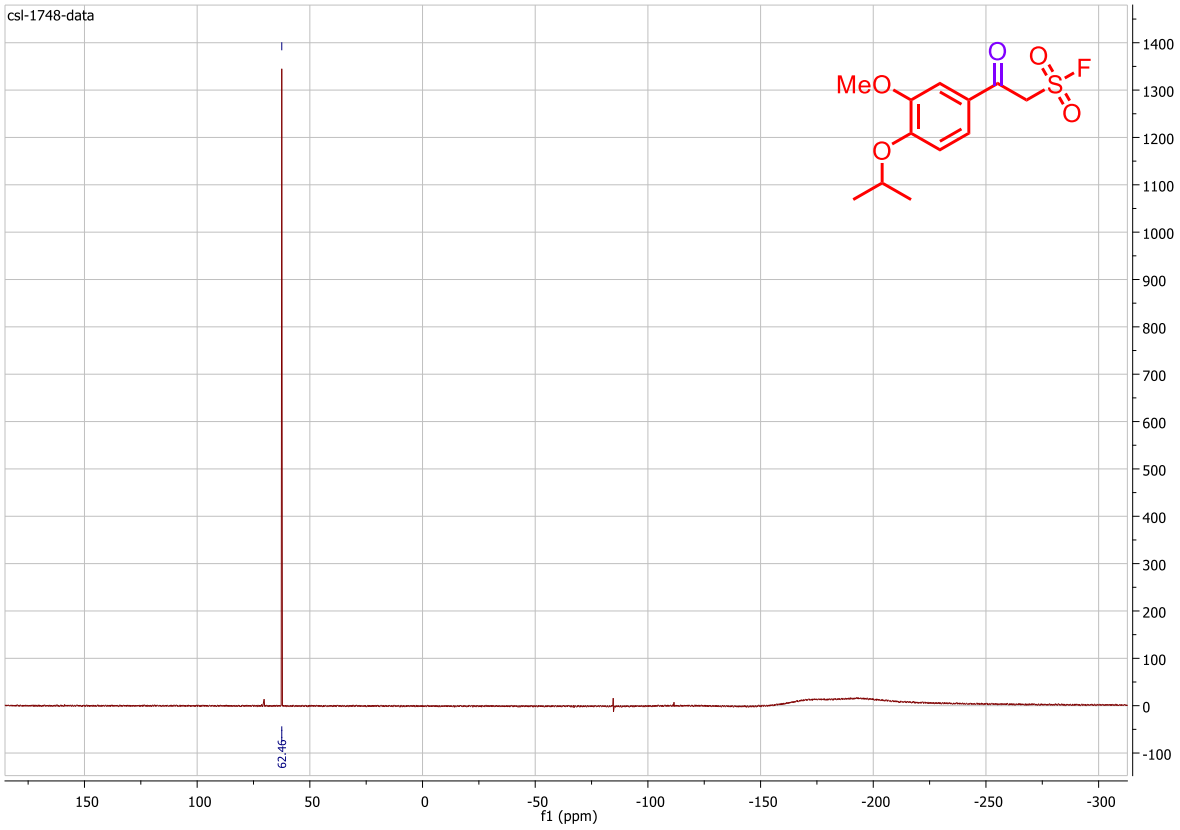
^{1}H NMR **14f**:



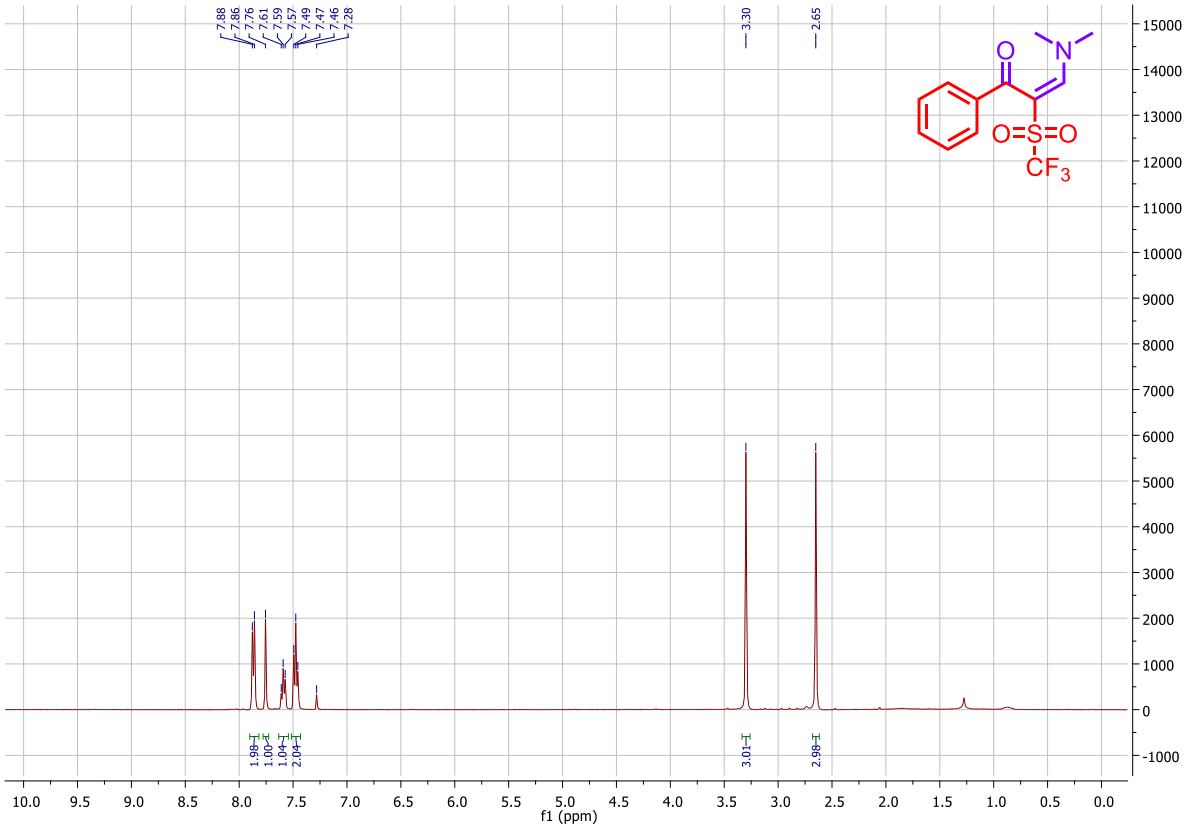
^{13}C NMR **14f**:



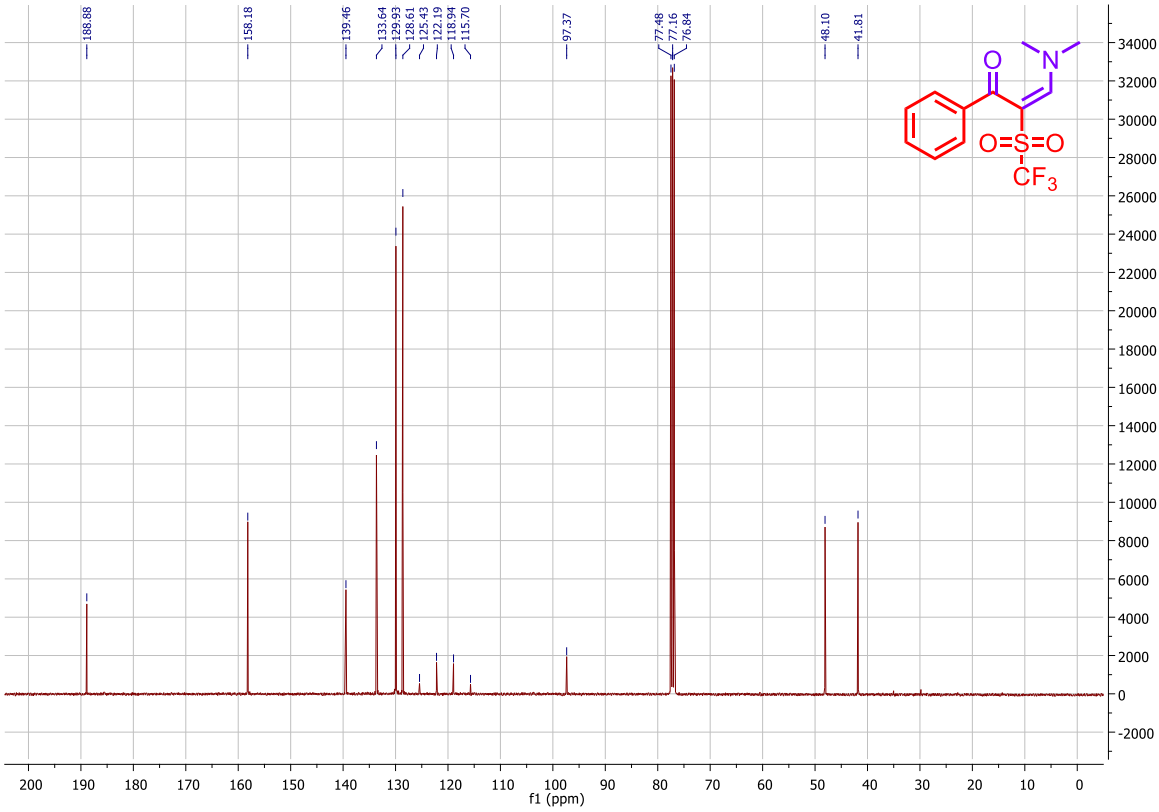
^{19}F NMR **14f**:


csl-1748-data
MeO
O
O
S
F
O
O
62.46
150
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

^{1}H NMR **9a-CF_3**:



^{13}C NMR **9a-CF_3**:



^{19}F NMR **9a-CF_3**: