Supporting Information

for

Synthesis of trifluoromethyl-substituted 1,2,6-thiadiazine 1-oxides from sulfonimidamides under mechanochemical conditions

Marco Thomas Passia,[a] Jan-Hendrik Schöbel,[a] Niklas Julian Lentelink,[a] Khai-Nghi Truong,[b] Kari Rissanen,[b] and Carsten Bolm*[a]

[a] Institute of Organic Chemistry, RWTH Aachen University, Landoltweg 1, 52074 Aachen, Germany

[b] Department of Chemistry, University of Jyvaskyla, P.O. Box 35, Survontie 9B, 40014 Jyväskylä, Finland

E-Mail: Carsten.Bolm@oc.rwth-aachen.de

Table of Content

1. General information and ball mill equipment

Unless otherwise noted, all solution-phase reactions were performed in oven-dried glassware under argon atmosphere and magnetic stirring. Anhydrous solvents were purchased from commercial suppliers as extra dry solvents stored over molecular sieves in sealed bottles or were taken from a MBRAUN® solvent purification system. Mechanochemical reactions were carried out in a RETSCH Mixer Mill MM400 in stainless steel jars (V = 5 mL or 10 mL; depending on the reaction scale) loaded with two stainless steel balls (d = 7 mm or 10 mm) under argon atmosphere. Sulfonimidamides **1a**-**k** and trifluoromethyl ketones **4b**-**d** were synthesized according to literature procedures (section 2). All other reagents were ordered from commercial suppliers und used without further purification.

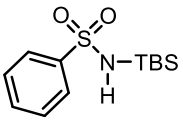
The reaction progress was monitored by thin layer chromatography (TLC) on silica gel 60 F_{254} covered aluminum sheets from Merck with UV-indicators and detected under UV-light (λ = 254 nm and 365 nm). Products were purified by flash column chromatography (FCC) on Acros Organics silica gel 60 Å (35 – 70 µm) as stationary phase and solvent mixtures as mobile phase. Nuclear magnetic resonance (NMR) spectra were measured at room temperature in Chloroform-*d* or DMSO-d_6 on a Bruker Avance Neo 400, Bruker Avance Neo 600, Agilent VNMRS 400 or Agilent VNMRS 600. The chemical shift (δ) is given in parts per million (ppm) and spectra are referenced on the residual solvent peaks (Chloroform-*d*: ^{1}H-NMR δ = 7.26 ppm, ^{13}C-NMR δ = 77.16 ppm; DMSO-d_6: ^{1}H-NMR δ = 2.50 ppm, ^{13}C-NMR δ = 39.52 ppm). Multiplicities are abbreviated as m (multiplet), s (singlet), d (doublet), dd (doublet of doublet), dt (doublet of triplet), ddt (doublet of doublet of triplet), t (triplet), td (triplet of doublet), q (quartet), p (quintet), or br (broad) and coupling constants (J) are reported in Hertz (Hz). Melting points (m.p.) were recorded on a Büchi B-540 in open-end capillaries with a heating rate of 2 °C/min. High resolution mass (HRMS) spectra were measured on a Thermo Scientific LTQ Orbitrap XL spectrometer with Orbitrap mass analyzer or Bruker maXis II spectrometer with TOF mass analyzer. The atomic mass and mass to charge ratio (m/z) are given as dimensionless values. Infrared (IR) spectra were recorded on a PerkinElmer 100 FT/IR spectrometer in combination with an UATR device Diamond KRS-5.

2. Procedure and analytical data of starting materials 1a-k and 4b-d

2. 1. Synthesis of sulfonimidamides (SIAs, 1a-k)

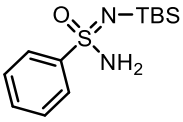
According to the literature procedure, sulfonimidamides **1a**-**k** were synthesized in a three-step reaction sequence from the corresponding sulfonamides.[S1] All analytical data are in full agreement with the published data.[S1,S2] Unreported sulfonimidamides **1b-j** were obtained following the same methodology. *N*-(*tert*-Butyldimethylsilyl)-4-methylbenzenesulfonimidamide (**6a**) and 4-methyl-benzenesulfonimidamide (**1a**) were taken from an earlier project and used without further purification.[S2]

N-(*tert*-Butyldimethylsilyl)benzenesulfonamide (1b-precursor)



Following the protocol from literature,[S1] the TBS-protected sulfonamide **1b-precursor** was obtained from benzenesulfonamide (314 mg, 2.00 mmol, 1.0 equiv.), *tert*-butyldimethylsilyl chloride (362 mg, 2.40 mmol, 1.2 equiv.) and triethylamine (405 mg, 0.556 mL, 4.00 mmol, 2.0 equiv.) as a colorless solid (543 mg, 2.00 mmol, quant.). **^{1}H NMR** (600 MHz, DMSO-d_6): δ = 7.82–7.80 (m, 2H), 7.65 (s, 1H), 7.60–7.54 (m, 3H), 0.86 (s, 9H), 0.09 (s, 6H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6): δ = 144.6, 131.7, 128.9 (2C), 125.4 (2C), 25.7 (3C), 17.4, –4.5 (2C) ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_{12}H_{21}O_2NSSiNa]^+$: 294.0954, found: 294.0947; **IR (ATR)**: ν = 3345, 3250, 2934, 2888, 2861, 2609, 2496, 2189, 2056, 1914, 1585, 1469, 1447, 1401, 1366, 1336, 1283, 1254, 1151, 1095, 1036, 931, 786, 756, 715, 689 cm^{-1}; **m.p.**: 85–87 °C.

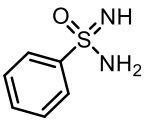
N-(*tert*-Butyldimethylsilyl)benzenesulfonimidamide (6b)



Following the protocol from literature,[S1] the TBS-protected sulfonimidamide **6b** was obtained from *N*-(*tert*-butyldimethylsilyl)benzenesulfonamide (**1b-precursor**, 500 mg, 1.84 mmol, 1.0 equiv.), PPh_3 (531 mg, 2.03 mmol, 1.1 equiv.), C_2Cl_6 (480 mg, 2.03 mmol, 1.1 equiv.), ammonia gas and triethylamine (280 mg, 0.384 mL, 2.76 mmol, 1.5 equiv.) after purification by use of column chromatography on silica gel (*n*-pentane:EtOAc 9/1 to 4/1) as a colorless solid (422 mg, 1.56 mmol, 85%). **^{1}H NMR** (600 MHz, DMSO-d_6): δ = 7.88–7.84 (m, 2H), 7.52–7.48 (m, 3H), 6.63 (s, 2H), 0.87 (s, 9H), 0.01 (s, 3H), 0.00 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6): δ = 148.34, 130.57, 128.38 (2C), 125.33 (2C), 26.02 (3C), 17.83, –2.46, –2.51 ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_{12}H_{22}ON_2SSiNa]^+$: 293.1114, found: 293.1109; **IR (ATR)**: ν = 3319, 3233, 3094, 2955, 2930, 2892, 2856, 2634, 2164, 2047,

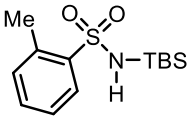
1997, 1923, 1811, 1553, 1469, 1442, 1407, 1277, 1142, 1090, 1003, 938, 899, 827, 778, 755, 689 cm^{-1}, **m.p.**: 129–131 °C.

Benzenesulfonimidamide (1b)



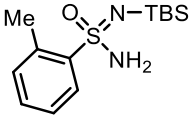
Following the protocol from literature,[S1] benzenesulfonimidamide (**1b**) was obtained after deprotection with 4 N HCl in dioxane (525 mg, 0.500 mL, 2.00 mmol, 2.0 equiv.) from *N*-(*tert*-butyldimethylsilyl)benzenesulfonimidamide (**6b**, 270 mg, 1.00 mmol, 1.0 equiv.) as a colorless solid (72.5 mg, 0.464 mmol, 46%). **^{1}H NMR** (600 MHz, DMSO-d_6): δ = 7.95–7.87 (m, 2H), 7.56–7.45 (m, 3H), 6.63 (br s, 2H) ppm [NH-Proton not detected]; **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6): δ = 146.7, 130.9, 128.4 (2C), 125.8 (2C) ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_6H_9ON_2S]^+$: 157.0430, found: 157.0428; **IR (ATR)**: ν = 3747, 3265, 2962, 2677, 2325, 2162, 2095, 1992, 1895, 1809, 1731, 1670, 1577, 1477, 1442, 1324, 1244, 1151, 1090, 1015, 906, 747, 715, 681 cm^{-1}; **m.p.**: 104–106 °C.

***N*-(*tert*-Butyldimethylsilyl)-2-methylbenzenesulfonamide (1c-precursor)**



Following the protocol from literature,[S1] the TBS-protected sulfonamide **1c-precursor** was obtained from 2-methylbenzenesulfonamide (1.71 g, 10.0 mmol, 1.0 equiv.), *tert*-butyldimethylsilyl chloride (1.81 g, 12.0 mmol, 1.2 equiv.) and triethylamine (2.02 g, 2.78 mL, 20.0 mmol, 2.0 equiv.) as a pale yellow solid (2.76 g, 9.68 mmol, 97%). **^{1}H NMR** (600 MHz, DMSO-d_6): δ = 7.83–7.80 (m, 1H), 7.63 (s, 1H), 7.47 (td, J = 7.4, 1.4 Hz, 1H), 7.36 (d, J = 7.6 Hz, 2H), 2.60 (s, 3H), 0.89 (s, 9H), 0.07 (s, 6H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6): δ = 142.5, 135.8, 132.1, 131.8, 127.0, 125.8, 25.7 (3C), 19.8, 17.5, –4.6 (2C) ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_{13}H_{23}O_2NSSiNa]^+$: 308.1111, found: 308.1107; **IR (ATR)**: ν = 3223, 2932, 2861, 2725, 2649, 2326, 2199, 2108, 2017, 1911, 1571, 1460, 1359, 1286, 1255, 1166, 1110, 1028, 951, 832, 795, 746, 717, 665 cm^{-1}; **m.p.**: 92–94 °C.

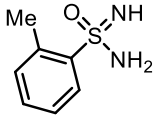
***N*-(*tert*-Butyldimethylsilyl)-2-methylbenzenesulfonimidamide (6c)**



Following the protocol from literature,[S1] the TBS-protected sulfonimidamide **6c** was obtained from *N*-(*tert*-butyldimethylsilyl)-2-methylbenzenesulfonamide (**1c-precursor**, 2.57 g, 9.00 mmol, 1.0 equiv.), PPh_3 (2.60 g, 9.90 mmol, 1.1 equiv.), C_2Cl_6 (2.32 g, 9.90 mmol, 1.1 equiv.), ammonia gas and triethylamine (1.37 g, 1.88 mL, 13.5 mmol, 1.5 equiv.) after purification by use of column chromatography on silica gel (*n*-pentane:EtOAc 9/1 to 4/1) as a colorless solid (832 mg, 2.92 mmol, 33%). **^{1}H NMR** (600 MHz,

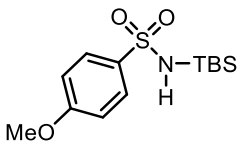
DMSO-d_6): δ = 7.95–7.92 (m, 1H), 7.38 (td, J = 7.3, 1.4 Hz, 1H), 7.30 (t, J = 7.3 Hz, 2H), 6.62 (s, 2H), 2.64 (s, 3H), 0.87 (s, 9H), 0.01 (s, 3H), 0.00 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6): δ = 146.01, 135.33, 131.99, 130.60, 126.51, 125.53, 26.00 (3C), 20.05, 17.81, –2.56, –2.61 ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_{13}H_{24}ON_2SSiNa]^+$: 307.1271; found: 307.1264; **IR (ATR)**: v = 3385, 3268, 3108, 3064, 2929, 2890, 2855, 2328, 2157, 2029, 1982, 1908, 1711, 1548, 1467, 1311, 1249, 1160, 1073, 1045, 1005, 936, 891, 828, 799, 775, 755, 705, 682 cm^{-1}; **m.p.**: 93–95 °C.

2-Methylbenzenesulfonimidamide (1c)



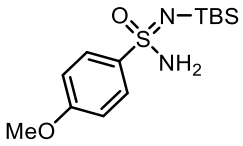
Following the protocol from literature,[S1] 2-methylbenzenesulfonimidamide (**1c**) was obtained after deprotection with formic acid (2.2 mL) and water (0.2 mL) from *N*-(*tert*-butyldimethylsilyl)-2-methylbenzenesulfonimidamide (**6c**, 142 mg, 0.500 mmol, 1.0 equiv.) as a colorless solid (85.0 mg, 0.499 mmol, quant.). **^{1}H NMR** (600 MHz, DMSO-d_6): δ = 7.99–7.90 (m, 1H), 7.40 (td, J = 7.4, 1.4 Hz, 1H), 7.30 (t, J = 6.7 Hz, 2H), 6.09 (br s, 3H), 2.65 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6): δ = 144.6, 135.9, 132.0, 130.9, 126.9, 125.6, 20.2 ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_7H_{11}ON_2S]^+$: 171.0587, found: 171.0584; **IR (ATR)**: v = 3867, 3312, 3279, 3177, 2988, 2627, 2323, 2187, 2064, 1982, 1914, 1829, 1720, 1573, 1455, 1381, 1351, 1314, 1244, 1196, 1140, 1110, 1037, 892, 804, 761, 706, 680 cm^{-1}; **m.p.**: 106–108 °C.

***N*-(*tert*-Butyldimethylsilyl)-4-methoxybenzenesulfonamide (1d-precursor)**



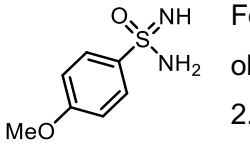
Following the protocol from literature,[S1] the TBS-protected sulfonamide **1d-precursor** was obtained from 4-methoxybenzenesulfonamide (1.87 g, 10.0 mmol, 1.0 equiv.), *tert*-butyldimethylsilyl chloride (1.81 g, 12.0 mmol, 1.2 equiv.) and triethylamine (2.02 g, 2.78 mL, 20.0 mmol, 2.0 equiv.) as a colorless solid (2.85 g, 9.45 mmol, 95%). **^{1}H NMR** (600 MHz, DMSO-d_6): δ = 7.73 (dd, J = 10.3, 3.6 Hz, 2H), 7.51 (s, 1H), 7.08 (dd, J = 10.0, 3.1 Hz, 2H), 3.82 (s, 3H), 0.86 (s, 9H), 0.08 (s, 6H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6): δ = 161.5, 136.7, 127.5 (2C), 113.9 (2C), 55.5, 25.7 (3C), 17.4, –4.5 (2C) ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_{13}H_{23}O_3NSSiNa]^+$: 324.1060, found: 324.1059; **IR (ATR)**: v = 3441, 3349, 3199, 2933, 2858, 2697, 2610, 2279, 2211, 2177, 2105, 2059, 1976, 1740, 1645, 1594, 1498, 1466, 1413, 1366, 1333, 1305, 1253, 1186, 1140, 1099, 1025, 935, 832, 784, 675 cm^{-1}; **m.p.**: 68–70 °C.

***N*-(*tert*-Butyldimethylsilyl)-4-methoxybenzenesulfonimidamide (6d)**



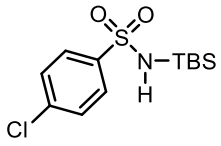
Following the protocol from literature,[S1] the TBS-protected sulfonimidamide **6d** was obtained from *N*-(*tert*-butyldimethylsilyl)-4-methoxybenzene-sulfonamide (**1d-precursor**, 2.71 g, 9.00 mmol, 1.0 equiv.), PPh_3 (2.60 g, 9.90 mmol, 1.1 equiv.), C_2Cl_6 (2.32 g, 9.90 mmol, 1.1 equiv.), ammonia gas and triethylamine (1.37 g, 1.88 mL, 13.5 mmol, 1.5 equiv.) after purification by use of column chromatography on silica gel (*n*-pentane:EtOAc 9/1 to 7/3) as a colorless solid (1.97 g, 6.55 mmol, 73%). **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 7.81–7.76 (m, 2H), 7.04–6.99 (m, 2H), 6.50 (s, 2H), 3.80 (s, 3H), 0.87 (s, 9H), 0.00 (s, 3H), -0.01 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ = 160.80, 140.60, 127.33 (2C), 113.39 (2C), 55.46, 26.03 (3C), 17.82, –2.46, –2.50 ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_{13}H_{24}O_2N_2SSiNa]^+$: 323,1220, found: 323,1218; **IR (ATR)**: ν = 3364, 3269, 3008, 2930, 2891, 9854, 2290, 2192, 2138, 2055, 2017, 1992, 1954, 1870, 1731, 1592, 1556, 1496, 1462, 1410, 1357, 1276, 1247, 1158, 1148, 1098, 1069, 1025, 961, 935, 875, 828, 772, 722 cm^{-1}; **m.p.**: 80–82 °C.

4-Methoxybenzenesulfonimidamide (1d)



Following the protocol from literature,[S1] 4-methoxysulfonimidamide (**1d**) was obtained after deprotection with 4 N HCl in dioxane (525 mg, 0.500 mL, 2.00 mmol, 2.0 equiv.) from *N*-(*tert*-butyldimethylsilyl)-4-methoxybenzene-sulfonamide (**6d**, 301 mg, 1.00 mmol, 1.0 equiv.) as a pale yellow solid (110 mg, 0.591 mmol, 59%). **^{1}H NMR** (600 MHz, DMSO-d_6): δ = 7.86–7.79 (m, 2H), 7.05–7.00 (m, 2H), 3.81 (s, 3H) ppm [NH and NH_2 protons not detected]; **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6): δ = 161.1, 138.7, 127.9 (2C), 113.5 (2C), 55.5 ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_7H_{11}O_2N_2S]^+$: 187.0536, found: 187.0536; **IR (ATR)**: ν = 3328, 3282, 2924, 2682, 2303, 2174, 2060, 1911, 1723, 1667, 1589, 1491, 1455, 1411, 1305, 1248, 1125, 1058, 1013, 812, 776 cm^{-1}; **m.p.**: 106–108 °C.

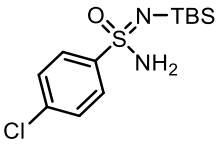
***N*-(*tert*-Butyldimethylsilyl)-4-chlorobenzenesulfonamide (1e-precursor)**



Following the protocol from literature,[S1] the TBS-protected sulfonamide **1e-precursor** was obtained from 4-chlorobenzenesulfonamide (1.92 g, 10.0 mmol, 1.0 equiv.), *tert*-butyldimethylsilyl chloride (1.81 g, 12.0 mmol, 1.2 equiv.) and triethylamine (2.02 g, 2.78 mL, 20.0 mmol, 2.0 equiv.) as a colorless solid (2.09 g, 9.48 mmol, 95%). **^{1}H NMR** (600 MHz, DMSO-d_6): δ = 7.81 (dd, J = 8.9, 2.3 Hz, 2H), 7.67–7.62 (m, 2H), 7.47 (s, 1H), 0.86 (s, 9H), 0.09 (s, 6H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6): δ = 143.5,

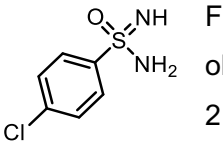
136.4, 129.1 (2C), 127.4(2C), 25.6 (3C), 17.4, –4.6 (2C) ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_{12}H_{20}O_2NClSSiNa]^+$:328.0565, found: 328.0564; **IR (ATR)**: *v* = 3244, 2937, 2861, 2650, 2563, 2290, 2170, 2030, 1913, 1740, 1644, 1576, 1471, 1396, 1336, 1282, 1149, 1088, 1011, 939, 848, 820, 788, 766, 704, 668 cm^{-1}; **m.p.**: 80–82 °C.

N-(tert-Butyldimethylsilyl)-4-chlorobenzenesulfonimidamide (6e)



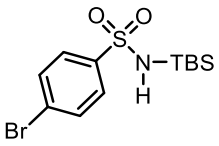
Following the protocol from literature,[S1] the TBS-protected sulfonimidamide **6e** was obtained from *N-(tert*-butyldimethylsilyl)-4-chlorobenzene-sulfonamide (**1e-precursor**, 2.75 g, 9.00 mmol, 1.0 equiv.), PPh_3 (2.60 g, 9.90 mmol, 1.1 equiv.), C_2Cl_6 (2.32 g, 9.90 mmol, 1.1 equiv.), ammonia gas and triethylamine (1.37 g, 1.88 mL, 13.5 mmol, 1.5 equiv.) after purification by use of column chromatography on silica gel (*n*-pentane:EtOAc 9/1 to 4/1) as a colorless solid (1.98 g, 6.48 mmol, 72%). **^{1}H NMR** (600 MHz, DMSO-d_6): δ = 7.86 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 6.73 (s, 2H), 0.87 (s, 9H), 0.01 (s, 3H), 0.01 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6): δ = 147.3, 135.3, 128.4 (2C), 127.3 (2C), 26.0 (3C), 17.8, –2.5, –2.6 ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_{12}H_{21}ON_2ClSSiNa]^+$: 237.0725, found: 327.0719; **IR (ATR)**: *v* = 3257, 3088, 2952, 2929, 2885, 2856, 2681, 2162, 1911, 1785, 1651, 1575, 1470, 1393, 1359, 1279, 1176, 1123, 1086, 1010, 938, 902, 823, 755, 692, 955 cm^{-1}; **m.p.**: 121–123 °C.

4-Chlorobenzenesulfonimidamide (1e)



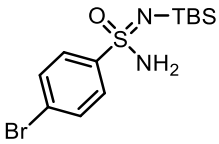
Following the protocol from literature,[S1] 4-chlorosulfonimidamide (**1e**) was obtained after deprotection with 4 N HCl in dioxane (525 mg, 0.500 mL, 2.00 mmol, 2.0 equiv.) from *N*-(*tert*-butyldimethylsilyl)-4-chlorobenzene-sulfonamide (**6e**, 305 mg, 1.00 mmol, 1.0 equiv.) as a colorless solid (122 mg, 0.642 mmol, 64%). **^{1}H NMR** (600 MHz, DMSO-d_6): δ = 7.92–7.88 (m, 2H), 7.61–7.57 (m, 2H), 6.73 (br s, 2H), 4.02 (br s, 1H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6): δ = 145.8, 135.6, 128.5 (2C), 127.8 (2C) ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_6H_8ON_2ClS]^+$: 191.0040, found: 191.0040; **IR (ATR)**: *v* = 3838, 3296, 3147, 3090, 3020, 2857, 2652, 2322, 2210, 2158, 2078, 1992, 1917, 1790, 1734, 1662, 1566, 1471, 1392, 1282, 1224, 1128, 1079, 952, 867, 825, 752, 711 cm^{-1}; **m.p.**: 101–103 °C.

***N-(tert*-Butyldimethylsilyl)-4-bromobenzenesulfonamide (1f-precursor)**



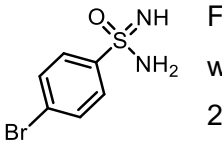
Following the protocol from literature,[S1] the TBS-protected sulfonamide **1f-precursor** was obtained from 4-bromobenzenesulfonamide (2.36 g, 10.0 mmol, 1.0 equiv.), *tert*-butyldimethylsilyl chloride (1.81 g, 12.0 mmol, 1.2 equiv.) and triethylamine (2.02 g, 2.78 mL, 20.0 mmol, 2.0 equiv.) as a colorless solid (3.46 g, 9.87 mmol, 99%). **^{1}H NMR** (600 MHz, DMSO-d_6): δ = 7.78 (dt, J = 6.3, 2.3 Hz, 2H), 7.74–7.72 (m, 2H), 7.47 (s, 1H), 0.86 (s, 9H), 0.09 (s, 6H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6): δ = 143.9, 132.0, 127.6 (2C), 125.3 (2C), 25.6 (3C), 17.4, –4.6 (2C) ppm. The estimated NMR-data is in full agreement with the reported data in literature.[S2]

***N-(tert*-Butyldimethylsilyl)-4-bromobenzenesulfonimidamide (6f)**



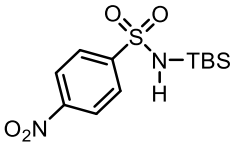
Following the protocol from literature,[S1] the TBS-protected sulfonimidamide **6f** was obtained from *N-(tert*-butyldimethylsilyl)-4-bromobenzene-sulfonamide (**1f-precursor**, 3.15 g, 9.00 mmol, 1.0 equiv.), PPh_3 (2.60 g, 9.90 mmol, 1.1 equiv.), C_2Cl_6 (2.32 g, 9.90 mmol, 1.1 equiv.), ammonia gas and triethylamine (1.37 g, 1.88 mL, 13.5 mmol, 1.5 equiv.) after purification by use of column chromatography on silica gel (*n*-pentane:EtOAc 9/1 to 4/1) as a colorless solid (2.60 g, 7.43 mmol, 83%). **^{1}H NMR** (600 MHz, DMSO-d_6): δ = 7.80–7.77 (m, 2H), 7.73–7.71 (m, 2H), 6.73 (s, 2H), 0.87 (s, 9H), 0.01 (s, 3H), 0.00 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6): δ = 147.72, 131.39 (2C), 127.54 (2C), 124.06, 25.98 (3C), 17.80, –2.49, –2.55 ppm. The estimated NMR-data is in full agreement with the reported data in literature.[S2]

4-Bromobenzenesulfonimidamide (1f)



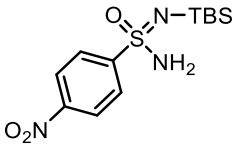
Following the protocol from literature,[S1] 4-bromobenzenesulfonimidamide (**1f**) was obtained after deprotection with 4 N HCl in dioxane (525 mg, 0.500 mL, 2.00 mmol, 2.0 equiv.) from *N*-(*tert*-butyldimethylsilyl)-4-bromobenzene-sulfonamide (**6f**, 349 mg, 1.00 mmol, 1.0 equiv.) as a colorless solid (171 mg, 0.727 mmol, 73%). **^{1}H NMR** (600 MHz, DMSO-d_6): δ = 7.82 (d, J = 8.2 Hz, 2H), 7.73 (d, J = 8.3 Hz, 2H), 6.73 (br s, 1H) ppm [NH_2-Protons not detected]; **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6): δ = 146.2, 131.4 (2C), 128.0 (2C), 124.4 ppm. The estimated NMR-data is in full agreement with the reported data in literature.[S2]

***N*-(*tert*-Butyldimethylsilyl)-4-nitrobenzenesulfonamide (1g-precursor)**



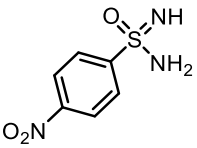
Following the protocol from literature,[S1] the TBS-protected sulfonamide **1g-precursor** was obtained from 4-nitrobenzenesulfonamide (505 mg, 2.50 mmol, 1.0 equiv.), *tert*-butyldimethylsilyl chloride (452 mg, 3.00 mmol, 1.2 equiv.) and triethylamine (506 mg, 0.695 mL, 5.00 mmol, 2.0 equiv.) as a brown solid (777 mg, 2.46 mmol, 98%). **^{1}H NMR** (600 MHz, DMSO-d_6): δ = 8.42–8.40 (m, 2H), 8.07–8.04 (m, 2H), 7.74 (s, 1H), 0.87 (s, 9H), 0.11 (s, 6H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6): δ = 149.8, 149.1, 127.1 (2C), 124.5 (2C), 25.6 (3C), 17.4, –4.6 (2C) ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_{12}H_{20}O_4N_2SSiNa]^+$: 339.0805, found: 339.0803; **IR (ATR)**: ν = 3437, 3253, 3110, 2934, 2862, 2576, 2189, 2104, 1996, 1953, 1739, 1643, 1608, 1528, 1471, 1402, 1346, 1289, 1259, 1228, 1094, 1014, 938, 845, 787, 735, 684 cm^{-1}; **m.p.**: 137–139 °C.

***N*-(*tert*-Butyldimethylsilyl)-4-nitrobenzenesulfonimidamide (6g)**



Following the protocol from literature,[S1] the TBS-protected sulfonimidamide **6g** was obtained from *N*-(*tert*-butyldimethylsilyl)-4-nitrobenzene-sulfonamide (**1g-precursor**, 633 mg, 2.00 mmol, 1.0 equiv.), PPh_3 (577 mg, 2.20 mmol, 1.1 equiv.), C_2Cl_6 (521 mg, 2.20 mmol, 1.1 equiv.), ammonia gas and triethylamine (304 mg, 0.417 mL, 3.00 mmol, 1.5 equiv.) after purification by use of column chromatography on silica gel (*n*-pentane:EtOAc 9/1 to 2/1) as a pale yellow solid (481 mg, 1.52 mmol, 76%). **^{1}H NMR** (600 MHz, DMSO-d_6): δ = 8.39–8.35 (m, 2H), 8.10–8.06 (m, 2H), 6.98 (s, 2H), 0.87 (s, 9H), 0.03 (s, 3H), 0.02 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6): δ = 153.86, 148.45, 126.83 (2C), 124.06 (2C), 25.96 (3C), 17.81, –2.49, –2.55 ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_{12}H_{22}O_3N_3SSi]^+$: 316.1146, found: 316.1139; **IR (ATR)**: ν = 3398, 3300, 3101, 3070, 2951, 2930, 2891, 2857, 2704, 2302, 2206, 2051, 1983, 1948, 1817, 1699, 1604, 1513, 1469, 1341, 1250, 1171, 1107, 1006, 939, 901, 857, 828, 772, 743, 683 cm^{-1}, **m.p.**: 179–181 °C.

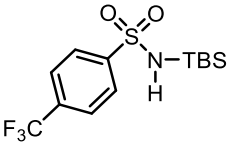
4-Nitrobenzenesulfonimidamide (1g)



Following the protocol from literature,[S1] 4-nitrosulfonimidamide (**1g**) was obtained after deprotection with 4 N HCl in dioxane (525 mg, 0.500 mL, 2.00 mmol, 2.0 equiv.) from *N*-(*tert*-butyldimethylsilyl)-4-nitrobenzene-sulfonamide (**6g**, 315 mg, 1.00 mmol, 1.0 equiv.) as a yellow solid (174 mg, 0.866 mmol, 87%). **^{1}H NMR** (600 MHz, DMSO-d_6): δ = 8.39–8.34 (m, 2H), 8.15–8.10 (m, 2H), 6.97 (br s, 2H) ppm [NH-Proton not detected]; **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6): δ = 152.6, 148.6, 127.3 (2C), 123.9 (2C) ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_6H_8O_3N_3S]^+$: 202.0281, found: 202.0280; **IR (ATR)**:

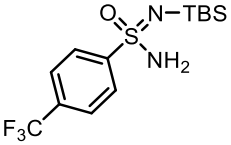
v = 3789, 3316, 3272, 3094, 3065, 2862, 2641, 2452, 2321, 2158, 2076, 1930, 1793, 1733, 1672, 1605, 1557, 1518, 1438, 1400, 1344, 1245, 1127, 1076, 997, 882, 849, 734, 681 cm^{-1}, **m.p.**: 127–129 °C.

***N*-(*tert*-Butyldimethylsilyl)-4-(trifluoromethyl)benzenesulfonamide (1h-precursor)**



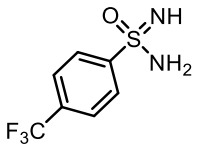
Following the protocol from literature,[S1] the TBS-protected sulfonamide **1h-precursor** was obtained from 4-(trifluoromethyl)benzenesulfonamide (2.25 g, 10.0 mmol, 1.0 equiv.), *tert*-butyldimethylsilyl chloride (1.81 g, 12.0 mmol, 1.2 equiv.) and triethylamine (2.02 g, 2.78 mL, 20.0 mmol, 2.0 equiv.) as a pale yellow solid (3.39 g, 10.0 mmol, quant.). **^{1}H NMR** (600 MHz, DMSO-d_6): δ = 8.02 (d, J = 8.3 Hz, 2H), 7.97 (d, J = 8.3 Hz, 2H), 7.90 (s, 1H), 0.87 (s, 9H), 0.10 (s, 6H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6): δ = 148.2, 131.6 (q, $^2J_{C\text{-}F}$ = 32.0 Hz), 126.4 (2C), 126.28 (q, $^3J_{C\text{-}F}$ = 3.8 Hz, 2C), 123.56 (q, $^1J_{C\text{-}F}$ = 272.7 Hz). 25.6 (3C), 17.4, –4.6 (2C) ppm; **^{19}F NMR** (564 MHz, DMSO-d_6): δ = –61.52 (s, CF_3) ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_{13}H_{20}O_2NSSiF_3Na]^+$: 362.0828, found: 362.0822; **IR (ATR)**: *v* = 3255, 2955, 2864, 2643, 2169, 2027, 1927, 1799, 1677, 1609, 1471, 1402, 1321, 1284, 1255, 1153, 1099, 1061, 1014, 942, 789, 759, 706, 666 cm^{-1}; **m.p.**: 112–114 °C.

***N*-(*tert*-Butyldimethylsilyl)- 4-(trifluoromethyl)benzenesulfonimidamide (6h)**



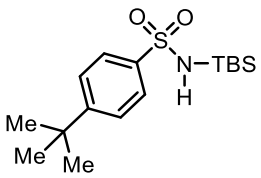
Following the protocol from literature,[S1] the TBS-protected sulfonimidamide **6h** was obtained from *N*-(*tert*-butyldimethylsilyl)-4-(trifluoromethyl)-benzenesulfonamide (**1h-precursor**, 3.06 g, 9.00 mmol, 1.0 equiv.), PPh_3 (2.60 g, 9.90 mmol, 1.1 equiv.), C_2Cl_6 (2.32 g, 9.90 mmol, 1.1 equiv.), ammonia gas and triethylamine (1.37 g, 1.88 mL, 13.5 mmol, 1.5 equiv.) after purification by use of column chromatography on silica gel (*n*-pentane:EtOAc 9/1 to 4/1) as a colorless solid (2.42 g, 7.14 mmol, 79%). **^{1}H NMR** (600 MHz, DMSO-d_6): δ = 8.05 (d, J = 8.2 Hz, 2H), 7.91 (d, J = 8.3 Hz, 2H), 6.86 (s, 2H), 0.87 (s, 9H), 0.02 (s, 3H), 0.01 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6): δ = 152.1, 130.6 (q, $^2J_{C\text{-}F}$ = 32.0 Hz), 126.2 (2C), 125.7 (q, $^3J_{C\text{-}F}$ = 3.8 Hz, 2C), 123.8 (q, $^1J_{C\text{-}F}$ = 272.4 Hz), 25.9 (3C), 17.8, –2.5, –2.6 ppm; **^{19}F NMR** (564 MHz, DMSO-d_6): δ = –61.25 (s, CF_3) ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_{13}H_{21}ON_2SSiF_3Na]^+$: 361.0988, found: 361.0981; **IR (ATR)**: *v* = 3856, 3748, 3237, 3102, 2933, 2890, 2859, 2662, 2324, 2255, 2161, 2107, 2071, 2024, 1982, 1911, 1741, 1681, 1608, 1562, 1469, 1401, 1320, 1161, 1128, 1086, 1061, 1011, 938, 893, 832, 778, 713, 688 cm^{-1}; **m.p.**: 94–96 °C.

4-(Trifluoromethyl)benzenesulfonimidamide (1h)



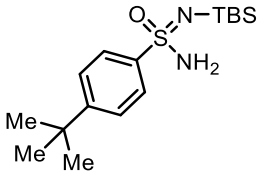
Following the protocol from literature,[S1] 4-(trifluoromethyl)sulfonimidamide (**1h**) was obtained after deprotection with 4 N HCl in dioxane (525 mg, 0.500 mL, 2.00 mmol, 2.0 equiv.) from *N*-(*tert*-butyldimethylsilyl)-4-(trifluoromethyl)-benzenesulfonamide (**6h**, 338 mg, 1.00 mmol, 1.0 equiv.) as a pale yellow solid (191 mg, 0.851 mmol, 85%). **^{1}H NMR** (600 MHz, DMSO-d_6): δ = 8.10 (d, J = 8.1 Hz, 2H), 7.91 (d, J = 8.2 Hz, 2H), 6.76 (br s, 2H) ppm [NH proton not detected]; **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6): δ = 150.7, 130.8 (q, $^{2}J_{C\text{-}F}$ = 32.0 Hz), 126.8 (2C), 125.7 (q, $^{3}J_{C\text{-}F}$ = 3.7 Hz, 2C), 123.78 (q, $^{1}J_{C\text{-}F}$ = 272.6 Hz) ppm; **^{19}F NMR** (564 MHz, DMSO-d_6): δ = –61.32 (s, CF_3) ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_7H_8ON_2SF_3]^+$: 225.0304, found: 225.0299; **IR (ATR)**: ν = 3269, 3051, 2973, 2862, 2680, 2161, 1927, 1800, 1673, 1577, 1453, 1401, 1320, 1248, 1159, 1119, 1062, 1009, 868, 833, 708 cm^{-1}; **m.p.**: 86–88 °C.

***4-(tert*-Butyl)-*N*-(*tert*-butyldimethylsilyl)benzenesulfonamide (1i-precursor)**



Following the protocol from literature,[S1] the TBS-protected sulfonamide **1i-precursor** was obtained from *4-(tert*-butyl)-benzenesulfonamide (1.07 g, 5.00 mmol, 1.0 equiv.), *tert*-butyldimethylsilyl chloride (0.904 g, 6.00 mmol, 1.2 equiv.) and triethylamine (1.01 g, 1.39 mL, 10.0 mmol, 2.0 equiv.) as a colorless solid (1.64 g, 5.00 mmol, quant.). **^{1}H NMR** (600 MHz, DMSO-d_6): δ = 7.73 (d, J = 8.5 Hz, 2H), 7.57 (d, J = 8.5 Hz, 2H), 7.27 (s, 1H), 1.29 (s, 9H), 0.88 (s, 9H), 0.10 (s, 6H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6): δ = 154.5, 141.8, 125.6 (2C), 125.4 (2C), 34.7, 30.9 (3C), 25.7 (3C), 17.4, –4.5 (2C) ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_{16}H_{29}O_2NSSiK]^+$: 366.1320, found: 366.1319; **IR (ATR)**: ν = 3317, 3218, 2956, 2865, 2715, 2222, 2182, 2112, 2010, 1926, 1779, 1699, 1596, 1516, 1468, 1398, 1362, 1331, 1279, 1256, 1199, 1150, 1112, 1012, 935, 831, 785, 668 cm^{-1}; **m.p.**: 69–71 °C.

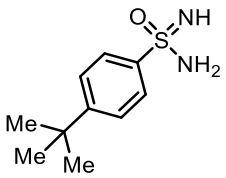
***4-(tert*-Butyl)-*N*-(*tert*-butyldimethylsilyl)benzenesulfonimidamide (6i)**



Following the protocol from literature,[S1] the TBS-protected sulfonimidamide **6i** was obtained from *4*-(*tert*-butyl)-*N*-(*tert*-butyldimethylsilyl)-benzenesulfonamide (**1i-precursor**, 1.47 g, 4.50 mmol, 1.0 equiv.), PPh_3 (1.30 g, 4.75 mmol, 1.1 equiv.), C_2Cl_6 (1.16 g, 4.75 mmol, 1.1 equiv.), ammonia gas and triethylamine (683 mg, 0.938 mL, 6.75 mmol, 1.5 equiv.) after purification by use of column chromatography on silica gel (*n*-pentane:EtOAc 9/1 to 4/1) as a colorless solid

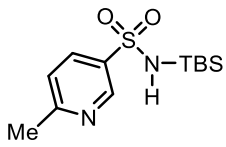
(985 mg, 3.02 mmol, 67%). **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 7.79 (d, J = 8.5 Hz, 2H), 7.51 (d, J = 8.5 Hz, 2H), 6.53 (s, 2H), 1.29 (s, 9H), 0.88 (s, 9H), 0.02 (s, 3H), 0.01 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ = 153.4, 145.5, 125.3 (2C), 125.1 (2C), 34.6, 30.9 (3C), 26.0 (3C), 17.8, –2.4, –2.5 ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_{16}H_{31}ON_2SSi]^+$: 327.1921, found: 327.1922; **IR (ATR)**: v = 3728, 3396, 3235, 3065, 2956, 2890, 2856, 2322, 2173, 2112, 2018, 1923, 1594, 1532, 1493, 1465, 1392, 1358, 1296, 1246, 1164, 1117, 1088, 1008, 936, 865, 832, 808, 775, 709, 665 cm^{-1}; **m.p.**: 114–116 °C.

4-(*tert*-Butyl)-benzenesulfonimidamide (1i)



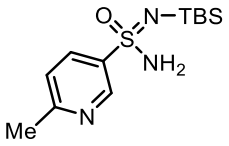
Following the protocol from literature,[S1] 4-(*tert*-butyl)-benzenesulfonimidamide (**1i**) was obtained after deprotection with 4 N HCl in dioxane (525 mg, 0.500 mL, 2.00 mmol, 2.0 equiv.) from 4-(*tert*-butyl)-*N*-(*tert*-butyldimethylsilyl)-benzenesulfonimidamide (**6i**, 327 mg, 1.00 mmol, 1.0 equiv.) as a colorless solid (196 mg, 0.925 mmol, 93%). **^{1}H NMR** (600 MHz, DMSO-d_6): δ = 7.84–7.81 (m, 2H), 7.53–7.51 (m, 2H), 1.30 (s, 9H) ppm [NH and NH_2 protons not detected]; **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6): δ = 153.7, 143.9, 125.8 (2C), 125.2 (2C), 34.6, 30.9 (3C) ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_{10}H_{17}ON_2S]^+$: 213.1056, found: 213.1056; **IR (ATR)**: v = 3269, 3072, 2958, 2868, 2662, 2325, 2175, 2079, 1897, 1663, 1596, 1564, 1469, 1395, 1362, 1228, 1143, 1100, 863, 830, 754 cm^{-1}; **m.p.**: 112–114 °C.

***N*-(*tert*-Butyldimethylsilyl)-6-methylpyridine-3-sulfonamide (1j-precursor)**



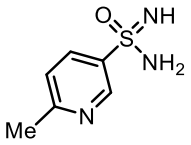
Following the protocol from literature,[S1] the TBS-protected sulfonamide **1j-precursor** was obtained from 6-methylpyridine-3-sulfonamide (861 mg, 5.00 mmol, 1.0 equiv.), *tert*-butyldimethylsilyl chloride (904 mg, 6.00 mmol, 1.2 equiv) and triethylamine (1.01 g, 1.39 mL, 10.0 mmol, 2.0 equiv.) as a colorless solid (1.42 g, 4.96 mmol, 99%). **^{1}H NMR** (600 MHz, DMSO-d_6): δ = 8.53 (d, J = 2.0 Hz, 1H), 7.86–7.83 (m, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.64 (s, 1H), 2.38 (s, 3H), 0.86 (s, 9H), 0.09 (s, 6H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6): δ = 157.6, 149.7, 138.2, 136.4, 120.0, 25.7(3C), 17.8, 17.5, –4.5 (2C) ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_{12}H_{22}O_2N_2SSiNa]^+$: 309.1064, found: 309.1063; **IR (ATR)**: v = 3223, 2932, 2861, 2725, 2649, 2326, 2199, 2108, 2017, 1911, 1571, 1460, 1359, 1286, 1255, 1166, 1110, 1228, 951, 832, 795, 746, 717, 665 cm^{-1}; **m.p.**: 92–94 °C.

***N-(tert*-Butyldimethylsilyl)-6-methylpyridine-3-sulfonimidamide (6j)**



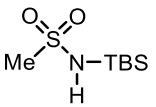
Following the protocol from literature,[S1] the TBS-protected sulfonimidamide **6j** was obtained from *N-(tert*-butyldimethylsilyl)-6-methylpyridine-3-sulfonamide (**1j-precursor**, 1.29 g, 4.50 mmol, 1.0 equiv.), PPh_3 (1.30 g, 4.95 mmol, 1.1 equiv.), C_2Cl_6 (1.17 g, 4.95 mmol, 1.1 equiv.), ammonia gas and triethylamine (683 mg, 0.938 mL, 6.75 mmol, 1.5 equiv.) after purification by use of column chromatography on silica gel (*n*-pentane:EtOAc 9/1 to 2/1) as a colorless solid (1.06 g, 3.70 mmol, 82 %). **^{1}H NMR** (600 MHz, DMSO-d_6): δ = 8.47 (dt, J = 2.0, 0.9 Hz, 1H), 7.85–7.77 (m, 2H), 6.57 (s, 2H), 2.36 (s, 3H), 0.86 (s, 9H), –0.01 (s, 3H), –0.04 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6): δ = 160.8, 148.9, 137.9, 135.2, 119.3, 26.0 (3C), 17.7, –2.5, –2.6 ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_{12}H_{23}ON_3SSiNa]^+$: 308.1223, found: 308.1218; **IR (ATR)**: ν = 3280, 3090, 2997, 2950, 2930, 2891, 2855, 2659, 2502, 2187, 2042, 1983, 1805, 1571, 1464, 1335, 1249, 1172, 1094, 1030, 1006, 940, 893, 830, 777, 696 cm^{-1}; **m.p.**: 109–111 °C.

6-Methylpyridine-3-sulfonimidamide (1j)



Following the protocol from literature,[S1] 6-methylpyridine-3-sulfonimidamide (**1j**) was obtained after deprotection with formic acid (2.2 mL) and water (0.2 mL) from *N*-(*tert*-butyldimethylsilyl)-6-methylpyridine-3-sulfonimidamide (**6j**, 143 mg, 0.500 mmol, 1.0 equiv.) as a colorless solid (85.5 mg, 0.499 mmol, quant.). **^{1}H NMR** (600 MHz, DMSO-d_6): δ = 8.48–8.47 (m, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 7.3 Hz, 1H), 5.95 (s, 3H, NH_2), 2.37 (s, 3H) ppm [NH- proton not detected]; **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6): δ = 159.7, 148.9, 138.0, 135.5, 119.7, 17.7 ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_6H_9ON_3SNa]^+$: 194.0359, found: 194.0354; **IR (ATR)**: ν = 3834, 3281, 3182, 3038, 2650, 2507, 2233, 2196, 2157, 2046, 1947, 1906, 1738, 1673, 1553, 1452, 1376, 1325, 1238, 1098, 1019, 908, 841, 690 cm^{-1}; **m.p.**: 108–110 °C.

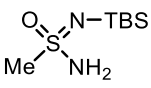
***N-(tert*-Butyldimethylsilyl)-methanesulfonamide (1k-precursor)**



Following the protocol from literature,[S1] the TBS-protected sulfonamide **1k-precursor** was obtained from methanesulfonamide (4.76 g, 50.0 mmol, 1.0 equiv.), *tert*-butyldimethylsilyl chloride (9.04 g, 60.0 mmol, 1.2 equiv.) and triethylamine (10.1 g, 13.9 mL, 100 mmol, 2.0 equiv.) as a colorless solid (9.09 g, 43.4 mmol, 87%). **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 4.82 (s, 1H), 2.99 (s, 3H), 0.92 (s, 9H), 0.26 (s, 6H) ppm; **^{13}C{^{1}H} NMR**

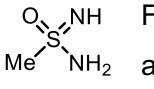
(151 MHz, Chloroform-*d*): δ = 44.2, 25.6 (3C), 17.1, –4.5 (2C) ppm. The estimated NMR-data is in full agreement with the reported data in literature.[S1]

***N-(tert*-Butyldimethylsilyl)-methanesulfonimidamide (6k)**



Following the protocol from literature,[S1] the TBS-protected sulfonimidamide **6k** was obtained from *N-(tert*-Butyldimethylsilyl)methanesulfonamide (**1k-precursor**, 1.88 g, 9.00 mmol, 1.0 equiv.), PPh_3 (2.60 g, 9.90 mmol, 1.1 equiv.), C_2Cl_6 (2.32 g, 9.90 mmol, 1.1 equiv.), ammonia gas and triethylamine (1.37 g, 1.88 mL, 13.5 mmol, 1.5 equiv.) after purification by use of column chromatography on silica gel (*n*-pentane:EtOAc 4/1 to 1/1) as a colorless solid (1.37 g, 6.54 mmol, 73%). **^{1}H NMR** (600 MHz, DMSO-d_6): δ = 6.17 (s, 2H), 2.93 (s, 3H), 0.85 (s, 9H), 0.01 (s, 3H), 0.01 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6): δ = 48.30, 26.06 (3C), 17.72, –2.35, –2.41 ppm. The estimated NMR-data is in full agreement with the reported data in literature.[S1]

Methanesulfonimidamide (1k)



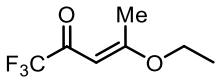
Following the protocol from literature,[S1] methanesulfonimidamide (**1k**) was obtained after deprotection with formic acid (2.2 mL) and water (0.2 mL) from *N*-(*tert*-butyldimethylsilyl)methanesulfonimidamide (**6k**, 104 mg, 0.500 mmol, 1.0 equiv.) as a colorless solid (46.9 mg, 0.498 mmol, quant.). **^{1}H NMR** (600 MHz, DMSO-d_6): δ = 5.18 (br s, 3H), 2.09 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6): δ = 45.6 ppm. The estimated NMR-data is in full agreement with the reported data in literature.[S1]

2. 2. Synthesis of Trifluoromethylketones 4b-d

(*E*)-4-Ethoxy-1,1,1-trifluoro-but-3-en-2-one (**4a**, ETFBO) was purchased from Sigma Aldrich. Methyl-substituted derivatives **4b** and **4c** as well as cyclic enone **4d** were synthesized according a procedure from literature.[S3] 1,3-Diphenylprop-2-yn-1-one (**2a**) was taken from an earlier project and used without further purification.[S2]

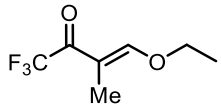
Note: Due to progressing decomposition of trifluoromethylketones **4b** and **4c**, improved yields were obtained with freshly prepared substrates. These enones should be stored under argon atmosphere at reduced temperatures (−18°C) and used as soon as possible.

(*E*)-4-Ethoxy-1,1,1-trifluoropent-3-en-2-one (4b)



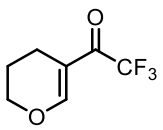
Following the protocol from literature,[S3] (*E*)-4-ethoxy-1,1,1-trifluoropent-3-en-2-one (**4b**) was obtained from 2-ethoxy-1-propene (258 mg, 3.00 mmol, 1.0 equiv.), pyridine (285 mg, 3.60 mmol, 1.2 equiv.) and trifluoroacetic anhydride (945 mg, 4.50 mmol, 1.5 equiv.) as a pale orange liquid (450 mg, 2.47 mmol, 82%). **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 5.66 (s, 1H), 4.00 (q, J = 7.0 Hz, 2H), 2.41 (s, 3H), 1.41 (t, J = 7.0 Hz, 3H); **^{13}C{^{1}H} NMR** (151 MHz, Chloroform-*d*): δ = 180.8, 178.9 (q, $^{2}J_{C\text{-}F}$ = 33.4 Hz), 116.7 (q, $^{1}J_{C\text{-}F}$ = 292.3 Hz), 91.9, 65.4, 21.4, 13.9 ppm; **^{19}F NMR** (564 MHz, Chloroform-*d*): δ = –78.41 (s, CF_3) ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_7H_9O_2F_3Na]^+$: 205.0447, found: 205.0445; **IR (ATR)**: v = 3402, 2991, 2947, 2513, 2084, 1997, 1783, 1702, 1570, 1475, 1445, 1411, 1362, 1316, 1258, 1194, 1139, 1099, 1050, 915, 868, 829, 801, 725 cm^{-1}.

(*E*)-4-Ethoxy-1,1,1-trifluoro-3-methylbut-3-en-2-one (4c)



Following the protocol from literature,[S3] (*E*)-4-ethoxy-1,1,1-trifluoro-3-methylbut-3-en-2-one (**4c**) was obtained from ethyl propenyl ether (258 mg, 3.00 mmol, 1.0 equiv.), pyridine (285 mg, 3.60 mmol, 1.2 equiv.) and trifluoroacetic anhydride (945 mg, 4.50 mmol, 1.5 equiv.) as a pale yellow liquid (452 mg, 2.48 mmol, 83%). **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.53 (s, 1H), 4.21 (q, J = 7.1 Hz, 2H), 1.80 (s, 3H), 1.40 (t, J = 7.1 Hz, 3H); **^{13}C{^{1}H} NMR** (151 MHz, Chloroform-*d*): δ = 180.0 (q, $^{2}J_{C\text{-}F}$ = 33.6 Hz), 164.1, 117.9 (q, $^{1}J_{C\text{-}F}$ = 293.4 Hz) 112.0, 71.5, 15.3, 8.1 ppm; **^{19}F NMR** (564 MHz, Chloroform-*d*): δ = –69.28 (s, CF_3) ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_7H_{10}O_2F_3]^+$: 183.0627, found: 183.0624; **IR (ATR)**: v = 3860, 3438, 3082, 2988, 2938, 2703, 2476, 2270, 2161, 2034, 2005, 1908, 1740, 1681, 1625, 1478, 1449, 1390, 1305, 1214, 1136, 1018, 921, 890, 808, 759, 706 cm^{-1}. The estimated NMR-data is in full agreement with the reported data in literature.[S4]

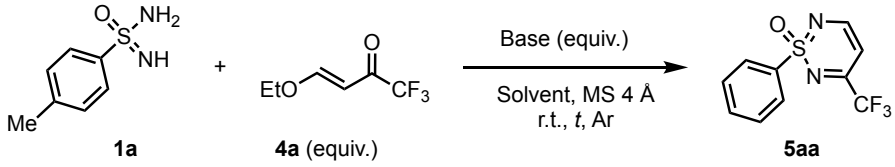
1-(3,4-Dihydro-2H-pyran-5-yl)-2,2,2-trifluoroethan-1-one (4d)



Following the protocol from literature,[S3] 1-(3,4-dihydro-2H-pyran-5-yl)-2,2,2-trifluoroethan-1-one (**4d**) was obtained from 3,4-dihydro-2H-pyran (421 mg, 5.00 mmol, 1.0 equiv.), pyridine (593 mg, 7.50 mmol, 1.5 equiv.) and trifluoroacetic anhydride (1.58 g, 7.50 mmol, 1.5 equiv.) as a pale orange liquid (778 mg, 4.32 mmol, 86%). **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 7.82 (s, 1H), 4.21 – 4.18 (m, 2H), 2.33 (t, J = 6.4 Hz, 2H), 1.95 (dt, J = 12.2, 6.0 Hz, 2H); **^{13}C{^{1}H} NMR** (151 MHz, Chloroform-*d*): δ = 179.34 (q, $^{2}J_{C\text{-}F}$ = 34.0 Hz), 162.47 (q, $^{3}J_{C\text{-}F}$ = 5.3 Hz), 116.92 (q, $^{1}J_{C\text{-}F}$ = 291.0 Hz), 111.5, 68.0, 20.7, 18.1 ppm;

^{19}F NMR (564 MHz, Chloroform-*d*): δ = –69.89 (s, CF_3) ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_7H_8O_2F_3]^+$: 181.0471, found: 181.0474; **IR (ATR)**: *v* = 3900, 3355, 3207, 3956, 2897, 2861, 2324, 2087, 1991, 1919, 1682, 1605, 1471, 1445, 1354, 1326, 1273, 1235, 1180, 1135, 1089, 1052, 997, 940, 893, 875, 844, 755, 723 cm^{-1}. The estimated NMR-data is in full agreement with the reported data in literature.[S4]

3. Optimization of the synthesis of 1,2,6-thiadiazine 1-oxide 5aa in solution



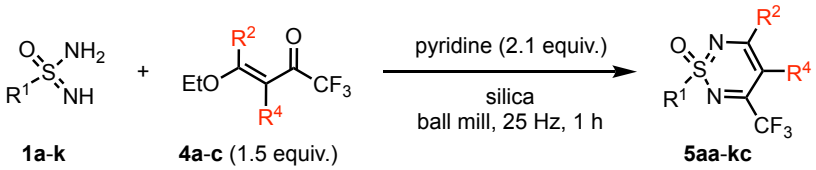
An oven-dried Schlenk-tube equipped with magnetic stirring bar and septum cap was charged with sulfonimidamide (**1a**, 0.1 mmol, 1.0 equiv.), MS 4 Å (80 mg · 1 mmol^{-1} of **1a**) and base (if solid) and subsequently evacuated and flushed with argon. Evacuating and flushing with argon was repeated three times, before the solvent (5.0 mL · 1 mmol^{-1}) and base (if liquid) was added by syringe. The reaction mixture was stirred for 15 minutes at ambient temperature and then, ETFBO (**4a**) dissolved in solvent (5.0 mL · 1 mmol^{-1}) was added dropwise by syringe. The reaction mixture was stirred for 3 h to 24 h at ambient temperature under argon. After completion of the reaction, a saturated $NaHCO_3$ solution (50 mL · 1 mmol^{-1}) was added. Then, the mixture was extracted with EtOAc (3 x 50 mL · 1 mmol^{-1}). The organic layers were collected, dried over anhydrous $MgSO_4$, and the volatiles were removed under reduced pressure. The product was purified by column chromatography on silica gel and dried under high vacuum for several hours.

Table S1: Optimization of reaction parameters in solution.

Entry	Base (equiv.)	4a (equiv.)	Solvent	*t* [h]	Yield of 5aa (%)
1	Cs_2CO_3 (2.1)	1.50	DMSO	3	67
2	Cs_2CO_3 (1.2)	1.50	DMSO	3	31
3	Cs_2CO_3 (2.5)	1.50	DMSO	3	57
7	**Cs_2CO_3 (2.1)**	**1.05**	**DMSO**	**3**	**76**
8	Cs_2CO_3 (2.1)	1.20	DMSO	3	58
19	Cs_2CO_3 (2.1)	2.50	DMSO	3	16
10[a]	Cs_2CO_3 (2.1)	1.00	DMSO	3	33
11[b]	Cs_2CO_3 (2.1)	1.00	DMSO	3	60
12	Cs_2CO_3 (2.1)	1.05	DMF	24	Trace
13	Cs_2CO_3 (2.1)	1.05	MeCN	24	35
14	Cs_2CO_3 (2.1)	1.05	HFIP	3	33
15	Cs_2CO_3 (2.1)	1.05	TFE	3	70 (72)[c]
16	K_2CO_3 (2.1)	1.05	DMSO	4	Trace
17	K_3PO_4 (2.1)	1.05	DMSO	4	9
18	KO*t*-Bu (2.1)	1.05	DMSO	4	4
19	NaH (2.1)	1.05	DMSO	24	Trace
20	DBU (2.1)	1.05	DMSO	24	37
21	Et_3N (2.1)	1.05	DMSO	3	72

[a] **1a** (0.1 mmol), **4a** (1.2 equiv.), else as described above; [b] **1a** (0.1 mmol), **4a** (1.5 equiv.), else as described above; [c] performed with 1.5 equiv. of **1a** (*t* = 5 h).

4. General procedure for the synthesis of 1,2,6-thiadiazine 1-oxides 5 under mechanochemical conditions (GP1)



1a-k **4a-c** (1.5 equiv.) **5aa-kc**

A ball milling container (stainless steel, *V* = 5.0 mL or 10 mL) equipped with two milling balls (stainless steel, *d* = 7.0 mm or 10 mm) was charged with ETFBO (**4a**, 1.5 equiv.) or its derivatives (**4b-d**, 1.5 equiv.), silica (1.0 mg per 1.0 mg of all reactants), sulfonimidamide (**1a-k**, 1.0 equiv.) and pyridine (2.1 equiv.) and flushed with argon for 30 s before closing. The reaction mixture was milled at 25 Hz for 1 h. After completion of the reaction, the solid powdery crude mixture was directly put on a column loaded with silica gel, and the product was purified by column chromatography. Then, the product was dried under high vacuum for several hours.

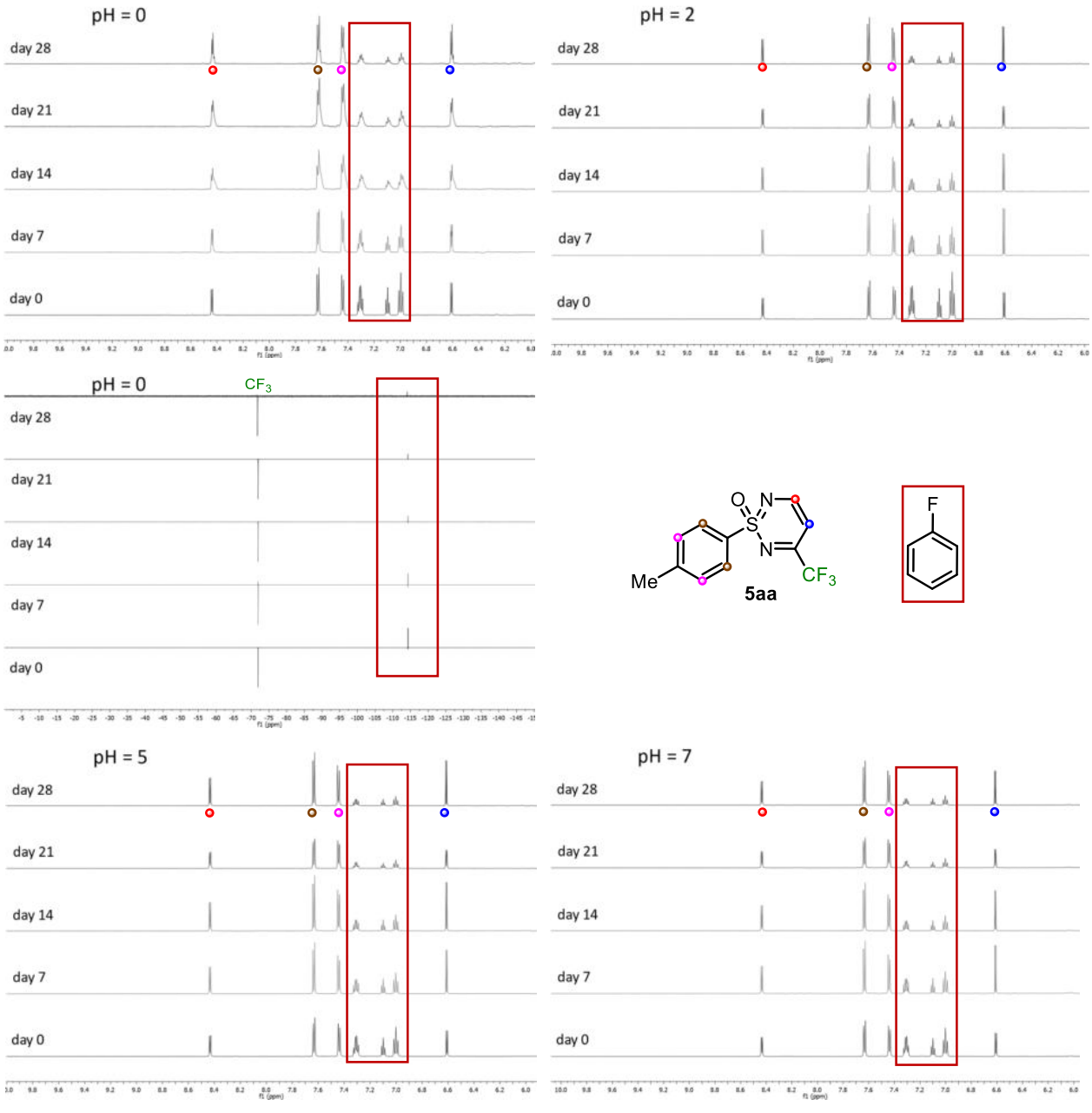
Table S2: Optimization of reaction parameters in ball mill reactor (for the reaction providing **5aa**).

Entry	Base (equiv.)	4a (equiv.)	Additive	Yield of 5aa (%)
1	Cs_2CO_3 (2.1)	1.50	---	55
2	Cs_2CO_3 (2.1)	1.50	$LaCl_3$[a]	58
3	Cs_2CO_3 (2.1)	1.50	Silica (110 mg), $LaCl_3$[a]	58
4	Cs_2CO_3 (2.1)	1.50	LAG: DMSO (55 µL)	18
5	Cs_2CO_3 (2.1)	1.50	Sand (110 mg)	33
6	Cs_2CO_3 (2.1)	1.50	Neutral Al_2O_3 (110 mg)	26
7	Cs_2CO_3 (2.1)	1.50	Silica (110 mg)	78
8	Cs_2CO_3 (2.1)	1.50	Silica (110 mg), 30 Hz	62
9	Cs_2CO_3 (2.1)	1.50	Silica (55 mg), 30 Hz	65
10[b]	Cs_2CO_3 (2.1)	1.00	Silica (110 mg)	58
11	Cs_2CO_3 (2.1)	1.05	Silica (105 mg)	58
12	Cs_2CO_3 (2.1)	2.00	Silica (120 mg)	66
13	Cs_2CO_3 (2.1)	2.50	Silica (125 mg)	59
14	Cs_2CO_3 (2.5)	1.50	Silica (125 mg)	59
15	Et_3N (2.1)	1.50	Silica (65 mg)	72
16	DMAP (2.1)	1.50	Silica (70 mg)	74
17	TMPDA (2.1)	1.50	Silica (65 mg)	68
18	DIPEA (2.1)	1.50	Silica (70 mg)	49
19	**Pyridine (2.1)**	**1.50**	**Silica (60 mg)**	**84**
20	Collidine (2.1)	1.50	Silica (70 mg)	76
21	Cy_2NEt (2.1)	1.50	Silica (85 mg)	61
22	DABCO (2.1)	1.50	Silica (65 mg)	31

[a] Use of 0.1 equiv. of $LaCl_3$; [b] Use of 0.1 mmol of **1a** and 1.5 equiv. of **4a**, else as described above.

5. Stability investigation of 1,2,6-thiadiazine 1-oxide 5aa

For the determination of the stability under aqueous acidic or basic conditions, compound **5aa** (0.05 mmol) was dissolved in acetone-d_6 (0.3 mL) and threated with aqueous HCl or NaOH solutions (0.3 mL) with pH-values = 0, 2, 5, 7, 9, 12 and 14. These solutions and fluorobenzene as internal standard were added to NMR-tubes and the relative amount of possible degradation of heterocycle **5aa** was examined. The mixture was homogenized by shaking twice per day and ^{1}H- and ^{19}F-NMR measurements were performed daily (first 7 days) and weekly for 28 days to observe potential decomposition of the product.



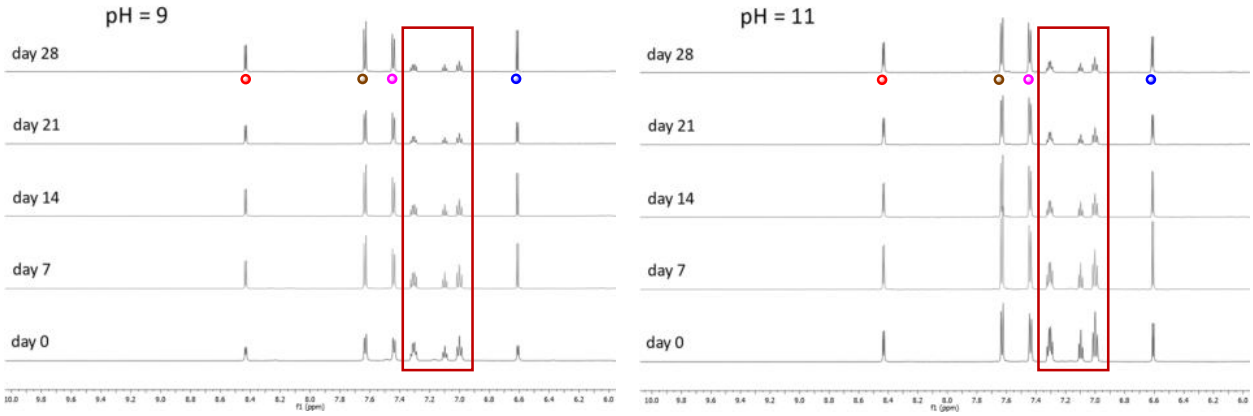
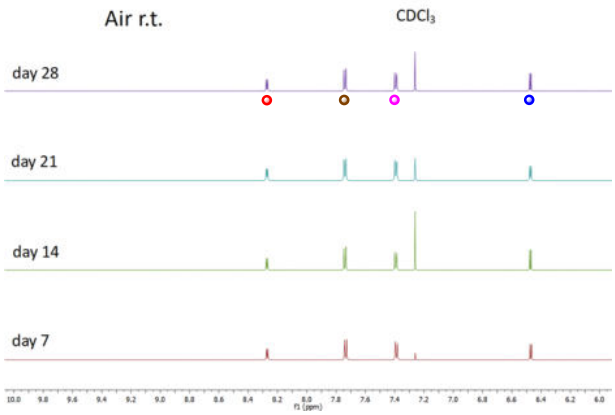
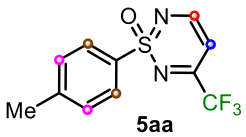


Figure S1. Degradation of **5aa** – pH dependence.

For determination of oxidation stability, product **5aa** (0.05 mmol) was stored at various conditions (1. air at room temperature, 2. air at 50 °C, 3. and O_2 at 50 °C) for 28 days, and potential decomposition was monitored weekly by ^{1}H- and ^{19}F-NMR measurements (2-3 mg of **5aa** dissolved in 0.7 mL chloroform-*d*). The stability investigation under oxygen atmosphere was carried out in a glass-container, sealed with alumina septum cap, then evacuated under high vacuum and flushed with pure oxygen after each sample-picking. Containers of reactions at 50 °C were placed in an alumina block as heating source.





5aa

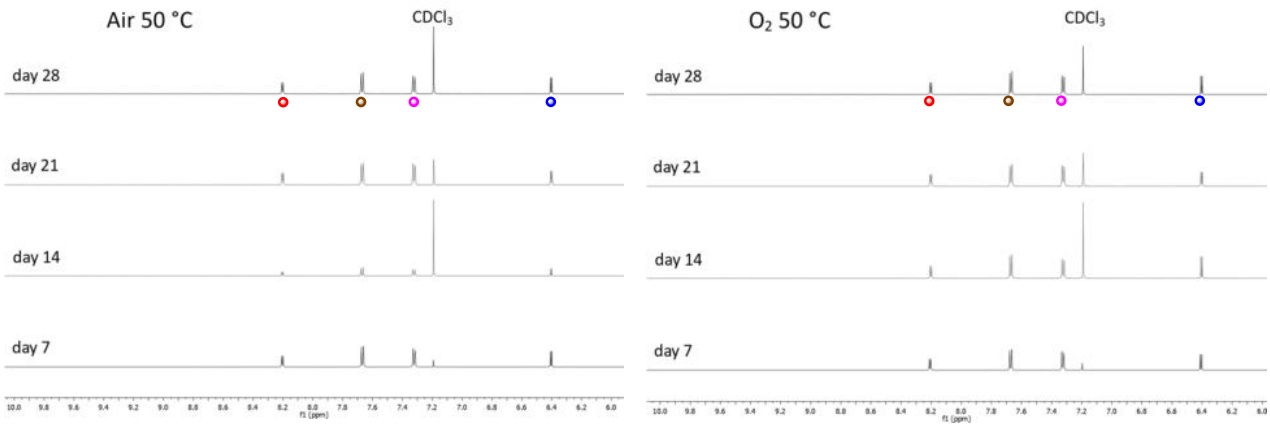
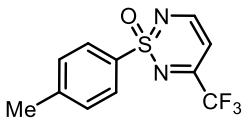


Figure S2. Degradation of **5aa** – oxidative conditions.

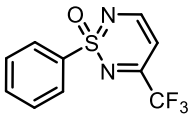
6. Analytical data of products 5aa-ka, 5ac, 5fc, 5kc, 5ad, 7ka, 3ka, and 8

1-(*p*-Tolyl)-3-(trifluoromethyl)-1,2,6-thiadiazine 1-oxide (5aa)



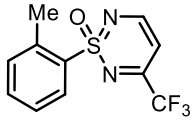
Following GP1, the title compound was obtained from 4-methylbenzenesulfonimidamide (**1a**, 34.0 mg, 0.200 mmol), ETFBO (**4a**, 50.4 mg, 42.7 µL, 0.300 mmol) and pyridine (33.2 mg, 34.0 µL, 0.420 mmol) in presence of silica (120 mg) after purification by column chromatography (*n*-pentane/EtOAc: 98/2 to 9/1) as a pale yellow solid (48.6 mg, 0.177 mmol, 89%). Furthermore, the product was obtained on a reaction scale of 1.00 mmol from 4-methylbenzenesulfonimidamide (**1a**, 170 mg, 1.00 mmol) in a yield of 85% (233 mg, 0.850 mmol) and from *N*-(*tert*-butyldimethylsilyl)-4-methylbenzenesulfonimidamide (**6a**, 285 mg, 1.00 mmol) in a yield of 84% (229 mg, 0.836 mmol). **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.27 (d, *J* = 5.6 Hz, 1H), 7.76–7.71 (m, 2H), 7.42–7.36 (m, 2H), 6.47 (d, *J* = 5.6 Hz, 1H), 2.47 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, Chloroform-*d*): δ = 161.4, 156.0 (q, $^2J_{C\text{-}F}$ = 36.4 Hz), 145.9, 135.7, 129.8 (2C), 128.5 (2C), 119.8 (q, $^1J_{C\text{-}F}$ = 277.1 Hz), 97.9 (q, $^3J_{C\text{-}F}$ = 3.0 Hz), 21.8 ppm; **^{19}F NMR** (564 MHz, Chloroform-*d*): δ = –71.53 (s, CF_3) ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_{11}H_9ON_2SF_3Na]^+$: 297.0280, found: 297.0284; **IR (ATR)**: *v* = 3119, 2967, 2595, 2193, 2161, 1927, 1727, 1654, 1561, 1512, 1450, 1381, 1313, 1274, 1239, 1188, 1140, 1103, 1080, 972, 815, 748, 663 cm^{-1}; **m.p.**: 59–61 °C.

1-Phenyl-3-(trifluoromethyl)-1,2,6-thiadiazine 1-oxide (5ba)



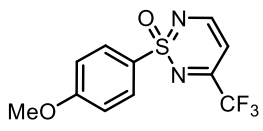
Following GP1, the title compound was obtained from benzenesulfonimidamide (**1b**, 31.2 mg, 0.200 mmol), ETFBO (**4a**, 50.4 mg, 42.7 µL, 0.300 mmol) and pyridine (33.2 mg, 34.0 µL, 0.420 mmol) in presence of silica (115 mg) after purification by column chromatography (*n*-pentane/EtOAc: 98/2 to 9/1) as a pale yellow solid (46.8 mg, 0.180 mmol, 90%). **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.30 (d, *J* = 5.6 Hz, 1H), 7.90–7.85 (m, 2H), 7.73–7.68 (m, 1H), 7.63–7.58 (m, 2H), 6.50 (d, *J* = 5.6 Hz, 1H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, Chloroform-*d*): δ = 161.6, 156.2 (q, $^2J_{C\text{-}F}$ = 36.6 Hz), 138.6, 134.5, 129.2 (2C), 128.5 (2C), 119.8 (q, $^1J_{C\text{-}F}$ = 277.2 Hz), 98.1 (q, $^3J_{C\text{-}F}$ = 3.1 Hz) ppm; **^{19}F NMR** (564 MHz, Chloroform-*d*): δ = –71.53 (s, CF_3) ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_{10}H_7ON_2SF_3Na]^+$: 283.0123, found: 283.0122; **IR (ATR)**: *v* = 3188, 3036, 2321, 2162, 2073, 1911, 1663, 1561, 1516, 1449, 1384, 1316, 1280, 1246, 1191, 1158, 1104, 1081, 969, 817, 752, 680 cm^{-1}; **m.p.**: 74–76 °C.

1-(*o*-Tolyl)-3-(trifluoromethyl)-1,2,6-thiadiazine 1-oxide (5ca)



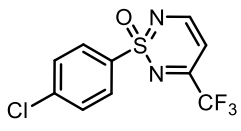
Following GP1, the title compound was obtained from 2-methylbenzene-sulfonimidamide (**1c**, 34.0 mg, 0.200 mmol), ETFBO (**4a**, 50.4 mg, 42.7 µL, 0.300 mmol) and pyridine (33.2 mg, 34.0 µL, 0.420 mmol) in presence of silica (120 mg) after purification by column chromatography (*n*-pentane/EtOAc: 98/2 to 9/1) as a pale yellow solid (36.6 mg, 0.133 mmol, 67%). **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.30 (d, *J* = 5.6 Hz, 1H), 8.16 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.59 (td, *J* = 7.5, 1.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 6.48 (d, *J* = 5.6 Hz, 1H), 2.22 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, Chloroform-*d*): δ = 161.9, 156.6 (q, $^{2}J_{C\text{-}F}$ = 36.5 Hz), 139.9, 135.9, 135.0, 133.2, 129.2, 126.5, 119.8 (q, $^{1}J_{C\text{-}F}$ = 277. Hz), 97.74 (q, $^{3}J_{C\text{-}F}$ = 3.0 Hz), 20.2 ppm; **^{19}F NMR** (564 MHz, Chloroform-*d*): δ = –71.64 (s, CF_3) ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_{11}H_9ON_2SF_3Na]^+$: 297.0278, found: 297.0277; **IR (ATR)**: *v* = 3108, 3067, 2928, 2163, 1949, 1712, 1642, 1563, 1511, 1467, 1379, 1313, 1275, 1245, 1188, 1141, 1078, 971, 911, 872, 828, 798, 758, 703, 683 cm^{-1}; **m.p.**: 36–38 °C.

1-(4-Methoxyphenyl)-3-(trifluoromethyl)-1,2,6-thiadiazine 1-oxide (5da)



Following GP1, the title compound was obtained from 4-methoxybenzene-sulfonimidamide (**1d**, 37.2 mg, 0.200 mmol), ETFBO (**4a**, 50.4 mg, 42.7 µL, 0.300 mmol) and pyridine (33.2 mg, 34.0 µL, 0.420 mmol) in presence of silica (120 mg) after purification by column chromatography (*n*-pentane/EtOAc: 98/2 to 4/1) as a yellow solid (42.2 mg, 0.145 mmol, 73%). **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.26 (d, *J* = 5.6 Hz, 1H), 7.80–7.75 (m, 2H), 7.07–7.02 (m, 2H), 6.46 (d, *J* = 5.6 Hz, 1H), 3.90 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, Chloroform-*d*): δ = 164.5, 161.3, 156.0 (q, $^{2}J_{C\text{-}F}$ = 36.5 Hz), 130.9 (2C), 130.0, 119.84 (q, $^{1}J_{C\text{-}F}$ = 277.3 Hz), 114.4 (2C), 97.7 (q, $^{3}J_{C\text{-}F}$ = 2.9 Hz) 56.0 ppm; **^{19}F NMR** (564 MHz, Chloroform-*d*): δ = –71.50 (s, CF_3) ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_{11}H_9O_2N_2SF_3Na]^+$: 313.0229, found: 313.0225; **IR (ATR)**: *v* = 3108, 3031, 2977, 2947, 2848, 2635, 2165, 2074, 1904, 1770, 1563, 1497, 1448, 1418, 1388, 1313, 1246, 1200, 1151, 1102, 1017, 972, 825, 798, 745, 663 cm^{-1}; **m.p.**: 72–74 °C.

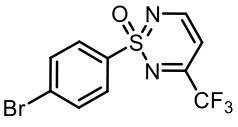
1-(4-Chlorophenyl)-3-(trifluoromethyl)-1,2,6-thiadiazine 1-oxide (5ea)



Following GP1, the title compound was obtained from 4-chlorobenzene-sulfonimidamide (**1e**, 38.1 mg, 0.200 mmol), ETFBO (**4a**, 50.4 mg, 42.7 µL, 0.300 mmol) and pyridine (33.2 mg, 34.0 µL, 0.420 mmol) in presence of

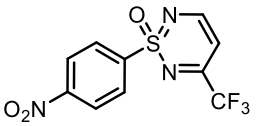
silica (120 mg) after purification by column chromatography (*n*-pentane/EtOAc: 98/2 to 9/1) as a pale yellow solid (51.1 mg, 0.173 mmol, 87%). **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.30 (d, *J* = 5.6 Hz, 1H), 7.81 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 6.51 (d, *J* = 5.6 Hz, 1H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, Chloroform-*d*): δ = 161.8, 156.4 (q, $^{2}J_{C\text{-}F}$ = 36.7 Hz), 141.6, 137.0, 129.8 (2C), 129.6 (2C), 119.7 (q, $^{1}J_{C\text{-}F}$ = 277.4 Hz), 98.3 (q, $^{3}J_{C\text{-}F}$ = 3.0 Hz) ppm; **^{19}F NMR** (564 MHz, Chloroform-*d*): δ = –71.54 (s, CF_3) ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_{10}H_6ON_2SF_3Na]^+$: 316.9734, found: 316.9735; **IR (ATR)**: *v* = 3096, 3040, 2166, 2024, 1917, 1782, 1649, 1566, 1517, 1478, 1391, 1318, 1254, 1197, 1158, 1127, 1086, 1012, 973, 824, 777 cm^{-1}; **m.p.**: 57–59 °C.

1-(4-Bromophenyl)-3-(trifluoromethyl)-1,2,6-thiadiazine 1-oxide (5fa)



Following GP1, the title compound was obtained from 4-bromobenzenesulfonimidamide (**1f**, 47.0 mg, 0.200 mmol), ETFBO (**4a**, 50.4 mg, 42.7 µL, 0.300 mmol) and pyridine (33.2 mg, 34.0 µL, 0.420 mmol) in presence of silica (130 mg) after purification by column chromatography (*n*-pentane/EtOAc: 98/2 to 9/1) as a pale yellow solid (61.2 mg, 0.182 mmol, 90%). **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.30 (d, *J* = 5.6 Hz, 1H), 7.77–7.69 (m, 4H), 6.51 (d, *J* = 5.6 Hz, 1H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, Chloroform-*d*): δ = 161.8, 156.3 (q, $^{2}J_{C\text{-}F}$ = 36.8 Hz), 137.6, 132.6 (2C), 130.2, 129.8 (2C), 119.7 (q, $^{1}J_{C\text{-}F}$ = 277.3 Hz), 98.3 (q, $^{3}J_{C\text{-}F}$ = 3.0 Hz) ppm; **^{19}F NMR** (564 MHz, Chloroform-*d*): δ = –71.54 (s, CF_3) ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_{10}H_7ON_2SF_3Br]^+$: 338.9409, found: 338.9411; **IR (ATR)**: *v* = 3095, 3038, 2293, 2196, 2025, 1916, 1785, 1647, 1566, 1516, 1476, 1389, 1318, 1253, 1196, 1156, 1097, 1068, 1009, 972, 821, 797, 772 cm^{-1}; **m.p.**: 83–85 °C.

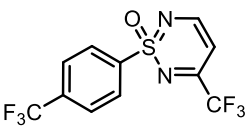
1-(4-Nitrophenyl)-3-(trifluoromethyl)-1,2,6-thiadiazine 1-oxide (5ga)



Following GP1, the title compound was obtained from 4-nitrobenzene-sulfonimidamide (**1g**, 40.2 mg, 0.200 mmol), ETFBO (**4a**, 50.4 mg, 42.7 µL, 0.300 mmol) and pyridine (33.2 mg, 34.0 µL, 0.420 mmol) in presence of silica (125 mg) after purification by column chromatography (*n*-pentane/EtOAc: 98/2 to 9/1) as a colorless solid (55.1 mg, 0.181 mmol, 90%).**^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.48–8.41 (m, 2H), 8.36 (d, *J* = 5.6 Hz, 1H), 8.13–8.07 (m, 2H), 6.58 (d, *J* = 5.6 Hz, 1H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, Chloroform-*d*): δ = 162.5, 156.8 (q, $^{2}J_{C\text{-}F}$ = 37.0 Hz), 151.0, 143.8, 129.6 (2C), 124.4 (2C), 119.6 (q, $^{1}J_{C\text{-}F}$ = 277.1 Hz), 99.0 (q, $^{3}J_{C\text{-}F}$ = 3.0 Hz) ppm; **^{19}F NMR** (564 MHz, Chloroform-*d*): δ = –71.56 (s, CF_3) ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_{10}H_7O_3N_3SF_3]^+$: 306.0155, found: 306.0153; **IR (ATR)**: *v* = 3112, 3073, 2881, 2638, 2288, 2165, 2072, 1994, 1938, 1804, 1693, 1647, 1609,

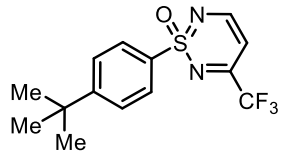
1563, 1534, 1354, 1315, 1268, 1188, 1144, 1103, 1018, 972, 856, 823, 771, 741, 676 cm^{-1}; **m.p.**: 100–102 °C.

3-(Trifluoromethyl)-1-[4-(trifluoromethyl)phenyl]-1,2,6-thiadiazine 1-oxide (5ha)



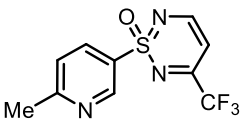
Following GP1, the title compound was obtained from 4-(trifluoromethyl)-benzenesulfonimidamide (**1h**, 44.8 mg, 0.200 mmol), ETFBO (**4a**, 50.4 mg, 42.7 µL, 0.300 mmol) and pyridine (33.2 mg, 34.0 µL, 0.420 mmol) in presence of silica (130 mg) after purification by column chromatography (*n*-pentane/EtOAc: 98/2 to 9/1) as a pale yellow solid (54.2 mg, 0.165 mmol, 83%). **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.33 (d, *J* = 5.6 Hz, 1H), 8.03 (d, *J* = 8.3 Hz, 2H), 7.88 (d, *J* = 8.3 Hz, 2H), 6.55 (d, *J* = 5.6 Hz, 1H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, Chloroform-*d*): δ = 162.2, 156.6 (q, $^{2}J_{C\text{-}F}$ = 37.1, 36.7 Hz), 141.9, 136.1 (q, $^{2}J_{C\text{-}F}$ = 33.3 Hz), 128.9 (2C), 126.4 (q, $^{3}J_{C\text{-}F}$ = 3.7 Hz, 2C), 121.4 (q, $^{1}J_{C\text{-}F}$ = 241.8 Hz), 117.8 (q, $^{1}J_{C\text{-}F}$ = 277.3 Hz) 98.7 (q, $^{3}J_{C\text{-}F}$ = 3.0 Hz) ppm; **^{19}F NMR** (564 MHz, Chloroform-*d*): δ = –63.34 (s, C_6H_4-CF_3), –71.51 (s, CF_3) ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_{11}H_7ON_2SF_6]^+$: 329.0178, found: 329.0176; **IR (ATR)**: *v* = 3109, 3060, 2170, 1931, 1804, 1673, 1567, 1516, 1405, 1385, 1319, 1279, 1256, 1184, 1115, 1058, 1017, 972, 835, 788, 746, 700 cm^{-1}; **m.p.**: 86–88 °C.

1-[4-(*tert*-Butyl)phenyl]-3-(trifluoromethyl)-1,2,6-thiadiazine 1-oxide (5ia)



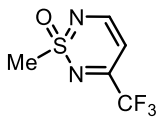
Following GP1, the title compound was obtained from 4-(*tert*-butyl)-benzenesulfonimidamide (**1i**, 42.5 mg, 0.200 mmol), ETFBO (**4a**, 50.4 mg, 42.7 µL, 0.300 mmol) and pyridine (33.2 mg, 34.0 µL, 0.420 mmol) in presence of silica (125 mg) after purification by column chromatography (*n*-pentane/EtOAc: 98/2 to 9/1) as a pale yellow solid (53.0 mg, 0.168 mmol, 84%). **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.26 (d, *J* = 5.6 Hz, 1H), 7.80–7.75 (m, 2H), 7.07–7.02 (m, 2H), 6.46 (d, *J* = 5.6 Hz, 1H), 3.90 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, Chloroform-*d*): δ = 161.6, 159.0, 156.3 (q, $^{2}J_{C\text{-}F}$ = 36.5 Hz), 135.7, 128.6 (2C), 126.5 (2C), 120.0 (q, $^{1}J_{C\text{-}F}$ = 277.1 Hz), 98.1 (q, $^{3}J_{C\text{-}F}$ = 3.0 Hz), 35.8, 31.4 (3C) ppm; **^{19}F NMR** (564 MHz, Chloroform-*d*): δ = –71.51 (s, CF_3) ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_{14}H_{15}ON_2SF_3Na]^+$: 339.0749, found: 339.0750; **IR (ATR)**: *v* = 3460, 3121, 2966, 2873, 2296, 2170, 2106, 2007, 1925, 1741, 1636, 1560, 1516, 1392, 1313, 1276, 1251, 1196, 1143, 1088, 972, 819, 782, 728 cm^{-1}; **m.p.**: 66–68 °C.

1-(6-Methylpyridin-3-yl)-3-(trifluoromethyl)-1,2,6-thiadiazine 1-oxide (5ja)



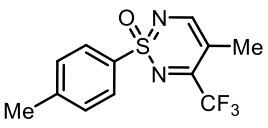
Following GP1, the title compound was obtained from 6-methylpyridine-3-sulfonimidamide (**1j**, 34.2 mg, 0.200 mmol), ETFBO (**4a**, 50.4 mg, 42.7 µL, 0.300 mmol) and pyridine (33.2 mg, 34.0 µL, 0.420 mmol) in presence of silica (120 mg) after purification by column chromatography (*n*-pentane/EtOAc: 98/2 to 2/1) as a pale yellow solid (46.1 mg, 0.167 mmol, 84%).**^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.62 (dd, *J* = 2.0, 1.0 Hz, 1H), 8.37 (d, *J* = 5.6 Hz, 1H), 8.17 (d, *J* = 8.0 Hz, 1H), 7.81 (ddt, *J* = 8.1, 2.0, 1.0 Hz, 1H), 6.48 (dd, *J* = 5.6, 0.9 Hz, 1H), 2.49 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, Chloroform-*d*): δ = 162.7, 156.8 (q, $^{2}J_{C\text{-}F}$ = 36.6 Hz), 153.0, 151.5, 139.3, 138.2, 123.1, 119.70 (q, $^{1}J_{C\text{-}F}$ = 277.2 Hz), 97.8 (q, $^{3}J_{C\text{-}F}$ = 3.0 Hz) ppm; **^{19}F NMR** (564 MHz, Chloroform-*d*): δ = –71.63 (s, CF_3) ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_{10}H_9ON_3SF_3]^+$: 276.0413, found: 276.0413; **IR (ATR)**: *v* = 3858, 3118, 2925, 2695, 2273, 2168, 2062, 2005, 1940, 1736, 1661, 1569, 1517, 1458, 1376, 1311, 1251, 1197, 1125, 1087, 974, 832, 794, 746, 662 cm^{-1}; **m.p.**: 107–109 °C.

1-Methyl-3-(trifluoromethyl)-1,2,6-thiadiazine 1-oxide (5ka)



Following GP1, the title compound was obtained from methanesulfonimidamide (**1k**, 18.8 mg, 0.200 mmol), ETFBO (**4a**, 50.4 mg, 42.7 µL, 0.300 mmol) and pyridine (33.2 mg, 34.0 µL, 0.420 mmol) in presence of silica (100 mg) after purification by column chromatography (*n*-pentane/EtOAc: 98/2 to 2/1) as a yellow solid (21.7 mg, 0.110 mmol, 55%). **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.16 (d, *J* = 5.6 Hz, 1H), 6.39 (d, *J* = 5.6 Hz, 1H), 3.49 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, Chloroform-*d*): δ = 161.9, 156.3 (q, $^{2}J_{C\text{-}F}$ = 36.5 Hz), 119.7 (q, $^{1}J_{C\text{-}F}$ = 276.8 Hz), 98.6 (q, $^{3}J_{C\text{-}F}$ = 3.0 Hz), 44.4 ppm; **^{19}F NMR** (564 MHz, Chloroform-*d*): δ = –71.69 (s, CF_3) ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_5H_6ON_2SF_3]^+$: 199.0148, found: 199.0142; **IR (ATR)**: *v* = 3127, 3034, 2944, 2162, 1985, 1704, 1567, 1516, 1384, 1318, 1268, 1233, 1179, 1134, 1083, 983, 845, 792, 742, 702 cm^{-1}; **m.p.**: 65–67 °C.

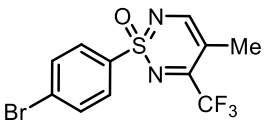
4-Methyl-1-(*p*-tolyl)-3-(trifluoromethyl)-1,2,6-thiadiazine 1-oxide (5ac)



Following GP1, the title compound was obtained from 4-methylbenzene-sulfonimidamide (**1a**, 34.0 mg, 0.200 mmol), (*E*)-4-Ethoxy-1,1,1-trifluoro-3-methylbut-3-en-2-one (**4c**, 54.6 mg, 0.300 mmol) and pyridine (33.2 mg, 34.0 µL, 0.420 mmol) in presence of silica (120 mg) after purification by column chromatography (*n*-pentane/EtOAc: 98/2 to 9/1) as a pale yellow oil (15.7 mg, 0.0545 mmol, 27%). **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.07 (s, 1H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 2.46 (s,

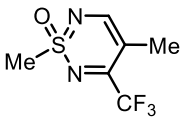
3H), 2.18 (q, *J* = 2.1 Hz, 3H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, Chloroform-*d*): *δ* = 163.2, 153.1 (q, $^{2}J_{C-F}$ = 35.0 Hz), 145.6, 135.5, 129.8 (2C), 128.7 (2C), 120.6 (q, $^{1}J_{C-F}$ = 278.7 Hz), 107.9, 21.8, 14.5 (q, $^{3}J_{C-F}$ = 2.5 Hz) ppm; **^{19}F NMR** (564 MHz, Chloroform-*d*): *δ* = –67.93 (s, CF_3) ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_{12}H_{12}ON_2SF_3]^+$: 289.0617, found: 289.0615; **IR (ATR)**: *v* = 2934, 2701, 2325, 2081, 1924, 1742, 1576, 1487, 1402, 1363, 1268, 1189, 1139, 1051, 942, 870, 812, 765, 742, 706 cm^{-1}.

4-Methyl-1-(4-Bromobenzene)-3-(trifluoromethyl)-1,2,6-thiadiazine 1-oxide (5fc)



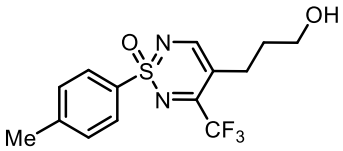
Following GP1, the title compound was obtained from 4-bromobenzene-sulfonimidamide (**1f**, 47.0 mg, 0.200 mmol), (*E*)-4-Ethoxy-1,1,1-trifluoro-3-methylbut-3-en-2-one (**4c**, 54.6 mg, 0.300 mmol) and pyridine (33.2 mg, 34.0 µL, 0.420 mmol) in presence of silica (135 mg) after purification by column chromatography (*n*-pentane/EtOAc: 98/2 to 9/1) as a pale yellow oil (14.2 mg, 0.0402 mmol, 20%). **^{1}H NMR** (600 MHz, Chloroform-*d*): *δ* = 8.10 (s, 1H), 7.73 (s, 4H), 2.19 (q, *J* = 2.2 Hz, 3H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, Chloroform-*d*): *δ* = 163.6, 153.4 (q, $^{2}J_{C-F}$ = 35.0 Hz), 132.5 (2C), 130.0 (2C), 120.49 (q, $^{1}J_{C-F}$ = 278.7 Hz), 108.5, 14.5 (q, $^{3}J_{C-F}$ = 2.7 Hz) ppm; **^{19}F NMR** (564 MHz, Chloroform-*d*): *δ* = –67.96 (s, CF_3) ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_{11}H_9ON_2SF_3Br]^+$: 352.9566, found: 352.9563; **IR (ATR)**: *v* = 3092, 2940, 2293, 2111, 1917, 1736, 1574, 1479, 1388, 1363, 1266, 1189, 1140, 1104, 1054, 1010, 943, 868, 822, 781, 741 cm^{-1}.

1,4-Dimethyl-3-(trifluoromethyl)-1,2,6-thiadiazine 1-oxide (5kc)



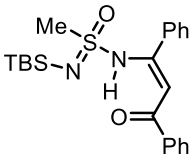
Following GP1, the title compound was obtained from methanesulfonimidamide (**1k**, 18.8 mg, 0.200 mmol), (*E*)-4-Ethoxy-1,1,1-trifluoro-3-methylbut-3-en-2-one (**4c**, 54.6 mg, 0.300 mmol) and pyridine (33.2 mg, 34.0 µL, 0.420 mmol) in presence of silica (110 mg) after purification by column chromatography (*n*-pentane/EtOAc: 98/2 to 4/1) as a colorless solid (20.9 mg, 0.0985 mmol, 49%). **^{1}H NMR** (600 MHz, Chloroform-*d*): *δ* = 7.96 (s, 1H), 3.48 (s, 3H), 2.11 (q, *J* = 2.1 Hz, 3H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, Chloroform-*d*): *δ* = 163.6, 153.4 (q, $^{2}J_{C-F}$ = 35.1 Hz), 120.51 (q, $^{1}J_{C-F}$ = 278.3 Hz), 108.7, 44.4, 14.4 (q, $^{3}J_{C-F}$ = 2.9 Hz) ppm; **^{19}F NMR** (564 MHz, Chloroform-*d*): *δ* = –68.10 (s, CF_3) ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_6H_8ON_2SF_3]^+$: 213.0304, found: 213.0304; **IR (ATR)**: *v* = 3035, 2979, 2944, 2653, 2440, 2269, 2195, 2161, 2082, 2047, 1972, 1906, 1851, 1739, 1581, 1489, 1453, 1408, 1367, 1335, 1267, 1221, 1189, 1137, 1052, 974, 896, 807, 738, 712 cm^{-1}; **m.p.**: 81–83 °C.

4-(3-Hydroxypropyl)-1-(*p*-tolyl)-3-(trifluoromethyl)-1,2,6-thiadiazine 1-oxide (5ad)



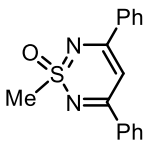
Using slightly modified reaction conditions from a previously reported protocol,[S2] the title compound was obtained from 4-methylbenzenesulfonimidamide (**1a**, 34.0 mg, 0.200 mmol), 1-(3,4-dihydro-2H-pyran-5-yl)-2,2,2-trifluoroethan-1-one (**4d**, 54.0 mg, 0.300 mmol, 1.5 equiv.) and Cs_2CO_3 (137 mg, 0.420 mmol, 2.1 equiv.) after purification by column chromatography (*n*-pentane/EtOAc: 3/1 to 1/1) as a yellow oil (25.3 mg, 0.0761 mmol, 38%). **^{1}H NMR** (400 MHz, Chloroform-*d*): δ = 8.16 (s, 1H), 7.75 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 3.73–3.66 (m, 2H), 2.77–2.67 (m, 1H), 2.61–2.51 (m, 1H), 2.46 (s, 3H), 1.90–1.69 (m, 2H) ppm [OH-proton not detected]; **^{13}C{^{1}H,^{19}F} NMR** (101 MHz, Chloroform-*d*): δ = 163.6, 152.6, 145.7, 135.4, 129.8 (2C), 128.7 (2C), 120.7, 112.4, 61.7, 34.3, 25.2, 21.8 ppm; **^{19}F NMR** (376 MHz, Chloroform-*d*): δ = –66.4 (s, CF_3) ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_{14}H_{15}O_2N_2SF_3Na]^+$: 355.0694, found: 355.0670; **IR (ATR)**: *v* = 3407, 2932, 2878, 2167, 1919, 1709, 1572, 1469, 1404, 1362, 1252, 1187, 1139, 1106, 1043, 954, 877, 811, 761, 703, 661 cm^{-1}.

***N*-(*tert*-Butyldimethylsilyl)-*N'*-(3-oxo-1,3-diphenylprop-1-en-1-yl) methanesulfonimidamide**



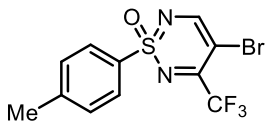
(7ka) Using slightly modified reaction conditions (without Al_2O_3 as grinding auxiliary) from a previously reported protocol,[S5] the title compound was obtained from *N*-(*tert*-butyldimethylsilyl)-methanesulfonimidamide (**6k**, 31.3 mg, 0.150 mmol), 1,3-diphenylprop-2-yn-1-one (**2a**, 46.4 mg, 0.225 mmol), Cs_2CO_3 (103 mg, 0.315 mmol, 2.1 equiv.), $LaCl_3$ (3.7 mg, 0.015 mmol, 0.10 equiv.), and molecular sieves (MS 4 Å, 5 mg) after purification by column chromatography (*n*-pentane/EtOAc: 98/2 to 4/1) as a yellow oil (56.1 mg, 0.135 mmol, 90%). **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 12.14 (s, 1H), 8.05–7.87 (m, 2H), 7.66–7.57 (m, 2H), 7.57–7.52 (m, 1H), 7.50–7.41 (m, 5H), 6.28 (s, 1H), 2.97 (s, 3H), 0.91 (s, 9H), 0.13 (s, 3H), 0.12 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, Chloroform-*d*): δ =191.3, 158.8, 138.7, 135.5, 132.7, 130.5, 129.0 (2C), 128.7 (2C), 128.2 (2C), 127.9 (2C), 103.8, 48.1, 26.0 (3C), 18.0, –2.7 (2C) ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_{22}H_{30}O_2N_2SSiNa]^+$: 437.1690, found: 437.1670; **IR (ATR)**: *v* = 3061, 2930, 2855, 2323, 2086, 1899, 1814, 1611, 1559, 1489, 1452, 1407, 1312, 1250, 1223, 1174, 1103, 1043, 1019, 962, 935, 827, 765, 730, 692 cm^{-1}.

1-Methyl-3,5-diphenyl-1,2,6-thiadiazine 1-oxide (3ka)



Using slightly modified reaction conditions (performing the reaction at 100 °C instead of room temperature) from a previously reported protocol,[S2] the title compound was synthesized from *N*-(*tert*-butyldimethylsilyl)-methanesulfonimidamide (**6k**, 41.7 mg, 0.200 mmol), 1,3-diphenylprop-2-yn-1-one (**2a**, 61.9 mg, 0.300 mmol), Cs_2CO_3 (137 mg, 0.420 mmol), $LaCl_3$ (4.9 mg, 0.020 mmol, 0.1 equiv.) and molecular sieves (MS 4 Å, 5 mg) in dry DMSO (3 mL) for 12 h at 100°C. The product **3ka** was obtained after purification by column chromatography (*n*-pentane/EtOAc: 98/2 to 4/1) as a yellow solid (53.0 mg, 0.188 mmol, 94%). **^{1}H NMR** (600 MHz, Chloroform-*d*): δ =8.09–7.99 (m, 4H), 7.57–7.46 (m, 6H), 7.04 (s, 1H), 3.51 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, Chloroform-*d*): δ =166.6 (2C), 137.0 (2C), 131.7 (2C), 128.8 (4C), 127.6 (4C), 95.9, 44.8 ppm. The observed NMR data are in full agreement with the reported data in the literature.[S2]

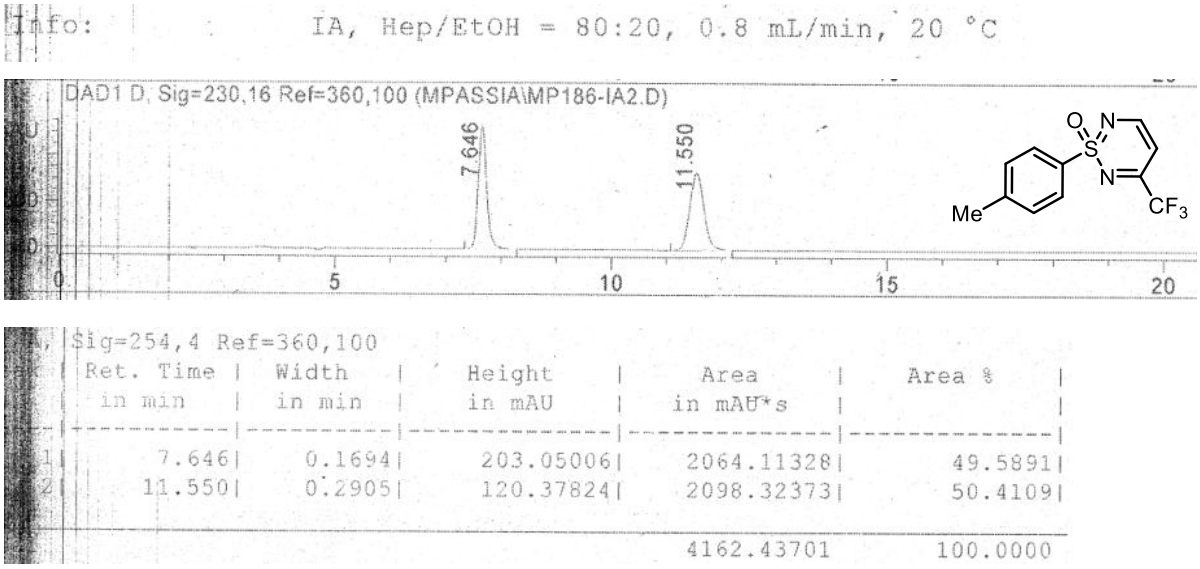
4-Bromo-1-(*p*-tolyl)-3-(trifluoromethyl)-1,2,6-thiadiazine 1-oxide (8)



Under an atmosphere of argon, 1-(*p*-tolyl)-3-(trifluoromethyl)-1,2,6-thiadiazine 1-oxide (**5aa**, 54.9 mg, 0.200 mmol) was loaded in an oven-dried Schlenk-tube, equipped with magnetic stirring bar and septum and dissolved in dry 1,4-dioxane (5 mL · 1 mmol^{-1}). Bromine (0.031 mL, 95.9 mg, 0.600 mmol, 3.0 equiv.) was added dropwise by syringe within 10 minutes, and the reaction mixture was stirred for 3 h at ambient temperature. After completion of the reaction (monitored by TLC), a $Na_2S_2O_3$ solution (1 M, 10 mL · 1 mmol^{-1}) was added and the reaction mixture was extracted with DCM (3 x 10 ml · 1 mmol^{-1}). The combined organic phases were washed with brine and dried over $MgSO_4$. The solvent was removed at reduced pressure and dried on high vacuum for several hours. Title compound **8** was obtained as a pale yellow solid (69.3 mg, 0.196 mmol, 98%) without further purification. **^{1}H NMR** (600 MHz, Chloroform-*d*): δ = 8.34 (s, 1H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 2.48 (s, 3H) ppm; **^{13}C{^{1}H} NMR** (151 MHz, Chloroform-*d*): δ = 163.4, 152.6 (q, $^2J_{C\text{-}F}$ = 35.8 Hz), 119.5 (q, $^1J_{C\text{-}F}$ = 278.6 Hz) 146.4, 134.3, 130.0 (2C), 128.7 (2C), 93.1, 21.9 ppm; **^{19}F NMR** (564 MHz, Chloroform-*d*): δ = –68.50 (s, CF_3) ppm; **HRMS (ESI)**: *m/z* calcd. for $[C_{11}H_9ON_2SBrF_3]^+$: 352.9566, found: 352.9557; **IR (ATR)**: *v* = 2923, 2853, 2311, 2201, 2113, 1920, 1739, 1652, 1591, 1551, 1492, 1454, 1376, 1252, 1196, 1155, 1100, 990, 835, 809, 757, 730, 702, 667 cm^{-1}; **m.p.**: 98–99 °C.

7. Analytical HPLC chromatogram of 5aa

Figure S3. HPLC trace of compound **5aa**.



	Ret. Time in min	Width in min	Height in mAU	Area in mAU*s	Area %
1	7.646	0.1694	203.05006	2064.11328	49.5891
2	11.550	0.2905	120.37824	2098.32373	50.4109
				4162.43701	100.0000

8. X-ray crystallographic studies (compounds 5aa and 8)

Single crystal X-ray data of **5aa** and **8** were measured using a dual-source Rigaku SuperNova diffractometer equipped with an Atlas detector and an Oxford Cryostream cooling system using mirror-monochromated Mo-K_α radiation (λ = 0.71073 Å). Data collection and reduction for both compounds were performed using the program *CrysAlisPro*[S6] and Gaussian face-index absorption correction method was applied.[S6] The structures were solved with Direct Methods (*SHELXS*)[S7] and refined by full-matrix least-squares based on F^2 using *SHELXL*-2015.[S7] Non-hydrogen atoms were assigned anisotropic displacement parameters unless stated otherwise. Hydrogen atoms were placed in idealized positions and included as riding. Isotropic displacement parameters for all H atoms were constrained to multiples of the equivalent displacement parameters of their parent atoms with $U_{iso}(H) = 1.2\ U_{eq}$(parent atom). The X-ray single crystal data and experimental details as well as CCDC numbers are given below.

Crystal data for **5aa** (obtained *via* slow evaporation from MeOH): CCDC-2109331, $C_{11}H_9F_3N_2OS$, M = 274.26 g•mol^{-1}, colourless plate, 0.29 × 0.18 × 0.04 mm^3, orthorhombic, space group *Pbca* (No. 61), a = 8.3925(6) Å, b = 11.7050(9) Å, c = 23.1584(19) Å, α = 90°, β = 90°, γ = 90°, V =

2274.9(3) Å^3, Z = 8, D_{calc} = 1.602 g•cm^{-3}, F(000) = 1120, μ = 0.313 mm^{-1}, T = 120(2) K, θ_{max} = 22.01°, 5469 total reflections, 1262 with $I_o > 2\sigma(I_o)$, R_{int} = 0.0857, 2291 data, 164 parameters, no restraints, GooF = 0.997, R_1 = 0.0724 and wR_2 = 0.0811 [$I_o > 2\sigma(I_o)$], R_1 = 0.1370 and wR_2 = 0.1043 (all reflections), 0.406 < dΔρ < -0.384 eÅ^{-3}.

Crystal data for **8** (obtained *via* slow evaporation from MeOH): CCDC-2109381, $C_{11}H_8BrF_3N_2OS$, M = 353.16 g•mol^{-1}, colourless plate, 0.28 × 0.20 × 0.06 mm^3, triclinic, space group *P*-1 (No. 2), a = 7.6104(12) Å, b = 7.8056(14) Å, c = 12.0015(19) Å, α = 90.867(2)°, β = 102.061(2)°, γ = 115.696(3)°, V = 623.71(18) Å^3, Z = 2, D_{calc} = 1.880 g•cm^{-3}, F(000) = 348, μ = 3.492 mm^{-1}, T = 120(2) K, θ_{max} = 26.37°, 4226 total reflections, 1815 with $I_o > 2\sigma(I_o)$, R_{int} = 0.0406, 2261 data, 173 parameters, no restraints, GooF = 1.071, R_1 = 0.0527 and wR_2 = 0.1167 [$I_o > 2\sigma(I_o)$], R_1 = 0.0693 and wR_2 = 0.1262 (all reflections), 1.236 < dΔρ < -0.622 eÅ^{-3}.

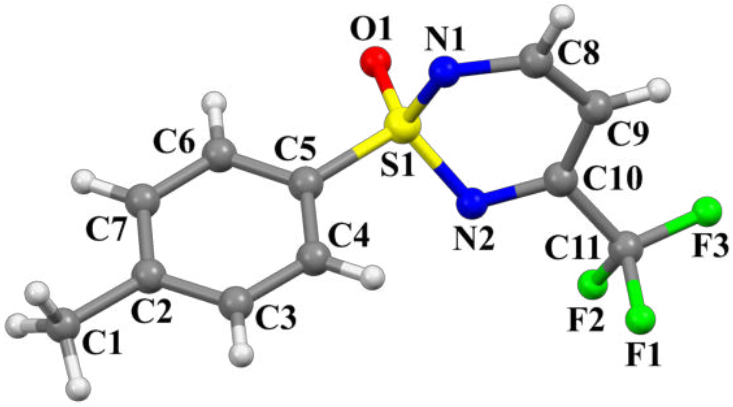


Figure S4 Ball-and-stick model of **5aa**.

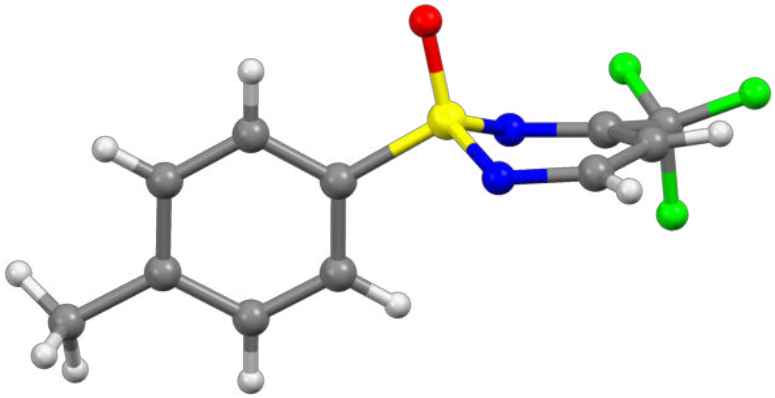


Figure S5 Ball-and-stick model of **5aa** showing the three-dimensional arrangement around the sulfur atom.

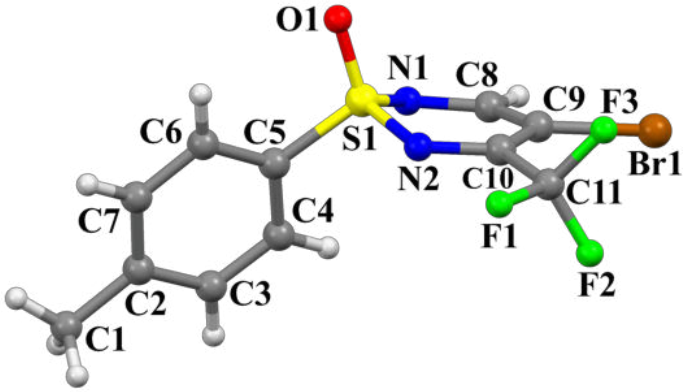


Figure S6 Ball-and-stick model of **8** showing the three-dimensional arrangement around the sulfur atom.

9. References

S1. Y. Chen and J. Gibson, A convenient synthetic route to sulfonimidamides from sulfonamides, *RSC Adv.*, 2015, **5**, 4171-4174.

S2. J.-H. Schöbel, M. T. Passia, N. A. Wolter, R. Puttreddy, K. Rissanen and C. Bolm, 1,2,6-Thiadiazine 1-Oxides: Unsaturated Three-Dimensional *S,N*-Heterocycles from Sulfonimidamides, *Org. Lett.*, 2020, **22**, 2702-2706.

S3. I. I. Gerus, M. G. Gorbunova and V. P. Kukhar, *β*-Ethoxyvinyl polyfluoroalkyl ketones — versatile synthones in fluoroorganic chemistry, *J. Fluor. Chem.*, 1994, **69**, 195-198.

S4. M. A. P. Martins, E. A. Guarda, C. P. Frizzo, E. Scapin, P. Beck, A. C. da Costa, N. Zanatta and H. G. Bonacorso, Synthesis of 1,1,1-trichloro[fluoro]-3-alken-2-ones using ionic liquids, *J. Mol. Catal. A Chem.*, 2007, **266**, 100-103.

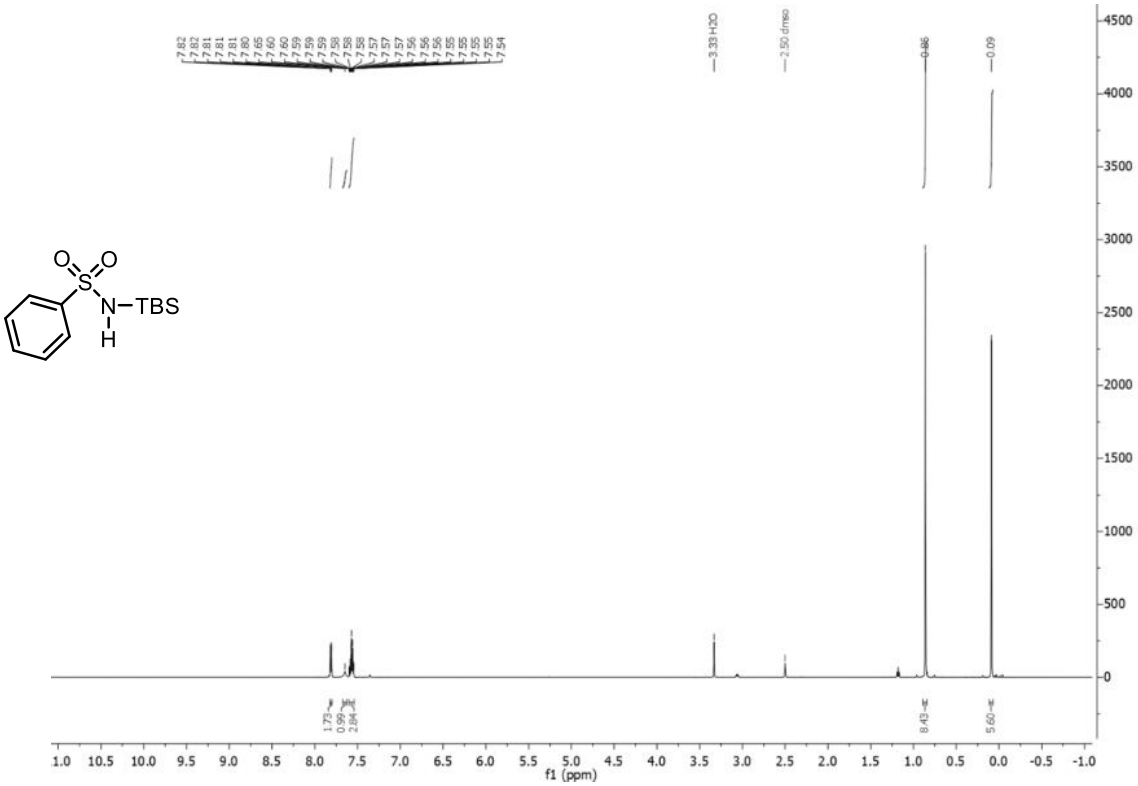
S5. J.-H. Schöbel, W. Liang, D. Wöll and C. Bolm, Mechanochemical Synthesis of 1,2,6-Thiadiazine 1-Oxides from Sulfonimidamides and the Fluorescence Properties of the Products, *J. Org. Chem.*, 2020, **85**, 15760-15766.

S6. Rigaku Oxford Diffraction, 2017, *CrysAlisPro* software system, version 38.46, Rigaku Corporation, Oxford, UK.

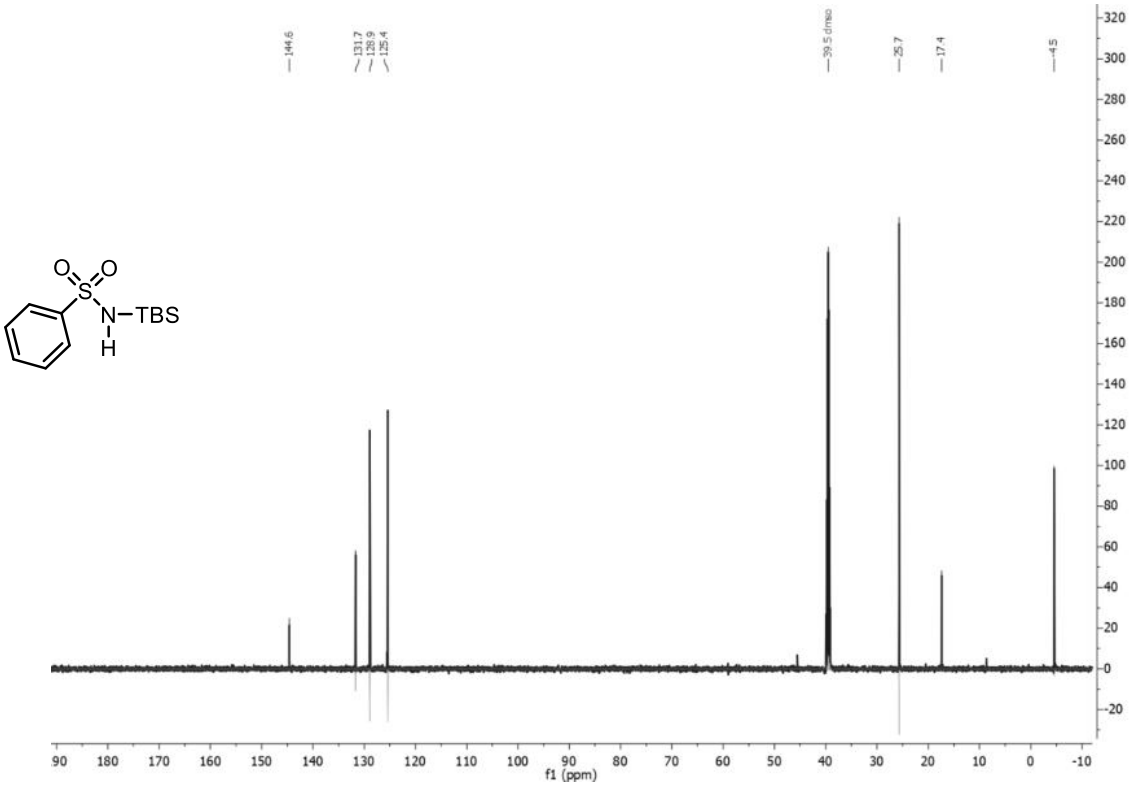
S7. a) G. M. Sheldrick, A short history of *ShelX*. *Acta Cryst.,* 2008, **A64**, 112-122. (b) G. M. Sheldrick, SHELXL13. Program package for crystal structure determination from single crystal diffraction data, University of Göttingen, Germany, 2013. (c) G. M. Sheldrick, Crystal structure refinement with *ShelXL*. *Acta Cryst.,* 2015, **C71**, 3-8.

10. NMR spectra

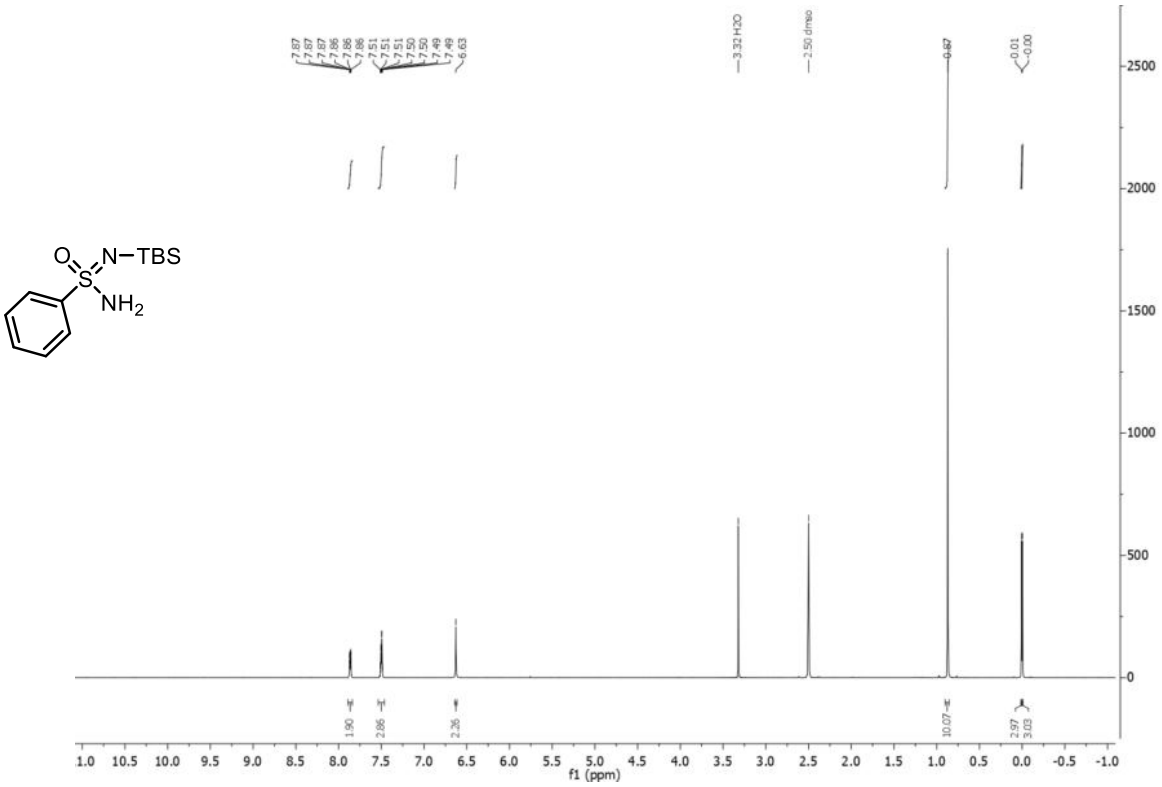
^{1}H NMR spectrum (DMSO-d_6, 600 MHz) of compound **1b-precursor**



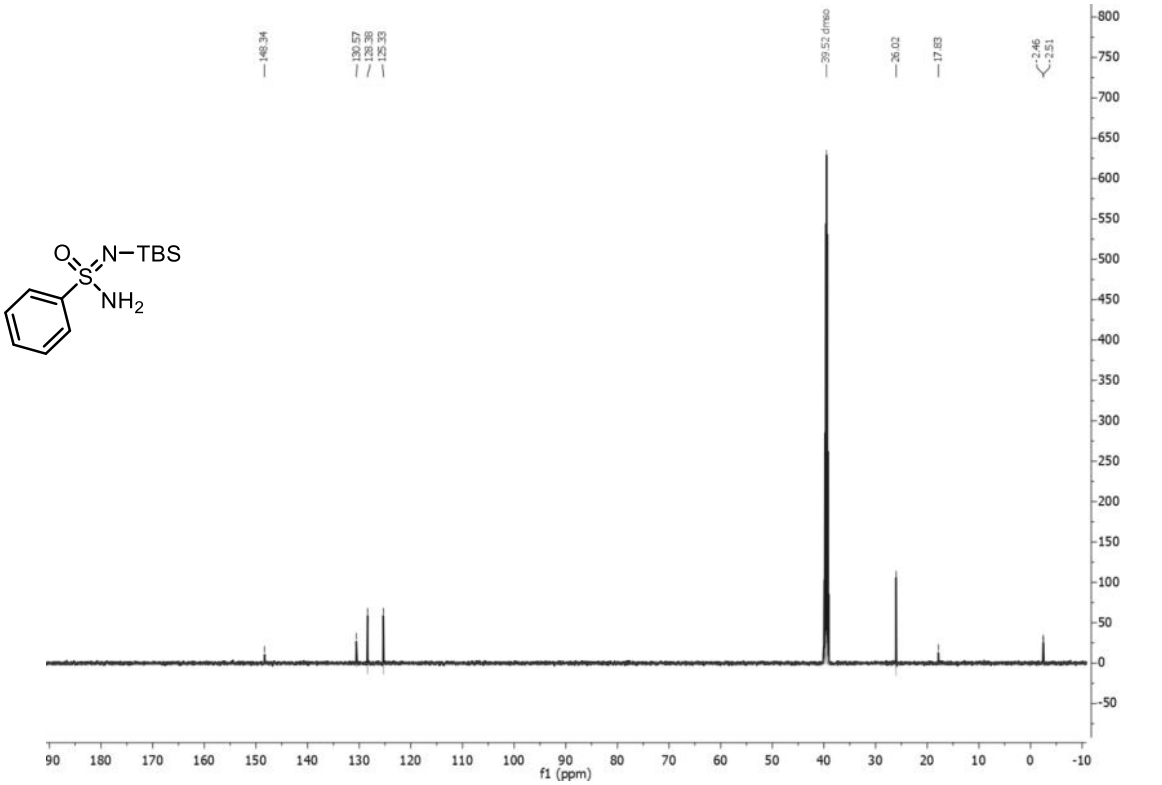
Stacked ^{13}C{^{1}H} DEPT NMR spectra (DMSO-d_6, 151 MHz) of compound **1b-precursor**



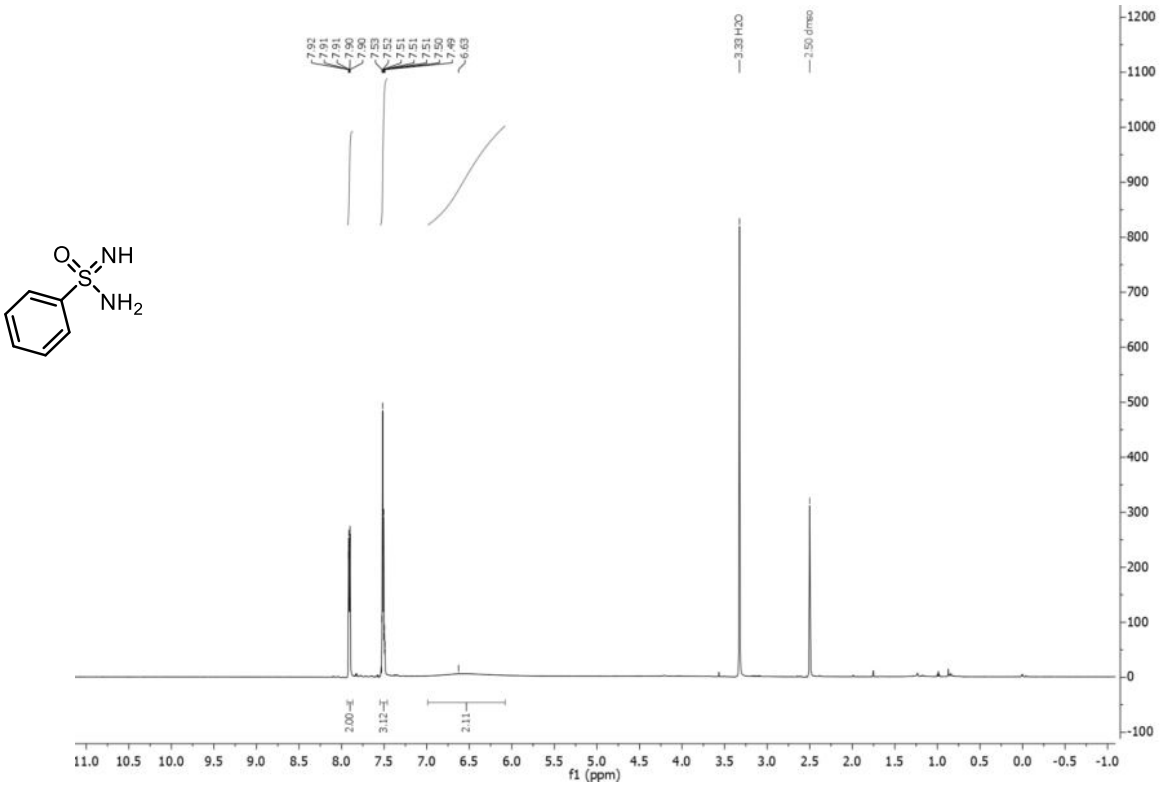
^{1}H NMR spectrum (DMSO-d_6, 600 MHz) of compound **6b**



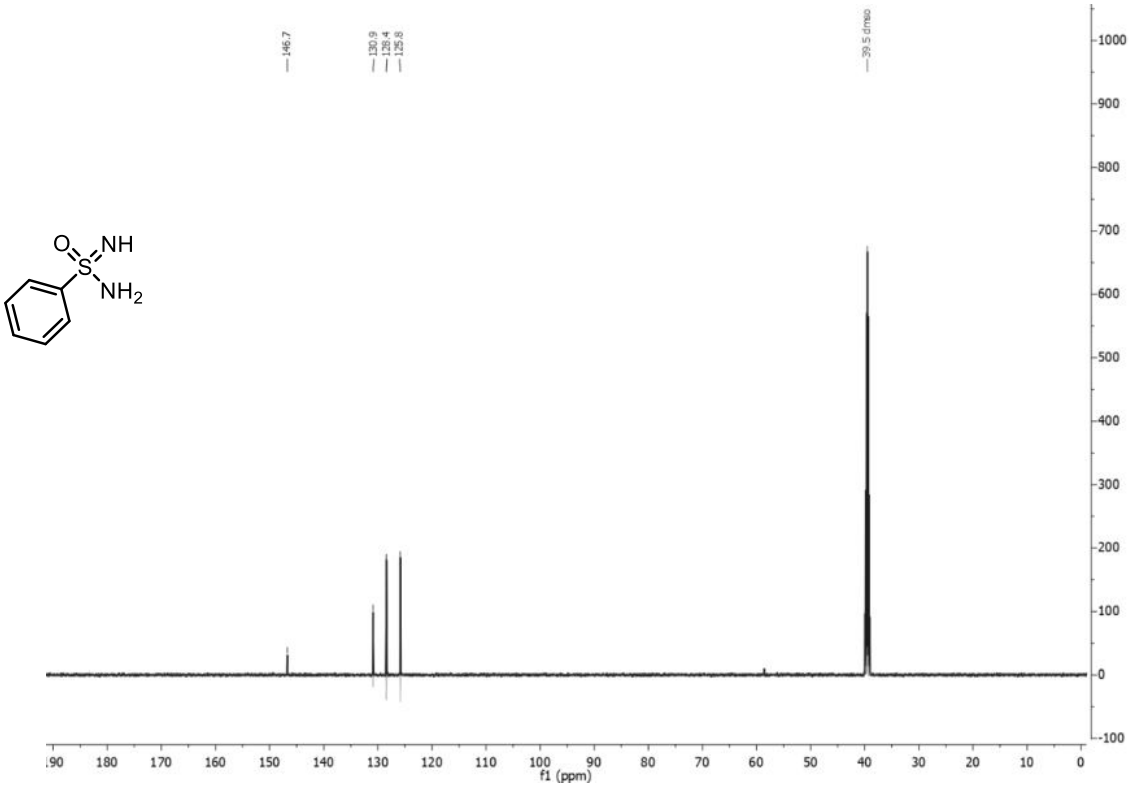
Stacked ^{13}C{^{1}H} DEPT NMR spectra (DMSO-d_6, 151 MHz) of compound **6b**



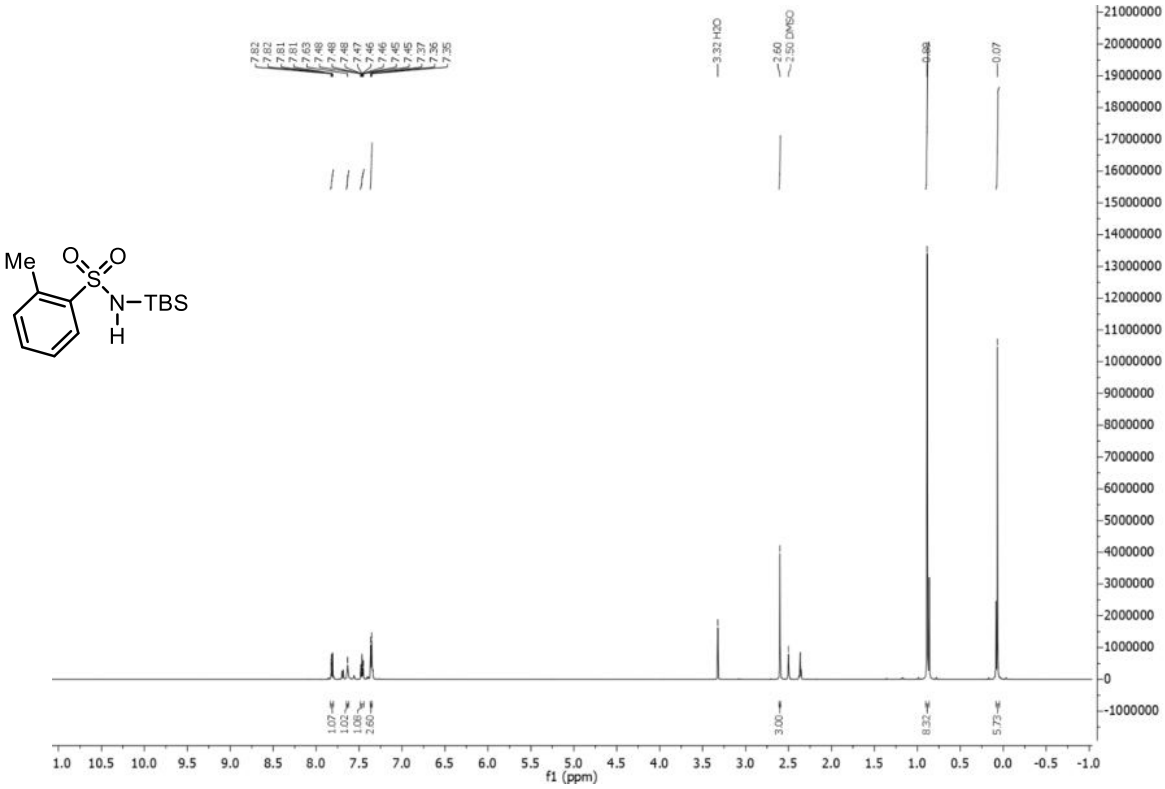
^{1}H NMR spectrum (DMSO-d_6, 600 MHz) of compound **1b**



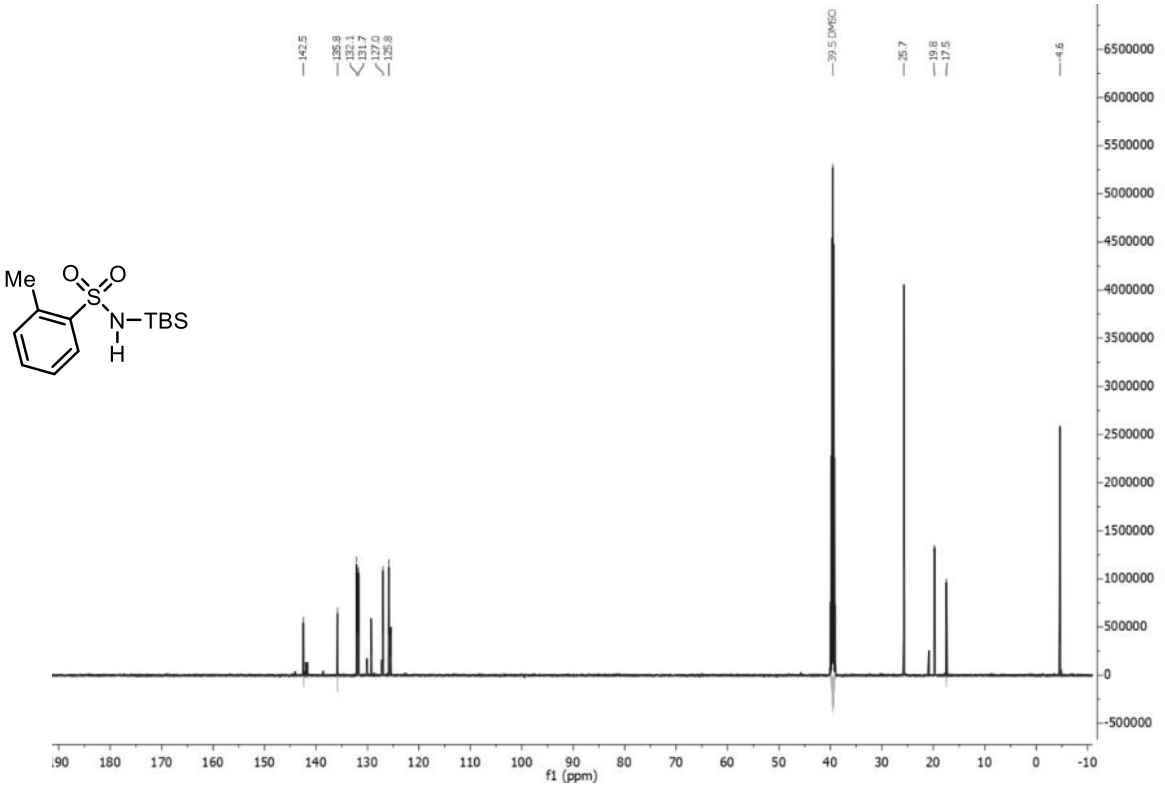
Stacked ^{13}C{^{1}H} DEPT NMR spectra (DMSO-d_6, 151 MHz) of compound **1b**



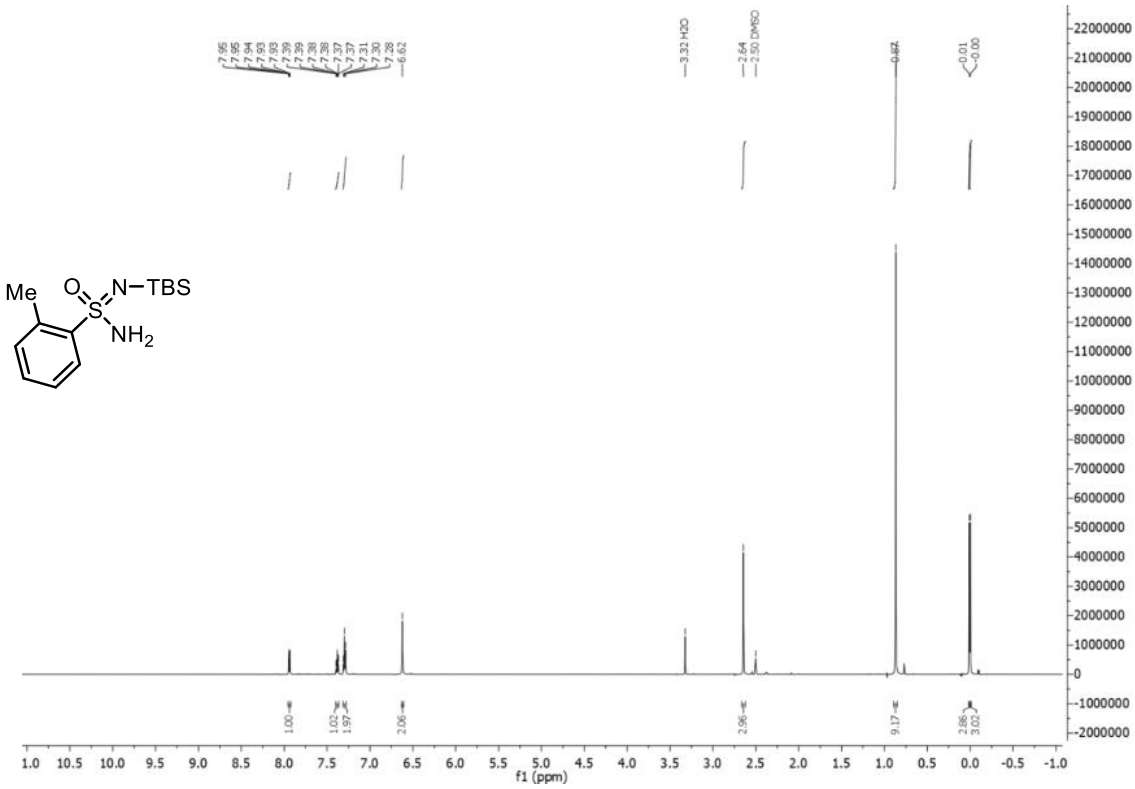
^{1}H NMR spectrum (DMSO-d_6, 600 MHz) of compound **1c-precursor**



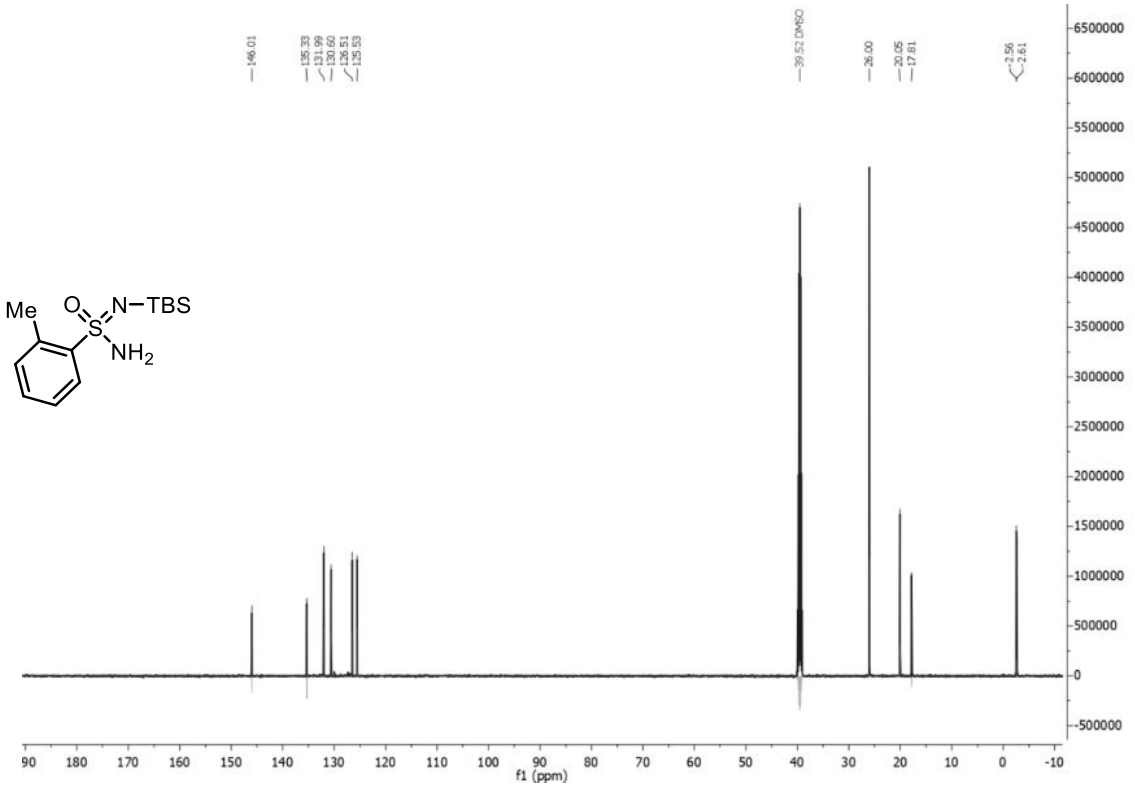
Stacked ^{13}C{^{1}H} DEPT NMR spectra (DMSO-d_6, 151 MHz) of compound **1c-precursor**



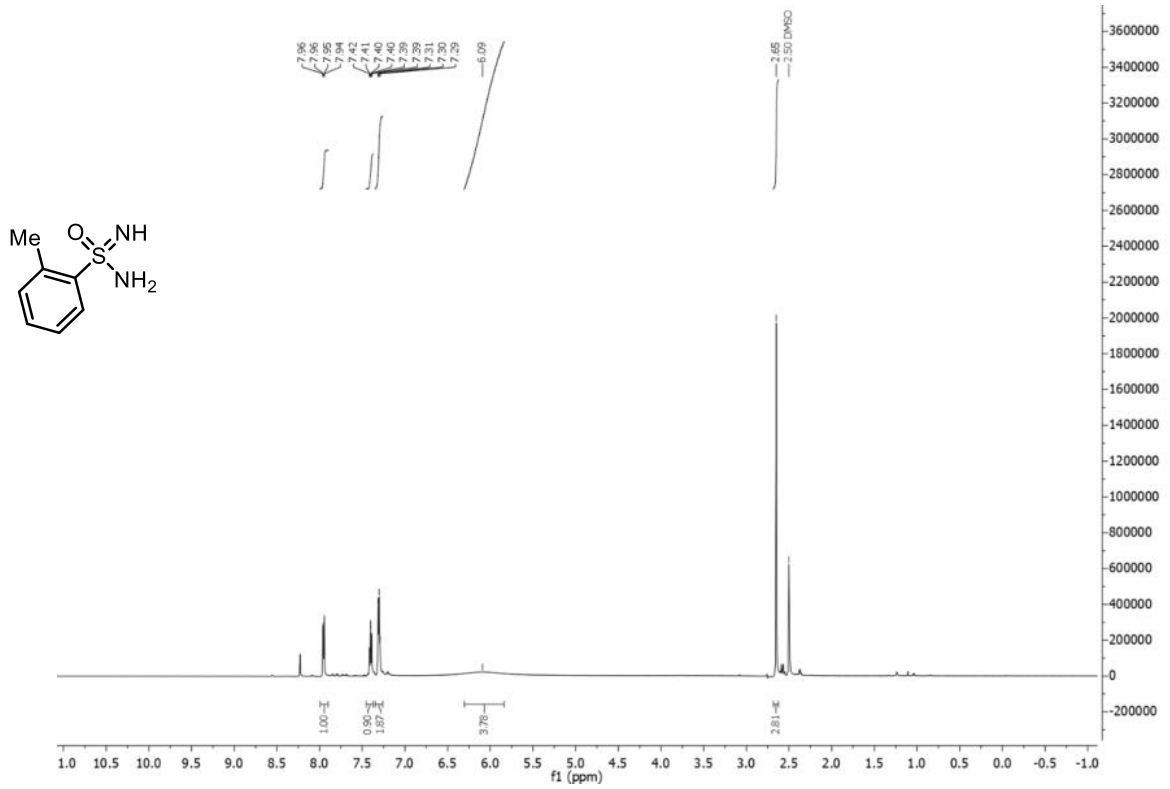
^{1}H NMR spectrum (DMSO-d_6, 600 MHz) of compound **6c**



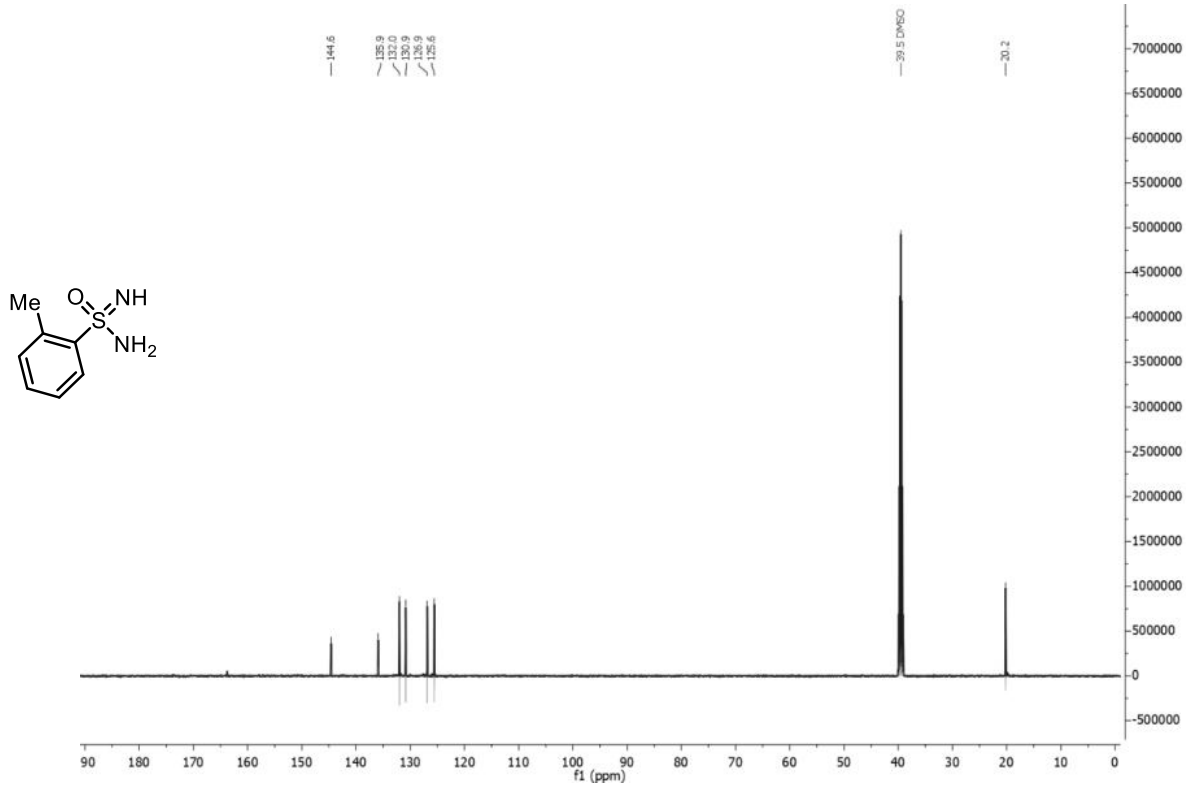
Stacked ^{13}C{^{1}H} DEPT NMR spectra (DMSO-d_6, 151 MHz) of compound **6c**



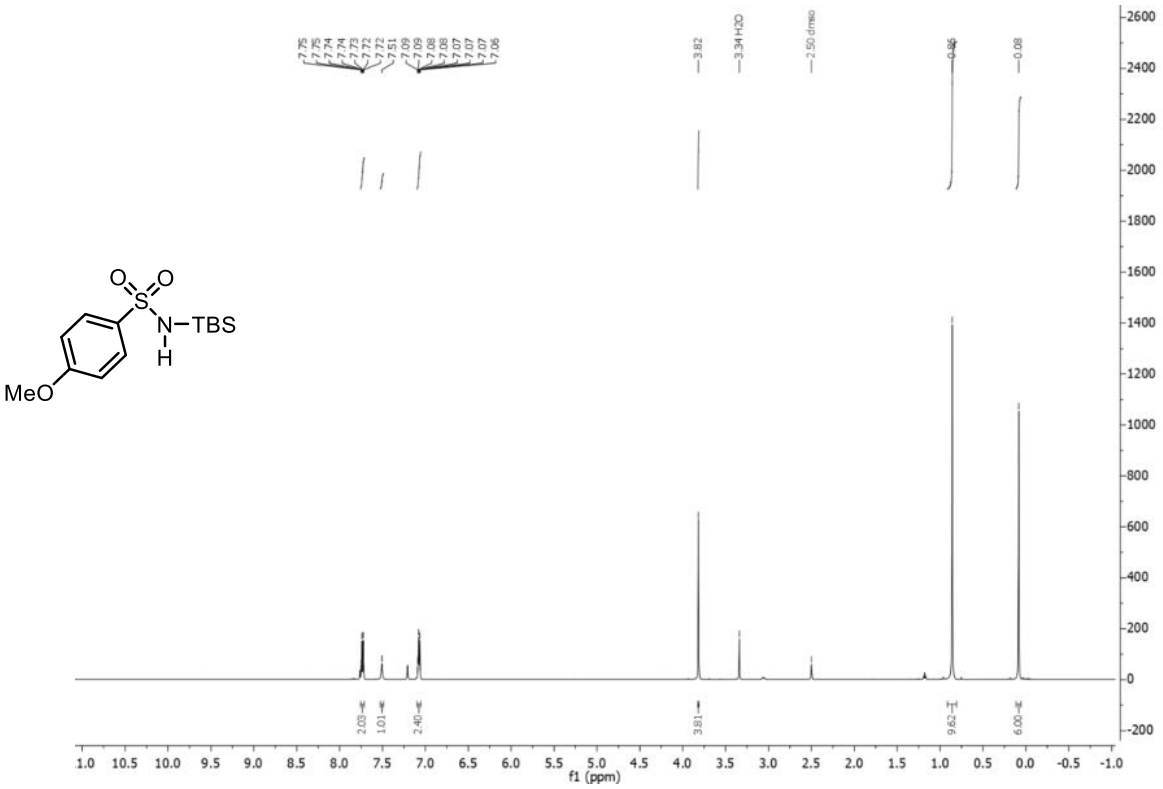
^{1}H NMR spectrum (DMSO-d_6, 600 MHz) of compound **1c**



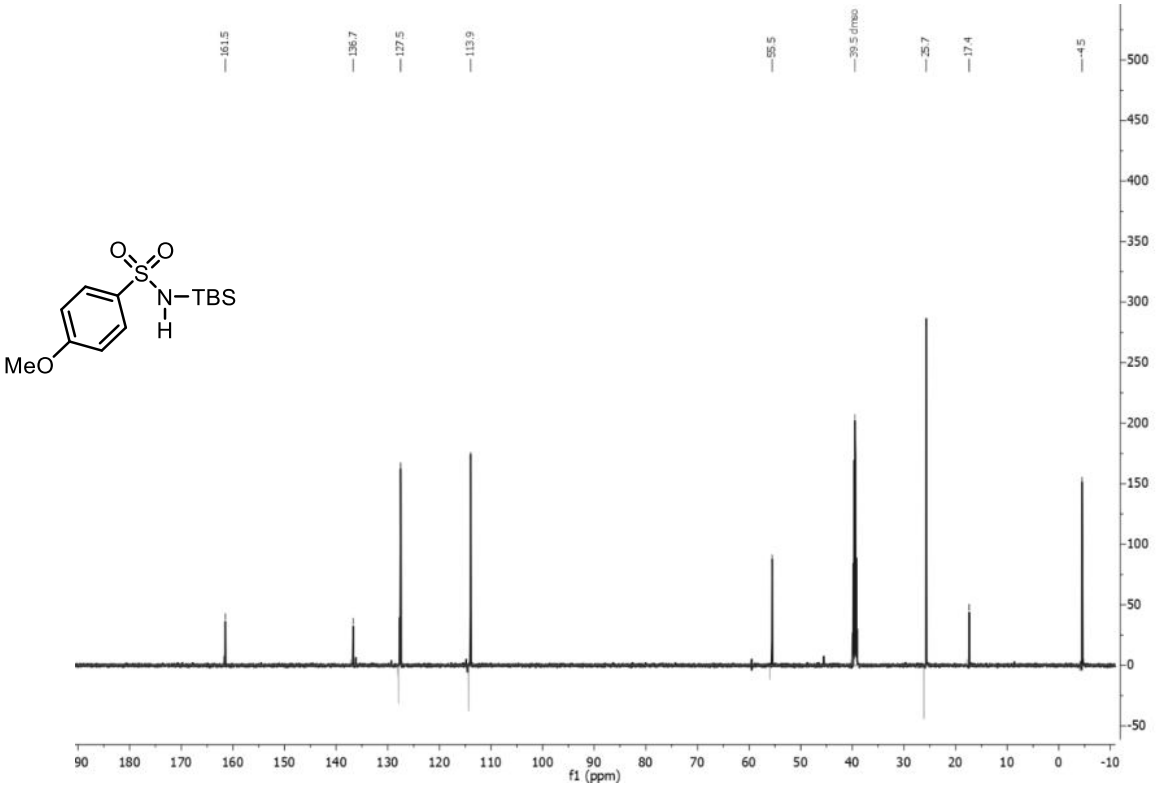
Stacked ^{13}C{^{1}H} DEPT NMR spectra (DMSO-d_6, 151 MHz) of compound **1c**



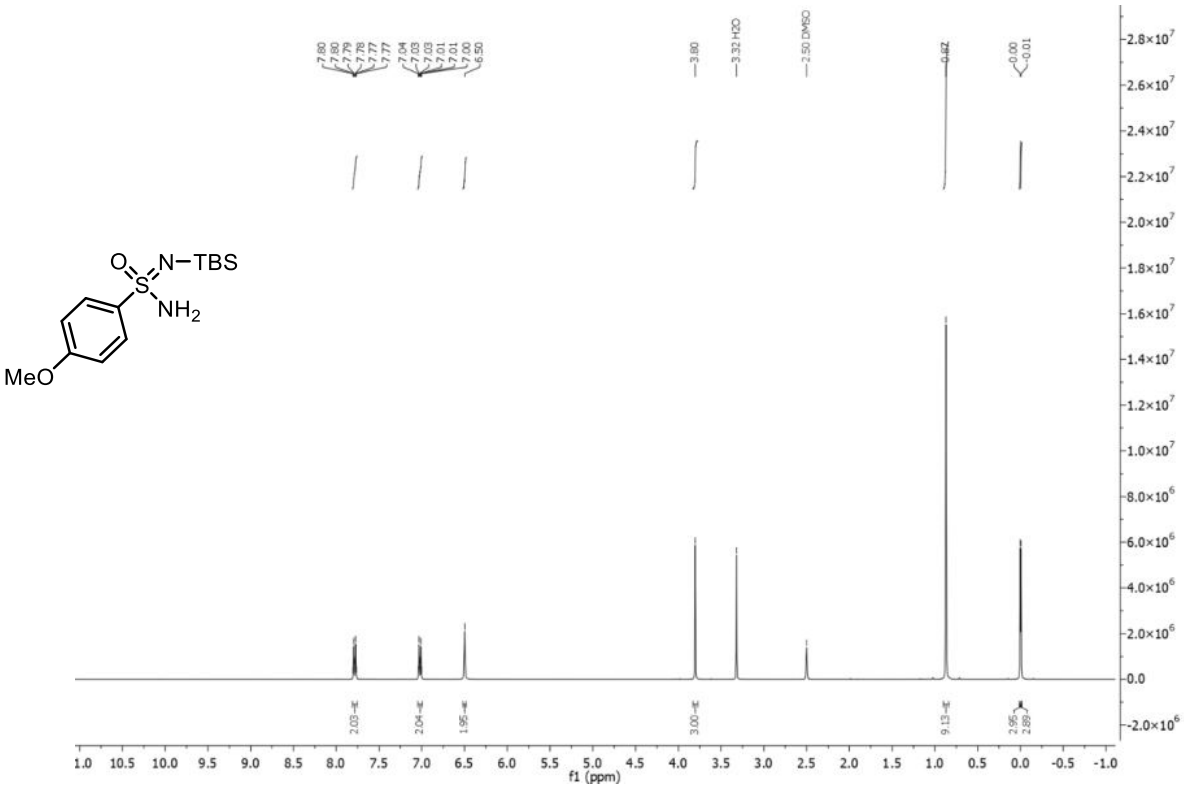
^{1}H NMR spectrum (DMSO-d_6, 600 MHz) of compound **1d-precursor**



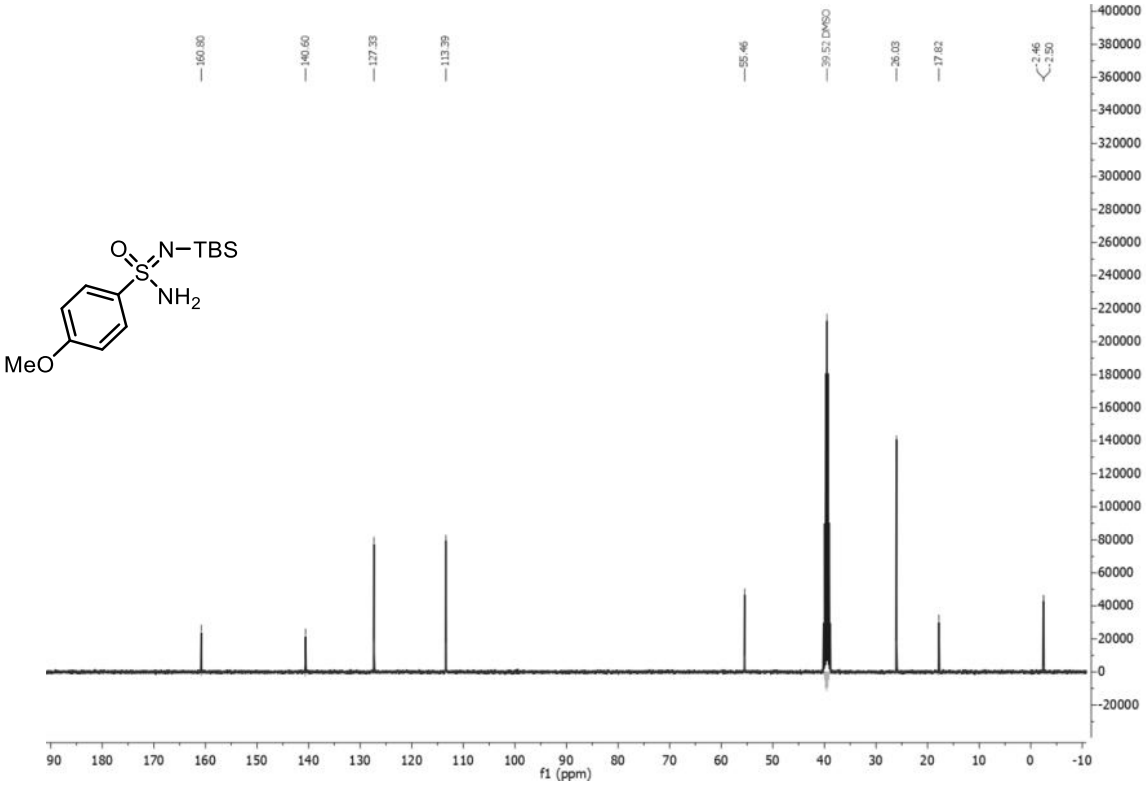
Stacked ^{13}C{^{1}H} DEPT NMR spectra (DMSO-d_6, 151 MHz) of compound **1d-precursor**



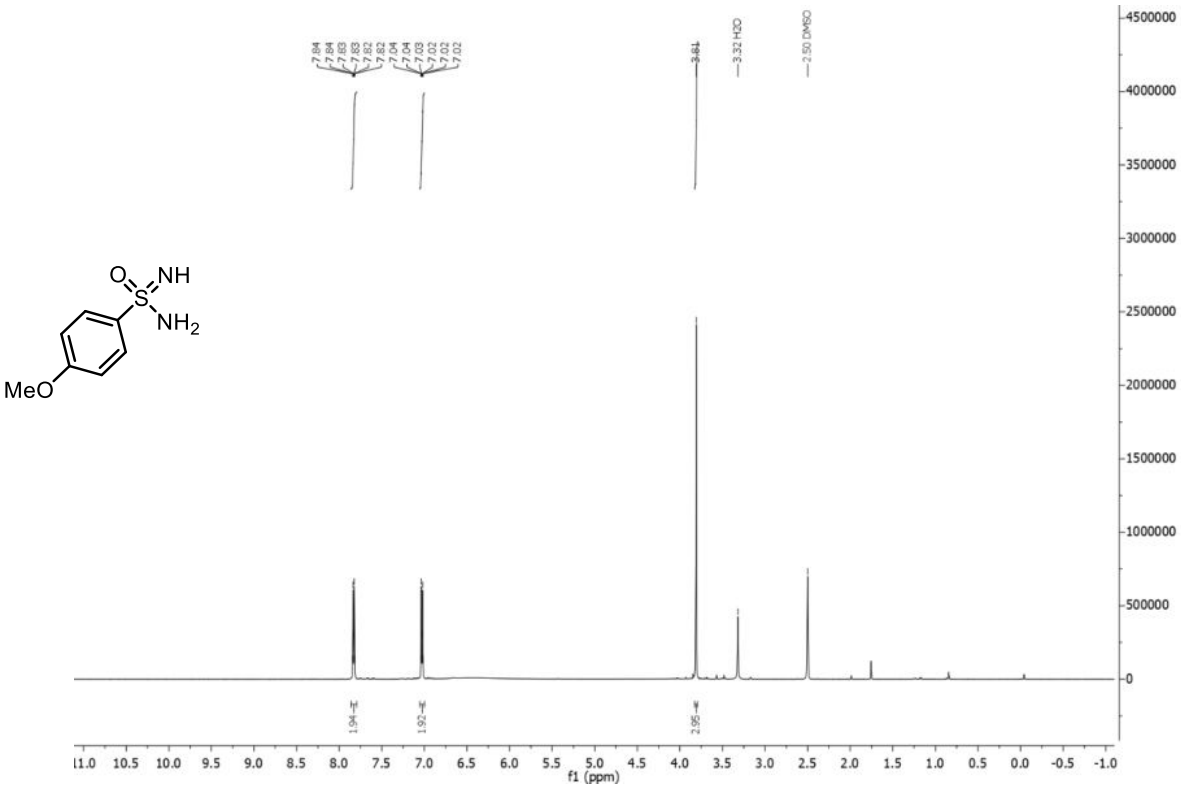
^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of compound **6d**



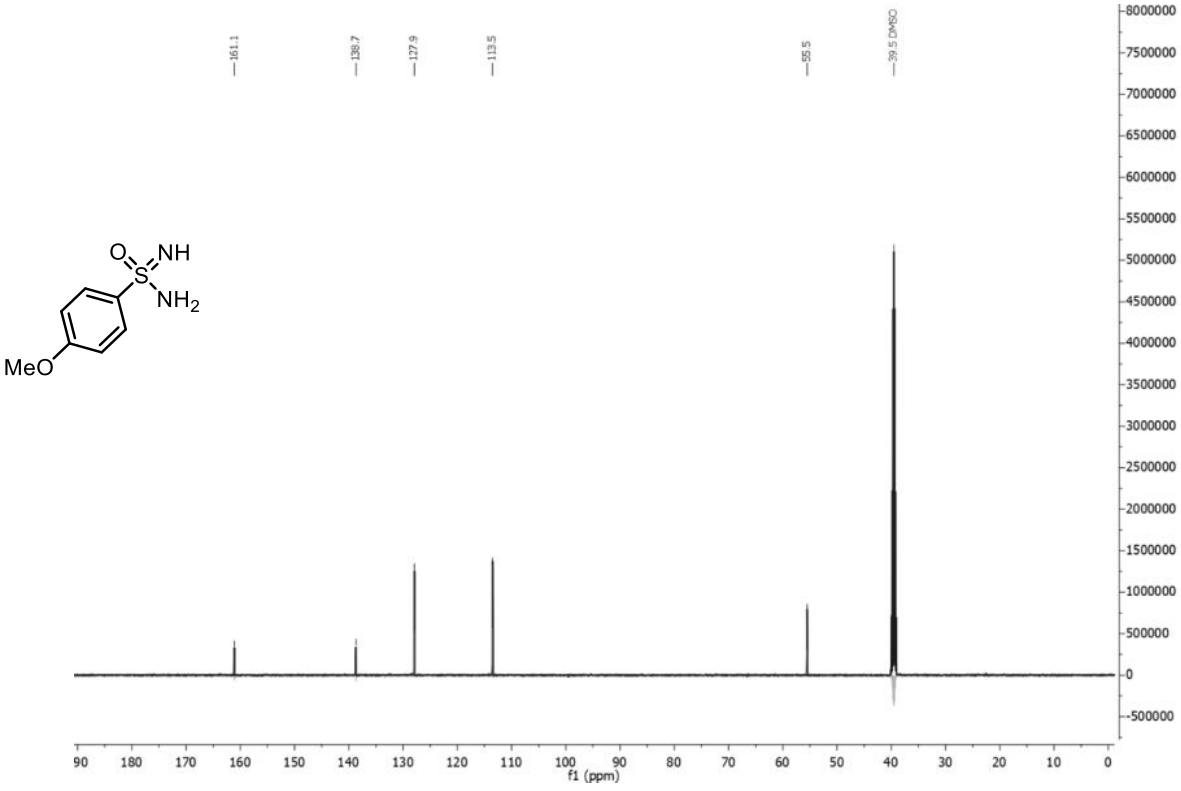
Stacked ^{13}C{^{1}H} DEPT NMR spectra (DMSO-d_6, 101 MHz) of compound **6d**



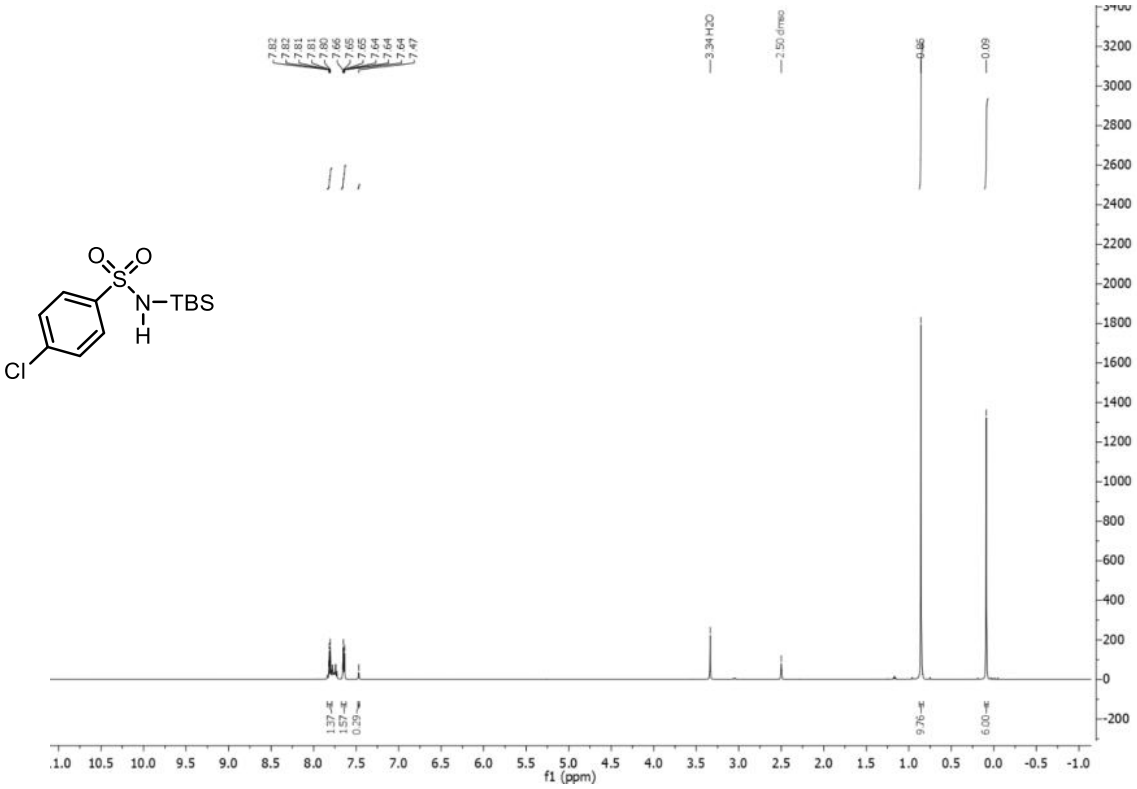
^{1}H NMR spectrum (DMSO-d_6, 600 MHz) of compound **1d**



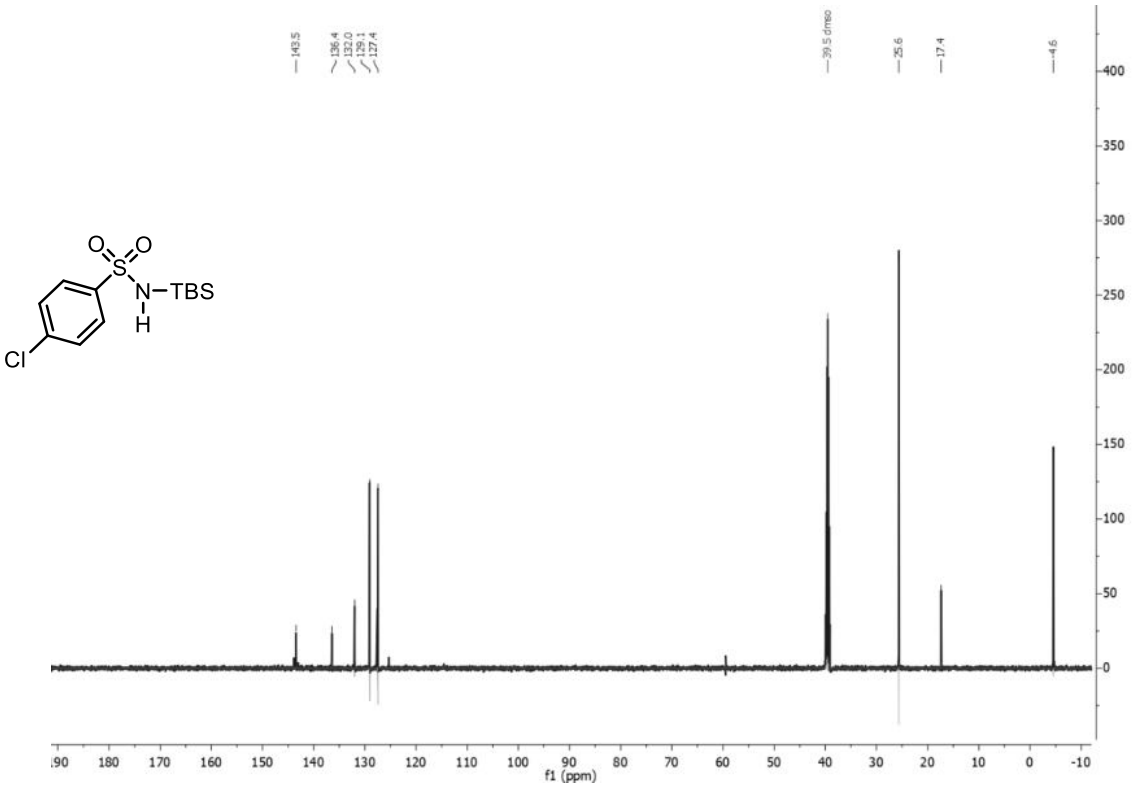
Stacked ^{13}C{^{1}H} DEPT NMR spectra (DMSO-d_6, 151 MHz) of compound **1d**



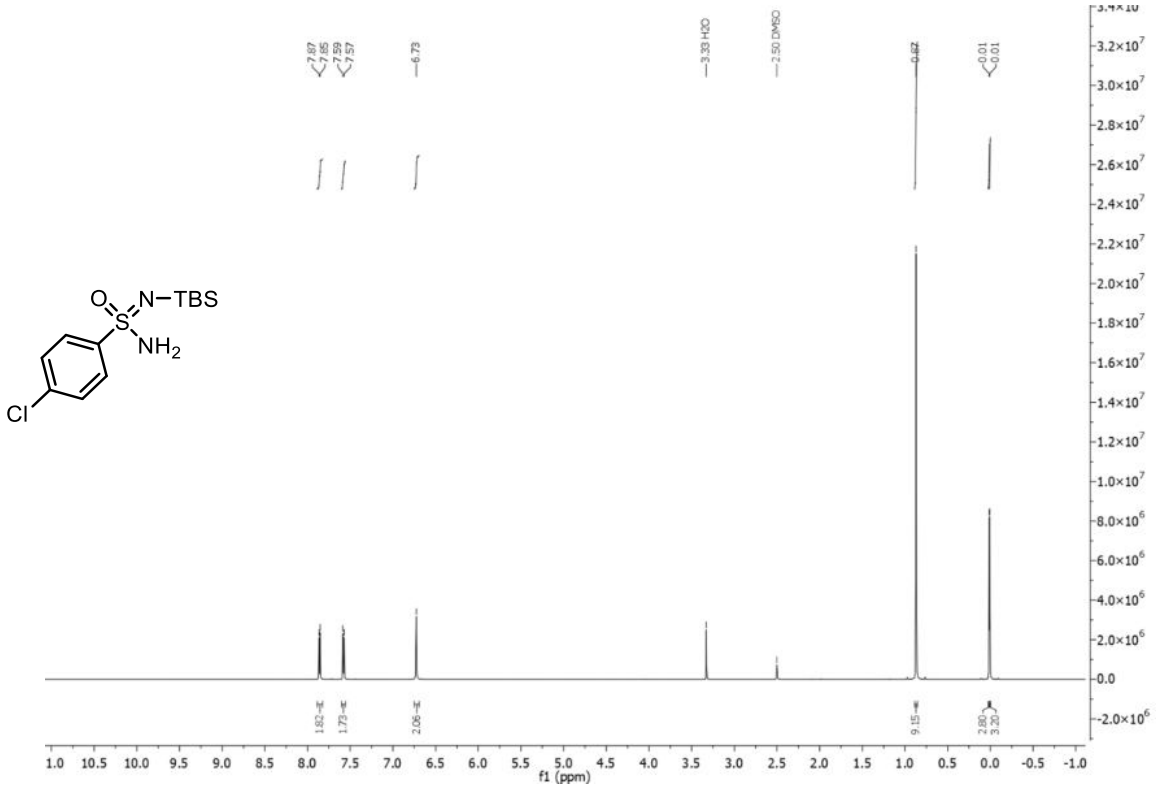
^{1}H NMR spectrum (DMSO-d_6, 600 MHz) of compound **1e-precursor**



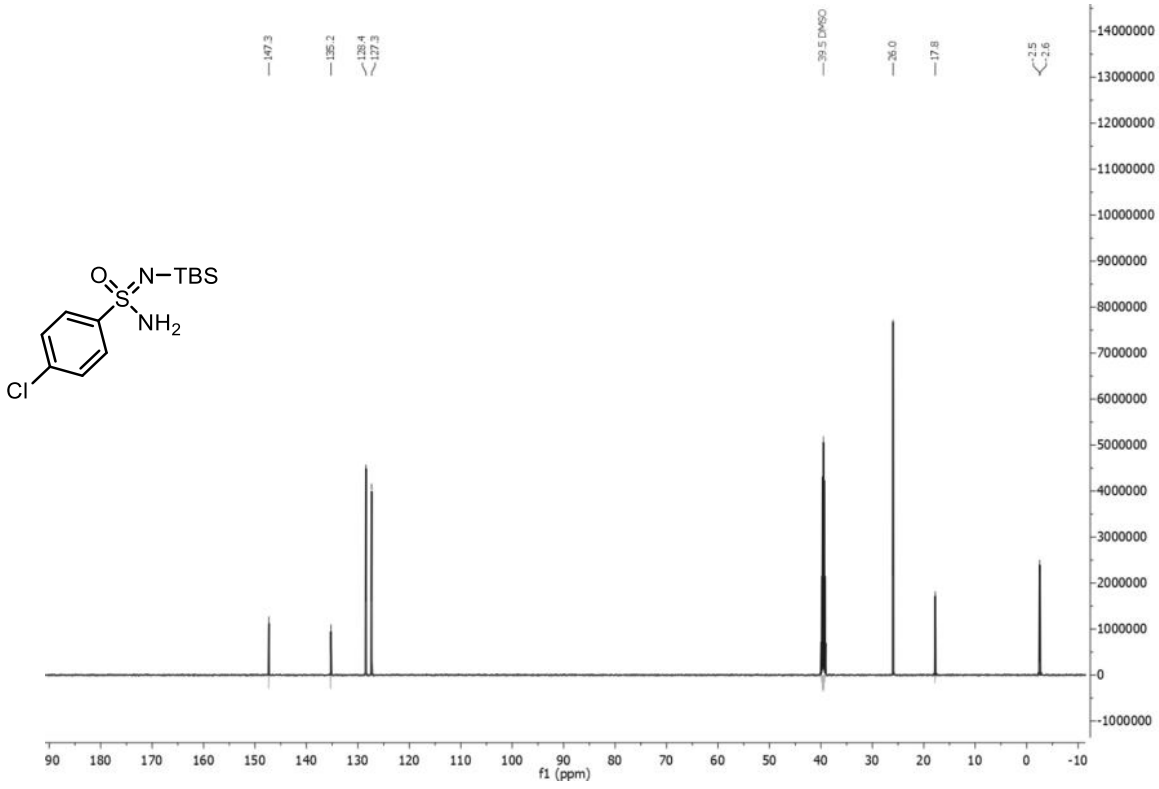
Stacked ^{13}C{^{1}H} DEPT NMR spectra (DMSO-d_6, 151 MHz) of compound **1e-precursor**



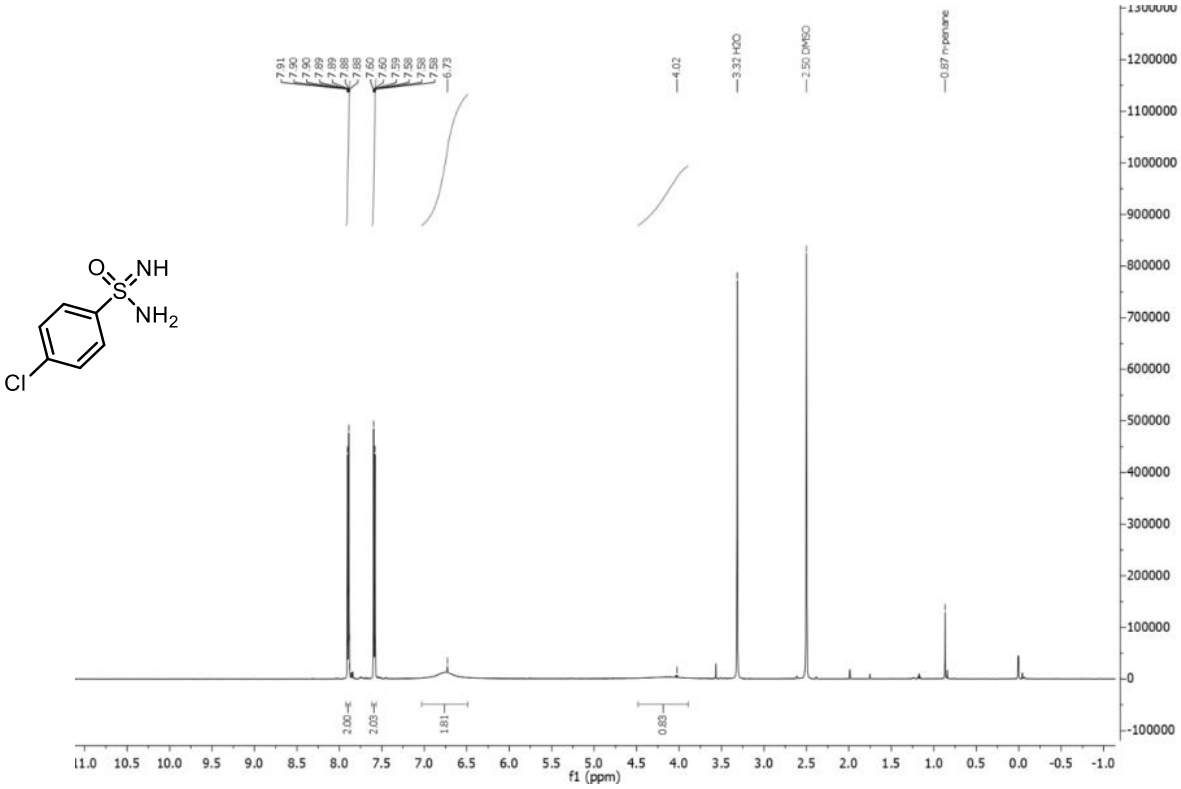
^{1}H NMR spectrum (DMSO-d_6, 600 MHz) of compound **6e**



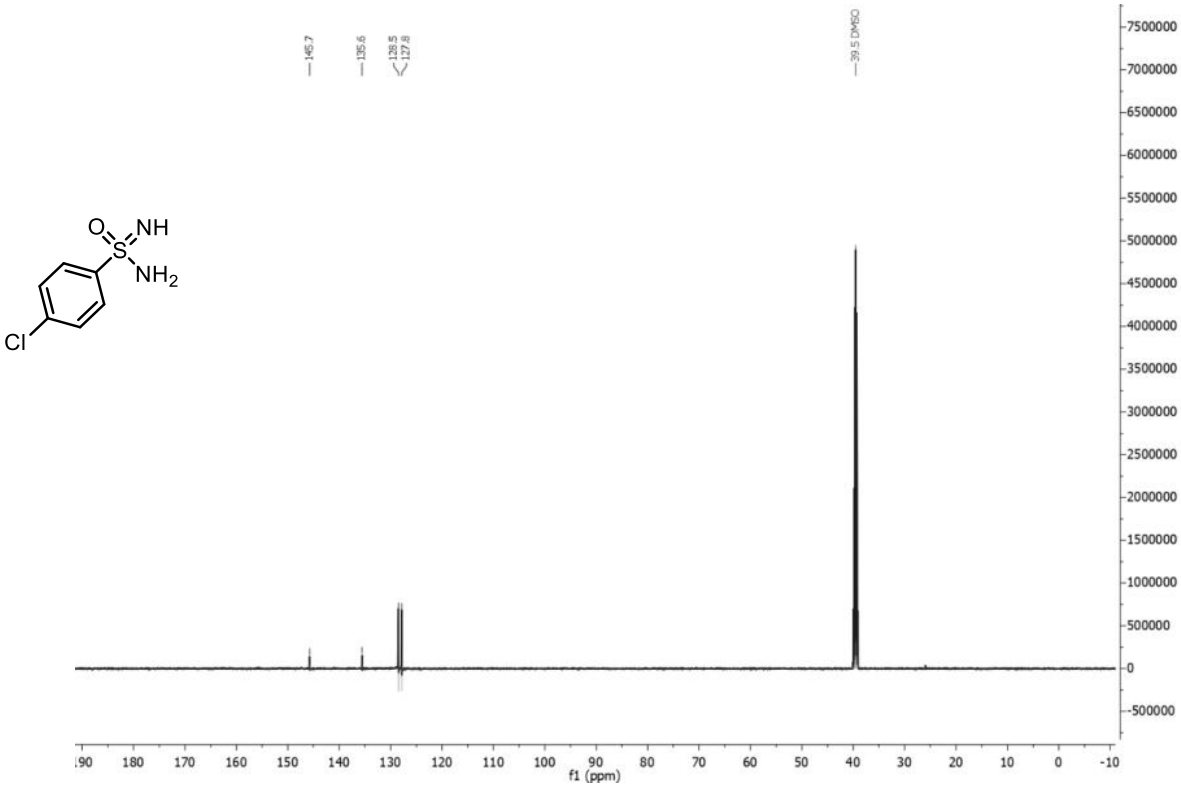
Stacked ^{13}C{^{1}H} DEPT NMR spectra (DMSO-d_6, 151 MHz) of compound **6e**



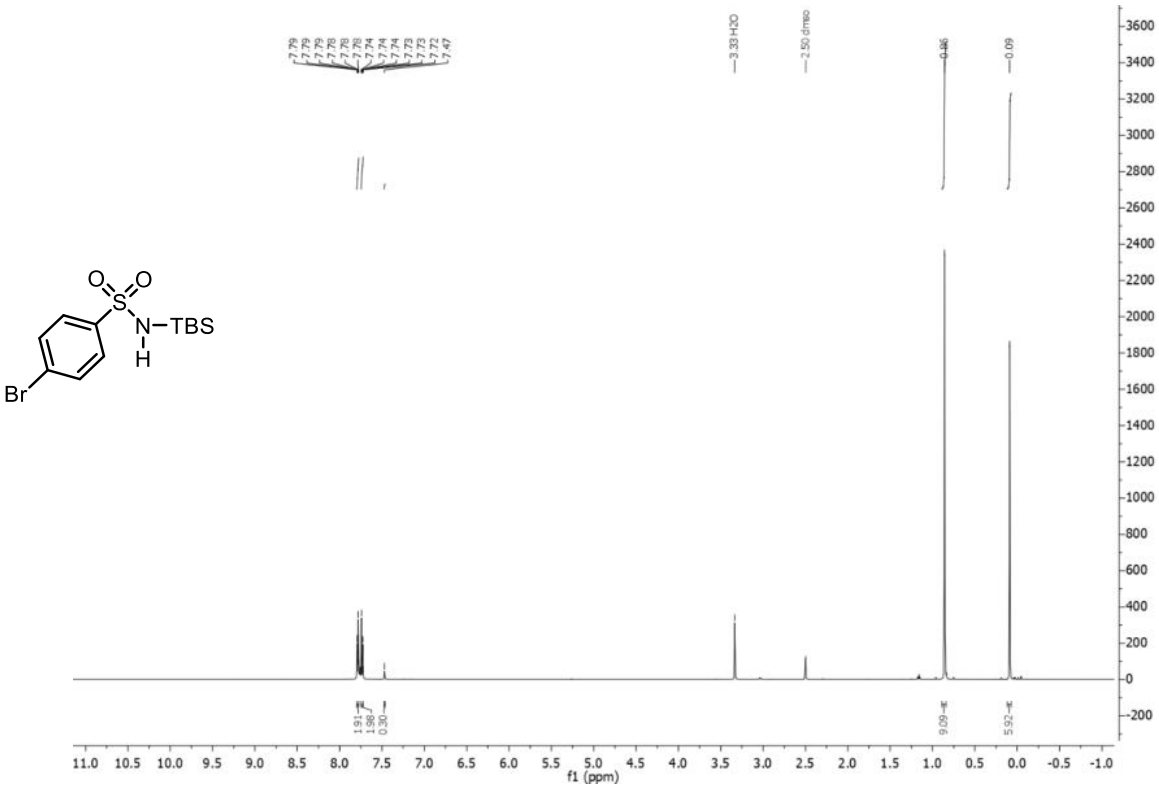
^{1}H NMR spectrum (DMSO-d_6, 600 MHz) of compound **1e**



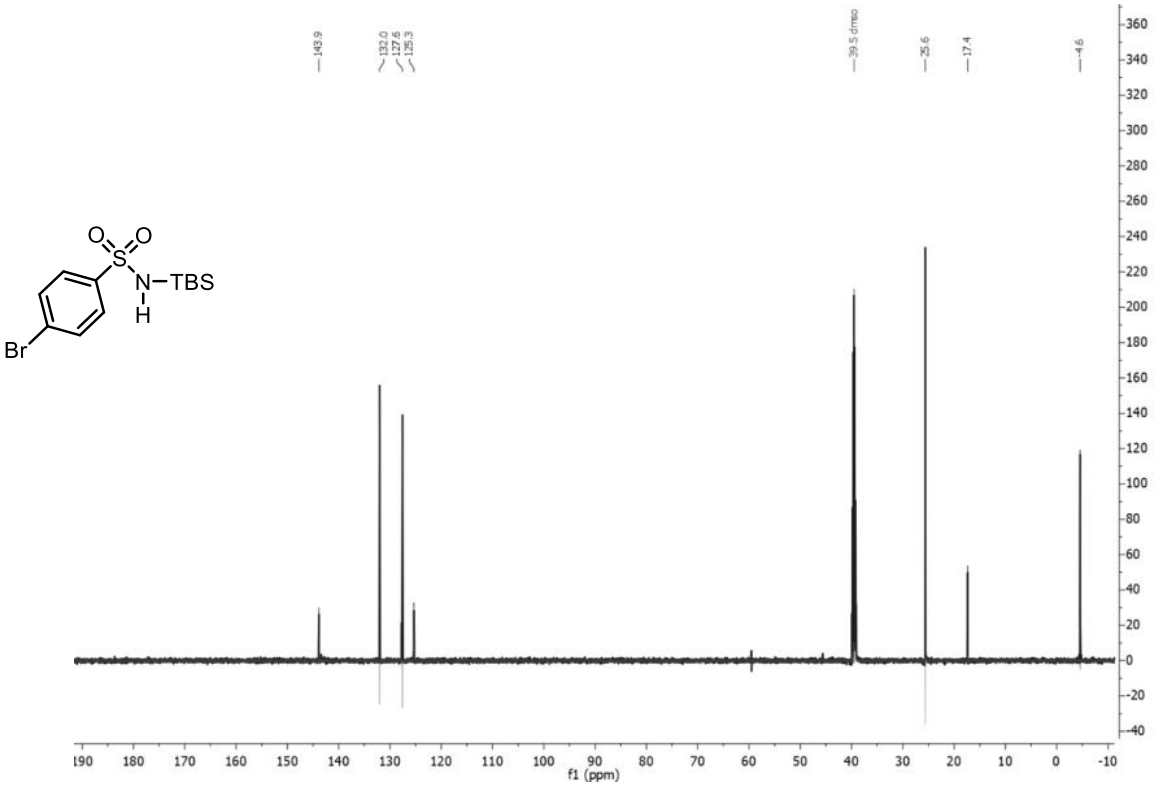
Stacked ^{13}C{^{1}H} DEPT NMR spectra (DMSO-d_6, 151 MHz) of compound **1e**



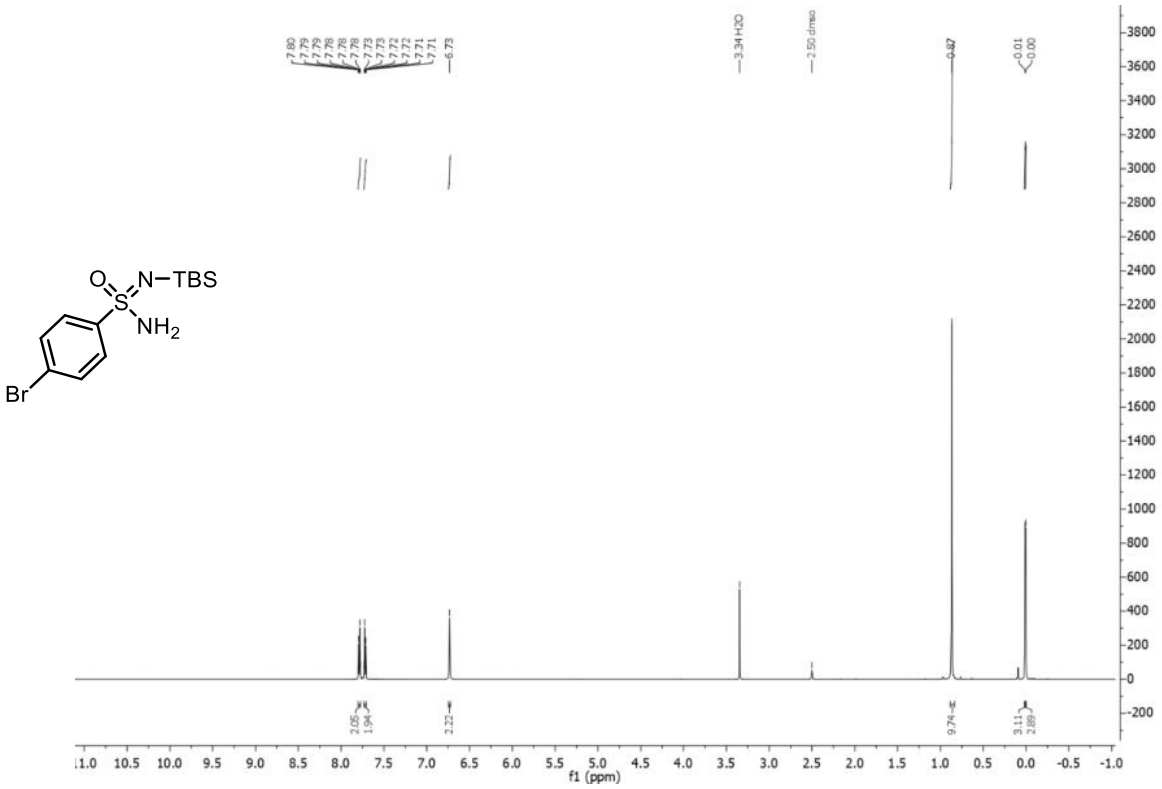
^{1}H NMR spectrum (DMSO-d_6, 600 MHz) of compound **1f-precursor**



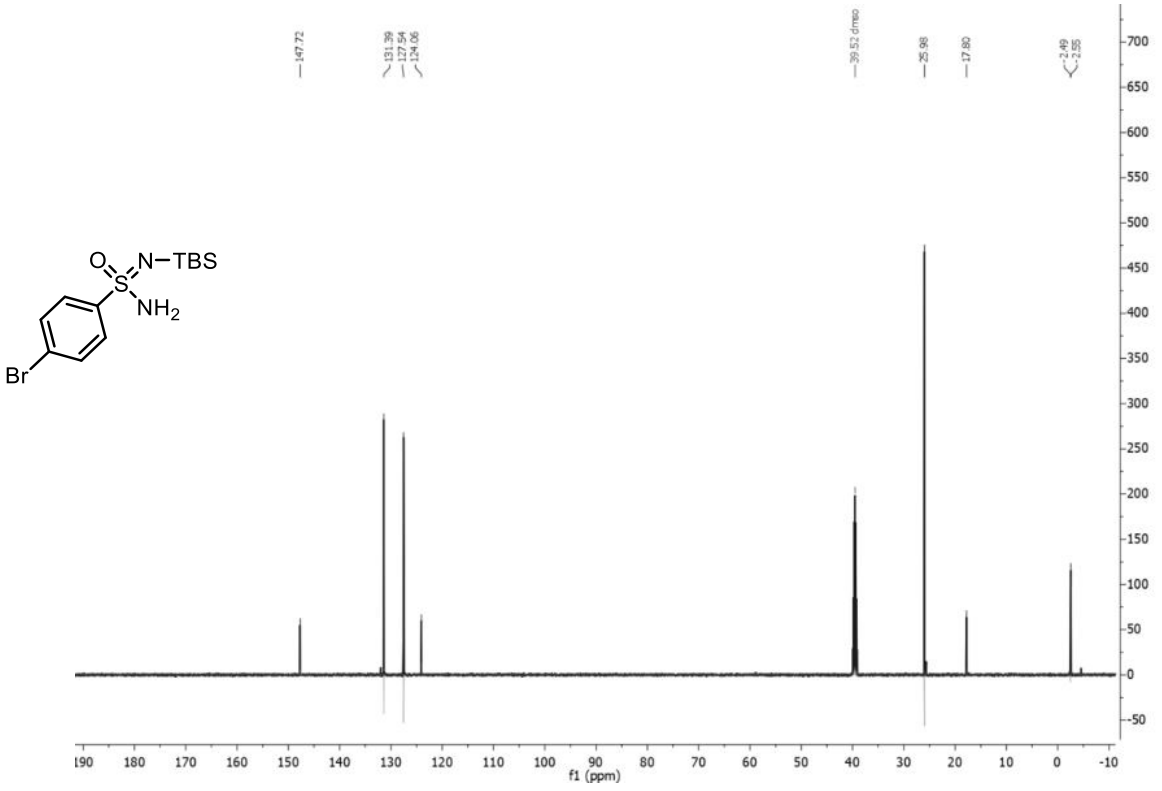
Stacked ^{13}C{^{1}H} DEPT NMR spectra (DMSO-d_6, 151 MHz) of compound **1f-precursor**



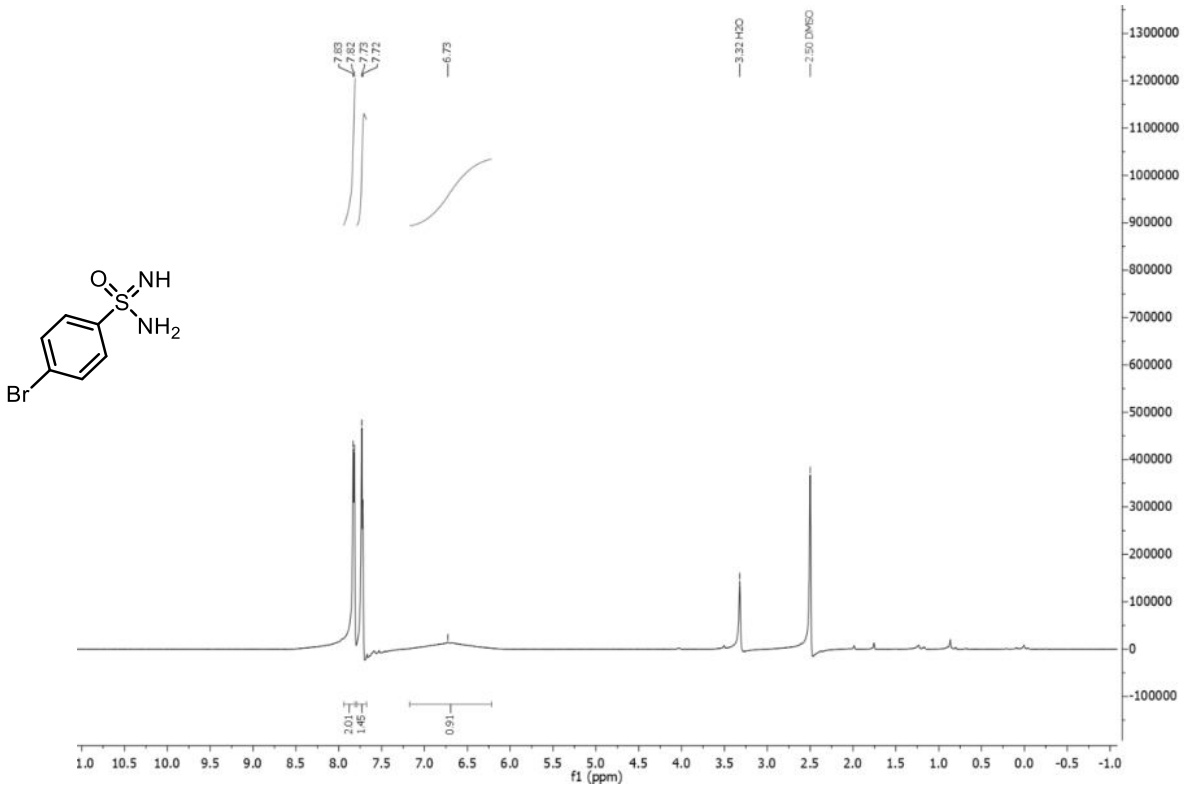
^{1}H NMR spectrum (DMSO-d_6, 600 MHz) of compound **6f**



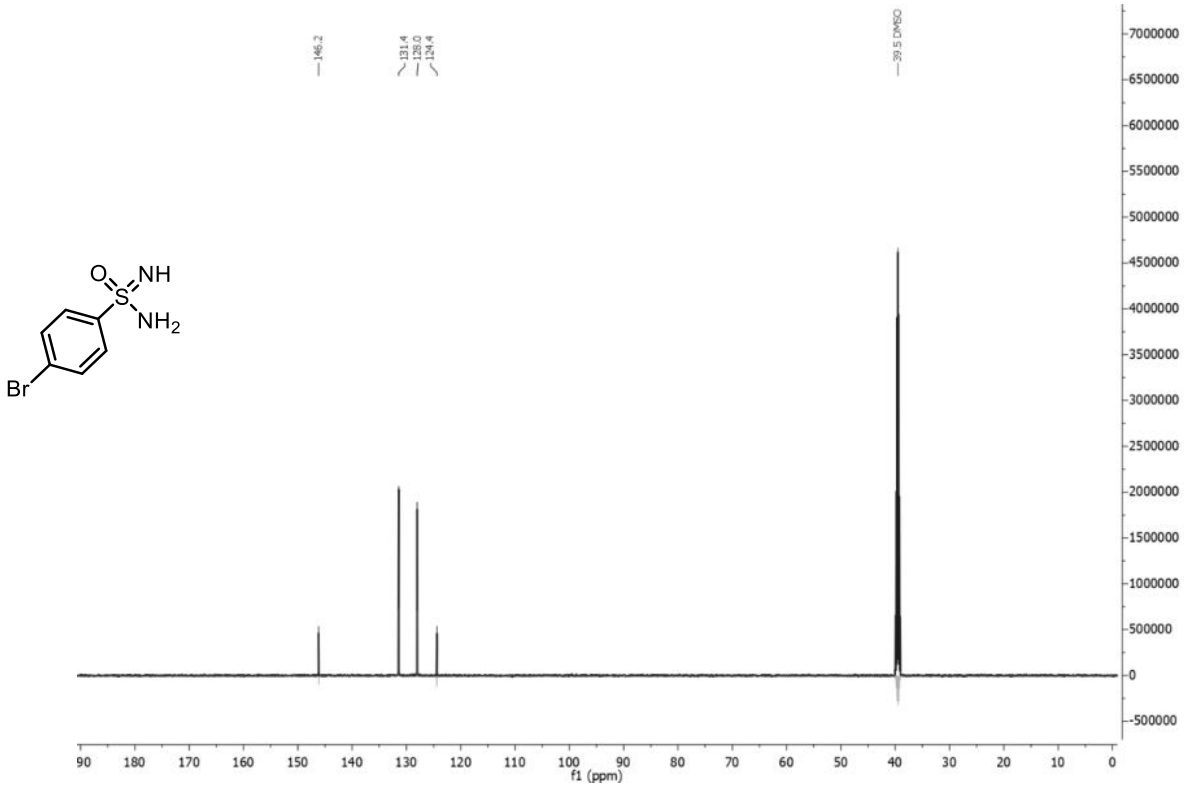
Stacked ^{13}C{^{1}H} DEPT NMR spectra (DMSO-d_6, 151 MHz) of compound **6f**



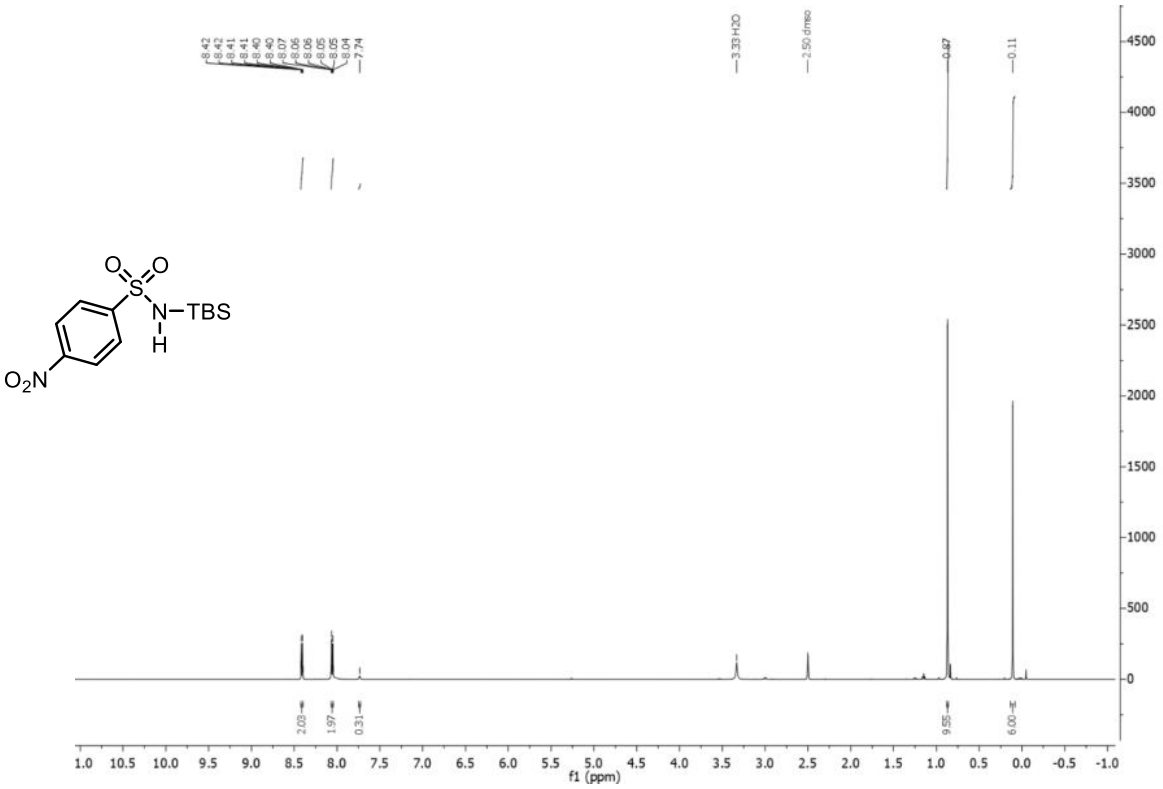
^{1}H NMR spectrum (DMSO-d_6, 600 MHz) of compound **1f**



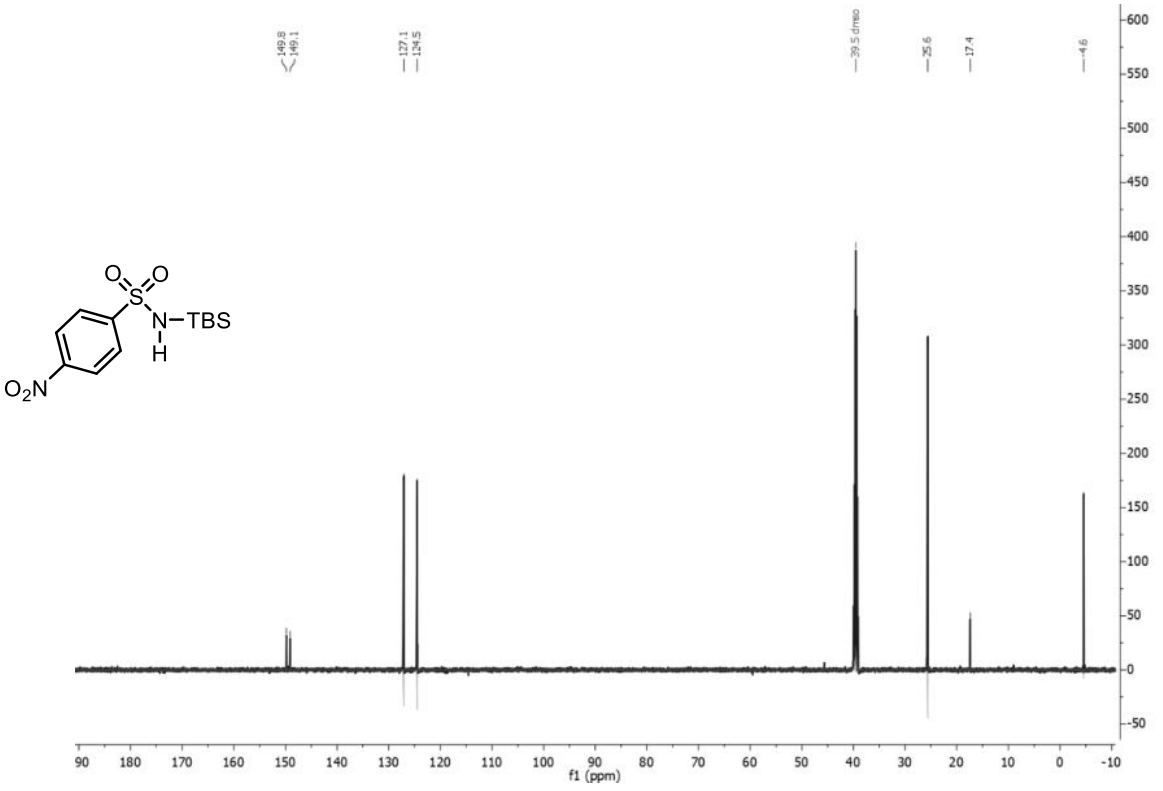
Stacked ^{13}C{^{1}H} DEPT NMR spectra (DMSO-d_6, 151 MHz) of compound **1f**



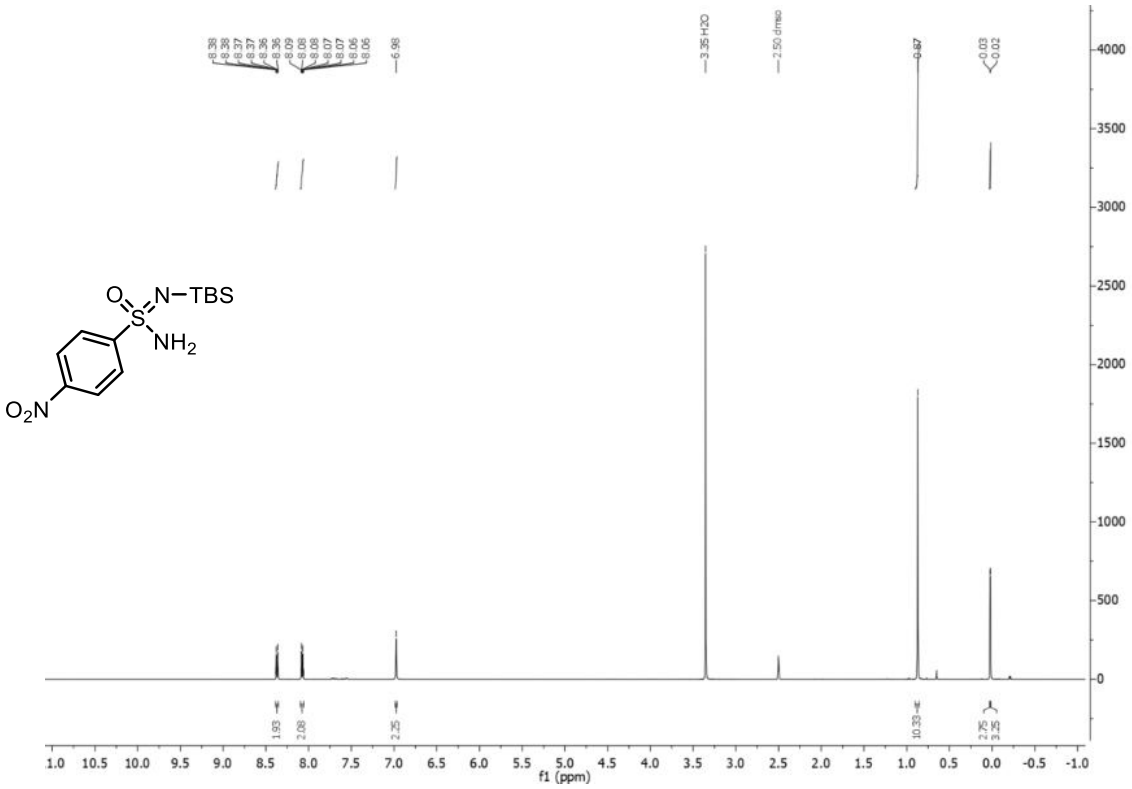
^{1}H NMR spectrum (DMSO-d_6, 600 MHz) of compound **1g-precursor**



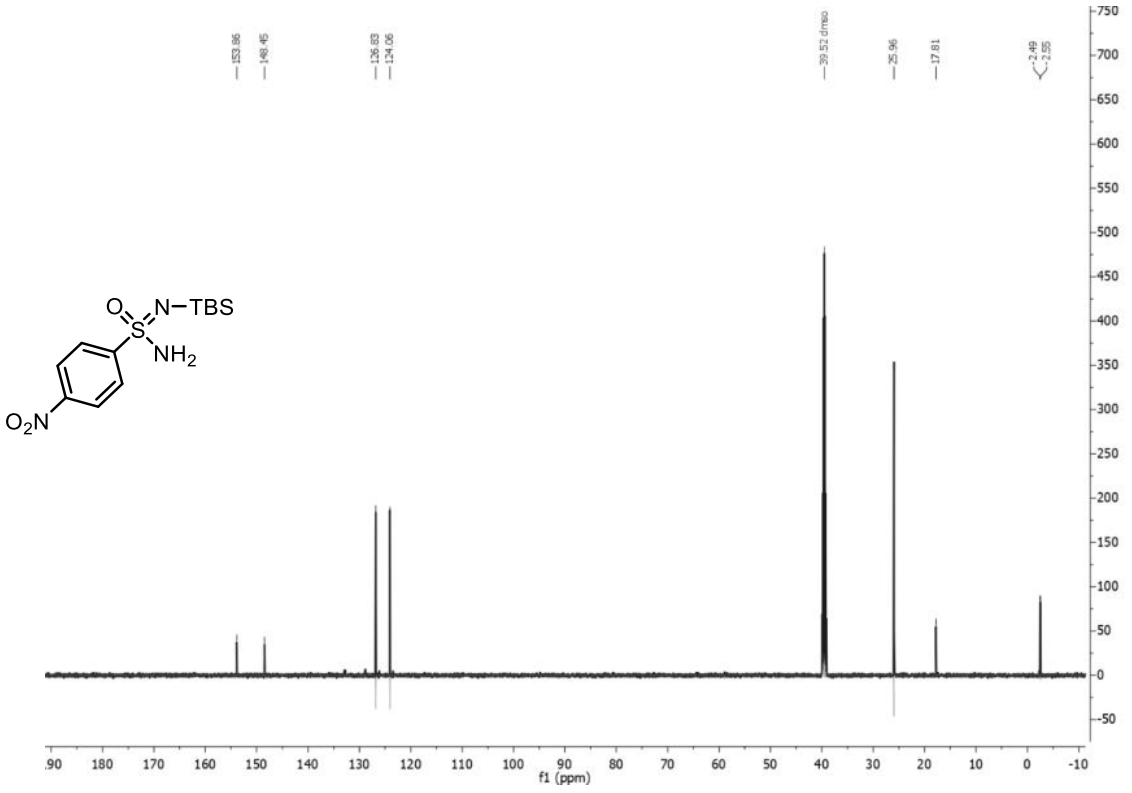
Stacked ^{13}C{^{1}H} DEPT NMR spectra (DMSO-d_6, 151 MHz) of compound **1g-precursor**



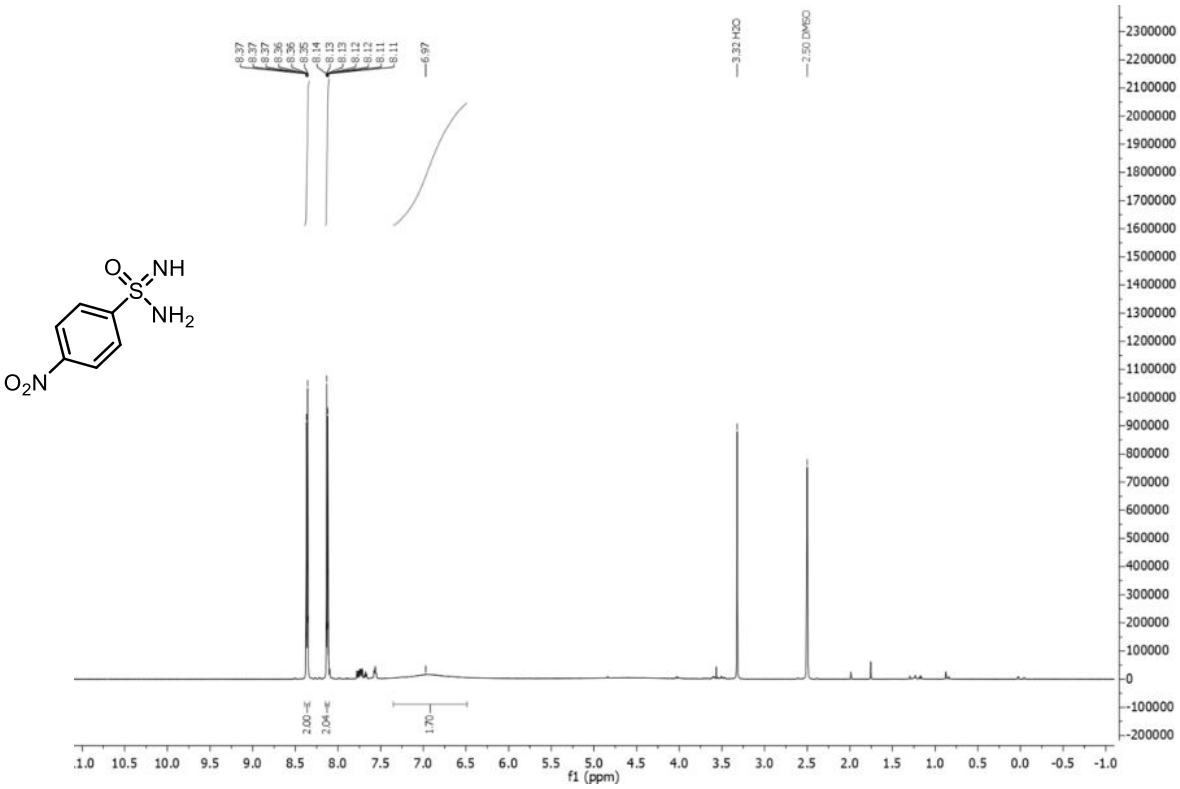
^{1}H NMR spectrum (DMSO-d_6, 600 MHz) of compound **6g**



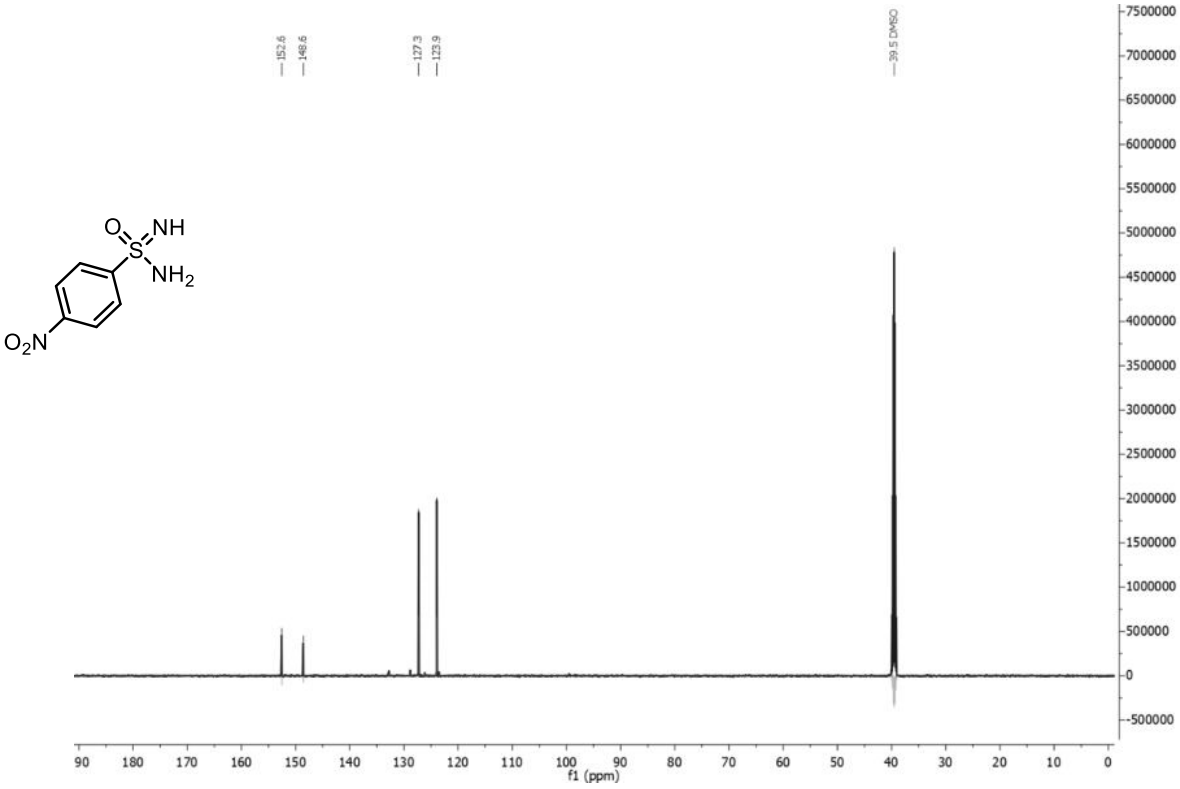
Stacked ^{13}C{^{1}H} DEPT NMR spectra (DMSO-d_6, 151 MHz) of compound **6g**



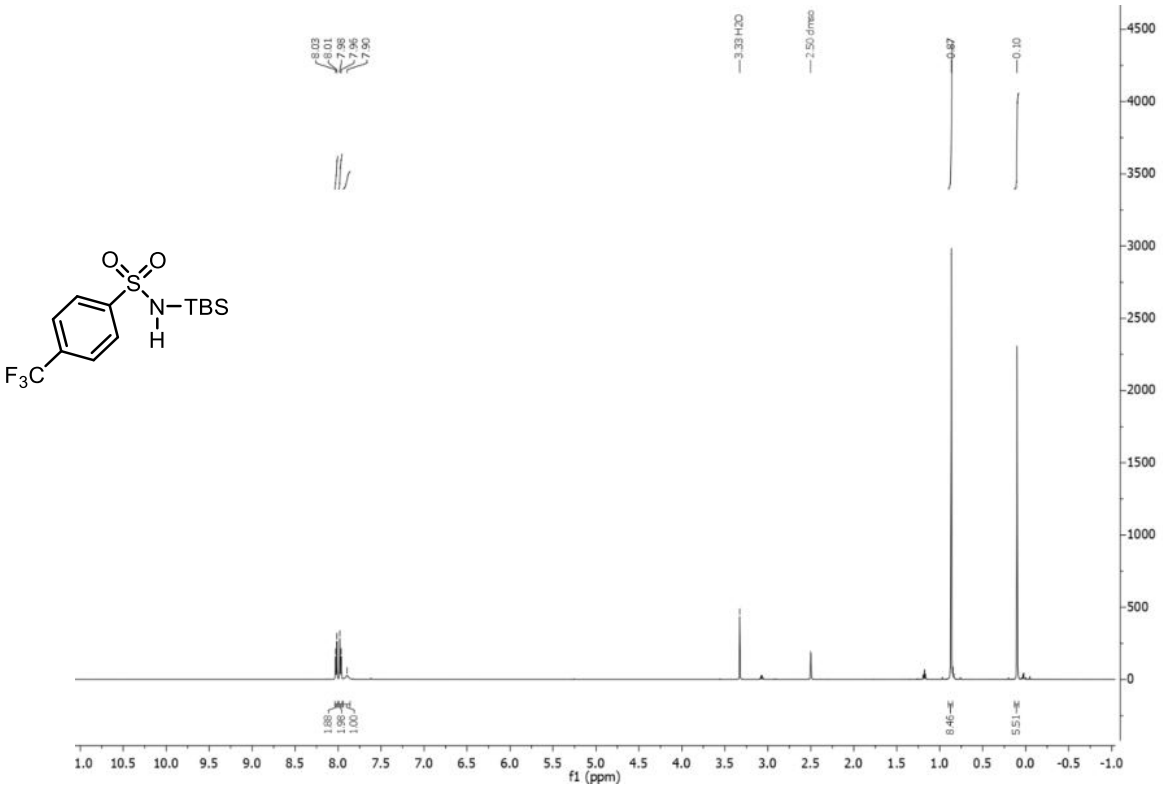
^{1}H NMR spectrum (DMSO-d_6, 600 MHz) of compound **1g**



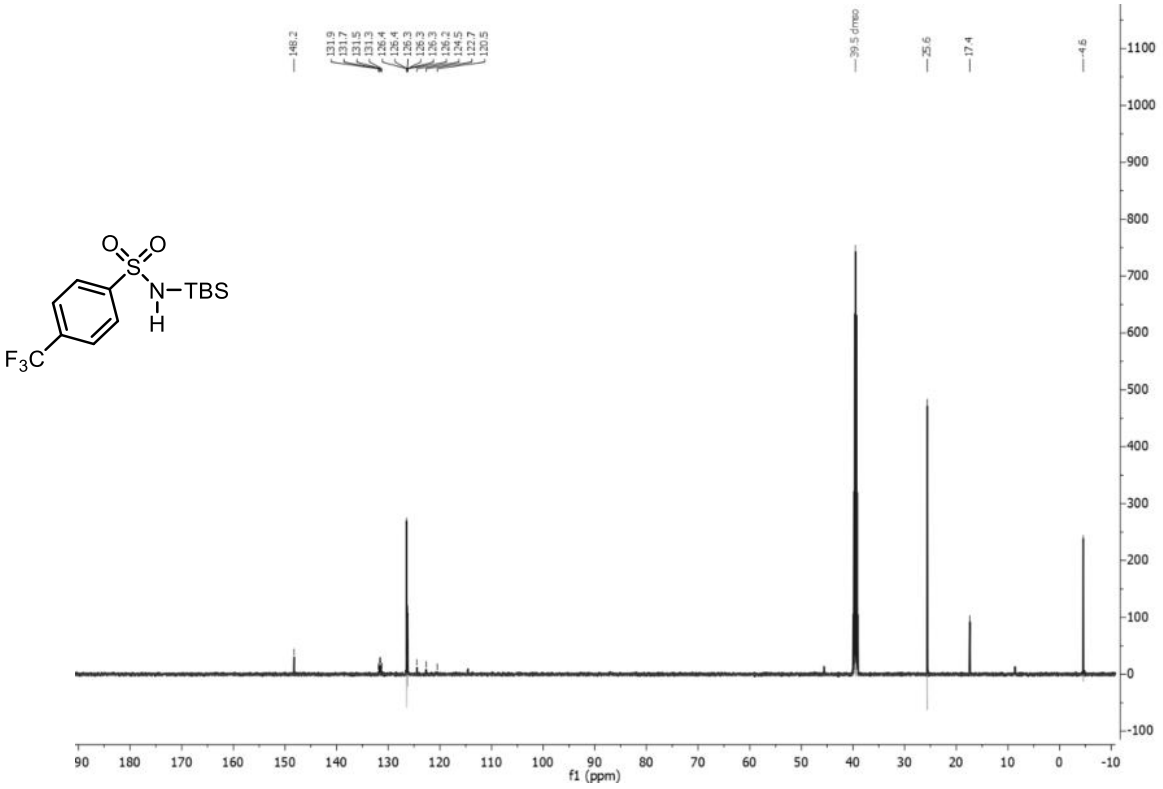
Stacked ^{13}C{^{1}H} DEPT NMR spectra (DMSO-d_6, 151 MHz) of compound **1g**



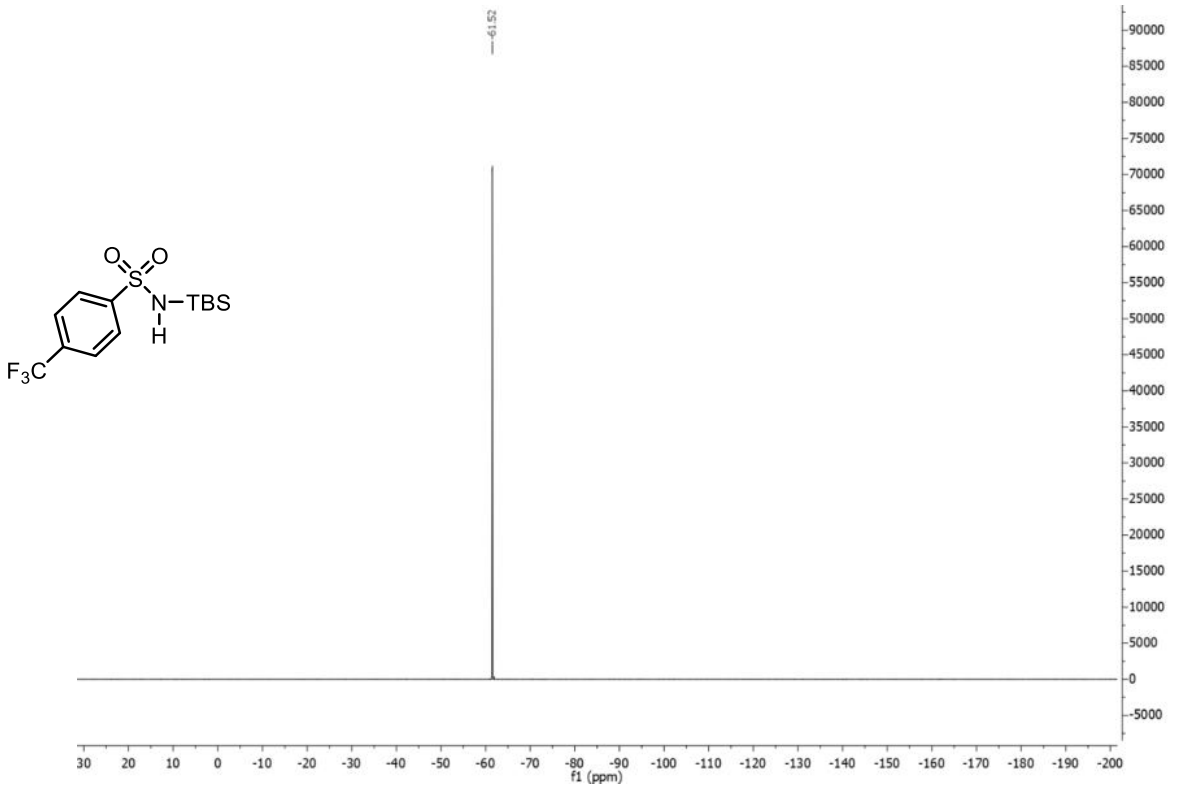
^{1}H NMR spectrum (DMSO-d_6, 600 MHz) of compound **1h-precursor**



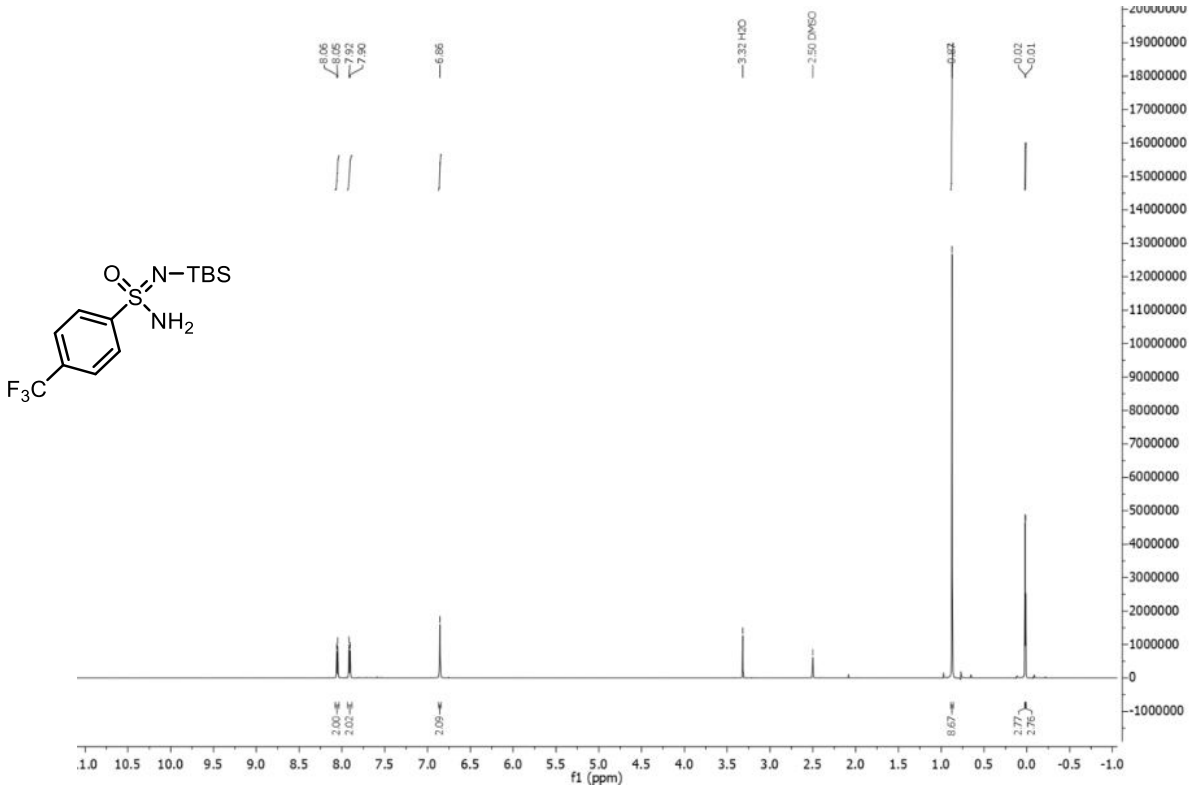
Stacked ^{13}C{^{1}H} DEPT NMR spectra (DMSO-d_6, 151 MHz) of compound **1h-precursor**



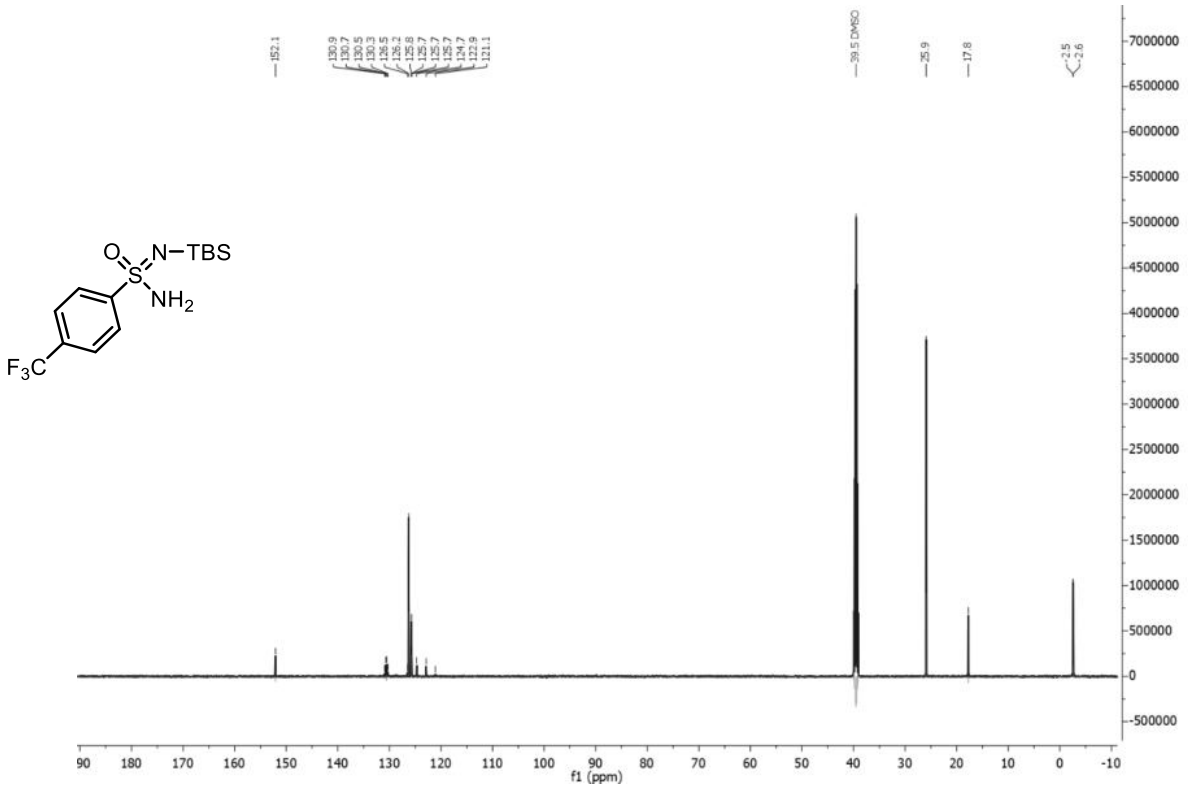
^{19}F NMR spectrum (DMSO-d_6, 564 MHz) of compound **1h-precursor**



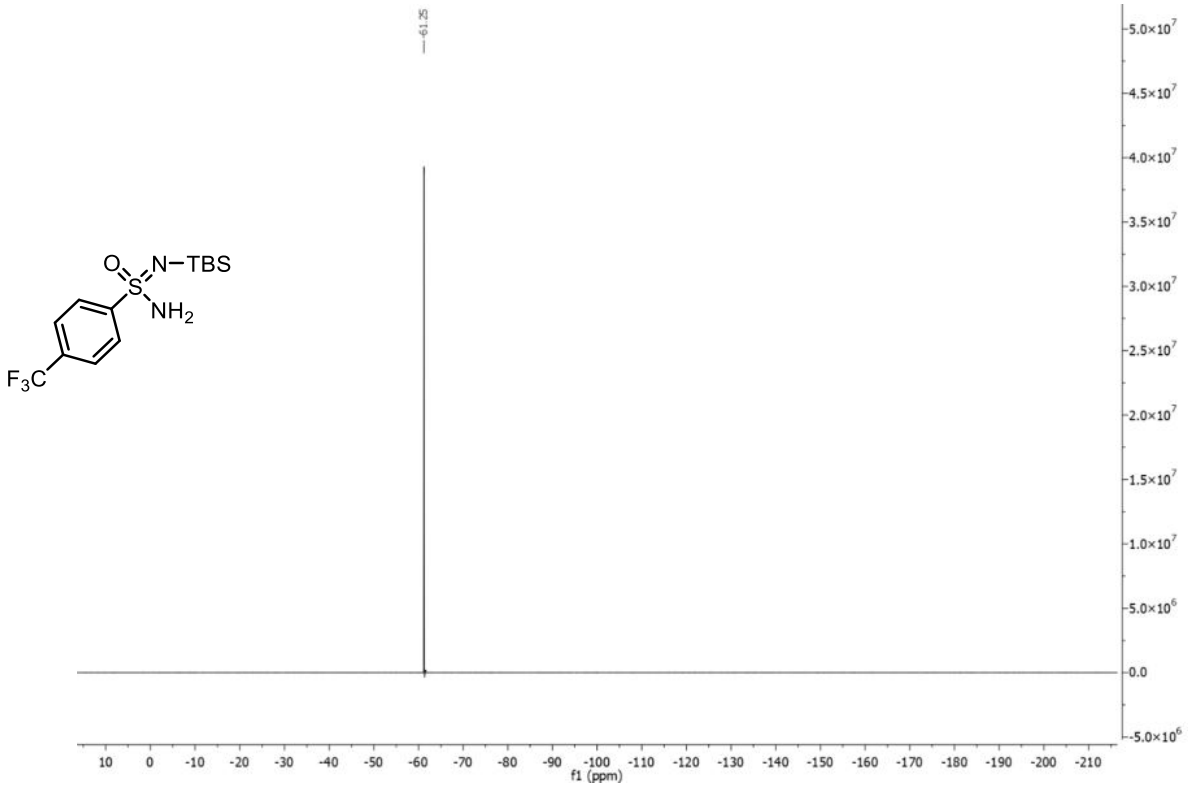
^{1}H NMR spectrum (DMSO-d_6, 600 MHz) of compound **6h**



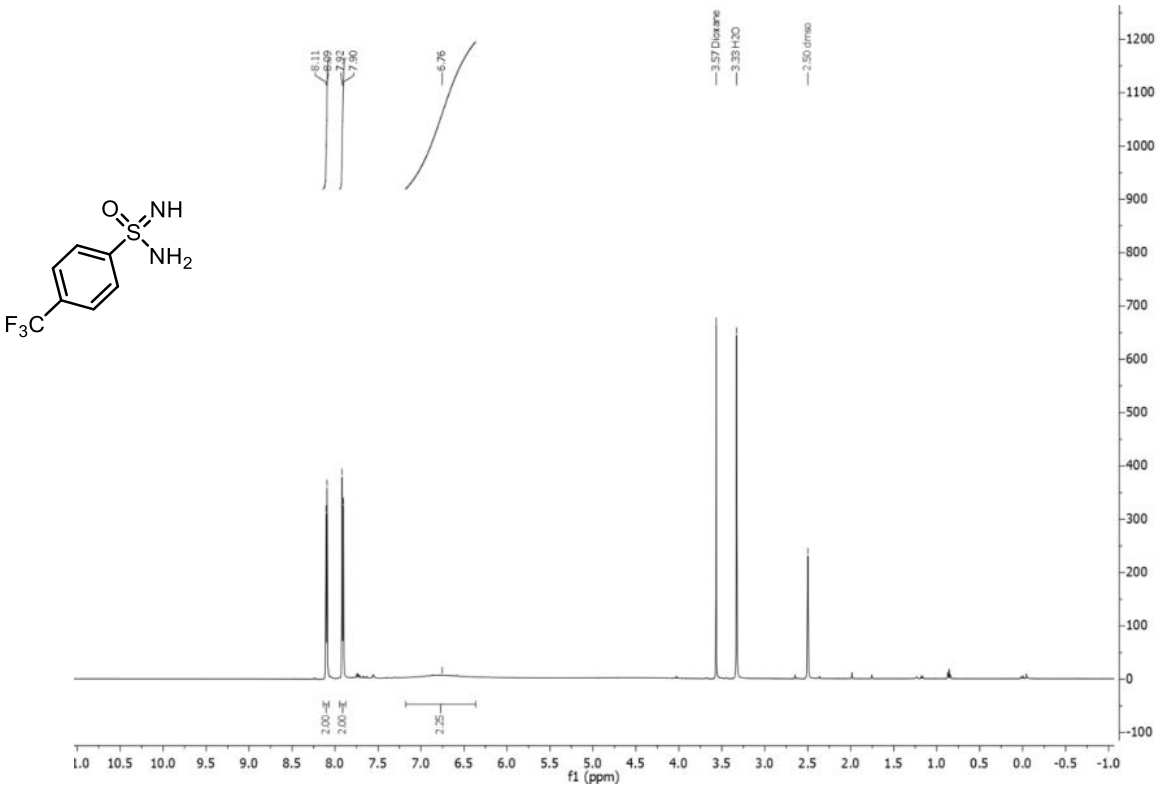
Stacked $^{13}C\{^{1}H\}$ DEPT NMR spectra (DMSO-d_6, 151 MHz) of compound **6h**



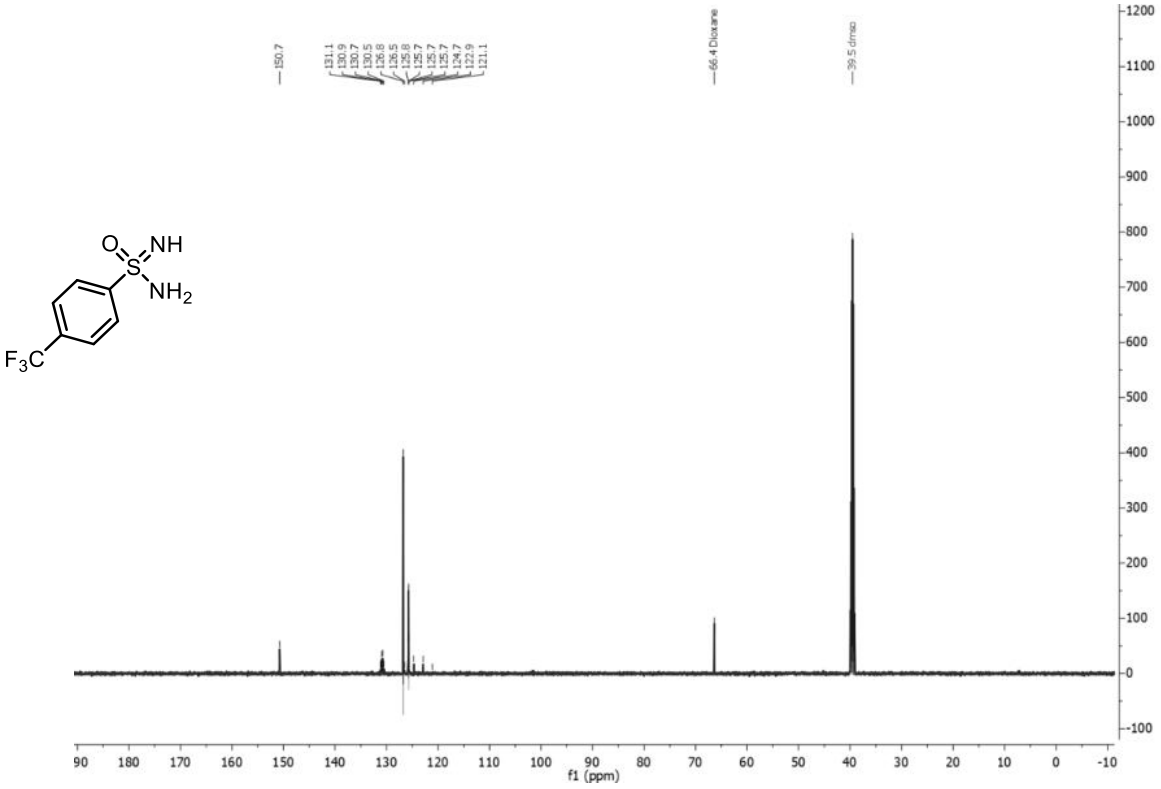
^{19}F NMR spectrum (DMSO-d_6, 564 MHz) of compound **6h**



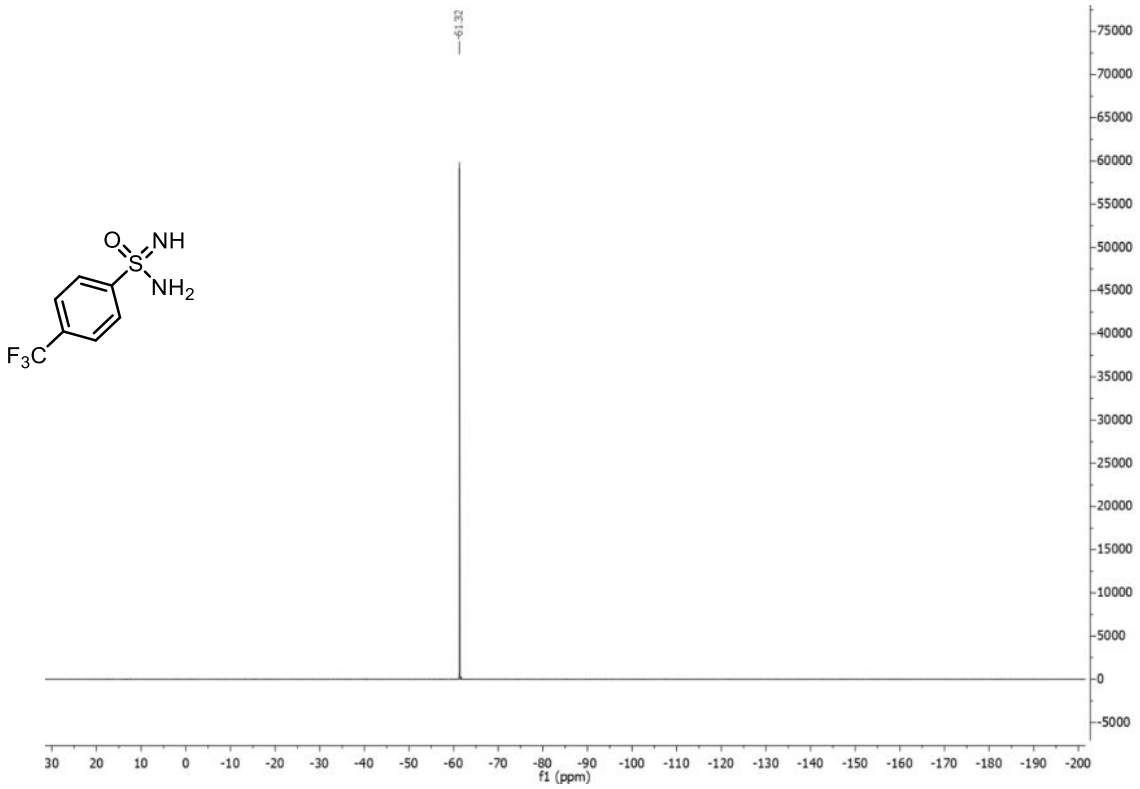
^{1}H NMR spectrum (DMSO-d_6, 600 MHz) of compound **1h**



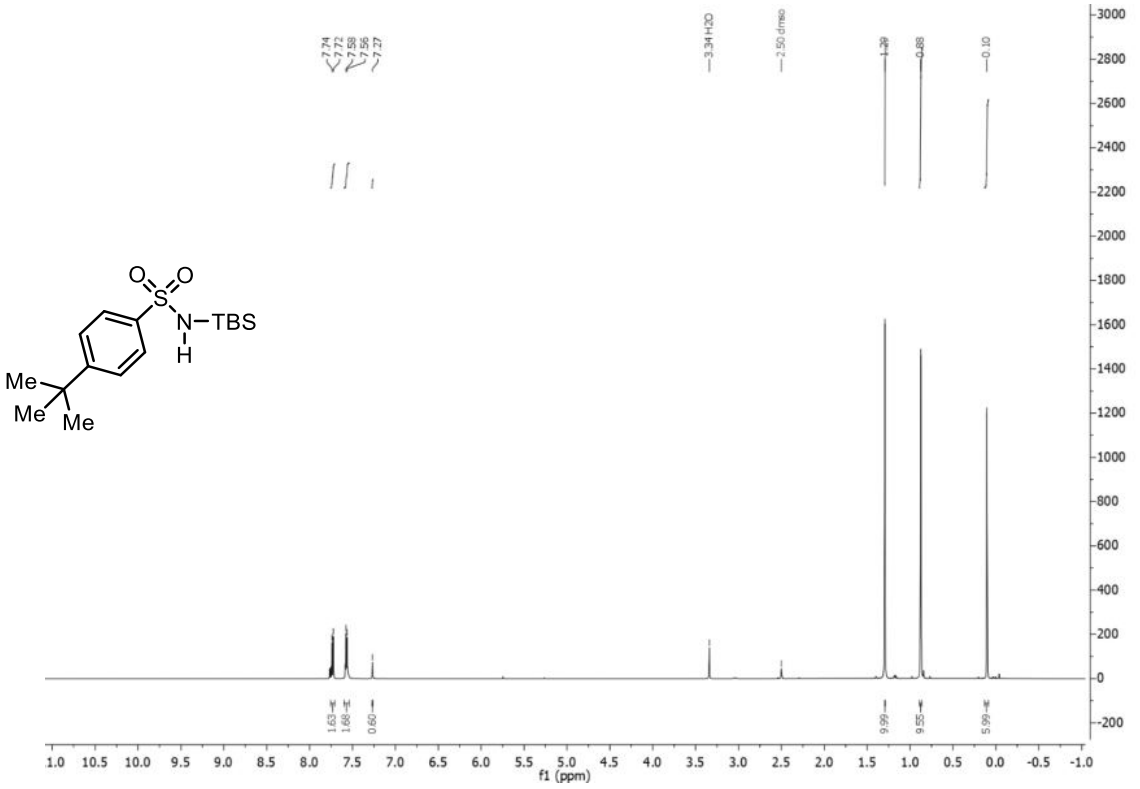
Stacked ^{13}C{^{1}H} DEPT NMR spectra (DMSO-d_6, 151 MHz) of compound **1h**



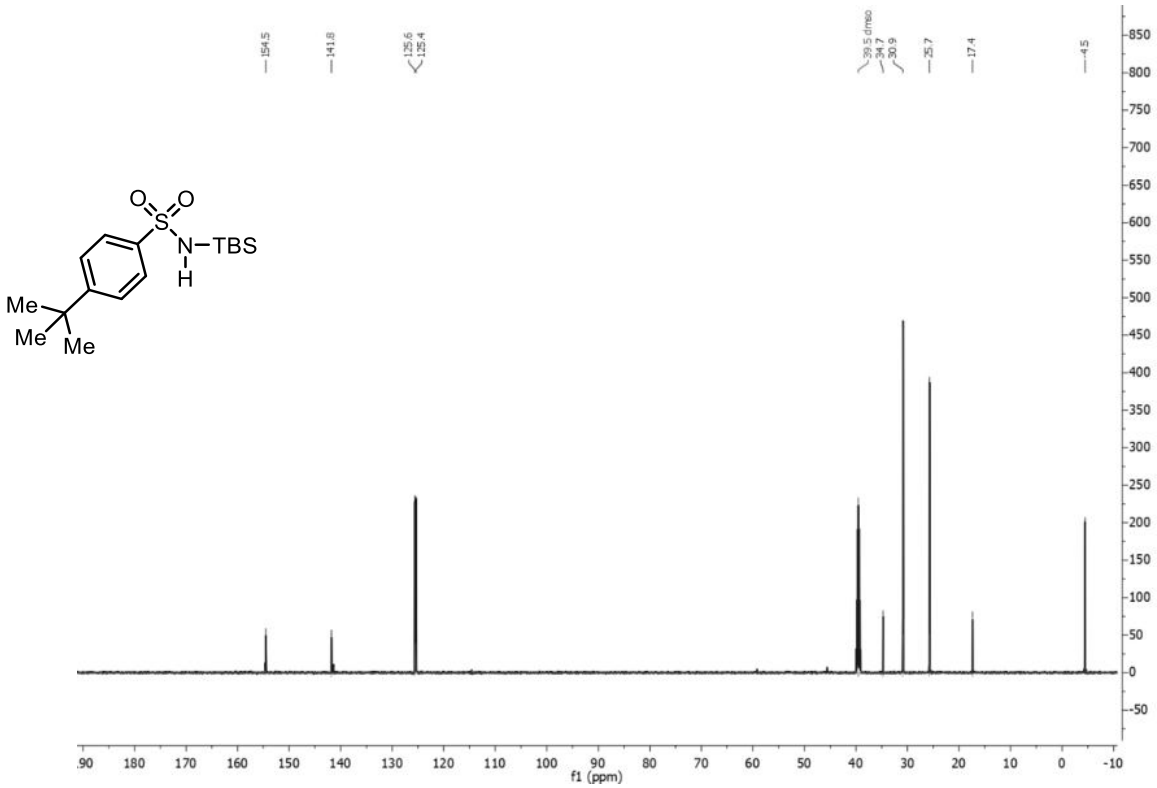
^{19}F NMR spectrum (DMSO-d_6, 564 MHz) of compound **1h**



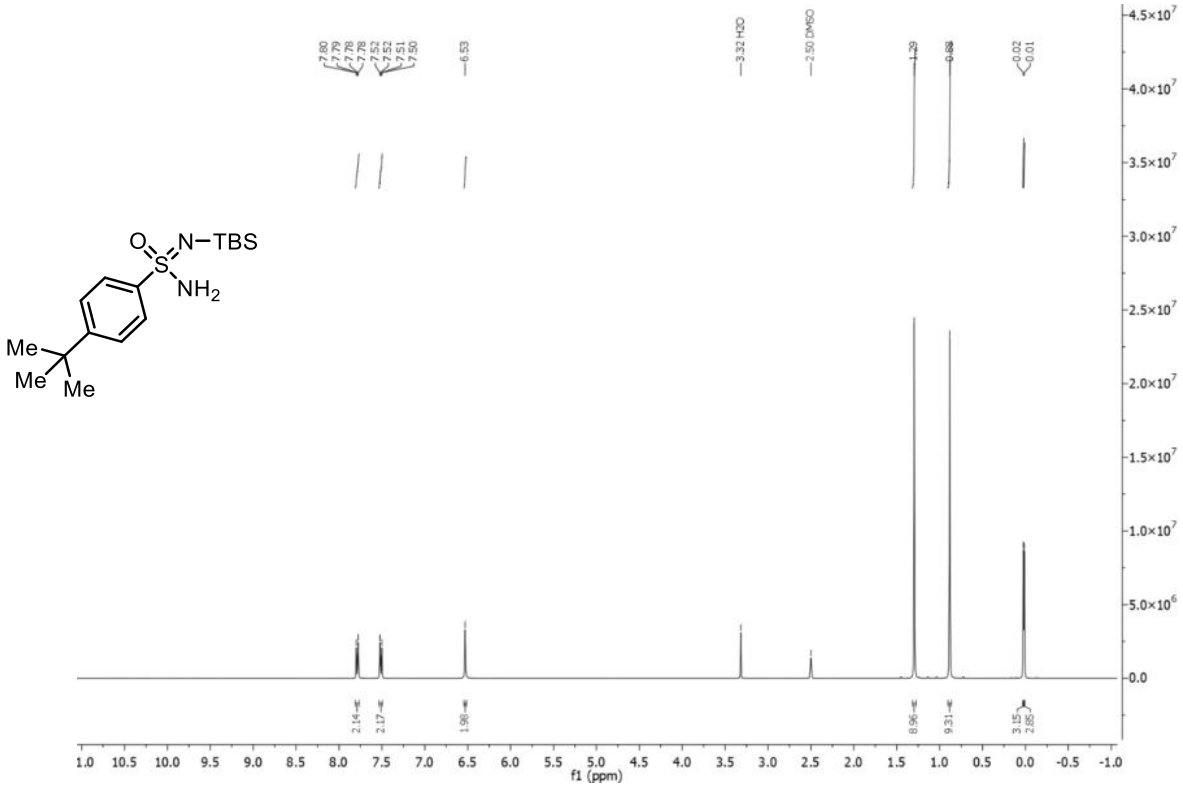
^{1}H NMR spectrum (DMSO-d_6, 600 MHz) of compound **1i-precursor**



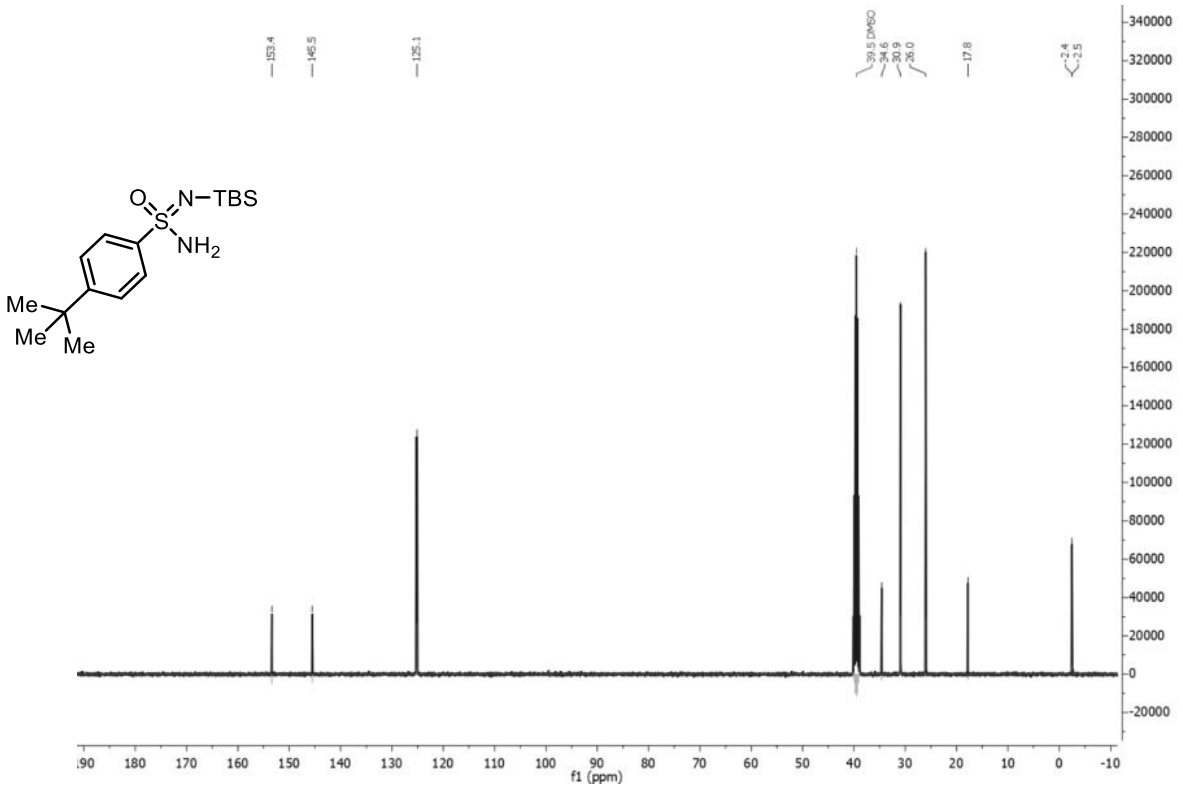
Stacked $^{13}C\{^{1}H\}$ DEPT NMR spectra (DMSO-d_6, 151 MHz) of compound **1i-precursor**



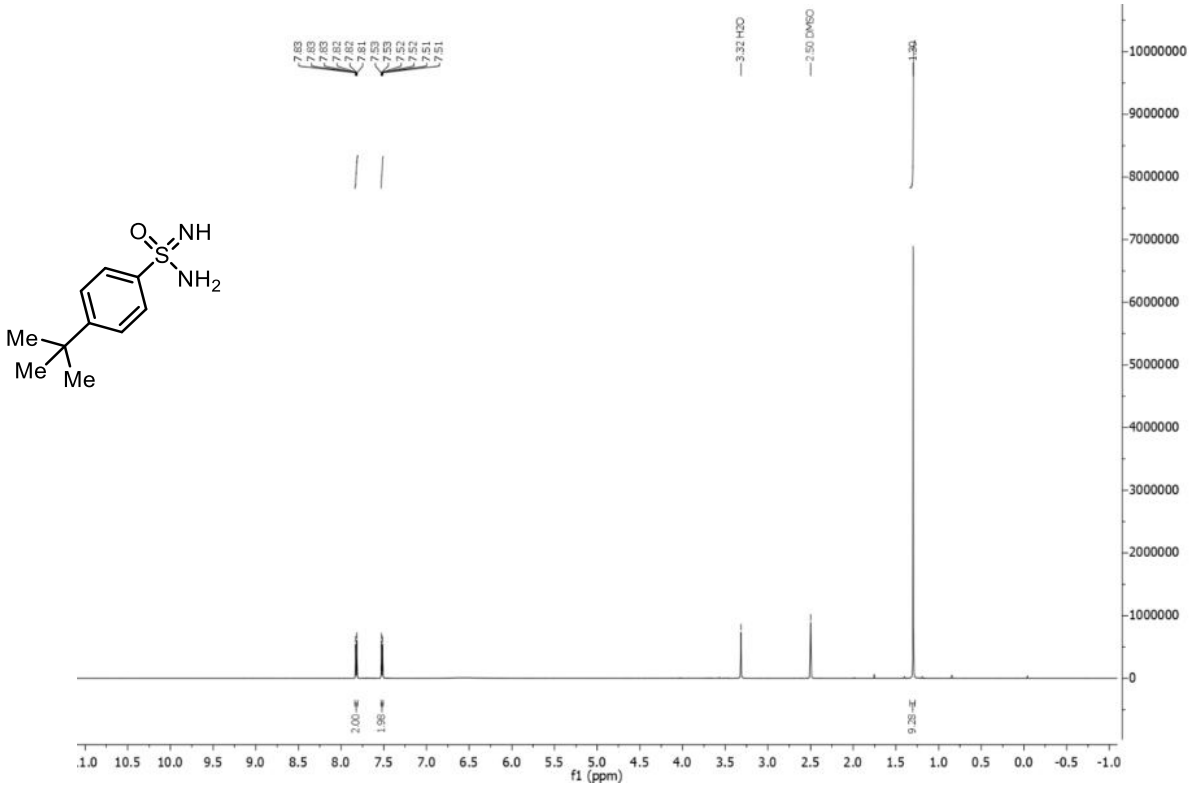
^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of compound **6i**



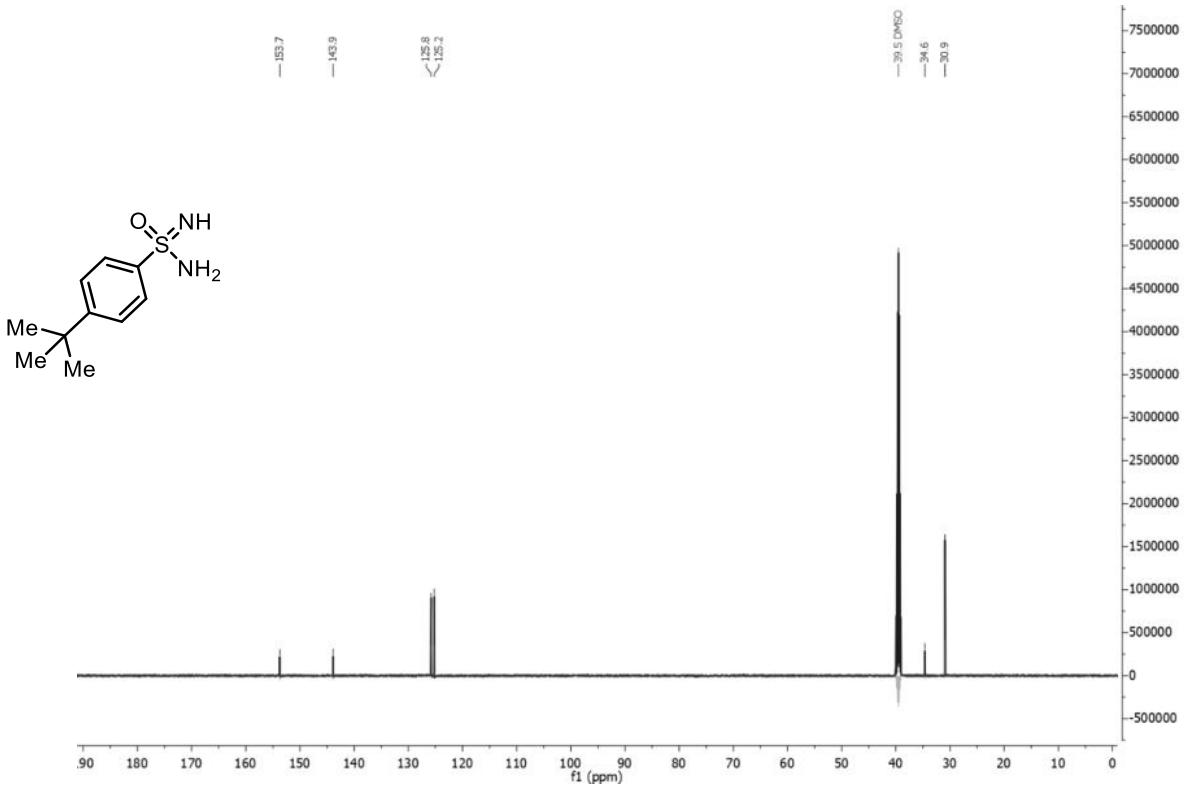
Stacked $^{13}C\{^{1}H\}$ DEPT NMR spectra (DMSO-d_6, 101 MHz) of compound **6i**



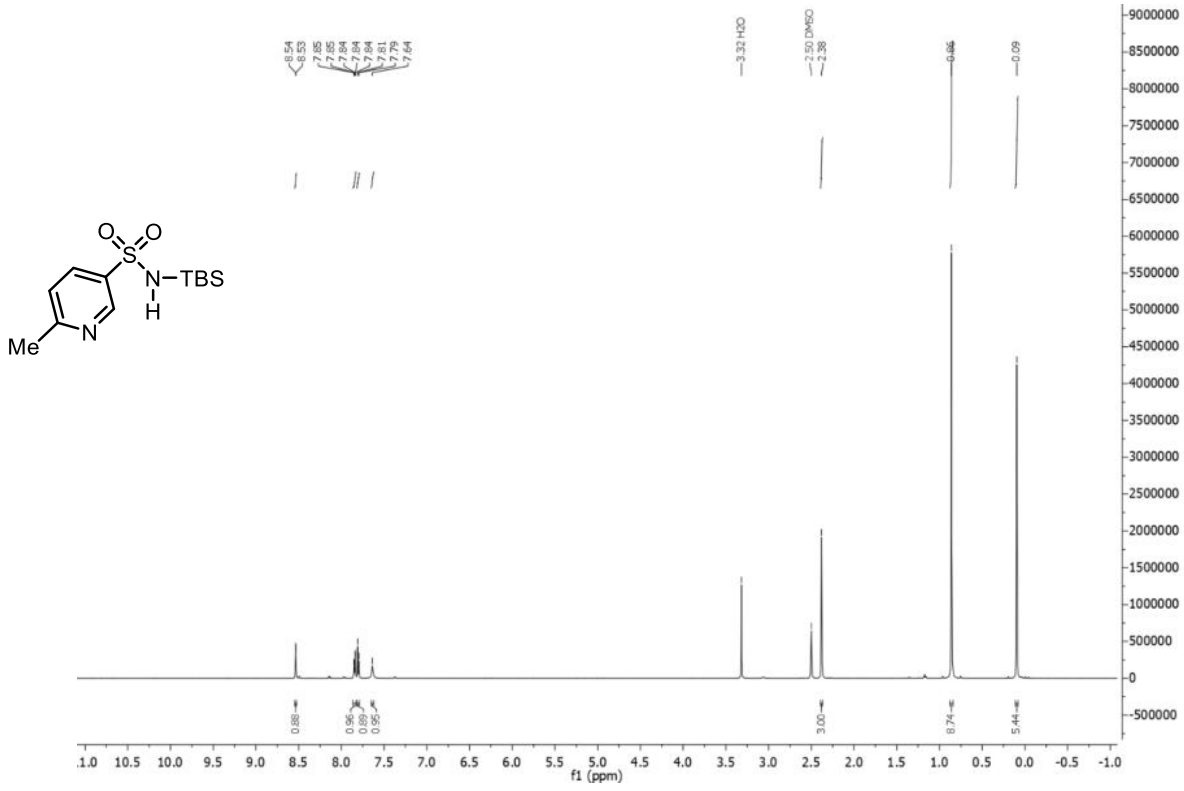
^{1}H NMR spectrum (DMSO-d_6, 600 MHz) of compound **1i**



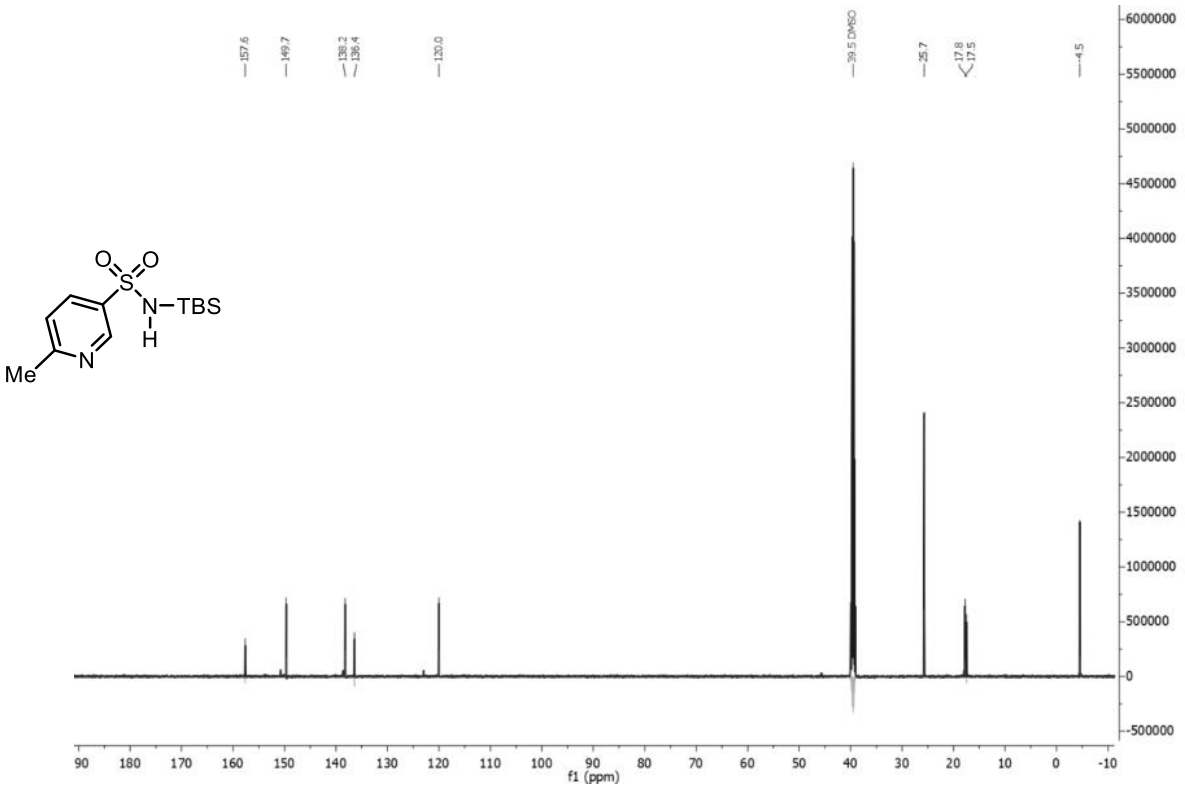
Stacked $^{13}C\{^{1}H\}$ DEPT NMR spectra (DMSO-d_6, 151 MHz) of compound **1i**



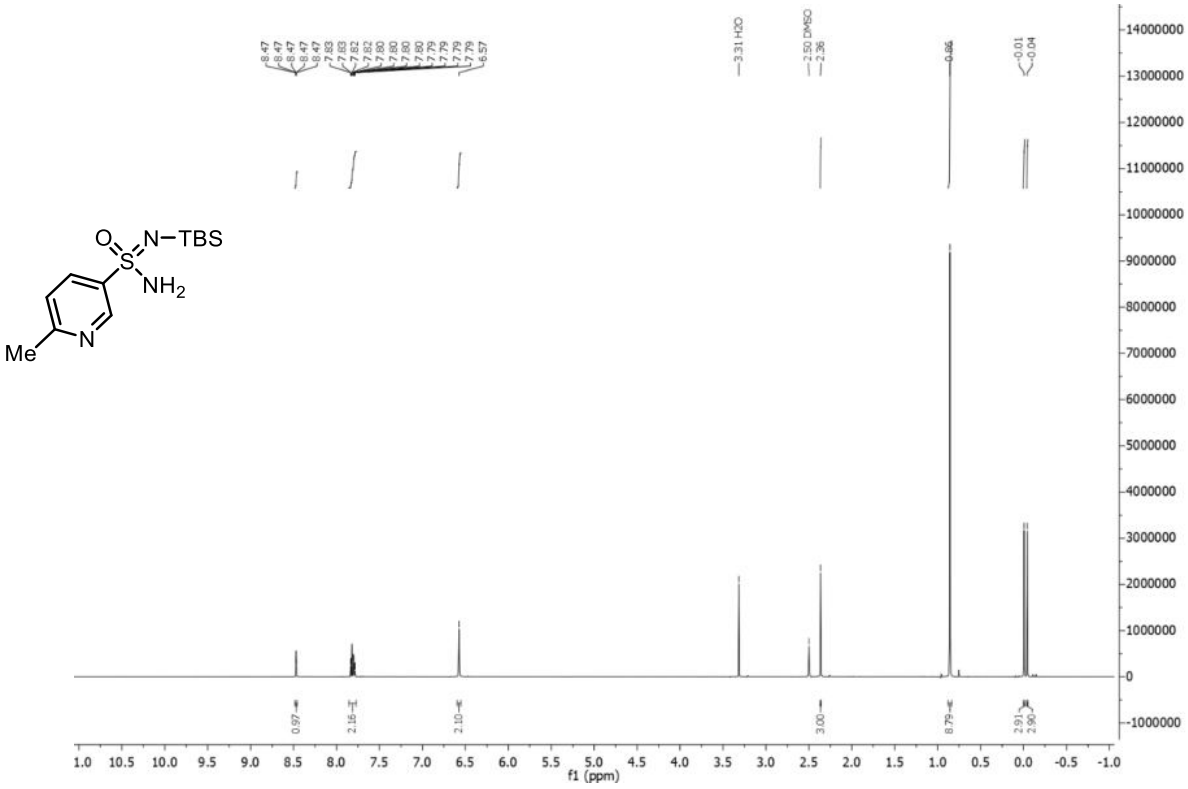
^{1}H NMR spectrum (DMSO-d_6, 600 MHz) of compound **1j-precursor**



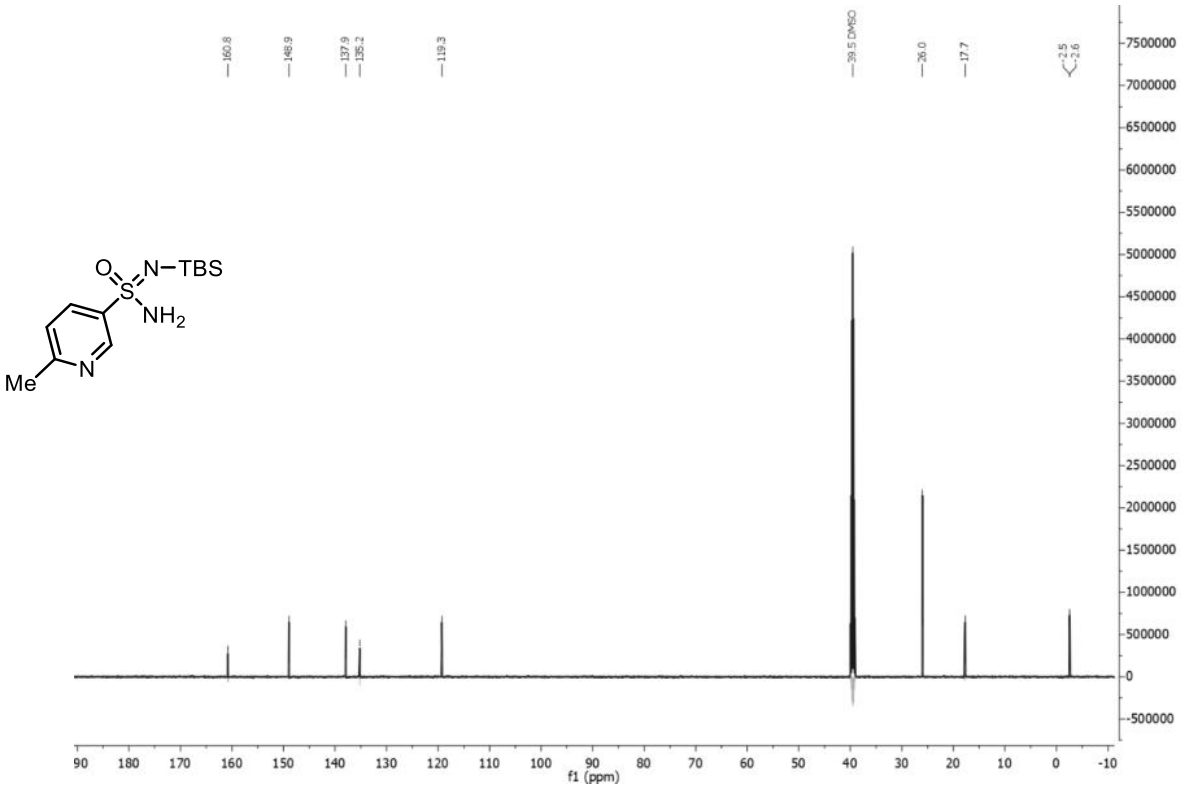
Stacked $^{13}C\{^{1}H\}$ DEPT NMR spectra (DMSO-d_6, 151 MHz) of compound **1j-precursor**



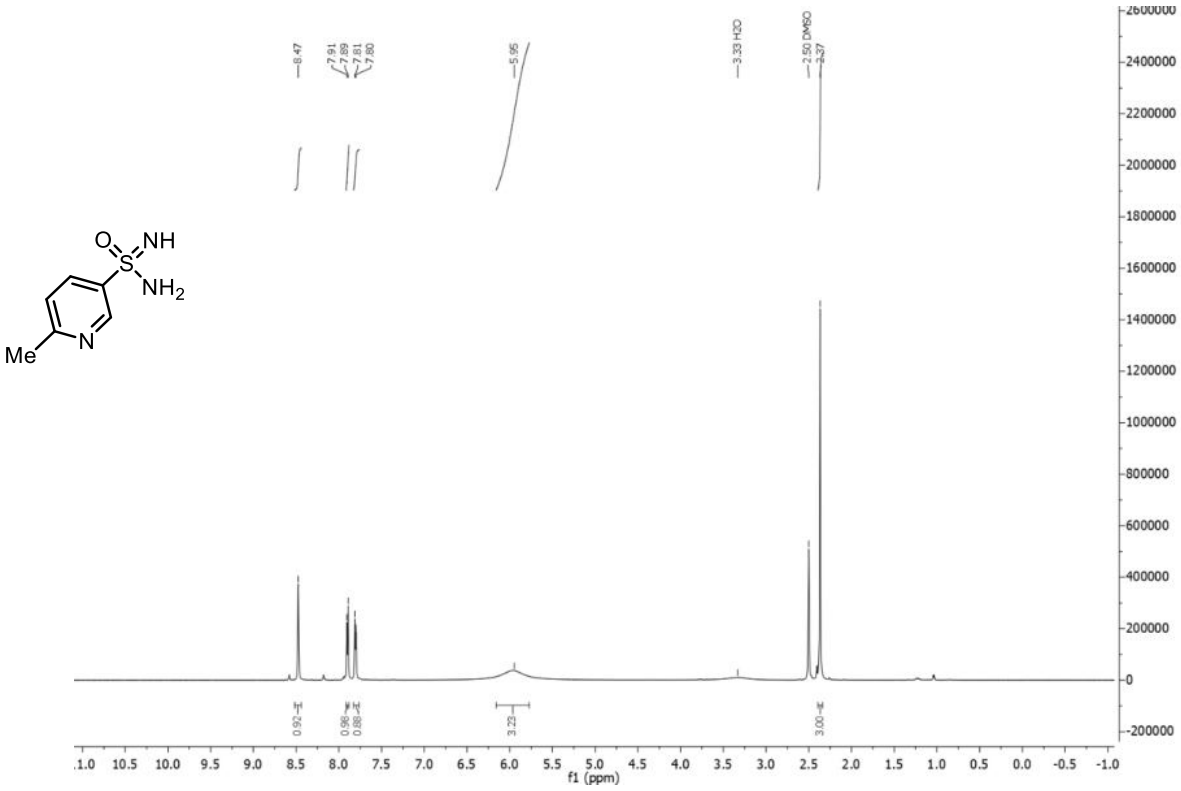
^{1}H NMR spectrum (DMSO-d_6, 600 MHz) of compound **6j**



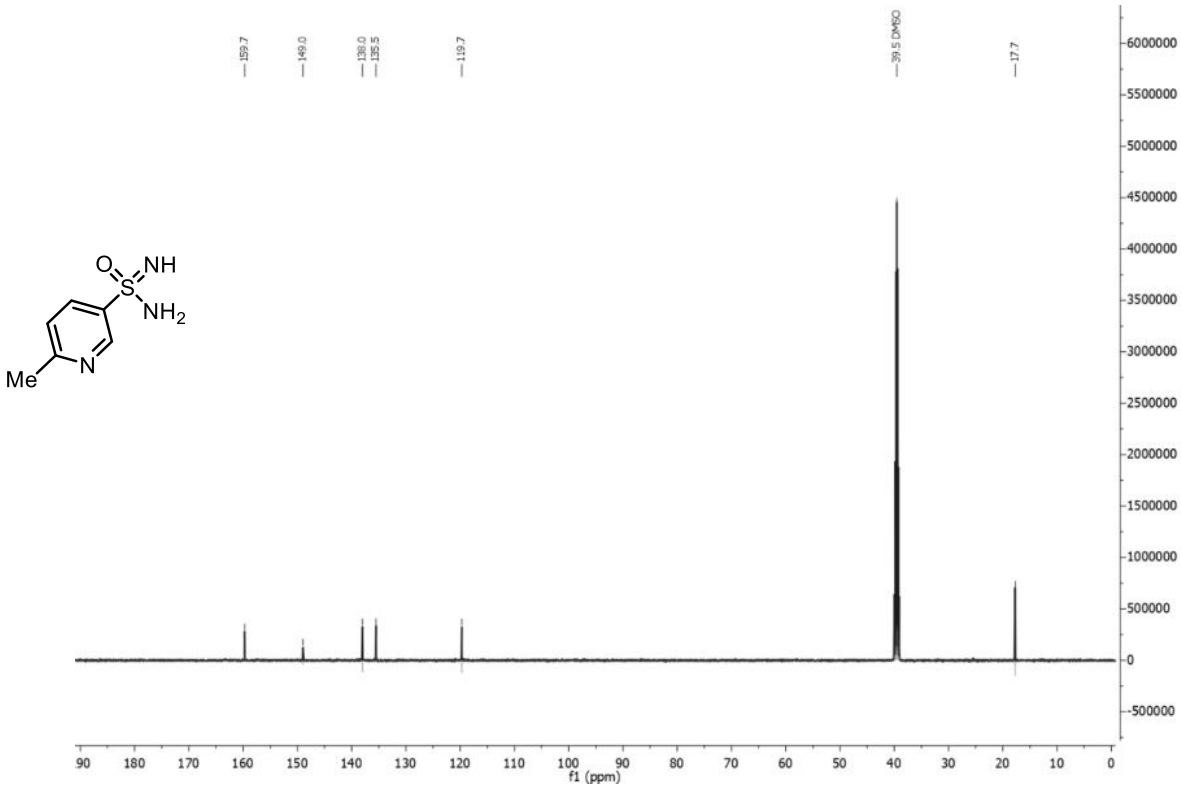
Stacked $^{13}C\{^{1}H\}$ DEPT NMR spectra (DMSO-d_6, 151 MHz) of compound **6j**



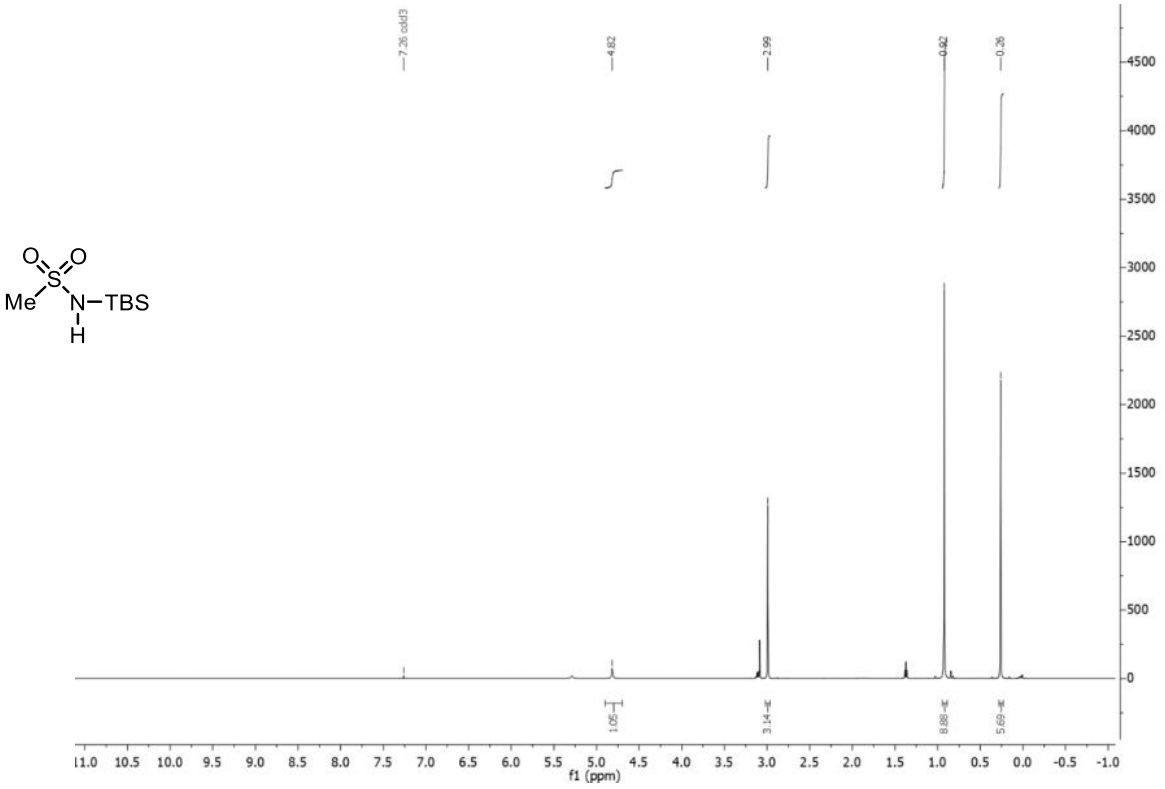
^{1}H NMR spectrum (DMSO-d_6, 600 MHz) of compound **1j**



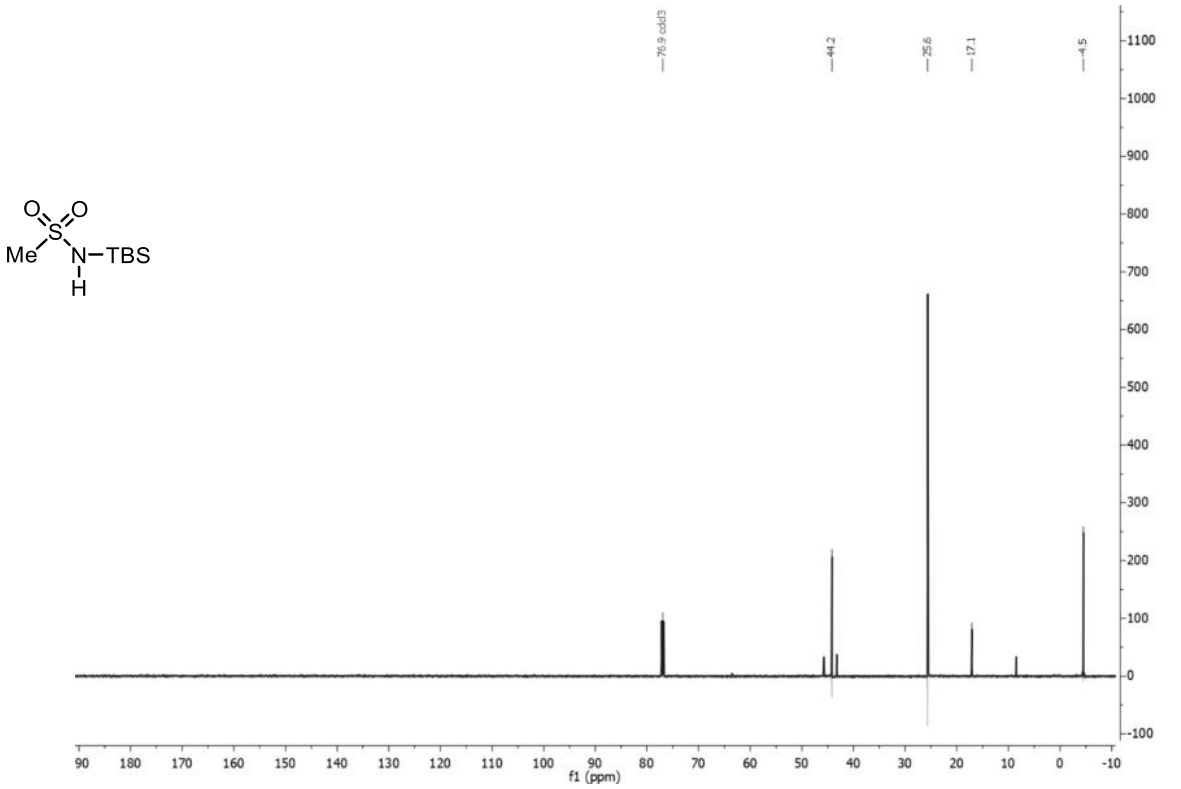
Stacked $^{13}C\{^{1}H\}$ DEPT NMR spectra (DMSO-d_6, 151 MHz) of compound **1j**



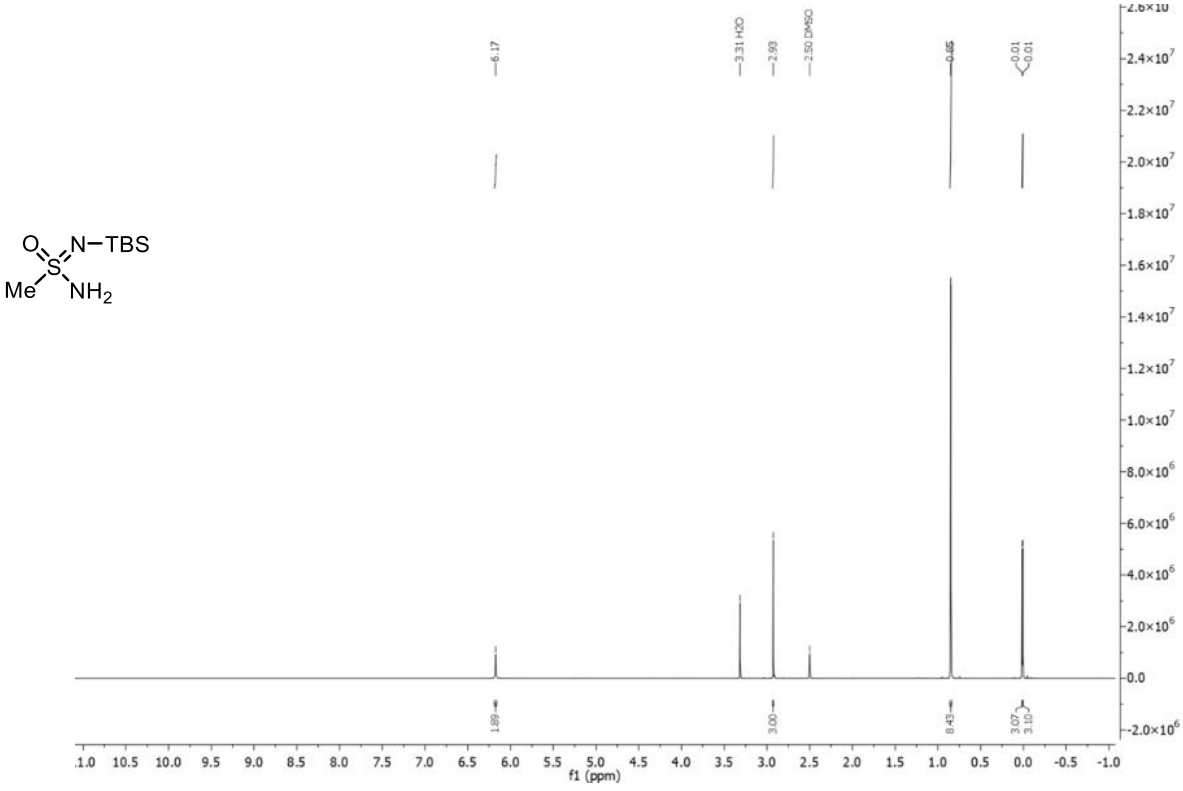
^{1}H NMR spectrum (Chloroform-d, 600 MHz) of compound **1k-precursor**



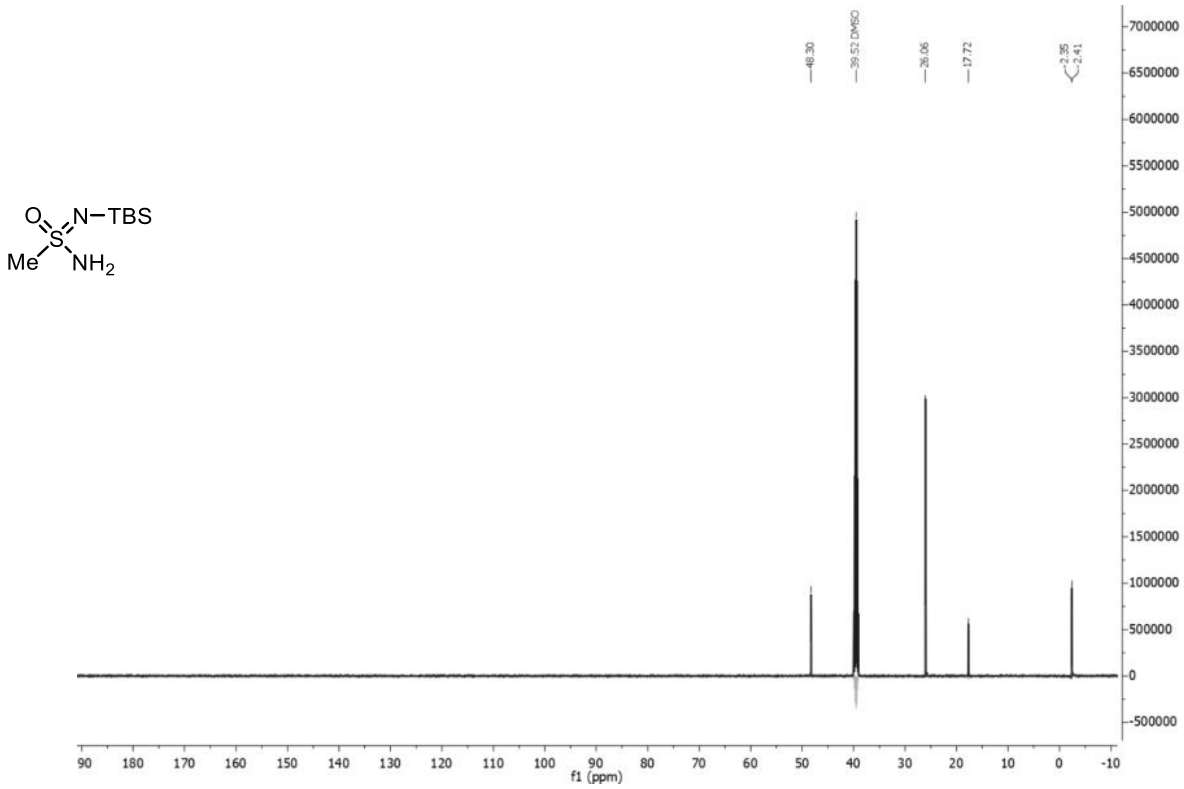
Stacked $^{13}C\{^{1}H\}$ DEPT NMR spectra (Chloroform-*d*, 151 MHz) of compound **1k-precursor**



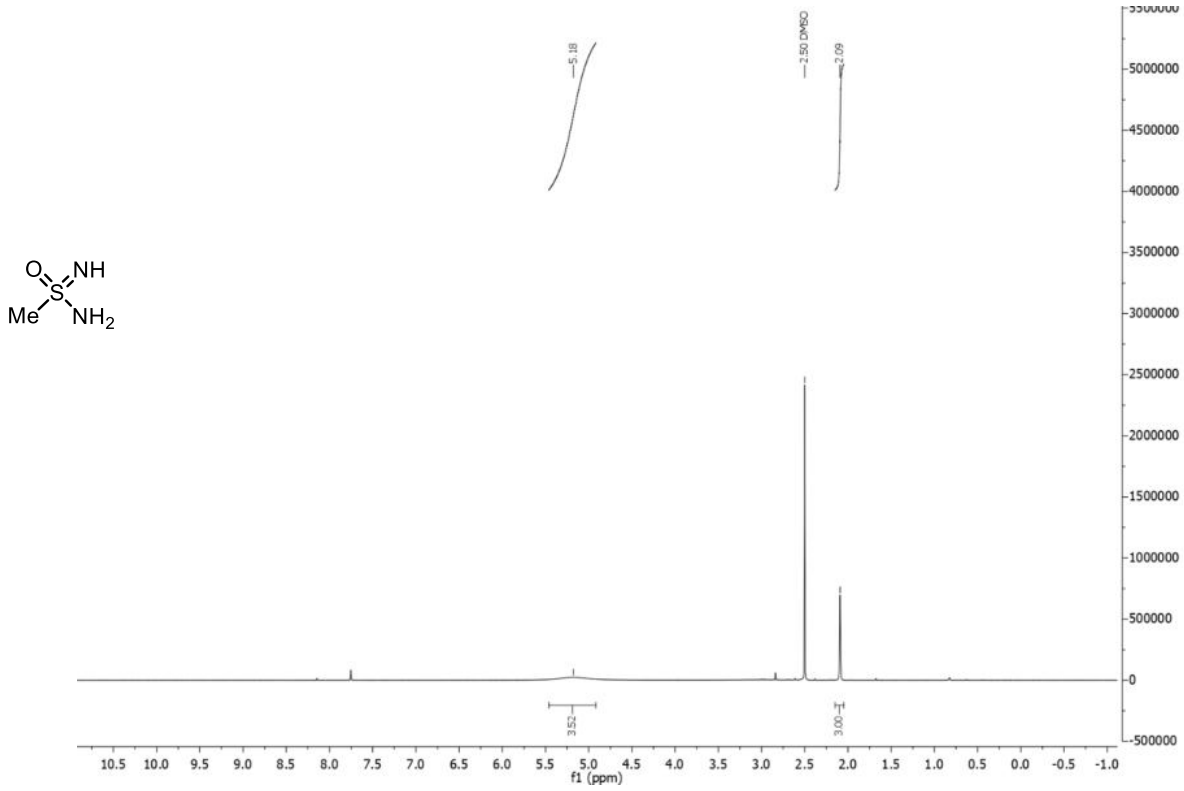
^{1}H NMR spectrum (DMSO-d_6, 600 MHz) of compound **6k**



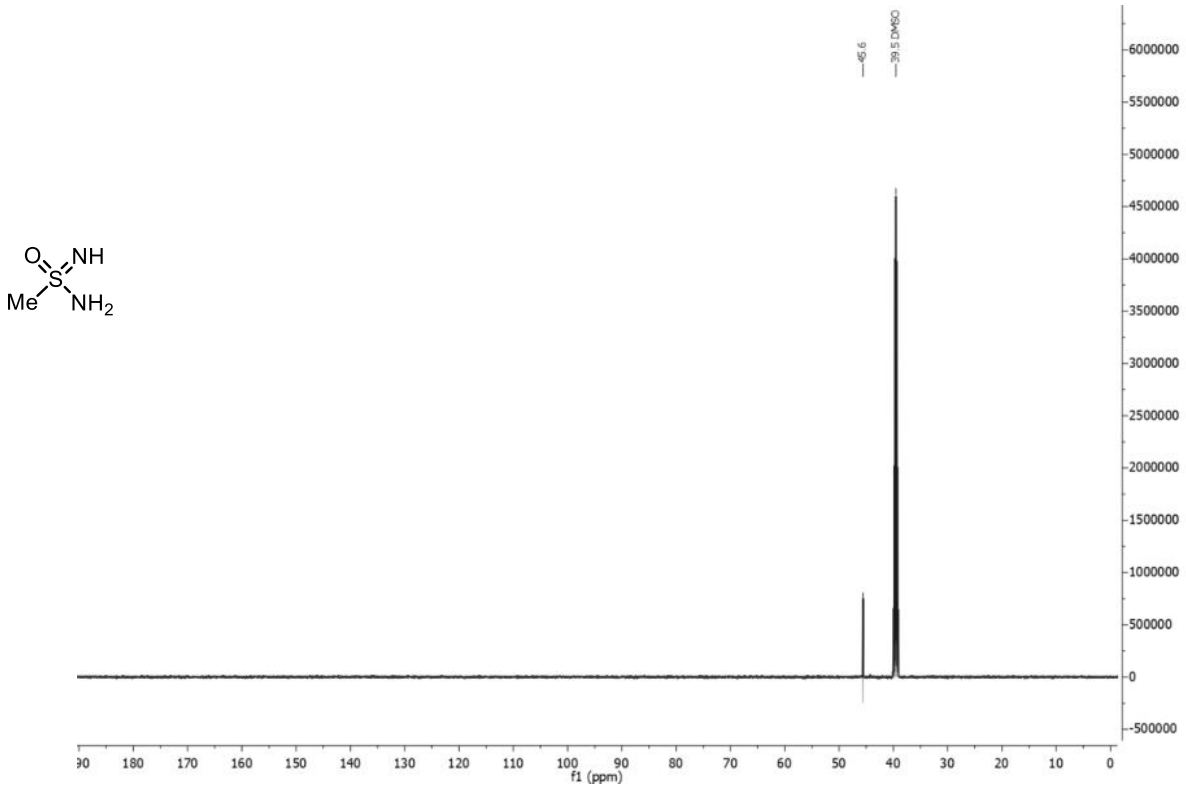
Stacked $^{13}C\{^{1}H\}$ DEPT NMR spectra (DMSO-d_6, 151 MHz) of compound **6k**



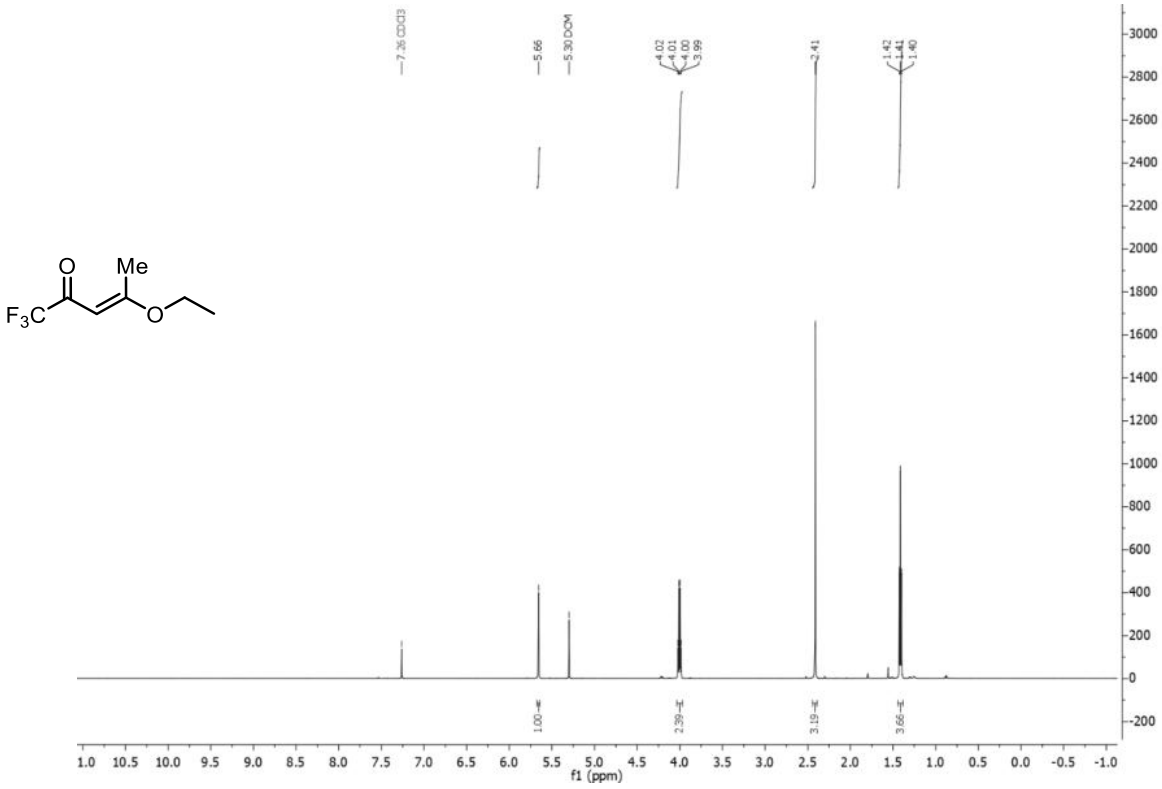
^{1}H NMR spectrum (DMSO-d_6, 600 MHz) of compound **1k**



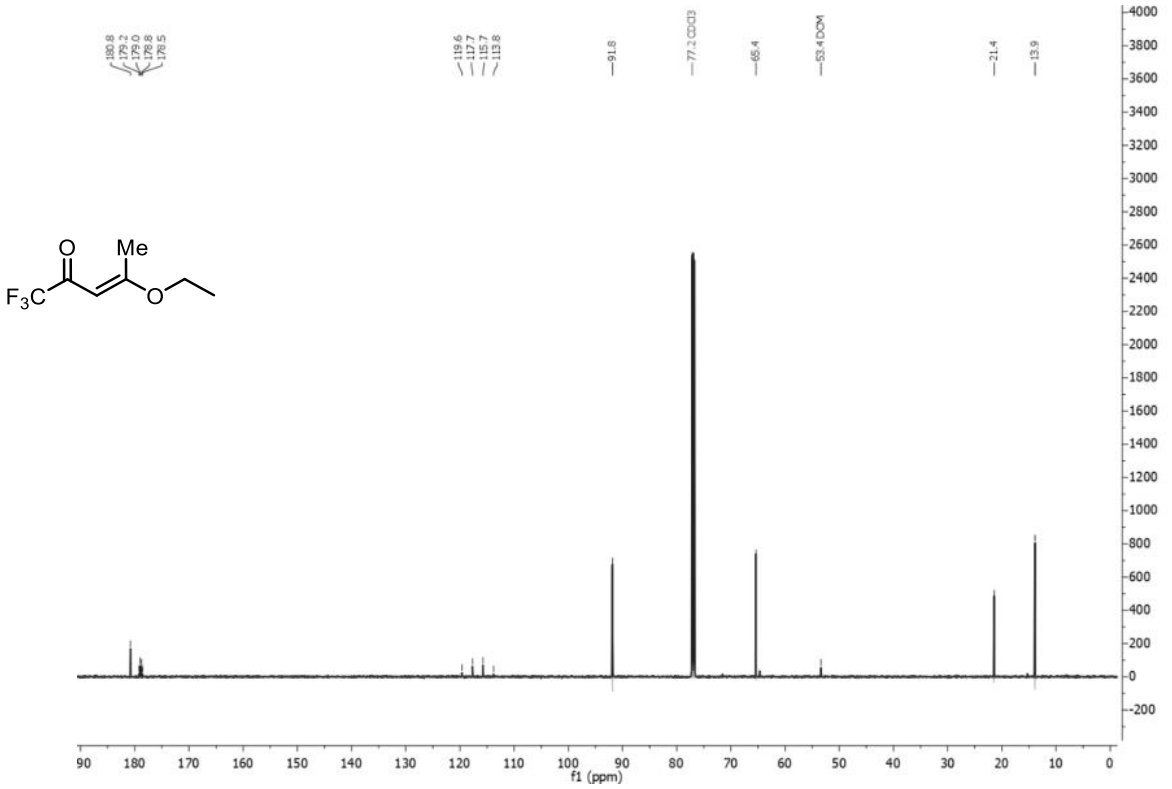
Stacked $^{13}C\{^{1}H\}$ DEPT NMR spectra (DMSO-d_6, 151 MHz) of compound **1k**



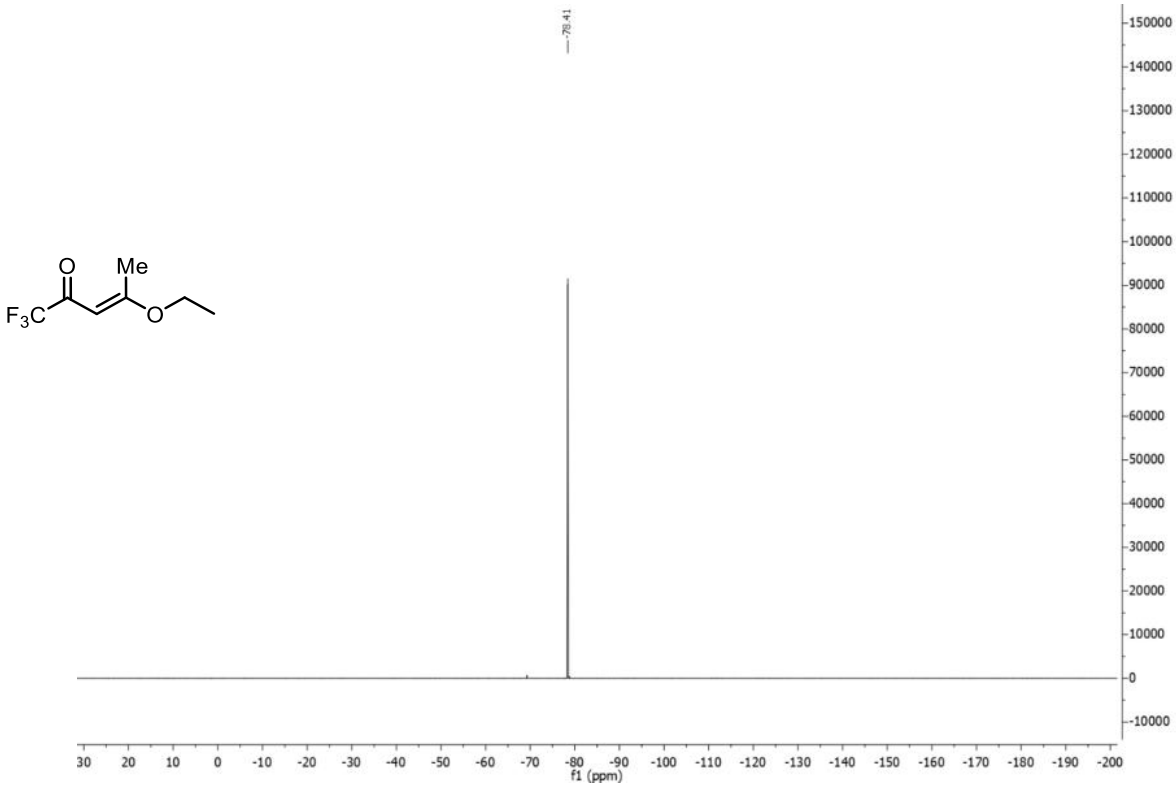
^{1}H NMR spectrum (Chloroform-*d*, 600 MHz) of compound **4b**



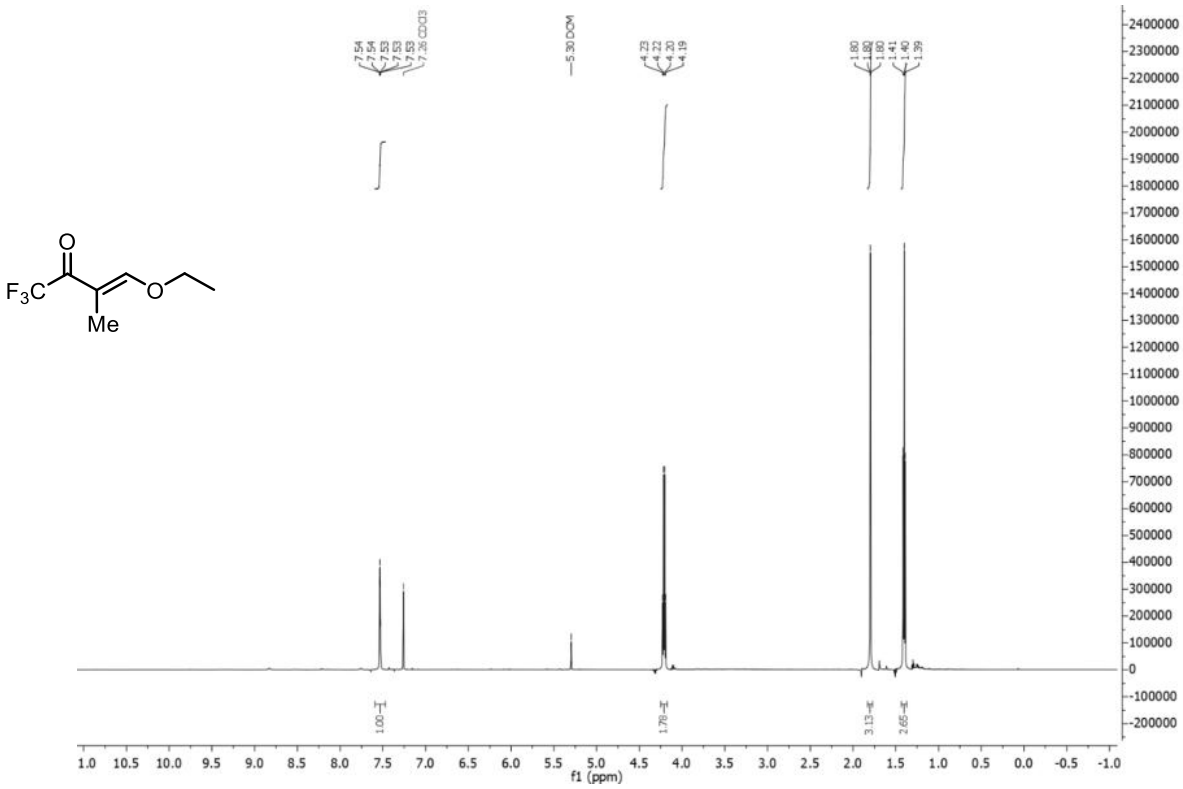
Stacked $^{13}C\{^{1}H\}$ DEPT NMR spectra (Chloroform-*d*, 151 MHz) of compound **4b**



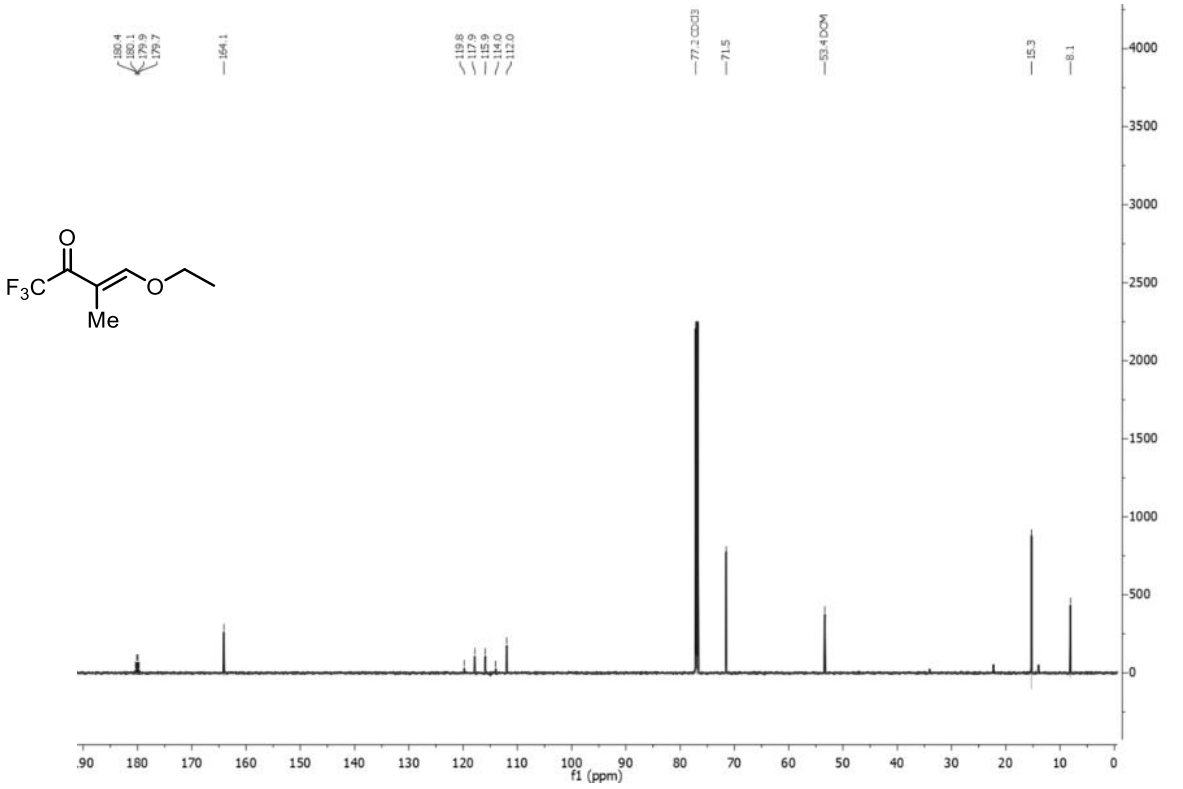
^{19}F NMR spectrum (Chloroform-*d*, 564 MHz) of compound **4b**



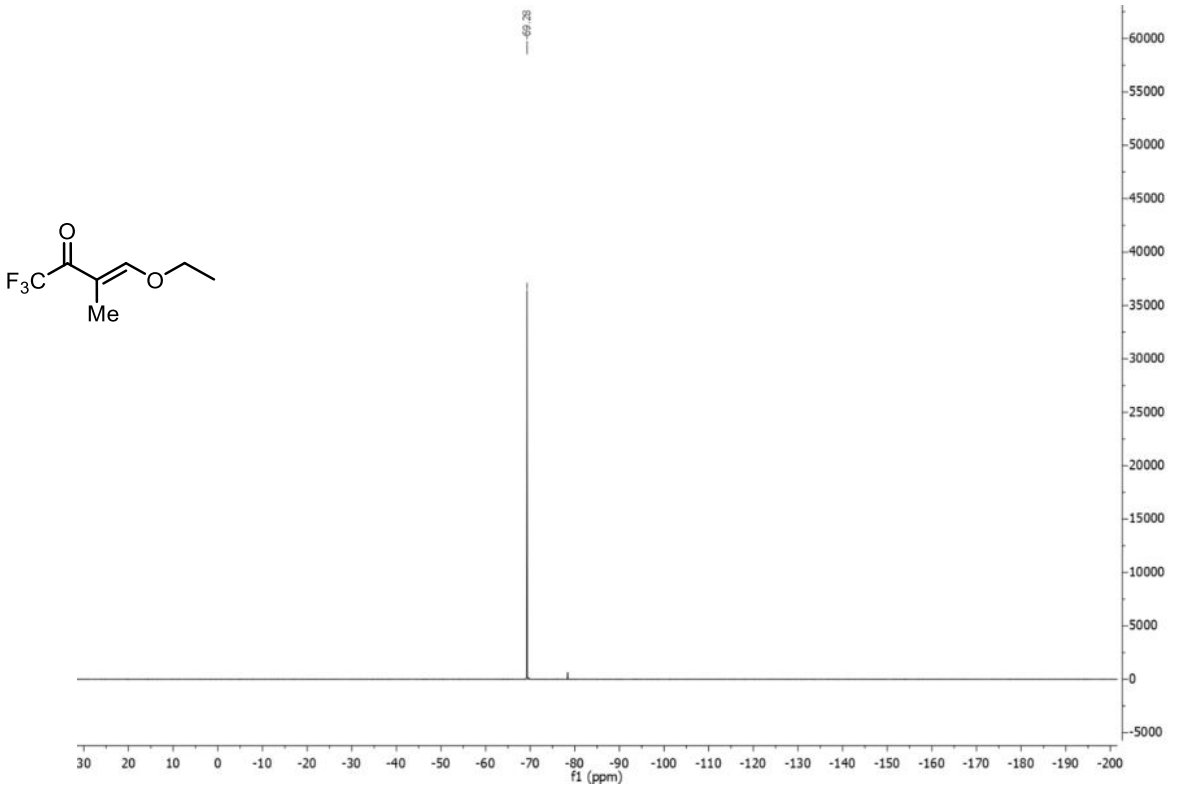
^{1}H NMR spectrum (Chloroform-*d*, 600 MHz) of compound **4c**



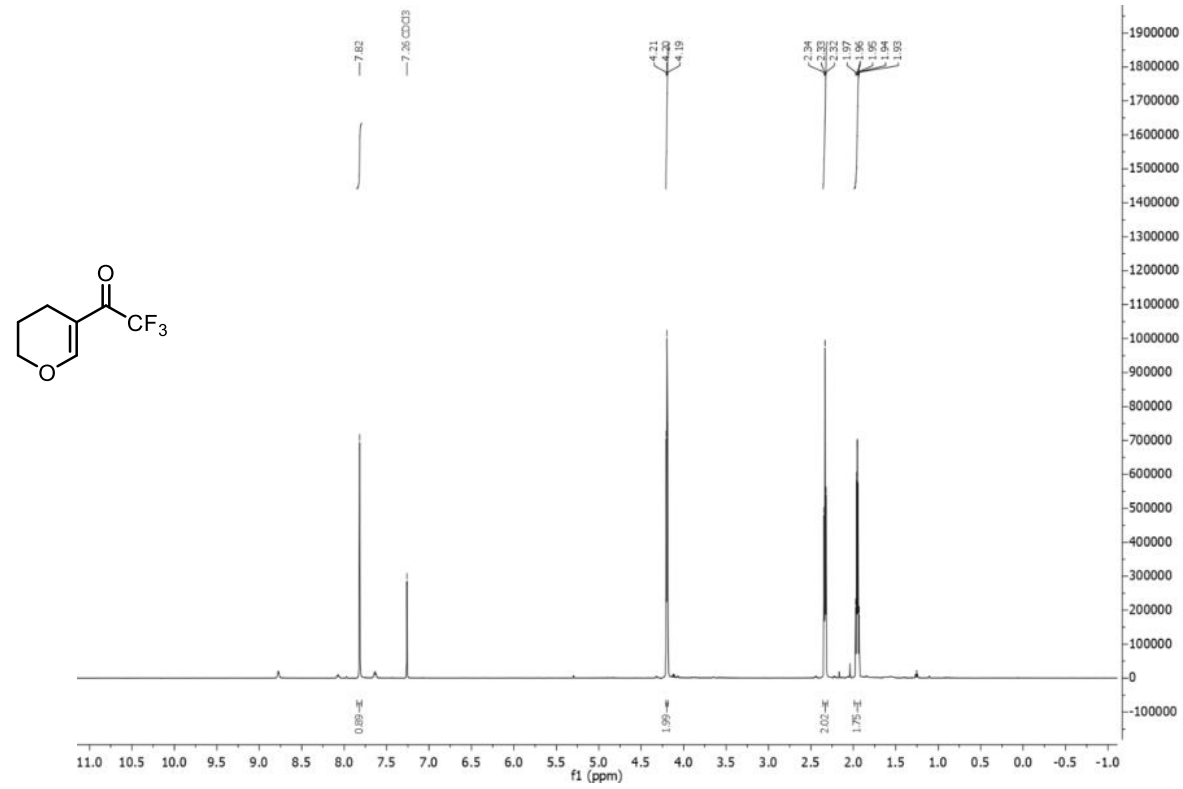
Stacked ^{13}C{^{1}H} DEPT NMR spectra (Chloroform-*d*, 151 MHz) of compound **4c**



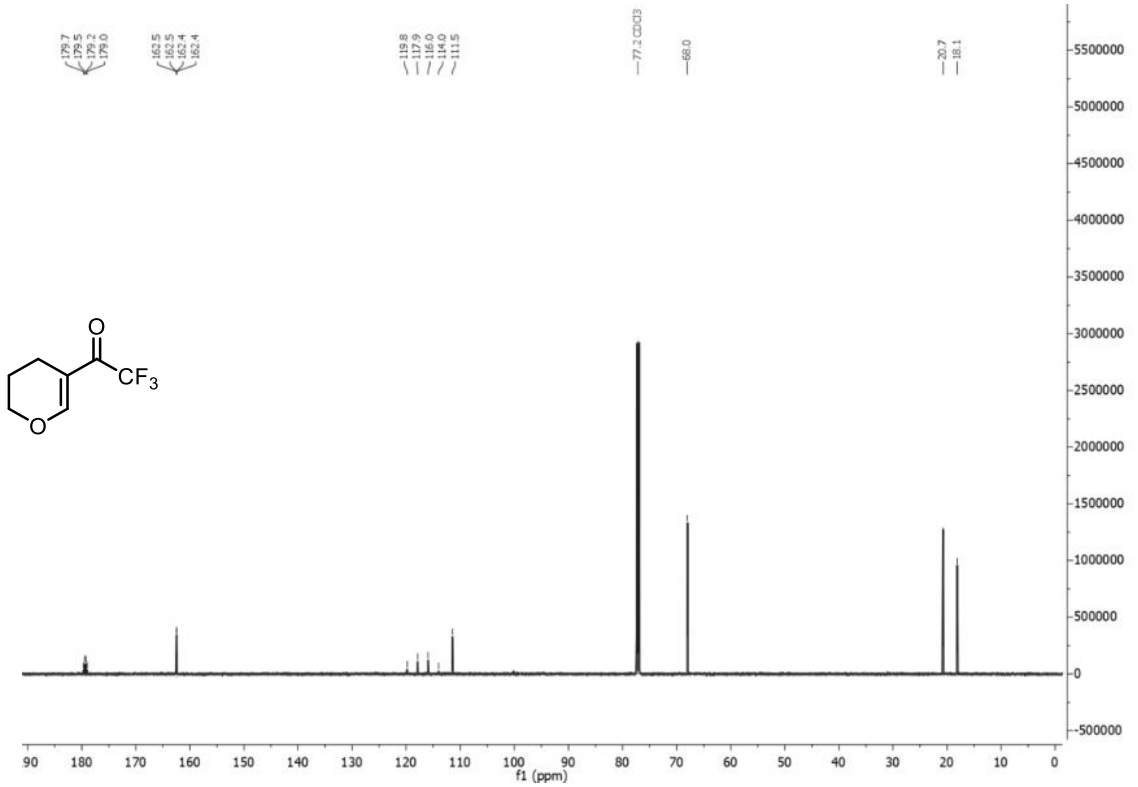
^{19}F NMR spectrum (Chloroform-*d*, 564 MHz) of compound **4c**



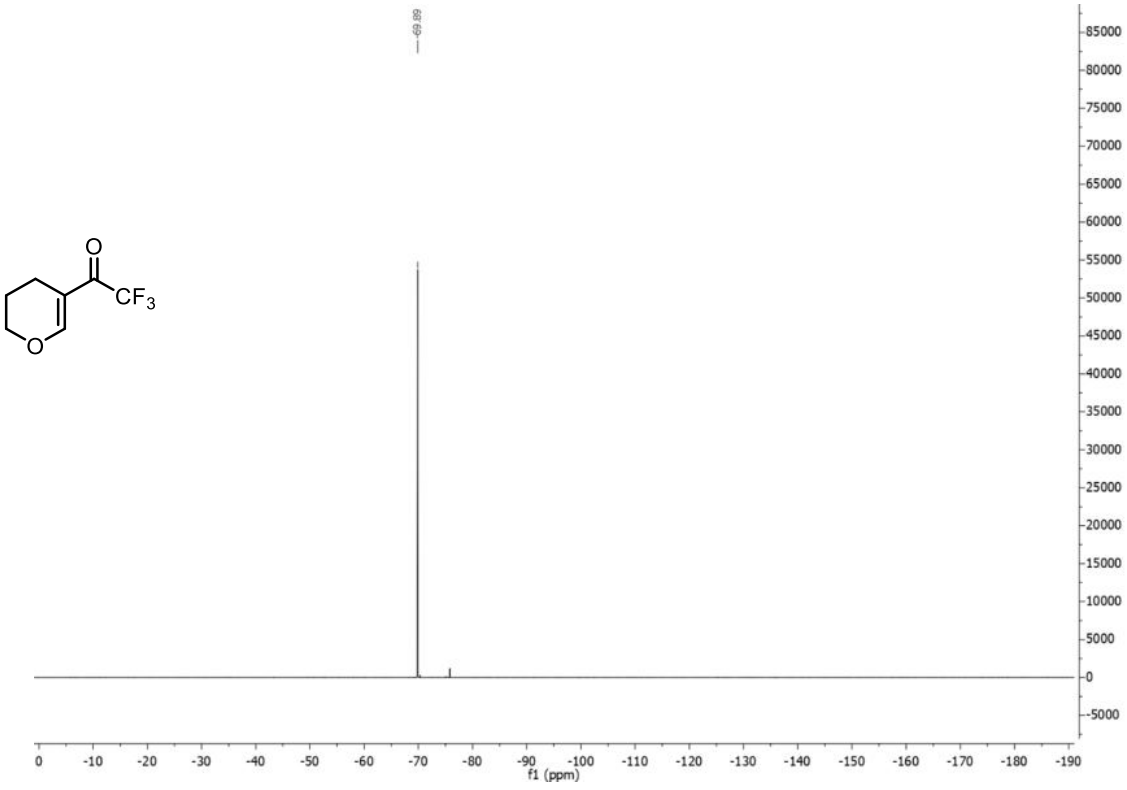
^{1}H NMR spectrum (Chloroform-*d*, 600 MHz) of compound **4d**



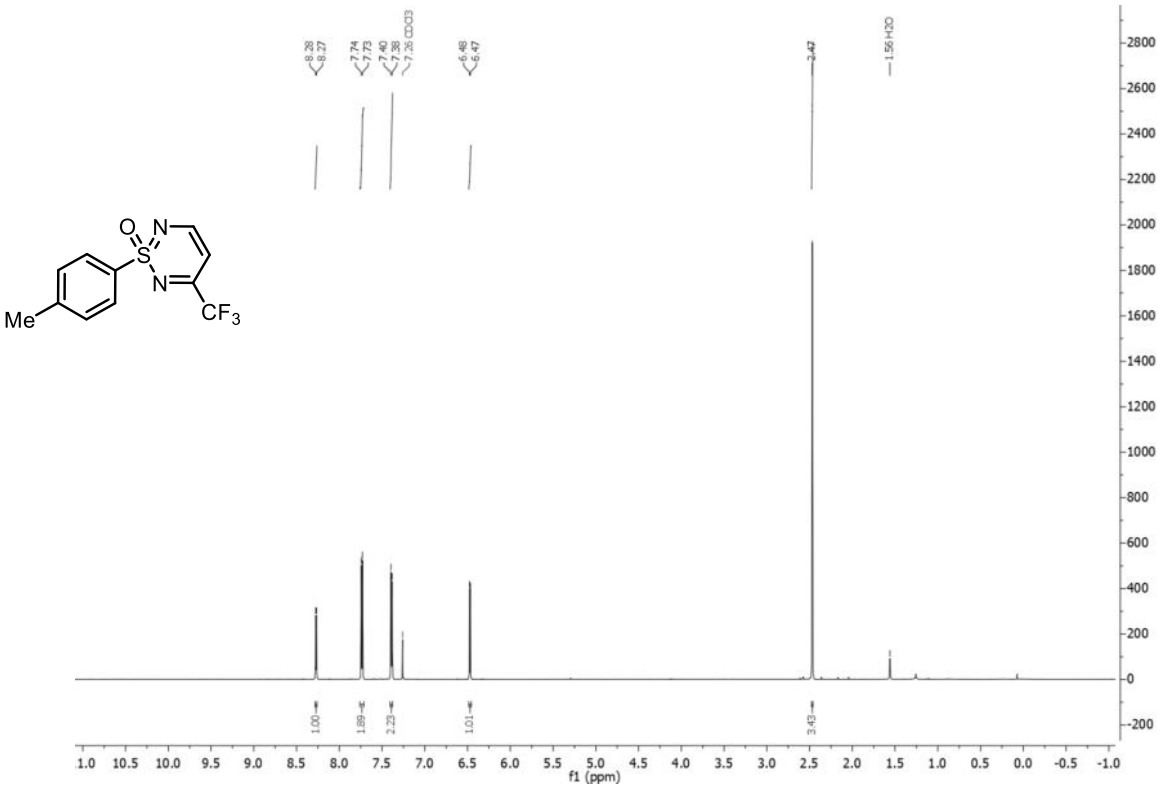
Stacked $^{13}C\{^{1}H\}$ DEPT NMR spectra (Chloroform-*d*, 151 MHz) of compound **4d**



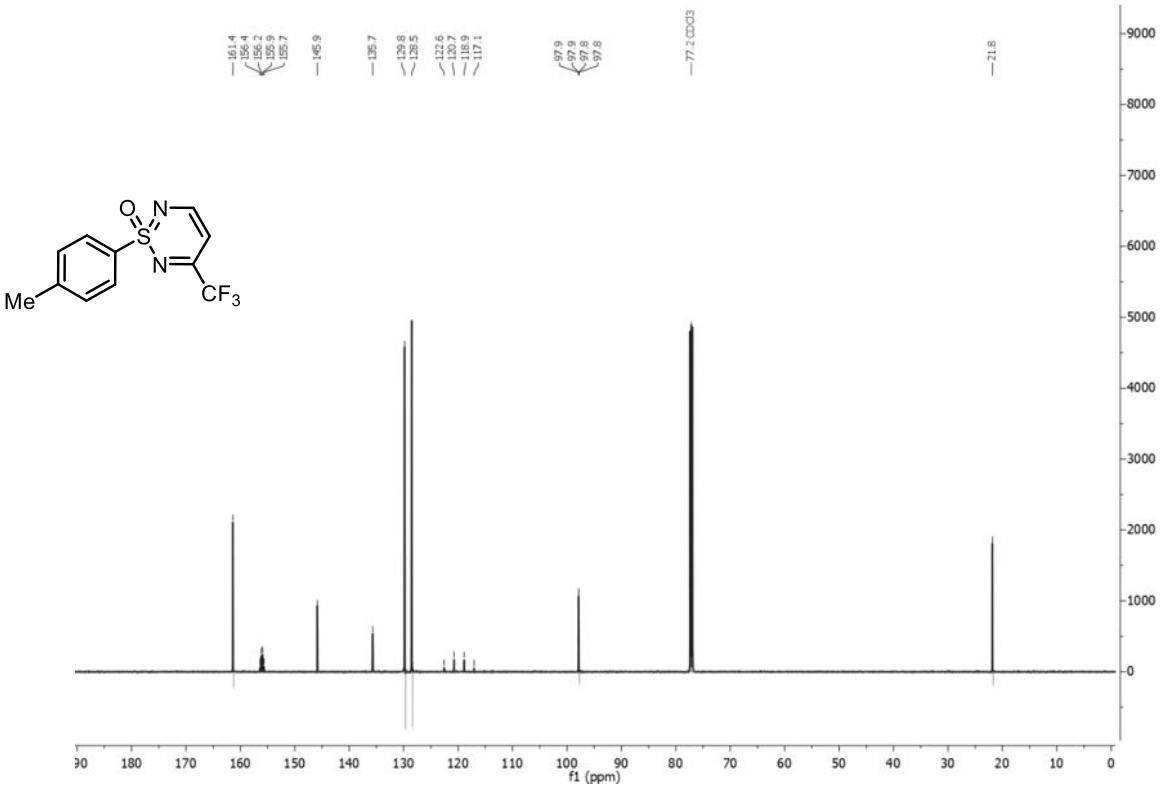
^{19}F NMR spectrum (Chloroform-*d*, 564 MHz) of compound **4d**



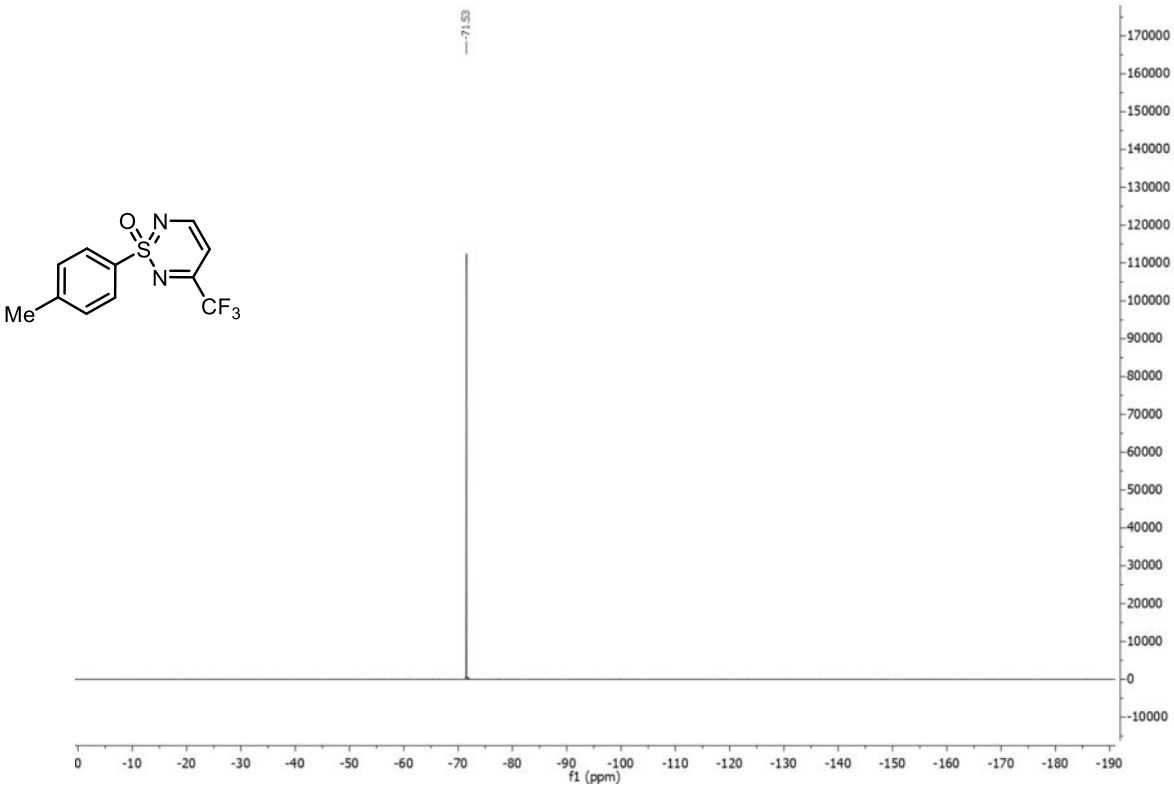
^{1}H NMR spectrum (Chloroform-*d*, 600 MHz) of compound **5aa**



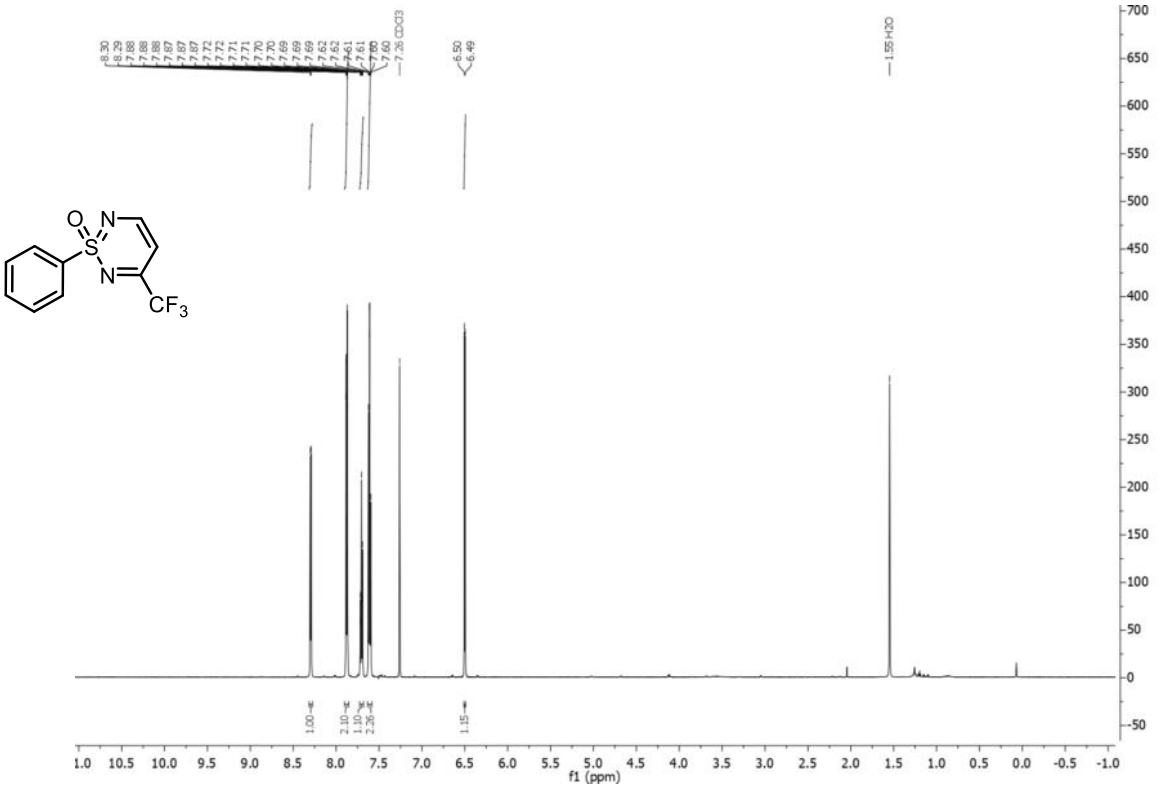
Stacked ^{13}C{^{1}H} DEPT NMR spectra (Chloroform-*d*, 151 MHz) of compound **5aa**



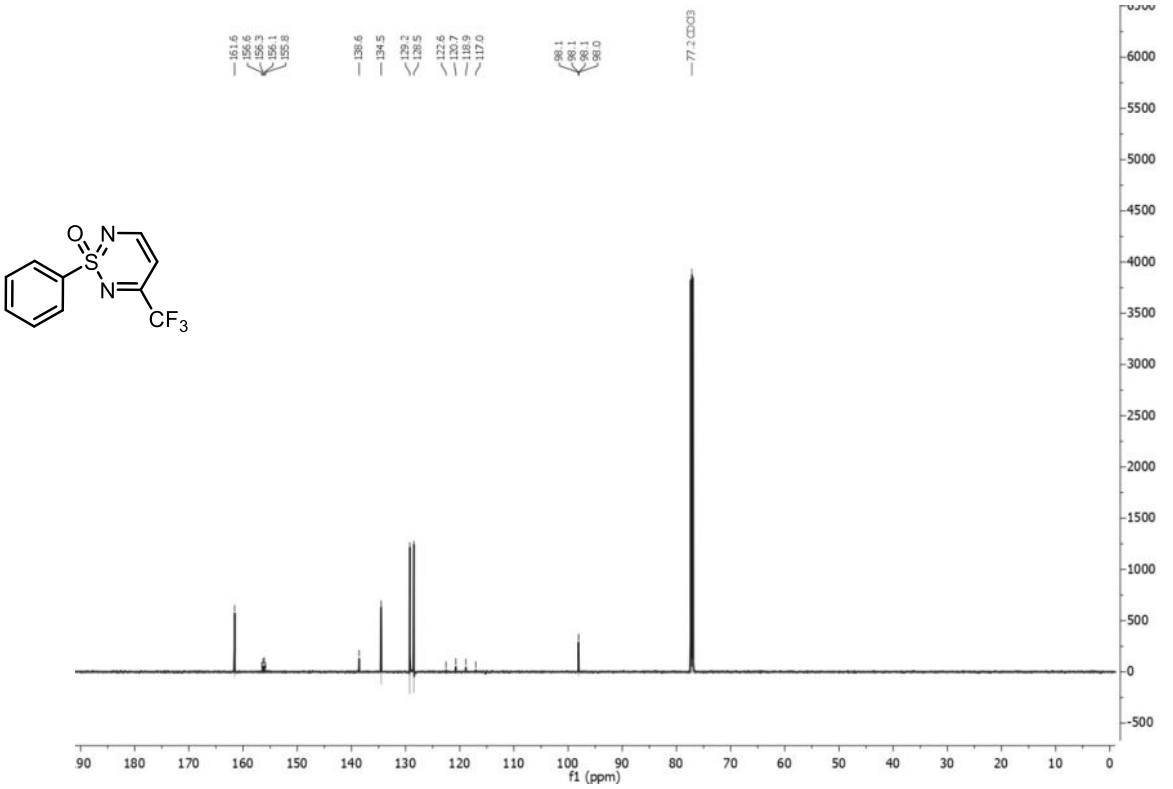
^{19}F NMR spectrum (Chloroform-*d*, 564 MHz) of compound **5aa**



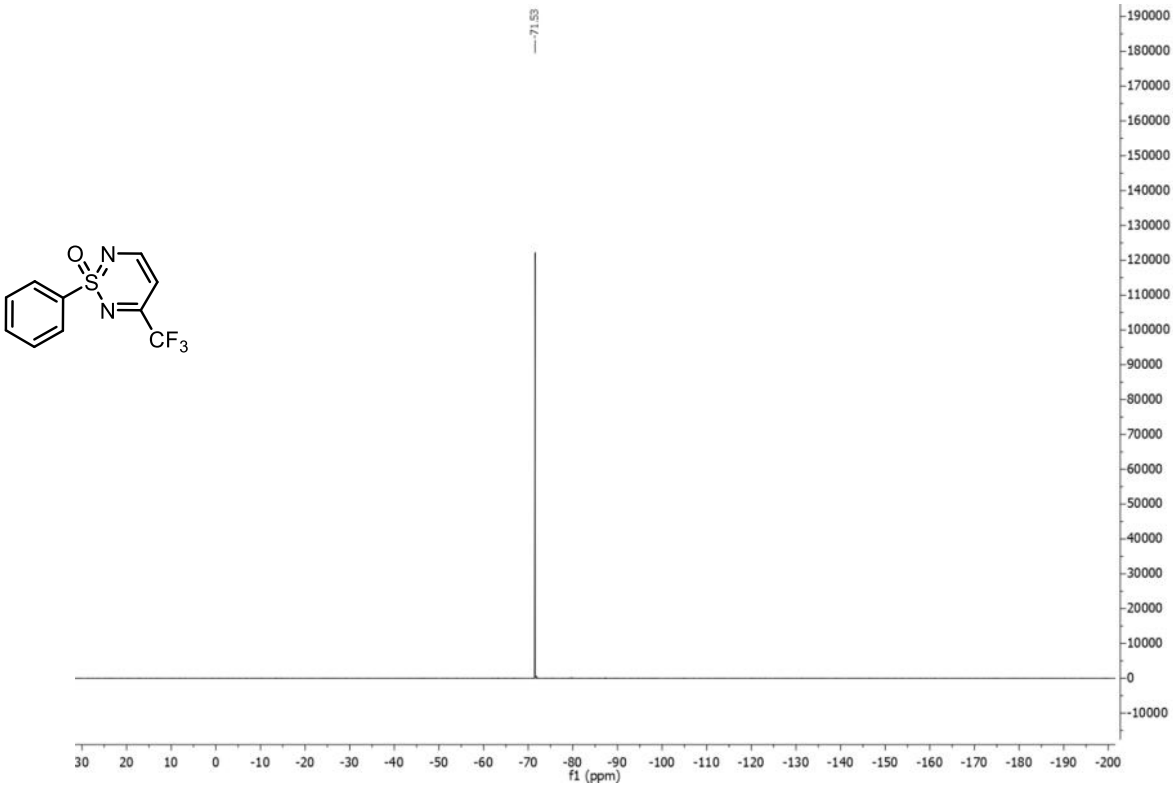
^{1}H NMR spectrum (Chloroform-*d*, 600 MHz) of compound **5ba**



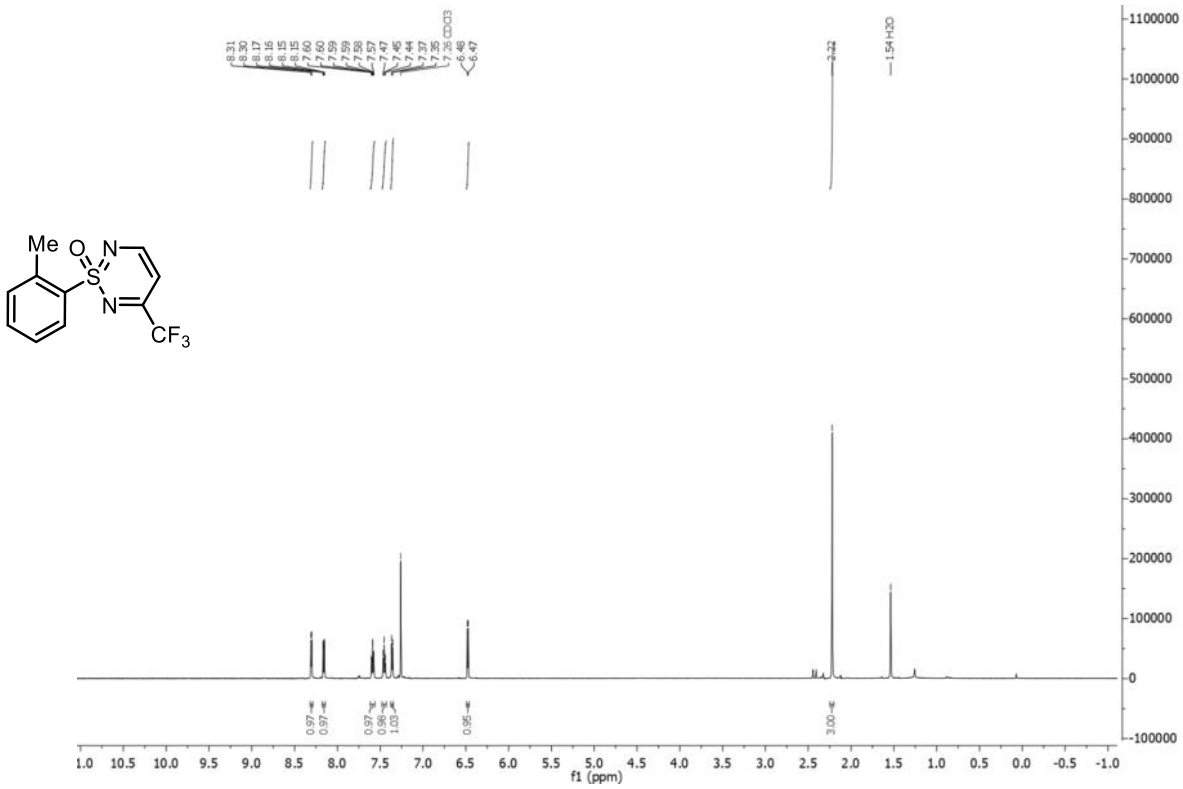
Stacked $^{13}C\{^{1}H\}$ DEPT NMR spectra (Chloroform-*d*, 151 MHz) of compound **5ba**



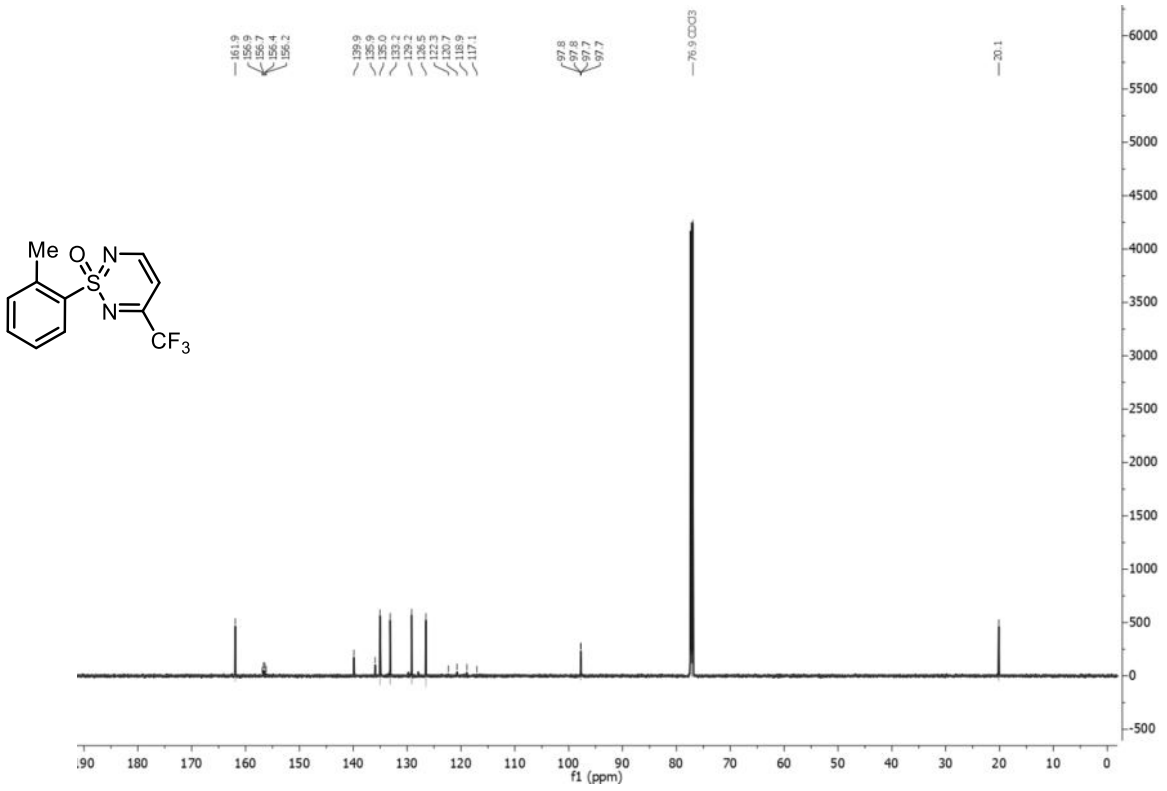
^{19}F NMR spectrum (Chloroform-*d*, 564 MHz) of compound **5ba**



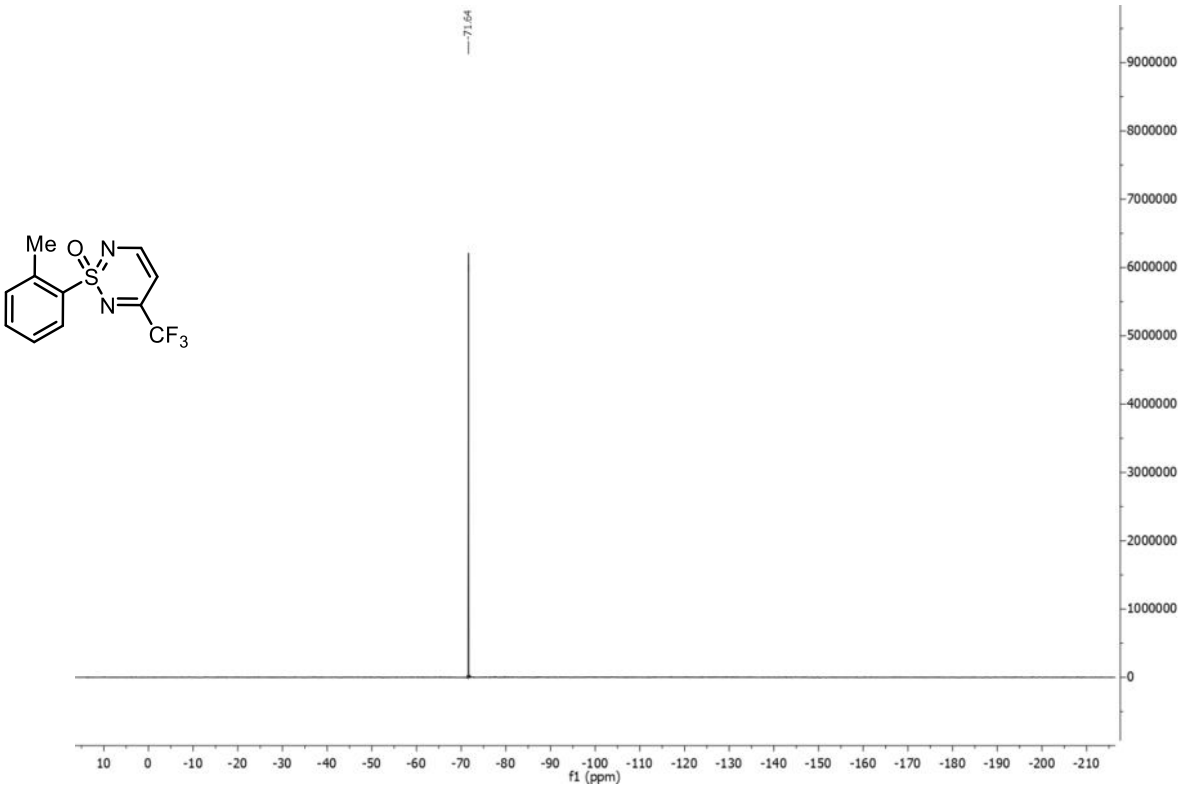
^{1}H NMR spectrum (Chloroform-*d*, 600 MHz) of compound **5ca**



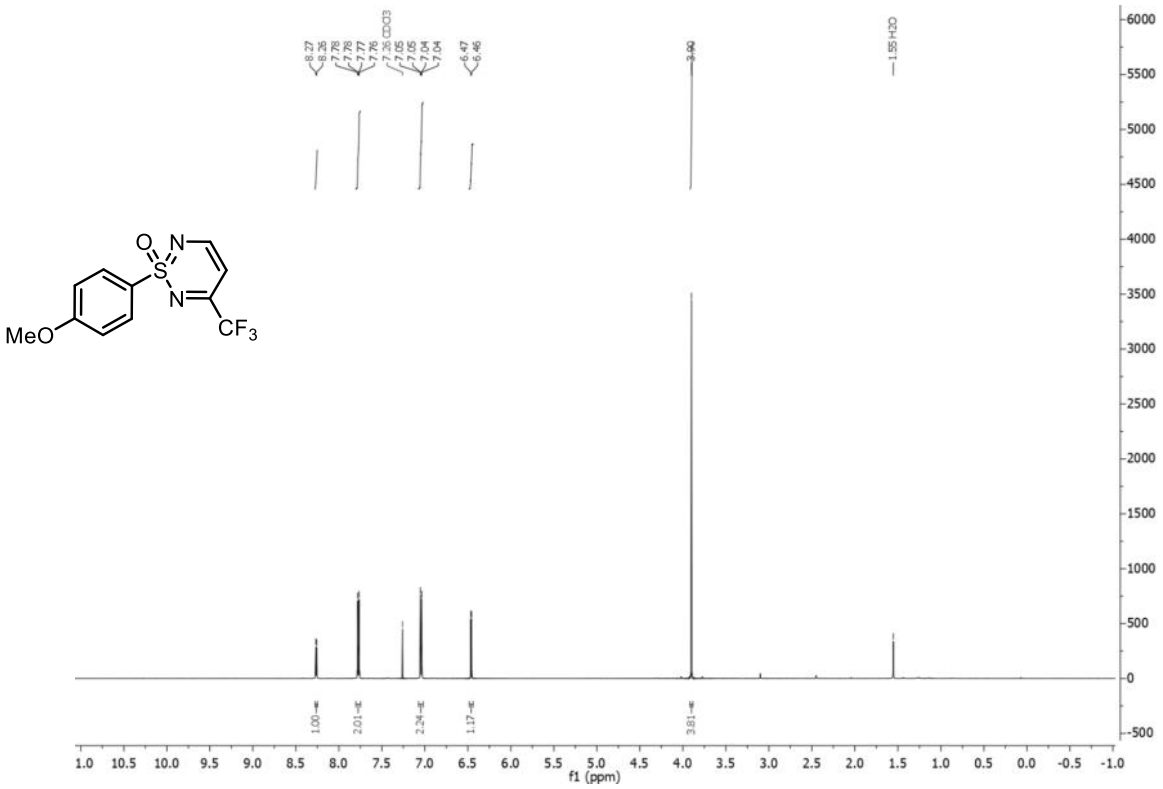
Stacked ^{13}C{^{1}H} DEPT NMR spectra (Chloroform-*d*, 151 MHz) of compound **5ca**



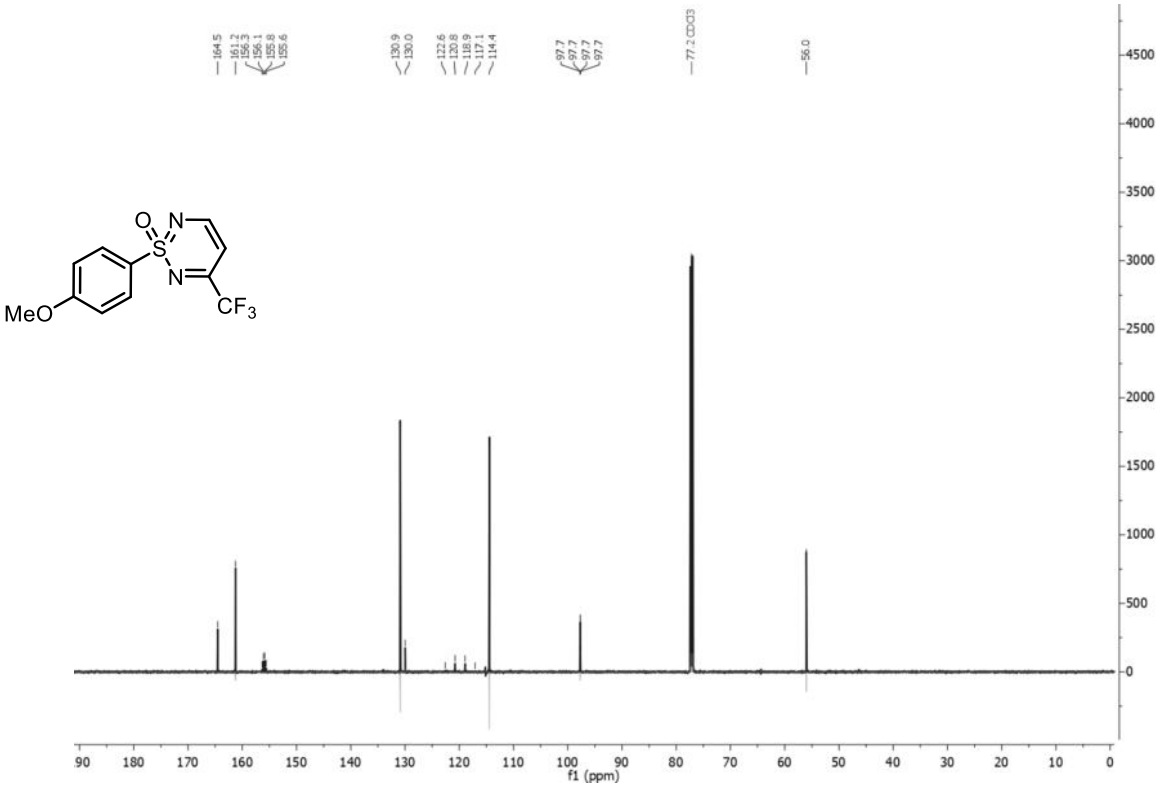
^{19}F NMR spectrum (Chloroform-*d*, 564 MHz) of compound **5ca**



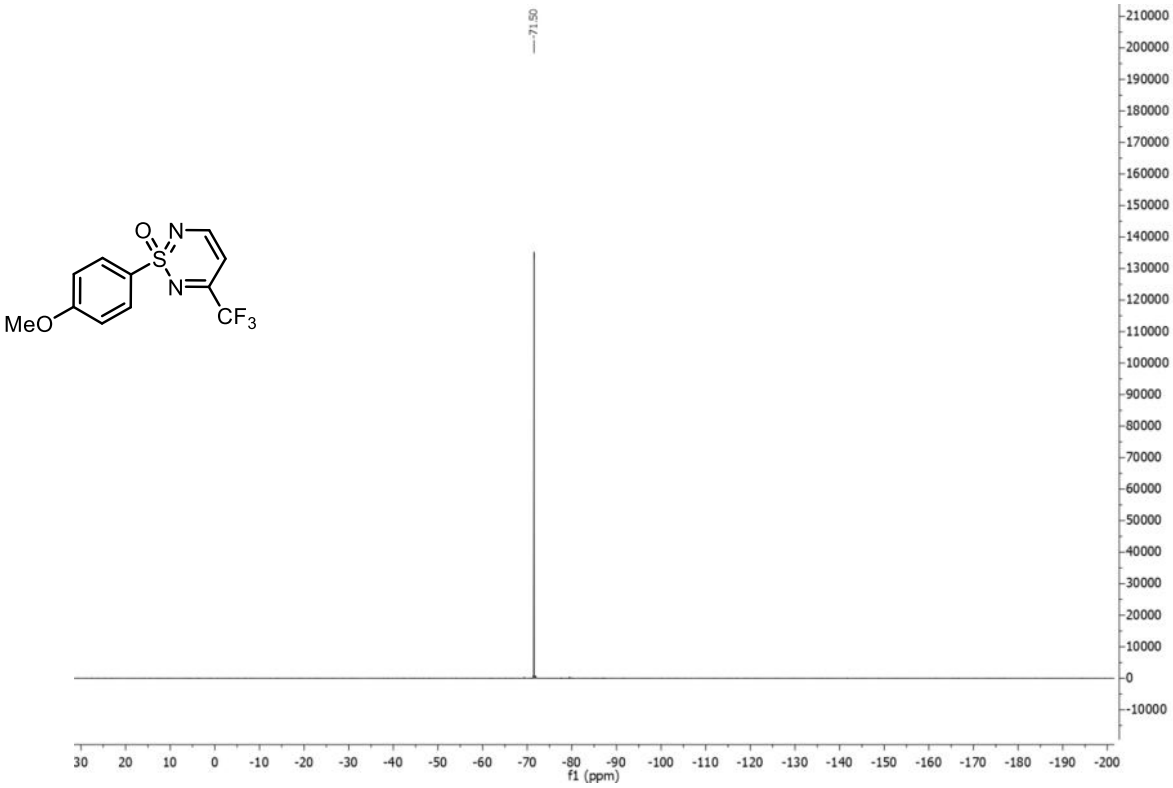
^{1}H NMR spectrum (Chloroform-*d*, 600 MHz) of compound **5da**



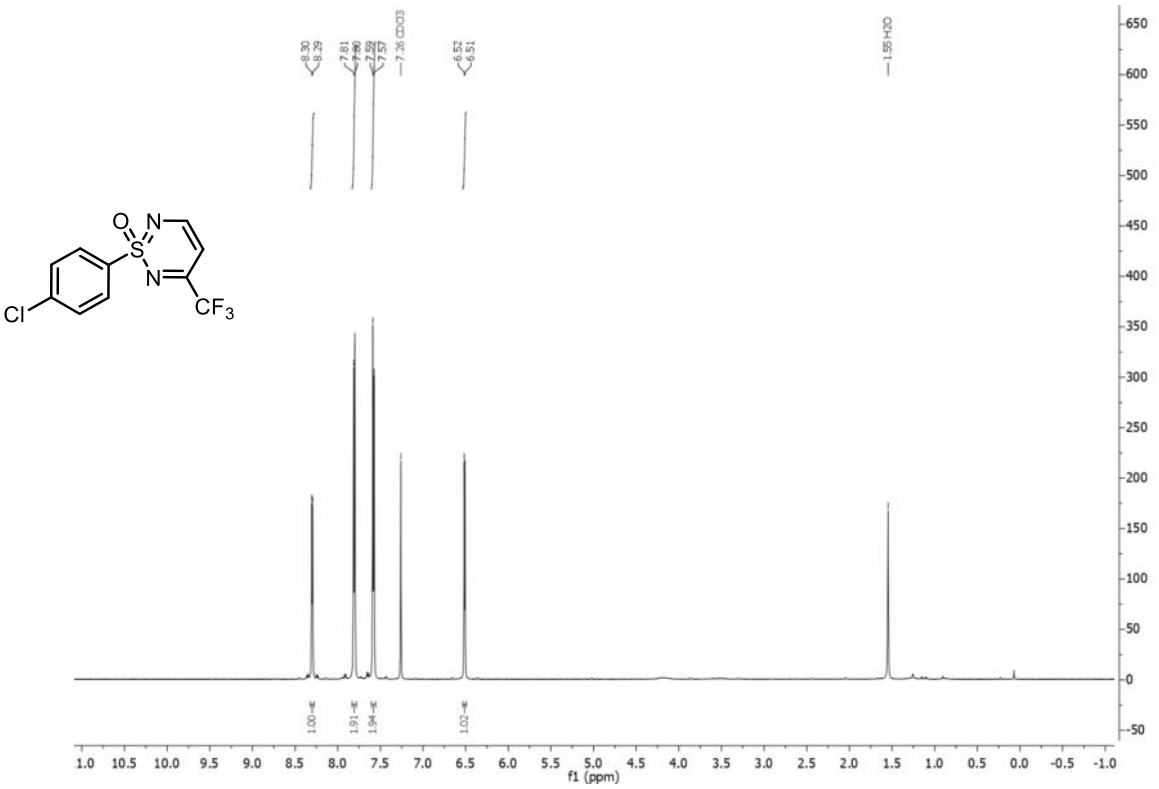
Stacked $^{13}C\{^{1}H\}$ DEPT NMR spectra (Chloroform-*d*, 151 MHz) of compound **5da**



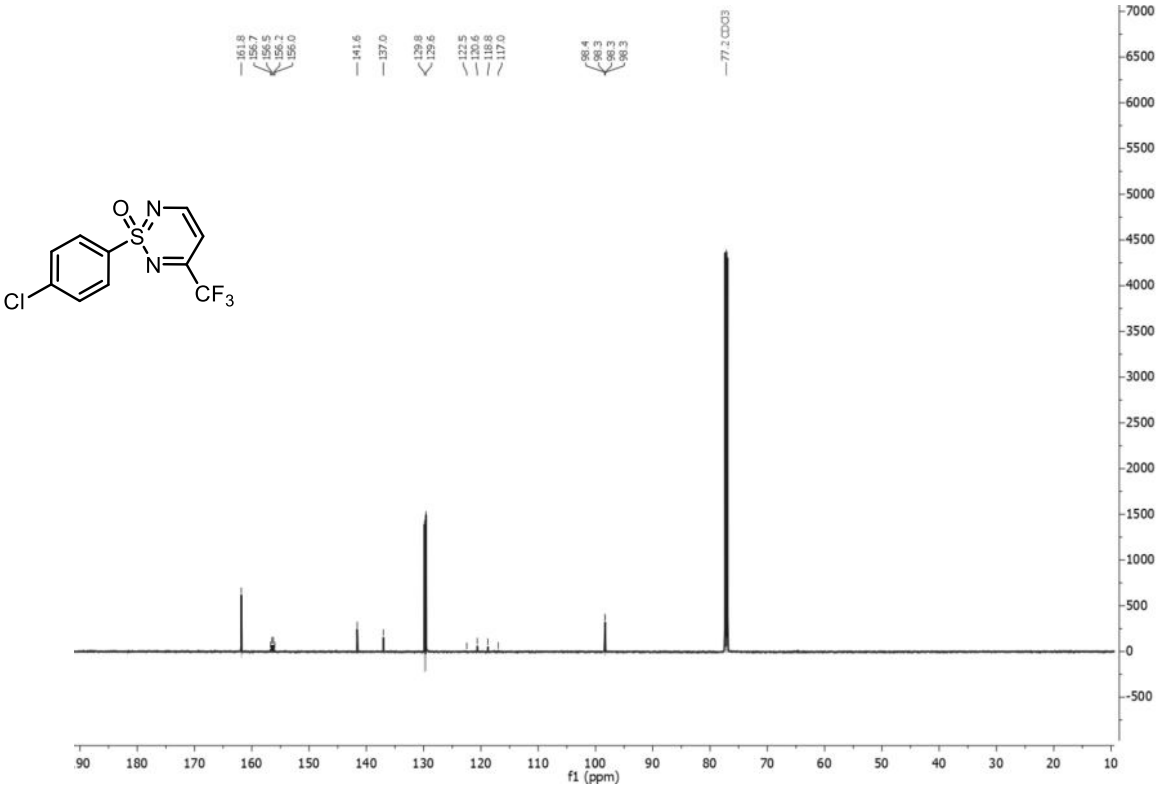
^{19}F NMR spectrum (Chloroform-*d*, 564 MHz) of compound **5da**



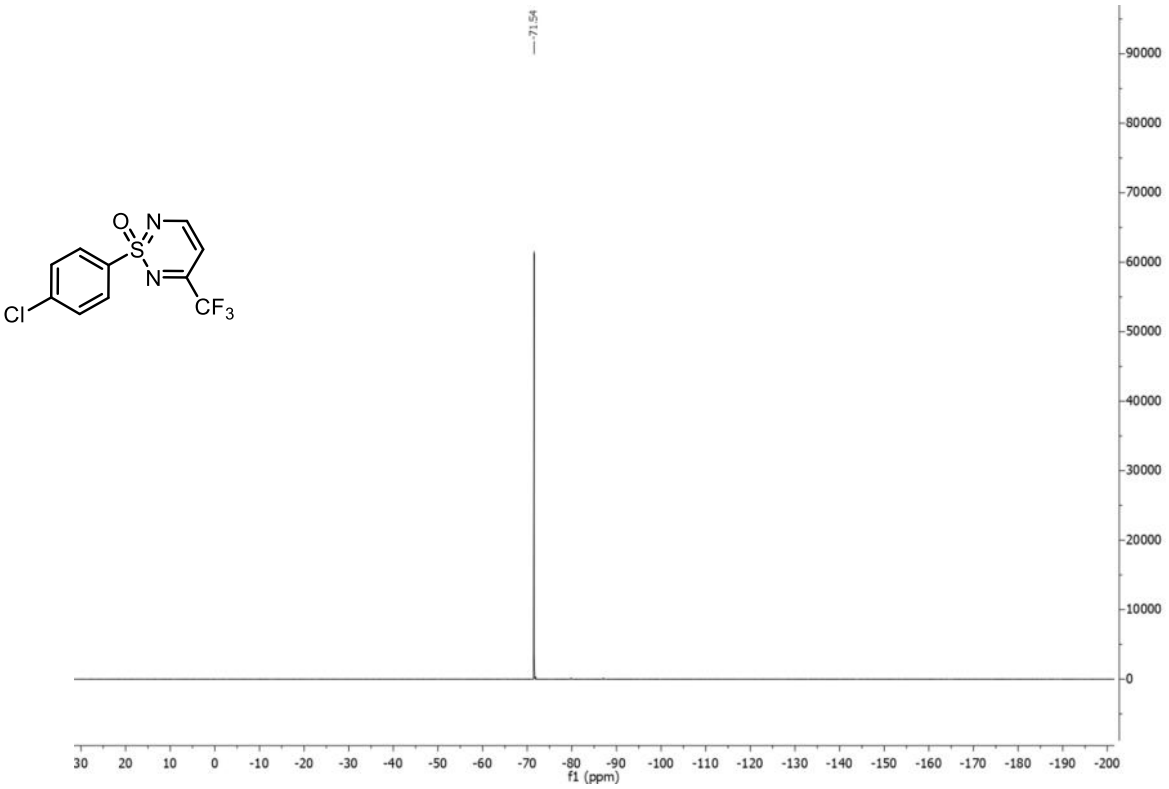
^{1}H NMR spectrum (Chloroform-*d*, 600 MHz) of compound **5ea**



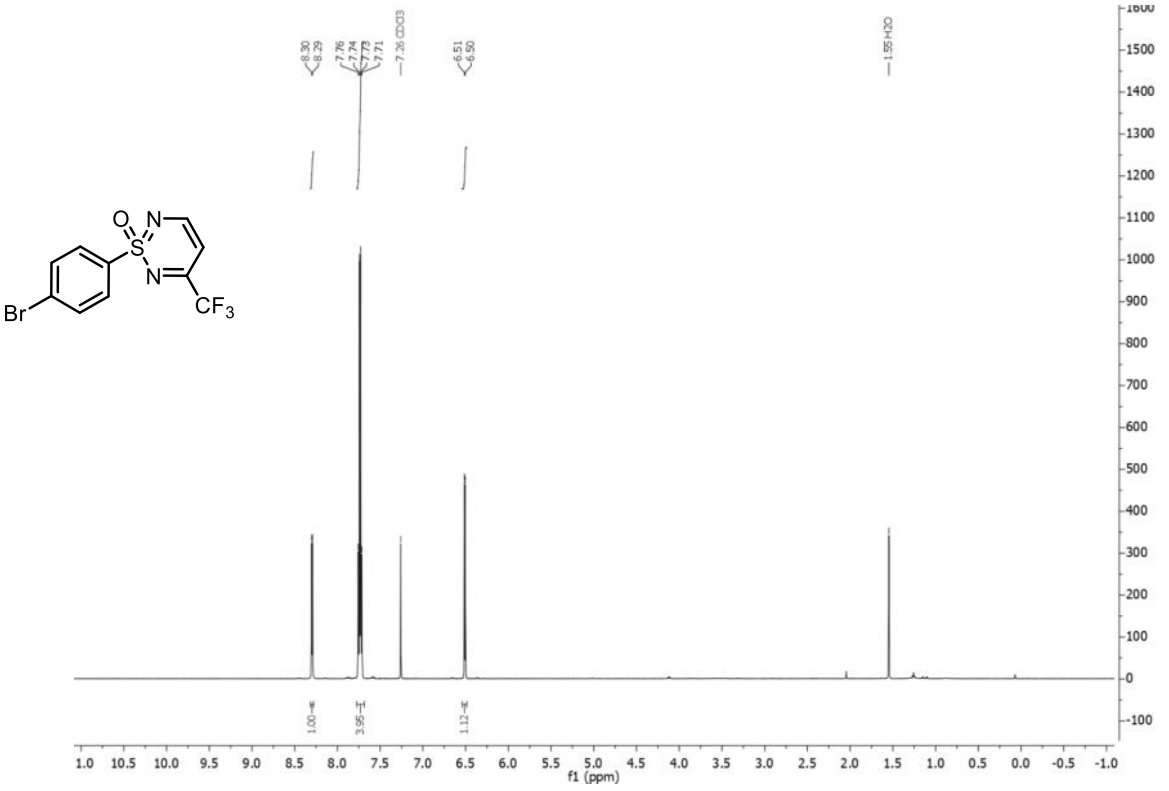
Stacked ^{13}C{^{1}H} DEPT NMR spectra (Chloroform-*d*, 151 MHz) of compound **5ea**



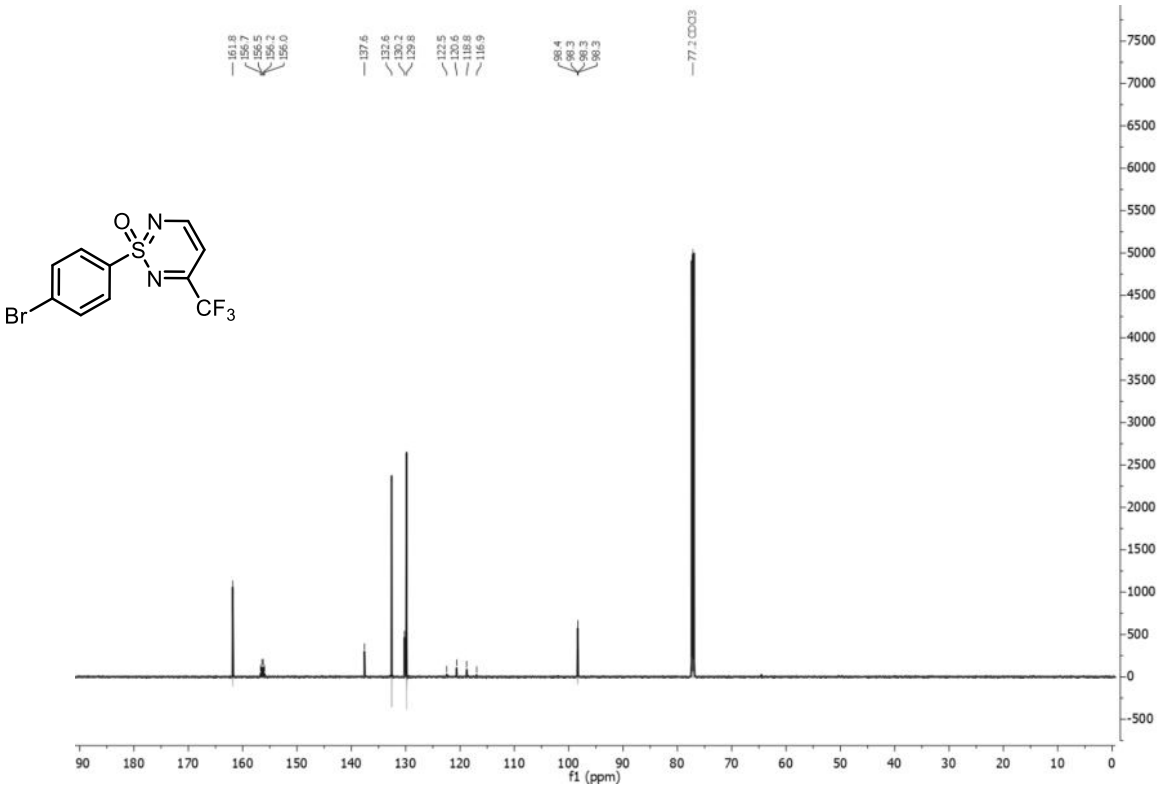
^{19}F NMR spectrum (Chloroform-*d*, 564 MHz) of compound **5ea**



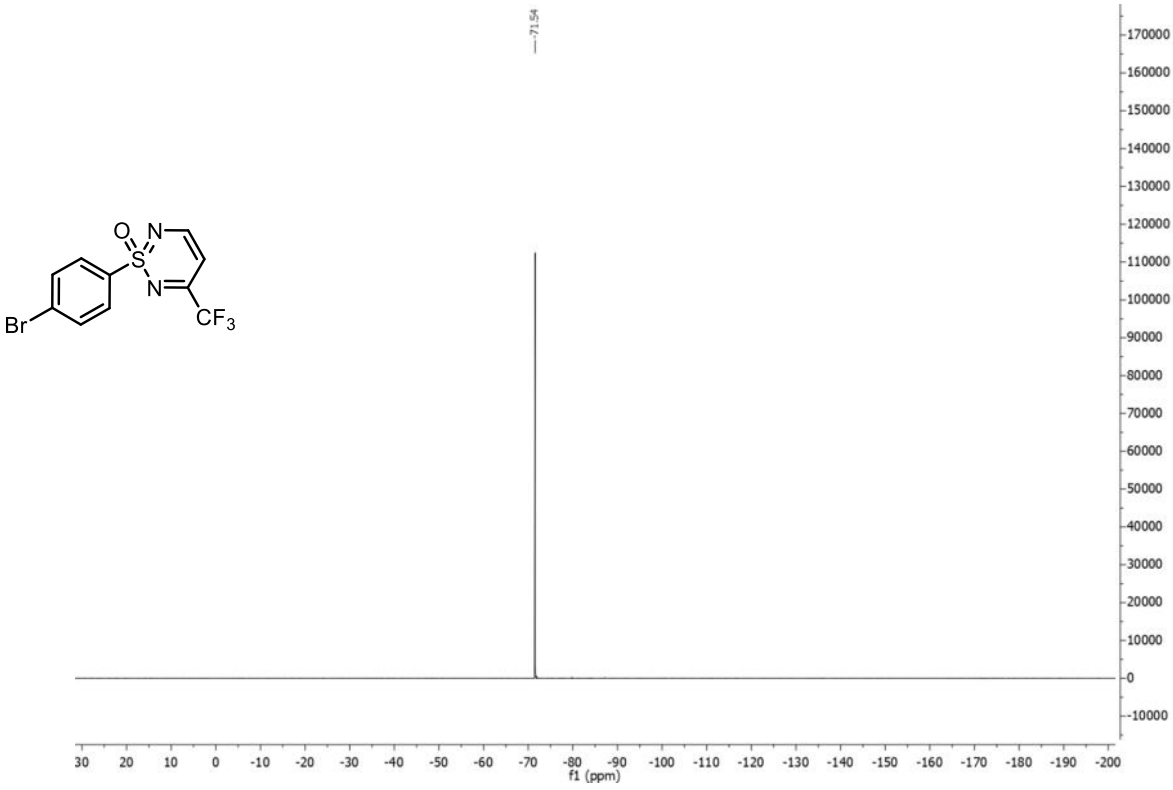
^{1}H NMR spectrum (Chloroform-*d*, 600 MHz) of compound **5fa**



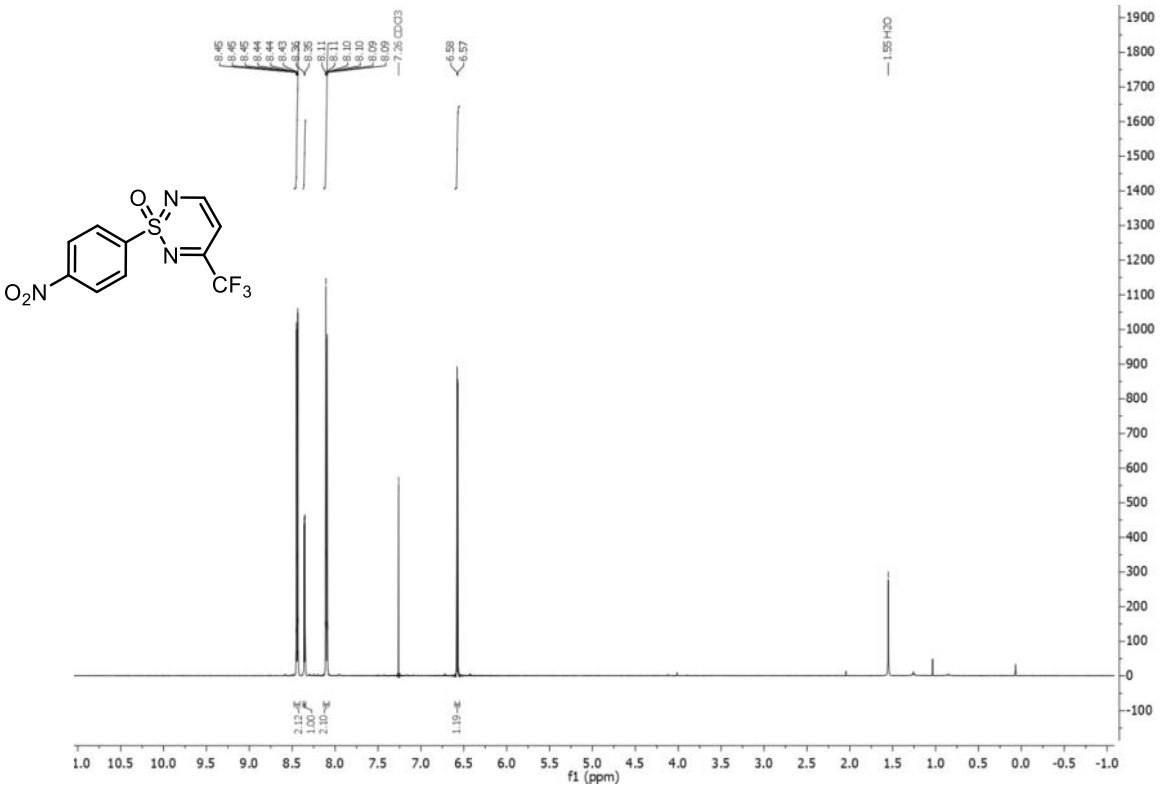
Stacked $^{13}C\{^{1}H\}$ DEPT NMR spectra (Chloroform-*d*, 151 MHz) of compound **5fa**



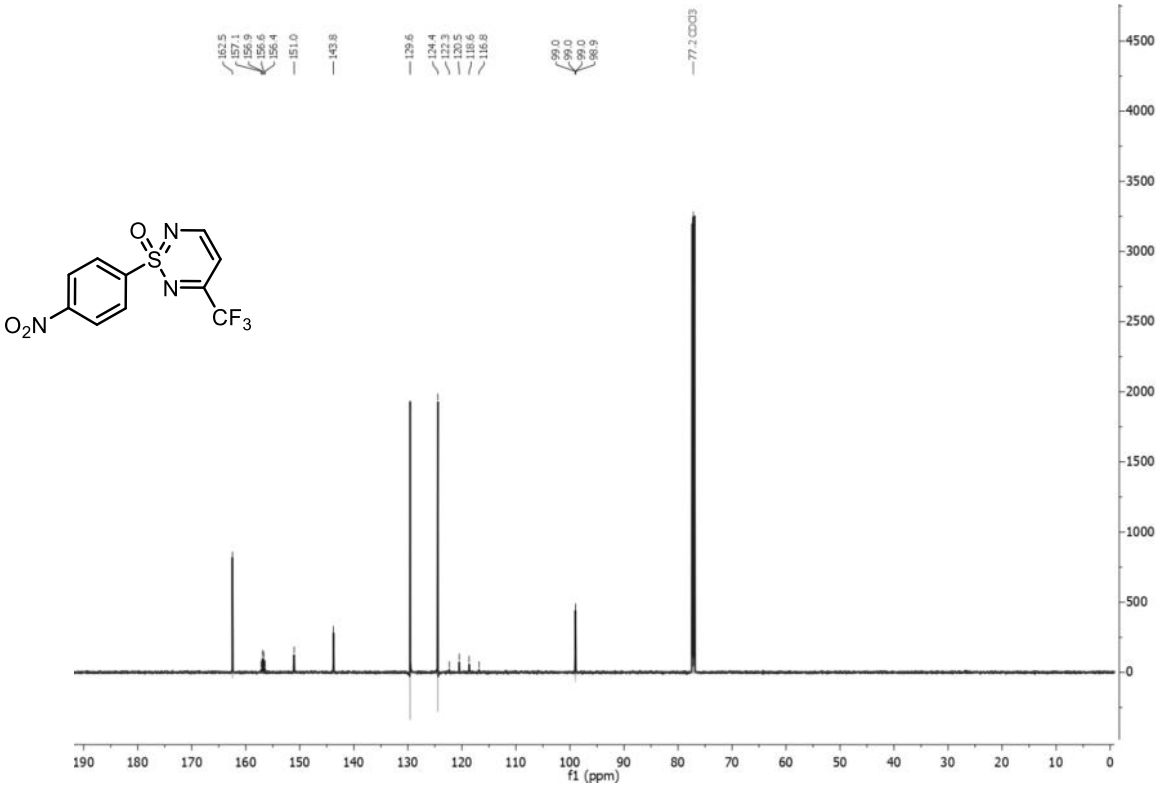
^{19}F NMR spectrum (Chloroform-*d*, 564 MHz) of compound **5fa**



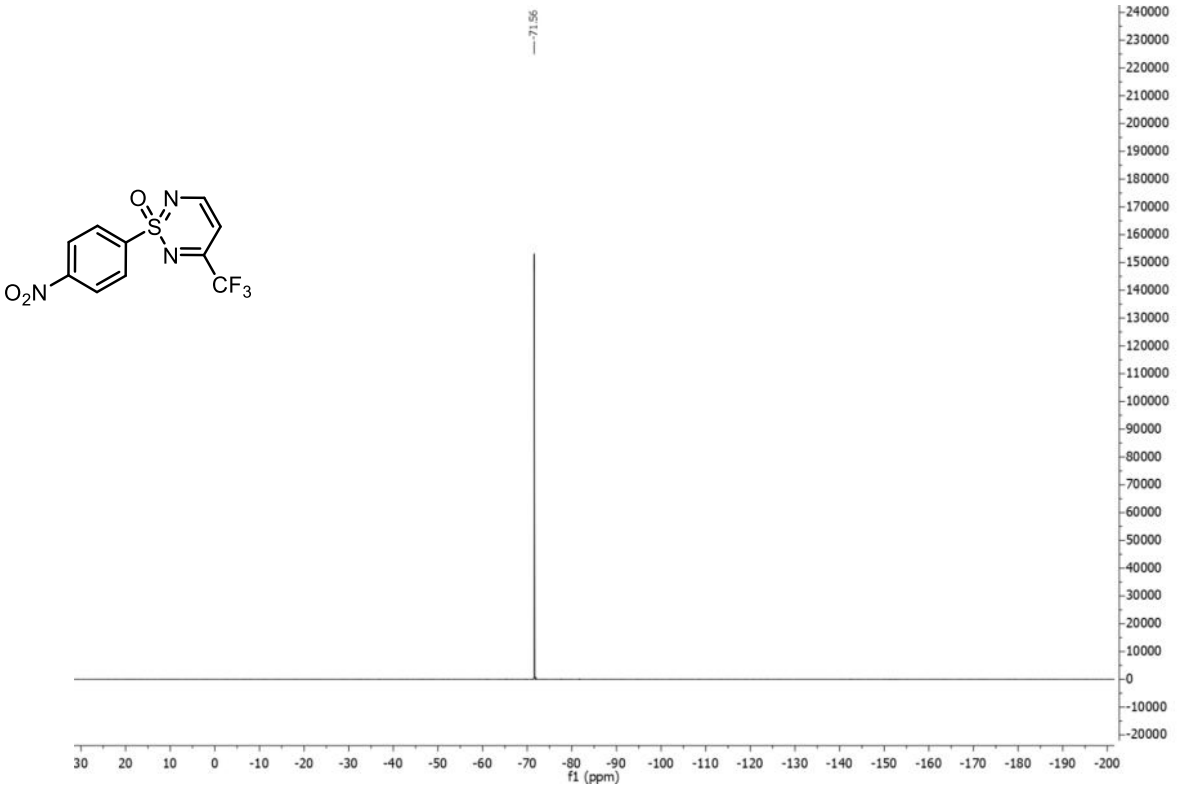
^{1}H NMR spectrum (Chloroform-*d*, 600 MHz) of compound **5ga**



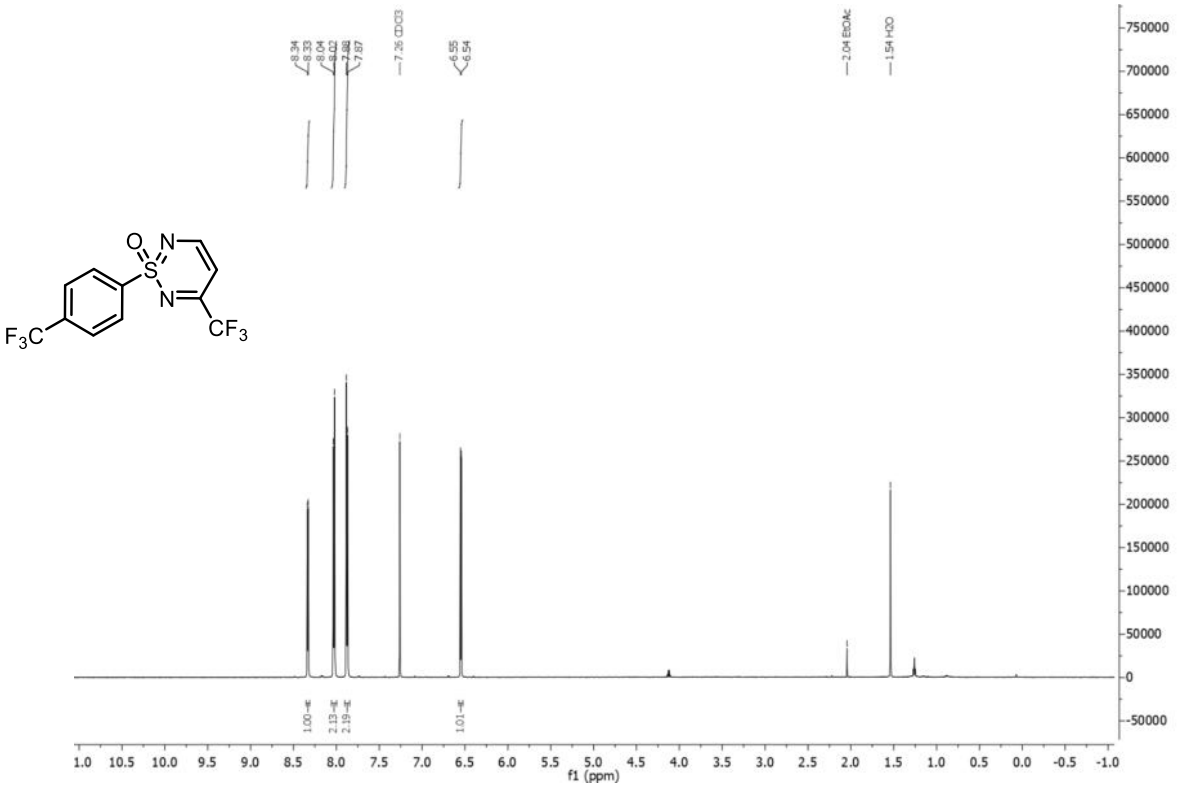
Stacked ^{13}C{^{1}H} DEPT NMR spectra (Chloroform-*d*, 151 MHz) of compound **5ga**



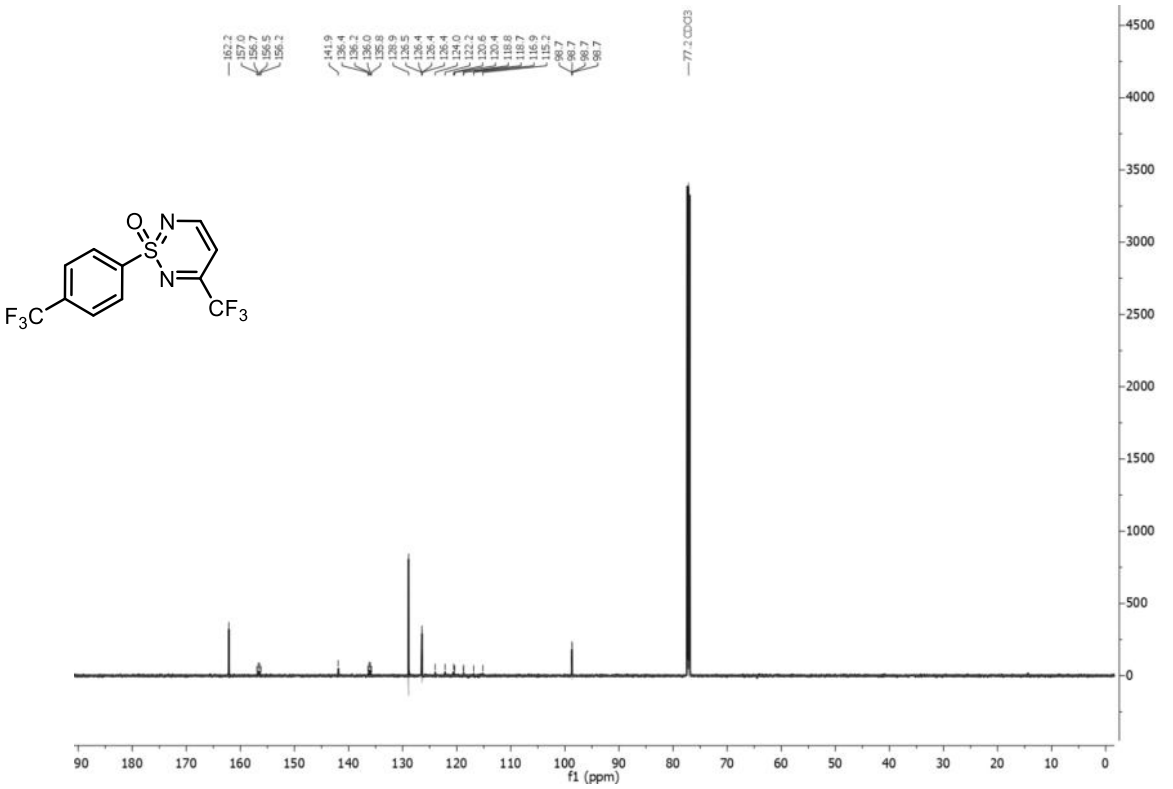
^{19}F NMR spectrum (Chloroform-*d*, 564 MHz) of compound **5ga**



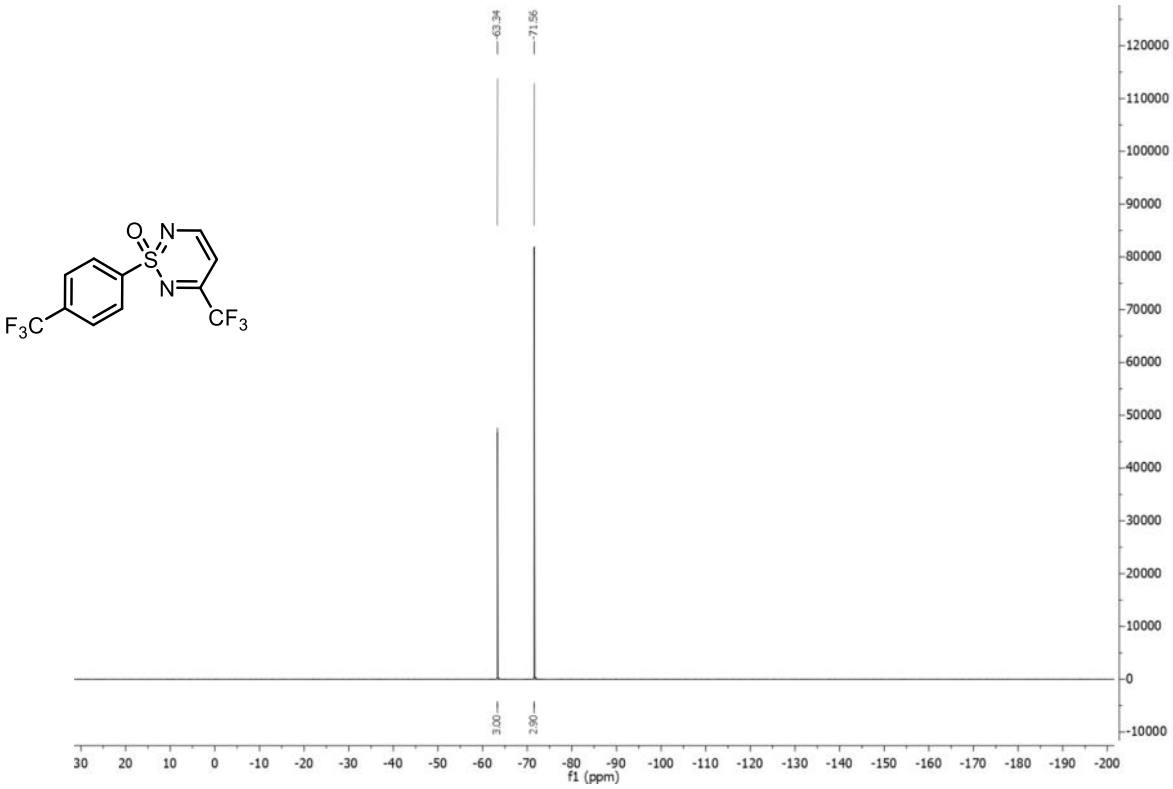
^{1}H NMR spectrum (Chloroform-*d*, 600 MHz) of compound **5ha**



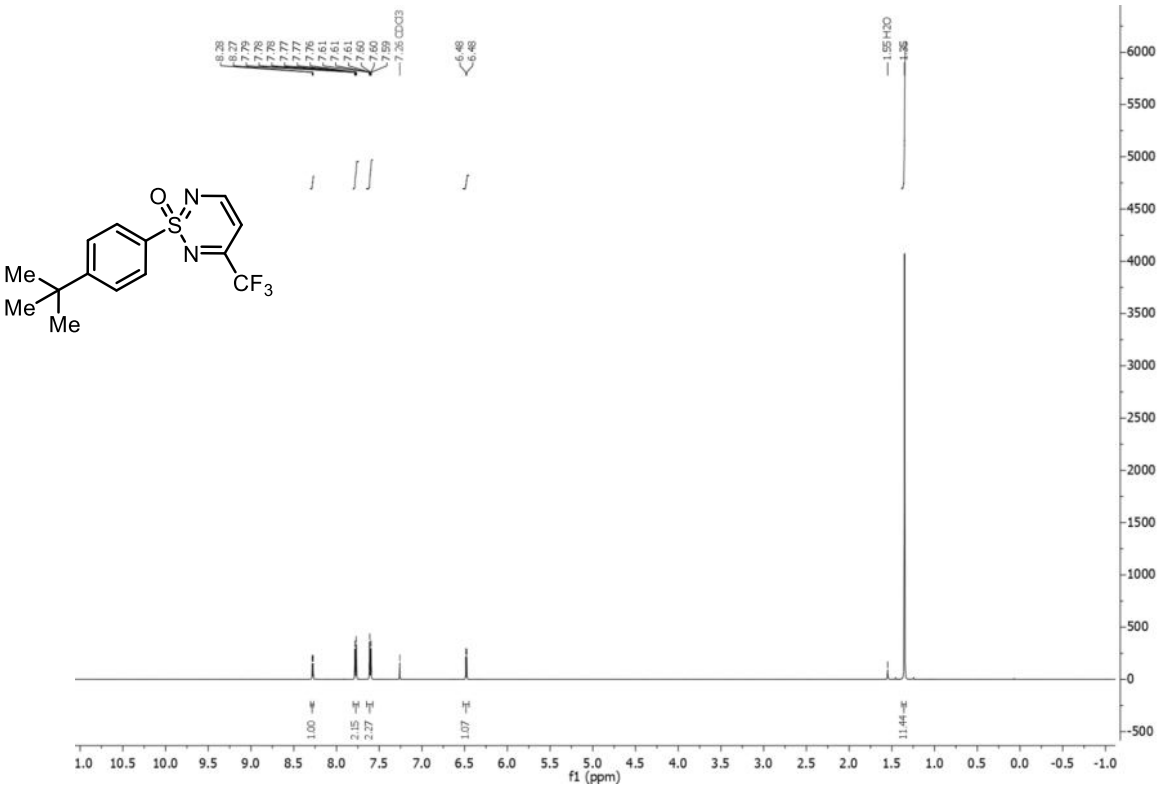
Stacked $^{13}C\{^{1}H\}$ DEPT NMR spectra (Chloroform-*d*, 151 MHz) of compound **5ha**



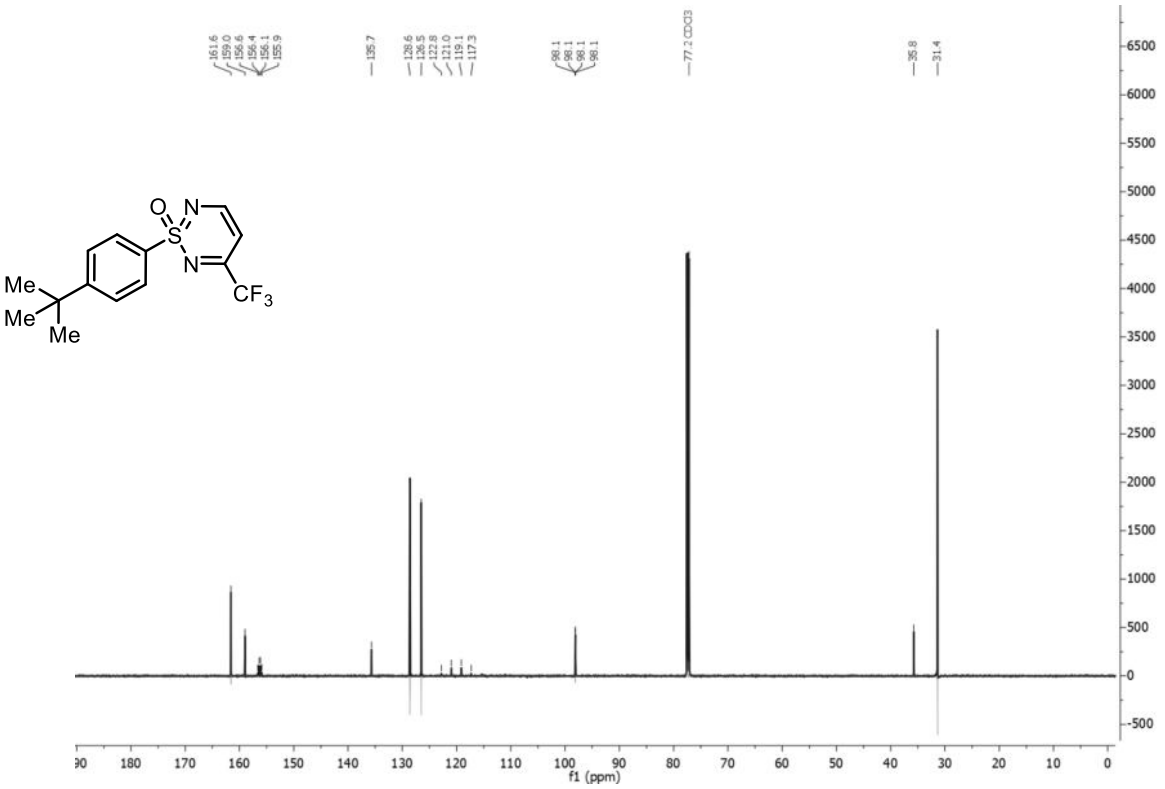
^{19}F NMR spectrum (Chloroform-*d*, 564 MHz) of compound **5ha**



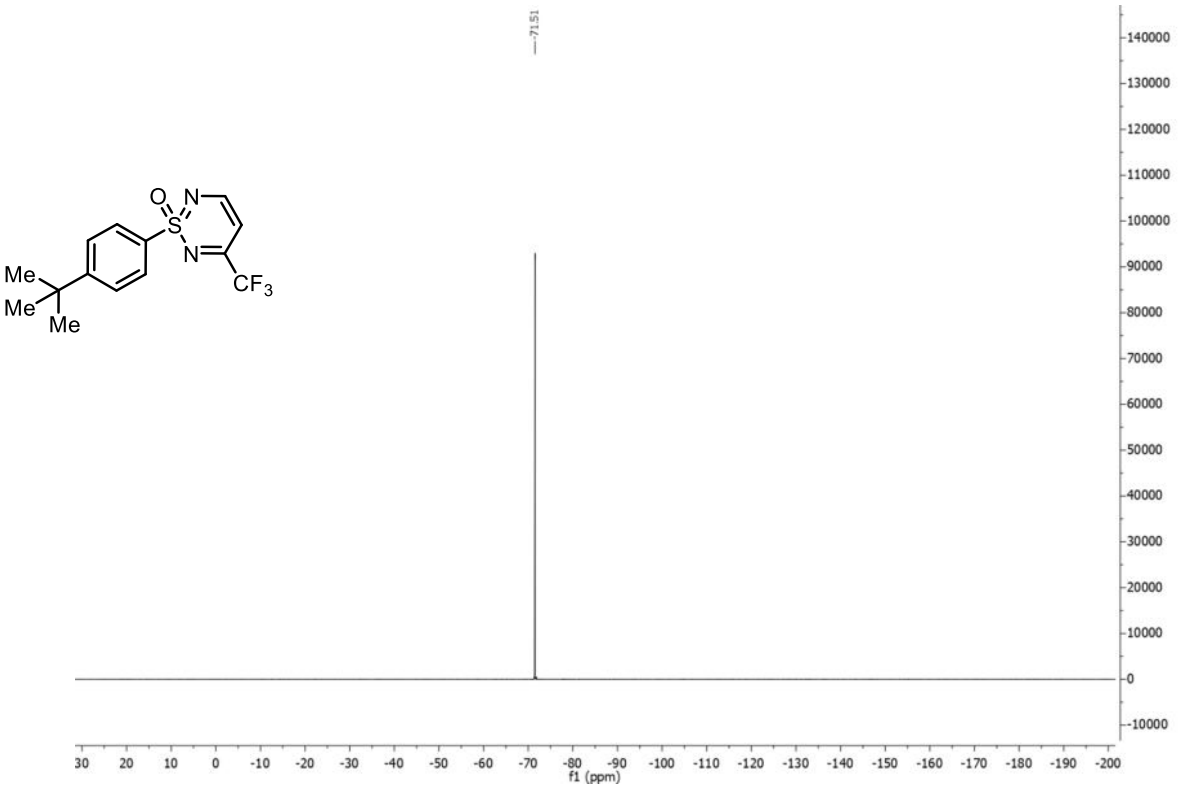
^{1}H NMR spectrum (Chloroform-*d*, 600 MHz) of compound **5ia**



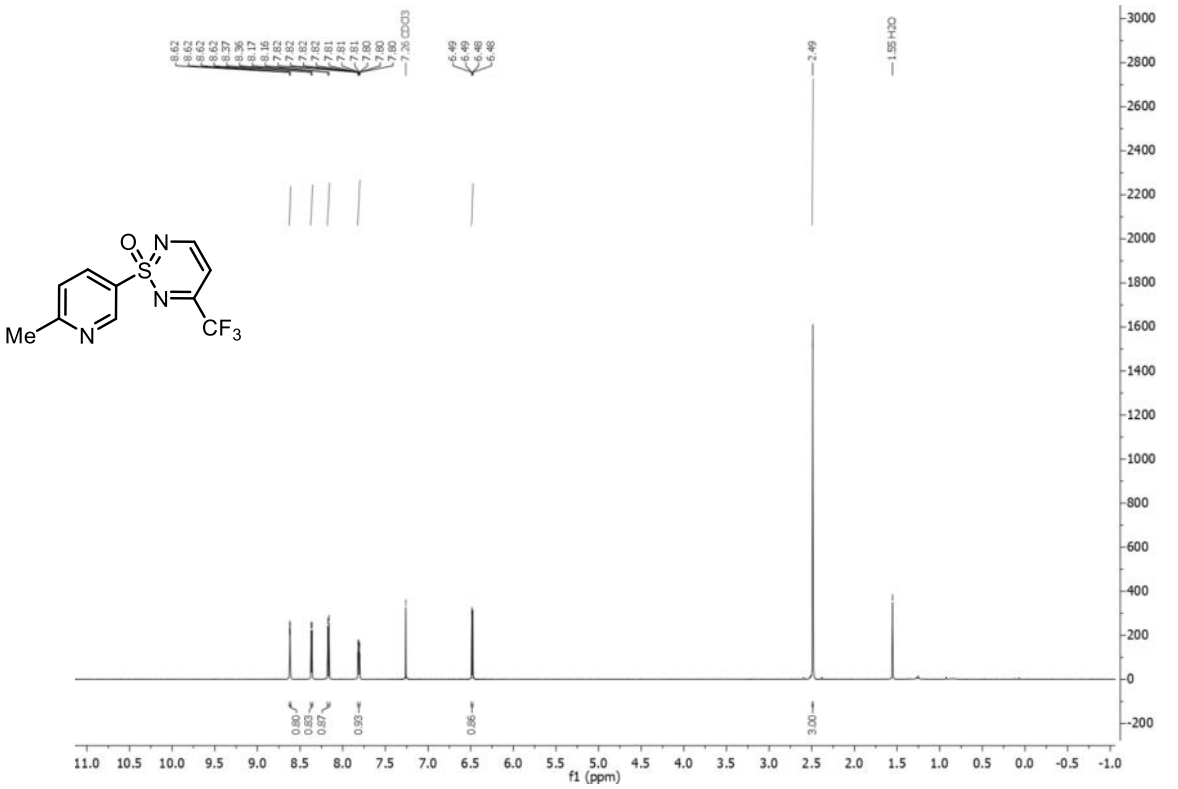
Stacked ^{13}C{^{1}H} DEPT NMR spectra (Chloroform-*d*, 151 MHz) of compound **5ia**



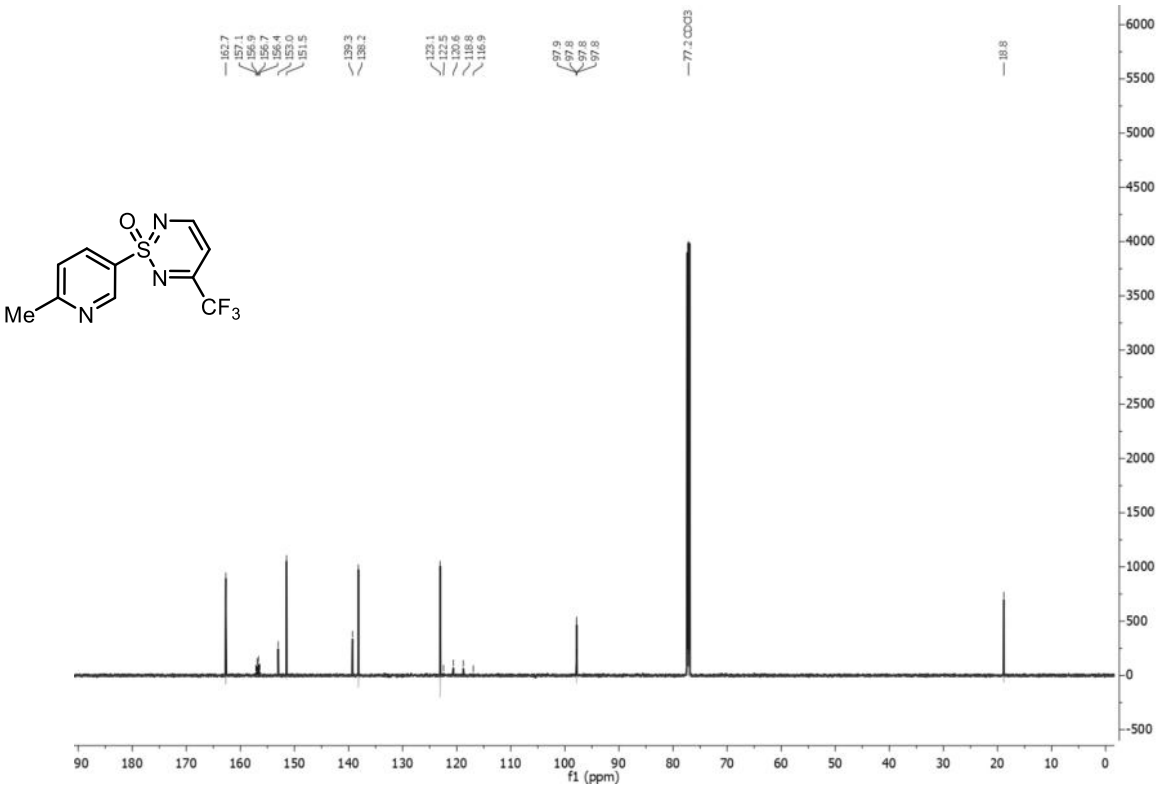
^{19}F NMR spectrum (Chloroform-*d*, 564 MHz) of compound **5ia**



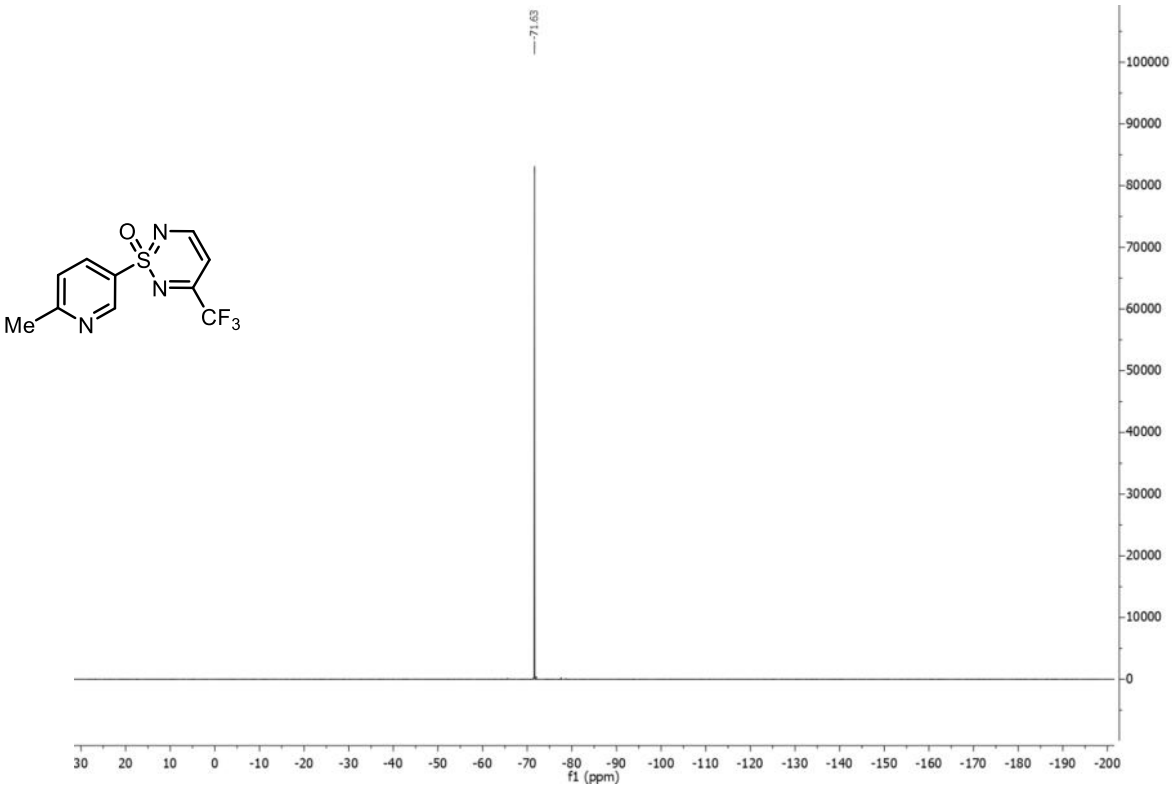
^{1}H NMR spectrum (Chloroform-*d*, 600 MHz) of compound **5ja**



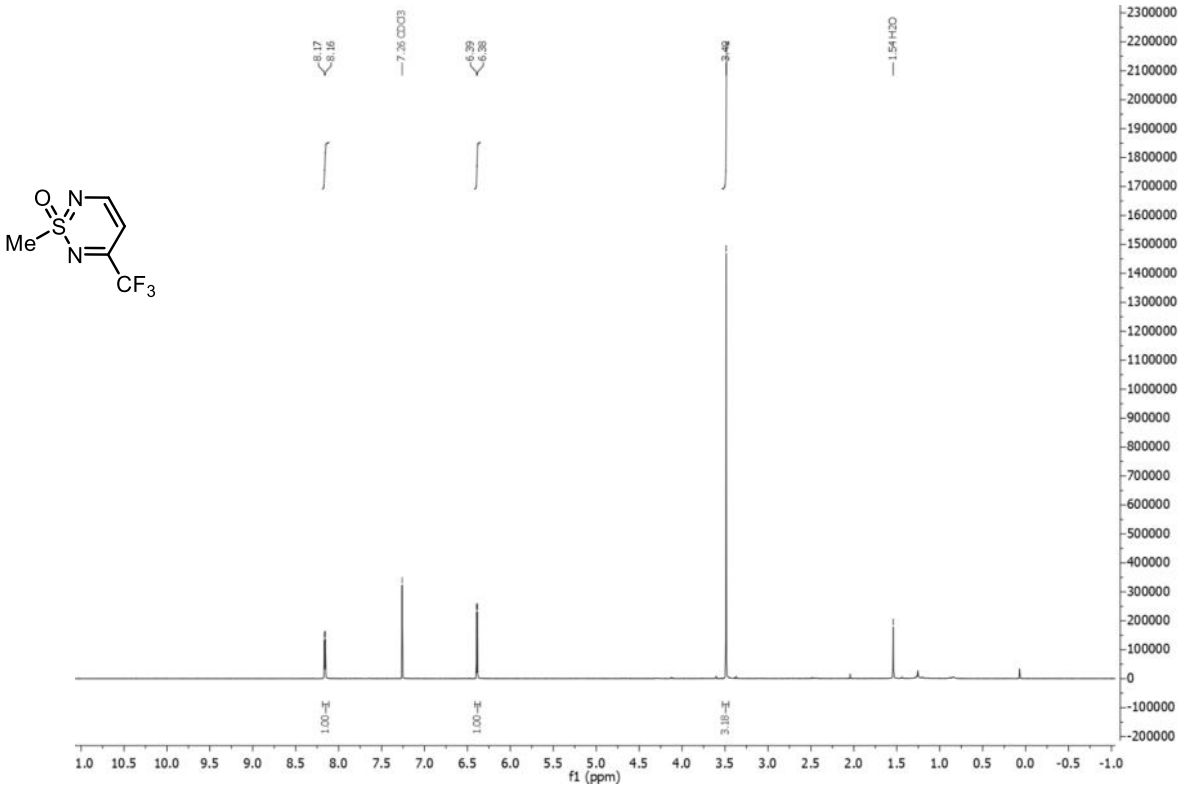
Stacked $^{13}C\{^{1}H\}$ DEPT NMR spectra (Chloroform-*d*, 151 MHz) of compound **5ja**



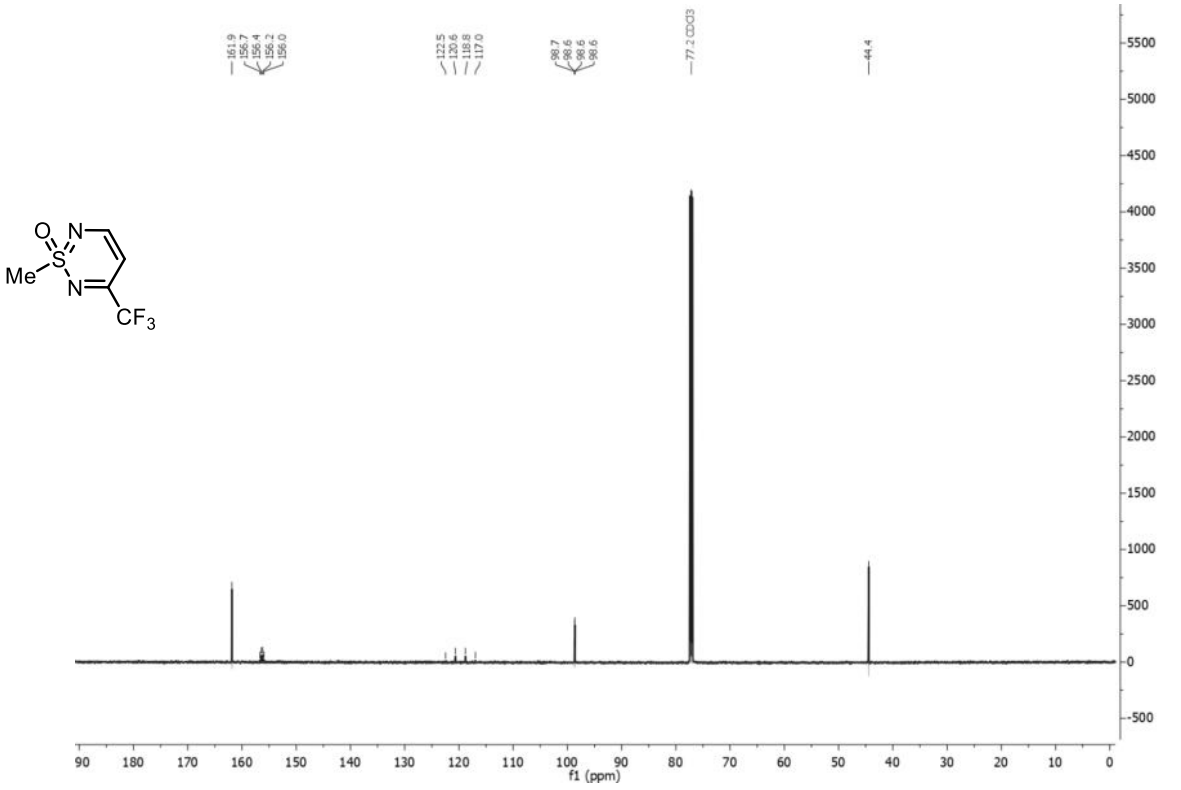
^{19}F NMR spectrum (Chloroform-*d*, 564 MHz) of compound **5ja**



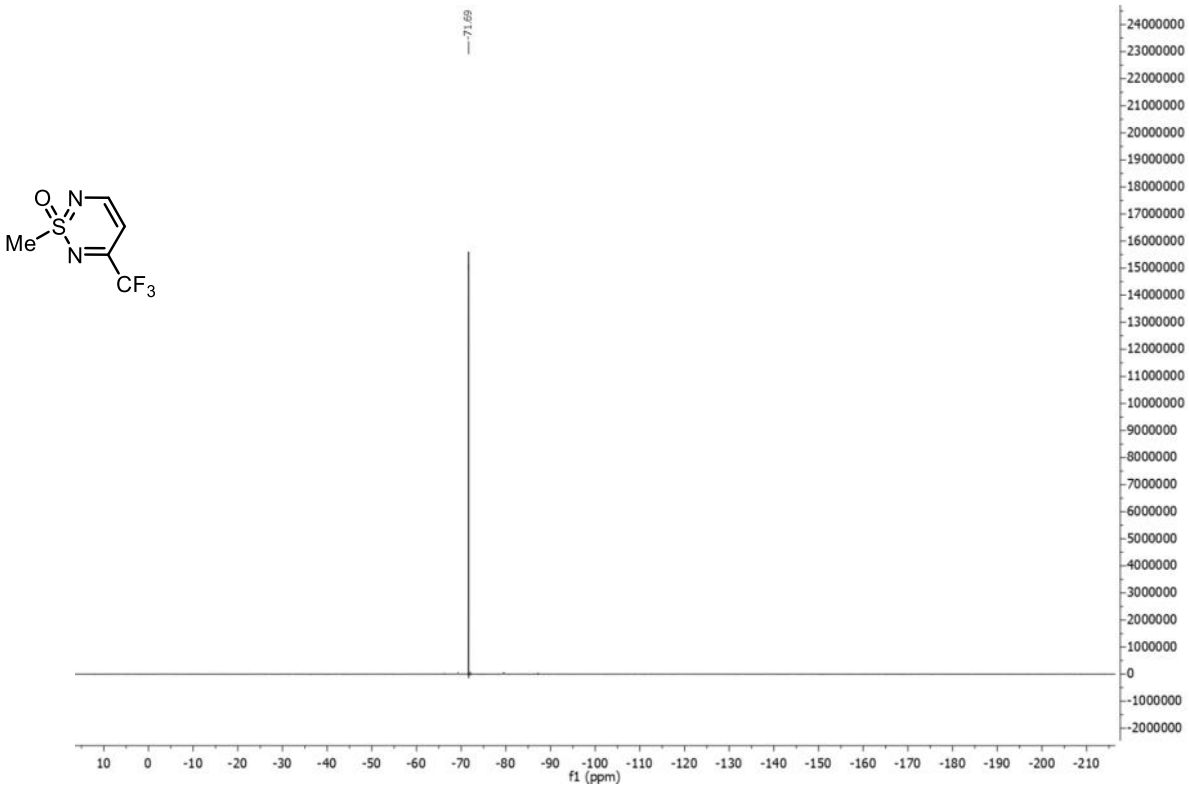
^{1}H NMR spectrum (Chloroform-*d*, 600 MHz) of compound **5ka**



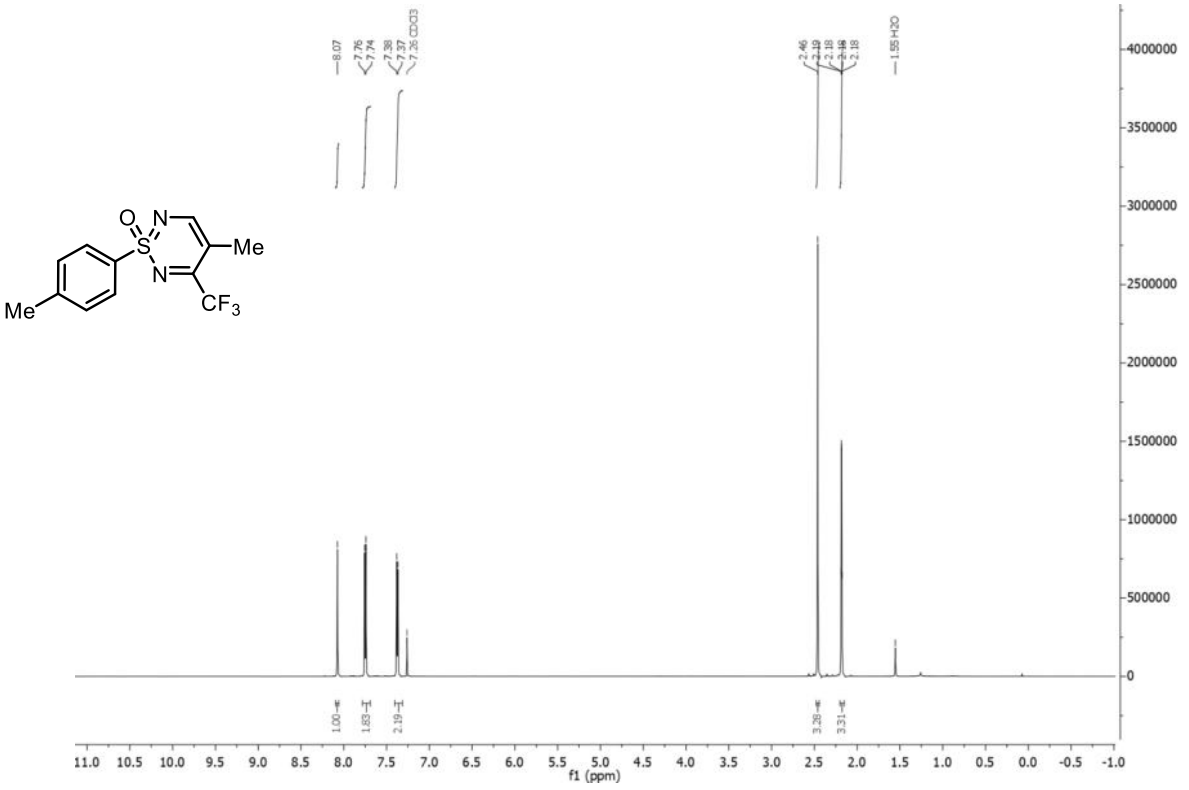
Stacked ^{13}C{^{1}H} DEPT NMR spectra (Chloroform-*d*, 151 MHz) of compound **5ka**



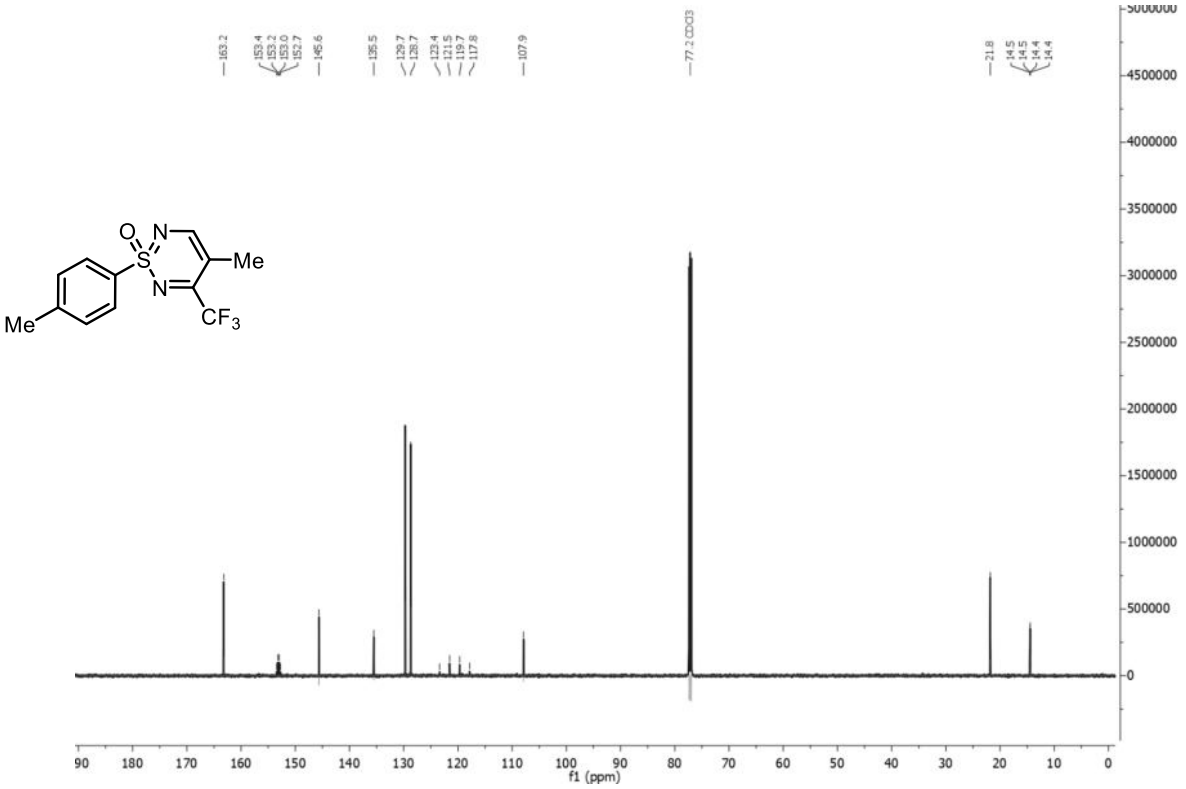
^{19}F NMR spectrum (Chloroform-*d*, 564 MHz) of compound **5ka**



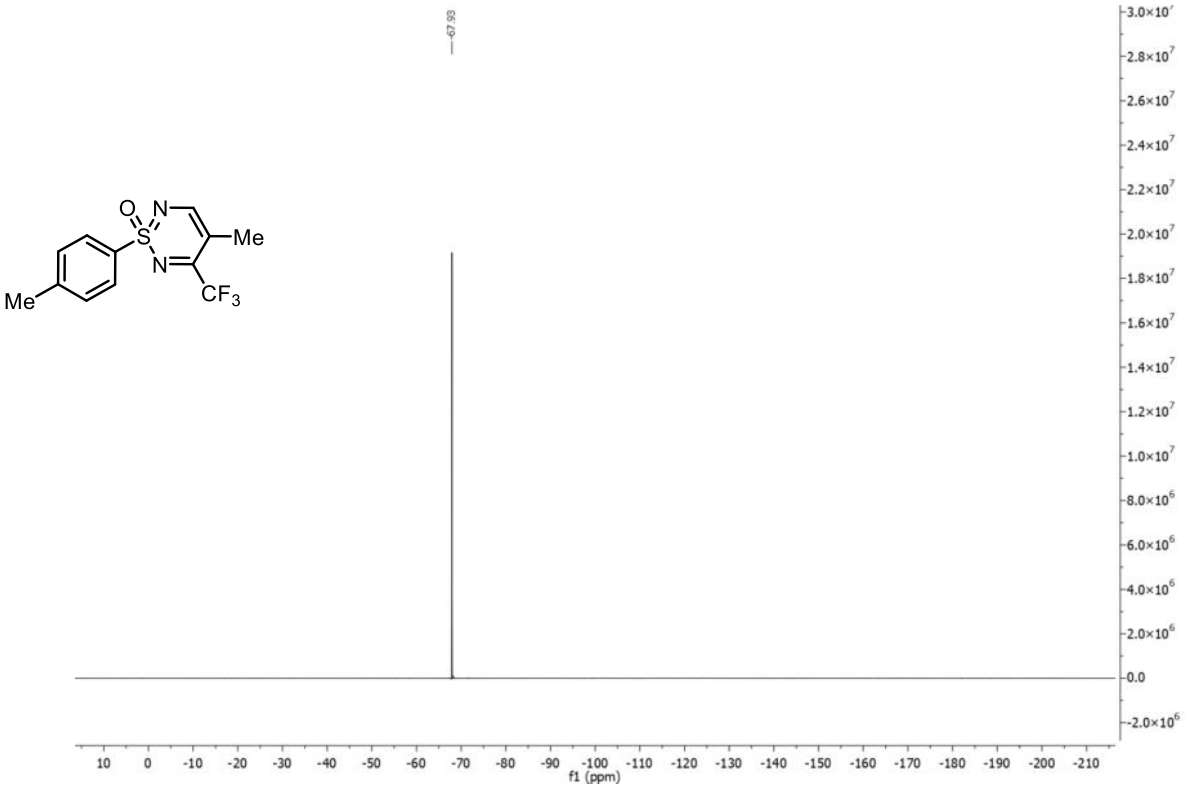
^{1}H NMR spectrum (Chloroform-*d*, 600 MHz) of compound **5ac**



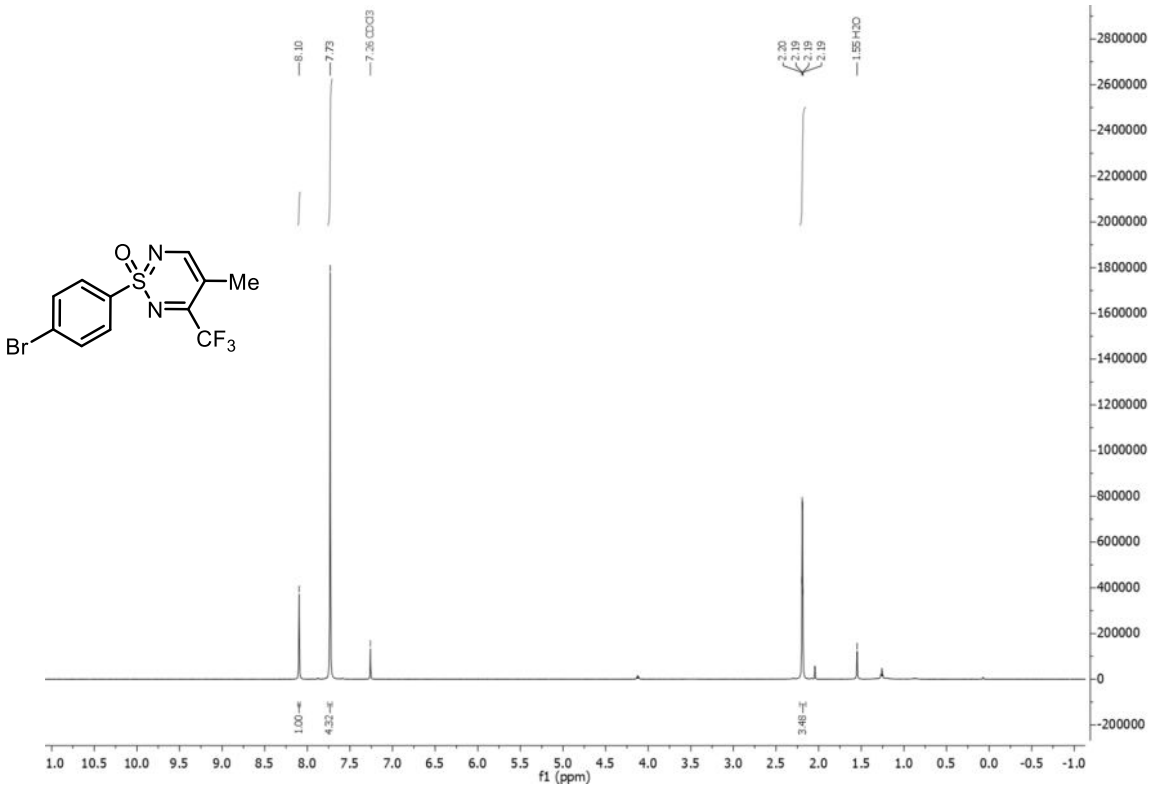
Stacked $^{13}C\{^{1}H\}$ DEPT NMR spectra (Chloroform-*d*, 151 MHz) of compound **5ac**



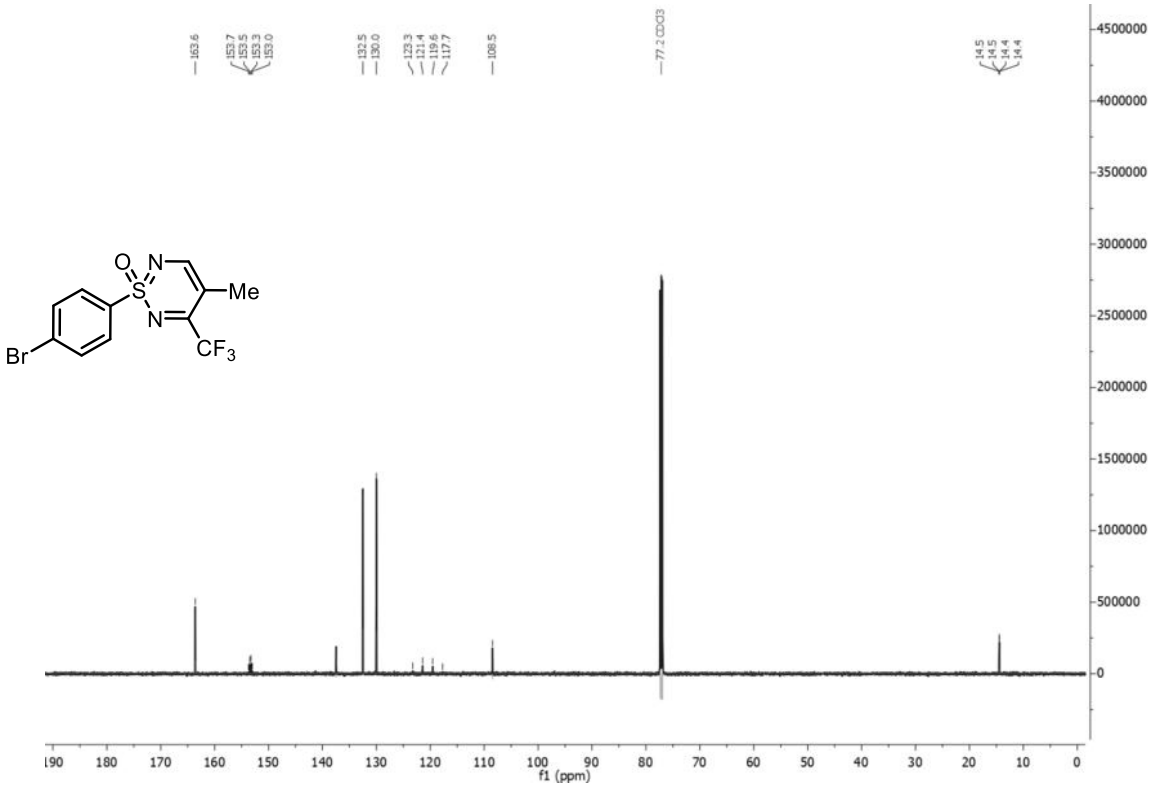
^{19}F NMR spectrum (Chloroform-*d*, 564 MHz) of compound **5ac**



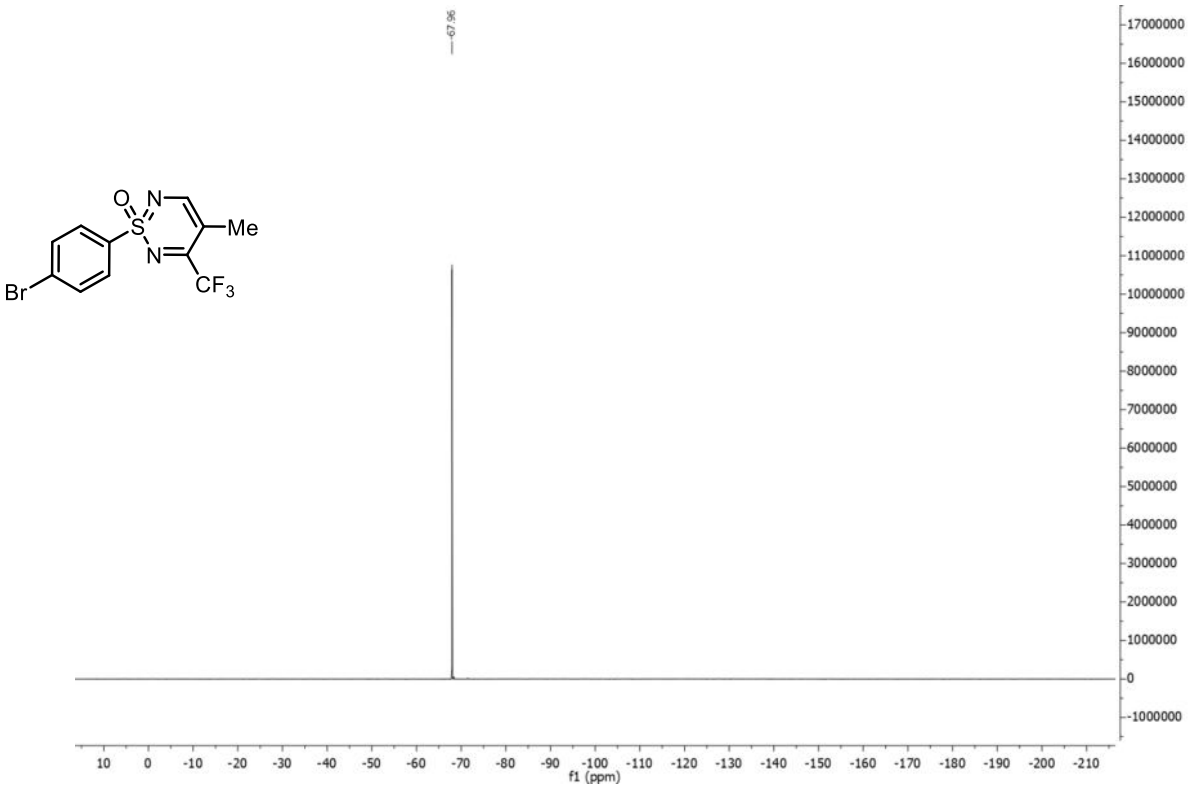
^{1}H NMR spectrum (Chloroform-*d*, 600 MHz) of compound **5fc**



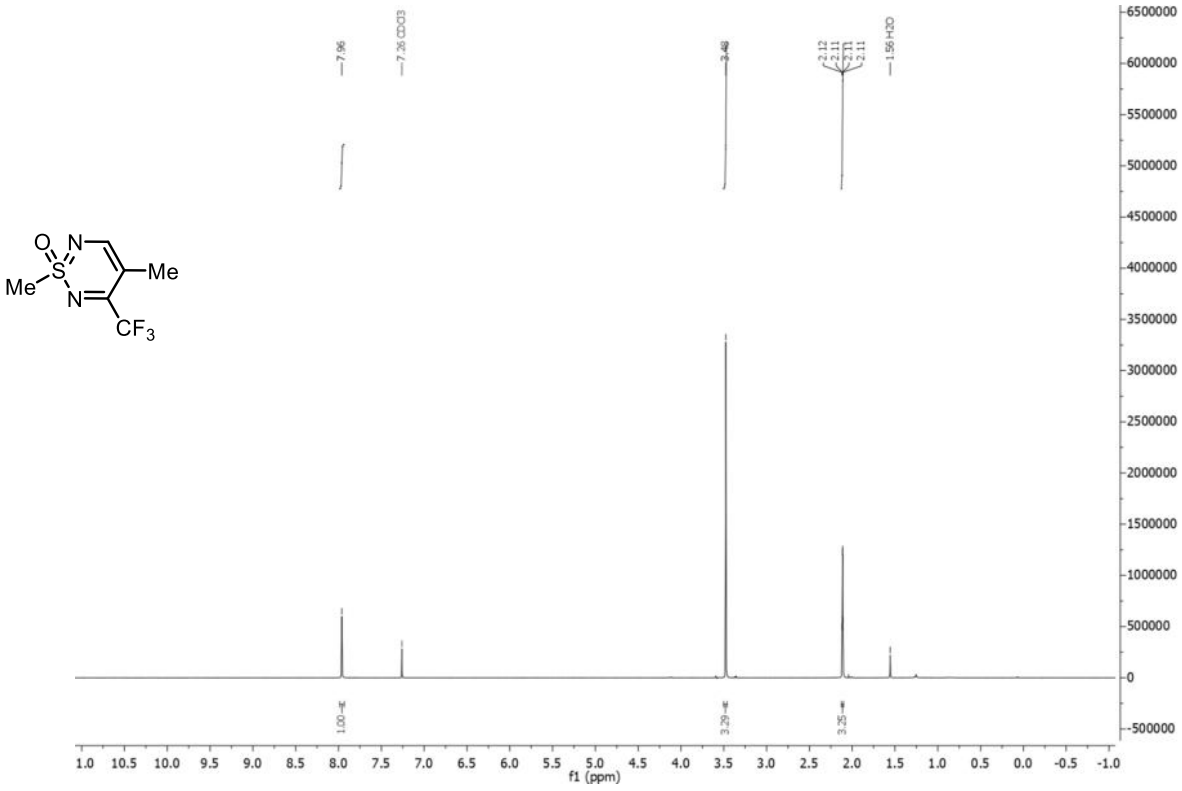
Stacked ^{13}C{^{1}H} DEPT NMR spectra (Chloroform-*d*, 151 MHz) of compound **5fc**



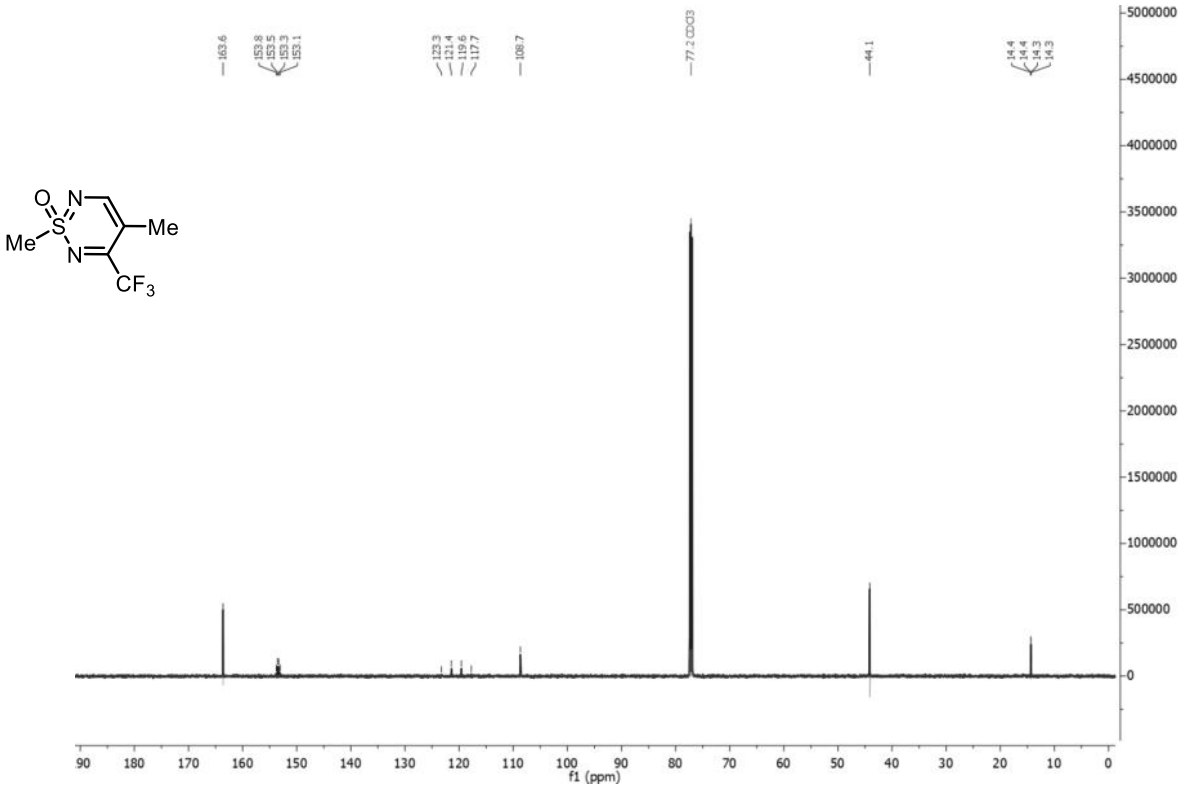
^{19}F NMR spectrum (Chloroform-*d*, 564 MHz) of compound **5fc**



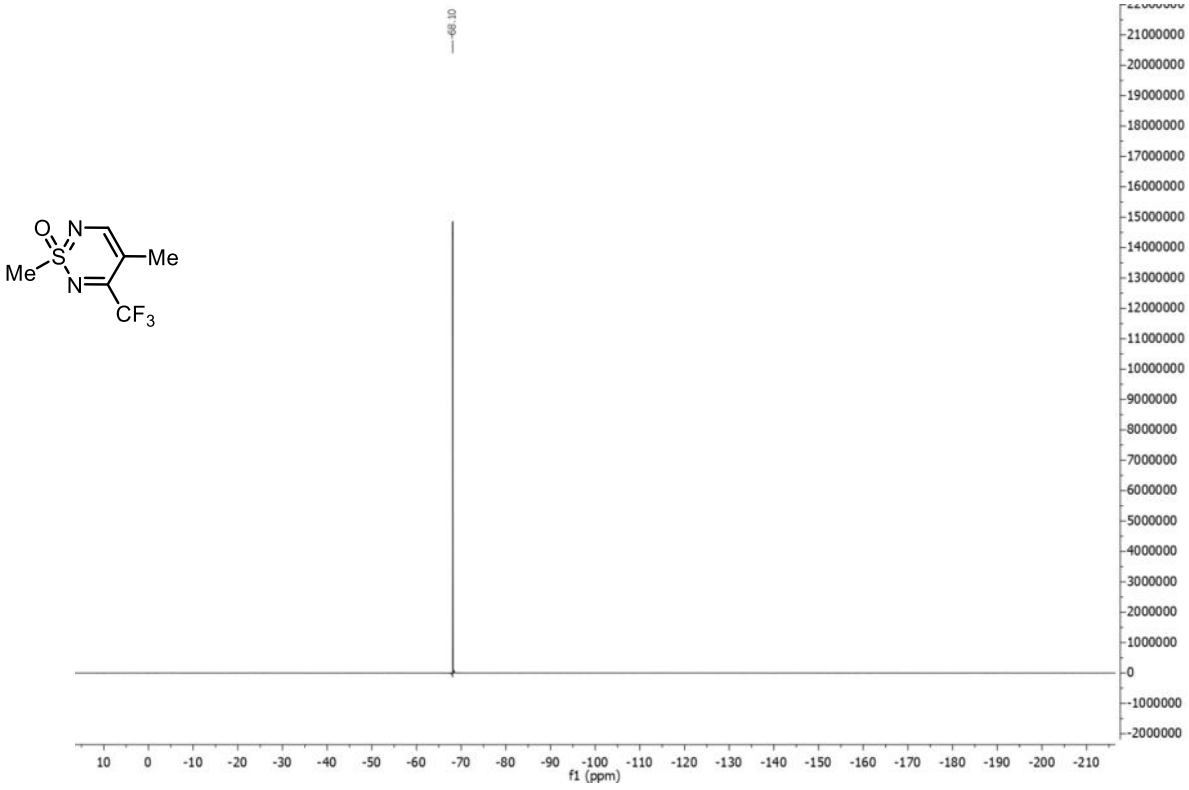
^{1}H NMR spectrum (Chloroform-*d*, 600 MHz) of compound **5kc**



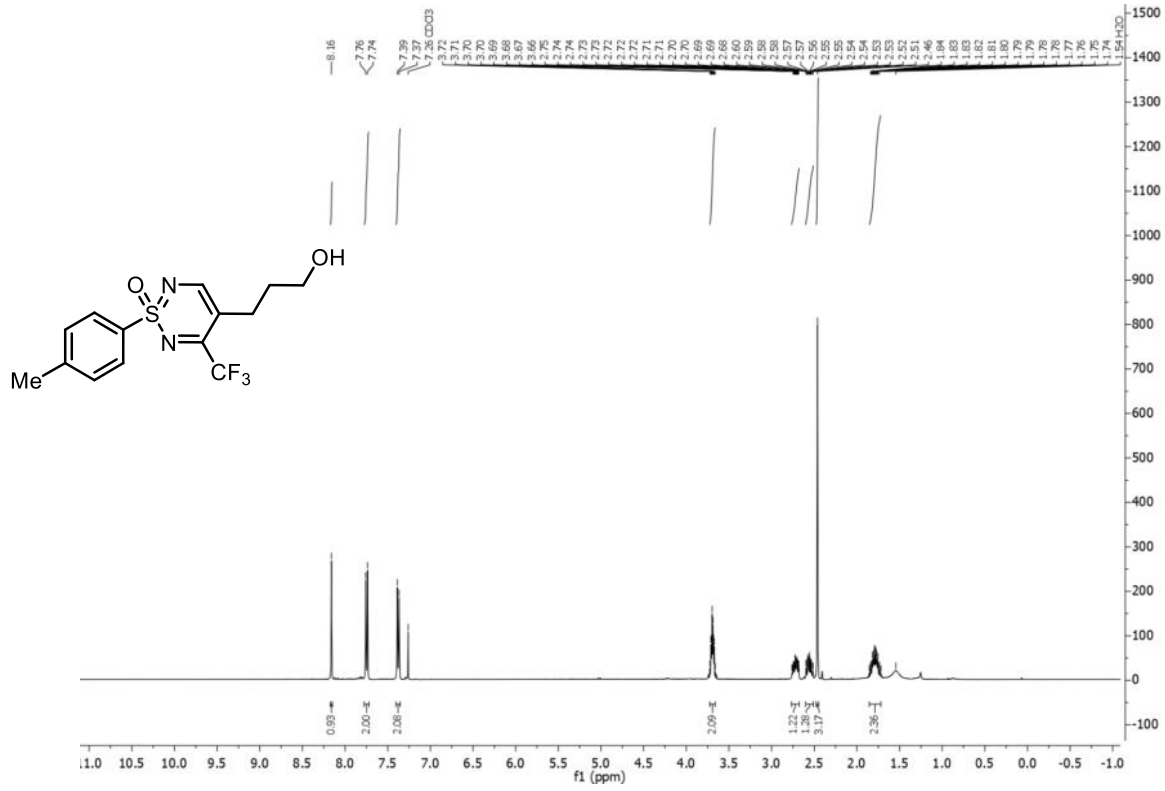
Stacked $^{13}C\{^{1}H\}$ DEPT NMR spectra (Chloroform-*d*, 151 MHz) of compound **5kc**



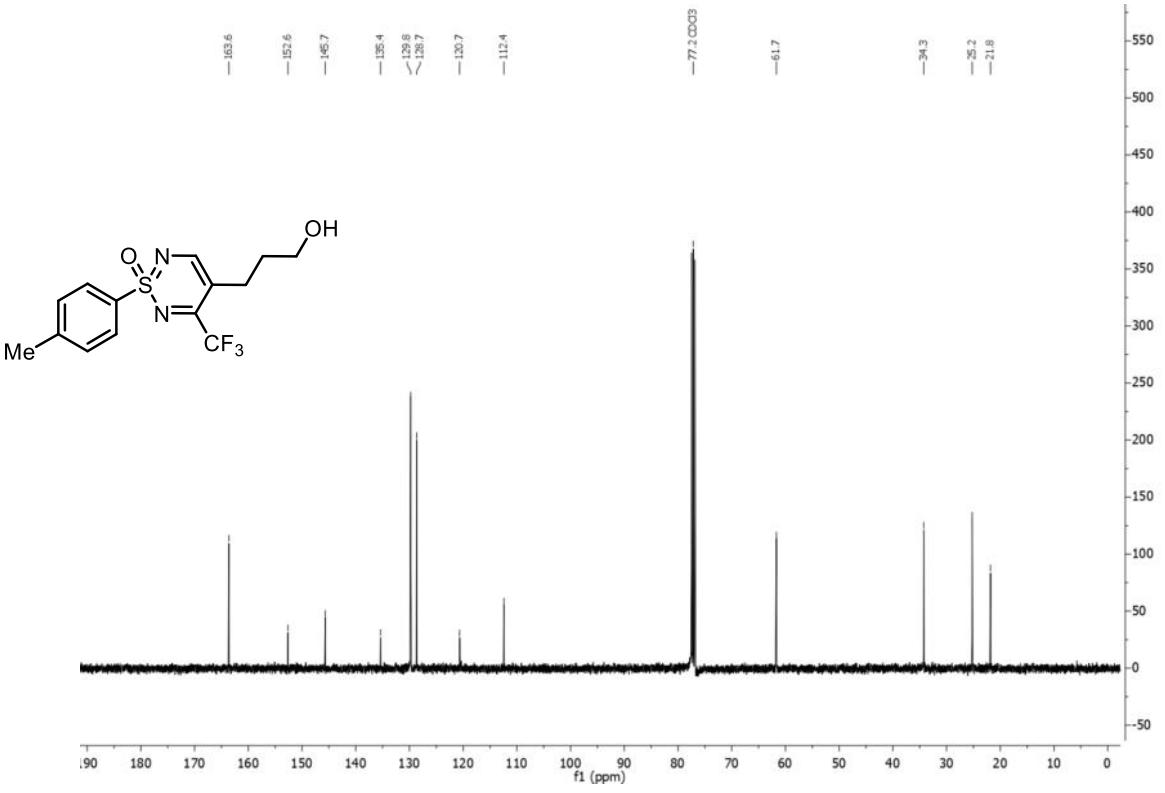
^{19}F NMR spectrum (Chloroform-*d*, 564 MHz) of compound **5kc**



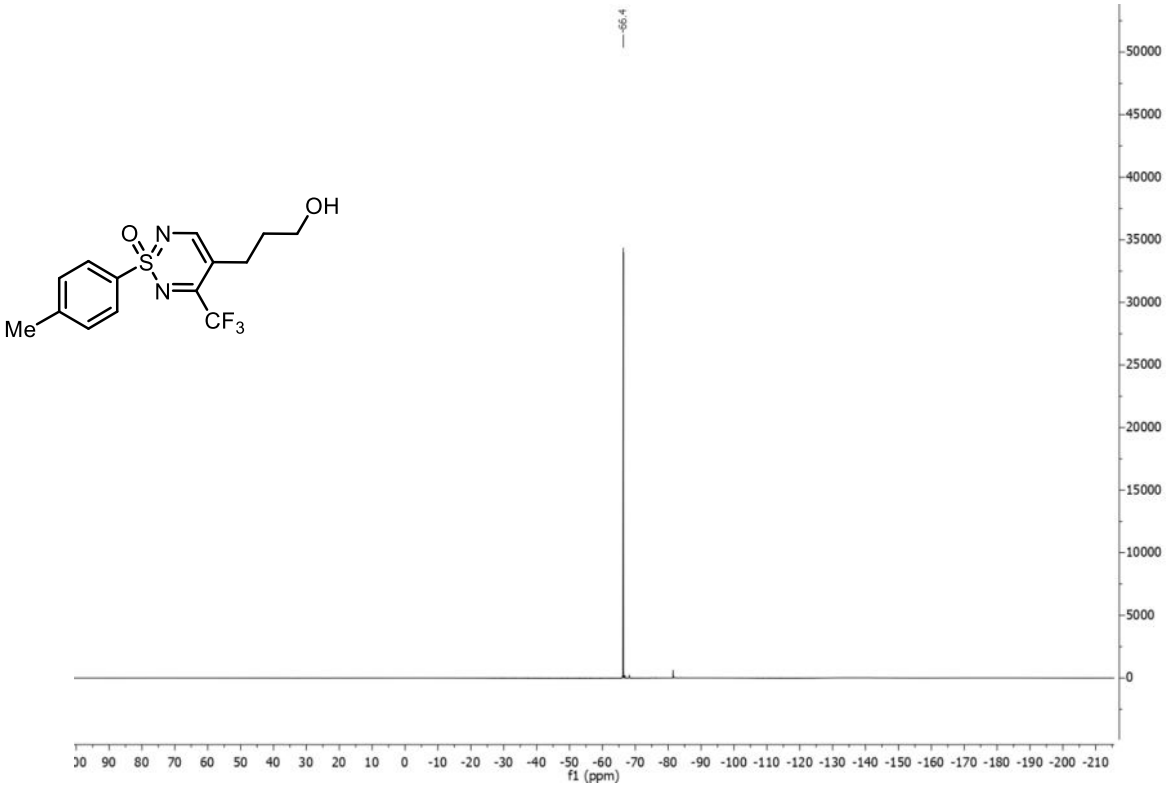
^{1}H NMR spectrum (Chloroform-*d*, 400 MHz) of compound **5ad**



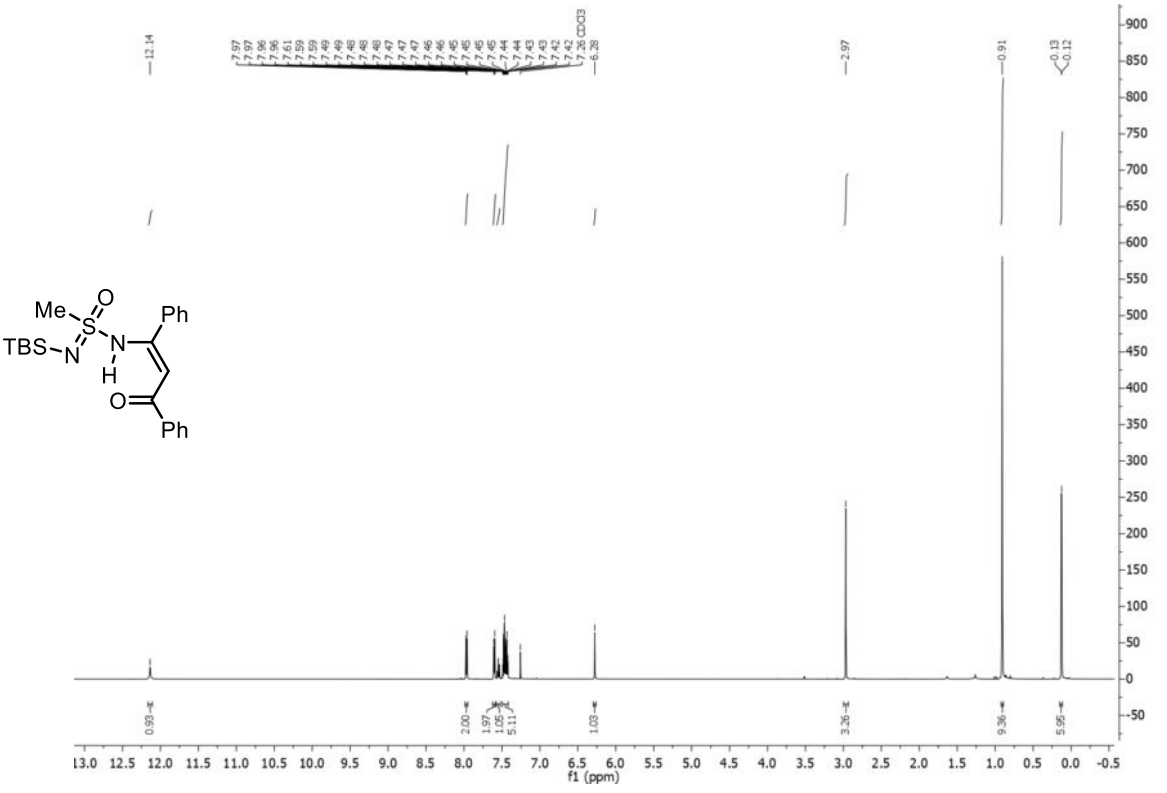
^{13}C{^{1}H, ^{19}F} NMR spectrum (Chloroform-*d*, 101 MHz) of compound **5ad**



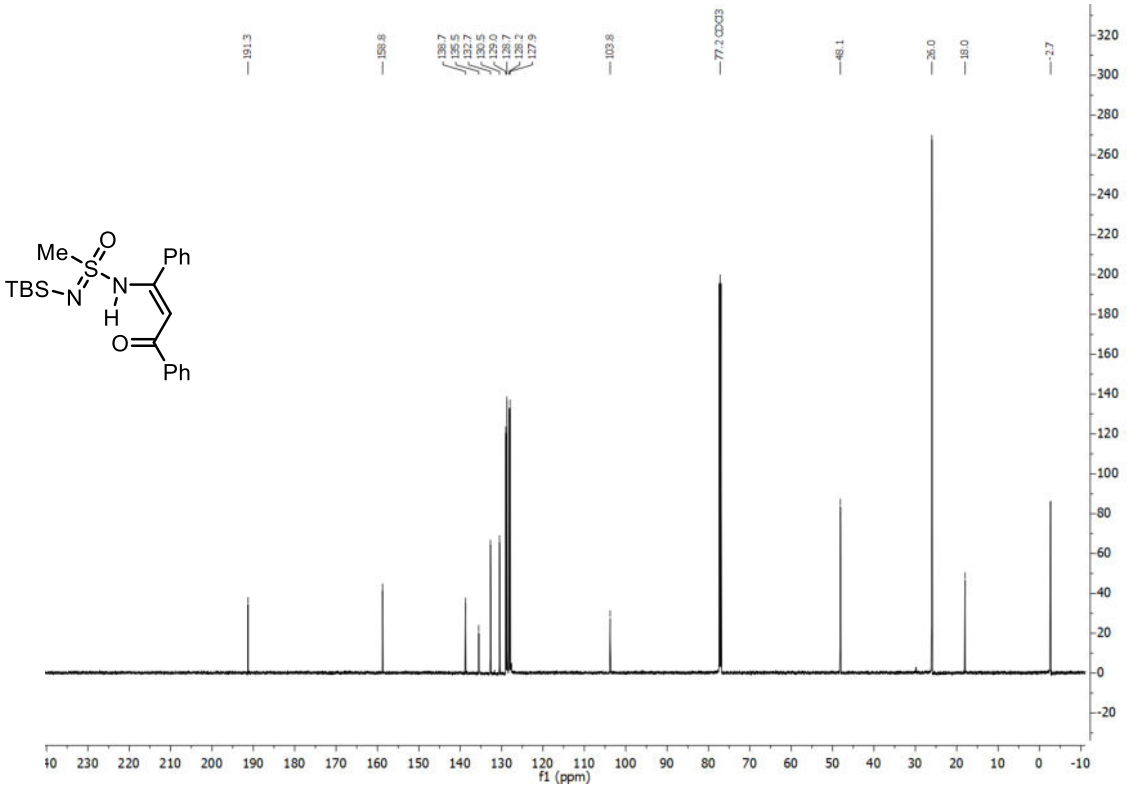
^{19}F NMR spectrum (Chloroform-*d*, 376 MHz) of compound **5ad**



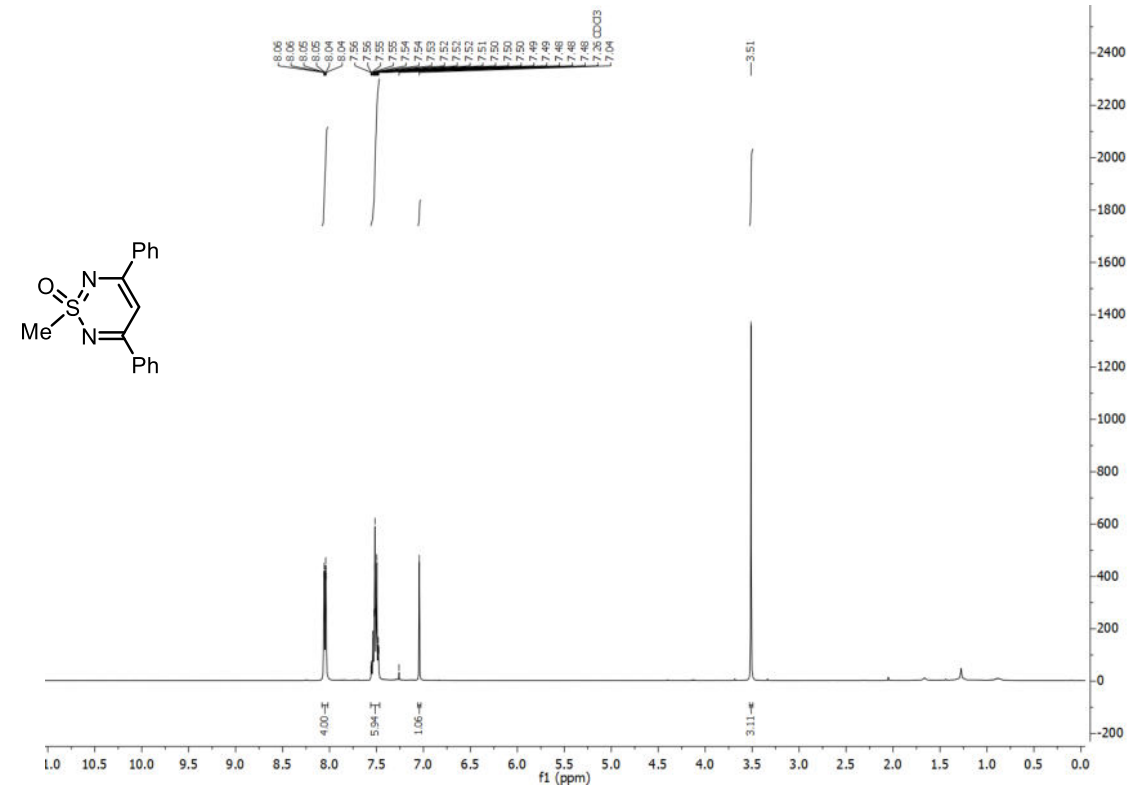
^{1}H NMR spectrum (Chloroform-*d*, 600 MHz) of compound **7ka**



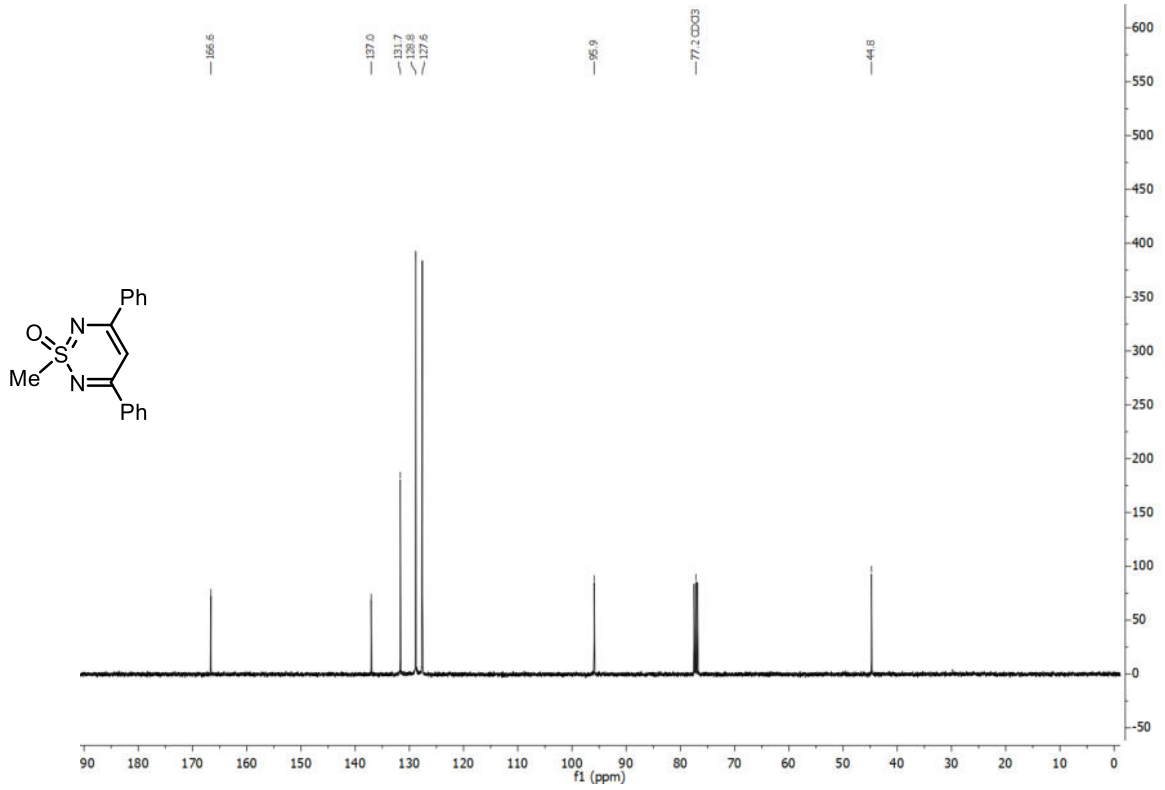
$^{13}C\{^{1}H\}$ NMR spectrum (Chloroform-*d*, 151 MHz) of compound **7ka**



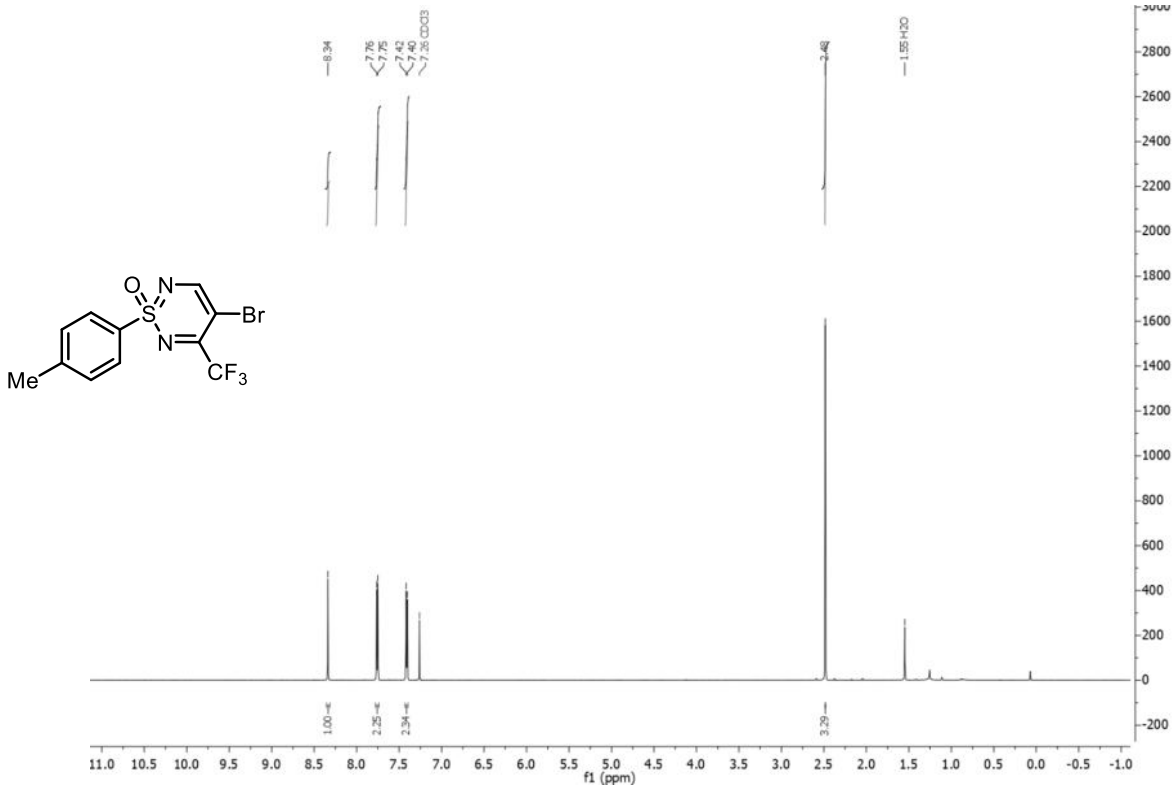
^{1}H NMR spectrum (Chloroform-*d*, 600 MHz) of compound **3ka**



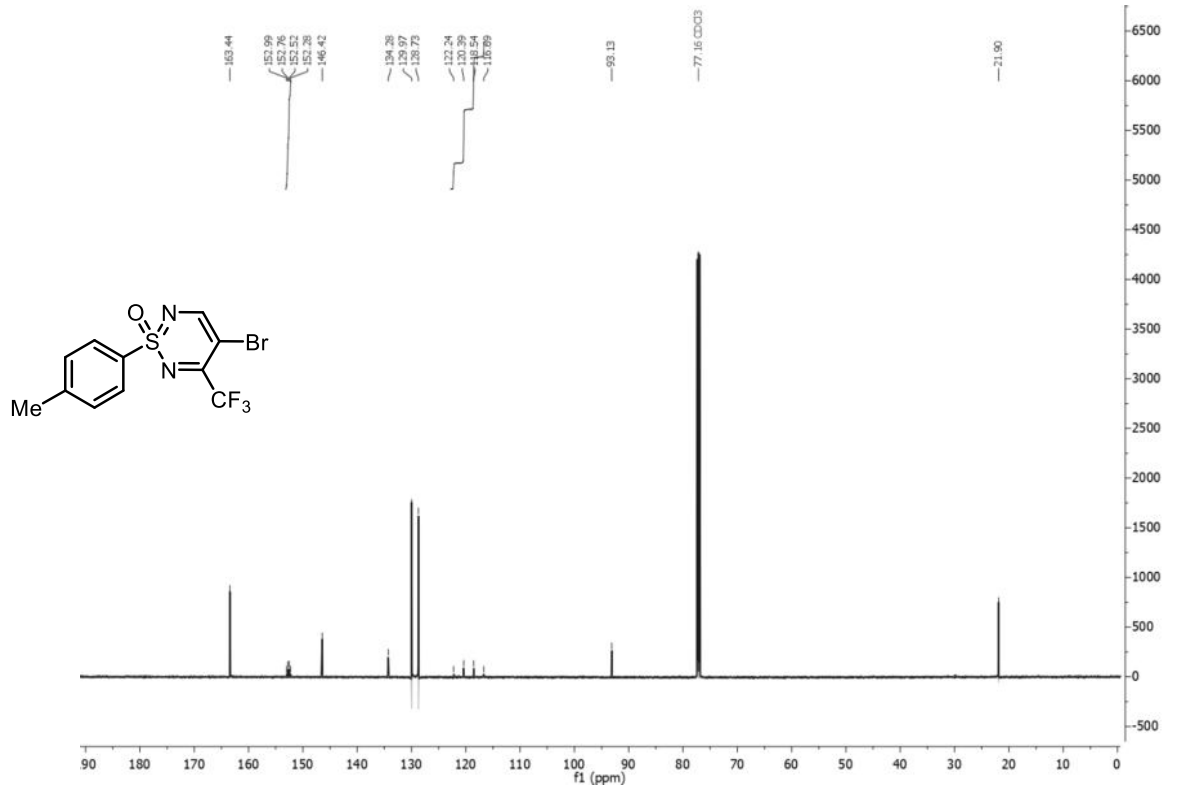
$^{13}C\{^{1}H\}$ NMR spectrum (Chloroform-*d*, 151 MHz) of compound **3ka**



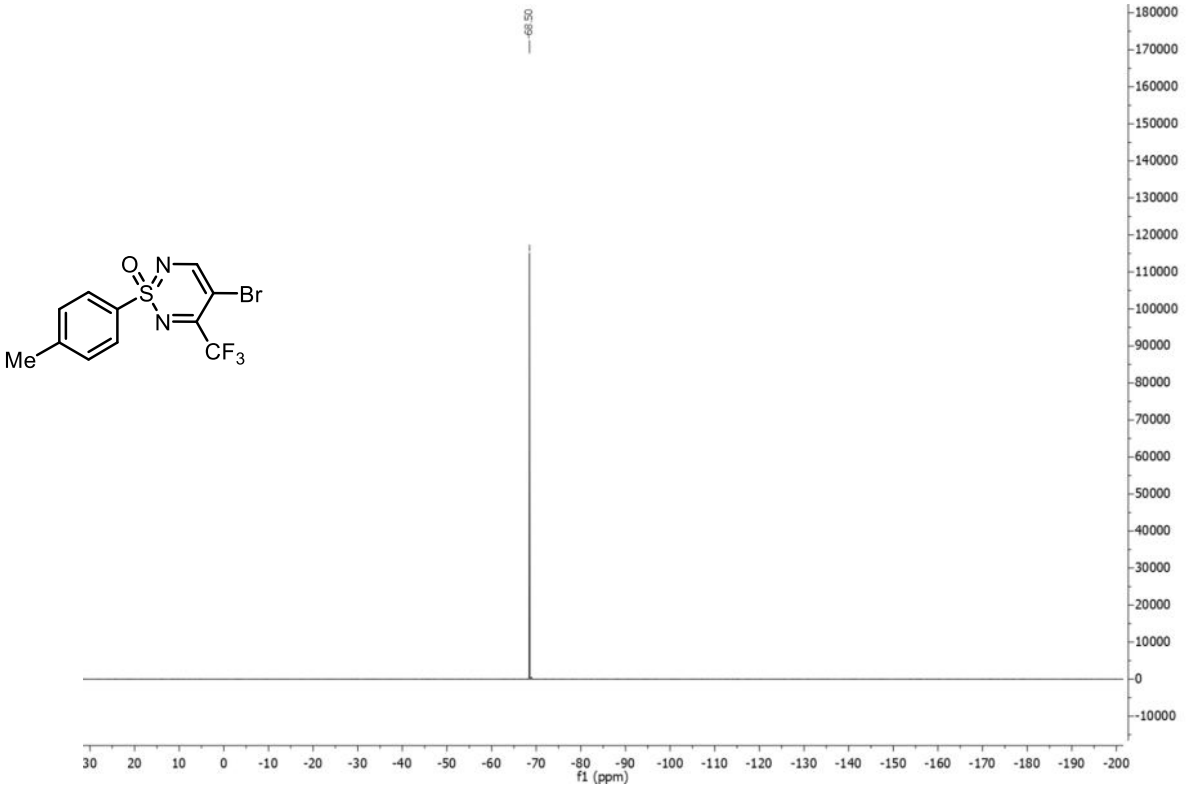
^{1}H NMR spectrum (Chloroform-*d*, 600 MHz) of compound **8**



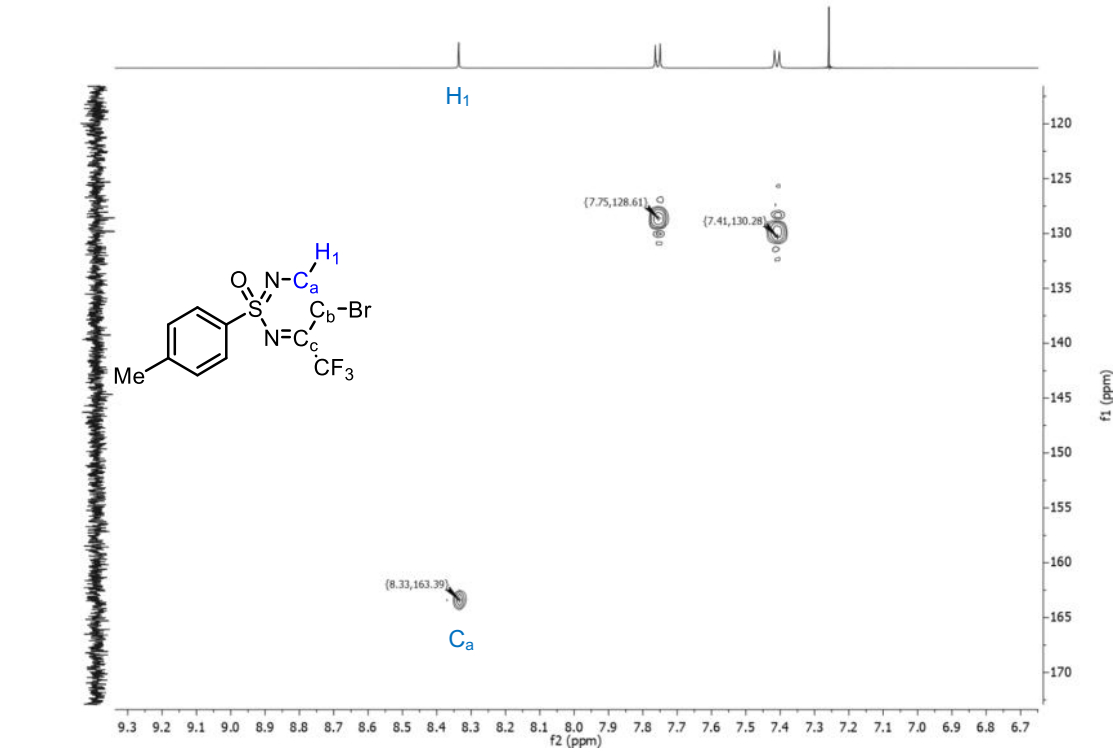
Stacked $^{13}C\{^{1}H\}$ DEPT NMR spectra (Chloroform-*d*, 151 MHz) of compound **8**



^{19}F NMR spectrum (Chloroform-*d*, 564 MHz) of compound **8**



HSQC 2D NMR spectrum of **8**



HMBC 2D NMR spectra of **8**