Supporting Information

N-Fluorobenzenesulfonimide (NFSI) analogs with deprotectable substituents: synthesis of β-fluoroamines via catalytic aminofluorination of styrenes

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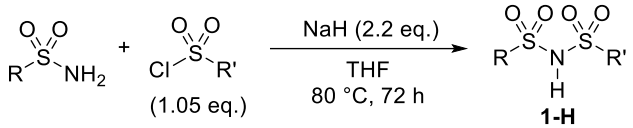
S1. General Information

^{1}H, ^{13}C, and ^{19}F NMR spectra were measured on JEOL JNM-ECZ400S (^{1}H NMR: 400 MHz, ^{13}C NMR: 100 MHz, ^{19}F NMR: 376 MHz) or on ECZ500R (^{1}H NMR: 500 MHz, ^{13}C NMR : 125 MHz, ^{19}F NMR: 470 MHz) spectrometers. ^{1}H NMR chemical shifts were determined relative to internal $(CH3)_4Si$ (TMS) at δ 0.0 or to the signal of the residual protonated solvent: $CDCl_3$ δ 7.26, acetone-d_6 δ 2.05, DMSO-d_6 δ 2.50. ^{13}C NMR chemical shifts were determined relative to internal TMS at δ 0.0 or to the signal of the residual protonated solvent: $CDCl_3$ δ 77.16, acetone-d_6 δ 29.84, 206.26. ^{19}F NMR chemical shifts were determined relative to $PhCF_3$ at δ −62.37. Data for ^{1}H, ^{13}C and ^{19}F NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad). **IR spectra** were measured on a Shimadzu FTIR-8400 spectrometer. **High-resolution mass spectra (HRMS)** were measured on a JEOL JMS-T100LP spectrometer in the electron spray ionization time-of-flight (ESI-TOF) mode or a Bruker Daltonics micrOTOF II mass spectrometer with the atmospheric pressure chemical ionization time-of-flight (APCI-TOF) method. **A single crystal X-ray diffraction** measurement was made on XtaLAB mini II diffractometer using graphite monochromated Mo-Kα radiation. **Thermogravimetric and differential thermal analysis (TG/DTA)** measurements were performed on a Seiko EXSTAR 6000 TG/DTA 6200 analyzer.

All reactions were carried out with commercial reagents and solvents. All reagents and starting materials were purchased from Sigma Aldrich, KANTO CHEMICAL, TCI, and/or FUJIFILM Wako Pure Chemical, and were used without further purification. All solvents were purchased from Sigma Aldrich, KANTO CHEMICAL, TCI, and/or FUJIFILM Wako Pure Chemical and used without further purification, unless otherwise mentioned.

S2. Preparation of Novel Electrophilic Fluorinating Reagents

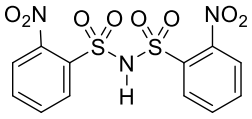
S2-1. Synthetic Procedure of sulfonimide 2'



Experimental Procedures:

A solution of sulfonamide in THF (0.1 M) was added to NaH (2.2 eq.) at 0 °C and stirred for 1 h at room temperature under N_2 atmosphere. Sulfonyl chloride (1.05 eq.) was added to the solution at 0 °C and stirred for another 48 h at 80 °C. The reaction mixture was quenched by 3M HCl and extracted with DCM twice. The organic extracts were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The resulting crude product was purified by silica-gel column chromatography to give the sulfonimide **1-H**.

***N*-(2,2'-Dinitro)benzenesulfonimide (1a-H)**



The title compound was obtained from 2-nitrobenzenesulfonamide (10.0 mmol) and 2-nitrobenzenesulfonyl chloride (10.5 mmol) following the procedure above. Purification by silica-gel column chromatography (DCM/MeOH = 10/1 to 0/1) gave the compound (3.55 g, 92% yield) as an orange solid.

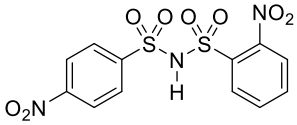
^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ 8.26 (d, *J* = 7.5 Hz, 2H), 8.02 (d, *J* = 4.6 Hz, 4H), 7.94-8.00 (m, 2H).

^{13}C NMR (125 MHz, $(CD_3)_2CO$) δ 148.97, 136.61, 133.85, 133.65, 132.74, 126.10.

HRMS (ESI-TOF) calcd for $C_{12}H_9N_3NaO_8S_2$ $[M+Na]^+$: 409.9729, found: 409.9711.

FT-IR (neat, cm^{-1}) 3558, 1537, 1353, 1240, 811, 784, 740, 694, 649, 580, 507, 455, 437, 424, 403.

***N*-(2,4'-Dinitro)benzenesulfonimide (1b-H)**



The title compound was obtained from 2-nitrobenzenesulfonamide (10.0 mmol) and 4-nitrobenzenesulfonyl chloride (10.5 mmol) following the procedure above. Purification by silica-gel column chromatography (DCM/MeOH = 10/1 to 0/1) gave the compound (3.87 g, 97% yield) as an orange solid.

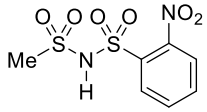
^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.45 (d, *J* = 8.7 Hz, 2H), 8.29 (d, *J* = 6.9 Hz, 1H), 8.22 (d, *J* = 8.7 Hz, 2H), 7.95-8.03 (m, 3H).

^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 151.59, 148.66, 146.73, 136.35, 133.65, 133.45, 132.73, 129.93, 125.91, 125.25.

HRMS (ESI-TOF) calcd for $C_{12}H_9N_3NaO_8S_2$ $[M+Na]^+$: 409.9729, found: 409.9717.

FT-IR (neat, cm^{-1}) 3556, 3103, 2158, 2015, 1965, 1544, 1529, 1388, 1352, 1307, 1191, 1170, 1143, 1120, 1110, 1091, 865, 850, 819, 786, 746, 736, 682, 649, 613, 595, 572, 540, 472, 435, 422, 410.

***N*-(2-Nitrobenzenesulfonyl)methanesulfonamide (1c-H)**



The title compound was obtained from methanesulfonamide (10.0 mmol) and 2-nitrobenzenesulfonyl chloride (10.5 mmol) following the procedure above. Purification by silica-gel column chromatography (DCM/MeOH = 10/1 to 0/1) gave the compound (2.72 g, 97% yield) as an orange solid.

^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ 8.27 (d, *J* = 7.5 Hz, 1H), 7.96-8.05 (m, 3H), 3.40 (s, 3H).

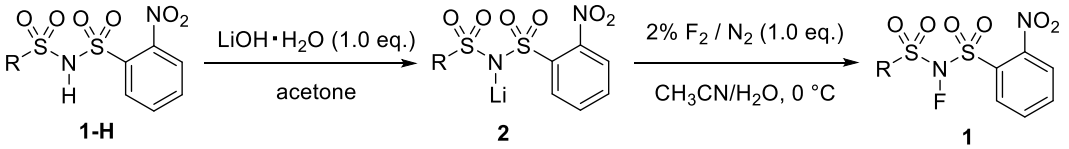
^{13}C NMR (125 MHz, $(CD_3)_2CO$) δ 148.82, 136.36, 133.66(2C), 132.81, 125.95, 44.27.

HRMS (ESI-TOF) calcd for $C_7H_8N_2NaO_6S_2$ $[M+Na]^+$: 302.9722, found: 302.9700.

FT-IR (neat, cm^{-1}) 3193, 1593, 1542, 1440, 1361, 1323, 1294, 1172, 1157, 1128, 1056, 968, 867, 850, 783, 744, 730, 702, 655, 595, 568, 514, 460, 439, 408

S2-2. Synthetic Procedure of Electrophilic Fluorinating Reagent 1[1], [2]

S2-2-1. Synthetic Procedure of reagent 1 using F_2 gas (Scheme 2a)

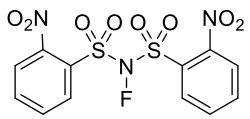


1-H 2 1

Experimental Procedures:

Sulfonimide **1-H** and lithium hydroxide monohydrate (1.0 eq.) were added to acetone (100 mL), and the mixture was stirred at room temperature for 1 h. Then, the solvent was distilled off under vacuum, and the residue was further dissolved in a mixed solvent of acetonitrile/water, filtered, and the solvent was distilled off under vacuum to provide lithium salt **2**, which is a brown solid. The solution of **2** in a mixture of acetonitrile (142.5 g) and H_2O (7.5 g) was stirred in a 250 mL PFA vessel and cooled to 0 °C. A gaseous mixture of 2% F_2 in N_2 (volume percent) was introduced at a rate of 100 mL/min to the solution (F_2: 1.0 eq.). N_2 gas was introduced to remove the residual F_2 gas for 30 min. The insoluble solid was filtered, and then the filtrate was evaporated under vacuum to give a yellow solid. The resulting crude product was purified by washing with a mixed solvent of hexane/dichloromethane to afford the desired product **1**.

***N*-Fluoro-*N*-(2,2'-dinitro)benzenesulfonimide (1a)**



The title compound was obtained from **2a** (3.25 g, 8.27 mmol) following the procedure above. Further purification by recrystallization (*n*-hexane/DCM) gave the compound (3.05 g, 91% yield) as a white solid.

^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ 8.37 (d, *J* = 8.6 Hz, 2H), 8.26 (t, *J* =7.7 Hz, 2H), 8.16 (d, *J* = 8.0 Hz, 2H), 8.12 (t, *J* = 7.7 Hz, 2H).

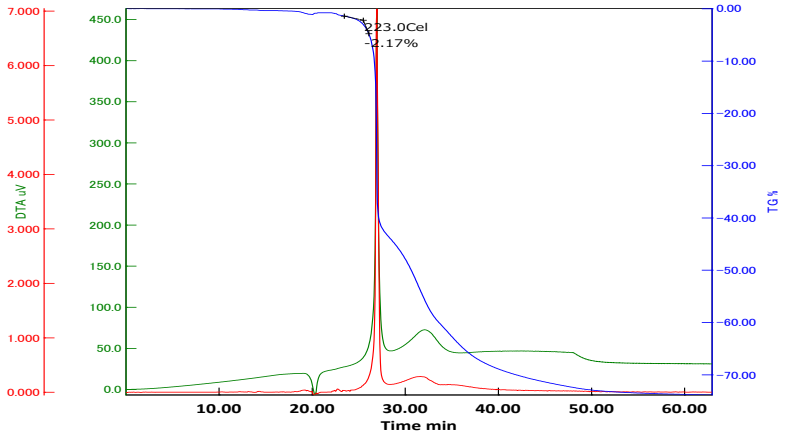
^{13}C NMR (125 MHz, $(CD_3)_2CO$) δ 149.85, 139.66, 134.10, 134.08, 127.50, 126.48.

^{19}F NMR (470 MHz, $(CD_3)_2CO$) δ -35.64.

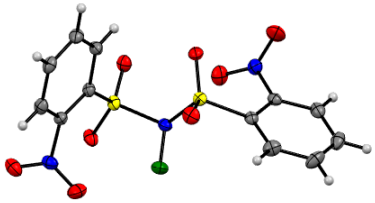
HRMS (ESI-TOF) calcd for $C_{12}H_8FN_3NaO_6S_2$ $[M+Na]^+$: 427.9635, found: 427.9626.

FT-IR (neat, cm^{-1}) 2507, 2158, 1974, 1548, 1411, 1390, 1371, 1361, 1184, 852, 808, 786, 773, 740, 727, 715, 700, 649, 617, 582, 559, 536, 443, 433, 422, 414.

Thermogravimetric and Differential Thermal Analysis (TG/DTA) measurements were performed at a heating rate of 10 °C/min. T_d of **1a** was observed at 223.0 °C.

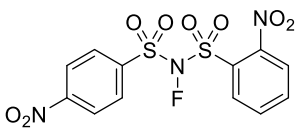


X-Ray crystallography of 1a



$C_{12}H_8FN_3O_6S_2$, clear light colorless block, M_W = 405.33, crystal dimensions = 0.27×0.24×0.22 mm^3, monoclinic, space group $P2_1/n$, a = 7.8287(6), b = 17.6965(12), c = 11.4149(10) Å, V = 1537.8(2) $Å^3$, Z = 4, λ = 0.71073 Å, T = 293 K, ρ_{calcd} = 1.751 g cm^{-3}, $\mu_{MoK\alpha}$ = 0.410 mm^{-1}, F_{000} = 824.0, 10101 total reflections ($2\theta_{max}$ = 28.371°), index ranges = -10≤h≤10, -23≤k≤21, -15≤l≤14, 3473 unique reflections, R_1 = 0.0368($I > 2\sigma(I)$), 0.0409(all data), wR_2 = 0.1030($I > 2\sigma(I)$), 0.1049(all data), goodness of fit = 1.060, S = 1.060 (235 parameters). CCDC 2234402 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

***N*-Fluoro-*N*-(2,4'-dinitro)benzenesulfonimide (1b)**



The title compound was obtained from **2b** (2.12 g, 5.4 mmol) following the procedure above. Further purification by silica-gel column chromatography (*n*-hexane/DCM = 1/1) gave the compound (1.84 g, 84% yield) as a white solid.

^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.62 (dt, J = 9.2, 2.3 Hz, 2H), 8.40 (dt, J = 9.2, 2.3 Hz, 2H), 8.32 (dd, J = 7.8, 1.4 Hz, 1H), 8.25 (td, J = 7.8, 1.4 Hz, 1H), 8.15 (dd, J = 8.0, 1.4, 0.9 Hz, 1H), 8.10 (td, J = 8.0, 1.4, 0.9 Hz, 1H).

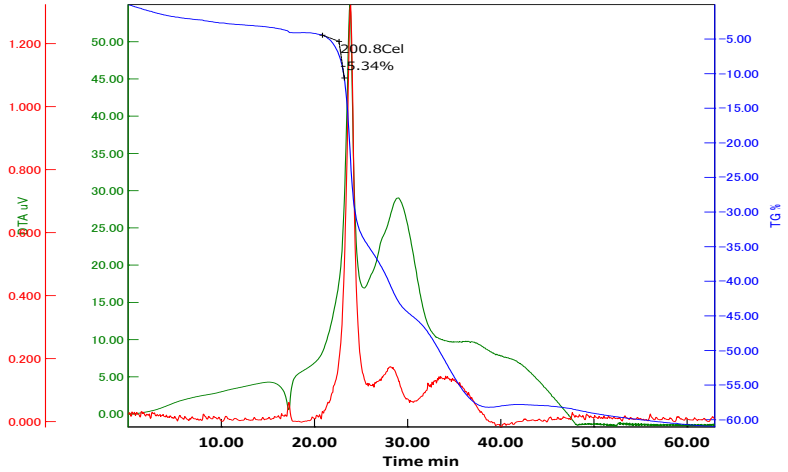
^{13}C NMR (100 MHz, $(CD_3)_2CO$) 153.55, 149.69, 140.08, 139.71, 134.18, 134.06, 132.70, 127.26, 126.61, 126.06.

^{19}F NMR (376 MHz, $(CD_3)_2CO$) δ -36.10.

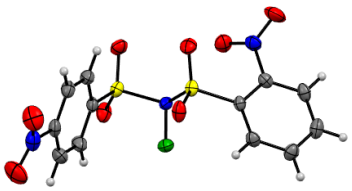
HRMS (ESI-TOF) calcd for $C_{12}H_9FN_2NaO_6S_2$ $[M+Na]^+$: 427.9635, found: 427.9682.

FT-IR (neat, cm^{-1}) 3115, 1933, 1607, 1592, 1547, 1530, 1442, 1402, 1392, 1378, 1359, 1345, 1309, 1294, 1188, 1125, 1082, 1055, 1012, 941, 884, 854, 796, 778, 736, 702, 677, 651, 628, 600, 571, 536, 463, 452, 404.

Thermogravimetric and Differential Thermal Analysis (TG/DTA) measurements were performed at a heating rate of 10 °C/min. T_d of **1b** was observed at 200.8 °C.

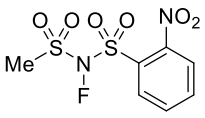


X-Ray crystallography of 1b



$C_{12}H_9FN_2O_6S_2$, clear light colorless needle, M_W = 405.33, crystal dimensions = 0.48×0.12×0.1 mm^3, monoclinic, space group $P2_1/c$, a = 7.6151(3), b = 12.0228(4), c = 17.3608(7) Å, V = 1585.35(10) Å^3, Z = 4, λ = 0.71073 Å, T = 170 K, ρ_{calcd} = 1.698 g cm^{-3}, $\mu_{MoK\alpha}$ = 0.398 mm^{-1}, F_{000} = 824.0, 7826 total reflections ($2\theta_{max}$ = 26.360°), index ranges = -9≤h≤9, -14≤k≤15, -18≤l≤21, 3042 unique reflections, R_1 = 0.0287 (I > 2σ(I)), 0.0352 (all data), wR_2 = 0.0729 (I > 2σ(I)), 0.0754 (all data), goodness of fit = 1.066, S = 1.066 (236 parameters). CCDC 2234407 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

***N*-Fluoro-*N*-(2-nitrobezenesulfonyl)methanesulfonamide (1c)**



The title compound was obtained from **2c** (1.92 g, 6.7 mmol) following the procedure above. Further purification by silica-gel column chromatography (*n*-hexane/DCM = 1/1) gave the compound (1.96 g, 99% yield) as a white solid.

^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ 8.37 (d, J = 9.2 Hz, 1H), 8.24 (t, J = 8.3 Hz, 1H), 8.15 (d, J = 9.2 Hz, 1H), 8.10 (t, J = 8.3 Hz, 1H), 3.67 (s, 3H).

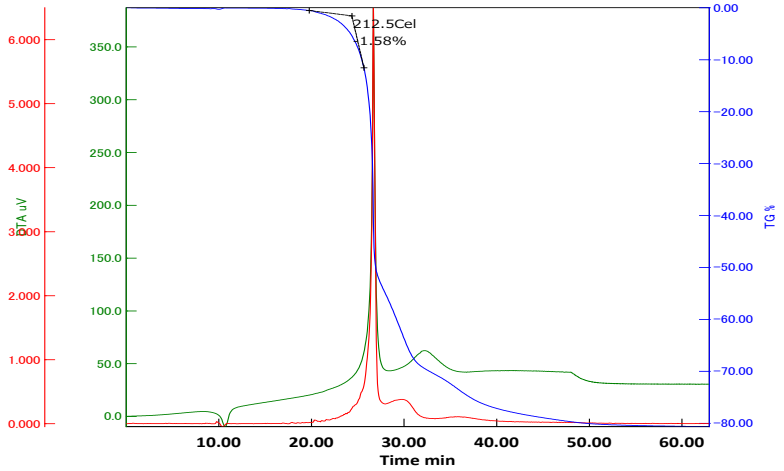
^{13}C NMR (125 MHz, $(CD_3)_2CO$) δ 149.78, 139.36, 134.03, 133.90, 127.38, 126.33, 40.93.

^{19}F NMR (470 MHz, $(CD_3)_2CO$) δ -40.84.

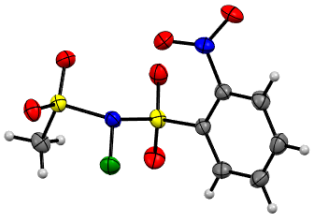
HRMS (ESI-TOF) calcd for $C_7H_7FN_2NaO_6S_2$ $[M+Na]^+$: 320.9627, found: 320.9651.

FT-IR (neat, cm^{-1}) 3109, 3022, 2943, 2162, 2015, 1976, 1591, 1537, 1440, 1417, 1382, 1353, 1326, 1178, 1147, 1122, 1053, 968, 927, 896, 854, 810, 784, 761, 740, 690, 651, 603, 580, 532, 507, 484, 462, 437, 406.

Thermogravimetric and Differential Thermal Analysis (TG/DTA) measurements were performed at a heating rate of 10 °C /min. T_d of **1c** was observed at 212.5 °C.



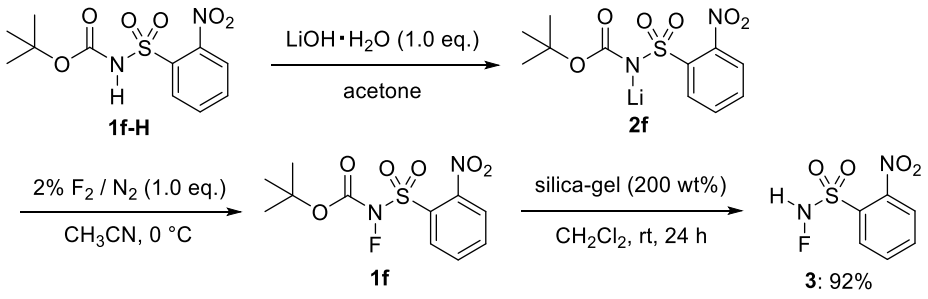
X-Ray crystallography of 1c



$C_7H_7FN_2O_6S_2$, clear light colorless block, M_W = 298.27, crystal dimensions = 0.27×0.24×0.22 mm^3, monoclinic, space group *C*2/c, *a* = 13.5187(3), *b* = 19.0911(5), *c* = 8.8331(2) Å, *V* = 2270.76(9) Å^3, *Z* = 8, λ = 0.71073 Å, *T* = 170 K, ρ_{calcd} = 1.745 g cm^{-3}, $\mu_{MoK\alpha}$ = 0.505 mm^{-1}, F_{000} = 1216.0, 7372 total reflections ($2\theta_{max}$ = 26.370°), index ranges = -16≤*h*≤16, -19≤*k*≤23, -11≤*l*≤11, 2318 unique reflections, R_1 = 0.0353($I > 2\sigma(I)$), 0.0353(all data), wR_2 = 0.0961($I > 2\sigma(I)$), 0.0998(all data), goodness of fit = 1.038, *S* = 1.038 (164 parameters). CCDC 2234405 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

S2-2-2. Synthetic Procedure of Reagent 1 via condensation (Scheme 2b and 2c)

S2-2-2-1. Synthetic Procedure of *N*-fluorosulfonamide

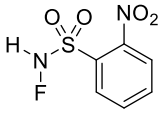


Experimental Procedures:

Commercially available *N*-(*tert*-butoxycarbonyl)-2-nitrobenzenesulfonamide **1f-H** (3.02 g, 10.0 mmol) and lithium hydroxide monohydrate (0.42 g, 10.0 mmol, 1.0 eq.) were added to acetone (100 mL), and the mixture was stirred at room temperature for 1 h. Then, the solvent was distilled off under vacuum, and the residue was further dissolved in a mixed solvent of acetonitrile/water, filtered, and the solvent was distilled off under vacuum to provide lithium salt **2f**, which is a brown solid. The solution of **2f** in acetonitrile (150 g) was stirred in a 250 mL PFA vessel and cooled to 0 °C. A gaseous mixture of 2% F_2 in N_2 (volume percent) was introduced at a rate of 100 mL/min to the solution

(F_2: 1.0 eq.). N_2 gas was introduced to remove the residual F_2 gas for 30 min. The insoluble solid was filtered, and then the filtrate was evaporated under vacuum to give **1f** as a yellow solid. A mixture of **1f** and silica-gel (6.00 g, 200 wt%) in dichloromethane (100 mL) were stirred at room temperature for 24 h in air. The reaction mixture was filtered and distilled off under vacuum to provide *N*-fluoro-2-nitrobenzenesulfonamide **3** (2.03 g, 92% yield) as an orange solid.

***N*-Fluoro-2-nitrobenzenesulfonimide (3)**



^{1}H NMR (500 MHz, $CDCl_3$) δ 9.82 (d, *J* = 52.1 Hz, 1H), 8.32 (d, *J* = 7.7 Hz, 1H), 8.00 (d, *J* = 7.7 Hz, 1H), 7.94 (t, *J* = 7.6 Hz, 1H), 7.89 (t, *J* = 7.6 Hz, 1H).

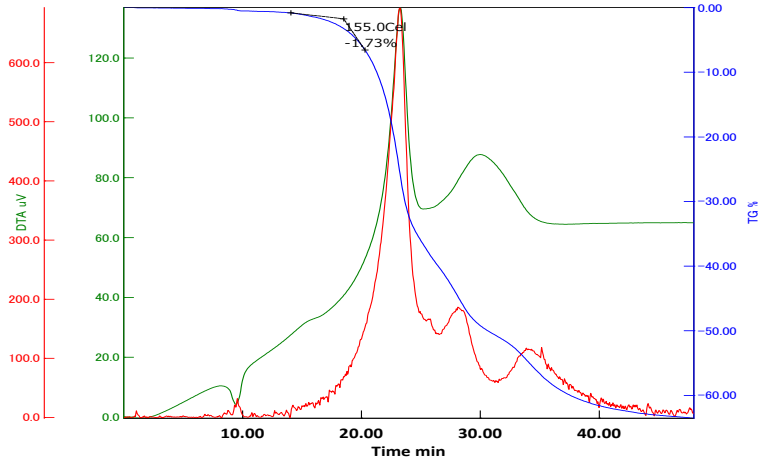
^{13}C NMR (125 MHz, $CDCl_3$) δ 148.69, 136.29, 134.56, 133.65, 128.52, 126.25.

^{19}F NMR (470 MHz, $CDCl_3$) δ -91.26 (d, *J* = 50.4 Hz, 1F).

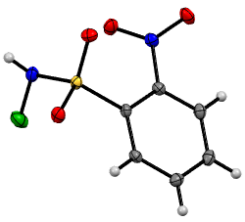
HRMS (APCI-TOF) calcd for $C_6H_4FN_2O_4S^-$ $[M-H]^-$: 218.9881, found: 218.9887.

FT-IR (neat, cm^{-1}) 3369, 3215, 3099, 3022, 1596, 1573, 1557, 1537, 1521, 1471, 1458, 1441, 1382, 1355, 1338, 1302, 1181, 1172, 1125, 1109, 1056, 1019, 980, 925, 890, 842, 750, 736, 696, 658, 644, 610, 565, 552.

Thermogravimetric and Differential Thermal Analysis (TG/DTA) measurements were performed at a heating rate of 10 °C/min. T_d of **3** was observed at 155.0 °C.

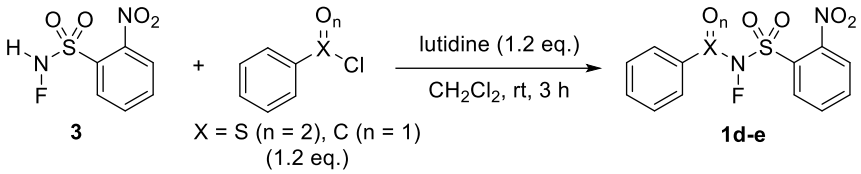


X-Ray crystallography of 3



$C_6H_5FN_2O_4S$, clear yellowish colorless plate, M_W = 220.18, crystal dimensions = 0.36×0.15×0.122 mm^3, orthorhombic, space group $P2_1/c$, a = 8.0042(7), b = 16.3141(10), c = 7.3230(6) Å, V = 1692.46(13) $Å^3$, Z = 8, λ = 0.71073 Å, T = 293 K, ρ_{calcd} = 1.728 g cm^{-3}, $\mu_{MoK\alpha}$ = 0.390 mm^{-1}, F_{000} = 896.0, 12145 total reflections ($2\theta_{max}$ = 29.469°), index ranges = -20≤*h*≤18, -9≤*k*≤9, -21≤*l*≤20, 2164 unique reflections, R_1 = 0.0337 ($I > 2\sigma(I)$), 0.0367 (all data), wR_2 = 0.1031 ($I > 2\sigma(I)$), 0.1052 (all data), goodness of fit = 1.081, S = 1.081 (127 parameters). CCDC 2260139 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

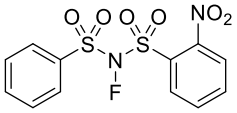
S2-2-2-2. Condensation of *N*-fluorosulfonamide 3[3]



Experimental Procedures

A solution of *N*-fluoro-2-nitrobenzenesulfonamide **3** and lutidine (1.2 eq.) in dicloromethane (0.2 M) was stirred for 1 h at room temperature under N_2 atmosphere. Benzenesulfonyl chloride or benzoyl chloride (1.2 eq.) was added to the solution at 0 °C and stirred for another 3 h at room temperature. The solvent was distilled off under vacuum, and the crude product was purified by silica-gel column chromatography to give the compounds **1d-e**.

***N*-Fluoro-*N*-(2-nitrobezenesulfonyl)benzenesulfonamide (1d)**



The title compound was obtained from **3** (0.2 mmol) and benzenesulfonyl chloride (0.24 mmol) following the procedure above. Purification by silica-gel column chromatography (*n*-hexane/DCM = 2/1 to 1/1) gave the compound (39.1 mg, 55% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.0 Hz, 1H), 8.09 (d, *J* = 8.6 Hz, 2H), 7.9 (t, *J* = 7.7 Hz, 1H), 7.82 (t, *J* = 7.7 Hz, 3H), 7.64-7.67 (m, 2H).

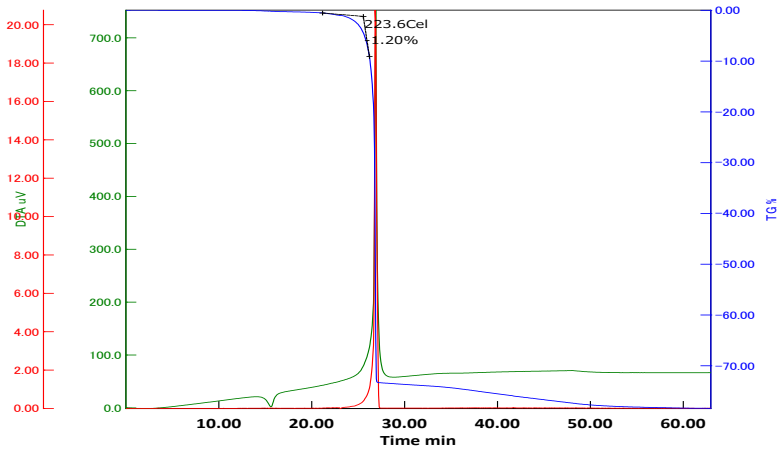
^{13}C NMR (125 MHz, $CDCl_3$) δ 148.94, 136.97, 136.43, 134.61, 132.95, 132.45, 130.19, 129.78, 128.35, 125.17.

^{19}F NMR (470 MHz, $CDCl_3$) δ -34.42.

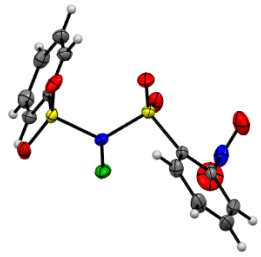
HRMS (ESI-TOF) calcd for $C_{12}H_9FN_2NaO_4S_2$ $[M+Na]^+$: 382.9784, found: 382.9787.

FT-IR (neat, cm^{-1}) 3098, 1580, 1544, 1474, 1449, 1441, 1392, 1369, 1312, 1303, 1270, 1184, 1125, 1083, 1036, 1023, 999, 967, 936, 849, 803, 778, 752, 742, 724, 712, 680, 651, 620, 587, 562, 538, 443, 404.

Thermogravimetric and Differential Thermal Analysis (TG/DTA) measurements were performed at a heating rate of 10 °C/min. T_d of **1d** was observed at 223.6 °C.

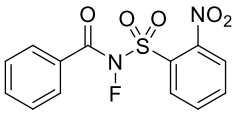


X-Ray crystallography of 1d



$C_{12}H_9FN_2O_4S_2$, clear light colorless needle, M_W = 360.33, crystal dimensions = 0.4×0.24×0.17 mm^3, monoclinic, space group $P2_1/n$, a = 11.9044(5), b = 7.9513(3), c = 15.0809(5) Å, V = 1423.63(9) Å^3, Z = 4, λ = 0.71073 Å, T = 170 K, ρ_{calcd} = 1.681 g cm^{-3}, $\mu_{MoK\alpha}$ = 0.420 mm^{-1}, F_{000} = 736.0, 6944 total reflections ($2\theta_{max}$ = 26.364°), index ranges = -14≤h≤14, -9≤k≤9, -18≤l≤18, 2826 unique reflections, R_1 = 0.0316 ($I > 2\sigma(I)$), 0.0403 (all data), wR_2 = 0.0857 ($I > 2\sigma(I)$), 0.0898 (all data), goodness of fit = 1.035, S = 1.035 (208 parameters). CCDC 2234403 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

***N*-Fluoro-*N*-(2-nitro)phenylsulfonyl)benzamide (1e)**[4]



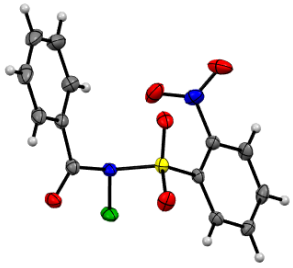
The title compound was obtained from **3** (0.2 mmol) and benzenecarbonyl chloride (0.24 mmol) following the procedure above. Purification by silica-gel column chromatography (*n*-hexane/DCM = 2/1 to 1/1) gave the compound (57.6 mg, 89% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 7.8 Hz, 1H), 7.96 (d, J = 7.8 Hz, 2H), 7.89 (t, J = 7.8 Hz, 1H), 7.76-7.83 (m, 2H), 7.66 (t, J = 7.3 Hz, 1H), 7.49 (t, J = 7.8 Hz, 2H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.27 (d, J = 3.8 Hz), 136.81, 135.16, 134.57 (d, J = 1.9 Hz), 132.42, 131.21 (d, J = 2.9 Hz), 130.73, 129.04, 128.69, 127.29, 125.15.

^{19}F NMR (376 MHz, $CDCl_3$) δ -50.06.

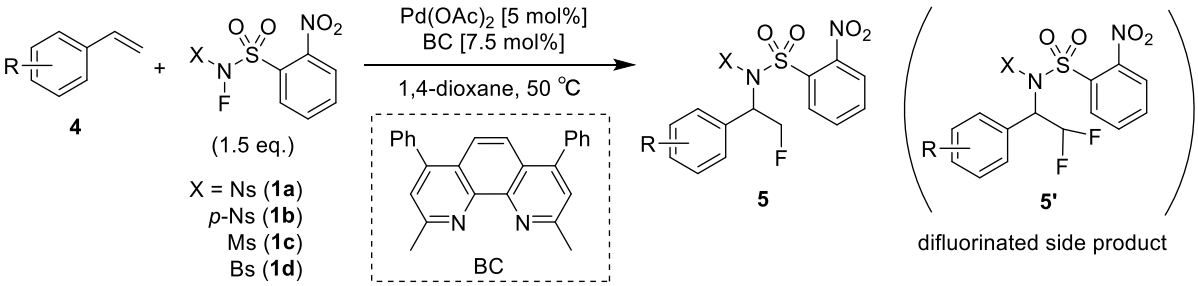
X-Ray crystallography of 1e



$C_{13}H_9FN_2O_5S$, clear light colorless cube, M_W = 324.28, crystal dimensions = 0.609×0.343×0.269 mm^3, triclinic, space group P-1, a = 7.0221(3), b = 7.3175(4), c = 13.1378(7) Å, V = 674.53(6) Å^3, Z = 2, λ = 0.71073 Å, T = 170 K, ρ_{calcd} = 1.597 g cm^{-3}, $\mu_{MoK\alpha}$ = 0.279 mm^{-1}, F_{000} = 332.0, 7601 total reflections ($2\theta_{max}$ = 26.369°), index ranges = -8≤h≤8, -9≤k≤9, -16≤l≤16, 2732 unique reflections, R_1 = 0.0466 ($I > 2\sigma(I)$), 0.0518 (all data), wR_2 = 0.1244 ($I > 2\sigma(I)$), 0.1283 (all data), goodness of fit = 1.085, S = 1.085 (199 parameters). CCDC 2234404 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

S3. Aminofluorination

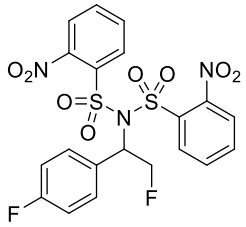
S3-1. Pd-catalyzed aminofluorination[5]



Experimental Procedures:

A solution of $Pd(OAc)_2$ (2.3 mg, 0.01 mmol, 5 mol%) and bathocuproine (5.4 mg, 0.015 mmol, 7.5 mol%) in 1,4-dioxane (1.0 mL) was stirred at room temperature for 1 h under N_2 atmosphere. N-F reagent **1** (0.3 mmol, 1.5 eq.) and styrene **4** (0.2 mmol) were added to the solution at room temperature and stirred at 50 °C under N_2 atmosphere. After stirring for 1-4 h, the yield was determined by ^{19}F NMR spectroscopy analysis using 2,3,5,6-tetrafluoro-*p*-xylene as an internal standard. The reaction mixture was directly loaded into a silica gel column and purified with a gradient eluant of hexane and dichloromethane to afford the aminofluorinated product **5**. In some cases, it was difficult to remove the difluorinated side product **5a'** [5] by silica-gel column chromatography. Therefore, the isolated yields of desired products decreased compared to the NMR yields.

***N*-[2-Fluoro-1-(4-fluorophenyl)ethyl]-*N*-(2-nitorobenzenesulfonyl)-2-nitrobenzenesulfonamide (5aa)**



The title compound was obtained from 4-fluorostyrene **4a** (0.2 mmol) and **1a** (0.3 mmol) following the procedure above. The yield (90%) was determined by ^{19}F NMR analysis using 2,3,5,6-tetrafluoro-*p*-xylene as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/DCM = 2/1 to 1/1) gave the compound (88.2 mg, 81% yield) as a white solid (containing 15% of difluorinated side product).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52-7.84 (m, 10H), 6.99 (t, *J* = 8.6 Hz, 2H), 6.04 (dt, *J* = 14.5, 7.5 Hz, 1H), 5.32 (ddd, *J* = 46.0, 9.5, 7.5 Hz, 1H), 5.05 (ddd, *J* = 46.4, 9.7, 6.9 Hz, 1H).

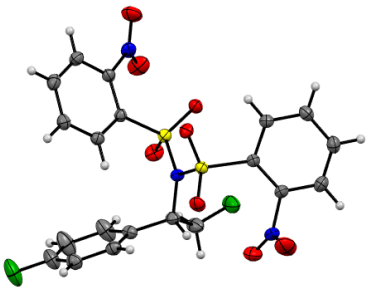
^{13}C NMR (125 MHz, $CDCl_3$) δ 163.32 (d, *J* = 251.1 Hz), 148.37, 134.99, 132.78, 132.20, 131.99 (d, *J* = 8.5 Hz), 131.28, 128.30, 124.28, 116.13 (d, *J* = 20.5 Hz), 82.09 (d, *J* = 175.0 Hz), 63.83 (d, *J* = 26.6 Hz).

^{19}F NMR (470 MHz, $CDCl_3$) δ -110.32 (1F), -216.13 (t, *J* = 43.2 Hz, 1F).

HRMS (ESI-TOF) calcd for $C_{20}H_{15}F_2N_3NaO_8S_2$ $[M+Na]^+$: 550.0166, found: 550.0226.

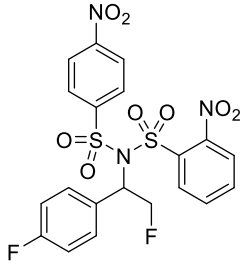
FT-IR (neat, cm^{-1}) 3527, 3099, 2918, 1603, 1589, 1470, 1443, 1302, 1197, 1057, 905, 665, 472, 434, 413, 405.

X-Ray crystallography of 5aa



$C_{20}H_{15}F_2N_3O_8S_2$, clear light colorless needle, M_W = 527.47, crystal dimensions = 0.371×0.2×0.056 mm^3, monoclinic, space group $P2_1/n$, a = 16.5286(5), b = 8.3039(2), c = 16.6083(5) Å, V = 2166.35(11) $Å^3$, Z = 4, λ = 0.71073 Å, T = 170 K, ρ_{calcd} = 1.617 g cm^{-3}, $\mu_{MoK\alpha}$ = 0.319 mm^{-1}, F_{000} = 1080.0, 41398 total reflections ($2\theta_{max}$ = 30.607°), index ranges = -23≤*h*≤23, -11≤*k*≤11, -23≤*l*≤23, 6519 unique reflections, R_1 = 0.0389 ($I > 2\sigma(I)$), 0.0554 (all data), wR_2 = 0.1016 ($I > 2\sigma(I)$), 0.1087 (all data), goodness of fit = 1.031, S = 1.031 (316 parameters). CCDC 2234408 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

***N*-[2-Fluoro-1-(4-fluorophenyl)ethyl]-*N*-(2-nitorobenzenesulfonyl)-4-nitrobenzenesulfonamide (5ab)**



The title compound was obtained from 4-fluorostyrene **4a** (0.2 mmol) and **1b** (0.3 mmol) following the procedure above. The yield (90%) was determined by ^{19}F NMR analysis using 2,3,5,6-tetrafluoro-*p*-xylene as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/DCM = 2/1 to 1/1) gave the compound (76.1 mg, 72% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (brs, 1H), 8.17 (d, *J* = 8.7 Hz, 2H), 7.62-7.82 (m, 5H), 7.44 (dd, *J* = 8.7, 5.0 Hz, 2H), 7.03 (t, *J* = 8.7 Hz, 2H), 5.96-6.02 (m, 1H), 5.34 (ddd, *J* = 46.4, 9.4, 8.2 Hz, 1H), 5.11 (ddd, *J* = 45.7, 9.2, 6.4 Hz, 1H).

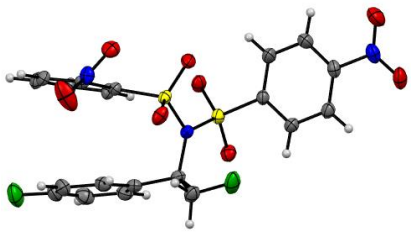
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.23 (d, *J* = 251.1 Hz), 150.61, 148.52, 144.99, 135.34, 132.20, 131.95, 131.53 (d, *J* = 8.6 Hz), 130.19, 128.26, 124.19, 123.97, 123.78, 116.10 (d, *J* = 21.1 Hz), 82.31 (d, *J* = 173.5 Hz), 63.05 (d, *J* = 24.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -110.26 (s, 1F), -217.08 (brs, 1F).

HRMS (ESI-TOF) calcd for $C_{20}H_{15}F_2N_3NaO_8S_2$ $[M+Na]^+$: 550.0166, found: 550.0079.

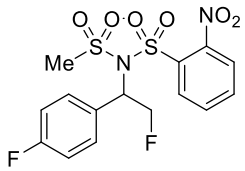
FT-IR (neat, cm^{-1}) 3627, 3523, 3515, 3114, 2987, 2032, 1967, 1903, 1602, 1512, 1469, 1404, 1367, 1319, 1253, 1118, 1024, 952, 854, 788, 705, 665, 632, 561, 530, 472.

X-Ray crystallography of 5ab



$C_{20}H_{15}F_2N_3O_8S_2$, clear light colorless block, M_W = 527.47, crystal dimensions = 0.64×0.31×0.3 mm^3, monoclinic, space group $P2_1/c$, a = 10.0255(3), b = 10.1690(4), c = 21.2063(9) Å, V = 2160.80(14) $Å^3$, Z = 4, λ = 0.71073 Å, T = 170 K, ρ_{calcd} = 1.621 g cm^{-3}, $\mu_{MoK\alpha}$ = 0.319 mm^{-1}, F_{000} = 1080.0, 36386 total reflections ($2\theta_{max}$ = 26.370°), index ranges = -12≤*h*≤12, -12≤*k*≤12, -26≤*l*≤26, 4416 unique reflections, R_1 = 0.0338 ($I > 2\sigma(I)$), 0.0389 (all data), wR_2 = 0.0932 ($I > 2\sigma(I)$), 0.0965 (all data), goodness of fit = 1.052, S = 1.052 (317 parameters). CCDC 2234410 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

***N*-[2-Fluoro-1-(4-fluorophenyl)ethyl]-*N*-(2-nitorobenzenesulfonyl)-methanesulfonamide (5ac)**



The title compound was obtained from 4-fluorostyrene **4a** (0.2 mmol) and **1b** (0.3 mmol) following the procedure above. The yield (93%) was determined by ^{19}F NMR analysis using 2,3,5,6-tetrafluoro-*p*-xylene as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/DCM = 2/1 to 1/1) gave the compound (74.0 mg, 90% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (brs, 1H), 7.63-7.74 (m, 3H), 7.56 (brs, 2H), 7.09 (t, *J* = 8.0 Hz, 2H), 5.94-6.00 (m, 1H), 5.09-5.37 (m, 2H), 2.91 (brs, 3H).

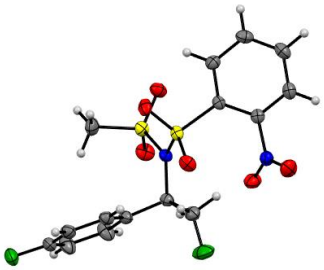
^{13}C NMR (125 MHz, $CDCl_3$) δ 163.15 (d, *J* = 249.9 Hz), 148.18, 134.89, 133.19, 132.26, 131.38 (d, *J* = 7.2 Hz), 128.59, 124.41,124.25, 112.26 (d, *J* = 21.7 Hz), 82.47 (d, *J* = 172.6 Hz), 62.34, 45.01.

^{19}F NMR (470 MHz, $CDCl_3$) δ -110.68 (s, 1F), -216.06 (brs, 1F).

HRMS (ESI-TOF) calcd for $C_{15}H_{14}F_2N_2NaO_6S_2$ $[M+Na]^+$: 443.0159, found: 443.0211.

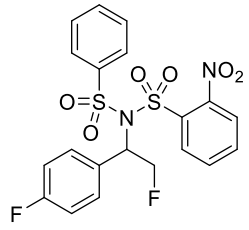
FT-IR (neat, cm^{-1}) 3664, 3541, 2507, 2158, 2032, 1974, 1541, 1512, 1377, 1353, 1319, 1228, 1163, 1124, 1002, 970, 887, 856, 831, 779, 736, 649, 592, 576, 570, 536, 514, 459.

X-Ray crystallography of 5ac



$C_{15}H_{14}F_2N_2O_6S_2$, clear light colorless block, M_W = 420.40, crystal dimensions = 0.446×0.318×0.237 mm^3, monoclinic, space group $P2_1/c$, a = 14.6054(6), b = 8.9495(3), c = 14.5067(6) Å, V = 1684.89(13) $Å^3$, Z = 4, λ = 0.71073 Å, T = 170 K, ρ_{calcd} = 1.657 g cm^{-3}, $\mu_{MoK\alpha}$ = 0.376 mm^{-1}, F_{000} = 864.0, 28297 total reflections ($2\theta_{max}$ = 26.371°), index ranges = -18≤h≤18, -11≤k≤11, -18≤l≤18, 3440 unique reflections, R_1 = 0.0291 ($I > 2\sigma(I)$), 0.0336 (all data), wR_2 = 0.0765 ($I > 2\sigma(I)$), 0.0787 (all data), goodness of fit = 1.061, S = 1.061 (253 parameters). CCDC 2234409 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

***N*-[2-Fluoro-1-(4-fluorophenyl)ethyl]-*N*-(2-nitorobenzenesulfonyl)-benzenesulfonamide (5ad)**



The title compound was obtained from 4-fluorostyrene **4a** (0.2 mmol) and **1d** (0.4 mmol) following the procedure above. The yield (74%) was determined by ^{19}F NMR analysis using 2,3,5,6-tetrafluoro-*p*-xylene as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/EtOAc = 7/1 to 5/1) gave the compound (72.9 mg, 72% yield) as a white solid.

^{1}H NMR (500MHz, $CDCl_3$) δ 8.28 (brs, 1H), 7.69-7.77 (m, 2H), 7.65 (d, J = 7.7 Hz, 1H), 7.49-7.56 (m, 3H), 7.41 (dd, J = 8.6, 5.2 Hz, 2H), 7.34 (t, J = 8.0, 7.5 Hz, 2H), 6.96 (t, J = 8.6 Hz, 2H), 5.93 (m, 1H), 5.09-5.30 (m, 2H).

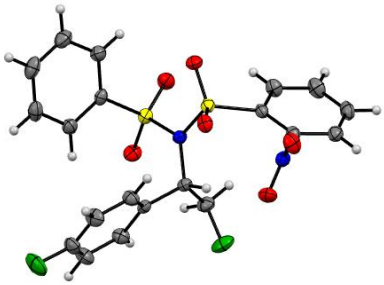
^{13}C NMR (125 MHz, $CDCl_3$) δ 162.99 (d, J = 249.89 Hz), 148.36, 139.48, 134.87, 134.22, 132.97, 132.11, 131.86, 131.29 (d, J = 8.45 Hz), 128.86, 128.72 (d, J = 7.24 Hz), 128.57, 124.08, 115.77 (d, J = 21.73 Hz), 82.46 (d, J = 172.63 Hz), 62.50 (d, J = 25.35 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -111.73 (s, 1F), -215.91 (t, J = 41.6 1F).

HRMS (ESI-TOF) calcd for $C_{20}H_{16}F_2N_2NaO_6S_2$ $[M+Na]^+$: 505.0316, found: 505.0332.

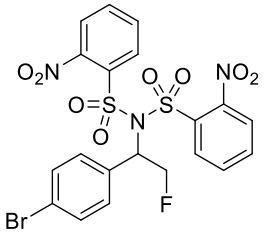
FT-IR (neat, cm^{-1}) 1605, 1583, 1537, 1511, 1478, 1449, 1441, 1383, 1362, 1296, 1274, 1168, 1129, 1085, 1059, 1009, 966, 941, 904, 852, 836, 815, 775, 719, 683, 651, 610, 579, 565, 549, 538, 476, 453, 443, 406.

X-Ray crystallography of 5ad



$C_{20}H_{16}F_2N_2O_6S_2$, clear light colorless plate, M_W = 482.47, crystal dimensions = 0.36×0.24×0.13 mm^3, monoclinic, space group $C2/c$, a = 16.0194(10), b = 11.6755(8), c = 21.8846(17) Å, V = 4087.7(5) $Å^3$, Z = 8, λ = 0.71073 Å, T = 175 K, ρ_{calcd} = 1.568 g cm^{-3}, $\mu_{MoK\alpha}$ = 0.321 mm^{-1}, F_{000} = 1984.0, 10657 total reflections ($2\theta_{max}$ = 26.369°), index ranges = -20≤h≤20, -14≤k≤13 -27≤l≤27 3971 unique reflections, R_1 = 0.0365 ($I > 2\sigma(I)$), 0.0465 (all data), wR_2 = 0.0935 ($I > 2\sigma(I)$), 0.0978 (all data), goodness of fit = 1.033, S = 1.033 (289 parameters). CCDC 2234411 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

***N*-[1-(4-Bromophenyl)-2-fluoroethyl]-*N*-(2-nitorobenzenesulfonyl)-2-nitrobenzenesulfonamide (5ba)**



The title compound was obtained from 4-bromostyrene **4b** (0.2 mmol) and **1b** (0.3 mmol) following the procedure above. The yield (87%) was determined by ^{19}F NMR analysis using 2,3,5,6-tetrafluoro-*p*-xylene as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/DCM = 2/1 to 1/1) gave the compound (90.1 mg, 77% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (brs, 2H), 7.73 (t, *J* = 7.8 Hz, 2H), 7.65-7.69 (m, 2H), 7.58 (t, *J* = 7.8 Hz, 2H), 7.40 (s, 4H), 6.01 (dt, *J* = 14.4, 7.2 Hz, 1H), 5.30 (ddd, *J* = 45.6, 9.5, 7.5 Hz, 1H), 5.08 (ddd, *J* = 46.1, 9.5, 7.0 Hz, 1H).

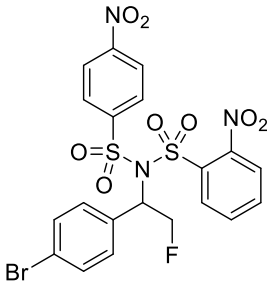
^{13}C NMR (100 MHz, $CDCl_3$) δ 148.34, 134.98, 132.69, 132.35, 132.26, 131.91, 131.43, 131.38 (d, *J* = 4.0 Hz), 124.30, 124.22, 81.87 (d, *J* = 173.8 Hz), 63.64 (d, *J* = 26.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -216.14 (td, *J* = 46.2, 11.6 Hz, 1F).

HRMS (ESI-TOF) calcd for $C_{20}H_{15}BrFN_3NaO_8S_2$ $[M+Na]^+$: 609.9366 , found: 609.9368.

FT-IR (neat, cm^{-1}) 3105, 2907, 1588, 1490, 1474, 1439, 1298, 1266, 1094, 950, 854, 678, 663, 642, 474, 461, 409.

***N*-[1-(4-Bromophenyl)-2-fluoroethyl]-*N*-(2-nitorobenzenesulfonyl)-4-nitrobenzenesulfonamide (5bb)**



The title compound was obtained from 4-bromostyrene **4b** (0.2 mmol) and **1b** (0.3 mmol) following the procedure above. The yield (94%) was determined by ^{19}F NMR analysis using 2,3,5,6-tetrafluoro-*p*-xylene as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/DCM = 2/1 to 1/1) gave the compound (99.1 mg, 84% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (brs, 1H), 8.13 (d, *J* = 8.7 Hz, 2H), 7.71-7.80 (m, 2H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.59 (brs, 2H), 7.40 (d, *J* = 8.7 Hz, 2H), 7.23 (d, *J* = 5.0 Hz, 2H), 5.90-5.96 (m, 1H), 5.03-5.36 (m, 2H).

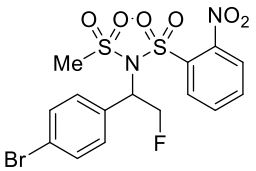
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.59, 148.50, 144.85, 135.38, 132.38, 132.28, 132.20, 131.38 (d, *J* = 4.8 Hz), 131.30, 131.07, 130.21, 124.26, 124.02, 123.80, 82.13 (d, *J* = 173.5 Hz), 62.84 (d, *J* = 24.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -217.11 (brs, 1F).

HRMS (ESI-TOF) calcd for $C_{20}H_{17}BrFN_3O_9S_2$ $[M+H_2O]^{\cdot+}$: 604.9574, found: 604.9566.

FT-IR (neat, cm^{-1}) 1589, 1528, 1488, 1442, 1388, 1316, 1168, 1042, 1020, 1012, 888, 852, 821, 773, 739, 729, 717, 681, 663, 650, 628, 595, 582, 559, 542, 465, 422, 406.

***N*-[1-(4-Bromophenyl)-2-fluoroethyl]-*N*-(2-nitorobenzenesulfonyl)-methanesulfonamide (5bc)**



The title compound was obtained from 4-bromostyrene **4b** (0.2 mmol) and **1c** (0.3 mmol) following the procedure above. The yield (85%) was determined by ^{19}F NMR analysis using 2,3,5,6-tetrafluoro-*p*-xylene as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/DCM = 2/1 to 1/1) gave the compound (81.8 mg, 85% yield) as a white solid (containing 9% of difluorinated side product).

^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ 8.11 (brs, 1H), 7.83-7.99 (m, 2H), 7.87 (t, *J* = 7.8 Hz, 1H), 7.6 (d, *J* = 8.7 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 5.91-5.98 (m, 1H), 5.14-5.42 (m, 2H), 3,17 (s, 3H).

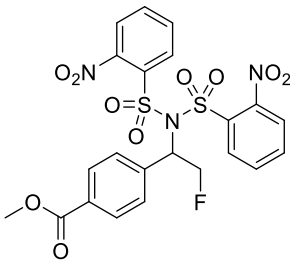
^{13}C NMR (125 MHz, $(CD_3)_2CO$) δ 149.14, 136.51, 133.44, 133.23, 133.02, 132.34, 132.07, 125.55, 125.45, 124.04, 83.32 (d, *J* = 170.5 Hz), 63.52 (d, *J* = 25.1 Hz), 45.56.

^{19}F NMR (470 MHz, $(CD_3)_2CO$) δ -217.59 (brs, 1F).

HRMS (ESI-TOF) calcd for $C_{17}H_{17}BrFN_3NaO_6S_2$ $[M+MeCN+Na]^+$:543.9624, found: 543.9589.

FT-IR (neat, cm^{-1}) 2502, 2222, 2206, 2029, 2023, 2004, 1994, 1593, 1495, 1443, 1412, 1323, 1126, 1076, 1055, 1011, 980, 878, 781, 725, 700, 689, 648, 500, 478, 447.

Methyl 4-[2-fluoro-1-[(2-nitrobenzenesulfonyl)-(2-nitrobenzenesulfonyl)amino]ethyl]benzoate (5ca)



The title compound was obtained from methyl 4-ethenylbenzoate **4c** (0.2 mmol) and **1b** (0.3 mmol) following the procedure above. The yield (60%) was determined by ^{19}F NMR analysis using 2,3,5,6-tetrafluoro-*p*-xylene as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/DCM = 2/1 to 1/1) twice gave the compound (47.3 mg, 42% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.82 (brs, 2H), 7.71 (t, *J* = 7.8 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.5 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 2H), 6.09 (dt, *J* = 12.4, 6.8 Hz, 1H), 5.35 (ddd, *J* = 45.7, 9.6, 7.4 Hz, 1H), 5.14 (ddd, *J* = 46.1, 9.8, 6.8 Hz, 1H), 3.93 (s, 3H).

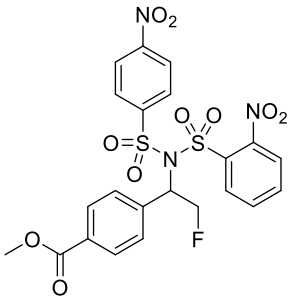
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.30, 148.37, 137.22 (d, *J* = 4.3 Hz), 135.09, 132.62, 132.22, 131.31, 130.34, 130.16, 129.77, 124.29, 81.90(d, *J* = 174.4 Hz), 63.69 (d, *J* = 26.0), 52.57.

^{19}F NMR (376 MHz, $CDCl_3$) δ -216.33 (td, *J* = 46.2 11.6 Hz, 1F).

HRMS (ESI-TOF) calcd for $C_{22}H_{18}FN_3NaO_{10}S_2$ $[M+Na]^+$: 590.0315, found: 590.0308.

FT-IR (neat, cm^{-1}) 3105, 2956, 2922, 1614, 1586, 1439, 1420, 1319, 818, 679, 665, 642, 487, 458, 434, 409, 403.

Methyl 4-[2-fluoro-1-[(2-nitrobenzenesulfonyl)-(4-nitrobenzenesulfonyl)amino]ethyl]benzoate (5cb)



The title compound was obtained from methyl 4-ethenylbenzoate **4c** (0.2 mmol) and **1b** (0.3 mmol) following the procedure above. The yield (85%) was determined by ^{19}F NMR analysis using 2,3,5,6-tetrafluoro-*p*-xylene as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/DCM = 2/1 to 1/1) twice gave the compound (43.8 mg, 39% yield) as a white solid. The isolated yield decreased compared to the NMR yield, because it was difficult to completely remove the difluorinated side product.

^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.26-8.33 (m, 3H), 8.00-8.06 (m, 3H), 7.94 (d, *J* = 8.7 Hz, 2H), 7.87 (d, *J* = 7.8 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 2H), 6.08-6.15 (m, 1H), 5.27-5.47 (m, 2H), 3.90 (s, 3H).

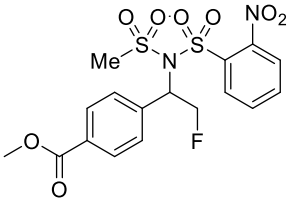
^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 166.54, 151.86, 149.26, 145.19, 138.18 (d, *J* = 5.8 Hz), 137.13, 133.62, 132.88, 132.17, 131.99, 131.17, 130.61, 130.19,125.66, 125.01, 82.98 (d, *J* = 171.6 Hz), 63.94 (d, *J* = 24.9 Hz), 52.66.

^{19}F NMR (376 MHz, $(CD_3)_2CO$) δ -217.85 (t, *J* = 46.2 Hz).

HRMS (ESI-TOF) calcd for $C_{22}H_{18}FN_3NaO_{10}S_2$ $[M+Na]^+$: 590.0315, found: 590.0329.

FT-IR (neat, cm^{-1}) 3102, 3081, 3038, 2953, 1606, 1594, 1576, 1483, 1449, 1428, 1417, 1404, 1034, 863, 636.

Methyl 4-[2-fluoro-1-[(methanesulfonyl)-(2-nitrobenzenesulfonyl)amino]ethyl]benzoate (5cc)



The title compound was obtained from methyl 4-ethenylbenzoate **4c** (0.2 mmol) and **1c** (0.4 mmol) following the procedure above. The yield (69%) was determined by ^{19}F NMR analysis using 2,3,5,6-tetrafluoro-*p*-xylene as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/DCM = 2/1 to 1/1) twice gave the compound (46,1 mg, 50% yield) as a white solid.

^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.16 (brs, 1H), 8.05 (d, *J* = 8.2, 2H), 7.87-8.00 (m, 3H), 7.67 (d, *J* = 8.7 Hz, 2H), 5.99-6.06 (m, 1H), 5.23-5.44 (m, 2H), 3.9 (s, 3H).

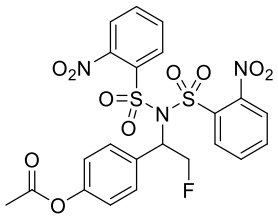
^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 166.68, 149.19, 138.95, 136.67, 133.47, 133.38, 132.49, 131.97, 130.79, 130.15, 125.58, 83.31 (d, *J* = 169.5 Hz), 63.57 (d, *J* = 26.0 Hz), 52.69, 45.64.

^{19}F NMR (376 MHz, $CDCl_3$) δ -216.19 (brs, 1F).

HRMS (ESI-TOF) calcd for $C_{19}H_{20}FN_3NaO_8S_2$ $[M+MeCN+Na]^+$: 524.0574, found: 524.0569.

FT-IR (neat, cm^{-1}) 3105, 2955, 1612, 1579, 1489, 1436, 1411, 1032, 676, 656, 650, 629, 428, 424, 411.

***N*-[1-(4-Acetyloxyphenyl)-2-fluoroethyl]-*N*-(2-nitorobenzenesulfonyl)-2-nitrobenzenesulfonamide (5da)**



The title compound was obtained from methyl 4-acetyloxystyrene **4d** (0.2 mmol) and **1b** (0.3 mmol) following the procedure above. The yield (74%) was determined by ^{19}F NMR analysis using 2,3,5,6-tetrafluoro-*p*-xylene as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/DCM = 2/1 to 1/1) twice gave the compound (59.6 mg, 53% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.72 (m, 10 H), 7.03 (d, *J* = 9.0 Hz, 2H), 6.06 (dt, *J* = 12.0, 7.6 Hz, 1H), 5.34 (ddd, *J* = 45.9, 9.4, 7.6 Hz, 1H), 5.11 (ddd, *J* = 46.1, 9.5, 7.0 Hz, 1H), 2.31 (s, 3H).

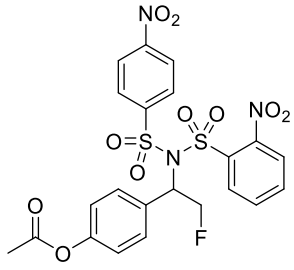
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.28, 151.72, 148.32, 135.06, 132.70, 132.40, 131.21, 130.16, 124.17, 122.58, 120.04, 82.05 (d, *J* = 173.8 Hz), 63.89 (d, *J* = 26.1 Hz), 21.24.

^{19}F NMR (376 MHz, $CDCl_3$) δ -216.06 (td, *J* = 46.2, 11.6 Hz, 1F).

HRMS (ESI-TOF) calcd for $C_{22}H_{18}FN_3NaO_{10}S_2$ $[M+Na]^+$: 590.0315, found: 590.0302.

FT-IR (neat, cm^{-1}) 3098, 3031, 2923, 2853, 1710, 1589, 1473, 1441, 1299, 1269, 673, 643, 482, 435, 409

***N*-[1-(4-Acetyloxyphenyl)-2-fluoroethyl]-*N*-(2-nitorobenzenesulfonyl)-4-nitrobenzenesulfonamide (5db)**



The title compound was obtained from methyl 4-acetyloxystyrene **4d** (0.2 mmol) and **1b** (0.3 mmol) following the procedure above. The yield (99%) was determined by ^{19}F NMR analysis using 2,3,5,6-tetrafluoro-*p*-xylene as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/DCM = 2/1 to 1/1) twice gave the compound (71.2 mg, 63% yield) as a white solid. The isolated yield decreased compared to the NMR yield, because it was difficult to remove the side products derived from reagent decomposition.

^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.25-8.33 (m, 3H), 7.99-8.08 (m, 3H), 7.66 (brs, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.5 Hz, 2H), 6.01-6.07 (m, 1H), 5.24-5.45 (m, 2H), 2.32 (s, 3H).

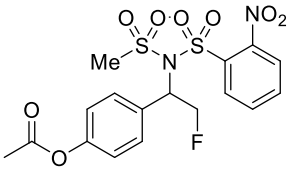
^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 170.10, 152.73, 151.88, 149.34, 145.46, 137.13, 137.53, 132.23, 131.56, 131.11, 130.92 (d, *J* = 4.8 Hz), 125.50, 125.02, 123.56, 83.11 (d, *J* = 171.6 Hz), 64.08 (d, *J* = 24.0 Hz), 55.06, 21.05.

^{19}F NMR (376 MHz, $(CD_3)_2CO$) δ -218.22 (t, *J* = 46.2 Hz).

HRMS (ESI-TOF) calcd for $C_{22}H_{18}FN_3NaO_{10}S_2$ $[M+Na]^+$: 590.0315, found: 590.0321.

FT-IR (neat, cm^{-1}) 3810, 3684, 3662, 3641, 3110, 2989, 1706, 1606, 1591, 1476, 1441, 1426, 1304, 1289, 1268, 1110, 916, 663, 431, 416, 405.

***N*-[1-(4-Acetyloxyphenyl)-2-fluoroethyl]-*N*-(2-nitorobenzenesulfonyl)-methanesulfonamide (5dc)**



The title compound was obtained from methyl 4-acetyloxystyrene **4d** (0.2 mmol) and **1c** (0.3 mmol) following the procedure above. The yield (86%) was determined by ^{19}F NMR analysis using 2,3,5,6-tetrafluoro-*p*-xylene as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/DCM = 2/1 to 1/1) twice gave the compound (56.6 mg, 60% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (brs, 1H), 7.68 (brs, 3H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 8.2 Hz, 2H), 5.94-6.01 (m, 1H), 5.35 (d, *J* = 47.6 Hz, 1H), 5.11 (d, *J* = 45.7 Hz, 1H), 2.93 (brs, 3H), 2.29 (s, 3H).

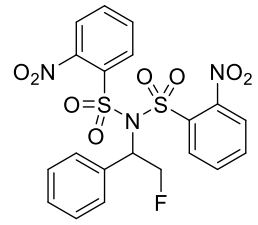
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.16, 151.46, 148.09,134.85, 133.14, 132.25, 130.59, 130.06, 124.36, 122.48, 82.47 (d, *J* = 171.6 Hz), 62.60 (d, *J* =22.0 Hz), 44.90, 29.79, 21.29.

^{19}F NMR (376 MHz, $CDCl_3$) δ -216.16 (brs, 1F).

HRMS (ESI-TOF) calcd for $C_{17}H_{17}FN_2NaO_8S_2$ $[M+Na]^+$: 483.0308, found: 483.0361.

FT-IR (neat, cm^{-1}) 3514, 3508, 3499, 3462, 3205, 3105, 3026, 2945, 1709, 1661, 1614, 1595, 1514, 1470, 1441, 1323, 1294, 1232, 1207, 1057, 1007, 968, 702.

***N*-[2-Fluoro-1-phenylethyl]-*N*-(2-nitorobenzenesulfonyl)-2-nitrobenzenesulfonamide (5ea)**



The title compound was obtained from styrene **4e** (0.2 mmol) and **1b** (0.3 mmol) following the procedure above. The yield (74%) was determined by ^{19}F NMR analysis using 2,3,5,6-tetrafluoro-*p*-xylene as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/DCM = 2/1 to 1/1) gave the compound (79.8 mg, 71% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.86 (m, 6H), 7.51-7.56 (m, 4H), 7.31 (dd, *J* = 3.2, 2.3 Hz, 3H), 6.06 (dt, *J* = 12.4, 7.2 Hz, 1H), 5.30-5.46 (dt, *J* = 45.2 , 8.8 Hz, 1H), 5.08 (ddd, *J* = 45.8, 9.6, 6.9 Hz, 1H).

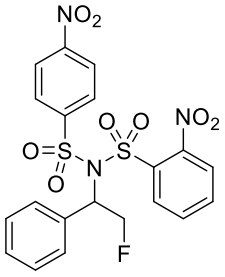
^{13}C NMR (100 MHz, $CDCl_3$) δ 148.34, 134.83, 132.85, 132.29 (d, *J* = 4.8 Hz), 132.13, 131.25, 130.36, 129.92, 129.14, 124.16, 82.12 (d, *J* = 173.5 Hz), 64.66 (d, *J* = 24.9 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -216.56 (t, *J* = 46.2 Hz, 1F).

HRMS (ESI-TOF) calcd for $C_{20}H_{16}FN_3NaO_8S_2$ $[M+Na]^+$: 532.0261, found: 532.0265.

FT-IR (neat, cm^{-1}) 3092, 3025, 1588, 1497, 1470, 1443, 1301, 1256, 1189, 1150, 1105, 1074, 1060, 669, 633, 622.

***N*-[2-Fluoro-1-phenylethyl]-*N*-(2-nitorobenzenesulfonyl)-4-nitrobenzenesulfonamide (5eb)**



The title compound was obtained from styrene **4e** (0.2 mmol) and **1b** (0.3 mmol) following the procedure above. The yield (90%) was determined by ^{19}F NMR analysis using 2,3,5,6-tetrafluoro-*p*-xylene as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/DCM = 2/1 to 1/1) gave the compound (80.5 mg, 79% yield) as a white solid.

^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.28 (d, *J* = 8.7 Hz, 2H), 8.19 (brs, 1H), 7.92-8.06 (m, 3H), 7.77 (d, *J* = 7.8 Hz, 2H), 7.35-7.48 (m, 5H), 6.03-6.09 (m, 1H), 5.20-5.47 (m, 2H).

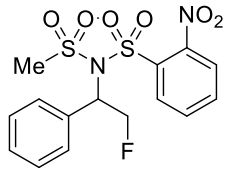
^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 151.69, 149.19, 145.36, 136.86, 133.36, 133.24 (d, *J* = 6.0 Hz), 132.95, 131.94, 131.05, 130.35, 130.08, 129.81, 125.43, 124.75, 83.07 (d, *J* = 169.7 Hz), 64.62 (d, *J* = 23.9 Hz).

^{19}F NMR (376 MHz, $(CD_3)_2CO$) δ -217.91 (t, *J* = 46.2 Hz).

HRMS (ESI-TOF) calcd for $C_{20}H_{16}FN_3NaO_8S_2$ $[M+Na]^+$: 532.0261, found: 532.0341.

FT-IR (neat, cm^{-1}) 1547, 1527, 1458, 1388, 1307, 1111, 1083, 1023, 957, 881, 852, 816, 772, 732, 707, 683, 664, 650, 630, 595, 541, 465.

***N*-[2-Fluoro-1-phenylethyl]-*N*-(2-nitorobenzenesulfonyl)-methanesulfonamide (5ec)**



The title compound was obtained from styrene **4e** (0.2 mmol) and **1c** (0.3 mmol) following the procedure above. The yield (89%) was determined by ^{19}F NMR analysis using 2,3,5,6-tetrafluoro-*p*-xylene as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/DCM = 2/1 to 1/1) gave the compound (62.4 mg, 77% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (brs, 1H), 7.70 (s, 2H), 7.65 (d, *J* = 6.0 Hz, 1H), 7.57 (d, *J* = 6.9 Hz, 2H), 7.40 (d, *J* =7.8 Hz, 3H), 5.98-6.04 (m, 1H), 5.12-5.43 (m, 2H), 2.85 (brs, 3H).

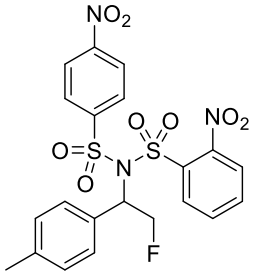
^{13}C NMR (100 MHz, $CDCl_3$) δ 148.15, 134.73, 133.38, 132.59, 132.20, 129.95, 129.68, 129.33, 129.21, 124.37, 82.53 (d, *J* = 171.6 Hz), 63.12 (d, *J* = 24.9 Hz), 44.80.

^{19}F NMR (376 MHz, $CDCl_3$) δ -216.47 (brs, 1F).

HRMS (ESI-TOF) calcd for $C_{15}H_{15}FN_2NaO_6S_2$ $[M+Na]^+$: 425.0253, found: 425.0259.

FT-IR (neat, cm^{-1}) 3690, 3647, 3595, 3568, 3562, 3543, 3529, 2532, 1259, 1117, 1105, 1070, 712, 629, 594, 442, 432.

***N*-[2-Fluoro-1-(4-methylphenyl)-ethyl]-*N*-(2-nitorobenzenesulfonyl)-4-nitrobenzenesulfonamide (5fb)**



The title compound was obtained from 4-methylstyrene **4f** (0.2 mmol) and **1b** (0.3 mmol) following the procedure above. The yield (74%) was determined by ^{19}F NMR analysis using 2,3,5,6-tetrafluoro-*p*-xylene as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/DCM = 2/1 to 1/1) gave the compound (67.9 mg, 65% yield) as a white solid.

^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.28 (d, *J* = 9.2 Hz, 2H), 8.21 (d, *J* = 8.7 Hz, 1H), 7.92-8.05 (m, 3H), 7.79 (d, *J* = 6.9 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.16 (d, *J* = 7.8 Hz, 2H), 5.99-6.06 (m, 1H), 5.16-5.46 (m, 2H), 2.34 (s, 3H).

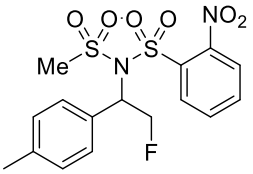
^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 151.67, 149.23, 145.48, 140.58, 136.76, 133.42, 133.14 (d, *J* = 5.8), 132.01, 131.07, 130.37, 130.17,130.07, 125.48, 124.76, 83.22 (d, *J* = 170.6 Hz), 64.59 (d, *J* = 30.7 Hz), 21.15.

^{19}F NMR (376 MHz, $(CD_3)_2CO$) δ -217.85 (t, *J* = 46.2 Hz).

HRMS (ESI-TOF) calcd for $C_{21}H_{18}FN_3NaO_8S_2$ $[M+Na]^+$: 546.0417, found: 546.0495.

FT-IR (neat, cm^{-1}) 3107, 3038, 2990, 2963, 2910, 1608, 1470, 1443, 1404, 1294, 1272, 1258, 1111, 1058, 666, 650, 640, 408.

***N*-[2-Fluoro 1-(4-methylphenyl)ethyl]-*N*-(2-nitorobenzenesulfonyl)-methanesulfonamide (5fc)**



The title compound was obtained from methyl 4-methylstyrene **4f** (0.2 mmol) and **1c** (0.3 mmol) following the procedure above. The yield (99%) was determined by ^{19}F NMR analysis using 2,3,5,6-tetrafluoro-*p*-xylene as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/DCM = 2/1 to 1/1) twice gave the compound (48.7 mg, 59% yield) as a white solid. The isolated yield decreased compared to the NMR yield, because it was difficult to remove the side products derived from reagent decomposition.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (brs, 1H), 7.70 (s, 2H), 7.65 (brs, 1H), 7.44 (d, *J* = 7.3 Hz, 2H), 7.19 (d, *J* = 7.3 Hz, 2H), 5.94-6.01 (m, 1H), 5.07-5.45 (m, 2H), 2.84 (brs, 3H), 2.34 (s, 3H).

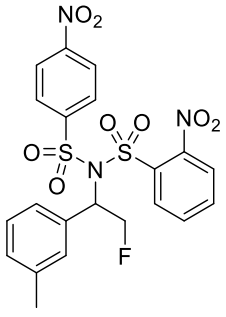
^{13}C NMR (100 MHz, $CDCl_3$) δ 148.19, 139.76, 134.58, 133.51, 132.18, 129.87, 129.51, 129.30, 124.34, 124.19, 83.50 (d, *J* = 170.6 Hz), 63.10 (d, *J* = 26.8 Hz), 44.83, 21.34.

^{19}F NMR (376 MHz, $CDCl_3$) δ -216.44 (brs, 1F).

HRMS (ESI-TOF) calcd for $C_{17}H_{21}FN_2NaO_7S_2$ $[M+Na+MeOH]^+$: 471.0672, found: 471.0683.

FT-IR (neat, cm^{-1}) 3624, 2497, 2158, 2030, 1976, 1593, 1539, 1519, 1479, 1444, 1411, 1371, 1352, 1321, 1161, 1128, 1054, 1016, 779, 729, 698, 686, 648, 437.

***N*-[2-Fluoro-1-(3-methylphenyl)-ethyl]-*N*-(2-nitorobenzenesulfonyl)-4-nitrobenzenesulfonamide (5gb)**



The title compound was obtained from 3-methylstyrene **4g** (0.2 mmol) and **1b** (0.3 mmol) following the procedure above. The yield (77%) was determined by ^{19}F NMR analysis using 2,3,5,6-tetrafluoro-*p*-xylene as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/DCM = 2/1 to 1/1) gave the compound (72.8 mg, 69% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (brs, 1H), 8.09 (d, *J* = 8.7 Hz, 2H), 7.72-7.80 (m, 2H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.56 (brs, 2H), 7.15-7.21 (m, 4H), 5.97-6.04 (m, 1H), 5.38 (ddd, *J* = 46.5, 9.6, 8.7 Hz, 1H), 5.13 (ddd, *J* = 45.7, 9.2, 6.4 Hz, 1H), 2.24 (s, 3H).

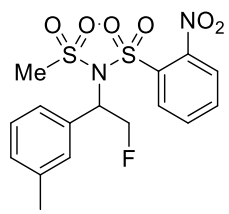
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.41, 148.48, 144.95, 138.91, 135.03, 132.55, 132.04, 131.98, 131.82, 130.23, 130.21, 130.08, 128.95, 126.31, 124.04, 123.44, 82.51 (d, *J* = 172.4 Hz), 63.69 (d, *J* = 23.1 Hz), 21.35.

^{19}F NMR (376 MHz, $(CD_3)_2CO$) δ -217.82 (t, *J* = 46.2 Hz).

HRMS (ESI-TOF) calcd for $C_{21}H_{18}FN_3NaO_8S_2$ $[M+Na]^+$: 546.0417, found: 546.0437.

FT-IR (neat, cm^{-1}) 3108, 3036, 2923, 1606, 1592, 1479, 1441, 1404, 1227, 1113, 1054, 917, 827, 758, 745, 413.

***N*-[2-fluoro 1-(3-methylphenyl)ethyl]-*N*-(2-nitorobenzenesulfonyl)-methanesulfonamide (5gc)**



The title compound was obtained from methyl 3-methylstyrene **4g** (0.2 mmol) and **1c** (0.3 mmol) following the procedure above. The yield (95%) was determined by ^{19}F NMR analysis using 2,3,5,6-tetrafluoro-*p*-xylene as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/DCM = 2/1 to 1/1) gave the compound (73.8 mg, 89% yield) as a white solid (containing 15% of difluorinated side product).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (brs, 1H), 7.68 (s, 2H), 7.63 (s, 1H), 7.32 (s, 2H), 7.24-7.28 (m, 1H), 7.15 (d, *J* = 7.3 Hz, 1H), 5.94-6.01 (m, 1H), 5.38 (d, *J* = 45.7 Hz, 1H), 5.12 (d, *J* = 45.7 Hz, 1H), 2.90 (brs, 3H), 2.35 (s, 3H).

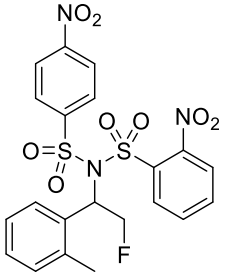
^{13}C NMR (100 MHz, $CDCl_3$) δ 148.22, 139.07, 134.57, 133.50, 132.09, 130.88, 130.41, 129.95, 129.07, 126.43, 124.27, 124.10, 82.69 (d, *J* = 170.5 Hz), 63.29 (d, *J* = 17.3 Hz), 44.83, 21.55.

^{19}F NMR (376 MHz, $CDCl_3$) δ -216.47 (brs, 1F).

HRMS (ESI-TOF) calcd for $C_{16}H_{17}FN_2NaO_6S_2$ $[M+Na]^+$: 439.0410, found: 439.0403.

FT-IR (neat, cm^{-1}) 3624, 2497, 2158, 2030, 1976, 1593, 1539, 1519, 1479, 1444, 1411, 1371, 1352, 1321, 1161, 1128, 1054, 1016, 995, 977, 875, 852, 837, 815, 779, 729, 698, 686, 648, 590, 578, 526, 516, 495, 478, 457, 437.

***N*-[2-Fluoro-1-(2-methylphenyl)-ethyl]-*N*-(2-nitorobenzenesulfonyl)-4-nitrobenzenesulfonamide (5hb)**



The title compound was obtained from 2-methylstyrene **4h** (0.2 mmol) and **1b** (0.3 mmol) following the procedure above. The yield (56%) was determined by ^{19}F NMR analysis using 2,3,5,6-tetrafluoro-*p*-xylene as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/DCM = 2/1 to 1/1) gave the compound (52.8 mg, 31% yield) as a white solid (it was difficult to isolate target molecules from deprotected compounds).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (brs, 1H), 8.07 (d, *J* = 6.4 Hz, 2H), 7.66-7.70 (m, 5H), 7.31 (d, *J* = 6.9 Hz, 1H), 7.18 (t, *J* = 6.0 Hz, 2H), 6.82 (d, *J* = 6.9 Hz, 1H), 6.18-6.25 (m, 1H), 5.60 (dt, *J* = 47.6, 9.6 Hz, 1H), 4.98 (dd, *J* = 45.1, 6.0 Hz, 1H), 2.20 (brs, 3H).

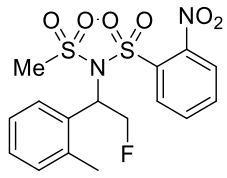
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.32, 148.37, 144.23, 139.14, 134.37, 134.15, 132.02, 131.19, 130.26, 130.16, 129.96, 128.79, 128.72, 126.64, 124.39, 123.42, 83.95 (d, *J* = 173.5 Hz), 61.92 (d, *J* = 21.1 Hz), 19.91.

^{19}F NMR (376 MHz, $CDCl_3$) δ -215.51 (brs, 1F).

HRMS (ESI-TOF) calcd for $C_{21}H_{18}FN_3NaO_8S_2$ $[M+Na]^+$: 546.0417, found: 546.0482.

FT-IR (neat, cm^{-1}) 3106, 1605, 1543, 1523, 1468, 1444, 1363, 1346, 1312, 1165, 1081, 1039, 1013, 954, 913, 852, 826, 776, 759, 739, 730, 683, 663, 648, 630, 601, 569, 538, 470, 419, 404.

***N*-[2-Fluoro 1-(2-methylphenyl)ethyl]-*N*-(2-nitorobenzenesulfonyl)-methanesulfonamide (5hc)**



The title compound was obtained from methyl 2-methylstyrene **4h** (0.2 mmol) and **1c** (0.3 mmol) following the procedure above. The yield (67%) was determined by ^{19}F NMR analysis using 2,3,5,6-tetrafluoro-*p*-xylene as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/DCM = 2/1 to 1/1) gave the compound (47.5 mg, 57% yield) as a white solid.

^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.11 (t, *J* = 4.6 Hz, 1H), 7.75 (t, *J* = 4.1 Hz, 2H), 7.69 (brs, 1H), 7.31 (t, *J* = 4.4 Hz, 1H), 7.13 (t, *J* = 4.4 Hz, 2H), 7.02 (brs, 1H), 6.16-6.23 (m, 1H), 5.59 (ddd, *J* = 47.6, 9.8 Hz, 1H), 4.97 (ddd, *J* = 44.5, 9.6, 4.6 Hz, 1H), 3.34 (brs, 3H), 2.40 (s, 3H).

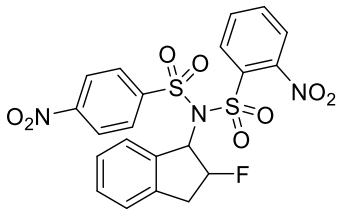
^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 148.86, 139.37, 135.51, 134.25, 132.91, 132.00, 130.54, 130.45, 130.18, 129.74, 127.21, 125.11, 85.13 (d, *J* = 169.7 Hz), 62.08 (d, *J* = 21.1 Hz), 45.05, 20.23.

^{19}F NMR (376 MHz, $CDCl_3$) δ -218.49 (brs, 1F).

HRMS (ESI-TOF) calcd for $C_{18}H_{20}FN_3NaO_6S_2$ $[M+MeCN+Na]^+$: 480.0675, found: 480.0765.

FT-IR (neat, cm^{-1}) 3102, 3038, 2956, 1494, 1441, 1416, 1268, 1182, 1126, 1075, 970, 953, 853, 792, 643, 629, 422.

***N*-(2-Fluoro-2,3-dihydro-1*H*-inden-1-yl)-*N*-(2-nitrobenzenesulfonyl)-4-nitrobenzenesulfonamide (5ib)**



The title compound was obtained from Indene **4i** (0.2 mmol) and **1b** (0.3 mmol) following the procedure above. The yield (99%, *trans* : *cis* = 5 : 1) was determined by ^{19}F NMR analysis using 2,3,5,6-tetrafluoro-*p*-xylene as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/DCM = 2/1 to 1/1) gave the compound (85.8 mg, 82% yield, *trans* : *cis* = 5 : 1) as a white solid. The ratio of *trans*/*cis* was determined by comparing with the chemical shifts of **5ib** analogues known in the literature.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62-8.66 (m, minor) and 8.46 (brs, major) (1H), 8.16 (d, *J* = 9.2 Hz, minor) and 8.05 (d, *J* = 7.8 Hz, major) (2H), 7.78-7.88 (m, major) and 7.84-7.86 (m, minor) (3H), 7.57 (d, *J* = 8.7 Hz, minor) and 7.40-7.47 (m, major) (2H), 7.35-7.37 (m, major) and 7.32-7.34 (m, minor) (2H), 7.07-7.17 (m, minor) and 6.89-6.94 (m, major) (2H), 6.18 (d, *J* = 27.0 Hz, major) and 6.10-6.13 (m, minor) (1H), 5.88 (dd, *J* = 51.1, 5.0 Hz, major) and 5.55-5.74 (m, minor) (1H), 3.81-3.95 (m, major), 3.53-3.66 (m, minor) (1H), 3.29-3.39 (m, minor) and 3.16 (dd, *J* = 30.7, 18.3 Hz, major) (1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.40 (major), 148.15 (major), 144.41 (major), 135.46 (major), 135.02 (major), 133.43 (major), 132.84 (major), 132.64 (major), 130.57 (major), 130.34 (major), 130.22 (major), 127.47 (major), 126.12 (major), 125.81 (major), 125.05 (major), 123.49 (major), 98.00 (d, *J* = 179.2 Hz, major), 73.11 (d, *J* = 36.4 Hz, major), 39.32 (d, *J* = 24.9 Hz, major),

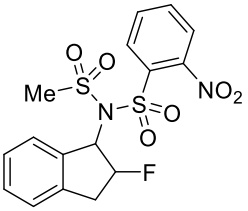
150.50 (minor), 145.81 (minor), 143.15 (minor), 135.47 (minor), 133.33 (minor), 132.29 (minor), 131.72 (minor), 130.48 (minor), 127.18 (minor), 126.46 (minor), 124.07 (minor), 123.55 (minor), 89.40 (d, *J* = 196.5 Hz, minor), 65.15 (d, *J* = 16.3 Hz, minor), 37.84 (d, *J* = 22.0 Hz, minor).

^{19}F NMR (376 MHz, $CDCl_3$) δ -160.81 (brs, major), -188.96 (brs, minor).

HRMS (ESI-TOF) calcd for $C_{21}H_{16}FN_3NaO_8S_2$ $[M+Na]^+$: 544.0261, found: 544.0261.

FT-IR (neat, cm^{-1}) 3110, 1608, 1461, 1443, 1216, 1127, 1082, 1055, 976, 962, 876, 838, 818, 702, 647, 487, 412.

***N*-(2-Fluoro-2,3-dihydro-1*H*-inden-1-yl)-*N*-(methylsulfonyl)-2-nitrobenzenesulfonamide (5ic)**



The title compound was obtained from Indene **4i** (0.2 mmol) and **1c** (0.3 mmol) following the procedure above. The yield (99%, *trans* : *cis* = 5 : 1) was determined by ^{19}F NMR analysis using 2,3,5,6-tetrafluoro-*p*-xylene as an internal standard. Purification by silica-gel column chromatography (*n*-hexane/DCM = 2/1 to 1/1) gave the compound (74.7 mg, 89% yield) as

a white solid. The ration of *trans*/*cis* was determined by comparing with the chemical shifts of **5ic** analogues known in the literature.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50-8.55 (m, minor) and 8.34 (dd, *J* = 7.6, 1.8, 1.4 Hz, major) (1H), 7.67-7.88 (m, major+minor, 3H), 7.71-7.73 (m, minor) and 7.54 (d, *J* = 7.3, major) (1H), 7.29-7.41 (m, major+minor, 3H), 6.15 (d, *J* = 27.4 Hz, major) and 6.06 (dd, *J* = 12.8, 7.3 Hz, minor) (1H), 5.79 (dd, *J* = 51.2, 6.4 Hz, major) and 5.60 (ddd, *J* = 52.6, 7.32, 4.12 Hz, minor) (1H), 3.67-3.81 (m, major, 1H), 3.59-3.23 (m, minor, 5H), 3.09 (dd, *J* = 30.4, 18.3, 17.8 Hz, major, 1H), 2.76 (s, major, 3H).

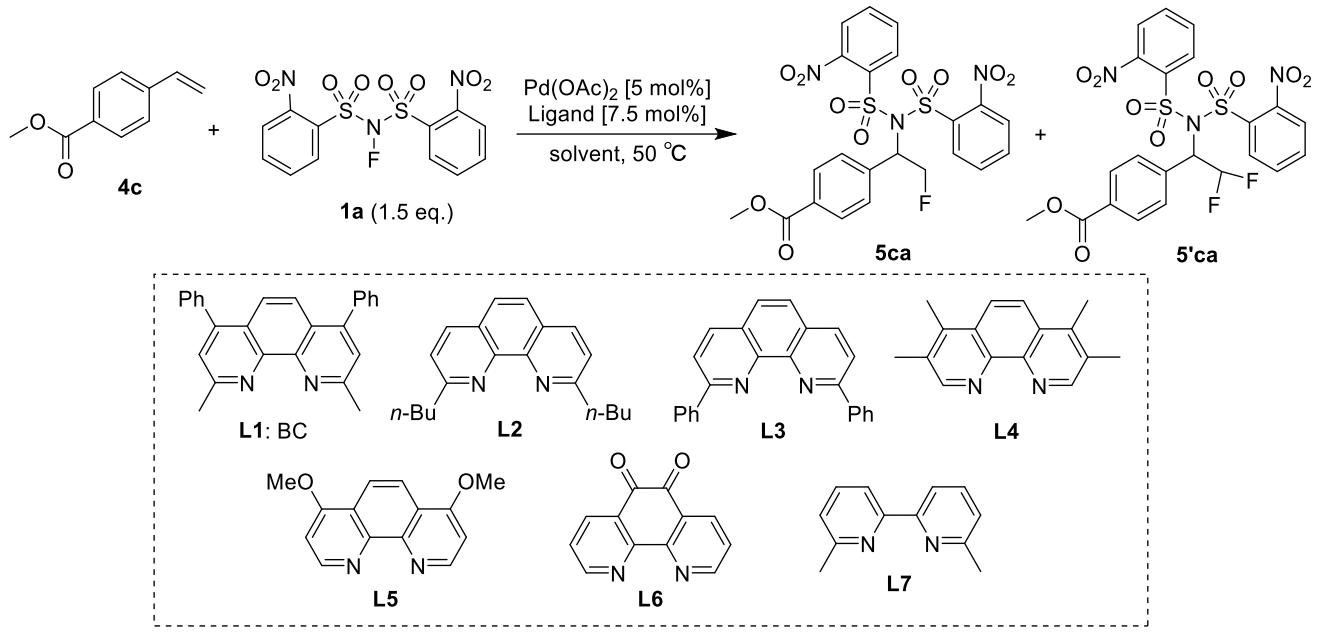
^{13}C NMR (100 MHz, $CDCl_3$) δ 148.47 (minor), 148.00 (major), 143.18 (major), 139.13 (minor), 136.10 (minor), 135.71 (major), 135.21 (minor), 135.15 (major), 133.82 (minor), 133.57 (major), 133.26 (major), 133.13 (minor), 132.50 (major), 132.35 (minor), 130.21 (major), 129.52 (minor), 127.70 (major), 127.34 (minor), 126.01 (major), 125.53 (major+minor), 124.98 (major), 124.91 (minor), 124.17 (minor), 98.09 (d, *J* = 178.2 Hz, major), 91.40 (d, *J* = 192.7 Hz, minor), 72.54 (d, *J* = 37.6 Hz, major), 66.00 (d, *J* = 16.4 Hz, minor), 46.43 (d, *J* = 6.7 Hz, minor), 44.99 (major), 39.34 (d, *J* = 25.1 Hz, major), 37.97 (d, *J* = 22.2 Hz, minor).

^{19}F NMR (376 MHz, $CDCl_3$) δ-162.17 (major), -186.17 (minor).

HRMS (ESI-TOF) calcd for $C_{18}H_{18}FN_3NaO_6S_2$ $[M+MeCN+Na]^+$: 478.0519, found: 478.0518.

FT-IR (neat, cm^{-1}) 2985, 1591, 1484, 1464, 1440, 1408, 1268, 1216, 1206, 1094, 1062, 873, 823, 673, 441, 411.

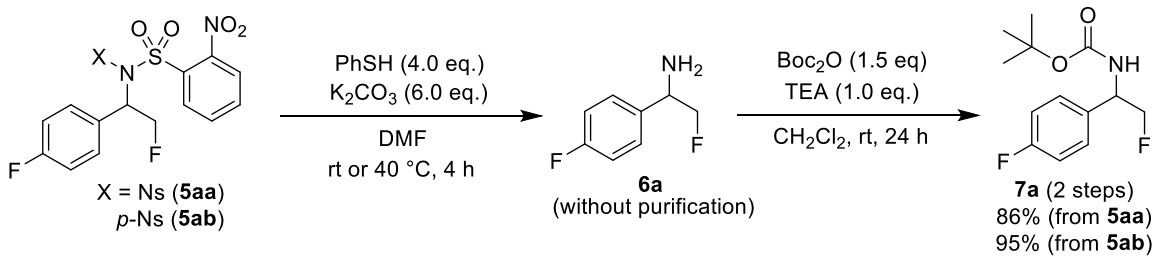
S3-2. Investigation of Solvents and Ligands



Solvent	Ligand	Reaction time [h]	^{19}F-NMR yield [%]		
			5ca	**5'ca**	other side products
1,4-dioxane	**L1**	2.5	60	9	3
DME	**L1**	2.5	44	3	35
DME (25 °C)	**L1**	48	38	0	44
toluene	**L1**	4	9	4	13
1,4-dioxane	**L2**	2.5	50	10	7
1,4-dioxane	**L3**	2.5	33	6	2
1,4-dioxane	**L4**	4	9	4	13
1,4-dioxane	**L5**	100	22	6	5
1,4-dioxane	**L6**	72	36	5	7
1,4-dioxane	**L7**	8	32	6	11

S4 Deprotection (Scheme 3)

S4-1. Synthesis of primary amine[6],[7]

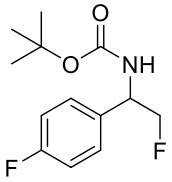


Experimental Procedures:

A mixture of **5aa** or **5ab** (52.7 mg, 0.1 mmol), benzene thiol (44.1 mg, 0.4 mmol), and K_2CO_3 (82.9 mg, 0.6 mmol) in DMF (1.0 mL) was stirred at room temperature (for **5aa**) or 40 °C (for **5ab**) for 4 h under N_2 atmosphere. The solvent was distilled off under vacuum to give an orange solid. A mixture of the obtained crude product, Boc_2O (32.7 mg,

0.15 mmol), and TEA (10.1 mg, 0.1 mmol) in dichloromethane (1.0 mL) was stirred at room temperature for 24 h under N_2 atmosphere. The reaction mixture was quenched by water and extracted with DCM twice. The organic extracts were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The resulting crude product was purified by silica-gel column chromatography to give the Boc-protected primary amine **7a**.

***tert*-Butyl (2-fluoro-1-(4-fluorophenyl)ethyl)carbamate (7a)**[8]



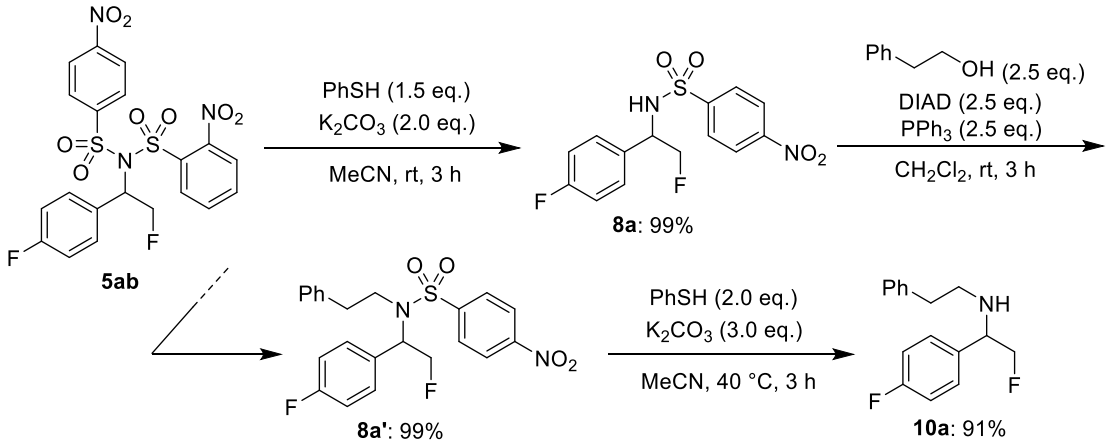
^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.45-7.50 (m, 2H), 7.13 (t, *J* = 9.2 Hz, 2H), 6.72 (brs, 1H), 4.97-5.03 (m, 1H), 4.48-4.66 (m, 2H), 1.39 (s, 9H).

^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 163.20 (d, *J* = 243.7 Hz), 156.21, 136.40, 130.02 (d, *J* = 8.7 Hz), 116.08 (d, *J* = 22.2 Hz), 85.49 (d, *J* = 175.3 Hz), 79.38, 55.13 (d, *J* = 19.3 Hz), 28.66.

^{19}F NMR (376 MHz, $(CD_3)_2CO$) δ -116.70 (s, 1F), -221.58 (td, *J* = 46.2, 17.3 Hz, 1F).

S4-2. Synthesis of secondary amine

S4-2-1. Synthesis of secondary amine from 5ab[7]



Experimental Procedures:

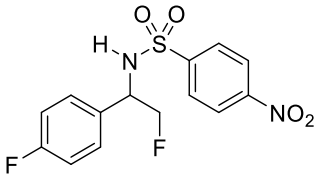
A mixture of **5ab** (52.7 mg, 0.1 mmol) and benzene thiol (16.5 mg, 0.15 mmol), and K_2CO_3 (27.6 mg, 0.2 mmol) in MeCN (1.0 mL) was stirred at room temperature for 3 h under N_2 atmosphere. Then, the mixture was quenched by water and extracted with DCM twice. The organic extracts were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The resulting crude product was purified by silica-gel column chromatography to give the sulfonamide **8a** (99% yield).

A mixture of **8a** (34.2 mg, 0.1 mmol), 2-phenethyl alcohol (30.5 mg, 0.25 mmol), DIAD (0.25 mmol, 1.9 M in toluene), and PPh_3 (65.6 mg, 0.25 mmol) in dichloromethane (1.0 mL) was stirred at room temperature for 3 h under N_2 atmosphere. The solvent was distilled off under vacuum to give a yellow solid. The resulting crude product was purified by silica-gel column chromatography to give the *p*-Ns-protected secondary amine **8a'** (99% yield).

A mixture of **8a'** (44.6 mg, 0.1 mmol), benzene thiol (22.0 mg, 0.2 mmol), and K_2CO_3 (41.5 mg, 0.3 mmol) in MeCN (1.0 mL) was stirred at 40 °C for 3 h under N_2 atmosphere. Then, the reaction was quenched by water and extracted with DCM twice. The organic extracts were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The

resulting crude product was purified by silica-gel column chromatography to give the secondary amine **10a** (91% yield).

***N*-[2-Fluoro-1-(4-fluorophenyl)ethyl]-4-nitrobenzenesulfonamide (8a)**



^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.27 (d, *J* = 9.3 Hz, 2H), 7.96 (d, *J* = 9.2 Hz, 2H), 7.31-7.36 (m, 2H), 6.99 (t, *J* = 8.7 Hz, 2H), 4.84-4.91 (m, 1H), 4.58-4.65 (m, 1H), 4.46-4.54 (m, 1H).

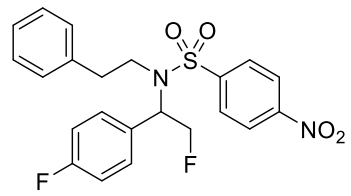
^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 163.28 (d, *J* = 244.4 Hz), 150.75, 148.22, 133.85, 130.40 (d, *J* = 8.6 Hz), 129.27, 124.96, 116.07 (d, *J* = 21.1 Hz), 85.5 (d, *J* = 177.3 Hz), 58.21 (d, *J* = 20.1 Hz).

^{19}F NMR (376 MHz, $(CD_3)_2CO$) δ -115.61 (s, 1F), -221.72 (t, *J* = 46.2 Hz, 1F).

HRMS (ESI-TOF) calcd for $C_{14}H_{12}F_2N_2NaO_4S$ $[M+Na]^+$: 365.0384, found: 365.03676.

FT-IR (neat, cm^{-1}) 3267, 3105, 2954, 2921, 2858, 2436, 1605, 1527, 1510, 1477, 1467, 1434, 1401, 1340, 1303, 1256, 1226, 1159, 1083, 1023, 1012, 964, 849, 832, 793, 746, 733, 683, 618, 574, 562, 538, 460, 420, 414.

***N*-[2-Fluoro-1-(4-fluorophenyl)ethyl]-*N*-(2-phenylethyl)-4-nitrobenzenesulfonamide (8a')**



^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.41 (d, *J* = 9.2 Hz, 2H), 8.20 (d, *J* = 8.7 Hz, 2H), 7.43-7.47 (m, 2H), 7.09-7.28 (m, 7H), 5.45-5.52 (m, 1H), 4.97-5.11 (m, 2H), 3.43-3.54 (m, 2H), 2.84-2.92 (m, 1H), 2.56 (td, *J* = 12.1, 5.0 Hz, 1H).

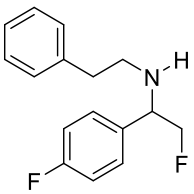
^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 162.84 (d, *J* = 248.7 Hz), 148.30, 138.20, 133.92, 131.84, 131.11, 130.16 (d, *J* = 8.5 Hz), 128.83, 128.76, 126.80, 124.34, 116.09 (d, *J* = 21.7 Hz), 82.80 (d, *J* = 176.3 Hz), 59.21 (d, *J* = 20.5 Hz), 47.94, 37.27.

^{19}F NMR (376 MHz, $(CD_3)_2CO$) δ -114.63 (s, 1F), -220.98 (t, *J* = 46.2 Hz, 1F).

HRMS (ESI-TOF) calcd for $C_{22}H_{20}F_2N_2NaO_4S$ $[M+Na]^+$: 469.1010, found: 469.0930.

FT-IR (neat, cm^{-1}) 3106, 3029, 2955, 1702, 1605, 1528, 1511, 1477, 1454, 1401, 1346, 1309, 1227, 1161, 1095, 1013, 993, 946, 854, 834, 793, 740, 699, 684, 610, 575, 546, 522, 463, 420, 407.

***N*-[2-Fluoro-1-(4-fluorophenyl)ethyl]-2-phenylethane (10a)**



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17-7.32 (m, 7H), 7.00-7.06 (m, 2H), 4.24-4.48 (m, 2H), 4.00-4.06 (m, 1H), 2.71-2.82 (m, 4H).

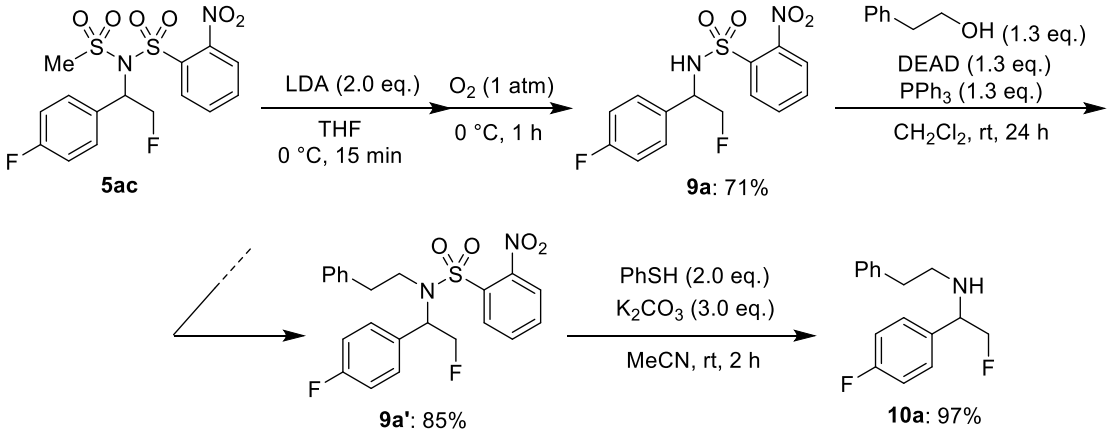
^{13}C NMR (125 MHz, $CDCl_3$) δ 162,55 (d, *J* = 246.27 Hz), 139.93, 134.35 (dd, *J* = 7.9, 2.4 Hz), 129.36 (d, *J* = 8.45 Hz), 128.80, 128.55, 126.31, 115.61 (d, *J* = 21.73 Hz), 86.94 (d, *J* = 175.04 Hz), 62.31 (d, *J* = 19.31 Hz), 48.68, 36.54.

^{19}F NMR (470 MHz, $CDCl_3$) δ -114.38 (s, 1F), -218.57 (td, *J* = 43.2, 14.4 Hz, 1F).

HRMS (ESI-TOF) calcd for $C_{16}H_{17}F_2NNa$ $[M+Na]^+$: 284.1227, found: 284.1224.

FT-IR (neat, cm^{-1}) 3560, 3526, 3518, 3022, 1967, 1603, 1539, 1475, 1454, 1441, 1418, 1379, 1344, 1294, 1198, 1157, 1126, 1034, 932, 906, 870, 852, 770, 654, 635, 611, 582, 480, 467, 461, 451, 432, 419.

S4-2-2. Synthesis of secondary amine from 5ac[7],[9]



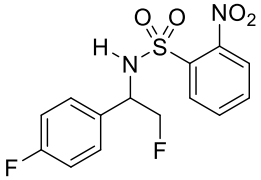
Experimental Procedures:

To a solution of **5ac** (0.1 mmol) in THF (0.1 mL) was added dropwise LDA (0.2 mmol, 0.2 M in THF) at 0 °C under N_2 atmosphere, and the mixture was stirred at 0 °C for 15 min. Then, the mixture was stirred at 0 °C under O_2 atmosphere for 1 h. The reaction mixture was quenched by water and extracted with DCM twice. The organic extracts were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The resulting crude product was purified by silica-gel column chromatography to give the sulfonamide **9a** (71% yield).

A mixture of **9a** (34.2 mg, 0.1 mmol), 2-phenethyl alcohol (15.9 mg, 0.13 mmol), DEAD (0.13 mmol, 2.2 M in toluene), and PPh_3 (34.1 mg, 0.13 mmol) in dichloromethane (1.0 mL) was stirred at room temperature for 24 h under N_2 atmosphere. The solvent was distilled off under vacuum to give a yellow solid. The resulting crude product was purified by silica-gel column chromatography to give the Ns-protected secondary amine **9a'** (85% yield).

A mixture of **9a'** (44.6 mg, 0.1 mmol), benzene thiol (22.0 mg, 0.2 mmol), and K_2CO_3 (41.5 mg, 0.3 mmol) in MeCN (1.0 mL) was stirred at room temperature for 2 h under N_2 atmosphere. Then, the mixture was quenched by water and extracted with DCM twice. The organic extracts were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The resulting crude product was purified by silica-gel column chromatography to give the secondary amine **10a** (97% yield).

***N*-[2-Fluoro-1-(4-fluorophenyl)ethyl]-2-nitrobenzenesulfonamide (9a)**



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.8 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.63 (t, *J* = 7.3 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.17 (dd, *J* = 7.8, 5.5 Hz, 2H), 6.85 (t, *J* = 9.6 Hz, 2H), 6.24 (d, *J* = 8.2 Hz, 1H), 4.45-4.84 (m, 3H).

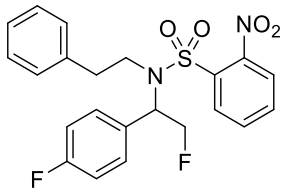
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.65 (d, *J* = 247.6 Hz), 147.52, 134.20, 133.55, 132.74, 131.74, 130.78, 129.09 (d, *J* = 8.7 Hz), 125.34, 115.72 (d, *J* = 21.2 Hz), 85.13 (*J* =179.2 Hz), 58.05 (d, *J* = 18.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -112.81 (s, 1F), -225.10 (td, *J* = 46.2, 23.1 Hz, 1F).

HRMS (ESI-TOF) calcd for $C_{14}H_{12}F_2N_2NaO_4S$ $[M+Na]^+$: 365.0384, found: 365.0364.

FT-IR (neat, cm^{-1}) 3744, 3647, 3628, 3572, 3566, 3555, 3524, 3516, 3510, 3348, 3171, 3157, 3097, 3078, 3057, 2968, 2891, 1960, 1906, 1595, 1578, 1487, 1466, 1389, 1263, 881, 415.

***N*-[2-Fluoro-1-(4-fluorophenyl)ethyl]-*N*-(2-phenylethyl)-2-nitrobenzenesulfonamide (9a')**



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.8 Hz, 1H), 7.63-7.74 (m, 3H), 7.39 (t, *J* = 6.0 Hz, 2H), 7.16-7.24 (m, 3H), 7.06 (t, *J* = 8.2 Hz, 2H), 7.00 (d, *J* = 6.9 Hz, 2H), 5.40 (dt, *J* = 20.6, 5.5 Hz, 1H), 4.94-5.02 (m, 1H), 4.82-4.90 (m, 1H), 3.41-3.53 (m, 2H), 2.78-2.85 (m,1H), 2.39-2.47 (m, 1H).

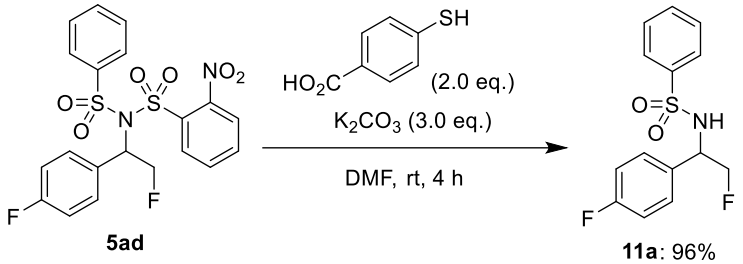
^{13}C NMR (125 MHz, $CDCl_3$) δ 162.84 (d, *J* = 248.68 Hz), 148.30, 138.20, 133.92(2C), 131.84, 131.11(2C), 130.16 (d, *J* = 8.45 Hz), 128.83, 128.76, 126.80, 124.34, 116.09 (d, *J* = 21.73 Hz), 82.80 (d, *J* = 176.25 Hz), 59.21 (d, *J* = 20.52 Hz), 47.94, 37.27.

^{19}F NMR (470 MHz, $CDCl_3$) δ -112.43 (s, 1F), -222.00 (td, *J* = 50.4, 14.4 Hz, 1F).

HRMS (ESI-TOF) calcd for $C_{22}H_{20}F_2N_2NaO_4S$ $[M+Na]^+$: 469.1010, found: 469.0993.

FT-IR (neat, cm^{-1}) 1603, 1497, 1475, 1460, 1441, 1421, 1296, 1273, 1251, 1198, 1103, 1084, 1061, 1034, 939, 908, 791, 725, 636, 611, 478, 451, 434, 413.

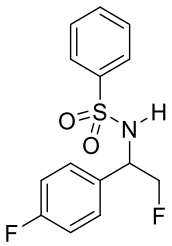
S4-3. Synthesis of sulfonamide[7]



Experimental Procedures:

A mixture of **5ad** (48.2 mg, 0.1 mmol), 4-mercaptobenzoic acid (22.0 mg, 0.2 mmol), and K_2CO_3 (41.5 mg, 0.3 mmol) in DMF (1.0 mL) was stirred at room temperature for 4 h under N_2 atmosphere. Then, the mixture was quenched by water and extracted with DCM twice. The organic extracts were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The resulting crude product was purified by silica-gel column chromatography to give the sulfonamide **11a**.

***N*-[2-Fluoro-1-(4-fluorophenyl)ethyl]-benzenesulfonamide (11a)**



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.50 (t, *J* = 7.1 Hz, 1H), 7.38 (t, *J* = 7.3 Hz, 2H), 7.08-7.12 (m, 2H), 6.88 (t, *J* = 8.7 Hz, 2H), 5.56 (brs, 1H), 4.39-4.63 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.65 (d, *J* = 247.6 Hz), 140.21, 132.86, 131.86, 129.13, 129.06, 127.16, 115.75 (d, *J* = 22.2 Hz), 84.87 (d, *J* =178.2 Hz), 57.08 (d, *J* = 19.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -113.26 (s, 1F), -223.39 (td, *J* = 46.2, 17.3 Hz, 1F).

HRMS (ESI-TOF) calcd for $C_{14}H_{13}F_2NNaO_2S$ $[M+Na]^+$: 320.0533, found: 320.0538.

FT-IR (neat, cm^{-1}) 3273, 3075, 2922, 2852, 1902, 1603, 1511, 1467, 1448, 1394, 1348, 1317, 1310, 1263, 1218, 1197, 1151, 1093, 1082, 1046, 1020, 973, 944, 857, 831, 791, 753, 719, 686, 614, 592, 568, 544, 515, 443, 429.

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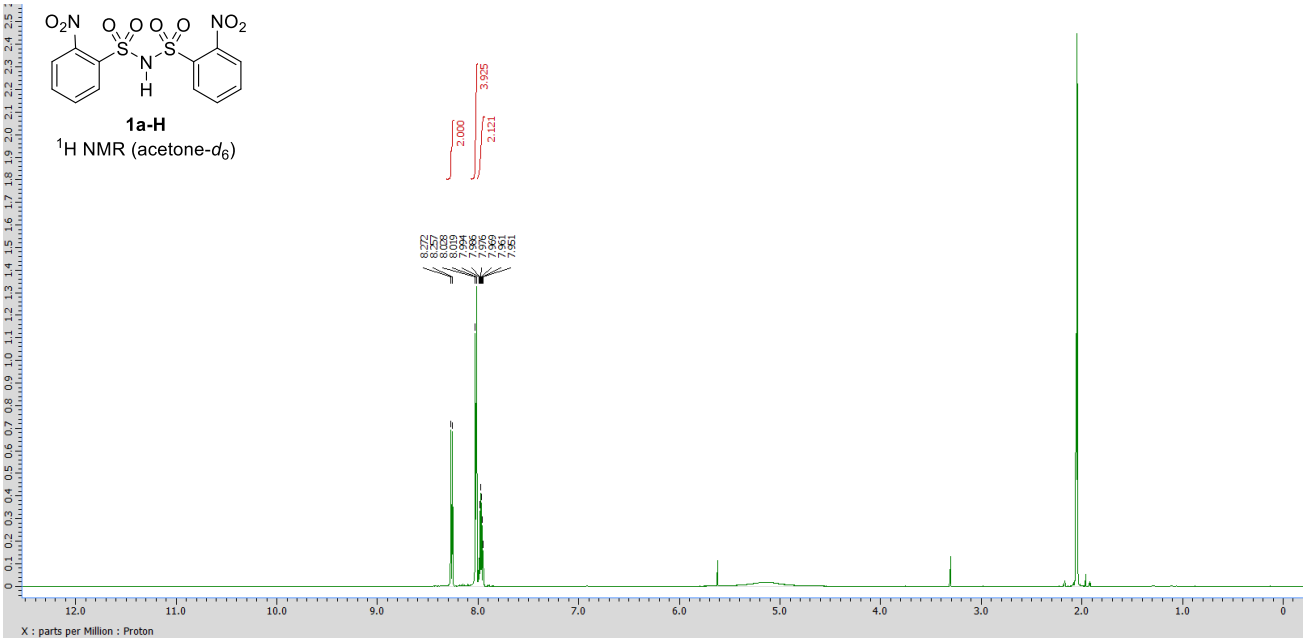
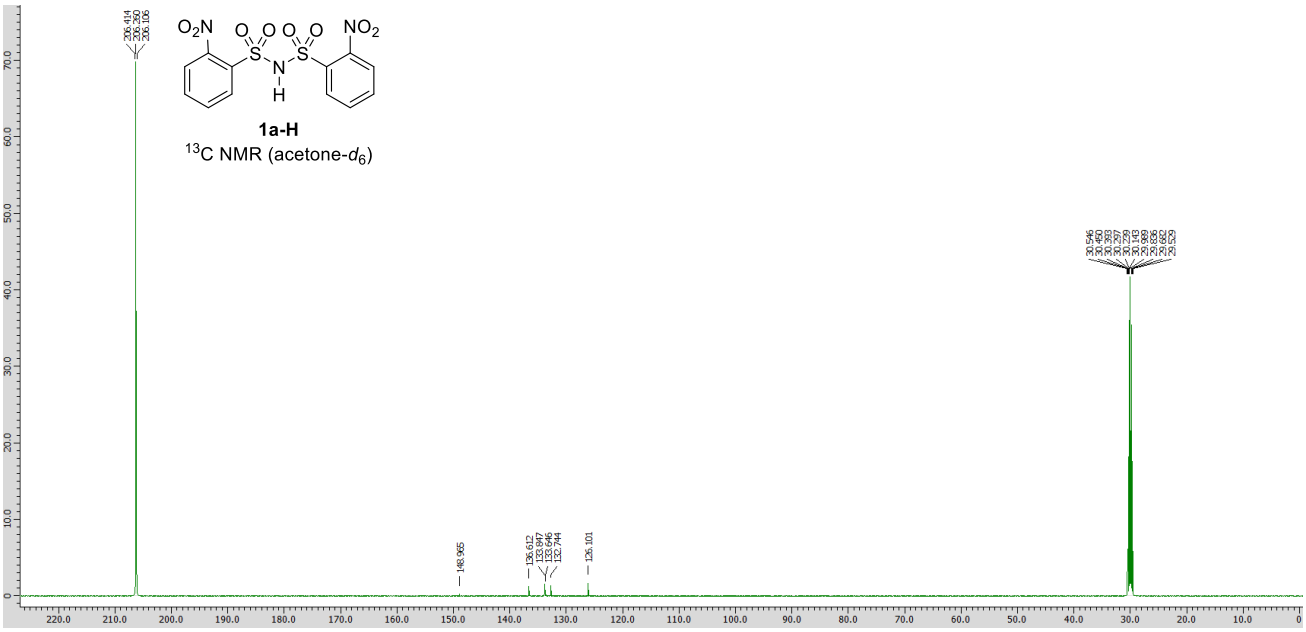
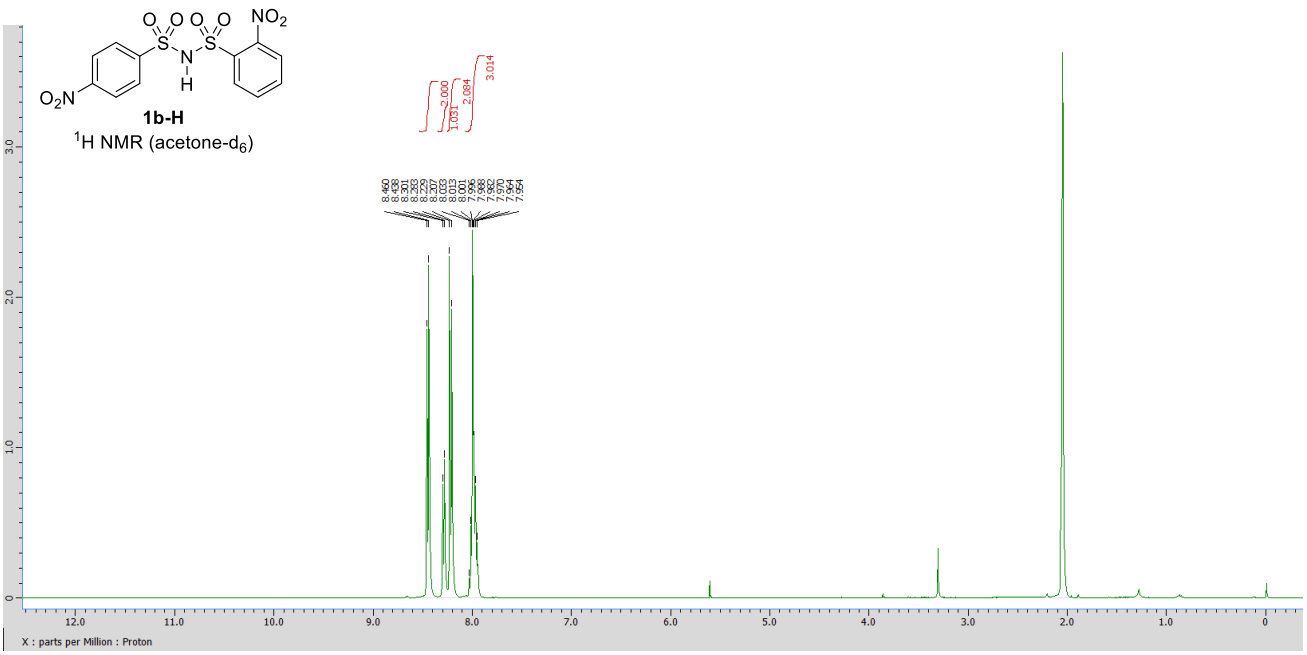
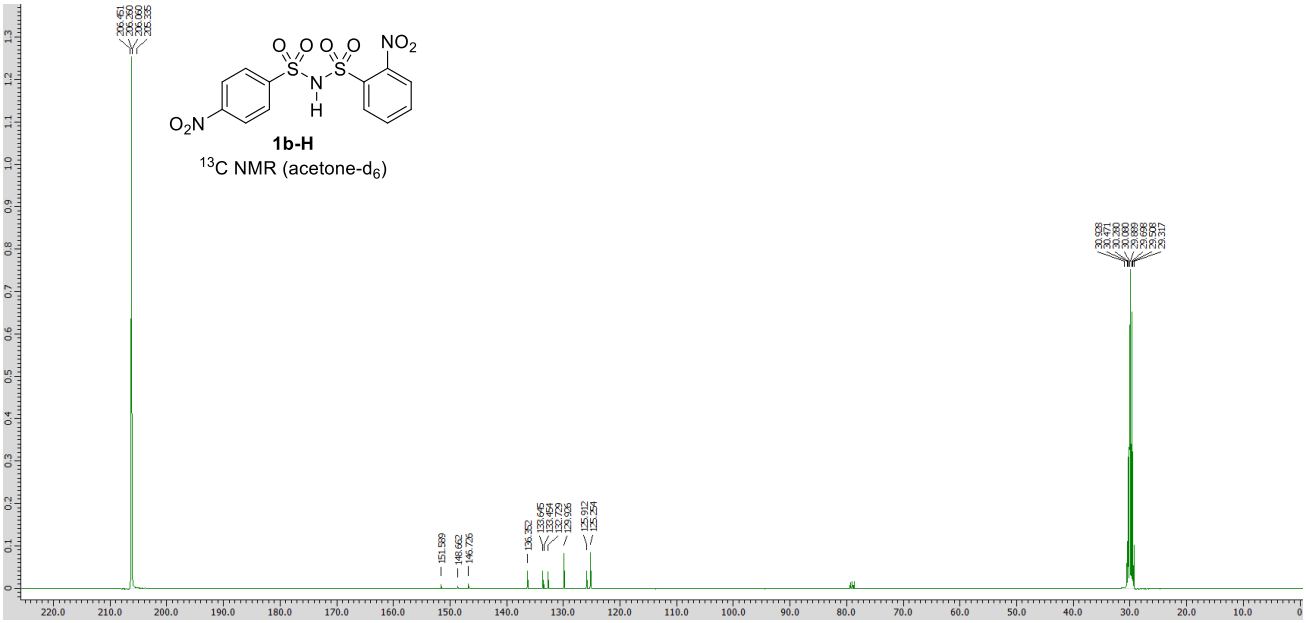
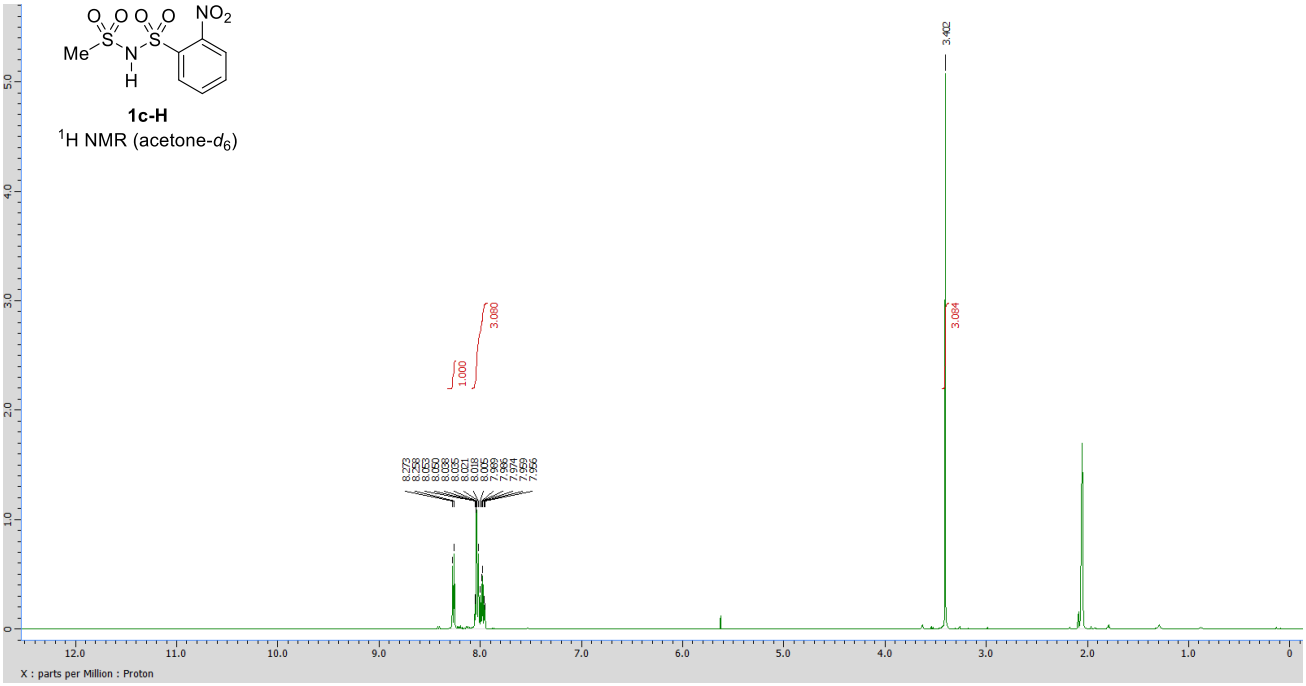
S6. NMR spectra

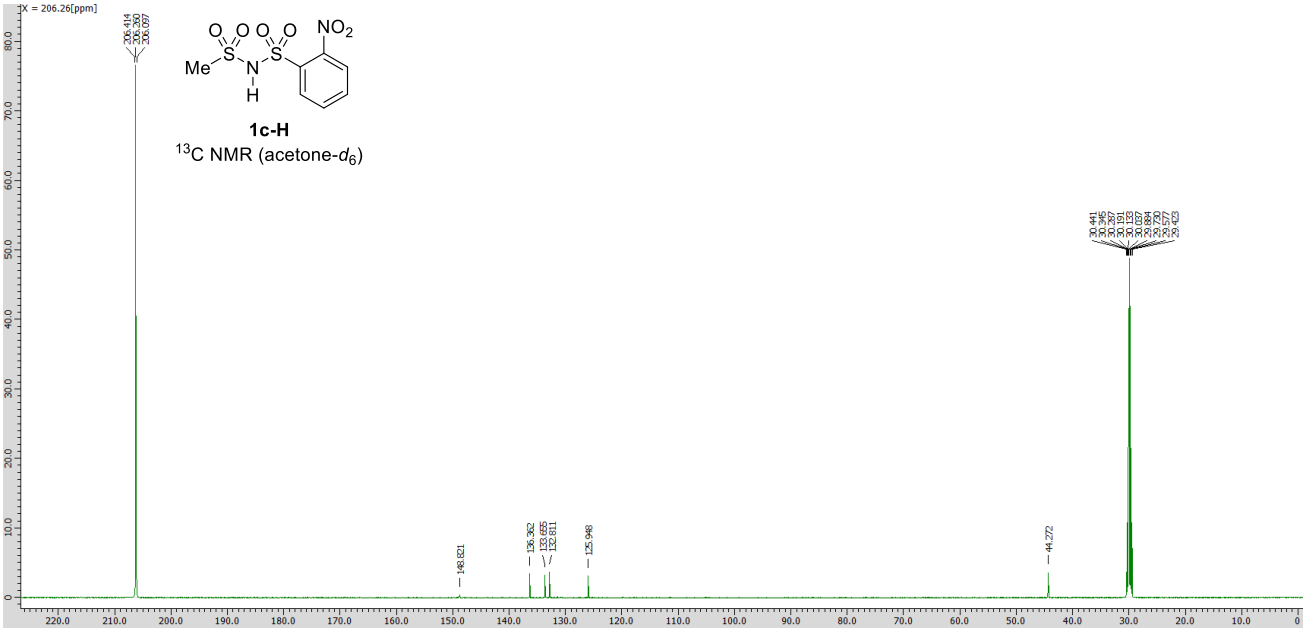


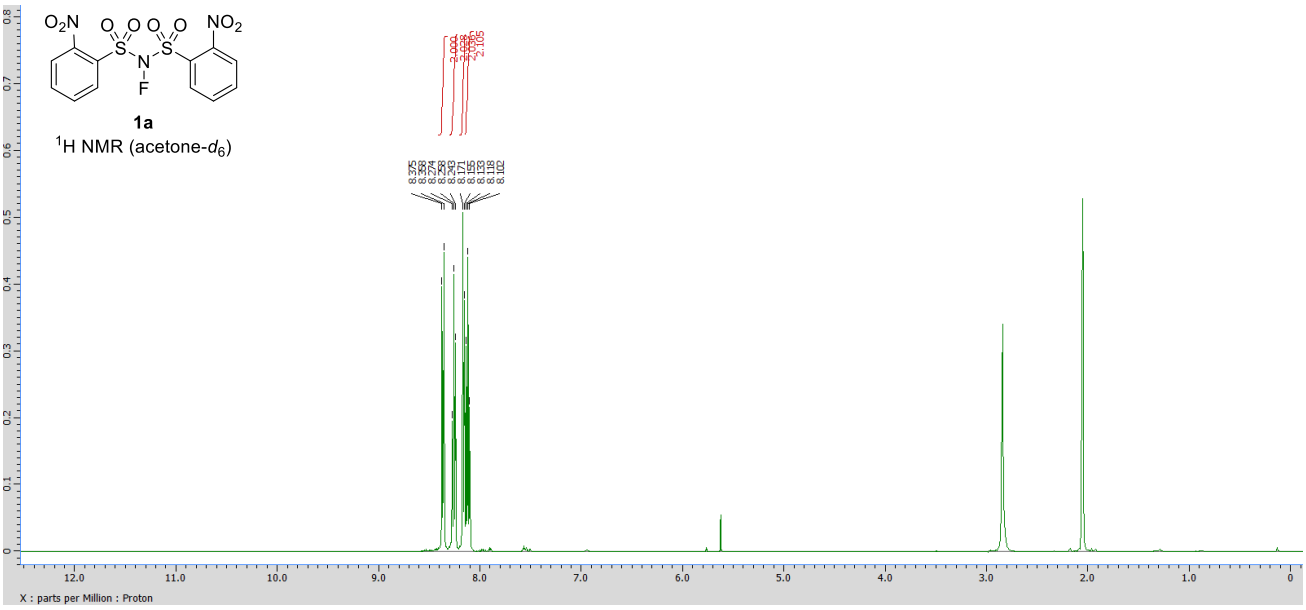


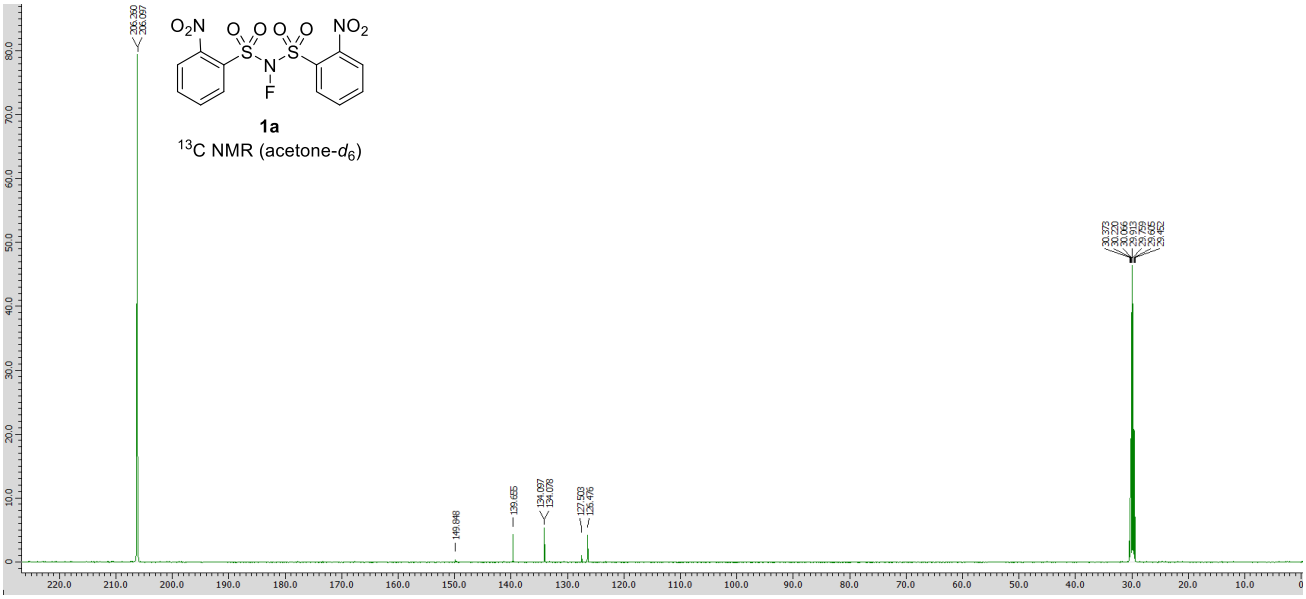

1b-H
1H NMR (acetone-d6)
X : parts per Million : Proton

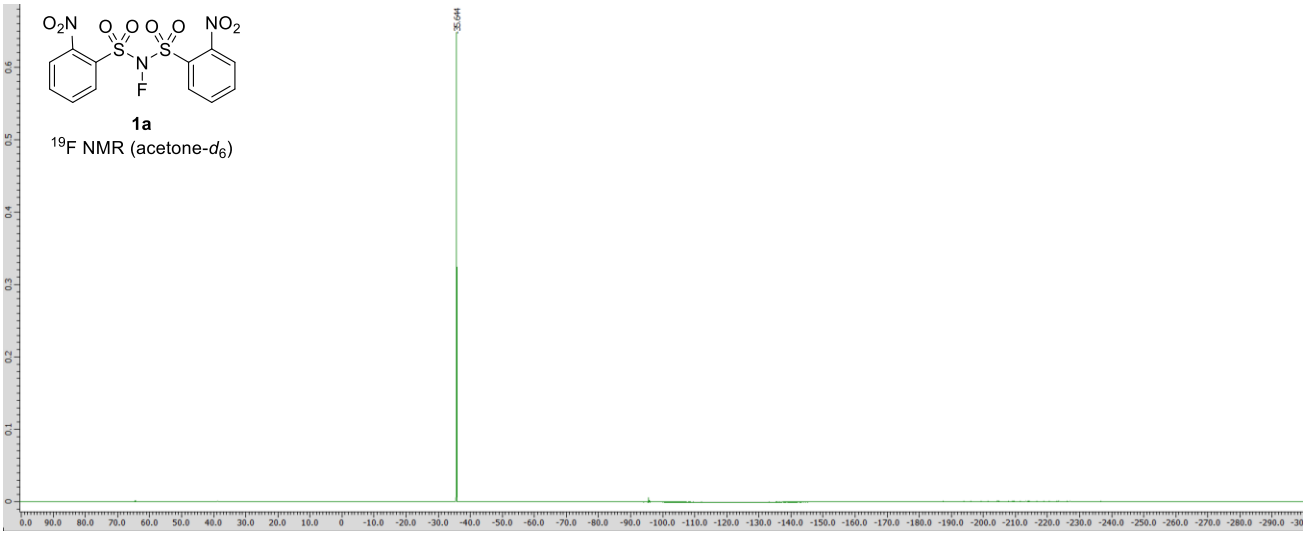

1b-H
13C NMR (acetone-d6)

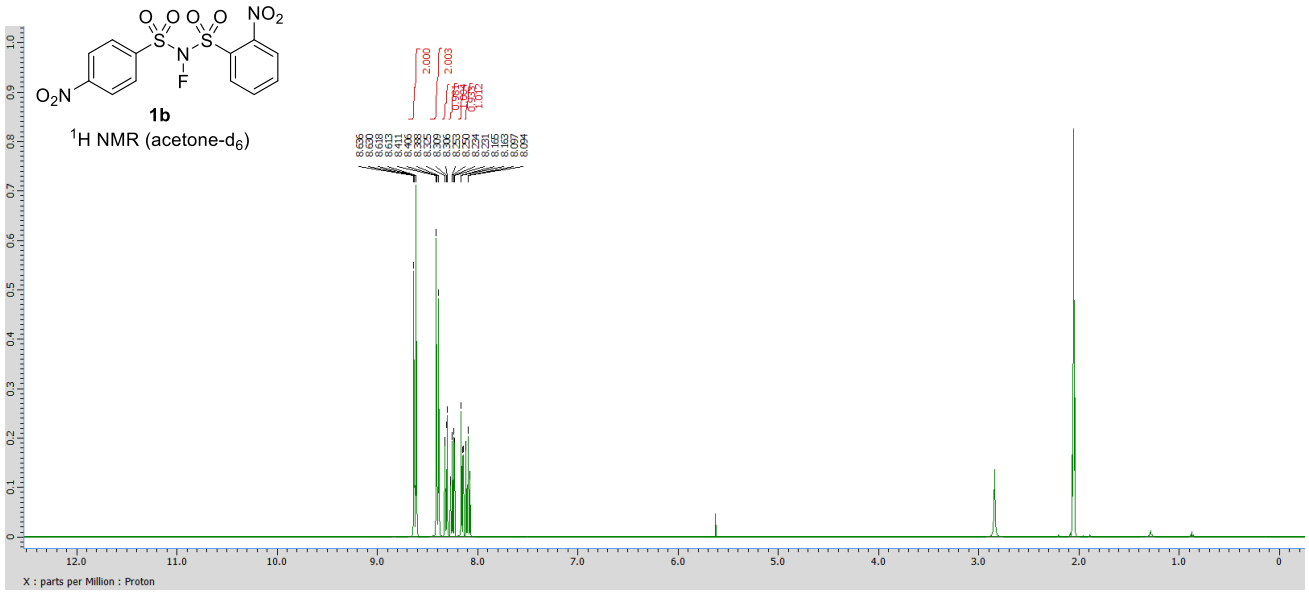

1c-H
1H NMR (acetone-d6)
X : parts per Million : Proton

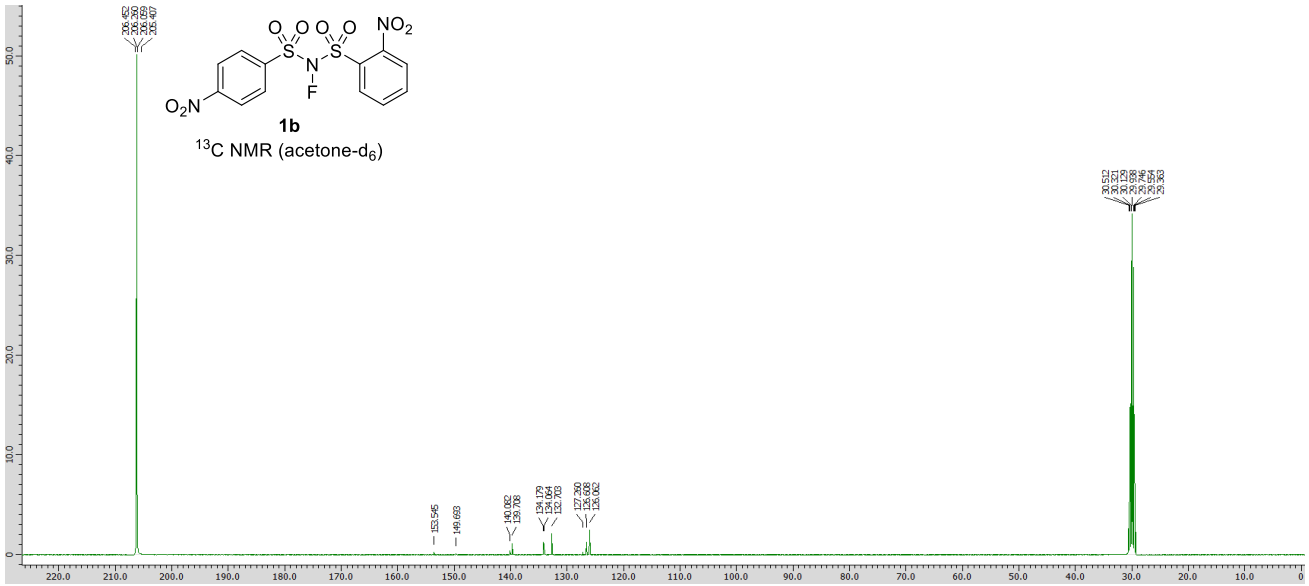

1c-H
13C NMR (acetone-d6)

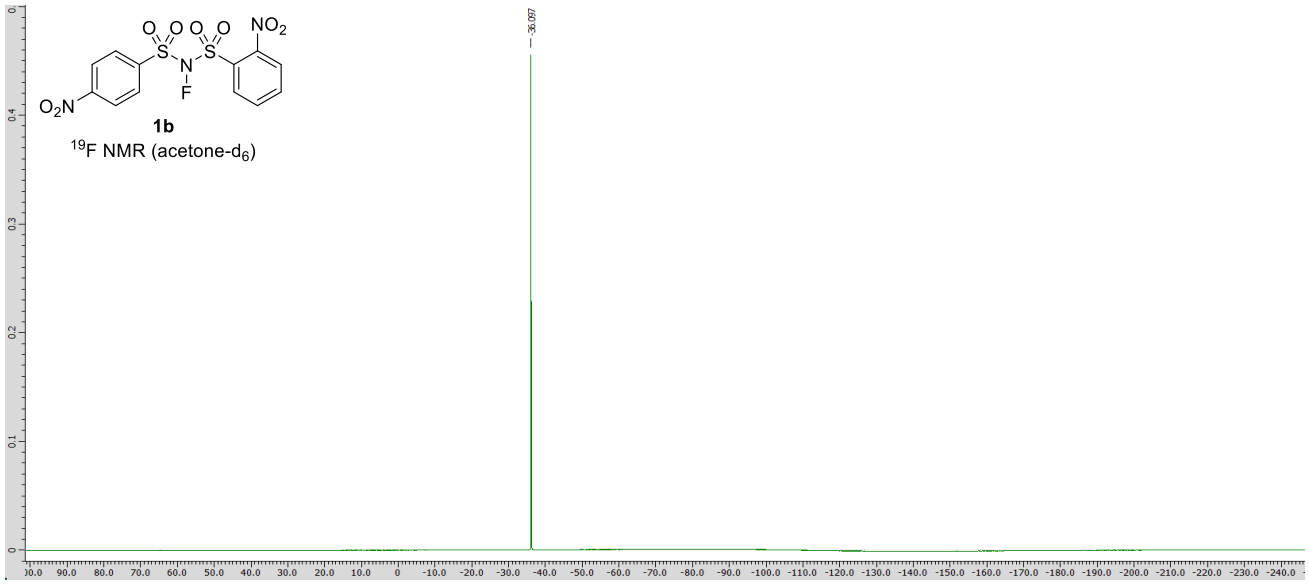

1a
1H NMR (acetone-d6)
X : parts per Million : Proton

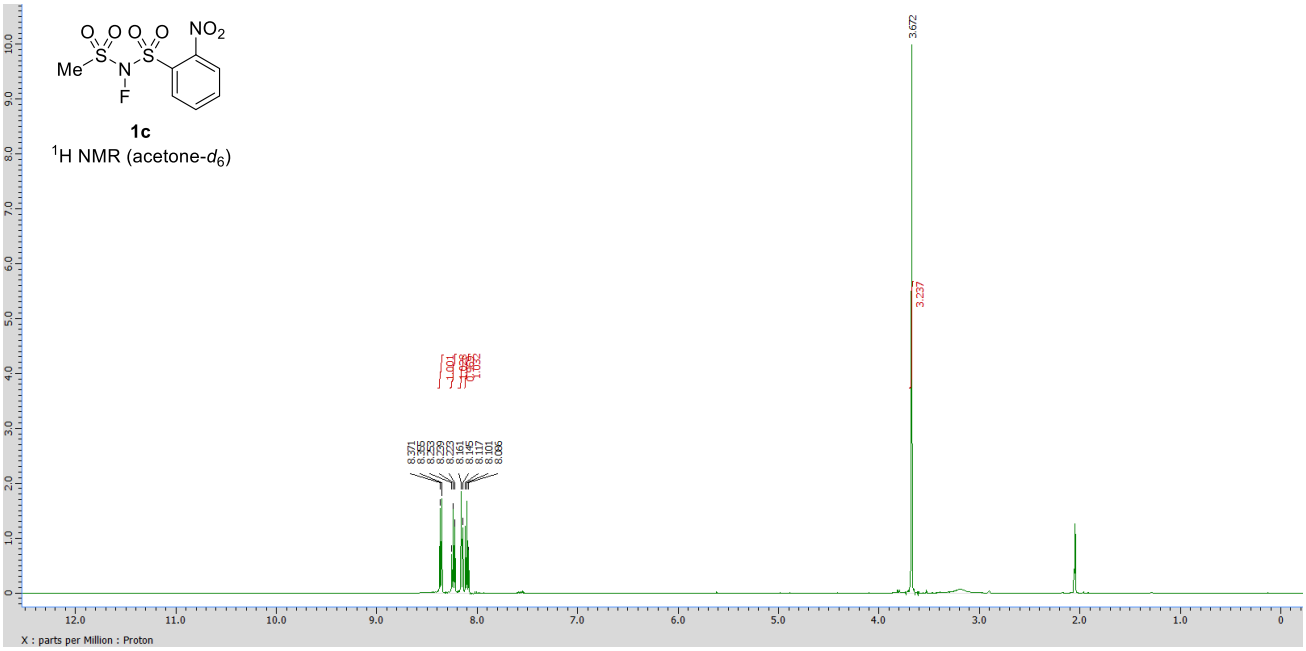

1a
13C NMR (acetone-d6)

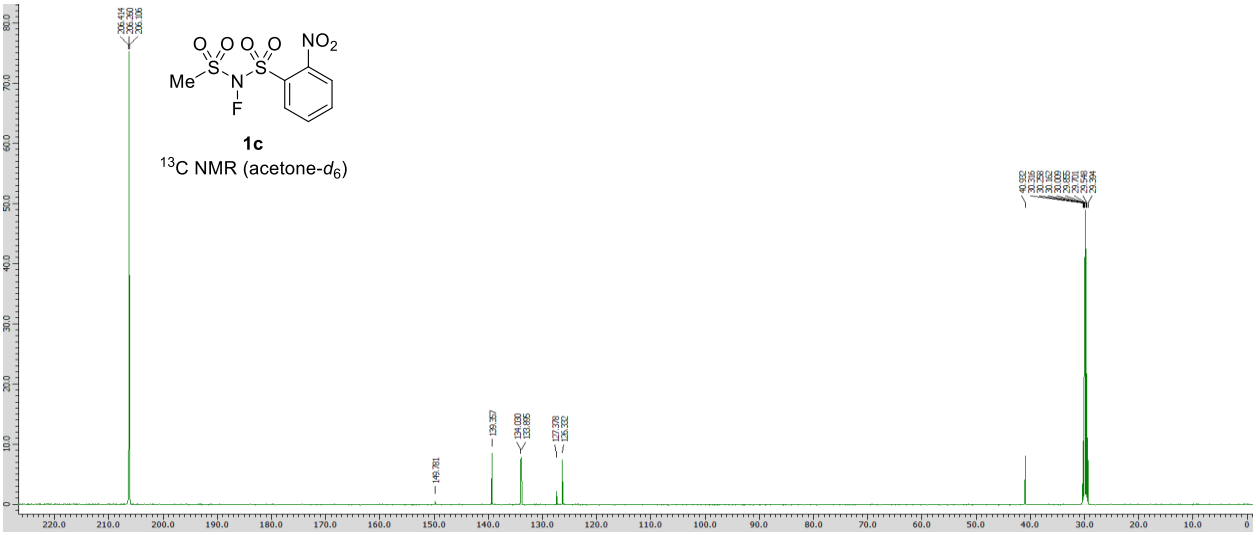

1a
19F NMR (acetone-d6)

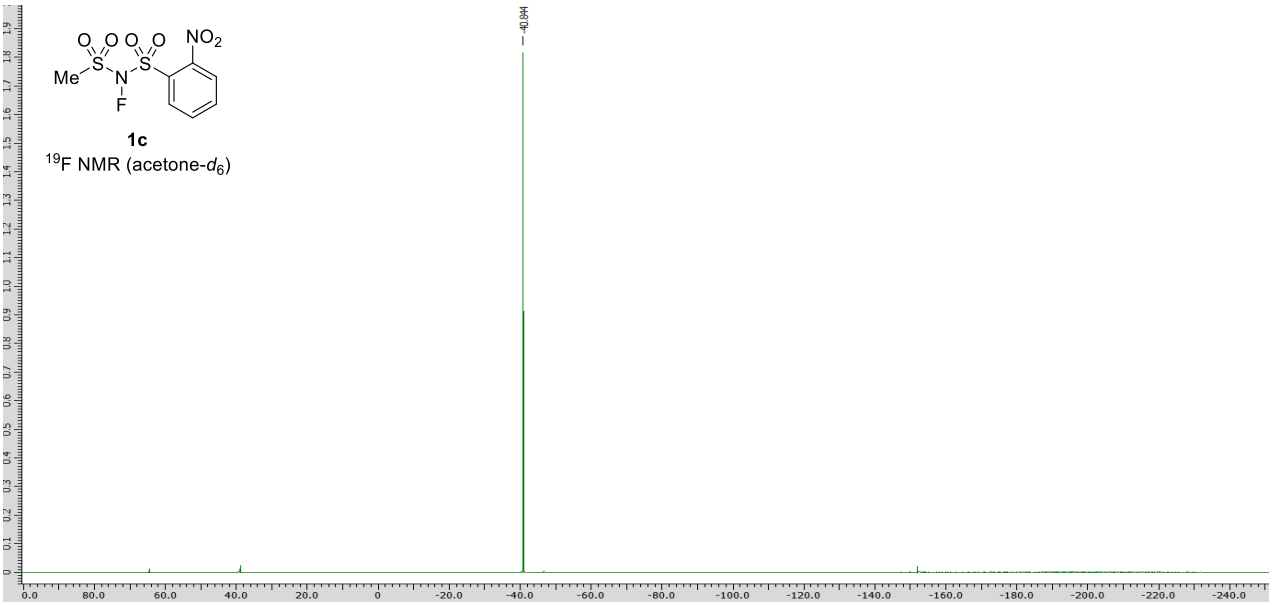

1b
^{1}H NMR (acetone-d$_6$)
X : parts per Million : Proton

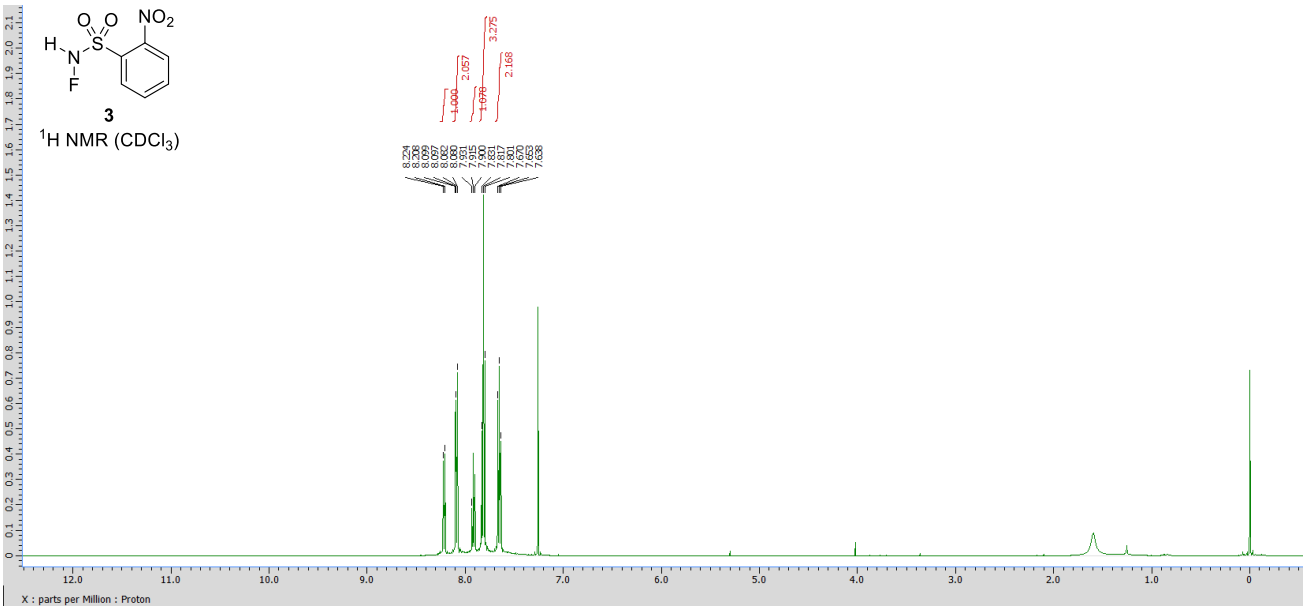

1b
^{13}C NMR (acetone-d$_6$)

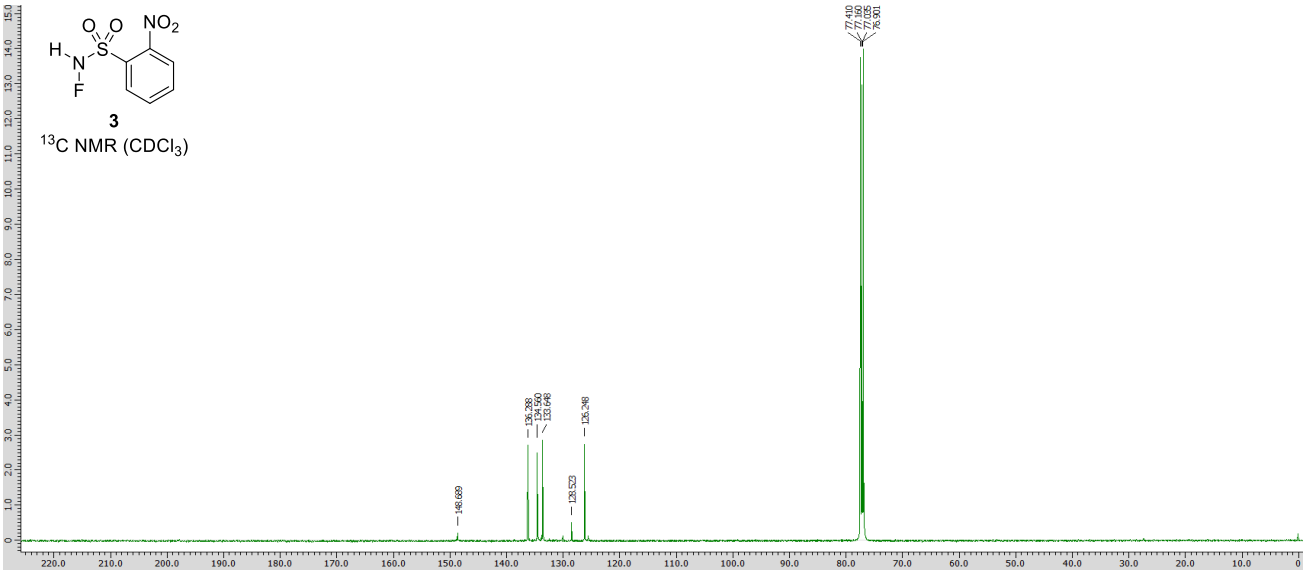

1b
^{19}F NMR (acetone-d$_6$)

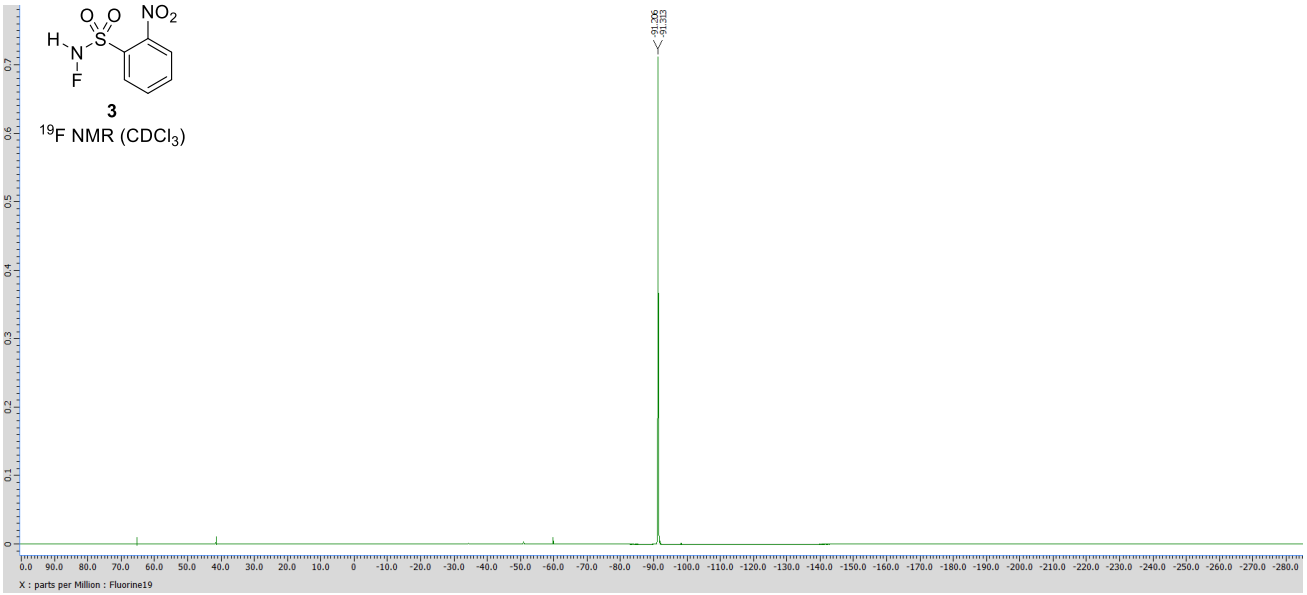

Me
N
F
NO2
1c
1H NMR (acetone-d6)
3.672
3.237
X : parts per Million : Proton

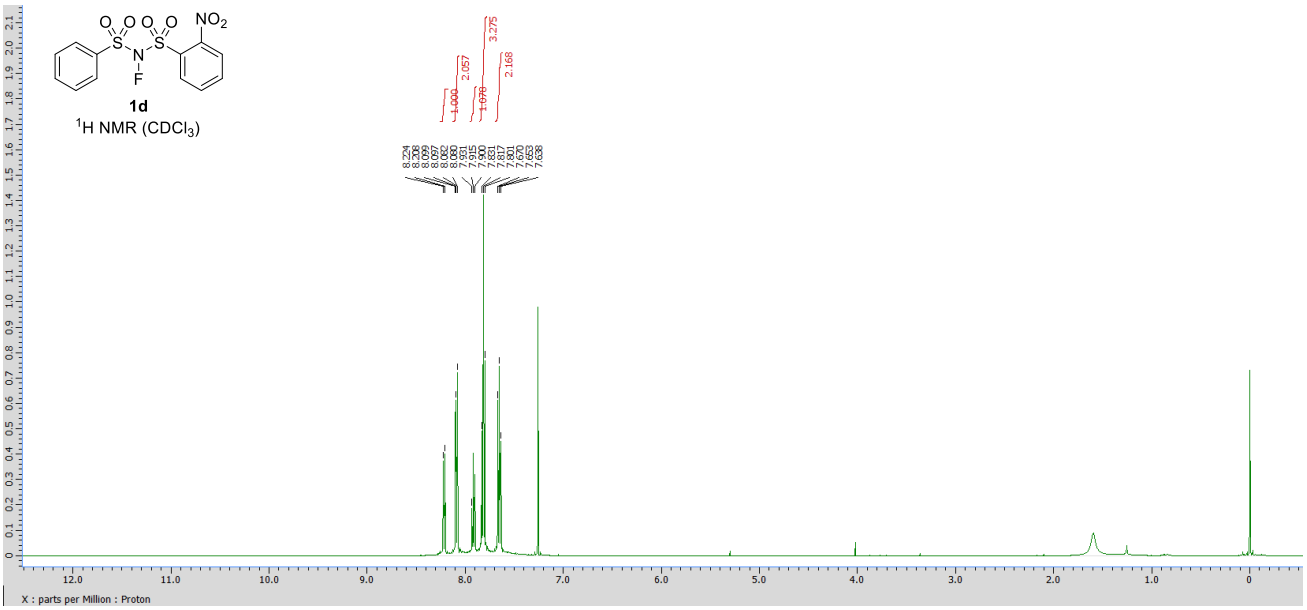

Me
N
F
NO2
1c
13C NMR (acetone-d6)

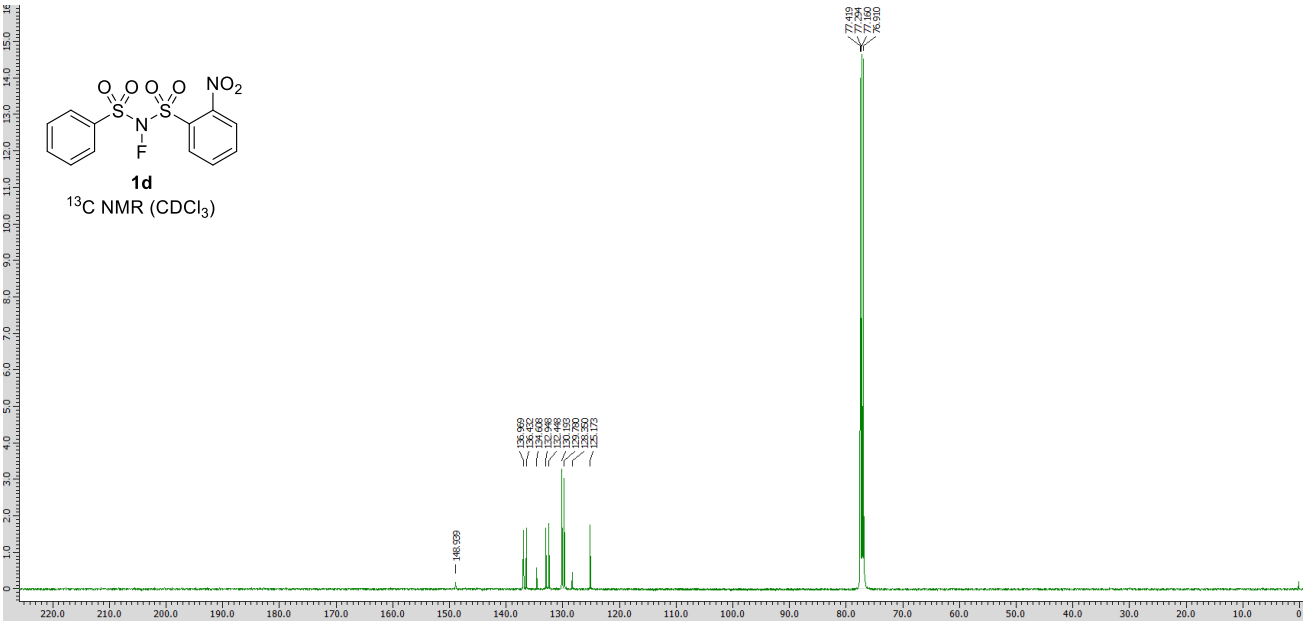

Me
N
F
NO2
1c
19F NMR (acetone-d6)
-40.944

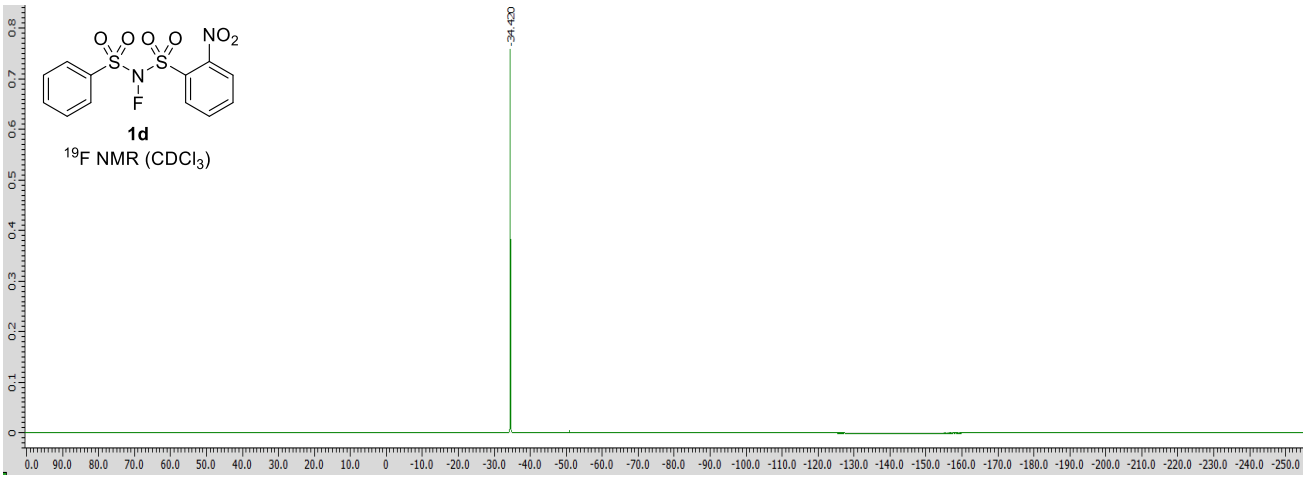

3
^{1}H NMR ($CDCl_3$)
X : parts per Million : Proton

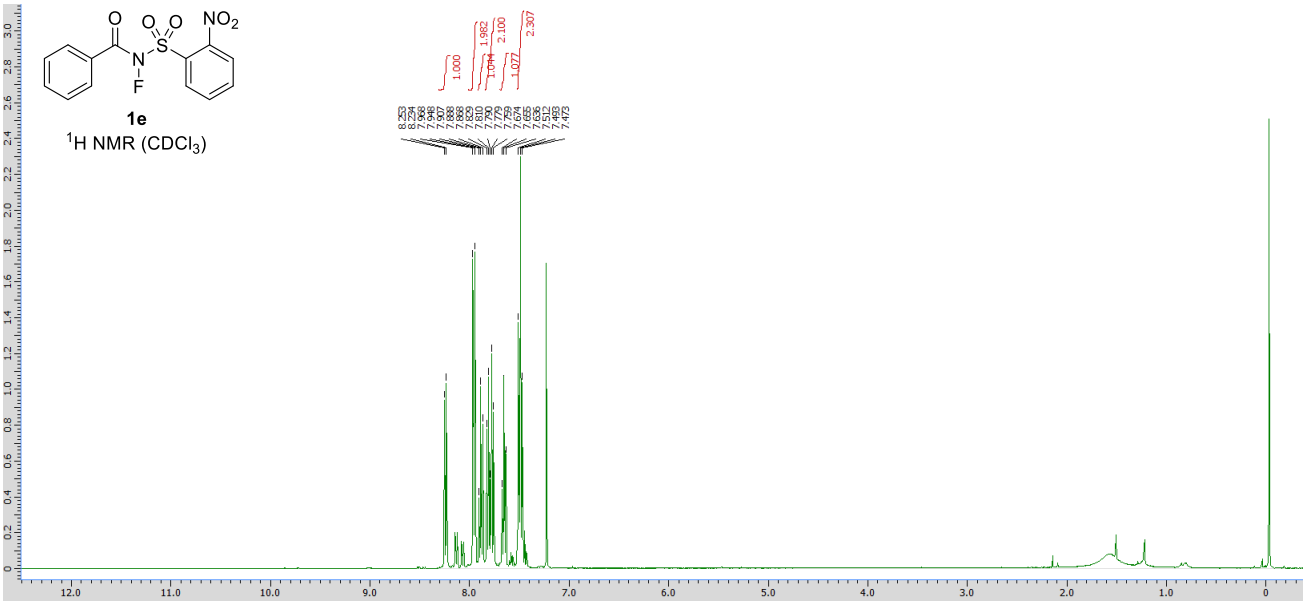

3
^{13}C NMR ($CDCl_3$)

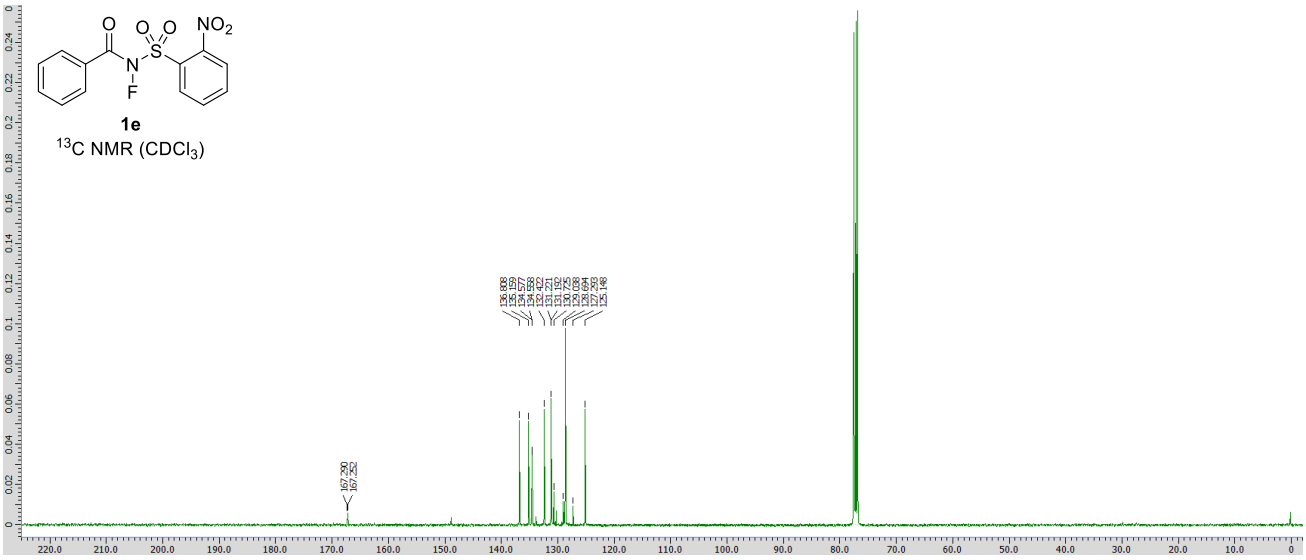

3
^{19}F NMR ($CDCl_3$)
X : parts per Million : Fluorine19

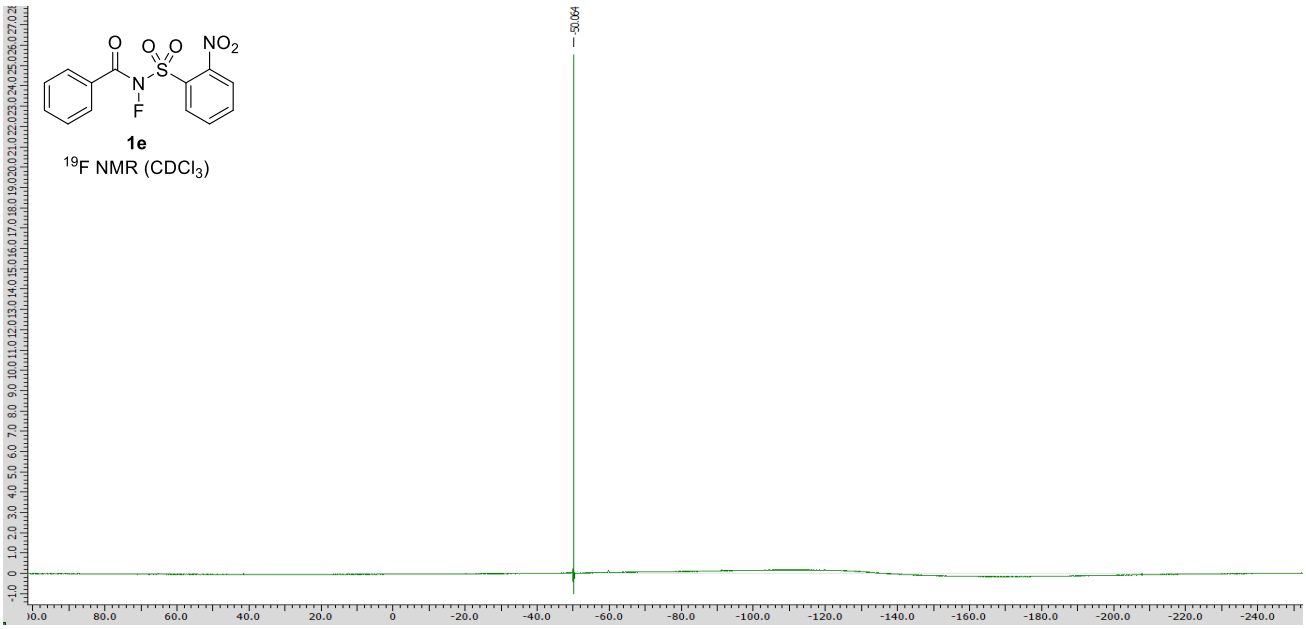

1d
1H NMR (CDCl3)
X : parts per Million : Proton

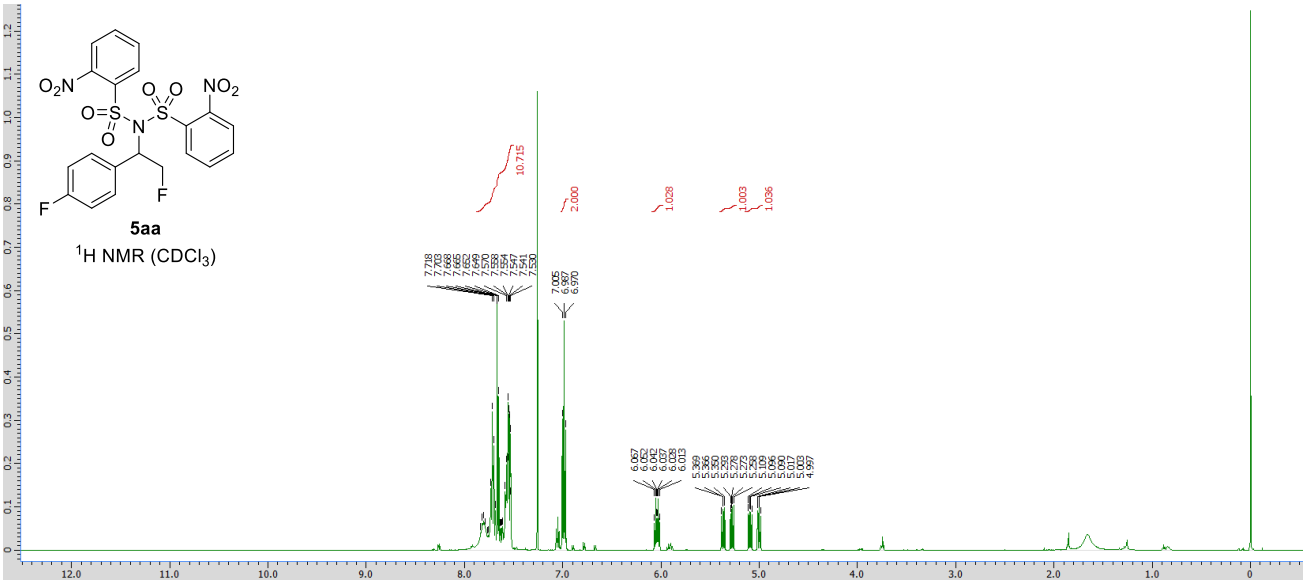

1d
13C NMR (CDCl3)

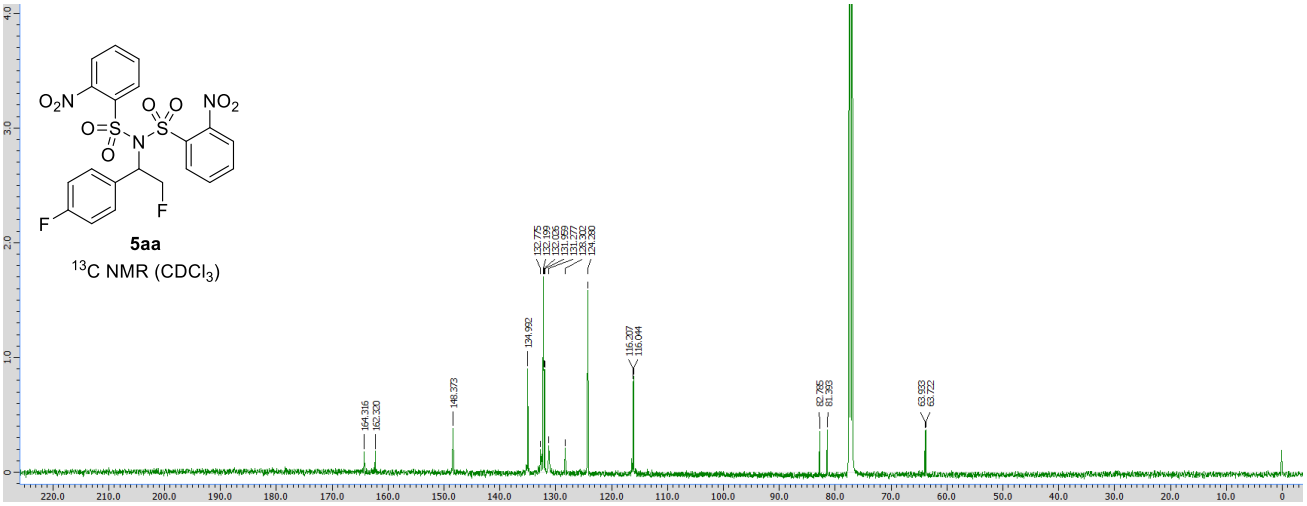

1d
19F NMR (CDCl3)

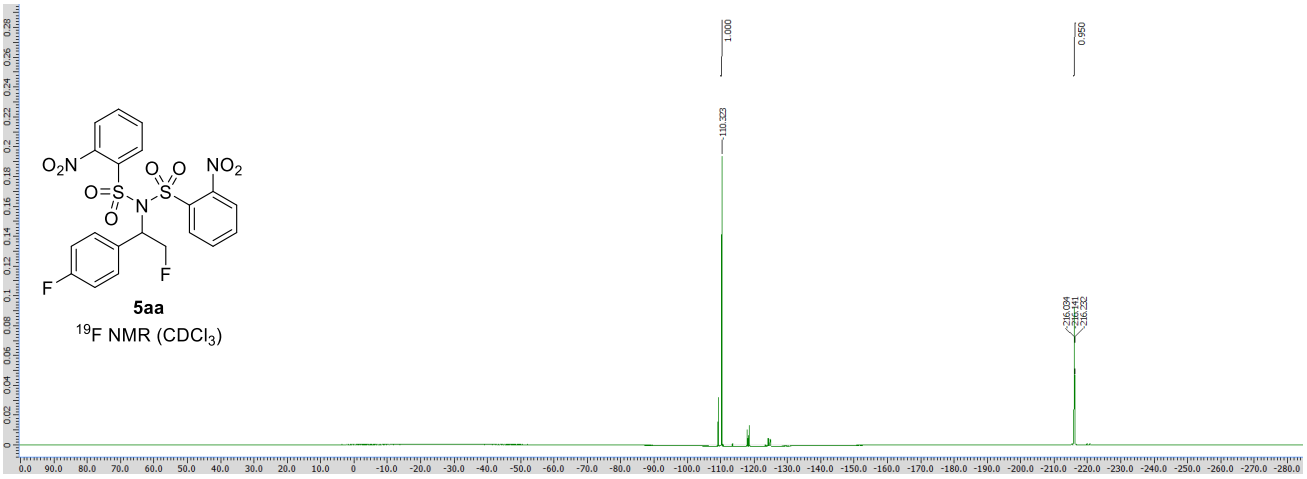

1e
^{1}H NMR ($CDCl_3$)

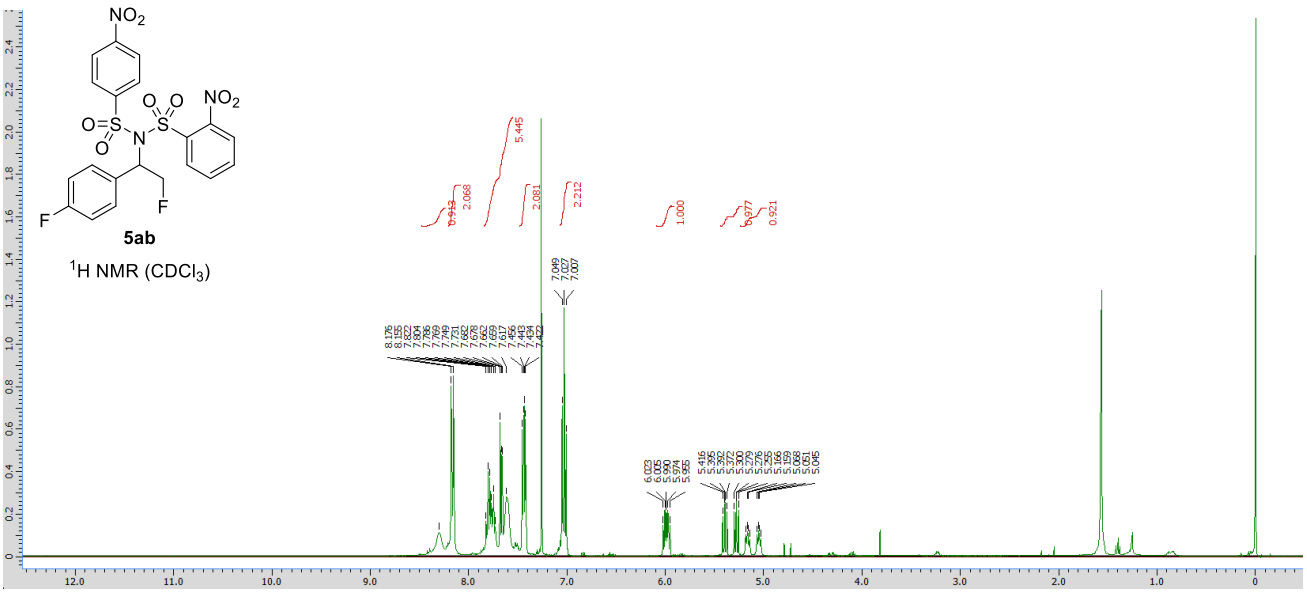

1e
^{13}C NMR ($CDCl_3$)

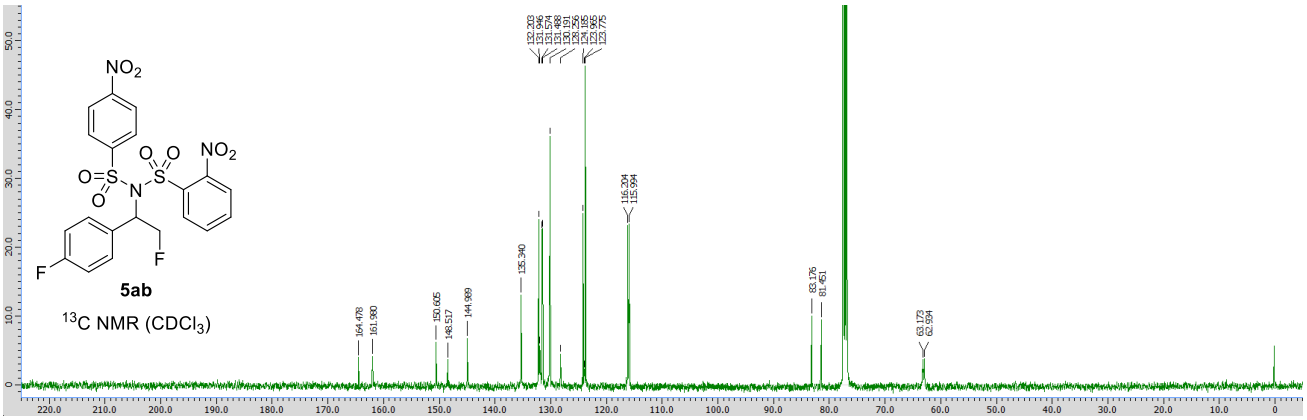

1e
^{19}F NMR ($CDCl_3$)

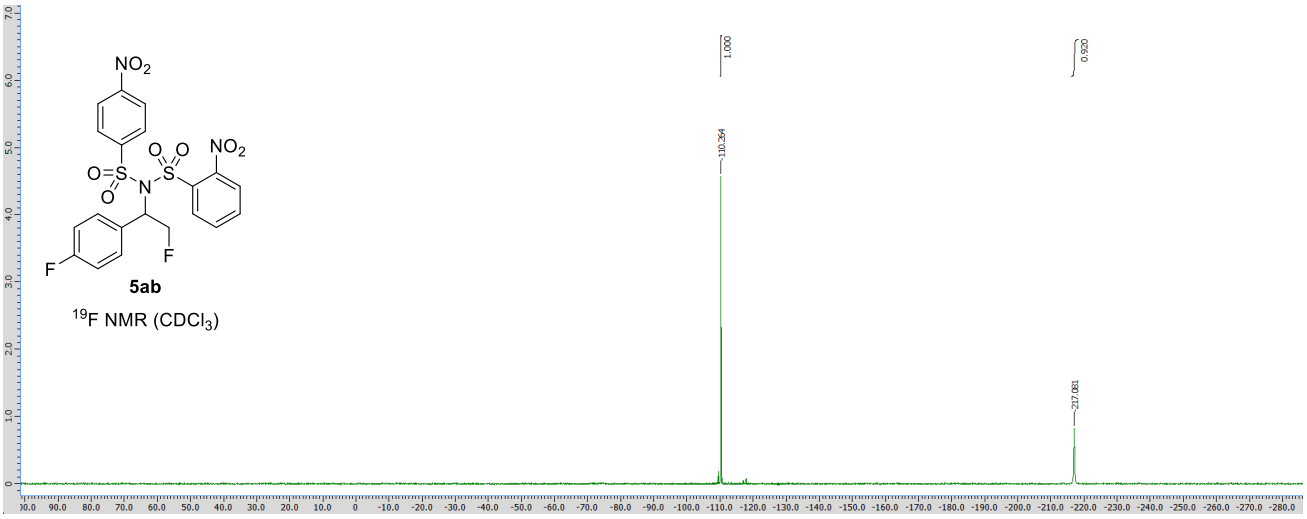

5aa
^{1}H NMR ($CDCl_3$)

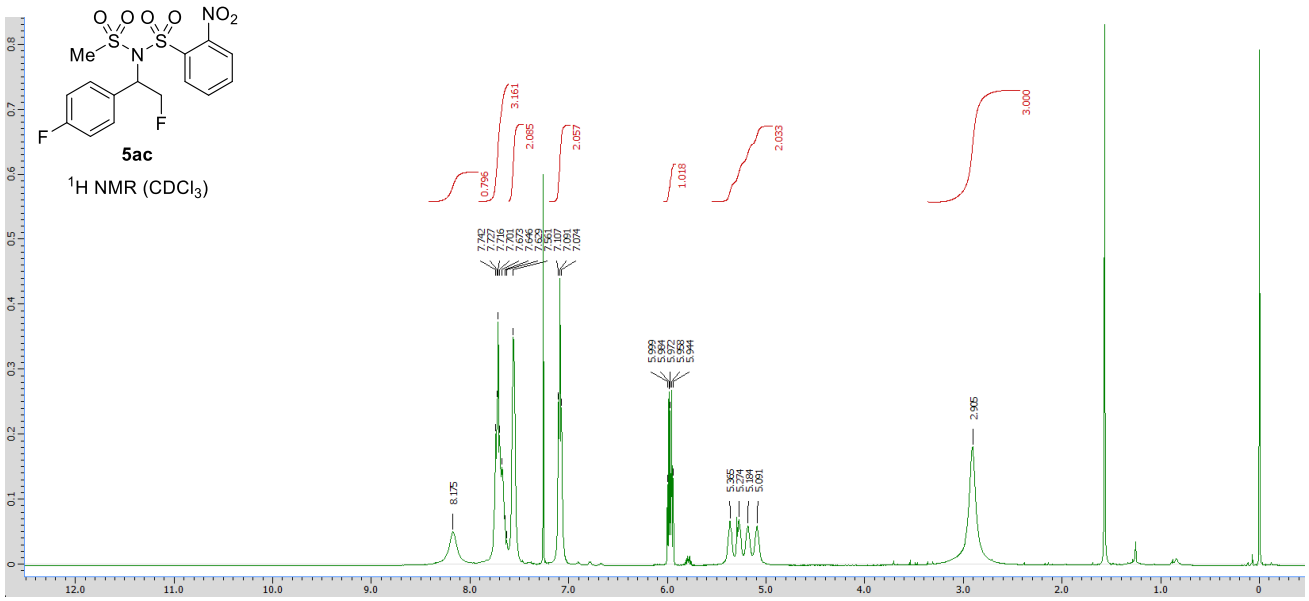

5aa
^{13}C NMR ($CDCl_3$)

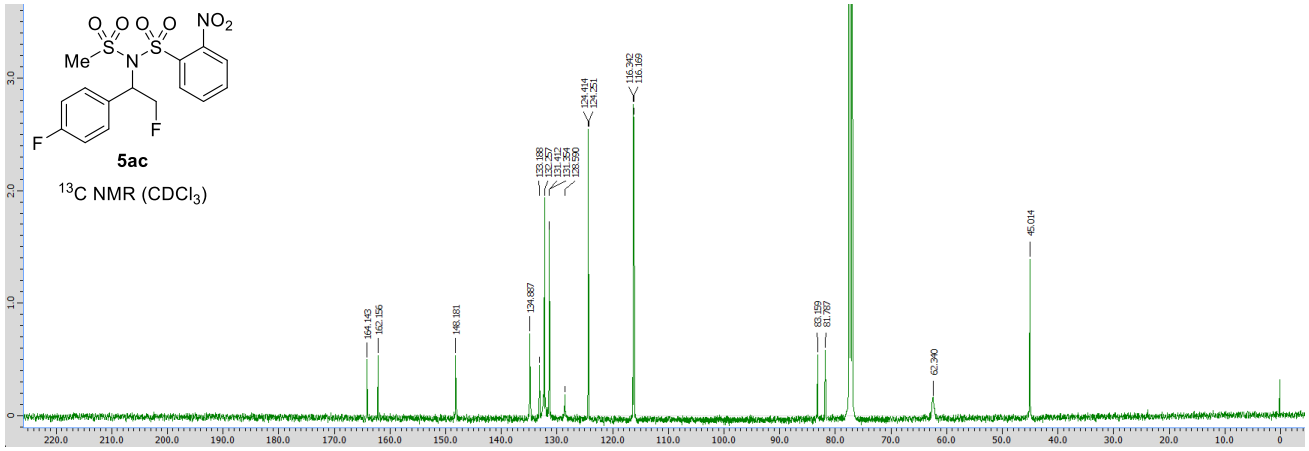

5aa
^{19}F NMR ($CDCl_3$)

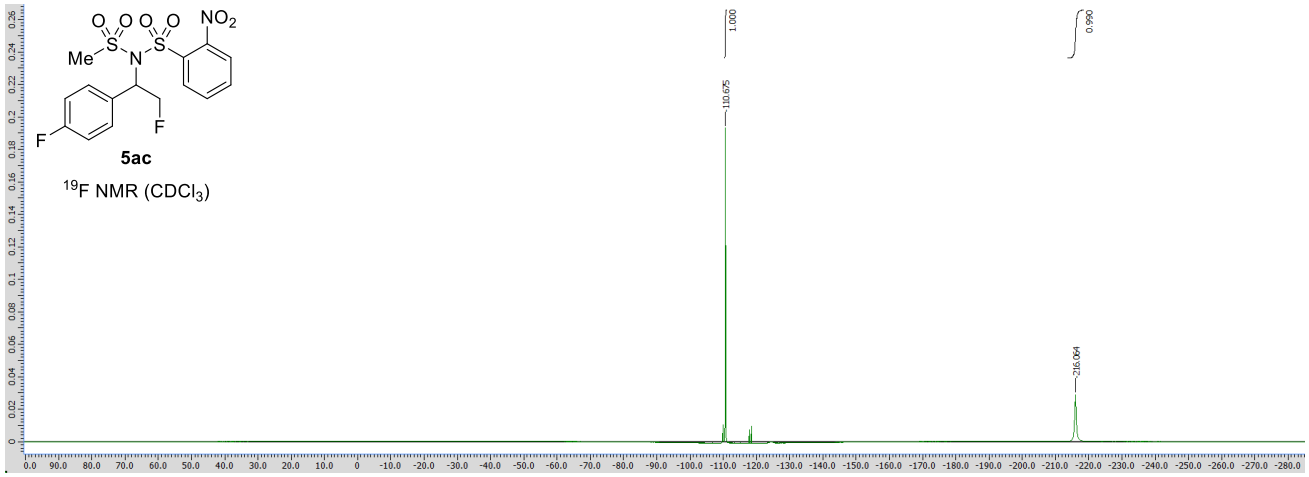

5ab
^{1}H NMR ($CDCl_3$)

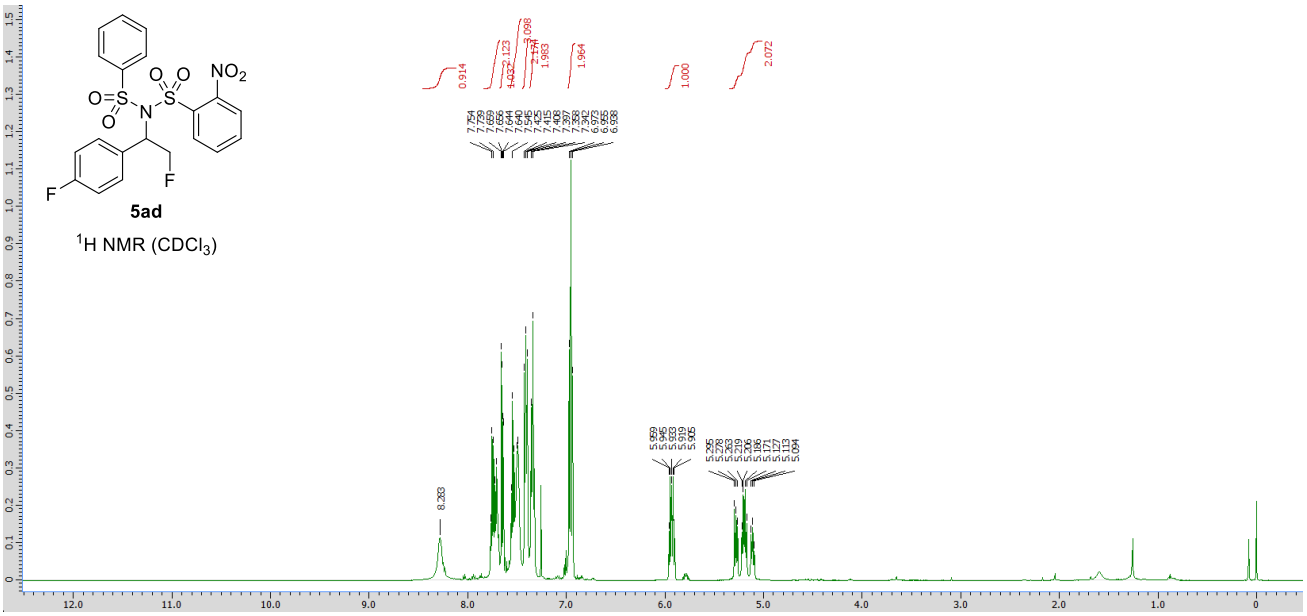

5ab
^{13}C NMR ($CDCl_3$)

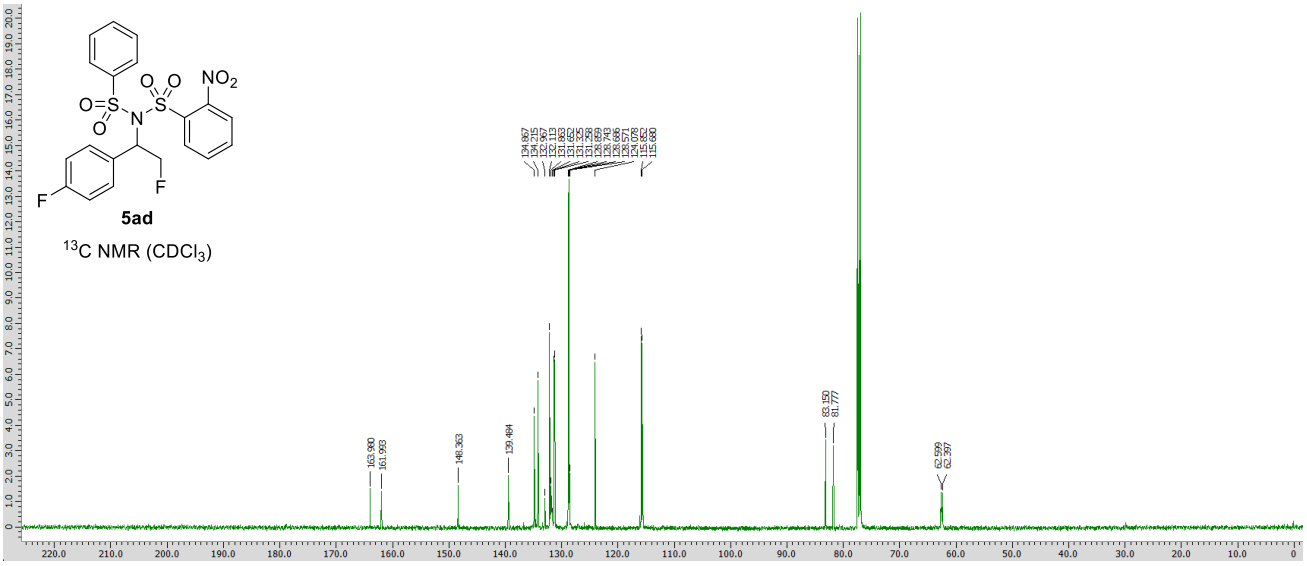

5ab
^{19}F NMR ($CDCl_3$)

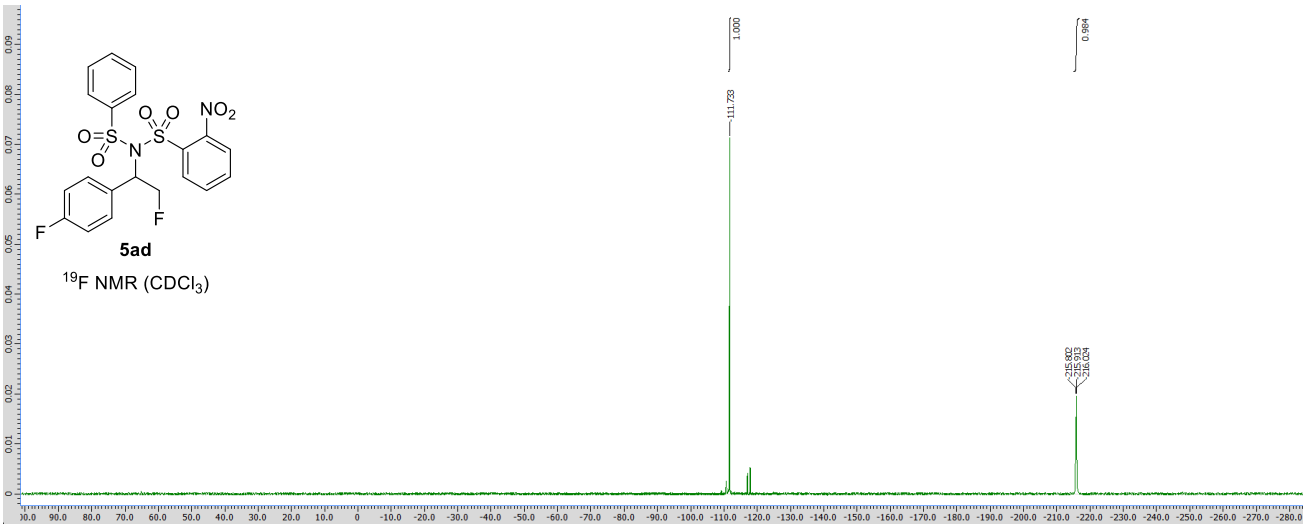

5ac
1H NMR (CDCl3)

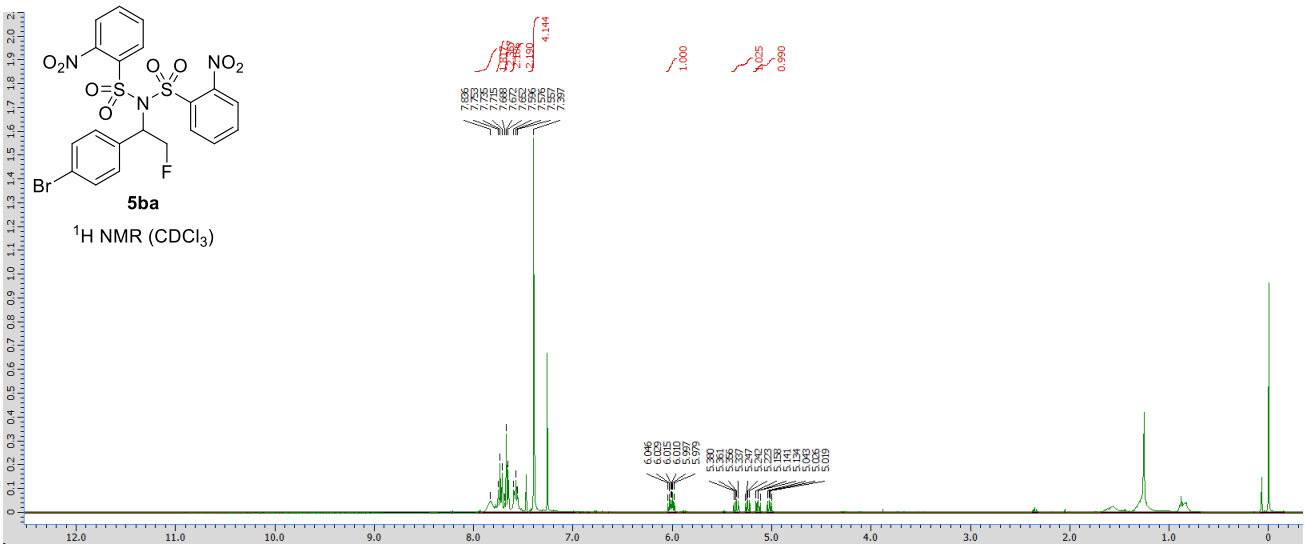

5ac
13C NMR (CDCl3)

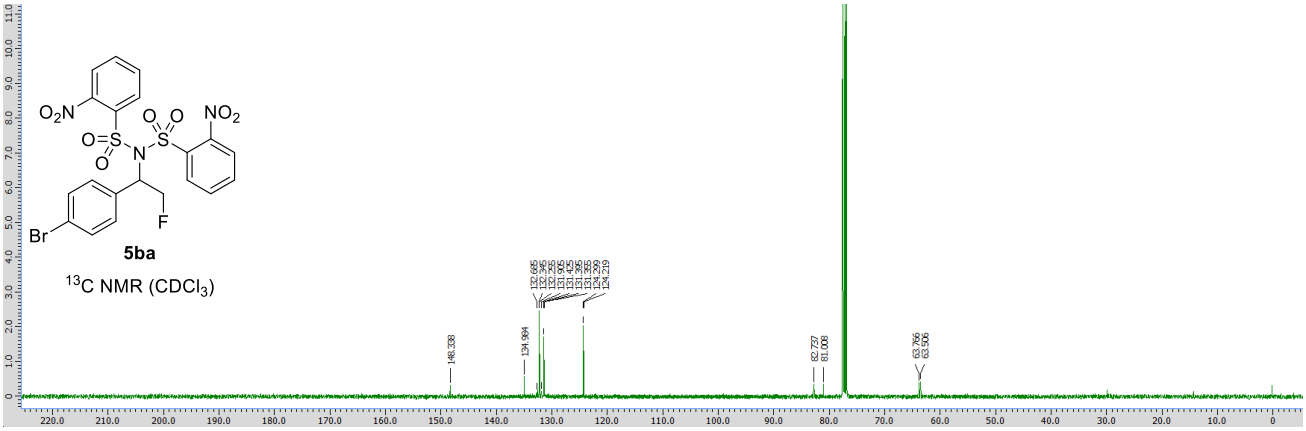

5ac
19F NMR (CDCl3)

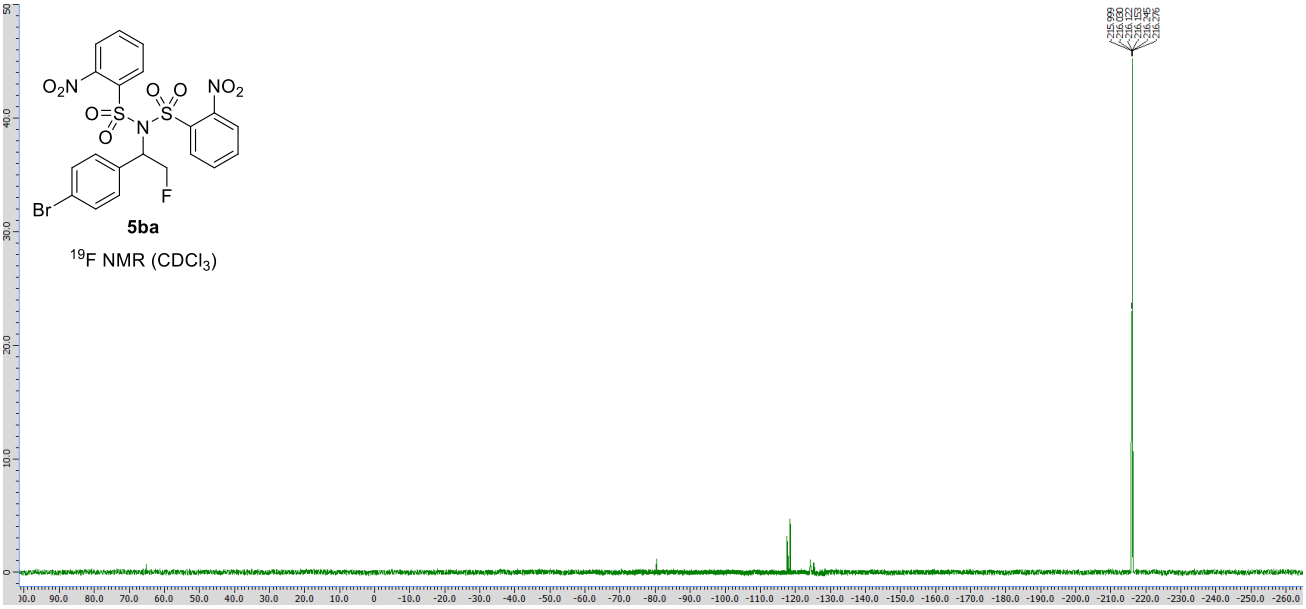

5ad
^{1}H NMR ($CDCl_3$)

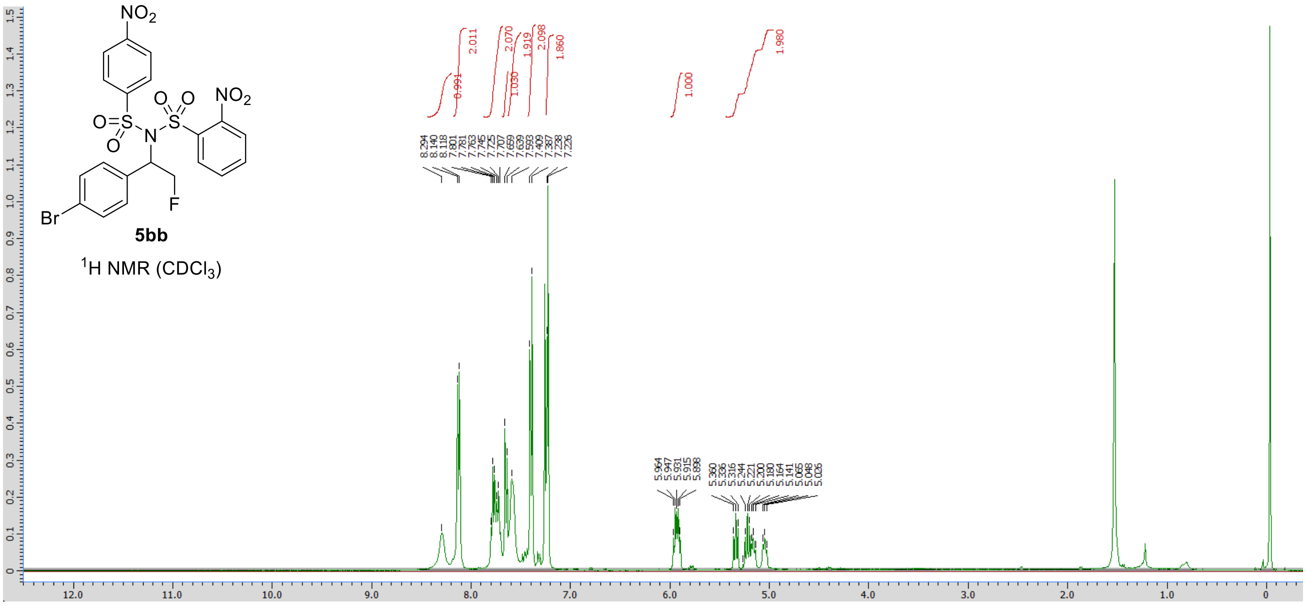

5ad
^{13}C NMR ($CDCl_3$)

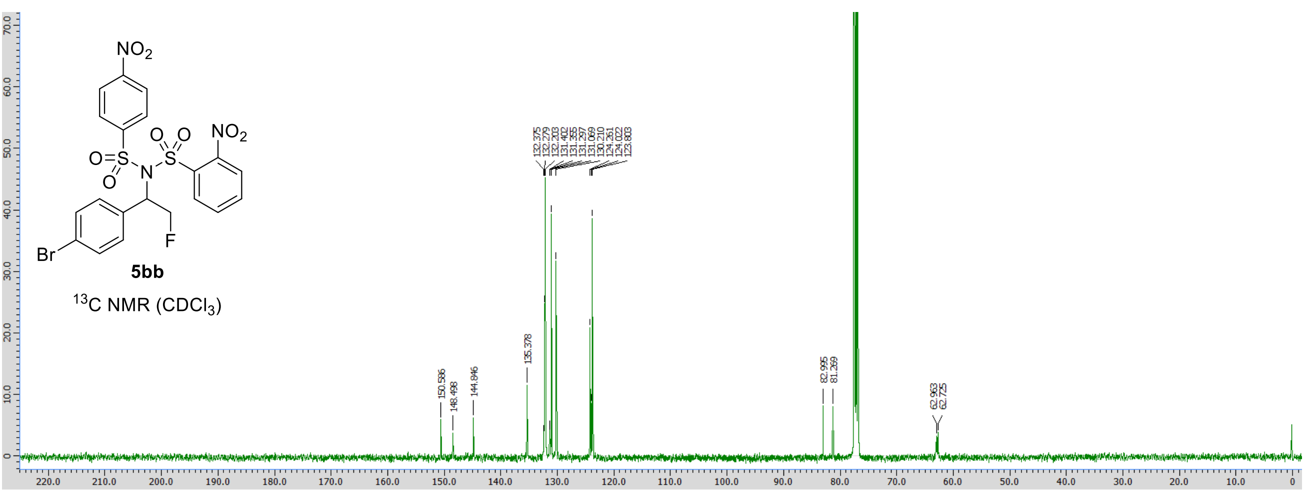

5ad
^{19}F NMR ($CDCl_3$)

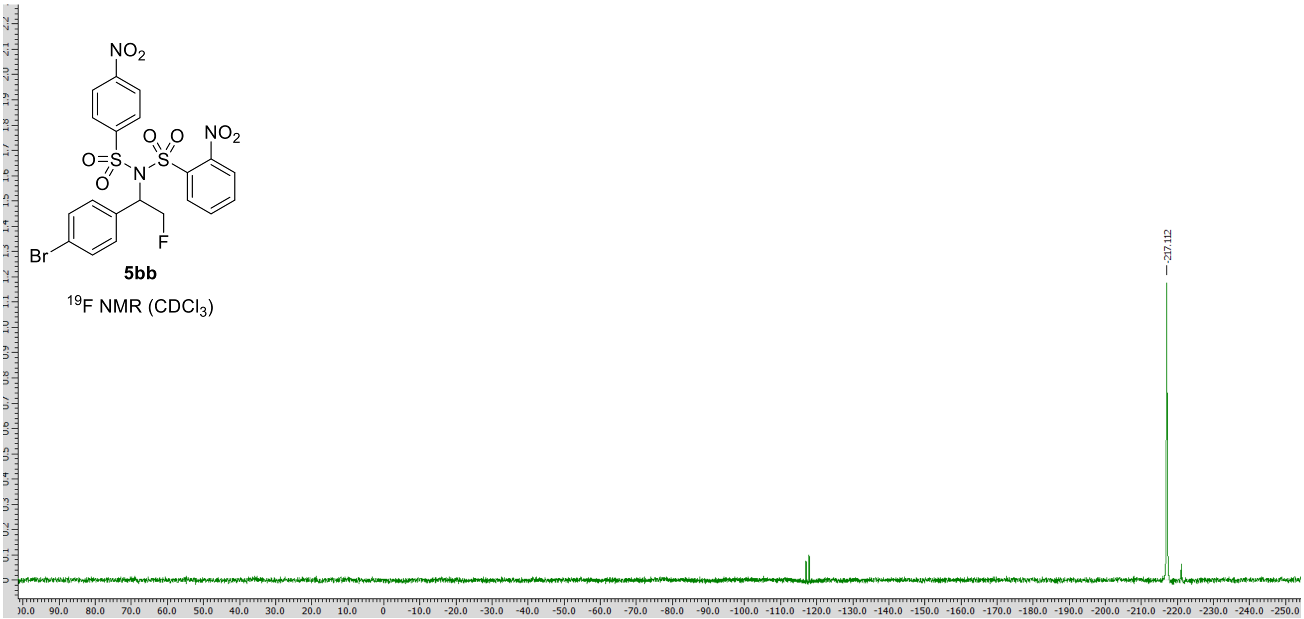

5ba
^{1}H NMR ($CDCl_3$)

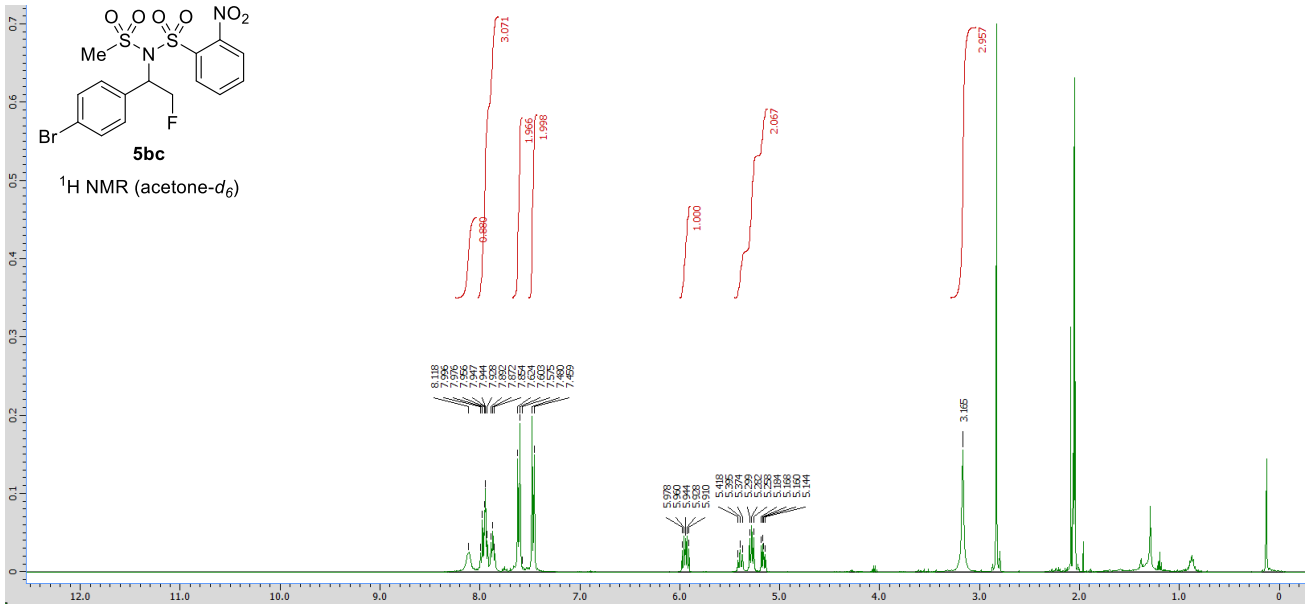

5ba
^{13}C NMR ($CDCl_3$)

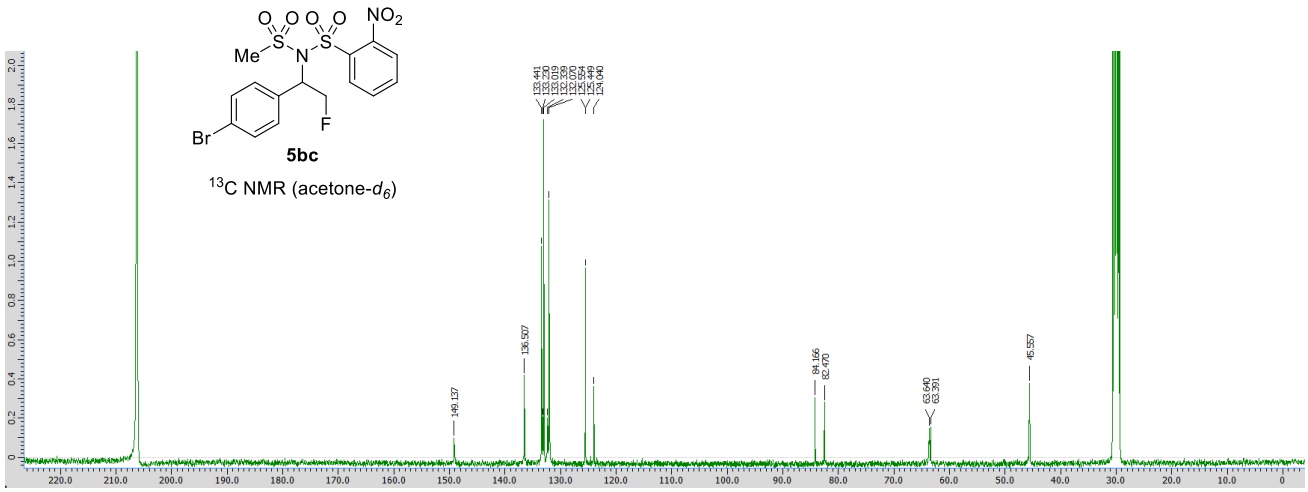

5ba
^{19}F NMR ($CDCl_3$)

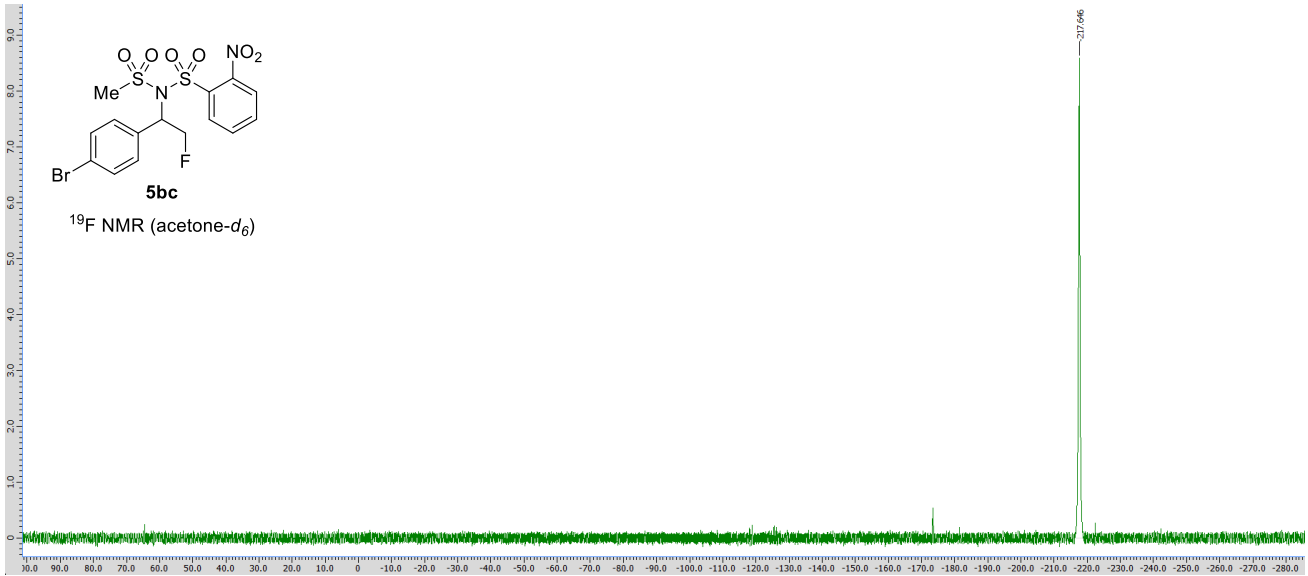

NO2
O=S
O
N
O O
S
NO2
Br
F
5bb
1H NMR (CDCl3)

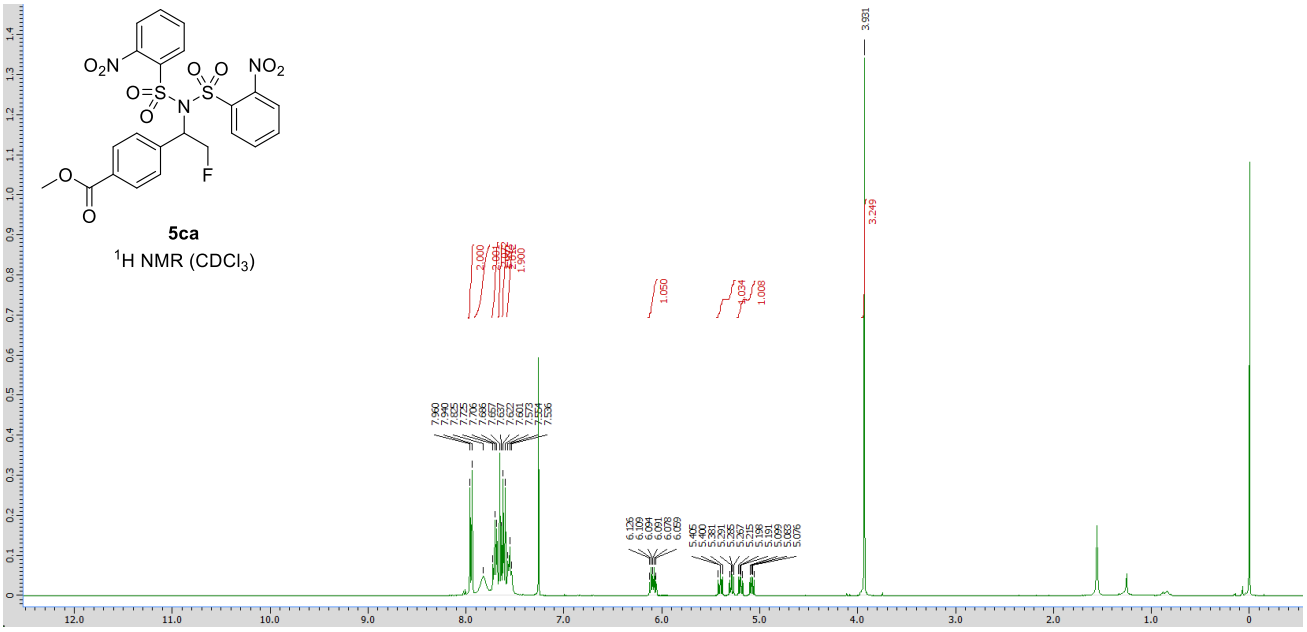

NO2
O=S
O
N
O O
S
NO2
Br
F
5bb
13C NMR (CDCl3)

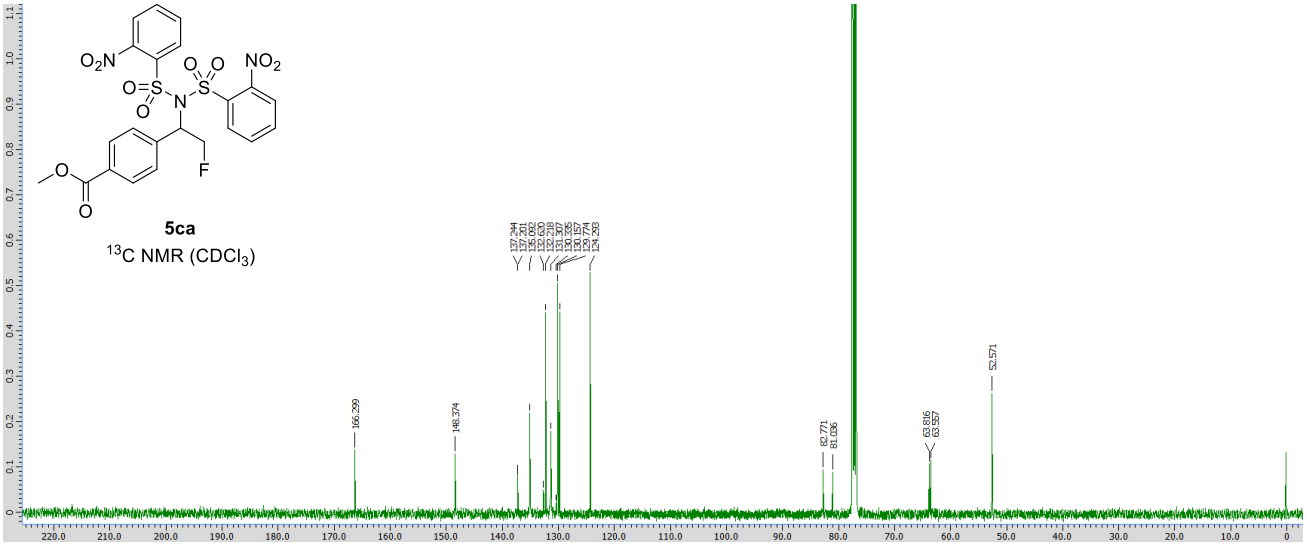

NO2
O=S
O
N
O O
S
NO2
Br
F
5bb
19F NMR (CDCl3)
-217.112

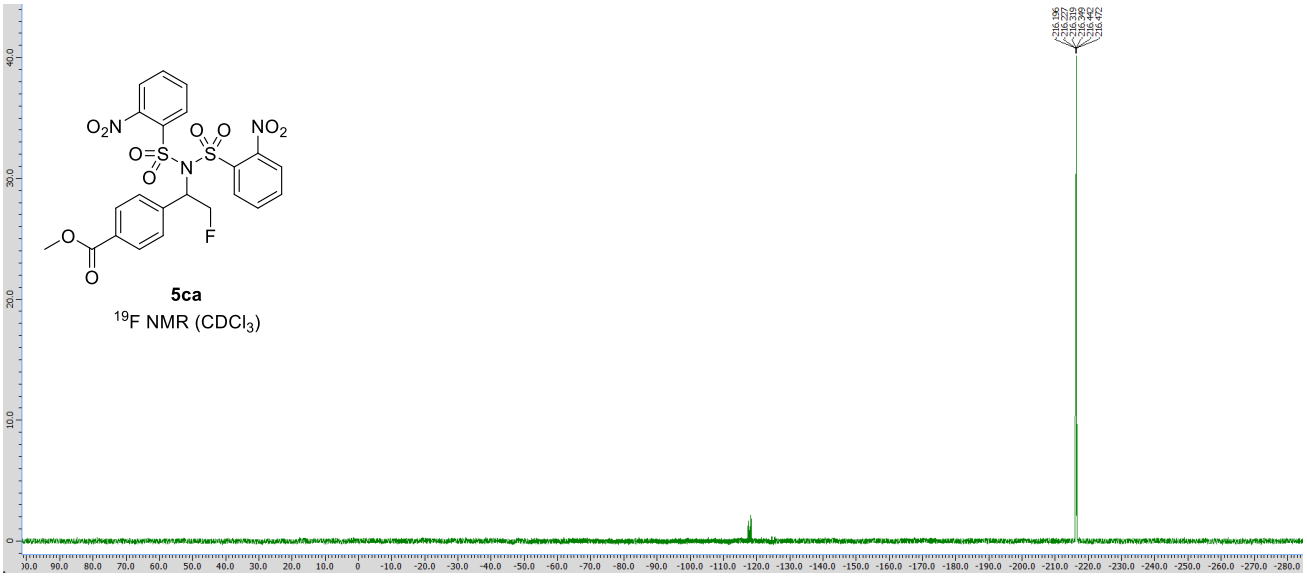

Me
Br
F
5bc
1H NMR (acetone-d6)

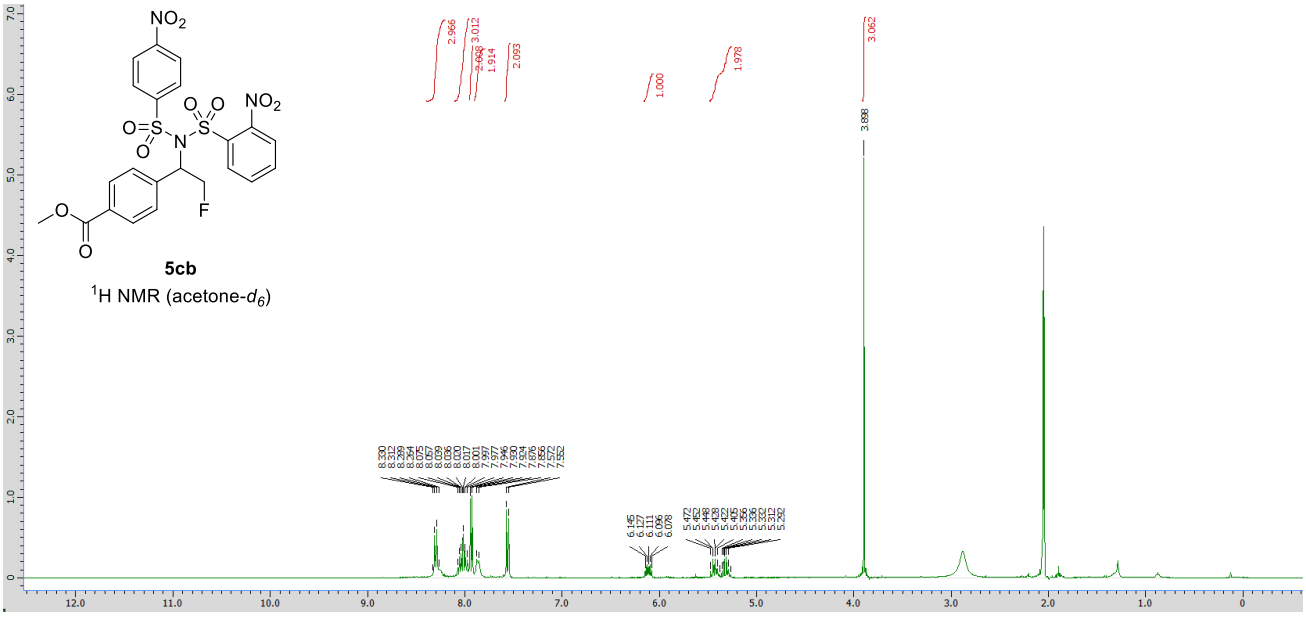

Me
Br
F
5bc
13C NMR (acetone-d6)

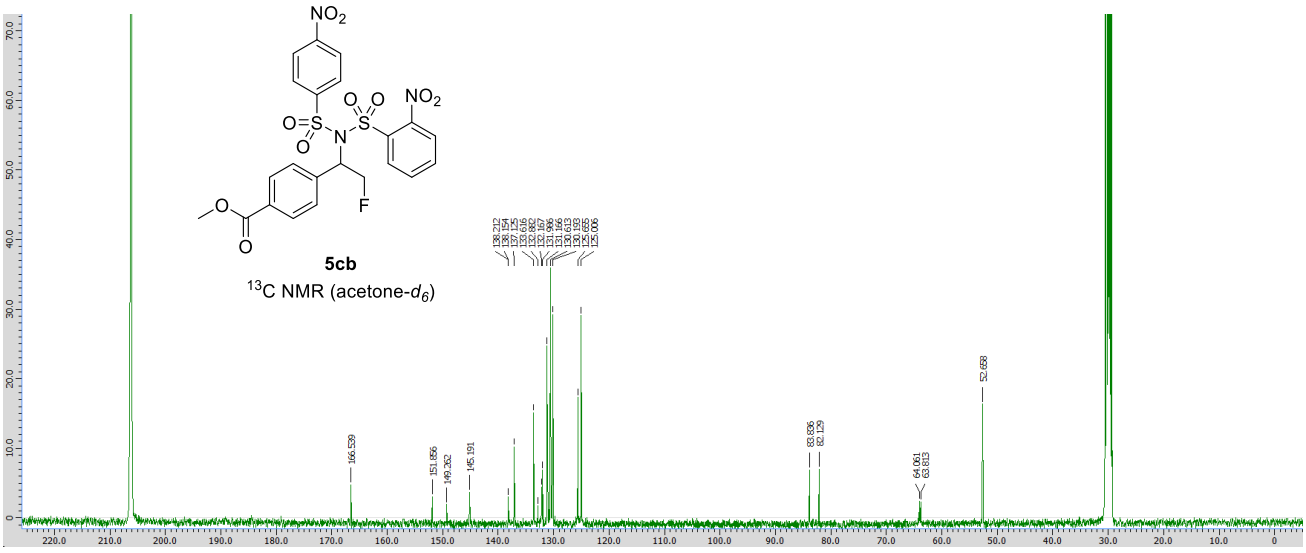

Me
Br
F
5bc
19F NMR (acetone-d6)

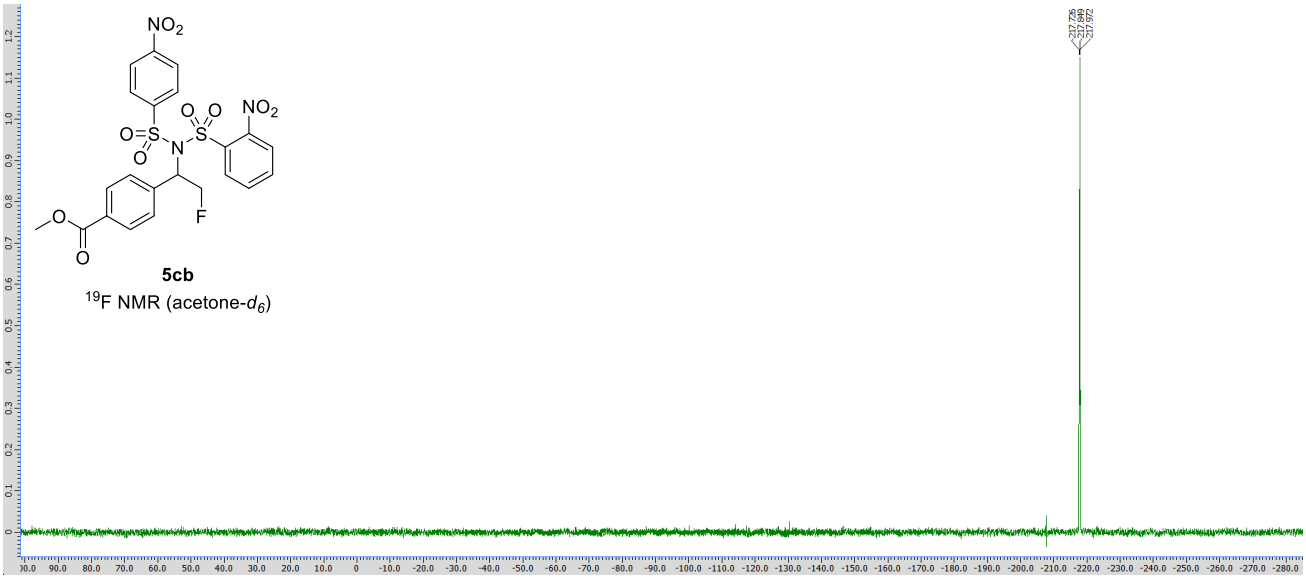

5ca
^{1}H NMR ($CDCl_3$)

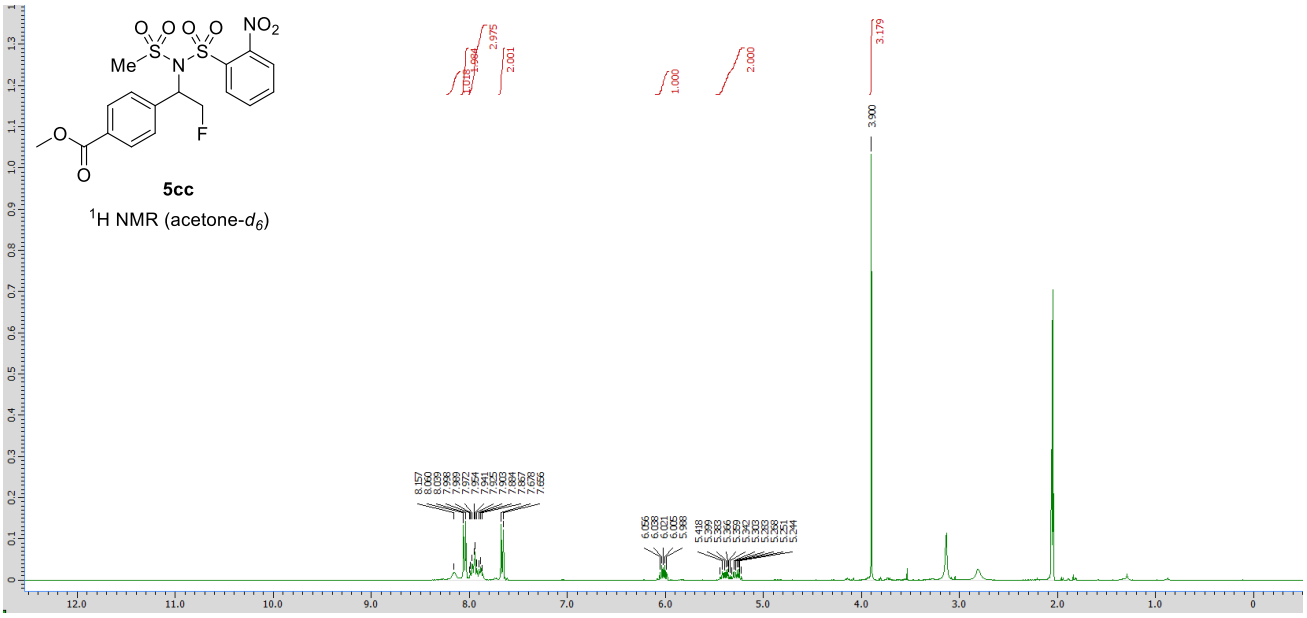

5ca
^{13}C NMR ($CDCl_3$)

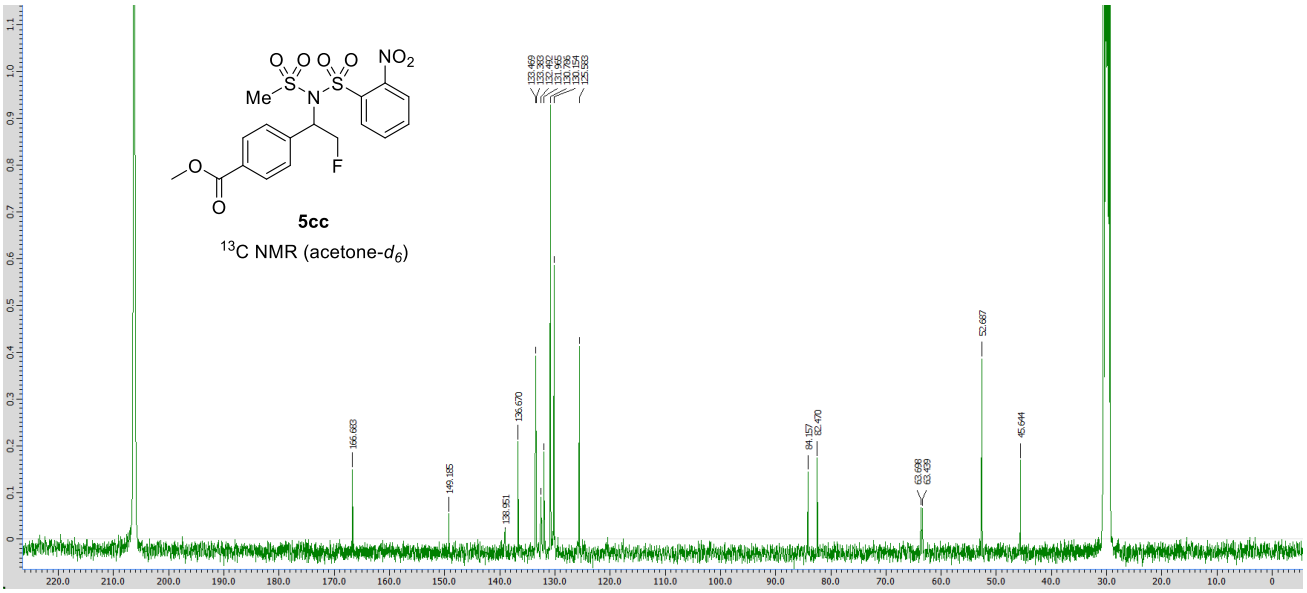

5ca
^{19}F NMR ($CDCl_3$)

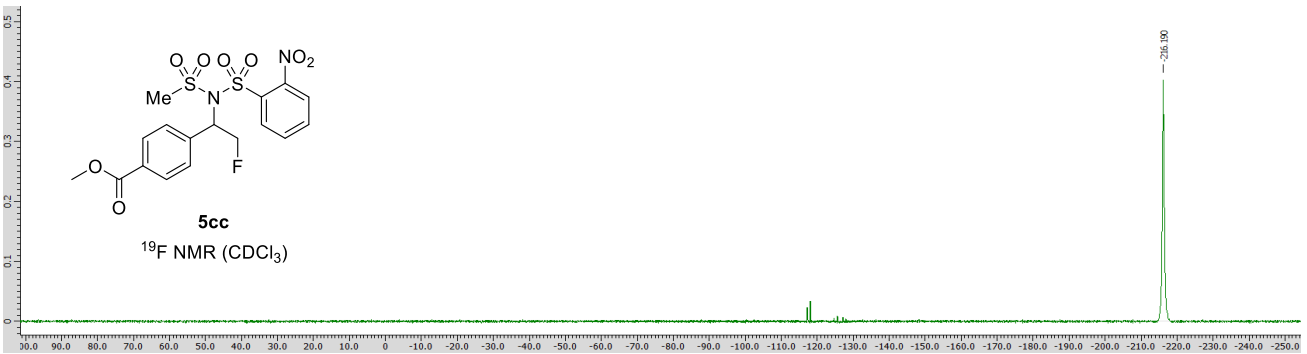

NO2
NO2
O
O
S
N
S
O
O
O
O
F
O
O
5cb
1H NMR (acetone-d6)

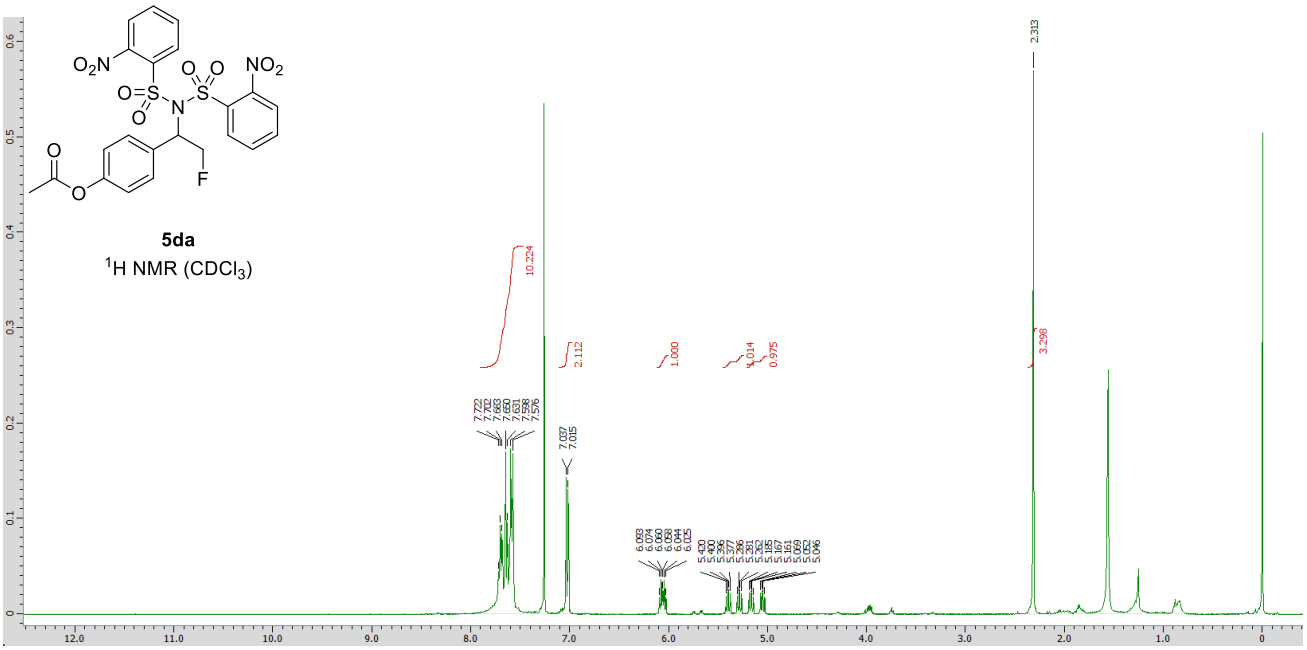

NO2
NO2
O
O
S
N
S
O
O
O
O
F
O
O
5cb
13C NMR (acetone-d6)


NO2
NO2
O
O
S
N
S
O
O
O
O
F
O
O
5cb
19F NMR (acetone-d6)


Me
N
F
NO2
5cc
1H NMR (acetone-d6)

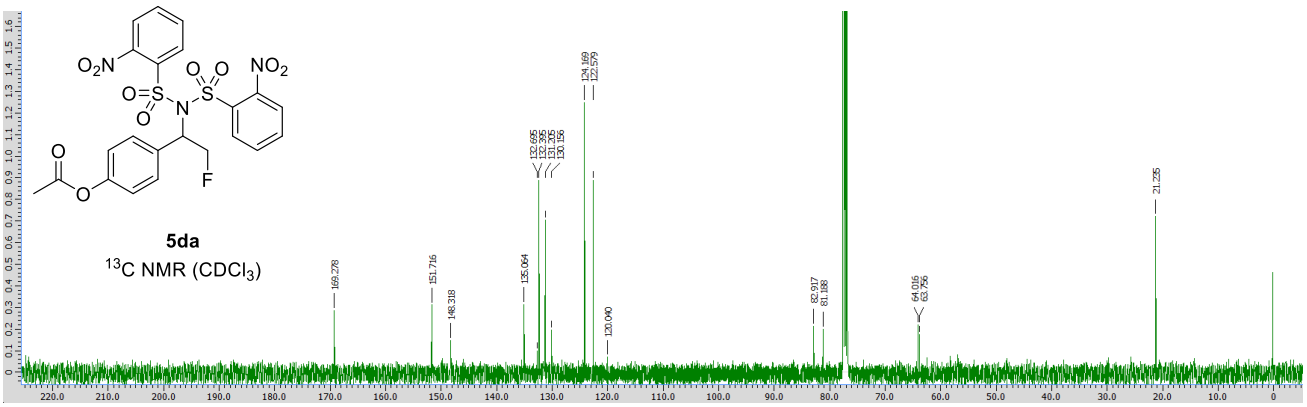

Me
N
F
NO2
5cc
13C NMR (acetone-d6)


Me
N
F
NO2
5cc
19F NMR (CDCl3)



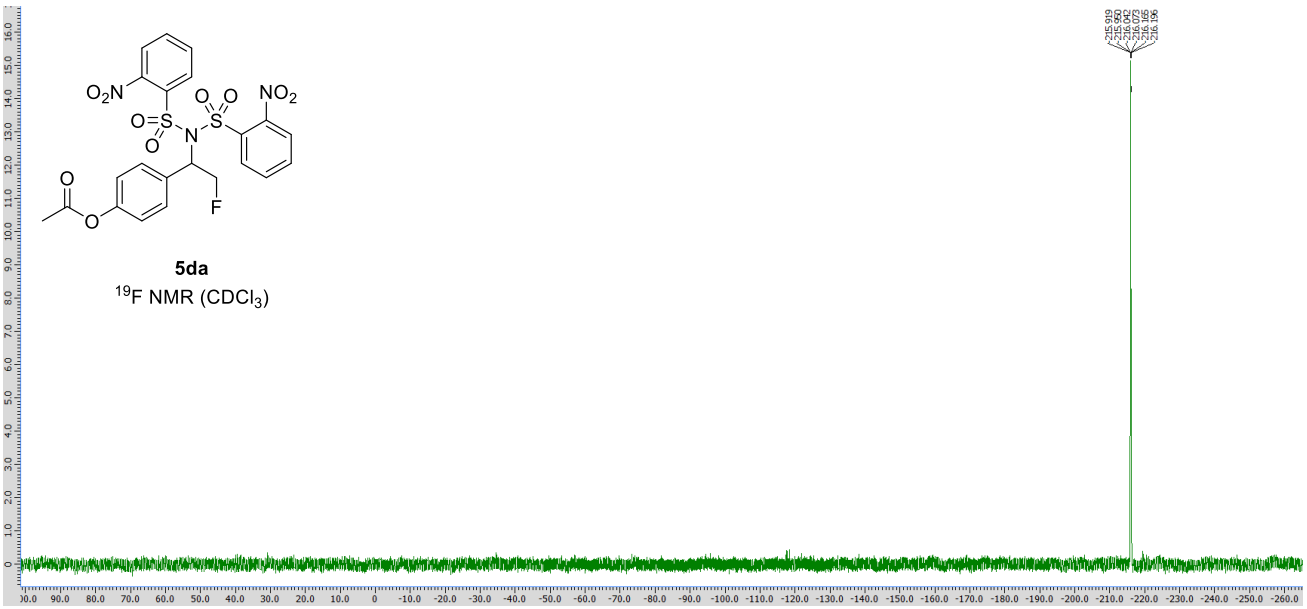
5da

^{1}H NMR ($CDCl_3$)



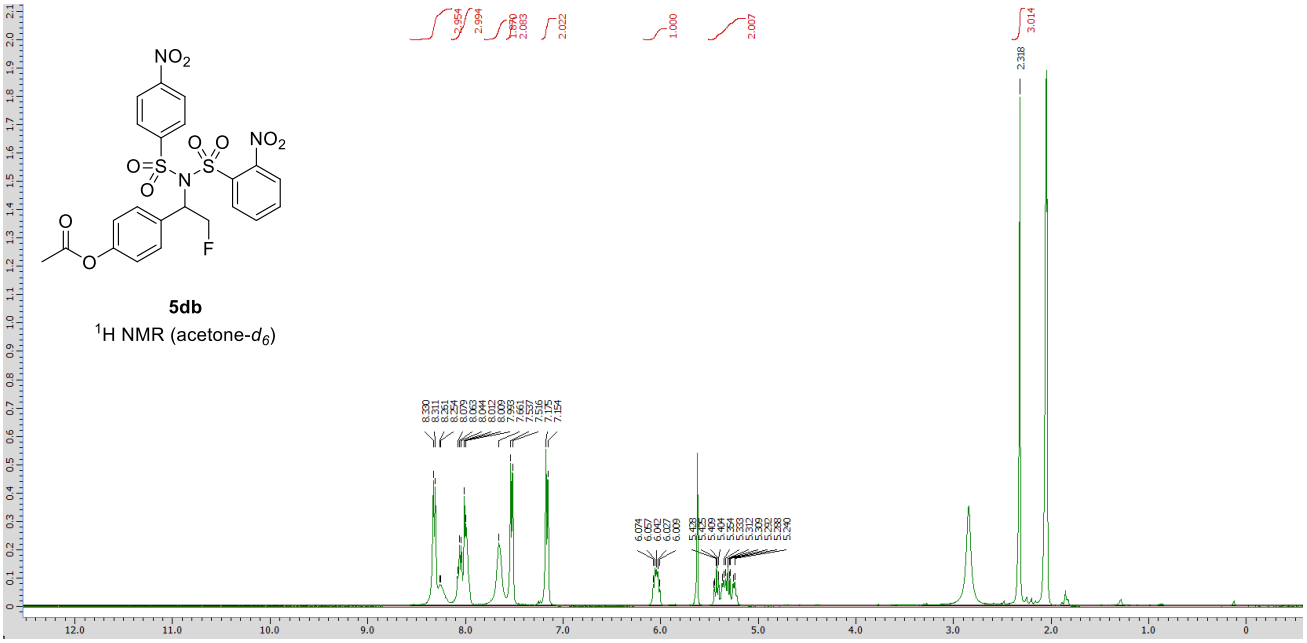
5da

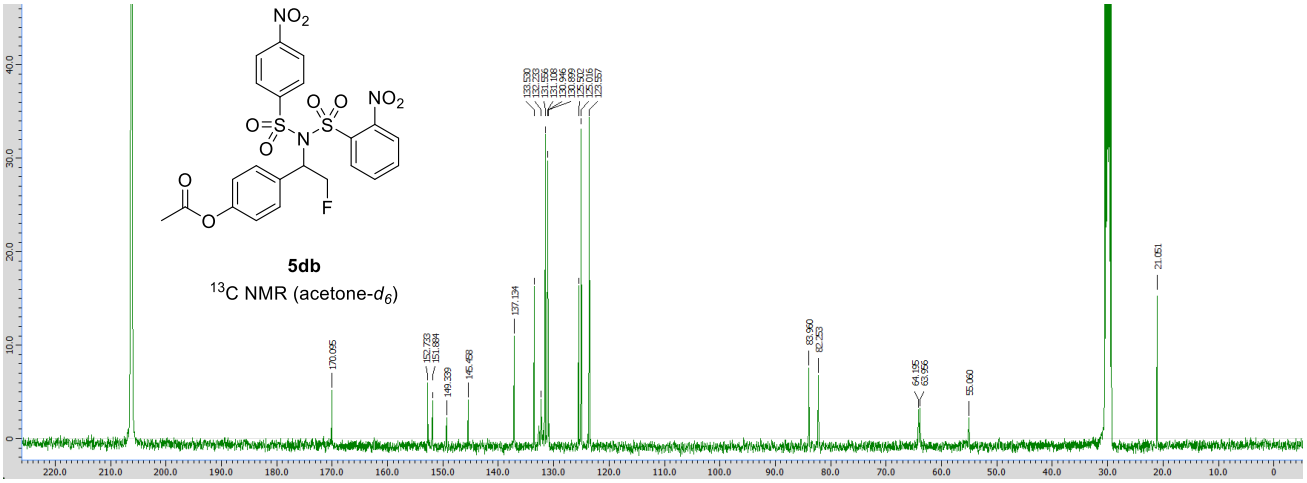
^{13}C NMR ($CDCl_3$)

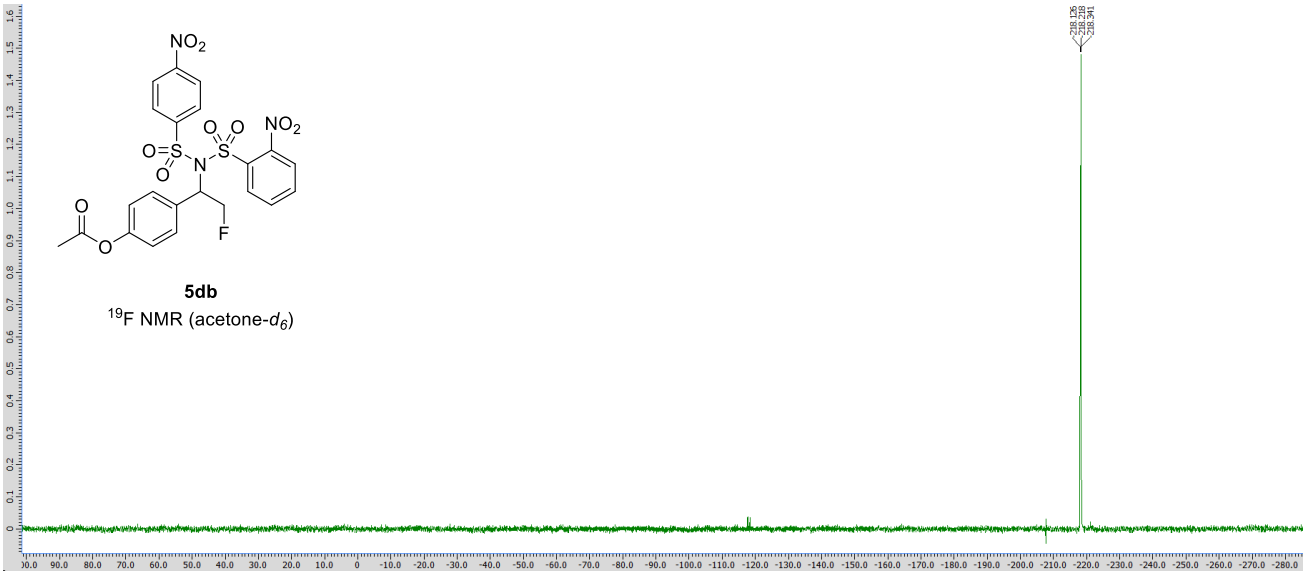


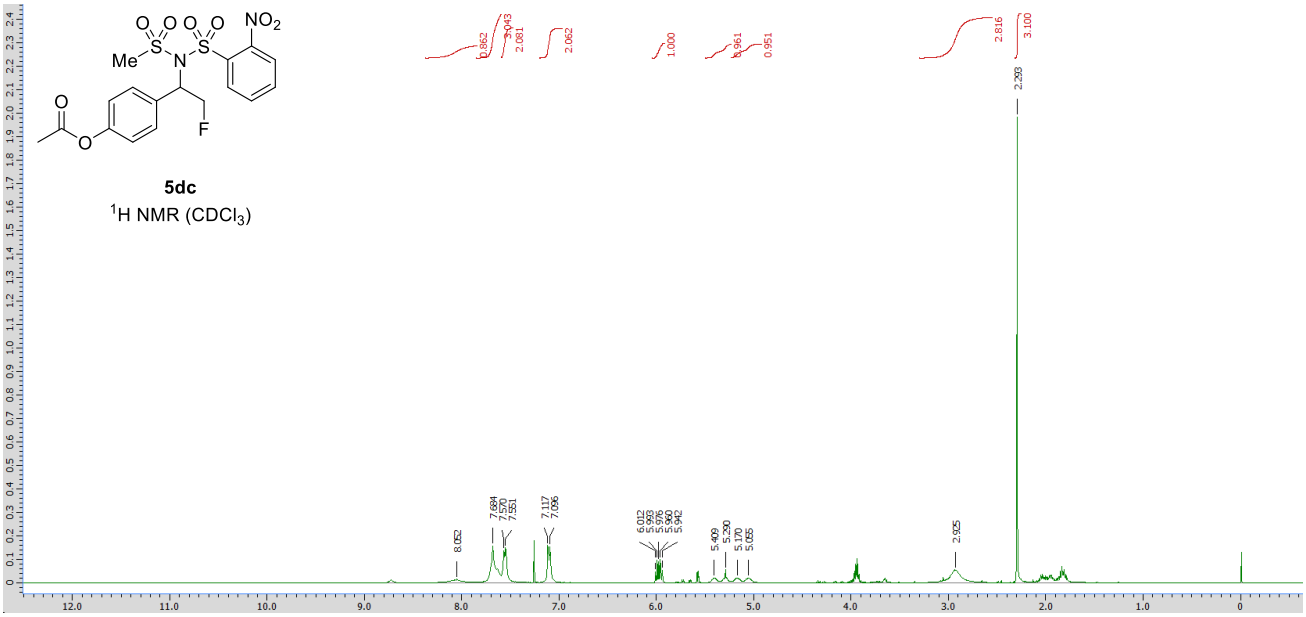
5da

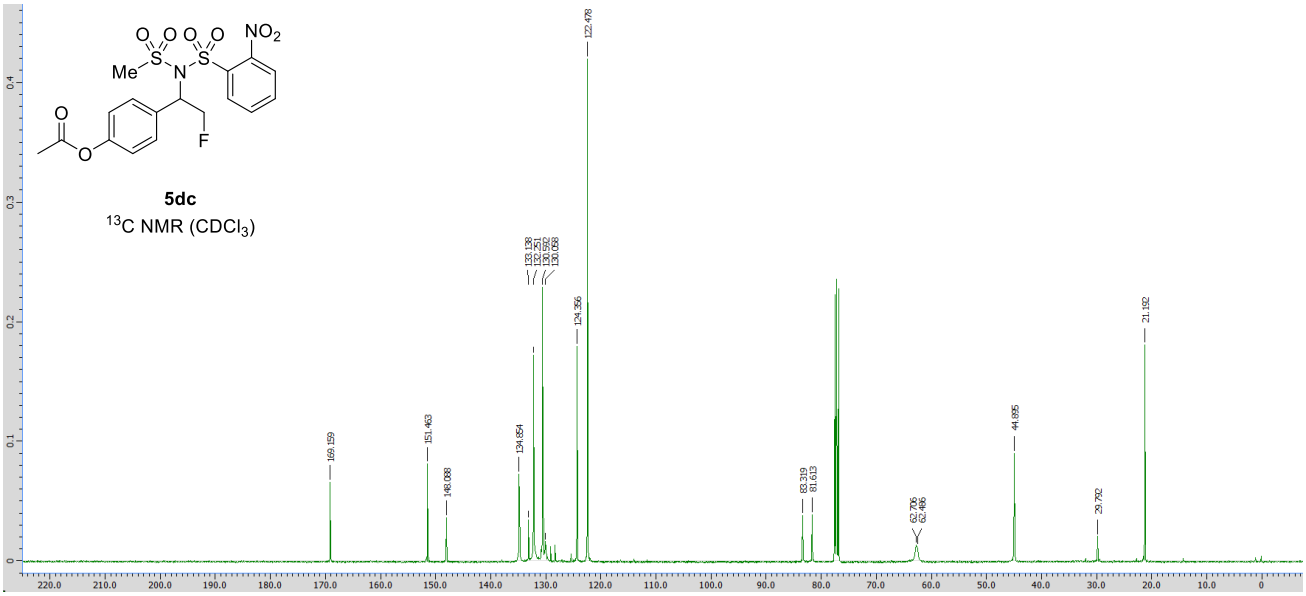
^{19}F NMR ($CDCl_3$)

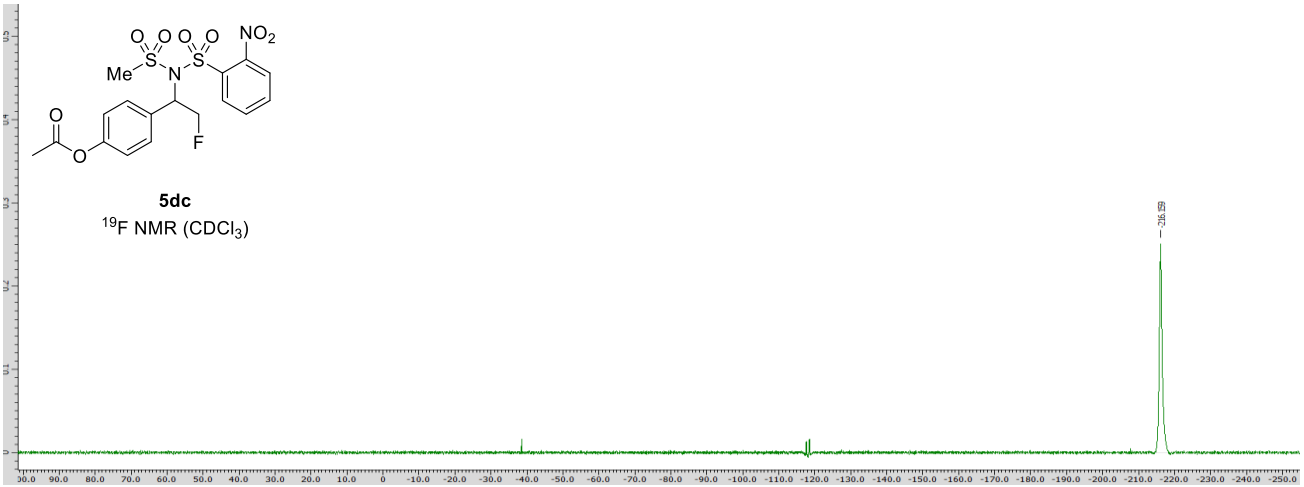

NO2
NO2
O=S
O
N
S
O
F
O
O
5db
1H NMR (acetone-d6)

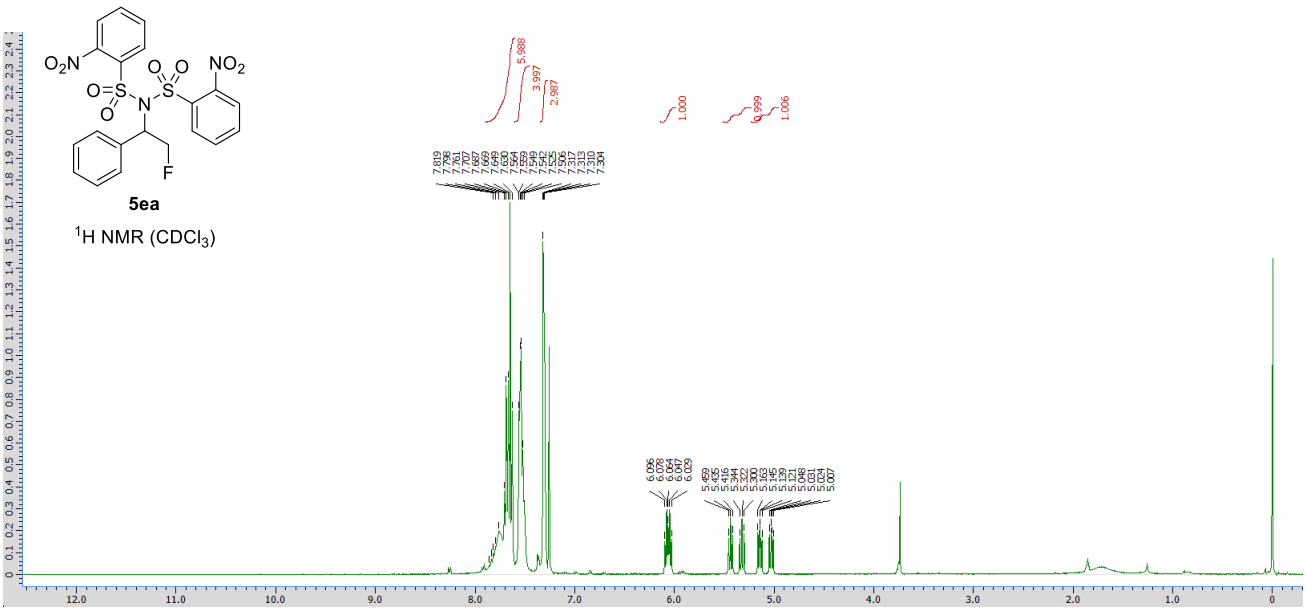

NO2
NO2
O=S
O
N
S
O
F
O
O
5db
13C NMR (acetone-d6)

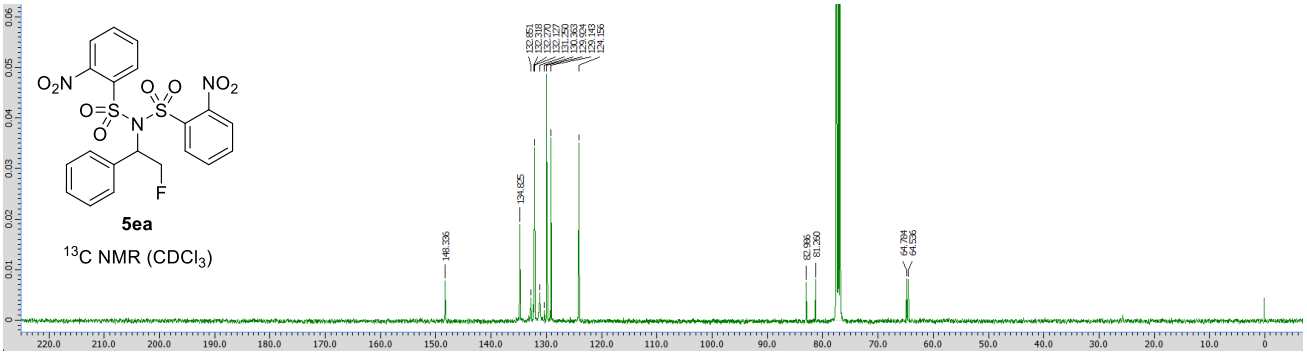

NO2
NO2
O=S
O
N
S
O
F
O
O
5db
19F NMR (acetone-d6)


5dc
^{1}H NMR ($CDCl_3$)

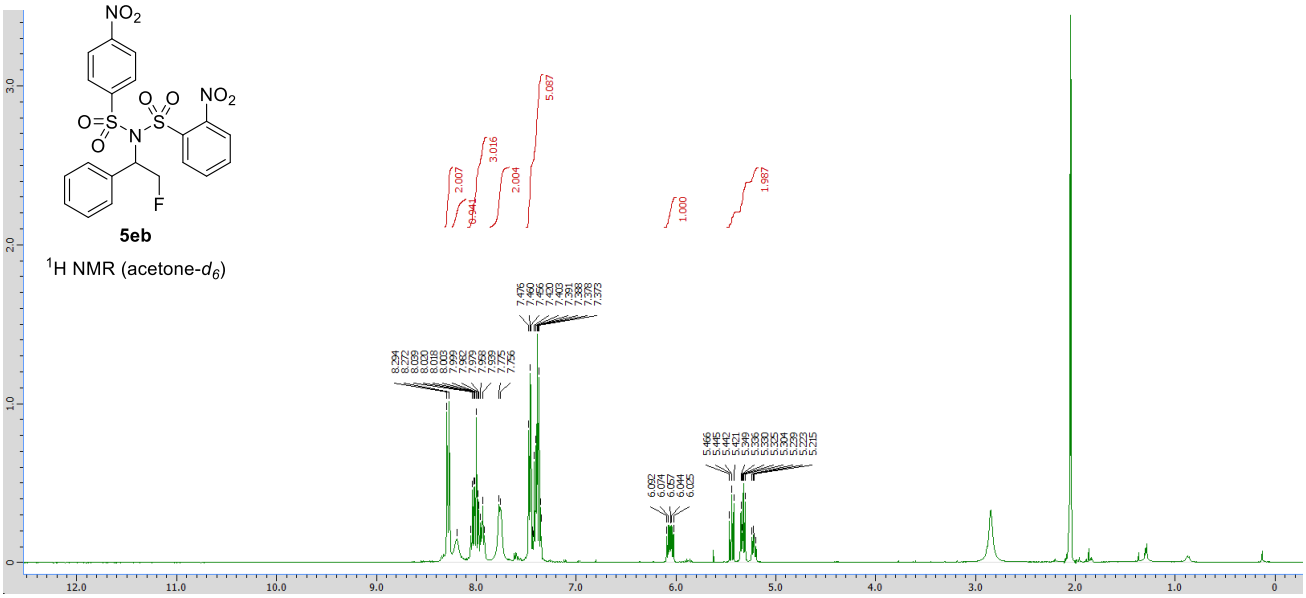

5dc
^{13}C NMR ($CDCl_3$)

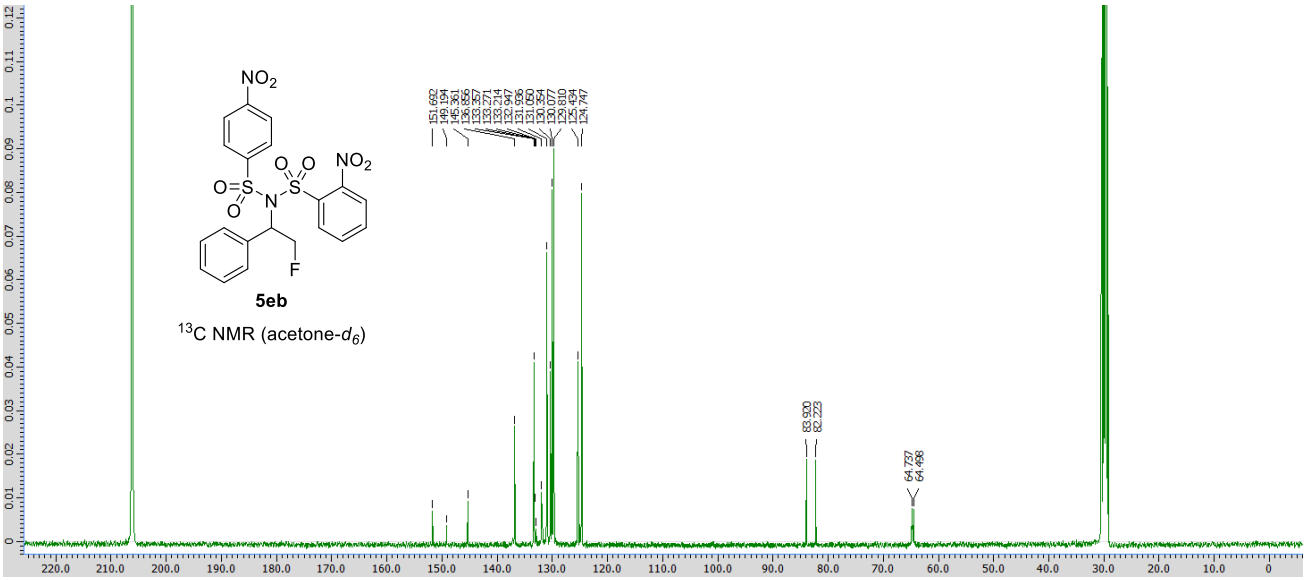

5dc
^{19}F NMR ($CDCl_3$)

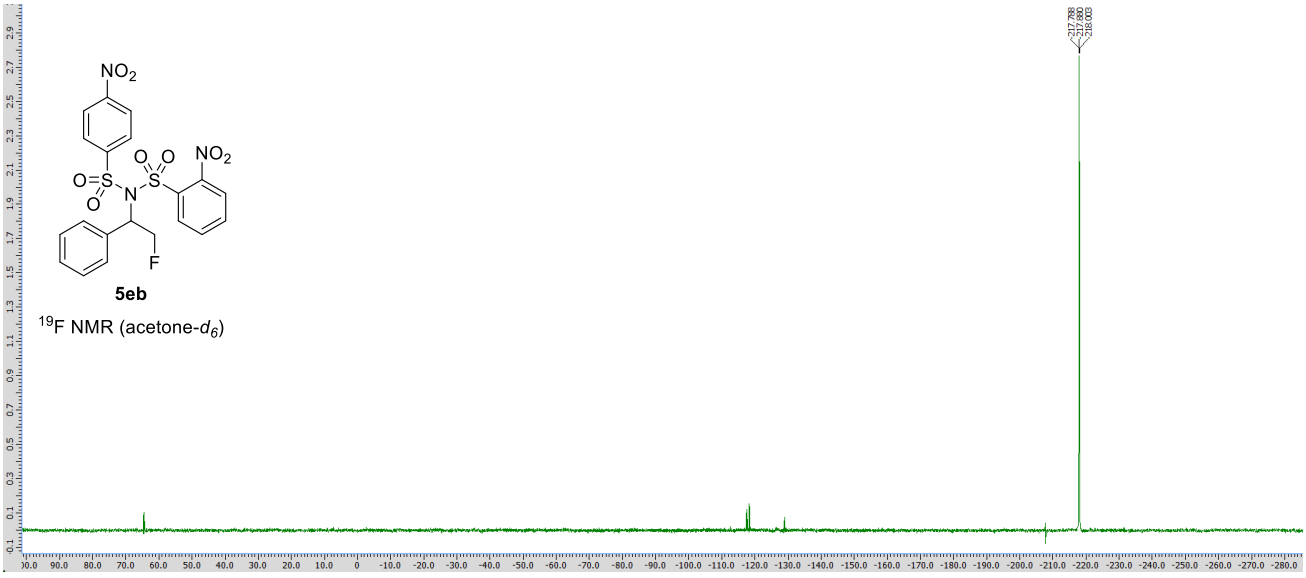

5ea
^{1}H NMR ($CDCl_3$)

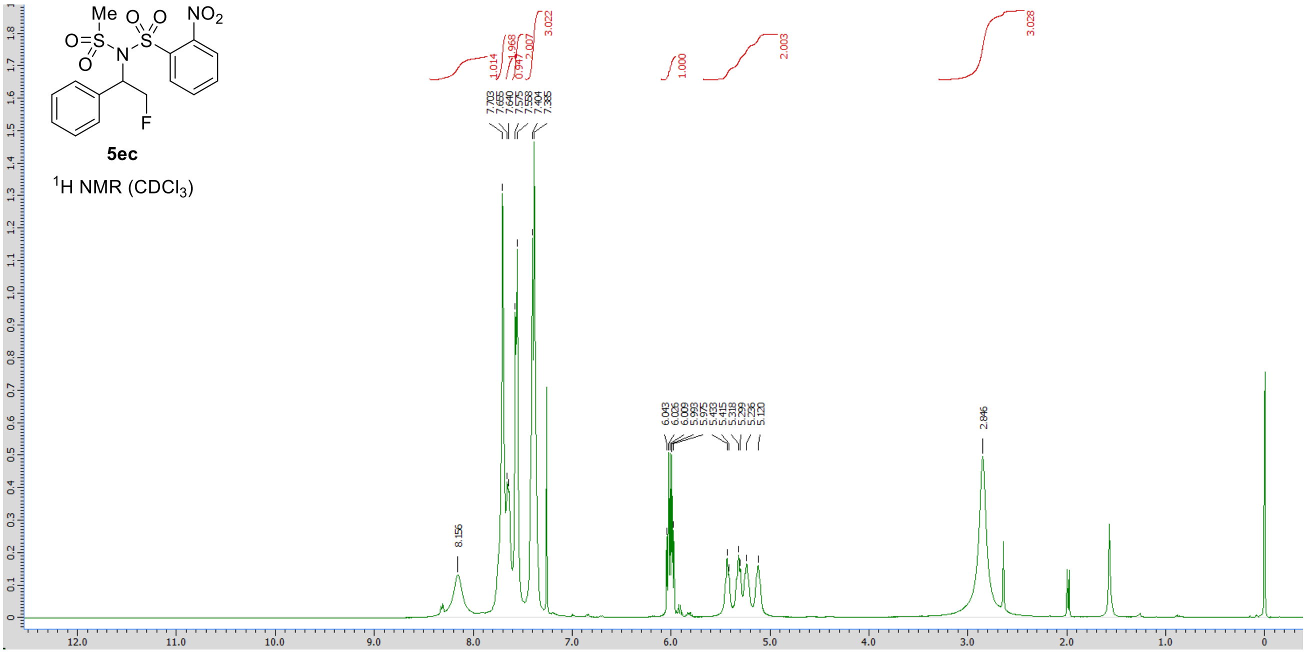

5ea
^{13}C NMR ($CDCl_3$)


5ea
^{19}F NMR ($CDCl_3$)

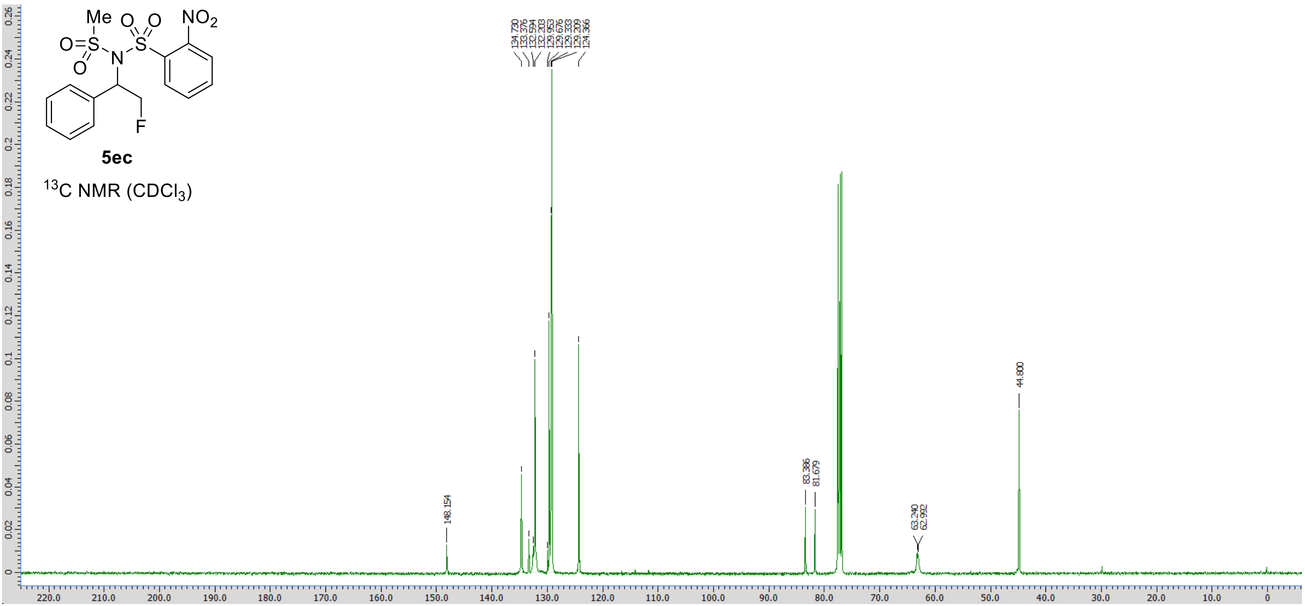

5eb
^{1}H NMR (acetone-d_6)


5eb
^{13}C NMR (acetone-d_6)

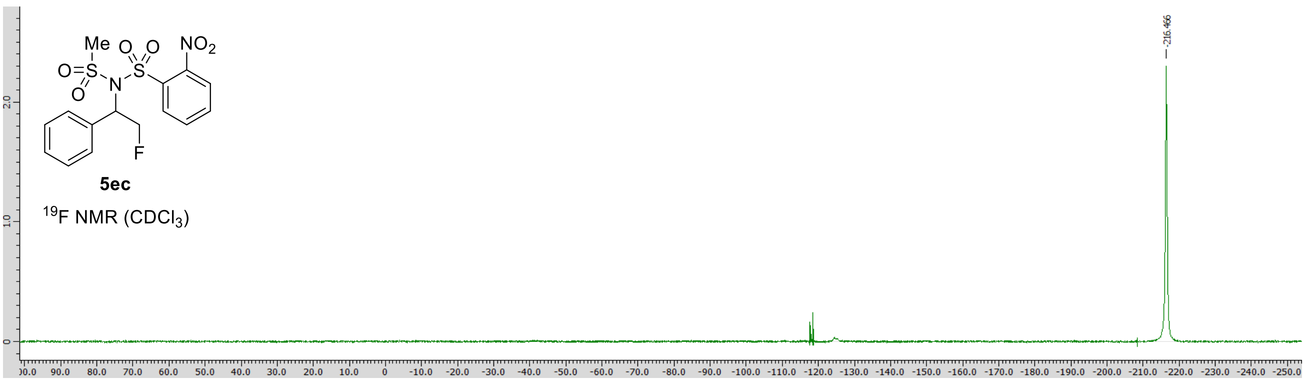

5eb
^{19}F NMR (acetone-d_6)



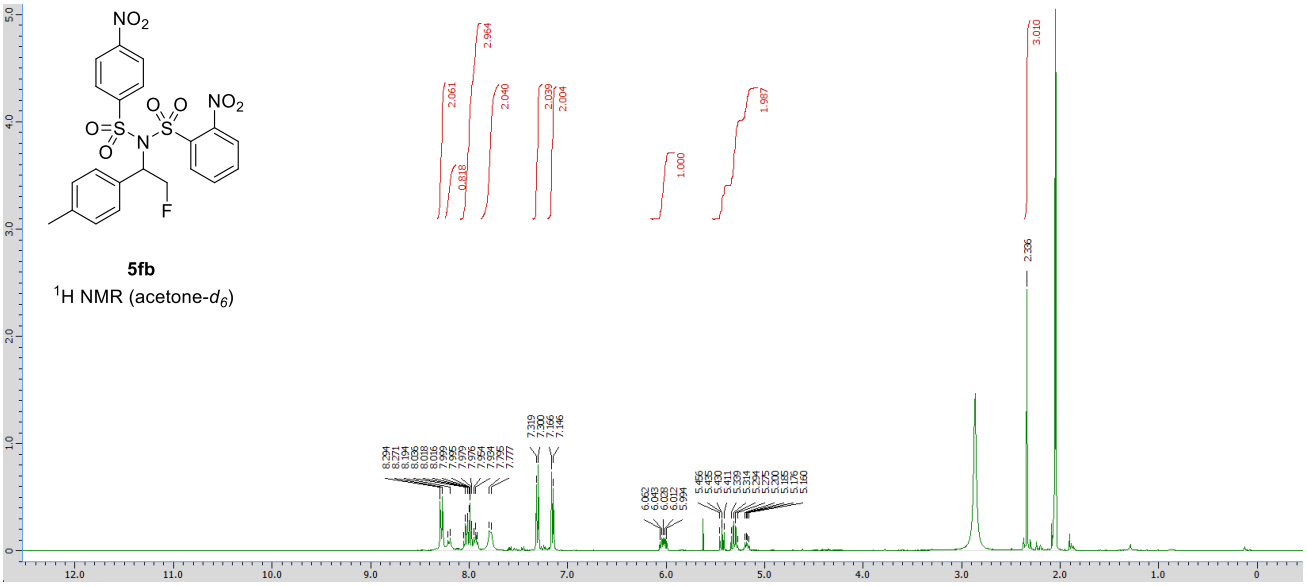
5ec
^{1}H NMR ($CDCl_3$)

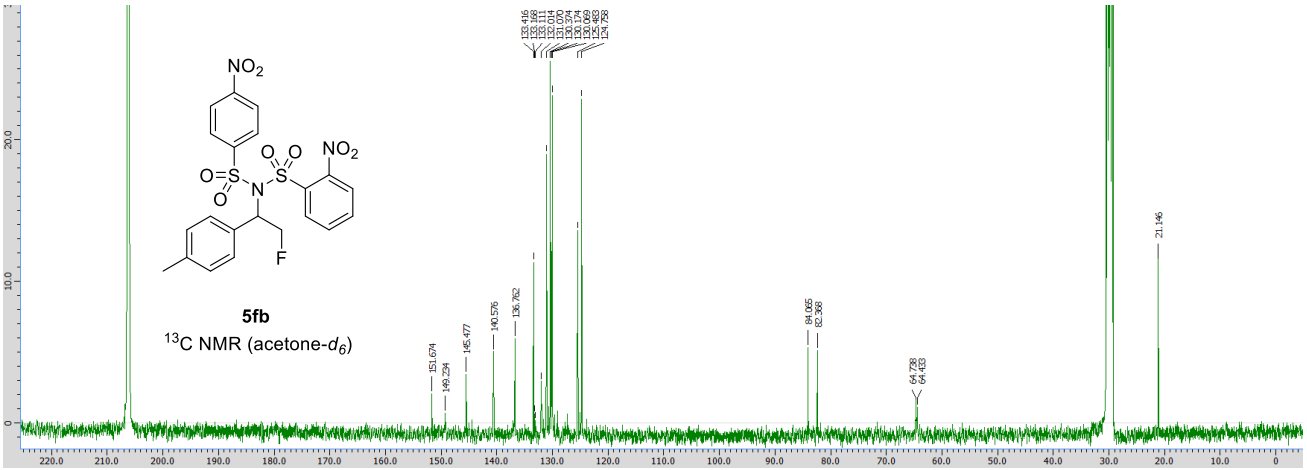


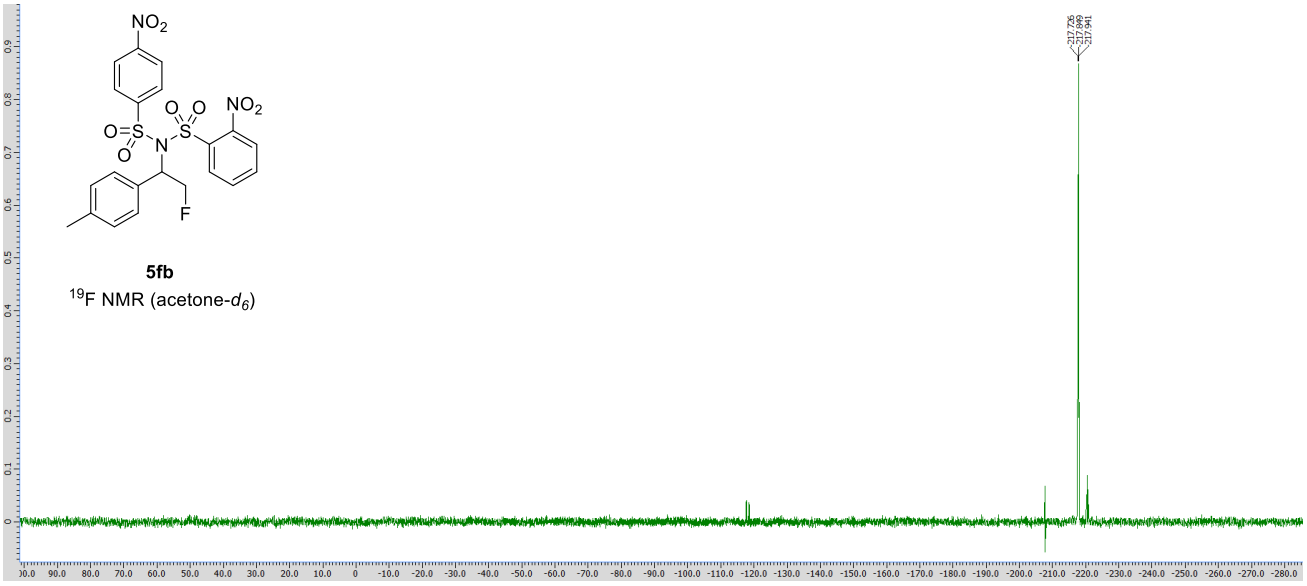
5ec
^{13}C NMR ($CDCl_3$)

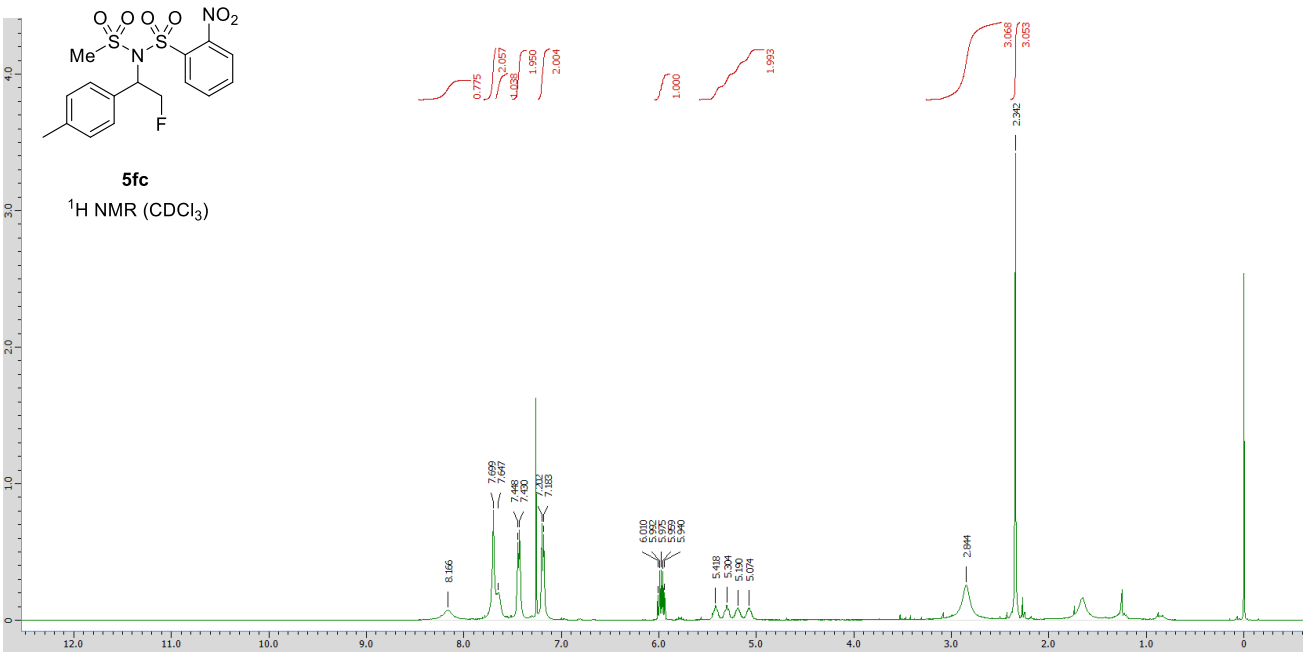


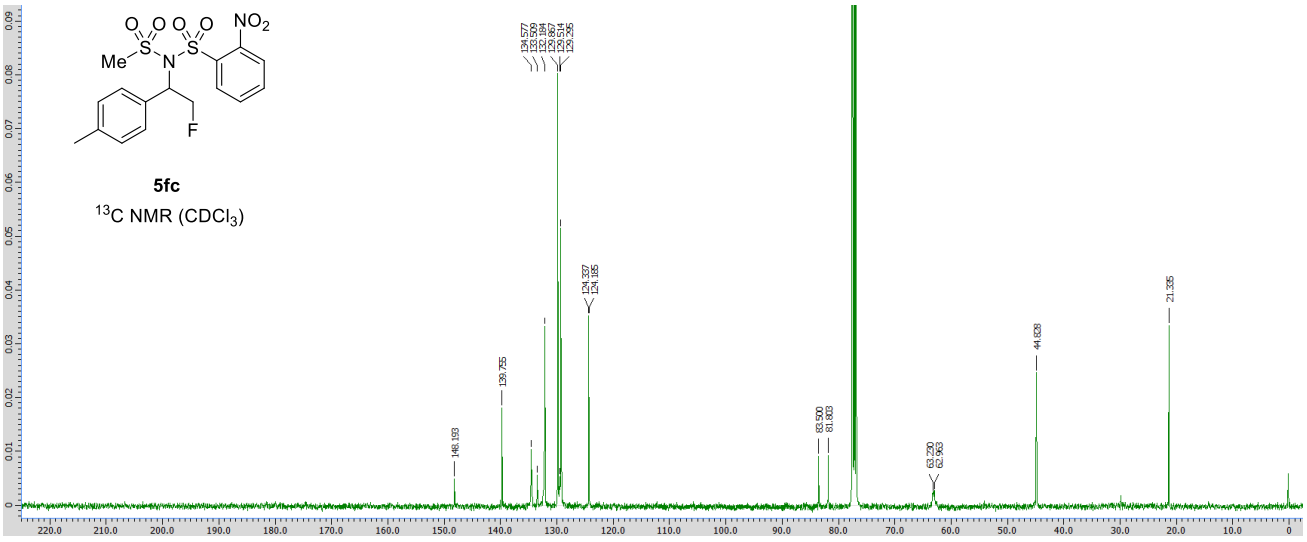
5ec
^{19}F NMR ($CDCl_3$)
-216.466

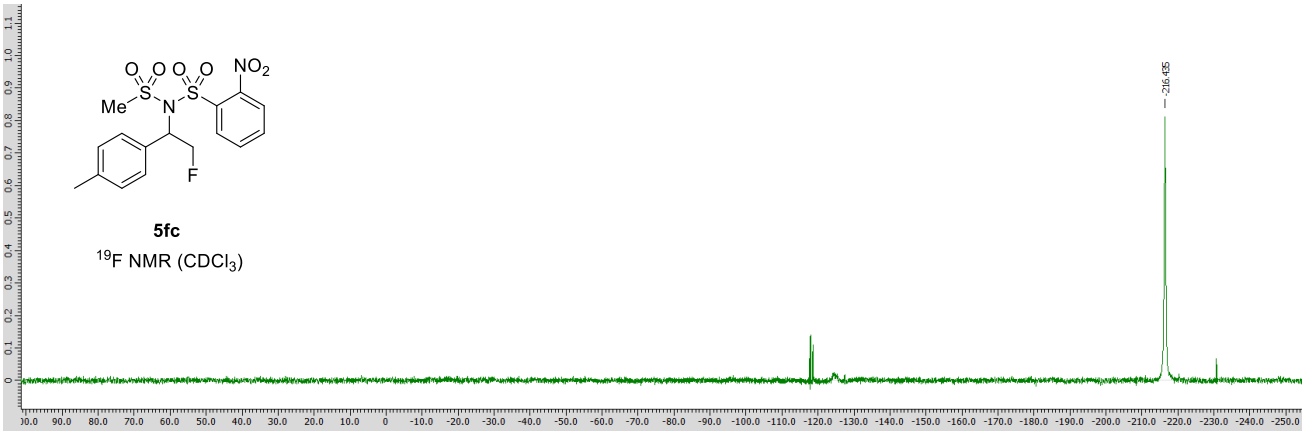

NO2
NO2
O
O
S
N
S
O
O
O
O
F
5fb
1H NMR (acetone-d6)

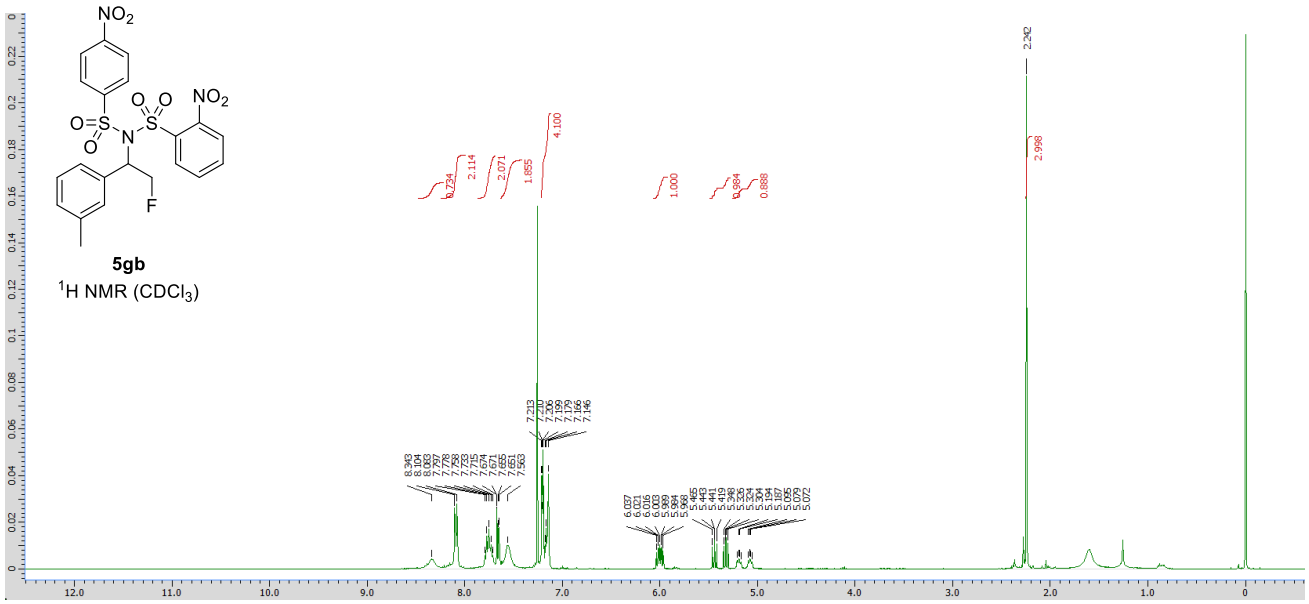

NO2
NO2
O
O
S
N
S
O
O
O
O
F
5fb
13C NMR (acetone-d6)


NO2
NO2
O
O
S
N
S
O
O
O
O
F
5fb
19F NMR (acetone-d6)


5fc
^{1}H NMR ($CDCl_3$)


5fc
^{13}C NMR ($CDCl_3$)


5fc
^{19}F NMR ($CDCl_3$)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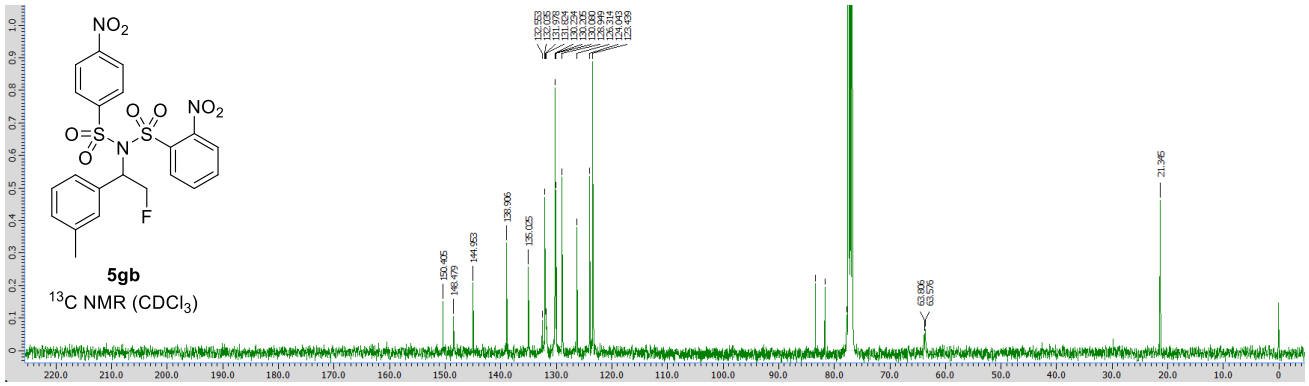
NO2
F
5gb
1H NMR (CDCl3)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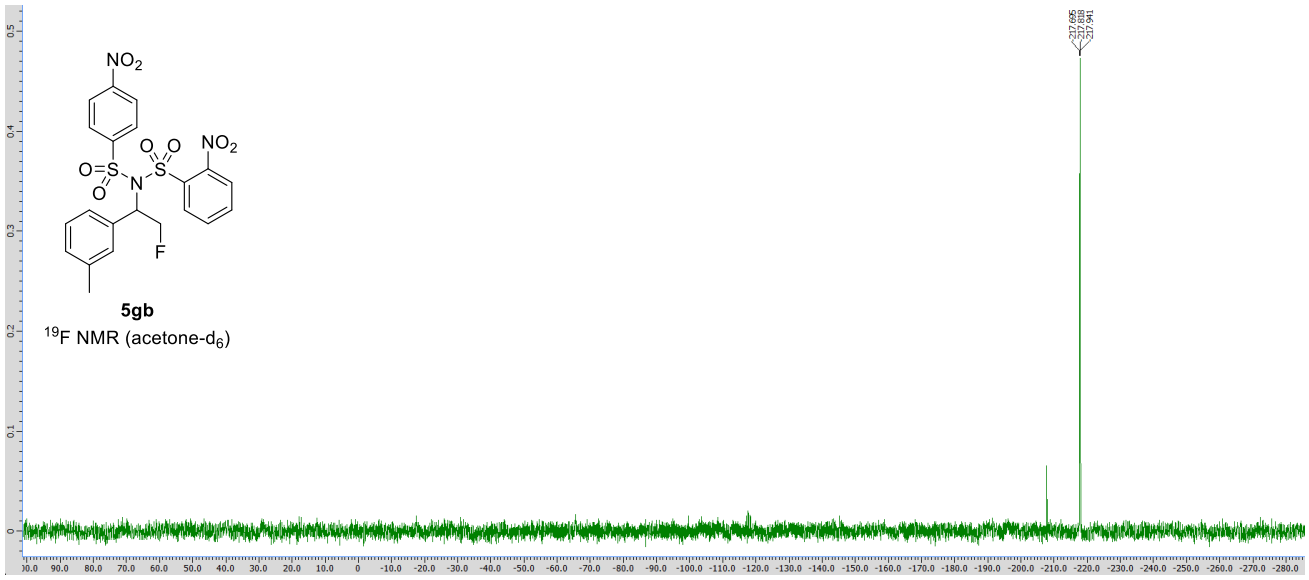
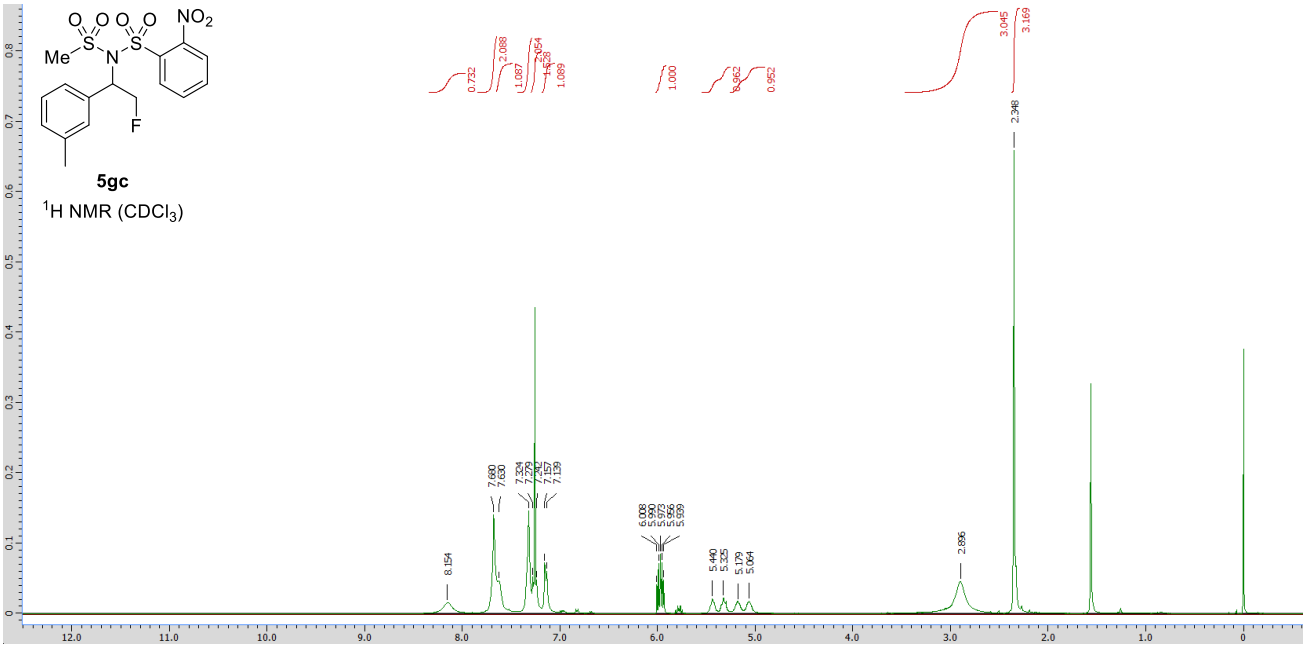
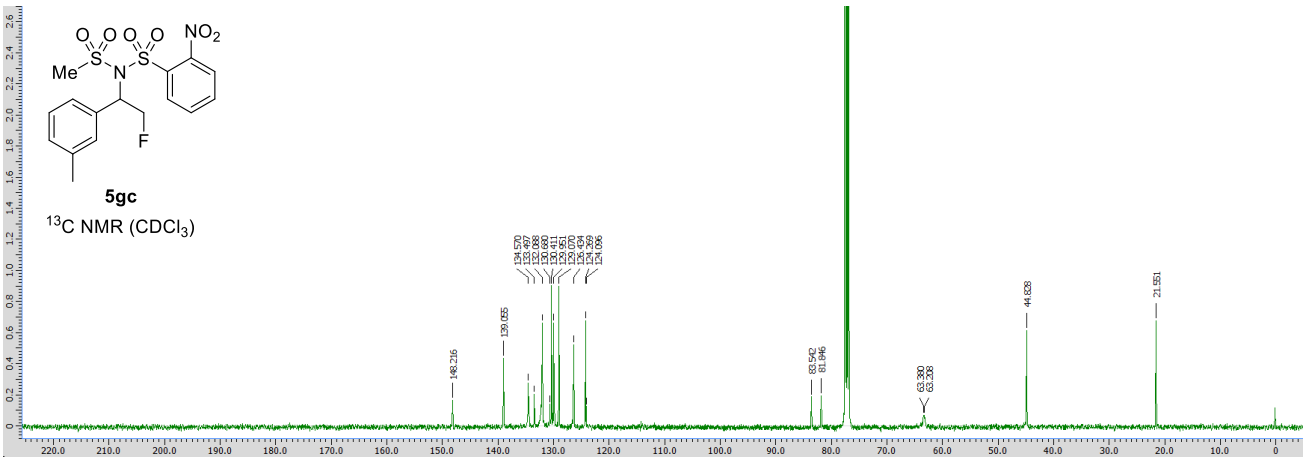
NO2
F
5gb
13C NMR (CDCl3)


NO2
NO2
F
5gb
19F NMR (acetone-d6)


Me
NO2
F
5gc
1H NMR (CDCl3)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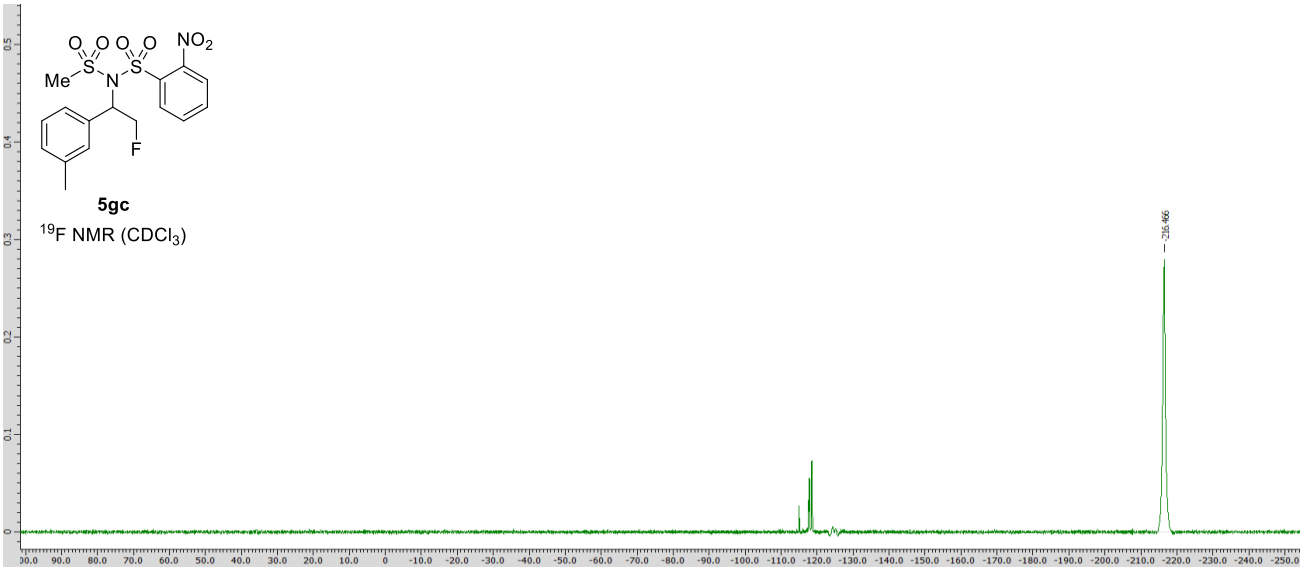
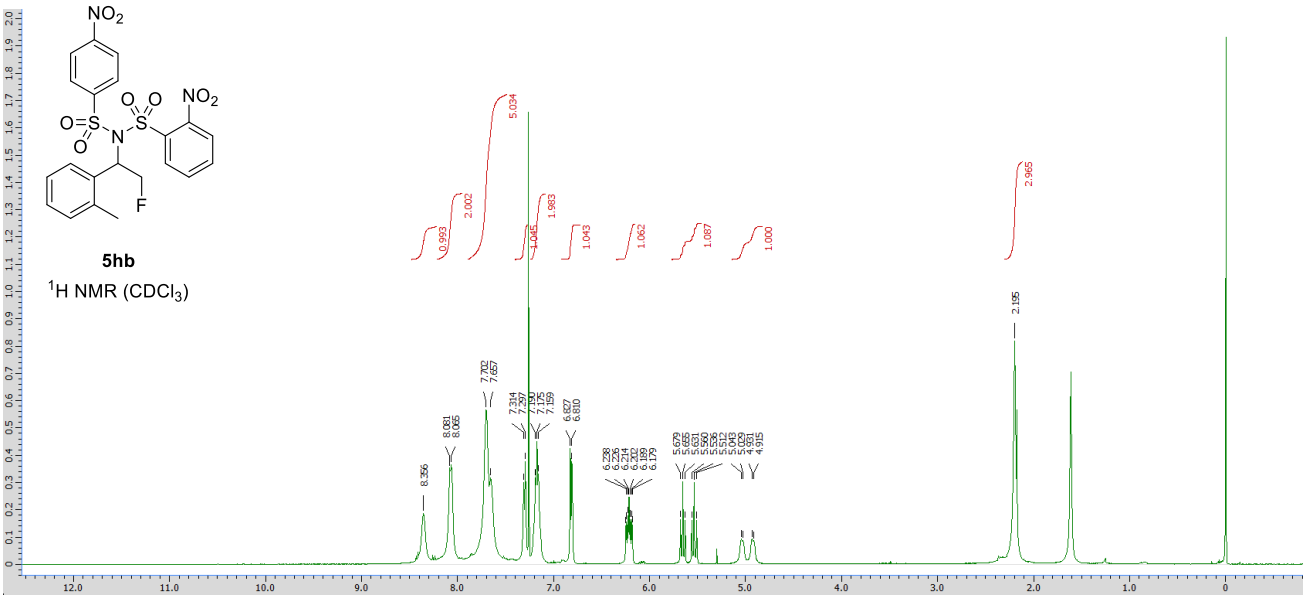
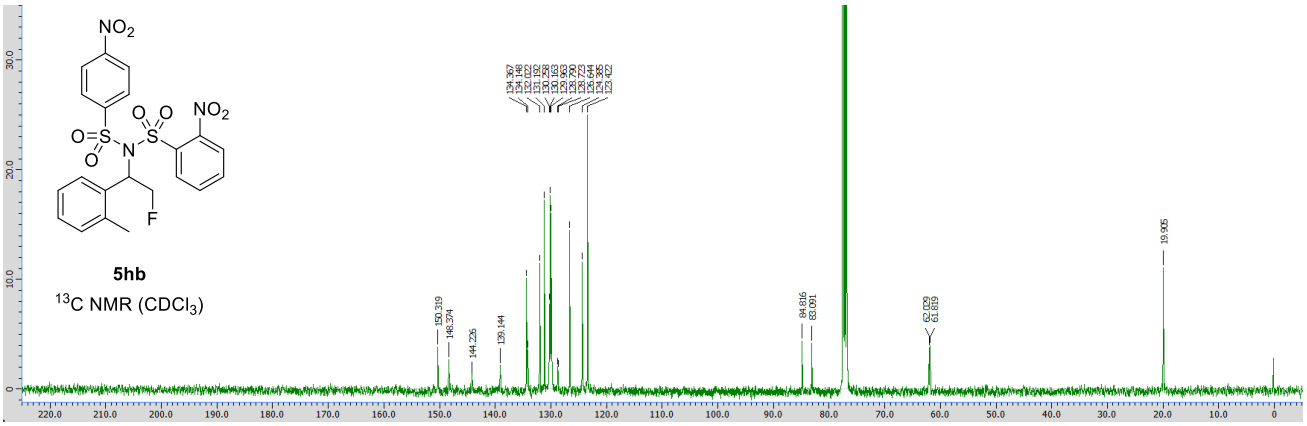
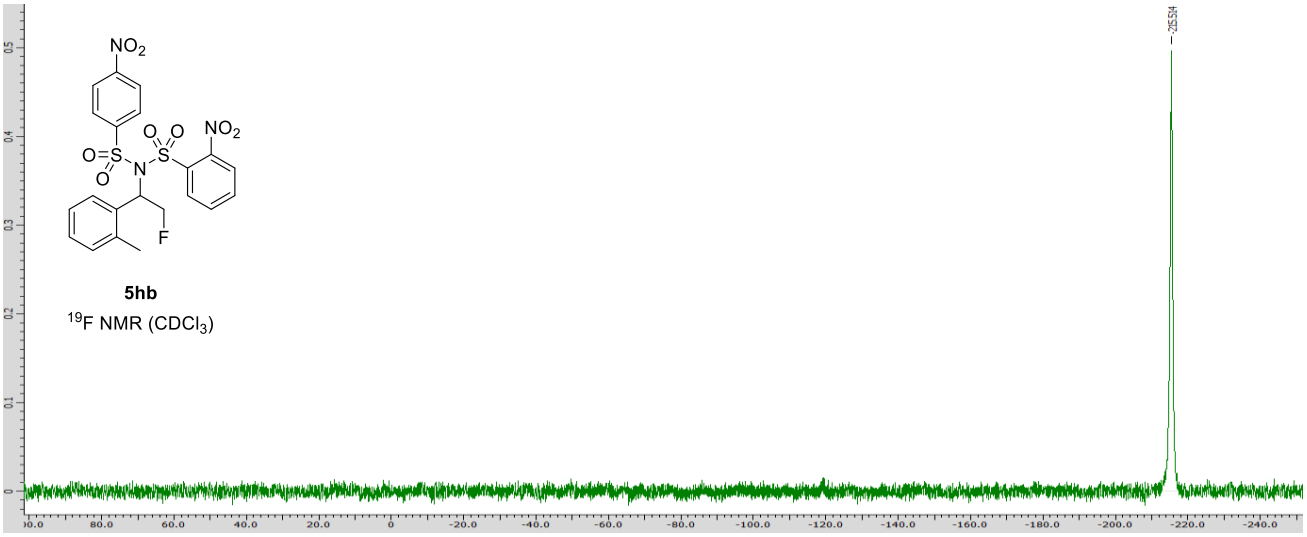
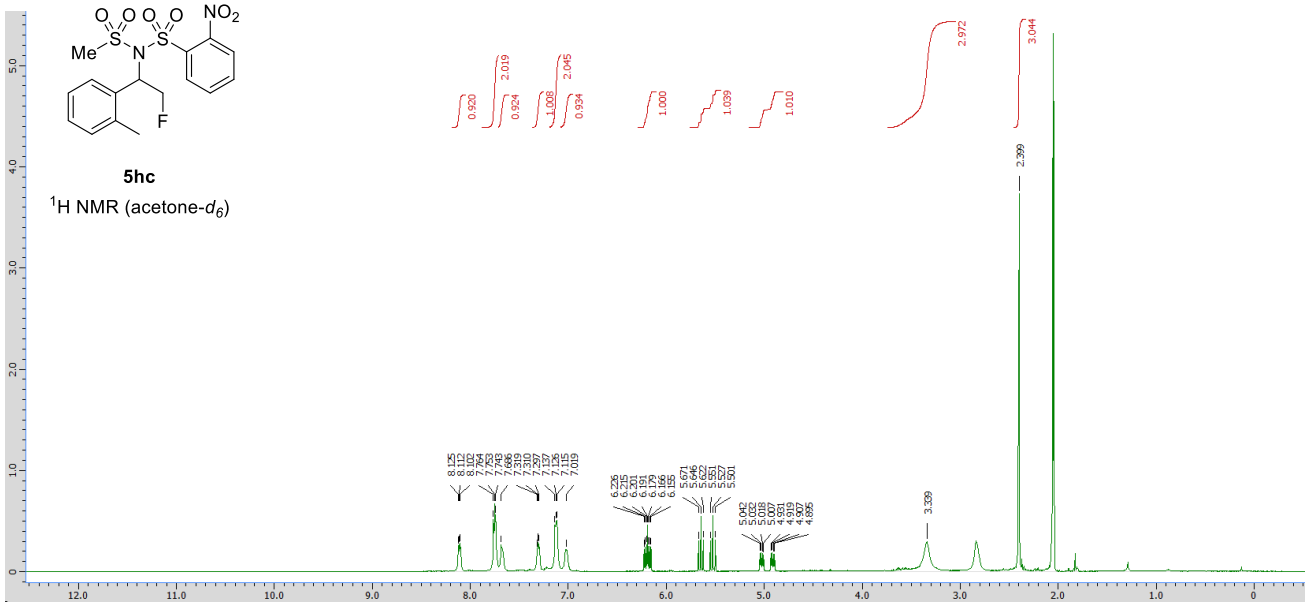
NO2
F
5gc
13C NMR (CDCl3)

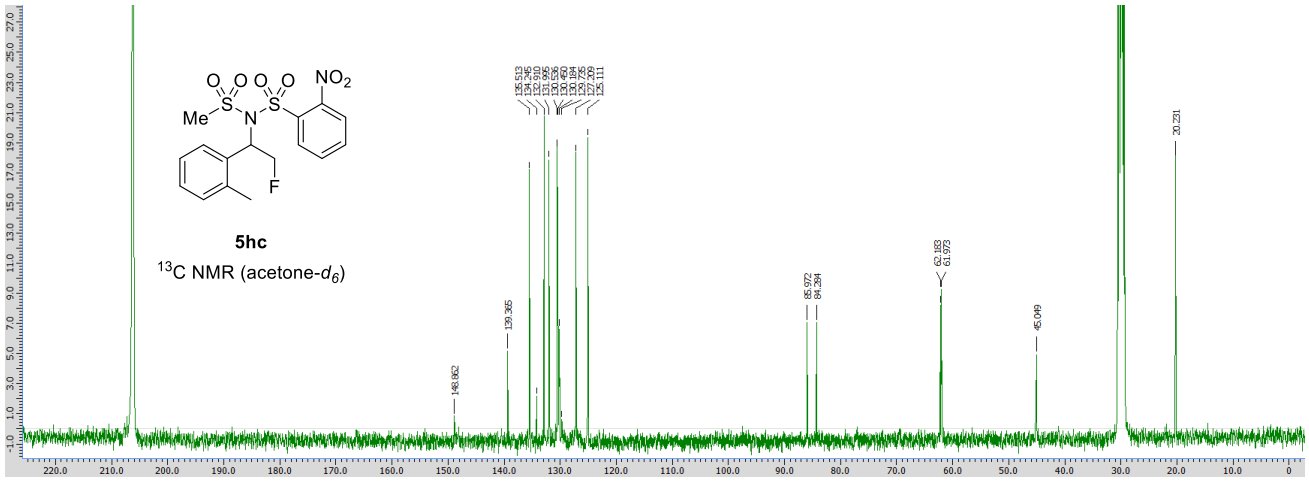

Me
NO2
F
5gc
19F NMR (CDCl3)


NO2
NO2
F
5hb
1H NMR (CDCl3)


NO2
NO2
F
5hb
13C NMR (CDCl3)


NO2
NO2
F
5hb
19F NMR (CDCl3)


Me
N
S
O
NO2
F
5hc
1H NMR (acetone-d6)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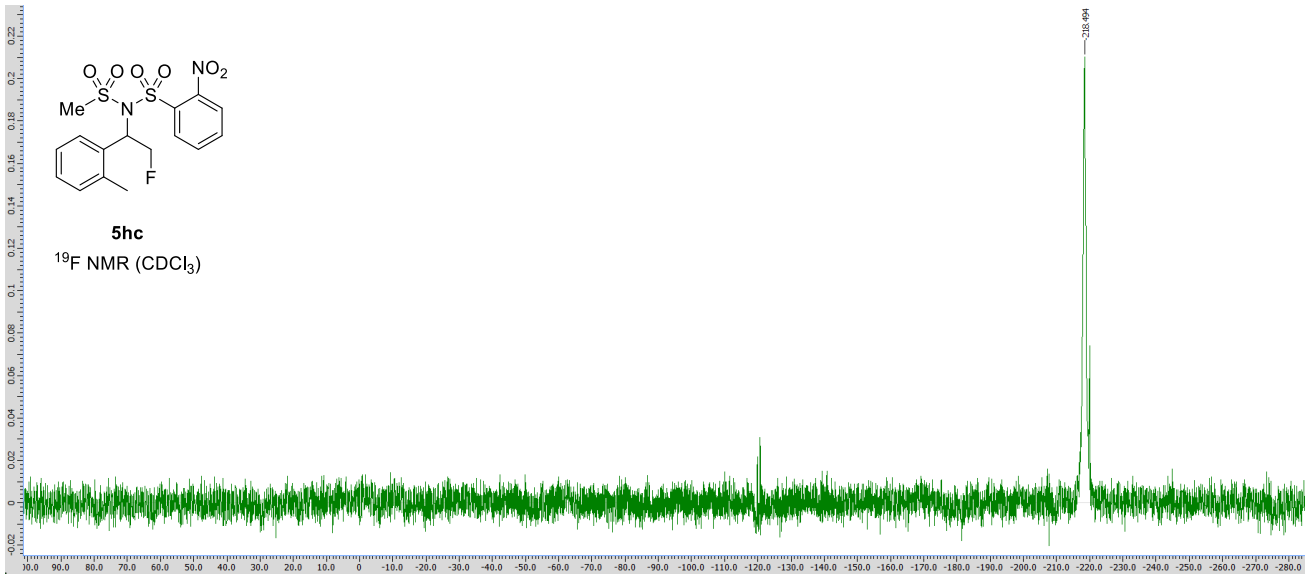
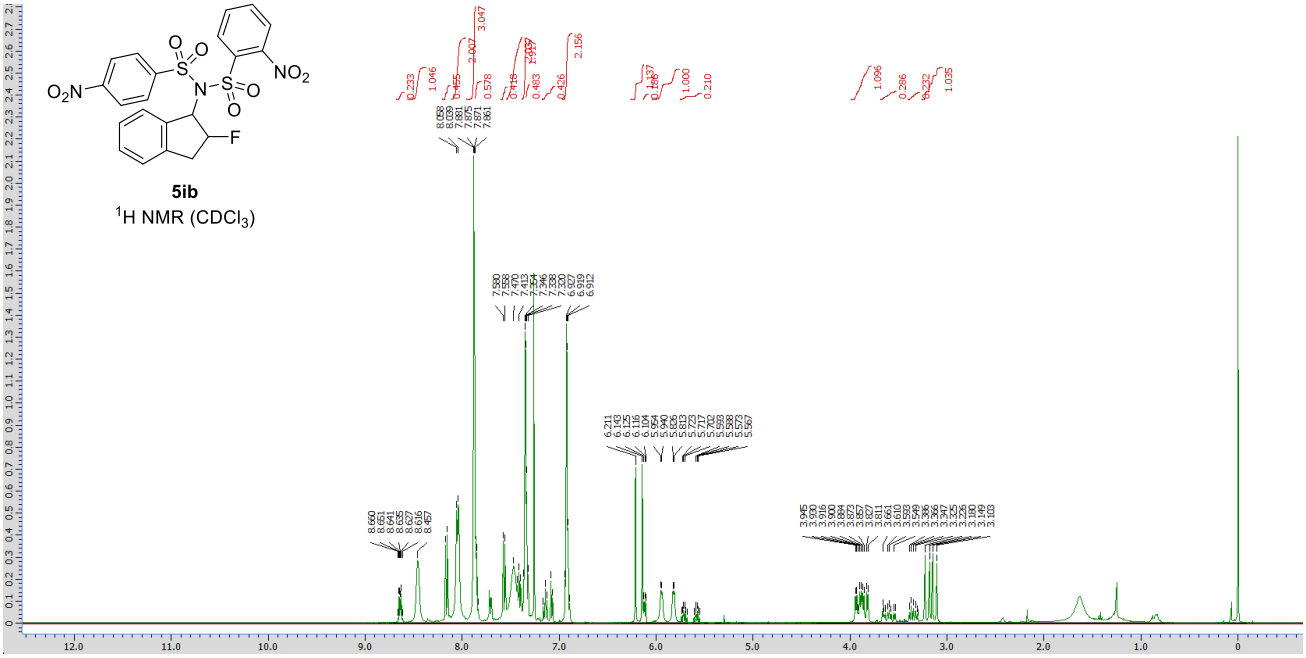
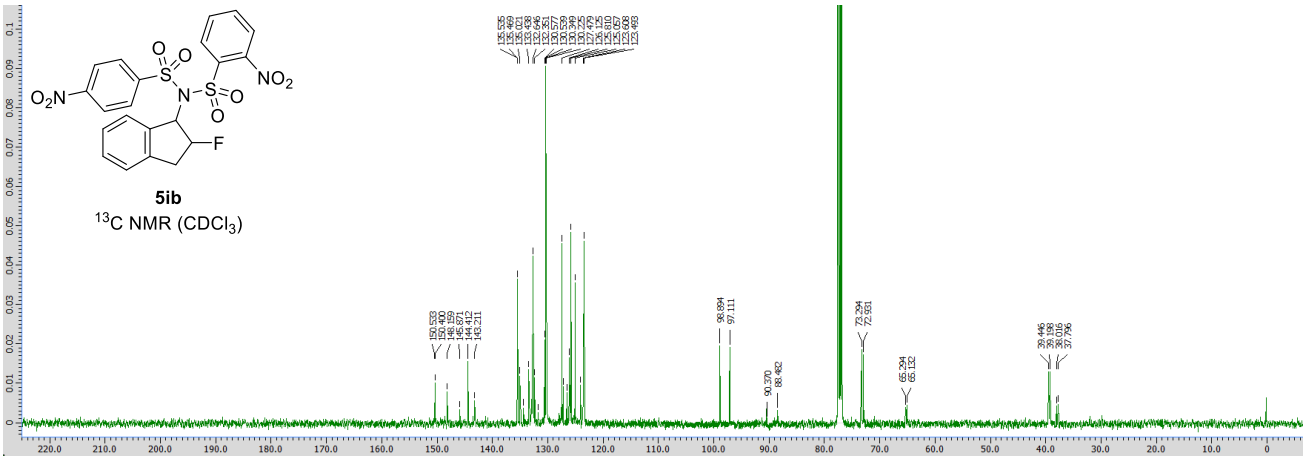
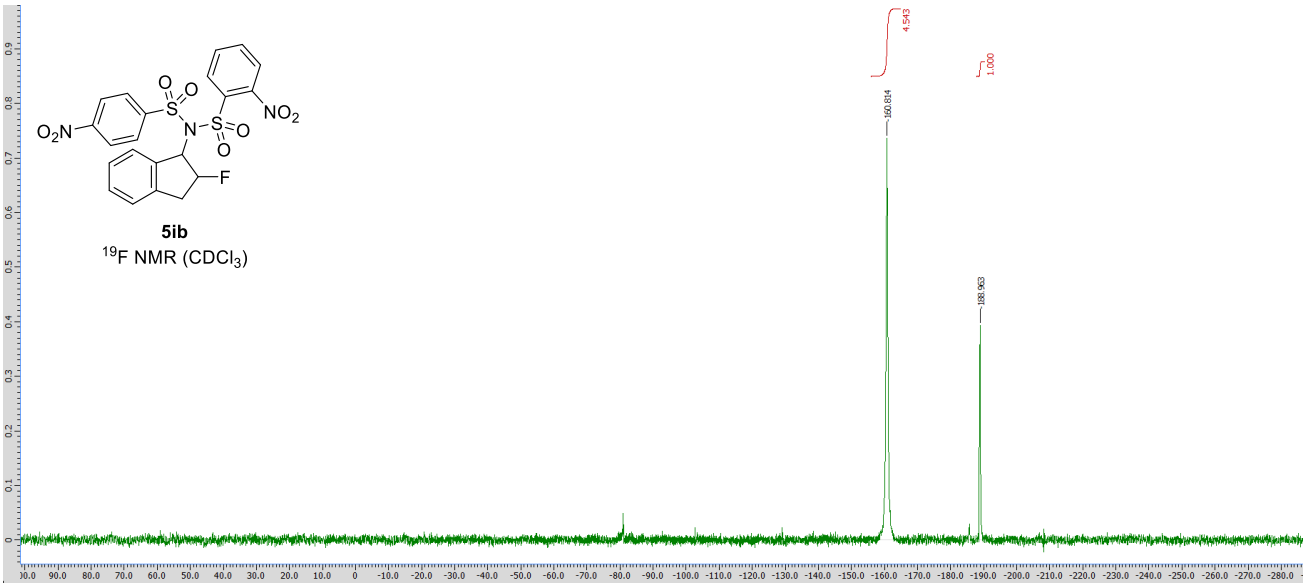
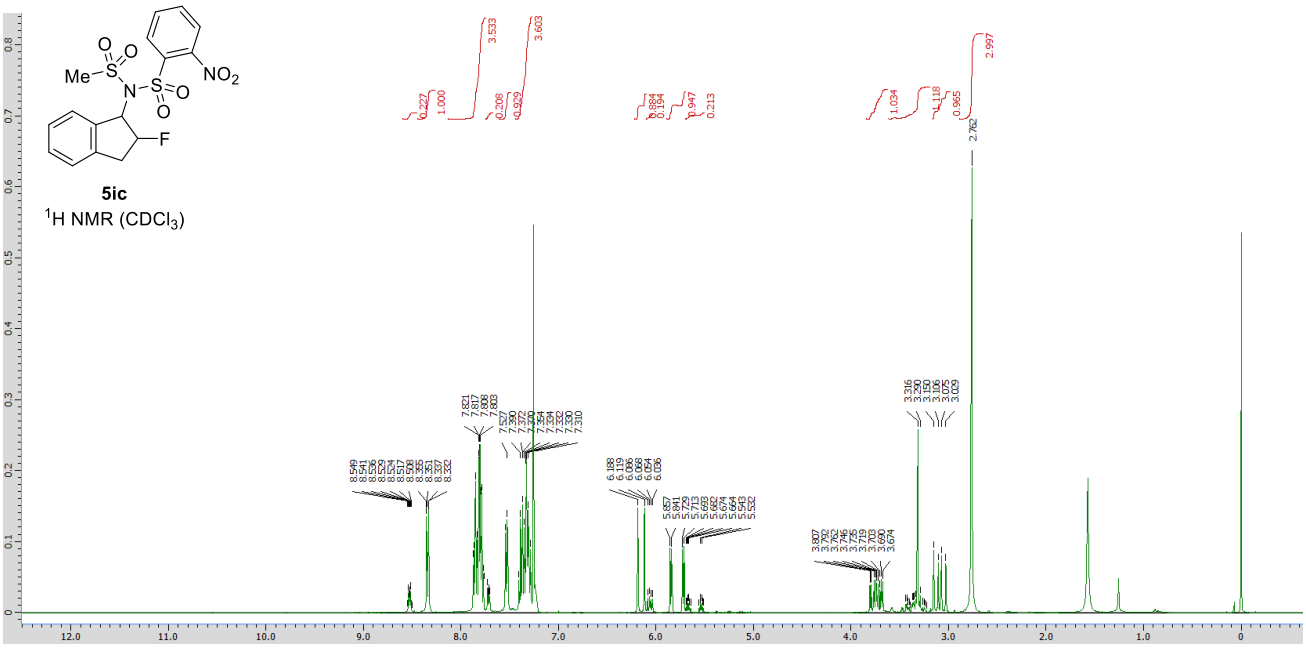
N
S
O
NO2
F
5hc
13C NMR (acetone-d6)

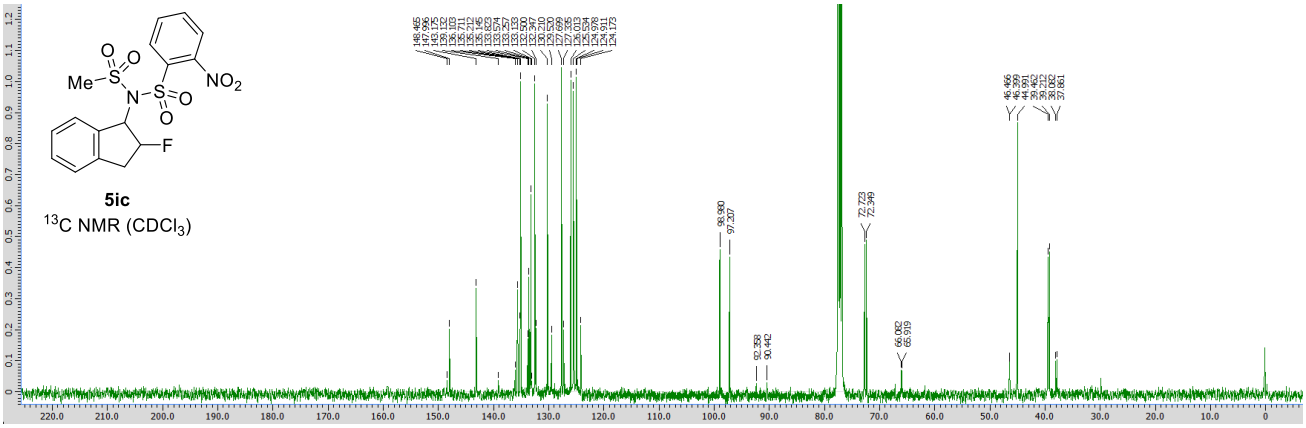

Me
N
S
O
NO2
F
5hc
19F NMR (CDCl3)

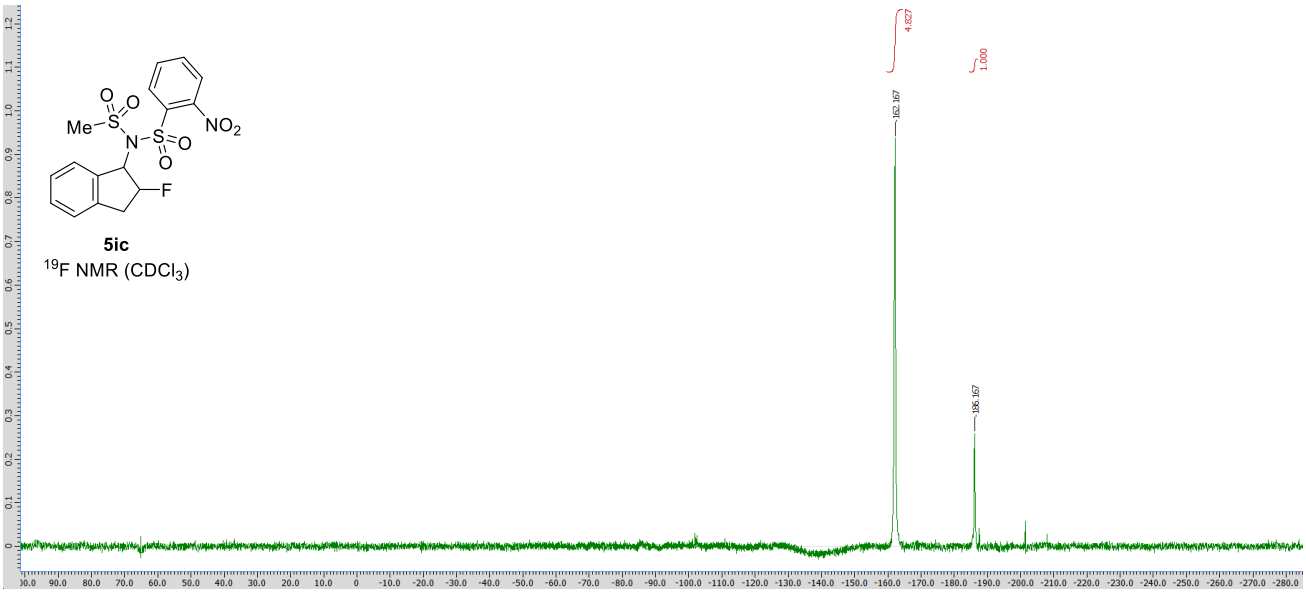

5ib
^{1}H NMR ($CDCl_3$)

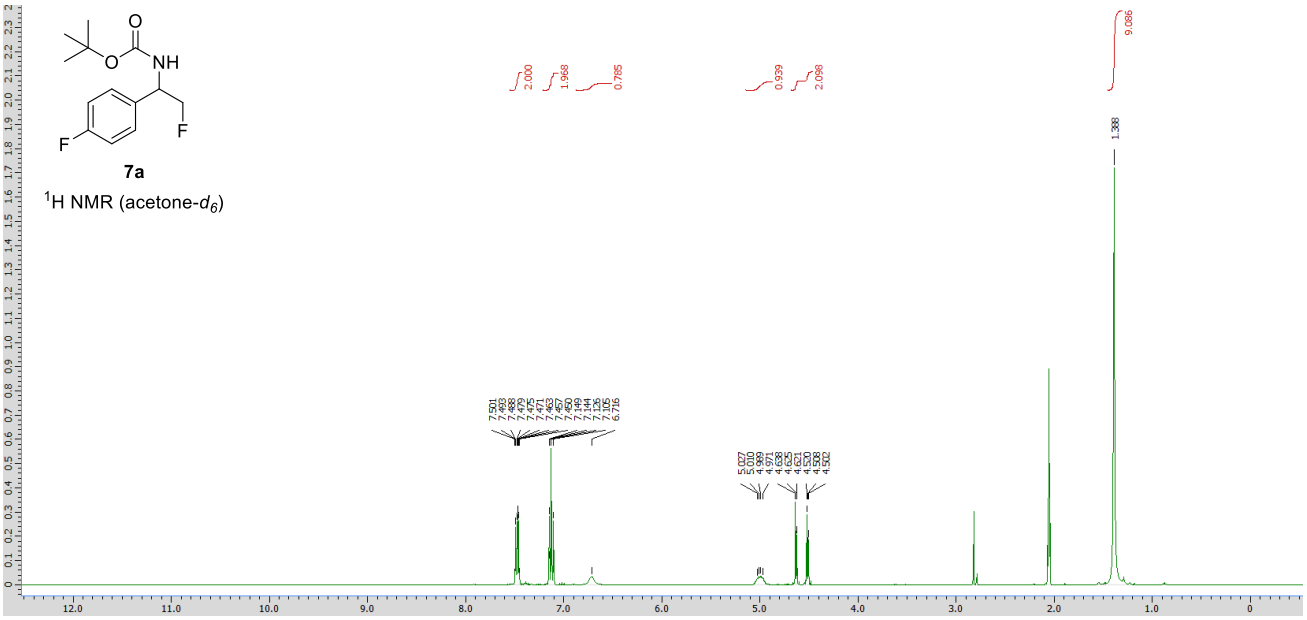

5ib
^{13}C NMR ($CDCl_3$)

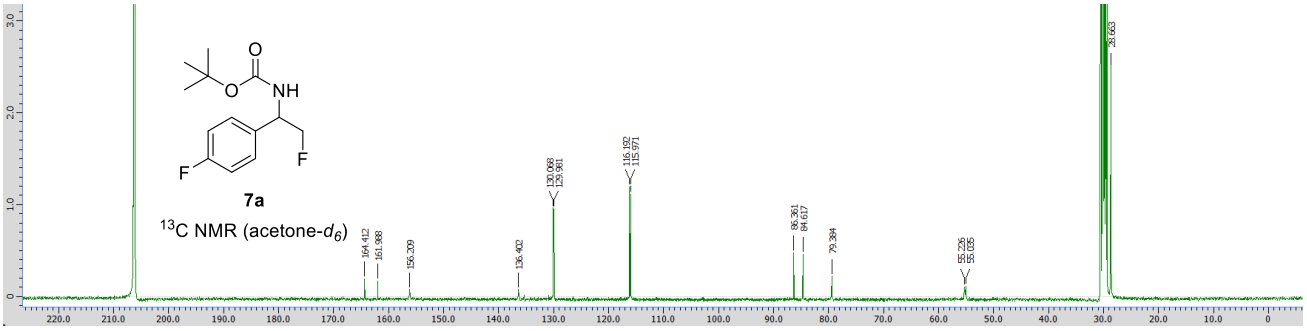

5ib
^{19}F NMR ($CDCl_3$)

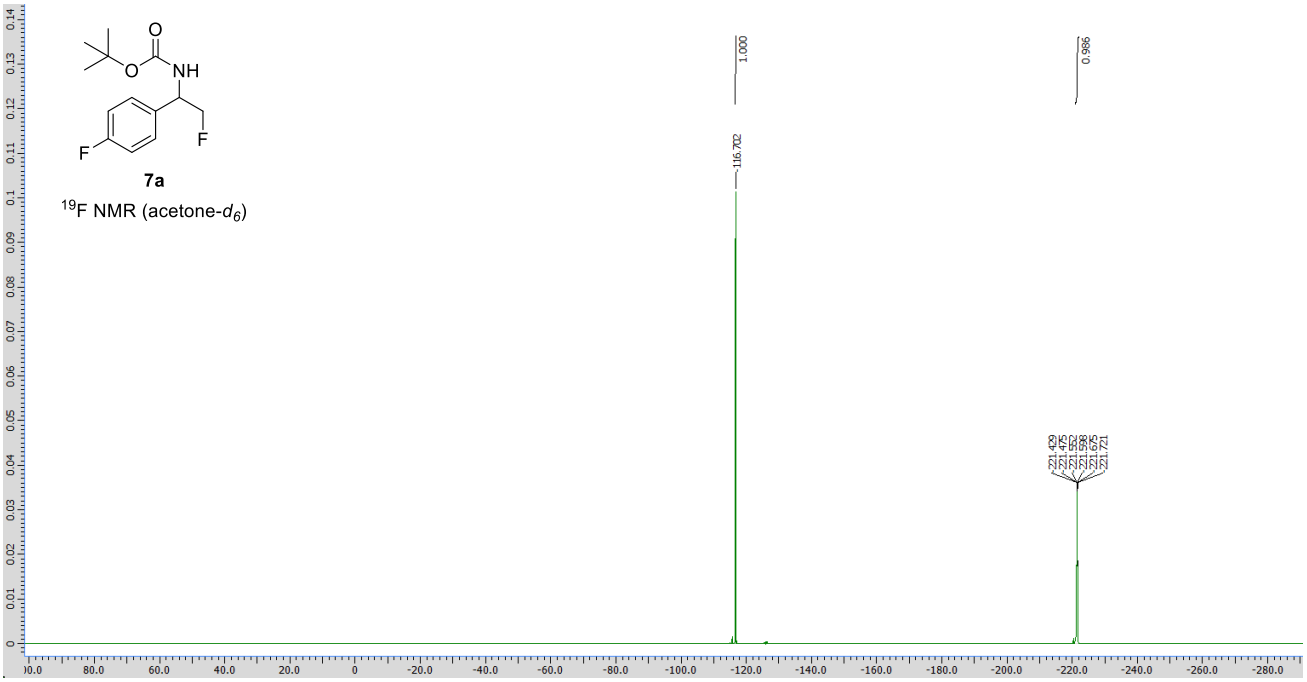

5ic
1H NMR (CDCl3)

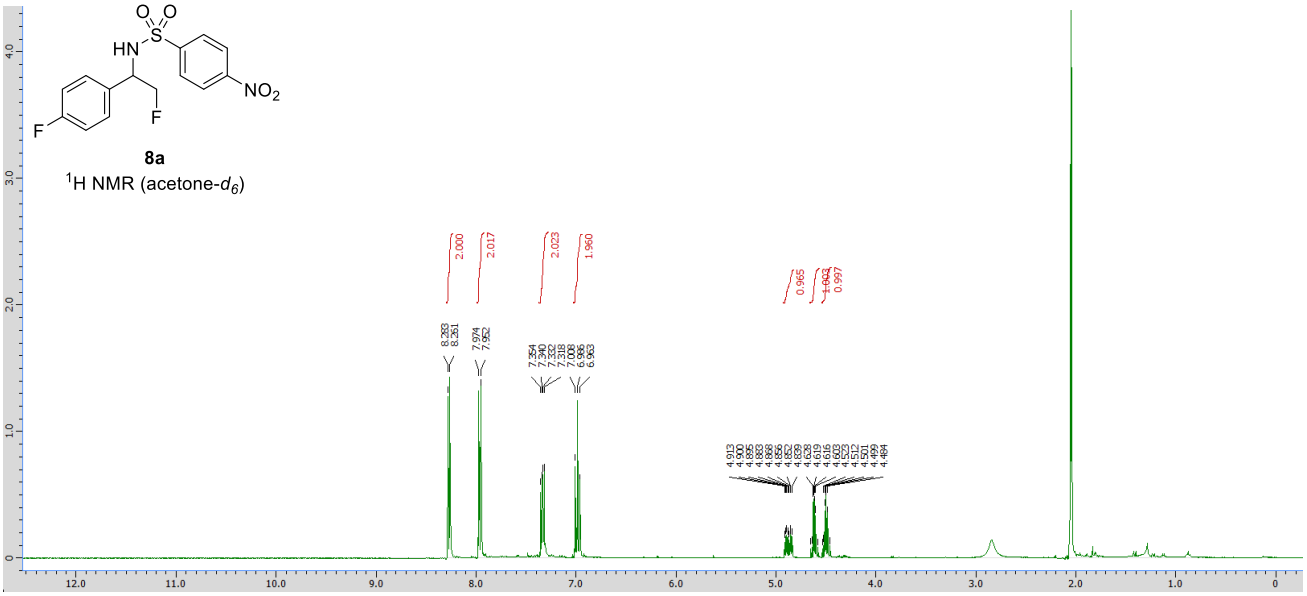

5ic
13C NMR (CDCl3)

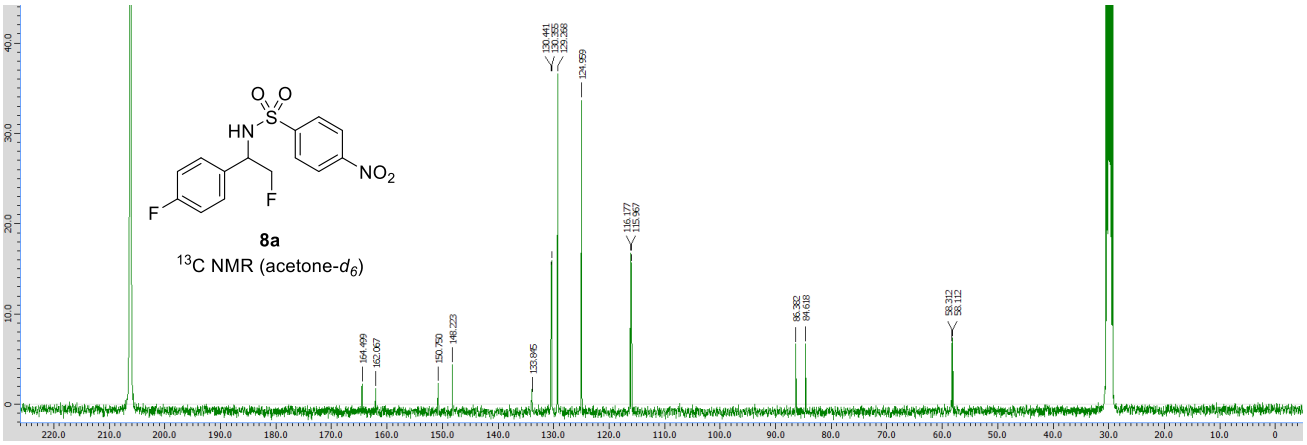

5ic
19F NMR (CDCl3)

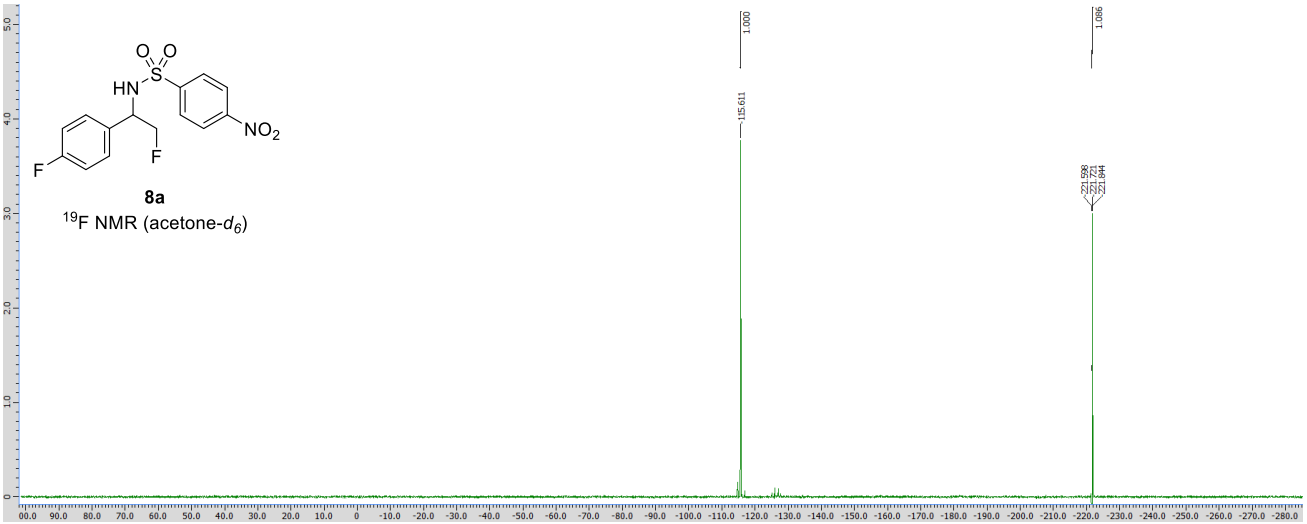

7a
1H NMR (acetone-d6)

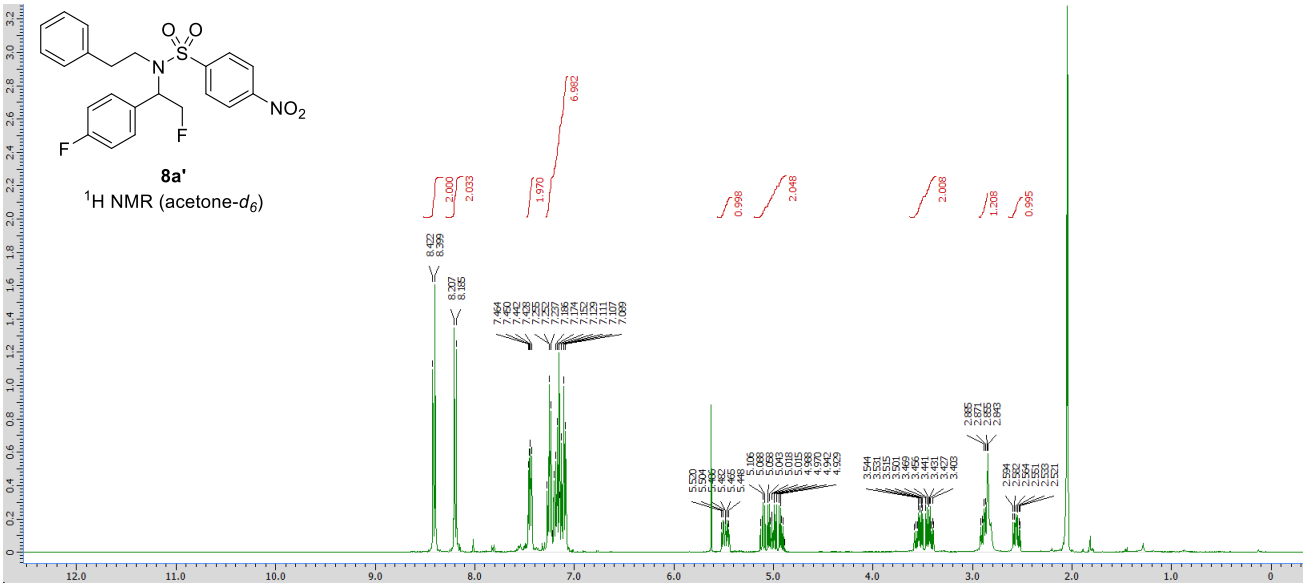

7a
13C NMR (acetone-d6)

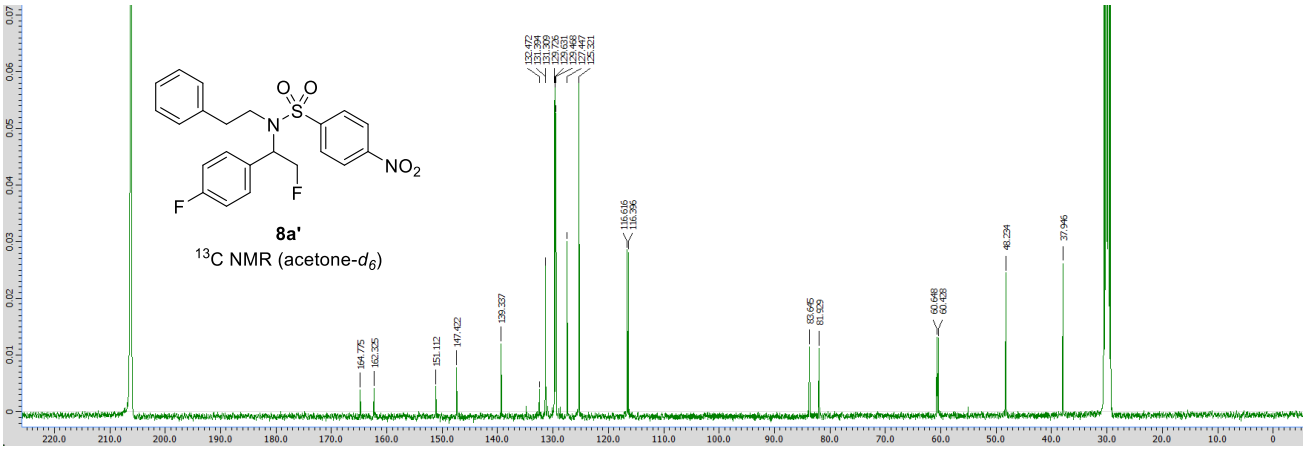

7a
19F NMR (acetone-d6)

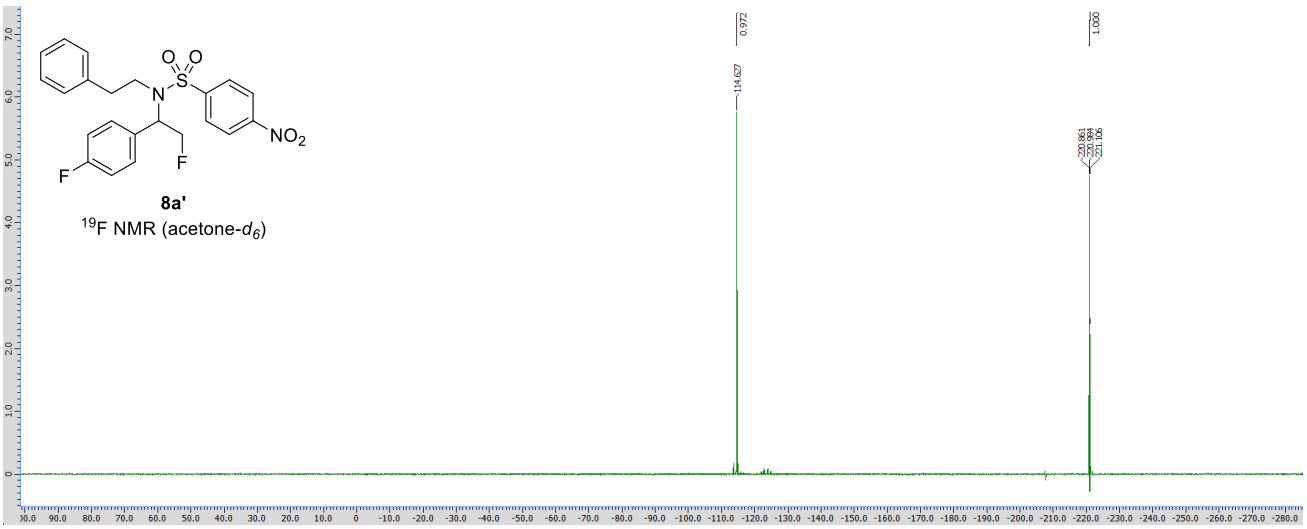

8a
^{1}H NMR (acetone-d_6)

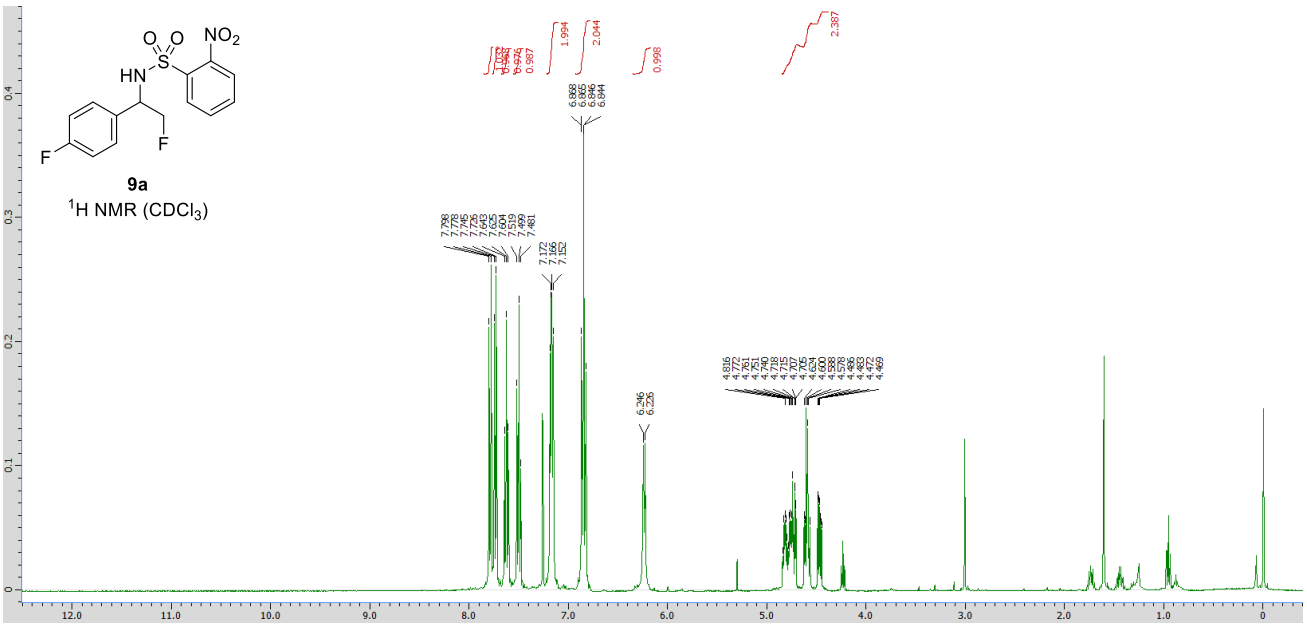

8a
^{13}C NMR (acetone-d_6)

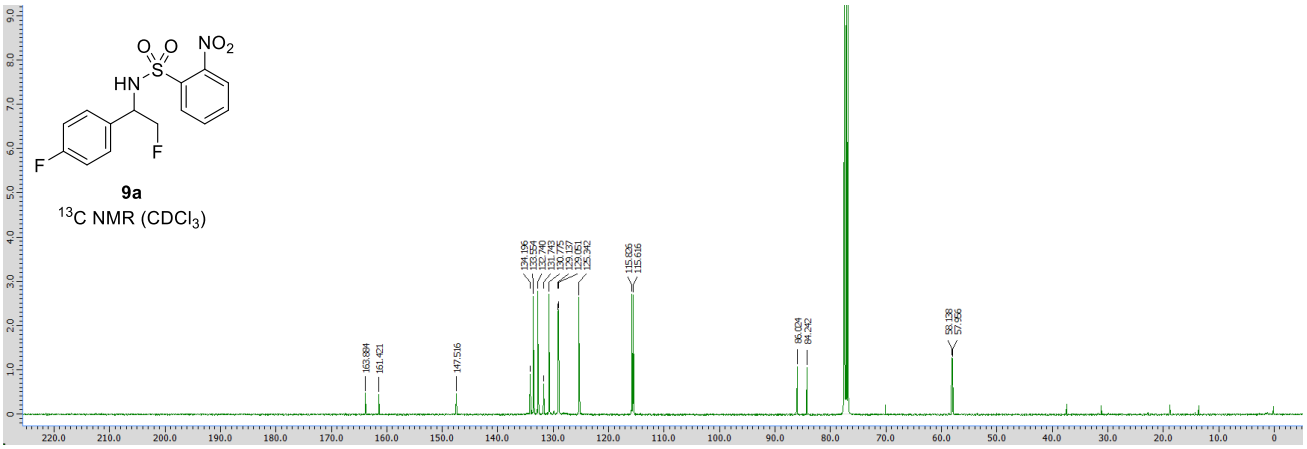

8a
^{19}F NMR (acetone-d_6)

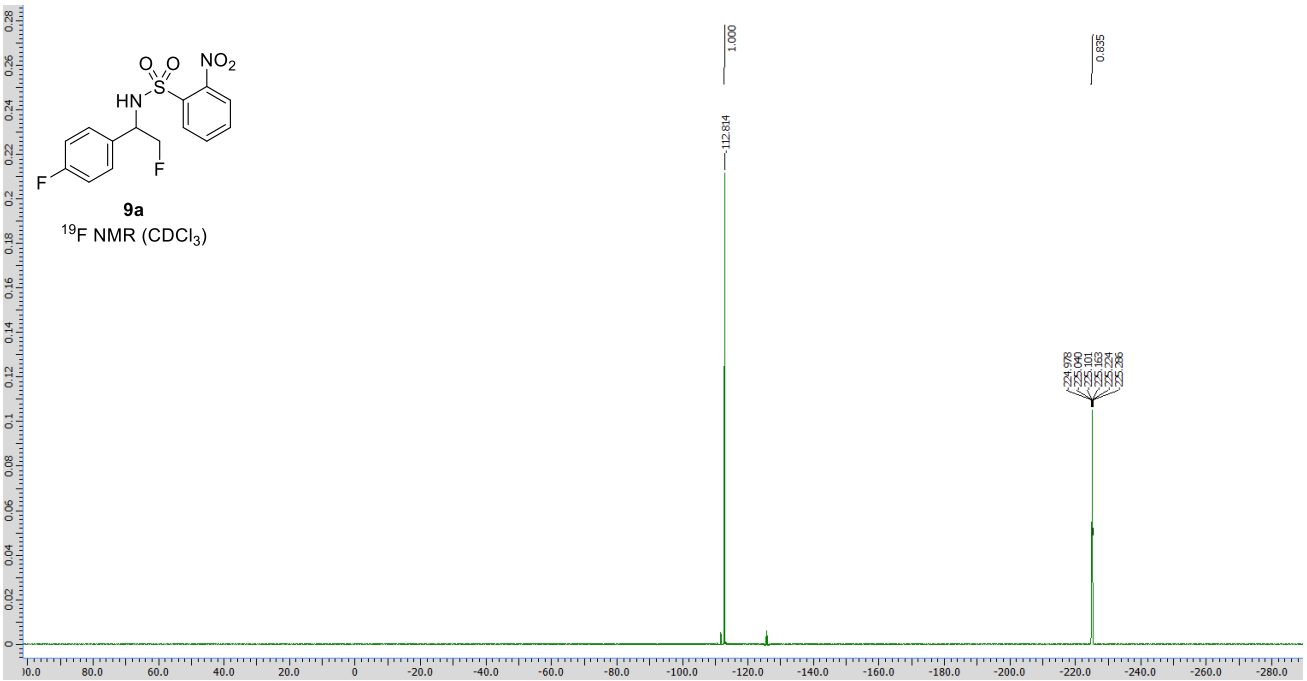

8a'
1H NMR (acetone-d6)

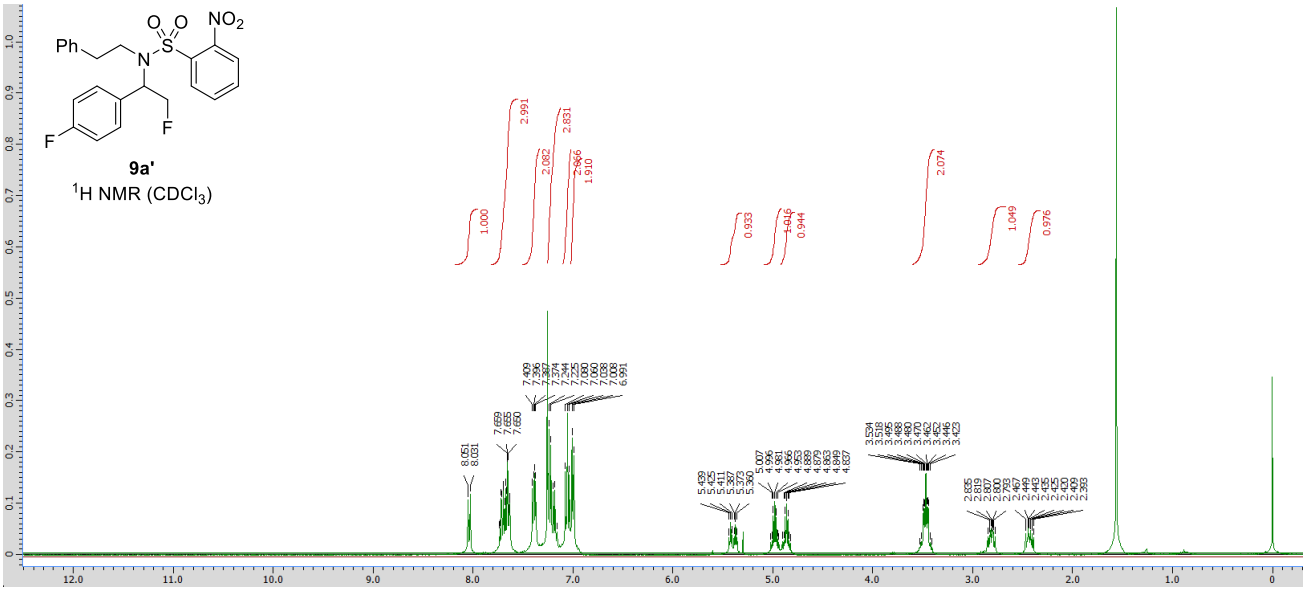

8a'
13C NMR (acetone-d6)

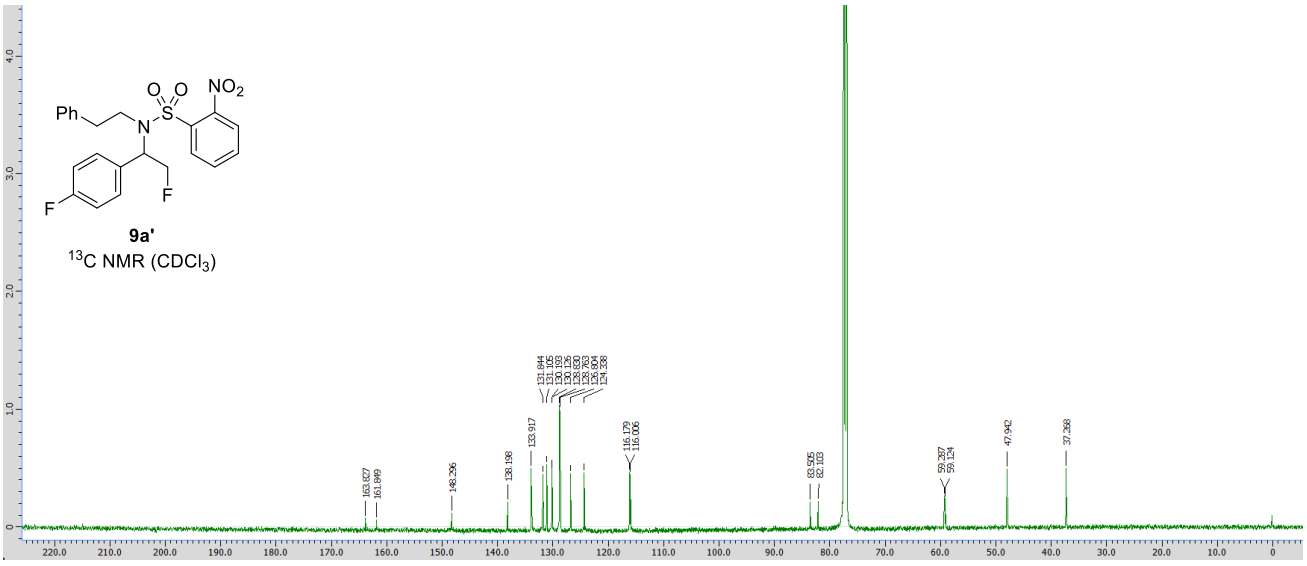

8a'
19F NMR (acetone-d6)

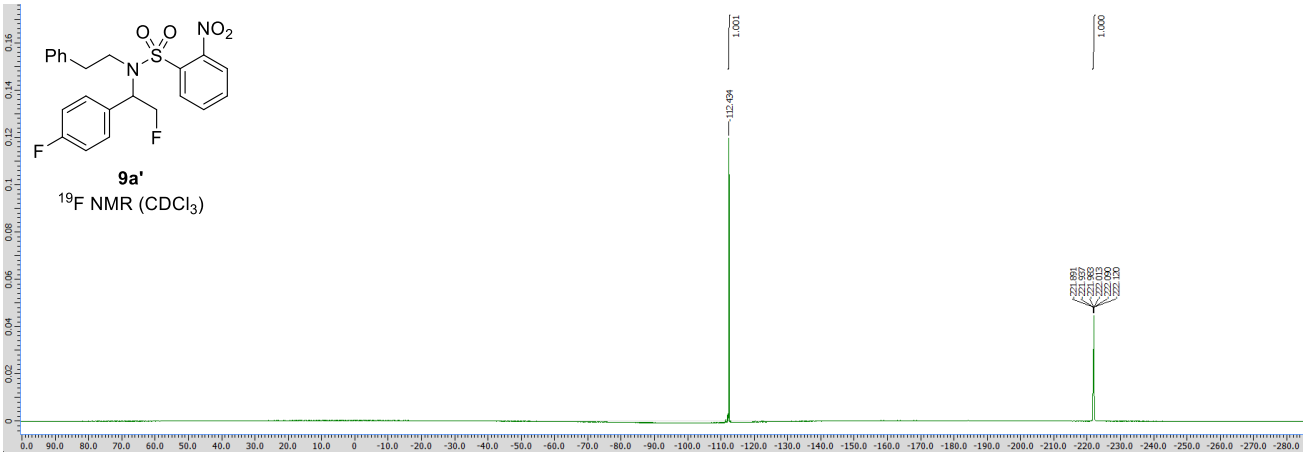

9a
^{1}H NMR ($CDCl_3$)

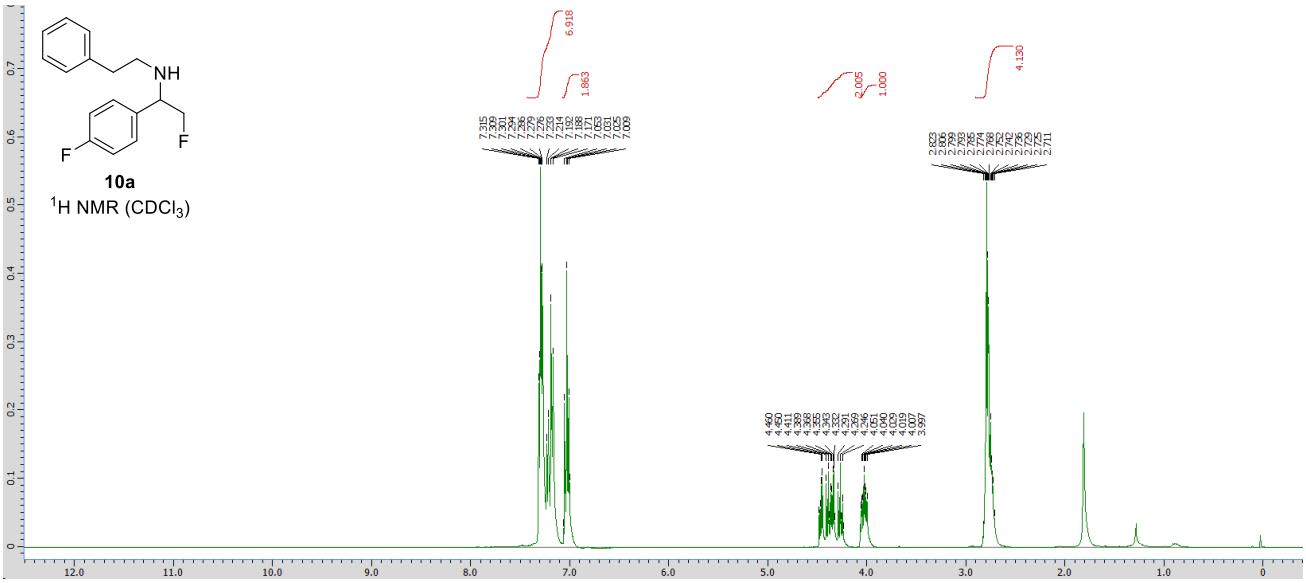

9a
^{13}C NMR ($CDCl_3$)

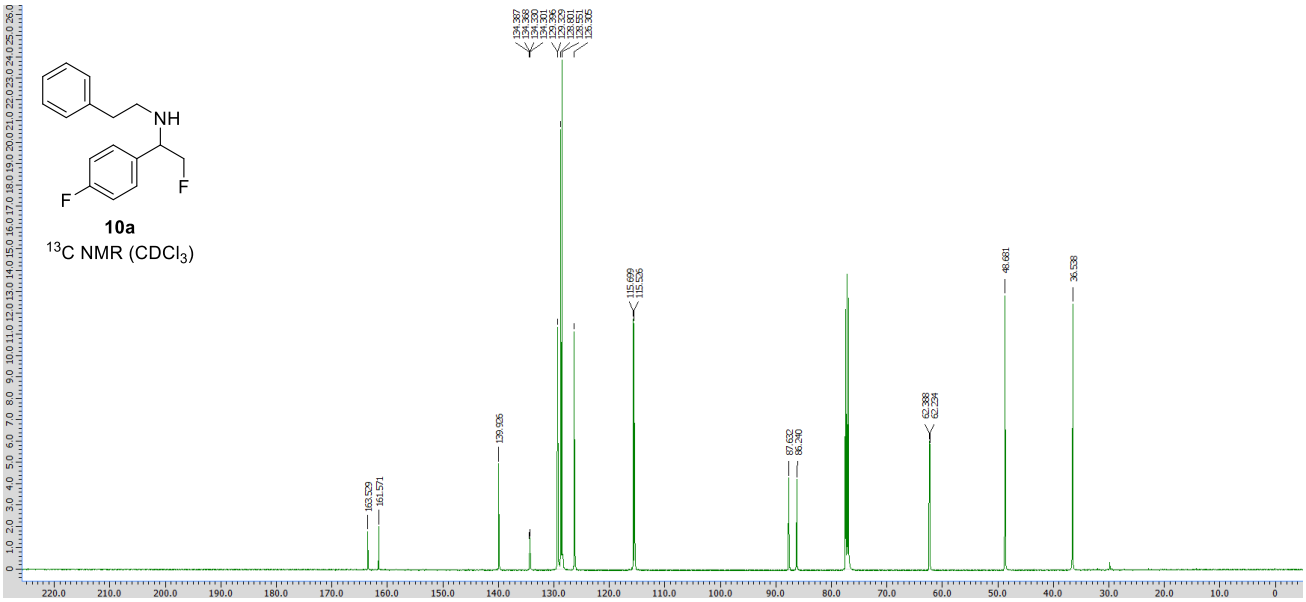

9a
^{19}F NMR ($CDCl_3$)

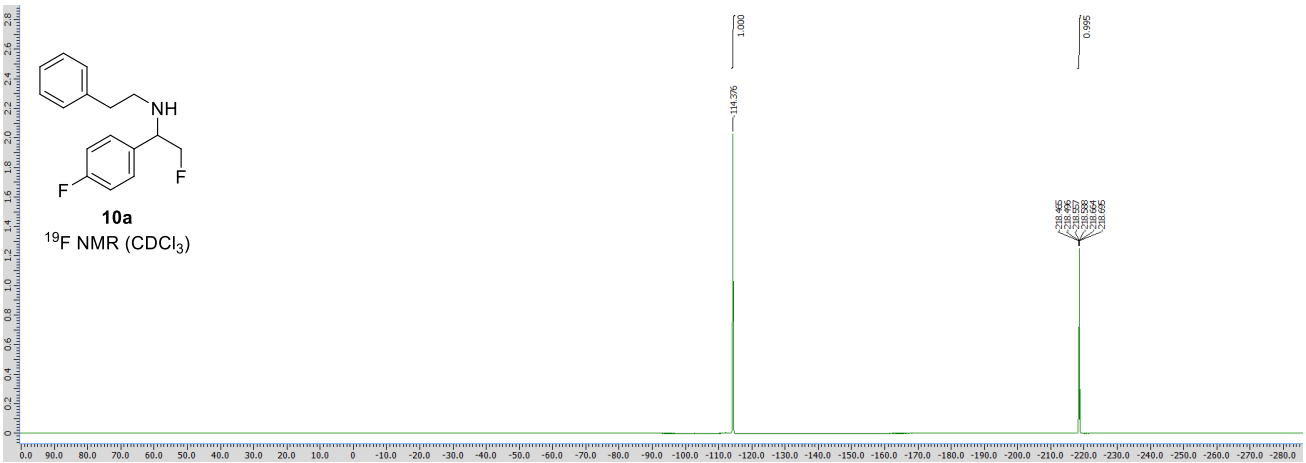

Ph
N
O
O
S
NO2
F
F
9a'
1H NMR (CDCl3)

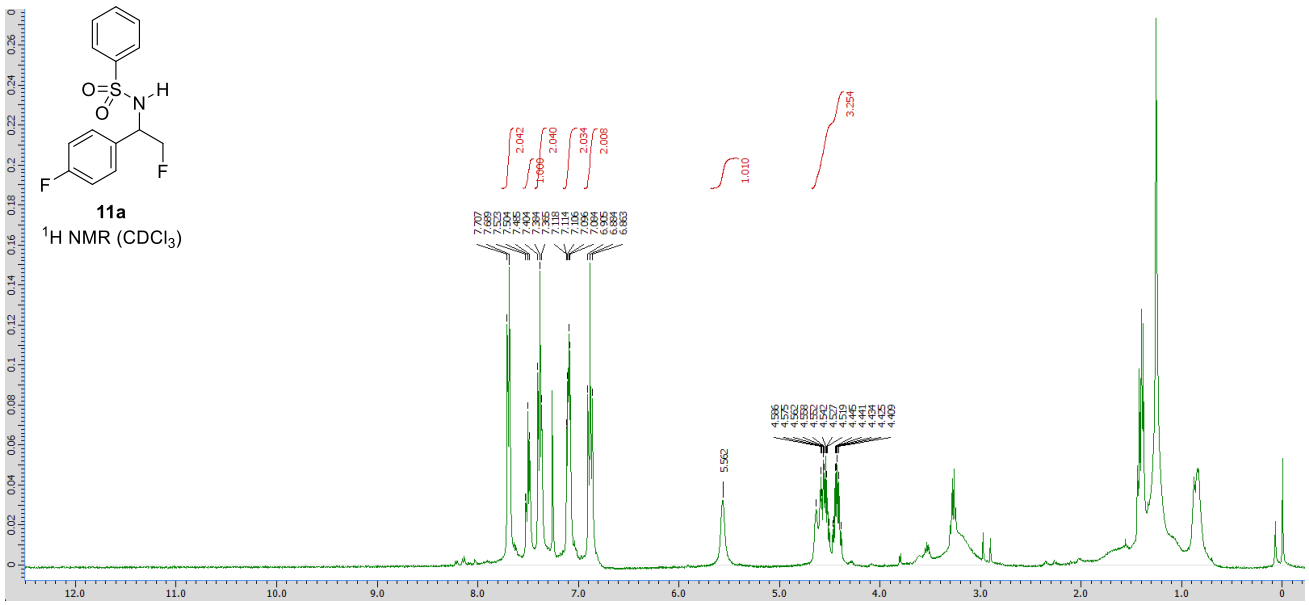

Ph
N
O
O
S
NO2
F
F
9a'
13C NMR (CDCl3)

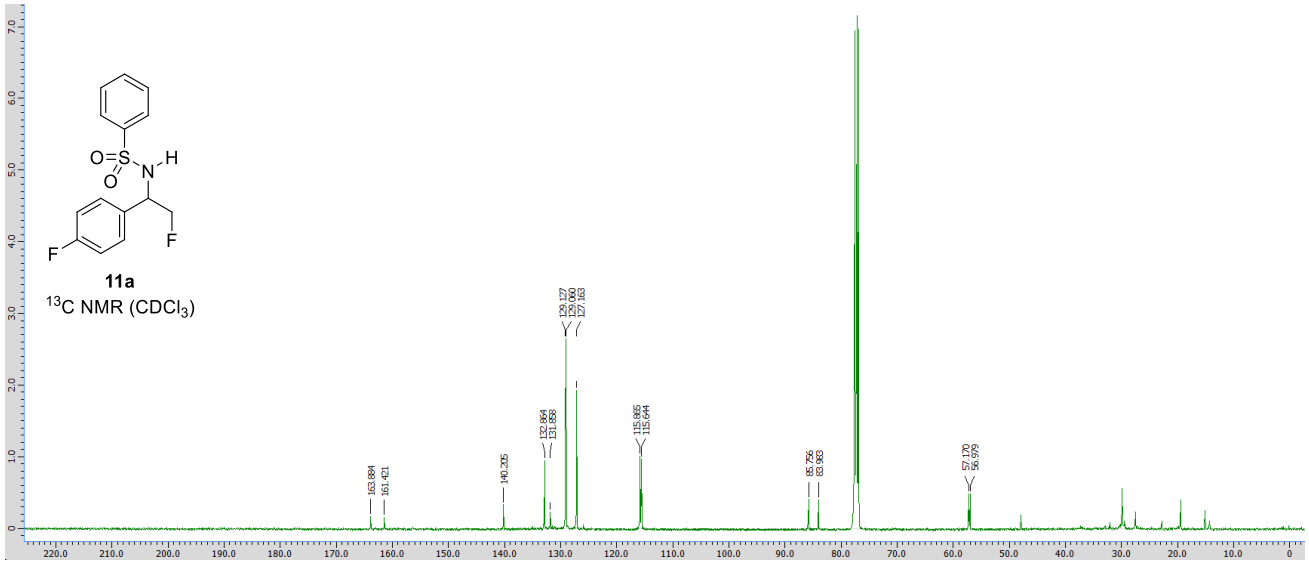

Ph
N
O
O
S
NO2
F
F
9a'
19F NMR (CDCl3)

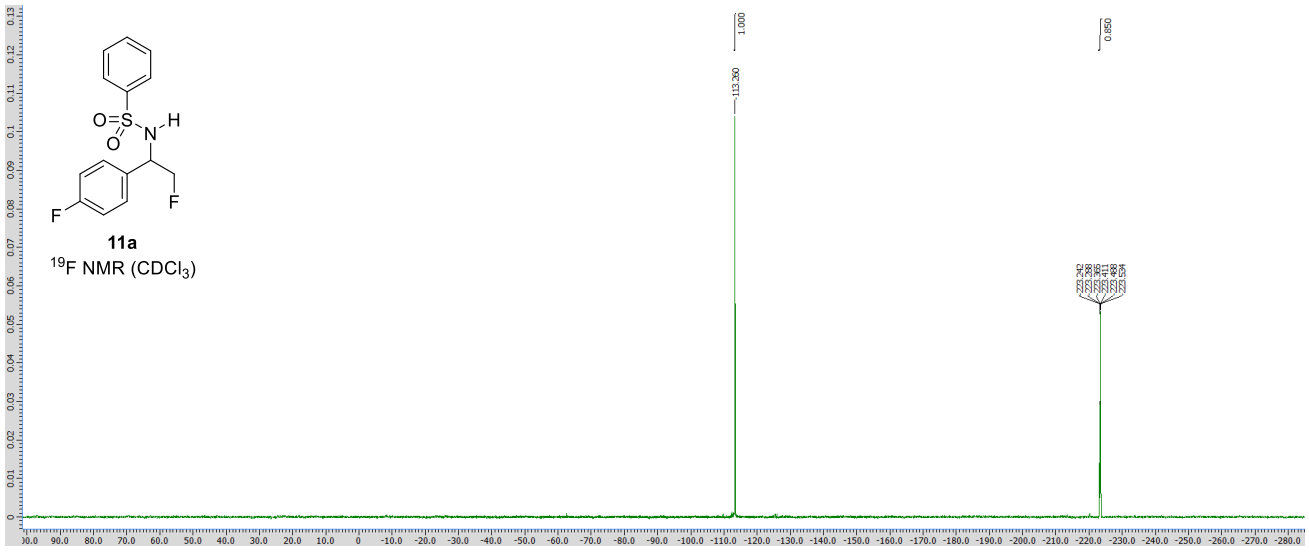

NH
F
F
10a
^{1}H NMR ($CDCl_3$)


NH
F
F
10a
^{13}C NMR ($CDCl_3$)


NH
F
F
10a
^{19}F NMR ($CDCl_3$)


11a
^{1}H NMR ($CDCl_3$)


11a
^{13}C NMR ($CDCl_3$)


11a
^{19}F NMR ($CDCl_3$)