

Copper-Catalyzed Synthesis of Activated Sulfonate Esters from Boronic Acids, DABSO and Pentafluorophenol

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1) General Considerations

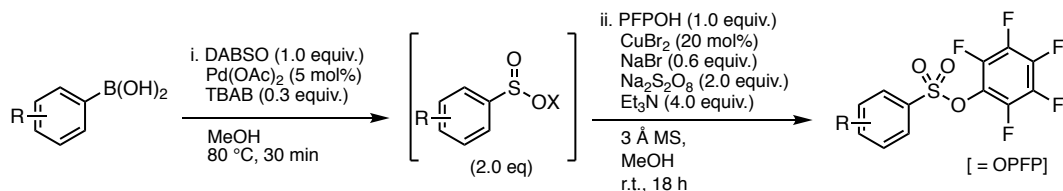
Reagents were purchased from Sigma-Aldrich, Alfa Aesar, Acros and Fluorochem and were used as supplied unless otherwise stated. DABSO was prepared from DABCO and SO₂ gas as previously reported by our group. Tetra-*n*-butylammonium bromide (TBAB) was recrystallised from ethyl acetate and dried *in vacuo* at 60 °C for two days. Sodium bromide was recrystallised from water and dried *in vacuo* at 140 °C overnight. Solvents were purchased from commercial suppliers and used without further purification unless otherwise stated. 1,4-Dioxane was dried over 4 Å molecular sieves and through anhydrous alumina columns using an Innovative Technology Inc. PS-400-7 solvent purification system. 'Pet. ether' refers to low boiling point (40-60 °C) petroleum ether. Organolithium reagents were titrated against *N*-benzylbenzamide in anhydrous THF.

Reactions were carried out with constant magnetic stirring and under air, unless otherwise stated. All glassware was dried in an oven (>200 °C, overnight) and allowed to cool down under positive flow of nitrogen prior to use. Standard Schlenk techniques were applied for the transfer of dry solvents and air sensitive reagents. Flash chromatography was carried out using silica gel (Merck silicagel 60, particle size 40-63 µm) with the indicated solvent. Crude reaction mixtures were dry-loaded on celite and pressure was applied at the column head from a nitrogen tap. Thin layer chromatography (TLC) analysis was performed on aluminum-backed silica sheets (Merck TLC Silica 60 F₂₅₄) and visualized by UV fluorescence (254 nm) and/or by staining with potassium permanganate (KMnO₄).

¹H NMR, ¹³C NMR and ¹⁹F NMR spectra were obtained on Bruker AVIII400 or a Bruker AVII500 NMR spectrometer using the residual solvent as an internal standard. Chemical shifts (δ) are reported in parts per million (ppm). Coupling constants *J* are quoted in the unit of hertz (Hz). Multiplicity are given as following: s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), sext (sextet), hept (heptet), m (multiplet), app (apparent). Low-resolution ESI mass spectra were recorded on a Waters LCT Premier spectrometer. High-resolution mass spectra were measured by internal service at the University of Oxford using a Bruker Daltronics microTOF (ESI) spectrometer or a Micromass LCT spectrometer using field ionization method (FI). Infrared spectra were recorded as thin films on a Bruker Tensor 27 FT-IR spectrometer. Melting points were determined using a Stuart Scientific Melting Point Apparatus SMP1.

2) General procedure for the synthesis of pentafluorophenyl sulfonate esters

General procedure A for the synthesis of pentafluorosulfonyl esters from boronic acids, DABSO and pentafluorophenol.



To a 10 mL round bottom flask was added DABSO (120 mg, 0.5 mmol), boronic acid (0.5 mmol), TBAB (48 mg, 0.15 mmol) and Pd(OAc)₂ (5.6 mg, 0.025 mmol). After the addition of methanol (3 mL), the reaction vessel was sealed using a rubber septum, and the reaction mixture was heated at 80 °C and stirred at this temperature for 30 minutes (t₁). After allowing the reaction mixture to cool to room temperature, pentafluorophenol (46 mg, 0.25 mmol), Na₂S₂O₈ (119 mg, 0.5 mmol), CuBr₂ (11.2 mg, 0.05 mmol), NaBr (15.5 mg, 0.15 mmol), powdered activated 3 Å molecular sieves (250 mg) and triethylamine (140 μL, 1.0 mmol) were added. The reaction vessel was resealed, and the mixture was stirred at room temperature for 18 hours. The reaction mixture was then diluted with EtOAc (5 mL), filtered through a plug of silica and washed with EtOAc (15 mL) before removing the solvent *in vacuo*. The desired product was isolated from the obtained crude material by flash column chromatography using the indicated solvents and gradient.

Notes:

- Reaction time for the first step (t₁) was 30 minutes unless otherwise stated.

General procedure B – Solvent MeOH/1,4-dioxane (1:1)

To a 10 mL round bottom flask was added DABSO (120 mg, 0.5 mmol), boronic acid (0.5 mmol), TBAB (48 mg, 0.15 mmol), and Pd(OAc)₂ (5.6 mg, 0.025 mmol). After the addition of methanol (1.5 mL) and 1,4-dioxane (1.5 mL), the reaction vessel was sealed using a rubber septum, and the reaction mixture was heated at 80 °C and stirred at this temperature for 30 minutes (t₁). After allowing the reaction mixture to cool to room temperature, pentafluorophenol (46 mg, 0.25 mmol), Na₂S₂O₈ (119 mg, 0.5 mmol), CuBr₂ (11.2 mg, 0.05 mmol), NaBr (15.5 mg, 0.15 mmol), powdered activated 3 Å molecular sieves (250 mg) and triethylamine (140 μL, 1.0 mmol) were added. The reaction vessel was resealed, and the mixture was stirred at room temperature for 18 hours. The reaction mixture was then diluted with EtOAc (5 mL), filtered through a plug of silica and washed with EtOAc (15 mL) before removing the solvent *in vacuo*. The desired product was isolated from the obtained crude material by flash column chromatography using the indicated solvents and gradient.

Notes:

- Reaction time for the first step (t₁) was 30 minutes unless otherwise stated.

General procedure C – No TBAB

To a 10 mL round bottom flask was added DABSO (120 mg, 0.5 mmol), boronic acid (0.5 mmol), and Pd(OAc)₂ (5.6 mg, 0.025 mmol). After the addition of methanol (3.0 mL), the reaction vessel was sealed using a rubber septum, the reaction mixture was heated at 80 °C and stirred at this temperature for 30

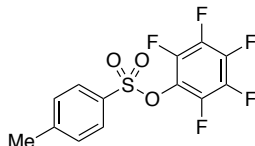
minutes (t_1). After allowing the reaction mixture to cool to room temperature, pentafluorophenol (46 mg, 0.25 mmol), $\text{Na}_2\text{S}_2\text{O}_8$ (119 mg, 0.5 mmol), CuBr_2 (11.2 mg, 0.05 mmol), NaBr (15.5 mg, 0.15 mmol), powdered activated 3 Å molecular sieves (250 mg) and triethylamine (140 μL , 1.0 mmol) were added. The reaction vessel was resealed, and the mixture was stirred at room temperature for 18 hours. The reaction mixture was then diluted with EtOAc (5 mL), filtered through a plug of silica and washed with EtOAc (15 mL) before removing the solvent *in vacuo*. The desired product was isolated from the obtained crude material by flash column chromatography using the indicated solvents and gradient.

Notes:

- Reaction time for the first step (t_1) was 30 minutes unless otherwise stated.

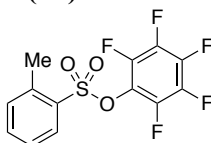
3) Characterisation of compounds

Pentafluorophenyl 4-methylphenylsulfonate ester (**2a**)



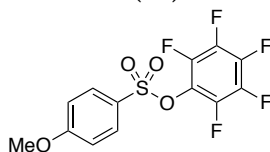
Prepared according to general procedure A using *p*-tolylboronic acid (68 mg, 0.5 mmol). Flash column chromatography (10% Et₂O in pet. ether) afforded the sulfonate as a white solid (73 mg, 86%). *R*_f = 0.59 (15% Et₂O in pet. ether); mp 61 °C (hexane); ¹H NMR (400 MHz; CDCl₃): δ 7.85 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 7.41 (dd, *J* = 8.4, 0.6 Hz, 2H, Ar-*H*), 2.50 (s, 3H, CH₃); ¹³C NMR (126 MHz; CDCl₃): δ 146.9, 142.4 (app. ddq, *J* = 255.7, 12.2, 3.8 Hz), 140.3 (app. dtt, *J* = 255.6, 13.7, 3.9 Hz), 138.0 (app. dtdd, *J* = 253.8, 13.5, 5.7, 3.1 Hz), 131.8, 130.3, 128.7, 124.3 (app. tdd, *J* = 14.3, 5.0, 2.5 Hz), 22.0; ¹⁹F NMR (377 MHz; CDCl₃): δ -150.6 (d, *J* = 18.2 Hz, 2F), -155.5 (t, *J* = 22.0 Hz, 1F), -161.2 (t, *J* = 20.2 Hz, 2F); IR ν_{max} (neat)/cm⁻¹ 1516, 1396 (SO₂), 1187 (SO₂), 994, 721 (C-O-S); HRMS (CI) found *m/z* 336.9959 [M-H]⁻, C₁₃H₆O₃F₅³²S requires *m/z* 336.9963.

Pentafluorophenyl 2-methylphenylsulfonate ester (**2b**)



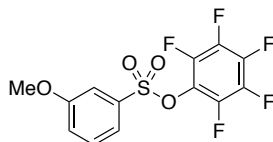
Prepared according to general procedure C using 2-methylphenylboronic acid (68 mg, 0.5 mmol). Flash column chromatography (10% Et₂O in pet. ether) afforded the sulfonate as a white solid (71 mg, 84%). *R*_f = 0.53 (15% Et₂O in pet. ether); mp 100 °C (hexane); ¹H NMR (400 MHz; CDCl₃): δ 7.89 (dd, *J* = 7.8, 1.3 Hz, 1H, Ar-*H*), 7.62 (td, *J* = 7.8, 1.3 Hz, 1H, Ar-*H*), 7.46 (ddt, *J* = 7.7, 1.2, 0.6 Hz, 1H, Ar-*H*), 7.35 (dddd, *J* = 8.0, 7.7, 1.2, 0.6 Hz, 1H, Ar-*H*), 2.81 (s, 3H, CH₃); ¹³C NMR (126 MHz; CDCl₃): δ 142.4 (app. ddq, *J* = 255.7, 12.4, 4.2 Hz), 140.4 (app. dtt, *J* = 254.0, 13.5, 3.8 Hz), 139.8, 137.9 (app. dtdd, *J* = 253.3, 13.8, 5.8, 3.0 Hz), 135.3, 133.7, 133.1, 130.3, 126.5, 124.3 (app. tdd, *J* = 14.5, 4.9, 2.3 Hz), 20.7; ¹⁹F NMR (377 MHz; CDCl₃): δ -150.7 (d, *J* = 17.4 Hz, 2F), -155.3 (t, *J* = 21.8 Hz, 1F), -161.1 (dd, *J* = 21.7, 17.6 Hz, 2F); IR ν_{max} (neat)/cm⁻¹ 1519, 1378 (SO₂), 1193 (SO₂), 995, 751, 718 (C-O-S); HRMS (CI) found *m/z* 336.9959 [M-H]⁻, C₁₃H₆O₃F₅³²S requires *m/z* 336.9963.

Pentafluorophenyl 4-methoxyphenylsulfonate ester (**2c**)



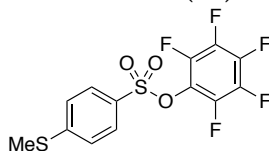
Prepared according to general procedure A using 4-methoxyphenylboronic acid (78 mg, 0.5 mmol). Flash column chromatography (10% Et₂O in pet. ether) afforded the sulfonate as a white solid (68 mg, 77%). *R*_f = 0.46 (10% Et₂O in pet. ether); mp 45 °C (hexane); ¹H NMR (500 MHz; CDCl₃): δ 7.91-7.88 (m, 2H, Ar-*H*), 7.07-7.04 (m, 2H, Ar-*H*), 3.93 (s, 3H, CH₃); ¹³C NMR (126 MHz, CDCl₃) δ 165.2, 143.5 (app. ddq, *J* = 255.5, 12.0, 3.7 Hz), 139.3 (app. dtt, *J* = 256.1, 13.6, 3.8 Hz), 137.0 (app. dtdd, *J* = 252.8, 14.7, 5.5, 3.1 Hz), 131.1, 125.9, 124.4 (app. tdt, *J* = 14.8, 5.1, 2.1 Hz), 114.9, 56.0; ¹⁹F NMR (377 MHz; CDCl₃): δ -150.8 (d, *J* = 13.5 Hz, 2F), -155.5 (t, *J* = 21.9 Hz, 1F), -161.2 (dd, *J* = 21.7, 17.8 Hz, 2F); IR ν_{max} (neat)/cm⁻¹ 1518, 1390 (SO₂), 1172 (SO₂), 996, 722 (C-O-S); HRMS (CI) found *m/z* 352.9908 [M-H]⁻, C₁₃H₆O₄F₅³²S requires *m/z* 352.9912.

Pentafluorophenyl 3-methoxyphenylsulfonate ester (**2d**)



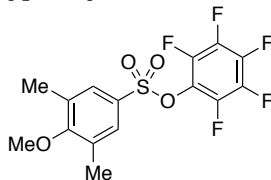
Prepared according to general procedure A using 3-methoxyphenylboronic acid (76 mg, 0.5 mmol). Time for SO₂ insertion (t_i) was adjusted from 30 minutes to 1 hour. After flash column chromatography (30% CH₂Cl₂ in pet. ether), the material was further purified by trituration in hexane at 0 °C to afford the sulfonate as a pale yellow oil (60 mg, 68%). R_f = 0.28 (30% CH₂Cl₂ in pet. ether); ¹H NMR (500 MHz; CDCl₃): δ 7.55 (dt, *J* = 7.8, 1.5 Hz, 1H, Ar-*H*), 7.51 (t, *J* = 7.8 Hz, 1H, Ar-*H*), 7.47 (t, *J* = 2.1 Hz, 1H, Ar-*H*), 7.28 (ddd, *J* = 8.1, 2.1, 1.3 Hz, 1H, Ar-*H*), 3.89 (s, 3H, OCH₃); ¹³C NMR (126 MHz; CDCl₃): δ 160.3, 142.4 (app. ddq, *J* = 255.6, 12.3, 4.1 Hz), 140.4 (app. dtt, *J* = 255.6, 13.5, 3.8 Hz), 138.0 (app. dtdd, *J* = 253.6, 13.8, 5.4, 3.0 Hz), 135.8, 130.7, 124.2 (app. tdd, *J* = 14.4, 4.8, 2.2 Hz), 122.0, 120.9, 113.0, 56.0; ¹⁹F NMR (377 MHz; CDCl₃): δ -150.5 (d, *J* = 17.6 Hz, 2F), -155.2 (t, *J* = 21.8 Hz, 1F), -161.0 (dd, *J* = 21.6, 17.9 Hz, 2F); IR ν_{max} (neat)/cm⁻¹ 1519, 1398 (SO₂), 1183 (SO₂), 995, 879, 722 (C-O-S); HRMS (ESI) found *m/z* 387.0319 [M+MeOH+H]⁺, C₁₄H₁₂O₅F₅³²S requires *m/z* 387.0320.

Pentafluorophenyl 4-(methylthio)phenylsulfonate ester (**2e**)



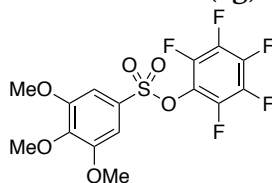
Prepared according to general procedure A using 4-(methylthio)phenylboronic acid (84 mg, 0.5 mmol). Time for SO₂ insertion (t_i) was adjusted from 30 minutes to 1 hour. Flash column chromatography (20% CH₂Cl₂ in pet. ether) afforded the sulfonate as a white solid (63 mg, 68%). R_f = 0.41 (30% CH₂Cl₂ in pet. ether); mp 90 °C (hexane); ¹H NMR (500 MHz; CDCl₃): δ 7.84-7.82 (m, 2H, Ar-*H*), 7.38-7.35 (m, 2H, Ar-*H*), 2.56 (s, 3H, CH₃); ¹³C NMR (126 MHz, CDCl₃) δ 150.0, 141.4 (app. ddq, *J* = 255.7, 12.3, 4.5 Hz), 139.4 (app. dtt, *J* = 256.7, 13.6, 3.9 Hz), 137.0 (app. tdd, *J* = 253.9, 13.7, 5.7, 3.1 Hz), 129.9, 128.8, 125.4, 124.3 (app. dddd, *J* = 16.9, 14.2, 4.8, 2.1 Hz), 14.8; ¹⁹F NMR (377 MHz; CDCl₃): -150.5 (d, *J* = 17.7 Hz, 2F), -155.4 (t, *J* = 21.9 Hz, 1F), -161.0 (dd, *J* = 21.9, 17.2 Hz, 2F); IR ν_{max} (neat)/cm⁻¹ 1519, 1393 (SO₂), 1184 (SO₂), 1079, 996, 766 (C-O-S), 716; HRMS (CI) found *m/z* 368.9679 [M-H]⁻, C₁₃H₇O₃F₅³²S requires *m/z* 368.9640.

Pentafluorophenyl 3,5-dimethyl-4-methoxyphenylsulfonate ester (**2f**)



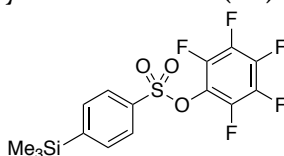
Prepared according to general procedure A using 3,5-dimethyl-4-methoxyphenylboronic acid (90 mg, 0.5 mmol). Flash column chromatography (30% CH₂Cl₂ in pet. ether), afford the sulfonate as a yellow oil (73 mg, 76%). R_f = 0.52 (30% CH₂Cl₂ in pet. ether); ¹H NMR (400 MHz; CDCl₃): δ 7.65 (s, 2H, Ar-*H*), 3.81 (s, 3H, OCH₃), 2.36 (s, 6H, Ar-CH₃); ¹³C NMR (126 MHz; CDCl₃): δ 163.1, 142.4 (app. ddq, *J* = 255.2, 12.2, 4.0 Hz), 140.3 (app. dtt, *J* = 255.2, 13.5, 3.8 Hz), 138.0 (app. dtdd, *J* = 253.4, 13.7, 5.6, 3.0 Hz), 133.1, 129.4, 129.2, 124.2 (app. tdd, *J* = 14.4, 4.6, 2.0 Hz), 60.0, 16.4; ¹⁹F NMR (377 MHz; CDCl₃): δ -150.6 (d, *J* = 17.8 Hz, 2F), -155.6 (t, *J* = 21.8 Hz, 1F), -161.3 (dd, *J* = 21.6, 18.1 Hz, 2F); IR ν_{max} (neat)/cm⁻¹ 2937, 1518, 1390 (SO₂), 1281, 1184 (SO₂), 996, 719 (C-O-S); HRMS (CI) found *m/z* 381.0221 [M-H]⁻, C₁₅H₁₀O₄F₅³²S requires *m/z* 381.0225.

Pentafluorophenyl 3,4,5-trimethoxyphenylsulfonate ester (**2g**)



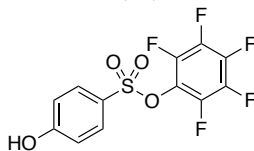
Prepared according to general procedure A using 3,4,5-trimethoxyphenylboronic acid (106 mg, 0.5 mmol). Flash column chromatography (70% CH₂Cl₂ in pet. ether), afford the sulfonate as a white solid (57 mg, 55%). R_f = 0.51 (70% CH₂Cl₂ in pet. ether); mp 102 °C (hexane); ¹H NMR (400 MHz; CDCl₃): δ 7.19 (s, 2H, Ar-H), 3.97 (s, 3H, OCH₃), 3.92 (s, 6H, 2 × OCH₃); ¹³C NMR (126 MHz; CDCl₃): δ 153.6, 144.1, 142.5 (app. ddq, *J* = 255.0, 12.4, 4.1 Hz), 140.4 (app. dtt, *J* = 255.6, 13.5, 3.8 Hz), 138.0 (app. dtdd, *J* = 252.3, 13.7, 5.6, 3.0 Hz), 128.9, 124.2 (app. tdd, *J* = 14.5, 4.8, 2.3 Hz), 106.1, 61.3, 56.8; ¹⁹F NMR (377 MHz; CDCl₃): δ -150.5 (d, *J* = 17.7 Hz, 2F), -155.2 (t, *J* = 21.8 Hz, 1F), -161.0 (dd, *J* = 21.6, 18.0 Hz, 2F); IR ν_{max} (neat)/cm⁻¹ 1519, 1516, 1413, 1375 (SO₂), 1313, 1178 (SO₂), 1125, 989, 746, 719 (C-O-S); HRMS (CI) found *m/z* 413.0118 [M-H]⁻, C₁₅H₁₀O₆F₅³²S requires *m/z* 413.0124.

Pentafluorophenyl 4-(trimethylsilyl)phenylsulfonate ester (**2h**)



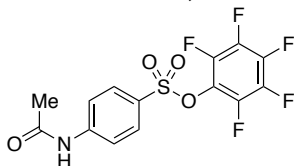
Prepared according to general procedure A using 4-(trimethylsilyl)phenylboronic acid (97 mg, 0.5 mmol). Flash column chromatography (20% CH₂Cl₂ in pet. ether) afforded the sulfonate as a white solid (67 mg, 68%). R_f = 0.44 (20% CH₂Cl₂ in pet. ether); mp 77 °C (hexane); ¹H NMR (400 MHz; CDCl₃): δ 7.94-7.91 (m, 2H, Ar-H), 7.76-7.74 (m, 2H, Ar-H), 0.33 (s, 9H, Si(CH₃)₃); ¹³C NMR (126 MHz; CDCl₃): δ 150.9, 142.4 (app. ddq, *J* = 255.4, 12.3, 4.1 Hz), 140.4 (app. dtt, *J* = 256.2, 13.6, 3.7 Hz), 138.0 (app. dtdd, *J* = 253.2, 13.7, 5.5, 3.0 Hz), 134.9, 134.4, 127.3, 124.3 (app. tdd, *J* = 14.3, 4.7, 2.1 Hz), -1.3; ¹⁹F NMR (377 MHz; CDCl₃): δ -150.5 (d, *J* = 17.6 Hz, 2F), -155.4 (t, *J* = 21.8 Hz, 1F), -161.1 (dd, *J* = 21.6, 17.9 Hz, 2F); IR ν_{max} (neat)/cm⁻¹ 1519, 1394 (SO₂), 1190 (SO₂), 997, 845, 762, 714 (C-O-S); HRMS (ESI) found *m/z* 395.0200 [M-H]⁻, C₁₅H₁₂O₃F₅³²S²⁸Si requires *m/z* 395.0202.

Pentafluorophenyl 4-hydroxyphenylsulfonate ester (**2i**)



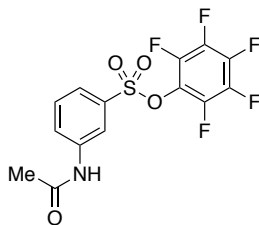
Prepared according to general procedure A using 4-hydroxyphenylboronic acid (69 mg, 0.5 mmol). Time for SO₂ insertion (t_i) was adjusted from 30 minutes to 1 hour. Flash column chromatography (30% Et₂O in pet. ether) afforded the sulfonate as colourless crystals (32 mg, 38%). R_f = 0.26 (30% Et₂O in pet. ether); mp 98 °C (hexane); ¹H NMR (400 MHz; CDCl₃): δ 7.87 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.01 (d, *J* = 8.8 Hz, 2H, Ar-H), 5.92 (s, 1H, OH); ¹³C NMR (126 MHz; CDCl₃): δ 162.0, 142.4 (app. ddq, *J* = 255.2, 12.4, 4.2 Hz), 140.3 (app. dtt, *J* = 256.3, 13.6, 3.8 Hz), 138.0 (app. dtdd, *J* = 253.2, 13.8, 5.7, 2.8 Hz), 131.4, 126.0, 124.3 (app. tdd, *J* = 14.3, 4.7, 2.2 Hz), 116.5; ¹⁹F NMR (377 MHz; CDCl₃): δ -150.7 (d, *J* = 17.5 Hz, 2F), -155.4 (t, *J* = 21.8 Hz, 1F), -161.1 (dd, *J* = 21.6, 17.8 Hz, 2F); IR ν_{max} (neat)/cm⁻¹ 3461, 1519, 1382 (SO₂), 1193, 1168 (SO₂), 996, 879, 726 (C-O-S); HRMS (ESI) found *m/z* 338.9754 [M-H]⁻, C₁₂H₄O₄NF₅³²S requires *m/z* 338.9756.

Pentafluorophenyl 4-acetamidophenylsulfonate ester (**2j**)



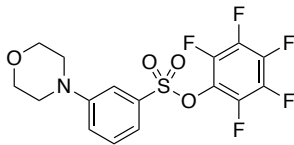
Prepared according to general procedure A using 4-acetamidophenylboronic acid (90 mg, 0.5 mmol). Time for SO₂ insertion (t_i) was adjusted from 30 minutes to 1 hour. Flash column chromatography (50% EtOAc in pet. ether) afforded the sulfonate as a beige solid (50 mg, 52%). R_f = 0.36 (50% EtOAc in pet. ether); mp 156-158 °C (hexane); ¹H NMR (500 MHz; CDCl₃): δ 7.91 (d, *J* = 8.9 Hz, 2H, Ar-*H*), 7.78 (d, *J* = 8.9 Hz, 2H, Ar-*H*), 7.63 (s, 1H, NH), 2.26 (s, 3H, CH₃); ¹³C NMR (126 MHz; CDCl₃): δ 168.9, 144.4, 142.4 (app. ddq, *J* = 255.4, 12.4, 4.1 Hz), 140.5 (app. dtt, *J* = 256.0, 13.5, 3.8 Hz), 138.0 (app. dtdd, *J* = 254.3, 13.7, 5.3, 3.0 Hz), 130.3, 128.9, 124.4 (app. tdd, *J* = 15.1, 5.1, 2.3 Hz), 119.4, 25.0; ¹⁹F NMR (377 MHz; CDCl₃): δ -150.6 (d, *J* = 17.7 Hz, 2F), -155.3 (t, *J* = 21.8 Hz, 1F), -161.0 (dd, *J* = 21.7, 17.7 Hz, 2F); IR ν_{max} (neat)/cm⁻¹ 3318, 1676, 1590, 1513, 1382 (SO₂), 1259, 1178 (SO₂), 992, 740, 710 (C-O-S); HRMS (ESI) found *m/z* 380.0020 [M-H]⁻, C₁₄H₇O₄NF₅³²S requires *m/z* 380.0021.

Pentafluorophenyl 3-acetamidophenylsulfonate ester (**2k**)



Prepared according to general procedure A using 3-acetamidophenylboronic acid (90 mg, 0.5 mmol). Time for SO₂ insertion (t_i) was adjusted from 30 minutes to 1 hour. Flash column chromatography (50% EtOAc in pet. ether) afforded the sulfonate as a beige solid (78 mg, 81%). R_f = 0.49 (50% EtOAc in pet. ether); mp 163 °C (hexane); ¹H NMR (400 MHz; CDCl₃): δ 8.11 (t, *J* = 1.7 Hz, 1H, Ar-*H*), 8.00 (dd, *J* = 8.0, 1.0 Hz, 1H, Ar-*H*), 7.69 (ddd, *J* = 8.0, 1.7, 1.0 Hz, 1H, Ar-*H*), 7.57 (t, *J* = 8.0 Hz, 1H, Ar-*H*), 7.47 (br. s, 1H, NH), 2.23 (s, 3H, CH₃); ¹³C NMR (126 MHz; CDCl₃): δ 168.6, 142.4 (app. ddq, *J* = 255.2, 12.4, 4.1 Hz), 140.5 (app. dtt, *J* = 256.0, 17.9, 4.4 Hz), 139.3, 138.0 (app. dtdd, *J* = 254.3, 13.7, 5.2, 2.8 Hz), 135.5, 130.4, 126.1, 124.2 (app. tdd, *J* = 15.1, 5.1, 2.3 Hz), 123.9, 119.1, 24.8; ¹⁹F NMR (377 MHz; CDCl₃): δ -150.5 (d, *J* = 17.4 Hz, 2F), -155.1 (t, *J* = 21.9 Hz, 1F), -161.2 (dd, *J* = 21.7, 18.1 Hz, 2F); IR ν_{max} (neat)/cm⁻¹ 3259, 1673, 1595, 1516, 1419 (SO₂), 1188 (SO₂), 995, 798, 748, 723 (C-O-S), 701; HRMS (ESI) found *m/z* 403.9986 [M+Na]⁺, C₁₄H₈O₄NF₅²³Na³²S requires *m/z* 403.9986.

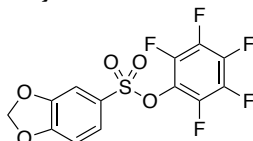
Pentafluorophenyl 3-morpholinophenylsulfonate ester (**2l**)



Prepared according to general procedure A using 3-(morpholino)phenylboronic acid (104 mg, 0.5 mmol). Flash column chromatography (90% CH₂Cl₂ in pet. ether) afforded the sulfonate as a yellow oil (60 mg, 58%). R_f = 0.49 (95% CH₂Cl₂ in pet. ether); ¹H NMR (400 MHz; CDCl₃): δ 7.47 (t, *J* = 8.0 Hz, 1H, Ar-*H*), 7.42 (t, *J* = 2.4 Hz, 1H, Ar-*H*), 7.41-7.38 (m, 1H, Ar-*H*), 7.23 (ddd, *J* = 8.0, 2.4, 1.0 Hz, 1H, Ar-*H*), 3.90-3.87 (m, 4H, O(CH₂)₂), 3.25-3.23 (m, 4H, N(CH₂)₂); ¹³C NMR (126 MHz; CDCl₃): δ 152.0, 142.4 (app. ddq, *J* =

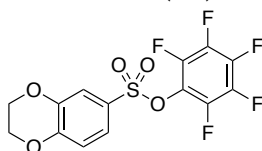
255.1, 12.1, 4.3 Hz), 140.4 (app. dtt, $J = 255.5, 13.4, 3.8$ Hz), 138.0 (app. dtdd, $J = 256.2, 13.7, 3.0$ Hz), 135.7, 130.4, 124.3 (app. tdd, $J = 14.3, 4.8, 2.2$ Hz), 121.6, 119.0, 114.2, 66.6, 48.5; ^{19}F NMR (377 MHz; CDCl_3): δ -150.4 (d, $J = 17.3$ Hz, 2F), -155.4 (t, $J = 21.9$ Hz, 1F), -161.1 (dd, $J = 21.7, 17.8$ Hz, 2F); IR ν_{max} (neat)/ cm^{-1} 2973, 2854, 1519, 1387 (SO_2), 1267, 1192 (SO_2), 997, 719 (C-O-S); HRMS (CI) found m/z 410.0476 $[\text{M}+\text{H}]^+$, $\text{C}_{16}\text{H}_{13}\text{O}_4\text{NF}_5^{32}\text{S}$ requires m/z 410.0480.

Pentafluorophenyl 3,4-(methylenedioxy)phenylsulfonate ester (**2m**)



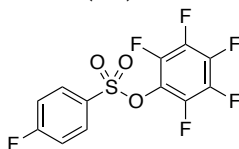
Prepared according to general procedure A using 3,4-(methylenedioxy)phenylboronic acid (83 mg, 0.5 mmol). Flash column chromatography (50% CH_2Cl_2 in pet. ether) afforded the sulfonate as an off white solid (57 mg, 62%). $R_f = 0.60$ (50% CH_2Cl_2 in pet. ether); mp 64°C (hexane); ^1H NMR (500 MHz; CDCl_3): δ 7.53 (dd, $J = 8.3, 1.9$ Hz, 1H, Ar-*H*), 7.36 (d, $J = 1.9$ Hz, 1H, Ar-*H*), 6.95 (d, $J = 8.2$ Hz, 1H, Ar-*H*), 6.17 (s, 2H, OCH_2O); ^{13}C NMR (126 MHz; CDCl_3): δ 153.9, 148.8, 142.4 (app. ddq, $J = 245.8, 12.3, 4.2$ Hz), 140.4 (app. dtt, $J = 250.9, 13.4, 3.8$ Hz), 138.0 (app. dtdd, $J = 253.6, 13.8, 5.2, 3.0$ Hz), 127.4, 125.4, 124.2 (app. tdd, $J = 14.4, 4.8, 2.2$ Hz), 108.7, 108.5, 103.1; ^{19}F NMR (377 MHz; CDCl_3): δ -150.6 (d, $J = 17.4$ Hz, 2F), -155.4 (t, $J = 21.8$ Hz, 1F), -161.0 (dd, $J = 21.7, 17.9$ Hz, 2F); IR ν_{max} (neat)/ cm^{-1} 1519, 1482, 1394 (SO_2), 1250, 1195 (SO_2), 996, 746, 724 (C-O-S); HRMS (ESI) found m/z 366.9701 $[\text{M}-\text{H}]^-$, $\text{C}_{13}\text{H}_4\text{O}_5\text{F}_5^{32}\text{S}$ requires m/z 366.9705.

Pentafluorophenyl 1,4-benzodioxane-6-sulfonate ester (**2n**)



Prepared according to general procedure A using 1,4-benzodioxane-6-boronic acid (90 mg, 0.5 mmol). Flash column chromatography (40% CH_2Cl_2 in pet. ether) afforded the sulfonate as a white solid (75 mg, 78%). $R_f = 0.48$ (50% CH_2Cl_2 in pet. ether); mp 88°C (hexane); ^1H NMR (500 MHz; CDCl_3): δ 7.49 (d, $J = 2.3$ Hz, 1H, Ar-*H*), 7.45 (dd, $J = 8.6, 2.3$ Hz, 1H, Ar-*H*), 7.03 (d, $J = 8.6$ Hz, 1H, Ar-*H*), 4.39-4.37 (m, 2H, OCH_2), 4.34-4.32 (m, 2H, OCH_2); ^{13}C NMR (126 MHz; CDCl_3): δ 149.9, 144.0, 142.4 (app. ddq, $J = 255.4, 12.4, 4.2$ Hz), 140.3 (app. dtt, $J = 255.4, 13.4, 3.8$), 138.0 (app. dtdd, $J = 255.7, 13.7, 5.5, 3.1$ Hz), 126.6, 124.3 (app. tdd, $J = 14.3, 4.5, 2.0$), 122.7, 118.4, 64.9, 64.2; ^{19}F NMR (377 MHz; CDCl_3): δ -150.6 (d, $J = 17.3$ Hz, 2F), -155.6 (t, $J = 21.9$ Hz, 1F), -161.2 (dd, $J = 21.8, 17.83$ Hz, 2F); IR ν_{max} (neat)/ cm^{-1} 1519, 1497, 1391 (SO_2), 1290, 1183 (SO_2), 995, 879, 722 (C-O-S); HRMS (ESI) found m/z 404.9827 $[\text{M}+\text{Na}]^+$, $\text{C}_{14}\text{H}_7\text{O}_5\text{F}_5^{32}\text{S}$ requires m/z 404.9827.

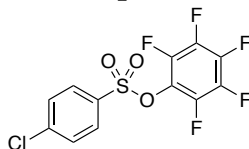
Pentafluorophenyl 4-fluorophenylsulfonate ester (**2o**)



Prepared according to general procedure A using 4-fluorophenylboronic acid (70 mg, 0.5 mmol). Flash column chromatography (5% CH_2Cl_2 and 5% Et_2O in pet. ether) afforded the sulfonate as a pale yellow oil (65 mg, 76%). $R_f = 0.42$ (5% CH_2Cl_2 and 5% Et_2O in pet. ether) ^1H NMR (500 MHz; CDCl_3): δ 8.04-8.00 (m, 2H, Ar-*H*), 7.33-7.28 (m, 2H, Ar-*H*); ^{13}C NMR (126 MHz, CDCl_3) δ 166.8 (d, $J = 259.5$ Hz), 141.3 (app. ddq, $J = 255.4, 12.1, 3.7$ Hz), 139.5 (app. dtt, $J = 256.3, 13.5, 3.8$ Hz), 137.0 (app. dtdd, $J = 253.7, 13.6, 5.7, 3.0$ Hz), 131.7 (d, $J = 10.0$ Hz), 130.9 (d, $J = 3.3$ Hz), 124.1 (app. tdd, $J = 12.5, 4.8, 2.6$ Hz), 117.2 (d, $J = 23.0$ Hz); ^{19}F NMR (377 MHz; CDCl_3): δ -99.8 (s, 1F), -150.6 (d, $J = 17.2$ Hz, 2F), -154.9 (t, $J = 21.9$ Hz, 1F), -160.8 (dd, $J =$

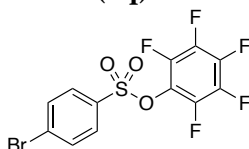
21.9, 17.2 Hz, 2F); IR ν_{\max} (neat)/cm⁻¹ 1518, 1394 (SO₂), 1195 (SO₂), 996, 751 (C-O-S), 725; HRMS (CI) found m/z 340.9708 [M-H]⁻, C₁₂H₃O₃F₆³²S requires m/z 340.9713.

Pentafluorophenyl 4-chlorophenylsulfonate ester (**2p**)



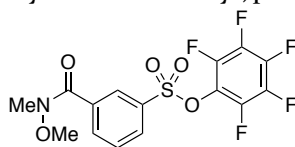
Prepared according to general procedure A using 4-chlorophenylboronic acid (78 mg, 0.5 mmol). Time for SO₂ insertion (t₁) was adjusted from 30 minutes to 1 hour. Flash column chromatography (5% Et₂O in pet. ether) afforded the sulfonate as an off-white solid (49 mg, 55%). R_f = 0.38 (5% Et₂O in pet. ether); mp 46 °C (hexane); ¹H NMR (400 MHz; CDCl₃): δ 7.77 (dd, J = 128.0, 8.4 Hz, 2H, Ar-H), 7.44 (dd, J = 37.3, 8.4 Hz, 2H, Ar-H); ¹³C NMR (126 MHz; CDCl₃): δ 142.5, 142.3 (app. ddq, J = 255.4, 12.5, 4.1 Hz), 140.6 (app. dtt, J = 256.4, 13.6, 3.9 Hz), 138.6, 138.0 (app. dtdd, J = 251.5, 13.7, 5.7, 3.0 Hz), 133.9, 133.3, 130.13, 130.05, 129.2, 128.4, 123.9 (app. tdd, J = 15.1, 5.4, 2.0 Hz); ¹⁹F NMR (377 MHz; CDCl₃): δ -150.5 (d, J = 17.3 Hz, 2F), -155.1 (t, J = 21.9 Hz, 1F), -160.6 (dd, J = 21.7, 17.8 Hz, 2F); IR ν_{\max} (neat)/cm⁻¹ 1514, 1395 (SO₂), 1193 (SO₂), 1089, 991, 825, 718 (C-O-S), 623; HRMS (CI) found m/z 356.9411 [M-H]⁻, C₁₂H₃O₄ClF₅23S requires m/z 356.9417.

Pentafluorophenyl 4-bromophenylsulfonate ester (**2q**)



Prepared according to general procedure A using 4-bromophenylboronic acid (100 mg, 0.5 mmol). Time for SO₂ insertion (t₁) was adjusted from 30 minutes to 1 hour. Flash column chromatography (20% CH₂Cl₂ in pet. ether) afforded the sulfonate as a white solid (68 mg, 67%). R_f = 0.53 (30% CH₂Cl₂ in pet. ether); mp 62 °C (hexane); ¹H NMR (500 MHz; CDCl₃): δ 7.86-7.83 (m, 2H, Ar-H), 7.79-7.76 (m, 2H, Ar-H); ¹³C NMR (126 MHz; CDCl₃): δ 141.3 (app. ddq, J = 255.6, 12.8, 4.0 Hz), 139.6 (app. dtt, J = 256.4, 13.4, 3.9 Hz), 137.0 (app. dtdd, J = 253.7, 13.5, 5.6, 3.0 Hz), 133.9, 133.1, 131.1, 130.0, 124.1 (app. dddd, J = 14.4, 12.6, 4.9, 2.5 Hz); ¹⁹F NMR (377 MHz; CDCl₃): δ -150.5 (d, J = 17.3 Hz, 2F), -154.7 (t, J = 21.9 Hz, 1F), -160.6 (dd, J = 21.7, 17.3 Hz, 2F); IR ν_{\max} (neat)/cm⁻¹ 1519, 1398 (SO₂), 1197 (SO₂), 996, 761 (C-O-S), 716; HRMS (CI) found m/z 400.8908 [M-H]⁻, C₁₂H₃O₃⁷⁹BrF₅³²S requires m/z 400.8912.

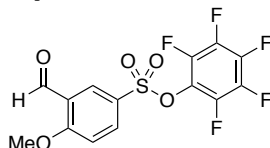
Pentafluorophenyl 3-(N,O-dimethylhydroxylaminocarbonyl)phenylsulfonate ester (**2r**)



Prepared according to general procedure A using 3-(N,O-dimethylhydroxylaminocarbonyl)benzeneboronic acid (105 mg, 0.5 mmol). Time for SO₂ insertion (t₁) was adjusted from 30 minutes to 3 hours. Flash column chromatography (70% Et₂O in pet. ether) afforded the sulfonate as a colourless oil (39 mg, 38%). R_f = 0.36 (70% Et₂O in pet. ether); ¹H NMR (400 MHz; CDCl₃): δ 8.33 (s, 1H, Ar-H), 8.09 (dd, J = 15.6, 7.9 Hz, 2H, Ar-H), 7.7 (t, J = 7.9 Hz, 1H, Ar-H), 3.54 (s, 3H, OCH₃), 3.40 (s, 3H, NCH₃); ¹³C NMR (126 MHz; CDCl₃): δ 167.0, 142.3 (app. ddq, J = 255.1, 12.6, 4.1 Hz),

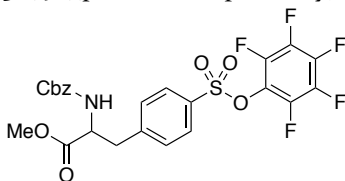
140.5 (app. dtt, $J = 256.4, 13.6, 4.0$ Hz), 138.0 (app. dtdd, $J = 253.8, 13.6, 5.3, 3.0$ Hz), 135.8, 135.3, 134.9, 130.3, 129.6, 128.7, 124.1 (app. tdd, $J = 14.4, 4.6, 2.3$ Hz), 61.5, 33.3; ^{19}F NMR (377 MHz; CDCl_3): δ -150.6 (d, $J = 17.7$ Hz, 2F), -154.8 (t, $J = 21.8$ Hz, 1F), -160.7 (dd, $J = 21.6, 17.8$ Hz, 2F); IR ν_{max} (neat)/ cm^{-1} 1647, 1518, 1392 (SO_2), 1189, 995, 794, 719 (C-O-S); HRMS (ESI) found m/z 412.0268 $[\text{M}+\text{H}]^+$, $\text{C}_{15}\text{H}_{11}\text{O}_5\text{NF}_5$ requires m/z 412.0273.

Pentafluorophenyl 3-formyl-4-methoxyphenylsulfonate ester (**2s**)



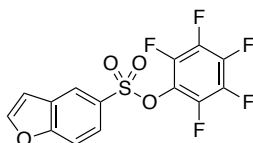
Prepared according to general procedure A using 3-formyl-4-methoxyphenylboronic acid (90.0 mg, 0.5 mmol). Flash column chromatography (60 to 70% CH_2Cl_2 in pet. ether) afforded the sulfonate as a white solid (80.6 mg, 84%). $R_f = 0.51$ (75% CH_2Cl_2 in pet. ether); mp 144 °C (hexane); ^1H NMR (400 MHz; CDCl_3): δ 10.46 (s, 1H, CHO), 8.41 (d, $J = 2.5$ Hz, 1H, Ar-H), 8.14 (dd, $J = 8.9, 2.5$ Hz, 1H, Ar-H), 7.22 (d, $J = 8.9$ Hz, 1H, Ar-H), 4.10 (s, 3H, OCH_3); ^{13}C NMR (101 MHz; CDCl_3): δ 187.4, 166.0, 142.3 (app. ddq, $J = 255.2, 12.3, 4.2$ Hz), 140.5 (app. dtt, $J = 256.3, 12.5, 4.1$ Hz), 138.0 (app. dtdd, $J = 254.2, 13.8, 5.6, 3.0$ Hz), 135.7, 130.1, 127.2, 125.2, 124.2 (app. tdd, $J = 13.8, 5.3, 1.8$ Hz), 113.0, 56.8; ^{19}F NMR (377 MHz; CDCl_3): δ -150.7 (d, $J = 17.4$ Hz, 2F), -154.9 (t, $J = 21.9$ Hz, 1F), -160.8 (dd, $J = 21.6, 17.7$ Hz, 2F); IR ν_{max} (neat)/ cm^{-1} 1681, 1592, 1518, 1395 (SO_2), 1289, 1257, 1192 (SO_2), 990, 912, 745, 711 (C-O-S); HRMS (ESI) found m/z 383.0008 $[\text{M}+\text{H}]^+$, $\text{C}_{14}\text{H}_8\text{O}_5\text{F}_5$ requires m/z 383.0007.

Methyl-2-(((benzyloxy)carbonyl)amino)-3-(4-((pentafluorophenoxy)sulfonyl ester)phenyl)propanoate (**2t**)



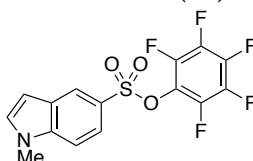
Prepared according to general procedure A using (4-(2-(((benzyloxy)carbonyl)amino)-3-methoxy-3-oxopropyl)phenyl)boronic acid (179 mg, 0.5 mmol). Time for SO_2 insertion (t_i) was adjusted from 30 minutes to 1 hour. Flash column chromatography (60% Et_2O in pet. ether) afforded the sulfonate as a pale-yellow oil (98 mg, 70%). $R_f = 0.42$ (65% Et_2O in pet. ether); ^1H NMR (500 MHz; CDCl_3): δ 7.86 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.36-7.32 (m, 7H, Ar-H), 5.37 (d, $J = 7.7$ Hz, 1H, Ar(CH_aH_b)O), 5.10 (app. q, $J = 10.6$ Hz, 2H, NH and NHCHCH_2), 4.72 (d, $J = 7.3$ Hz, 1H, Ar(CH_aH_b)O), 3.73 (s, 3H, OCH_3), 3.24 (ddd, $J = 65.7, 13.8, 6.1$ Hz, 2H, CH_2CH); ^{13}C NMR (126 MHz; CDCl_3): δ 171.3, 155.6, 144.7, 142.3 (app. ddq, $J = 255.5, 12.3, 4.0$ Hz), 140.4 (app. dtt, $J = 255.7, 13.6, 3.7$ Hz), 138.0 (app. dtdd, $J = 253.9, 13.7, 5.5, 3.0$ Hz), 136.1, 133.5, 130.6, 128.82, 128.69, 128.5, 128.3, 124.2 (app. tdd, $J = 15.3, 4.9, 2.3$ Hz), 67.3, 54.6, 52.7, 38.5; ^{19}F NMR (377 MHz; CDCl_3): δ -150.6 (d, $J = 17.8$ Hz, 2F), -155.1 (t, $J = 22.0$ Hz, 1F), -160.9 (dd, $J = 21.7, 18.1$ Hz, 2F); IR ν_{max} (neat)/ cm^{-1} 1734, 1722, 1518, 1391 (SO_2), 1200 (SO_2), 996, 747, 718 (C-O-S); HRMS (ESI) found m/z 560.0795 $[\text{M}+\text{H}]^+$, $\text{C}_{24}\text{H}_{19}\text{O}_7\text{NF}_5$ requires m/z 560.0797.

Pentafluorophenyl benzofuran-5-sulfonate ester (**2u**)



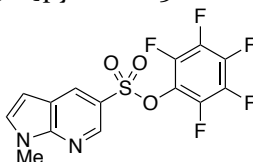
Prepared according to general procedure A using benzofuran-5-ylboronic acid (81 mg, 0.5 mmol). Flash column chromatography (20% Et₂O in pet. ether) afforded the sulfonate as a yellow solid (59 mg, 65%). *R*_f = 0.44 (20% Et₂O in pet. ether); mp 74 °C (hexane); ¹H NMR (500 MHz; CDCl₃): δ 8.30 (d, *J* = 2.0 Hz, 1H, Ar-*H*), 7.93 (dd, *J* = 8.8, 2.0 Hz, 1H, Ar-*H*), 7.83 (d, *J* = 2.3 Hz, 1H, Ar-*H*), 7.71 (ddd, *J* = 8.8, 0.9, 0.6 Hz, 1H, OCH), 6.95 (dd, *J* = 2.3, 0.9 Hz, 1H, OCHCH); ¹³C NMR (126 MHz; CDCl₃): δ 158.1, 148.1, 142.4 (app. ddq, *J* = 255.7, 12.4, 4.1 Hz), 140.4 (app. dtt, *J* = 255.8, 13.6, 3.9 Hz), 138.0 (app. dtdd, *J* = 255.8, 13.8, 5.5, 3.1 Hz), 129.4, 128.3, 124.7, 124.5-124.2 (m), 123.5, 112.9, 107.4; ¹⁹F NMR (377 MHz; CDCl₃): δ -150.6 (d, *J* = 17.5 Hz, 2F), -155.4 (t, *J* = 21.9 Hz, 1F), -161.1 (dd, *J* = 21.7, 17.9 Hz, 2F); IR ν_{max} (neat)/cm⁻¹ 1515, 1396 (SO₂), 1259, 1196 (SO₂), 1170, 990, 845, 746, 718 (C-O-S), 625; HRMS (CI) found *m/z* 363.9834 [M]⁺, C₁₄H₅O₄F₅³²S requires *m/z* 363.9834.

Pentafluorophenyl 1-methyl-1H-indole-5-sulfonate ester (2v)



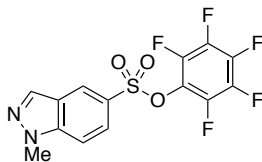
Prepared according to general procedure A using *N*-methylindole-5-boronic acid (88 mg, 0.5 mmol). Flash column chromatography (10% CH₂Cl₂ and 10% Et₂O in pet. ether) afforded the sulfonate as a white solid (68 mg, 72%). *R*_f = 0.31 (10% CH₂Cl₂ and 10% Et₂O in pet. ether); mp 108-110 °C (hexane); ¹H NMR (400 MHz; CDCl₃): δ 8.28 (dd, *J* = 1.9, 0.7 Hz, 1H, Ar-*H*), 7.78 (dd, *J* = 8.8, 1.9 Hz, 1H, Ar-*H*), 7.48 (dt, *J* = 8.8, 0.7 Hz, 1H, Ar-*H*), 7.25 (d, *J* = 3.3 Hz, 1H, NCH), 6.68 (dd, *J* = 3.3, 0.7 Hz, 1H, NCHCH), 3.90 (s, 3H, CH₃); ¹³C NMR (126 MHz; CDCl₃): δ 142.5 (app. ddq, *J* = 255.3, 12.2, 3.8 Hz), 140.2 (app. dtt, *J* = 254.8, 13.9, 3.8 Hz), 139.7, 137.9 (app. dtdd, *J* = 254.8, 13.5, 5.7, 2.9 Hz), 132.1, 128.0, 124.74-124.47 (m), 124.66, 123.7, 121.2, 110.2, 103.5, 33.4; ¹⁹F NMR (377 MHz; CDCl₃): δ -150.6 (d, *J* = 17.3 Hz, 2F), -156.1 (t, *J* = 22.0 Hz, 1F), -161.5 (dd, *J* = 21.9, 17.8 Hz, 2F); IR ν_{max} (neat)/cm⁻¹ 1518, 1382 (SO₂), 1249, 1175 (SO₂), 1153, 995, 763 (C-O-S), 629; HRMS (ESI) found *m/z* 400.0037 [M+Na]⁺, C₁₅H₈O₃NF₅²³Na³²S requires *m/z* 400.0037.

Pentafluorophenyl 1-methyl-1H-pyrrolo[2,3-b]pyridine-5-sulfonate ester (2w)



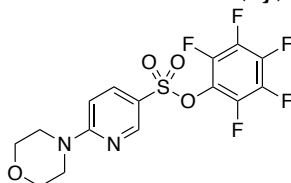
Prepared according to general procedure B using 1-methyl-1H-pyrrolo[2,3-b]pyridine-5-boronic acid (88 mg, 0.5 mmol). Flash column chromatography (30-60% Et₂O in pet. ether), afford the sulfonate as a yellow solid (57 mg, 60%). *R*_f = 0.50 (60% Et₂O in pet. ether); mp 99 °C (hexane); ¹H NMR (400 MHz; CDCl₃): δ 8.84 (d, *J* = 0.5 Hz, 1H, Ar-*H*), 8.49 (d, *J* = 0.5 Hz, 1H, Ar-*H*), 7.41 (d, *J* = 3.5 Hz, 1H, Ar-*H*), 6.67 (d, *J* = 3.5 Hz, 1H, Ar-*H*), 3.98 (s, 3H, NCH₃); ¹³C NMR (126 MHz; CDCl₃): δ 149.8, 142.7, 142.4 (app. ddq, *J* = 255.6, 12.3, 4.1 Hz), 140.4 (app. dtt, *J* = 254.6, 13.4, 3.8), 138.0 (app. dtdd, *J* = 256.3, 13.8, 5.3, 2.9 Hz), 132.7, 130.0, 124.3 (app. tdd, *J* = 14.2, 4.7, 2.0), 122.9, 119.7, 101.9, 31.9; ¹⁹F NMR (377 MHz; CDCl₃): δ -150.6 (d, *J* = 17.8 Hz, 2F), -155.4 (t, *J* = 21.8 Hz, 1F), -161.0 (dd, *J* = 21.6, 18.1 Hz, 2F); IR ν_{max} (neat)/cm⁻¹ 2922, 1591, 1515, 1381 (SO₂), 1206, 1174 (SO₂), 991, 879, 738, 715 (C-O-S), 640; HRMS (ESI) found *m/z* 379.0166 [M+H]⁺, C₁₄H₈O₃N₂F₅³²S requires *m/z* 379.0170.

Pentafluorophenyl 1-methyl-1H-indazole-5-sulfonate ester (2x)



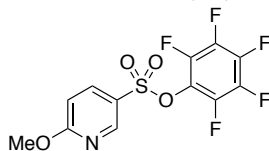
Prepared according to general procedure A using 1-methyl-1*H*-indazole-5-boronic acid (88 mg, 0.5 mmol). After flash column chromatography (20 - 40% EtOAc in pet. ether), the material was further purified by dissolving in EtOAc (10 mL) and washed with saturated NaHCO_{3(aq)} (5 mL × 2), dried on MgSO₄ and concentrated to afford the sulfonate as a yellow solid (25 mg, 26%). *R*_f = 0.28 (20% EtOAc in pet. ether); mp 114 °C (hexane); ¹H NMR (400 MHz; CDCl₃): δ 8.44 (s, 1H, Ar-*H*), 8.19 (s, 1H, Ar-*H*), 7.94 (d, *J* = 8.9 Hz, 1H, Ar-*H*), 7.59 (d, *J* = 8.9 Hz, 1H, Ar-*H*), 4.18 (s, 3H, NCH₃); ¹³C NMR (126 MHz; CDCl₃): δ 142.4 (app. ddq, *J* = 256.9, 12.2, 4.1 Hz), 141.8, 140.4 (app. dtt, *J* = 253.8, 13.6, 3.8 Hz), 138.0 (app. dtdd, *J* = 253.6, 13.7, 5.7, 3.0 Hz), 135.2, 126.6, 125.05, 125.01, 123.3, 124.5-124.2 (app. m), 110.4, 36.2; ¹⁹F NMR (377 MHz; CDCl₃): δ -150.7 (d, *J* = 18.0 Hz, 2F), -155.4 (t, *J* = 21.8 Hz, 1F), -161.0 (dd, *J* = 21.5, 18.4 Hz, 2F); IR ν_{max} (neat)/cm⁻¹ 2922, 2853, 1607, 1515, 1467, 1399 (SO₂), 1290, 1176 (SO₂), 1061, 987, 926, 800, 703 (C-O-S), 640; HRMS (ESI) found *m/z* 379.0170 [M+H]⁺, C₁₄H₈O₃N₂F₅³²S requires *m/z* 379.0173.

Pentafluorophenyl 2-morpholino-5-pyridinesulfonate ester (**2y**)



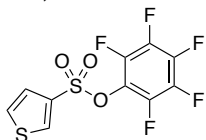
Prepared according to general procedure B using 2-morpholino-5-pyridineboronic acid (104 mg, 0.5 mmol). Flash column chromatography (50% CH₂Cl₂ in pet. ether) afforded the sulfonate as a white solid (17 mg, 17%). *R*_f = 0.68 (60% CH₂Cl₂ in pet. ether); mp 125 °C (hexane); ¹H NMR (400 MHz; CDCl₃): δ 8.61 (s, 1H, Ar-*H*), 7.90 (d, *J* = 9.7 Hz, 1H, Ar-*H*), 6.65 (d, *J* = 9.7 Hz, 1H, Ar-*H*), 3.83 (t, *J* = 4.2 Hz, 4H, N(CH₂)₂), 3.75 (t, *J* = 4.2 Hz, 4H, O(CH₂)₂); ¹³C NMR (126 MHz; CDCl₃): δ 161.0, 150.3, 142.3 (app. ddq, *J* = 255.1, 12.4, 4.3 Hz), 140.2 (app. dtt, *J* = 258.6, 13.4, 3.9 Hz), 137.9 (app. dtdd, *J* = 253.3, 13.5, 5.2, 2.8 Hz), 137.2, 124.2 (app. tdd, *J* = 13.6, 4.9, 2.3 Hz), 117.9, 105.4, 66.6, 45.0; ¹⁹F NMR (377 MHz; CDCl₃): δ -150.7 (d, *J* = 17.9 Hz, 2F), -155.6 (t, *J* = 21.8 Hz, 1F), -161.1 (dd, *J* = 21.7, 18.5 Hz, 2F); IR ν_{max} (neat)/cm⁻¹ 1590, 1518, 1389 (SO₂), 1191 (SO₂), 996, 747, 711 (C-O-S); HRMS (ESI) found *m/z* 411.0428 [M+H]⁺, C₁₅H₁₂O₄N₂F₅³²S requires *m/z* 411.0432.

Pentafluorophenyl 2-methoxypyridine-5-sulfonate ester (**2z**)



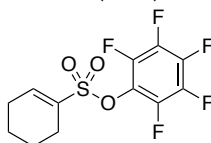
Prepared according to general procedure B using 2-methoxy-5-pyridineboronic acid (77 mg, 0.5 mmol). Flash column chromatography (10% EtOAc in pet. ether) afforded the sulfonate as a brown oil (30 mg, 34%). *R*_f = 0.57 (15% EtOAc in pet. ether); ¹H NMR (500 MHz; CDCl₃): δ 8.72 (dd, *J* = 2.6, 0.5 Hz, 1H, Ar-*H*), 8.07 (dd, *J* = 8.9, 2.6 Hz, 1H, Ar-*H*), 6.92 (dd, *J* = 8.9, 0.5 Hz, 1H, Ar-*H*), 4.06 (s, 3H, OCH₃); ¹³C NMR (126 MHz; CDCl₃): δ 168.2, 149.4, 142.4 (app. ddq, *J* = 255.7, 12.4, 4.1 Hz), 140.4 (app. dtt, *J* = 255.8, 13.6, 3.9 Hz), 138.2, 138.0 (app. dtdd, *J* = 255.8, 13.8, 5.5, 3.1 Hz), 124.3, 123.9 (app. tdd, *J* = 13.3, 5.0, 2.3 Hz), 112.3, 54.9; ¹⁹F NMR (377 MHz; CDCl₃): δ -150.7 (d, *J* = 17.4 Hz, 2F), -154.9 (t, *J* = 21.8 Hz, 1F), -160.7 (dd, *J* = 21.7, 17.6 Hz, 2F); IR ν_{max} (neat)/cm⁻¹ 1591, 1519, 1487, 1384 (SO₂), 1196 (SO₂), 997, 726 (C-O-S); HRMS (ESI) found *m/z* 356.0010 [M+H]⁺, C₁₂H₇O₄NF₅³²S requires *m/z* 356.0011.

Pentafluorophenyl 3-thienylsulfonate ester (**2aa**)



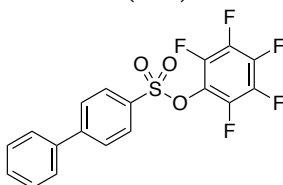
Prepared according to general procedure A using 3-thienylboronic acid (64 mg, 0.5 mmol). Time for SO₂ insertion (t_i) was adjusted from 30 minutes to 1 hour. Flash column chromatography (10% Et₂O in pet. ether) afforded the sulfonate as an off-white solid (22 mg, 27%). R_f = 0.34 (15% Et₂O in pet. ether); mp 88 °C (hexane); ¹H NMR (500 MHz; CDCl₃): δ 8.20 (dd, *J* = 3.1, 1.3 Hz, 1H, Ar-*H*), 7.56 (dd, *J* = 5.2, 3.1 Hz, 1H, Ar-*H*), 7.51 (dd, *J* = 5.2, 1.3 Hz, 1H, Ar-*H*); ¹³C NMR (126 MHz; CDCl₃): δ 142.6 (app. ddq, *J* = 255.6, 12.4, 4.2 Hz), 140.5 (app. dtt, *J* = 255.7, 13.6, 3.7 Hz), 138.0 (app. dtdd, *J* = 254.0, 13.8, 5.6, 3.0 Hz), 134.9, 133.8, 129.0, 126.3, 124.2 (app. tdd, *J* = 14.4, 4.7, 2.2 Hz); ¹⁹F NMR (377 MHz; CDCl₃): δ -150.8 (d, *J* = 17.5 Hz, 2F), -155.1 (t, *J* = 21.8 Hz, 1F), -160.9 (dd, *J* = 21.6, 17.7 Hz, 2F); IR ν_{max} (neat)/cm⁻¹ 2975, 2922, 1515, 1381 (SO₂), 1178 (SO₂), 992, 807, 754, 719 (C-O-S), 622; HRMS (CI) found *m/z* 328.9367 [M-H]⁻, C₁₀H₂O₃NF₅³²S₂ requires *m/z* 328.9371.

Pentafluorophenyl cyclohex-1-ene-1-sulfonate ester (**2ab**)



Prepared according to general procedure B using 1-cyclohexene-1-ylboronic acid (63 mg, 0.5 mmol). Time for SO₂ insertion (t_i) was adjusted from 30 minutes to 1 hour. Flash column chromatography (20% Et₂O in pet. ether) afforded the sulfonate as a yellow oil (32 mg, 38%). R_f = 0.58 (20% Et₂O in pet. ether); ¹H NMR (500 MHz; CDCl₃): δ 7.01 (tt, *J* = 3.5, 2.1 Hz, 1H, CH₂CHCS), 2.60 (tq, *J* = 6.2, 2.1 Hz, 2H, SCCHCH₂), 2.35 (tq, *J* = 6.2, 3.5 Hz, 2H, SCCH₂), 1.89-1.84 (m, 2H, CH₂), 1.75-1.70 (m, 2H, CH₂); ¹³C NMR (101 MHz; CDCl₃): δ 143.9, 142.5 (app. ddq, *J* = 254.6, 12.4, 4.2 Hz), 140.3 (app. dtt, *J* = 255.4, 12.8, 4.2 Hz), 138.0 (app. dtdd, *J* = 255.8, 13.9, 5.6, 3.1 Hz), 135.4, 124.1 (app. tdd, *J* = 14.3, 4.7, 2.0 Hz), 26.0, 23.7, 21.8, 20.6; ¹⁹F NMR (377 MHz; CDCl₃): δ -151.0 (d, *J* = 17.9 Hz, 2F), -155.8 (t, *J* = 21.8 Hz, 1F), -161.2 (dd, *J* = 21.6, 18.2 Hz, 2F); IR ν_{max} (neat)/cm⁻¹ 2921, 1518, 1389 (SO₂), 1188 (SO₂), 997, 754, 707 (C-O-S), 619; HRMS (CI) found *m/z* 328.0195 [M]⁻, C₁₂H₉O₃F₅³²S requires *m/z* 328.0198.

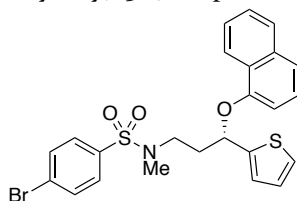
Pentafluorophenyl [1,1'-biphenyl]-4-sulfonate ester (**2ac**)



A glass reaction tube was charged with DABSO (72 mg, 0.3 mmol), PdCl₂(AmPhos)₂ (18 mg, 0.025 mmol) and 4-bromobiphenyl (117 mg, 0.5 mmol), sealed with a rubber septum and evacuated and filled with N₂ four times. Anhydrous isopropanol (1.9 mL) and anhydrous triethylamine (209 μL, 1.5 mmol), were added sequentially through the septum and the reaction mixture stirred under positive pressure of N₂ in a pre-heated aluminium heating block at 75 °C for 16 hours. After allowing the reaction mixture to cool to room temperature, pentafluorophenol (46 mg, 0.25 mmol), Na₂S₂O₈ (119 mg, 0.5 mmol), CuBr₂ (11 mg, 0.05 mmol), NaBr (16 mg, 0.15 mmol), powdered activated 3 Å molecular sieves (250 mg) and triethylamine (140 μL, 1.0 mmol) were added. The reaction vessel was resealed, and the mixture was stirred at room temperature for 18 hours. The reaction mixture was then diluted with EtOAc (5 mL), filtered through a

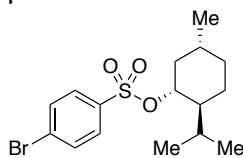
plug of silica and washed with EtOAc (15 mL) before removing the solvent *in vacuo*. Flash column chromatography (2 to 5% Et₂O in pet. ether) afforded the sulfonate as a white solid (49 mg, 49%). *R*_f = 0.41 (30% Et₂O in pet. ether); mp 73 °C (hexane); ¹H NMR (400 MHz; CDCl₃): δ 8.05 (d, *J* = 8.5 Hz, 2H, Ar-*H*), 7.82 (d, *J* = 8.5 Hz, 2H, Ar-*H*), 7.66-7.64 (m, 2H, Ar-*H*), 7.54-7.45 (m, 3H, Ar-*H*); ¹³C NMR (126 MHz; CDCl₃): δ 148.5, 142.4 (app. ddq, *J* = 255.1, 12.3, 4.0 Hz), 140.5 (app. dtt, *J* = 255.7, 13.4, 3.8 Hz), 138.7, 137.0 (app. dtdd, *J* = 253.7, 13.5, 5.6, 3.0 Hz), 133.3, 129.4, 129.26, 129.13, 128.2, 127.6, 124.3 (app. tdd, *J* = 14.3, 4.5, 2.1 Hz); ¹⁹F NMR (377 MHz; CDCl₃): δ -150.5 (d, *J* = 17.8 Hz, 2F), -155.3 (t, *J* = 21.8 Hz, 1F), -161.0 (dd, *J* = 21.6, 17.8 Hz, 2F); IR *v*_{max} (neat)/cm⁻¹ 1516, 1389 (SO₂), 1196 (SO₂), 990, 844, 767 (C-O-S), 711; HRMS (CI) found *m/z* 400.0195 [M]⁺, C₁₈H₉O₃F₅³²S requires *m/z* 400.400.0187.

(*S*)-4-bromo-*N*-methyl-*N*-(3-(naphthalen-1-yloxy)-3-(thiophen-2-yl)propyl)phenylsulfonamide ester (**4**)



To a glass reaction tube was added pentafluoro 4-bromophenylsulfonate ester **2q** (202 mg, 0.5 mmol). Acetonitrile (1.5 mL) and (*S*)-Duloxetine (164 mg, 0.55 mmol) were added sequentially, and stirred 16 hours at room temperature. The reaction mixture was diluted with solution of 10% KH₂PO_{4(aq)} (10 mL) and extracted with CH₂Cl₂ (3 × 10 mL). The combined organic phase was dried over MgSO₄, and the solvent was removed *in vacuo*. Flash column chromatography (20% Et₂O in pet. ether) afforded the sulfonamide as an off brown solid (158.2 mg, 61%). [α]_D²⁵ = +42.6 (*c* = 1.0, CHCl₃); *R*_f = 0.33 (30% Et₂O in pet. ether); mp 118 °C; ¹H NMR (400 MHz; CDCl₃): δ 8.30-8.28 (m, 1H, Ar-*H*), 7.79 (dd, *J* = 5.3, 3.3 Hz, 1H, Ar-*H*), 7.62-7.60 (m, 4H, 4 × Ar-*H*), 7.50-7.48 (m, 2H, Ar-*H*), 7.41 (d, *J* = 8.2 Hz, 1H, Ar-*H*), 7.29 (d, *J* = 8.2 Hz, 1H, Ar-*H*), 7.22 (d, *J* = 5.3 Hz, 1H, Ar-*H*), 7.11 (d, *J* = 3.3 Hz, 1H, Ar-*H*), 6.95 (t, *J* = 4.2 Hz, 1H, Ar-*H*), 6.86 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 5.79-5.75 (m, 1H, OCH), 3.32-3.20 (m, 2H, NCH₂), 2.77 (s, 3H, CH₃), 2.53-2.46 (m, 1H, OCHCH_aH_b), 2.37-2.30 (m, 1H, OCHCH_aH_b); ¹³C NMR (101 MHz; CDCl₃): δ 153.1, 144.4, 136.4, 134.7, 132.5, 129.0, 127.81, 127.73, 126.9, 126.5, 126.1, 125.9, 125.46, 125.27, 125.17, 122.0, 121.1, 107.3, 73.7, 47.3, 37.7, 35.8; IR *v*_{max} (neat)/cm⁻¹ 2977, 2921, 1576, 1462, 1391 (SO₂), 1265, 1239, 1161 (SO₂), 1092, 937, 768, 641; HRMS (ESI) found *m/z* 538.0116 [M+Na]⁺, C₂₄H₂₂O₃N⁷⁹Br²³Na³²S₂ requires *m/z* 538.0117.

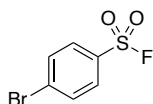
(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4-bromobenzenesulfonate ester (**5**)



A glass reaction tube was charged with (1*R*,2*S*,5*S*)-(-)-menthol (78 mg, 0.5 mmol), sealed with a rubber septum and evacuated and filled with N₂ four times. Anhydrous THF (0.5 mL) was added through the septum, and the reaction mixture was cooled down at 0 °C before *n*-BuLi (0.22 mL, 2.24 M in hexane, 0.5 mmol) was added dropwise. The reaction mixture for stirred at 0 °C for 1 hour. A 10 mL round bottom flask was charged with pentafluoro 4-bromophenylsulfonate ester **2q** (202 mg, 0.5 mmol), sealed with a rubber septum and evacuated and filled with N₂ four times, before anhydrous THF (1.5 mL) was added. The lithiated menthol solution was cannulated on the sulfonate ester solution at 0 °C. The reaction mixture was then warmed to room temperature and stirred 1 hour at this temperature. The reaction mixture was diluted with water (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic phase was dried over MgSO₄, filtered, and the solvent was removed on *vacuo*. Flash column chromatography (5% Et₂O in pet.) afforded the desired sulfonate ester as a beige solid (126 mg, 67%). [α]_D²⁵ = -51.9 (*c* = 1.0, CHCl₃); *R*_f = 0.56 (5% Et₂O in pet. ether); mp 89 °C (hexane/CH₂Cl₂); ¹H NMR (400 MHz; CDCl₃): δ 7.78

(d, $J = 8.5$ Hz, 2H, Ar-*H*), 7.68 (d, $J = 8.5$ Hz, 2H, Ar-*H*), 4.45 (td, $J = 10.8, 4.5$ Hz, 1H, SOCH), 2.13 (dt, $J = 12.3, 4.5$ Hz, 1H, SOCHCH_aH_b), 1.86 (dtd, $J = 13.9, 6.9, 2.0$ Hz, 1H, CH(CH₃)₂), 1.69-1.63 (m, 2H, CH₃CHCH_aH_b and (CH₃)₂CHCHCH_aCH_b), 1.48-1.34 (m, 2H, CH₃CH and (CH₃)₂CHCH), 1.19 (q, $J = 11.7$ Hz, 1H, SOCHCH_aH_b), 0.98 (qd, $J = 13.0, 3.1$ Hz, 1H, (CH₃)₂CHCHCH_aCH_b), 0.89 (d, $J = 6.5$ Hz, 3H, CH₂CHCH₃), 0.85-0.78 (m, 4H, CHCHCH_{3a} and CH₃CHCH_aH_b), 0.56 (d, $J = 6.9$ Hz, 3H, CHCHCH_{3b}); ¹³C NMR (101 MHz; CDCl₃): δ 137.0, 132.5, 129.3, 128.6, 84.7, 47.7, 42.1, 33.8, 31.8, 25.7, 23.1, 22.0, 20.9, 15.4; IR ν_{max} (neat)/cm⁻¹ 2955, 2867, 1577, 1454, 1357 (SO₂), 1180 (SO₂), 1068, 941, 907, 818, 739 (C-O-S); HRMS (ESI) found m/z 397.0443 [M+Na]⁺, C₁₆H₂₃O₃⁷⁹Br²³Na³²S requires m/z 397.0444.

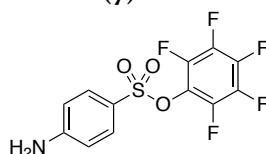
4-Bromophenylsulfonyl fluoride (6)



In a 5 mL round bottom flask was charged perfluoro 4-bromophenylsulfonate ester **2q** (100.8 mg, 0.25 mmol) and methanol (2.0 mL). To the resulting mixture was added dropwise a solution of KF (75 μL, 10 M in methanol, 0.75 mmol). The reaction mixture was stirred at room temperature for 16 hours. The solution was dissolved in water (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic phase was dried on MgSO₄, filtered, and the solvent removed on vacuo. Flash column chromatography (10% CH₂Cl₂ in pet. ether) afforded the desired sulfonyl fluoride as white crystal (47 mg, 78%) with spectroscopic data in accordance with the literature.¹ R_f = 0.40 (10% CH₂Cl₂ in pet. ether); mp 58 °C; ¹H NMR (400 MHz; CDCl₃): δ 7.88 (d, $J = 8.6$ Hz, 2H, Ar-*H*), 7.79 (d, $J = 8.2$ Hz, 2H, Ar-*H*); ¹³C NMR (101 MHz; CDCl₃): δ 133.3, 132.2, 131.5, 130.0; ¹⁹F NMR (377 MHz; CDCl₃): δ 66.4; HRMS (CI) found m/z 237.9101 [M]⁺, C₆H₄BrO₂F³²S requires m/z 237.9094.

(1) Chen, G.; Chen, F.; Zhang, Y.; Yang, X.; Yuan, X.; Wu, F.; Yang, X. *Journal of Fluorine Chemistry* 2012, 133, 155.

Pentafluorophenyl 4-aminophenylsulfonate ester (7)

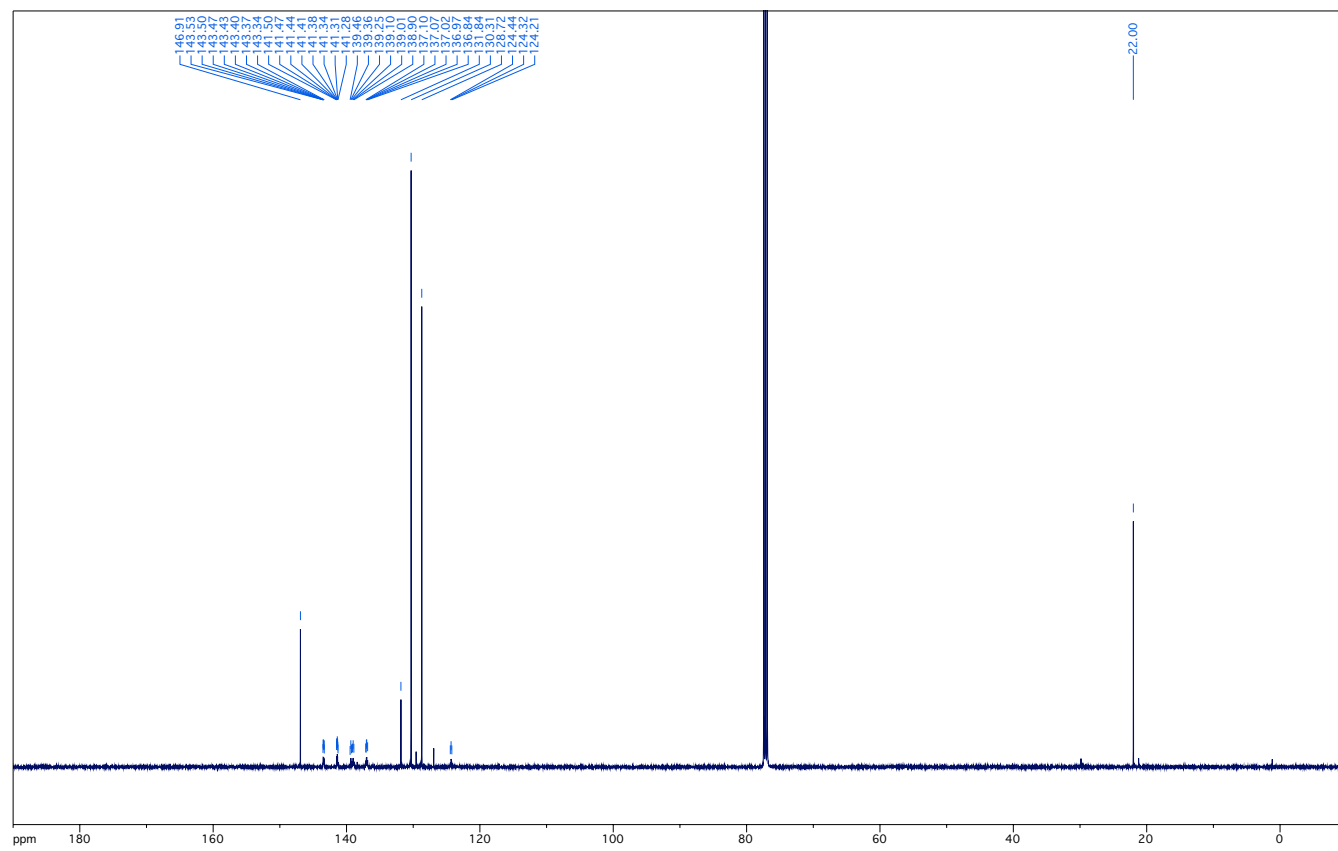
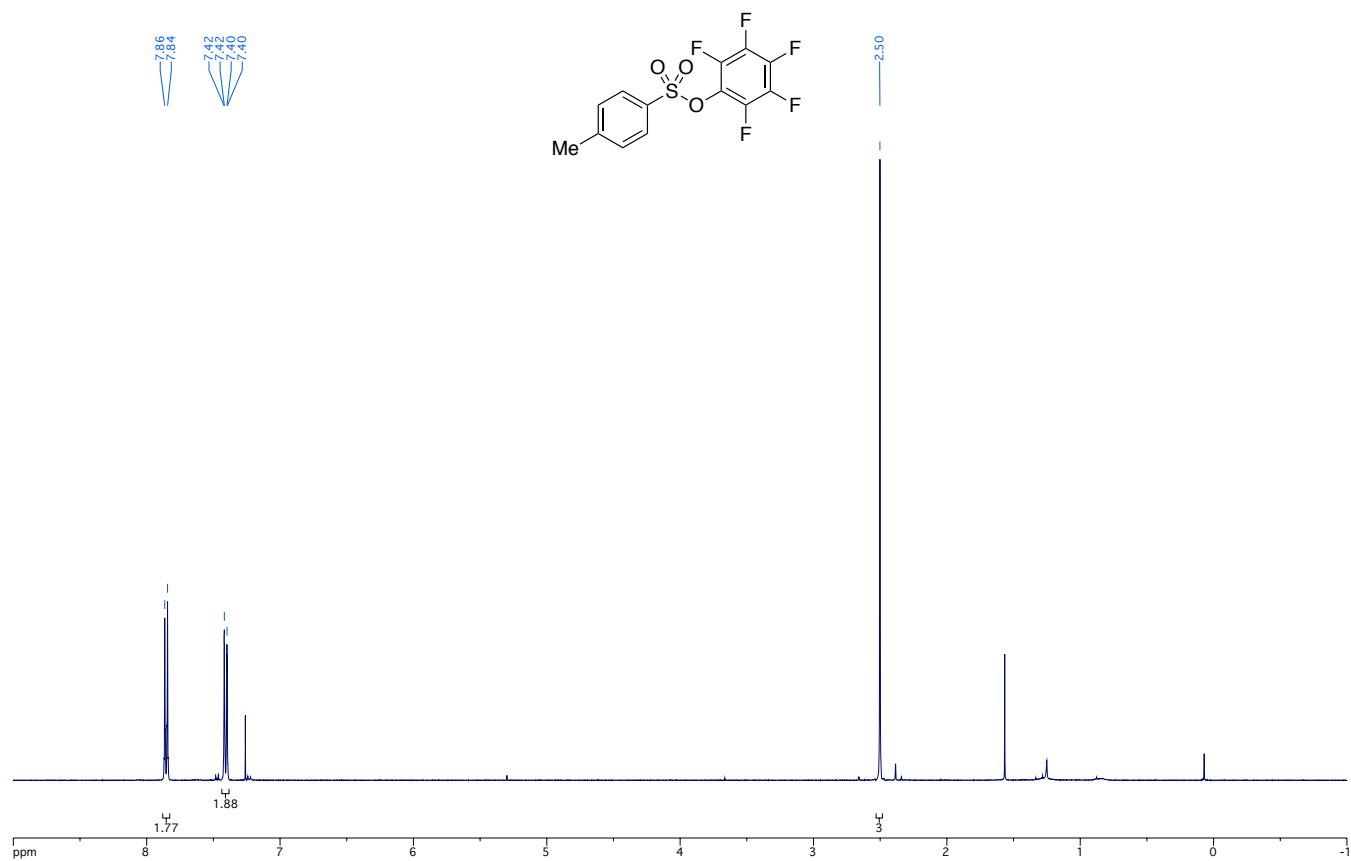


A 150 mL Schlenk flask was charged with perfluoro 4-bromophenylsulfonate ester **2q** (100.8 mg, 0.25 mmol), Pd₂(dba)₃ (4.6 mg, 0.005 mmol), BINAP (7.8 mg, 0.0125 mmol), and sodium tertbutoxide (33.7 mg, 0.35 mmol), sealed with a rubber septum and was evacuated and filled with N₂ four times. Anhydrous toluene (1.6 mL), and benzophenone imine (50 μL, 0.3 mmol) were added sequentially through the rubber septum. The reaction mixture was stirred under positive pressure of N₂ and heated at 80 °C for 18 hours. The reaction mixture was cooled to ambient temperature, filtered through celite and rinsed several times with CH₂Cl₂. After concentrating the solution under reduced pressure, the residue was diluted with THF (1.6 mL). To the reaction mixture was added a solution of 10% HCl_(aq) (1.6 mL). The resulting mixture was stirred vigorously at room temperature for 1 hour. The reaction mixture was neutralised by adding a solution of saturated NaHCO_{3(aq)}. The resulting solution was extracted with EtOAc (3 × 10 mL) and the combined organic layer was dried over MgSO₄, filtered, and the solvent removed under vacuo. Flash column chromatography (5 to 50% Et₂O in pet. ether) afforded the desired product as an off white solid (38 mg, 45%). R_f = 0.46 (50% Et₂O in pet. ether); mp 147 °C; ¹H NMR (500 MHz; CDCl₃): δ 7.71 (d, $J = 8.8$ Hz, 2H, Ar-*H*), 6.71 (d, $J = 8.8$ Hz, 2H, Ar-*H*), 4.38 (s, 2H, NH₂); ¹³C NMR (126 MHz; CDCl₃): δ 152.9, 142.5 (app. ddq, $J = 254.9, 12.5, 4.1$ Hz), 140.2 (app. dtt, $J = 255.0, 17.9, 4.5$ Hz), 138.0 (app. dtdd, $J = 257.4, 14.0, 5.7, 2.9$ Hz), 131.2, 124.5 (app. tdd, $J = 14.1, 4.9, 2.0$ Hz), 121.7, 114.1; ¹⁹F NMR (377 MHz; CDCl₃): δ -150.7 (d, $J = 17.8$ Hz, 2F), -156.1 (t, $J = 21.8$ Hz, 1F), -161.5 (dd, $J = 21.8, 17.6$ Hz, 2F); IR ν_{max} (neat)/cm⁻¹ 3489, 3390,

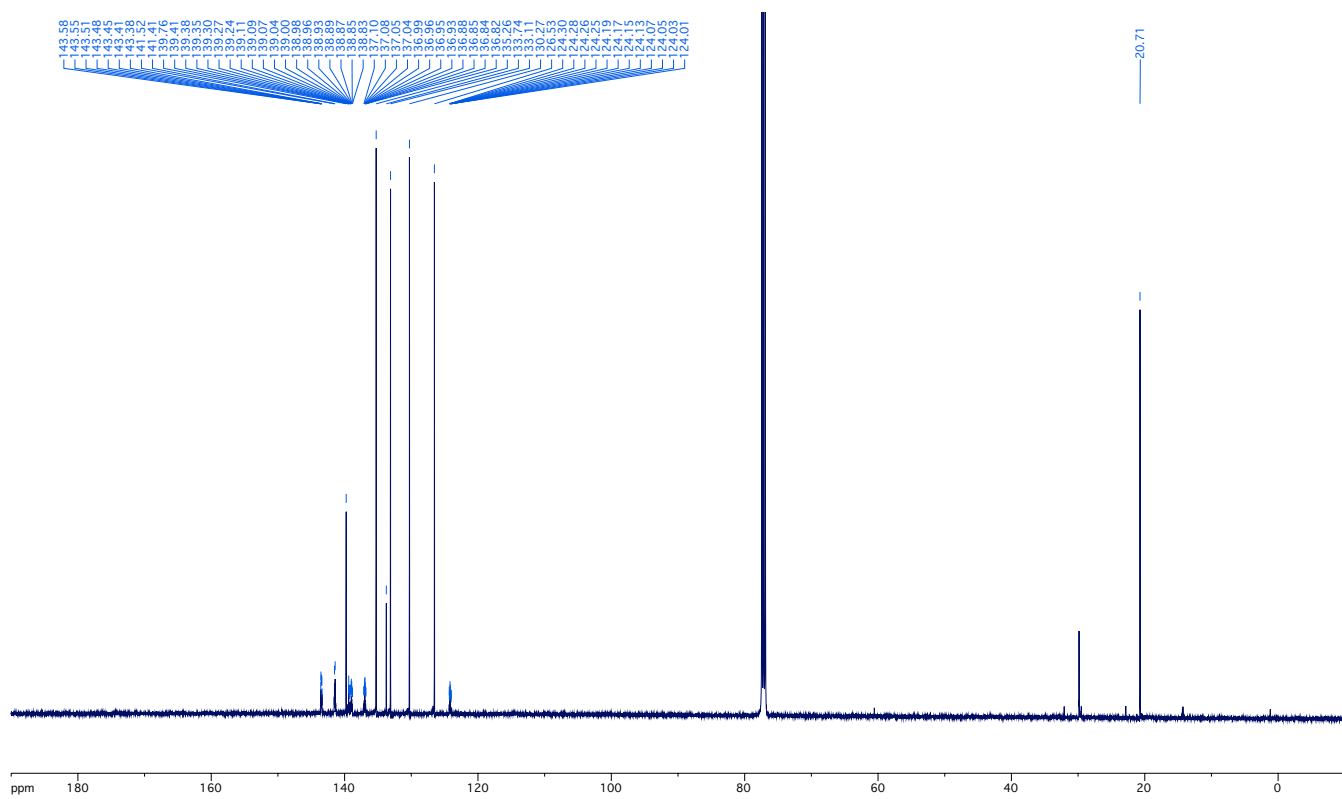
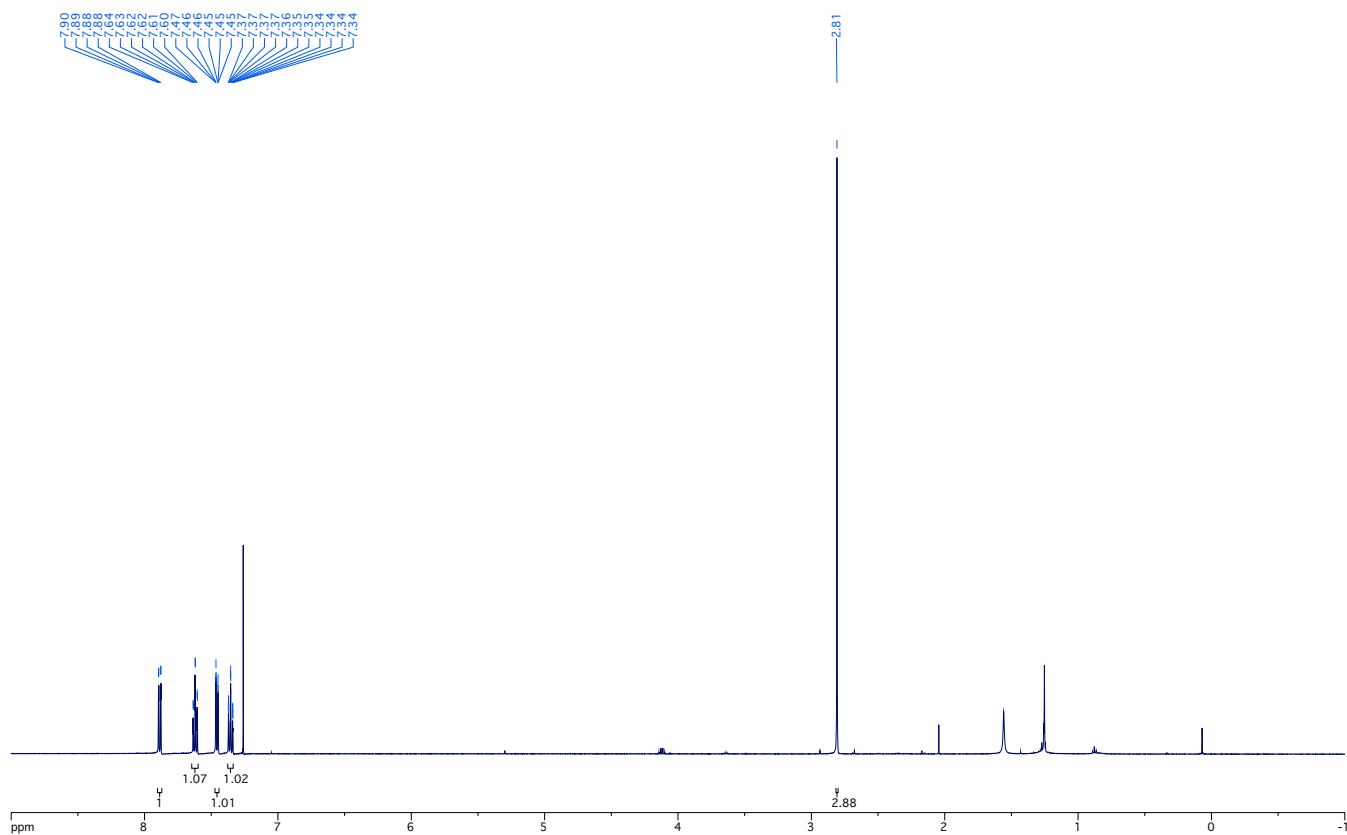
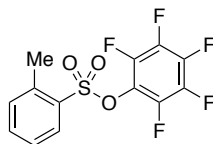
1636, 1598, 1365 (SO₂), 1201, 1168 (SO₂), 1091, 993, 830, 759 (C-O-S); HRMS (ESI) found m/z 361.9883 [M+Na]⁺, C₁₂H₆O₃NF₅²³Na³²S requires m/z 361.9881.

4) ^1H and ^{13}C NMR Spectra

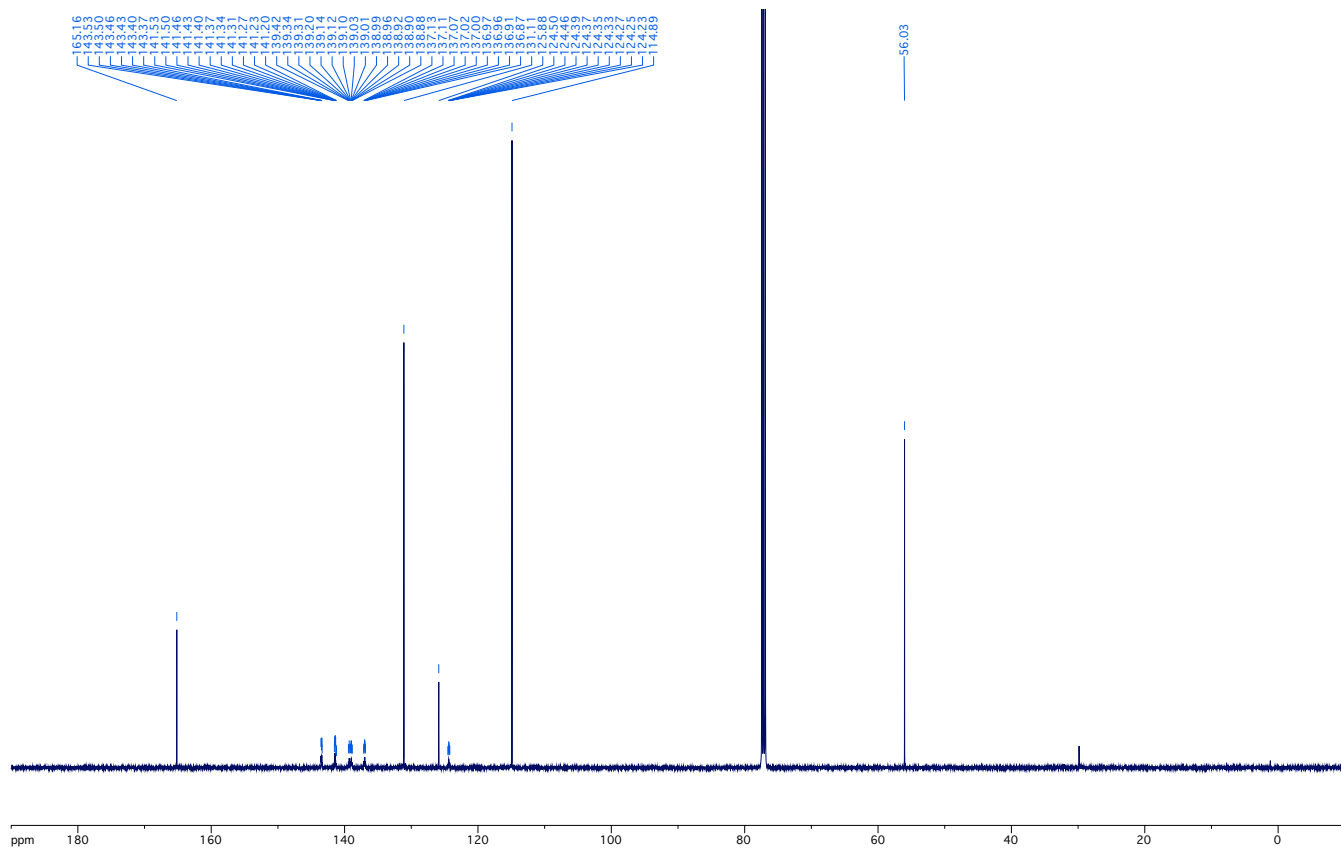
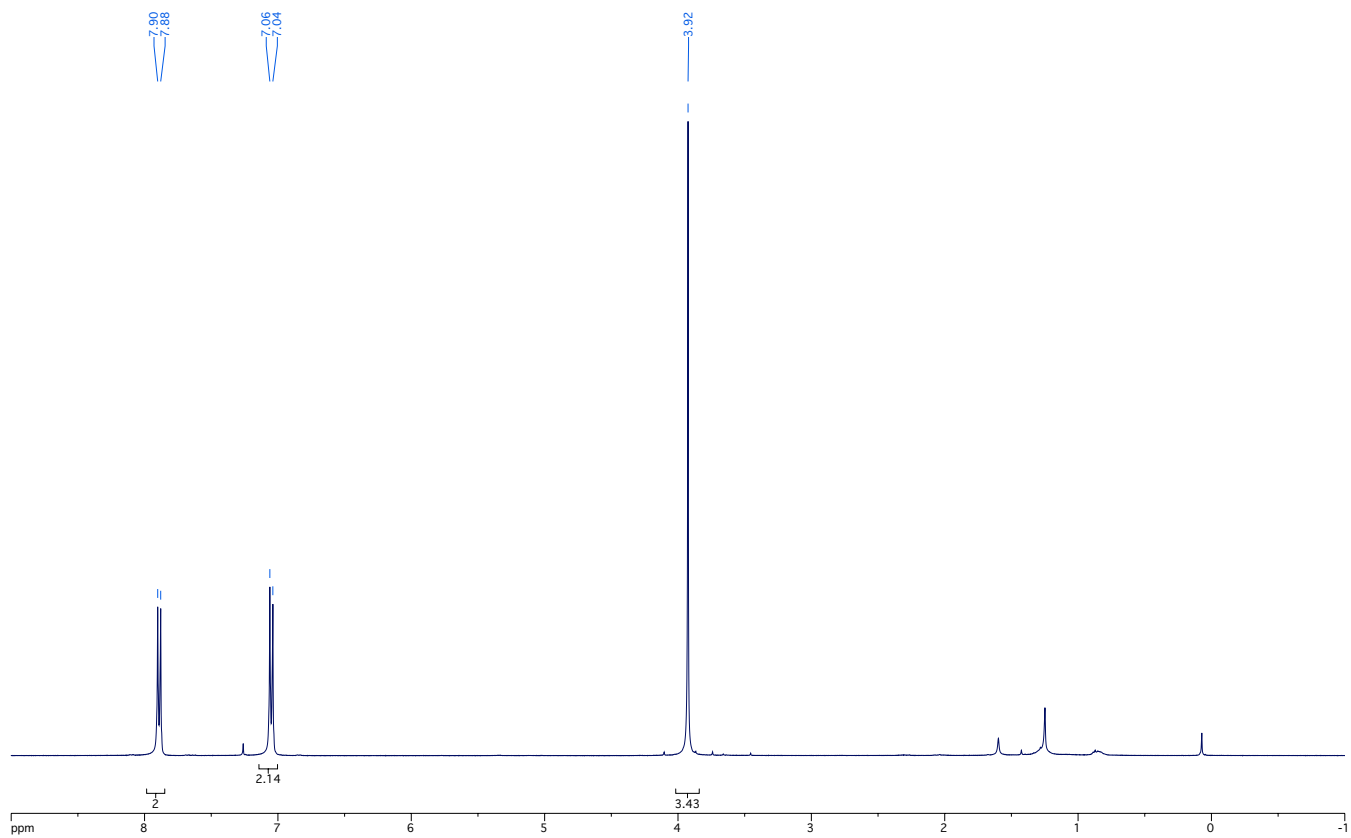
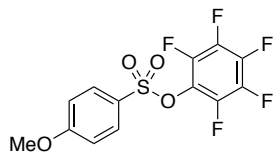
Compound **2a**



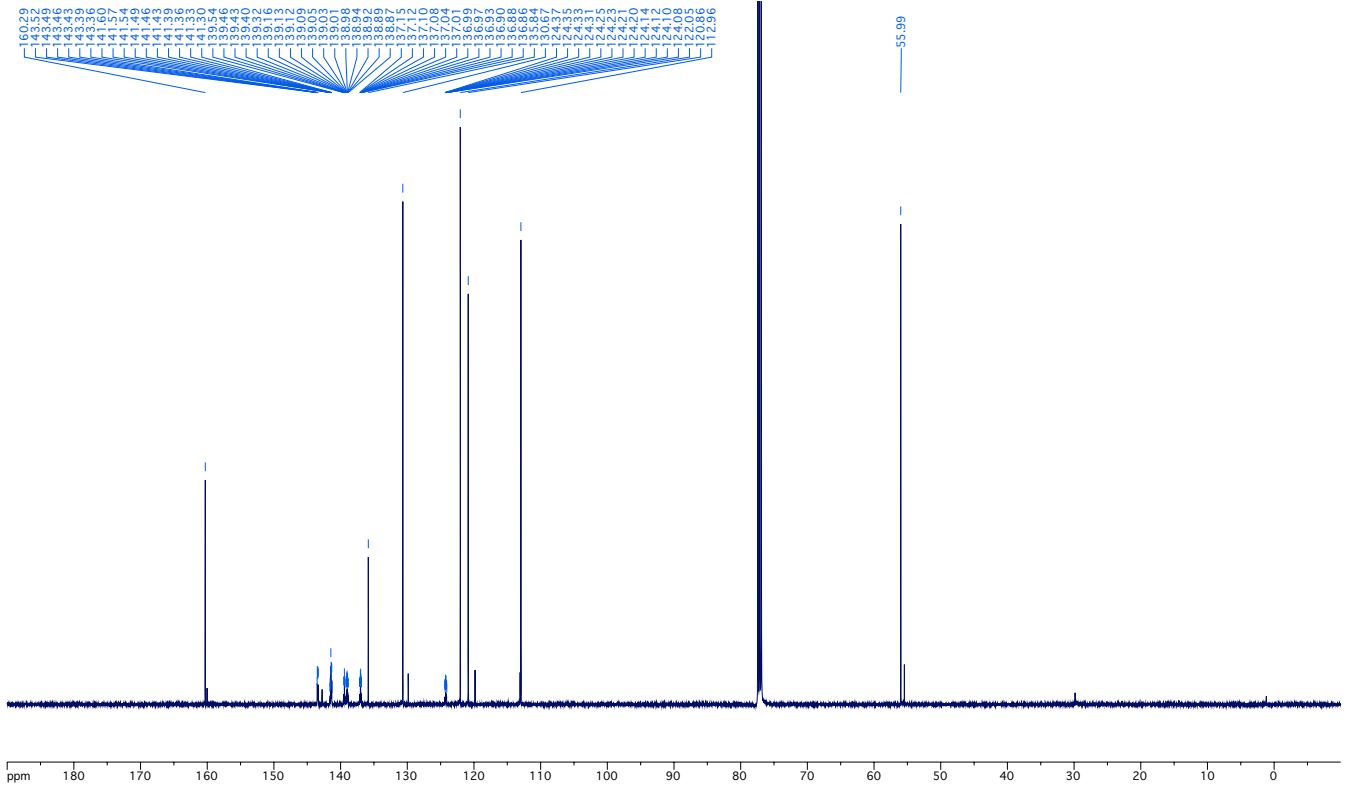
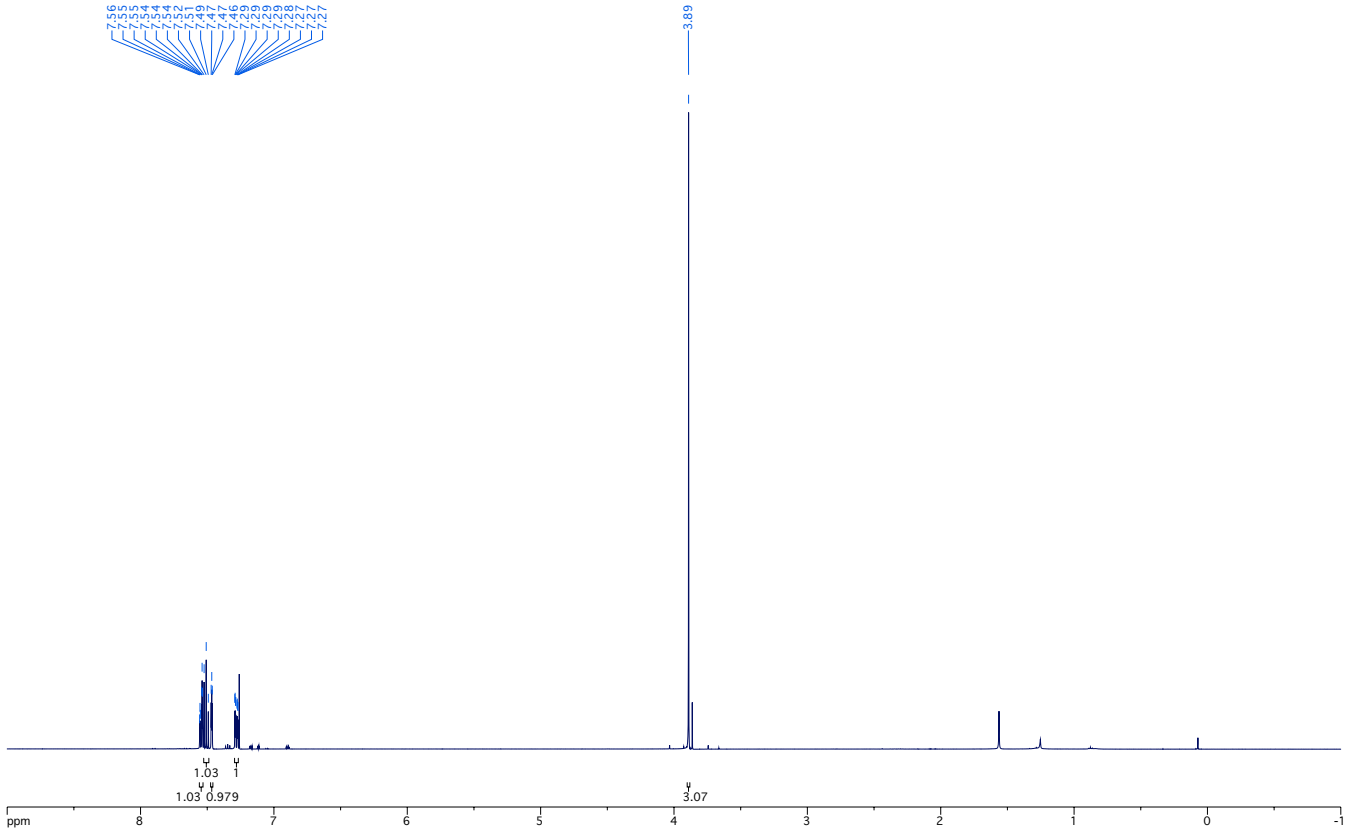
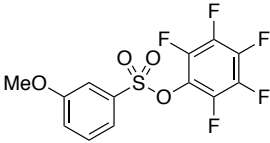
Compound 2b



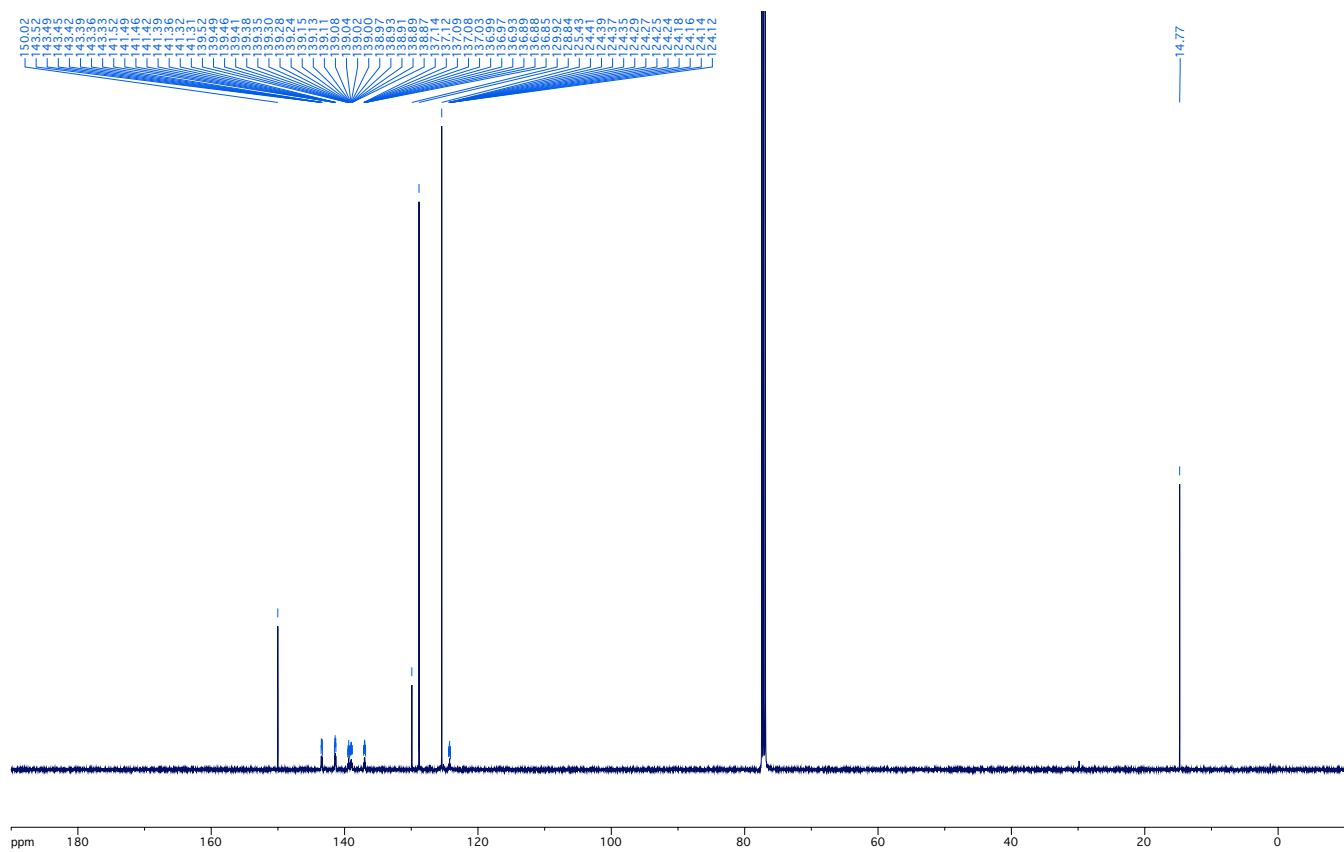
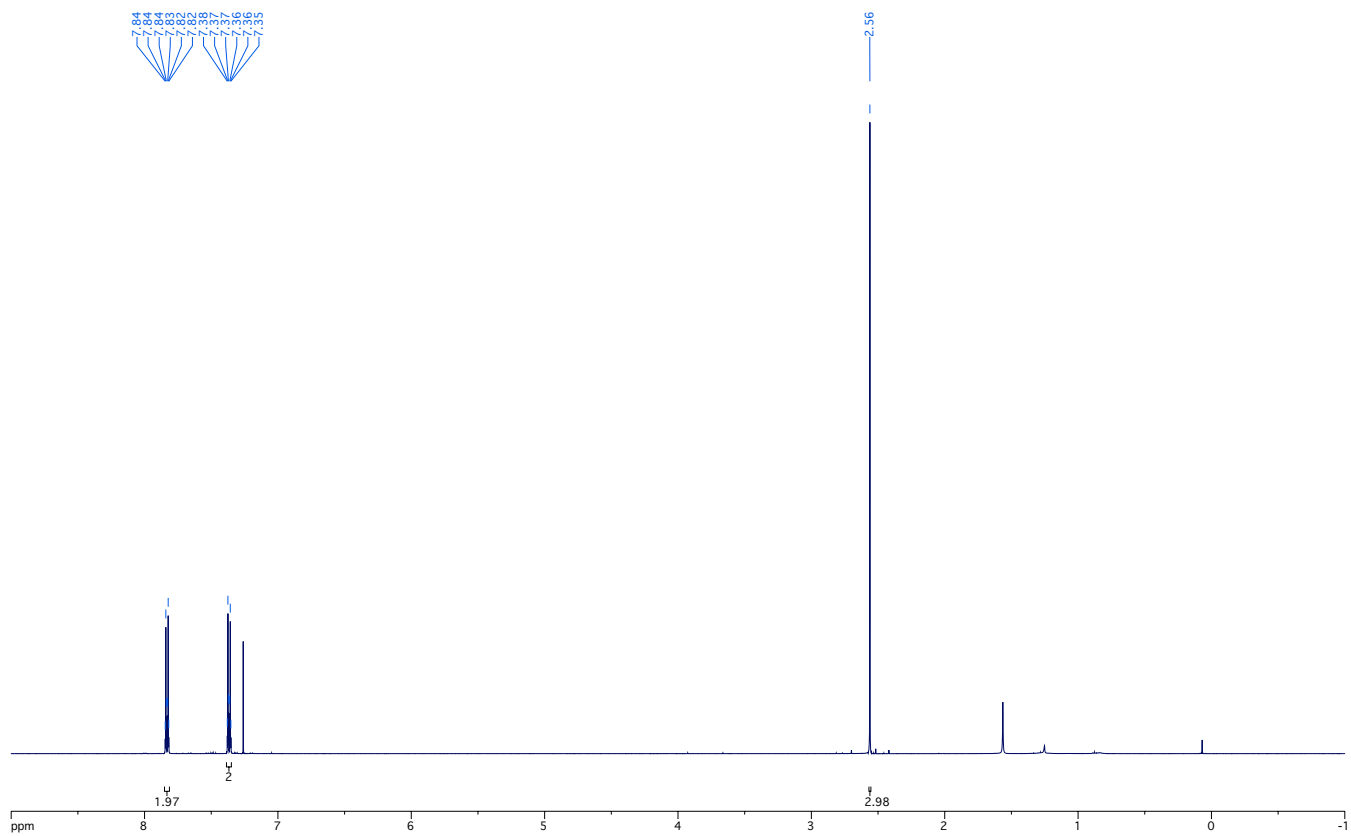
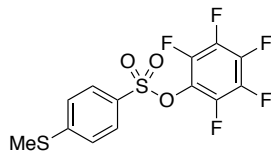
Compound 2c



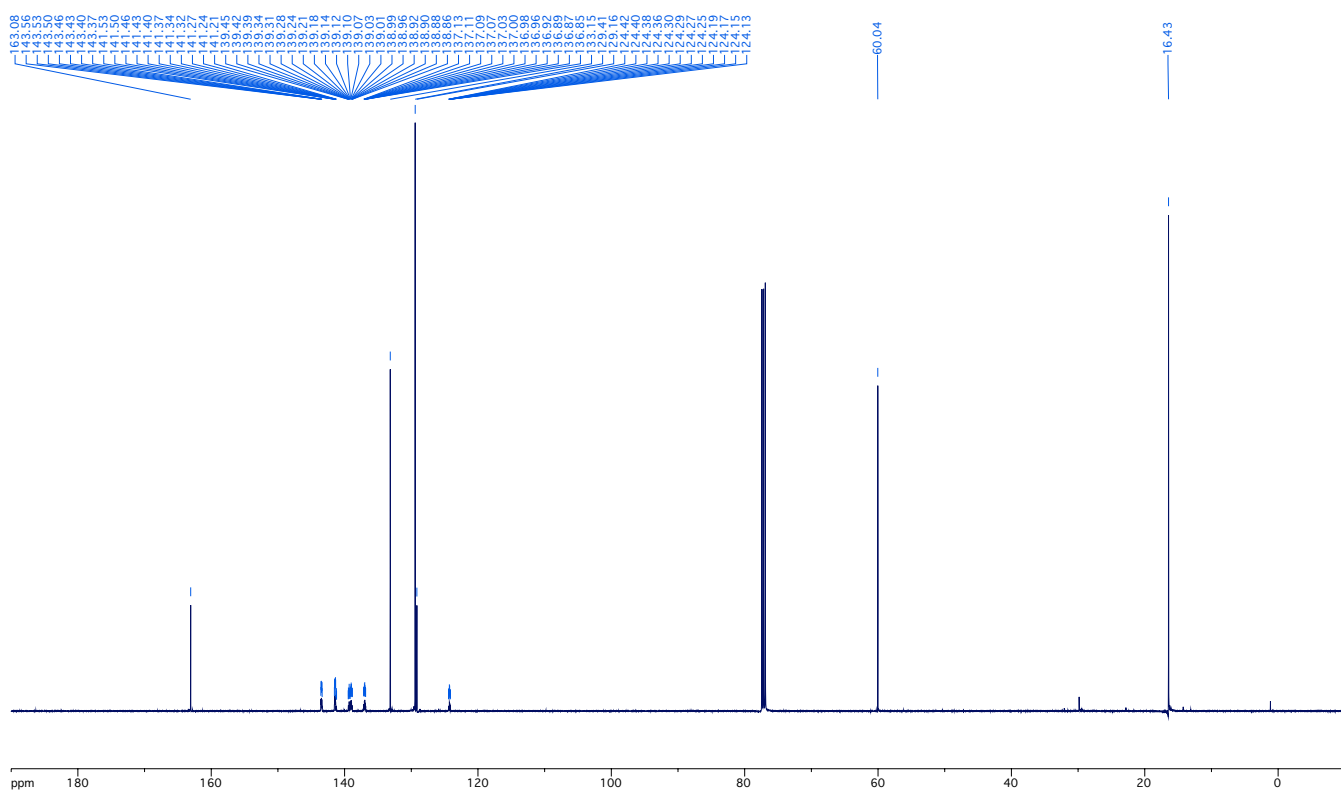
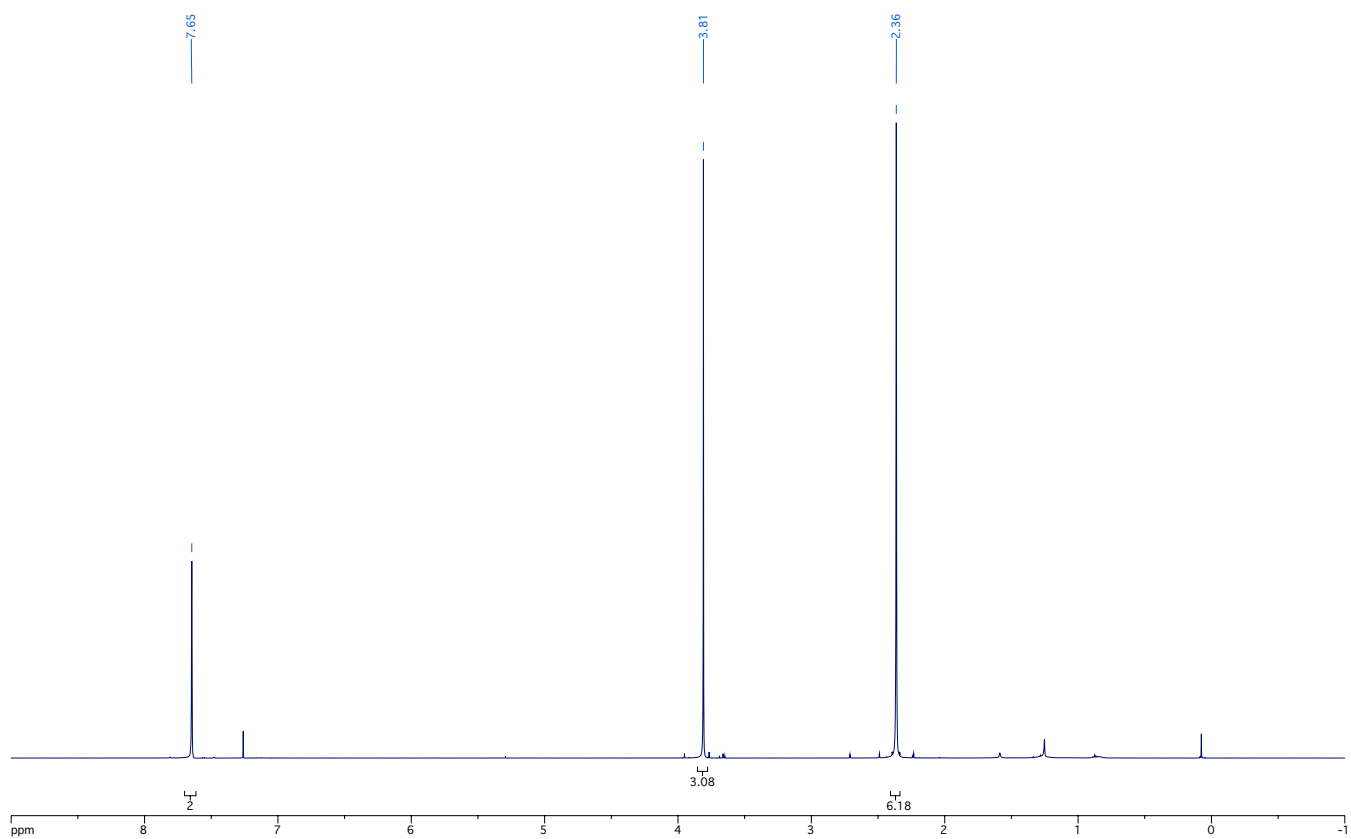
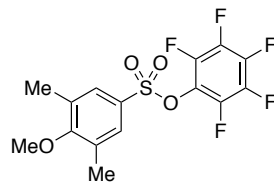
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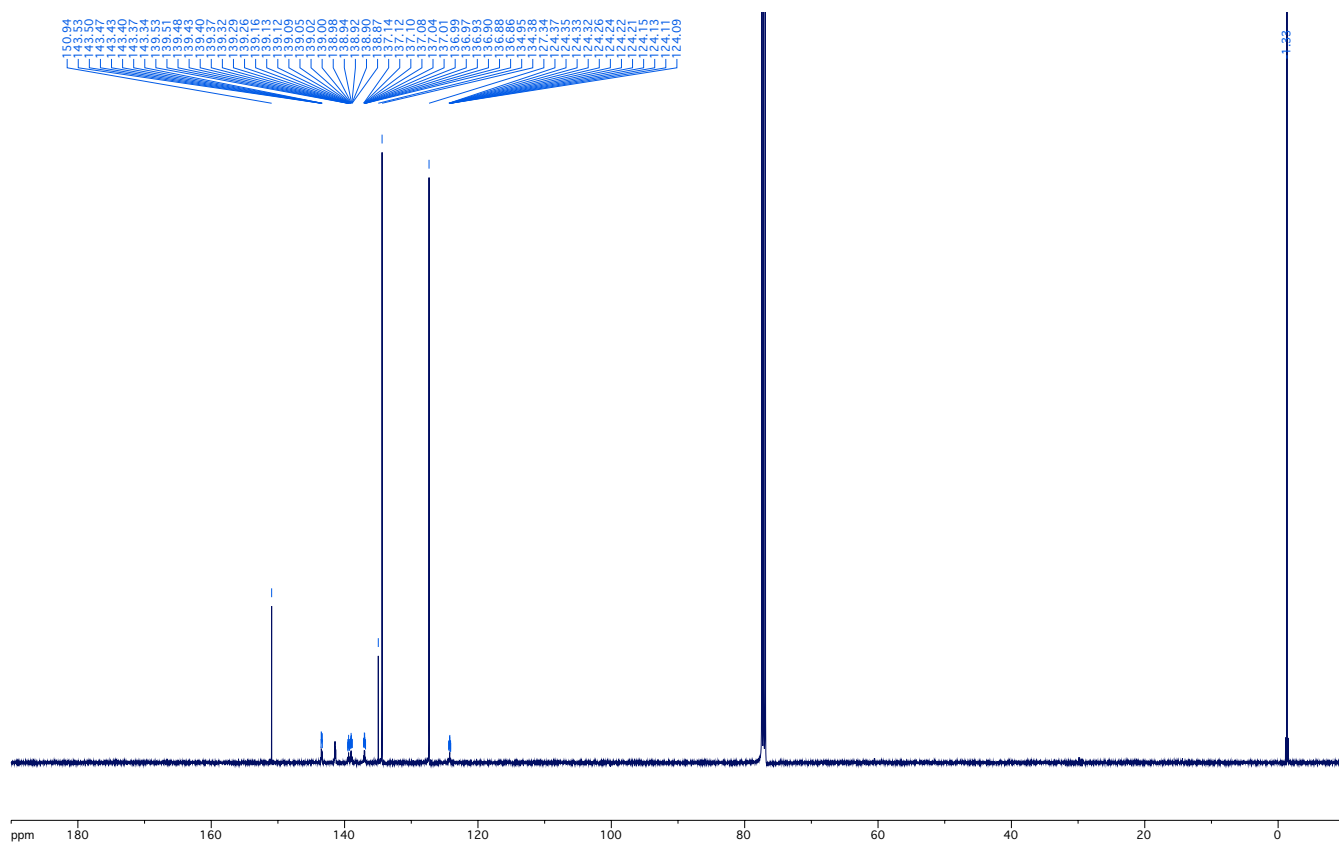
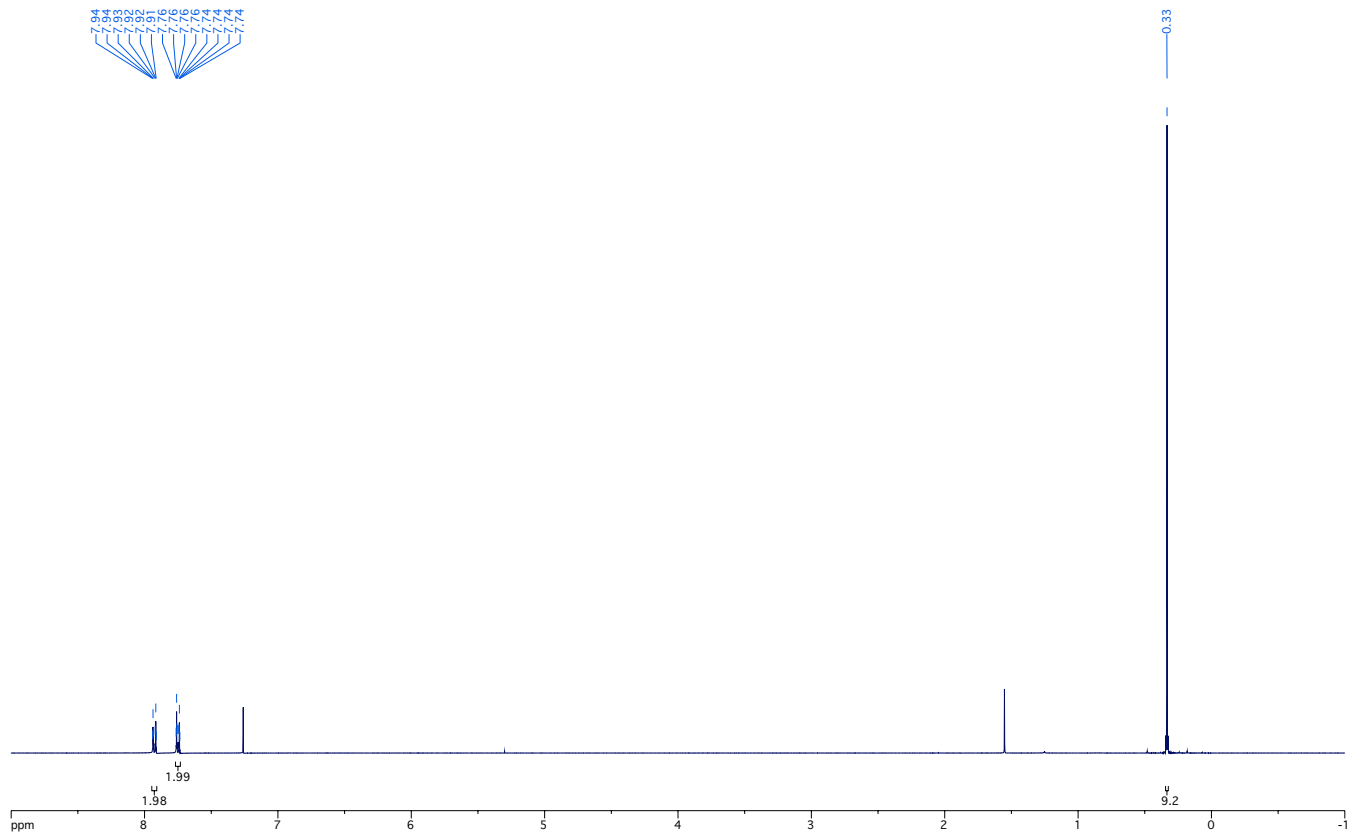
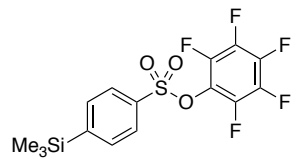
Compound 2e



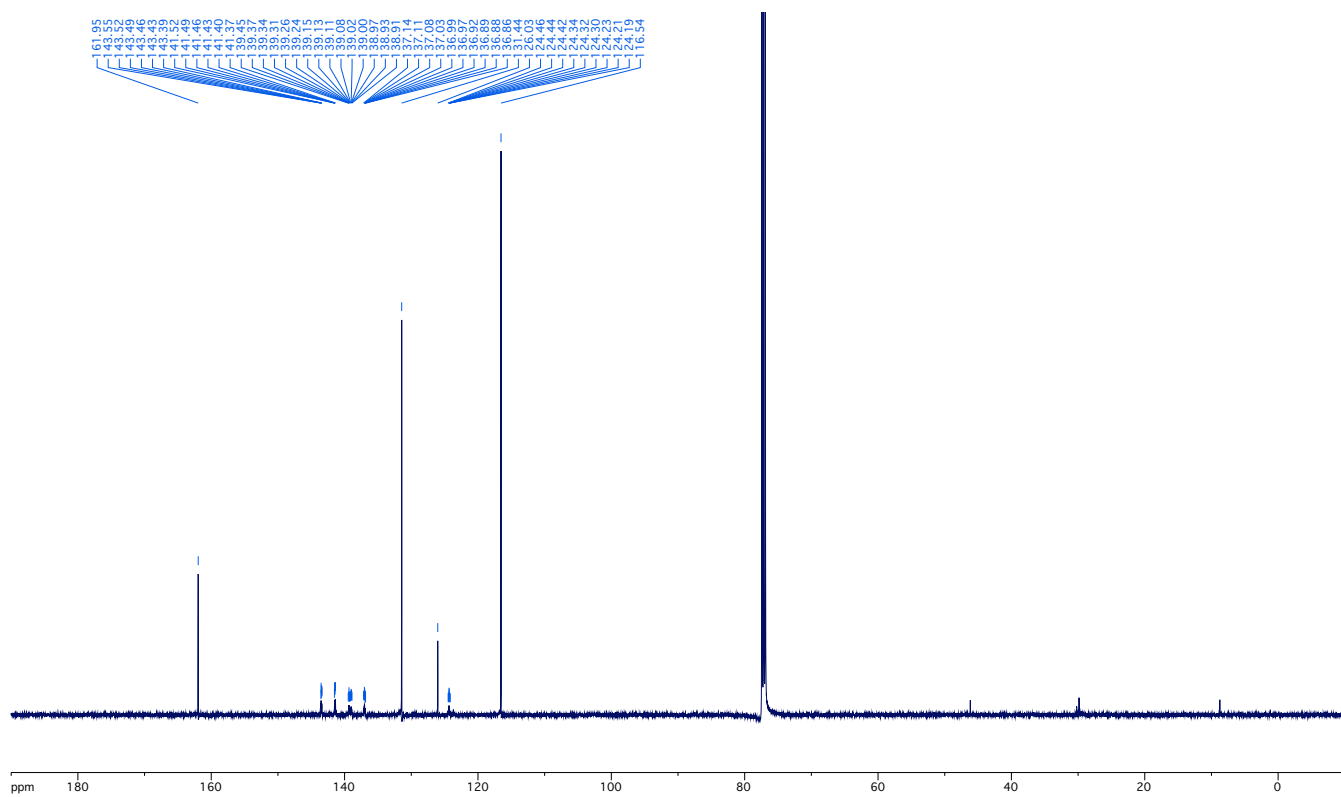
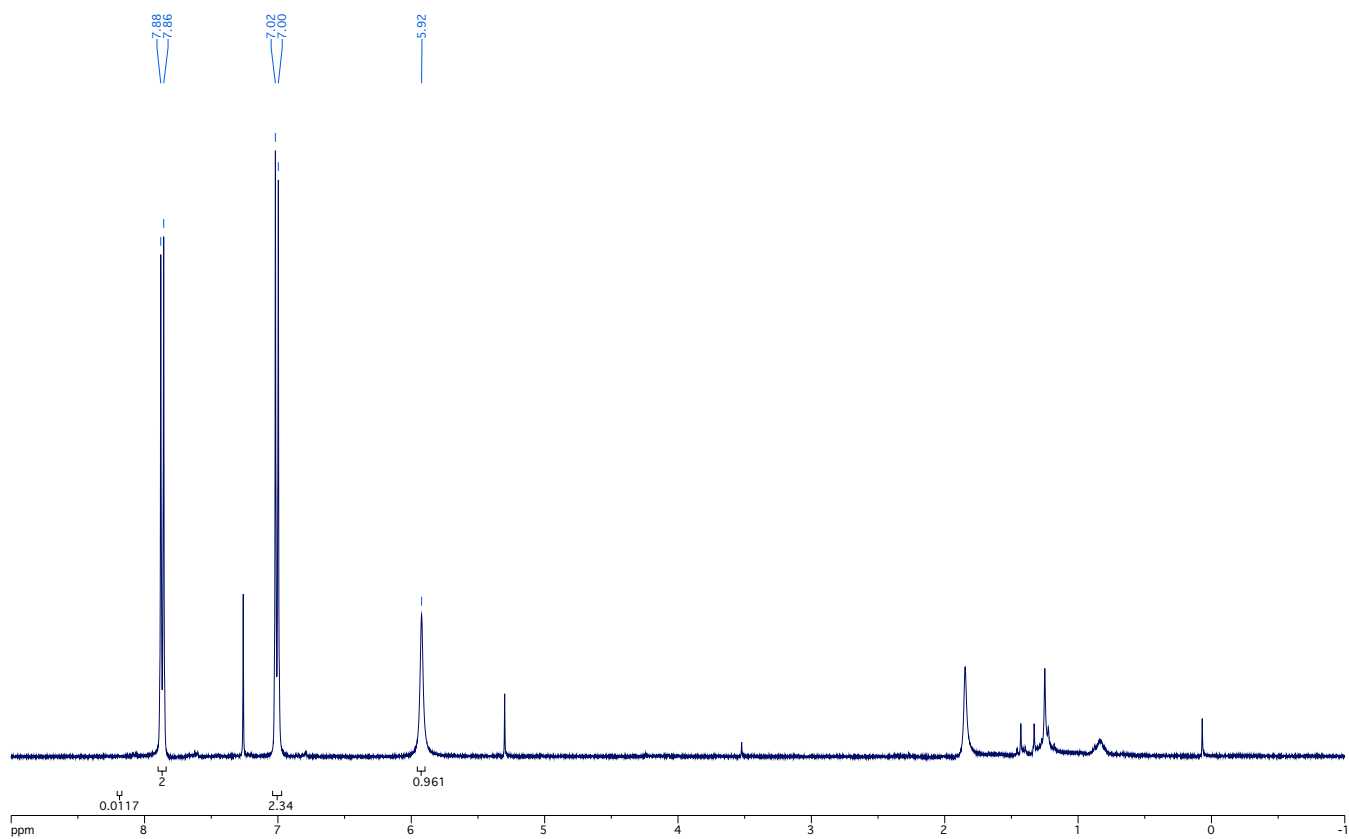
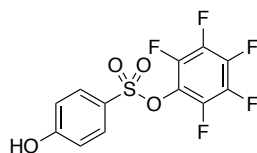
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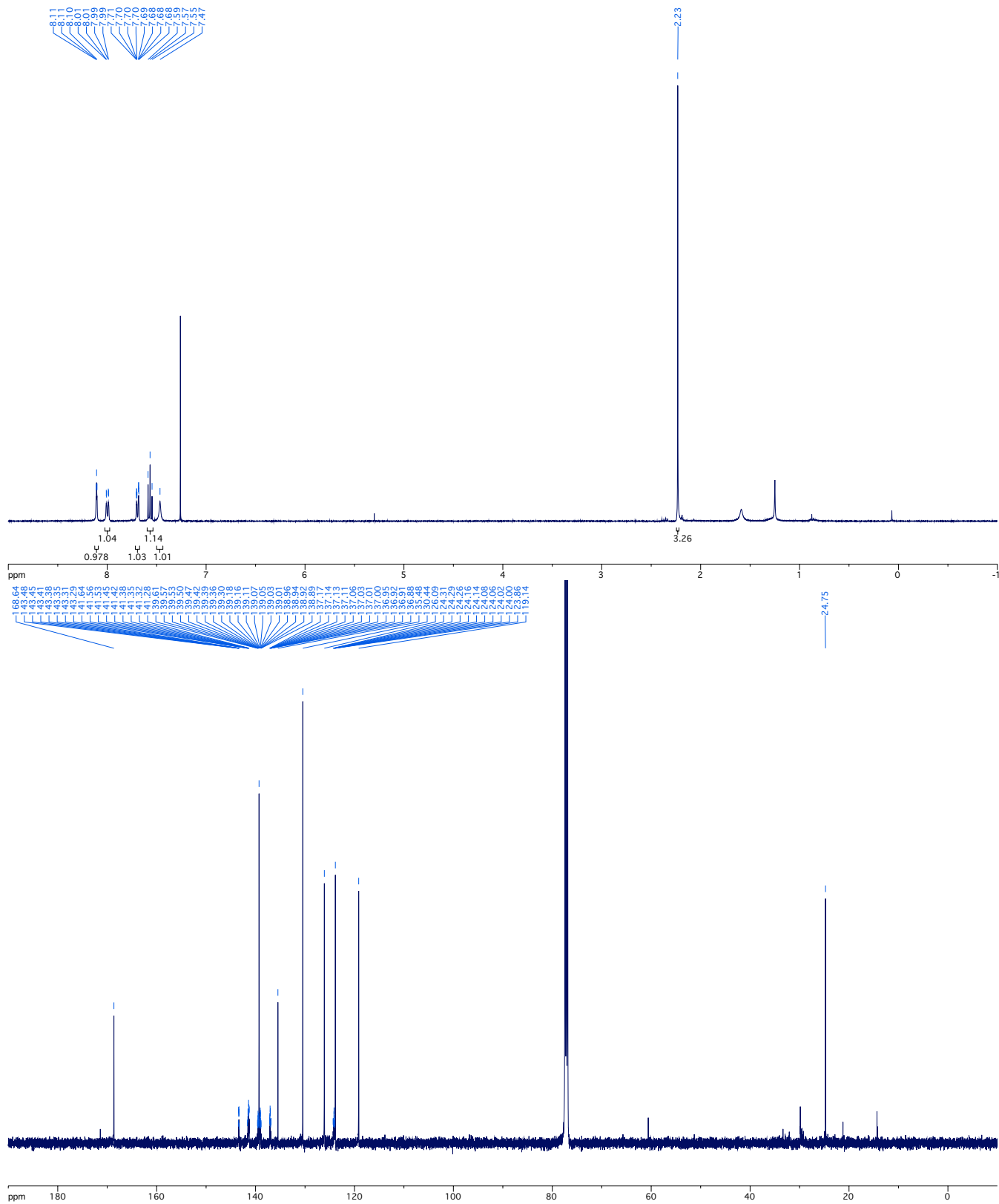
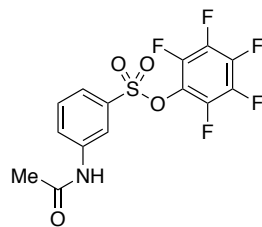
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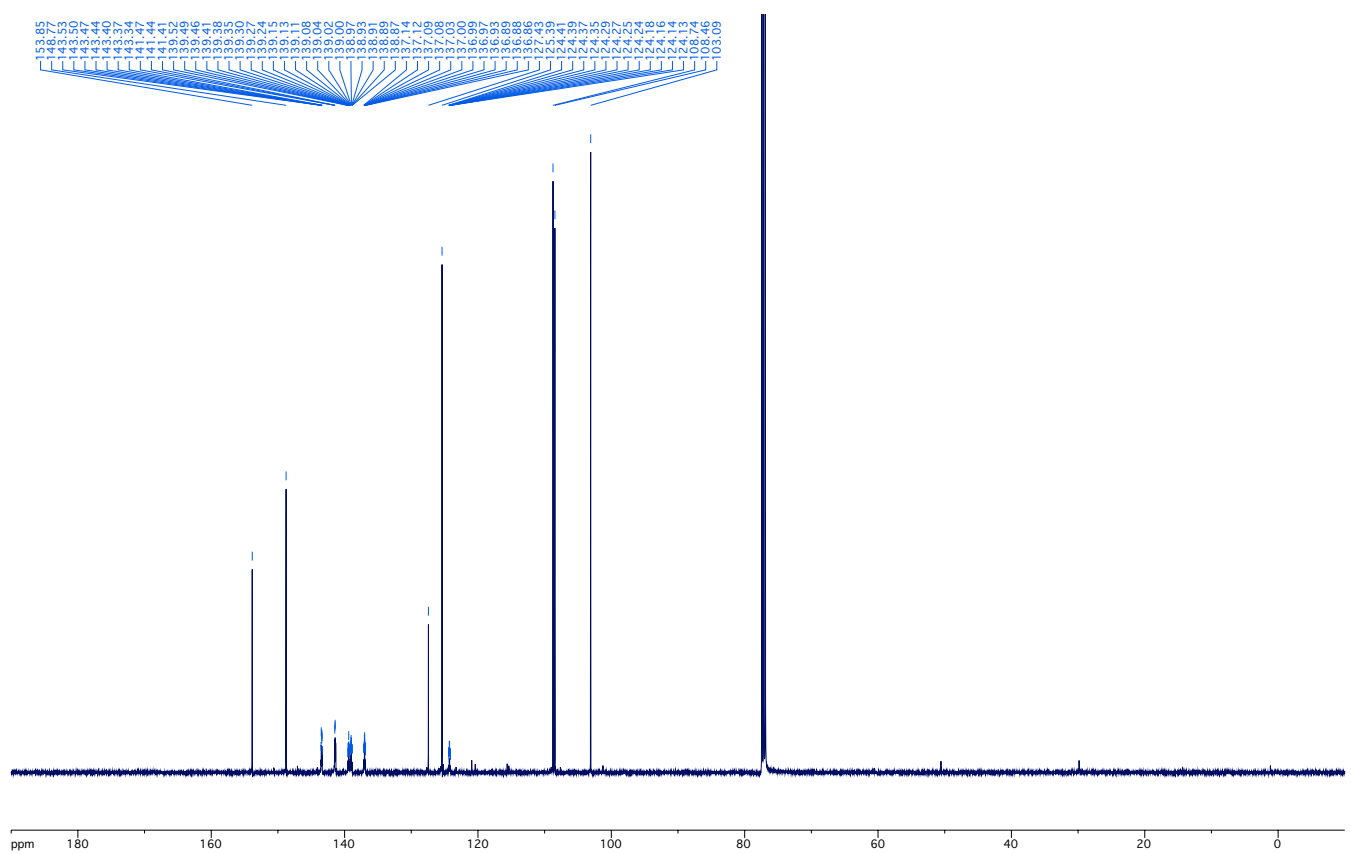
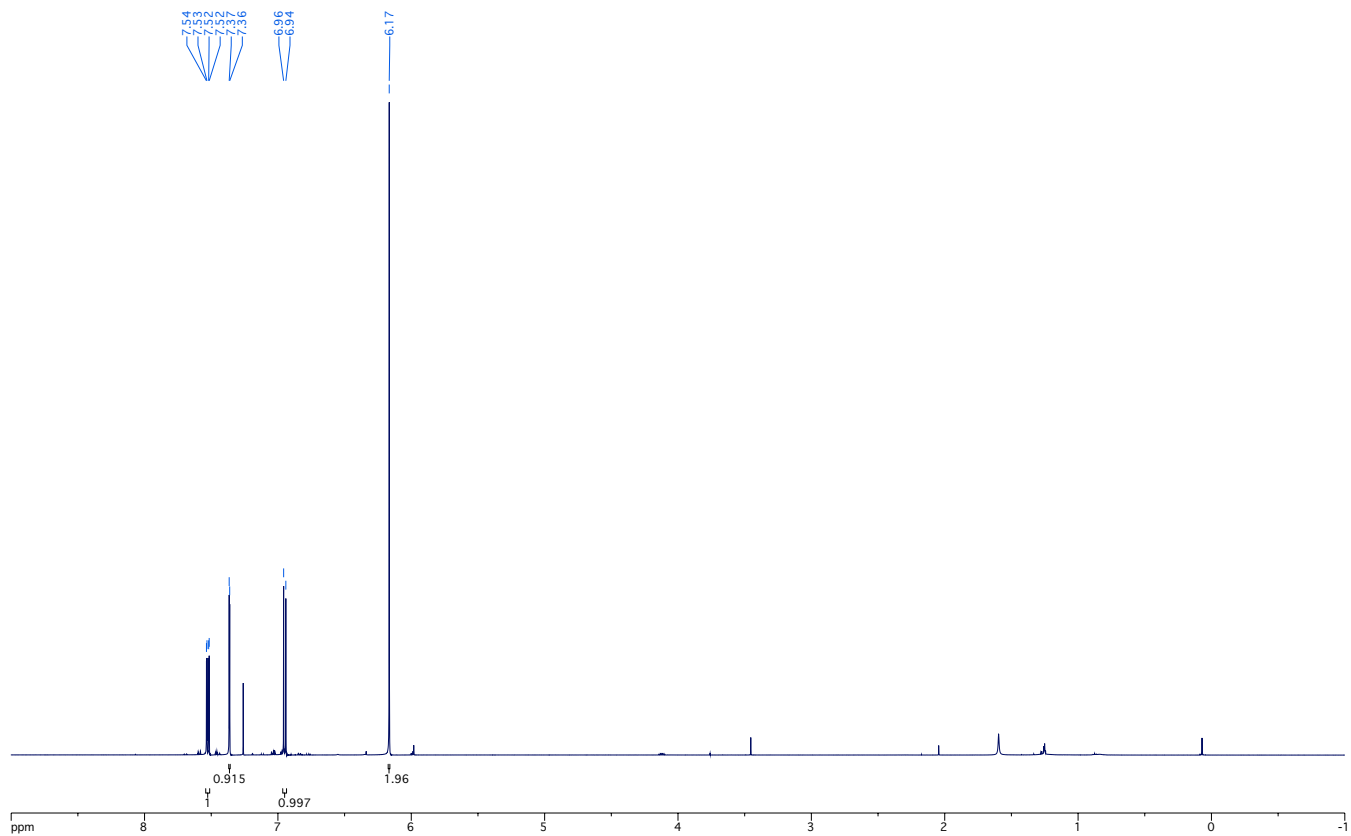
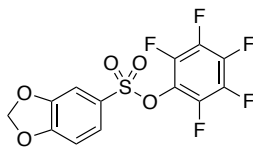
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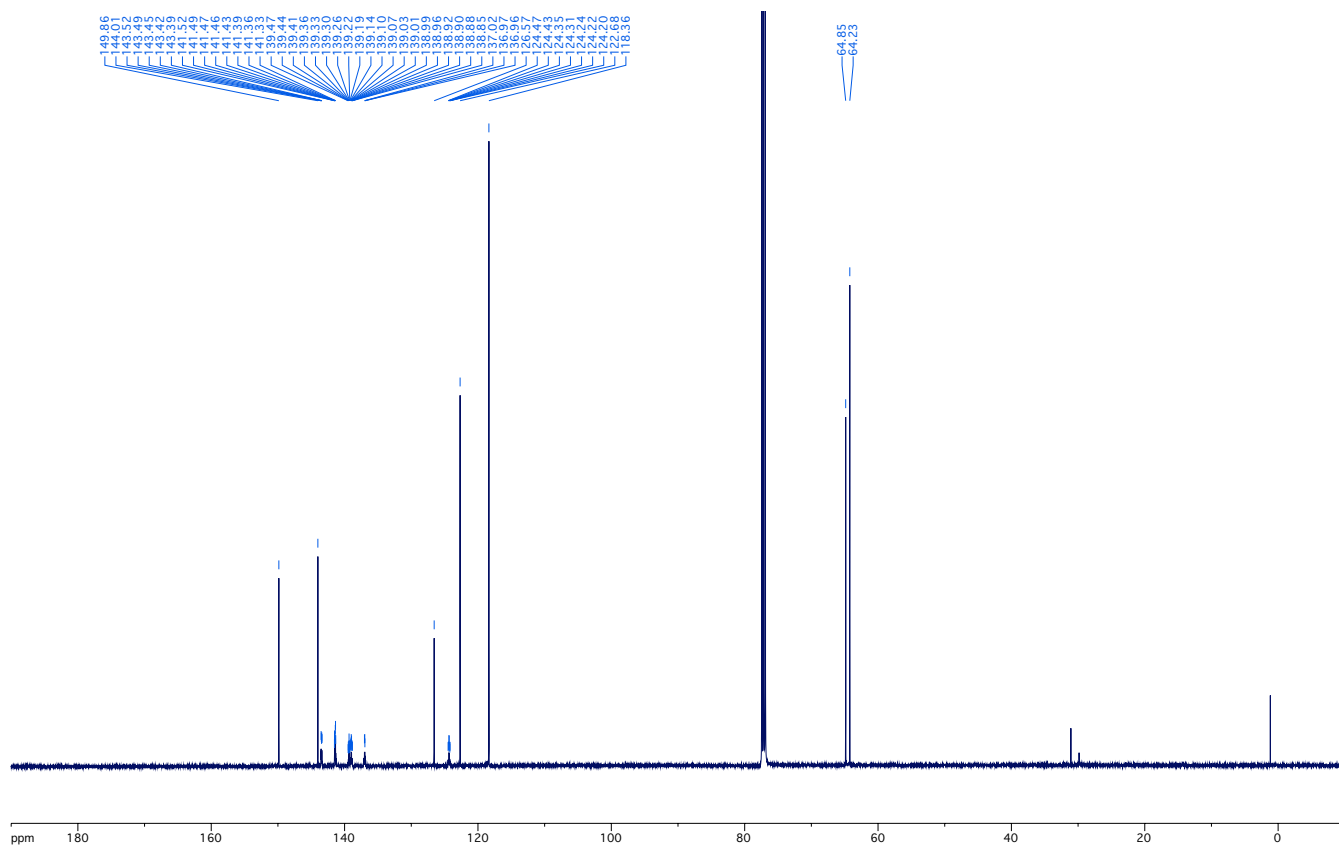
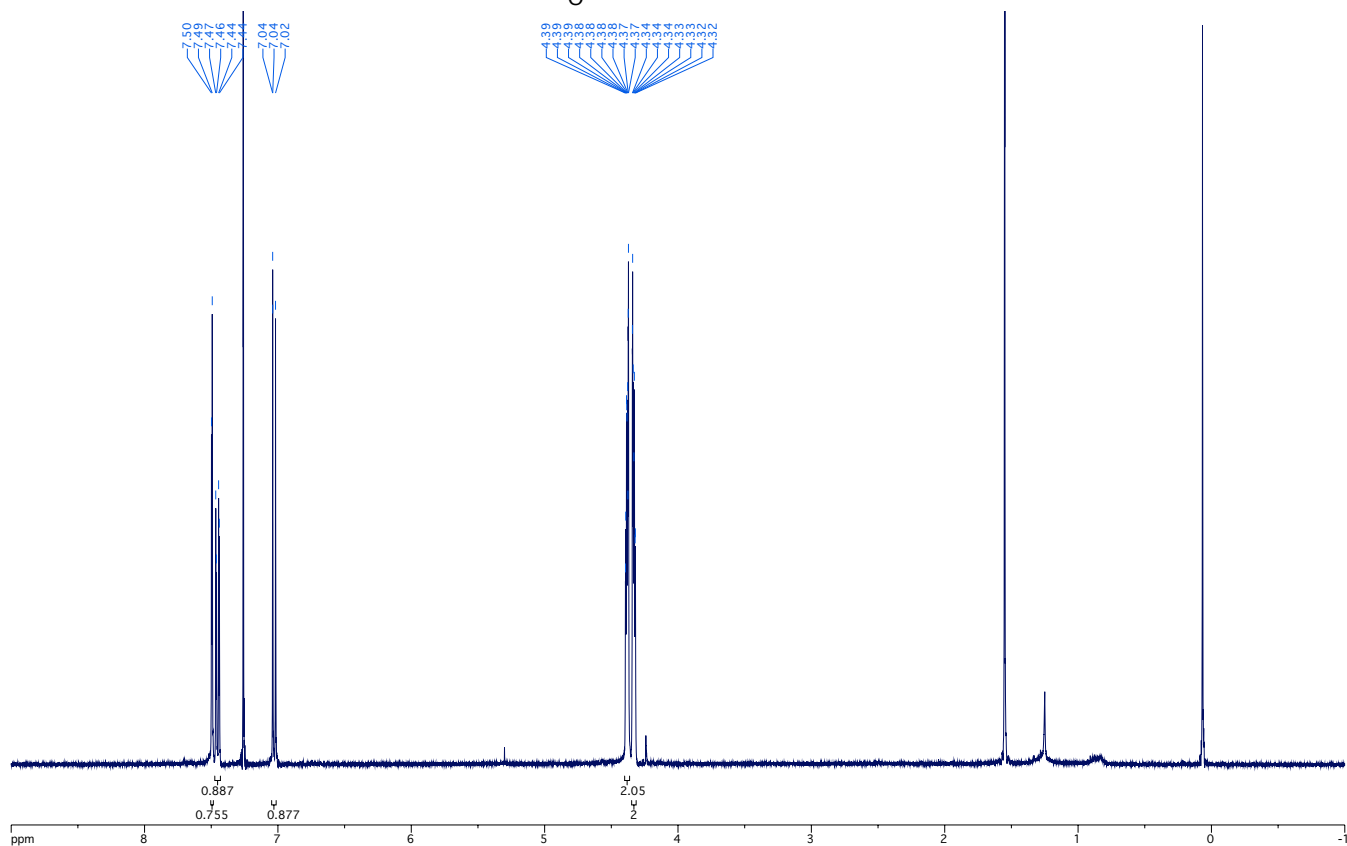
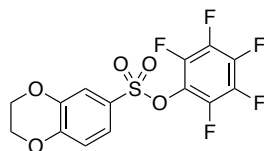
Compound 2k



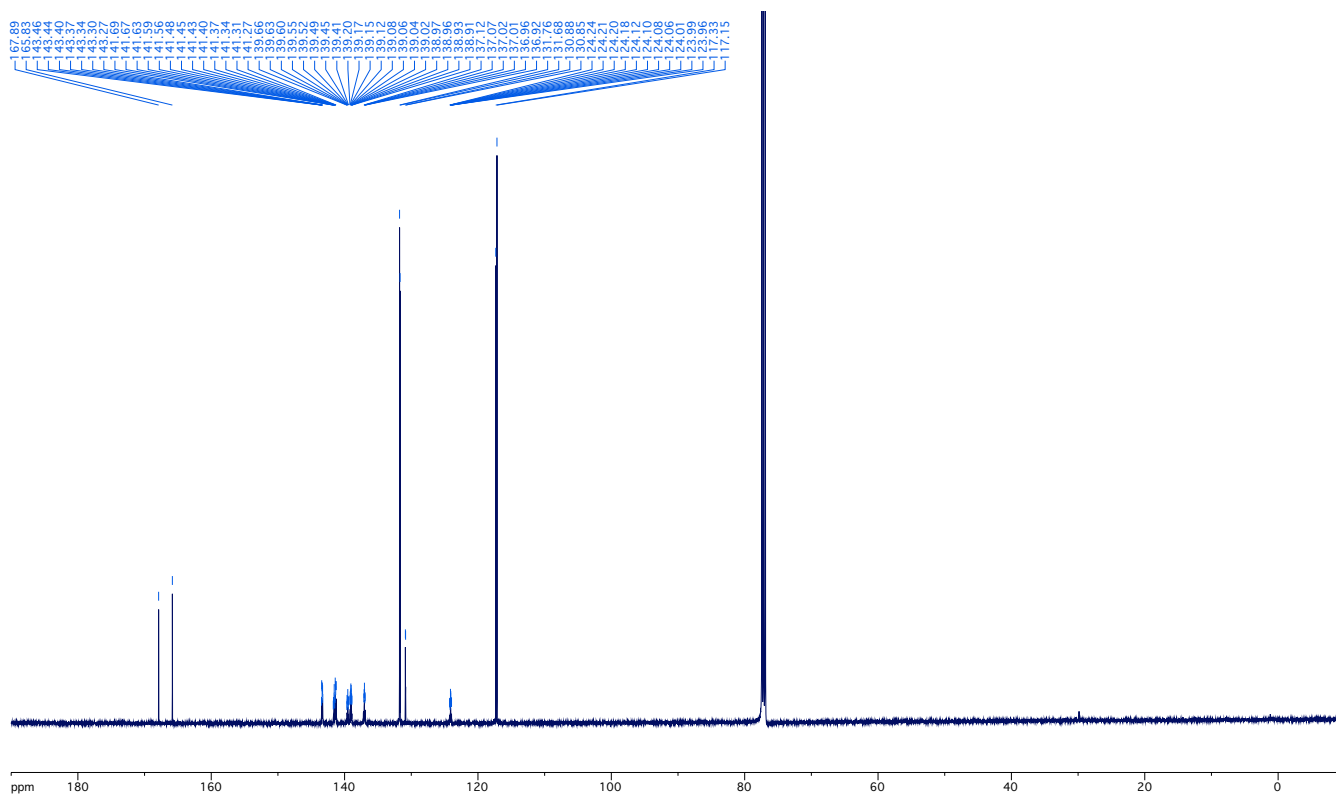
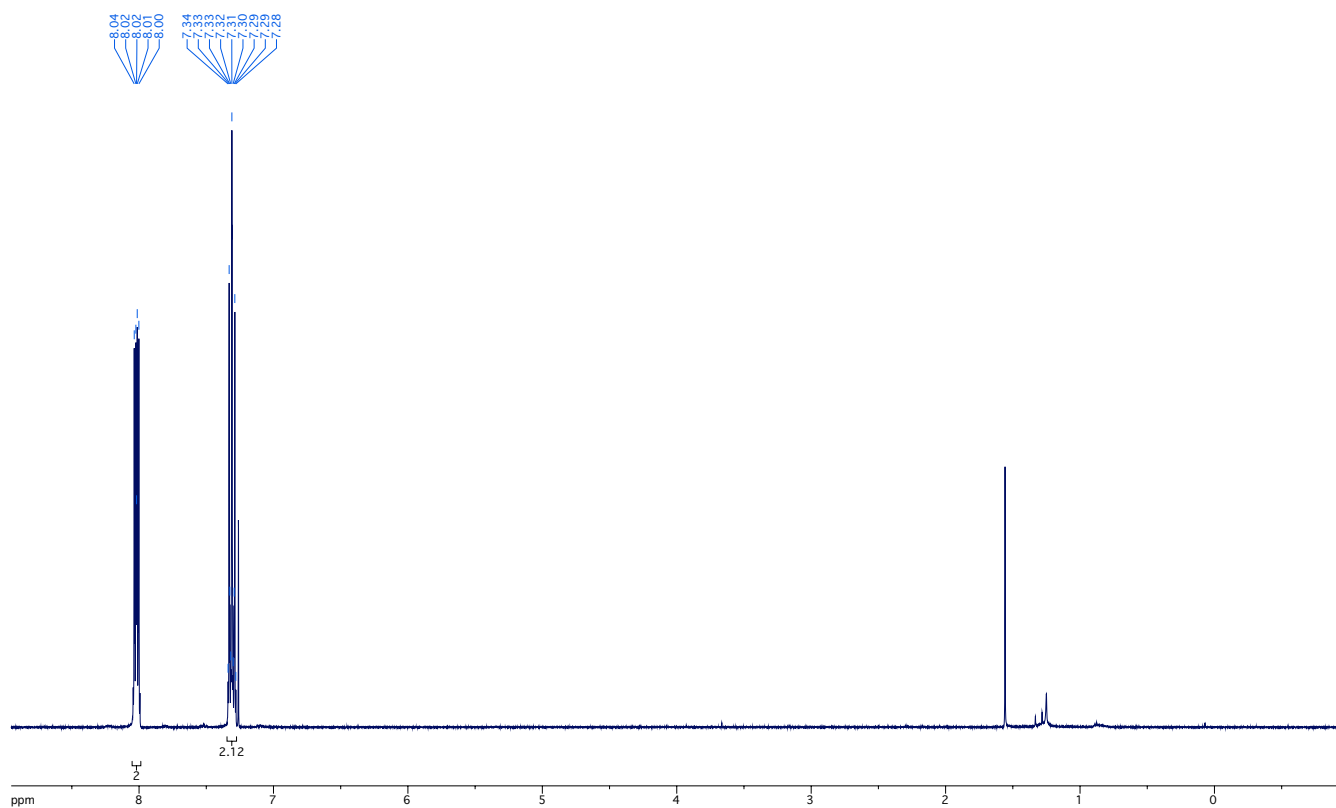
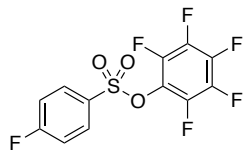
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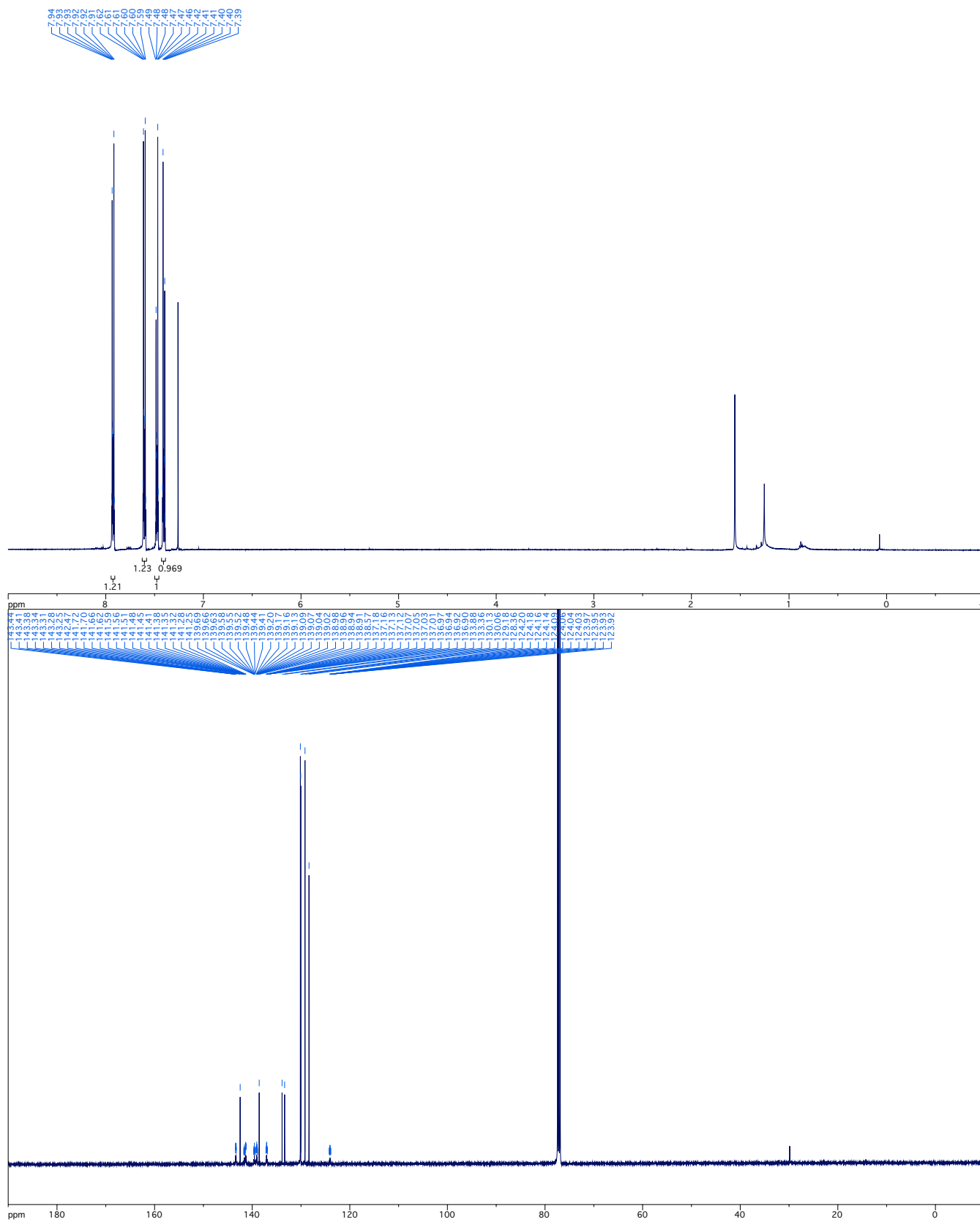
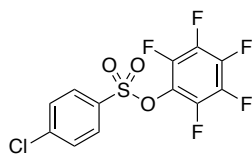
Compound 2n



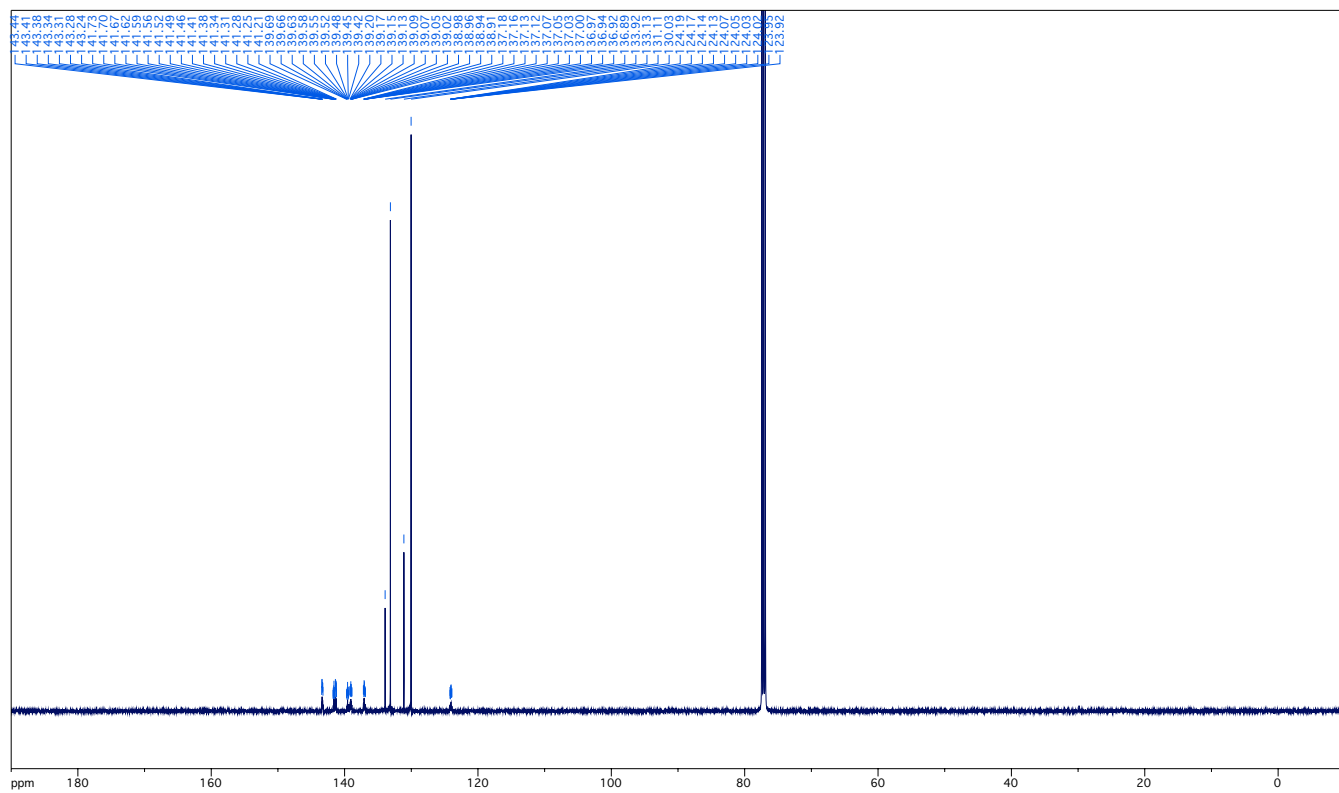
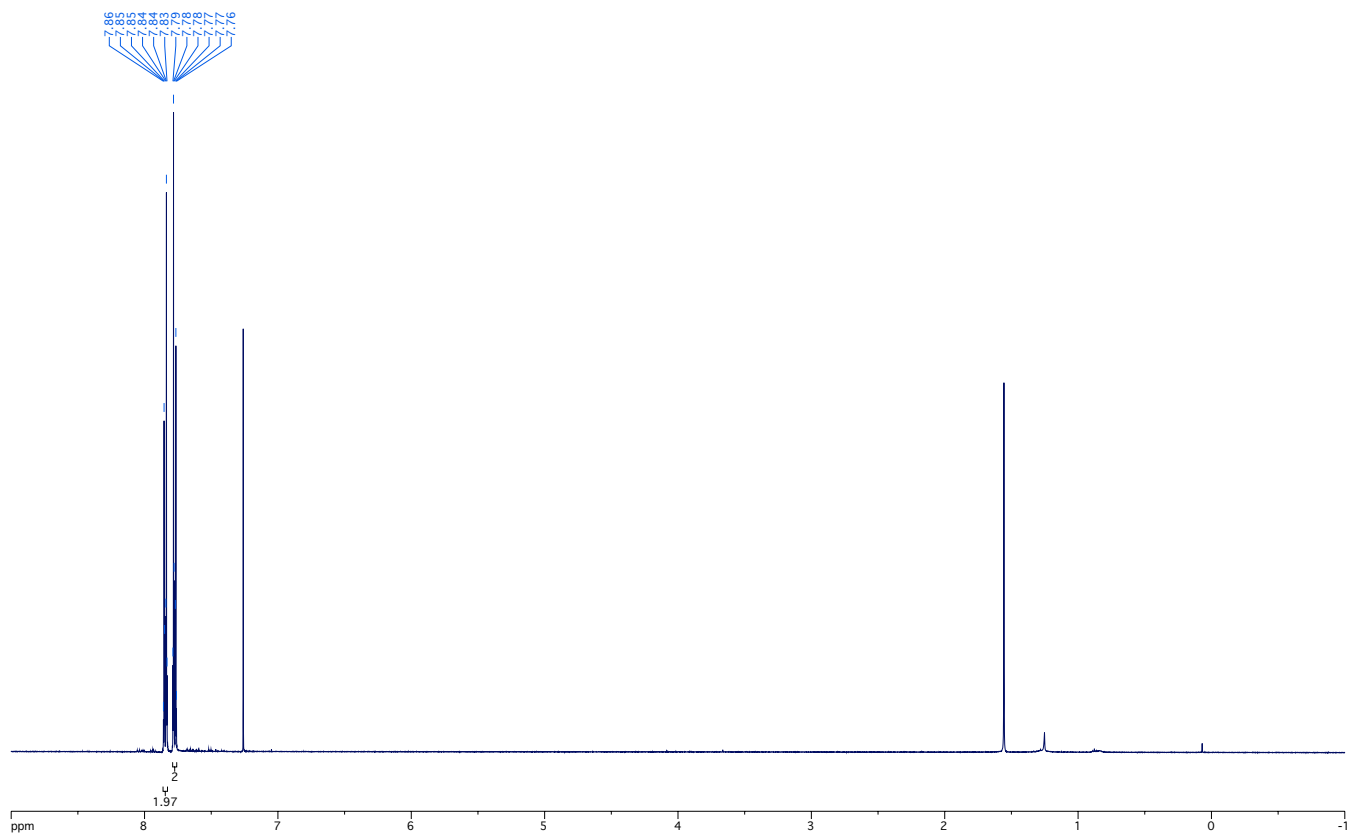
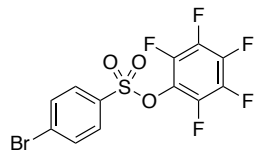
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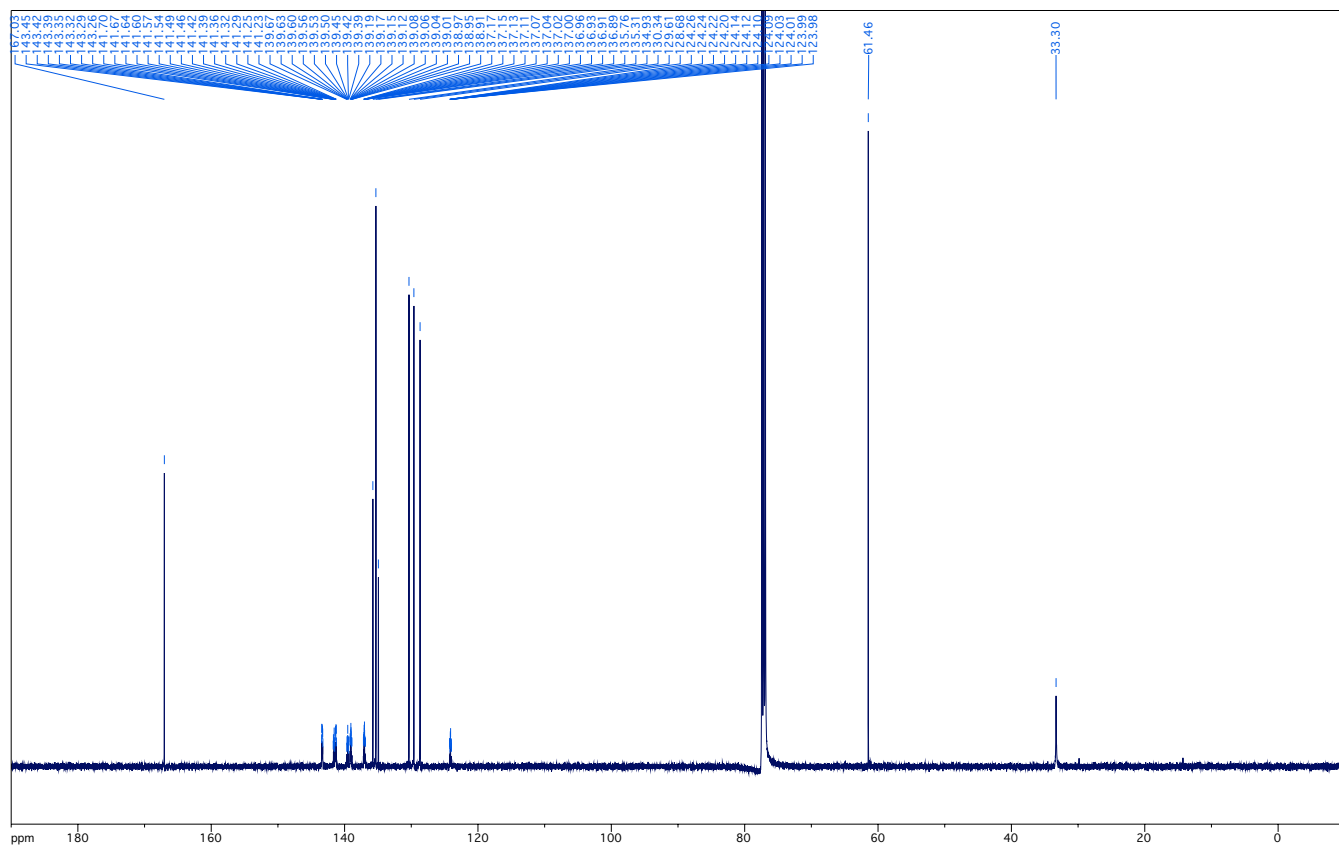
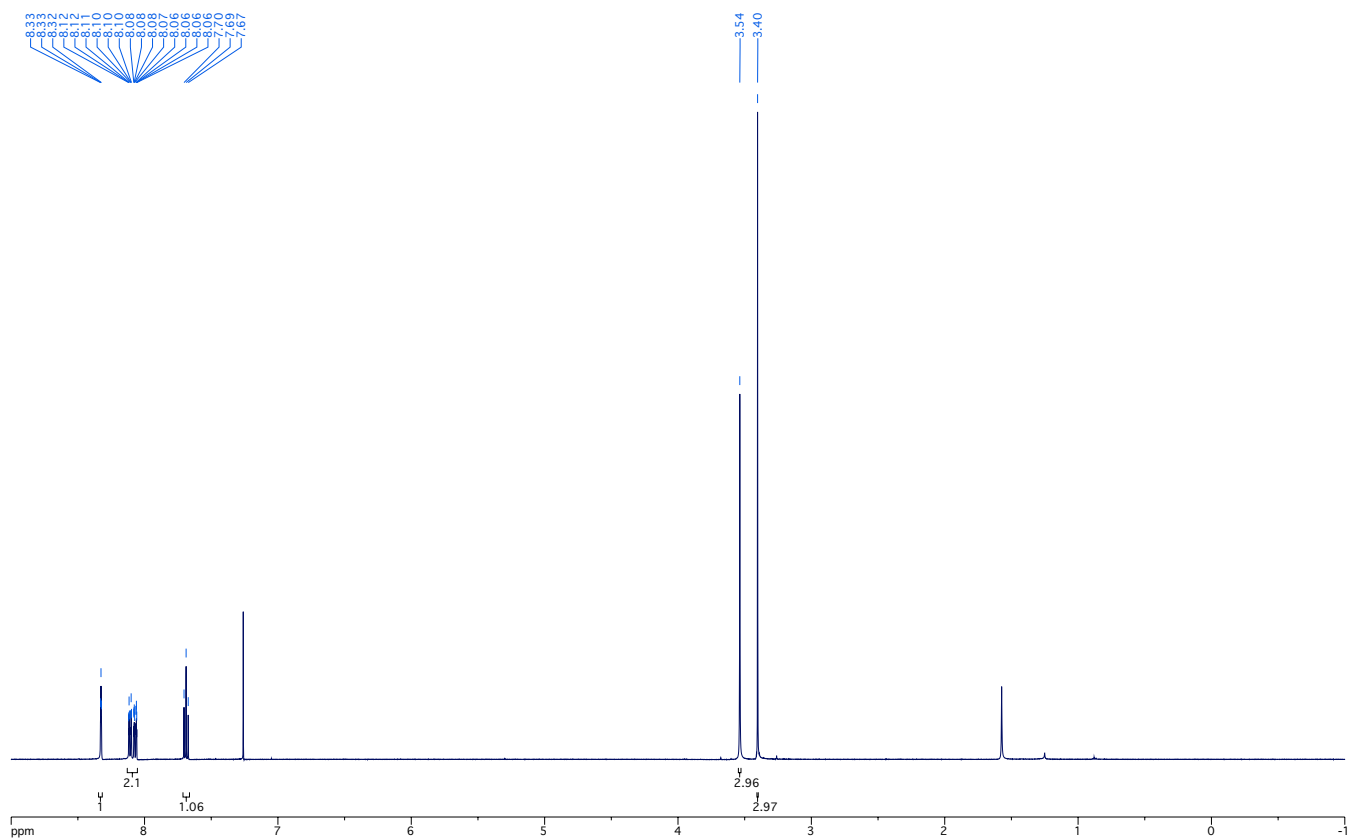
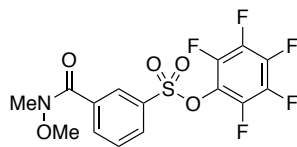
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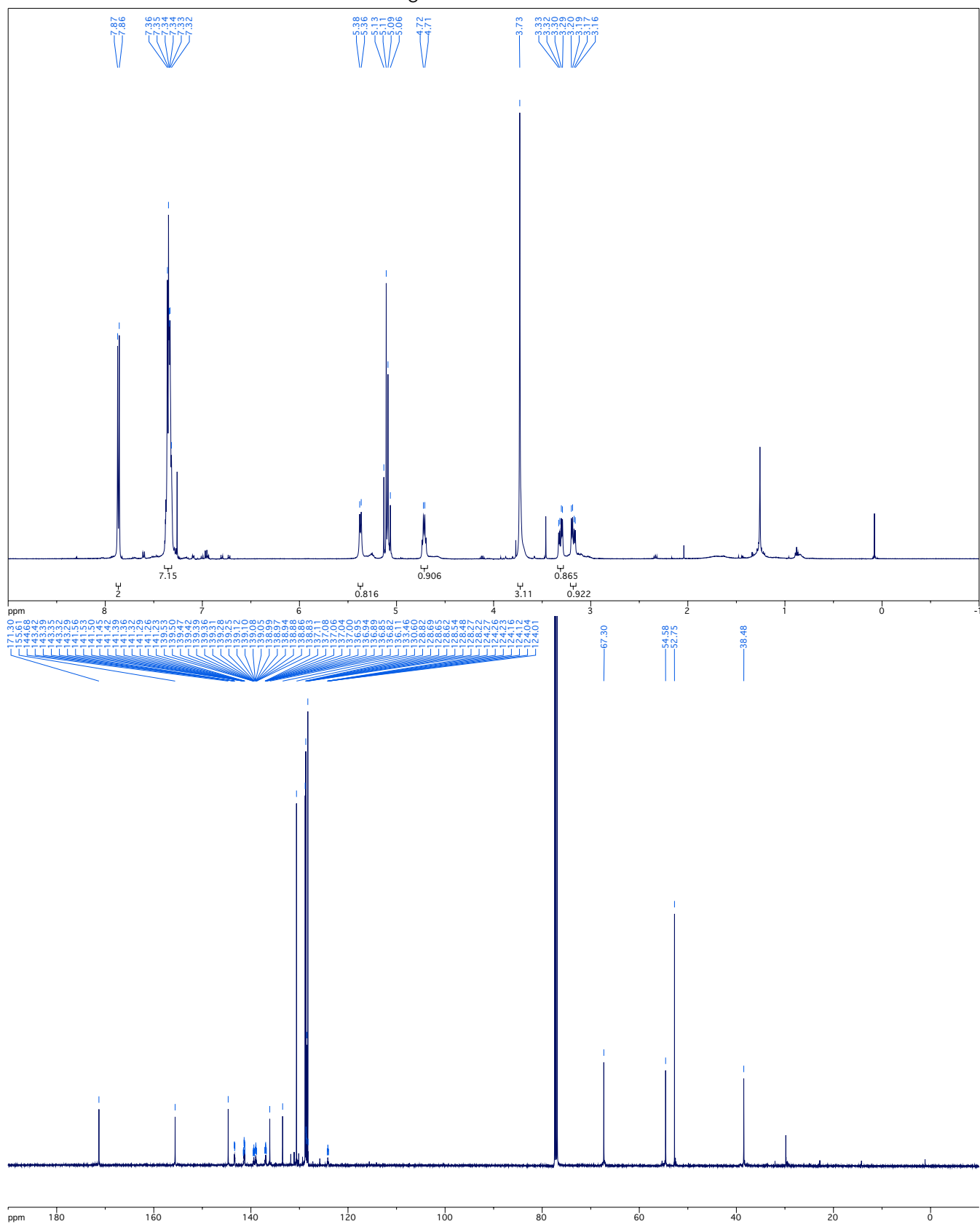
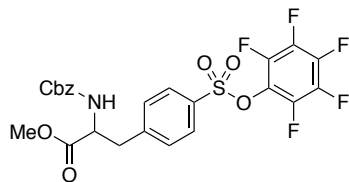
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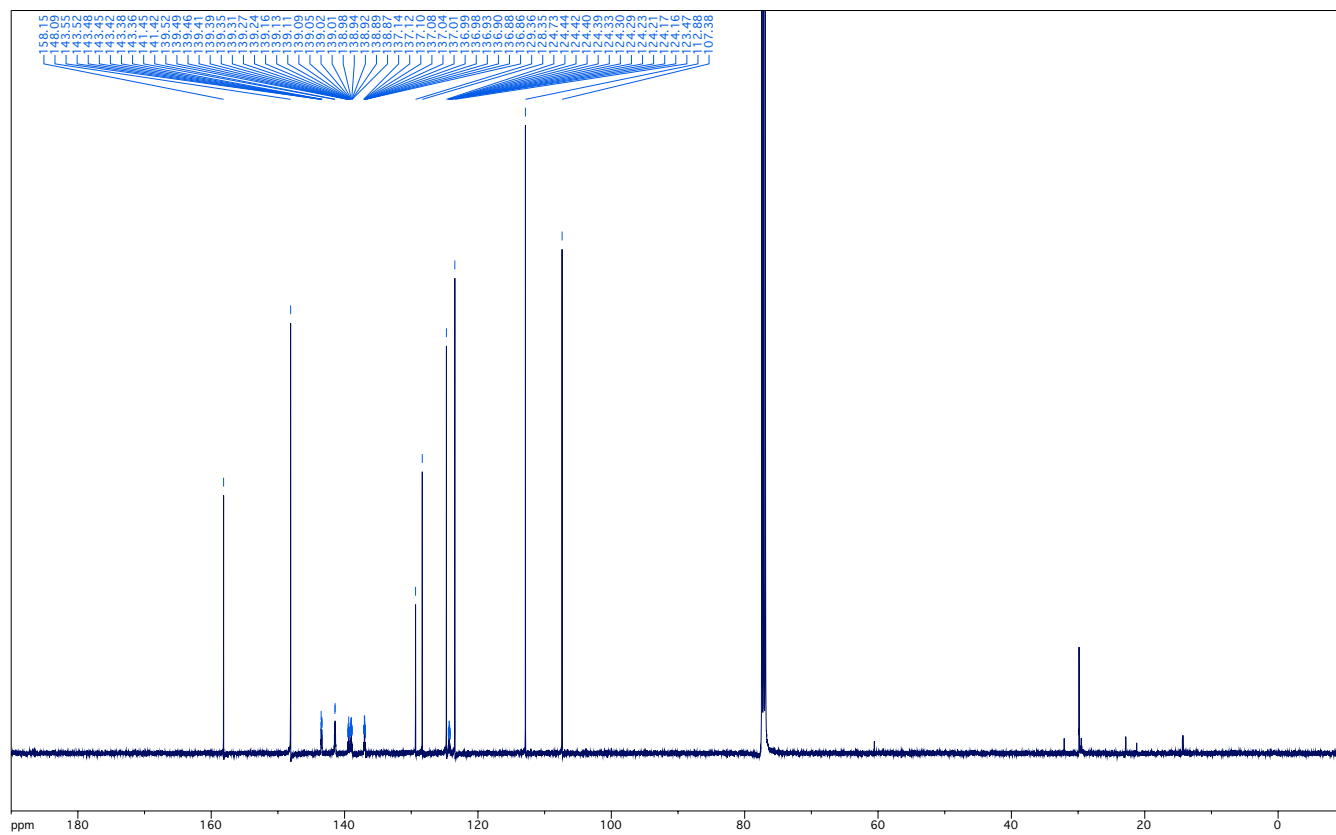
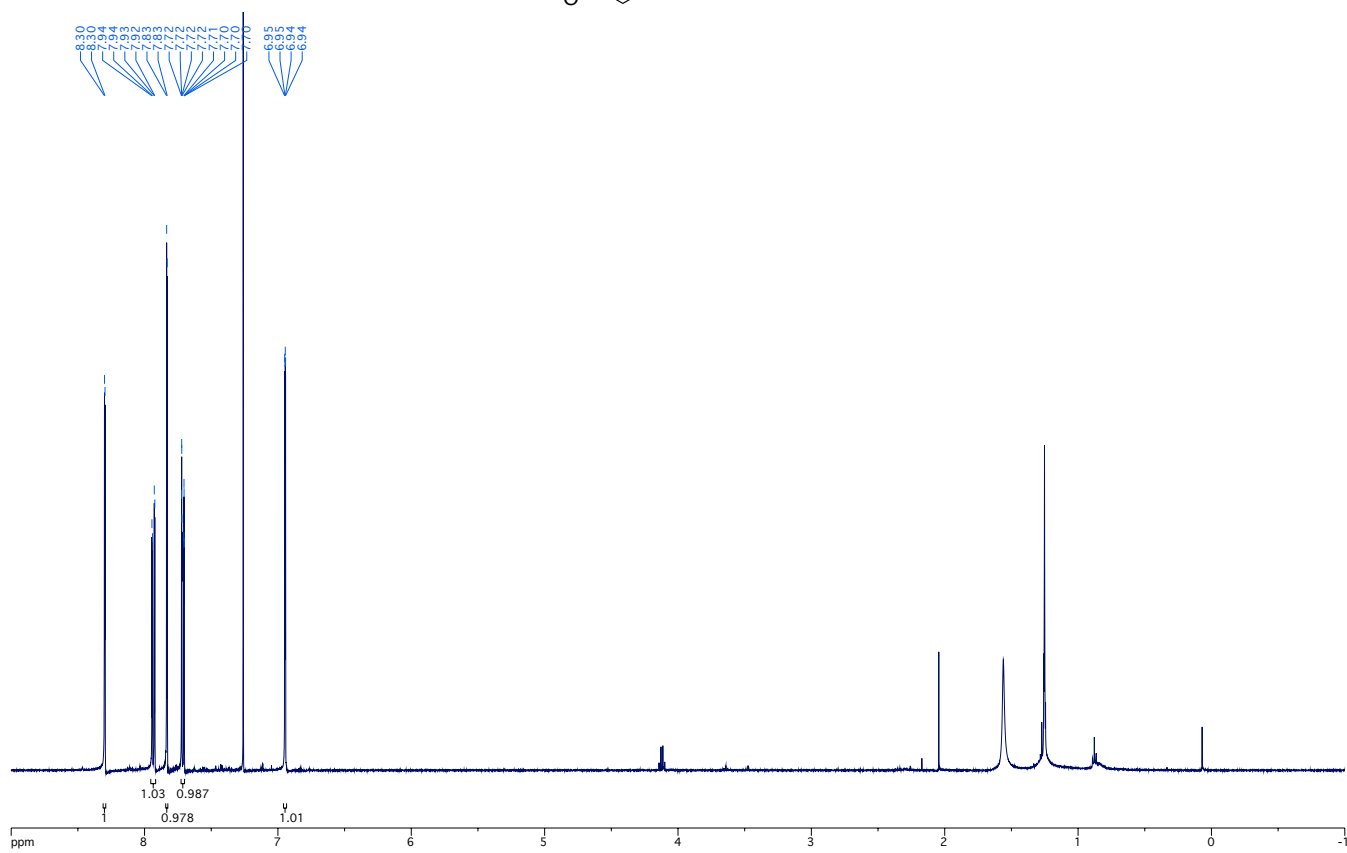
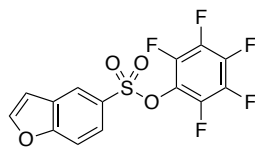
Compound 2r



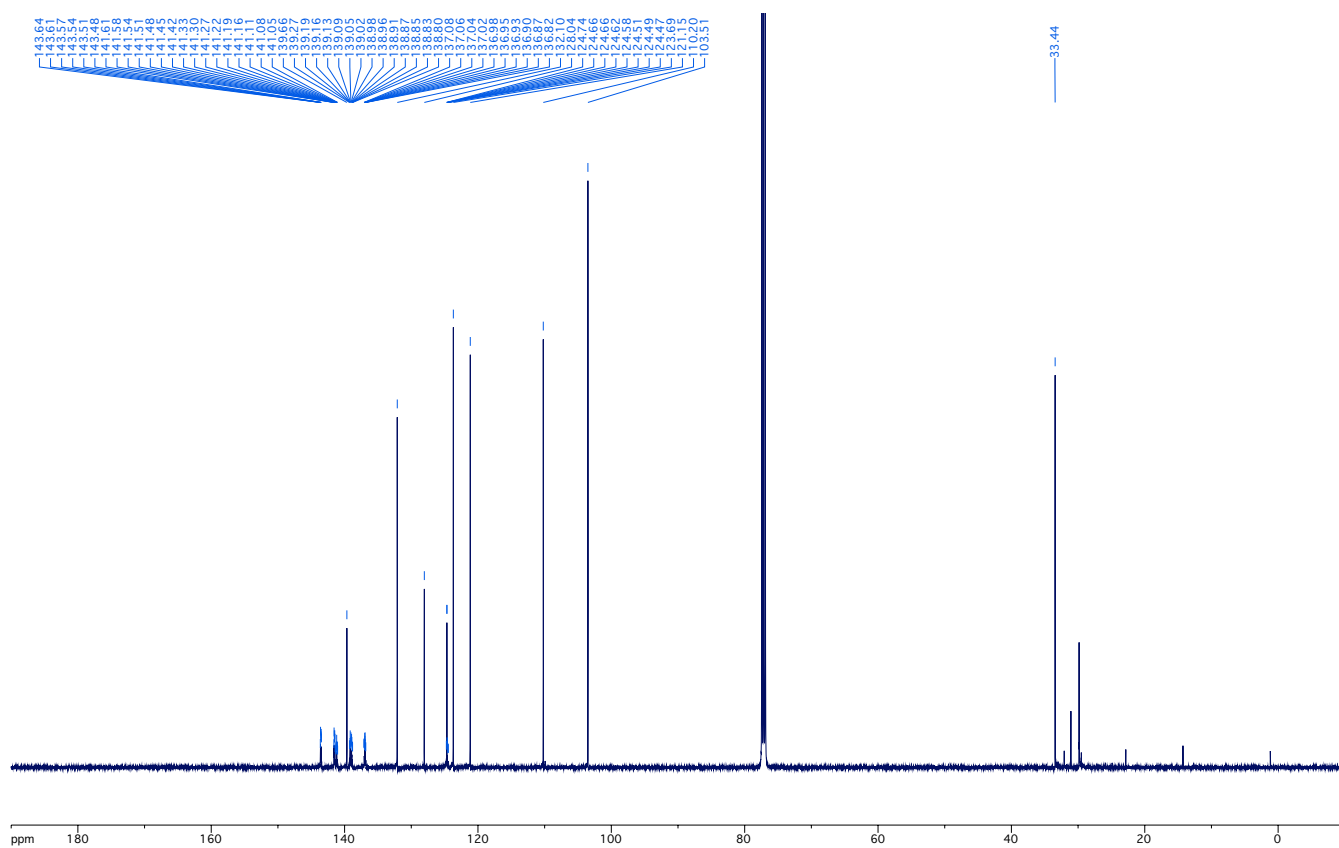
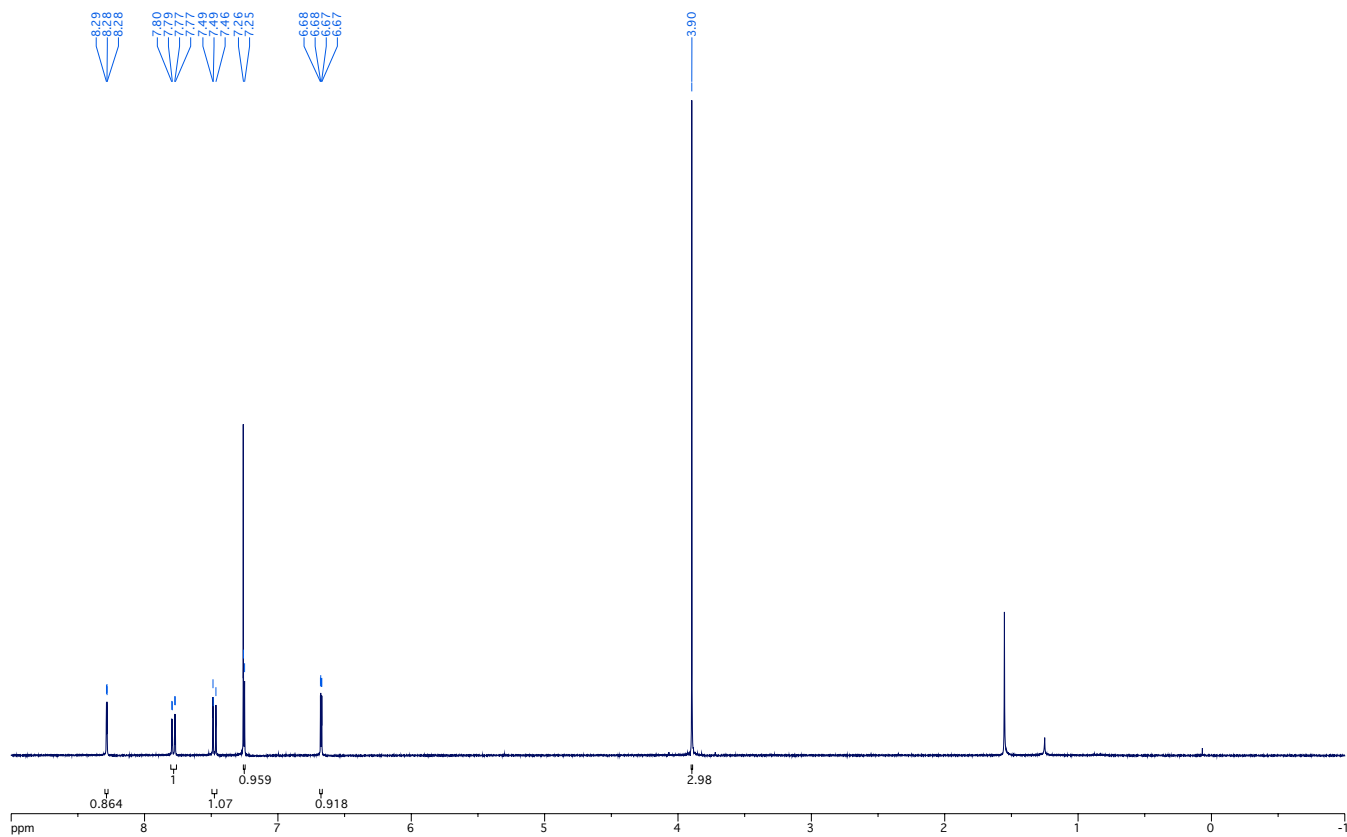
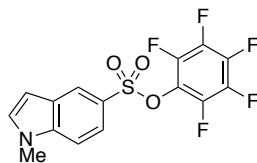
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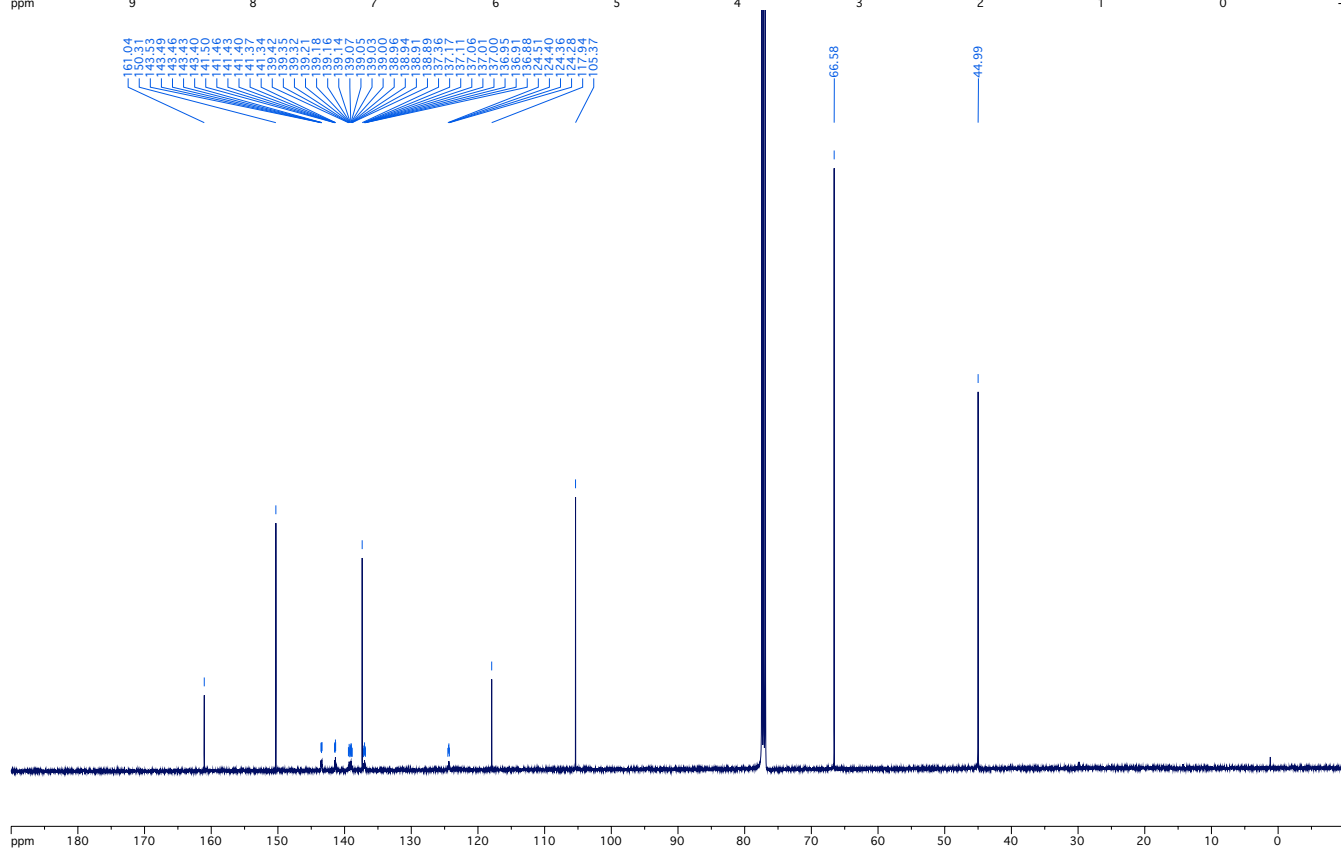
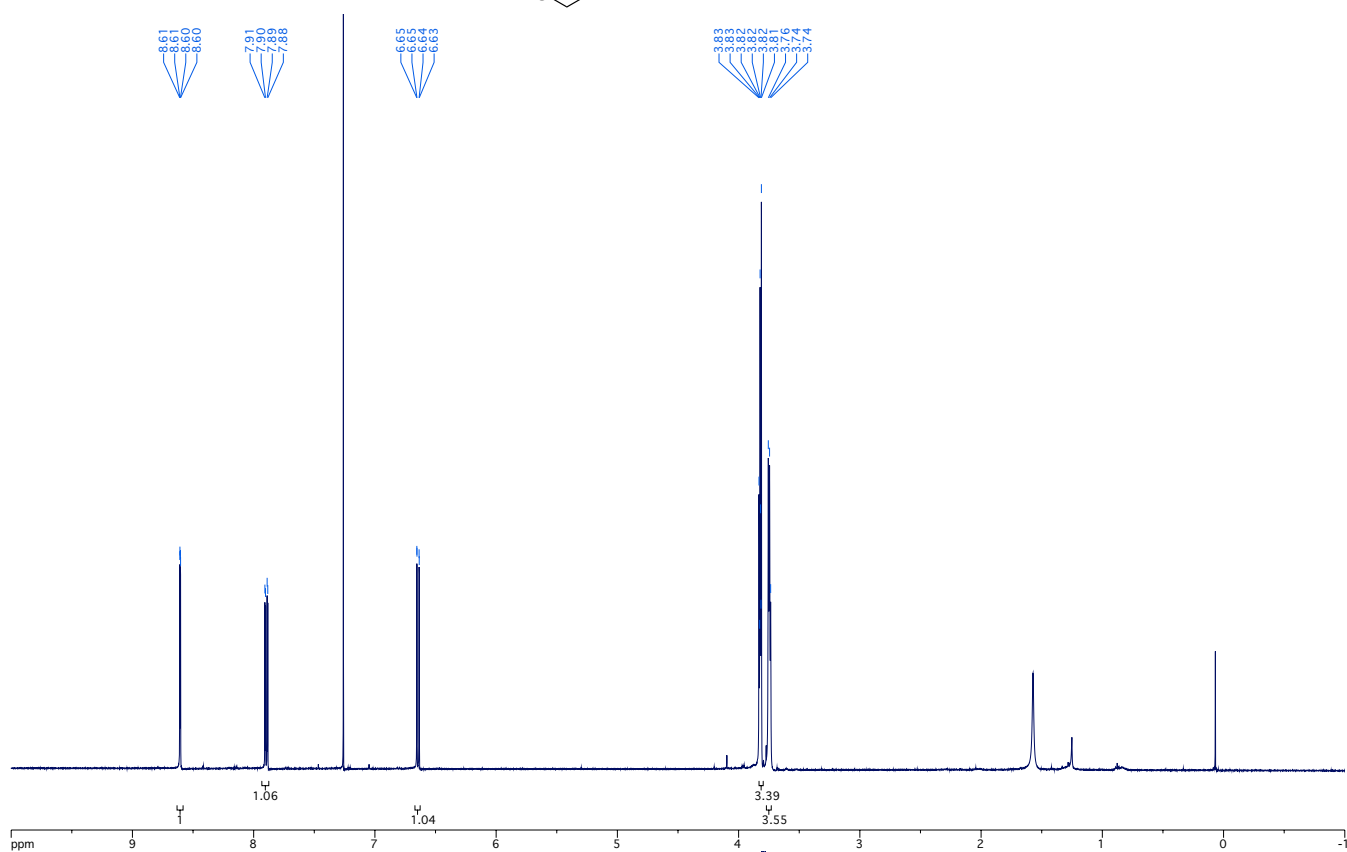
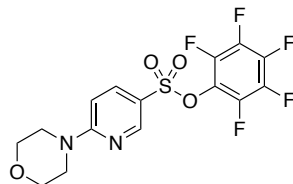
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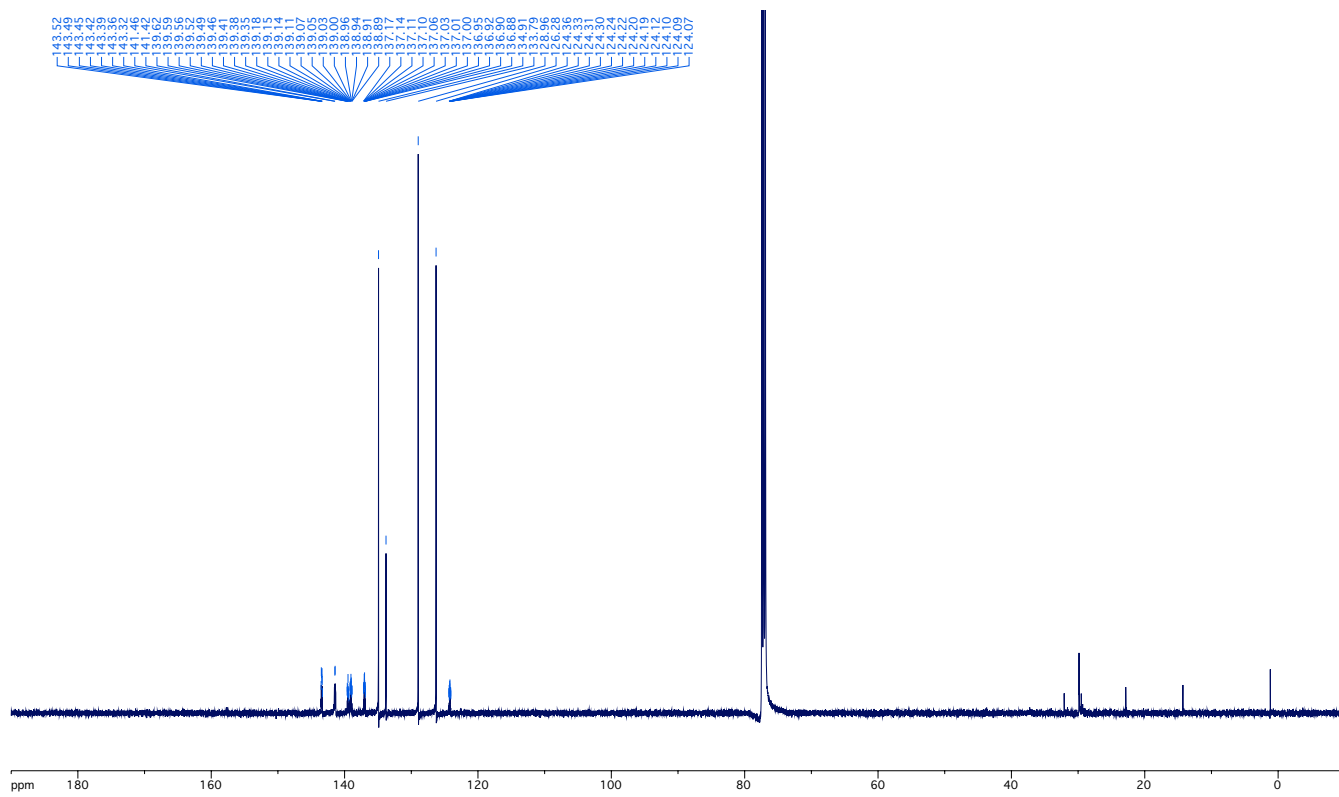
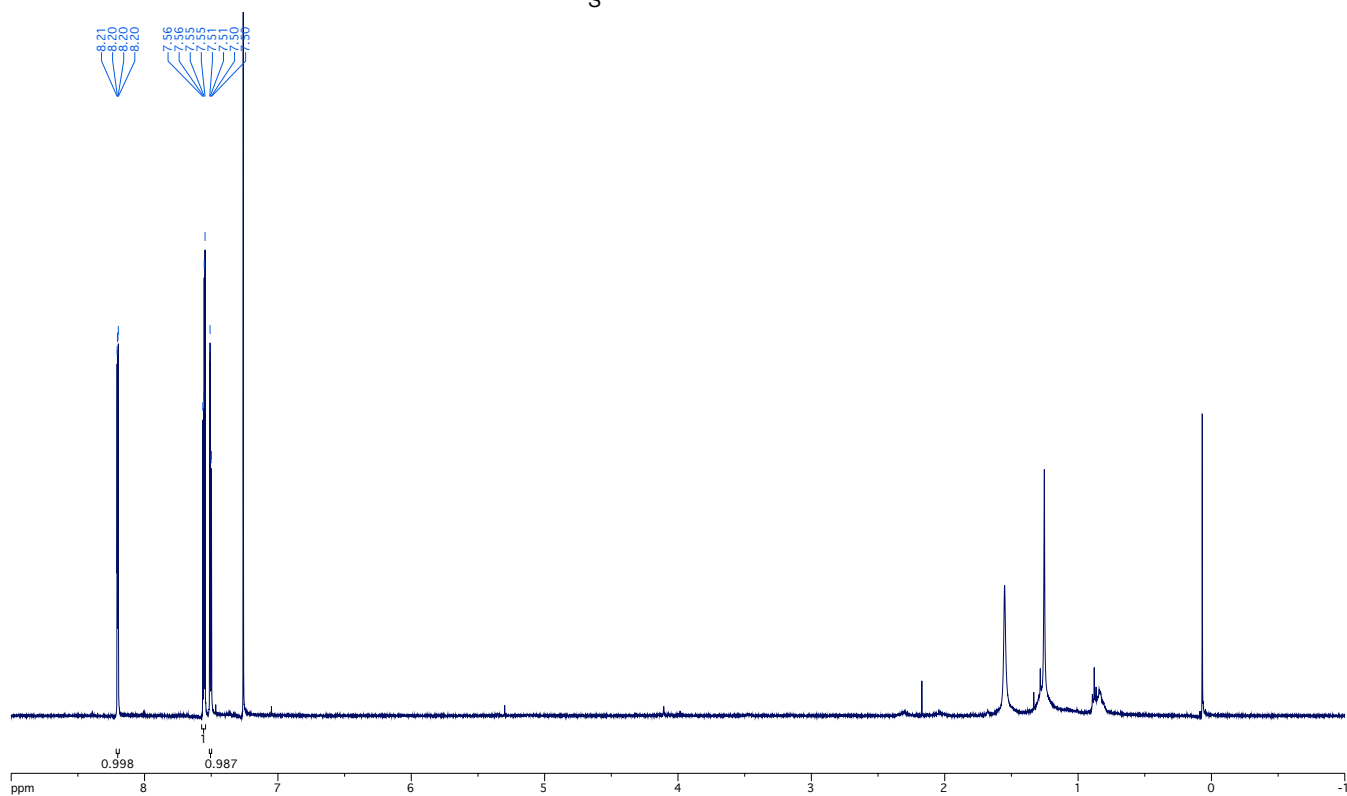
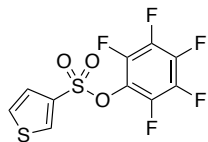
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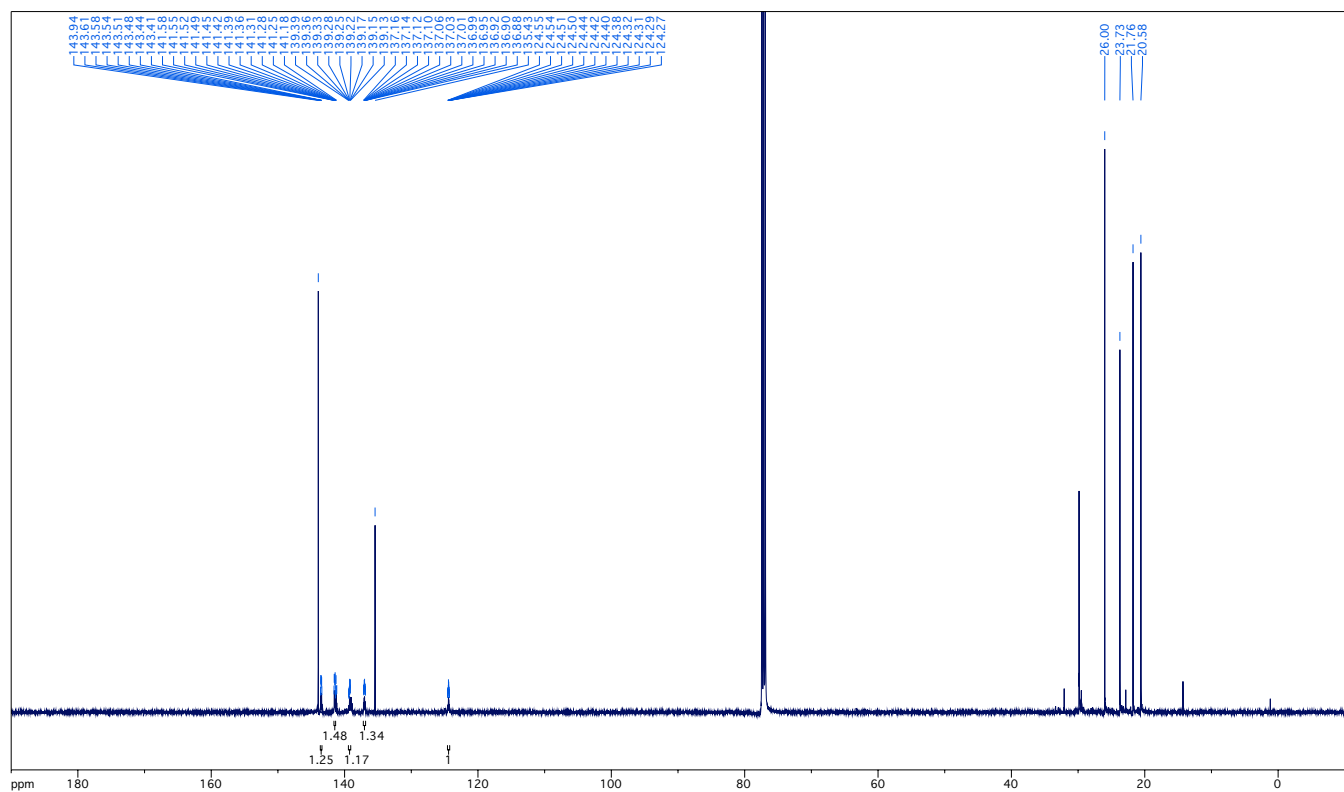
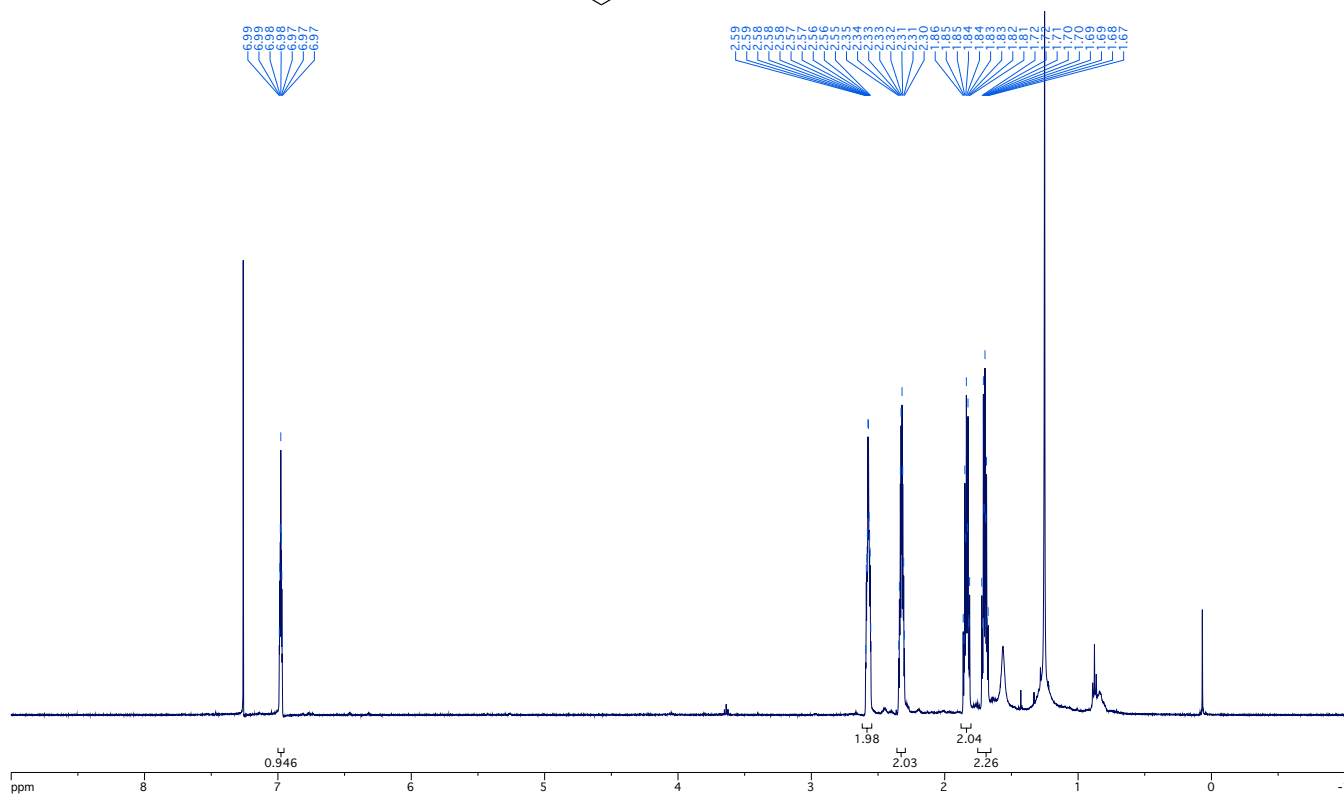
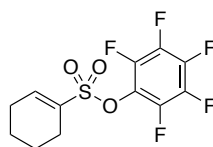
Compound 2y



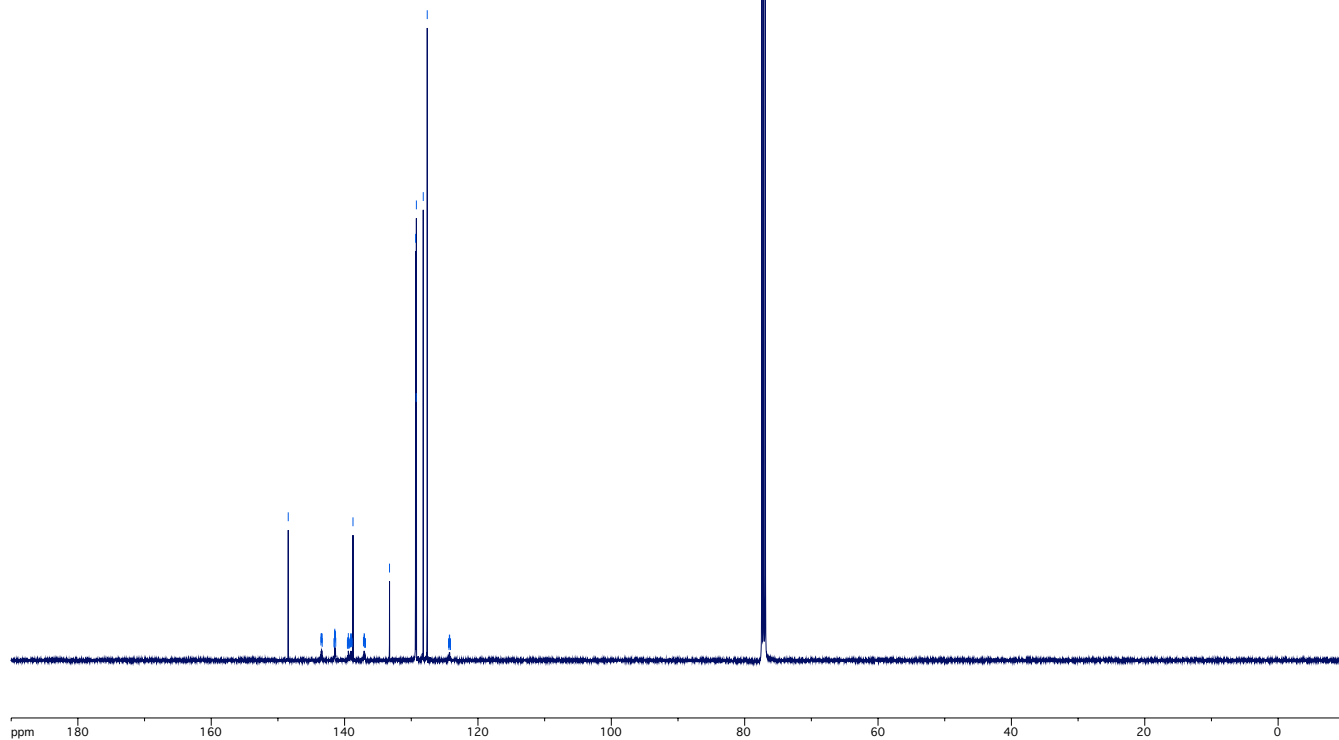
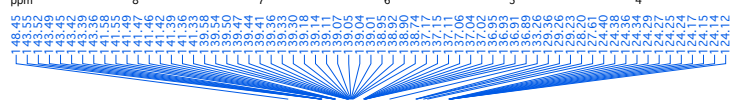
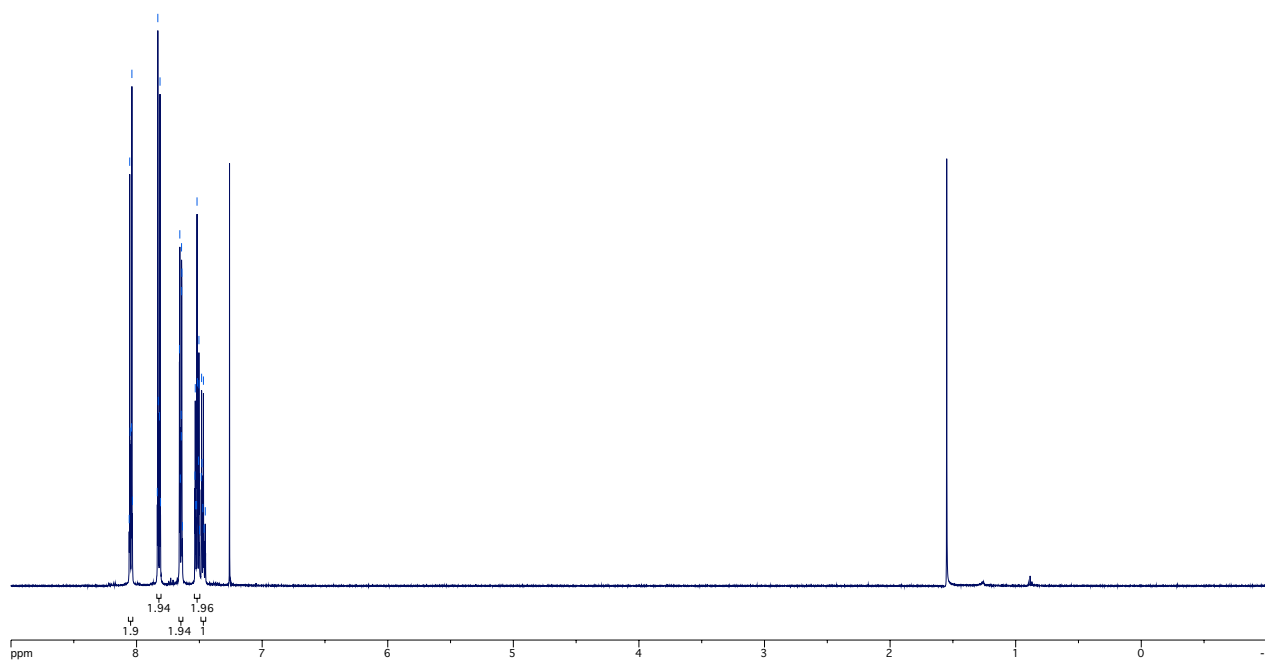
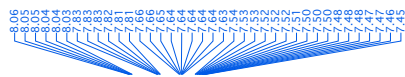
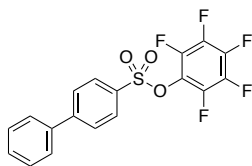
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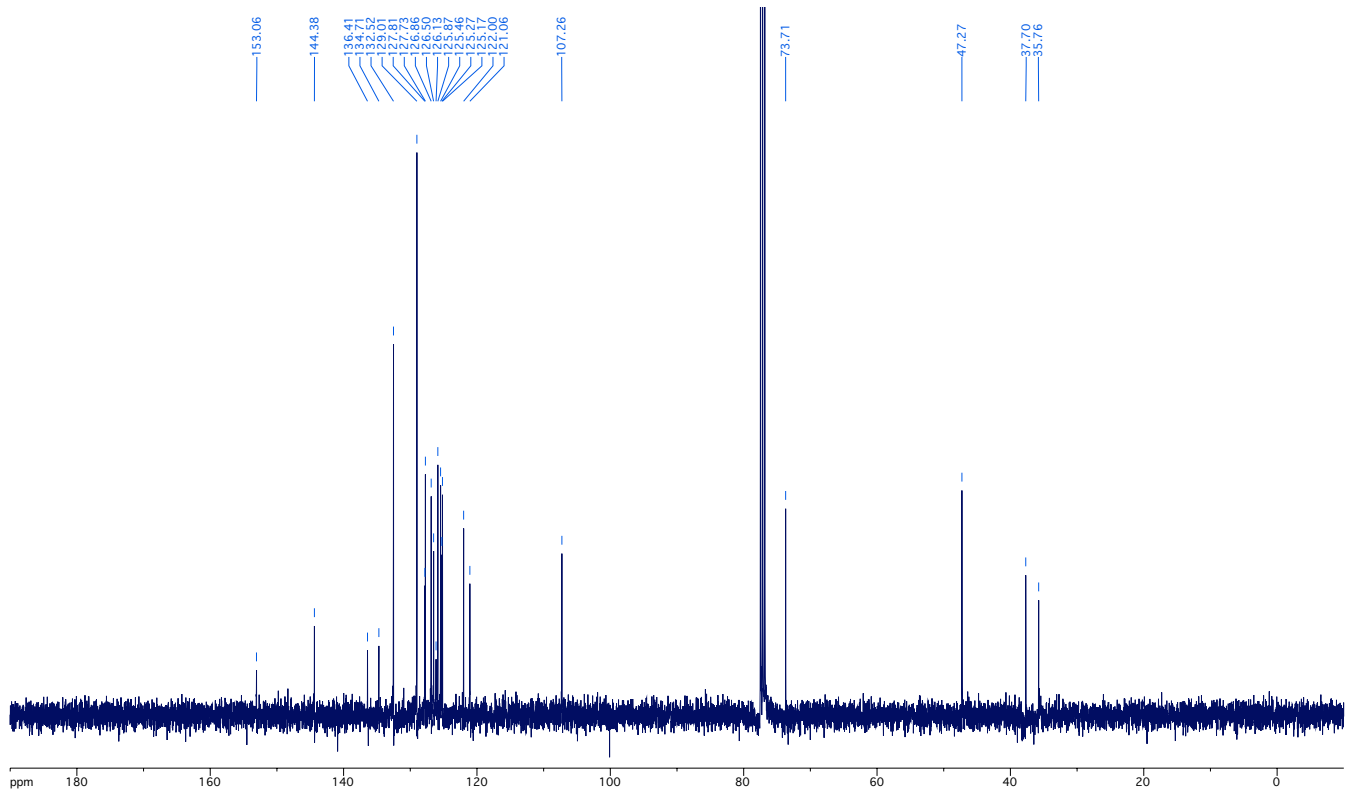
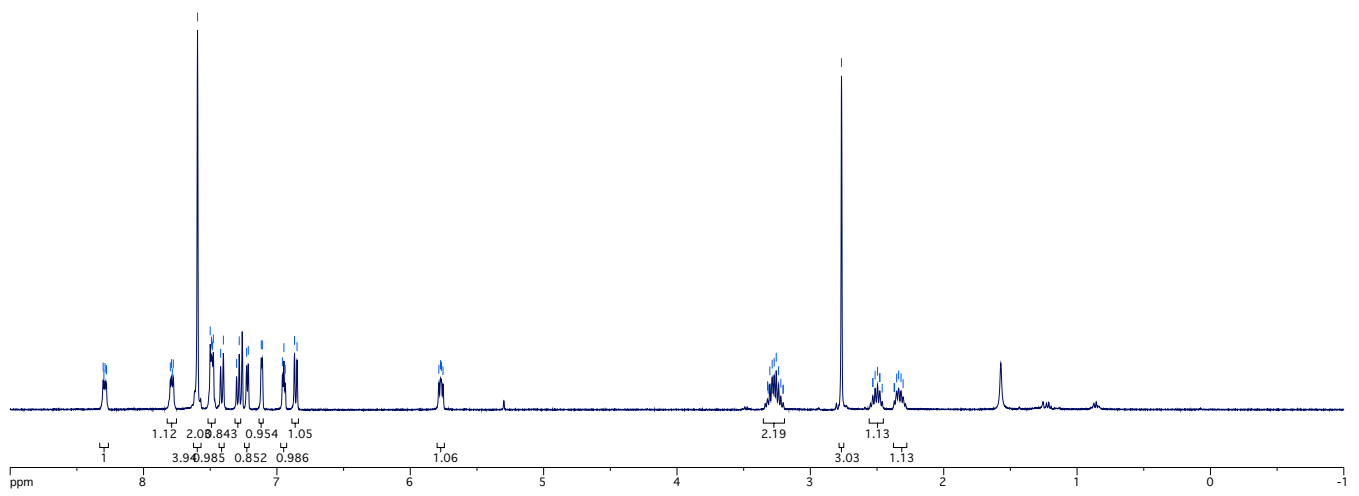
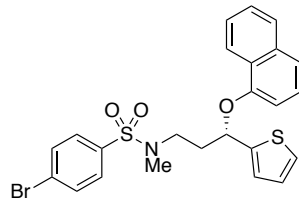
Compound 2ab



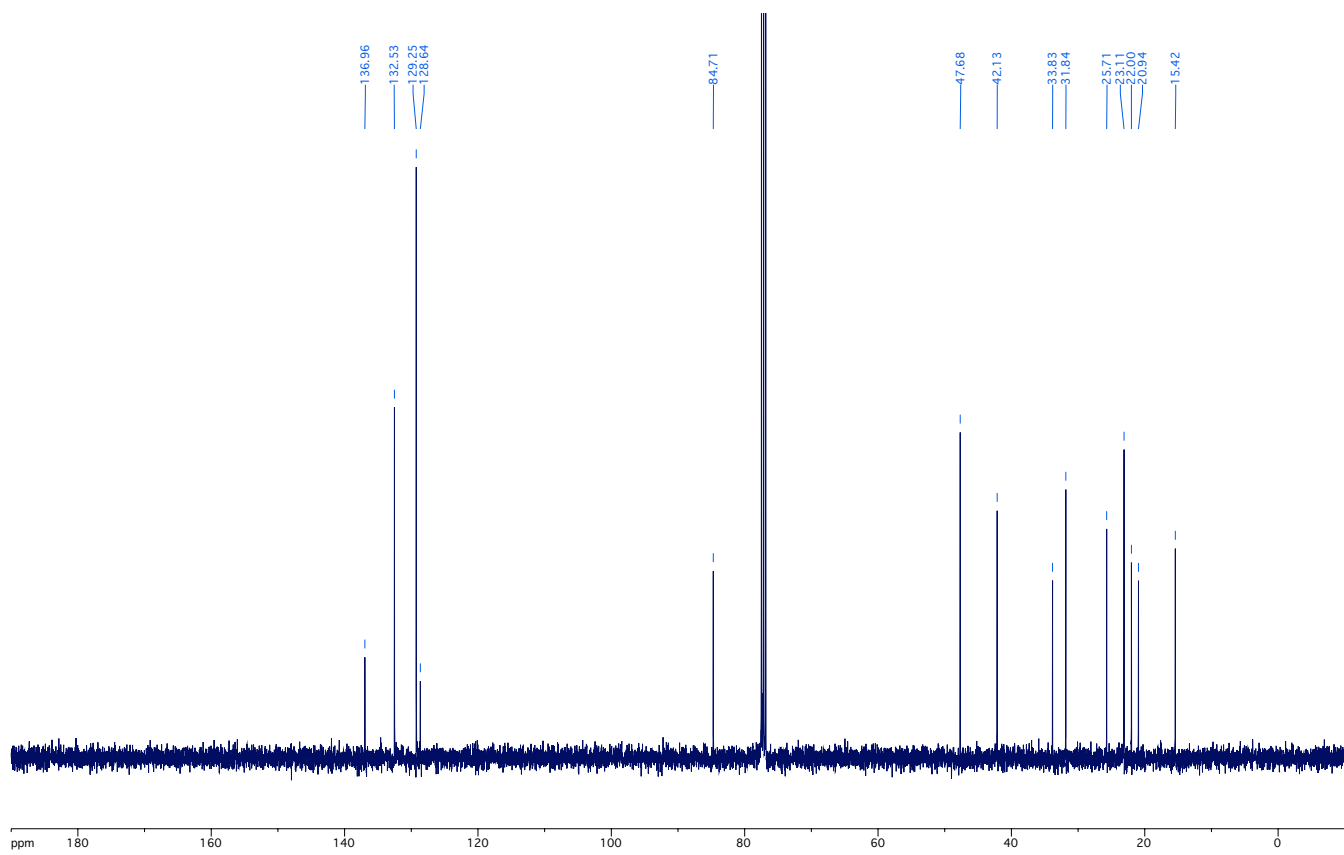
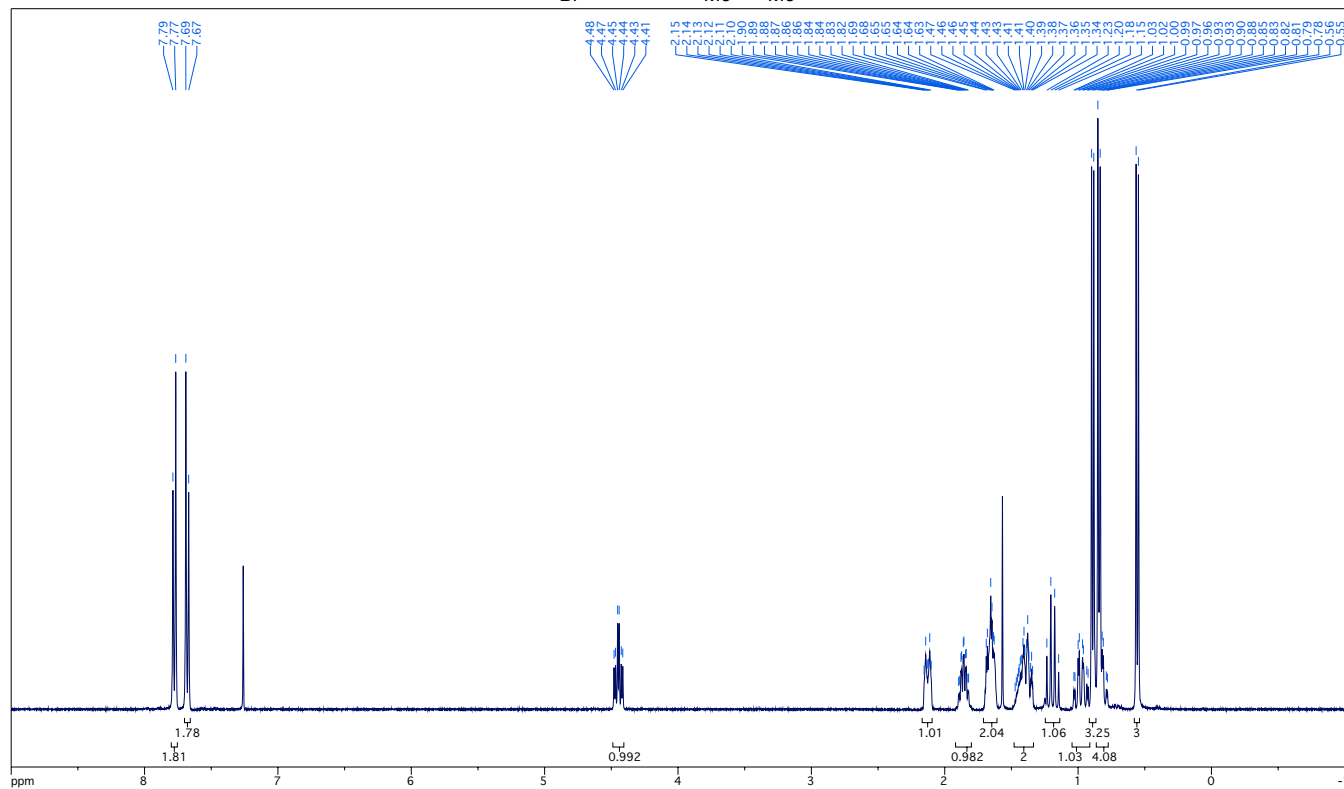
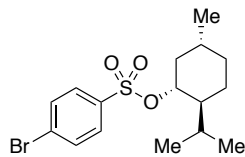
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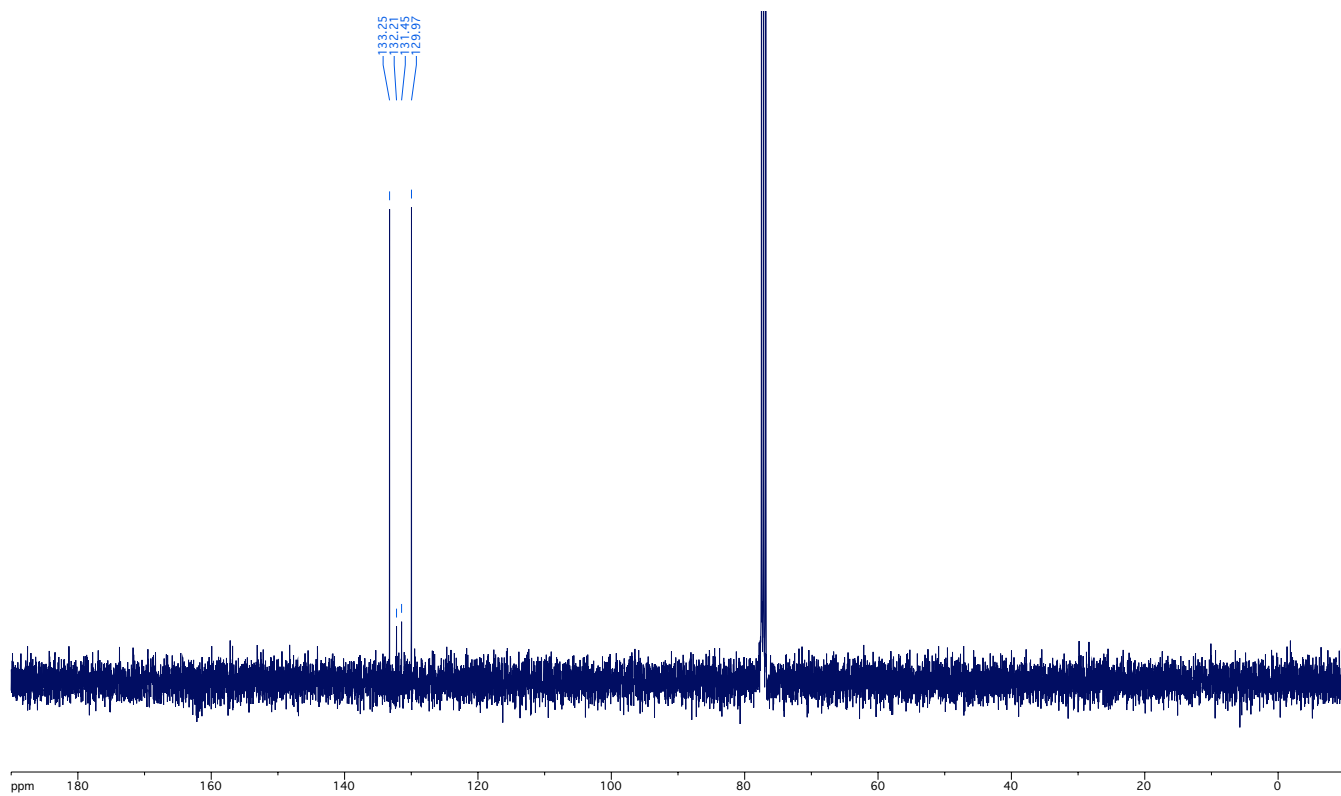
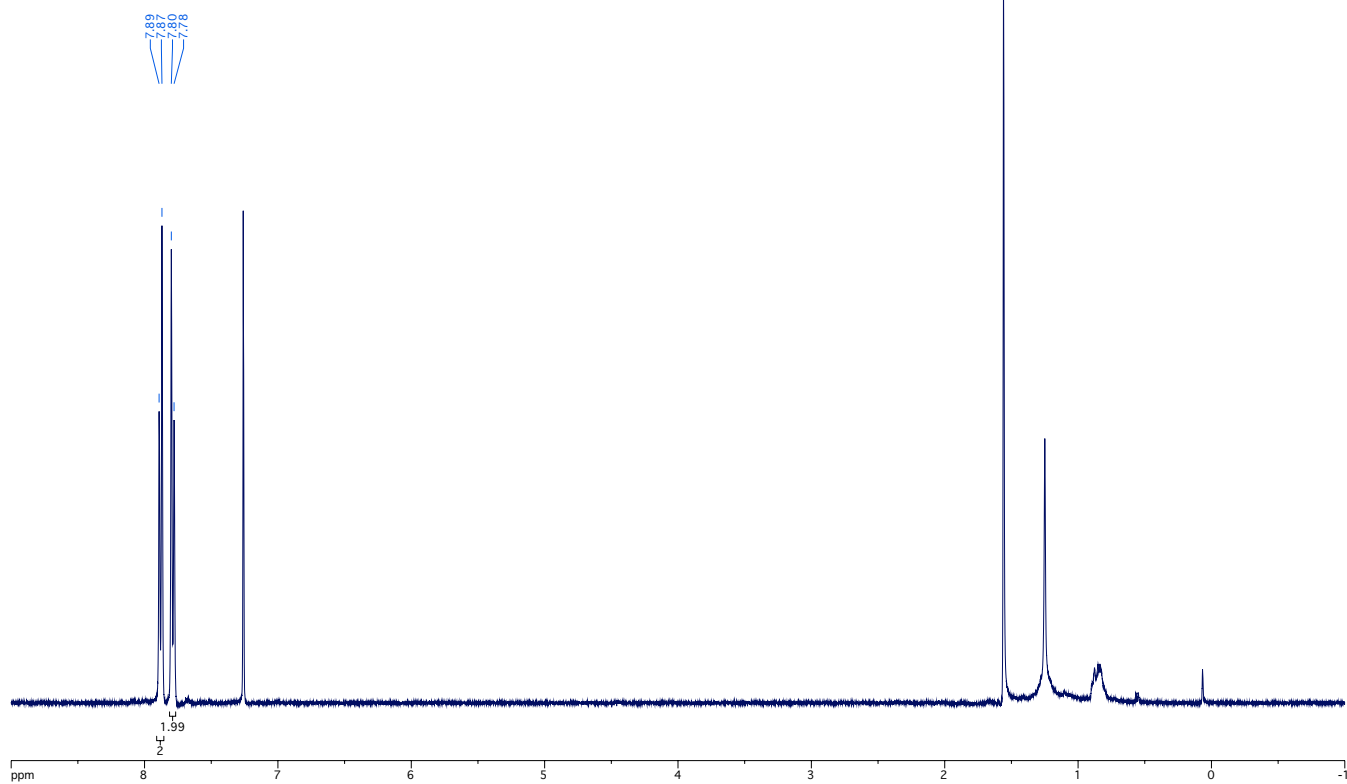
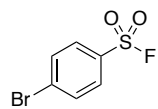
Compound 4



Compound 5



Compound 6



Compound 7

