

Supporting Information

Arenesulfonyl Fluoride Synthesis via Copper-catalyzed Fluorosulfonylation of Arenediazonium Salts

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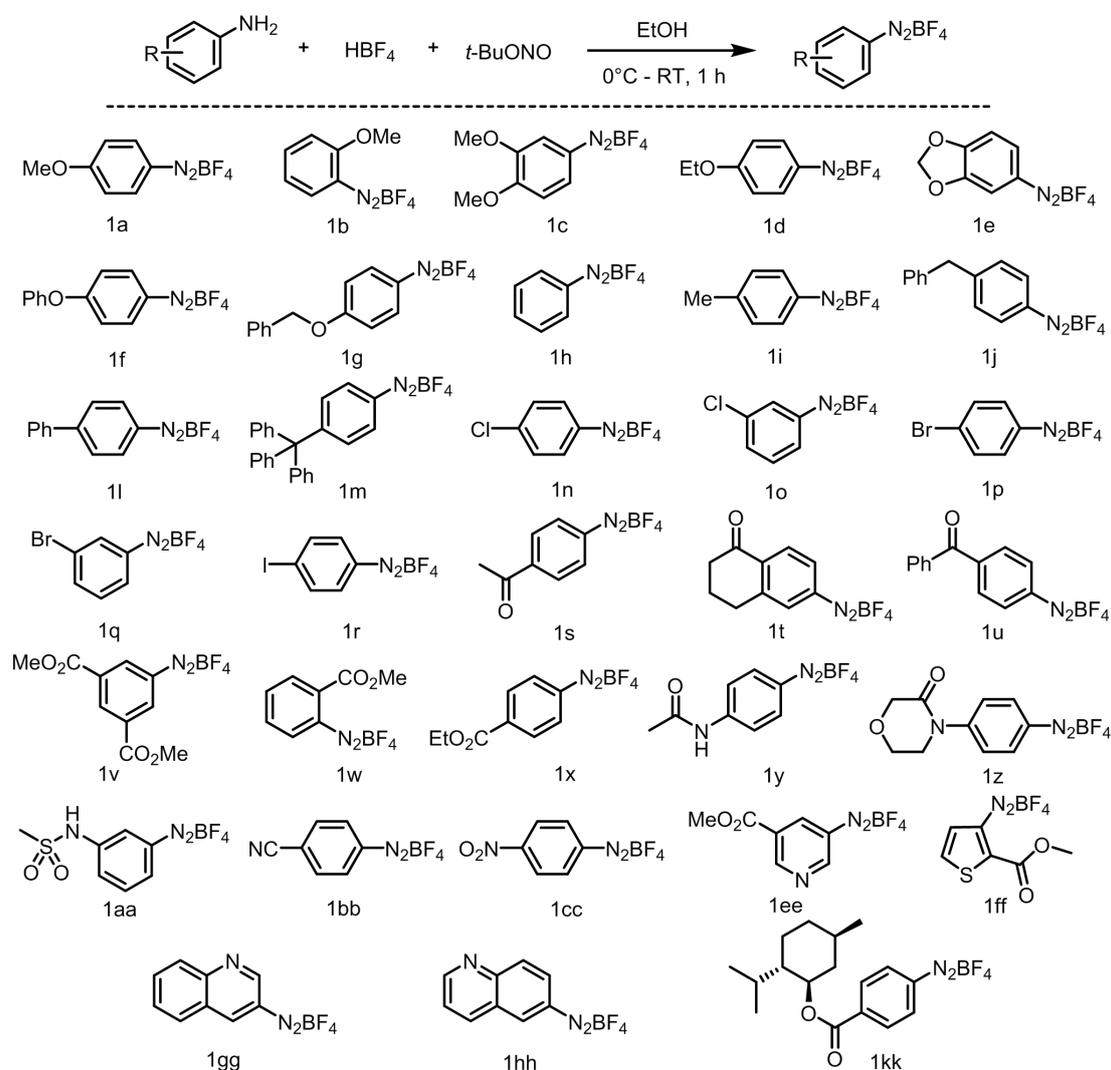
1. General information

Unless otherwise noted, all reagents were purchased from commercial source and used as received. The solvent MeCN, dichloroethane (DCE), dimethyl sulfoxide (DMSO) and N, N-dimethylformamide (DMF) were distilled from CaH₂ and kept over activated 4Å MS. 1,4-diazabicyclo[2.2.2]octane-1,4-dium-1,4-disulfinate (DABSO) was purchased from TCI and Acros. KHF₂ was purchased from Adamas, and before it was used, we usually crush it into powder. CuCl₂ and 6,6'-dimethyl-2,2'-dipyridyl were purchased from Energy Chemical and J&K respectively. The arenediazonium tetrafluoroborates were synthesized according to reported literature.^[1] ¹H, ¹⁹F and ¹³C NMR spectra were obtained on 400 MHz spectrometer. ¹H NMR and ¹³C NMR chemical shifts were determined relative to internal (CH₃)₄Si (TMS) at δ 0.0 ppm and ¹⁹F NMR chemical shifts were determined relative to CFCl₃ at δ 0.0 ppm. Data for ¹H, ¹⁹F and ¹³C NMR were recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad). Coupling constants are reported in hertz (Hz). Flash column chromatograph was carried out using 300-400 mesh silica gel at medium pressure.

2. Synthesis of various arenediazonium tetrafluoroborates^[1]

Method A

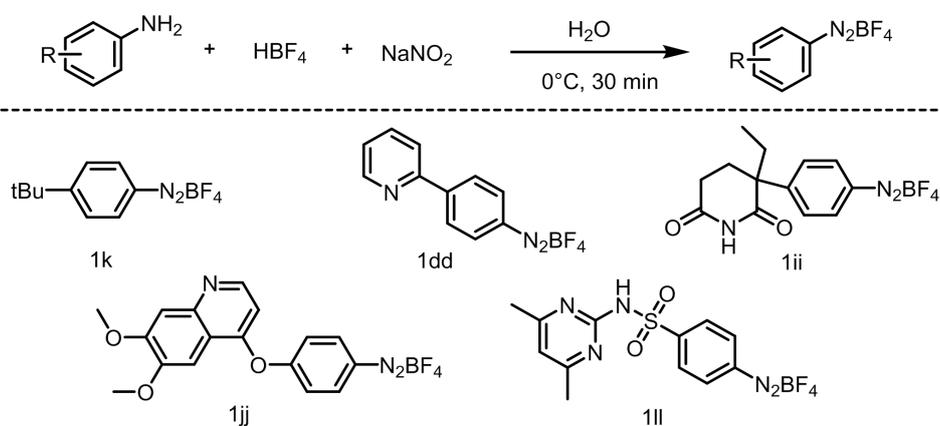
To a stirred solution of aniline (10 mmol) in absolute ethanol (3 – 9 mL) was added an aqueous solution of HBF₄ (50 %, 2.5 mL). The tert-butyl nitrite (2.7 mL) was added dropwise to the solution at 0 °C. The reaction mixture was stirred at room temperature for 1 h and Et₂O (30 mL) was added to precipitate the arenediazonium tetrafluoroborate. The solid was filtered off and washed with Et₂O (3 × 10 mL). The product was dried in vacuo (10⁻³ mbar) for 10 minutes and stored in refrigerator under N₂ atmosphere.



Scheme S1. Preparation of arenediazonium tetrafluoroborate (Method A)

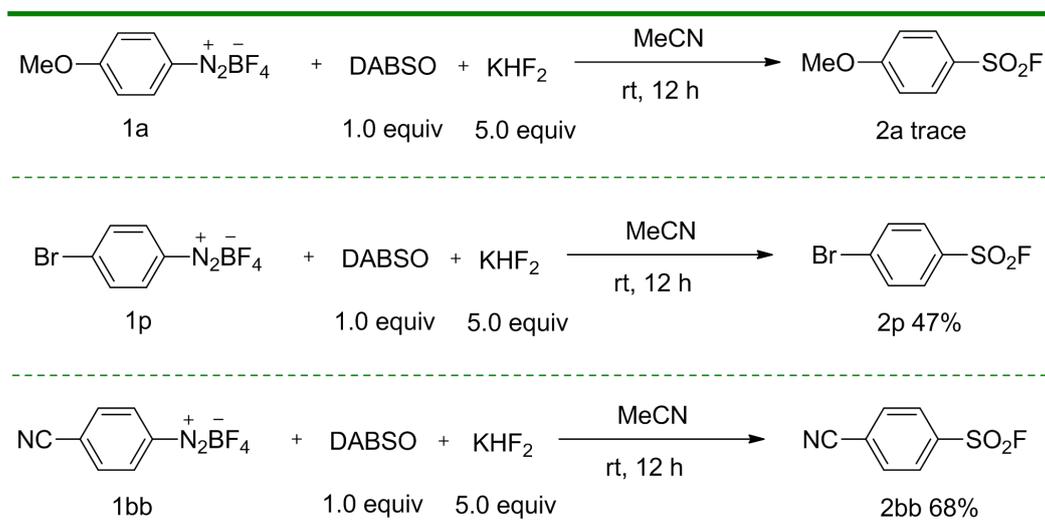
Method B

In a 50 mL round-bottom flask, aniline (5.0 mmol) was dissolved in a mixture of H₂O (1 mL) and an aqueous solution of HBF₄ (50 %, 1.9 mL). The mixture was cooled at 0 °C with an ice bath and an aqueous solution of NaNO₂ (0.68 g, in 1.0 mL H₂O) was added dropwise. The reaction mixture was stirred at 0 °C for 30 minutes. The arenediazonium tetrafluoroborate was removed by filtration, washed successively with a small amount ice water, EtOH, and Et₂O. The product was dried in vacuo (10⁻³ mbar) for 10 minutes and stored in refrigerator under N₂ atmosphere.



Scheme S2. Preparation of arenediazonium tetrafluoroborate (Method B)

3. Screening reaction conditions for the Sandmeyer fluorosulfonylation



Scheme S3. Initial survey on different substrates

Table S1. Survey of the copper salts as oxidant

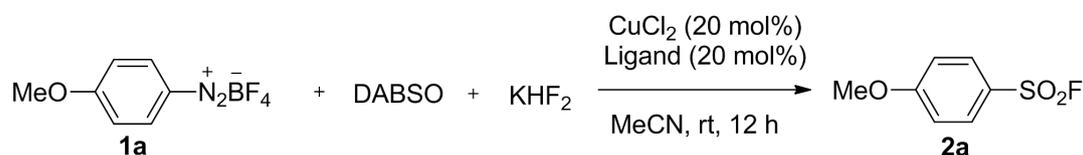
| Entry ^a | [Cu] (1.0 equiv) | Yield (%) ^b |
|--------------------|---------------------------------------|------------------------|
| 1 | CuO | 1 |
| 2 | CuF ₂ | 2 |
| 3 | Cu(OAc) ₂ | 1 |
| 4 | CuSO ₄ | 2 |
| 5 | CuBr ₂ | 33 |
| 6 | CuCl ₂ | 38 |
| 7 | CuCl | 21 |
| 8 | CuI | 14 |
| 9 | Cu(MeCN) ₄ BF ₄ | n.d. |

^a Reaction conditions: 4-methoxyphenyldiazonium tetrafluoroborate (0.2 mmol), DABSO (1.0 equiv), KHF_2 (5.0 equiv), [Cu] (1.0 equiv) in MeCN (1.0 mL) at rt for 12 hours. ^b Yields were determined by ¹⁹F NMR analysis of the crude reaction mixture with 1-methoxy-4-(trifluoromethoxy)benzene as an internal standard. n.d. = not detectable.

Table S2. Survey of the equivalent of CuCl₂

| Entry ^a | CuCl ₂ (X equiv) | Yield (%) ^b |
|--------------------|-----------------------------|------------------------|
| 1 | 0.1 | 44 |
| 2 | 0.2 | 58 |
| 3 | 0.5 | 51 |
| 4 | 1.0 | 38 |
| 5 | 1.5 | 21 |
| 6 | 2.0 | trace |

^a Reaction conditions: 4-methoxyphenyldiazonium tetrafluoroborate (0.2 mmol), DABSO (1.0 equiv), KHF₂ (5.0 equiv), CuCl₂ (X equiv) in MeCN (1.0 mL) at rt for 12 hours. ^b Yields were determined by ¹⁹F NMR analysis of the crude reaction mixture with 1-methoxy-4-(trifluoromethoxy)benzene as an internal standard.

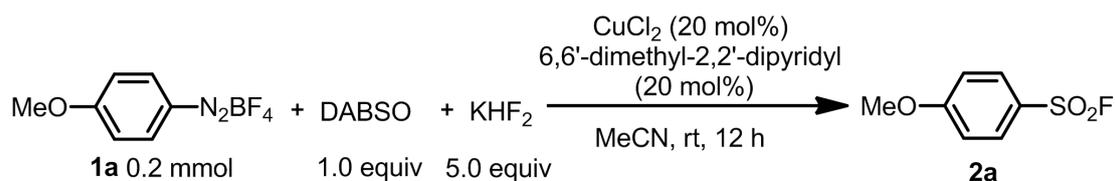
Table S3. Survey of the ligands

| Entry ^a | Ligand | Yield (%) ^b |
|--------------------|--|------------------------|
| 1 | 2,2'-bipyridine | 53 |
| 2 | 4,4'-dimethyl-2,2'-bipyridyl | 50 |
| 3 | 4,4'-dimethoxy-2,2'-bipyridine | 54 |
| 4 | 4,4'-di-tert-butyl-2,2'-bipyridine | 41 |
| 5 | 4,4'-dinitro-2,2'-bipyridine | 51 |
| 6 | 5,5'-dimethyl-2,2'-bipyridyl | 59 |
| 7 | 6,6'-dimethyl-2,2'-dipyridyl | 70 |
| 8 | 6,6'-dimethoxycarbonyl-2,2'-bipyridine | 46 |
| 9 | 6,6'-dicyano-2,2'-bipyridine | 39 |
| 10 | 2,2'-biquinoline | 61 |
| 11 | 1,10-phenanthroline | 17 |

| | | |
|----|-----------------------------------|----|
| 12 | neocuproine | 63 |
| 13 | bathophenanthroline | 58 |
| 14 | 4,7-dimethoxy-1,10-phenanthroline | 49 |
| 15 | 1,10-phenanthroline-5,6-dione | 63 |
| 16 | 2,2'-bis(2-oxazoline) | 61 |
| 17 | 2,2':6',2''-terpyridine | 38 |
| 18 | tetramethylethylenediamine | 45 |

^a Reaction conditions: **1a** (0.2 mmol), DABSO (1.0 equiv), KHF₂ (5.0 equiv), CuCl₂ (0.2 equiv), ligand (0.2 equiv) in MeCN (1.0 mL) at rt for 12 hours. ^b Yields were determined by ¹⁹F NMR analysis of the crude reaction mixture with 1-methoxy-4-(trifluoromethoxy)benzene as an internal standard.

Table S4. Control experiments



| Entry ^a | Variation from the standard conditions | Yield (%) ^b |
|--------------------|--|------------------------|
| 1 | none | 70% |
| 2 | without CuCl ₂ | trace |
| 3 | 110 °C | 59 ^c |
| 4 | without 6,6'-dimethyl-2,2'-dipyridyl | 58 |
| 5 | PhMe, THF, or DMF instead of MeCN | <20 |
| 6 | 0.1 mL of H ₂ O as co-solvent | n.d. |
| 7 | Na ₂ S ₂ O ₄ or K ₂ S ₂ O ₅ instead of DABSO | <15 |
| 8 | Selectfluor or NFSI instead of KHF ₂ | <10 |
| 9 | KF instead of KHF ₂ | 48 |

^a Reaction conditions: **1a** (0.2 mmol), DABSO (1.0 equiv), KHF₂ (5.0 equiv), CuCl₂ (0.2 equiv), 6,6'-dimethyl-2,2'-dipyridyl (0.2 equiv) in MeCN (1.0 mL) at rt for 12 hours. ^b Yields were determined by ¹⁹F NMR analysis of the crude reaction mixture with 1-methoxy-4-(trifluoromethoxy)benzene as an internal standard. ^c No formation of Balz-Schiemann fluorination byproduct was observed. n.d. = not detectable

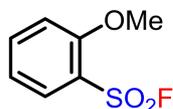
4. General procedures for the Sandmeyer fluorosulfonylation

To an oven-dried sealed tube (10 mL) equipped with a magnetic stirring bar were added ArN_2BF_4 (0.4 mmol, 1.0 equiv), DABSO (0.4 mmol, 1.0 equiv), KHF_2 (2.0 mmol, 5.0 equiv), CuCl_2 (0.08 mmol, 20 mol%), 6,6'-dimethyl-2,2'-dipyridyl (0.08 mmol, 20 mol%). The tube was then evacuated and backfilled with Ar (3 times) and anhydrous MeCN (2 mL) was added via syringe under Ar atmosphere. The mixture was sealed and stirred smoothly at room temperature for 12 hours. The reaction mixture was filtered through a pad of celite. After removal of the solvent under reduced pressure with a rotary evaporator, the crude product was purified by column chromatography on silica gel to give the desired fluorosulfonylated product.

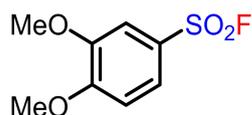
5. Characterization data of the products



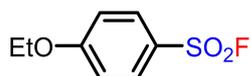
4-methoxybenzenesulfonyl fluoride (2a): Obtained as a colorless oil in 66% yield (50.0 mg) by silica gel flash column chromatography eluted with petroleum ether : dichloromethane = 10:3 v/v. **¹H NMR** (400 MHz, CDCl₃): δ 7.93 (d, *J* = 9.0 Hz, 2H), 7.06 (d, *J* = 9.0 Hz, 2H), 3.91 (s, 3H); **¹⁹F NMR** (376 MHz, CDCl₃): δ 67.3 (s, 1F); **¹³C NMR** (101 MHz, CDCl₃): δ 165.3, 131.0, 124.2 (d, *J* = 24.7 Hz), 115.0, 56.1 ppm. **GC-MS** (EI): *m/z* = 190.1 (M⁺). The analytical data are consistent with literature values.^[2]



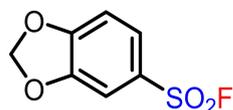
2-methoxybenzenesulfonyl fluoride (2b): Obtained as a colorless oil in 58% yield (44.0 mg) by silica gel flash column chromatography eluted with petroleum ether : dichloromethane = 1:1 v/v. **¹H NMR** (400 MHz, CDCl₃): δ 7.92 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.74 – 7.66 (m, 1H), 7.15 – 7.07 (m, 2H), 4.00 (s, 3H); **¹⁹F NMR** (376 MHz, CDCl₃): δ 58.5 (s, 1F); **¹³C NMR** (101 MHz, CDCl₃): δ 158.2 (d, *J* = 1.2 Hz), 137.5, 131.3 (d, *J* = 1.4 Hz), 121.5 (d, *J* = 23.3 Hz), 120.6, 112.9, 56.6 ppm. **GC-MS** (EI): *m/z* = 190.0 (M⁺). The analytical data are consistent with literature values.^[3]



3,4-dimethoxybenzenesulfonyl fluoride (2c): Obtained as a white solid in 59% yield (51.9 mg) by silica gel flash column chromatography eluted with petroleum ether : dichloromethane = 1:1 v/v. **¹H NMR** (400 MHz, CDCl₃): δ 7.63 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.37 (d, *J* = 2.2 Hz, 1H), 7.00 (d, *J* = 8.5 Hz, 1H), 3.96 (s, 3H), 3.93 (s, 3H); **¹⁹F NMR** (376 MHz, CDCl₃): δ 67.2 (s, 1F); **¹³C NMR** (101 MHz, CDCl₃): δ 155.1, 149.6, 124.1 (d, *J* = 24.5 Hz), 123.3, 110.9, 110.3, 56.5, 56.4 ppm. **HRMS** (EI) *m/z*: [M⁺] Calcd for C₈H₉FO₄S 220.0206; Found 220.0211. **Melting point:** 56 – 58 °C. **IR** (film) *v*_{max}: 3026, 3011, 2978, 2937, 1583, 1511, 1441, 1401, 1272, 1245, 1182, 1147, 1097, 1030, 1013 cm⁻¹.



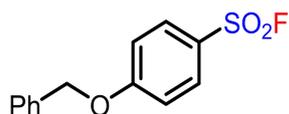
4-ethoxybenzenesulfonyl fluoride (2d): Obtained as a white solid in 60% yield (48.6 mg) by silica gel flash column chromatography eluted with petroleum ether : dichloromethane = 5:1 v/v. **¹H NMR** (400 MHz, CDCl₃): δ 7.91 (d, *J* = 8.9 Hz, 2H), 7.03 (d, *J* = 8.9 Hz, 2H), 4.13 (q, *J* = 7.0 Hz, 2H), 1.46 (t, *J* = 7.0 Hz, 3H); **¹⁹F NMR** (376 MHz, CDCl₃): δ 67.3 (s, 1F); **¹³C NMR** (101 MHz, CDCl₃): δ 164.8, 130.9, 123.8 (d, *J* = 24.6 Hz), 115.4, 64.6, 14.6 ppm. **HRMS** (EI) *m/z*: [M]⁺ Calcd for C₈H₉FO₃S 204.0256; Found 204.0258. **Melting point:** 30 – 32 °C. **IR** (film) *v*_{max}: 3052, 2974, 1781, 1710, 1615, 1468, 1456, 1403, 1368, 1336, 1287, 1192, 1165, 1122, 1078, 1030 cm⁻¹.



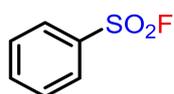
benzo[d][1,3]dioxole-5-sulfonyl fluoride (2e): Obtained as a white solid in 54% yield (44.2 mg) by silica gel flash column chromatography eluted with petroleum ether : dichloromethane = 5:1 v/v. **¹H NMR** (400 MHz, CDCl₃): δ 7.62 – 7.56 (m, 1H), 7.36 (d, *J* = 1.8 Hz, 1H), 6.96 (d, *J* = 8.3 Hz, 1H), 6.15 (s, 2H); **¹⁹F NMR** (376 MHz, CDCl₃): δ 66.8 (s, 1F); **¹³C NMR** (101 MHz, CDCl₃): δ 154.0, 148.8, 125.7 (d, *J* = 25.0 Hz), 125.3, 108.9, 108.3, 103.1 ppm. **GC-MS** (EI): *m/z* = 204.0 (M⁺). The analytical data are consistent with literature values.^[4]



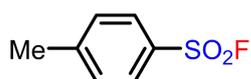
4-phenoxybenzenesulfonyl fluoride (2f): Obtained as a colorless oil in 56% yield (56.9 mg) by silica gel flash column chromatography eluted with petroleum ether : dichloromethane = 4:1 v/v. **¹H NMR** (400 MHz, CDCl₃): δ 7.98 – 7.91 (m, 2H), 7.50 – 7.41 (m, 2H), 7.32 – 7.26 (m, 1H), 7.11 (d, *J* = 8.5 Hz, 4H); **¹⁹F NMR** (376 MHz, CDCl₃): δ 67.1 (s, 1F); **¹³C NMR** (101 MHz, CDCl₃): δ 164.3, 154.4, 131.1, 130.5, 125.9 (d, *J* = 24.2 Hz), 125.8, 120.7, 117.8 ppm. **HRMS** (EI) *m/z*: [M]⁺ Calcd for C₁₂H₉FO₃S 252.0256; Found 252.0252. **IR** (film) *v*_{max}: 1585, 1489, 1406, 1302, 1259, 1212, 1170, 1100, 1022 cm⁻¹.



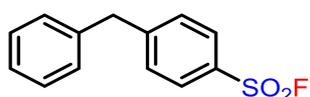
4-(benzyloxy)benzenesulfonyl fluoride (2g): Obtained as a white solid in 63% yield (67.0 mg) by silica gel flash column chromatography eluted with petroleum ether : dichloromethane = 3:1 v/v. **¹H NMR** (400 MHz, CDCl₃): δ 7.94 (d, *J* = 8.9 Hz, 2H), 7.48 – 7.42 (m, 4H), 7.41 – 7.35 (m, 1H), 7.14 (d, *J* = 8.9 Hz, 2H), 5.19 (s, 2H); **¹⁹F NMR** (376 MHz, CDCl₃): δ 67.3 (s, 1F); **¹³C NMR** (101 MHz, CDCl₃): δ 164.4, 135.4, 131.0, 129.0, 128.8, 127.6, 124.5 (d, *J* = 24.8 Hz), 115.8, 70.8 ppm. **HRMS** (EI) *m/z*: [M]⁺ Calcd for C₁₃H₁₁FO₃S 266.0413; Found 266.0411. **Melting point:** 94 – 96 °C. **IR** (film) *v*_{max}: 1593, 1577, 1499, 1469, 1420, 1395, 1317, 1265, 1205, 1173, 1118, 1099, 1029, 1001 cm⁻¹.



benzenesulfonyl fluoride (2h): Obtained as a colorless oil in 57% yield (36.3 mg) by silica gel flash column chromatography eluted with petroleum ether : dichloromethane = 20:3 v/v. **¹H NMR** (400 MHz, CDCl₃): δ 8.02 (d, *J* = 7.8 Hz, 2H), 7.79 (t, *J* = 7.5 Hz, 1H), 7.64 (t, *J* = 7.8 Hz, 2H); **¹⁹F NMR** (376 MHz, CDCl₃): δ 65.9 (s, 1F); **¹³C NMR** (101 MHz, CDCl₃): δ 135.7, 133.3 (d, *J* = 24.3 Hz), 129.8, 128.5 ppm. **GC-MS** (EI): *m/z* = 160.0 (M⁺). The analytical data are consistent with literature values.^[2]



4-methylbenzenesulfonyl fluoride (2i): Obtained as a colorless oil in 60% yield (42.0 mg) by silica gel flash column chromatography eluted with petroleum ether : ethyl acetate = 40:1 v/v. **¹H NMR** (400 MHz, CDCl₃): δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 2.50 (s, 3H); **¹⁹F NMR** (376 MHz, CDCl₃): δ 66.3 (s, 1F) ppm. **GC-MS** (EI): *m/z* = 174.1 (M⁺). The analytical data are consistent with literature values.^[2]

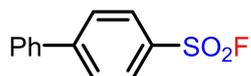


4-benzylbenzenesulfonyl fluoride (2j): Obtained as a colorless oil in 58% yield

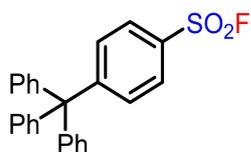
(58.5 mg) by silica gel flash column chromatography eluted with petroleum ether : dichloromethane = 4:1 v/v. **¹H NMR** (400 MHz, CDCl₃): δ 7.93 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 2H), 7.28 (t, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 7.1 Hz, 2H), 4.12 (s, 2H); **¹⁹F NMR** (376 MHz, CDCl₃): δ 66.3 (s, 1F); **¹³C NMR** (101 MHz, CDCl₃): δ 150.2, 138.9, 130.8 (d, *J* = 24.3 Hz), 130.2, 129.1, 129.0, 128.8, 127.0, 42.0 ppm. **HRMS** (EI) *m/z*: [M]⁺ Calcd for C₁₃H₁₁FO₂S 250.0464; Found 250.0471. **IR** (film) *v*_{max}: 3087, 3064, 3030, 2924, 1595, 1496, 1455, 1414, 1214, 1185, 1113, 1098, 1075, 1030, 1018 cm⁻¹.



4-(tert-butyl)benzenesulfonyl fluoride (2k): Obtained as a white solid in 64% yield (55.4 mg) by silica gel flash column chromatography eluted with petroleum ether : dichloromethane = 20:3 v/v. **¹H NMR** (400 MHz, CDCl₃): δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 1.37 (s, 9H); **¹⁹F NMR** (376 MHz, CDCl₃): δ 66.2 (s, 1F); **¹³C NMR** (101 MHz, CDCl₃): δ 160.1, 130.1 (d, *J* = 24.2 Hz); 128.5, 126.8, 35.7, 31.1 ppm. **GC-MS** (EI): *m/z* = 216.0 (M⁺). The analytical data are consistent with literature values.^[2]

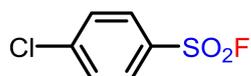


[1,1'-biphenyl]-4-sulfonyl fluoride (2l): Obtained as a white solid in 56% yield (53.0 mg) by silica gel flash column chromatography eluted with petroleum ether : dichloromethane = 8:1 v/v. **¹H NMR** (400 MHz, CDCl₃): δ 8.08 (d, *J* = 8.4 Hz, 2H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 7.2 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 2H), 7.48 (dd, *J* = 8.4, 5.8 Hz, 1H); **¹⁹F NMR** (376 MHz, CDCl₃): δ 66.5 (s, 1F); **¹³C NMR** (101 MHz, CDCl₃): δ 148.8, 138.7, 131.5 (d, *J* = 24.6 Hz), 129.4, 129.3, 129.1, 128.3, 127.6 ppm. **GC-MS** (EI): *m/z* = 236.0 (M⁺). The analytical data are consistent with literature values.^[4]

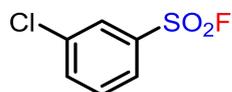


4-tritylbenzenesulfonyl fluoride (2m): Obtained as a white solid in 53% yield (86.0

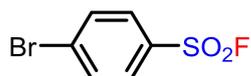
mg) by silica gel flash column chromatography eluted with petroleum ether : dichloromethane = 5:1 v/v. **¹H NMR** (400 MHz, CDCl₃): δ 7.90 (d, *J* = 8.6 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.34 – 7.28 (m, 6H), 7.27 – 7.24 (m, 3H), 7.23 – 7.19 (m, 6H); **¹⁹F NMR** (376 MHz, CDCl₃): δ 66.0 (s, 1F); **¹³C NMR** (101 MHz, CDCl₃): δ 155.8, 145.5, 132.3, 131.0, 130.5 (d, *J* = 24.5 Hz), 128.1, 127.8, 126.7, 65.5 ppm. **HRMS** (EI) *m/z*: [M]⁺ Calcd for C₂₅H₁₉FO₂S 402.1090; Found 402.1094. **Melting point**: 227 – 229 °C. **IR** (film) *v*_{max}: 1590, 1492, 1443, 1410, 1215, 1194, 1096, 1036, 1015 cm⁻¹.



4-chlorobenzenesulfonyl fluoride (2n): Obtained as a white solid in 49% yield (38.0 mg) by silica gel flash column chromatography eluted with petroleum ether : dichloromethane = 20:3 v/v. **¹H NMR** (400 MHz, CDCl₃): δ 7.96 (d, *J* = 8.5 Hz, 2H), 7.62 (d, *J* = 8.5 Hz, 2H); **¹⁹F NMR** (376 MHz, CDCl₃): δ 66.5 (s, 1F); **¹³C NMR** (101 MHz, CDCl₃): δ 142.8, 131.6 (d, *J* = 25.7 Hz), 130.3, 130.0 ppm. **GC-MS** (EI): *m/z* = 194.0 (M⁺). The analytical data are consistent with literature values.^[2]

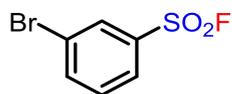


3-chlorobenzenesulfonyl fluoride (2o): Obtained as a colorless oil in 47% yield (36.9 mg) by silica gel flash column chromatography eluted with petroleum ether : dichloromethane = 20:3 v/v. **¹H NMR** (400 MHz, CDCl₃): δ 8.00 (t, *J* = 1.8 Hz, 1H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.78 – 7.73 (m, 1H), 7.60 (td, *J* = 8.0, 0.6 Hz, 1H); **¹⁹F NMR** (376 MHz, CDCl₃): δ 66.1 (s, 1F); **¹³C NMR** (101 MHz, CDCl₃): δ 136.2, 135.9, 134.7 (d, *J* = 25.6 Hz), 131.1, 128.6, 126.7 ppm. **HRMS** (EI) *m/z*: [M]⁺ Calcd for C₆H₄ClFO₂S 193.9605; Found 193.9610. **IR** (film) *v*_{max}: 3095, 1583, 1470, 1417, 1214, 1124, 1078 cm⁻¹.

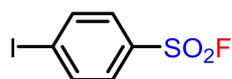


4-bromobenzenesulfonyl fluoride (2p): Obtained as a white solid in 60% yield (57.0 mg) by silica gel flash column chromatography eluted with petroleum ether : dichloromethane = 20:3 v/v. **¹H NMR** (400 MHz, CDCl₃): δ 7.88 (d, *J* = 8.4 Hz, 2H),

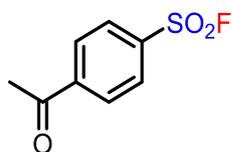
7.79 (d, $J = 8.4$ Hz, 2H); ^{19}F NMR (376 MHz, CDCl_3): δ 66.4 (s, 1F); ^{13}C NMR (101 MHz, CDCl_3): δ 133.3, 132.1 (d, $J = 25.8$ Hz), 131.4, 130.0 ppm. **GC-MS** (EI): $m/z = 239.9$ (M^+). The analytical data are consistent with literature values.^[2]



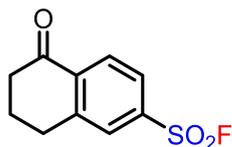
3-bromobenzenesulfonyl fluoride (2q): Obtained as a colorless oil in 51% yield (48.4 mg) by silica gel flash column chromatography eluted with petroleum ether : dichloromethane = 20:3 v/v. ^1H NMR (400 MHz, CDCl_3): δ 8.15 (t, $J = 1.8$ Hz, 1H), 7.96 (d, $J = 7.9$ Hz, 1H), 7.91 (dd, $J = 8.1, 0.8$ Hz, 1H), 7.53 (td, $J = 8.0, 0.7$ Hz, 1H); ^{19}F NMR (376 MHz, CDCl_3): δ 66.2 (s, 1F); ^{13}C NMR (101 MHz, CDCl_3): δ 138.8, 134.8 (d, $J = 25.4$ Hz), 131.4, 131.3, 127.1, 123.7 ppm. **HRMS** (EI) m/z : [M]⁺ Calcd for $\text{C}_6\text{H}_4\text{BrFO}_2\text{S}$ 237.9099; Found 237.9106. **IR** (film) ν_{max} : 3091, 1574, 1467, 1420, 1300, 1213, 1115, 1102, 1070 cm^{-1} .



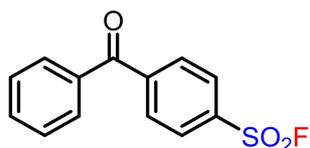
4-iodobenzenesulfonyl fluoride (2r): Obtained as a white solid in 45% yield (51.7 mg) by silica gel flash column chromatography eluted with petroleum ether : dichloromethane = 20:3 v/v. ^1H NMR (400 MHz, CDCl_3): δ 8.00 (d, $J = 8.3$ Hz, 2H), 7.71 (d, $J = 8.3$ Hz, 2H); ^{19}F NMR (376 MHz, CDCl_3): δ 66.2 (s, 1F); ^{13}C NMR (101 MHz, CDCl_3): δ 139.2, 132.7 (d, $J = 25.6$ Hz), 129.6, 104.2 ppm. **GC-MS** (EI): $m/z = 285.9$ (M^+). The analytical data are consistent with literature values.^[5]



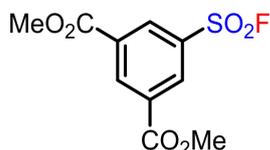
4-acetylbenzenesulfonyl fluoride (2s): Obtained as a white solid in 61% yield (49.6 mg) by silica gel flash column chromatography eluted with petroleum ether : ethyl acetate = 8:1 v/v. ^1H NMR (400 MHz, CDCl_3): δ 8.16 (d, $J = 8.4$ Hz, 2H), 8.10 (d, $J = 8.4$ Hz, 2H), 2.68 (s, 3H); ^{19}F NMR (376 MHz, CDCl_3): δ 65.8 (s, 1F); ^{13}C NMR (101 MHz, CDCl_3): δ 196.3, 142.3, 136.6 (d, $J = 25.4$ Hz), 129.4, 128.9, 27.0 ppm. **GC-MS** (EI): $m/z = 202.0$ (M^+). The analytical data are consistent with literature values.^[3]



5-oxo-5,6,7,8-tetrahydronaphthalene-2-sulfonyl fluoride (2t): Obtained as a white solid in 57% yield (51.6 mg) by silica gel flash column chromatography eluted with petroleum ether : ethyl acetate = 10:1 v/v. **¹H NMR** (400 MHz, CDCl₃): δ 8.22 (d, *J* = 8.2 Hz, 1H), 7.92 (s, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 3.09 (t, *J* = 6.1 Hz, 2H), 2.74 (t, *J* = 6.0 Hz, 2H), 2.26 – 2.16 (m, 2H); **¹⁹F NMR** (376 MHz, CDCl₃): δ 65.5 (s, 1F); **¹³C NMR** (101 MHz, CDCl₃): δ 196.4, 145.8, 137.5, 136.5 (d, *J* = 24.7 Hz), 129.2, 128.8, 126.2, 38.9, 29.6, 22.7 ppm. **HRMS** (EI) *m/z*: [M]⁺ Calcd for C₁₀H₉FO₃S 228.0256; Found 228.0265. **Melting point:** 95 – 97 °C. **IR** (film) *v*_{max}: 2958, 1687, 1458, 1439, 1409, 1280, 1215, 1187, 1024 cm⁻¹.

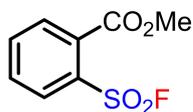


4-benzoylbenzenesulfonyl fluoride (2u): Obtained as a white solid in 64% yield (67.4 mg) by silica gel flash column chromatography eluted with petroleum ether : ethyl acetate = 50:3 v/v. **¹H NMR** (400 MHz, CDCl₃): δ 8.13 (d, *J* = 8.2 Hz, 2H), 7.98 (d, *J* = 8.2 Hz, 2H), 7.83 – 7.75 (m, 2H), 7.69 – 7.62 (m, 1H), 7.53 (t, *J* = 7.7 Hz, 2H); **¹⁹F NMR** (376 MHz, CDCl₃): δ 65.9 (s, 1F); **¹³C NMR** (101 MHz, CDCl₃): δ 194.7, 144.1, 136.1, 135.8 (d, *J* = 25.4 Hz), 133.8, 130.7, 130.3, 128.9, 128.6 ppm. **HRMS** (EI) *m/z*: [M]⁺ Calcd for C₁₃H₉FO₃S 264.0256; Found 264.0257. **Melting point:** 131 – 133 °C. **IR** (film) *v*_{max}: 1652, 1594, 1415, 1280, 1221 cm⁻¹.

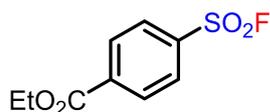


dimethyl 5-(fluorosulfonyl)isophthalate (2v): Obtained as a white solid in 45% yield (49.2 mg) by silica gel flash column chromatography eluted with petroleum ether : ethyl acetate = 8:1 v/v. **¹H NMR** (400 MHz, CDCl₃): δ 9.01 (s, 1H), 8.80 (d, *J* = 1.2 Hz, 2H), 4.01 (s, 6H); **¹⁹F NMR** (376 MHz, CDCl₃): δ 66.1 (s, 1F); **¹³C NMR** (101 MHz, CDCl₃): δ 164.0, 137.0, 134.5 (d, *J* = 27.0 Hz), 133.1, 132.8, 53.3 ppm.

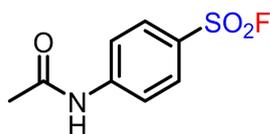
HRMS (EI) m/z : $[M]^+$ Calcd for $C_{10}H_9FO_6S$ 276.0104; Found 276.0103. **Melting point**: 70 – 72 °C. **IR** (film) ν_{max} : 3078, 1729, 1447, 1415, 1327, 1263, 1214, 1149 cm^{-1} .



methyl 2-(fluorosulfonyl)benzoate (2w): Obtained as a white solid in 61% yield (53.1 mg) by silica gel flash column chromatography eluted with petroleum ether : ethyl acetate = 13:1 v/v. **1H NMR** (400 MHz, $CDCl_3$): δ 8.15 (d, J = 7.9 Hz, 1H), 7.87 (d, J = 7.6 Hz, 1H), 7.82 (td, J = 7.5, 1.0 Hz, 1H), 7.73 (t, J = 7.7 Hz, 1H), 3.98 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$): δ 64.4 (s, 1F); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 165.9, 135.4, 133.1, 132.0 (d, J = 26.1 Hz), 131.8, 130.9, 130.6 (d, J = 1.3 Hz), 53.6 ppm. **GC-MS** (EI): m/z = 218.0 (M^+). The analytical data are consistent with literature values.^[2]

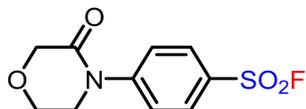


ethyl 4-(fluorosulfonyl)benzoate (2x): Obtained as a white solid in 53% yield (49.0 mg) by silica gel flash column chromatography eluted with petroleum ether : ethyl acetate = 20:1 v/v. **1H NMR** (400 MHz, $CDCl_3$): δ 8.27 (d, J = 8.2 Hz, 2H), 8.08 (d, J = 8.2 Hz, 2H), 4.44 (q, J = 7.1 Hz, 2H), 1.42 (t, J = 7.1 Hz, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$): δ 65.8 (s, 1F); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 164.5, 137.0, 136.7 (d, J = 25.3 Hz), 130.8, 128.6, 62.3, 14.3 ppm. **HRMS** (EI) m/z : $[M]^+$ Calcd for $C_9H_9FO_4S$ 232.0206; Found 232.0207. **Melting point**: 37 – 39 °C. **IR** (film) ν_{max} : 3105, 2989, 1948, 1717, 1578, 1475, 1411, 1369, 1279, 1213, 1104, 1012 cm^{-1} .

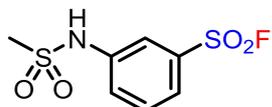


4-acetamidobenzenesulfonyl fluoride (2y): Obtained as a white solid in 68% yield (58.8 mg) by silica gel flash column chromatography eluted with petroleum ether : acetone = 5:1 v/v. **1H NMR** (400 MHz, CD_3CN): δ 8.85 (br, 1H), 7.94 (d, J = 9.0 Hz, 2H), 7.85 (d, J = 9.0 Hz, 2H), 2.12 (s, 3H); **^{19}F NMR** (376 MHz, CD_3CN): δ 65.7 (s,

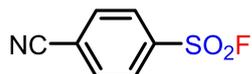
1F); ^{13}C NMR (101 MHz, CD_3CN): δ 170.5, 147.0, 130.8, 126.2 (d, $J = 24.3$ Hz), 120.0, 24.6 ppm. **GC-MS** (EI): $m/z = 217.0$ (M^+). The analytical data are consistent with literature values.^[2]



4-(3-oxomorpholino)benzenesulfonyl fluoride (2z): Obtained as a white solid in 69% yield (71.2 mg) by silica gel flash column chromatography eluted with petroleum ether : ethyl acetate = 1:1 v/v. ^1H NMR (400 MHz, CDCl_3): δ 8.00 (d, $J = 8.7$ Hz, 2H), 7.69 (d, $J = 8.7$ Hz, 2H), 4.34 (s, 2H), 4.05 (t, $J = 4.0$ Hz, 2H), 3.84 (t, $J = 4.0$ Hz, 2H); ^{19}F NMR (376 MHz, CDCl_3): δ 69.0 (s, 1F); ^{13}C NMR (101 MHz, CDCl_3): δ 166.9, 147.7, 129.7 (d, $J = 25.2$ Hz), 129.5, 124.9, 68.6, 63.9, 48.7 ppm. **HRMS** (EI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{10}\text{H}_{10}\text{FNO}_4\text{S}$ 259.0315; Found 259.0306. **Melting point:** 104 – 106 °C. **IR** (film) ν_{max} : 3100, 3068, 2981, 2881, 1671, 1587, 1500, 1463, 1409, 1346, 1214, 1193, 1124, 1100, 1000 cm^{-1} .



3-(methylsulfonylamido)benzenesulfonyl fluoride (2aa): Obtained as a white solid in 45% yield (46.0 mg) by silica gel flash column chromatography eluted with petroleum ether : acetone = 4:1 v/v. ^1H NMR (400 MHz, CD_3CN): δ 8.05 (br, 1H), 7.88 (s, 1H), 7.83 – 7.77 (m, 1H), 7.72 – 7.65 (m, 2H), 3.03 (s, 3H); ^{19}F NMR (376 MHz, CD_3CN): δ 64.4 (s, 1F); ^{13}C NMR (101 MHz, CD_3CN): δ 140.5, 134.3 (d, $J = 24.5$ Hz), 132.3, 127.8, 124.7, 119.6, 40.3 ppm. **HRMS** (EI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_7\text{H}_8\text{FNO}_4\text{S}_2$ 252.9879; Found 252.9872. **Melting point:** 112 – 114 °C. **IR** (film) ν_{max} : 3283, 3033, 1607, 1487, 1417, 1402, 1334, 1298, 1241, 1203, 1160, 1101 cm^{-1} .

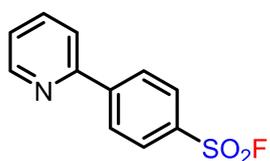


4-cyanobenzenesulfonyl fluoride (2bb): Obtained as a white solid in 65% yield (48.3 mg) by silica gel flash column chromatography eluted with petroleum ether : dichloromethane = 1:1 v/v. ^1H NMR (400 MHz, CDCl_3): δ 8.15 (d, $J = 8.5$ Hz, 2H), 7.95 (d, $J = 8.5$ Hz, 2H); ^{19}F NMR (376 MHz, CDCl_3): δ 66.0 (s, 1F) ppm. **GC-MS**

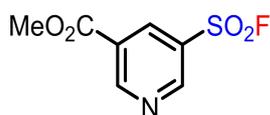
(EI): $m/z = 185.0$ (M^+). The analytical data are consistent with literature values.^[3]



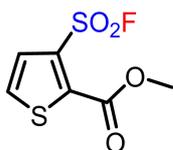
4-nitrobenzenesulfonyl fluoride (2cc): Obtained as a white solid in 55% yield (45.0 mg) by silica gel flash column chromatography eluted with petroleum ether : ethyl acetate = 25:1 v/v. **¹H NMR** (400 MHz, CDCl₃): δ 8.49 (d, $J = 8.9$ Hz, 2H), 8.25 (d, $J = 8.9$ Hz, 2H); **¹⁹F NMR** (376 MHz, CDCl₃): δ 66.1 (s, 1F); **¹³C NMR** (101 MHz, CDCl₃): δ 152.0, 138.5 (d, $J = 26.9$ Hz), 130.1, 125.0 ppm. **GC-MS** (EI): $m/z = 205.0$ (M^+). The analytical data are consistent with literature values.^[5]



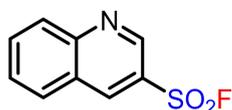
4-(pyridin-2-yl)benzenesulfonyl fluoride (2dd): Obtained as a white solid in 49% yield (46.9 mg) by silica gel flash column chromatography eluted with petroleum ether : acetone = 12:1 v/v. **¹H NMR** (400 MHz, CDCl₃): δ 8.74 (d, $J = 4.7$ Hz, 1H), 8.25 (d, $J = 8.3$ Hz, 2H), 8.08 (d, $J = 8.3$ Hz, 2H), 7.86 – 7.77 (m, 2H), 7.35 (ddd, $J = 6.6, 4.8, 1.7$ Hz, 1H); **¹⁹F NMR** (376 MHz, CDCl₃): δ 66.3 (s, 1F); **¹³C NMR** (101 MHz, CDCl₃): δ 154.5, 150.3, 146.3, 137.4, 132.9 (d, $J = 24.6$ Hz), 129.0, 128.0, 123.9, 121.4 ppm. **HRMS** (EI) m/z : [M]⁺ Calcd for C₁₁H₈FNO₂S 237.0260; Found 237.0265. **Melting point:** 76 – 78 °C. **IR** (film) ν_{\max} : 1587, 1565, 1467, 1403, 1317, 1211, 1186, 1091, 1011 cm⁻¹.



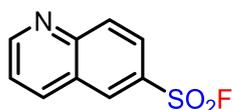
methyl 5-(fluorosulfonyl)nicotinate (2ee): Obtained as a white solid in 41% yield (35.8 mg) by silica gel flash column chromatography eluted with petroleum ether : ethyl acetate = 8:1 v/v. **¹H NMR** (400 MHz, CDCl₃): δ 9.54 (d, $J = 1.8$ Hz, 1H), 9.34 (d, $J = 1.3$ Hz, 1H), 8.86 (t, $J = 2.1$ Hz, 1H), 4.03 (s, 3H); **¹⁹F NMR** (376 MHz, CDCl₃): δ 68.2 (s, 1F); **¹³C NMR** (101 MHz, CDCl₃): δ 163.4, 156.6, 152.1, 137.3, 130.5 (d, $J = 26.9$ Hz), 127.0, 53.4 ppm. **HRMS** (EI) m/z : [M]⁺ Calcd for C₇H₆FNO₄S 219.0002; Found 218.9998. **Melting point:** 92 – 94 °C. **IR** (film) ν_{\max} : 3026, 1727, 1586, 1453, 1426, 1300, 1216, 1172, 1128, 1117, 1020 cm⁻¹.



methyl 3-(fluorosulfonyl)thiophene-2-carboxylate (2ff): Obtained as a white solid in 41% yield (37.2 mg) by silica gel flash column chromatography eluted with petroleum ether : ethyl acetate = 10:1 v/v. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.66 (d, J = 5.3 Hz, 1H), 7.60 (d, J = 5.3 Hz, 1H), 3.97 (s, 3H); $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ 62.8 (s, 1F); $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 159.0, 137.2, 134.5 (d, J = 29.8 Hz), 131.0 (d, J = 1.3 Hz), 130.5 (d, J = 2.4 Hz), 53.6 ppm. **HRMS** (EI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_6\text{H}_5\text{FO}_4\text{S}_2$ 223.9613; Found 223.9621. **Melting point:** 64 – 66 °C. **IR** (film) ν_{max} : 3125, 2962, 1734, 1508, 1440, 1402, 1256, 1219, 1100, 1079 cm^{-1} .

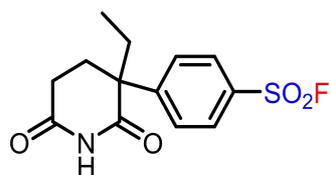


quinoline-3-sulfonyl fluoride (2gg): Obtained as a white solid in 32% yield (27.1 mg) by silica gel flash column chromatography eluted with petroleum ether : ethyl acetate = 8:1 v/v. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 9.33 (d, J = 2.1 Hz, 1H), 8.89 (d, J = 2.1 Hz, 1H), 8.26 (d, J = 8.5 Hz, 1H), 8.06 – 7.95 (m, 2H), 7.78 (t, J = 7.6 Hz, 1H); $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ 68.8 (s, 1F); $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 150.5, 146.2, 139.0, 134.3, 130.1, 129.5, 129.3, 126.5 (d, J = 25.4 Hz), 125.9 ppm. **GC-MS** (EI): m/z = 211.0 (M^+). The analytical data are consistent with literature values.^[4]

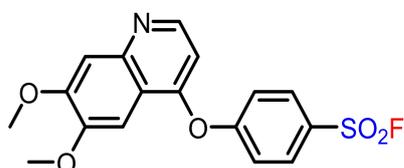


quinoline-6-sulfonyl fluoride (2hh): Obtained as a white solid in 42% yield (35.4 mg) by silica gel flash column chromatography eluted with petroleum ether : acetone = 5:1 v/v. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 9.14 (dd, J = 4.1, 1.4 Hz, 1H), 8.61 (d, J = 1.7 Hz, 1H), 8.39 – 8.29 (m, 2H), 8.17 (dd, J = 8.9, 2.0 Hz, 1H), 7.63 (dd, J = 8.3, 4.3 Hz, 1H); $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ 66.4 (s, 1F); $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 154.5, 150.3, 137.7, 132.0, 131.2 (d, J = 0.6 Hz), 130.8 (d, J = 25.4 Hz), 127.3, 126.1, 123.4 ppm. **HRMS** (EI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_9\text{H}_6\text{FNO}_2\text{S}$ 211.0103; Found 211.0108. **Melting point:** 103 – 105 °C. **IR** (film) ν_{max} : 3010, 1494, 1401, 1321, 1238,

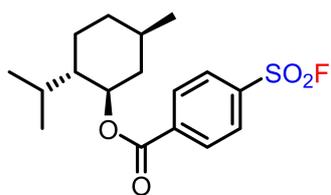
1214, 1190, 1080 cm^{-1} .



4-(3-ethyl-2,6-dioxopiperidin-3-yl)benzenesulfonyl fluoride (2ii): Obtained as a white solid in 66% yield (79.5 mg) by silica gel flash column chromatography eluted with petroleum ether : acetone = 4:1 v/v. **$^1\text{H NMR}$** (400 MHz, CDCl_3): δ 8.93 (br, 1H), 7.99 (d, $J = 8.6$ Hz, 2H), 7.59 (d, $J = 8.6$ Hz, 2H), 2.72 – 2.61 (m, 1H), 2.48 – 2.38 (m, 1H), 2.36 – 2.55 (m, 2H), 2.12 – 2.03 (m, 1H), 1.99 – 1.89 (m, 1H), 0.86 (t, $J = 7.4$ Hz, 3H); **$^{19}\text{F NMR}$** (376 MHz, CDCl_3): δ 66.1 (s, 1F); **$^{13}\text{C NMR}$** (101 MHz, CDCl_3): δ 174.3, 172.2, 147.8, 132.2 (d, $J = 25.1$ Hz), 129.1, 128.0, 51.4, 32.8, 29.1, 26.9, 9.0 ppm. **HRMS** (EI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{13}\text{H}_{14}\text{FNO}_4\text{S}$ 299.0628; Found 299.0630. **Melting point:** 120 – 122 $^\circ\text{C}$. **IR** (film) ν_{max} : 3215, 3107, 2981, 2943, 1731, 1698, 1595, 1459, 1414, 1348, 1270, 1217, 1197, 1099 cm^{-1} .

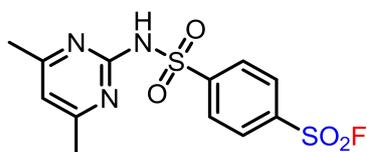


4-((6,7-dimethoxyquinolin-4-yl)oxy)benzenesulfonyl fluoride (2jj): Obtained as a white solid in 48% yield (69.5 mg) by silica gel flash column chromatography eluted with petroleum ether : acetone = 2:1 v/v. **$^1\text{H NMR}$** (400 MHz, CDCl_3): δ 8.61 (d, $J = 5.1$ Hz, 1H), 8.04 (d, $J = 9.0$ Hz, 2H), 7.45 (s, 1H), 7.32 (d, $J = 9.0$ Hz, 2H), 7.30 (s, 1H), 6.71 (d, $J = 5.1$ Hz, 1H), 4.03 (s, 3H), 3.97 (s, 3H); **$^{19}\text{F NMR}$** (376 MHz, CDCl_3): δ 66.8 (s, 1F); **$^{13}\text{C NMR}$** (101 MHz, CDCl_3): δ 161.7, 157.8, 153.4, 150.4, 148.8, 147.7, 131.3, 128.3 (d, $J = 25.5$ Hz), 120.1, 116.8, 108.2, 106.7, 98.9, 56.3, 56.2 ppm. **HRMS** (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{15}\text{FNO}_5\text{S}$ 364.0649; Found 364.0649. **Melting point:** 152 – 154 $^\circ\text{C}$. **IR** (film) ν_{max} : 1597, 1574, 1506, 1479, 1433, 1414, 1348, 1233, 1248, 1211, 1174 cm^{-1} .



(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 4-(fluorosulfonyl)benzoate (2kk):

Obtained as a colorless oil in 59% yield (80.6 mg) by silica gel flash column chromatography eluted with petroleum ether : dichloromethane = 4:1 v/v. **¹H NMR** (400 MHz, CDCl₃): δ 8.27 (d, *J* = 8.1 Hz, 2H), 8.08 (d, *J* = 8.1 Hz, 2H), 4.98 (td, *J* = 10.9, 4.4 Hz, 1H), 2.16 – 2.07 (m, 1H), 1.95 – 1.85 (m, 1H), 1.78 – 1.69 (m, 2H), 1.62 – 1.52 (m, 2H), 1.19 – 1.06 (m, 2H), 0.99 – 0.94 (m, 1H), 0.92 (t, *J* = 6.7 Hz, 6H), 0.78 (d, *J* = 6.9 Hz, 3H); **¹⁹F NMR** (376 MHz, CDCl₃): δ 65.8 (s, 1F); **¹³C NMR** (101 MHz, CDCl₃): δ 164.0, 137.4, 136.6 (d, *J* = 25.3 Hz), 130.8, 128.6, 76.5, 47.3, 40.9, 34.3, 31.6, 26.7, 23.7, 22.1, 20.8, 16.6 ppm. **HRMS** (EI) *m/z*: [M-CH₃]⁺ Calcd for C₁₆H₂₀FO₄S 327.1066; Found 327.1064. **IR** (film) *v*_{max}: 2957, 2871, 1721, 1457, 1417, 1277, 1215, 1179, 1119, 1095, 1017 cm⁻¹.

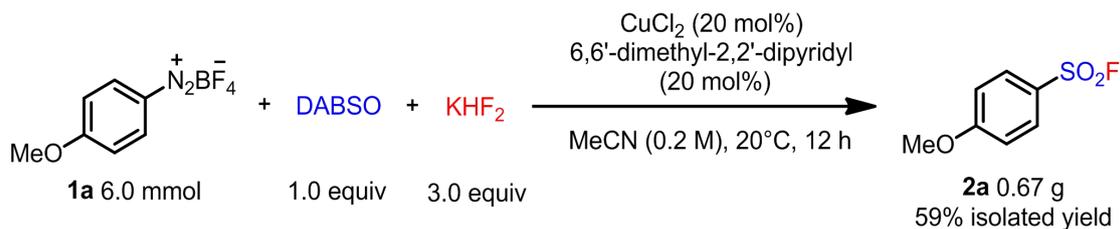


4-(N-(4,6-dimethylpyrimidin-2-yl)sulfamoyl)benzenesulfonyl fluoride (2ll):

Obtained as a white solid in 48% yield (67.7 mg) by silica gel flash column chromatography eluted with petroleum ether : acetone = 2:1 v/v. **¹H NMR** (400 MHz, (CD₃)₂CO): δ 8.52 (d, *J* = 8.4 Hz, 2H), 8.33 (d, *J* = 8.4 Hz, 2H), 6.80 (s, 1H), 2.31 (s, 6H); **¹⁹F NMR** (376 MHz, (CD₃)₂CO): δ 64.6 (s, 1F); **¹³C NMR** (101 MHz, (CD₃)₂CO): δ 169.1, 157.0, 149.3, 136.6 (d, *J* = 25.5 Hz), 131.1, 129.7, 114.9, 23.2 ppm. **HRMS** (ESI) *m/z*: [M + H]⁺ Calcd for C₁₂H₁₃FN₃O₄S₂ 346.0326; Found 346.0322. **Melting point** could not be measured due to the decomposition temperature lower than melting point. **IR** (film) *v*_{max}: 3078, 2968, 2850, 1626, 1602, 1413, 1311, 1150, 1082 cm⁻¹.

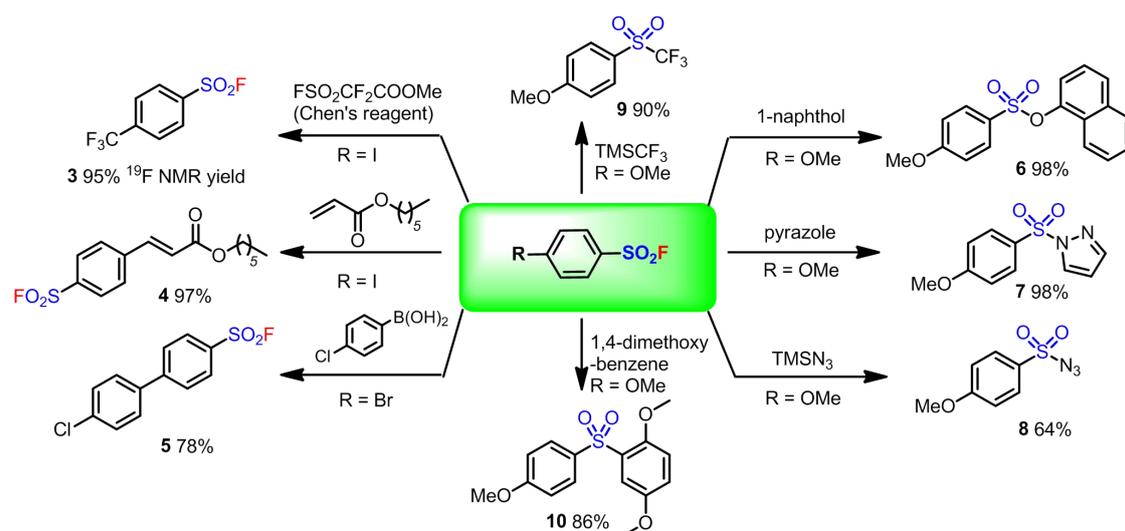
6. Application of the Sandmeyer fluorosulfonylation of arenediazonium salts

(a) Synthesis of 4-methoxybenzenesulfonyl fluoride on gram scale



To a 100 mL round bottom flask equipped with a magnetic stirring bar were added 4-MeO-C₆H₄N₂BF₄ (6.0 mmol, 1.0 equiv), DABSO (6.0 mmol, 1.0 equiv), KHF₂ (18.0 mmol, 3.0 equiv), CuCl₂ (1.2 mmol, 20 mol%), 6,6'-dimethyl-2,2'-dipyridyl (1.2 mmol, 20 mol%). The flask was then evacuated and backfilled with Ar (3 times). To this flask was added anhydrous MeCN (30 mL) via syringe and the mixture was stirred smoothly at rt for 12 hours. The reaction mixture was filtered through a short plug of silica gel and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to give the final product (0.67 g, 59%).

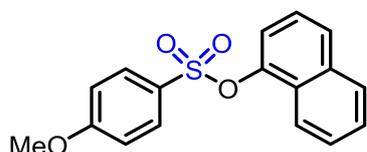
(b) Transformations of 4-methoxybenzenesulfonyl fluoride



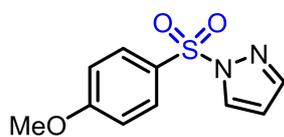
Scheme S4. Transformations of 4-methoxybenzenesulfonyl fluoride

The procedure for the preparation of sulfonic esters and sulfonamides^[3]

A 10 mL sealed tube equipped with a magnetic stirring bar was charged with 4-methoxybenzenesulfonyl fluoride (0.3 mmol, 1.0 equiv), appropriate alcohol or amine (0.33 mmol, 1.1 equiv), Cs₂CO₃ (0.6 mmol, 2.0 equiv) and anhydrous MeCN (1.5 mL). The reaction mixture was stirred vigorously at room temperature under argon atmosphere for 75 minutes (for alcohol) or 3 hours (for amine). The mixture was filtered through a short plug of silica gel and concentrated under reduced pressure. The residue was subjected to flash column chromatography to afford the desired product.



naphthalen-1-yl 4-methoxybenzenesulfonate (6): Known compound.^[6] Obtained as a white solid in 98% yield (92.3 mg) by silica gel flash column chromatography eluted with petroleum ether : ethyl acetate = 8:1 v/v. ¹H NMR (400 MHz, CDCl₃): δ 7.97 – 7.89 (m, 1H), 7.83 – 7.76 (m, 3H), 7.72 (d, *J* = 8.3 Hz, 1H), 7.49 – 7.40 (m, 2H), 7.36 (t, *J* = 7.9 Hz, 1H), 7.24 – 7.18 (m, 1H), 6.92 – 6.85 (m, 2H), 3.79 (s, 3H); ¹³C NMR (101 MHz, CDCl₃): δ 164.2, 145.8, 134.7, 130.7, 127.7, 127.3, 127.1, 126.9, 126.8, 126.7, 125.2, 121.8, 118.5, 114.4, 55.7 ppm. GC-MS (EI): *m/z* = 314.1 (M⁺).



1-((4-methoxyphenyl)sulfonyl)-1H-pyrazole (7): Obtained as a white solid in 98% yield (70.0 mg) by silica gel flash column chromatography eluted with petroleum ether : ethyl acetate = 2:1 v/v. ¹H NMR (400 MHz, CDCl₃): δ 8.07 (d, *J* = 2.7 Hz, 1H), 7.91 (d, *J* = 9.1 Hz, 2H), 7.68 (d, *J* = 1.1 Hz, 1H), 6.95 (d, *J* = 9.1 Hz, 2H), 6.35 (dd, *J* = 2.7, 1.6 Hz, 1H), 3.82 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 164.5, 145.0, 131.0, 130.5, 128.2, 114.7, 108.6, 55.8 ppm. HRMS (EI) *m/z*: [M]⁺ Calcd for C₁₀H₁₀N₂O₃S

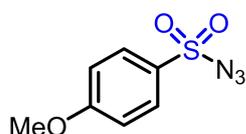
238.0412; Found 238.0421. **Melting point:** 101 – 103 °C. **IR** (film) ν_{max} : 3098, 1593, 1499, 1404, 1272, 1170, 1116, 1046 cm^{-1} .

The procedure for the preparation of 4-ethylphenyl 4-methoxybenzenesulfonate^[7]

To a stirred solution of 4-methoxybenzenesulfonyl fluoride (0.3 mmol, 1.0 equiv) in MeCN (1 mL) was added tert-butyl(4-ethylphenoxy)dimethylsilane (0.3 mmol, 1.0 equiv) followed by DBU (0.06 mmol, 0.2 equiv). The resulting mixture was stirred at 80 °C under argon atmosphere for 2 hours. After the solvent was removed under reduced pressure, the crude product was purified with silica gel chromatography to give a colorless oil (86 mg, 98%).

The procedure for the preparation of 4-methoxybenzenesulfonyl azide^[8]

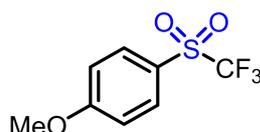
To a stirred solution of 4-methoxybenzenesulfonyl fluoride (0.3 mmol, 1.0 equiv) in MeCN (1 mL) was added DBU (0.3 mmol, 1.0 equiv) followed by TMSN₃ (0.675 mmol, 2.25 equiv). The resultant solution was stirred at 60 °C for 90 minutes, then a further portion of TMSN₃ (0.45 mmol, 1.5 equiv) was added. The reaction mixture was stirred for a further 2 hours, filtered through a silica plug, eluted with DCM, and concentrated under reduced pressure. The residue was subjected to flash column chromatography to provide a white solid (40.8 mg, 64%).



4-methoxybenzenesulfonyl azide (8): Known compound.^[8] **¹H NMR** (400 MHz, CDCl₃): δ 7.88 (d, J = 9.0 Hz, 2H), 7.05 (d, J = 9.0 Hz, 2H), 3.91 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 164.7, 130.0, 129.9, 115.0, 56.0 ppm. **LRMS** (EI): calcd for C₇H₇N₃O₃S (M⁺) 213.0, found 213.0.

The procedure for the preparation of 1-methoxy-4-((trifluoromethyl)sulfonyl)benzene^[9]

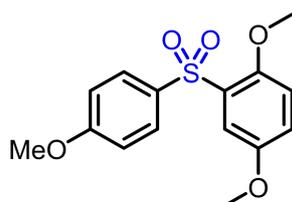
To a mixture of 4-methoxybenzenesulfonyl fluoride (0.5 mmol, 1.0 equiv) and KHF_2 (0.05, 0.1 equiv) in anhydrous DMSO (0.8 mL) was added TMSCF_3 (0.55 mmol, 1.1 equiv) under argon atmosphere. The mixture was stirred at room temperature for 2 hours and then diluted with DCM and H_2O . The aqueous layer was then re-extracted with DCM. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 , filtered and the solvent was then removed under reduced pressure to obtain analytically pure product (108 mg, 90%).



1-methoxy-4-((trifluoromethyl)sulfonyl)benzene (9): Known compound.^[9] Obtained as a yellow oil. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.93 (d, $J = 9.0$ Hz, 2H), 7.10 (d, $J = 9.0$ Hz, 2H), 3.92 (s, 3H); $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -79.1 (s, 3F) ppm. **GC-MS** (EI): $m/z = 240.0$ (M^+).

The procedure for the preparation of 1,4-dimethoxy-2-((4-methoxyphenyl)sulfonyl)benzene^[10]

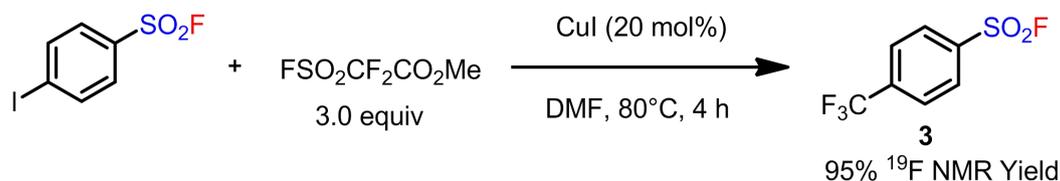
To an oven-dried sealed tube equipped with a magnetic stirring bar were added 4-methoxybenzenesulfonyl fluoride (0.4 mmol, 1.0 equiv), 1,4-dimethoxybenzene (3.4 mmol, 8.5 equiv), AlCl_3 (0.6 mmol, 1.5 equiv) and anhydrous DCE under argon atmosphere. The tube was sealed and the reaction mixture was stirred at 50 °C for 2 hours. The mixture was diluted with H_2O and extracted with DCM. The organic phase was dried with anhydrous Na_2SO_4 and stripped of solvent. The residue was subjected to flash column chromatography to provide a white solid (105.9 mg, 86%).



1,4-dimethoxy-2-((4-methoxyphenyl)sulfonyl)benzene (10): Known compound.^[11] $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.86 (d, $J = 9.0$ Hz, 2H), 7.62 (d, $J = 3.2$ Hz, 1H), 7.00 (dd, $J = 9.0, 3.2$ Hz, 1H), 6.90 (d, $J = 9.0$ Hz, 2H), 6.80 (d, $J = 9.0$ Hz, 1H), 3.79

(s, 3H), 3.77 (s, 3H), 3.67 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 163.3, 153.2, 151.0, 132.8, 130.6, 130.1, 121.1, 114.2, 113.7, 113.7, 56.5, 56.0, 55.6 ppm. GC-MS (EI): $m/z = 308.1$ (M^+).

(c) The transformations of 4-iodobenzenesulfonyl fluoride



A sealed tube was charged with CuI (0.1 mmol, 0.2 equiv), 4-iodobenzenesulfonyl fluoride (0.5 mmol, 1.0 equiv), $\text{FSO}_2\text{CF}_2\text{CO}_2\text{Me}$ (1.5 mmol, 3.0 equiv) and anhydrous DMF (2.5 mL) under argon atmosphere. The tube was sealed and put into a preheated oil bath (80°C). After stirring for 4 hours, the reaction mixture was cooled to room temperature. 1-methoxy-4-(trifluoromethoxy)benzene (75 μL , 0.5 mmol) was added as an internal standard, and the crude reaction mixture was analyzed by ^{19}F NMR spectroscopy. 95% yield of the desired product was detected.^[12]

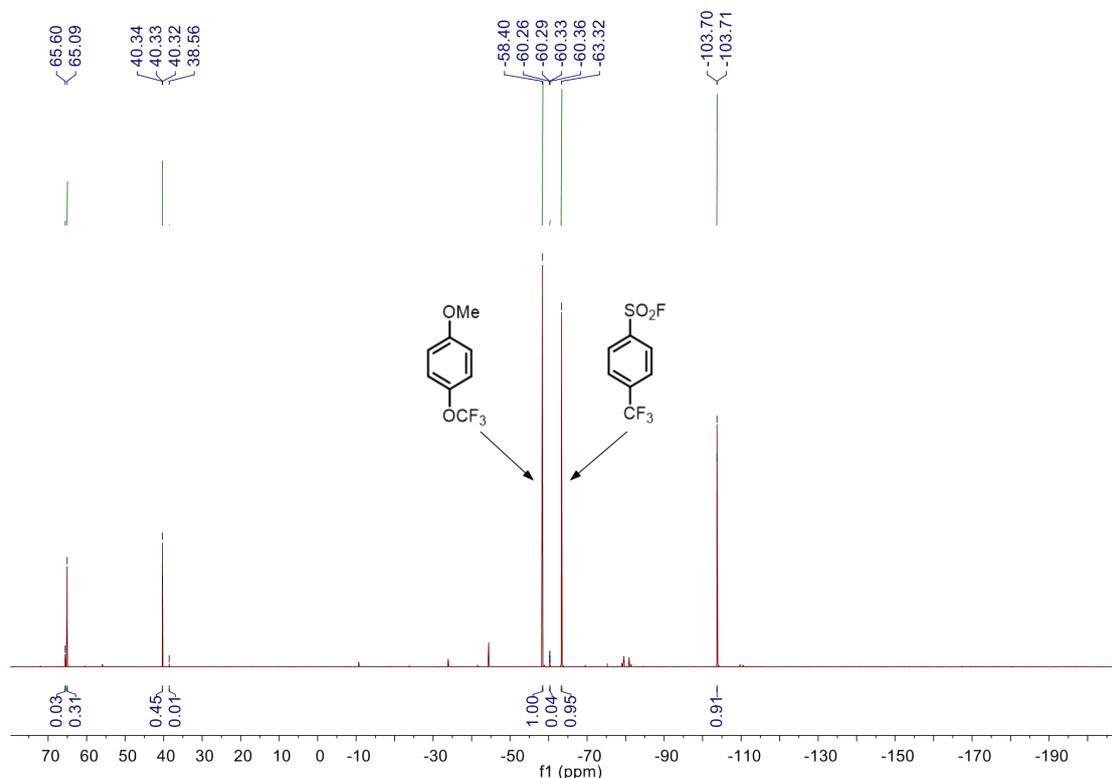
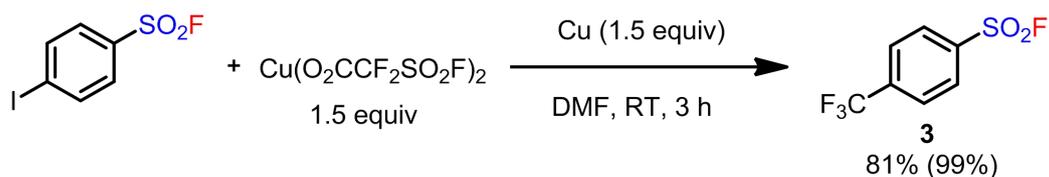


Figure S1. Crude ^{19}F NMR spectrum of 4-(trifluoromethyl)benzenesulfonyl fluoride



A sealed tube was charged with Cu (0.6 mmol, 1.5 equiv), 4-iodobenzenesulfonyl fluoride (0.4 mmol, 1.0 equiv) and Cu(O2CCF2SO2F)2 (0.6 mmol, 1.5 equiv) under argon atmosphere. Anhydrous DMF (4 mL) was added under argon atmosphere while keeping the sealed tube at $-78\text{ }^{\circ}\text{C}$. The mixture was then warmed stepwise and stirred at room temperature for 3 hours. 1-methoxy-4-(trifluoromethoxy)benzene (60 μL , 0.4 mmol) was added as an internal standard to calculate the ^{19}F NMR yield (99%). The reaction mixture was filtered, diluted with H_2O and extracted with DCM. The organic phase was washed with brine, dried with anhydrous Na2SO4, filtered and concentrated. The residue was subjected to flash column chromatography to provide a white solid (74.3 mg, 81%).^[13]

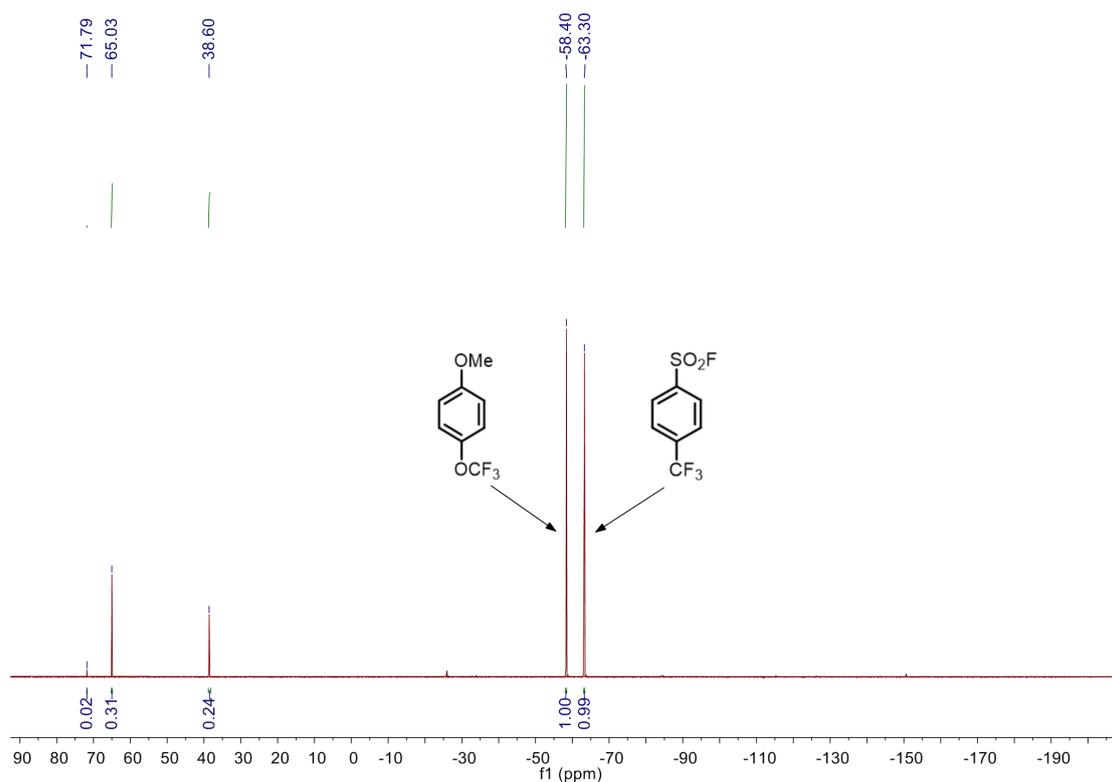
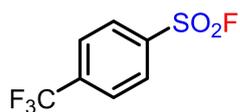
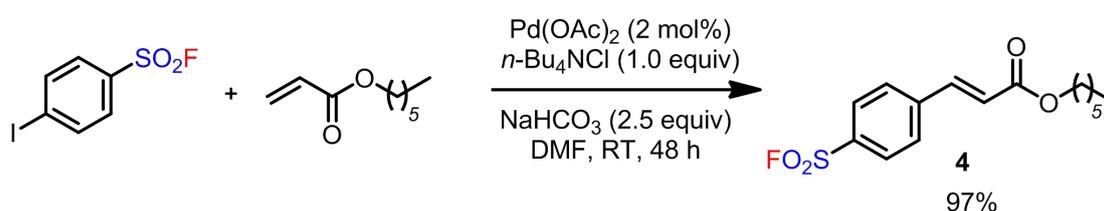


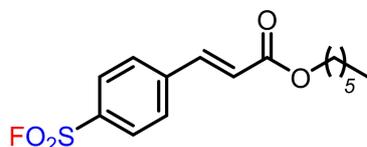
Figure S2. Crude ^{19}F NMR spectrum of 4-(trifluoromethyl)benzenesulfonyl fluoride



4-(trifluoromethyl)benzenesulfonyl fluoride (3): Known compound.^[2] $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.17 (d, $J = 8.3$ Hz, 2H), 7.92 (d, $J = 8.3$ Hz, 2H); $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ 65.7 (s, 1F), -63.6 (s, 3F); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 137.3 (dd, $J = 67.3, 33.7$ Hz), 136.7 (dd, $J = 26.3, 0.8$ Hz), 129.3, 127.1 (q, $J = 3.7$ Hz), 122.9 (q, $J = 273.1$ Hz) ppm. **GC-MS** (EI): $m/z = 228.0$ (M^+).



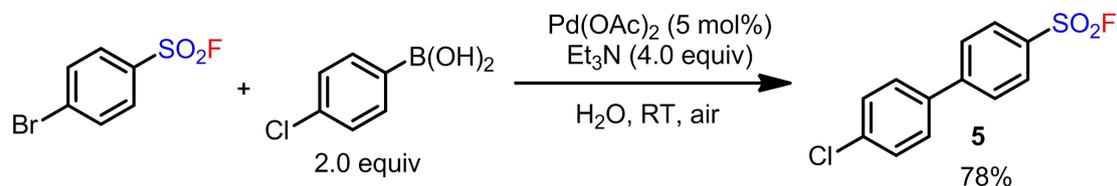
To an oven-dried sealed tube equipped with a magnetic stirring bar were added 4-iodobenzene-1-sulfonyl fluoride (0.4 mmol, 1.0 equiv), NaHCO_3 (1.0 mmol, 2.5 equiv), tetrabutylammonium chloride (0.4 mmol, 1.0 equiv), $\text{Pd}(\text{OAc})_2$ (0.008 mmol, 2 mol%), hexyl acrylate (0.8 mmol, 2.0 equiv) and anhydrous DMF (4 mL) under argon atmosphere. The tube was sealed and the reaction mixture was stirred at room temperature for 2 days. The reaction mixture was diluted with water and extracted with DCM. The organic layers were washed with brine, dried with anhydrous sodium sulfate, filtered and concentrated. The residue was subjected to flash column chromatography to provide a colorless oil (122.4 mg, 97%).^[14]



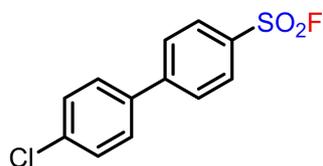
hexyl (E)-3-(4-(fluorosulfonyl)phenyl)acrylate (4): $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.99 (d, $J = 8.5$ Hz, 2H), 7.73 (d, $J = 8.5$ Hz, 2H), 7.68 (d, $J = 16.1$ Hz, 1H), 6.58 (d, $J = 16.1$ Hz, 1H), 4.20 (t, $J = 6.7$ Hz, 2H), 1.73 – 1.63 (m, 2H), 1.44 – 1.34 (m, 2H), 1.32 – 1.26 (m, 4H), 0.87 (t, $J = 6.5$ Hz, 3H); $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ 66.1 (s, 1F); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 166.0, 141.7, 141.3, 133.6 (d, $J = 25.2$ Hz), 129.1, 128.8, 123.4, 65.3, 31.5, 28.7, 25.6, 22.6, 14.0 ppm. **HRMS** (EI) m/z : $[\text{M}]^+$

Calcd for C₁₅H₁₉FO₄S 314.0988; Found 314.0996. **IR** (film) ν_{max} : 2962, 2860, 1716, 1643, 1596, 1468, 1413, 1312, 1261, 1215, 1178, 1099, 1016 cm⁻¹.

(d) The transformations of 4-bromobenzenesulfonyl fluoride



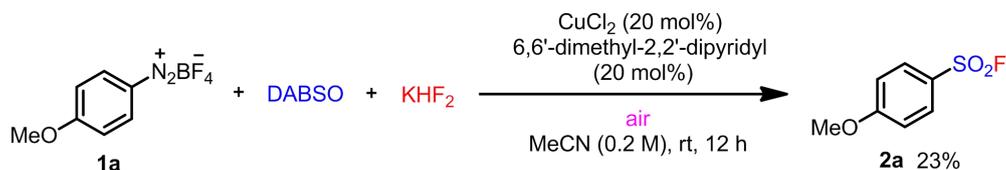
To a pear-shaped round-bottom flask equipped with a magnetic stirring bar were added 4-bromobenzenesulfonyl fluoride (0.2 mmol, 1.0 equiv), 4-chlorophenylboronic acid (0.4 mmol, 2.0 equiv), Pd(OAc)₂ (0.01, 5 mol%), H₂O (2.5 mL) and Et₃N (0.8 mmol, 4.0 equiv). The reaction mixture was stirred at room temperature in open air for 2 hours. The mixture was diluted with DCM and washed with water, follow by brine solution. The organic layer was dried with anhydrous sodium sulfate and concentrated under vacuum. The residue was subjected to flash column chromatography to provide a white solid (42 mg, 78%).^[15]



4'-chloro-[1,1'-biphenyl]-4-sulfonyl fluoride (5): Known compound.^[15] **¹H NMR** (400 MHz, CDCl₃): δ 8.08 (d, J = 8.5 Hz, 2H), 7.79 (d, J = 8.2 Hz, 2H), 7.59 – 7.53 (m, 2H), 7.50 – 7.46 (m, 2H); **¹⁹F NMR** (376 MHz, CDCl₃): δ 66.5 (s, 1F); **¹³C NMR** (100 MHz, CDCl₃): δ 147.5, 137.1, 135.7, 131.9 (d, J = 24.8 Hz), 129.6, 129.2, 128.8, 128.2 ppm. **GC-MS** (EI): m/z = 270.0 (M⁺).

7. Preliminary mechanistic studies

(a) Radical inhibition experiments

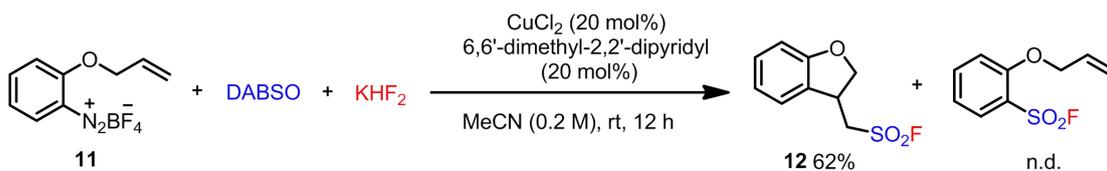


To an oven-dried sealed tube (10 mL) equipped with a magnetic stirring bar were added PMPN₂BF₄ (0.2 mmol, 1.0 equiv), DABSO (0.2 mmol, 1.0 equiv), KHF₂ (1.0 mmol, 5.0 equiv), CuCl₂ (0.04 mmol, 20 mol%), 6,6'-dimethyl-2,2'-dipyridyl (0.04 mmol, 20 mol%) and anhydrous MeCN (1.0 mL). The mixture was sealed and stirred smoothly at rt under air for 12 hours. 1-methoxy-4-(trifluoromethoxy)benzene (10 μL) was added as an internal standard, and the crude reaction mixture was analyzed by ¹⁹F NMR spectroscopy. The desired reaction was greatly suppressed and only 23% of the target product was detected.

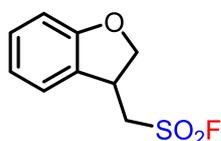


To an oven-dried sealed tube (10 mL) equipped with a magnetic stirring bar were added PMPN₂BF₄ (0.4 mmol, 1.0 equiv), DABSO (0.4 mmol, 1.0 equiv), KHF₂ (2.0 mmol, 5.0 equiv), CuCl₂ (0.08 mmol, 20 mol%), 6,6'-dimethyl-2,2'-dipyridyl (0.08 mmol, 20 mol%) and TEMPO (0.4 mmol, 1.0 equiv). The tube was then evacuated and backfilled with Ar (3 times) and anhydrous MeCN (2 mL) was added via syringe under Ar atmosphere. The mixture was sealed and stirred smoothly at rt for 12 hours. 1-methoxy-4-(trifluoromethoxy)benzene (20 μL) was added as an internal standard. ¹⁹F NMR analysis of the reaction mixture revealed that 31% of the desired product was generated. However, the TEMPO-PMP adducts derived from $\cdot\text{PMP}$ was not detected by GC-MS analysis.

(b) Radical probe experiment



According to the general procedure for Sandmeyer fluorosulfonylation of arenediazonium salts, a tailored substrate was used for radical cyclization reaction. This reaction proceeded smoothly, giving rise to the corresponding product in 62% isolated yield. The product of direct fluorosulfonylation on the benzene ring was not detected. These results revealed that the aryl radical would be formed initially.



(2,3-dihydrobenzofuran-3-yl)methanesulfonyl fluoride (12): $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.26 – 7.19 (m, 2H), 6.94 (t, $J = 7.5$ Hz, 1H), 6.86 (d, $J = 8.4$ Hz, 1H), 4.75 (t, $J = 9.2$ Hz, 1H), 4.58 – 4.51 (m, 1H), 4.14 – 4.05 (m, 1H), 3.75 (dt, $J = 14.8, 3.1$ Hz, 1H), 3.62 – 3.52 (m, 1H); $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ 56.6 (t, $J = 7.5$ Hz, 1F); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 159.8, 130.2, 125.5, 124.4, 121.5, 110.6, 75.1 (d, $J = 1.4$ Hz), 54.9 (d, $J = 14.5$ Hz), 37.9 ppm. **HRMS** (EI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_9\text{H}_9\text{FO}_3\text{S}$ 216.0256; Found 216.0262. **Melting point**: 129 – 131 $^\circ\text{C}$. **IR** (film) ν_{max} : 2930, 1596, 1497, 1464, 1409, 1316, 1274, 1261, 1206, 1178, 1148, 1095, 1018 cm^{-1} .

(c) The reducibility study of DABSO^[16]

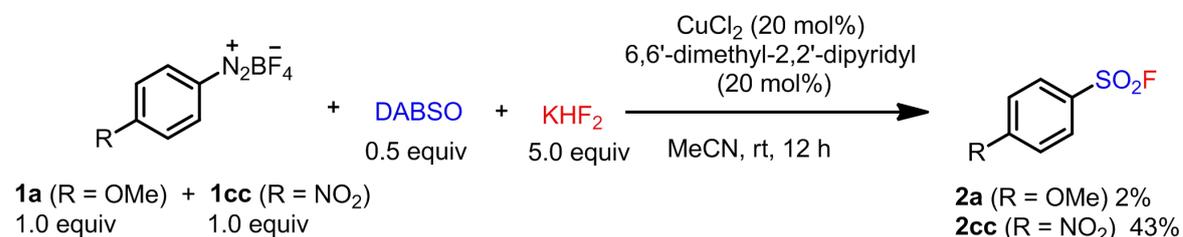
The three tubes below are: **A**) CuCl (14.7 mg) and 6,6'-dimethyl-2,2'-dipyridyl (27.4 mg) in anhydrous MeCN (3 mL) under argon atmosphere, stirred at room temperature for 5 minutes; **B**) CuCl_2 (20 mg) and 6,6'-dimethyl-2,2'-dipyridyl (27.4 mg) in anhydrous MeCN (3 mL) under argon atmosphere, stirred at room temperature for 5 minutes; **C**) CuCl_2 (20 mg), DABSO (45 mg) and 6,6'-dimethyl-2,2'-dipyridyl (27.4 mg) in anhydrous MeCN (3 mL) under argon atmosphere, stirred at room temperature for 5 minutes. The tube C turned deep red (the color of tube A) and the color of tube B is faint yellow. This experiment revealed that DABSO could reduce Cu(II) to Cu(I) easily. DABSO or Cu(I) may trigger the decomposition of

arene diazonium salt via single electron transfer pathway to produce aryl radical.



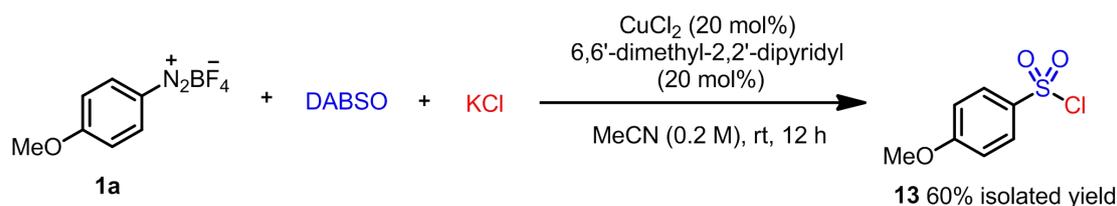
Figure S3. The reducibility study of DABSO

(d) Competition experiment

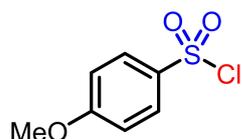


Following the general procedure for sandmeyer fluorosulfonylation of arene diazonium salts, a competition experiment between a methoxy- (0.2 mmol, 1.0 equiv) and nitro- (0.2 mmol, 1.0 equiv) substituted diazonium salts, in the presence of 0.5 equivalent of DABSO, led to a higher reactivity of the electron-deficiency substrate, consistent with the results in the part of screening reaction conditions (even without copper catalyst and ligand, electron-deficiency substrates could give the corresponding products in moderate yields). The presence of CuCl₂ and 6,6'-dimethyl-2,2'-dipyridyl must afford another possible reaction pathway, especially for the electron-rich substrates.

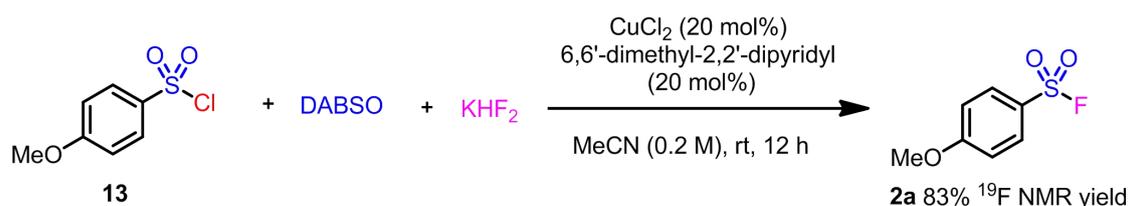
(e) The possibility of arenesulfonyl chlorides as reaction intermediate



To an oven-dried sealed tube (10 mL) equipped with a magnetic stirring bar were added PMPN₂BF₄ (0.4 mmol, 1.0 equiv), DABSO (0.4 mmol, 1.0 equiv), KCl (2.0 mmol, 5.0 equiv), CuCl₂ (0.08 mmol, 20 mol%) and 6,6'-dimethyl-2,2'-dipyridyl (0.08 mmol, 20 mol%). The tube was then evacuated and backfilled with Ar (3 times) and anhydrous MeCN (2 mL) was added via syringe under Ar atmosphere. The mixture was sealed and stirred smoothly at rt for 12 hours. The mixture was filtered through a short plug of silica gel and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to give a white solid (49.4 mg, 60%).



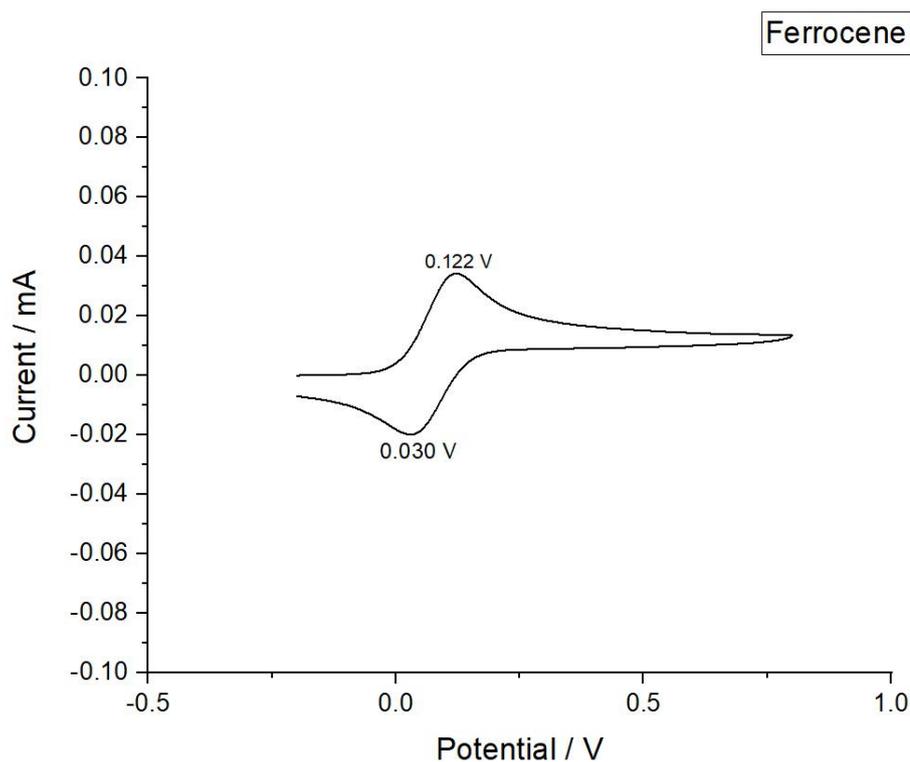
4-methoxybenzenesulfonyl chloride (13): Known compound.^[17] ¹H NMR (400 MHz, CDCl₃): δ 7.97 (d, *J* = 9.0 Hz, 2H), 7.04 (d, *J* = 9.0 Hz, 2H), 3.92 (s, 3H). GC-MS (EI): *m/z* = 206.0 (M⁺).



Following the general procedure for sandmeyer fluorosulfonylation of arenediazonium salts, 4-methoxybenzenesulfonyl chloride was used as a replacement of 4-methoxyphenyldiazonium tetrafluoroborate. 83% yield of the desired product was detected by ¹⁹F NMR spectroscopy. Sulfonyl chlorides could be turned to the corresponding fluorides under the standard conditions.

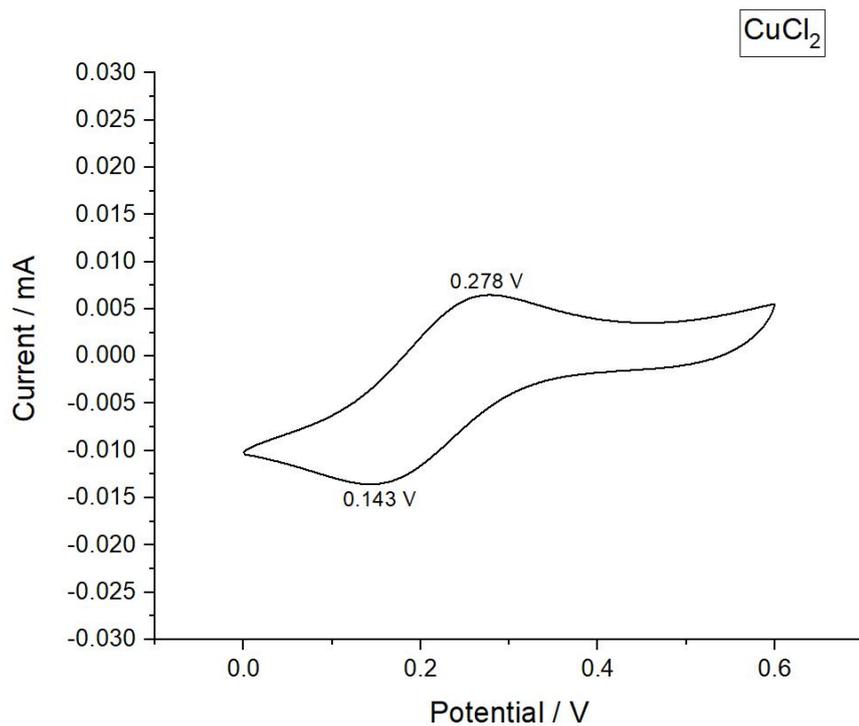
(f) Cyclic voltammetry studies

Cyclic voltammetry (CV) was performed on a CHI 660C instrument with a standard three-electrode cell using a glassy carbon as working electrode, a platinum wire as counter electrode and Ag/AgNO₃ as reference electrode. For all studies, tetrabutylammonium hexafluorophosphate (ⁿBu₄NPF₆) was used as electrolyte in a solution of MeCN. Samples were prepared by adding the reagent (0.02 mmol) to be measured into a solution of ⁿBu₄NPF₆ (10 mL, 0.1 M) in dry and degassed MeCN. Cyclic voltammetry with the following settings: Scan Rates = 0.1 V/s, Sweep Segments = 2, Sample Interval = 0.001 V, Quiet Time = 2 sec, Sensitivity = 1e-5 A/V. The obtained values were referenced to Ag/Ag⁺ electrode and were further converted to values referenced to saturated calomel electrode (SCE) by using Ferrocene (Fc) as an external standard. The redox potential of Ferrocene was 0.400 V vs SCE.^[18]



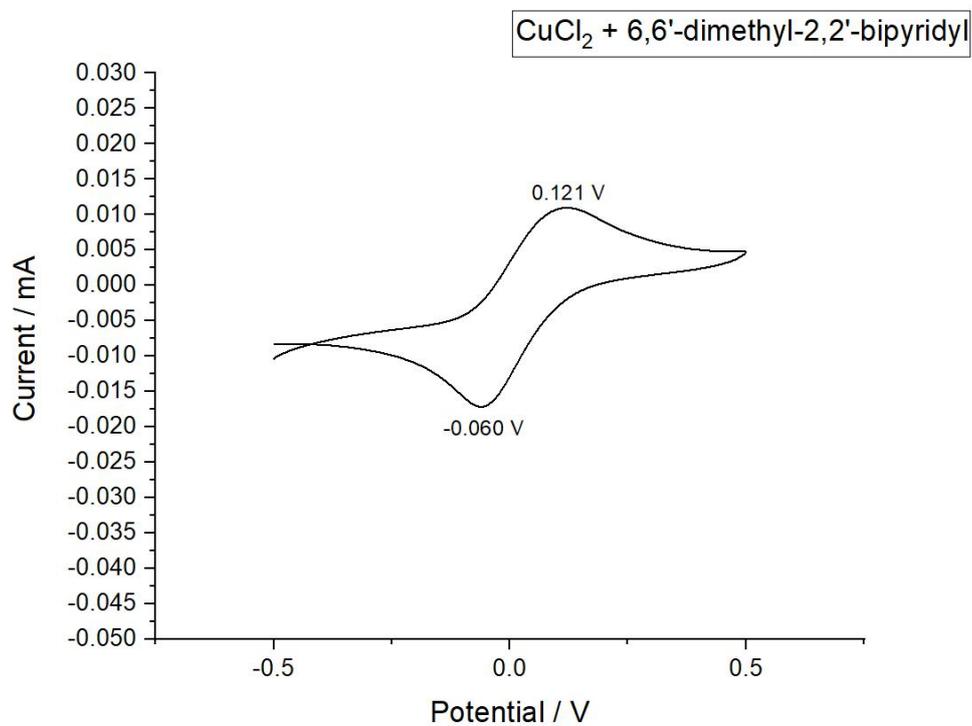
$$E_{1/2} = 0.076 \text{ V vs Ag/Ag}^+$$

$$E_{1/2} = 0.400 \text{ V vs SCE}$$



$$E_{1/2} = 0.211 \text{ V vs Ag/Ag}^+$$

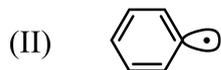
$$E_{1/2} = 0.535 \text{ V vs SCE}$$



$$E_{1/2} = 0.031 \text{ V vs Ag/Ag}^+$$

$$E_{1/2} = 0.355 \text{ V vs SCE}$$

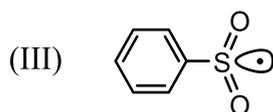
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SO₂

| | | | |
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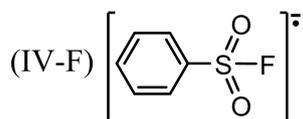
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F⁻

| | | | |
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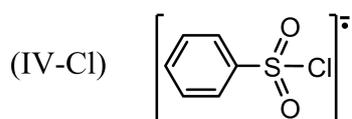
Cl⁻

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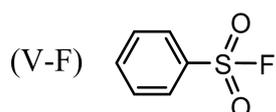


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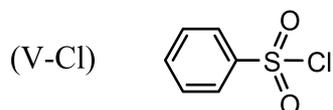


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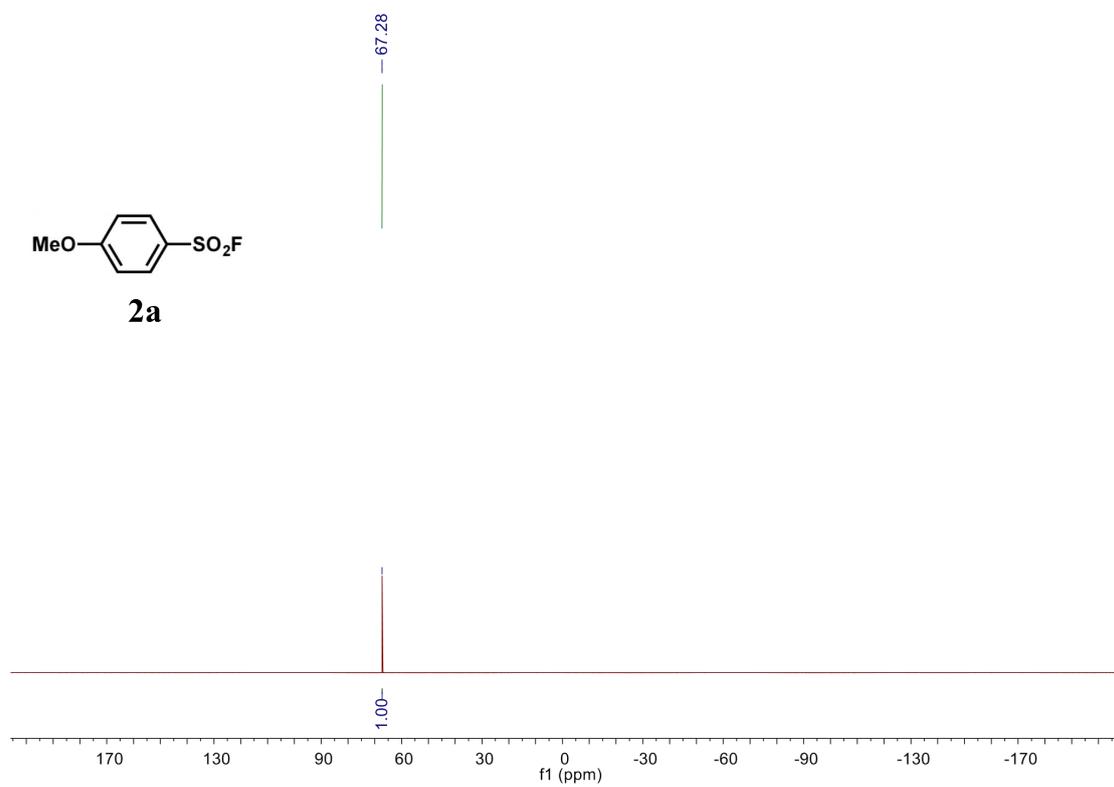
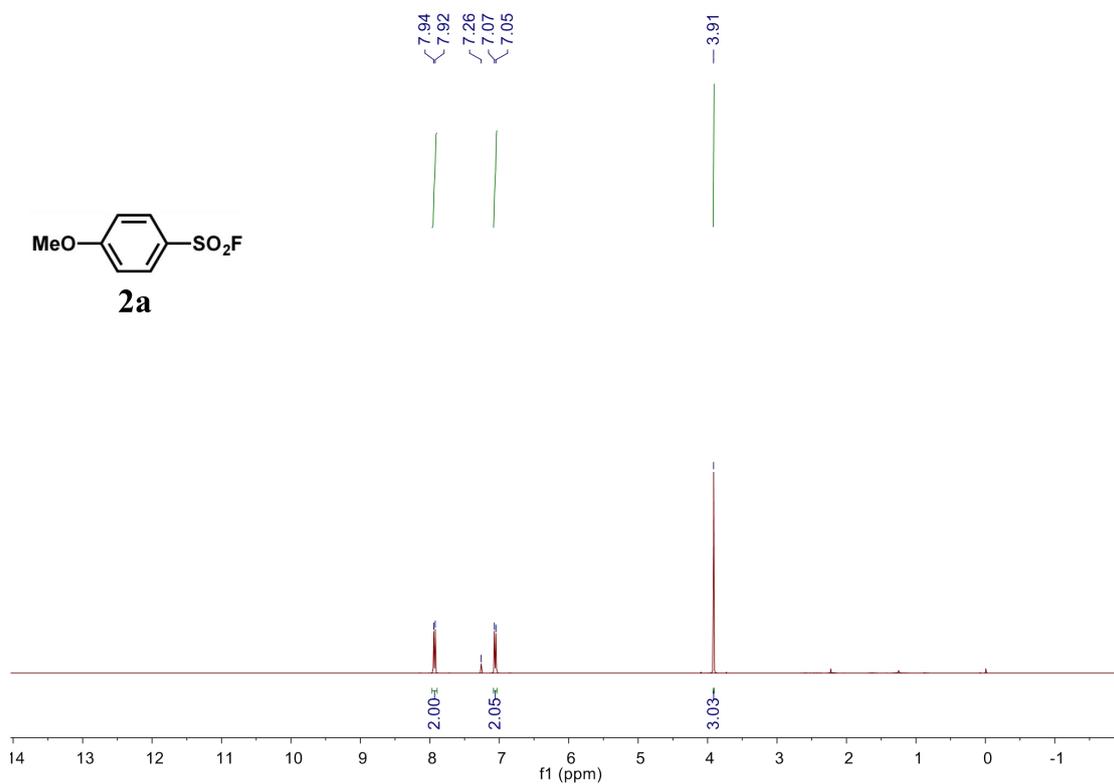


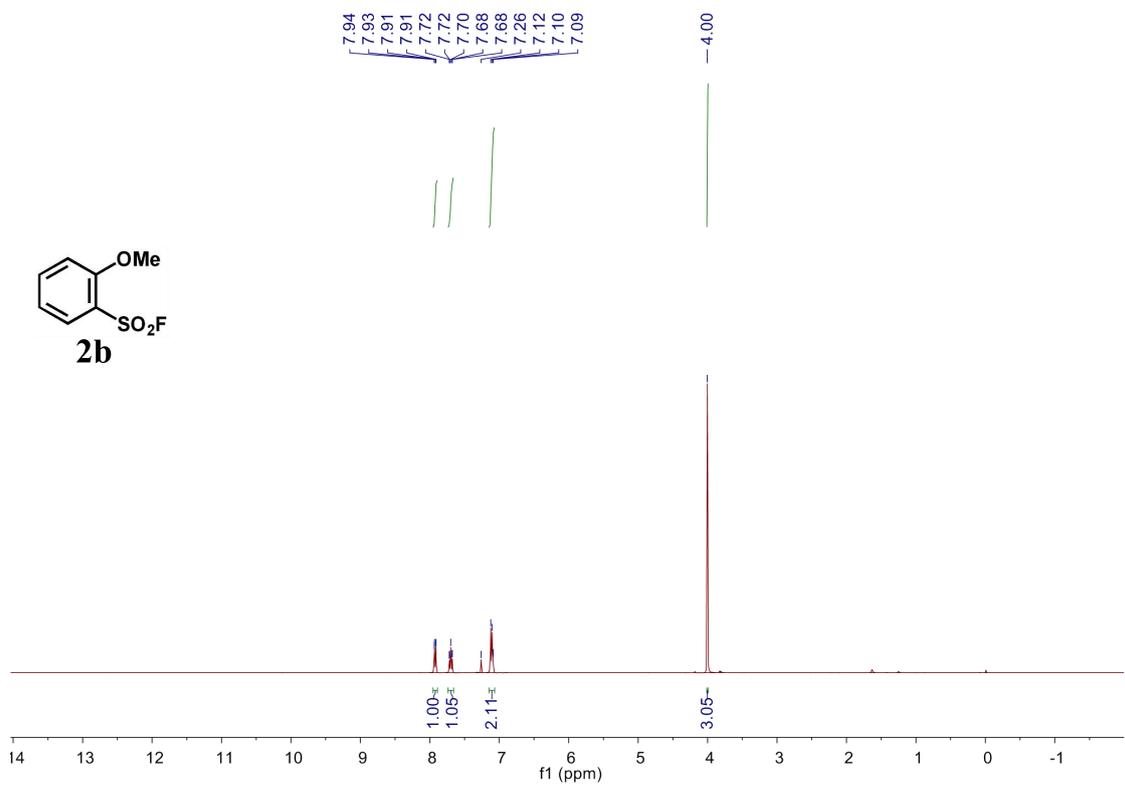
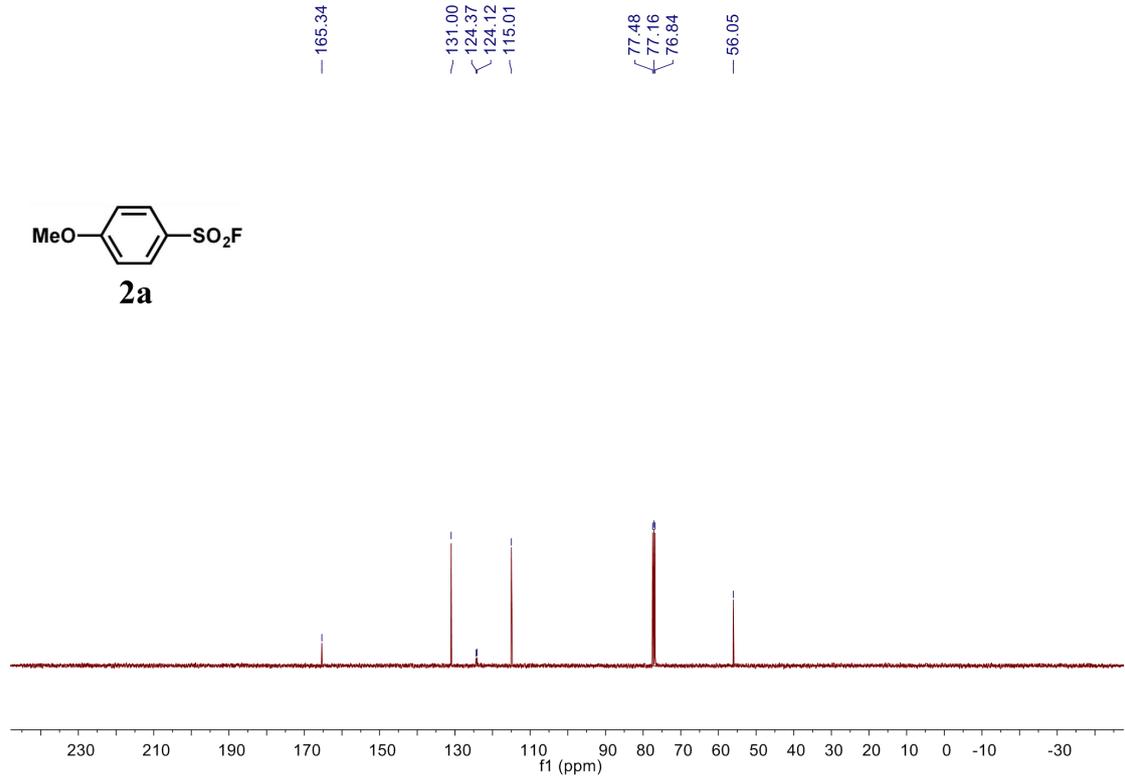
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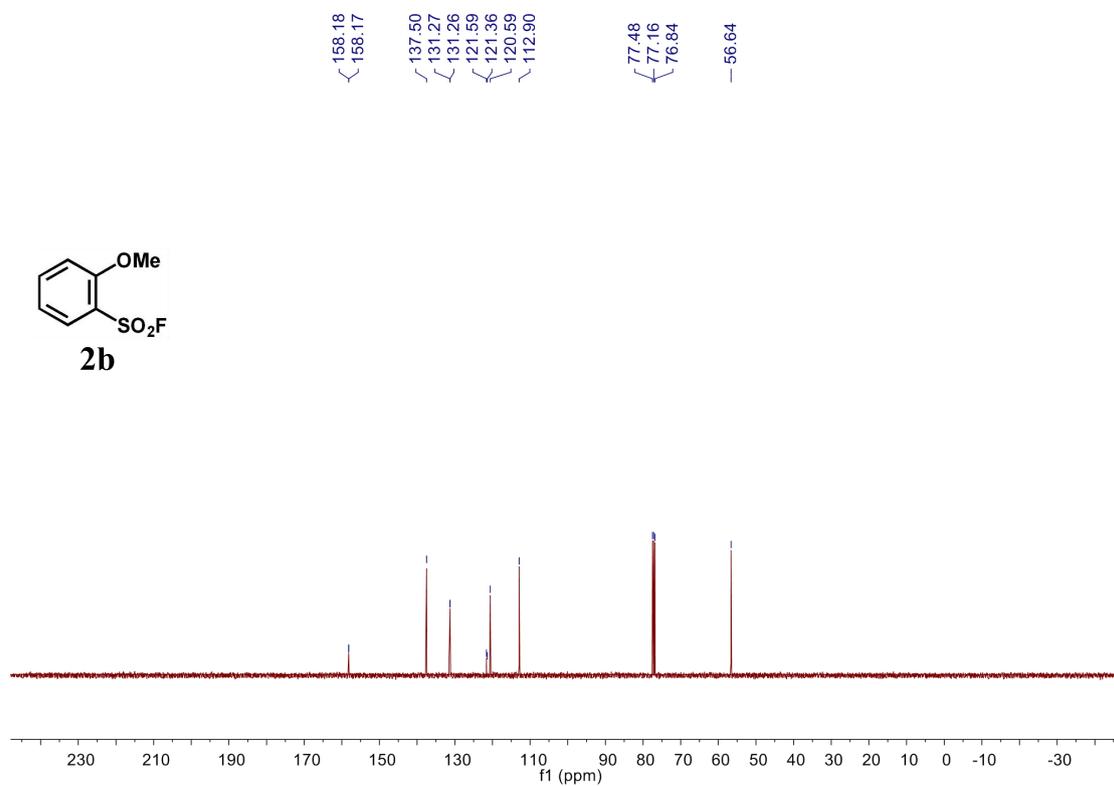
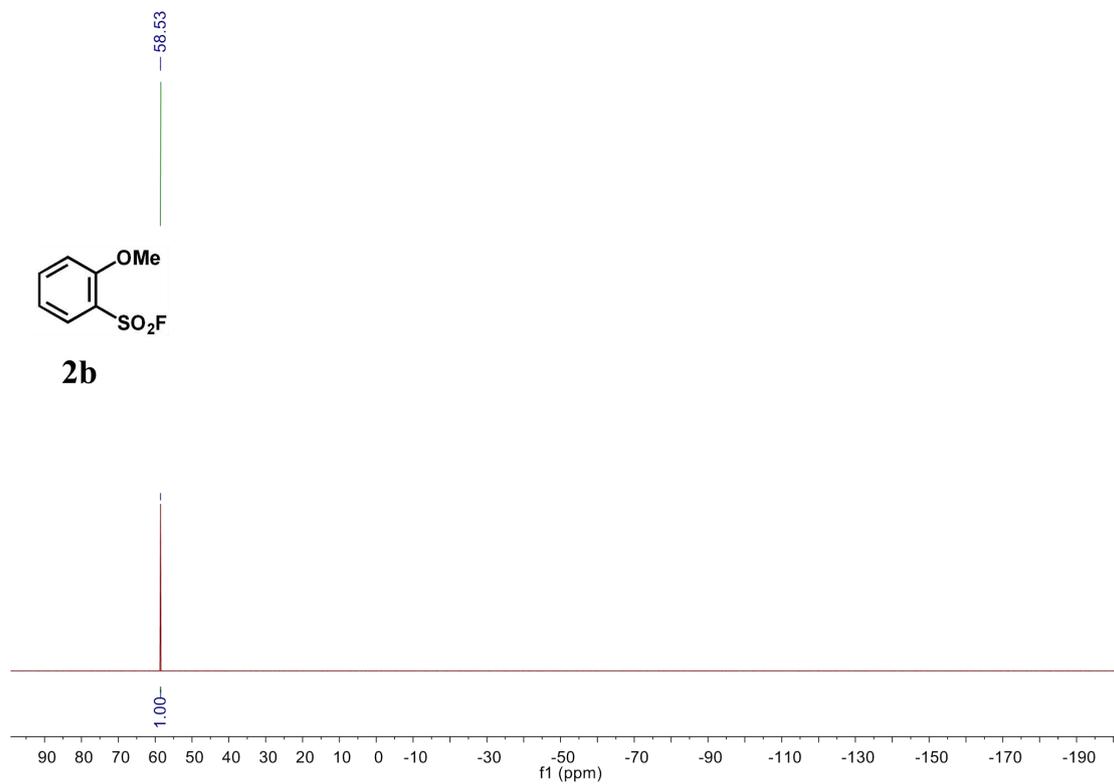
8. References

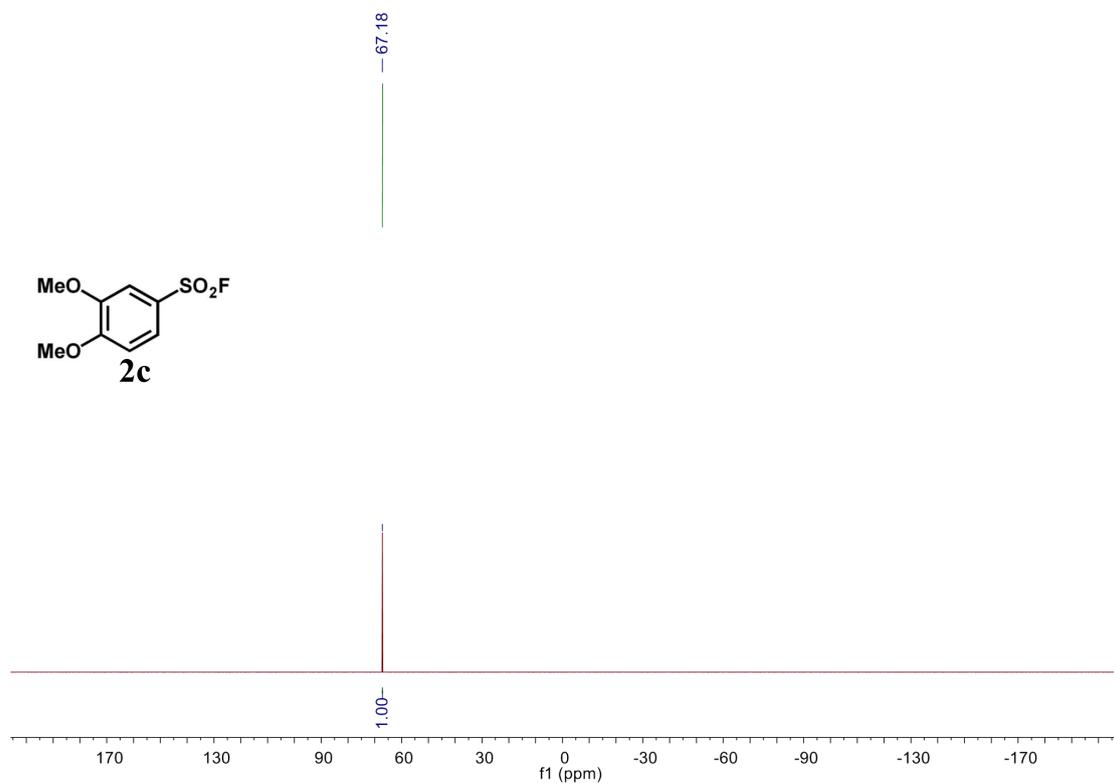
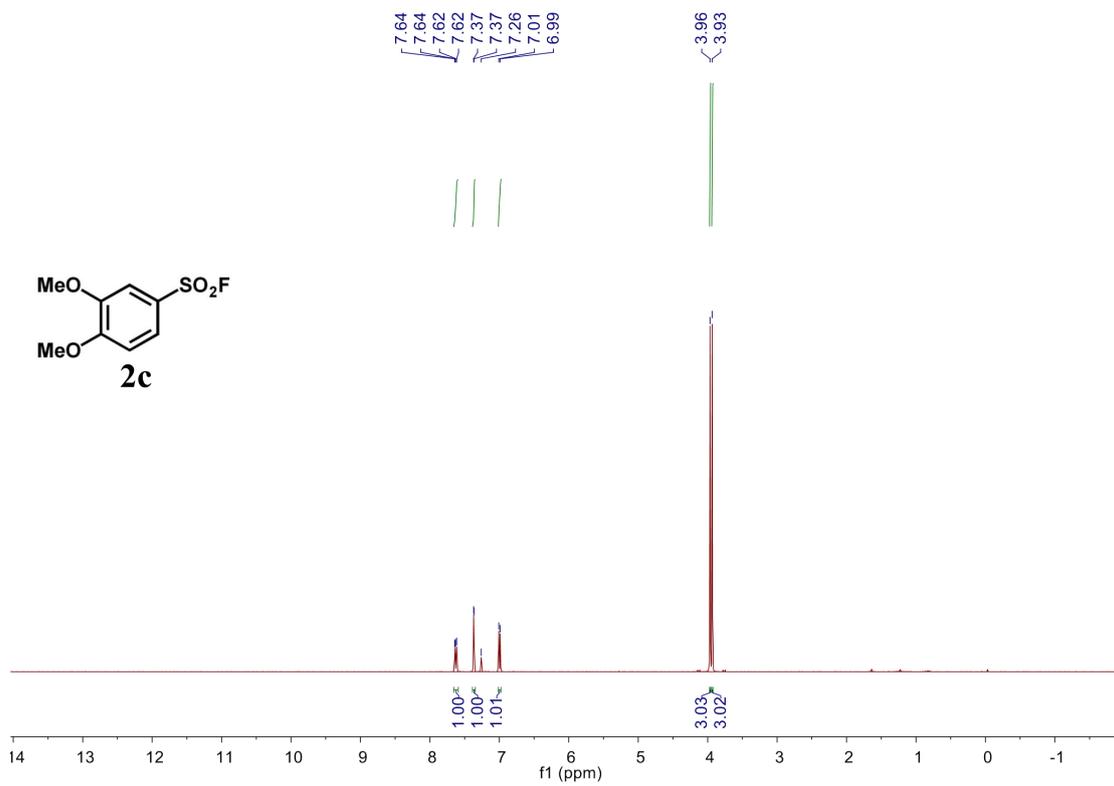
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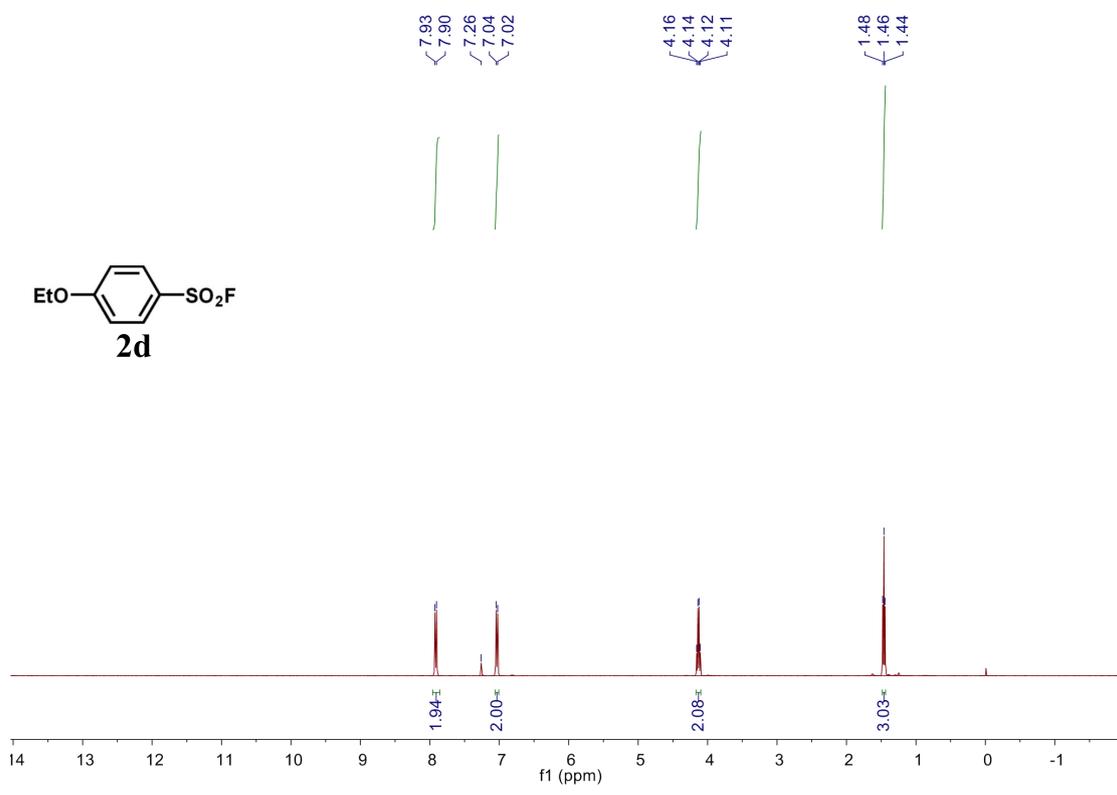
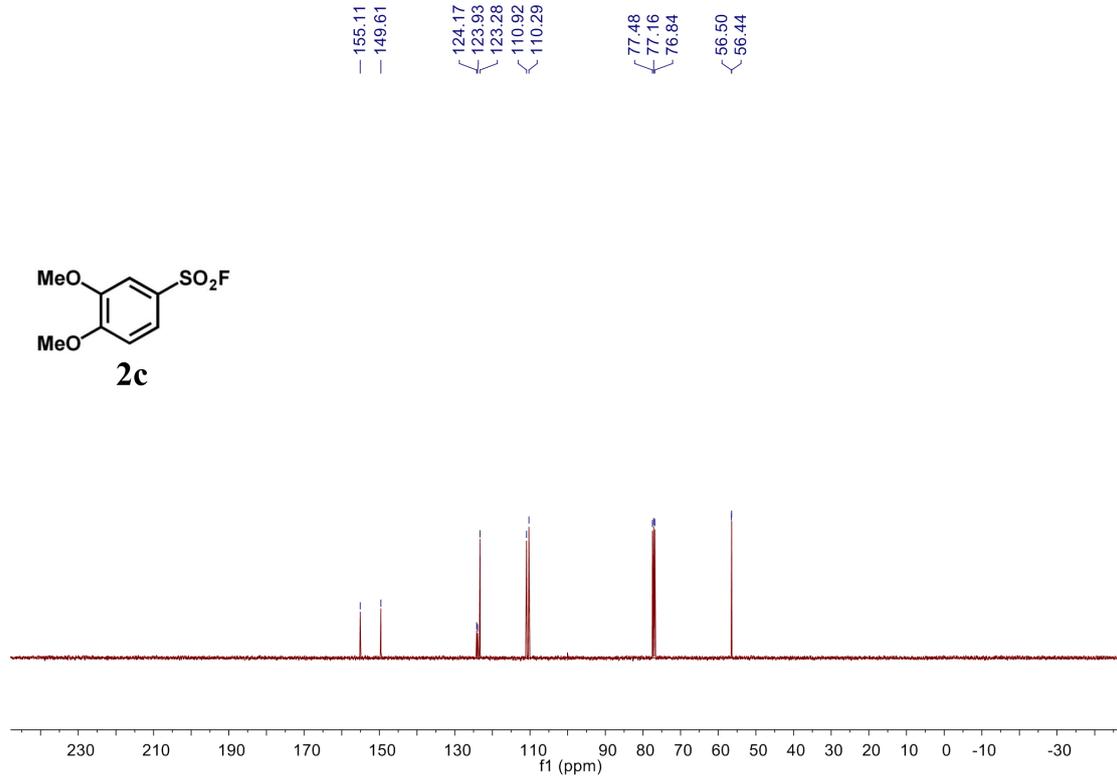
9. Copies of ^1H NMR, ^{19}F NMR and ^{13}C NMR spectra of products

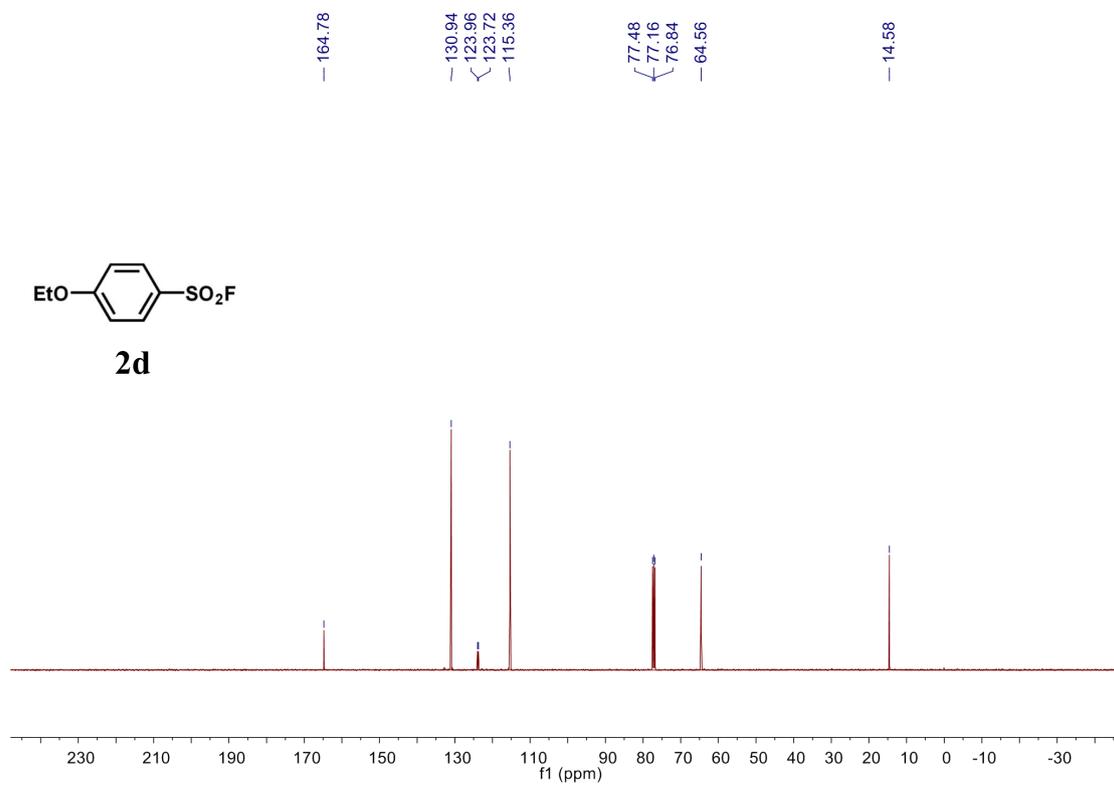
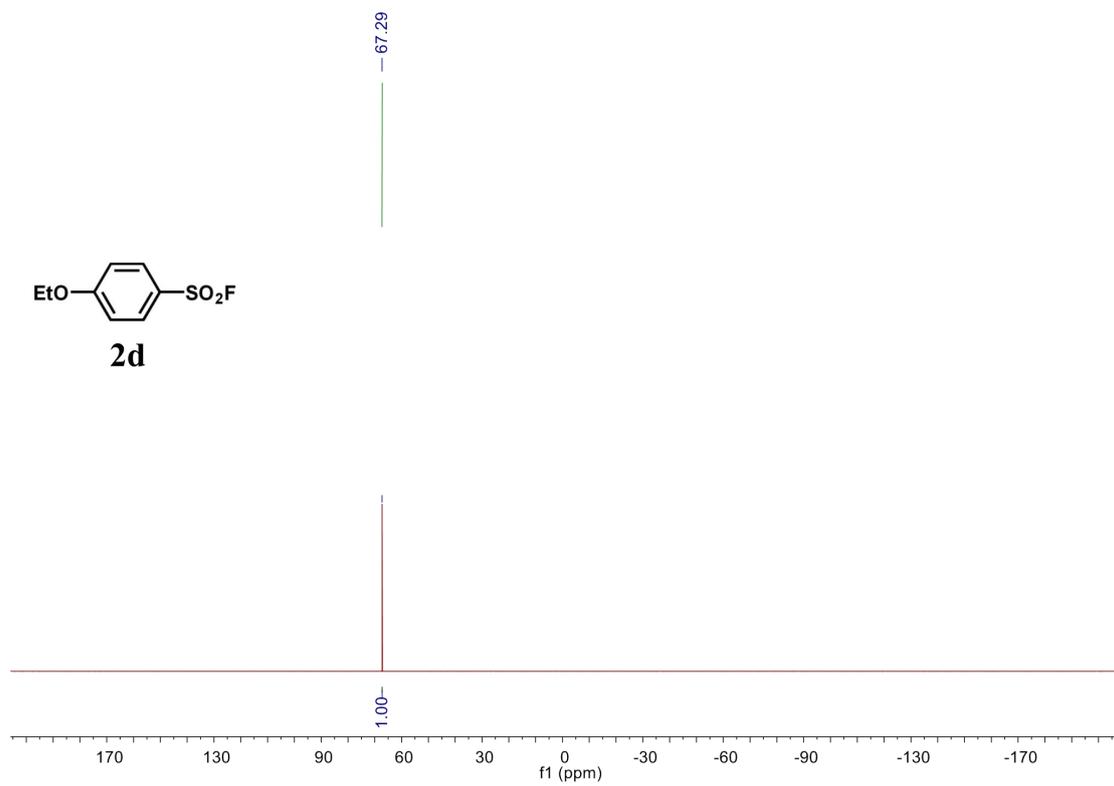


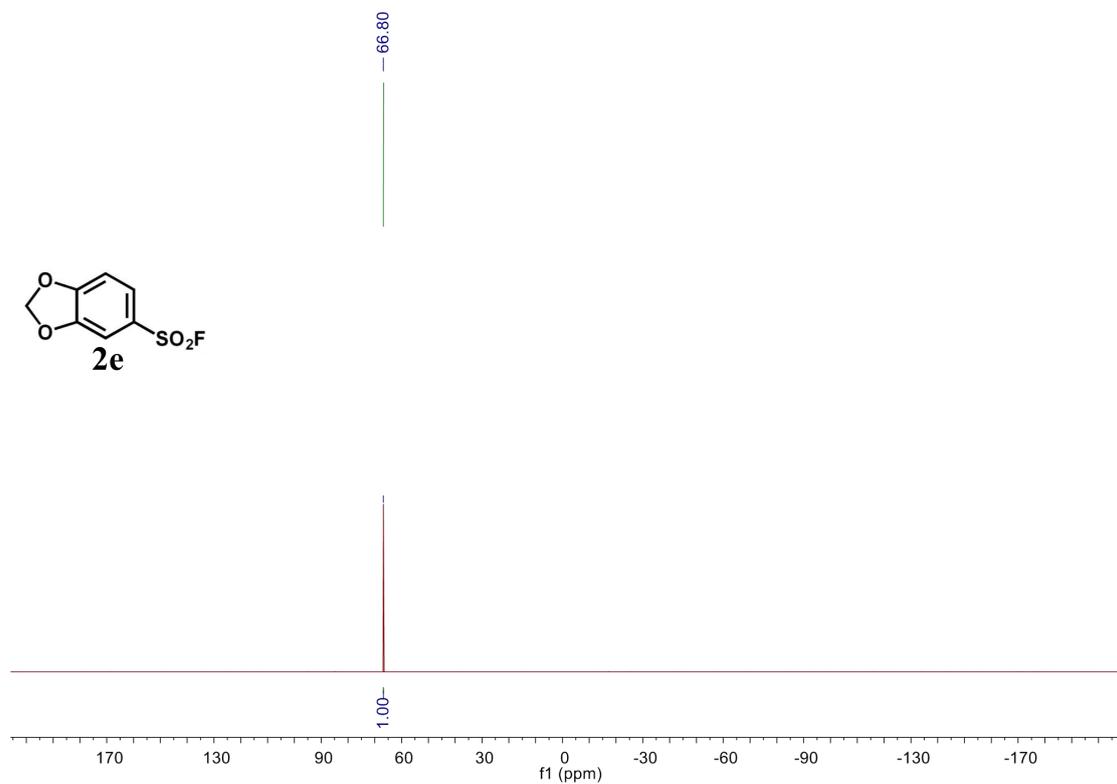
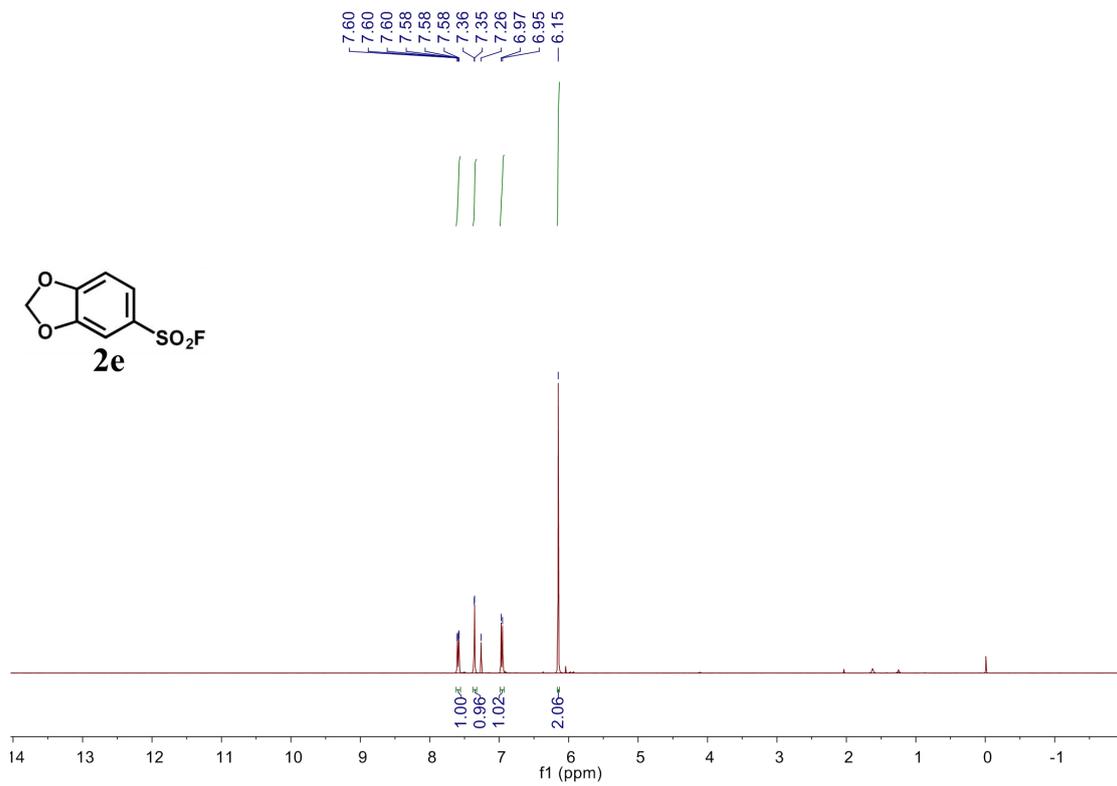


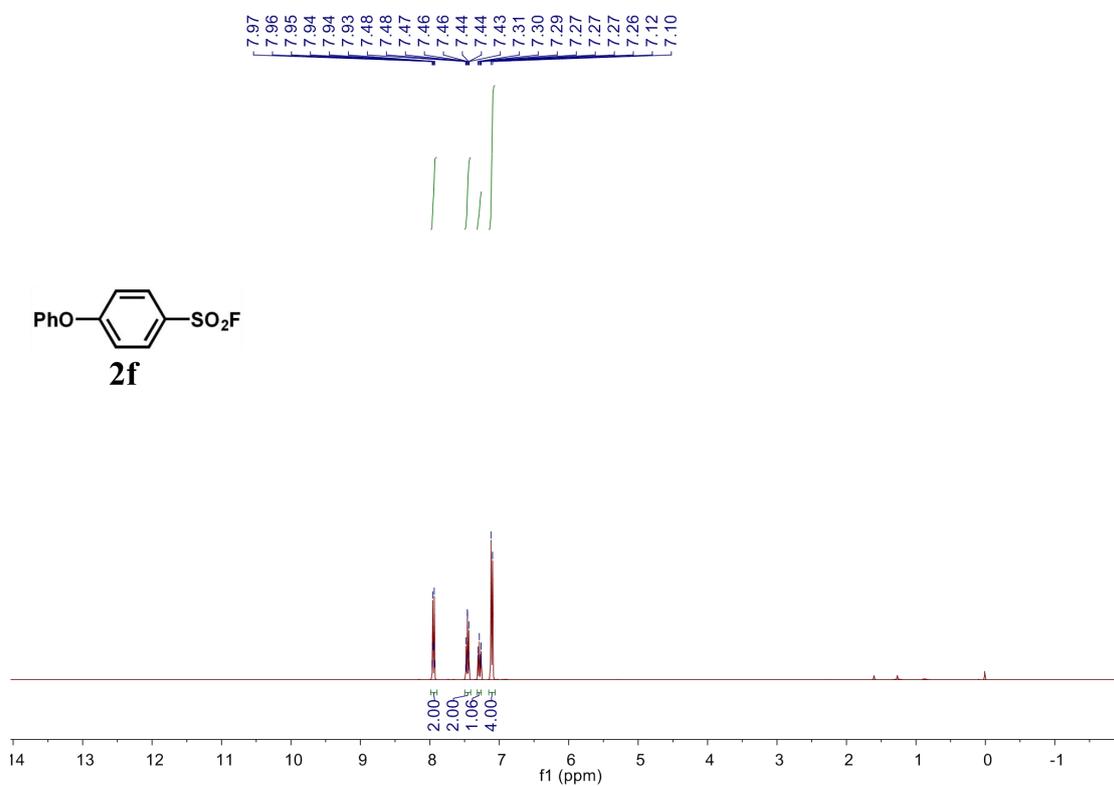
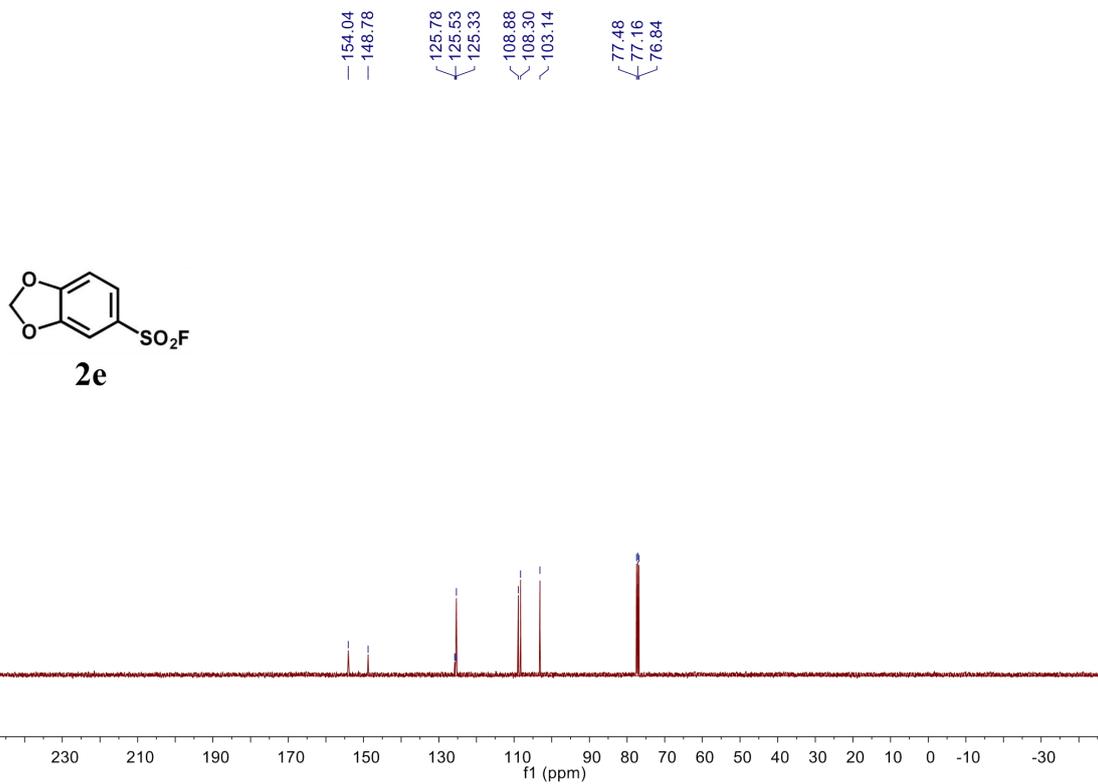


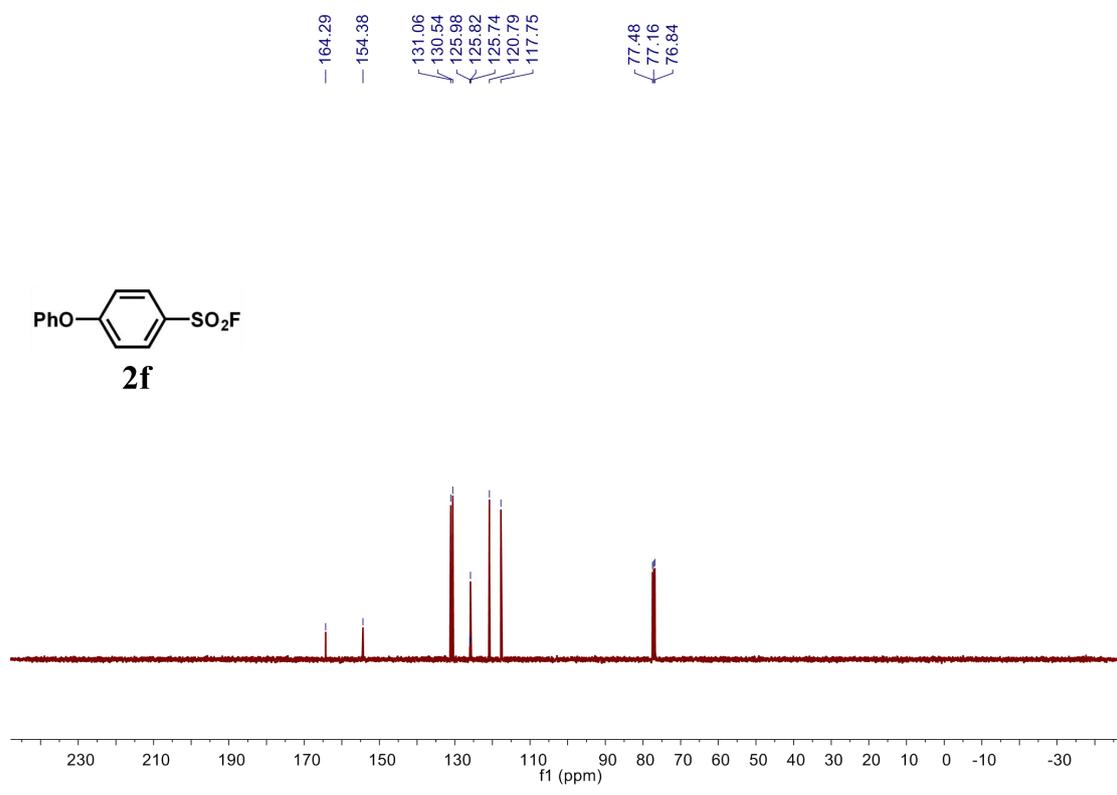
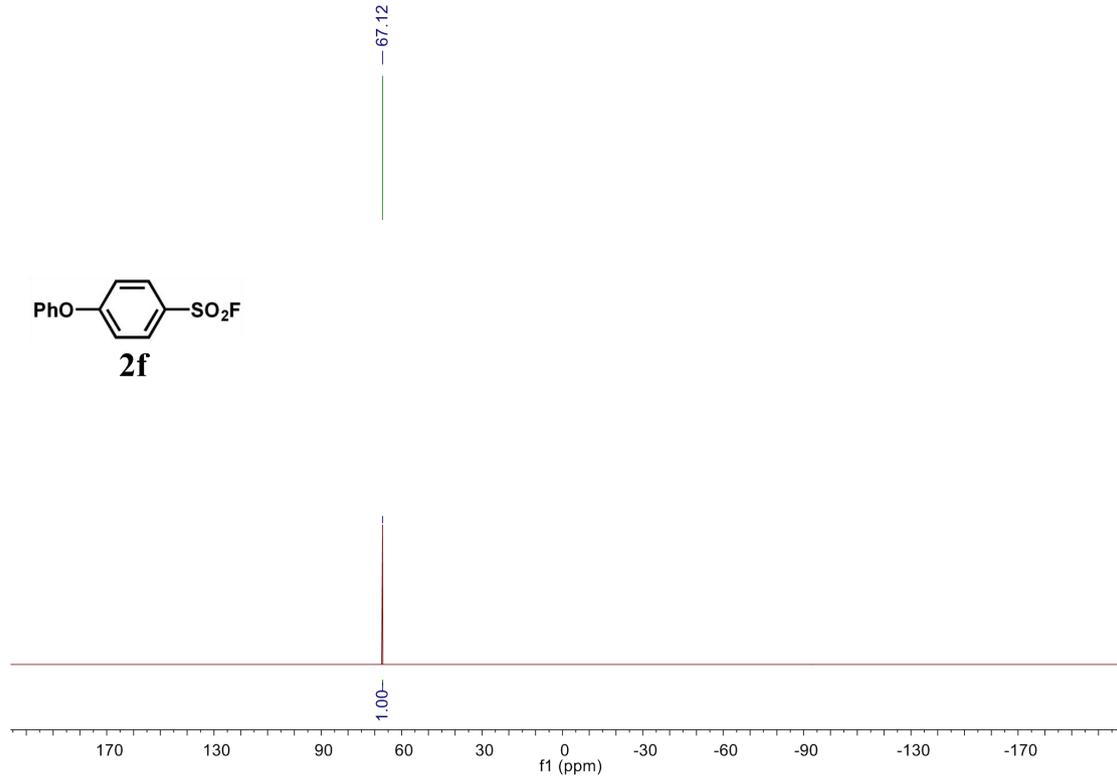


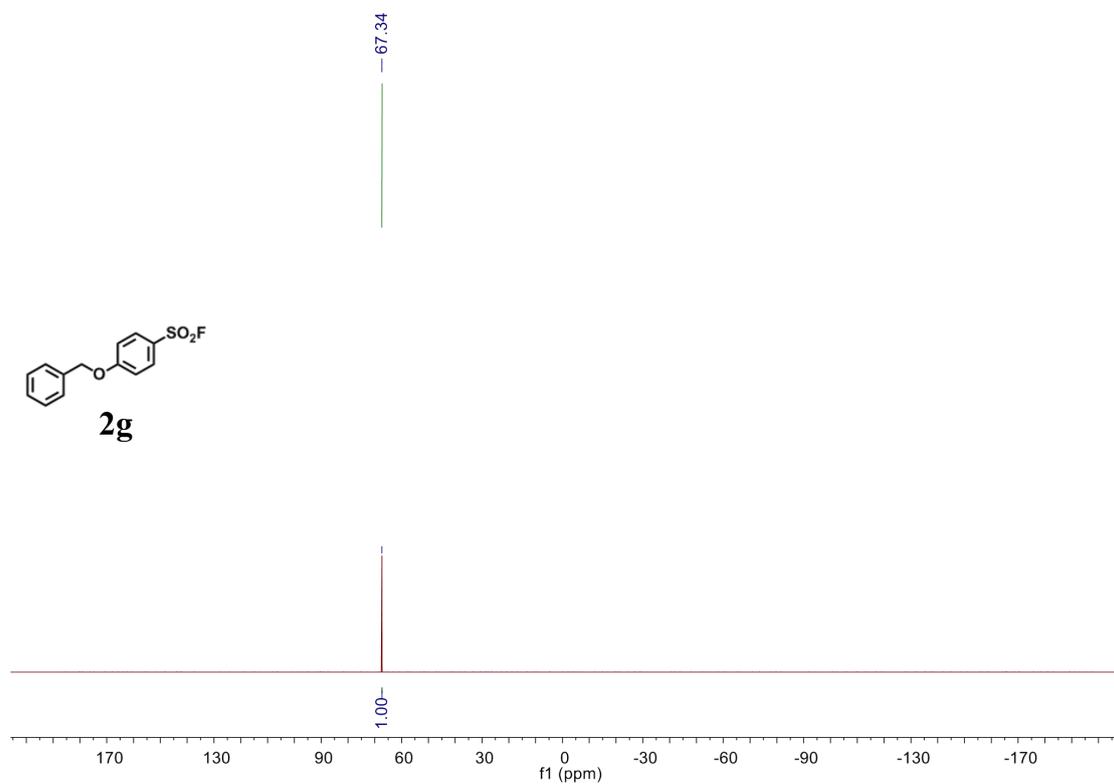
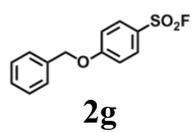
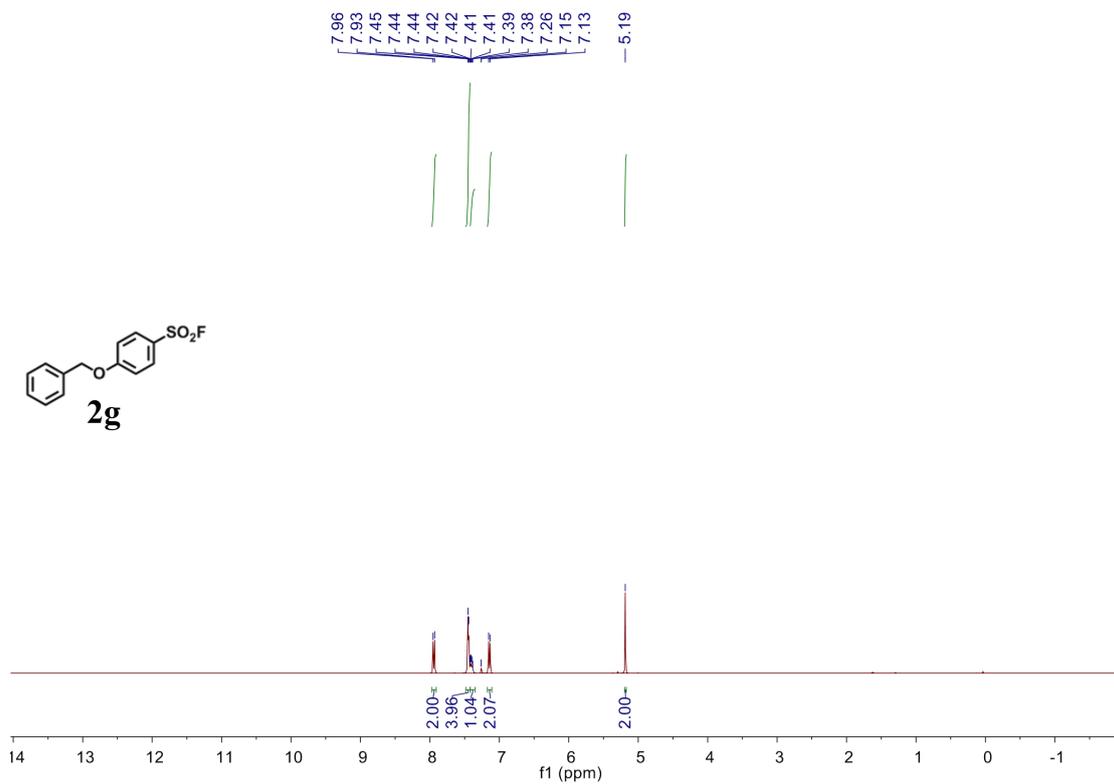
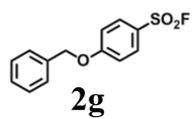


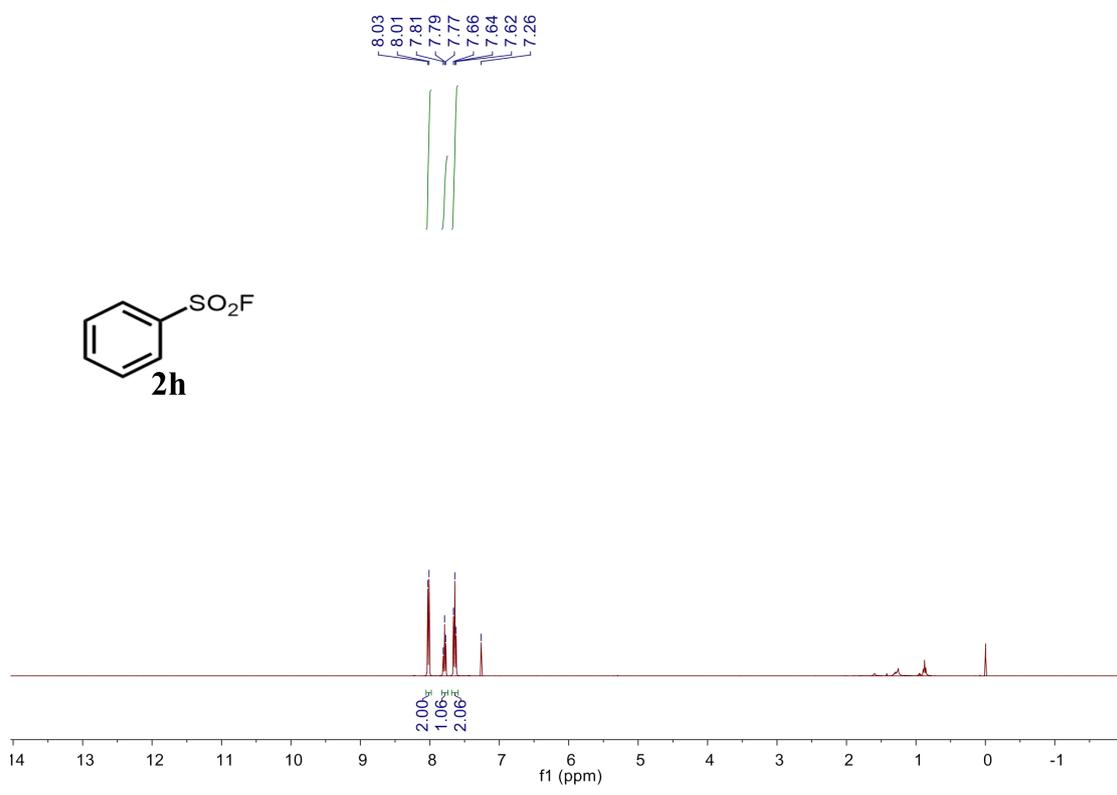
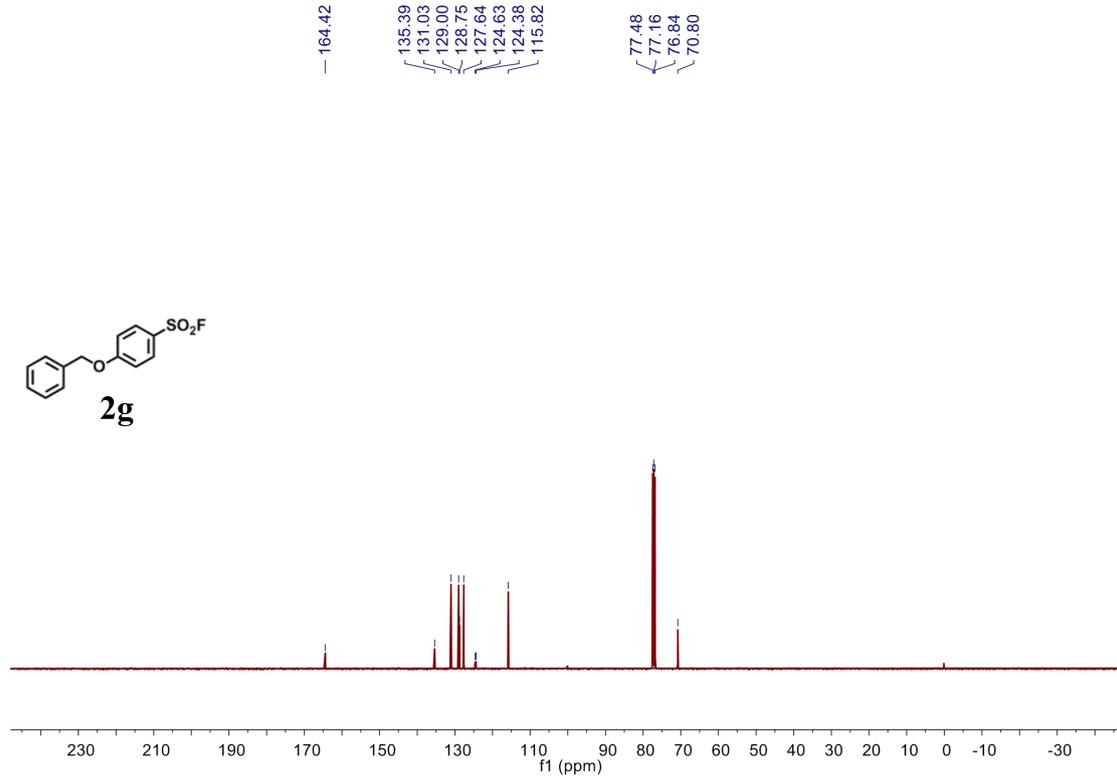


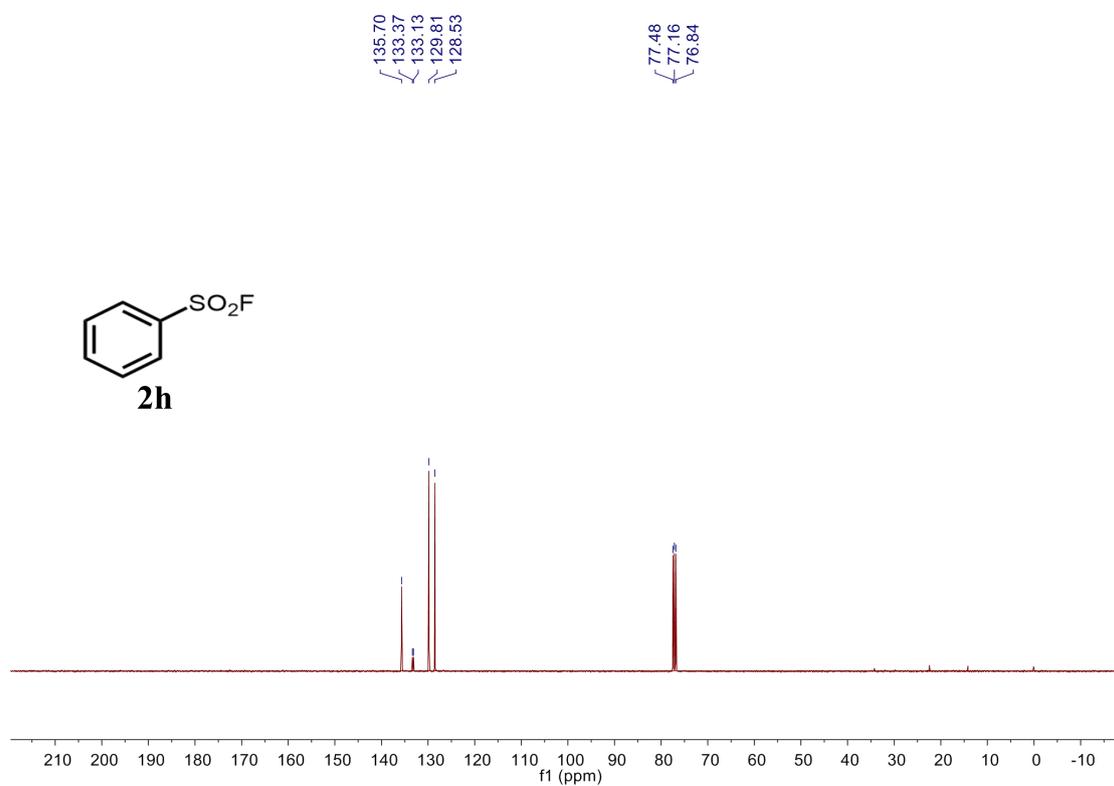
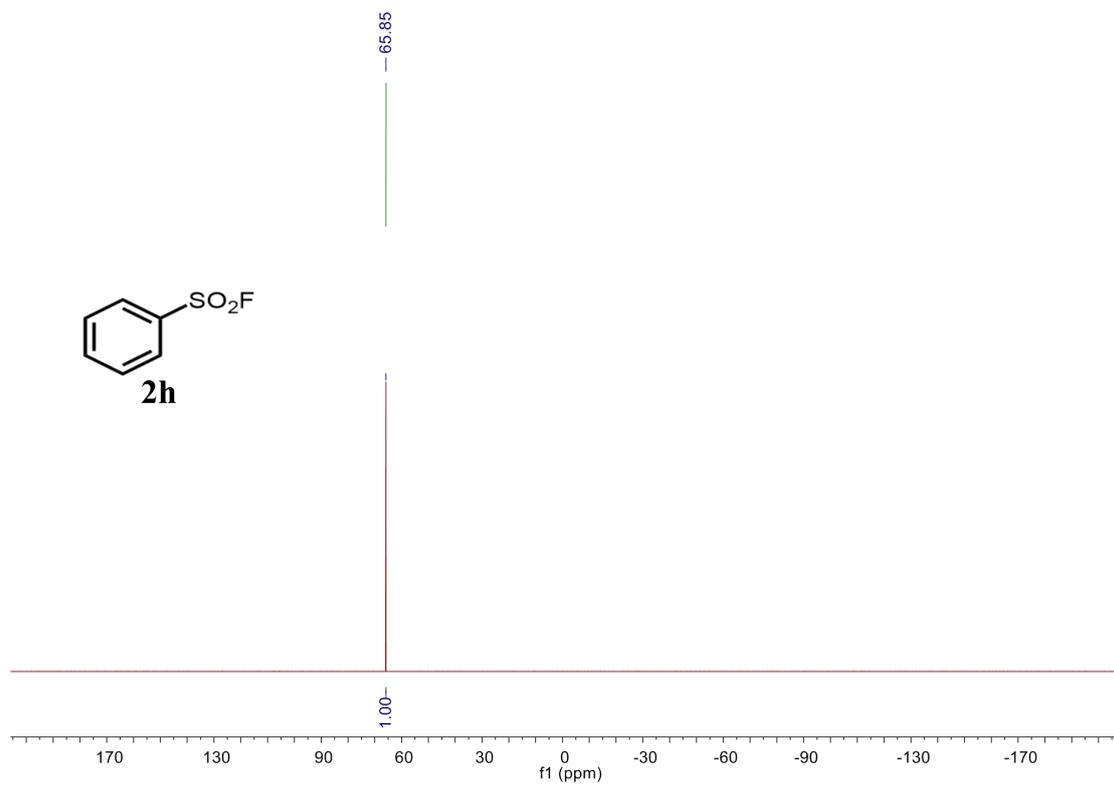


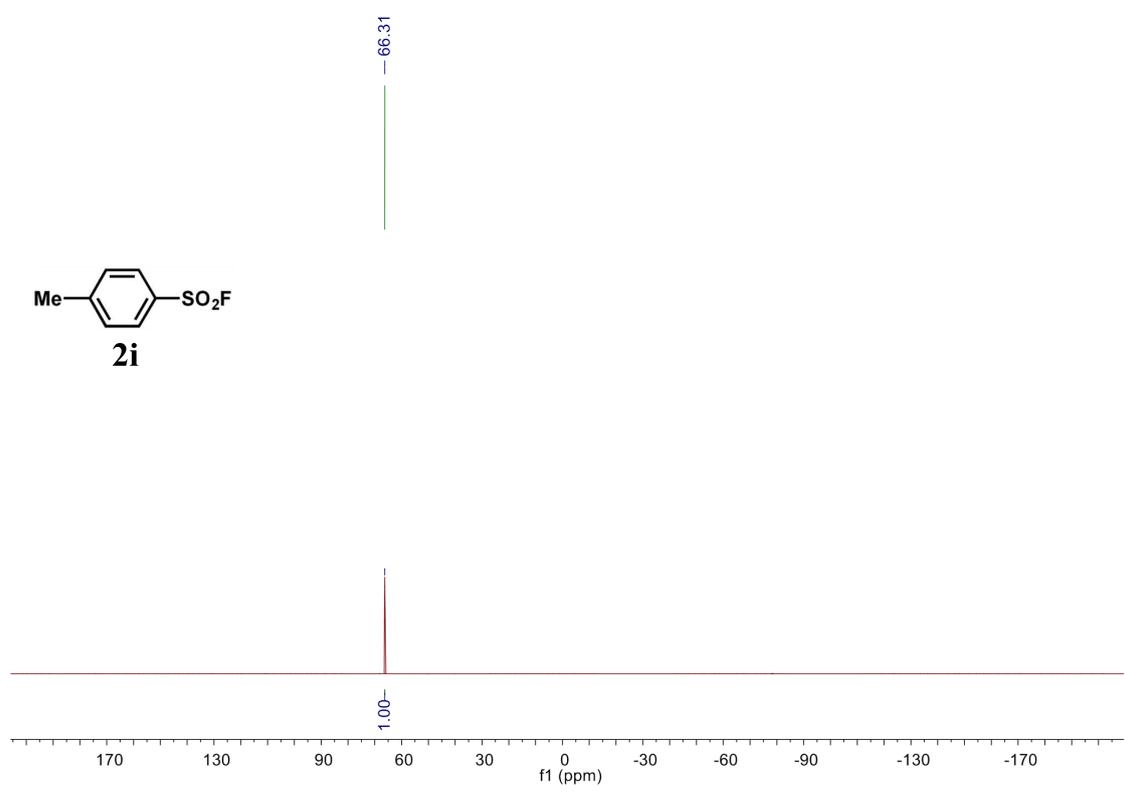
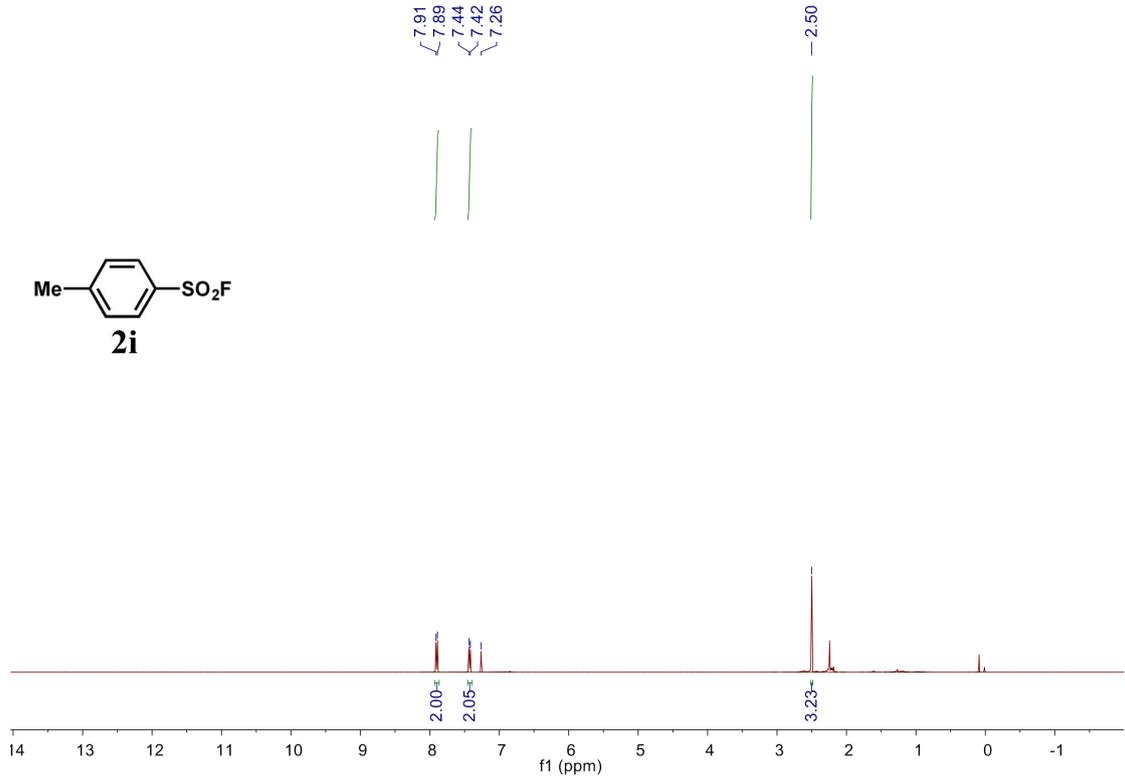


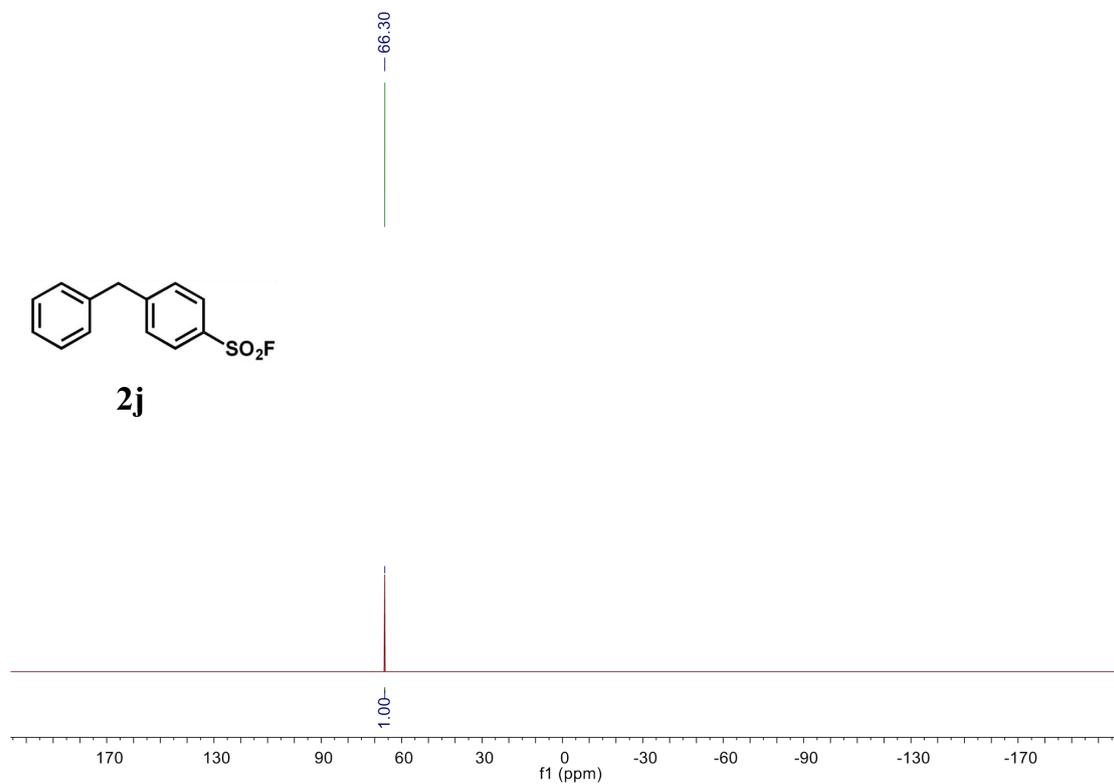
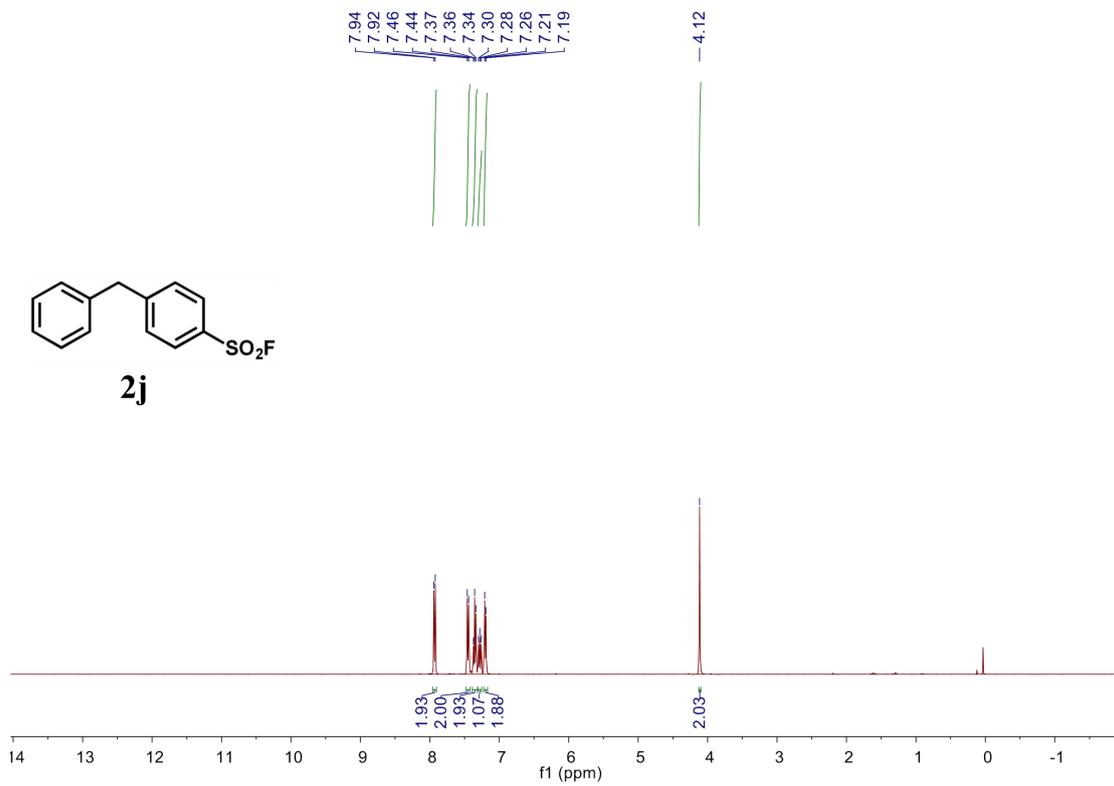


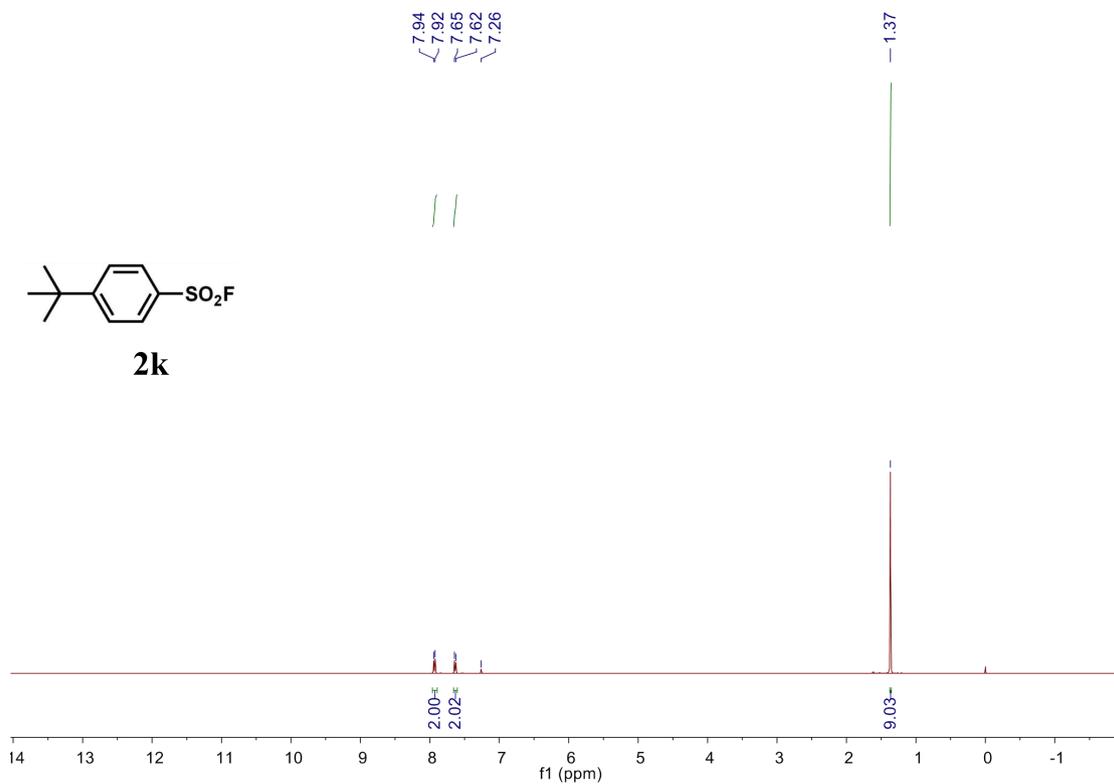
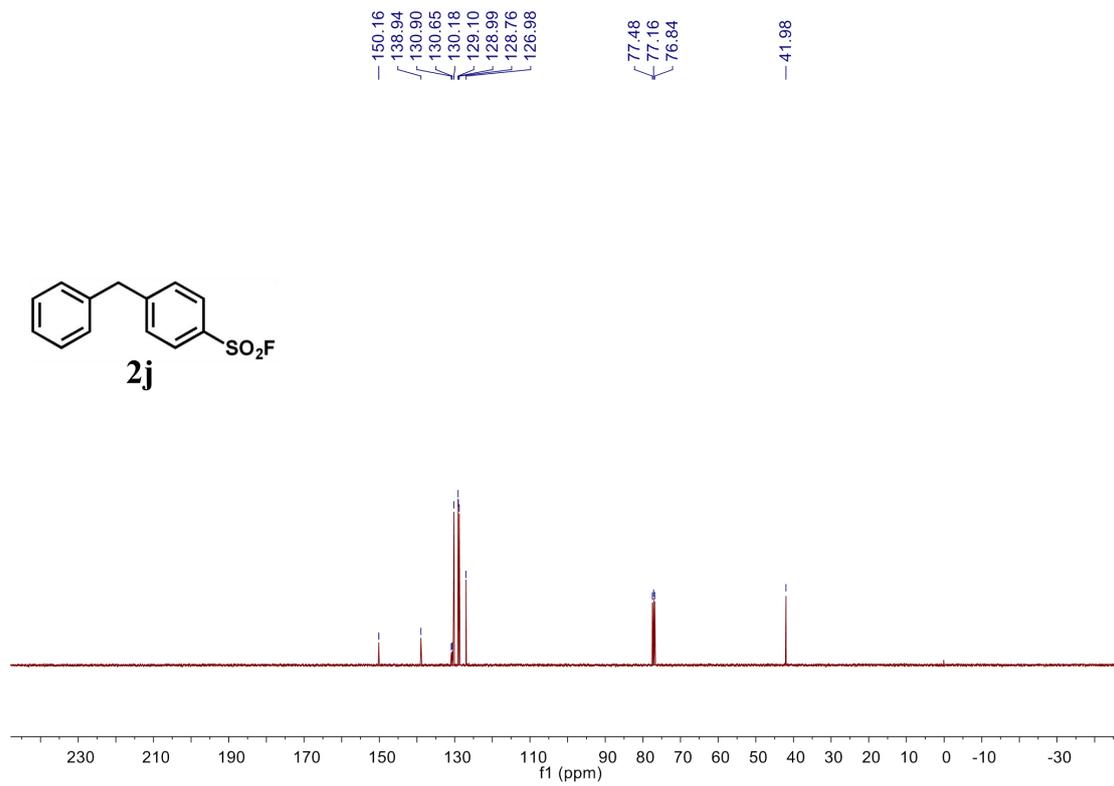


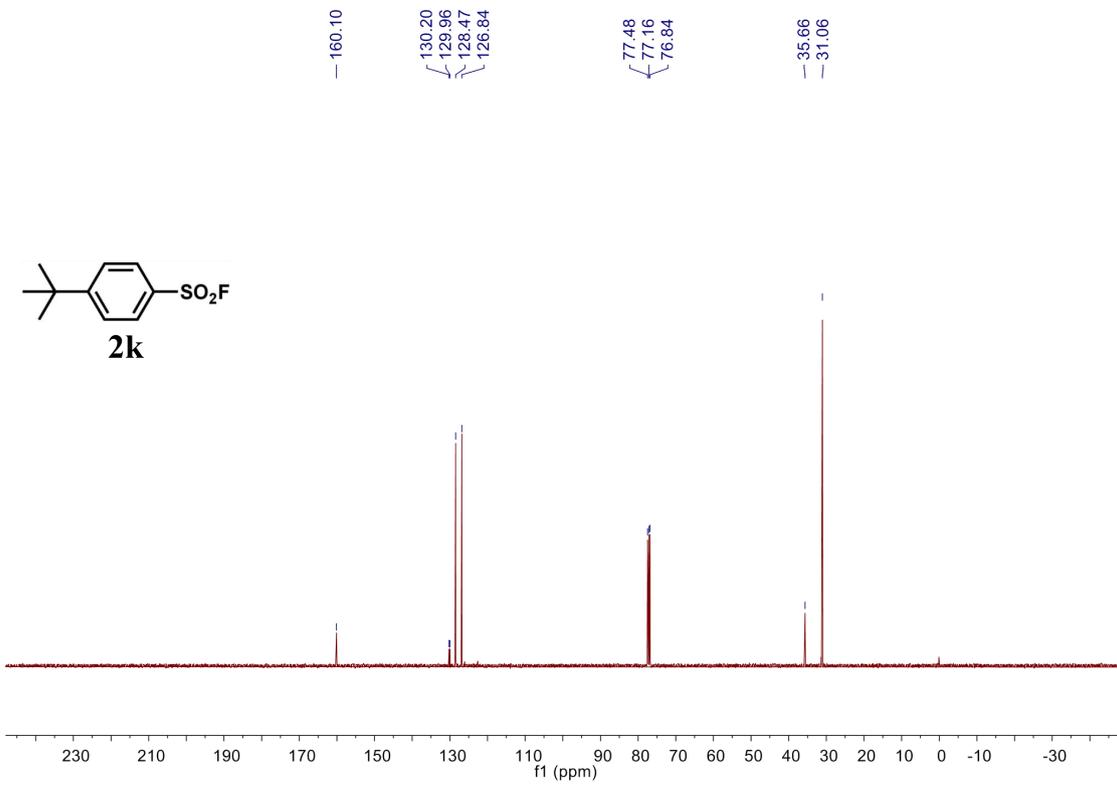
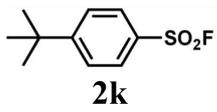
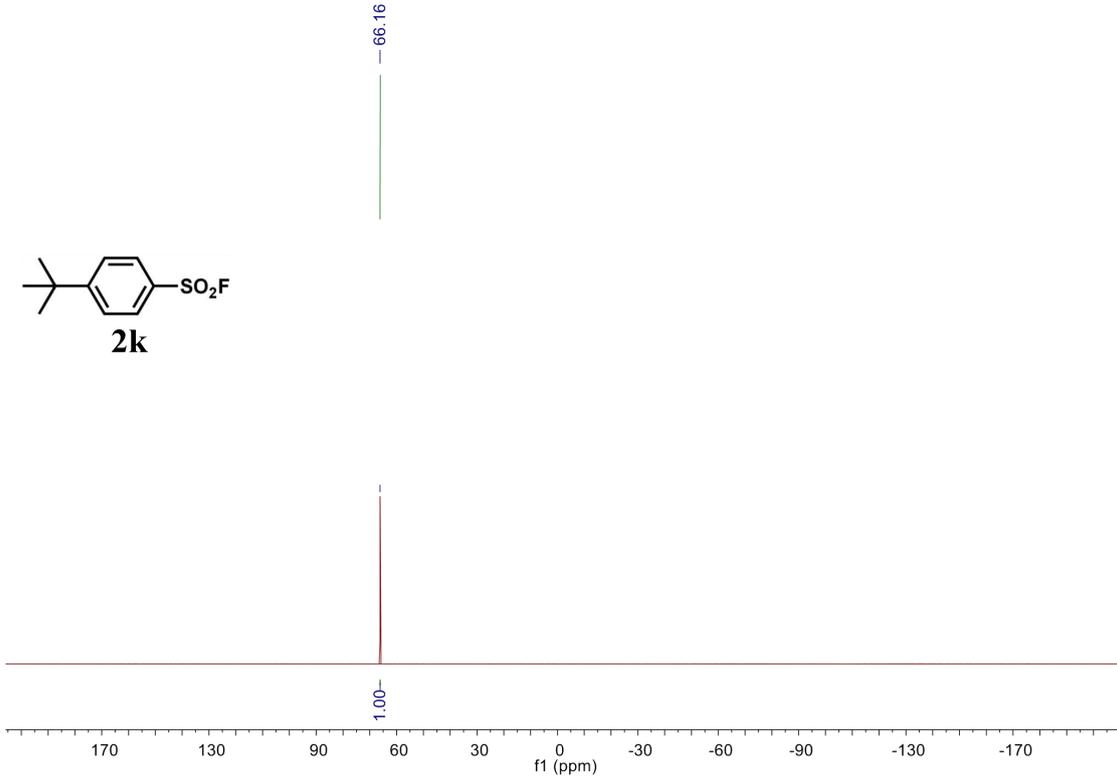
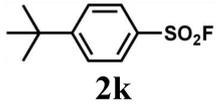


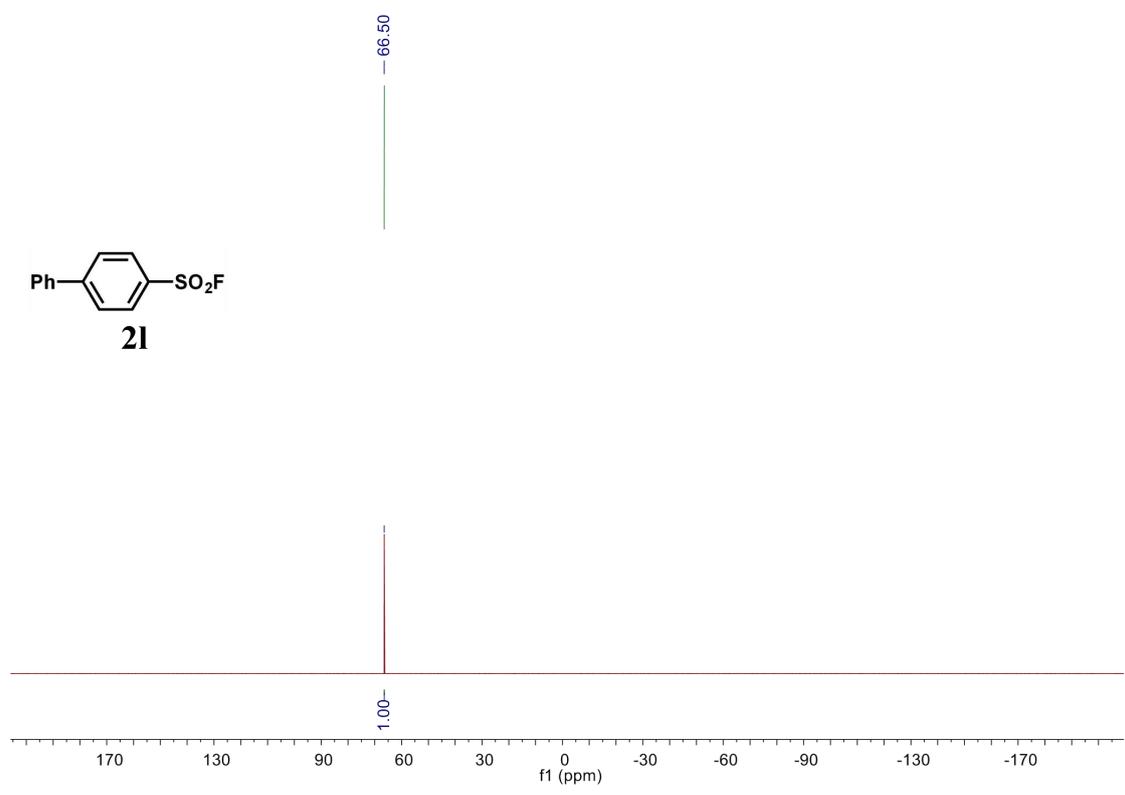
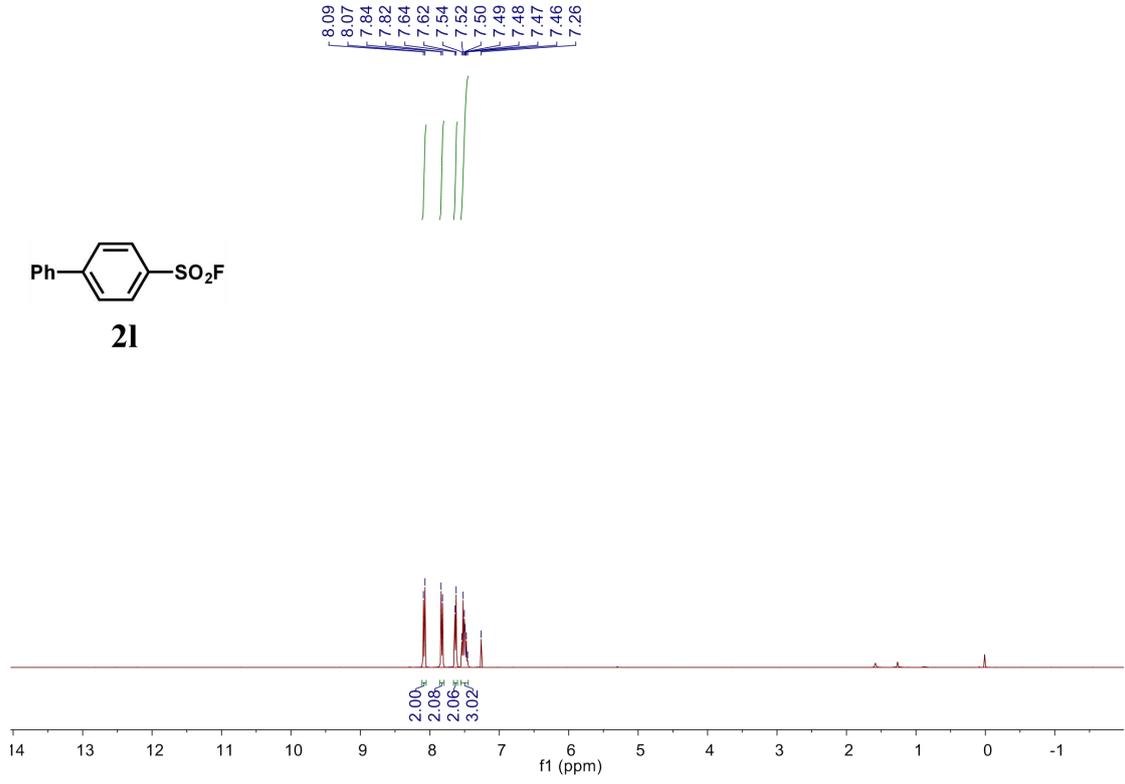


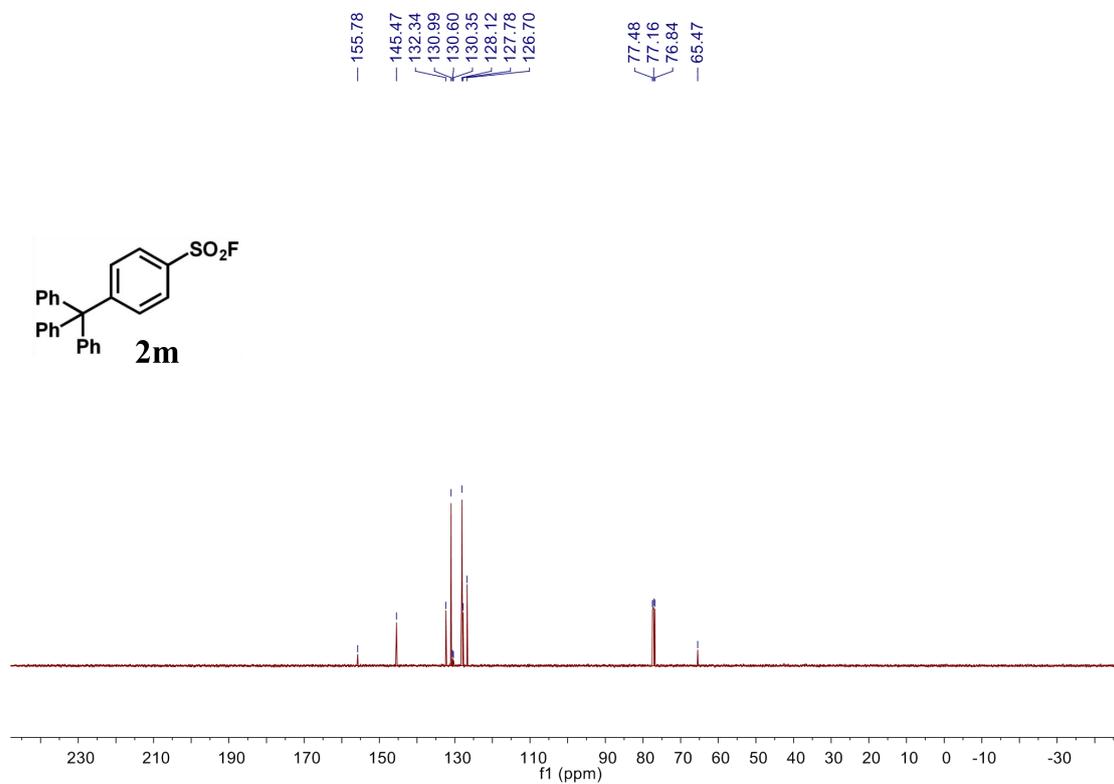
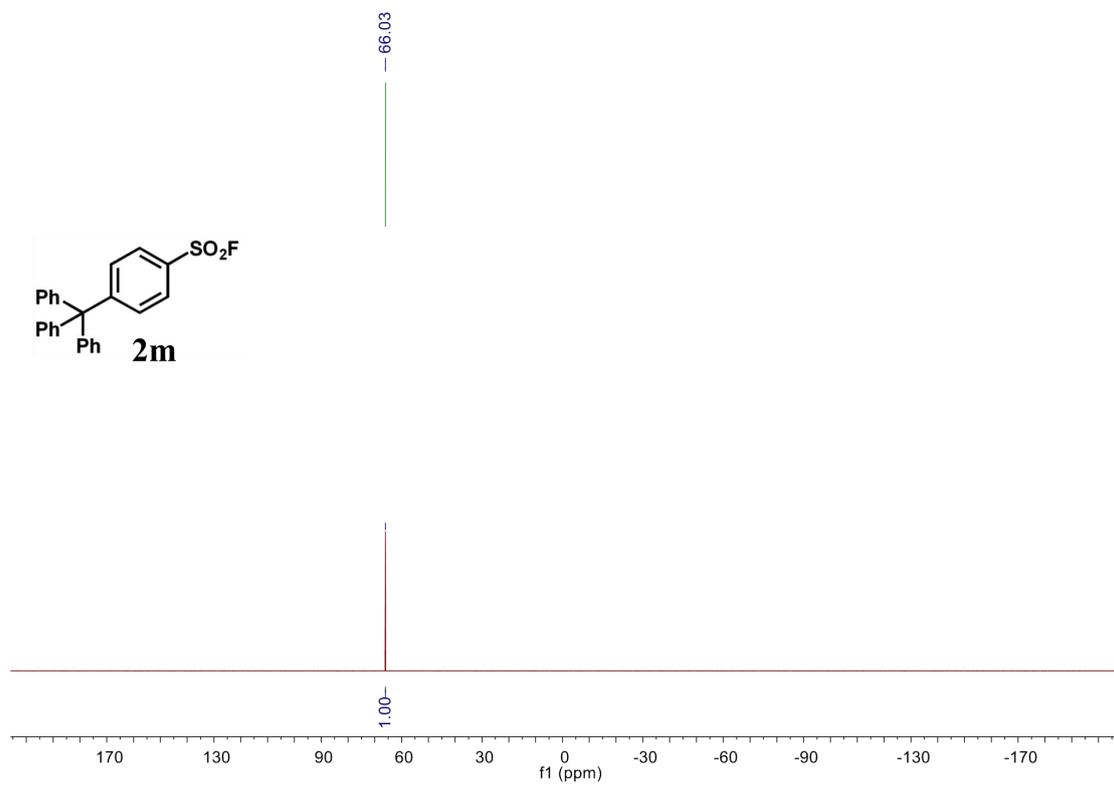


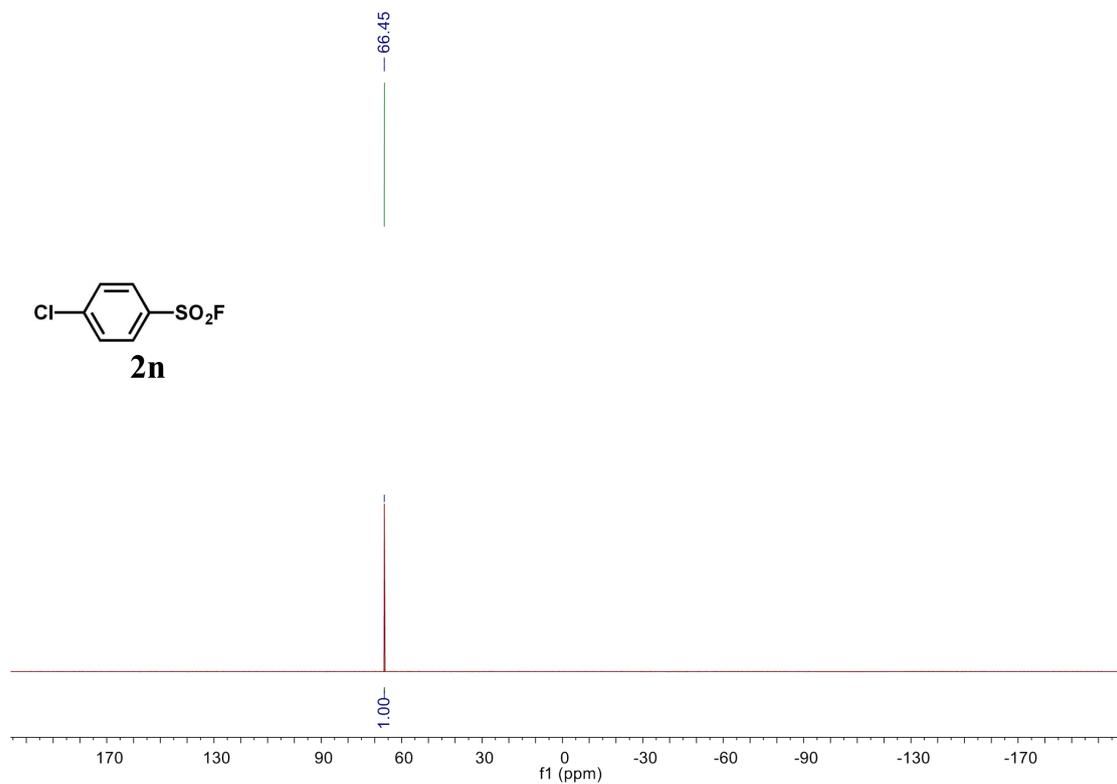
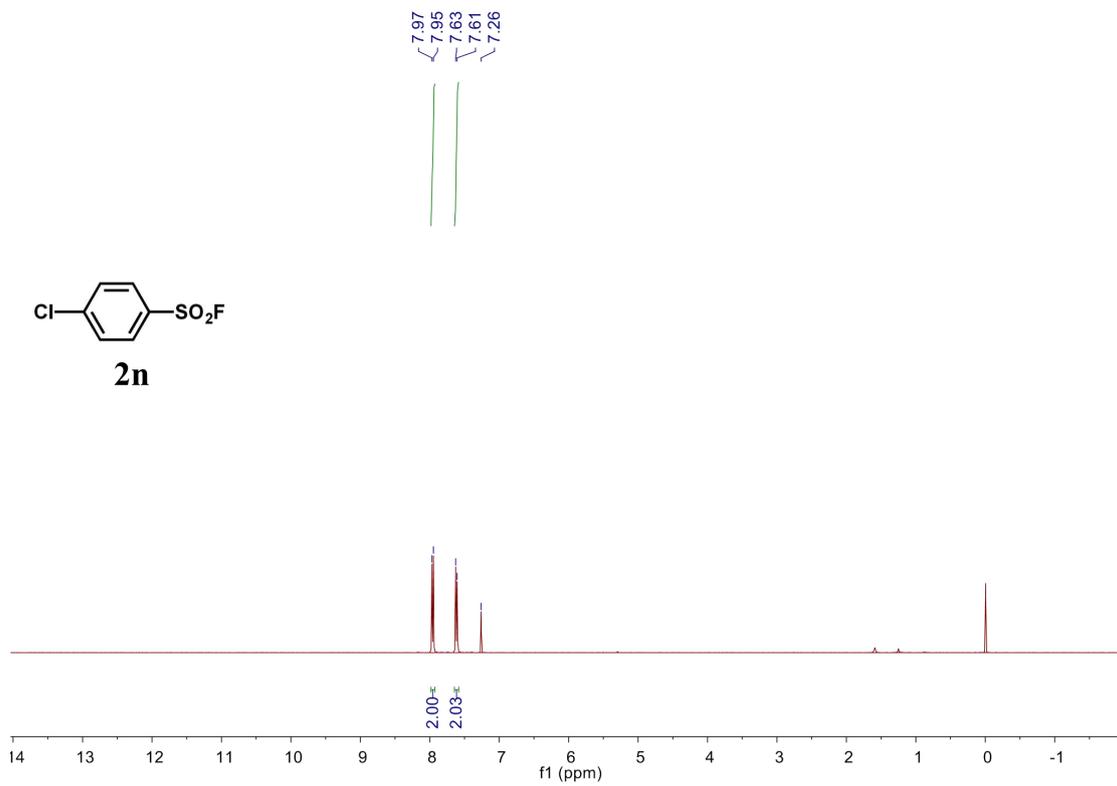


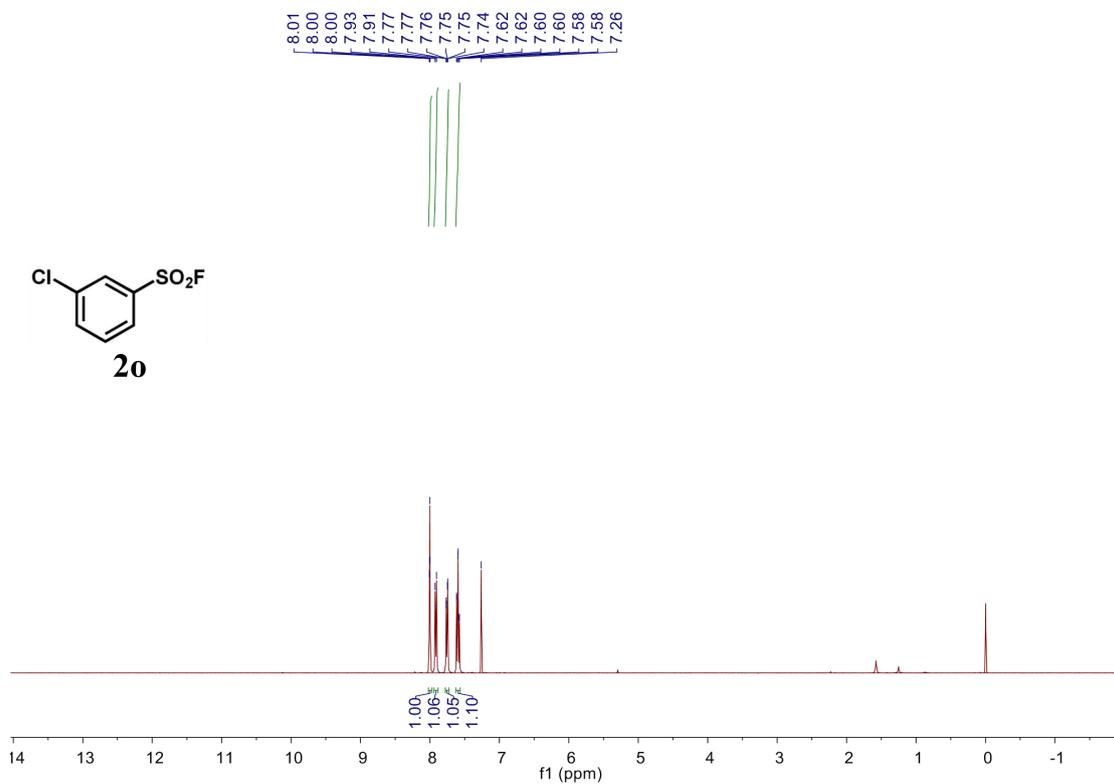
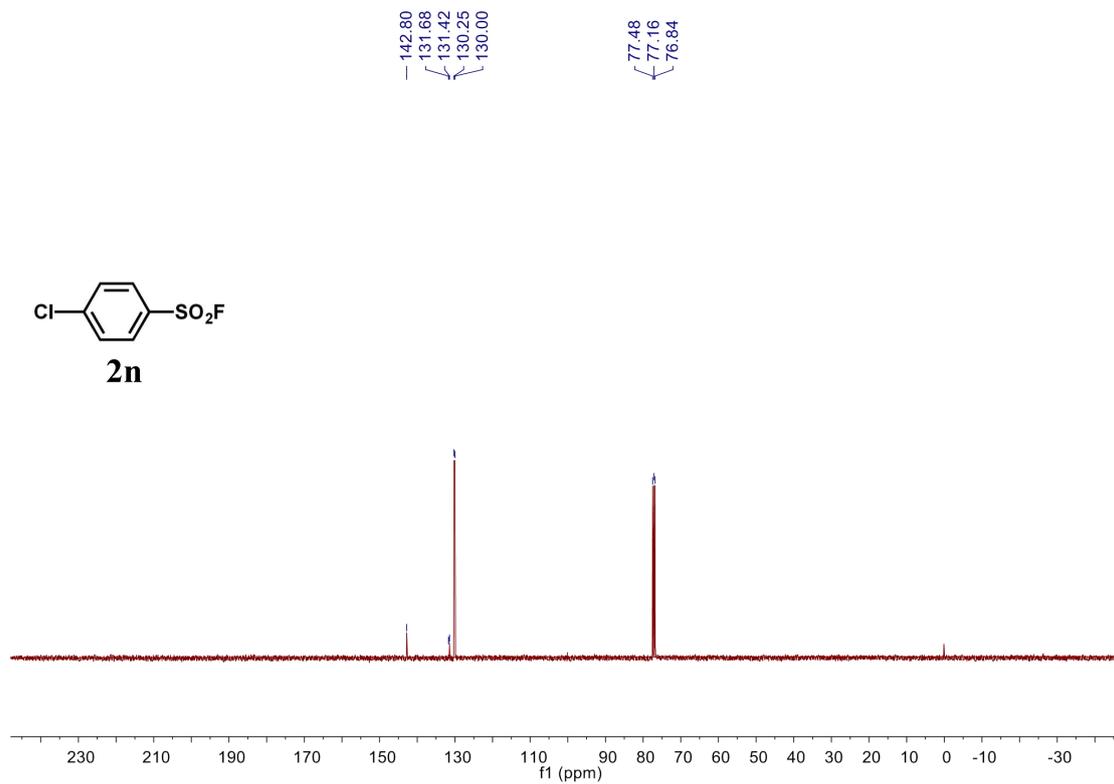


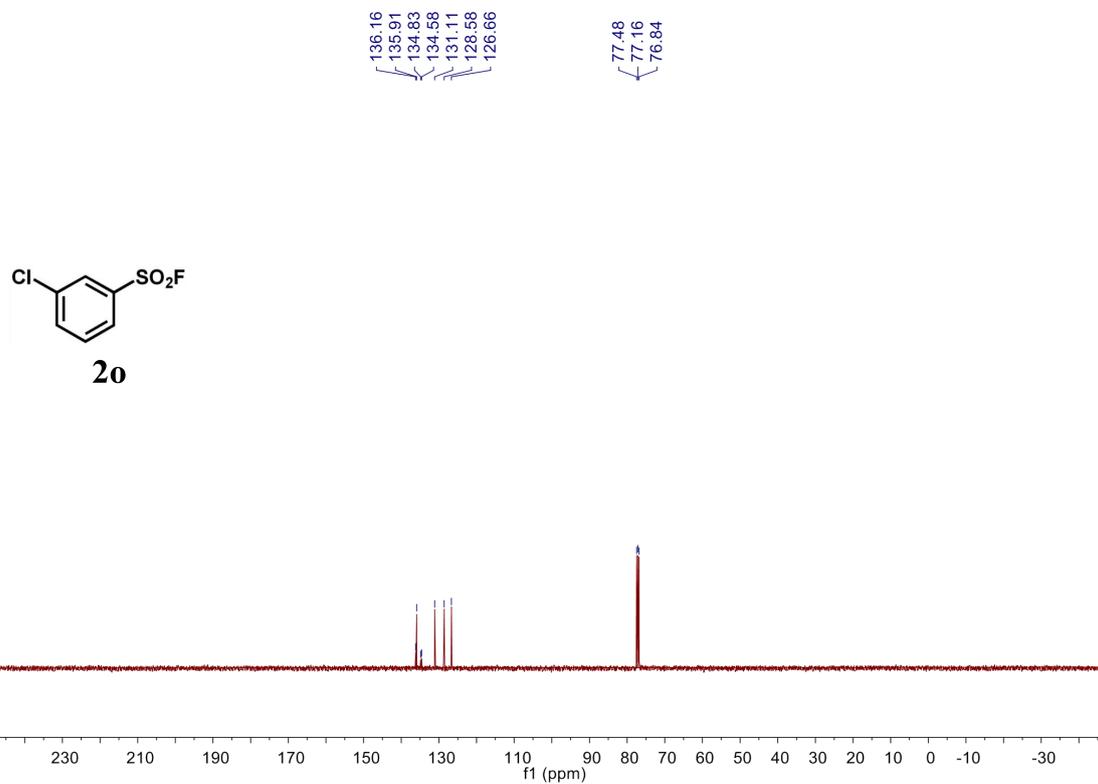
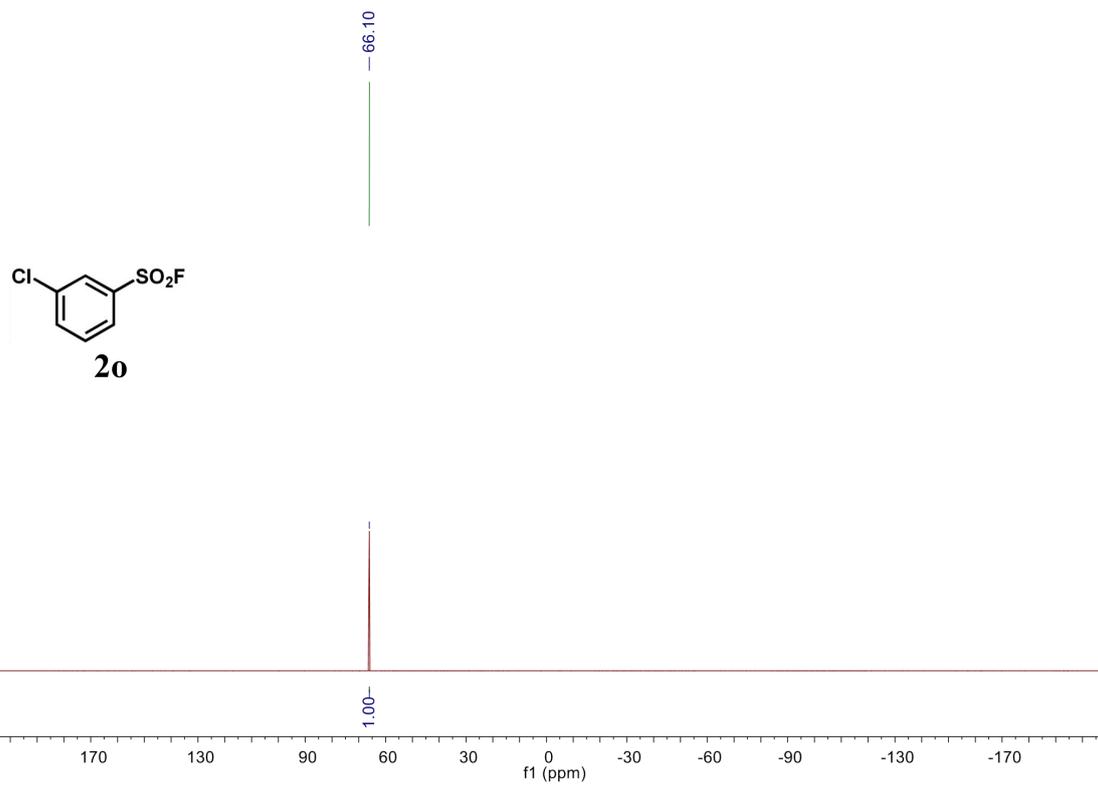


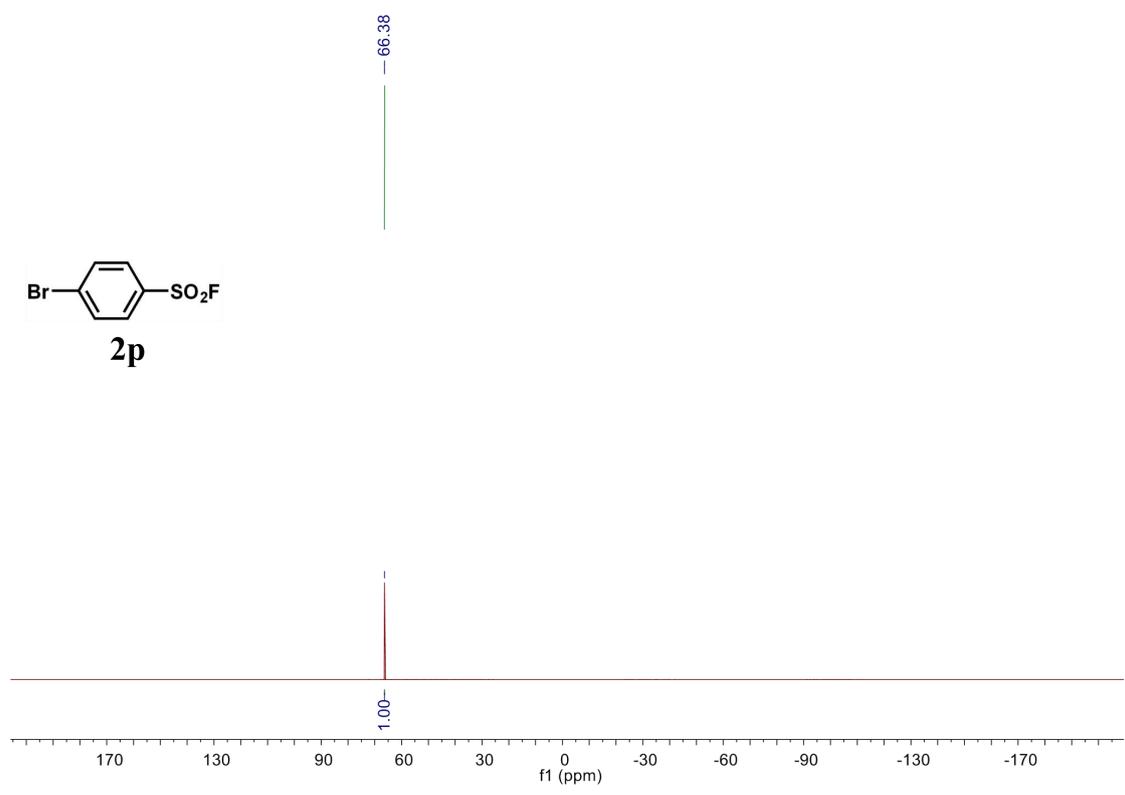
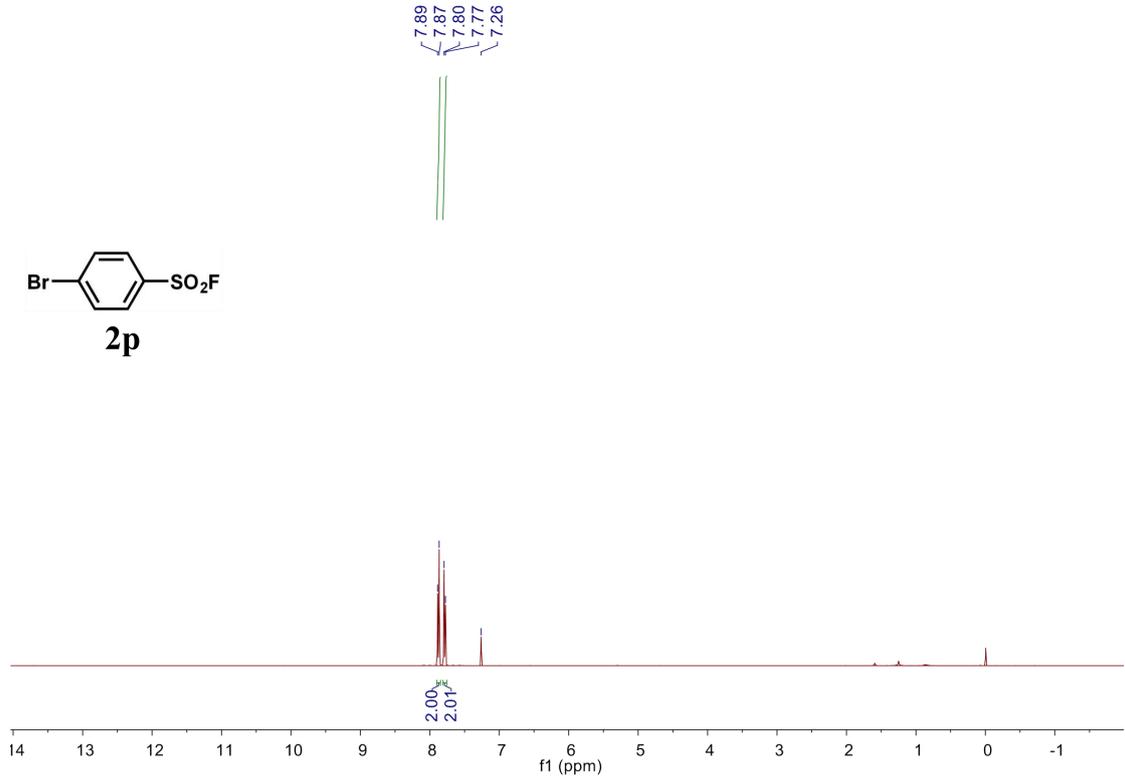


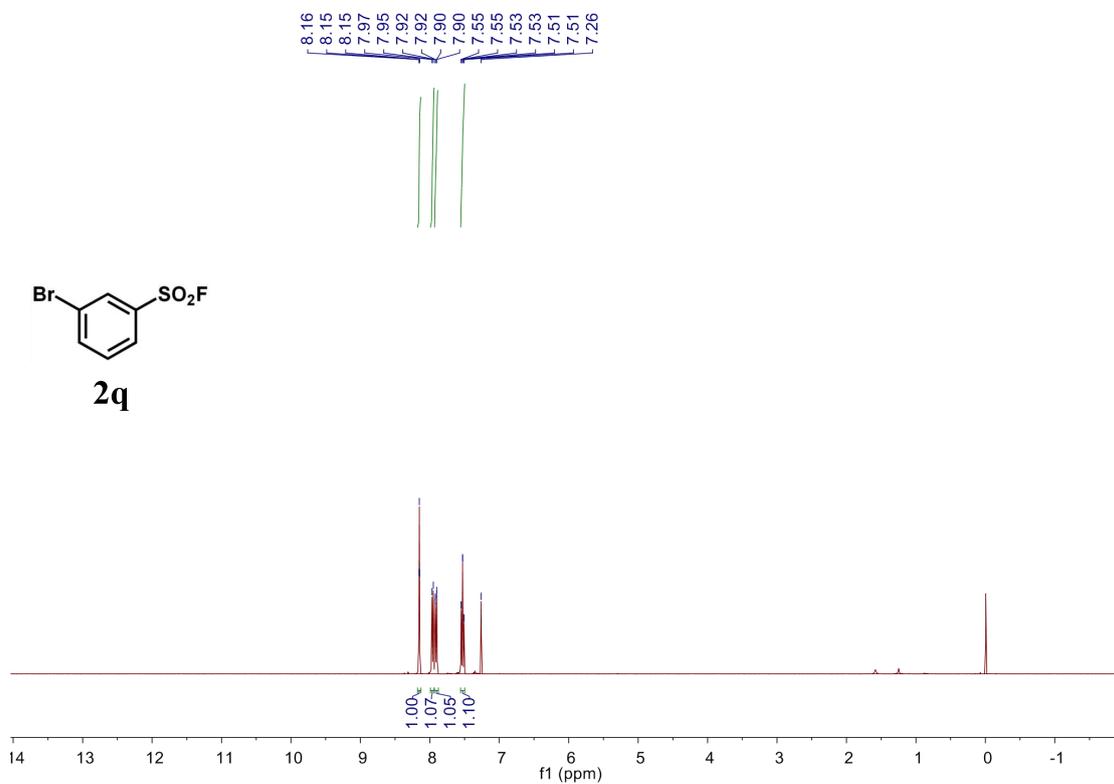
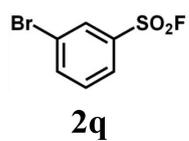
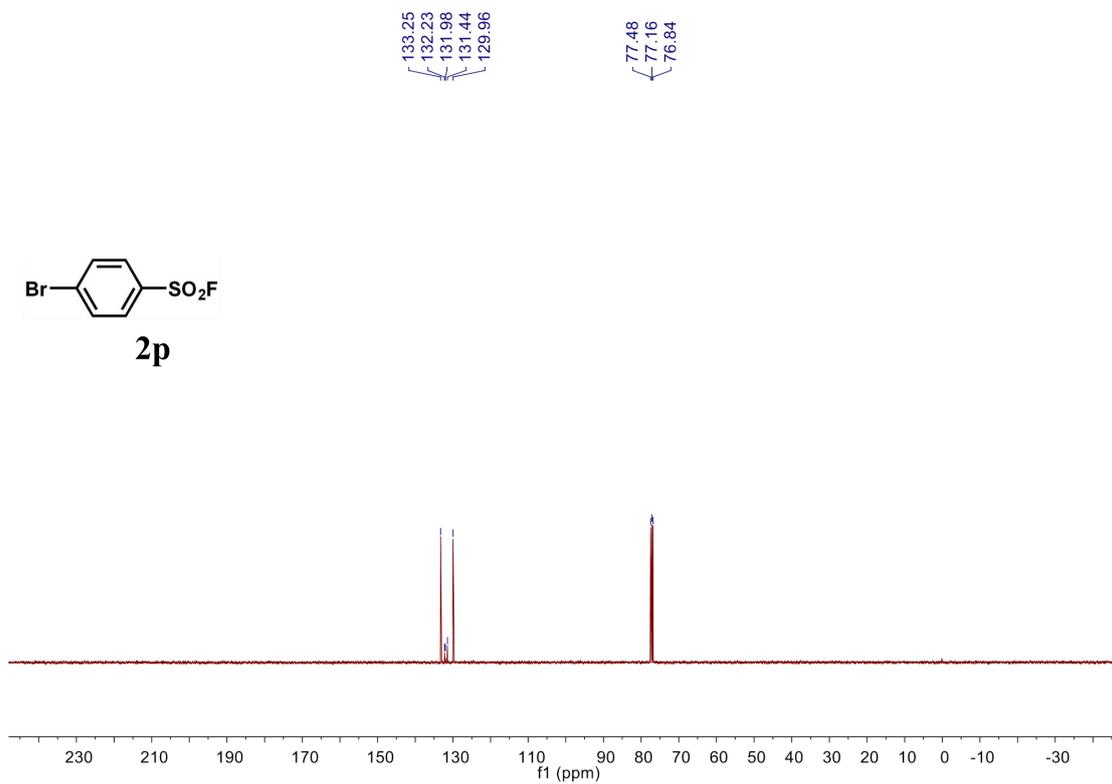
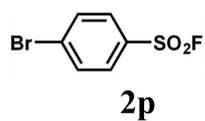


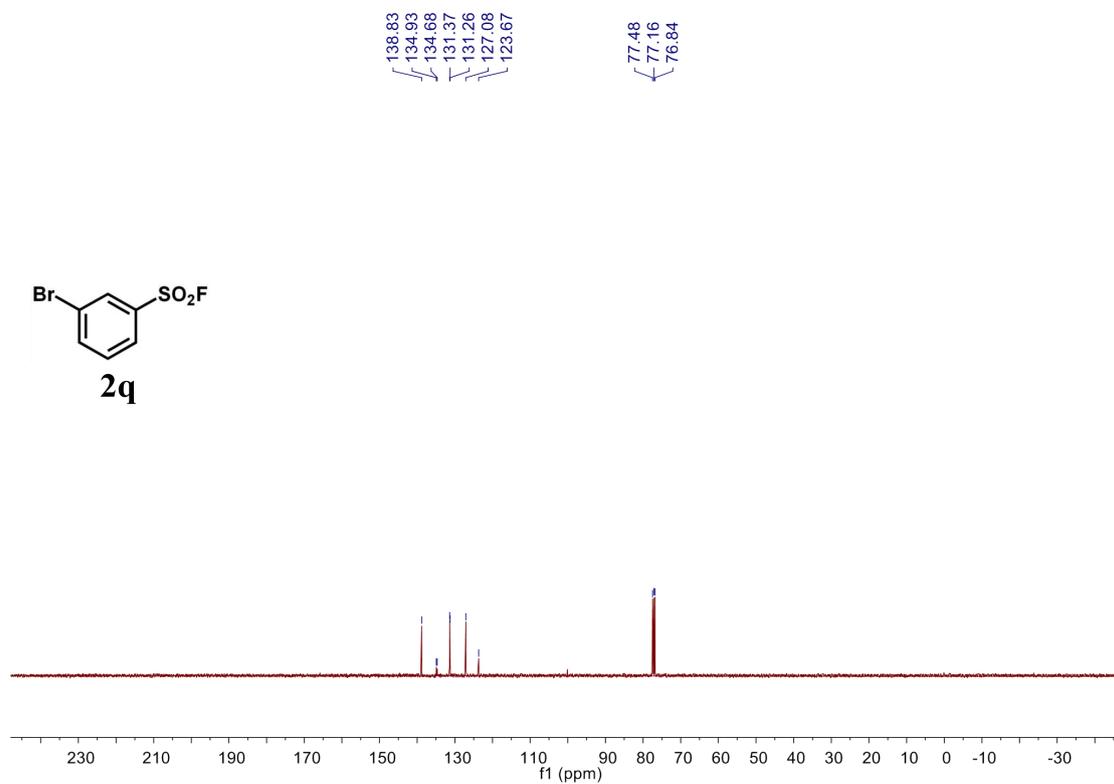
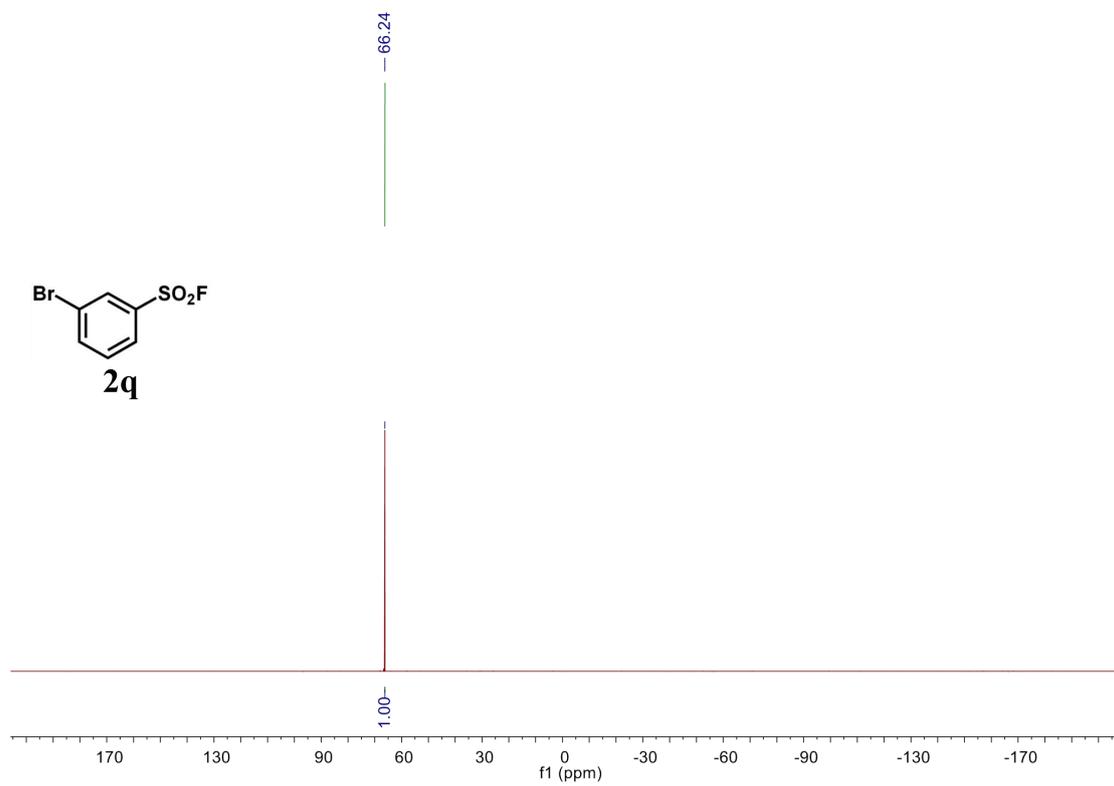


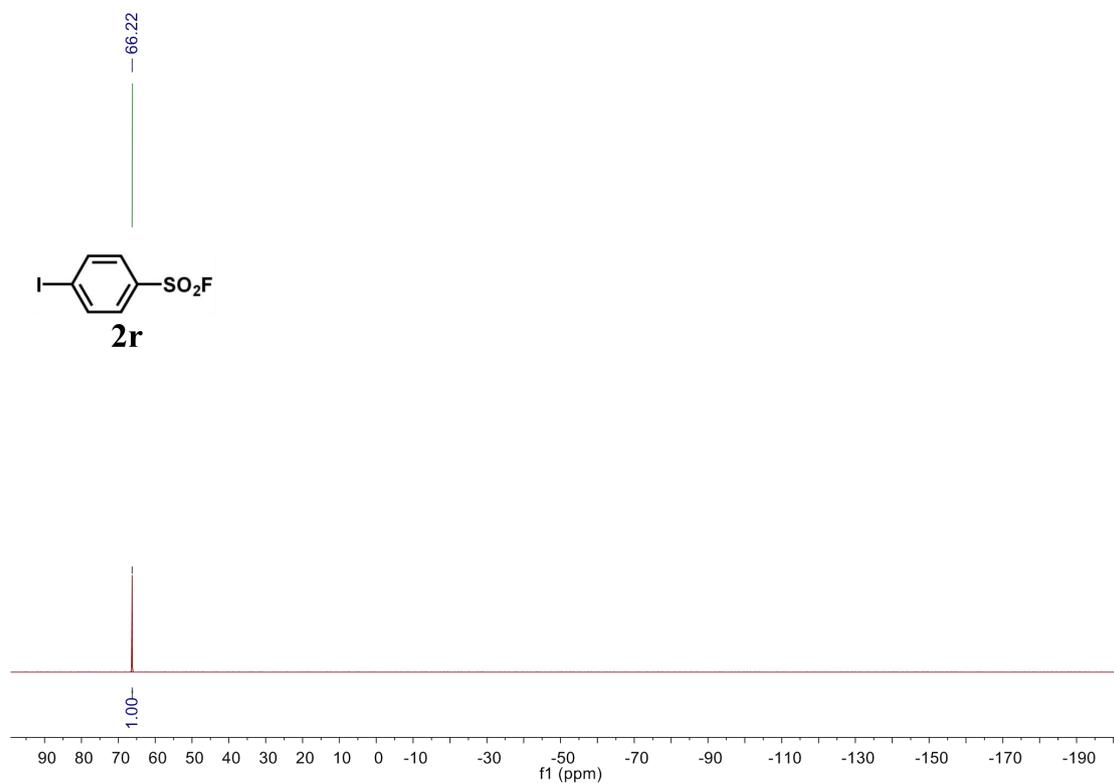
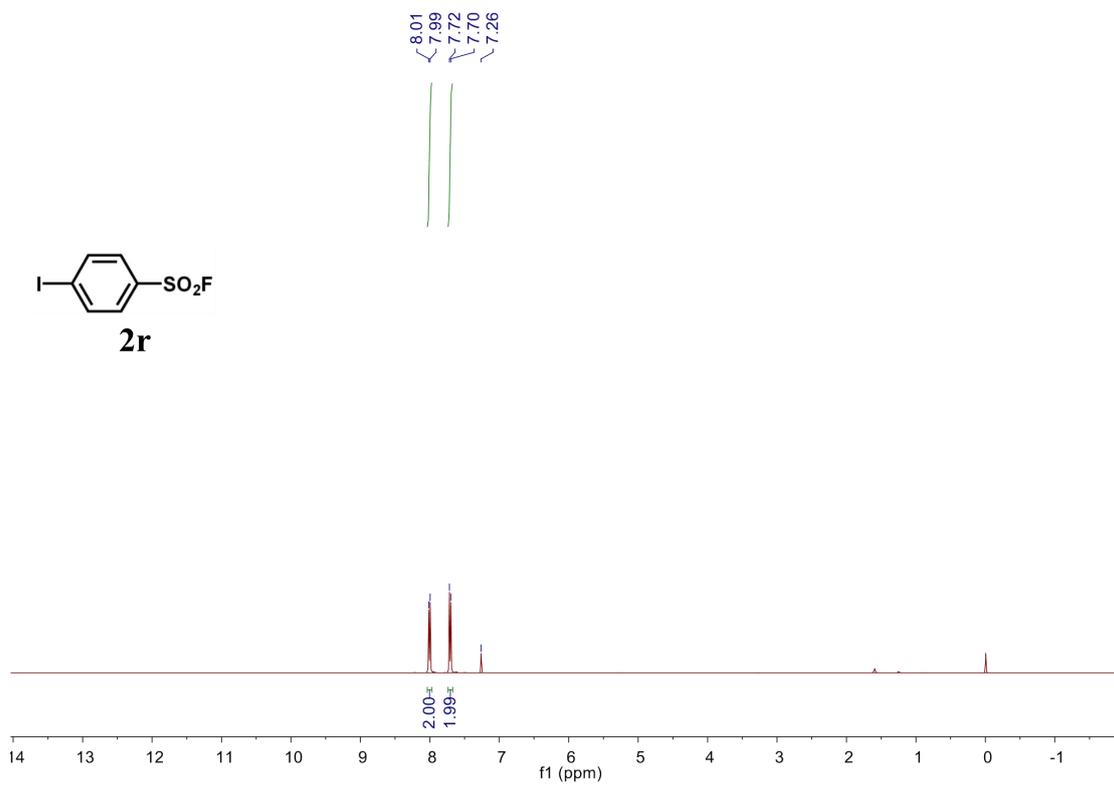


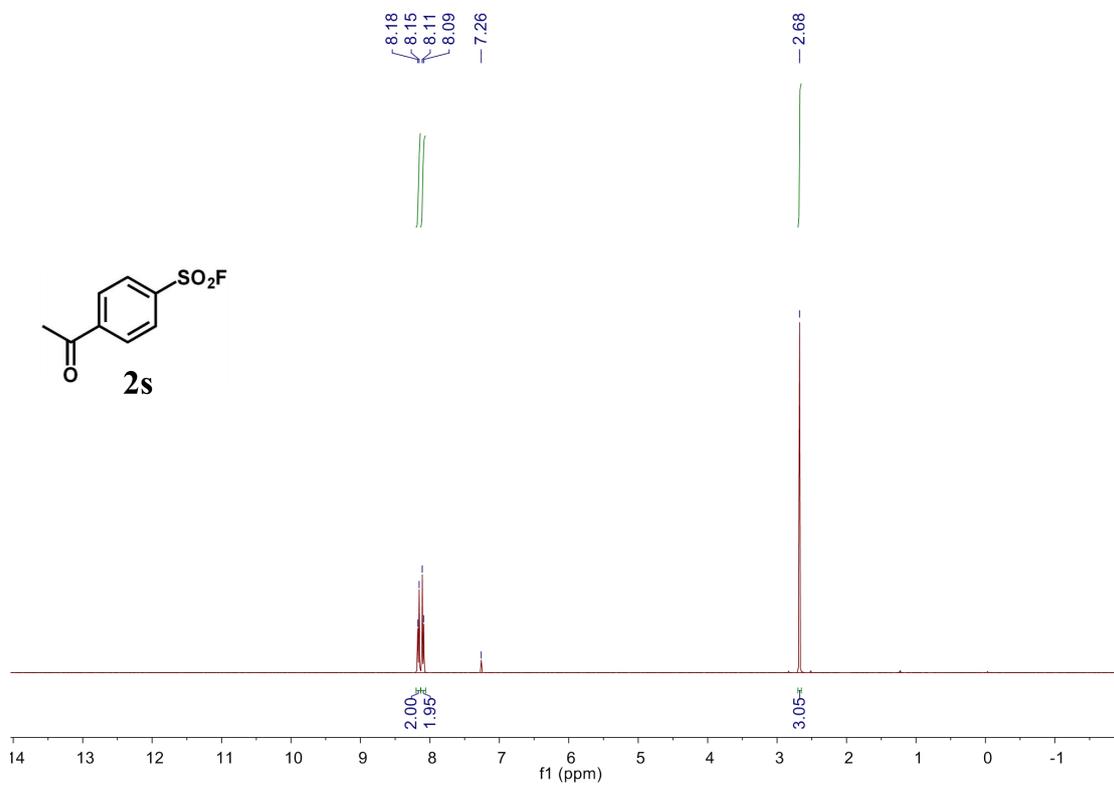
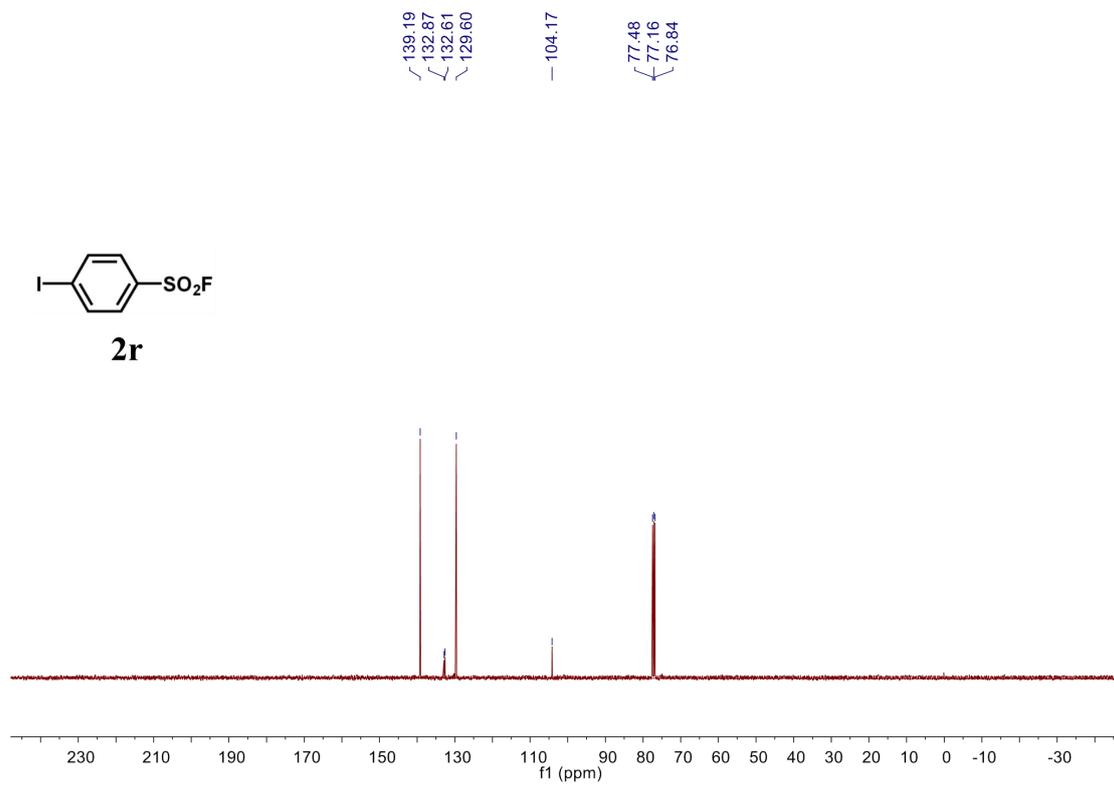


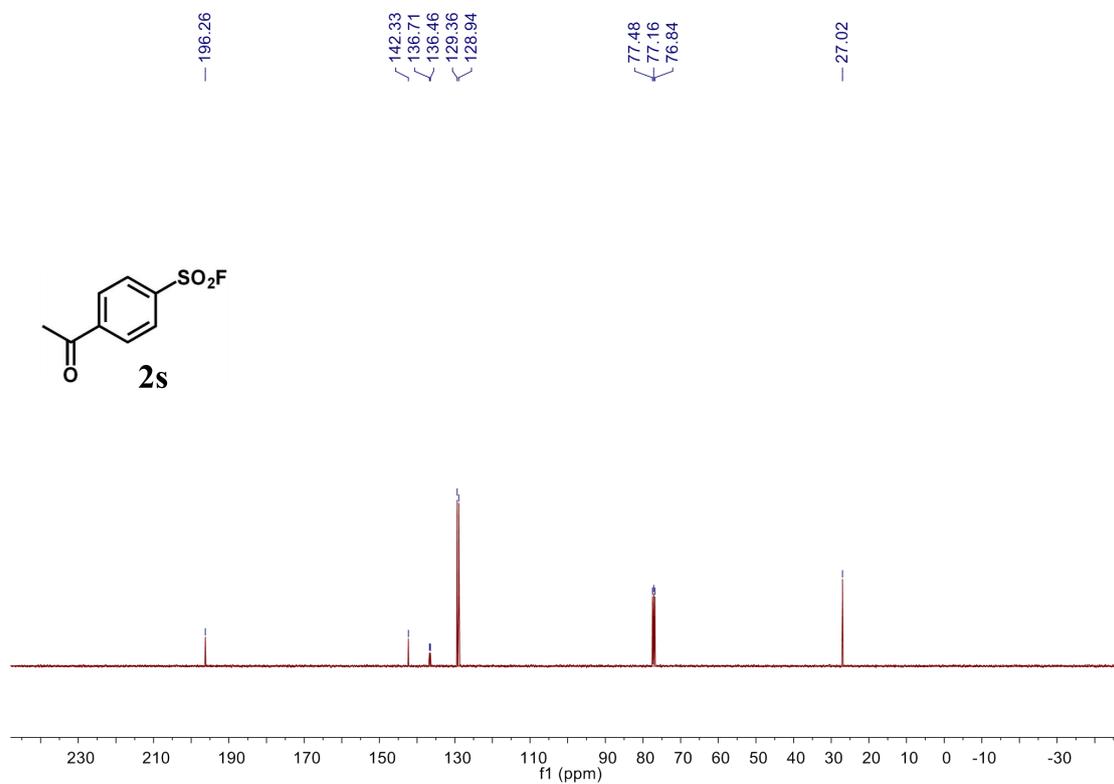
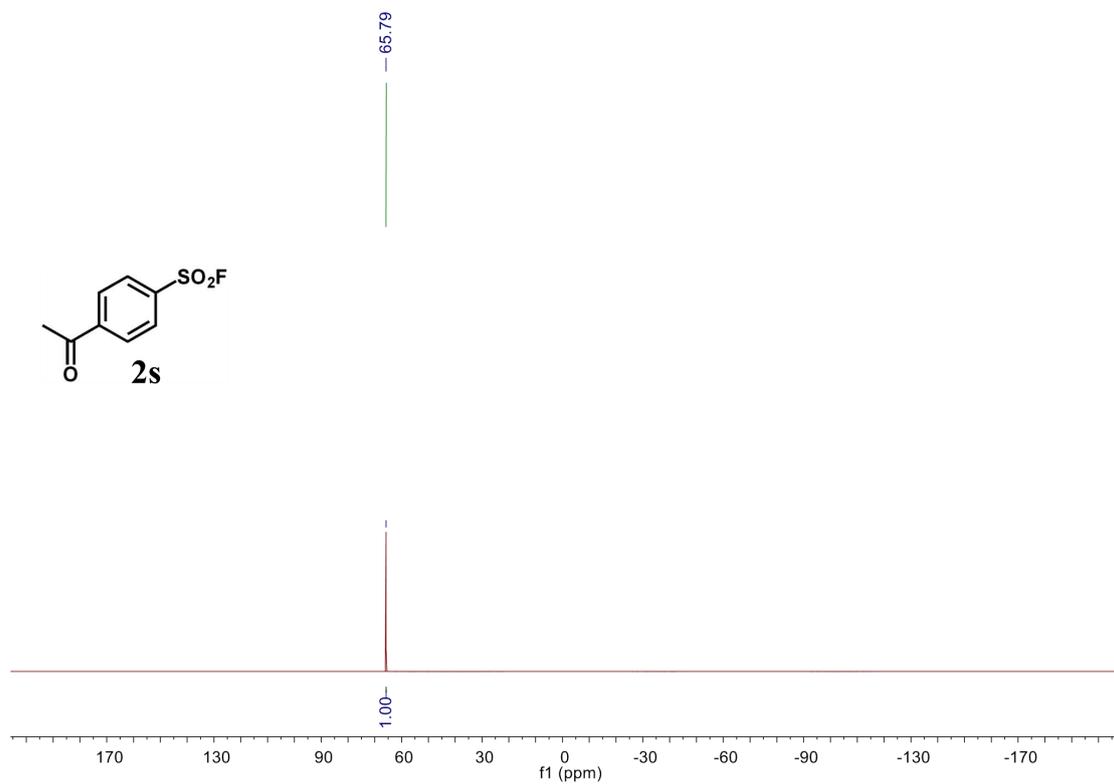


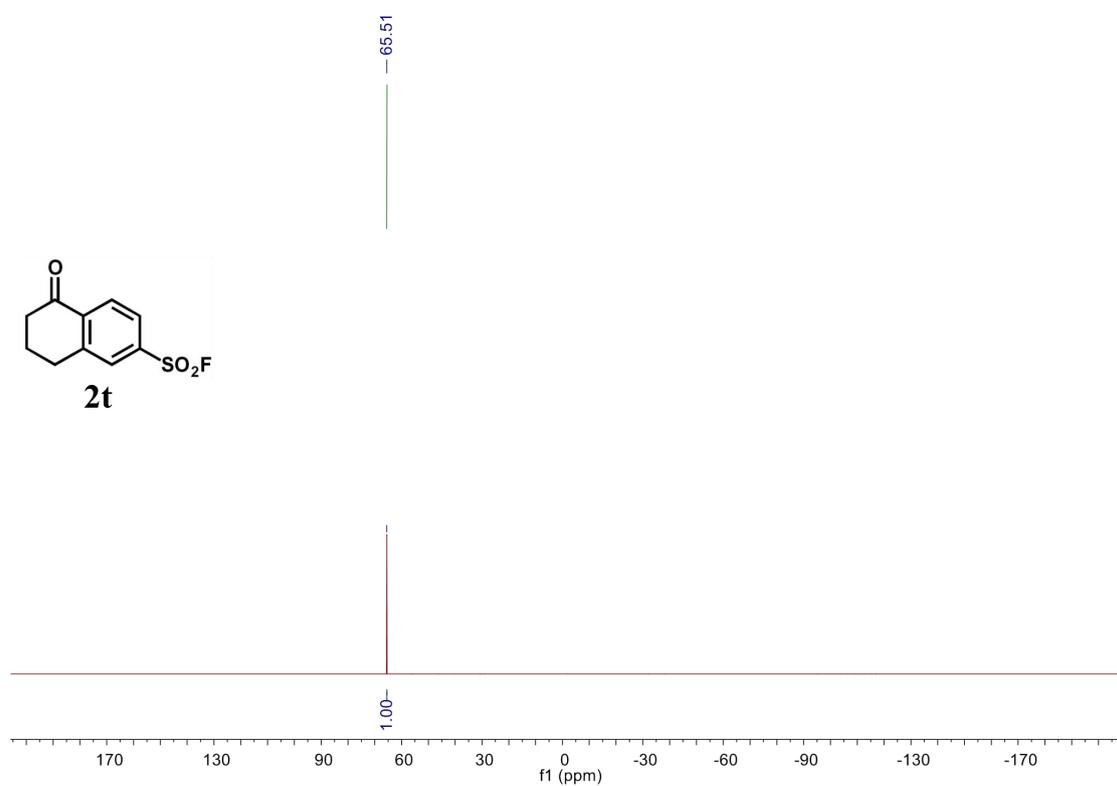
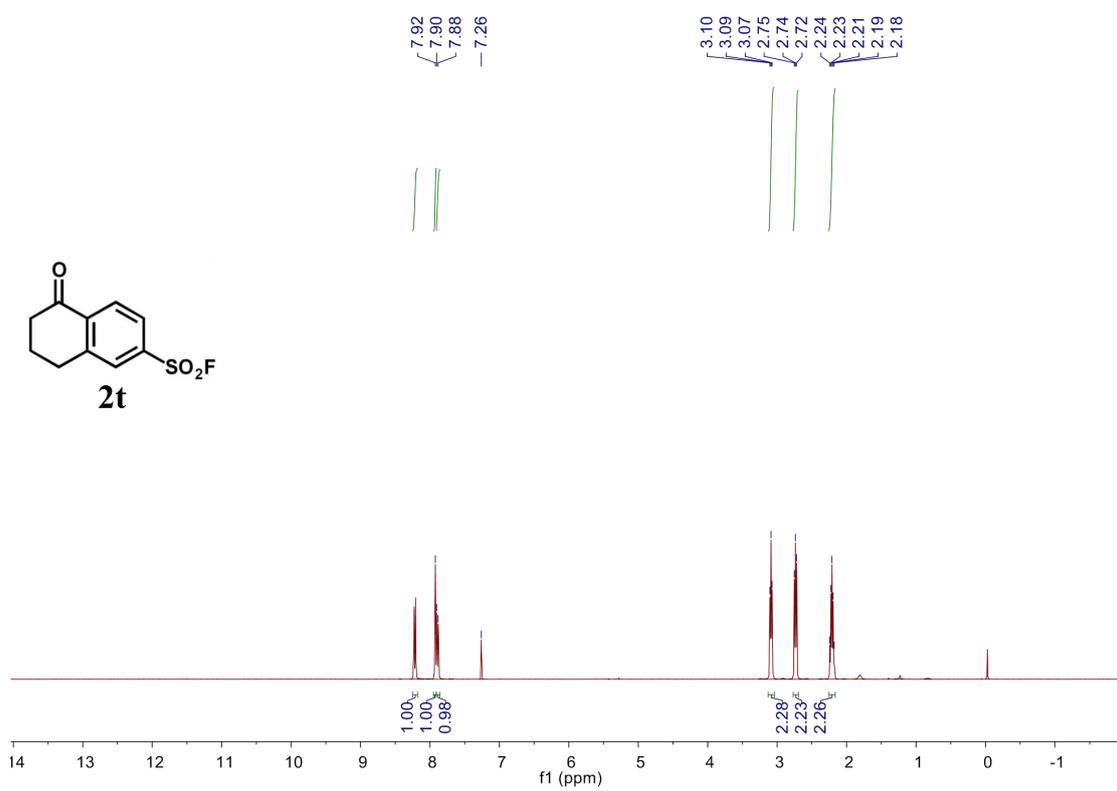


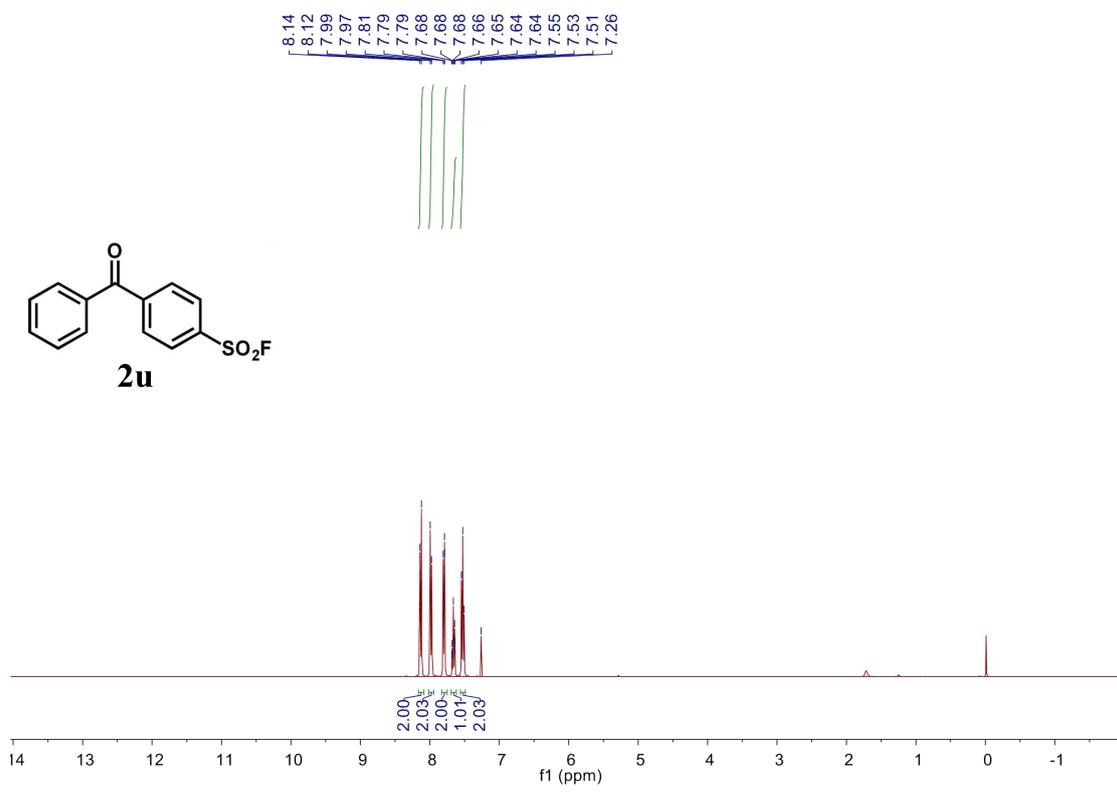
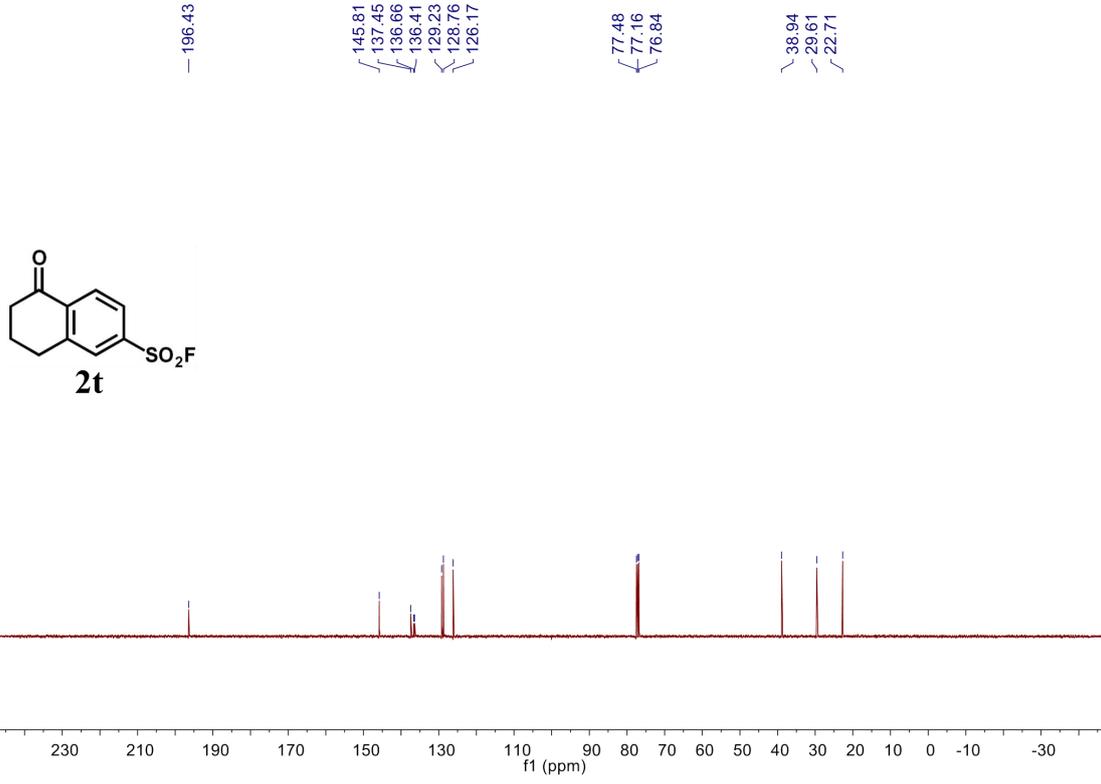


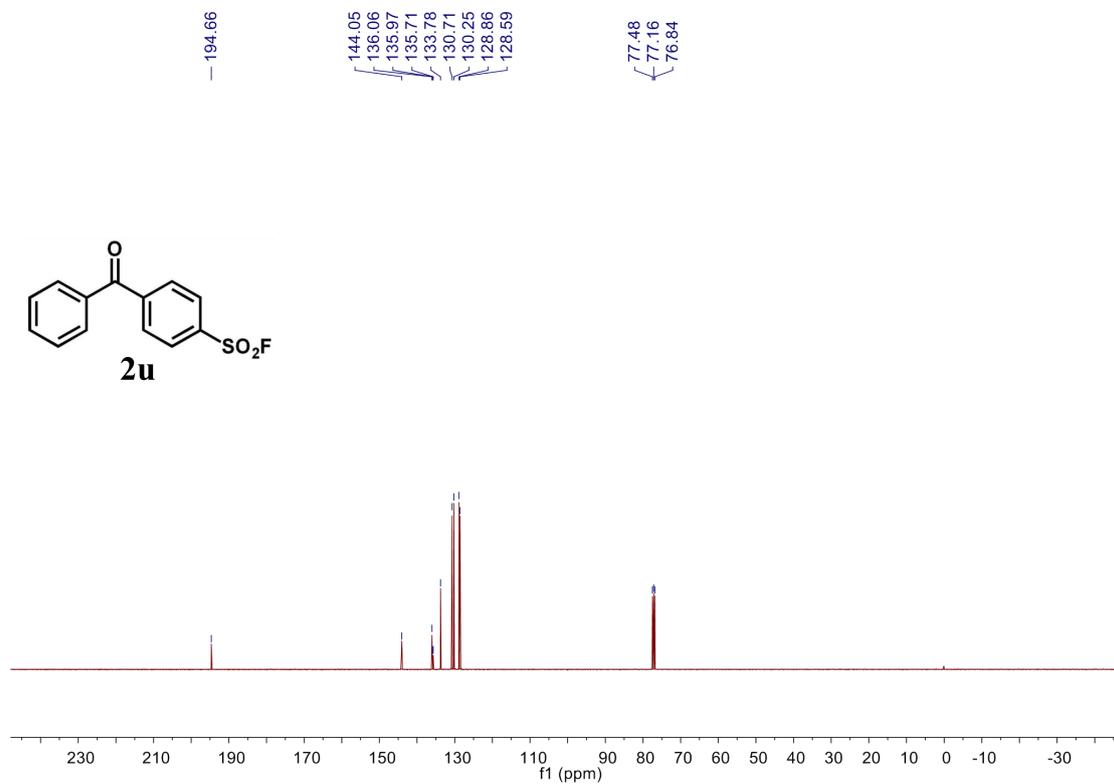
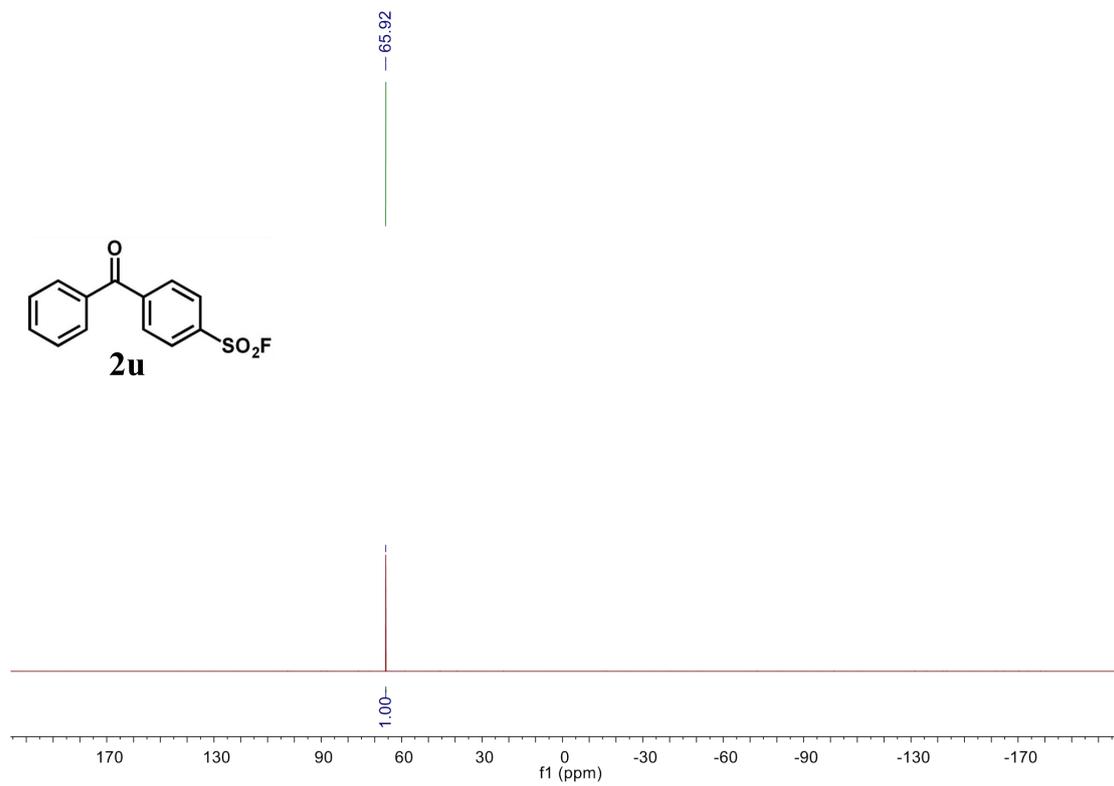


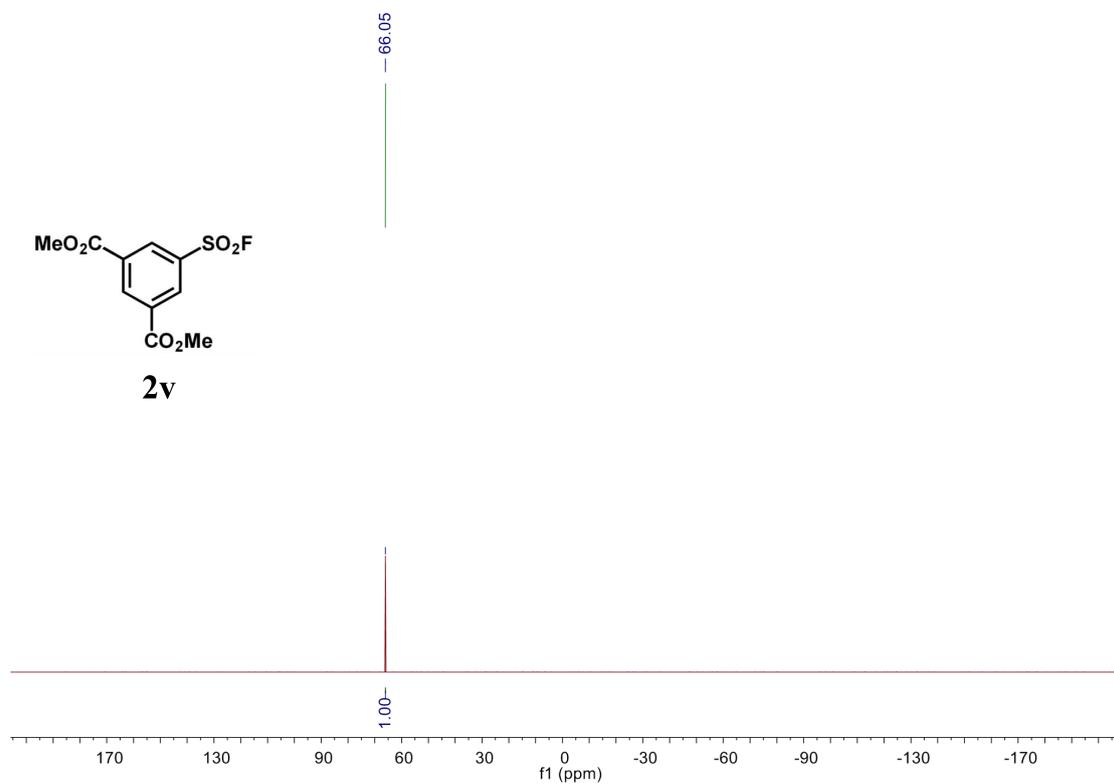
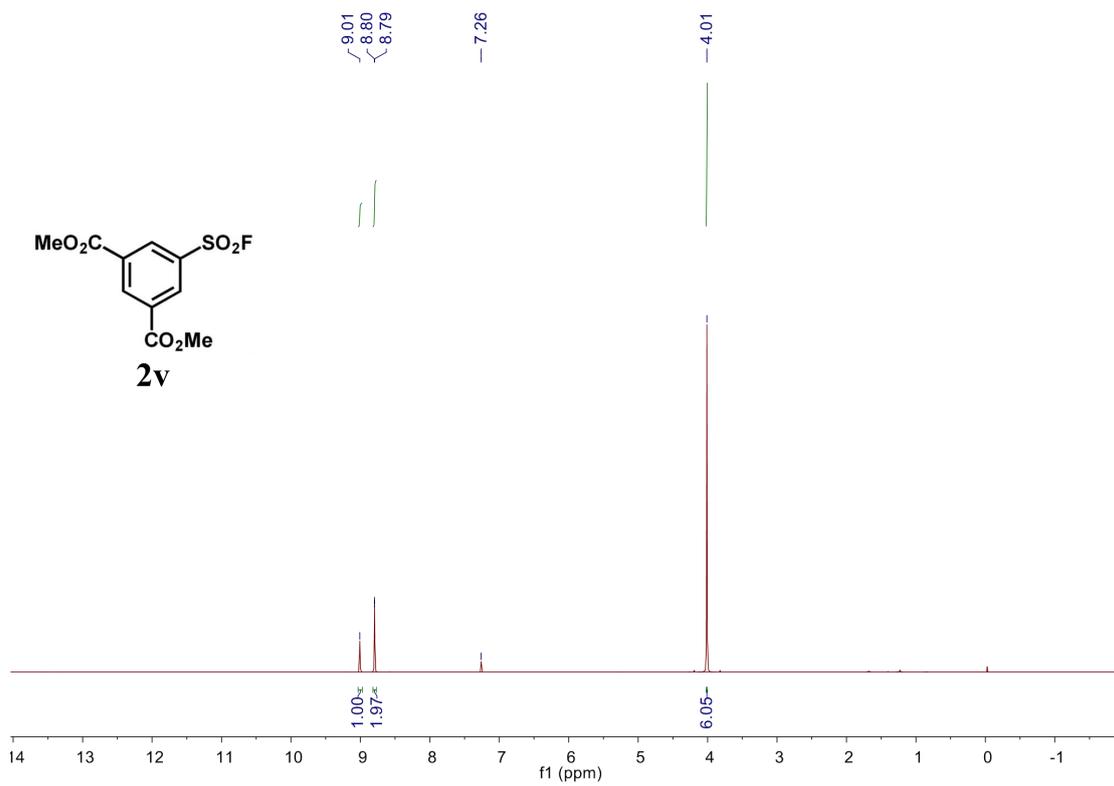


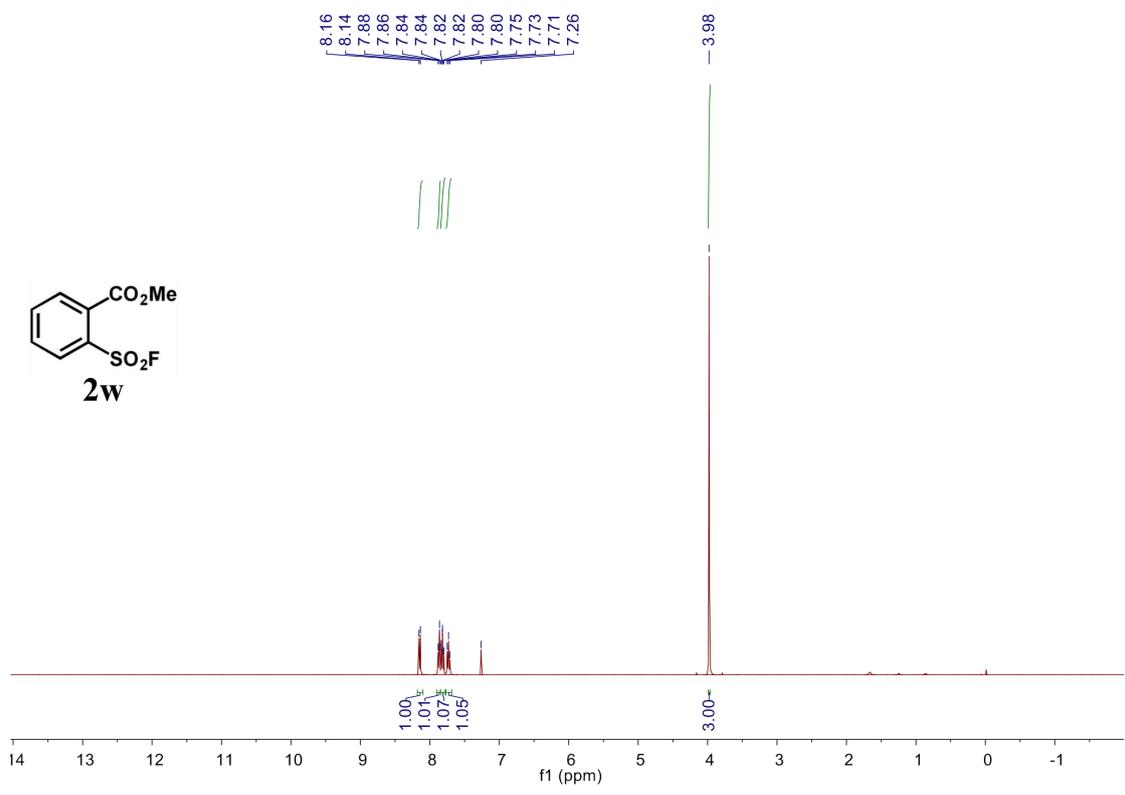
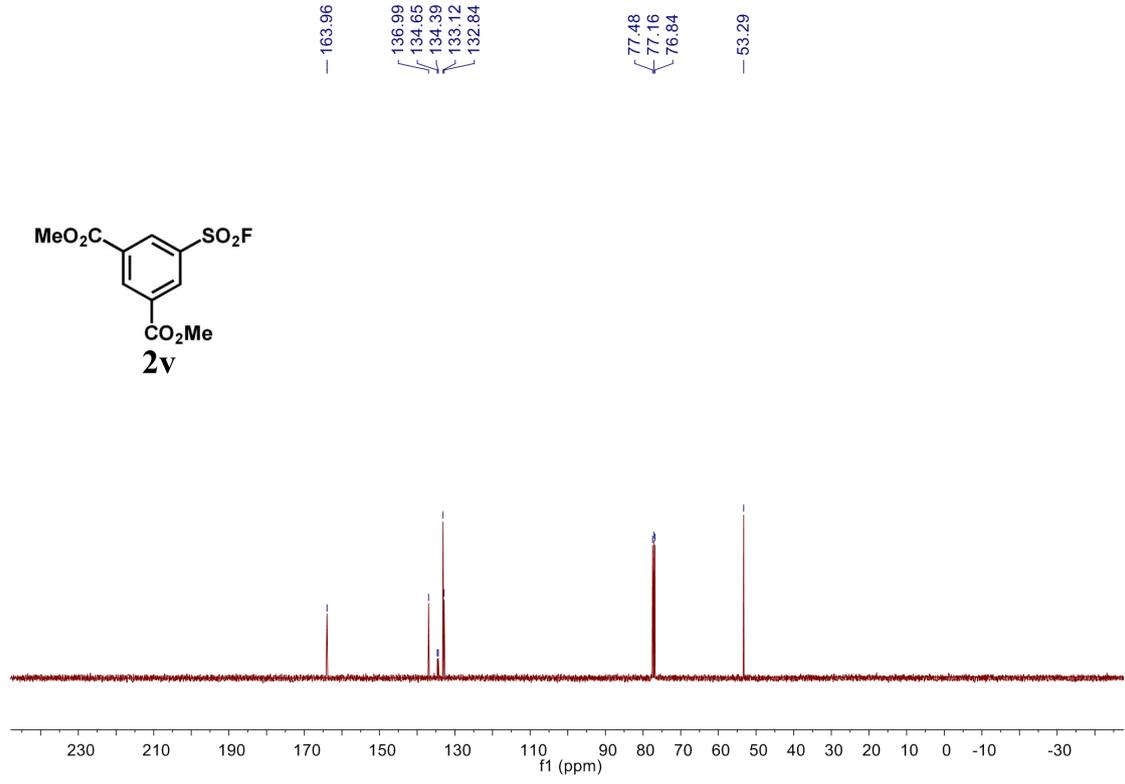


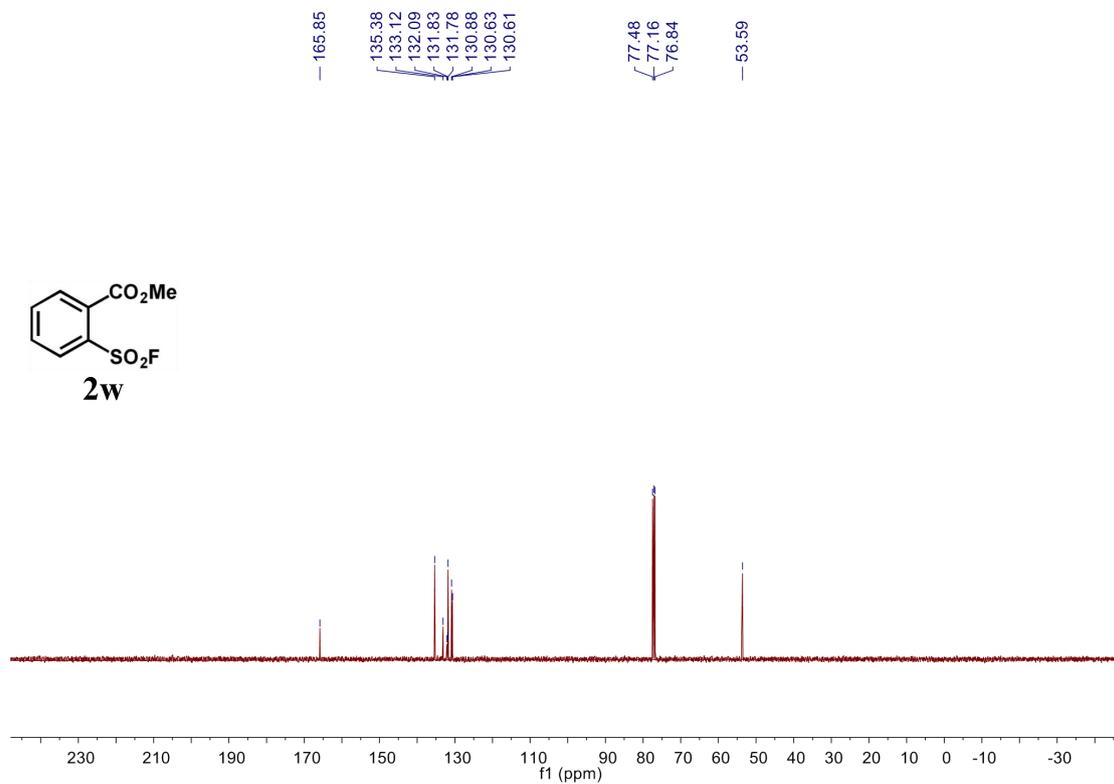
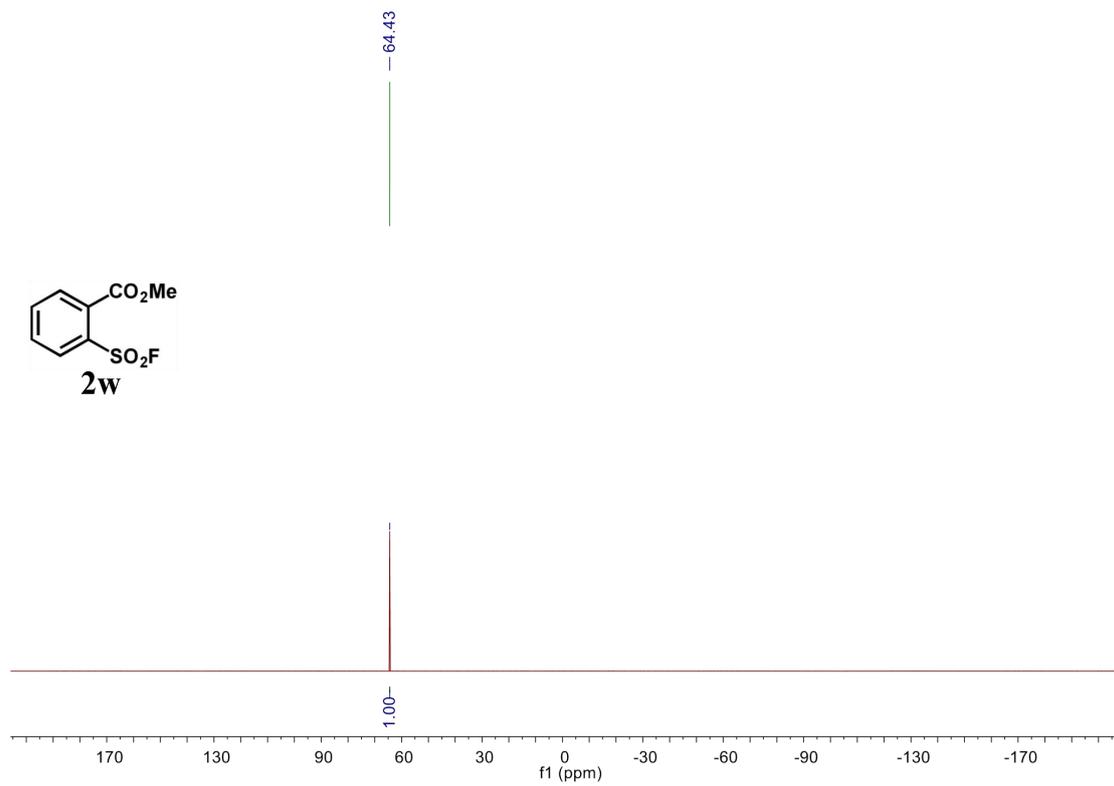


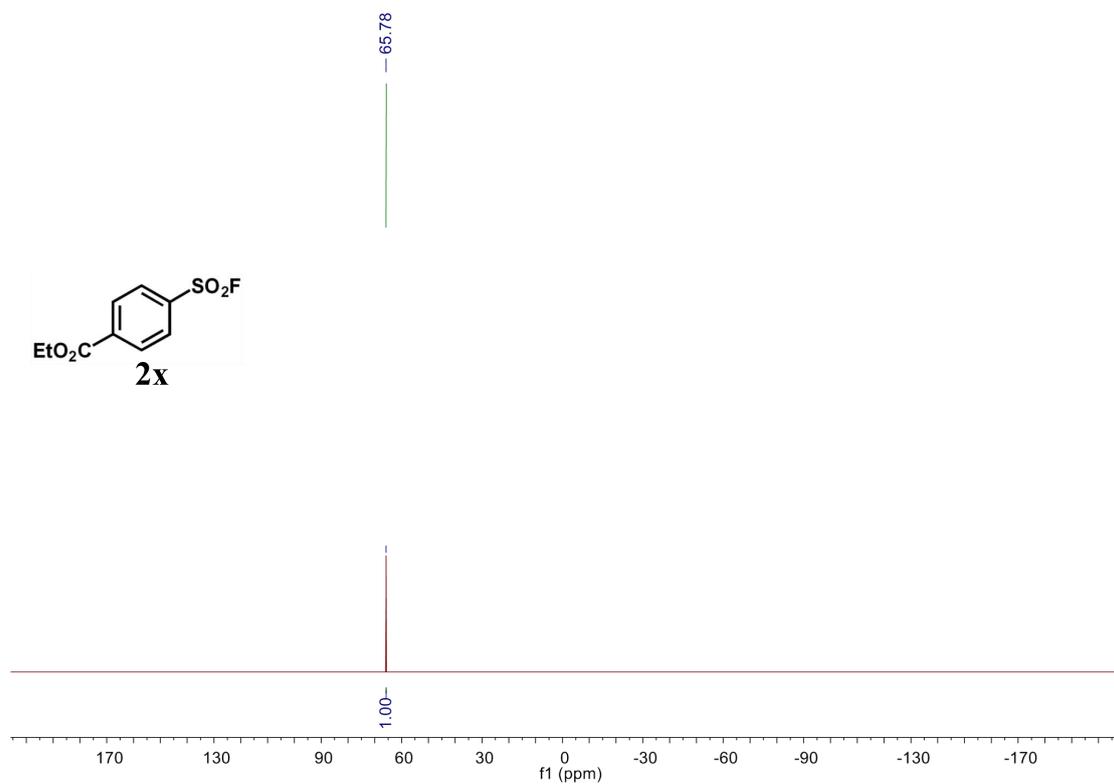
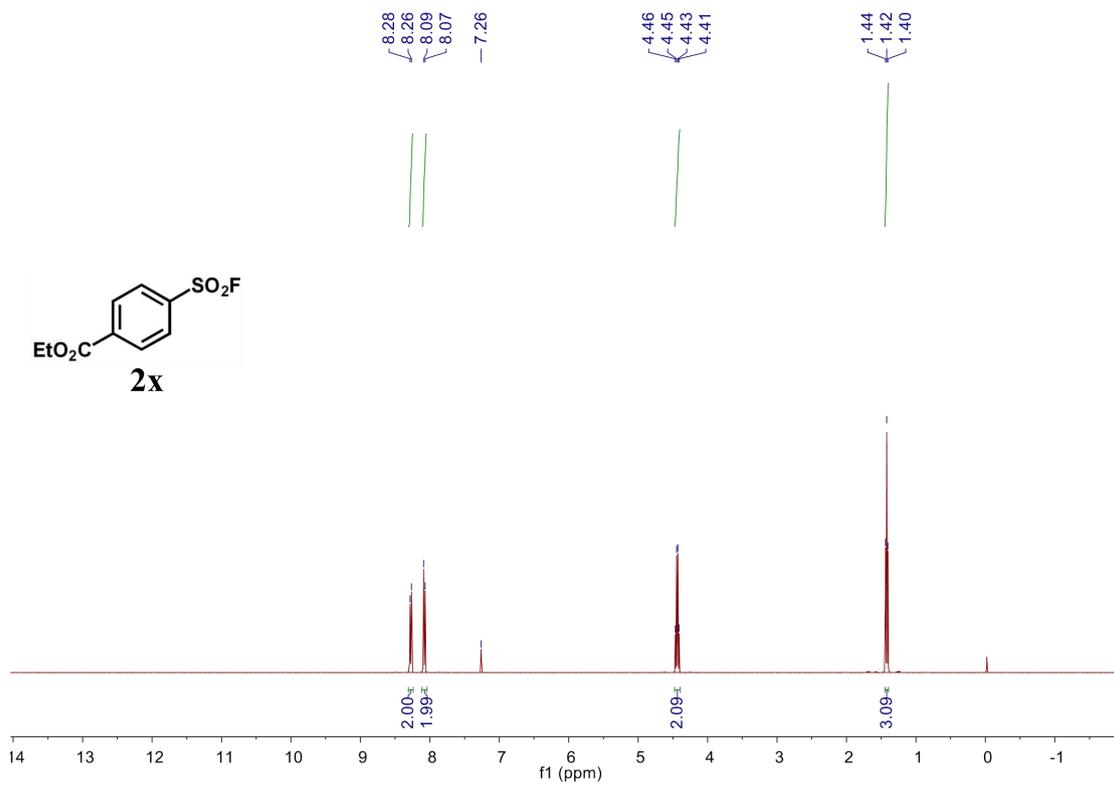


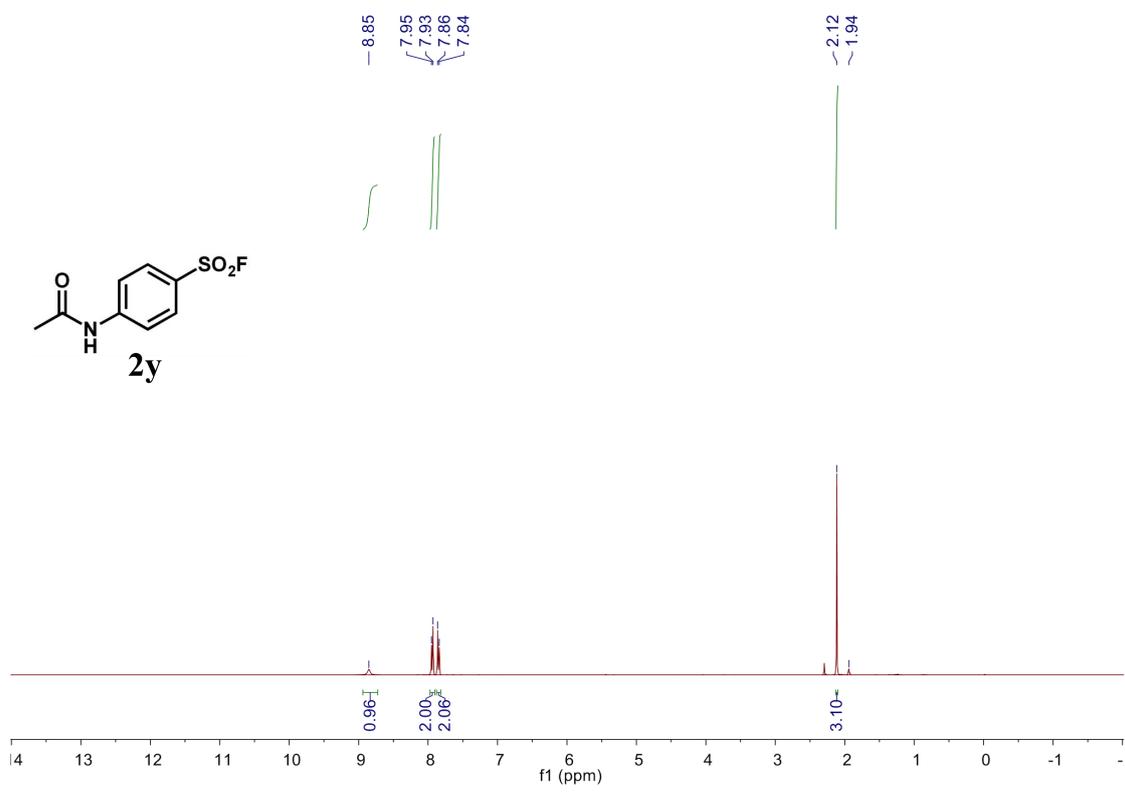
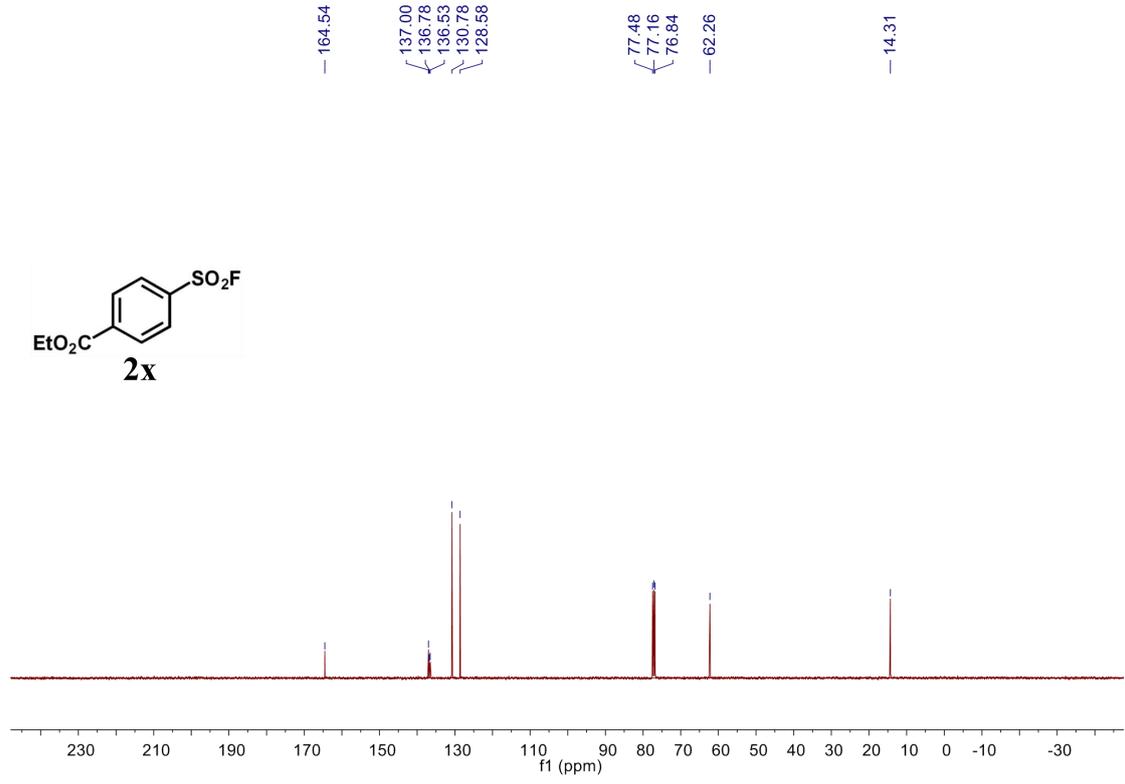


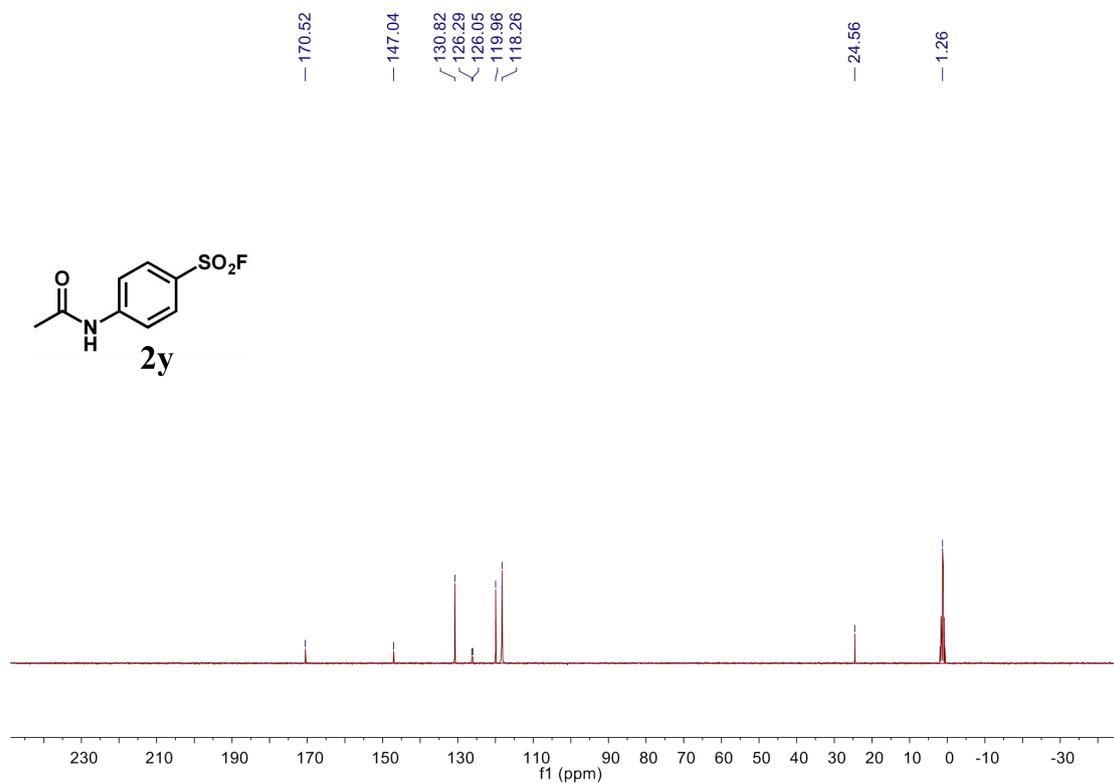
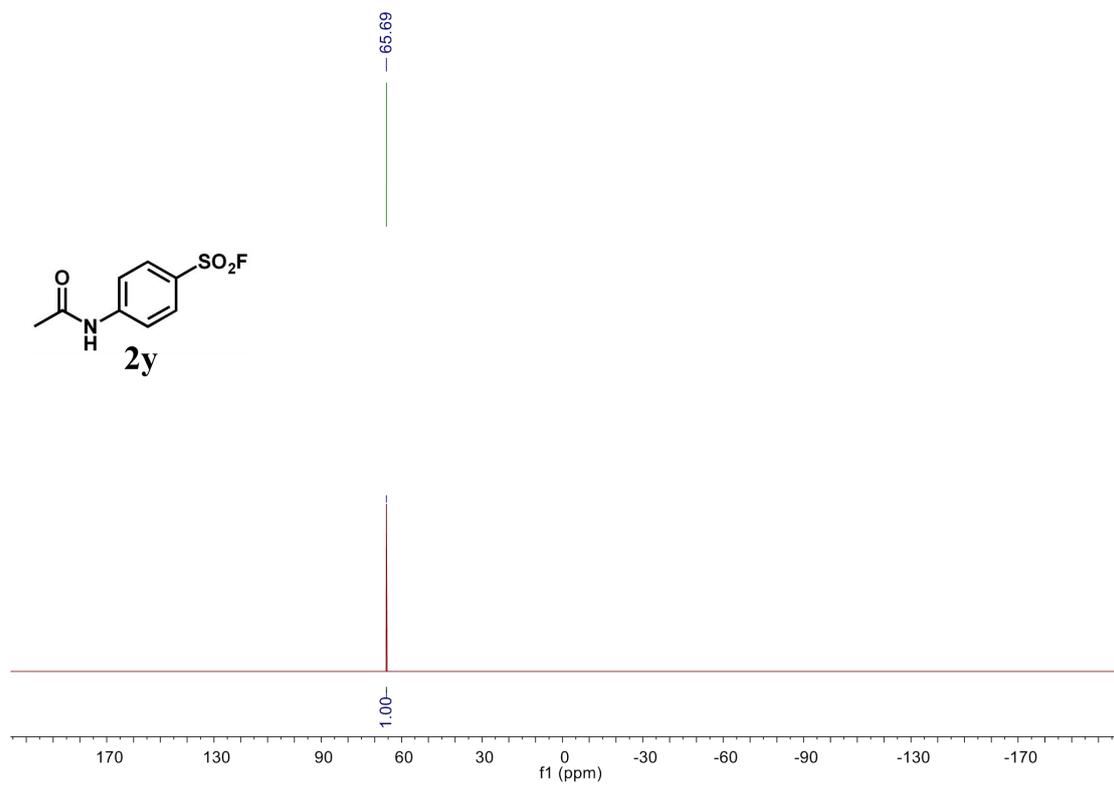


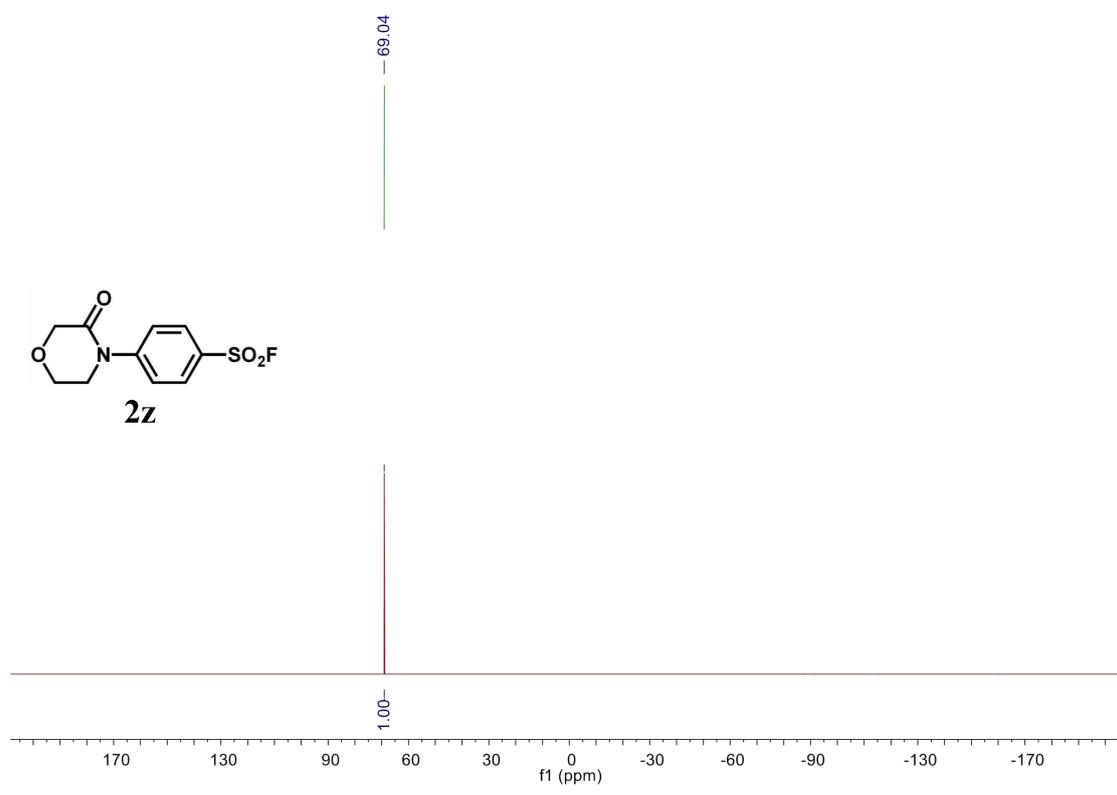
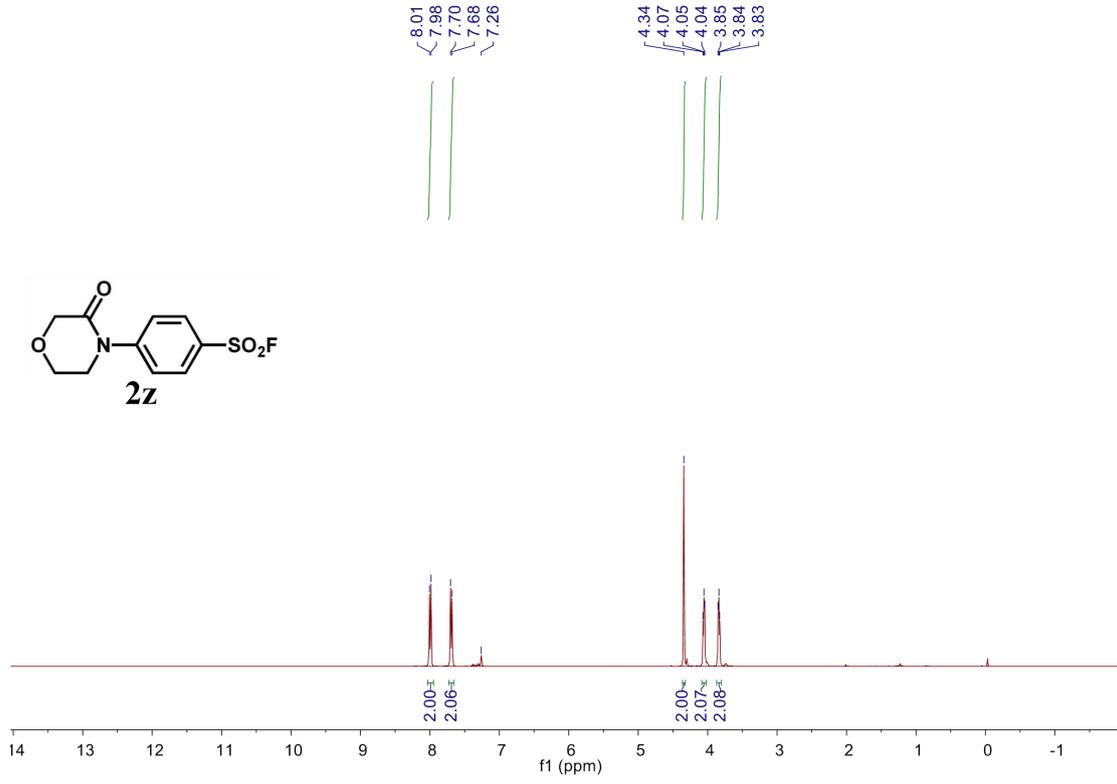


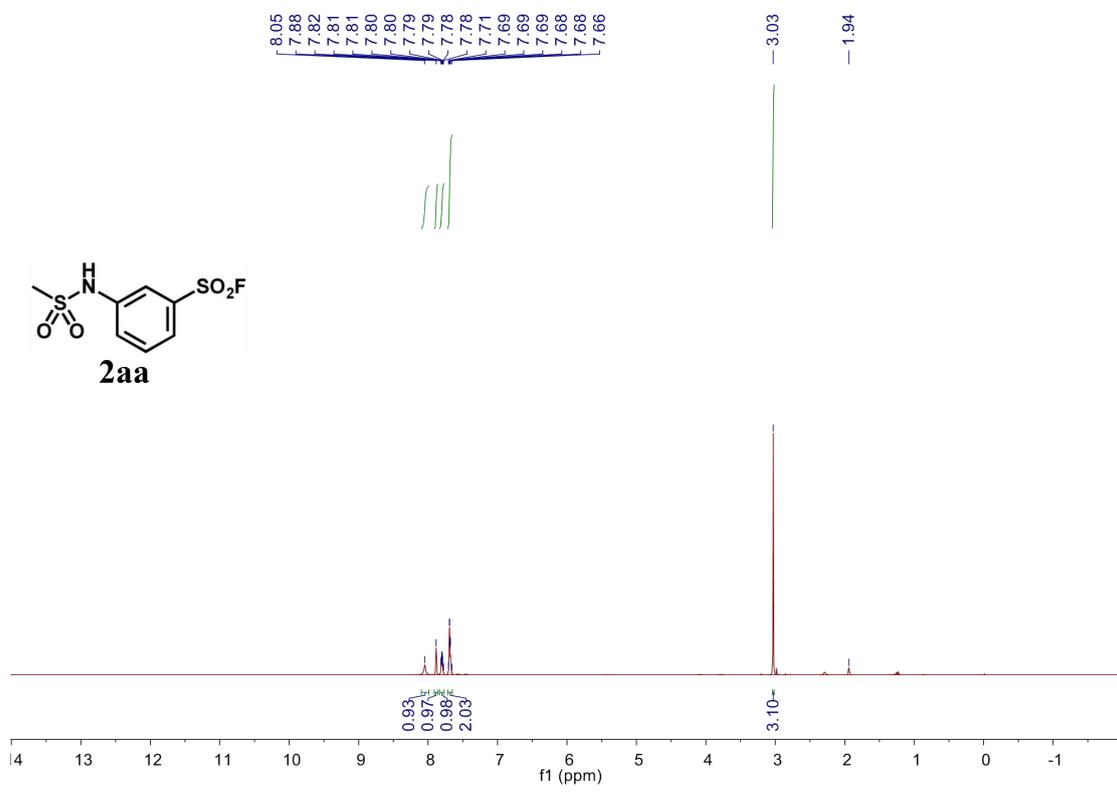
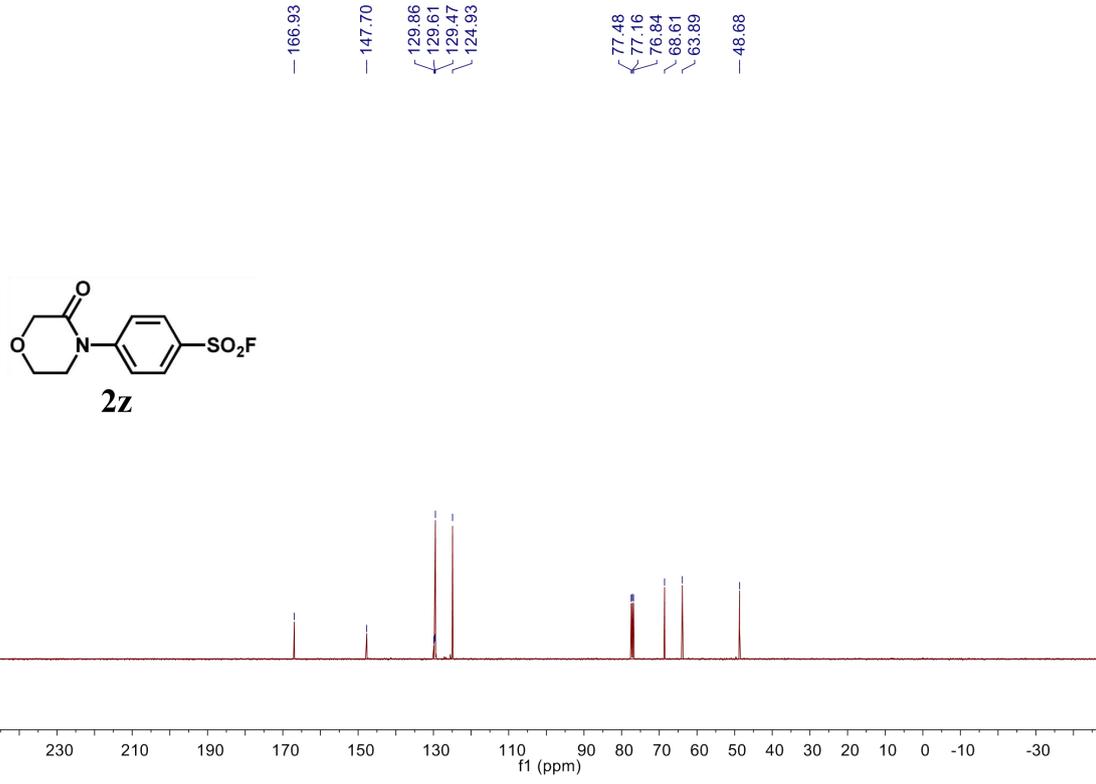


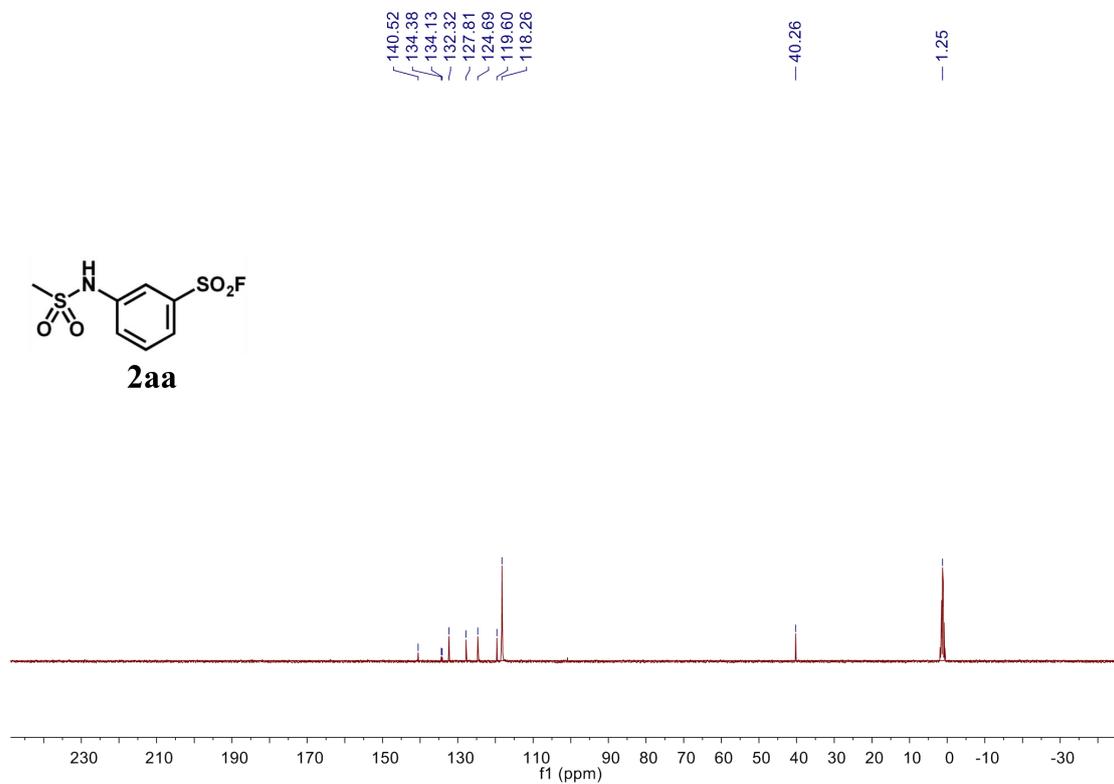
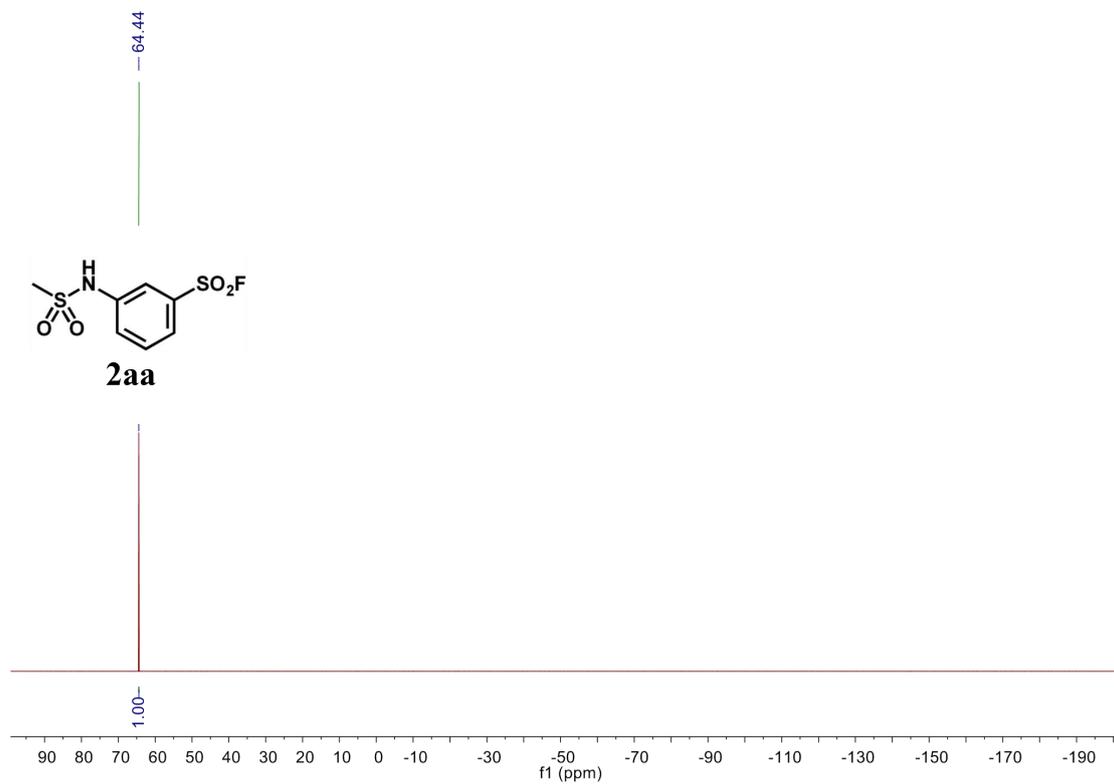


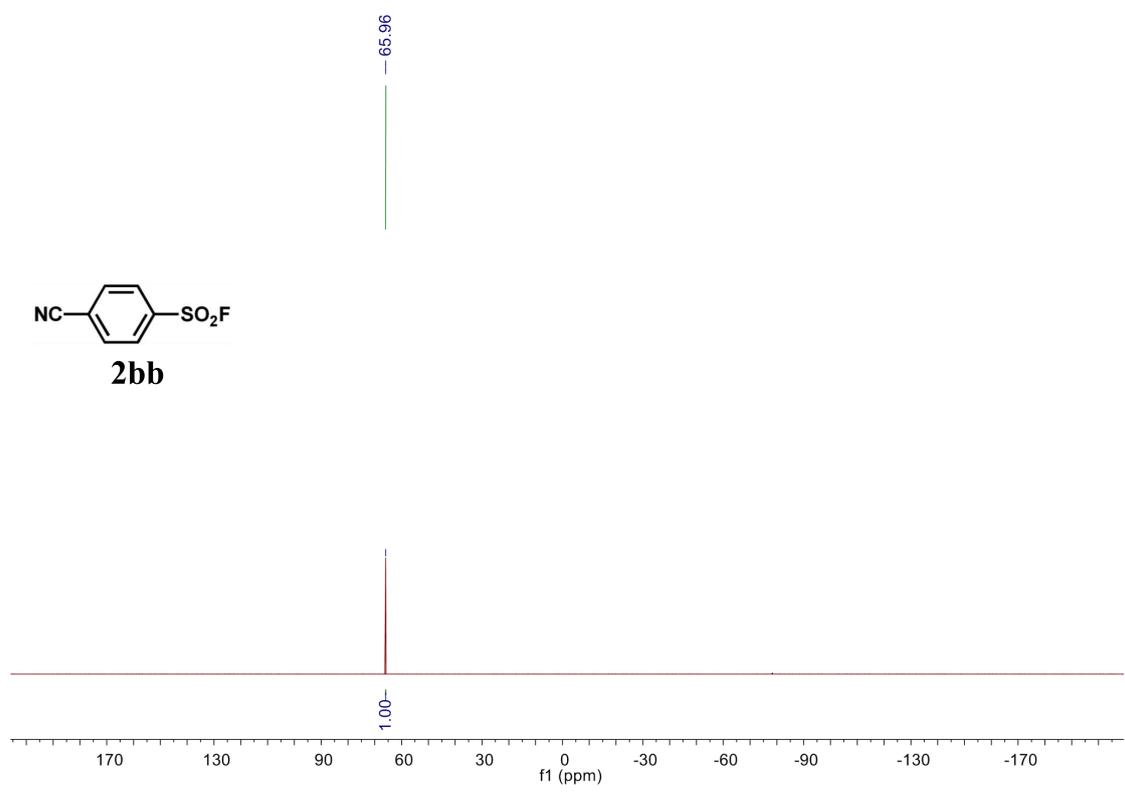
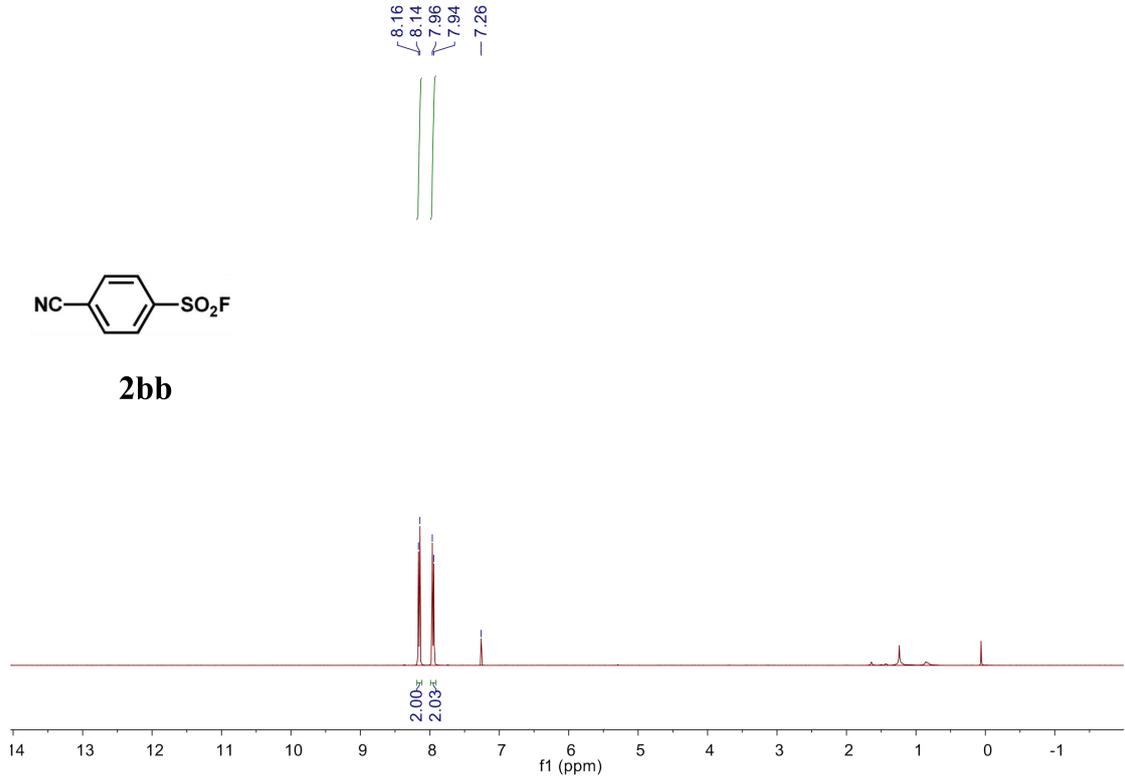


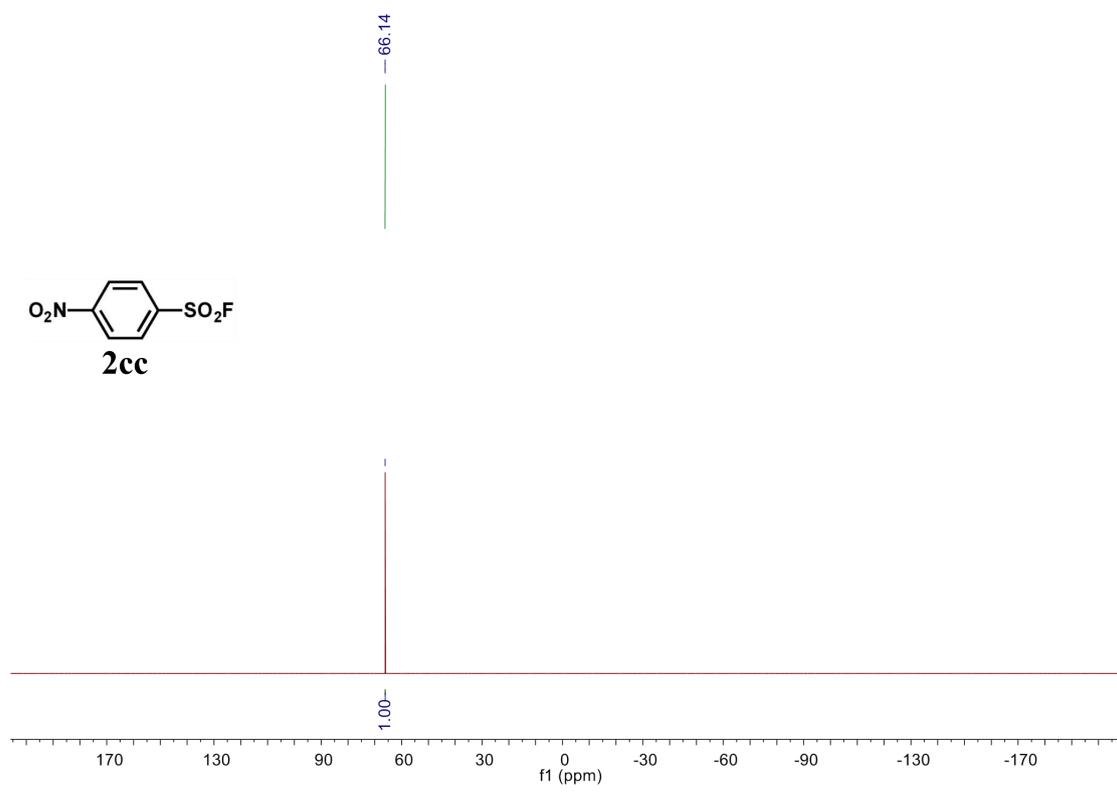
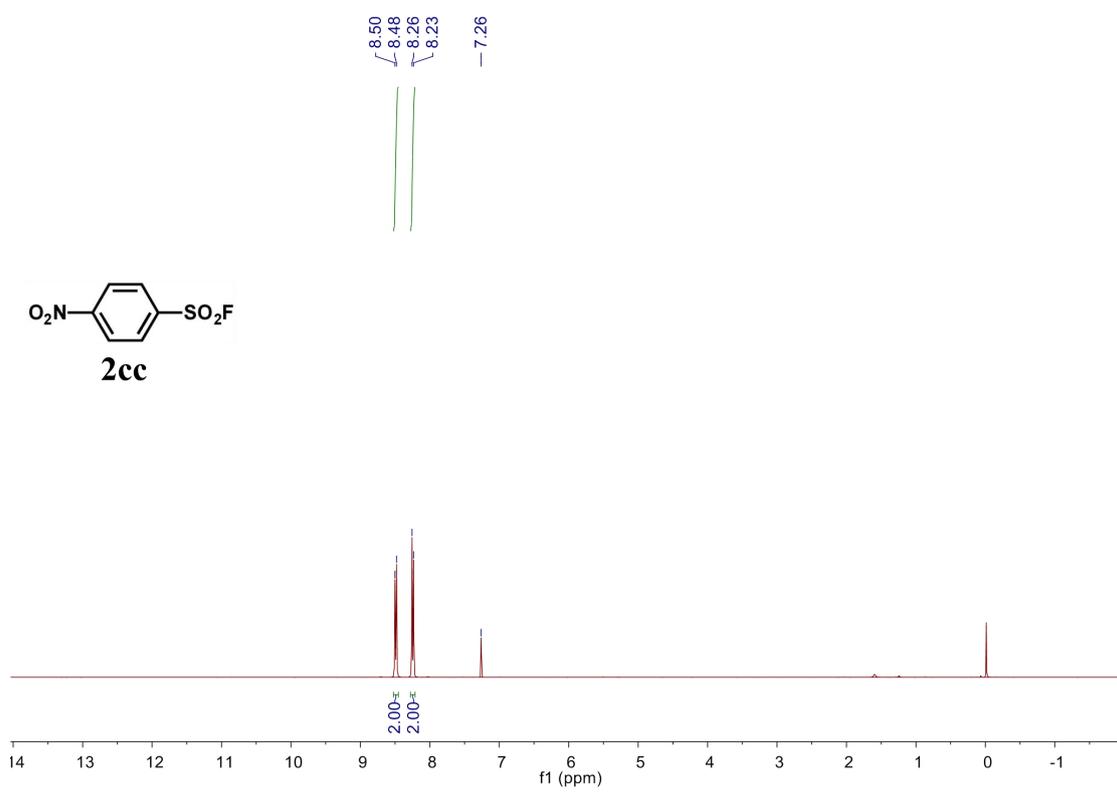


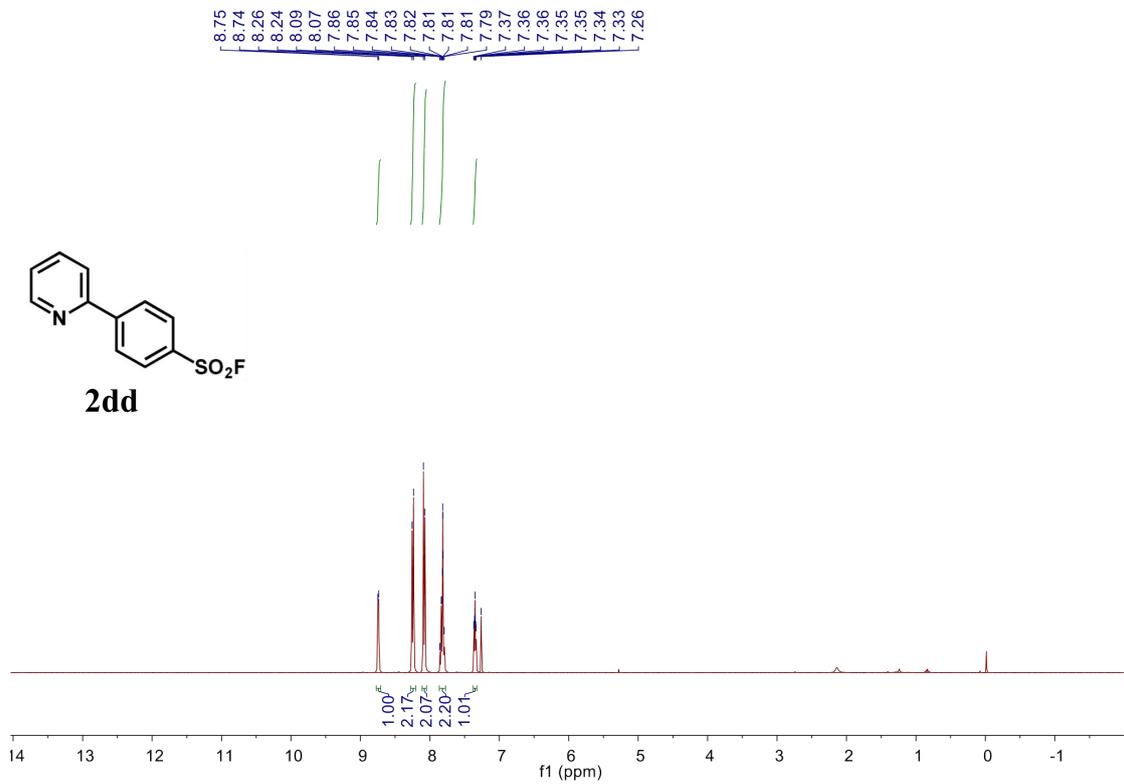
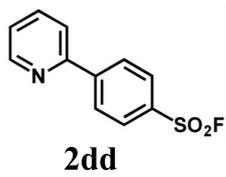
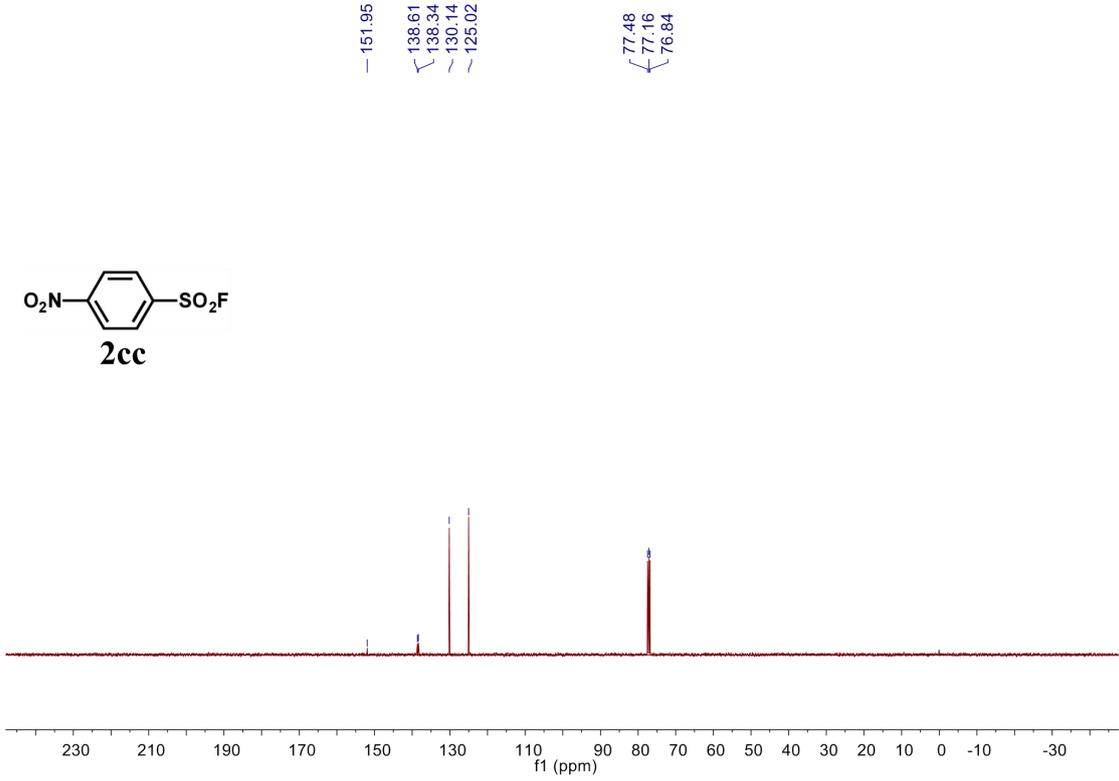
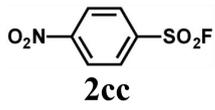


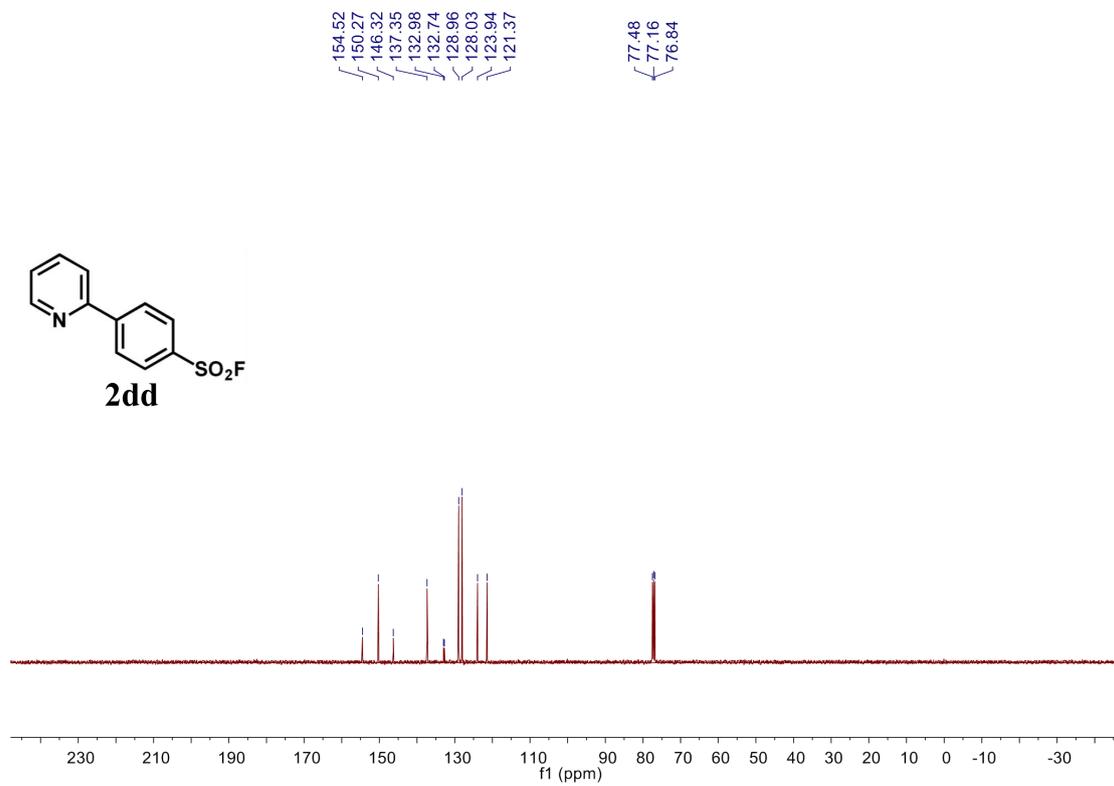
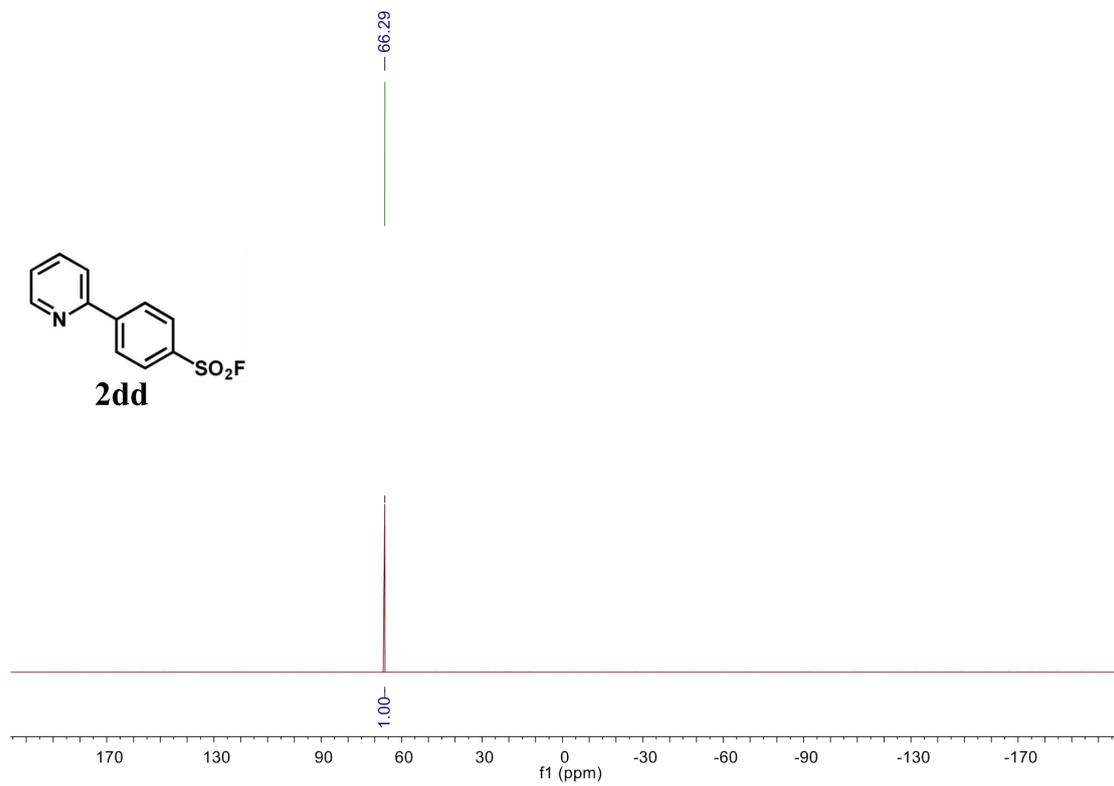


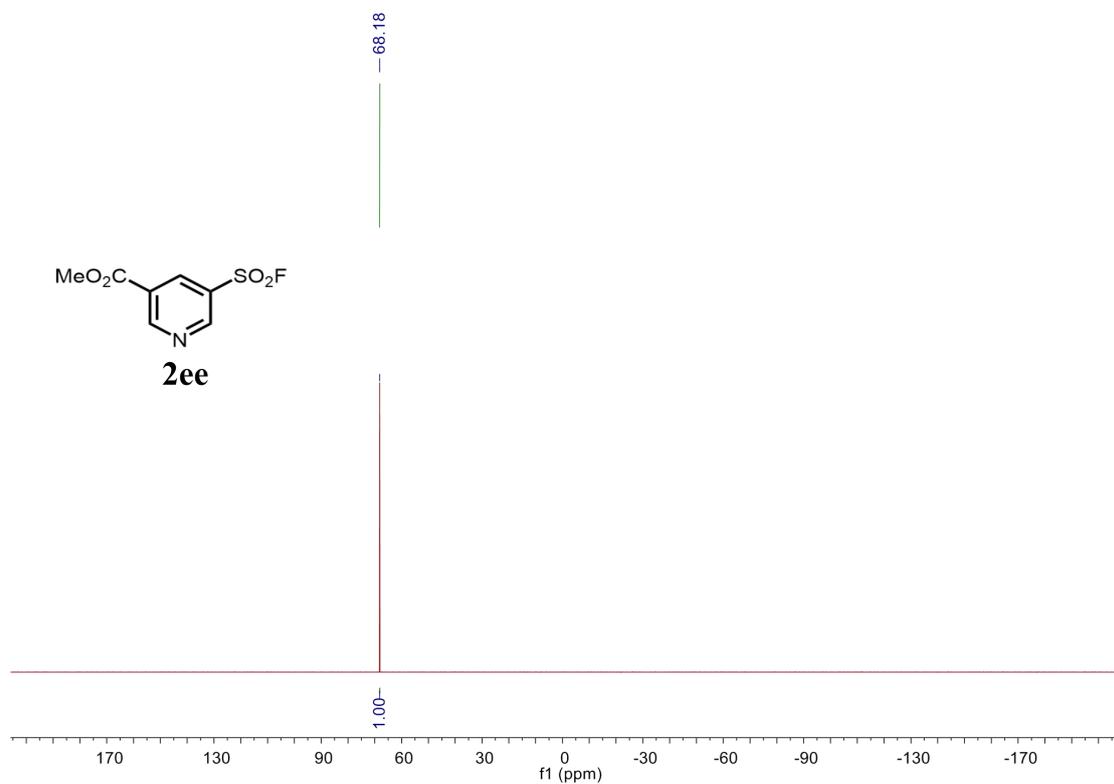
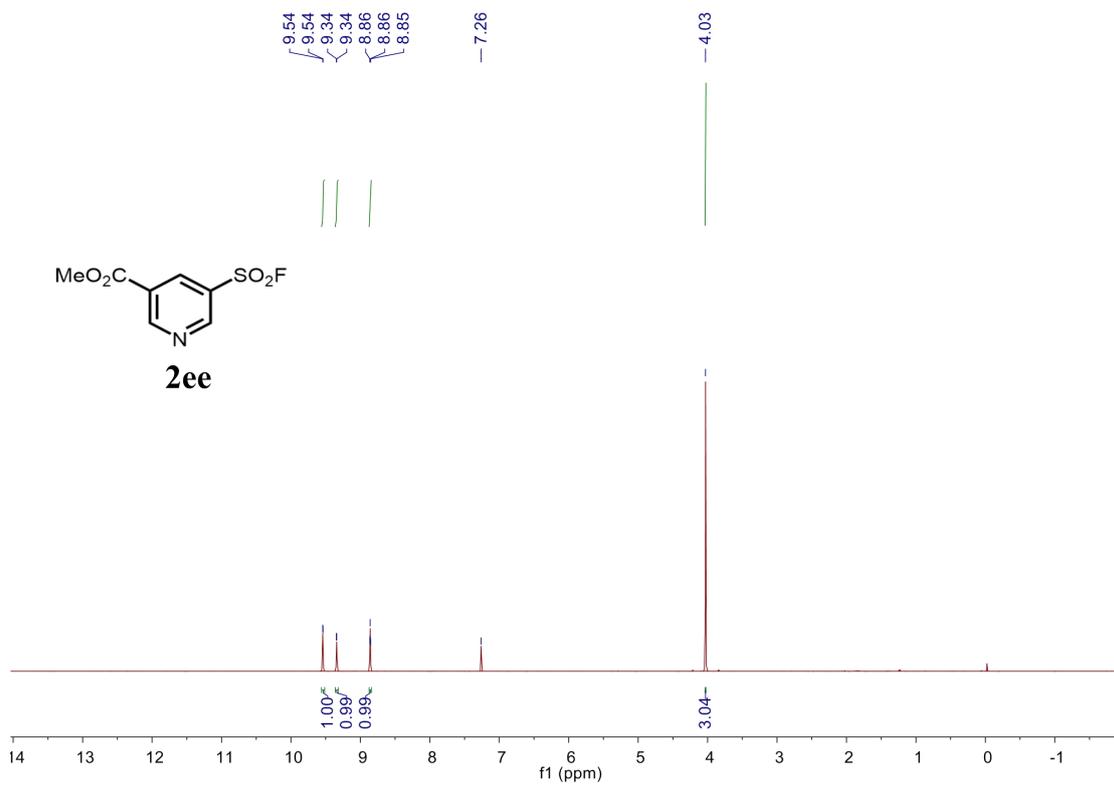


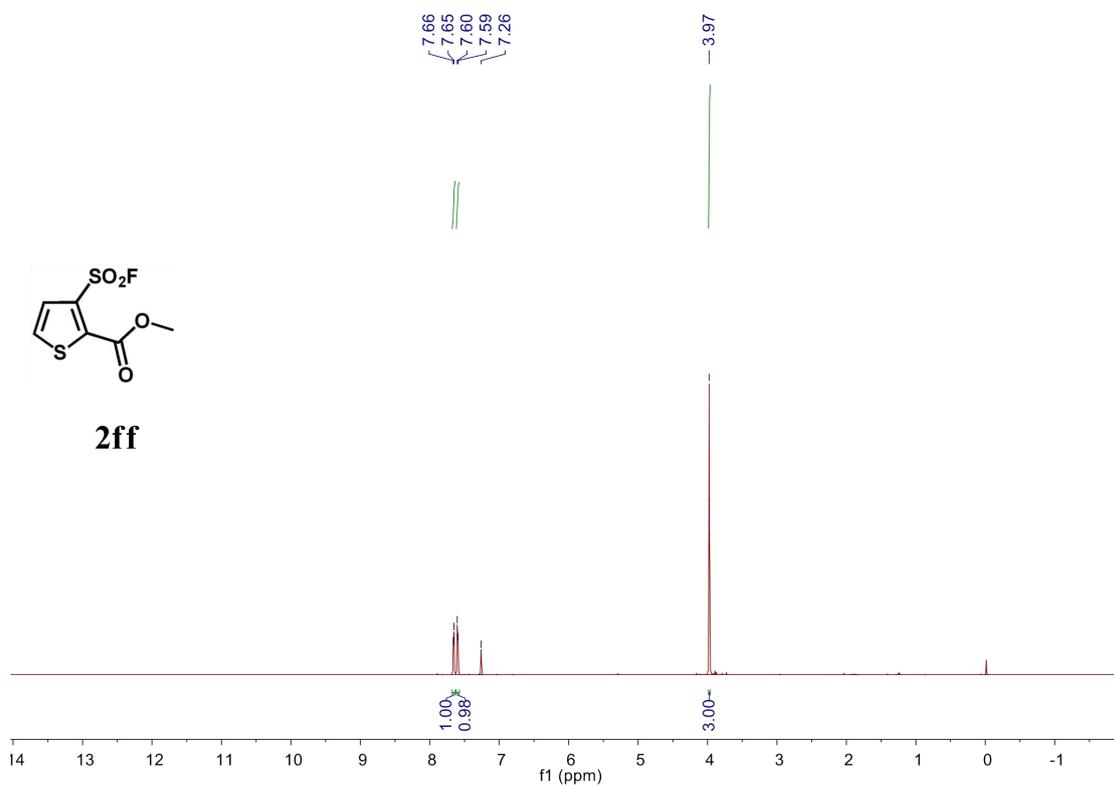
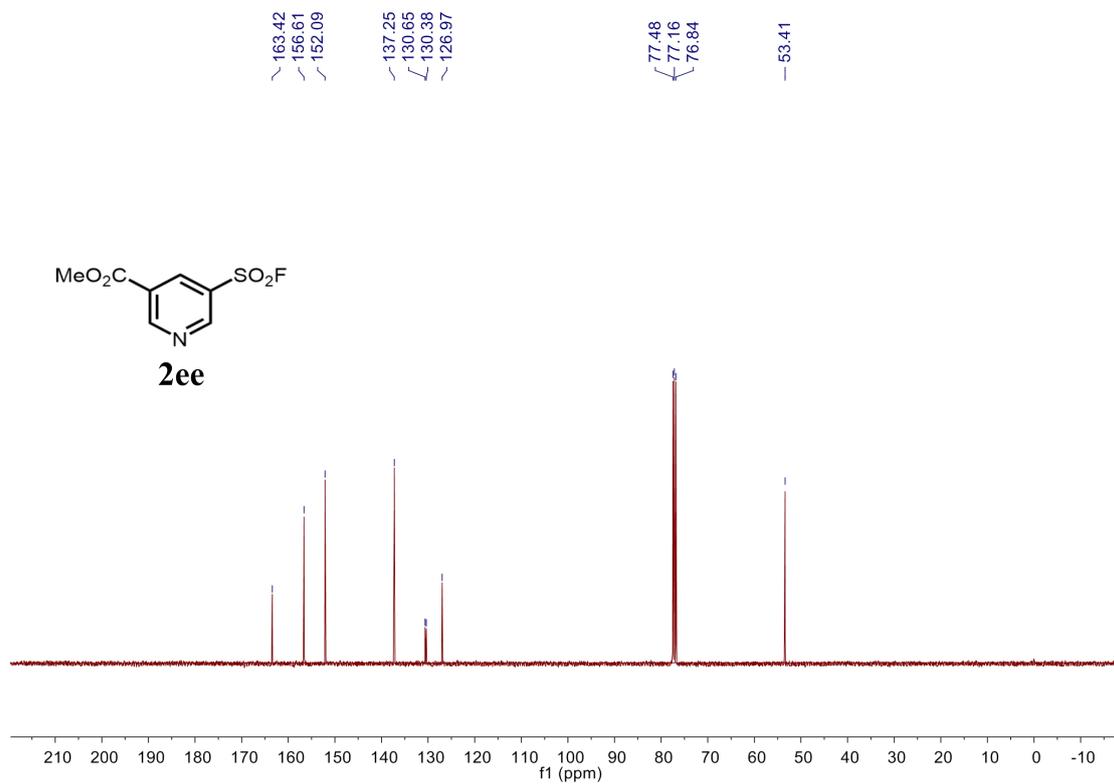


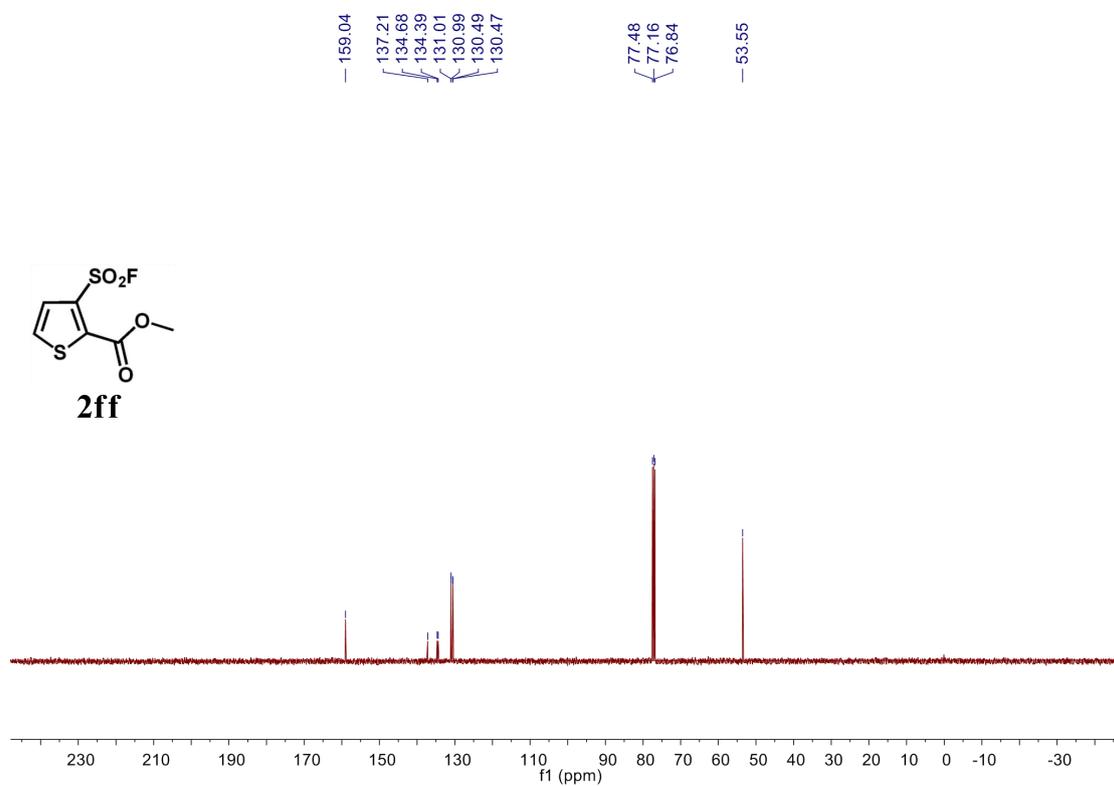
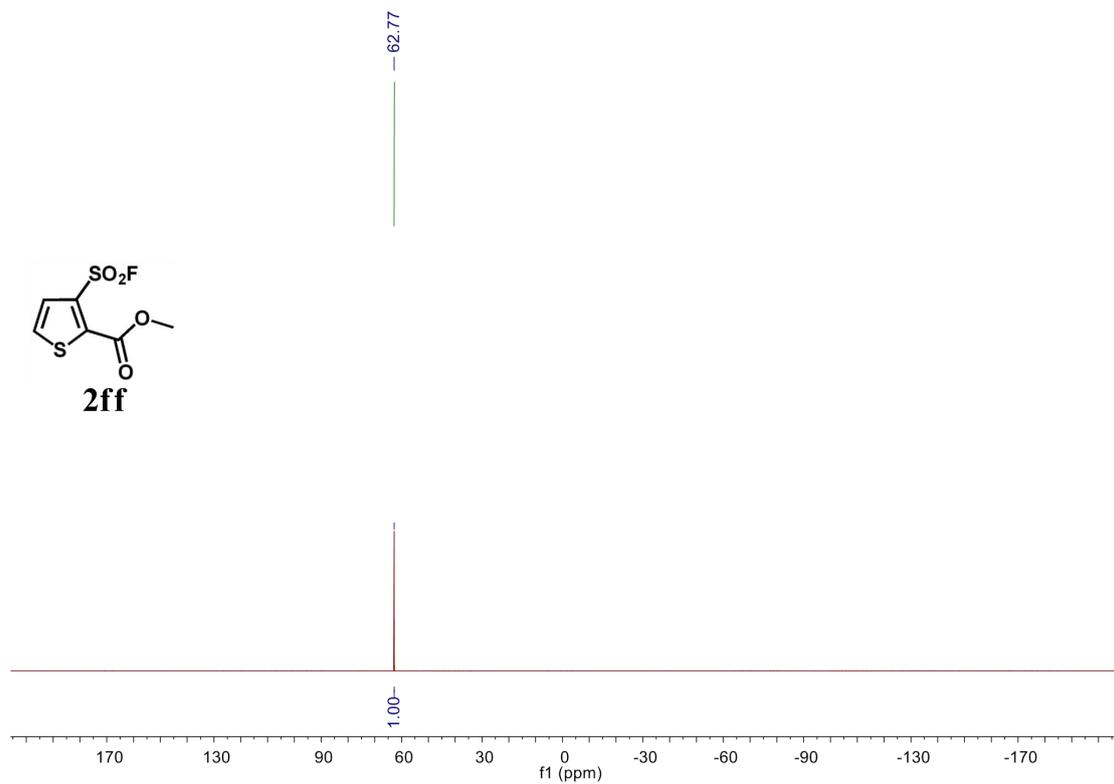


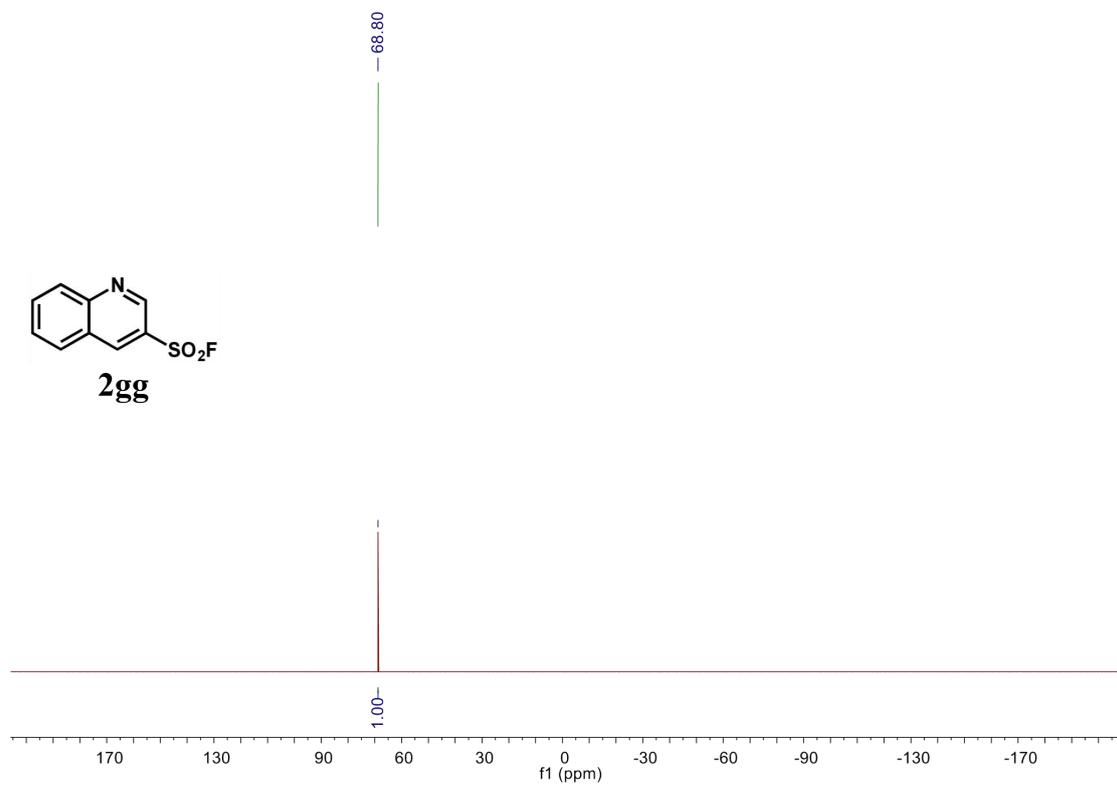
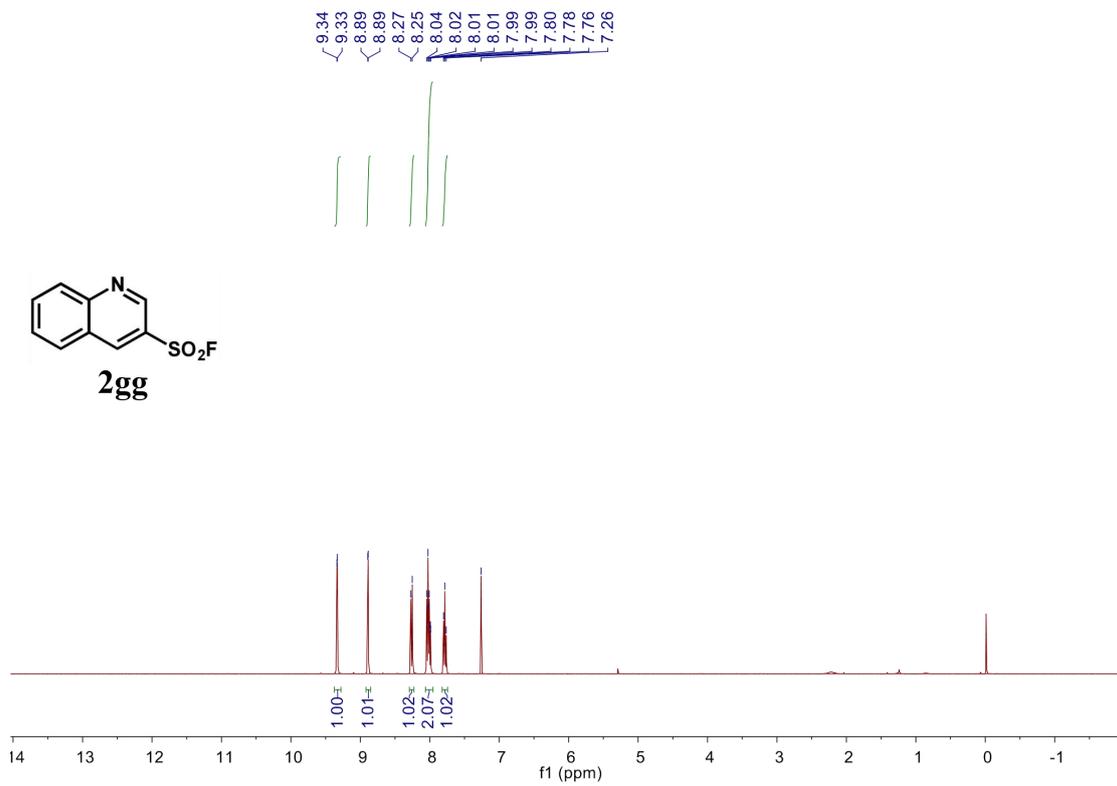


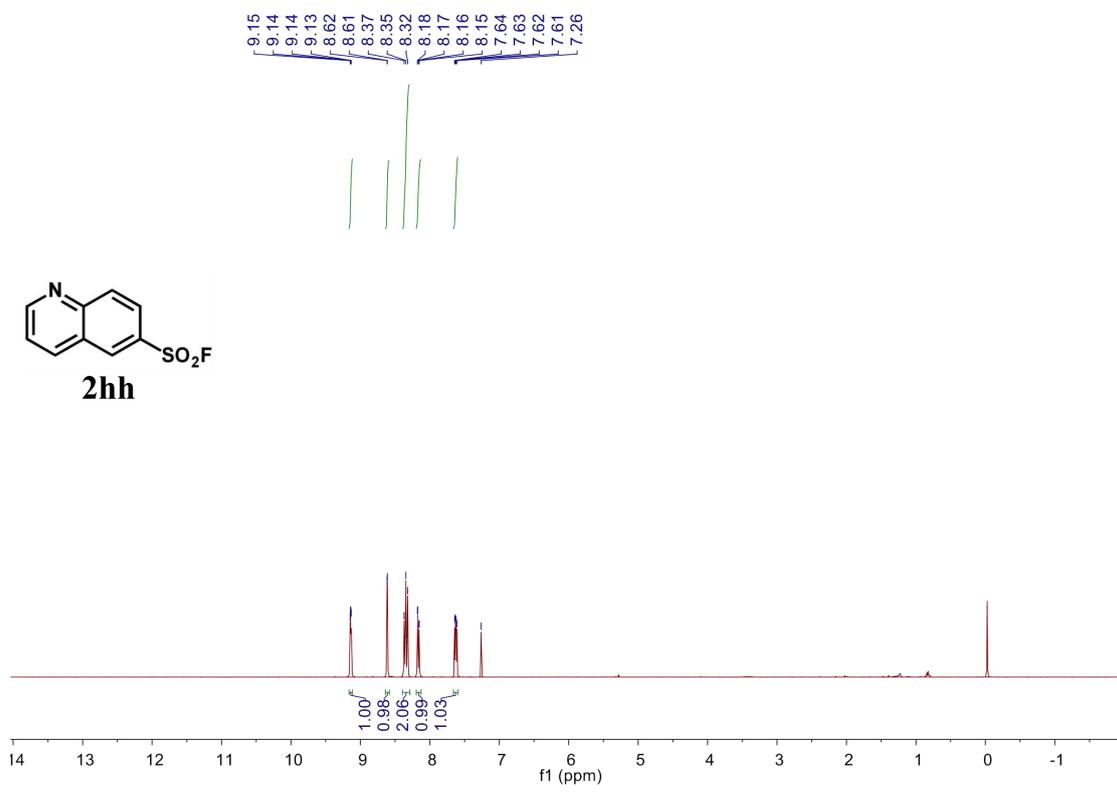
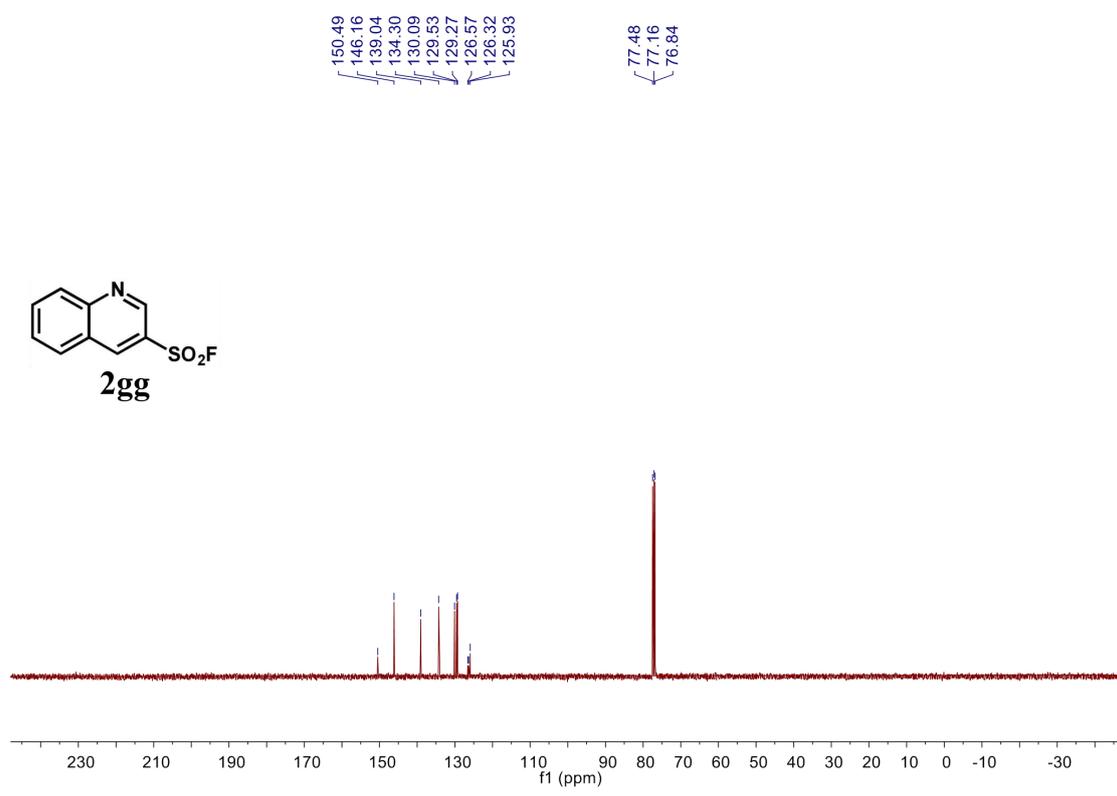


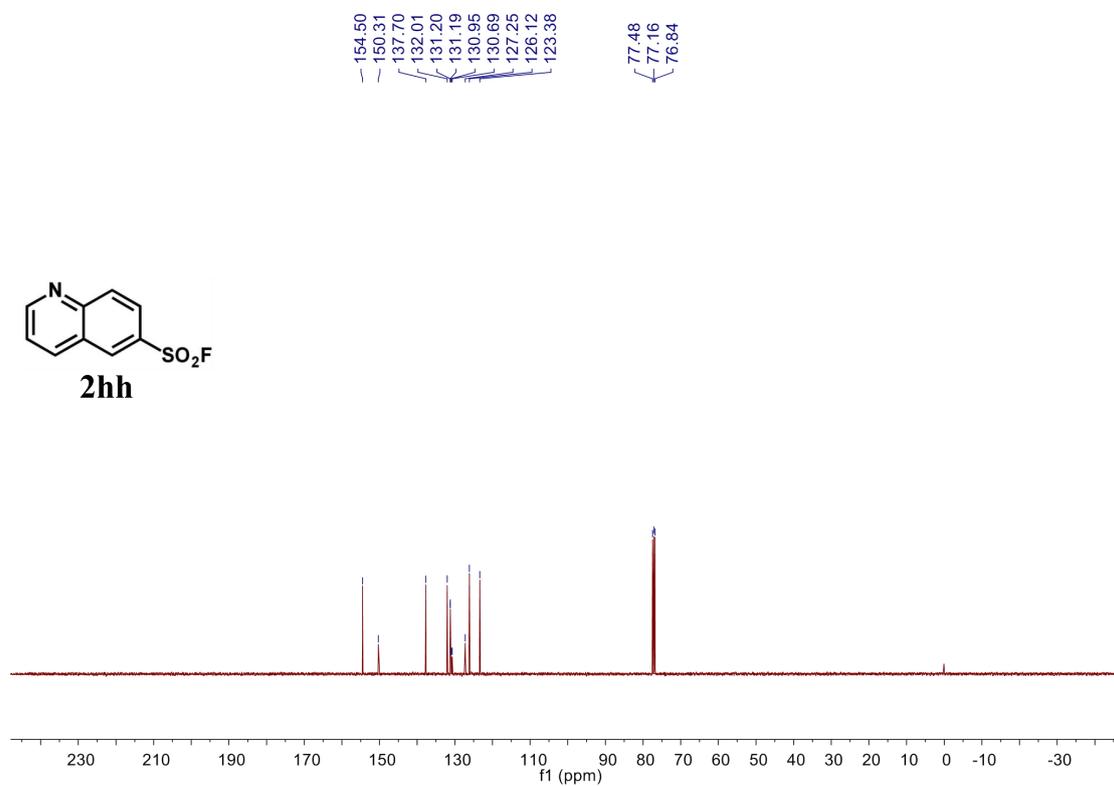
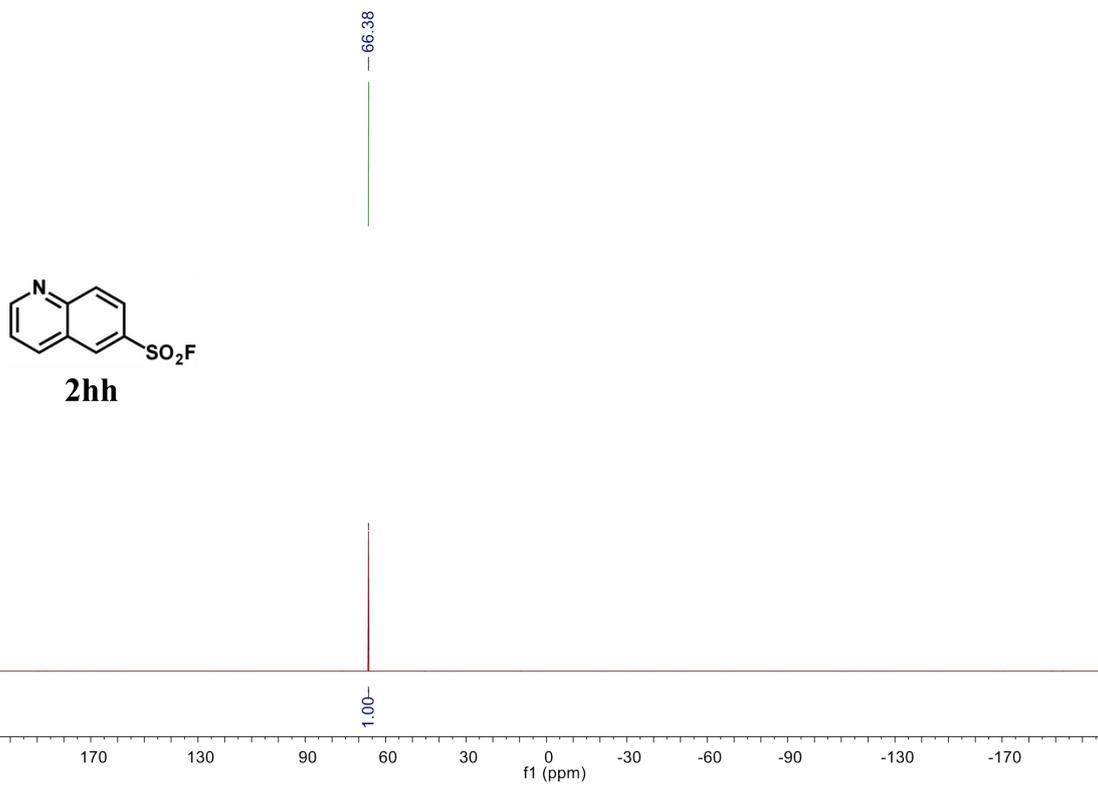


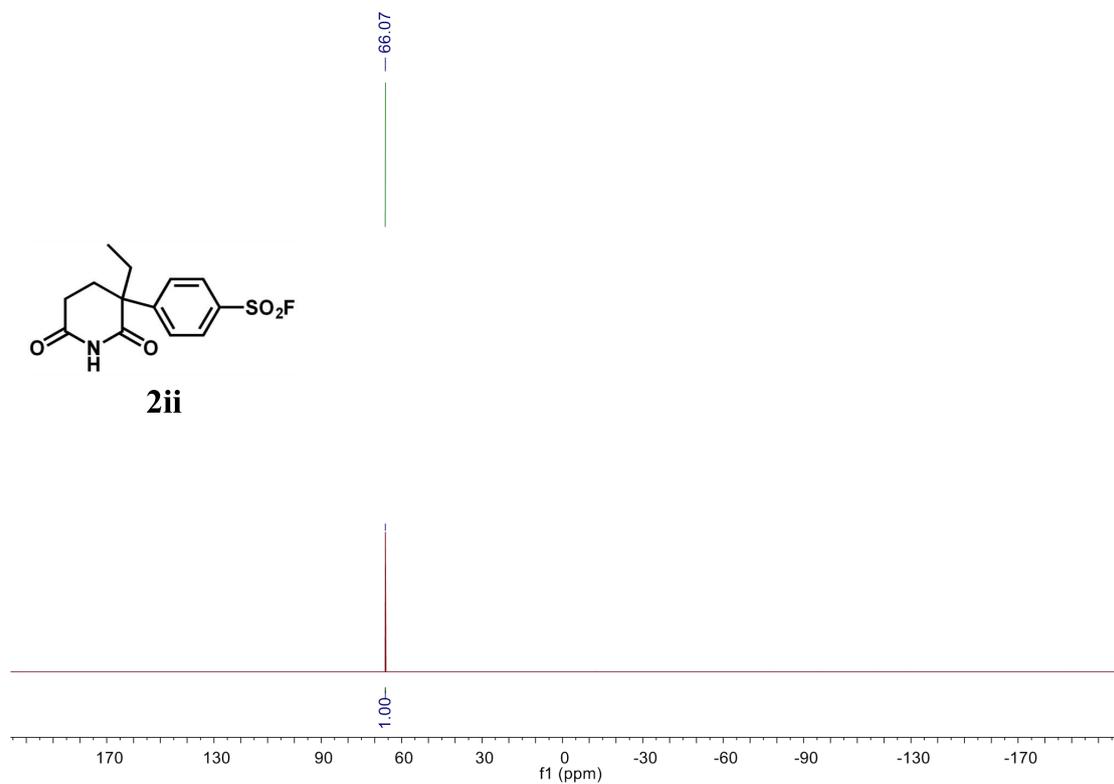
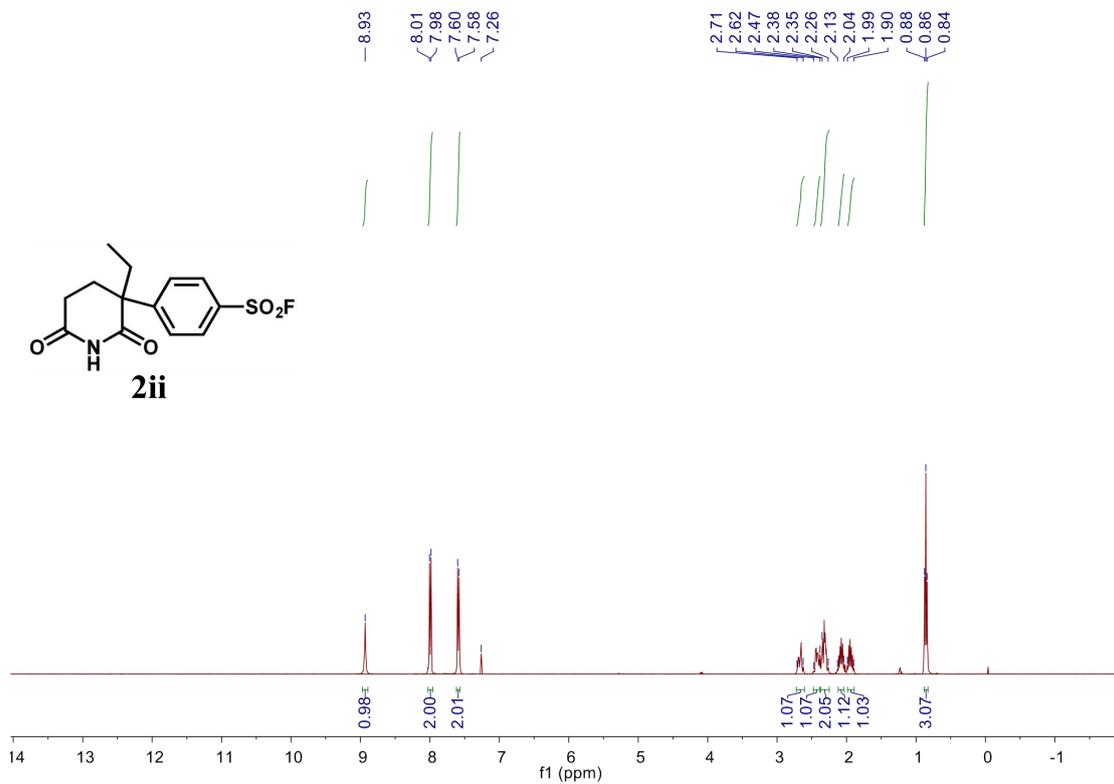


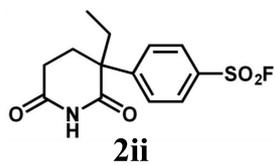




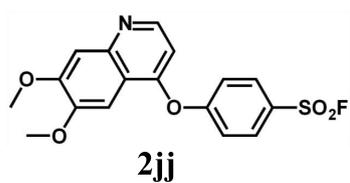
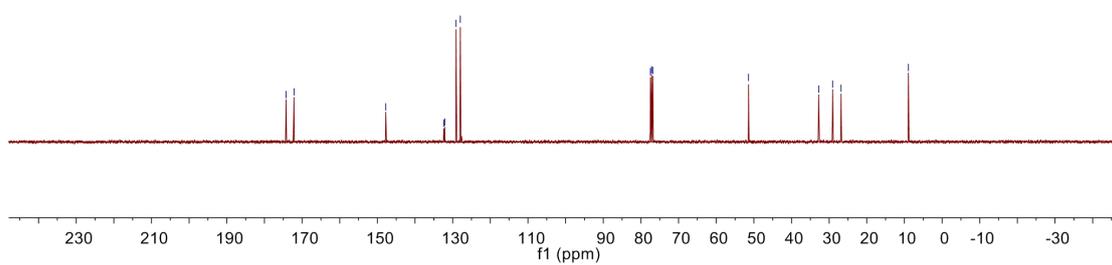




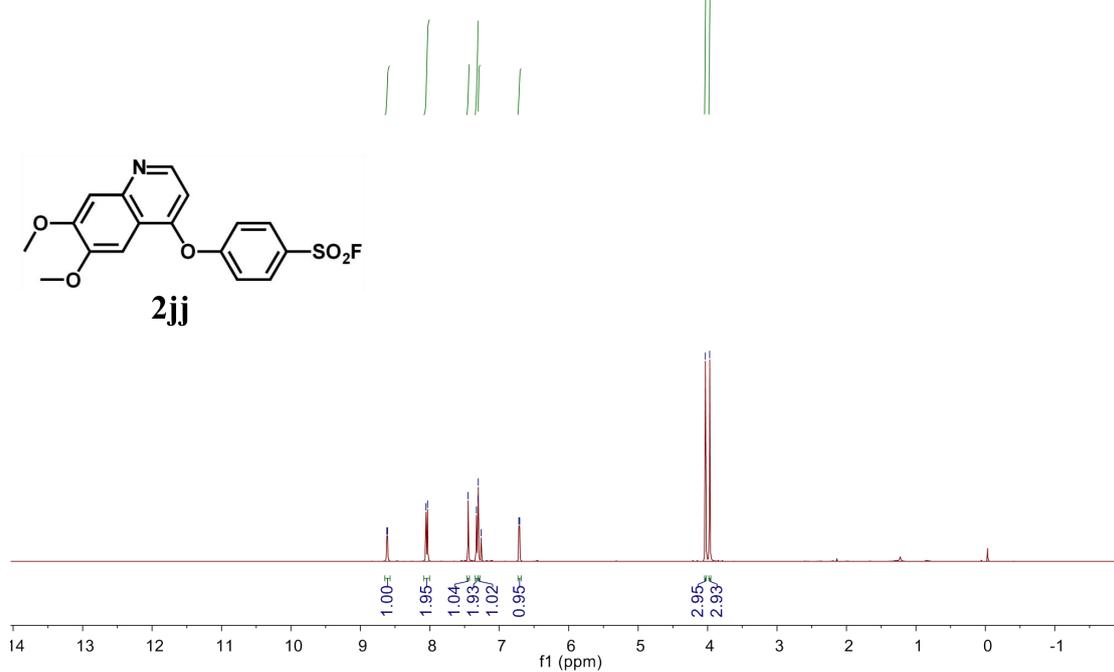


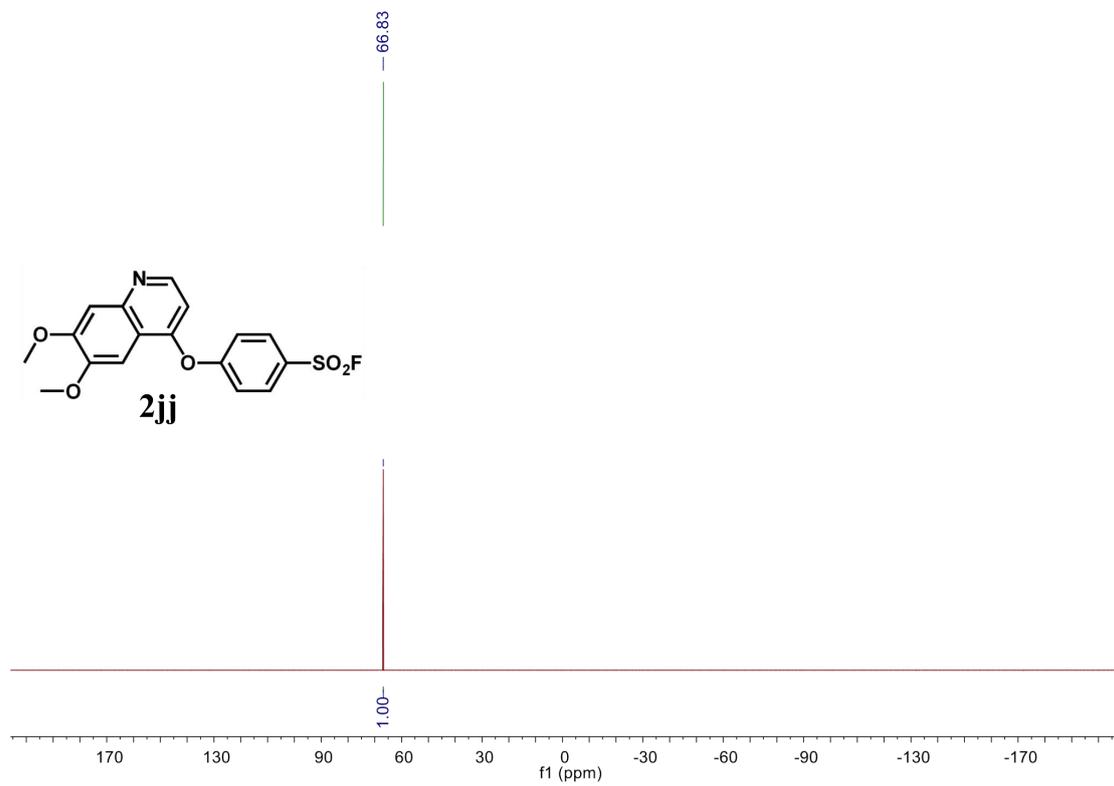


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 29.07
 26.85
 8.95

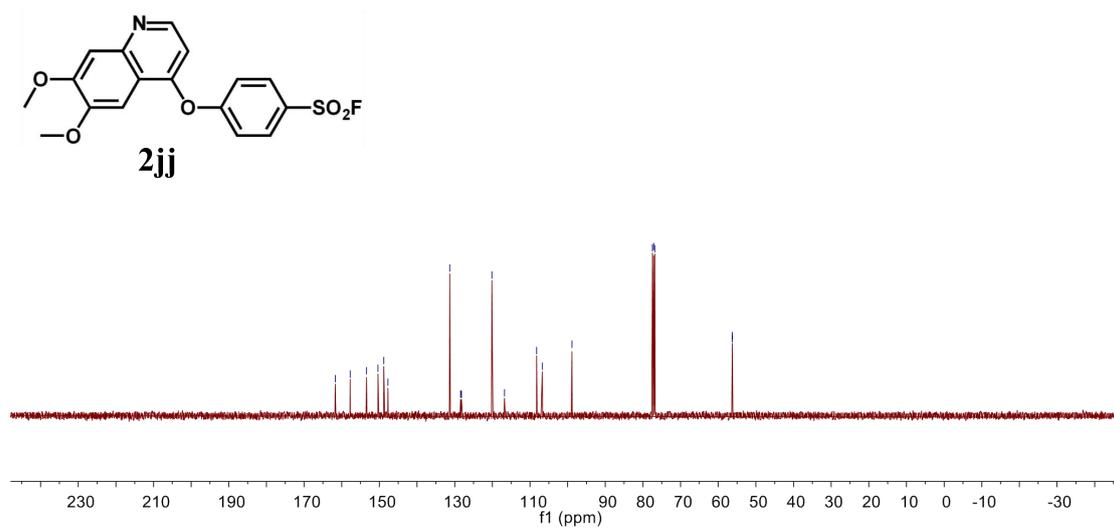


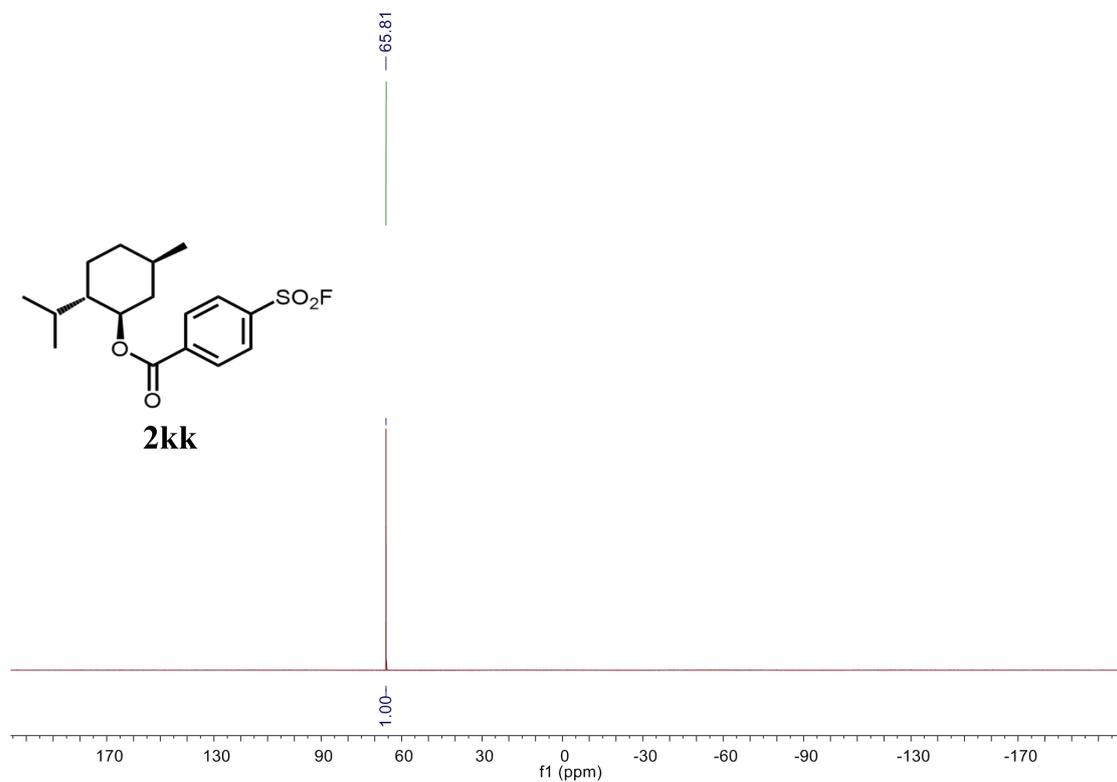
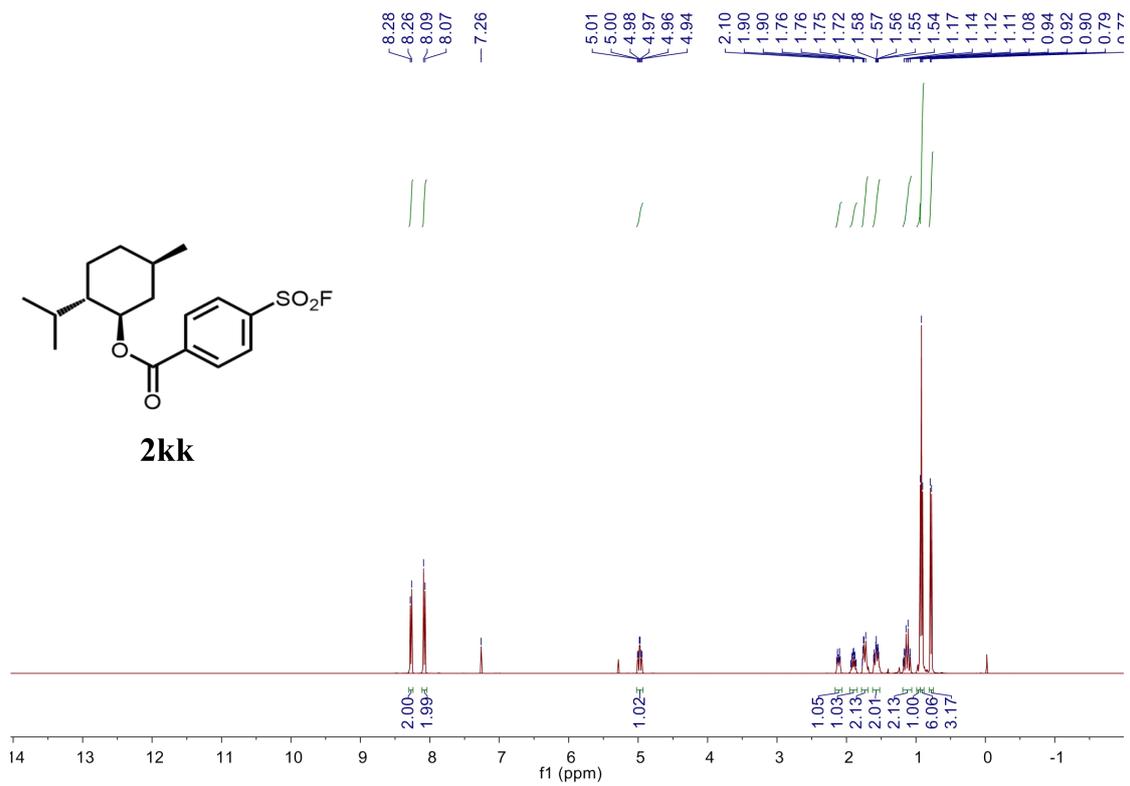
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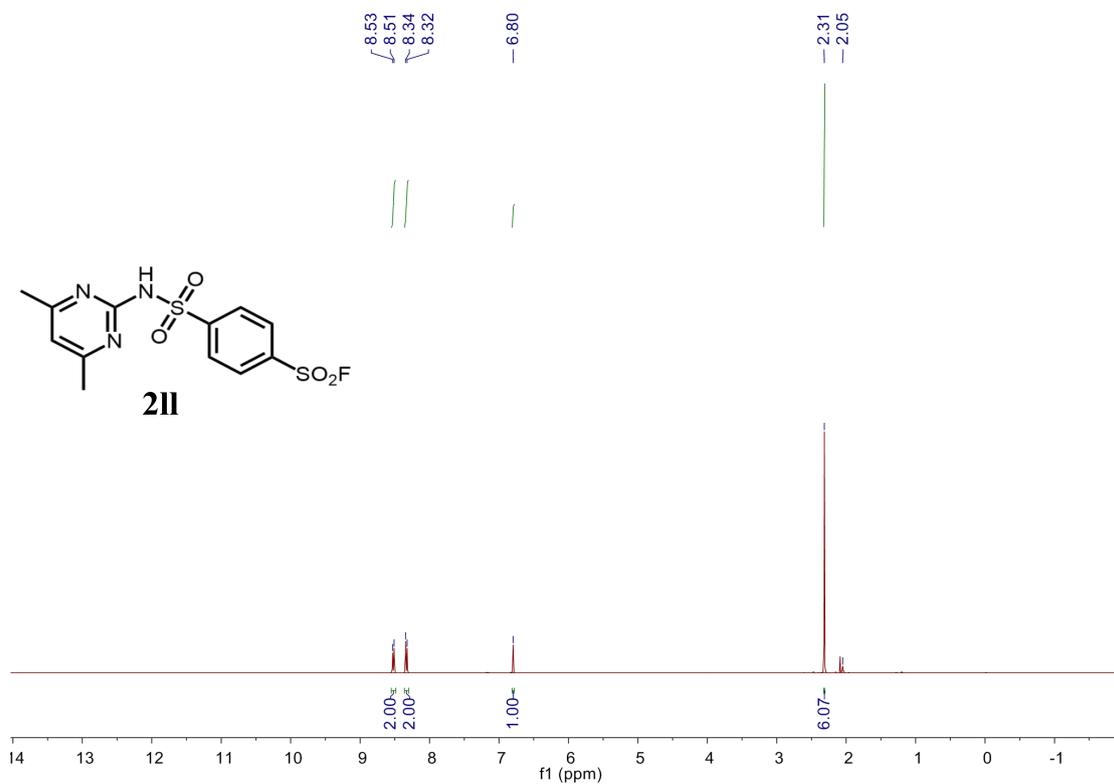
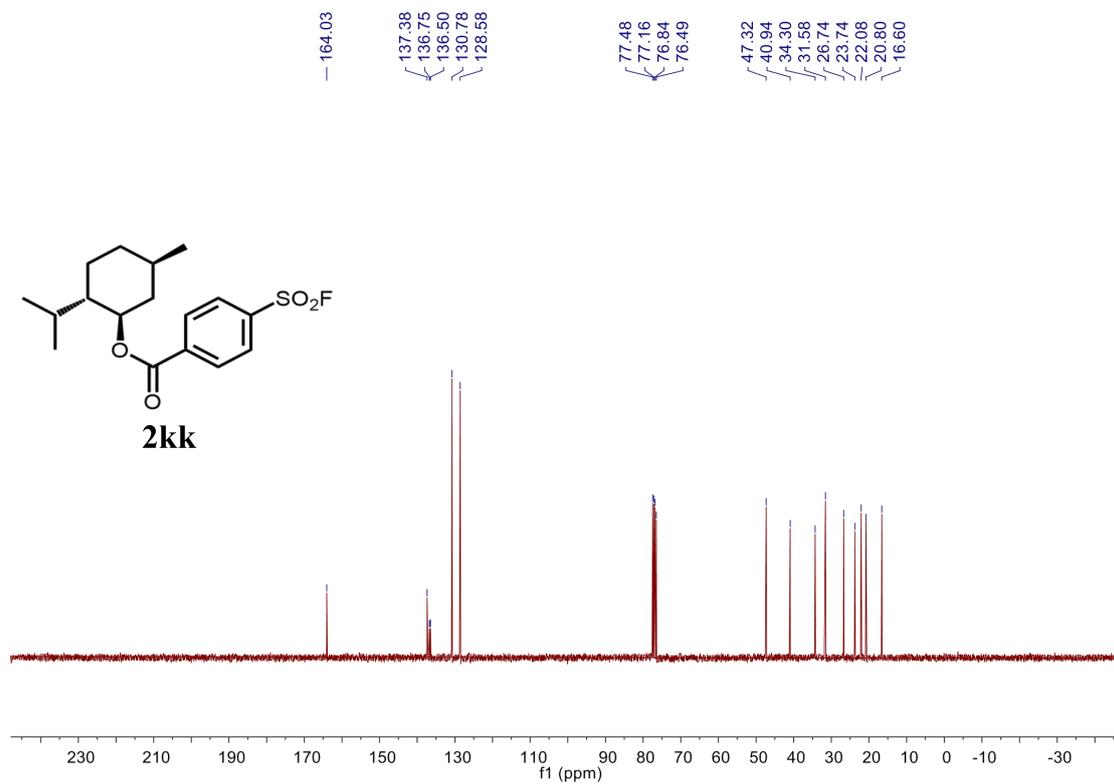


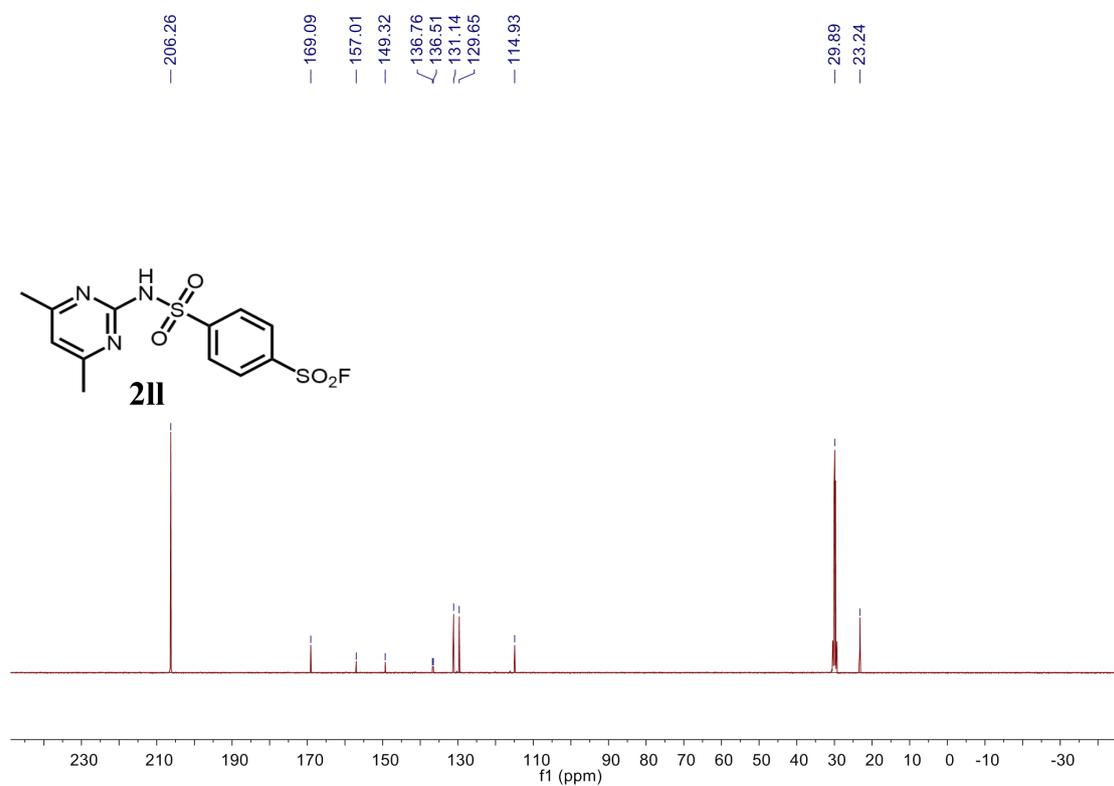
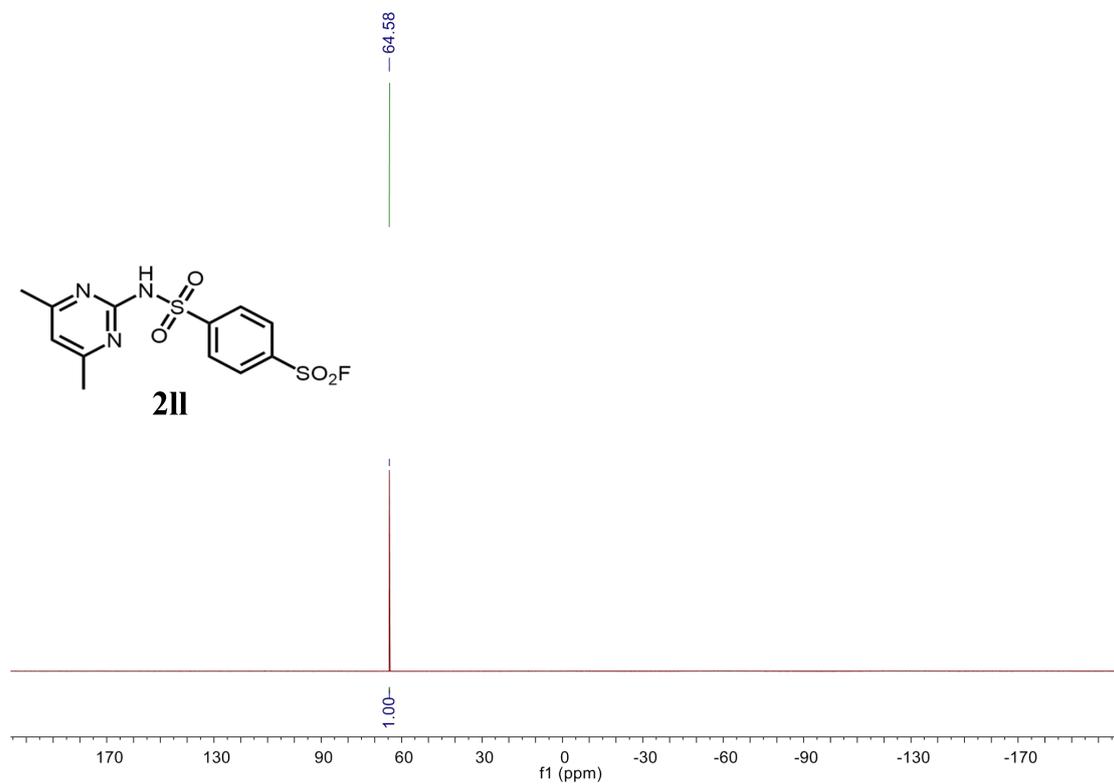


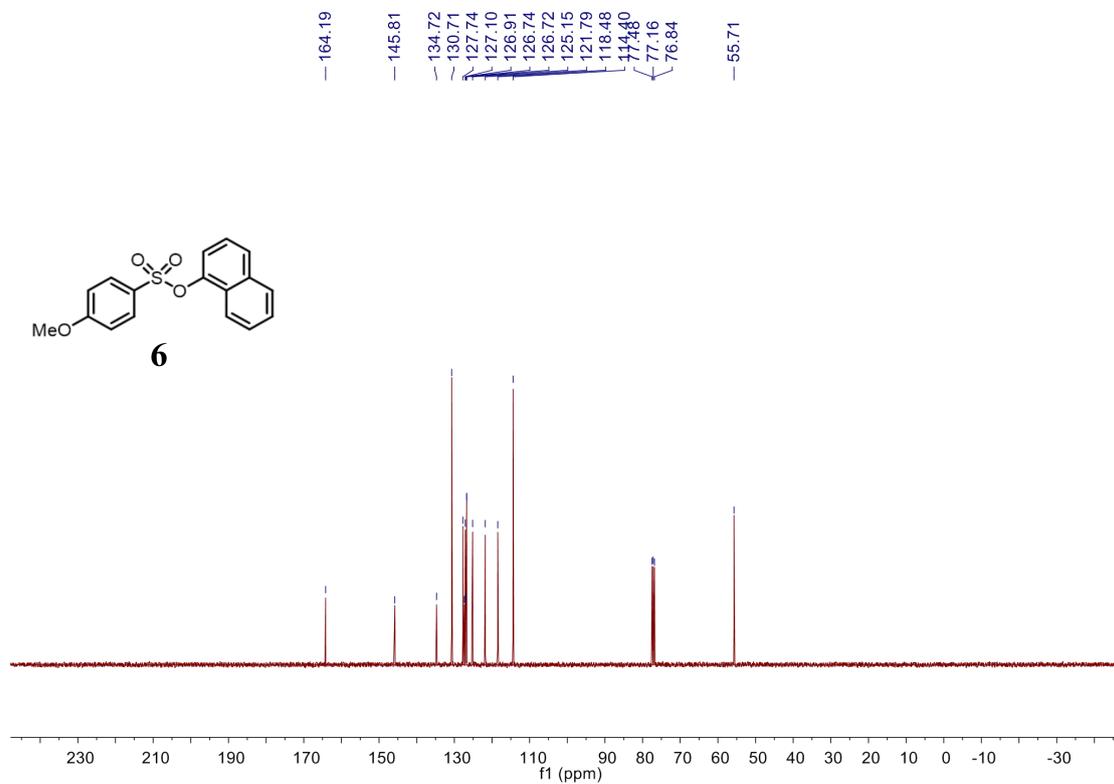
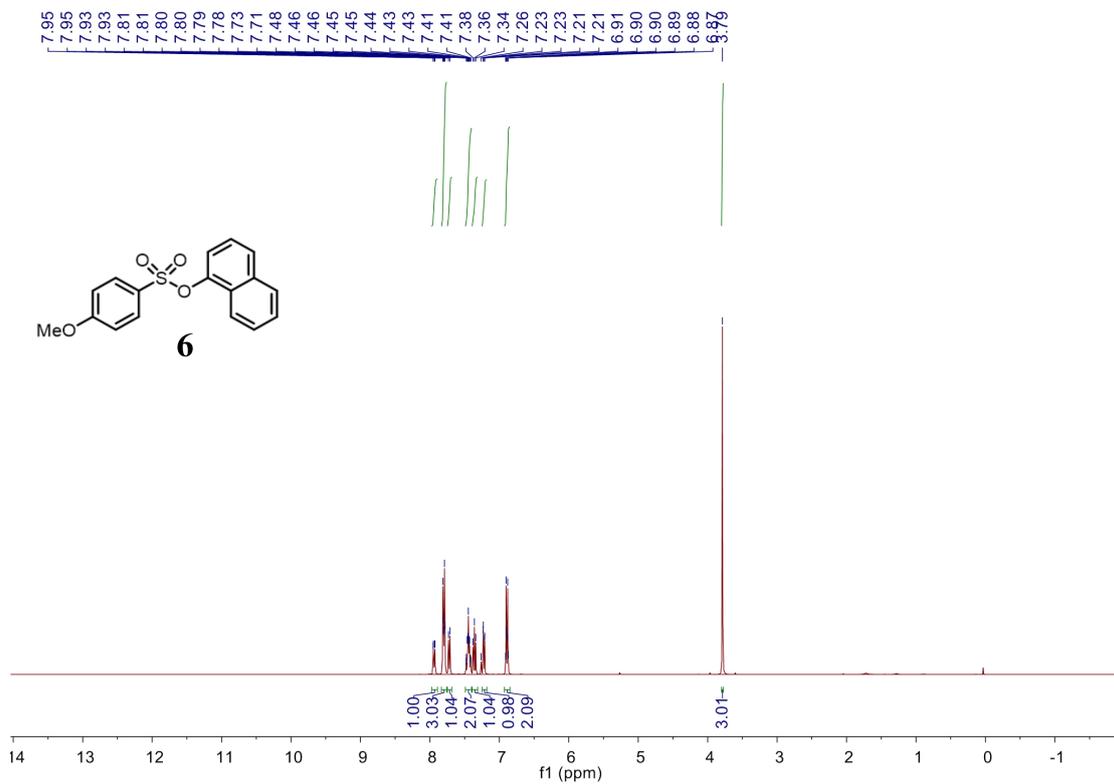
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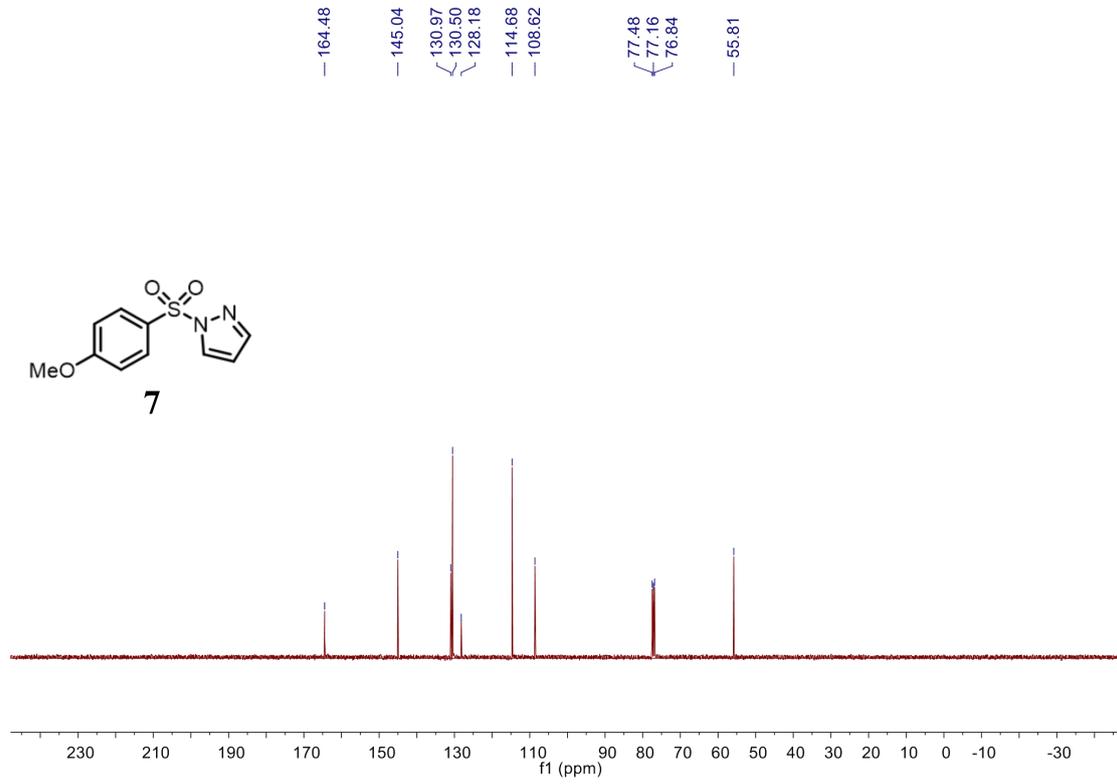
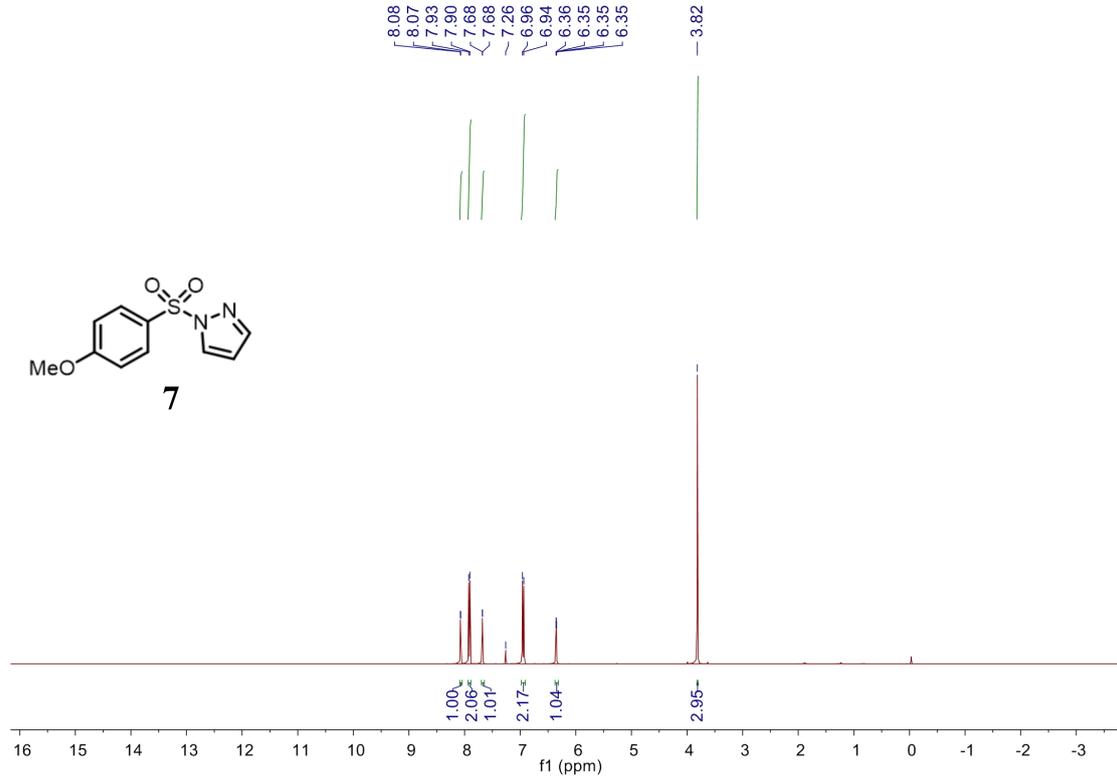


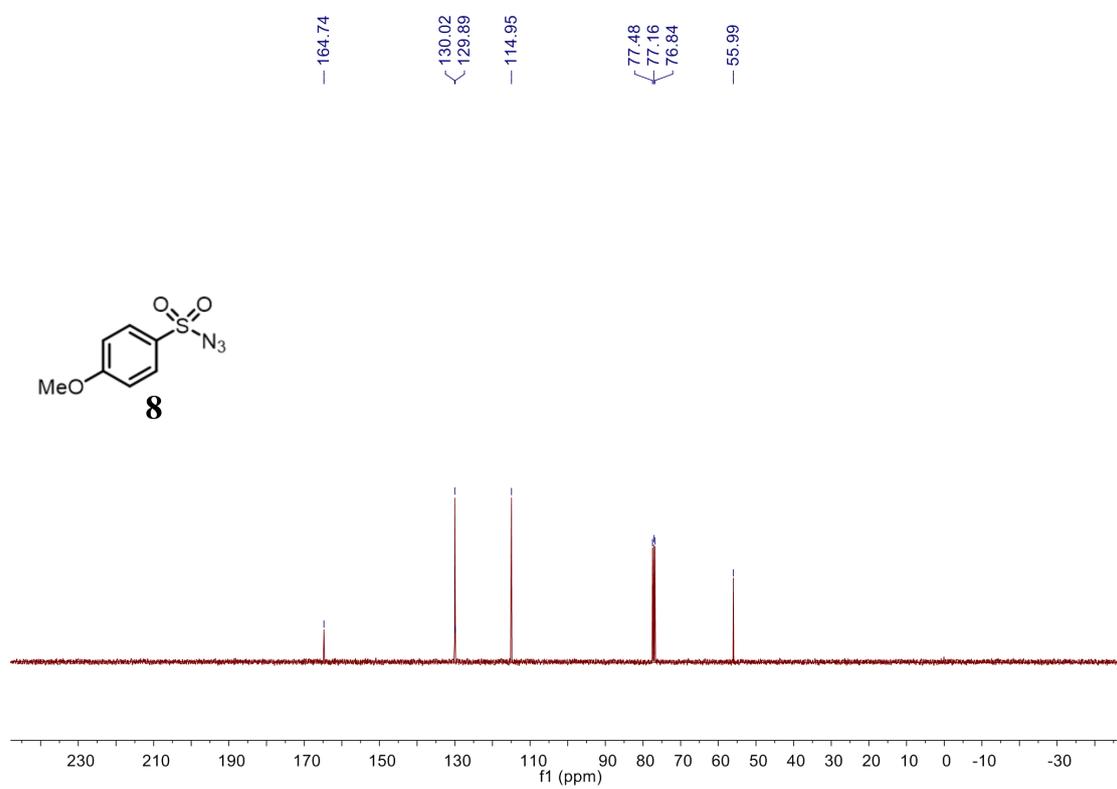
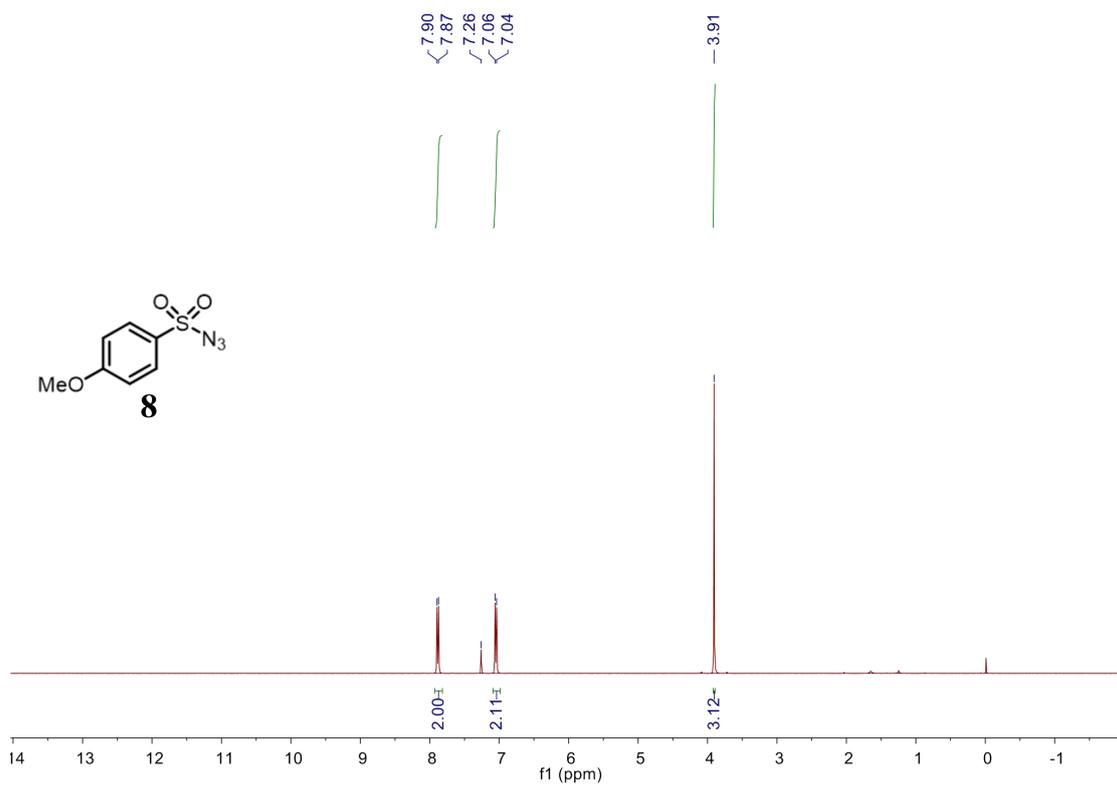


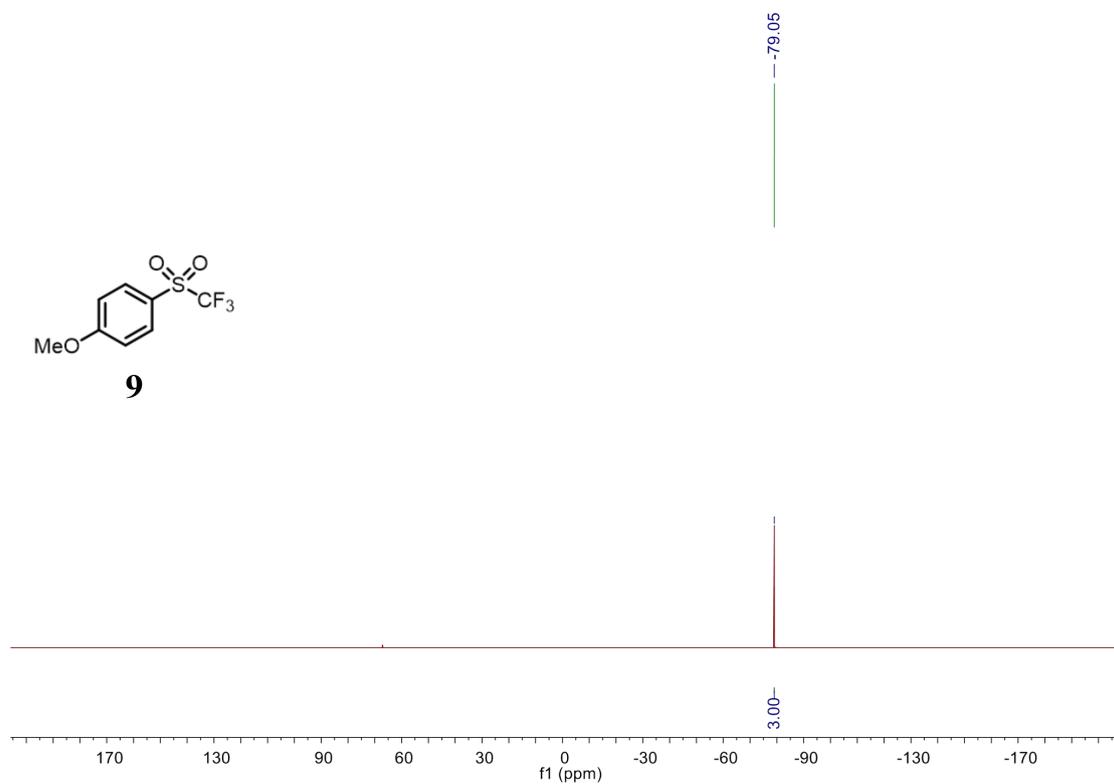
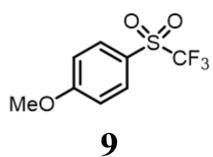
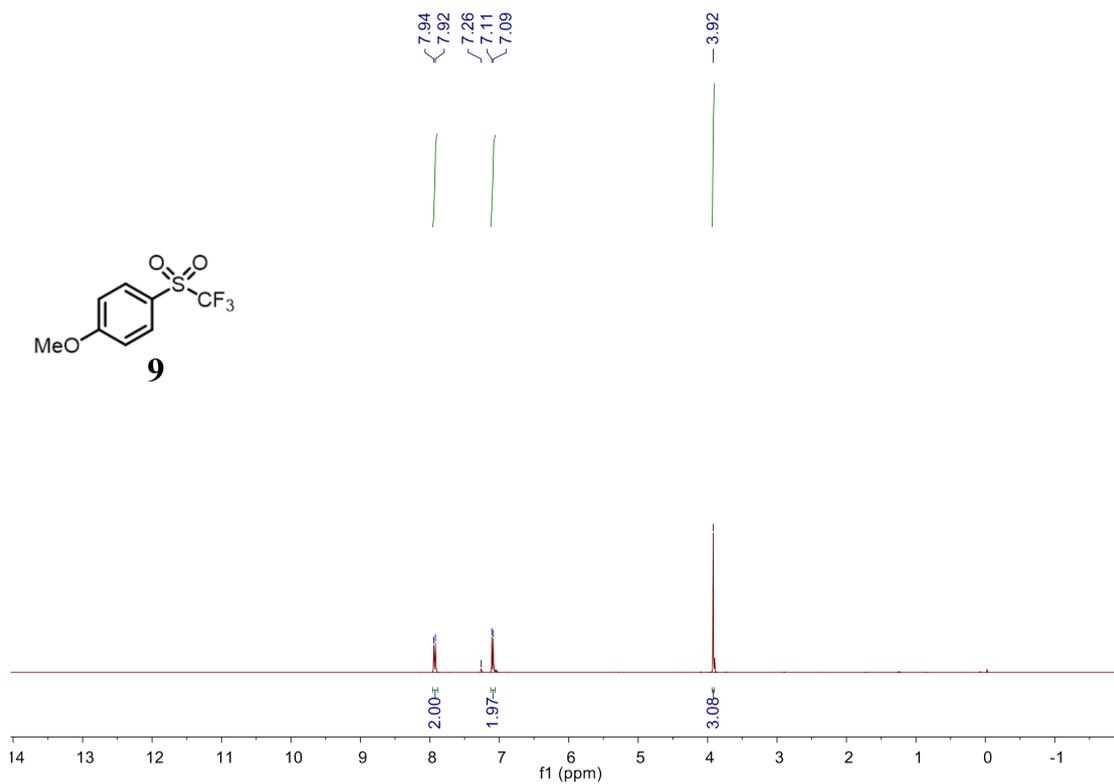
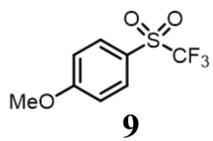


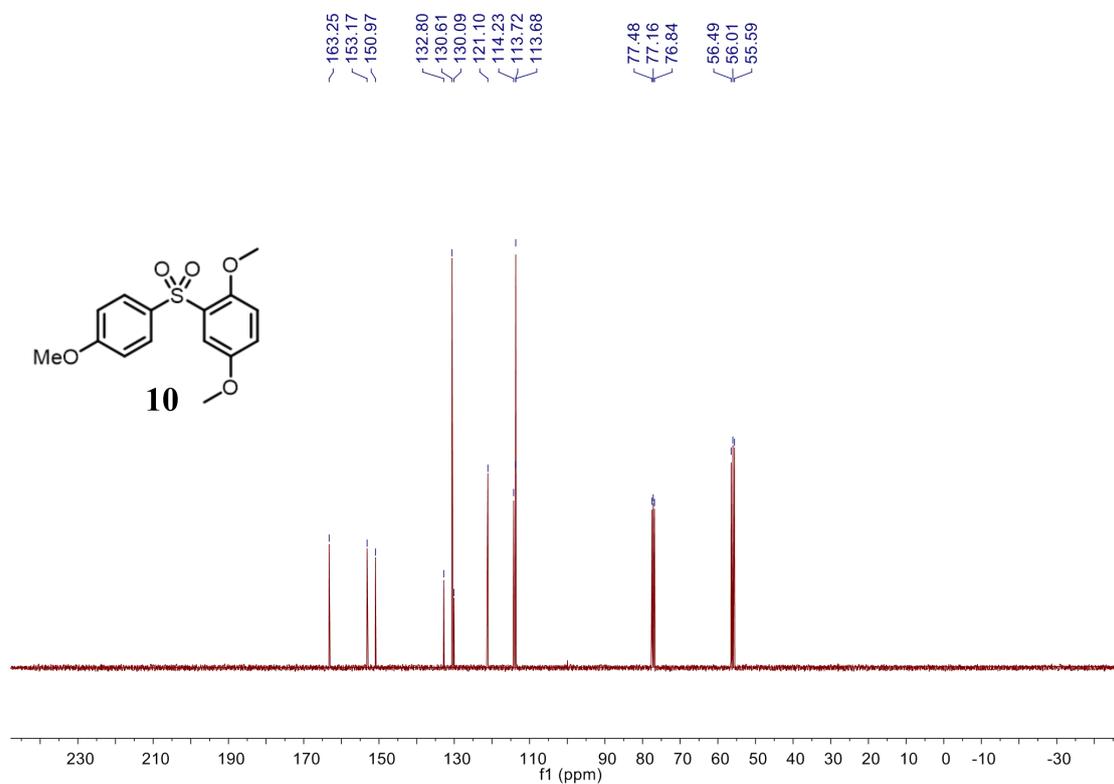
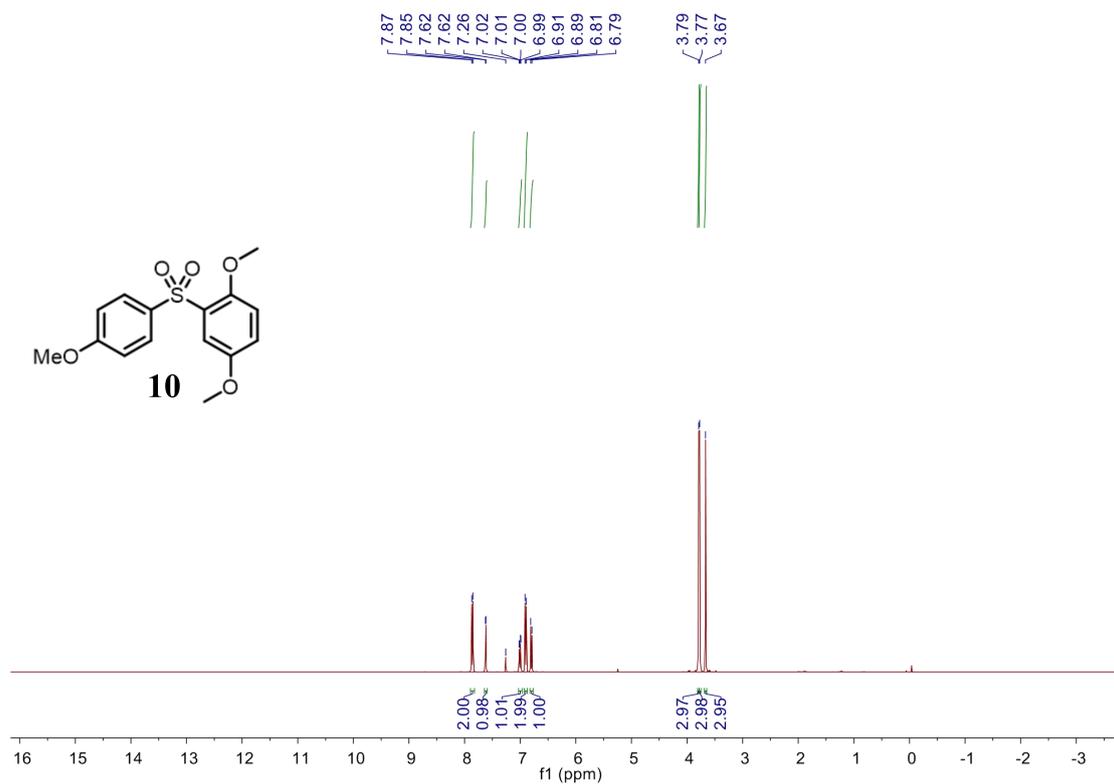


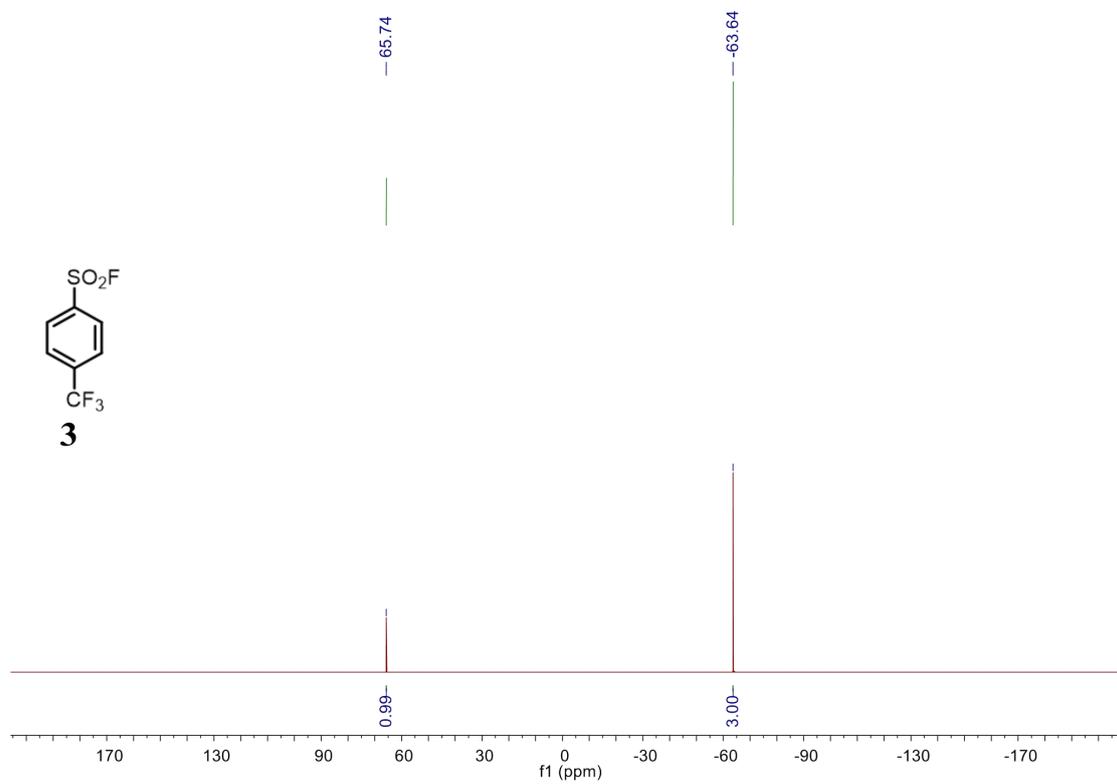
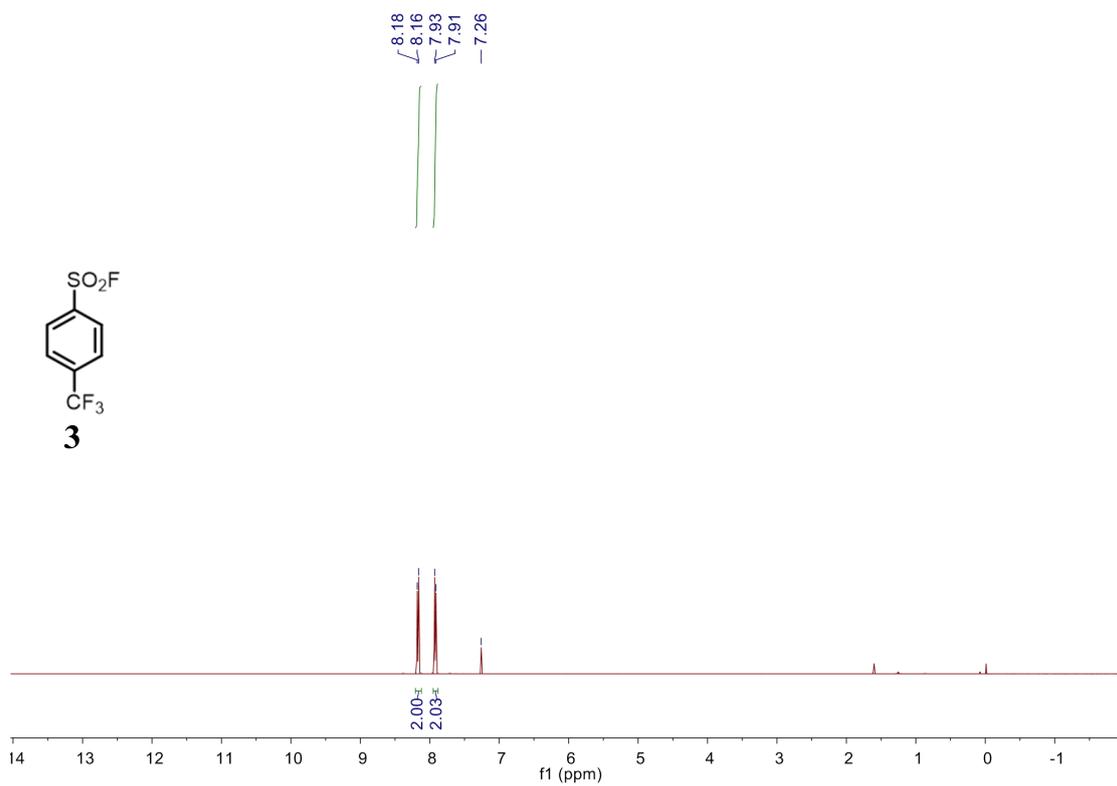


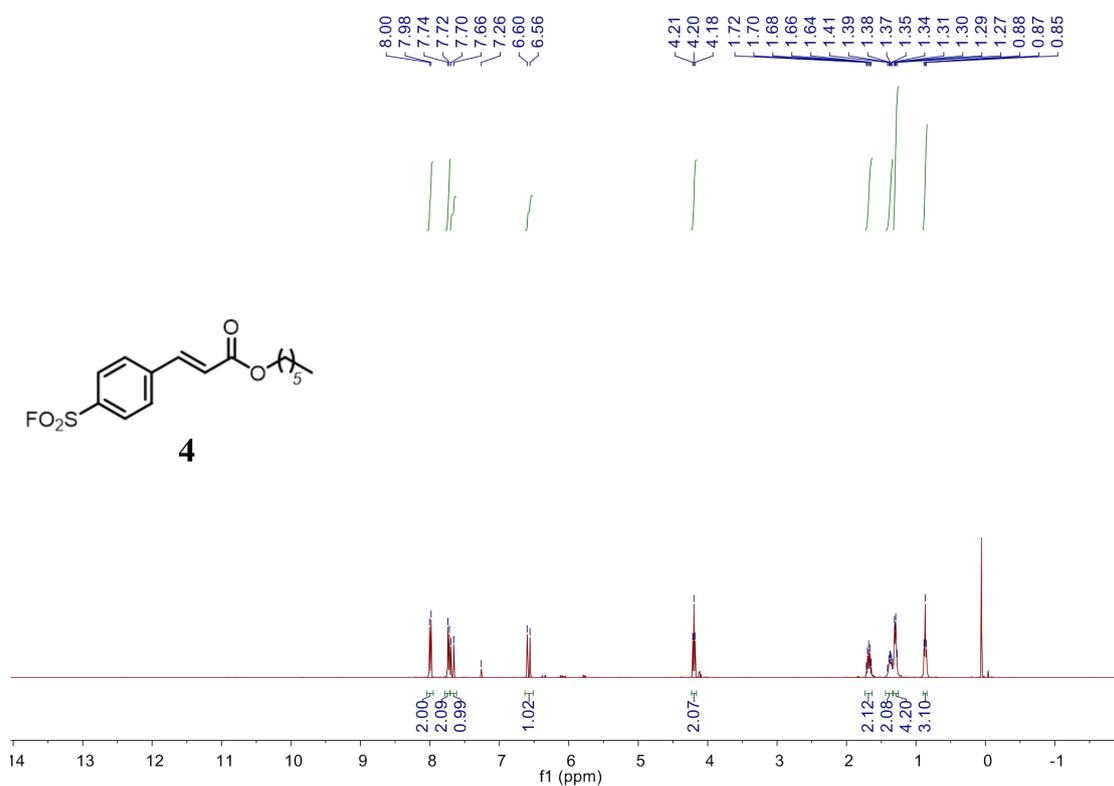
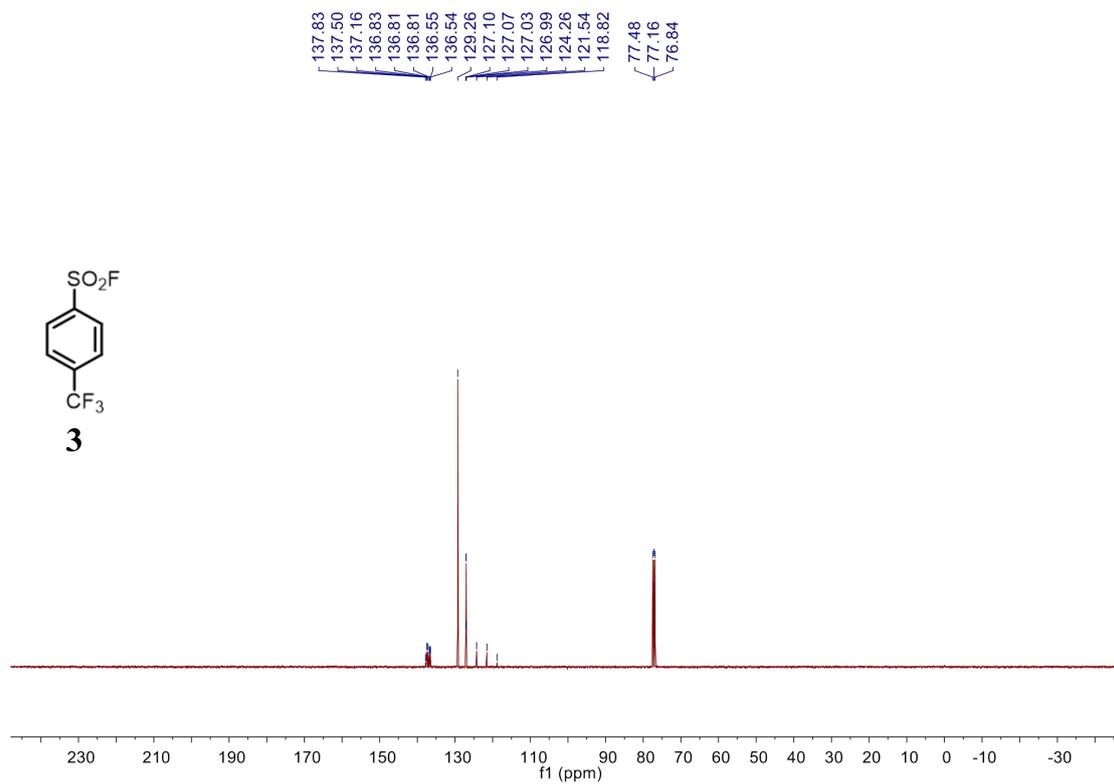


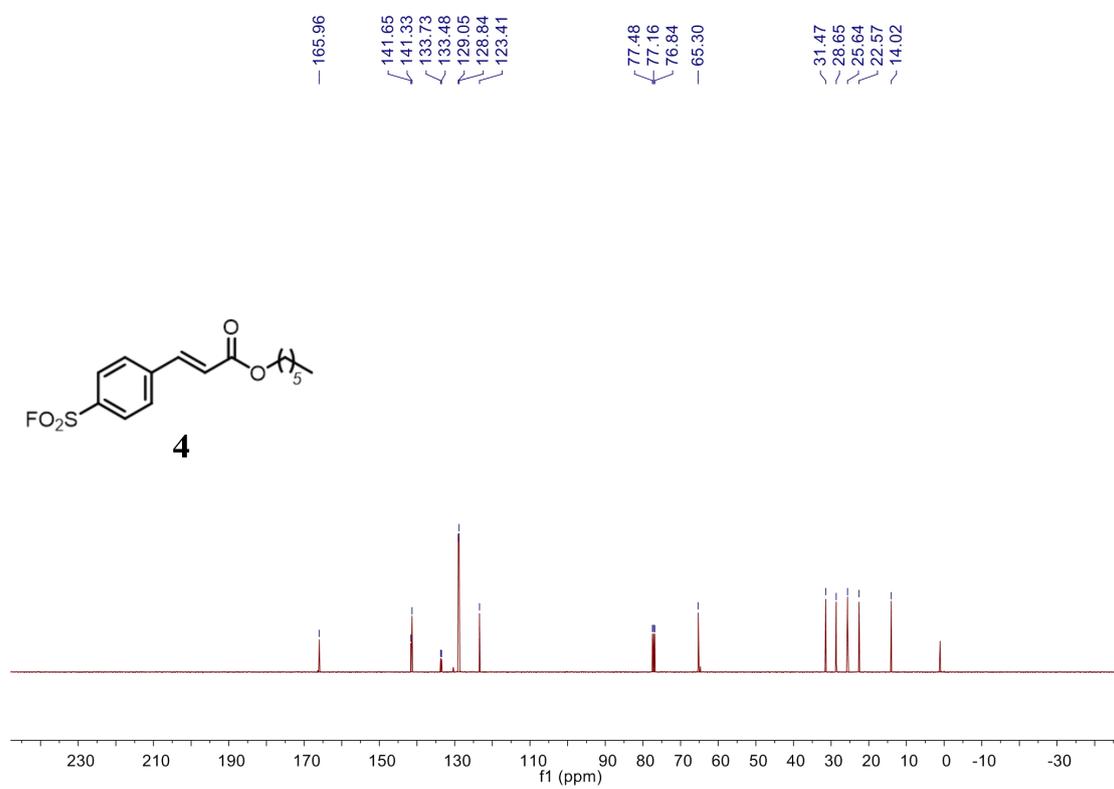
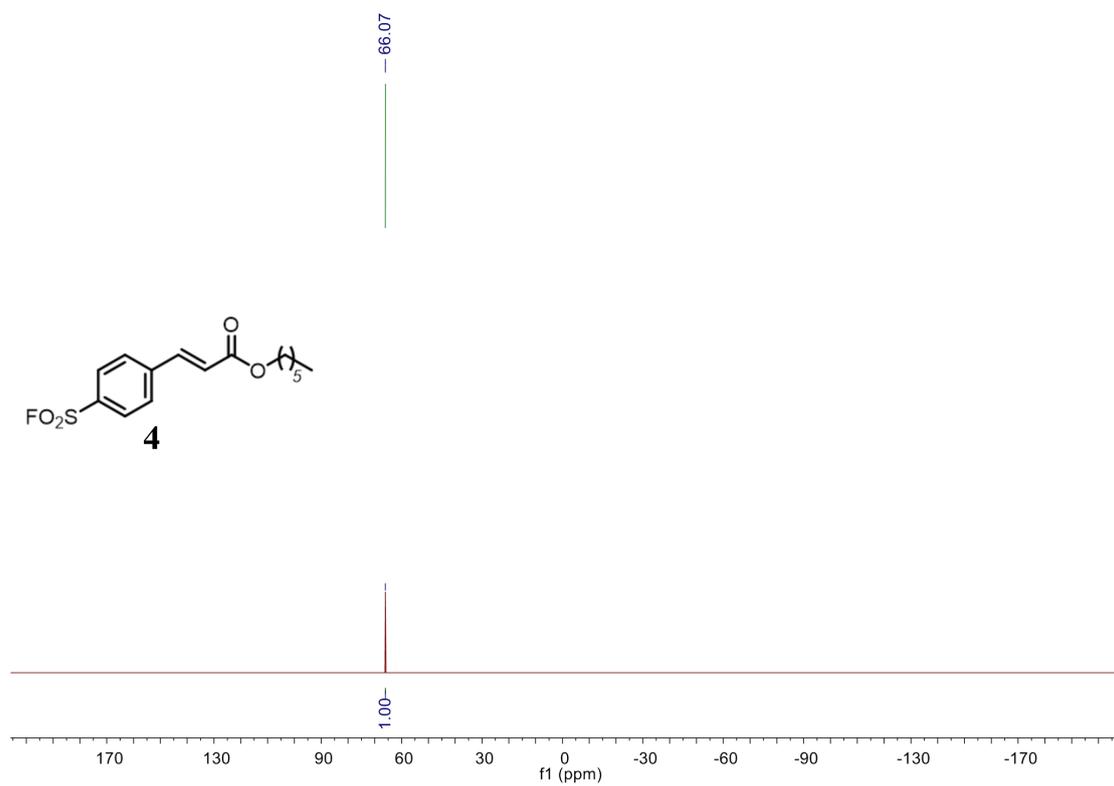


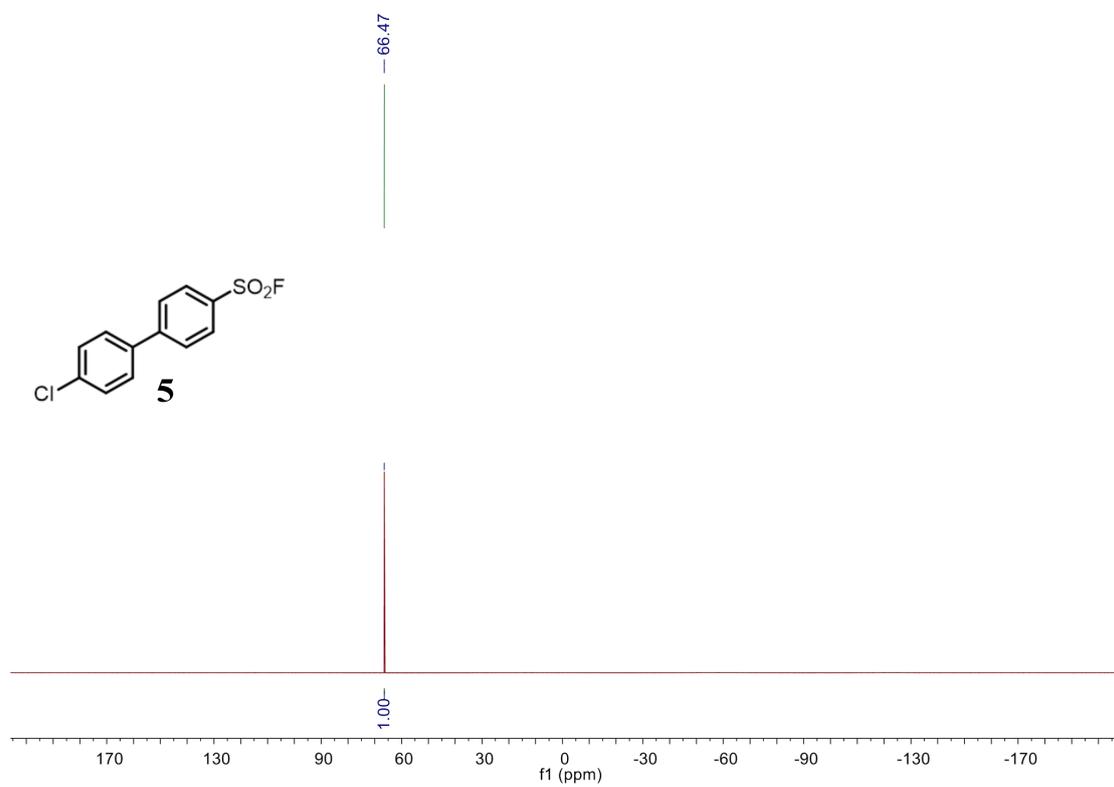
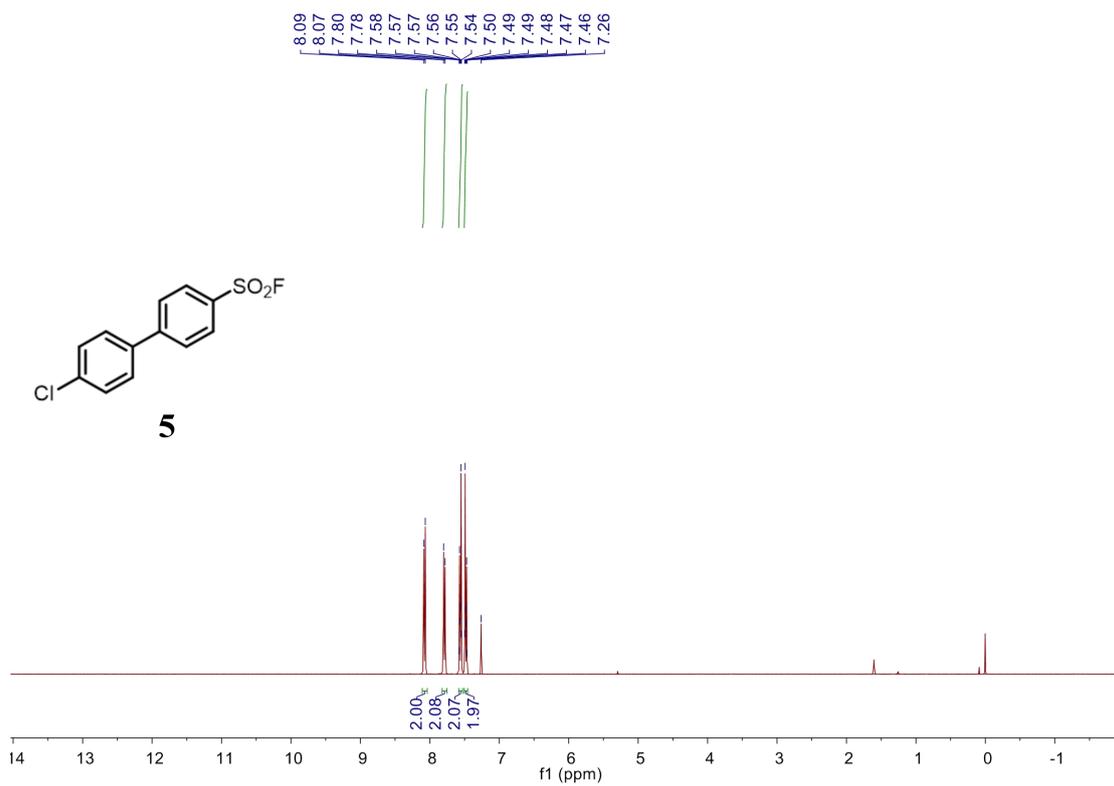


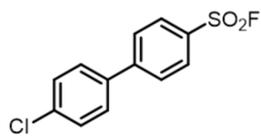




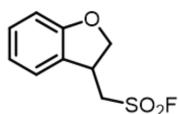
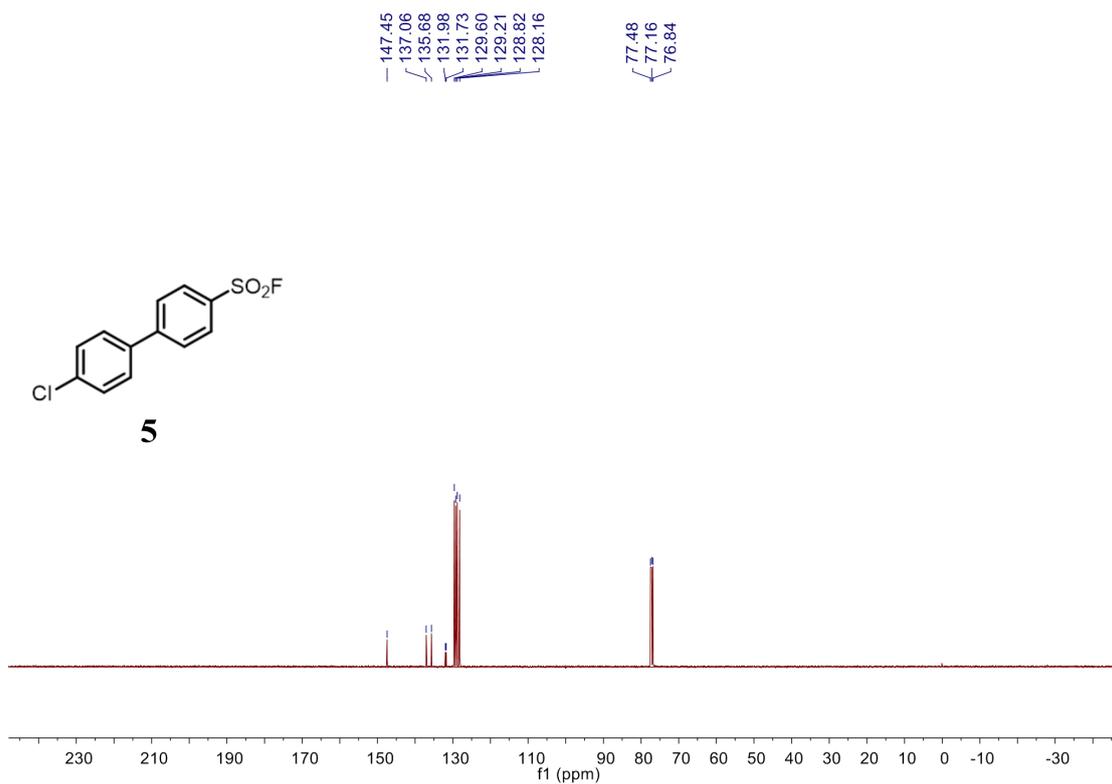




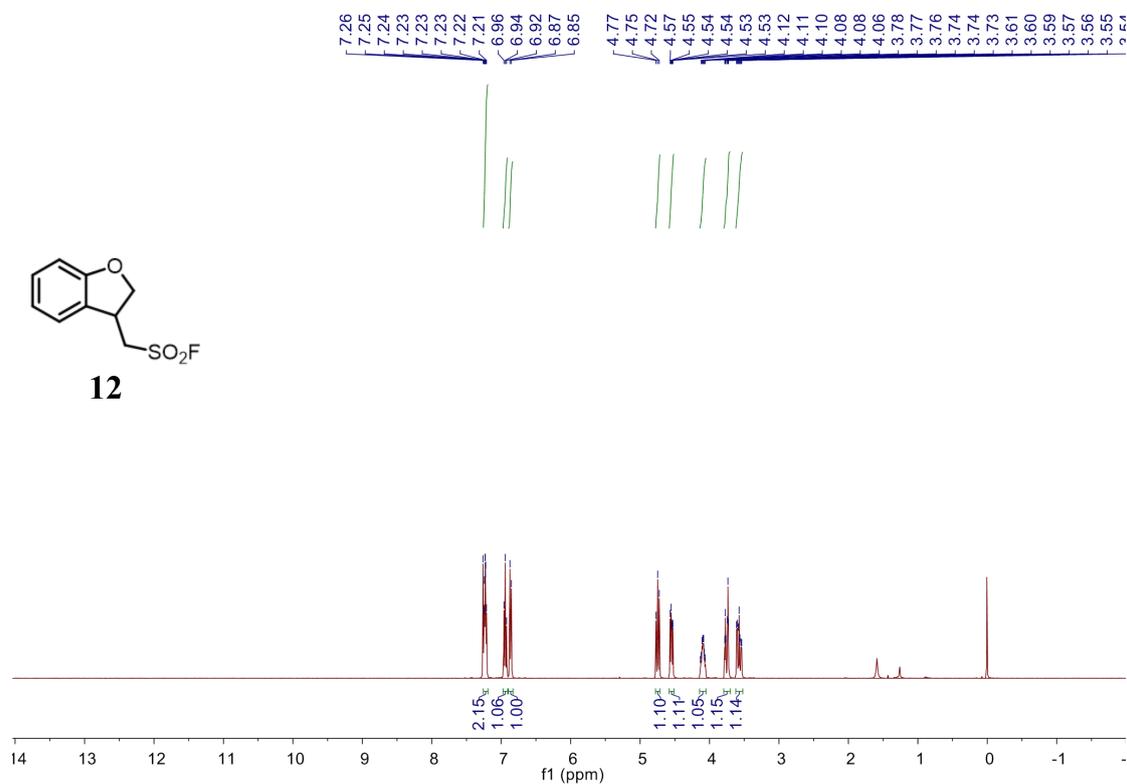


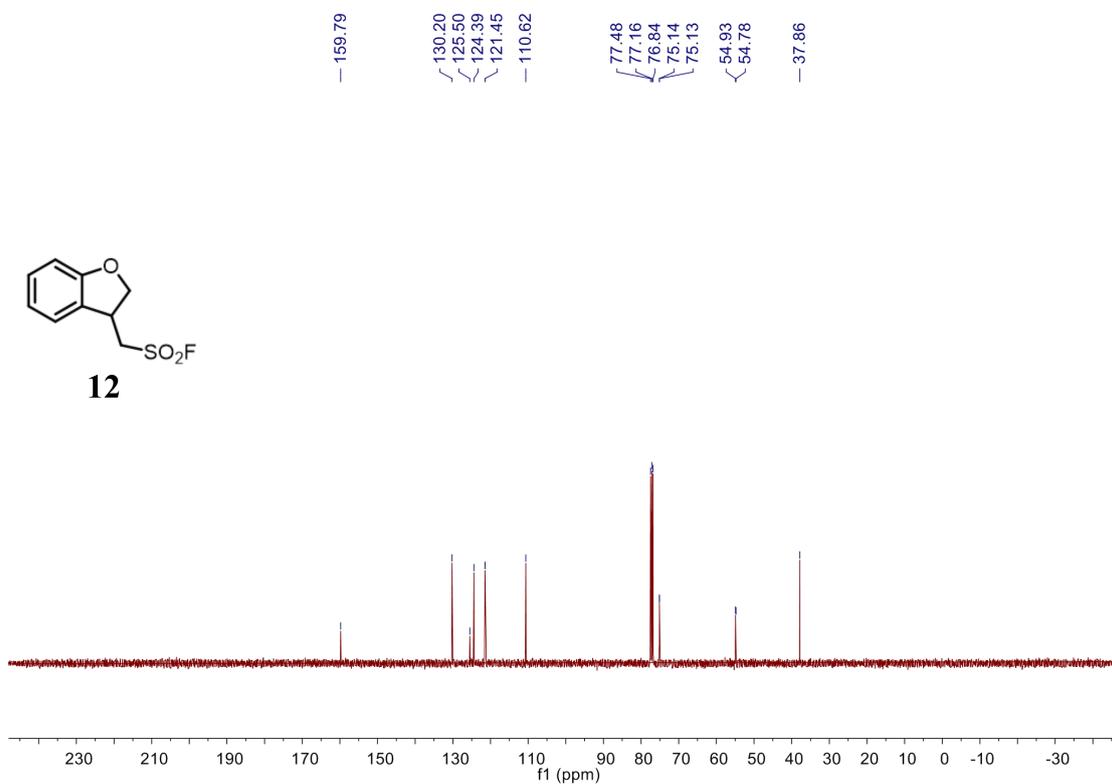
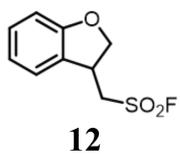
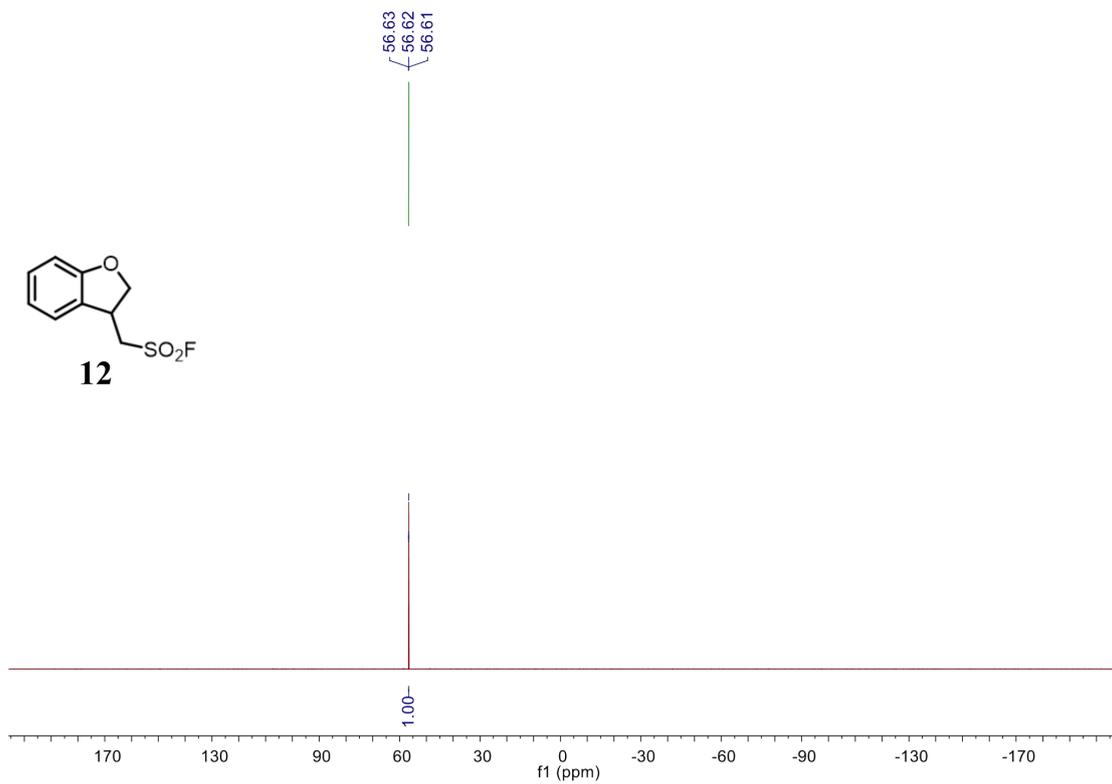
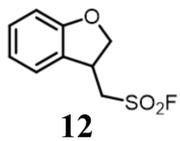


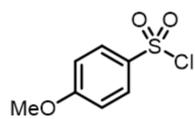
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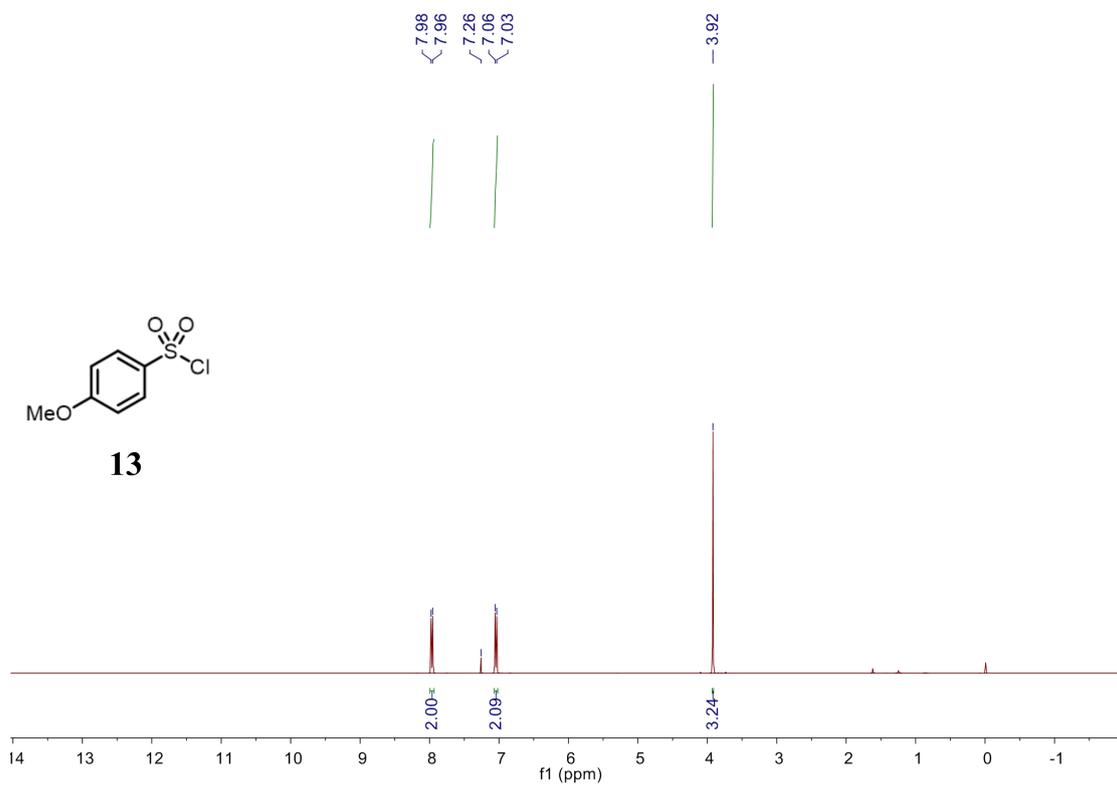
12







13



10. Single crystal structure data of 2ii

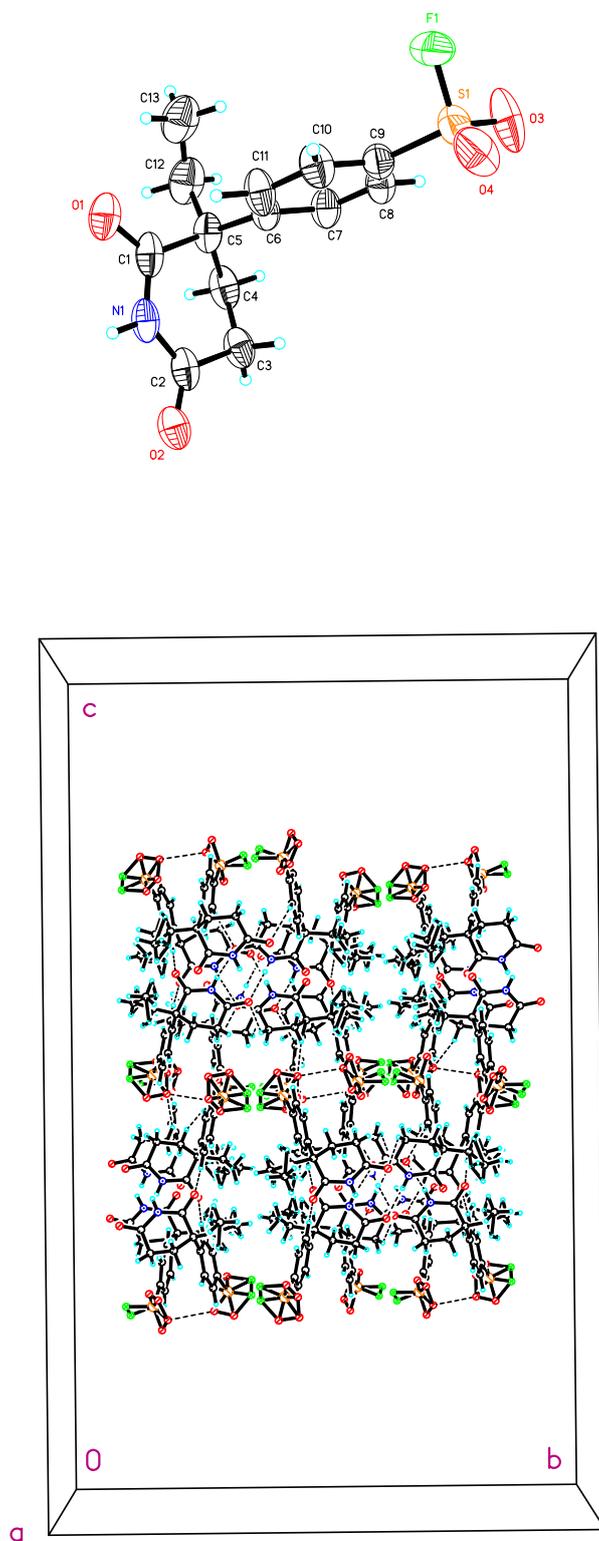


Figure S5. ORTEP diagram of 2ii. Ellipsoids are shown at the 50% probability level.

Table S5. Crystal data and structure refinement for mo_d8v19977_0m.

| | | |
|-----------------------------------|---|-----------------------|
| Identification code | mo_d8v19977_0m | |
| Empirical formula | C13 H14 F N O4 S | |
| Formula weight | 299.31 | |
| Temperature | 293(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | F d d d | |
| Unit cell dimensions | a = 14.9474(4) Å | $\alpha = 90^\circ$. |
| | b = 30.7863(10) Å | $\beta = 90^\circ$. |
| | c = 49.8938(17) Å | $\gamma = 90^\circ$. |
| Volume | 22959.9(12) Å ³ | |
| Z | 64 | |
| Density (calculated) | 1.385 Mg/m ³ | |
| Absorption coefficient | 0.248 mm ⁻¹ | |
| F(000) | 9984 | |
| Crystal size | 0.200 x 0.160 x 0.120 mm ³ | |
| Theta range for data collection | 2.442 to 25.498°. | |
| Index ranges | -18<=h<=17, -37<=k<=31, -53<=l<=60 | |
| Reflections collected | 26555 | |
| Independent reflections | 5331 [R(int) = 0.0373] | |
| Completeness to theta = 25.242° | 99.6 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.7456 and 0.6400 | |
| Refinement method | Full-matrix least-squares on F ² | |
| Data / restraints / parameters | 5331 / 74 / 456 | |
| Goodness-of-fit on F ² | 1.012 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0689, wR2 = 0.1843 | |
| R indices (all data) | R1 = 0.1082, wR2 = 0.2222 | |
| Extinction coefficient | 0.00038(10) | |
| Largest diff. peak and hole | 0.489 and -0.374 e.Å ⁻³ | |

Table S6. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for mo_d8v19977_0m. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

| | x | y | z | U(eq) |
|-------|----------|----------|---------|---------|
| S(1) | 7595(1) | 1785(1) | 7370(1) | 102(1) |
| S(2) | 2357(2) | 4341(1) | 4974(1) | 150(1) |
| N(1) | 4872(2) | 2973(1) | 6406(1) | 80(1) |
| N(2) | 5256(2) | 4077(1) | 6057(1) | 85(1) |
| O(1) | 4938(2) | 2315(1) | 6217(1) | 107(1) |
| O(2) | 4743(2) | 3660(1) | 6552(1) | 92(1) |
| F(1) | 7805(9) | 1351(3) | 7244(2) | 172(5) |
| O(3) | 7279(6) | 1672(6) | 7637(2) | 167(4) |
| O(4) | 8357(7) | 2023(3) | 7350(3) | 138(5) |
| F(1') | 7456(15) | 1355(5) | 7408(7) | 257(15) |
| O(3') | 7632(12) | 2041(5) | 7594(3) | 153(5) |
| O(4') | 8377(12) | 1818(7) | 7215(3) | 156(7) |
| O(5) | 4783(3) | 4716(1) | 6211(1) | 124(1) |
| O(6) | 5699(2) | 3415(1) | 5930(1) | 104(1) |
| F(2) | 2326(12) | 3843(5) | 4975(3) | 139(4) |
| O(7) | 1488(10) | 4459(5) | 5065(4) | 204(10) |
| O(8) | 2687(9) | 4488(5) | 4691(2) | 181(5) |
| F(2') | 2630(20) | 3913(10) | 4868(6) | 231(15) |
| O(7') | 1593(18) | 4294(9) | 5137(6) | 234(15) |
| O(8') | 2245(11) | 4609(7) | 4819(3) | 165(7) |
| C(1) | 4775(2) | 2532(2) | 6417(1) | 84(1) |
| C(2) | 4649(2) | 3269(2) | 6595(1) | 79(1) |
| C(3) | 4286(3) | 3096(2) | 6853(1) | 92(1) |
| C(4) | 3848(2) | 2661(2) | 6815(1) | 94(1) |
| C(5) | 4471(2) | 2330(1) | 6681(1) | 79(1) |
| C(6) | 5289(2) | 2226(1) | 6855(1) | 70(1) |
| C(7) | 5184(2) | 2152(1) | 7126(1) | 84(1) |
| C(8) | 5886(3) | 2019(1) | 7282(1) | 89(1) |
| C(9) | 6713(3) | 1961(1) | 7171(1) | 77(1) |
| C(10) | 6843(2) | 2041(1) | 6904(1) | 92(1) |
| C(11) | 6131(2) | 2174(2) | 6748(1) | 92(1) |
| C(12) | 3901(10) | 1931(4) | 6624(6) | 123(2) |
| C(13) | 4395(6) | 1552(3) | 6548(2) | 133(3) |

| | | | | |
|--------|----------|---------|---------|--------|
| C(12') | 4026(16) | 1864(6) | 6641(9) | 124(3) |
| C(13') | 3163(8) | 1825(5) | 6497(3) | 132(3) |
| C(14) | 5099(3) | 4515(2) | 6026(1) | 87(1) |
| C(15) | 5677(2) | 3803(2) | 5884(1) | 89(1) |
| C(16) | 6083(3) | 4006(2) | 5639(1) | 111(2) |
| C(17) | 6203(2) | 4494(2) | 5667(1) | 107(2) |
| C(18) | 5336(2) | 4712(1) | 5755(1) | 83(1) |
| C(19) | 4576(2) | 4619(1) | 5561(1) | 68(1) |
| C(20) | 4745(3) | 4587(1) | 5287(1) | 82(1) |
| C(21) | 4077(4) | 4501(1) | 5108(1) | 96(1) |
| C(22) | 3223(3) | 4445(1) | 5199(1) | 95(1) |
| C(23) | 3017(3) | 4486(1) | 5467(1) | 99(1) |
| C(24) | 3698(2) | 4573(1) | 5646(1) | 89(1) |
| C(25) | 5371(10) | 5222(4) | 5773(5) | 137(3) |
| C(26) | 6034(9) | 5442(4) | 5934(2) | 153(3) |
| C(25') | 5617(14) | 5178(5) | 5789(8) | 139(3) |
| C(26') | 4872(9) | 5474(5) | 5806(3) | 150(3) |

Table S7. Bond lengths [\AA] and angles [$^\circ$] for mo_d8v19977_0m.

| | |
|-------------|-----------|
| S(1)-F(1') | 1.353(11) |
| S(1)-O(4) | 1.358(9) |
| S(1)-O(3') | 1.370(11) |
| S(1)-O(4') | 1.40(2) |
| S(1)-O(3) | 1.456(7) |
| S(1)-F(1) | 1.507(8) |
| S(1)-C(9) | 1.739(4) |
| S(2)-O(8') | 1.144(16) |
| S(2)-O(7') | 1.41(4) |
| S(2)-O(7) | 1.423(18) |
| S(2)-F(2') | 1.48(4) |
| S(2)-F(2) | 1.532(15) |
| S(2)-O(8) | 1.565(11) |
| S(2)-C(22) | 1.741(4) |
| N(1)-C(2) | 1.354(5) |
| N(1)-C(1) | 1.366(5) |
| N(1)-H(1) | 0.8600 |
| N(2)-C(15) | 1.362(5) |
| N(2)-C(14) | 1.376(5) |
| N(2)-H(2) | 0.8600 |
| O(1)-C(1) | 1.226(5) |
| O(2)-C(2) | 1.230(5) |
| O(5)-C(14) | 1.206(5) |
| O(6)-C(15) | 1.217(5) |
| C(1)-C(5) | 1.526(5) |
| C(2)-C(3) | 1.494(5) |
| C(3)-C(4) | 1.502(6) |
| C(3)-H(3A) | 0.9700 |
| C(3)-H(3B) | 0.9700 |
| C(4)-C(5) | 1.534(6) |
| C(4)-H(4A) | 0.9700 |
| C(4)-H(4B) | 0.9700 |
| C(5)-C(12) | 1.522(12) |
| C(5)-C(6) | 1.532(5) |
| C(5)-C(12') | 1.594(16) |
| C(6)-C(11) | 1.376(5) |

| | |
|---------------|-----------|
| C(6)-C(7) | 1.380(5) |
| C(7)-C(8) | 1.372(5) |
| C(7)-H(7) | 0.9300 |
| C(8)-C(9) | 1.367(5) |
| C(8)-H(8) | 0.9300 |
| C(9)-C(10) | 1.367(5) |
| C(10)-C(11) | 1.379(5) |
| C(10)-H(10) | 0.9300 |
| C(11)-H(11) | 0.9300 |
| C(12)-C(13) | 1.431(15) |
| C(12)-H(12A) | 0.9700 |
| C(12)-H(12B) | 0.9700 |
| C(13)-H(13A) | 0.9600 |
| C(13)-H(13B) | 0.9600 |
| C(13)-H(13C) | 0.9600 |
| C(12')-C(13') | 1.482(17) |
| C(12')-H(12C) | 0.9700 |
| C(12')-H(12D) | 0.9700 |
| C(13')-H(13D) | 0.9600 |
| C(13')-H(13E) | 0.9600 |
| C(13')-H(13F) | 0.9600 |
| C(14)-C(18) | 1.528(5) |
| C(15)-C(16) | 1.499(5) |
| C(16)-C(17) | 1.520(6) |
| C(16)-H(16A) | 0.9700 |
| C(16)-H(16B) | 0.9700 |
| C(17)-C(18) | 1.523(6) |
| C(17)-H(17A) | 0.9700 |
| C(17)-H(17B) | 0.9700 |
| C(18)-C(25') | 1.503(16) |
| C(18)-C(19) | 1.519(5) |
| C(18)-C(25) | 1.574(12) |
| C(19)-C(24) | 1.387(5) |
| C(19)-C(20) | 1.393(5) |
| C(20)-C(21) | 1.366(6) |
| C(20)-H(20) | 0.9300 |
| C(21)-C(22) | 1.365(6) |
| C(21)-H(21) | 0.9300 |

| | |
|------------------|-----------|
| C(22)-C(23) | 1.379(7) |
| C(23)-C(24) | 1.380(5) |
| C(23)-H(23) | 0.9300 |
| C(24)-H(24) | 0.9300 |
| C(25)-C(26) | 1.446(14) |
| C(25)-H(25A) | 0.9700 |
| C(25)-H(25B) | 0.9700 |
| C(26)-H(26A) | 0.9600 |
| C(26)-H(26B) | 0.9600 |
| C(26)-H(26C) | 0.9600 |
| C(25')-C(26') | 1.442(17) |
| C(25')-H(25C) | 0.9700 |
| C(25')-H(25D) | 0.9700 |
| C(26')-H(26D) | 0.9600 |
| C(26')-H(26E) | 0.9600 |
| C(26')-H(26F) | 0.9600 |
| | |
| F(1')-S(1)-O(3') | 117.0(14) |
| F(1')-S(1)-O(4') | 106.1(15) |
| O(3')-S(1)-O(4') | 111.9(9) |
| O(4)-S(1)-O(3) | 117.8(7) |
| O(4)-S(1)-F(1) | 106.0(7) |
| O(3)-S(1)-F(1) | 103.7(7) |
| F(1')-S(1)-C(9) | 105.6(7) |
| O(4)-S(1)-C(9) | 115.2(4) |
| O(3')-S(1)-C(9) | 108.5(5) |
| O(4')-S(1)-C(9) | 107.2(6) |
| O(3)-S(1)-C(9) | 110.6(4) |
| F(1)-S(1)-C(9) | 101.3(5) |
| O(8')-S(2)-O(7') | 110.2(11) |
| O(8')-S(2)-F(2') | 116.2(17) |
| O(7')-S(2)-F(2') | 109.8(16) |
| O(7)-S(2)-F(2) | 103.1(10) |
| O(7)-S(2)-O(8) | 120.1(8) |
| F(2)-S(2)-O(8) | 107.5(9) |
| O(8')-S(2)-C(22) | 114.2(10) |
| O(7')-S(2)-C(22) | 104.6(10) |
| O(7)-S(2)-C(22) | 115.2(6) |

| | |
|------------------|-----------|
| F(2')-S(2)-C(22) | 101.0(12) |
| F(2)-S(2)-C(22) | 101.9(6) |
| O(8)-S(2)-C(22) | 107.1(5) |
| C(2)-N(1)-C(1) | 127.9(3) |
| C(2)-N(1)-H(1) | 116.1 |
| C(1)-N(1)-H(1) | 116.1 |
| C(15)-N(2)-C(14) | 128.2(3) |
| C(15)-N(2)-H(2) | 115.9 |
| C(14)-N(2)-H(2) | 115.9 |
| O(1)-C(1)-N(1) | 119.2(4) |
| O(1)-C(1)-C(5) | 122.7(5) |
| N(1)-C(1)-C(5) | 118.1(4) |
| O(2)-C(2)-N(1) | 120.5(3) |
| O(2)-C(2)-C(3) | 122.7(4) |
| N(1)-C(2)-C(3) | 116.8(4) |
| C(2)-C(3)-C(4) | 111.6(4) |
| C(2)-C(3)-H(3A) | 109.3 |
| C(4)-C(3)-H(3A) | 109.3 |
| C(2)-C(3)-H(3B) | 109.3 |
| C(4)-C(3)-H(3B) | 109.3 |
| H(3A)-C(3)-H(3B) | 108.0 |
| C(3)-C(4)-C(5) | 112.5(3) |
| C(3)-C(4)-H(4A) | 109.1 |
| C(5)-C(4)-H(4A) | 109.1 |
| C(3)-C(4)-H(4B) | 109.1 |
| C(5)-C(4)-H(4B) | 109.1 |
| H(4A)-C(4)-H(4B) | 107.8 |
| C(12)-C(5)-C(1) | 109.6(11) |
| C(12)-C(5)-C(6) | 112.5(7) |
| C(1)-C(5)-C(6) | 109.6(3) |
| C(12)-C(5)-C(4) | 106.1(8) |
| C(1)-C(5)-C(4) | 106.7(3) |
| C(6)-C(5)-C(4) | 112.1(3) |
| C(1)-C(5)-C(12') | 112.4(17) |
| C(6)-C(5)-C(12') | 102.5(9) |
| C(4)-C(5)-C(12') | 113.6(13) |
| C(11)-C(6)-C(7) | 117.6(3) |
| C(11)-C(6)-C(5) | 122.4(3) |

| | |
|----------------------|-----------|
| C(7)-C(6)-C(5) | 119.8(3) |
| C(8)-C(7)-C(6) | 121.4(4) |
| C(8)-C(7)-H(7) | 119.3 |
| C(6)-C(7)-H(7) | 119.3 |
| C(9)-C(8)-C(7) | 119.9(3) |
| C(9)-C(8)-H(8) | 120.1 |
| C(7)-C(8)-H(8) | 120.1 |
| C(10)-C(9)-C(8) | 120.1(3) |
| C(10)-C(9)-S(1) | 120.3(3) |
| C(8)-C(9)-S(1) | 119.6(3) |
| C(9)-C(10)-C(11) | 119.5(4) |
| C(9)-C(10)-H(10) | 120.3 |
| C(11)-C(10)-H(10) | 120.3 |
| C(6)-C(11)-C(10) | 121.5(3) |
| C(6)-C(11)-H(11) | 119.2 |
| C(10)-C(11)-H(11) | 119.2 |
| C(13)-C(12)-C(5) | 114.8(11) |
| C(13)-C(12)-H(12A) | 108.6 |
| C(5)-C(12)-H(12A) | 108.6 |
| C(13)-C(12)-H(12B) | 108.6 |
| C(5)-C(12)-H(12B) | 108.6 |
| H(12A)-C(12)-H(12B) | 107.6 |
| C(12)-C(13)-H(13A) | 109.5 |
| C(12)-C(13)-H(13B) | 109.5 |
| H(13A)-C(13)-H(13B) | 109.5 |
| C(12)-C(13)-H(13C) | 109.5 |
| H(13A)-C(13)-H(13C) | 109.5 |
| H(13B)-C(13)-H(13C) | 109.5 |
| C(13')-C(12')-C(5) | 119.9(15) |
| C(13')-C(12')-H(12C) | 107.3 |
| C(5)-C(12')-H(12C) | 107.3 |
| C(13')-C(12')-H(12D) | 107.3 |
| C(5)-C(12')-H(12D) | 107.3 |
| H(12C)-C(12')-H(12D) | 106.9 |
| C(12')-C(13')-H(13D) | 109.5 |
| C(12')-C(13')-H(13E) | 109.5 |
| H(13D)-C(13')-H(13E) | 109.5 |
| C(12')-C(13')-H(13F) | 109.5 |

| | |
|----------------------|-----------|
| H(13D)-C(13')-H(13F) | 109.5 |
| H(13E)-C(13')-H(13F) | 109.5 |
| O(5)-C(14)-N(2) | 119.1(4) |
| O(5)-C(14)-C(18) | 124.4(5) |
| N(2)-C(14)-C(18) | 116.5(4) |
| O(6)-C(15)-N(2) | 120.1(4) |
| O(6)-C(15)-C(16) | 123.6(4) |
| N(2)-C(15)-C(16) | 116.3(5) |
| C(15)-C(16)-C(17) | 112.7(4) |
| C(15)-C(16)-H(16A) | 109.1 |
| C(17)-C(16)-H(16A) | 109.1 |
| C(15)-C(16)-H(16B) | 109.1 |
| C(17)-C(16)-H(16B) | 109.1 |
| H(16A)-C(16)-H(16B) | 107.8 |
| C(16)-C(17)-C(18) | 111.2(3) |
| C(16)-C(17)-H(17A) | 109.4 |
| C(18)-C(17)-H(17A) | 109.4 |
| C(16)-C(17)-H(17B) | 109.4 |
| C(18)-C(17)-H(17B) | 109.4 |
| H(17A)-C(17)-H(17B) | 108.0 |
| C(25')-C(18)-C(19) | 117.4(11) |
| C(25')-C(18)-C(17) | 102.4(10) |
| C(19)-C(18)-C(17) | 111.7(3) |
| C(25')-C(18)-C(14) | 110.2(16) |
| C(19)-C(18)-C(14) | 108.4(3) |
| C(17)-C(18)-C(14) | 106.1(3) |
| C(19)-C(18)-C(25) | 104.4(6) |
| C(17)-C(18)-C(25) | 115.3(8) |
| C(14)-C(18)-C(25) | 110.8(10) |
| C(24)-C(19)-C(20) | 117.7(3) |
| C(24)-C(19)-C(18) | 122.2(3) |
| C(20)-C(19)-C(18) | 120.1(3) |
| C(21)-C(20)-C(19) | 121.5(4) |
| C(21)-C(20)-H(20) | 119.3 |
| C(19)-C(20)-H(20) | 119.3 |
| C(22)-C(21)-C(20) | 119.5(4) |
| C(22)-C(21)-H(21) | 120.3 |
| C(20)-C(21)-H(21) | 120.3 |

| | |
|----------------------|-----------|
| C(21)-C(22)-C(23) | 121.2(4) |
| C(21)-C(22)-S(2) | 120.4(4) |
| C(23)-C(22)-S(2) | 118.4(4) |
| C(22)-C(23)-C(24) | 118.8(4) |
| C(22)-C(23)-H(23) | 120.6 |
| C(24)-C(23)-H(23) | 120.6 |
| C(23)-C(24)-C(19) | 121.4(4) |
| C(23)-C(24)-H(24) | 119.3 |
| C(19)-C(24)-H(24) | 119.3 |
| C(26)-C(25)-C(18) | 121.4(11) |
| C(26)-C(25)-H(25A) | 107.0 |
| C(18)-C(25)-H(25A) | 107.0 |
| C(26)-C(25)-H(25B) | 107.0 |
| C(18)-C(25)-H(25B) | 107.0 |
| H(25A)-C(25)-H(25B) | 106.7 |
| C(25)-C(26)-H(26A) | 109.5 |
| C(25)-C(26)-H(26B) | 109.5 |
| H(26A)-C(26)-H(26B) | 109.5 |
| C(25)-C(26)-H(26C) | 109.5 |
| H(26A)-C(26)-H(26C) | 109.5 |
| H(26B)-C(26)-H(26C) | 109.5 |
| C(26')-C(25')-C(18) | 113.3(15) |
| C(26')-C(25')-H(25C) | 108.9 |
| C(18)-C(25')-H(25C) | 108.9 |
| C(26')-C(25')-H(25D) | 108.9 |
| C(18)-C(25')-H(25D) | 108.9 |
| H(25C)-C(25')-H(25D) | 107.7 |
| C(25')-C(26')-H(26D) | 109.5 |
| C(25')-C(26')-H(26E) | 109.5 |
| H(26D)-C(26')-H(26E) | 109.5 |
| C(25')-C(26')-H(26F) | 109.5 |
| H(26D)-C(26')-H(26F) | 109.5 |
| H(26E)-C(26')-H(26F) | 109.5 |

Symmetry transformations used to generate equivalent atoms:

Table S8. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for mo_d8v19977_0m. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

| | U ¹¹ | U ²² | U ³³ | U ²³ | U ¹³ | U ¹² |
|-------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| S(1) | 106(1) | 99(1) | 100(1) | 11(1) | -36(1) | 0(1) |
| S(2) | 180(2) | 100(1) | 172(2) | 26(1) | -120(2) | -14(1) |
| N(1) | 57(2) | 133(3) | 51(2) | 14(2) | 5(1) | -9(2) |
| N(2) | 67(2) | 134(3) | 53(2) | 16(2) | -1(1) | -9(2) |
| O(1) | 95(2) | 160(3) | 66(2) | -6(2) | 9(1) | 0(2) |
| O(2) | 71(2) | 129(2) | 74(2) | 20(2) | 6(1) | 11(2) |
| F(1) | 220(11) | 98(7) | 199(8) | -47(6) | -106(7) | 64(8) |
| O(3) | 149(7) | 271(13) | 82(4) | 75(6) | -20(4) | 13(9) |
| O(4) | 108(6) | 105(6) | 201(12) | 49(6) | -82(8) | -46(5) |
| F(1') | 220(20) | 92(11) | 450(40) | 140(17) | -180(20) | -80(12) |
| O(3') | 171(13) | 173(12) | 116(9) | -29(8) | -85(9) | 12(9) |
| O(4') | 125(10) | 210(20) | 136(11) | 27(10) | -58(9) | 23(12) |
| O(5) | 156(3) | 148(3) | 67(2) | -15(2) | 16(2) | -16(2) |
| O(6) | 80(2) | 149(3) | 83(2) | 29(2) | 5(1) | 14(2) |
| F(2) | 173(8) | 74(4) | 171(7) | -2(4) | -82(6) | -16(4) |
| O(7) | 132(8) | 174(11) | 300(20) | -62(13) | -160(12) | 69(9) |
| O(8) | 196(12) | 263(13) | 83(6) | 69(7) | -73(6) | -46(10) |
| F(2') | 250(30) | 144(19) | 300(30) | -52(19) | -150(20) | 26(15) |
| O(7') | 170(20) | 210(20) | 330(30) | 102(19) | -170(20) | -63(17) |
| O(8') | 132(13) | 240(17) | 122(12) | 86(14) | -63(9) | -7(11) |
| C(1) | 50(2) | 148(4) | 55(2) | 8(2) | -1(1) | -2(2) |
| C(2) | 46(2) | 131(3) | 59(2) | 17(2) | 0(1) | 7(2) |
| C(3) | 82(2) | 132(4) | 63(2) | 18(2) | 19(2) | 21(2) |
| C(4) | 57(2) | 156(4) | 68(2) | 27(2) | 16(2) | 1(2) |
| C(5) | 57(2) | 120(3) | 60(2) | 9(2) | 3(2) | -16(2) |
| C(6) | 62(2) | 90(2) | 56(2) | 9(2) | 4(1) | -11(2) |
| C(7) | 73(2) | 119(3) | 60(2) | 9(2) | 8(2) | -8(2) |
| C(8) | 96(3) | 111(3) | 61(2) | 14(2) | -3(2) | -9(2) |
| C(9) | 83(2) | 78(2) | 71(2) | 7(2) | -12(2) | -9(2) |
| C(10) | 67(2) | 130(3) | 80(3) | 17(2) | 1(2) | 5(2) |
| C(11) | 67(2) | 149(4) | 60(2) | 24(2) | 7(2) | -1(2) |
| C(12) | 97(5) | 167(6) | 105(4) | -6(5) | -6(4) | -46(4) |
| C(13) | 127(5) | 161(6) | 113(5) | -15(5) | -5(4) | -53(5) |

| | | | | | | |
|--------|--------|--------|--------|--------|--------|--------|
| C(12') | 98(5) | 167(6) | 105(5) | -7(5) | -7(4) | -43(5) |
| C(13') | 108(6) | 173(7) | 116(6) | -3(6) | -14(5) | -41(6) |
| C(14) | 75(2) | 134(4) | 53(2) | -2(2) | -2(2) | -21(2) |
| C(15) | 52(2) | 151(4) | 63(2) | 28(3) | -3(2) | 14(2) |
| C(16) | 71(2) | 178(5) | 85(3) | 48(3) | 24(2) | 42(3) |
| C(17) | 58(2) | 185(5) | 79(3) | 41(3) | 3(2) | -15(3) |
| C(18) | 75(2) | 114(3) | 60(2) | 9(2) | -5(2) | -24(2) |
| C(19) | 66(2) | 81(2) | 58(2) | 8(2) | -2(2) | 1(2) |
| C(20) | 89(2) | 97(3) | 61(2) | 13(2) | -2(2) | 9(2) |
| C(21) | 125(4) | 101(3) | 62(2) | 13(2) | -28(2) | 9(3) |
| C(22) | 116(4) | 68(2) | 100(3) | 15(2) | -54(3) | 3(2) |
| C(23) | 70(2) | 99(3) | 129(4) | 10(3) | -23(2) | -5(2) |
| C(24) | 71(2) | 116(3) | 79(2) | 1(2) | 0(2) | -11(2) |
| C(25) | 150(8) | 145(6) | 115(4) | -10(5) | -18(6) | -49(5) |
| C(26) | 168(8) | 160(7) | 130(5) | -9(5) | -22(6) | -45(6) |
| C(25') | 154(8) | 146(6) | 117(5) | -9(5) | -19(7) | -50(5) |
| C(26') | 171(8) | 151(7) | 130(5) | -12(6) | -17(6) | -43(6) |

Table S9. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for mo_d8v19977_0m.

| | x | y | z | U(eq) |
|--------|------|------|------|-------|
| H(1) | 5104 | 3075 | 6261 | 96 |
| H(2) | 5065 | 3963 | 6203 | 101 |
| H(3A) | 3852 | 3299 | 6925 | 111 |
| H(3B) | 4769 | 3069 | 6982 | 111 |
| H(4A) | 3316 | 2697 | 6706 | 112 |
| H(4B) | 3663 | 2550 | 6988 | 112 |
| H(7) | 4625 | 2194 | 7204 | 101 |
| H(8) | 5800 | 1967 | 7464 | 107 |
| H(10) | 7407 | 2006 | 6828 | 111 |
| H(11) | 6223 | 2229 | 6567 | 110 |
| H(12A) | 3555 | 1864 | 6784 | 148 |
| H(12B) | 3482 | 2001 | 6482 | 148 |
| H(13A) | 4696 | 1606 | 6381 | 200 |
| H(13B) | 3992 | 1312 | 6528 | 200 |
| H(13C) | 4827 | 1486 | 6684 | 200 |
| H(12C) | 4457 | 1684 | 6547 | 148 |
| H(12D) | 3945 | 1738 | 6817 | 148 |
| H(13D) | 2713 | 1990 | 6589 | 199 |
| H(13E) | 2987 | 1525 | 6490 | 199 |
| H(13F) | 3228 | 1933 | 6318 | 199 |
| H(16A) | 5703 | 3947 | 5486 | 134 |
| H(16B) | 6661 | 3873 | 5605 | 134 |
| H(17A) | 6393 | 4615 | 5497 | 129 |
| H(17B) | 6667 | 4553 | 5798 | 129 |
| H(20) | 5327 | 4625 | 5225 | 99 |
| H(21) | 4203 | 4481 | 4926 | 115 |
| H(23) | 2430 | 4456 | 5526 | 119 |
| H(24) | 3566 | 4600 | 5827 | 106 |
| H(25A) | 5436 | 5330 | 5591 | 164 |
| H(25B) | 4789 | 5318 | 5835 | 164 |
| H(26A) | 5872 | 5421 | 6120 | 229 |
| H(26B) | 6062 | 5743 | 5883 | 229 |

| | | | | |
|--------|------|------|------|-----|
| H(26C) | 6607 | 5309 | 5907 | 229 |
| H(25C) | 5975 | 5203 | 5950 | 167 |
| H(25D) | 5990 | 5261 | 5638 | 167 |
| H(26D) | 4406 | 5381 | 5687 | 226 |
| H(26E) | 5066 | 5761 | 5757 | 226 |
| H(26F) | 4649 | 5478 | 5986 | 226 |

Table S10. Torsion angles [°] for mo_d8v19977_0m.

| | |
|------------------------|------------|
| C(2)-N(1)-C(1)-O(1) | 173.4(3) |
| C(2)-N(1)-C(1)-C(5) | -7.1(5) |
| C(1)-N(1)-C(2)-O(2) | -177.0(3) |
| C(1)-N(1)-C(2)-C(3) | 2.8(5) |
| O(2)-C(2)-C(3)-C(4) | 153.7(3) |
| N(1)-C(2)-C(3)-C(4) | -26.2(4) |
| C(2)-C(3)-C(4)-C(5) | 54.4(4) |
| O(1)-C(1)-C(5)-C(12) | -33.5(7) |
| N(1)-C(1)-C(5)-C(12) | 147.0(6) |
| O(1)-C(1)-C(5)-C(6) | 90.4(4) |
| N(1)-C(1)-C(5)-C(6) | -89.1(4) |
| O(1)-C(1)-C(5)-C(4) | -148.0(4) |
| N(1)-C(1)-C(5)-C(4) | 32.5(4) |
| O(1)-C(1)-C(5)-C(12') | -22.9(10) |
| N(1)-C(1)-C(5)-C(12') | 157.6(9) |
| C(3)-C(4)-C(5)-C(12) | -172.8(11) |
| C(3)-C(4)-C(5)-C(1) | -56.1(4) |
| C(3)-C(4)-C(5)-C(6) | 63.9(4) |
| C(3)-C(4)-C(5)-C(12') | 179.5(15) |
| C(12)-C(5)-C(6)-C(11) | 100.3(12) |
| C(1)-C(5)-C(6)-C(11) | -21.9(5) |
| C(4)-C(5)-C(6)-C(11) | -140.1(4) |
| C(12')-C(5)-C(6)-C(11) | 97.7(17) |
| C(12)-C(5)-C(6)-C(7) | -75.2(12) |
| C(1)-C(5)-C(6)-C(7) | 162.6(4) |
| C(4)-C(5)-C(6)-C(7) | 44.4(5) |
| C(12')-C(5)-C(6)-C(7) | -77.8(17) |
| C(11)-C(6)-C(7)-C(8) | -2.0(6) |
| C(5)-C(6)-C(7)-C(8) | 173.8(4) |
| C(6)-C(7)-C(8)-C(9) | 0.8(6) |
| C(7)-C(8)-C(9)-C(10) | 0.7(6) |
| C(7)-C(8)-C(9)-S(1) | -179.2(3) |
| F(1')-S(1)-C(9)-C(10) | -104.0(17) |
| O(4)-S(1)-C(9)-C(10) | 50.0(8) |
| O(3')-S(1)-C(9)-C(10) | 129.9(11) |
| O(4')-S(1)-C(9)-C(10) | 8.8(10) |

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| O(3)-S(1)-C(9)-C(10) | -173.3(9) |
| F(1)-S(1)-C(9)-C(10) | -63.8(7) |
| F(1')-S(1)-C(9)-C(8) | 76.0(17) |
| O(4)-S(1)-C(9)-C(8) | -130.0(8) |
| O(3')-S(1)-C(9)-C(8) | -50.2(11) |
| O(4')-S(1)-C(9)-C(8) | -171.2(9) |
| O(3)-S(1)-C(9)-C(8) | 6.6(9) |
| F(1)-S(1)-C(9)-C(8) | 116.1(6) |
| C(8)-C(9)-C(10)-C(11) | -1.0(6) |
| S(1)-C(9)-C(10)-C(11) | 178.9(3) |
| C(7)-C(6)-C(11)-C(10) | 1.7(6) |
| C(5)-C(6)-C(11)-C(10) | -173.9(4) |
| C(9)-C(10)-C(11)-C(6) | -0.2(7) |
| C(1)-C(5)-C(12)-C(13) | 77.1(17) |
| C(6)-C(5)-C(12)-C(13) | -45(2) |
| C(4)-C(5)-C(12)-C(13) | -168.1(15) |
| C(12')-C(5)-C(12)-C(13) | -31(14) |
| C(12)-C(5)-C(12')-C(13') | 9(12) |
| C(1)-C(5)-C(12')-C(13') | -67(3) |
| C(6)-C(5)-C(12')-C(13') | 176(3) |
| C(4)-C(5)-C(12')-C(13') | 54(4) |
| C(15)-N(2)-C(14)-O(5) | -173.6(4) |
| C(15)-N(2)-C(14)-C(18) | 6.9(5) |
| C(14)-N(2)-C(15)-O(6) | -173.9(3) |
| C(14)-N(2)-C(15)-C(16) | 5.1(5) |
| O(6)-C(15)-C(16)-C(17) | -163.4(4) |
| N(2)-C(15)-C(16)-C(17) | 17.6(5) |
| C(15)-C(16)-C(17)-C(18) | -51.7(5) |
| C(16)-C(17)-C(18)-C(25') | 176.2(15) |
| C(16)-C(17)-C(18)-C(19) | -57.4(4) |
| C(16)-C(17)-C(18)-C(14) | 60.6(4) |
| C(16)-C(17)-C(18)-C(25) | -176.4(9) |
| O(5)-C(14)-C(18)-C(25') | 31.5(10) |
| N(2)-C(14)-C(18)-C(25') | -149.0(9) |
| O(5)-C(14)-C(18)-C(19) | -98.2(4) |
| N(2)-C(14)-C(18)-C(19) | 81.3(4) |
| O(5)-C(14)-C(18)-C(17) | 141.6(4) |
| N(2)-C(14)-C(18)-C(17) | -38.8(4) |

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|---------------------------|------------|
| O(5)-C(14)-C(18)-C(25) | 15.7(7) |
| N(2)-C(14)-C(18)-C(25) | -164.7(6) |
| C(25')-C(18)-C(19)-C(24) | -96.4(16) |
| C(17)-C(18)-C(19)-C(24) | 145.7(4) |
| C(14)-C(18)-C(19)-C(24) | 29.1(5) |
| C(25)-C(18)-C(19)-C(24) | -89.0(10) |
| C(25')-C(18)-C(19)-C(20) | 82.2(16) |
| C(17)-C(18)-C(19)-C(20) | -35.6(5) |
| C(14)-C(18)-C(19)-C(20) | -152.2(4) |
| C(25)-C(18)-C(19)-C(20) | 89.7(10) |
| C(24)-C(19)-C(20)-C(21) | -1.7(6) |
| C(18)-C(19)-C(20)-C(21) | 179.6(4) |
| C(19)-C(20)-C(21)-C(22) | 0.0(6) |
| C(20)-C(21)-C(22)-C(23) | 1.8(6) |
| C(20)-C(21)-C(22)-S(2) | 179.4(3) |
| O(8')-S(2)-C(22)-C(21) | -60.6(13) |
| O(7')-S(2)-C(22)-C(21) | 178.8(11) |
| O(7)-S(2)-C(22)-C(21) | -155.7(9) |
| F(2')-S(2)-C(22)-C(21) | 64.8(12) |
| F(2)-S(2)-C(22)-C(21) | 93.4(8) |
| O(8)-S(2)-C(22)-C(21) | -19.3(7) |
| O(8')-S(2)-C(22)-C(23) | 117.0(13) |
| O(7')-S(2)-C(22)-C(23) | -3.6(12) |
| O(7)-S(2)-C(22)-C(23) | 21.9(9) |
| F(2')-S(2)-C(22)-C(23) | -117.6(12) |
| F(2)-S(2)-C(22)-C(23) | -88.9(8) |
| O(8)-S(2)-C(22)-C(23) | 158.4(7) |
| C(21)-C(22)-C(23)-C(24) | -1.9(6) |
| S(2)-C(22)-C(23)-C(24) | -179.5(3) |
| C(22)-C(23)-C(24)-C(19) | 0.2(6) |
| C(20)-C(19)-C(24)-C(23) | 1.6(6) |
| C(18)-C(19)-C(24)-C(23) | -179.7(4) |
| C(25')-C(18)-C(25)-C(26) | -25(8) |
| C(19)-C(18)-C(25)-C(26) | -178.3(16) |
| C(17)-C(18)-C(25)-C(26) | -55(2) |
| C(14)-C(18)-C(25)-C(26) | 65.2(19) |
| C(19)-C(18)-C(25')-C(26') | 43(3) |
| C(17)-C(18)-C(25')-C(26') | 165(2) |

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|---------------------------|--------|
| C(14)-C(18)-C(25')-C(26') | -82(3) |
| C(25)-C(18)-C(25')-C(26') | 13(7) |

Symmetry transformations used to generate equivalent atoms:

Table S11. Hydrogen bonds for mo_d8v19977_0m [\AA and $^\circ$].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | $\angle(\text{DHA})$ |
|-----------------------|--------|----------|----------|----------------------|
| C(23)-H(23)...O(6)#1 | 0.93 | 2.50 | 3.188(6) | 131.0 |
| C(16)-H(16B)...O(2)#2 | 0.97 | 2.46 | 3.125(5) | 125.8 |
| N(2)-H(2)...O(2) | 0.86 | 2.03 | 2.891(4) | 173.8 |
| N(1)-H(1)...O(6) | 0.86 | 2.15 | 3.003(4) | 171.9 |

Symmetry transformations used to generate equivalent atoms:

#1 $-x+3/4, -y+3/4, z$ #2 $-x+5/4, y, -z+5/4$