Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

A Modular Synthesis of Functionalised Phenol Enabled by Controlled Boron Speciation

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Contents

1. General

All reagents and solvents were obtained from commercial suppliers and were used without further purification unless otherwise stated. Purification was carried out according to standard laboratory methods.[1]

1.1 Purification of Solvents

Dry THF was obtained from a PureSolv SPS-400-5 solvent purification system. This solvent was transferred to and stored in a septum-sealed oven-dried flask over previously activated 4 Å molecular sieves and purged with and stored under N_2. CH_2Cl_2, Et_2O, EtOAc, MeCN, and petroleum ether 40-60° for purification purposes were used as obtained from suppliers without further purification.

1.2 Drying of Inorganic Bases

K_3PO_4 was dried in a Heraeus Vacutherm oven at 60 °C under vacuum for a minimum of 24 hours before use.

1.3 Experimental Details

Reactions were carried out using conventional glassware (preparation of intermediates) or in capped 5 mL microwave vials (optimisation reactions and reactions for Table 1, Scheme 1, Figure 2, and Scheme 2). The glassware was oven-dried (150 °C) and purged with N_2 before use. Purging refers to a vacuum/nitrogen-refilling procedure. Room temperature was generally 18 °C. Reactions were carried out at elevated temperatures using a temperature-regulated hotplate/stirrer.

1.4 Purification of Products

Thin layer chromatography was carried out using Merck silica plates coated with fluorescent indicator UV254. These were analysed under 254 nm UV light or developed using potassium permanganate solution. Normal phase flash chromatography was carried out using ZEOprep 60 HYD 40-63 μm silica gel. Reverse phase flash chromatography was carried out using IST Isolute C18 cartridges.

1.5 Analysis of Products

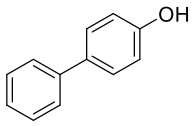
Fourier Transformed Infra-Red (FTIR) spectra were obtained on a Shimadzu IRAffinity-1 machine. ^{19}F NMR spectra were obtained on a Bruker AV 400 spectrometer at 376 MHz. ^{11}B NMR spectra were obtained on a Bruker AV 400 spectrometer at 128 MHz. ^{1}H and ^{13}C, NMR spectra were obtained on either a Bruker AV 400 at 400 MHz and 101 MHz, respectively, or Bruker DRX 500 at 500 MHz and 126 MHz, respectively. Chemical shifts are reported in ppm and coupling constants are reported in Hz: $CDCl_3$ is referenced at 7.26 (^{1}H) and 77.0 (^{13}C), DMSO-d_6 referenced at 2.50 (^{1}H) and 39.5 (^{13}C), and CD_3CN referenced at 1.94 (^{1}H) and 118.3, 1.3 (^{13}C). High-resolution mass spectra were

obtained through analysis at the EPSRC UK National Mass Spectrometry Facility at Swansea University. Reversed phase HPLC data was obtained on an Agilent 1200 series HPLC using a Machery-Nagel Nucleodur C18 column, which was maintained at a constant temperature of 40 °C. Analysis was performed using a gradient method, eluting with 5 – 80% MeCN/H_2O over 16 minutes at a flow rate of 2 mL/min. Samples for HPLC analysis were prepared through the addition of 2 mL of caffeine standard (to the completed reaction mixture, the resulting solution was then stirred before the removal of a 200 µL aliquot. The aliquot was diluted to 1 mL with MeCN, a 200 µL aliquot of the diluted solution was then filtered through cotton wool and further diluted with 800 µL MeCN and 500 µL H_2O for HPLC analysis against established conversion factors.

2. General Experimental Procedures

General Procedure A: Optimised Reaction (Scheme 1 and Figure 2)

For example, synthesis of [1,1'-biphenyl]-4-ol, **3a**



To an oven-dried 5 mL microwave vial was added 4-bromophenylboronic acid MIDA ester (70.6 mg, 0.226 mmol, 1 equiv), 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (69.3 mg, 0.339 mmol, 1.5 equiv), Pd(dppf)Cl_2·DCM (7.4 mg, 0.009 mmol, 4 mol%), and K_3PO_4 (144 mg, 0.678 mmol, 3 equiv). The vial was then capped and purged with N_2 before addition of THF (0.9 mL, 0.25 M) and H_2O (20 µL, 1.13 mmol, 5 equiv). The reaction mixture was then heated to 90 °C in a sand bath for 24 h. The reaction mixture was allowed to cool to room temperature then decapped, cooled to 0 ˚C, and 30% wt. aq. H_2O_2 (177 µL, 2.26 mmol, 10 equiv) was added dropwise. The reaction mixture was then stirred at room temperature for 3 h. The reaction mixture was then cooled to 0 ˚C and quenched with sodium metabisulphite (176 mg, 0.904 mmol, 4 equiv) before being concentrated under vacuum. The residue was then dissolved in EtOAc (10 mL) and washed with sat. aq. NH_4Cl (2x10 mL) and brine (10 mL). The aqueous washings were re-extracted with EtOAc (10 mL), the combined organics were filtered through a hydrophobic frit packed with Celite®, and concentrated under vacuum before being purified by column chromatography (C18 silica gel, 0-60% H_2O in MeCN) to afford the title compound as a white solid (31 mg, 80%).

υ_{max} (solid): 3399, 3098, 3062, 1597, 1485 cm^{-1}.

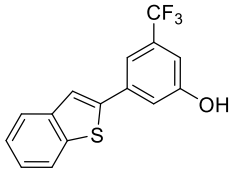
^{1}H NMR (CD_3CN, 500 MHz): δ 7.56-7.59 (m, 2H), 7.48-7.51 (m, 2H), 7.42 (t, *J* = 8.2 Hz, 2H), 7.30 (tt, *J* = 8.0, 2.0 Hz, 1H), 6.99 (s, 1H), 6.89 (d, *J* = 8.3 Hz, 2H).

^{13}C NMR (DMSO-d_6, 126 MHz): δ 157.1, 140.2, 130.9, 128.7, 127.7, 126.3, 125.9, 115.8.

HRMS: exact mass calculated for $[M-H]^-$ ($C_{12}H_9O$) requires *m/z* 169.0659, found *m/z* 169.0658.

General Procedure B: Optimised Reaction (Figure 2)

For example, synthesis of 3-(benzo[b]thiophen-2-yl)-5-(trifluoromethyl)phenol, **3b**



To an oven dried 5 mL microwave vial was added 3-bromo-5-(trifluoromethyl)phenylboronic acid MIDA ester (86 mg, 0.226 mmol, 1 equiv), benzo[b]thiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (88.2 mg, 0.339 mmol, 1.5 equiv), $Pd(OAc)_2$ (2 mg, 0.009 mmol, 4 mol%), SPhos (7.4 mg, 0.018 mmol, 8 mol%), and K_3PO_4 (144 mg, 0.678 mmol, 3 equiv). The vial was then capped and purged with N_2 before addition of THF (0.9 mL, 0.25 M) and H_2O (20 µL, 1.13 mmol, 5 equiv). The reaction mixture was then heated to 90 °C in a sand bath for 24 h. The reaction mixture was allowed to cool to room temperature then decapped, cooled to 0 ˚C, and 30% wt. aq. H_2O_2 (177 µL, 2.26 mmol, 10 equiv) was added dropwise. The reaction mixture was then stirred at room temperature for 3 h. The reaction mixture was then cooled to 0 ˚C and quenched with sodium metabisulphite (176 mg, 0.904 mmol, 4 equiv) before being concentrated under vacuum. The residue was then dissolved in EtOAc (10 mL) and washed with sat. aq. NH_4Cl (2x10 mL) and brine (10 mL). The aqueous washings were re-extracted with EtOAc (10 mL), the combined organics filtered through a hydrophobic frit packed with Celite®, and concentrated under vacuum before being purified by column chromatography (silica gel, 0-30% Et_2O in petroleum ether) to afford the title compound as an orange solid (58 mg, 88%).

υ_{max} (solid): 3305, 3067, 3052, 2923, 1610, 1450, 1439, 1351, 1327 cm^{-1}.

^{1}H NMR (CD_3CN, 500 MHz): δ 7.93 (d, *J* = 7.5 Hz, 1H), 7.86 (dd, *J* = 6.9, 1.6 Hz, 1H), 7.77 (s, 1H), 7.64 (s, 1H), 7.56 (s, 1H), 7.37 - 7.46 (m, 3H), 7.10 (s, 1H).

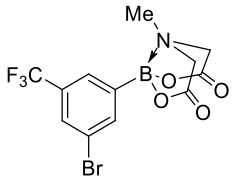
^{13}C NMR (CD_3CN, 126 MHz): δ 157.9, 141.9, 140.5, 139.4, 136.6, 132.1 (d, $^{2}J_{C\text{-}F}$ = 32.4 Hz), 125.2, 125.0, 124.0, 123.9 (d, $^{1}J_{C\text{-}F}$ = 271.8 Hz) 122.3, 121.4, 116.6, 114.3 (d, $^{3}J_{C\text{-}F}$ = 3.2 Hz) 111.9 (d, $^{3}J_{C\text{-}F}$ = 3.2 Hz).

^{19}F NMR (CD_3CN, 376 MHz): δ –64.24 (s, 3F).

HRMS: exact mass calculated for $[M\text{-}H]^-$ ($C_{15}H_8F_3OS$) requires *m/z* 293.0253, found *m/z* 293.0245.

General Procedure C: Synthesis of MIDA Esters from Boronic Acids

For example, for the preparation of 3-bromo-5-(trifluoromethyl)phenylboronic acid MIDA ester, **S1**



A mixture of 3-bromo-5-(trifluoromethyl)phenylboronic acid (2.0 g, 7.6 mmol, 1 equiv), *N*-methyliminodiacetic acid (1.17 g, 8 mmol, 1.05 equiv) in DMF (100 mL) was heated to 90 °C for 18 h under air. The reaction mixture was allowed to cool to room temperature and concentrated under vacuum to give an off-white slurry. EtOAc (100 mL) was added and the resulting precipitate was collected by filtration. The precipitate was washed with H_2O (2×50 mL) and Et_2O (2×50 mL) before being dried under vacuum to afford the title compound as a white crystalline solid (1.63 g, 57%).

υ_{max} (film): 3344, 3014, 2978, 1760, 1323, 1286, 1201, 1159, 1103, 1035 cm^{-1}.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 7.96 (s, 1H), 7.92 (s, 1H), 7.79 (s, 1H), 4.38 (d, *J* = 17.2 Hz, 2H), 4.21 (d, *J* = 17.2 Hz, 2H), 2.62 (s, 3H).

^{13}C NMR (DMSO-d_6, 101 MHz): δ 169.2, 139.4, 130.4 (d, $^{2}J_{C\text{-}F}$ = 31.9 Hz), 128.3 (d, $^{3}J_{C\text{-}F}$ = 3.7 Hz), 128.0 (d, $^{3}J_{C\text{-}F}$ = 3.1 Hz), 123.4 (d, $^{1}J_{C\text{-}F}$ = 272.8 Hz), 122.2, 62.4, 48.0. Carbon bearing boron not observed.

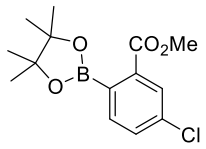
^{11}B NMR (DMSO-d_6, 128 MHz): δ 10.0.

^{19}F NMR (DMSO-d_6, 376 MHz): δ –61.0 (s, 3F).

HRMS: exact mass calculated for $[M+H]^+$ ($C_{12}H_{11}BBrF_3NO_4$) requires *m/z* 379.9911, found *m/z* 379.9911.

General Procedure D: Miyaura Borylation of Aryl Bromides

For example, for the preparation of methyl 5-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate, **S2**



Methyl 2-bromo-5-chlorobenzoate (3.15 g, 12.63 mmol, 1 equiv), bis(pinacolato)diboron (5.35 g, 13.89 mmol, 1.1 equiv), Pd(dppf)Cl_2·DCM (413 mg, 0.51 mmol, 4 mol%), and KOAc (3.72 g, 37.89 mmol, 3 equiv) were dissolved in 1,4-dioxane (80 mL) and degassed with N_2. The reaction was heated to 90 ˚C for 24 h. The mixture was cooled to room temperature, filtered through a plug of silica, washing with EtOAc (50 mL), and the filtrate evaporated. Purification of the residue by column chromatography (silica gel, 0-10% EtOAc in petroleum ether) afforded the title compound as a clear oil (2.76 g, 74%).

υ_{max} (film): 2978, 1721, 1344, 1294, 1258, 1142, 1096, 1055 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.94 (d, *J* = 2.0 Hz, 1H), 7.51 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 3.94 (s, 3H), 1.43 (s, 12H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ 166.8, 134.9, 134.8, 133.1, 131.3, 128.4, 83.8, 52.1, 24.4.

^{11}B NMR ($CDCl_3$, 128 MHz): δ 31.6.

HRMS: exact mass calculated for $[M+H]^+$ ($C_{14}H_{19}BClO_4$) requires *m/z* 297.1059, found *m/z* 297.1058.

General Procedure E: Oxidation of BPin

To an oven-dried 5 mL microwave vial was added 2-([1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (50 mg, 0.178 mmol, 1 equiv) and K_3PO_4 (114 mg, 0.534 mmol, 3 equiv). The reaction mixture was suspended in THF (0.6 mL, 0.3 M) and H_2O (16 µL, 0.892 mmol, 5 equiv). 30% wt. aq. H_2O_2 (139.5 µL, 1.78 mmol, 1 equiv) was added at 0 °C and the reaction was stirred at room temperature for 3 h. The reaction was quenched with sodium metabisulphite (135 mg, 0.712 mmol, 4 equiv) and the conversion to product(s) was determined by HPLC against an internal standard (caffeine).

General Procedure F: Oxidation of BMIDA

To an oven-dried 5 mL microwave vial was added 4-biphenylboronic acid MIDA ester (50 mg, 0.162 mmol, 1 equiv) and K_3PO_4 (103 mg, 0.486 mmol, 3 equiv). The reaction mixture was suspended in THF (0.54 mL, 0.3 M) and H_2O (14 µL, 0.81 mmol, 5 equiv). 30% wt. aq. H_2O_2 (126.4 µL, 1.62 mmol, 1 equiv) was added at 0 °C and the reaction was stirred at room temperature for 3 hours. The reaction was quenched with sodium metabisulphite (123 mg, 0.648 mmol, 4 equiv) and the conversion to product(s) was determined by HPLC against an internal standard (caffeine).

3. Reaction Optimisation Data

3.1 Oxidation of BPin – Oxidant Study

Reactions were carried out according to General Procedure E using 2-([1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (50 mg, 0.178 mmol, 1 equiv), K_3PO_4 (114 mg, 0.534 mmol, 3 equiv), THF (0.6 mL, 0.3 M), H_2O (16 µL, 0.892 mmol, 5 equiv), and **Oxidant** (1.78 mmol, 10 equiv).

Entry	Oxidant	Conversion
1	30% wt. aq. H_2O_2 (139.5 µL)	98%
2	aq. Oxone® (0.54 M, 3.3 mL)	9%
3	$NaBO_3 \cdot 4H_2O$ (274.5 mg)	18%
4	NaOCl (110 µL)	-
5	UHP (167 mg)	87%

3.2 Oxidation of BMIDA – Oxidant Study

Reactions were carried out according to General Procedure F using 4-biphenylboronic acid MIDA ester (50 mg, 0.162 mmol, 1 equiv), K_3PO_4 (103 mg, 0.486 mmol, 3 equiv), THF (0.54 mL, 0.3 M), H_2O (14 µL, 0.81 mmol, 5 equiv), and **Oxidant** (1.62 mmol, 10 equiv).

Entry	Oxidant	Conversion
1	30% wt. aq. H_2O_2 (126.4 µL)	10%
2	aq. Oxone® (0.54 M, 3 mL)	-
3	$NaBO_3 \cdot 4H_2O$ (274.5 mg)	1%
4	NaOCl (100 µL)	-
5	UHP (152 mg)	2%

3.3 BPin Oxidant Equivalent/Temperature Study

Reactions were carried out according to General Procedure E using 2-([1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (50 mg, 0.178 mmol, 1 equiv), K_3PO_4 (114 mg, 0.534 mmol, 3 equiv), THF (0.6 mL, 0.3 M), H_2O (16 µL, 0.892 mmol, 5 equiv), and **Oxidant** (**X equiv**). Reactions were run for 24 h.

Entry	Oxidant	Temperature	Conversion
1	30% wt. aq. H_2O_2 (14.0 µL, 0.178 mmol, 1 equiv)	r.t.	36%
2	30% wt. aq. H_2O_2 (41.9 µL, 0.534 mmol, 3 equiv)	r.t.	71%
3	30% wt. aq. H_2O_2 (69.8 µL, 0.89 mmol, 5 equiv)	r.t.	93%
4	30% wt. aq. H_2O_2 (139.5 µL, 1.78 mmol, 10 equiv)	r.t.	98%
5	30% wt. aq. H_2O_2 (14.0 µL, 0.178 mmol, 1 equiv)	50 °C	37%
6	30% wt. aq. H_2O_2 (41.9 µL, 0.534 mmol, 3 equiv)	50 °C	84%
7	30% wt. aq. H_2O_2 (69.8 µL, 0.89 mmol, 5 equiv)	50 °C	98%
8	30% wt. aq. H_2O_2 (139.5 µL, 1.78 mmol, 10 equiv)	50 °C	99%
9	aq. Oxone® (0.54 M, 0.33 mL, 0.178 mmol, 1 equiv)	r.t.	6%
10	aq. Oxone® (0.54 M, 0.99 mL, 0.534 mmol, 3 equiv)	r.t.	59%
11	aq. Oxone® (0.54 M, 1.65 mL, 0.89 mmol, 5 equiv)	r.t.	50%
12	aq. Oxone® (0.54 M, 3.3 mL, 1.78 mmol, 10 equiv)	r.t.	32%
13	aq. Oxone® (0.54 M, 0.33 mL, 0.178 mmol, 1 equiv)	50 °C	4%
14	aq. Oxone® (0.54 M, 0.99 mL, 0.534 mmol, 3 equiv)	50 °C	23%
15	aq. Oxone® (0.54 M, 1.65 mL, 0.89 mmol, 5 equiv)	50 °C	42%
16	aq. Oxone® (0.54 M, 3.3 mL, 1.78 mmol, 10 equiv)	50 °C	57%

3.4 BMIDA Oxidant Equivalent/Temperature Study

Reactions were carried out according to General Procedure F using 4-biphenylboronic acid MIDA ester (50 mg, 0.162 mmol, 1 equiv), K_3PO_4 (103 mg, 0.486 mmol, 3 equiv), THF (0.54 mL, 0.3 M), H_2O (14 µL, 0.81 mmol, 5 equiv), and **Oxidant** (**X equiv**). Reactions were run for 24 h.

Entry	Oxidant	Temperature	Conversion
1	30% wt. aq. H_2O_2 (12.6 µL, 0.162 mmol, 1 equiv)	r.t.	5%
2	30% wt. aq. H_2O_2 (37.9 µL, 0.486 mmol, 3 equiv)	r.t.	8%
3	30% wt. aq. H_2O_2 (63.2 µL, 0.81 mmol, 5 equiv)	r.t.	12%
4	30% wt. aq. H_2O_2 (126.4 µL, 1.62 mmol, 10 equiv)	r.t.	22%
5	30% wt. aq. H_2O_2 (12.6 µL, 0.162 mmol, 1 equiv)	50 °C	34%

6	30% wt. aq. H_2O_2 (37.9 µL, 0.486 mmol, 3 equiv)	50 °C	6%
7	30% wt. aq. H_2O_2 (63.2 µL, 0.81 mmol, 5 equiv)	50 °C	7%
8	30% wt. aq. H_2O_2 (126.4 µL, 1.62 mmol, 10 equiv)	50 °C	55%
9	aq. Oxone® (0.54 M, 0.3 mL, 0.162 mmol, 1 equiv)	r.t.	3%
10	aq. Oxone® (0.54 M, 0.9 mL, 0.486 mmol, 3 equiv)	r.t.	15%
11	aq. Oxone® (0.54 M, 1.5 mL, 0.81 mmol, 5 equiv)	r.t.	26%
12	aq. Oxone® (0.54 M, 3.0 mL, 1.62 mmol, 10 equiv)	r.t.	2%
13	aq. Oxone® (0.54 M,0.3 mL, 0.162 mmol, 1 equiv)	50 °C	3%
14	aq. Oxone® (0.54 M, 0.9 mL, 0.486 mmol, 3 equiv)	50 °C	29%
15	aq. Oxone® (0.54 M, 1.5 mL, 0.81 mmol, 5 equiv)	50 °C	70%
16	aq. Oxone® (0.54 M, 3.0 mL, 1.62 mmol, 10 equiv)	50 °C	76%

3.5 BPin Oxidation Time Study

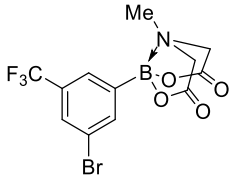
Reactions were carried out according to General Procedure E using 2-([1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (50 mg, 0.178 mmol, 1 equiv), K_3PO_4 (114 mg, 0.534 mmol, 3 equiv), THF (0.6 mL, 0.3 M), H_2O (16 µL, 0.892 mmol, 5 equiv), and 30% wt. aq. H_2O_2 (139.5 µL, 1.78 mmol, 10 equiv) for **X h**.

Entry	Time	Conversion
1	1.5 h	59%
2	2 h	68%
3	3 h	92%
4	18 h	93%
5	24 h	98%

4. Compound Characterisation Data

4.1 Intermediates

3-Bromo-5-(trifluoromethyl)phenylboronic acid MIDA ester, **S1**



Prepared according to General Procedure C using 3-bromo-5-(trifluoromethyl)phenylboronic acid (2.0 g, 7.6 mmol, 1 equiv) and *N*-methyliminodiacetic acid (1.17 g, 8 mmol, 1.05 equiv) in DMF (100 mL) to afford the title compound as a white crystalline solid (1.63 g, 57%).

υ_{max} (film): 3344, 3014, 2978, 1760, 1323, 1286, 1201, 1159, 1103, 1035 cm^{-1}.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 7.96 (s, 1H), 7.92 (s, 1H), 7.79 (s, 1H), 4.38 (d, J = 17.2 Hz, 2H), 4.21 (d, J = 17.2 Hz, 2H), 2.62 (s, 3H).

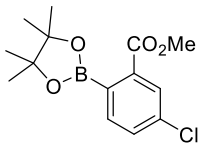
^{13}C NMR (DMSO-d_6, 101 MHz): δ 169.2, 139.4, 130.4 (d, $^{2}J_{C\text{-}F}$ = 31.9 Hz), 128.3 (d, $^{3}J_{C\text{-}F}$ = 3.7 Hz), 128.0 (d, $^{3}J_{C\text{-}F}$ = 3.1 Hz), 123.4 (d, $^{1}J_{C\text{-}F}$ = 272.8 Hz), 122.2, 62.4, 48.0. Carbon bearing boron not observed.

^{11}B NMR (DMSO-d_6, 128 MHz): δ 10.0.

^{19}F NMR (DMSO-d_6, 376 MHz): δ –61.0 (s, 3F).

HRMS: exact mass calculated for $[M+H]^+$ ($C_{12}H_{11}BBrF_3NO_4$) requires *m/z* 379.9911, found *m/z* 379.9911.

Methyl 5-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate, **S2**



Prepared according to General Procedure D using methyl 2-bromo-5-chlorobenzoate (3.15 g, 12.63 mmol, 1 equiv), bis(pinacolato)diboron (5.35 g, 13.89 mmol, 1.1 equiv), Pd(dppf)Cl_2·DCM (413 mg, 0.51 mmol, 4 mol%), and KOAc (3.72 g, 13.89 mmol, 3 equiv) in 1,4-dioxane (80 mL) to afford the title compound as a clear oil (2.76 g, 74%).

υ_{max} (film): 2978, 1721, 1344, 1294, 1258, 1142, 1096, 1055 cm^{-1}.

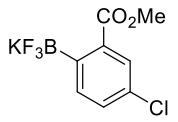
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.94 (d, J = 2.0 Hz, 1H), 7.51 (dd, J = 8.0, 2.0 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H), 3.94 (s, 3H), 1.43 (s, 12H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ 166.8, 134.9, 134.8, 133.1, 131.3, 128.4, 83.8, 52.1, 24.4.

^{11}B NMR ($CDCl_3$, 128 MHz): δ 31.6.

HRMS: exact mass calculated for $[M+H]^+$ ($C_{14}H_{19}BClO_4$) requires *m/z* 297.1059, found *m/z* 297.1058.

Potassium (4-chloro-2-(methoxycarbonyl)phenyl)trifluoroborate, **S3**



4-Chloro-2-(methoxycarbonyl)phenylboronic acid pinacol ester (**S2**, 2.7 g, 9.10 mmol, 1 equiv) was dissolved in MeOH (25 mL). Potassium hydrogen fluoride (4.5 M aq., 10.0 mL, 45.0 mmol, 5 equiv) was added and the resulting thick white slurry was stirred at room temperature for 30 min. The reaction mixture was then concentrated under vacuum. The residue was suspended in hot acetone and filtered. The filtrate was evaporated and the residue azeotroped with 1:1 MeOH:H_2O (30 mL) three times to afford the title compound (1.28 g, 51%) as a white solid.

υ_{max} (film): 1697, 1292, 1244 cm^{-1}.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 7.46 (d, *J* = 8.0 Hz, 1H), 7.25-7.29 (m, 1H), 7.21 (d, *J* = 2.5 Hz, 1H), 3.69 (s, 3H).

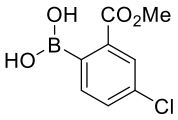
^{13}C NMR (DMSO-d_6, 101 MHz): δ 170.7, 138.5, 134.8, 129.5, 128.0, 125.2, 51.5. Carbon bearing boron not observed.

^{19}F NMR (DMSO-d_6, 376 MHz): δ –137.6 (s, 3F).

^{11}B NMR (DMSO-d_6, 128 MHz): δ 2.59.

HRMS: exact mass calculated for $[M-K]^-$ ($C_8H_6BClF_3O_2$) requires *m/z* 237.0107 found *m/z* 237.0104.

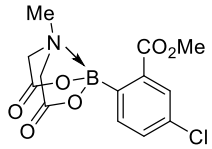
4-Chloro-2-(methoxycarbonyl)phenylboronic acid, **S4**



Potassium (4-chloro-2-(methoxycarbonyl)phenyl)trifluoroborate (**S3**, 1.25 g, 4.52 mmol, 1 equiv) was dissolved in MeCN (45 mL). H_2O (0.24 mL, 13.56 mmol, 3 equiv) and TMSCl (1.72 mL, 13.56 mmol, 3 equiv) were added and the reaction was stirred for 1 h at room temperature, then quenched with sat. aq. $NaHCO_3$ (7 mL). The mixture was diluted with EtOAc (40 mL), the organics were separated and washed with water (2x20 mL), and the aqueous extracts were re-extracted with EtOAc (2x10 mL). The combined organics were dried over Na_2SO_4, filtered, and concentrated to afford the crude title compound (967 mg, 100%), which was taken forward directly to the preparation of **S5**.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 7.98 (br. s., 2H), 7.83 (d, *J* = 2.0 Hz, 1H), 7.63 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 3.83 (s, 3H).

4-Chloro-2-(methoxycarbonyl)phenylboronic acid MIDA ester, **S5**



Prepared according to General Procedure C using 4-chloro-2-(methoxycarbonyl)phenylboronic acid (crude **S4**, 915 mg, 4.27 mmol, 1 equiv) and *N*-methyliminodiacetic acid (690 mg, 4.69 mmol, 1.1 equiv) in DMF (20 mL) to afford the title compound as an off-white solid (1.10 g, 79%).

υ_{max} (film): 1763, 1740, 1724, 1346, 1315, 1290, 1236, 1188, 1148, 1030 cm^{-1}.

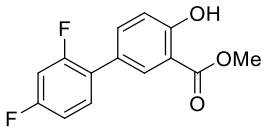
^{1}H NMR (DMSO-d_6, 400 MHz): δ 7.55-7.62 (m, 3H), 4.39 (d, *J* = 17.5 Hz, 2H), 4.17 (d, *J* = 17.5 Hz, 2H), 3.78 (s, 3H), 2.77 (s, 3H).

^{13}C NMR (DMSO-d_6, 101 MHz): δ 169.8, 169.4, 138.8, 136.5, 133.7, 129.8, 127.4, 63.9, 52.9, 49.4. Carbon bearing boron not observed.

^{11}B NMR (DMSO-d_6, 128 MHz): δ 10.9.

HRMS: exact mass calculated for $[M+H]^+$ ($C_{13}H_{14}BClNO_6$) requires *m/z* 326.0597, found *m/z* 326.0596.

Methyl 2',4'-difluoro-4-hydroxy-[1,1'-biphenyl]-3-carboxylate (Diflunisal methyl ester), **S6**



Prepared according to General Procedure B using 4-chloro-2-(methoxycarbonyl)phenylboronic acid MIDA ester (81 mg, 0.25 mmol, 1 equiv), 4,4,5,5-tetramethyl-2-(2,4-difluorophenyl)-1,3,2-dioxaborolane (90 mg, 0.375 mmol, 1.5 equiv), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol, 4 mol%), SPhos (8.2 mg, 0.02 mmol, 8 mol%), K_3PO_4 (159 mg, 0.75 mmol, 3 equiv), THF (1 mL, 0.25 M), H_2O (22.5 µL, 1.25 mmol, 5 equiv), and 30% wt. aq. H_2O_2 (195 µL, 2.5 mmol, 10 equiv). After 27 h, the reaction

mixture was subjected to the purification outlined in the General Procedure (silica gel, 0-5% Et_2O in petroleum ether) to afford the title compound as a white solid (33 mg, 50%).

υ_{max} (film): 3113, 1676, 1483, 1441, 1258, 1213, 1094 cm^{-1}.

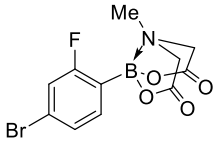
^1H NMR ($CDCl_3$, 400 MHz): δ 10.86 (s, 1H), 8.00 (dd, *J* = 2.1, 1.3 Hz, 1H), 7.63 (dt, *J* = 8.7, 2.0 Hz, 1H), 7.39 (td, *J* = 8.7, 6.4 Hz, 1H), 7.09 (d, *J* = 8.6 Hz, 1H), 6.89-7.00 (m, 2H), 4.00 (s, 3H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ 169.9, 161.7 (dd, $^1J_{C\text{-}F}$ = 250.0 Hz, $^3J_{C\text{-}F}$ = 11.0 Hz), 160.7, 159.2 (dd, $^1J_{C\text{-}F}$ = 250.0 Hz, $^3J_{C\text{-}F}$ = 11.0 Hz), 135.7, 130.6 (dd, $^3J_{C\text{-}F}$ = 11.0, 5.4 Hz), 129.7 (d, $^3J_{C\text{-}F}$ = 2.7 Hz), 125.6, 123.8 (dd, $^2J_{C\text{-}F}$ = 13.5 Hz, $J_{C\text{-}F}$ = 5.4 Hz), 117.4, 112.0, 111.2 (dd, $^2J_{C\text{-}F}$ = 21.5 Hz, $J_{C\text{-}F}$ = 2.7 Hz), 103.9 (dd, $^2J_{C\text{-}F}$ = 26.5, 26.5 Hz), 52.0.

^{19}F NMR ($CDCl_3$, 376 MHz): δ –111.4 (d, *J* = 7.4 Hz, 1F), –113.8 (d, *J* = 7.4 Hz, 1F).

HRMS: exact mass calculated for $[M\text{-}H]^-$ ($C_{14}H_9F_2O_3$) requires *m/z* 263.0525, found *m/z* 263.0520.

4-Bromo-2-fluorophenylboronic acid MIDA ester, **S7**



Prepared according to General Procedure D using 4-bromo-2-fluorophenylboronic acid (875 mg, 4 mmol, 1 equiv), *N*-methyliminodiacetic acid (618 mg, 4.2 mmol, 1.05 equiv), and DMF (50 mL) to afford the title compound as a white crystalline solid (994 mg, 75%).

υ_{max} (film): 3014, 2978, 1761, 1575, 1340, 1292, 1255, 1193, 1033 cm^{-1}.

^1H NMR (DMSO-d_6, 400 MHz): δ 7.40-7.48 (m, 3H), 4.42 (d, *J* = 17.3 Hz, 2H), 4.10 (d, *J* = 17.3 Hz, 2H), 2.63 (s, 3H).

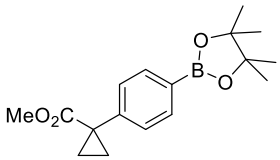
^{13}C NMR (DMSO-d_6, 101 MHz): δ 168.8, 165.3 (d, $^1J_{C\text{-}F}$ = 246.1), 136.4 (d, $^3J_{C\text{-}F}$ = 10.0 Hz), 127.4, 123.3 (d, $^3J_{C\text{-}F}$ = 10.0 Hz), 118.3 (d, $^2J_{C\text{-}F}$ = 28.8 Hz), 62.4, 47.5. Carbon bearing boron not observed.

^{11}B NMR (DMSO-d_6, 128 MHz): δ 10.7.

^{19}F NMR (DMSO-d_6, 376 MHz): δ –102.9 (s, 1F).

HRMS: exact mass calculated for $[M+H]^+$ ($C_{11}H_{11}BBrFNO_4$) requires *m/z* 329.9943, found *m/z* 329.9944.

Methyl 1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)cyclopropane-1-carboxylate, **S8**



Prepared according to General Procedure D using methyl 1-(4-bromophenyl)cyclopropanecarboxylate (2.50 g, 9.8 mmol, 1 equiv), bis(pinacolato)diboron (2.51 g, 9.9 mmol, 1.01 equiv), KOAc (2.88 g, 29.4 mmol, 3 equiv), Pd(dppf)Cl_2·CH_2Cl_2 (240 mg, 0.29 mmol, 0.03 equiv), and 1,4-dioxane (49 mL, 0.2 M). After 18 h, the reaction mixture was subjected to the purification outlined in the General Procedure (silica gel, 3-8% Et_2O in petroleum ether) to afford the title compound as a white solid (1.2 g, 40%).

υ_{max} (film): 2978, 1708, 1614, 1372, 1298, 1168, 1101 cm^{-1}.

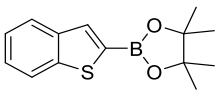
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.79 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 3.64 (s, 3H), 1.63 (q, *J* = 4.0 Hz, 2H), 1.36 (s, 12H), 1.22 (q, *J* = 4.0 Hz, 2H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 174.4, 142.1, 134.2, 129.4, 83.3, 51.9, 28.6, 24.3, 16.2. Carbon bearing boron not observed.

^{11}B NMR ($CDCl_3$, 128 MHz): δ 31.0.

HRMS: exact mass calculated for $[M+H]^+$ ($C_{17}H_{24}BO_4$) requires *m/z* 303.1762, found *m/z* 313.1767.

2-(Benzo[b]thiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, **S9**



A mixture of benzo[b]thiophene-2-boronic acid (1.25 g, 7 mmol, 1 equiv), pinacol (830 mg, 7 mmol, 1 equiv), and trifluoroacetic acid (53.7 µL, 0.7 mmol, 0.1 equiv) in Et_2O (35 mL, 0.2 M) was stirred at room temperature for 2 h under N_2. The mixture was then concentrated under vacuum to give a residue that was diluted with hexane (30 mL), filtered, and concentrated under vacuum to afford the title compound as an off-white solid (1.79 g, 98%).

υ_{max} (film): 2978, 1526, 1348, 1338, 1137 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.91-7.93 (m, 2H), 7.86-7.88 (m, 1H), 7.35-7.40 (m, 2H), 1.40 (s, 12H).

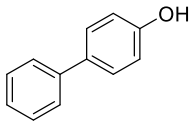
^{13}C NMR ($CDCl_3$, 101 MHz): δ 143.8, 140.5, 134.5, 125.3, 124.4, 124.1, 122.5, 84.5, 24.8. Carbon bearing boron not observed.

^{11}B NMR ($CDCl_3$, 128 MHz): δ 29.1.

HRMS: exact mass calculated for $[M+H]^+$ ($C_{14}H_{18}BO_2S$) requires *m/z* 261.1115, found *m/z* 261.1115.

4.2 Products from Figure 2 and Scheme 2

[1,1'-Biphenyl]-4-ol, **3a**



Prepared according to General Procedure A using 4-bromophenylboronic acid MIDA ester (70.6 mg, 0.226 mmol, 1 equiv), 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (69.3 mg, 0.339 mmol, 1.5 equiv), Pd(dppf)Cl_2·DCM (7.4 mg, 0.009 mmol, 4 mol%), K_3PO_4 (144 mg, 0.678 mmol, 3 equiv), THF (0.9 mL, 0.25 M), H_2O (20 µL, 1.13 mmol, 5 equiv) and 30% wt. aq. H_2O_2 (177 µL, 2.26 mmol, 10 equiv). After 27 h, the reaction mixture was subjected to the purification outlined in the General Procedure (C18 silica gel, 0-60% H_2O in MeCN) to afford the title compound as a white solid (31 mg, 80%).

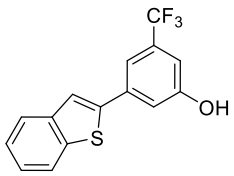
υ_{max} (solid): 3399, 3098, 3062, 1597, 1485 cm^{-1}.

^{1}H NMR (CD_3CN, 500 MHz): δ 7.56-7.59 (m, 2H), 7.48-7.51 (m, 2H), 7.42 (t, *J* = 8.2 Hz, 2H), 7.30 (tt, *J* = 8.0, 2.0 Hz, 1H), 6.99 (s, 1H), 6.89 (d, *J* = 8.3 Hz, 2H).

^{13}C NMR (DMSO-d_6, 126 MHz): δ 157.1, 140.2, 130.9, 128.7, 127.7, 126.3, 125.9, 115.8.

HRMS: exact mass calculated for $[M-H]^-$ ($C_{12}H_9O$) requires *m/z* 169.0659, found *m/z* 169.0658.

3-(Benzo[b]thiophen-2-yl)-5-(trifluoromethyl)phenol, **3b**



Prepared according to General Procedure B using 3-bromo-5-(trifluoromethyl)phenylboronic acid MIDA ester (86 mg, 0.226 mmol, 1 equiv), benzo[b]thiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (88.2 mg, 0.339 mmol, 1.5 equiv), $Pd(OAc)_2$ (2 mg, 0.01 mmol, 4 mol%), SPhos (7.4 mg, 0.02 mmol, 8 mol%), K_3PO_4 (144 mg, 0.678 mmol, 3 equiv), THF (0.9 mL, 0.25 M), H_2O (20 µL, 1.13 mmol, 5 equiv) and 30% wt. aq. H_2O_2 (177 µL, 2.26 mmol, 10 equiv). After 27 h, the reaction mixture was subjected to the purification outlined in the General Procedure (silica gel, 0-30% Et_2O in petroleum ether) to afford the title compound as an orange solid (58 mg, 88%).

υ_{max} (solid): 3305, 3067, 3052, 2923, 1610, 1450, 1439, 1351, 1327 cm^{-1}.

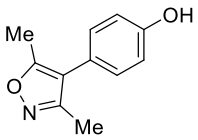
^1H NMR (CD_3CN, 500 MHz): δ 7.93 (d, J = 7.5 Hz, 1H), 7.86 (dd, J = 6.9, 1.6 Hz, 1H), 7.77 (s, 1H), 7.64 (s, 1H), 7.56 (s, 1H), 7.37-7.46 (m, 3H), 7.10 (s, 1H).

^{13}C NMR (CD_3CN, 126 MHz): δ 157.9, 141.9, 140.5, 139.4, 136.6, 132.2 (d, $^2J_{C\text{-}F}$ = 32.4 Hz), 132.1 (d, $^2J_{C\text{-}F}$ = 32.4 Hz), 125.2, 125.0, 124.0, 123.9 (d, $^1J_{C\text{-}F}$ = 271.8 Hz) 122.3, 121.4, 116.6, 114.3 (d, $^3J_{C\text{-}F}$ = 3.2 Hz) 111.9 (d, $^3J_{C\text{-}F}$ = 3.2 Hz).

^{19}F NMR (CD_3CN, 376 MHz): δ –64.2 (s, 3F).

HRMS: exact mass calculated for $[M\text{-}H]^-$ ($C_{15}H_8F_3OS$) requires *m/z* 293.0253, found *m/z* 293.0245.

4-(3,5-Dimethylisoxazol-4-yl)phenol, **3c**



Prepared according to General Procedure A using 4-bromophenylboronic acid MIDA ester (70.6 mg, 0.226 mmol, 1 equiv), 3,5-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)isoxazole (75.6 mg, 0.339 mmol, 1.5 equiv), $Pd(dppf)Cl_2$·DCM (7.4 mg, 0.009 mmol, 4 mol%), K_3PO_4 (144 mg, 0.678 mmol, 3 equiv), THF (0.9 mL, 0.25 M), H_2O (20 µL, 1.13 mmol, 5 equiv), and 30% wt. aq. H_2O_2 (177 µL, 2.26 mmol, 10 equiv). After 27 h, the reaction mixture was subjected to the purification outlined in the General Procedure (silica gel, 0-30% Et_2O in petroleum ether) to afford the title compound as a white solid (37 mg, 87%).

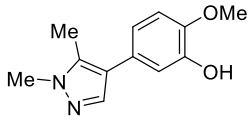
υ_{max} (solid): 3194, 3025, 2926, 1612, 1591, 1424 cm^{-1}.

^1H NMR (CD_3CN, 500 MHz): δ 7.18 (d, J = 8.8 Hz, 2H), 7.05 (br. s., 1H), 6.90 (d, J = 8.8 Hz, 2H), 2.35 (s, 3H), 2.20 (s, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 165.0, 158.9, 155.6, 130.4, 122.3, 116.4, 115.8, 11.5, 10.7.

HRMS: exact mass calculated for $[M+H]^+$ ($C_{11}H_{12}NO_2$) requires *m/z* 190.0863, found *m/z* 190.0861.

5-(1,5-Dimethyl-1*H*-pyrazol-4-yl)-2-methoxyphenol, **3d**



Prepared according to General Procedure B using 5-bromo-2-methoxyphenylboronic acid MIDA ester (85 mg, 0.25 mmol, 1 equiv), 1,5-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrazole (83 mg, 0.375 mmol, 1.5 equiv), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol, 4 mol%), SPhos (8.2 mg, 0.02 mmol, 8 mol%), K_3PO_4 (159 mg, 0.75 mmol, 3 equiv), THF (1 mL, 0.25 M), H_2O (22.5 µL, 1.25 mmol, 5 equiv), and 30% wt. aq. H_2O_2 (195 µL, 2.5 mmol, 10 equiv). After 27 h, the reaction mixture was subjected to the purification outlined in the General Procedure (silica gel, 20-70% EtOAc in petroleum ether) to afford the desired product as a white solid (42 mg, 77%).

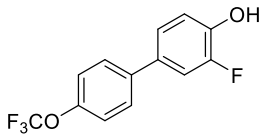
υ_{max} (film): 3341, 3204, 2920, 2851, 1464, 1034 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.53 (s, 1H), 6.96 (d, *J* = 2.0 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 6.85 (dd, *J* = 8.2, 2.0 Hz, 1H), 3.93 (s, 3H), 3.86 (s, 3H), 2.38 (s, 3H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ 145.3, 144.9, 136.4, 134.5, 126.8, 120.1, 118.9, 113.8, 110.6, 55.6, 35.9, 9.8.

HRMS: exact mass calculated for $[M+H]^+$ ($C_{12}H_{15}N_2O_2$) requires *m/z* 219.1128, found *m/z* 219.1126.

3-Fluoro-4'-(trifluoromethoxy)-[1,1'-biphenyl]-4-ol, **3e**



Prepared according to General Procedure A using 4-bromo-2-fluorophenylboronic acid MIDA ester (82.5 mg, 0.25 mmol, 1 equiv), 4,4,5,5-tetramethyl-2-(4-(trifluoromethoxy)phenyl)-1,3,2-dioxaborolane (86 mg, 0.375 mmol, 1.5 equiv), $Pd(dppf)Cl_2$·DCM (8.2 mg, 0.01 mmol, 4 mol%), K_3PO_4 (159 mg, 0.75 mmol, 3 equiv), THF (1 mL, 0.25 M), H_2O (22.5 µL, 1.25 mmol, 5 equiv), and 30% wt. aq. H_2O_2 (195 µL, 2.5 mmol, 10 equiv). After 27 h, the reaction mixture was subjected to the

purification outlined in the General Procedure (silica gel, 0-10% EtOAc in petroleum ether) to afford the title compound as a white solid (58 mg, 85%).

υ_{max} (film): 3395, 1503, 1256, 1200, 1159, 1117 cm^{-1}.

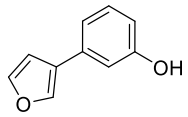
^1H NMR ($CDCl_3$, 400 MHz): δ 7.50-7.58 (m, 2H), 7.23-7.35 (m, 4H), 7.10 (t, *J* = 8.5 Hz, 1H), 5.23 (br. s., 1H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ 151.2 (d, $^1J_{C\text{-}F}$ = 237.0 Hz), 148.6, 143.3 (d, $^2J_{C\text{-}F}$ = 14.6 Hz), 138.5, 133.1 (d, $^3J_{C\text{-}F}$ = 5.9 Hz), 128.0, 123.4 (d, $^3J_{C\text{-}F}$ = 5.9 Hz), 121.3, 120.5 (q, $^1J_{C\text{-}F}$ = 257.5 Hz), 117.7, 114.2 (d, $^2J_{C\text{-}F}$ = 20.5 Hz).

^{19}F NMR ($CDCl_3$, 376 MHz): δ –57.8 (s, 3F), –140.4 (s, 1F).

HRMS: exact mass calculated for $[M]^+$ ($C_{13}H_8F_4O_2$) requires *m/z* 272.0455, found *m/z* 272.0459.

3-(Furan-3-yl)phenol, **3f**



Prepared according to General Procedure A using 3-bromophenylboronic acid MIDA ester (70.6 mg, 0.226 mmol, 1 equiv), 2-(furan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (65.8 mg, 0.339 mmol, 1.5 equiv), Pd(dppf)Cl_2·DCM (7.4 mg, 0.009 mmol, 4 mol%), K_3PO_4 (144 mg, 0.678 mmol, 3 equiv), THF (0.9 mL, 0.25 M), H_2O (20 µL, 1.13 mmol, 5 equiv), and 30% wt. aq. H_2O_2 (177 µL, 2.26 mmol, 10 equiv). After 27 h, the reaction mixture was subjected to the purification outlined in the General Procedure (silica gel, 0-30% Et_2O in petroleum ether) to afford the title compound as a white solid (32 mg, 87%).

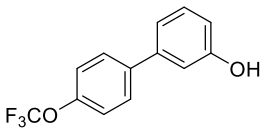
υ_{max} (solid): 3477, 3401, 3150, 3127, 1591, 1513, 1457 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ 7.72 (s, 1H), 7.47-7.50 (m, 1H), 7.26 (t, *J* = 7.9 Hz, 1H), 7.09 (td, *J* = 7.8, 1.1 Hz, 1H), 6.97-6.99 (m, 1H), 6.72-6.79 (m, 1H), 6.65-6.71 (m, 1H), 4.88 (br. s., 1H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 155.9, 143.7, 138.7, 134.1, 130.1, 126.1, 118.6, 113.9, 112.8, 108.9.

HRMS: exact mass calculated for $[M\text{-}H]^-$ ($C_{10}H_7O_2$) requires *m/z* 159.0452, found *m/z* 159.0448.

4'-(Trifluoromethoxy)-[1,1'-biphenyl]-3-ol, **3g**



Prepared according to General Procedure A using 3-bromophenylboronic acid MIDA ester (70.6 mg, 0.226 mmol, 1 equiv), 4,4,5,5-tetramethyl-2-(4-(trifluoromethoxy)phenyl)-1,3,2-dioxaborolane (97.7 mg, 0.339 mmol, 1.5 equiv), Pd(dppf)Cl_2·DCM (7.4 mg, 0.009 mmol, 4 mol%), K_3PO_4 (144 mg, 0.678 mmol, 3 equiv), THF (0.9 mL, 0.25 M), H_2O (20 µL, 1.13 mmol, 5 equiv), and 30% wt. aq. H_2O_2 (177 µL, 2.26 mmol, 10 equiv). After 27 h, the reaction mixture was subjected to the purification outlined in the General Procedure (C18 silica gel, 0-60% H_2O in MeCN) to afford the title compound as a pale yellow solid (47 mg, 81%).

υ_{max} (solid): 3304, 3047, 2928, 1597, 1485, 1457 cm^{-1}.

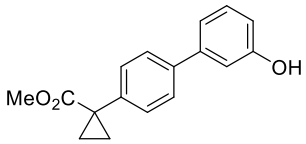
^{1}H NMR (CD_3CN, 500 MHz): δ 7.72-7.68 (m, 2H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.31 (t, *J* = 7.9 Hz, 1H), 7.15-7.12 (m, 1H), 7.09-7.07 (m, 2H), 6.89-6.83 (m, 1H).

^{13}C NMR (CD_3CN, 126 MHz): δ 157.4, 148.5, 141.0, 140.0, 130.2, 128.6, 121.3, 120.6 (d, $^1J_{C\text{-}F}$ = 255.3 Hz), 118.6, 114.7, 113.8, 29.4.

^{19}F NMR (CD_3CN, 376 MHz): δ –57.8 (s, 3F).

HRMS: exact mass calculated for $[M\text{-}H]^-$ ($C_{13}H_8F_3O$) requires *m/z* 253.0482, found *m/z* 253.0482.

Methyl 1-(3'-hydroxy-[1,1'-biphenyl]-4-yl)cyclopropane-1-carboxylate, **3h**



Prepared according to General Procedure A using 3-bromophenylboronic acid MIDA ester (70.6 mg, 0.226 mmol, 1 equiv), methyl 1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)cyclopropane-1-carboxylate (102.4 mg, 0.339 mmol, 1.5 equiv), Pd(dppf)Cl_2·DCM (7.4 mg, 0.009 mmol, 4 mol%), K_3PO_4 (144 mg, 0.678 mmol, 3 equiv), THF (0.9 mL, 0.25 M), H_2O (20 µL, 1.13 mmol, 5 equiv), and 30% wt. aq. H_2O_2 (177 µL, 2.26 mmol, 10 equiv). After 27 h, the reaction mixture was subjected to the purification outlined in the General Procedure (silica gel, 0-30% Et_2O in petroleum ether) to afford the title compound as a white solid (45 mg, 75%).

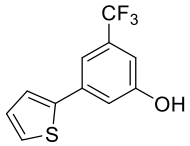
υ_{max} (solid): 3440, 3040, 2954, 2926, 2852 , 1698, 1590 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz) δ 7.51 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.27-7.32 (m, 1H), 7.15 (d, *J* = 7.9 Hz, 1H), 7.01-7.07 (m, 1H), 6.80 (dd, *J* = 8.0, 2.5 Hz, 1H), 3.66 (s, 3H), 1.63-1.66 (m, 2H), 1.22-1.25 (m, 2H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 175.2, 155.9, 142.6, 139.6, 138.8, 130.9, 129.9, 126.9, 119.7, 114.2, 114.0, 52.5, 28.7, 16.8.

HRMS: exact mass calculated for $[M-H]^-$ ($C_{17}H_{15}O_3$) requires *m/z* 267.1027, found *m/z* 267.1019.

3-(Thiophen-2-yl)-5-(trifluoromethyl)phenol, **3i**



Prepared according to General Procedure B using 3-bromo-5-(trifluoromethyl)phenylboronic acid MIDA ester (95 mg, 0.25 mmol, 1 equiv), 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane (79 mg, 0.375 mmol, 1.5 equiv), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol, 4 mol%), SPhos (8.2 mg, 0.02 mmol, 8 mol%), K_3PO_4 (159 mg, 0.75 mmol, 3 equiv), THF (1 mL, 0.25 M), H_2O (22.5 µL, 1.25 mmol, 5 equiv), and 30% wt. aq. H_2O_2 (195 µL, 2.5 mmol, 10 equiv). After 27 h, the reaction mixture was subjected to the purification outlined in the General Procedure (silica gel, 0-15% Et_2O in petroleum ether) to afford the title compound as a brown solid (53 mg, 87%).

υ_{max} (film): 3318, 1599, 1115, 1099 cm^{-1}.

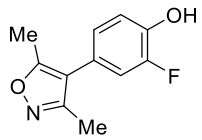
^1H NMR ($CDCl_3$, 400 MHz): δ 7.44-7.47 (m, 1H), 7.35-7.39 (m, 2H), 7.26 (t, *J* = 2.0 Hz, 1H), 7.13 (dd, *J* = 5.0, 3.5 Hz, 1H), 7.00-7.03 (m, 1H), 5.16 (s, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ 156.2, 142.3, 136.9, 132.7 (q, $^2J_{C-F}$ = 33.1 Hz), 128.2, 126.0, 124.4, 123.7 (q, $^1J_{C-F}$ = 272.1 Hz), 116.0, 115.3, 111.2.

^{19}F NMR ($CDCl_3$, 376 MHz): δ –62.9 (s, 3F).

HRMS: exact mass calculated for $[M-H]^-$ ($C_{11}H_6F_3OS$) requires *m/z* 243.0097, found *m/z* 243.0097.

4-(3,5-Dimethylisoxazol-4-yl)-2-fluorophenol, **3j**



Prepared according to General Procedure A using 4-bromo-2-fluorophenylboronic acid MIDA ester (82.5 mg, 0.25 mmol, 1 equiv), 4,4,5,5-tetramethyl-4-(3,5-dimethylisoxazol-4-yl)-1,3,2-dioxaborolane (84 mg, 0.375 mmol, 1.5 equiv), Pd(dppf)Cl_2·DCM (8.2 mg, 0.01 mmol, 4 mol%), K_3PO_4 (159 mg, 0.75 mmol, 3 equiv), THF (1 mL, 0.25 M), H_2O (22.5 µL, 1.25 mmol, 5 equiv), and 30% wt. aq. H_2O_2 (195 µL, 2.5 mmol, 10 equiv). After 27 h, the reaction mixture was subjected to the purification outlined in the General Procedure (silica gel, 10-20% Et_2O in petroleum ether) to afford the title compound as a white solid (41 mg, 79%).

υ_{max} (film): 3075, 1460, 1410, 1308, 1244, 1213, 1121 cm^{-1}.

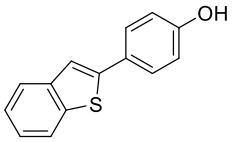
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.13-7.08 (m, 1H), 7.00 (dd, *J* = 11.5, 2.0 Hz, 1H), 6.94 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H), 5.98 (br. s., 1H), 2.42 (s, 3H), 2.28 (s, 3H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ 164.8, 158.2, 150.6 (d, $^1J_{C\text{-}F}$ = 237.0 Hz), 142.8 (d, $^2J_{C\text{-}F}$ = 16.2 Hz), 125.2 (d, $J_{C\text{-}F}$ = 2.7 Hz), 122.4 (d, $^3J_{C\text{-}F}$ = 8.1 Hz), 117.3 (d, $^3J_{C\text{-}F}$ = 5.4 Hz), 115.9 (d, $^2J_{C\text{-}F}$ =18.8 Hz), 115.2, 11.0, 10.2.

^{19}F NMR ($CDCl_3$, 376 MHz): δ –139.3 (s, 1F).

HRMS: exact mass calculated for $[M+H]^+$ ($C_{11}H_{11}FNO_2$) requires *m/z* 208.0768, found *m/z* 208.0768.

4-(Benzo[b]thiophen-2-yl)phenol, **3k**



Prepared according to General Procedure A using 4-bromophenylboronic acid MIDA ester (70.6 mg, 0.226 mmol, 1 equiv), 2-(benzo[b]thiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (88.2 mg, 0.339 mmol, 1.5 equiv), Pd(dppf)Cl_2·DCM (7.4 mg, 0.009 mmol, 4 mol%), K_3PO_4 (144 mg, 0.678 mmol, 3 equiv), THF (0.9 mL, 0.25 M), H_2O (20 µL, 1.13 mmol, 5 equiv), and 30% wt. aq. H_2O_2 (177 µL, 2.26 mmol, 10 equiv). After 27 h, the reaction mixture was subjected to the purification outlined in the General Procedure (silica gel, 0-30% Et_2O in petroleum ether) to afford the title compound as an off-white solid (47 mg, 92%).

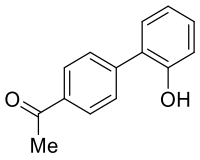
υ_{max} (solid): 3388, 3052, 3042, 2923, 1610, 1597, 1507 cm^{-1}.

^1H NMR (DMSO-d_6, 500 MHz): δ 9.78 (s, 1H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.63 (s, 1H), 7.57-7.61 (m, 2H), 7.35 (dt, *J* = 7.5, 1.3 Hz, 1H), 7.27-7.31 (m, 1H), 6.86 (d, *J* = 8.5 Hz, 2H).

^{13}C NMR (DMSO-d_6, 126 MHz): δ 158.5, 144.3, 141.2, 138.5, 128.0, 125.1, 125.0, 124.5, 123.7, 122.7, 118.3, 116.4.

HRMS: exact mass calculated for $[M-H]^-$ ($C_{14}H_9OS$) requires *m/z* 225.0380, found *m/z* 225.0385.

1-(2'-Hydroxy-[1,1'-biphenyl]-4-yl)ethanone, **3l**



Prepared according to General Procedure A using 2-bromophenylboronic acid MIDA ester (92 mg, 0.25 mmol, 1 equiv), 1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethanone (92 mg, 0.375 mmol, 1.5 equiv), Pd(dppf)Cl_2·DCM (8.2 mg, 0.01 mmol, 4 mol%), K_3PO_4 (159 mg, 0.75 mmol, 3 equiv), THF (1 mL, 0.25 M), H_2O (22.5 µL, 1.25 mmol, 5 equiv), and 30% wt. aq. H_2O_2 (195 µL, 2.5 mmol, 10 equiv). After 27 h, the reaction mixture was subjected to the purification outlined in the General Procedure (silica gel, 5-20% EtOAc in petroleum ether) to afford the title compound as a white solid (38 mg, 72%).

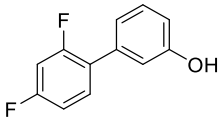
υ_{max} (film): 3285, 1667, 1479, 1277, 1190, 1179, 1155 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ 8.11-8.05 (m, 2H), 7.63-7.68 (m, 2H), 7.29-7.34 (m, 2H), 7.08-6.98 (m, 2H), 2.67 (s, 3H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ 197.4, 152.0, 142.1, 135.6, 129.9, 129.3, 128.9, 128.5, 126.7, 120.7, 115.8, 26.2.

HRMS: exact mass calculated for $[M+H]^+$ ($C_{14}H_{13}O_2$) requires *m/z* 213.0910, found *m/z* 213.0909.

2',4'-Difluoro-[1,1'-biphenyl]-3-ol, **3m**



Prepared according to General Procedure A using 3-bromophenylboronic acid MIDA ester (78 mg, 0.25 mmol, 1 equiv), 2-(2,4-difluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (90 mg, 0.375 mmol, 1.5 equiv), Pd(dppf)Cl_2·DCM (8.2 mg, 0.01 mmol, 4 mol%), K_3PO_4 (159 mg, 0.75 mmol, 3 equiv), THF (1 mL, 0.25 M), H_2O (22.5 µL, 1.25 mmol, 5 equiv), and 30% wt. aq. H_2O_2 (195 µL, 2.5 mmol, 10 equiv). After 27 h, the reaction mixture was subjected to the purification outlined in the General Procedure (silica gel, 0-10% Et_2O in petroleum ether) to afford the title compound as a white solid (43 mg, 83%).

υ_{max} (film) 3260, 1597, 1479, 1306, 1265, 1229, 1192, 1140, 1099 cm^{-1}.

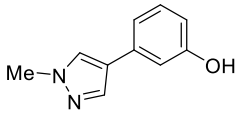
^1H NMR ($CDCl_3$, 400 MHz): δ 7.41 (td, J = 8.8, 6.5 Hz, 1H), 7.34 (t, J = 8.0 Hz, 1H), 7.10 (dq, J = 7.6, 1.5 Hz, 1H), 7.00-7.04 (m, 1H), 6.86-7.00 (m, 3H), 5.06 (s, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ 161.5 (dd, $^1J_{C\text{-}F}$ = 250.4 Hz, $^3J_{C\text{-}F}$ = 5.4), 159.2 (dd, $^1J_{C\text{-}F}$ = 250.4 Hz, $^3J_{C\text{-}F}$ = 5.4), 155.0, 136.1, 130.9 (dd, $^3J_{C\text{-}F}$ = 6.7, 5.4 Hz), 129.3, 124.4 (dd, $^2J_{C\text{-}F}$ = 18.9 Hz, $J_{C\text{-}F}$ = 5.4 Hz), 121.0, 115.5, 114.3, 111.0 (dd, $^2J_{C\text{-}F}$ = 21.5 Hz, $J_{C\text{-}F}$ = 2.7 Hz), 103.9 (dd, $^2J_{C\text{-}F}$ = 24.2, 26.9 Hz).

^{19}F NMR ($CDCl_3$, 376 MHz): δ –111.3 (d, J = 7.5 Hz, 1F), –113.2 (d, J = 7.5 Hz, 1F).

HRMS: exact mass calculated for $[M+H]^+$ ($C_{12}H_9F_2O$) requires *m/z* 207.0616, found *m/z* 207.0619.

3-(1-Methyl-1*H*-pyrazol-4-yl)phenol, **3n**



Prepared according to General Procedure A using 3-bromophenylboronic acid MIDA ester (70.6 mg, 0.226 mmol, 1 equiv), 1-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrazole (71.2 mg, 0.339 mmol, 1.5 equiv), Pd(dppf)Cl_2·DCM (7.4 mg, 0.009 mmol, 4 mol%), K_3PO_4 (144 mg, 0.678 mmol, 3 equiv), THF (0.9 mL, 0.25 M), H_2O (20 µL, 1.13 mmol, 5 equiv), and 30% wt. aq. H_2O_2 (177 µL, 2.26 mmol, 10 equiv). After 27 h, the reaction mixture was subjected to the purification outlined in the General Procedure (silica gel, 20-80% Et_2O in petroleum ether) to afford the title compound as a yellow solid (33 mg, 83%).

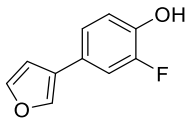
υ_{max} (solid): 3107, 2926, 2855, 1616, 1569, 1588, 1374 cm^{-1}.

^1H NMR (CD_3CN, 500 MHz): δ 7.79 (s, 1H), 7.72 (s, 1H), 7.19 (t, J = 8.0 Hz, 1H), 7.03 (td, J = 7.6, 1.4 Hz, 1H), 6.98-6.96 (m, 1H), 6.94 (br. s., 1H), 6.74-6.61 (m, 1H), 3.87 (s, 3H).

^{13}C NMR (DMSO-d_6, 126 MHz): δ 157.7, 135.9, 133.8, 129.7, 127.6, 122.0, 115.9, 113.0, 111.8, 38.6.

HRMS: exact mass calculated for $[M+H]^+$ ($C_{10}H_{11}N_2O$) requires *m/z* 175.0866, found *m/z* 175.0864.

2-Fluoro-4-(furan-3-yl)phenol, **3o**



Prepared according to General Procedure A using 4-bromo-2-fluorophenylboronic acid MIDA ester (83 mg, 0.25 mmol, 1 equiv), 2-(furan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (73 mg, 0.375 mmol, 1.5 equiv), Pd(dppf)Cl_2·DCM (8.2 mg, 0.01 mmol, 4 mol%), K_3PO_4 (159 mg, 0.75 mmol, 3 equiv), THF (1 mL, 0.25 M), H_2O (22.5 µL, 1.25 mmol, 5 equiv), and 30% wt. aq. H_2O_2 (195 µL, 2.5 mmol, 10 equiv). After 27 h, the reaction mixture was subjected to the purification outlined in the General Procedure (silica gel, 0-10% EtOAc in petroleum ether) to afford the title compound as off-white solid (32 mg, 72%).

υ_{max} (film): 3362, 1520, 1497, 1279, 1250, 1231, 1155, 1117, 1086, 1049, 1016 cm^{-1}.

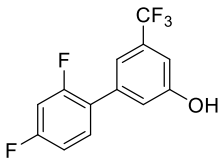
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.67 (dd, *J* = 1.4, 1.0 Hz, 1H), 7.48 (t, *J* = 1.7 Hz, 1H), 7.22 (dd, *J* = 11.5, 2.0 Hz, 1H), 7.18 (ddd, *J* = 8.4, 2.1, 1.0 Hz, 1H), 7.07-6.99 (m, 1H), 6.64 (dd, *J* = 1.8, 0.9 Hz, 1H), 5.14 (br. s., 1H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ 150.7 (d, $^1J_{C\text{-}F}$ = 237.0 Hz), 143.3, 141.9 (d, $^2J_{C\text{-}F}$ = 13.5 Hz), 137.6, 125.4 (d, $^2J_{C\text{-}F}$ = 8.1 Hz), 124.9 (d, $J_{C\text{-}F}$ = 2.7 Hz), 121.8 (d, $^3J_{C\text{-}F}$ = 5.4 Hz), 117.1, 112.6 (d, $^3J_{C\text{-}F}$ = 18.8 Hz), 108.3.

^{19}F NMR ($CDCl_3$, 376 MHz): δ –140.7 (s, 1F).

HRMS: exact mass calculated for $[M+H]^+$ ($C_{10}H_8FO_2$) requires *m/z* 179.0503, found *m/z* 179.0502.

3-(2,4-Difluorophenyl)-5-(trifluoromethyl)phenol, **3p**



Prepared according to General Procedure B using 3-bromo-5-(trifluoromethyl)phenylboronic acid MIDA ester (95 mg, 0.25 mmol, 1 equiv), 4,4,5,5-tetramethyl-2-(2,4-difluorophenyl)-1,3,2-dioxaborolane (90 mg, 0.375 mmol, 1.5 equiv), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol, 4 mol%), SPhos (8.2 mg, 0.02 mmol, 8 mol%), K_3PO_4 (159 mg, 0.75 mmol, 3 equiv), THF (1 mL, 0.25 M), H_2O (22.5 µL, 1.25 mmol, 5 equiv), and 30% wt. aq. H_2O_2 (195 µL, 2.5 mmol, 10 equiv). After 27 h, the reaction mixture was subjected to the purification outlined in the General Procedure (silica gel, 0-20% Et_2O in petroleum ether) to afford the title compound as a brown solid (60 mg, 88%).

υ_{max} (film): 3331, 1607, 1364, 1271, 1121, 1103 cm^{-1}.

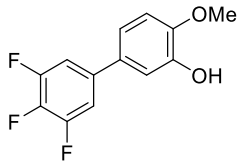
^1H NMR ($CDCl_3$, 400 MHz): δ 7.43 (td, J = 8.7, 6.3 Hz, 1H), 7.34 (s, 1H), 7.19 (d, J = 1.5 Hz, 1H), 7.14-7.11 (m, 1H), 7.03-6.92 (m, 2H), 5.30 (br. s, 1H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ 162.8 (dd, $^1J_{C\text{-}F}$ = 250.0 Hz, $^3J_{C\text{-}F}$ = 11.0 Hz), 159.7 (dd, $^1J_{C\text{-}F}$ = 250.0 Hz, $^3J_{C\text{-}F}$ = 11.0 Hz), 155.8, 137.4, 132.4 (q, $^2J_{C\text{-}F}$ = 33.1 Hz), 131.4 (dd, $^3J_{C\text{-}F}$ = 7.5, 7.5 Hz), 123.6 (dd, $^2J_{C\text{-}F}$ = 13.5 Hz, $J_{C\text{-}F}$ = 5.4 Hz), 123.7 (q, $^1J_{C\text{-}F}$ = 272.1 Hz), 119.3, 118.2, 111.9 (dd, $^2J_{C\text{-}F}$ = 21.5 Hz, $J_{C\text{-}F}$ = 3.0 Hz), 111.7, 104.6 (dd, $^2J_{C\text{-}F}$ = 25.7, 25.7 Hz).

^{19}F NMR ($CDCl_3$, 376 MHz): δ –62.8 (s, 3F), –109.7 (d, J = 8.0 Hz, 1F), –113.1 (d, J = 8.0 Hz, 1F).

HRMS: exact mass calculated for $[M+H]^+$ ($C_{13}H_8F_5O$) requires *m/z* 275.0490, found *m/z* 275.0490.

3',4',5'-Trifluoro-3-methoxy-[1,1'-biphenyl]-4-ol, **3q**



Prepared according to General Procedure B using 5-bromo-2-methoxyphenylboronic acid MIDA ester (85 mg, 0.25 mmol, 1 equiv), 4,4,5,5-tetramethyl-2-(3,4,5-trifluorophenyl)-1,3,2-dioxaborolane (97 mg, 0.375 mmol, 1.5 equiv), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol, 4 mol%), SPhos (8.2 mg, 0.02 mmol, 8 mol%), K_3PO_4 (159 mg, 0.75 mmol, 3 equiv), THF (1 mL, 0.25 M), H_2O (22.5 µL, 1.25 mmol, 5 equiv), and 30% wt. aq. H_2O_2 (195 µL, 2.5 mmol, 10 equiv). After 27 h, the reaction mixture was subjected to the purification outlined in the General Procedure (silica gel, 5-20% EtOAc in petroleum ether) to afford the title compound as an off-white solid (41 mg, 65%).

υ_{max} (film): 3530, 2941, 2361, 1503, 1263, 1231, 1211, 1136, 1038, 1022 cm^{-1}.

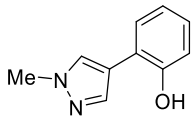
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.17-7.12 (m, 2H), 7.10 (d, J = 2.5 Hz, 1H), 7.01 (dd, J = 8.1, 2.5 Hz, 1H), 6.93 (d, J = 8.1 Hz, 1H), 5.73 (br. s., 1H), 3.96 (s, 3H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ 151.5 (ddd, $^{1}J_{C\text{-}F}$ = 248.9 Hz, $^{2}J_{C\text{-}F}$ = 10.0 Hz, $^{3}J_{C\text{-}F}$ = 4.1 Hz), 147.1, 146.2, 139.0 (dt, $^{1}J_{C\text{-}F}$ = 251.1 Hz, $^{2}J_{C\text{-}F}$ = 15.6 Hz), 137.1 (td, $^{3}J_{C\text{-}F}$ = 8.0 Hz, $J_{C\text{-}F}$ = 4.3 Hz), 131.8, 118.7, 113.2, 111.1, 110.7 (dd, $^{2}J_{C\text{-}F}$ = 15.8 Hz, $^{3}J_{C\text{-}F}$ = 6.0 Hz), 56.2.

^{19}F NMR ($CDCl_3$, 376 MHz): δ –134.5 (d, J = 20.4 Hz, 2F), –163.6 (t, J = 20.4 Hz, 1F).

HRMS: exact mass calculated for $[M\text{-}H]^-$ ($C_{13}H_8F_3O_2$) requires *m/z* 253.0482, found *m/z* 253.0477.

2-(1-Methyl-1*H*-pyrazol-4-yl)phenol, **3r**



Prepared according to General Procedure A using 2-bromophenylboronic acid MIDA ester (70.6 mg, 0.226 mmol, 1 equiv), 1-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrazole (71.2 mg, 0.339 mmol, 1.5 equiv), Pd(dppf)Cl_2·DCM (7.4 mg, 0.009 mmol, 4 mol%), K_3PO_4 (144 mg, 0.678 mmol, 3 equiv), THF (0.9 mL, 0.25 M), H_2O (20 μL, 1.13 mmol, 5 equiv), and 30% wt. aq. H_2O_2 (177 μL, 2.26 mmol, 10 equiv). After 27 h, the reaction mixture was subjected to the purification outlined in the General Procedure (silica gel, 20-80% Et_2O in petroleum ether) to afford the title compound as a yellow solid (30 mg, 75%).

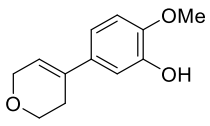
υ_{max} (solid): 3060, 2928, 2852, 1566, 1457, 1355 cm^{-1}.

^{1}H NMR (CD_3CN, 500 MHz): δ 7.96 (s, 1H), 7.82 (s, 1H), 7.51 (dd, J = 7.7, 1.7 Hz, 1H), 7.20 (s, 1H), 7.05-7.11 (m, 1H), 6.87-6.93 (m, 2H), 3.89 (s, 3H).

^{13}C NMR (CD_3CN, 126 MHz): δ 153.0, 137.3, 129.4, 127.4, 127.0, 120.2, 119.8, 118.3, 115.8, 38.3.

HRMS: exact mass calculated for $[M+H]^+$ ($C_{10}H_{11}N_2O$) requires *m/z* 175.0866, found *m/z* 175.0864.

5-(3,6-Dihydro-2*H*-pyran-4-yl)-2-methoxyphenol, **3s**



Prepared according to General Procedure B using (5-bromo-2-methoxyphenyl)boronic acid MIDA ester (85 mg, 0.25 mmol, 1 equiv), 2-(3,6-dihydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (79 mg, 0.375 mmol, 1.5 equiv), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol, 4 mol%), SPhos (8.2 mg, 0.02 mmol, 8 mol%), K_3PO_4 (159 mg, 0.75 mmol, 3 equiv), THF (1 mL, 0.25 M), H_2O (22.5 µL, 1.25 mmol, 5 equiv), and 30% wt. aq. H_2O_2 (195 µL, 2.5 mmol, 10 equiv). After 27 h, the reaction mixture was subjected to the purification outlined in the General Procedure (silica gel, 10-20% EtOAc in petroleum ether) to afford the title compound as an off-white solid (35 mg, 67%).

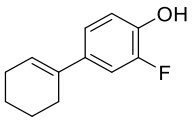
υ_{max} (film): 3302, 2916, 1510, 1276, 1118, 1028, 1014 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ 7.00 (d, *J* = 2.2 Hz, 1H), 6.89 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 6.03 (tt, *J* = 3.0, 1.5 Hz, 1H), 5.60 (br. s, 1H), 4.31 (q, *J* = 2.8 Hz, 2H), 3.92 (t, *J* = 5.5 Hz, 2H), 3.89 (s, 3H), 2.45-2.50 (m, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ 145.5, 145.0, 133.5, 132.9, 120.6, 115.9, 110.6, 109.9, 65.4, 64.0, 55.5, 26.7.

HRMS: exact mass calculated for $[M+H]^+$ ($C_{12}H_{15}O_3$) requires *m/z* 207.1016, found *m/z* 207.1012.

3-Fluoro-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-4-ol, **3t**



Prepared according to General Procedure A using 4-bromo-2-fluorophenylboronic acid MIDA ester (82.5 mg, 0.25 mmol, 1 equiv), 2-(cyclohex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (78 mg, 0.375 mmol, 1.5 equiv), $Pd(dppf)Cl_2$·DCM (8.2 mg, 0.01 mmol, 4 mol%), K_3PO_4 (159 mg, 0.75 mmol, 3 equiv), THF (1 mL, 0.25 M), H_2O (22.5 µL, 1.25 mmol, 5 equiv), and 30% wt. aq. H_2O_2 (195 µL, 2.5 mmol, 10 equiv). After 27 h, the reaction mixture was subjected to the purification outlined in the General Procedure (silica gel, 0-10% EtOAc in petroleum ether) to afford the title compound as an off-white solid (36 mg, 75%).

υ_{max} (film): 3314, 2928, 2859, 2359, 1593, 1516, 1431, 1290, 1267 cm^{-1}.

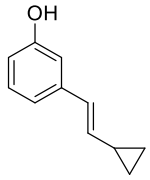
^1H NMR ($CDCl_3$, 400 MHz): δ 7.13 (dd, *J* = 12.5, 2.0 Hz, 1H), 7.08 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H), 6.99-6.89 (m, 1H), 6.10-6.04 (m, 1H), 5.18 (d, *J* = 3.5 Hz, 1H), 2.41-2.30 (m, 2H), 2.27-2.13 (m, 2H), 1.84-1.72 (m, 2H), 1.71-1.60 (m, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ 150.4 (d, $^{1}J_{C\text{-}F}$ = 237.0 Hz), 141.5 (d, $^{2}J_{C\text{-}F}$ = 16.2 Hz), 135.7 (d, $^{3}J_{C\text{-}F}$ = 8.1 Hz), 134.6 (d, $J_{C\text{-}F}$ = 2.7 Hz), 123.7, 120.6 (d, $^{3}J_{C\text{-}F}$ = 5.4 Hz), 116.2, 111.5 (d, $^{2}J_{C\text{-}F}$ = 18.8 Hz), 26.9, 25.3, 22.5, 21.6.

^{19}F NMR ($CDCl_3$, 376 MHz): δ –141.4 (s, 1F).

HRMS: exact mass calculated for $[M+H]^+$ ($C_{12}H_{14}FO$) requires *m/z* 193.1023, found *m/z* 193.1023.

(*E*)-3-(2-Cyclopropylvinyl)phenol, **3u**



Prepared according to General Procedure B using 3-bromophenylboronic acid MIDA ester (78 mg, 0.25 mmol, 1 equiv), (*E*)-2-(2-cyclopropylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (73 mg, 0.375 mmol, 1.5 equiv), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol, 4 mol%), SPhos (8.2 mg, 0.02 mmol, 8 mol%), K_3PO_4 (159 mg, 0.75 mmol, 3 equiv), THF (1 mL, 0.25 M), H_2O (22.5 µL, 1.25 mmol, 5 equiv), and 30% wt. aq. H_2O_2 (195 µL, 2.5 mmol, 10 equiv). After 27 h, the reaction mixture was subjected to the purification outlined in the General Procedure (silica gel, 0-15% EtOAc in petroleum ether) to afford the title compound as an off-white solid (29 mg, 72%).

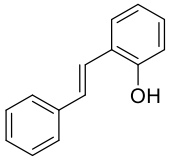
υ_{max} (film): 3321, 3005, 2359, 1649, 1607, 1580, 1491, 1449, 1277, 1252, 1229, 1153 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.17 (t, *J* = 8.0 Hz, 1H), 6.94-6.88 (m, 1H), 6.77-6.84 (m, 1H), 6.68 (ddd, *J* = 8.0, 2.5, 1.0 Hz, 1H), 6.43 (d, *J* = 15.7 Hz, 1H), 5.73 (dd, *J* = 15.7, 8.8 Hz, 1H), 4.99 (s, 1H), 1.64-1.52 (m, 1H), 0.89-0.81 (m, 2H), 0.57-0.49 (m, 2H).

^{13}C NMR ($CDCl_3$, 101 MHz): δ 155.2, 139.1, 135.1, 129.2, 126.5, 118.0, 113.1, 111.7, 14.0, 6.8.

HRMS: exact mass calculated for $[M+H]^+$ ($C_{11}H_{13}O$) requires *m/z* 161.0959, found *m/z* 161.0959.

(*E*)-2-Styrylphenol, **3v**



Prepared according to General Procedure A using 2-bromophenylboronic acid MIDA ester (70.6 mg, 0.226 mmol, 1 equiv), (*E*)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (78.0 mg, 0.339 mmol, 1.5 equiv), Pd(dppf)Cl_2·DCM (7.4 mg, 0.009 mmol, 4 mol%), K_3PO_4 (144 mg, 0.678 mmol, 3 equiv), THF (0.9 mL, 0.25 M), H_2O (20 µL, 1.13 mmol, 5 equiv), and 30% wt. aq. H_2O_2 (177 µL, 2.26 mmol, 10 equiv). After 27 h, the reaction mixture was subjected to the purification outlined in the General Procedure (silica gel, 0-30% Et_2O in petroleum ether) to afford the title compound as a yellow solid (38 mg, 85%).

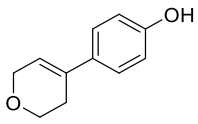
υ_{max} (solid): 3526, 3042, 2927, 1584, 1497, 1454, 1329 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ 7.52-7.57 (m, 3H), 7.35-7.41 (m, 3H), 7.28 (s, 1H), 7.11-7.19 (m, 2H), 6.97 (dt, *J* = 7.5, 0.8 Hz, 1H), 6.82 (dd, *J* = 8.2, 0.9 Hz, 1H), 4.97 (br. s., 1H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 153.0, 137.6, 130.2, 128.7, 127.7, 127.3, 126.6, 124.7, 123.0, 121.2, 116.0.

HRMS: exact mass calculated for $[M-H]^-$ ($C_{14}H_{11}O$) requires *m/z* 195.0815, found *m/z* 195.0821.

4-(3,6-Dihydro-2*H*-pyran-4-yl)phenol, **3w**



Prepared according to General Procedure A using 4-bromophenylboronic acid MIDA ester (70.6 mg, 0.226 mmol, 1 equiv), 2-(3,6-dihydro-2*H*-pyran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (71.2 mg, 0.339 mmol, 1.5 equiv), Pd(dppf)Cl_2·DCM (7.4 mg, 0.009 mmol, 4 mol%), K_3PO_4 (144 mg, 0.678 mmol, 3 equiv), THF (0.9 mL, 0.25 M), H_2O (20 µL, 1.13 mmol, 5 equiv), and 30% wt. aq. H_2O_2 (177 µL, 2.26 mmol, 10 equiv). After 27 h, the reaction mixture was subjected to the purification outlined in the General Procedure (silica gel, 0-30% Et_2O in petroleum ether) to afford the title compound as a white solid (48 mg, 93%).

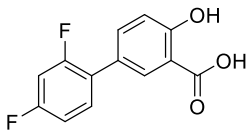
υ_{max} (solid): 3271, 2924, 2872, 1610, 1588, 1515, 1442 cm^{-1}.

^1H NMR (CD_3CN, 500 MHz): δ 7.30 (d, *J* = 8.8 Hz, 2H), 6.91 (br. s., 1H), 6.79 (d, *J* = 8.8 Hz, 2H), 6.06 (tt, *J* = 2.9, 1.5 Hz, 1H), 4.23 (q, *J* = 2.8 Hz, 2H), 3.86 (t, *J* = 5.5 Hz, 2H), 2.47-2.42 (m, 2H).

^{13}C NMR (CD_3CN, 126 MHz): δ 156.3, 133.3, 132.1, 125.8, 120.4, 115.1, 65.4, 64.0, 26.9.

HRMS: exact mass calculated for $[M+H]^+$ ($C_{11}H_{13}O_2$) requires *m/z* 177.0910, found *m/z* 177.0906.

2',4'-Difluoro-4-hydroxy-[1,1'-biphenyl]-3-carboxylic acid (Diflunisal), **7**



To a solution of methyl 2',4'-difluoro-4-hydroxy-[1,1'-biphenyl]-3-carboxylate (13 mg, 0.049 mmol, 1 equiv) in THF (1 mL) and water (1 mL) was added KOH (3 mg, 0.054 mmol, 1.1 equiv). The reaction was heated to 80 ˚C for 3 h before being allowed to cool to room temperature and concentrated under vacuum. The residue was partitioned between EtOAc (10 mL) and 2 M HCl (5 mL) and the aqueous extracted with EtOAc (2x10 mL). The combined organics were dried through a hydrophobic frit and evaporated to dryness to afford the desired product (12 mg, 98%) as a white solid.

υ_{max} (film): 2961, 2614, 1668, 1618, 1587, 1483, 1449, 1300, 1267, 1236, 1209 cm^{-1}.

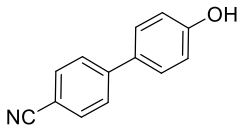
^1H NMR (DMSO-d_6, 400 MHz): δ 7.94-7.91 (m, 1H), 7.70-7.67 (m, 1H), 7.59 (td, *J* = 8.9, 6.6 Hz, 1H), 7.35 (ddd, *J* = 11.4, 9.1, 2.5 Hz, 1H), 7.21-7.16 (m, 1H), 7.08 (d, *J* = 8.5 Hz, 1H). Exchangeable protons were not observed.

^{13}C NMR (DMSO-d_6, 101 MHz): δ 171.5, 160.7, 160.1, 161.5 (dd, $^1J_{C\text{-}F}$ = 250.0 Hz, $^3J_{C\text{-}F}$ = 11.0 Hz), 159.0 (dd, $^1J_{C\text{-}F}$ = 250.0 Hz, $^3J_{C\text{-}F}$ = 11.0 Hz), 135.8, 131.5 (dd, $^3J_{C\text{-}F}$ = 5.4 Hz, $^3J_{C\text{-}F}$ = 8.8 Hz), 130.3, 125.1, 123.7 (dd, $^2J_{C\text{-}F}$ = 17.6 Hz, $J_{C\text{-}F}$ = 2.7 Hz), 117.6, 113.2, 112.0 (dd, $^2J_{C\text{-}F}$ = 20.5 Hz, $J_{C\text{-}F}$ = 2.7 Hz), 104.5 (dd, $^2J_{C\text{-}F}$ = 26.5, 26.5 Hz).

^{19}F NMR (DMSO-d_6, 376 MHz): δ -111.40 (d, *J* = 8.2 Hz, 1F), -114.17 (d, *J* = 8.2 Hz, 1F).

HRMS: exact mass calculated for $[M-H]^-$ ($C_{13}H_7F_2O_3$) requires *m/z* 249.0369, found *m/z* 249.0370.

4'-Hydroxy-[1,1'-biphenyl]-4-carbonitrile, **8**



Prepared according to General Procedure A using 4-bromophenylboronic acid MIDA ester (78 mg, 0.25 mmol, 1 equiv), 2-(4-cyanophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (86 mg, 0.375 mmol, 1.5 equiv), Pd(dppf)Cl_2·DCM (8.2 mg, 0.01 mmol, 4 mol%), K_3PO_4 (159 mg, 0.75 mmol, 3

equiv), THF (1 mL, 0.25 M), H_2O (22.5 µL, 1.25 mmol, 5 equiv), and 30% wt. aq. H_2O_2 (195 µL, 2.5 mmol, 10 equiv). After 27 h, the reaction mixture was subjected to the purification outlined in the General Procedure (silica gel, 0-15% Et_2O in petroleum ether) to afford the desired product as a white solid (39 mg, 80%).

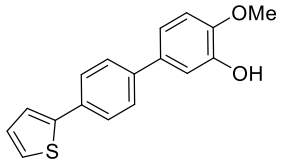
υ_{max} (film): 3375, 2228, 1601, 1587, 1491, 1204, 1179 cm^{-1}.

^1H NMR (DMSO-d_6, 400 MHz) δ 9.79 (s, 1H), 7.85 (d, *J* = 8.5 Hz, 2H), 7.82 (dd, *J* = 22.4, 8.7 Hz, 4H), 6.89 (d, *J* = 8.5 Hz, 2H).

^{13}C NMR (DMSO-d_6, 101 MHz): δ 158.3, 144.6, 132.7, 128.8, 128.3, 126.5, 119.1, 116.0, 108.7.

HRMS: exact mass calculated for $[M-H]^-$ ($C_{13}H_8NO$) requires *m/z* 194.0611, found *m/z* 194.0606.

4-Methoxy-4'-(thiophen-2-yl)-[1,1'-biphenyl]-3-ol, **9**



To an oven dried 5 mL microwave vial was added 4-bromophenylboronic acid MIDA ester (78 mg, 0.25 mmol, 1 equiv), 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane (79 mg, 0.375 mmol, 1.5 equiv), Pd(dppf)Cl_2·DCM (8.2 mg, 0.01 mmol, 4 mol%), and K_3PO_4 (159 mg, 1 mmol, 4 equiv). The vial was then capped and purged with N_2 before addition of THF (1 mL, 0.25 M) and H_2O (90 µL, 5 mmol, 20 equiv). The reaction mixture was then heated to 90 °C in a sand bath for 24 h. The reaction mixture was allowed to cool to room temperature before adding (5-bromo-2-methoxyphenyl)boronic acid MIDA ester (85 mg, 0.25 mmol, 1 equiv). The vial was then recapped and purged again with N_2 before being heated to 90 °C for a further 24 h. The reaction mixture was allowed to cool to room temperature then decapped, cooled to 0 ˚C and 30% wt. aq. H_2O_2 (195 µL, 2.5 mmol, 10 equiv) was added dropwise. The reaction mixture was then stirred at room temperature for 3 h. The reaction mixture was then cooled to 0 ˚C and quenched with sodium metabisulphite (190 mg, 1 mmol, 4 equiv) before being concentrated under vacuum. The residue was then dissolved in EtOAc (10 mL) and washed with sat. aq. NH_4Cl (2x10 mL) and brine (10 mL). The aqueous extracts were extracted with EtOAc (10 mL), the combined organics filtered through a hydrophobic frit packed with Celite® and concentrated under vacuum before being purified by column chromatography (silica gel, 10-20% Et_2O in petroleum ether) to afford the title compound as an off-white solid (64 mg, 91%).

υ_{max} (film): 3377, 2980, 1502, 1263, 1219 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.55-7.49 (m, 2H), 7.23 (ddd, *J* = 4.8, 4.3, 1.1 Hz, 2H), 7.10-7.06 (m, 2H), 6.99 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.89-6.85 (m, 2H), 6.74 (d, *J* = 8.6 Hz, 1H), 5.65 (br. s., 1H), 3.90 (s, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 154.6, 146.0, 145.4, 143.7, 127.4, 127.1, 127.0, 123.4, 122.3, 121.6, 117.4, 115.3, 112.8, 111.4, 55.6

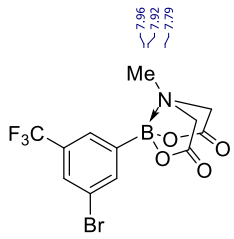
HRMS: exact mass calculated for $[M+H]^+$ ($C_{17}H_{15}O_2S$) requires *m/z* 283.0787, found *m/z* 283.0788.

5. References

1. W. L. F. Armarego and C. Chai, *Purification of Laboratory Chemicals, 7th ed.*, Elsevier, Oxford, 2013.

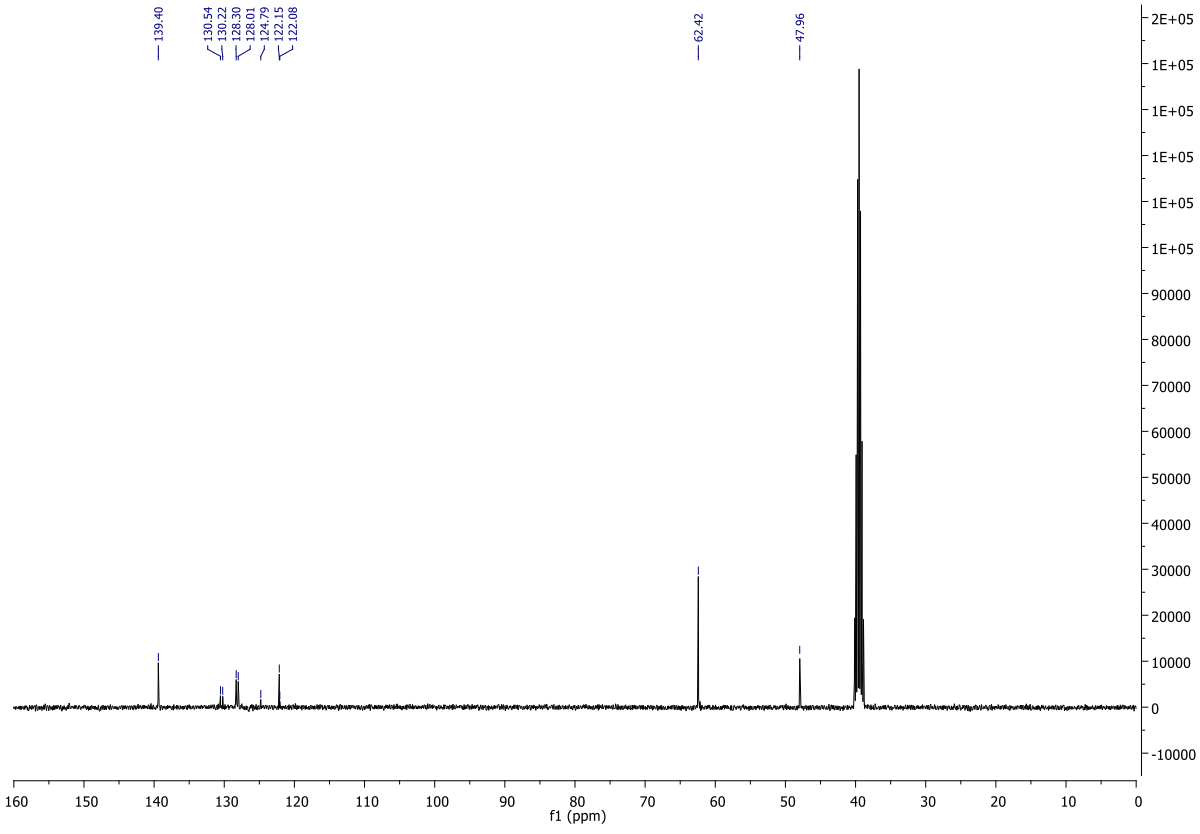
6. NMR and HRMS spectra for intermediates and products

^{1}H NMR of S1, DMSO-d_6, 400 MHz

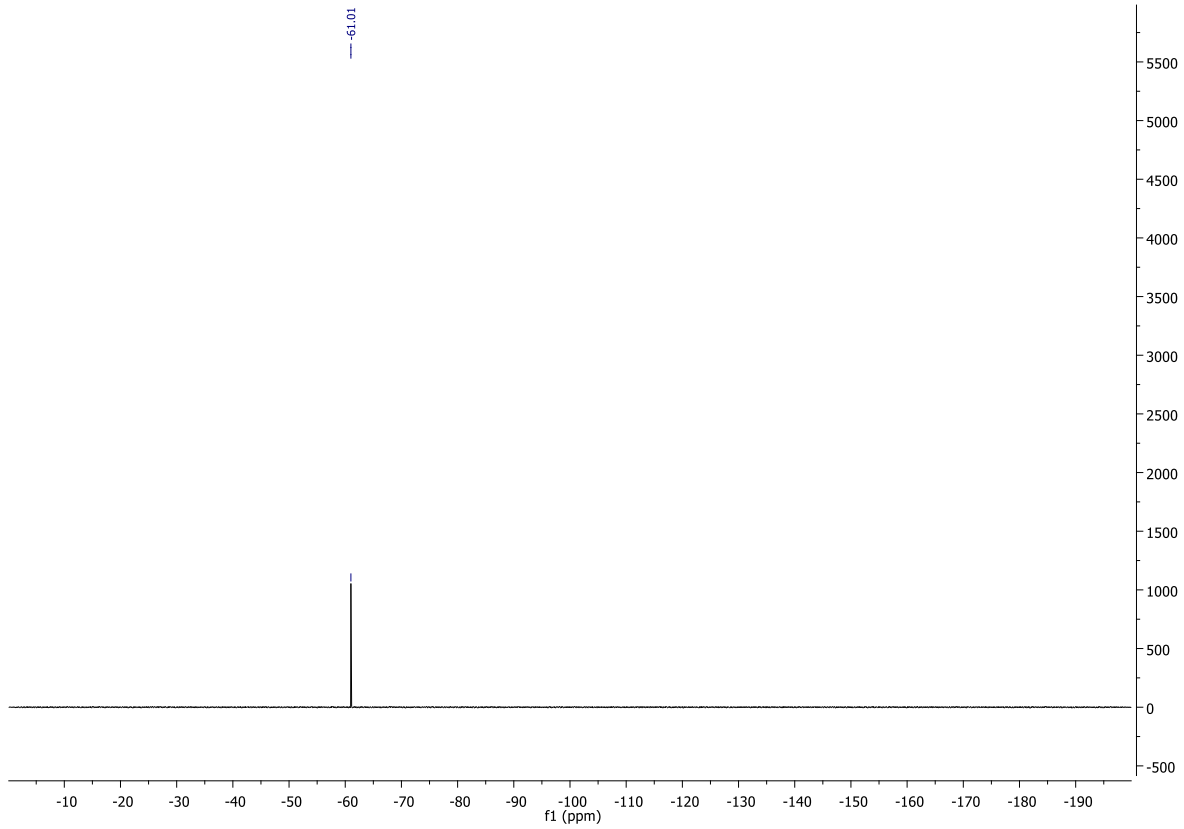


S1

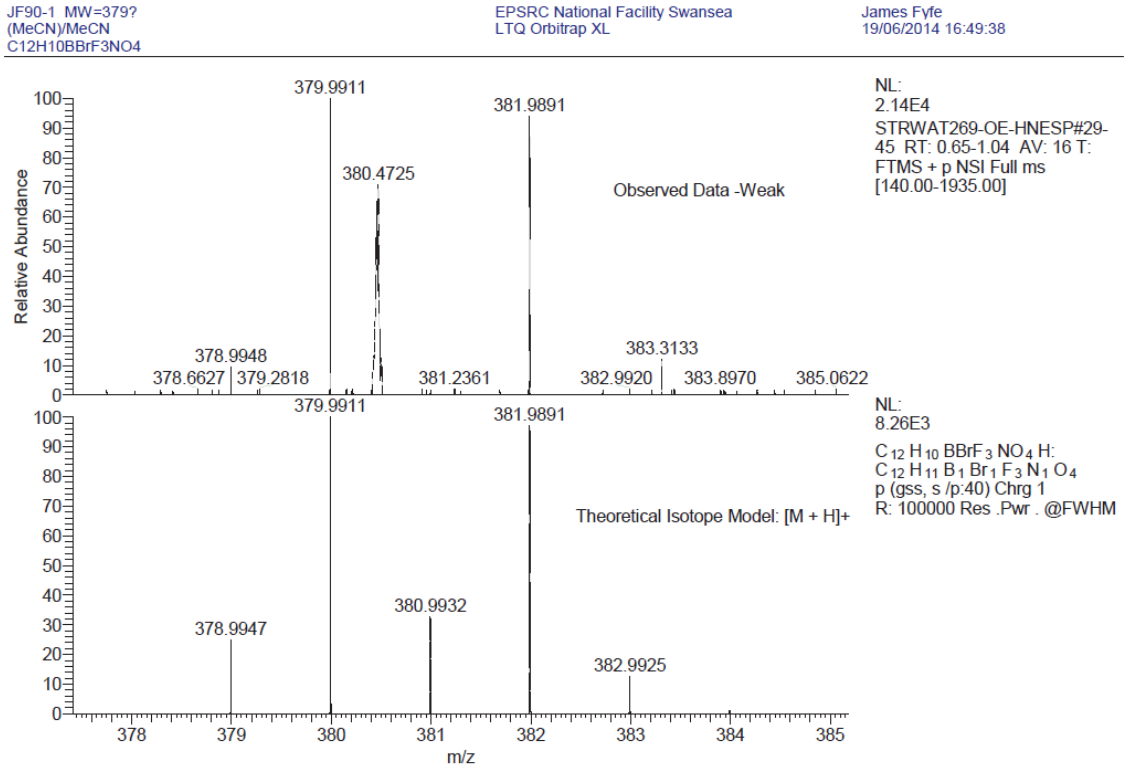
^{13}C NMR of S1, DMSO-d_6, 101 MHz



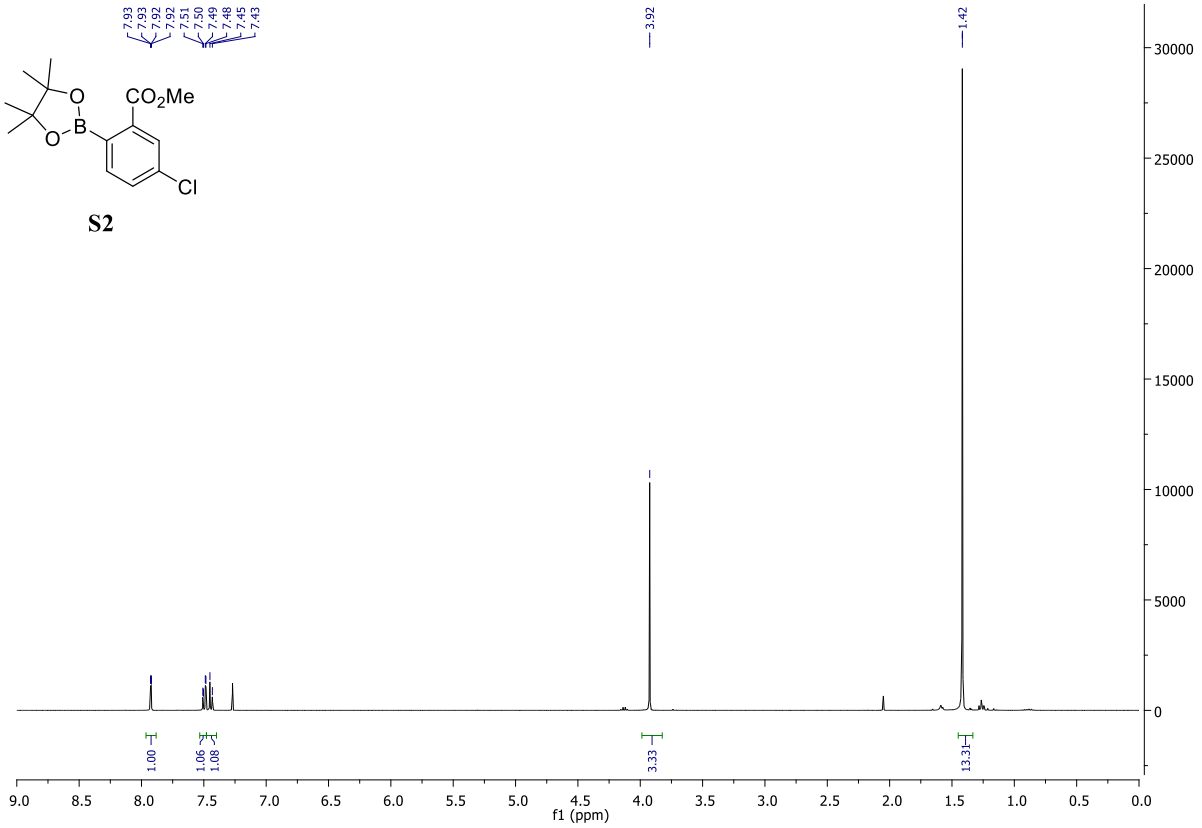
^{19}F NMR of S1, DMSO-d_6, 376 MHz



HRMS of S1

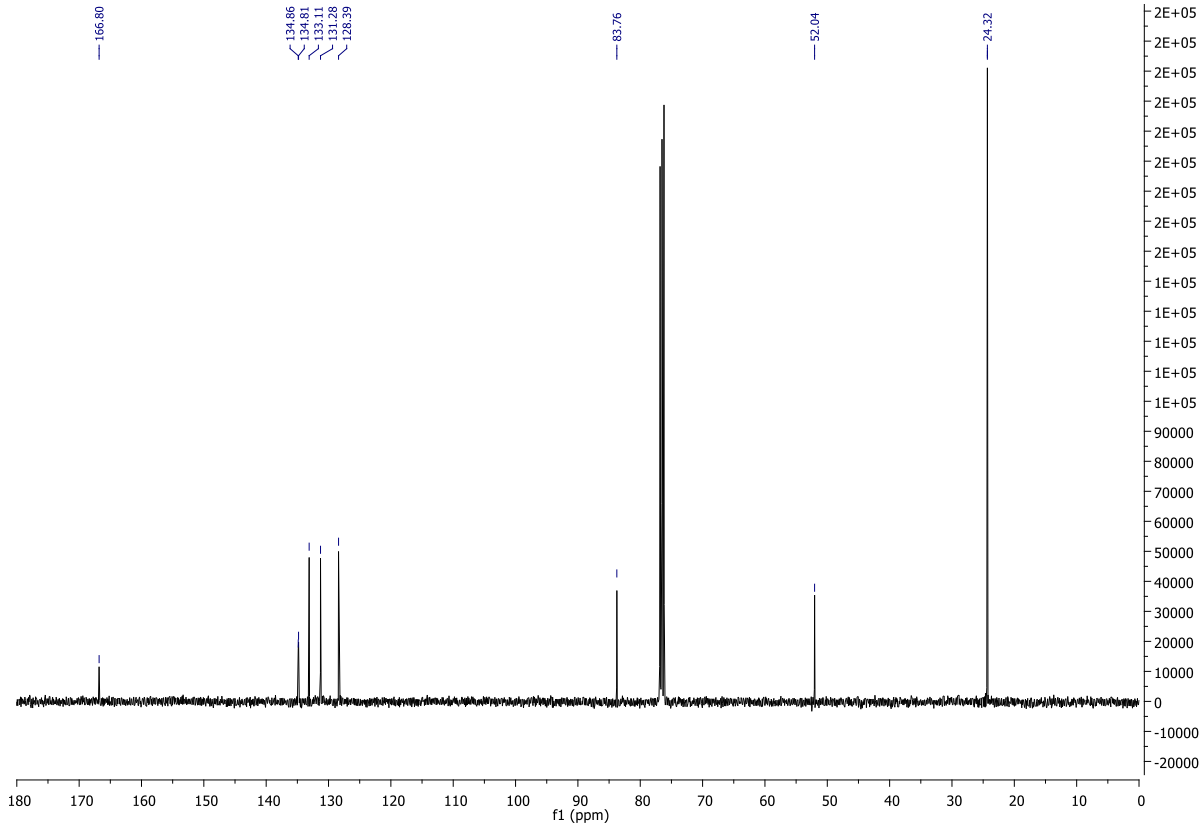


^{1}H NMR of S2, $CDCl_3$, 400 MHz

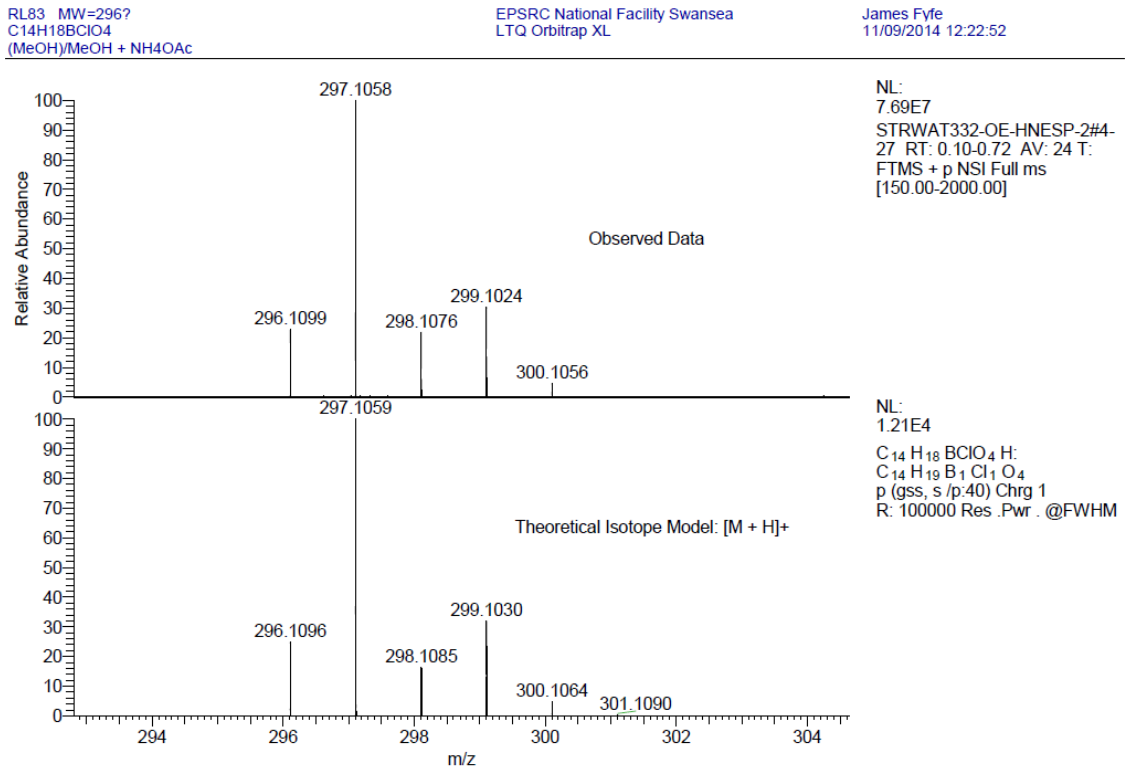


S2

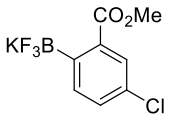
^{13}C NMR of S2, $CDCl_3$, 101 MHz



HRMS of S2

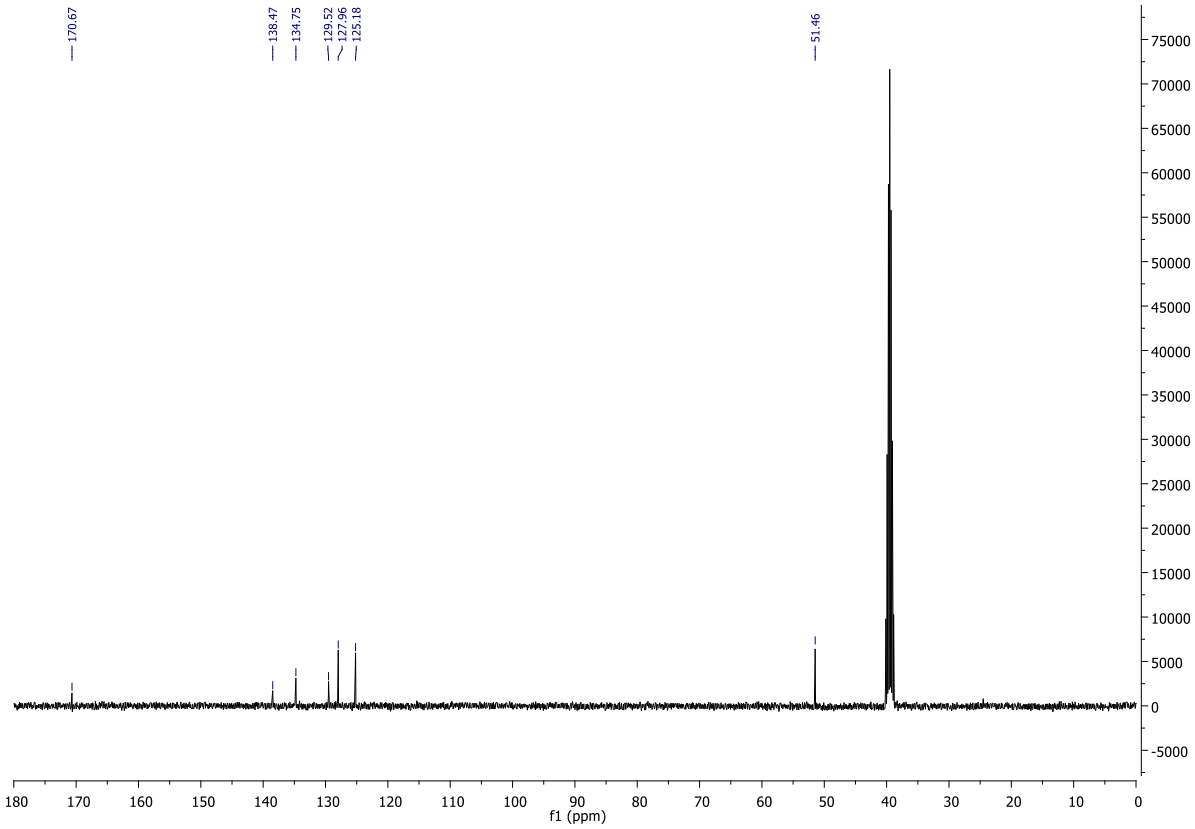


^{1}H NMR of S3, DMSO-d_6, 400 MHz

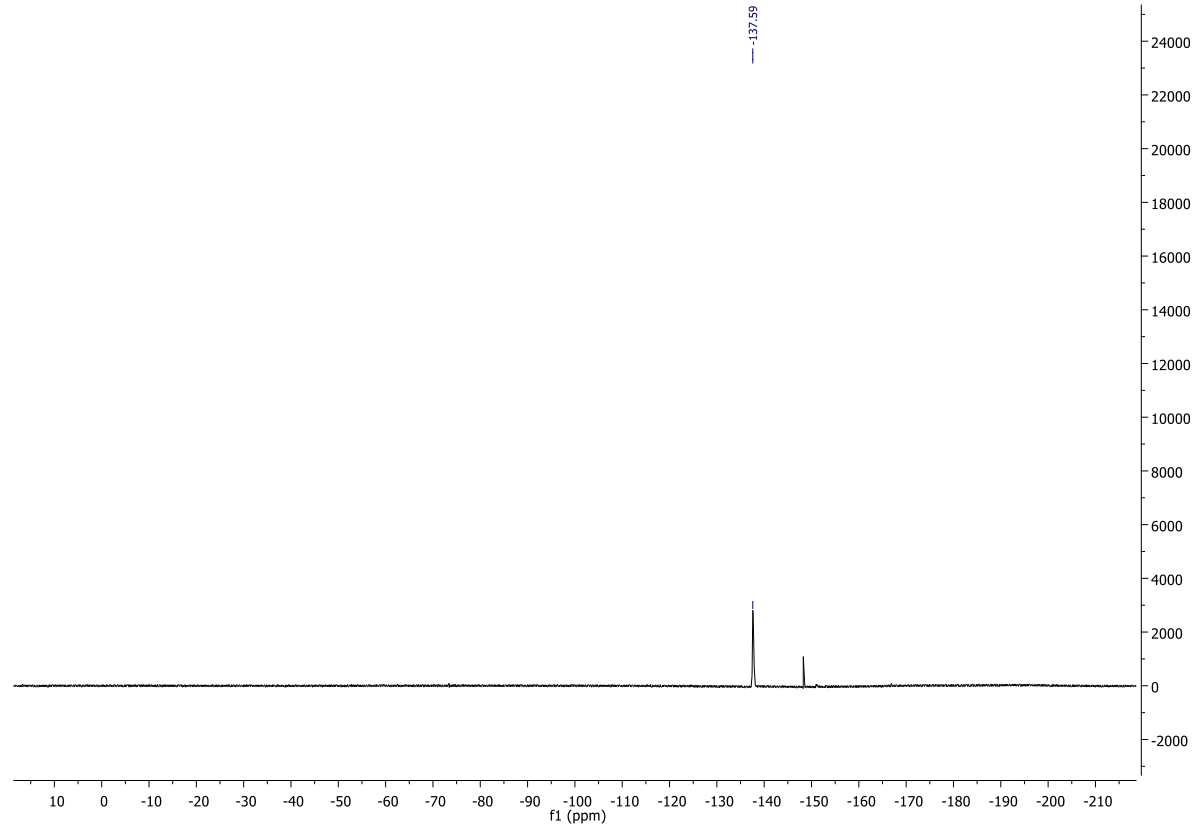


S3

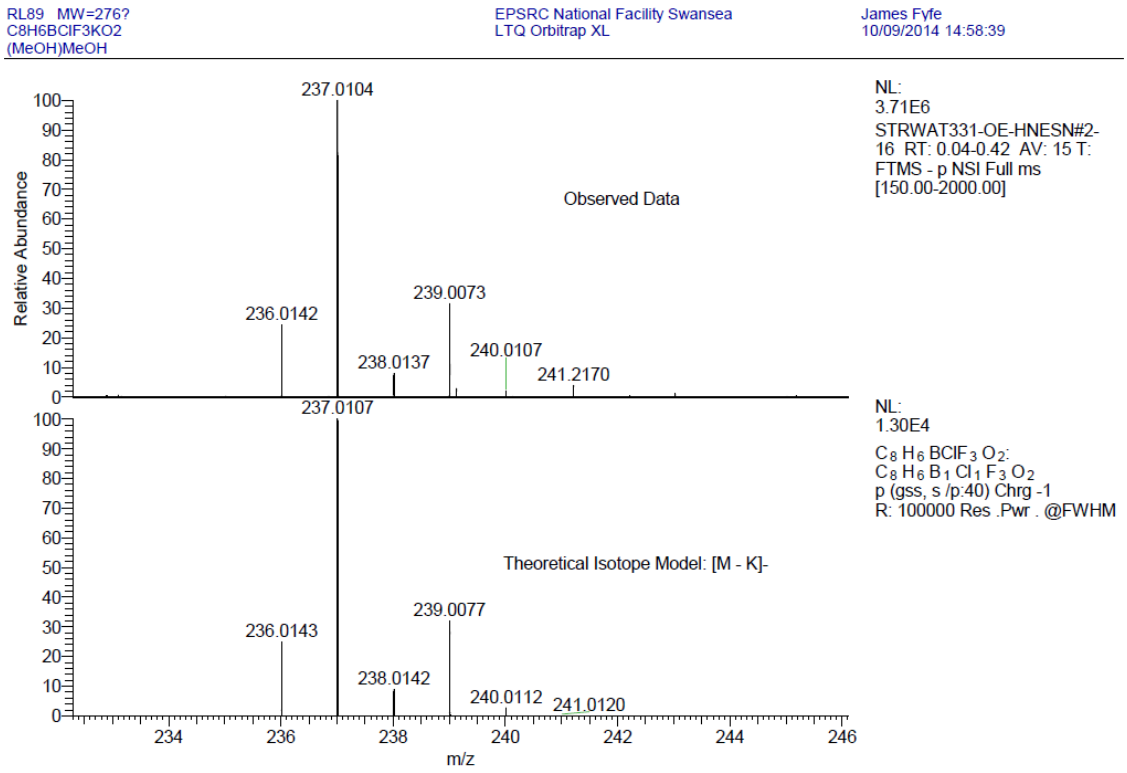
^{13}C NMR of S3, DMSO-d_6, 101 MHz



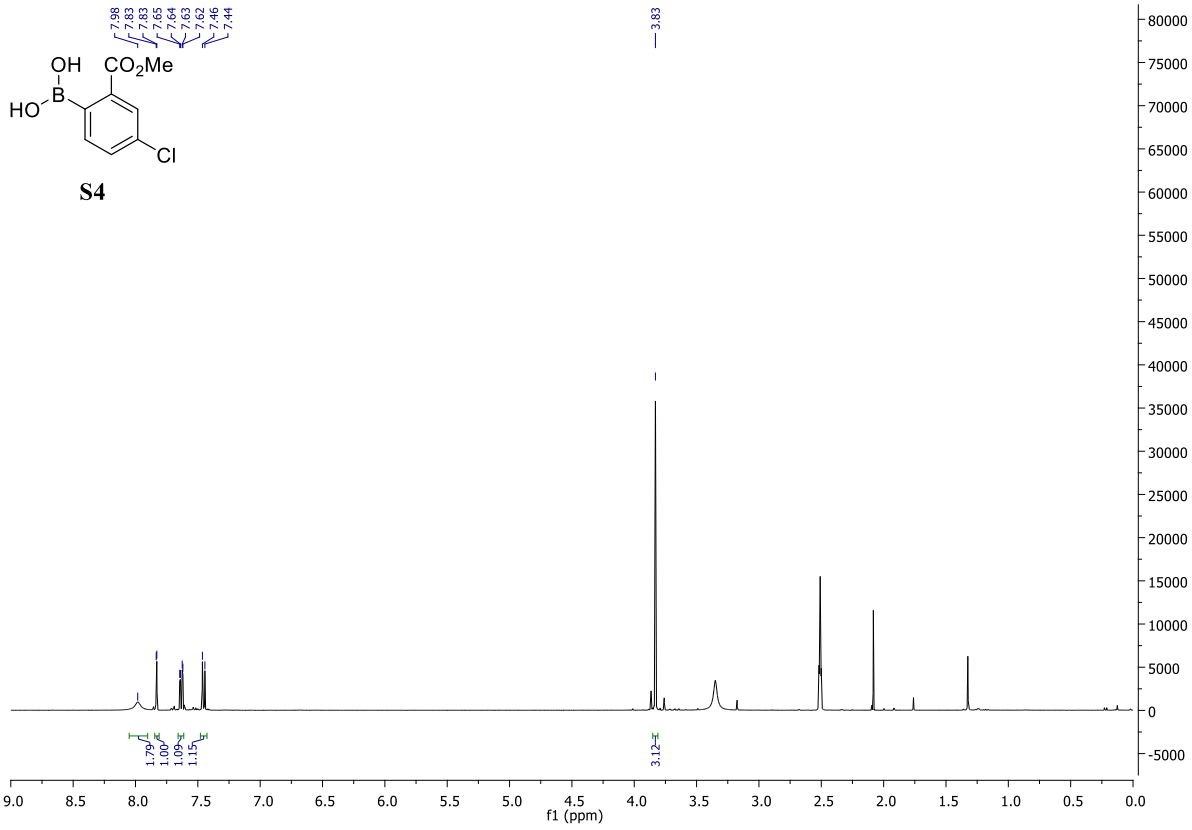
^{19}F NMR of S3, DMSO-d_6, 376 MHz



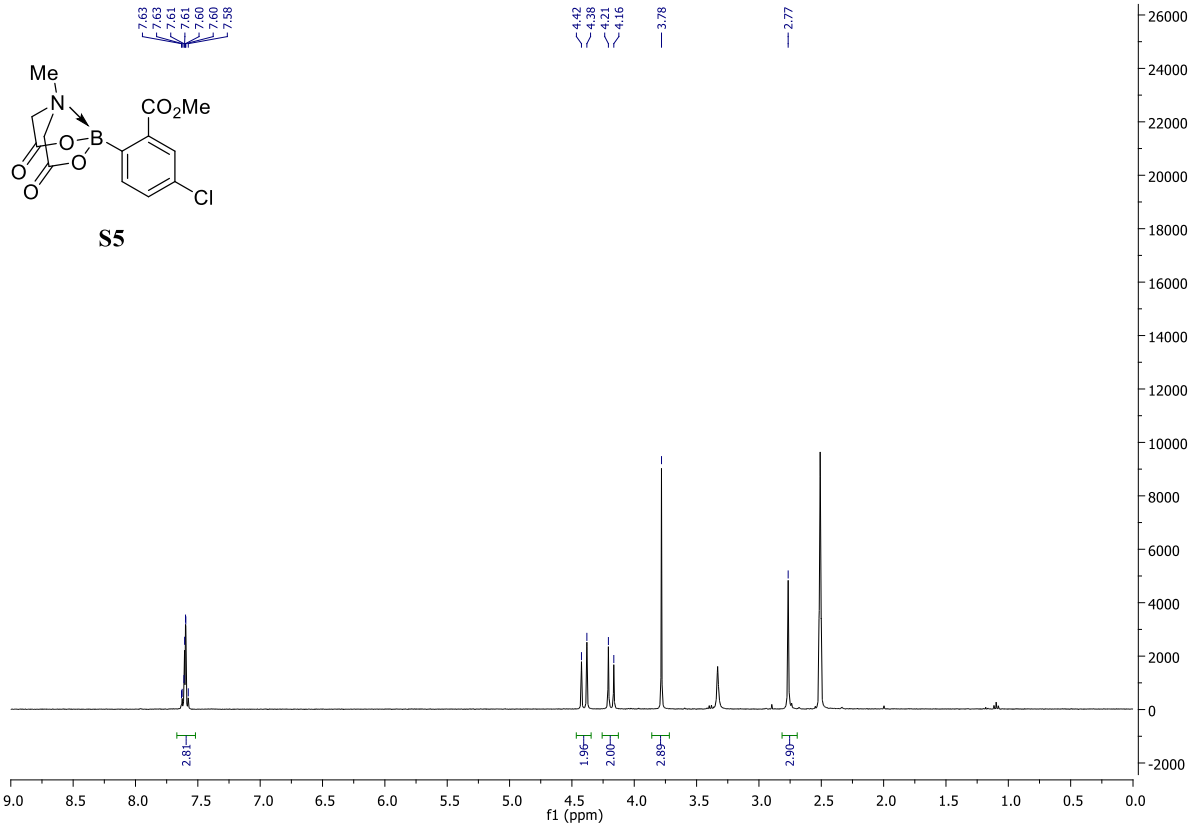
HRMS of S3



^{1}H NMR of S4, DMSO-d_6, 400 MHz

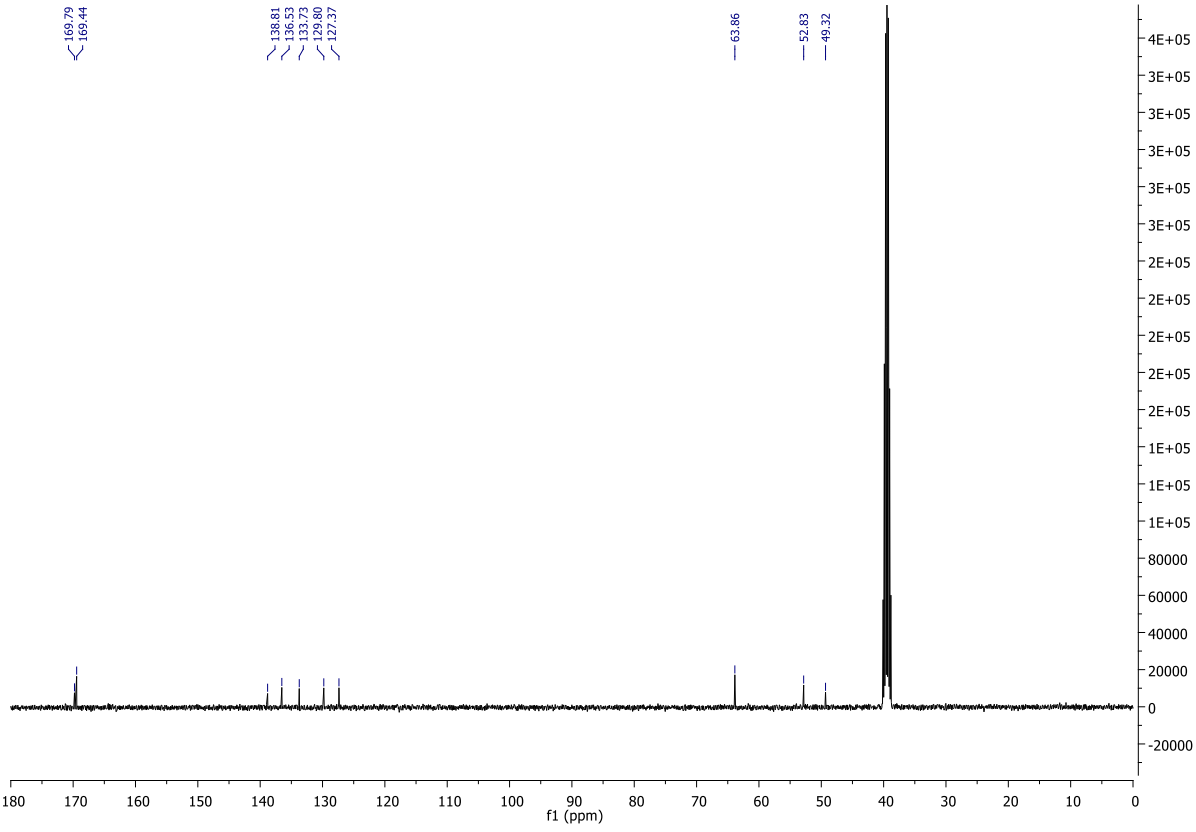


^{1}H NMR of S5, DMSO-d_6, 400 MHz

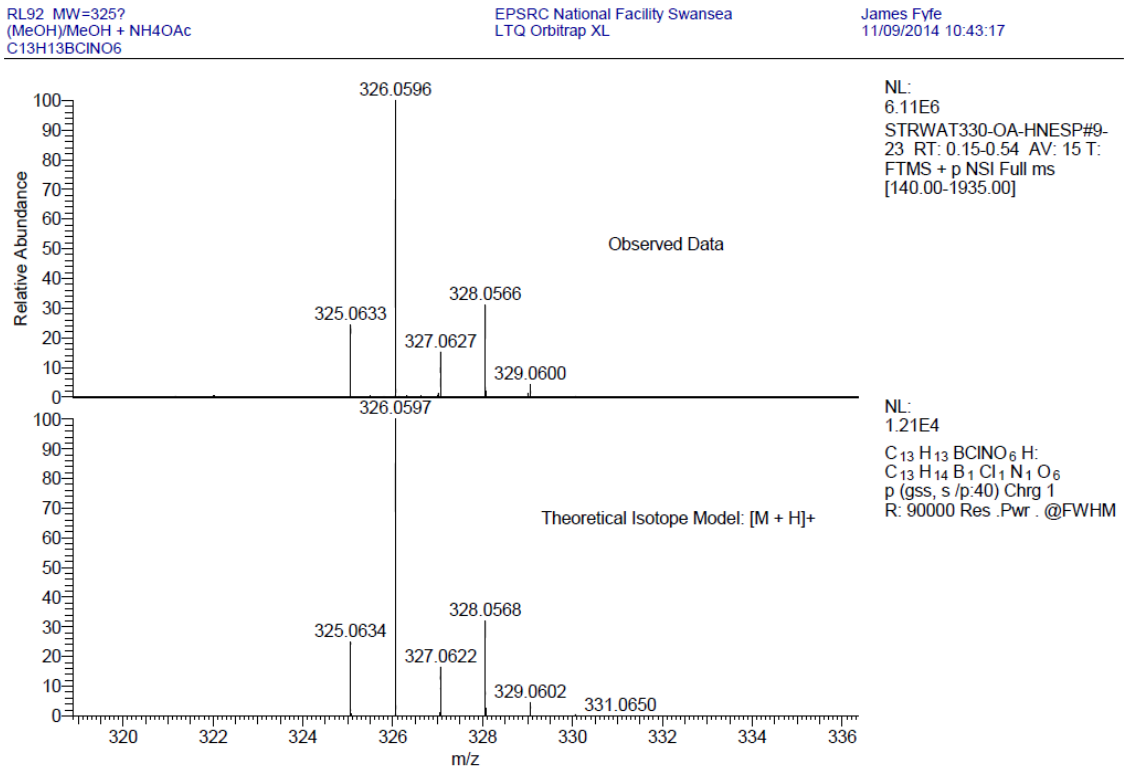


S5

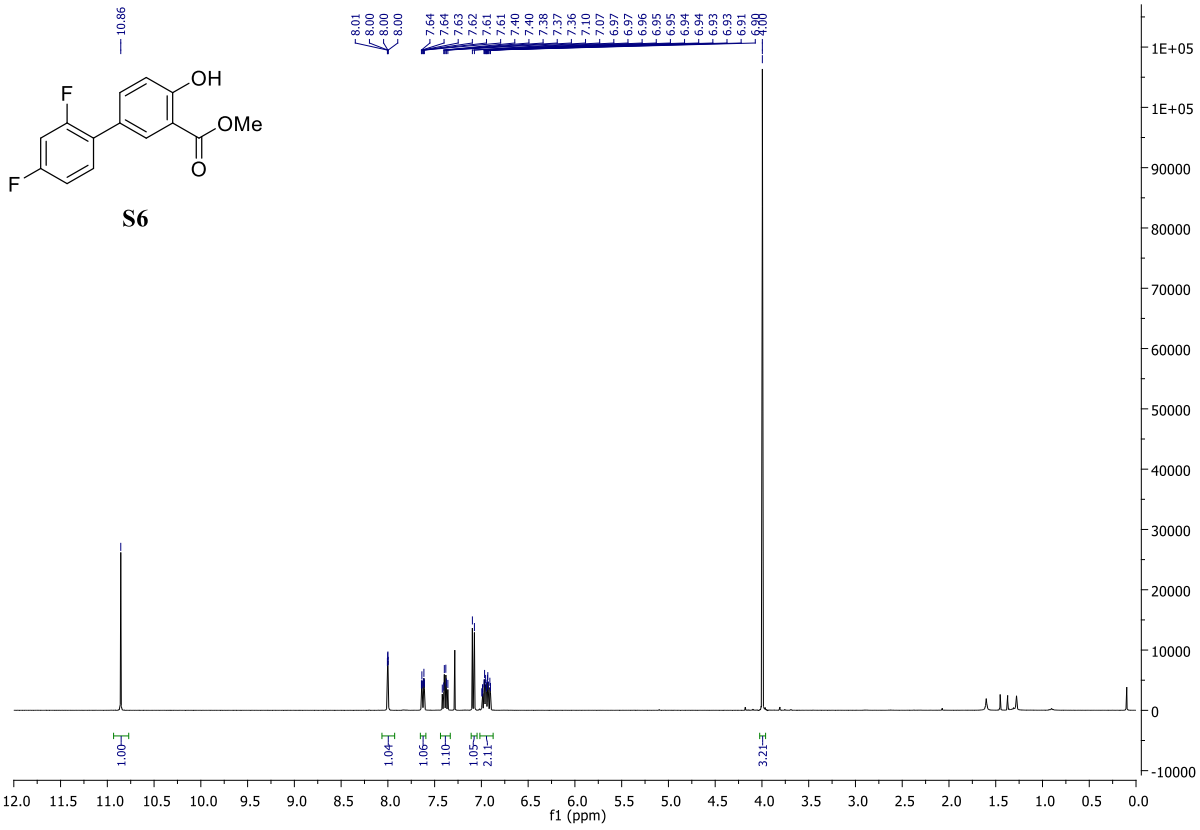
^{13}C NMR of S5, DMSO-d_6, 101 MHz



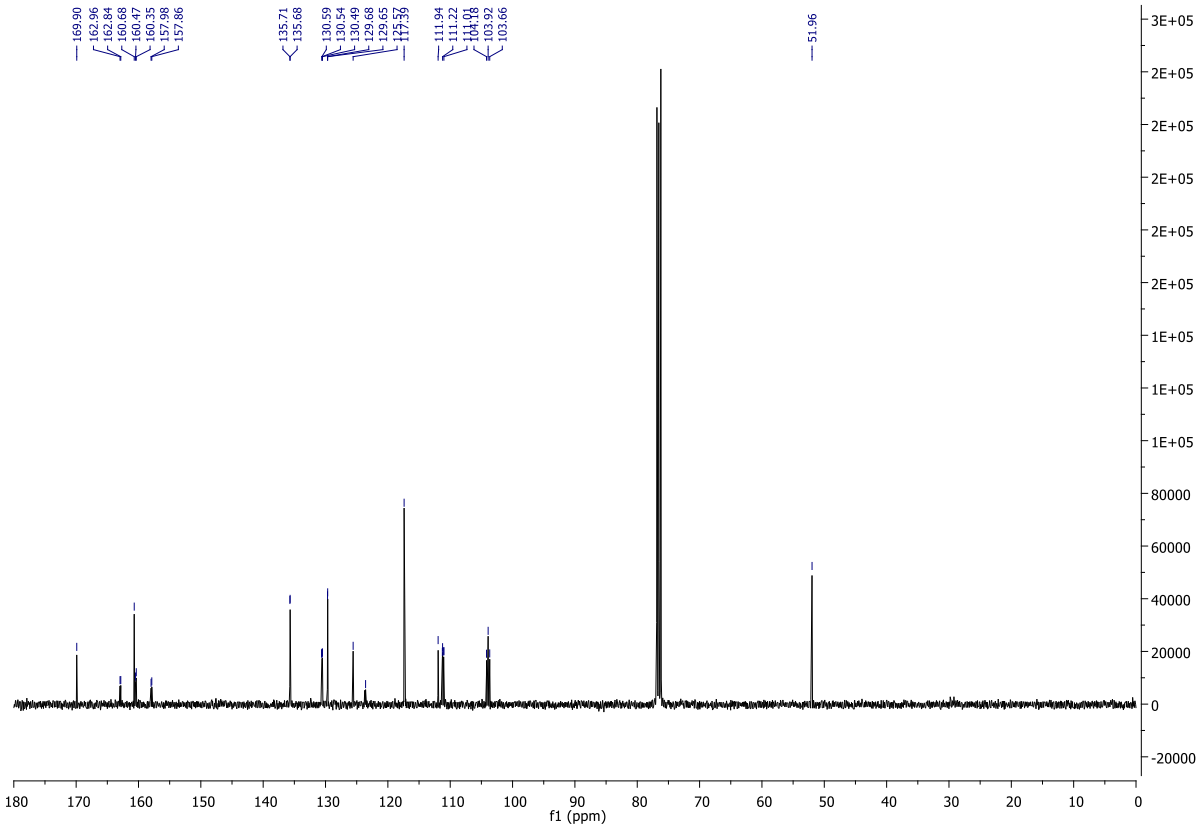
HRMS of S5



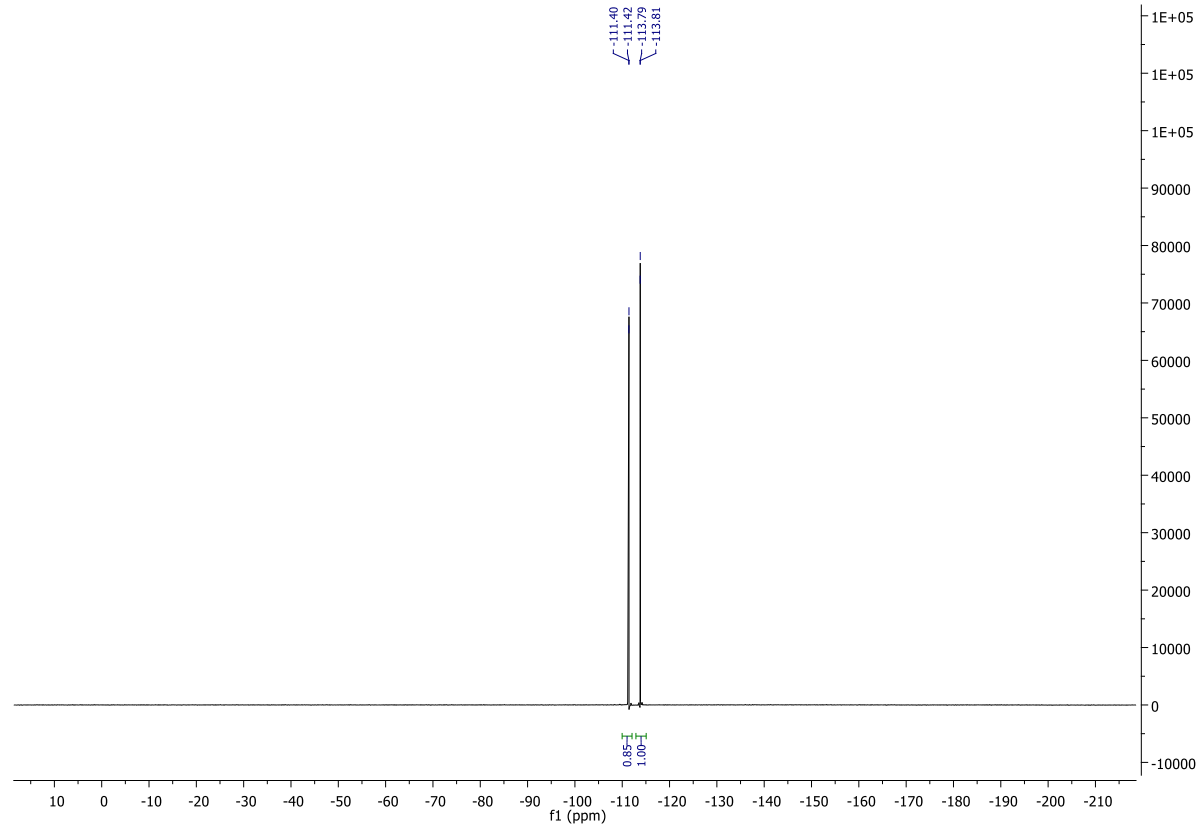
^{1}H NMR of S6, $CDCl_3$, 400 MHz



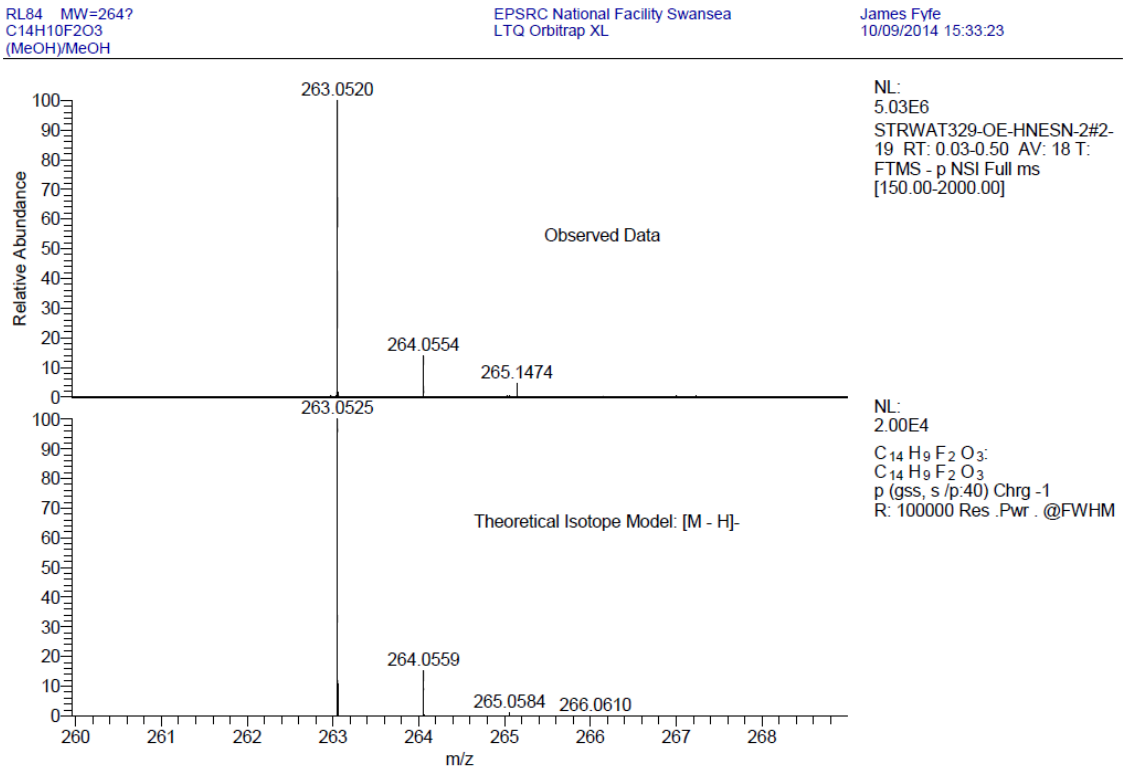
^{13}C NMR of S6, $CDCl_3$, 101 MHz



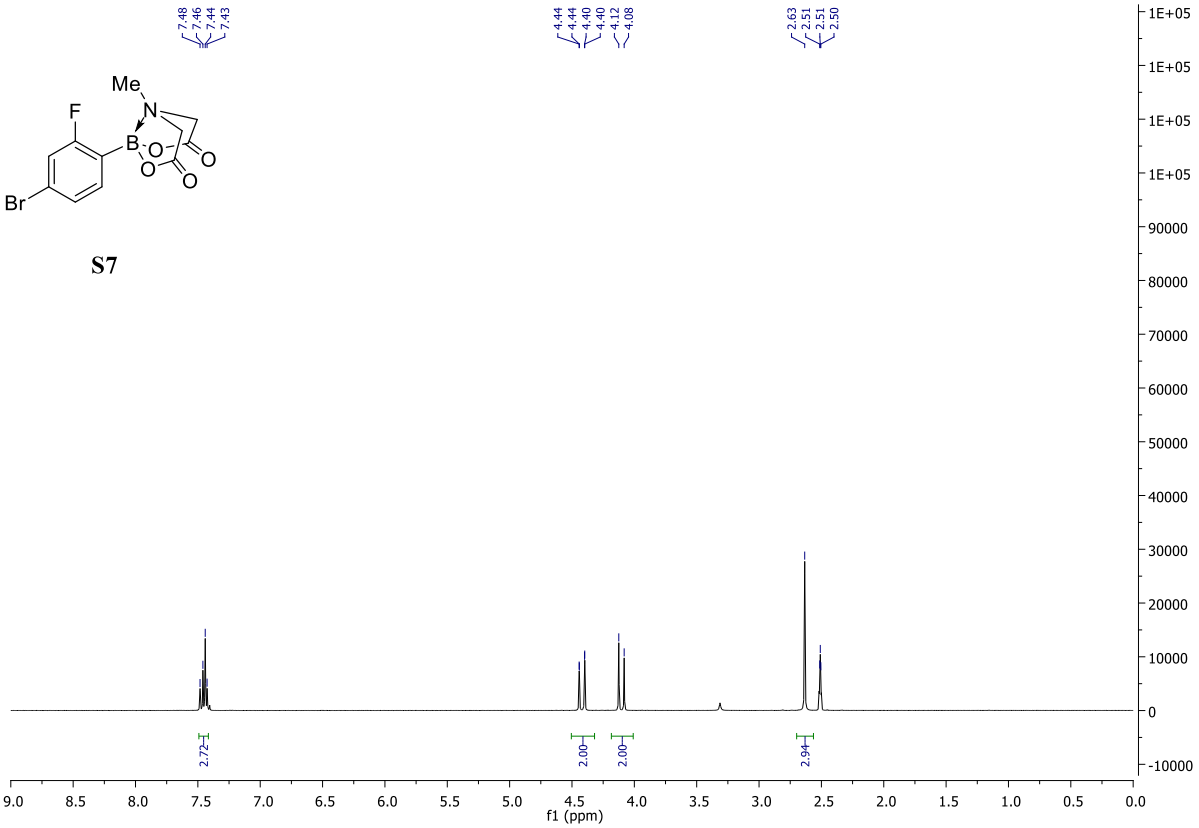
^{19}F NMR of S6, $CDCl_3$, 376 MHz



HRMS of S6

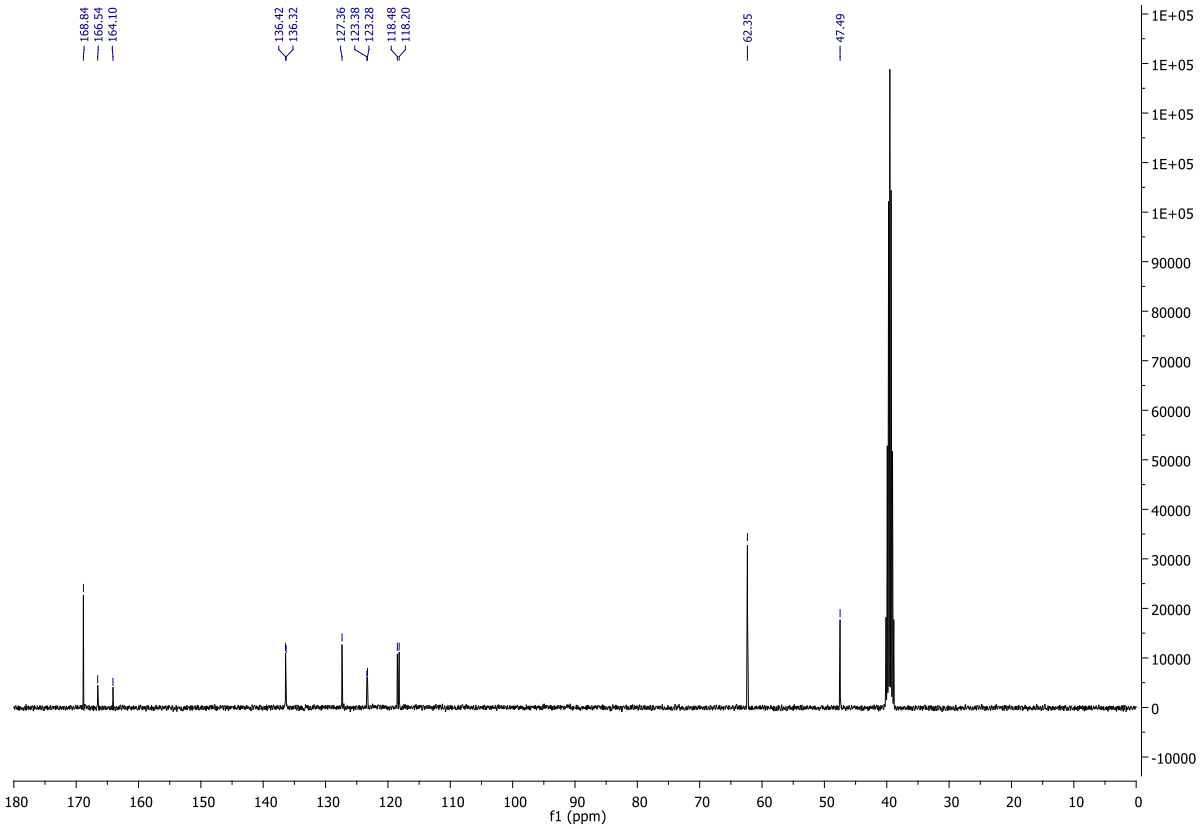


^{1}H NMR of S7, DMSO-d_6, 400 MHz

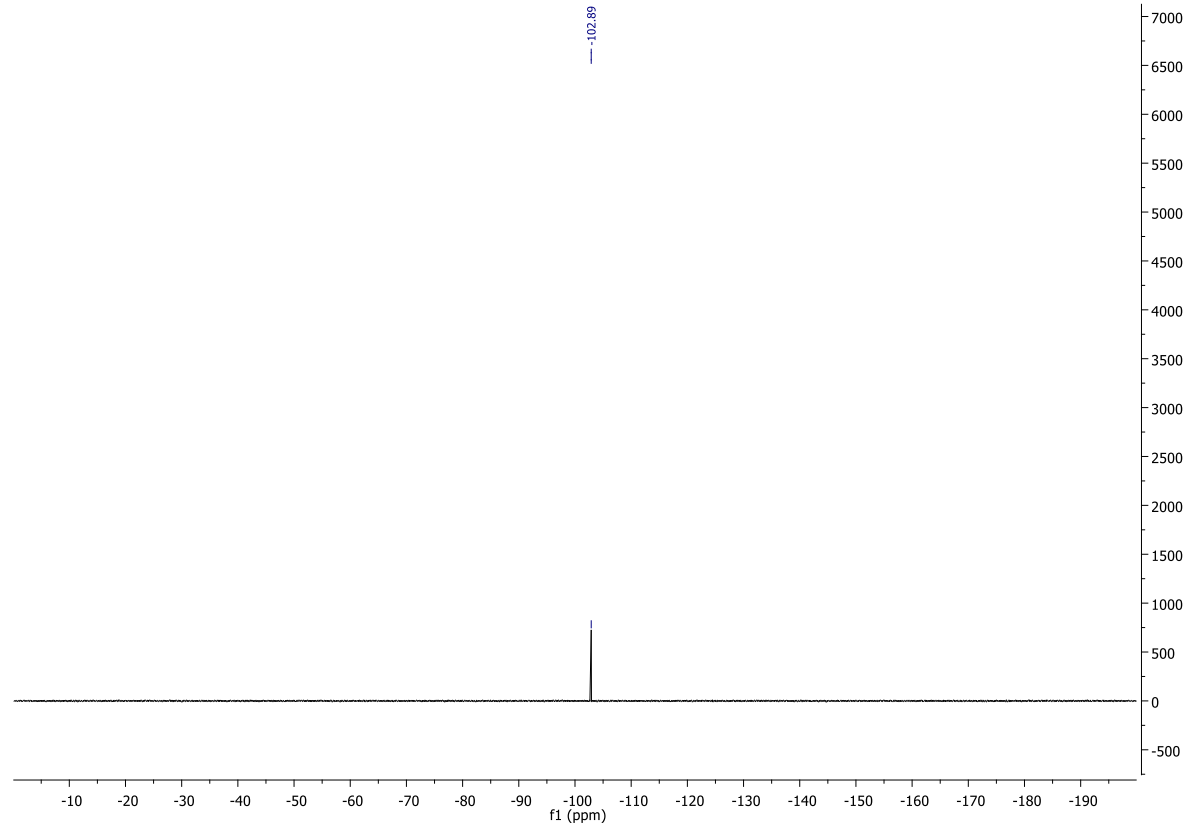


S7

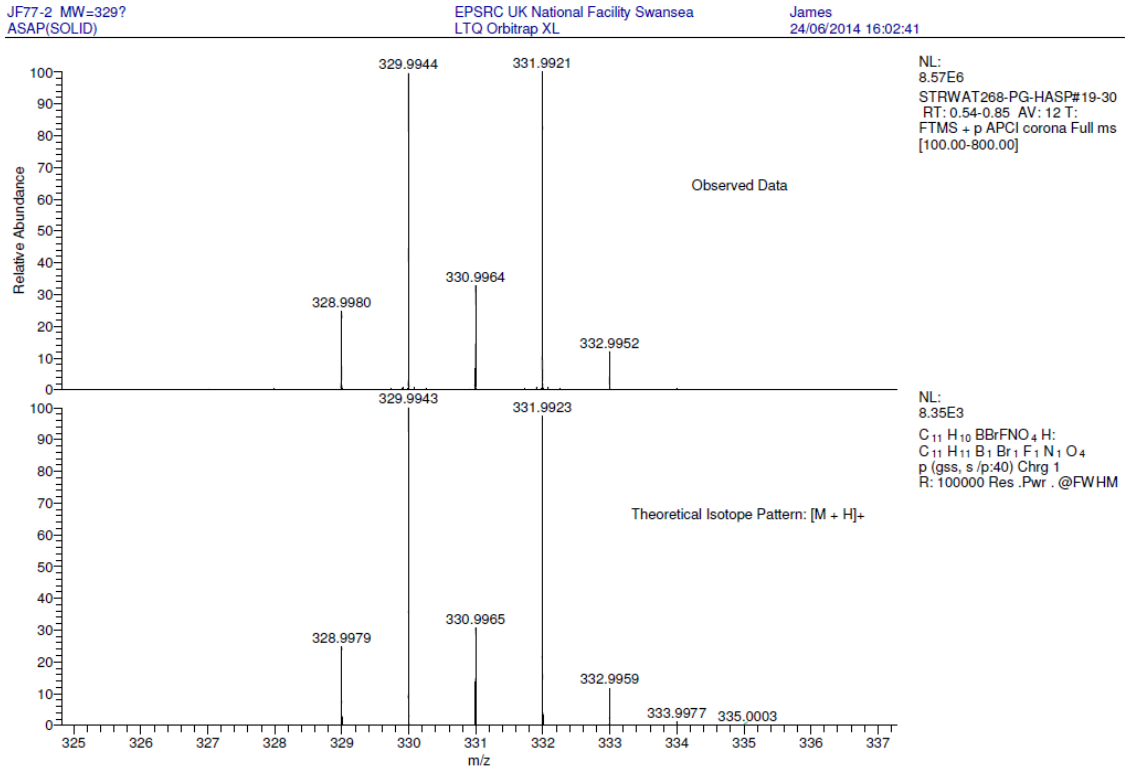
^{13}C NMR of S7, DMSO-d_6, 101 MHz



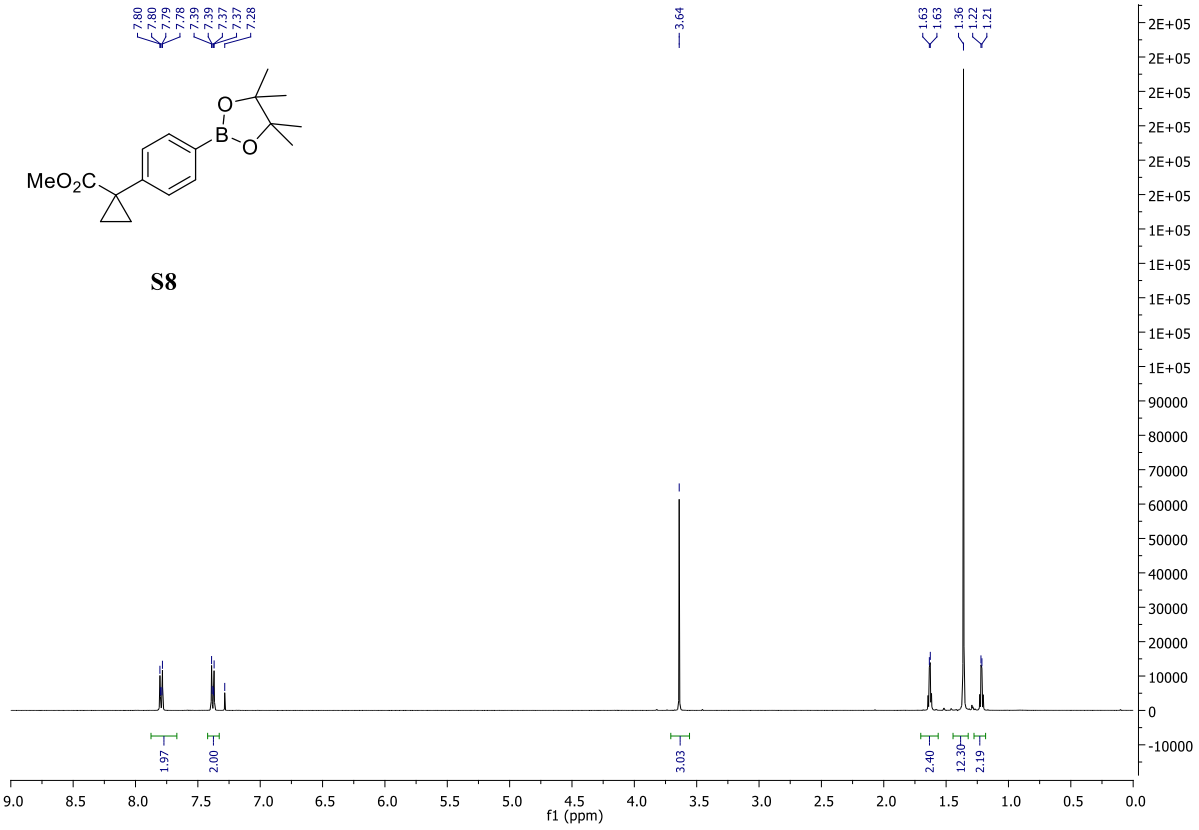
^{19}F NMR of S7, DMSO-d_6, 376 MHz



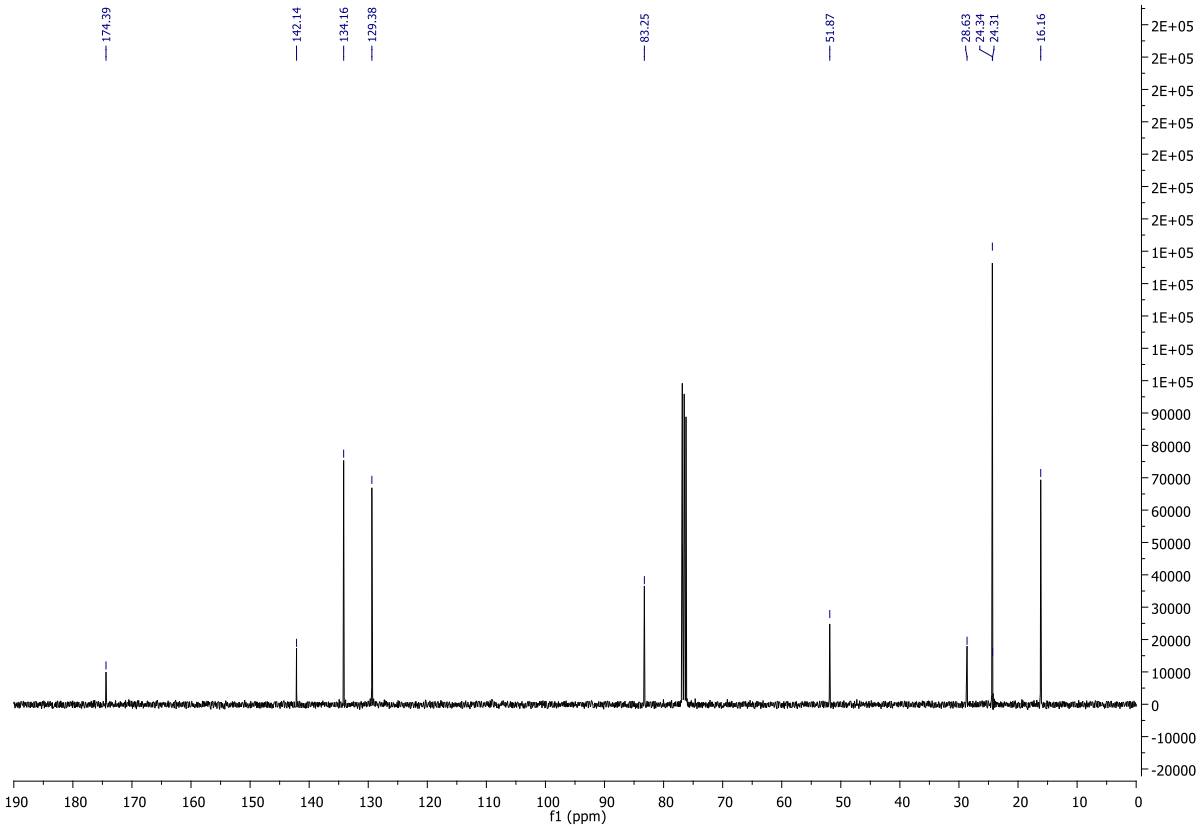
HRMS of S7



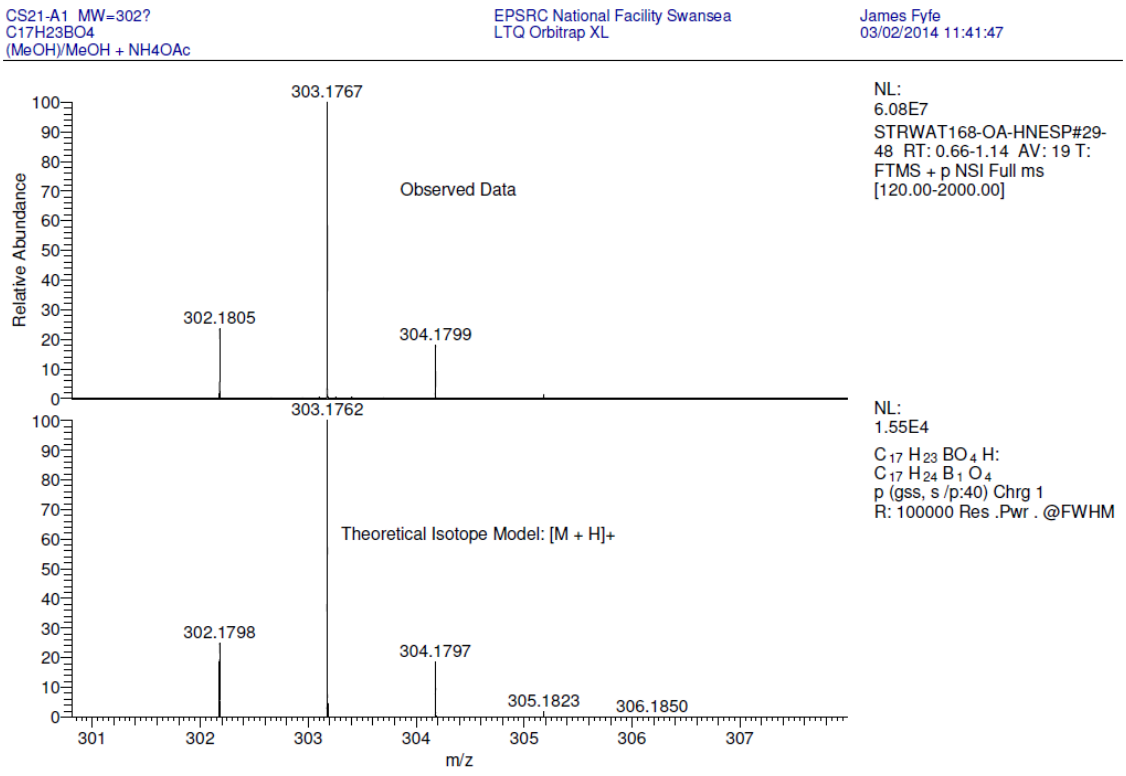
^{1}H NMR of S8, $CDCl_3$, 400 MHz



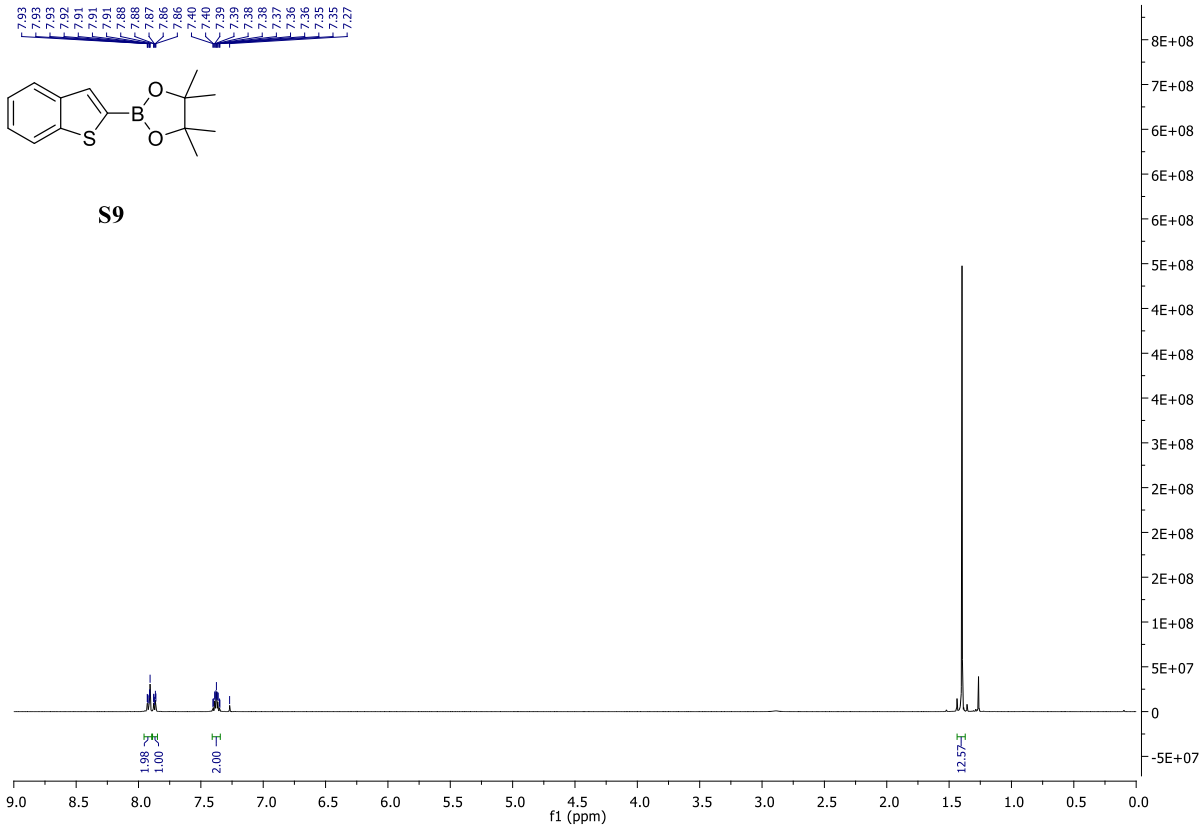
^{13}C NMR of S8, $CDCl_3$, 101 MHz



HRMS of S8

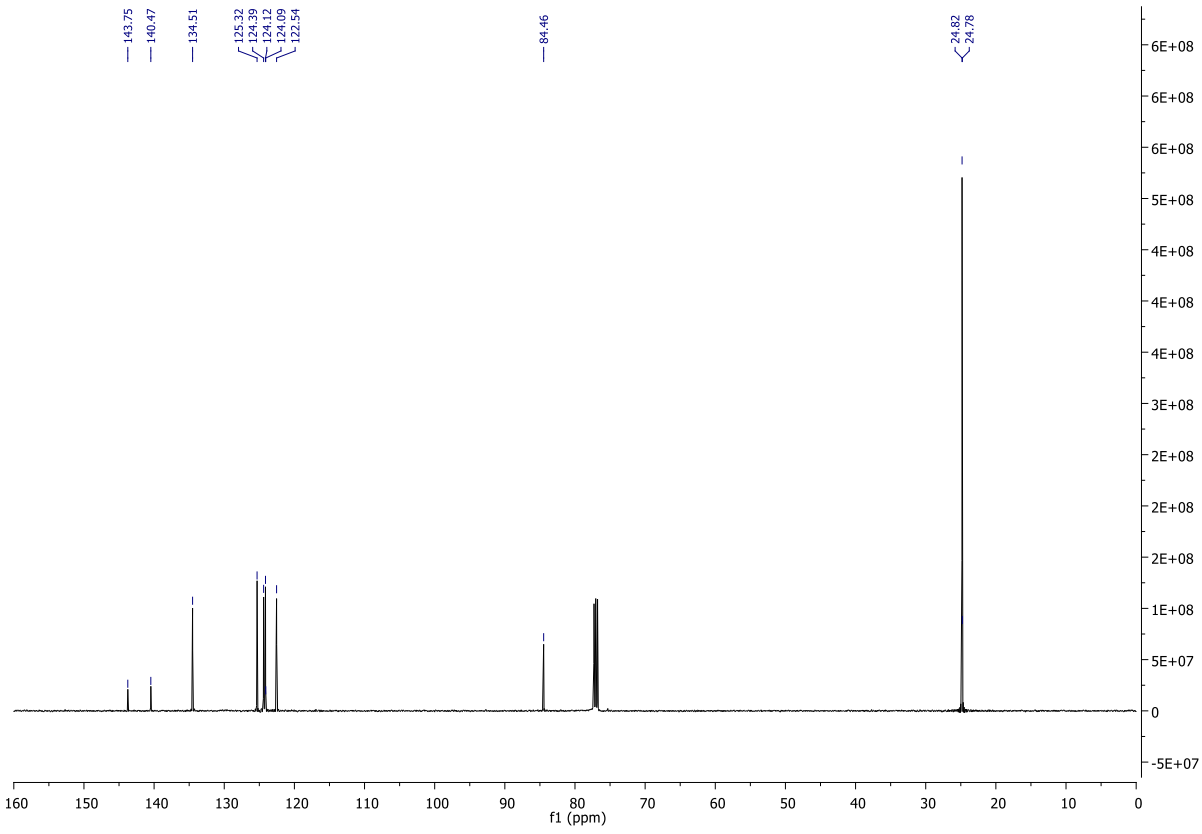


^{1}H NMR of S9, $CDCl_3$, 400 MHz

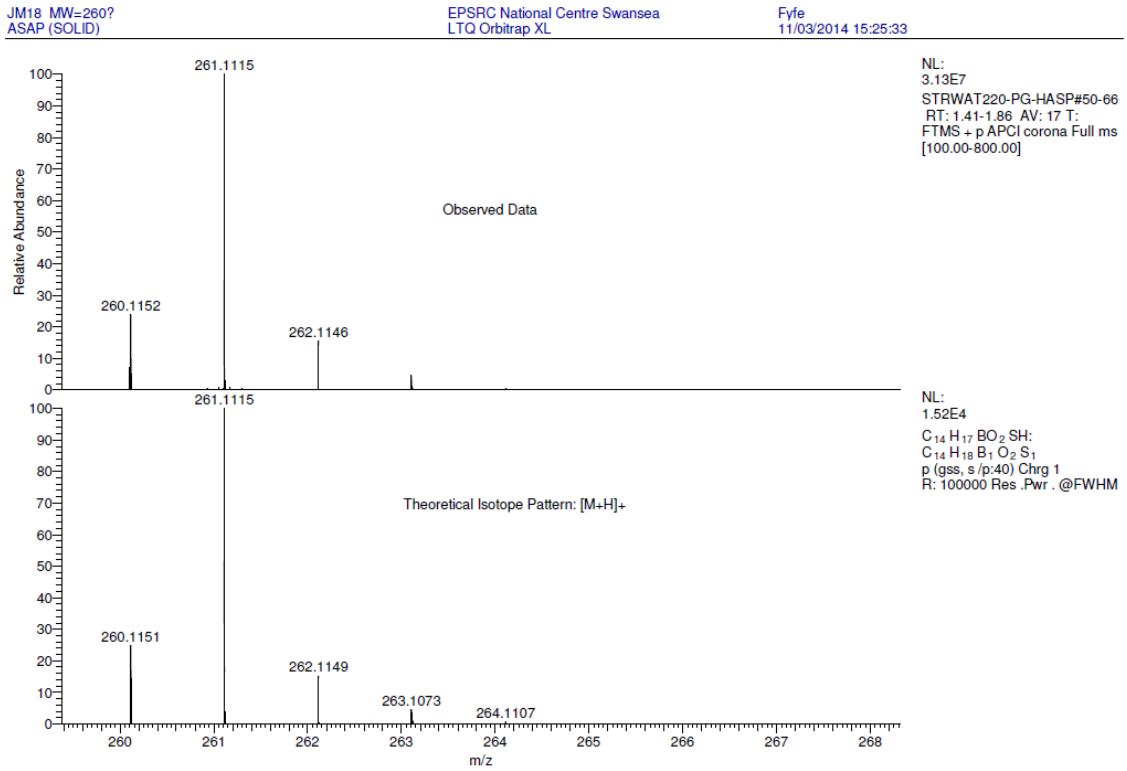


S9

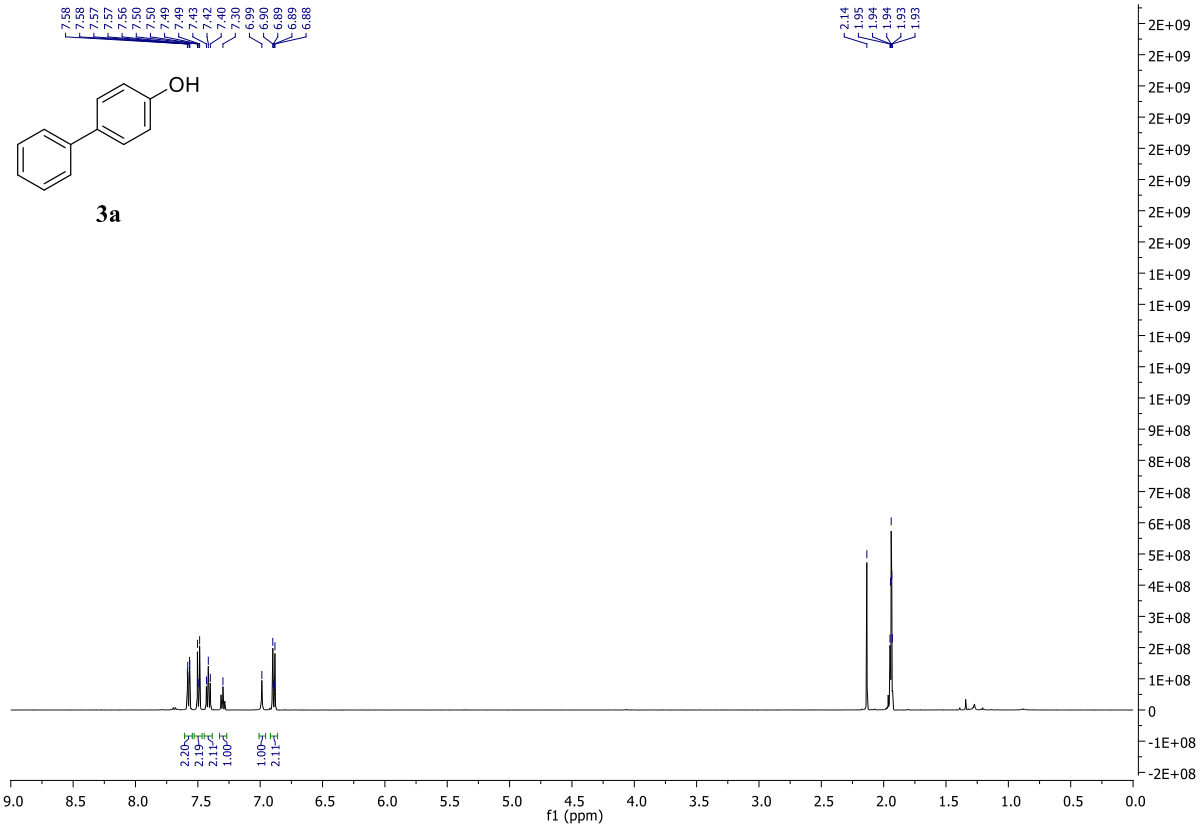
^{13}C NMR of S9, $CDCl_3$, 101 MHz



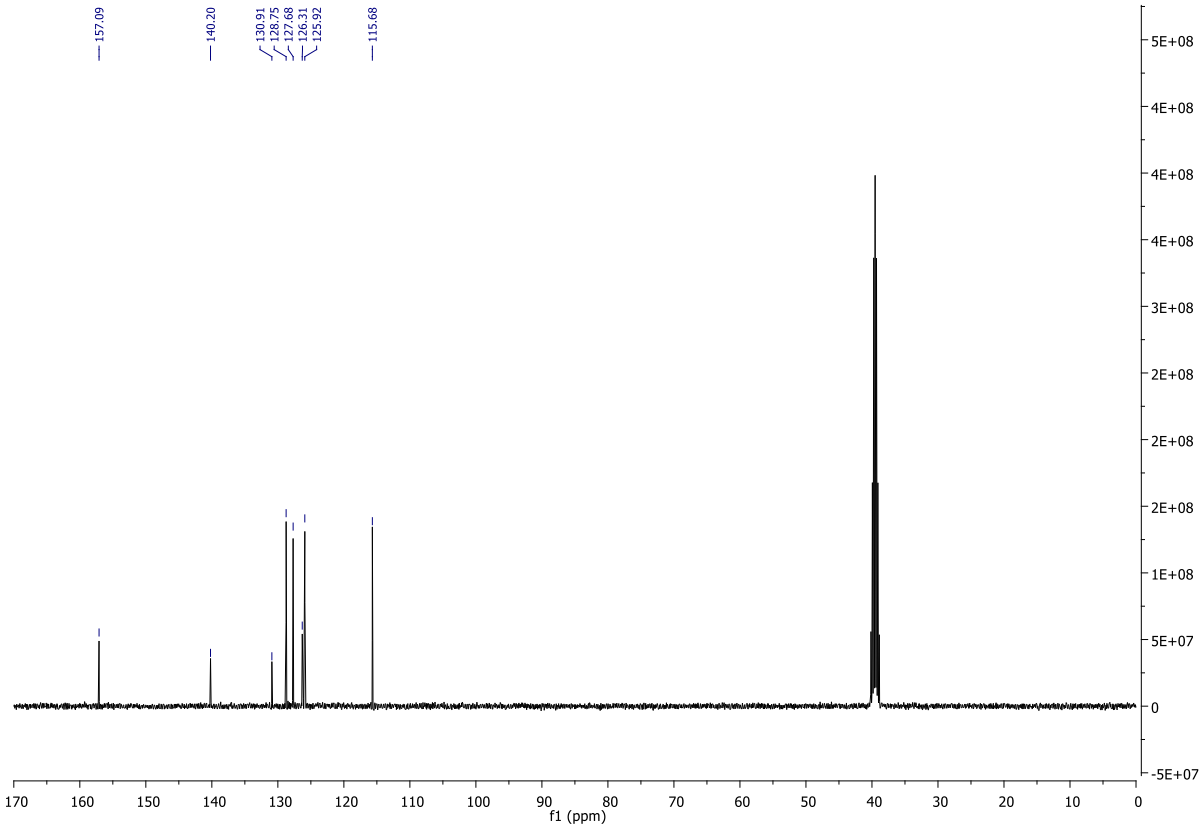
HRMS of S9



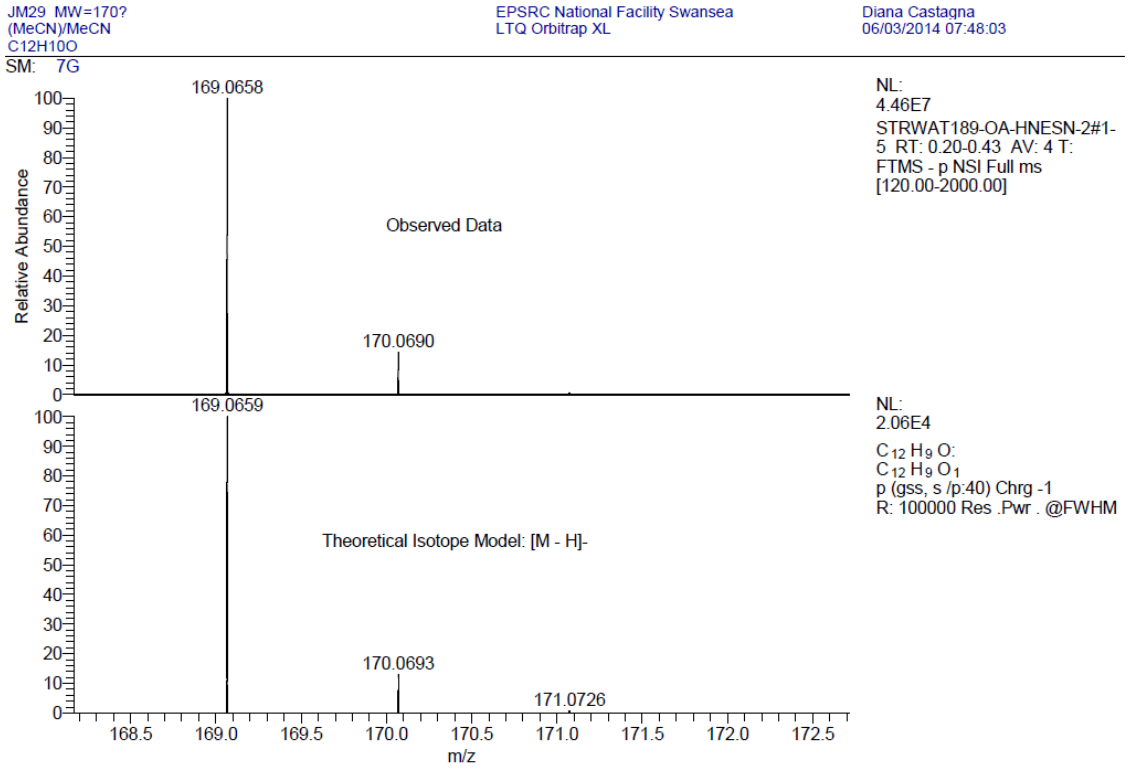
^{1}H NMR of 3a, CD_3CN, 500 MHz



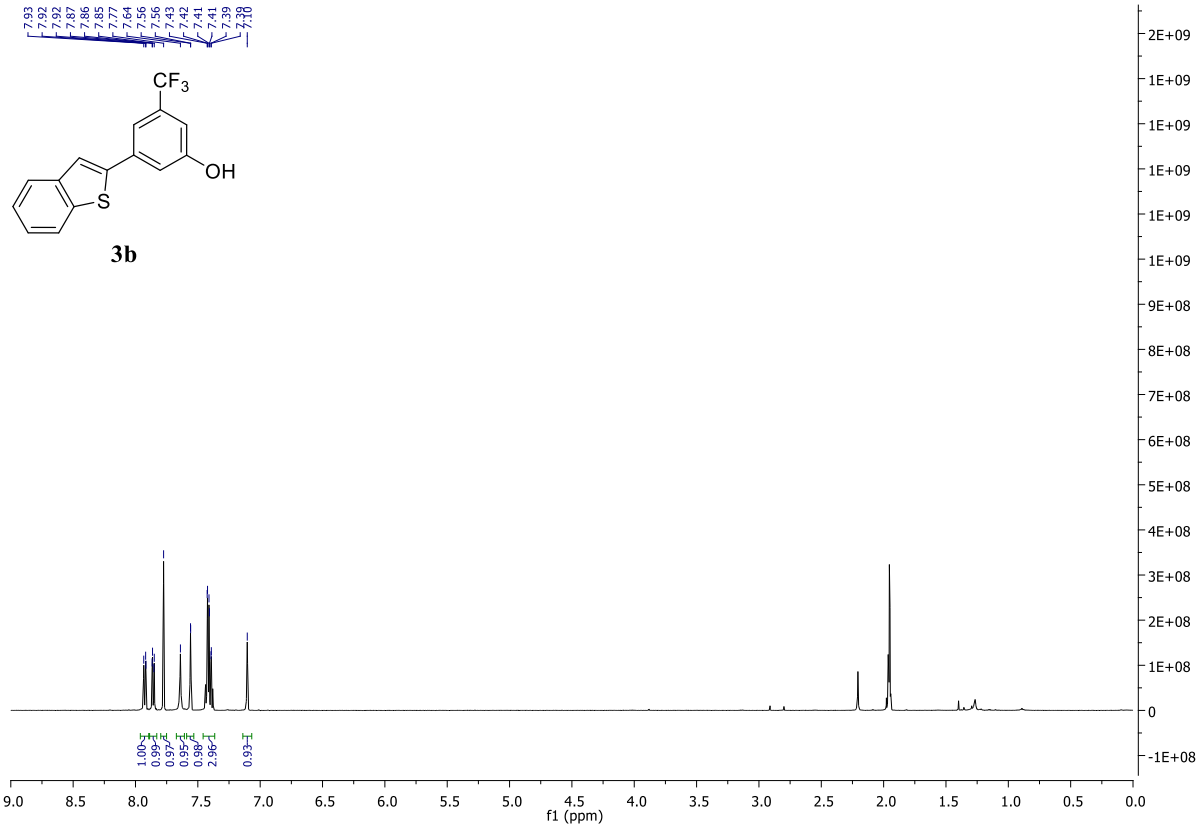
^{13}C NMR of 3a, DMSO-d_6, 126 MHz



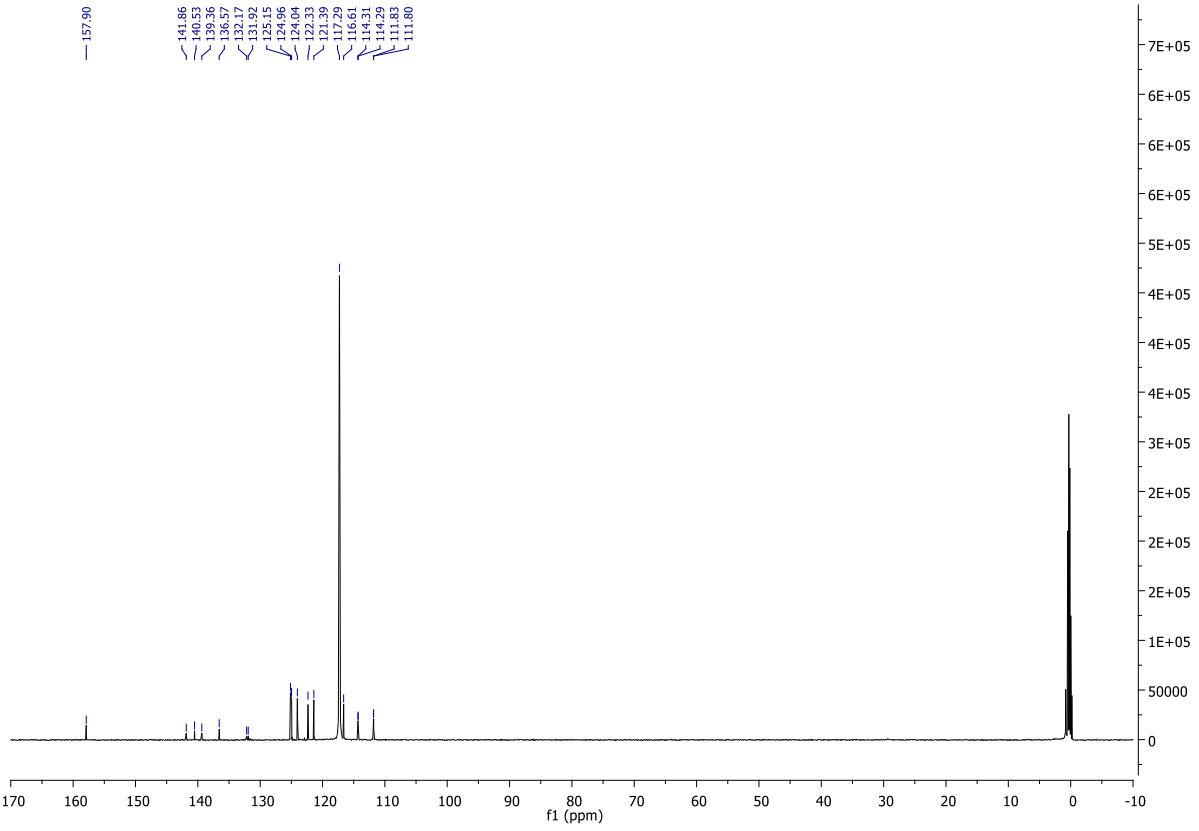
HRMS of 3a



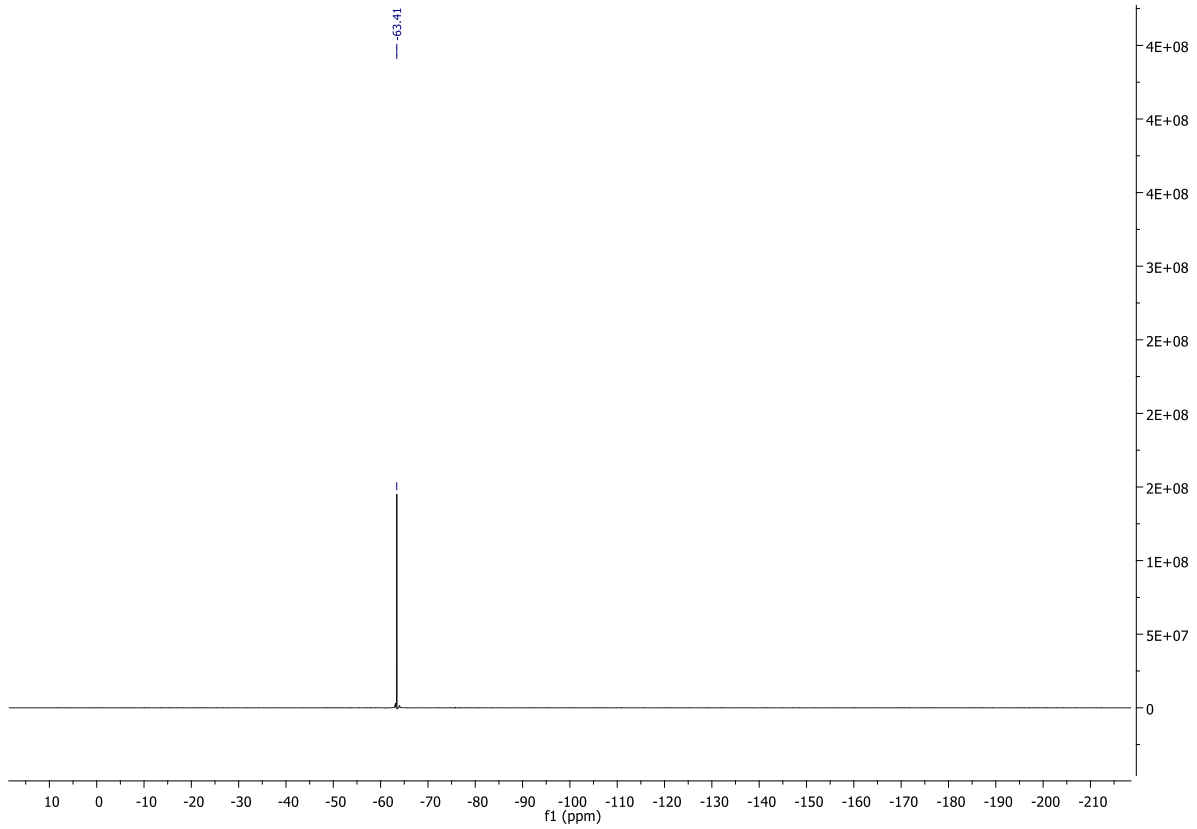
^{1}H NMR of 3b, CD_3CN, 500 MHz



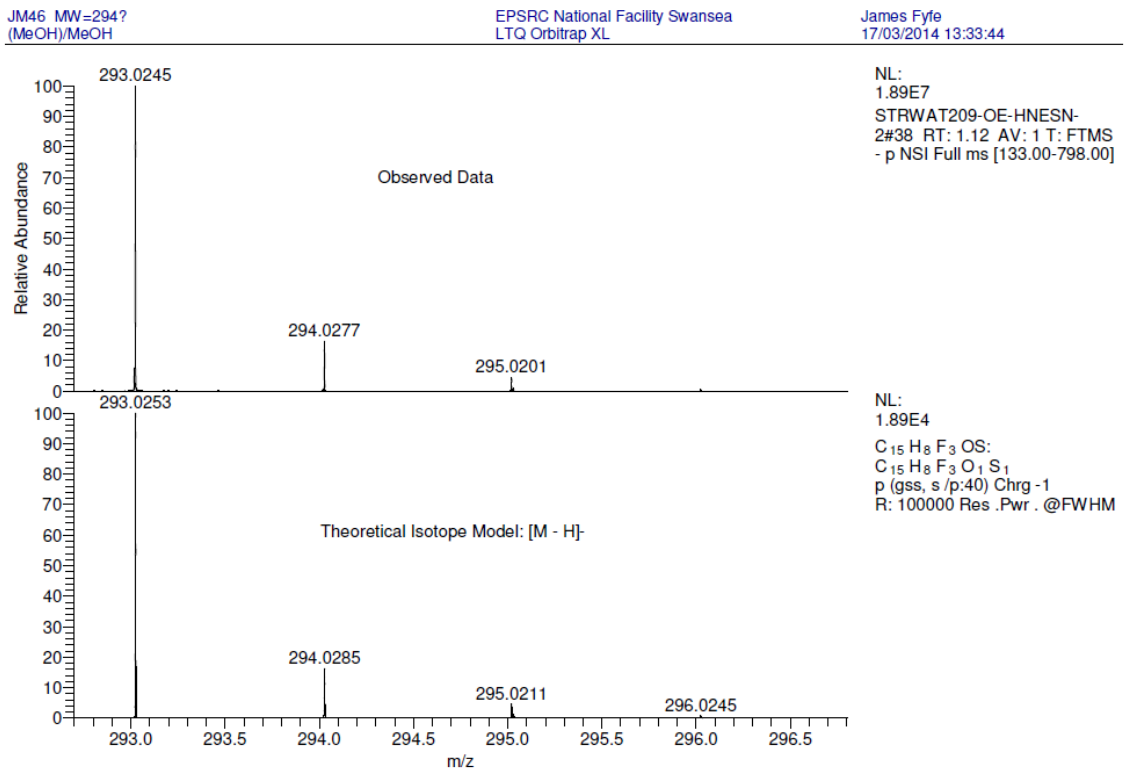
^{13}C NMR of 3b, CD_3CN, 126 MHz



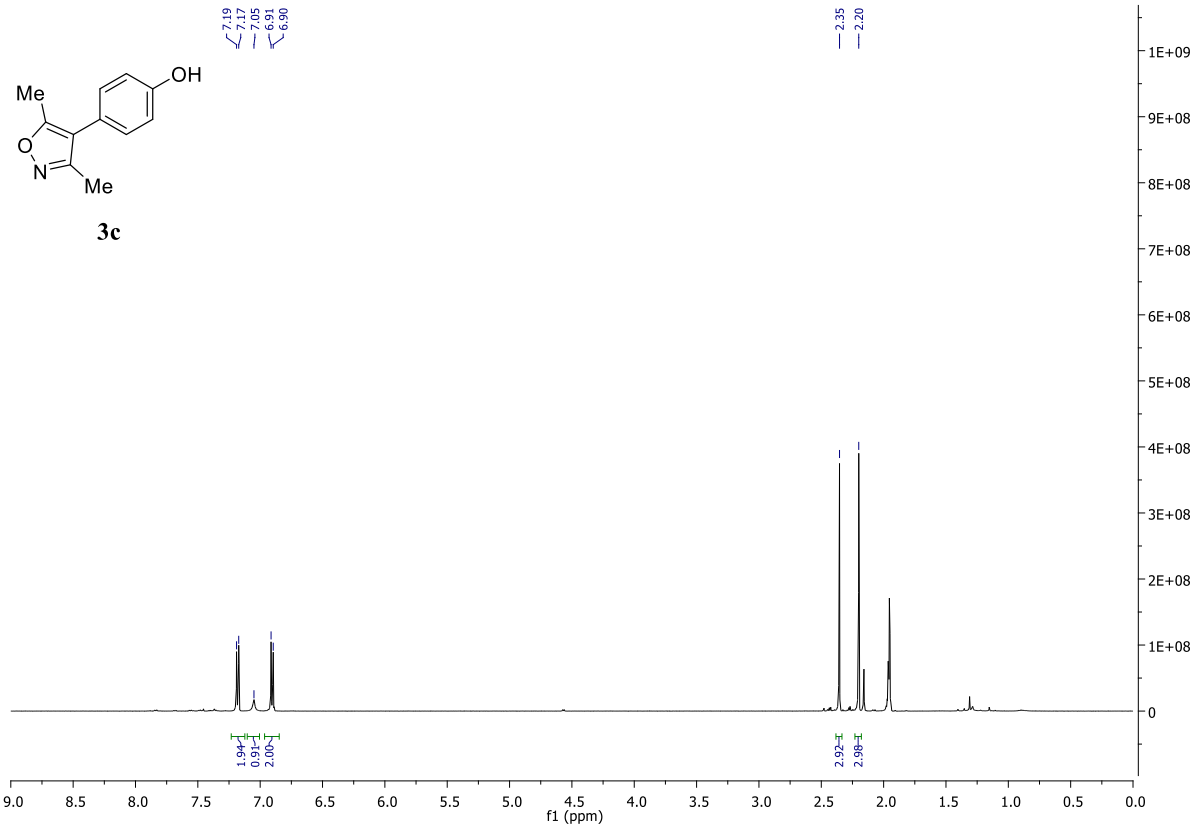
^{19}F NMR of 3b, CD_3CN, 376 MHz



HRMS of 3b

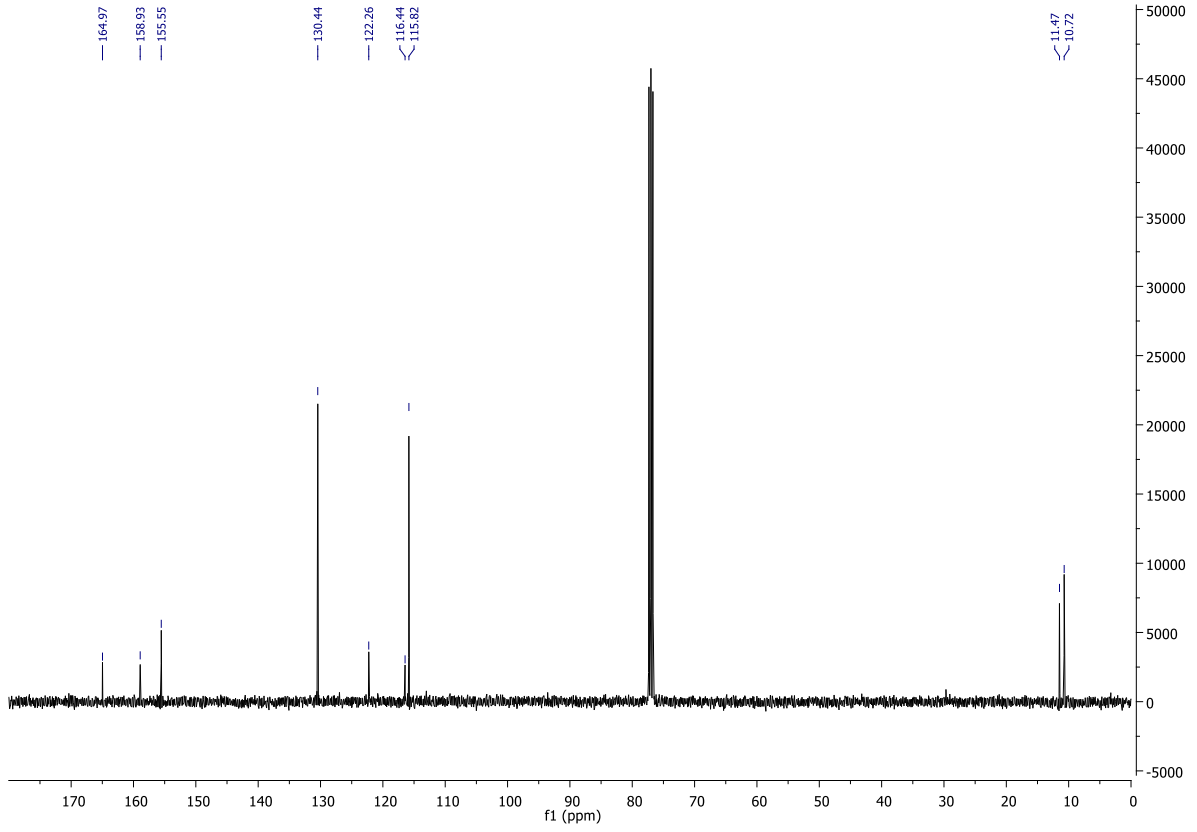


^{1}H NMR of 3c, CD_3CN, 500 MHz

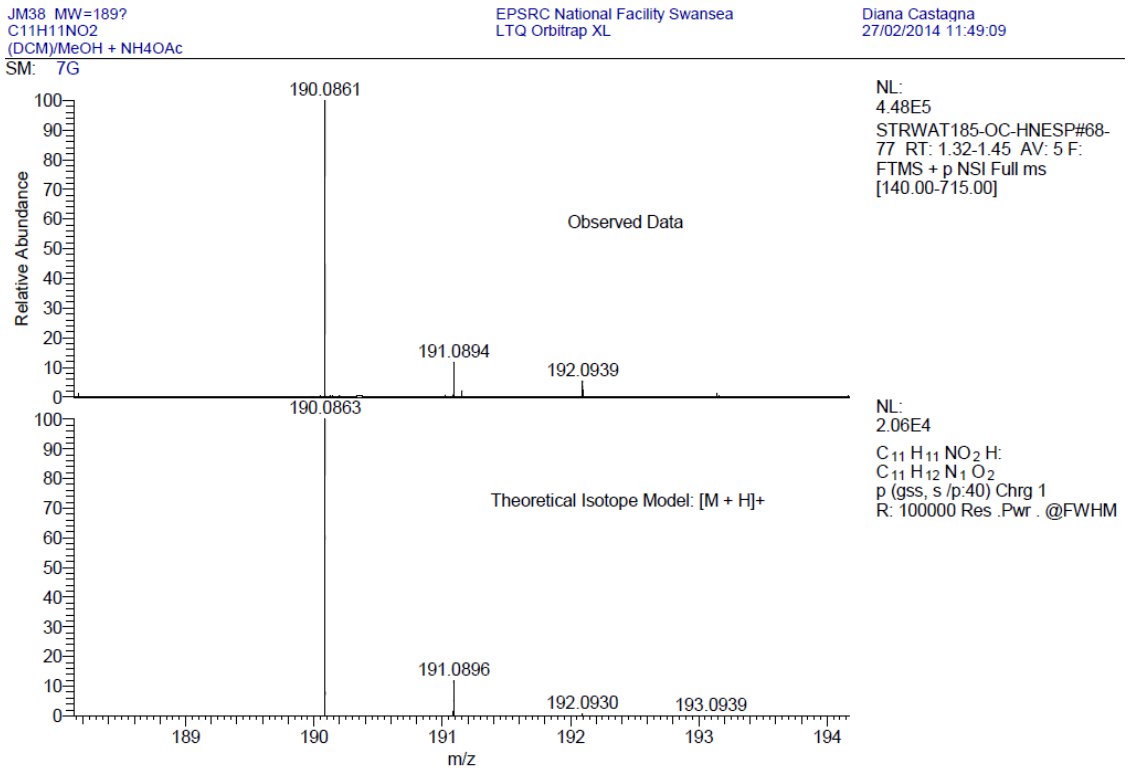


3c

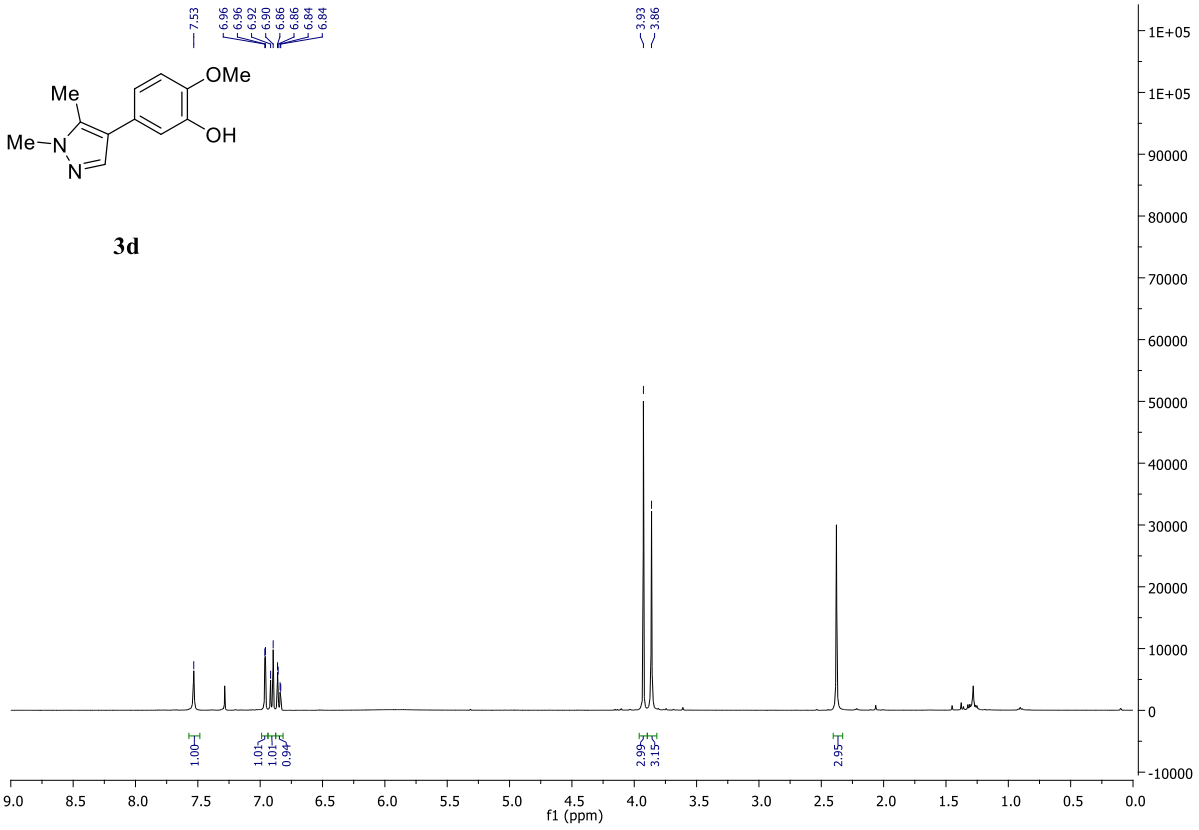
^{13}C NMR of 3c, $CDCl_3$, 126 MHz



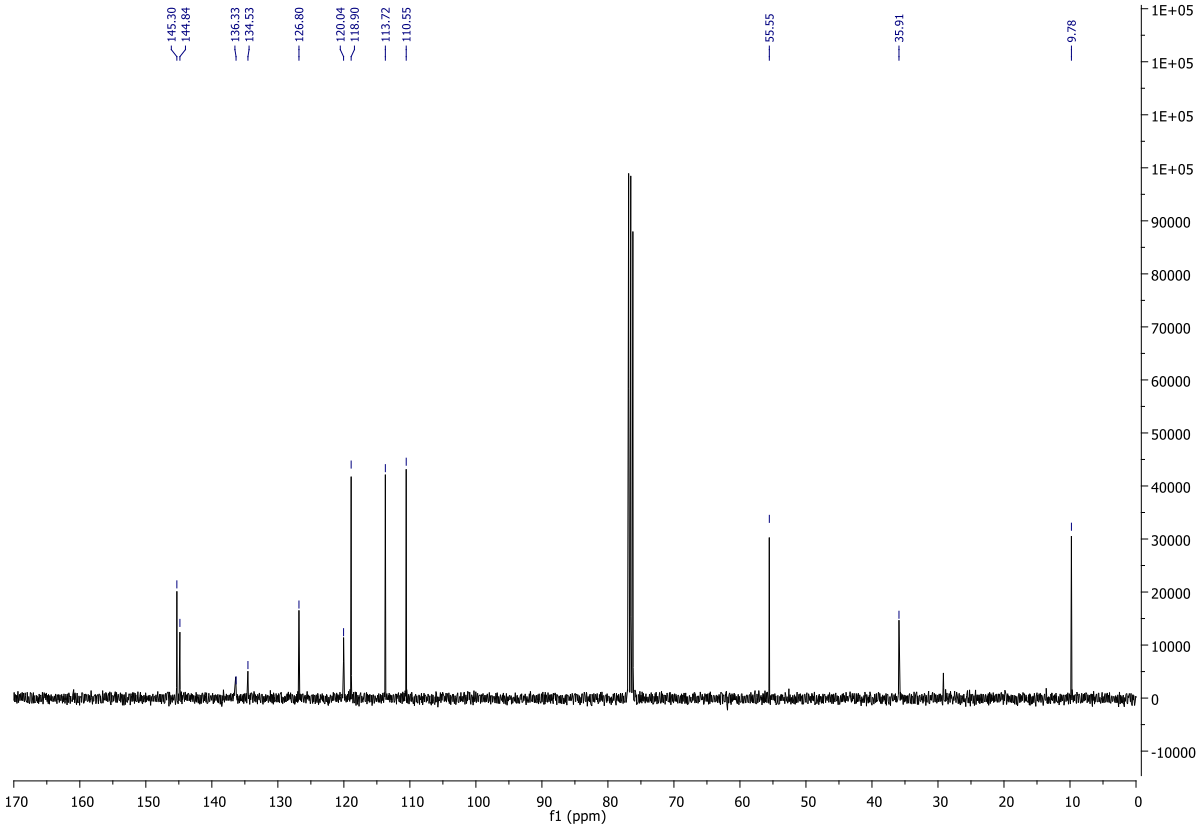
HRMS of 3c



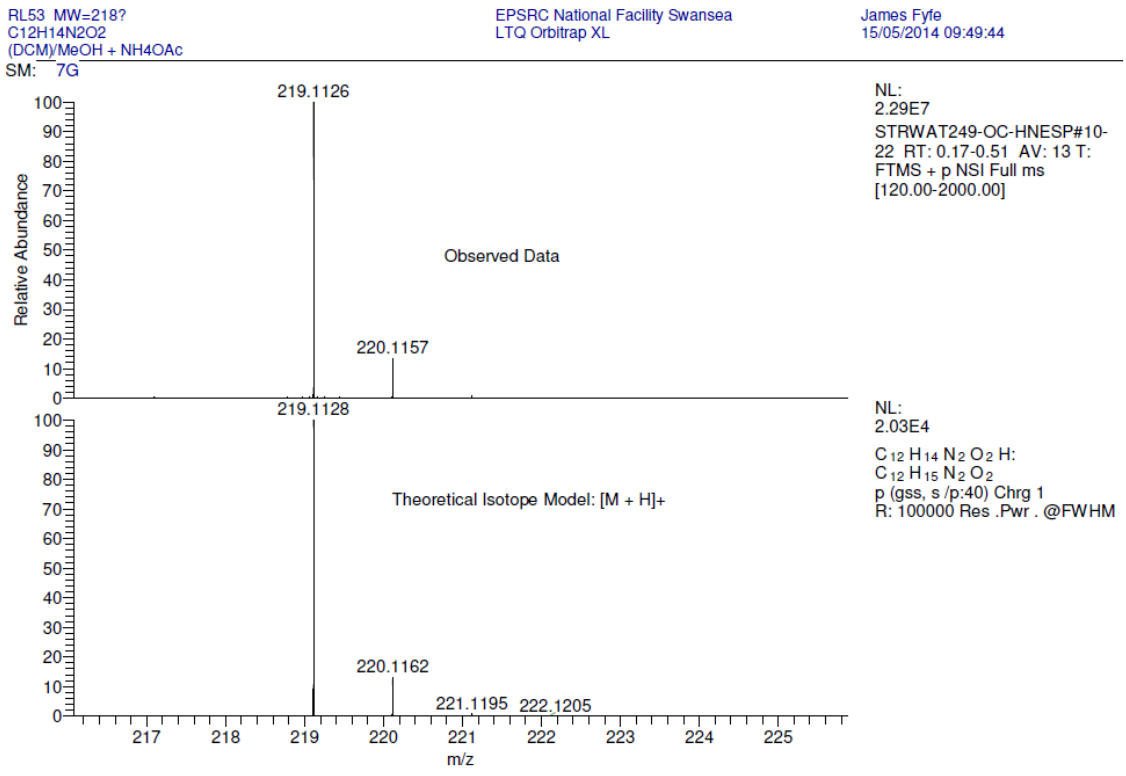
^{1}H NMR of 3d, $CDCl_3$, 400 MHz



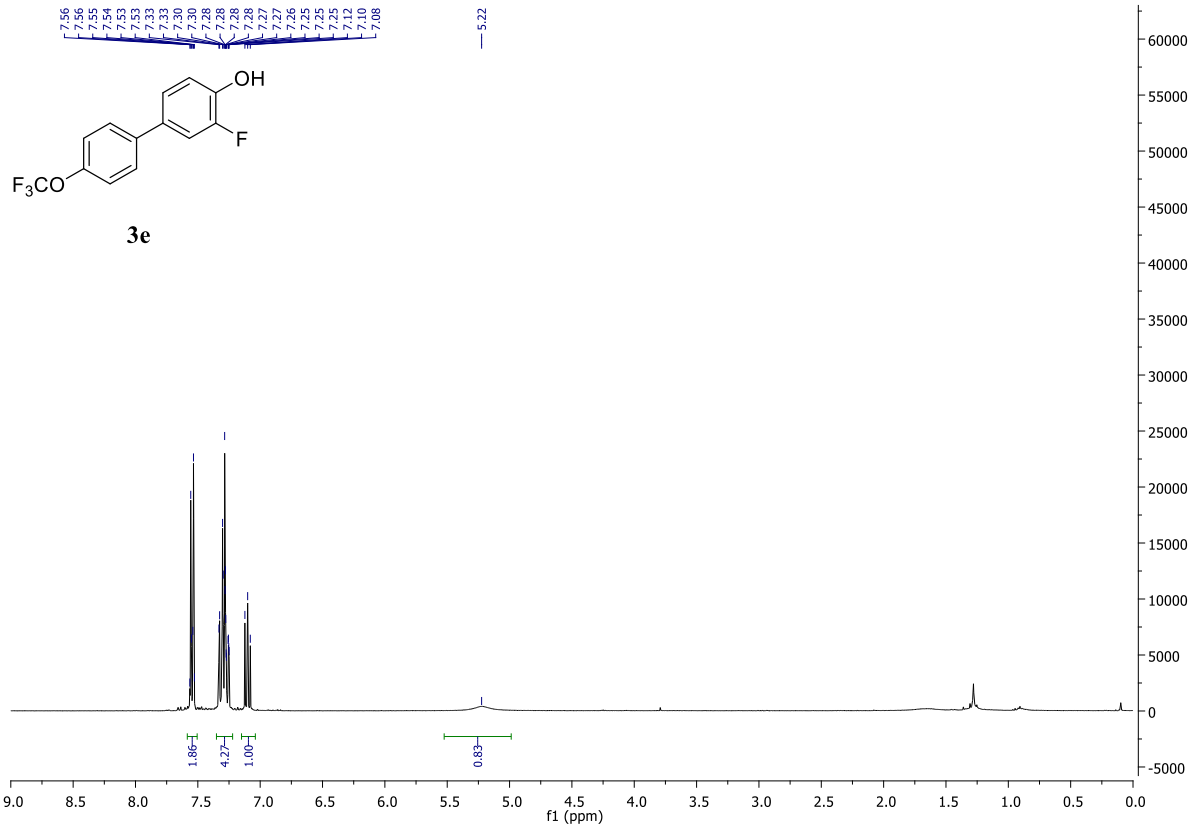
^{13}C NMR of 3d, $CDCl_3$, 101 MHz



HRMS of 3d

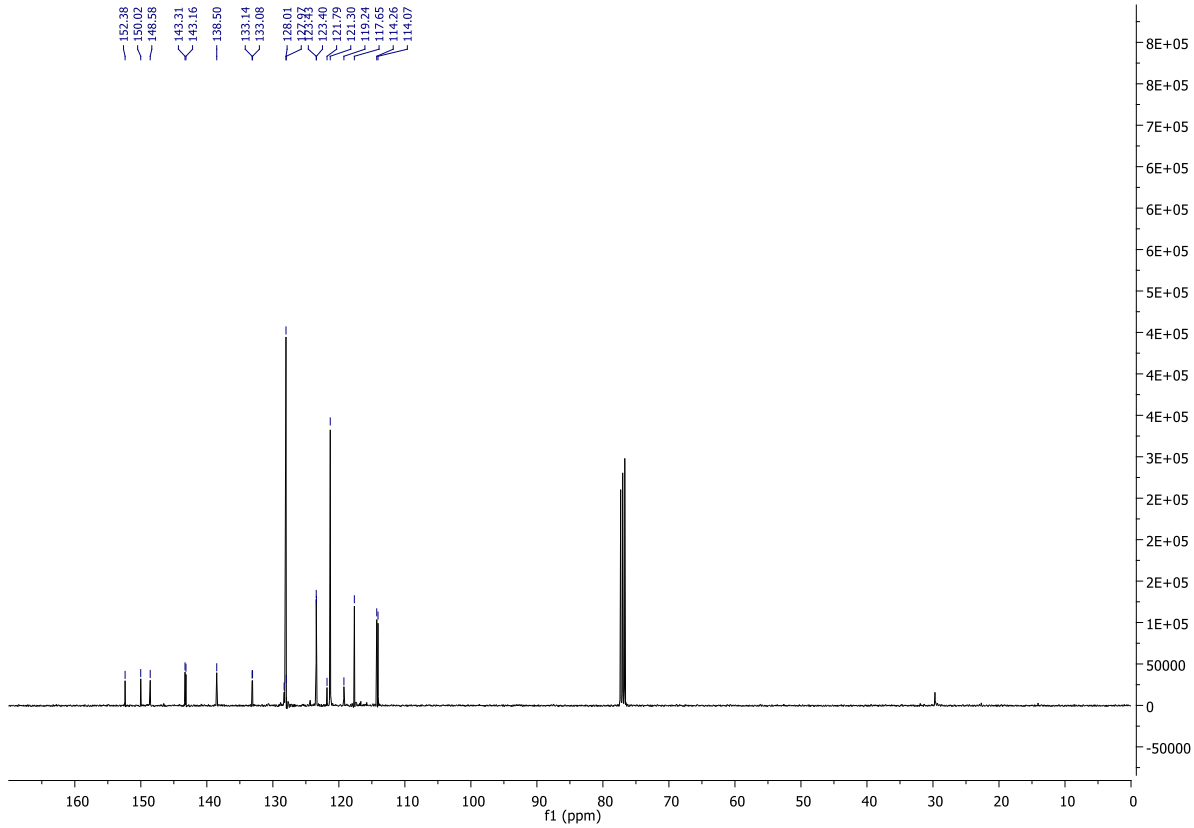


^{1}H NMR of 3e, $CDCl_3$, 400 MHz

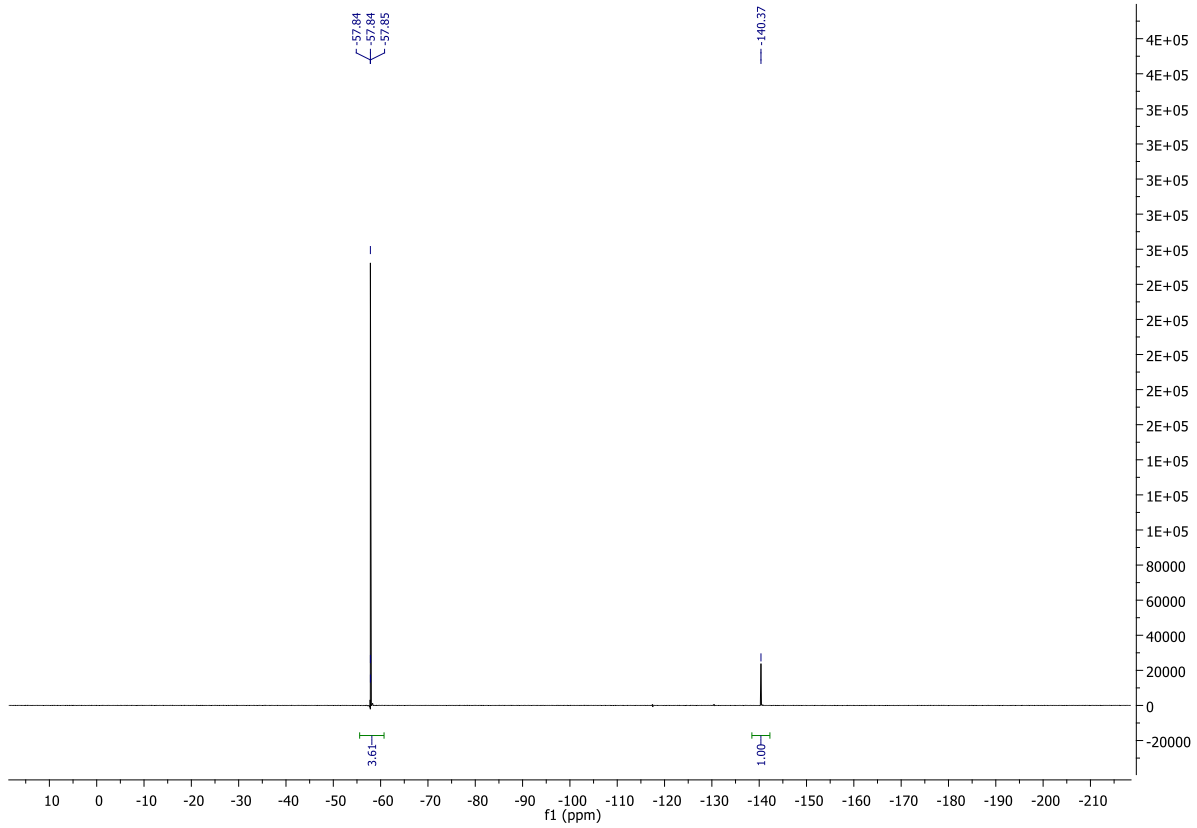


3e

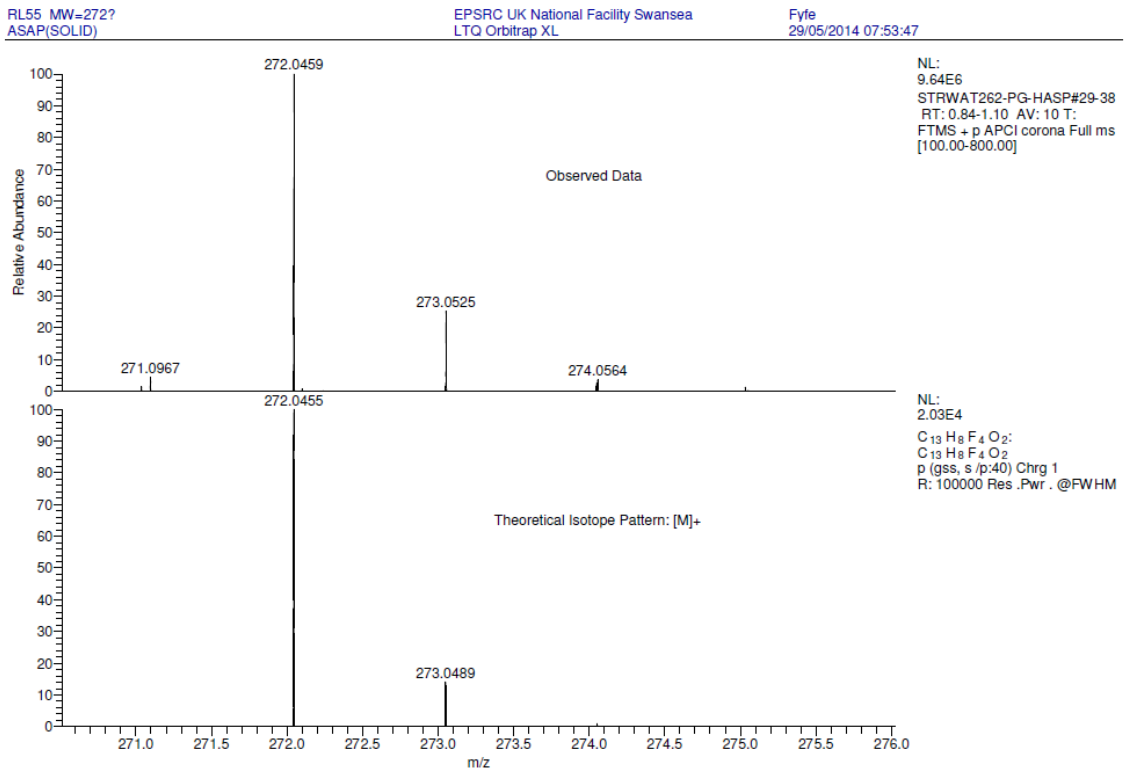
^{13}C NMR of 3e, $CDCl_3$, 101 MHz



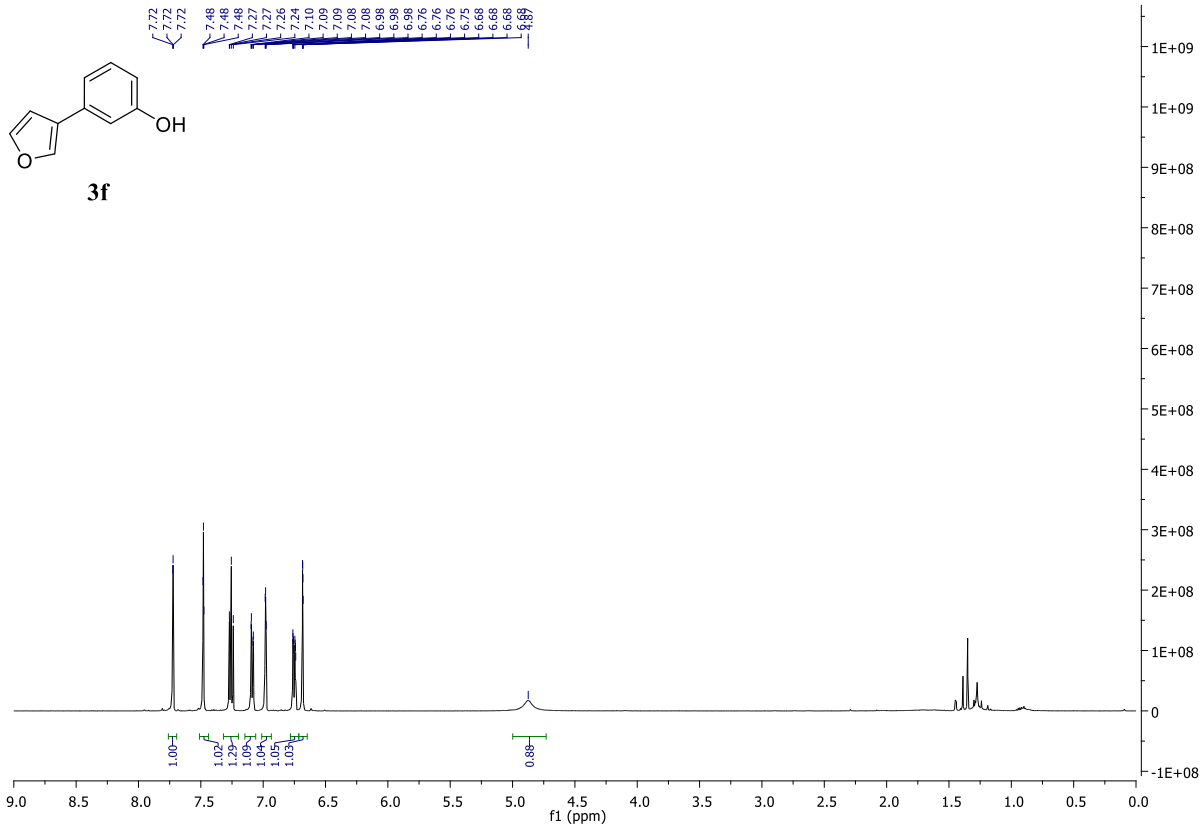
^{19}F NMR of 3e, $CDCl_3$, 376 MHz



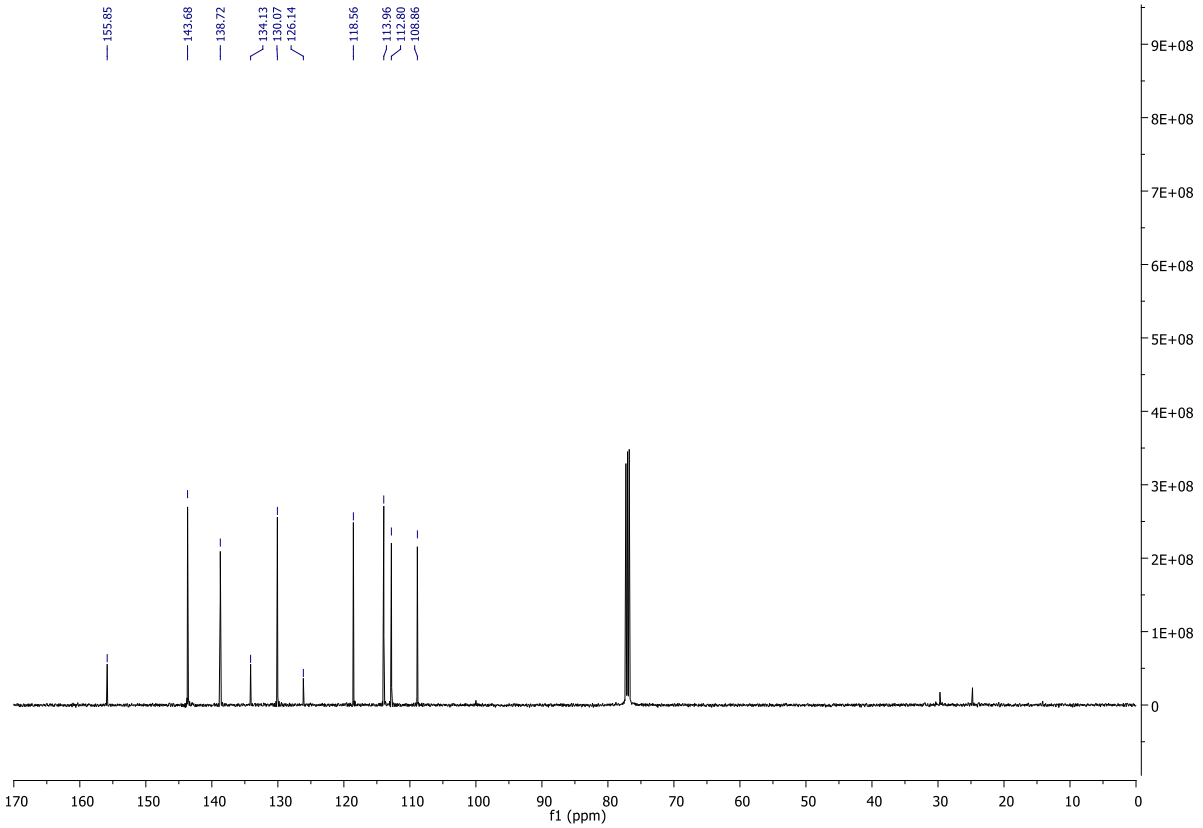
HRMS of 3e



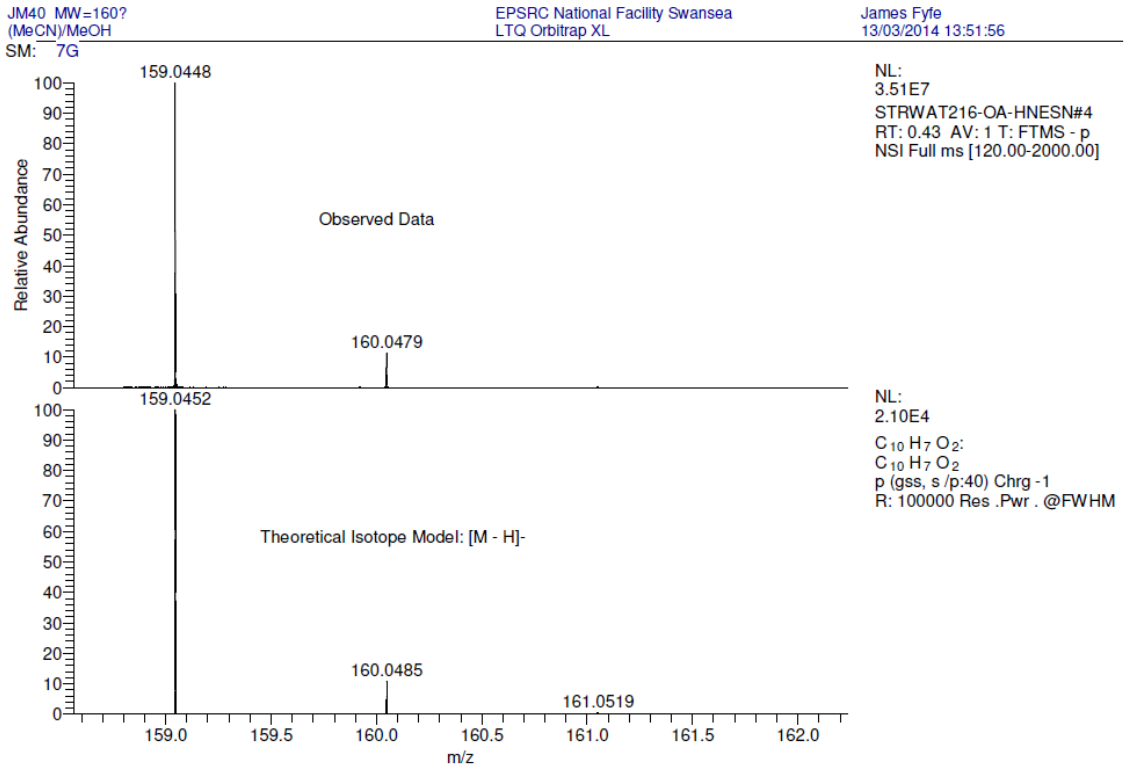
^{1}H NMR of 3f, $CDCl_3$, 500 MHz



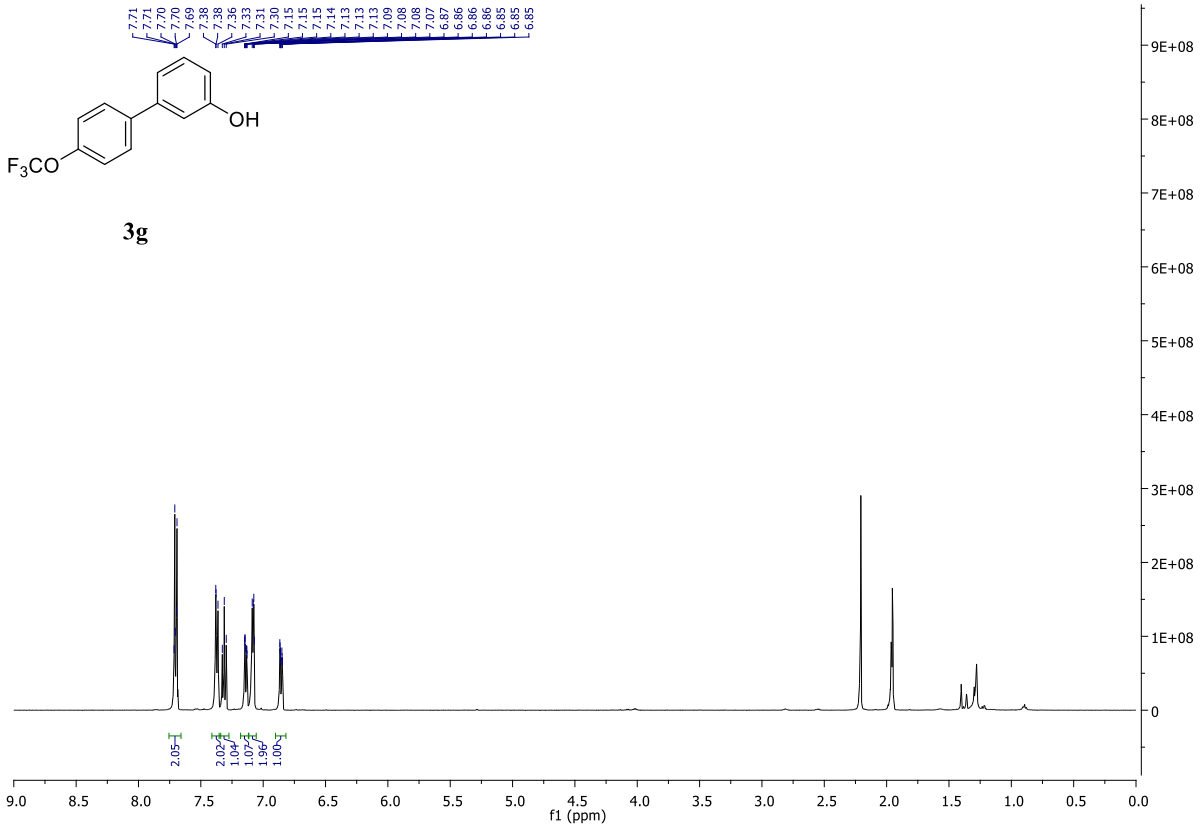
^{13}C NMR of 3f, $CDCl_3$, 126 MHz



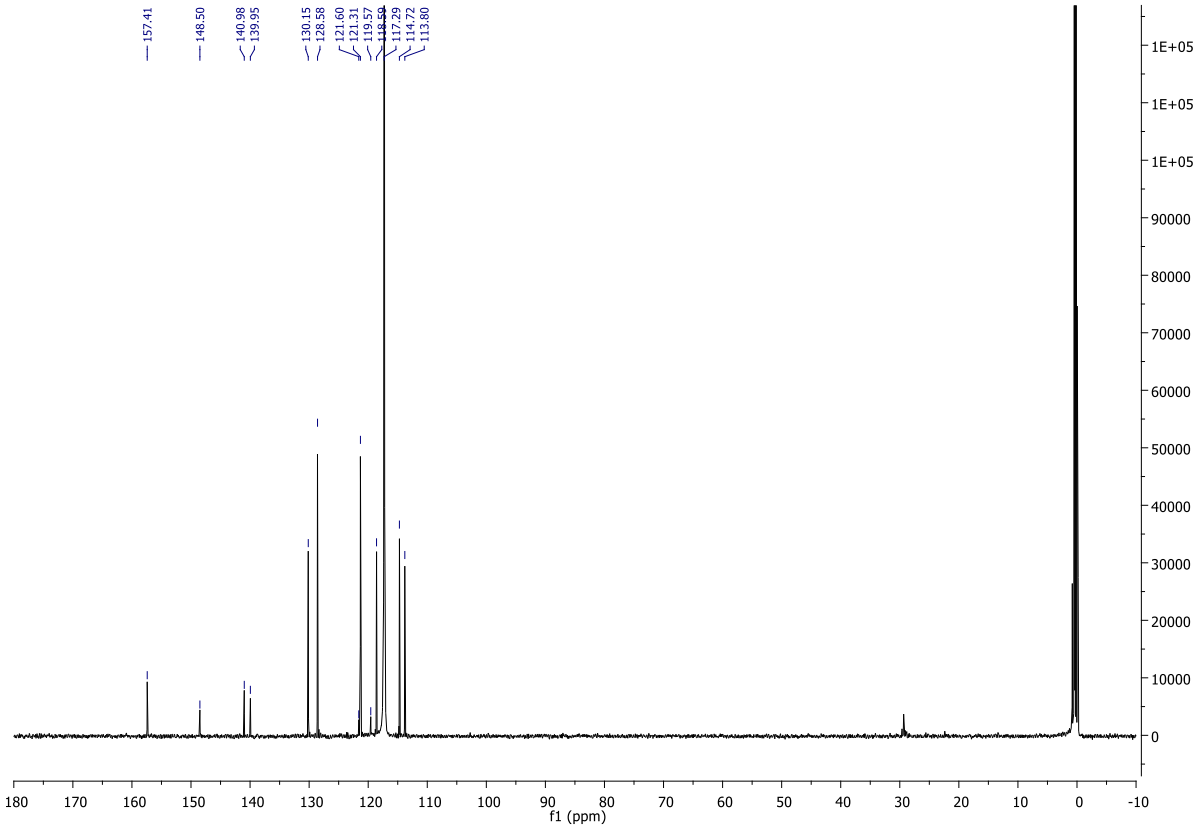
HRMS of 3f



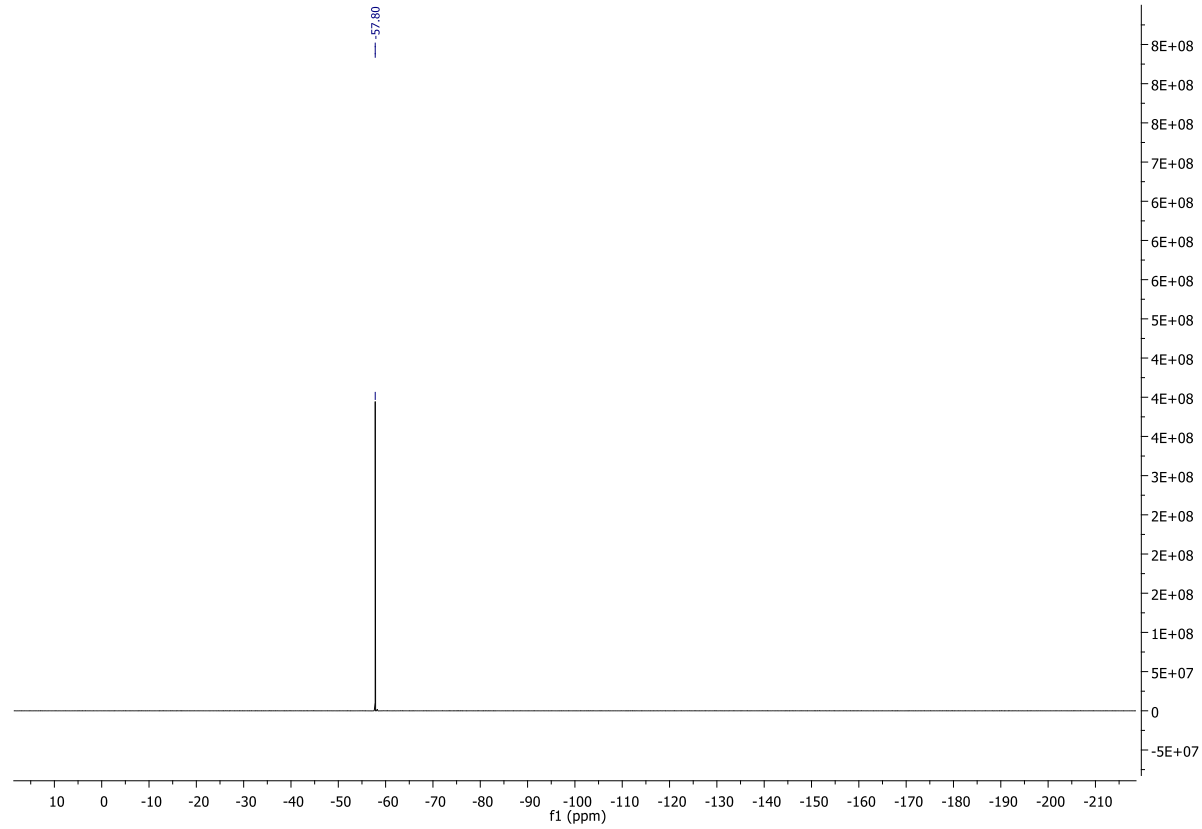
^{1}H NMR of 3g, CD_3CN, 500 MHz



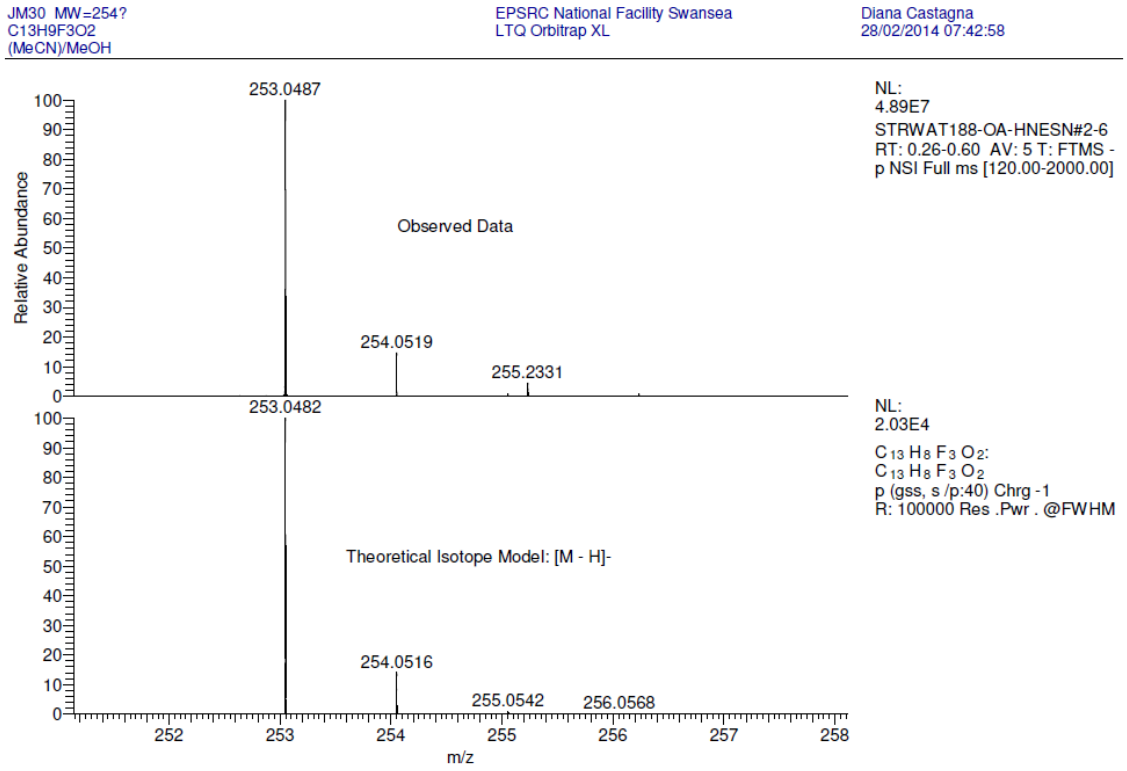
^{13}C NMR of 3g, CD_3CN, 126 MHz



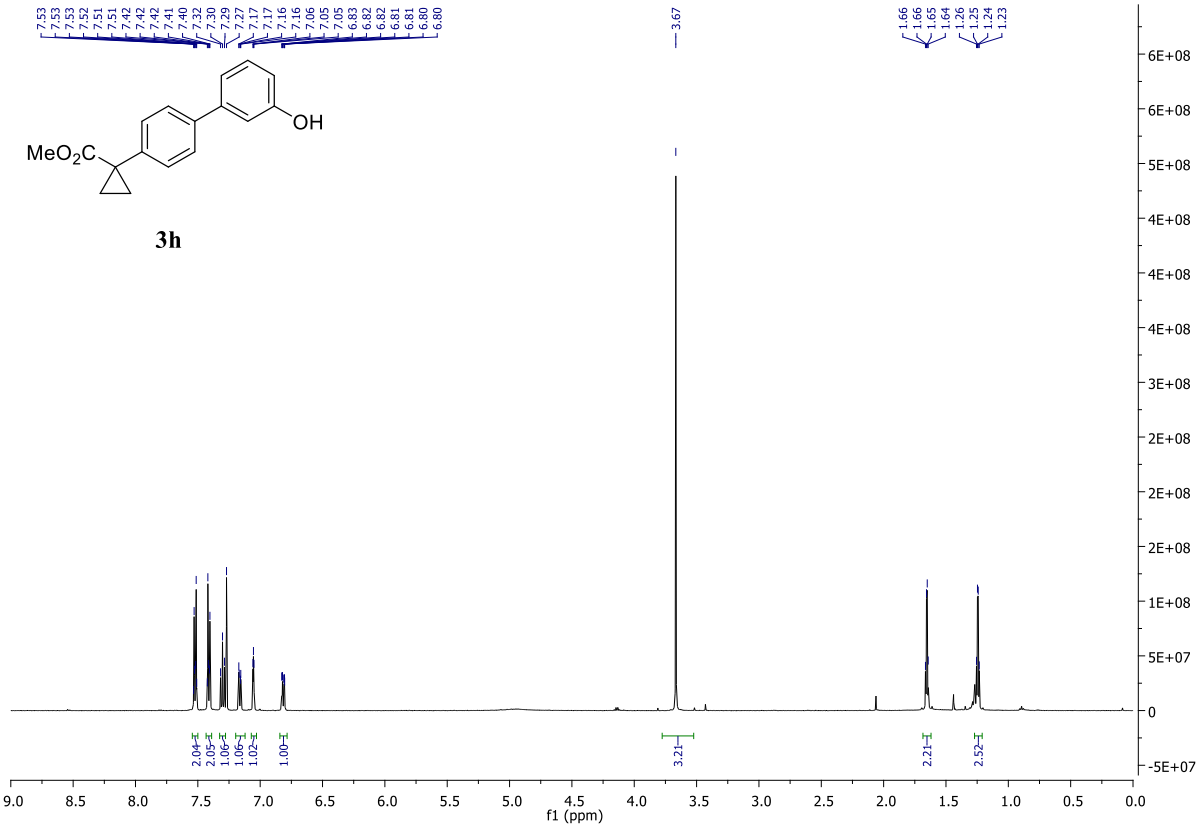
^{19}F NMR of 3g, CD_3CN, 376 MHz



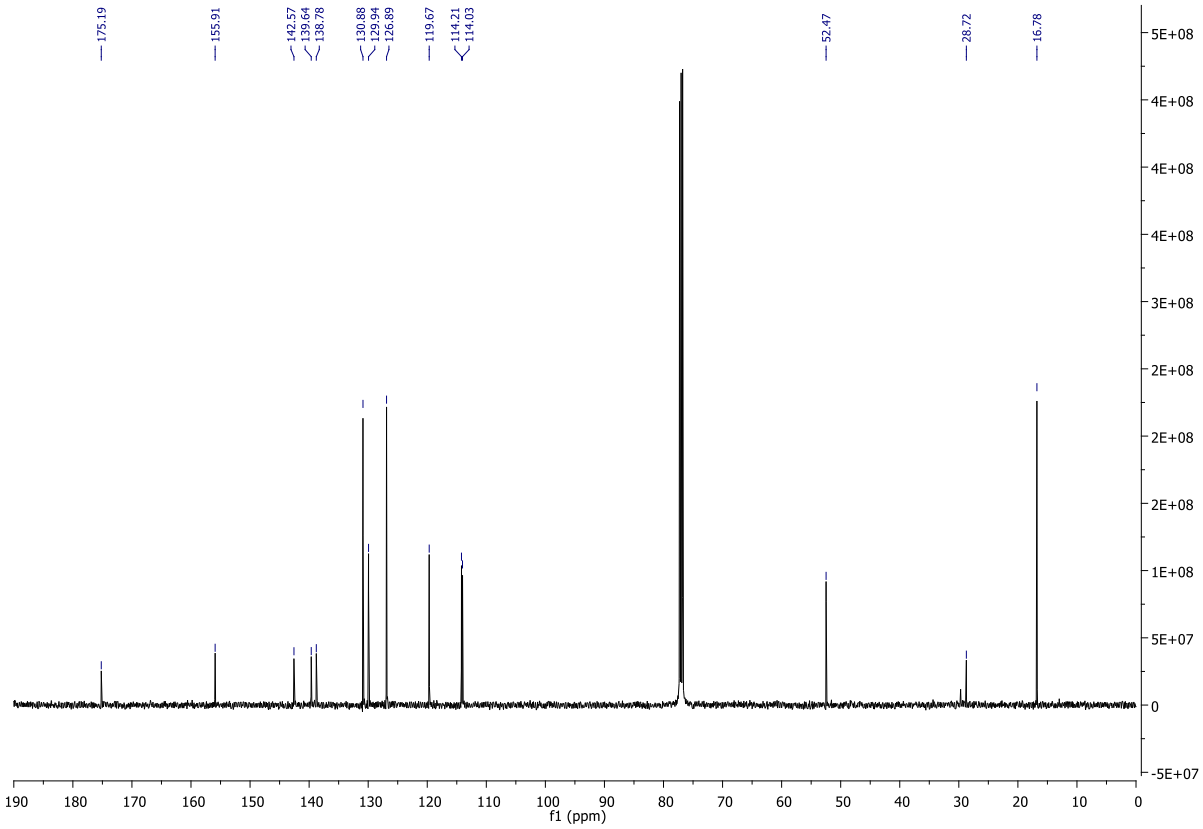
HRMS of 3g



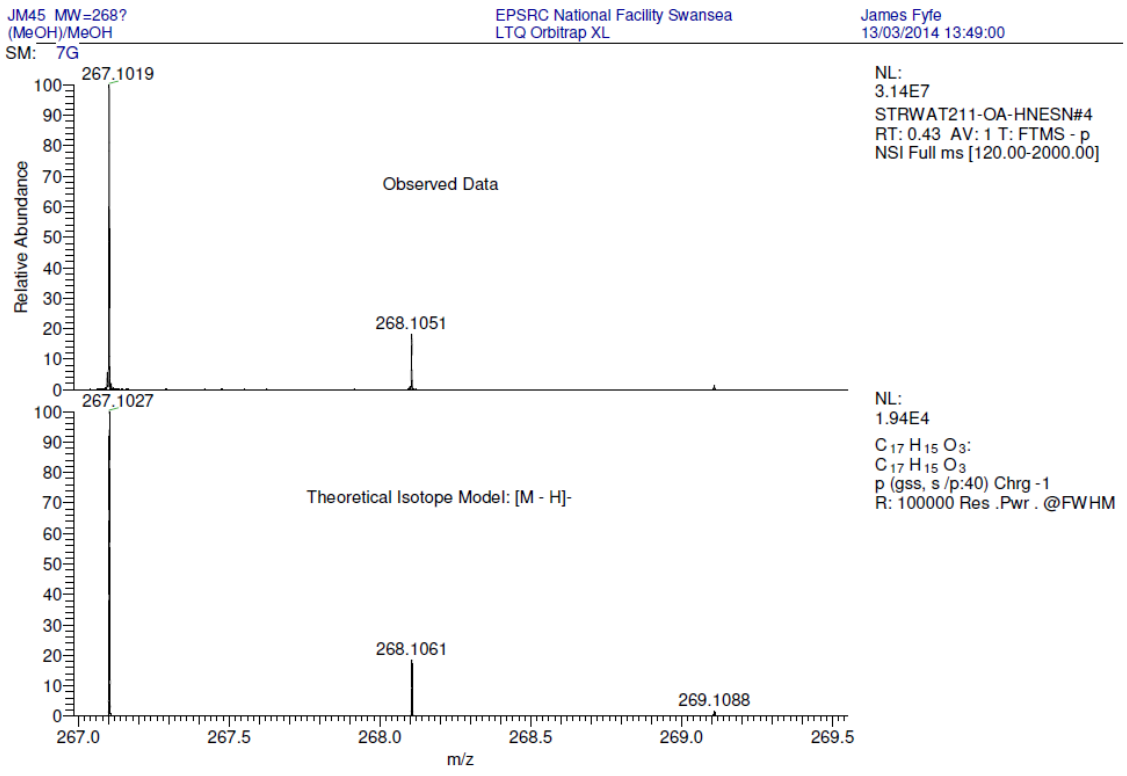
^{1}H NMR of 3h, $CDCl_3$, 500 MHz



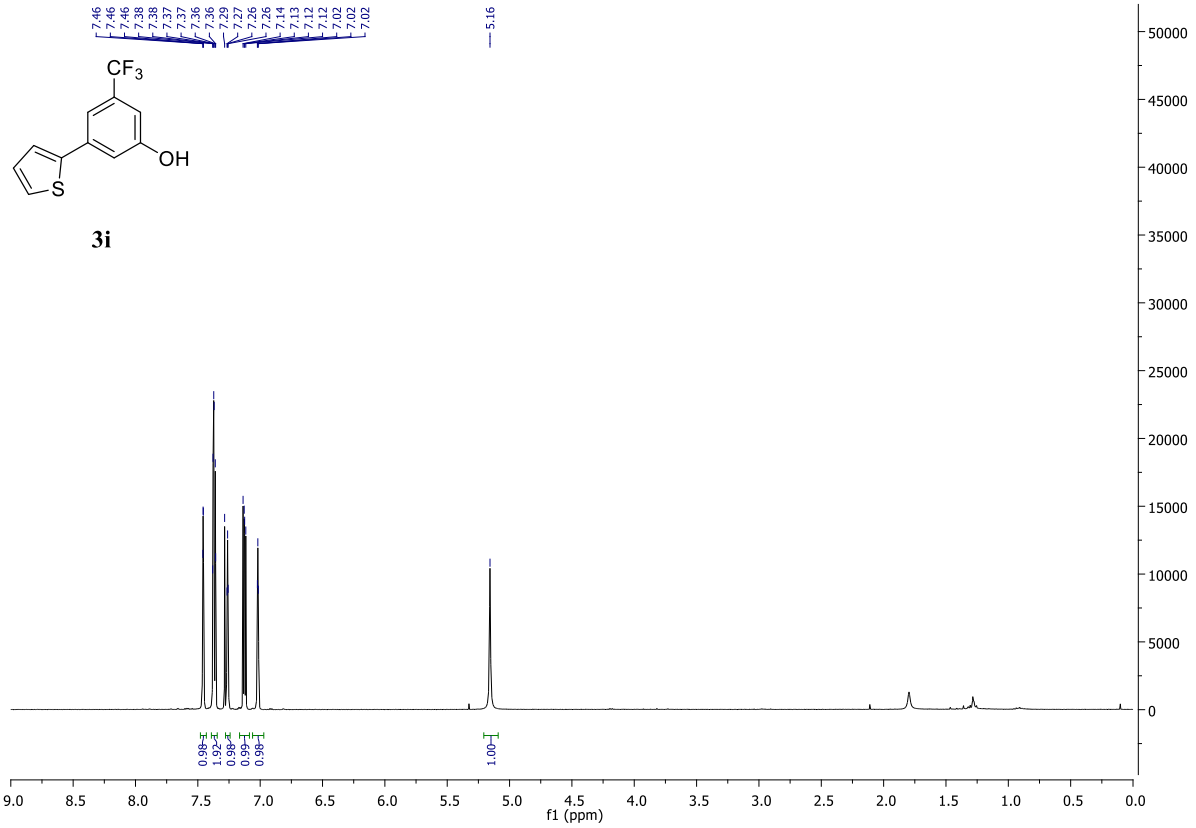
^{13}C NMR of 3h, $CDCl_3$, 126 MHz



HRMS of 3h

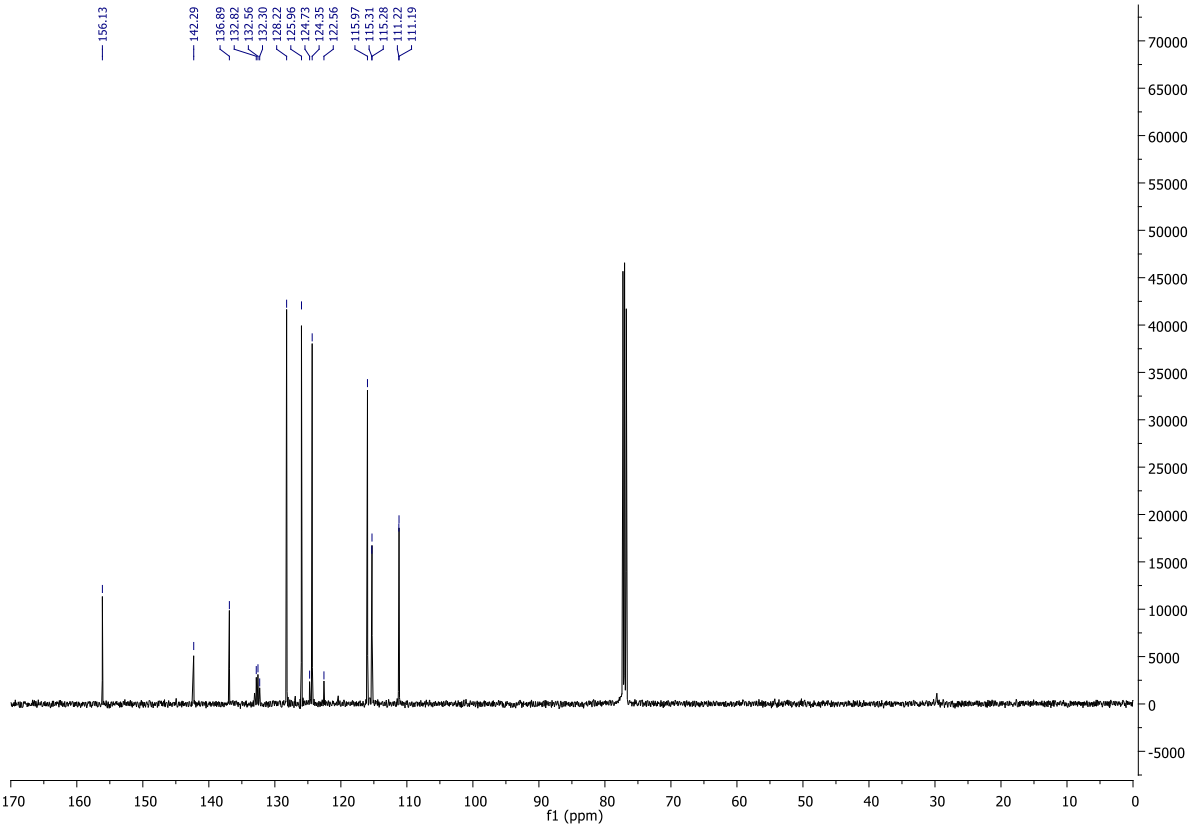


^{1}H NMR of 3i, $CDCl_3$, 400 MHz

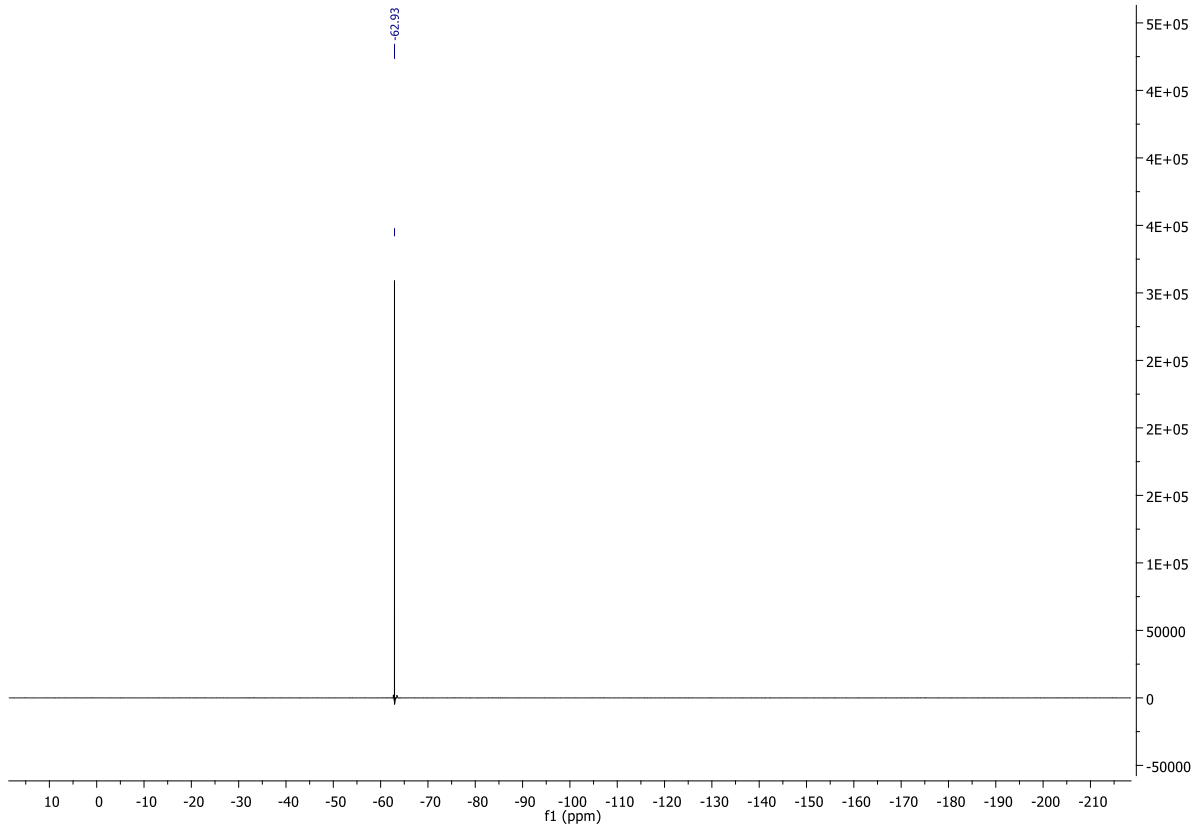


3i

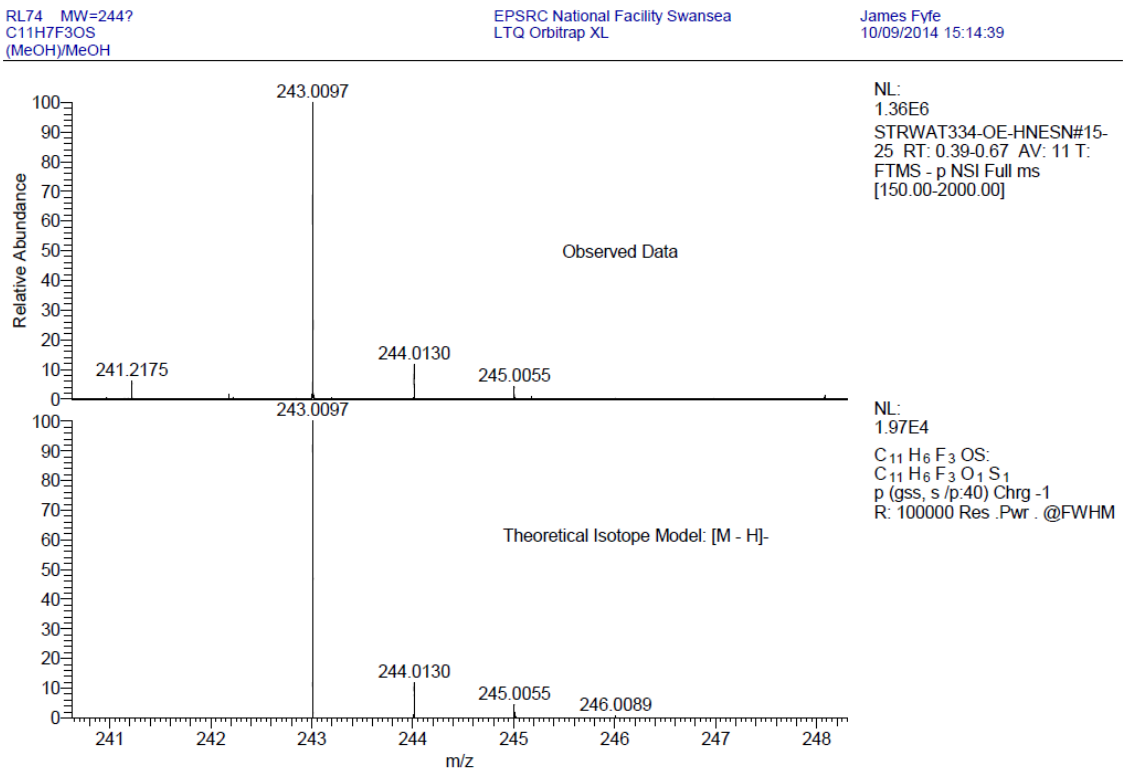
^{13}C NMR of 3i, $CDCl_3$, 101 MHz



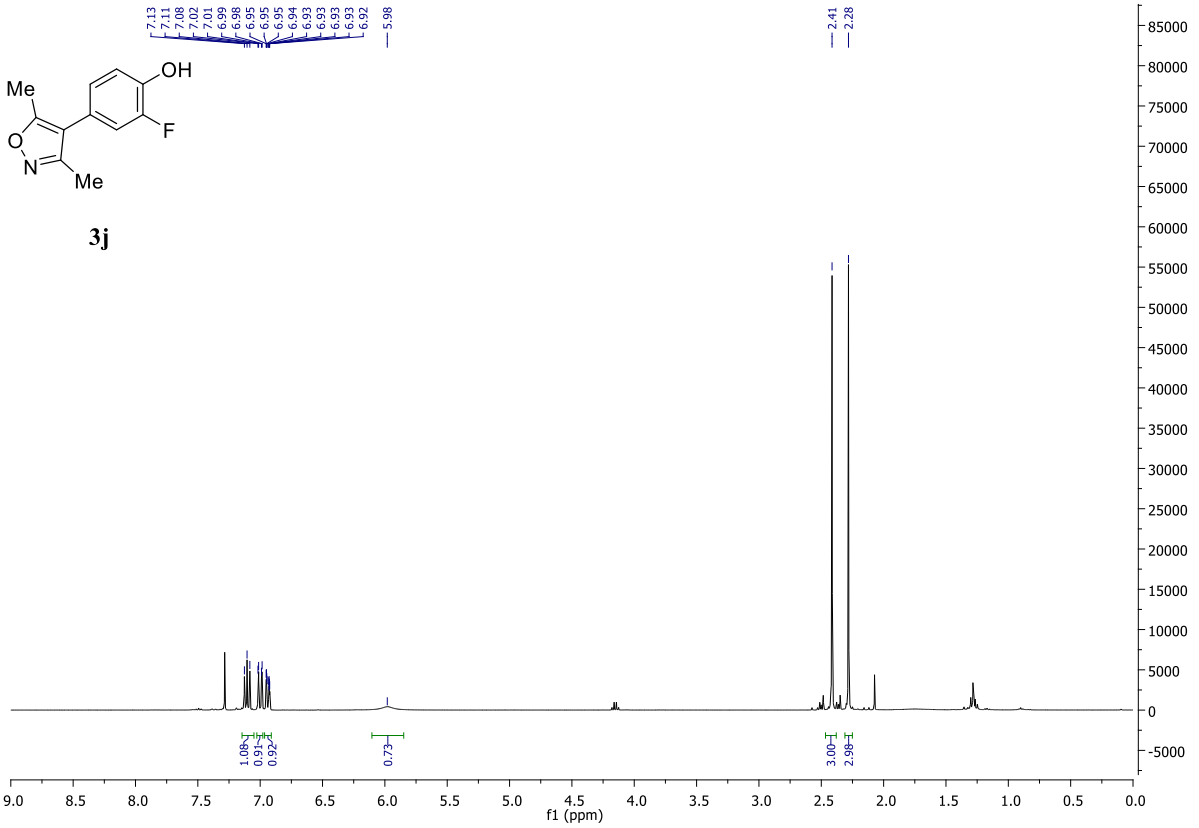
^{19}F NMR of 3i, $CDCl_3$, 376 MHz



HRMS of 3i

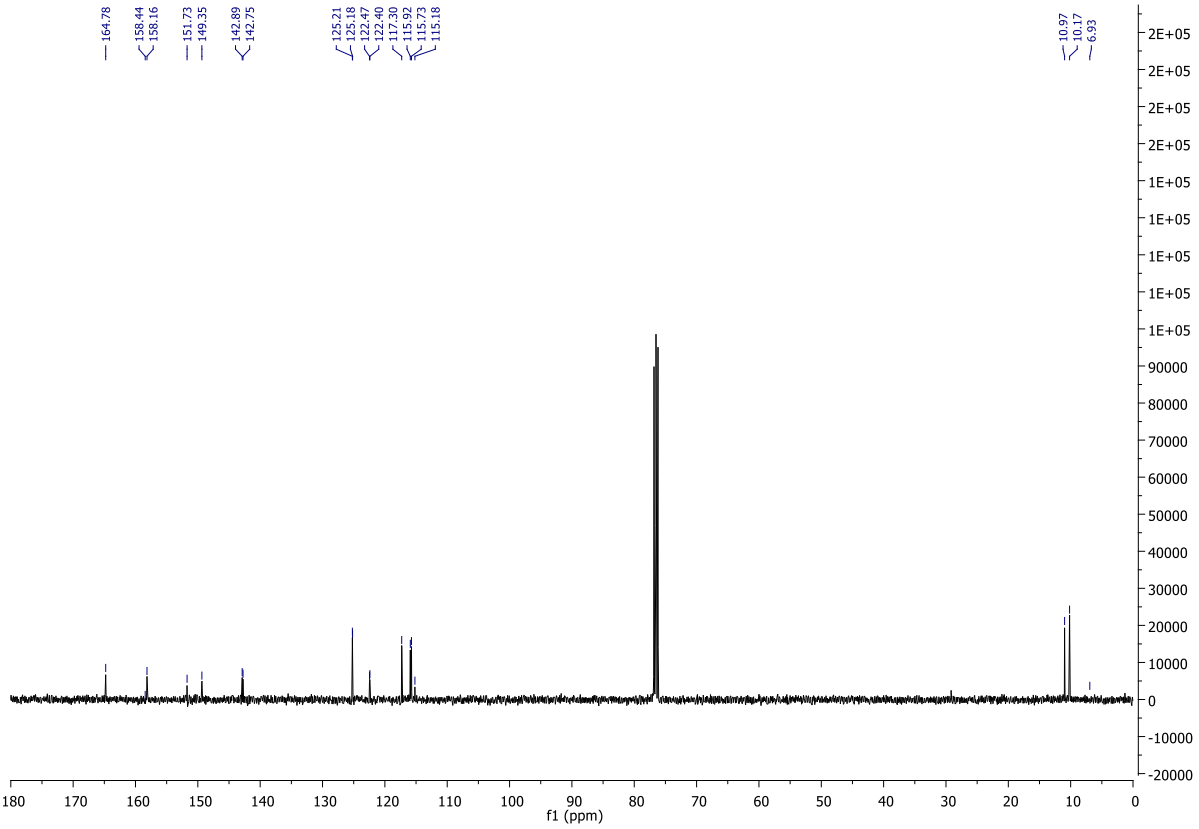


^{1}H NMR of 3j, $CDCl_3$, 400 MHz

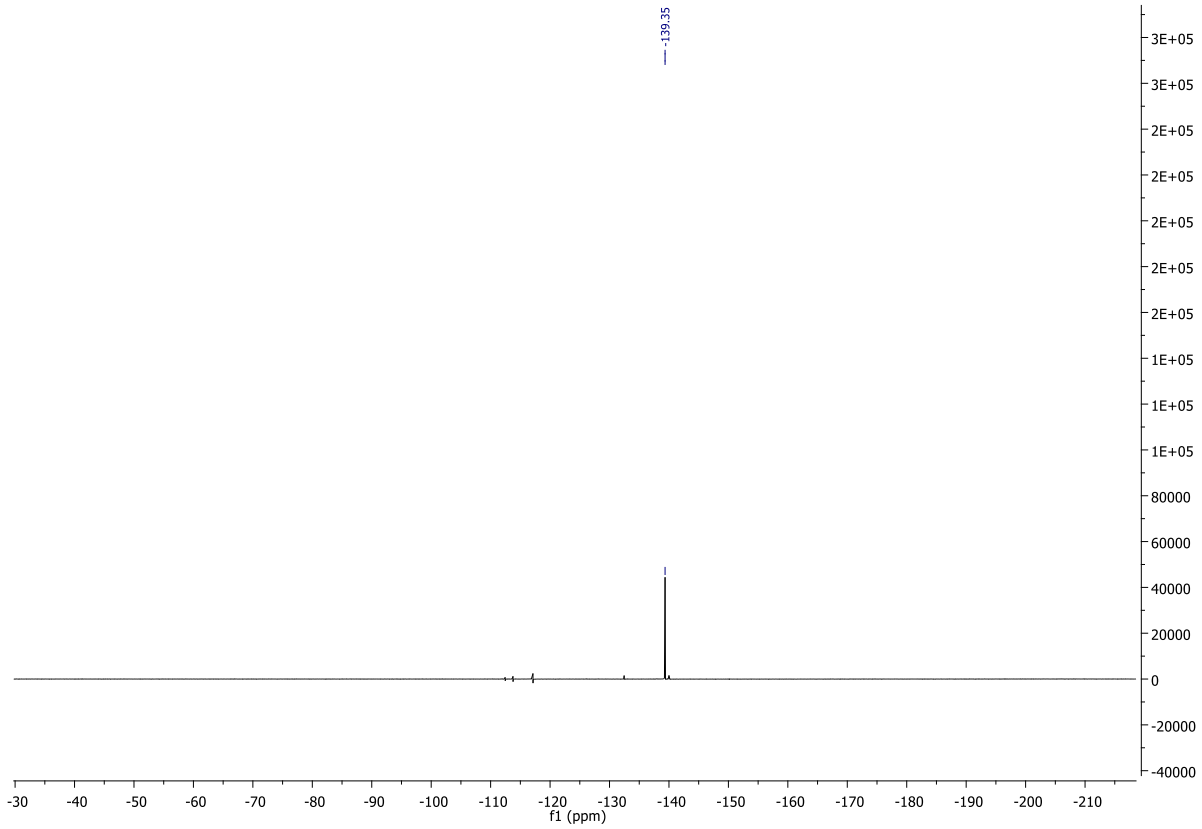


3j

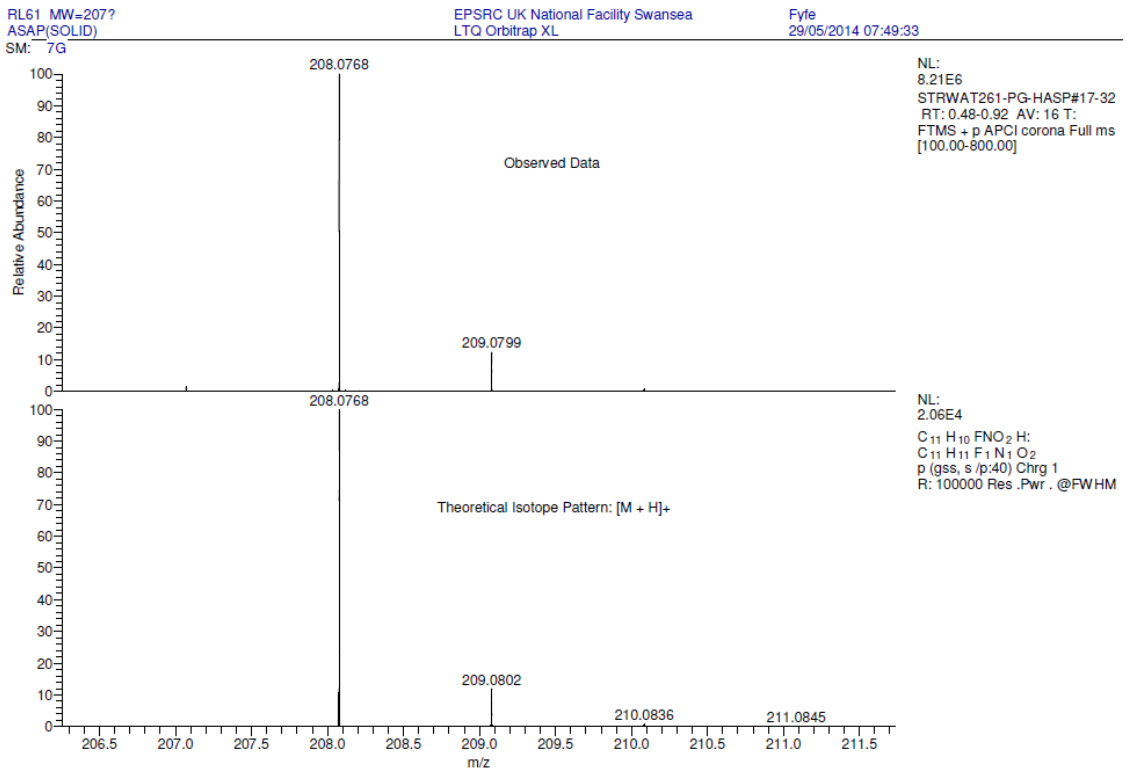
^{13}C NMR of 3j, $CDCl_3$, 101 MHz



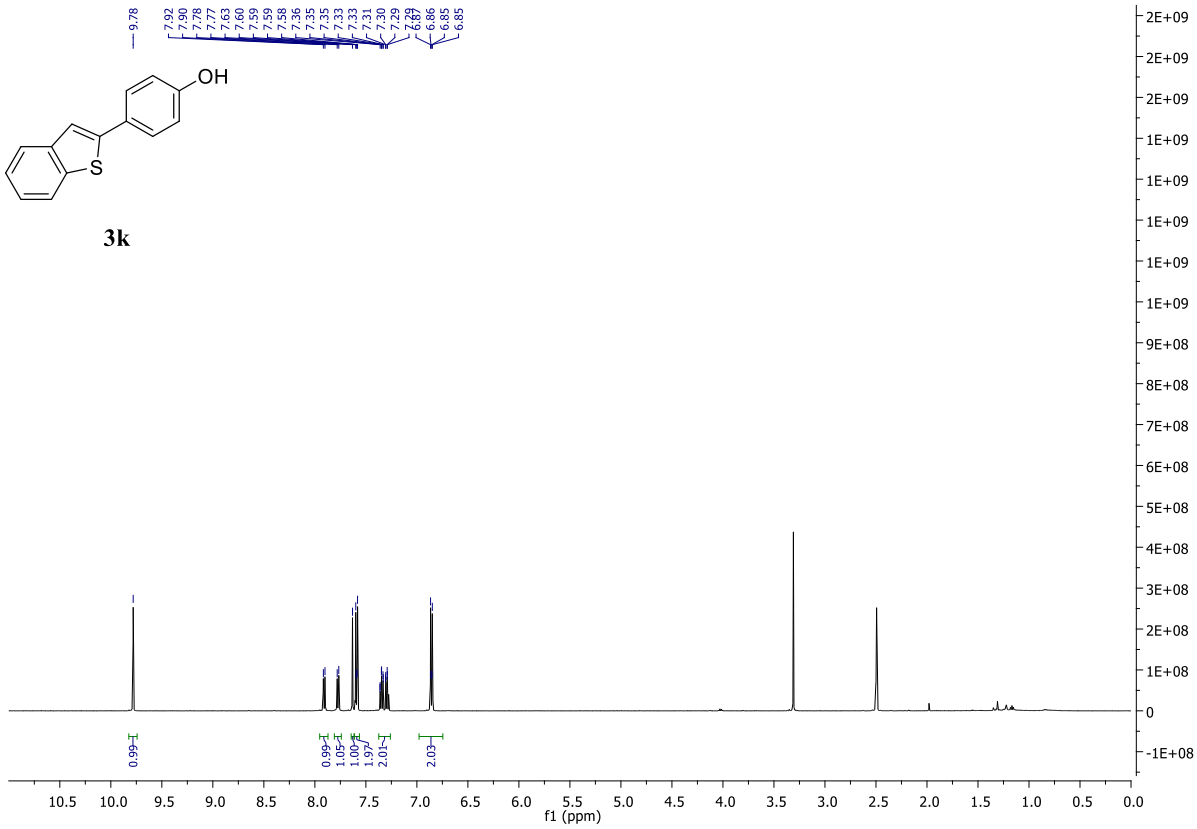
^{19}F NMR of 3j, $CDCl_3$, 376 MHz



HRMS of 3j

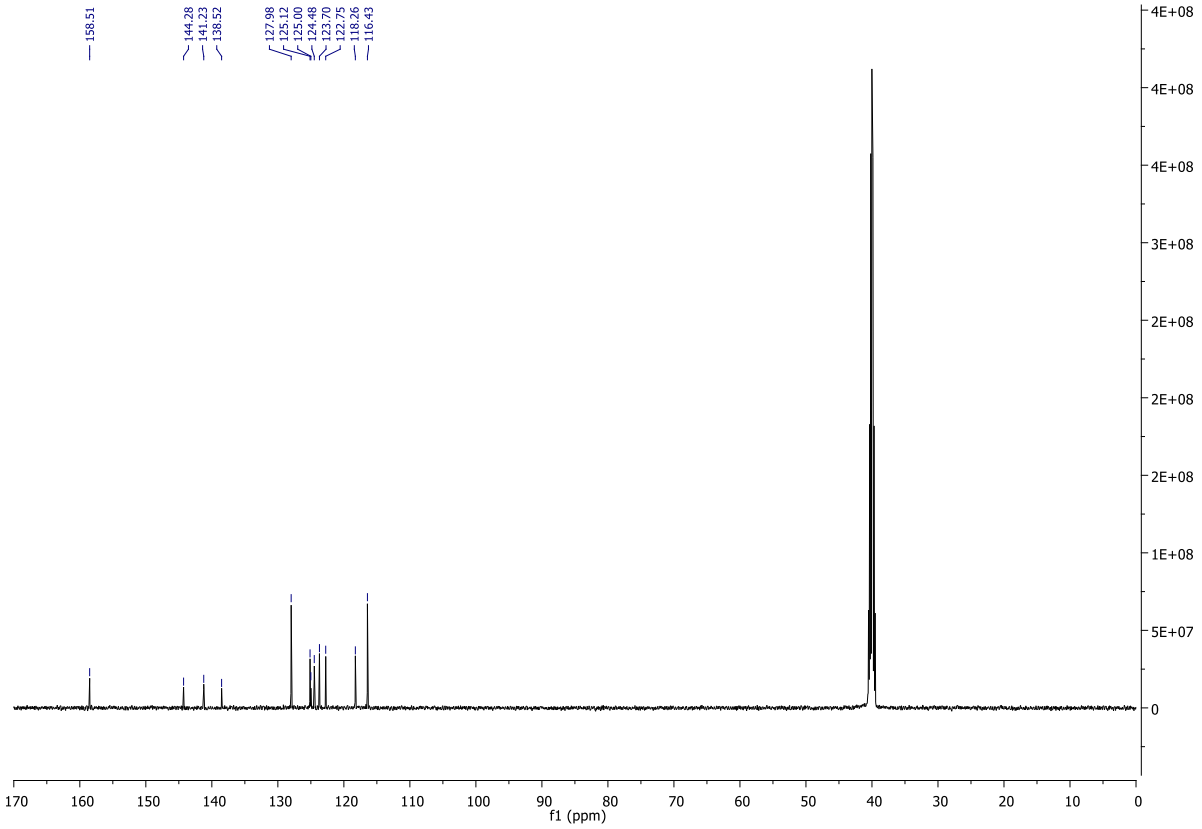


^{1}H NMR of 3k, DMSO-d$_6$, 500 MHz

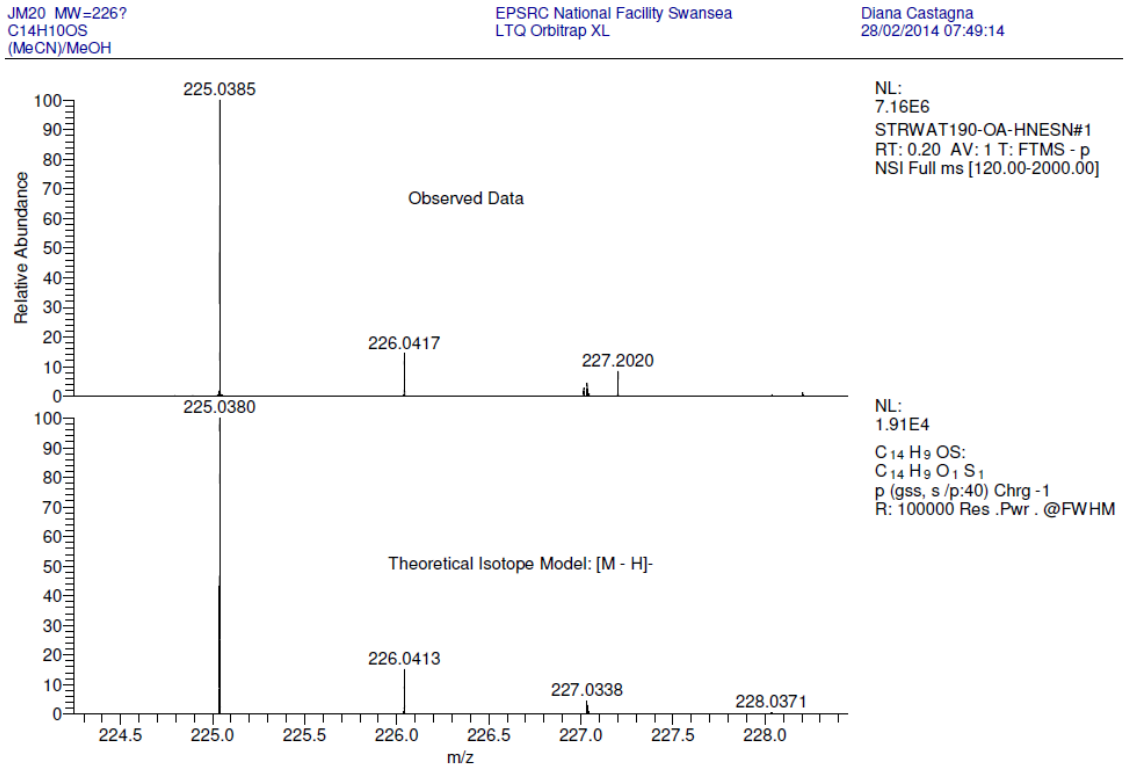


3k

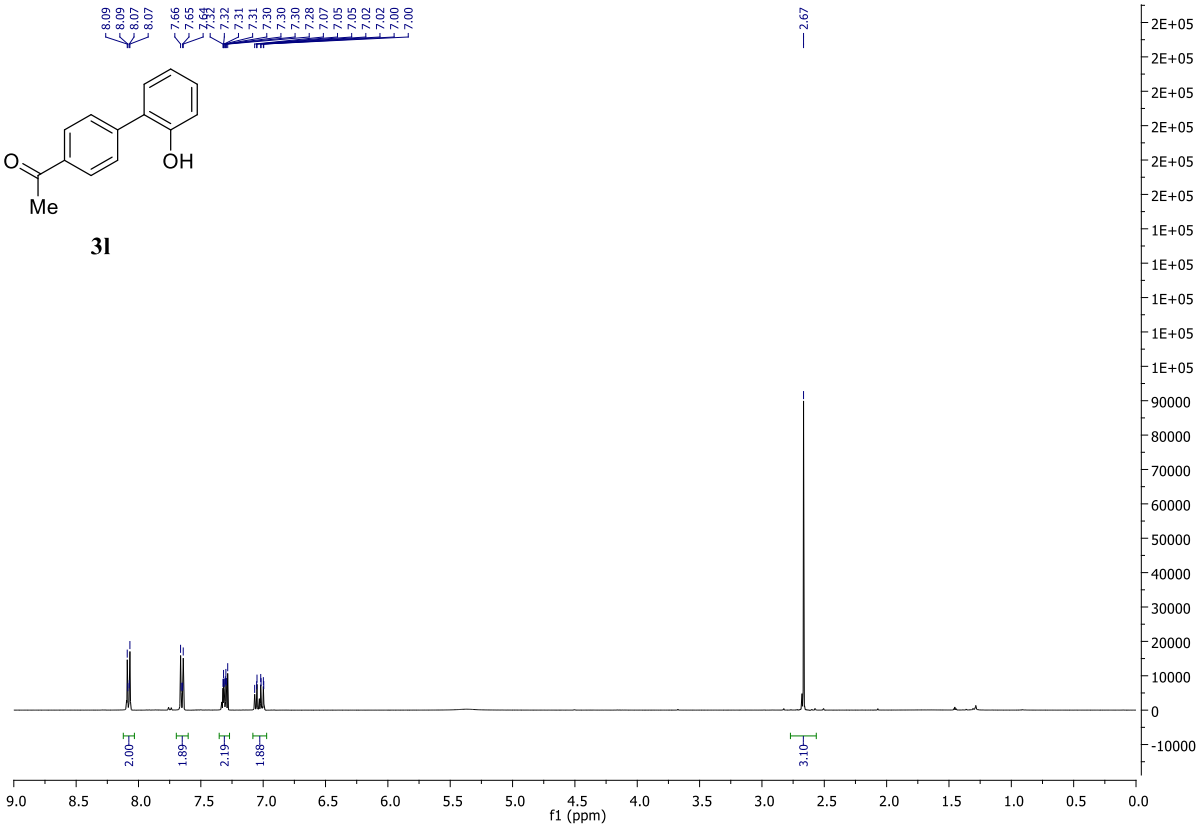
^{13}C NMR of 3k, DMSO-d$_6$, 126 MHz



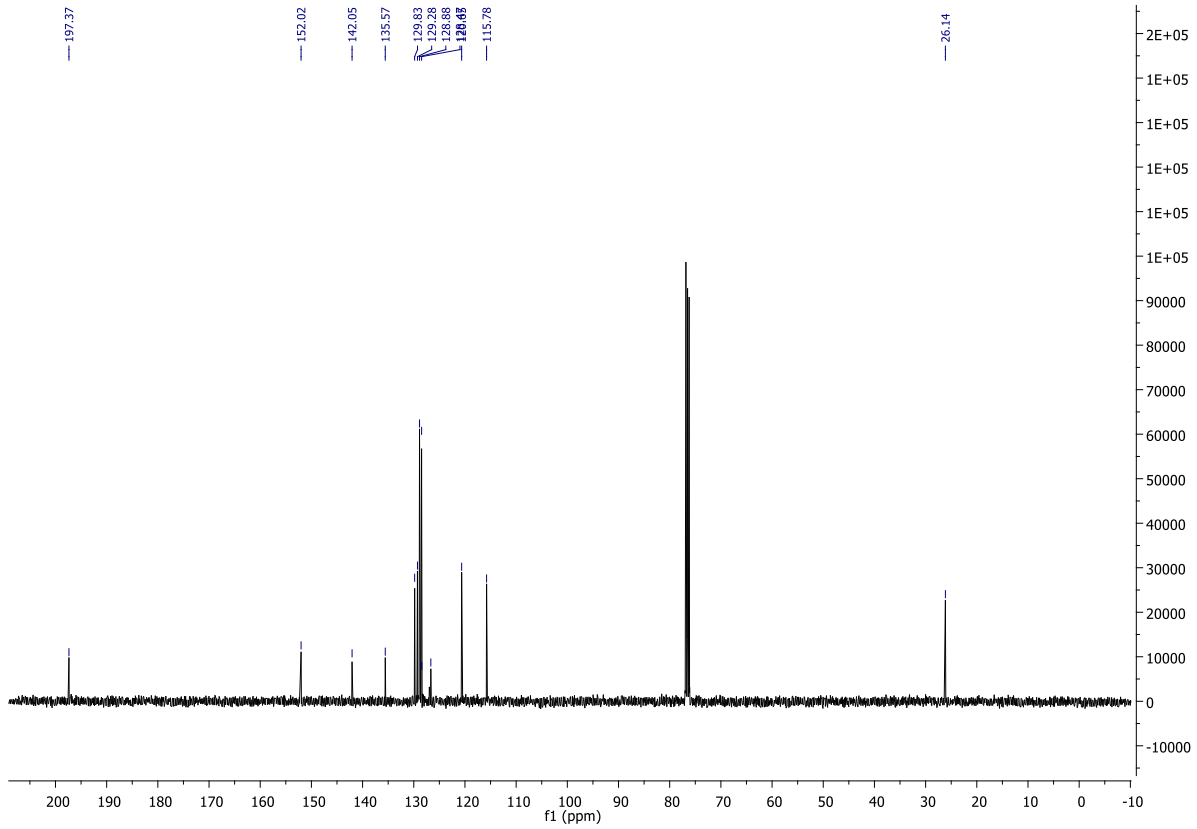
HRMS of 3k



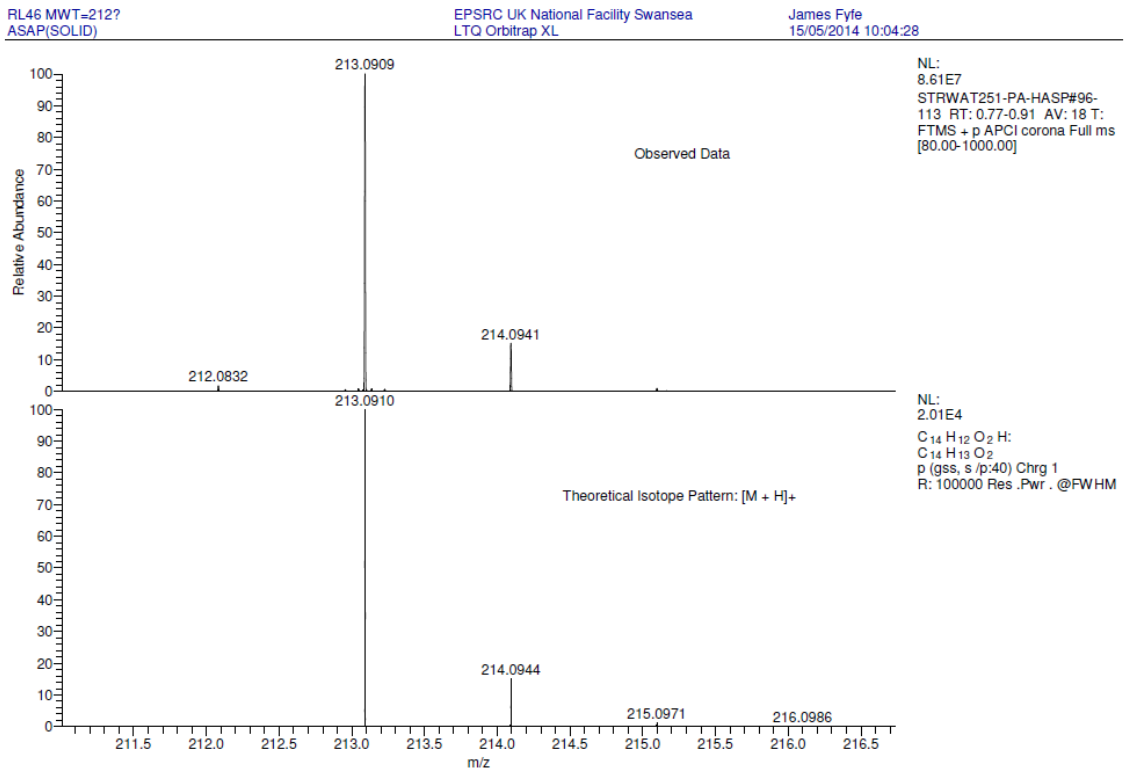
^{1}H NMR of 3l, $CDCl_3$, 400 MHz



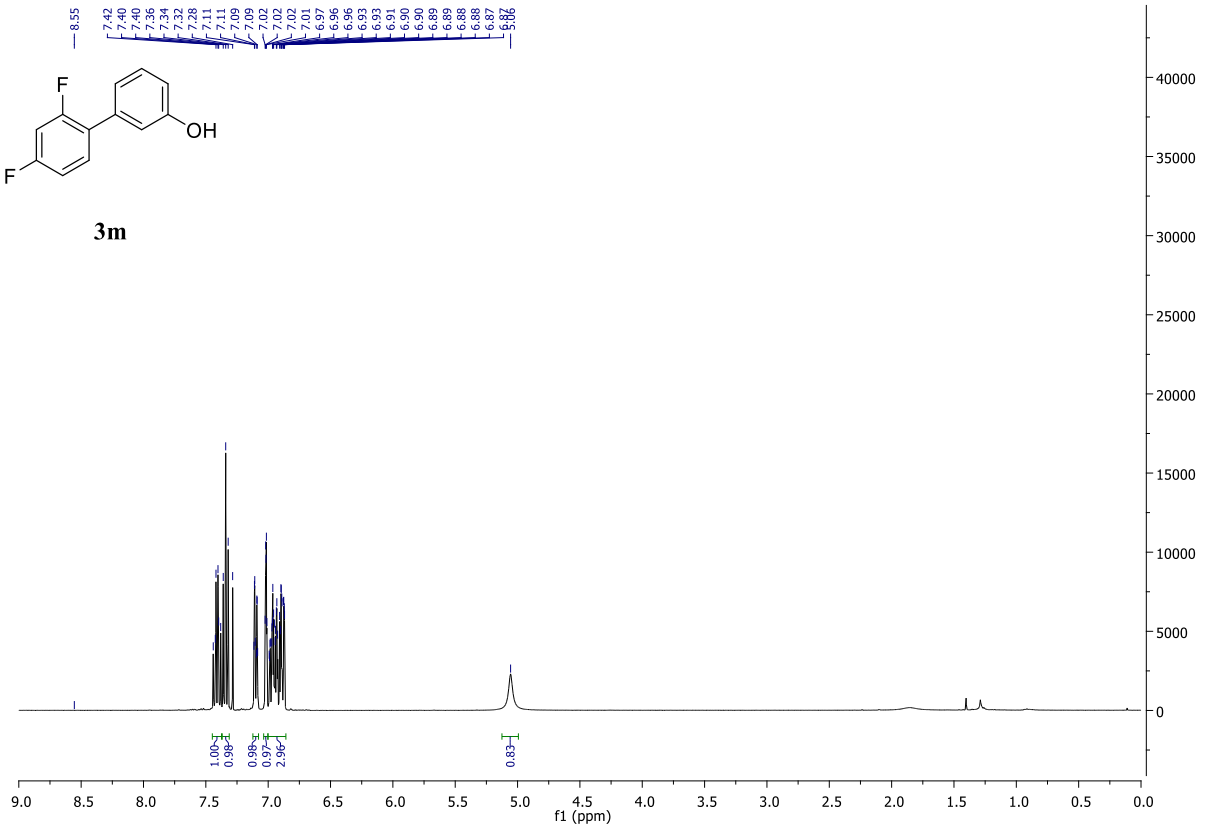
^{13}C NMR of 3l, $CDCl_3$, 101 MHz



HRMS of 3l

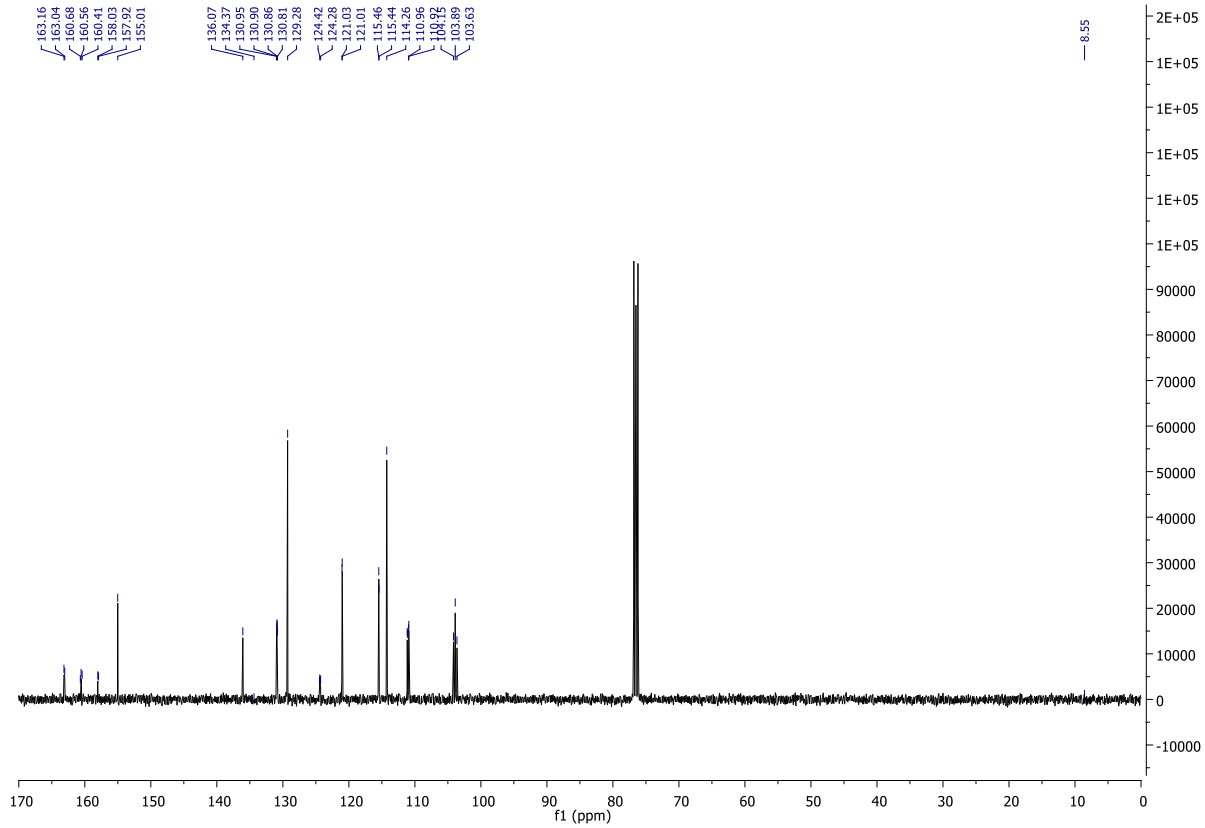


^{1}H NMR of 3m, $CDCl_3$, 400 MHz

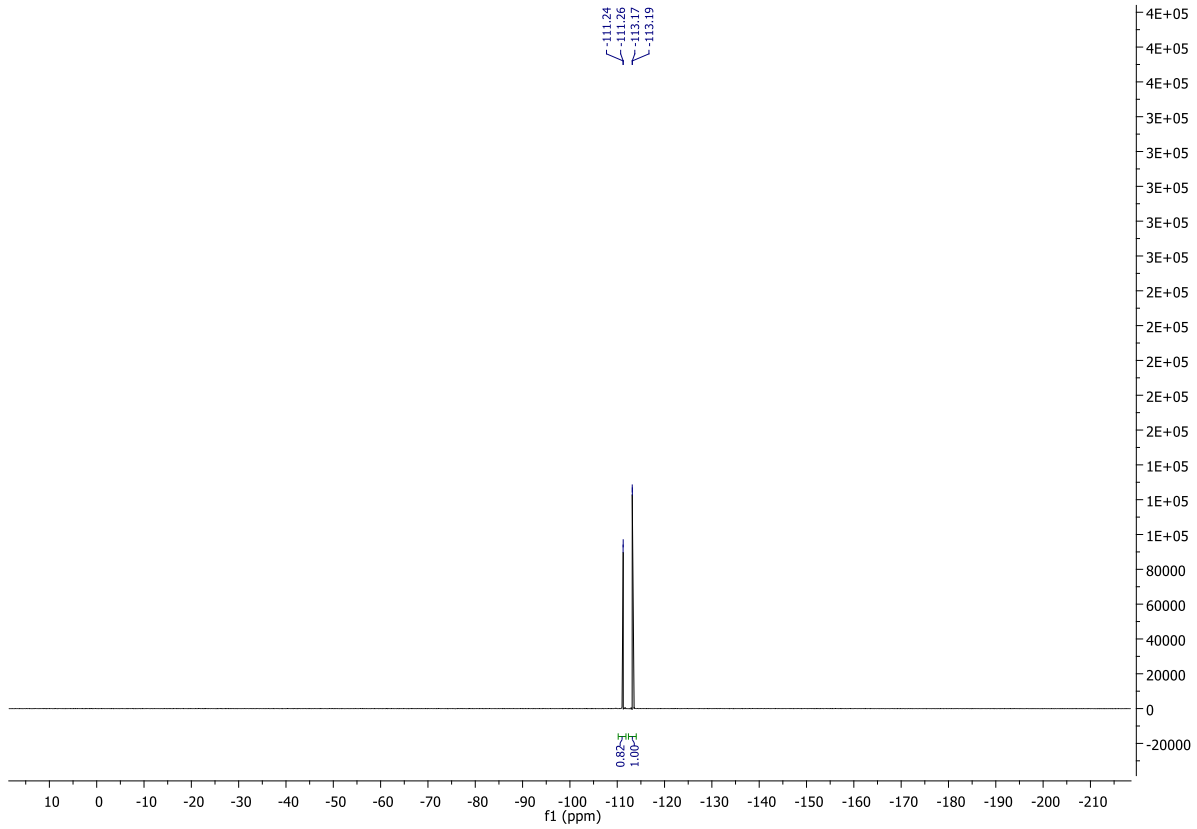


3m

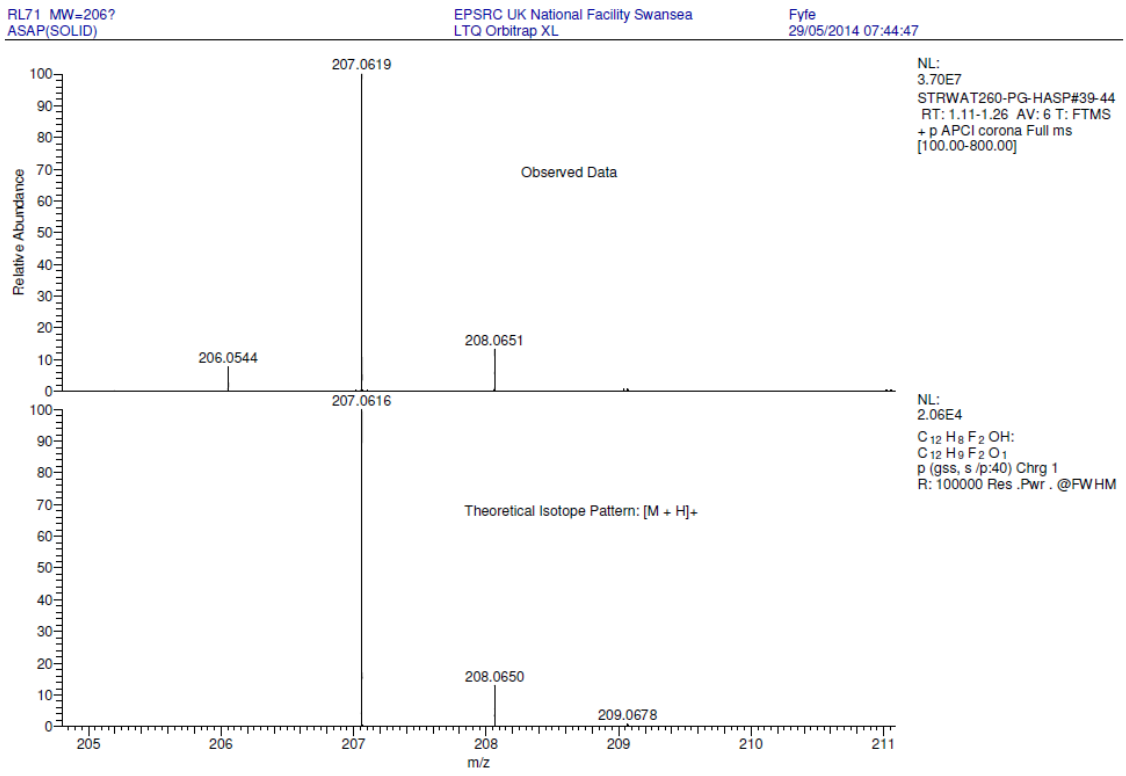
^{13}C NMR of 3m, $CDCl_3$, 101 MHz



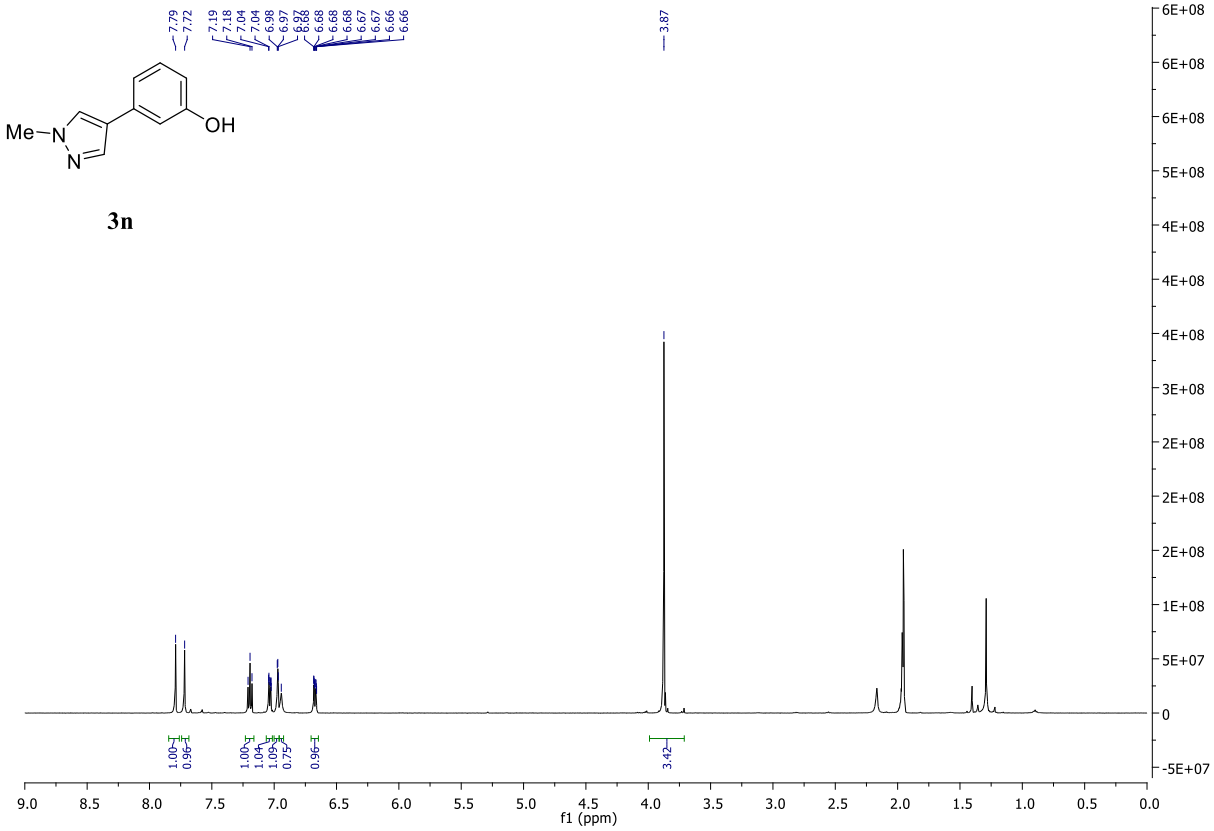
^{19}F NMR of 3m, $CDCl_3$, 376 MHz



HRMS of 3m

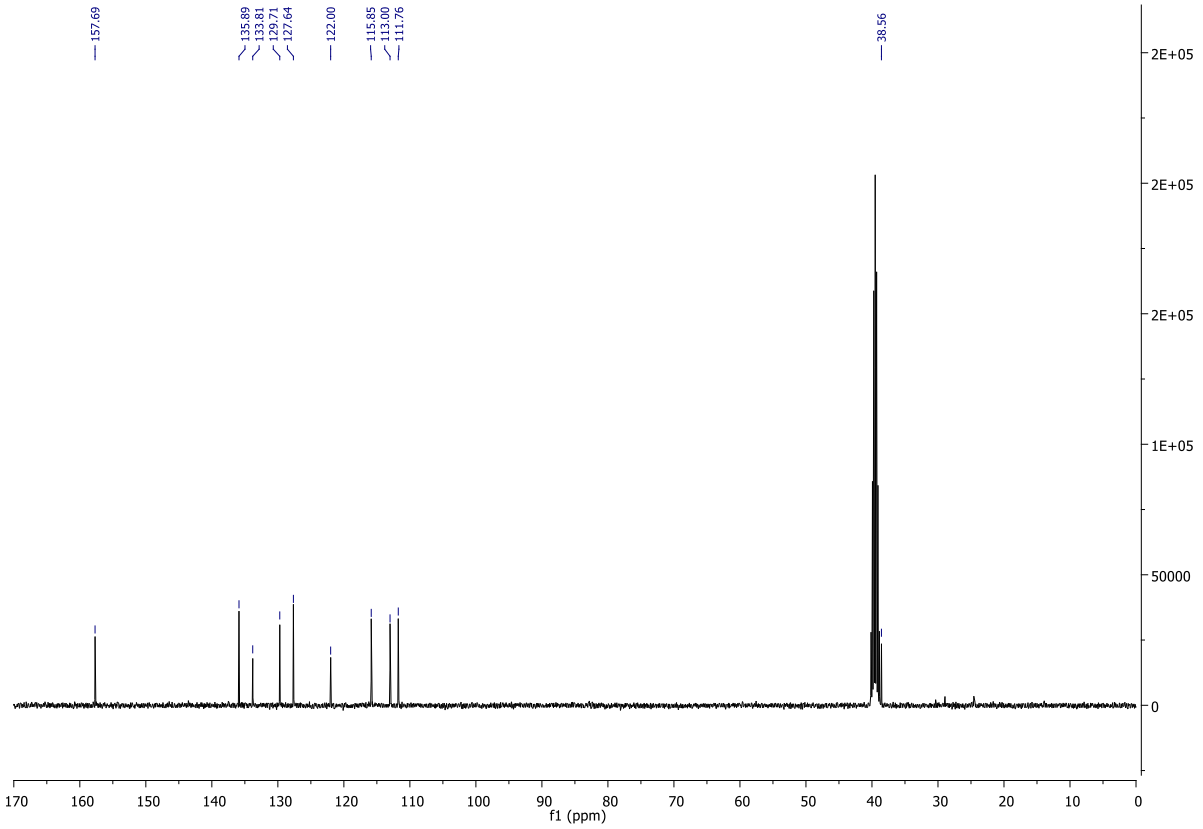


^{1}H NMR of 3n, CD_3CN, 500 MHz

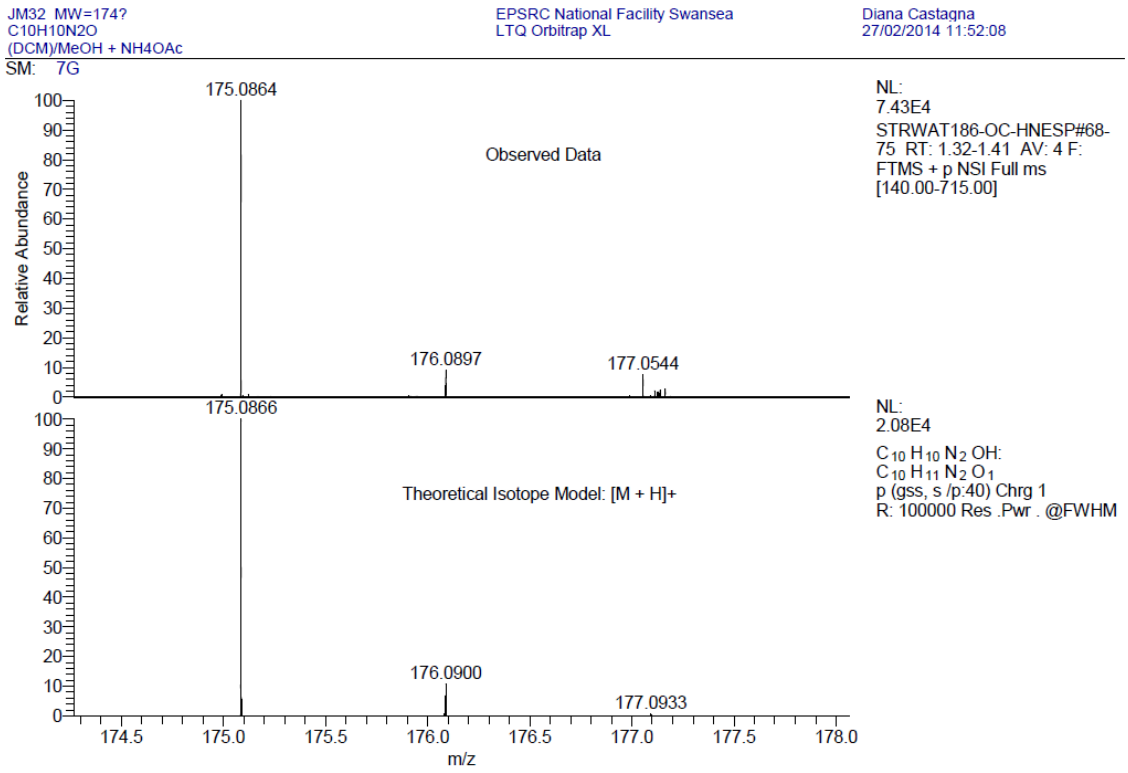


3n

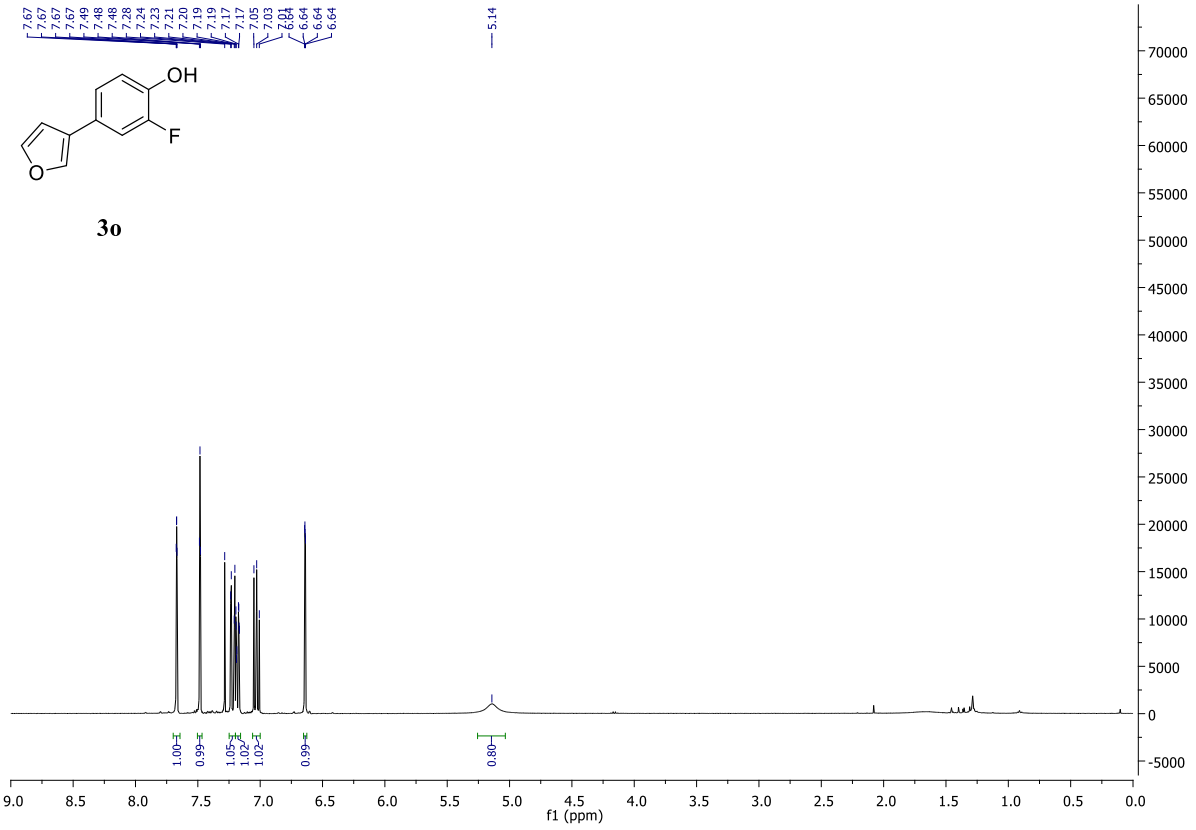
^{13}C NMR of 3n, DMSO-d_6, 126 MHz



HRMS of 3n

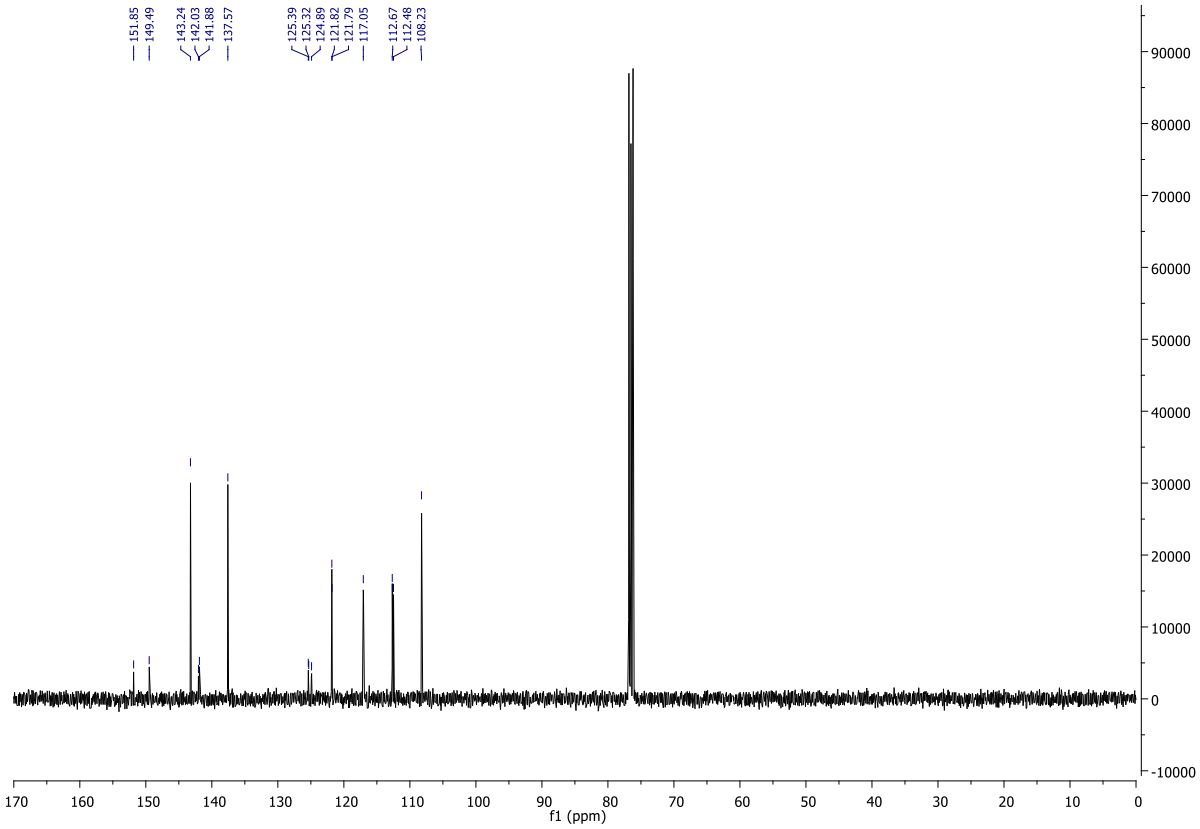


^{1}H NMR of 3o, $CDCl_3$, 400 MHz

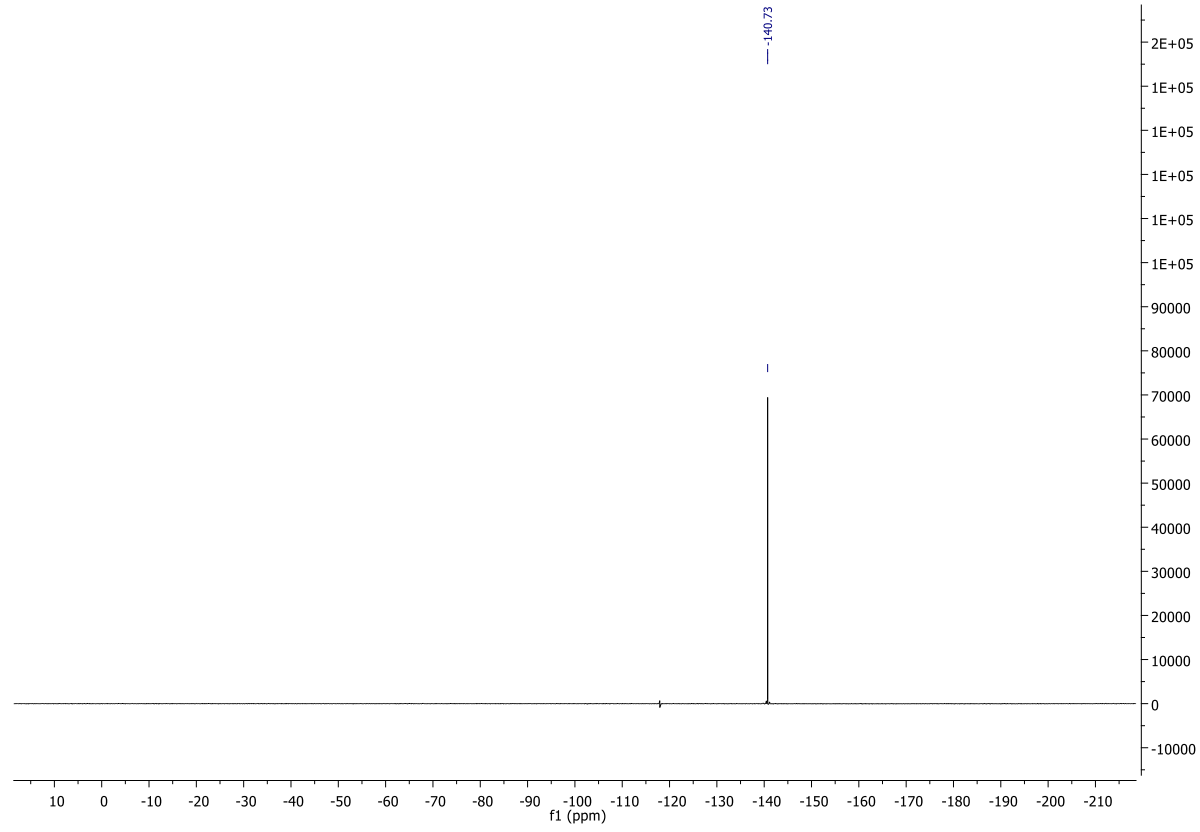


3o

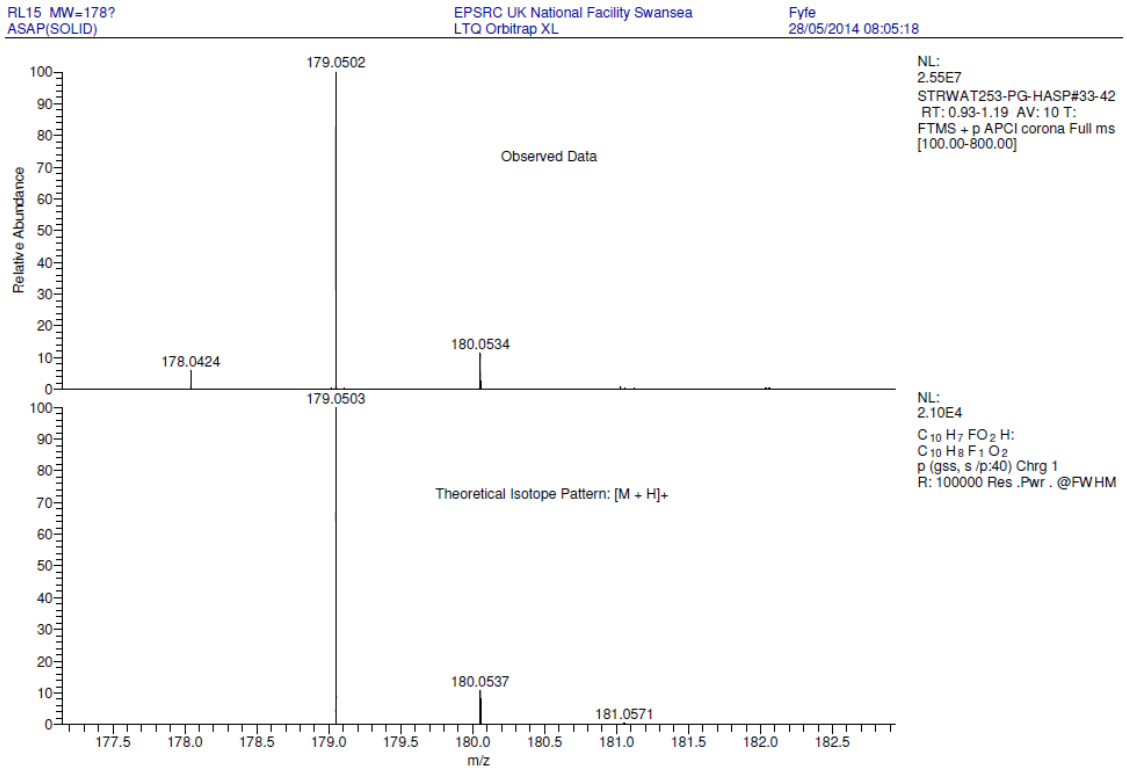
^{13}C NMR of 3o, $CDCl_3$, 101 MHz



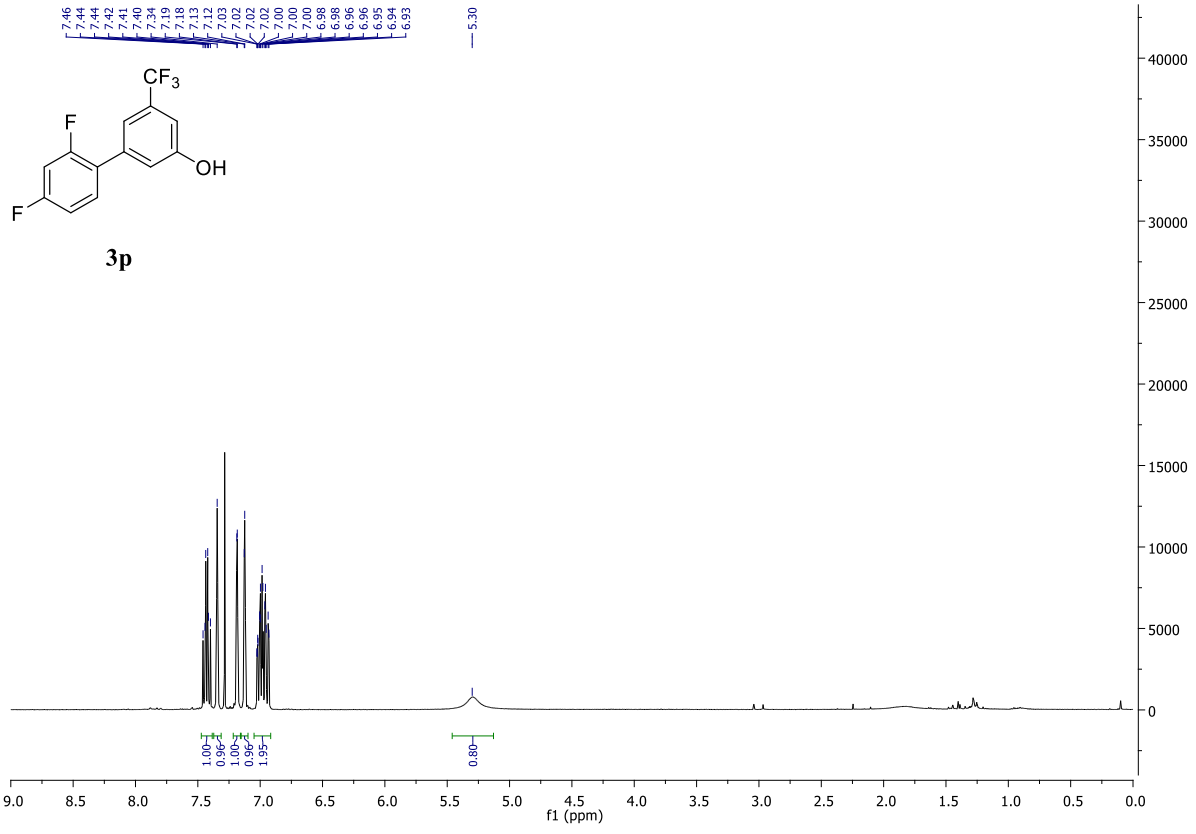
^{19}F NMR of 3o, $CDCl_3$, 376 MHz



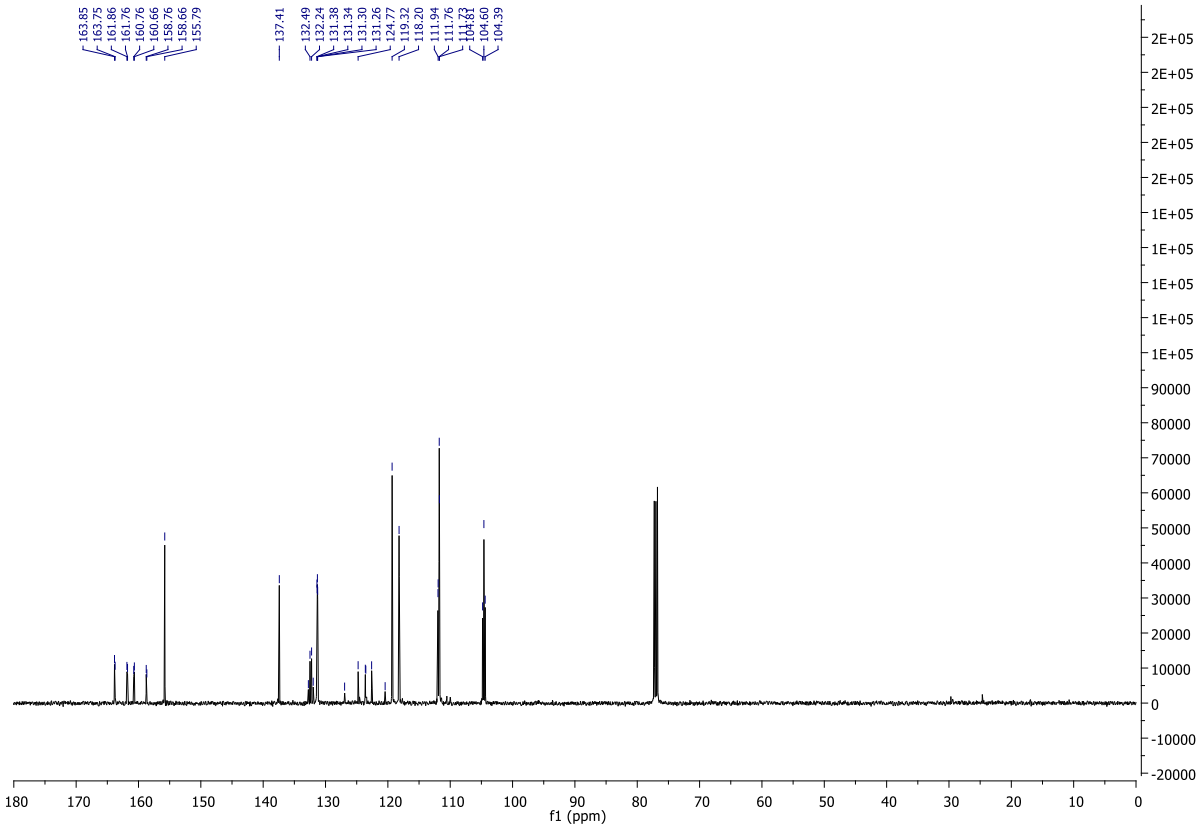
HRMS of 3o



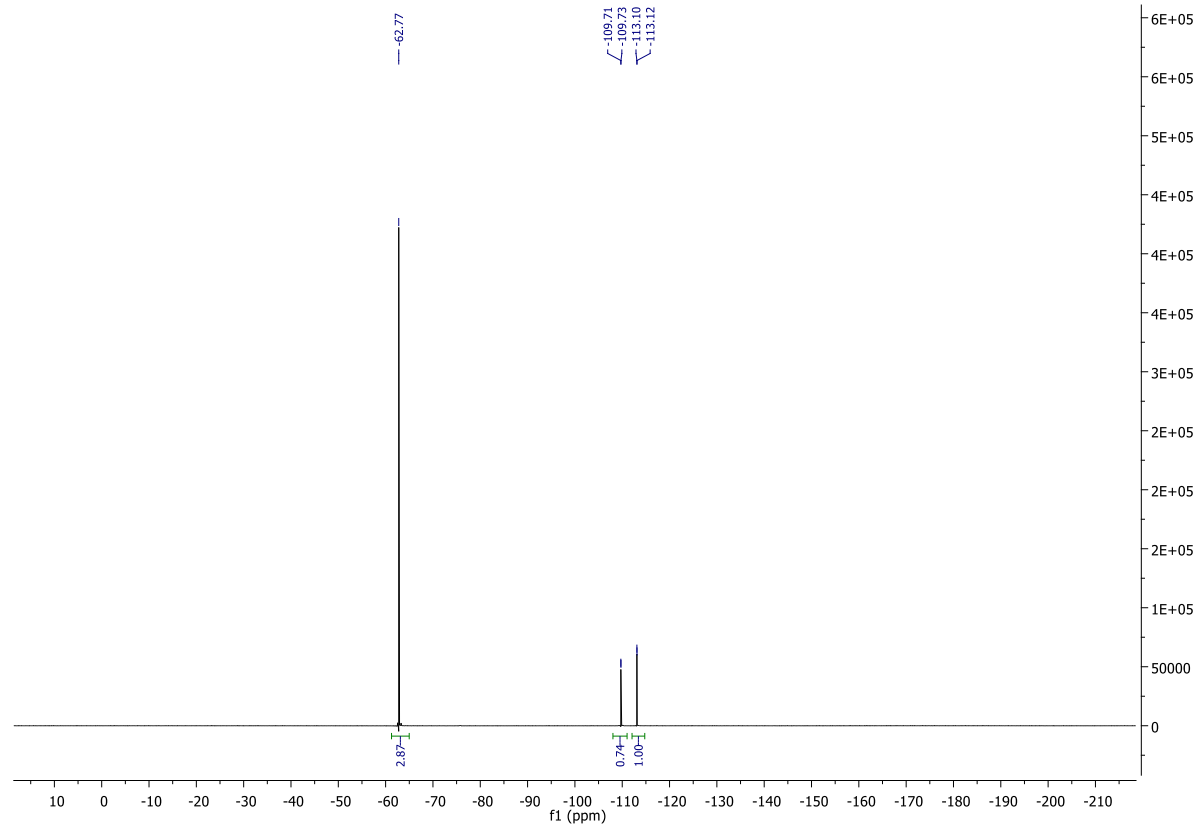
^{1}H NMR of 3p, $CDCl_3$, 400MHz



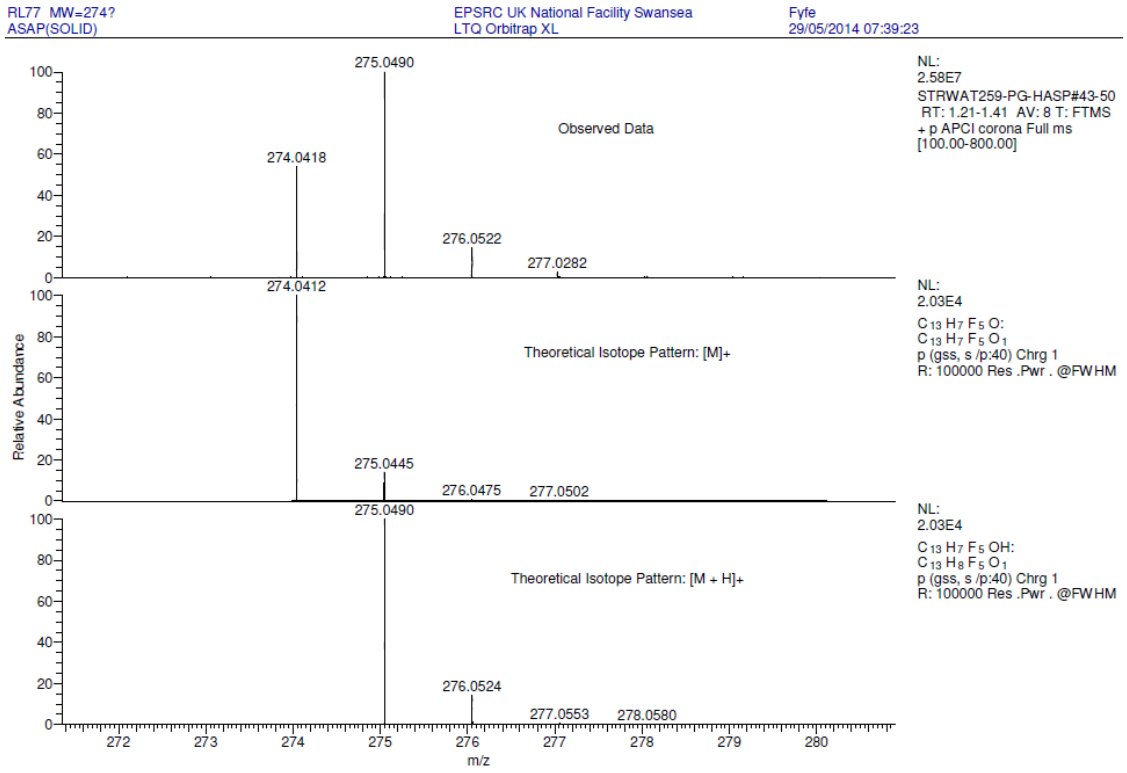
^{13}C NMR of 3p, $CDCl_3$, 101 MHz



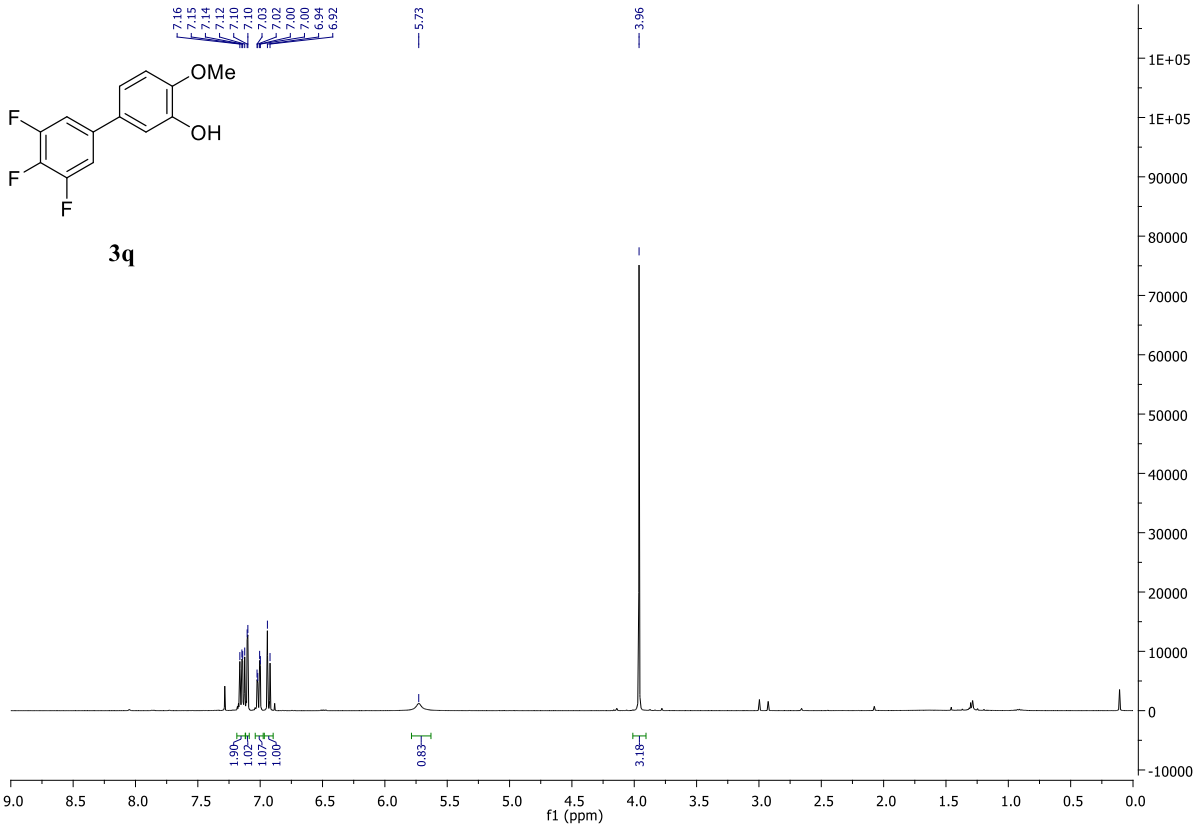
^{19}F NMR of 3p, $CDCl_3$, 376 MHz



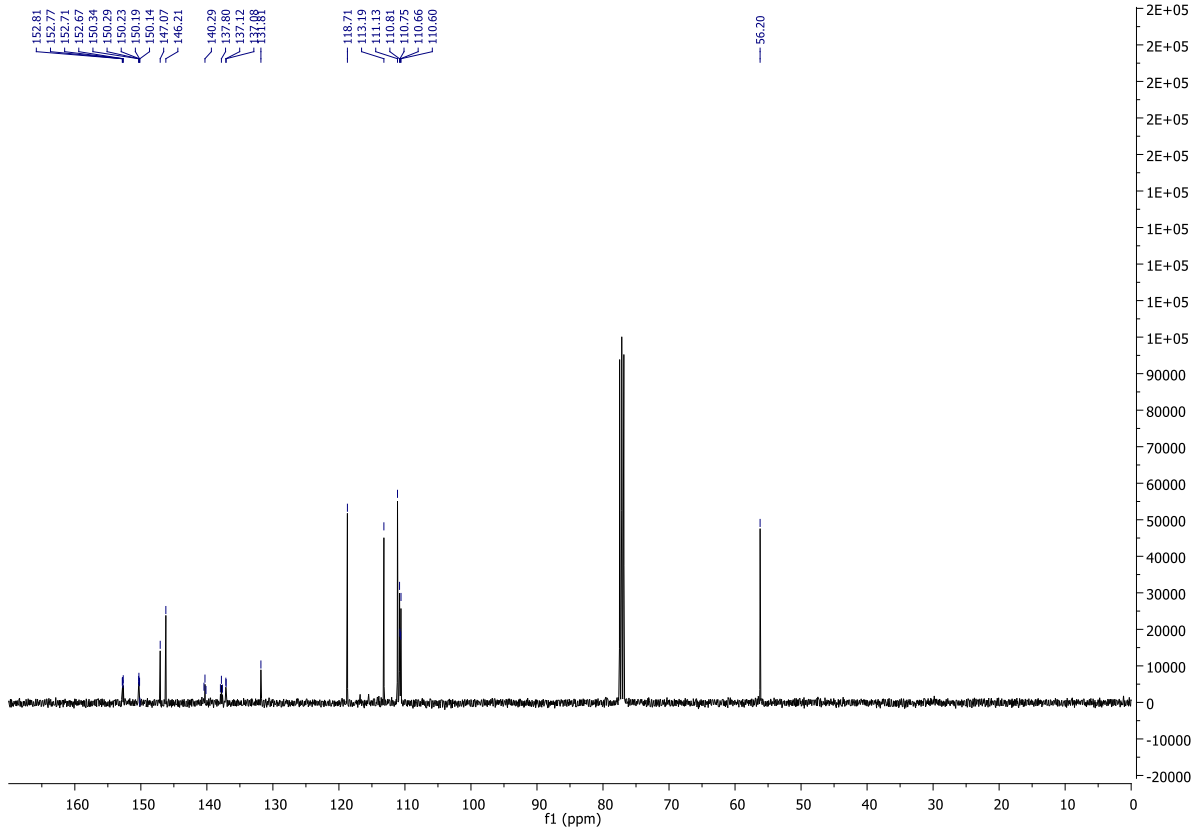
HRMS of 3p



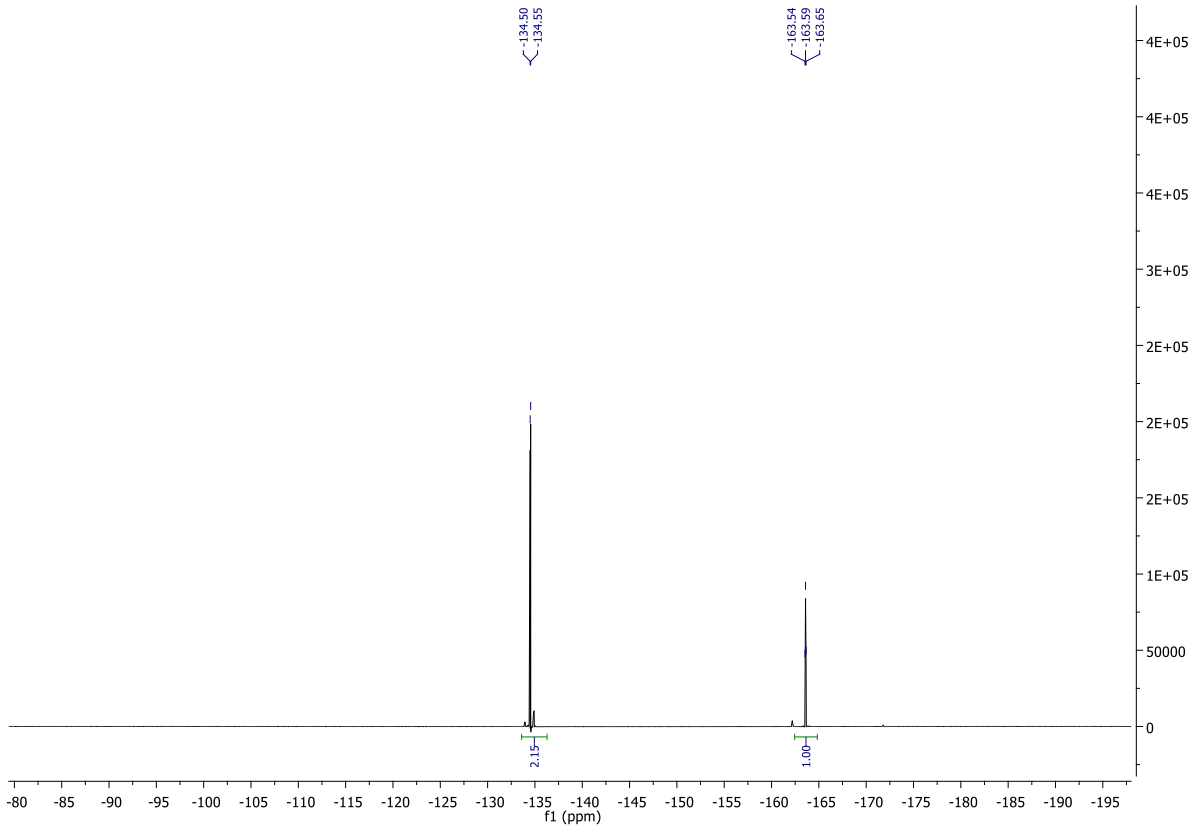
^{1}H NMR of 3q, $CDCl_3$, 400 MHz



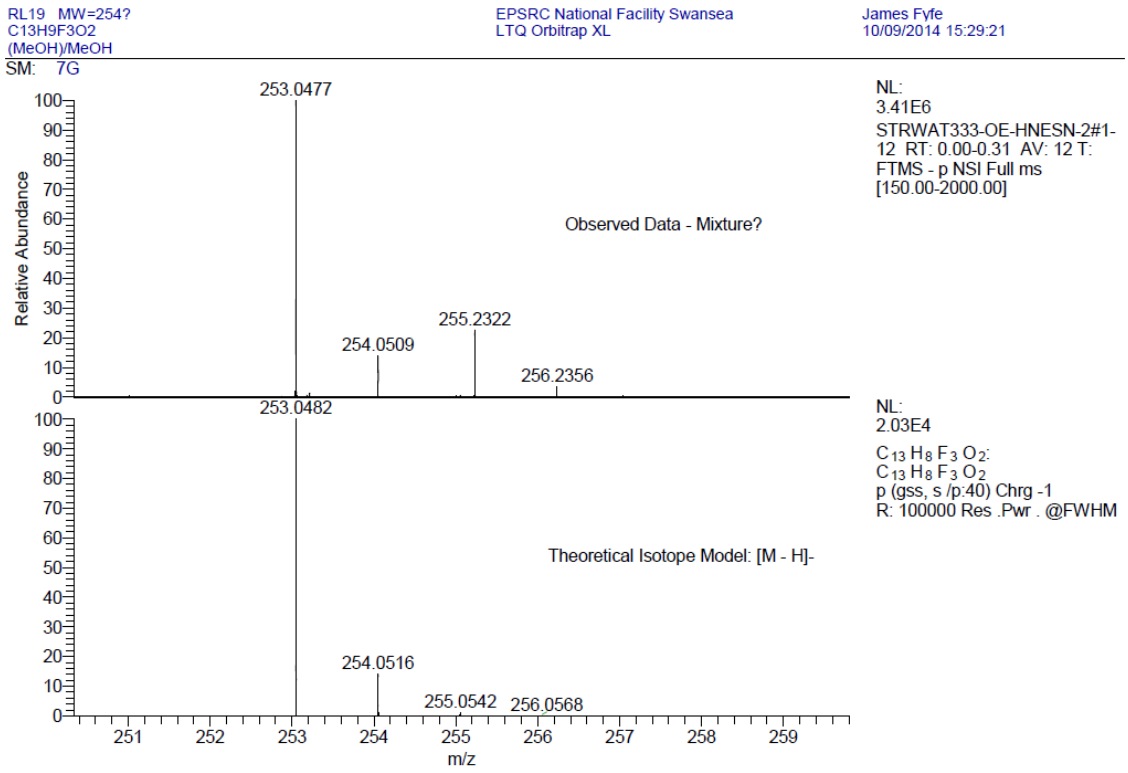
^{13}C NMR of 3q, $CDCl_3$, 101 MHz



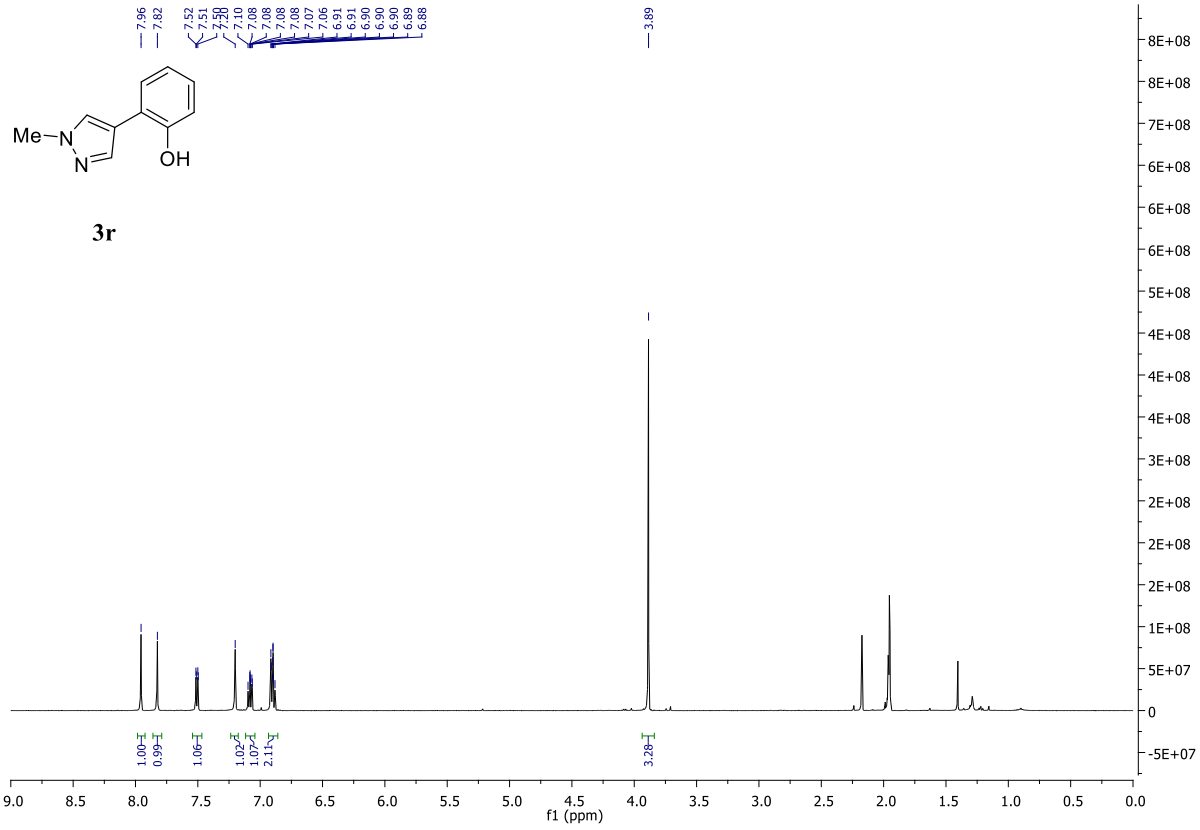
^{19}F NMR of 3q $CDCl_3$, 376 MHz



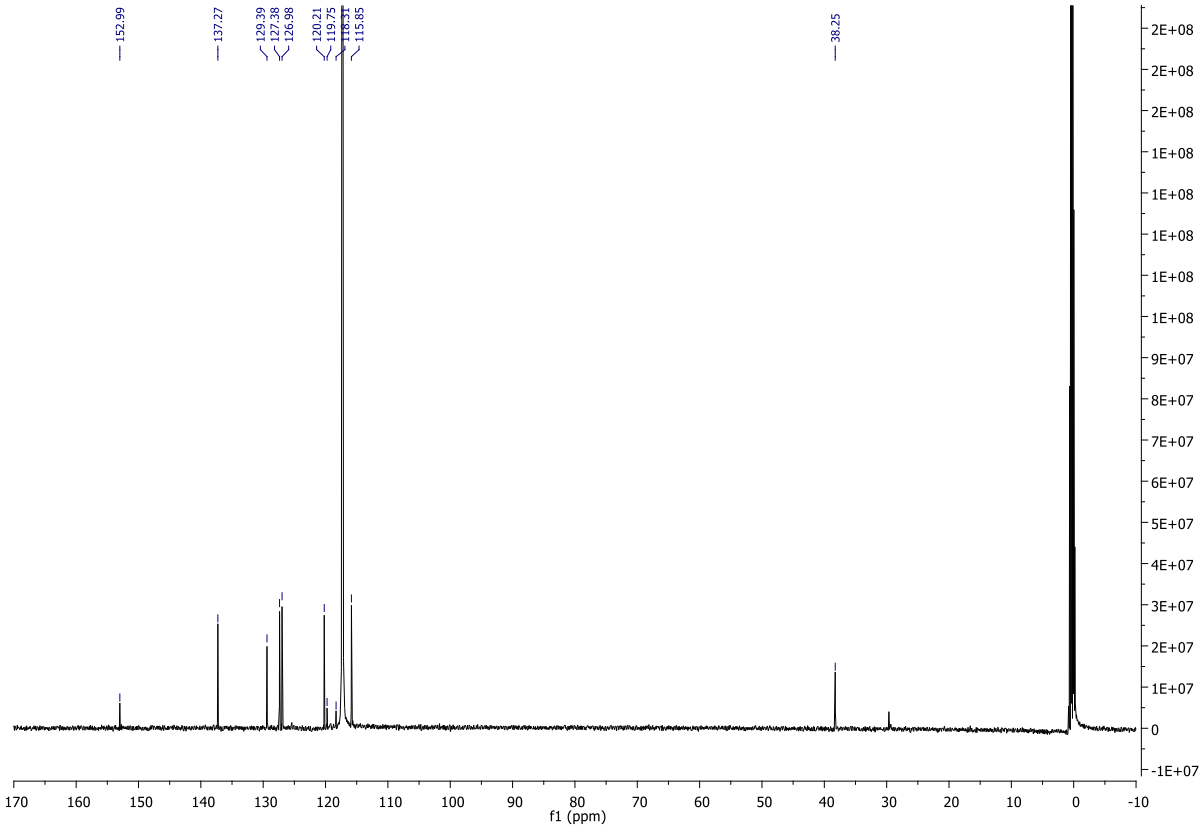
HRMS of 3q



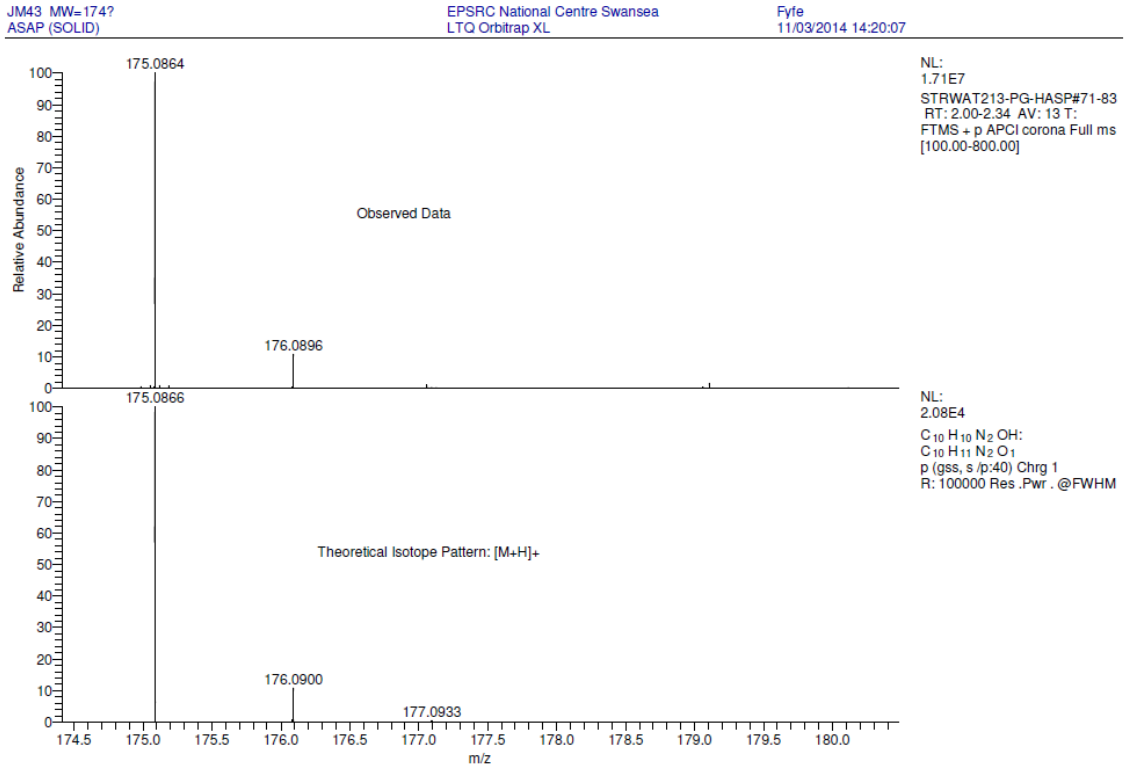
^{1}H NMR of 3r, CD_3CN, 500 MHz



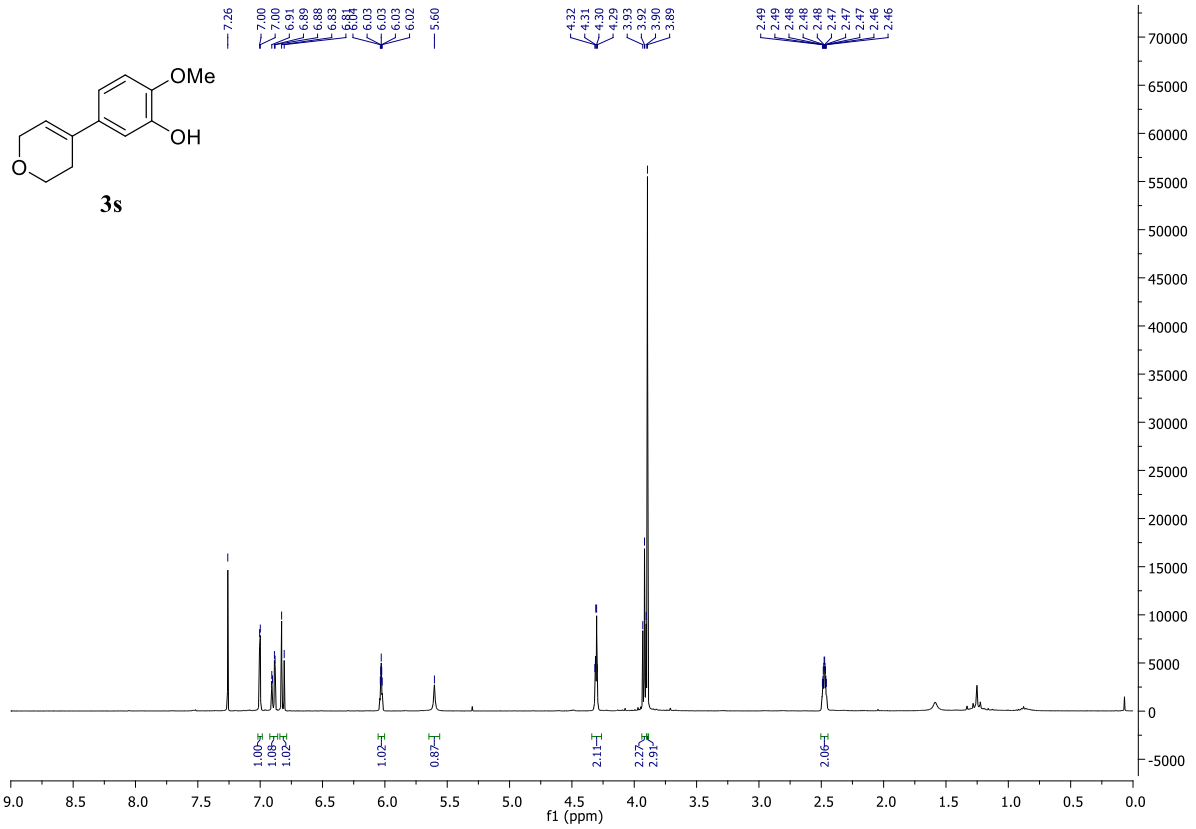
^{13}C NMR of 3r, CD_3CN, 126 MHz



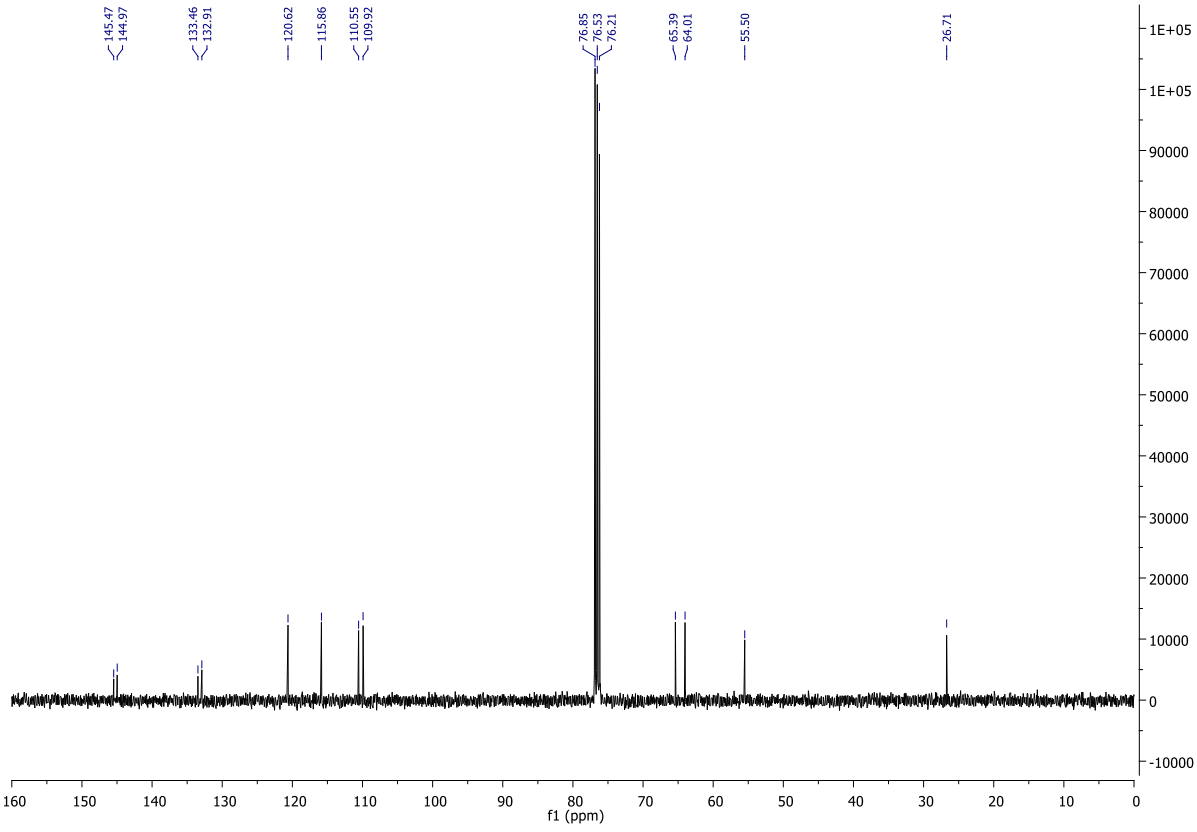
HRMS of 3r



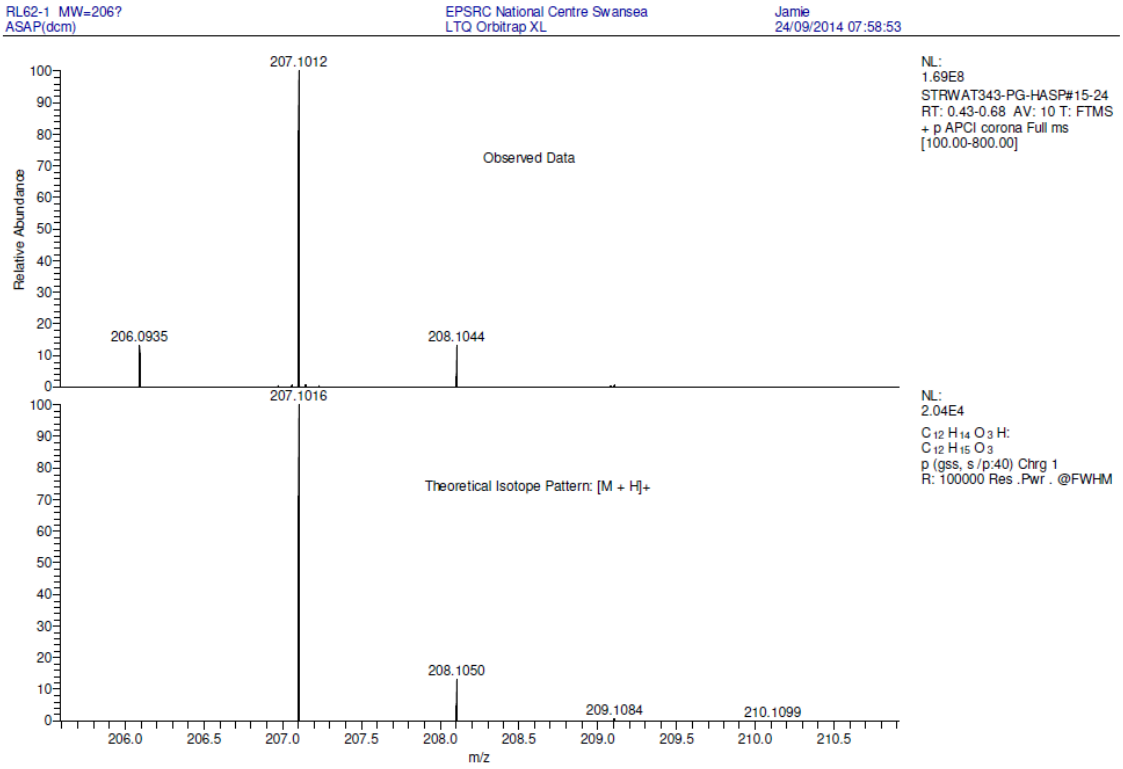
^{1}H NMR of 3s, $CDCl_3$, 400 MHz



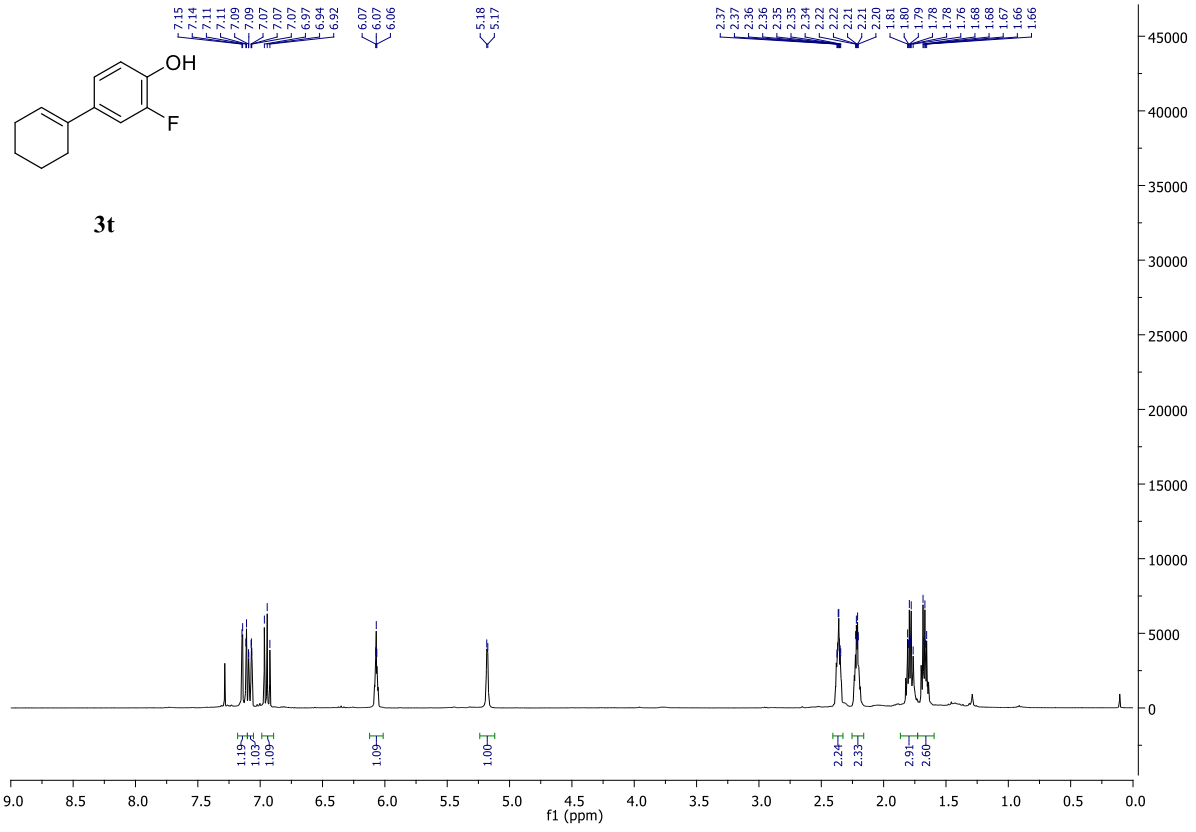
^{13}C NMR of 3s, $CDCl_3$, 101 MHz



HRMS of 3s

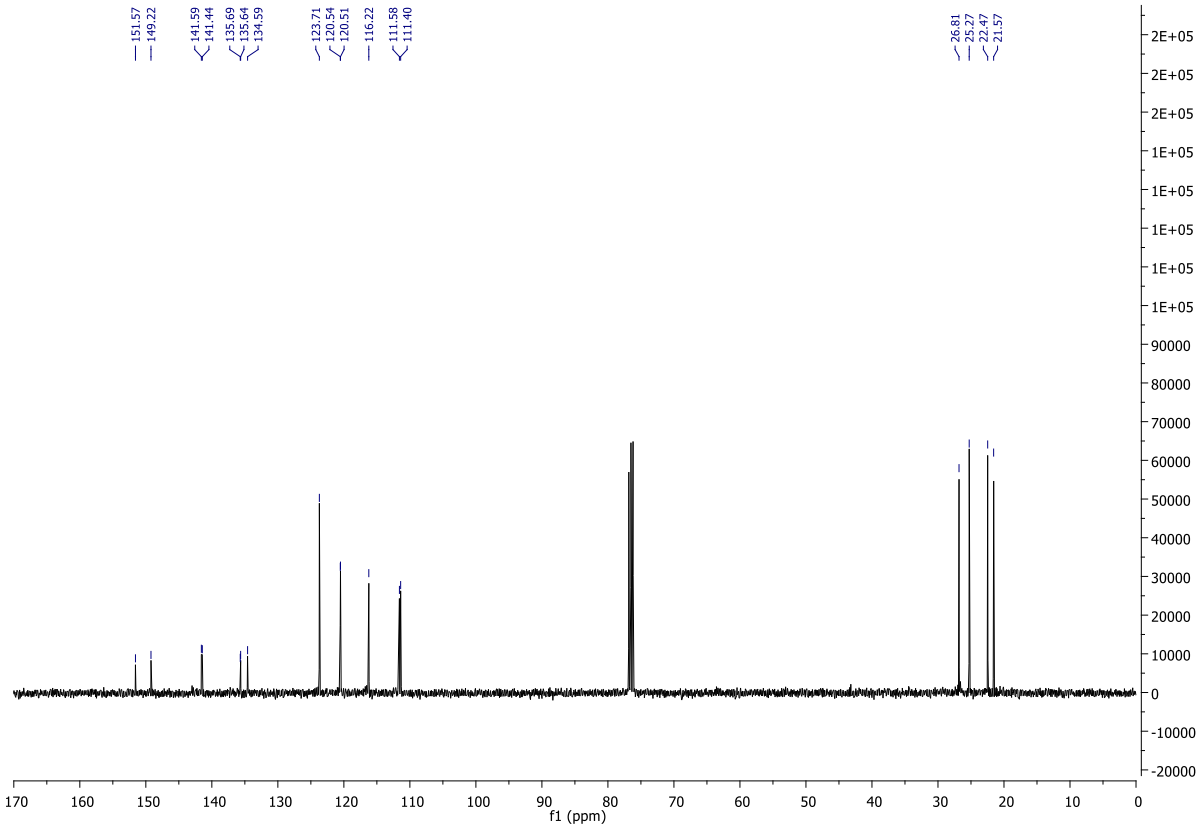


^{1}H NMR of 3t, $CDCl_3$, 400 MHz

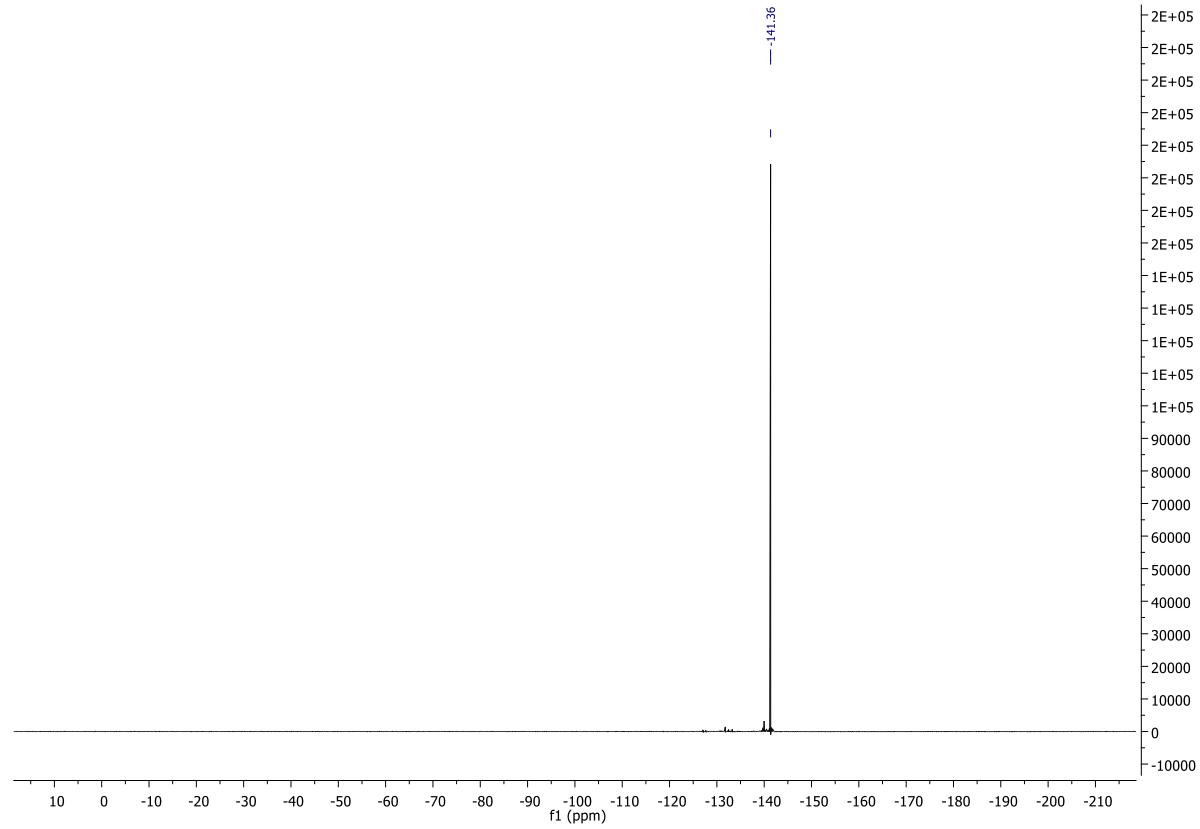


3t

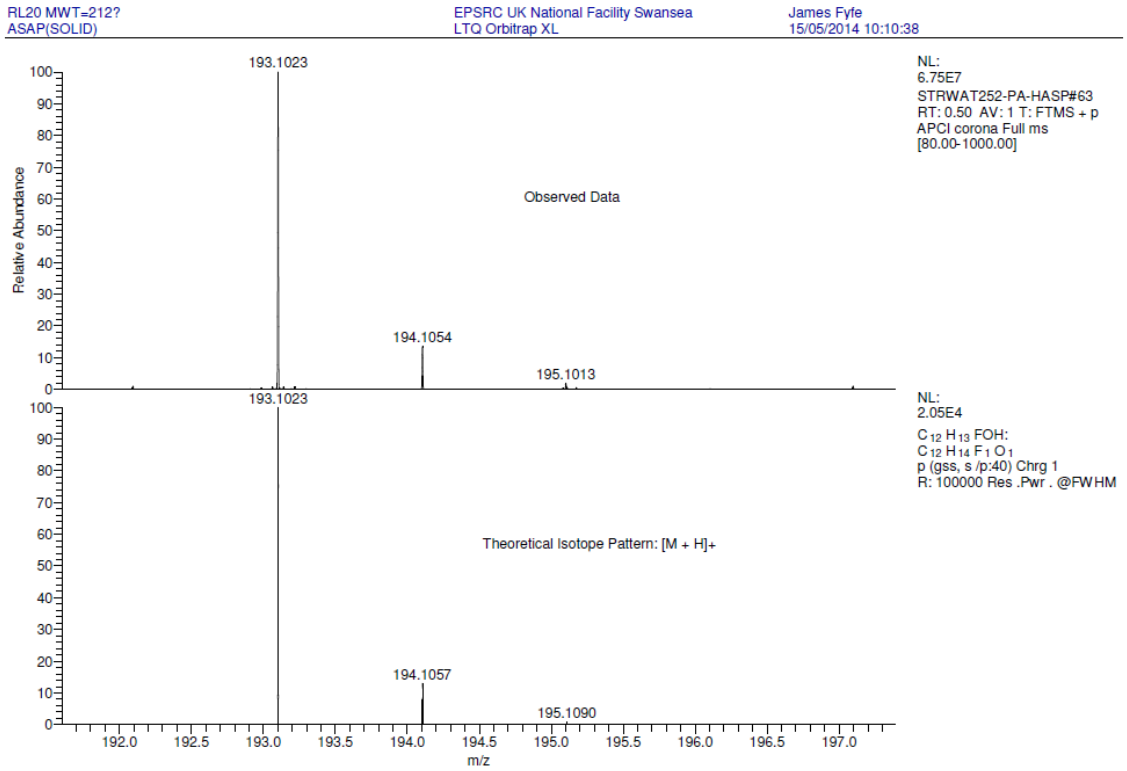
^{13}C NMR of 3t, $CDCl_3$, 101 MHz



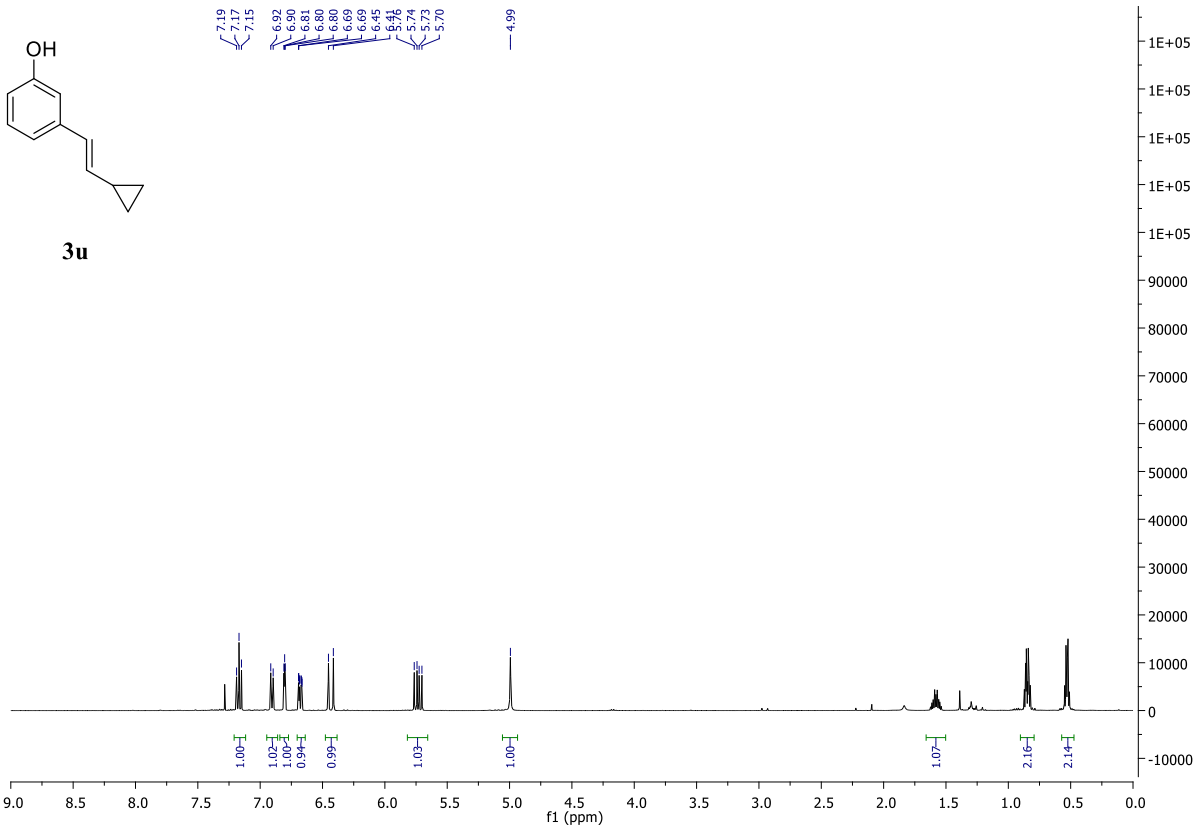
^{19}F NMR of 3t, $CDCl_3$, 376 MHz



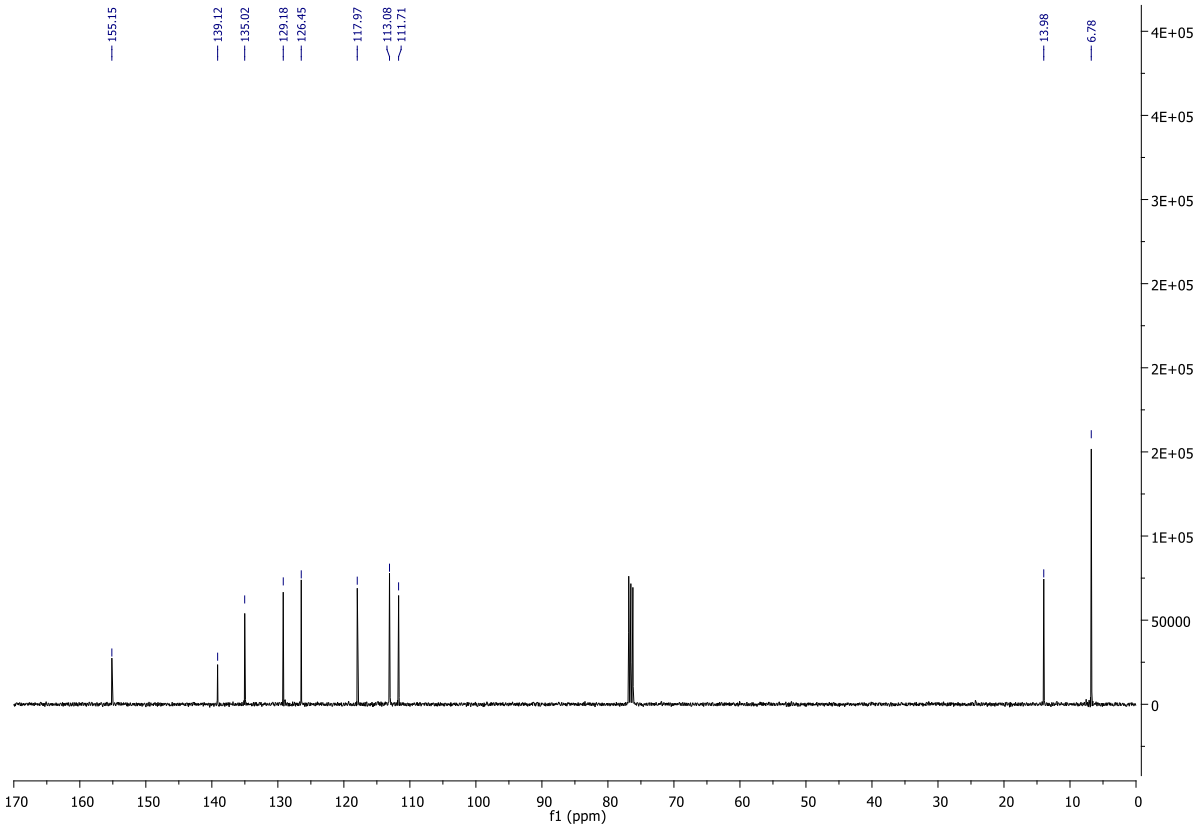
HRMS of 3t



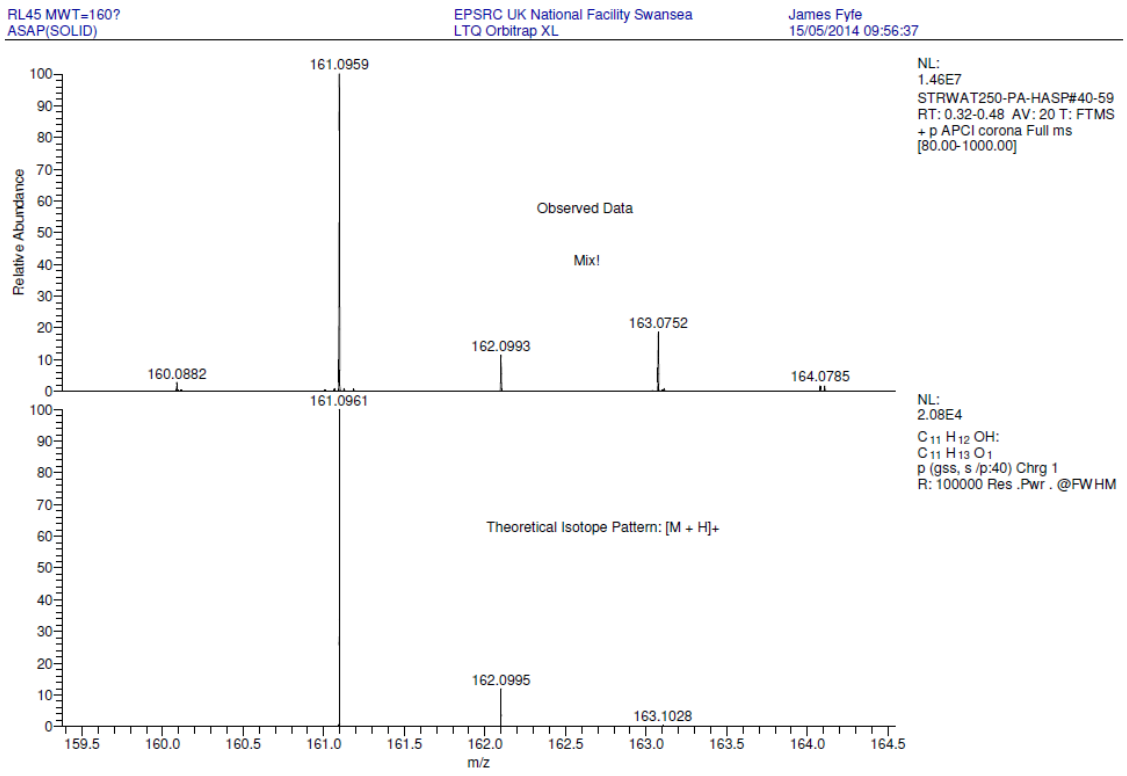
^{1}H NMR of 3u, $CDCl_3$, 400 MHz



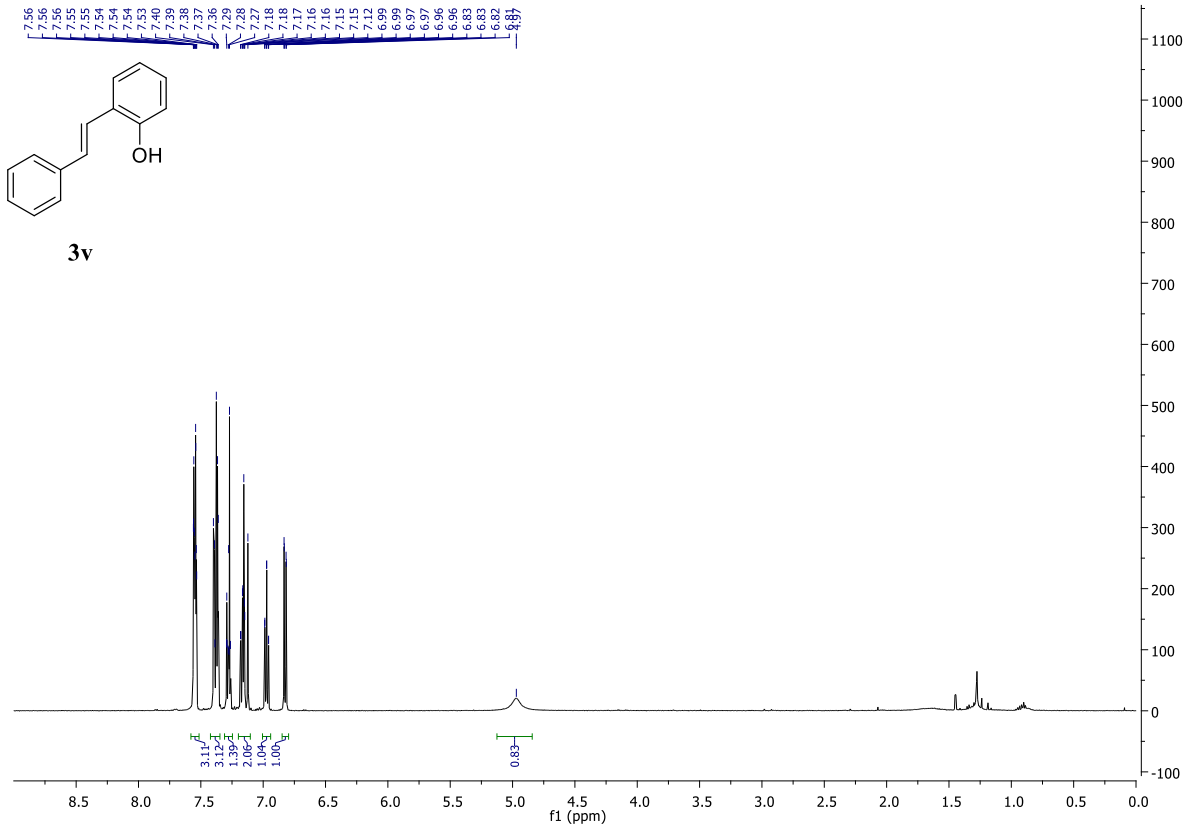
^{13}C NMR of 3u, $CDCl_3$, 101 MHz



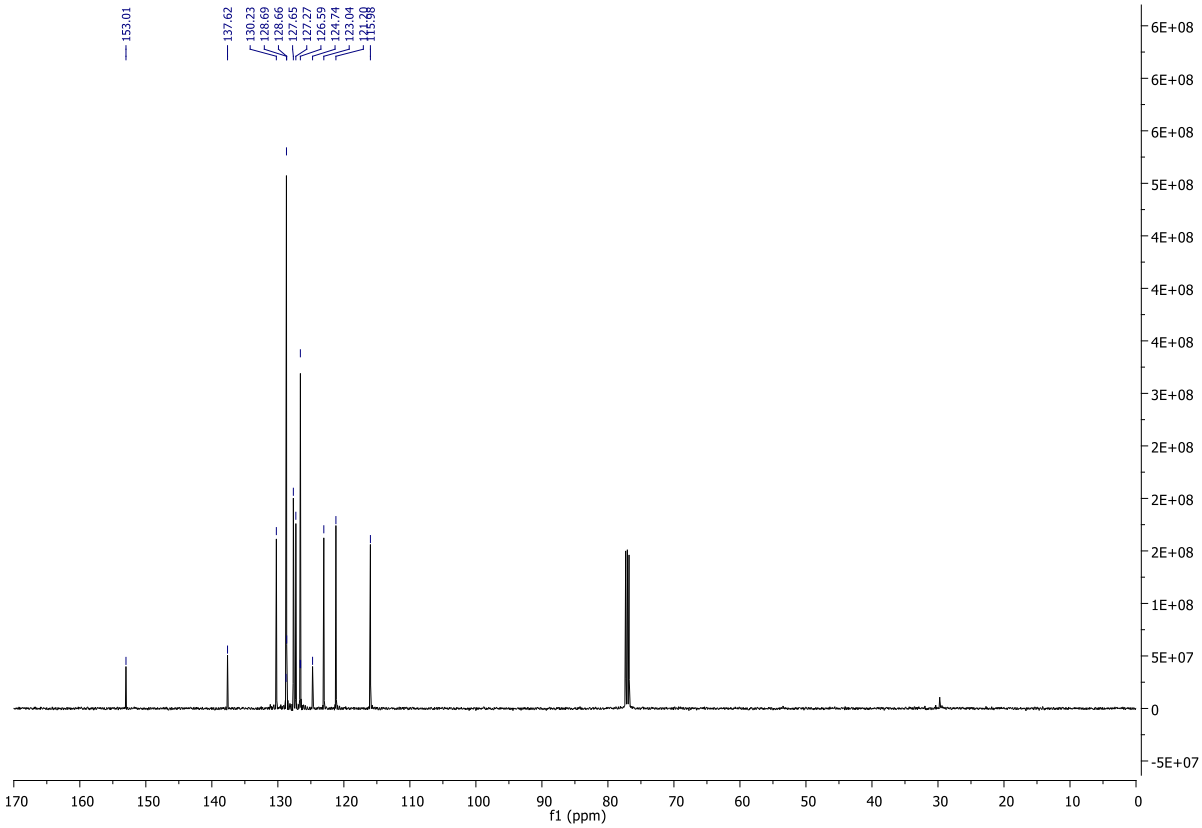
HRMS of 3u



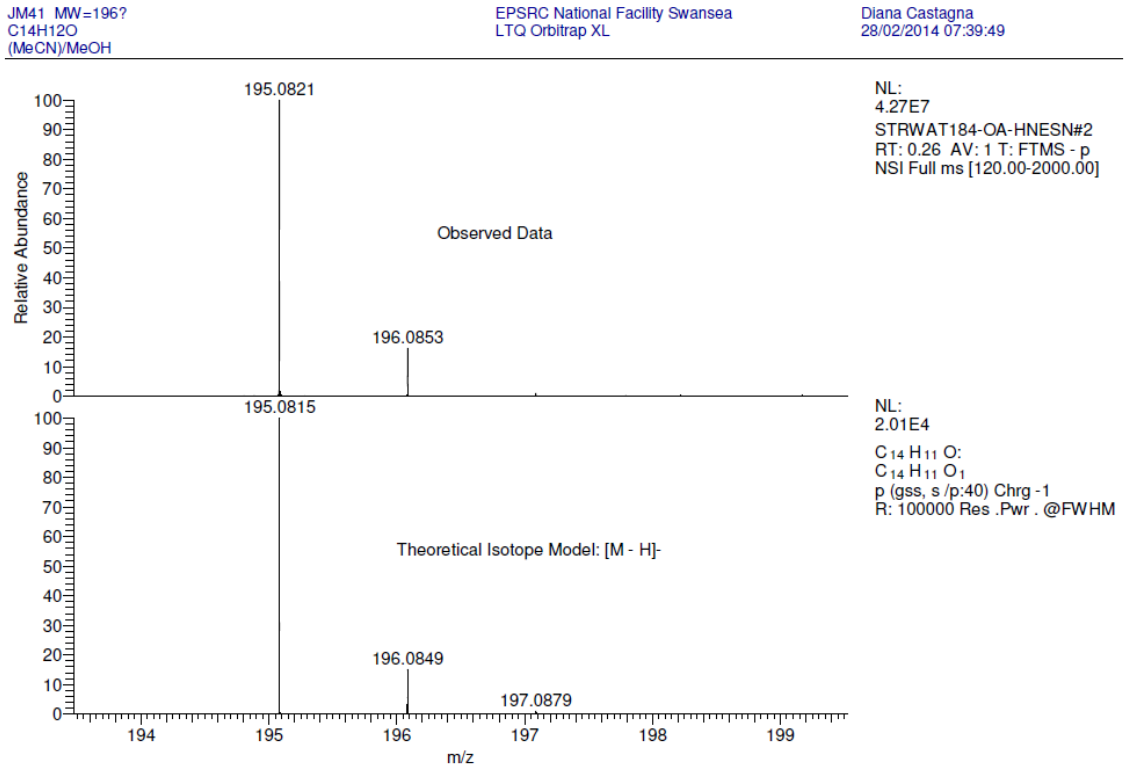
^{1}H NMR of 3v, $CDCl_3$, 500 MHz



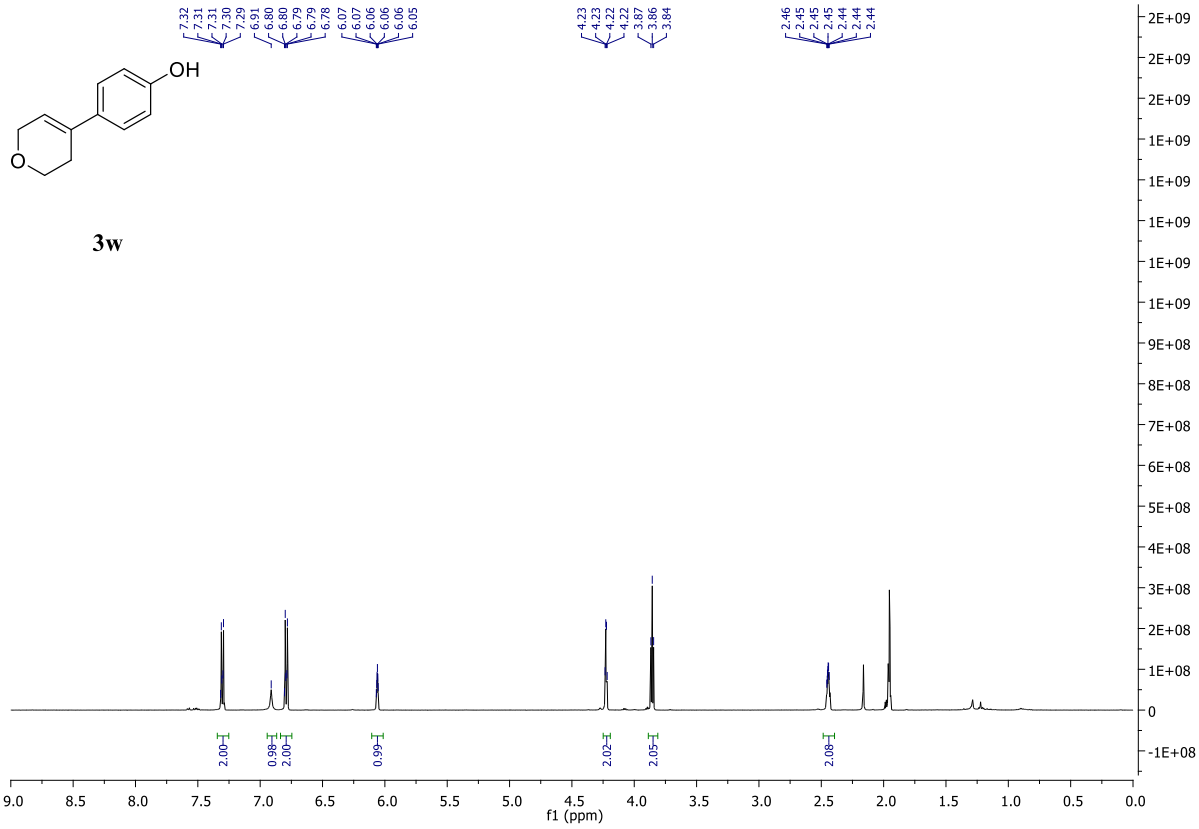
^{13}C NMR of 3v, $CDCl_3$, 126 MHz



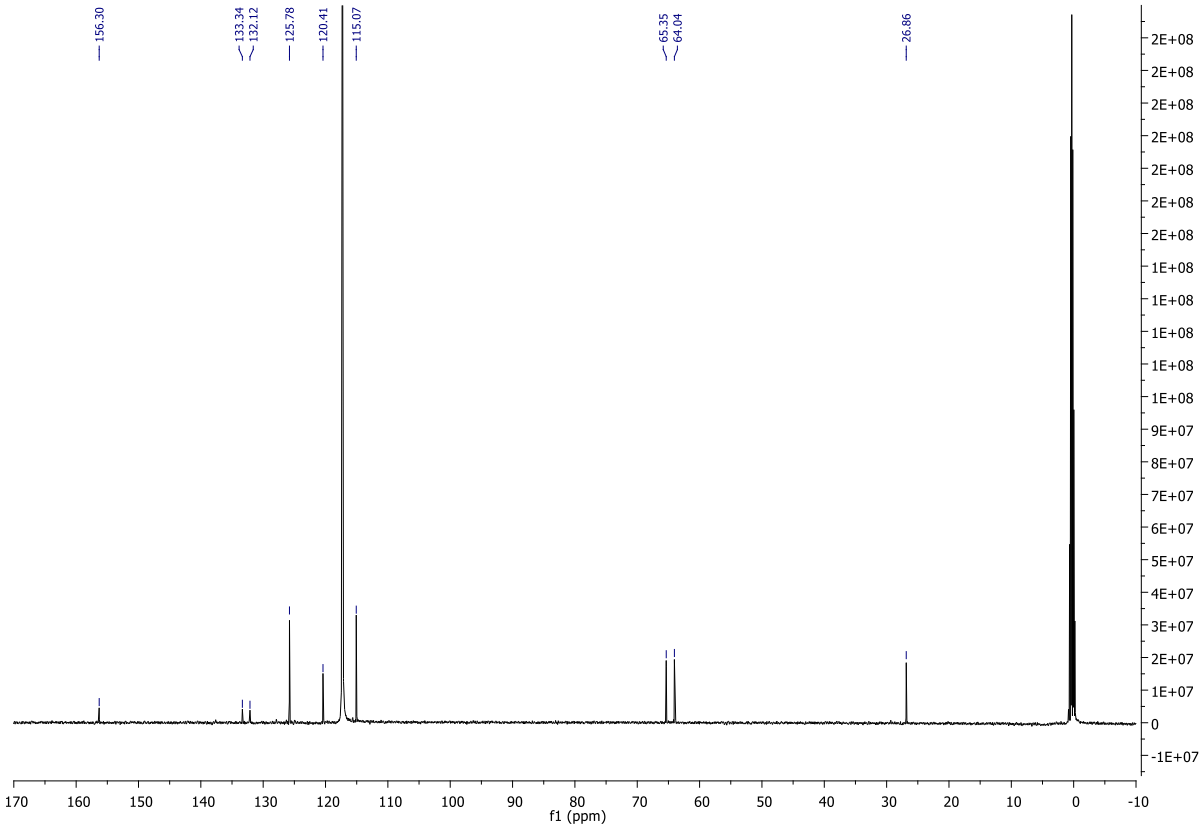
HRMS of 3v



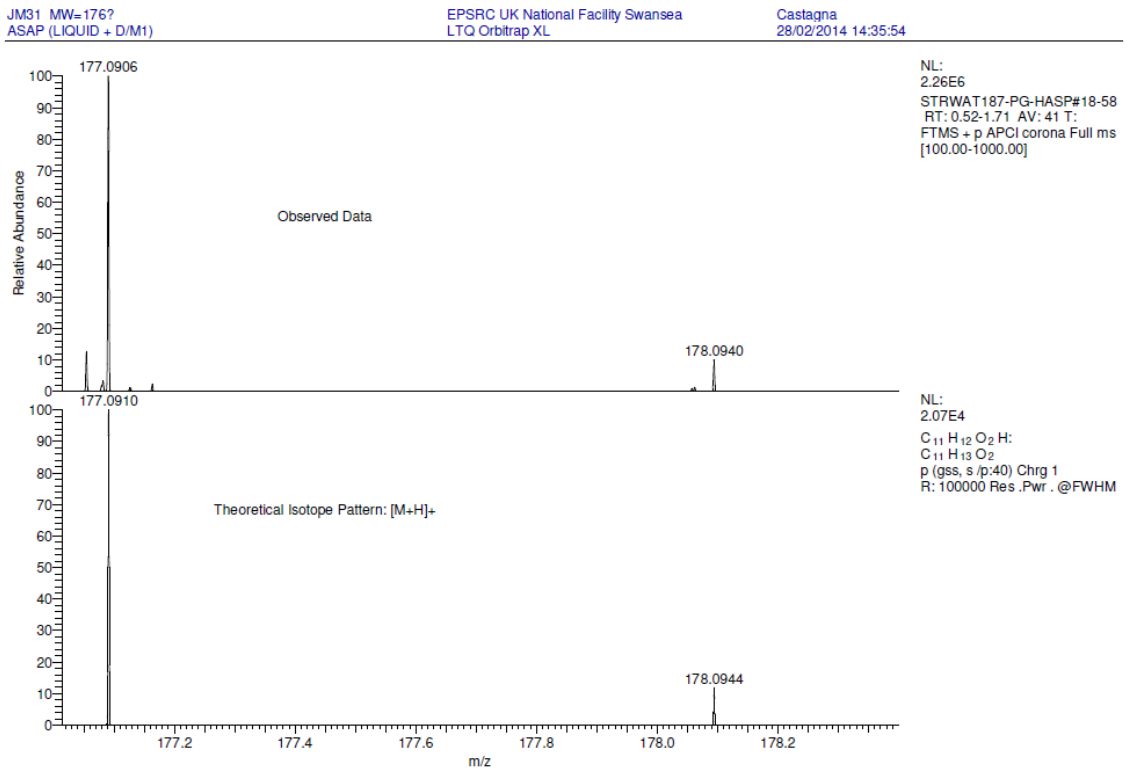
^{1}H NMR of 3w, CD_3CN, 500 MHz



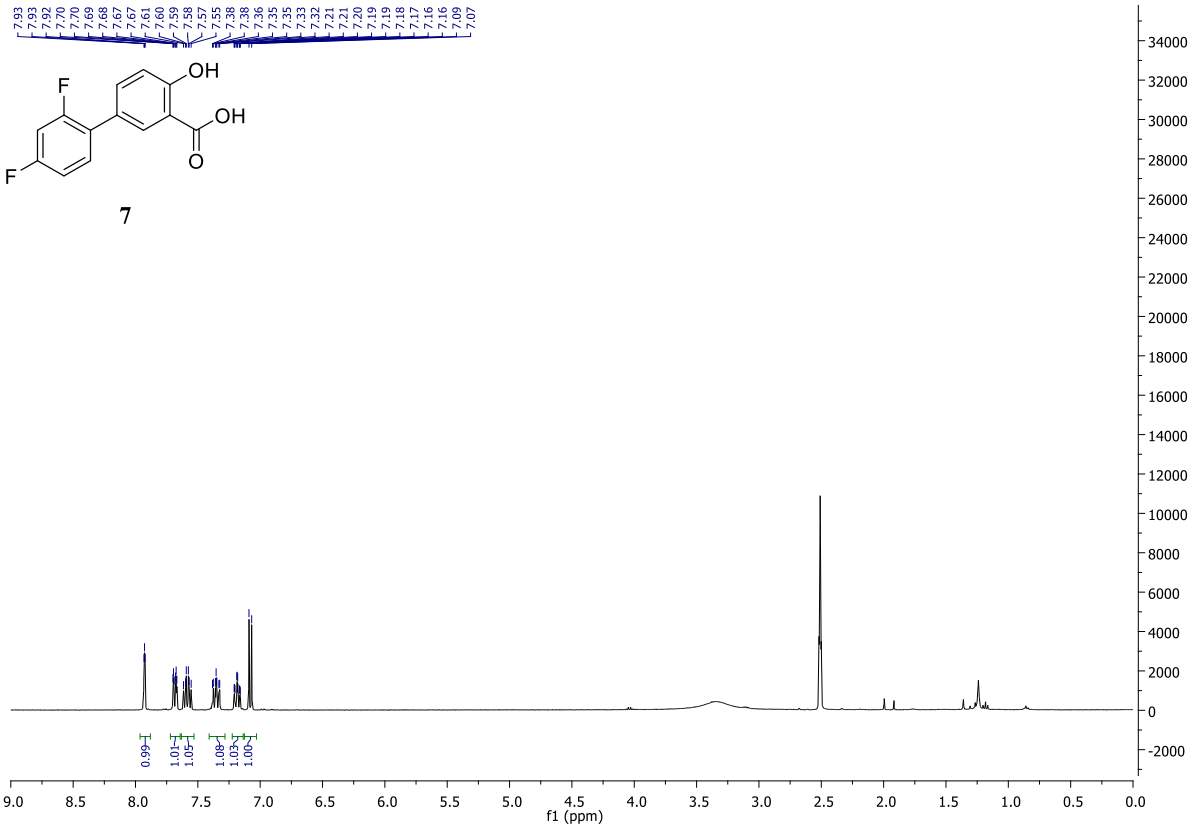
^{13}C NMR of 3w, CD_3CN, 126 MHz



HRMS of 3w

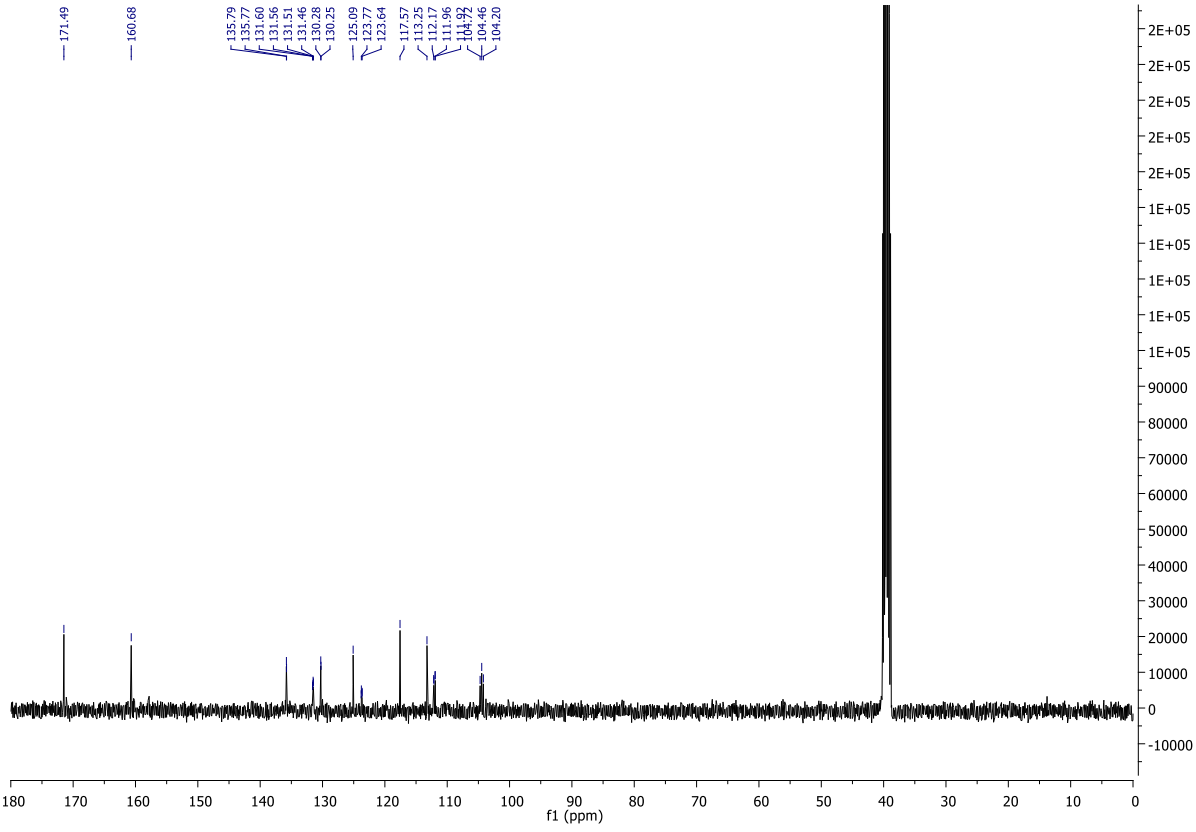


^{1}H NMR of 7, DMSO-d_6, 400 MHz

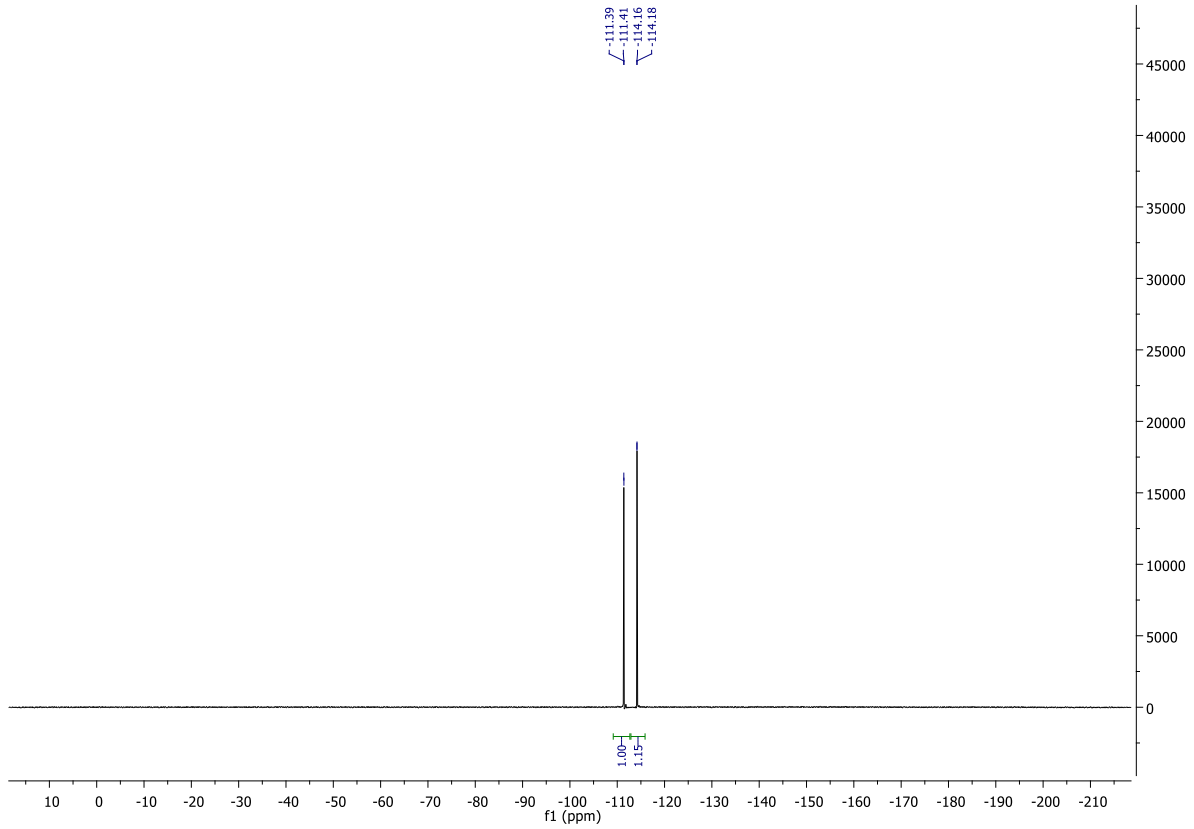


7

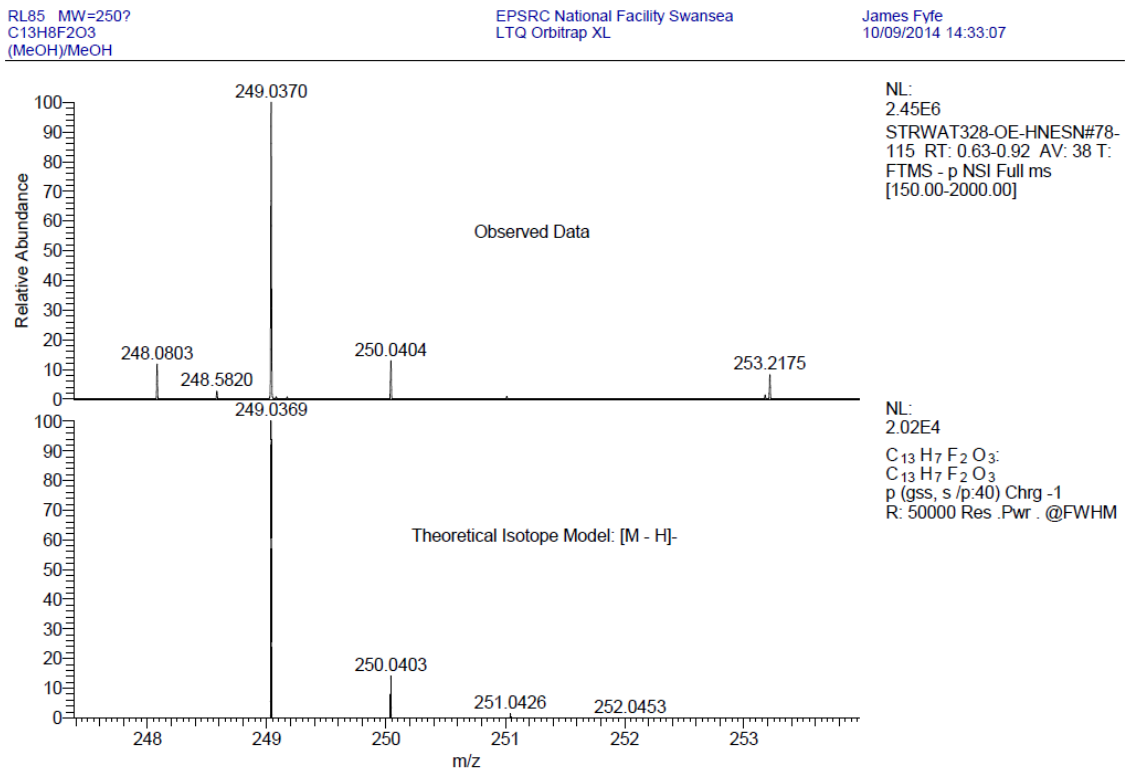
^{13}C NMR of 7, DMSO-d_6, 101 MHz



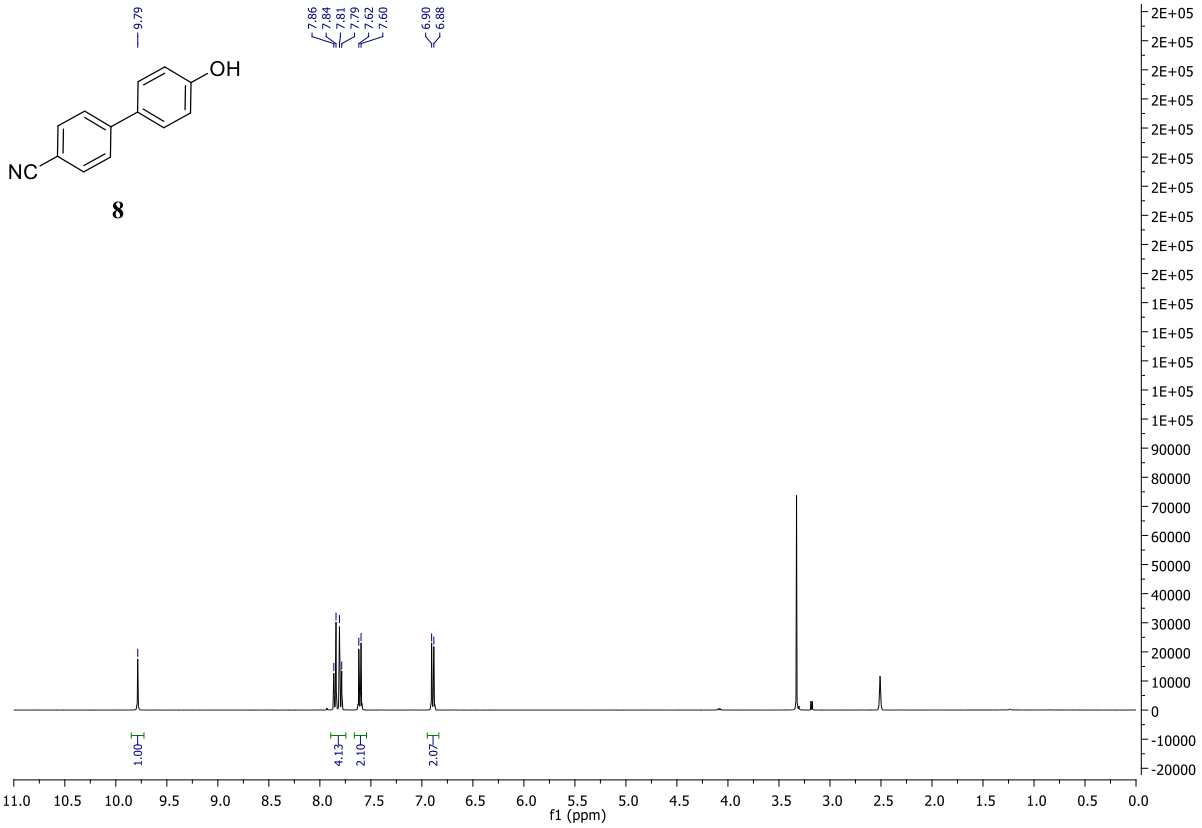
^{19}F NMR of 7, DMSO-d_6, 376 MHz



HRMS of 7

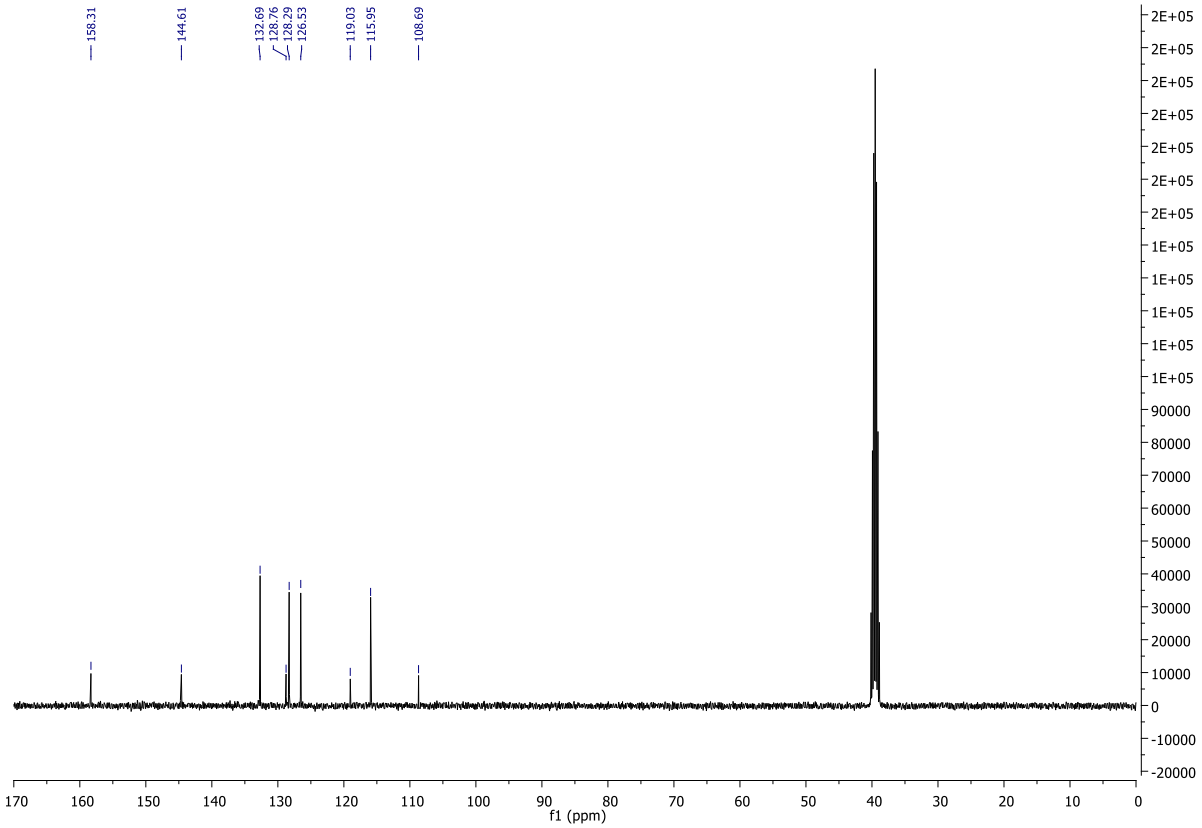


^{1}H NMR of 8, DMSO-d_6, 400 MHz

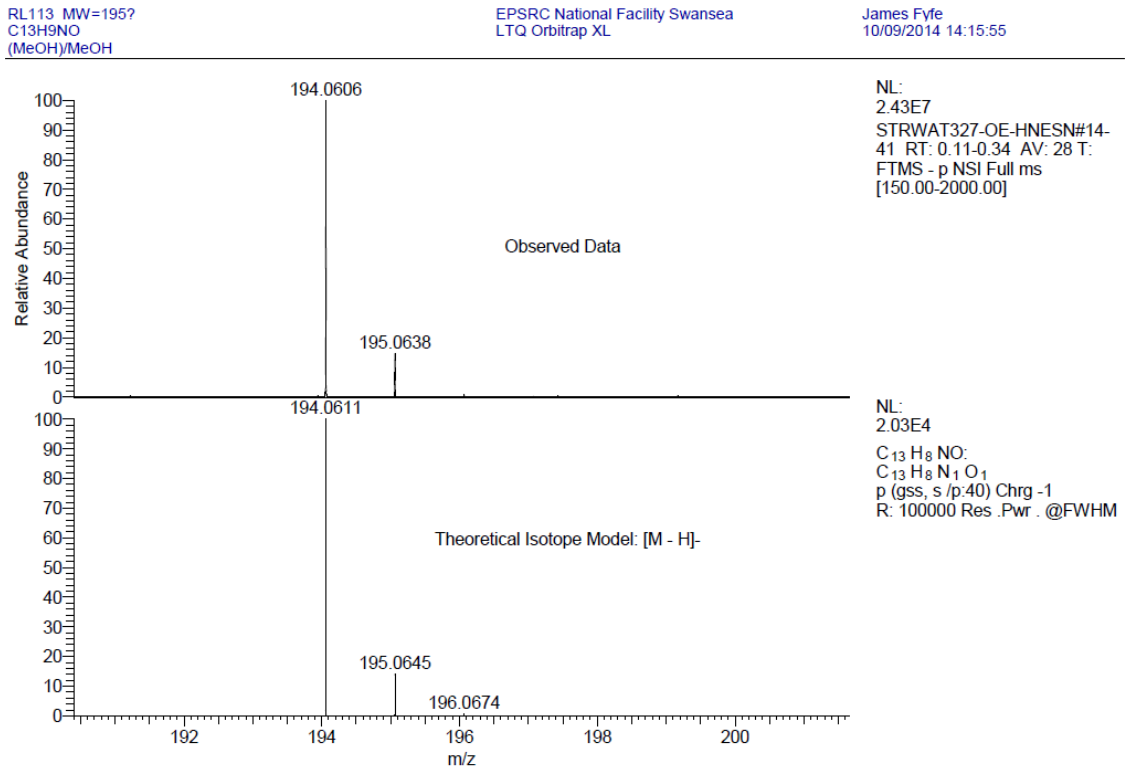


8

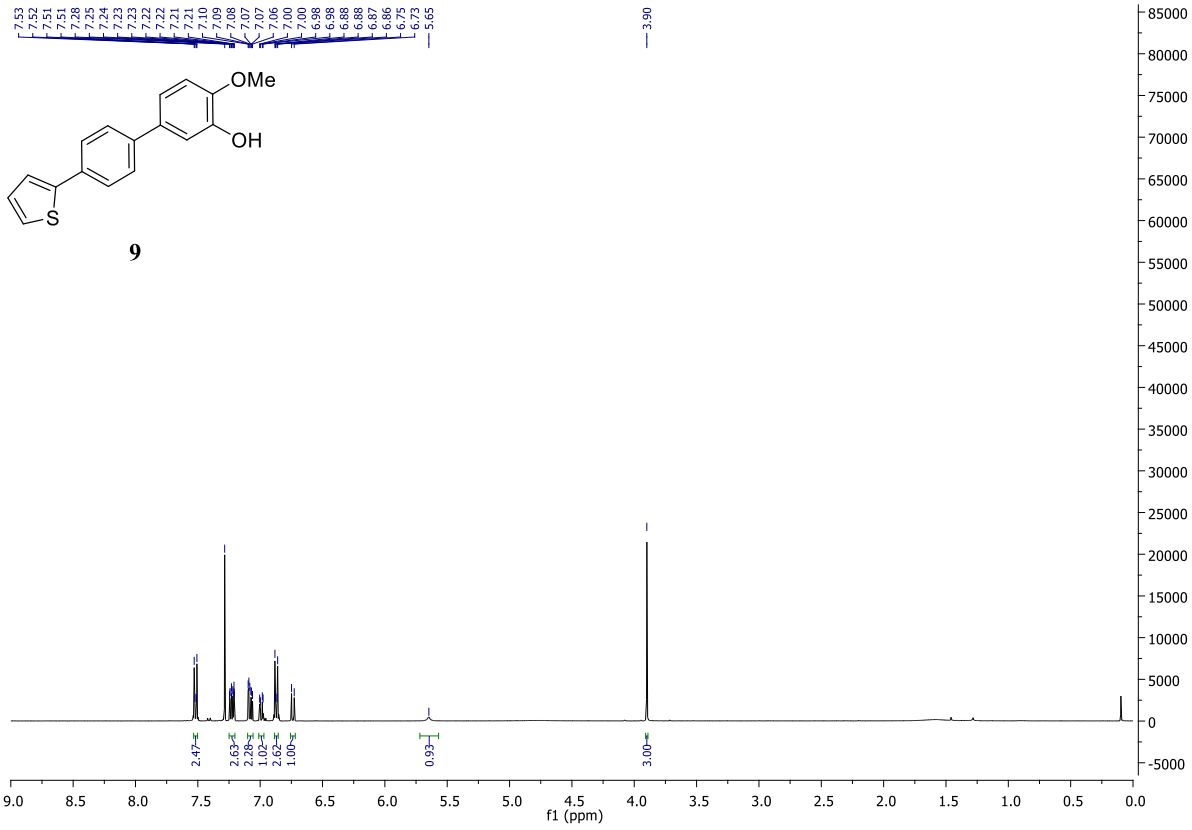
^{13}C NMR of 8, DMSO-d_6, 101 MHz



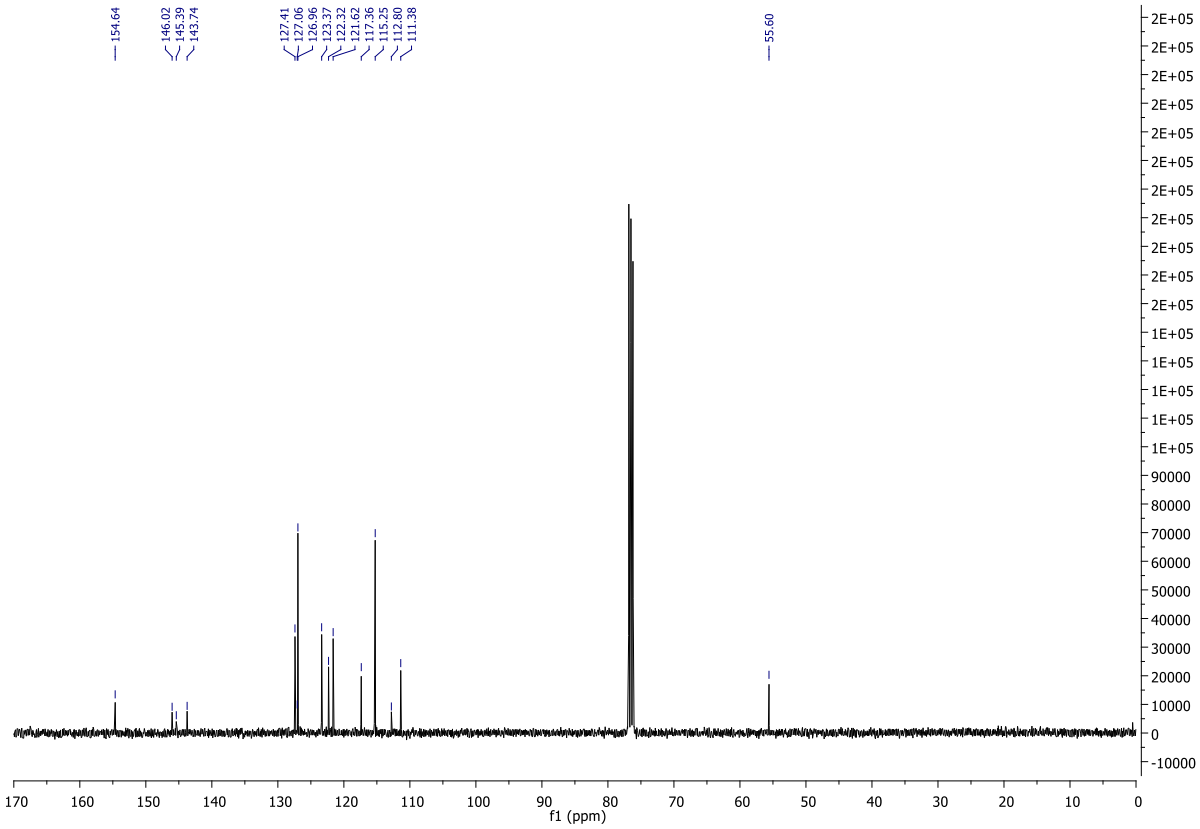
HRMS of 8



^{1}H NMR of 9, $CDCl_3$, 500 MHz



^{13}C NMR of 9, $CDCl_3$, 126 MHz



HRMS of 9