

Continuous Flow Synthesis of Trimethylsilylphenyl Perfluorosulfonate Benzyne Precursors

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Supporting Information

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General Instrumentation

¹H-NMR, ¹³C{¹H}-NMR and ¹⁹F-NMR were recorded at 500/400/300 MHz, 125/100/75 MHz, 470/376 MHz on a Bruker Avance 500, 400 or 300 spectrometers. All spectra are referenced to CDCl₃ residual CHCl₃ peak (¹H-NMR δ = 7.26 ppm; ¹³C{¹H}-NMR δ = 77.0 ppm). All chemical shifts are quoted in parts per million (ppm), measured from the centre of the signal except in the case of multiplets of more than one proton, which are quoted as a range. Coupling constants are quoted to the nearest 0.1 Hz. Splitting patterns are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), quintet (quin.), heptet (hept.), multiplet (m), broad singlet (brs) and combinations thereof.

Low resolution mass spectrometry was performed on a Agilent 6100 mass spectrometer (ESI ionisation), Thermo Finnigan MAT95XP (EI) and Hewlett Packard 5971 MSD (GC/MS with EI). High resolution mass spectrometry was performed on a Waters QTOF with ESI ionisation.

GC analysis were performed on a Dani Master GC, fitted with a BPX5 column 30 m length, 0.32 mm width, with a 0.25 μm non polar film. The maximum temperature was 300 °C and a gradient of 5 °C per minute was used. All the analysis were performed using dodecane as internal standard and helium as carrier gas.

Flow experiments were conducted in PTFE-FEP tubing with 1/32" inner diameter, 1/16" outer diameter and 1/64" wall thickness. Flangeless PEEK fittings with PEEK ferrules were used in conjunctions with PEEK PTFE Y-adapters with 0.02" channel diameter. Syringes were connected via PTFE female luer to female 1/4-28 thread.

One type of syringe pumps employed was a Razel Scientific Instruments A-99 with a manual stepped motor and a customized syringe mount to hold multiple syringes at the same time. The second type were multiple non-programmable New Era Pumpsystems Ltd. NE-300 Just Infusion™ Syringe Pumps.

All chemicals were purchased from Sigma-Aldrich, Alfa-Aesar or Fisher Scientific and used without further purification. Dry ether and hexane were purchased from Sigma Aldrich and stored over 10 A molecular sieves.

Trimethylsilylphenolethers (**6a – g**) were prepared via a standard literature procedure.^[1]

N'-cyclohexylidene-4-methylbenzenesulfonohydrazide was prepared following a procedure reported by Magrath *et. al.*^[2]

General Procedures

General Procedure A – Synthesis of TMS protected phenols.

In a round bottomed flask 1 equivalent of phenol is mixed with 1.1 equivalents of hexamethyldisilazane and diluted with THF (1 mL per mmol). The mixture is heated to reflux for 45 minutes. After completion the reaction is left to cool to room temperature. The title compound is obtained in excellent yield and purity by evaporation of the solvent and amine residues.

General Procedure B – Continuous Flow Synthesis of 2-Trimethylsilyl phenols.

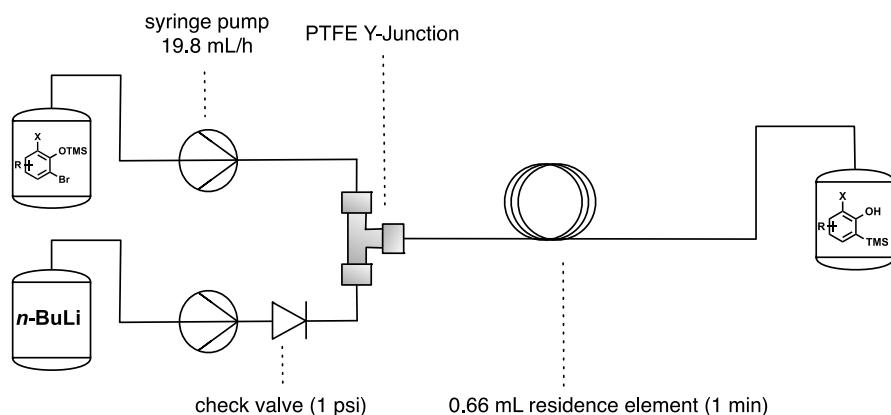
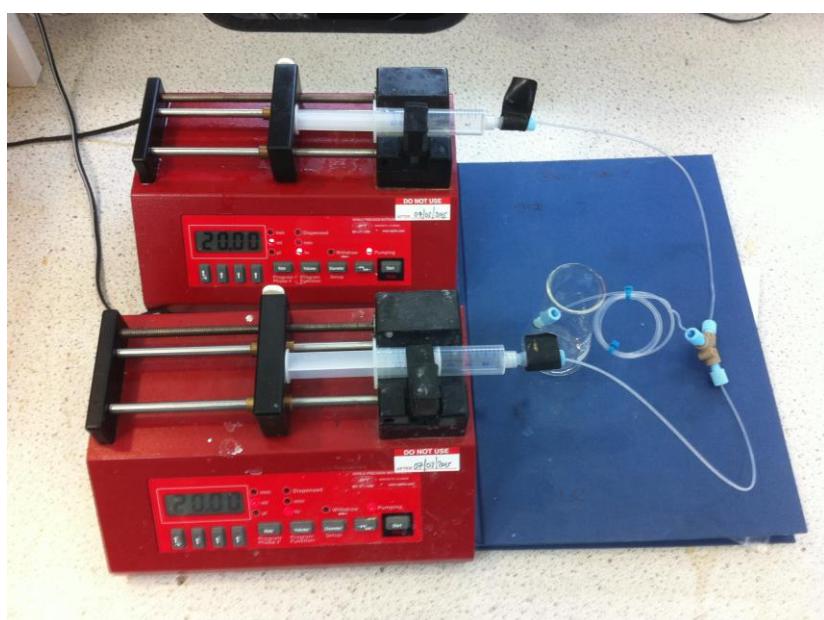


Figure 1. Flow diagram for general procedure B.

In a continuous flow reactor consisting of two syringe pumps set to 19.8 mL/h each, a Y-shaped mixing element and a 0.66 mL residence element a solution of (2-bromoaryloxy) trimethylsilane (1 eq.) in diethylether and a solution of *n*-butyllithium (1.2 eq.) in ether are mixed and reacted at room temperature. The effective residence time is 1 minute. The crude reaction mixture is poured onto a plug of silica and eluted with chloroform. The pure product is obtained by evaporation without further purification.



General Procedure C – Continuous Flow Synthesis of 2-Trimethylsilylaryl Trifluoromethylsulfonates.

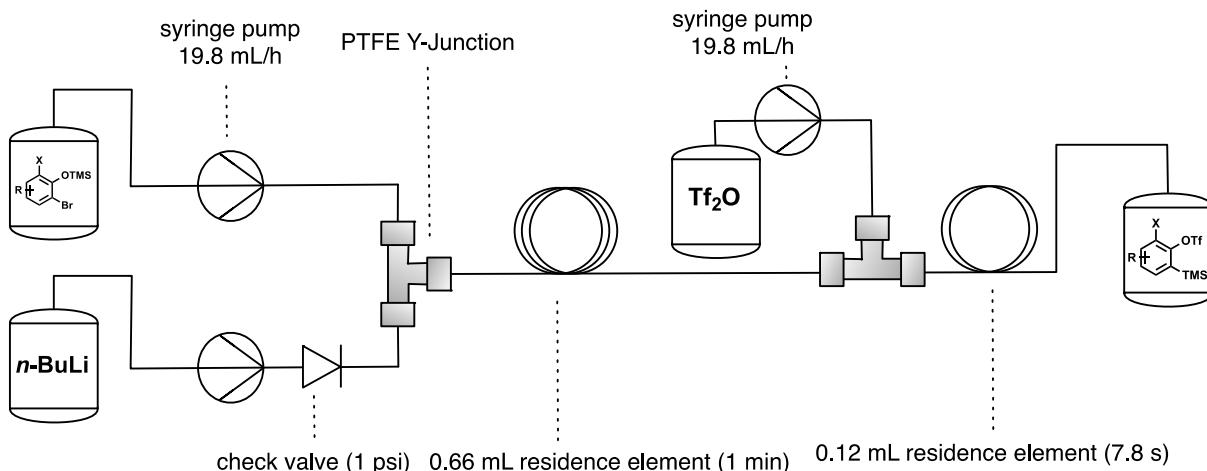


Figure 2. Flow diagram for general procedure C.

In a continuous flow reactor consisting of three syringe pumps set to 19.8 mL/h each, two Y-shaped mixing element, a 0.66 mL and a 0.12 mL residence element a solution of (2-bromoaryloxy) trimethylsilane (1 eq.) in diethylether and a solution of *n*-butyllithium (1.2 eq.) in ether are mixed and reacted at room temperature. To this stream is added a stream of triflic anhydride (1.2 eq.) in diethyl ether. The effective residence time for step 1 is 1 minute, for step 2 7.3 seconds. The crude reaction mixture is poured onto a plug of silica and eluted with pentane. The pure product is obtained by evaporation without further purification.

In reaction scales above 3 mmol (accumulated product) higher yields were obtained when the excess triflic anhydride was quenched with aqueous sodium carbonate solution and the product extracted with hexane.



General Procedure D – Continuous Flow Synthesis of 2-Trimethylsilylaryl Perfluorobutylsulfonates.

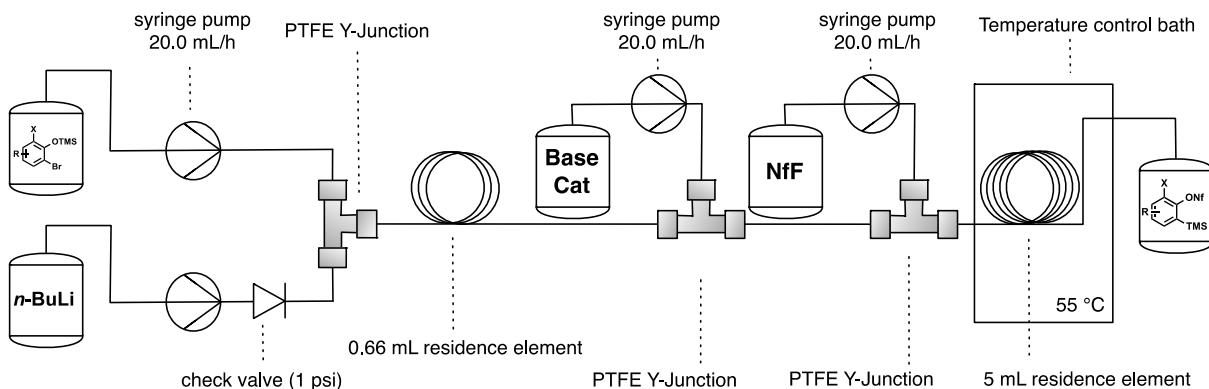
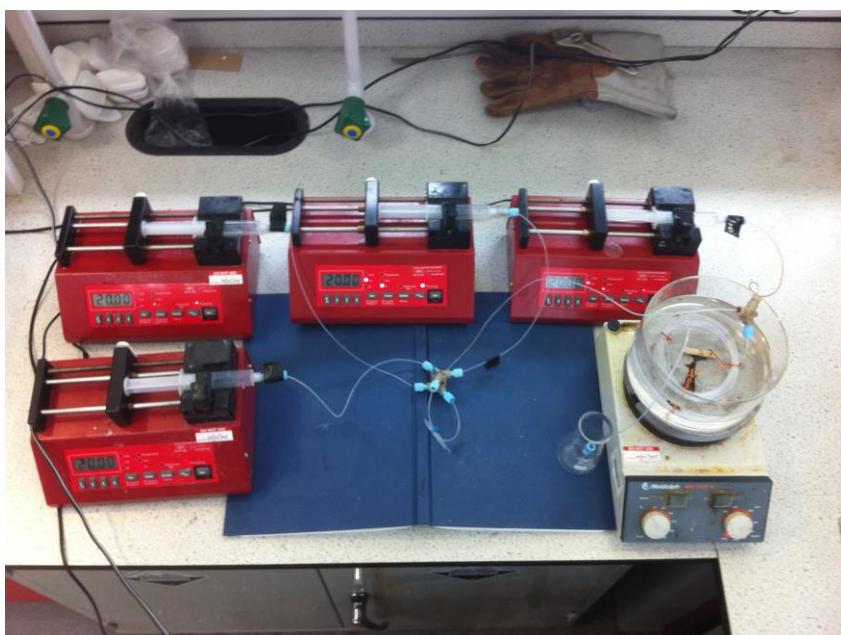


Figure 3. Flow diagram for general procedure D.

In a continuous flow reactor consisting of four syringe pumps set to 20.0 mL/h each, three Y-shaped mixing element, a 0.66 mL for step 1 and a 5 mL heated (55 °C) residence element for step 2, a solution of (2-bromoaryloxy) trimethylsilane (1 eq.) in THF and a solution of n-butyllithium (1.2 eq.) in hexanes are mixed and reacted at room temperature. The effective residence time is 1 minute. This stream is then mixed with triethylamine (30 eq.) and 4-pyrollidino pyridine (3 mol-%) in THF and immediately after with a solution of nonafluyl fluoride (1.6 eq.) in THF. The reaction mixture is conveyed into the heated residence element for an effective residence time of 3.75 minutes. The crude reaction mixture is poured onto a plug of silica and eluted with pentane. The pure product is obtained by evaporation without further purification.



Base screen for continuous flow synthesis of nonaflates.

Entry	Base ^[a]	Amount [eq.]	Conv. [%]
1	NEt ₃ ^[b]	2	19
2	NEt ₃ ^[b]	10	25
3	NEt ₃ ^[b]	40	61
4	DIPEA	40	0
5	TMG	10	- ^[c]
6	DBU	7	- ^[d]
7	Pyridine	40	0

[a] DIPEA = diisopropylethylamine, TMG = 1,1,3,3-Tetramethylguanidine, DBU = 1,8-Diazabicycloundec-7-ene. [b] Distilled triethylamine used yields significantly lower with “wet” base. [c] Upon mixing TMG with nonafluyl fluoride imminent precipitation of a white solid occurred indicating non-compatibility. [d] The reaction with DBU led to immediate blockage upon mixing the substrate stream with the base/NfF mixture.

Continuous flow synthesis of nonaflates via nucleophilic catalysis by DMAP.

Entry	Base	Cat. Loading [%]	Conv. [%]
1	NEt ₃	10	50
2	NEt ₃	30	80
3	NEt ₃	30 ^[a]	82
4	NEt ₃	30 ^[b]	83
5	DIPEA	10	0
6	DIPEA	80	80
7	-	100	0
8	-	120	0

DMAP = 4-N,N-Dimethylaminopyridine [a] The loading of NfF was increased from 1.6 eq. to 3.0 eq. [b] The residence element was submerged in an oil bath heated to 55 °C.

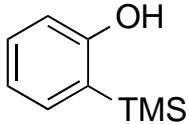
Continuous flow synthesis of nonaflates via nucleophilic catalysis catalyst screen.

Entry	Catalyst	Cat. Loading [%]	Conv. [%]
1	DMAP	30	83
2	4-PPY ^[a]	30	>99
3	4-PPY ^[a]	3	>99

Conditions as in general procedure D with catalyst loadings as indicated. [a] 4-PPY = 4-Pyrrolidinopyridine

Characterisation data for 2-trimethylsilyl phenols

2-(Trimethylsilyl)phenol (7a):



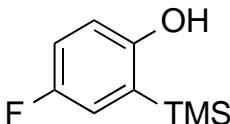
The title compound was synthesised *via* **General Procedure B** from (2-bromophenoxy)trimethylsilane (1.22 g, 5 mmol) diluted to 0.5 M to give 2-(trimethylsilyl)phenol as a colourless oil (763 mg, 4.6 mmol, 92%).

¹H-NMR (400 MHz, CDCl₃): δ 7.41 (dd, J = 7.2, 1.7 Hz, 1H, ArH), 7.27 (ddd, J = 8.0, 7.4, 1.8 Hz, 1H, ArH), 6.97 (td, J = 7.3, 0.9 Hz, 1H, ArH), 6.69 (ddd, J = 8.0, 0.9, 0.3 Hz, 1H, ArH), 4.90 (br s, 1H, OH), 0.35 (s, 9H Si(CH₃)₃).

¹³C-NMR (75 MHz, CDCl₃): δ 160.24 (C), 135.27 (CH), 130.65 (CH), 125.35 (CH), 120.47 (CH), 114.43 (C), -0.98 (CH₃).

The characterisation data was in agreement with the literature.^[3]

4-Fluoro-2-(trimethylsilyl)phenol (7b):



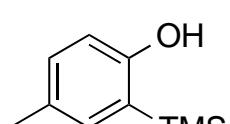
The title compound was synthesised *via* **General Procedure B** from (2-bromo-4-fluorophenoxy)trimethylsilane (262 mg, 1 mmol) diluted to 0.1 M to give 4-fluoro-2-(trimethylsilyl)phenol as a colourless oil (169 mg, 0.92 mmol, 92%).

¹H-NMR (600 MHz, CDCl₃): δ 7.03-7.01 (m, 1H, ArH), 6.89 (td, J = 8.4, 3.1 Hz, 1H, ArH), 06.61 (dd, J = 8.7, 3.9 Hz, 1H, ArH), 4.71 (d, J = 0.5 Hz, 1H, OH), 0.30 (s, 8H, Si(CH₃)₃).

¹³C-NMR (151 MHz, CDCl₃): δ 157.22 (C, d, J_{CF} = 239.1 Hz), 156.01 (C, d, J_{CF} = 2.89 Hz), 127.64 (C, d, J_{CF} = 3.11 Hz), 120.98 (CH, d, J_{CF} = 20.39 Hz), 116.62 (CH, d, J_{CF} = 23.37 Hz), 115.35 (CH, d, J_{CF} = 7.49 Hz), -1.22 (CH₃).

Characterisation data was in agreement with the literature.^[5]

4-Methyl-2-(trimethylsilyl)phenol (7c):



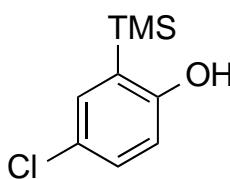
The title compound was synthesised *via* **General Procedure B** from (2-bromo-4-methylphenoxy)trimethylsilane (258 mg, 1 mmol) diluted to 0.1 M to give 2-(trimethylsilyl)phenol as a colourless oil (160 mg, 0.89 mmol, 89%).

¹H-NMR (600 MHz, CDCl₃): δ 7.14 (s, 1H, ArH), 7.02 (d, J = 8.0 Hz, 1H, ArH), 6.57 (d, J = 8.1 Hz, 1H, ArH), 4.67 (s, 1H, OH), 2.27 (s, 3H, CH₃), 0.29 (d, J = 2.5 Hz, 9H Si(CH₃)₃).

¹³C-NMR (151 MHz, CDCl₃): δ 158.13 (C), 135.66 (C), 131.07 (CH), 129.35 (CH), 125.08 (CH), 114.30 (C), 20.52 (CH₃), -0.94 (CH₃).

Characterisation data was in agreement with the literature.^[4]

4-Chloro-2-(trimethylsilyl)phenol (7d):



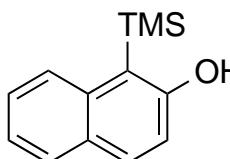
The title compound was synthesised *via* **General Procedure B** from (2-bromo-4-chlorophenoxy)trimethylsilane (278 mg, 1 mmol) diluted to 0.1 M to give 4-chloro-2-(trimethylsilyl)phenol as a colourless oil (182 mg, 0.91 mmol, 91%).

¹H-NMR (600 MHz, CDCl₃): δ 7.27 (d, J = 2.6 Hz, 1H, ArH), 7.16 (dd, J = 8.5, 2.6 Hz, 1H, ArH), 6.61 (d, J = 8.5 Hz, 1H, ArH), 5.11 (s, 1H, OH), 0.31 (s, 9H, Si(CH₃)₃).

¹³C-NMR (151 MHz, CDCl₃): δ 158.78 (C), 134.67 (CH), 130.10 (CH), 128.04 (C), 125.54 (C), 115.78 (CH), -1.21 (CH₃).

Characterisation data was in agreement with the literature.^[8]

1-(Trimethylsilyl)naphthalen-2-ol (7e):

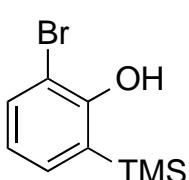


The title compound was synthesised *via* **General Procedure B** from ((1-bromonaphthalen-2-yl)oxy)trimethylsilane (294 mg, 1 mmol) diluted to 0.1 M to give 1-(trimethylsilyl)naphthalen-2-ol as a colourless oil (196 mg, 0.96 mmol – 96%). The product was quite unstable, with rapid degradation and colouring observed, to form a brown oil in minutes and a black solid after days. Immediate NMR spectroscopy of the freshly prepared material gave data in agreement with the literature.^[9]

¹H-NMR (300 MHz, CDCl₃): δ 8.07 (d, J = 8.5 Hz, 1H, ArH), 7.79-7.74 (m, 2H, ArH), 7.45 (ddd, J = 8.5, 6.9, 1.6 Hz, 1H, ArH), 7.33 (ddd, J = 8.0, 6.9, 1.1 Hz, 1H, ArH), 6.96 (d, J = 8.8 Hz, 1H, ArH), 5.51 (d, J = 3.9 Hz, 1H, ArH), 0.58 (s, 9H, Si(CH₃)₃).

¹³C-NMR (75 MHz, CDCl₃): δ 159.17 (C), 138.35 (C), 132.01 (CH), 129.34 (C), 128.90 (CH), 127.05 (CH), 125.98 (CH), 122.82 (CH), 118.02 (CH), 2.35 (CH₃).

2-Bromo-6-(trimethylsilyl)phenol (7f):



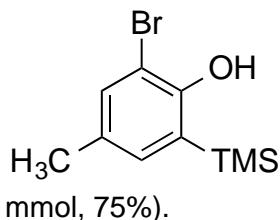
The title compound was synthesised *via* **General Procedure B**, with the mixing and residence elements cooled to -78 °C, from (2,6-dibromophenoxy)trimethylsilane (322 mg, 1 mmol) diluted to 0.1 M to give 2-bromo-6-(trimethylsilyl)phenol as a colourless oil (185 mg, 0.76 mmol, 76%).

¹H-NMR (300 MHz, CDCl₃): δ 7.47 (dd, J = 7.9, 1.6 Hz, 1H, ArH), 7.31 (dd, J = 7.2, 1.5 Hz, 1H, ArH), 6.80 (dd, J = 7.9, 7.2 Hz, 1H, ArH), 5.73 (s, 1H, OH), 0.32 (s, 9H, Si(CH₃)₃).

¹³C-NMR (151 MHz, CDCl₃): δ 156.03 (C), 134.49 (CH), 132.95 (CH), 127.07 (C), 121.55 (CH), 110.44 (C), -1.19 (CH₃).

Characterisation data was in agreement with the literature.^[6]

(2,6-Dibromo-4-methylphenoxy)trimethylsilane (7g):



The title compound was synthesised *via* **General Procedure B**, with the mixing and residence elements cooled to $-78\text{ }^{\circ}\text{C}$, from (2,6-dibromo-4-methylphenoxy)trimethylsilane (335 mg, 1 mmol) diluted to 0.1 M to give 2-bromo-4-methyl-6-(trimethylsilyl)phenol as a colourless oil (191 mg, 0.75 mmol, 75%).

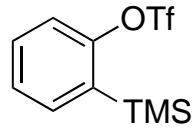
$^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.29-7.28 (m, 1H, ArH), 7.08-7.07 (m, 1H, ArH), 5.55 (s, 1H, OH), 2.27 (t, $J = 0.7$ Hz, 3H, CH_3), 0.31 (s, 9H, $\text{Si}(\text{CH}_3)_3$).

$^{13}\text{C-NMR}$ (151 MHz, CDCl_3): δ 153.84 (C), 135.04 (CH), 133.06 (CH), 130.89 (C), 126.58 (C), 110.06 (C), 20.20 (CH_3), -1.15 (CH_3).

Characterisation data was in agreement with the literature.^[7]

Characterisation data for 2-trimethylsilylaryl trifluoromethylsulfonates

2-(Trimethylsilyl)phenyl trifluoromethanesulfonate (1a):



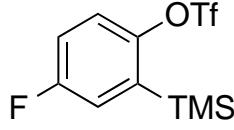
The title compound was synthesised *via* **General Procedure C** from (2-bromophenoxy)trimethylsilane (244 mg, 1 mmol) diluted to 0.1 M to give 2-(trimethylsilyl)phenyl trifluoromethanesulfonate as a colourless oil (270 mg, 0.91 mmol, 91%).

$^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.56 (dd, $J = 7.4, 2.0$ Hz, 1H, ArH), 7.50-7.44 (m, 1H, ArH), 7.39-7.34 (m, 2H, ArH), 0.39 (s, 9H, $\text{Si}(\text{CH}_3)_3$).

$^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ 155.09 (CH), 136.24 (CH), 132.53 (CH), 131.22 (CH), 127.45 (CH), 118.47 (C, q, $J_{\text{CF}} = 317.72$ Hz), 119.47 (C, q, $J_{\text{CF}} = 1.51$ Hz), -0.85 (CH_3).

The characterisation data was in agreement with the literature.^[10]

4-Fluoro-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (1b):



The title compound was synthesised *via* **General Procedure C** from (2-bromo-4-fluorophenoxy)trimethylsilane (262 mg, 1 mmol) diluted to 0.1 M to give 4-fluoro-2-(trimethylsilyl)phenyl trifluoromethanesulfonate as a colourless oil (275 mg, 0.87 mmol – 87%).

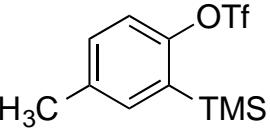
$^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.32 (dd, $J = 9.0, 4.0$ Hz, 1H, ArH), 7.21 (dd, $J = 8.1, 3.1$ Hz, 1H, ArH), 7.12 (ddd, $J = 9.0, 7.3, 3.2$ Hz, 1H, ArH), 0.39 (s, 9H, $\text{Si}(\text{CH}_3)_3$).

$^{13}\text{C-NMR}$ (151 MHz, CDCl_3): δ 160.97 (C, d, $J_{\text{CF}} = 234.81$ Hz), 150.16 (C, d, $J_{\text{CF}} = 3.12$ Hz), 135.88 (C, d, $J_{\text{CF}} = 5.14$ Hz), 122.35 (CH, d, $J_{\text{CF}} = 22.0$ Hz), 121.46 (C, d, $J_{\text{CF}} = 7.08$ Hz), 118.41 (C, q, $J_{\text{CF}} = 316.05$ Hz), 117.69 (CH, d, $J_{\text{CF}} = 24.22$ Hz), 1.04 (CH_3).

¹⁹F-NMR (376 MHz, CDCl₃): δ -73.86 (s, 3F), -114.37 (s, 1F).

HRMS (EI+): Calcd. for C₉H₉O₃F₄Si₁: 300.9979, found: 300.9972

4-Methyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (1c):

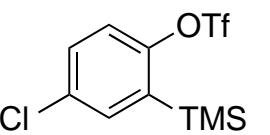
 The title compound was synthesised *via* **General Procedure C** from (2-bromo-4-methylphenoxy)trimethylsilane (258 mg, 1 mmol) diluted to 0.1 M to give 4-methyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate as a colourless oil (273 mg, 0.88 mmol, 88%).

¹H-NMR (300 MHz, CDCl₃): δ 7.34-7.32 (m, 1H, ArH), 7.25-7.23 (m, 2H, ArH), 2.39 (s, 3H, CH₃), 0.39 (s, 8H, Si(CH₃)₃).

¹³C-NMR (151 MHz, CDCl₃): δ 153.04 (C), 137.20 (C), 136.65 (CH), 132.18 (CH), 131.65 (CH), 118.46 (C, q, J_{CF} = 320.19 Hz) 119.27 (C), 20.83 (CH₃), -0.80 (CH₃).

The characterisation data was in agreement with that reported in the literature.^[11]

4-Chloro-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (1d):

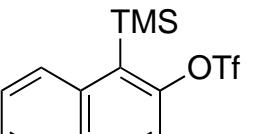
 The title compound was synthesised *via* **General Procedure C** from (2-bromo-4-chlorophenoxy)trimethylsilane (278 mg, 1 mmol) diluted to 0.1 M to give 4-chloro-2-(trimethylsilyl)phenyl trifluoromethanesulfonate as a colourless oil (302 mg, 0.91 mmol – 91%).

¹H-NMR (300 MHz, CDCl₃): δ 7.48 (dd, J = 2.7, 0.3 Hz, 1H, ArH), 7.41 (dd, J = 8.8, 2.7 Hz, 1H, ArH), 7.29 (d, J = 8.4 Hz, 1H, ArH), 0.39 (s, 9H, Si(CH₃)₃).

¹³C-NMR (75 MHz, CDCl₃): δ 153.04 (C), 135.83 (CH), 135.28 (C), 133.51 (CH), 130.96 (CH), 120.96 (C), -1.02 (CH₃). Trifluoromethyl carbon not resolved.

The characterisation data was in agreement with that in the literature.^[13]

1-(Trimethylsilyl)naphthalen-2-yl trifluoromethanesulfonate (1e):

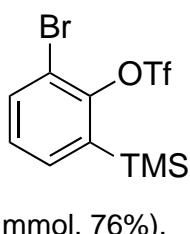
 The title compound was synthesised *via* **General Procedure B** from ((1-bromonaphthalen-2-yl)oxy)trimethylsilane (294 mg, 1 mmol) diluted to 0.1 M to give 1-(trimethylsilyl)naphthalen-2-yl trifluoromethanesulfonate as a colourless oil (339 mg, 0.97 mmol – 97%).

¹H-NMR (300 MHz, CDCl₃): δ 8.24-8.21 (m, 1H, ArH), 7.93-7.88 (m, 2H, ArH), 7.61-7.52 (m, 2H, ArH), 7.41 (d, J = 9.1 Hz, 1H, ArH), 0.60 (s, 9H, Si(CH₃)₃).

¹³C-NMR (75 MHz, CDCl₃): δ 152.46 (C), 137.52 (C), 132.41 (CH), 132.34 (C), 129.25 (C), 129.01 (CH), 128.77 (CH), 126.65 (CH), 126.25 (CH), 118.64 (C, q, J_{CF} = 320.48 Hz), 119.09 (C), 2.21 (CH₃).

The characterisation data was in agreement with that reported in the literature.^[10]

2-Bromo-6-(trimethylsilyl)phenyl trifluoromethanesulfonate: (1f)



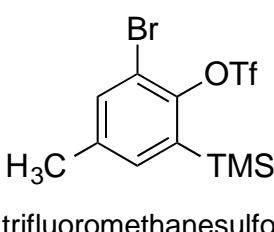
The title compound was synthesised *via* an altered **General Procedure C** from (2,6-dibromophenoxy)trimethylsilane (322 mg, 1 mmol) diluted to 0.1 M and an exact equivalent of n-butyllithium 0.1 M in diethyl ether to give 2-bromo-6-(trimethylsilyl)phenyl trifluoromethanesulfonate as a colourless oil (284 mg, 0.76 mmol, 76%).

¹H-NMR (300 MHz, CDCl₃): δ 7.67 (dd, J = 7.8, 1.7 Hz, 1H, ArH), 7.51 (dd, J = 7.4, 1.7 Hz, 1H, ArH), 7.23 (dd, J = 7.5, 7.8, 1H, ArH), 0.40 (s, 9H, Si(CH₃)₃).

¹³C-NMR (101 MHz, CDCl₃): δ 148.73 (C), 137.74 (C), 135.78 (CH), 135.72 (CH), 129.09 (CH), 118.59 (C, q, J_{CF} = 324.29 Hz) 116.52 (C), 0.01 (CH₃).

The characterisation data was in agreement with that reported in the literature.^[12]

2-Bromo-4-methyl-6-(trimethylsilyl)phenyl trifluoromethanesulfonate (1g):



The title compound was synthesised *via* an altered **General Procedure C** from (2,6-dibromo-4-methylphenoxy)trimethylsilane (335 mg, 1 mmol) diluted to 0.1 M and an exact equivalent of n-butyllithium 0.1 M in diethyl ether to give 2-bromo-4-methyl-6-(trimethylsilyl)phenyl trifluoromethanesulfonate as a colourless oil (293 mg, 0.75 mmol – 75%).

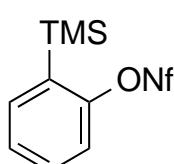
¹H-NMR (400 MHz, CDCl₃): δ 7.53 (td, J = 1.4, 0.7 Hz, 1H, ArH), 7.31 (td, J = 1.4, 0.6 Hz, 1H, ArH), 2.40 (s, 3H, ArCH₃), 0.44 (s, 9H, Si(CH₃)₃).

¹³C-NMR (151 MHz, CDCl₃): δ 146.66 (C), 139.33 (C), 137.01 (C), 136.23 (CH), 136.12 (CH), 118.59 (C, q, J_{CF} = 320.31 Hz), 115.99 (C), 20.54 (CH₃), 0.04 (CH₃).

The characterisation data was in agreement with that reported in the literature.^[7]

Characterisation data for 2-trimethylsilyl perfluorobutylsulfonates

2-(Trimethylsilyl)phenyl 1,1,2,2,3,3,4,4,4-nona-fluorobutane-1-sulfonate (8a):



The title compound was synthesised *via* **General Procedure D** from (2-bromophenoxy)trimethylsilane (244 mg, 1 mmol) diluted to 0.1 M to give 2-(trimethylsilyl)phenyl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate as a colourless oil (408 mg, 0.91 mmol – 91%).

¹H-NMR (600 MHz, CDCl₃): δ 7.57 (dd, J = 7.3, 1.9 Hz, 1H, ArH), 7.48 (ddd, J = 8.3, 7.4, 1.8 Hz, 1H, ArH), 7.37 (td, J = 7.3, 0.9 Hz, 1H, ArH), 7.36 (d, J = 8.3 Hz, 1H, ArH), 0.42-0.39 (m, 9H, Si(CH₃)₃).

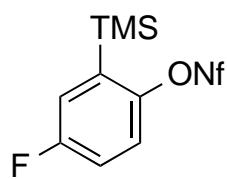
¹³C-NMR (101 MHz, CDCl₃): δ 155.37 (C), 136.19 (CH), 132.61 (C), 131.25 (CH), 127.48 (CH), 119.64 (C, t, *J*_{CF} = 2.30 Hz), -0.88 (CH₃).

¹⁹F-NMR (376 MHz, CDCl₃): δ -80.63 (t, *J* = 9.8 Hz, 3F), -109.70–109.78 (m, 2F), -120.88–120.99 (m, 2F), -125.75–125.82 (m, 2F).

LRMS (GC/MS-EI): [M-Me]⁺ = 433.0 (TMS demethylated)

HRMS (EI+): Calcd. for C₁₂H₁₀O₃F₉S₁Si₁: 432.9971, found: 432.9984

4-Fluoro-2-(trimethylsilyl)phenyl 1,1,2,2,3,3,4,4,4-nona-fluorobutane-1-sulfonate (8b):



The title compound was synthesised *via* **General Procedure D** from (2-bromo-4-fluorophenoxy)trimethylsilane (262 mg, 1 mmol) diluted to 0.1 M to give 4-fluoro-2-(trimethylsilyl)phenyl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate as a colourless oil (422 mg, 0.91 mmol – 91%).

¹H-NMR (300 MHz, CDCl₃): δ 7.30 (dd, *J* = 9.1, 4.0 Hz, 1H, ArH), 7.19 (dd, *J* = 8.1, 3.2 Hz, 1H, ArH), 7.10 (ddd, *J* = 9.1, 7.3, 3.2 Hz, 1H, ArH), 0.38 (s, 9H, Si(CH₃)₃).

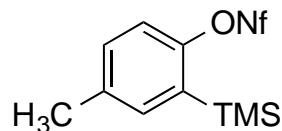
¹³C-NMR (151 MHz, CDCl₃): δ 160.87 (C, d, *J*_{CF} = 249.9 Hz), 150.36 (C, d, *J*_{CF} = 3.0 Hz), 135.89 (CH, d, *J*_{CF} = 4.4 Hz), 122.22 (CH, d, *J*_{CF} = 22.0 Hz), 121.58 (C, dt, *J*_{CF} = 8.2, 2.3 Hz), 117.65 (CH, d, *J*_{CF} = 24.2 Hz), -1.14 (CH₃).

¹⁹F-NMR (376 MHz, CDCl₃): δ -80.66 (t, *J* = 9.9 Hz, 3F), -109.67 (t, *J* = 13.9 Hz, 2F), -114.42 (s, 1F), -120.94–121.00 (m, 2F), -125.77–125.86 (m, 2F).

LRMS (GC/MS-EI): [M-Me]⁺ = 451.0 (TMS demethylated)

HRMS (EI+): Calcd. for C₁₂H₉O₃F₁₀S₁Si₁: 450.9883, found: 450.9876

4-Methyl-2-(trimethylsilyl)phenyl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate (8c):



The title compound was synthesised *via* **General Procedure D** from (2-bromo-4-methylphenoxy)trimethylsilane (258 mg, 1 mmol) diluted to 0.1 M to give 4-methyl-2-(trimethylsilyl)phenyl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate as a colourless oil (378 mg, 0.82 mmol – 82%).

¹H-NMR (300 MHz, CDCl₃): δ 7.32 (td, *J* = 1.3, 0.6 Hz, 1H, ArH), 7.27–7.20 (m, 2H, ArH), 2.39 (s, 3H, ArCH₃), 0.38 (s, 9H, Si(CH₃)₃).

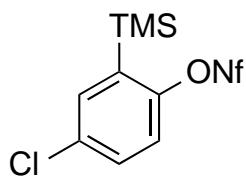
¹³C-NMR (75 MHz, CDCl₃): δ 153.37 (C), 137.23 (CH), 136.60 (CH), 132.28 (C), 131.68 (CH), 119.44 (C, t *J*_{CF} = 2.59 Hz), 20.81 (CH₃), -0.83 (CH₃).

¹⁹F-NMR (471 MHz, CDCl₃): δ -80.66 (t, *J* = 10.9 Hz, 3F), -109.74–109.81 (m, 2F), -120.98 (dd, *J* = 17.8, 10.1 Hz, 2F), -125.75–125.85 (m, 2F).

LRMS (GC/MS-EI): [M-Me]⁺ = 447.1 (TMS demethylated)

HRMS (EI+): Calcd. for C₁₃H₁₂O₃F₉S₁Si₁: 447.0142, found: 447.0127

4-Chloro-2-(trimethylsilyl)phenyl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate (8d):



The title compound was synthesised *via General Procedure D* from (2-bromo-4-chlorophenoxy)trimethylsilane (278 mg, 1 mmol) diluted to 0.1 M to give 4-chloro-2-(trimethylsilyl)phenyl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate as a colourless oil (438 mg, 0.91 mmol – 91%).

¹H-NMR (300 MHz, CDCl₃): δ 7.46 (d, J = 2.6 Hz, 1H, ArH), 7.39 (dd, J = 8.8, 2.7 Hz, 1H, ArH), 7.27 (d, J = 8.8 Hz, 1H, ArH), 0.38 (s, J = 6.8 Hz, 9H, Si(CH₃)₃).

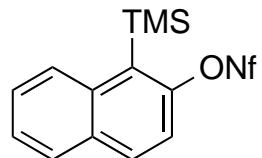
¹³C-NMR (126 MHz, CDCl₃): δ 153.33 (C), 135.78 (C), 135.36 (CH), 133.56 (CH), 130.99 (CH), 121.14 (C, t, J_{CF} = 2.49 Hz), -1.04 (CH₃).

¹⁹F-NMR (471 MHz, CDCl₃): δ -80.65 (t, J = 10.9 Hz, 3F), -109.54 (t, J = 15.9 Hz, 2F), -120.94 (dd, J = 9.9, 4.5 Hz, 2F), -125.78 (dd, J = 20.8, 14.3 Hz, 2F).

LRMS (GC/MS-EI): [M-Me]⁺ = 466.9 (TMS demethylated).

HRMS (EI+): Calcd. for C₁₃H₁₂O₃Cl₁F₉S₁Si₁: 481.9793, found: 481.9816.

1-(Trimethylsilyl)naphthalen-2-yl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate (8e):



The title compound was synthesised *via General Procedure B* from ((1-bromonaphthalen-2-yl)oxy)trimethylsilane (294 mg, 1 mmol) diluted to 0.1 M to give 1-(trimethylsilyl)naphthalen-2-yl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate as a colourless oil (463 mg, 0.93 mmol – 93%).

¹H-NMR (500 MHz, CDCl₃): δ 8.22-8.20 (m, 1H, ArH), 7.92-7.88 (m, 2H, ArH), 7.59-7.52 (m, 2H, ArH), 7.41 (d, J = 9.1 Hz, 1H, ArH), 0.59 (s, 9H, Si(CH₃)₃).

¹³C-NMR (126 MHz, CDCl₃): δ 152.70 (C), 137.53 (C), 132.40 (CH), 132.34 (C), 129.31 (C), 129.01 (CH), 128.79 (CH), 126.64 (CH), 126.26 (CH), 119.21 (C, t, J_{CF} = 2.43 Hz), 2.23 (CH₃).

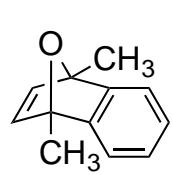
¹⁹F-NMR (471 MHz, CDCl₃): δ -80.62 (t, J = 10.9 Hz, 1F), -108.99 (t, J = 15.7 Hz, 1F), -120.79–120.85 (m, 1F), -125.71–125.78 (m, 1F).

LRMS (GC/MS-EI): [M-Me]⁺ = 483.0 (TMS demethylated)

HRMS (EI+): Calcd. for C₁₃H₁₂O₃Cl₁F₉S₁Si₁: 498.0353, found: 498.0362.

Characterisation data for products of benzyne reactions

1,4-dimethyl-1,4-dihydro-1,4-epoxynaphthalene (10):



2-(trimethylsilyl)phenyl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate (224 mg, 0.5 mmol, 1 eq.), 2,5-dimethylfuran (146 mg, 1 mmol, 2 eq.) and tetrabutylammonium difluorotriphenylsilicate (859 mg, 1.5 mmol, 3 eq.) were combined in a microwave vial, sealed and purged. The mixture was dissolved in 5 mL of dry THF and irradiated in a microwave at 100 °C for 30 minutes. The crude reaction mixture was loaded onto

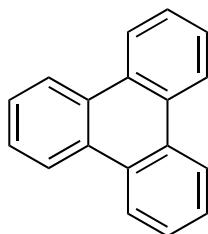
silica and purified by column chromatography (5% EtOAc in hexanes) (76 mg, 0.44 mmol – 89%).

¹H-NMR (300 MHz, CDCl₃): δ 7.17-7.11 (m, 2H, ArH), 7.01-6.95 (m, 2H, ArH), 6.79 (s, 2H, CHC=CHC), 1.90 (s, 6H, CH₃).

¹³C-NMR (75 MHz, CDCl₃): δ 152.67, 146.76, 124.68, 118.29, 88.58, 15.23.

The characterisation data were in agreement with that in the literature.^[14]

Triphenylene (11):



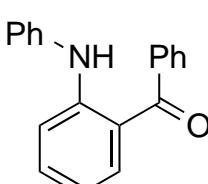
2-(trimethylsilyl)phenyl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate (112 mg, 0.25 mmol, 1 eq.), caesium fluoride (75.9 mg, 0.5 mmol, 2 eq.) and tetrakis-triphenylphosphine palladium(0) (28 mg, 0.025 mmol, 10 mol-%) were combined in a 5 mL microwave vial. The vial was sealed, purged and filled with 2 mL of dry acetonitrile. The reaction was stirred over night at 55 °C. The crude mixture was loaded onto silica and purified by column chromatography (Hexane). (17 mg, 7.4 mmol – 90%)

¹H-NMR (400 MHz, CDCl₃): δ 8.69-8.65 (m, 6H, ArH), 7.69-7.66 (m, 6H, ArH).

¹³C-NMR (101 MHz, CDCl₃): δ 129.75 (C), 127.20 (CH), 123.27 (CH).

The characterisation data was in agreement with that reported in the literature.^[15]

Phenyl(2-(phenylamino)phenyl)methanone (12):



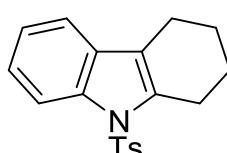
2-(trimethylsilyl)phenyl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate (168 mg, 0.38 mmol, 1.5 eq.), Tetrabutylammonium difluorotriphenylsilicate (269 mg, 0.5 mmol, 2 eq.) and benzilide (49.3 mg, 0.25 mmol, 1 eq.) were combined in a 5 mL microwave vial. The vial was sealed, purged and filled with 2 mL of dry toluene. The reaction was stirred over night at 55 °C. The crude mixture was loaded onto silica and purified by column chromatography (Hexane/DCM – 1:1) (51.5 mg, 0.2 mmol- 80%).

¹H-NMR (400 MHz, CDCl₃): δ 10.12 (s, 1H, NH), 7.72-7.69 (m, 2H, ArH), 7.58-7.53 (m, 2H, ArH), 7.50-7.46 (m, 2H, ArH), 7.39-7.33 (m, 4H, ArH), 7.32-7.29 (m, 2H, ArH), 7.10 (ddt, J = 7.4, 7.1, 1.3 Hz, 1H, ArH), 6.71 (ddd, J = 8.1, 6.6, 1.5 Hz, 1H, ArH).

¹³C-NMR (151 MHz, CDCl₃): δ 199.17 (C), 148.02 (C), 140.52 (C), 139.78 (C), 134.99 (CH), 134.21 (CH), 131.37 (CH), 129.41 (CH), 129.38 (CH), 128.13 (CH), 123.51 (CH), 122.18 (CH), 119.71 (C), 116.54 (CH), 114.61 (CH).

The characterisation data was in agreement with that reported in the literature.^[16]

9-Tosyl-2,3,4,9-hexahydro-1H-carbazole (13):



The title compound was prepared according to a procedure previously reported in the literature using 2-(trimethylsilyl)phenyl 1,1,2,2,3,3,4,4,4-

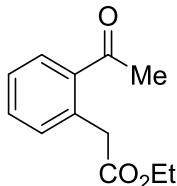
nonafluorobutane-1-sulfonate (201 mg, 0.45 mmol, 1.5 eq.), N'-cyclohexylidene-4-methylbenzenesulfonohydrazide (266 mg, 0.3 mmol, 1.0 eq.), cesium fluoride (151.90 mg, 0.9 mmol, 3.0 eq.) and boron trifluoride diethyletherate (0.6 mmol, 2.0 eq.) to give the title compound as a colourless oil (78 mg, 24 mmol - 80%)

¹H NMR (500 MHz, CDCl₃) δ 8.18 – 8.11 (m, 1H, TsH), 7.68 – 7.62 (m, 2H, TsH), 7.36 – 7.15 (m, 6H, ArH), 3.00 (ddd, *J* = 8.1, 4.0, 1.9 Hz, 2H, CycH), 2.58 (ddd, *J* = 8.0, 4.0, 1.9 Hz, 2H, CycH), 2.33 (s, 3H, ArCH₃), 1.96 – 1.84 (m, 2H, CycH), 1.84 – 1.71 (m, 2H, CycH).

¹³C NMR (126 MHz, CDCl₃) δ 144.39 (C), 136.25 (C), 136.17 (C), 135.34 (C), 130.30 (C), 129.75 (CH), 126.32 (CH), 123.83 (CH), 123.13 (CH), 118.54 (C), 117.92 (CH), 114.35 (CH), 24.63 (CH₂), 23.25 (CH₂), 22.04 (CH₂), 21.53 (CH₂), 21.07 (CH₃).

The characterisation data was in agreement with that reported in the literature.^[17]

Methyl 2-(2-oxopropyl)benzoate (14):



The title compound was prepared according to a procedure reported by Stoltz et. al. from 2-(trimethylsilyl)phenyl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate (168 mg, 0.38 mmol, 1.25 eq.), Methyl acetoacetate (34.8 mg, 0.3 mmol, 1.00 eq.) and cesium fluoride (136 mg, 0.9 mmol, 3.00 eq.) to give the title compound as a colourless oil (39 mg, 20 mmol, 68%).

¹H NMR (600 MHz, CDCl₃) δ 7.83 (dd, *J* = 1.1, 7.5 Hz, 1H, ArH), 7.47 (td, *J* = 7.5, 1.1 Hz, 1H, ArH), 7.40 (td, *J* = 7.5, 1.1 Hz, 1H, ArH), 7.24 – 7.27 (m, 1H, ArH), 3.94 (s, 2H, CH₂), 3.70 (s, 1H, C(O)CH₃), 2.60 (s, 1H, C(O)OCH₃).

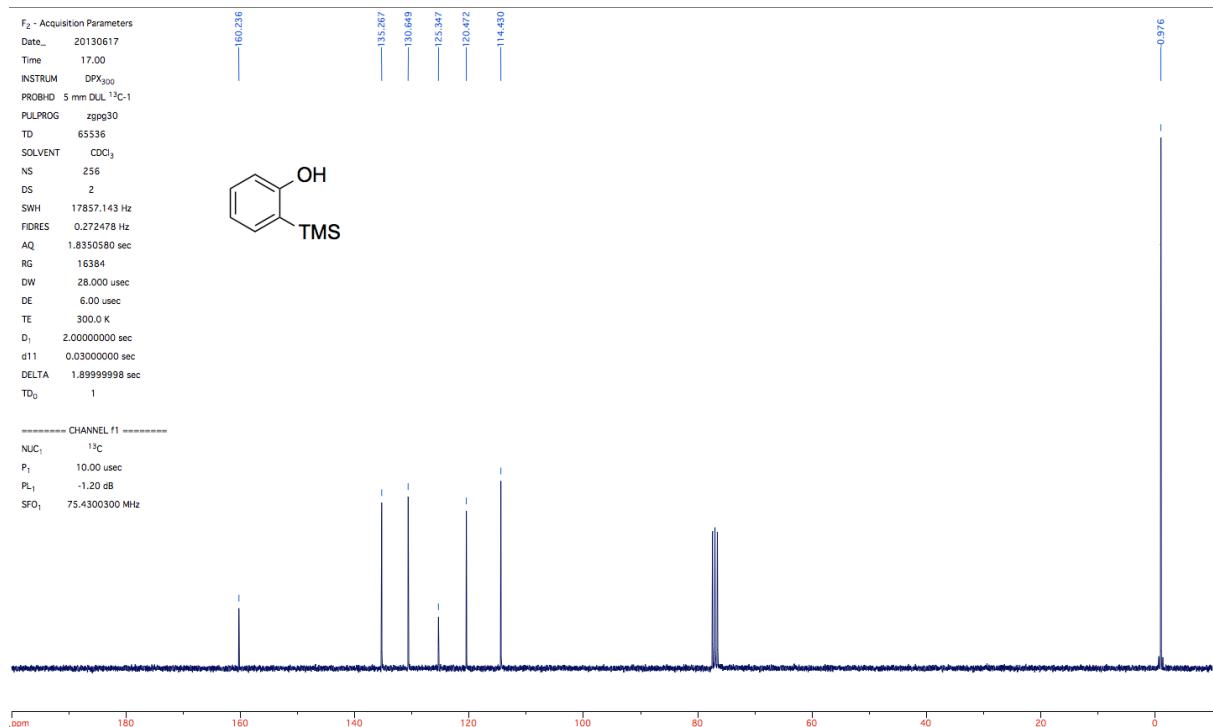
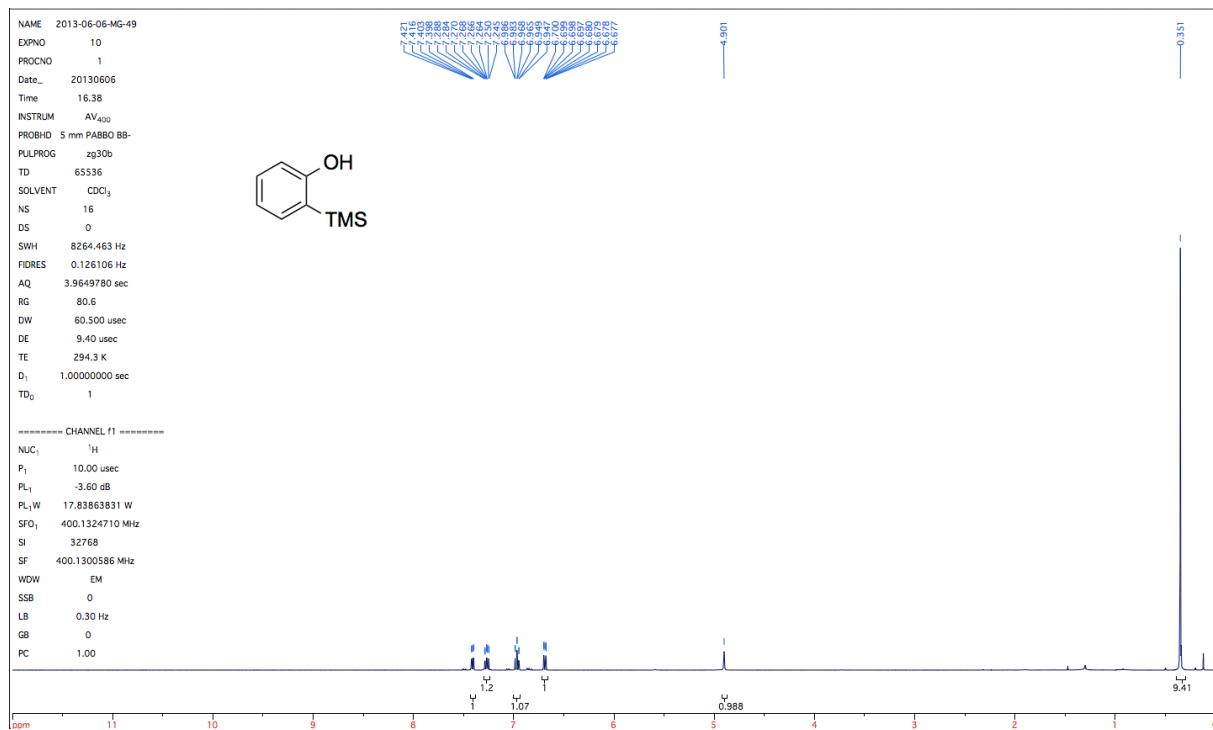
¹³C NMR (151 MHz, CDCl₃) δ 201.24 (C), 172.04 (C), 137.07 (C), 134.36 (C), 132.71 (CH), 132.06 (CH), 130.02 (C), 127.47 (CH), 51.88 (CH₂), 40.18 (CH₃), 28.78 (CH₃). The characterisation data was in agreement with that reported in the literature.^[18]

References

- [1] M. Jereb, *Tetrahedron* **2012**, *68*, 3861–3867.
- [2] P.-L. Wu, S.-Y. Peng, J. Magrath, *Synthesis* **1996**, *1996*, 249–252.
- [3] L. Hevesi, M. Dehon, R. Crutzen, A. Lazarescu-Grigore, *J. Org. Chem.* **1997**, *62*, 2011–2017.
- [4] R. Tello-Aburto, K. A. Kalstabakken, K. A. Volp, A. M. Harned, *Org. Biomol. Chem.* **2011**, *9*, 7849–59.
- [5] K. Tamao, H. Yao, Y. Tsutsumi, H. Abe, T. Hayashi, Y. Ito, *Tetrahedron Lett.* **1990**, *31*, 2925–2928.
- [6] J. E. M. Booker, A. Boto, G. H. Churchill, C. P. Green, M. Ling, G. Meek, J. Prabhakaran, D. Sinclair, A. J. Blake, G. Pattenden, *Org. Biomol. Chem.* **2006**, *4*, 4193.
- [7] S. Akai, T. Ikawa, S. Takayanagi, Y. Morikawa, S. Mohri, M. Tsubakiyama, M. Egi, Y. Wada, Y. Kita, *Angew. Chem. Int. Ed.* **2008**, *47*, 7673–6.
- [8] T. Ikawa, T. Nishiyama, T. Nosaki, A. Takagi, S. Akai, *Org. Lett.* **2011**, *13*, 1730–1733.
- [9] S. V. Sunthankar, H. Gilman, *J. Am. Chem. Soc.* **1950**, *72*, 4884–4887.
- [10] D. Peña, A. Cobas, D. Pérez, E. Guitián, *Synthesis* **2002**, 1454–1458.
- [11] A. T. Biju, F. Glorius, *Angew. Chem. Int. Ed.* **2010**, *122*, 9955–9958.
- [12] M. Dai, Z. Wang, S. J. Danishefsky, *Tetrahedron Lett.* **2008**, *49*, 6613–6616.
- [13] D. Peña, A. Cobas, D. Pérez, E. Guitián, *Synthesis* **2002**, *2002*, 1454–1458.
- [14] Y. Sumida, T. Kato, T. Hosoya, *Org. Lett.* **2013**, *15*, 2806–2809.
- [15] D. Peña, S. Escudero, D. Pérez, E. Guitián, L. Castedo, *Angew. Chem. Int. Ed.* **1998**, *37*, 2659–2661.
- [16] D. G. Pintori, M. F. Greaney, *Org. Lett.* **2009**, *12*, 168–171.
- [17] D. McAusland, S. Seo, D. G. Pintori, J. Finlayson, M. F. Greaney, *Org. Lett.* **2011**, *13*, 3667–9.
- [18] U. K. Tambar, B. M. Stoltz, *J. Am. Chem. Soc.* **2005**, *127*, 5340–1.

Spectroscopic Data

2-(Trimethylsilyl)phenol (7a):



4-Fluoro-2-(trimethylsilyl)phenol (7b):

F2 - Acquisition Parameters

Date... 20130622

Time 16.20

INSTRUM spect

PROBHD 5 mm CPDCH ^{13}C

PULPROG zg30

TD 65536

SOLVENT CDCl_3

NS 16

DS 2

SWH 12019.230 Hz

FIDRES 0.183399 Hz

AQ 2.7262976 sec

RG 32

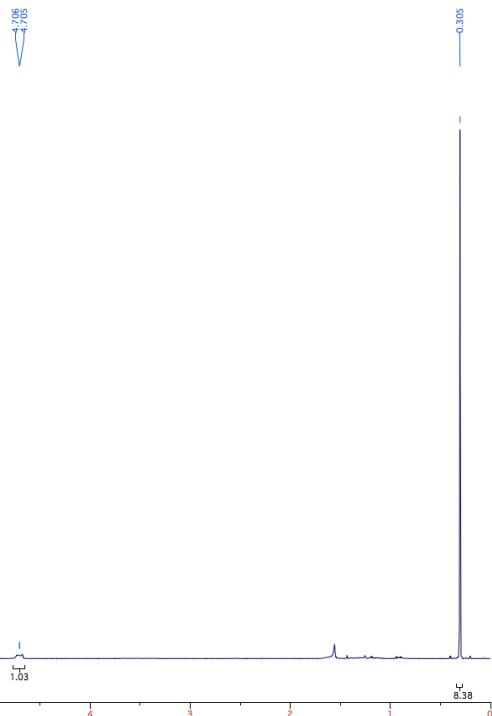
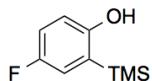
DW 41.600 usec

DE 16.39 usec

TE 295.0 K

D1 1.00000000 sec

TD0 1



F2 - Acquisition Parameters

Date... 20130622

Time 16.23

INSTRUM spect

PROBHD 5 mm CPDCH ^{13}C

PULPROG zgpg30

TD 65536

SOLVENT CDCl_3

NS 32

DS 4

SWH 36057.691 Hz

FIDRES 0.550197 Hz

AQ 0.9097659 sec

RG 362

DW 13.867 usec

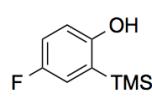
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TE 295.0 K

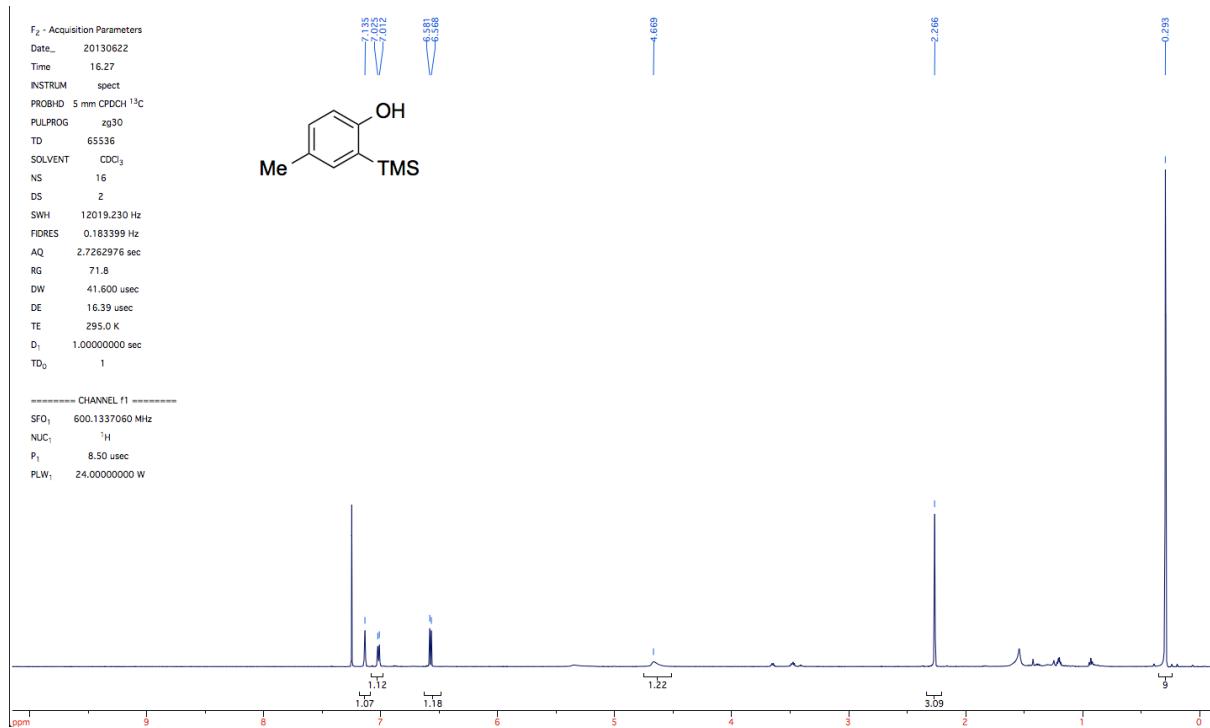
D1 2.00000000 sec

D11 0.03000000 sec

TD0 1



4-Methyl-2-(trimethylsilyl)phenol (7c):



4-Chloro-2-(trimethylsilyl)phenol (7d):

F2 - Acquisition Parameters

Date_ 20130702

Time 15.12

INSTRUM spect

PROBHD 5 mm CPDCH¹³C

PULPROG zg30

TD 65536

SOLVENT CDCl₃

NS 16

DS 2

SWH 12019.230 Hz

FIDRES 0.183399 Hz

AQ 2.7262976 sec

RG 32

DW 41.600 usec

DE 16.39 usec

TE 295.0 K

D1 1.00000000 sec

TD0 1

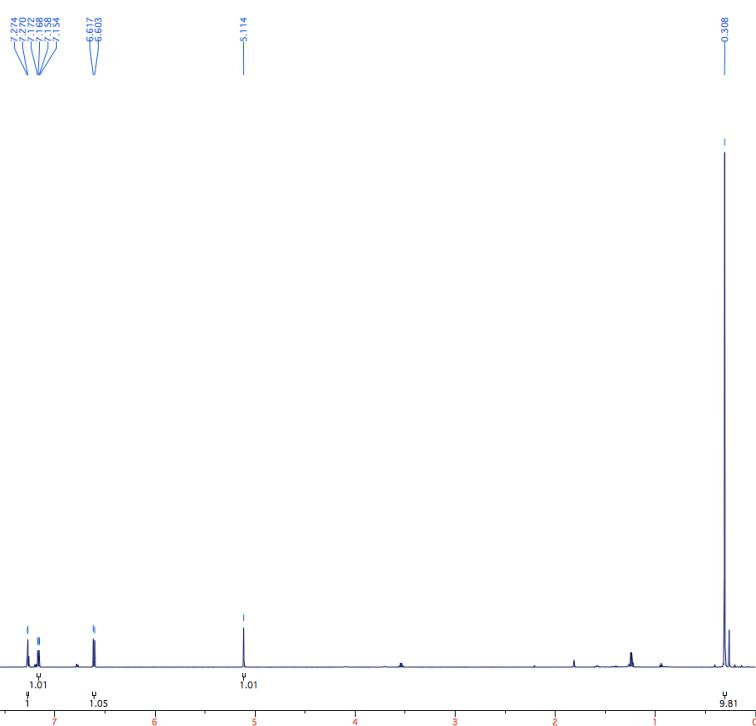
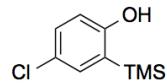
===== CHANNEL f1 =====

SFO1 600.1337060 MHz

NUC1 ¹H

P1 8.50 usec

PLW1 24.00000000 W



F2 - Acquisition Parameters

Date_ 20130703

Time 12.25

INSTRUM DPX₅₀₀

PROBHD 5 mm DUL ¹³C-1

PULPROG zgpg30

TD 65536

SOLVENT CDCl₃

NS 64

DS 2

SWH 17857.143 Hz

FIDRES 0.272478 Hz

AQ 1.8350580 sec

RG 16384

DW 28.000 usec

DE 6.00 usec

TE 300.0 K

D1 2.00000000 sec

d11 0.03000000 sec

DELTA 1.89999998 sec

TD0 1

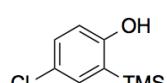
===== CHANNEL f1 =====

NUC1 ¹³C

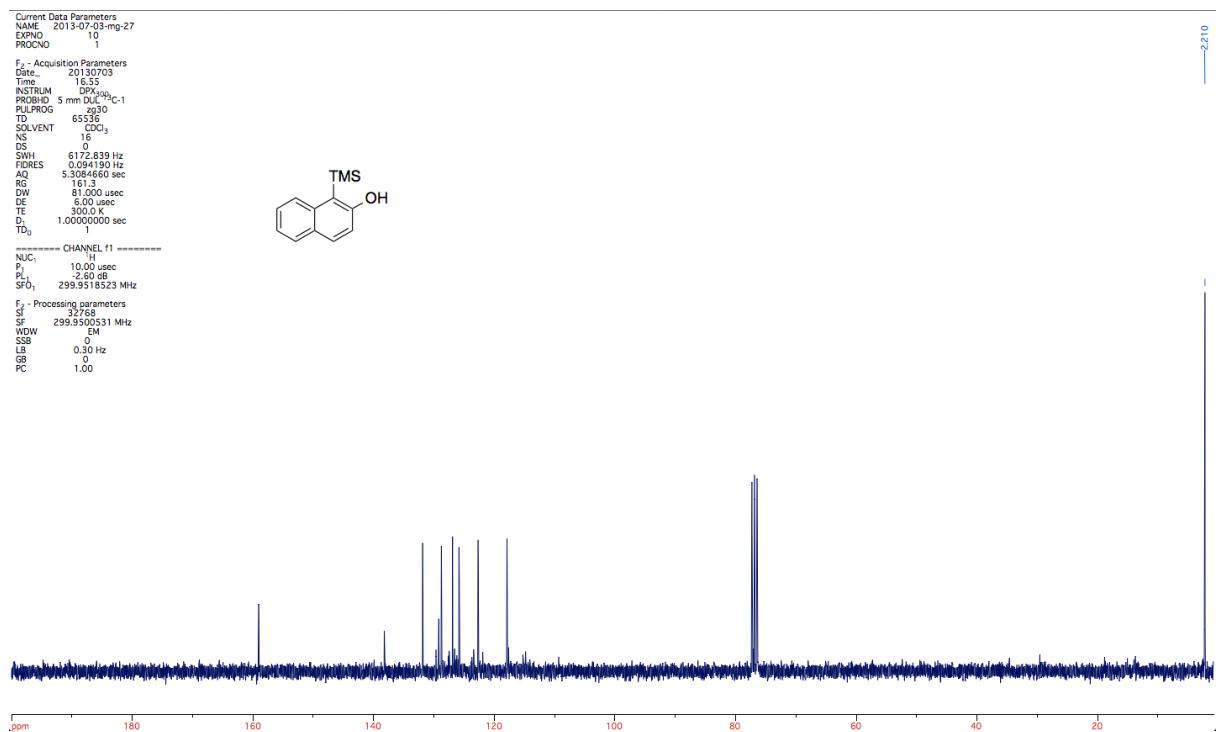
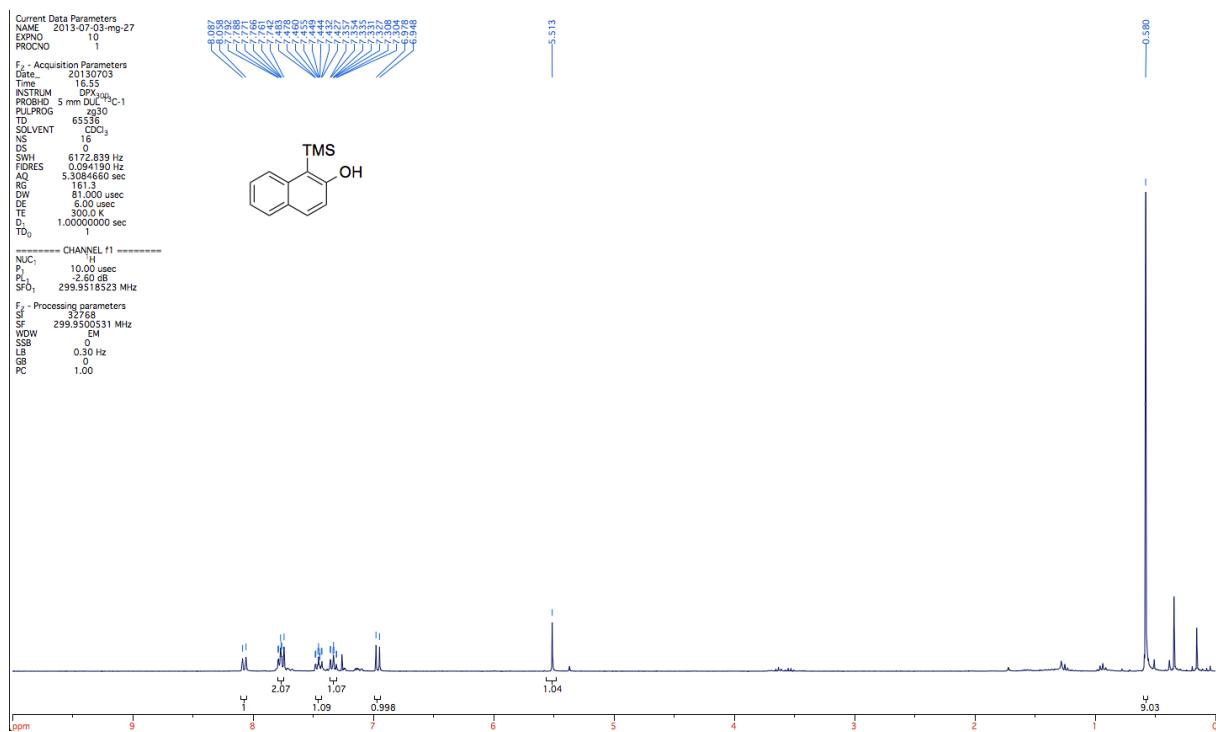
P1 10.00 usec

PL1 -1.20 dB

SFO1 75.4300300 MHz

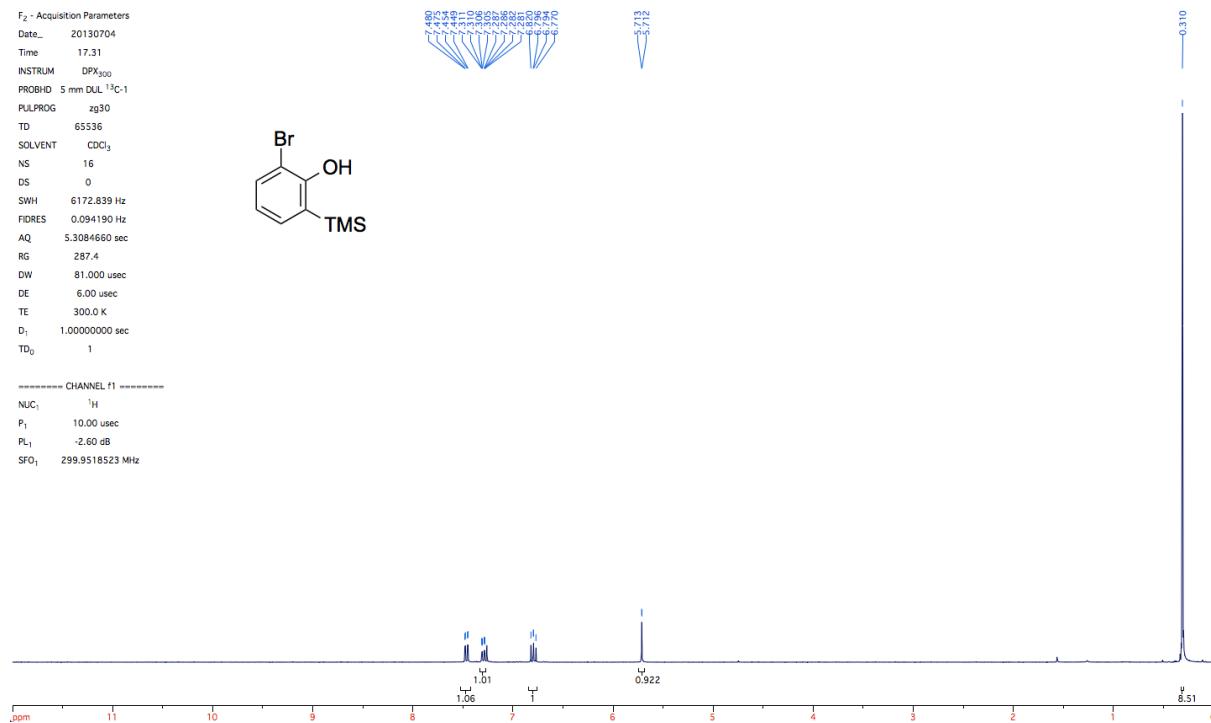
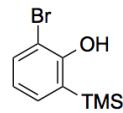


1-(Trimethylsilyl)naphthalen-2-ol (7e):

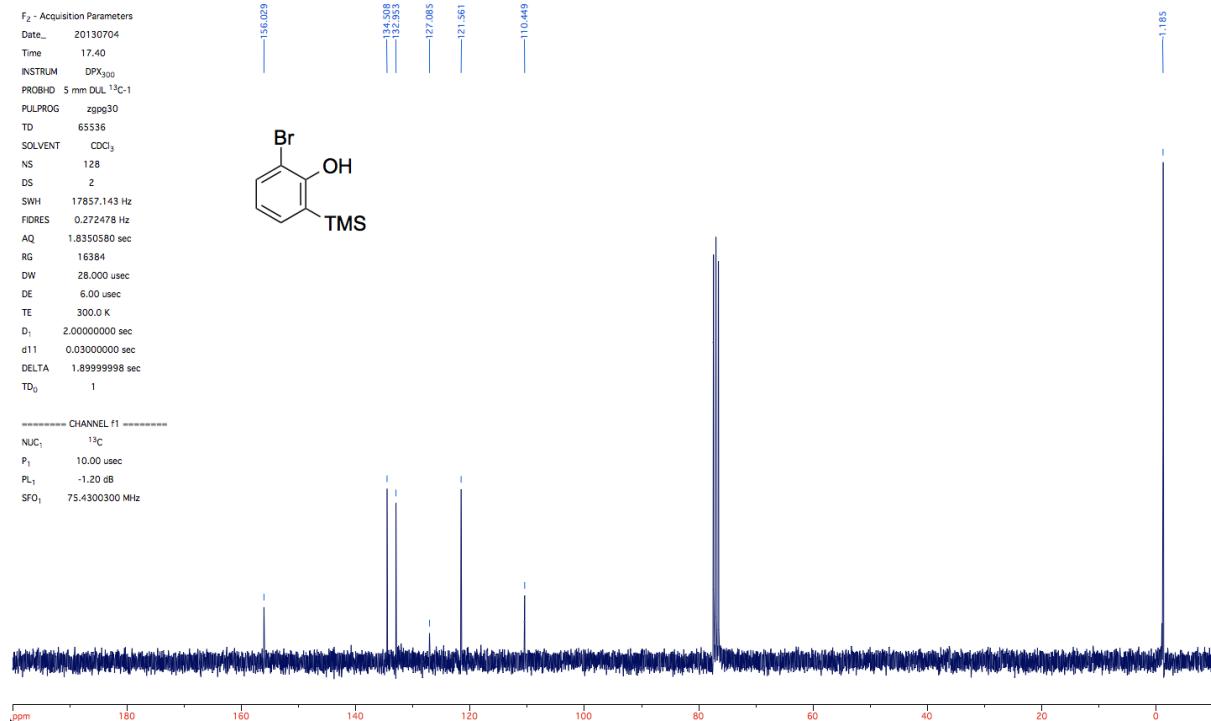
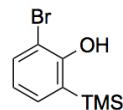


2-Bromo-6-(trimethylsilyl)phenol (7f):

F2 - Acquisition Parameters
 Date 20130704
 Time 17.31
 INSTRUM DPX₅₀₀
 PROBID 5 mm DUL 13-C1
 PULPROG zg30
 TD 65536
 SOLVENT CDCl₃
 NS 16
 DS 0
 SWH 6172.839 Hz
 FIDRES 0.094190 Hz
 AQ 5.3084660 sec
 RG 287.4
 DW 81.000 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.0000000 sec
 DT₀ 1



F2 - Acquisition Parameters	
Date_	20130704
Time	17.40
INSTRUM	DPX300
PROBHD	5 mm DUL-13C-1
PULPROG	zgpp30
TD	65536
SOLVENT	CDCl3
NS	128
DS	2
SWH	17857.143 Hz
FIRES	0.272748 Hz
AQ	1.8350580 sec
RG	16384
DW	28.000 usec
DE	6.00 usec
TE	300.0 K
D1	2.00000000 sec
d11	0.03000000 sec
DELTA	1.8999998 sec
TDn	1



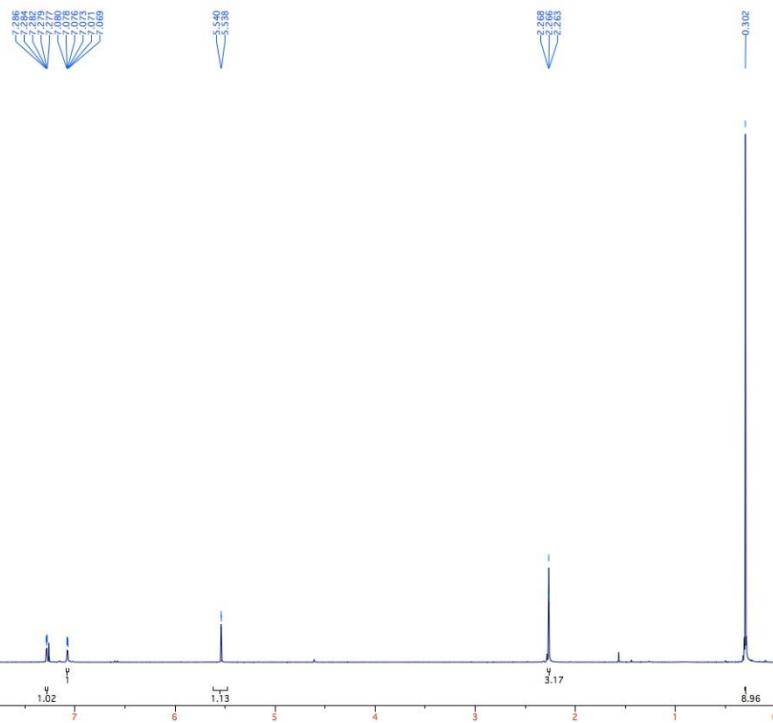
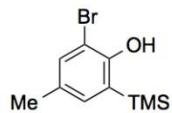
(2,6-Dibromo-4-methylphenoxy)trimethylsilane (7g):

F₂ - Acquisition Parameters

Date... 20130704
 Time 17.46
 INSTRUM DPX₃₀₀
 PROBHD 5 mm DUL ¹³C-1
 PULPROG zg30
 TD 65536
 SOLVENT CDCl₃
 NS 16
 DS 0
 SWH 6172.839 Hz
 FIDRES 0.094190 Hz
 AQ 5.3084660 sec
 RG 256
 DW 81.000 usec
 DE 6.00 usec
 TE 300.0 K
 D₁ 1.0000000 sec
 TD₀ 1

----- CHANNEL F1 -----

NUC₁ ¹H
 P₁ 10.00 usec
 PL₁ -2.60 dB
 SFO₁ 299.9518523 MHz

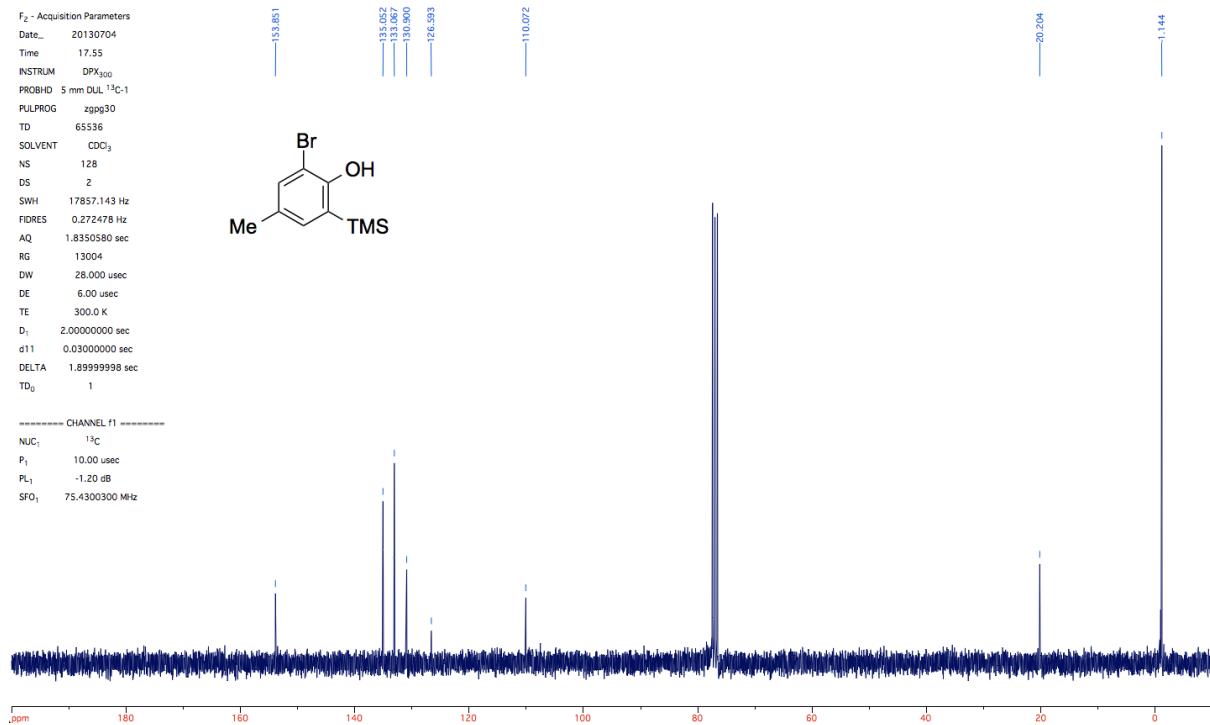
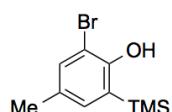


F₂ - Acquisition Parameters

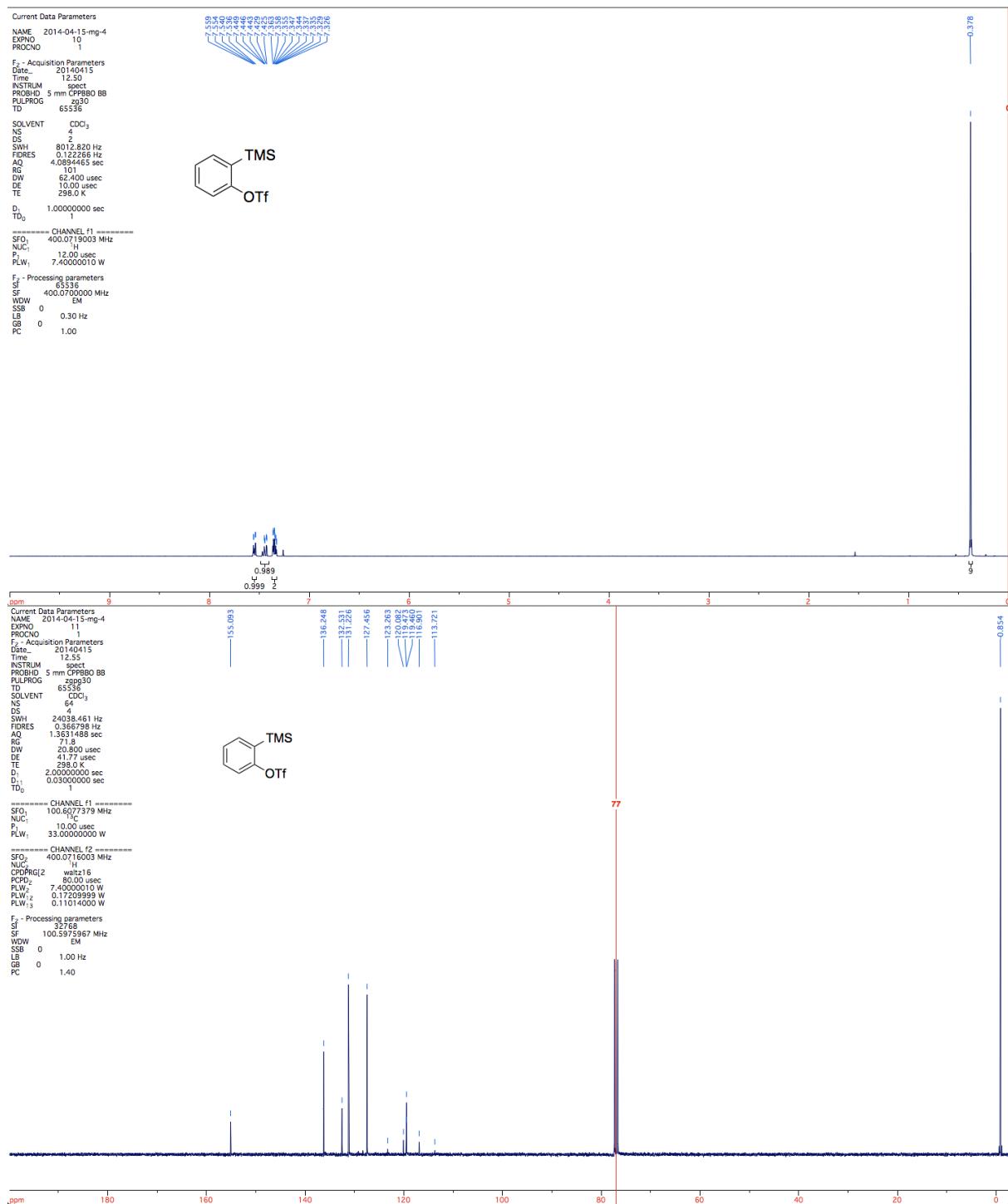
Date... 20130704
 Time 17.55
 INSTRUM DPX₃₀₀
 PROBHD 5 mm DUL ¹³C-1
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl₃
 NS 128
 DS 2
 SWH 17857.143 Hz
 FIDRES 0.272478 Hz
 AQ 1.8350580 sec
 RG 13004
 DW 28.000 usec
 DE 6.00 usec
 TE 300.0 K
 D₁ 2.0000000 sec
 d11 0.03000000 sec
 DELTA 1.8999998 sec
 TD₀ 1

----- CHANNEL F1 -----

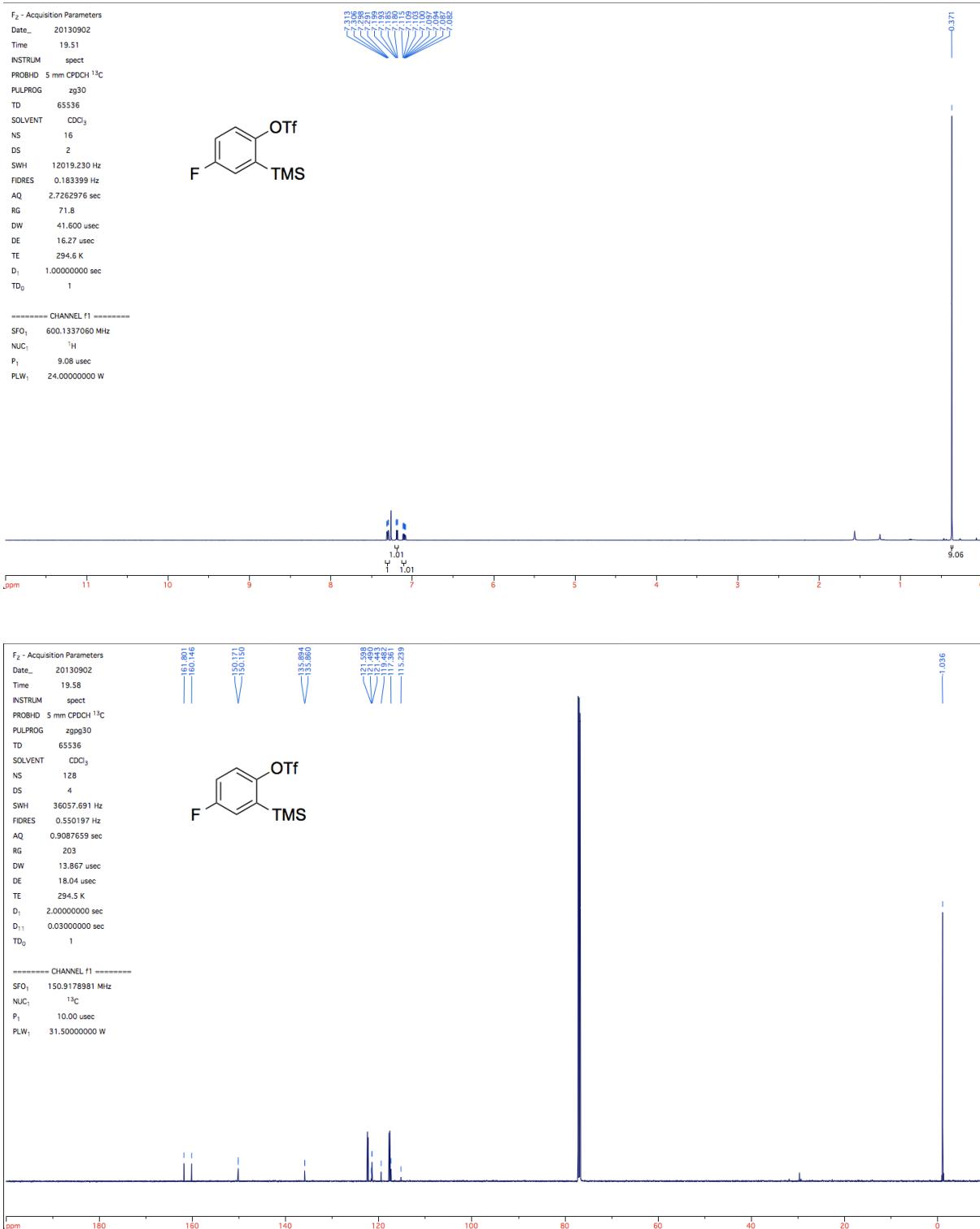
NUC₁ ¹³C
 P₁ 10.00 usec
 PL₁ -1.20 dB
 SFO₁ 75.4300300 MHz

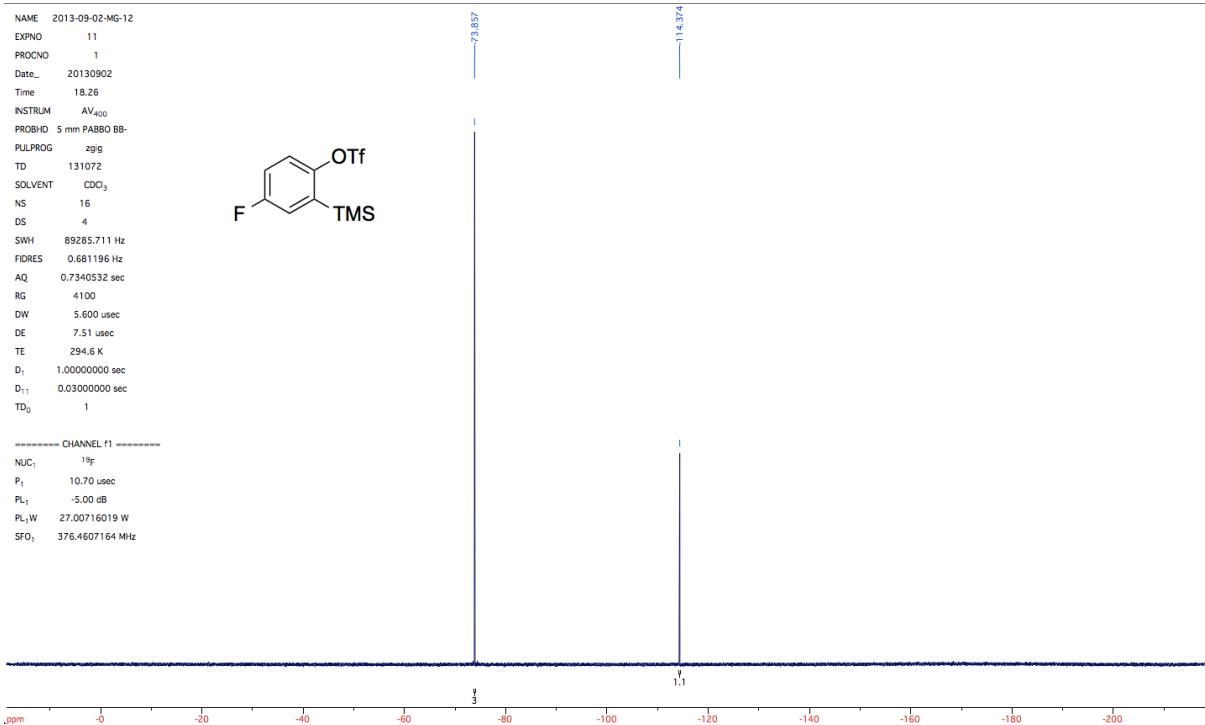


2-(Trimethylsilyl)phenyl trifluoromethanesulfonate (1a):

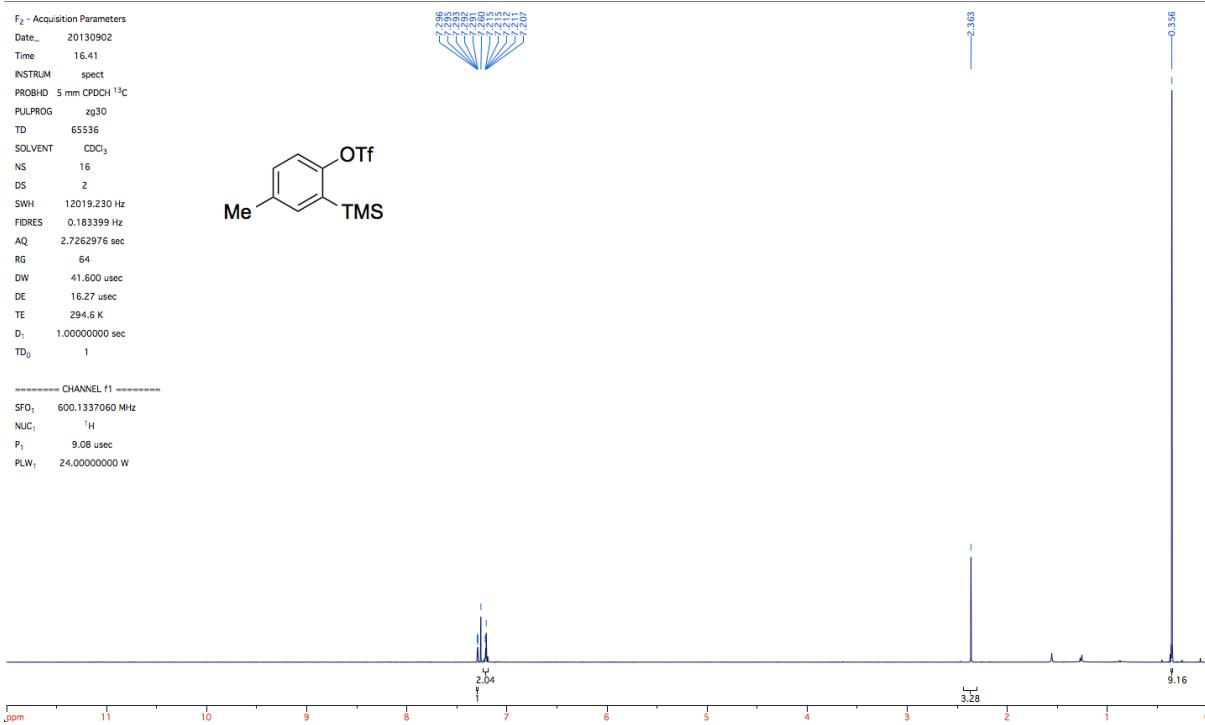


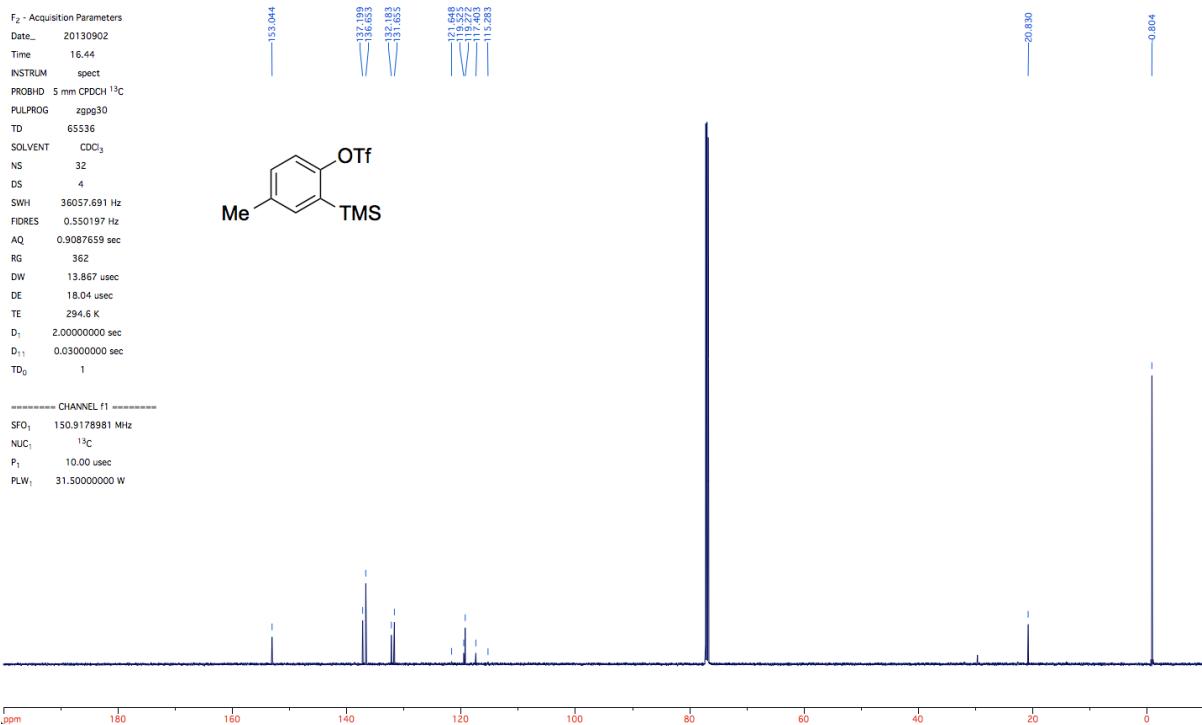
4-Fluoro-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (1b):



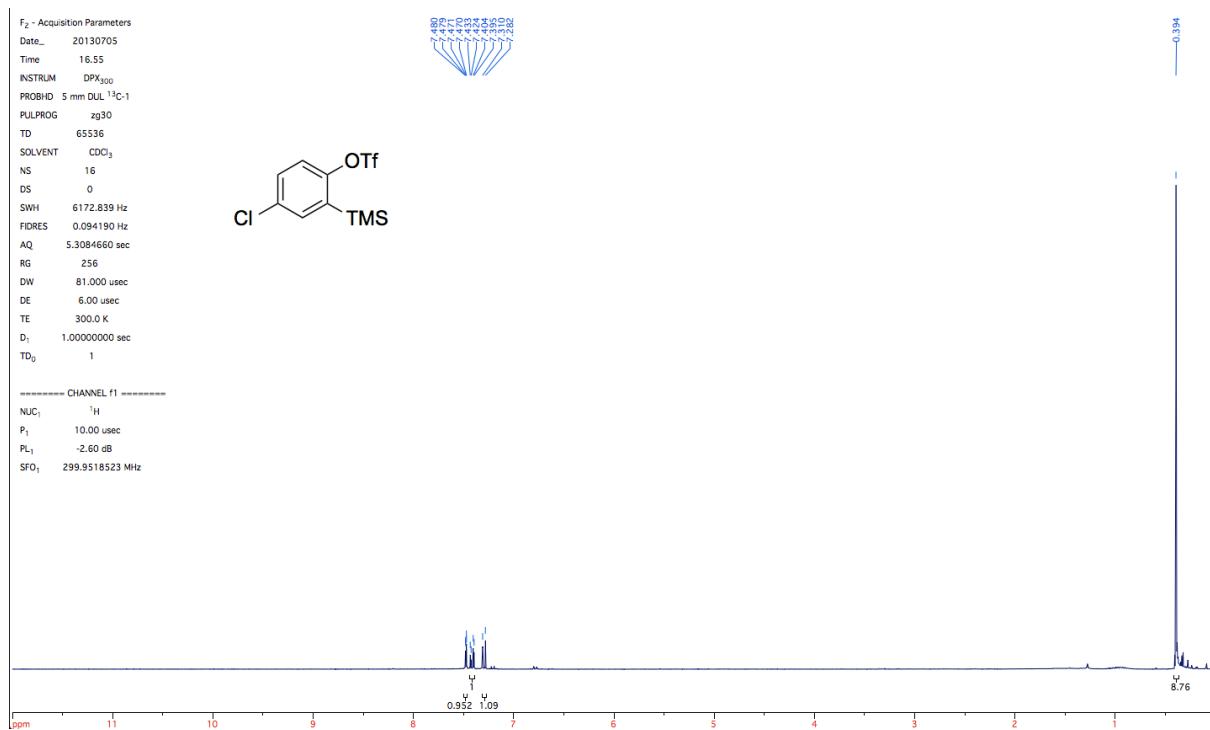


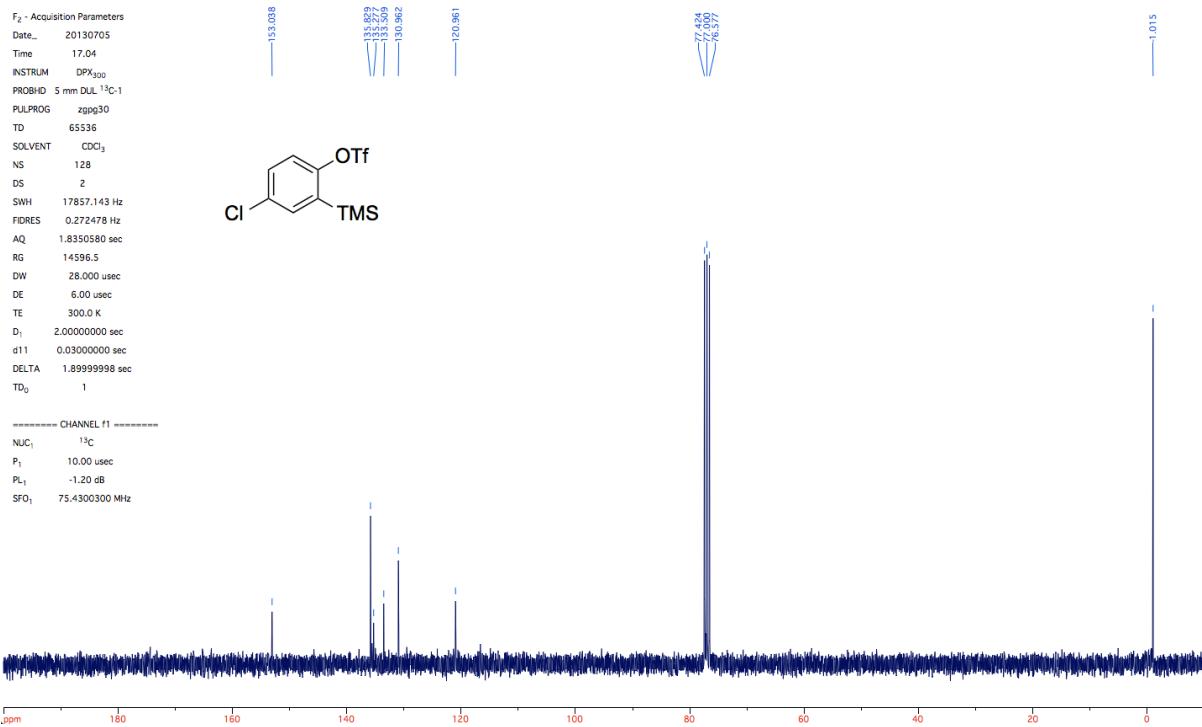
4-Methyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (1c):



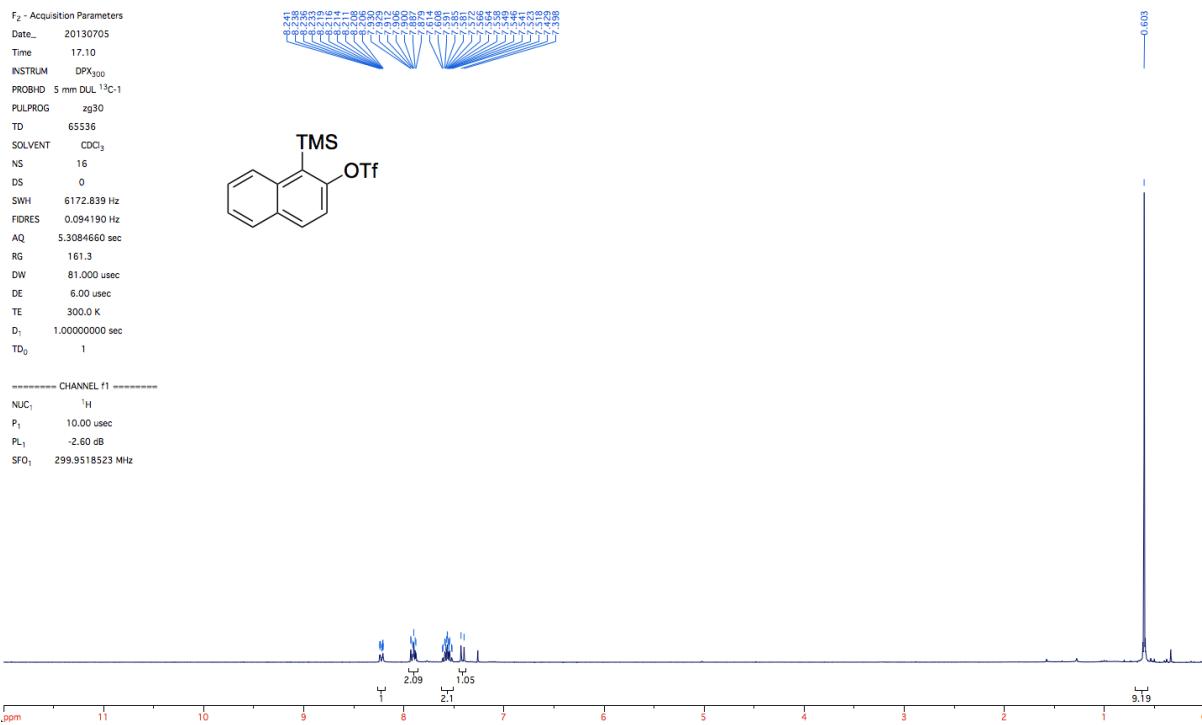


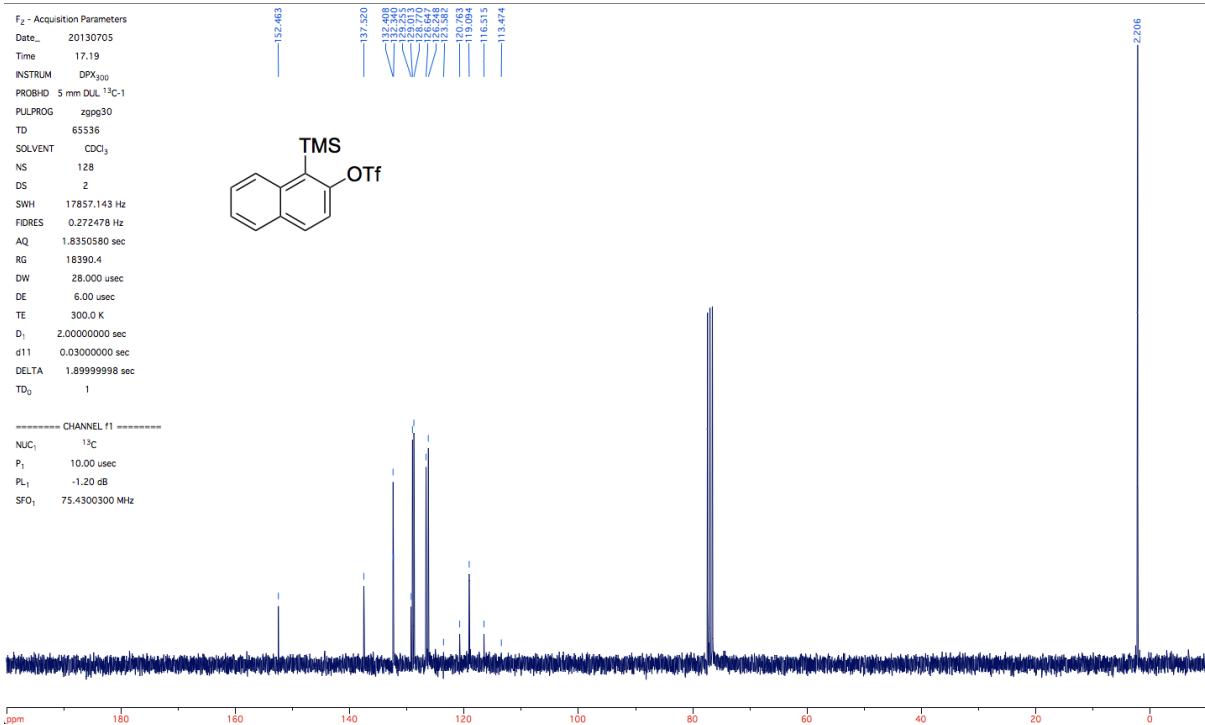
4-Chloro-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (1d):



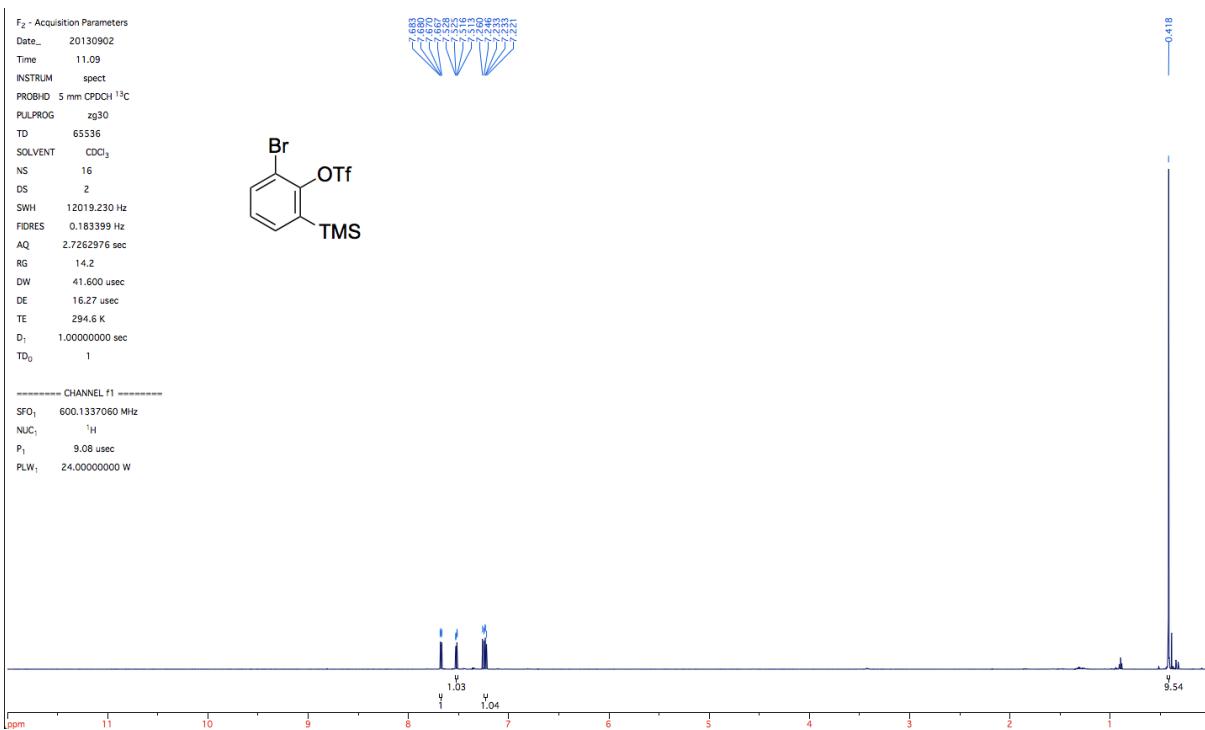


1-(Trimethylsilyl)naphthalen-2-yl trifluoromethanesulfonate (1e):



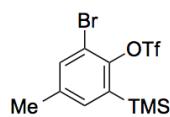


2-Bromo-6-(trimethylsilyl)phenyl trifluoromethanesulfonate (1f):

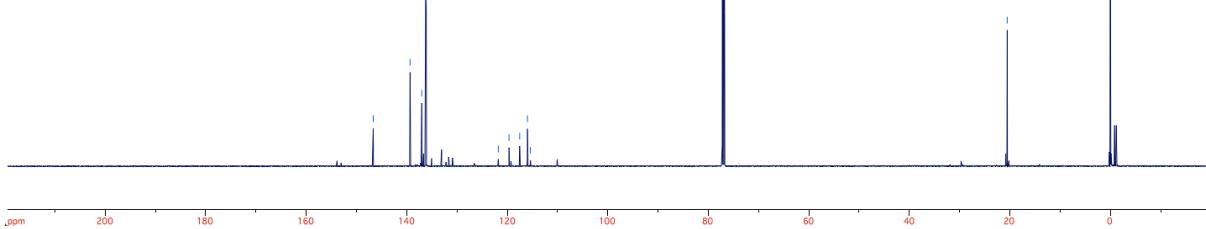


F2 - Acquisition Parameters

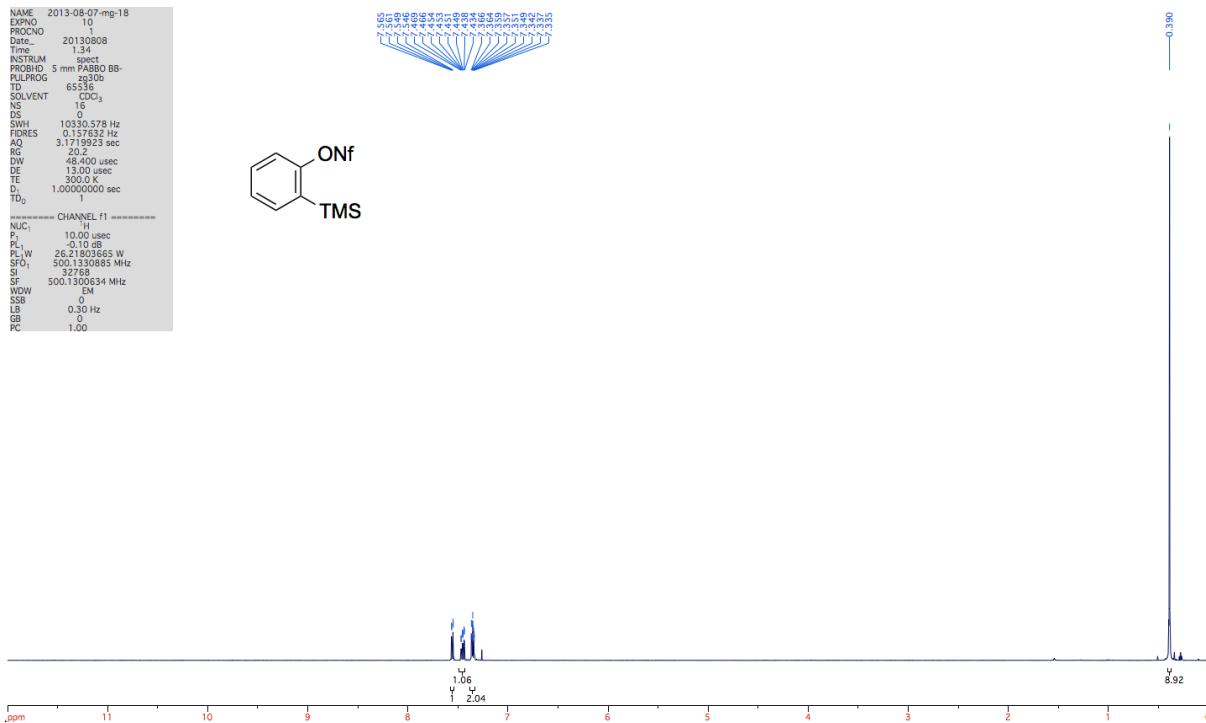
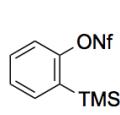
Date_ 20130902
 Time 11:05
 INSTRUM spect
 PROBHD 5 mm CPDCH ^{13}C
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl_3
 NS 32
 DS 4
 SWH 36057.691 Hz
 FIDRES 0.550197 Hz
 AQ 0.9087659 sec
 RG 322
 DW 13.867 usec
 DE 18.04 usec
 TE 294.6 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1



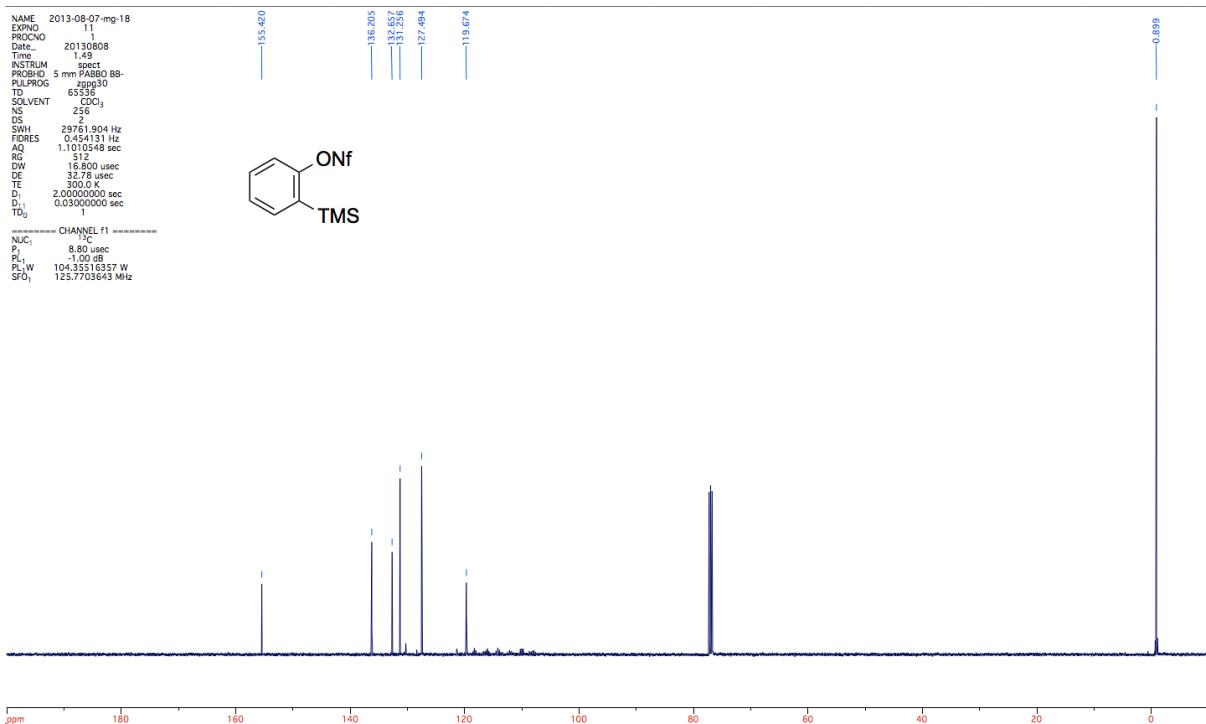
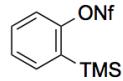
----- CHANNEL f1 -----
 SFO1 150.9178981 MHz
 NUC1 ^{13}C
 P1 10.00 usec
 PLW1 31.5000000 W

**2-(Trimethylsilyl)phenyl 1,1,2,2,3,3,4,4,4-nona-fluorobutane-1-sulfonate (8a):**

NAME 2013-08-07-mg-18
 EXPNO 10
 PROCN0 1
 Date_ 20130808
 Time 10:44
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl_3
 NS 16
 DS 0
 SWH 1035.573 Hz
 FIDRES 0.157532 Hz
 AQ 3.1719923 sec
 RG 20
 DW 48,400 usec
 DE 13.00 usec
 TE 300.0 K
 D1 1.0000000 sec
 TD0 1



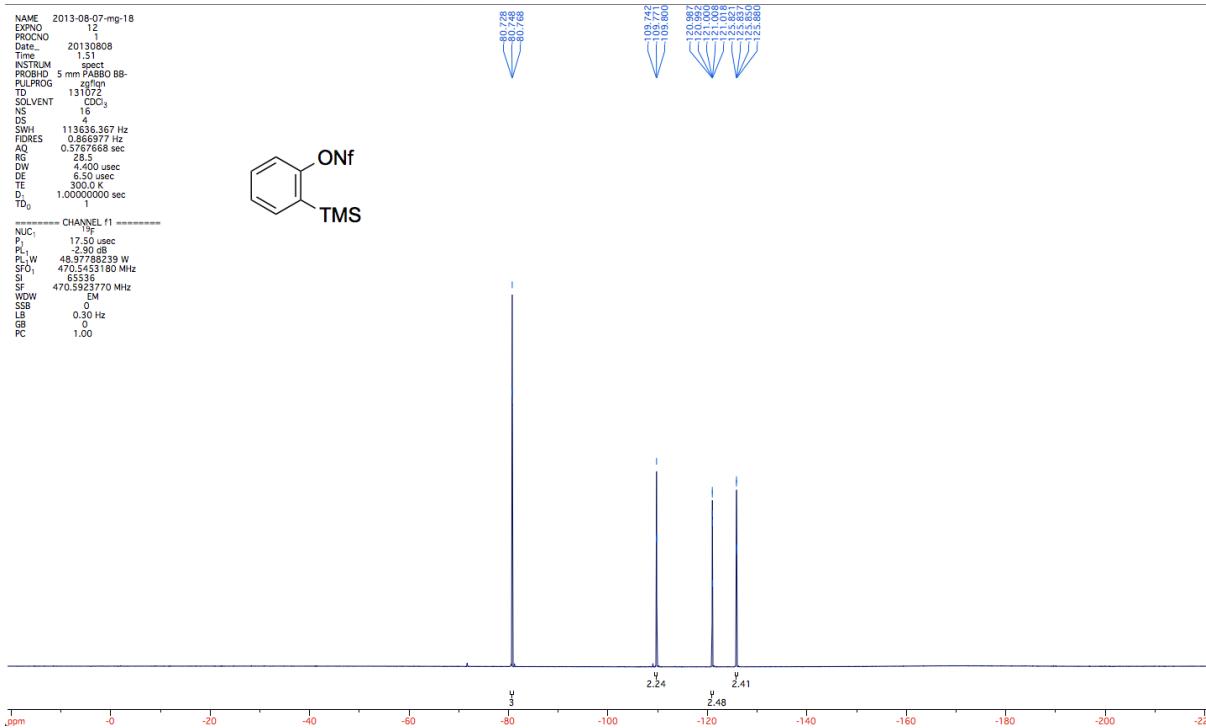
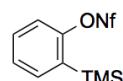
NAME	2013-08-07-mg-18
EXPNO	11
PROCNO	
Time	20130808
INSTRUM	spec
PROBHD	5 mm PABBO BB
ULPROM	zgng30
TD	65536
SOLVENT	ODCI ₃
NS	256
DS	2
SWH	29761.904 Hz
FIDRES	0.454131 Hz
AQ	1.1010548 sec
RG	
DW	18.000 usec
DE	32.78 usec
TE	300.0 K
D1	2.00000000 sec
D1 ₁	0.03000000 sec
TD ₀	1



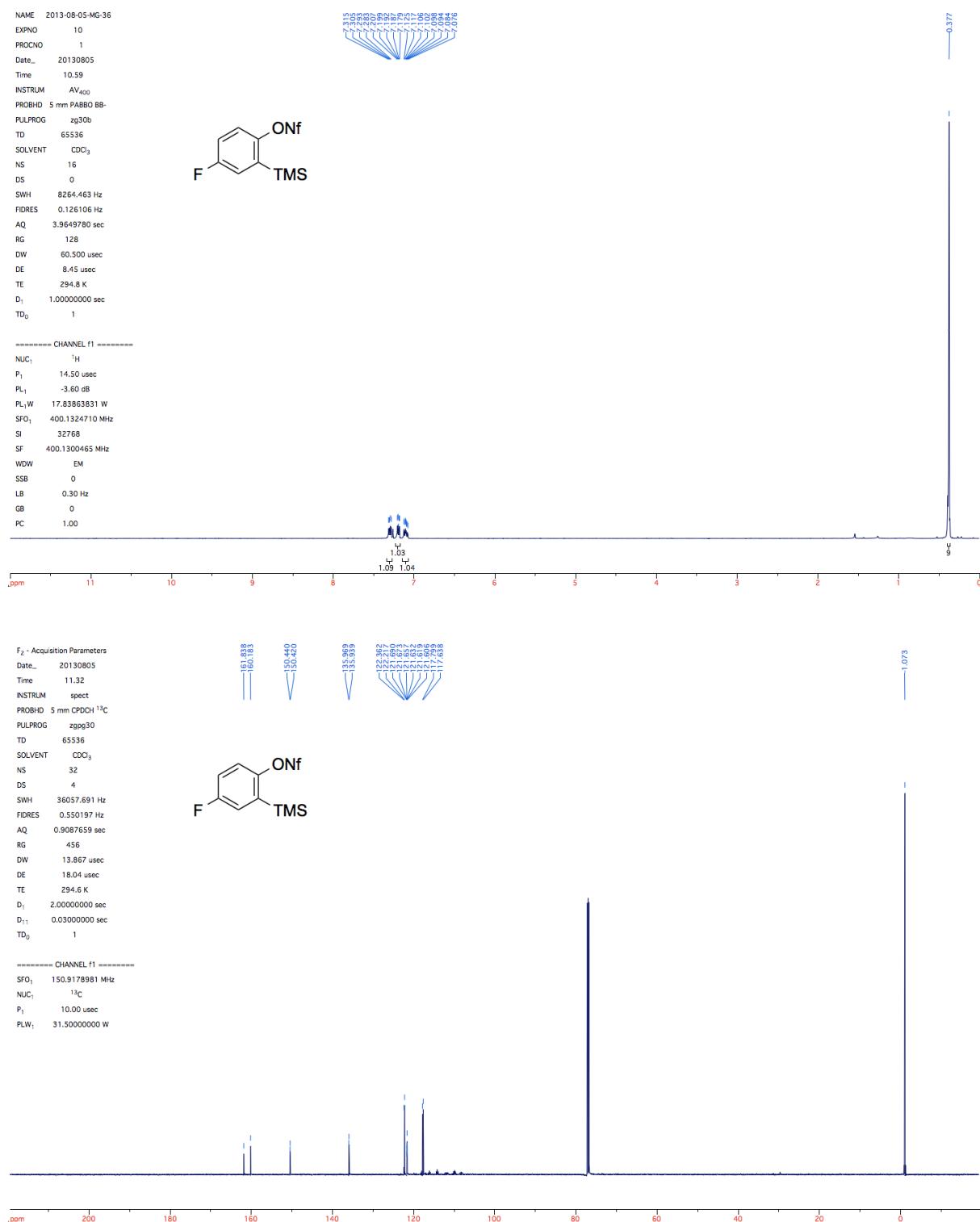
```

NAME 2013-08-07-mg-1
EXPNO 12
PROCNO 1
Date_ 20130808
Time 1.51
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zqflgr3
TD 131072
SOLVENT CDCl3
NS 16
DS 4
SWH 11363.367 Hz
FIDRES 0.866977 Hz
AQ 0.5767686 sec
RG 256
DW 4.400 usec
DE 6.50 usec
TE 3000.0 K
D1 1.0000000 sec
D2 1
DT0 1

```



4-Fluoro-2-(trimethylsilyl)phenyl 1,1,2,2,3,3,4,4,4-nona-fluorobutane-1-sulfonate (8b):



NAME 2013-08-05-MG-36

EXPNO 12

PROCNO 1

Date.. 20130805

Time 11.08

INSTRUM AV400

PROBHD 5 mm PABBO BB-

PULPROG zg3g

TD 131072

SOLVENT CDCl₃

NS 16

DS 4

SWH 89285.711 Hz

FIDRES 0.681196 Hz

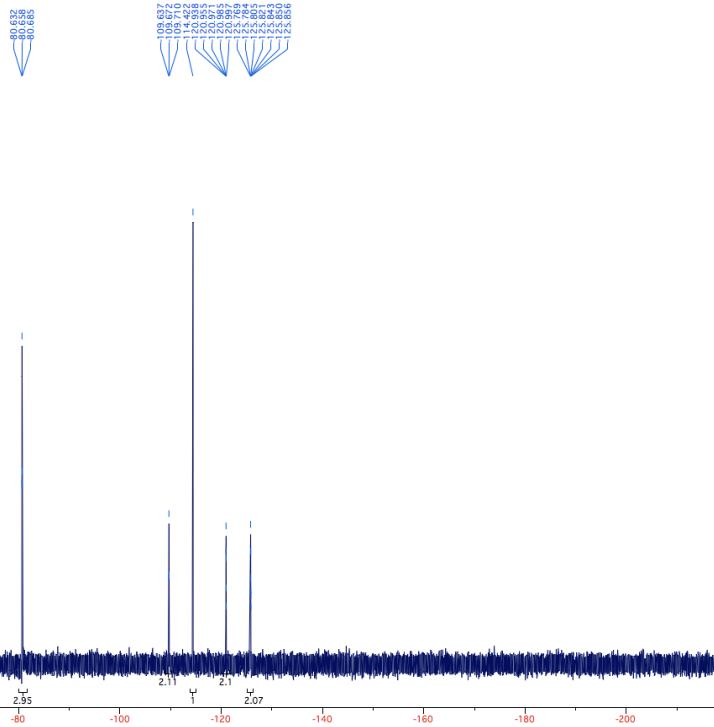
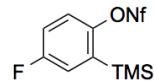
AQ 0.7340532 sec

RG 4100

DW 5.600 usec

DE 7.51 usec

TE 295.2 K

D₁ 1.00000000 secD₁₁ 0.03000000 secTD₀ 1

4-Methyl-2-(trimethylsilyl)phenyl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate (8c):

NAME 2013-08-02-MG-3

EXPNO 10

PROCNO 1

Date.. 20130802

Time 17.54

INSTRUM AV400

PROBHD 5 mm PABBO BB-

PULPROG zg30b

TD 65536

SOLVENT CDCl₃

NS 16

DS 0

SWH 8264.463 Hz

FIDRES 0.126106 Hz

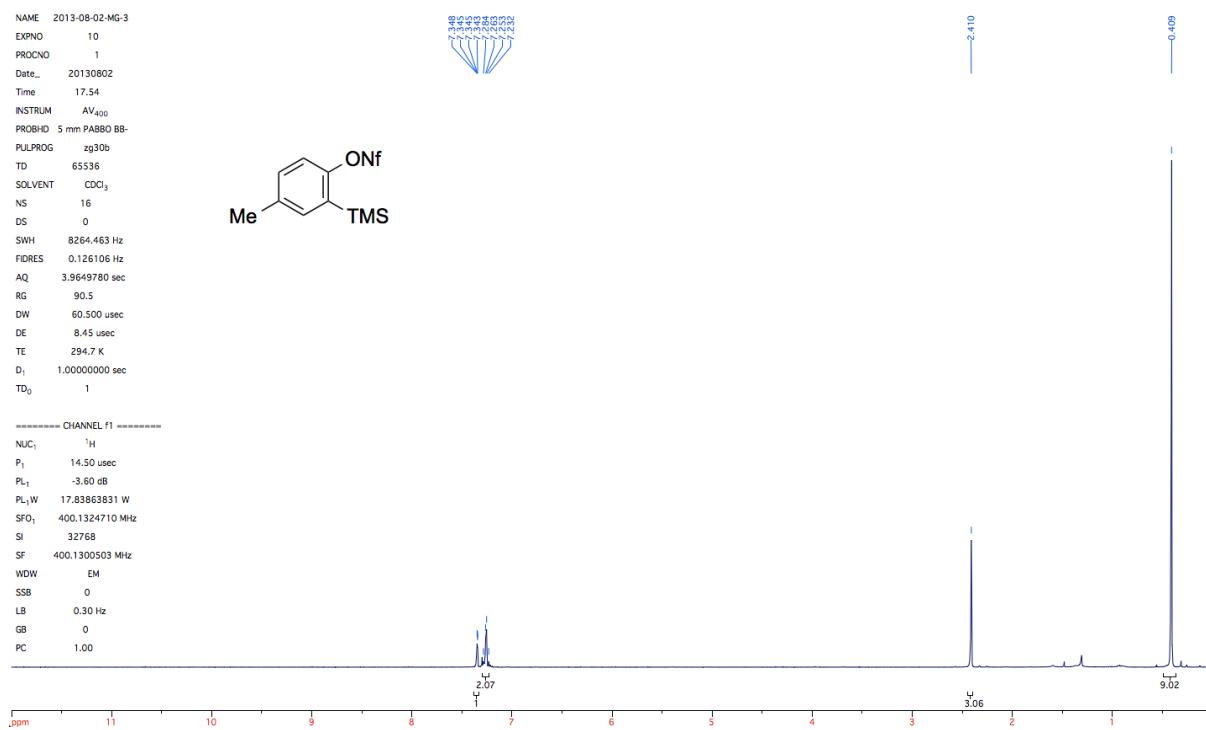
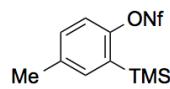
AQ 3.9649780 sec

RG 90.5

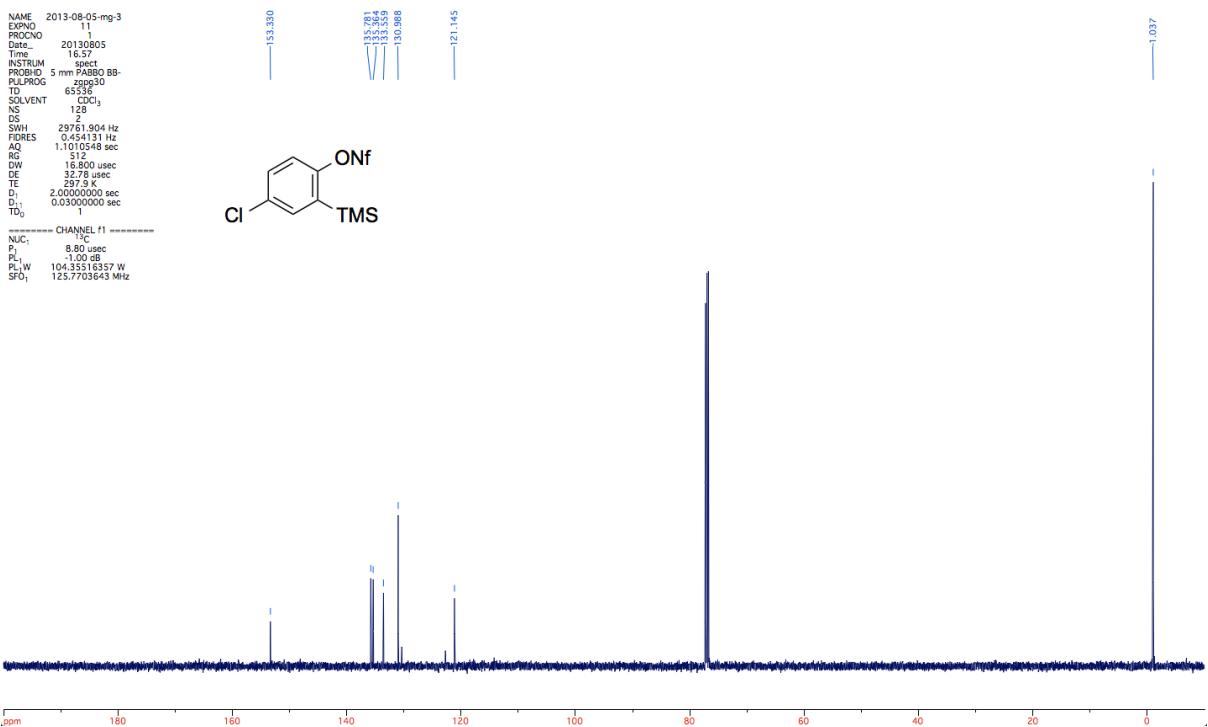
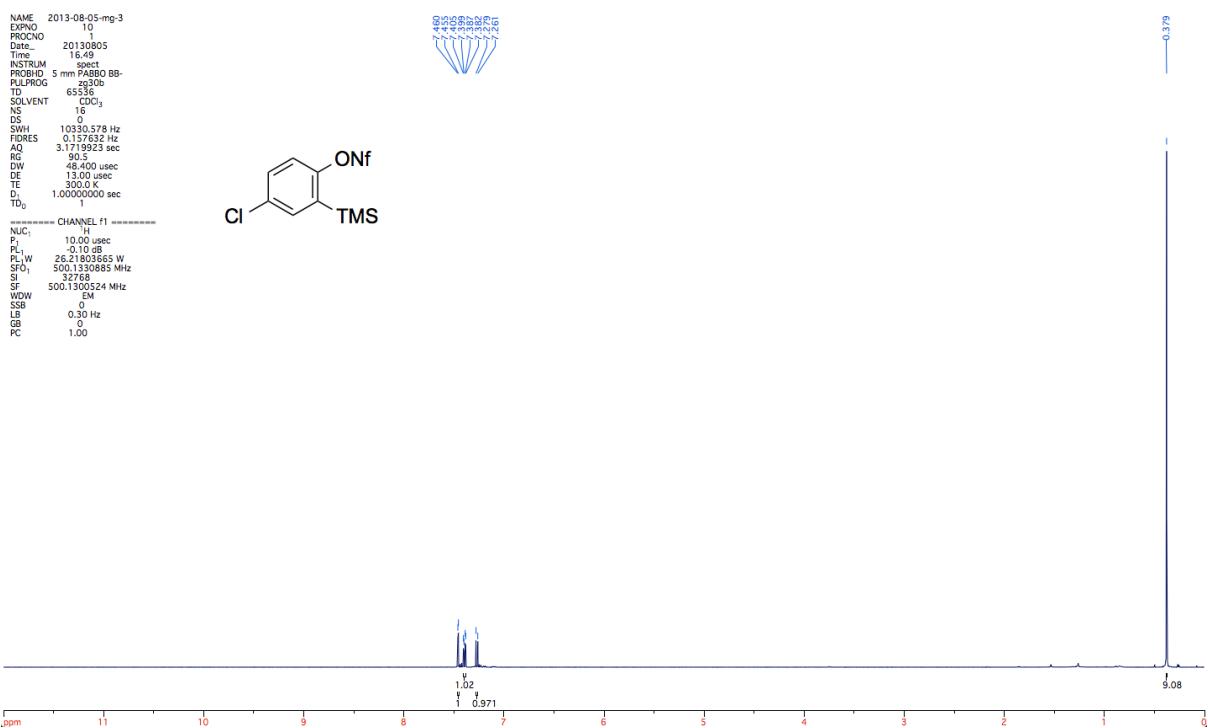
DW 60.500 usec

DE 8.45 usec

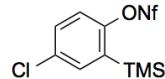
TE 294.7 K

D₁ 1.00000000 secTD₀ 1

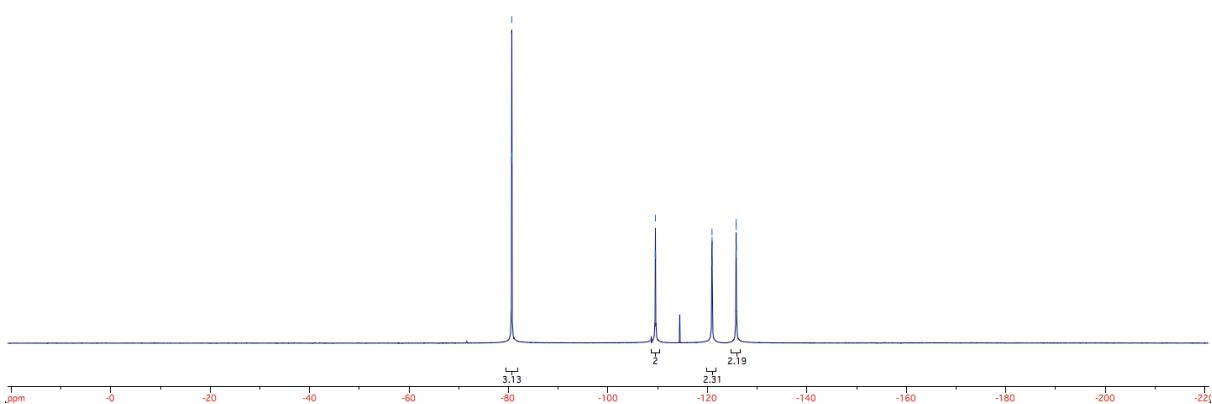
4-Chloro-2-(trimethylsilyl)phenyl 1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonate (8d):

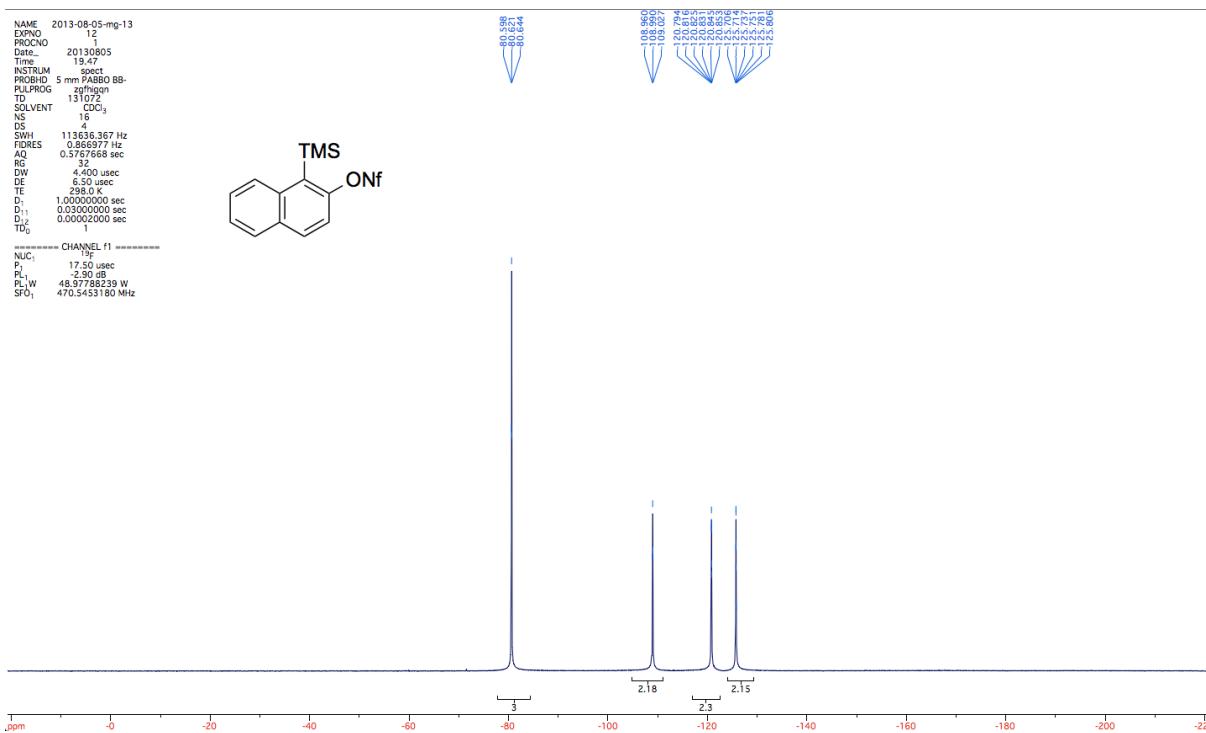
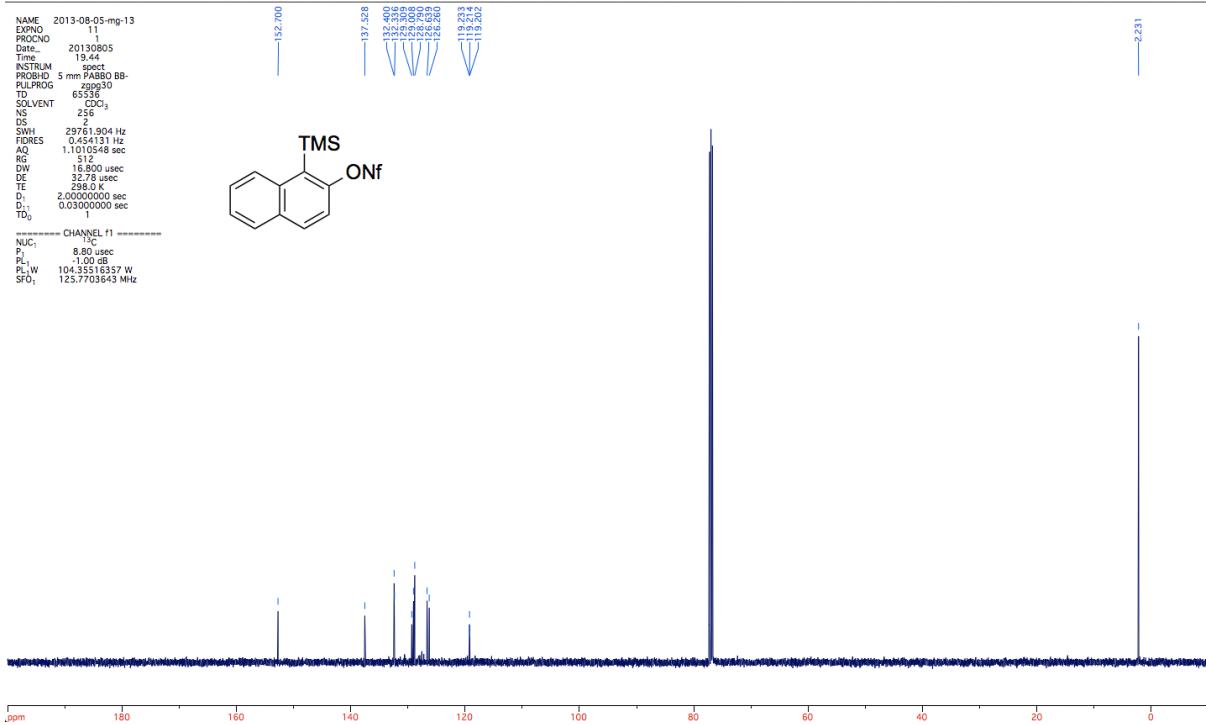


NAME 2013-08-05-mg-3
 EXPNO 12
 PROCN0 1
 Date_ 20130805
 Time 11:11
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zg3d90deg90
 TD 131072
 SOLVENT CDCl₃
 NS 1
 DS 4
 SWH 113636.367 Hz
 FIDRES 0.0102412 Hz
 AQ 0.5767688 sec
 RG 32
 DW 4000 usec
 DE 6.50 usec
 TE 300.0 K
 D1 1.0000000 sec
 D11 0.03000000 sec
 D12 0.00002000 sec
 TD0 1

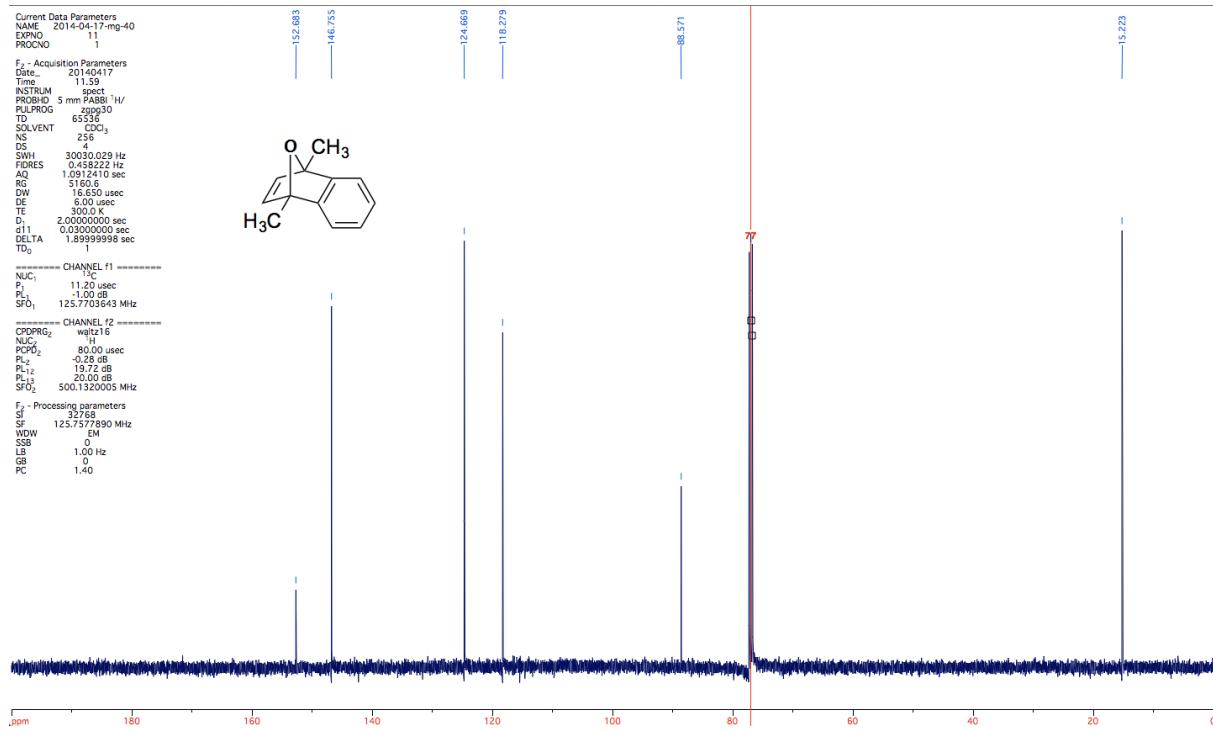
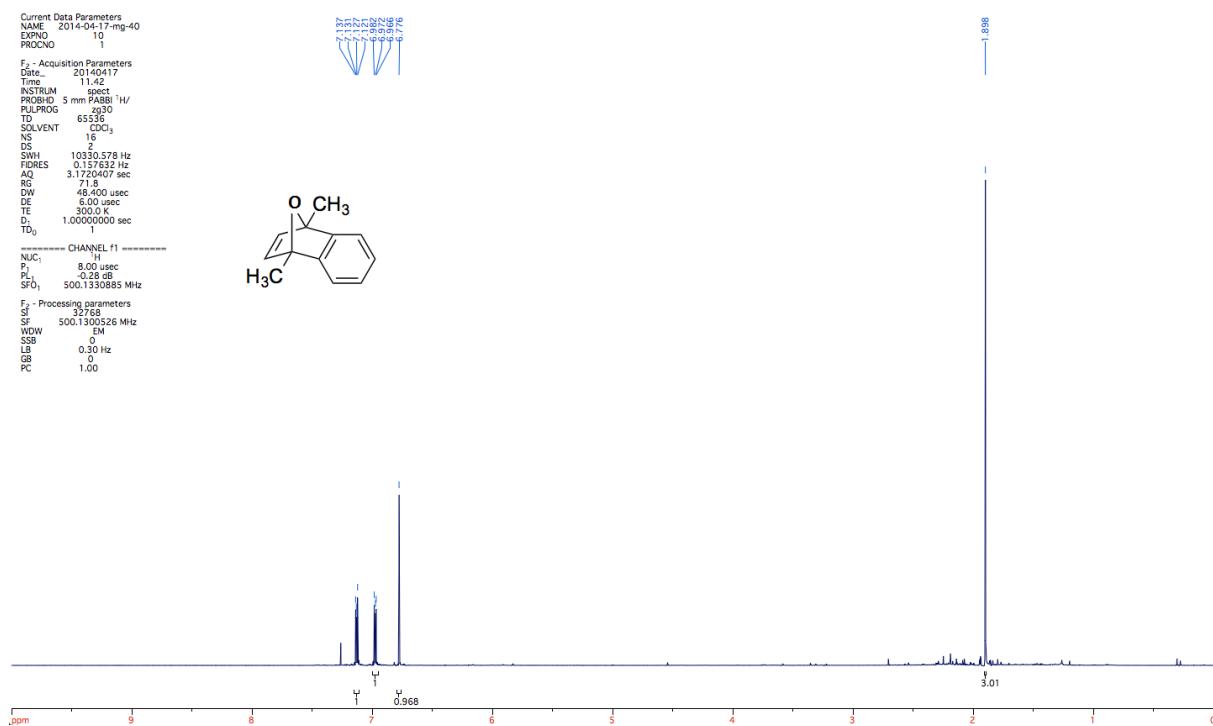


----- CHANNEL f1 -----
 NUC: ¹H
 P1 17.50 usec
 PL -9.90 dB
 PL_W 48.3203639 W
 SF_U 470.5453180 MHz

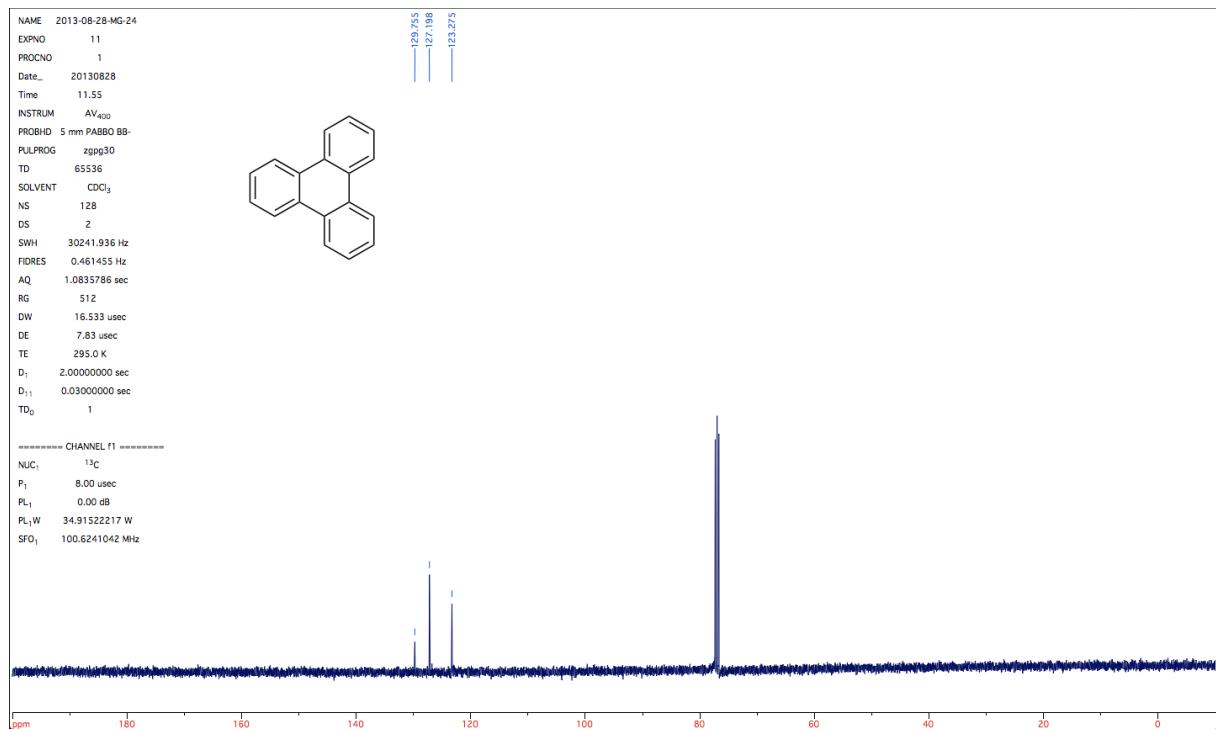
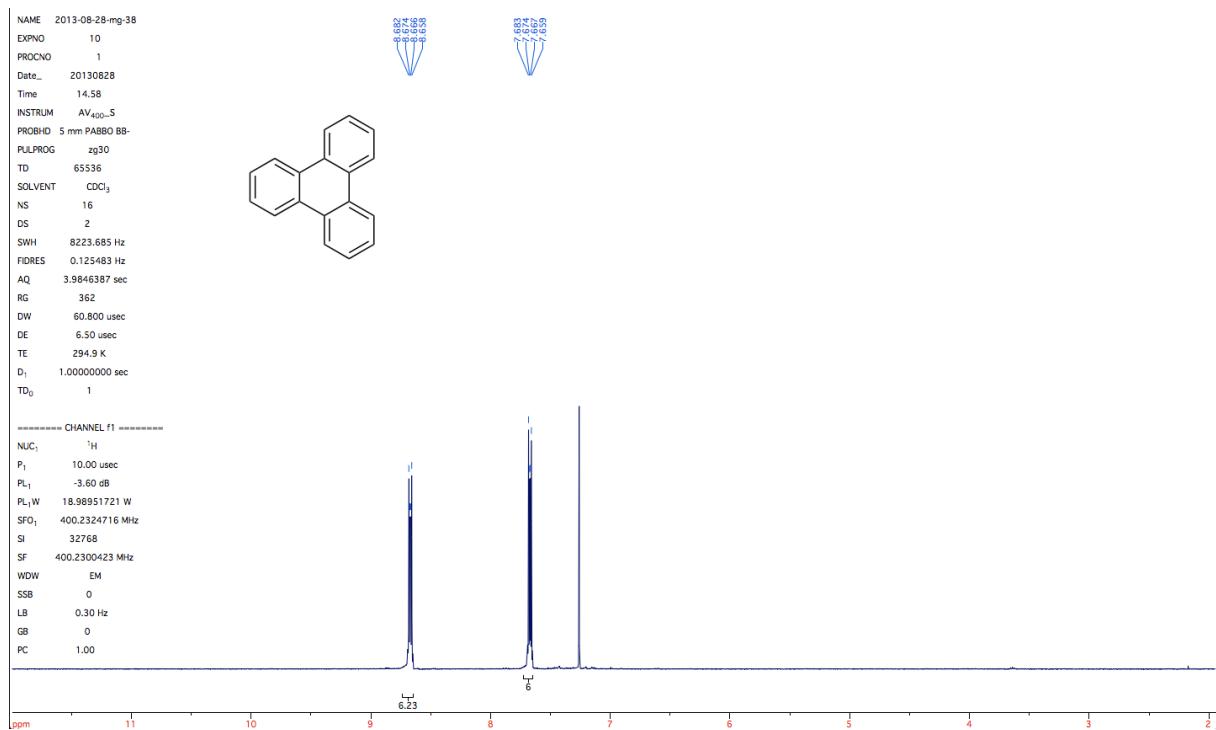




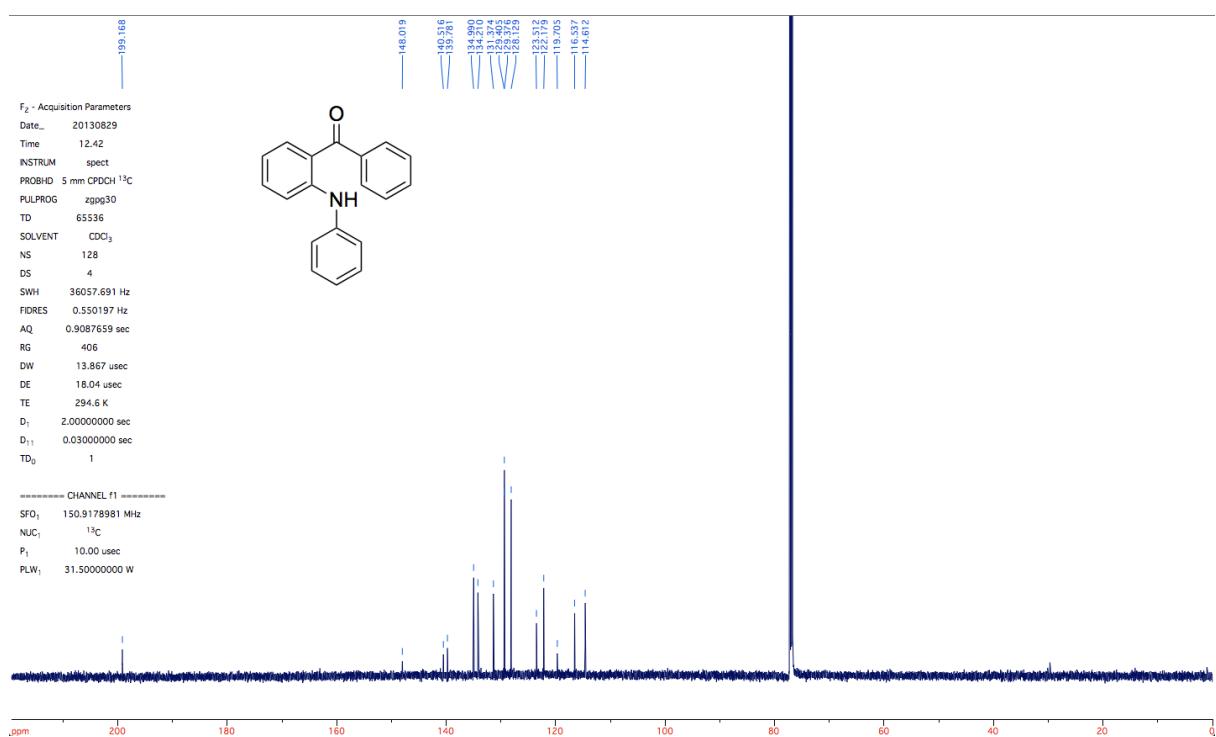
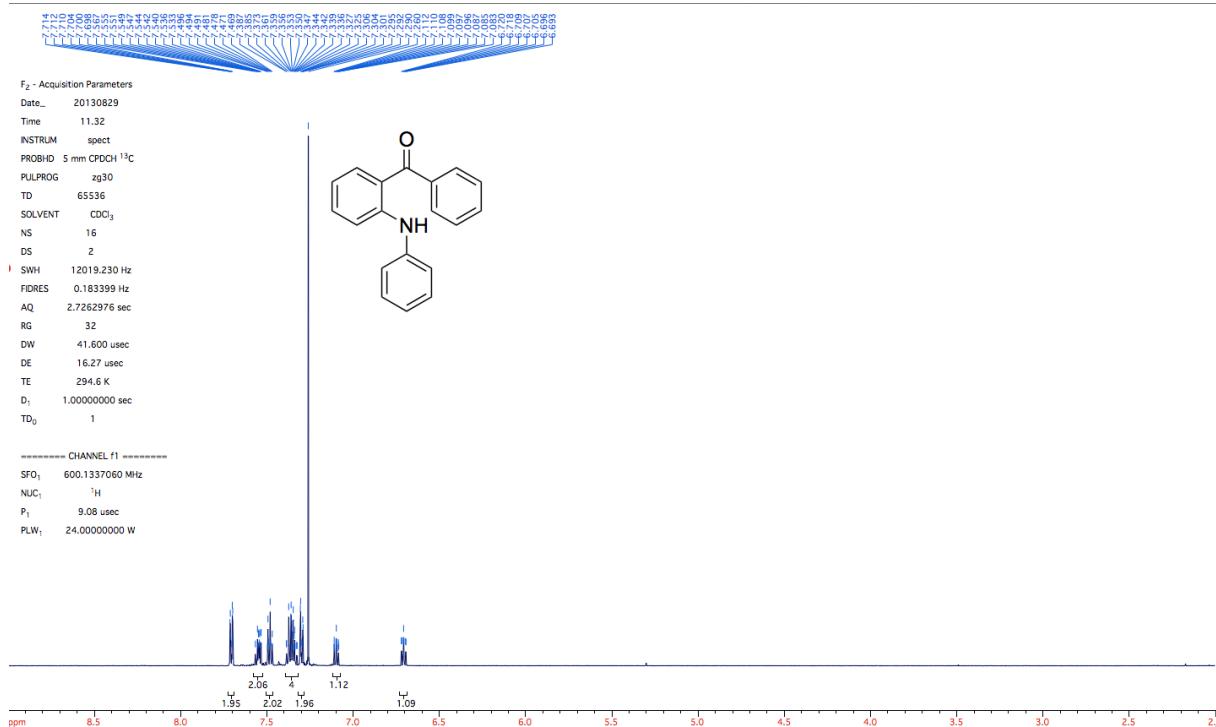
1,4-dimethyl-1,4-dihydro-1,4-epoxynaphthalene (10):



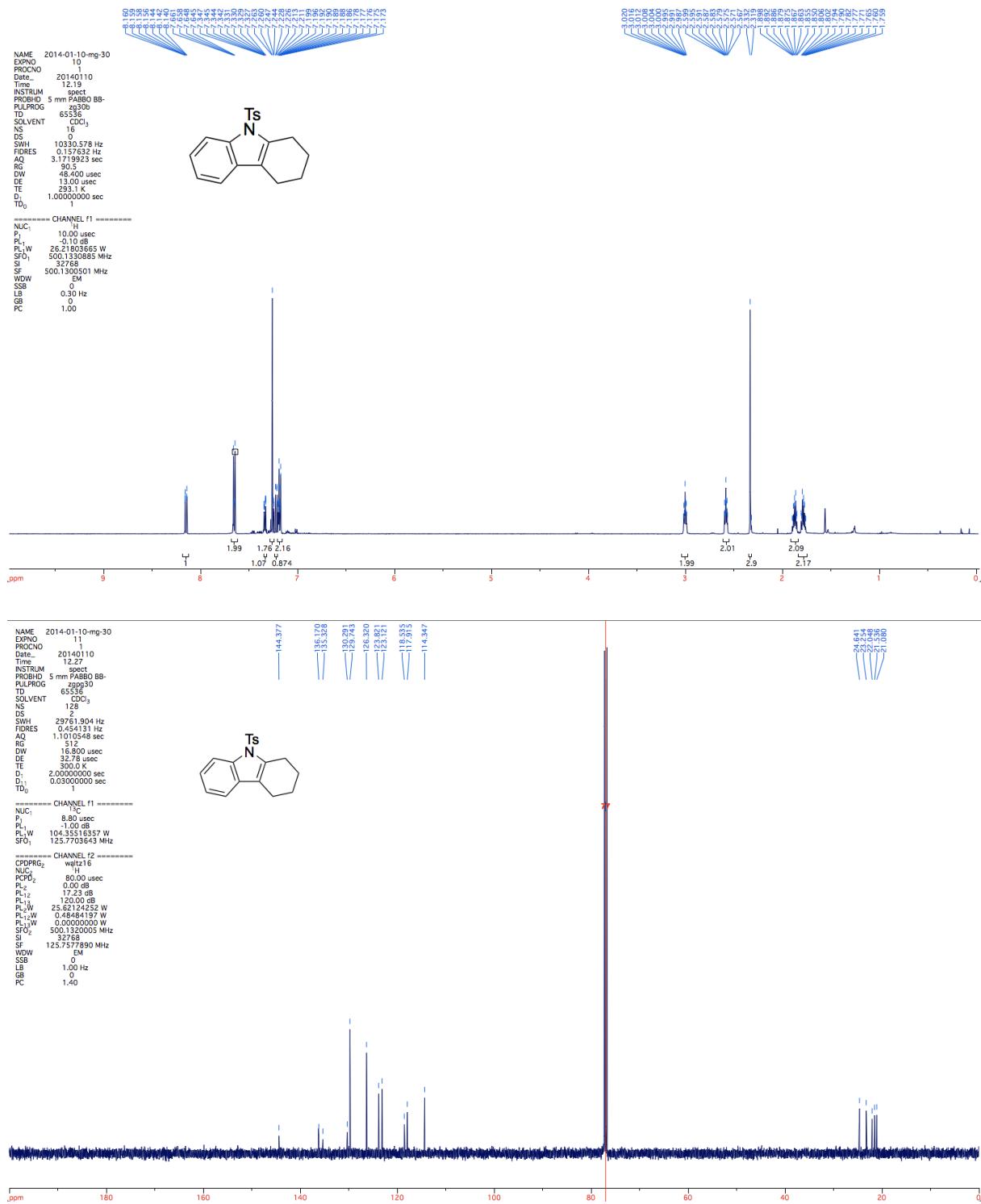
Triphenylene (11):



Phenyl(2-(phenylamino)phenyl)methanone (12):



9-Tosyl-2,3,4,9-hexahydro-1H-carbazole (13):



Methyl 2-(2-oxopropyl)benzoate (14):

