Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

A novel reaction of gem-difluorocyclopropyl ketones with nitriles leading to 2-fluoropyrroles

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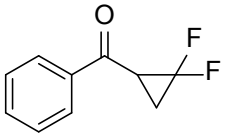
General Methods

All reactions were carried out under nitrogen atmosphere. All the reagents used were purchased from commercial sources and used without further purification. m-xylene and CH_3CN were freshly distilled from CaH_2. ^1H, ^{13}C NMR spectra were recorded in $CDCl_3$ on a spectrometer operating at 300 and 100 MHz, respectively. Chemical shifts are reported in parts per million relative to the appropriate standard: TMS for ^1H and ^{13}C NMR spectra. High Resolution Mass spectra were recorded on a Waters Micromass GCT instrument. The IR spectra were recorded on a Shimadzu IR-440 spectrometer. Column chromatography was carried out on silica gel (300-400 mm).

General Procedure A (methenylation reactions of Aryl ketones)

Into an oven dried Schlenk tube was weighed aryl vinyl ketones (20 mmol), anhydrous sodium fluoride (2 mmol). m-xylene (1 mL) were added to the mixture under the atmosphere of nitrogen. The mixture was heated to 110°C and stirred for 5 min. Then, TFDA ($FSO_2CF_2CO_2SiMe_3$, 40 mmol) was added dropwise in 30 min. Then the mixture was stirred for further 30 min at 110°C after addition of TFDA. When the substrate was completely transformed via TLC, the mixture was cooled to room temperature. After removal of the solvent under reduced pressure the crude product was purified by column chromatography (Hexane : Et_2O = 20 : 1).

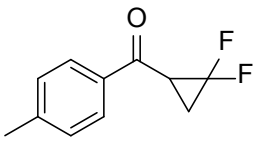
Phenyl 2,2-Difluorocyclopropyl Ketone



1a

Coloress liquid (77%). ^1H NMR (300 MHz, $CDCl_3$): δ 8.01 (d, J = 7.3 Hz, 2 H), 7.63 (t, J = 7.3 Hz, 1 H), 7.52 (t, J = 7.3 Hz, 2 H), 3.39 (m, 1 H), 2.43 (m, 1 H), 1.81 (m, 1 H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ: -124.16 (dtd,J = 149.0, 13.0, 6.0 Hz, 1 F), -140.04 (ddd, J = 149.0, 12.2, 4.8 Hz, 1 F) ppm;

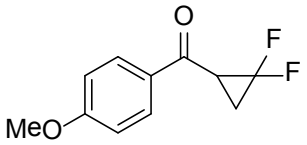
4-methylphenyl 2,2-Difluorocyclopropyl Ketone



1b

White solid (38%) ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.0 Hz, 2 H), 7.31 (d, *J* = 8.1 Hz, 2 H), 3.37 (m, 1 H), 2.41 (m, 1 H), 2.44 (s, 3 H), 1.78 (m, 1 H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ = -124.18 (dtd, *J* = 149.0, 12.4, 5.9 Hz 1 F), -140.13 (ddd, *J* = 148.7, 12.1, 4.7 Hz, 1 F) ppm

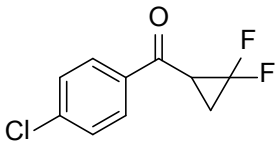
4-methoxyphenyl 2,2-Difluorocyclopropyl Ketone



1c

Faint yellow liquid (41%) ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.7 Hz, 2 H), 6.98 (d, *J* = 8.7 Hz, 2 H), 3.89 (s, 3 H), 3.34 (m, 1 H), 2.40 (m, 1 H), 1.77 (m, 1 H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ = -124.39 (dtd, *J* = 149.0, 13.0, 5.8 Hz, 1 F), -140.35 (ddd, *J* = 149.0, 12.2, 4.6 Hz, 1 F) ppm

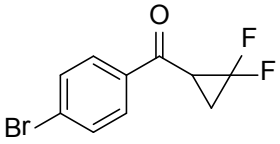
4-Chlorophenyl 2,2-Difluorocyclopropyl Ketone



1d

Faint yellow solid (22%) ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.4 Hz, 2 H), 7.49 (d, *J* = 8.4 Hz, 2 H), 3.34(m, 1 H), 2.43 (m, 1 H), 1.82 (m, 1 H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ -124.07 (dtd, *J* = 148.7, 12.3, 5.7 Hz, 1 F), -139.90 (ddd, J = 148.7, 12.2, 4.9 Hz, 1 F) ppm;

4-Bromophenyl 2,2-Difluorocyclopropyl Ketone



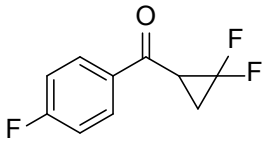
1e

White solid (m.p. 67-69°C, 32%) ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.8 Hz, 2 H), 7.66 (d, *J* = 8.8 Hz, 2 H), 3.35 (m, 1 H), 2.43 (m, 1 H), 1.84 (m, 1 H) ppm; ^{19}F

NMR (282 MHz, $CDCl_3$): δ -124.56 (dtd, *J* = 148.3, 12.3, 5.9 Hz, 1 F), -140.36 (ddd, J = 148.3, 12.1, 4.7 Hz, 1 F) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 189.5, 135.7, 132.3, 129.9, 129.1, 111.5 (t, *J* = 287.6 Hz), 29.7 (dd, *J* = 11.7, 9.6 Hz), 15.8 (dd, *J* = 11.0, 8.8 Hz) ppm; EI-MS (m/z, %): 183 (100), 185 (92.6), 76 (54.0), 155 (50.2), 157 (49.6), 75 (47.3), 50 (44.1), 133 (39.2). IR (KBr): 3117, 3095, 3075, 3060, 1671, 1582, 1453, 1400, 1381, 1319, 1247, 1180, 1008, 846, 703, 658, 515, 479cm^{-1}.

HRMS for $C_{10}H_7OF_2Br$: 259.9648; Found: 259.9649.

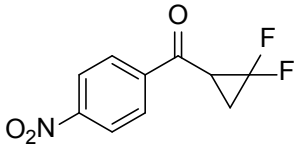
4-fluorophenyl 2,2-Difluorocyclopropyl Ketone



1f

Coloress liquid (28%) ^1H NMR (300 MHz, $CDCl_3$): δ 8.08-8.02 (m, 2 H), 7.23-7.16 (m, 2 H), 3.35 (m, 1 H), 2.43 (m, 1 H), 1.82 (m, 1 H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ -103.89 (m, 1 F), -124.28 (dtd, *J* = 148.5, 12.7, 5.9 Hz, 1 F), -140.07 (ddm, *J* = 149.2, 12.0 Hz, 1 F) ppm

4-nitrophenyl 2,2-Difluorocyclopropyl Ketone

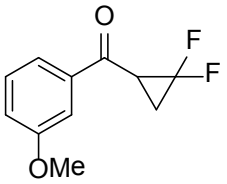


1g

White solid (m.p. 62-64°C,44%) ^1H NMR (300 MHz, $CDCl_3$): δ 8.38 (d, *J* = 8.5 Hz, 2 H), 8.18 (d, *J* = 8.5 Hz, 2 H), 3.44 (m, 1 H), 2.50 (m, 1 H), 1.94 (m, 1 H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ = -123.66 (dtd, *J* = 148.1, 12.2, 6.0 Hz, 1 F), -139.32 (ddd, *J* = 148.1, 12.0, 4.7 Hz, 1 F) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.3, 150.7, 141.3, 129.4, 124.1, 123.8, 111.4 (t, *J* = 288.5 Hz), 30.2 (dd, *J* = 11.8, 10.3 Hz), 16.3 (dd, *J* = 11.4, 9.1Hz) ppm; EI-MS (m/z, %): 150 (100), 104 (58.4), 76 (54.2), 133 (41.3), 50 (37.8), 51 (26.3), 75 (25.6), 77 (25.5). IR (KBr): 3113, 3087, 3052, 1677, 1607, 1451, 1413, 1321, 1298, 1208, 1052, 963, 923, 856, 729, 703, 685, 479cm^{-1}.

HRMS for $C_{10}H_7NO_3F_2$: 227.0394; Found: 227.0397

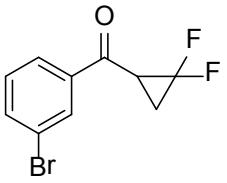
3-methoxyphenyl 2,2-Difluorocyclopropyl Ketone



1h

Coloress liquid (71%) ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60 (d, *J* = 7.9 Hz, 1 H), 7.52 (s, 1 H), 7.43 (t, *J* = 7.9 Hz, 1 H), 7.17 (dd, *J* = 7.9, 2.6 Hz, 1 H), 3.87 (s, 3 H), 3.38 (m, 1 H), 2.43 (m, 1 H), 1.81 (m, 1 H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ = -124.73 (dm, J = 148.0 Hz, 1 F), -140.65 (dm, J = 148.0 Hz, 1 F) ppm

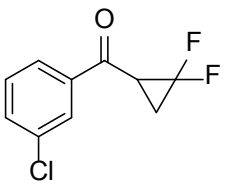
3-Bromophenyl 2,2-Difluorocyclopropyl Ketone



1i

White solid (62%) ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.12 (s, 1 H), 7.93 (d, *J* = 7.9 Hz, 1 H), 7.75 (d, *J* = 7.9 Hz, 1 H), 7.41 (t, *J* = 7.9 Hz, 1 H), 3.37 (m, 1 H), 2.44 (m, 1 H), 1.85 (m, 1 H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ = -124.48 (dtd, *J* = 148.5, 12.2, 6.0 Hz, 1 F), -140.28 (ddd, *J* = 148.5, 12.1, 4.8 Hz, 1 F) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.3, 138.7, 136.6, 131.4, 130.4, 127.0, 123.2, 111.5 (dd, *J* = 288.4, 286.9 Hz), 29.8 (dd, *J* = 11.7, 10.3 Hz), 15.9 (dd, *J* = 11.0, 8.8 Hz) ppm; EI-MS (m/z, %): 183 (100), 185 (99), 155 (48.6), 157 (47.7), 133 (28.6), 76 (28.0), 181 (26.6), 75 (22.9). IR (KBr): 3116, 3062, 3026, 1669, 1566, 1459, 1374, 1316, 1247, 1203, 1055, 1008, 929, 919, 908, 817, 773, 704, 679, 667, 478 cm^{-1}. HRMS for $C_{10}H_7OF_2Br$: 259.9648; Found: 259.9651.

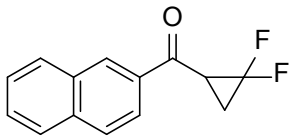
3-Chlorophenyl 2,2-Difluorocyclopropyl Ketone



1j

White solid (70%) ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97 (t, *J* = 1.8 Hz, 1 H), 7.89 (dt, *J* = 7.9, 1.8 Hz, 1 H), 7.60 (ddd, *J* = 7.9, 1.8, 1.1 Hz, 1H), 7.47 (t, *J* = 7.9 Hz, 1 H), 3.36 (m, 1 H), 2.45 (m, 1 H), 1.84 (m, 1 H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ = -124.52 (dm, *J* = 148. 1 Hz, 1 F), -140.36 (dm, *J* = 148.1 Hz, 1 F) ppm

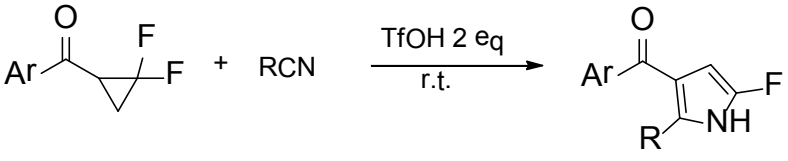
Naphthalen-2-yl 2,2-difluorocyclopropyl ketone



1k

White solid (m.p. 91-93 °C, 57%) ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.52 (s, 1 H), 8.07-7.98 (m, 2 H), 7.91 (t, *J* = 8.8 Hz, 2 H), 7.65-7.55 (m, 2 H), 3.56 (m, 1 H), 2.49 (m, 1 H), 1.86 (m, 1 H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ -124.51 (dtd, J = 147.9, 12.5, 5.9 Hz, 1 F), -140.43 (ddd, *J* = 147.9, 12.3, 5.1 Hz, 1 F) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.4, 135.9, 134.5, 132.5, 130.5, 129.7, 128.9, 128.8, 127.9, 127.1, 123.8, 111.7 (dd, *J* = 288.1, 286.6 Hz), 29.84 (dd, *J* = 11.8, 9.6 Hz), 15.76 (dd, *J* = 11.0, 9.0 Hz) ppm; EI-MS (m/z, %): 127 (100), 155 (75.2), 232 (46.3), 128 (24.8), 126 (24.1), 183 (21.0), 77 (18.6), 51 (14.4). IR (KBr): 3113, 3053, 3021, 1676, 1624, 1453, 1373, 1237,1061, 1043, 1008, 925, 768, 744, 690, 484, 478cm^{-1}. HRMS for $C_{14}H_{10}OF_2$: 232.0700; Found: 232.0702.

General Procedure B (The Reaction of Difluorocyclopropyl Ketones with Nitriles)

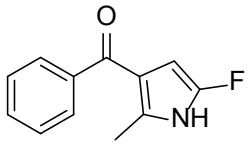


1a-k 2a-l

Under nitrogen, aryl difluorocyclopropyl ketones (0.2 mmol), triflic acid (0.4 mmol) was added into acetonitrile (1 mL). And the mixture was stirred for 0.5 h at room temperature. When TLC showed the complete transformation of the substrate, the mixture

was quenched at -20°C with triethylamine carefully. After removal of the solvent under reduced pressure the crude product was purified by column chromatography (Hexane : EtOAc = 8 : 1).

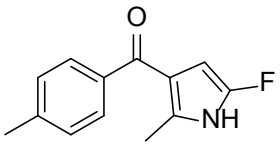
(5-fluoro-2-methyl-1H-pyrrol-3-yl) (phenyl) methanone



2a

White solid（m.p. 120-122 °C, 64 %）^{1}H NMR (300 MHz, $CDCl_3$): δ 8.61 (br, 1 H), 7.77 (d, *J* = 7.0 Hz, 2 H),7.52 (t, *J* = 7.0 Hz, 1 H), 7.44 (t, *J* = 7.0 Hz, 2 H), 5.68 (t, *J* = 3.2 Hz, 1 H), 2.47 (s, 3 H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ -141.02 (s, 1 F) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.7 (d, *J* = 15.4 Hz), 145.1 (dd, *J* = 260.1, 5.9 Hz), 140.1, 131.5, 128.9, 128.6 (d, *J* = 14.7 Hz), 128.2, 117.2 (t, *J* = 3.6 Hz), 87.64 (d, *J* = 8.8 Hz), 13.3 ppm；EI-MS (m/z, %): 203 (100), 202 (85.3), 126 (78.1), 182 (42.1), 77 (38.1), 51 (32.3), 57 (27.0), 71 (18.2). IR (KBr): 3211, 1625, 1600, 1574, 1530, 1448, 1430, 1371, 1252, 762, 721, 694, 675, 606 cm^{-1}. HRMS for $C_{12}H_{10}NOF$: 203.0746; Found: 203.0749.

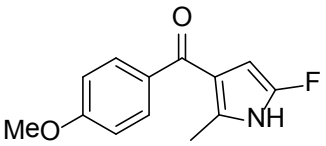
(5-fluoro-2-methyl-1H-pyrrol-3-yl)(p-tolyl) methanone



2b

White solid (m.p. 149-151°C, 49 %) ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.99 (br, 1 H), 7.68 (d, *J* = 7.8 Hz, 2 H), 7.23 (d, *J* = 7.8 Hz, 2 H), 5.67 (s, 1 H), 2.43 (s, 3 H), 2.41 (s, 3 H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ -140.87 (s, 1 F) ppm；^{13}C NMR (100 MHz, $CDCl_3$): δ 192.3 (d, *J* = 2.9 Hz), 145.0 (d, *J* = 260.0 Hz), 142.1, 137.4, 129.2, 128.8, 128.0, 117.4 (d, *J* = 2.9 Hz), 87.6 (d, *J* = 8.8 Hz), 21.6, 13.2 ppm； EI-MS (m/z, %): 217 (100), 202 (83.7), 216 (60.0), 126 (55.3), 196 (36.9), 91 (26.7), 182 (19.1), 218 (15.6). IR (KBr): 3176, 1633, 1533, 1427, 1371, 1178, 911, 836, 795, 755, 605. HRMS for $C_{13}H_{12}NOF$: 217.0903; Found: 217.0901.

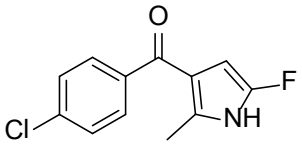
(5-fluoro-2-methyl-1H-pyrrol-3-yl) (4-methoxyphenyl) methanone



2c

White solid (m.p. 126-128 °C, 54 %) ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.98 (br, 1 H), 7.81 (d, *J* = 8.7 Hz, 2 H), 6.94 (d, *J* = 8.7 Hz, 2 H), 5.68 (s, 1 H), 3.87 (s, 3 H), 2.44 (s, 3 H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ -141.05 (s, 1 F) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.4 (d, *J* = 3.0 Hz), 162.5, 145.0 (d, *J* = 259.9 Hz), 132.6, 131.4, 127.7 (d, *J* = 1.5 Hz), 117.4 (d, *J* = 2.9 Hz), 113.4, 87.5 (d, *J* = 8.8 Hz), 55.4, 13.1 ppm; EI-MS (m/z, %): 233 (100), 232 (65.9), 126 (57.5), 202 (39.1), 135 (31.4), 212 (27.0), 77 (19.4), 92 (15.9). IR (KBr): 3207, 1623, 1537, 1433, 1371, 1249, 1170, 1032, 915, 834, 761, 619 cm^{-1}. HRMS for $C_{13}H_{12}NO_2F$: 233.0852; Found: 233.0854.

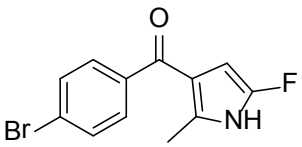
(4-chlorophenyl) (5-fluoro-2-methyl-1H-pyrrol-3-yl) methanone



2d

White solid (m.p. 138-140 °C, 57 %) ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.40 (br, 1 H), 7.72 (d, *J* = 8.5 Hz, 2 H), 7.42 (d, *J* = 8.5 Hz, 2 H), 5.65 (t, *J* = 3.1 Hz, 1 H), 2.48 (s, 3 H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ = -140.91 (s, 1 F) ppm; ^{13}C NMR (100 MHz, CD_3COCD_3): δ 189.3 (d, *J* = 3.7 Hz), 145.4 (d, *J* = 255.8 Hz), 139.2, 136.6, 130.3, 128.4, 128.3, 116.5 (d, J = 3.0 Hz), 86.6 (d, *J* = 9.5 Hz), 12.2 ppm; EI-MS (m/z, %): 126 (100), 237 (81.0), 202 (67.4), 201 (53.8), 236 (46.9), 238 (32.2), 111 (31.0), 182 (26.9). IR (KBr): 3251, 1629, 1587, 1530, 1433, 1371, 1253, 1091, 1015, 914, 844, 765, 764, 606 cm^{-1}. HRMS for $C_{12}H_9NOFCl$: 237.0357; Found: 237.0357.

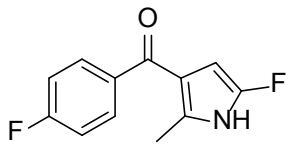
(4-bromophenyl) (5-fluoro-2-methyl-1H-pyrrol-3-yl) methanone



2e

White solid (m.p. 141-143 ^{o}C, 65 %) ^{1}H NMR (300 MHz, CD_3Cl_3): δ 8.22 (br, 1 H), 7.65 (d, *J* = 8.4 Hz, 2 H), 7.58 (d, *J* = 8.4 Hz, 2 H) 5.65 (t, *J* = 2.8 Hz, 1 H), 2.49 (s, 3 H) ppm; ^{19}F NMR (282 MHz, CD_3COCD_3): δ -143.11 (s, 1 F) ppm; ^{13}C NMR (100 MHz, CD_3COCD_3): δ 189.4 (d, *J* = 2.9 Hz), 145.4 (d, *J* = 256.3 Hz), 139.6, 131.3, 130.5, 128.4, 125.1, 116.5 (d, *J* = 2.9 Hz), 86.6 (d, *J* = 9.5 Hz), 12.2 ppm; EI-MS (m/z, %): 126 (100), 201 (54.8), 202 (53.2), 283 (51.7), 281 (49.4), 282 (31.8), 182 (28.3), 280 (25.5). HRMS for $C_{12}H_9NOFBr$: 280.9852; Found: 280.9849.

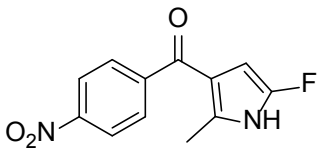
(5-fluoro-2-methyl-1H-pyrrol-3-yl) (4-fluorophenyl) methanone



2f

White solid (m.p. 144-145 ^{o}C, 60 %) ^{1}H NMR (300 MHz, CD_3COCD_3): δ 11.03 (br, 1 H), 7.83 (dd, *J* = 8.6, 5.6 Hz, 2 H), 7.25 (t, *J* = 8.6 Hz, 2 H), 5.68 (d, *J* = 2.6 Hz, 1 H), 2.43 (s, 3 H) ppm; ^{19}F NMR (282 MHz, CD_3COCD_3): δ = -110.97 (m, 1 F), -144.10 (s, 1F) ppm; ^{13}C NMR (100 MHz, CD_3COCD_3) δ 189.1 (d, *J* = 2.9 Hz), 164.5 (d, *J* = 249.1 Hz), 145.3 (d, *J* = 255.6 Hz), 137.0 (d, *J* = 2.9 Hz), 131.2 (d, *J* = 9.5 Hz), 128.1, 116.6, 114.9 (d, *J* = 21.9 Hz), 86.6 (d, *J* = 9.5 Hz), 12.2 ppm; EI-MS (m/z, %): 221 (100), 126 (78.0), 220 (59.4), 200 (31.4), 95 (27.4), 123 (19.6), 98 (15.0), 222 (14.3). IR (KBr): 3187, 1625, 1529, 1429, 1257, 1244, 848, 757 cm^{-1}. HRMS for $C_{12}H_9NOF_2$: 221.0652; Found: 221.0648

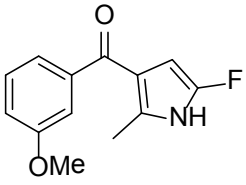
(5-fluoro-2-methyl-1H-pyrrol-3-yl) (4-nitrophenyl) methanone



2g

White solid (m.p. 193-195 °C, 61 %) ^{1}H NMR (400 MHz, CD_3COCD_3): δ = 11.10 (br, 1 H), 8.34 (d, *J* = 8.8 Hz, 2 H), 7.94 (d, *J* = 8.8 Hz, 2 H), 5.67 (d, *J* = 3.5 Hz, 1 H), 2.45 (s, 3 H) ppm; ^{19}F NMR (282 MHz, CD_3COCD_3): δ = -141.79 (s, 1 F) ppm; ^{13}C NMR (100 MHz, CD_3COCD_3): δ 188.9 (d, *J* = 2.9 Hz), 149.2, 146.0, 145.5 (d, *J* = 257.0 Hz), 129.5, 129.4, 123.4, 116.2 (d, *J* = 3.7 Hz), 86.6 (d, *J* = 10.2 Hz), 12.4 ppm; EI-MS (m/z, %): 126 (100), 248 (61.0), 201 (51.6), 231 (30.8), 247 (21.7), 172 (16.1), 98 (16.0), 71 (15.1). IR (KBr): 3284, 1637, 1515, 1426, 1349, 1244, 868, 852, 771, 728 cm^{-1}。HRMS for $C_{12}H_9N_2O_3F$: 248.0597; Found: 248.0595.

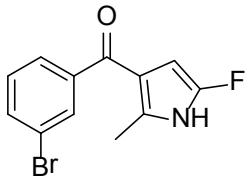
(5-fluoro-2-methyl-1H-pyrrol-3-yl) (3-methoxyphenyl) methanone



2h

White solid (m.p. 130-132 °C, 74 %) ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.48 (br, 1H), 7.28-7.22 (m, 3 H), 7.01-6.97 (m, 1 H), 5.61 (t, *J* = 2.9 Hz, 1 H), 3.77 (s, 3 H), 2.37 (s, 3 H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ -140.79 (s, 1 F) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.4 (d, *J* = 2.6 Hz), 159.5, 145.1 (d, *J* = 260.2 Hz), 141.5, 129.2, 128.7, 121.6, 117.8, 117.2, 113.6, 87.6 (d, *J* = 8.8 Hz), 55.4, 13.3 ppm; EI-MS (m/z, %): 233 (100), 126 (94.2), 232 (58.9), 212 (22.6), 202 (20.1), 71 (18.6), 77 (18.0), 97 (16.2). IR (KBr): 3242, 1625, 1582, 1484, 1432, 1372, 1267, 1045, 864, 818, 753 cm^{-1}. HRMS for $C_{13}H_{12}NO_2F$: 233.0852; Found: 233.0853.

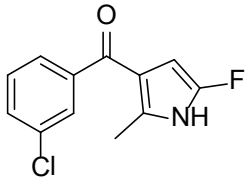
(3-bromophenyl) (5-fluoro-2-methyl-1H-pyrrol-3-yl) methanone



2i

White solid (m.p. 191-193 ^{o}C, 79 %) ^{1}H NMR (400 MHz, CD_3COCD_3): δ 11.02 (br, 1 H), 7.87 (s, 1 H), 7.75 (d, J = 7.8 Hz, 2 H), 7.48 (t, J = 7.8 Hz, 1 H), 5.69 (d, J = 3.1 Hz, 1 H), 2.46 (s, 3 H) ppm; ^{19}F NMR (282 MHz, CD_3COCD_3): δ -143.85 (s, 1 F) ppm; ^{13}C NMR (100 MHz, CD_3COCD_3) δ 188.9 (d, J = 3.0 Hz), 145.4 (d, J = 257.2 Hz), 142.7, 133.8, 131.2, 130.2, 128.7, 127.4, 121.8, 116.3 (d, J = 3.7 Hz), 86.6 (d, J = 9.5 Hz), 12.2 ppm; EI-MS (m/z, %): 126 (100), 201 (39.1), 281 (38.7), 283 (38.3), 282 (27.5), 280 (23.2), 202 (19.0), 182 (17.0). IR (KBr): 3180, 1623, 1561, 1530, 1247, 793, 709, 686 cm^{-1}. HRMS for $C_{12}H_9NOBrF$: 280.9852; Found: 280.9855.

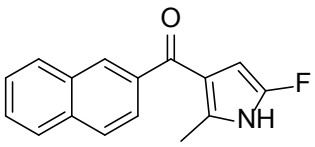
(3-chlorophenyl)(5-fluoro-2-methyl-1H-pyrrol-3-yl)methanone



2j

White solid (m.p. 197-200 ^{o}C, 66 %) ^{1}H NMR (300 MHz, CD_3COCD_3): δ 11.13 (br, 1 H), 7.69-7.67 (m, 2 H), 7.58-7.52 (m, 2 H), 5.68 (d, J = 2.6 Hz), 2.43 (s, 3 H) ppm; ^{19}F NMR (282 MHz, CD_3COCD_3): δ -143.00 (s, 1 F) ppm; ^{13}C NMR (100 MHz, CD_3COCD_3) δ 189.0 (d, J = 3.2 Hz), 145.4 (d, J = 257.1 Hz), 142.5, 133.8, 130.8, 130.0, 128.7, 128.2, 127.0, 116.4 (d, J = 3.2 Hz), 86.6 (d, J = 9.6 Hz), 11.8 ppm; EI-MS (m/z, %): 126 (100), 237 (63.8), 236 (39.2), 201 (29.4), 239 (22.8), 238 (22.1), 200(19.6), 111 (16.4). IR (KBr): 3177, 1622, 1530, 1249, 756, 724, 686cm^{-1}. HRMS for $C_{12}H_9NOClF$: 237.0357; Found: 237.0360

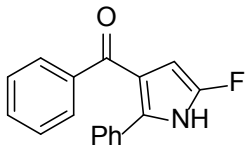
(5-fluoro-2-methyl-1H-pyrrol-3-yl)(naphthalen-2-yl)methanone



2k

White solid (m.p. 202-204 ^{o}C, 52 %) ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.28 (s, 1 H), 8.13 (br, 1 H), 7.95-7.89 (m, 4 H), 7.60-7.52 (m ,2 H), 5.76 (m, 1 H), 2.51 (s, 3 H) ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ -140.42 (s, 1 F) ppm; ^{13}C NMR (100 MHz, CD_3COCD_3,): δ 190.5 (d, J = 2.8 Hz), 145.3 (d, J = 256.4 Hz), 137.8, 134.7, 132.6, 129.3, 129.1, 127.9, 127.9, 127.7, 127.6, 126.6, 125.3, 117.0 (d, J = 3.1 Hz), 86.8 (d, J = 9.2 Hz), 12.2 ppm; EI-MS (m/z, %): 254 (100), 253 (64.0), 126 (54.9), 44 (48.7), 127 (34.0), 237 (26.7), 234 (20.5), 232 (20.1). IR (KBr): 3197, 1622, 1528, 1429, 1377, 1255, 907, 780, 751, 608, 479 cm^{-1}. HRMS for $C_{16}H_{12}NOF$: 253.0903; Found: 253.0908.

(5-fluoro-2-phenyl-1H-pyrrol-3-yl) (phenyl) methanone

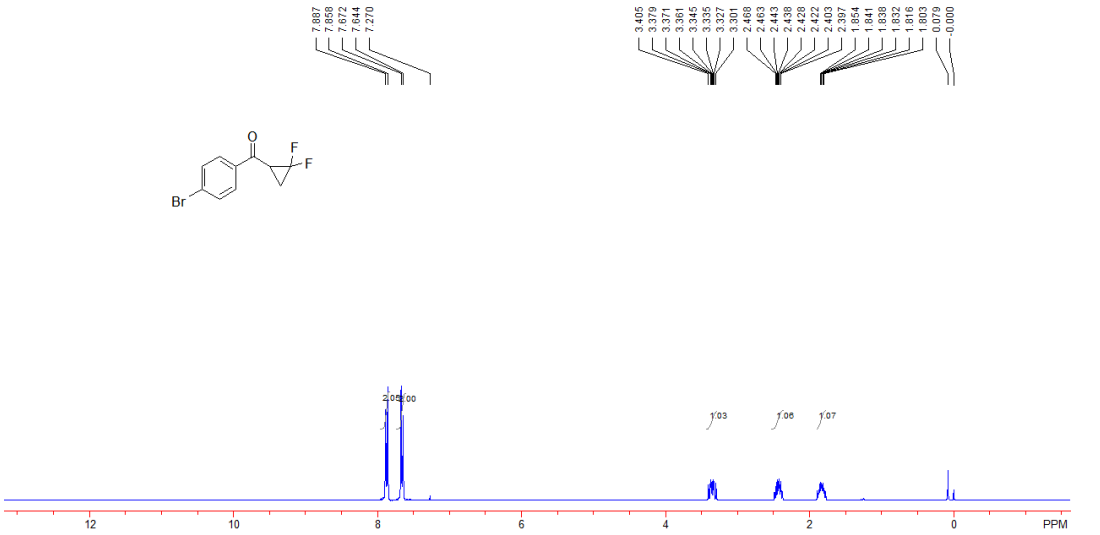


2L

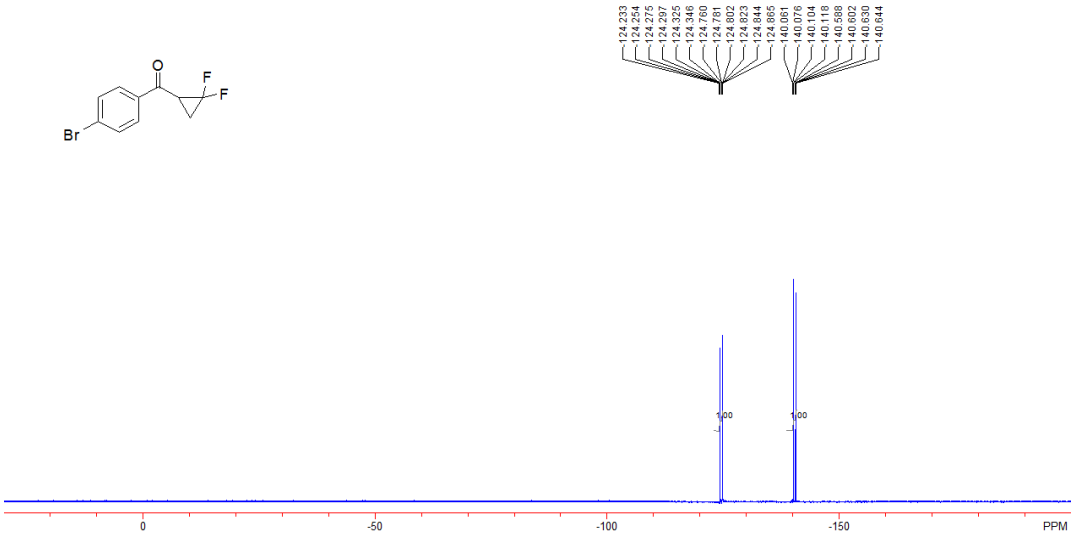
White solid (m.p. 166-169 ^{o}C, 45 %) ^{1}H NMR (300 MHz, $CDCl_3$): δ: 8.81 (br, 1H), 7.71 (d, J = 7.2 Hz, 2 H), 7.39 (t, J = 7.2 Hz, 1 H), 7.31-7.25 (m, 4 H), 7.19-7.18 (m, 3H), 5.87 (t, J = 3.0 Hz, 1H);^{19}F NMR (282 MHz, $CDCl_3$): δ -138.8 (s, 1 F) ppm;^{13}C NMR (100 MHz, $CDCl_3$): δ 192.3 (d, J = 2.2 Hz), 146.9 (d, J = 262.6 Hz), 139.0, 131.8, 131.2, 129.6, 128.8, 128.5, 128.4, 128.1, 128.0, 118.2 (d, J = 2.2 Hz), 89.42 (d, J = 9.5 Hz); EI-MS (m/z, %): 265 (100), 188 (94.9), 264 (57.2), 77 (29.4), 133 (23.9), 266 (17.4), 105 (14.4), 189 (14.0); IR (KBr): 3162, 3025, 1609, 1594, 1574, 1528, 1485, 1452, 1428, 1340, 1286, 1271, 1232, 1159, 1123, 911, 901, 802, 772, 733, 693, 672, 648 cm^{-1}; HRMS for $C_{17}H_{12}NOF$: 265.0903; Found: 265.0905;

NMR spectra of the new products

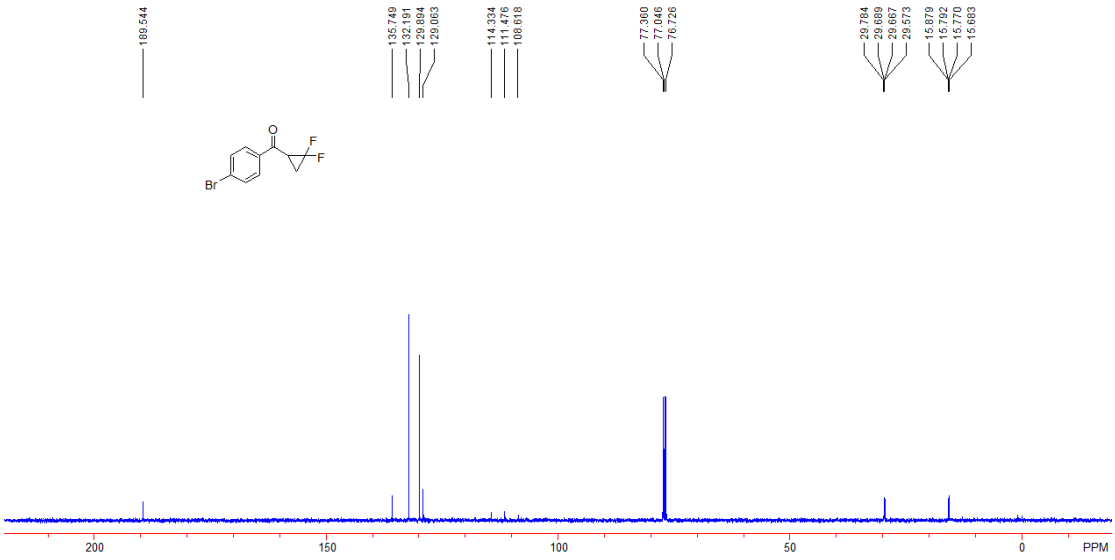
^{1}H NMR of **1e**



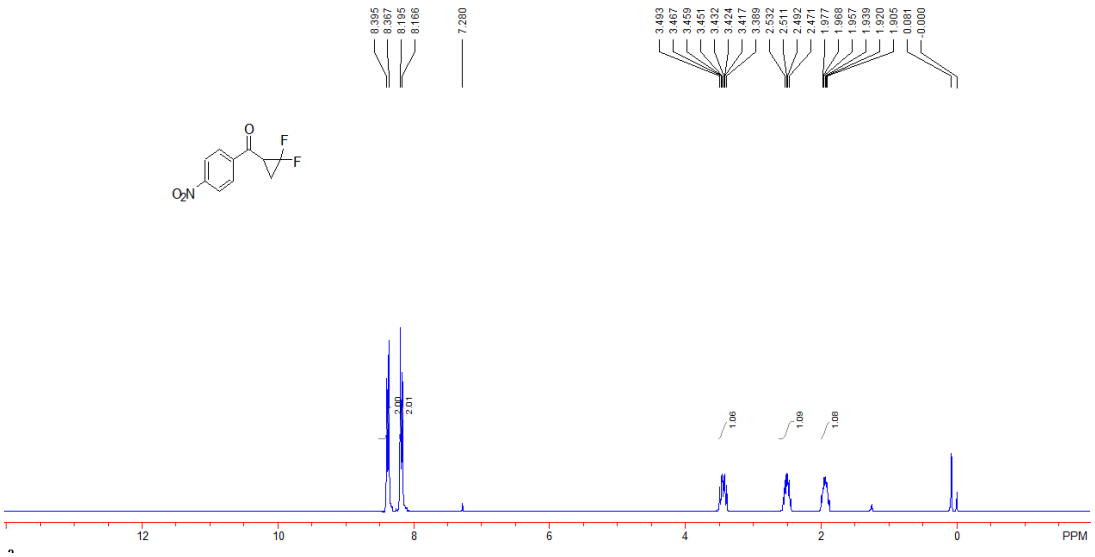
^{19}F NMR of **1e**



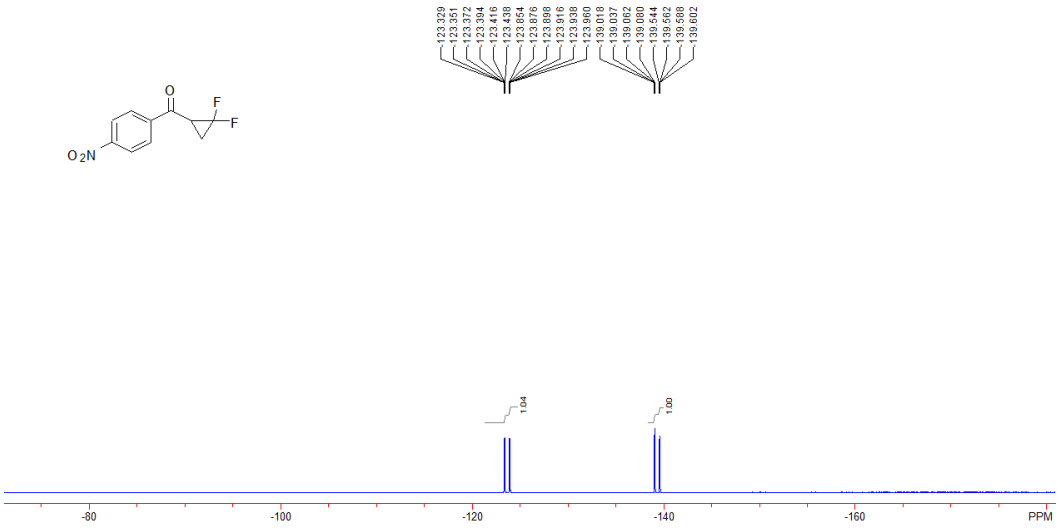
^{13}C NMR of **1e**



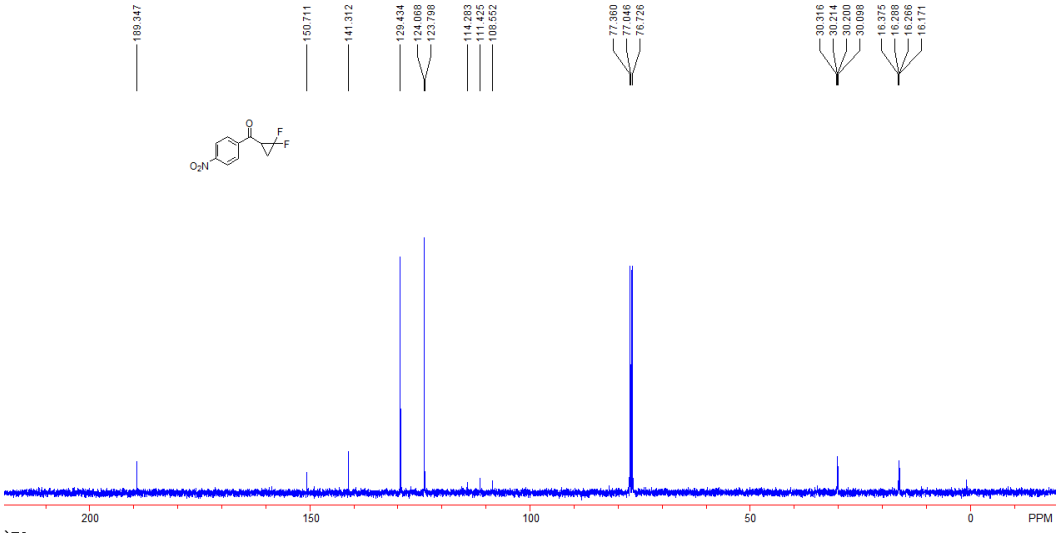
^{1}H NMR of **1g**



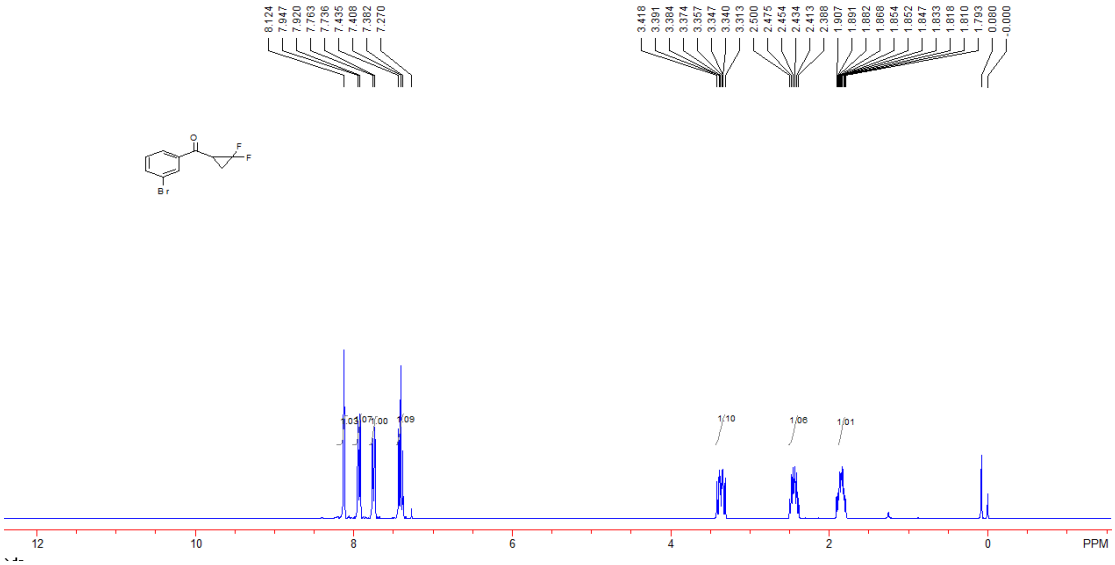
^{19}F NMR of **1g**



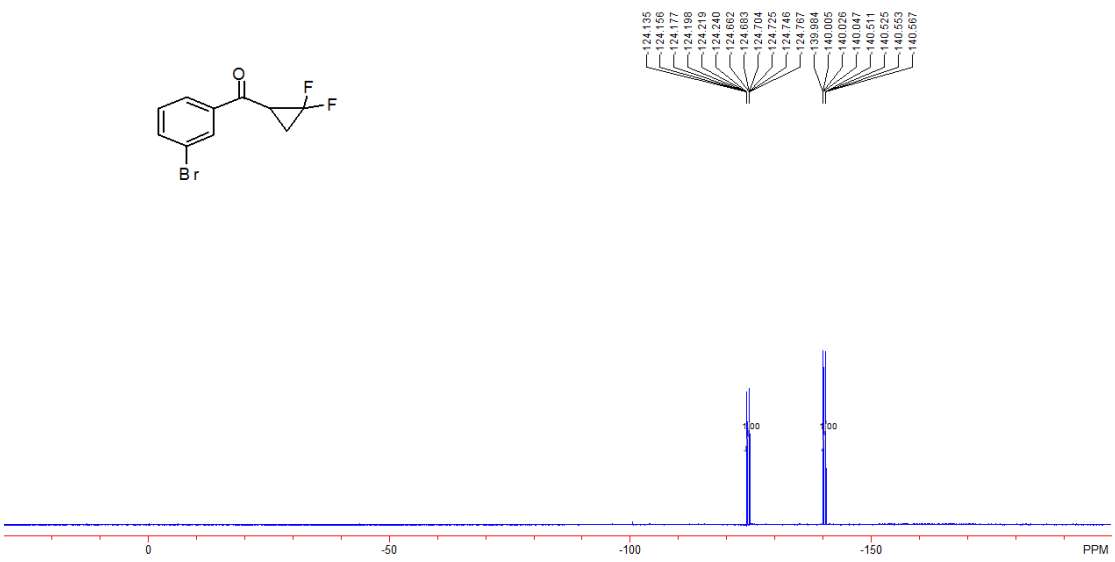
^{13}C NMR of **1g**



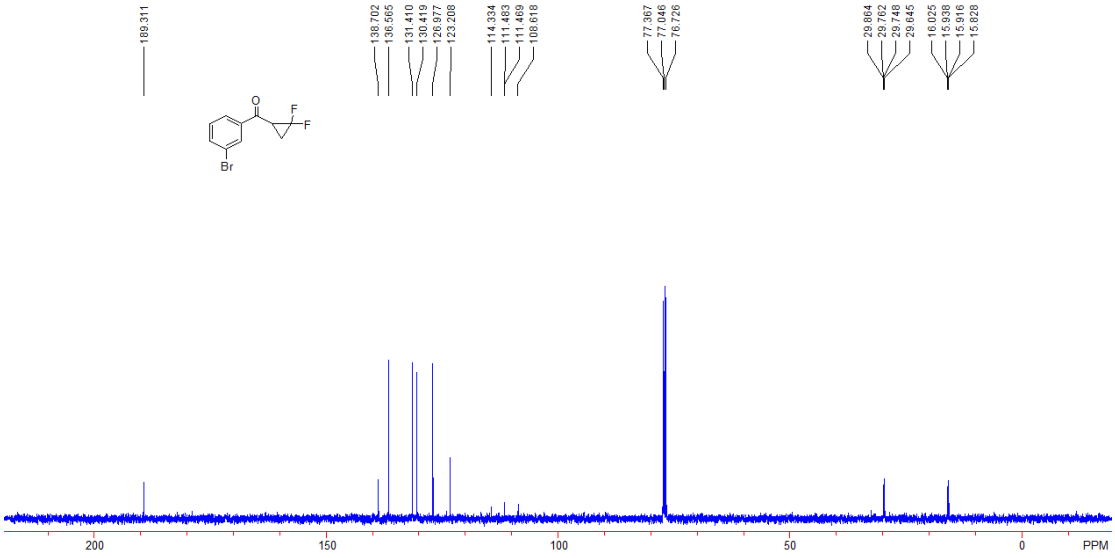
^{1}H NMR of **1i**



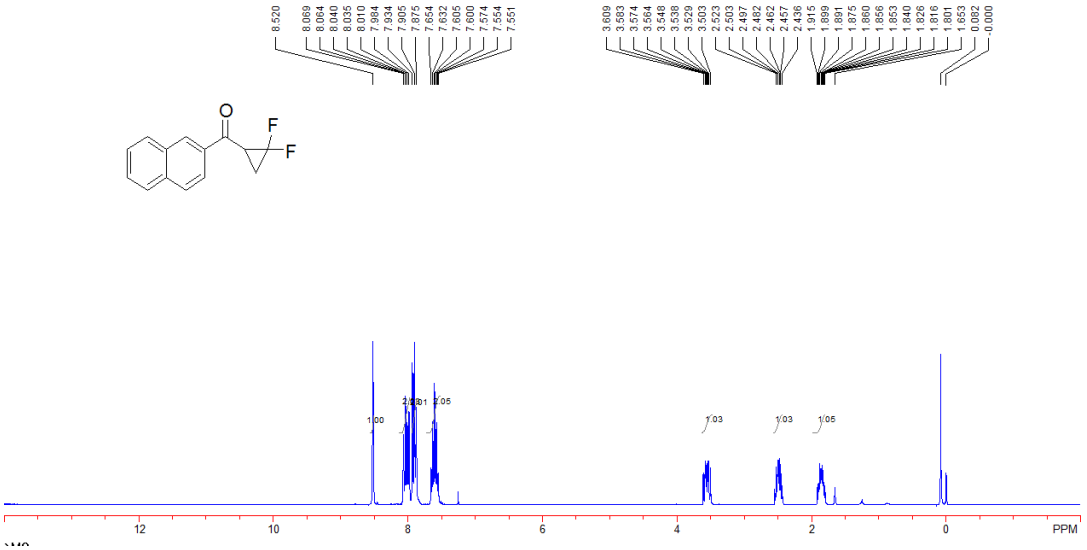
^{19}F NMR of **1i**



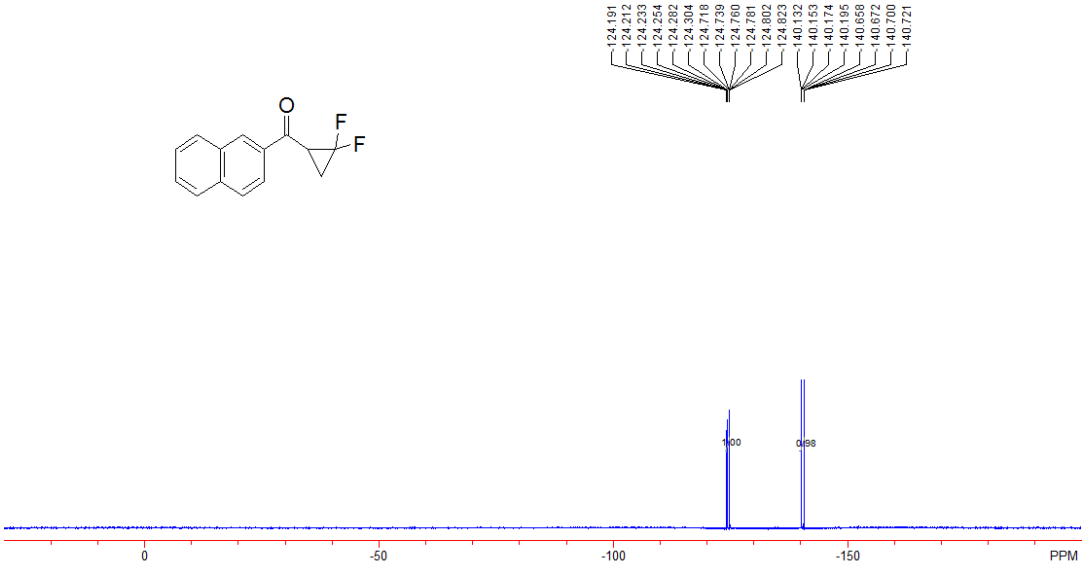
^{13}C NMR of **1i**



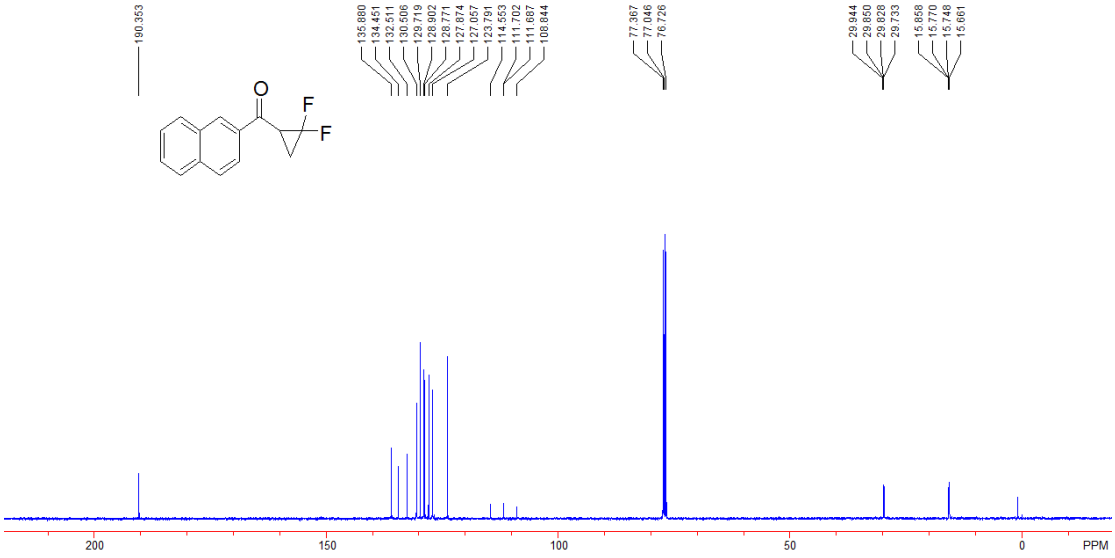
^{1}H NMR of **1k**



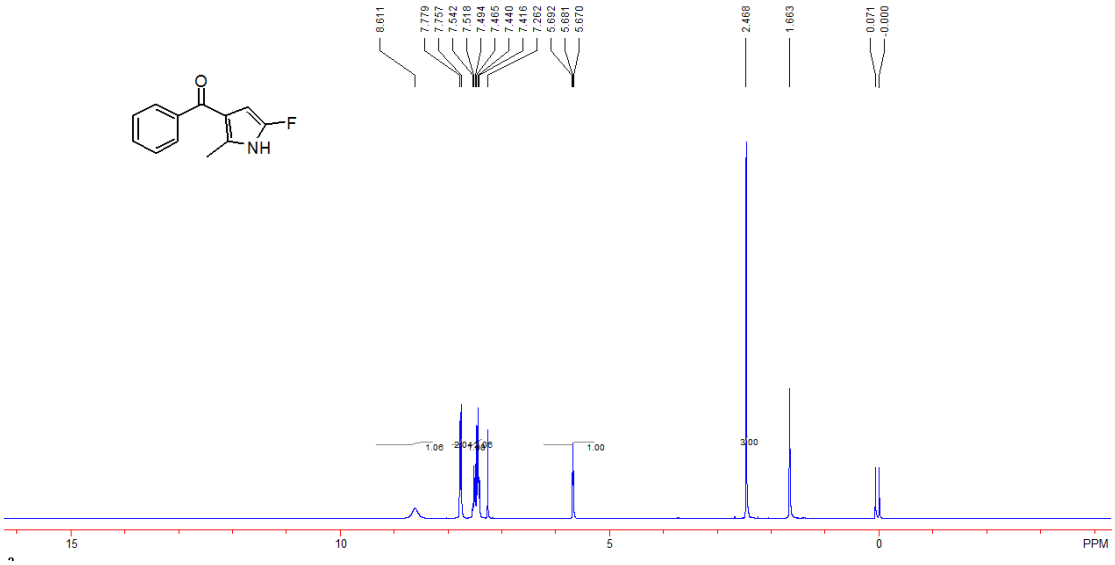
^{19}F NMR of **1k**



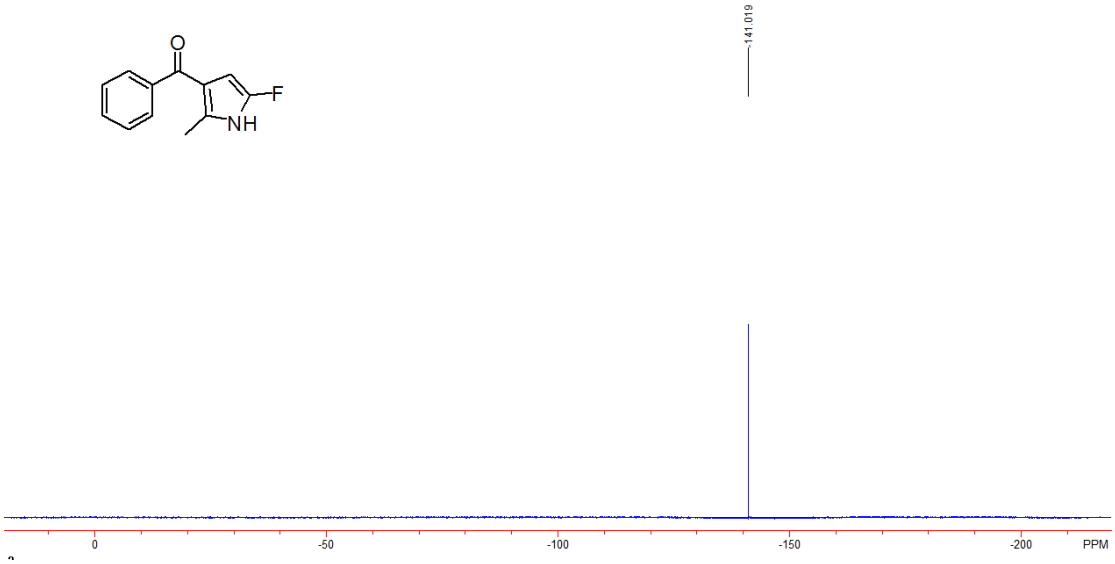
^{13}C NMR of **1k**



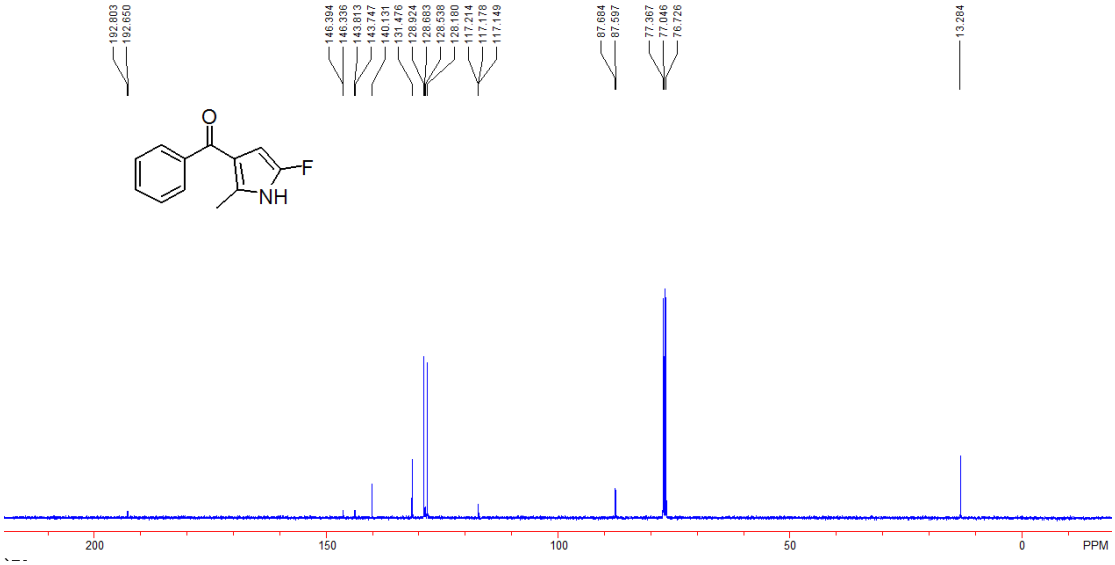
^{1}H NMR of **2a**



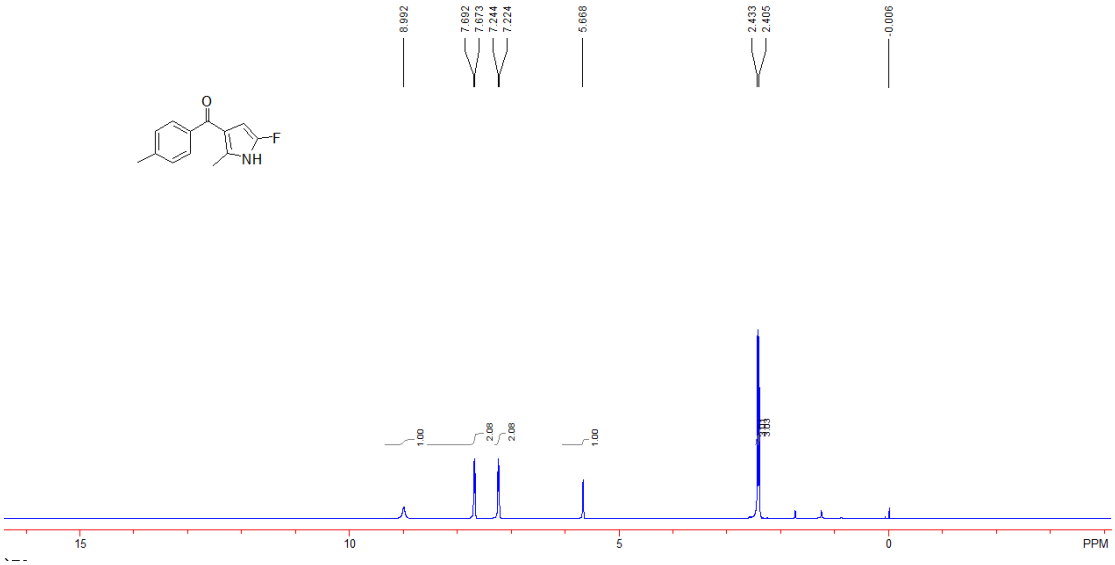
^{19}F NMR of **2a**



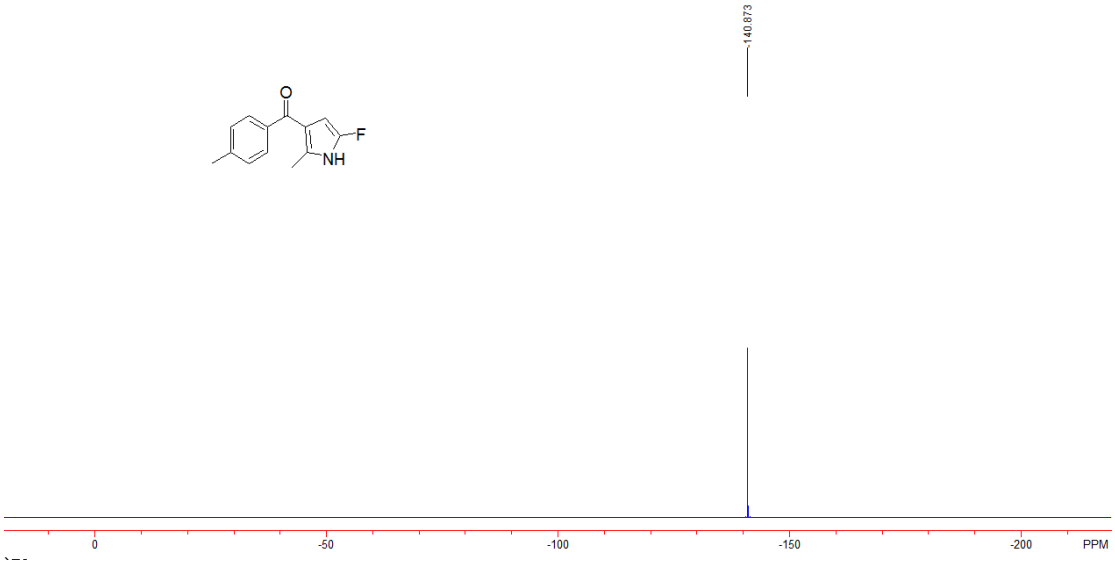
^{13}C NMR of **2a**



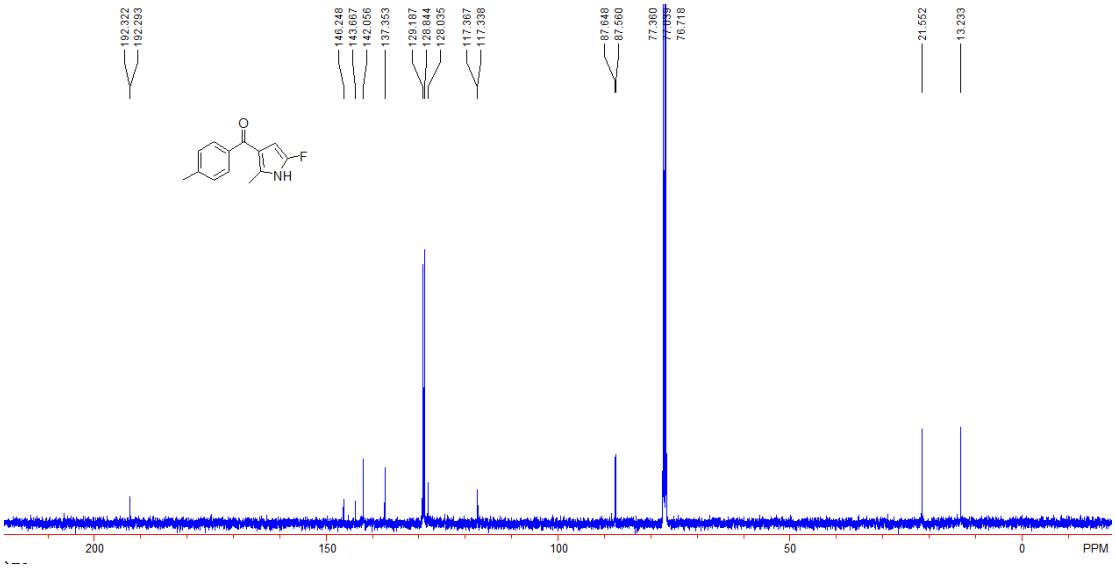
^{1}H NMR of **2b**



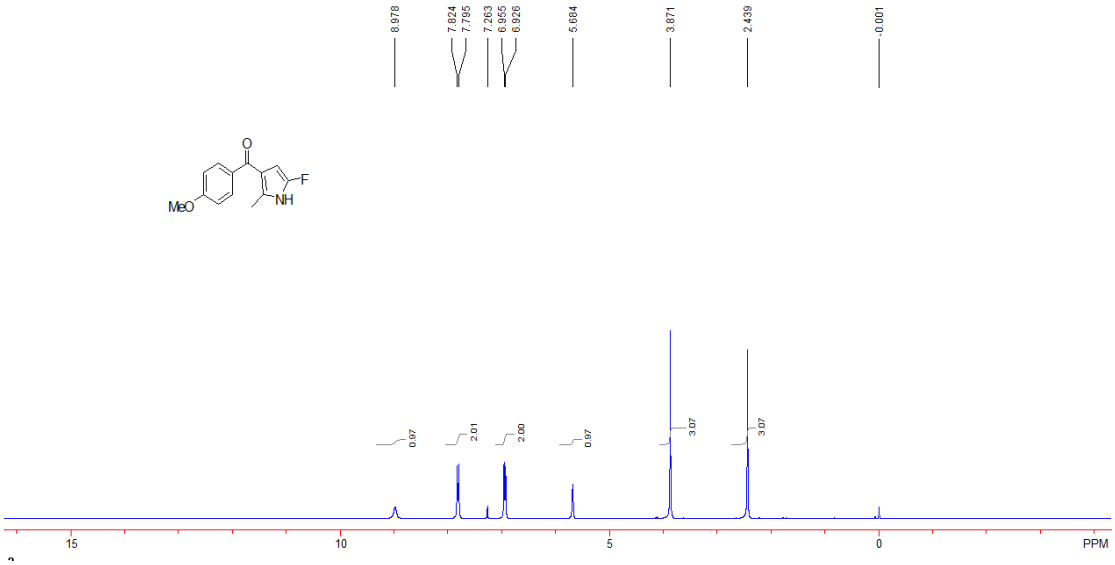
^{19}F NMR of **2b**



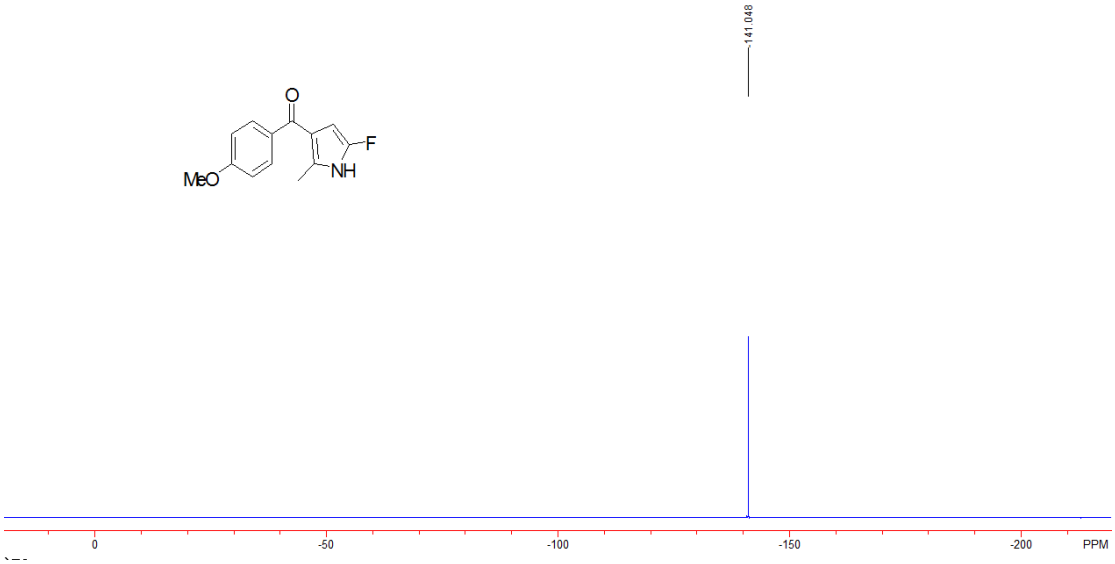
^{13}C NMR of **2b**



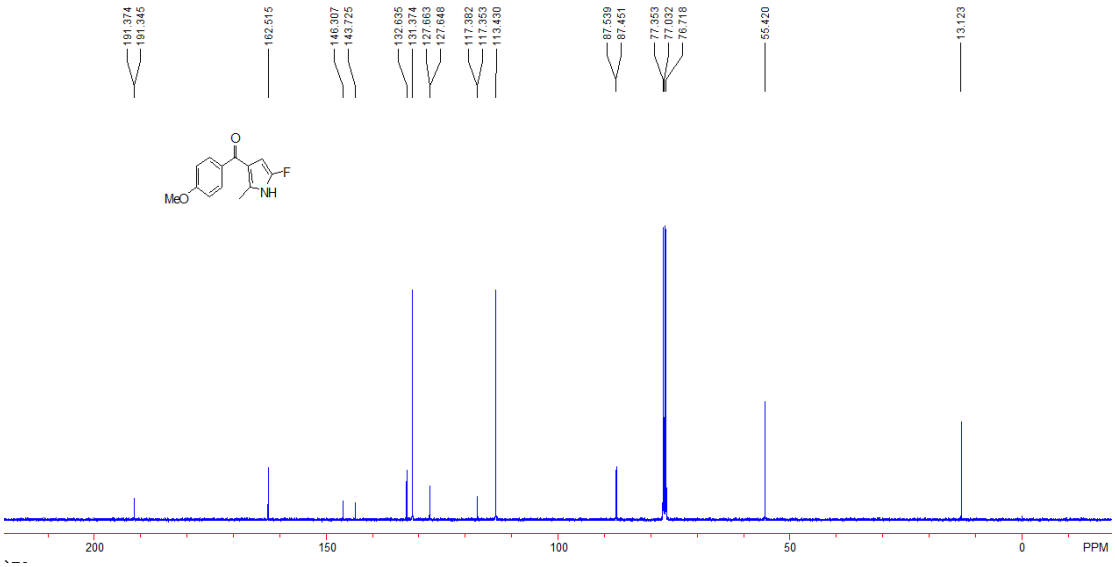
^{1}H NMR of **2c**



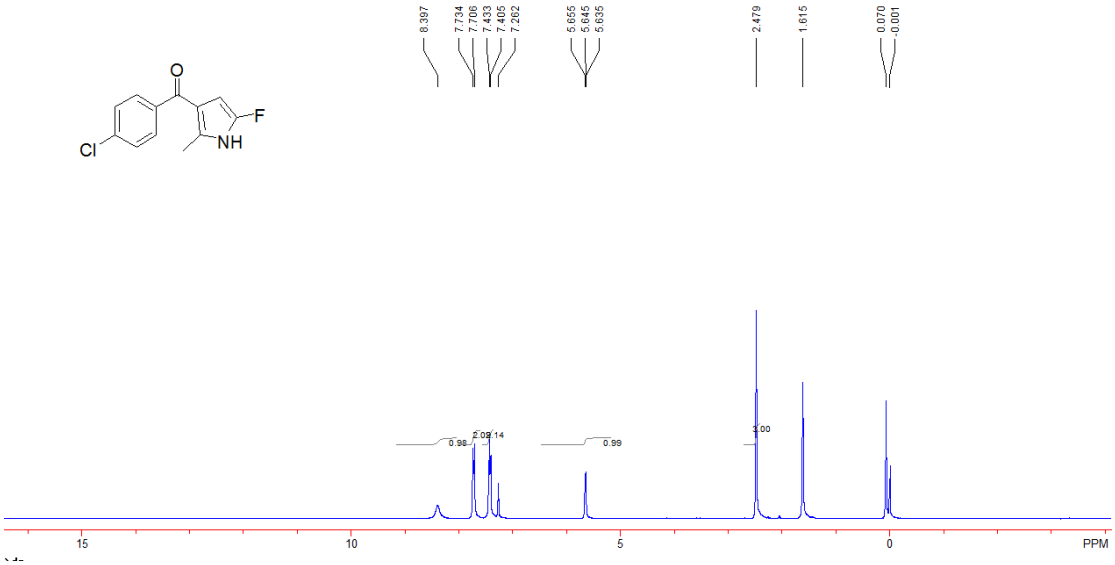
^{19}F NMR of **2c**



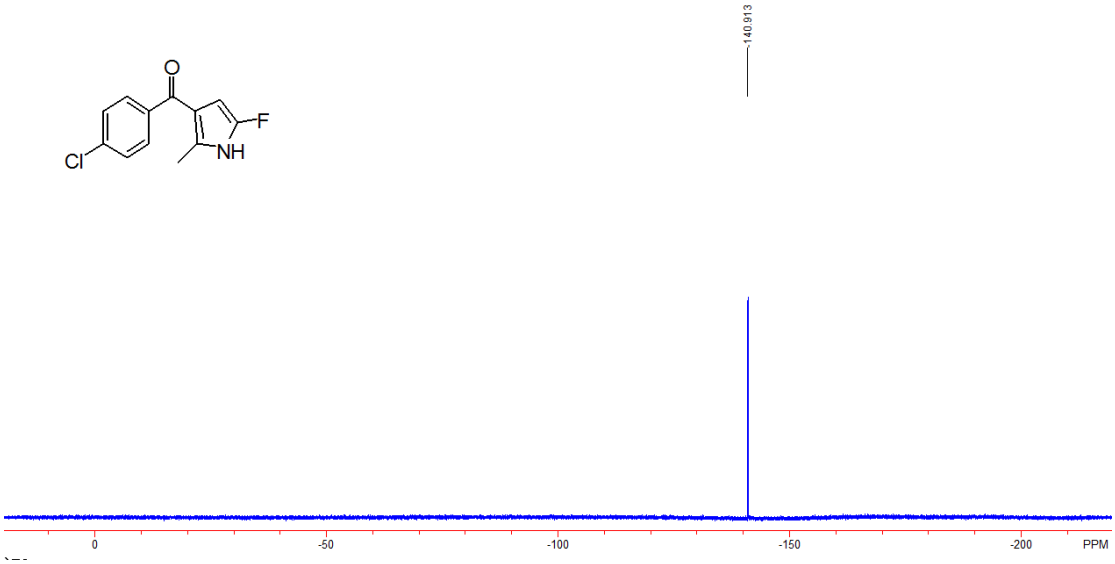
^{13}C NMR of **2c**



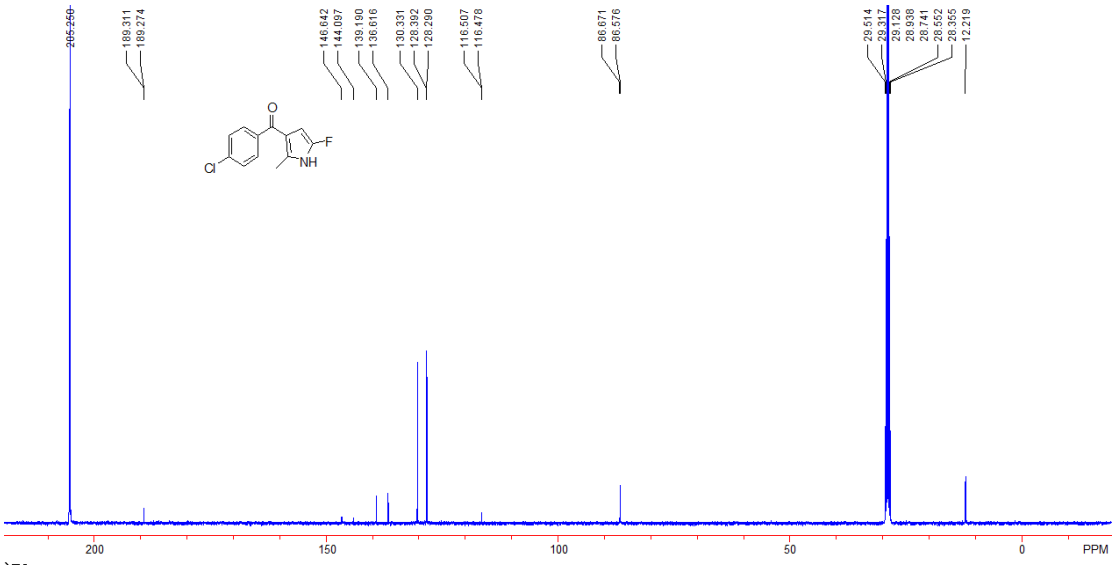
^{1}H NMR of **2d**



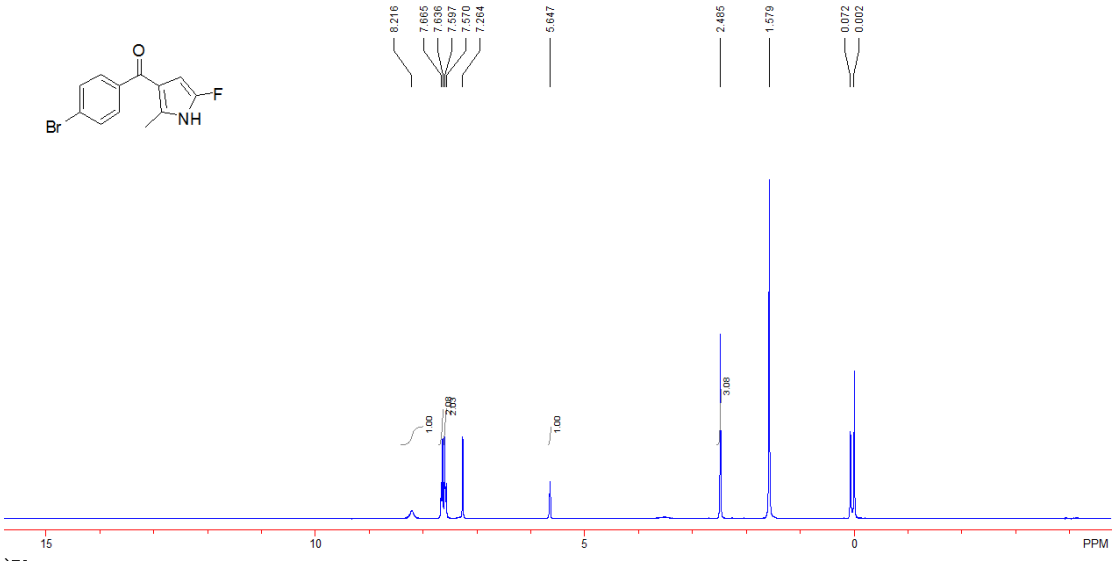
^{19}F NMR of **2d**



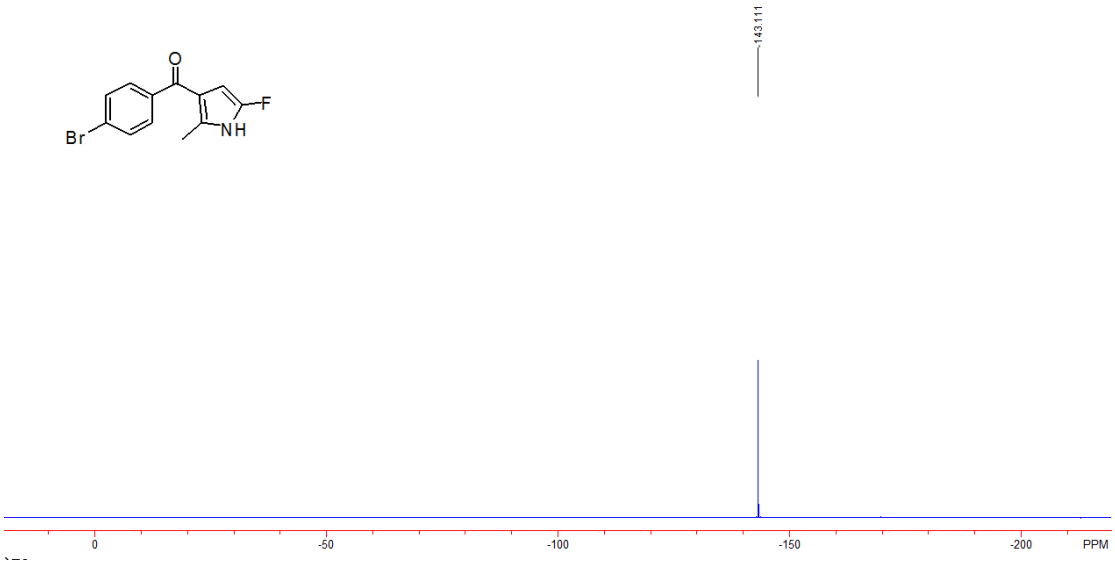
^{13}C NMR of **2d**



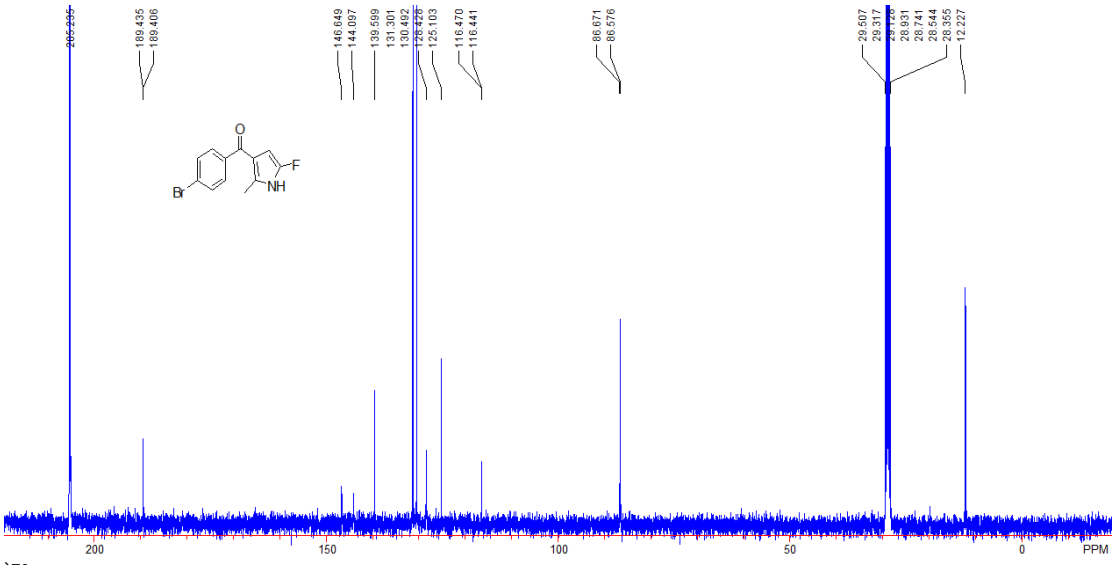
^{1}H NMR of **2e**



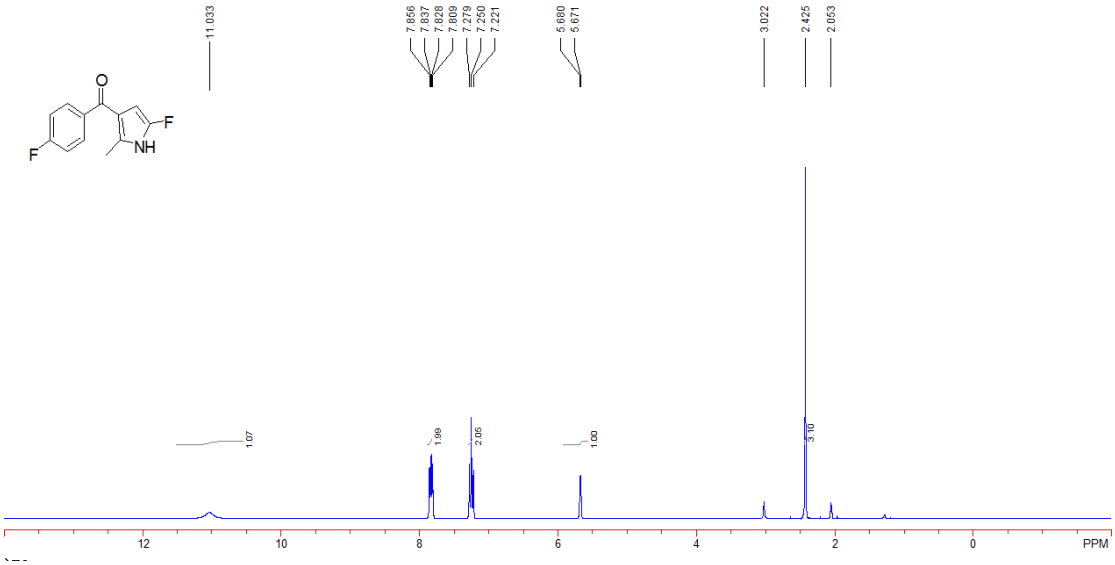
^{19}F NMR of **2e**



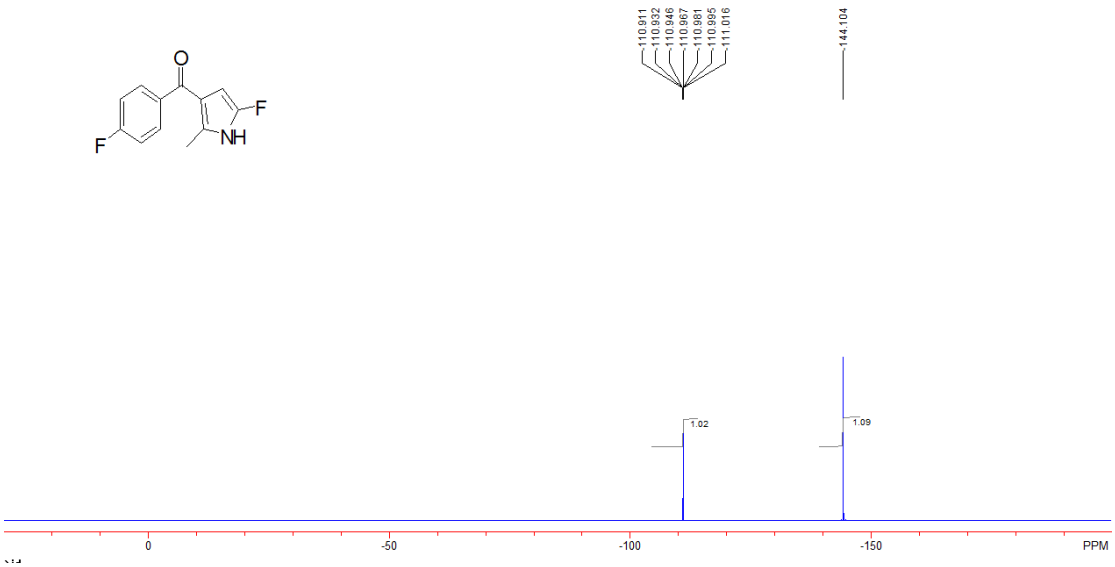
^{13}C NMR of **2e**



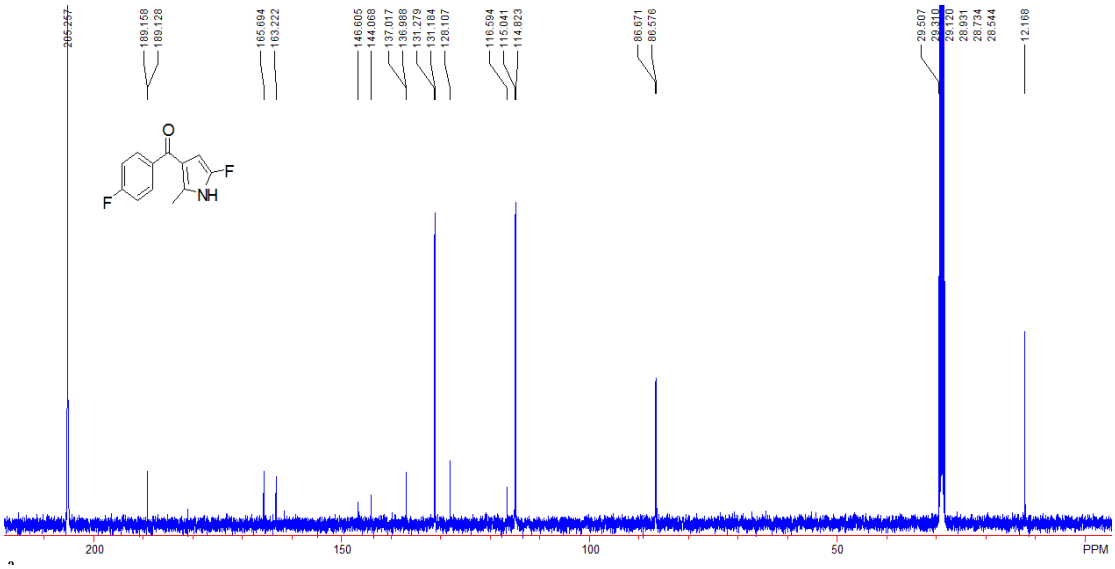
^{1}H NMR of **2f**



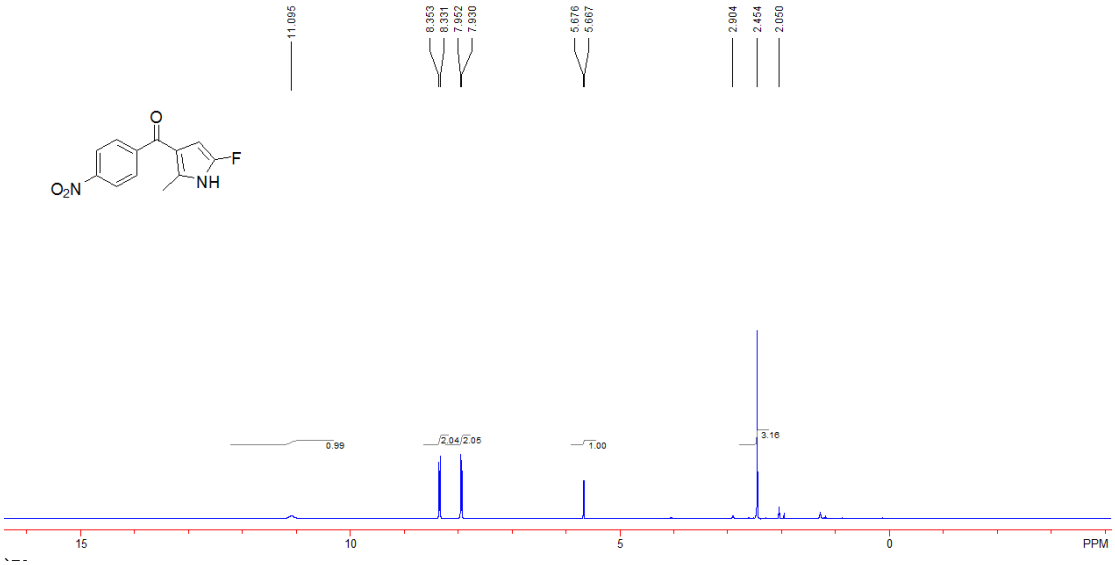
^{19}F NMR of **2f**



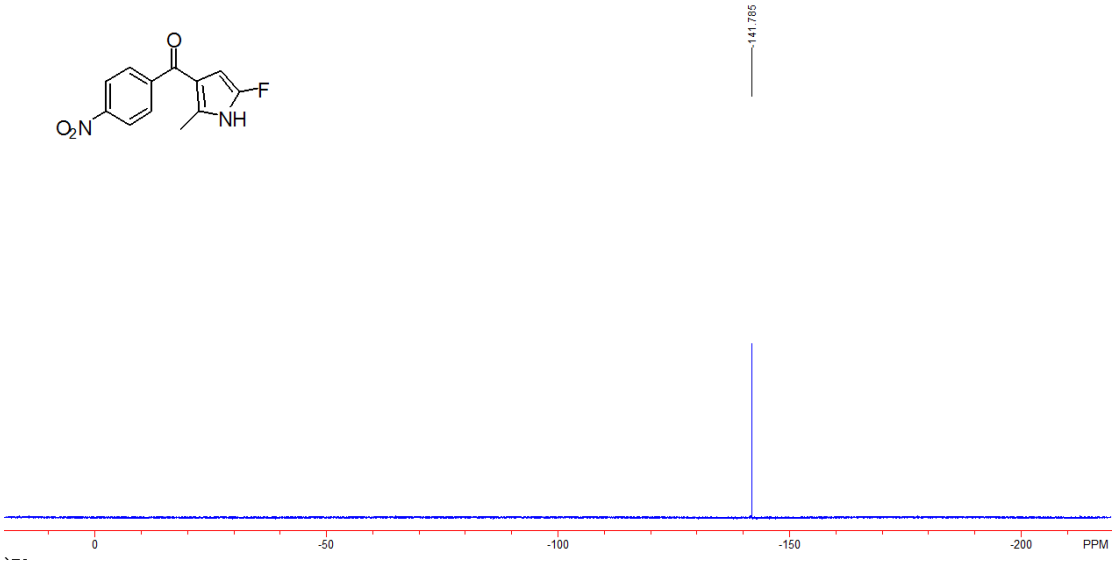
^{13}C NMR of **2f**



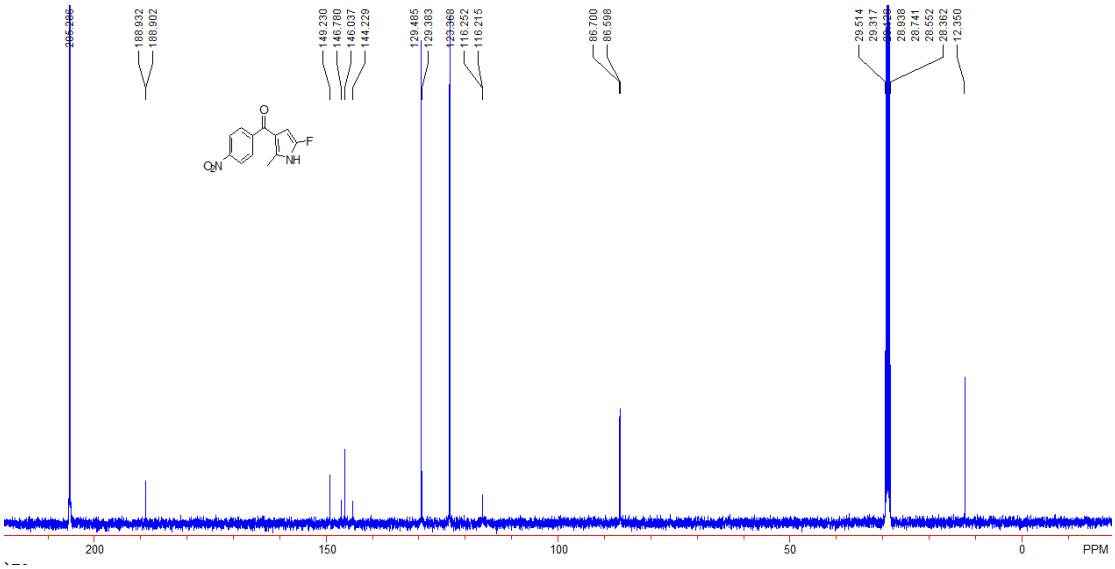
^{1}H NMR of **2g**



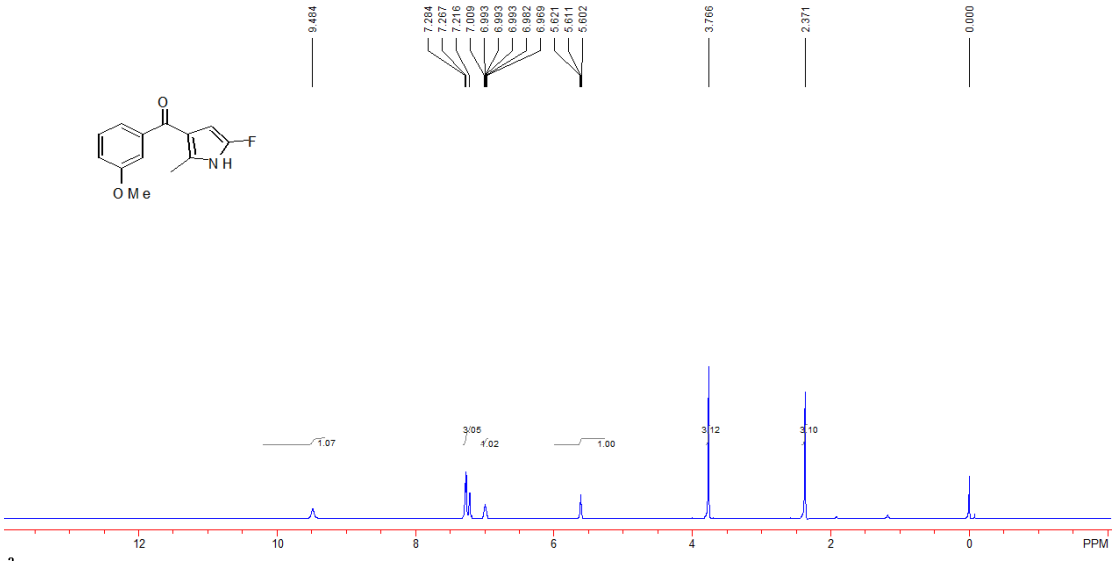
^{19}F NMR of **2g**



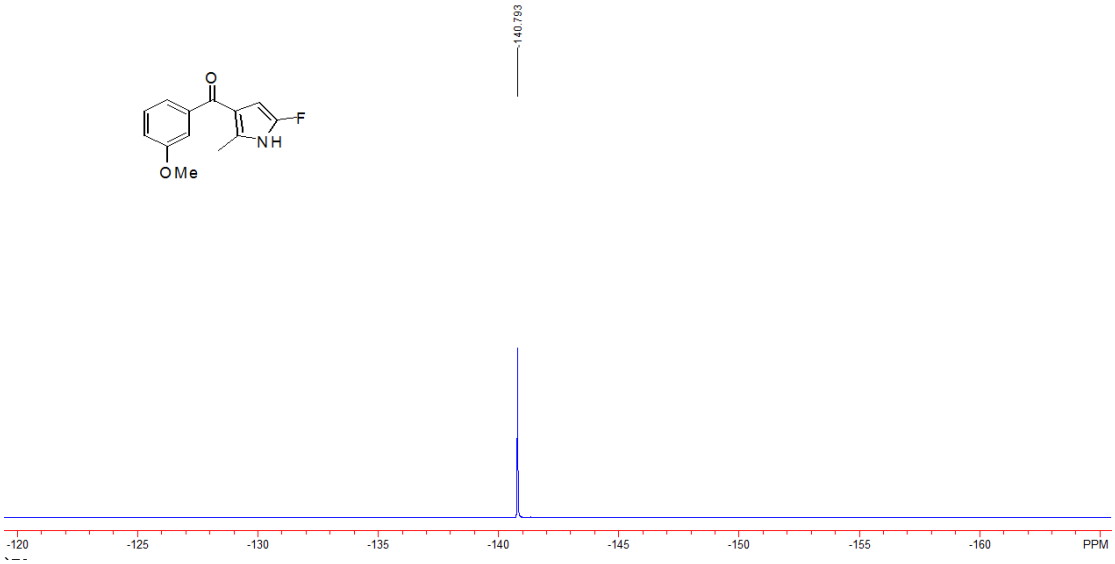
^{13}C NMR of **2g**



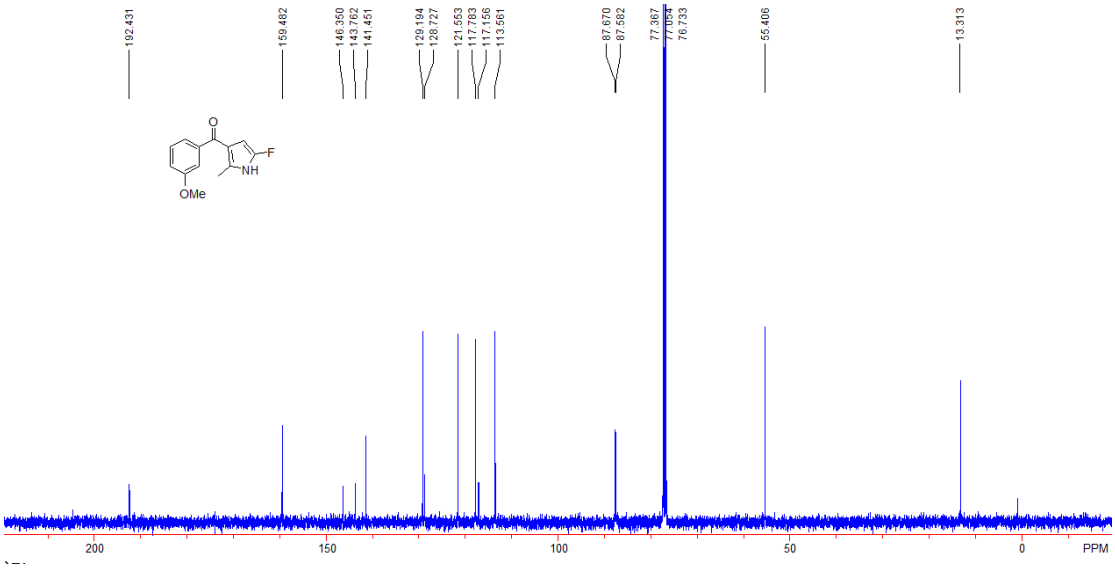
^{1}H NMR of **2h**



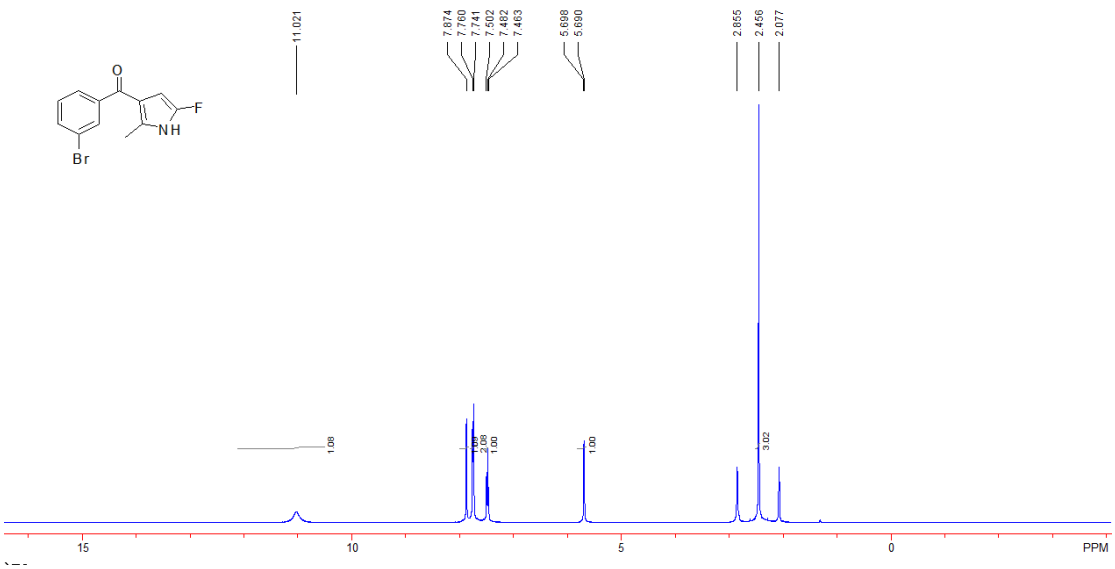
^{19}F NMR of **2h**



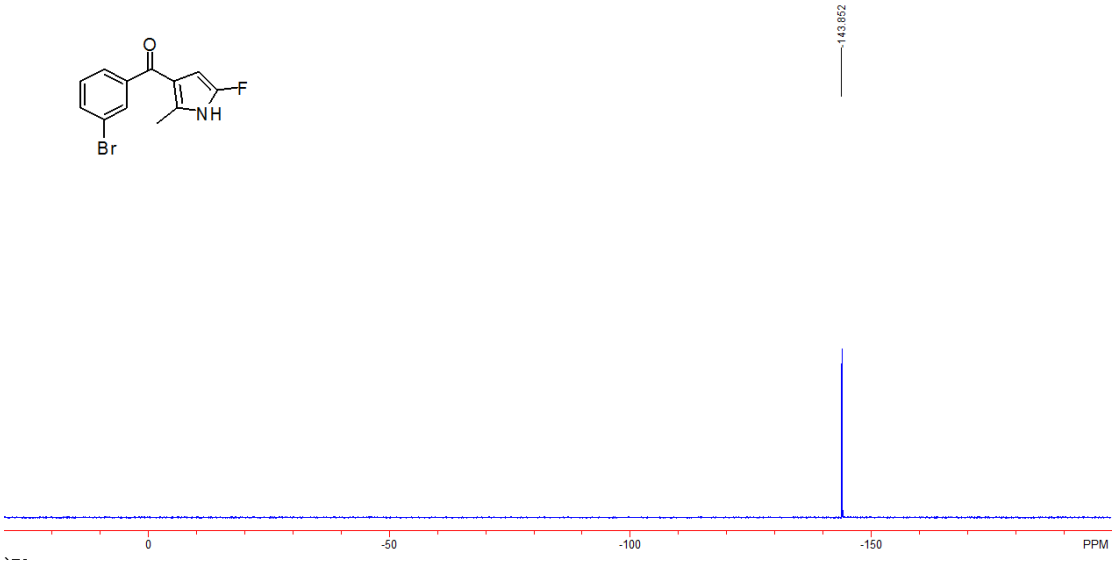
^{13}C NMR of **2h**



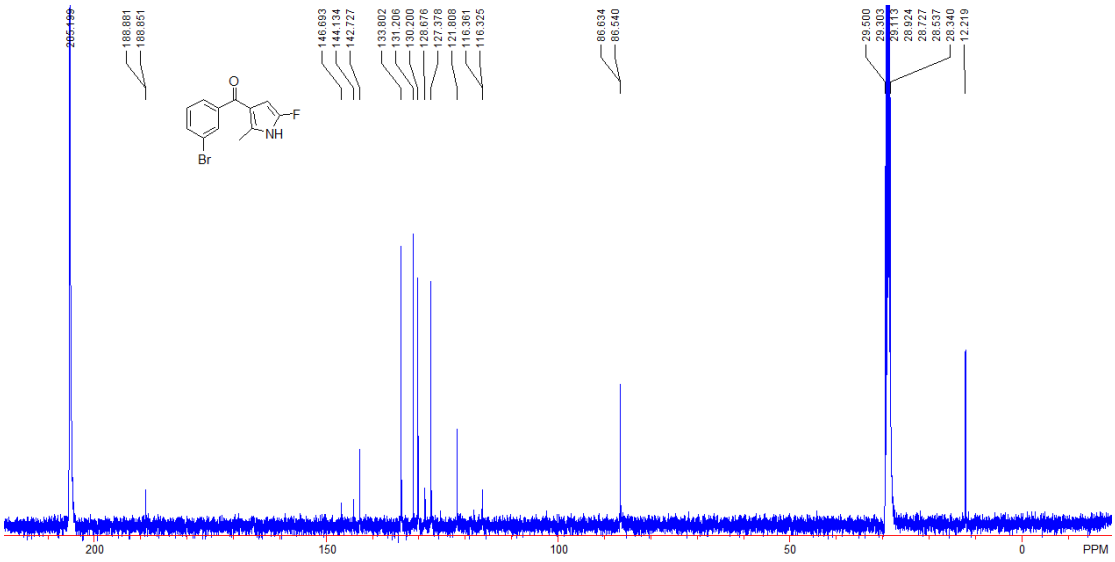
^{1}H NMR of **2i**



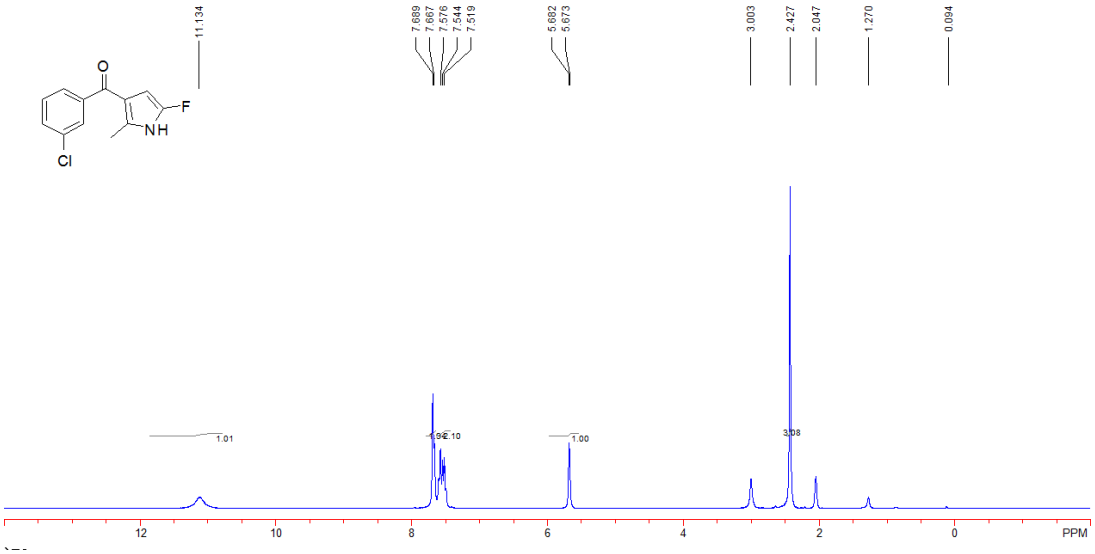
^{19}F NMR of **2i**



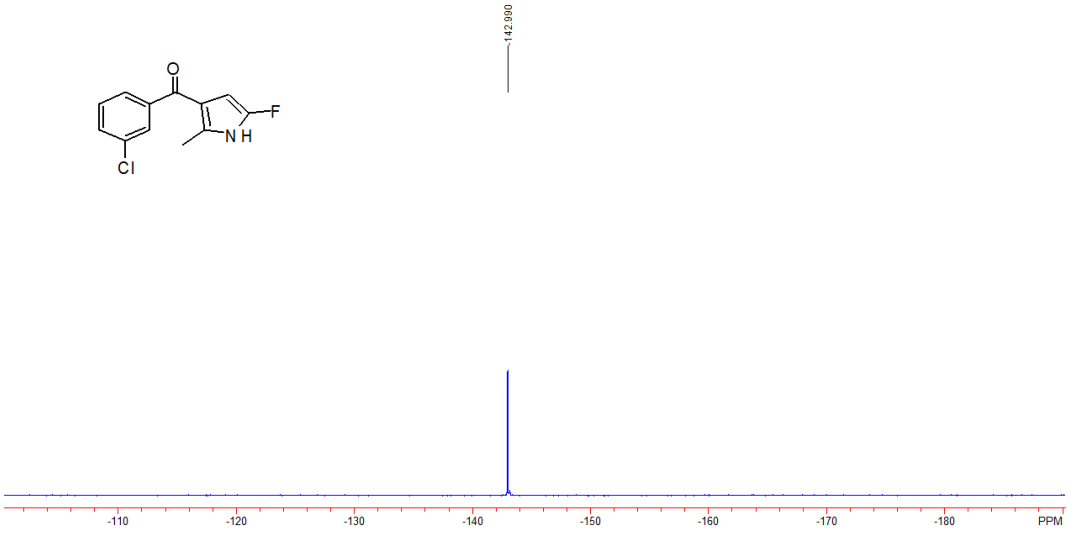
^{13}C NMR of **2i**



^{1}H NMR of **2j**



^{19}F NMR of **2j**



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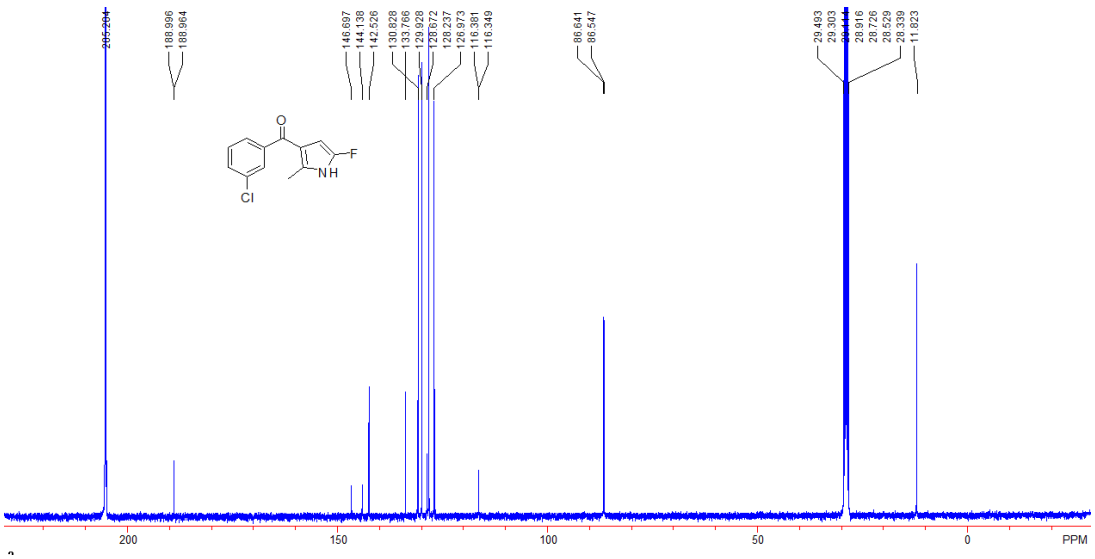

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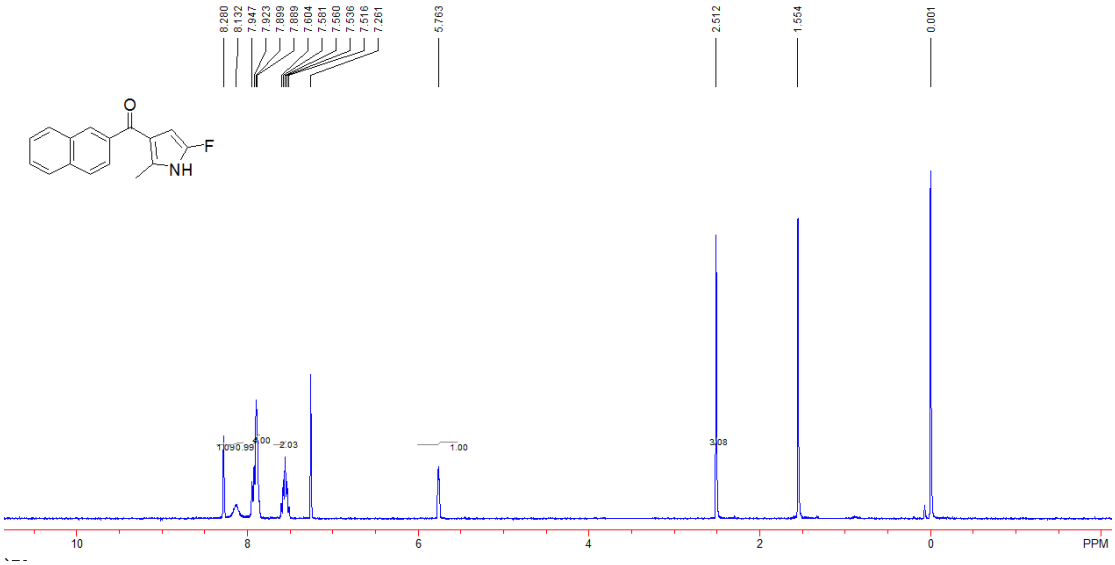
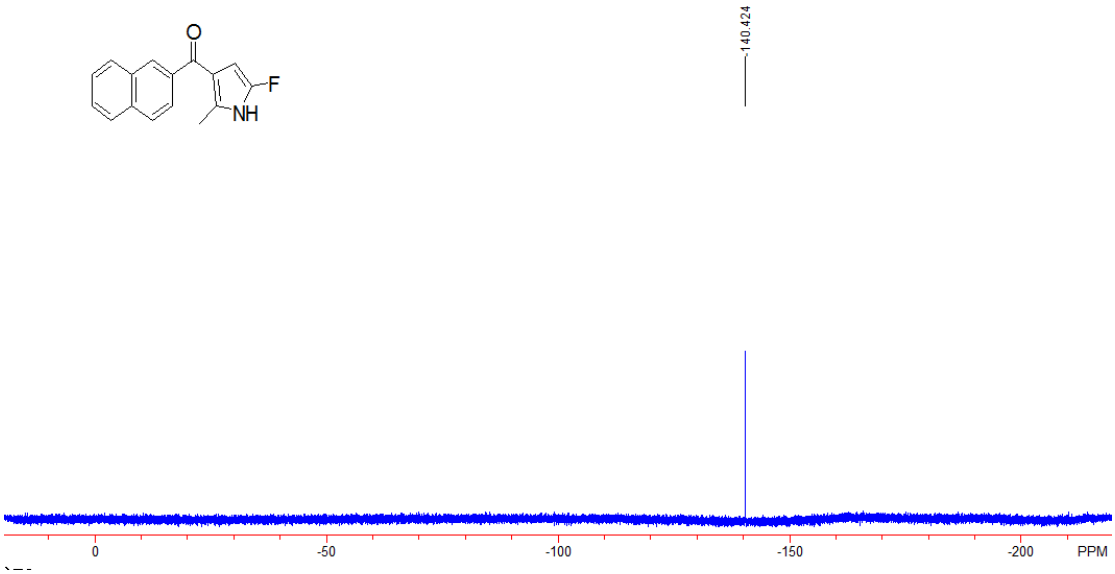


^{19}F NMR of **2k**



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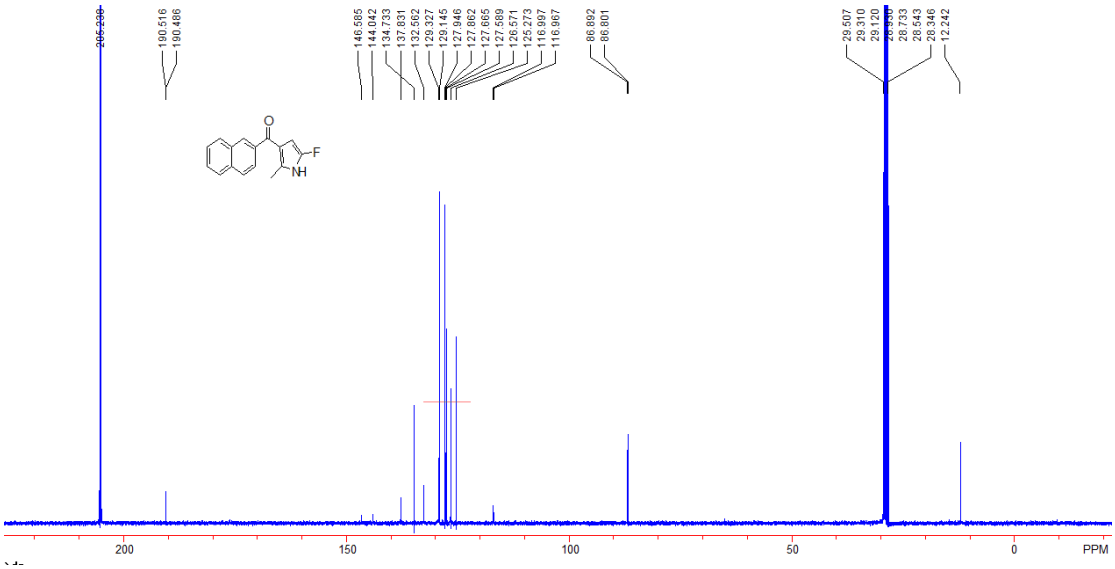
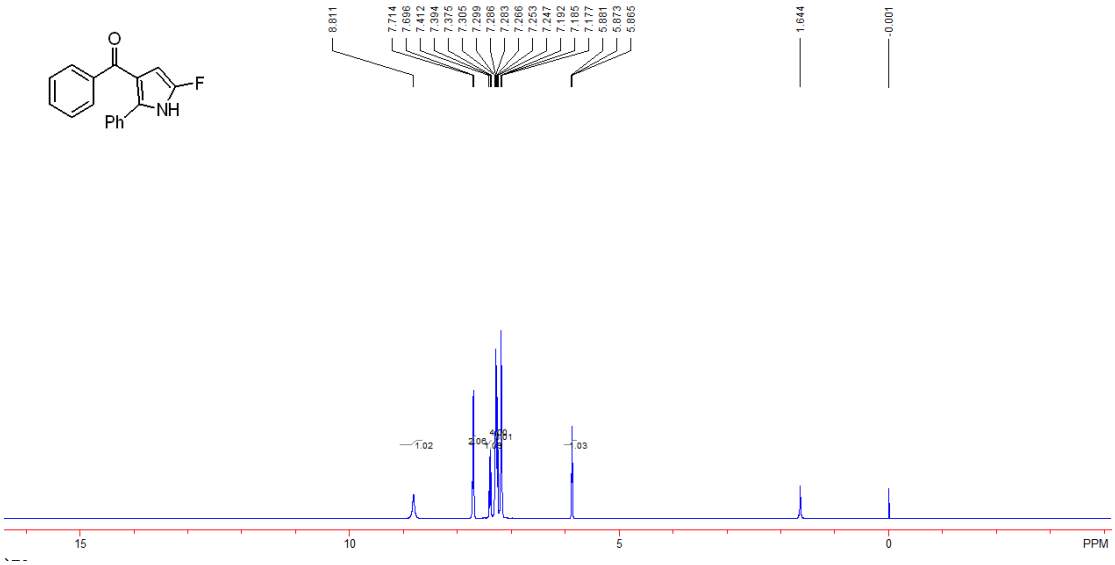
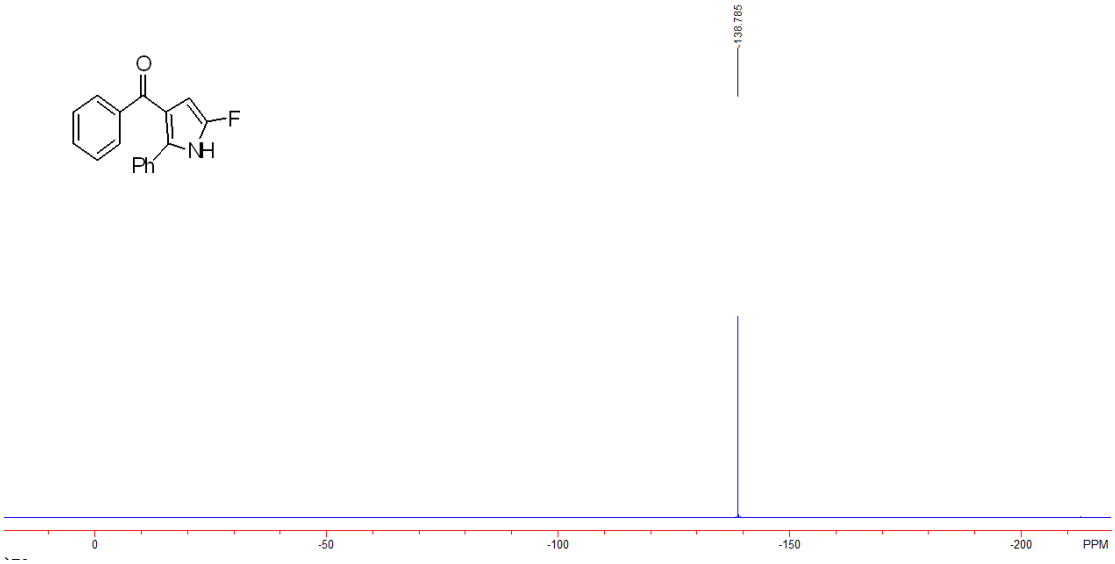


^{1}H NMR of **2l**



^{19}F NMR of **2l**



^{13}C NMR of **2l**