Supporting Information

for

Decarboxylative Cross-Coupling of Acyl Fluorides with Potassium Perfluorobenzoates

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1. General

Instrumentation

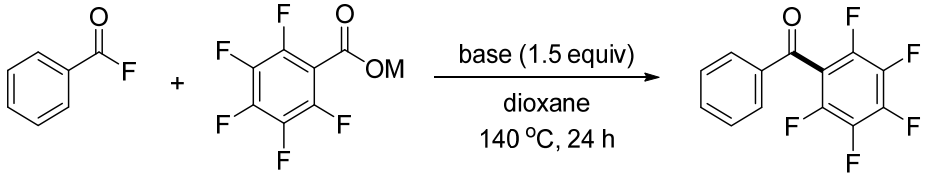
Unless otherwise noted, all the reactions were carried out under an Ar atmosphere using standard Schlenk techniques and heated in an oil bath. Solvents were employed as eluents for all other routine operation, as well as dehydrated solvent were purchased from commercial suppliers and employed without any further purification. Glassware was dried in an oven (130 °C) and heated under reduced pressure before use. For thin layer chromatography (TLC) analyses throughout this work, Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were used. Silica gel column chromatography was carried out using Silica gel 60 N (spherical, neutral, 40–100 μm) from Kanto Chemicals Co., Ltd. NMR spectra (^1H, $^{13}C\{^1H\}$, and $^{19}F\{^1H\}$) were recorded on Varian INOVA-600 (600 MHz) or Mercury-400 (400 MHz) spectrometers. Chemical shifts (δ) are in parts per million relative to $CDCl_3$ at 7.26 ppm for ^1H and at 77.16 ppm for $^{13}C\{^1H\}$, respectively. The $^{19}F\{^1H\}$ NMR spectra were measured by using CCl_3F (δ = 0.00 ppm) as an external standard. The GC yields were determined by GC analysis of the crude mixture, using *n*- tetradecane as an internal standard. GC analyses were performed on a Shimadzu GC-14A equipped with a flame ionization detector using Shimadzu Capillary Column (CBP1-M25-025) and Shimadzu C-R6A-Chromatopac integrator. Infrared spectra were recorded on a Shimadzu IR Prestige-21 spectrophotometer. Elemental analyses were carried out with a Perkin-Elmer 2400 CHN elemental analyzer at Okayama University. HRMS analyses were obtained by using a double focusing magnetic sector mass spectrometer (JEOL JMS-700 MStation).

Chemicals

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Benzoyl fluoride (**1a**) (purity > 98%) were purchased from TCI. 1,4-Dioxane (super dehydrated) was purchased from FUJIFILM Wako Pure Chem. Benzoic acid-α-^{13}C (99 atom % ^{13}C) was purchased from Sigma-Aldrich. Acyl fluorides **1a**-α-^{13}C, **1b**-**1z**[1] and benzoates **2b**-**2f**[2] were prepared according to the literatures and showed the identical spectra reported.

2. Optimization of Reaction Conditions

Table S1. Screening of benzoates and bases[a]

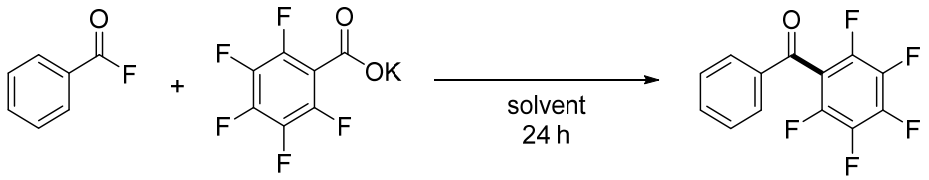


1a **2** (1.5 equiv) **3a**

entry	M	base	conversion[b] of **1a**/%	yield[b] of **3a**/%
1	H	K_2CO_3	100	2
2	H	K_3PO_4	100	0
3	H	KF	73	2
4	H	KO^{t}Bu	89	0
5	Li	-	100	0
6	Na	-	100	11
7	**K**	-	**100**	**85**

[a]Reactions were carried out with **1a** (0.2 mmol, 1.0 equiv), **2** (0.3 mmol, 1.5 equiv) and base (0.3 mmol, 1.5 equiv) in dioxane (1 mL) at 140 °C for 24 h. [b]GC yields, using *n*-tetradecane as the internal standard.

Table S2. Screening of solvent and temperature[a]

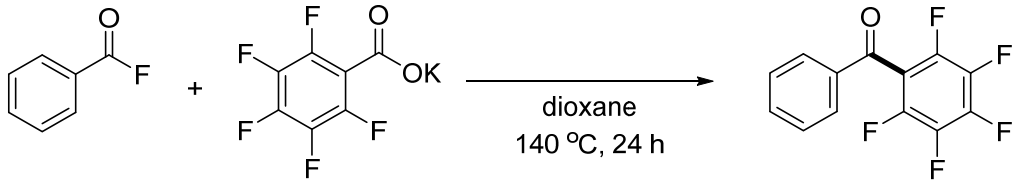


1a **2d** (1.5 equiv) **3a**

entry	solvent	T (°C)	conversion[b] of **1a**/%	yield[b] of **3a**/%
1	1,4-dioxane	25	56	0
2	1,4-dioxane	100	63	1
3	1,4-dioxane	110	67	5
4	1,4-dioxane	120	89	36
5	1,4-dioxane	130	100	68
6	1,4-dioxane	**140**	**100**	**85**
7	1,4-dioxane	150	100	70
8	toluene	150	75	0
9	acetone	80	100	0
10	THF	80	90	28
11	MeCN	80	100	53
12	MeCN	90	100	55
13	MeCN	100	100	52
14	MeCN	110	100	36
15	DME	110	100	0
16	DCE	110	64	0

[a]Reactions were carried out with **1a** (0.2 mmol, 1.0 equiv) and **2d** (0.3 mmol, 1.5 equiv) in solvent (1 mL) for 24 h. [b]GC yields, using *n*-tetradecane as the internal standard.

Table S3. Screening of ratios of substrates[a]

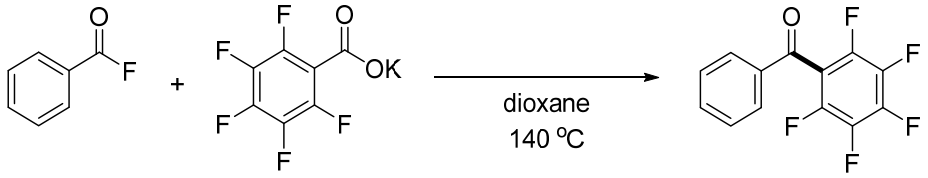


1 (x equiv) **2d** (y equiv) **3a**

entry	x	y	conversion[b] of **1a**/%	yield[b] of **3a**/%
1	1.5	1.0	82	54
2	1.0	1.0	100	66
3	1.0	1.2	100	78
4	**1.0**	**1.5**	**100**	**85**
5	1.0	2.0	100	56

[a]Reactions were carried out with **1a** and **2d** in dioxane (1 mL) at 140 °C for 24 h, 1.0 equiv equal to 0.2 mmol. [b]GC yields, using *n*-tetradecane as the internal standard.

Table S4. Optimization of reaction time[a]

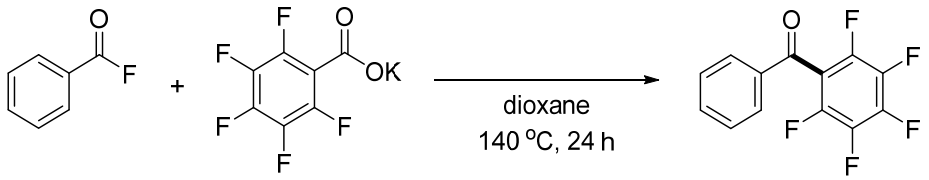


1a **2d** (1.5 equiv) **3a**

entry	time (h)	conversion[b] of **1a**/%	yield[b] of **3a**/%
1	3	88	52
2	6	100	74
3	**12**	**100**	**85 (82[c])**
4	24	100	85

[a]Reactions were carried out with **1a** (0.2 mmol, 1.0 equiv) and **2d** (0.3 mmol, 1.5 equiv) in dioxane (1 mL) at 140 °C. [b]GC yields, using *n*-tetradecane as the internal standard. [c]An isolated yield by using column chromatography.

Table S5. Control experiments[a]



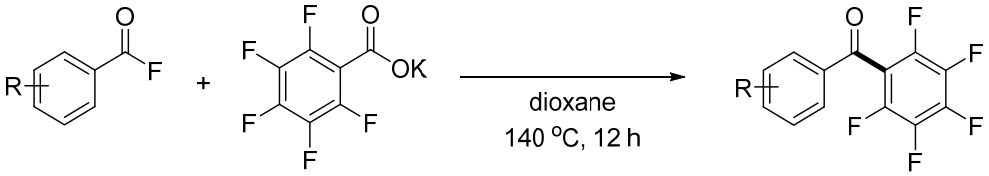
1a **2d** (1.5 equiv) **3a**

entry	Deviations from the standard conditions	conversion[b] of **1a**/%	yield[b] of **3a**/%
1	**None**	**100**	**85**
2	in Air	85	40
3	benzoyl chloride instead of **1a**	100	43
4	TEMPO (1.0 equiv)	100	64
5	18-crown-6 (1.0 equiv)	100	2
6[c]	10 mol % $Pd(OAc)_2$/20 mol % PPh_3	100	61
7[c]	10 mol % $Ni(cod)_2$/20 mol % PPh_3	100	60
8[c]	10 mol % CuI/10 mol % Phen	100	64

[a]Reactions were carried out with **1a** (0.2 mmol, 1.0 equiv) and **2d** (0.3 mmol, 1.5 equiv) in dioxane (1 mL) at 140 °C for 24 h. [b]GC yields, using *n*-tetradecane as the internal standard. [c]130 ºC.

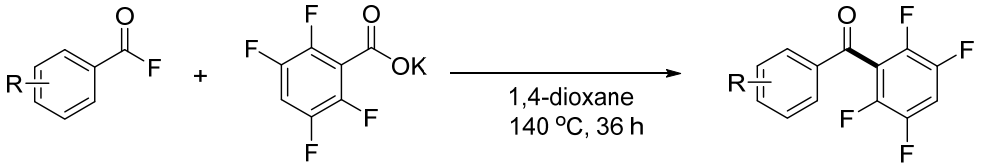
3. Experimental Procedures and Spectroscopic Data for the Products

3.1 General procedure for decarboxylative cross-coupling of acyl fluorides 1 with potassium perfluorobenzoates 2.



1 **2d** (1.5 equiv) **3**

Method A: An oven-dried Schlenk tube (25 mL) containing a magnetic stirring bar was charged with acyl fluoride **1** (0.2 mmol, 1.0 equiv) and potassium pentafluorobenzoates **2d** (0.3 mmol, 1.5 equiv) in 1,4-dioxane (1 mL) under argon. The mixture was heated at 140 ºC with stirring for 12 h. After being at room temperature, the mixture was quenched with saturated NH_4Cl and the aqueous solution was extracted with Et_2O. The combined organic extracts were dried over anhydrous $MgSO_4$, then filtered and evaporated under vacuum to obtain the crude product which was purified by column chromatography (Et_2O/hexane) on silica gel to afford the desired products **3**.

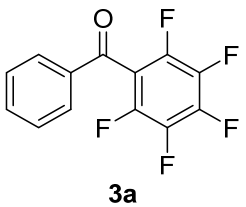


1 **2e** (1.5 equiv) **3z, 3aa, 3ab**

Method B: An oven-dried Schlenk tube (25 mL) containing a magnetic stirring bar was charged with acyl fluoride **1** (0.2 mmol, 1.0 equiv) and potassium perfluorobenzoates **2** (0.3 mmol, 1.5 equiv) in 1,4-dioxane (2 mL) under argon. The mixture was heated at 140 ºC with stirring for 36 h. After being at room temperature, the mixture was quenched with saturated NH_4Cl and the aqueous solution was extracted with Et_2O. The combined organic extracts were dried over anhydrous $MgSO_4$, then filtered and evaporated under vacuum to obtain the crude product which was purified by column chromatography (Et_2O/hexane) on silica gel to afford the desired products **3z**, **3aa**, or **3ab**.

3.2 Spectroscopic Data for the Products.

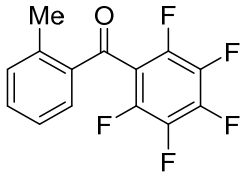
(Pentafluorophenyl)(phenyl)methanone (3a)[3]



3a

Colorless oil. R_f = 0.35 (Et_2O:hexane = 1:20). Isolated yield is 82% (44.7 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 7.86-7.84 (m, 2H), 7.71-7.66 (m, 1H), 7.55-7.51 (m, 2H); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, rt): δ –140.2 (m), –150.8 (m), –160.2 (m).

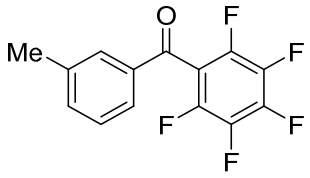
(2-Methylphenyl)(pentafluorophenyl)methanone (3b)[3]



3b

White solid. R_f = 0.45 (Et_2O:hexane = 1:20). Isolated yield is 78% (44.6 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 7.50 (td, J = 7.6, 1.2 Hz, 1H), 7.43 (d, J = 8.4 Hz, 1H), 7.36 (d, J = 7.6 Hz, 1H), 7.30-7.27 (m, 1H), 2.66 (s, 3H); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, rt): δ –141.0 (m), –151.0 (m), –160.4 (m).

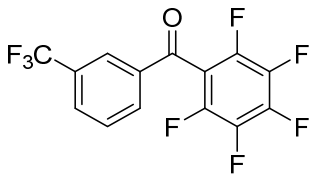
(3-Methylphenyl)(pentafluorophenyl)methanone (3c)[3]



3c

Colorless oil. R_f = 0.38 (Et_2O:hexane = 1:20). Isolated yield is 87% (49.6 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 7.67 (s, 1H), 7.61 (d, J = 7.6 Hz, 1H), 7.50 (d, J = 7.6 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 2.43 (s, 3H); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, rt): δ –140.3 (m), –150.9 (m), –160.2 (m).

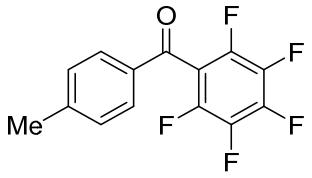
(Pentafluorophenyl)(3-(trifluoromethyl)phenyl)methanone (3d)[3]



3d

Colorless oil. R_f = 0.32 (Et_2O:hexane = 1:20). Isolated yield is 82% (55.7 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 8.12 (s, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.69 (t, J = 7.8 Hz, 1H); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, rt): δ –63.3 (s), –139.8 (m), –149.2 (m), –159.5 (m).

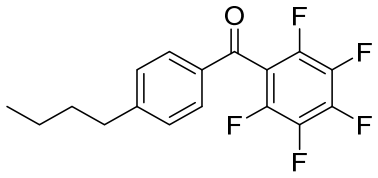
(4-Methylphenyl)(pentafluorophenyl)methanone (3e)[3]



3e

White solid. R_f = 0.40 (Et_2O:hexane = 1:20). Isolated yield is 83% (47.3 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 2.46 (s, 3H); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, rt): δ –140.3 (m), –151.1 (m), –160.3 (m).

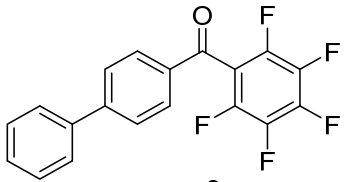
(4-Butylphenyl)(pentafluorophenyl)methanone (3f)[4]



3f

Colorless oil. R_f = 0.42 (Et_2O:hexane = 1:20). Isolated yield is 83% (54.4 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.8 Hz, 2H), 2.70 (t, J = 7.8 Hz, 2H), 1.67-1.59 (m, 2H), 1.42-1.32 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, rt): δ –140.4 (m), –151.2 (m), –160.3 (m).

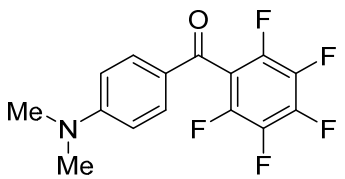
[1,1'-Biphenyl]-4-yl(pentafluorophenyl)methanone (3g)[3]



3g

White solid. R_f = 0.36 (Et_2O:hexane = 1:20). Isolated yield is 87% (60.4 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, J = 8.8 Hz, 2H), 7.74 (d, J = 8.4 Hz, 2H), 7.65-7.63 (m, 2H), 7.52-7.42 (m, 3H); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, rt): δ –140.1 (m), –150.7 (m), –160.1 (m).

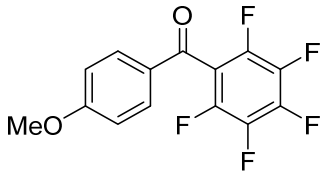
(4-(Dimethylamino)phenyl)(pentafluorophenyl)methanone (3h)[3]



3h

Yellow solid. R_f = 0.23 (Et_2O:hexane = 1:5). Isolated yield is 88% (55.9 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.8 Hz, 2H), 6.75 (d, J = 9.2 Hz, 2H), 3.12 (s, 6H); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, rt): δ –140.8 (m), –152.6 (m), –160.8 (m).

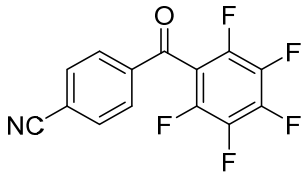
(4-Methoxyphenyl)(pentafluorophenyl)methanone (3i)[3]



3i

White solid. R_f = 0.36 (Et_2O:hexane = 1:5). Isolated yield is 93% (56.3 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J = 8.8 Hz, 2H), 6.98 (d, J = 9.2 Hz, 2H), 3.91 (s, 3H); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, rt): δ –140.5 (m), –151.5 (m), –160.3 (m).

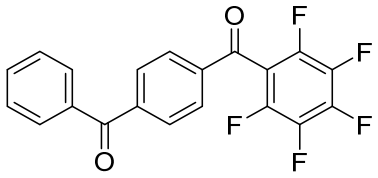
4-(Pentafluorobenzoyl)benzonitrile (3j)



3j

Colorless oil. R_f = 0.43 (Et_2O:hexane = 1:5). Isolated yield is 97% (57.8 mg). ^1H NMR (600 MHz, $CDCl_3$): δ 7.95 (d, J = 8.4 Hz, 2H), 7.84 (d, J = 9.0 Hz, 2H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 184.2, 144.2 (dm), 143.2 (dm), 138.9, 137.9 (dm), 133.0, 130.0, 118.2, 117.6, 112.9 (m); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, rt): δ –139.4 (m), –148.5 (m), –159.2 (m). FT-IR (cm^{-1}): 2235, 1690, 1653, 1605, 1518, 1416, 1321, 1294, 1229, 1180, 1113, 999, 964, 960, 931, 902, 765, 727, 627, 544. Anal. Calcd for $C_{14}H_4F_5NO$: C, 56.58; H, 1.36; N, 4.71%; Found: C, 56.56; H, 1.40; N, 4.61%.

(4-Benzoylphenyl)(pentafluorophenyl)methanone (3k)

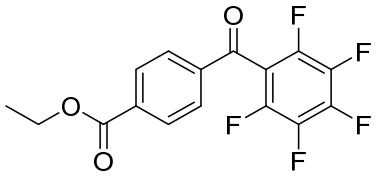


3k

White solid. Melting point: 149-150 °C. R_f = 0.32 (Et_2O:hexane = 1:10). Isolated yield is 92% (69.5 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, J = 8.4 Hz, 2H), 7.92-7.89 (m, 2H), 7.83-7.81 (m, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 195.6, 184.9, 144.1 (dm), 143.1,

142.9 (dm), 138.4, 137.8 (dm), 136.6, 133.4, 130.4, 130.3, 129.6, 128.7, 113.6 (m); $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$, rt): δ –139.7 (m), –149.6 (m), –159.6 (m). FT-IR (cm^{-1}): 1676, 1659, 1524, 1491, 1323, 1234, 1115, 999, 980, 735, 702, 690. Anal. Calcd for $C_{20}H_9F_5O_2$: C, 63.84; H, 2.41%; Found: C, 63.91; H, 2.69%.

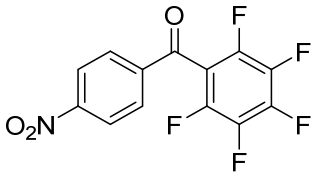
Ethyl 4-(pentafluorobenzoyl)benzoate (3l)[5]



3l

White solid. R_f = 0.35 (Et_2O:hexane = 1:10). Isolated yield is 97% (66.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, J = 8.8 Hz, 2H), 7.90 (d, J = 8.4 Hz, 2H), 4.43 (q, J = 7.2 Hz, 2H), 1.42 (t, J = 7.0 Hz, 3H); $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$, rt): δ –139.8 (m), –149.6 (m), –159.7 (m).

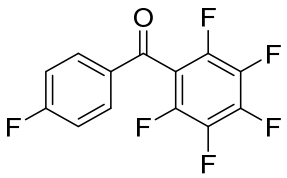
(4-Nitrophenyl)(pentafluorophenyl)methanone (3m)[6]



3m

Yellow solid. R_f = 0.53 (Et_2O:hexane = 1:5). Isolated yield is 76% (47.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (d, J = 8.8 Hz, 2H), 8.02 (d, J = 9.2 Hz, 2H); $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$, rt): δ –139.0 (m), –147.9 (m), –158.7 (m).

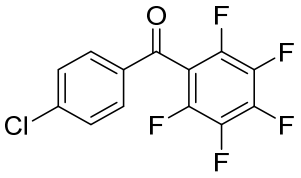
(4-Fluorophenyl)(pentafluorophenyl)methanone (3n)[3]



3n

Colorless oil. R_f = 0.35 (Et_2O:hexane = 1:20). Isolated yield is 95% (55.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90-7.87 (m, 2H), 7.23-7.18 (m, 2H); $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$, rt): δ –101.4 (s), –140.1 (m), –150.3 (m), –159.9 (m).

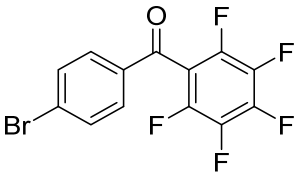
(4-Chlorophenyl)(pentafluorophenyl)methanone (3o)[3]



3o

White solid. R_f = 0.39 (Et_2O:hexane = 1:20). Isolated yield is 85% (52.3 mg). ^1H NMR (600 MHz, $CDCl_3$): δ 7.79 (d, J = 9.0 Hz, 2H), 7.51 (d, J = 9.0 Hz, 2H); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, rt): δ –140.0 (m), –150.0 (m), –159.7 (m).

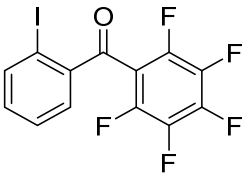
(4-Bromophenyl)(pentafluorophenyl)methanone (3p)[6]



3p

White solid. R_f = 0.44 (Et_2O : hexane = 1:20). Isolated yield is 86% (60.7 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 7.72-7.66 (m, 4H); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, rt): δ –139.9 (m), –149.9 (m), –159.7 (m).

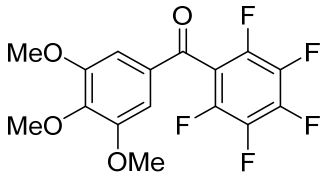
(2-Iodophenyl)(pentafluorophenyl)methanone (3q)



3q

Pale yellow oil. R_f = 0.46 (Et_2O : hexane = 1:20). Isolated yield is 96% (76.2 mg). ^1H NMR (600 MHz, $CDCl_3$): δ 8.01 (dd, J = 8.7, 0.9 Hz, 1H), 7.51-7.46 (m, 2H), 7.26-7.24 (m, 1H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$*):* δ 186.9, 145.1 (dm), 143.9 (dm), 141.7, 141.5, 137.8 (dm), 133.8, 131.2, 128.6, 110.1 (m), 92.5; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, rt): δ –139.3 (m), –148.4 (m), –160.4 (m). FT-IR (cm^{-1}): 1682, 1650, 1580, 1528, 1487, 1393, 1329, 1242, 1121, 1009, 995, 984, 824, 793. Anal. Calcd for $C_{13}H_4F_5IO$: C, 39.22; H, 1.01. Found: C, 39.62; H, 0.91.

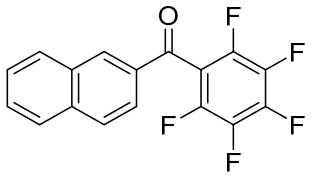
(Pentafluorophenyl)(3,4,5-trimethoxyphenyl)methanone (3r)[3]



3r

White solid. R_f = 0.33 (Et_2O:hexane = 1:5). Isolated yield is 95% (68.7 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 7.08 (s, 2H), 3.97 (s, 3H), 3.88 (s, 6H); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, rt): δ –140.2 (m), –150.6 (m), –159.9 (m).

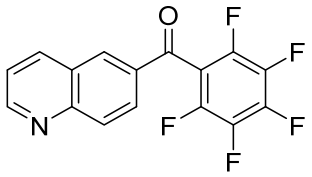
Naphthalen-2-yl(pentafluorophenyl)methanone (3s)



3s

White solid. Melting point: 69-71 °C. R_f = 0.30 (Et_2O:hexane = 1:20). Isolated yield is 97% (62.7 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 8.23 (s, 1H), 8.03-7.91 (m, 4H), 7.69-7.65 (m, 1H), 7.61-7.57 (m, 1H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$)*:* δ 185.3, 144.0 (dm), 142.6 (dm), 137.8 (dm), 136.6, 133.6, 133.1, 132.5, 123.0, 129.8, 129.3, 128.1, 127.5, 123.9, 114.3 (m); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, rt): δ –140.1 (m), –150.7 (m), –160.0 (m). FT-IR (cm^{-1}): 1670, 1626, 1522, 1500, 1354, 1321, 1225, 1190, 1132, 1100, 999, 995, 810, 800. Anal. Calcd for $C_{17}H_7F_5O$: C, 63.37; H, 2.19%; Found: C, 63.54; H, 2.27%.

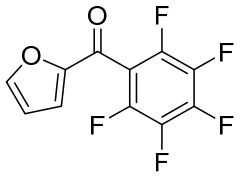
(Pentafluorophenyl)(quinolin-6-yl)methanone (3t)



3t

White solid. Melting point: 113-114 °C. R_f = 0.28 (Et_2O:hexane = 1:1). Isolated yield is 99% (63.9 mg). ^1H NMR (600 MHz, $CDCl_3$): δ 9.06 (dd, J = 4.2, 1.8 Hz, 1H), 8.28-8.21 (m, 4H), 7.52 (dd, J = 8.4, 4.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$)*:* δ 184.7, 153.6, 150.8, 144.0 (dm), 142.8 (dm), 138.0, 137.8 (dm), 134.0, 132.6, 131.0, 127.8, 127.6, 122.6, 113.8 (m); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, rt): δ –139.8 (m), –149.8 (m), –159.6 (m). FT-IR (cm^{-1}): 1684, 1620, 1518, 1495, 1356, 1318, 1231, 1175, 1123, 1105, 988, 916, 781. Anal. Calcd for $C_{16}H_6F_5NO$: C, 59.46; H, 1.87; N, 4.33%; Found: C, 59.34; H, 1.74; N, 4.32%.

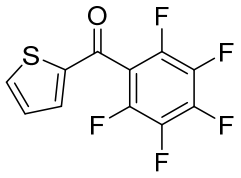
Furan-2-yl(pentafluorophenyl)methanone (3u)[6]



3u

Orange oil. R_f = 0.40 (Et_2O : hexane = 1:5). Isolated yield is 83% (43.3 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 7.71-7.71 (m, 1H), 7.30-7.29 (m, 1H), 6.66-6.65 (m, 1H); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, rt): δ –140.1 (m), –149.9 (m), –160.0 (m).

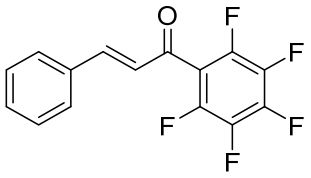
(Pentafluorophenyl)(thiophen-2-yl)methanone (3v)[6]



3v

Purple oil. R_f = 0.35 (Et_2O:hexane = 1:10). Isolated yield is 72% (39.8 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 7.87-7.86 (m, 1H), 7.54-7.52 (m, 1H), 7.20-7.18 (m, 1H); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, rt): δ –140.2 (m), –150.5 (m), –159.9 (m).

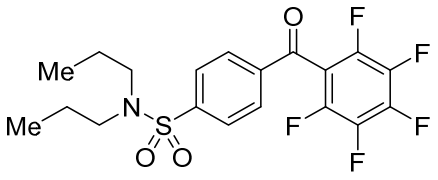
1-(Pentafluorophenyl)-3-phenylprop-2-en-1-one (3w)[7]



3w

White solid. R_f = 0.30 (Et_2O:hexane = 1:20). Isolated yield is 88% (52.6 mg). ^1H NMR (600 MHz, $CDCl_3$): δ 7.59 (d, J = 6.6 Hz, 2H), 7.53 (d, J = 16.2 Hz, 1H), 7.48-7.42 (m, 3H), 7.04 (d, J = 16.2 Hz, 1H); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, rt): δ –140.8 (m), –150.5 (m), –160.2 (m).

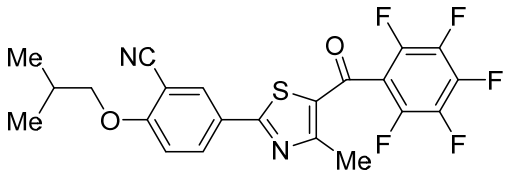
4-(Pentafluorobenzoyl)-N,N-dipropylbenzenesulfonamide (3x)



3x

White solid. Melting point: 72-73 °C. R_f = 0.40 (Et_2O:hexane = 1:5). Isolated yield is 87% (75.5 mg). ^1H NMR (600 MHz, $CDCl_3$): δ 7.94 (m, 4H), 3.13-3.10 (m, 4H), 1.58-1.52 (m, 4H), 0.86 (t, J = 7.5 Hz, 6H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$*): δ* 184.4, 146.1, 144.1 (dm), 143.1 (dm), 138.5, 137.9 (dm), 130.3, 113.3 (m), 127.7, 50.1, 22.1, 11.2; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, rt): δ –139.6 (m), –149.1 (m), –159.5 (m). FT-IR (cm^{-1}): 2976, 2940, 2880, 1686, 1522, 1503, 1344, 1317, 1233, 1159, 990, 610. HRMS (FAB^+): Calcd for $C_{19}H_{19}F_5NO_3S^+$: 436.1000. Found: 436.1004 $[M+H]^+$.

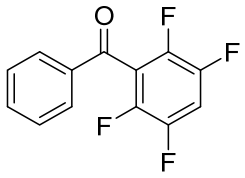
2-Isobutoxy-5-(4-methyl-5-(pentafluorobenzoyl)thiazol-2-yl)benzonitrile (3y)



3y

White solid. Melting point: 156-158 °C. R_f = 0.34 (Et_2O:hexane = 1:5). Isolated yield is 81% (75.5 mg). ^1H NMR (600 MHz, $CDCl_3$): δ 8.19 (d, J = 2.4 Hz, 1H), 8.10 (dd, J = 9.0, 2.4 Hz, 1H), 7.02 (d, J = 9.0 Hz, 1H), 3.91 (d, J = 6.6 Hz, 2H), 2.71 (s, 3H), 2.24-2.17 (m, 1H), 1.09 (d, J = 6.6 Hz, 6H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$*): δ* 175.9, 170.2, 163.2, 163.0, 143.5 (dm), 142.9 (dm), 137.9 (dm), 133.0, 132.6, 131.2, 125.4, 115.6 (m), 115.2, 112.9, 103.4, 75.9, 28.3, 19.2, 18.5; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, rt): δ –140.8 (m), –149.8 (m), –159.3 (m). FT-IR (cm^{-1}): 2968, 2200, 1634, 1603, 1514, 1497, 1427, 1414, 1341, 1294, 995, 789. Anal. Calcd for $C_{22}H_{15}F_5N_2O_2S$: C, 56.65; H, 3.24; N, 6.01%; Found: C, 56.75; H, 3.26; N, 5.90%.

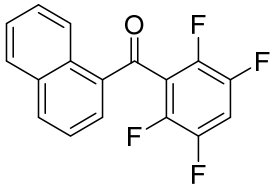
Phenyl(2,3,5,6-tetrafluorophenyl)methanone (3z)[8]



3z

Colorless oil. R_f = 0.30 (Et_2O:hexane = 1:20). Isolated yield is 58% (29.3 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 7.88-7.86 (m, 2H), 7.70-7.66 (m, 1H), 7.55-7.51 (m, 2H), 7.27-7.18 (m, 1H); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, rt): δ –137.4 (m), –141.1 (m).

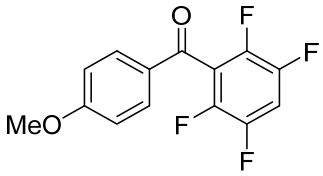
Naphthalen-1-yl(2,3,5,6-tetrafluorophenyl)methanone (3aa)[8]



3aa

White solid. R_f = 0.24 (Et_2O:hexane = 1:20). Isolated yield is 45% (27.6 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 9.15-9.13 (m, 1H), 8.14 (d, J = 8.0 Hz, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.78-7.72 (m, 2H), 7.66-7.62 (m, 1H), 7.52-7.49 (m, 1H), 7.27-7.18 (m, 1H); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, rt): δ –137.6 (m), –141.6 (m).

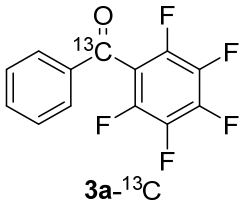
(4-Methoxyphenyl)(2,3,5,6-tetrafluorophenyl)methanone (3ab)[3]



3ab

White solid. R_f = 0.32 (Et_2O : hexane = 1:5). Isolated yield is 64% (36.5 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, J = 9.2 Hz, 2H), 7.24-7.15 (m, 1H), 6.98 (d, J = 9.2 Hz, 2H), 3.90 (s, 3H); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, rt): δ –137.6 (m), –141.4 (m).

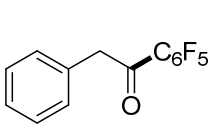
(Pentafluorophenyl)(phenyl)methanone-α-^{13}C (3a-^{13}C)[3]



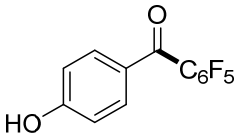
3a-^{13}C

Colorless oil. R_f = 0.35 (Et_2O:hexane = 1:20). Isolated yield is 51% (28.1 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 7.87-7.84 (m, 2H), 7.71-7.67 (m, 1H), 7.55-7.52 (m, 2H).; $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$*): δ* 185.4 (^{13}C), 143.9 (dm), 142.6 (dm), 137.8 (dm), 136.1 (d, J = 60.1 Hz), 135.2, 129.9 (d, J = 3.5 Hz), 129.2 (d, J = 4.7 Hz), 114.1 (m); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, rt): δ –140.1 (m), –150.7 (m), –160.1 (m).

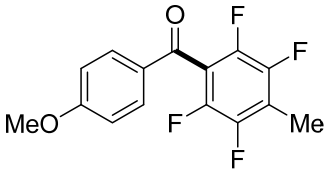
Negative scope (for reference only)



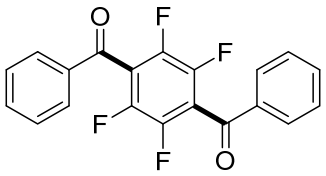
0%



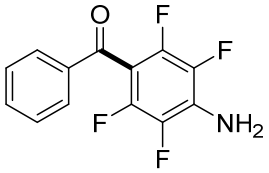
0%



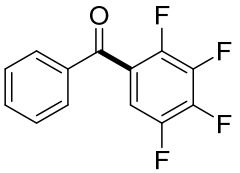
15%



0%



8%



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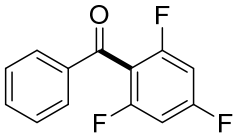
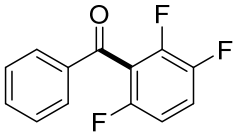


trace



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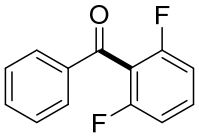
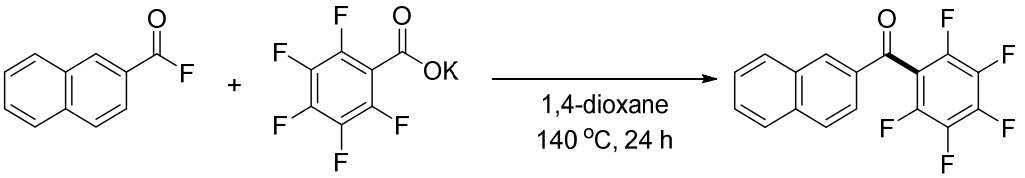


0%

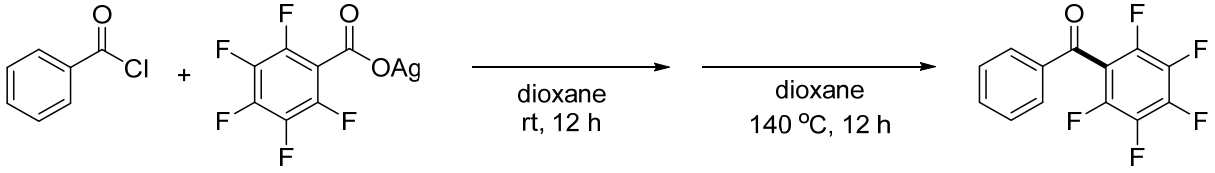
3.4 Gram-Scale Synthesis of 3s



1s **2d** **3s**

An oven-dried two-necked flask (500 mL) containing a magnetic stirring bar was charged with acyl fluoride **1s** (6.0 mmol, 1.0 equiv) and potassium pentafluorobenzoates **2d** (9.0 mmol, 1.5 equiv) in 1,4-dioxane (30 mL) under argon. The mixture was heated at 140 ºC with stirring for 24 h. After being at room temperature, the mixture was quenched with saturated NH_4Cl and the aqueous solution was extracted with Et_2O. The combined organic extracts were dried over anhydrous $MgSO_4$, then filtered and evaporated under vacuum to obtain the crude product which was purified by column chromatography (Et_2O/hexane = 1:20) on silica gel to afford the desired products **3s** (1.40 g, 4.35 mmol) in 72% yield.

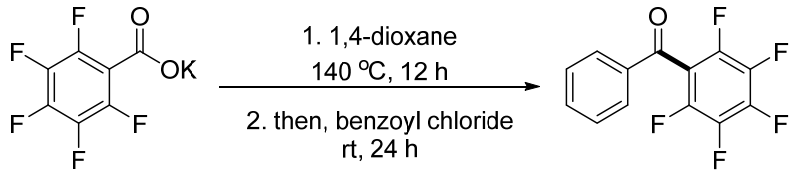
3.5 Mixed Anhydride Synthesis



2f **3a**

An oven-dried Schlenk tube (25 mL) containing a magnetic stirring bar was charged with benzoyl chloride (0.2 mmol, 1.0 equiv) and silver pentafluorobenzoates **2e** (0.3 mmol, 1.5 equiv) in 1,4-dioxane (1 mL) under argon. The mixture was stirred under room temperature for 12 h in dark. The measurements of $^{19}F\{^{1}H\}$ NMR showed the three complex signals assignable to three types of fluorine atoms at δ –137.7 (m), –146.9 (m), –160.7 (m), which are different from those of **2f** (δ –144.8 (m), –155.5 (m), –162.4 (m)), implying the formation of the mixed anhydride as the intermediate. However, even heating of the mixture at 140 °C for 12 h gave **3a** in 3% GC yield.

3.6 Trapping C_6F_5K Species

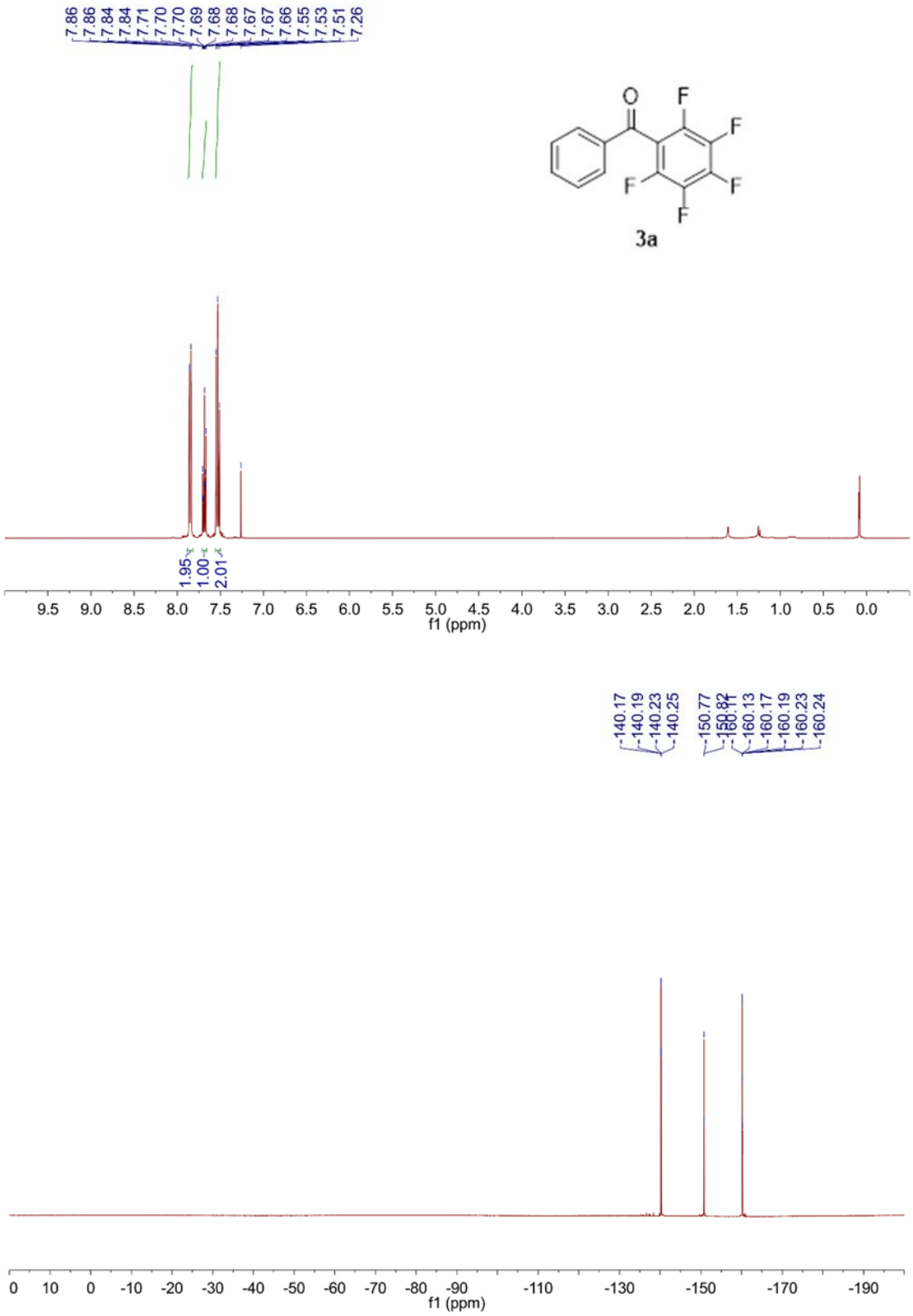


2d (1.5 equiv) **3a**

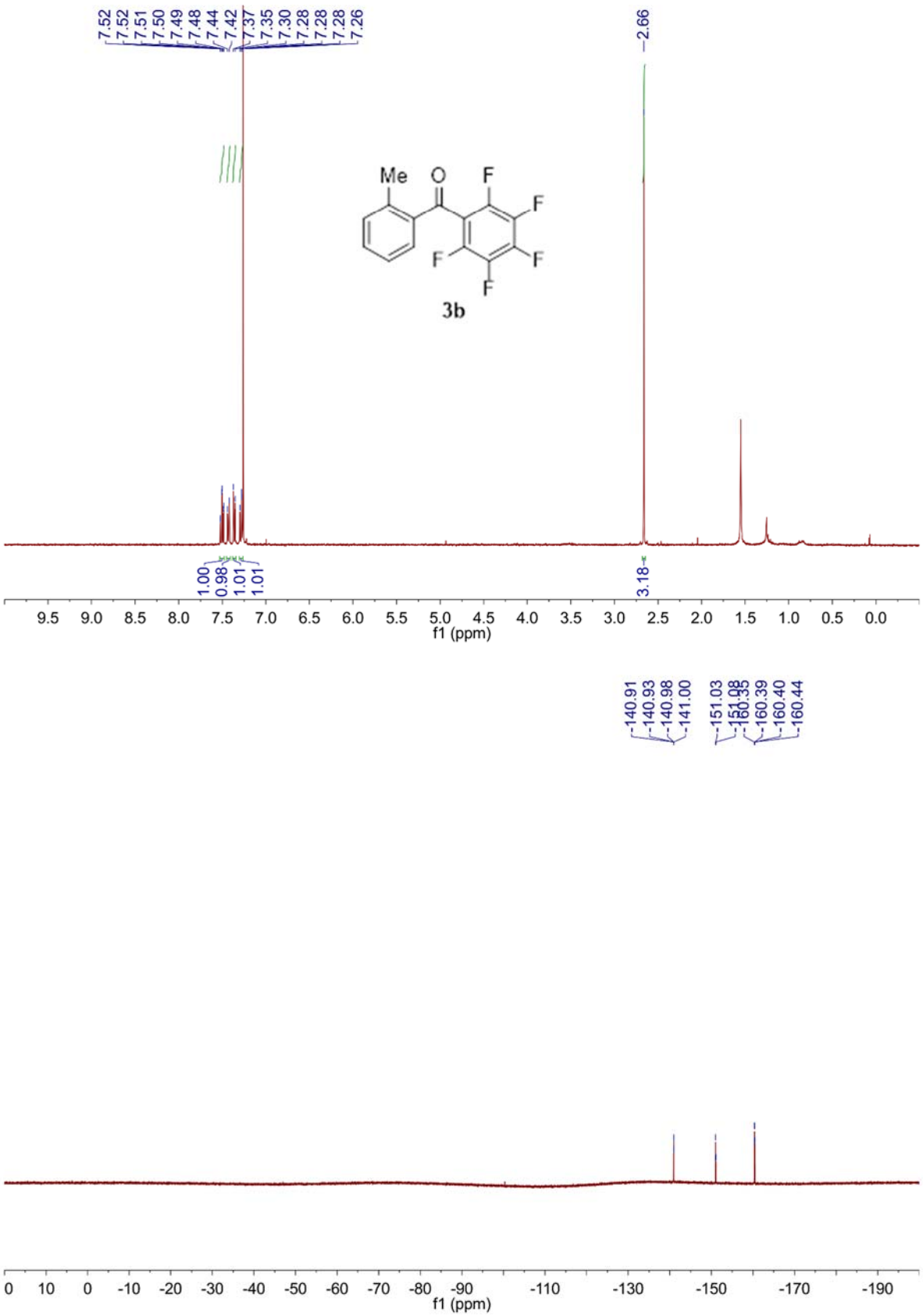
An oven-dried Schlenk tube (25 mL) containing a magnetic stirring bar was charged potassium pentafluorobenzoates **2d** (0.3 mmol, 1.5 equiv) in 1,4-dioxane (1 mL) under argon. The mixture was heated at 140 °C with stirring for 12 h. After being at room temperature, benzoyl chloride (0.2 mmol, 1.0 equiv) was added under argon. The mixture was stirred for 24 h at room temperature. Then the mixture was quenched with saturated NH_4Cl and the aqueous solution was extracted with Et_2O. The combined organic extracts were dried over anhydrous $MgSO_4$, then filtered and evaporated under vacuum to obtain the crude product in 3% GC yield.

Attempt to trap C_6F_5K species with benzoyl fluoride and I_2 instead of benzoyl chloride gave no desired products.

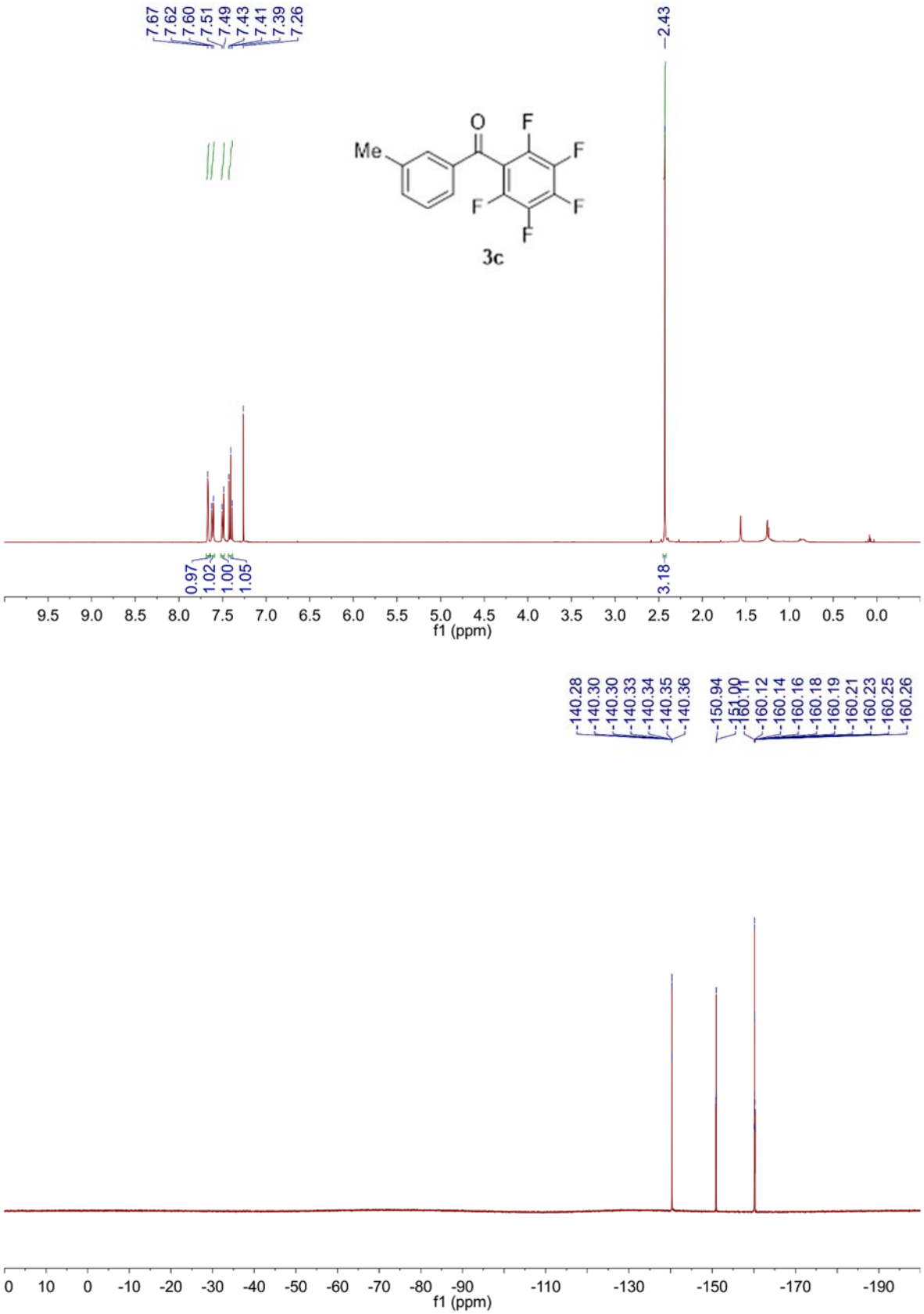
4. *Copies of ^{1}H, $^{13}C\{^{1}H\}$, and $^{19}F\{^{1}H\}$ NMR Charts for the Products*



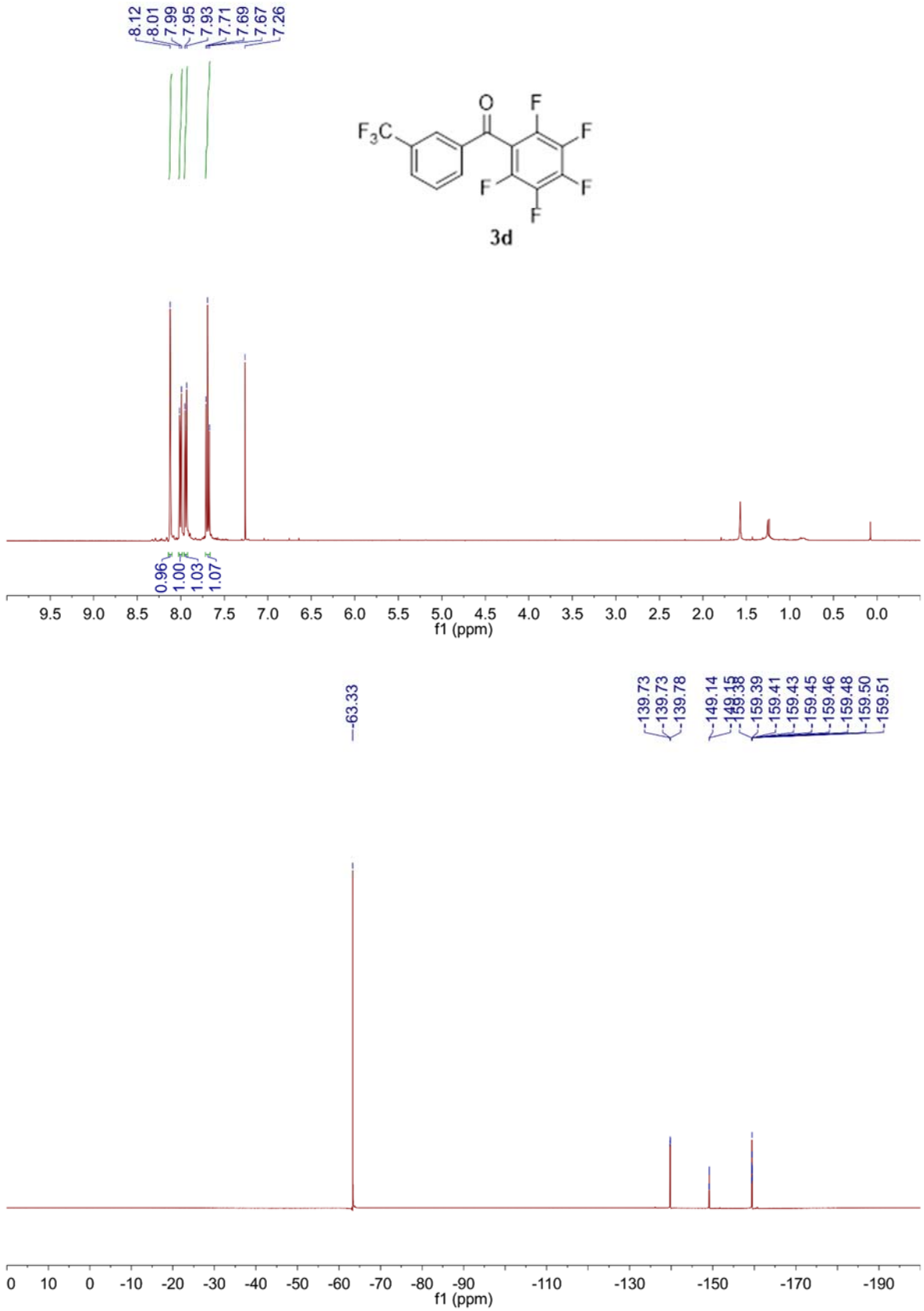
^{1}H NMR (400 MHz) and $^{19}F\{^{1}H\}$ NMR (376 MHz) spectra of **3a** (rt, $CDCl_3$).



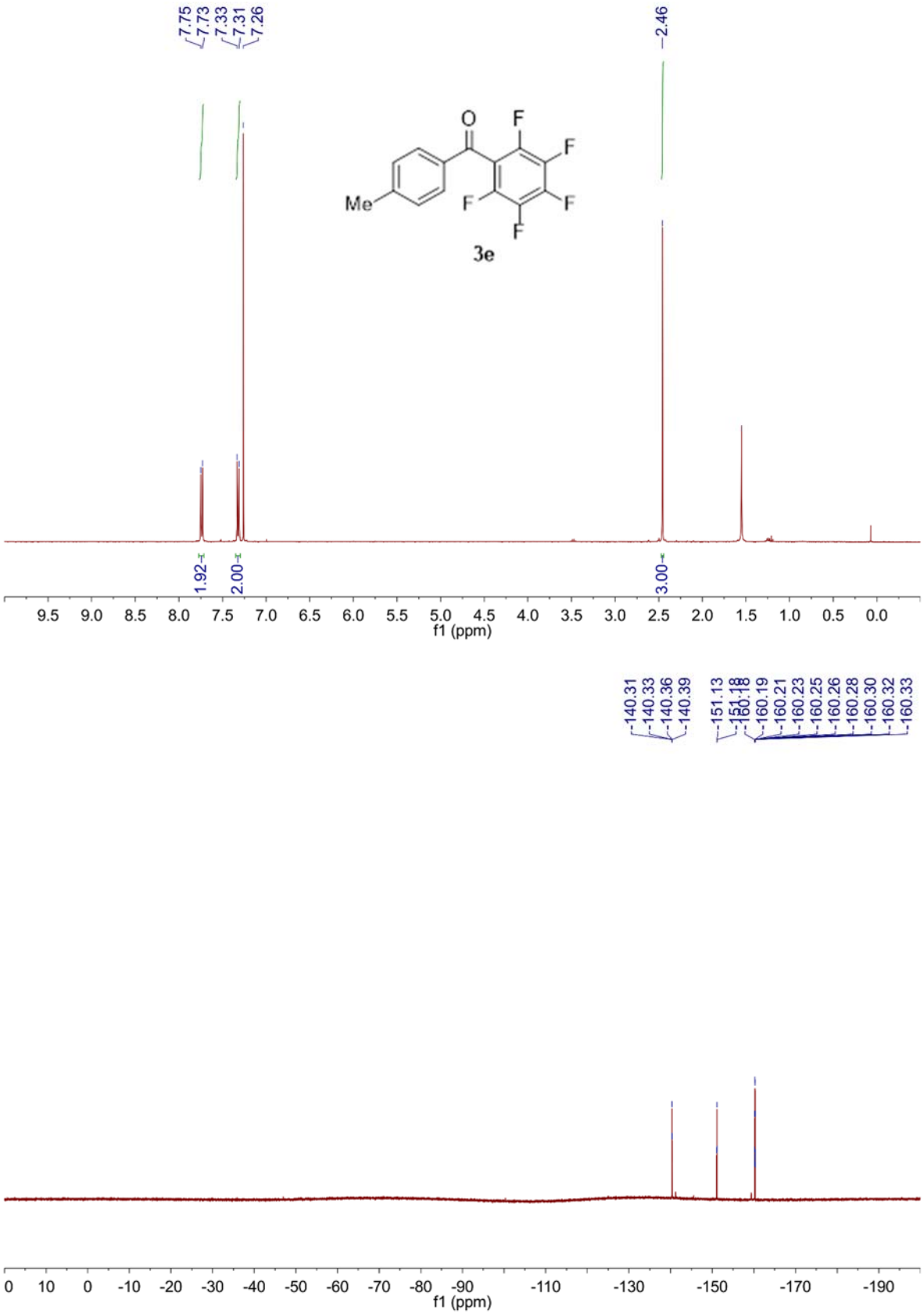
^{1}H NMR (400 MHz) and ^{19}F{^{1}H} NMR (376 MHz) spectra of **3b** (rt, $CDCl_3$).



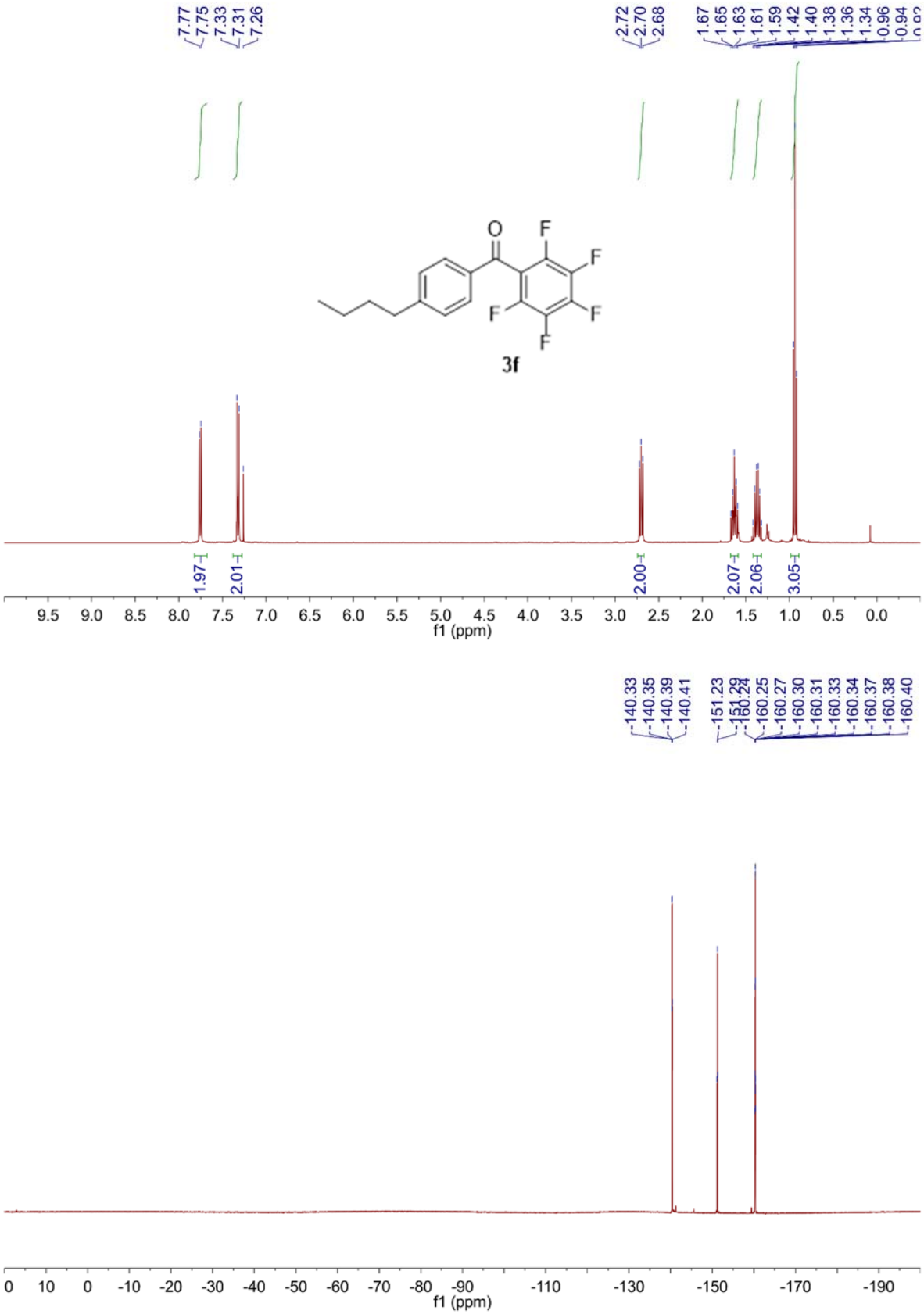
^{1}H NMR (400 MHz) and ^{19}F{^{1}H} NMR (376 MHz) spectra of **3c** (rt, $CDCl_3$).



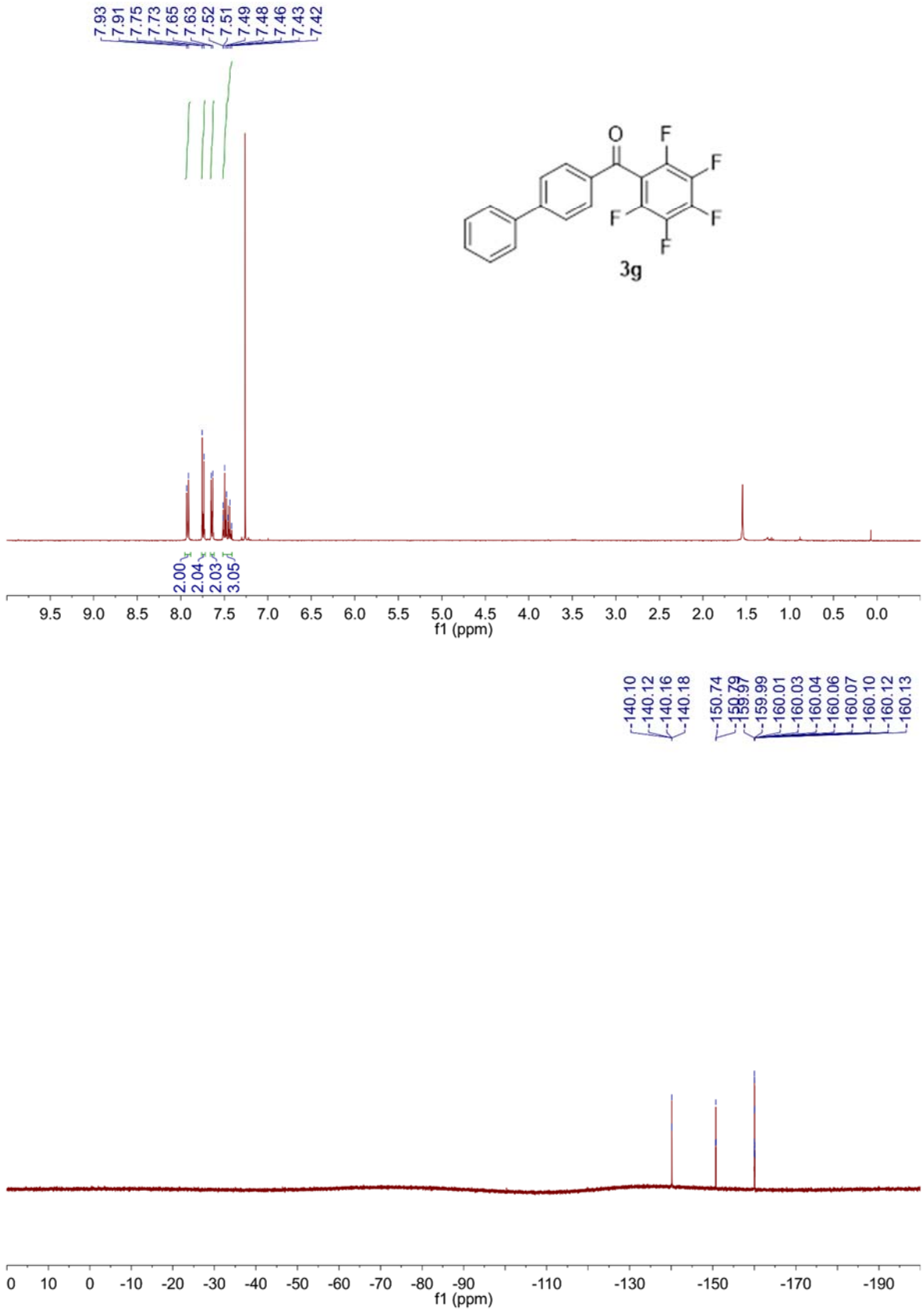
^{1}H NMR (400 MHz) and ^{19}F{^{1}H} NMR (376 MHz) spectra of **3d** (rt, $CDCl_3$).



^{1}H NMR (400 MHz) and ^{19}F{^{1}H} NMR (376 MHz) spectra of **3e** (rt, $CDCl_3$).

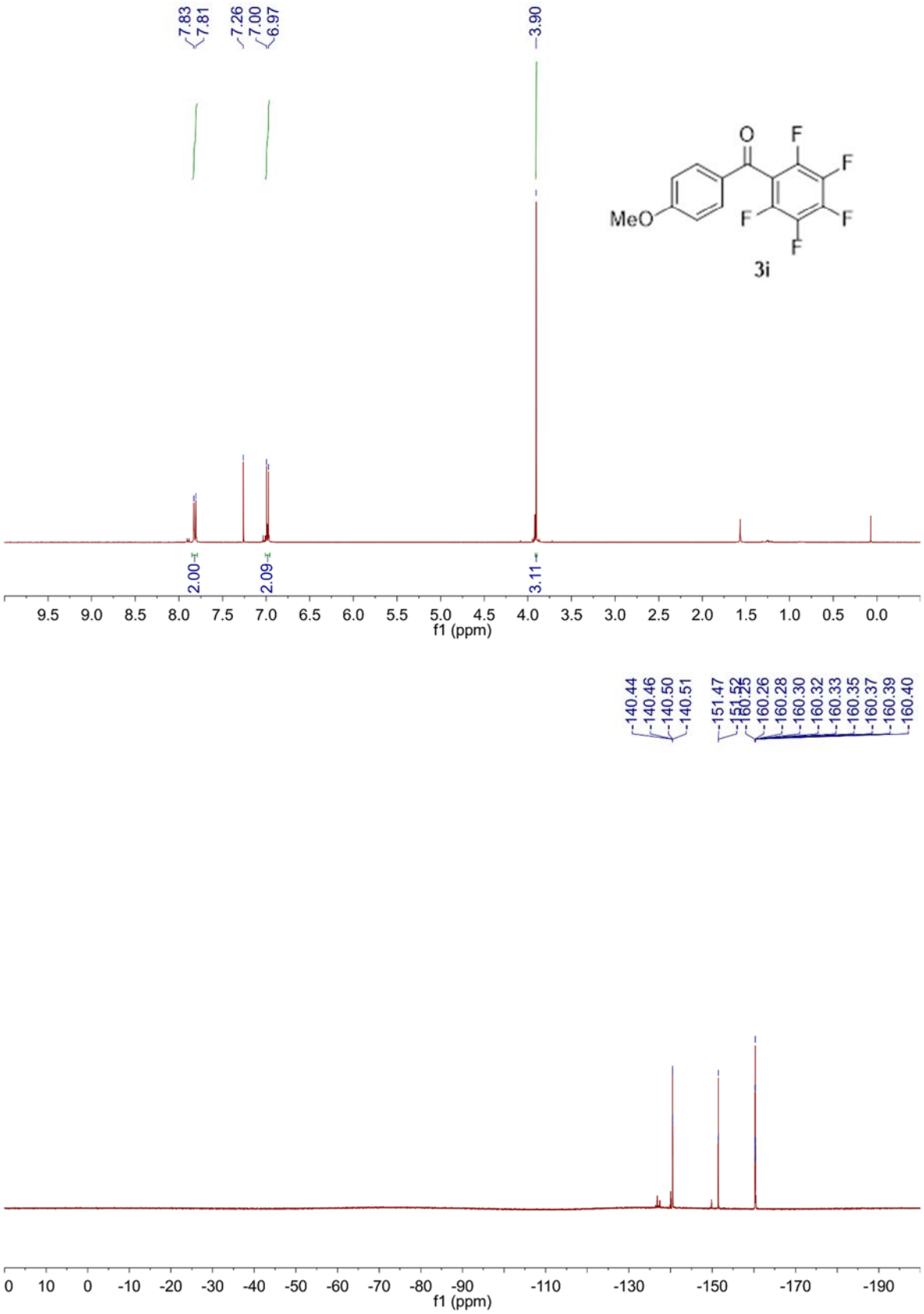


^{1}H NMR (400 MHz) and ^{19}F{^{1}H} NMR (376 MHz) spectra of **3f** (rt, $CDCl_3$).

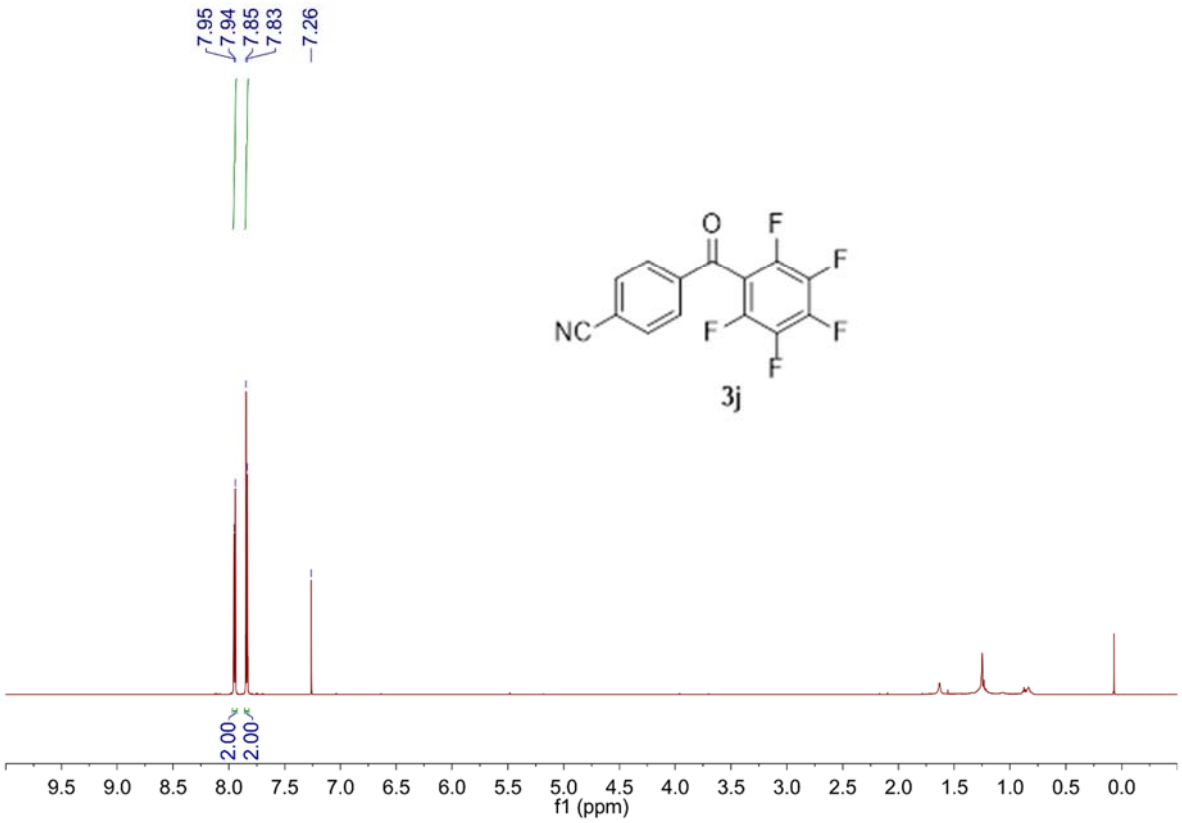


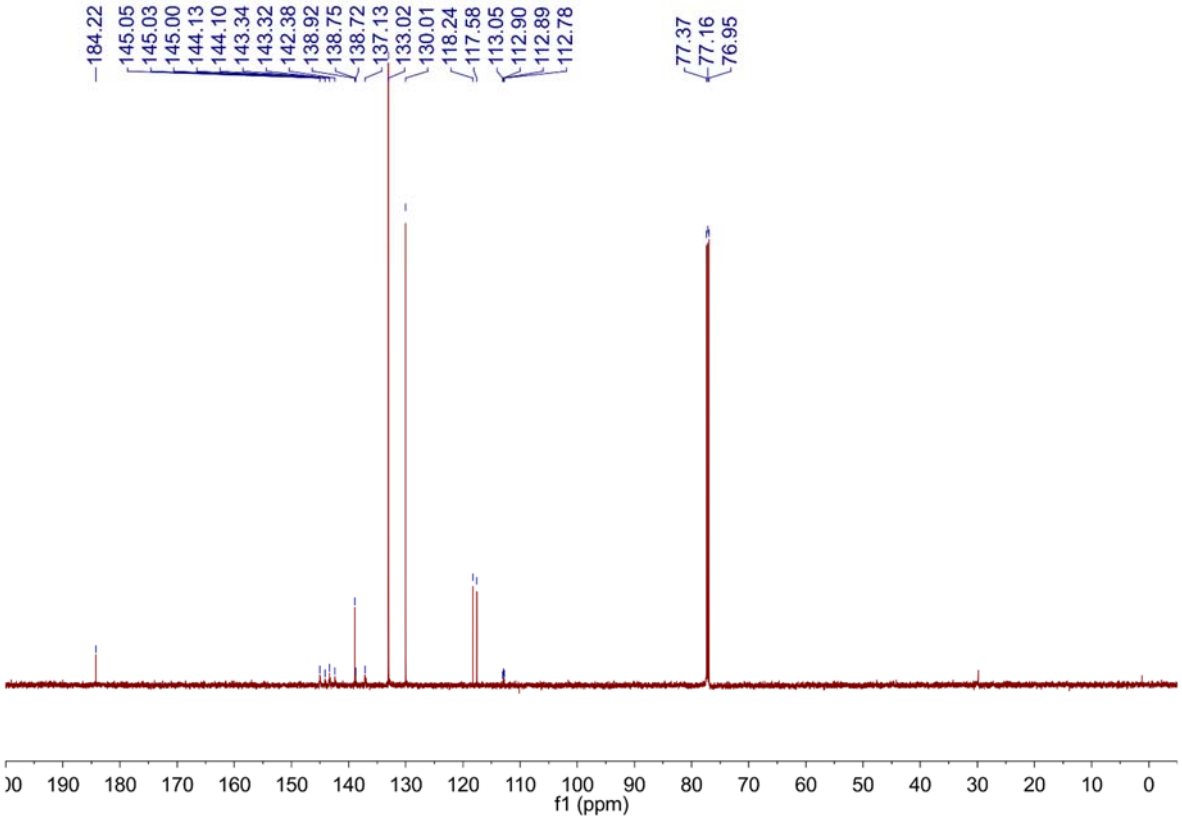
^{1}H NMR (400 MHz) and ^{19}F{^{1}H} NMR (376 MHz) spectra of **3g** (rt, $CDCl_3$).

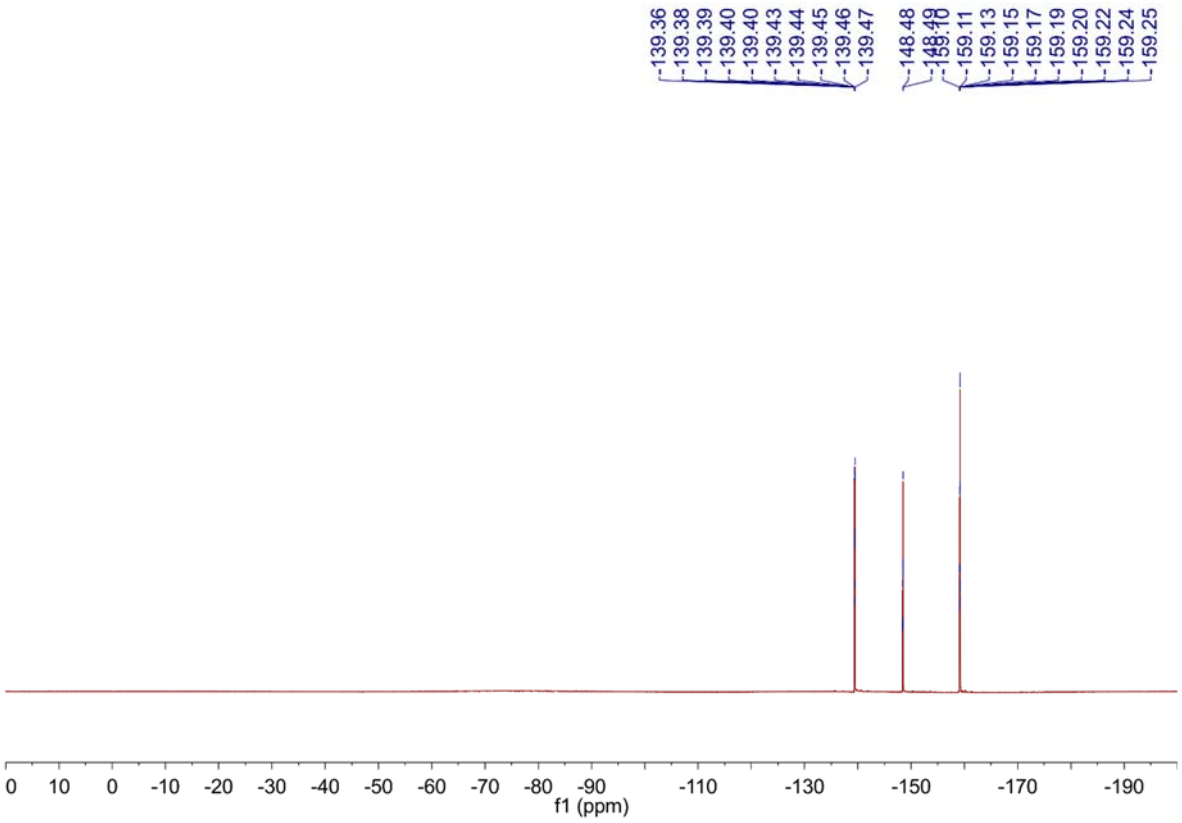
^{1}H NMR (400 MHz) and ^{19}F{^{1}H} NMR (376 MHz) spectra of **3h** (rt, $CDCl_3$).



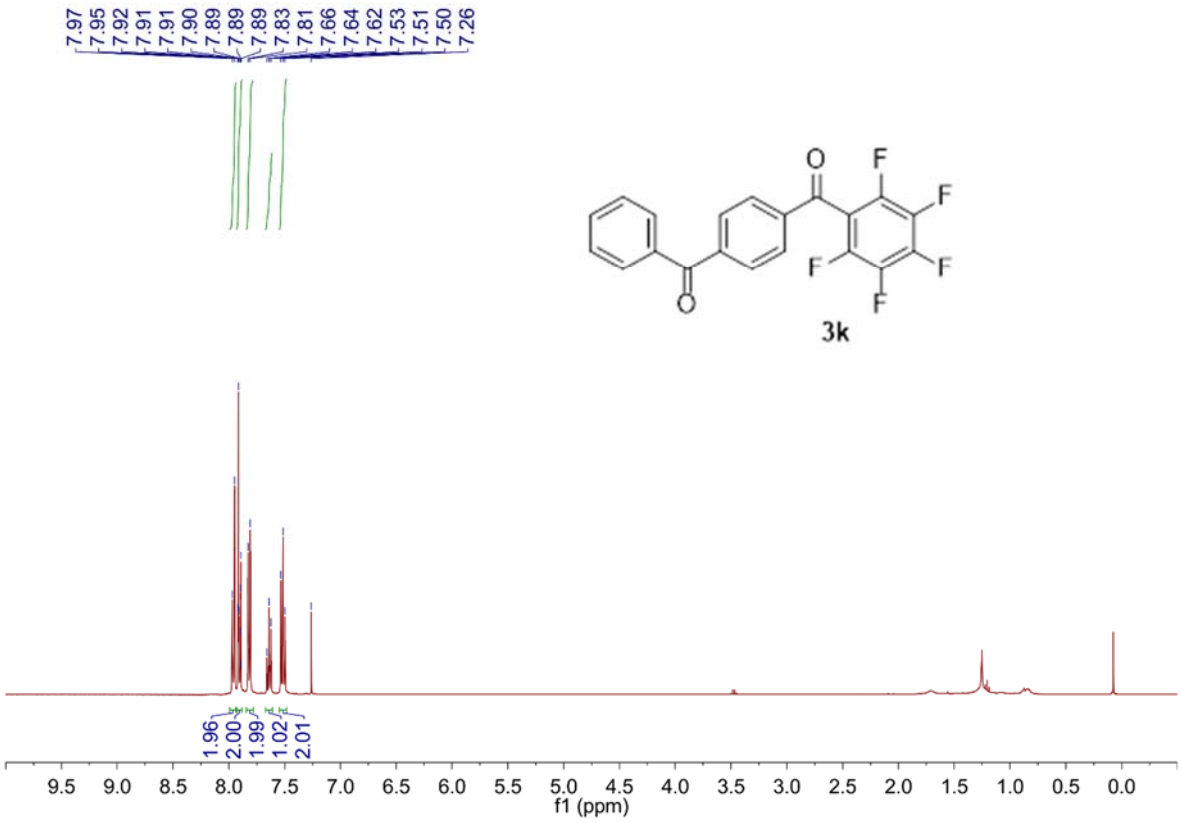
^{1}H NMR (400 MHz) and ^{19}F{^{1}H} NMR (376 MHz) spectra of **3i** (rt, $CDCl_3$).

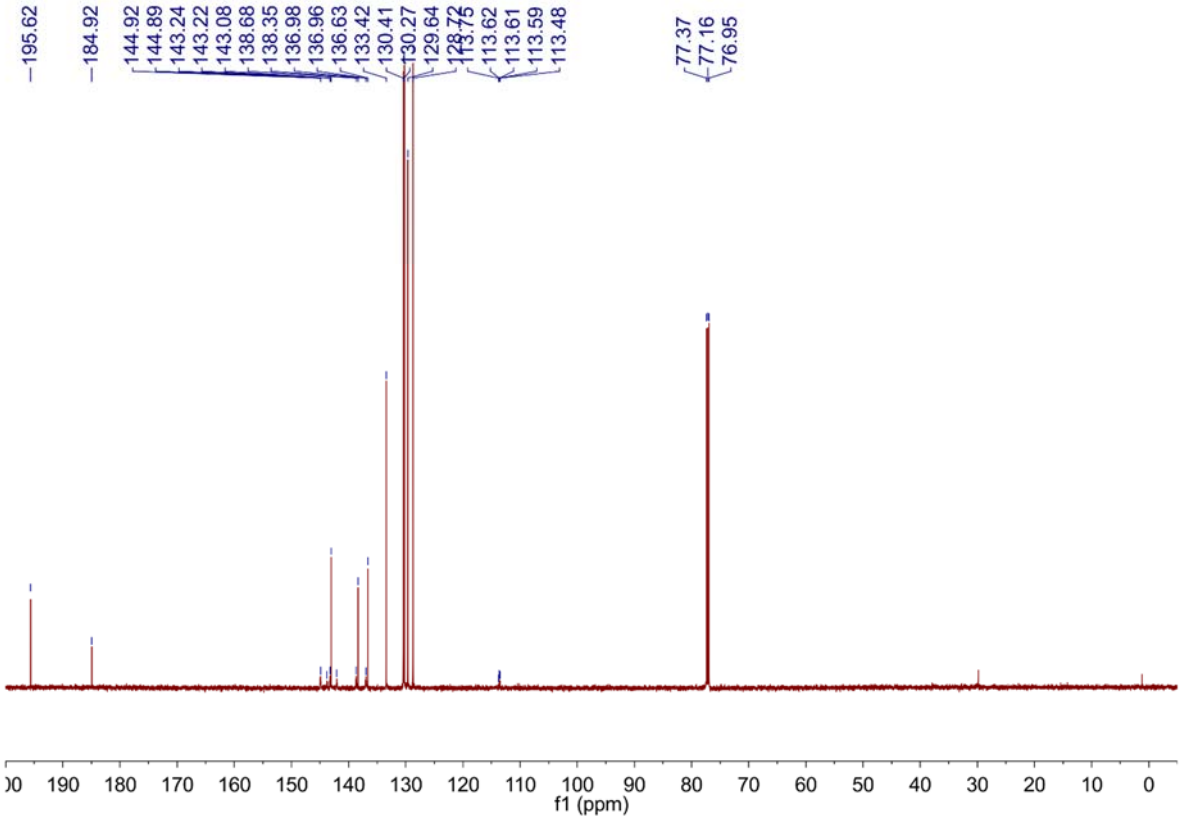

7.95
7.94
7.85
7.83
7.26
O
F
F
F
F
F
NC
3j
2.00
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

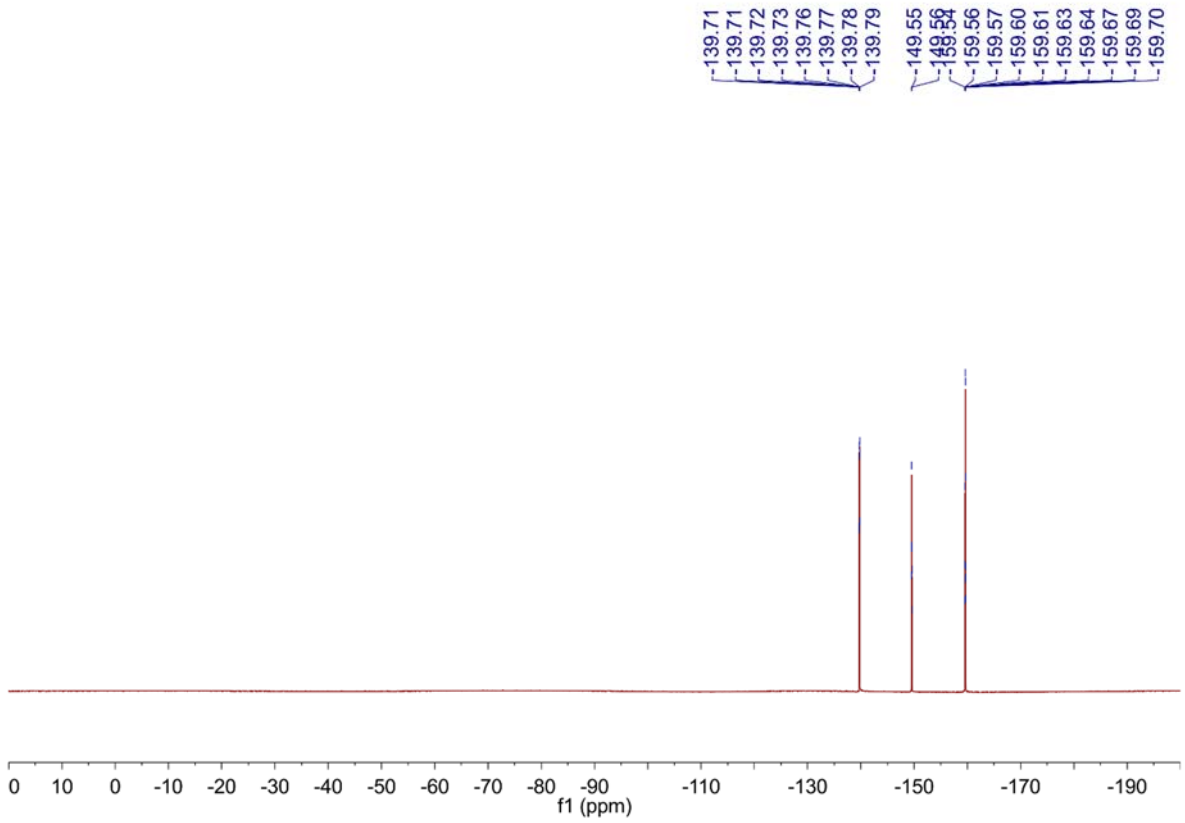

184.22
145.05
145.03
145.00
144.13
144.10
143.34
143.32
142.38
138.92
138.75
138.72
137.13
133.02
130.01
118.24
117.58
113.05
112.90
112.89
112.78
77.37
77.16
76.95
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



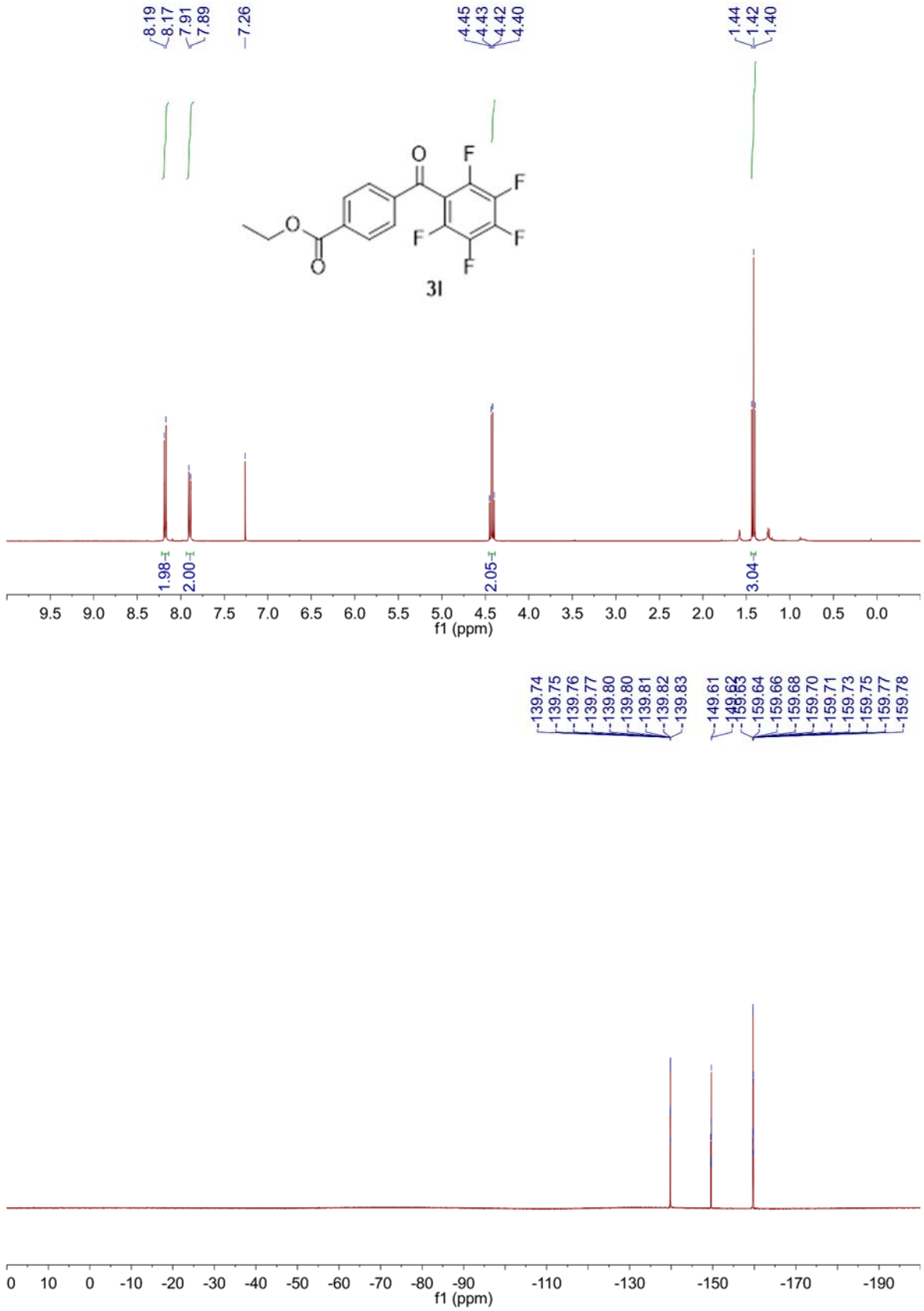
^{1}H NMR (600 MHz), ^{13}C{^{1}H} NMR (151 MHz) and ^{19}F{^{1}H} NMR (376 MHz) spectra of **3j** (rt, $CDCl_3$).


7.97
7.95
7.92
7.91
7.91
7.90
7.89
7.89
7.89
7.83
7.81
7.66
7.64
7.62
7.53
7.51
7.50
7.26
O
F
F
F
F
O
F
3k
1.96
2.00
1.99
1.02
2.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

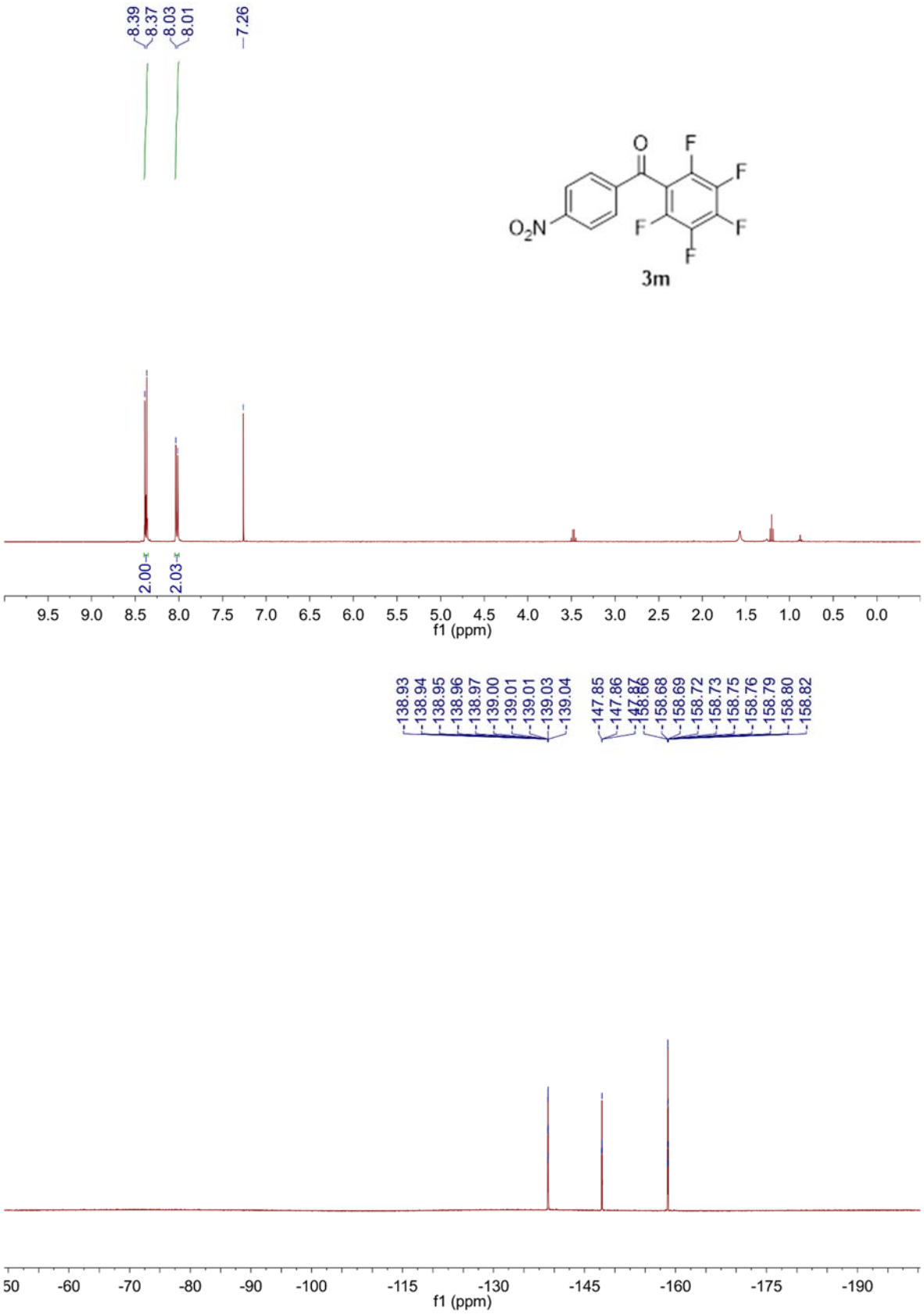

195.62
184.92
144.92
144.89
143.24
143.22
143.08
138.68
138.35
136.98
136.96
136.63
133.42
130.41
130.27
129.64
128.72
113.75
113.62
113.61
113.59
113.48
77.37
77.16
76.95
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



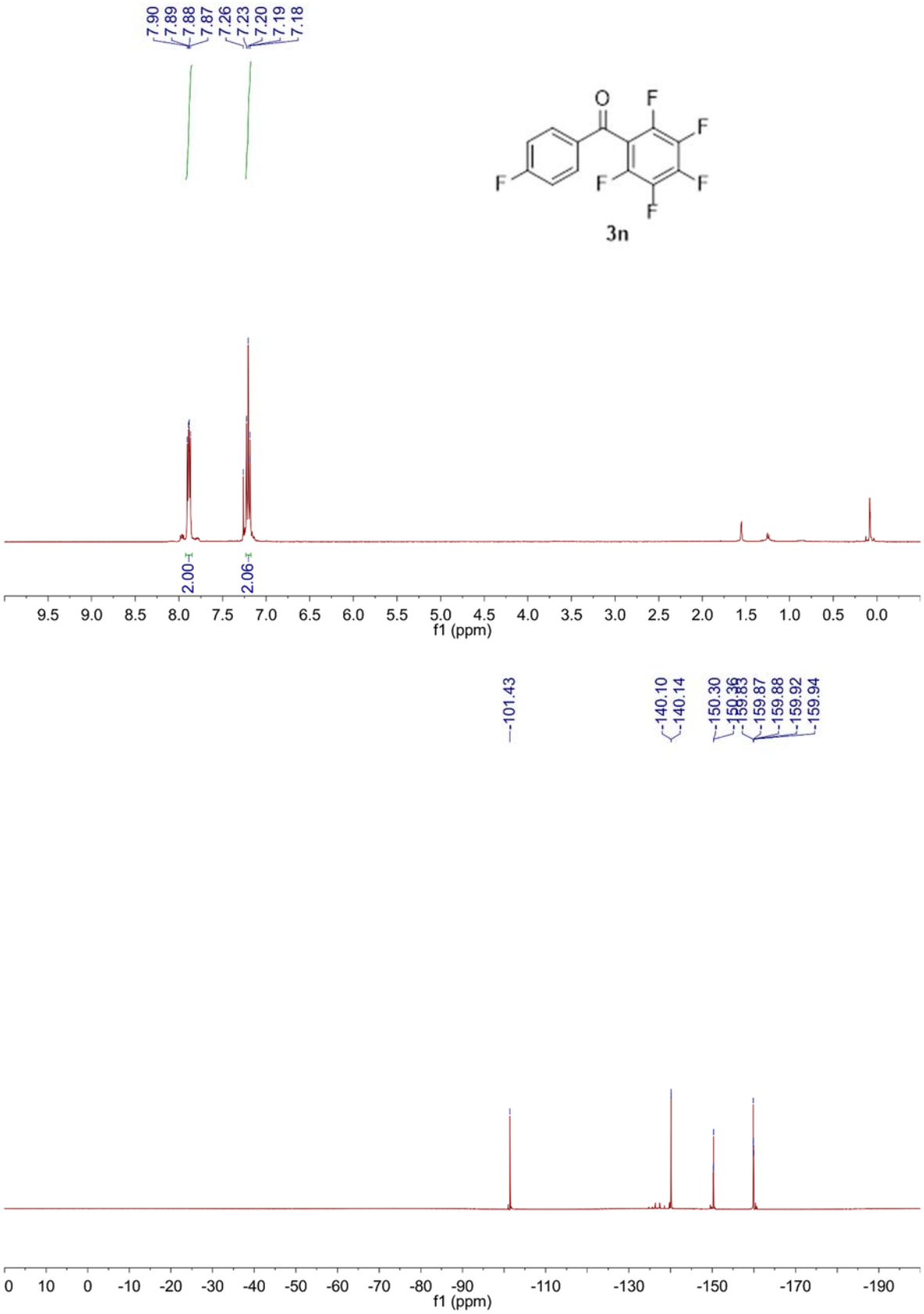
^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (151 MHz) and ^{19}F{^{1}H} NMR (376 MHz) spectra of **3k** (rt, $CDCl_3$).



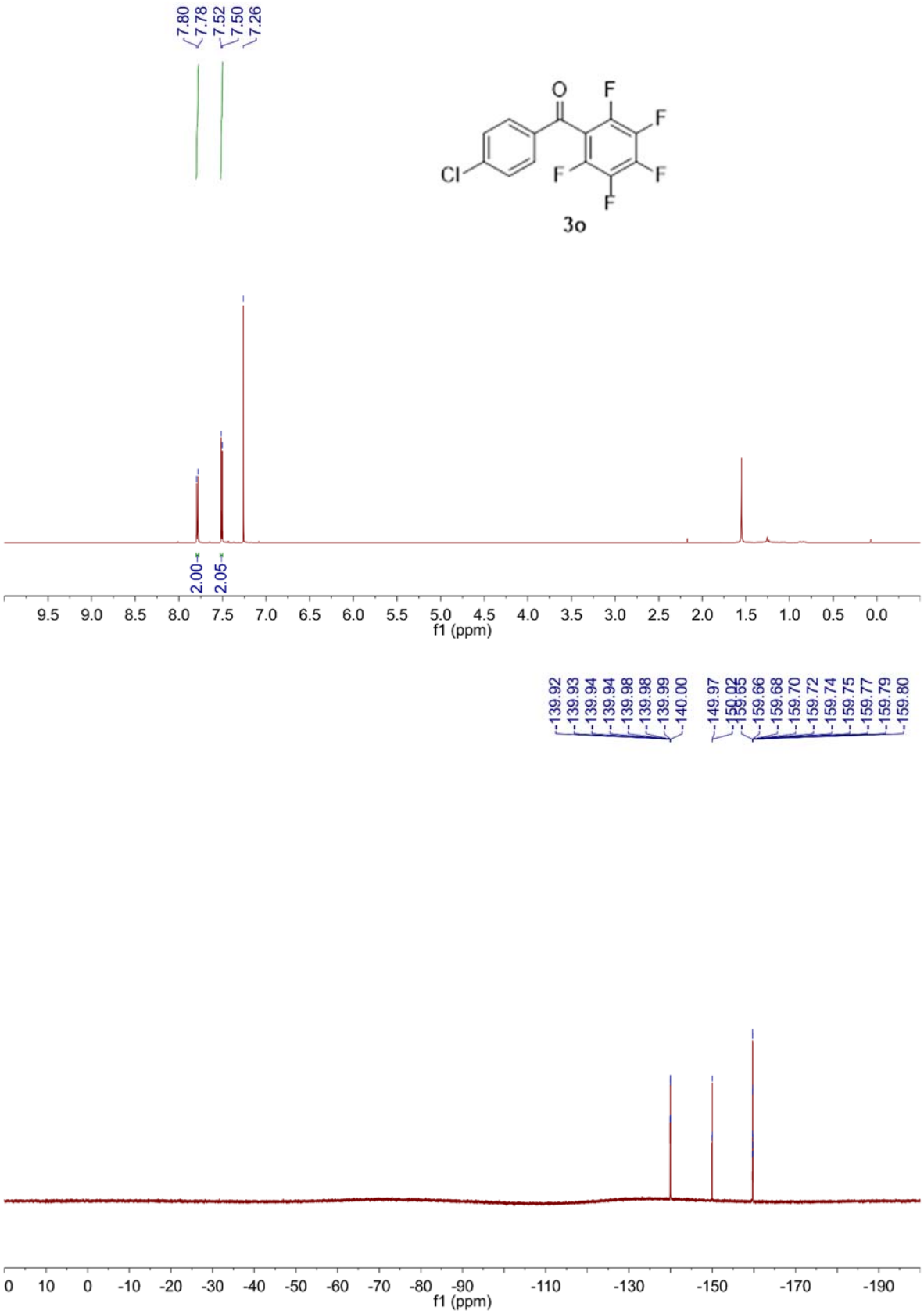
^{1}H NMR (400 MHz) and ^{19}F{^{1}H} NMR (376 MHz) spectra of **3l** (rt, $CDCl_3$).



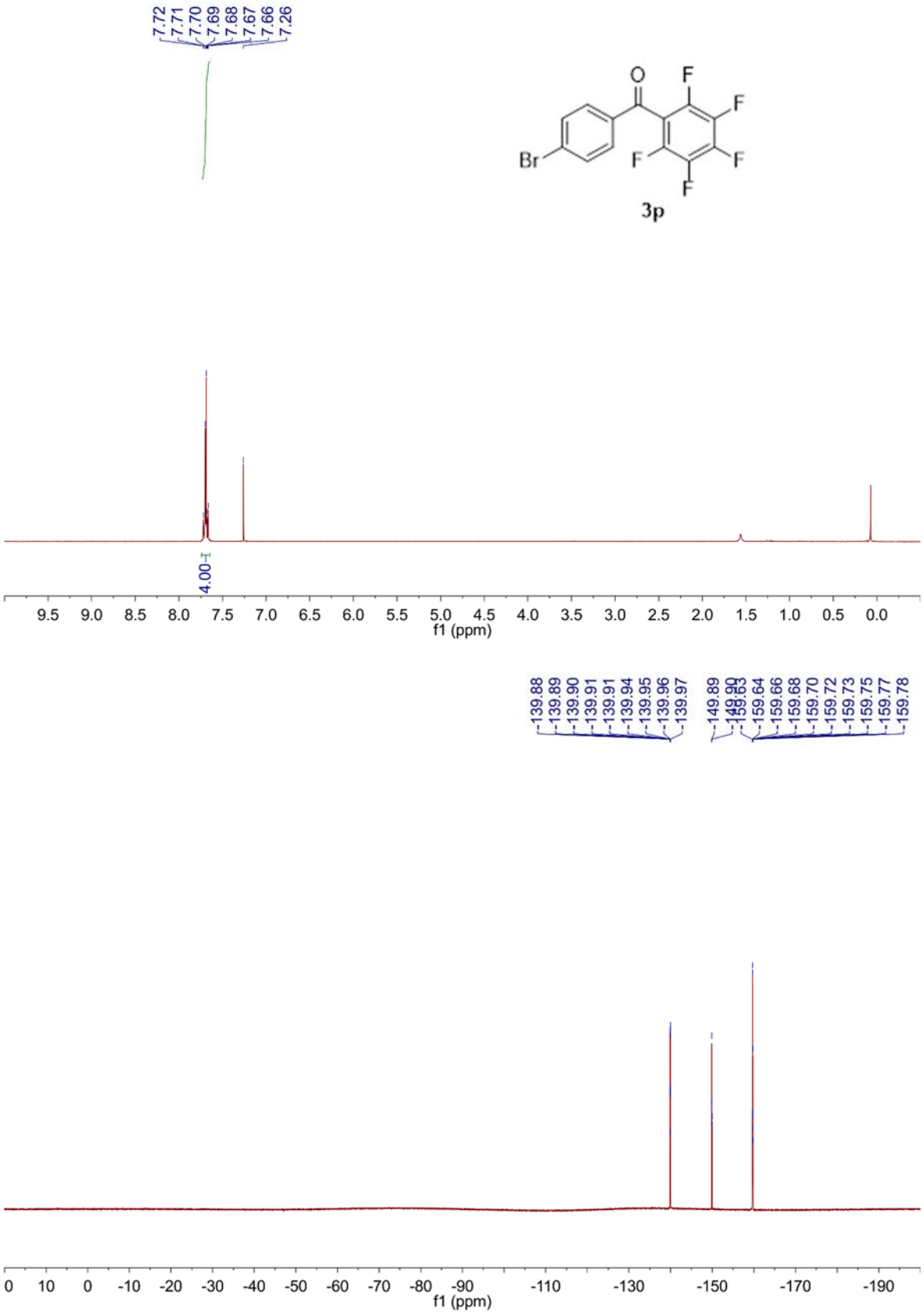
^{1}H NMR (400 MHz) and ^{19}F{^{1}H} NMR (376 MHz) spectra of **3m** (rt, $CDCl_3$).



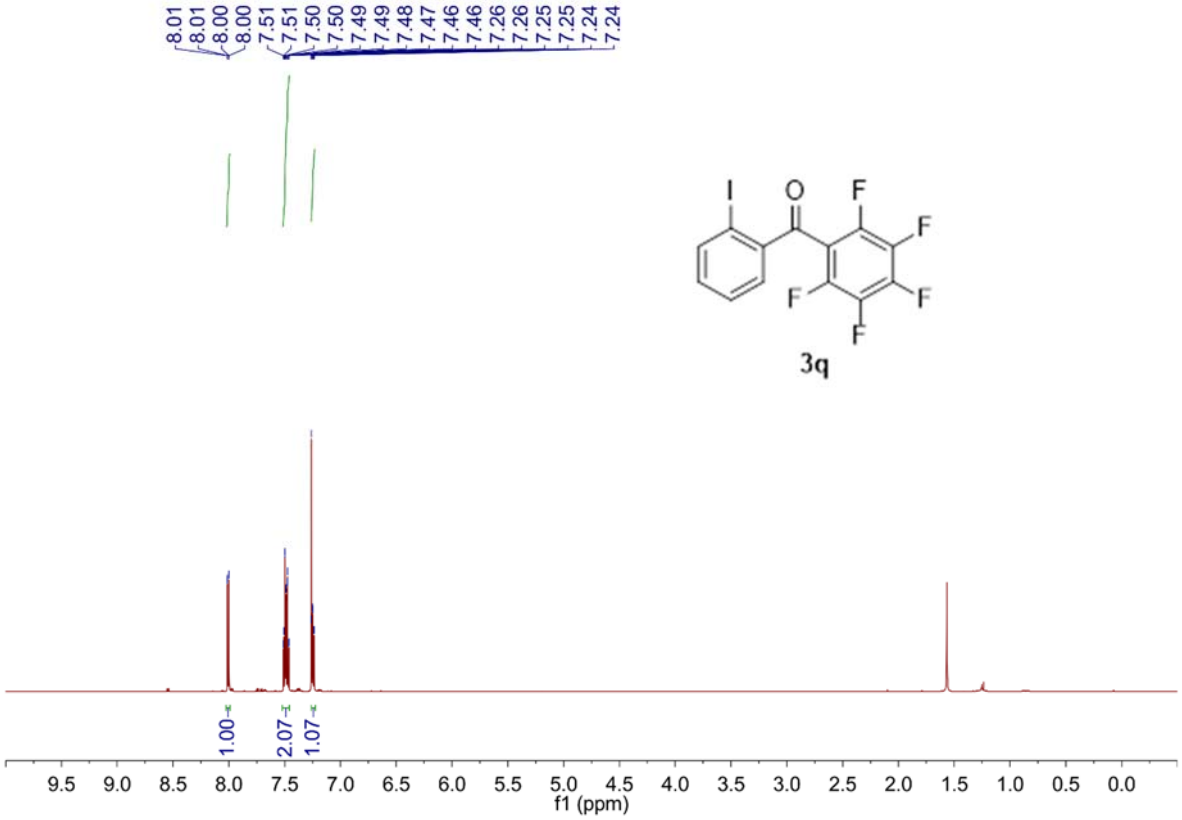
^{1}H NMR (400 MHz) and ^{19}F{^{1}H} NMR (376 MHz) spectra of **3n** (rt, $CDCl_3$).



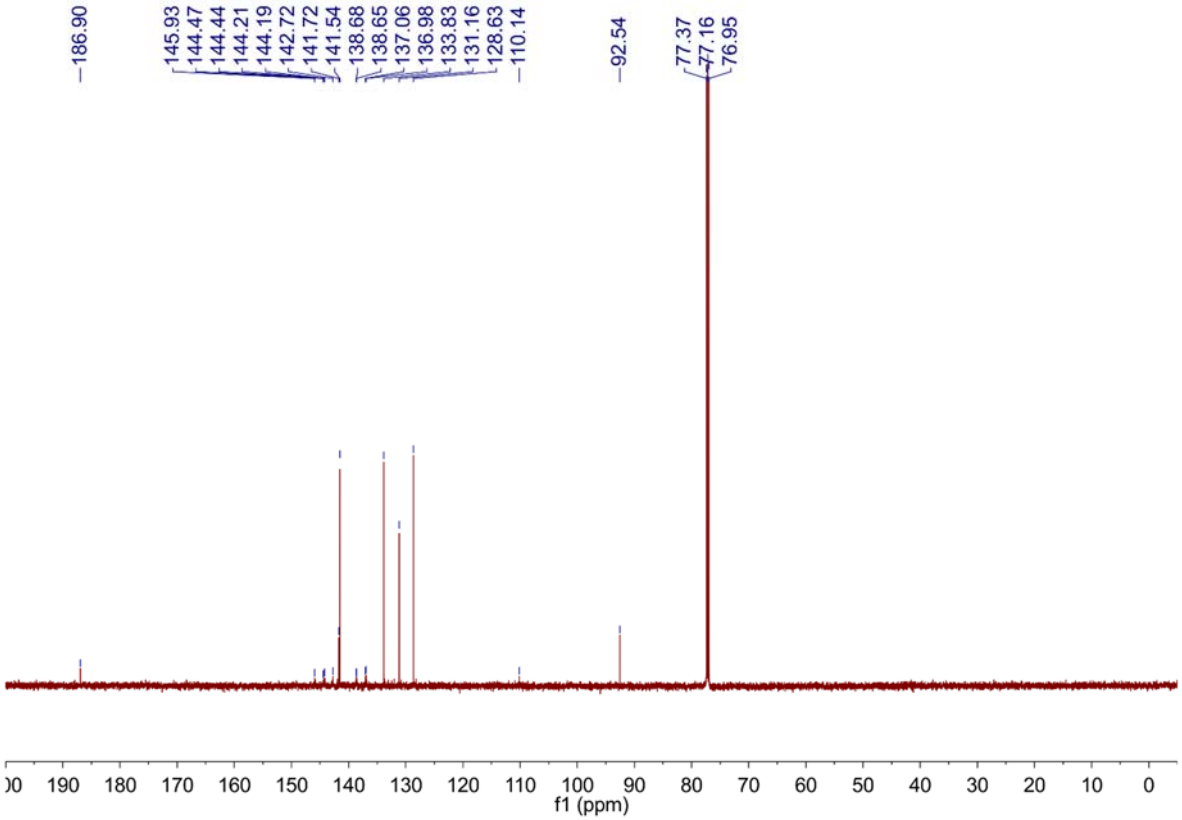
^{1}H NMR (600 MHz) and ^{19}F{^{1}H} NMR (376 MHz) spectra of **3o** (rt, $CDCl_3$).

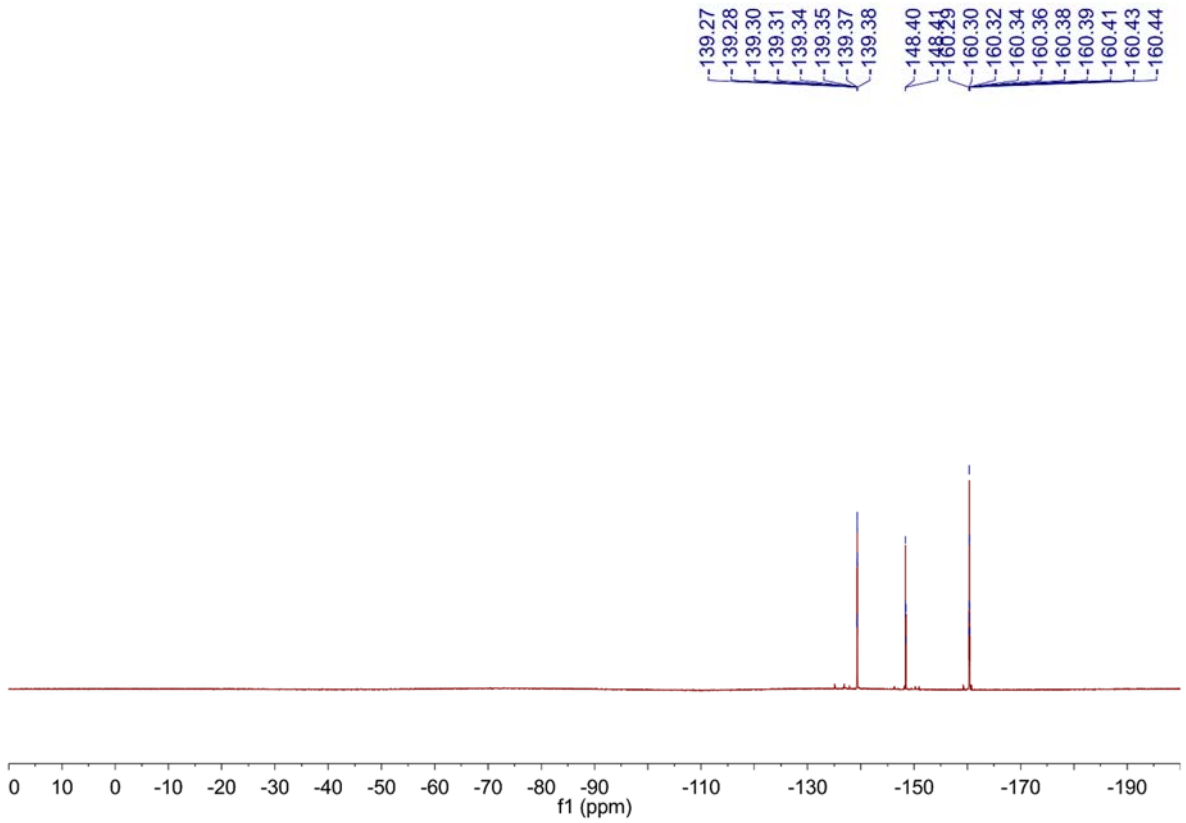


^{1}H NMR (400 MHz) and ^{19}F{^{1}H} NMR (376 MHz) spectra of **3p** (rt, $CDCl_3$).

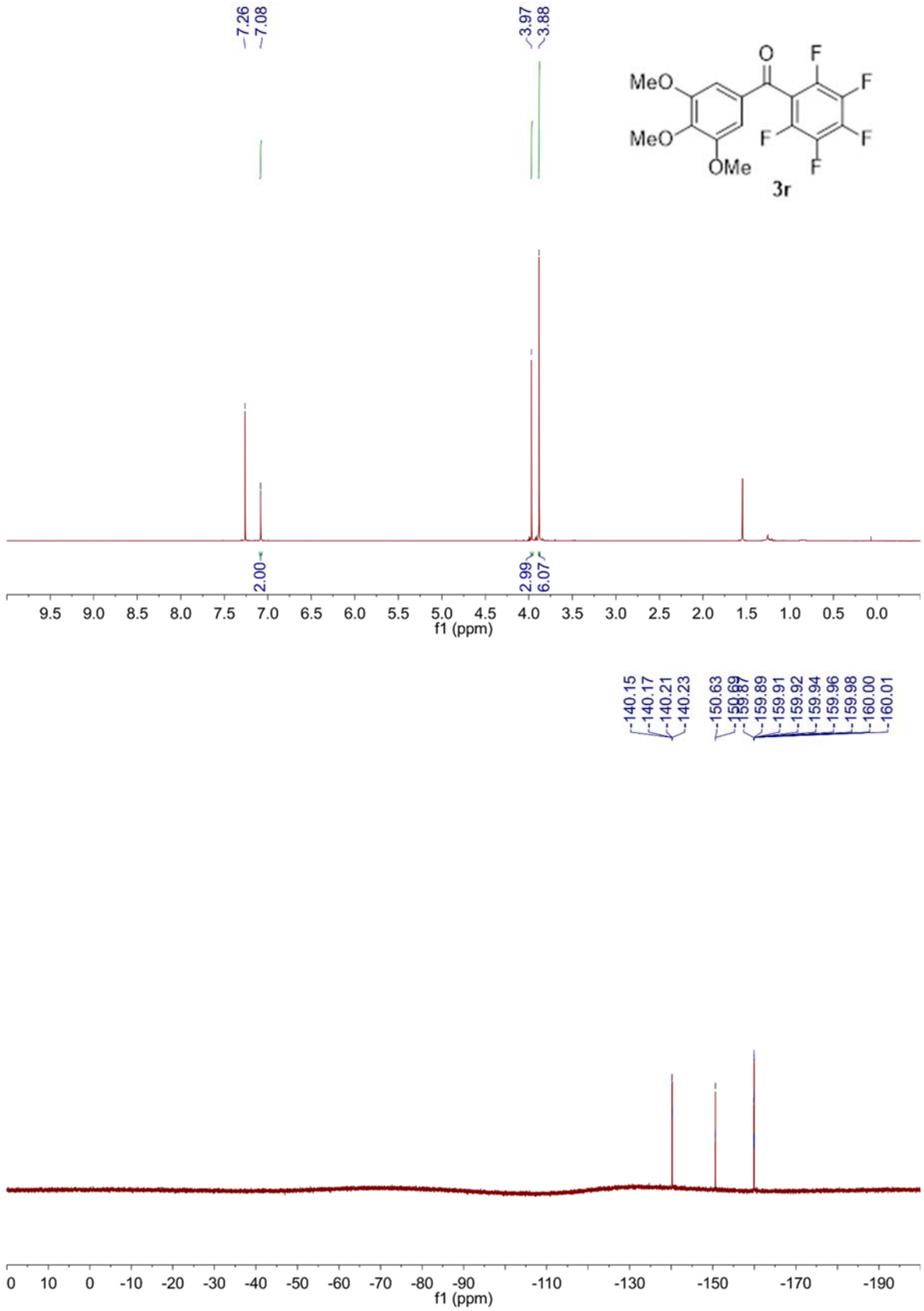

8.01
8.01
8.00
8.00
7.51
7.51
7.50
7.50
7.49
7.49
7.48
7.47
7.46
7.46
7.26
7.26
7.25
7.25
7.24
7.24
I
O
F
F
F
F
F
1.00
2.07
1.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3q

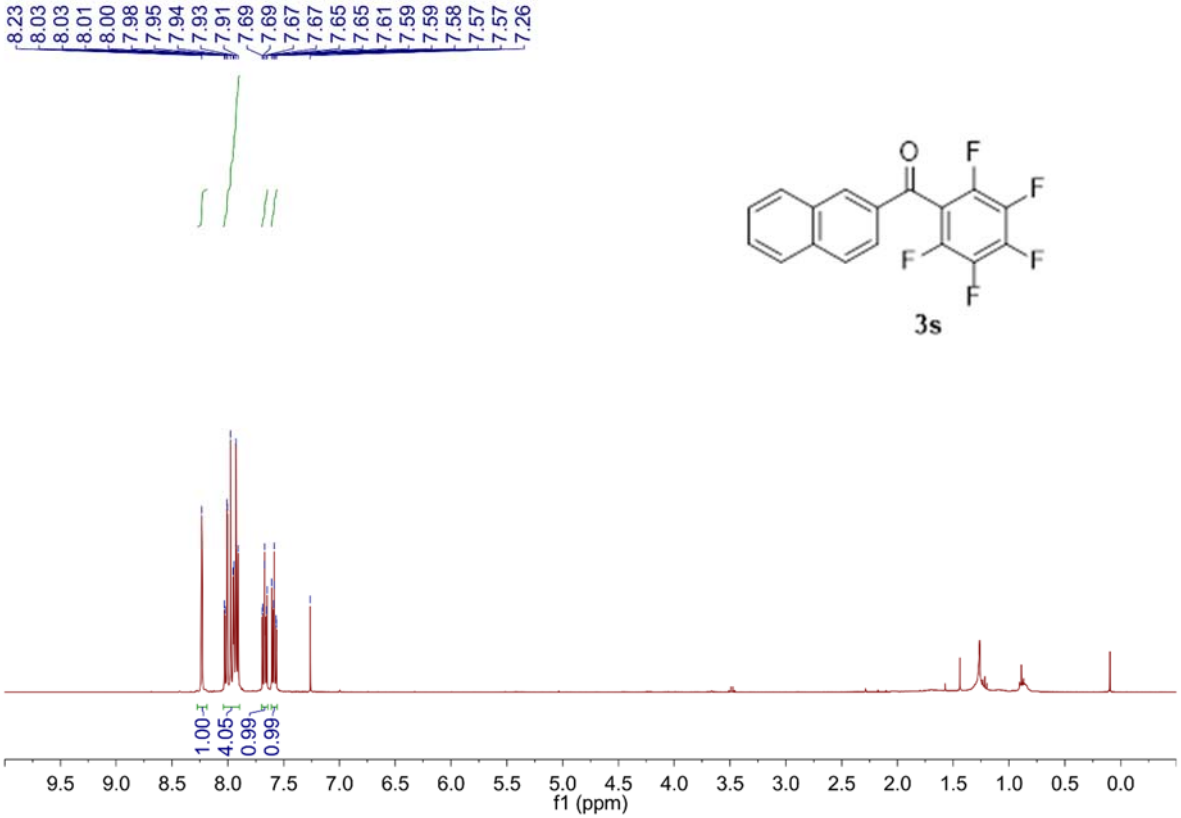

186.90
145.93
144.47
144.44
144.21
144.19
142.72
141.72
141.54
138.68
138.65
137.06
136.98
133.83
131.16
128.63
110.14
92.54
77.37
77.16
76.95
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

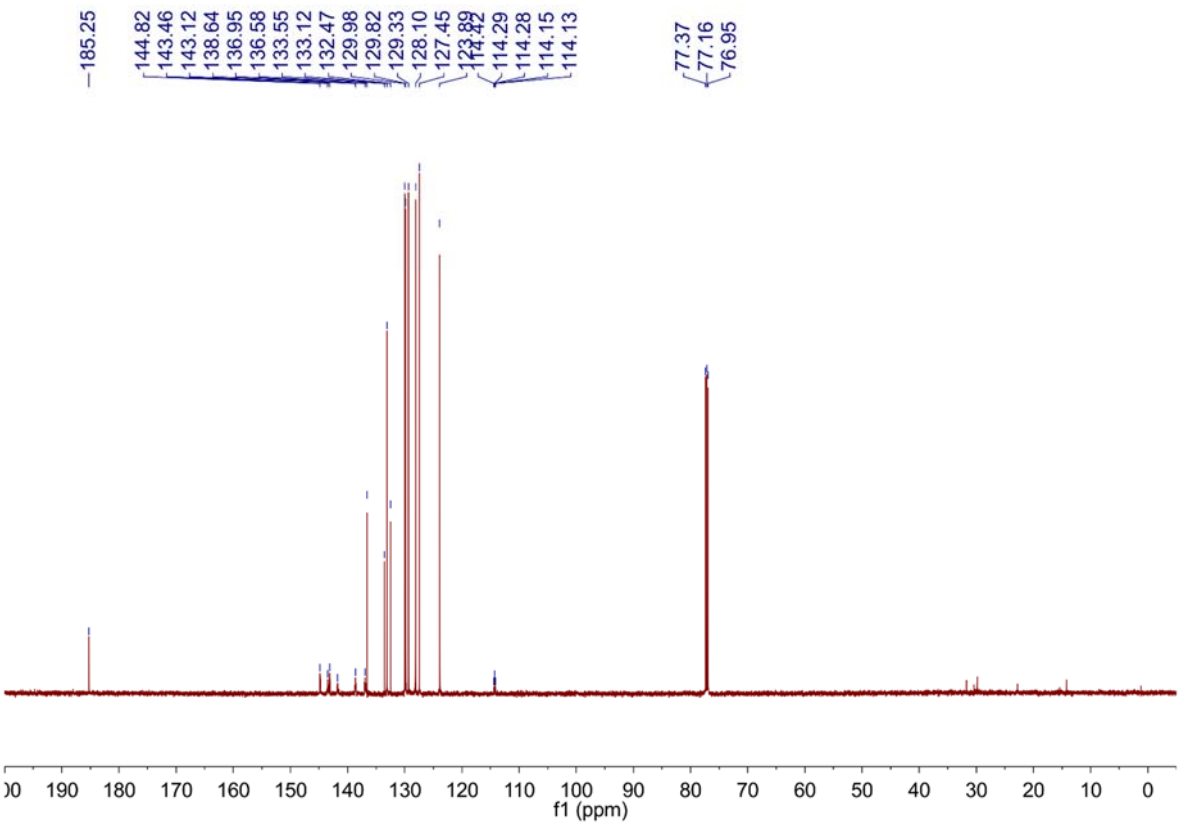


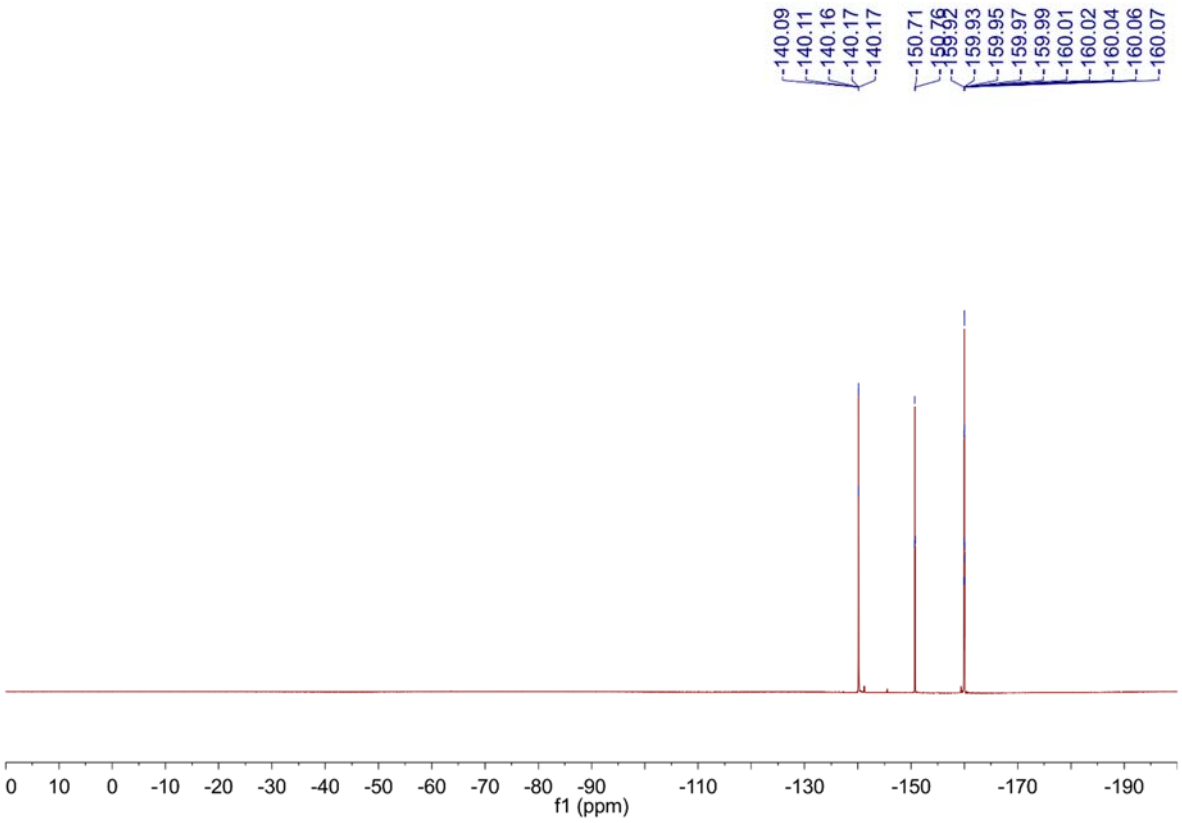
^{1}H NMR (600 MHz), ^{13}C{^{1}H} NMR (151 MHz) and ^{19}F{^{1}H} NMR (376 MHz) spectra of **3q** (rt, $CDCl_3$).



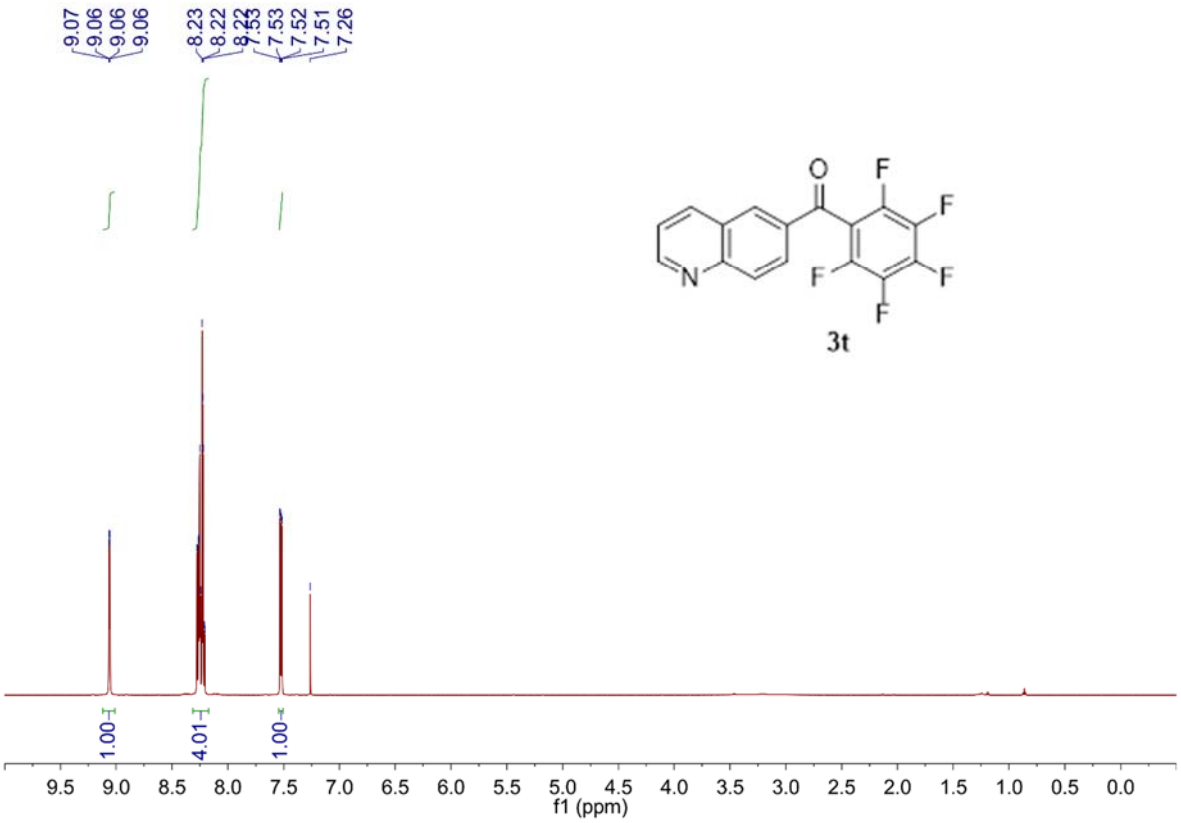
^{1}H NMR (400 MHz) and ^{19}F{^{1}H} NMR (376 MHz) spectra of **3r** (rt, $CDCl_3$).

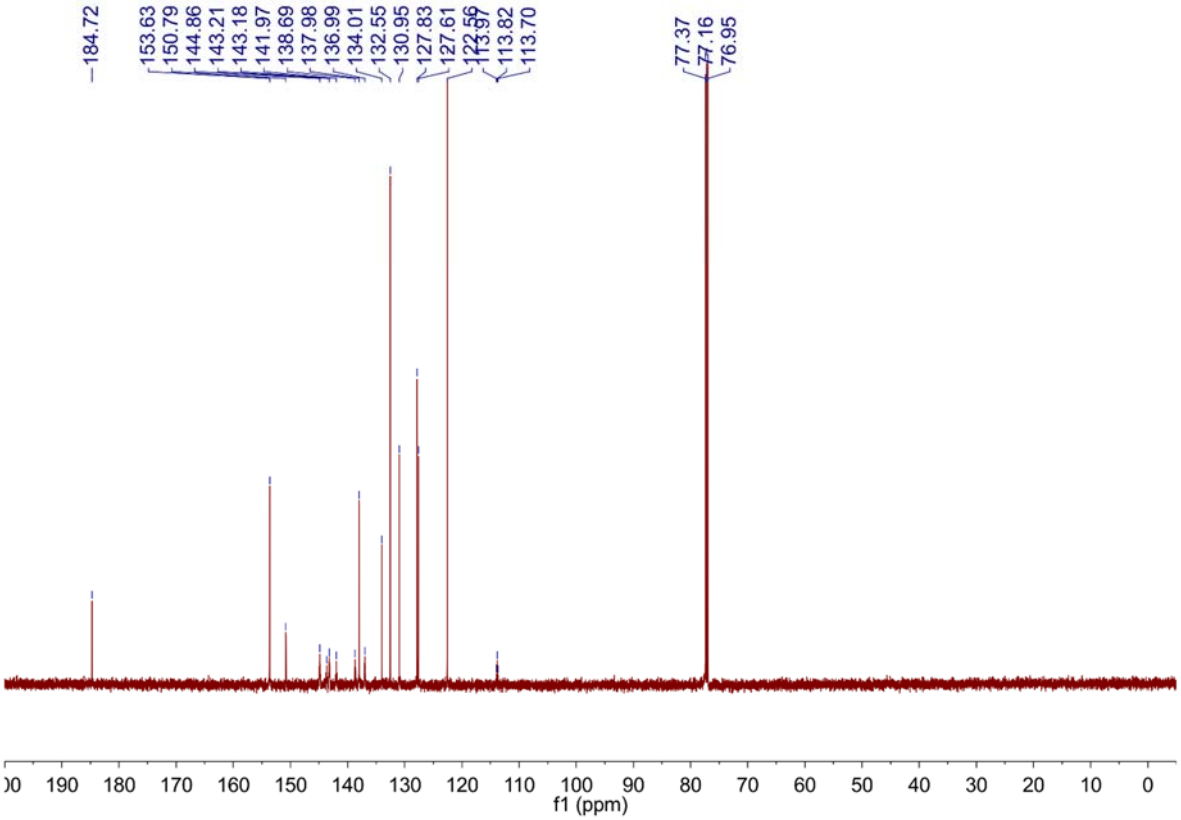

8.23
8.03
8.03
8.01
8.00
7.98
7.95
7.94
7.93
7.91
7.69
7.69
7.67
7.67
7.65
7.65
7.61
7.59
7.59
7.58
7.57
7.57
7.26
O
F
F
F
F
F
3s
1.00
4.05
0.99
0.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

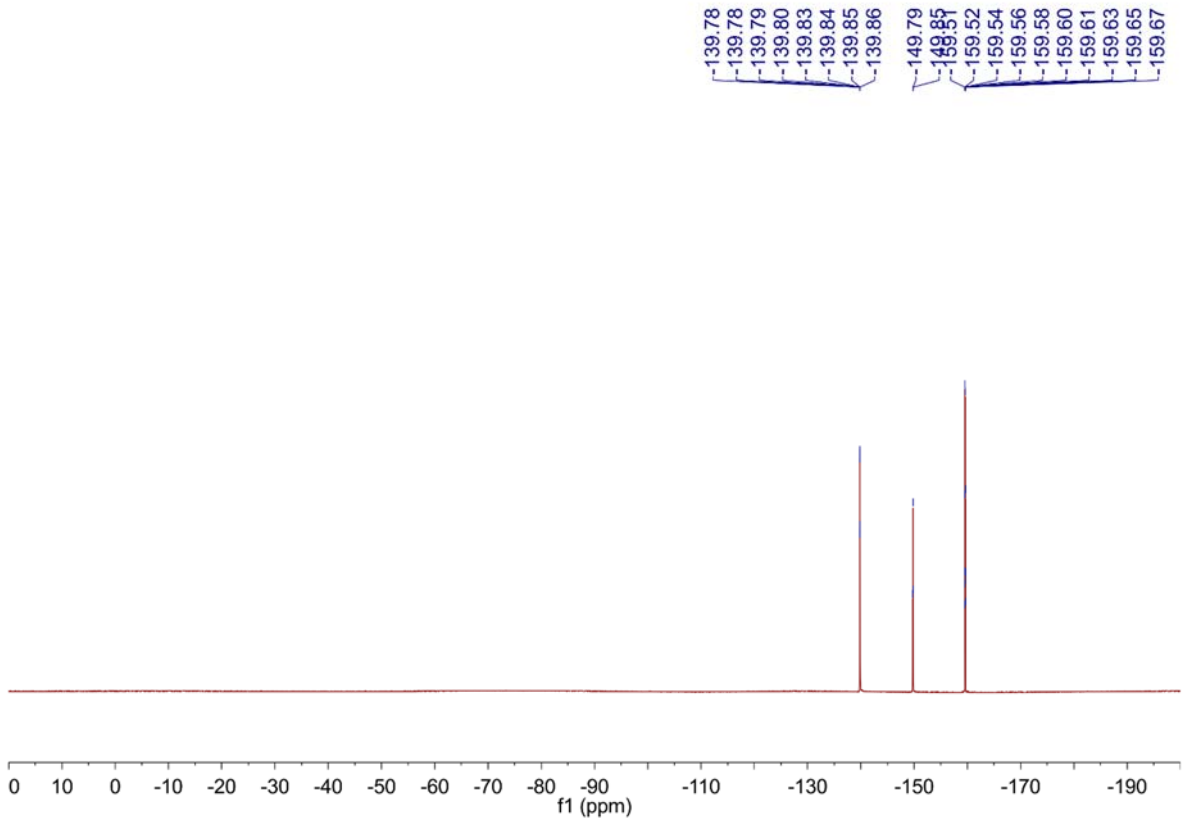

185.25
144.82
143.46
143.12
138.64
136.95
136.58
133.55
133.12
132.47
129.98
129.82
129.33
128.10
127.45
123.89
114.29
114.28
114.15
114.13
77.37
77.16
76.95
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



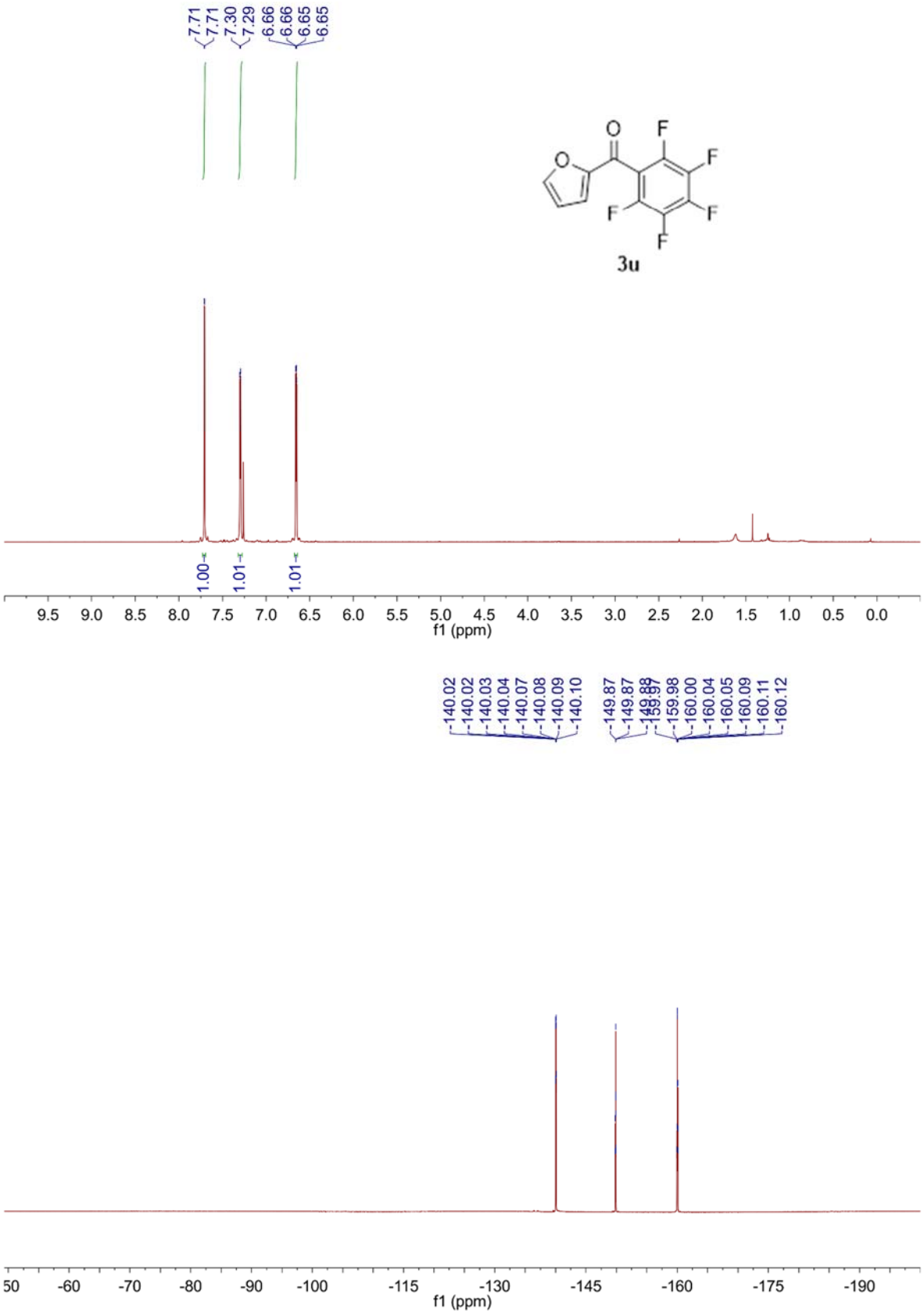
^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (151 MHz) and ^{19}F{^{1}H} NMR (376 MHz) spectra of **3s** (rt, $CDCl_3$).


9.07
9.06
9.06
9.06
8.23
8.22
7.53
7.52
7.51
7.26
O
F
F
F
F
F
N
3t
1.00
4.01
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

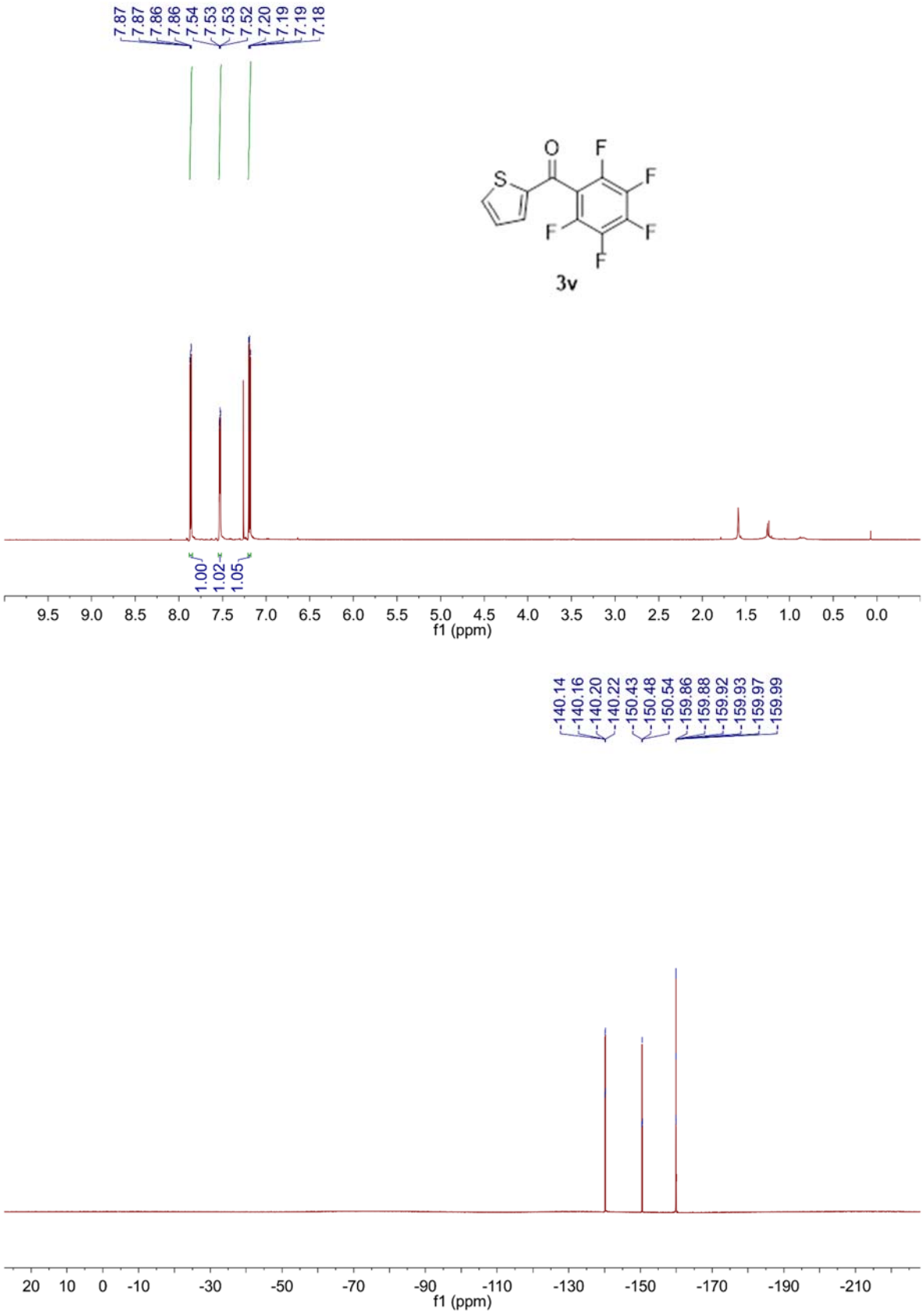

184.72
153.63
150.79
144.86
143.21
143.18
141.97
138.69
137.98
136.99
134.01
132.55
130.95
127.83
127.61
113.82
113.70
77.37
77.16
76.95
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



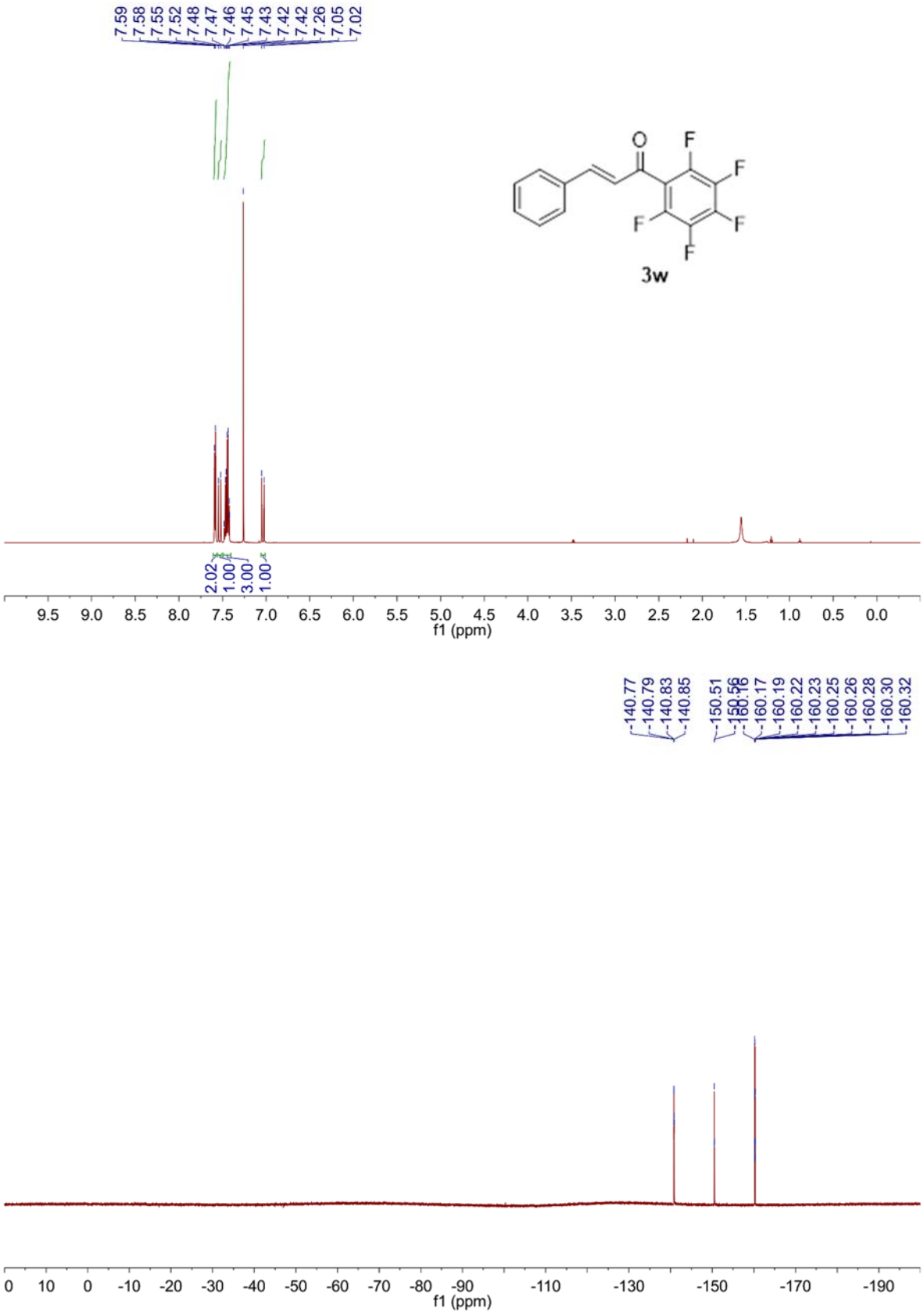
^{1}H NMR (600 MHz), ^{13}C{^{1}H} NMR (151 MHz) and ^{19}F{^{1}H} NMR (376 MHz) spectra of **3t** (rt, $CDCl_3$).



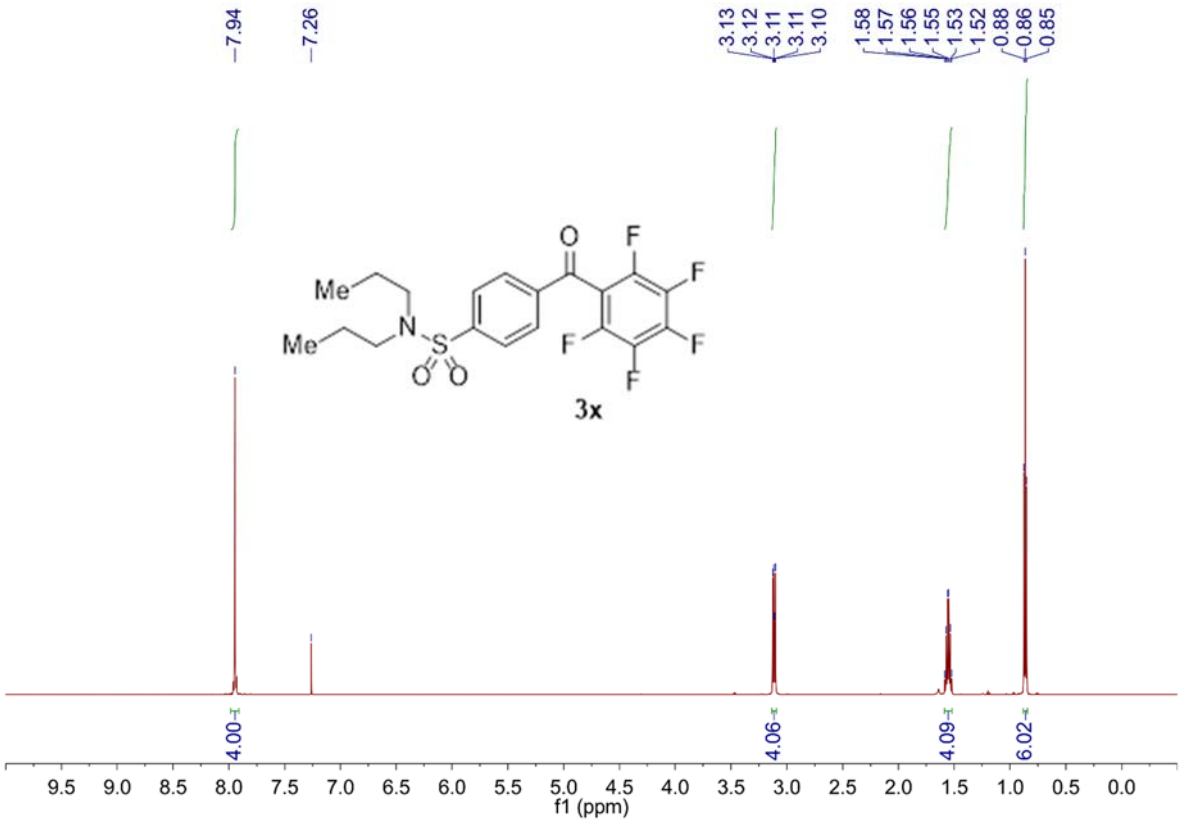
^{1}H NMR (400 MHz) and ^{19}F{^{1}H} NMR (376 MHz) spectra of **3u** (rt, $CDCl_3$).

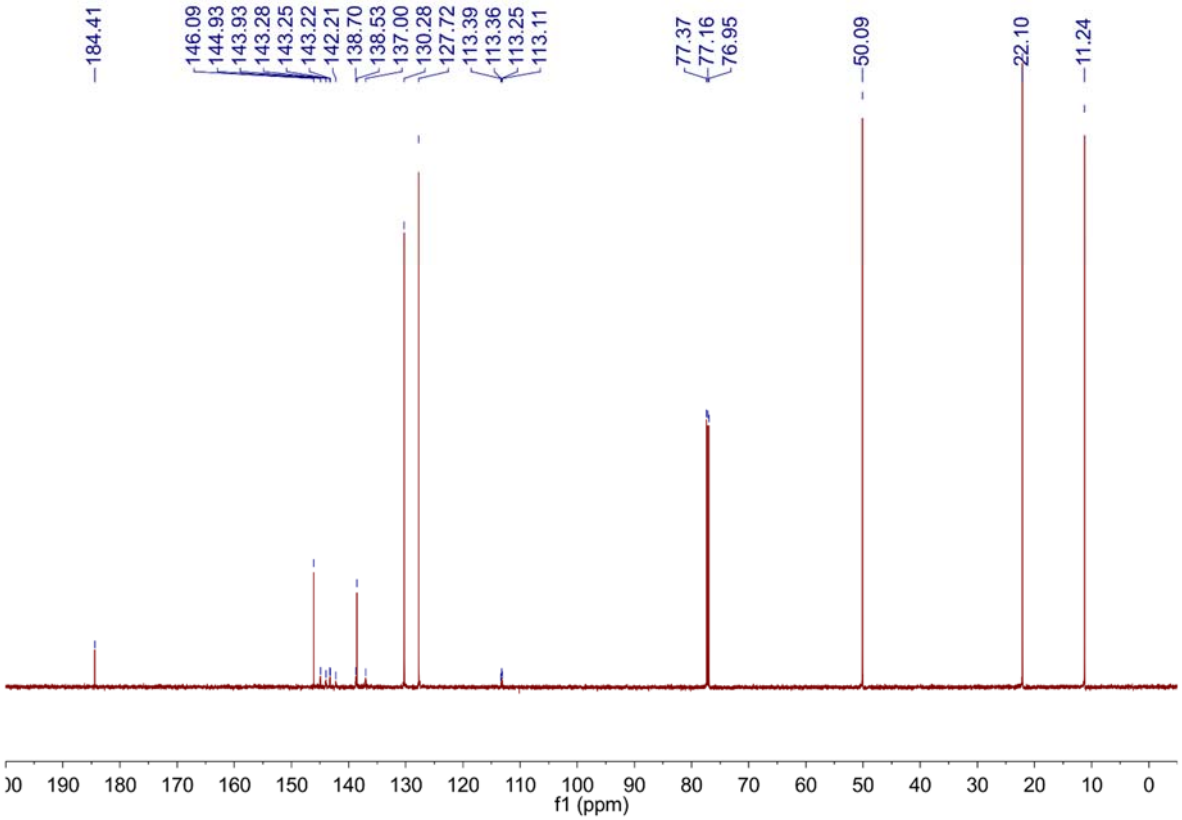


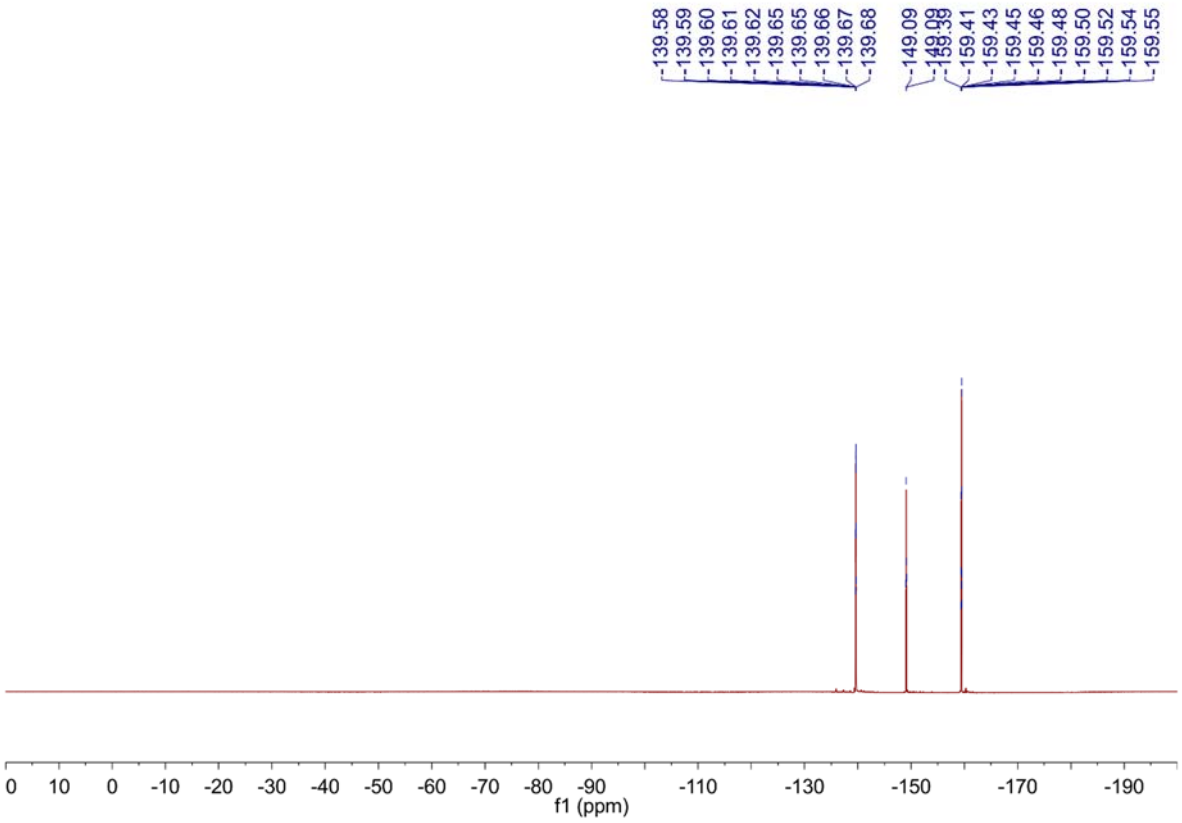
^{1}H NMR (400 MHz) and ^{19}F{^{1}H} NMR (376 MHz) spectra of **3v** (rt, $CDCl_3$).



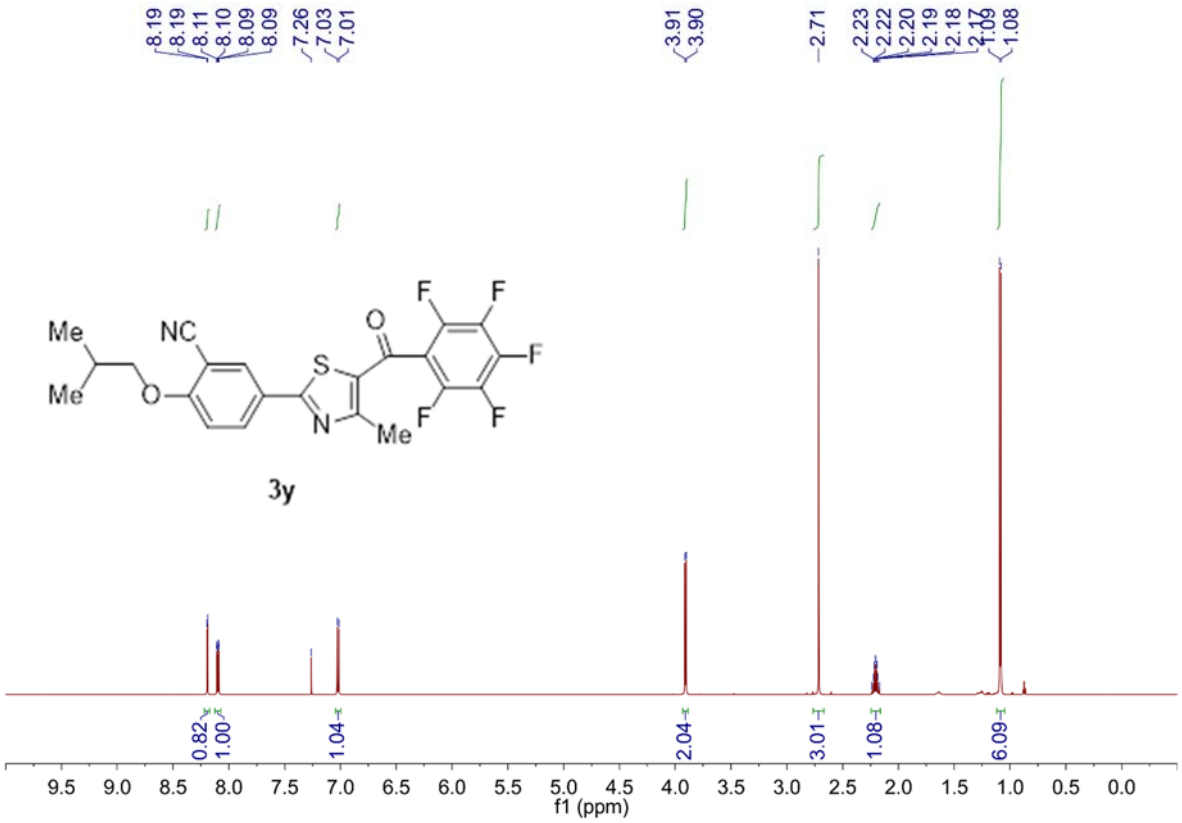
^{1}H NMR (600 MHz) and ^{19}F{^{1}H} NMR (376 MHz) spectra of **3w** (rt, $CDCl_3$).

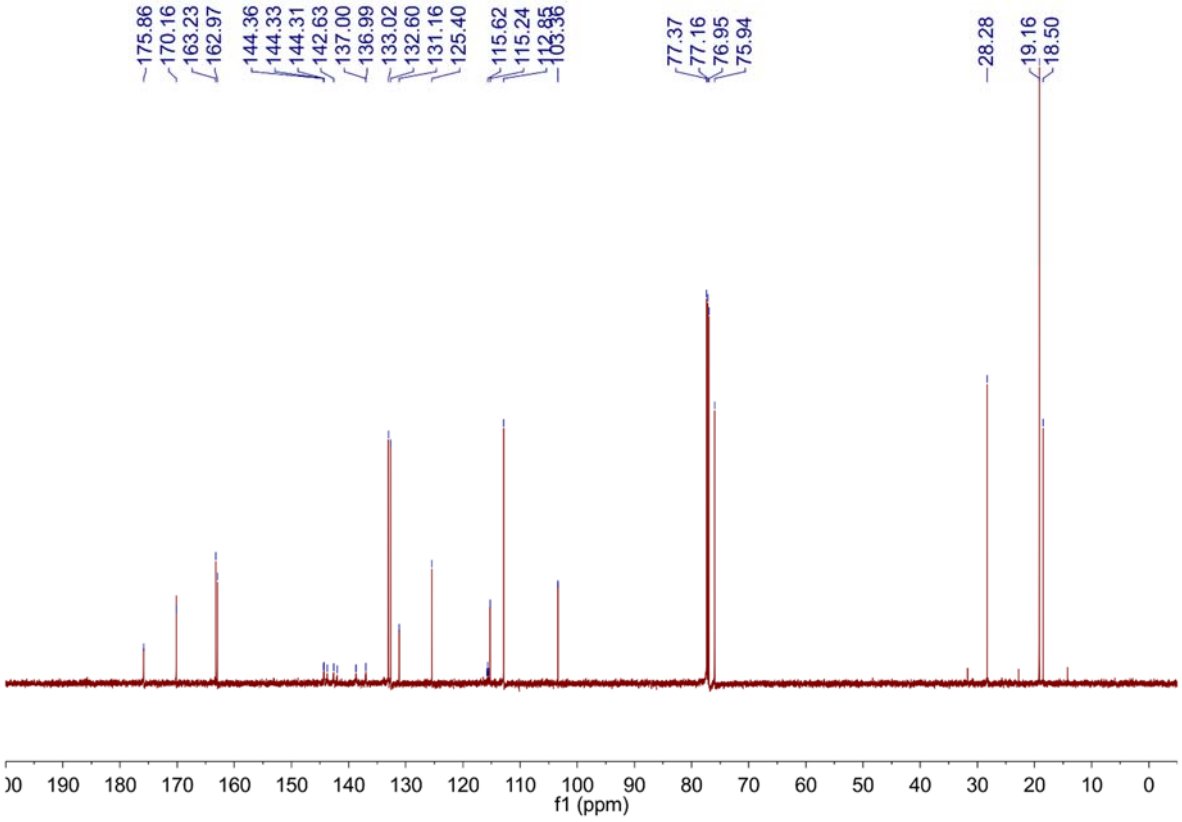

7.94
7.26
3.13
3.12
3.11
3.11
3.10
1.58
1.57
1.56
1.55
1.53
1.52
0.88
0.86
0.85
Me
Me
N
S
O
O
O
F
F
F
F
F
3x
4.00
4.06
4.09
6.02
f1 (ppm)

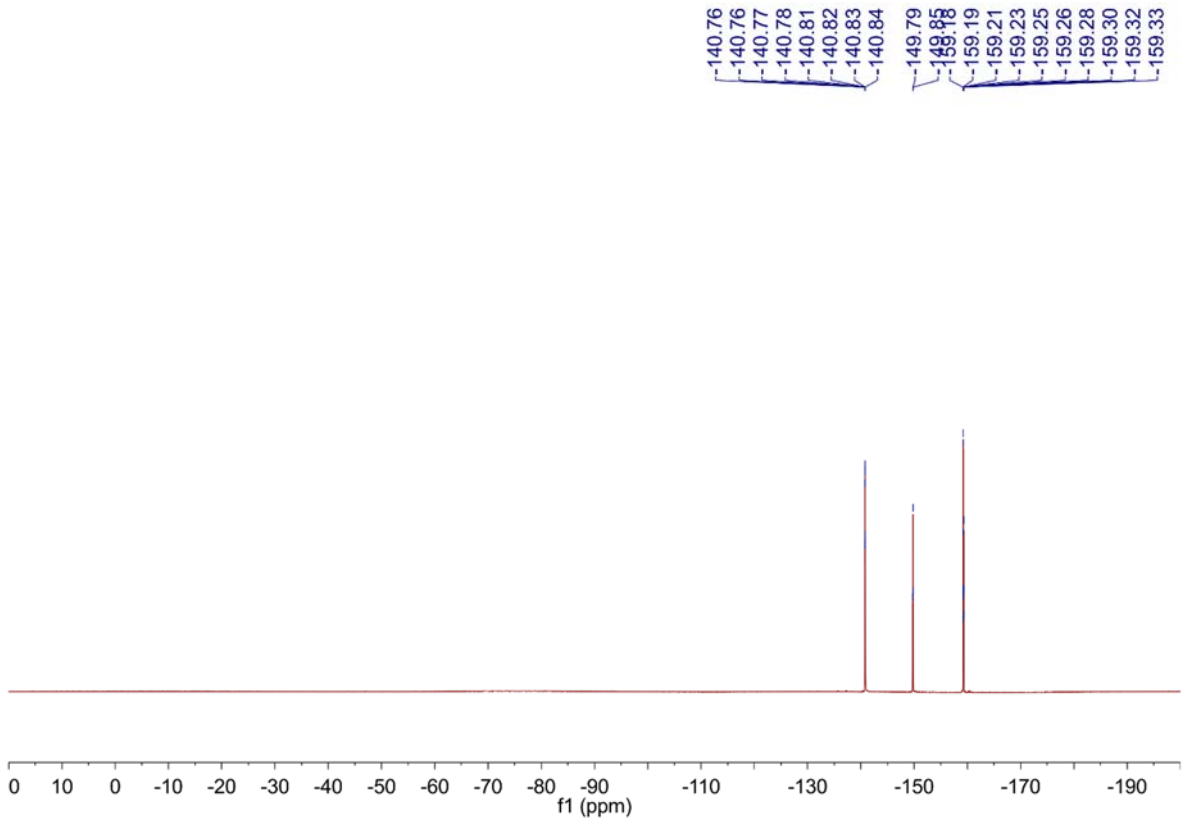

184.41
146.09
144.93
143.93
143.28
143.25
143.22
142.21
138.70
138.53
137.00
130.28
127.72
113.39
113.36
113.25
113.11
77.37
77.16
76.95
50.09
22.10
11.24
f1 (ppm)



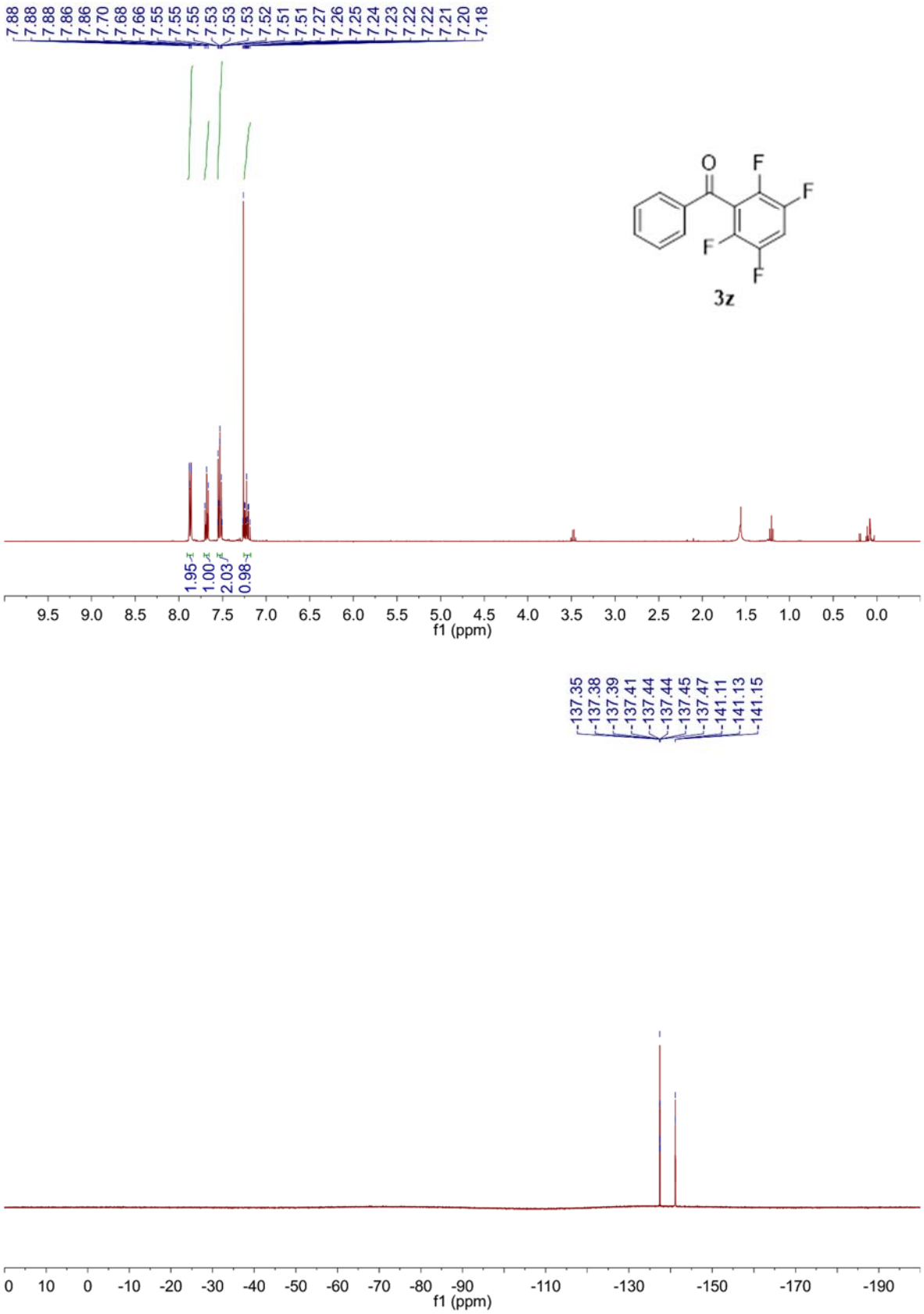
^{1}H NMR (600 MHz), ^{13}C{^{1}H} NMR (151 MHz) and ^{19}F{^{1}H} NMR (376 MHz) spectra of **3x** (rt, $CDCl_3$).


8.19
8.19
8.11
8.10
8.09
8.09
7.26
7.03
7.01
3.91
3.90
2.71
2.23
2.22
2.20
2.19
2.18
2.17
2.09
1.08
Me
Me
NC
O
S
N
Me
O
F
F
F
F
F
3y
0.82
1.00
1.04
2.04
3.01
1.08
6.09
f1 (ppm)

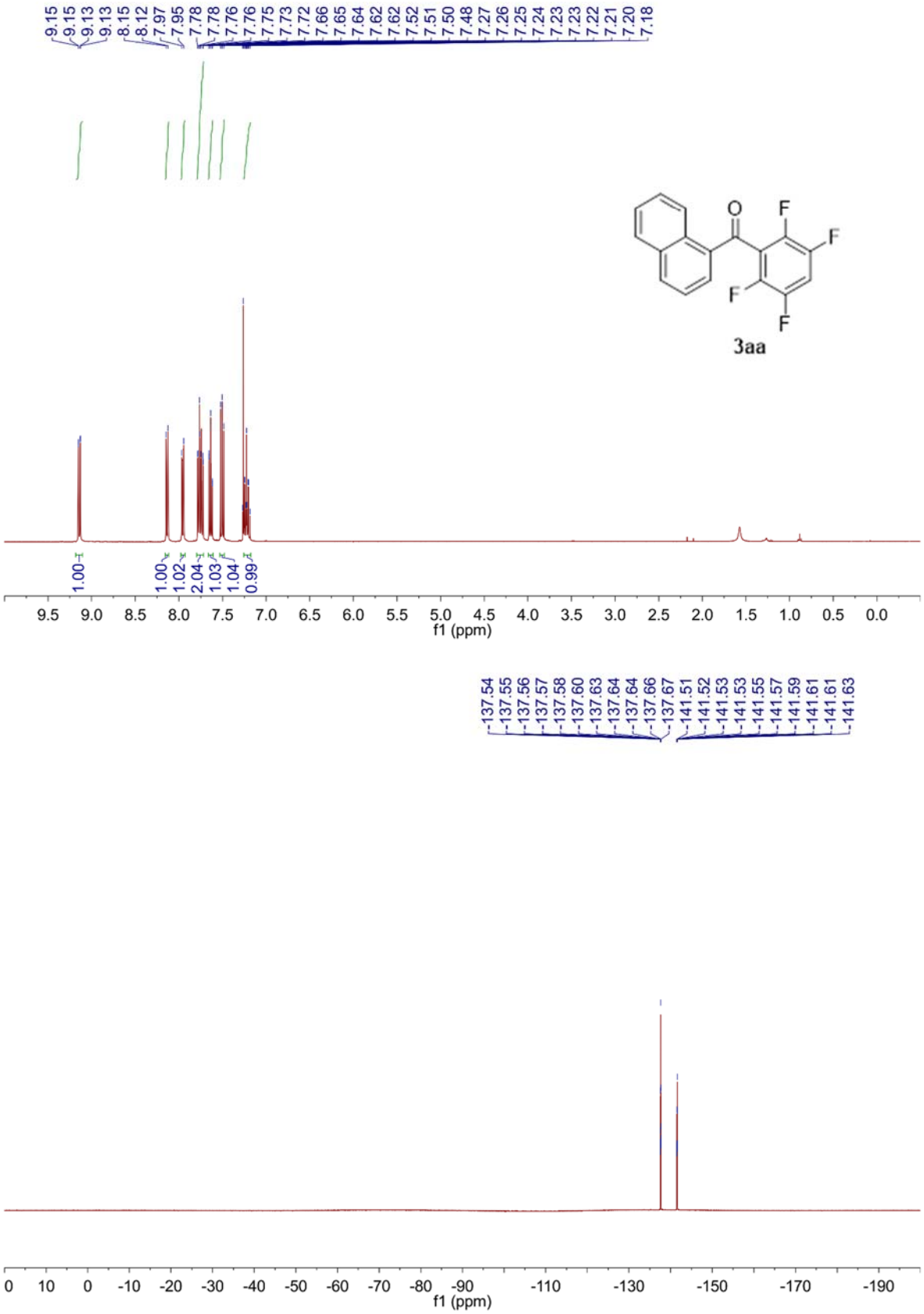

175.86
170.16
163.23
162.97
144.36
144.33
144.31
142.63
137.00
136.99
133.02
132.60
131.16
125.40
115.62
115.24
77.37
77.16
76.95
75.94
28.28
19.16
18.50
f1 (ppm)



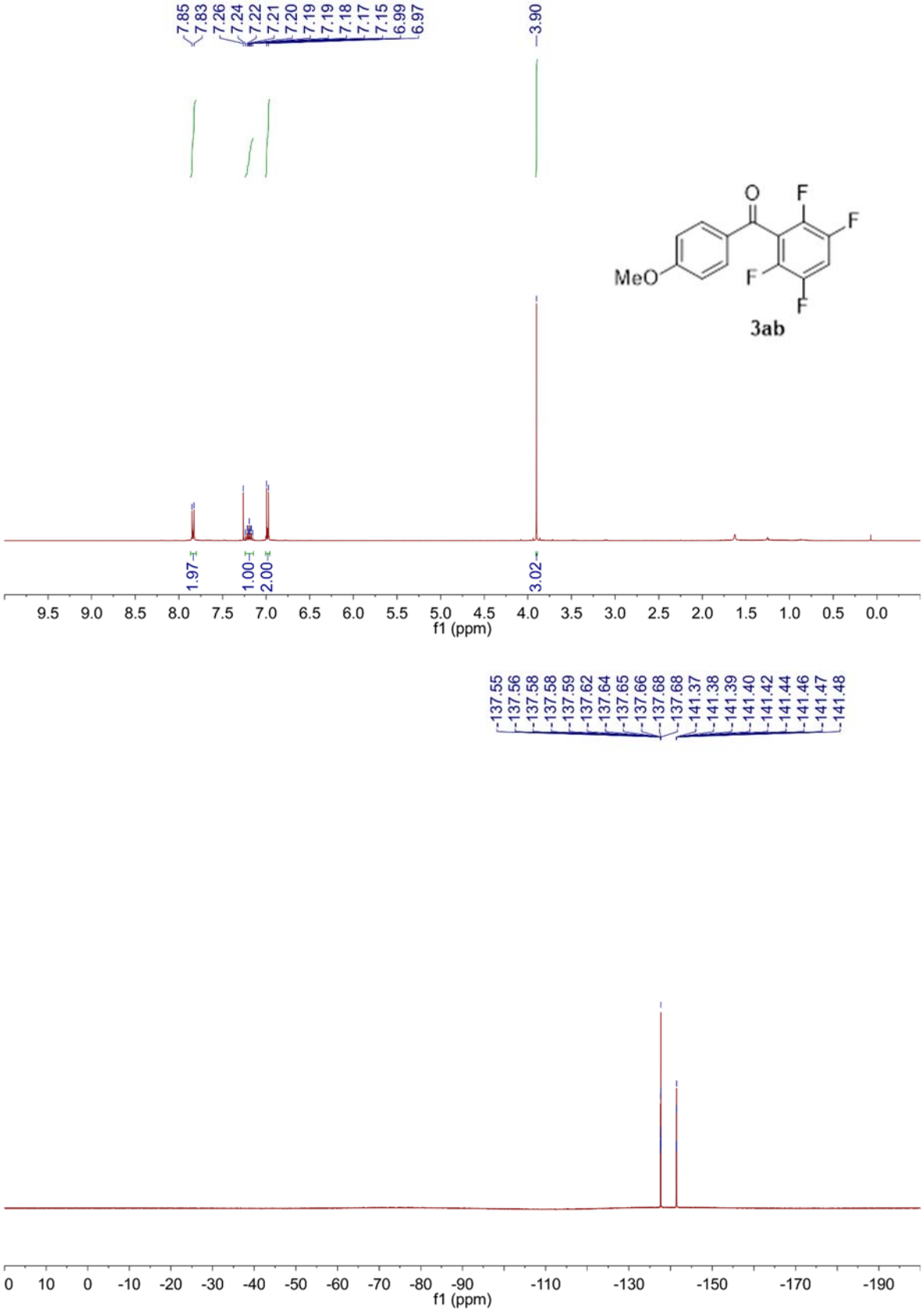
^{1}H NMR (600 MHz), ^{13}C{^{1}H} NMR (151 MHz) and ^{19}F{^{1}H} NMR (376 MHz) spectra of **3y** (rt, $CDCl_3$).



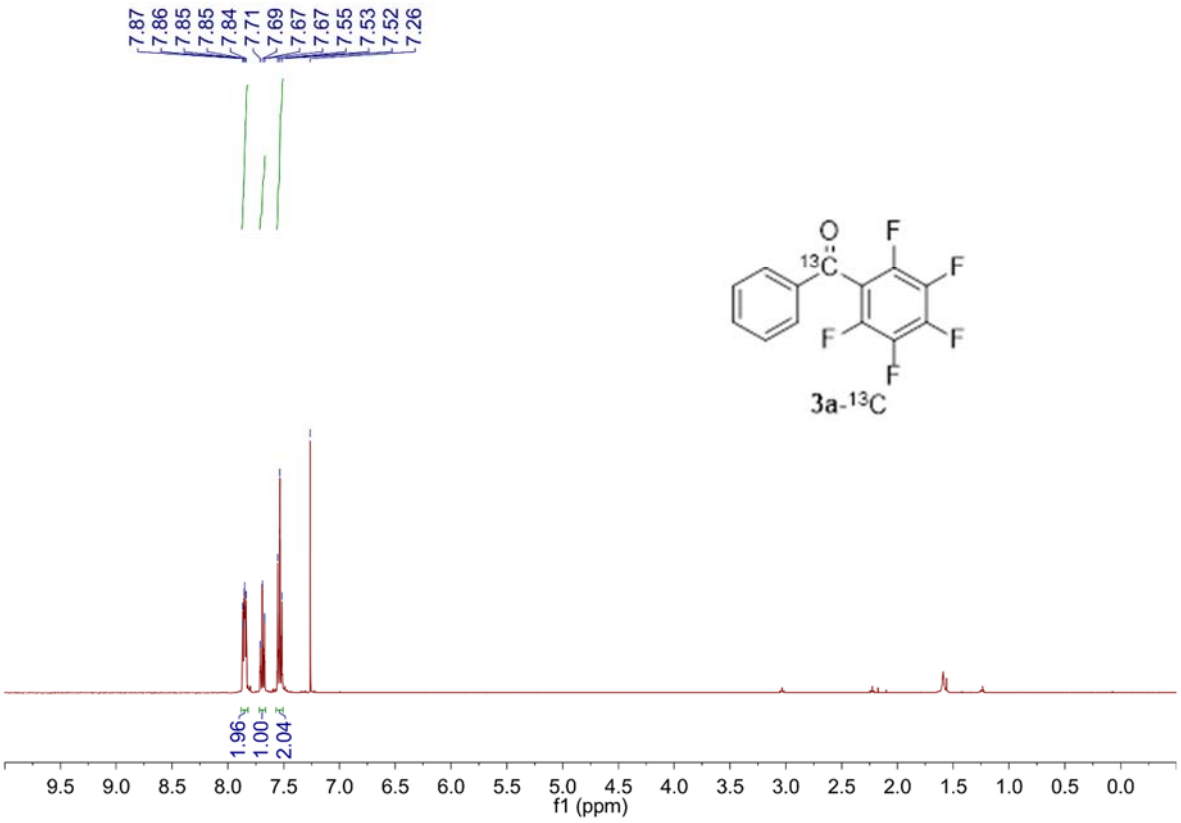
^{1}H NMR (400 MHz) and ^{19}F{^{1}H} NMR (376 MHz) spectra of **3z** (rt, $CDCl_3$).

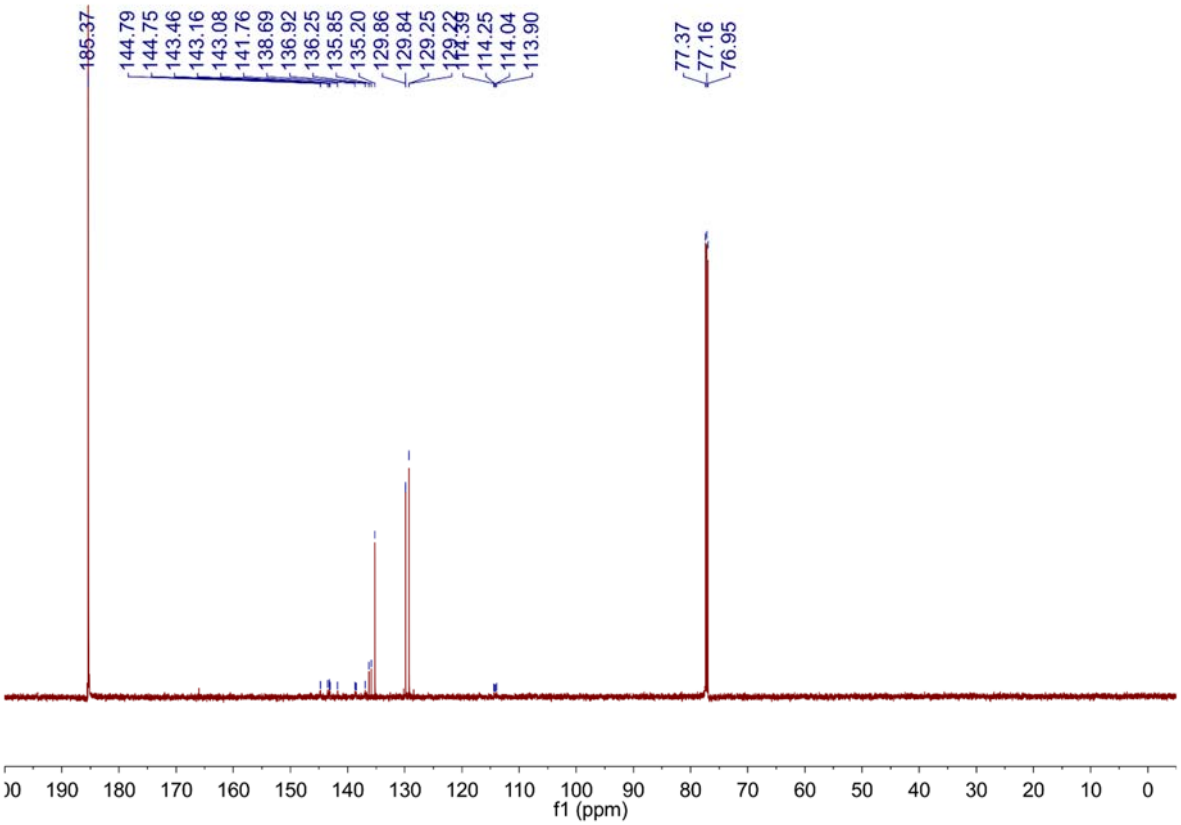


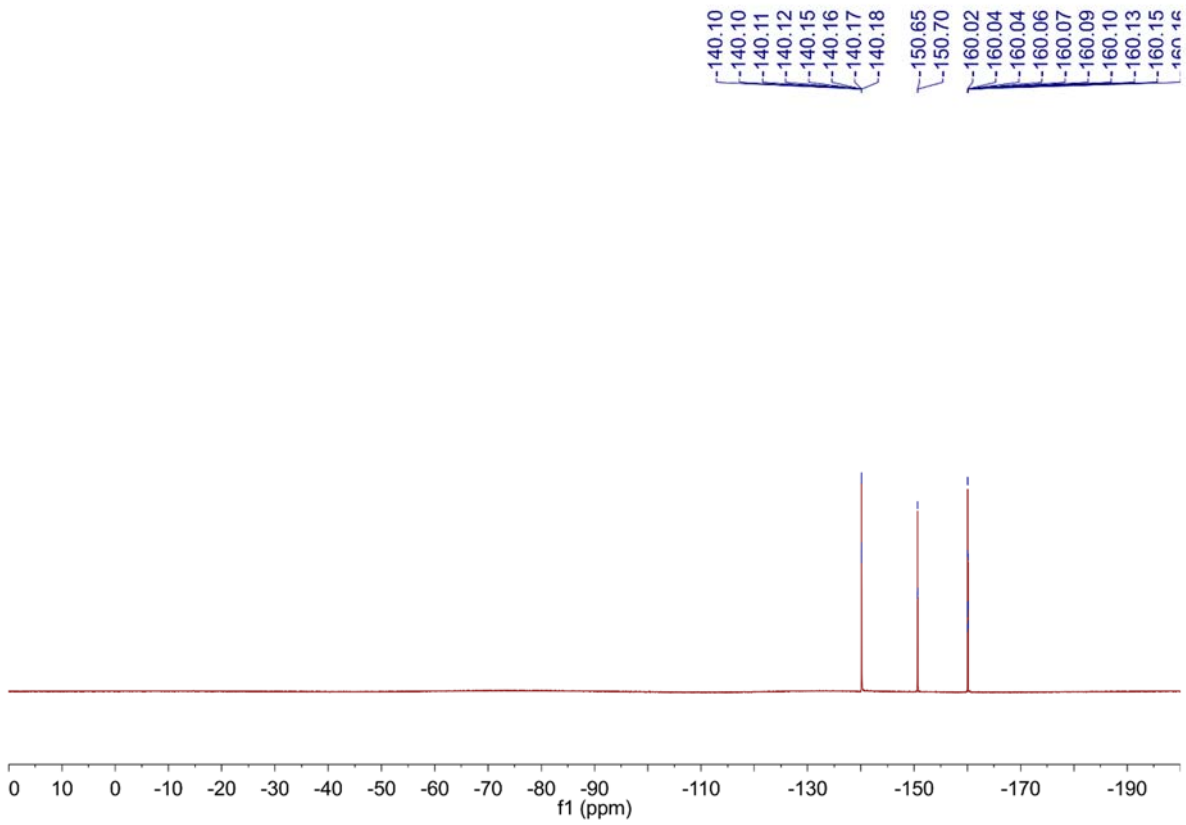
^{1}H NMR (400 MHz) and ^{19}F{^{1}H} NMR (376 MHz) spectra of **3aa** (rt, $CDCl_3$).



^{1}H NMR (400 MHz) and ^{19}F{^{1}H} NMR (376 MHz) spectra of **3ab** (rt, $CDCl_3$).


7.87
7.86
7.85
7.85
7.84
7.71
7.69
7.67
7.67
7.55
7.53
7.52
7.26
O
F
13C
F
F
F
F
3a-13C
1.96
1.00
2.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


185.37
144.79
144.75
143.46
143.16
143.08
141.76
138.69
136.92
136.25
135.85
135.20
129.86
129.84
129.25
114.25
114.04
113.90
77.37
77.16
76.95
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (151 MHz) and ^{19}F{^{1}H} NMR (376 MHz) spectra of **3a**-^{13}C (rt, $CDCl_3$).

4. References

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