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Supporting Information

On the Reactivity of Tetrakis(trifluoromethyl)cyclopentadienone towards Carbon-Based Lewis Bases

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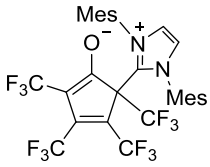
Experimental procedures:

General: All reactions were carried out in flame-dried glassware under Ar. All solvents were purified by distillation over the appropiate drying agents and were transferred under Ar. IR: Nicolet FT-7199 spectrometer, wavenumbers in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), ESIMS: Finnigan MAT 95, accurate mass determinations: Bruker APEX III FT-MS (7 T magnet). NMR: Spectra were recorded on a Bruker AV 600, AV 400 or DPX 300; ^{1}H and ^{13}C chemical shifts (δ) are given in ppm relative to TMS, coupling constants (*J*) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale. Column chromatography was performed on Merck 60 silica gel (40-63 µm). Thin-layer chromatography (TLC) analysis was performed using Merck silica gel 60 F254 TLC plates, and visualized by UV. All commercially available compounds (ABCR, Acros, Aldrich, Fischer) were used as received

Compound **4a**:



1 (90.5 mg, 0.257 mmol) and IMes (78 mg, 0.257 mmol) were solved at -78°C in toluene (2 ml) and the mixture allowed to warm up to room temperature overnight. Removal of the solvents in vacuum afforded crude **4a** as a brown precipitate. Purification by silica gel flash chromatography (10:7 hexene : ethyl acetate) produced analytically pure **4a** as a yellow solid (61.8 mg, 37%).

Yellow crystals suitable for X-ray crystallography could be obtained from pentene/CH_2Cl_2 mixtures.

HRMS calcd. for $[C_{30}H_{24}F_{12}N_2ONa]^+$ 678.158924, found: 679.159473.

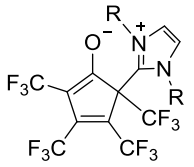
IR (solid): 3068, 1655, 1557, 1451, 1359, 1294, 1235, 1201, 1160, 1074, 982, 909, 847, 703 cm^{-1}.

^{1}H-NMR (400 MHz, CD_2Cl_2): 2.09 (s, 6H), 2.11 (s, 3H), 2.30 (s, 3H), 2.37 (s, 3H), 2.41 (s, 3H), 6.92 (d, *J* = 11.5 Hz, 2H), 7.04 (s, 1H), 7.06 (s, 1H), 7.17 (d, *J* = 1.6 Hz, 1H), 7.32 (d, *J* = 1.6 Hz, 1H) ppm.

^{19}F-NMR (470 MHz, CD_2Cl_2, 273 K): -75.07 (1F), -67.23 (1F), -60.00 (sep, *J* = 11.3 Hz, 3F), -55.25 (q, *J* = 9.3 Hz, 3F), -54.16 (1F), -50.63 (3F) ppm.

^{13}C-NMR (100 MHz CD_2Cl_2): 17.42, 18.12, 18.31, 20.99, 21.19, 63.50 (q, $J_{C,F}$ = 28 Hz), 92.40 (q, $J_{C,F}$ = 34 Hz), 95.30 (q, $J_{C,F}$ = 37 Hz), 120.64 (q, $J_{C,F}$ = 277 Hz), 121.37 (q, $J_{C,F}$ = 285 Hz), 122.75 (q, $J_{C,F}$ = 267 Hz), 124.14 (q, $J_{C,F}$ = 267 Hz), 126.29, 126.72, 129.23, 129.36, 129.67, 129.82, 129.93, 133.65, 134.97, 135.30, 136.31, 137.54, 141.74, 142.84, 142.95, 151.3 (q, $J_{C,F}$ = 35 Hz), 176.67 ppm.

Compound **4b**:



R = 2,6-diisopropylphenyl

1 (78.0 mg, 0.222 mmol) and IPr (86.3 mg, 0.222 mmol) were solved at -78°C in pentane (5 ml) and the mixture allowed to warm to r.t. overnight. Removal of the solvent in vacuum afforded **4b** as a brown precipitate that was purified by silica gel flash chromatography (10:7 hexene : ethyl acetate) giving **4b** as a yellow solid (39 mg, 24%).

Yellow crystals suitable for X-ray crystallography were obtained from pentene/CH_2Cl_2 mixtures.

ESI(pos) (*m/z*): 741 = $[C_{36}H_{37}F_{12}N_2O]^+$ and 763 = $[C_{36}H_{36}F_{12}N_2ONa]^+$.

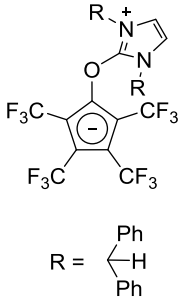
IR (solid): 2963, 1675, 1547, 1445, 1288, 1242, 1224, 1201, 1187, 1165, 1153, 1111, 1074, 1050, 905, 847, 799, 756, 699 cm^{-1}**.**

^{1}H-NMR (600 MHz, CD_2Cl_2): 0.94 (d, *J* = 6.0 Hz, 3H), 1.02 (d, *J* = 6.0 Hz, 3H), 1.09 (d, *J* = 5.3 Hz, 3H), 1.21 (d, *J* = 5.7 Hz, 3H), 1.31 (d, *J* = 5.7 Hz, 3H), 1.39 (d, *J* = 5.3 Hz, 6H), 1.46 (d, *J* = 5.3 Hz, 3H), 2.29 (s, 1H), 2.71 (1H), 2.78 (s, 1H), 3.17 (s, 1H), 7.22 (s, 1H), 7.29-7.40 (m, 4H), 7.49 (s, 1H), 7.52-7.60 (m, 2H) ppm.

^{19}F-NMR (282 MHz CD_2Cl_2, 273 K): -75.80 (1F), -65.55 (1F), -59.68 (3F), -54.08 (3F), -51.62 (1F), -51.00 (3F) ppm.

^{13}C-NMR (151 MHz CD_2Cl_2): 20.6, 21.1, 21.9, 22.1, 26.0, 26.3, 28.0, 28.1, 28.8, 28.9, 29.5, 30.3, 63.4 (q, $J_{C,F}$ = 28 Hz), 90.5 (q, $J_{C,F}$ = 36 Hz), 93.7 (q, $J_{C,F}$ = 36 Hz), 120.6 (q, $J_{C,F}$ = 272 Hz), 121.2 (q, $J_{C,F}$ = 286 Hz), 122.8 (q, $J_{C,F}$ = 268 Hz), 123.7 (q, $J_{C,F}$ = 268 Hz), 123.8, 124.1, 124.9, 125.0, 127.0, 127.1, 130.5, 132.1, 133.1, 133.8, 144.2, 145.6, 145.7, 147.0, 147.9, 151.9 (q, $J_{C,F}$ = 35 Hz), 176.4 ppm.

Compound **5c:**



1 (93.3 mg, 0.265 mmol) and carbene **6** (225.0 mg, 0.265 mmol) were solved at -78°C in pentene (15 ml) and the mixture allowed to warm to room temperature overnight. Removal of the solvents in vacuum afforded crude **5c** as a brown precipitate that was purified by silica gel flash chromatography (6:1 pentene : ethyl acetate). Yellow solid (107.5 mg, 32%). Crystals suitable for X-ray crystallography were obtained from pentane/CH_2Cl_2 mixtures.

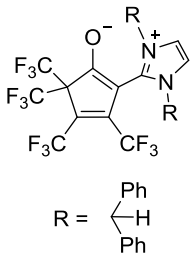
ESI(pos) (*m/z*): 1265 = $[C_{78}H_{57}F_{12}N_2O]^+$ and 1287 = $[C_{78}H_{56}F_{12}N_2ONa]^+$.

^{1}H-NMR (400 MHz, CD_2Cl_2): 2.18 (s, 6H), 4.50 (s, 2H), 5.28 (s, 4H), 6.61 (d, *J* = 7.5 Hz, 8H), 6.83 (s, 4H), 6.97 (d, *J* = 7.5 Hz, 8H), 7.07-7.14 (m, 12H), 7.26-7.32 (m, 12H) ppm.

^{19}F-NMR (376 MHz, CD_2Cl_2): -52.0 (6F), -49.9 (6F) ppm.

^{13}C-NMR (100 MHz CD_2Cl_2): 21.8, 52.3, 118.8, 127.4, 128.3, 128.8, 129.0, 129.4, 130.6, 131.2, 141.8, 141.9, 143.9. (Lack of solubility prevented the detection of the cyclopentadiene signals).

Compound **8**:



1 (93.3 mg, 0.265 mmol) and carbene **6** (225.0 mg, 0.265 mmol) were solved at -78°C in pentane (15 ml) and the mixture allowed to warm up to room temperature overnight. Removal of the solvents in vacuum afforded **8** as a brown precipitate that could be further purified by silica gel flash chromatography (6:1 pentene : ethyl acetate) Yellow solid (164,3 mg, 49%). Crystals suitable for X-ray crystallography were obtained from pentane/CH_2Cl_2 mixtures.

ESI(pos): 1265 = $[C_{78}H_{57}F_{12}N_2O]^+$, 1287 = $[C_{78}H_{56}F_{12}N_2ONa]^+$.

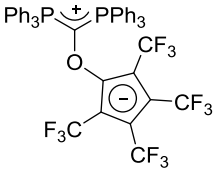
IR (solid): 3161, 3061, 3026, 2923, 1665, 1557, 1494, 1446, 1319, 1212, 1183, 1133, 1086, 964, 851, 752, 698, 604 cm^{-1}.

^{1}H-NMR (400 MHz, CD_2Cl_2): 2.19 (s, 6H), 4.86 (s, 2H), 5.17 (s, 2H), 5.63 (s, 2H), 6.63-6.69 (m, 8H), 6.82 (d, *J* = 7.8 Hz, 4H), 7.00 (d, *J* = 7.8 Hz, 4H), 7.06-7.14 (m, 12H), 7.22-7.31 (m, 16H) ppm.

^{19}F-NMR (376 MHz, CD_2Cl_2): -65.60 (6F), -58.07 (3F), -52.17 (3F) ppm.

^{13}C-NMR (151 MHz CD_2Cl_2): 21.8, 51.5, 51.8, 63.4 (q, $J_{C,F}$ = 27 Hz), 63.5 (q, $J_{C,F}$ = 27 Hz), 83.0, 97.6 (q, $J_{C,F}$ = 39 Hz), 121.7 (q, $J_{C,F}$ = 274 Hz), 121.7 (q, $J_{C,F}$ = 284 Hz), 122.4 (q, $J_{C,F}$ = 266 Hz), 122.7, 126.8(7), 126.9, 127.2, 128.4, 128.7, 128.8, 129.0, 129.3, 129.5, 130.4, 131.0, 131.1, 131.1(7), 131.4, 140.5, 141.0, 142.5, 142.7, 143.1, 144.0, 144.5, 146.5, 150.6 (q, $J_{C,F}$ = 33 Hz), 179.1 ppm.

Compound **9:**



1 (70.4 mg, 0.265 mmol) and carbodiphosphorane **7** (107.2 mg, 0.200 mmol) were solved at -78°C in toluene (15 ml) and the mixture allowed to warm up to room temperature overnight. Removal of the solvents in vacuum afforded **9** as a yellow precipitate that could be further purified by silica gel flash chromatography (6:1 pentene : ethyl acetate) (161,3 mg, 91%).Yellow crystals suitable for X-ray crystallography were obtained from pentane/CH_2Cl_2 mixtures.

ESI(pos): 889 = $[C_{46}H_{31}F_{12}OP_2]^+$.

HRMS calcd. for $[C_{46}H_{31}F_{12}OP_2]$ 889.165309, found: 889.16453.

IR (solid)**:** 1503, 1435, 1285, 1208, 1189, 1089, 1040, 997, 832, 736, 721, 688 cm^{-1}.

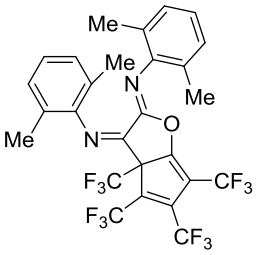
^{1}H-NMR (400 MHz, CD_2Cl_2): 7.28-7.34 (m, 12H), 7.47-7.52 (m, 6H), 7.53-7.59 (m, 12H) ppm.

^{31}P-NMR (162 MHz, CD_2Cl_2): 21.37 ppm.

^{19}F-NMR (376 MHz, CD_2Cl_2): -48.20 (6F), -50.60 (6F) ppm.

^{13}C-NMR (100 MHz, CD_2Cl_2): 135.5(t, *J* = 4.9 Hz), 133.5 (br.s.), 129.2 (t, *J* = 6.2 Hz), 125.0 (*J* = 45.0 Hz), (the signals from the cyclopentadiene moiety were not detected after overnight adquisition).

Compound **11a:**



1 (32.8 mg, 0.093 mmol) and 2,6-(dimethylphenyl)isocianide (24.4 mg, 0.186 mmol) were solved at -78°C in CH_2Cl_2 (3 ml) and the mixture was allowed to warm to room temperature overnight. REemoval of the solvents in vacuum to afforded crude **11a** as orange oil (50.9 mg, 89%). Yellow crystals suitable for X-ray crystallography were obtained by cooling to -20°C a pentene solution.

HRMS calcd. for $[C_{27}H_{19}F_{12}N_2O]^+$ 615.130029, found: 615.129560.

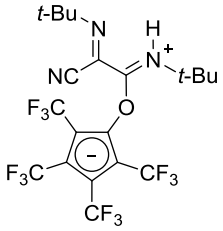
IR (neat): 2959, 1789, 1658, 1585, 1471, 1364, 1293, 1161, 1066, 994, 897, 859, 764 cm^{-1}.

^{1}H-NMR (400 MHz, $CDCl_3$): 1.86 (s, 6H), 1.95 (s, 3H), 2.16 (s, 3H), 6.92-6.98 (m, 4H), 7.00-7.05 (m, 2H) ppm.

^{19}F-NMR 376 MHz, $CDCl_3$, 300 K: -65.57 (q, *J* = 6.8 Hz, 3F), -60.19 (sep., *J* = 10.0 Hz, 3F), -59.16 (q, *J* = 8.8 Hz, 3F), -54.84 (m, 3F).

^{13}C-NMR 100 MHz $CDCl_3$, 300 K: 17.7, 17.8, 17.8, 67.8 (q, $J_{C,F}$ = 29 Hz), 109.2 (q, $J_{C,F}$ = 40 Hz, 2C), 118.7 (q, $J_{C,F}$ = 275 Hz), 119.3 (q, $J_{C,F}$ = 271 Hz), 119.6 (q, $J_{C,F}$ = 272 Hz), 121.8 (q, $J_{C,F}$ = 289 Hz), 121.8, 124.6, 125.1, 125.7, 126.9, 127.9, 128.1, 128.2, 140.6, 141.4, 142.9 (q, $J_{C,F}$ = 39 Hz), 146.2, 146.5, 161.5.

Compound **13:**



1 (43.1 mg, 0.122 mmol) and *terc*-butylisonitrile (30.7 mg, 0.367 mmol) were solved at -78°C in CH_2Cl_2 (4 ml) and the mixture allowed to warm up to room temperature slowly overnight. Removal of the solvents in vacuum afforded **13** as orange solid. (53.9 mg, 81%). Yellow crystals suitable for X-ray crystallography were obtained from a pentene/CH_2Cl_2 solution.

ESI(pos) (m/z): 546 $[C_{20}H_{20}F_{12}N_3O]^+$.

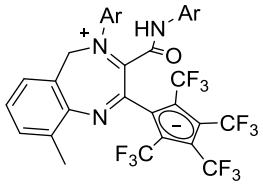
IR (solid): 3273, 2996, 1660, 1532, 1471, 1402, 1311, 1280, 1213, 1190, 1114, 920, 763, 673 cm^{-1}.

^{1}H-NMR (300 MHz, $CDCl_3$): 1.48 (s, 9H), 1.69 (s, 9H), 8.56 (br.s, 1H) ppm.

^{19}F-NMR (282 MHz, $CDCl_3$): -52.60 (6F), -51.84 (6F) ppm.

^{13}C-NMR (100 MHz CD_2Cl_2): 28.1, 28.6, 62.3, 64.4, 100.8 (q, $J_{C,F}$ = 34 Hz, 2C), 105.6, 123.5 (q, $J_{C,F}$ = 269 Hz), 123.7 (q, $J_{C,F}$ = 269 Hz), 126.3, 129.8, 139.4, 146.4, 163.8 ppm.

Compound **14a**:



1 (32.5 mg, 0.092 mmol) and 2,6-(dimethylphenyl)isocianide (36.3 mg, 0.277 mmol) were solved at -78°C in CH_2Cl_2 (3 ml) and the mixture was allowed to slowly warm to room temperature overnight. Removal of the solvents in vacuum afforded **14a** as orange oil (24.6 mg, 36%). Alternatively, 2,6-(dimethylphenyl)isocianide (12.1 mg, 0.0923 mmol) can be added at -78°C to a solution of **11a** in CH_2Cl_2 (3 ml) obtaining the same result. Red crystals suitable for X-ray crystallography were obtained from pentene/CH_2Cl_2 mixtures.

ESI(pos) (m/z)= 746 $[C_{36}H_{28}F_{12}N_3O]$.

HRMS calcd. for $[C_{36}H_{28}F_{12}N_3O]^+$ 746.203528, found: 746.203720.

IR (solid): 3406, 1697, 1496, 1200, 1111, 781, 622, 500, 458 cm^{-1}.

^{1}H-NMR (600 MHz, CD_2Cl_2): 1.31 (s, 6H), 1.35 (s, 3H), 2.69 (s, 3H), 2.72 (s, 3H), 4.87 (d, *J* = 12.77 Hz, 1H), 5.11 (d, *J* = 12.77 Hz, 1H), 6.89 (d, *J* = 7.62 Hz, 2H), 7.03 (t, *J* = 7.50 Hz, 1H), 7.10 (m, 3H), 7.36 (d, *J* = 6.76 Hz, 1H), 7.41 (t, *J* = 7.68 Hz, 1H), 7.56 (t, *J* = 7.62 Hz, 1H), 7.65 (d, *J* = 6.56 Hz, 1H) ppm.

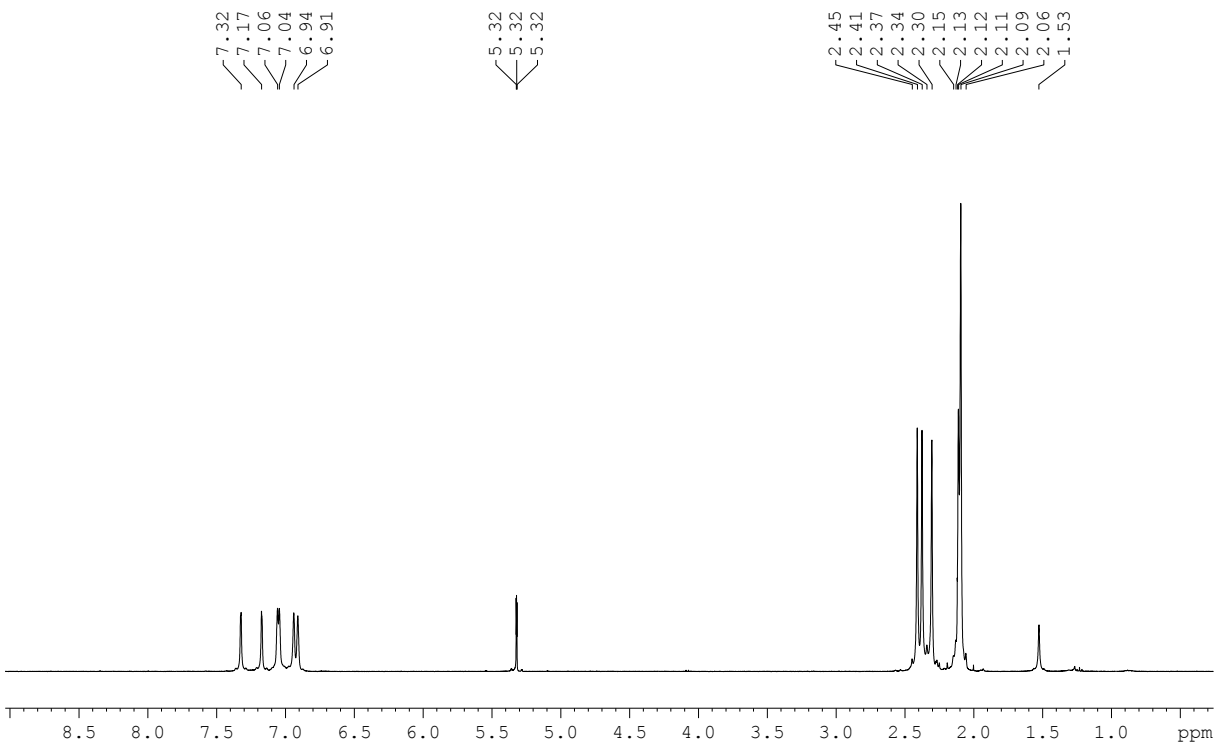
^{19}F-NMR (282 MHz, $CDCl_3$): -52.82 (sep, *J* = 10.6 Hz, 3F), -52.40 (sep, *J* = 10.6 Hz, 3F), -49.10 (q, *J* = 10.4 Hz, 3F), -46.15 (q, *J* = 10.4 Hz, 3F) ppm.

^{13}C-NMR (151 MHz CD_2Cl_2): 16.6, 18.1, 18.7, 18.9, 63.8 (d, $J_{C,F}$ = 4 Hz), 110.3 (q, $J_{C,F}$ = 35 Hz), 111.6 (q, $J_{C,F}$ = 35 Hz), 112.3 (q, $J_{C,F}$ = 37 Hz), 113.7 (q, $J_{C,F}$ = 37 Hz), 116.2, 122.5, 123.7 (q, $J_{C,F}$ = 268 Hz), 124.5 (q, $J_{C,F}$ = 269 Hz), 125.7 (q, $J_{C,F}$ = 268 Hz), 126.5, 128.8, 129.1, 130.5, 130.7, 130.8, 132.4, 133.2, 133.8, 133.8, 134.5, 136.1, 140.3, 140.3, 145.4, 150.5, 155.0, 158.3 ppm.

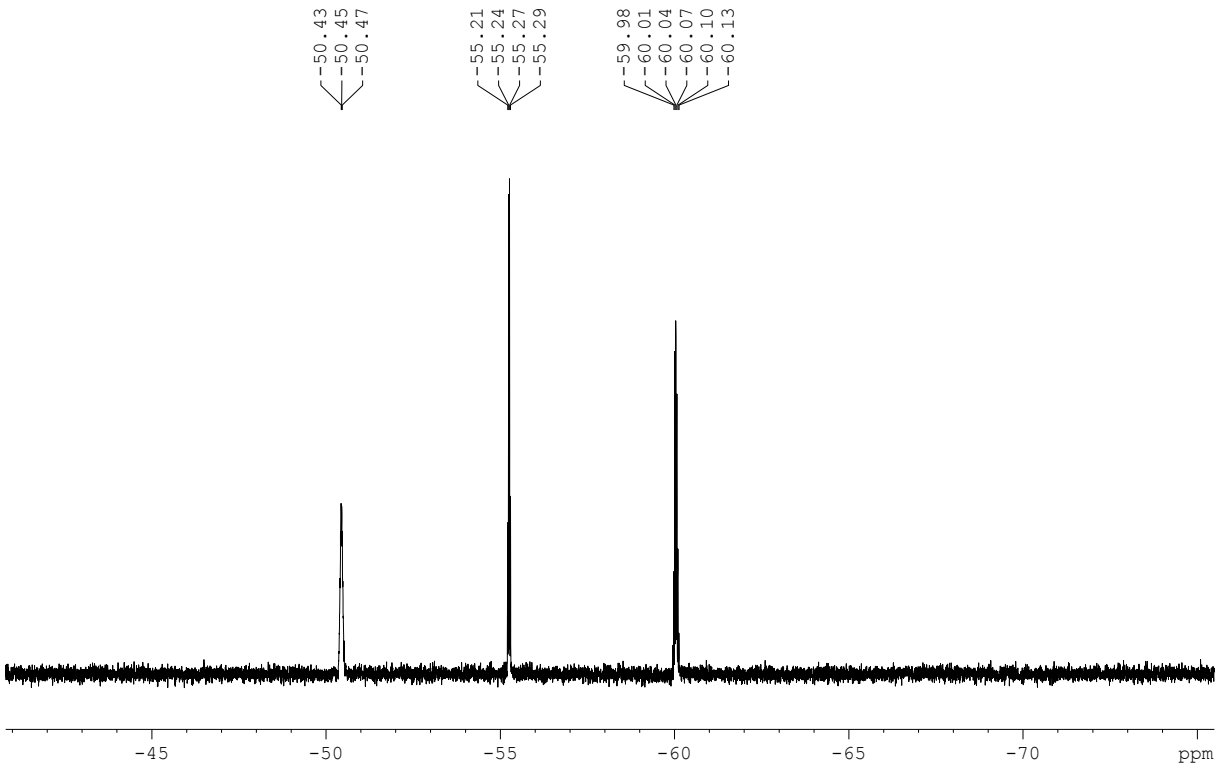
Selected NMR Spectra

Compound **4a**

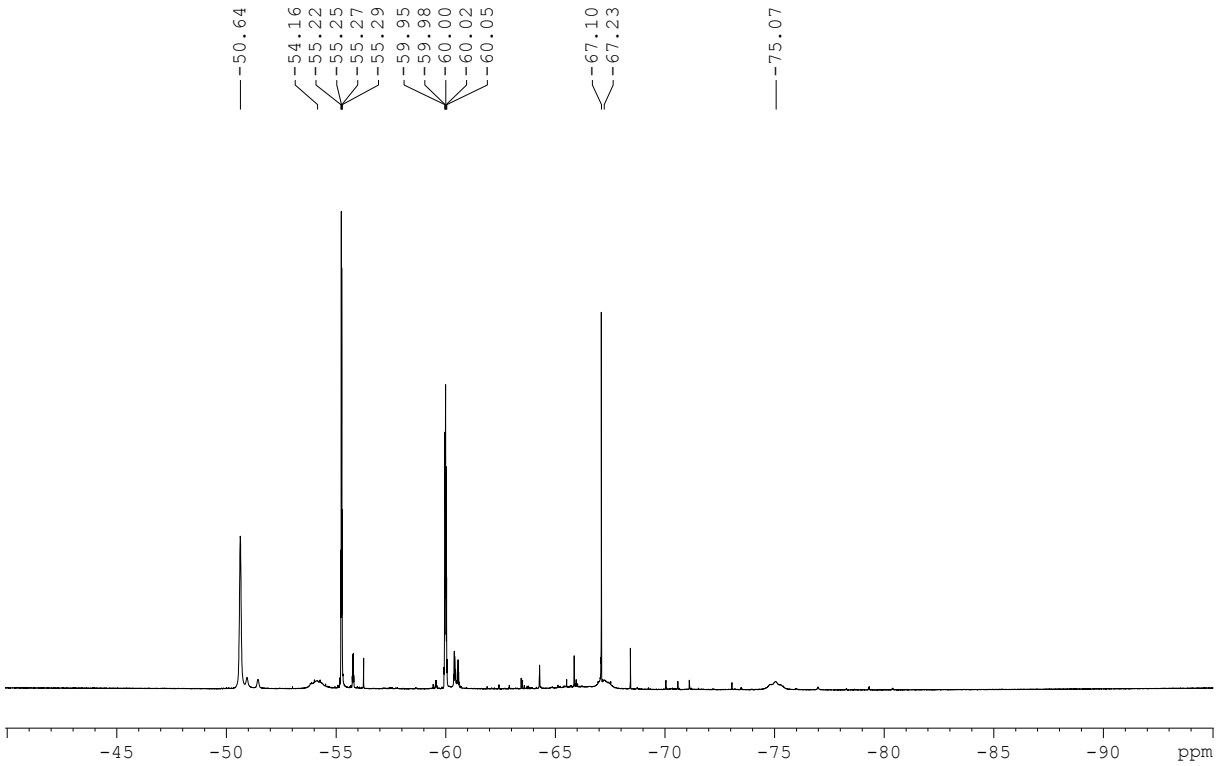
^{1}H-NMR



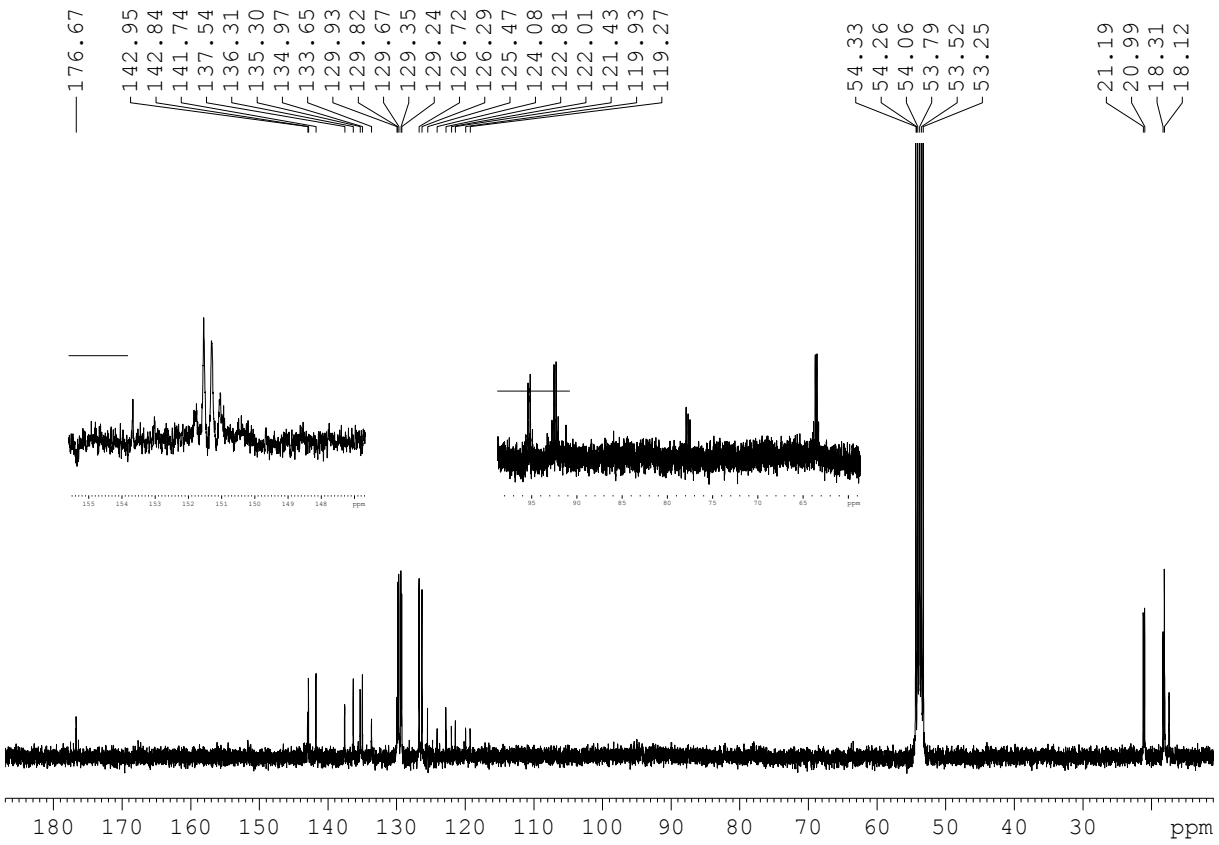
^{19}F-NMR at 300 K:



^{19}F-NMR at 193 K:

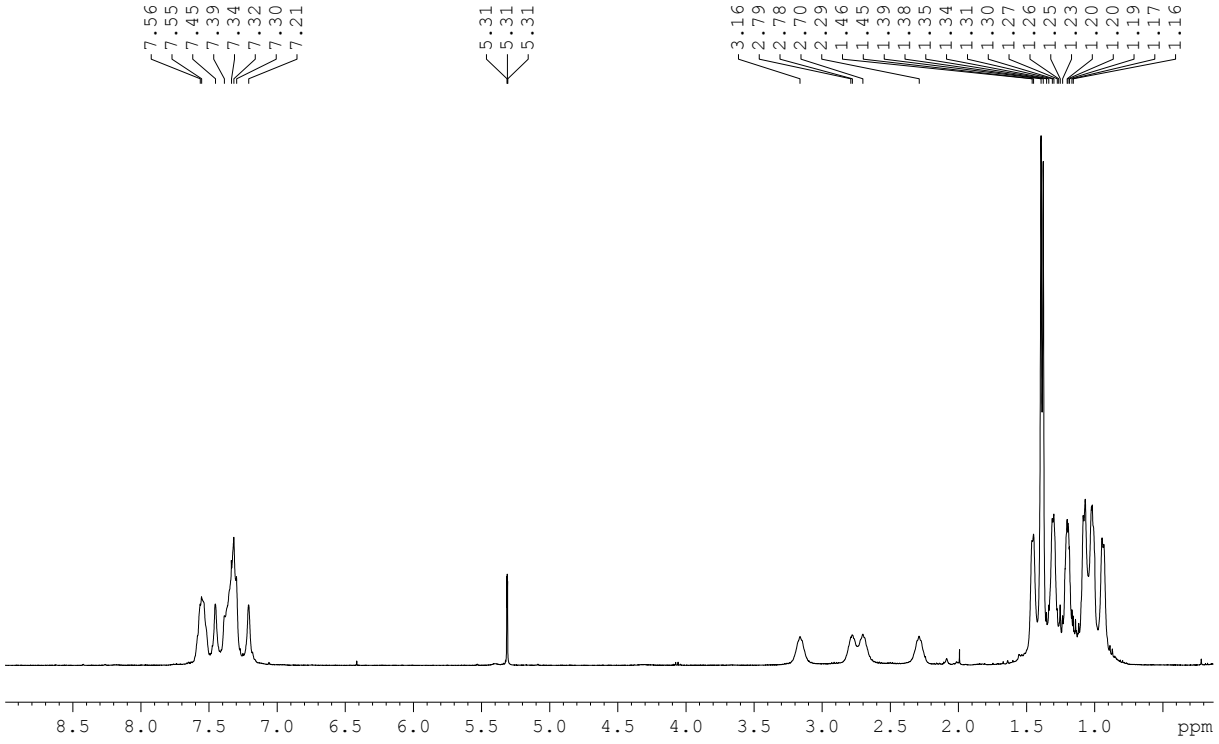


^{13}C-NMR

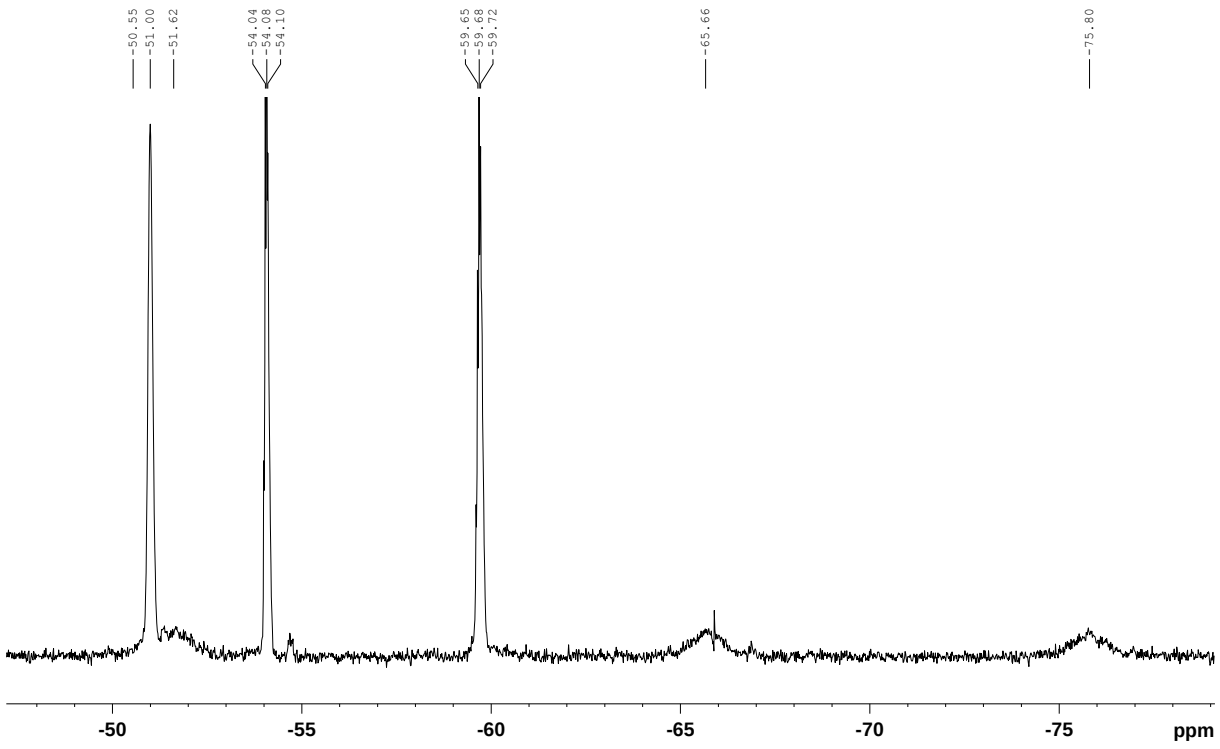


Compound **4b**

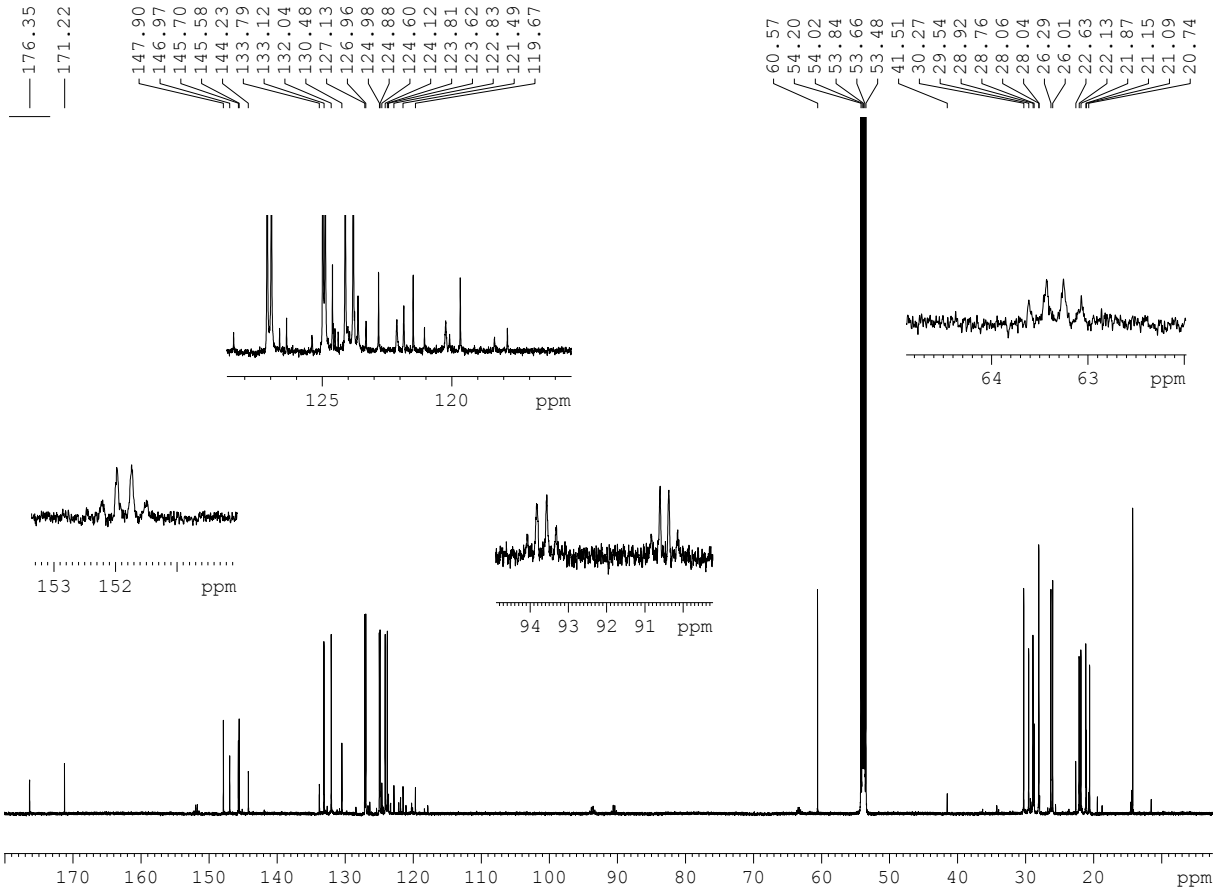
^{1}H-NMR



^{19}F-NMR

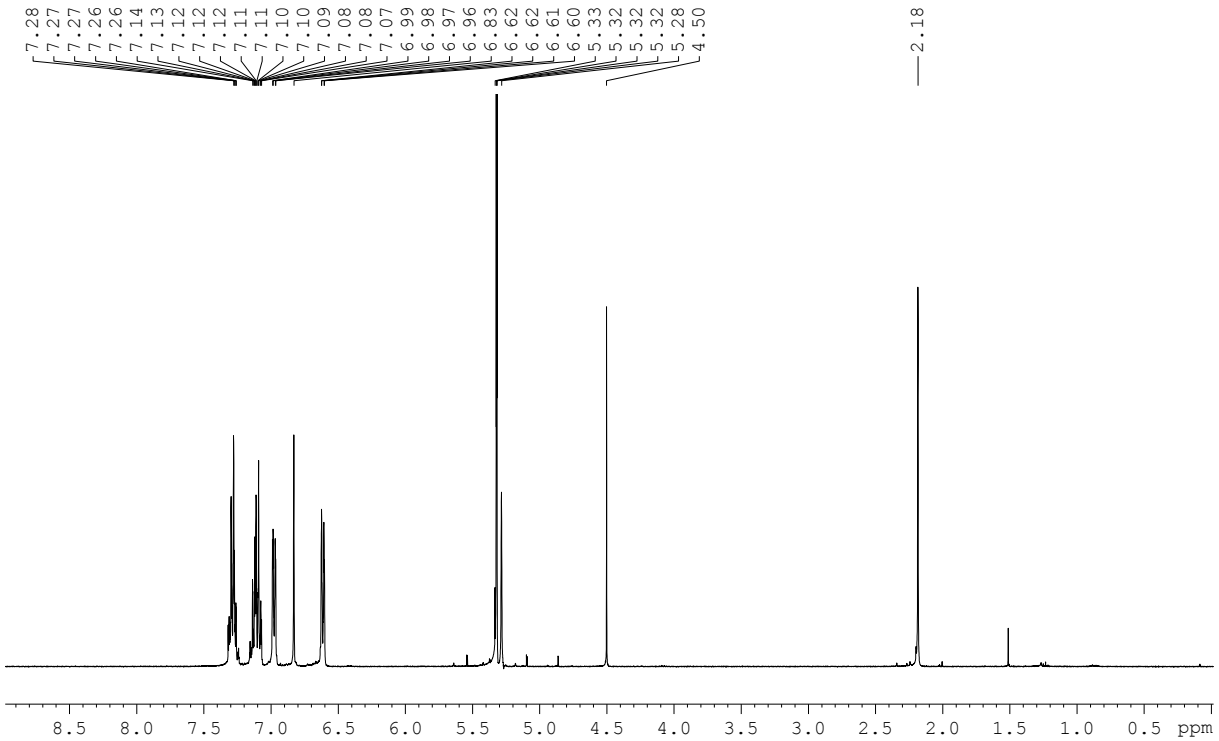


^{13}C-NMR

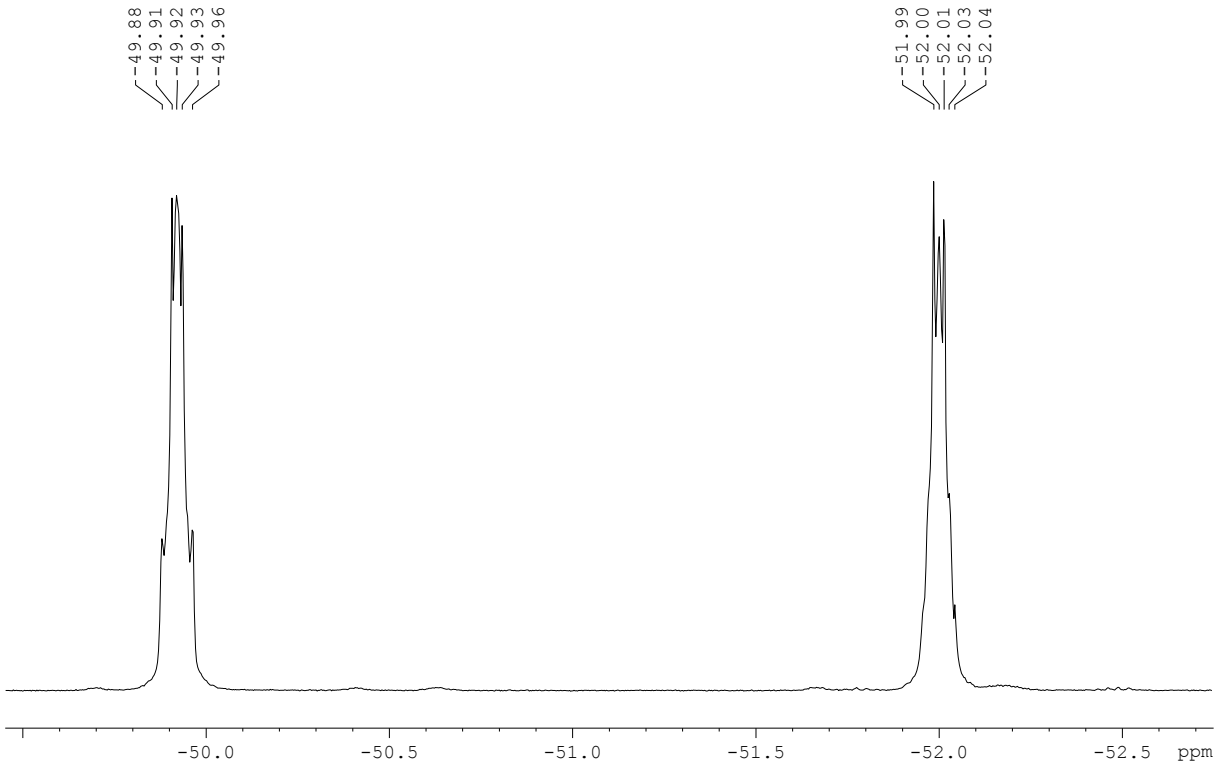


Compound **5c**

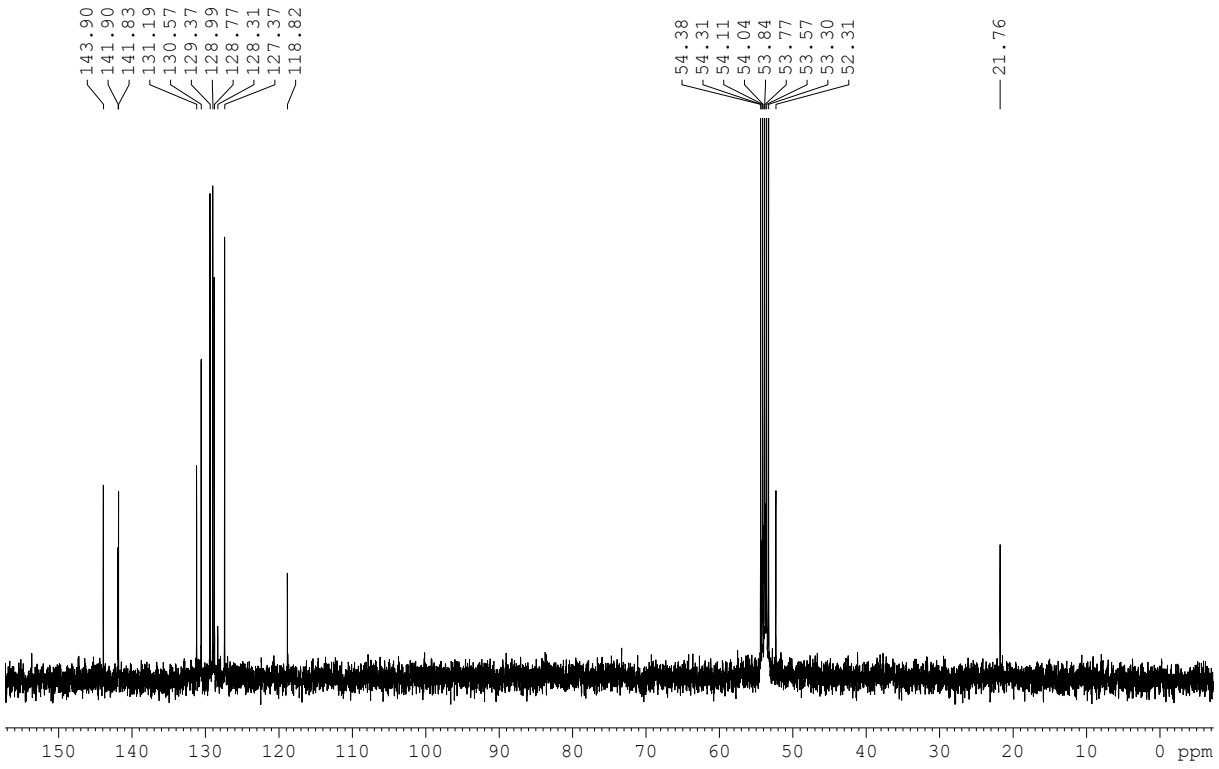
^{1}H-NMR



^{19}F-NMR

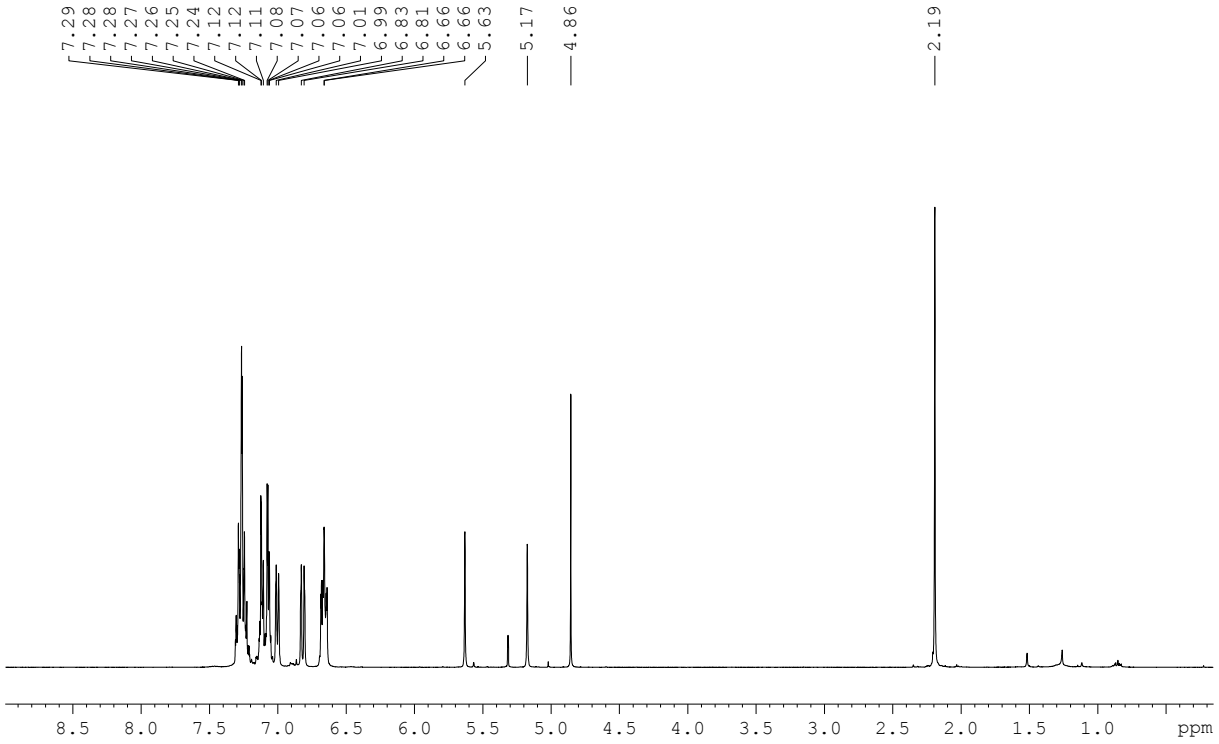


^{13}C-NMR

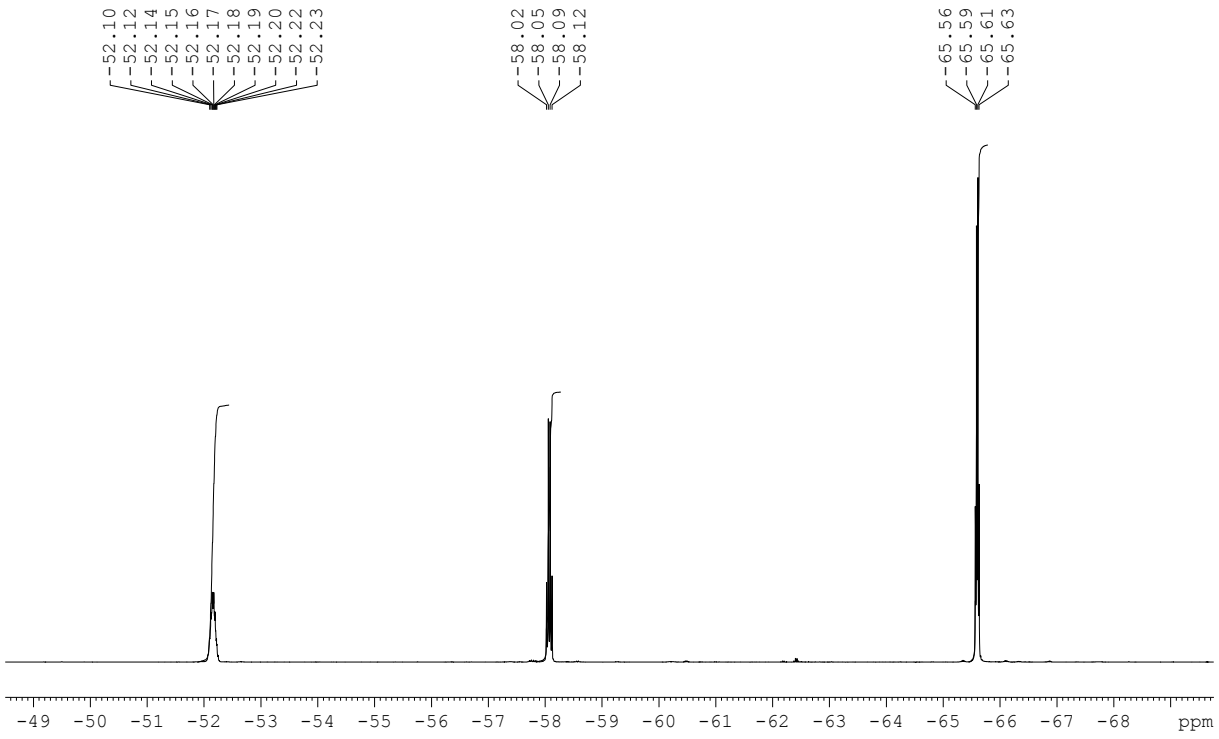


Compound **8**

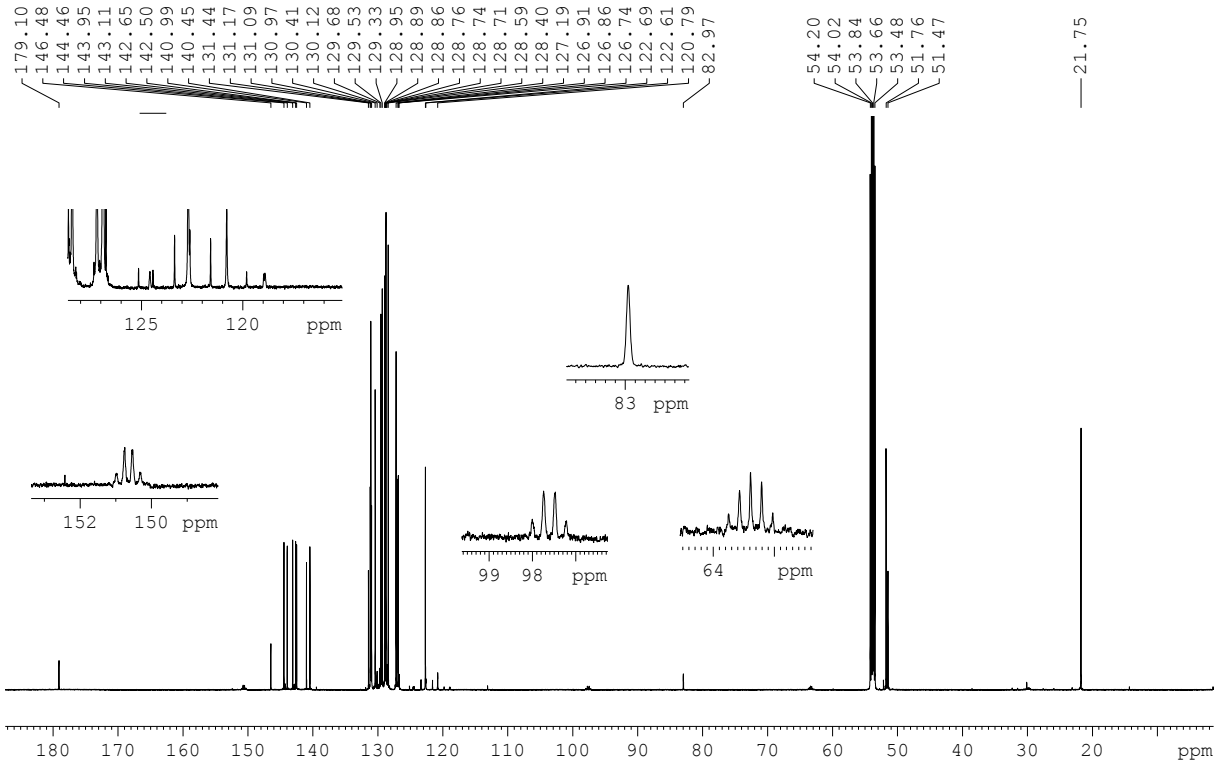
^{1}H-NMR



^{19}F-NMR

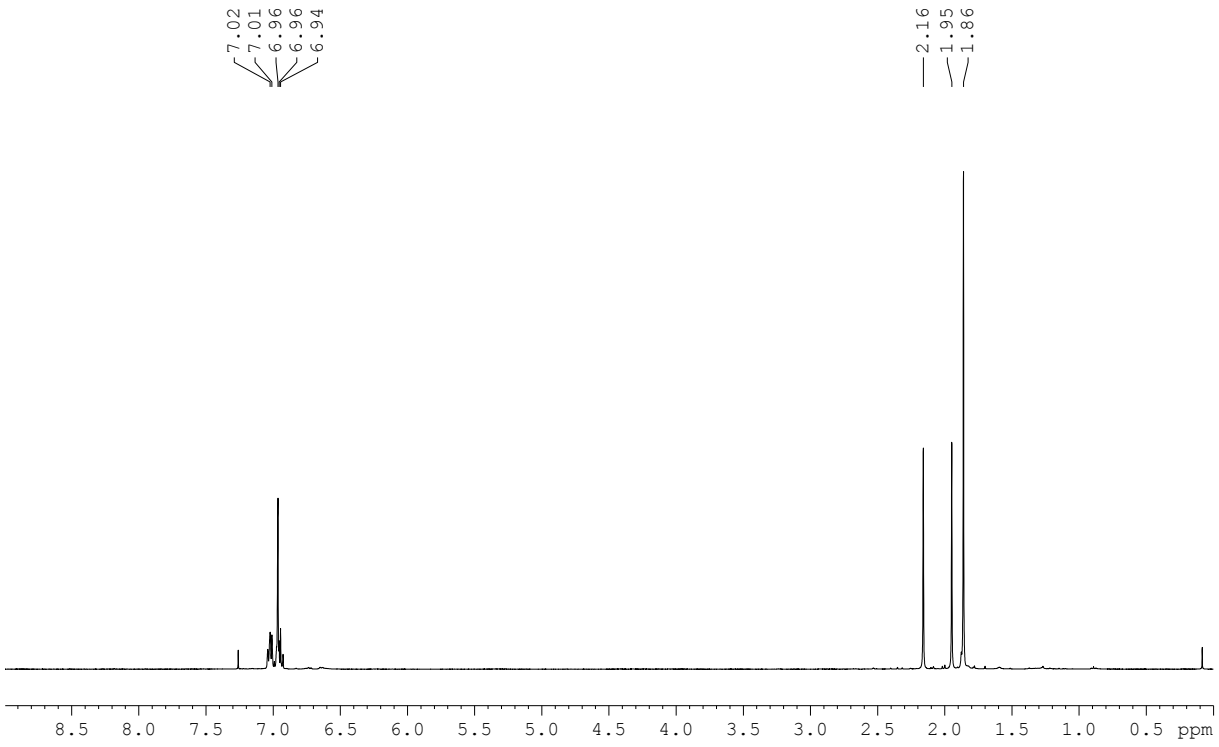


^{13}C-NMR

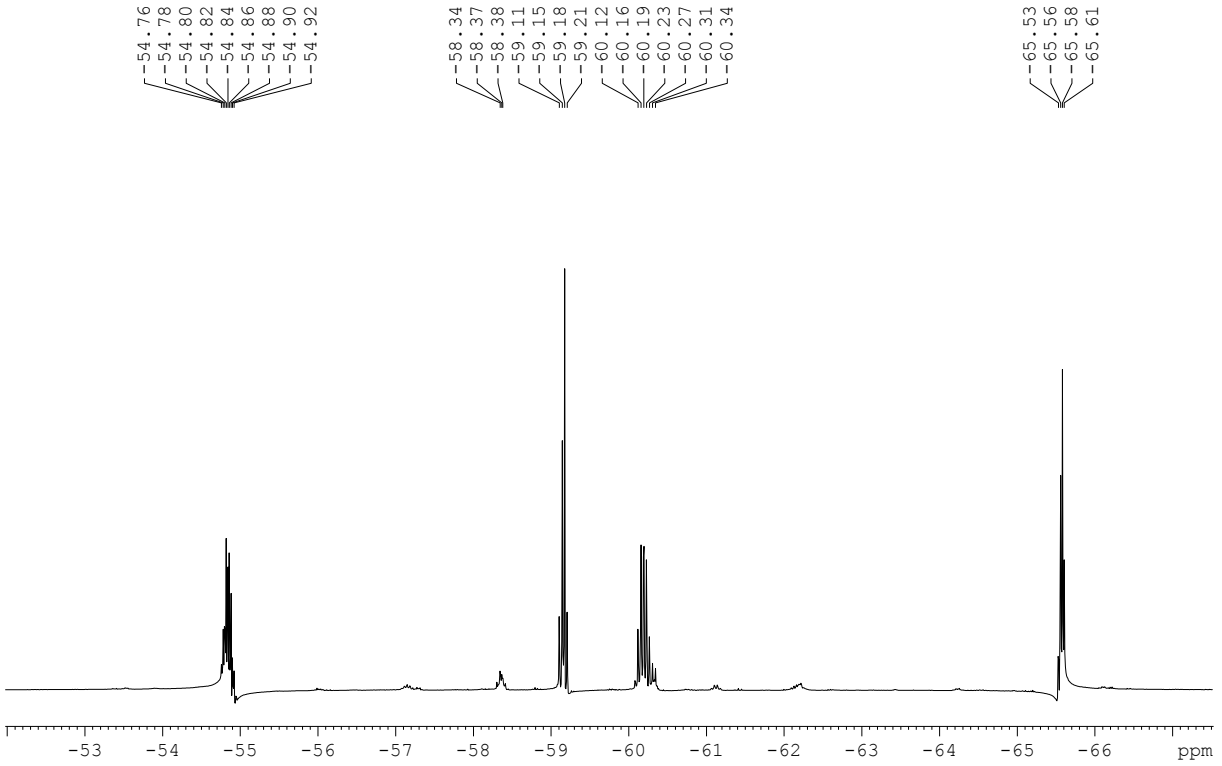


Compound **11a**

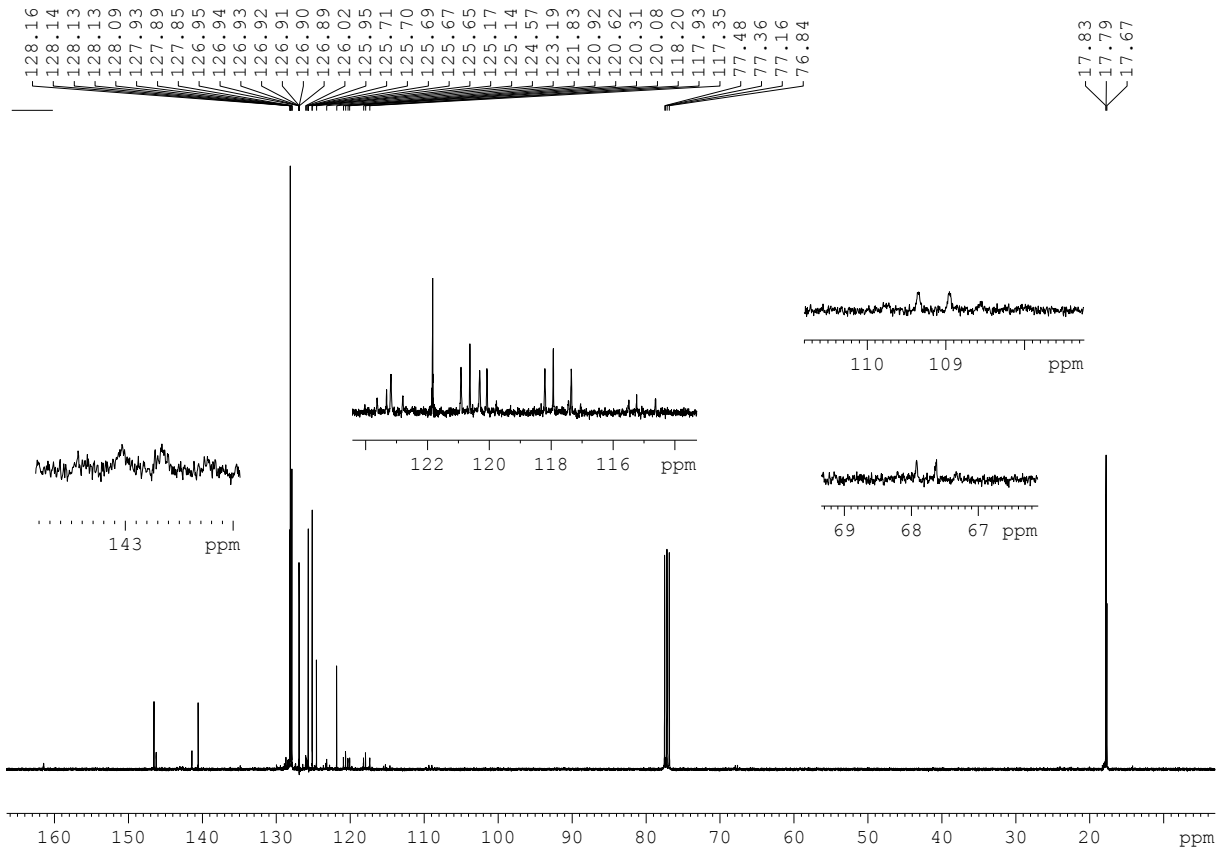
^{1}H-NMR



^{19}F-NMR

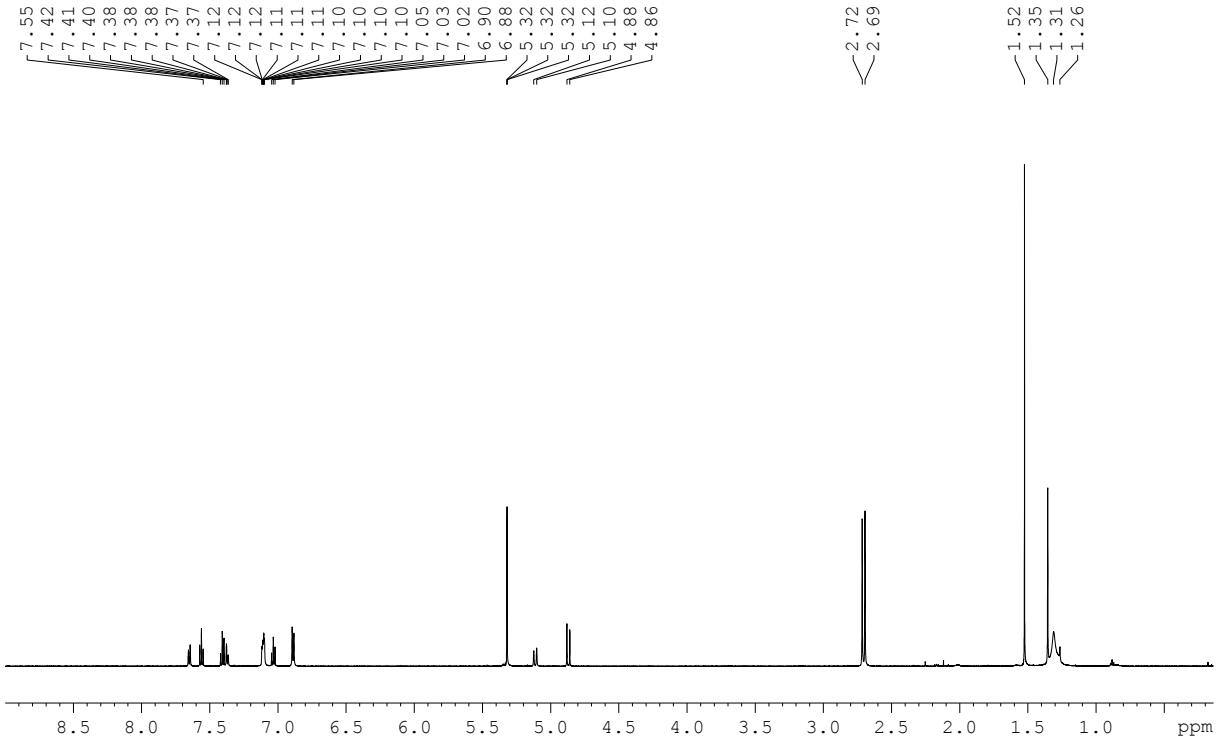


^{13}C-NMR

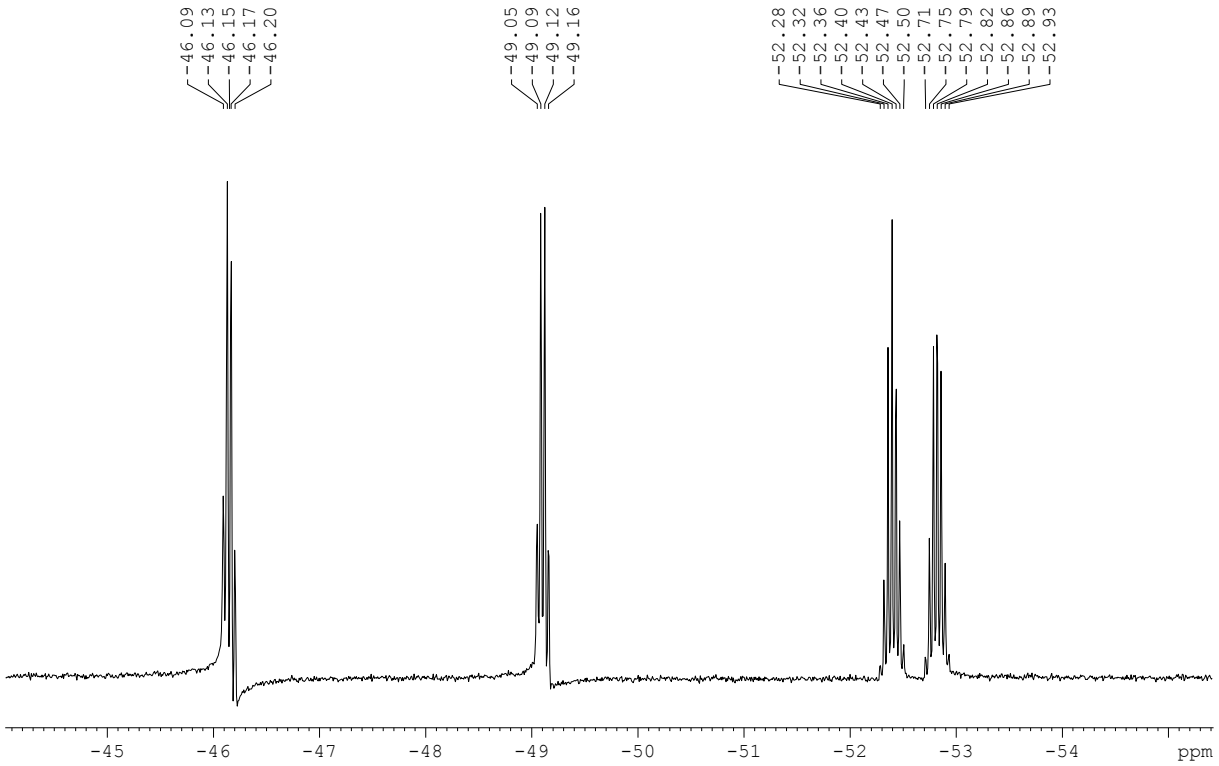


Compound **14a**

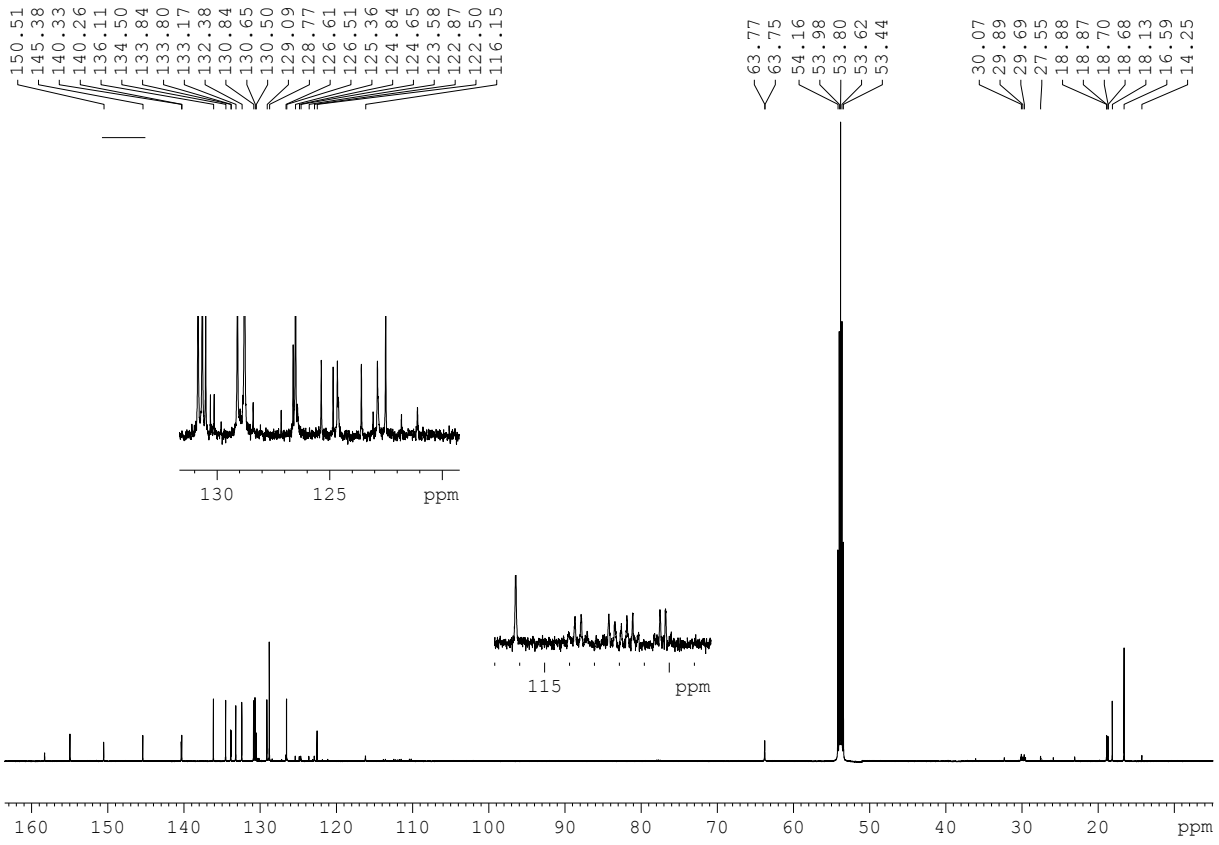
^{1}H-NMR



^{19}F-NMR

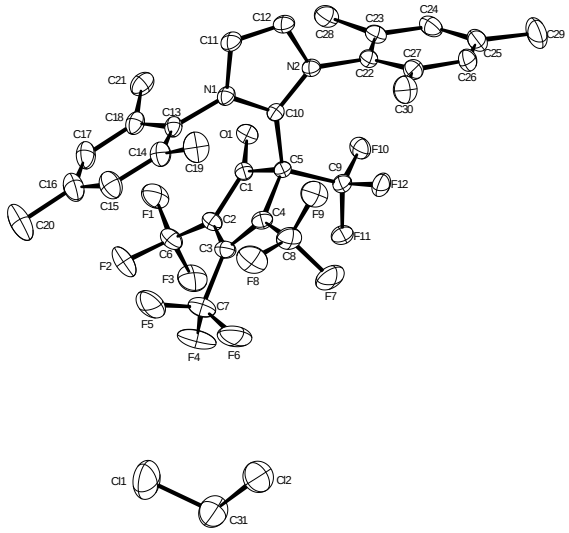


^{13}C-NMR


150.51
145.38
140.33
140.26
136.11
134.50
133.84
133.80
133.17
132.38
130.84
130.65
130.50
129.09
128.77
126.61
126.51
125.36
124.84
124.65
123.58
122.87
122.50
116.15
63.77
63.75
54.16
53.98
53.80
53.62
53.44
30.07
29.89
29.69
27.55
18.88
18.87
18.70
18.68
18.13
16.59
14.25
130
125
ppm
115
ppm
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

X-ray diffraction analyses:

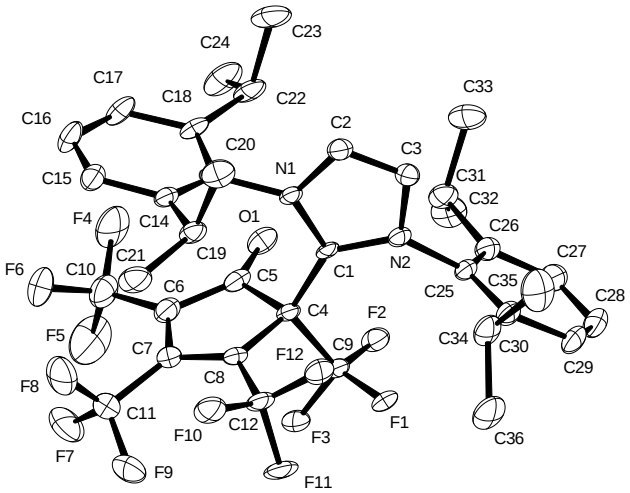
Compound **4a**



Crystal data and structure refinement.

Identification code	7904sadabs	
Empirical formula	$C_{31}\ H_{26}\ Cl_2\ F_{12}\ N_2\ O$	
Color	yellow	
Formula weight	741.44 g · mol^{-1}	
Temperature	150 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	p 21/c, (no. 14)	
Unit cell dimensions	a = 8.9704(15) Å	α= 90°.
	b = 12.518(2) Å	β= 98.175(3)°.
	c = 28.283(5) Å	γ = 90°.
Volume	3143.6(9) $Å^3$	
Z	4	
Density (calculated)	1.567 Mg · m^{-3}	
Absorption coefficient	0.308 mm^{-1}	
F(000)	1504 e	
Crystal size	0.48 x 0.38 x 0.14 mm^3	
θ range for data collection	1.78 to 31.05°.	
Index ranges	-13 ≤ h ≤ 12, -14≤ k ≤ 18, -40≤ l ≤ 38	
Reflections collected	53779	
Independent reflections	10017 [R_{int} = 0.0237]	
Reflections with I>2σ(I)	8303	
Completeness to θ = 27.50°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.98207 and 0.94447	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10017 / 0 / 439	
Goodness-of-fit on F^2	1.026	
Final R indices [I>2σ(I)]	R_1 = 0.0457	w R^2 = 0.1234
R indices (all data)	R_1 = 0.0561	w R^2 = 0.1313
Largest diff. peak and hole	0.621 and -0.917 e ·$Å^{-3}$	

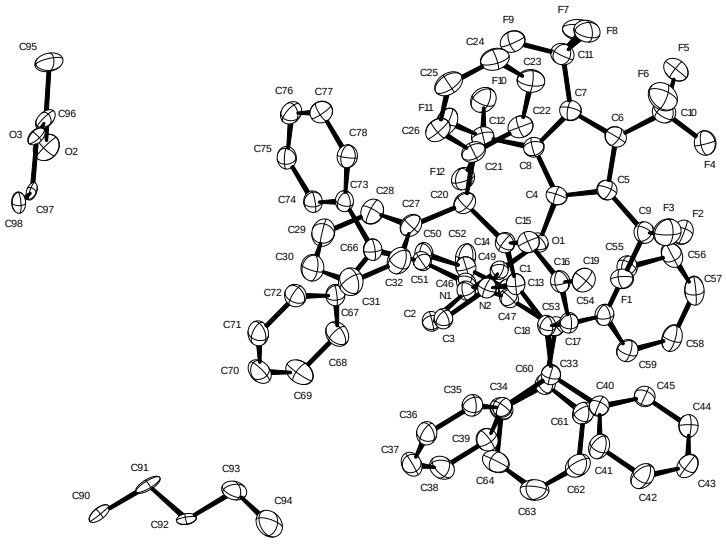
Compound **4b**



Crystal data and structure refinement.

Identification code	7120	
Empirical formula	$C_{41}H_{48}F_{12}N_2O$	
Color	yellow	
Formula weight	812.81 g · mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	**$P2_1/c$, (no. 14)**	
Unit cell dimensions	a = 18.7977(16) Å	α= 90°.
	b = 10.1829(12) Å	β= 102.454(9)°.
	c = 21.494(3) Å	γ = 90°.
Volume	4017.4(8) Å^3	
Z	4	
Density (calculated)	1.344 Mg · m^{-3}	
Absorption coefficient	0.119 mm^{-1}	
F(000)	1696 e	
Crystal size	0.29 x 0.18 x 0.14 mm^3	
θ range for data collection	2.61 to 32.43°.	
Index ranges	-26 ≤ h ≤ 28, -15≤ k ≤ 15, -32≤ l ≤ 32	
Reflections collected	75523	
Independent reflections	14415 [R_{int} = 0.0846]	
Reflections with I>2σ(I)	8890	
Completeness to θ = 27.50°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.99 and 0.97	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14415 / 0 / 513	
Goodness-of-fit on F^2	1.049	
Final R indices [I>2σ(I)]	R_1 = 0.0761	wR^2 = 0.1884
R indices (all data)	R_1 = 0.1261	wR^2 = 0.2265
Largest diff. peak and hole	0.694 and -0.605 e · Å^{-3}	

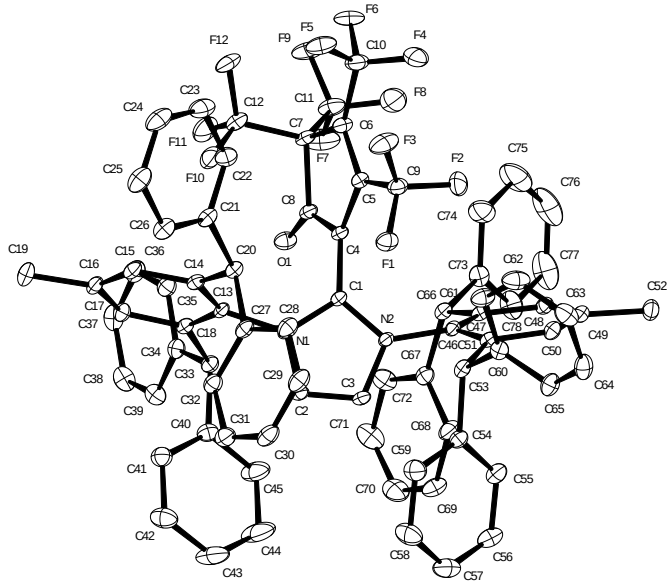
Compound **5c**



Crystal data and structure refinement.

Identification code	7300	
Empirical formula	$C_{82.50}H_{66}F_{12}N_2O_2$	
Color	colourless	
Formula weight	1345.37 g · mol^{-1}	
Temperature	100 K	
Wavelength	1.54184 Å	
Crystal system	MONOCLINIC	
Space group	**$P2_1/n$, (no. 14)**	
Unit cell dimensions	a = 14.9970(5) Å	α= 90°.
	b = 23.3819(8) Å	β= 103.047(2)°.
	c = 21.4481(7) Å	γ = 90°.
Volume	7326.8(4) Å^3	
Z	4	
Density (calculated)	1.220 Mg · m^{-3}	
Absorption coefficient	0.786 mm^{-1}	
F(000)	2796 e	
Crystal size	0.30 x 0.20 x 0.10 mm^3	
θ range for data collection	2.84 to 67.17°.	
Index ranges	-17 ≤ h ≤ 17, -27≤ k ≤ 27, -25 ≤ l ≤ 23	
Reflections collected	201826	
Independent reflections	12937 [R_{int} = 0.0862]	
Reflections with I>2σ(I)	10552	
Completeness to θ = 67.17°	98.7 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.81 and 0.65	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12937 / 0 / 944	
Goodness-of-fit on F^2	1.059	
Final R indices [I>2σ(I)]	R_1 = 0.0685	wR^2 = 0.2096
R indices (all data)	R_1 = 0.0814	wR^2 = 0.2274
Extinction coefficient	0.00124(13)	
Largest diff. peak and hole	1.118 and -0.328 e · Å^{-3}	

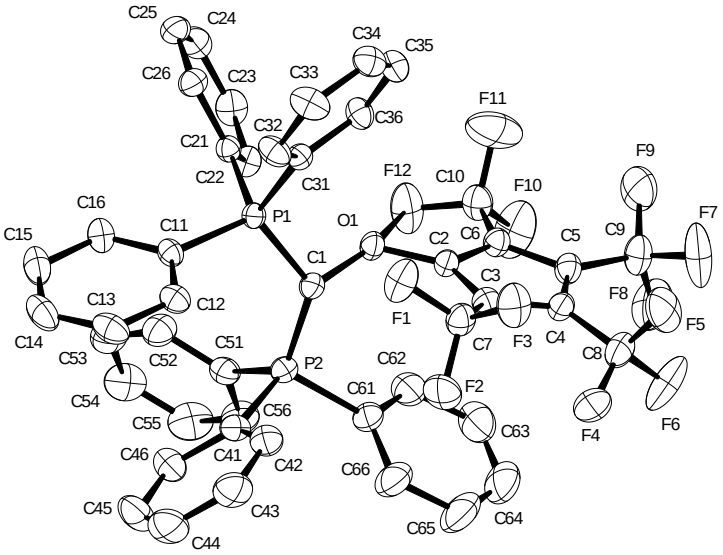
Compound **8**



Crystal data and structure refinement.

Identification code	7499	
Empirical formula	$C_{78}H_{56}F_{12}N_2O$	
Color	yellow	
Formula weight	1265.25 g · mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	**$P2_1/n$, (no. 14)**	
Unit cell dimensions	a = 13.782(3) Å	α= 90°.
	b = 22.193(5) Å	β= 94.270(4)°.
	c = 20.837(4) Å	γ = 90°.
Volume	6355(2) Å^3	
Z	4	
Density (calculated)	1.322 Mg · m^{-3}	
Absorption coefficient	0.102 mm^{-1}	
F(000)	2616 e	
Crystal size	0.200 x 0.080 x 0.060 mm^3	
θ range for data collection	1.34 to 31.10°.	
Index ranges	$-19 \le h \le 20$, $-32 \le k \le 30$, $-30 \le l \le 30$	
Reflections collected	182273	
Independent reflections	20374 [R_{int} = 0.1150]	
Reflections with I>2σ(I)	14288	
Completeness to θ = 27.50°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.99 and 0.98	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	20374 / 0 / 840	
Goodness-of-fit on F^2	1.013	
Final R indices [I>2σ(I)]	R_1 = 0.0484	wR^2 = 0.1092
R indices (all data)	R_1 = 0.0818	wR^2 = 0.1267
Largest diff. peak and hole	0.437 and -0.484 e · Å^{-3}	

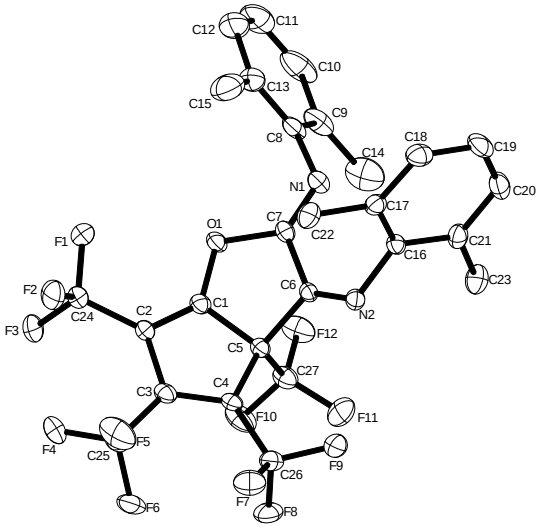
Compound **9**



Crystal data and structure refinement.

Identification code	7161	
Empirical formula	$C_{46}H_{30}F_{12}OP_2$	
Color	colourless	
Formula weight	888.64 g · mol^{-1}	
Temperature	200 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	**$P2_1/c$, (no. 14)**	
Unit cell dimensions	a = 17.4554(12) Å	α= 90°.
	b = 13.4948(11) Å	β= 112.675(6)°.
	c = 18.2231(16) Å	γ = 90°.
Volume	3960.8(5) Å^3	
Z	4	
Density (calculated)	1.490 Mg · m^{-3}	
Absorption coefficient	0.204 mm^{-1}	
F(000)	1808 e	
Crystal size	0.30 x 0.24 x 0.02 mm^3	
θ range for data collection	2.72 to 33.11°.	
Index ranges	-26 ≤ h ≤ 26, -20≤ k ≤ 20, -27 ≤ l ≤ 27	
Reflections collected	208528	
Independent reflections	15038 [R_{int} = 0.0742]	
Reflections with I>2σ(I)	10155	
Completeness to θ = 27.50°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.00 and 0.95	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15038 / 0 / 550	
Goodness-of-fit on F^2	1.144	
Final R indices [I>2σ(I)]	R_1 = 0.0739	wR^2 = 0.1331
R indices (all data)	R_1 = 0.1214	wR^2 = 0.1586
Largest diff. peak and hole	1.102 and -0.675 e · Å^{-3}	

Compound **11a**



Crystal data and structure refinement.

Identification code	8931sadabs	
Empirical formula	$C_{27}H_{18}F_{12}N_2O$	
Color	yellow	
Formula weight	614.43 g·mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	TRICLINIC	
Space group	p -1, (no. 2)	
Unit cell dimensions	a = 9.6967(19) Å	α= 86.858(3)°.
	b = 12.110(2) Å	β= 80.692(3)°.
	c = 13.572(3) Å	γ = 81.476(3)°.
Volume	1554.6(5) Å^3	
Z	2	
Density (calculated)	1.313 Mg·m^{-3}	
Absorption coefficient	0.130 mm^{-1}	
F(000)	620 e	
Crystal size	0.34 x 0.13 x 0.01 mm^3	
θ range for data collection	1.521 to 30.505°.	
Index ranges	-13 ≤ h ≤ 13, -17≤ k ≤ 17, -19≤ l ≤ 19	
Reflections collected	39101	
Independent reflections	9495 [R_{int} = 0.0487]	
Reflections with I>2σ(I)	6131	
Completeness to θ = 25.242°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.99871 and 0.97093	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9495 / 0 / 383	
Goodness-of-fit on F^2	0.988	
Final R indices [I>2σ(I)]	R_1 = 0.0525	wR^2 = 0.1333
R indices (all data)	R_1 = 0.0849	wR^2 = 0.1451
Extinction coefficient	0	
Largest diff. peak and hole	0.528 and -0.393 e·Å^{-3}	

Compound **11b**

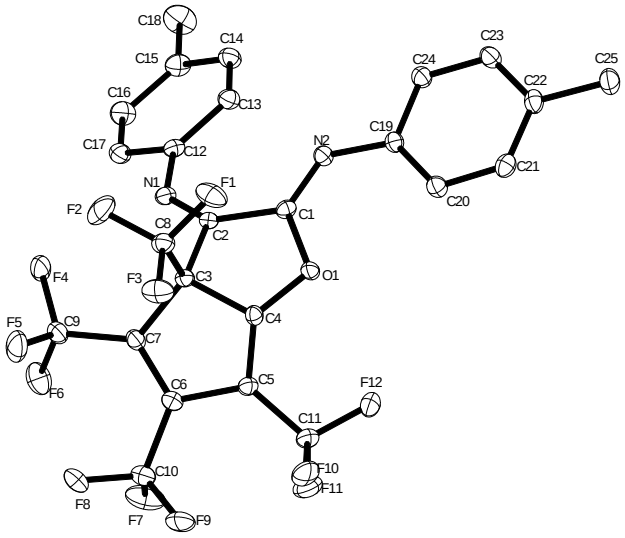


Table 1. Crystal data and structure refinement.

Identification code	8917sadabs	
Empirical formula	$C_{25}H_{14}F_{12}N_2O$	
Color	yellow	
Formula weight	586.38 g·mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	TRICLINIC	
Space group	p -1, (no. 2)	
Unit cell dimensions	a = 9.0983(10) Å	α= 79.451(2)°.
	b = 9.6805(11) Å	β= 74.919(2)°.
	c = 14.2614(16) Å	γ = 76.643(2)°.
Volume	1169.9(2) Å^3	
Z	2	
Density (calculated)	1.665 Mg·m^{-3}	
Absorption coefficient	0.169 mm^{-1}	
F(000)	588 e	
Crystal size	0.12 x 0.05 x 0.05 mm^3	
θ range for data collection	2.181 to 30.928°.	
Index ranges	-13 ≤ h ≤ 13, -13≤ k ≤ 13, -20≤ l ≤ 20	
Reflections collected	34458	
Independent reflections	7364 [R_{int} = 0.0457]	
Reflections with I>2σ(I)	5388	
Completeness to θ = 25.242°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.99276 and 0.98286	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7364 / 0 / 363	
Goodness-of-fit on F^2	1.033	
Final R indices [I>2σ(I)]	R_1 = 0.0409	wR^2 = 0.0937
R indices (all data)	R_1 = 0.0639	wR^2 = 0.1039
Extinction coefficient	0	
Largest diff. peak and hole	0.390 and -0.383 e·Å^{-3}	

Compound **13**

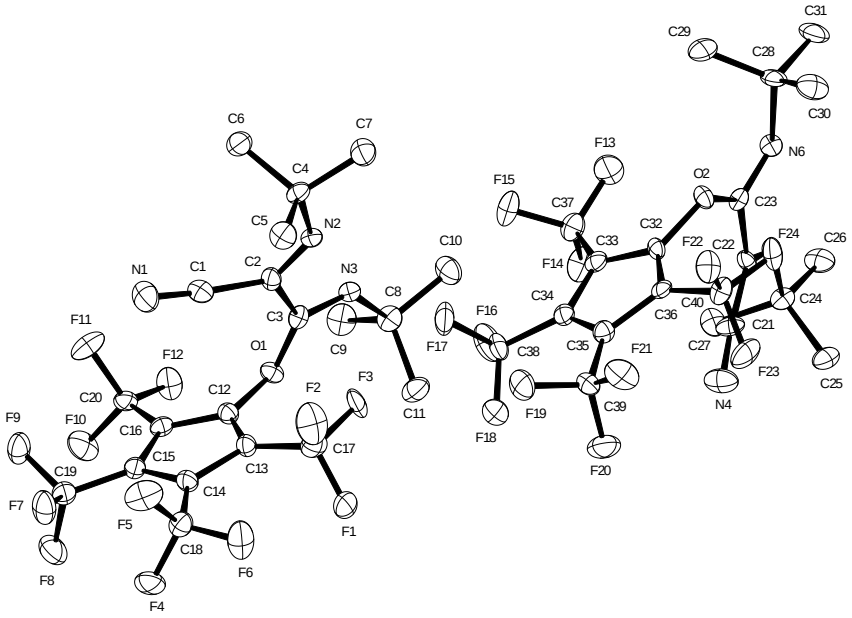
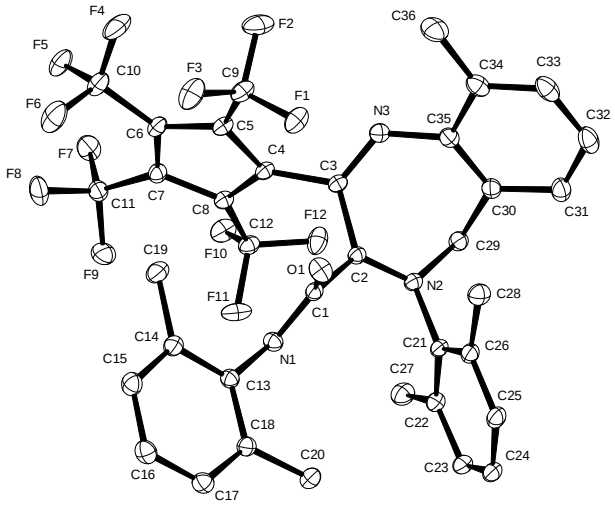


Table 1. Crystal data and structure refinement.

Identification code	8164	
Empirical formula	$C_{20}H_{19}F_{12}N_3O$	
Color	orange	
Formula weight	545.38 g · mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	**Pc, (no. 7)**	
Unit cell dimensions	a = 12.8818(15) Å	α= 90°.
	b = 11.7546(14) Å	β= 92.543(2)°.
	c = 15.2119(18) Å	γ = 90°.
Volume	2301.1(5) Å^3	
Z	4	
Density (calculated)	1.574 Mg · m^{-3}	
Absorption coefficient	0.165 mm^{-1}	
F(000)	1104 e	
Crystal size	0.15 x 0.08 x 0.08 mm^3	
θ range for data collection	1.58 to 27.41°.	
Index ranges	-16 ≤ h ≤ 16, -15≤ k ≤ 15, -19 ≤ l ≤ 19	
Reflections collected	10449	
Independent reflections	10449 [R_{int} = 0.0000]	
Reflections with I>2σ(I)	8598	
Completeness to θ = 27.41°	99.8 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.99 and 0.98	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10449 / 2 / 661	
Goodness-of-fit on F^2	1.129	
Final R indices [I>2σ(I)]	R_1 = 0.0783	wR^2 = 0.1670
R indices (all data)	R_1 = 0.1005	wR^2 = 0.1751
Absolute structure parameter	-0.3(8)	
Largest diff. peak and hole	0.438 and -0.436 e · Å^{-3}	

Compound **14a**



Crystal data and structure refinement.

Identification code	8858	
Empirical formula	$C_{36}H_{27}F_{12}N_3O$	
Color	orange	
Formula weight	745.60 g · mol^{-1}	
Temperature	100.15 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	**$P2_1/c$, (no. 14)**	
Unit cell dimensions	a = 9.5593(10) Å	α= 90°.
	b = 19.7906(10) Å	β= 105.511(12)°.
	c = 17.385(2) Å	γ = 90°.
Volume	3169.2(6) Å^3	
Z	4	
Density (calculated)	1.563 Mg · m^{-3}	
Absorption coefficient	0.144 mm^{-1}	
F(000)	1520 e	
Crystal size	0.24 x 0.10 x 0.10 mm^3	
θ range for data collection	2.641 to 33.134°.	
Index ranges	-14 ≤ h ≤ 14, -30≤ k ≤ 30, -26 ≤ l ≤ 26	
Reflections collected	68701	
Independent reflections	12042 [R_{int} = 0.0269]	
Reflections with I>2σ(I)	10570	
Completeness to θ = 25.242°	99.3 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.99 and 0.97	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12042 / 0 / 478	
Goodness-of-fit on F^2	1.063	
Final R indices [I>2σ(I)]	R_1 = 0.0349	wR^2 = 0.0927
R indices (all data)	R_1 = 0.0415	wR^2 = 0.0981
Largest diff. peak and hole	0.7 and -0.3 e · Å^{-3}	

Computational details

Geometry optimizations of all minima and transition states were carried out using the B3LYP functional[1],[2] in combination with the 6-311+G* basis set. Gibbs reaction free energies were computed at the same level of theory. The nature of the stationary points (either minima or transition states) was confirmed by computing the Hessian at the same level of theory. Natural population analysis (NPA) charges were computed by performing a Natural Bond Orbital (NBO) analysis using the NBO program, version 3.1.[3] All the calculations were performed with the Gaussian09 program package.[4]

Table S1. Computed Gibbs reaction free energies (ΔG^o) and activation barriers ($\Delta G^{\neq}$) (B3LYP/6-311+G*) for the reactions under study.

Reaction	ΔG^o (kcal/mol)	$\Delta G^{\neq}$ (kcal/mol)
1 + 1,3-dimethylimidazol-2-ylidene (C_2 pathway)	-22.0	+7.5
1 + 1,3-dimethylimidazol-2-ylidene (O pathway)	-29.1	+13.7
1 + *tert*-butylisonitrile (C_2 pathway)	0.0	+18.8
1 + *tert*-butylisonitrile (O pathway)	+7.5	+34.4
1 + 10a (C_2 pathway)	-0.8	+19.0
1 + 10a (O pathway)	+9.0	+31.6

[1] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.

[2] C. T. Lee, W. T. Yang, R. G. Parr, *Phys. Rev. B.* **1988**, *37*, 785.

[3] NBO Version 3.1. E. D. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold.

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