Supporting information

Deconstructing the Catalytic, *Vicinal* Difluorination of Alkenes: HF-Free Synthesis and Structural Study of *p*-TolIF$_2$

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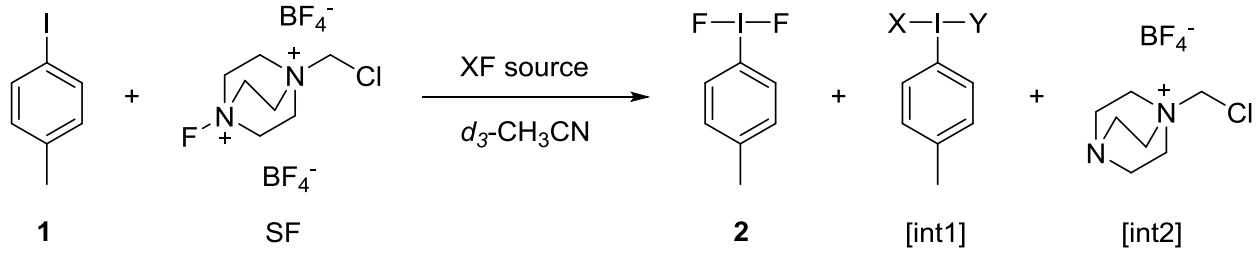
I. Conversion in Table 1

I.1 General Procedure

4-Iodotoluene (9 mg, 0.04 mmol, 1 eq.), the indicated XF source and Selectfluor® and d_3-CH_3CN (1 mL) were added into a borosilicate NMR tube. In some cases the reaction mixture was protected from light by wrapping the NMR tube with aluminum foil (entry 3-9, 11-13) and left to react at ambient temperature for the indicated reaction time. Then the mixture was characterized by ^{1}H NMR (200 MHz, 299 K) experiments. (***1**: p-TolI; SF: Selectfluor®; **2**: p-TolIF$_2$; [int1]: Intermediate with tolyl moiety; [int2]: Intermediate with DABCO moiety, w: water*).



Entry	Selectfluor® (eq.)	XF source	XF (eq.)	Time (h)	Conversion (%)[a]
1	2.6	-	-	4	26
2	2.6	Et_3N•3HF	2 drops	4	56[b]
3	2.6	Et_3N•3HF	2 drops	4	66
4	2.6	Et_3N•3HF	2 drops	22	59
5	5.0	Et_3N•3HF	2 drops	4	66
6	5.0	Et_3N•3HF	2 drops	22	80
7	2.6	Et_3N•3HF	0.9	4	49
8	2.6	Et_3N•3HF	2.3	4	63
9	2.6	Et_3N•3HF	4.6	4	54
10	3.5	Et_3N•3HF	3.7	22	91[c]
11	2.6	TBAF•3H_2O	5	8	0[d]
12	2.6	LiF	5	8	23
13	2.6	CsF	5	24	72
14	4.0	CsF	5	14	62[c]

(a) All reactions were performed in a borosilicate NMR tube with d_3-CH_3CN as solvent. (b) Et_3N•3HF was added at the end of the reaction in accordance with the literature.[2] (c) Yield.

Figure S1: General scheme of oxidation of *p*-TolI (**1**) and Table 1: Reaction optimization.

I.2 Results ^{1}H NMR experiments

The conversion of the respective reaction was determined by analysis of the corresponding ^{1}H NMR spectrum using the program MestReNova (Version 11.0.2, Mestrelab Research S.L.). After suitable baseline correction, the integral values of signals with the same number of hydrogens were compared to each other (e.g., entry 8: *p*-TolI H^{1a} (2H) compared with *p*-TolIF$_2$ H^{2a} (2H), see Figure S2 & S3).
[Comment: impurities were taken into account with two protons (respective examples see below)].

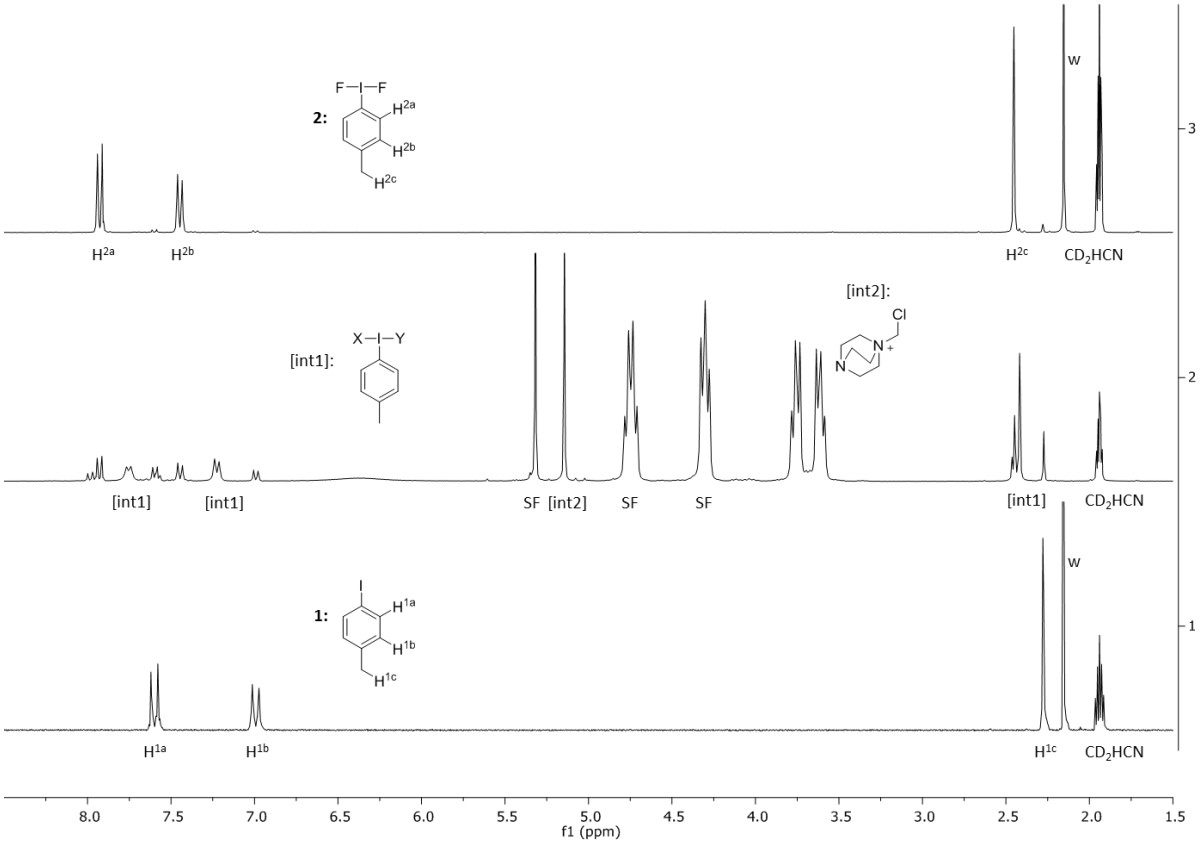


Figure S2: ^{1}H NMR (200 MHz, 299 K, d_3-CH_3CN) spectra of 1) *p*-TolI (**1**), 2) Reaction mixture (table 1, entry 1), and 3) *p*-TolIF$_2$ (**2**).

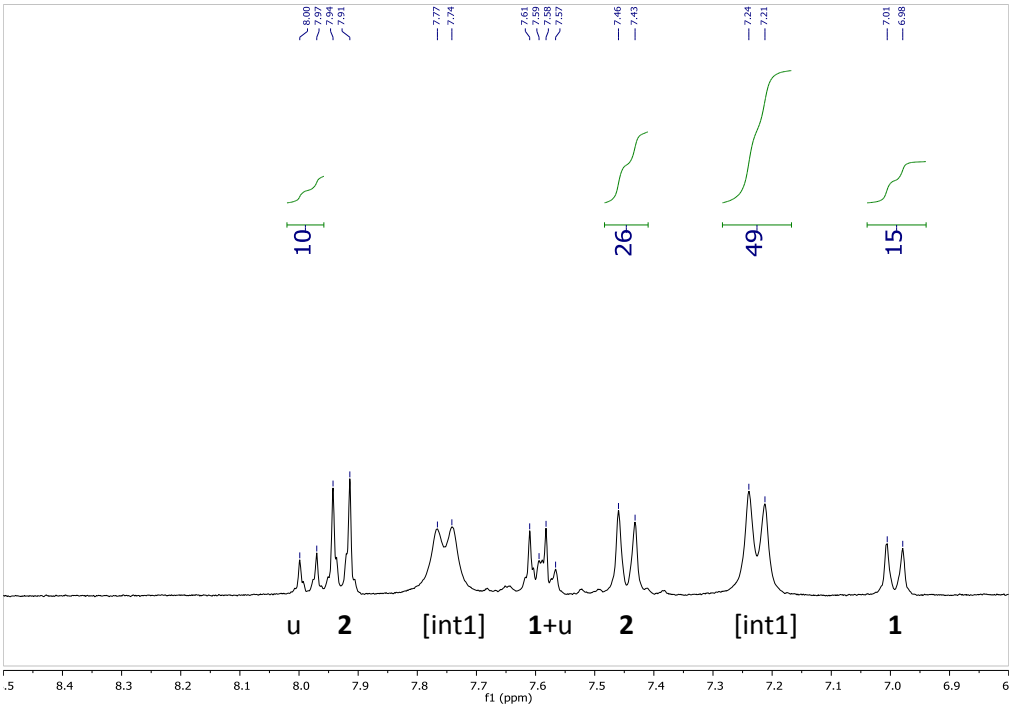


Figure S3: Zoom [8.5 ppm to 6.8 ppm] of the ^{1}H NMR (200 MHz, 299 K, d_3-CH_3CN) spectrum of the reaction mixture (table 1, entry 1). u: compound not identified yet.

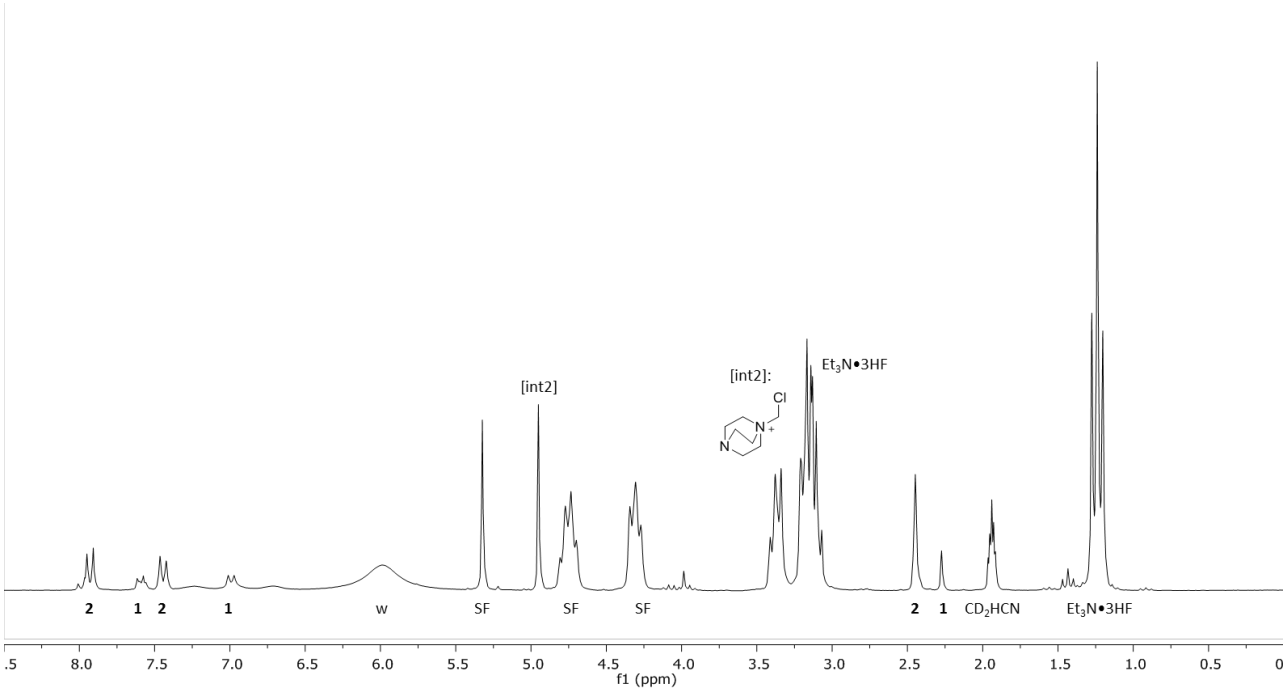


Figure S4: ^{1}H NMR (200 MHz, 299 K, d_3-CH_3CN) spectrum of the reaction mixture (table 1, entry 2).

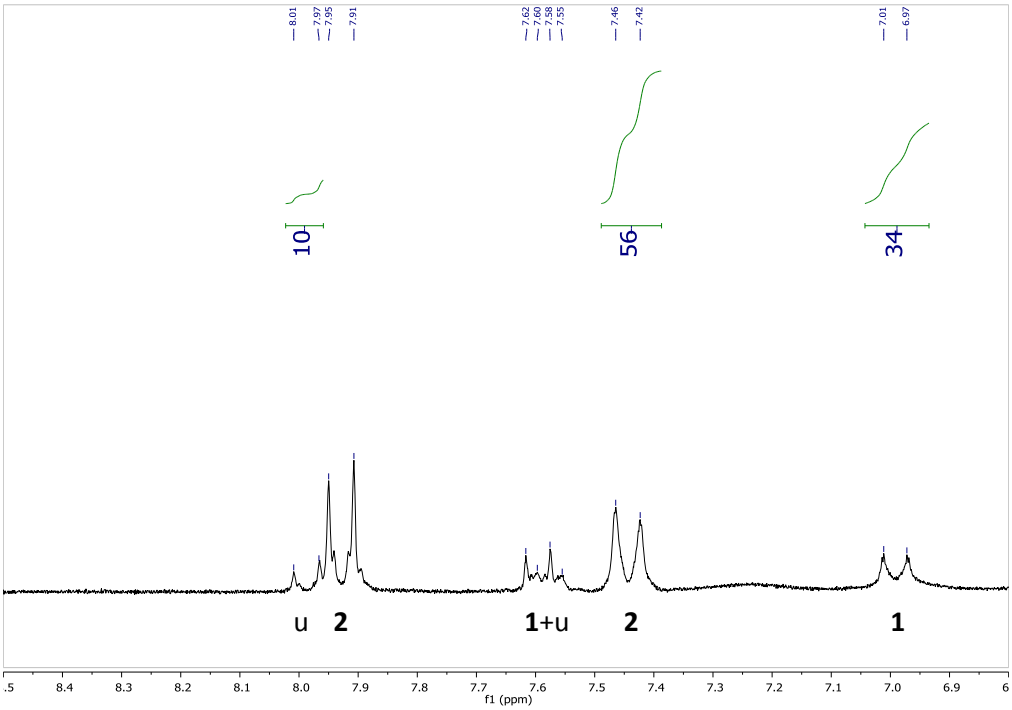


Figure S5: Zoom [8.5 ppm to 6.8 ppm] of the ^{1}H NMR (200 MHz, 299 K, d_3-CH_3CN) spectrum of the reaction mixture (table 1, entry 2). u: compound not identified yet.

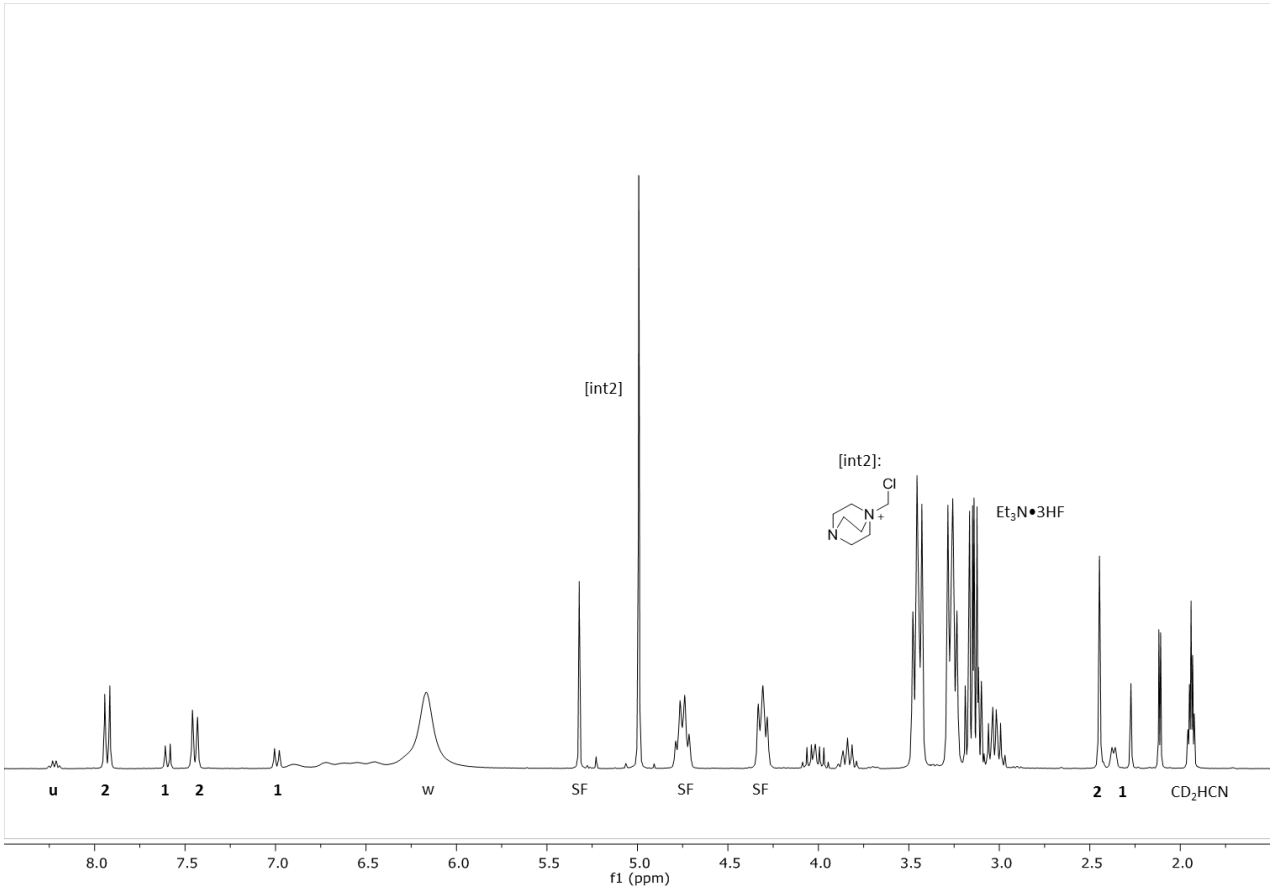


Figure S6: ^{1}H NMR (200 MHz, 299 K, d_3-CH_3CN) spectrum of the reaction mixture (table 1, entry 3).

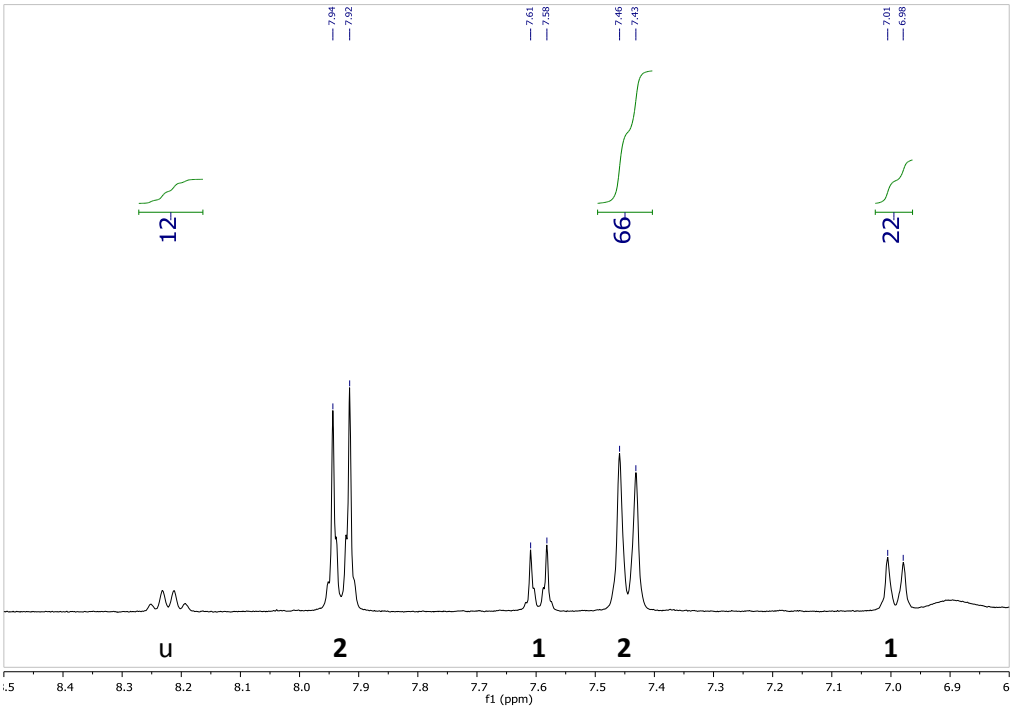


Figure S7: Zoom [8.5 ppm to 6.8 ppm] of the ^{1}H NMR (200 MHz, 299 K, d_3-CH_3CN) of the reaction mixture (table 1, entry 3). u: compound not identified yet.

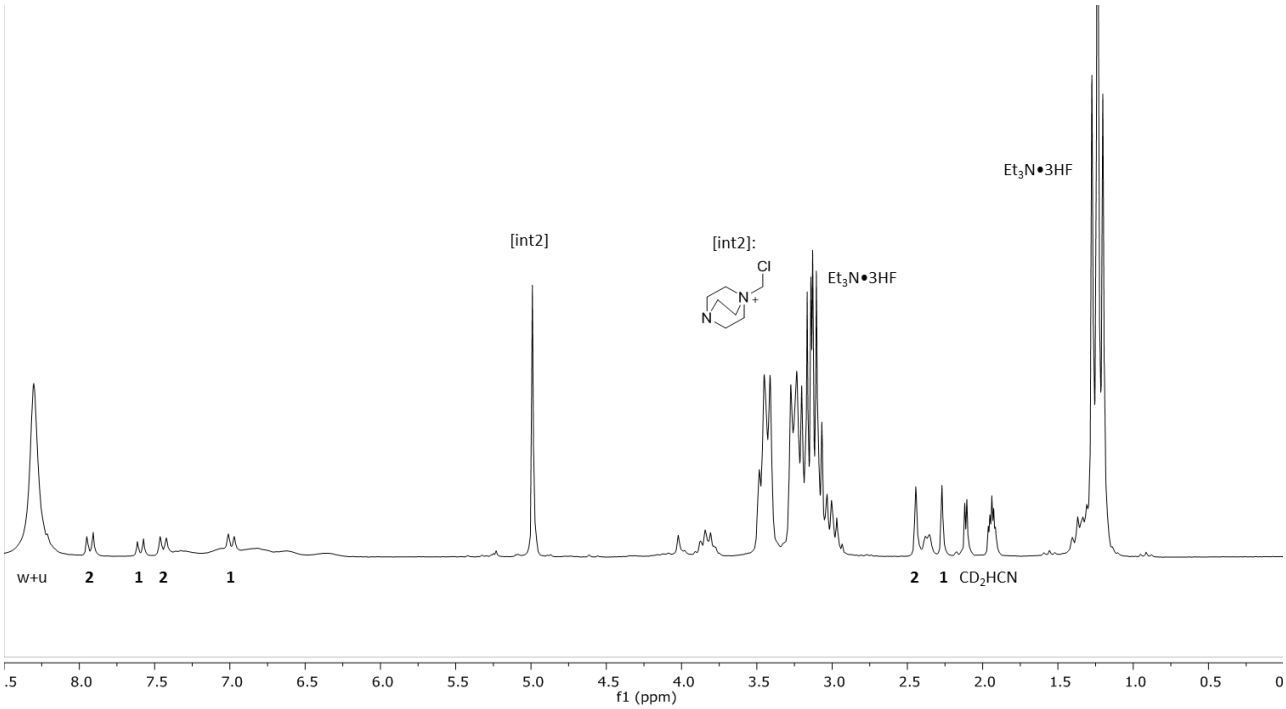


Figure S8: ^{1}H NMR (200 MHz, 299 K, d_3-CH_3CN) spectrum of the reaction mixture (table 1, entry 4). w+u: water and unidentified species.

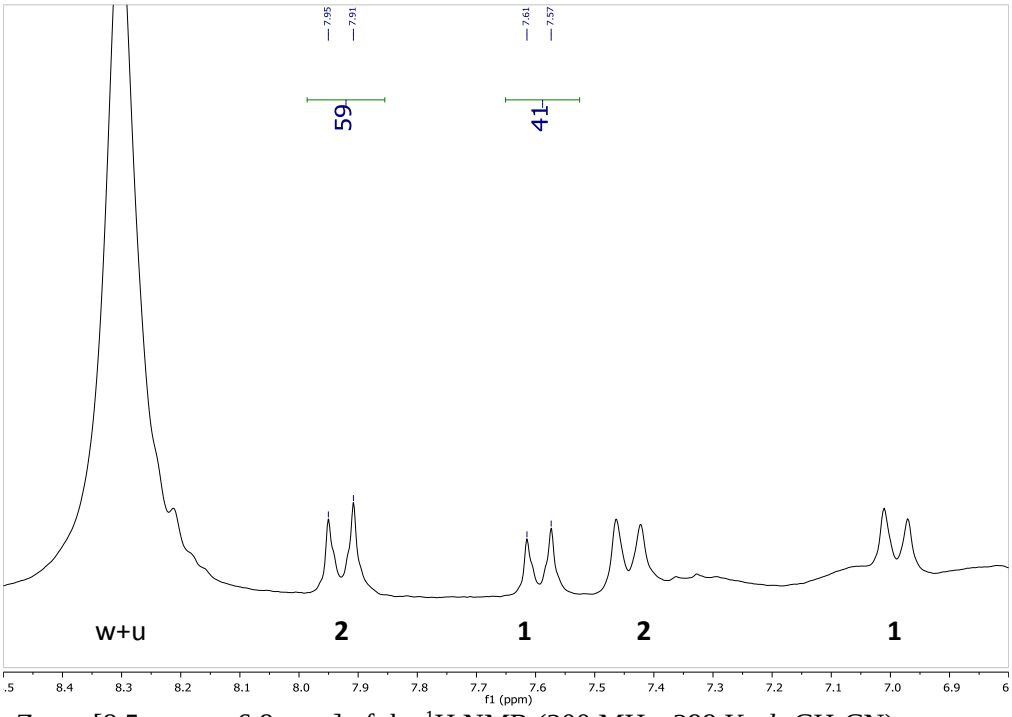


Figure S9: Zoom [8.5 ppm to 6.8 ppm] of the ^{1}H NMR (200 MHz, 299 K, d_3-CH_3CN) spectrum of the reaction mixture (table 1, entry 4). u: unidentified species.

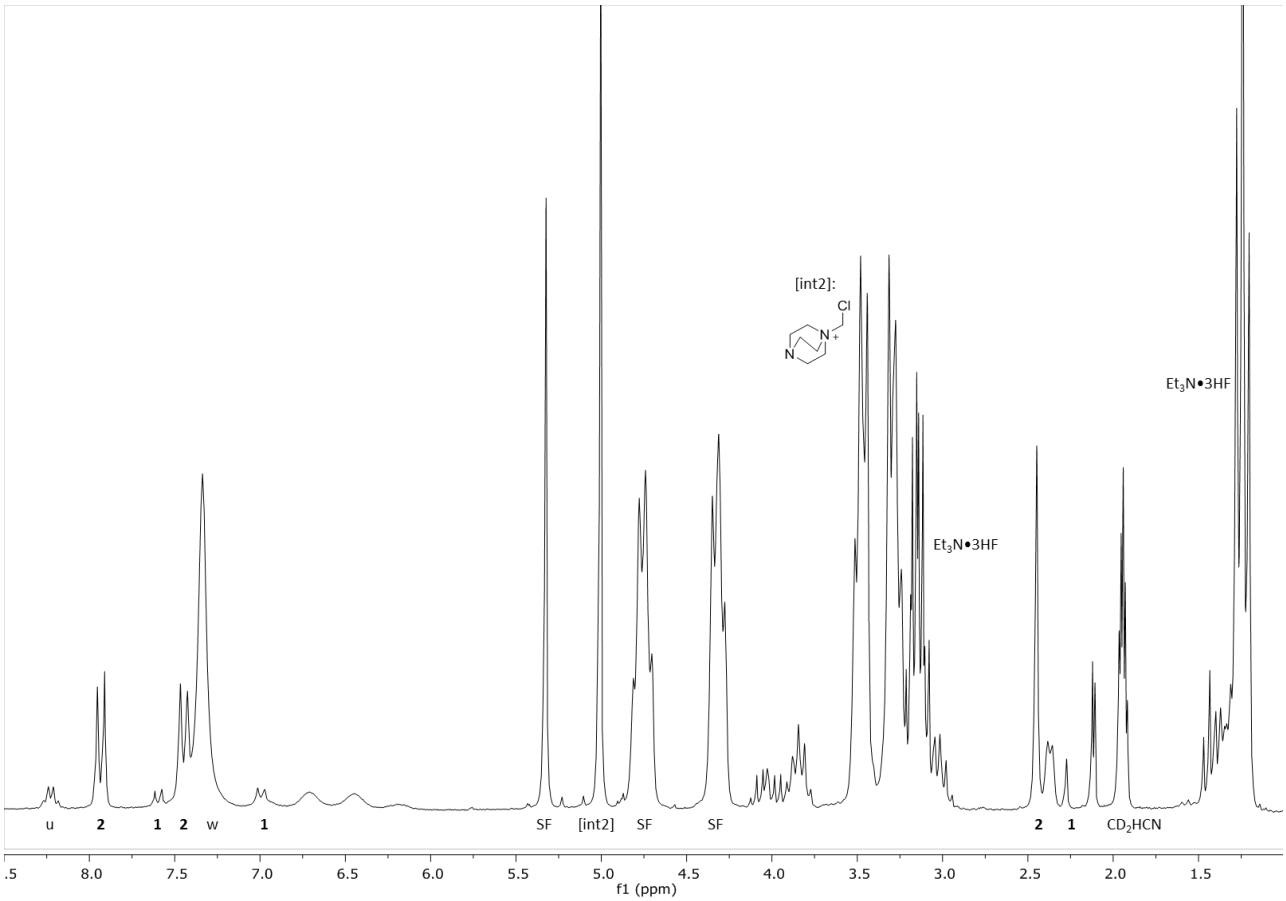


Figure S10: ^{1}H NMR (200 MHz, 299 K, d_3-CH_3CN) spectrum of the reaction mixture (table 1, entry 5). u: unidentified species.

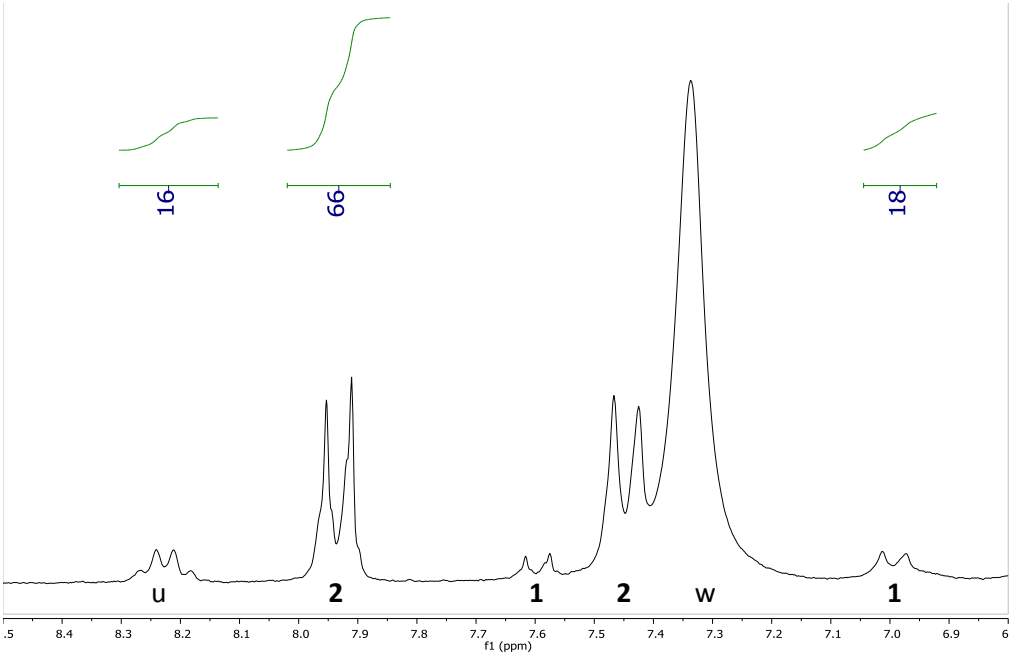


Figure S11: Zoom [8.5 ppm to 6.8 ppm] of the ^{1}H NMR (200 MHz, 299 K, d_3-CH_3CN) spectrum of the reaction mixture (table 1, entry 5). u: unidentified species.

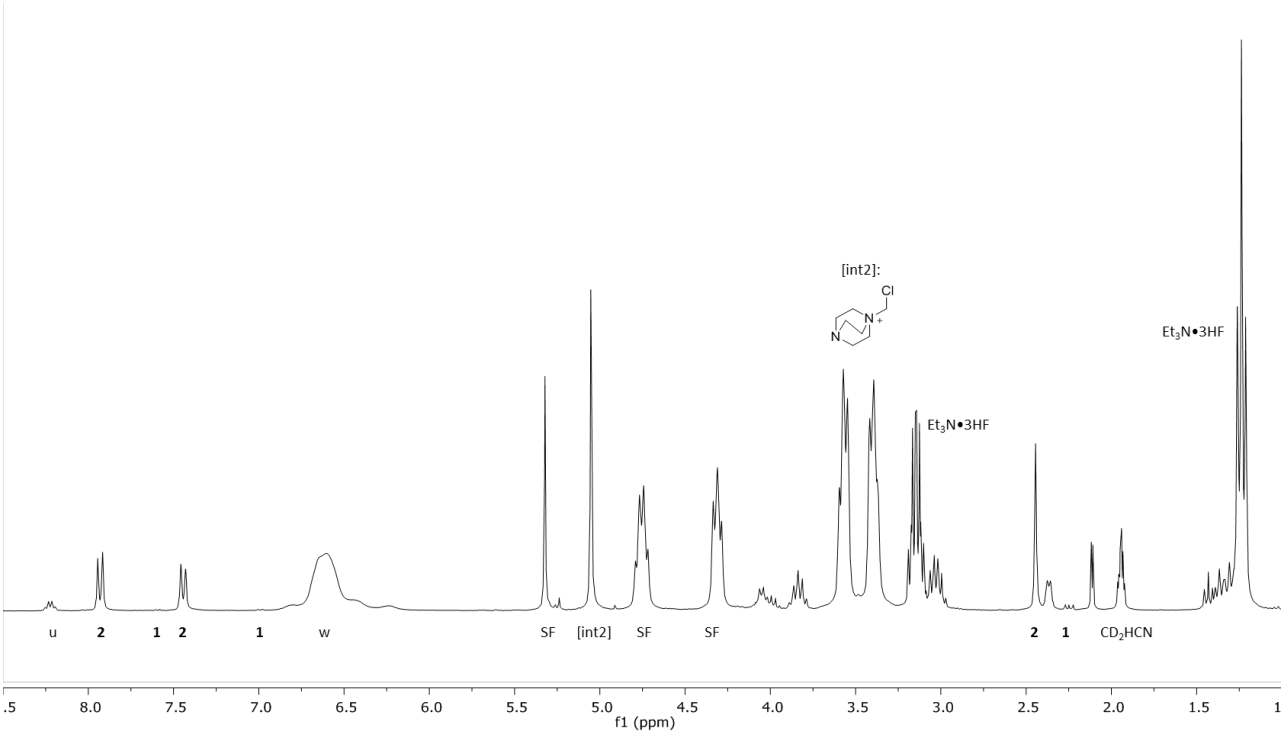


Figure S12: ^{1}H NMR (200 MHz, 299 K, d_3-CH_3CN) spectrum of the reaction mixture (table 1, entry 6). u: unidentified species.

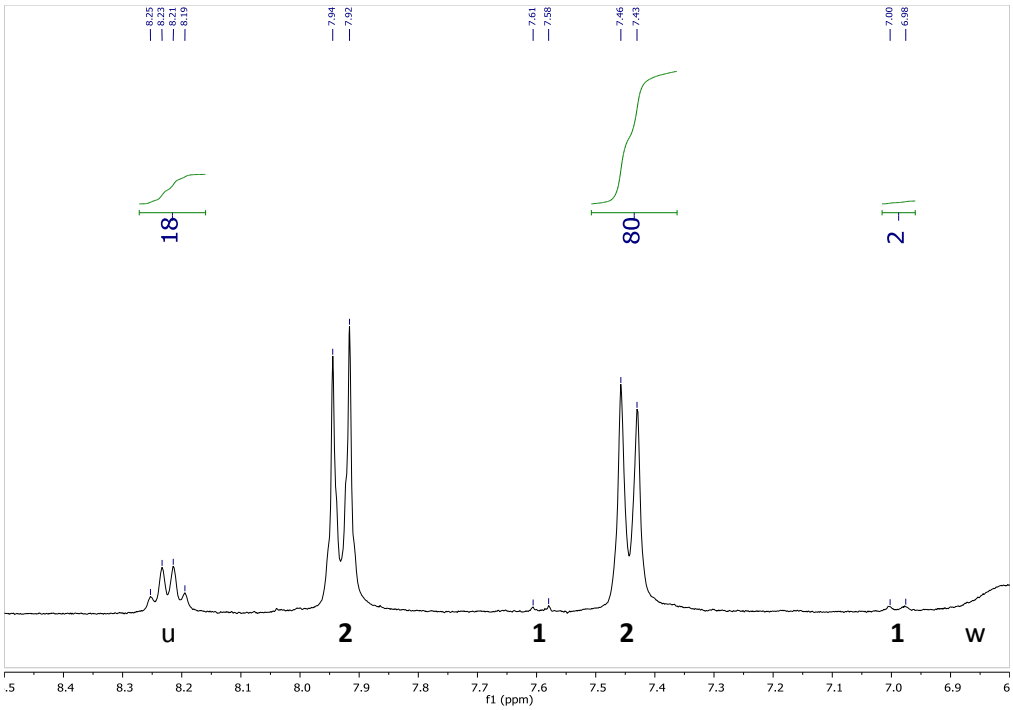


Figure S13: Zoom [8.5 ppm to 6.8 ppm] of the ^{1}H NMR (200 MHz, 299 K, d_3-CH_3CN) spectrum of the reaction mixture (table 1, entry 6). u: unidentified species.

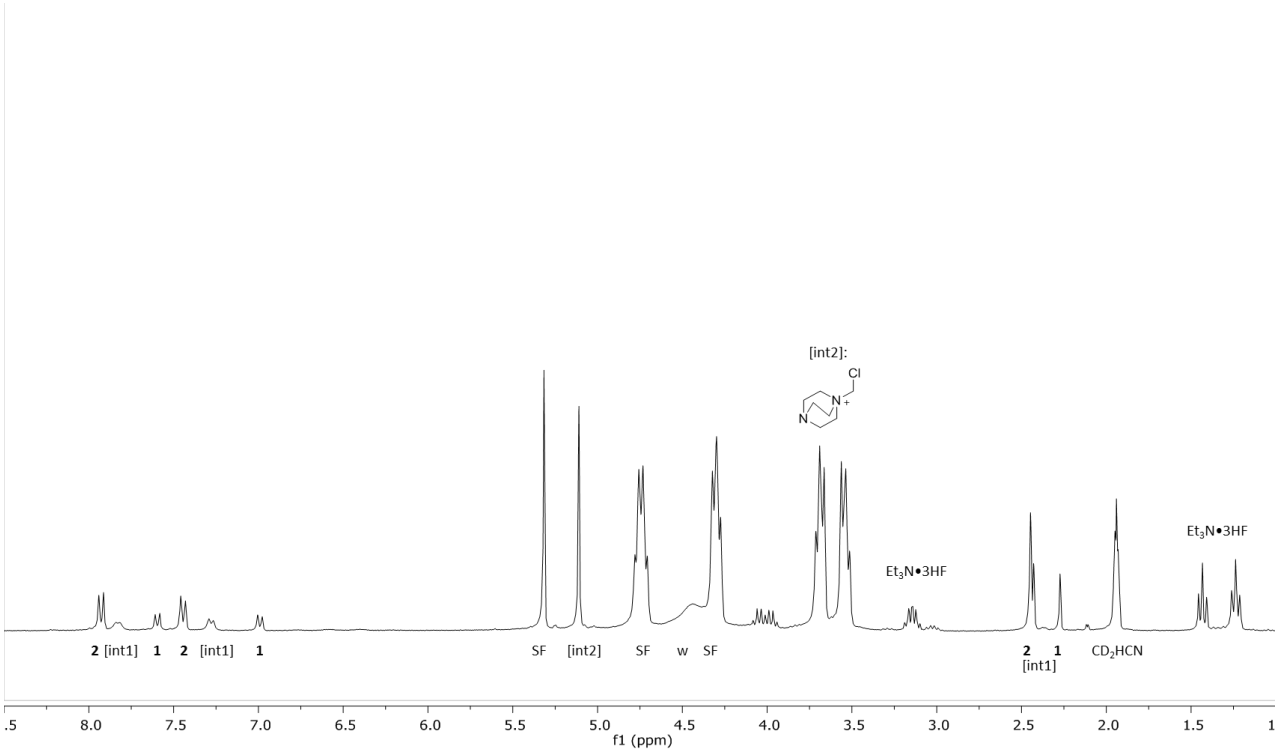


Figure S14: ^{1}H NMR (200 MHz, 299 K, d_3-CH_3CN) spectrum of the reaction mixture (table 1, entry 7).

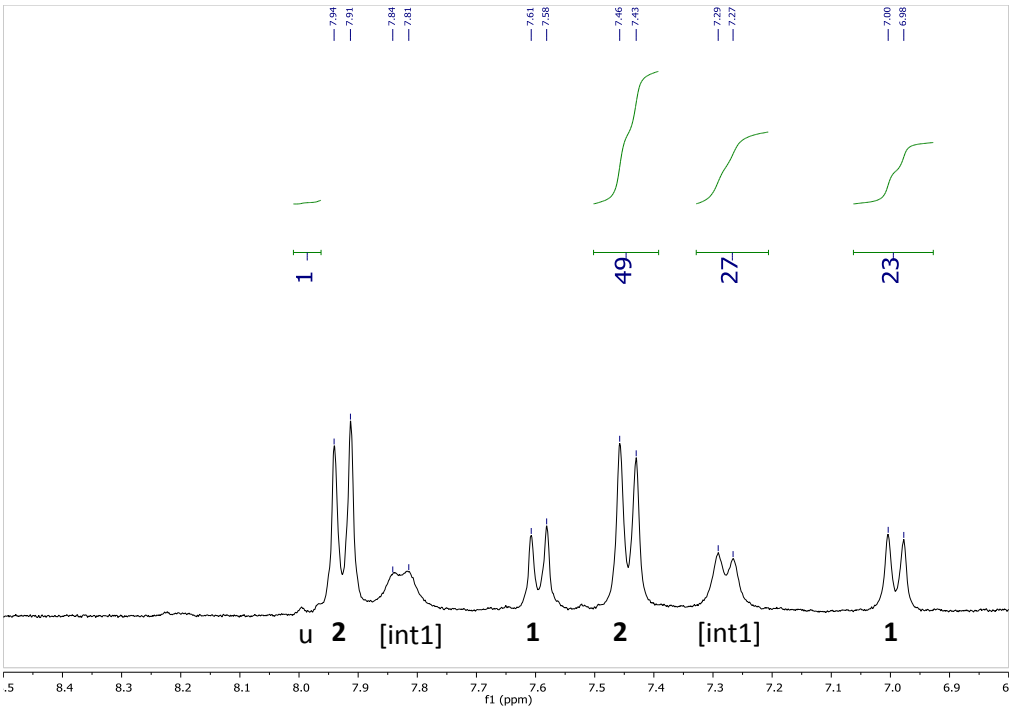


Figure S15: Zoom [8.5 ppm to 6.8 ppm] of the ^{1}H NMR (200 MHz, 299 K, d_3-CH_3CN) spectrum of the reaction mixture (table 1, entry 7). u: unidentified species.

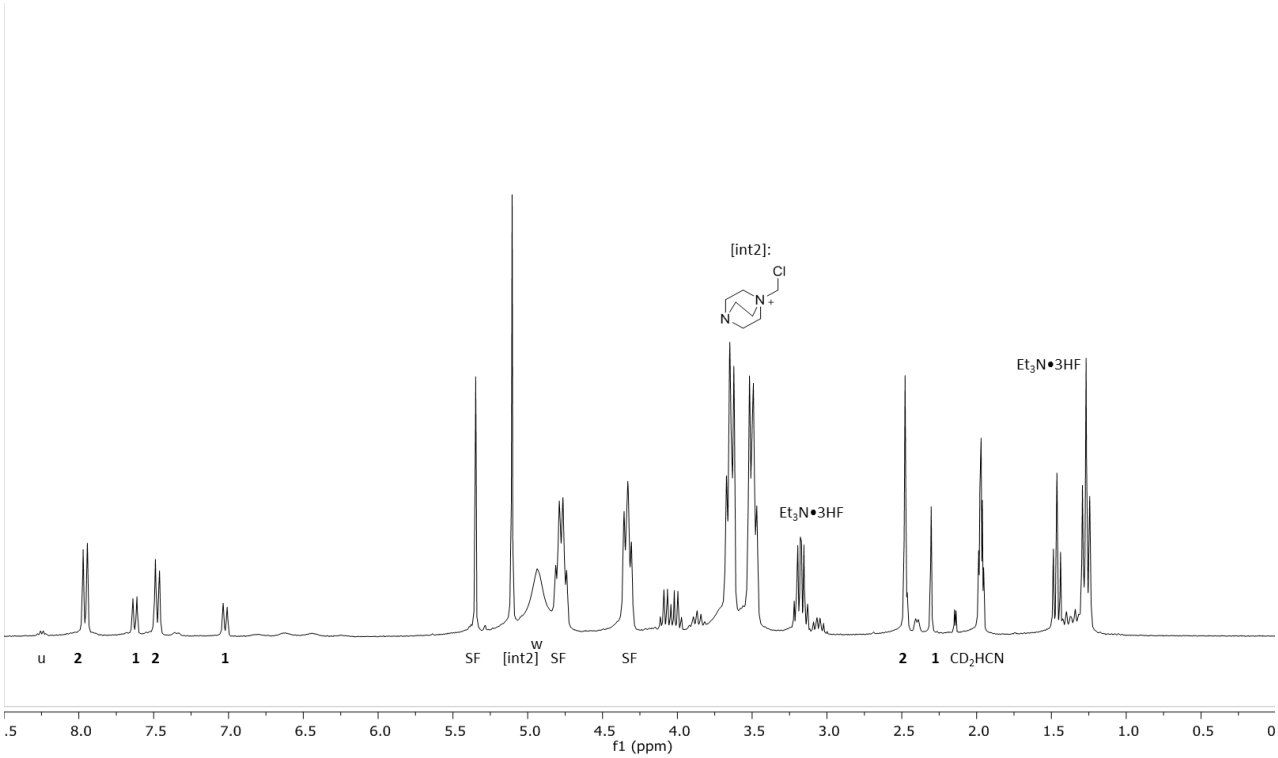


Figure S16: ^{1}H NMR (200 MHz, 299 K, d_3-CH_3CN) spectrum of the reaction mixture (table 1, entry 8).

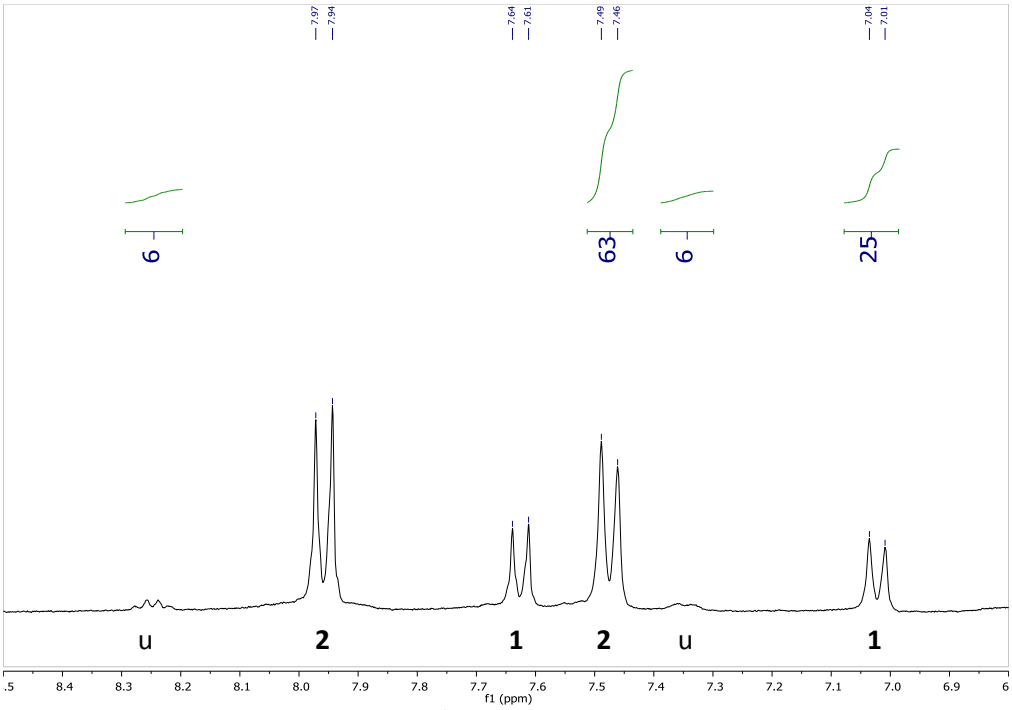


Figure S17: Zoom [8.5 ppm to 6.8 ppm] of the ^{1}H NMR (200 MHz, 299 K, d_3-CH_3CN) spectrum of the reaction mixture (table 1, entry 8). u: unidentified species.

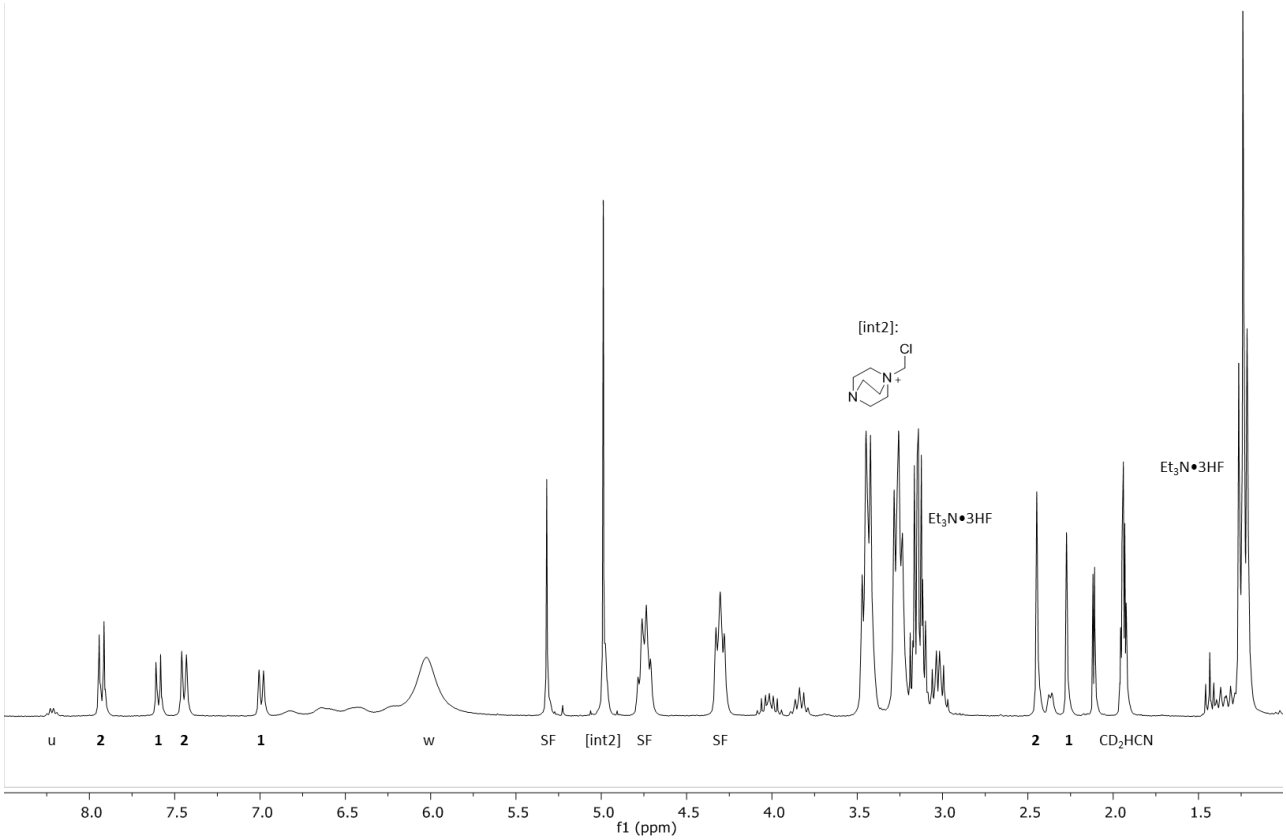


Figure S18: ^{1}H NMR (200 MHz, 299 K, d_3-CH_3CN) spectrum of the reaction mixture (table 1, entry 9).

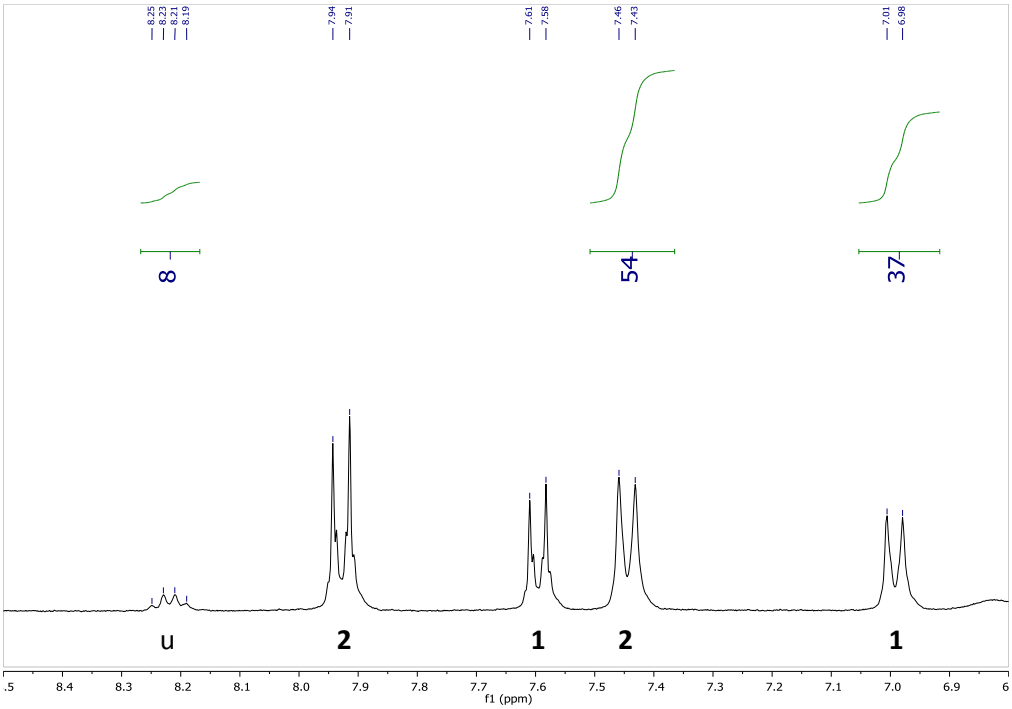


Figure S19: Zoom [8.5 ppm to 6.8 ppm] of the ^{1}H NMR (200 MHz, 299 K, d_3-CH_3CN) spectrum of the reaction mixture (table 1, entry 9). u: unidentified species.

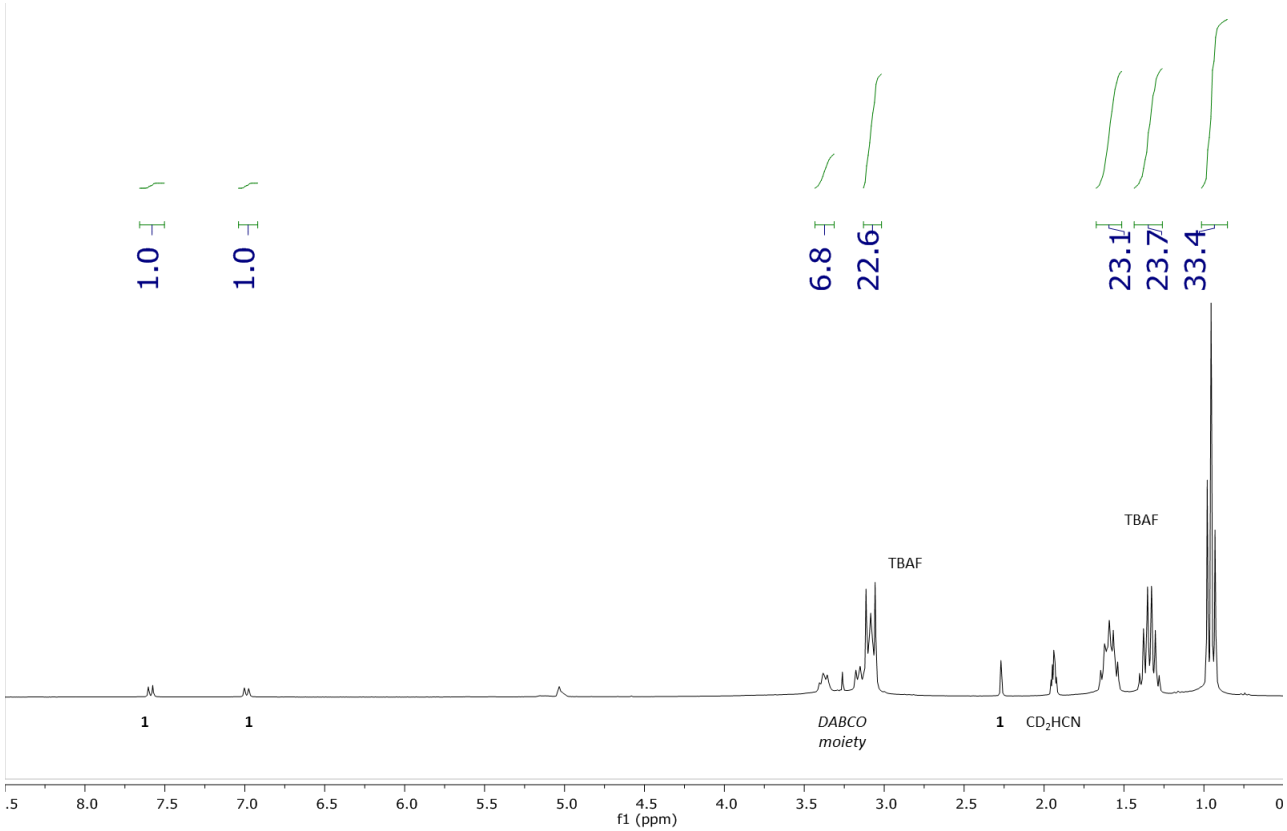


Figure S20: ^{1}H NMR (200 MHz, 299 K, d_3-CH_3CN) spectrum of the reaction mixture (table 1, entry 11) using TBAF·3H_2O.

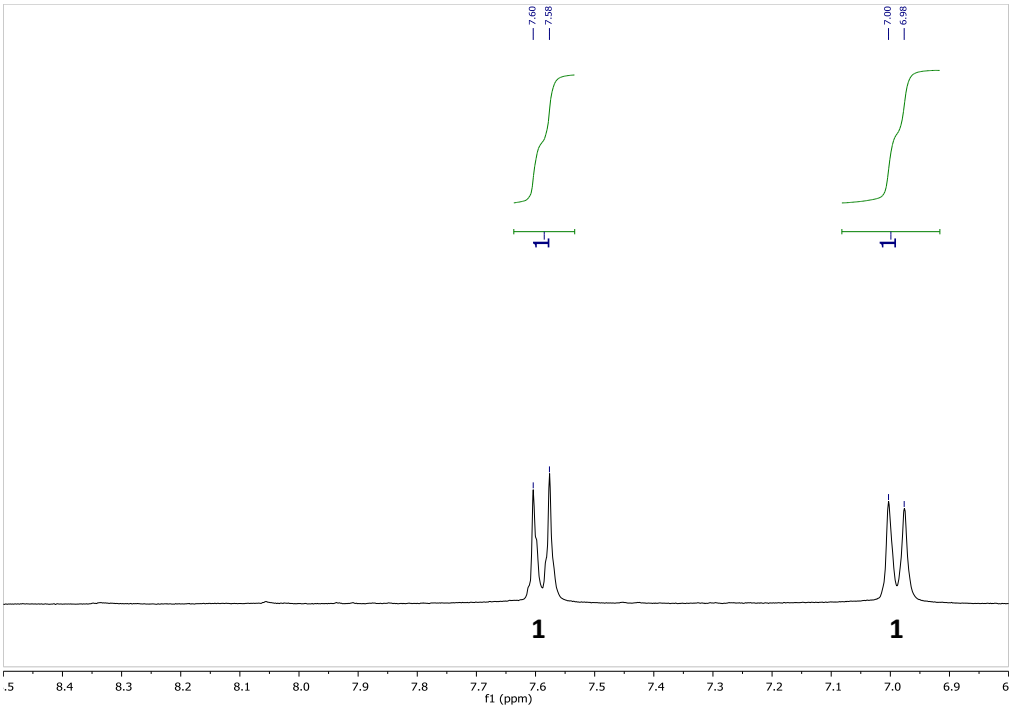


Figure S21: Zoom [8.5 ppm to 6.8 ppm] of the ^{1}H NMR (200 MHz, 299 K, d_3-CH_3CN) spectrum of the reaction mixture (table 1, entry 11) using TBAF·3H_2O.

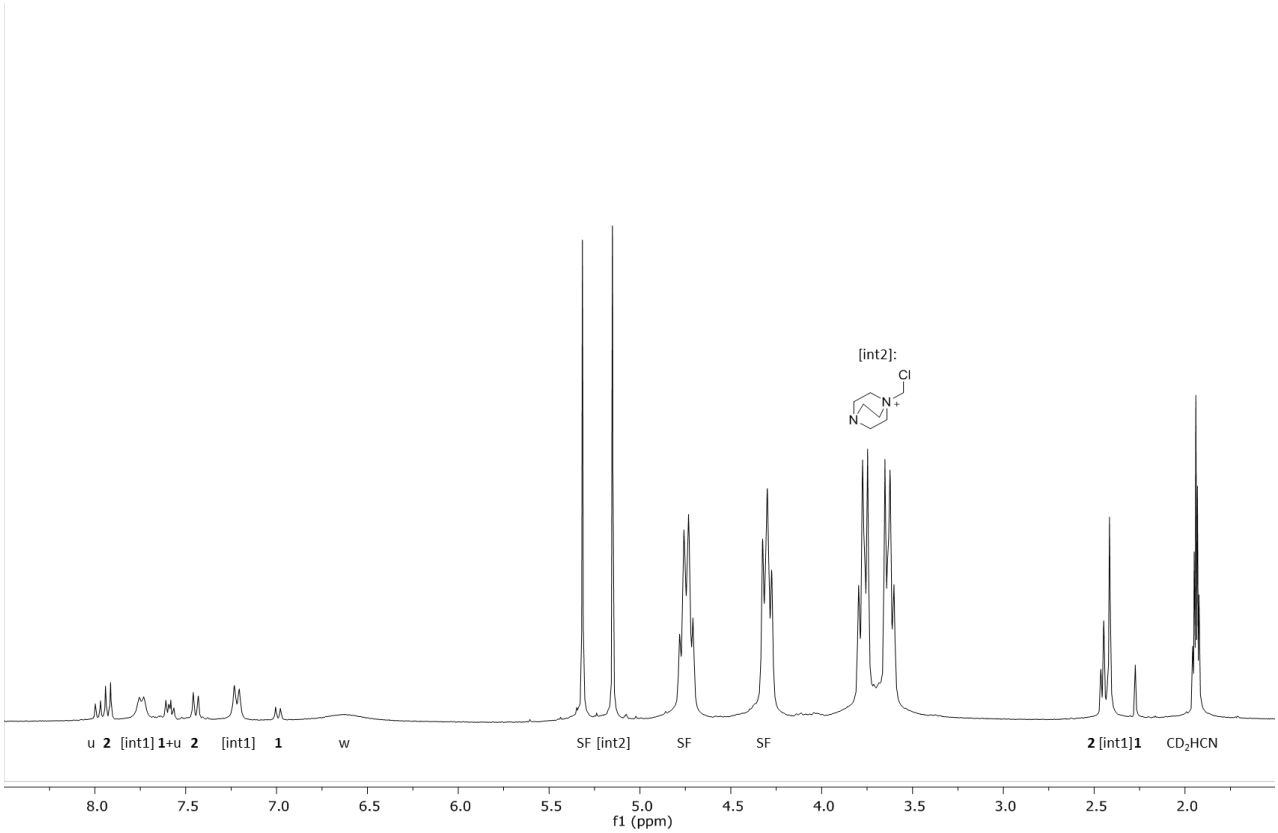


Figure S22: ^{1}H NMR (200 MHz, 299 K, d_3-CH_3CN) spectrum of the reaction mixture (table 1, entry 12).

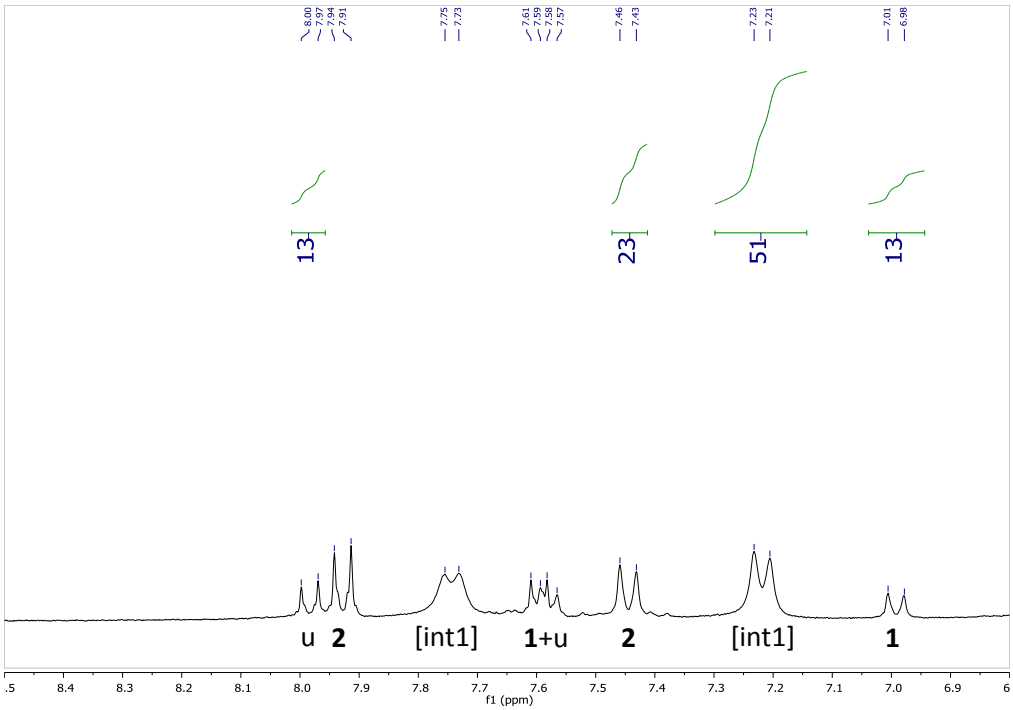


Figure S23: Zoom [8.5 ppm to 6.8 ppm] of the ^{1}H NMR (200 MHz, 299 K, d_3-CH_3CN) spectrum of the reaction mixture (table 1, entry 12).

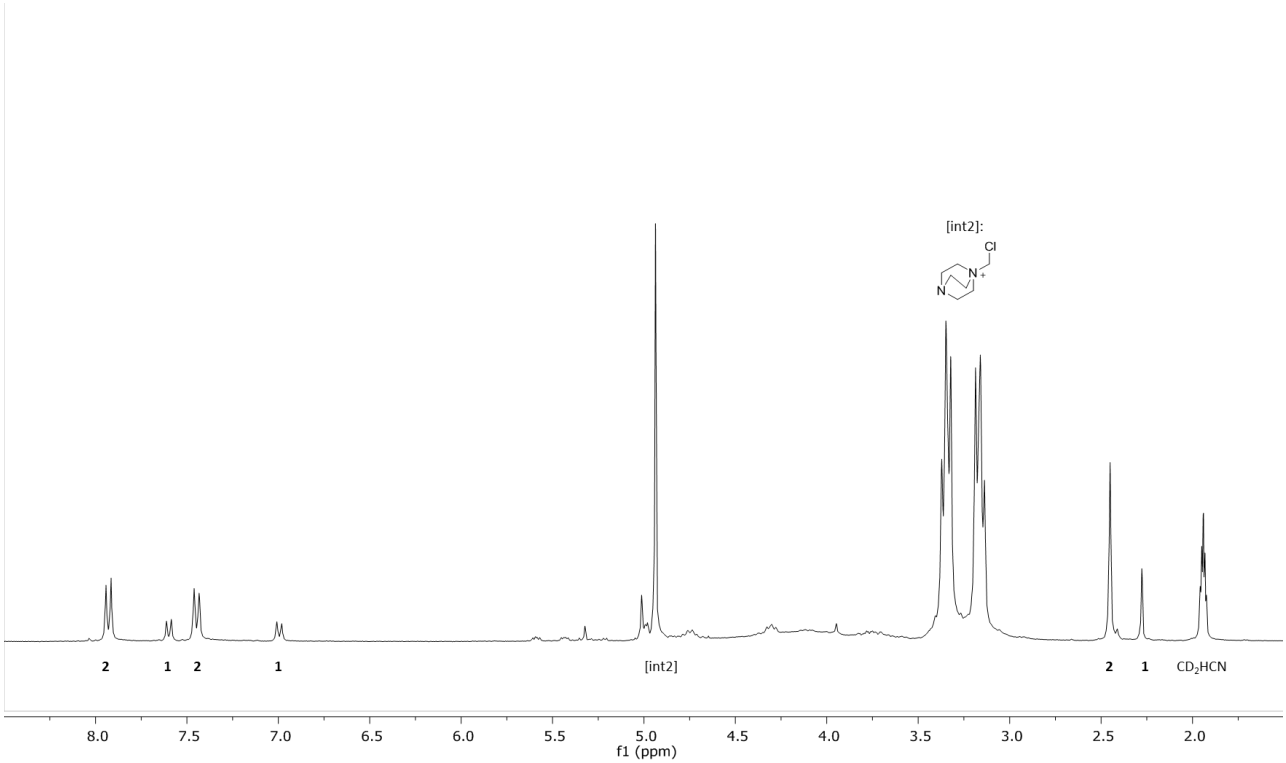


Figure S24: ^{1}H NMR (200 MHz, 299 K, d_3-CH_3CN) spectrum of the reaction mixture (table 1, entry 13).

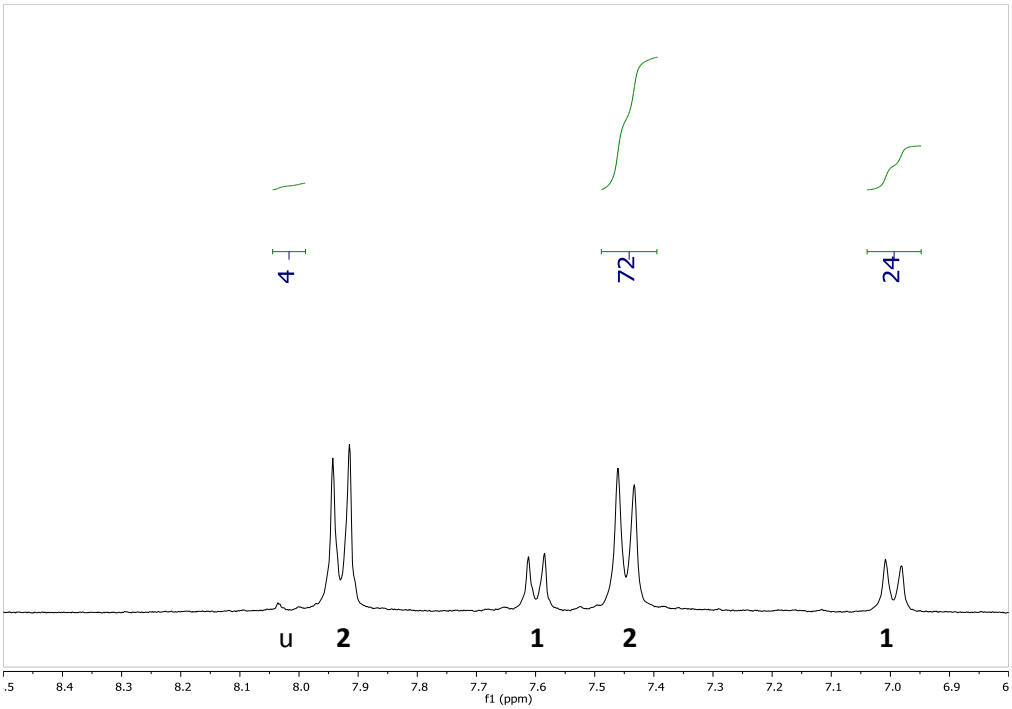


Figure S25: Zoom [8.5 ppm to 6.8 ppm] of the ^{1}H NMR (200 MHz, 299 K, d_3-CH_3CN) spectrum of the reaction mixture (table 1, entry 13).

II. Exploring oxidant

II.1 1-Fluoropyridinium tetrafluoroborate

4-Iodotoluene (9 mg, 0.04 mmol, 1 eq.), 1-fluoropyridinium tetrafluoroborate (18.5 mg, 0.10 mmol, 2.6 eq.) and d_3-CH_3CN (1 mL) was added in a NMR tube. After the reaction mixture was protected against light by using aluminum foil and stored at ambient temperature for 8 h, it was characterized by ^{1}H and ^{19}F NMR experiments.

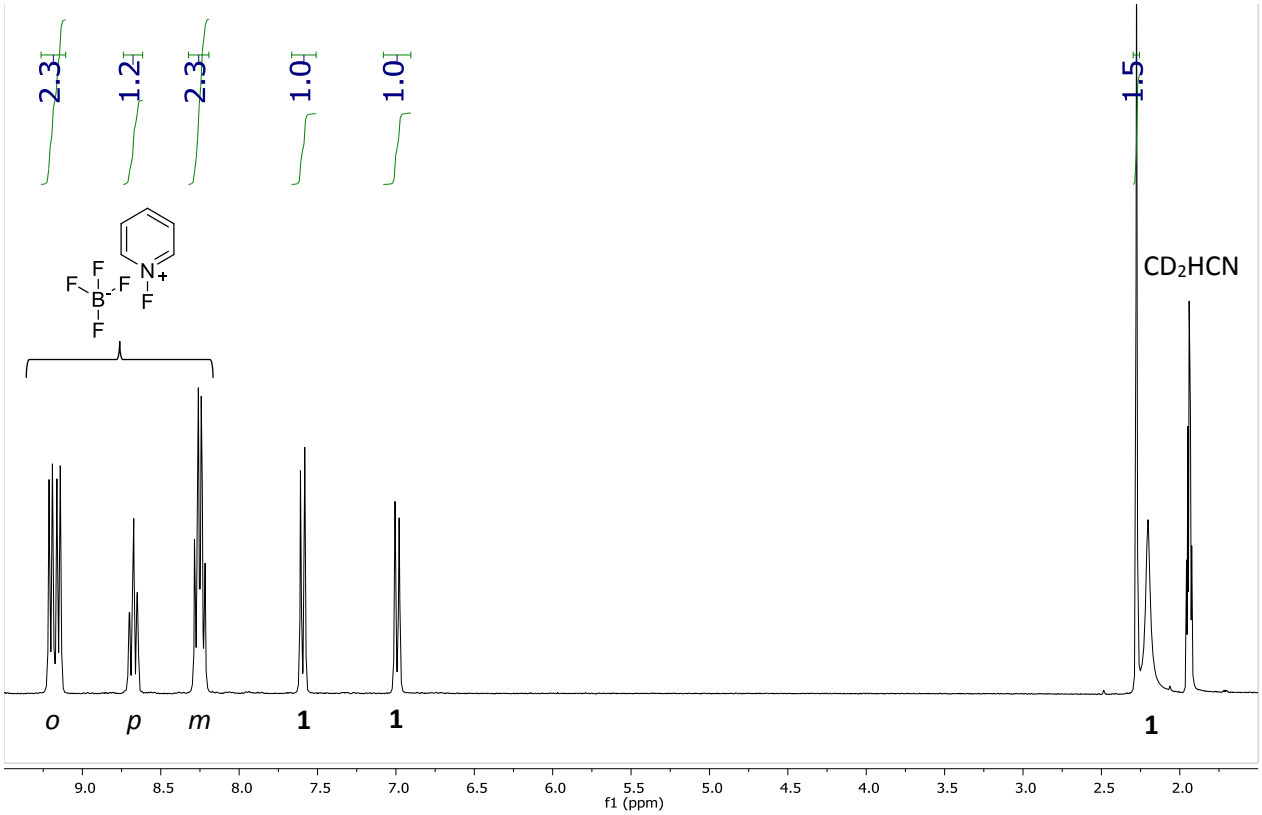


Figure S26: ^{1}H NMR (300 MHz, 299 K, d_3-CH_3CN) spectrum of the reaction mixture.

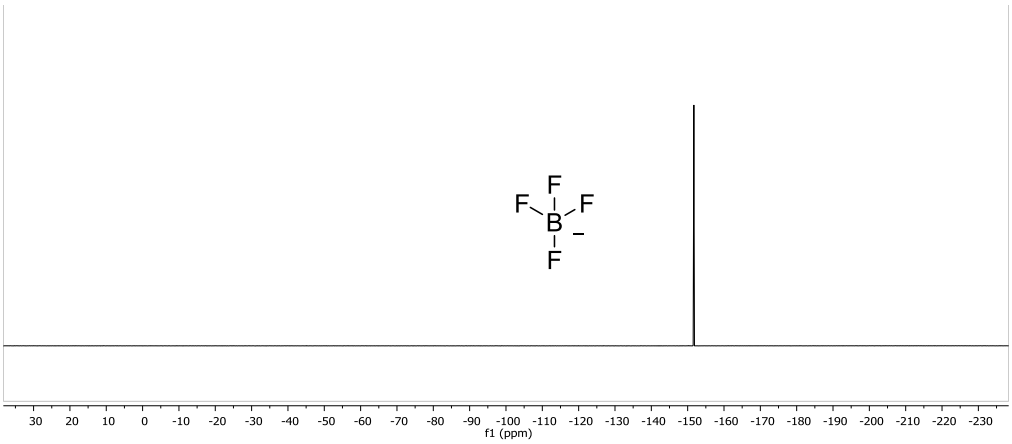


Figure S27: ^{19}F NMR (282 MHz, 299 K, d_3-CH_3CN) spectrum of the reaction mixture.

II.2 N-Fluorobenzenesulfonimide (NFSI)

4-Iodotoluene (9 mg, 0.04 mmol, 1 eq.), N-fluorobenzenesulfonimide (31.5 mg, 0.10 mmol, 2.6 eq.) and d_3-CH_3CN (1 mL) were added in a NMR tube. After the reaction mixture was protected against light by using aluminum foil and stored at ambient temperature for 4 h, it was characterized by a ^{1}H NMR experiment.

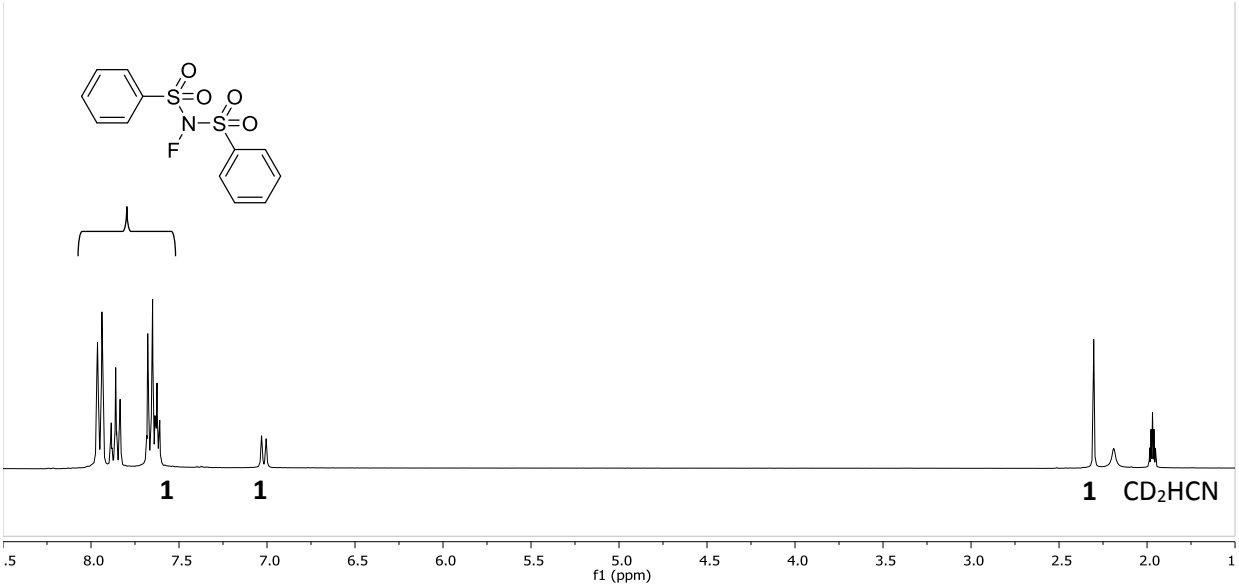
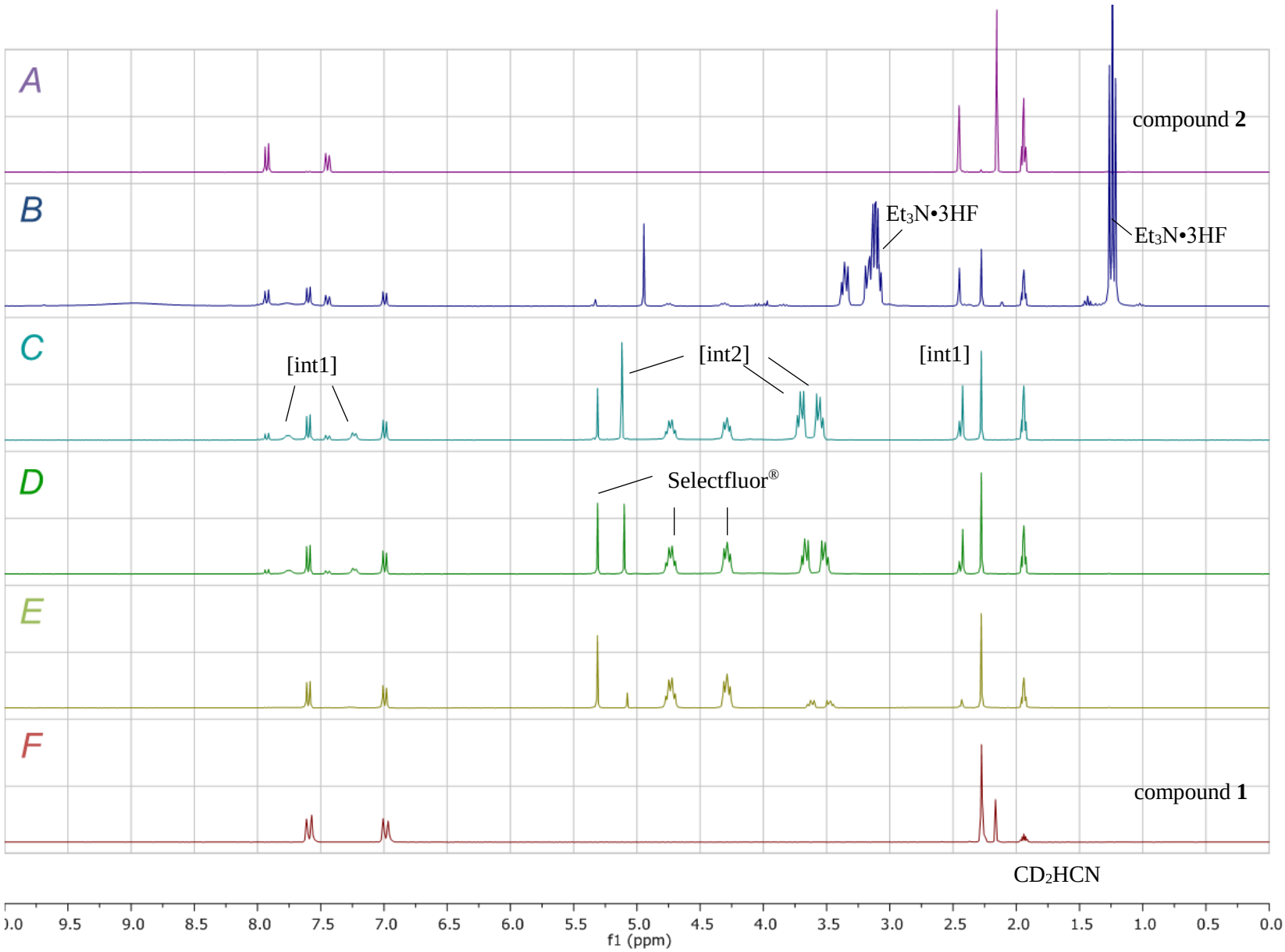


Figure S28: ^{1}H NMR (300 MHz, 299 K, d_3-CH_3CN) NMR spectrum of the reaction mixture.

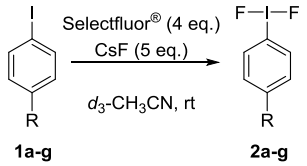
III. Figure S31: full ^{1}H NMR spectra corresponding to Figure 1

Experiments B to E:
4-Iodotoluene (9 mg, 0.04 mmol, 1 eq.), Selectfluor® (14 mg, 0.04 mmol, 1 eq.) and d_3-CH_3CN (1 mL) were added in a NMR tube. The obtained reaction mixture was characterized by ^{1}H NMR (300MHz, 299K, d_3-CH_3CN) experiments after the respective reaction time at ambient temperature.

A: Reference spectrum of *p*-$TolIF_2$ (**2**).
B: Reaction mixture 240 min after addition of 2 drops of Et_3N•3HF.
C: Reaction mixture 240 min prior to addition of 2 drops of Et_3N•3HF.
D: Reaction mixture after 130 min.
E: Reaction mixture after 26 min.
F: Reference *p*-TolI (**1**) (200 MHz, 299 K).


A
compound 2
B
Et3N•3HF
Et3N•3HF
C
[int1]
[int2]
[int1]
D
Selectfluor®
E
F
compound 1
CD2HCN
f1 (ppm)

IV. Conversion in Table 2



Entry	n°	R	Time (h)	Conversion (%)
1	2a	NO_2	48	13
2	2b	CF_3	48	14
3	2c	CO_2Et	48	51
4	2d	Cl	24	54
5	2e	H	24	80
6	2	CH_3	24	74
7	2f	OBn	6	75
8	2g	OMe	6	89

Figure S29: Exploring the effect of electronic modulation on the oxidation of *p*-substituted aryl iodides using Selectfluor® and CsF.

IV.1 General Procedure

The respective iodoarene (0.04 mmol, 1 eq.), CsF (0.2 mmol, 5 eq.), Selectfluor® (0.16 mmol, 4 eq.) and d_3-CH_3CN (1 mL) were added in a borosilicate NMR tube. After the reaction mixture was protected against light by using aluminum foil and stored at ambient temperature for the indicated time, it was characterized by a ^1H NMR (200 MHz, 299 K) experiment.

IV.2 Results ^{1}H NMR experiments

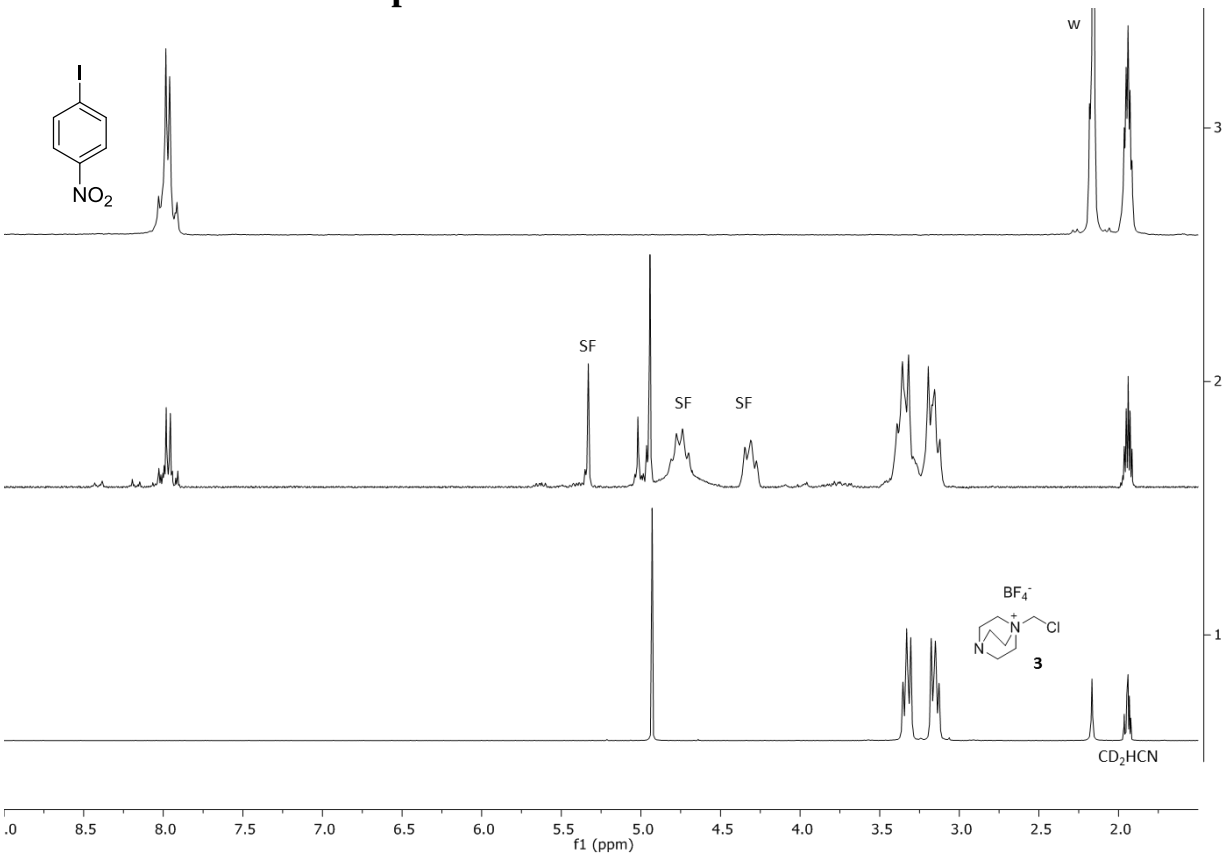


Figure S30: ^{1}H NMR (200 MHz, 299 K, d_3-CH_3CN) spectra of 1) Compound **3** (300 MHz, 299 K, d_3-CH_3CN), 2) the reaction mixture (table 2, entry 1) after 48 h and 3) the starting material.

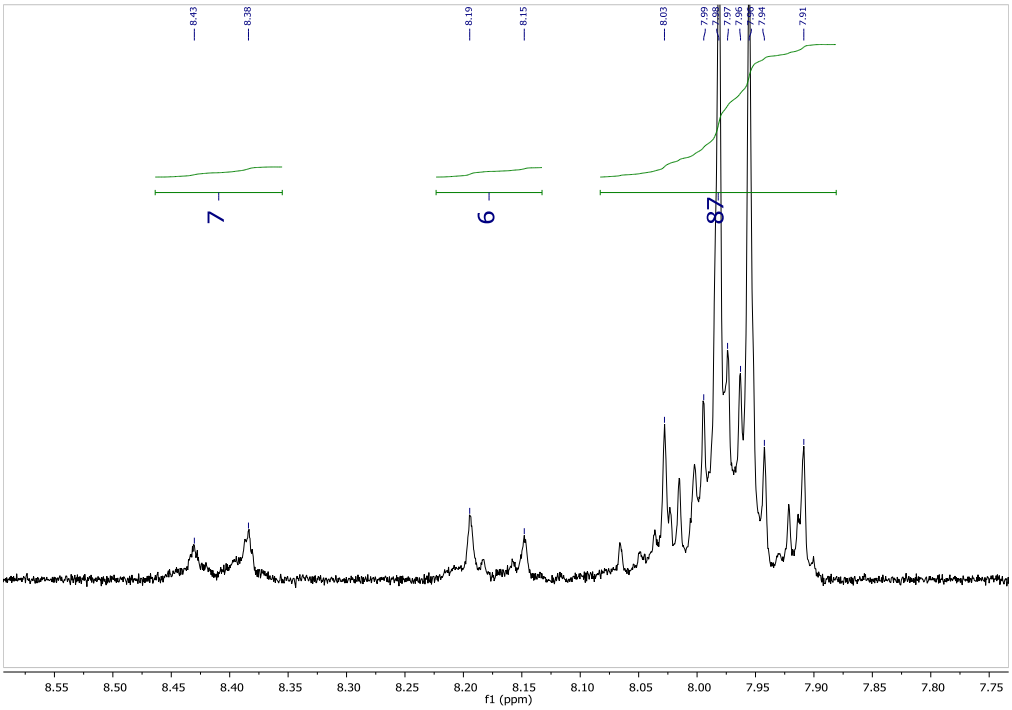


Figure S31: Zoom [8.6 ppm to 7.7 ppm] of the ^{1}H NMR (200 MHz, 299 K, d_3-CH_3CN) spectrum of the reaction mixture (table 2, entry 1) after 48 h.

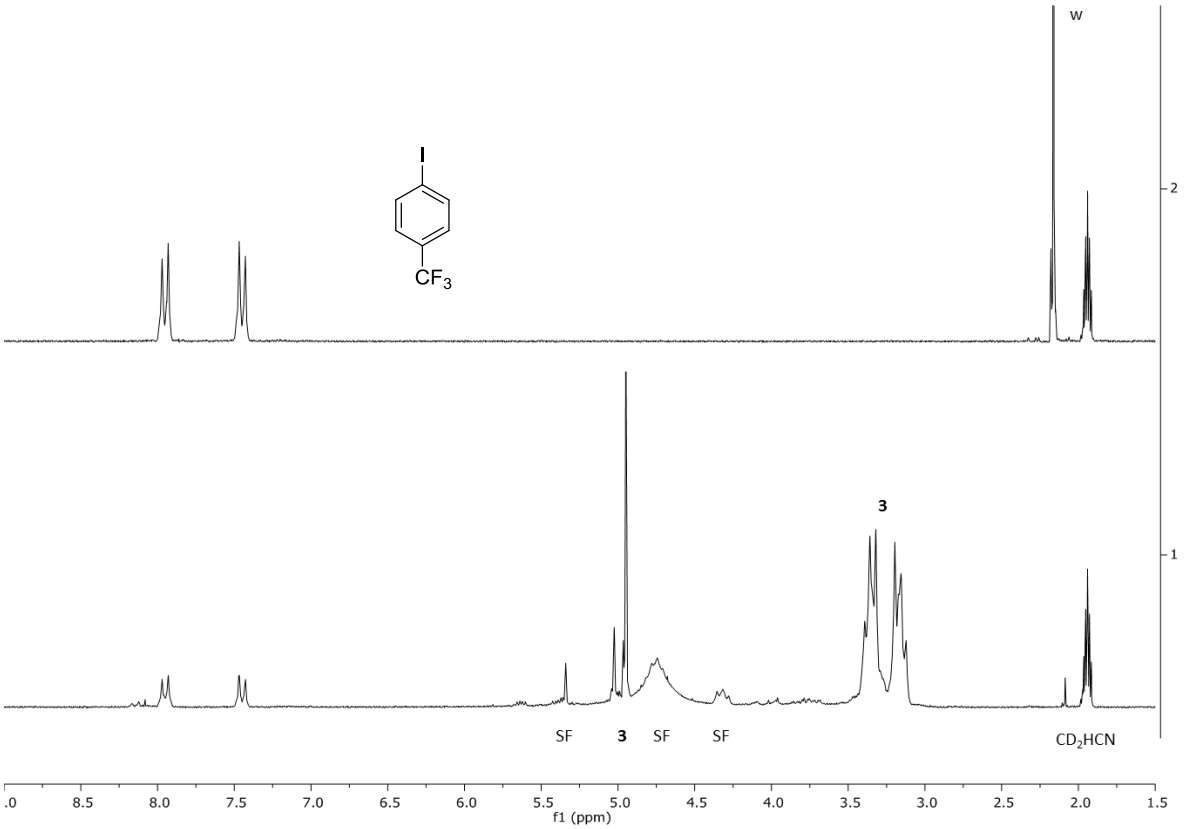


Figure S32: ^{1}H NMR (200 MHz, 299 K, d_3-CH_3CN) spectra of 1) the reaction mixture (table 2, entry 2) after 48 h and 2) the starting material.

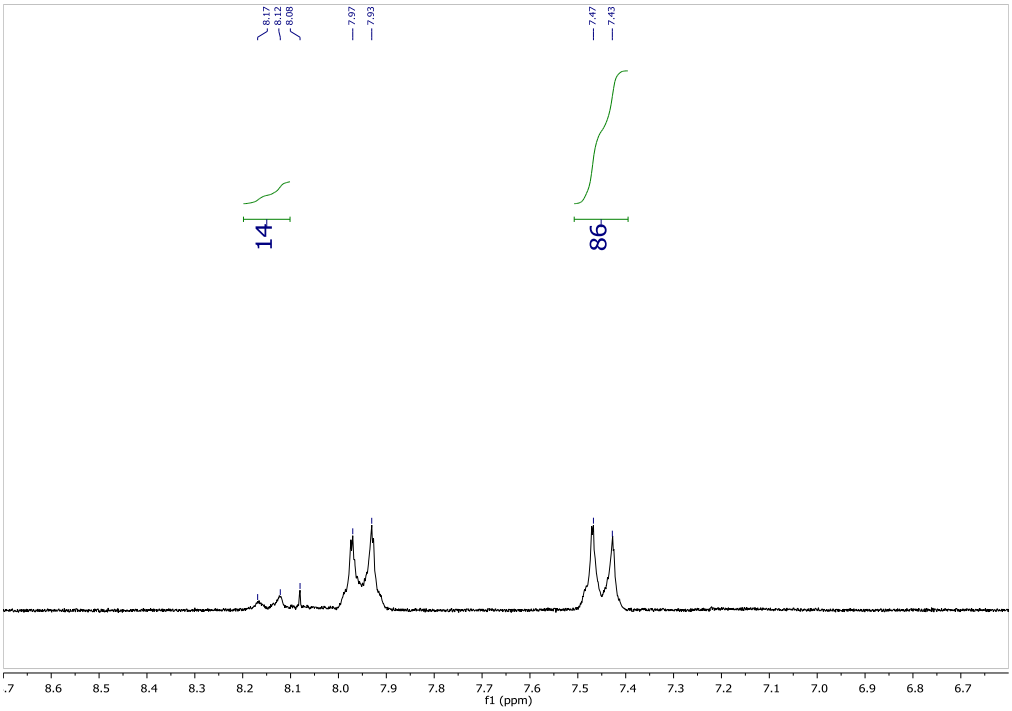


Figure S33: Zoom [8.7 to 6.6 ppm] of the ^{1}H NMR (200 MHz, 299 K, d_3-CH_3CN) spectrum of the reaction mixture (table 2, entry 2) after 48 h. (The second resonance of the product is obscured by a resonance of the starting material at 7.95].

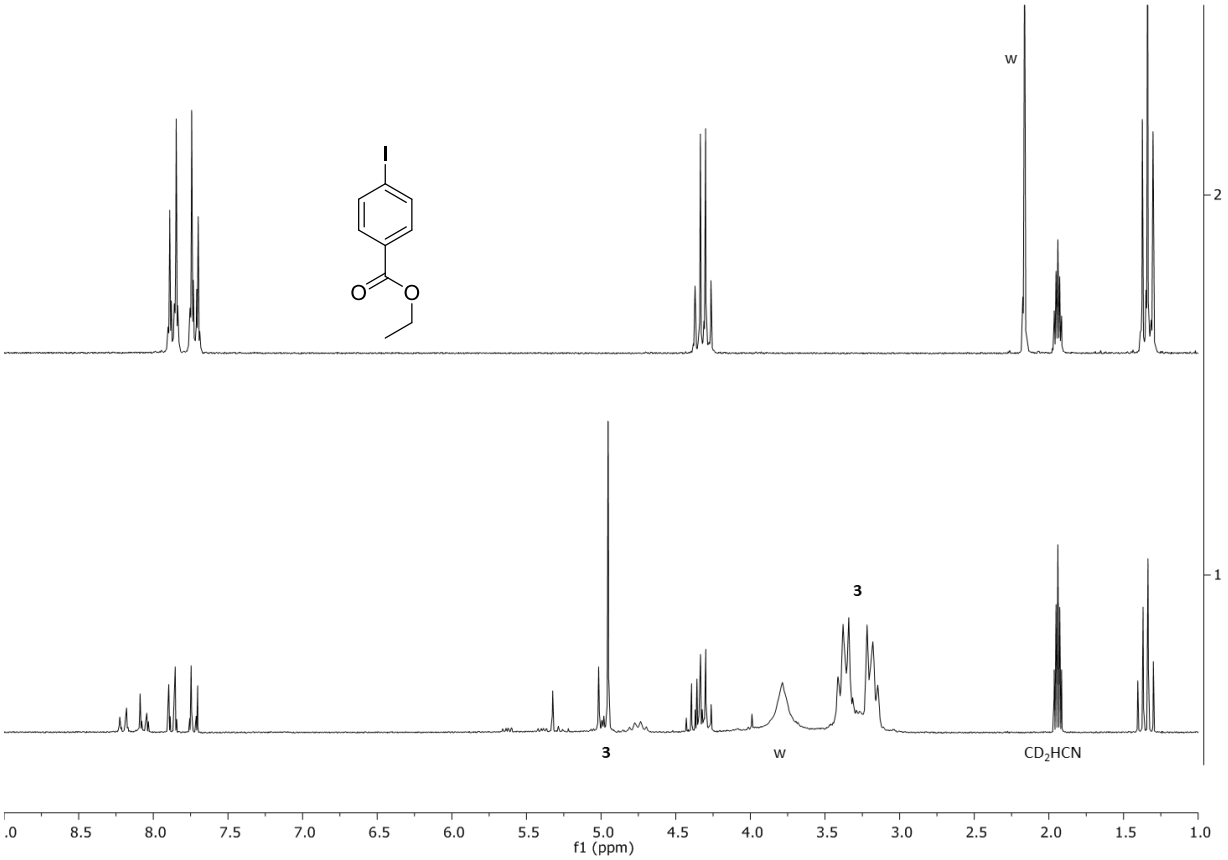


Figure S34: ^{1}H NMR (200 MHz, 299 K, d_3-CH_3CN) spectra of 1) the reaction mixture (table 2, entry 3) after 48 h and 2) the starting material.

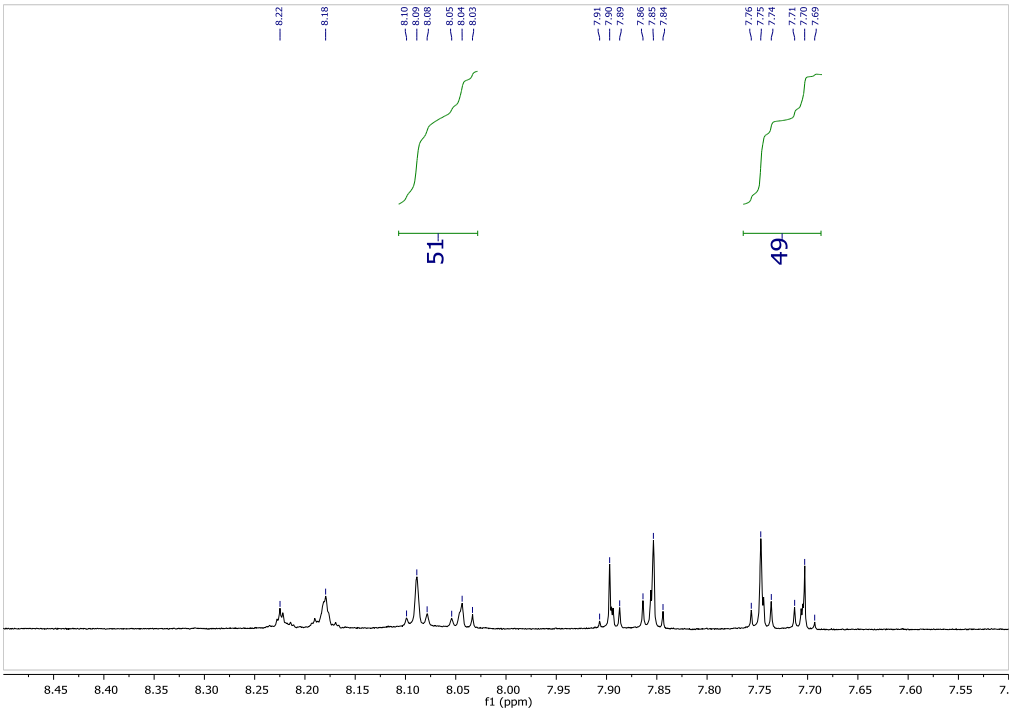


Figure S35: Zoom [8.5 to 7.5 ppm] of the ^{1}H NMR (200 MHz, 299 K, d_3-CH_3CN) spectrum of the reaction mixture (table 2, entry 3) after 48 h.

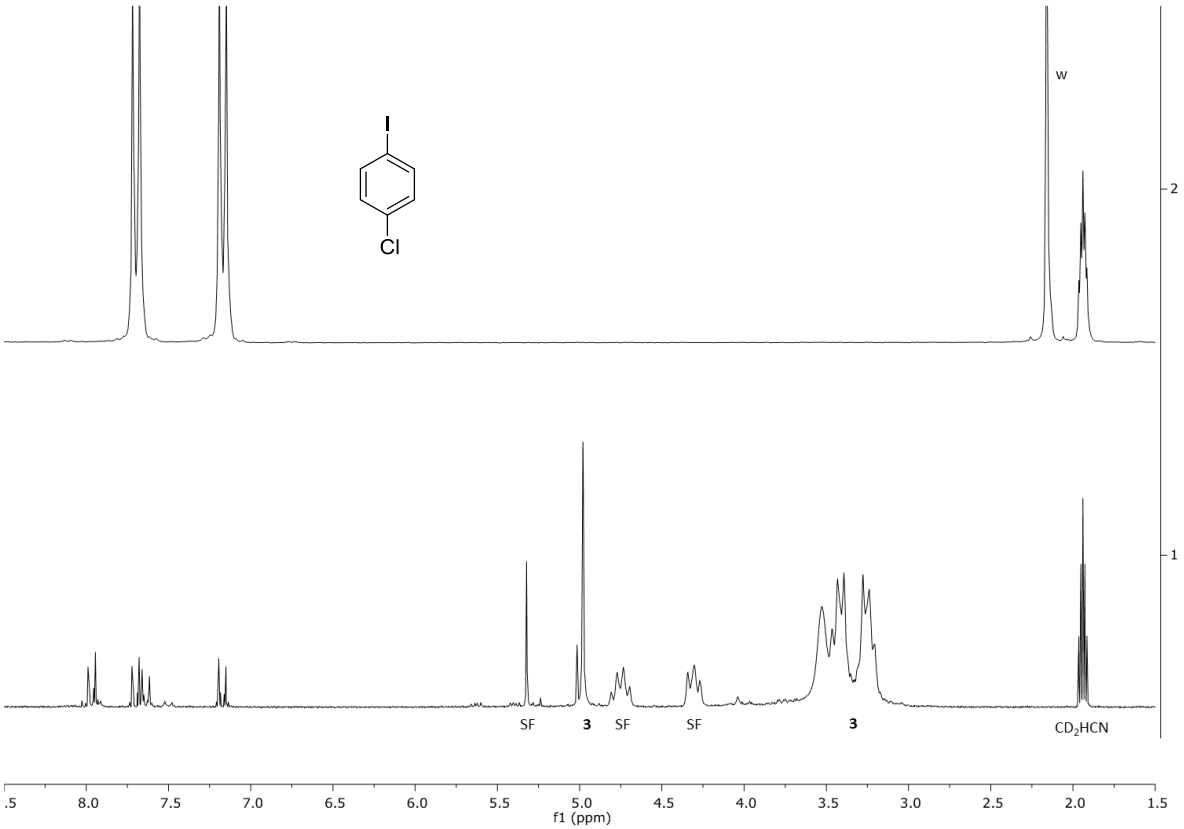


Figure S36: ^{1}H NMR (200 MHz, 299 K, d_3-CH_3CN) spectra of 1) the reaction mixture (table 2, entry 4) after 24 h and 2) the starting material.

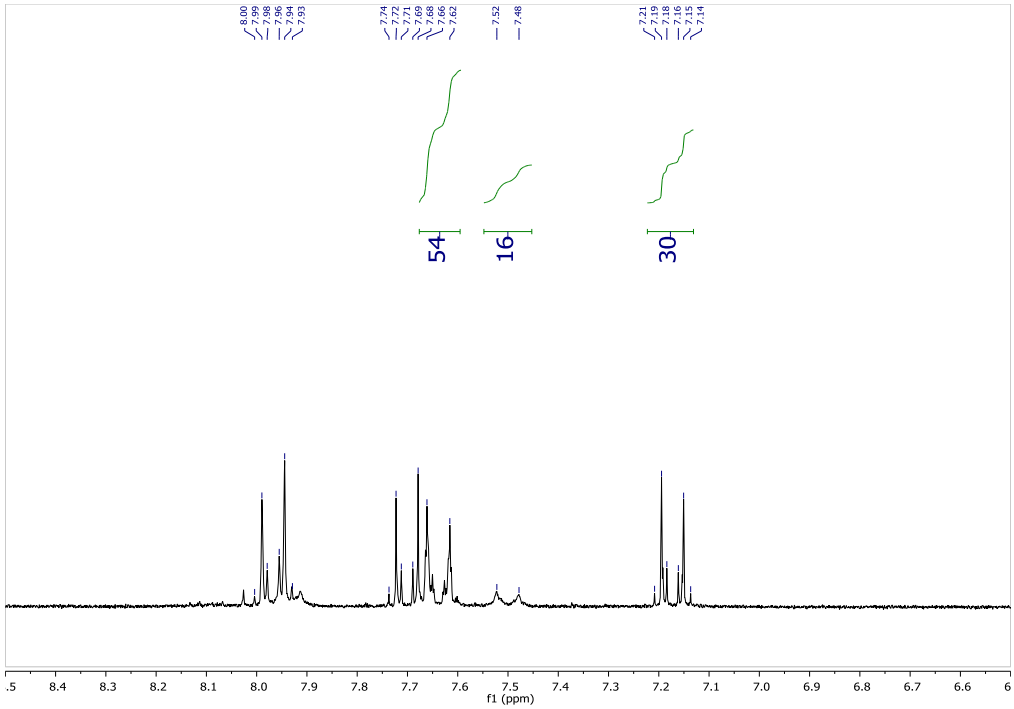


Figure S37: Zoom [8.5 to 6.5 ppm] of the ^{1}H NMR (200 MHz, 299 K, d_3-CH_3CN) spectrum of the reaction mixture (table 2, entry 4) after 24 h.

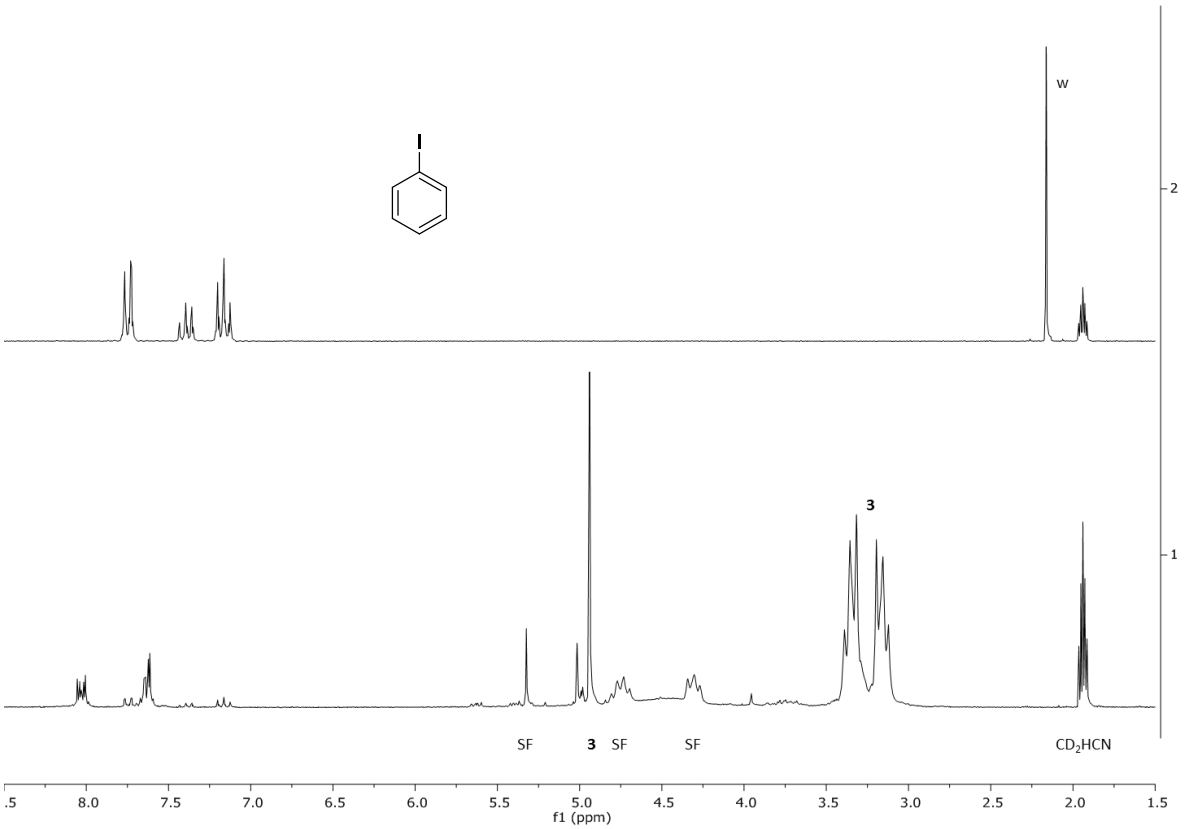


Figure S38: ^{1}H NMR (200 MHz, 299 K, d_3-CH_3CN) spectra of 1) the reaction mixture (table 2, entry 5) after 24 h and 2) the starting material.

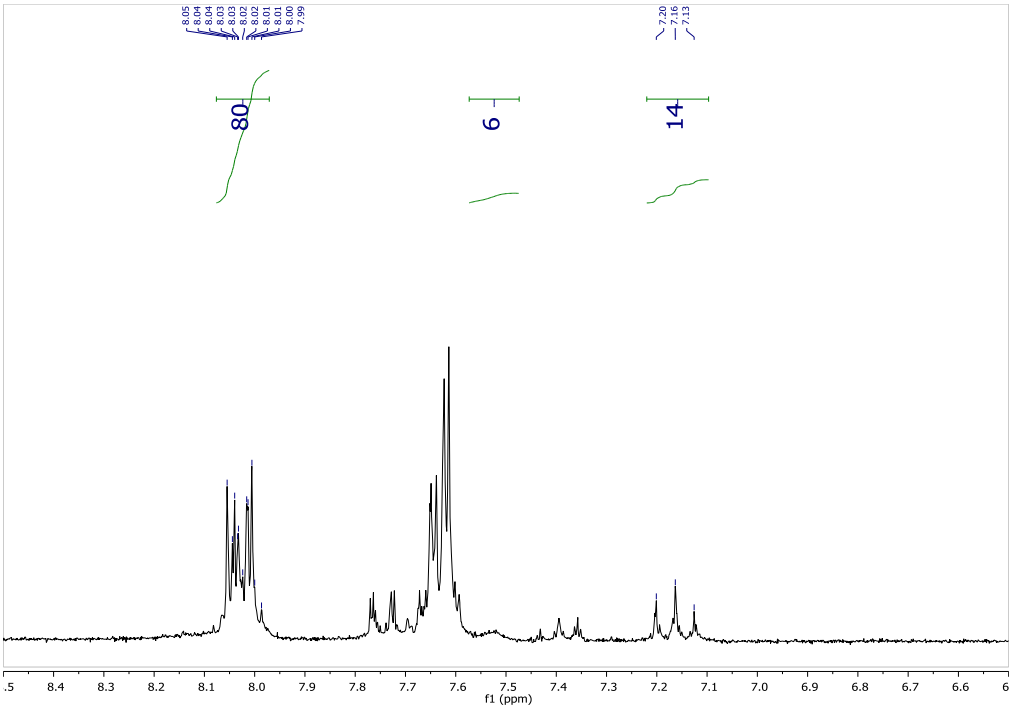


Figure S39: Zoom [8.5 to 6.5 ppm] of the ^{1}H NMR (200 MHz, 299 K, d_3-CH_3CN) spectrum of the reaction mixture (table 2, entry 5) after 24 h.

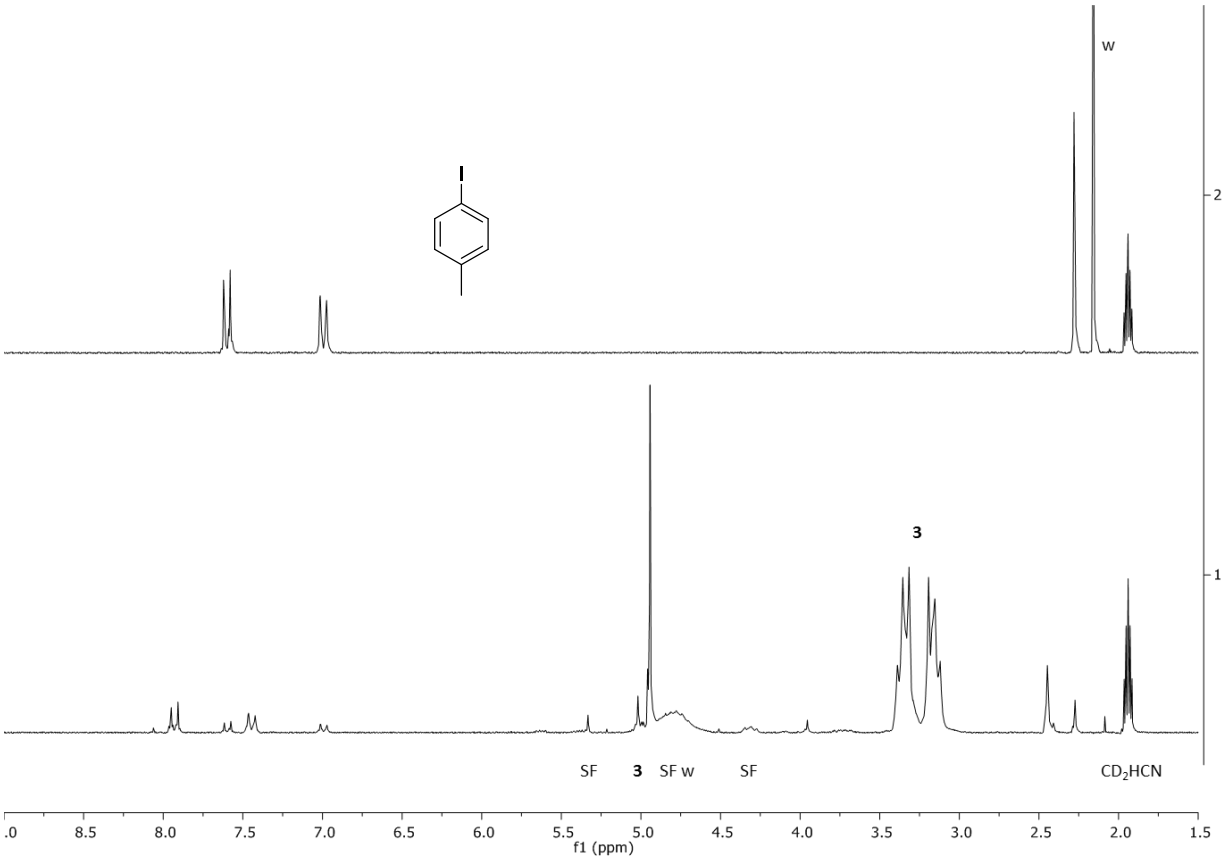


Figure S40: ^{1}H NMR (200 MHz, 299 K, d_3-CH_3CN) spectra of 1) the reaction mixture (table 2, entry 6) after 24 h and 2) the starting material.

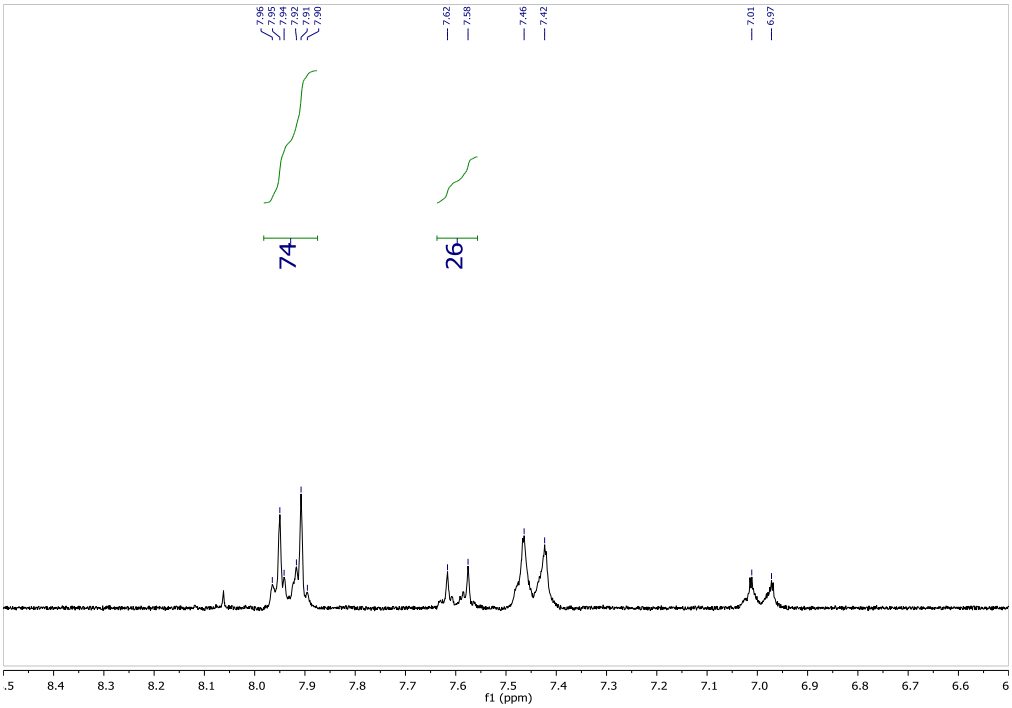


Figure S41: Zoom [8.5 to 6.5 ppm] of the ^{1}H NMR (200 MHz, 299 K, d_3-CH_3CN) spectrum of the reaction mixture (table 2, entry 6) after 24 h.

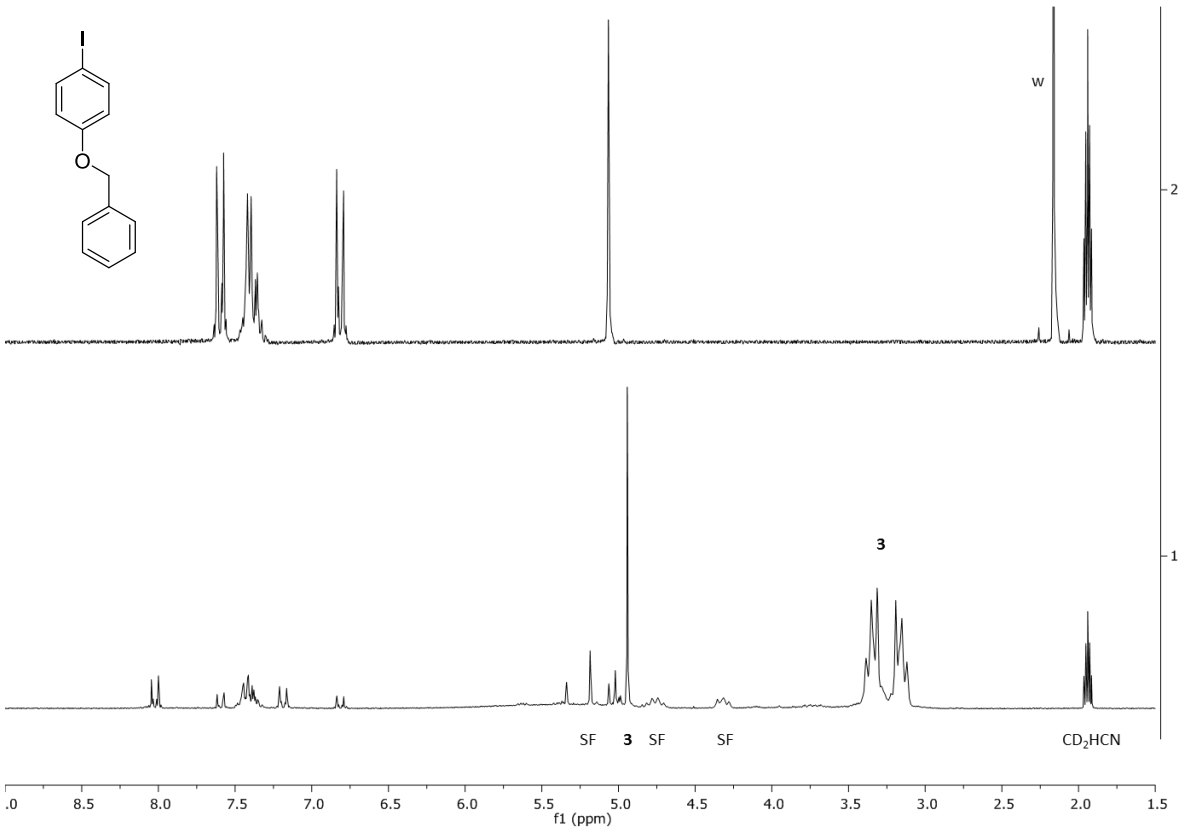


Figure S42: ^{1}H NMR (200 MHz, 299 K, d_3-CH_3CN) spectra of 1) the reaction mixture (table 2, entry 7) after 6 h and 2) the starting material.

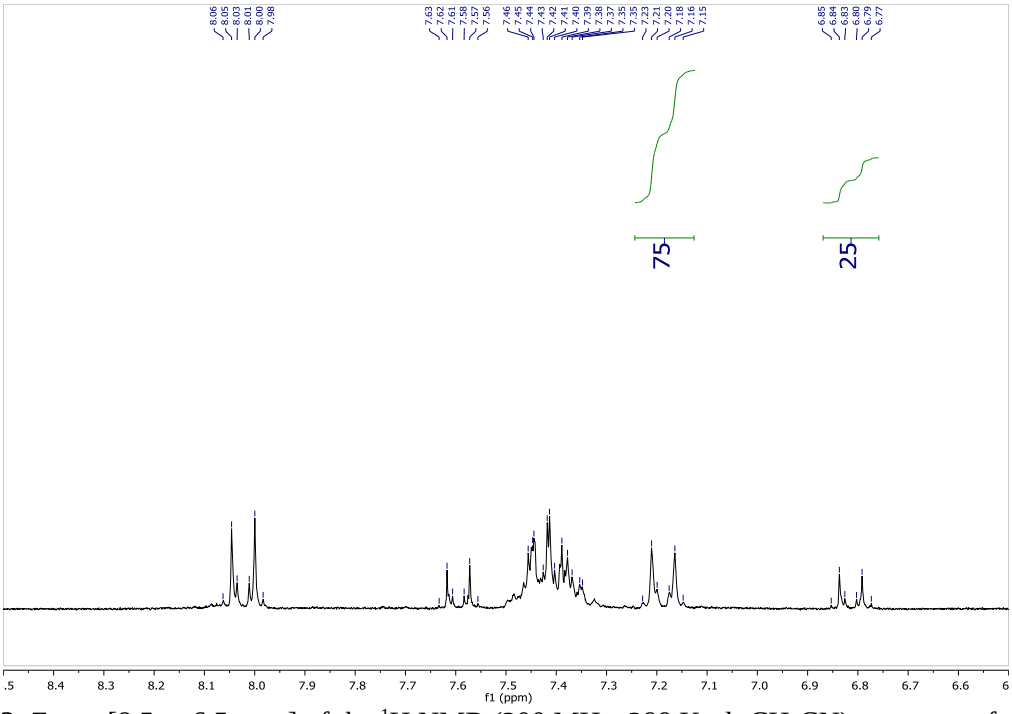


Figure S43: Zoom [8.5 to 6.5 ppm] of the ^{1}H NMR (200 MHz, 299 K, d_3-CH_3CN) spectrum of the reaction mixture (table 2, entry 7) after 6 h.

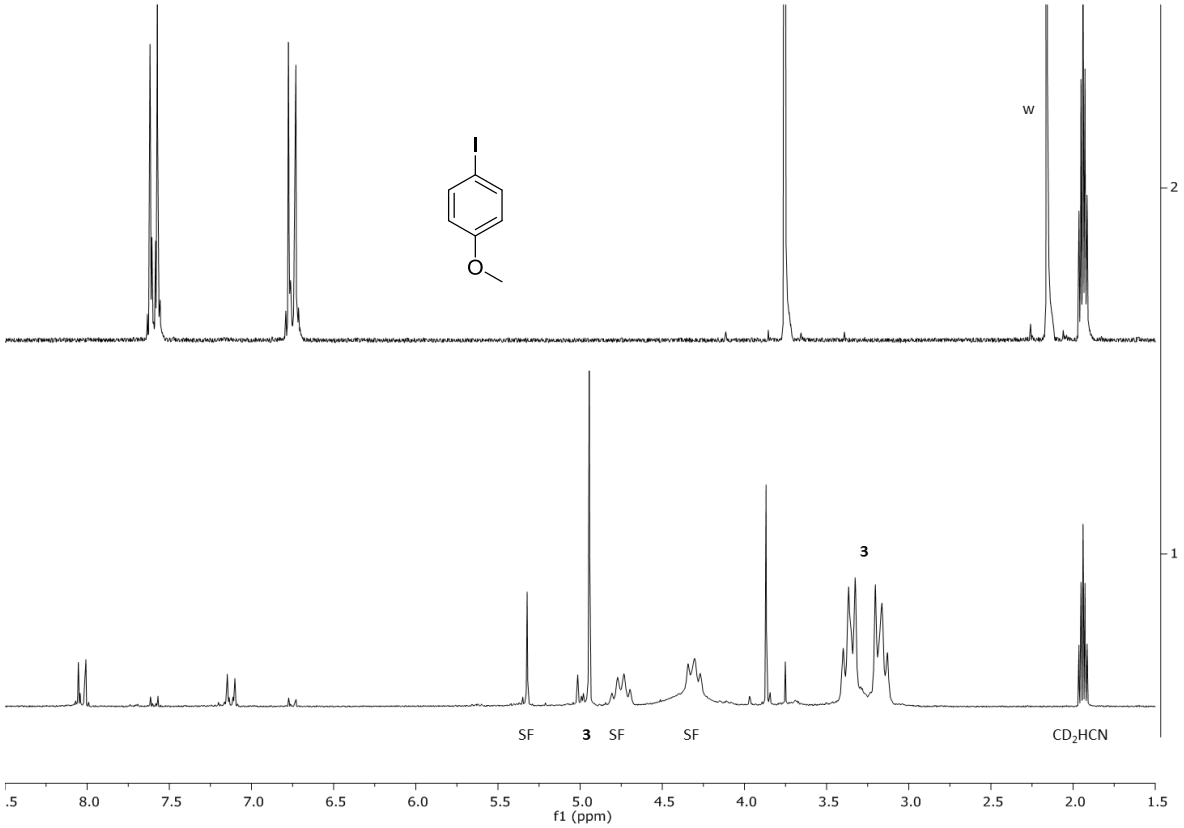


Figure S44: ^{1}H NMR (200 MHz, 299 K, d_3-CH_3CN) spectra of 1) the reaction mixture (table 2, entry 8) after 6 h and 2) the starting material.

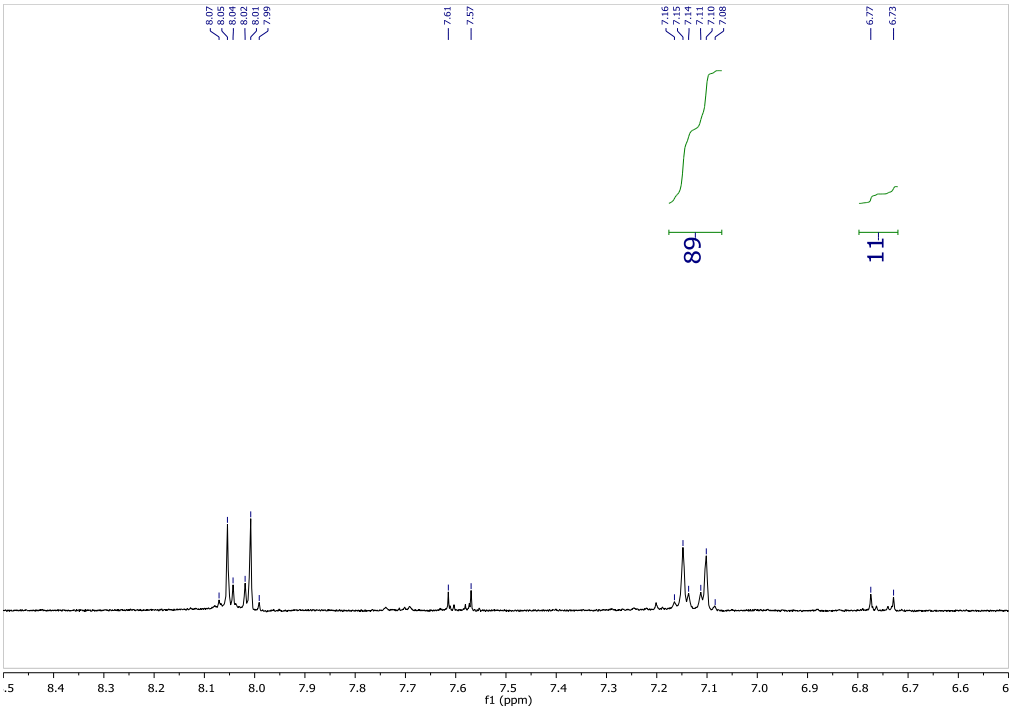


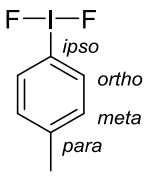
Figure S45: Zoom [8.5 to 6.5 ppm] of the ^{1}H NMR (200 MHz, 299 K, d_3-CH_3CN) of the reaction mixture (table 2, entry 8) after 6 h.

V. Reaction of 4-iodotoluene and Selectfluor® monitored by NMR

Comment: the line width of the resonances of the appearing intermediate depend on the concentration of the reaction (see Figure S47). Therefore we select the following procedure for our NMR study:

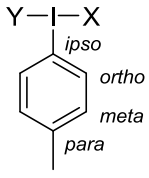
4-Iodotoluene (44 mg, 0.2 mmol, 1 eq.), Selectfluor® (71 mg, 0.2 mmol, 1 eq.) and CH_3CN (5 mL) were added in a Schlenk tube. After the reaction mixture was prodected from light by using in aluminum foil and stirred at ambient temperature for 4h, the formed yellow solution was dried in vacuo. Then the yellow residue was dissolved in d_3-CH_3CN (1 mL) and the mixture was characterized by NMR experiments.

[Comment: a mixture of compound **1** (ca. 13 mol%), compound **2** (ca. 9 mol%), intermediate [int1] (ca. 26 mol%), Selectfluor® (ca. 18 mol%), and intermediate [int2] (ca. 34 mol%) was observed]



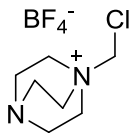
2

δ^{19}F: -174.7
δ^{1}H^{ortho}: 7.92 (m, 2H)
δ^{1}H^{meta}: 7.44 (m, 2H)
δ^{1}H(Me): 2.45 (s, 3H)
δ^{13}C^{ipso}: 122.9 (t, J_{FC} = 12.0 Hz)
δ^{13}C^{ortho}: 132.3 (t, J_{FC} = 2.6 Hz)
δ^{13}C^{meta}: 132.9
δ^{13}C^{para}: 143.9 (t, J_{FC} ~ 1Hz)
δ^{13}C(Me): 21.3



[int1]

δ^{1}H^{ortho}: 7.70 (m, 2H)
δ^{1}H^{meta}: 7.20 (m, 2H)
δ^{1}H(Me): 2.40 (s, 3H)
δ^{13}C^{ipso}: 119.8 (br)
δ^{13}C^{ortho}: 135.7
δ^{13}C^{meta}: 133.2
δ^{13}C^{para}: 145.7 (br)
δ^{13}C(Me): 21.7



[int2]

δ^{1}H(CH_2N): 3.49 (m, 6H)
δ^{1}H(CH_2N^+): 3.67 (m, 6H)
δ^{1}H(CH_2Cl): 5.10 (s, 2H)
δ^{13}C(CH_2N): 45.4
δ^{13}C(CH_2N^+): 51.5
δ^{13}C(CH_2Cl): 69.8

Figure S46: The given assignment was supported by 1D and 2D NMR experiments for this reaction mixture.

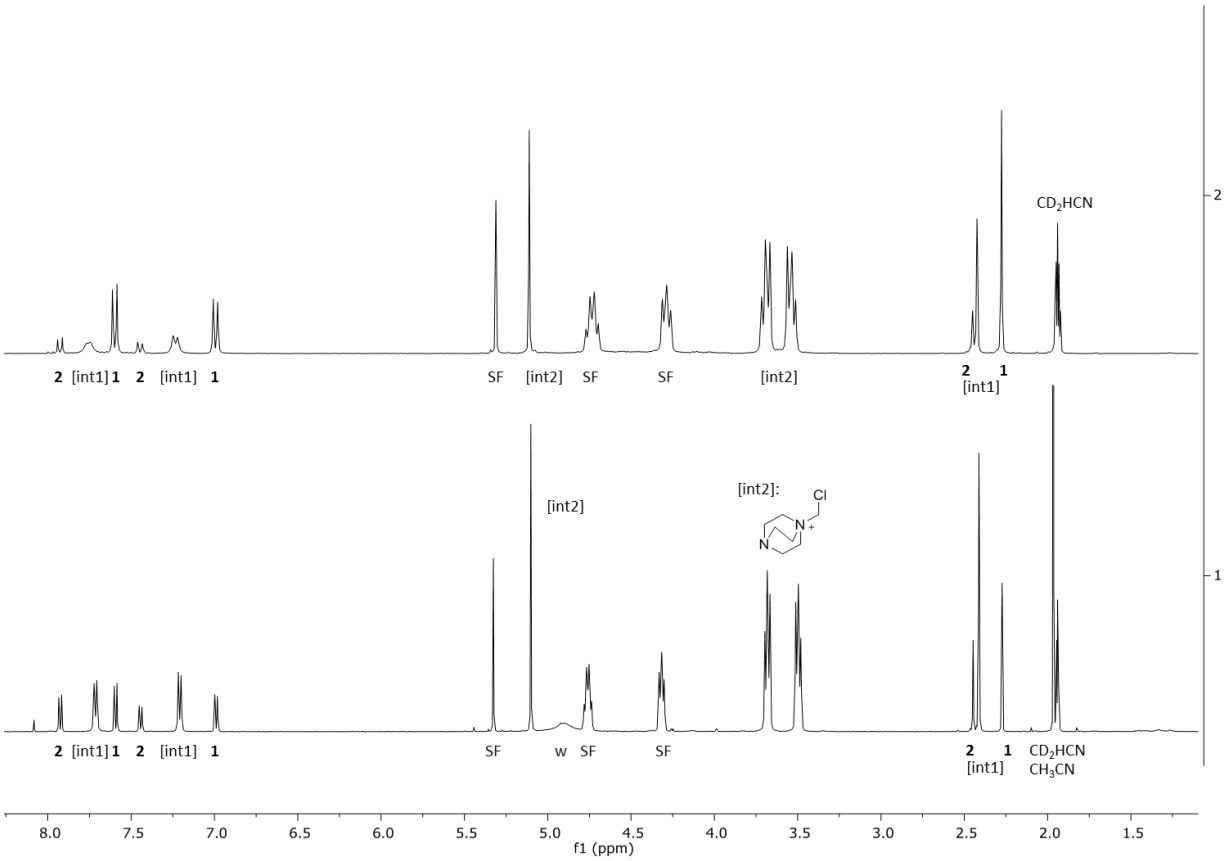


Figure S47: 1) ^{1}H NMR (600 MHz, 299 K, d_3-CH_3CN) of the reaction mixture with a concentration of 200 mM of compound **1** (see experimental part of chapter 5; page S28). 2) ^{1}H NMR (300 MHz, 299 K, d_3-CH_3CN) of the reaction mixture with a concentration 40 mM.

.

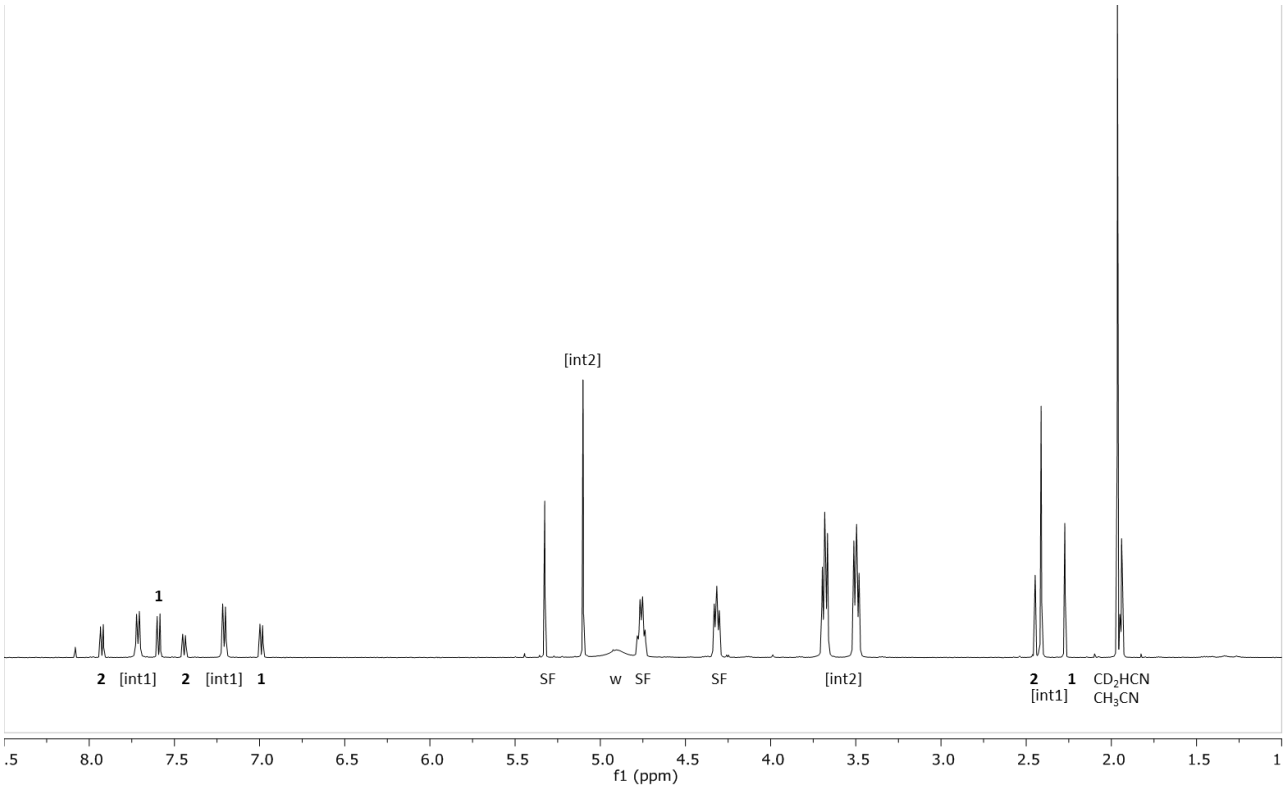


Figure S48: ^{1}H NMR (600 MHz, 299 K, d_3-CH_3CN) spectrum of the obtained mixture.

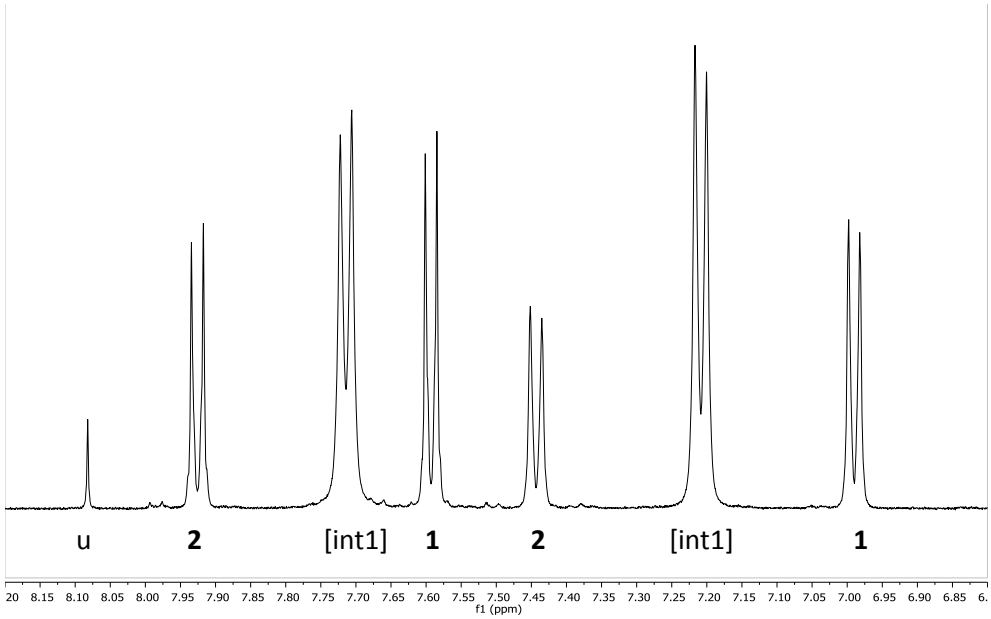


Figure S49: Zoom [8.2 ppm to 6.8 ppm] of the ^{1}H NMR (600 MHz, 299 K, d_3-CH_3CN) spectrum of the obtained mixture.

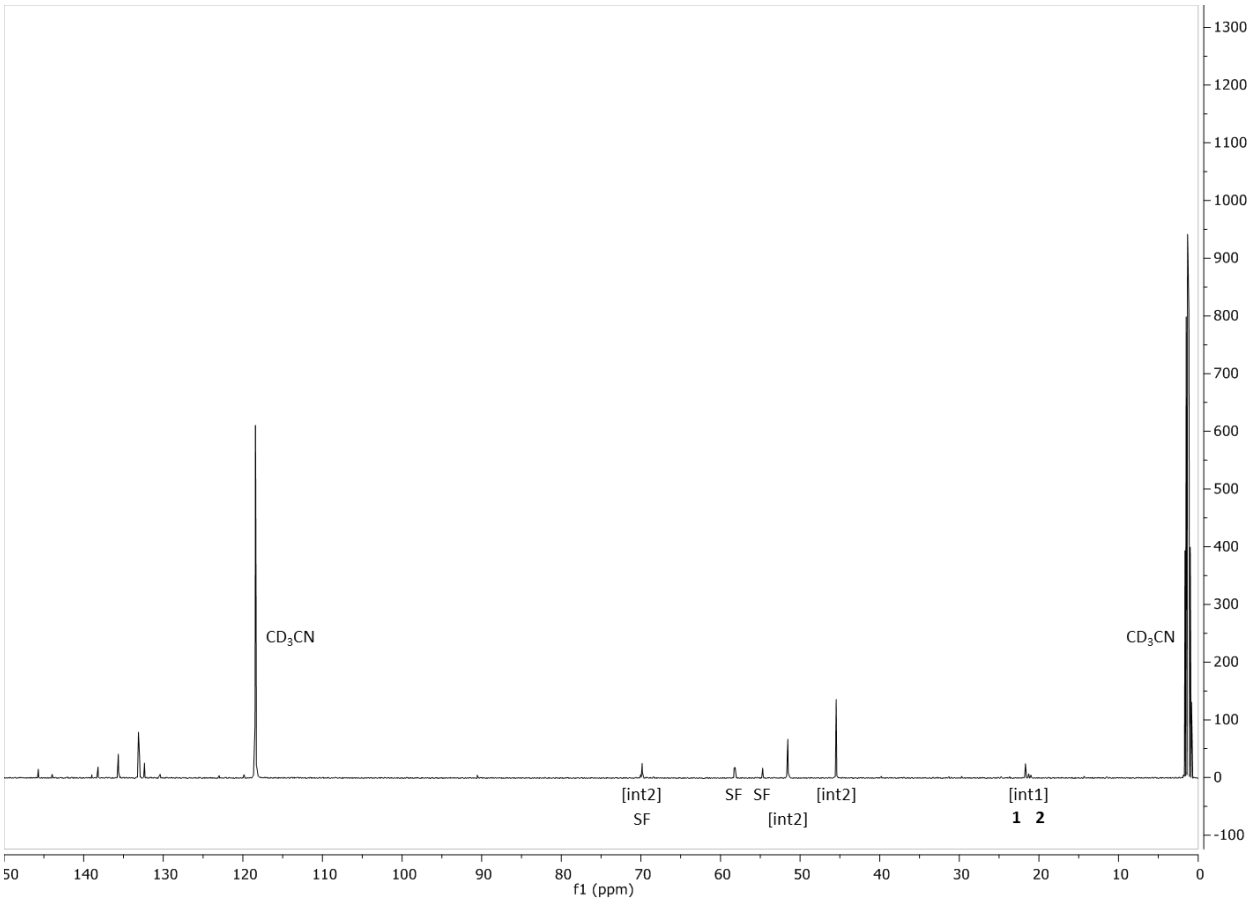


Figure S50: $^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, d_3-CH_3CN) spectrum of the obtained mixture.

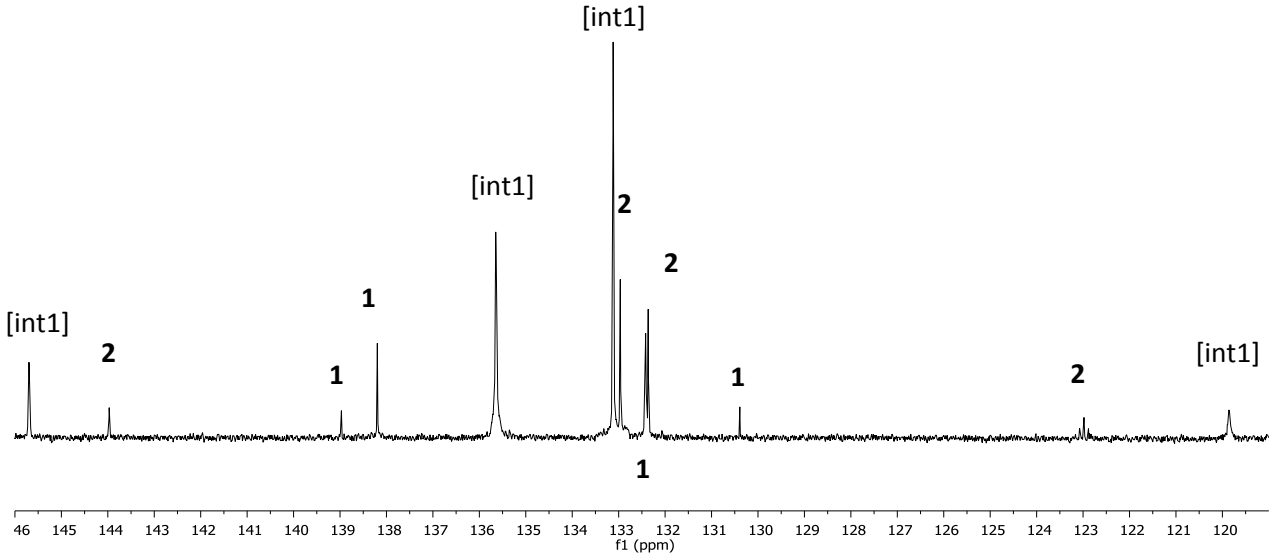


Figure S51: Zoom [146 ppm to 119 ppm] of $^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, d_3-CH_3CN) spectrum of the obtained mixture.

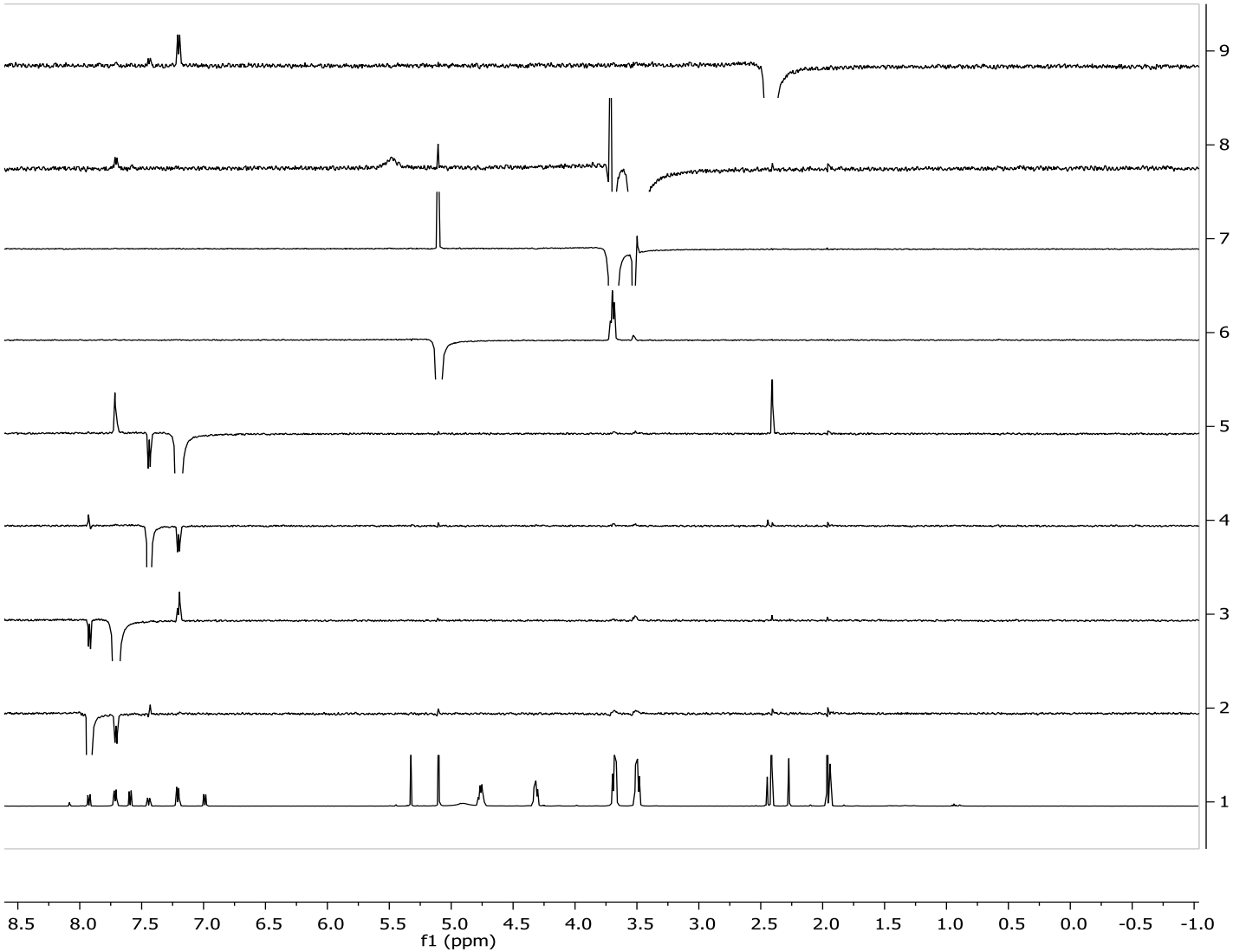


Figure S52: 1) ^{1}H NMR (600 MHz, 299 K, d_3-CH_3CN) spectrum of the obtained mixture and 2 to 9) ^{1}H{^{1}H} NOEDIF (600 MHz, 299 K, d_3-CH_3CN) experiments.

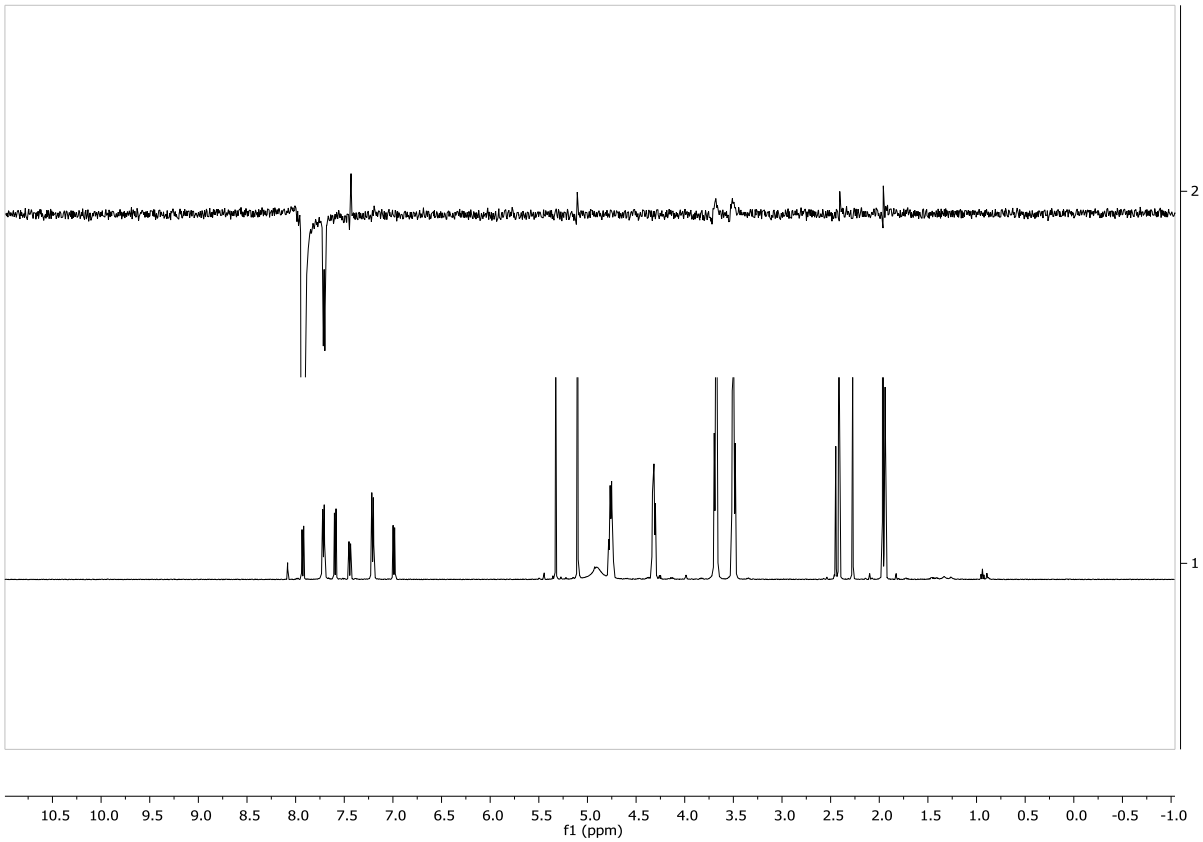


Figure S53: 1) ^{1}H NMR (600 MHz, 299 K, d_3-CH_3CN) spectrum of the obtained mixture and 2) $^{1}H\{^{1}H\}$ NOEDIF (600MHz, 299K, d_3-CH_3CN) experiment: $\delta^{1}H_{irr}/\delta^{1}H_{res}$: 7.92 / 7.70(-), 7.44(+), 5.10(+), 3.67(+), 3.49(+), 2.40(+) (*o-Tol(**2**)/ o-Tol([int1]), m-Tol(**2**), CH_2Cl([int2]), CH_2N([int2]), CH_2N^+([int2]), Me([int1])).*

[Comment: +/- denoted the phase of the 'response': - in phase with the irradiated resonance, + anti phase with the irradiated resonance]

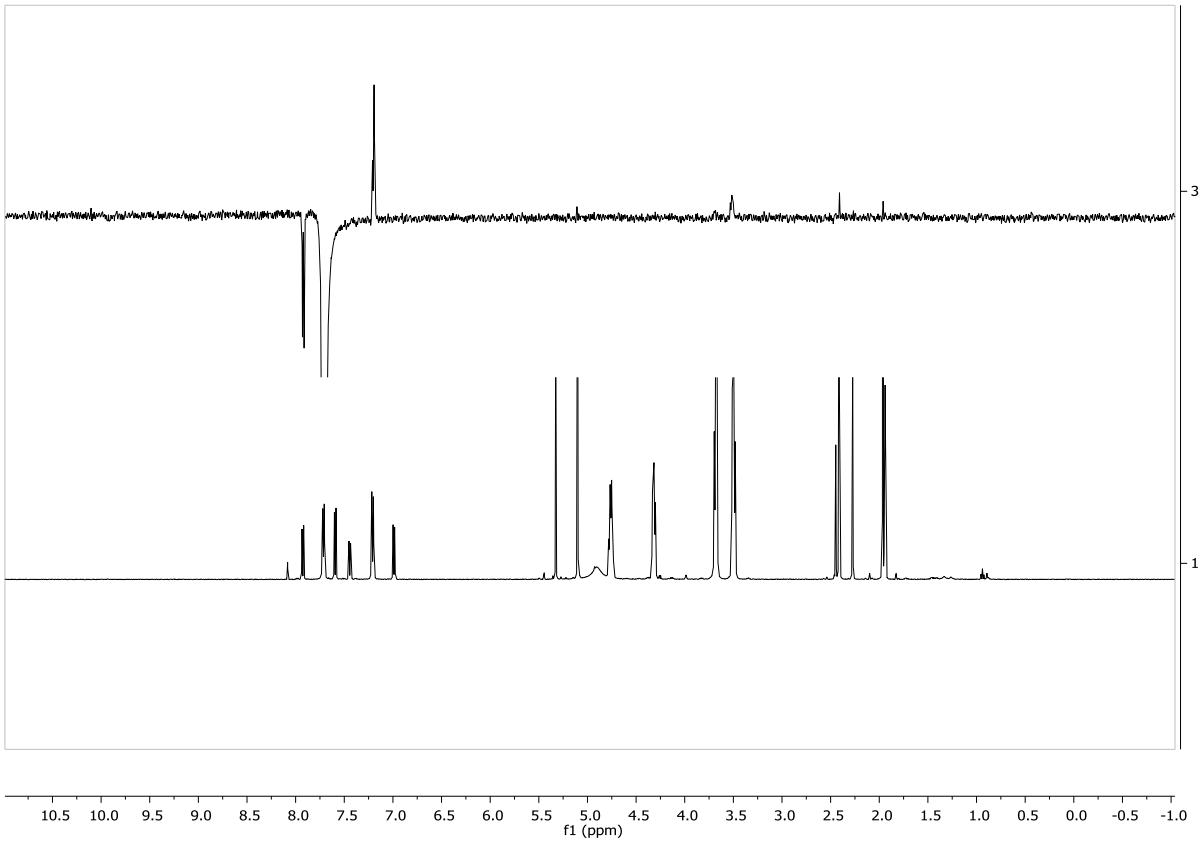


Figure S54: 1) ^{1}H NMR (600 MHz, 299 K, d_3-CH_3CN) spectrum of the obtained mixture and 2) ^{1}H{^{1}H} NOEDIF (600 MHz, 299 K, d_3-CH_3CN) experiment: $\delta^{1}H_{irr}/\delta^{1}H_{res}$: 7.70 / 7.92(-), 7.20(+), 5.10(+), 3.49(+), 2.40(+) (*o-Tol([int1]/ o-Tol(**2**), m-Tol([int1]*, *CH_2Cl([int2]), CH_2N([int2]), Me([int1])).*
[Comment: +/- denoted the phase of the 'response': - in phase with the irradiated resonance, + anti phase with the irradiated resonance]

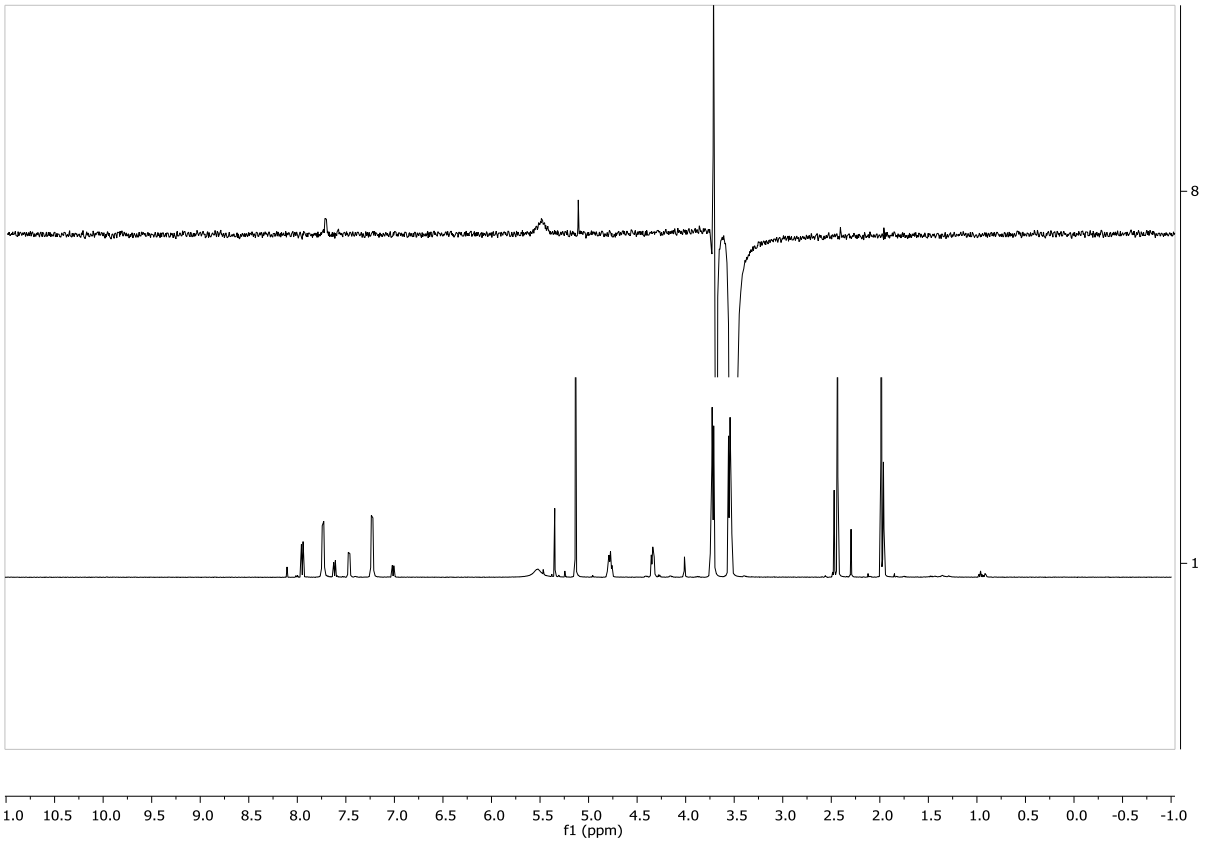


Figure S55: 1) ^{1}H NMR (600 MHz, 299 K, d_3-CH_3CN) spectrum of the obtained mixture and 2) ^{1}H{^{1}H} NOEDIF (600 MHz, 299 K, d_3-CH_3CN) experiment: $\delta^{1}H_{irr}/\delta^{1}H_{res}$: 3.49 / 7.70(+), 5.49(+), 5.10(+), 3.67(-) (*CH_2N([int2])/o-Tol([int1]), water (tentative assignment), CH_2Cl([int2]), CH_2N^+([int2])*).
[Comment: +/- denoted the phase of the 'response': - in phase with the irradiated resonance, + anti phase with the irradiated resonance]

VI. Calculation of [HF] in $Et_3N{\cdot}3HF$:

In 1 mol of $Et_3N{\cdot}3HF$, there is:

25% of Et_3N → 0.250 mol
75% of HF → 0.750 mol

$\delta(Et_3N{\cdot}3HF)$= 0.989 g/mL; $M(Et_3N)$= 101.19 g/mol; M(HF)= 20.01 g/mol.

So,

$m(Et_3N)$ = 0.250 x 101.19
$m(Et_3N)$ = 25.30 g

m(HF) = 0.750x20.01
m(HF) = 15 g

m(total) = 40.30 g
V(total) = 40.75 mL

In conclusion,
[HF]= 0.750/ 0.04075
[HF] = 18.4 mol/L

Or,

For 1 mol of $Et_3N{\cdot}3HF$,

$\delta(Et_3N{\cdot}3HF)$= 0.989 g/mL; $M(Et_3N{\cdot}3HF)$ = 161.21 g/mol

$m(Et_3N{\cdot}3HF)$ = 161.21 g
$V(Et_3N{\cdot}3HF)$ = 163.00 mL

$[Et_3N{\cdot}3HF]$ = 1/ 0.163
$[Et_3N{\cdot}3HF]$ = 6.13 mol/L

In conclusion,
[HF] = 3x$[Et_3N{\cdot}3HF]$ = 3x6.13
[HF] = 18.4 mol/L

VII. X-ray diffraction

X-Ray diffraction: Data sets were collected with a D8 Venture Dual Source 100 CMOS diffractometer. Programs used: data collection: APEX3 V2016.1-0 (Bruker AXS Inc., **2016**); cell refinement: SAINT V8.37A (Bruker AXS Inc., **2015**); data reduction: SAINT V8.37A (Bruker AXS Inc., **2015**); absorption correction, SADABS V2014/7 (Bruker AXS Inc., **2014**); structure solution SHELXT-2015 (Sheldrick, **2015**); structure refinement SHELXL-2015 (Sheldrick, **2015**) and graphics XP (Bruker AXS Inc., **1998**). *R*-values are given for observed reflections, and wR^2 values are given for all reflections.

X-ray crystal structure analysis of *p*-TolI(III)F_2: A colorless needle-like specimen of $C_7H_7F_2I$, approximate dimensions 0.072 mm x 0.073 mm x 0.249 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 246 frames were collected. The total exposure time was 1.37 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 12280 reflections to a maximum θ angle of 27.50° (0.77 Å resolution), of which 3384 were independent (average redundancy 3.629, completeness = 99.6%, R_{int} = 3.54%, R_{sig} = 3.49%) and 3134 (92.61%) were greater than $2\sigma(F^2)$. The final cell constants of a = 17.9542(8) Å, b = 11.5049(5) Å, c = 7.3428(3) Å, volume = 1516.74(11) $Å^3$, are based upon the refinement of the XYZ-centroids of 7847 reflections above 20 σ(I) with 4.537° < 2θ < 54.96°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.892. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.4230 and 0.7530. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *P*ca2_1, with Z = 8 for the formula unit, $C_7H_7F_2I$. The final anisotropic full-matrix least-squares refinement on F^2 with 184 variables converged at R1 = 1.97%, for the observed data and wR2 = 3.99% for all data. The goodness-of-fit was 1.044. The largest peak in the final difference electron density synthesis was 0.410 $e^-/Å^3$ and the largest hole was -0.551 $e^-/Å^3$ with an RMS deviation of 0.107 $e^-/Å^3$. On the basis of the final model, the calculated density was 2.242 g/cm^3 and F(000), 960 e^-.

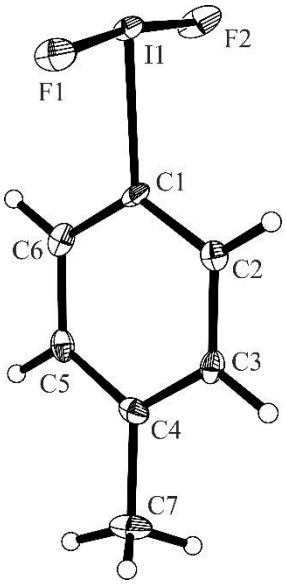
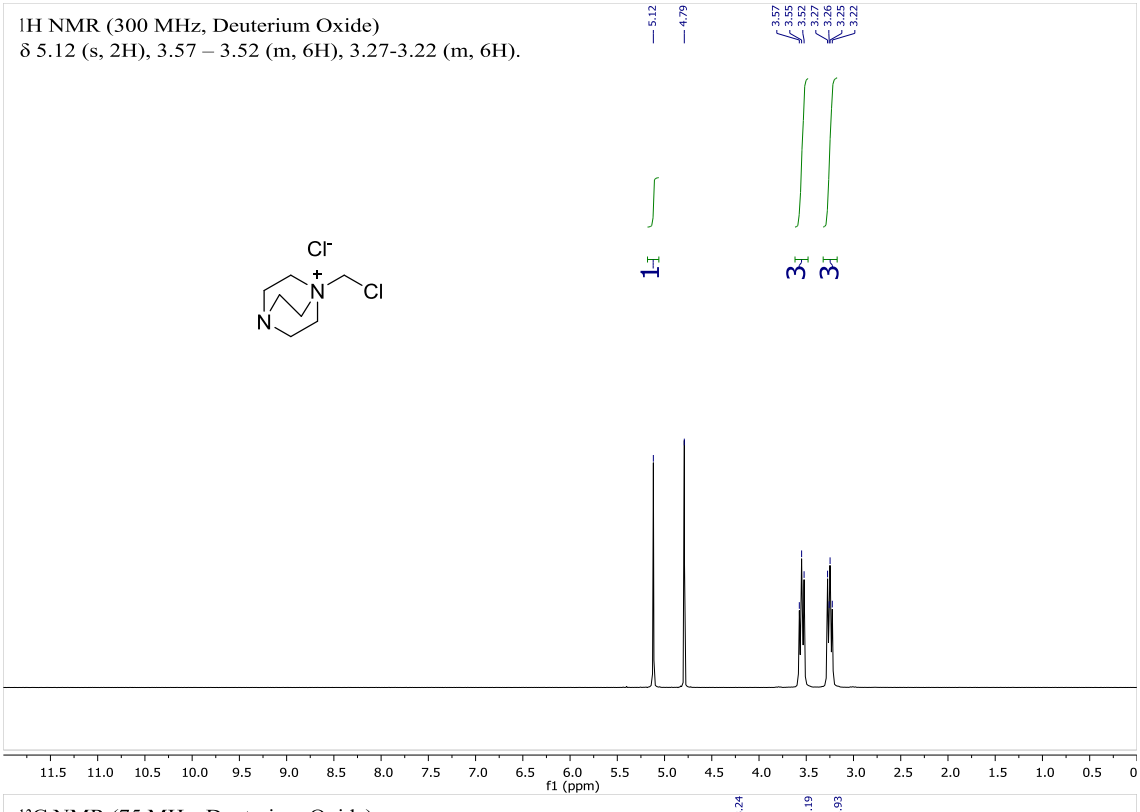


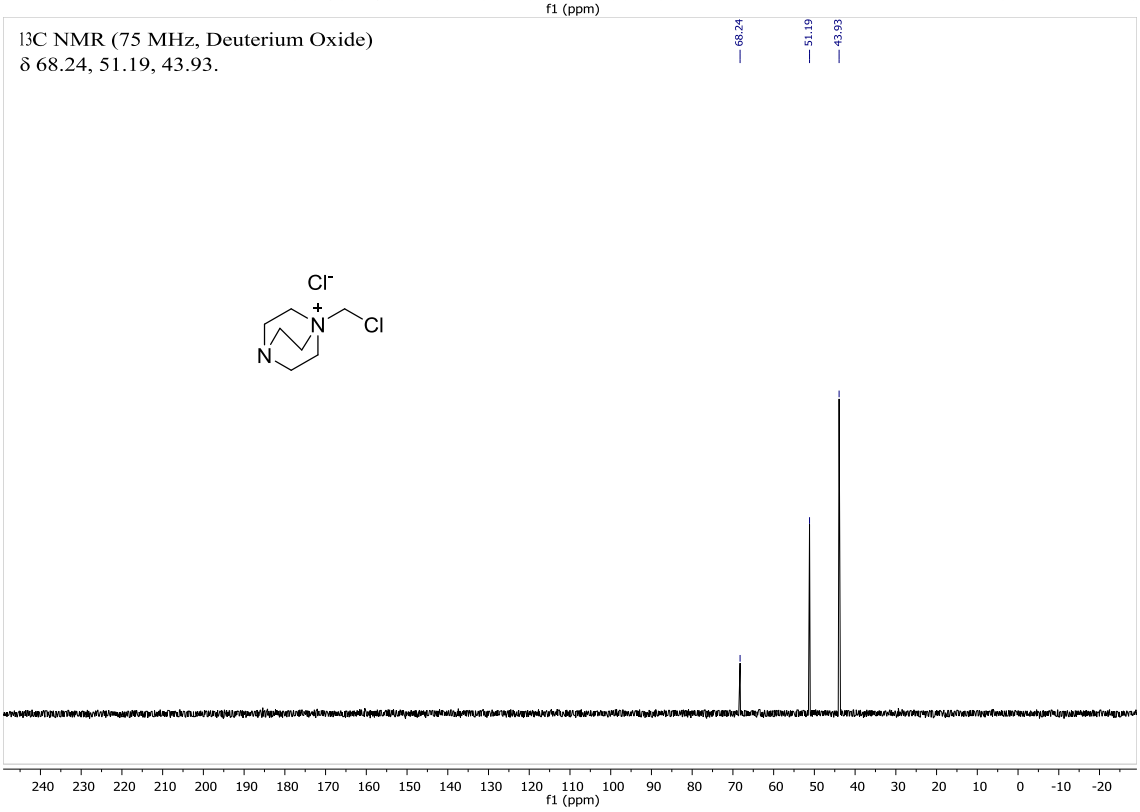
Figure S56: Crystal structure of compound ***p*-TolI(III)F_2**.
Only one molecule of two found in the asymmetric unit is shown.
Thermal ellipsoids are set at 50% probability.

1. *APEX3* (**2016**), *SAINT* (**2015**) and *SADABS* (**2015**), Bruker AXS Inc., Madison, Wisconsin, USA.
2. *SHELX* software: Sheldrick, G. M. *Acta Cryst.,* **2015**, *A71*, 3-8.
3. *XP – Interactive molecular graphics, Version 5.1,* Bruker AXS Inc., Madison, Wisconsin, USA, **1998**.

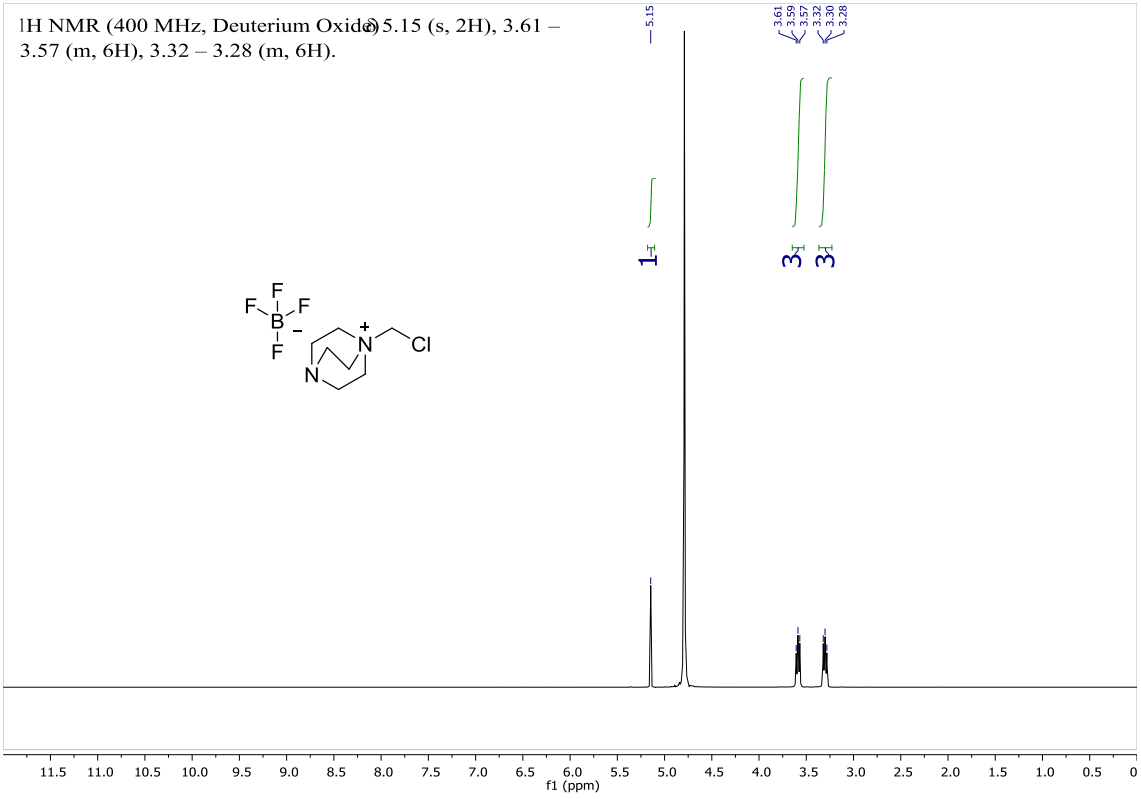
VIII. NMR spectra

VIII.1 1-chloromethyl-1,4-diazabicyclo[2.2.2]octan-1-ium chloride (4)[3]

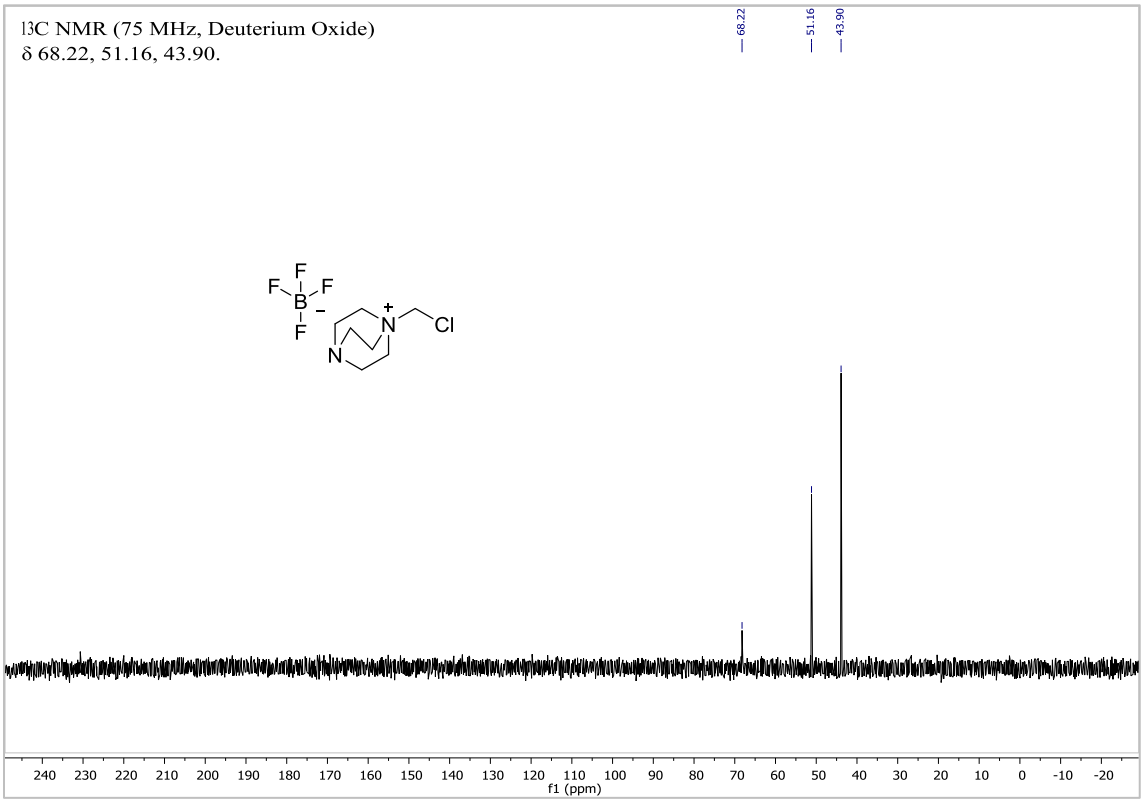




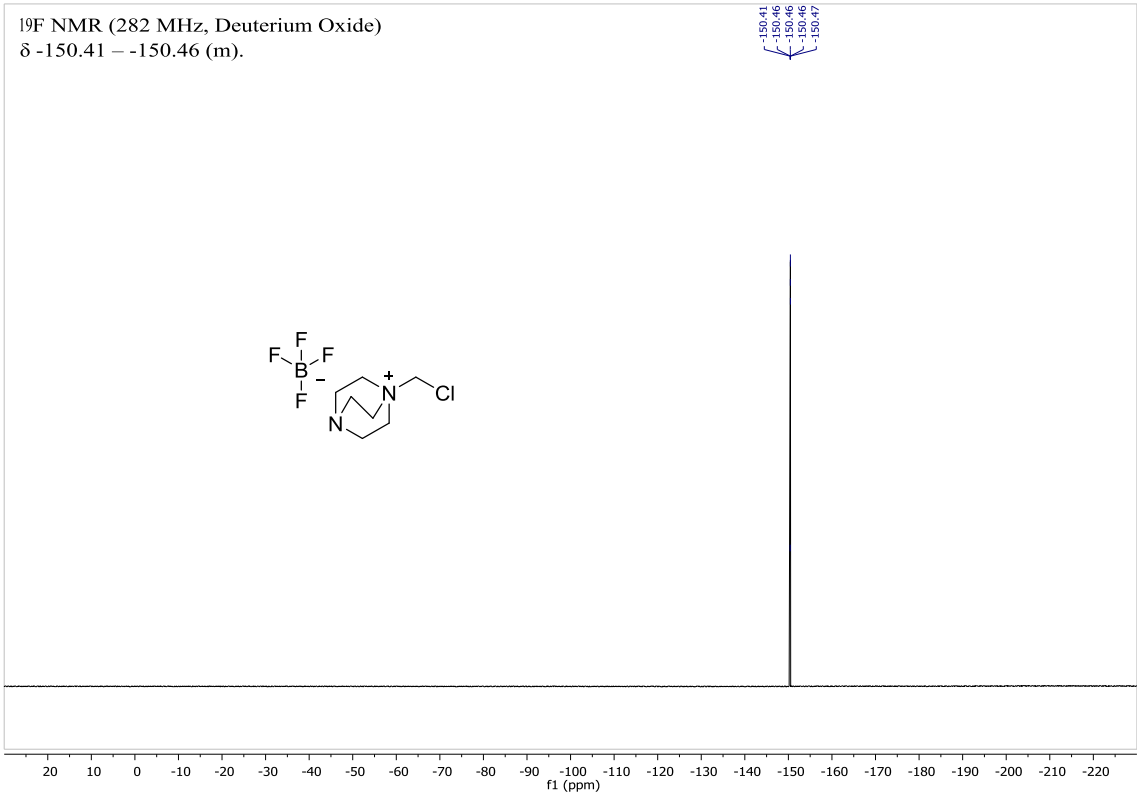
VIII.2 1-chloromethyl-1,4-diazabicyclo[2.2.2]octan-1-ium tetrafluoroborate (3)[3]



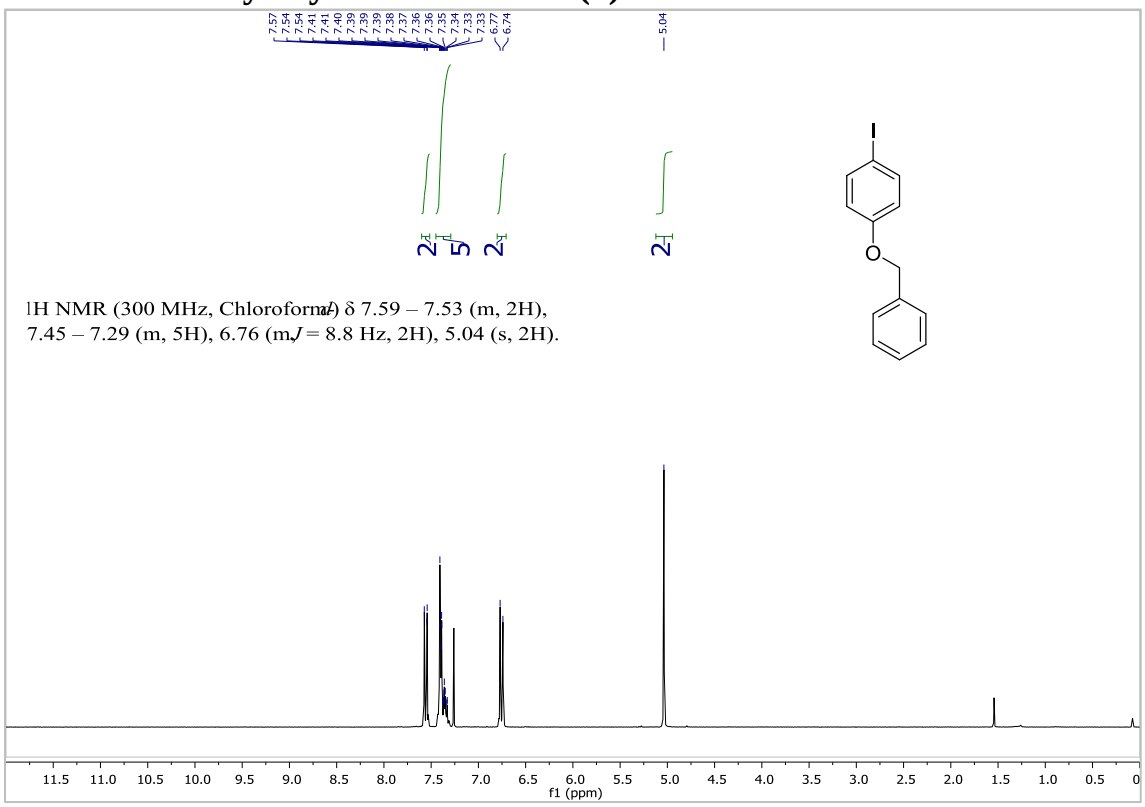
13C NMR (75 MHz, Deuterium Oxide)
δ 68.22, 51.16, 43.90.



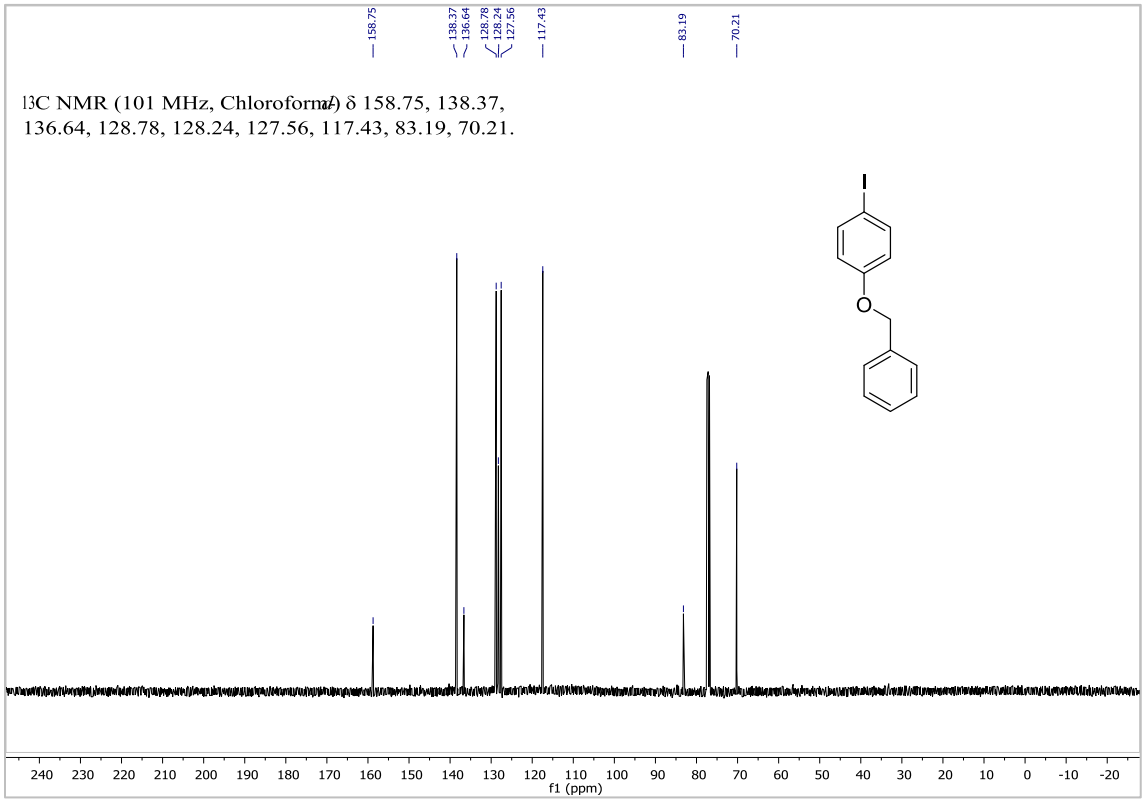
19F NMR (282 MHz, Deuterium Oxide)
δ -150.41 – -150.46 (m).



VIII.3 1-benzyloxy-4-iodobenzene (5)[4]



^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.59 – 7.53 (m, 2H), 7.45 – 7.29 (m, 5H), 6.76 (m, *J* = 8.8 Hz, 2H), 5.04 (s, 2H).

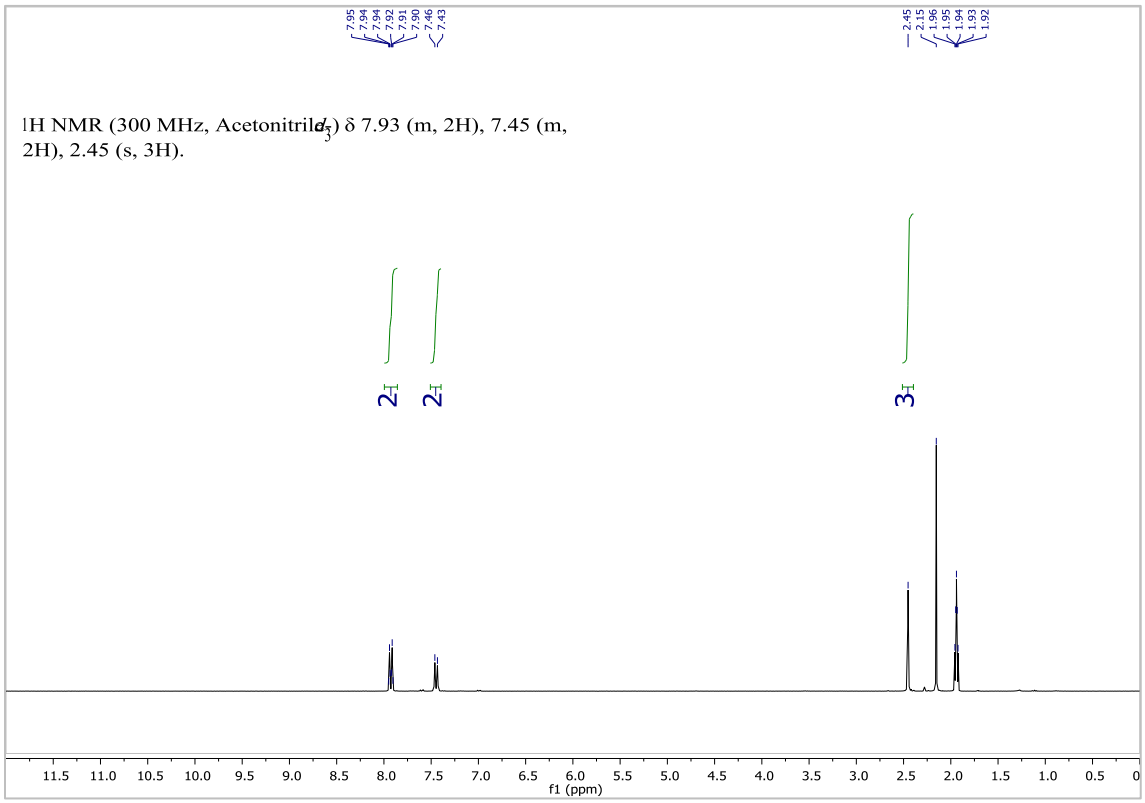


^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.75, 138.37, 136.64, 128.78, 128.24, 127.56, 117.43, 83.19, 70.21.

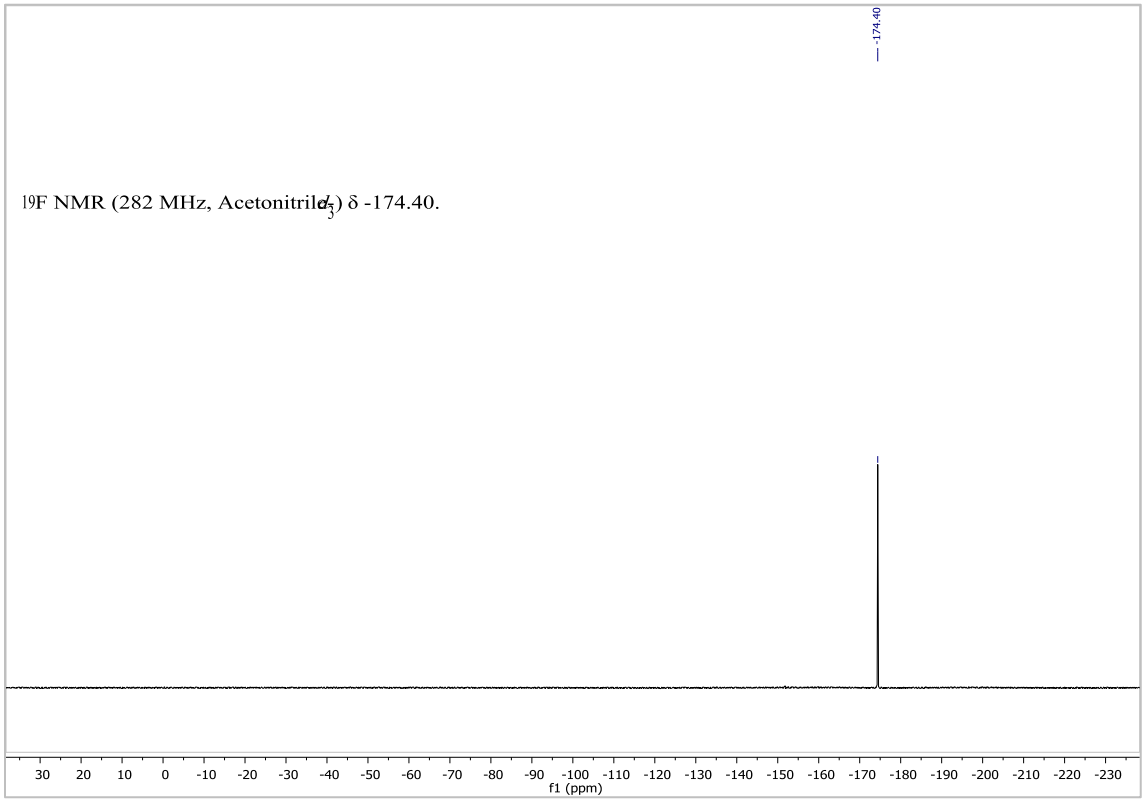
IX. Characterization of $ArIF_2$

IX.1 *p*-$TolIF_2$ (2)[1]

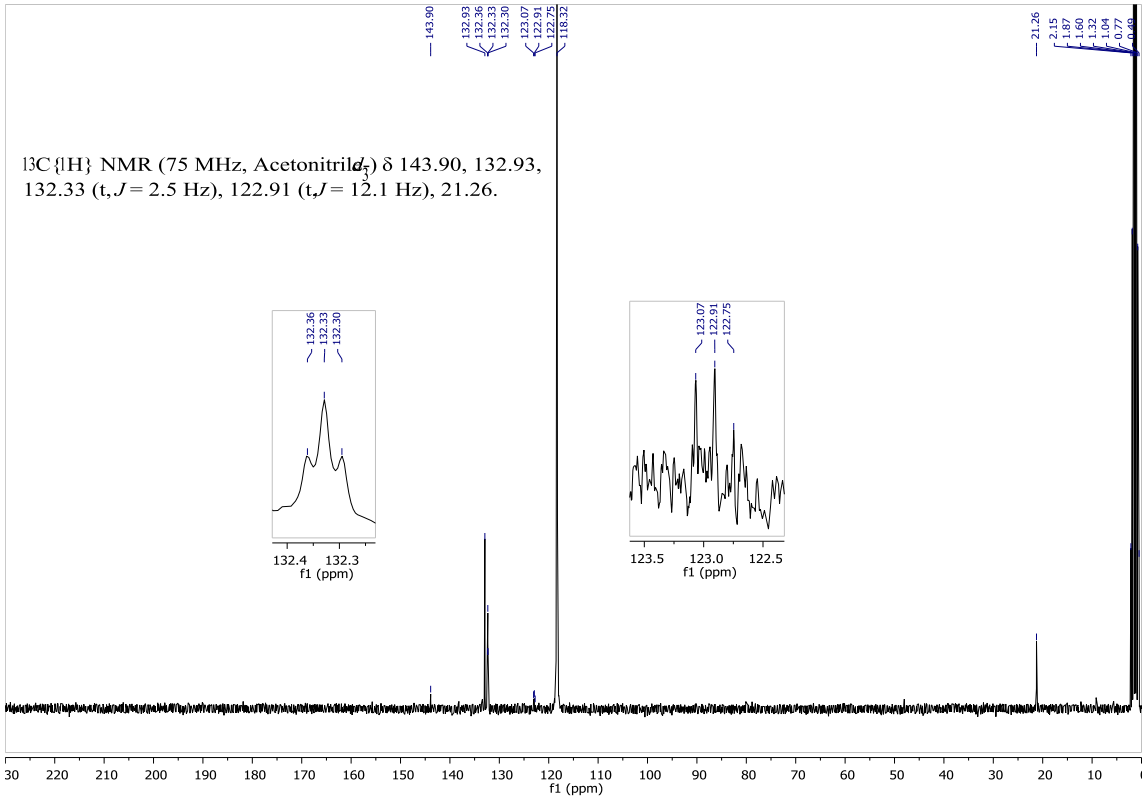
General Procedure 1 (Selectfluor® and CsF)



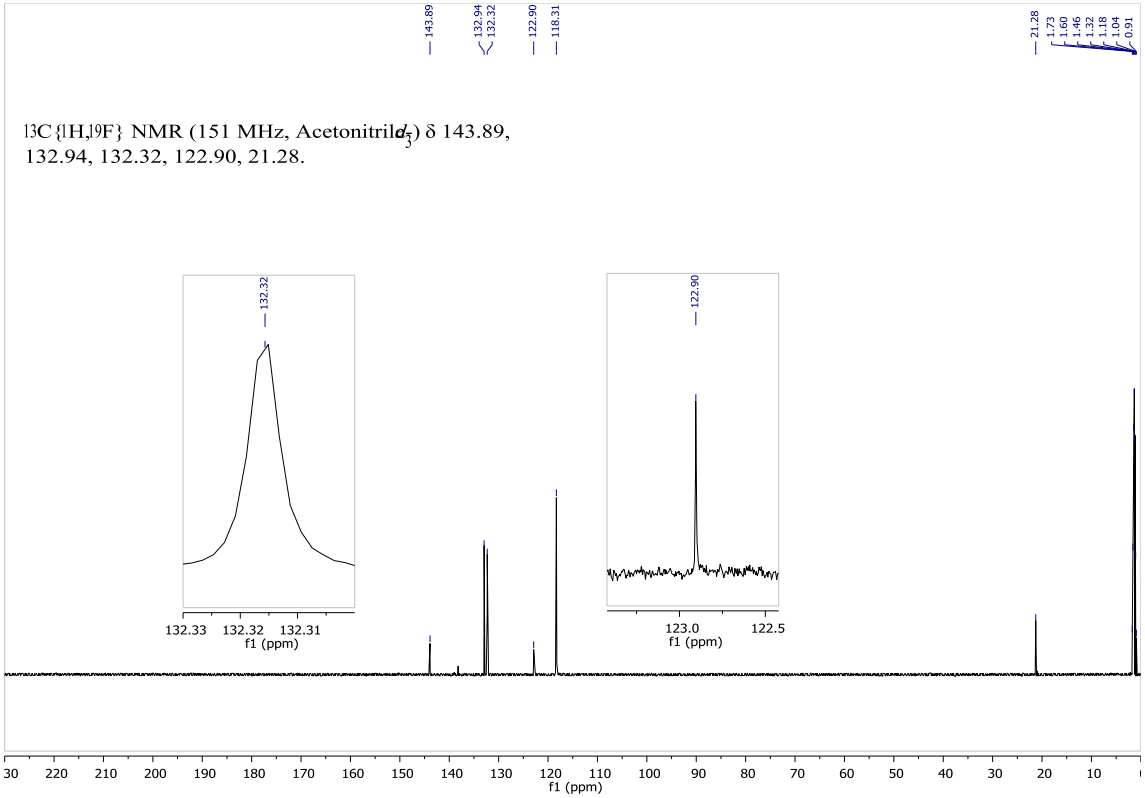
^{1}H NMR (300 MHz, Acetonitrile-d_3) δ 7.93 (m, 2H), 7.45 (m, 2H), 2.45 (s, 3H).



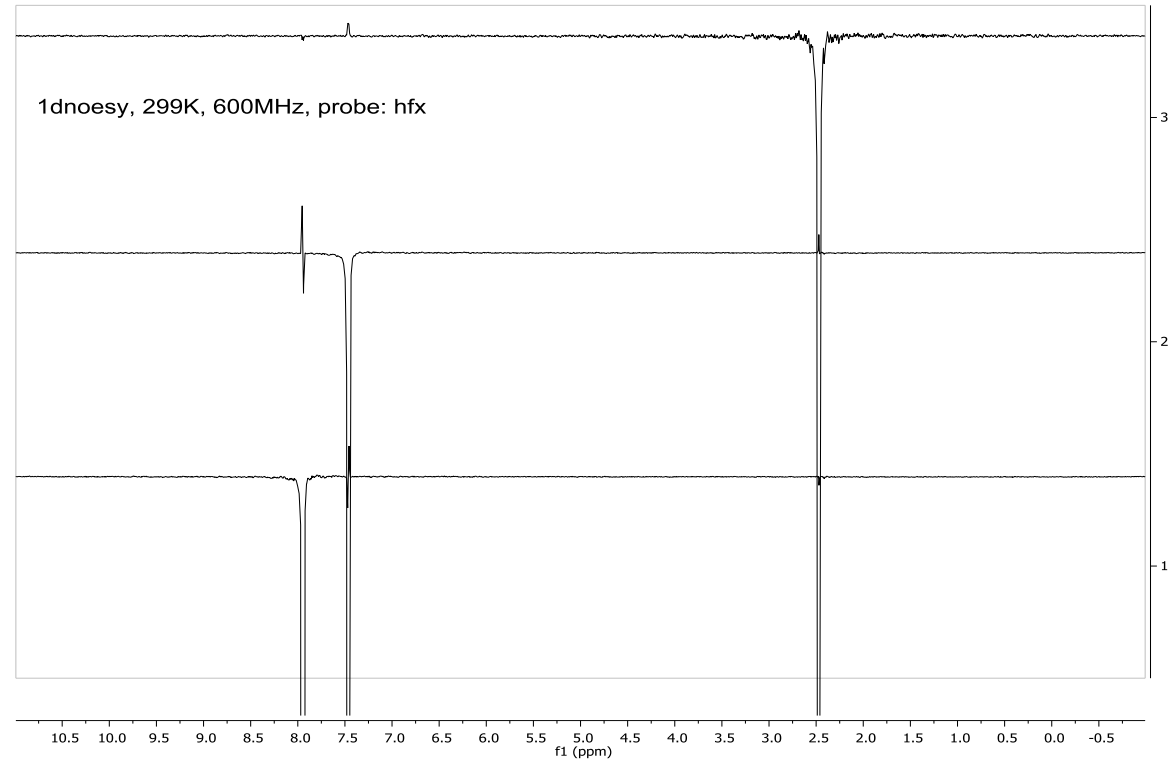
^{19}F NMR (282 MHz, Acetonitrile-d_3) δ -174.40.

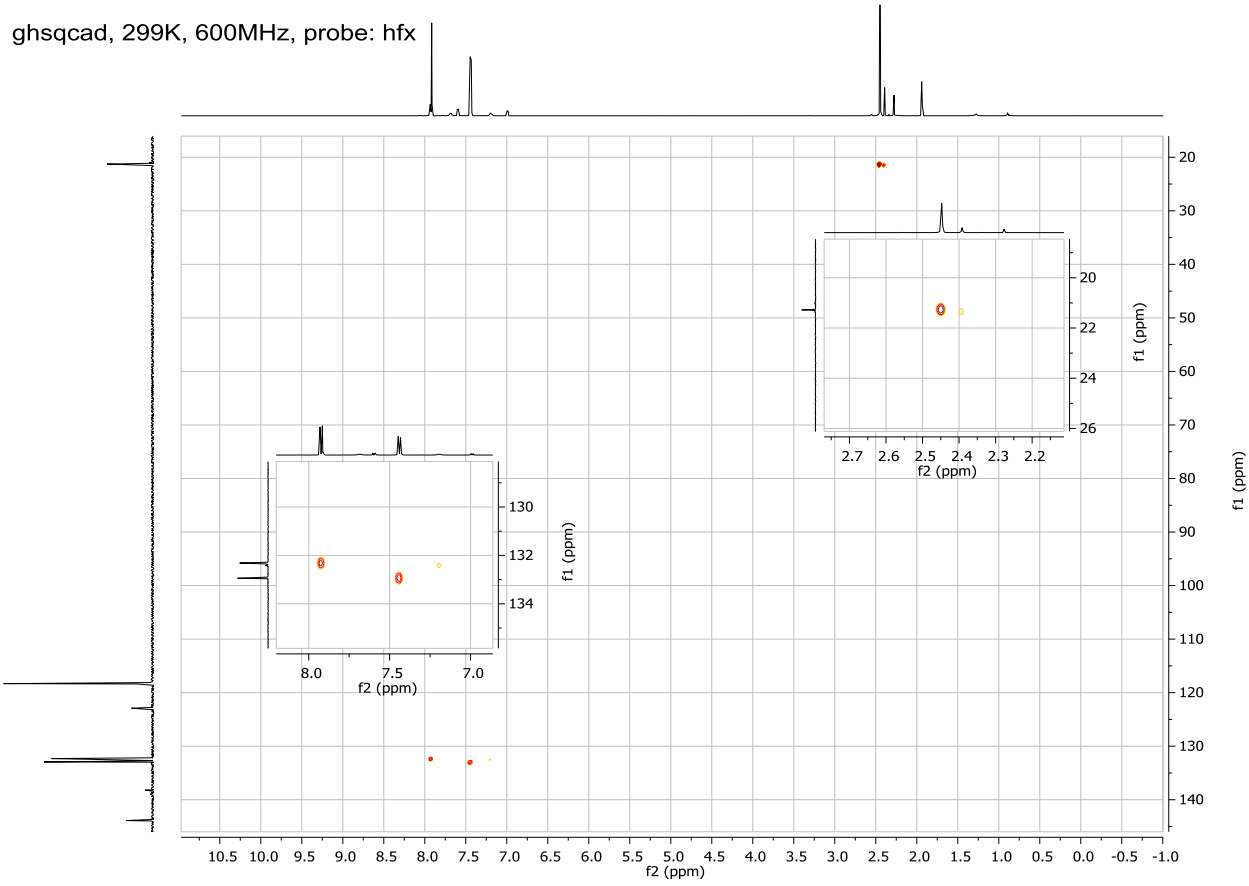


$^{13}C\{^{1}H\}$ NMR (75 MHz, Acetonitrile-d_3) δ 143.90, 132.93, 132.33 (t, J = 2.5 Hz), 122.91 (t, J = 12.1 Hz), 21.26.

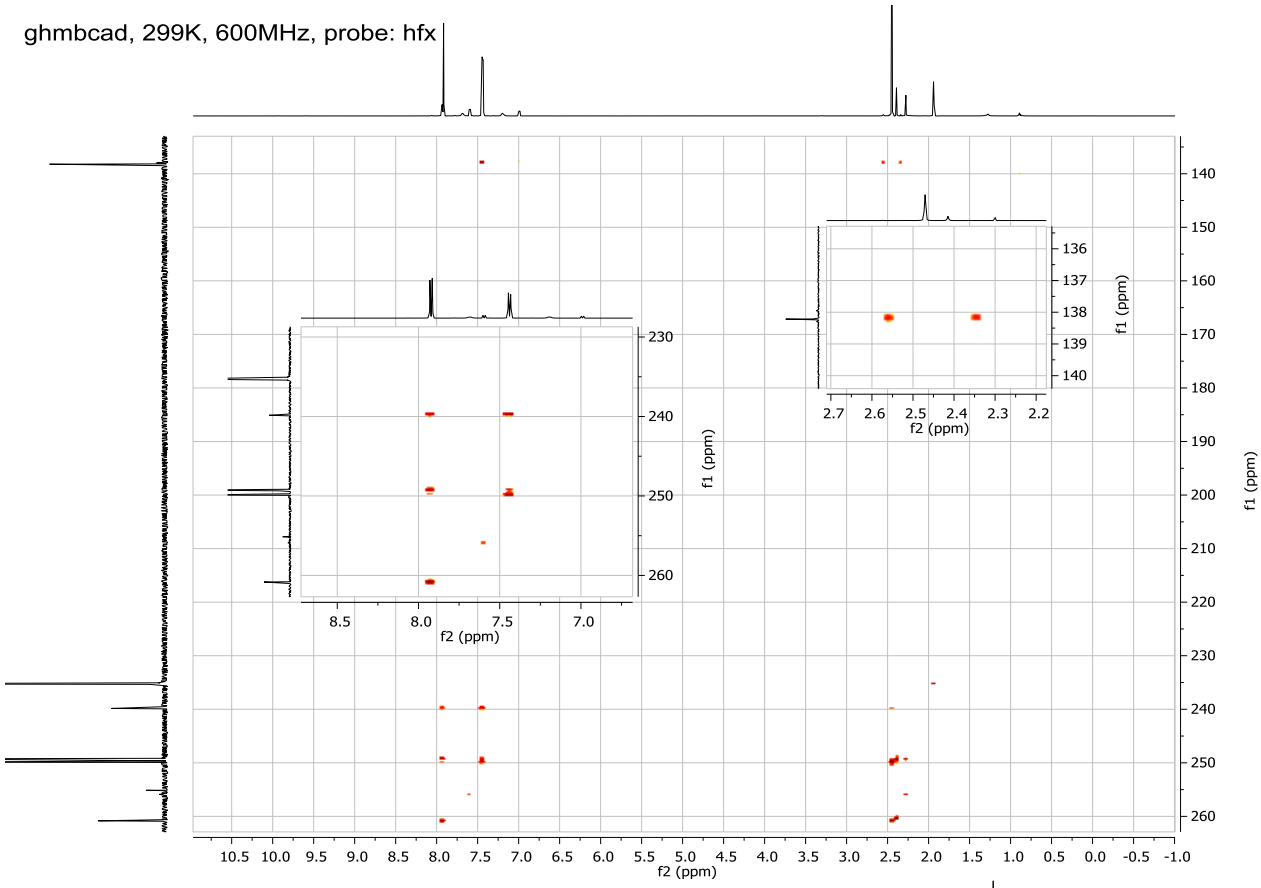


$^{13}C\{^{1}H,^{19}F\}$ NMR (151 MHz, Acetonitrile-d_3) δ 143.89, 132.94, 132.32, 122.90, 21.28.

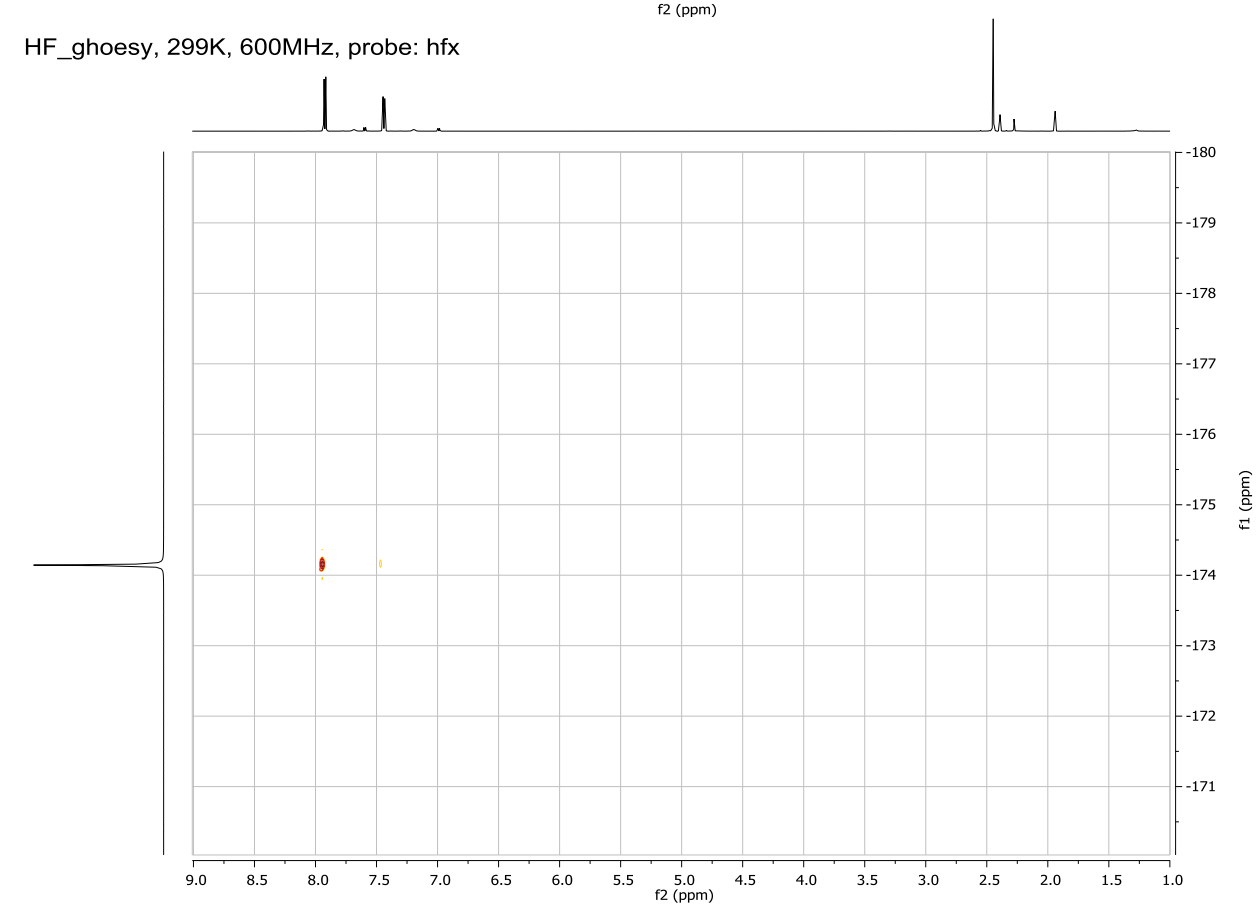

1dnoesy, 299K, 600MHz, probe: hfx
f1 (ppm)

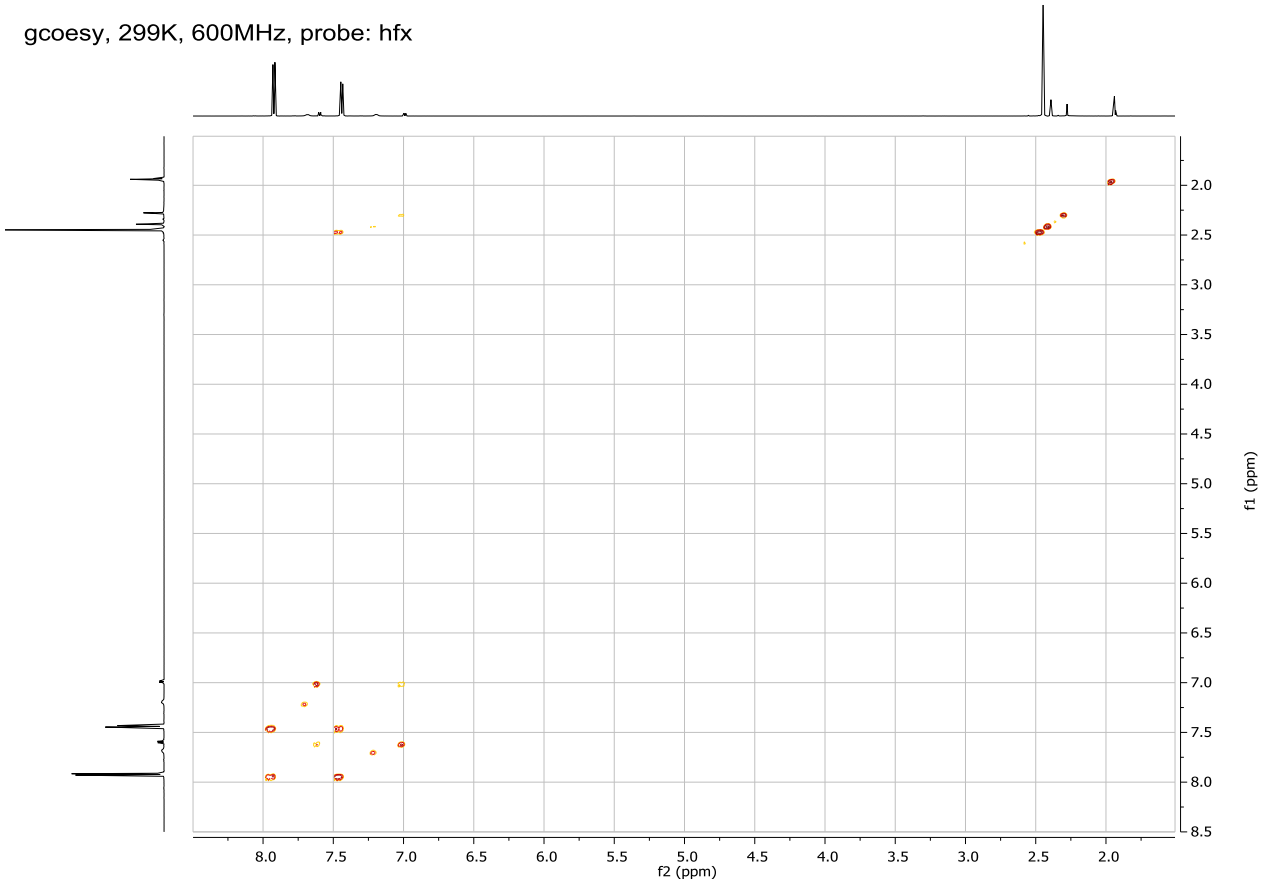

ghsqcad, 299K, 600MHz, probe: hfx
f2 (ppm)
f1 (ppm)

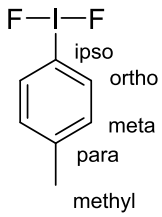
ghmbcad, 299K, 600MHz, probe: hfx



HF_ghoesy, 299K, 600MHz, probe: hfx

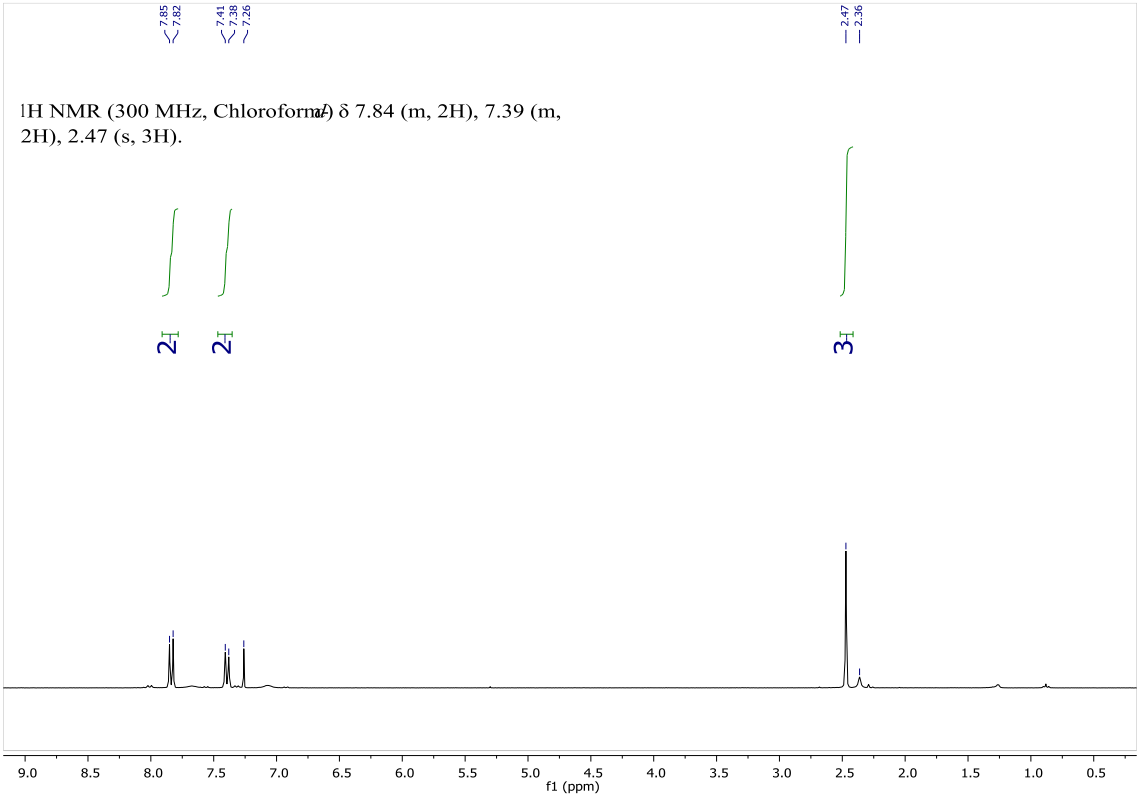




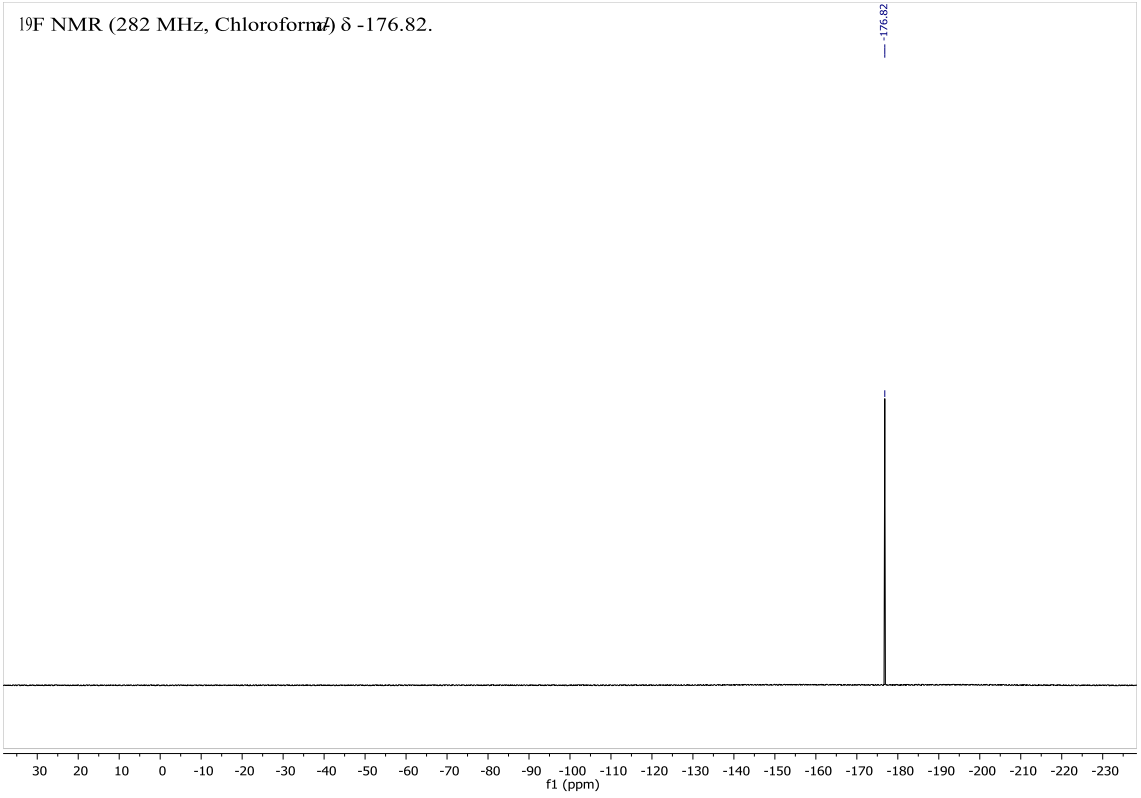


^{19}F: -174.4 ppm, s
$^{1}H^{ortho}$: 7.93 ppm, m
$^{1}H^{meta}$: 7.45 ppm, m
^{1}H(Me): 2.45 ppm, s
$^{13}C^{ipso}$: 122.9 ppm, t, 12.0 Hz
$^{13}C^{ortho}$: 132.3 ppm, t, 2.6 Hz
$^{13}C^{meta}$: 132.9 ppm, bs
$^{13}C^{para}$: 143.9 ppm, t, 1 Hz
^{13}C(Me): 21.3 ppm, s

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.84 (m, 2H), 7.39 (m, 2H), 2.47 (s, 3H).



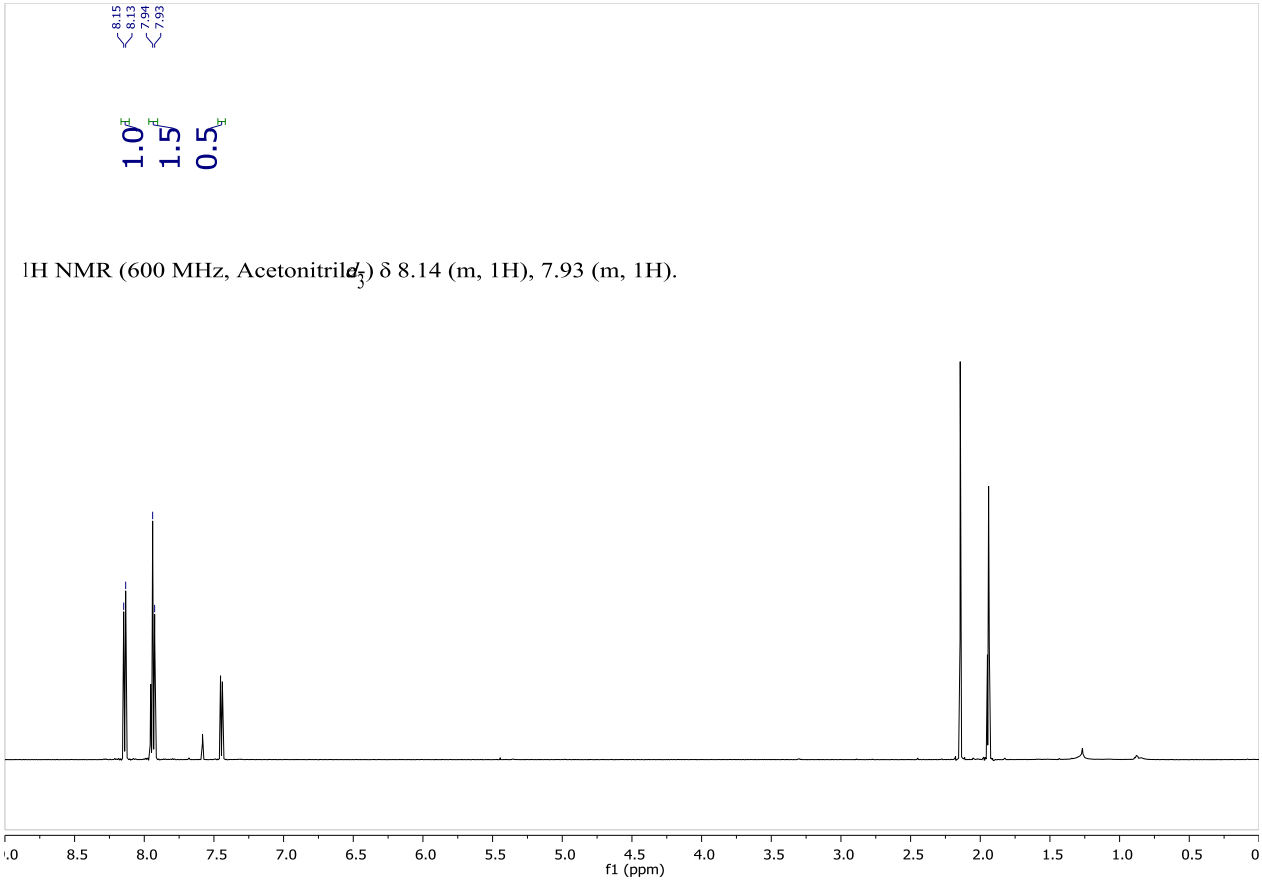
^{19}F NMR (282 MHz, Chloroform-*d*) δ -176.82.

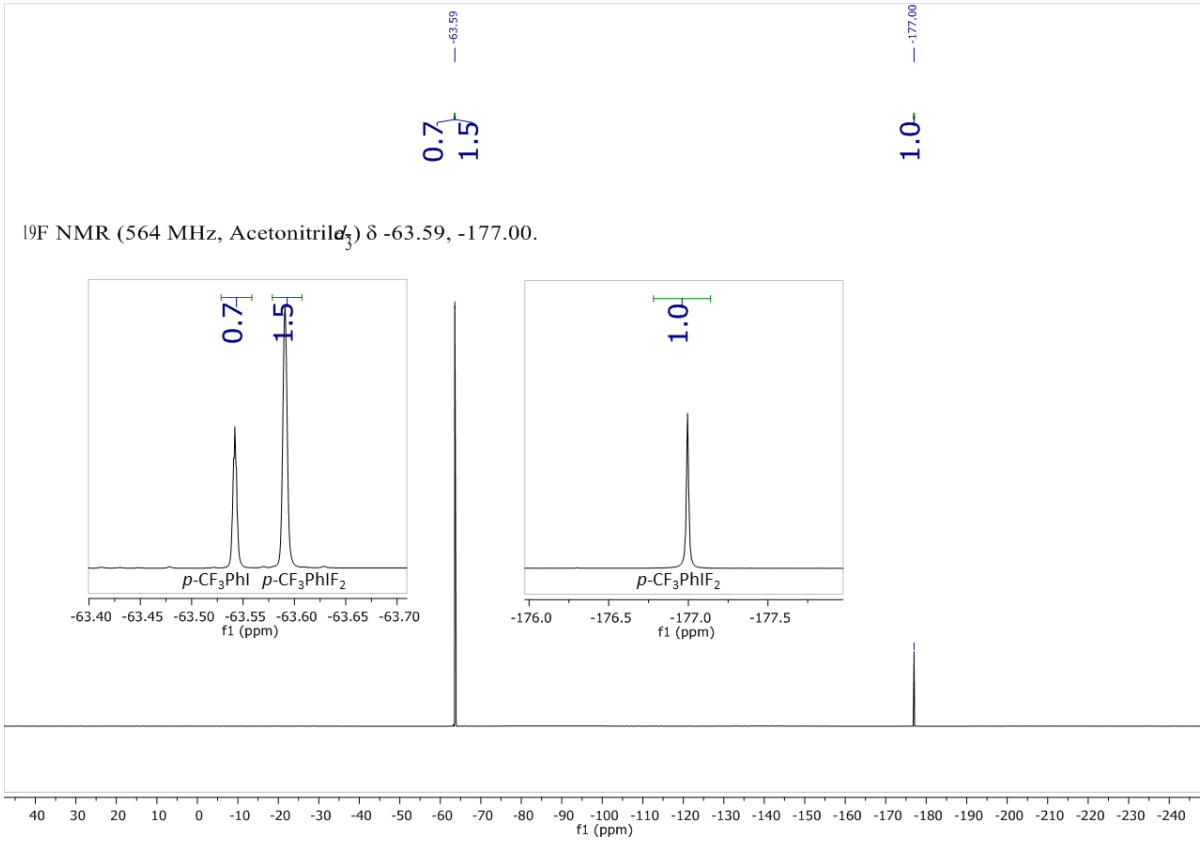


IX.2 *p*-CF_3PhIF_2 (2b) [5]

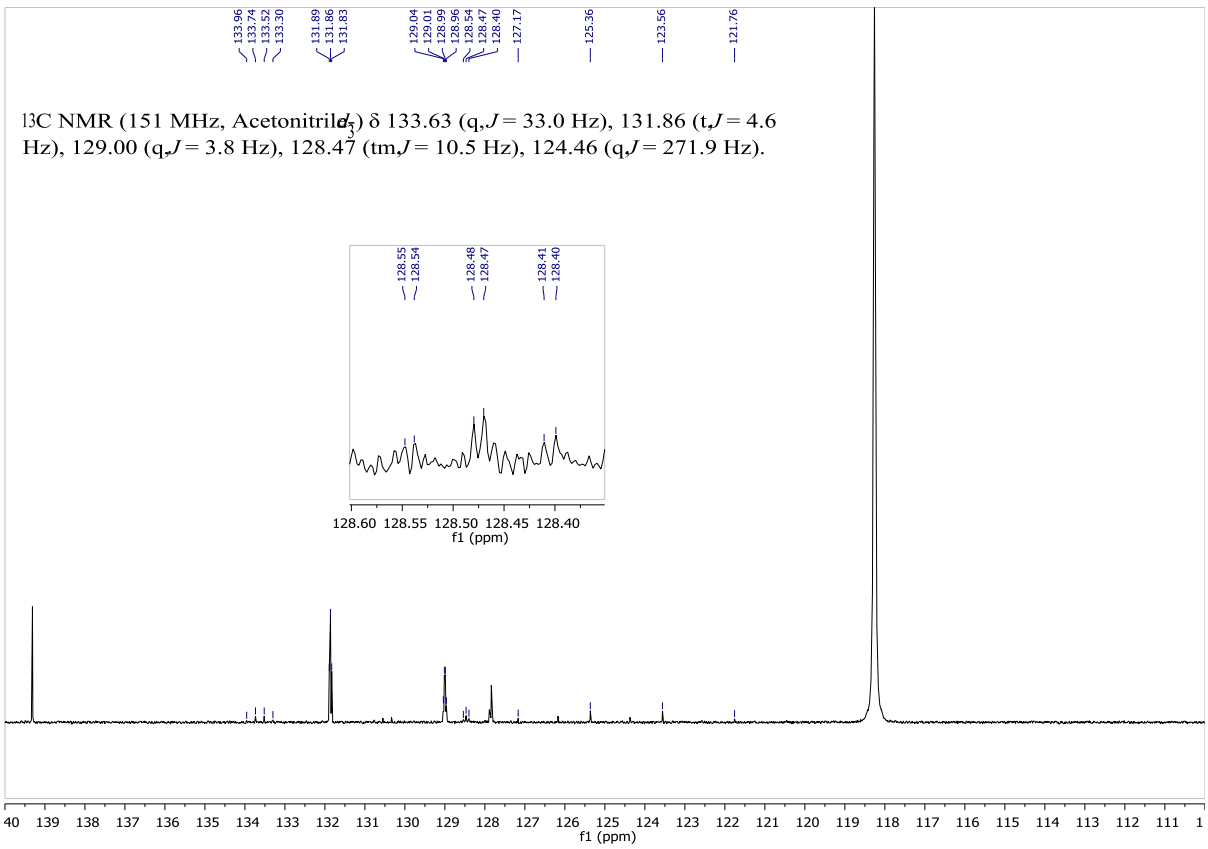
General Procedure 1 using *p*-CF_3PhI (272 mg, 1 mmol), Selectfluor® (1410 mg. 4 mmol, 4 eq.) and CsF (760 mg, 5 mmol, 5 eq.) in dry acetonitrile (previously distilled and stored on 4Å molecular sieves) (25 mL). Reaction time: 48 h.

Conditions for extraction: To the reaction residue was added *n*-hexane (4 mL) to dissolve the product. The organic material was transferred by syringe to a flame-dried Schlenk. The solvent was evaporated to dryness at 0°C (ice bath) to give 34 mg (7%) of a white solid. A solution of the solid in d_3-CH_3CN showed a mixture of starting material and compound 2b (ca. 1:2).





^{19}F NMR (564 MHz, Acetonitrile-d_3) δ -63.59, -177.00.

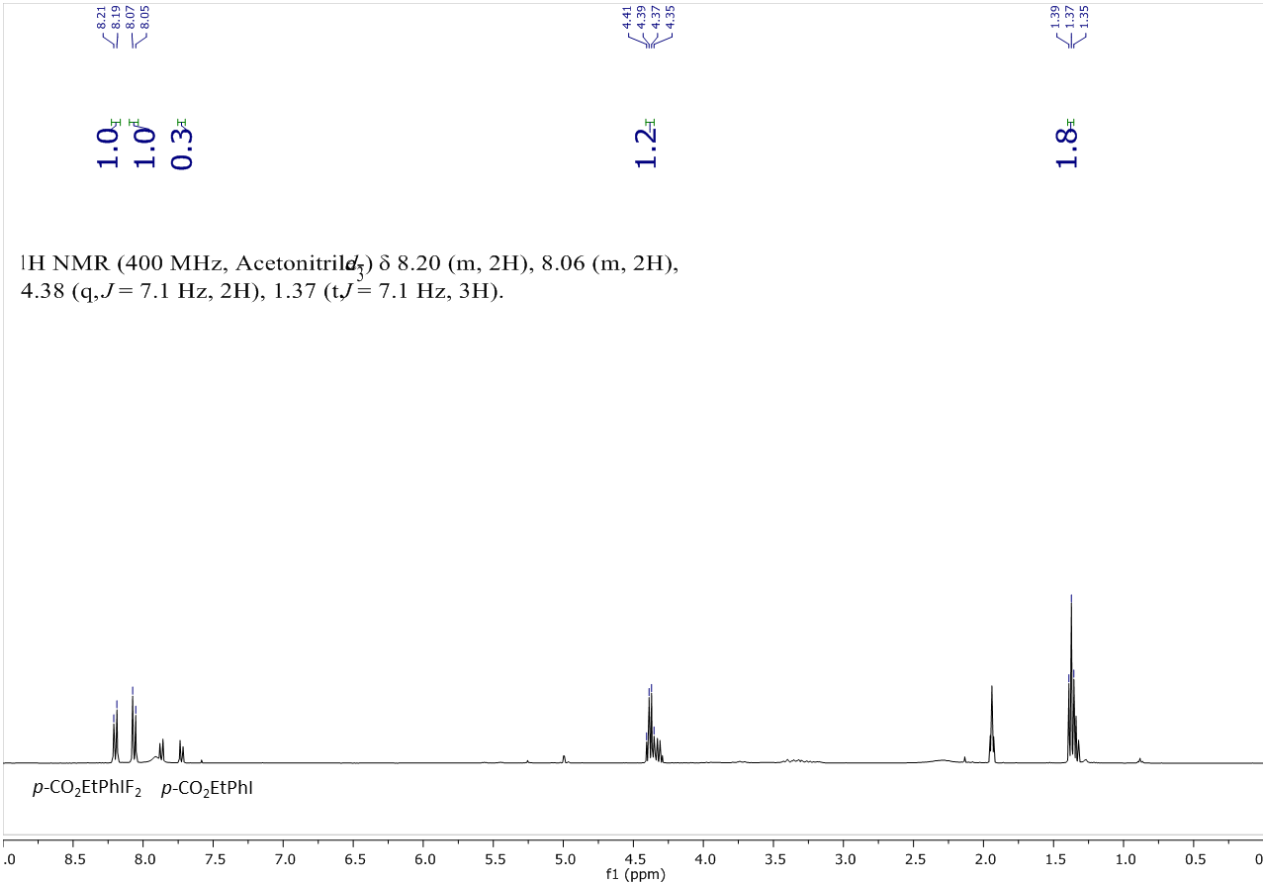


^{13}C NMR (151 MHz, Acetonitrile-d_3) δ 133.63 (q, J = 33.0 Hz), 131.86 (t, J = 4.6 Hz), 129.00 (q, J = 3.8 Hz), 128.47 (tm, J = 10.5 Hz), 124.46 (q, J = 271.9 Hz).

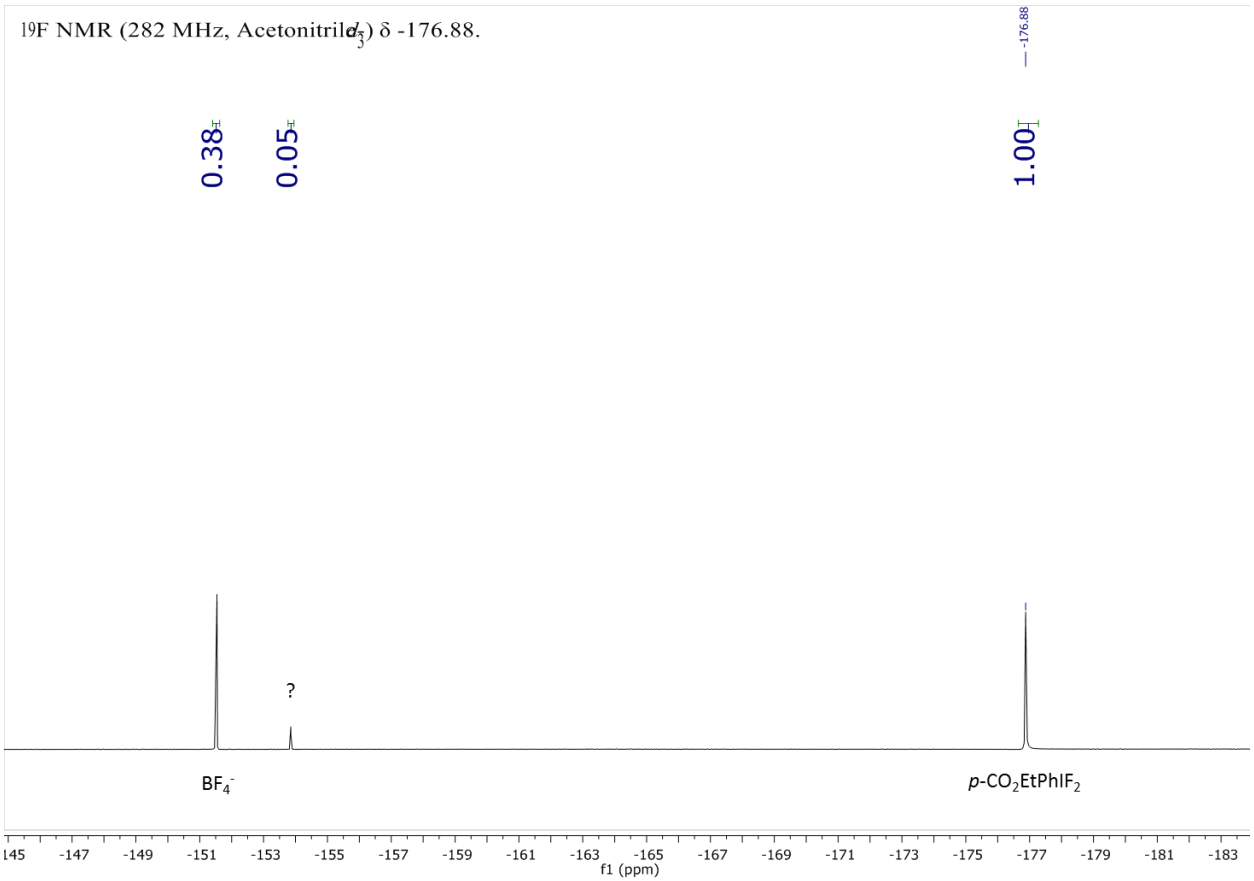
IX.3 *p*-CO_2EtPhIF_2 (2c)

General Procedure 1 using *p*-CO_2EtPhI (276 mg, 168 µL, 1 mmol), Selectfluor® (1410 mg. 4 mmol, 4 eq.) and CsF (760 mg, 5 mmol, 5 eq.) in dry acetonitrile (previously distilled and stored on 4Å molecular sieves) (25 mL). Reaction time: 88 h.

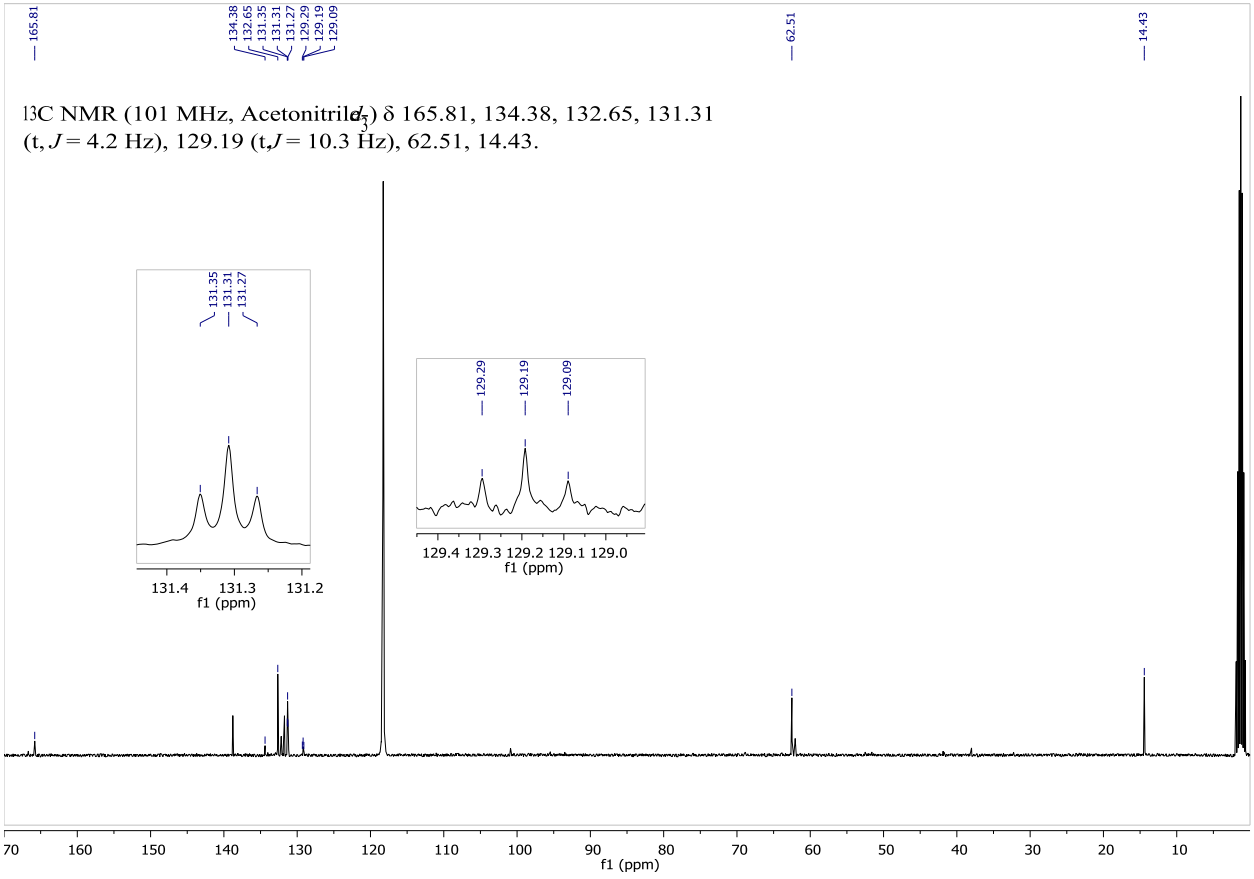
Conditions for extraction: To the reaction residue was added a mixture of $CHCl_3$:*n*-hexane 1:1 to dissolve the product (4 mL). The organic material was transferred by syringe to a flame-dried Schlenk tube and the process was repeated two times. The solvent was evaporated to dryness at 0°C (ice bath) to give 142 mg (35%) of a white solid. A solution of the solid in d_3-CH_3CN showed a mixture of starting material and compound 2c (ca. 1:3.4).



^{19}F NMR (282 MHz, Acetonitrile-d_3) δ -176.88.



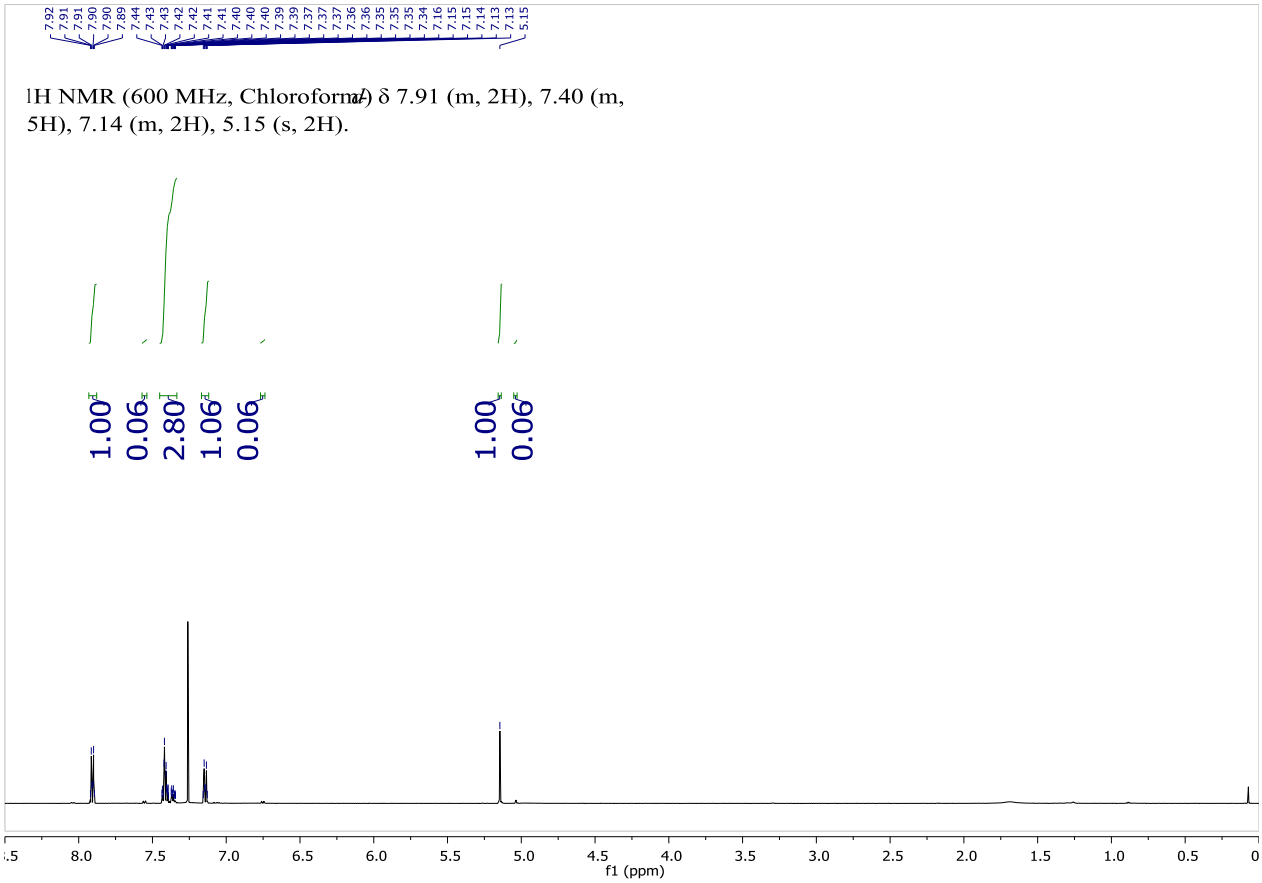
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 165.81, 134.38, 132.65, 131.31 (t, J = 4.2 Hz), 129.19 (t, J = 10.3 Hz), 62.51, 14.43.



IX.4 *p*-BnOPhIF$_2$ (2f)

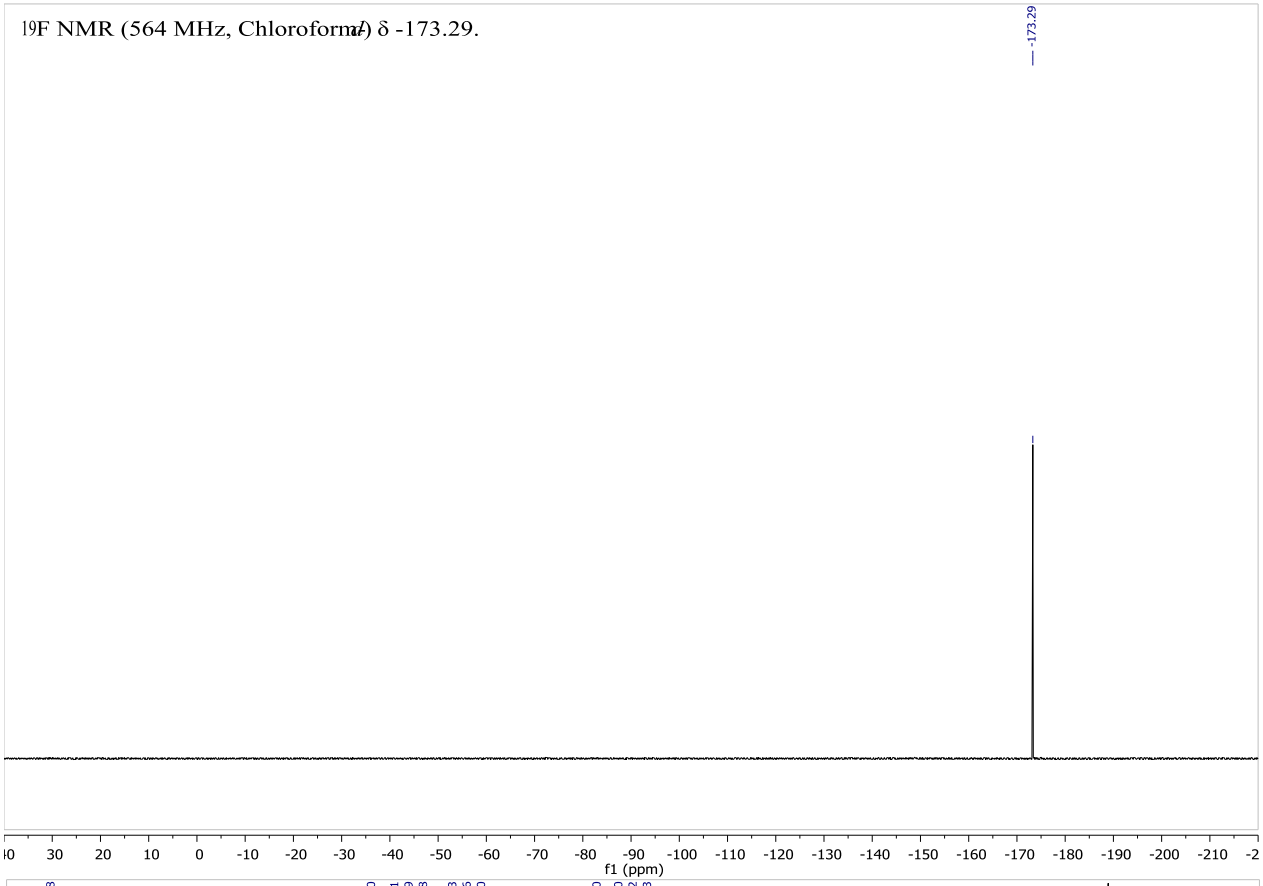
General Procedure 1 using *p*-BnOPhI (310 mg, 1 mmol), Selectfluor® (1410 mg. 4 mmol, 4 eq.) and CsF (760 mg, 5 mmol, 5 eq.) in dry acetonitrile (previously distilled and stored on 4Å molecular sieves) (25 mL). Reaction time: 6 h.

Conditions for extraction: To the reaction residue was added a mixture of $CHCl_3$:*n*-hexane 1:3 to dissolve the product (4 mL). The organic material was transferred by syringe to a flame-dried Schlenk tube and the process was repeated four times. The solvent was evaporated to dryness at 0°C (ice bath) to give 46 mg of a 1:1 mixture SM:Product. To the remaining residue was added a mixture of $CHCl_3$:*n*-hexane 1:1 to dissolve the product (4 mL). The organic material was transferred by syringe to a flame-dried Schlenk tube and the process was repeated one time.[1] The solvent was evaporated to dryness at 0°C (ice bath) to give 76 mg of a 1:1.7 mixture SM:Product. This fraction was dissolved in $CHCl_3$:*n*-hexane 1:1 (1 mL) and stored in the freezer overnight causing precipitation of a white solid (30 mg, SM:Product 6:94, 9%) which was isolated by removal of the remaining solvent and dried under vacuum. The obtained solid was characterized by NMR experiments.

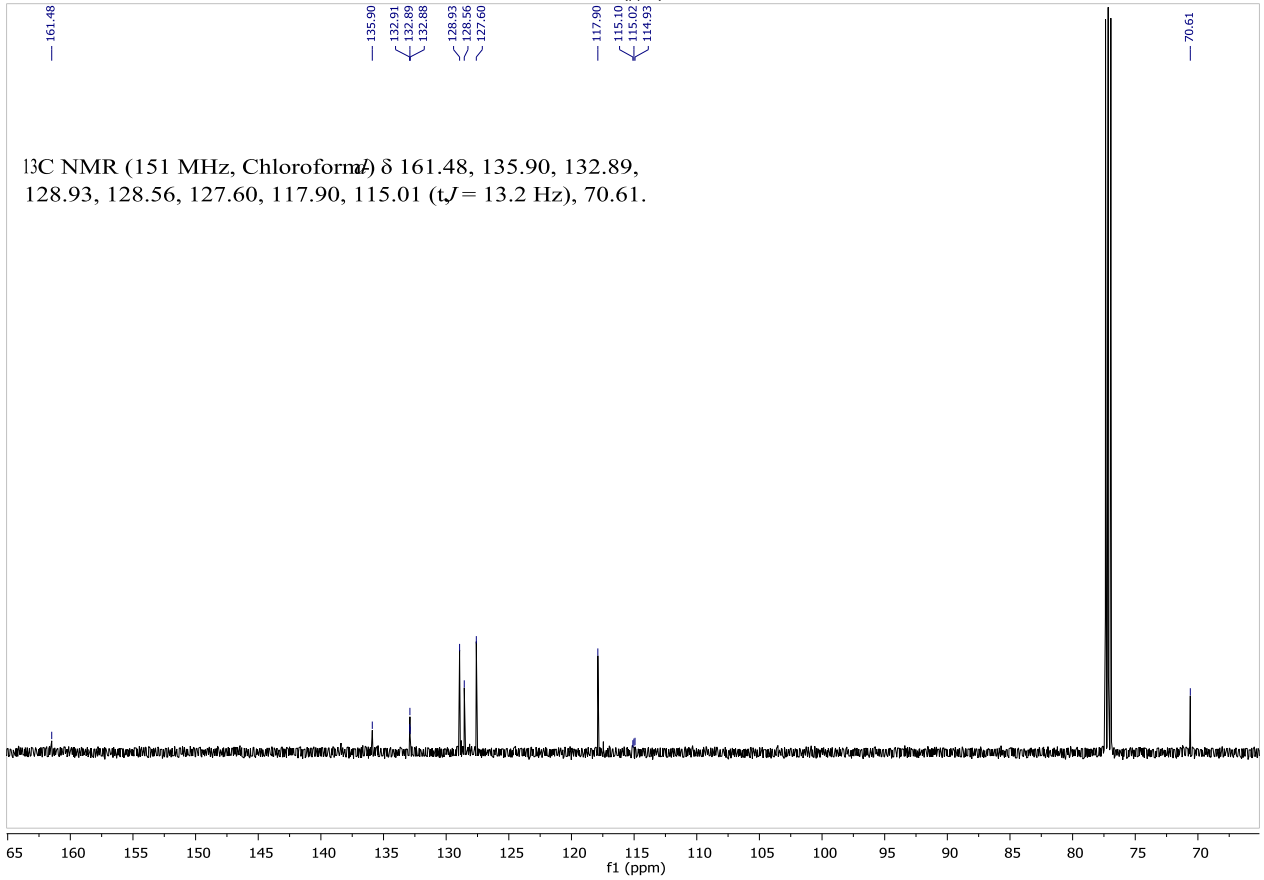


[1] The obtained residue was further extracted using $CHCl_3$:*n*-hexane 1:1 and the organic phase was evaporated to dryness at 0°C (ice bath). This light yellow solid was characterized by ^{1}H and ^{13}C NMR experiments, see page S55.

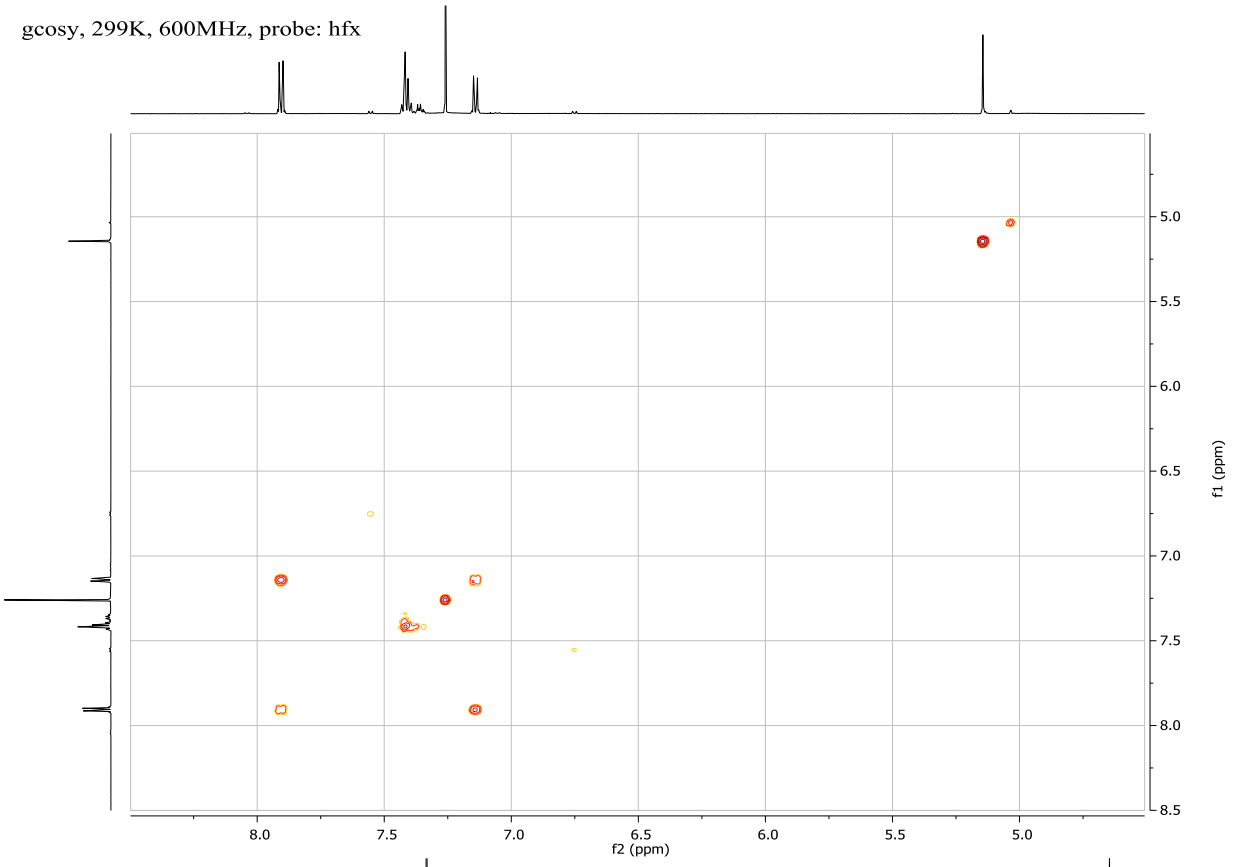
^{19}F NMR (564 MHz, Chloroform-*d*) δ -173.29.



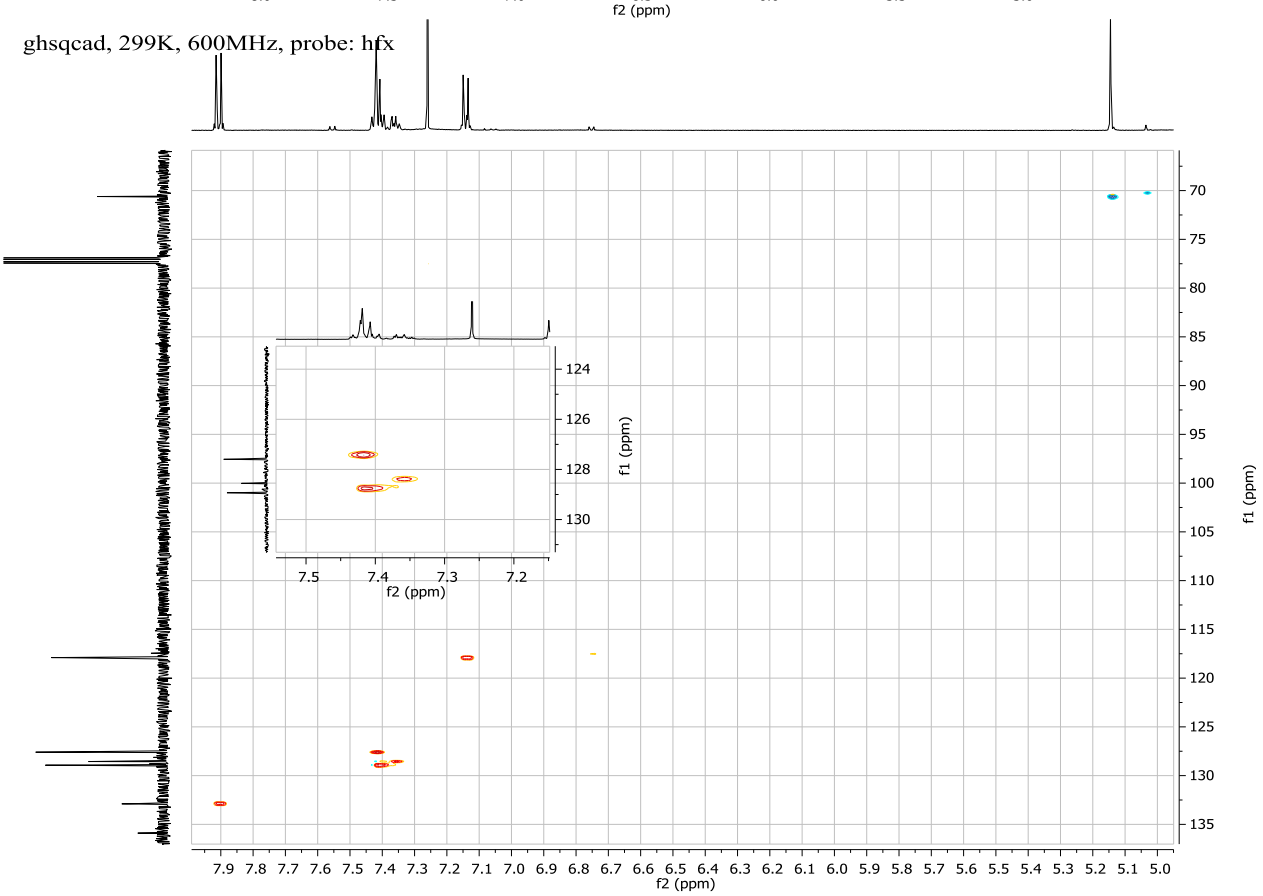
^{13}C NMR (151 MHz, Chloroform-*d*) δ 161.48, 135.90, 132.89, 128.93, 128.56, 127.60, 117.90, 115.01 (t, *J* = 13.2 Hz), 70.61.

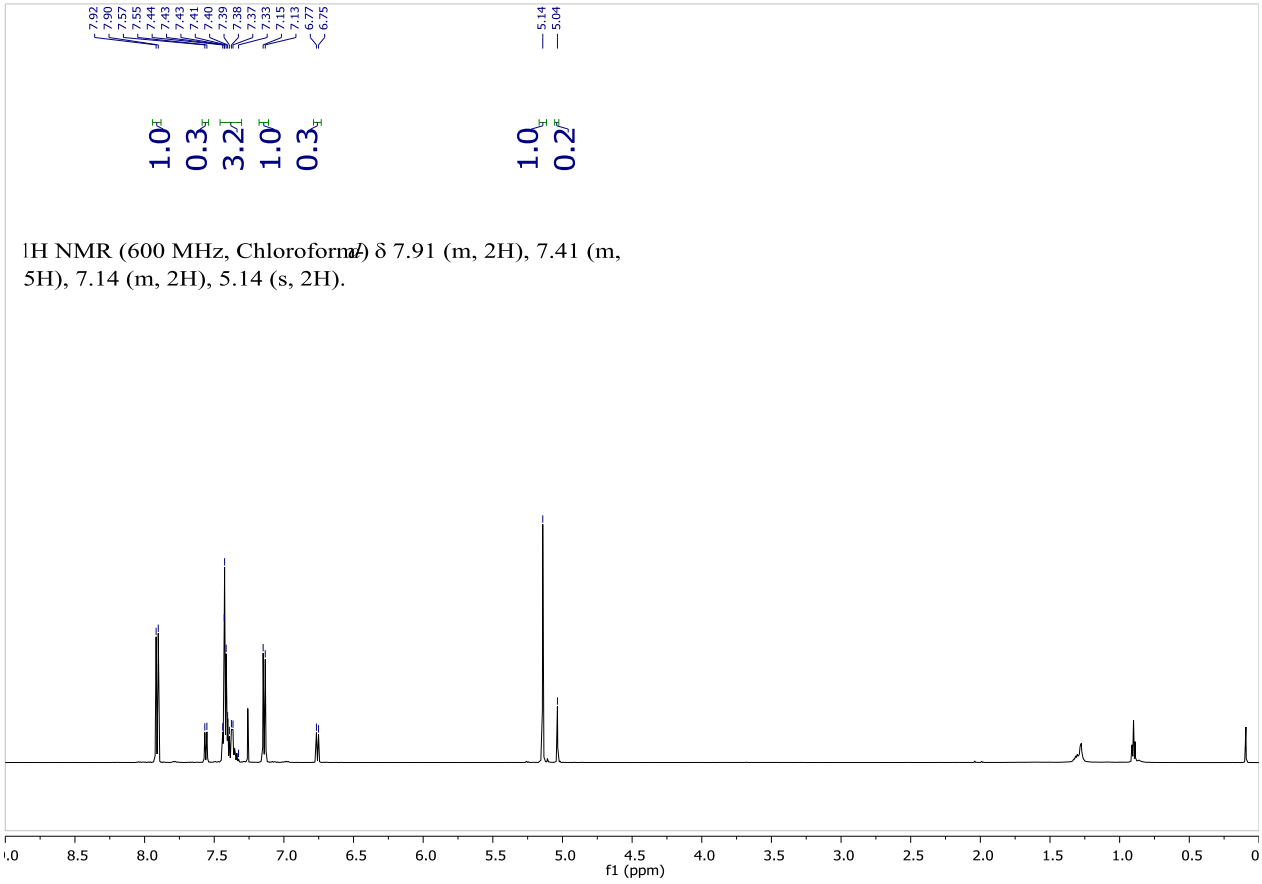


gcosy, 299K, 600MHz, probe: hfx

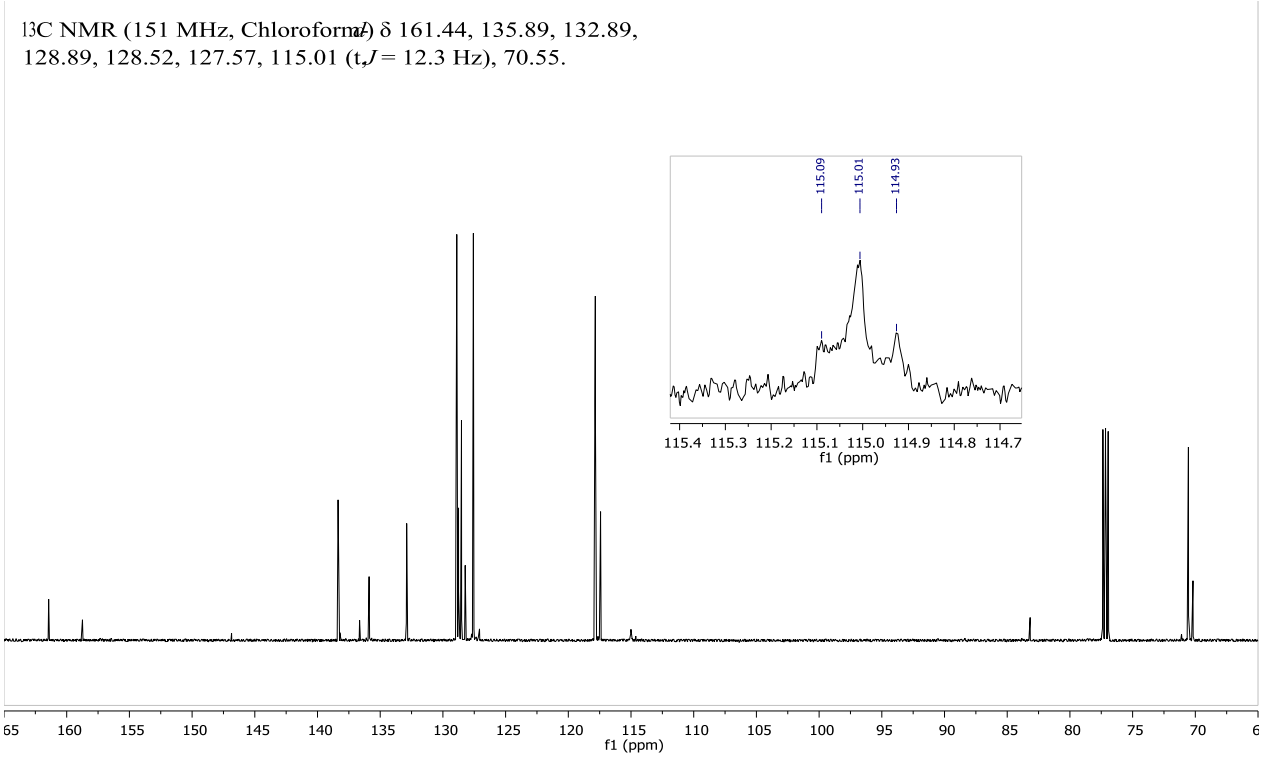


ghsqcad, 299K, 600MHz, probe: hfx





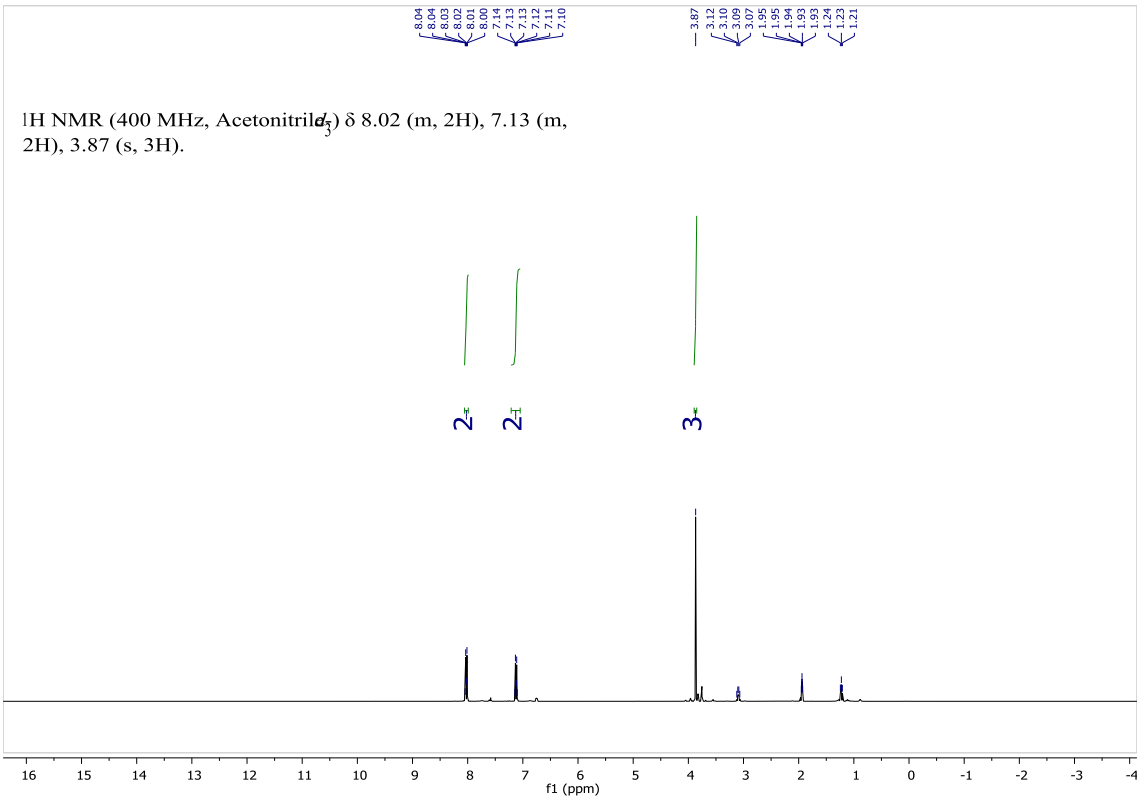
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.91 (m, 2H), 7.41 (m, 5H), 7.14 (m, 2H), 5.14 (s, 2H).



^{13}C NMR (151 MHz, Chloroform-*d*) δ 161.44, 135.89, 132.89, 128.89, 128.52, 127.57, 115.01 (t, J = 12.3 Hz), 70.55.

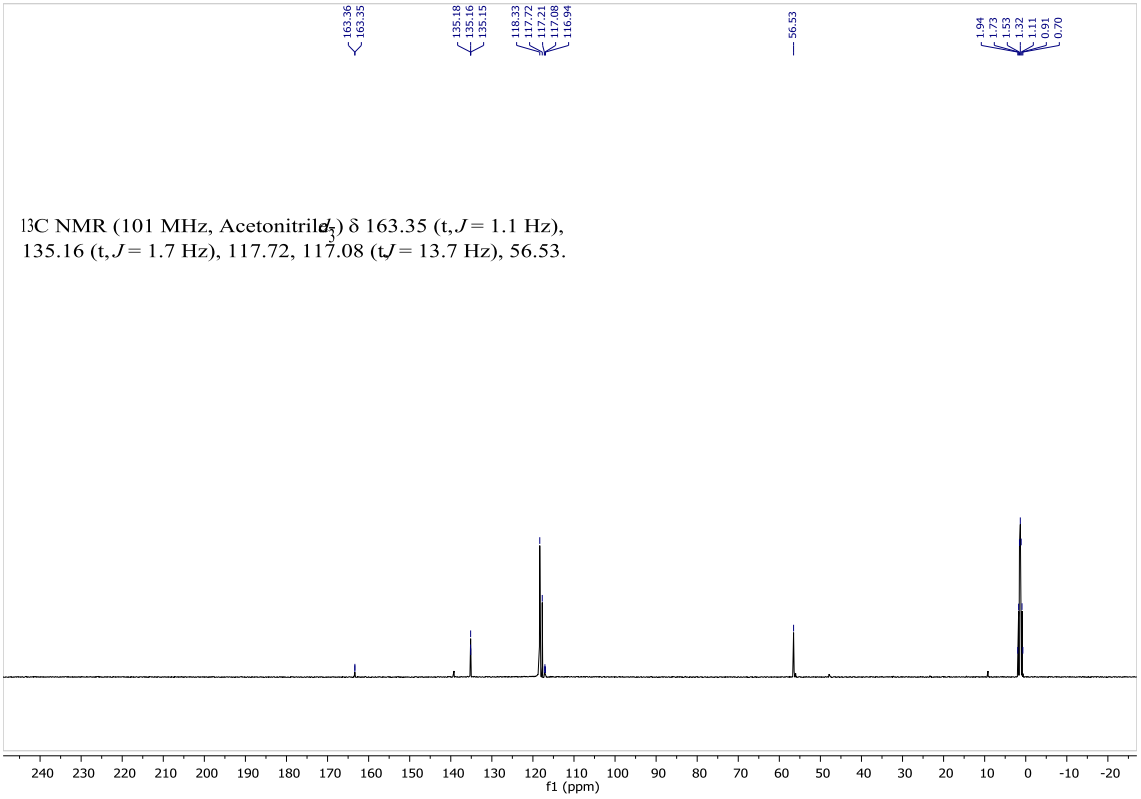
IX.5 *p*-MeOPhIF$_2$ (2g)

General Procedure 2 (Selectfluor® and Et_3N•3HF)

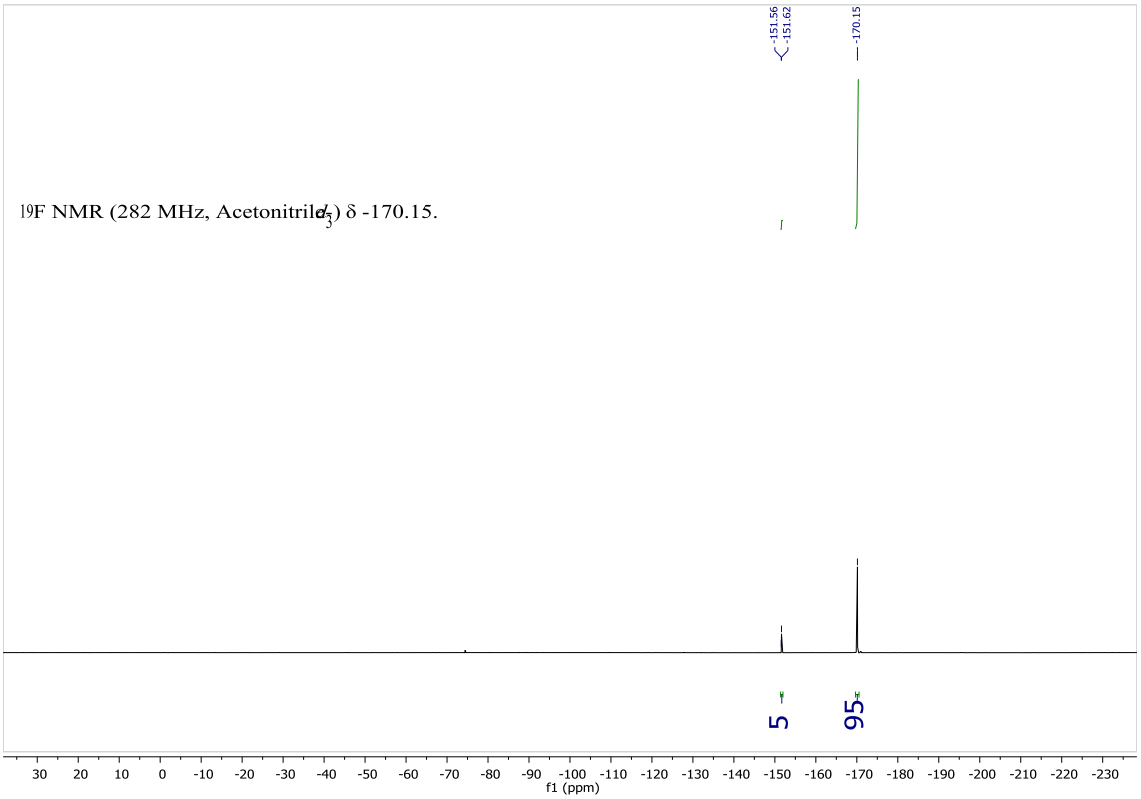


^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 8.02 (m, 2H), 7.13 (m, 2H), 3.87 (s, 3H).

Contains traces of starting material and TEA salts (3.12-3.07 and 1.24-1.21).

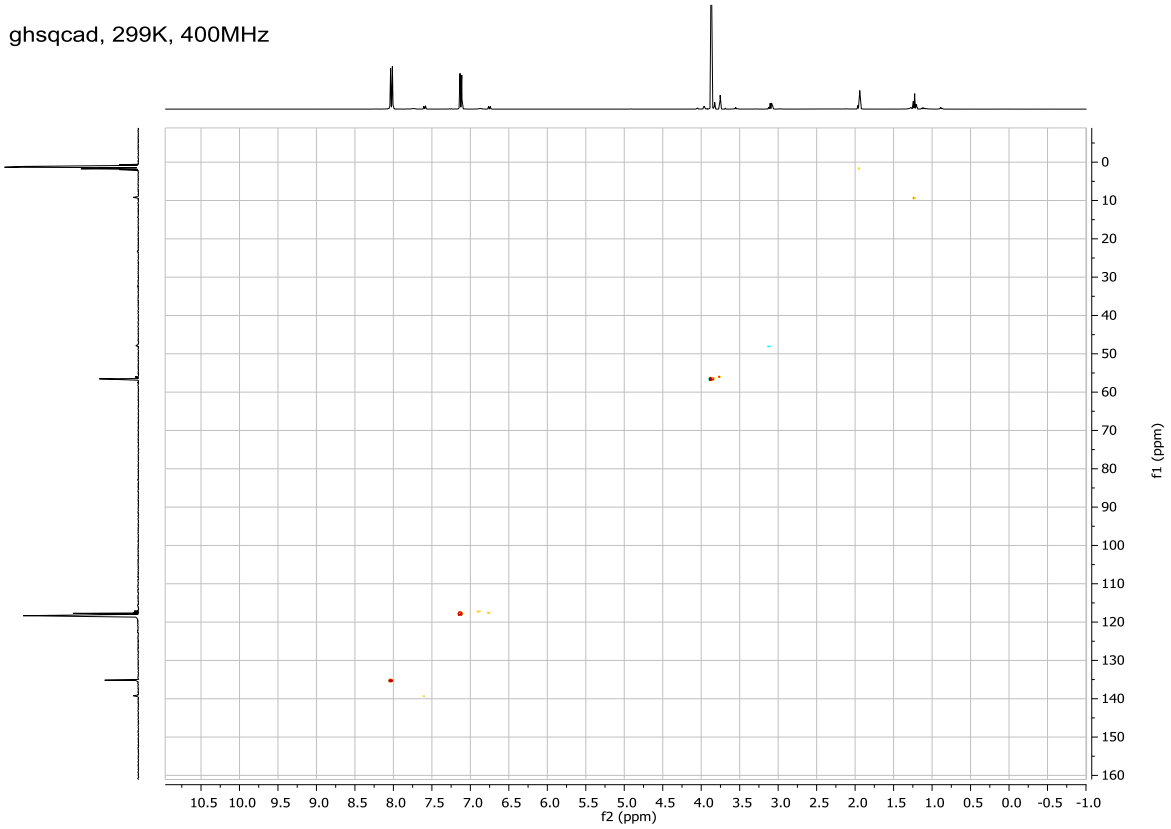


^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 163.35 (t, J = 1.1 Hz), 135.16 (t, J = 1.7 Hz), 117.72, 117.08 (t, J = 13.7 Hz), 56.53.



^{19}F NMR (282 MHz, Acetonitrile-d_3) δ -170.15.

Contains traces of tetrafluoroborate (-151.56 - -151.62 ppm)



X. References

[2] Ye, C.; Twamley, B.; Shreeve, J. *Org. Lett.* **2005**, *7*, 3961–3964.
[3] Laali, K.; Jamalian, A.; Zhao, C. *Tetrahedron Lett*. **2014**, *55*, 6643–6646.
[4] Uchiyama, M.; Furuyama, T.; Kobayashi, M.; Matsumoto, Y.; Tanaka, K. *J. Am. Chem. Soc.*, **2006**, *128*, 8404–8405.
[5] Ochiai, M.; Yoshimura, A.; Mori, T.; Nishi, Y.; Hirobe, M. *J. Am. Chem. Soc.*, **2008**, *130*, 3742–3743.