Electronic Supplementary Material (ESI) for Green Chemistry
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Supported Ionic Liquid-Like Phases as Orgonocatalysts for the Solvent-Free Cyanosilylation of Carbonyl Compounds: From Batch to Continuous Flow Process.

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Supporting information index

1. General procedures

2. Characterization

3. NMR Spectra.

4. Calculations of E-factor and Productivity.

5. Swelling of the supported catalysts.

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1. General procedures

Reagents were supplied by Aldrich and were used without further purification (octanal was distilled before being used).^{1}H NMR experiments were obtained using a Varian INOVA 500 (^{1}H, 500 MHz) spectrometer. The chemical shifts are given in delta (δ) values (ppm). Samples were analyzed by GC VARIAN 3900.

2. Characterization.

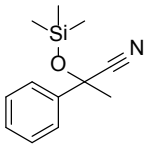
All the products here synthesized were previously reported and purified by medium pressure column chromatography (Combi-Flash Teledyne ISCO) with n-Hexane-Ethylacetate. According to bibliography data the compounds were characterized as following:

Compound (**13**) and compounds entries 1, 3 and 5, Table 2, were analyzed by the following GC method (VARIAN 3900). Analysis time: 60 min., Column Cyclodex B Pressure: 15.00 Psi Oven Temperature: To= 60ºC, Tf=130ºC. Rate: 1.2ºC/min Detector: T: 300ºC, Injector: T: 230ºC, Helium flow: 25mL/min, Nitrogen flow: 30mL/min, Air flow: 300mL/min.

Compound entry 2, Table 2 was analyzed by GC VARIAN 3900. Analysis time: 30 min., Column CyclodexB Pressure: 15.00 Psi Oven Temperature: To= 60ºC, Tf=130ºC. Rate: 10ºC/min Detector: T: 300ºC, Injector: T: 230ºC, Helium flow: 25mL/min, Nitrogen flow: 30mL/min, Air flow: 300mL/min.

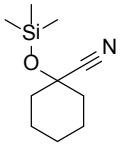
Compounds entry 4, 6 and 7, Table 2 were analyzed by using a Varian INOVA 500 (^{1}H, 500 MHz) spectrometer.

2-phenyl-2-((trimethylsilyl)oxy)propanenitrile (13)



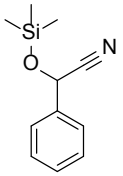
^{1}H-RMN ($CDCl_3$, 500 MHz): δ 0.181 (s, 9H, 3xCH_3), 1.868 (s, 3H, CH_3), 7.515-7.403 (m, 5H, Ph).

1-((trimethylsilyl)oxy)cyclohexanecarbonitrile (Table 2 entry 1).



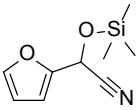
^{1}H-RMN ($CDCl_3$, 500 MHz): δ 0.230 (s, 9H, 3xCH_3), 1.519-2.027 (m, 10H, cyclohexyl).

2-phenyl-2-((trimethylsilyl)oxy)acetonitrile (Table 2 entry 2).



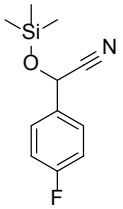
^{1}H-RMN ($CDCl_3$, 500 MHz): δ 0.181 (s, 9H, 3xCH_3), 5.503 (s, 1H, CH), 7.400-7.499 (m, 5H, Ph).

2-(furan-2-yl)-2-((trimethylsilyl)oxy)acetonitrile (Table 2 entry 3).



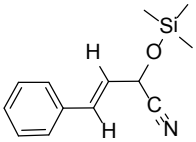
^{1}H-RMN ($CDCl_3$, 500 MHz): δ 0.226 (s, 9H, 3xCH_3), 5.559 (s, 1H, CH), 6.427-6.539 (m, 1H, 2xfuran), 7.445-7.454 (m, 1H, furan).

2-(4-fluorophenyl)-2-((trimethylsilyl)oxy)acetonitrile (Table 2 entry 4).



^{1}H-RMN ($CDCl_3$, 500 MHz): δ 0.246 (s, 9H, 3xCH_3), 5.478 (s, 1H, CH), 7.056-7.126 (m, 2H, Ph), 7.433-7.480 (m, 2H, Ph).

(E)-4-phenyl-2-((trimethylsilyl)oxy)but-3-enenitrile (Table 2 entry 5).



^{1}H-RMN ($CDCl_3$, 500 MHz): δ 0.275 (s, 9H, 3xCH_3), 5.117-5.132 (m, 1H, CH), 6.172-6.216 (m, 1H, CH), 6.800-6.834 (m, 1H, CH), 7.239-7.419 (m, 5H, Ph).

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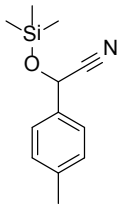
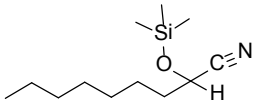
2-(p-tolyl)-2-((trimethylsilyl)oxy)acetonitrile (Table 2 entry 6).



^{1}H-RMN ($CDCl_3$, 500 MHz): δ 0.221 (s, 9H, 3xCH_3), 2.372 (s, 3H, CH_3), 5.458 (s, 1H, CH), 7.226-7.380 (m, 4H, Ph).

2-((trimethylsilyl)oxy)nonanenitrile (Table 2 entry 7).



^{1}H-RMN ($CDCl_3$, 500 MHz): δ 0.180 (s, 9H, 3xCH_3), 0.892 (s, 3H, CH_3), 1.270-1.538 (m, 10H, CH_2), 1.756-1.801 (m, 2H, CH_2), 4.369-4.395 (m, 1H, CH).

4. Productivity calculation

Productivity= (mol product/mol cat.) x (1/time(h))

REF. 6:

Mol product= mol benzaldehyde x Yield= 0,001mol x 99%= 0,00099 mol

Mol cat. = V x ρ/Fw = (0,5mL x 1,231g/mL) / (340,29g/mol)= 0,0018087 mol

Time= 24h

Productivity= (0,00099mol/0,0018087mol) x (1/24h) **= 0,023**

REF. 7:

Mol product= mol benzaldehyde x Yield= 0,005mol x >99% = 0,005 mol

Mol cat.= 0,01% Mol product= 0,005mol x(0,01/100)=0,0000005 mol

Time= 30min= 0,5h

Productivity= (0,005mol/0,0000005mol) x (1/0,5h) = **20000**

REF. 26:

Mol product= mol acetophenone x Yield= 0,200mol x 99%= 0,198 mol

Mol cat. = 0,125g x 3,2mmol/g = 0,4mmol = 0,0004mol

Time= 20h

Productivity= (0,198mol/0,0004mol) x (1/20h) = **25**

E factor calculation

E factor= kg waste/kg product

E factor=[(mol benzaldehyde x Fw benzaldehyde) + (mol TMSCN x Fw TMSCN)+(mL solvent x ρ solvent) – (mol benzaldehyde x Yield x Fw product)]/ [mol benzaldehyde x Yield x Fw product]

REF. 6:

Solvent= 3x15mL diethyl ether

ρ diethyl ether= 0,7134 g/mL

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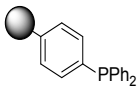
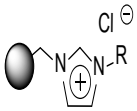
E factor= [(0,001mol x 106g/mol)+(0,002mol x 99,21g/mol)+(3x15mL x 0,7134g/mL)-(0,001mol x (99/100) x 205,09g/mol)]/[0,001mol x (99/100) x 205,09g/mol]= **158,6**

REF. 7:

Solvent= 3x50mL hexane

ρ hexane= 0,6548 g/mL

E factor= [(0,005mol x 106g/mol)+(0,006mol x 99,21g/mol)+(3x50mL x 0,6548g/mL)-(0,005mol x >99% x 205,09g/mol)]/[0,005mol x >99% x 205,09g/mol]= **95,8 ≈ 96**

	SOLVENT	CAT.	CONDITIONS	YIELD	TIME	TEMP.	TYPE OF REACTOR
REF. 6	[OMIM]PF_6	[OMIM]PF_6 0,5 mL	1mmol benzaldehyde/ 2 mmol TMSCN	99%	24 h	r.t.	batch
REF. 7	[BMIM]SBF_6	$Sc(OTf)_3$ 0,01%	5 mmol benzaldehyde/ 6 mmol TMSCN	>99%	30 min	r.t.	batch
REF. 26	SolFC	 0,125g	200 mmol acetophenone/ 220 mmol TMSCN	99%	20 h	60°C	flow
OUR	SolFC	 600 mg	114 mmol acetophenone/ 125 mmol TMSCN	99%	4 min[a]	r.t.	flow

a) **Residence time for a flow rate of 0.1 mL/min**

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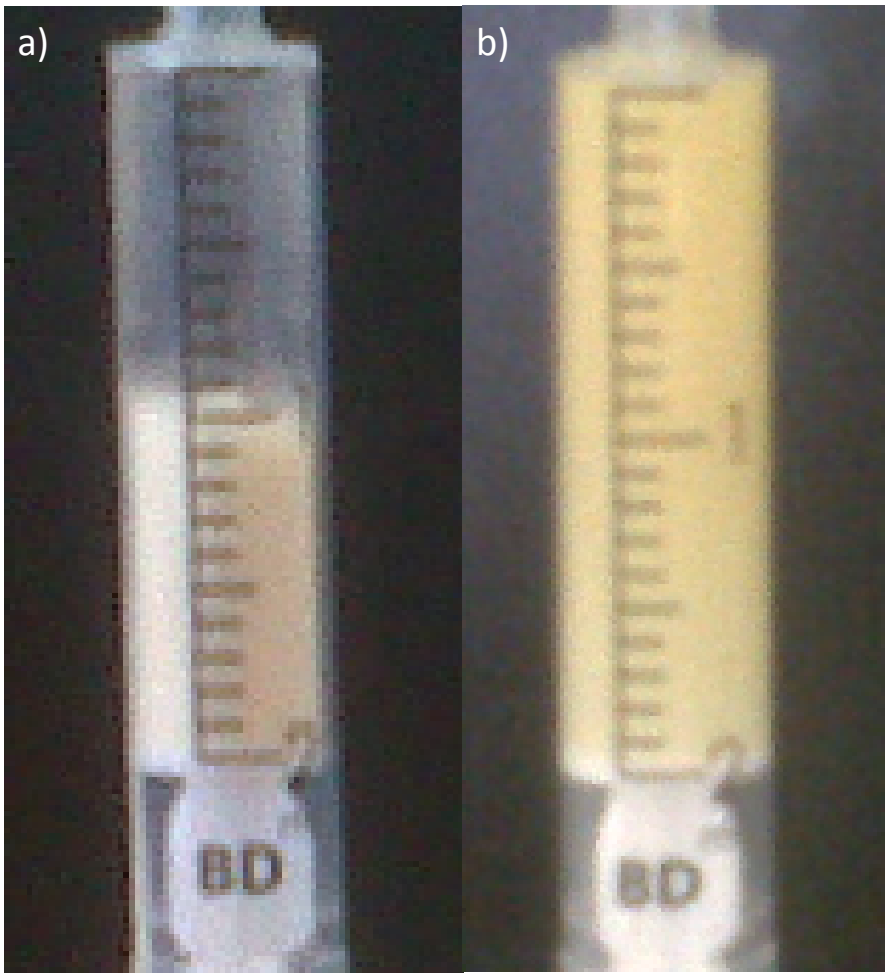
5. Swelling of the supported catalyst.



a) Dry volume = 1 ml
b) Wet volume at 25,5h = 2mL

Swelling (vf-vi/vi x 100).

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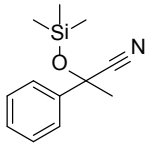
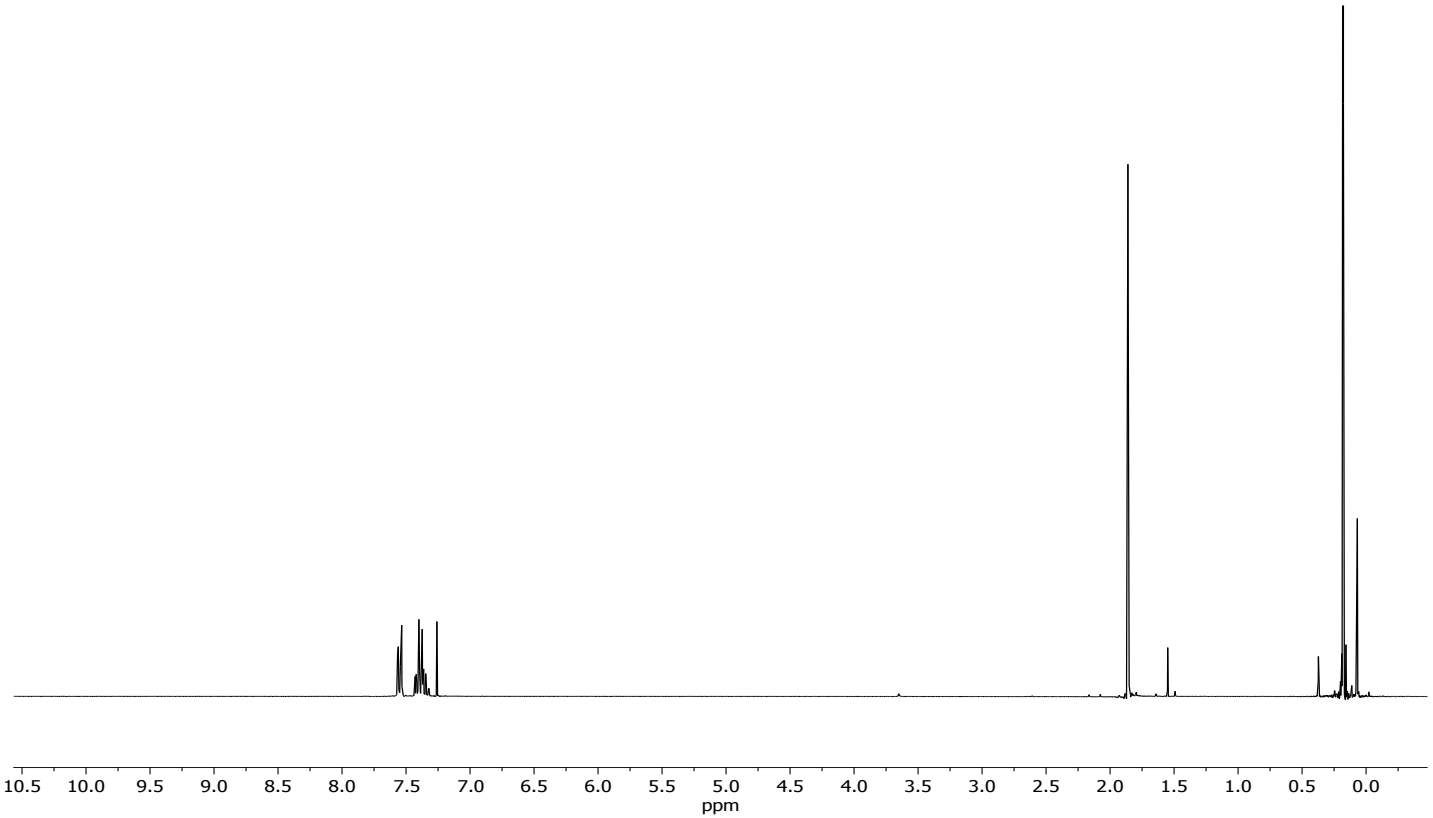
3. NMR Spectra (corresponding with the reaction crude).



(**13**)



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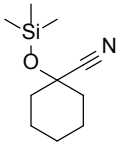
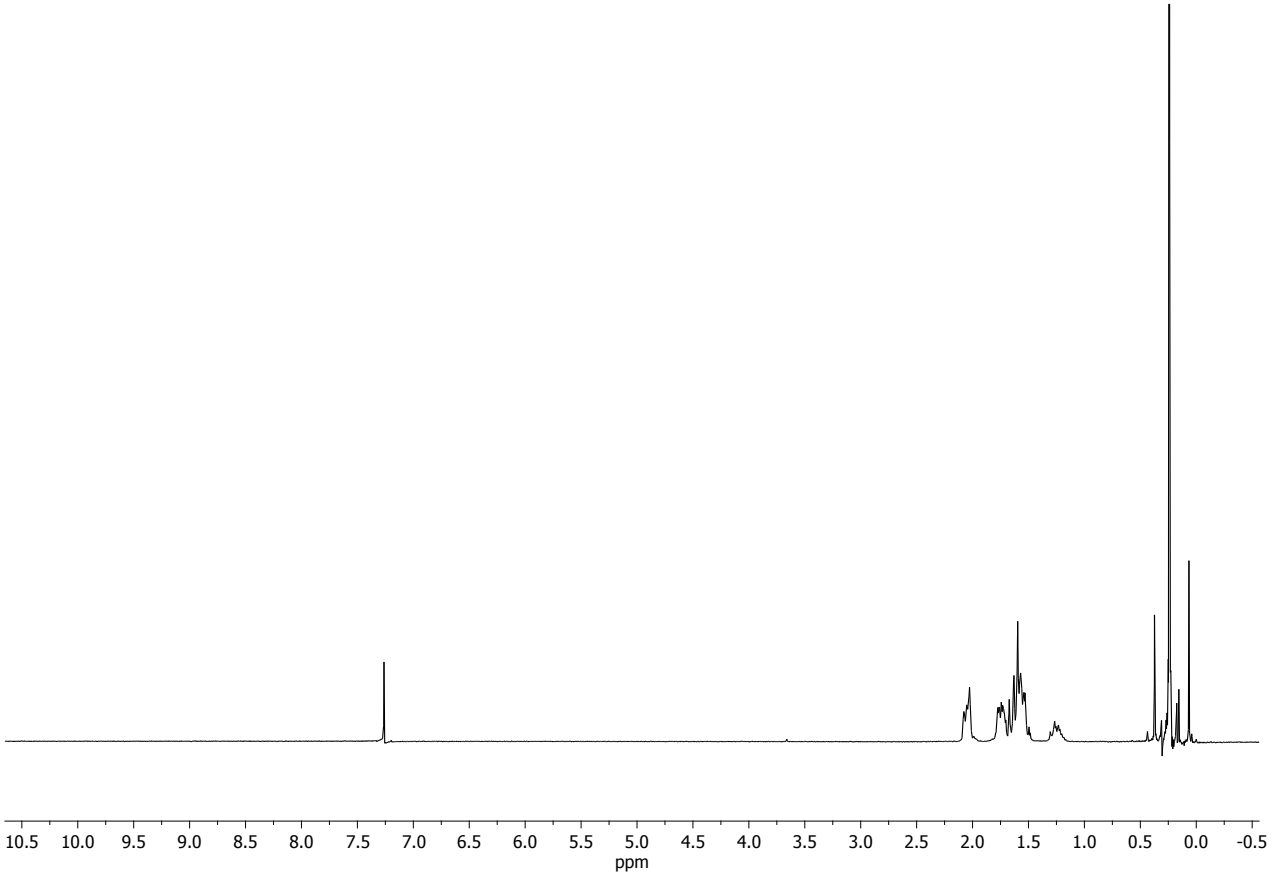


(Table 2 Entry 1)



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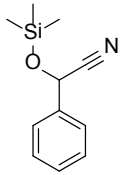
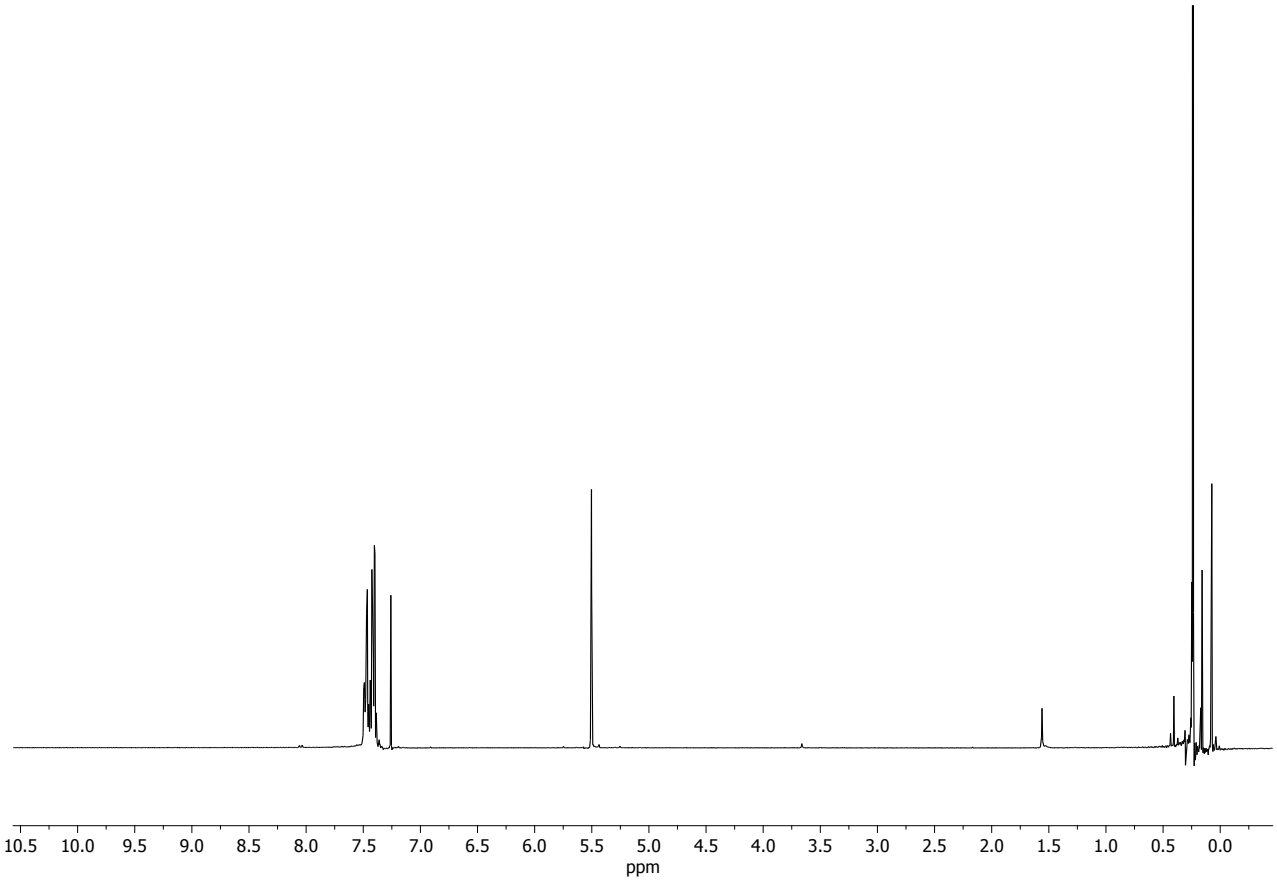


(Table 2 Entry 2)



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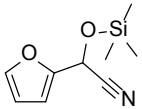
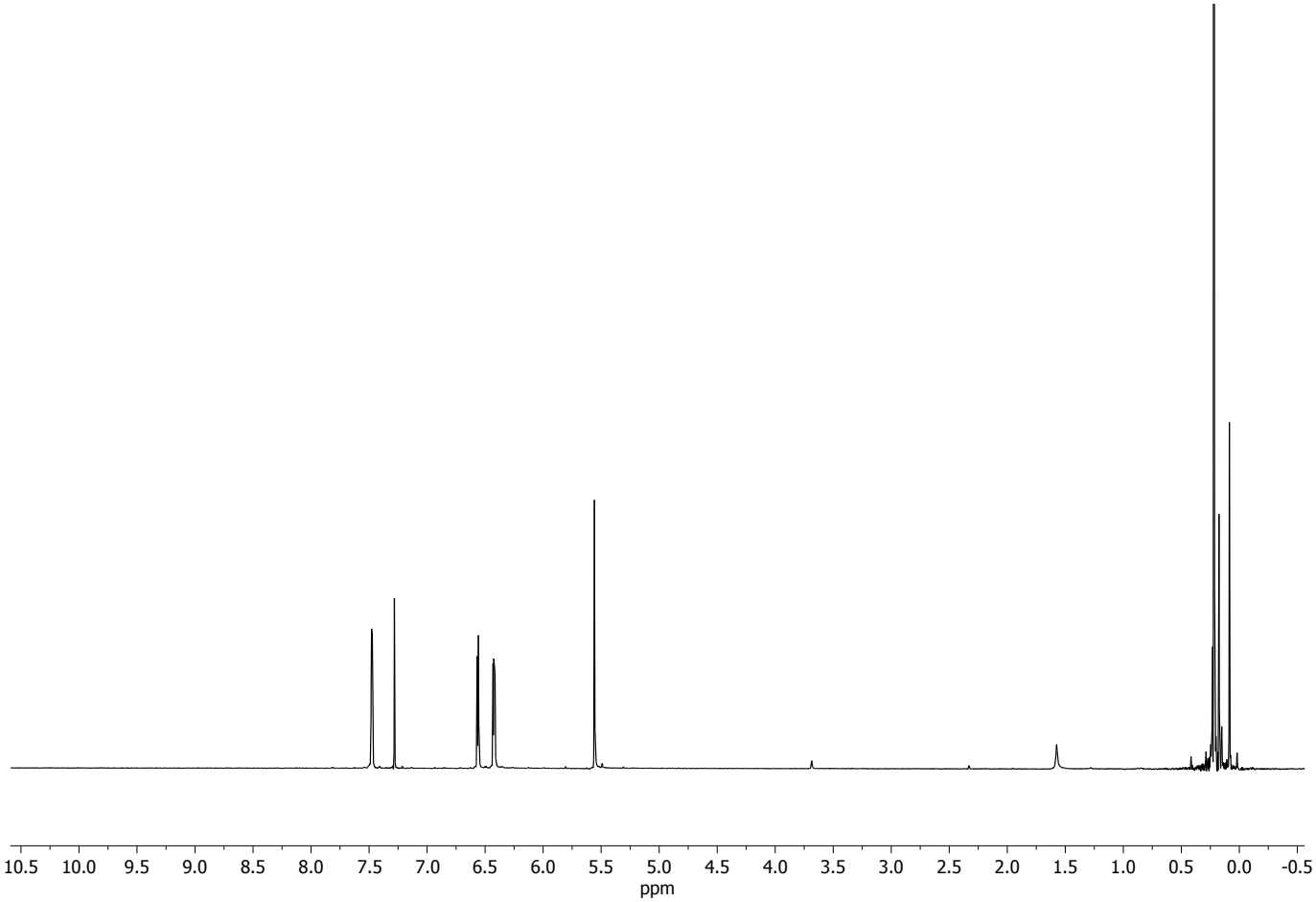


(Table 2 Entry 3)



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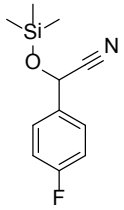

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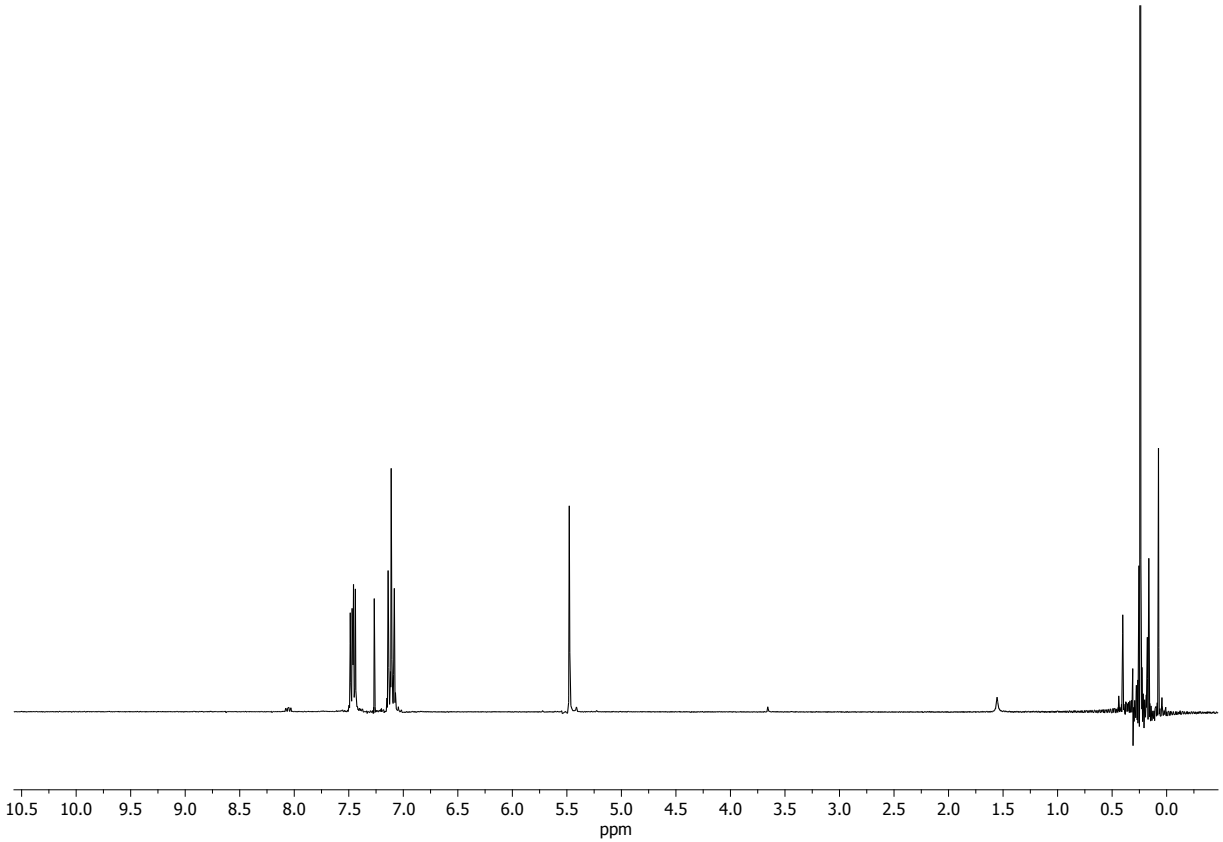

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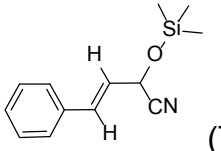

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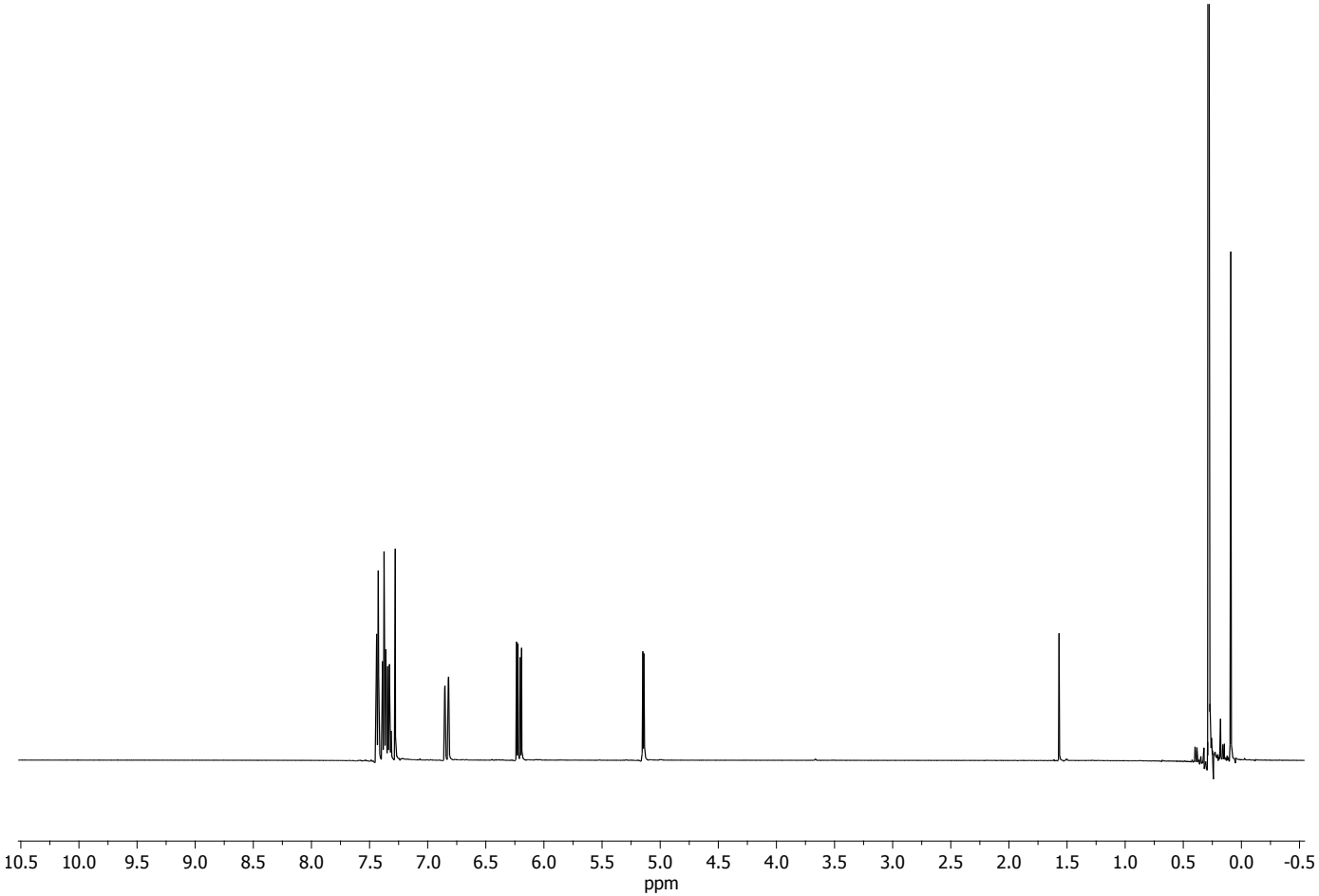

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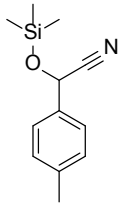

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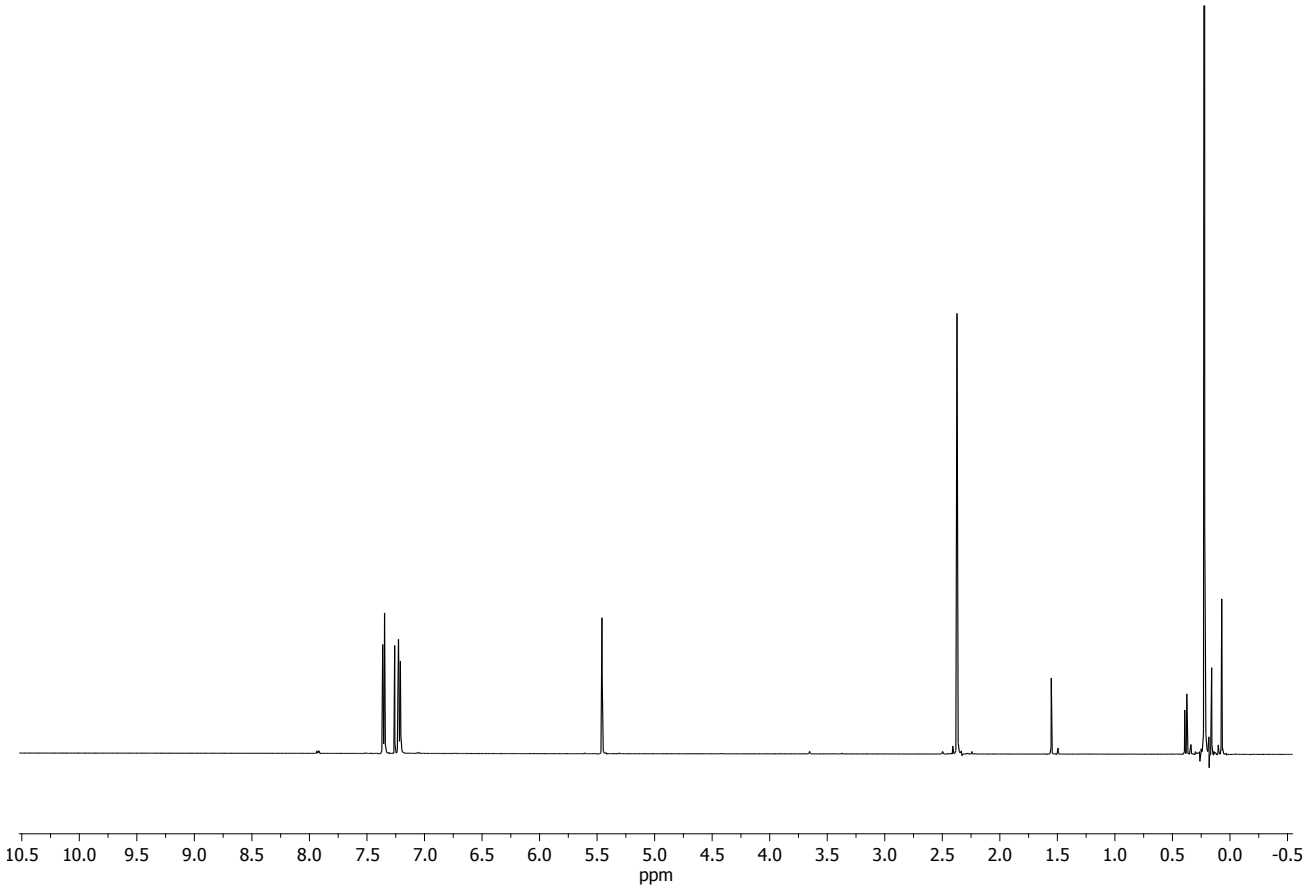

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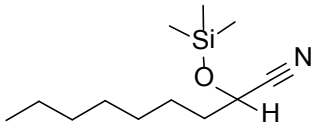
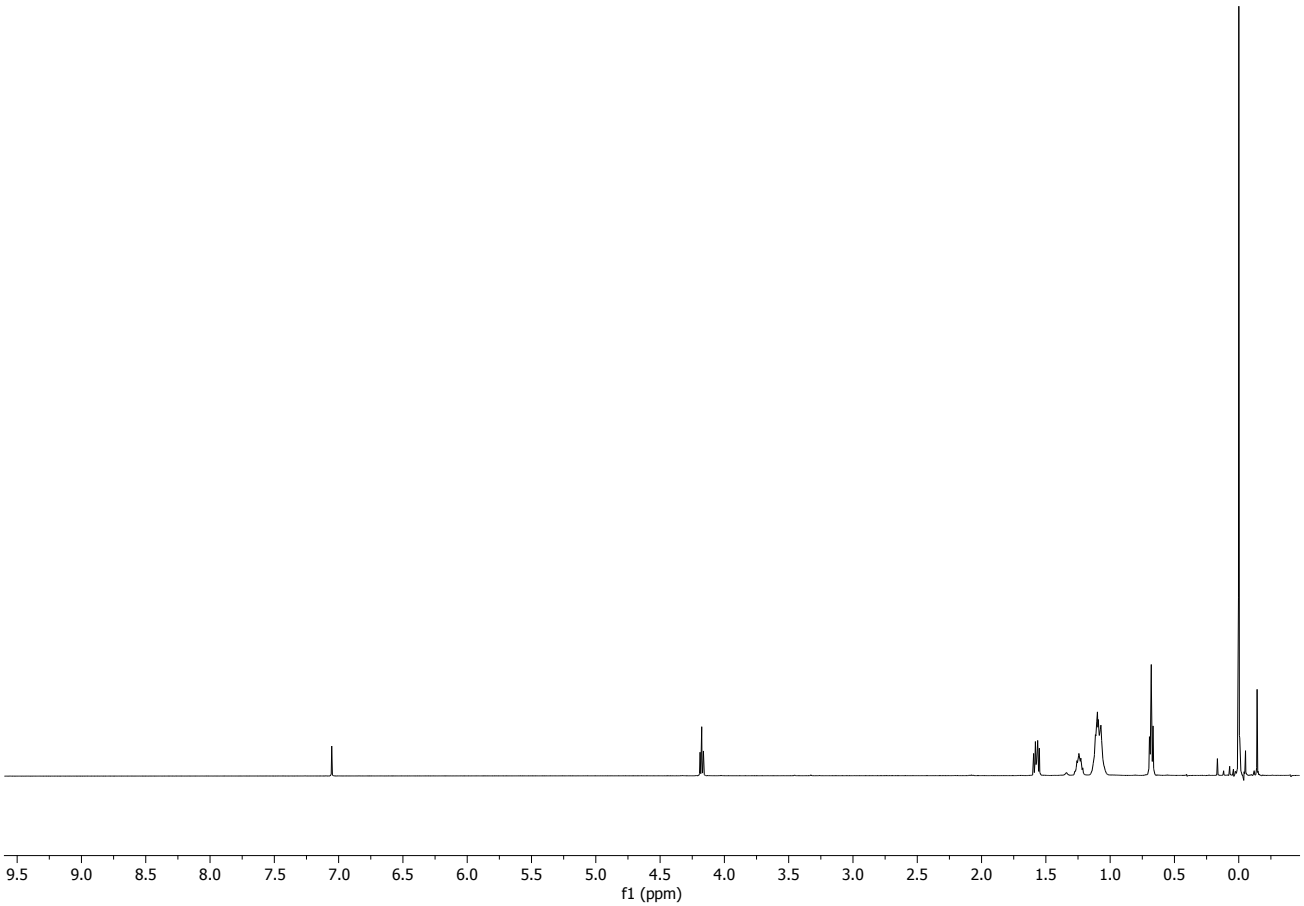
(Table 2 Entry 7)