Electronic Supplementary Information

Pickering emulsion droplets hosting ionic liquid catalysts for continuous-flow cyanosilylation reaction

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Experimental section

Chemicals and materials. Trimethylsilyl cyanide (TMSCN) (98%) were purchased from Adamas Reagent Co., Ltd, (China). Acetophenone (98%), benzaldehyde (98%), *p*-chloroacetophenone (97%), *p*-methylacetophenone (99%), cyclohexanone (99%) and fluorescein isothiocyanate isomer I (FITC-I, CAS No.3326-32-7) were purchased from Aladdin (China). Nile red (CAS No. 7385-67-3) was obtained from Sigma-Aldrich. Propiophenone (99%), butanone (99%), 2-hexanone (98%) were purchased from Alfa Aesar. 1-Butyl-3-methylimidazolium hexafluorophosphate (99%), 1-butyl-3-methylimidazolium tetrafluoroborate (99%), 1-butyl-3-methylimidazolium chloride (99%), 1-butyl-3-methylimidazolium bromide (99%) and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (99%) were purchased from Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. Water used in this study was de-ionized water.

Characterization. Nitrogen-sorption analysis of silica emulsifier was performed at -196 ^{o}C on a Micromeritics ASAP 2020 analyzer. Before measurement, samples were out gassed at 120 ^{o}C under vacuum for 6 h. The specific surface area was calculated from the adsorption branch in the relative pressure range of 0.05–0.15 using the Brunauer-Emmett-Teller (BET) method. Samples for transmission electron microscopy (TEM) observation were prepared by dispersing the sample powder in ethanol using ultrasound and then allowing a drop of the suspension to evaporate on a copper gird covered with a holey carbon film. TEM images were obtained on a JEOL-JEM-2000EX instrument. Emulsion droplets were observed using an optical microscope analyzer (XSP-8CA, Shanghai, China) equipped with 4 or 10 × magnification lens. X-ray photoelectron spectra (XPS) ware recorded on a Kratos Axis Ultra DLD. The contact angles of water in air on silica particle disks were measured using a Krüss DSA100 instrument. Before measurement, the powder sample was compressed into a disk of thickness approximately 1 mm (ca. 2 MPa). A drop of water (1 µL) was formed on the sample disk. The appearance of the water droplet was recorded at ca. 0.1 s with a digital camera. The value of the contact angle was determined by a photogoniometric method. Gas chromatography (GC) analysis was carried out on an Agilent 7890 analyzer (Agilent HP-5) with a flame ionization detector. The identification of products by mass spectrometry (MS) was performed on a GC-MS instrument (7890A-5977A, HP-5, Agilent). Confocal laser scanning microscopy images were obtained on a Carl Zeiss LSM880 instrument (Germany). The concentration of FITC-I in ionic liquid was 2×10^{-6} M and the excitation wavelength is 488 nm (green). The concentration of Nile Red in n-octane was 5×10^{-6} M and the excitation wavelength is 559 nm (red).

Preparation of the FITC-I-Labelled Emulsifier. 1.0 g of dimethyl-modified silica particles and 0.1 mmol $(CH_3CH_2O)_3SiCH_2CH_2CH_2NH_2$ were dispersed into toluene (8 mL). This mixture was stirred under a N_2 atmosphere at 60 ^{o}C. After refluxing for 2 h, the resultant silica nanospheres were collected through centrifugation, washed four times with toluene and dried, resulting in bifunctionalized silica nanospheres. 0.5 g of this bifunctionalized silica particles and 0.005 g fluorescein isothiocyanate isomer I (FITC-I) were dispersed into 50 mL ethanol. The mixture was stirred overnight at room temperature in the dark. After centrifugation, the solid was washed five times with ethanol and dried yielding FITC-I-labelled emulsifier.

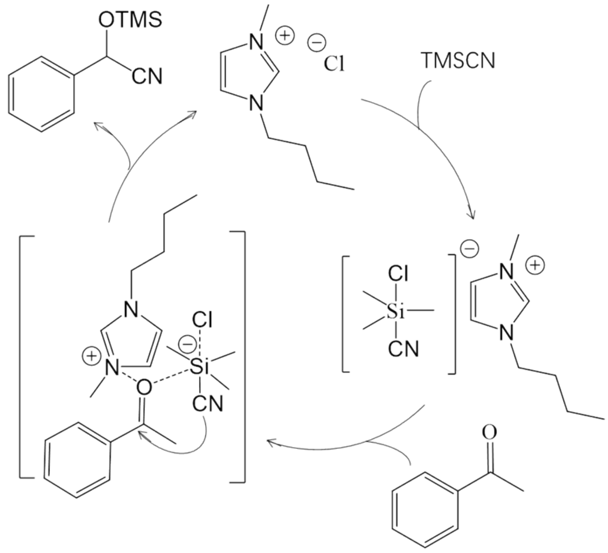
Permeability of IL droplet to Probe Molecules. IL-in-oil Pickering emulsion droplets were deposited on a glass slide and diluted with *n*-octane. 5 µL of Nile Red solution (5 µM in *n*-octane) was gently dropped on the glass slide. The diffusion of Nile Red molecules into the droplets was recorded by fluorescence microscopy at intervals.

Determination of the Partition Coefficient of reactant molecules between IL and Oil. A mixture of 1 mL of oil containing a given organic compound (0.1 M) and 1 mL of ionic liquid was stirred for 12 h at room temperature to reach equilibrium. After phase separation, the concentration of the compound in the oil phase was determined by GC. The concentration of this compound in the ionic liquid is calculated from the difference between the initial concentration in oil and the determined concentration after equilibrium. This experiment was repeated three times to obtain an average value. The partition coefficient ($K_{IL/oil}$) between ionic liquid and oil is the ratio of the compound concentration in the ionic liquid to that in the oil after reaching equilibrium.

Partition coefficient of reactant molecules between [bmim]BF_4 and *n*-octane.

Reactant molecules (0.1 M)	acetophenone	TMSCN
$K_{IL/oil}$	5.5	1.9

Batch Reactions. Batch biphasic reactions were conducted in a 20 mL glass vial. 0.6 g [bmim]BF_4, 0.006 g [bmim]Cl, 0.1 M acetophenone and 0.36 M TMSCN in *n*-octane (17 mL) and were charged into this vial. The mixture was stirred with a magnetic stir bar (10 mm in length, 2600 rpm) at 25 ^oC. To determine the kinetic profiles, an aliquot were regularly taken (10 min, 20 min, 40 min, 1 h, 2 h, 3 h, 4 h, 5 h, 6 h, 7 h, 8 h) for GC analysis.



Scheme S1. Proposed mechanism for the acetophenone cyanosilylation. Synergistic mode of activation by Cl⁻ together with the imidazolium cation of [bmim]Cl.

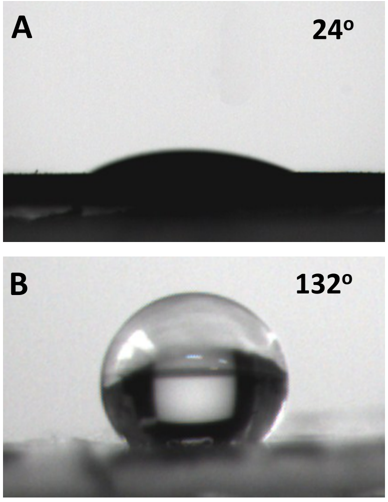


Fig. S1. Appearance of a water droplet in air on a disk of compressed silica particles. (A) Unmodified silica and (B) hydrophobically modified silica nanoparticles (emulsifiers).

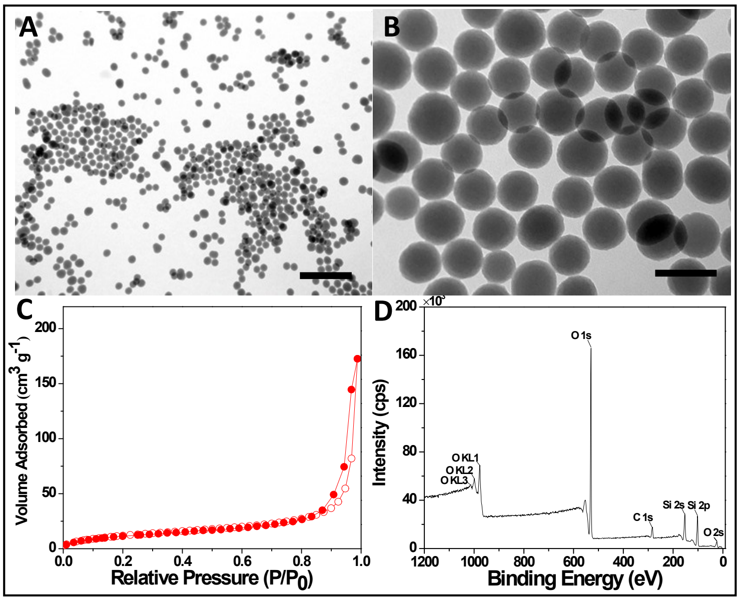


Fig. S2. Characterization of silica particle emulsifier. (A) TEM image, scale bar = 500 nm; (B) higher magnification TEM image, scale bar = 100 nm; (C) N_2 adsorption (open points)–desorption (filled points) isotherms. Specific surface area is 47 $m^2 g^{-1}$; (D) XPS spectrum. According to the results of elemental analysis, the methyl loading on the silica emulsifier was estimated as 1.14 mmol g^{-1}.

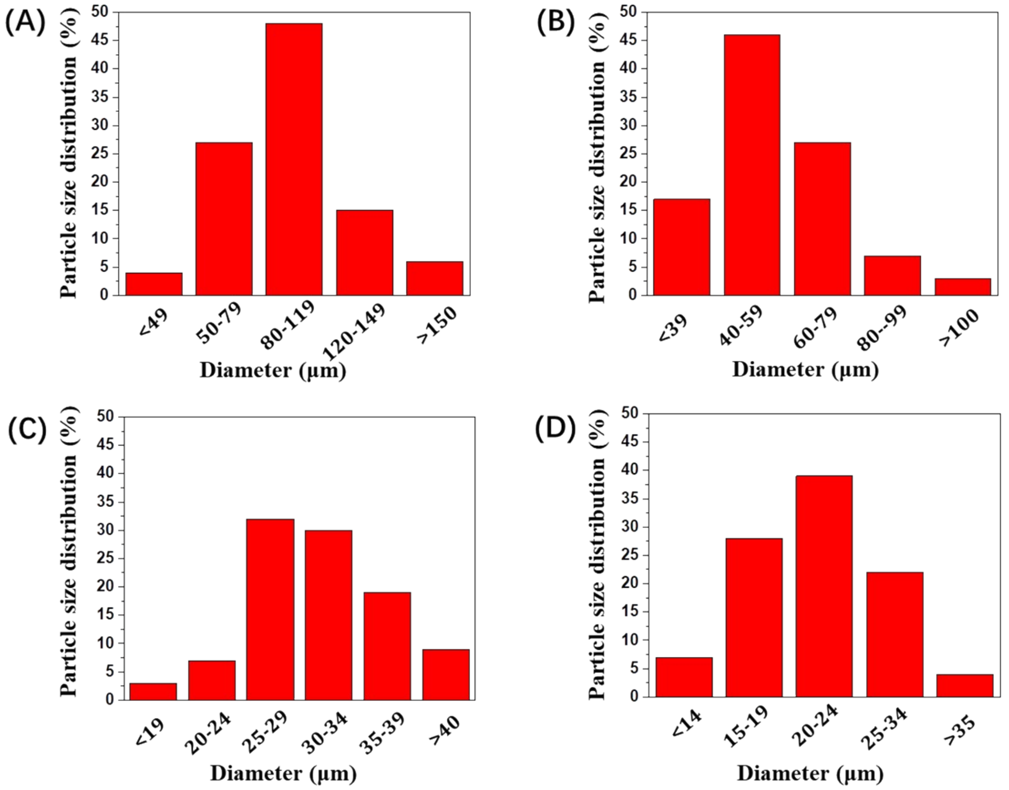


Fig. S3. Droplet size distributions of IL-in-oil Pickering emulsion systems prepared with different amounts of emulsifier: (A) 1 wt%, (B) 2 wt%, (C) 3 wt%, (D) 4 wt%.

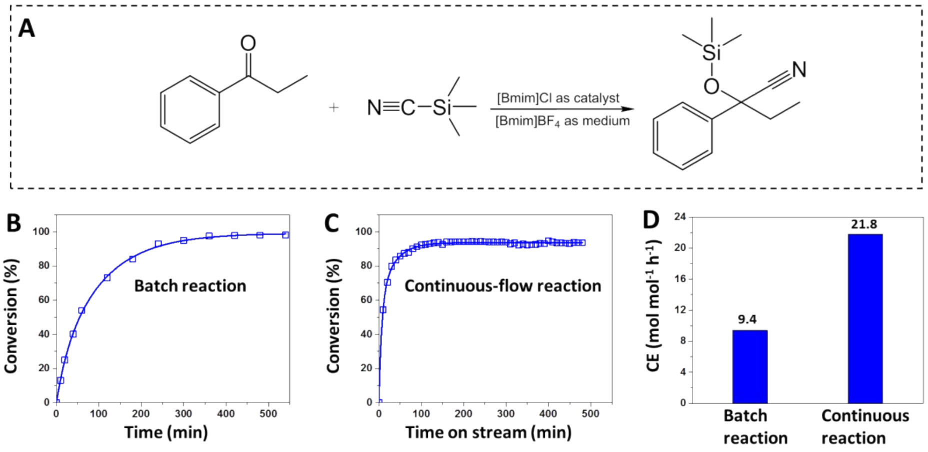


Fig. S4. Comparison of [bmim]Cl-catalyzed cyanosilylation reactions in the batch system and in the IL droplet-based continuous-flow system. (A) Propiophenone cyanosilylation reaction. (B) Kinetic profile for substrates propiophenone cyanosilylation in the batch system. (C) Conversions of propiophenone with time in the IL droplet-based flow system. (D) Catalysis efficiency (CE) comparison for the propiophenone cyanosilylation in the batch system and in the IL droplet-based flow system. For the batch reaction, CE is calculated according to the conversion within the first 300 min. For the flow reaction, CE is calculated after the conversion levelled off. Batch reaction conditions: 0.6 g [bmim]BF_4, 0.006 g [bmim]Cl, 0.1 M propiophenone and 0.36 M TMSCN in *n*-octane (17 mL), 25 ^{o}C, 2600 rpm. Reaction conditions for the continuous-flow system: the IL-based Pickering emulsions consist of 0.45 g [bmim]BF_4, 0.0045 g [bmim]Cl, 0.2 mL *n*-octane and 0.014 g emulsifier, 0.1 M propiophenone and 0.36 M TMSCN in *n*-octane (17 mL) as mobile phase, 25 ^{o}C, flow velocity = 6 mL h^{-1}.

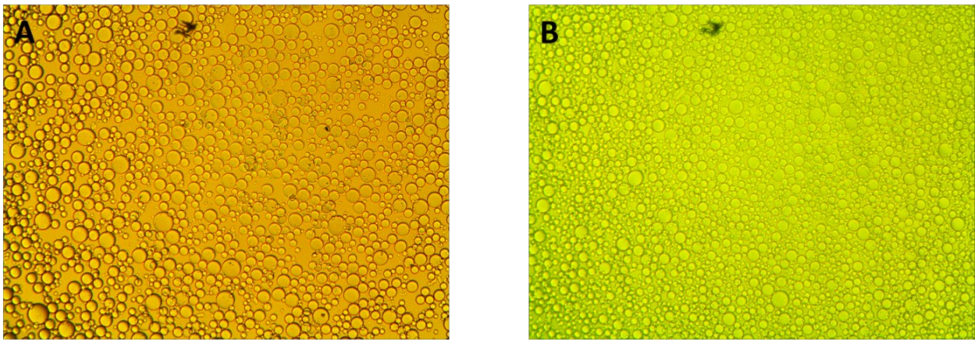
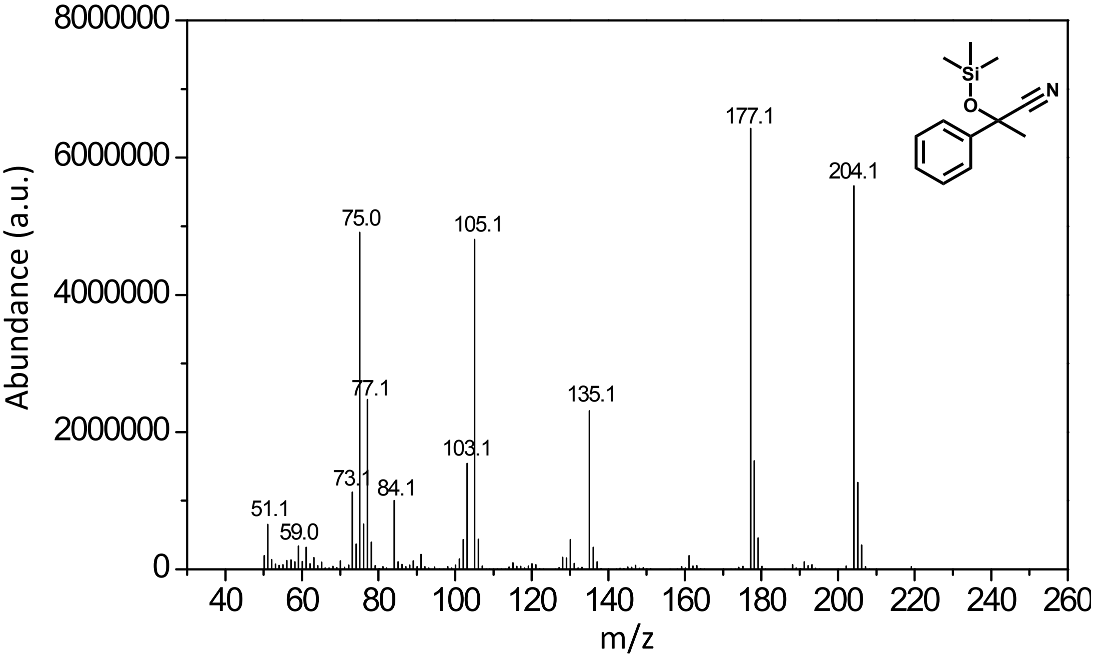
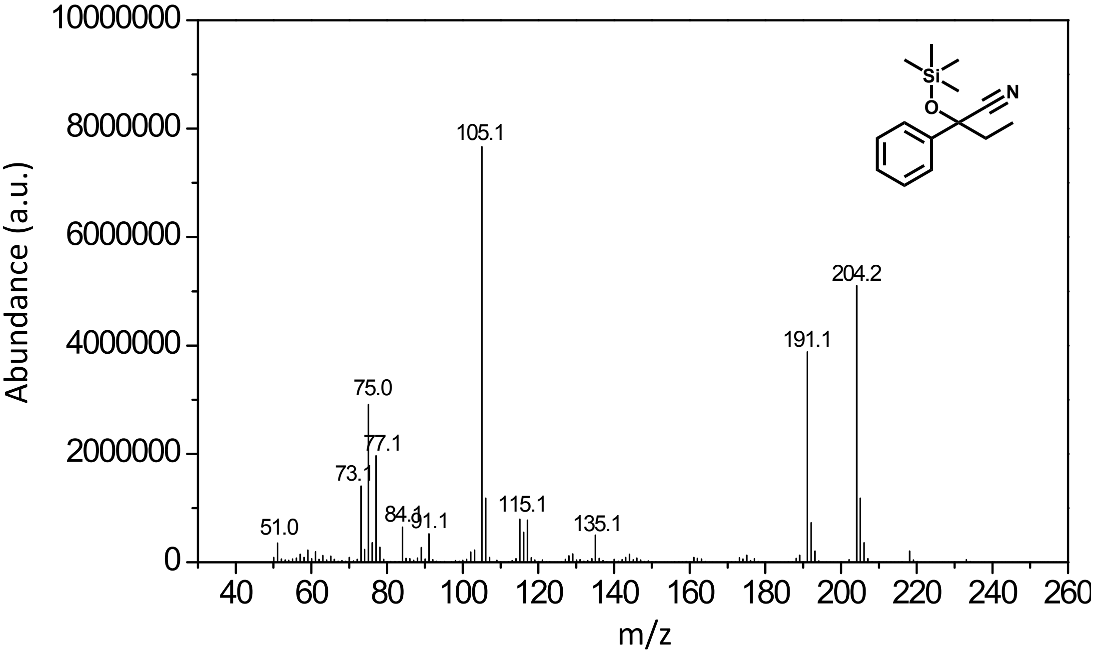


Fig. S5. Optical micrographs for the IL-in-oil Pickering emulsions before and after flowing for 100 h at 25 ^{o}C. (A) Before flowing for 100 h. (B) After flowing for 100 h, Scale bar = 100 µm. The emulsion consists of 5.6 g [bmim]BF_4, 0.168 g [bmim]Cl (3 wt % with respect to [bmim]BF_4), 2 mL *n*-octane and 0.168 g emulsifier.

Mass Spectrometry Spectra





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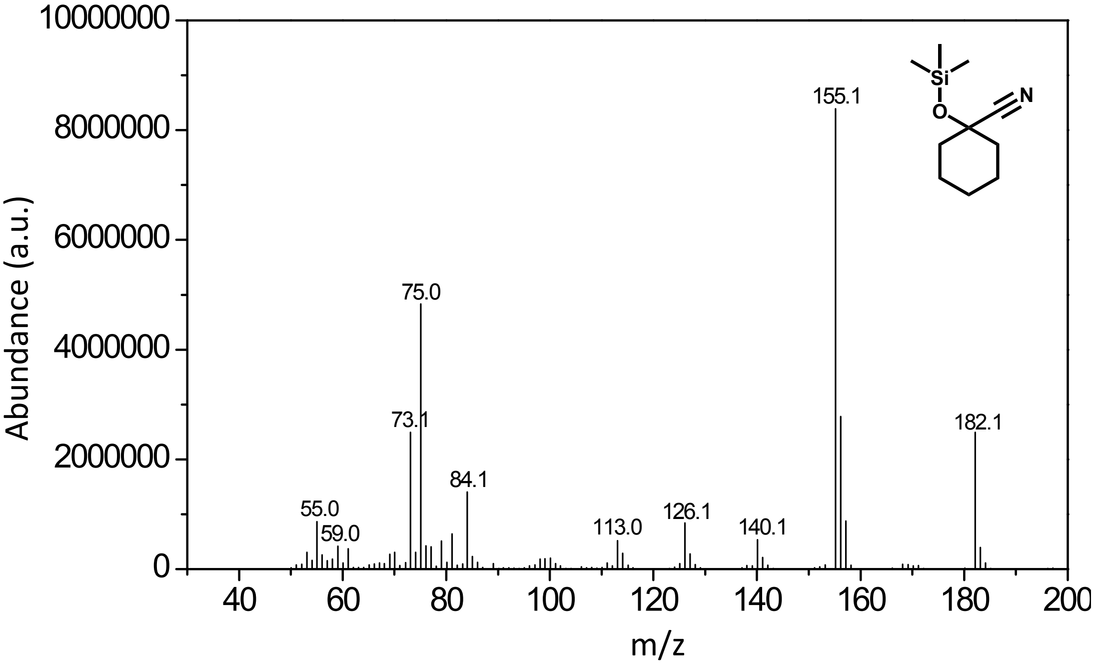
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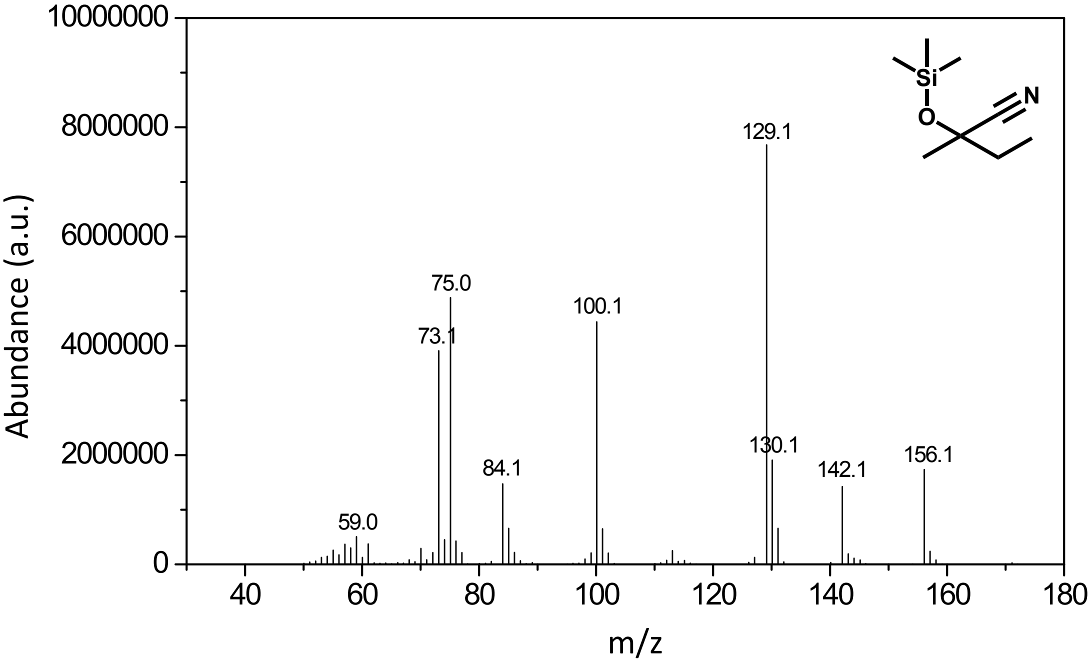
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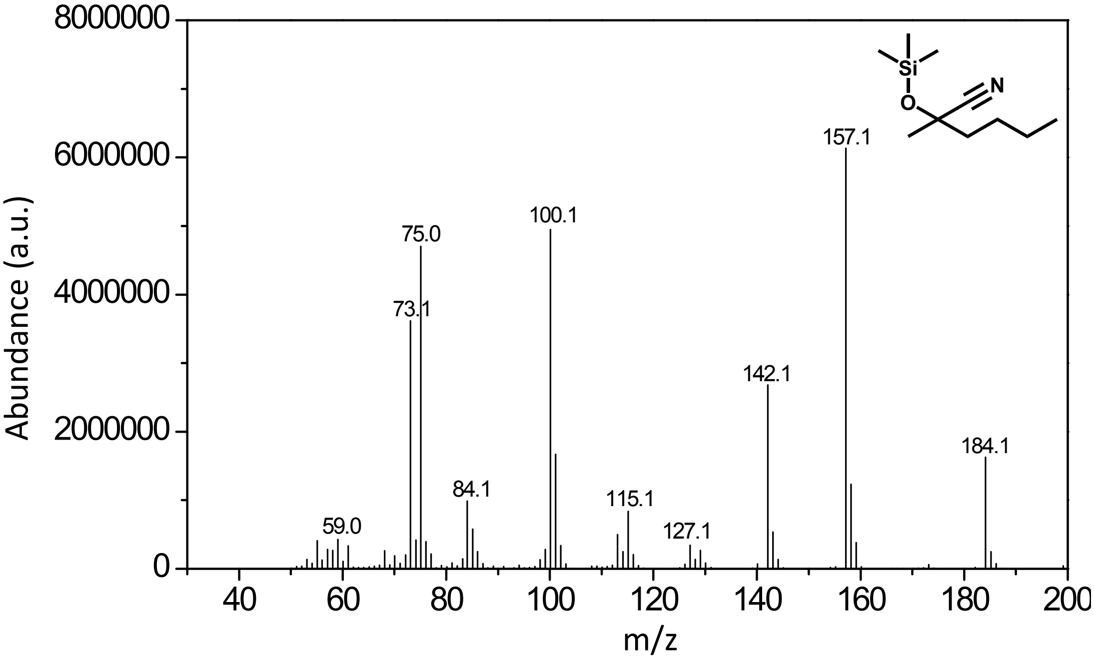
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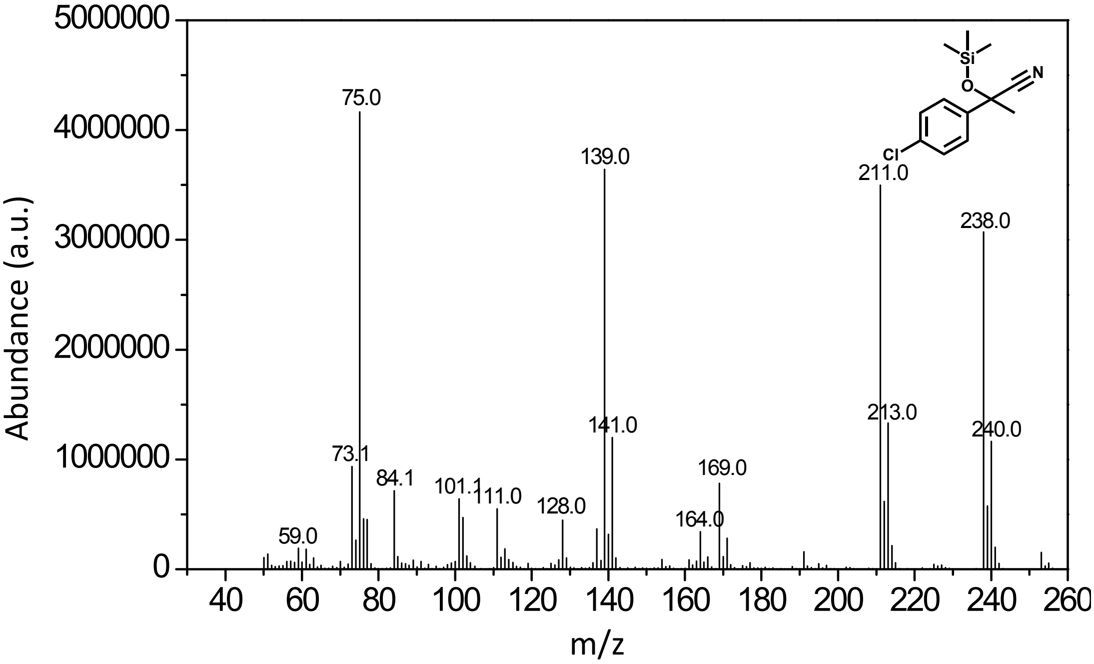
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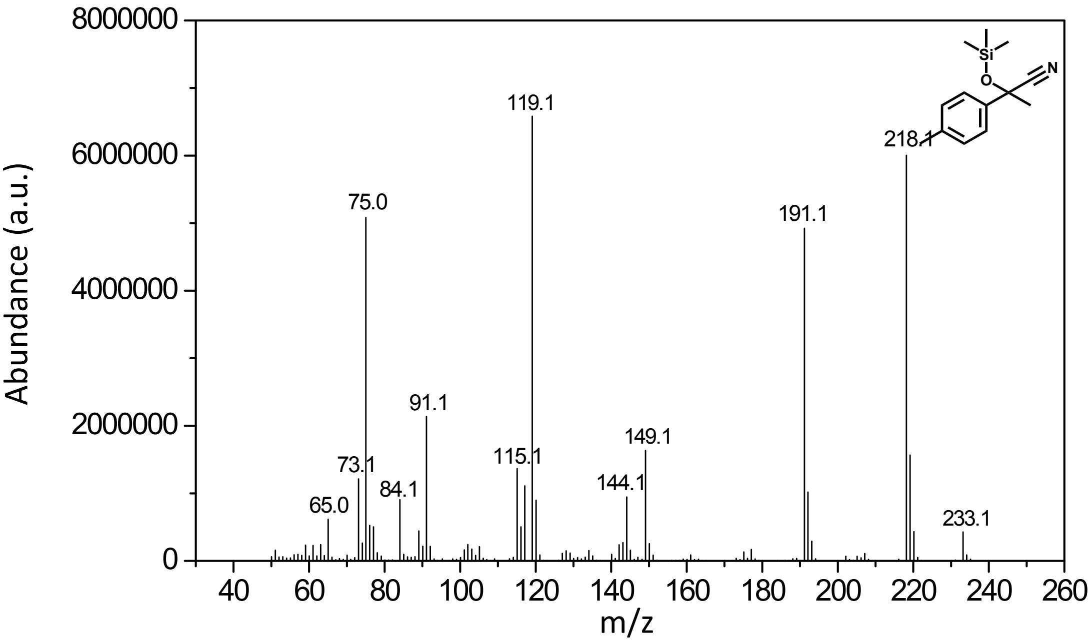

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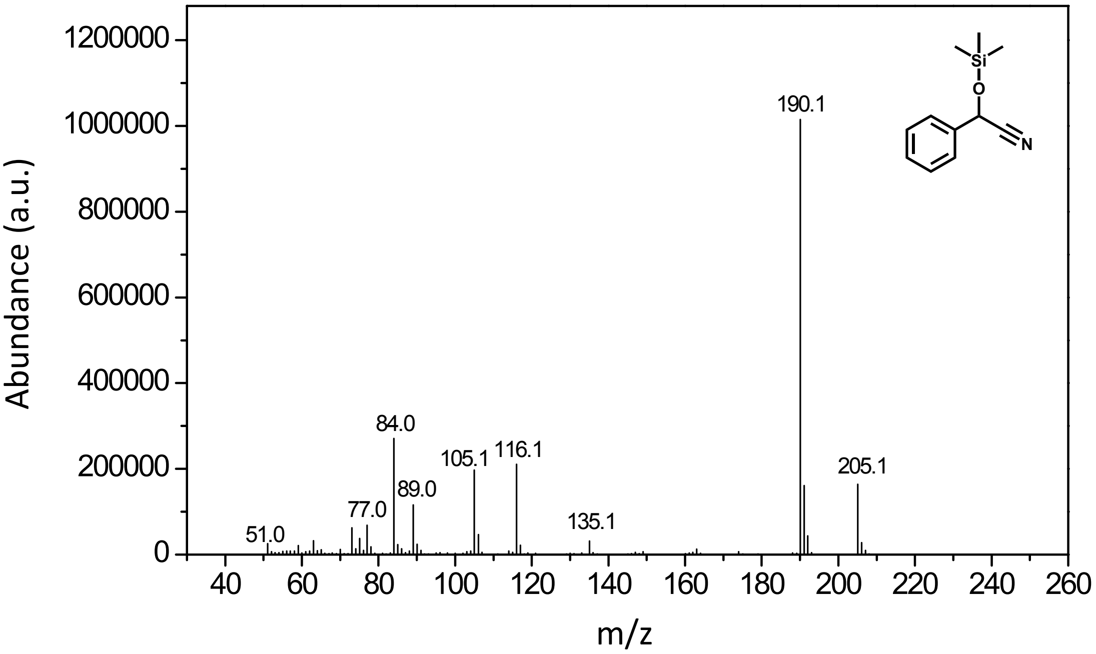
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