

## Supplementary information

# TIPS-benzene-based two-dimensional perovskites

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## 1. Experimental section

### *Materials*

All materials were of reagent grade and used as received. *N, N*-Dimethylformamide and  $\text{PbBr}_2$  were purchased from Sigma-Aldrich. All other reagents were purchased from Tokyo Chemical Industry Co., Ltd.

### *Synthesis of TIPS-PEA amine*

4-Bromophenethylamine (34.8 g, 208 mmol), triisopropylsilylacetylene (38.0 g, 174 mmol), bis(triphenylphosphine)palladium(II) dichloride (6.03 g, 8.6 mmol), tri-*tert*-butylphosphonium tetrafluoroborate (2.49 g, 8.06 mmol), and copper(I) iodide (1.64 g, 8.6 mmol) were mixed in toluene (3 L) under stirring. The resulting solution was degassed by argon bubbling, followed by the addition of triethylamine (780 mL). The mixture was heated at 333 K for 6 h under an argon atmosphere and then naturally cooled down to room temperature. The mixture was passed through a 150 g silica gel plug and eluted with toluene (18 L). The eluate was concentrated on a rotary evaporator (yield: 58 g). The residue was purified by column chromatography on silica gel (4 kg), using chloroform/methanol (1:1, v/v), and the collected material was concentrated on a rotary evaporator (yield: 33 g). The formation of 4-(triisopropylsilylethynyl)-2-phenylethylamine was confirmed by NMR.

### *Synthesis of TIPS-PEABr and TIPS-PEAI salts*

TIPS-PEABr and TIPS-PEAI salts were synthesized using a neutralization method.<sup>1-3</sup> First, ethanol solutions of as-prepared TIPS-PEA and HBr or HI aqueous solutions were prepared with equal volumes and concentrations. HBr or HI solution was gradually added dropwise to the TIPS-PEA solution under stirring in an ice bath. After stirring for 2 h, ethanol was removed using a vacuum evaporator for 3 h. We note that to avoid overlapping optical properties between TIPS-PEA and 2D perovskites, we choose bromide and iodide TIPS-PEA salts and the corresponding 2D perovskites.

### *2D Perovskite sample preparation*

The 2D perovskites of (TIPS-PEA)<sub>2</sub>PbBr<sub>4</sub> and (TIPS-PEA)<sub>2</sub>PbI<sub>4</sub> layers were deposited by spin-coating the precursor solution, which is an *N, N*-dimethylformamide solution containing 1 M TIPS-PEABr or TIPS-PEAI and 0.5 M PbBr<sub>2</sub> or PbI<sub>2</sub>, on quartz substrates at 3000 rpm for 30 s, followed by annealing at 100 °C for 10 min in a dry room (temperature: 291 K, dew point: <243 K).

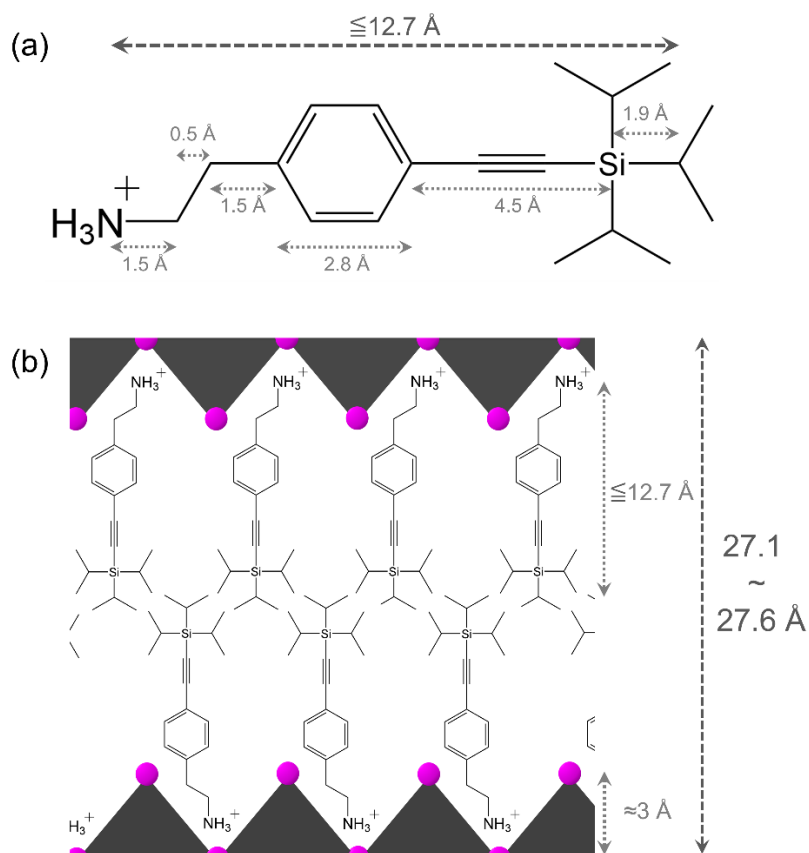
For the coating of TIPS-PEAI over a 3D perovskite (Fig. S2), 3D perovskite (Cs<sub>0.06</sub>FA<sub>0.94</sub>PbI<sub>3</sub>) was deposited on titanium oxide/fluorine-doped tin oxide substrate, along with previously reported methods<sup>1-4</sup>, and then, 15 mM TIPS-PEAI isopropyl alcohol solution was spin-coated at 3000 rpm for 30 s over the 3D perovskite, followed by heating at 353 K for 10 min.

## *Characterization*

The photoluminescence (PL) and excitation spectra were measured using a fluorescence spectrometer (Fluorolog-QM, Horiba). The 50  $\mu\text{L}/\text{mL}$  TIPS-PEA solution filled in a 1 mm path cuvette with  $\text{N}_2$  atmosphere was excited at 295 nm for the PL measurement (Fig. 2). As for excitation spectra (Fig. 2), the emission at 340 nm was swept. For  $(\text{TIPS-PEA})_2\text{PbBr}_4$  and  $(\text{TIPS-PEA})_2\text{PbI}_4$ , the PL spectra (Fig. 4) were measured with excitations at 350 nm and 450 nm, respectively, from the glass side. The PL lifetime (Fig. S1) was measured by fluorescence spectrometer (Fluorolog-QM, Horiba) equipped with a time-correlated single-photon counting system; the sample was excited at 409 nm and PL was detected at 520 nm. The PL stability (Fig. S2) was evaluated using the fluorescence spectrometer with a fixed sample position under a continuous irradiation from a 409 nm laser (Delta diode, Horiba) with a fluence of  $0.23 \text{ W cm}^{-2}$  in ambient air (approximately 23% relative humidity at 292 K). The relative PL intensities at 510 nm were plotted. Ultraviolet–visible absorption spectra were measured using a spectrophotometer (UV3600, Shimadzu). XRD patterns of the 2D perovskites were acquired using a SmartLab 2080A202 diffractometer (Rigaku). The contact angle of water droplets on the 2D perovskite was measured using a contact angle meter (Kyowa Interface Science Co.; DMo-401), and the contact angle values were determined as the average of eight measurements, and these error bars

represented by the standard deviation. NMR measurements were performed using a JNM-ECZ400S/L1 (JEOL Co. Ltd).

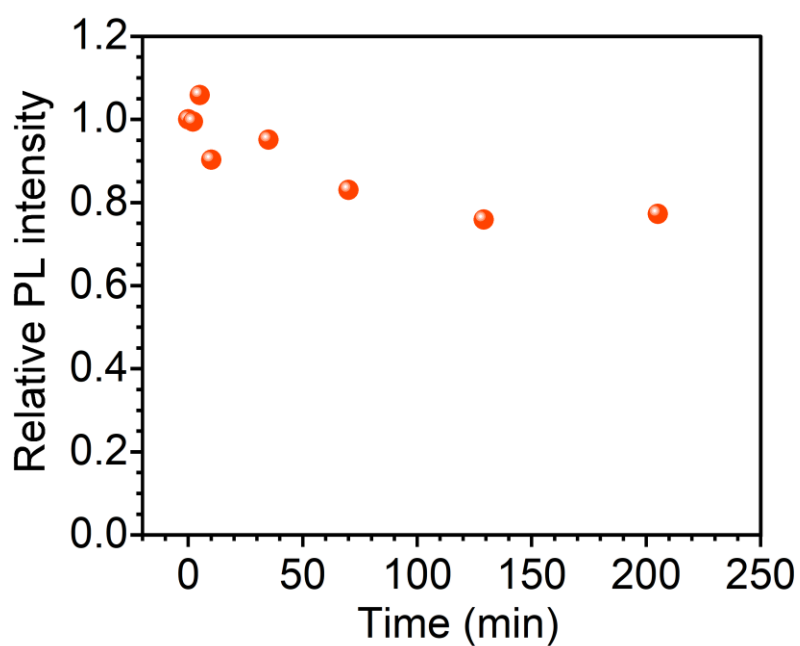
## 2. Structural calculations of TIPS-PEA and the 2D perovskites



**Fig S1.** (a) Size calculation for TIPS-PEA molecule, (b) structural calculation for 2D perovskites

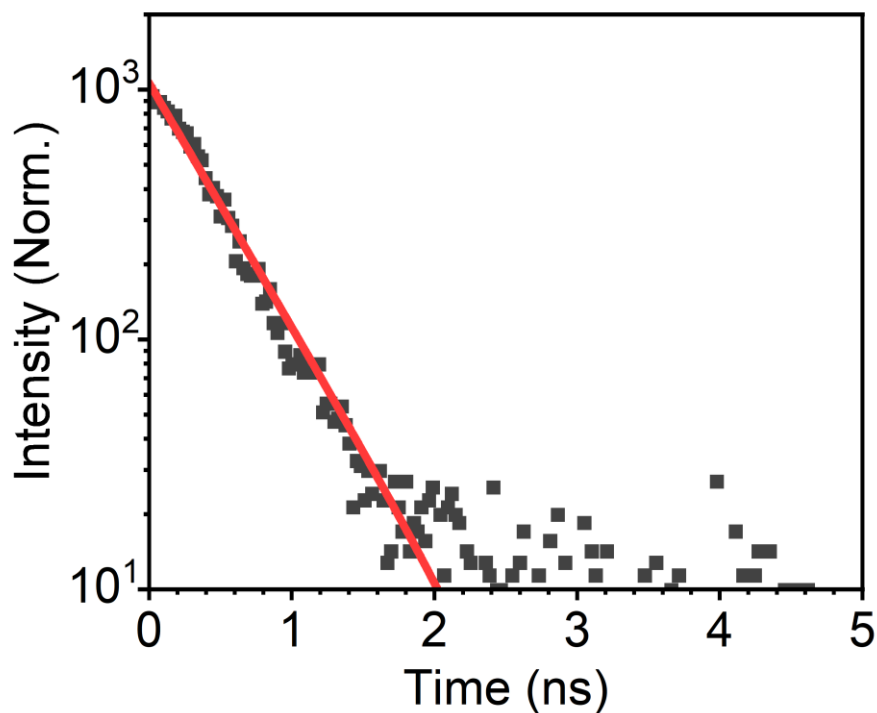
The length of the TIPS-PEA molecule, from the ammonium N ( $\text{NH}_3^+$ ) to the outermost C on isopropyl group, was calculated to be  $\leq 12.7 \text{ \AA}$  based on the bond lengths, which is maximum possible geometric extent (Fig. S1a). For the 2D perovskite structure, taking account of the  $\text{NH}_3^+$  head group in TIPS-PEA embedded to the approximately half of Pb-X slab (original  $\approx 6 \text{ \AA}$ <sup>5 6</sup>;  $\approx 3 \text{ \AA}$  for the half), the estimated  $d$ -values (27.1–27.6  $\text{\AA}$ ) for (001) crystal plane of  $(\text{TIPS-PEA})_2\text{PbX}_4$  ( $X = \text{Br, I}$ ) match the calculated length of TIPS-PEA (Fig. S1b;  $(12.7 \times 2) + 3 \approx 28 \text{ \AA}$ , which is close to 27.1–27.6  $\text{\AA}$ ).

### 3. PL Stability of TIPS-PEA-based 2D perovskite



**Fig. S2** PL stability of  $(\text{TIPS-PEA})_2\text{PbI}_4$  at 510 nm under continuous excitation at 409 nm with a fluence of  $0.23 \text{ W cm}^{-2}$  in an ambient air (approximately 23% relative humidity at 292 K)

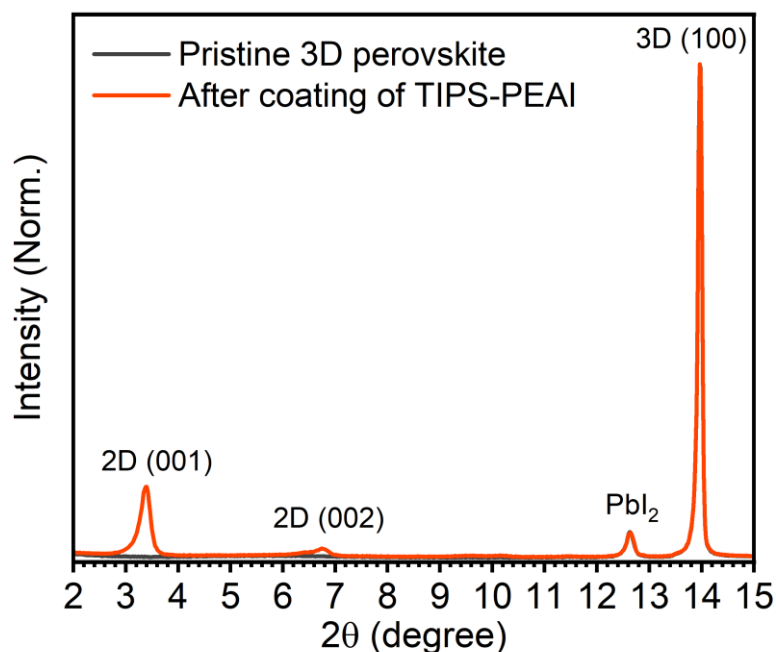
#### 4. PL lifetime of TIPS-PEA-based 2D perovskite



**Fig. S3** PL lifetime of  $(\text{TIPS-PEA})_2\text{PbI}_4$

The estimated PL lifetime with a single exponential fitting was  $0.45 \pm 0.01$  ns, indicating that the observed PL was directly via exciton not via charge separation. This is attributed to the strong confinement effects of the 2D perovskite, supporting the formation of the  $(\text{TIPS-PEA})_2\text{PbI}_4$  2D perovskite.

## 5. Supporting data for TIPS-PEA-based 2D perovskite formation

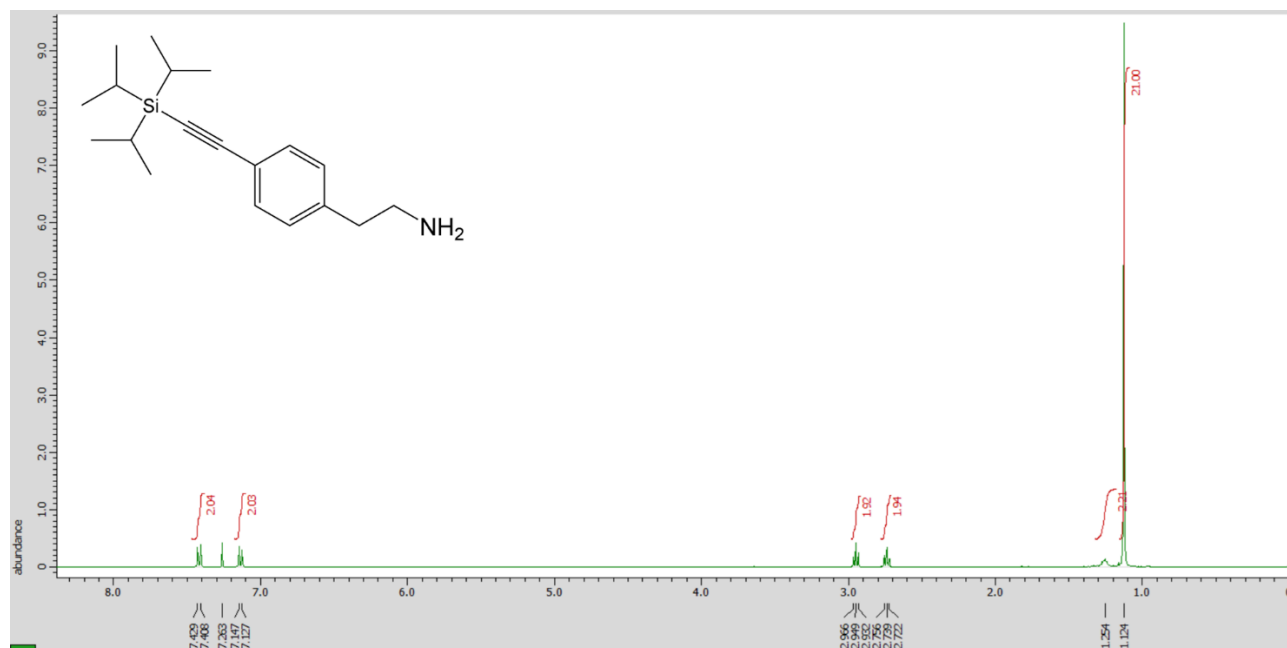


**Fig. S4** XRD patterns of 3D perovskites before and after coating of TIPS-PEAI

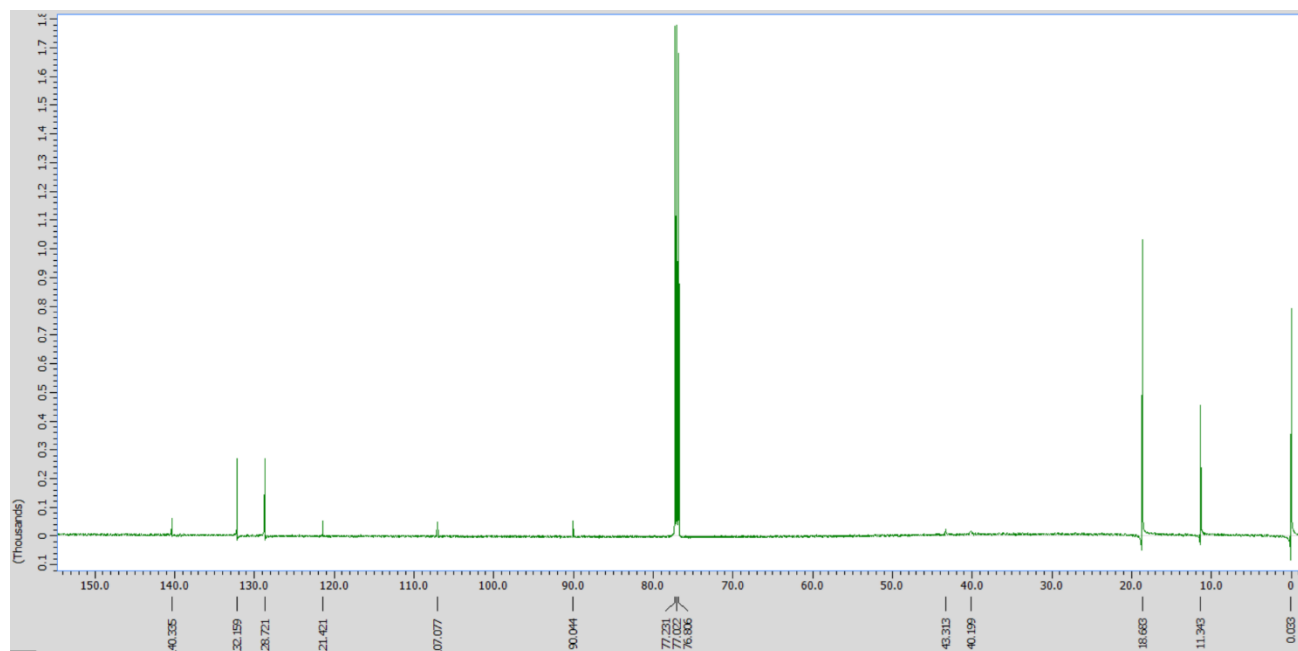
The coating of TIPS-PEAI over perovskite led to additional XRD peaks corresponding to (001) and (002) planes of 2D perovskites, indicating applicability of TIPS-PEA-based 2D perovskite passivation over 3D perovskites.

In addition, one of the advantages for the perovskite passivation is hydrophobicity of the 2D perovskite overlayer, blocking moistures. Indeed, contact angle of water droplet to (TIPS-PEA)<sub>2</sub>PbI<sub>4</sub> was  $99 \pm 2^\circ$ , which is highly hydrophobic presumably owing to the presence of TIPS moiety.

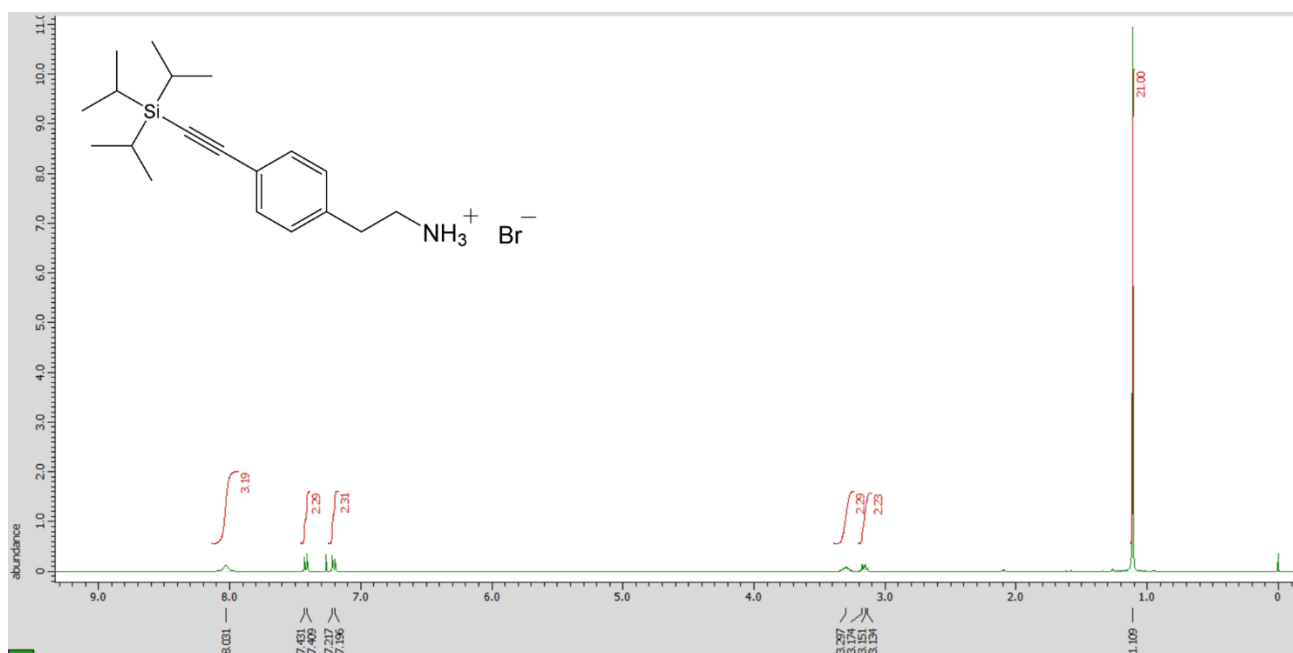
## 6. NMR spectra



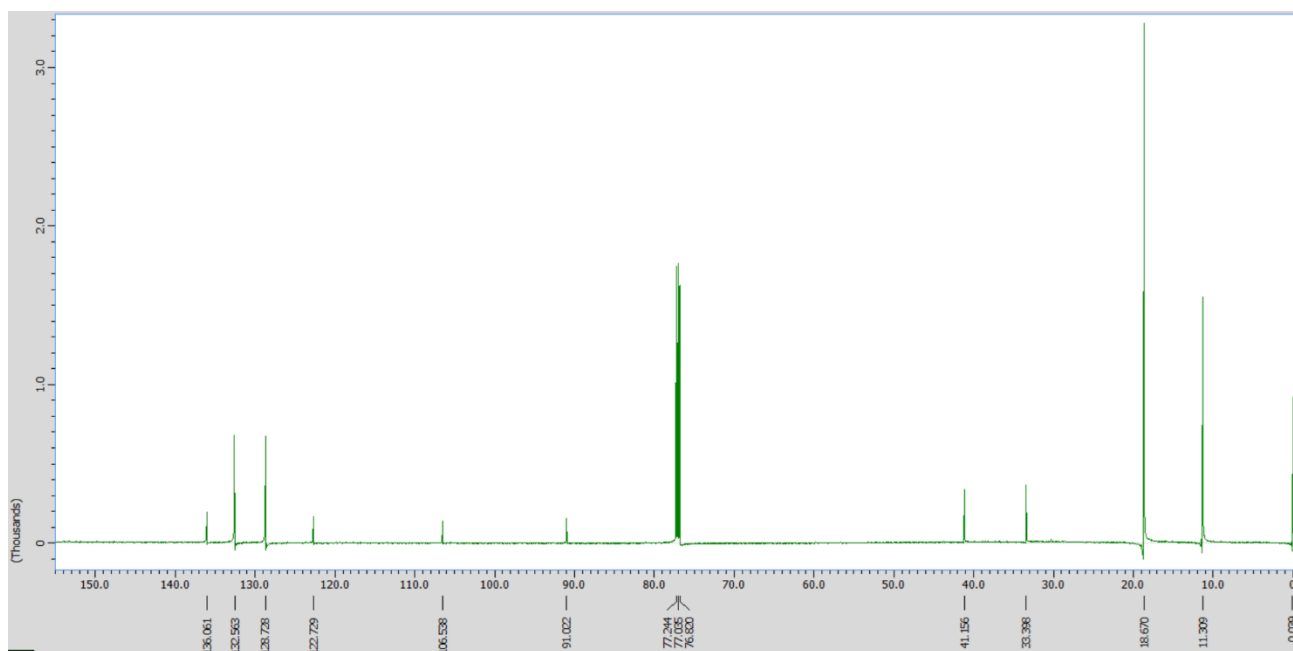
**Fig. S5** <sup>1</sup>H NMR spectrum of TIPS-PEA; (400 MHz, CDCl<sub>3</sub>): δ=7.41–7.43 (m, 2H, Ar), 7.13–7.15 (m, 2H, Ar), 2.93–2.97 (t, 2H; CH<sub>2</sub>), 2.72–2.76 (t, 2H; CH<sub>2</sub>), 1.25 (Br, 2H; NH<sub>2</sub>), 1.12 (s, 21H; CH<sub>3</sub>).



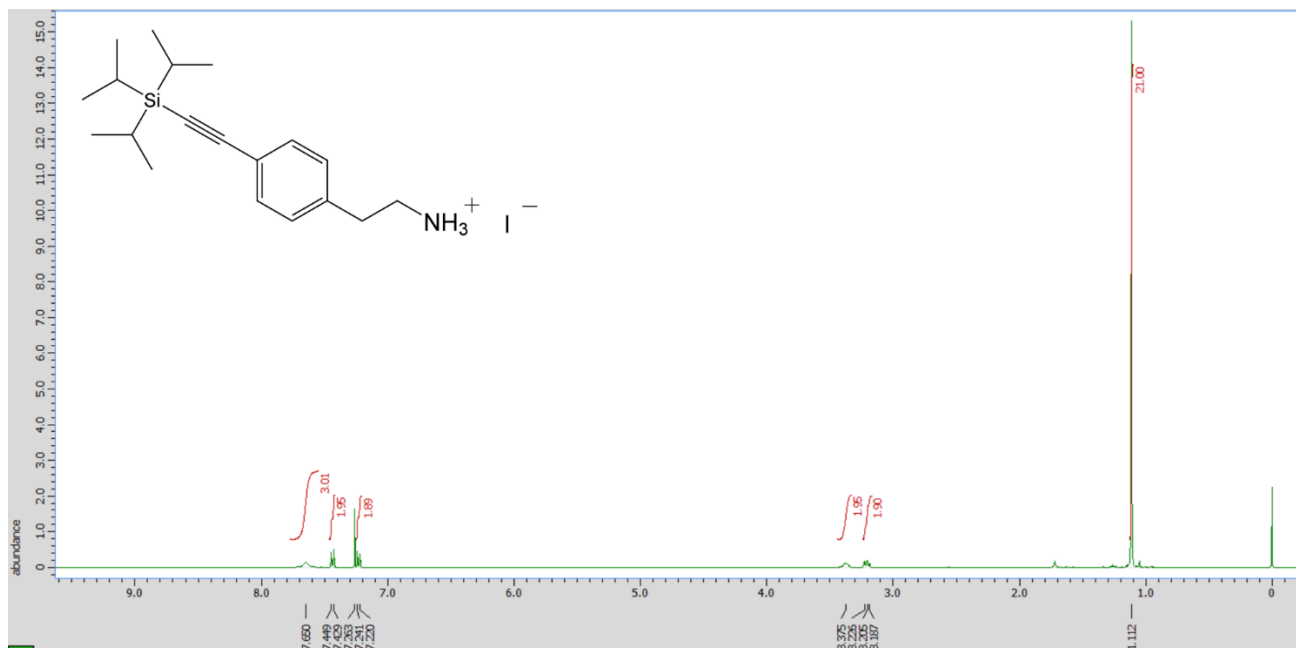
**Fig. S6** <sup>13</sup>C NMR spectrum of TIPS-PEA; (100 MHz, CDCl<sub>3</sub>).



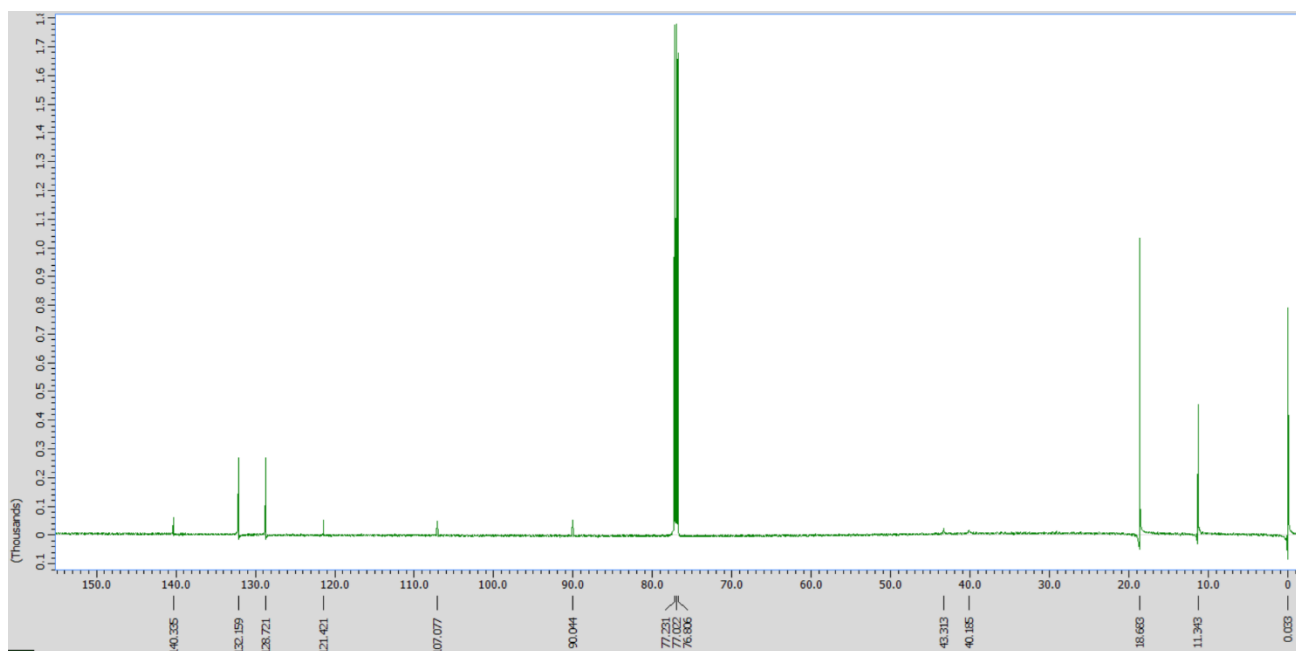
**Fig. S7**  $^1\text{H}$  NMR spectrum of TIPS-PEABr; (400 MHz,  $\text{CDCl}_3$ ):  $\delta=8.03$  (Br, 3H;  $\text{NH}_3$ ), 7.41–7.43 (m, 2H, Ar), 7.20–7.22 (m, 2H, Ar), 3.30 (m, 2H;  $\text{CH}_2$ ), 3.13–3.15 (m, 2H;  $\text{CH}_2$ ), 1.11 (s, 21H;  $\text{CH}_3$ ).



**Fig. S8**  $^{13}\text{C}$  NMR spectrum of TIPS-PEABr; (100 MHz,  $\text{CDCl}_3$ ).



**Fig. S9**  $^1\text{H}$  NMR spectrum of TIPS-PEAI; (400 MHz,  $\text{CDCl}_3$ ):  $\delta=7.65$  (Br, 3H;  $\text{NH}_3$ ), 7.43–7.45 (m, 2H, Ar), 7.22–7.26 (m, 2H, Ar), 3.38 (m, 2H;  $\text{CH}_2$ ), 3.19–3.23 (m, 2H;  $\text{CH}_2$ ), 1.1 (s, 21H;  $\text{CH}_3$ ).



**Fig. S10**  $^{13}\text{C}$  NMR spectrum of TIPS-PEABr; (100 MHz,  $\text{CDCl}_3$ ).

## References

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