Support information

Exploring π-Extended Chiral Ligands for Direct Detection of Circularly Polarized Light in 2D Chiral Perovskites

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Experimental sections:

Materials

[1,1′-Bis(diphenylphosphino)ferrocene]dichloropalladium(II), triethylamine and hydriodic acid, contains no stabilizer, distilled, 57 wt. % in H_2O, 99.99%, lead iodide (PbI_2), dimethyl sulfoxide (DMSO) and anhydrous chlorobenzene (CB) were purchased form Sigma-Aldrich. Di-tert-butyl decarbonate and 2-Phenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane were purchased form TCI Chemical. CH_2Cl_2, 1,4-dioxane and NaOH were purchased form DAEJUNG. (R/S)-1-(4-bromophenyl)ethan-1-amine were purchased from J's Science (South Korea). All chemicals were used without further purification.

Synthesis of (*R/S*)-BPEAs:

tert-butyl (*R/S*)-(1-(4-bromophenyl)ethyl)carbamate (1)

To a solution of (*R/S*)-1-(4-bromophenyl)ethan-1-amine (3 g, 15 mmol), triethylamine (2.28g, 22.5 mmol, 3.14 ml) in CH_2Cl_2 (30 ml) was slowly added di-tert-butyl decarbonate (3.27 g, 15 mmol, 3.44 ml) and stirred at room temperature over 3h. The mixture was washed several times with H_2O and brine. The combined organic layers were dried with anhydrous $MgSO_4$, filtered, and evaporated under reduced pressure. The crude product washed with hexane many times and used without further purification. Compound **1** was obtained as a white solid (4.14 g, 92%). ^{1}H NMR (600 MHz, CDCl$_3$): δ (ppm): 7.44 (d, J = 7.8 Hz, 2 H), 7.17 (d, J = 7.8 Hz, 2 H), 4.74 (br, 2 H), 1.42 (br, 12 H). ^{13}C NMR (151 MHz, CDCl$_3$): δ (ppm): 155.10, 143.33, 131.74, 127.74, 120.95, 79.74, 49.83, 28.50, 22.74

tert-butyl (*R*/*S*)-(1-([1,1'-biphenyl]-4-yl)ethyl)carbamate (2)

Compound **1** (1 g, 3.33 mmol), 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (0.68 g, 3.33 mmol) and $PdCl_2(dppf)$ (37 mg, 0.05 mmol) were dissolved in 1,4-dioxane (20 ml) under N_2 atmosphere and stirred until 80 °C. To this was added dropwise aqueous solution of NaOH (0.27 g, 6.66 mmol, 3.4 ml) and refluxed at 80 °C for 16h. The mixture was extracted with CH_2Cl_2 and washed several times with H_2O and brine. The combined organic layers were dried with anhydrous $MgSO_4$, filtered, and evaporated under reduced pressure. The crude product purified by column chromatography on silica gel using ethyl acetate/hexane (v/v, 1/8). Compound **2** was obtained as a white solid (855 mg, 86.3%). ^1H NMR (600MHz, $CDCl_3$): δ (ppm): 7.57 (d, J = 7.8 Hz, 2 H), 7.55 (d, J = 8.4 Hz, 2 H), 7.43 (t, J = 7.8 Hz, 2H), 7.37 (d, J = 7.8 Hz, 2 H), 7.34 (t, J = 7.2 Hz, 1 H), 4.84 (br, 2H), 1.48 (d, J = 6 Hz, 3H), 1.44 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm): 155.22, 143.20, 140.98, 140.19, 128.87, 127.47, 127.34, 127.20, 126.43

(*R*/*S*)-1-([1,1'-biphenyl]-4-yl)ethan-1-aminium iodide (BPEA)

To a solution of compound **2** (1g, 3.36 mmol) in 1,4-dioxane (15ml) was added 57 wt% hydroiodic acid and stirred under N_2 atmosphere at room temperature over 4h. After the monitoring by thin layer chromatography, the mixture was poured into diethyl ether (400ml) to precipitate the crude product. The crude product was filtered and washed with diethyl ether several times. Compound (R/S)-BPEA was obtained as a white solid (874 mg, 80%). ^1H NMR (600MHz, DMSO-d6): δ (ppm): 8.23 (s, 3 H), 7.74 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 7.2 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H), 7.48 (t, J = 7.8 Hz, 2H), 7.39 (t, J = 7.2 Hz, 1H), 4.49 (q, 1H), 1.52 (d, J = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, DMSO-d6): δ (ppm): 140.39, 139.46, 138.25, 129.04, 127.77, 127.41, 127.06, 126.76, 49.70

Perovskites Precursor Solution Preparation

Thin films and single crystals were prepared with a Pb perovskite precursor solution by dissolving 92.2mg of lead iodide, 130mg of (*R/S*)-1-([1,1'-biphenyl]-4-yl) ethan-1-aminium iodide into 1ml of DMSO. Before fabricating the perovskite film, the solutions were stirred for overnight at 60°C.

Fabrication of Chiral Perovskites Thin Film Devices

Glasses were rinsed sequentially with deionized water, acetone, and isopropyl alcohol. Rinsed substrates were treated with O_2 plasma for 20 min at 100 W. After that, perovskite precursor solutions were spin-coated at 4000 rpm for 30 s on glass substrate followed by annealing at 150°C for 10min. Then, 40nm thick Au layers were thermally evaporated under vacuum through a shadow mask, the channel length (L) and width (W) are 50 and 1000 μm.

Fabrication of Chiral Perovskites Single Crystals

Perovskite single crystals were prepared with a PbI_2 perovskite precursor solution by dissolving 115.25 mg of Lead iodide, 162.5 mg of (*R/S*)-1-([1,1'-biphenyl]-4-yl) ethan-1-aminium iodide into 0.5 ml of DMSO with about 5ml of chlorobenzene. The precursor solutions were stirred for overnight at 60°C first before mixing with chlorobenzene. Then, the solutions were mixed with chlorobenzene and let it stay in the glovebox for overnight until the crystals grew up completely.

Material Characterization

^{1}H NMR and ^{13}C NMR spectra were recorded on VARIAN VNMRS 600 MHz NMR spectroscopy, with tetramethylsilane as an internal reference. The absorption and CD spectra of organic ligands were measured on a Jasco V-730 model UV-visible spectrophotometers and J-1500 model CD spectroscopy. The background was air, and the CD spectra were obtained at a scan rate of 100 nm/min, with a data pitch of 0.1 nm using 10 mm quartz cell. The absorption and CD spectra of perovskite film were measured on a J-815 model CD spectroscopy. Cyclic voltammetry was performed on a Won a Tech ZIVE sp1 electrochemical analyzer with a three-electrode cell and Ag/Ag$^+$ reference electrode in a 0.1 mol L^{-1} Bu$_4$NBF$_4$ solution in acetonitrile at a scan rate of 100 mV s^{-1}. The synthesized organic monomers were dissolved in electrolyte. Electrochemical potential of the materials was calculated with respect to ionization potential of ferrocene/ferrocenium ion (Fc/Fc+) as an internal standard, -4.8 eV. X-ray diffraction analyses were conducted using an X-ray diffractometer (Smart Lab, Rigaku) with Cu Kα radiation (λ = 1.5406 Å) at 40 kV/40 mA.

Device Characterization

The current–voltage (I–V) characteristics of the perovskites photoconductors were measured inside a vacuum chamber (< 5.0×10^{-5} Torr) using a Keithley 4200-SCS semiconductor parametric analyzer. To investigate the photocurrent of photoconductor devices, laser instrument (Lasertrack, maximum power of 55 mW) was used to generate monochromatic light. Circularly polarized illumination was created by passing the beam through a linear polarizer and a quarter-wave plate (Thorlabs), which were installed between the light source and samples.

The dissymmetry factor (g_{CD}), which stands for the ratio of CD to absorbance of the sample, was calculated from the equation below:

$$g_{CD} = 2\frac{A^L - A^R}{A^L + A^R} = \frac{CD}{32980 \times A}$$

where A^L is the absorption for LCPL, A^R is the absorption for RCPL, CD is the extracted value from CD spectroscopy, and A is the absorbance of the sample. In chiral optoelectronics, the dissymmetry factor can be defined in terms of measured photocurrents under LCPL and RCPL illumination. The equation can be redefined as follows,

$$g_{res} = 2\frac{I_{ph}^L - I_{ph}^R}{I_{ph}^L + I_{ph}^R}$$

where I_{Ph}^L and I_{Ph}^R are measured photocurrent under LCPL and RCPL illumination, respectively.
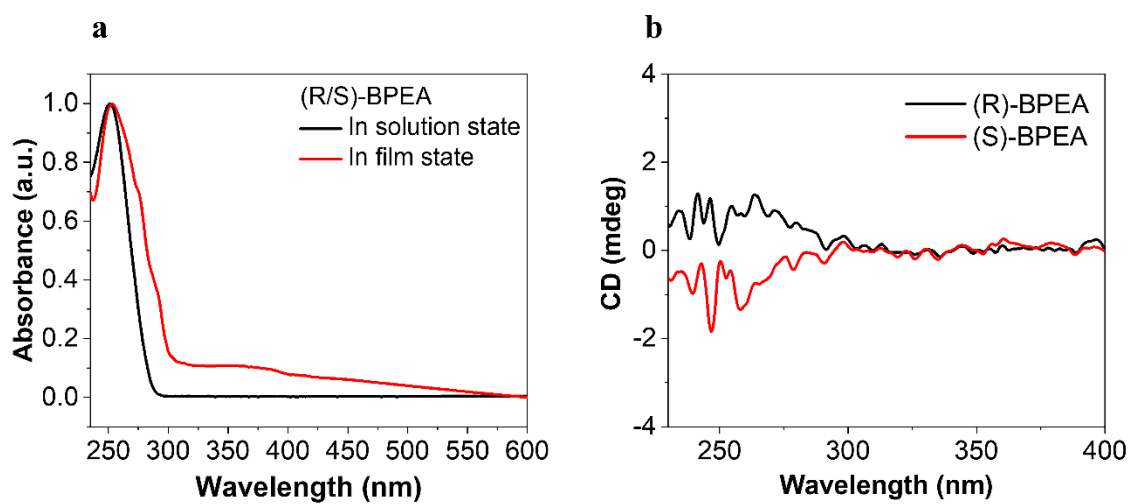
Figure S1. Chiroptical characteristics of (*R*/*S*)-BPEA a. absorption spectra, b. CD spectra.
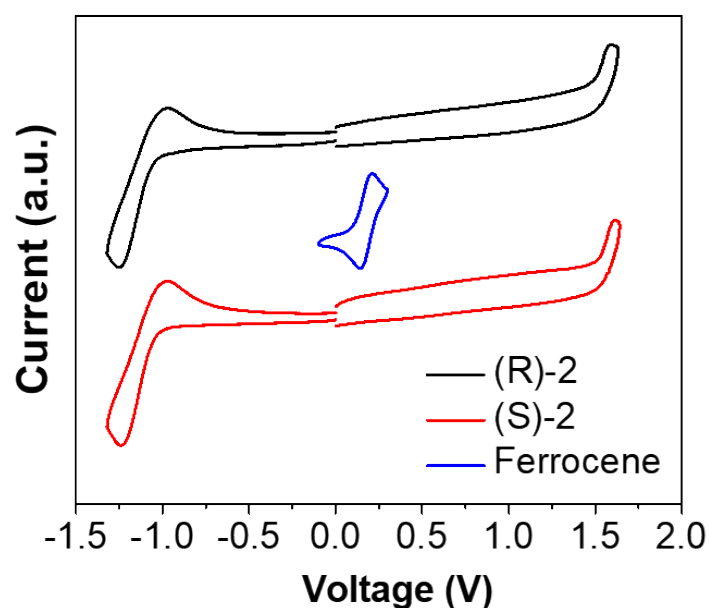
Materials	Electrochemical properties			
	E_{ox}/E_{HOMO} (V/eV)	E_{re}/E_{LUMO} (V/eV)	$E^{1/2}_{Ferr}$ (V)	E^{CV}_{g} (eV)
(R)-2	1.5 / -6.1	-1.0 / -3.6	0.176	2.5
(S)-2	1.5 / -6.1	-1.0 / -3.6	0.176	2.5

Figure S2. Cyclic voltammograms (CV) of Precursor (R/S)-BPEA

Cyclic voltammograms (CV) of (*R/S*)-2 and Ferrocene measured in Acetonitrile (0.1 mol L^{-1} Bu_4NPF_6) at a scan rate of 100mV s^{-1}

For organic cations, iodide precursors are not suitable for CV method due to the oxidation of iodide, so we measured the Boc groups, in this way the measured oxidation and reduction characteristics originate from their conjugation parts.
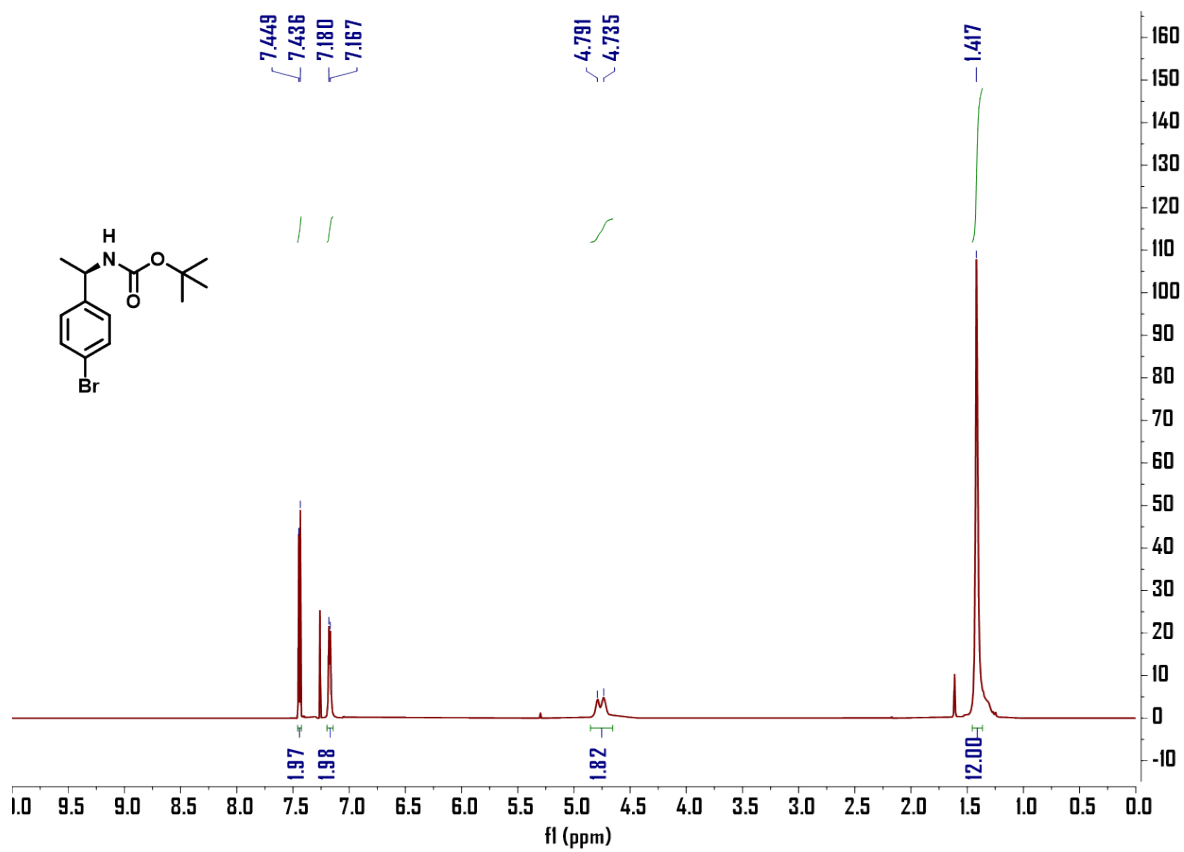
Figure S3. ^{1}H NMR spectrum of (**R**)-**1**
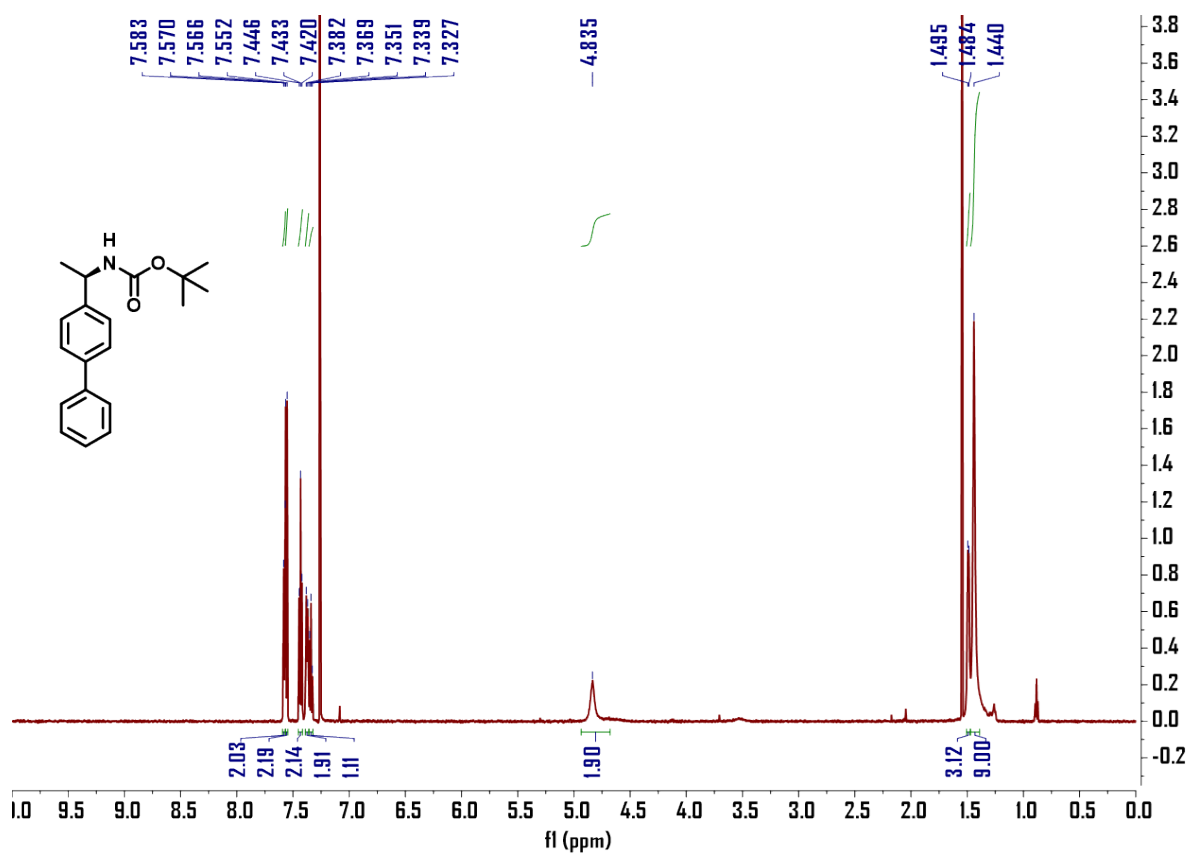
Figure S4. ^{1}H NMR spectrum of (*R*)-**2**
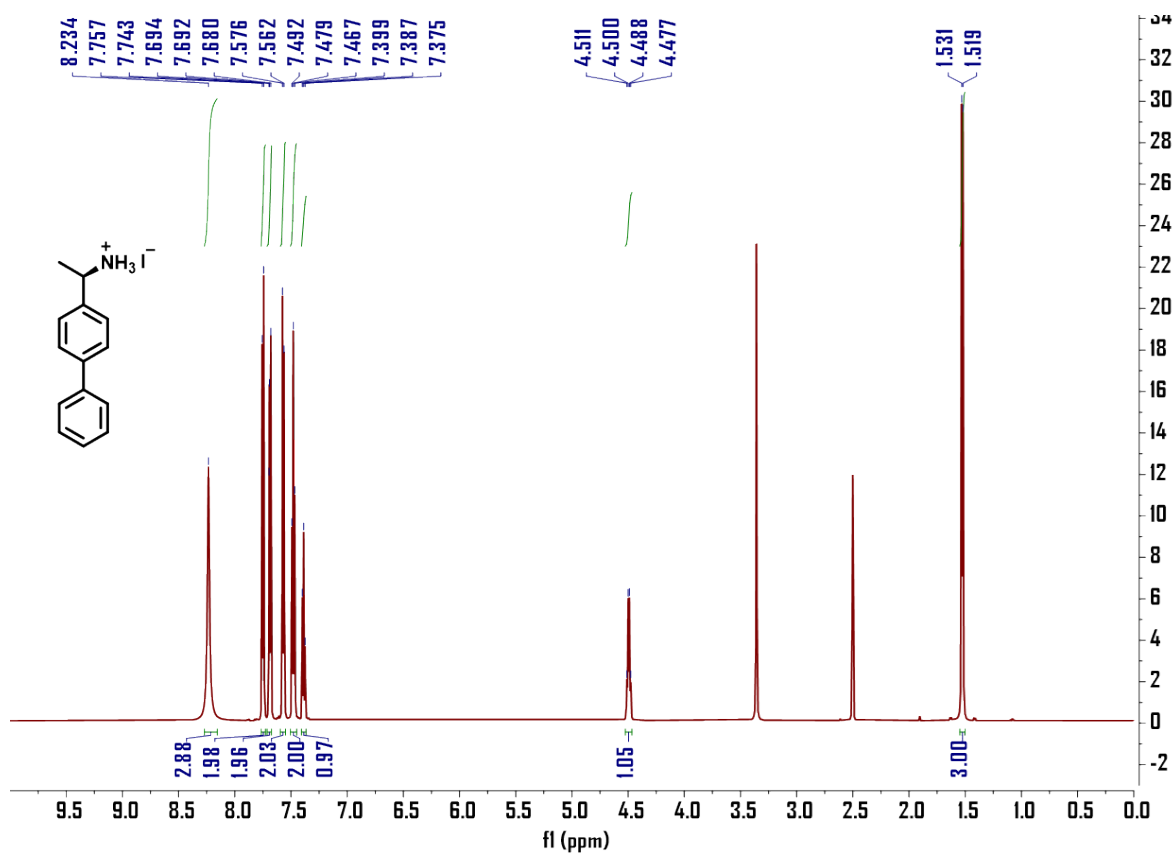
Figure S5. ¹H NMR spectrum of (*R*)-BPEA
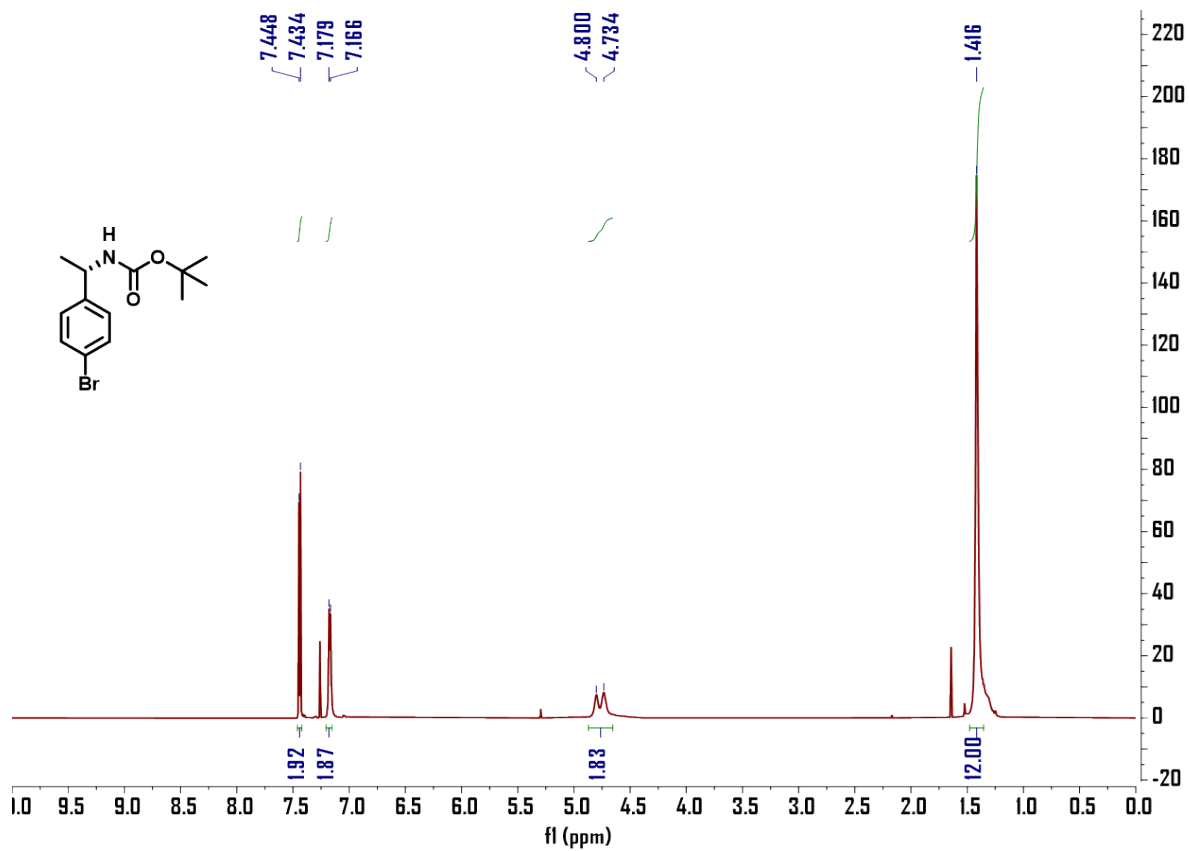
Figure S6. ¹H NMR spectrum of (*S*)-1
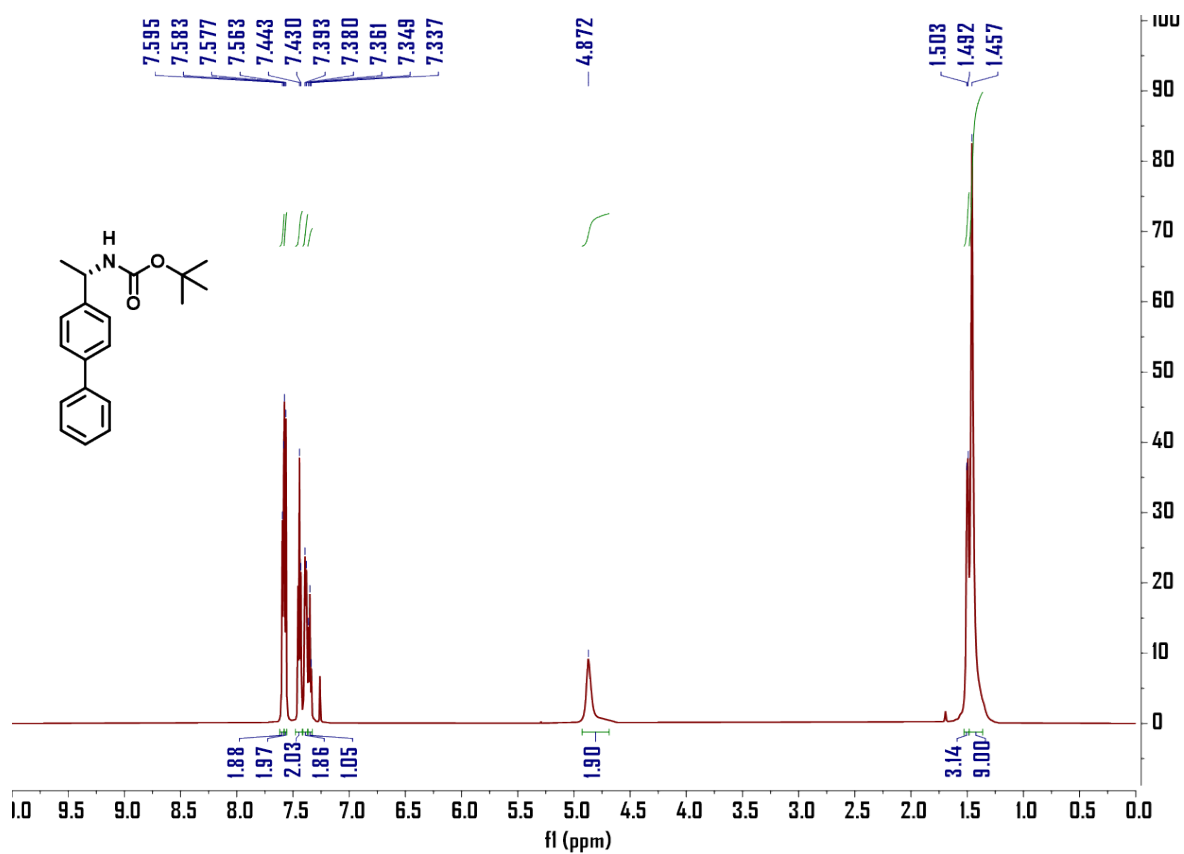
Figure S7. ^{1}H NMR spectrum of **(S)-2**
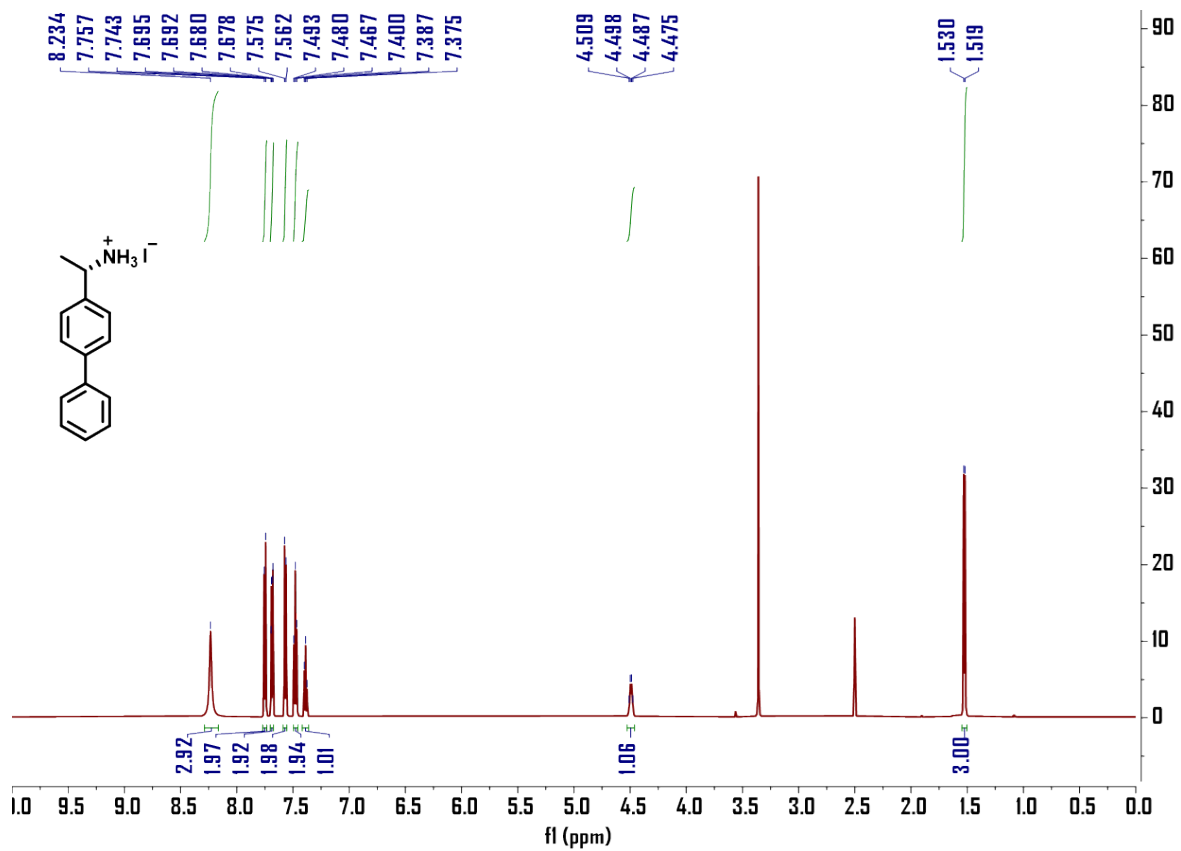
Figure S8. ^{1}H NMR spectrum of **(S)-BPEA**
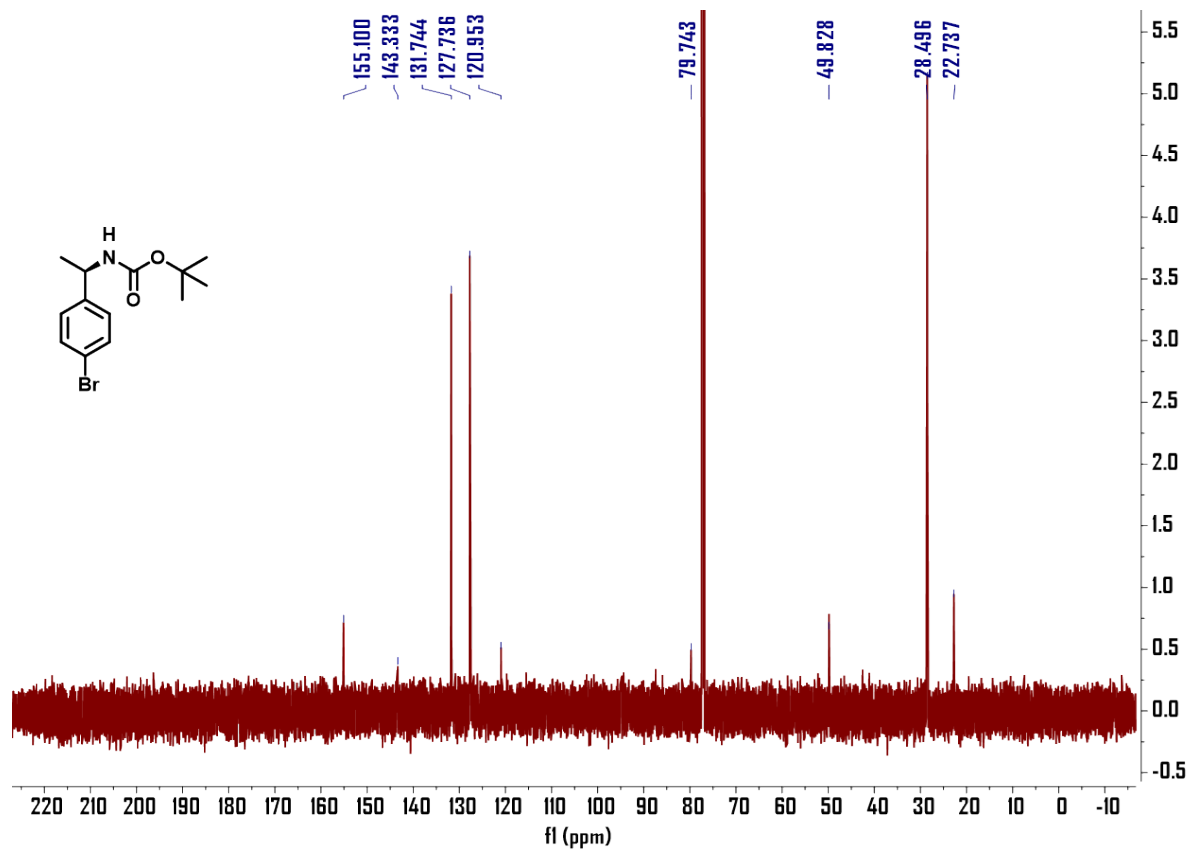
Figure S9. ^{13}C NMR spectrum of (**R**)-**1**
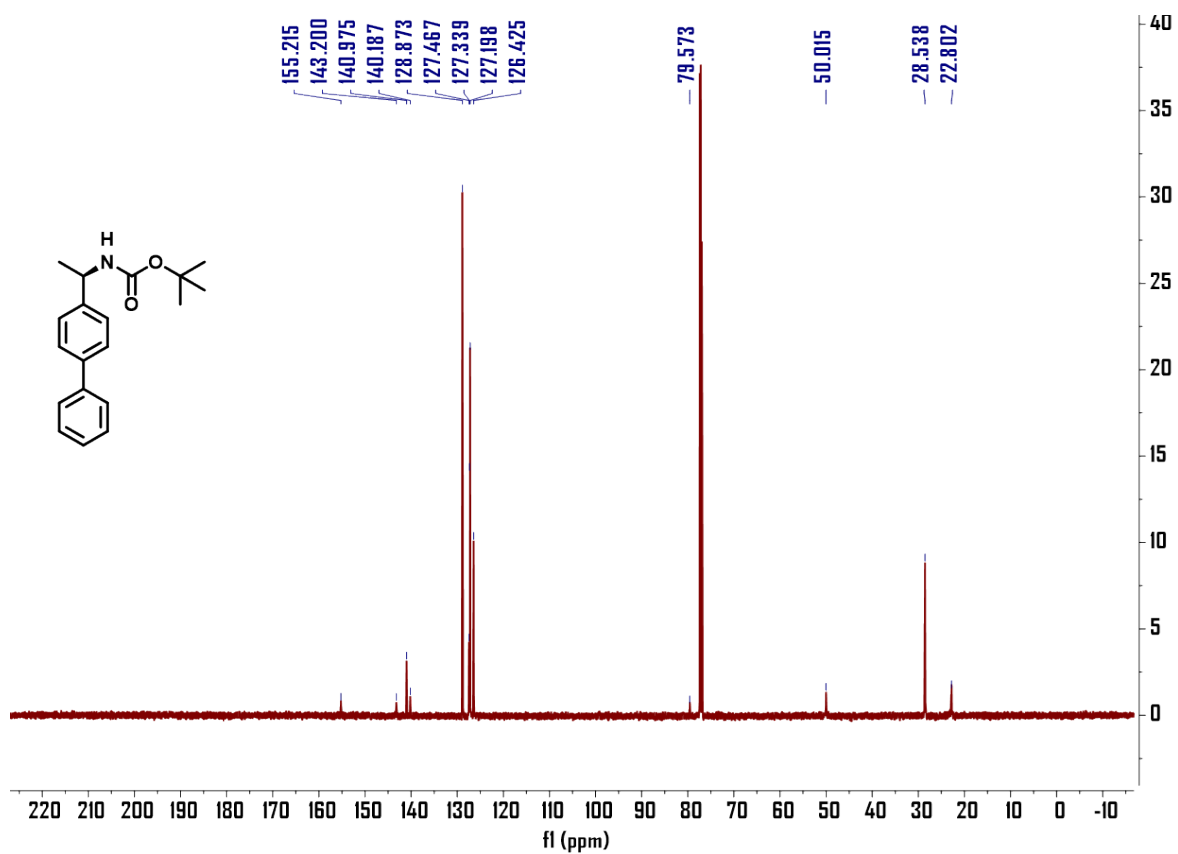
Figure S10. ^{13}C NMR spectrum of **(R)-2**
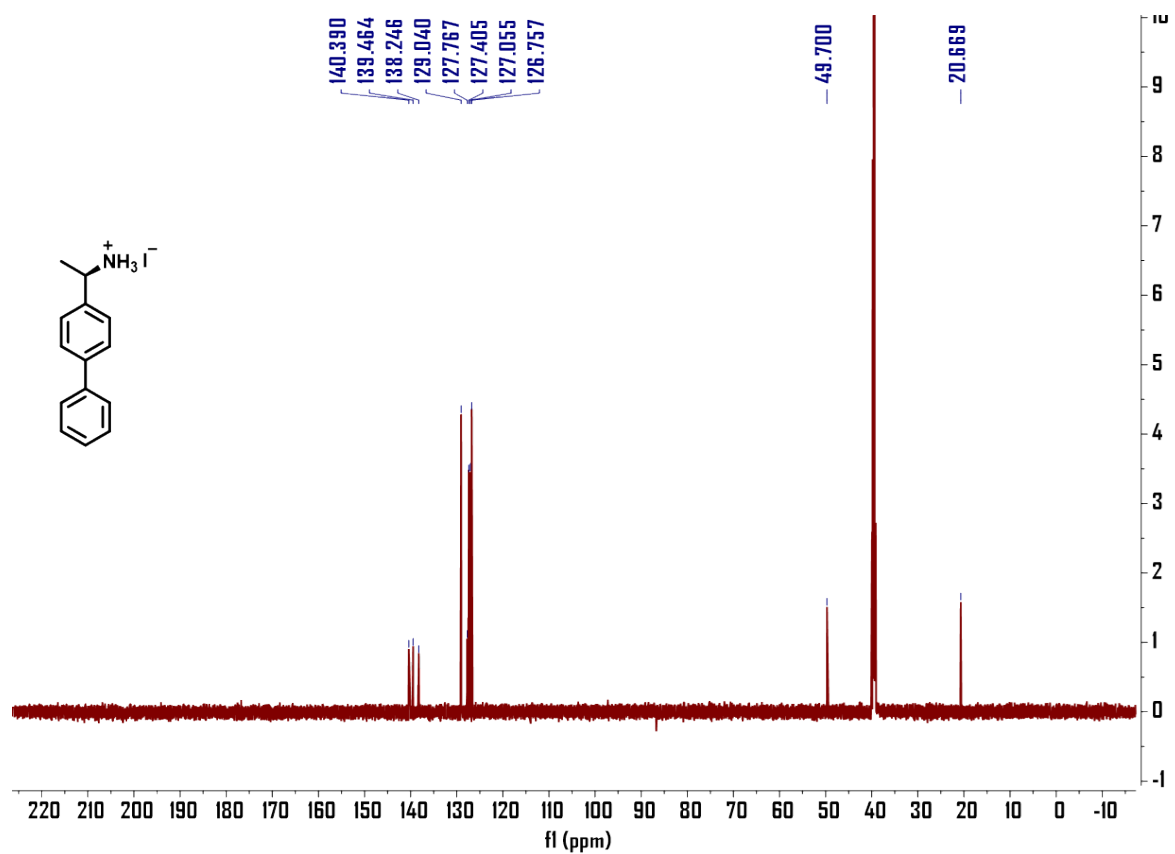
Figure S11. ^{13}C NMR spectrum of **(R)-BPEA**
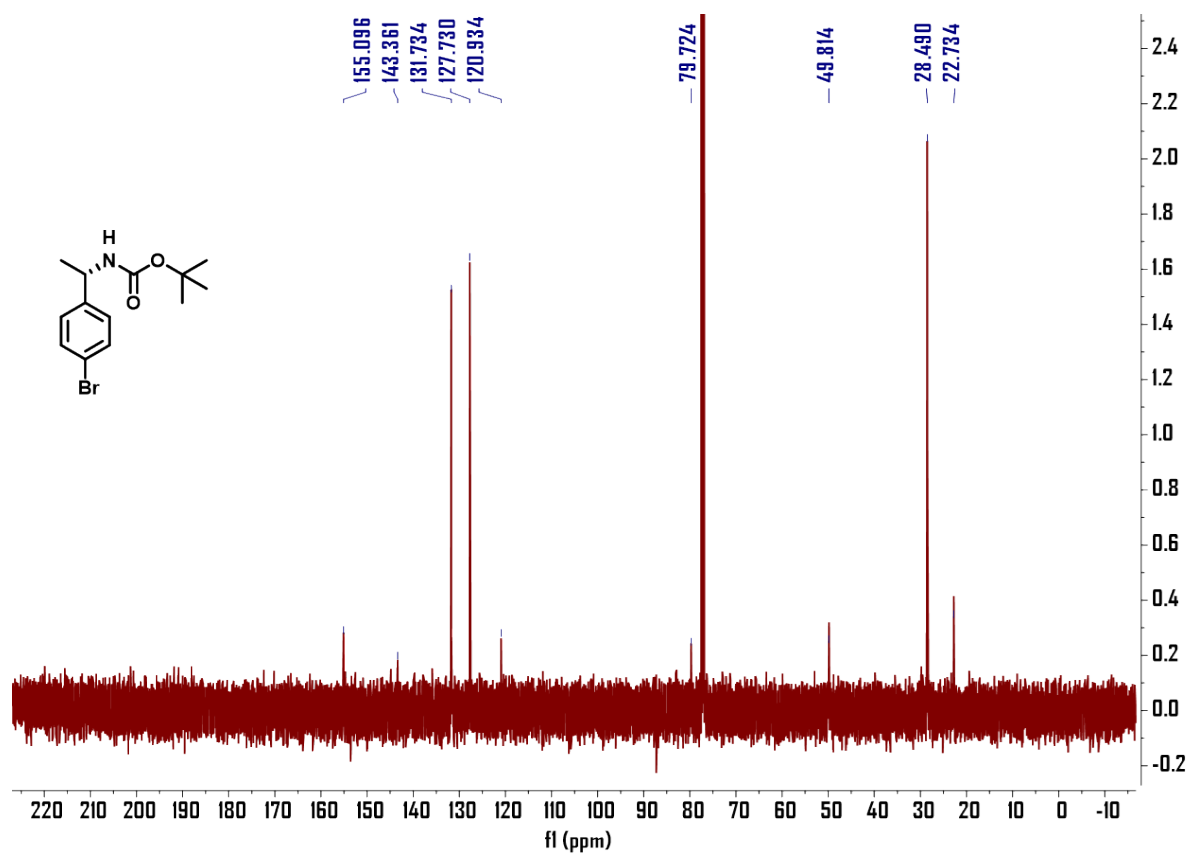
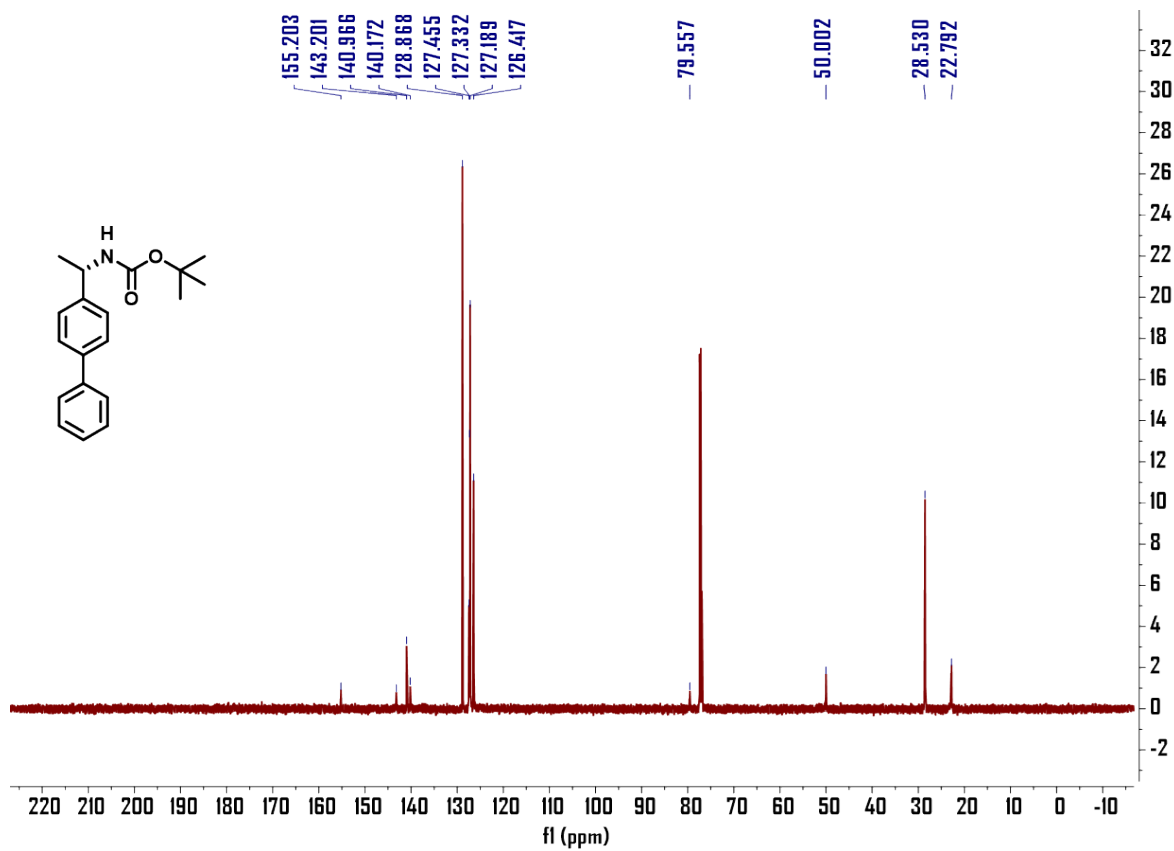**Figure S12.** ^{13}C NMR spectrum of (*S*)-1

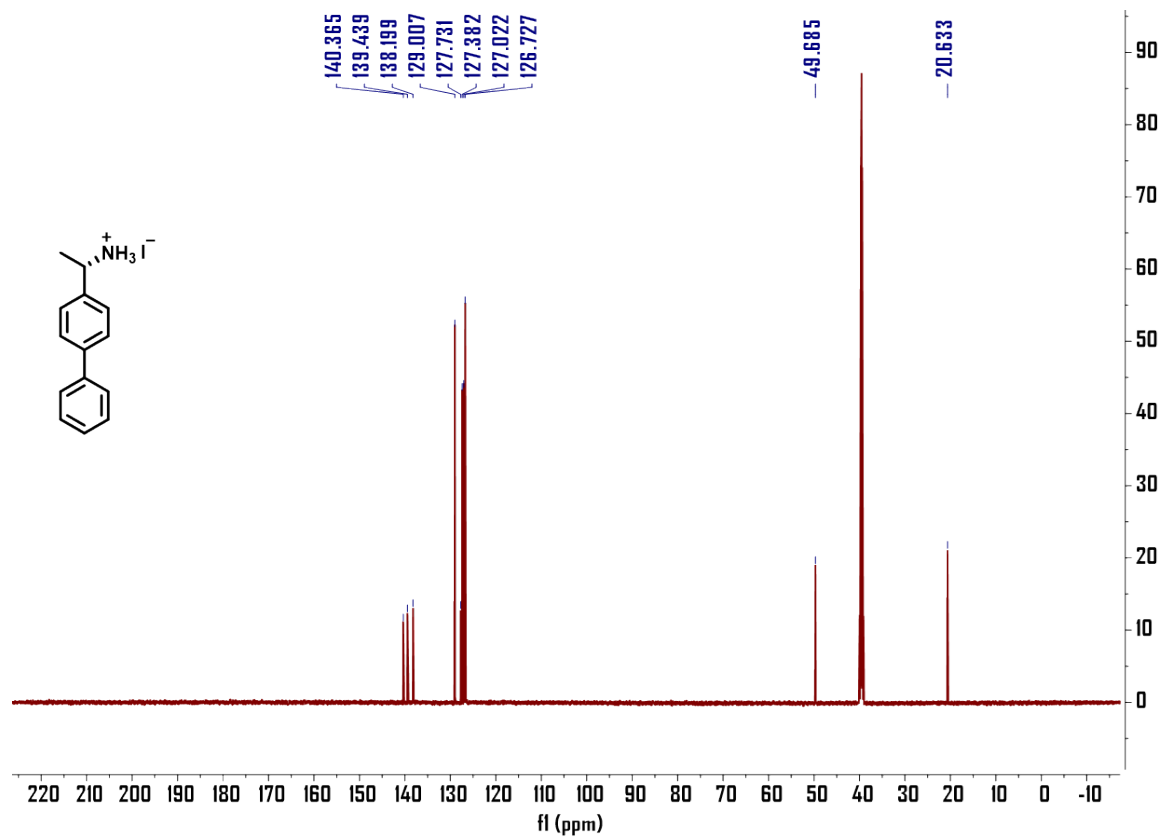**Figure S13.** ^{13}C NMR spectrum of (*S*)-2

Figure S14. ^{13}C NMR spectrum of **(S)-BPEA**

Figure S15. Schematic illustration of fabrication process for a. chiral perovskites photoconductor, b. chiral perovskites crystal.

a

b

c

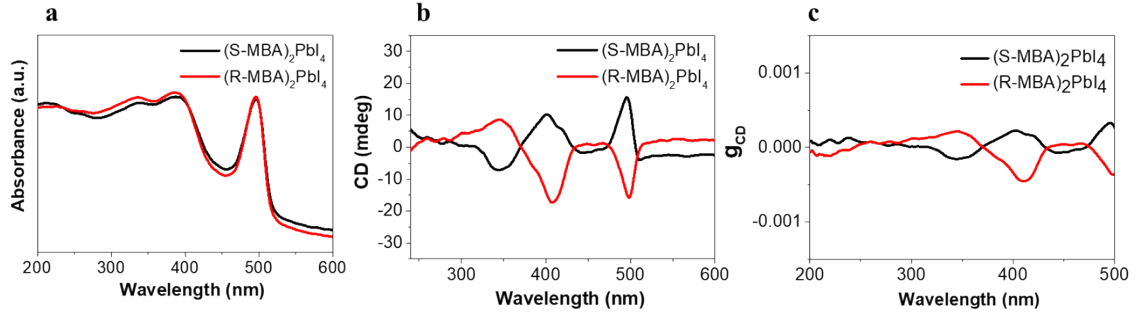**Figure S16.** Optical image of a. (*R)*-, b. (*S*)- and c. (*rac*)-chiral perovskites crystal

Figure S17. Characterization of $[(R/S)\text{-MBA}]_2\text{PbI}_4$ film. a. absorption spectra, b. CD spectra and c. g_{CD} spectra.

Calculation of the important optoelectronic parameters

To demonstrate optoelectrical characteristics of photoconductor, photoresponsivity (R), photosensitivity (P), external quantum efficiency (EQE) and detectivity (D*) were calculated from current-voltage curves of the devices under illumination and dark condition. The R and P values are generally defined by the following equations:

$$R = \frac{I_{ph}}{P_{in}} = \frac{I_{light} - I_{dark}}{P_{in}}$$

(1)

$$P = \frac{I_{ph}}{I_{dark}}$$

(2)

where I_{ph} is the photocurrent, I_{light} is the photocurrent under illumination, I_{dark} is the current in the dark condition and P_{in} is the incident illumination power, respectively. Also, EQE of devices can be defined as the ratio of number of photogenerated charge carriers to the number of incident photons on the devices. The EQE was calculated using the following equation:

$$EQE = \frac{(I_{light} - I_{dark})hc}{eP_{in}A\lambda}$$

(3)

where h is the Plank constant, c is the speed of light, e is the fundamental unit of charge, A is the area of the device channel, and λ the wavelength of the incident light, respectively. Detectivity usually describes the minimum detectable signal, as follows,

$$D^* = \frac{\sqrt{A}}{NEP}$$

(4)

$$NEP = \frac{I_n}{R\sqrt{\Delta f}}$$

(5)

In these equations, NEP the noise equivalent power, I_n is the measured noise current, and Δf is the bandwidth. If the major limit to detectivity is shot noise from the drain current under dark condition, D^* can be simplified as follows,

$$D^* = \frac{R}{\sqrt{(2e \cdot I_{dark}/A)}}$$

(6)