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Supporting information for

Modulating the glassy and crystalline ordering of carbazole small molecules in bulk

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1. Materials and methods:

Phenylacetylene (98%), molecular sieves (3 Å) and triphenylphosphine for synthesis, were purchased from Sigma Aldrich. Bromoacetic acid (99%), *p*-toluenesulfonic acid monohydrate ACS (99%), *n*-octanol (>99%) *n*-butanol (99.5%), potassium iodide (99.8%), potassium carbonate anhydrous (99.5%), triethylamine (99.5%) and potassium iodate (99.9%) were purchased from SRL. Glacial acetic acid ACS ISO, ethyl bromoacetate (96%), copper iodide (>98%) were purchased from Spectrochem India Limited. $Pd(PPh_3)_4$ (99%) was purchased from Chempure. Dodecanol was purchased from BLD Pharma. Carbazole (>97%) and bromoacetyl bromide (>98%) were purchased from TCI. Cetyl alcohol (98%) was purchased from Loba Chemie. Analytical grade solvents (Toluene, THF, DMF, DCM) solvents were purchased from SRL. AR grade solvents were distilled and dried over activated molecular sieves (3 Å). Silica gel of mesh size (100 – 200 and 230 – 400 mesh) was purchased from SRL and Merck, respectively. Bulk grade solvents for column chromatography were purchased from Memba Chem Limited or Merck and were distilled over rotavapor before use. Thin layer chromatography (TLC) was performed on Merck silica gel 60 F_{254} plates coated on aluminium. The TLC was visualized using UV lamps (254 nm or 365 nm), and other suitable staining agents (PMA, Iodine, Vanillin, $KMnO_4$ and Ninhydrin stains). (*S*)-3,7-dimethyloctan-1-ol[1] and (*S*)-1-amino-3,7-dimethyloctane[2] were synthesised according to known literature procedure.

Nuclear Magnetic Resonance (NMR) spectra were recorded on either Bruker 400 spectrometer or Bruker 500 spectrometer operating at room temperature. Chemical shifts (δ) are stated in parts per million (ppm) using the residual $CHCl_3$ ($\delta = 7.26$ ppm for ^1H and 77.16 ppm for ^{13}C [$CDCl_3$]) or DMSO ($\delta = 2.50$ ppm for ^1H and $\delta = 39.52$ for ^{13}C [DMSO-d_6]) Coupling constants *J* are given in Hz. Multiplicities are described as singlet (s), broad signal (br), doublet (d), triplet (t), quartet (q), quintet (quint) and multiplet (m).

HRMS were recorded with Agilent 6545 LCMS Mass Spectrometer **(**Agilent Technologies, G6545B) with ESI-TOF and APCI techniques in positive mode by dissolving the compound in either methanol or acetonitrile. and in MALDI-TOF with DCTB matrix.

FTIR spectra were recorded on Bruker Alpha II instrument in attenuated total reflectance (ATR) mode.

UV-vis absorption spectra were recorded on Shimadzu UV-Vis-NIR 3600 spectrophotometer or JASCO V-770 spectrophotometer. All spectra were recorded using Quartz cuvette (Hellma

QS) with pathlength of 10 mm, 2mm and 1 mm respectively. All measurements were performed with a bandwidth of 1 nm, data interval of 0.5 nm and scan speed of 400 nm/min.

Thermogravimetric analysis (TGA) measurements were recorded on TGA-Q500 analyzer under N_2 atmosphere at a heating rate of 10 °C min^{-1}.

Differential Scanning Calorimeter (DSC) used to analyse the thermal property were recorded on RIGAKU DSC vesta instrument. 1-3 mg sample was taken in an aluminium pan and was hermetically sealed. The samples were heated/cooled under N_2 atmosphere for 3 cycles at 10 and 2 °C min^{-1}.

Polarizing Optical Microscope (POM) were recorded on Olympus (BX53) brightfield polarizing optical microscope equipped with cross-polarizer and objectives (5x, 10x, 20x and 50x). Images were recorded either in transmission or reflection mode. A Linkam T96-S heating and cooling stage and a Linkam LNP96-S temperature controller were used to investigate the thermal properties and different phases. Phase change behaviour of the sample was studied by placing sample on a glass cover slip or quartz substrate and placing it in Linkam stage (THMS600). Controlled heating and cooling at varying rates were performed and the temperature were halted to record different phases.

SEM microscopy was performed using ZEISS Ultra 5 operating on voltage 3 to 5 kV. A drop cast and dried sample on silicon wafer with a 5 nm gold coating were used for SEM imaging. Before drop casting, the silicon wafer was cleaned by sonicating 10 min in chloroform, acetone, distilled water and acetone respectively followed by drying it in an oven. Then 3 to 4 drops of sample were drop casted on silicon wafer and kept in closed petri-dish for slow solvent evaporation. After complete evaporation of solvent, the drop casted sample were kept in high vacuum for 12 hours to ensure complete evaporation of the solvent.

Melting point of the sample were recorded on Buchi M-560 with a heating rate of 10°C/min.

Sample preparation: All spectroscopic measurements were performed on freshly prepared solutions. Sample weights were measured using an aluminium boat placed on a Sartorius Quintix® Semi-Micro Balance (QUINTIX125D-1OIN). Stock solutions were prepared using chloroform as the solvent. The required volume of stock solution was transferred to separate vials, and the chloroform was removed by gentle heating. Subsequently, a fixed volume of the desired solvent was added to each vial. All solvent measurements were performed using a Hamilton syringe to ensure precision.

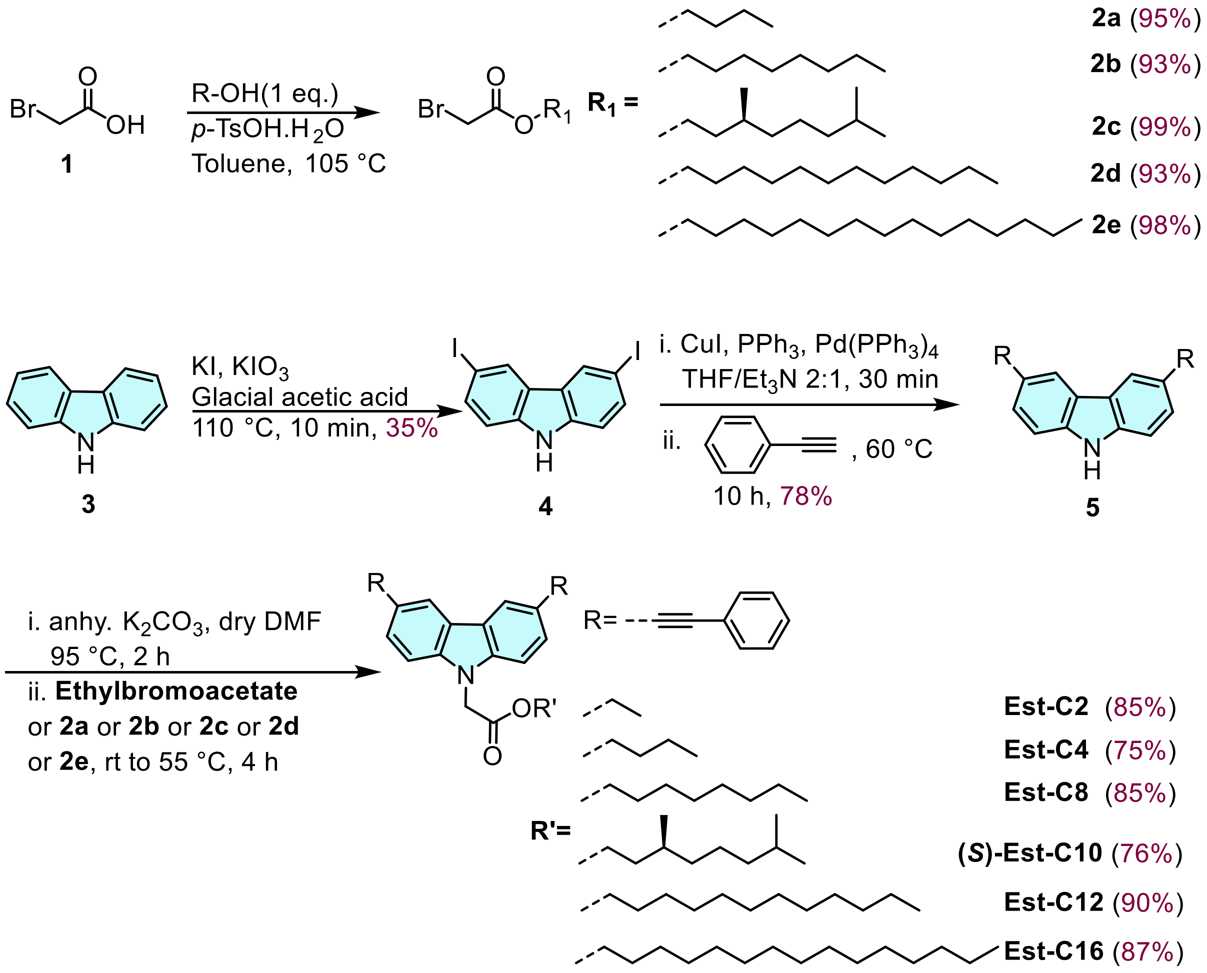
Thin Film preparation: Thin Films were prepared by placing the compound (1 – 1.2 mg) between two quartz slides. The assembly was placed on IKA hot plate and heated till the isotropic melt was observed. Upon isotropic melting, the upper quartz slide was uniformly rotated to facilitate the formation of uniform film. This was followed by cooling the assembly to room temperature to obtain a solid thin film.

Single Crystal XRD: The single-crystal X-ray diffraction was measured on a Bruker D8 Quest single-crystal X-ray diffractometer comprised of low temperature attachment. Data collection was done at 100 K using graphite-monochromated MoKα radiation (λα =0.71073 Å) by the ω-scan technique. The reduction was performed using CrysalisPro Red 171.41_64.93a software.[3] The chemical structures were solved using Olex2 1.5[4] with the ShelXT[5] structure solution program using intrinsic phasing and refined with the SHELXL[5] refinement package using least-squares minimization. An empirical absorption correction by multi scans was applied and all of the non-hydrogen atoms were S3 refined with anisotropic displacement factors. CCDC no. 2477502 and 2477503 contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Powder X-ray diffraction was carried out using a Rigaku Smartlab SE X-ray diffractometer with Cu Kα (λ = 0.1514 nm) as an incident wavelength in the 2θ range of 3-40°, with a step scan speed of 1°/min or 0.5 °/min. The samples were annealed by placing them between a quartz slide and a glass coverslip. After the annealing process, the slides were gently peeled apart, leaving the sample on the coverslip. The sample on the coverslip was then used for X-ray diffraction (XRD) measurements.

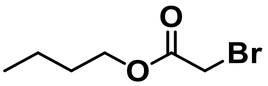
Film thickness measurements were performed using a Dektak XT stylus profilometer (Bruker). A diamond stylus was scanned across the sample surface under a stylus force of 2 mg at a constant scan speed of 55.55 µm/s. The film thickness was determined from the step height between the film-coated region and the bare substrate. The recorded line profiles were analyzed using the instrument’s built-in software. The films used for thickness measurement were annealed by placing them between a quartz slide and a glass coverslip. After annealing, the slides were gently separated, leaving the film on the coverslip, which was then used for further characterization

2. Synthetic details:

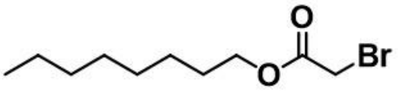


Scheme S1: Synthetic route to obtain bromoacetates and carbazole ester derivatives.

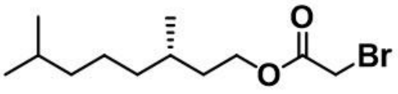
General procedure for the synthesis of alkyl bromoacetates (2a–2e): In an oven-dried, two-neck round-bottom flask equipped with a reflux condenser, compound **1** (1.2 equiv.) was dissolved in dry toluene under an inert atmosphere. To this stirred solution, the corresponding alkyl alcohol (1.0 equiv.) and *p*-toluenesulfonic acid monohydrate (0.01 equiv.) were added dropwise. The reaction mixture was heated to 105°C and stirred until completion, as monitored by thin-layer chromatography (TLC) and $KMnO_4$ stain. Upon completion, the reaction mixture was cooled to room temperature and quenched with water. The organic phase was sequentially washed with saturated ammonium chloride solution, saturated sodium bicarbonate solution, and brine. The organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure using a rotary evaporator to afford the desired esters (**2a**–**2e**) in excellent yields.



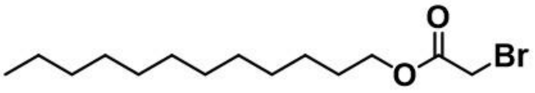
Synthesis of butyl-2-bromoacetate (2a): Bromoacetic acid (2.25 g, 16.2 mmol, 1.2 equiv.) was dissolved in toluene (15 mL). To this stirred solution, add *n*-butanol (1g, *d*= 0.810 g/ml, 13.5 mmol, 1 equiv.) and *p*-toluenesulfonic acid monohydrate (25 mg, 0.13 mmol, 0.01 equiv.) to obtain yellow liquid (2.5 g, 95%). **R_f** = 0.56 (Petroleum ether/EtOAc (19:1)). **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) = 4.15 (t, ^3J = 6.50 Hz, 2H), 3.81 (s, 2H), 1.63 (quint, ^3J = 6.5 Hz, 2H), 1.39 (quint, ^3J = 7.5 Hz, 2H), 0.92 (t, ^3J = 7.5 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ (ppm) = 167.41, 66.23, 30.52, 26.03, 19.07, 13.72; **HRMS** (ESI-TOF): *m/z* $[M+H]^+$ calcd. for $C_6H_{12}BrO_2$ = 195.0015; Found = 195.0007.



Synthesis of octyl-2-bromoacetate (2b): Bromoacetic acid (636 mg, 4.61 mmol, 1.2 equiv.) was dissolved in toluene (8 mL). To this stirred solution, add *n*-octanol (500 mg, *d*= 0.827 g/ml, 3.84 mmol, 1 equiv.) and *p*-toluenesulfonic acid monohydrate (7.3 mg, 0.038 mmol, 0.01 equiv.) to obtain yellow liquid (900 mg, 93%). **R_f** = 0.60 (Petroleum ether/EtOAc (19:1)). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 4.16 (t, ^3J = 6.8 Hz, 2H), 3.83 (s, 2H), 1.66 (quint, ^3J = 6.8 Hz, 2H), 1.37–1.27 (m, 10H), 0.88 (t, ^3J = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 167.52, 66.63, 31.89, 29.27 (2C), 28.54, 26.09, 25.88, 22.76, 14.22; **HRMS** (ESI-TOF): *m/z* $[M+H]^+$ calcd. for $C_{10}H_{20}BrO_2$ = 251.0641; Found = 251.0611.

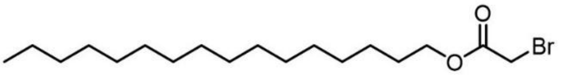


Synthesis of (*S*)-3,7-dimethyloctyl-2-bromoacetate (2c): Bromoacetic acid (523 mg, 3.79 mmol, 1.2 equiv.) was dissolved in toluene (10 mL). To this stirred solution, add (*S*)-3,7-dimethyloctanol (500 mg, 3.16 mmol, 1 equiv.) and *p*-toluenesulfonic acid monohydrate (6 mg, 0.032 mmol, 0.01 eq.) to obtain yellow liquid (900 mg, 99%). **R_f** = 0.56 (Petroleum ether/EtOAc (19:1)). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 4.24–4.17 (m, 2H), 3.82 (s, 2H), 1.72–1.68 (m, 1H), 1.67–1.44 (m, 3H), 1.32–1.09 (m, 6H), 0.90 (d, ^3J = 6.5 Hz, 3H), 0.86 (d, ^3J = 6.6 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 167.39, 64.99, 39.18, 37.08, 35.30, 29.72, 27.96, 26.06, 24.61, 22.72, 22.62, 19.51; **HRMS** (ESI-TOF): *m/z* $[M+H]^+$ calcd. for $C_{12}H_{24}BrO_2$ = 279.0954; Found = 279.0928.

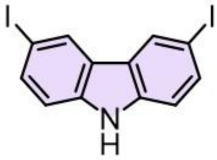


Synthesis of dodecyl-2-bromoacetate (2d): Bromoacetic acid (0.89 g, 6.44 mmol, 1.2 equiv.) was dissolved in toluene (10 mL). To this stirred solution, add dodecanol (1 g, *d*= 0.831 g/ml, 5.37 mmol, 1 equiv.) and *p*-toluenesulfonic acid monohydrate (10 mg, 0.05 mmol, 0.01 equiv.) to obtain yellow liquid (1.52 g, 93%). **R_f** = 0.62 (Petroleum ether/EtOAc (19:1)). **^{1}H NMR** (400

MHz, $CDCl_3$): δ (ppm) = 4.16 (t, ^3J = 6.8 Hz, 2H), 3.82 (s, 2H), 1.65 (quint, ^3J = 6.8 Hz, 2H), 1.34–1.25 (m, 18H), 0.87 (t, ^3J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 167.46, 66.60, 32.04, 29.75, 29.67 (2C), 29.60, 29.47, 29.30, 28.53, 26.07, 25.86, 22.81, 14.24; **HRMS** (ESI-TOF): *m/z* $[M+H]^+$ calcd. for $C_{14}H_{28}BrO_2$ = 307.1267; Found = 307.1266.

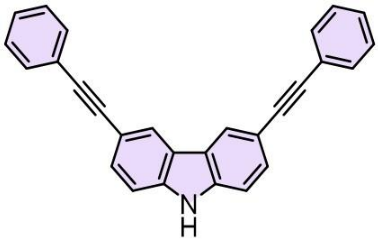


Synthesis of hexadecyl-2-bromoacetate (2e): Bromoacetic acid (688 mg, 4.95 mmol, 1.2 equiv.) was dissolved in toluene (8 mL). To this stirred solution, add hexadecanol (1.00 g, 4.13 mmol, 1 equiv.) and *p*-toluenesulfonic acid monohydrate (7.8 mg, 0.04 mmol, 0.01 equiv.) to obtain colourless liquid (1.62 g, 98%). **R_f** = 0.62 (Petroleum ether/EtOAc (19:1)). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 4.16 (t, ^3J = 6 Hz, 2H), 3.82 (s, 2H), 1.65 (quint, ^3J = 6 Hz, 2H), 1.35–1.25 (m, 26H), 0.88 (t, ^3J = 6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 167.45, 66.59, 32.06, 29.82 (2C), 29.79, 29.76, 29.68, 29.61, 29.50, 29.31, 28.53, 26.05, 25.87, 22.82, 14.24; **HRMS** (ESI-TOF): *m/z* $[M+H]^+$ calcd. for $C_{18}H_{36}BrO_2$= 363.1893; Found = 363.1896.



Synthesis of 3,6-Diiodocarbazole (4)[6]: In an oven-dried, two-neck round-bottom flask, compound **3** (1.00 g, 5.98 mmol, 1.0 equiv.) and potassium iodide (1.50 g, 8.98 mmol, 1.5 equiv.) were dissolved in glacial acetic acid (10 mL) and stirred at room temperature. To this solution, potassium iodate (1.70 g, 7.96 mmol, 1.3 equiv.) was added portion-wise over 5 minutes. After the complete addition, the reaction mixture was refluxed for 10 minutes. Upon completion, the reaction was quenched with water and extracted with ethyl acetate (3 × 20 mL). The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, concentrated under reduced pressure and the residue was purified by silica gel column chromatography using (petroleum ether/$CHCl_3$ (9:1)) as eluent to afford compound **4** as a solid (880 mg, 35% yield). **R_f** = 0.15 (petroleum ether/$CHCl_3$ (9:1)). Note: Triiodo carbazole is also formed in a substantial amount. **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 11.55 (s, 1H), 8.56 (d, ^3J = 1.60 Hz, 2H), 7.66 (dd, ^3J = 8.4 Hz, ^4J = 1.6 Hz, 2H), 7.36 (d, ^3J = 8.4 Hz, 2H). **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) = 139.31, 134.58, 129.66, 124.35, 114.04, 82.38; **MS** (Maldi-TOF): *m/z* $[M]^+$ calcd. for $C_{12}H_7I_2N$= 418.866; Found = 418.962.

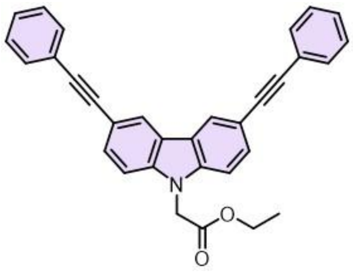
Synthesis of 3,6-Bis(phenylethynyl)-9H-carbazole (5)[7]**:** In an oven-dried, two-neck round-bottom flask under a positive flow of nitrogen, compound 4 (0.50 g, 1.19 mmol, 1.0 equiv.), Pd(PPh_3)$_4$ (0.06 mmol, 5 mol%), triphenylphosphine (63 mg, 0.24 mmol, 0.2 equiv.), and CuI (23 mg, 0.12 mmol, 0.1 equiv.) were added. A freshly distilled mixture of tetrahydrofuran (THF) and triethylamine (Et_3N) in a 2:1 ratio was added to the flask, and the reaction mixture was stirred at room temperature for 30 minutes. Phenylacetylene (0.40 g, 3.94 mmol, 3.3 equiv.) was then added dropwise under a nitrogen atmosphere. The resulting mixture was refluxed with continuous stirring for 18 hours. Upon completion of the reaction, the reaction mixture was concentrated under reduced pressure. The residue was dissolved in ethyl acetate and washed sequentially with 1 M HCl solution (2 × 5 mL) and saturated ammonium chloride solution (2 × 10 mL). The organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure and the residue was purified by silica gel flash column chromatography using (petroleum ether/EtOAc (19:1)) as eluent to afford compound **5** as a yellow solid (0.44 g, 78% yield). **R_f** = 0.2 (petroleum ether/EtOAc (19:1)). **Melting point** = 214.5–220.2 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.27 (s, 2H), 8.20 (brs, 1H), 7.63–7.59 (m, 6H), 7.39–7.32 (m, 8H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 139.51, 131.64, 130.09, 128.50, 128.07, 124.27, 123.83, 123.09, 114.70, 110.99, 90.56, 88.01. **MS** (MALDI-TOF): *m/z* $[M]^+$ calcd. for $C_{28}H_{17}N$ = 367.135; Found = 367.221.



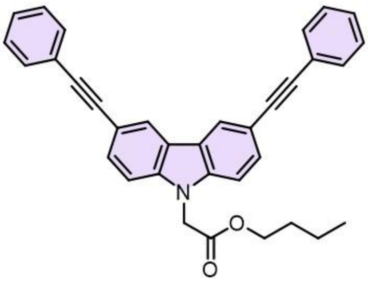
General procedure for synthesis of Carbazole esters:

In an oven-dried 30 mL reaction tube under an inert atmosphere, 3,6-bis(phenylethynyl)-9H-carbazole (1.0 equiv.) and anhydrous potassium carbonate (3.0 equiv.) were added. Dry N,N-dimethylformamide (DMF, 2 mL) was introduced, and the reaction mixture was stirred at 95 °C for 2 hours. After cooling to room temperature, bromoacetate (1.2 equiv.) was added, and the reaction was stirred further at 55 °C for 4 hours. Upon completion, the reaction mixture was quenched with water, resulting in immediate precipitation. The precipitate was collected by filtration through Whatman filter paper, washed thoroughly with water, and dried under vacuum to afford the corresponding carbazole ester derivatives as solid products.

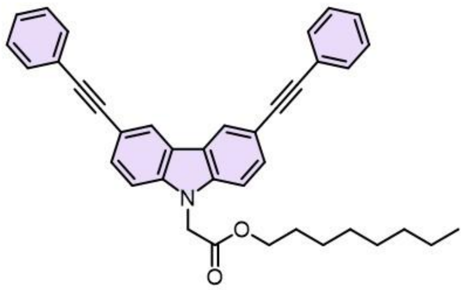
Synthesis of Ethyl-2-(3,6-bis(phenylethynyl)-9H-carbazol-9-yl)acetate (Est-C2): The titled compound was prepared from 3,6-bis(phenylethynyl)-9H-carbazole (100 mg, 0.27 mmol, 1 equiv.), anhydrous potassium carbonate (113 mg, 0.82 mmol, 3 equiv.) and ethyl bromoacetate (55 mg, 0.33 mmol, 1.2 equiv.) by following the general procedure to afford Yellowish brown solid. (105 mg 85%). $\mathbf{R_f}$ = 0.16 (12% $CHCl_3$ in Pet Ether)). **IR** $\boldsymbol{\nu_{max}}$ (cm^{-1}) = 3053, 2987, 2207, 1738. **Melting point** = 168.9–169.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.29 (d, ^4J = 1.14 Hz, 2H), 7.67 (dd, ^3J = 8.46 Hz, ^4J = 1.53 Hz, 2H), 7.59 – 7.57 (dd, ^3J = 8.37 Hz, ^4J = 1.72 Hz, 4H), 7.39 – 7.25 (m, 8H), 5.0 (s, 2H), 4.22 (q, ^3J = 7.13 Hz, 2H), 1.23 (t, ^3J = 7.15 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 168.05, 140.69, 131.67, 130.22, 128.50, 128.09, 124.39, 123.83, 123.05, 115.05, 108.88, 90.42, 88.20, 62.09, 45.08, 14.27; **MS** (HRMS, ESI mode): m/z calculated for $C_{32}H_{24}NO_2$= 454.1802 $[M+H]^+$; Found= 454.1796.



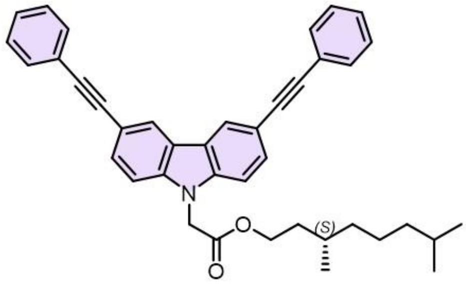
Synthesis of butyl-2-(3,6-bis(phenylethynyl)-9H-carbazol-9-yl)acetate (Est-C4): The titled compound was prepared from 3,6-bis(phenylethynyl)-9H-carbazole (50 mg, 0.136 mmol, 1 equiv.), anhydrous potassium carbonate (57 mg, 0.408, 3 equiv.) and butyl bromoacetate (32 mg, 0.163 mmol, 1.2 equiv.) by following the general procedure to afford light brown solid. (50 mg, 75%). $\mathbf{R_f}$ = 0.16 (Petroleum ether/$CHCl_3$ (8:1)). **IR** $\boldsymbol{\nu_{max}}$ (cm^{-1}) = 3051, 2948, 2203, 1732. **Melting point** = 124.7–128.8 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.28 (d, ^4J = 1.2 Hz, 2H), 7.66 (dd, ^3J = 8.4 Hz, ^4J = 1.5 Hz, 2H), 7.59 (dd, ^3J = 8.02 Hz, ^4J = 1.7 Hz, 4H), 7.39–7.30 (m, 8H), 5.0 (s, 2H), 4.14 (t, ^3J = 6.6 Hz, 2H), 1.55–1.51 (m, 2H), 1.22 (quint, ^3J = 7.6 Hz, 2H), 0.84 (t, ^3J = 7.3 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.16, 140.71, 131.66, 130.22, 128.50, 128.09, 124.39, 123.83, 123.06, 115.05, 108.88, 90.43, 88.20, 65.88, 45.10, 30.54, 19.03, 13.67 ppm; **HRMS** (ESI-TOF): *m/z* $[M+H]^+$ calcd. for $C_{34}H_{28}NO_2$ = 482.2115; Found = 482.2113.



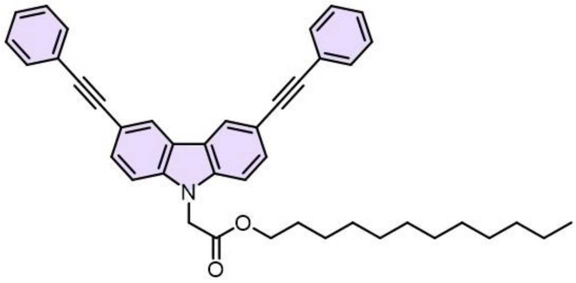
Synthesis of octyl-2-(3,6-bis(phenylethynyl)-9H-carbazol-9-yl)acetate (Est-C8): The titled compound was prepared from 3,6-bis(phenylethynyl)-9H-carbazole (50 mg, 0.14 mmol, 1 equiv.), anhydrous potassium carbonate (57 mg, 0.41 mmol, 3 equiv.) and octyl bromoacetate (41 mg, 0.16 mmol, 1.2 equiv.) by following the general procedure to afford white crystal solid (62 mg, 85%). **R_f** = 0.19 (Petroleum ether/$CHCl_3$ (8:1)). **IR** ν_{max} (cm^{-1}) = 3057, 2916, 2209, 1740. **Melting point** = 129.0–130.2 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.28 (d, $^{3}J = 1.2$ Hz, 2H), 7.66 (dd, $^{3}J = 8.4$, $^{3}J = 1.6$ Hz, 2H), 7.58 (dd, $^{3}J = 8.0$, $^{4}J = 1.6$ Hz, 4H), 7.39–7.30 (m, 8H), 5.00 (s, 2H), 4.12 (t, $^{3}J = 6.8$ Hz, 2H), 1.54–1.50 (m, 2H), 1.29–1.25 (m, 2H), 1.19–1.11 (m, 8H), 0.88 (t, $^{3}J = 7.2$ Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 168.16, 140.70, 131.66, 130.21, 128.50, 128.08, 124.38, 123.84, 123.05, 115.06, 108.89, 90.43, 88.20, 66.14, 45.13, 31.87, 29.28, 29.18, 28.54, 25.81, 22.80, 14.25. **HRMS** (ESI-TOF): *m/z* $[M+H]^+$ calcd. for $C_{38}H_{36}NO_2$ = 538.2741; Found = 538.2734.



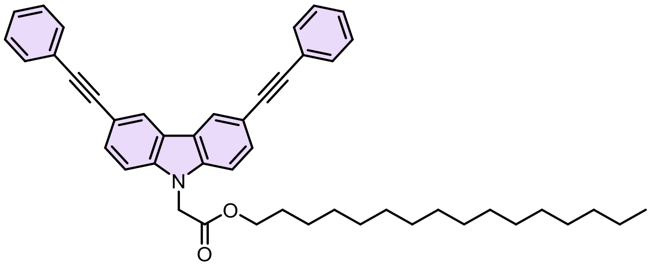
Synthesis of (*S*)-3,7-dimethyloctyl-2-(3,6-bis(phenylethynyl)-9H-carbazol-9-yl)acetate ((*S*)-Est-C10): The titled compound was prepared from 3,6-bis(phenylethynyl)-9H-carbazole (100 mg, 0.27 mmol, 1 equiv.), anhydrous potassium carbonate (113 mg, 0.82 mmol, 3 equiv.) and (*S*)-3,7-dimethyloctylbromoacetate (91 mg, 0.33 mmol, 1.2 equiv.) by following the general procedure to afford white solid (117 mg, 76%). **R_f** = 0.19 (Petroleum ether/$CHCl_3$ (8:1)). **IR** ν_{max} (cm^{-1}) = 3047, 2922, 2203, 1752. **Melting point** = 98.4–101.2 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.28 (d, $^{3}J = 1.20$ Hz, 2H), 7.66 (dd, $^{3}J = 8.4$, $^{3}J = 1.2$ Hz, 2H), 7.58 (dd, $^{3}J = 8$, $^{4}J = 1.6$ Hz, 4H), 7.39–7.23 (m, 8H), 5.00 (s, 2H), 4.19–4.15 (m, 2H), 1.54–1.51 (m, 2H), 1.34–1.25 (m, 2H), 1.17–1.07 (m, 6H), 0.86 (d, $^{3}J = 6.4$ Hz, 6H) 0.77 (d, $^{3}J = 6.4$ Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 168.16, 140.66, 131.65, 130.19, 128.49, 128.08, 124.36, 123.83, 123.02, 115.03, 108.86, 90.44, 88.19, 64.59, 45.11, 39.28, 37.14, 35.47, 29.79, 28.09, 24.75, 22.84, 22.75, 19.40; **HRMS** (ESI-TOF): *m/z* $[M+H]^+$ calcd. for $C_{40}H_{40}NO_2$ = 566.3054; Found = 566.3050.

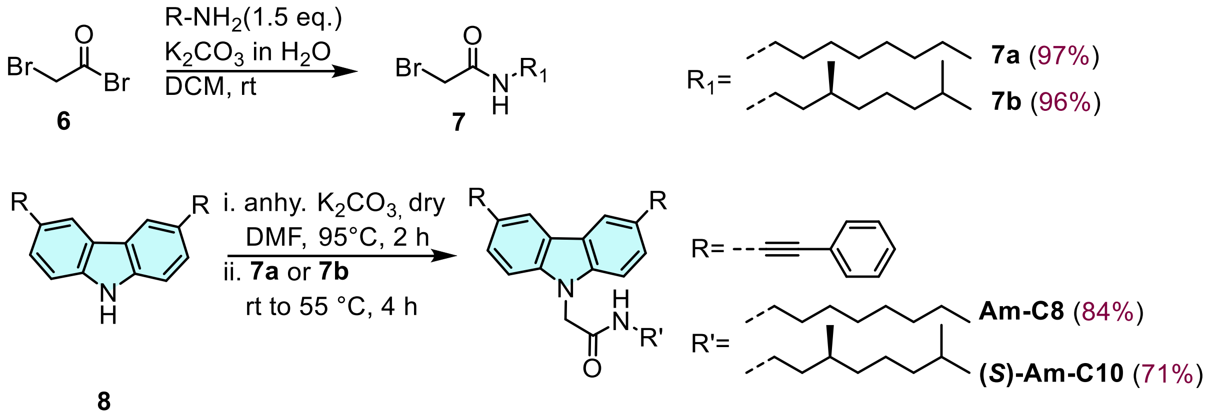


Synthesis of dodecyl-2-(3,6-bis(phenylethynyl)-9H-carbazol-9-yl)acetate (Est-C12): The titled compound was prepared from 3,6-bis(phenylethynyl)-9H-carbazole (100 mg, 0.27 mmol, 1 equiv.), anhydrous potassium carbonate (113 mg, 0.82 mmol, 3 equiv) and dodecylbromoacetate (100 mg, 0.33 mmol, 1.2 equiv.) by following the general procedure to afford white solid (145 mg, 90%). **R_f** = 0.2 (Petroleum ether/$CHCl_3$ (8:1)). **IR ν_{max}** (cm^{-1}) = 3051, 2916, 2846, 2207, 1726. **Melting point** = 121.7–123.0 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 8.28 (d, ^4J = 1.2 Hz, 2H), 7.66 (dd, ^3J = 8.6, ^4J = 1.6 Hz, 2H), 7.59 (d, ^3J = 8.23 Hz, 4H), 7.39–7.30 (m, 8H), 4.99 (s, 2H), 4.12 (t, ^3J = 6.6 Hz, 2H), 1.56–1.51 (m, 2H), 1.31–1.29 (m, 12H) 1.17–1.12 (m, 6H), 0.87 (t, ^3J = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 168.15, 140.68, 131.65, 130.19, 128.48, 128.08, 124.37, 123.83, 123.03, 115.03, 108.87, 90.42, 88.19, 66.12, 45.10, 32.07, 29.82, 29.81, 29.69, 29.62, 29.52, 29.22, 28.53, 25.80, 22.84, 14.28; **HRMS** (ESI-TOF): *m/z* $[M+H]^+$ calcd. for $C_{42}H_{44}NO_2$ = 594.3367; Found = 594.3360.

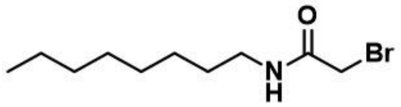


Synthesis of hexadecyl-2-(3,6-bis(phenylethynyl)-9H-carbazol-9-yl)acetate (Est-C16): The titled compound was prepared from 3,6-bis(phenylethynyl)-9H-carbazole (50 mg, 0.14 mmol, 1 equiv.), anhydrous potassium carbonate (57 mg, 0.41 mmol, 3 equiv.) and hexadecylbromoacetate (60 mg, 0.16mmol, 1.2 equiv.) by following the general procedure to afford white semi solid (77 mg, 87%). **R_f** = 0.23 (Petroleum ether/$CHCl_3$ (8:1)). **IR ν_{max}** (cm^{-1}) = 3053, 2918, 2848, 2207, 1726; **Melting point** = 90.4–92.5 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) = 8.28 (d, ^4J = 1.1 Hz, 2H), 7.66 (dd, ^3J = 9.5, ^4J = 1 Hz, 2H), 7.59 –7.57 (m, 4H), 7.39–7.30 (m, 8H), 5.00 (s, 2H), 4.12 (t, ^3J = 6.5, 2H), 1.55–1.49 (m, 2H), 1.30–1.24 (m, 20H), 1.16 (brs, 6H), 0.88 (t, ^3J = 7 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ (ppm) = 168.17, 140.69, 131.65, 130.20, 128.49, 128.08, 124.38, 123.82, 123.04, 115.04, 108.88, 90.41, 88.19, 66.14, 45.12, 32.07, 29.86, 29.81, 29.70, 29.63, 29.51, 29.22, 28.53, 25.80, 22.84, 14.28; **HRMS** (ESI-TOF): *m/z* $[M+H]^+$ calcd. for $C_{46}H_{52}NO_2$= 650.3993 Found = 650.3984.

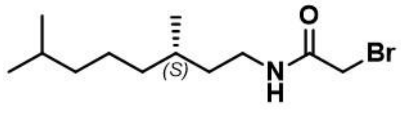




Scheme S2: Synthetic route to obtain amide functionalized carbazole derivatives.

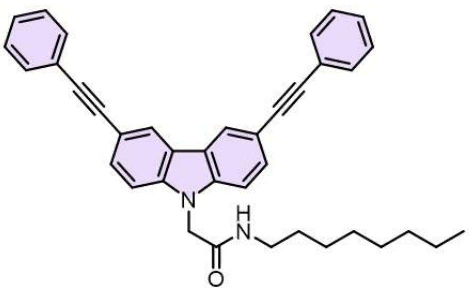


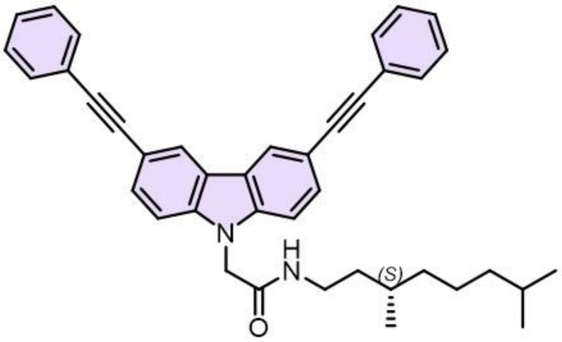
Synthesis of octyl-2-bromoacetamide (7a): To a stirred solution of octylamine (1.00 g, 7.74 mmol, 1.0 equiv.) in dichloromethane (15 mL) at room temperature was added an aqueous solution of potassium carbonate (1.60 g, 11.61 mmol, 1.5 equiv.) in water. The reaction mixture was cooled to using an ice bath. Bromoacetyl bromide (2.34 g, 11.61 mmol, 1.5 equiv.), dissolved in dichloromethane (5 mL), was added dropwise over 30 min. After the complete addition, the reaction mixture was stirred at room temperature until full consumption of the starting amine (monitored by TLC). The organic layer was separated and washed sequentially with 1 M HCl, distilled water, and brine solution. The organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure and the residue was purified by silica gel column chromatography using (petroleum ether/EtOAc (9:1)) as eluent to afford compound **7a** as a colourless oil (0.94g, 97% yield). **R_f** = 0.2 (Petroleum ether/$CHCl_3$: 7:3)).**^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) = 6.51 (s, 1H), 3.87 (s, 2H), 3.27 (q, ^3J = 10 Hz, 2H), 1.55–1.50 (m, 2H), 1.29–1.25 (m, 10H), 0.87 (t, ^3J = 7.5 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ (ppm) = 165.34, 40.39, 31.87, 29.53, 29.37, 29.30, 29.27, 26.92, 22.74, 14.20; **HRMS** (ESI-TOF): *m/z* $[M+H]^+$ calcd. for $C_{10}H_{21}BrNO$= 250.0801, Found = 250.0817.



Synthesis of 3,7-dimethyloctyl-2-bromoacetamide (7b): To a stirred solution of 3,7-dimethyloctan-1-amine (100 mg, 0.63 mmol, 1.0 equiv.) in dichloromethane (3 mL) at room temperature was added an aqueous solution of potassium carbonate (132 mg, 0.95 mmol, 1.5 equiv.) under continuous stirring. The reaction mixture was cooled to 4–5 °C, and a solution of bromoacetyl bromide (192 mg, 0.95 mmol, 1.5 equiv.) in dichloromethane (2 mL) was added dropwise over 30 min. Upon complete addition, the reaction mixture was allowed to warm to room temperature and stirred until the starting amine was fully consumed (monitored by TLC). The reaction mixture was then diluted with dichloromethane and the organic layer was successively washed with 1 M HCl, distilled water, and brine. The organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure and the residue was purified by silica gel column chromatography using (petroleum ether/EtOAc (9:1)) as eluent to afford compound **7b** as a colourless oil (0.94g, 96% yield). **R$_f$** = 0.15 (Petroleum ether/EtOAc (9:1)). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 6.48 (s, 1H), 3.87 (s, 2H), 3.33–3.26 (m, 2H), 1.56–1.46 (m, 3H), 1.38-1.26 (m, 4H), 1.13-1.11 (m, 3H), 0.89 (d, ^3J = 6.52 Hz, 3H), 0.85 (d, ^3J = 6.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 165.38, 39.29, 38.55, 37.16, 36.40, 30.75, 29.49, 28.05, 24.73, 22.80, 22.70, 19.60. **HRMS** (ESI-TOF): *m/z* $[M+H]^+$ calcd. for $C_{12}H_{25}BrNO$= 278.1114; Found= 278.1112.

Synthesis of octyl-2-(3,6-bis(phenylethynyl)-9H-carbazol-9-yl)acetamide (Am-C8): In an oven-dried reaction tube under an inert atmosphere, 3,6-bis(phenylethynyl)-9H-carbazole (50 mg, 0.14 mmol, 1.0 equiv.) and anhydrous potassium carbonate (52 mg, 0.41 mmol, 3.0 equiv.) were added. Dry DMF (2 mL) was introduced, and the reaction mixture was stirred at 95 °C for 2 h. After cooling to room temperature, octyl-2-bromoacetamide (41 mg, 0.16 mmol, 1.2 equiv.) was added, and the reaction mixture was stirred at 55 °C for an additional 4 h. The reaction was quenched by the addition of water, and the resulting mixture was extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure and the residue was purified by silica gel flash column chromatography using (petroleum ether/EtOAc (9:1)) as eluent to afford compound as slightly yellowish-white solid (61 mg, 84% yield). **R$_f$** = 0.10 (Petroleum ether/$CHCl_3$: 7:3)). **IR ν_{max}** (cm^{-1}) = 3307, 2926, 2852, 2211, 1658. **Melting point**= 211.2–215.3 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) = 8.31 (d, ^4J = 1 Hz, 2H), 7.69 (dd, ^3J = 8.5 Hz, ^4J = 1.5 Hz, 2H), 7.59–7.57 (m, 4H), 7.40–7.34 (m, 8H), 5.43 (t, ^3J = 6 Hz, 1H, NH), 4.93 (s, 2H), 3.16 (q, ^3J = 6.75, 2H) , 1.30–1.04 (m, 12H), 0.85 (t, ^3J = 7.25 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ (ppm) = 167.17, 140.23, 131.68, 130.69, 128.54, 128.26, 124.50, 123.62, 123.20, 115.86, 109.05, 89.96, 88.65, 47.31, 39.61, 31.83, 29.38, 29.26, 29.18, 26.71, 22.77, 14.23. **HRMS** (ESI-TOF): *m/z* $[M+H]^+$ calcd. for $C_{38}H_{37}N_2O$ = 537.2900; Found = 537.2897.

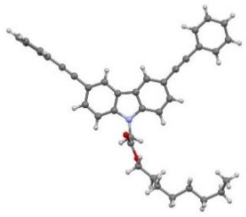
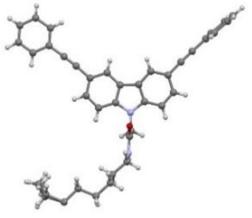




Synthesis of (*S*)-3,7-dimethyloctyl-2-(3,6-bis(phenylethynyl)-9H-carbazol-9-yl)acetamide ((*S*)-Am-C10): In an oven-dried reaction tube under an inert atmosphere, 3,6-bis(phenylethynyl)-9H-carbazole (100 mg, 0.27 mmol, 1.0 equiv.) and anhydrous potassium carbonate (113 mg, 0.82 mmol, 3.0 equiv.) were added. Dry DMF (3 mL) was introduced, and the reaction mixture was stirred at 95 °C for 2 h. After cooling to room temperature, 3,7-dimethyloctyl-2-bromoacetamide (91 mg, 0.33 mmol, 1.2 equiv.) was added, and the reaction was stirred at 55 °C for 4 h. The reaction was quenched by the addition of water, and the mixture was extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure and the residue was purified by silica gel flash column chromatography using (Petroleum ether/EtOAc (9:1)) as eluent to afford compound as slightly yellowish-white solid (110 mg, 71% yield). **R_f** = 0.10, (Petroleum ether/$CHCl_3$: 7:3)). **IR ν_{max}** (cm^{-1}) = 3253, 2924, 2207, 1648. **Melting point** = 184.8–185.9 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.30 (d, ^4J = 0.8 Hz, 2H), 7.69 (dd, ^3J = 8.4 Hz, ^4J = 1.6 Hz, 2H), 7.59–7.57 (m, 4H), 7.39–7.33 (m, 8H), 5.39 (t, 1H, NH), 4.92 (s, 2H), 3.20 (q, ^3J = 6.39, 2H), 1.52–1.42 (m, 1H), 1.32–1.24 (m, 1H), 1.17–1.03 (m, 8H), 0.83 (d, ^3J = 6.61 Hz, 6H), 0.75 (d, ^3J = 6.33 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 167.11, 140.23, 131.67, 130.68, 128.54, 128.26, 124.49, 123.61, 123.19, 115.84, 109.04, 89.97, 88.65, 47.31, 39.24, 37.78, 37.11, 36.51, 30.64, 28.06, 24.77, 22.82, 22.72, 19.42. **HRMS** (ESI-TOF): *m/z* $[M+H]^+$ calcd. for $C_{40}H_{41}N_2O$= 565.3213; Found = 565.3209.

3. Supporting Figures and Tables:

Table S1: SC-XRD details of **Est-C8** and **Am-C8**.

		
	Est-C8	**Am-C8**
Empirical Formula	$C_{38}H_{35}NO_2$	$C_{38}H_{35}N_2O$
Formula Weight	537.67	537.29
Temperature (K)	150	100
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a, b, c (Å)	5.4040(10), 13.518(3), 20.795(4)	4.9248(2), 14.1036(8), 21.9940(9)
α, β, γ (°)	83.148(6), 86.034(6), 83.367(6)	78.503(4), 86.972(4), 82.765(4)
Volume (Å)^3	1495.8(5)	1484.47(12)
Z	2	2
ρ_{calc} (g/cm^3)	1.194	1.169
M (mm^{-1})	0.073	0.070
F (000)	572.0	556.0
Crystal size/mm^3	0.633 × 0.135 × 0.089	0.2 × 0.12 × 0.08
Radiation	MoK$_\alpha$ (λ = 0.71073)	MoK$_\alpha$ (λ = 0.71073)
2θ range for data collections/°	3.818 to 50.406	3.194 to 64.738
Reflections collected	42218	55438
Independent Reflections	5354	9756
Goodness-of-fit on F^2	1.052	1.040

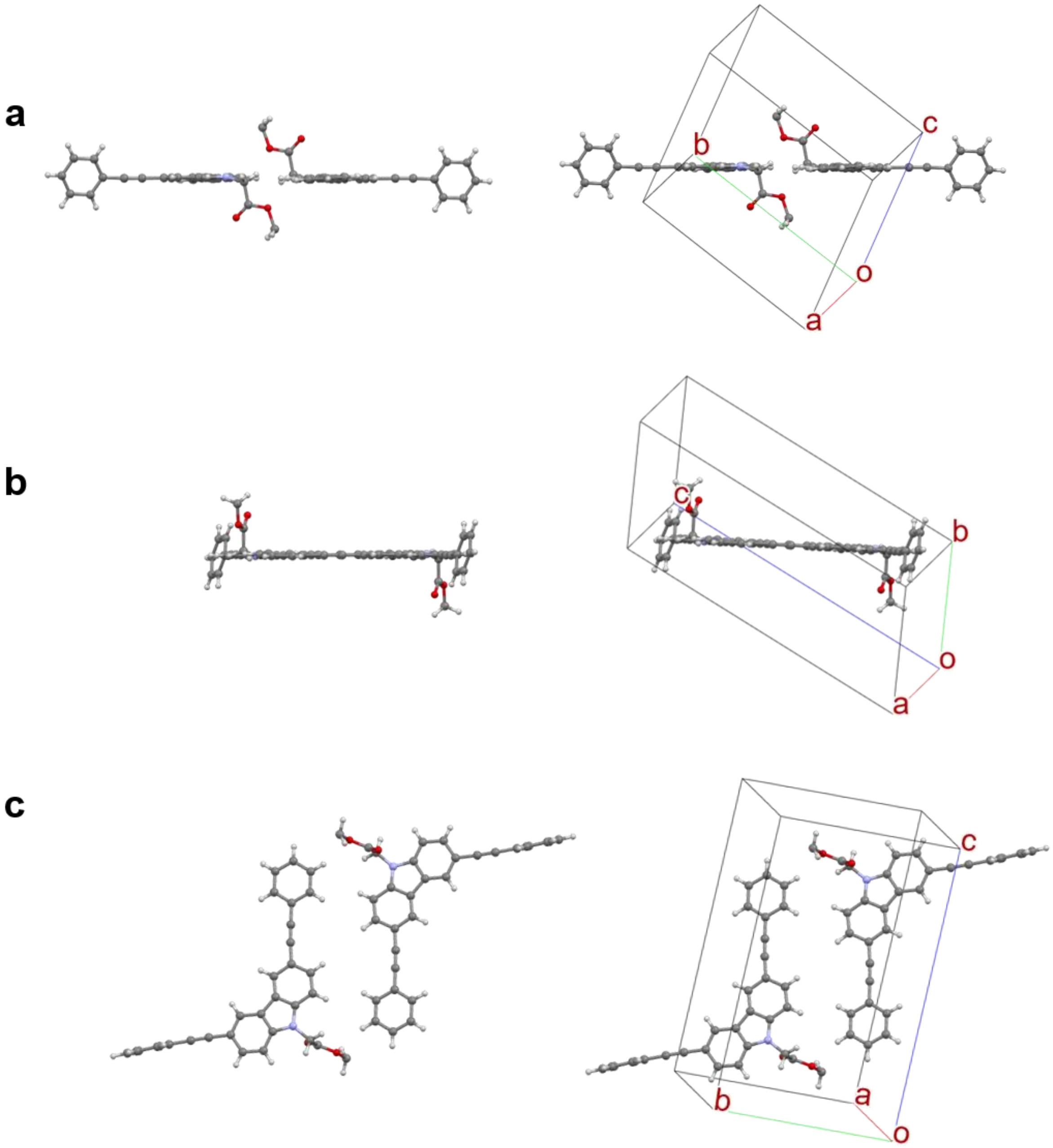


Figure S1: Unit Cell packing of **Est-C8** viewed along different axis (Representation with and without axis). The alkyl chain was truncated to methyl for clarity.

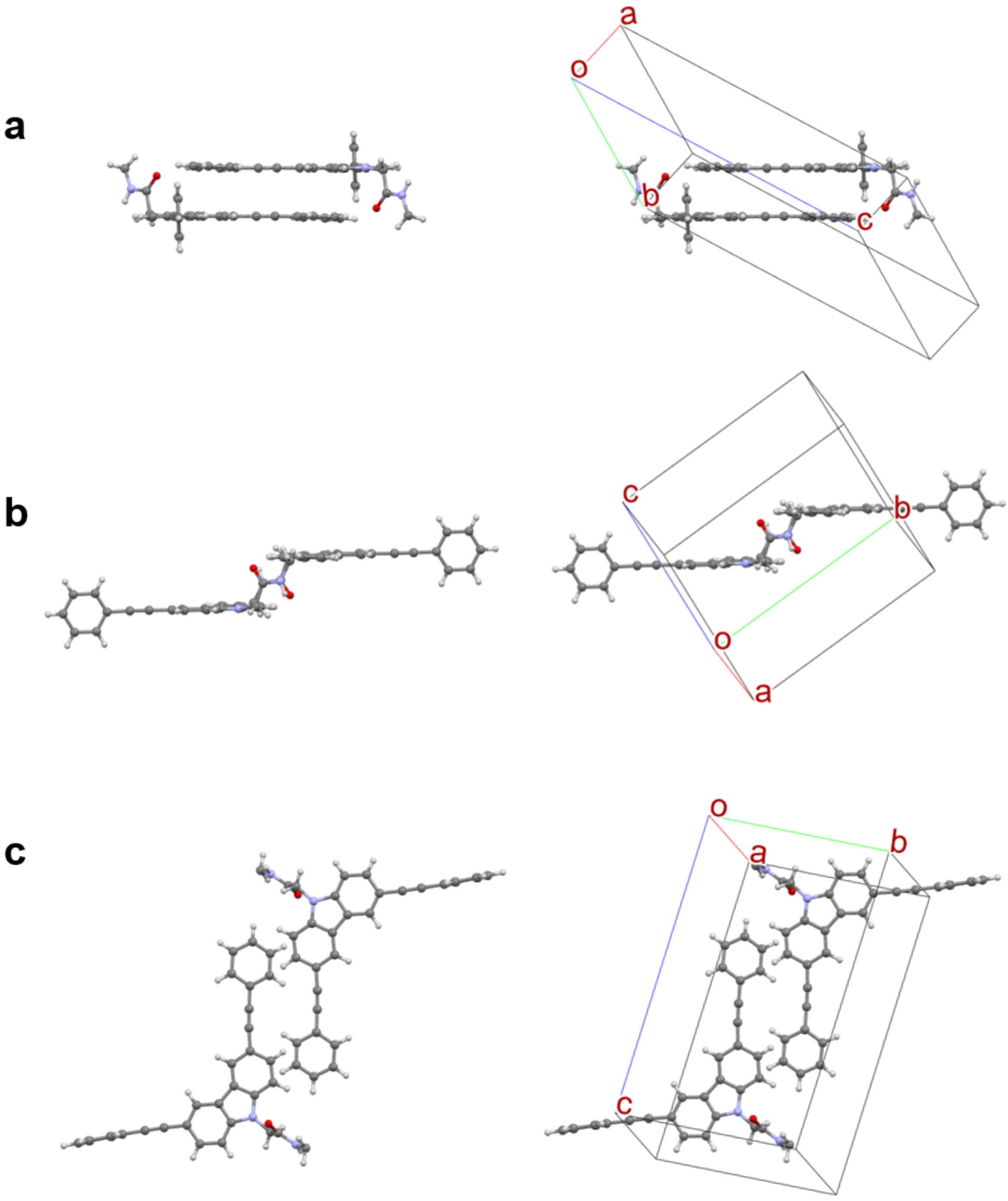


Figure S2: Unit cell packing of **Am-C8** viewed along different axis (Representation with and without axis). The alkyl chain was truncated to methyl for clarity.

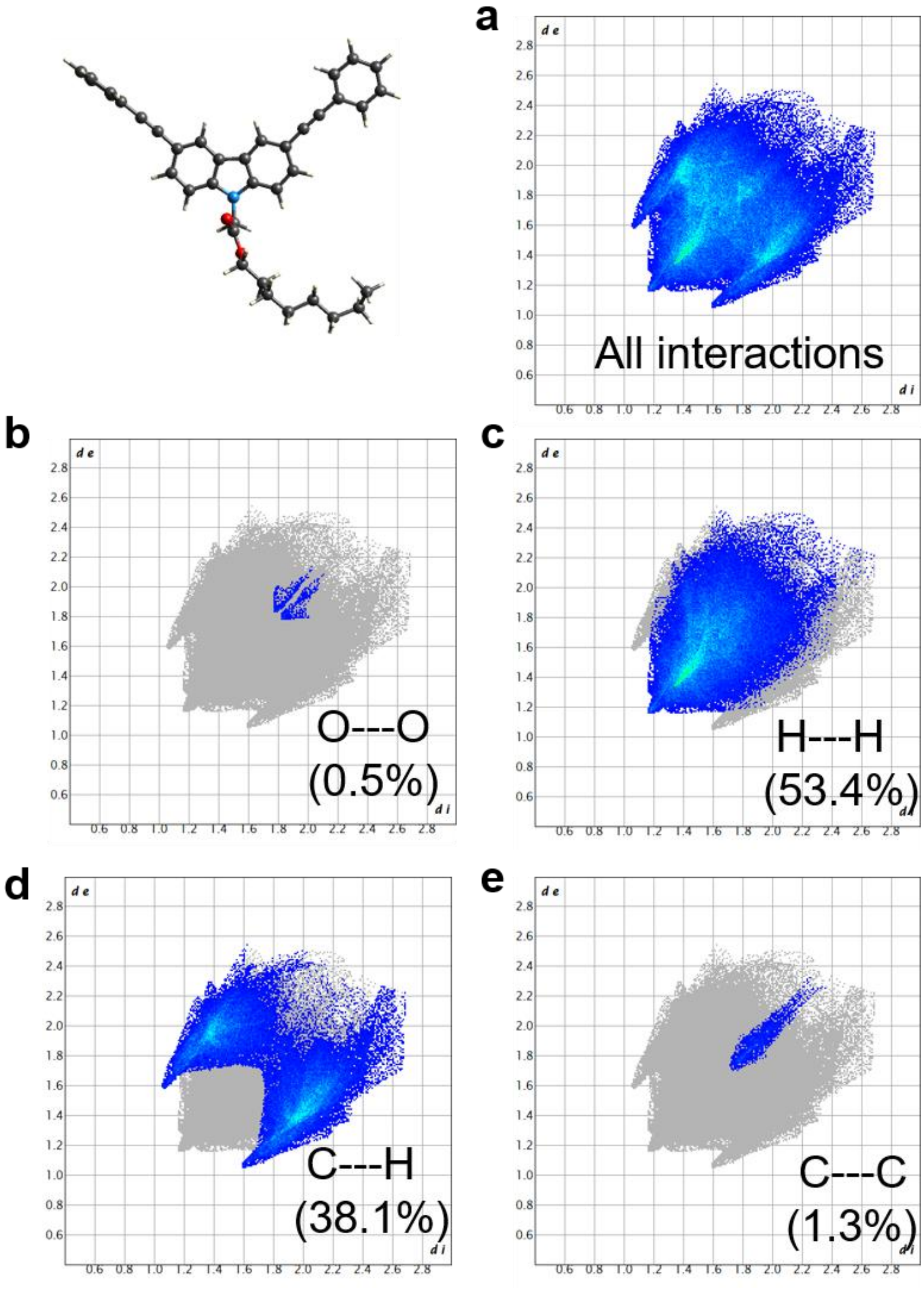


Figure S3: 2D Fingerprint plots of **Est-C8** obtained from Hirshfeld analysis (via crystal explorer software) showing the different interactions.

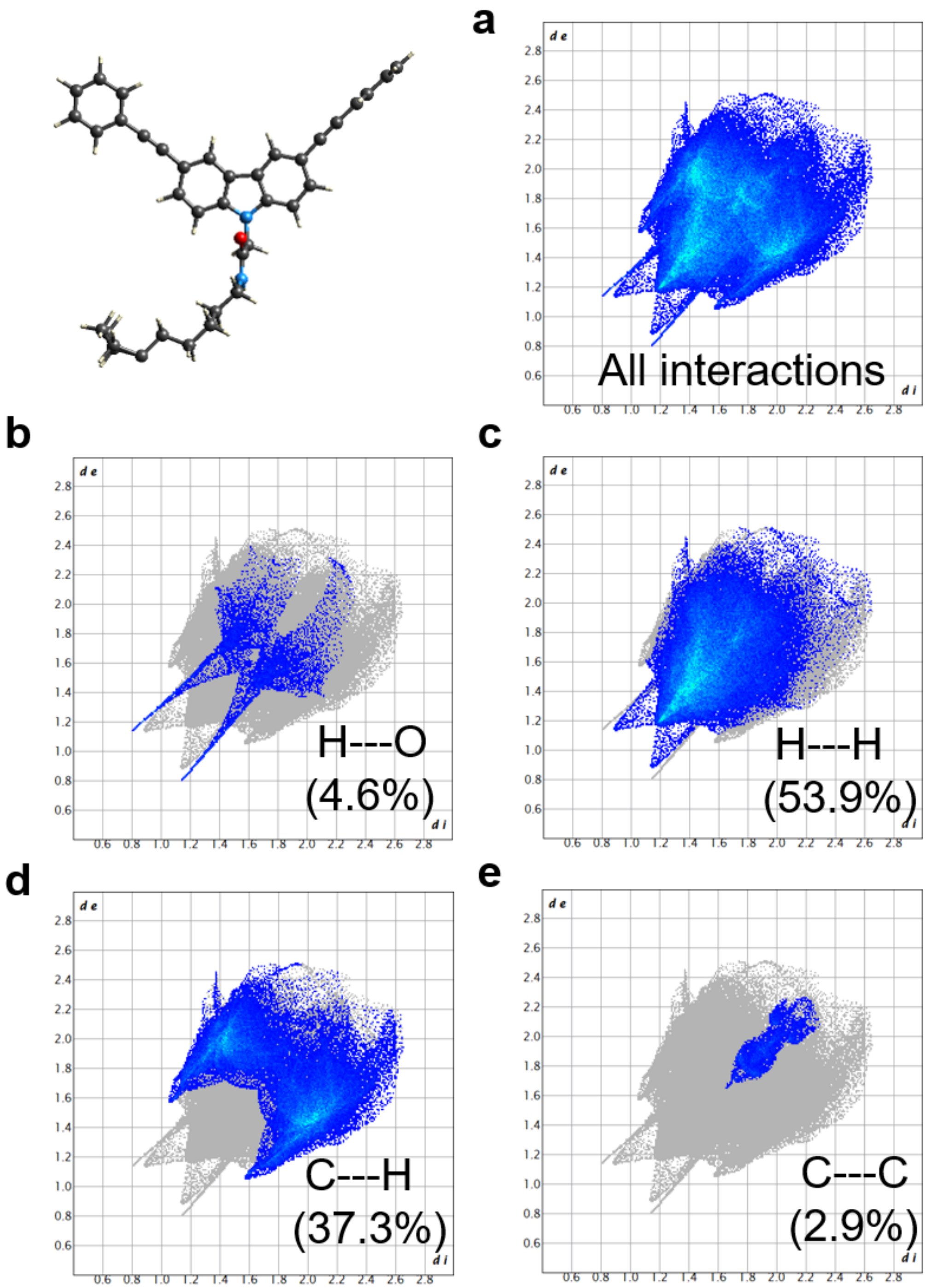


Figure S4: 2D Fingerprint plots of **Am-C8** obtained from Hirshfeld analysis (via crystal explorer software) showing the different interactions.

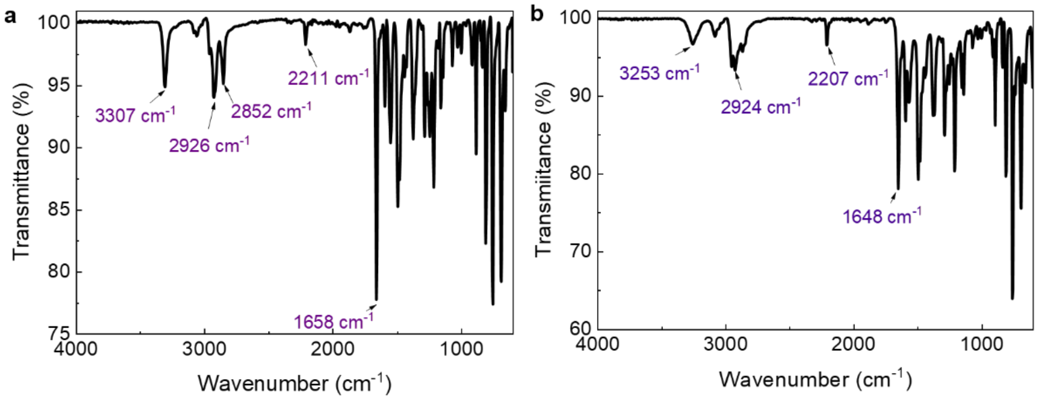


Figure S5: a) and b) Solid state FTIR spectra (ATR mode) of **Am-C8** and **(*S*)-Am-C10**, respectively.

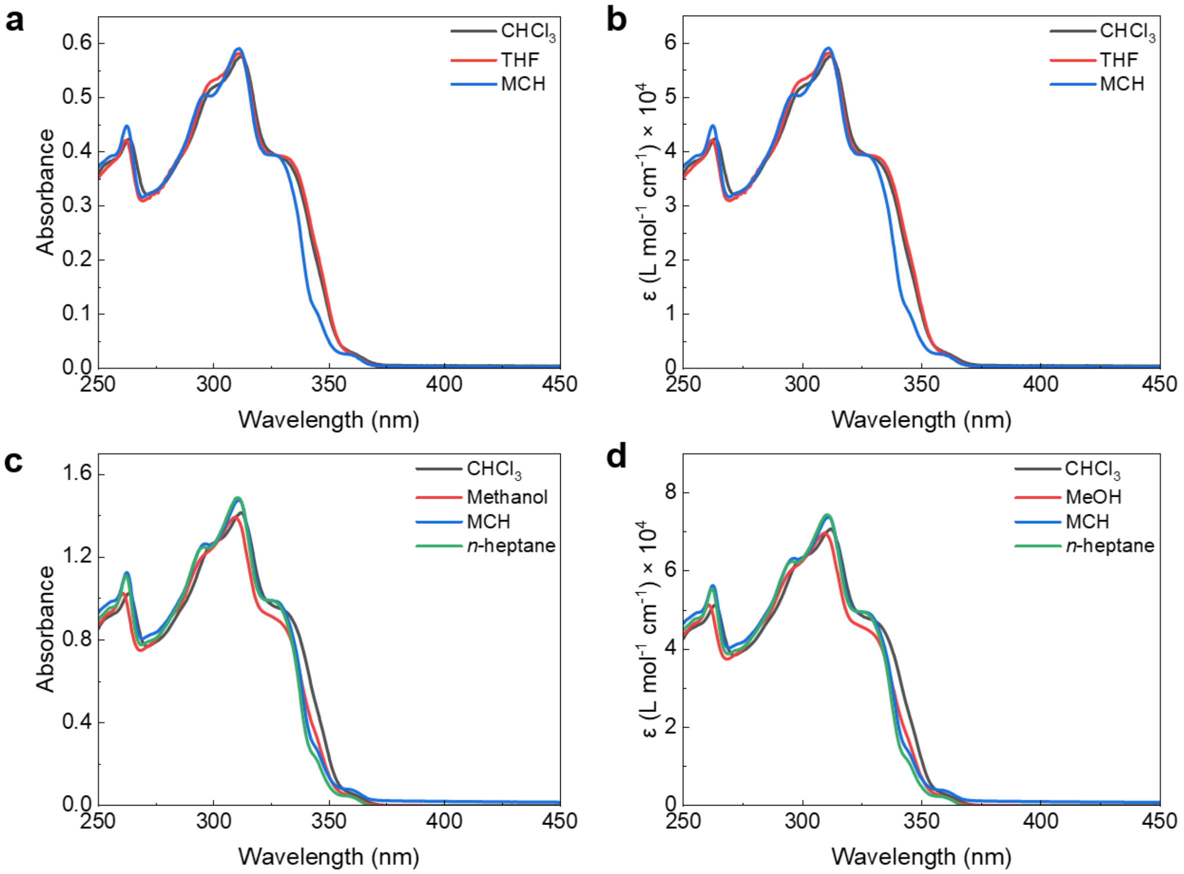


Figure S6: a) and b) UV-vis absorption and molar absorptivity spectra, respectively of **Est-C8** in various solvents (c = 10 µM, l = 10 mm). c) and d) UV-vis absorption and molar absorptivity spectra, respectively of **Est-C8** in various solvents (c = 100 µM, l = 2 mm).

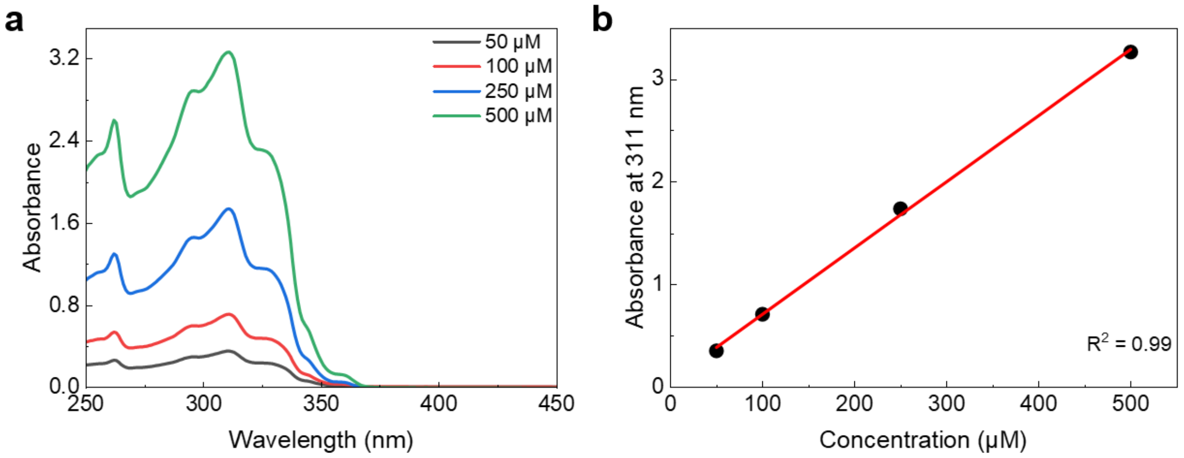


Figure S7: a) Concentrated-dependent UV-vis absorption spectra of **(*S*)-Est-C10** in *n*-heptane ($l = 1$ mm). b) Variation of absorbance of **(*S*)-Est-C10** at 311 nm as a function of concentration in *n*-heptane. The linear-dependence of absorbance with concentration suggests that **(*S*)-Est-C10** follows Beer-Lambert's law and shows no aggregation.

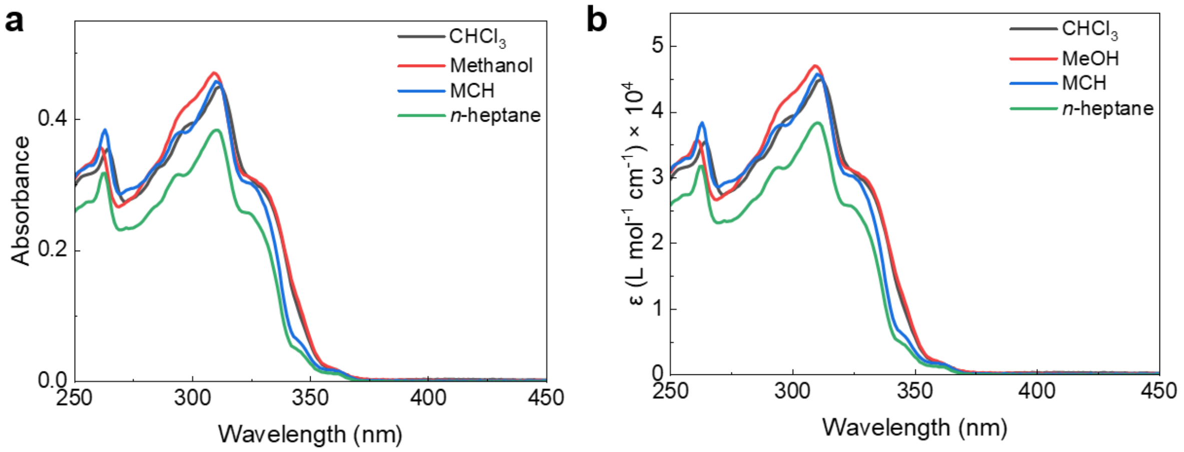


Figure S8: a) and b) UV-vis absorption and molar absorptivity spectra, respectively of **Am-C8** in various solvents ($c = 10$ μM, $l = 10$ mm).

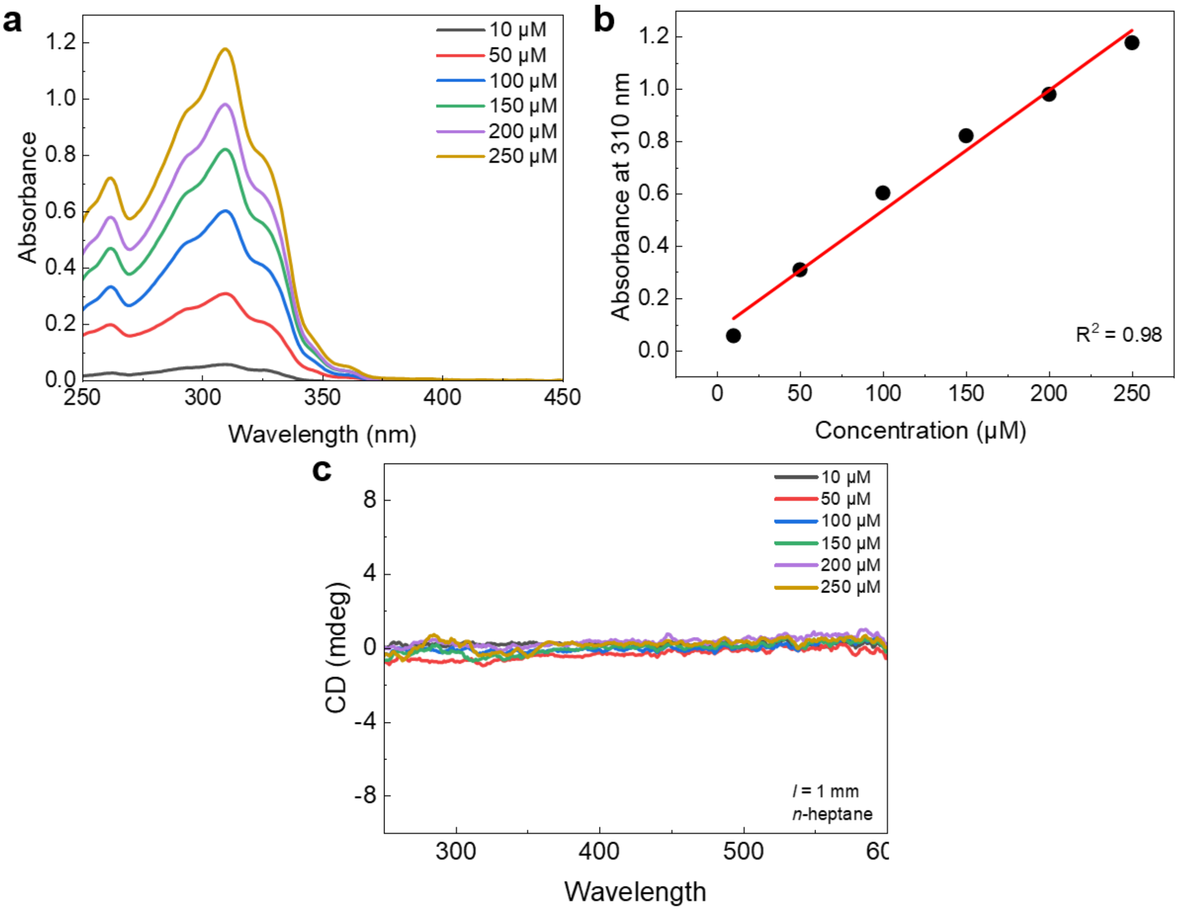


Figure S9: a) Concentration-dependent UV-Vis absorption spectra of **(*S*)-Am-C10** in *n*-heptane (*l* = 1 mm). b) Variation of absorbance of **(*S*)-Am-C10** at 310 nm as a function of concentration in *n*-heptane. The linear-dependence of absorbance with concentration suggests that **(*S*)-Am-C10** follows Beer-Lambert's law and shows no aggregation. c) Concentration-dependent circular dichroism (CD) spectra of **(*S*)-Am-C10** in *n*-heptane.

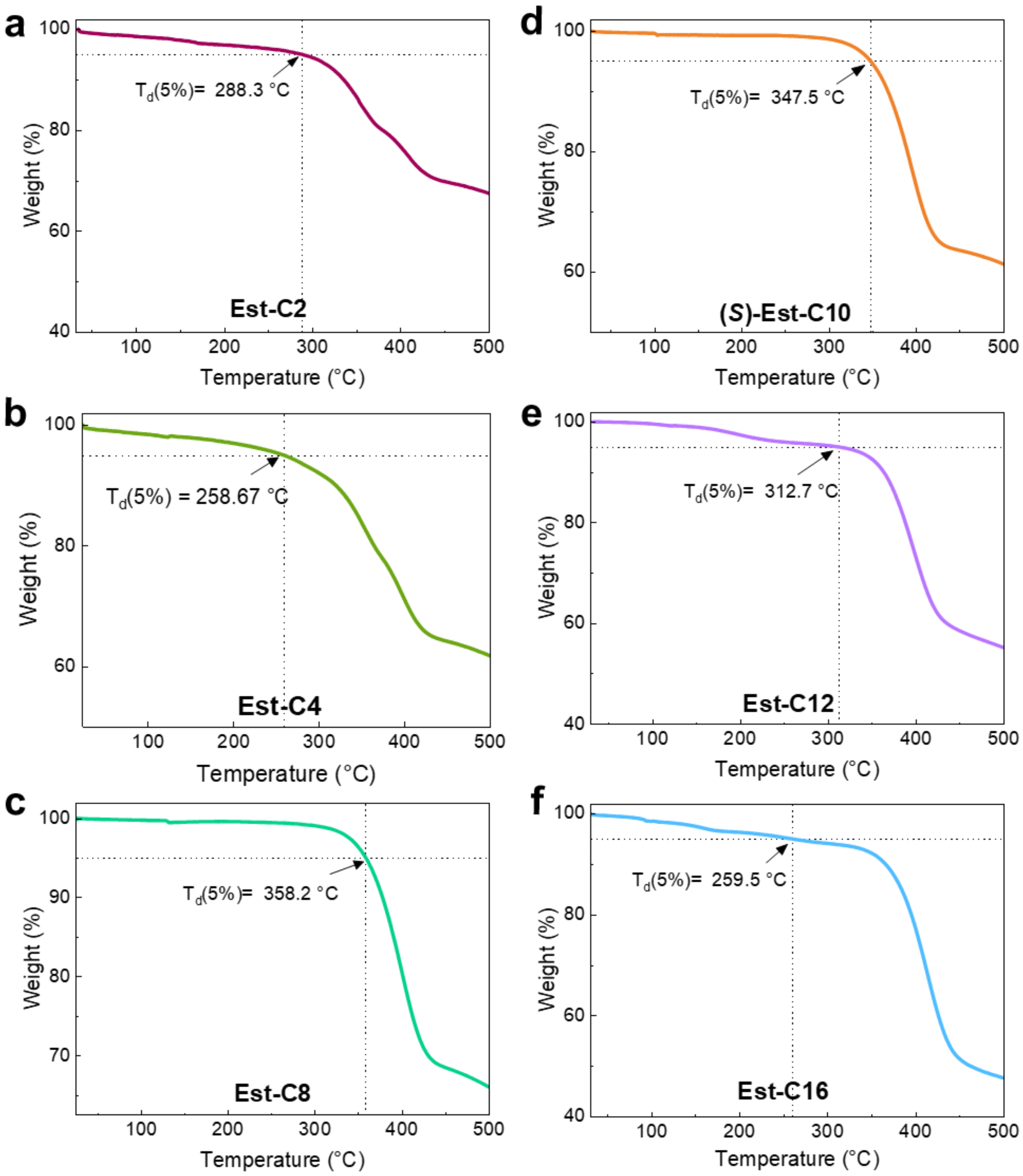


Figure S10: Thermogravimetric analysis of **Est-C2**, **Est-C4**, **Est-C8**, **(*S*)-Est-C10, Est-C12** and **Est-C16** at the rate of 10 °C/min.

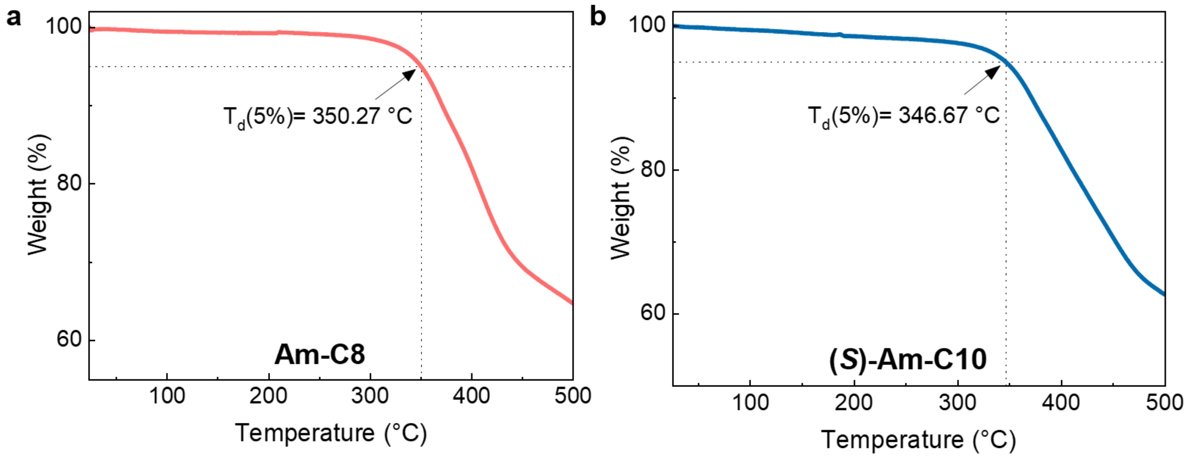


Figure S11: Thermogravimetric analysis of **Am-C8** and **(*S*)-Am-C10** at the rate of 10 °C/min.

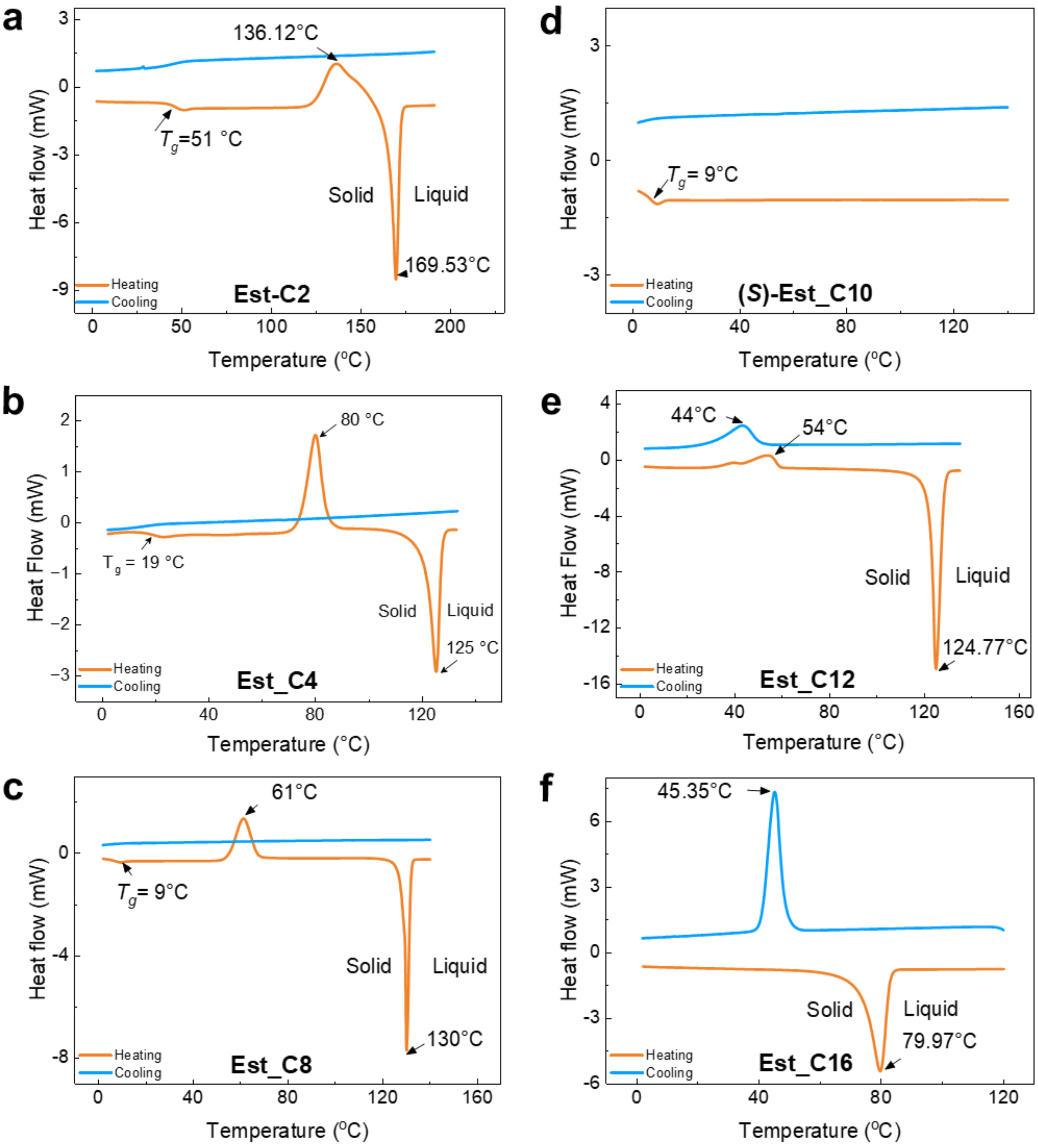


Figure S12: DSC profile of **Est-C2**, **Est-C4**, **Est-C8**, **(S)-Est-C10, Est-C12** and **Est-C16 and** (second heating/cooling cycle) at the rate of 10 °C/min.

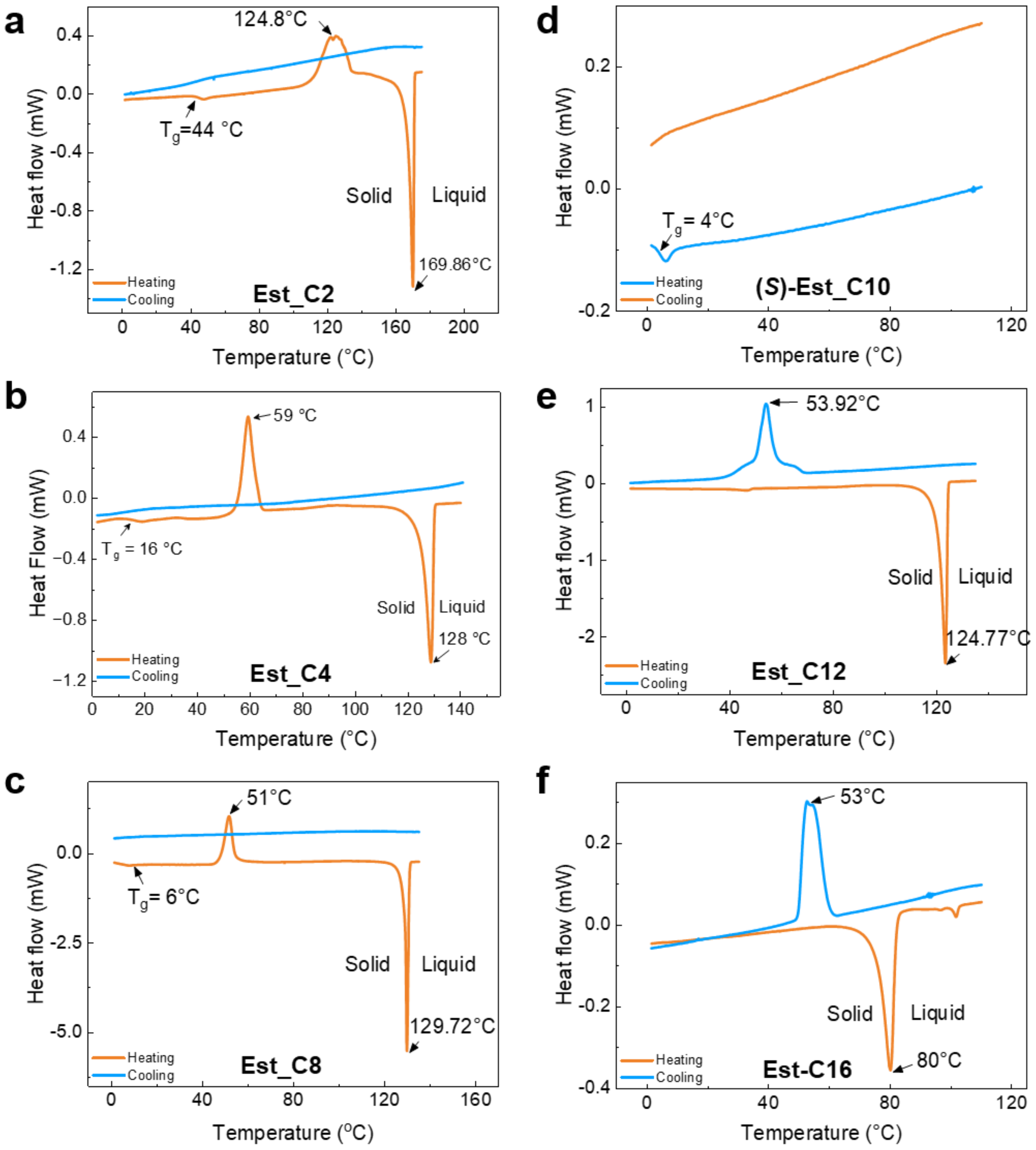


Figure S13: DSC profile of **Est-C2**, **Est-C4**, **Est-C8**, **(*S*)-Est-C10**, **Est-C12** and **Est-C16** (second heating/cooling cycle) at the rate of 2 °C/min.

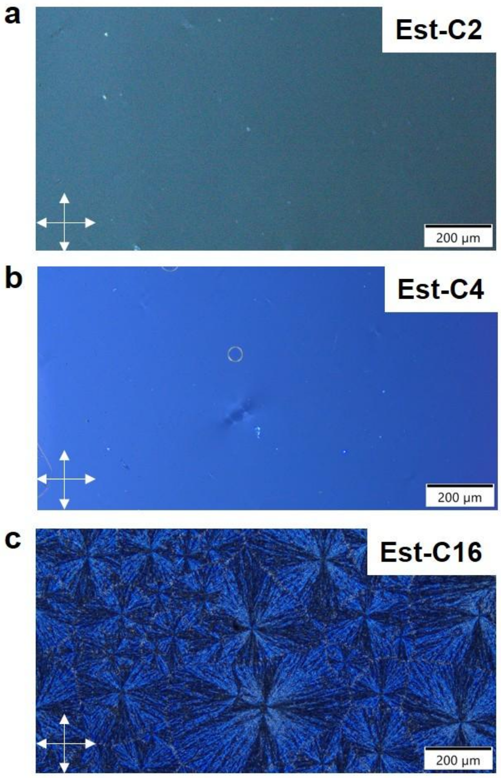


Figure S14: POM images (10x) under cross polarizer of **Est-C2**, **Est-C4** and **Est-C16** recorded in thin film at room temperature after first heating and cooling cycle at the rate of 10 °C/min.

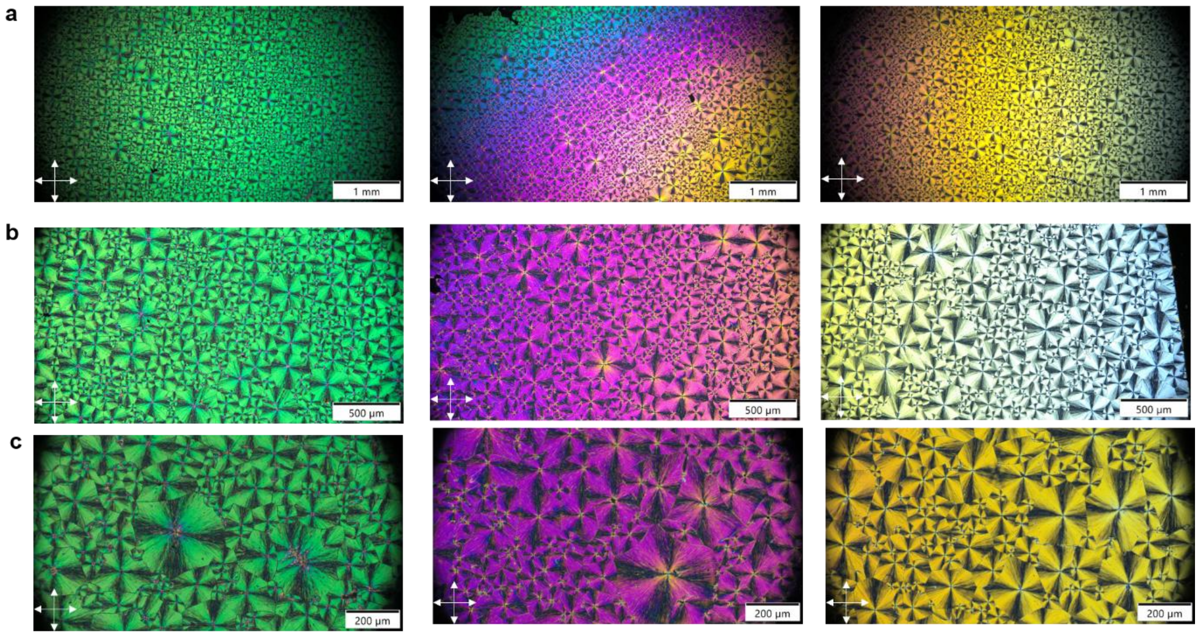


Figure S15: a), b) and c) POM images at 5x, 10x and 20x magnification, respectively under cross polarizer of **Am-C8** recorded in thin film at room temperature after first heating and cooling cycle at the rate of 10 °C/min.

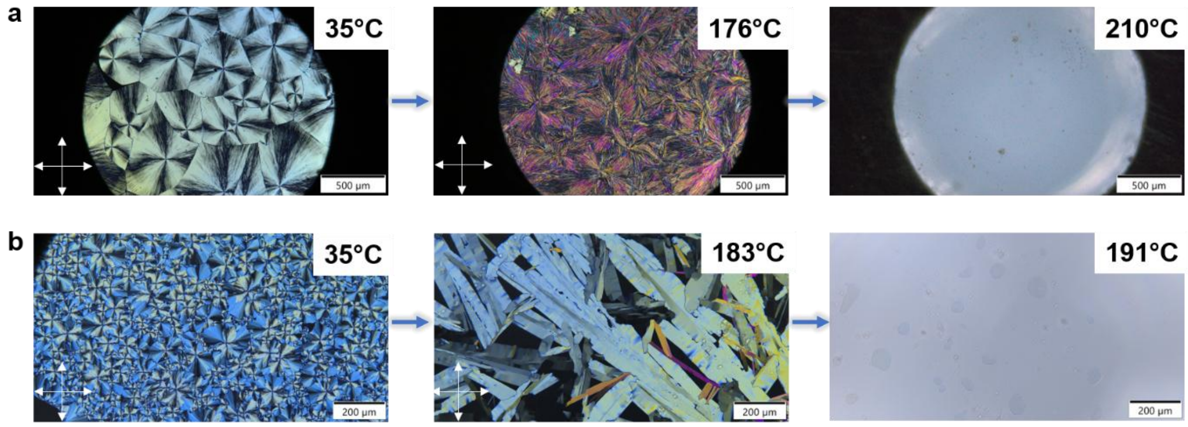


Figure S16: a) and b) Morphological change (POM images) of **Am-C8** and **(*S*)-Am-C10**, respectively during second heating cycle under cross polarizer at the rate of 10 °C/min.

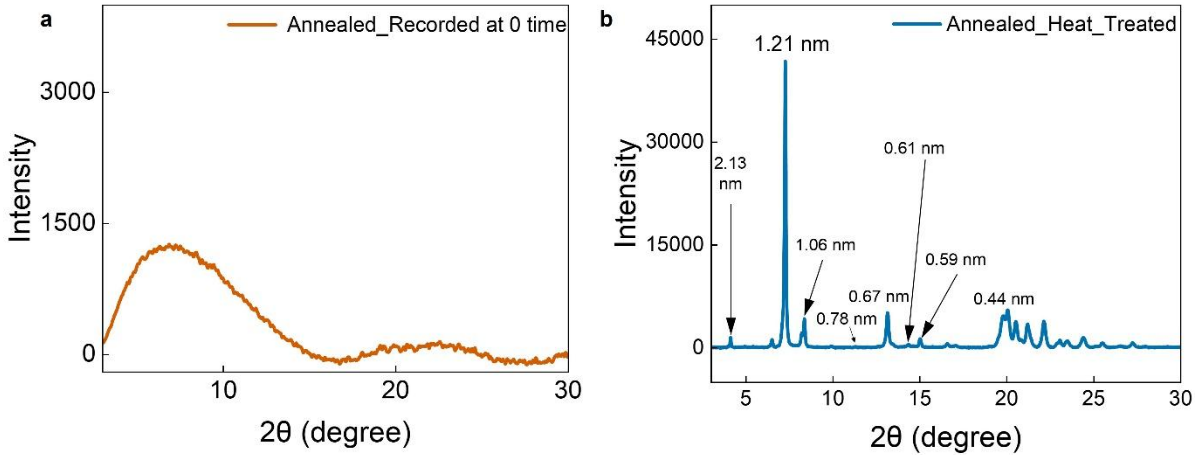


Figure S17: a) XRD of **Est-C8** annealed on coverslip and recorded at room temperature. b) XRD of **Est-C8** annealed on coverslip followed by heating till 70 °C and recorded at room temperature.

Table S2: Details of XRD pattern of **Est-C8** (after heating to 70 °C during the second cycle).

2θ (°)	d-spacing (nm)	Miller indices (hkl)	Ratio of Miller indices = d(hkl)/d(100)	Expected ratio of Miller indices for columnar hexagonal phase
4.14	2.13	(100)	1	1
7.28	1.21	(110)	0.568	0.577 (1/√3)
8.38	1.06	(200)	0.497	0.50 (1/2)
11.29	0.78	(210)	0.366	0.377 (1/√7)
13.17	0.67	(300)	0.314	0.333 (1/3)
14.41	0.61	(220)	0.286	0.288 (1/√12)
15.05	0.59	(310)	0.276	0.277 (1/√13)

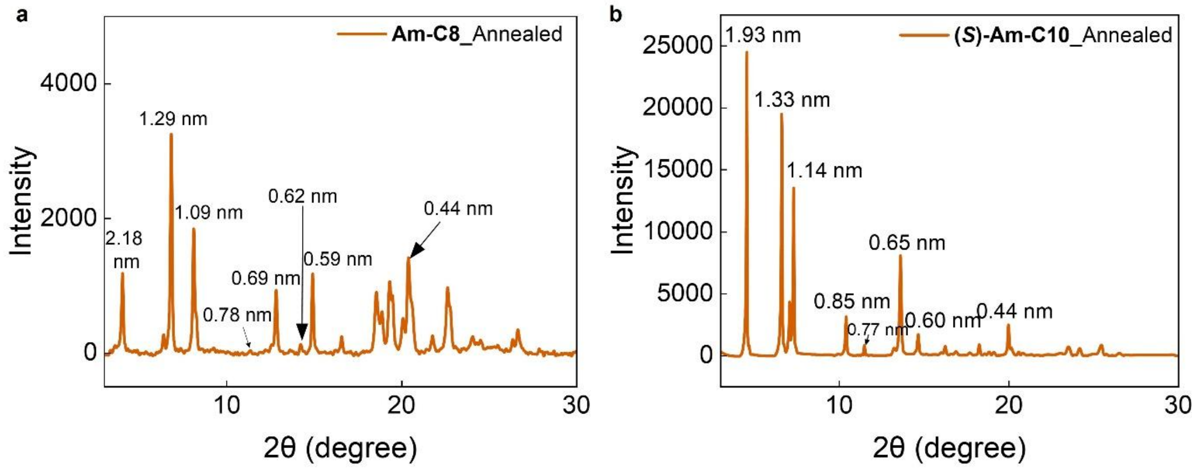


Figure S18: a) and b) XRD of **Am-C8** and **(*S*)-Am-C10**, respectively annealed on coverslip and recorded at room temperature.

Table S3: Details of XRD pattern of **Am-C8**.

2θ (°)	d-spacing (nm)	Miller indices (hkl)	Ratio of Miller indices = d(hkl)/d(100)	Expected ratio of Miller indices for columnar hexagonal phase
4.14	2.18	(100)	1	1
7.28	1.29	(110)	0.591	0.577 (1/√3)
8.38	1.09	(200)	0.500	0.50 (1/2)
11.36	0.78	(210)	0.357	0.377 (1/√7)
13.17	0.69	(300)	0.316	0.333 (1/3)
15.05	0.62	(220)	0.284	0.288 (1/√12)
19.84	0.59	(310)	0.270	0.277 (1/√13)

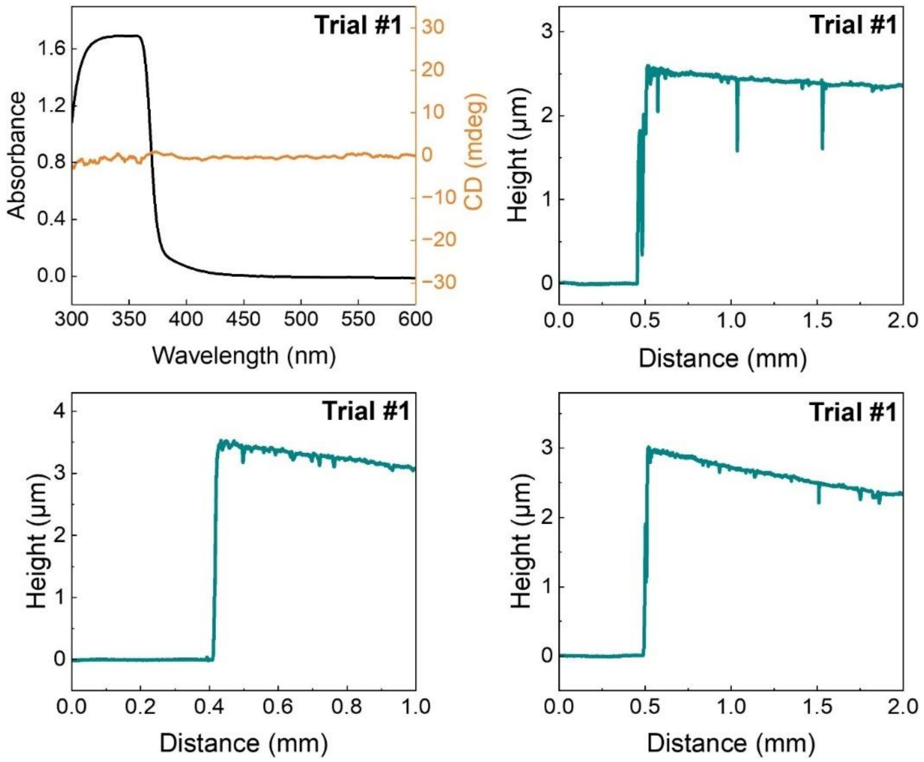


Figure S19: UV-vis absorption and CD spectrum of annealed films of **(*S*)-Est-C10** (**trial #1**). The corresponding height profile of film measured using Dektak profilometer (average thickness = 2.79 ± 0.5 µm).

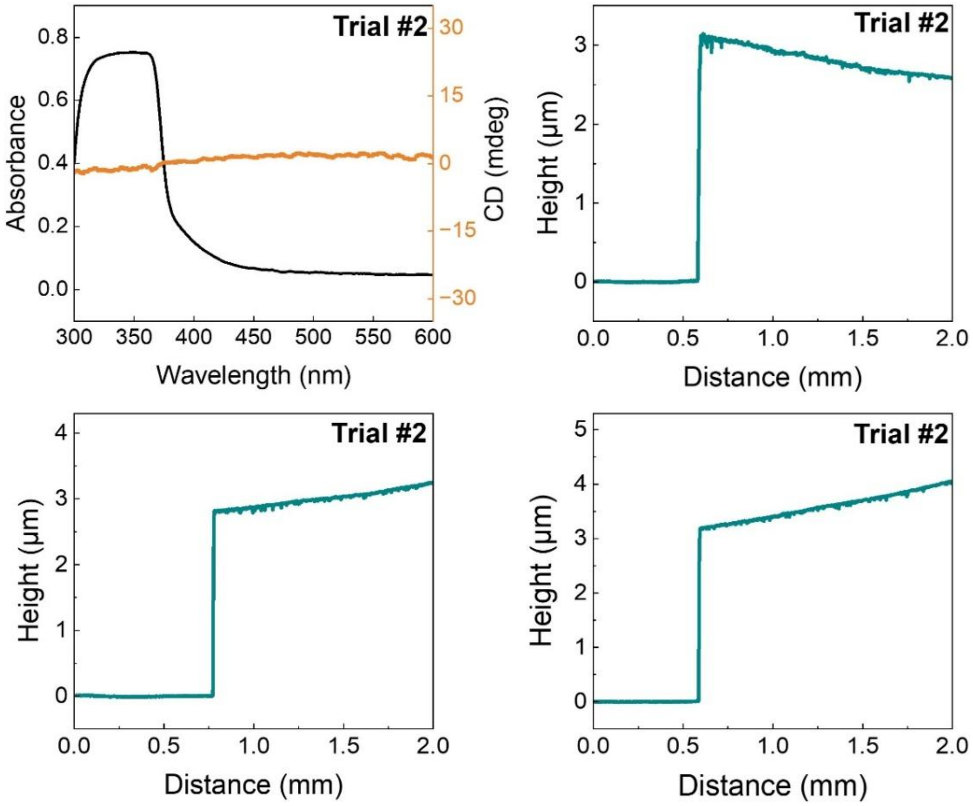


Figure S20: UV-vis absorption and CD spectrum of annealed films of **(*S*)-Est-C10** (**trial #2**). The corresponding height profile of film measured using Dektak profilometer (average thickness =3.73 ± 0.8 µm).

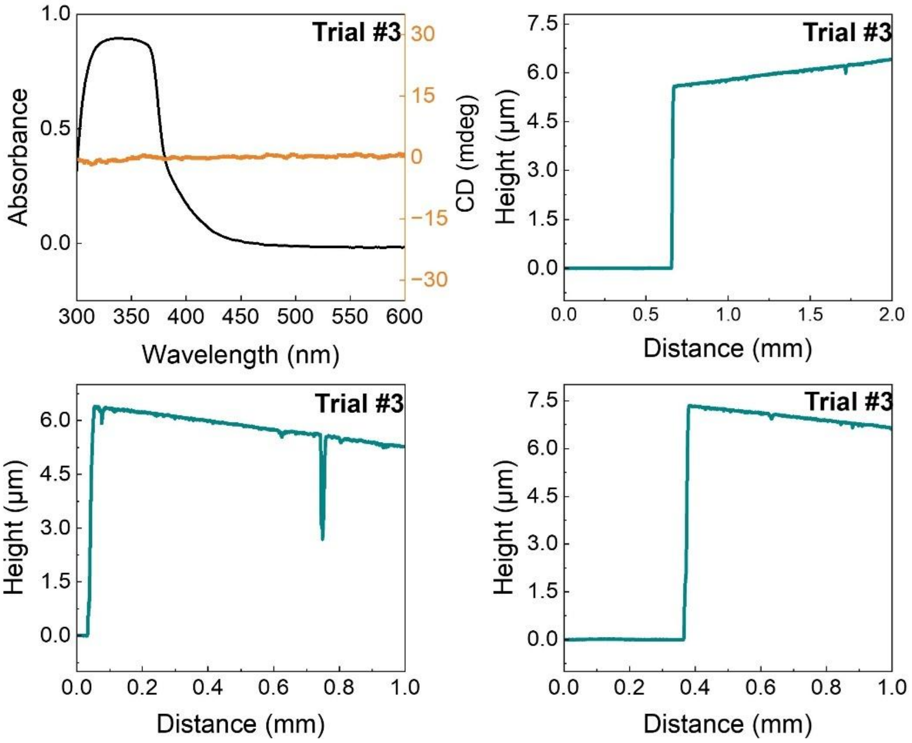


Figure S21: UV-vis absorption and CD spectrum of annealed films of **(*S*)-Est-C10** (**trial #3**). The corresponding height profile of film measured using Dektak profilometer (average thickness = 6.28 ± 0.6 µm).

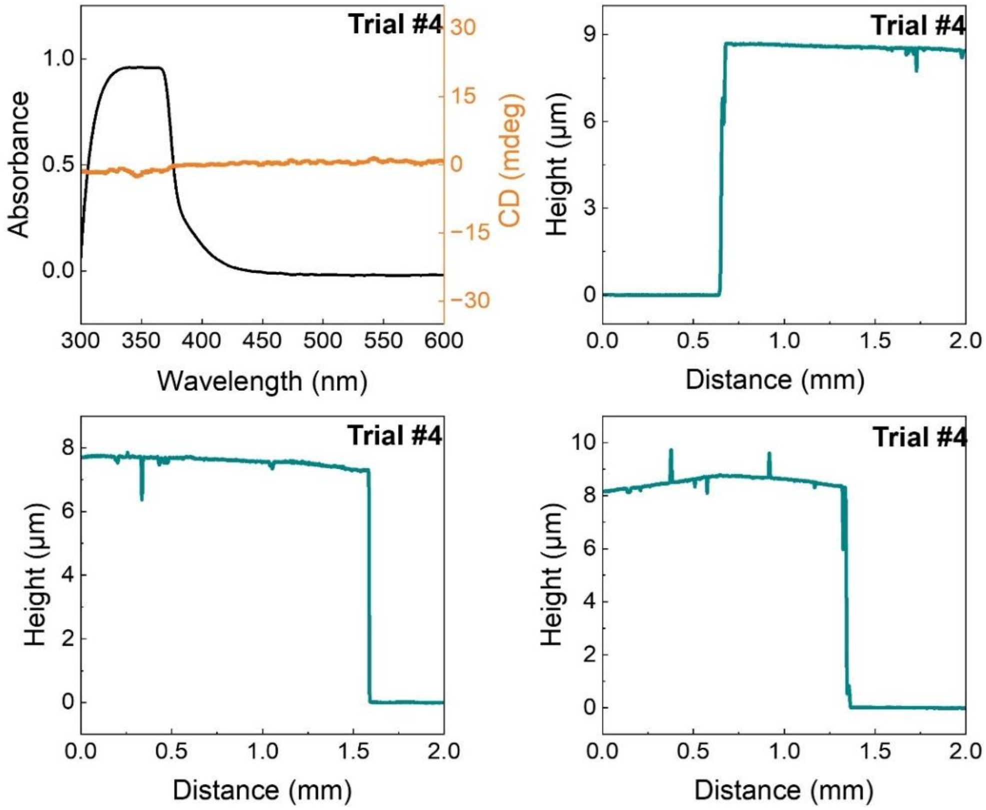


Figure S22: UV-vis absorption and CD spectrum of annealed films of **(*S*)-Est-C10** (**trial #4**). The corresponding height profile of film measured using Dektak profilometer (average thickness = 8.56 ± 1.2 µm).

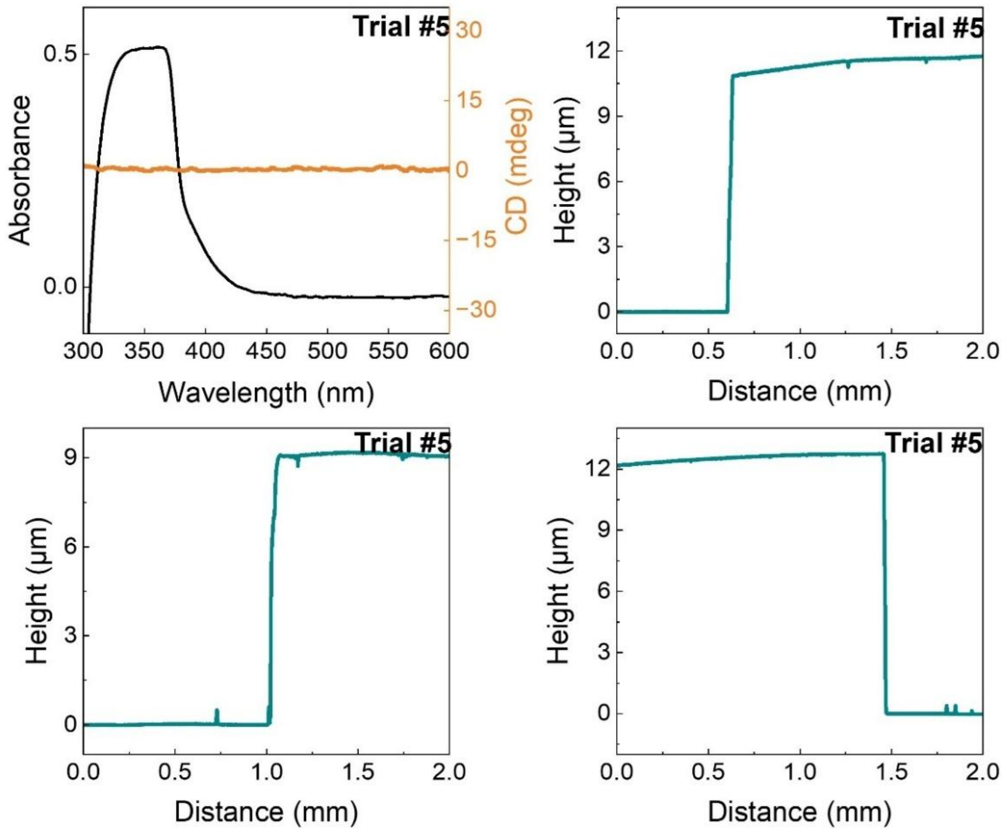


Figure S23: UV-vis absorption and CD spectrum of annealed films of **(*S*)-Est-C10** (**trial #5**). The corresponding height profile of film measured using Dektak profilometer (average thickness = 10.89 ± 1.4 µm.).

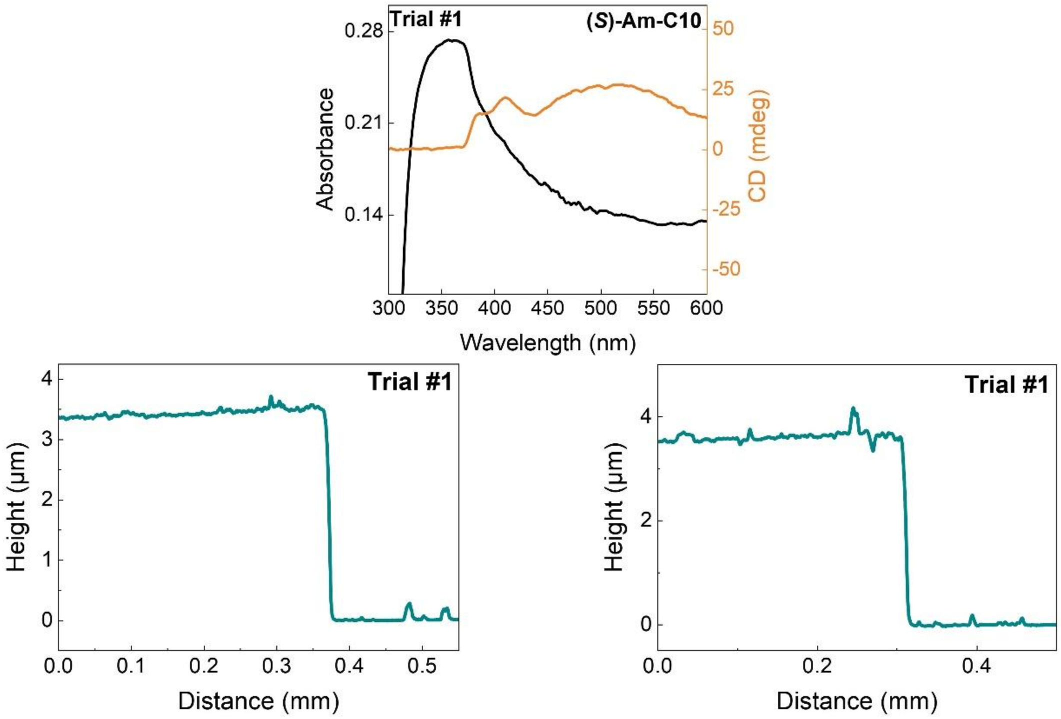


Figure S24: UV-vis absorption and CD spectrum of annealed films of **(*S*)-Am-C10** (**trial #1**). The corresponding height profile of film measured using Dektak profilometer (average thickness = 3.48 ± 0.09 µm).

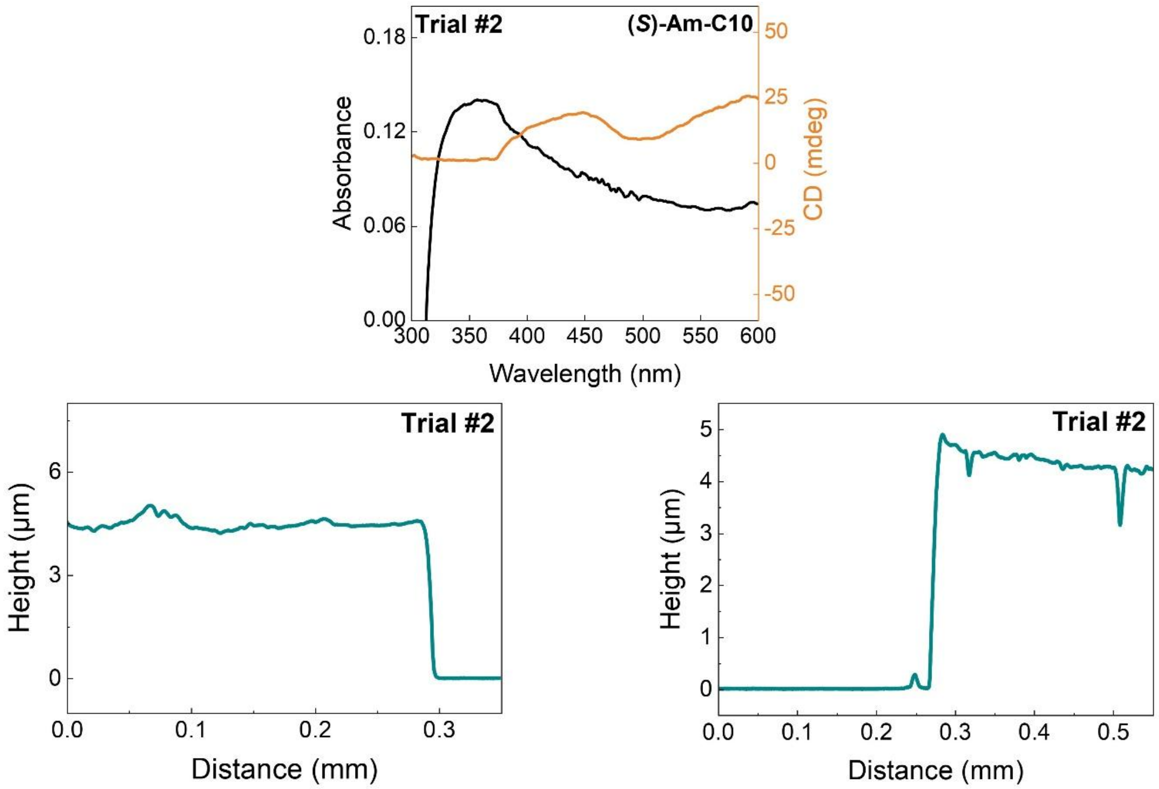


Figure S25: UV-vis absorption and CD spectrum of annealed films of **(*S*)-Am-C10** (**trial #2**). The corresponding height profile of film measured using Dektak profilometer (average thickness = 4.53 ± 0.04 µm).

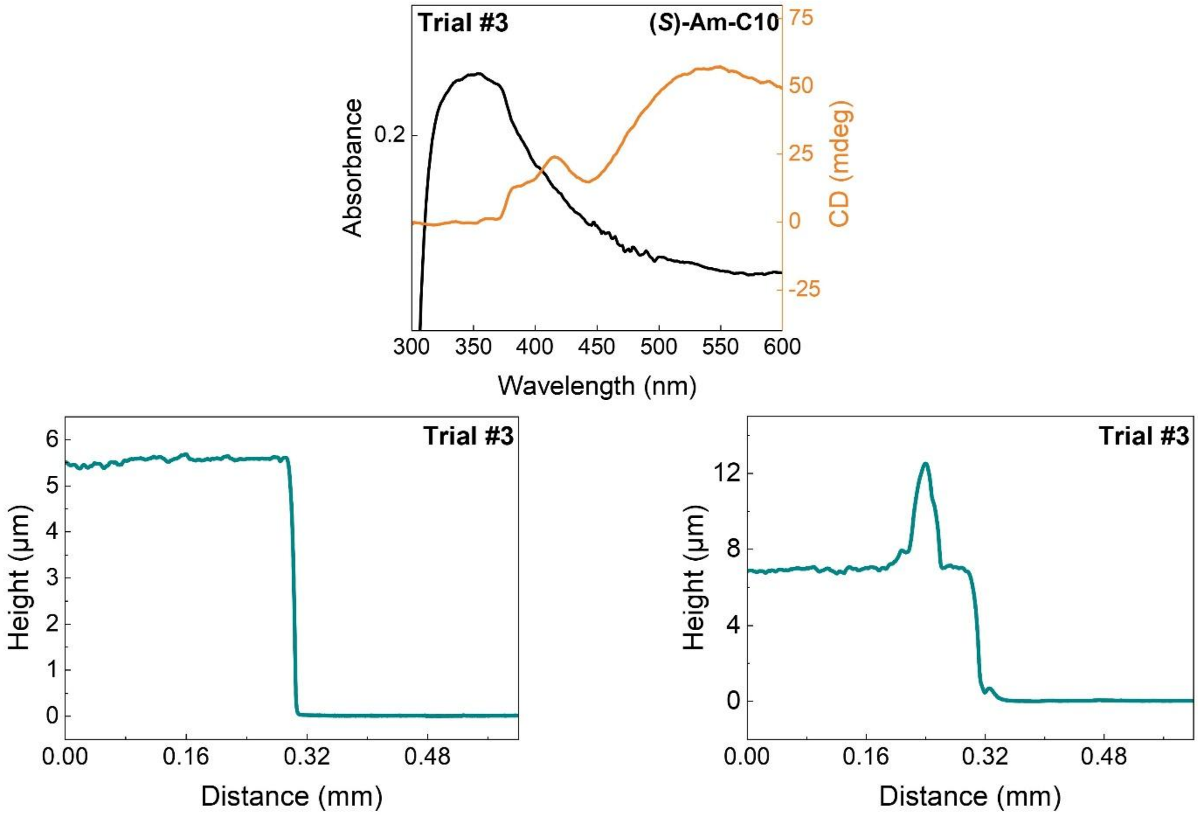


Figure S26: UV-vis absorption and CD spectrum of annealed films of **(*S*)-Am-C10** (**trial #3**). The corresponding height profile of film measured using Dektak profilometer (average thickness = 6.15 ± 0.87 µm).

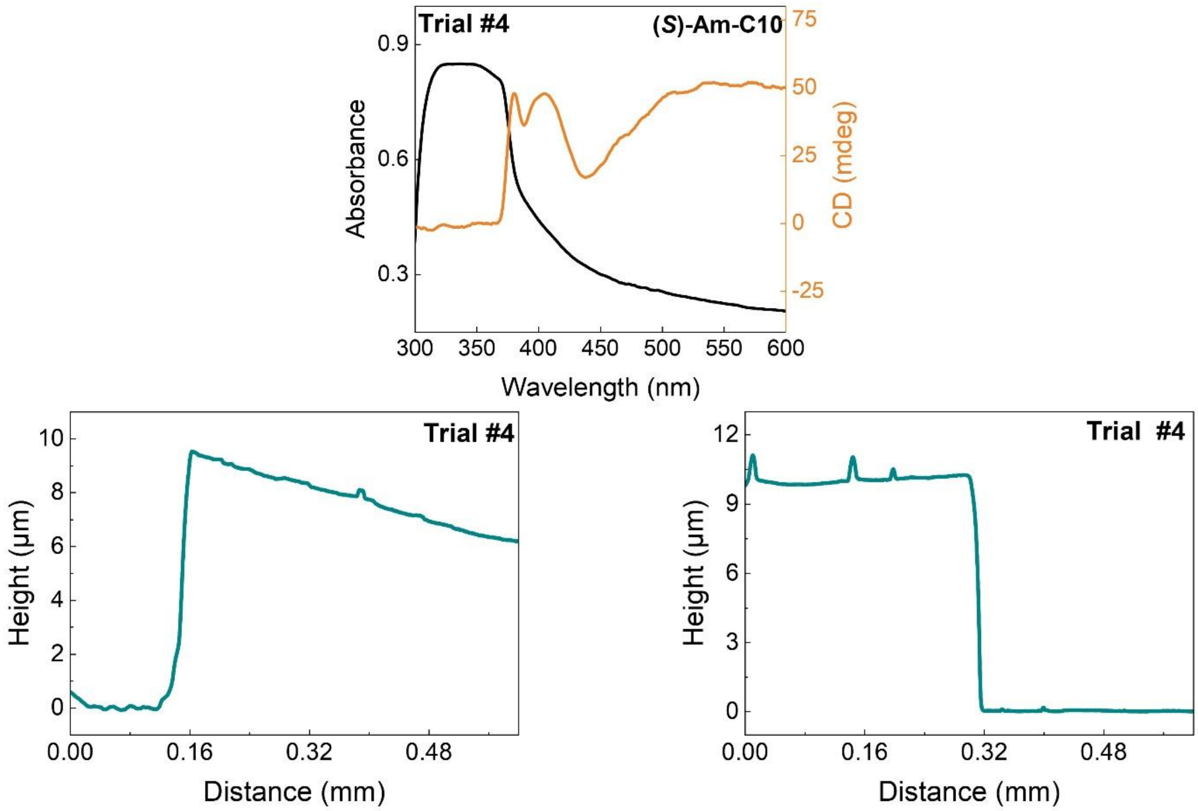


Figure S27: UV-vis absorption and CD spectrum of annealed films of **(*S*)-Am-C10** (**trial #4**). The corresponding height profile of film measured using Dektak profilometer (average thickness = 8.9 ± 1.5 µm).

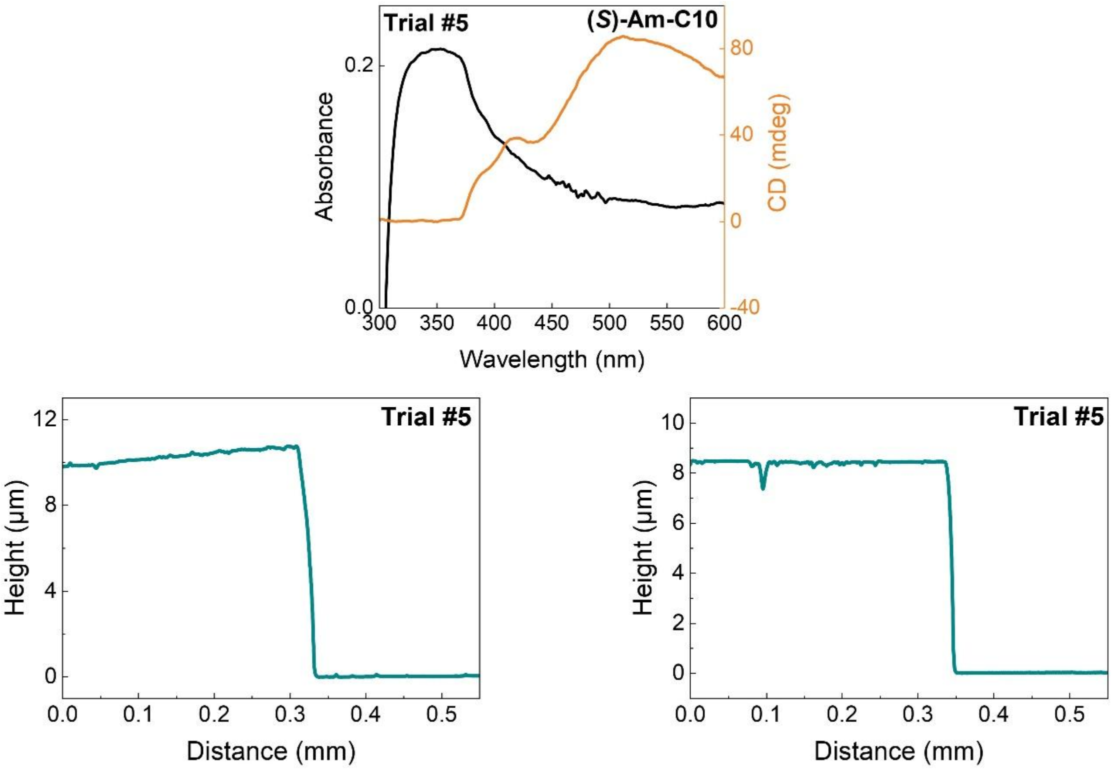


Figure S28: UV-vis absorption and CD spectrum of annealed films of **(*S*)-Am-C10** (**trial #5**). The corresponding height profile of film measured using Dektak profilometer (average thickness = 9.3 ± 1.2 µm).

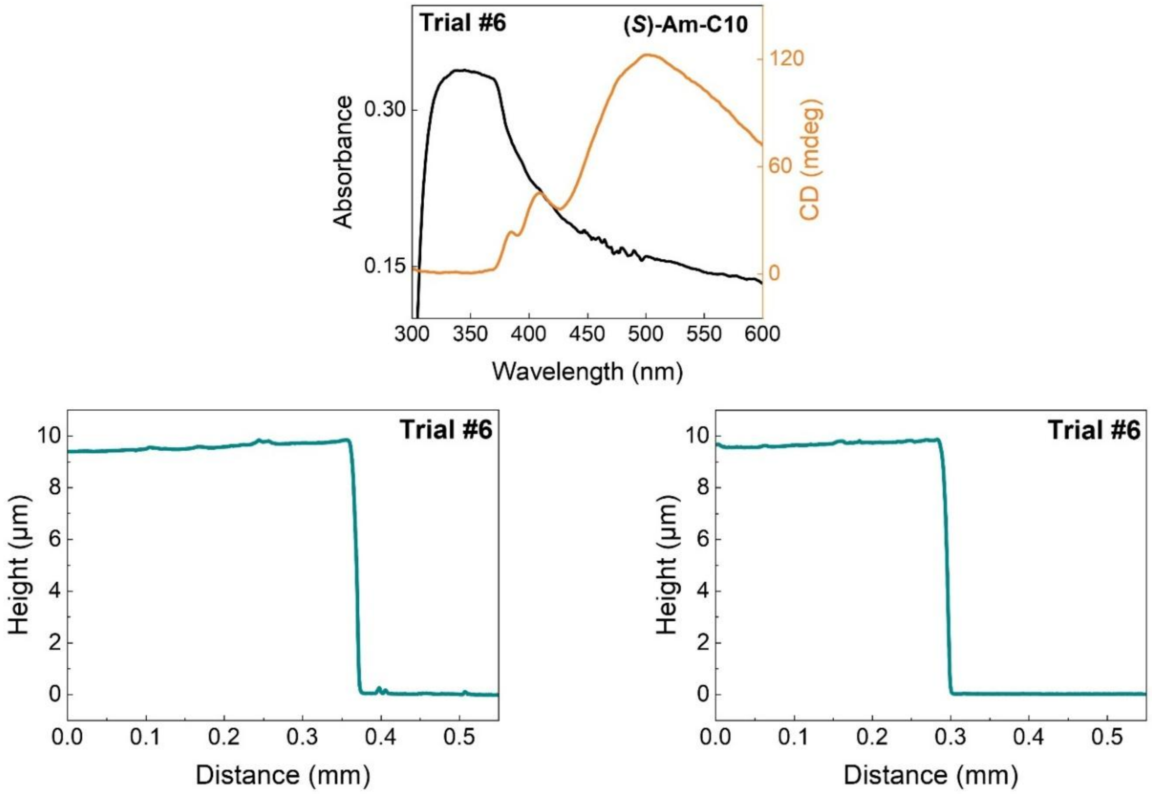


Figure S29: UV-vis absorption and CD spectrum of annealed films of **(*S*)-Am-C10** (**trial #6**). The corresponding height profile of film measured using Dektak profilometer (average thickness = 9.65 ± 0.12 µm).

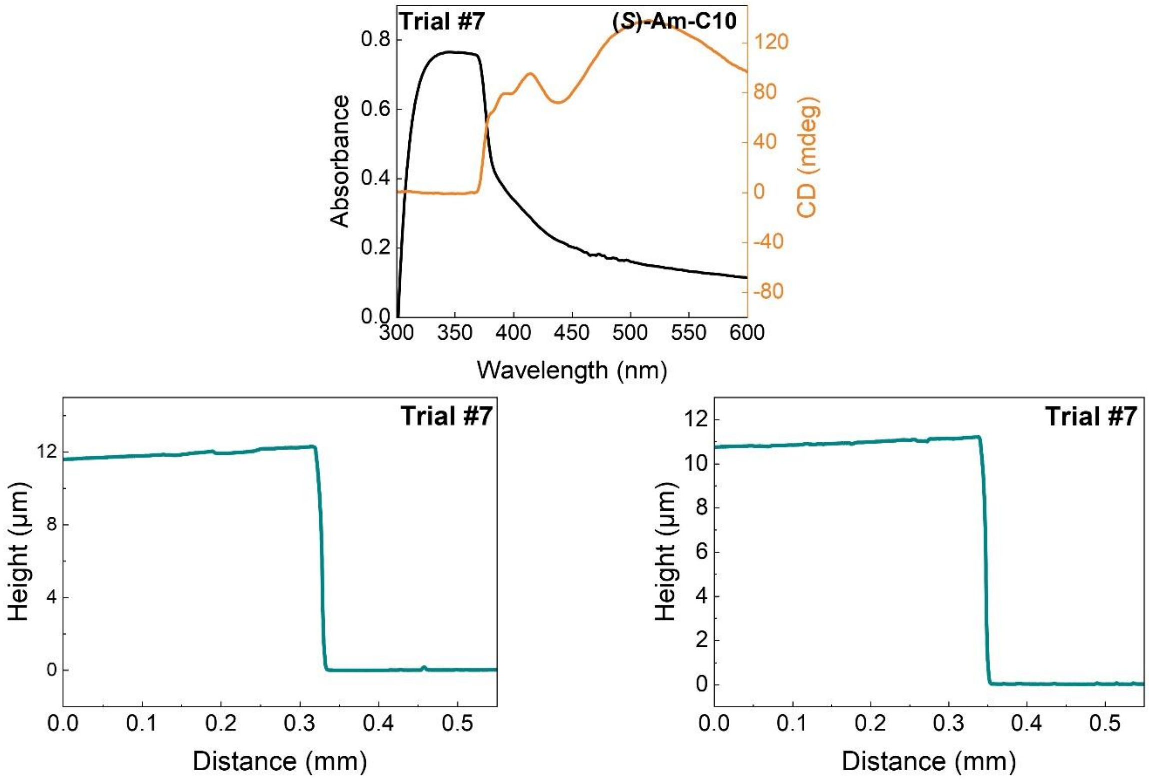


Figure S30: UV-vis absorption and CD spectrum of annealed films of **(*S*)-Am-C10** (**trial #7**). The corresponding height profile of film measured using Dektak profilometer (average thickness = 11.43 ± 0.69).

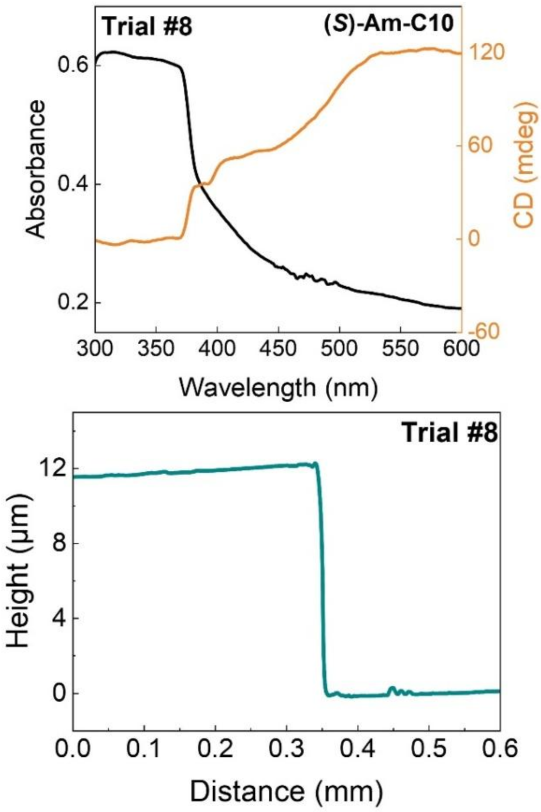


Figure S31: UV-vis absorption and CD spectrum of annealed films of **(*S*)-Am-C10** (**trial #8**). The corresponding height profile of film measured using Dektak profilometer (average thickness = 14.2 ± 3.3 µm).

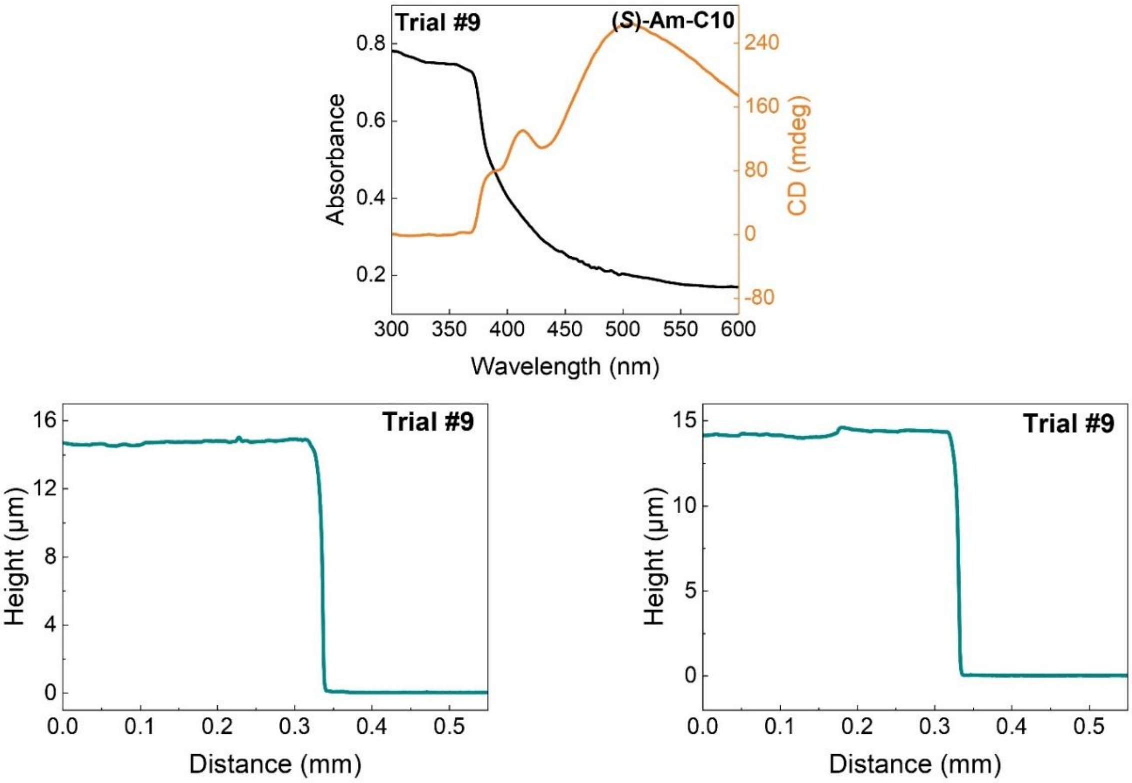
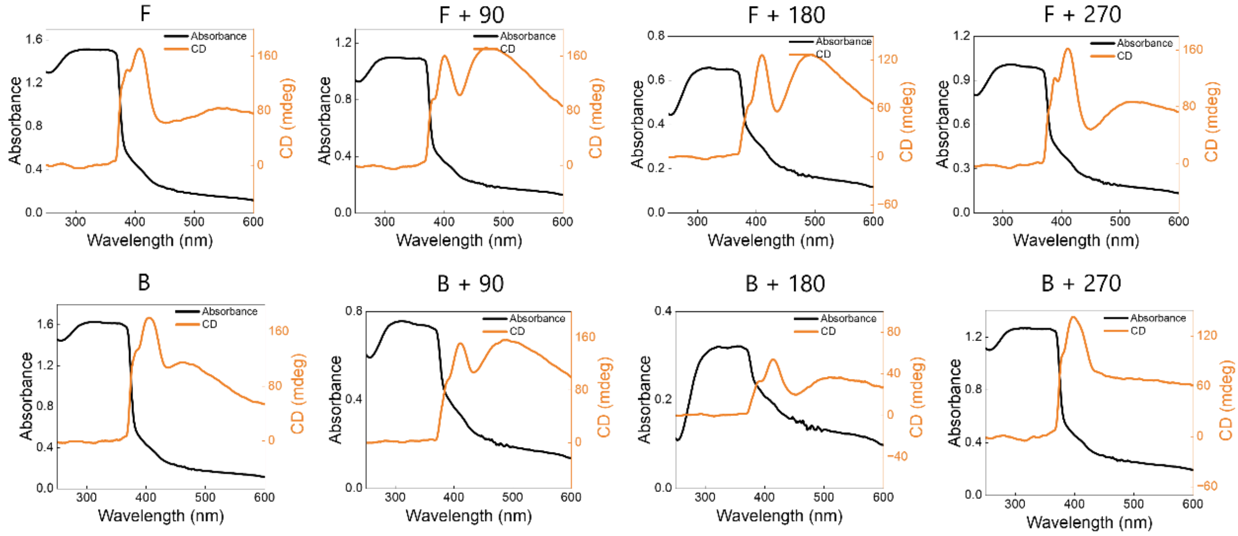


Figure S32: UV-vis absorption and CD spectrum of annealed films of **(*S*)-Am-C10** (**trial #9**). The corresponding height profile of film measured using Dektak profilometer (average thickness = 14.5 ± 0.38 µm).

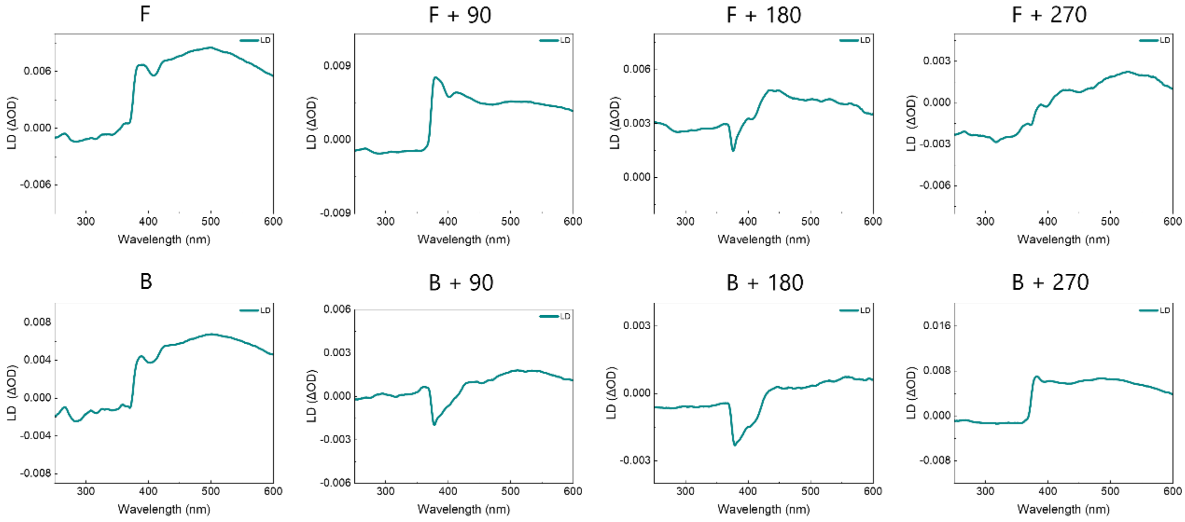


F – Front or coated side of the film

B – Back side of the film facing the light source

The F/B + X indicates the ‘X’ degree in-plane rotation

Figure S33: UV-vis absorption and CD spectra of an annealed film of **(*S*)-Am-C10** in different orientations.



F – Front or coated side of the film

B – Back side of the film facing the light source

The F/B + X indicates the ‘X’ degree in-plane rotation

Figure S34: Linear dichroism (LD) spectra of an annealed film of **(*S*)-Am-C10** in different orientations.

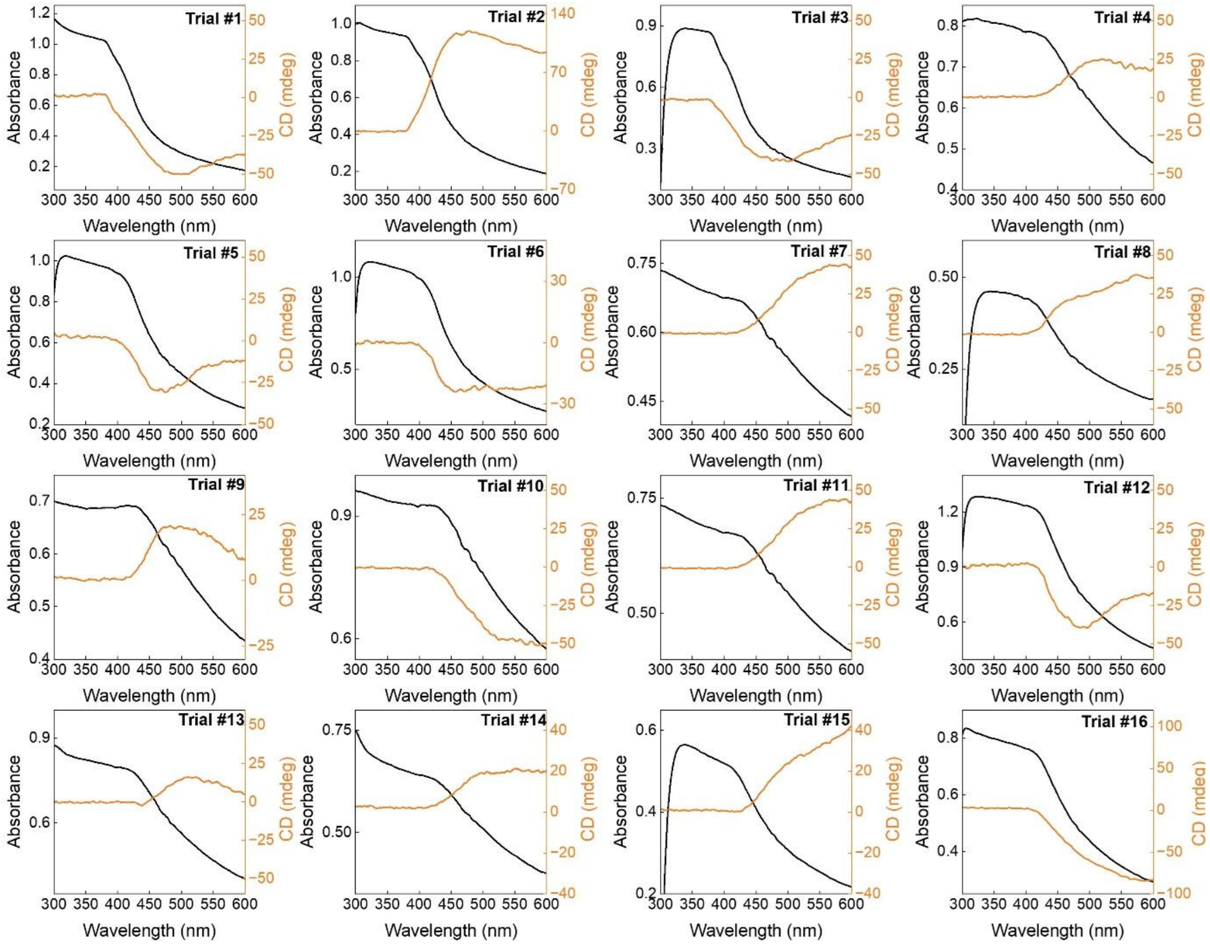


Figure S35: UV-vis absorption and CD spectra of annealed films of **Am-C8**. Each graph corresponds to different trials.

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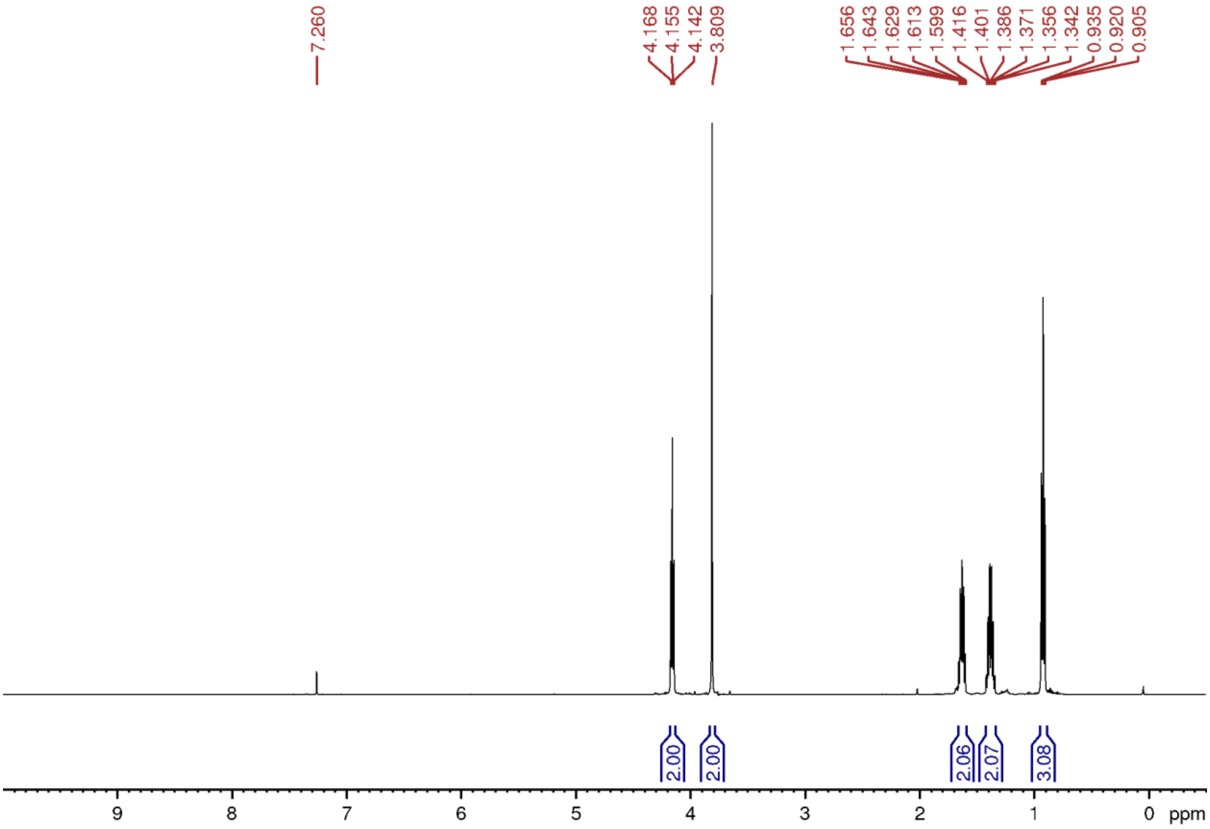


Figure S36: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of butyl-2-bromoacetate (**2a**).

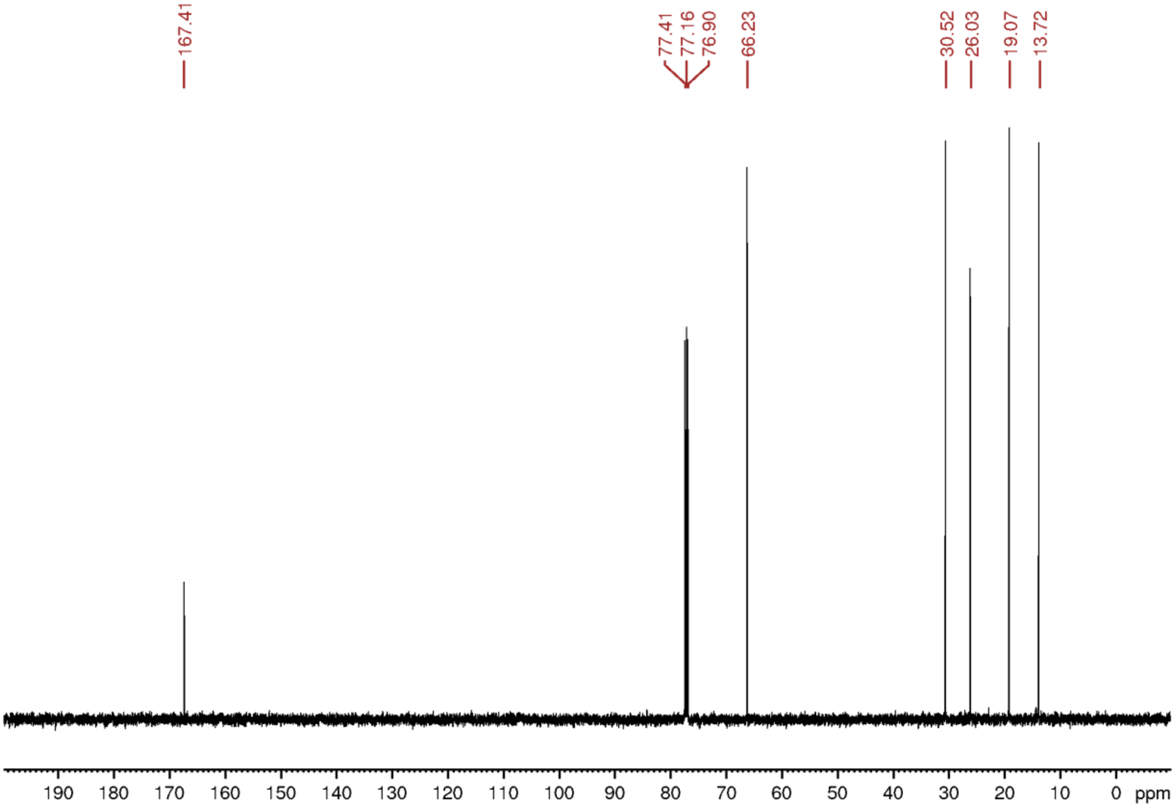


Figure S37: $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) spectrum of butyl-2-bromoacetate (**2a**).

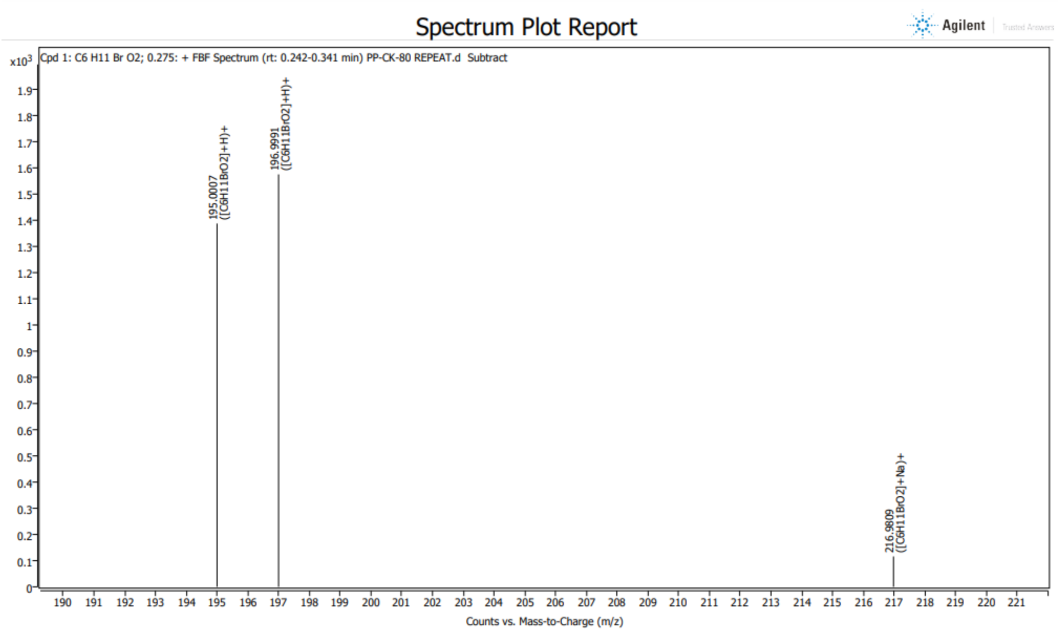


Figure S38: HRMS (ESI-mode) of butyl-2-bromoacetate (**2a**).

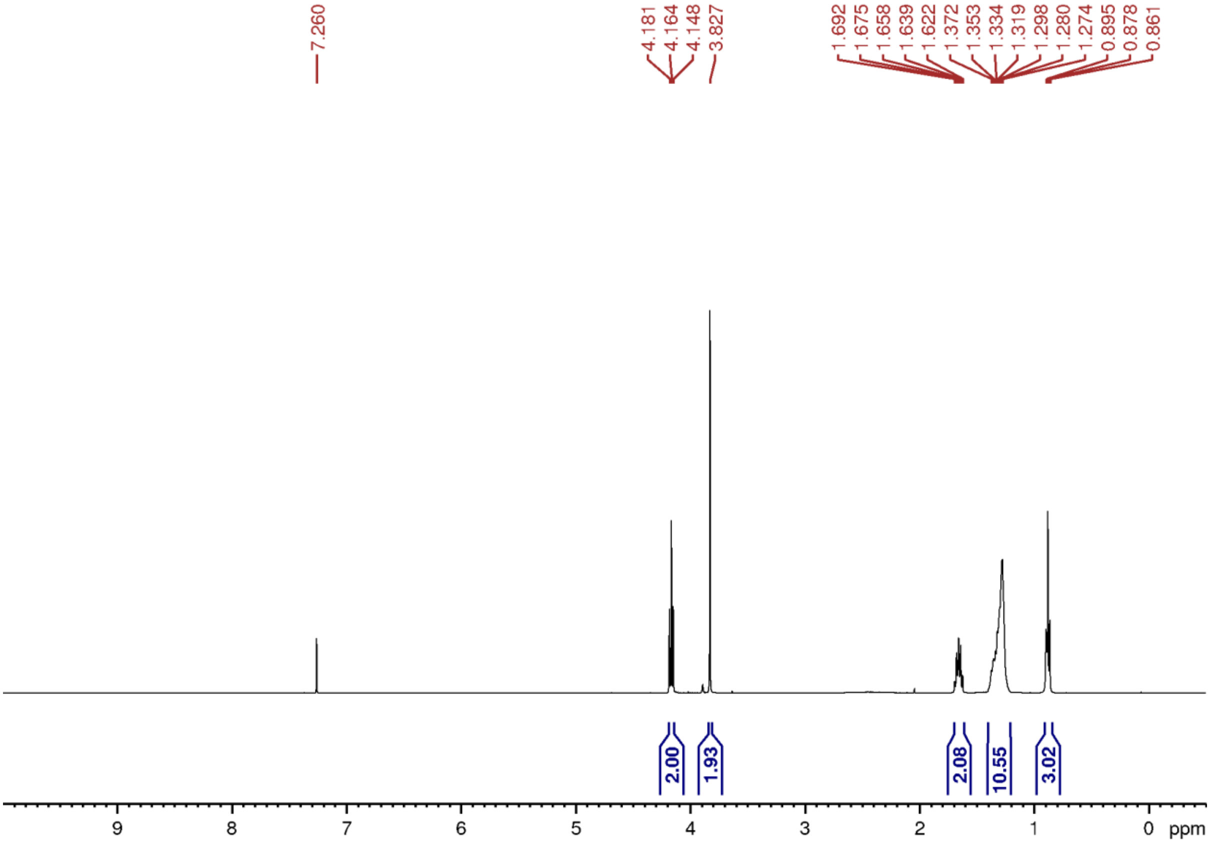


Figure S39: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of octyl-2-bromoacetate (**2b**).

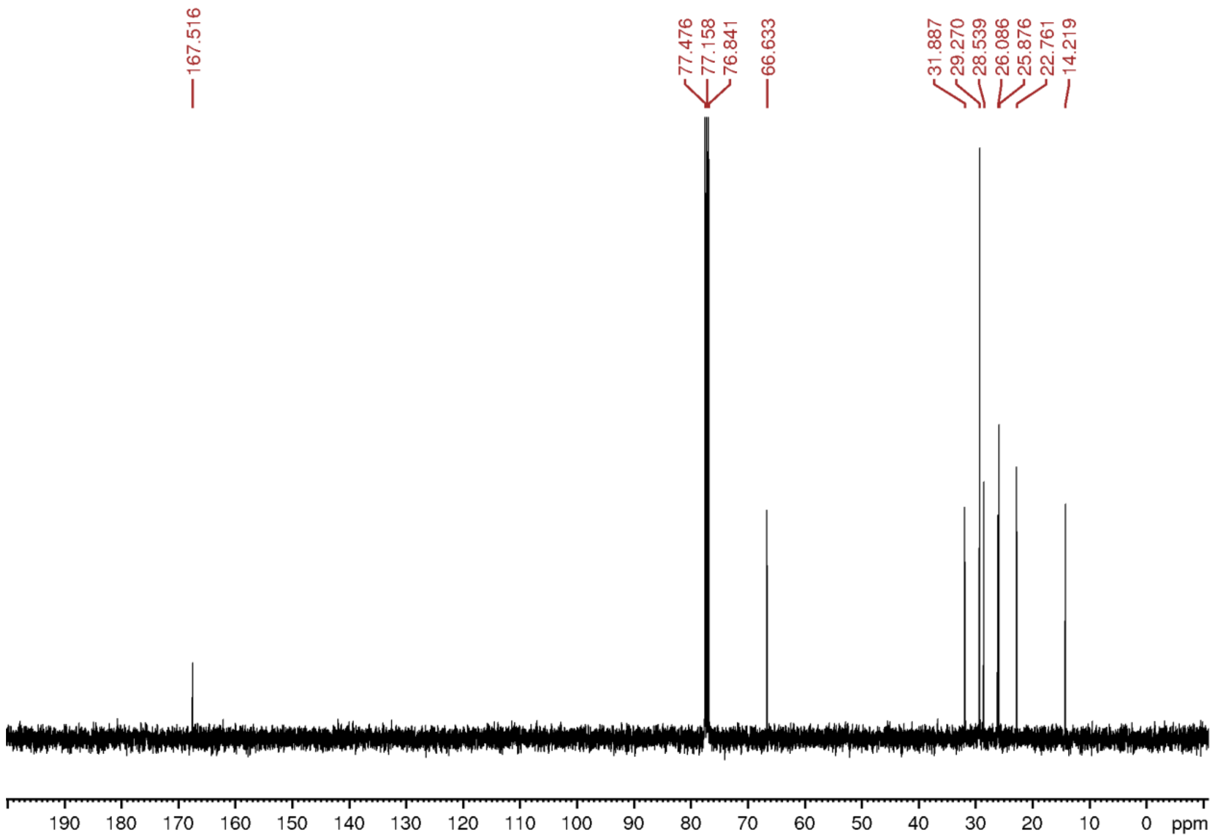


Figure S40: $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of octyl-2-bromoacetate (**2b**).

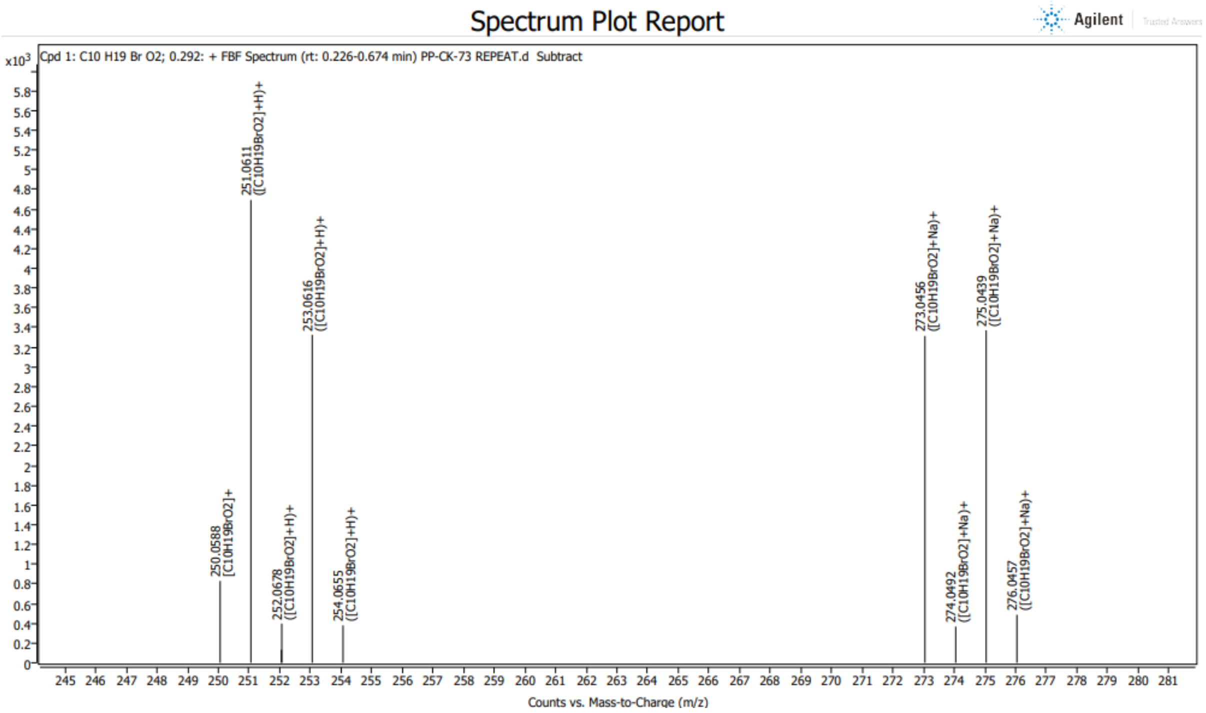


Figure S41: HRMS (ESI-mode) of octyl-2-bromoacetate (**2b**).

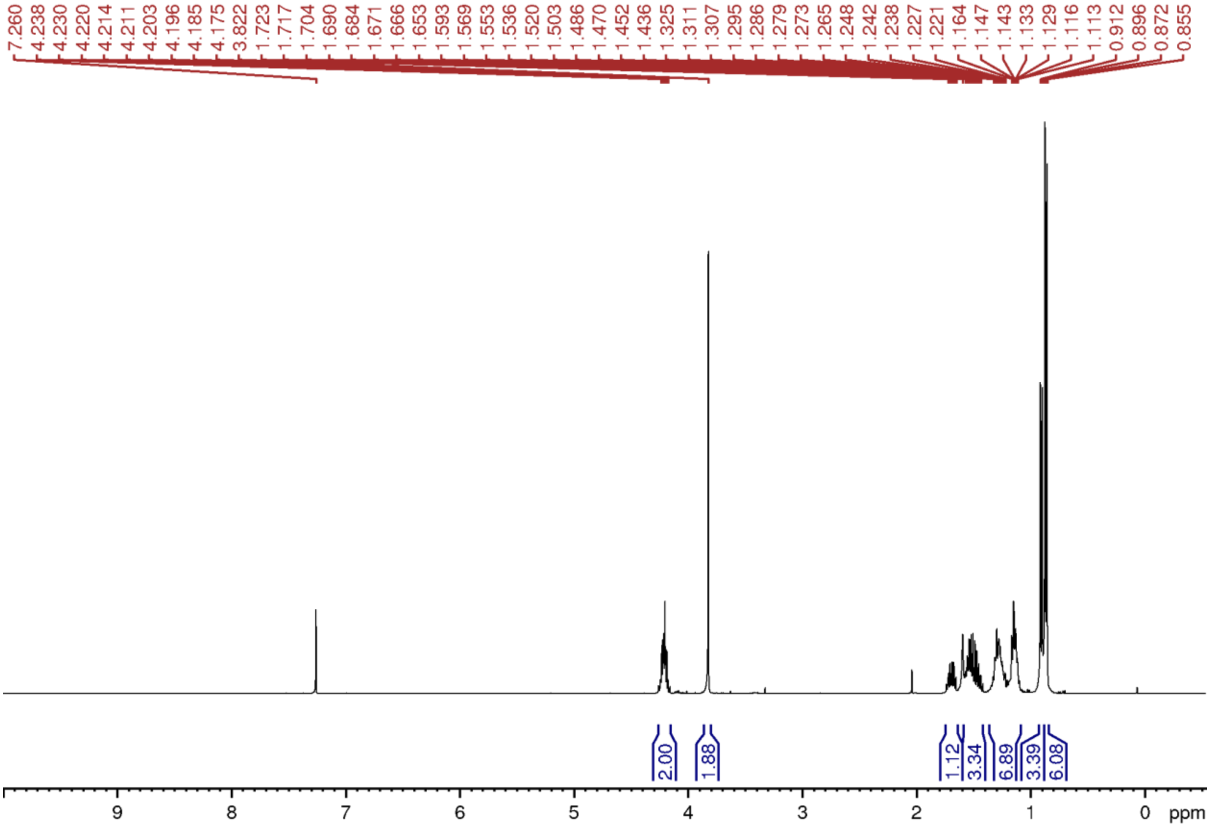


Figure S42: ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of (*S*)-3,7-dimethyloctyl-2-bromoacetate (**2c**).

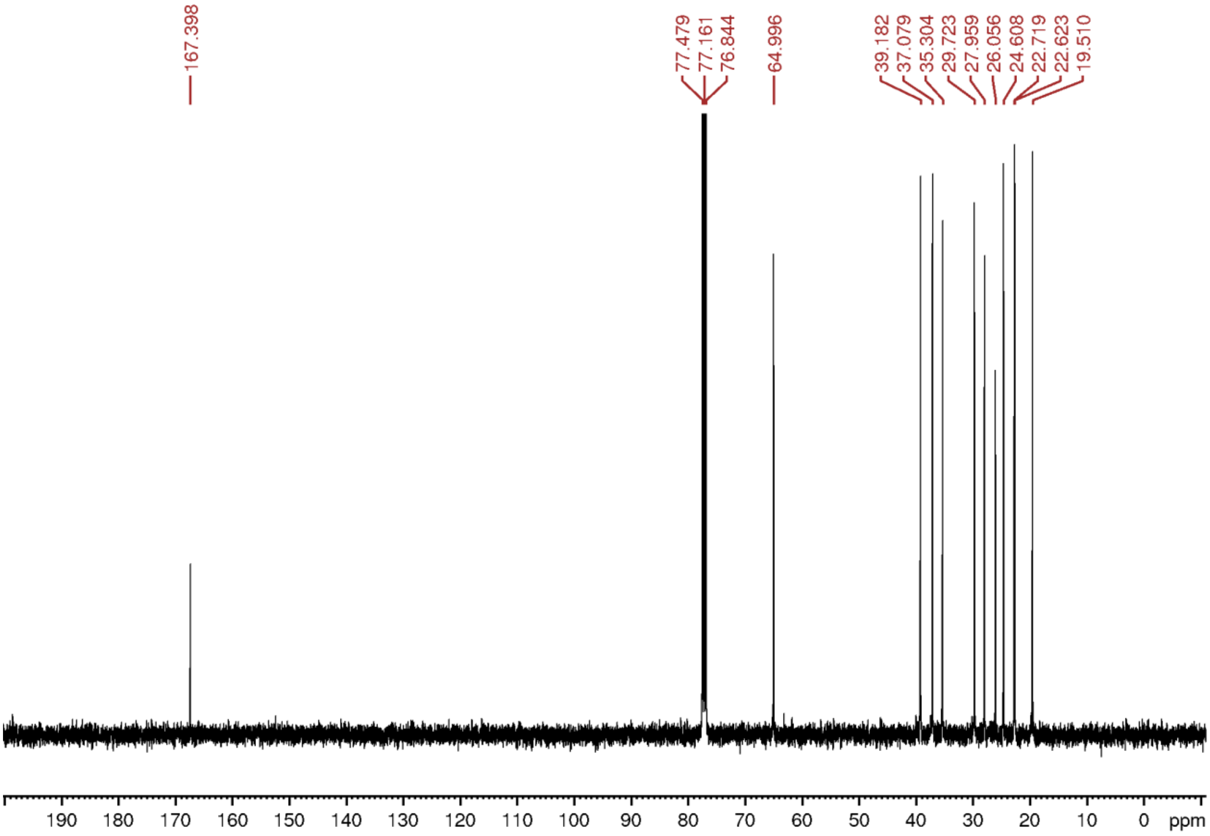


Figure S43: ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of (*S*)-3,7-dimethyloctyl-2-bromoacetate (**2c**).

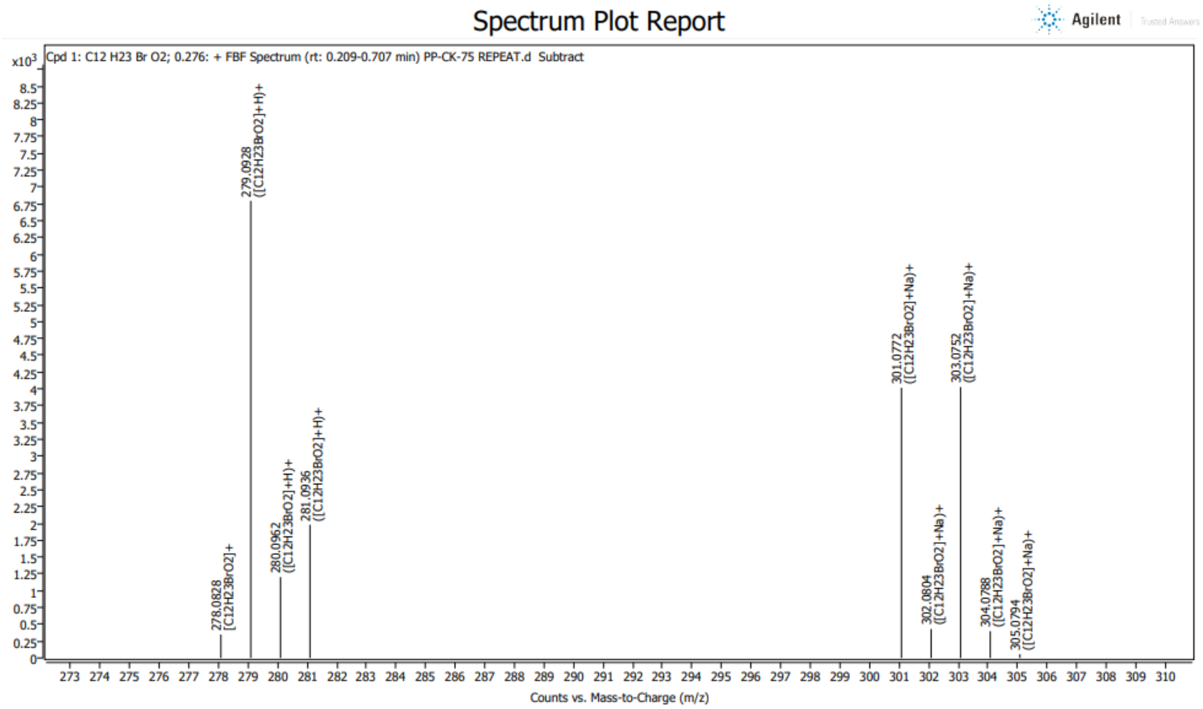


Figure S44: HRMS (ESI-mode) of (*S*)-3,7-dimethyloctyl-2-bromoacetate (**2c**).

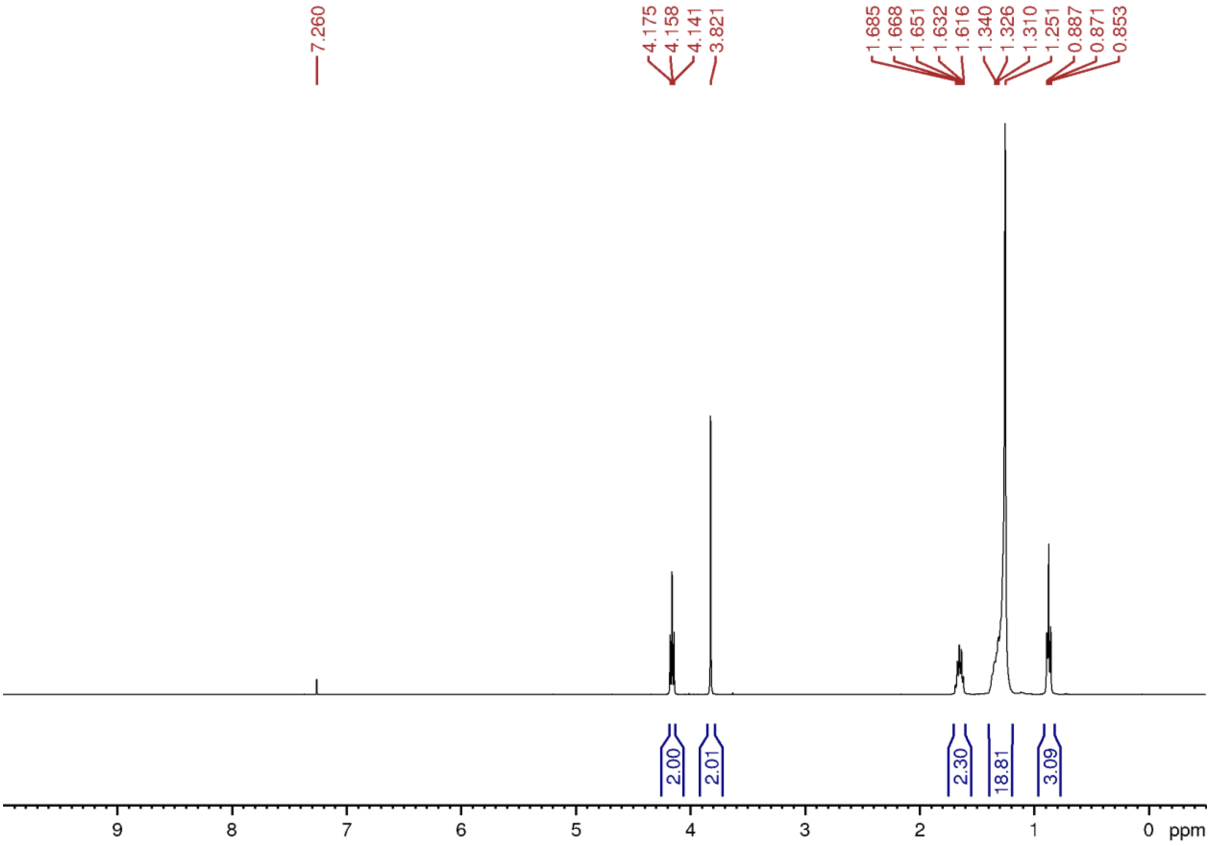


Figure S45: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of dodecyl-2-bromoacetate (**2d**).

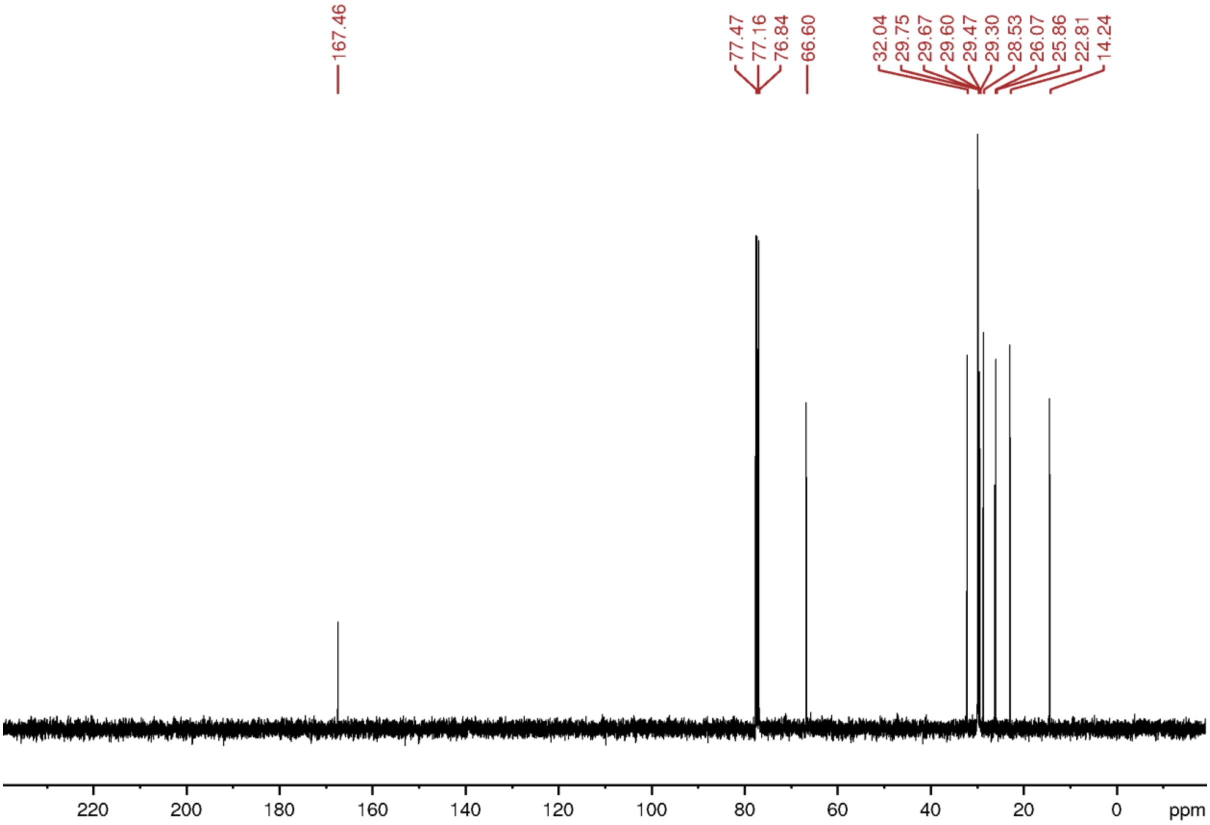


Figure S46: $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of dodecyl-2-bromoacetate (**2d**).

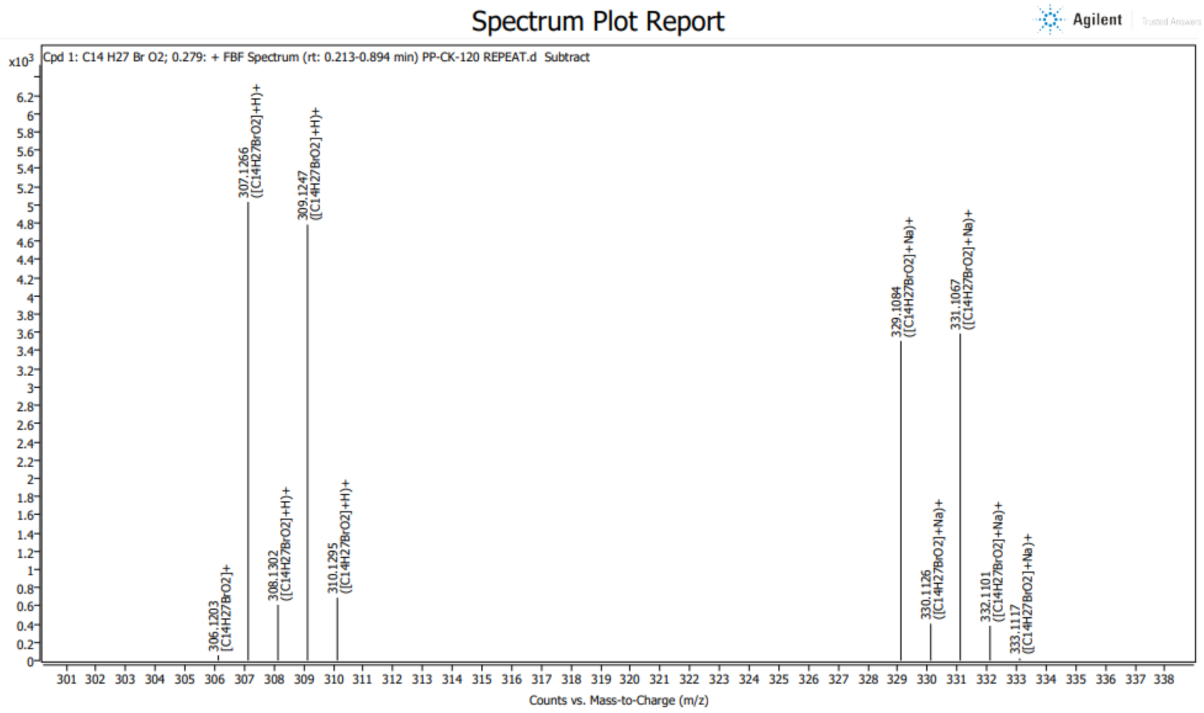


Figure S47: HRMS (ESI-mode) of dodecyl-2-bromoacetate (**2d**).

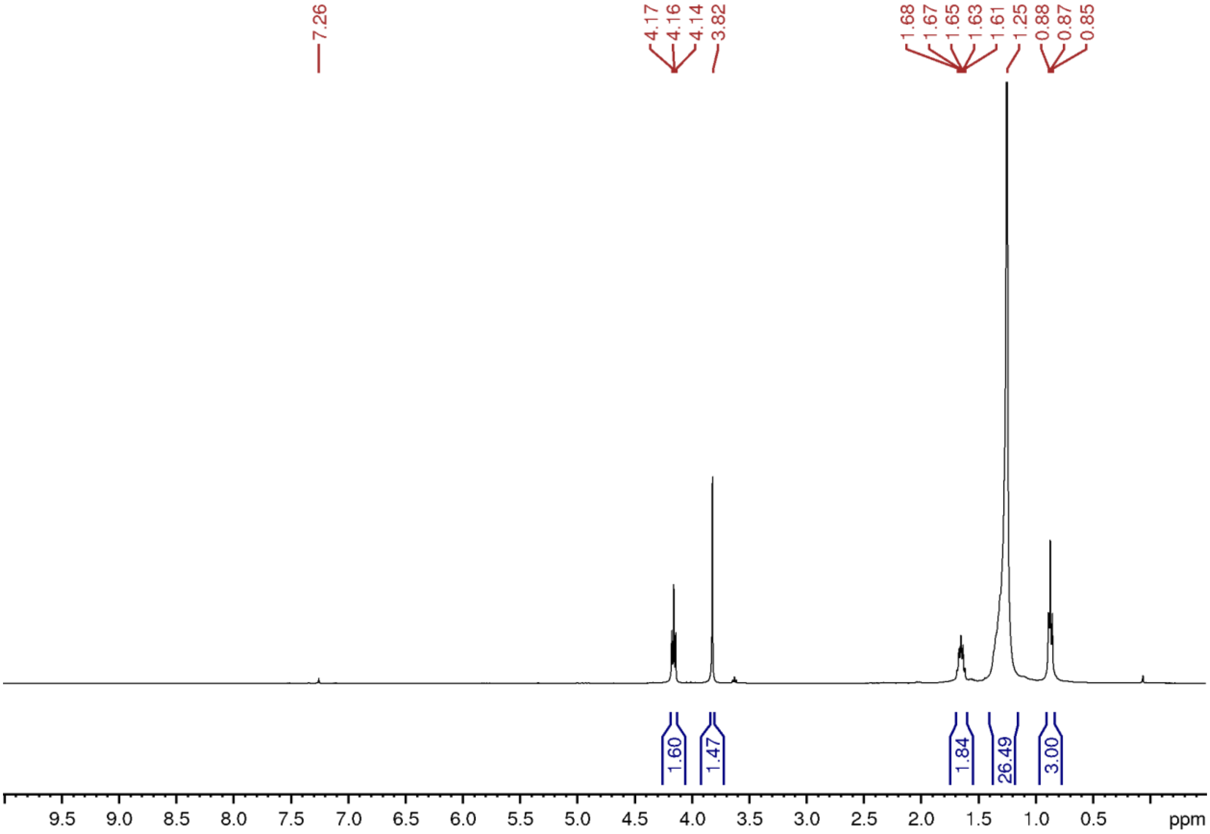


Figure S48: ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of hexadecyl-2-bromoacetate (**2e**).

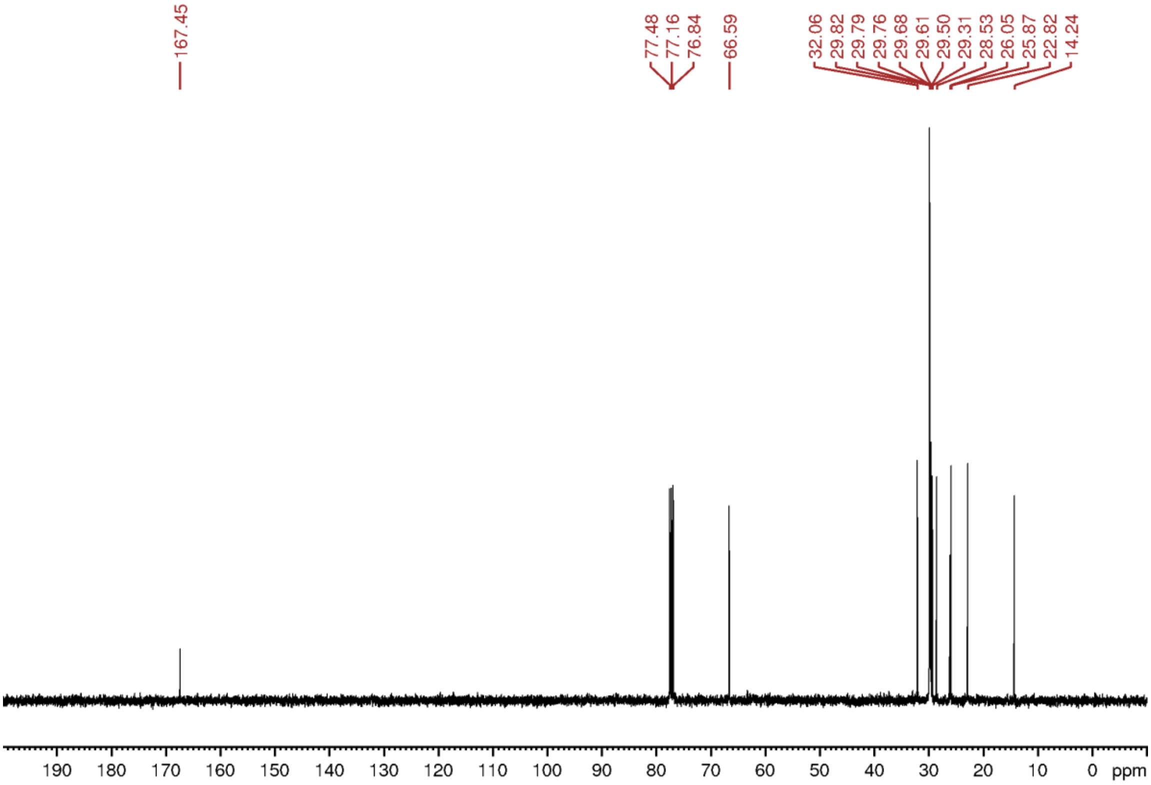


Figure S49: ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of hexadecyl-2-bromoacetate (**2e**).

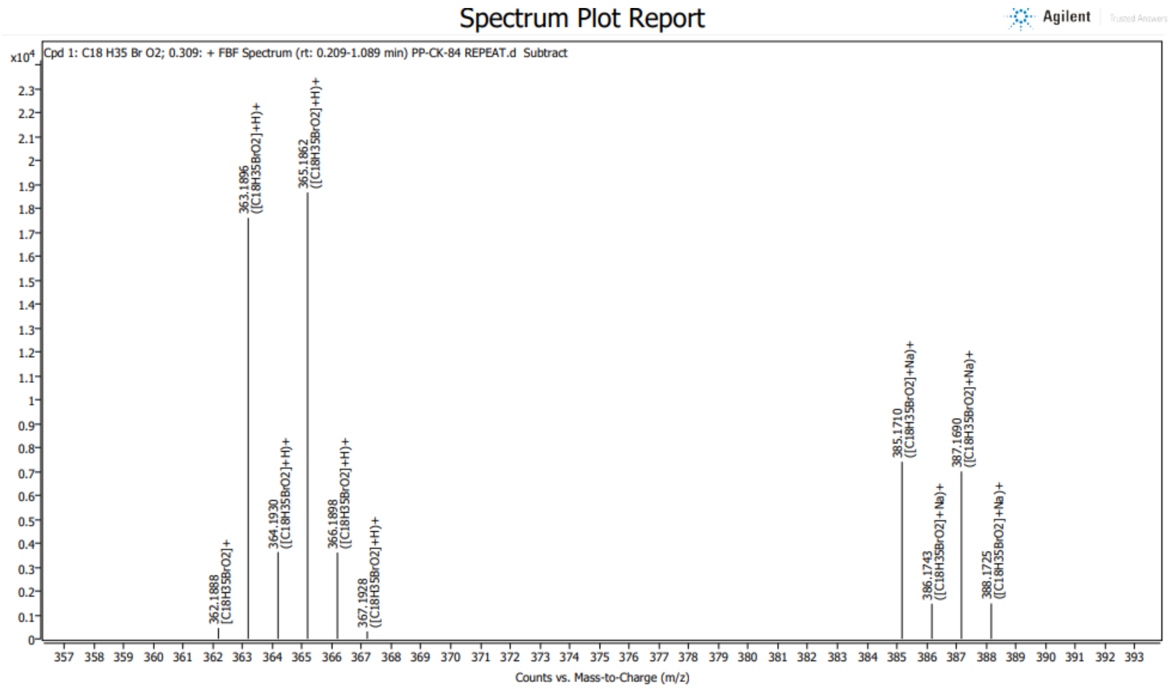


Figure S50: HRMS (ESI-mode) of hexadecyl-2-bromoacetate (**2e**).

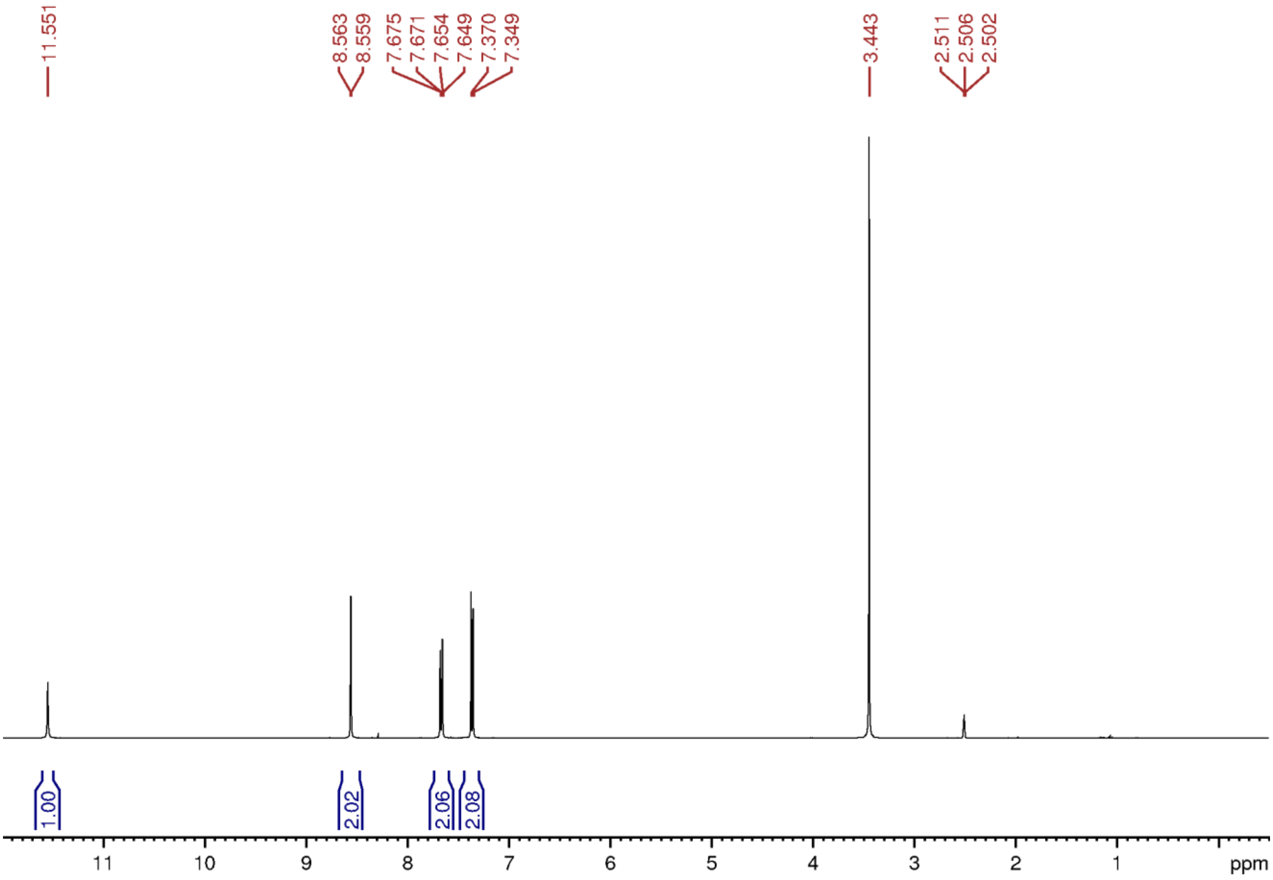


Figure S51: ^{1}H NMR (400 MHz, DMSO-d6) spectrum of 3,6-Diiodocarbazole (**4**).

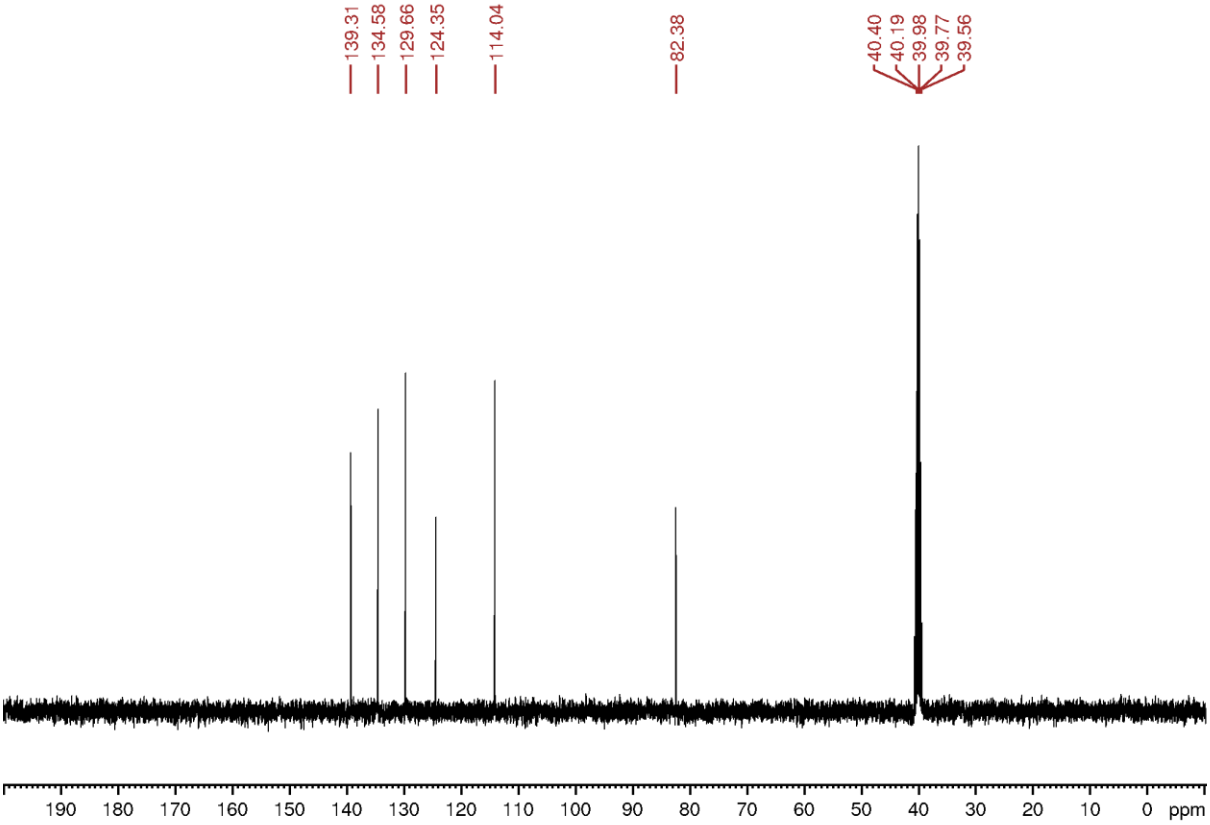


Figure S52: $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d6) spectrum of 3,6-Diiodocarbazole (**4**).

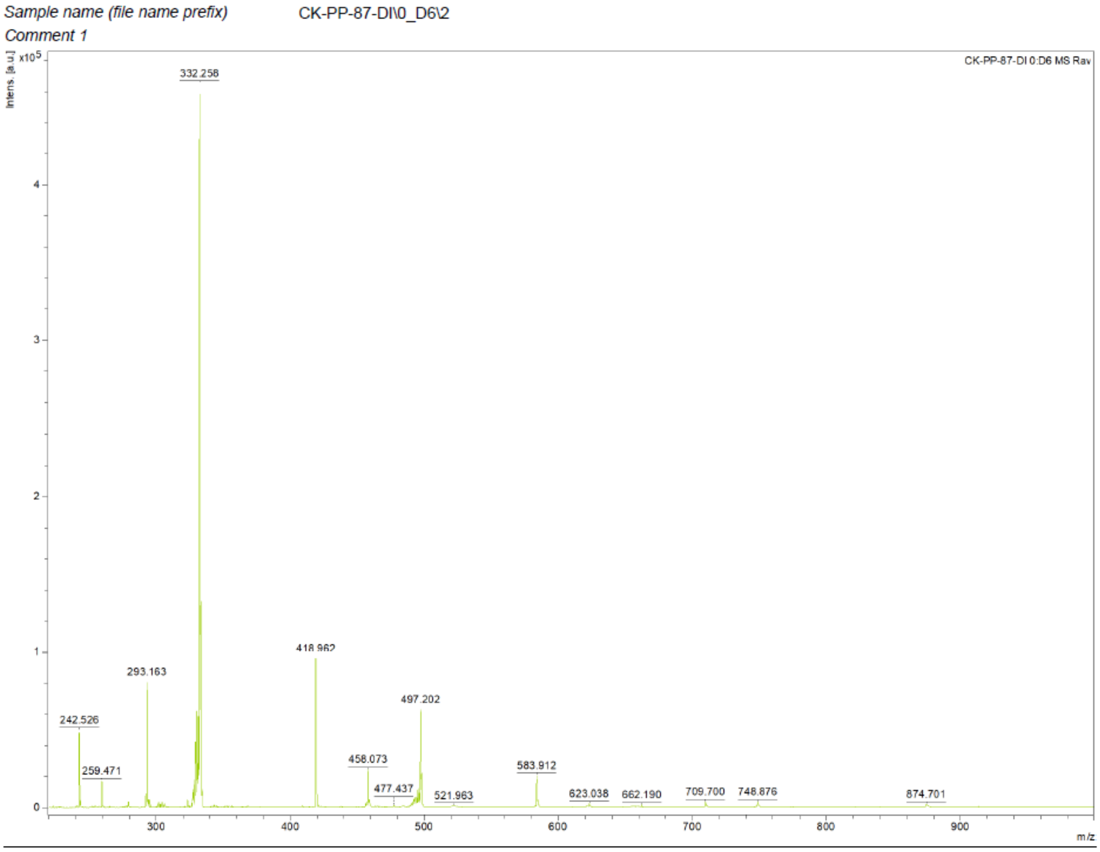


Figure S53: MALDI-TOF mass spectrum of 3,6-Diiodocarbazole (**4**) with DCTB matrix.

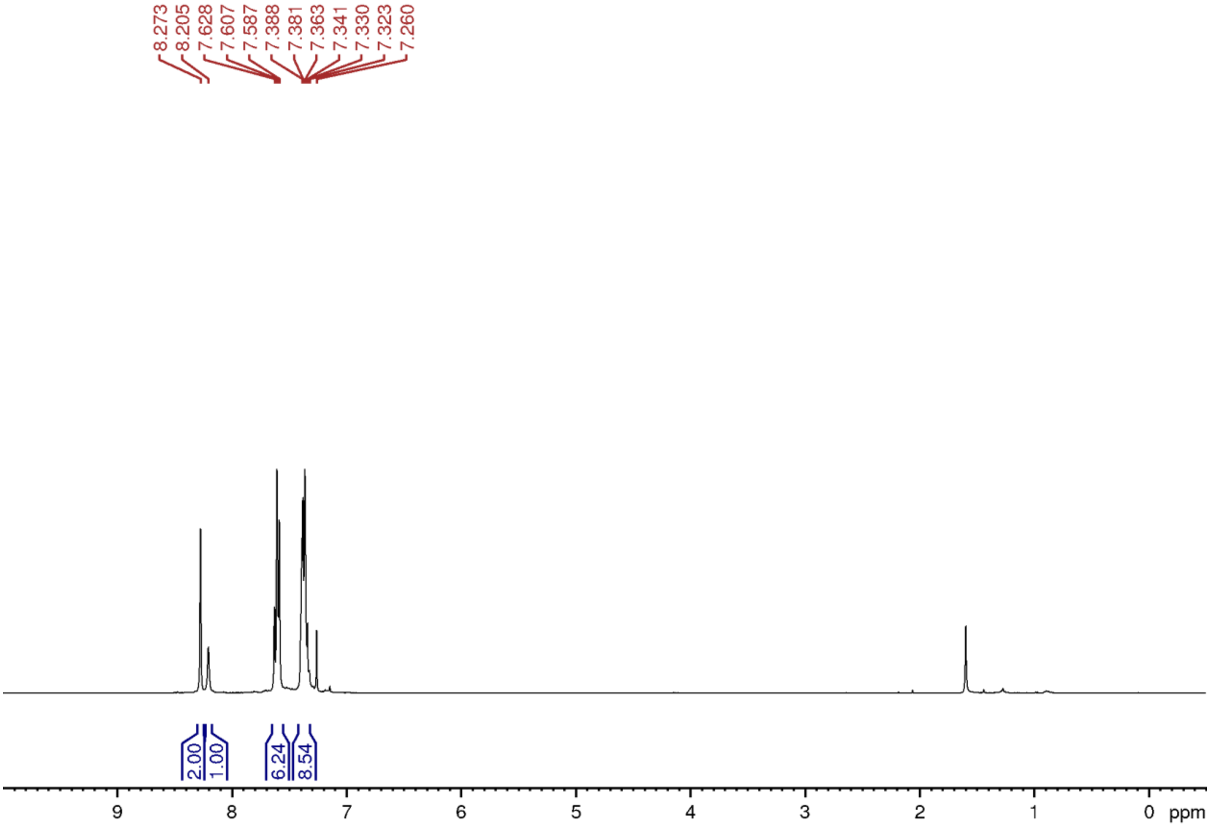


Figure S54: ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of 3,6-Bis(phenylethynyl)-9H-carbazole (**5**).

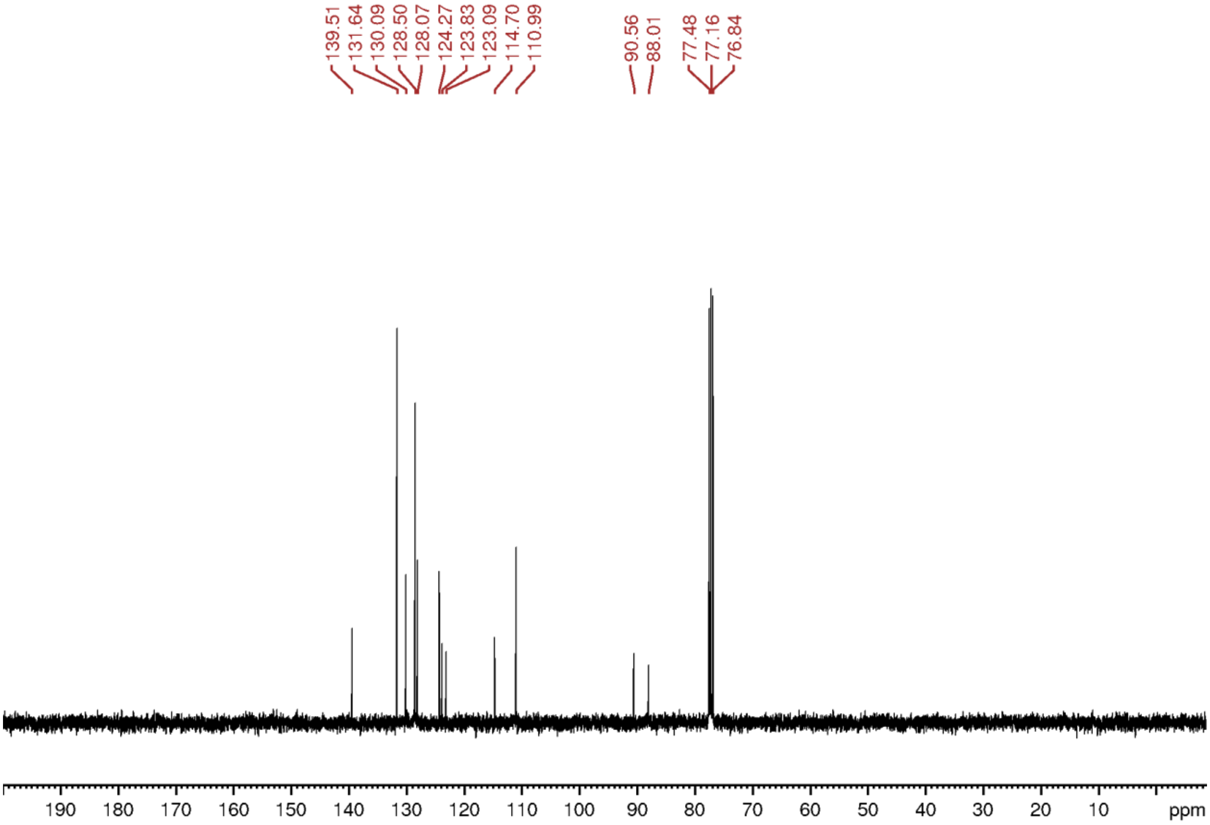


Figure S55: ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of 3,6-Bis(phenylethynyl)-9H-carbazole (**5**).

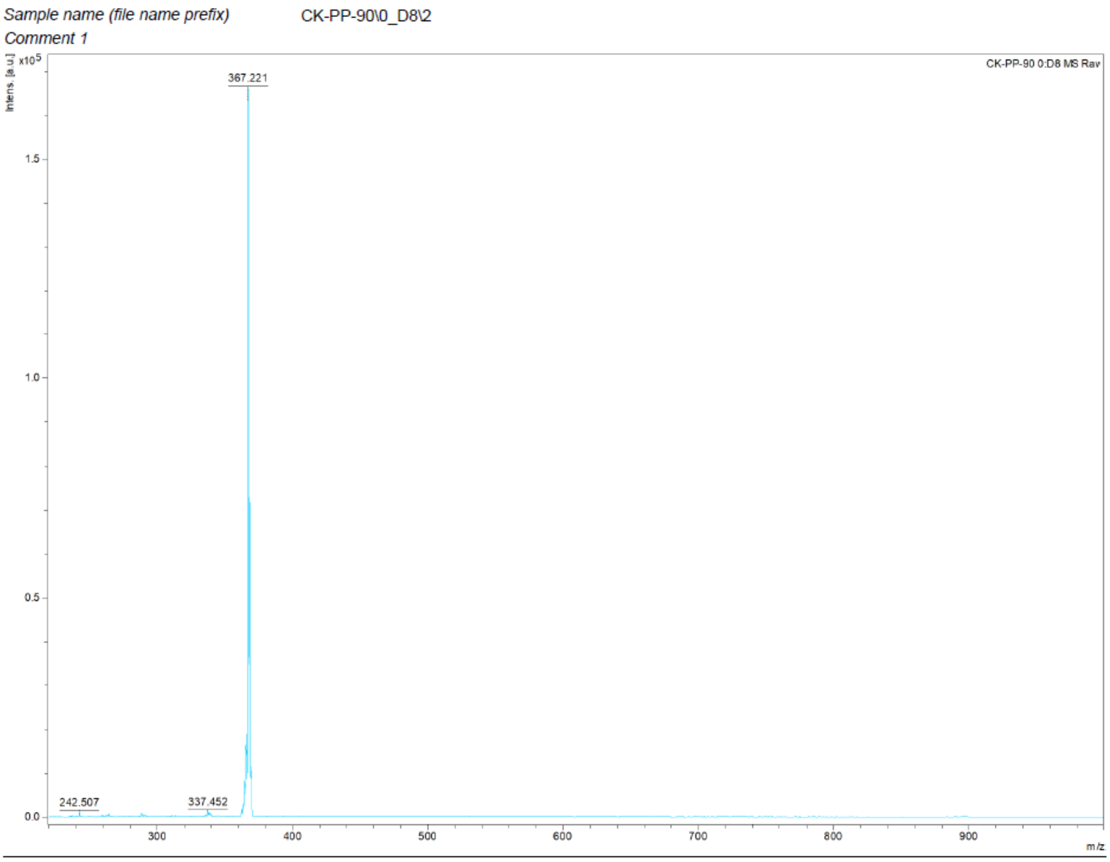


Figure S56: MALDI-TOF mass spectrum of 3,6-Bis(phenylethynyl)-9H-carbazole (**5**) with DCTB matrix.

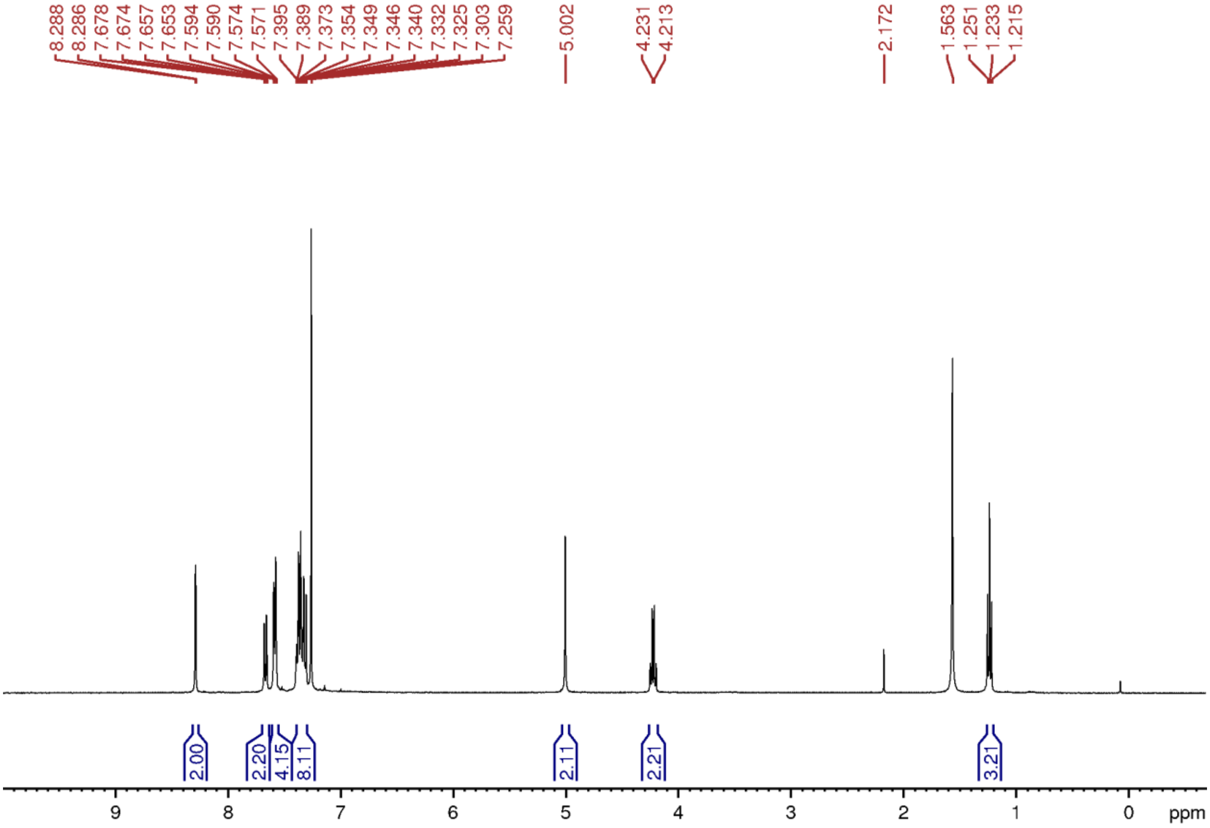


Figure S57: ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of ethyl-2-(3,6-bis(phenylethynyl)-9H-carbazol-9-yl)acetate (**Est-C2**).

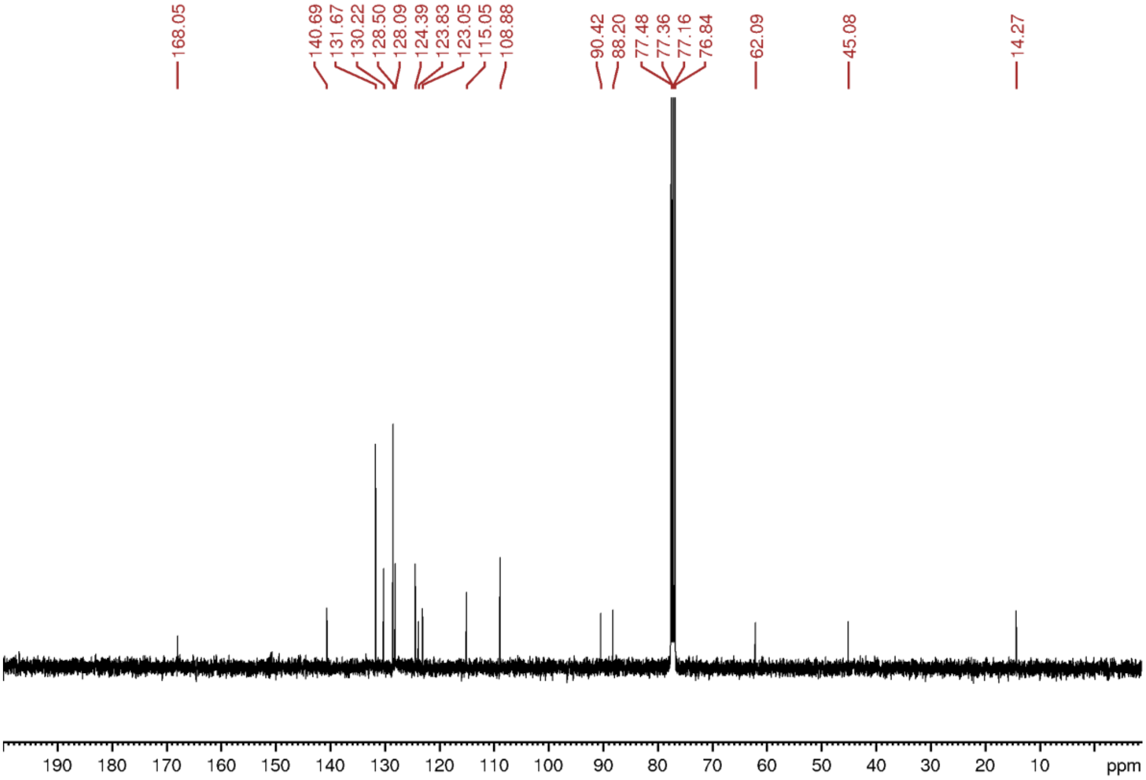
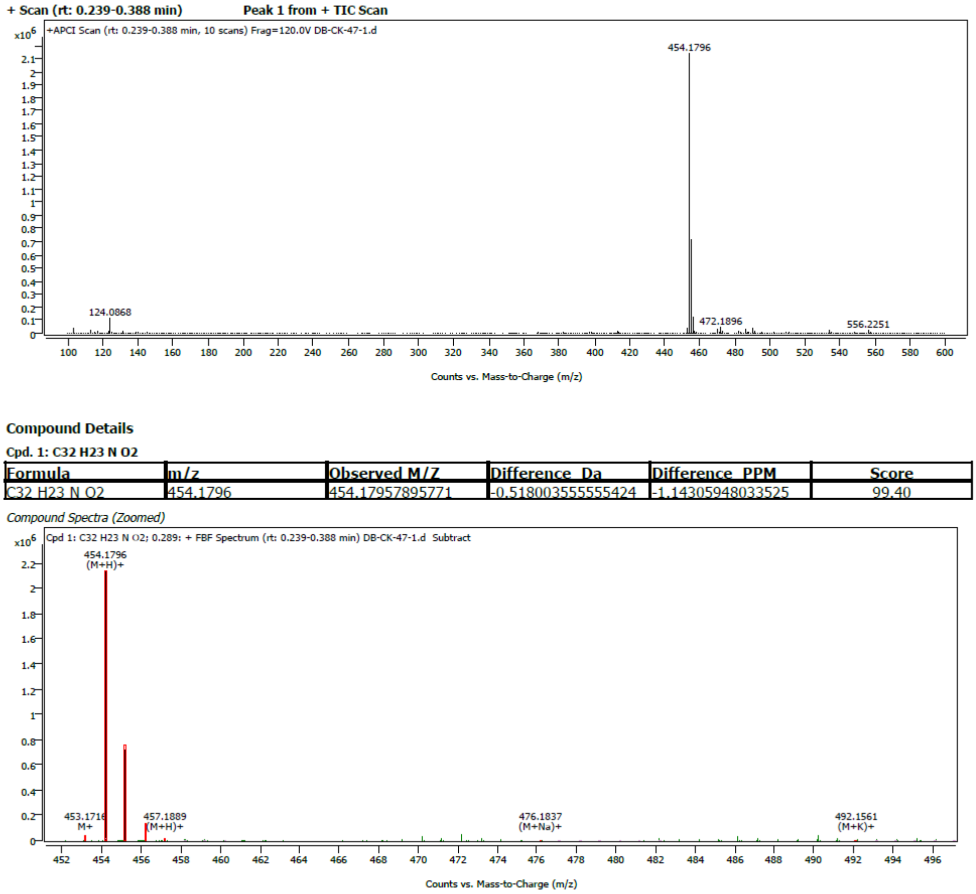


Figure S58: $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of ethyl-2-(3,6-bis(phenylethynyl)-9H-carbazol-9-yl)acetate (**Est-C2**).



Compound Details

Cpd. 1: C32 H23 N O2

Formula	m/z	Observed M/Z	Difference_Da	Difference_PPM	Score
C32 H23 N O2	454.1796	454.17957895771	-0.518003555555424	-1.14305948033525	99.40

Compound Spectra (Zoomed)

Figure S59: HRMS (APCI-mode) of ethyl-2-(3,6-bis(phenylethynyl)-9H-carbazol-9-yl)acetate (**Est-C2**).

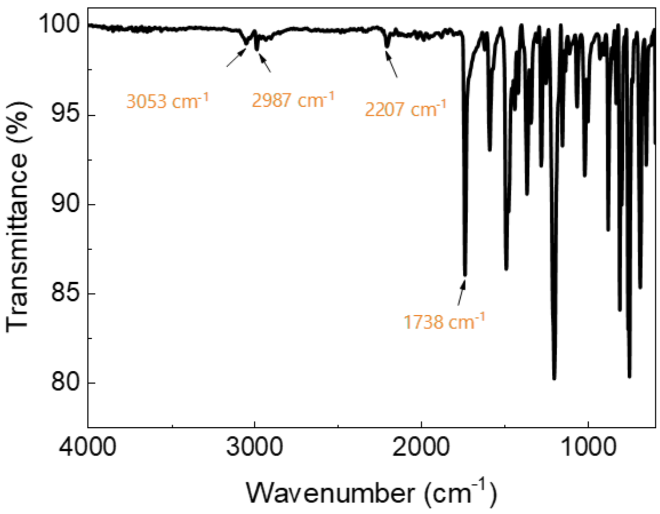


Figure S60: Solid-state FTIR spectrum (ATR mode) of ethyl-2-(3,6-bis(phenylethynyl)-9H-carbazol-9-yl)acetate (**Est-C2**).

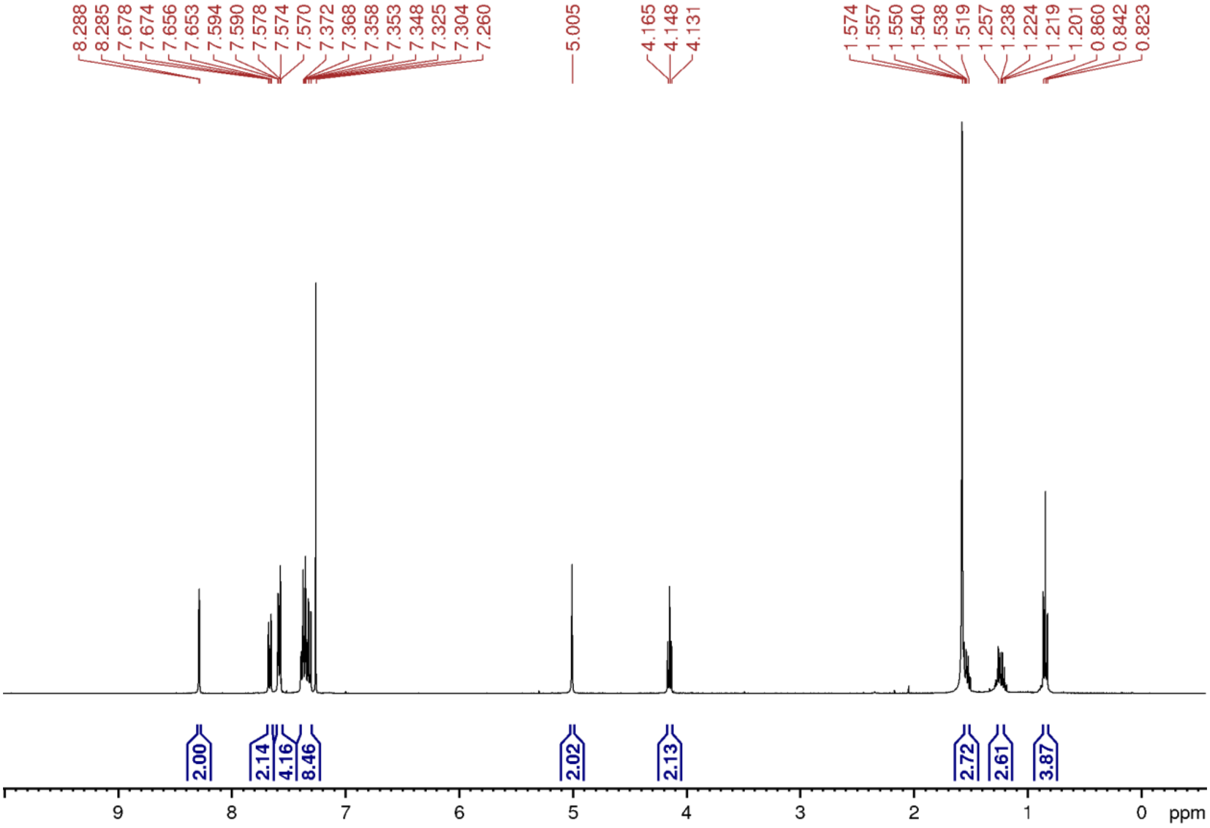


Figure S61: ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of butyl-2-(3,6-bis(phenylethynyl)-9H-carbazol-9-yl)acetate (**Est-C4**).

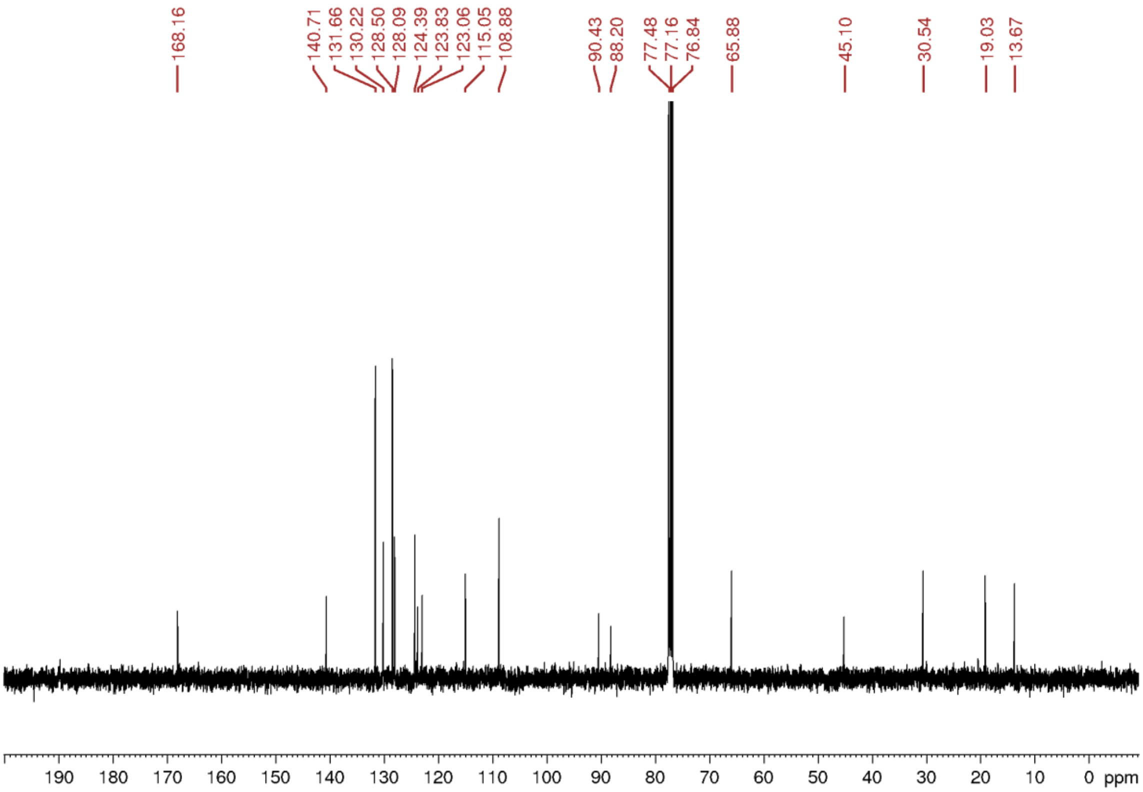
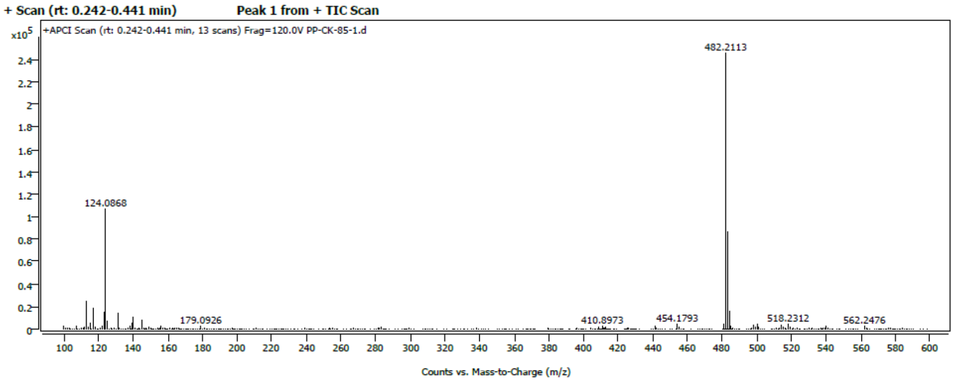


Figure S62: $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of butyl-2-(3,6-bis(phenylethynyl)-9H-carbazol-9-yl)acetate (**Est-C4**).



Compound Details

Cpd. 1: C34 H27 N O2

Formula	m/z	Observed M/Z	Difference Da	Difference PPM	Score
C34 H27 N O2	482.2113	482.211298005989	-0.317446314113567	-0.659691515353246	99.24

Compound Spectra (Zoomed)

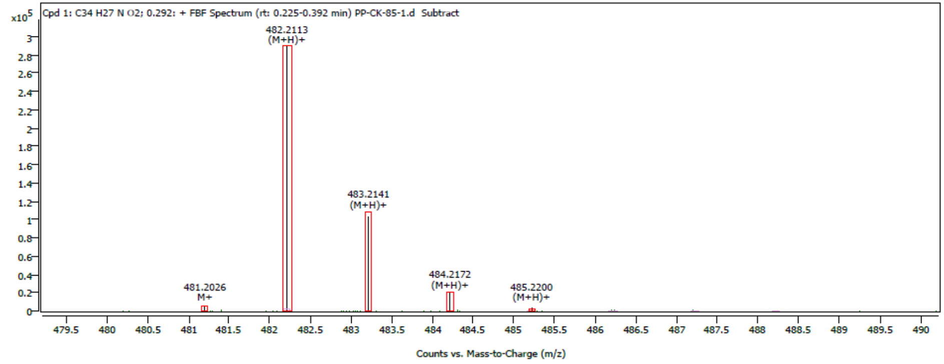


Figure S63: HRMS (APCI-mode) of butyl-2-(3,6-bis(phenylethynyl)-9H-carbazol-9-yl)acetate (**Est-C4**).

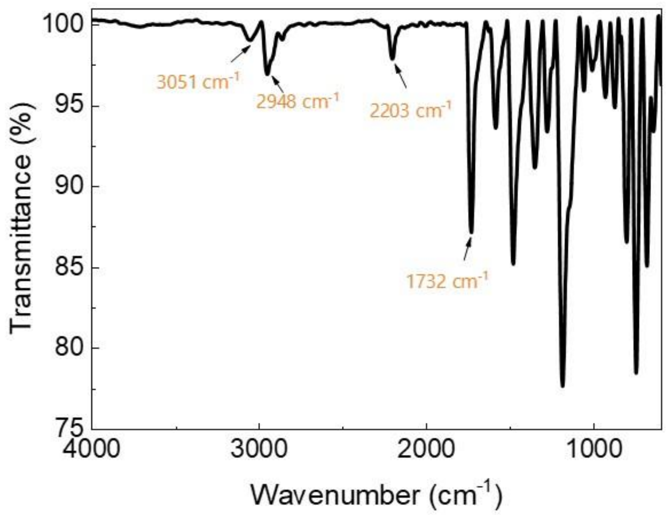


Figure S64: Solid-state FTIR spectrum (ATR mode) of butyl-2-(3,6-bis(phenylethynyl)-9H-carbazol-9-yl)acetate (**Est-C4**).

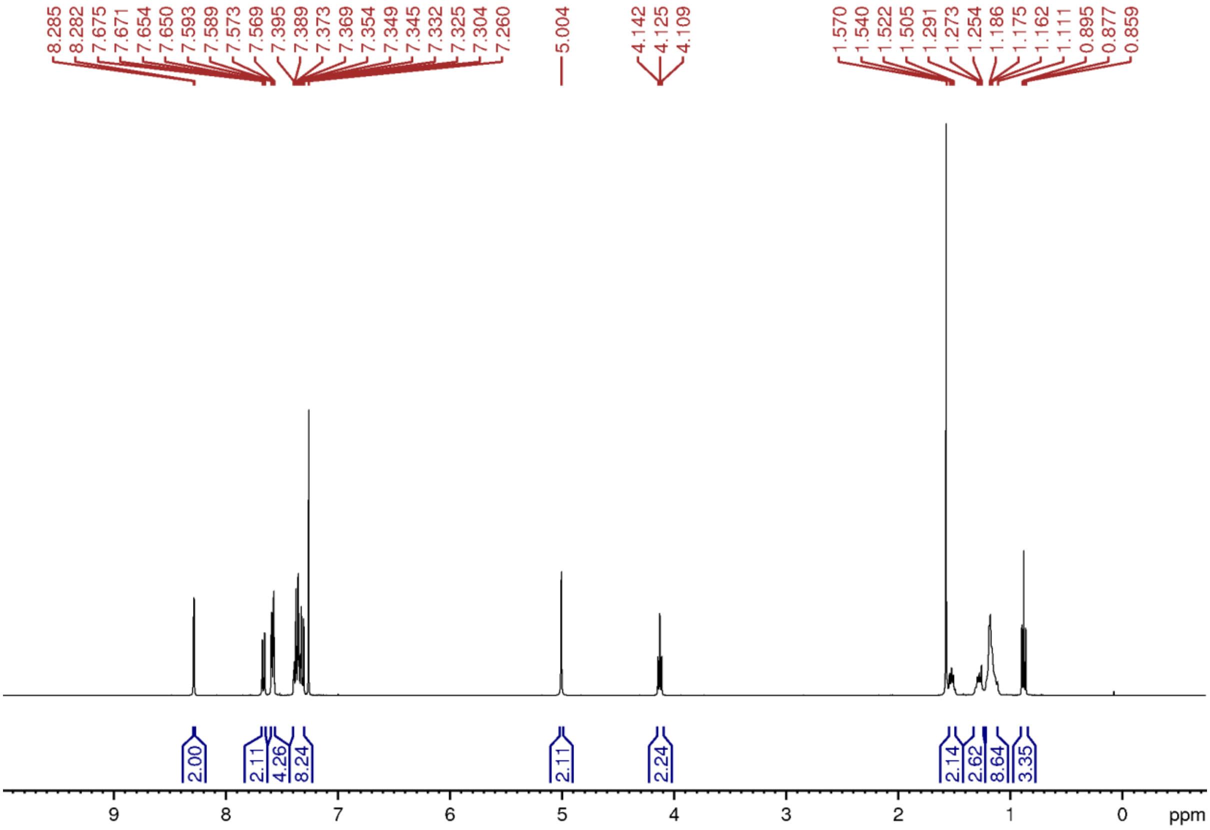


Figure S65: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of octyl-2-(3,6-bis(phenylethynyl)-9H-carbazol-9-yl)acetate (**Est-C8**).

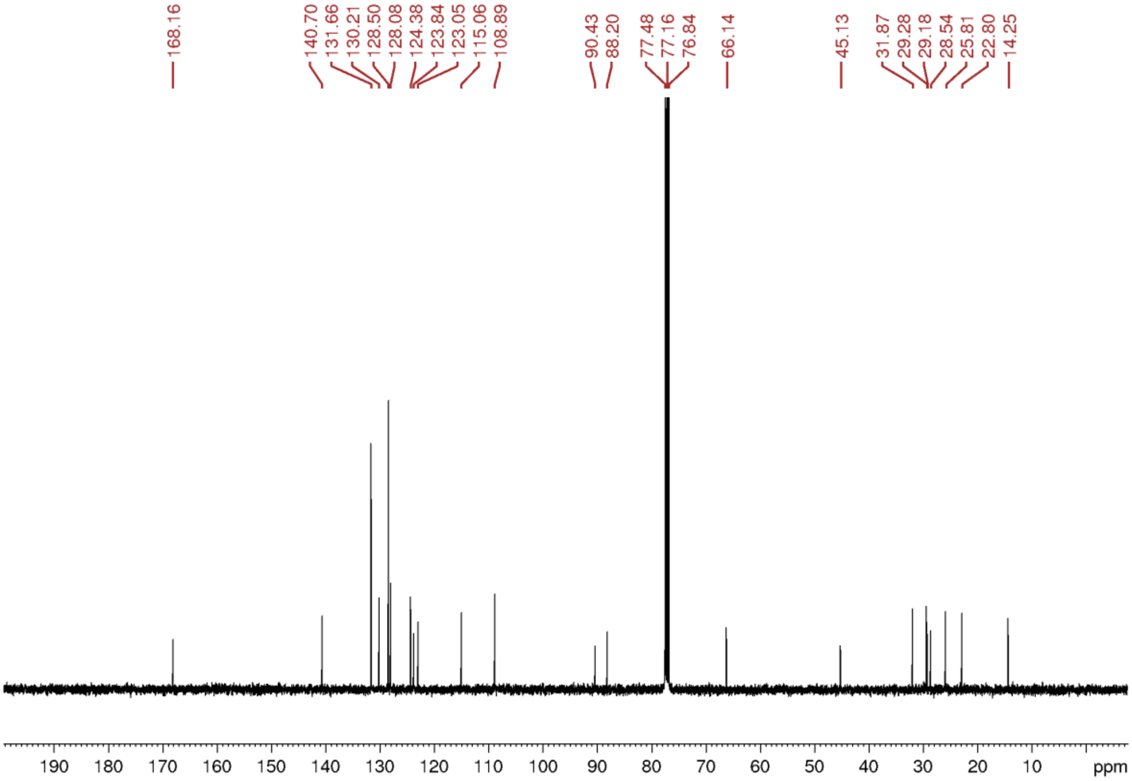
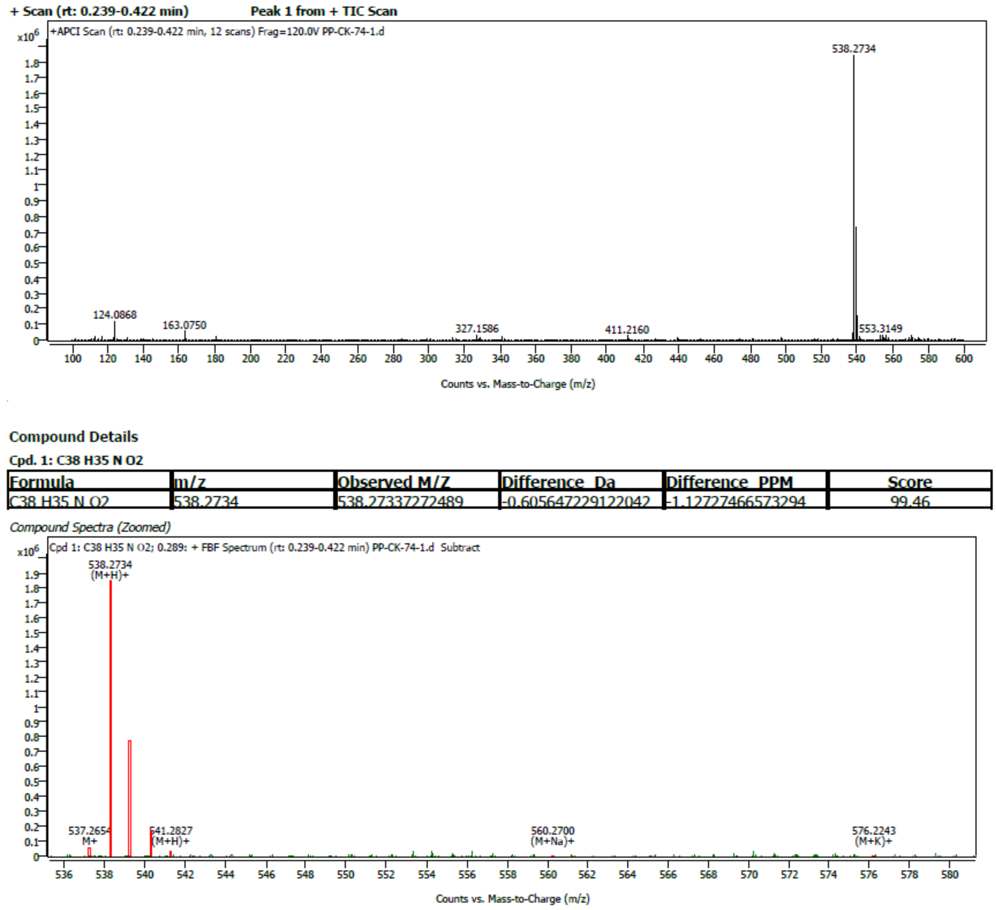


Figure S66: $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of octyl-2-(3,6-bis(phenylethynyl)-9H-carbazol-9-yl)acetate (**Est-C8**).



Compound Details

Cpd. 1: C38 H35 N O2

Formula	m/z	Observed M/Z	Difference Da	Difference PPM	Score
C38 H35 N O2	538.2734	538.27337272489	-0.605647229122042	-1.12727466573294	99.46

Compound Spectra (Zoomed)

Figure S67: HRMS (APCI-mode) of octyl-2-(3,6-bis(phenylethynyl)-9H-carbazol-9-yl)acetate (**Est-C8**).

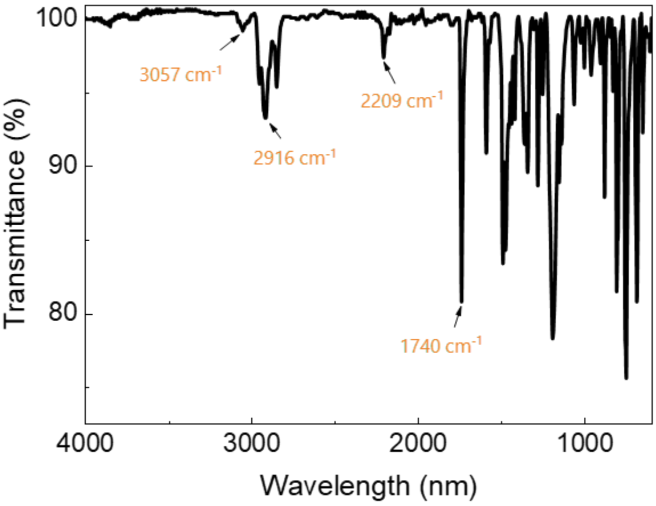


Figure S68: Solid-state FTIR spectrum (ATR mode) of octyl-2-(3,6-bis(phenylethynyl)-9H-carbazol-9-yl)acetate (**Est-C8**).

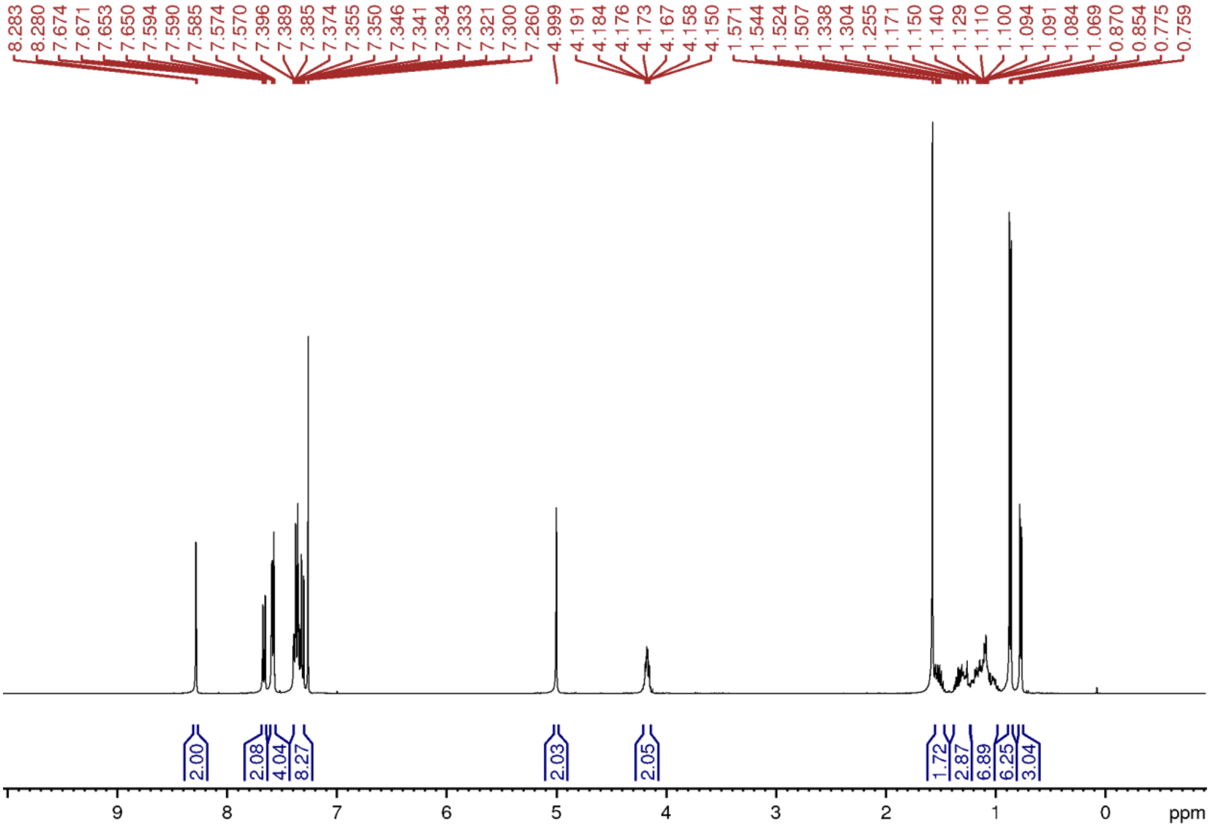


Figure S69: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*)-3,7-dimethyloctyl-2-(3,6-bis(phenylethynyl)-9H-carbazol-9-yl)acetate (**(*S*)-Est-C10**).

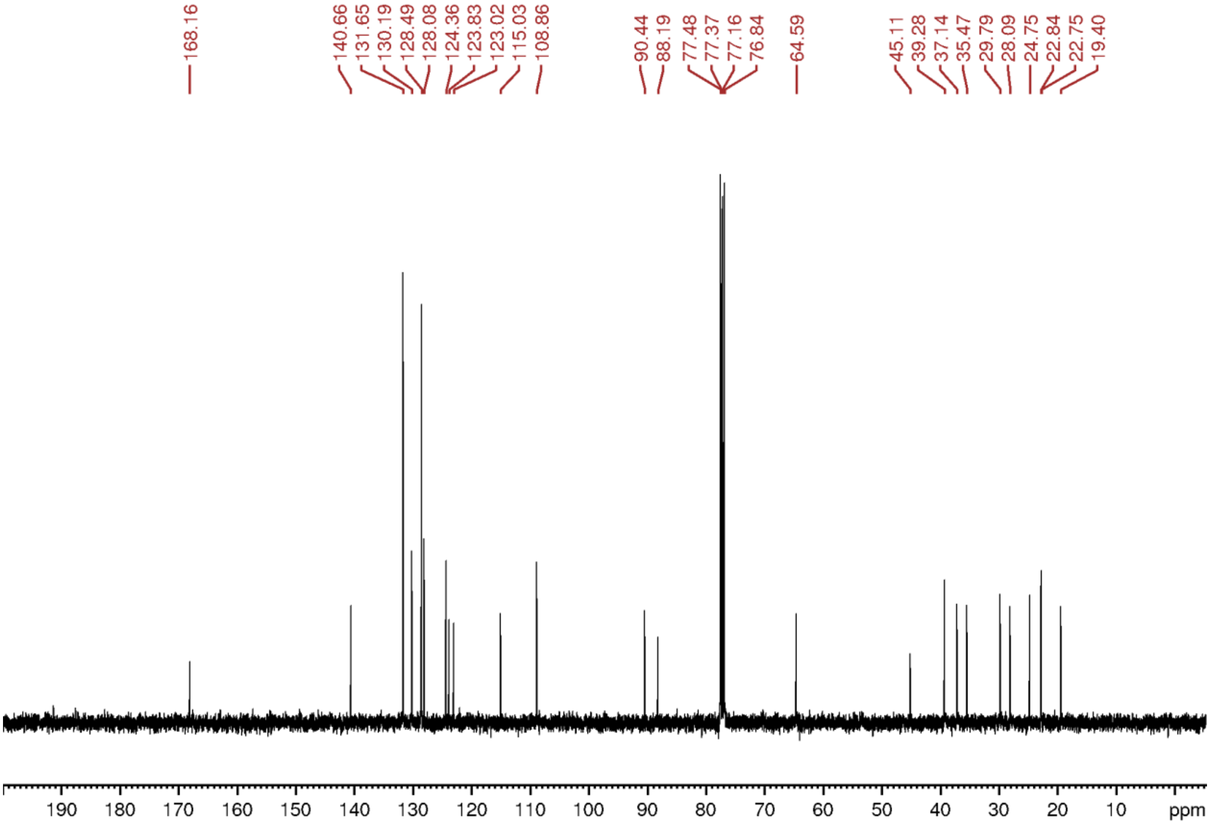
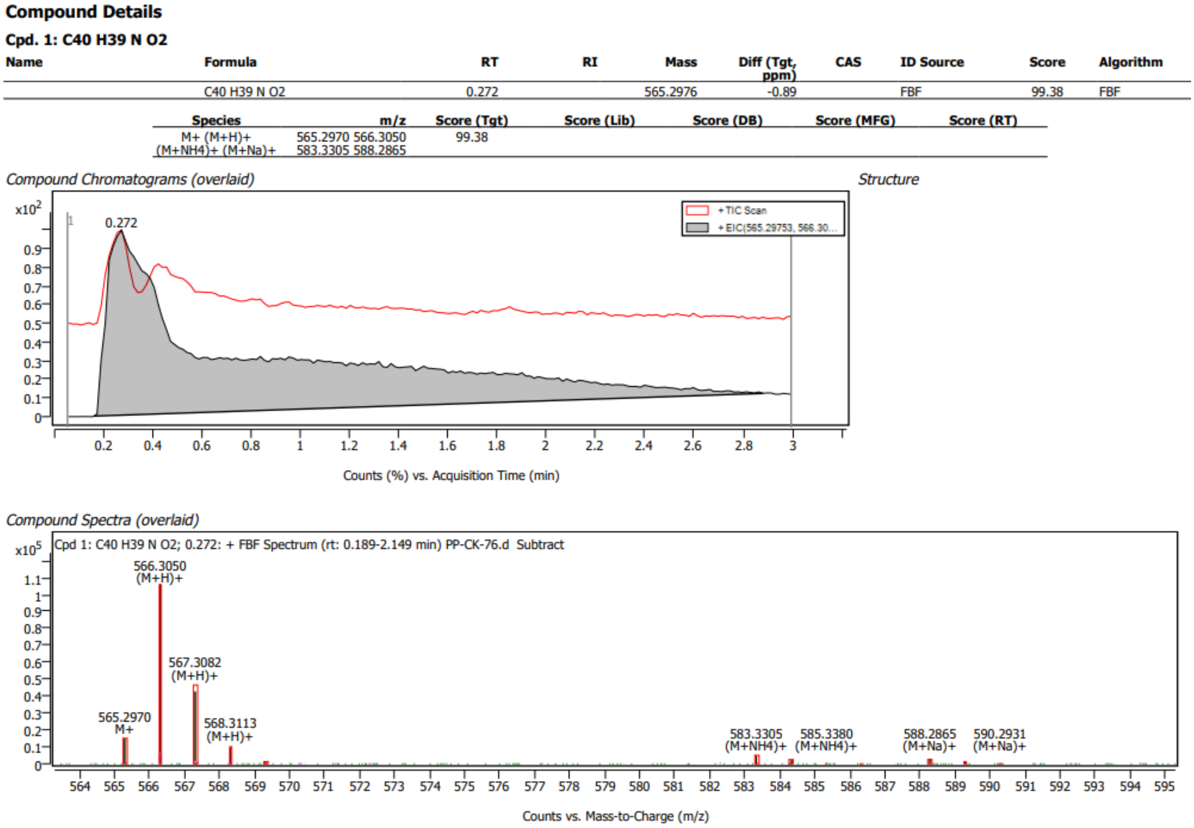


Figure S70: $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of (S)-3,7-dimethyloctyl-2-(3,6-bis(phenylethynyl)-9H-carbazol-9-yl)acetate **(S)-Est-C10**.



Compound Details

Cpd. 1: C40 H39 N O2

Name	Formula	RT	RI	Mass	Diff (Tgt, ppm)	CAS	ID Source	Score	Algorithm
	C40 H39 N O2	0.272		565.2976	-0.89		FBF	99.38	FBF

Species	m/z	Score (Tgt)	Score (Lib)	Score (DB)	Score (MFG)	Score (RT)
M+ (M+H)+ (M+NH4)+ (M+Na)+	565.2970 566.3050 583.3305 588.2865	99.38				

Compound Chromatograms (overlaid)

Structure

Compound Spectra (overlaid)

Cpd 1: C40 H39 N O2; 0.272: + FBF Spectrum (rt: 0.189-2.149 min) PP-CK-76.d Subtract

Figure S71: HRMS (ESI-mode) of (*S*)-3,7-dimethyloctyl-2-(3,6-bis(phenylethynyl)-9H-carbazol-9-yl)acetate **(*S*)-Est-C10**.

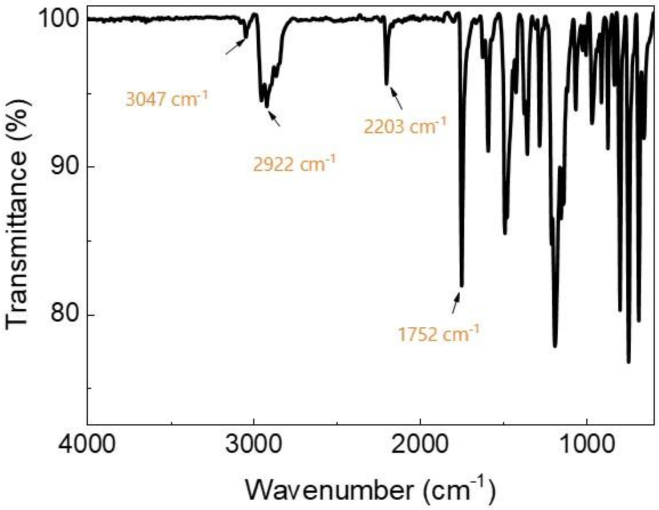


Figure S72: Solid-state FTIR spectrum (ATR mode) of (*S*)-3,7-dimethyloctyl-2-(3,6-bis(phenylethynyl)-9H-carbazol-9-yl)acetate (**(*S*)-Est-C10**).

z

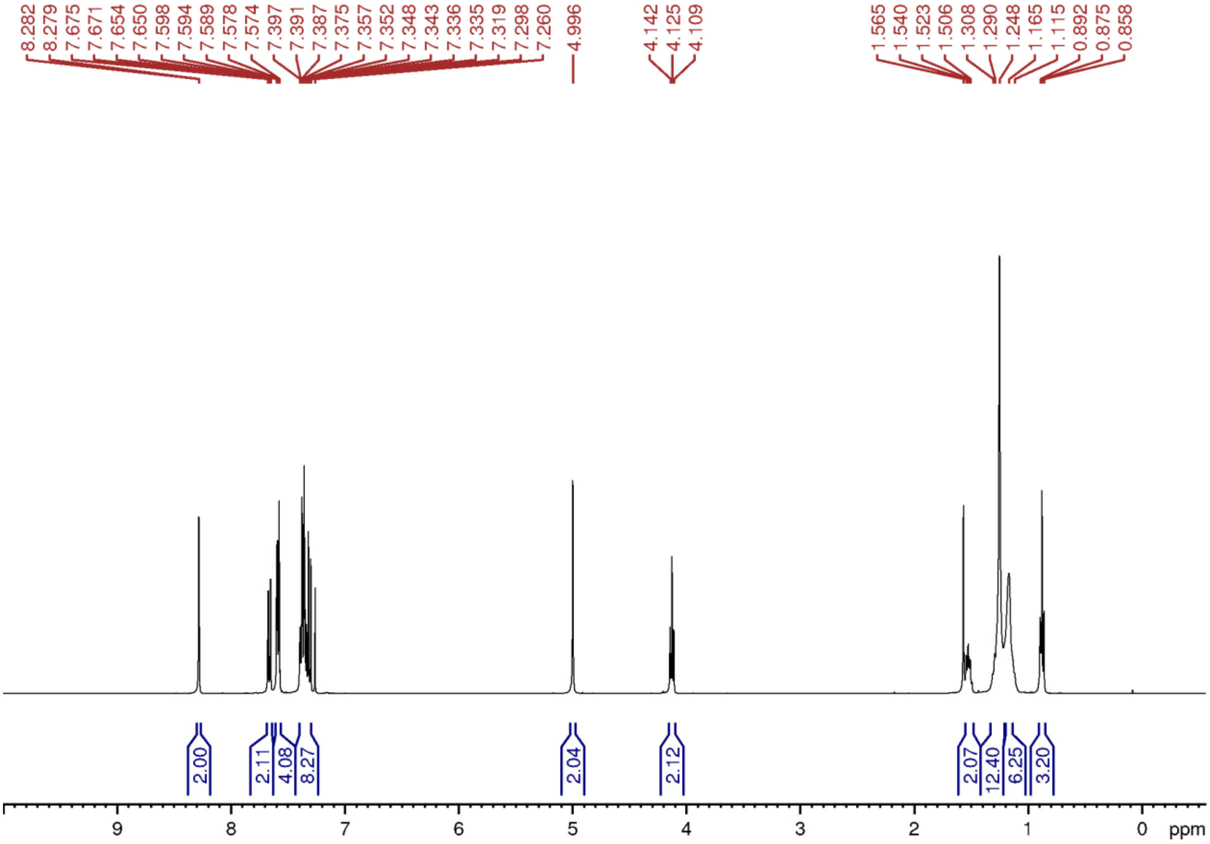


Figure S73: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of dodecyl-2-(3,6-bis(phenylethynyl)-9H-carbazol-9-yl)acetate (**Est-C12**).

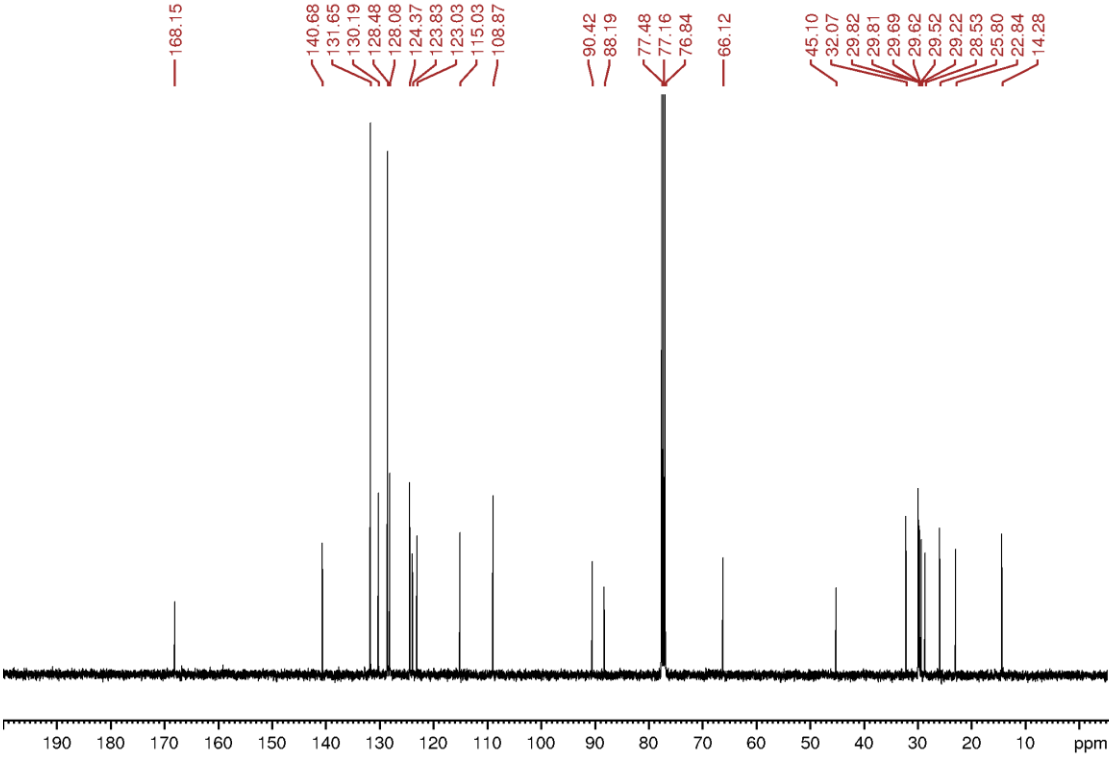
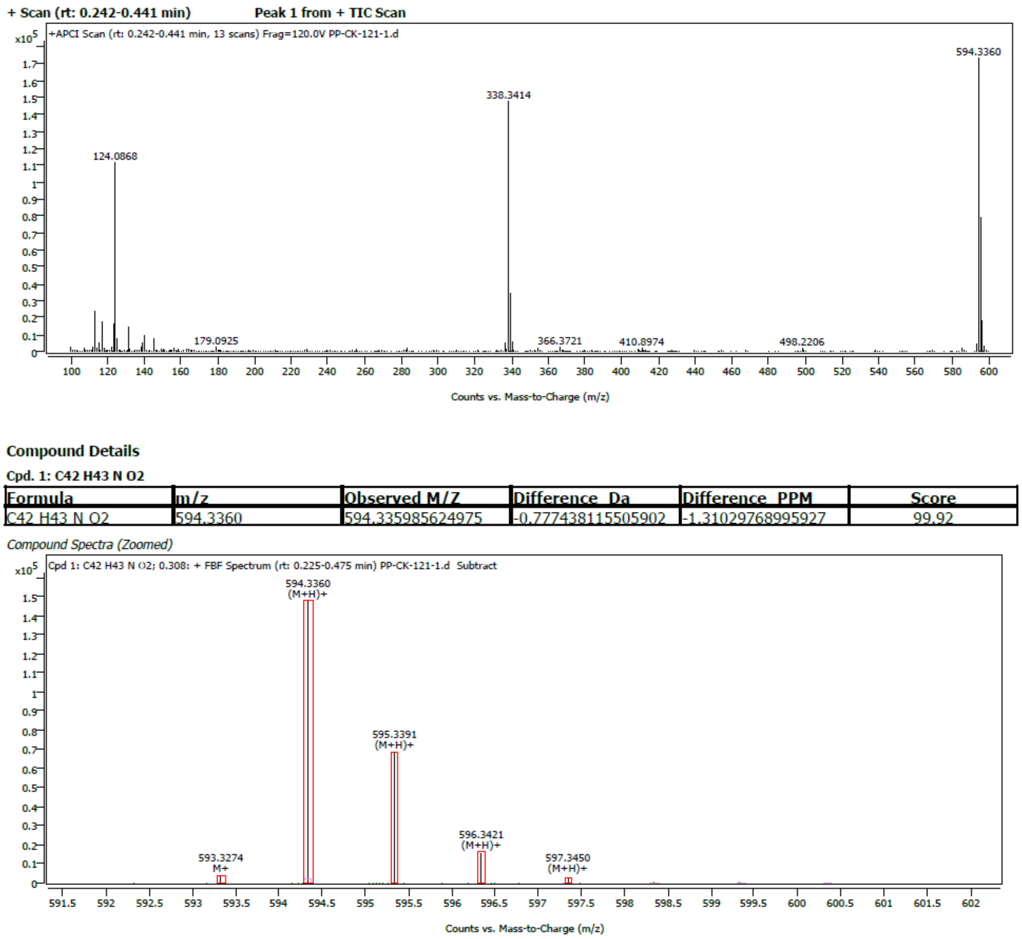


Figure S74: $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of dodecyl-2-(3,6-bis(phenylethynyl)-9H-carbazol-9-yl)acetate (**Est-C12**).



Compound Details

Cpd. 1: C42 H43 N O2

Formula	m/z	Observed M/Z	Difference Da	Difference PPM	Score
C42 H43 N O2	594.3360	594.335985624975	-0.777438115505902	-1.31029768995927	99.92

Compound Spectra (Zoomed)

Figure S75: HRMS (APCI-mode) of dodecyl-2-(3,6-bis(phenylethynyl)-9H-carbazol-9-yl)acetate (**Est-C12**).

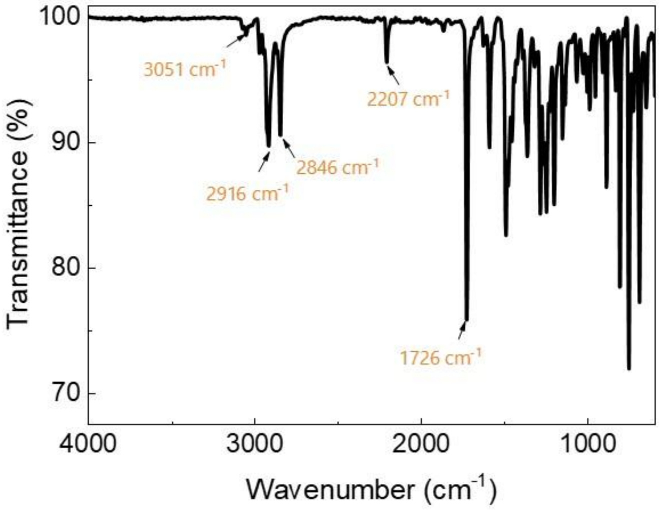


Figure S76: Solid-state FTIR spectrum (ATR mode) of dodecyl-2-(3,6-bis(phenylethynyl)-9H-carbazol-9-yl)acetate (**Est-C12**).

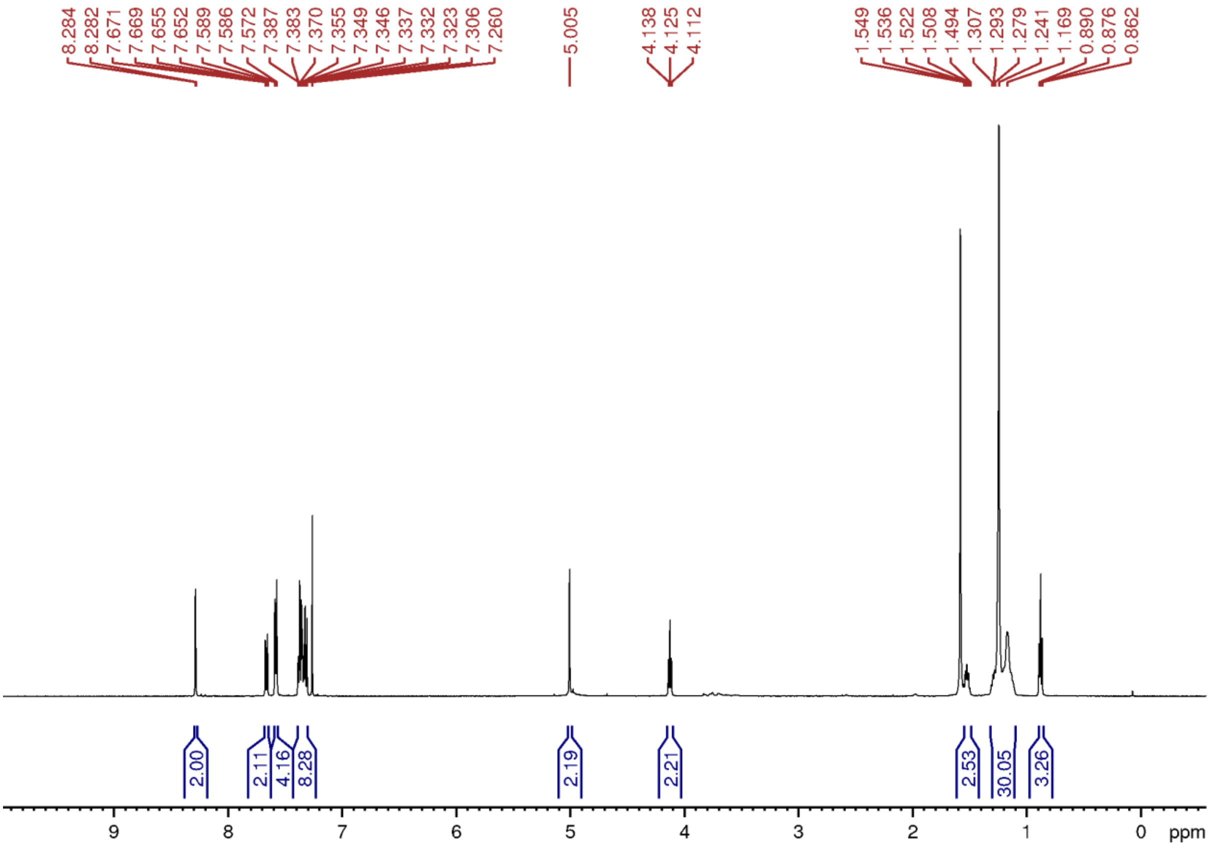


Figure S77: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of hexadecyl-2-(3,6-bis(phenylethynyl)-9H-carbazol-9-yl)acetate (**Est-C16**).

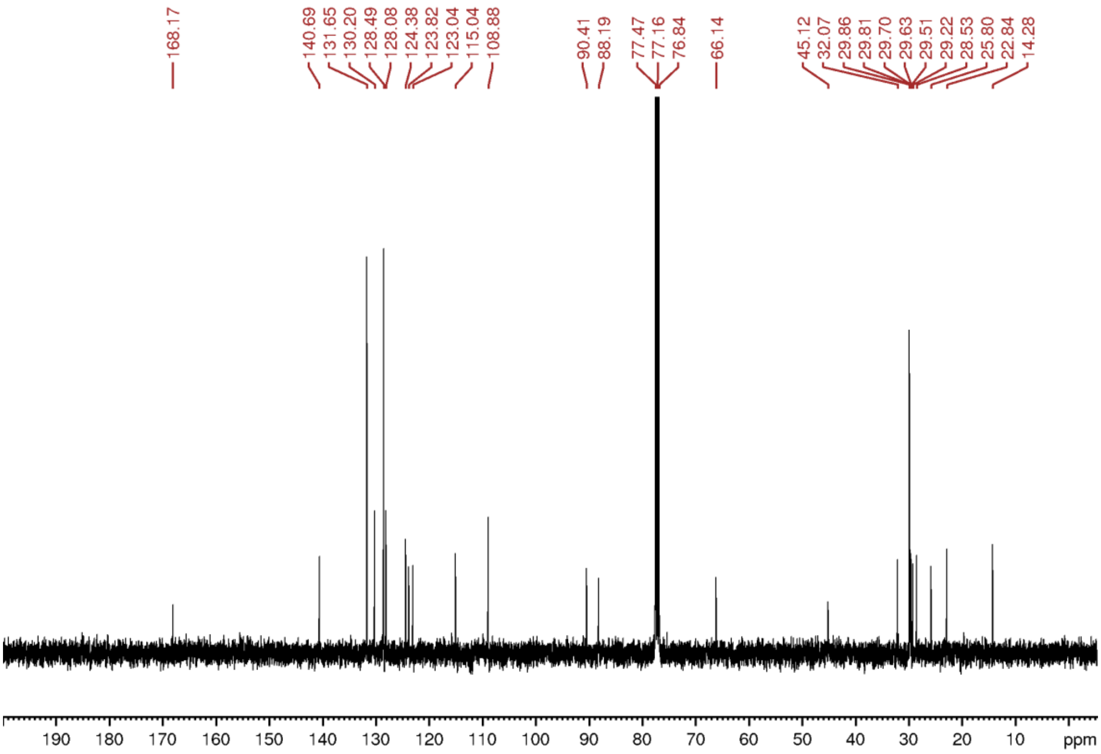
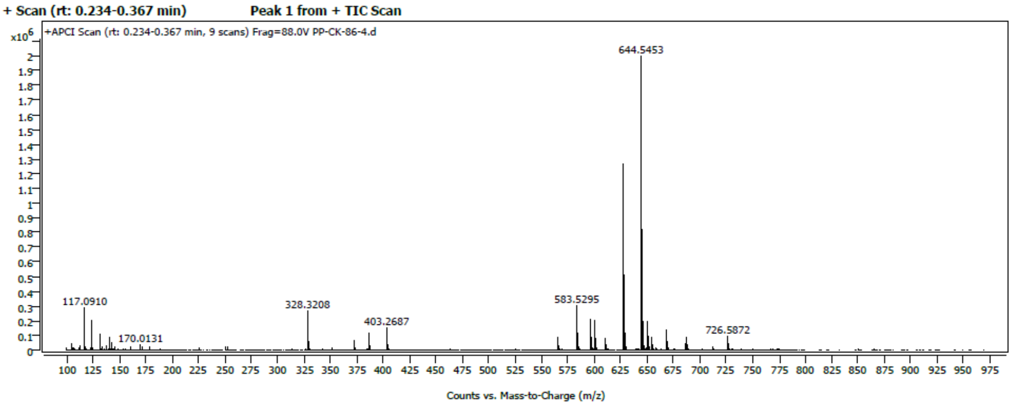


Figure S78: $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of hexadecyl-2-(3,6-bis(phenylethynyl)-9H-carbazol-9-yl)acetate (**Est-C16**).



Compound Details

Cpd. 1: C46 H51 N O2

Formula	m/z	Observed M/Z	Difference_Da	Difference_PPM	Score
C46 H51 N O2	650.3984	650.398401925334	-0.91474823648241	-1.40862262674232	99.54

Compound Spectra (Zoomed)

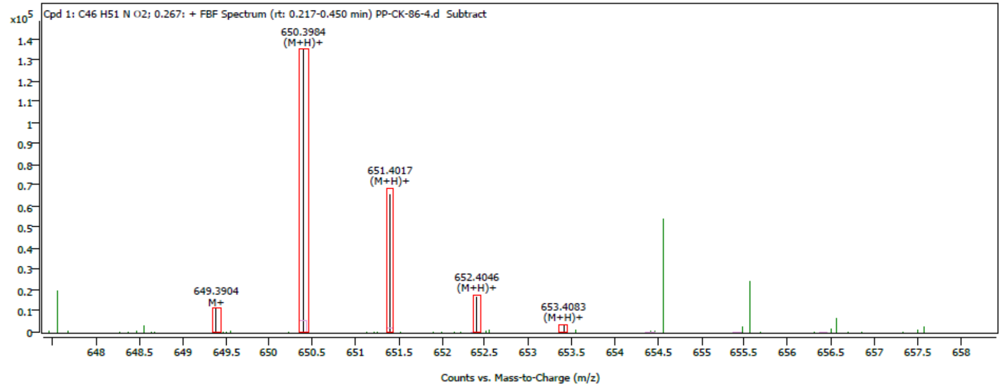


Figure S79: HRMS (APCI-mode) spectrum of hexadecyl-2-(3,6-bis(phenylethynyl)-9H-carbazol-9-yl)acetate (**Est-C16**).

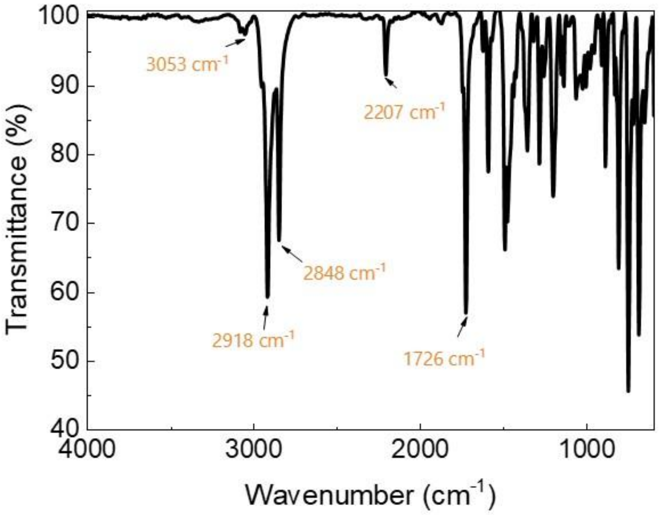


Figure S80: Solid-state FTIR spectrum (ATR mode) of hexadecyl-2-(3,6-bis(phenylethynyl)-9H-carbazol-9-yl)acetate (**Est-C16**).

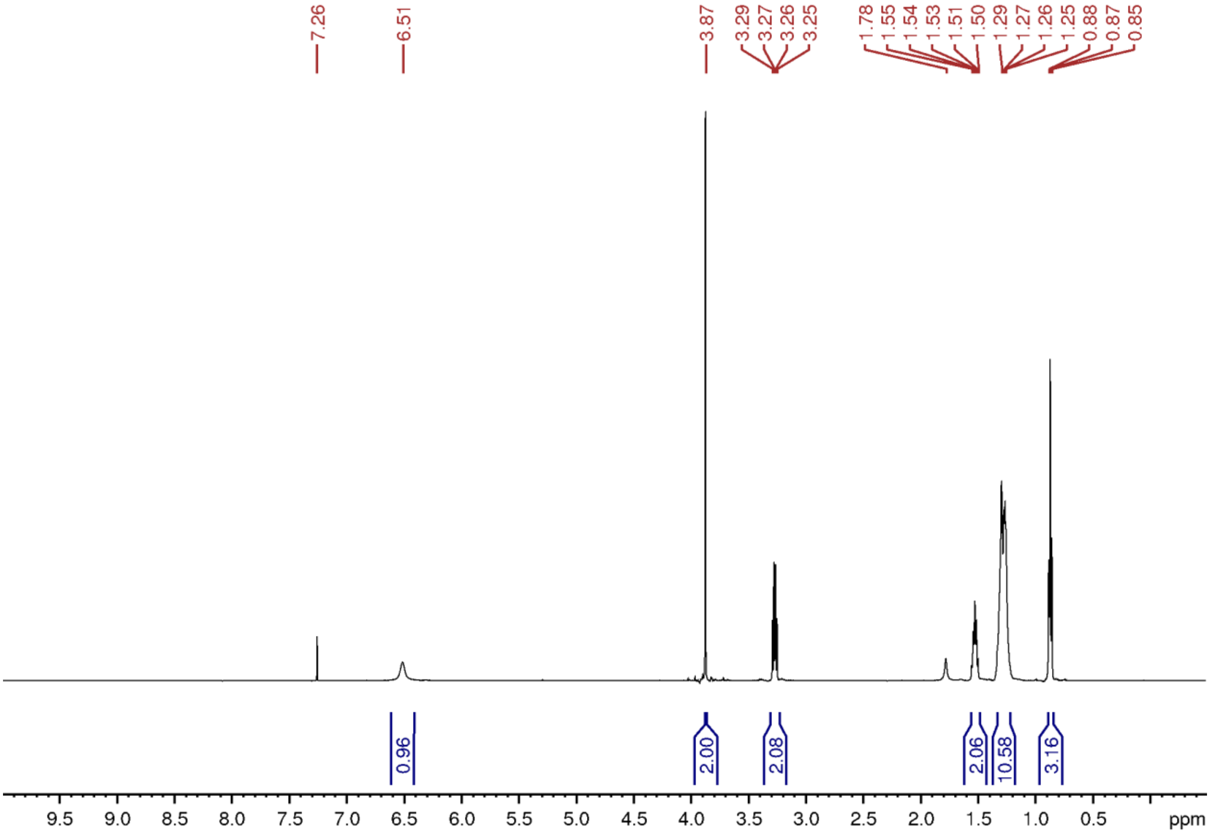


Figure S81: ^{1}H NMR (500 MHz, CDCl$_3$) spectrum of octyl-2-bromoacetamide (**7a**).

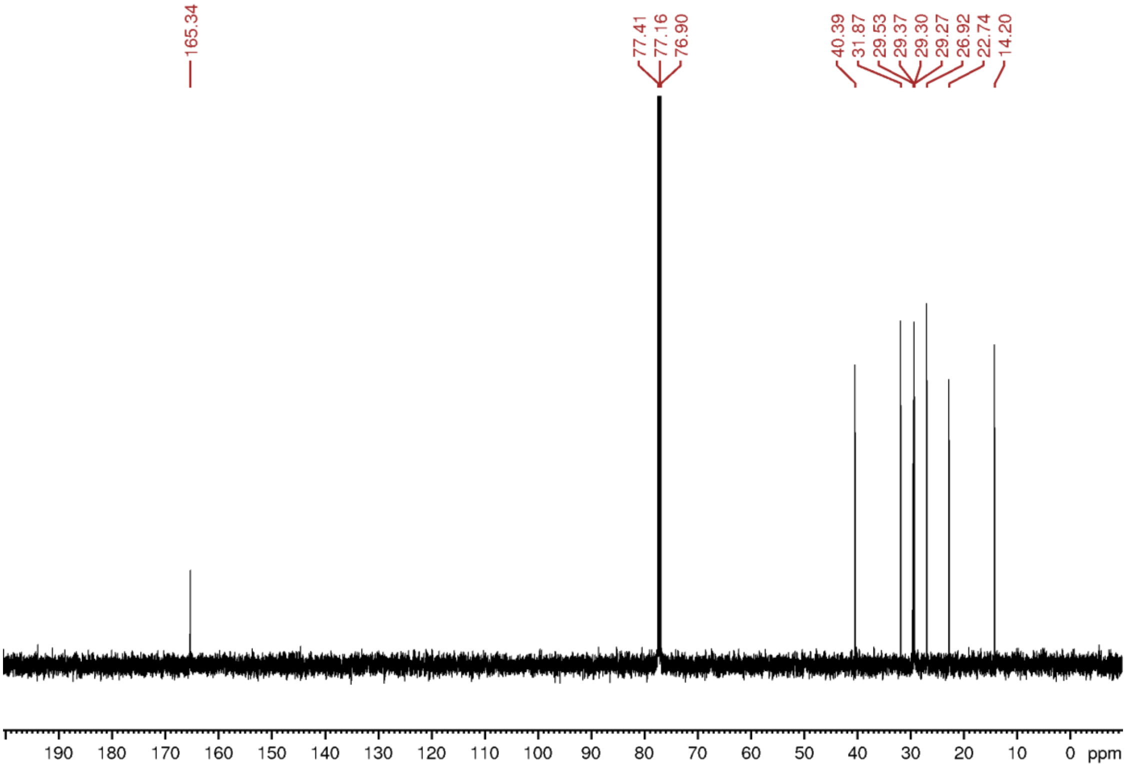
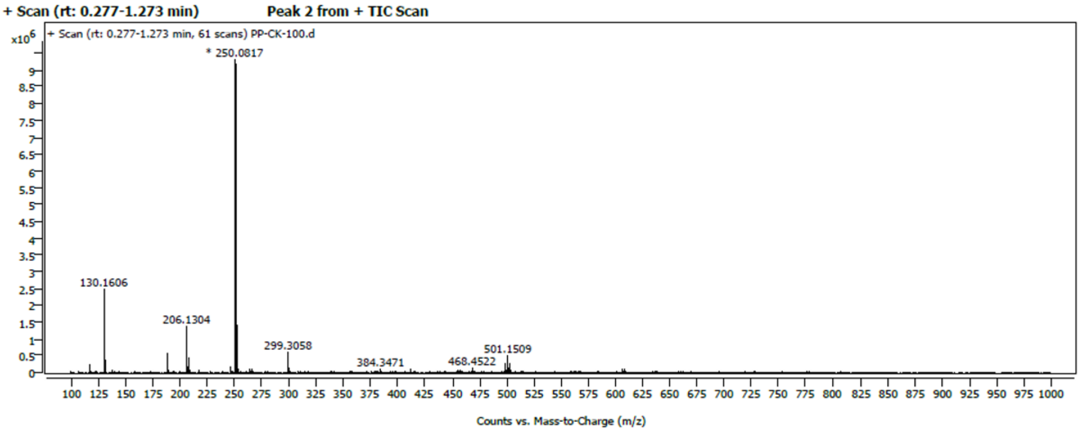


Figure S82: $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) spectrum of octyl-2-bromoacetamide (**7a**).



Compound Details

Cpd. 1: C10 H20 Br N O

Formula	m/z	Observed M/Z	Difference Da	Difference PPM	Score
C10 H20 Br N O	250.0814	250.081383141811	1.08688472610652	4.36372260461284	90.83

Compound Spectra (Zoomed)

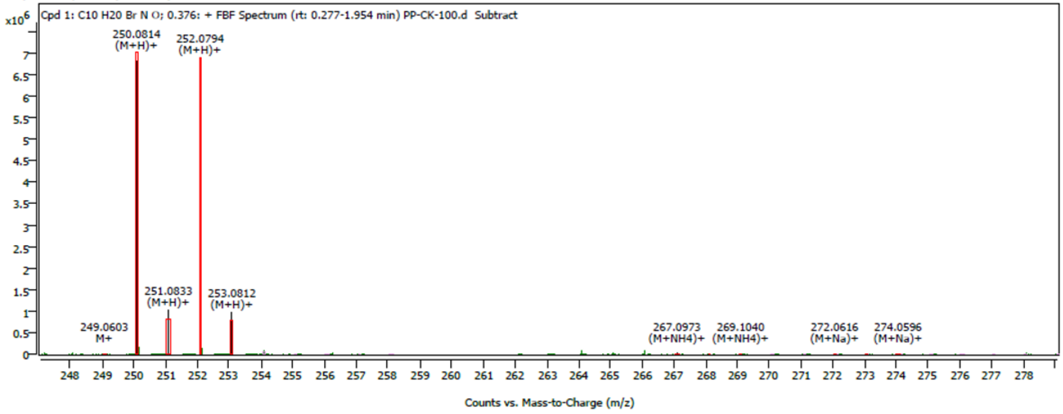


Figure S83: HRMS (ESI-mode) of octyl-2-bromoacetamide (**7a**).

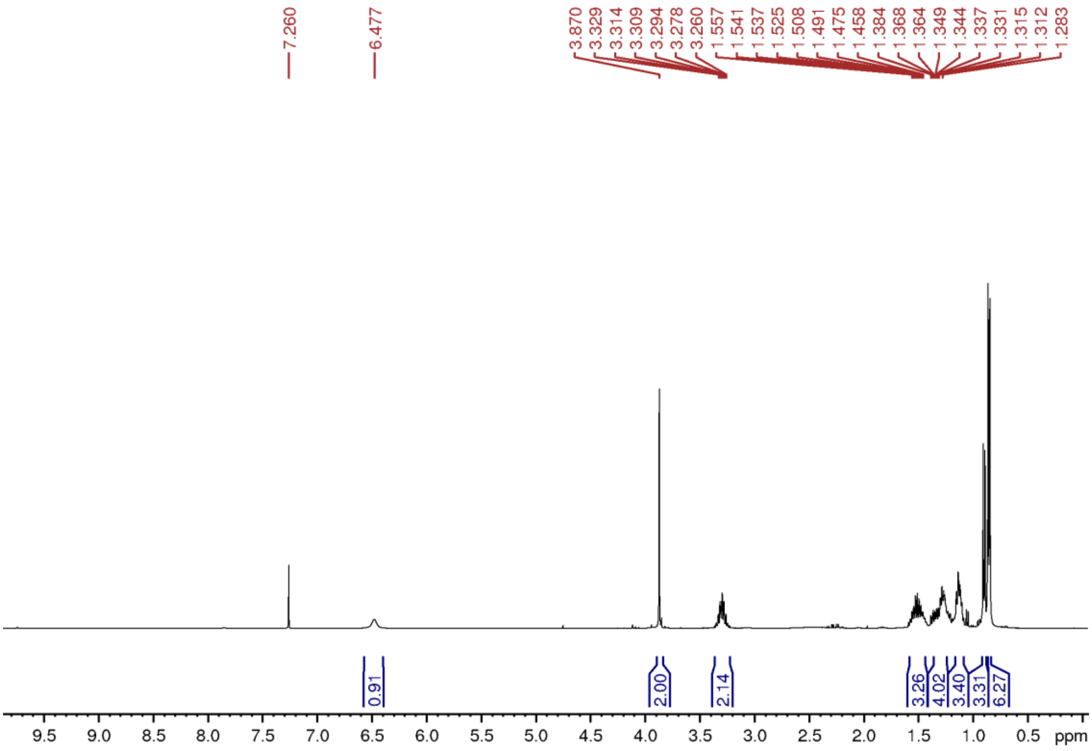


Figure S84: ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of (*S*)-3,7-dimethyloctyl-2-bromoacetamide (**7b**).

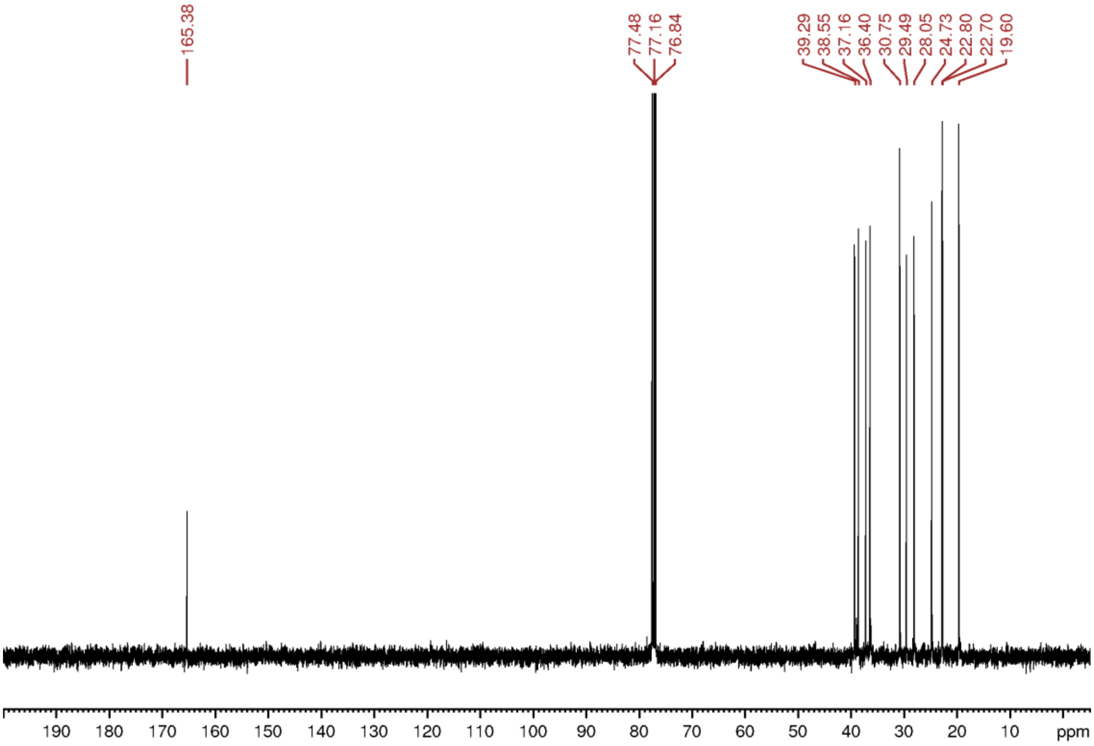
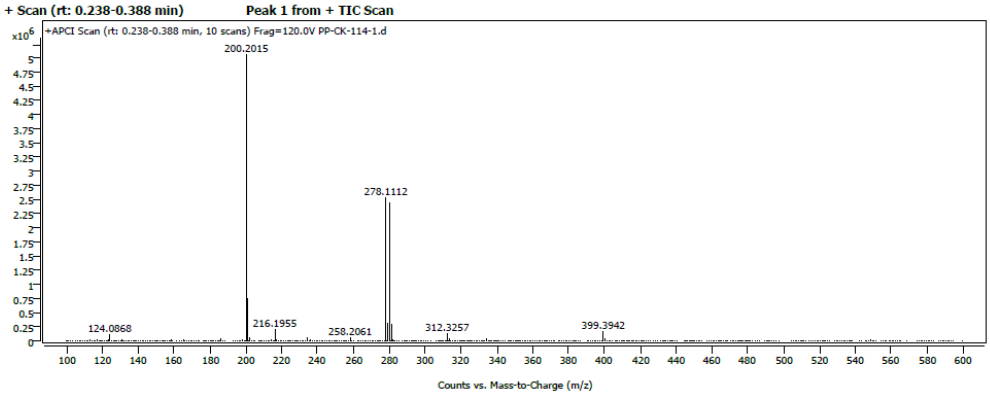


Figure S85: ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of (*S*)-3,7-dimethyloctyl-2-bromoacetamide (**7b**).



Compound Details

Cpd. 1: C12 H24 Br N O

Formula	m/z	Observed M/Z	Difference_Da	Difference_PPM	Score
C12 H24 Br N O	278.1112	278.111179739974	-0.242847646518385	-0.876376865580175	99.70

Compound Spectra (Zoomed)

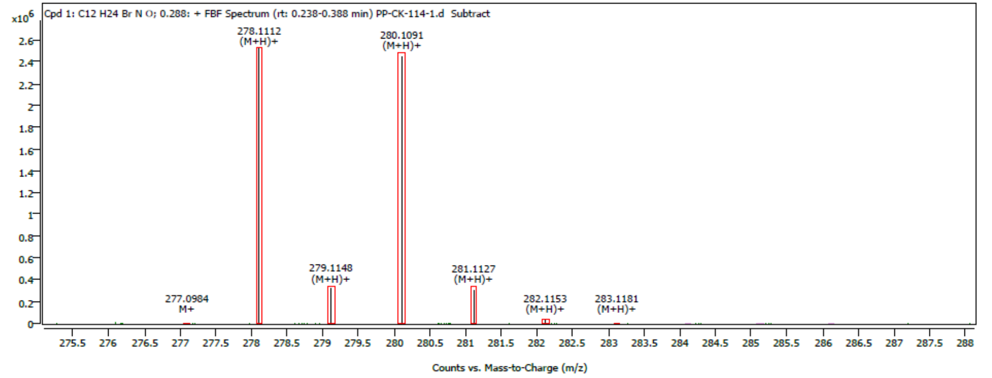


Figure S86: HRMS (APCI-mode) of (*S*)-3,7-dimethyloctyl-2-bromoacetamide (**7b**).

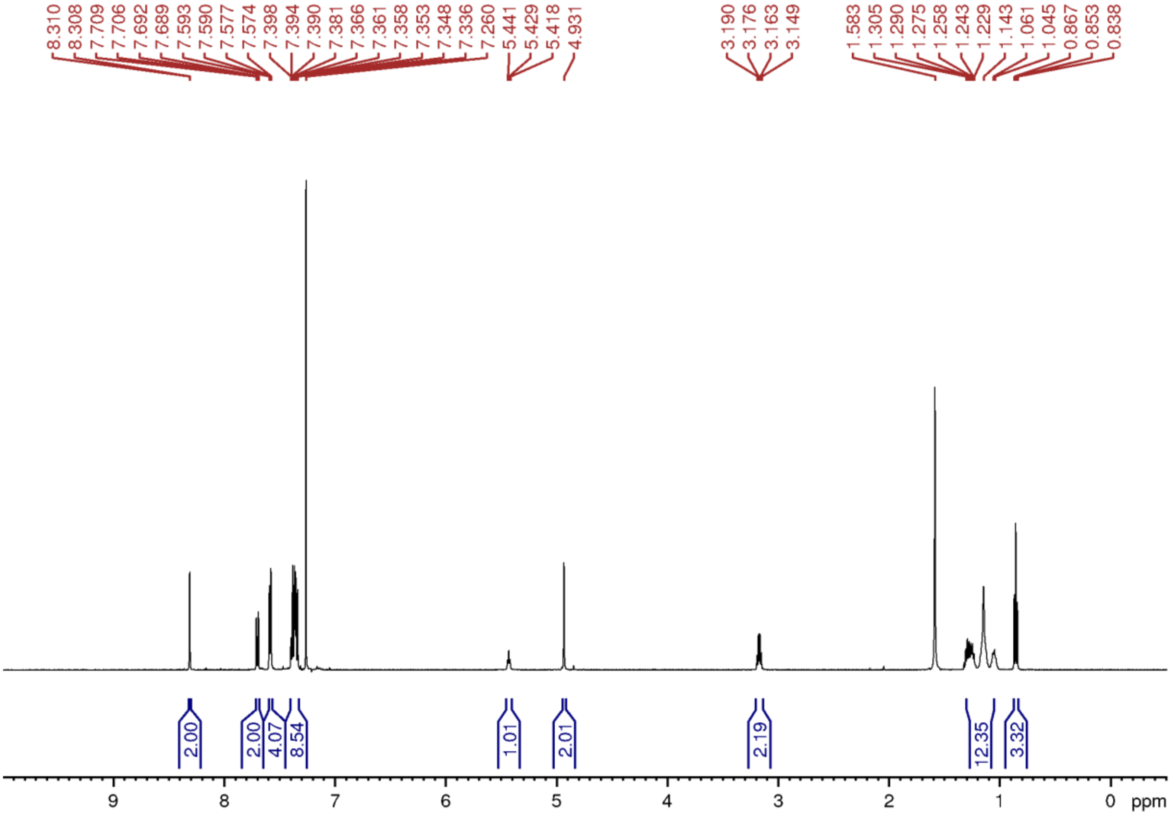


Figure S87: ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of octyl-2-(3,6-bis(phenylethynyl)-9H-carbazol-9-yl)acetamide (**Am-C8**).

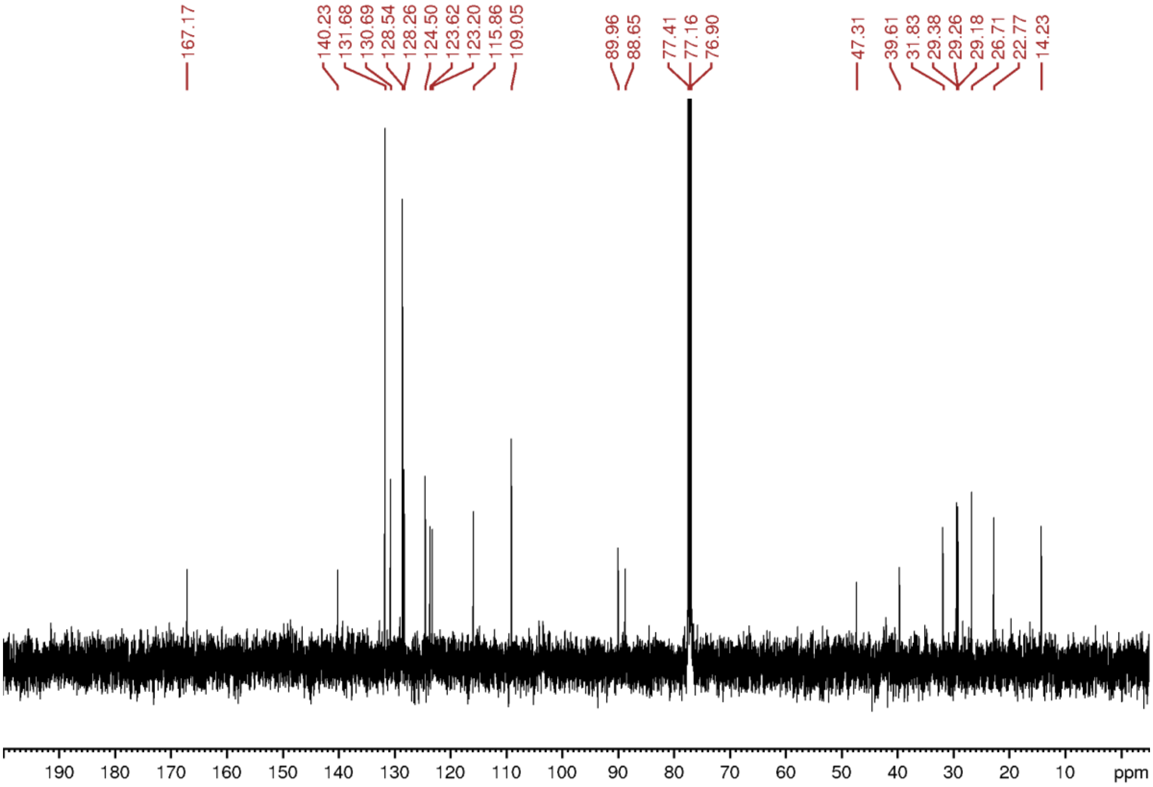
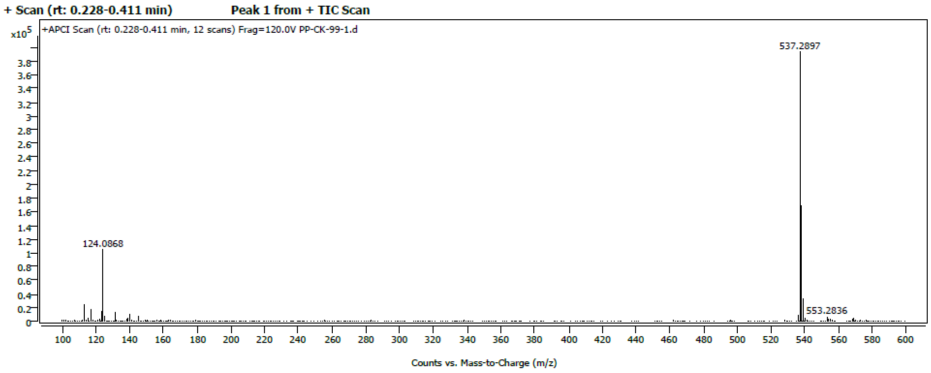


Figure S88: $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of octyl-2-(3,6-bis(phenylethynyl)-9H-carbazol-9-yl)acetamide (**Am-C8**).



Compound Details

Cpd. 1: C38 H36 N2 O

Formula	m/z	Observed M/Z	Difference Da	Difference PPM	Score
C38 H36 N2 O	537.2897	537.289748453342	-0.423836764412044	-0.790323301499149	99.82

Compound Spectra (Zoomed)

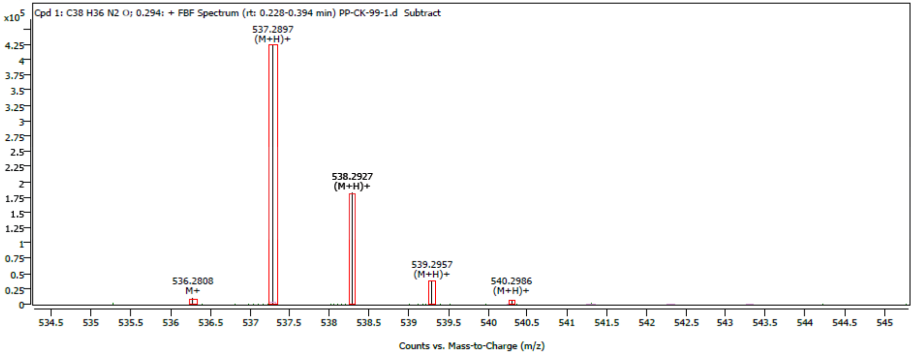


Figure S89: HRMS (APCI-mode) of octyl-2-(3,6-bis(phenylethynyl)-9H-carbazol-9-yl)acetamide (**Am-C8**).

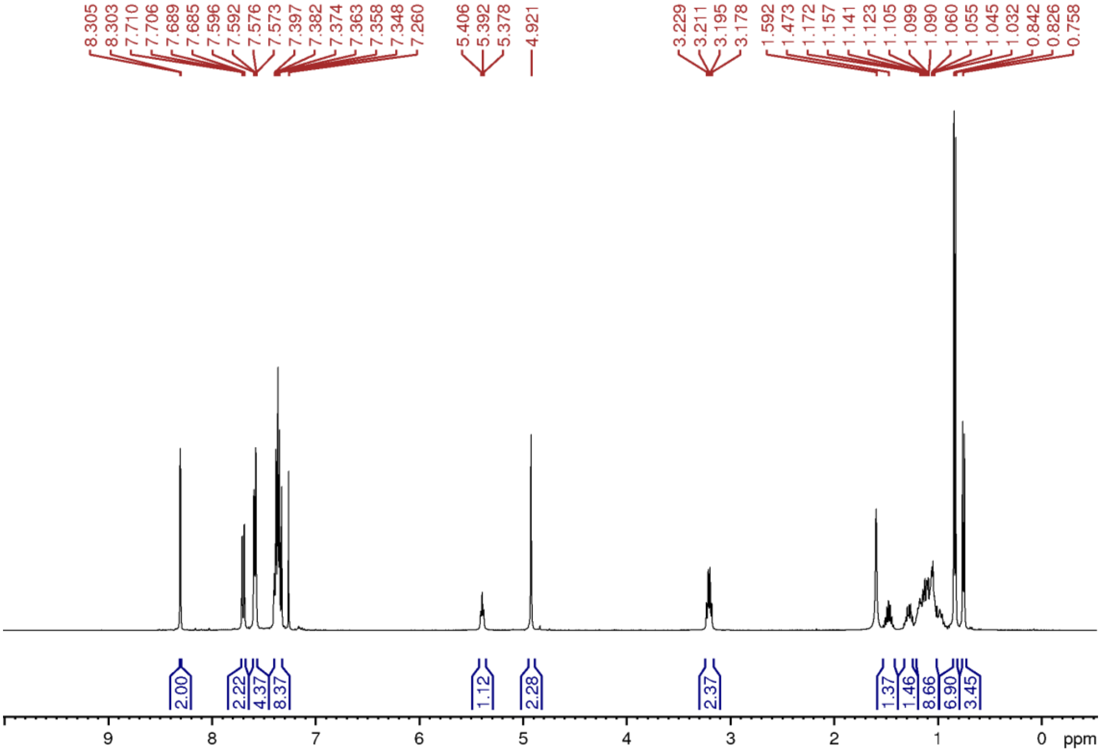


Figure S90: ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of (*S*)-3,7-dimethyloctyl-2-(3,6-bis(phenylethynyl)-9H-carbazol-9-yl)acetamide (**(*S*)-Am-C10**).

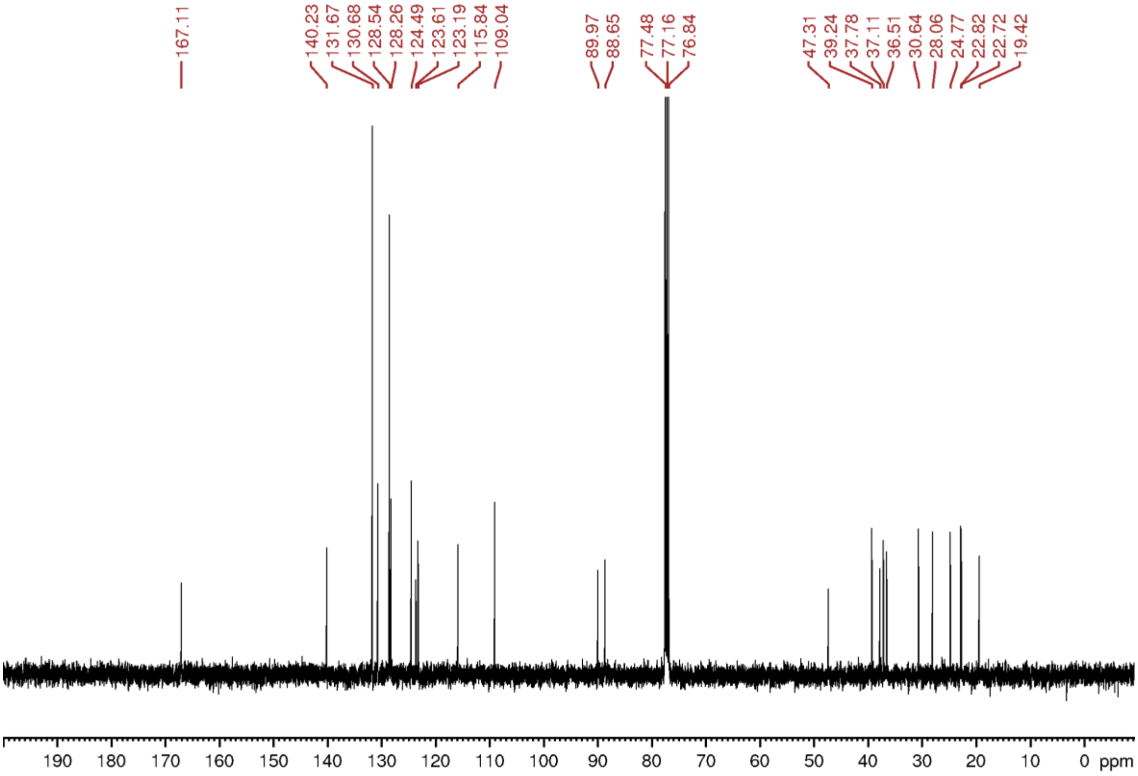
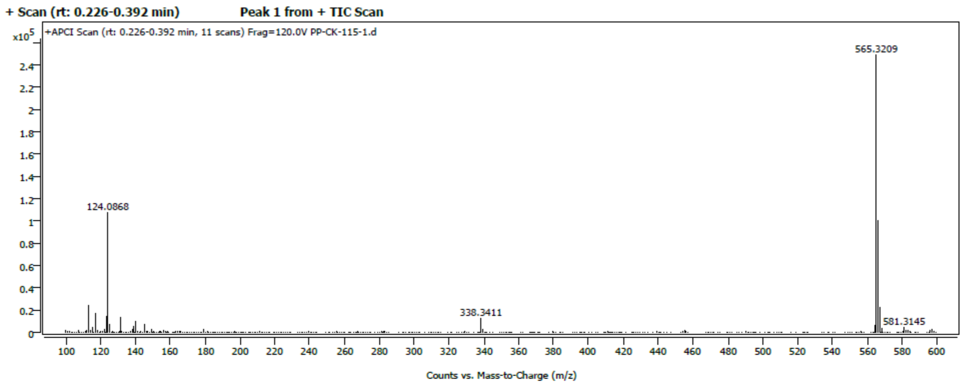


Figure S91: ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of (*S*)-3,7-dimethyloctyl-2-(3,6-bis(phenylethynyl)-9H-carbazol-9-yl)acetamide (**(*S*)-Am-C10**).



Compound Details

Cpd. 1: C40 H40 N2 O

Formula	m/z	Observed M/Z	Difference_Da	Difference_PPM	Score
C40 H40 N2 O	565.3209	565.320922801205	-0.568518844488608	-1.00745113553675	98.08

Compound Spectra (Zoomed)

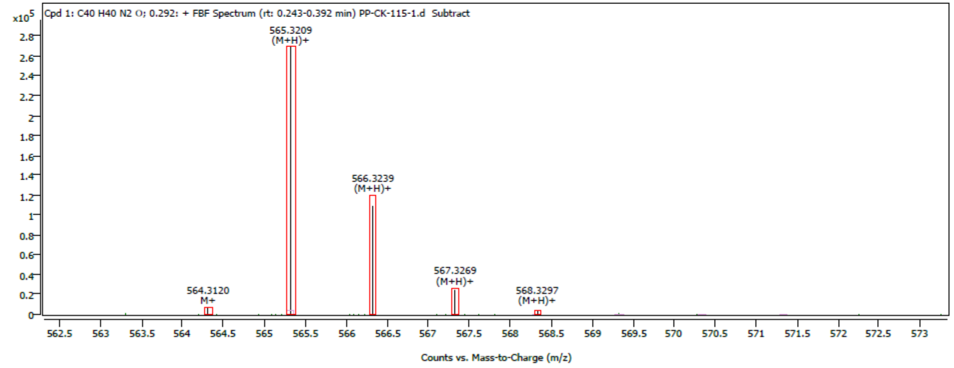


Figure S92: HRMS (APCI-mode) of (*S*)-3,7-dimethyloctyl-2-(3,6-bis(phenylethynyl)-9H-carbazol-9-yl)acetamide (**(*S*)-Am-C10**).

5. References

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