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Supporting Information

Highly-stable, green-solvent-processable organic thin-film transistors: angular- *vs* linear-shaped carbazoledioxazine derivatives

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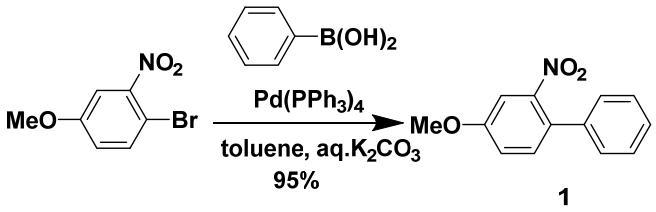
Content

1. Synthetic details of compounds 1-3

All chemicals were purchased from Tokyo Chemical Industry (TCI), Kanto Chemical, and Sigma Aldrich and used as received unless otherwise stated.

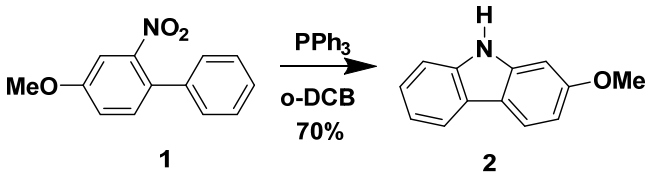
Synthesis of 4-methoxy-2-nitro-1,1'-biphenyl (1)



This compound was synthesized using a modified method according to literature[S1]. Under N_2 atmosphere, phenylboronic acid (3.30 g, 26.7 mmol) and 1-bromo-4-methoxy-2-nitrobenzene (5.00 g, 21.6 mmol) were dissolved in degassed toluene (30 mL). Degassed K_2CO_3 aqueous solution (2 M, 25 mL) was then injected by a syringe. Subsequently, $Pd(PPh_3)_4$ (0.15 g, 0.13 mmol) was quickly added under N_2 flow. After stirring overnight at 110 ^oC, the reaction was quenched with H_2O (100 mL) and the organic phase was extracted with ethyl acetate (150 mL). Evaporation of the solvent followed by column chromatography (SiO_2, hexane/CH_2Cl_2 = 5:2) afforded the title compound as a yellow solid (4.90 g, 95%).

^1H NMR (300 MHz, $CDCl_3$): δ = 7.61 (d, J = 9 Hz, 1H), 7.42-7.39 (m, 4H), 7.30 (t, 6 Hz, 1H), 7.17 (d, J = 6 Hz, 1H), 7.01 (d, J =6 Hz, 1H), 3.90 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 159.1, 149.6, 137.3, 135.4, 132.8, 128.6, 128.0, 119.9, 118.6, 110.7, 109.0, 104.5, 56.0 ppm.

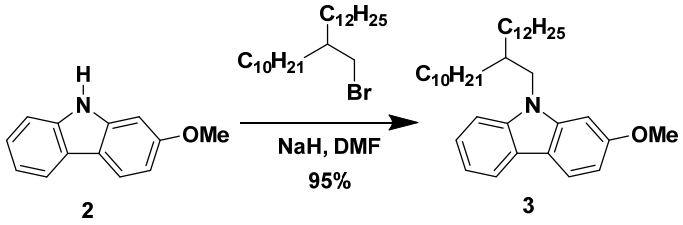
Synthesis of 2-methoxy-9*H*-carbazole (2)



This compound was synthesized using a modified method according to literature[S2]. Under N_2 atmosphere, 4-methoxy-2-nitro-1,1'-biphenyl (4.00 g, 17.4 mmol) and PPh_3 (11.0 g, 41.9 mmol) were dissolved in 1,2-dichlorobenzene (32 mL). After refluxing overnight, the solvent was removed by reduced pressure. The residue was then purified by column chromatography (SiO_2, hexane/CH_2Cl_2= 5:2) afforded the desired compound as a white solid (2.40 g, 70%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.90–8.02 (m, 2H), 7.15–7.43 (m, 3H), 6.92 (d, J = 2.0 Hz, 1H), 6.88 (dd, J = 2.4, 8.5 Hz, 1H), 3.91 ppm (s, 3H).

Synthesis of 9-(2-decyltetradecyl)-2-methoxy-9*H*-carbazole (3)



This compound was synthesized using a modified method according to literature[S3]. Under N_2 atmosphere, 2-methoxy-9*H*-carbazole (4.10 g, 20.8 mmol) was dissolved in dry DMF (45 mL). NaH (1.3 g, 3.3 mmol) was then added quickly under N_2 flow. After stirring for 30 min at room temperature, 2-decyltetradecylbromide (9.60 g, 22.9 mmol) was injected by a syringe. After stirring overnight at room temperature, the reaction mixture was quenched with MeOH (5 mL) and water (100 mL) was added.

The organic phase was extracted with CH_2Cl_2 (150 mL). Evaporation of the solvent followed by column chromatography (SiO_2, hexane/CH_2Cl_2 = 3:1) afforded the desired compound as a white solid (10.6 g, 95%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.00-7.93 (m, 2H), 7.40-7.31 (m, 2H), 7.20 (t, J = 6.0 Hz, 1H), 6.88-6.82 (m, 2H), 4.04 (s, 2H), 3.90 (s, 3H), 2.10 (br,1H), 1.50-1.26 (m, 40 H), 0.86 ppm (t, J = 6.0 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.58, 142.61, 141.75, 124.82, 123.52, 121.41, 120.14, 119.29, 117.15, 109.33, 107.59, 94.01, 55.84, 48.22, 39.94, 36.33, 33.12, 29.95, 27.02, 23.60, 14.47; MALDI-TOF MS (M_w = 533.87): m/z = 533.77 [M^+].

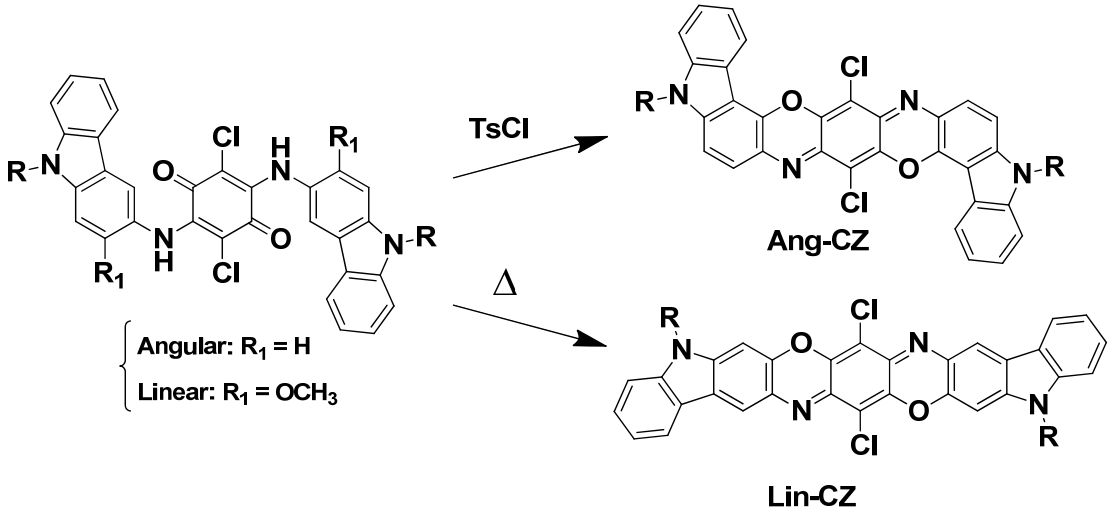
References

[S1] M. Yuan, L. Chen, J. Wang, S. Chen, K. Wang, Y. Xue, G. Yao, Z. Luo and Y. Zhang, *Org. Lett.*, 2015, **17**, 346-349.

[S2] A. W. Freeman, M. Urvoy and M. E. Criswell, *J. Org. Chem.*, 2005, **70**, 5014-5019.

[S3] R. Otsuka, Y. Wang, T. Mori and T. Michinobu, *RSC Adv.*, 2018, **8**, 9822-9832.

2. Synthetic protocols towards angular- and linear-type carbazoledioxazines (CZ)



Scheme S1 Different synthetic protocols towards angular-shaped (**Ang-CZ**) and linear-shaped (**Lin-CZ**) carbazoledioxazine derivatives.

3. TGA curves

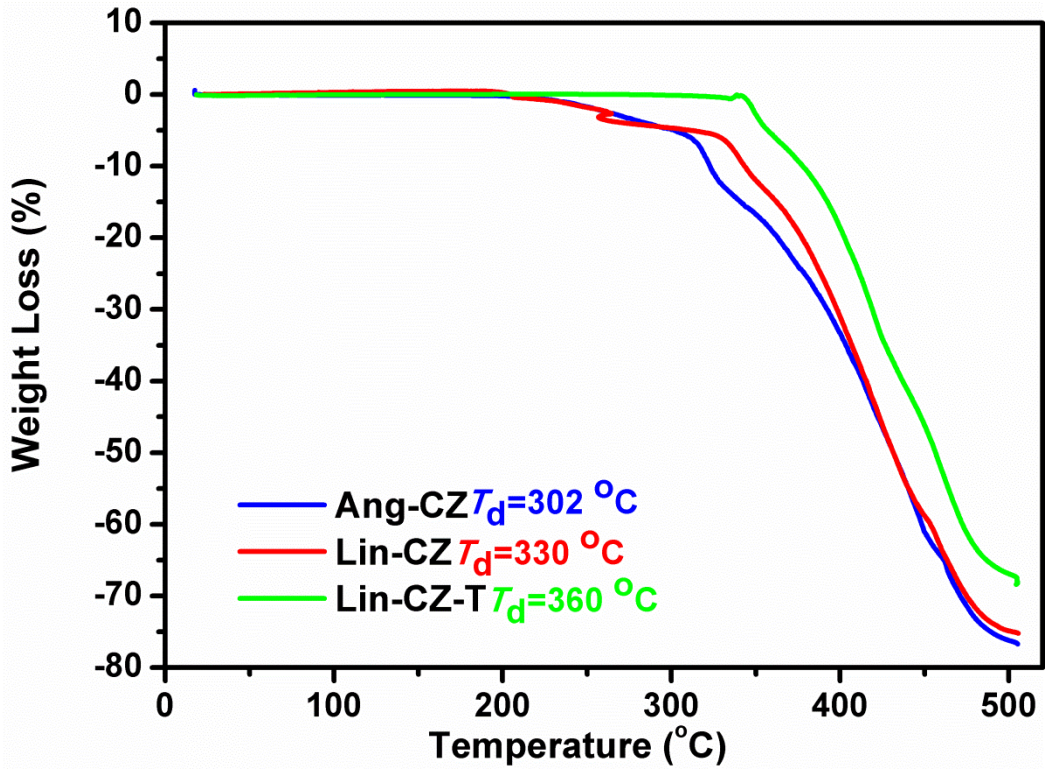


Fig. S1 Thermogravimetric analysis (TGA) under a nitrogen atmosphere at the heating rate of 10 °C min^{-1}.

4. DSC curves

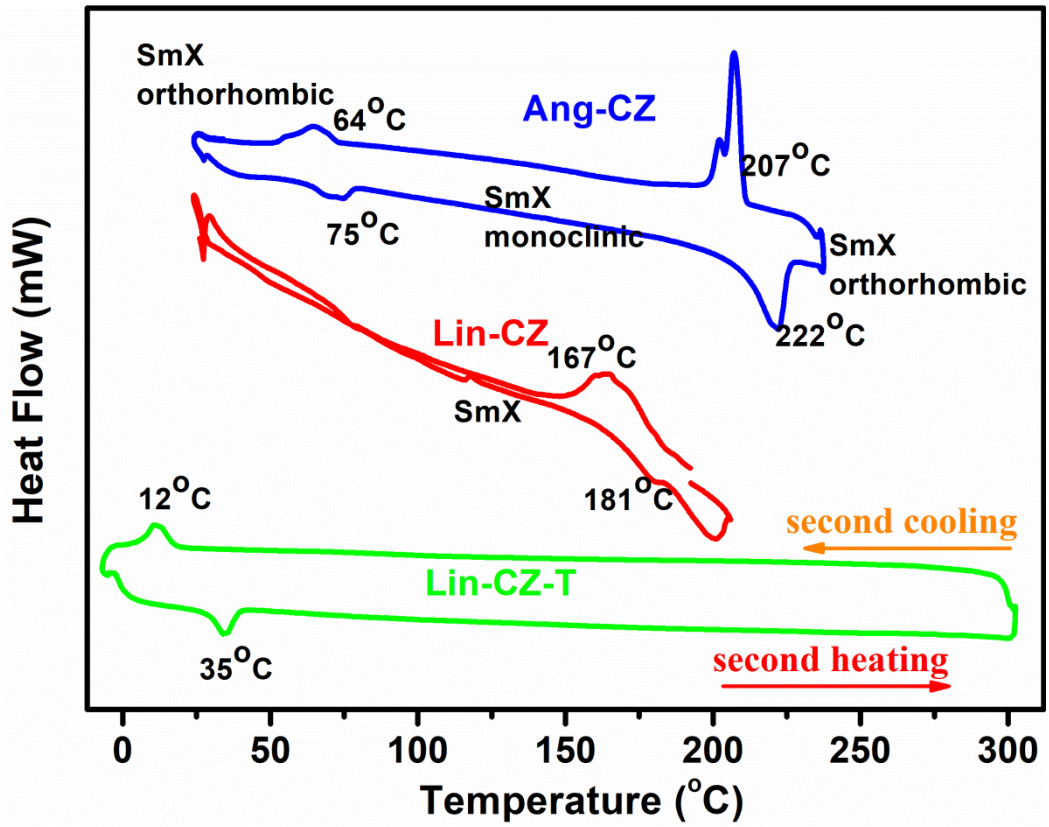


Fig. S2 Differential scanning calorimetry (DSC) curves of **Ang-CZ**, **Lin-CZ**, and **Lin-CZ-T** at the scanning rate of 10 °C min^{-1}.

5. Side-view molecular geometry optimized by DFT calculations

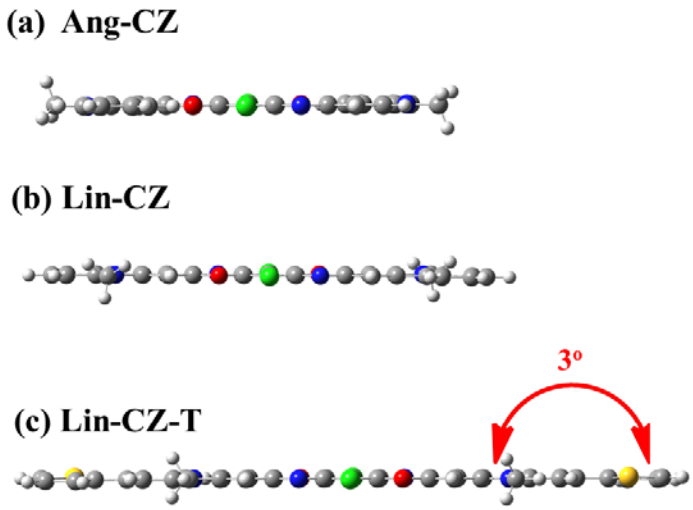


Fig. S3 Calculated side-view molecular geometry of (a) **Ang-CZ**; (b) **Lin-CZ**; (c) **Lin-CZ-T** (using DFT B3LYP/6-31G(d), long and branched alkyl chains are substituted by the methyl group).

6. 1D in-plane profile of GIWAXS

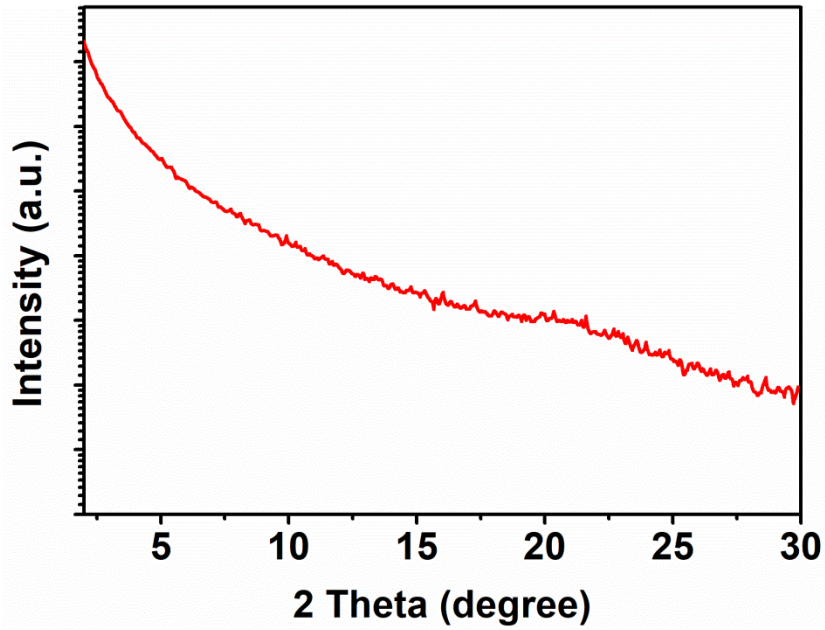


Fig. S4 The 1D in-plane profile of the GIWAXS of **Lin-CZ**.

7. Crystal domain sizes illustrated by AFM images

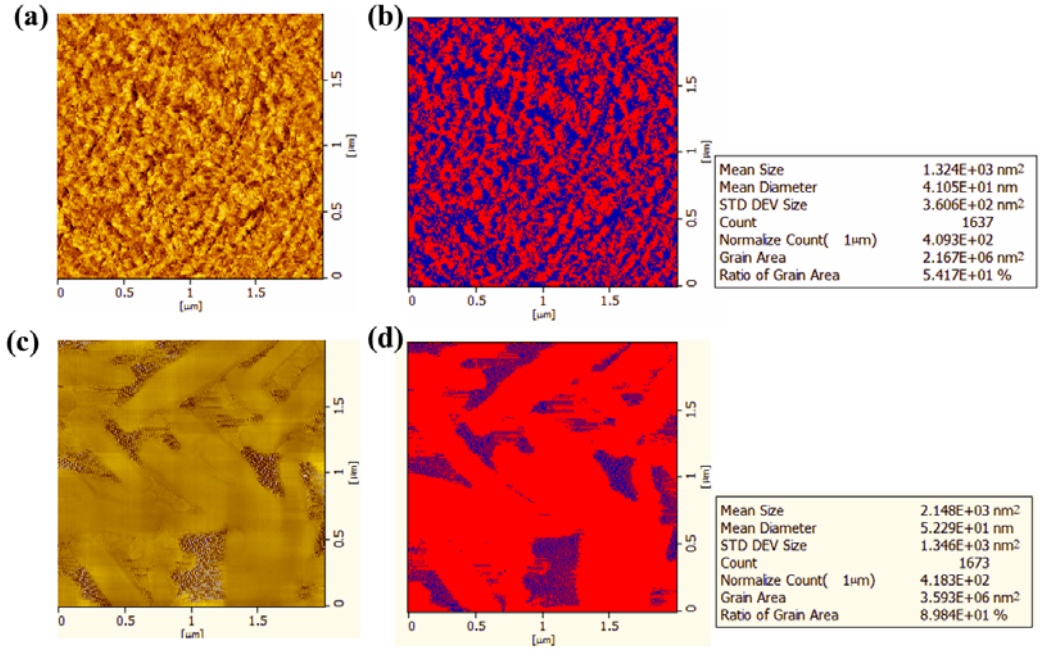


Fig. S5 The size of the crystal domains illustrated by atomic force microscopy (AFM) images (the films were prepared under the best conditions of TFT performances): (a) phase image and (b) the corresponding domain size of **Ang-CZ**; (c) phase image and (d) the corresponding domain size of **Lin-CZ**.

8. Images of Lin-CZ-T dissolved in different solvents

Fig. S6 Images of **Lin-CZ-T** dissolved in $CHCl_3$ (left), THF (middle) and hexane (right) at a concentration of 5 mg mL^{-1}.

9. UV-vis absorption spectra of Lin-CZ-T in THF/HEX mixtures

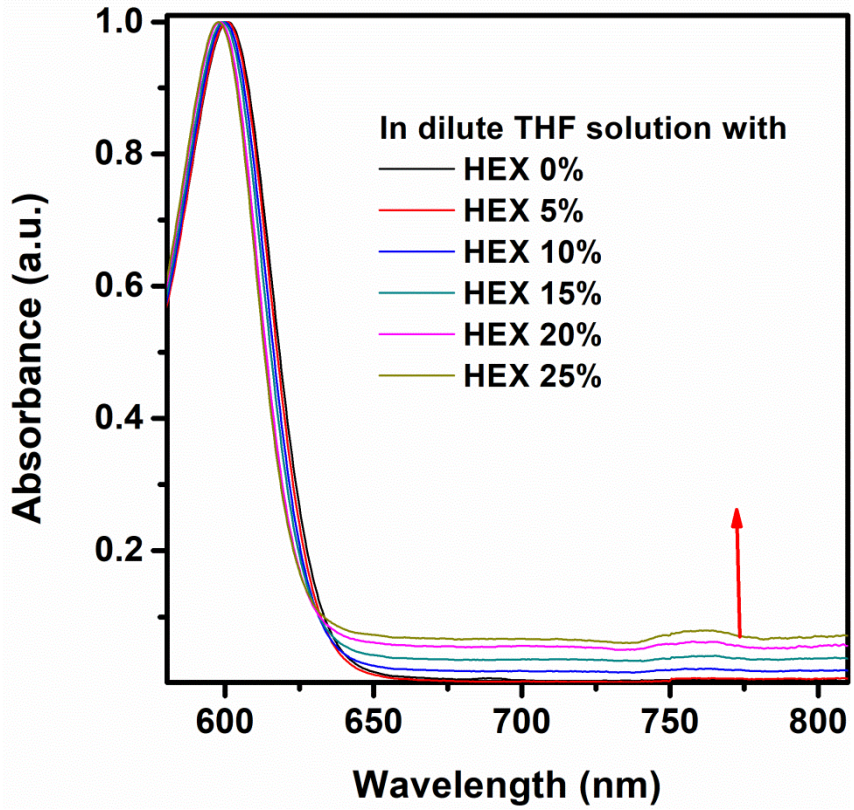


Fig. S7 UV-vis absorption spectral changes of the diluted solution of **Lin-CZ-T** in tetrahydrofuran (THF) by adding hexane (HEX).

10. NMR spectra

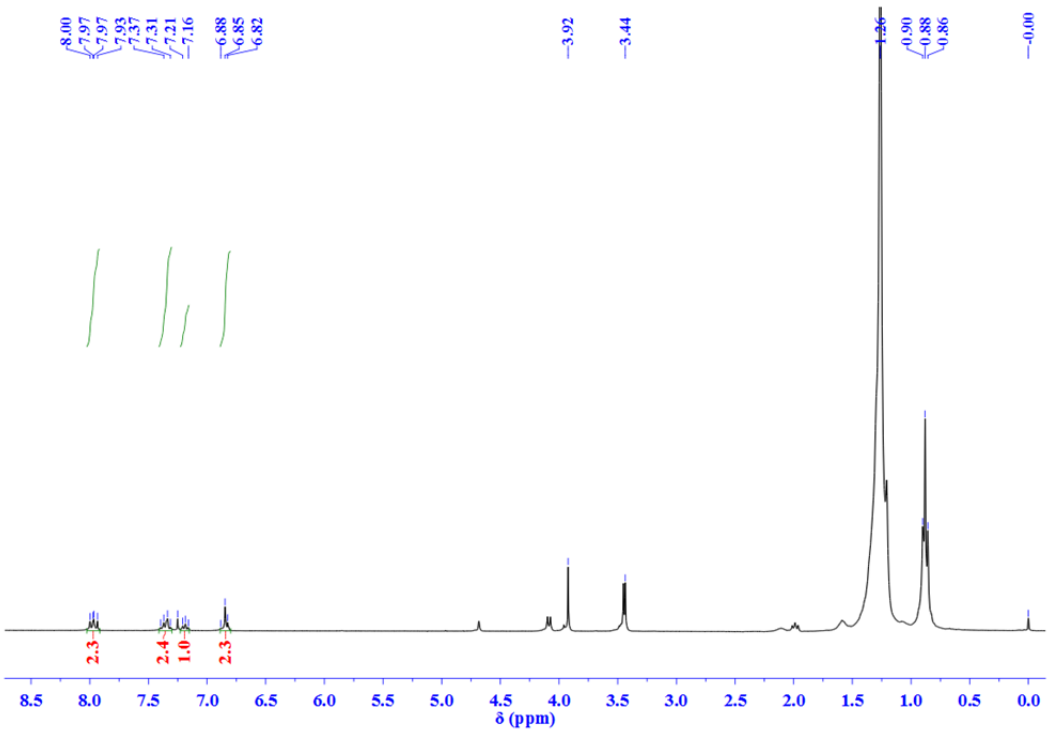


Fig. S8 ^{1}H NMR of compound **3** in $CDCl_3$.

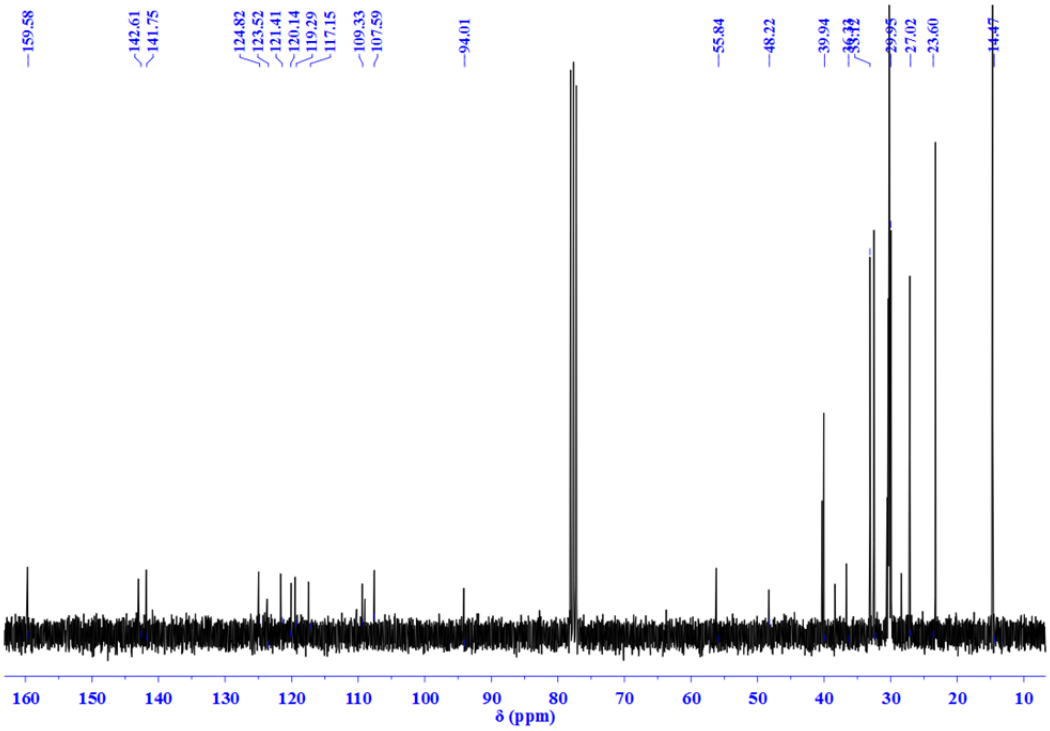


Fig. S9 ^{13}C NMR of compound **3** in $CDCl_3$.

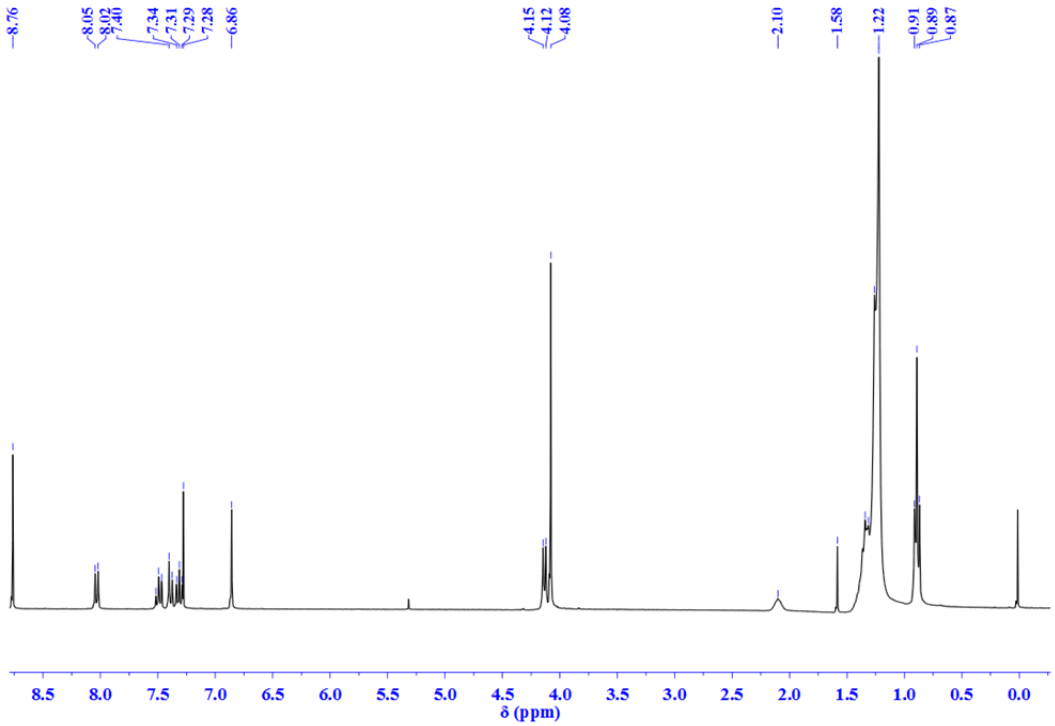


Fig. S10 ^{1}H NMR of compound **4** in $CDCl_3$.

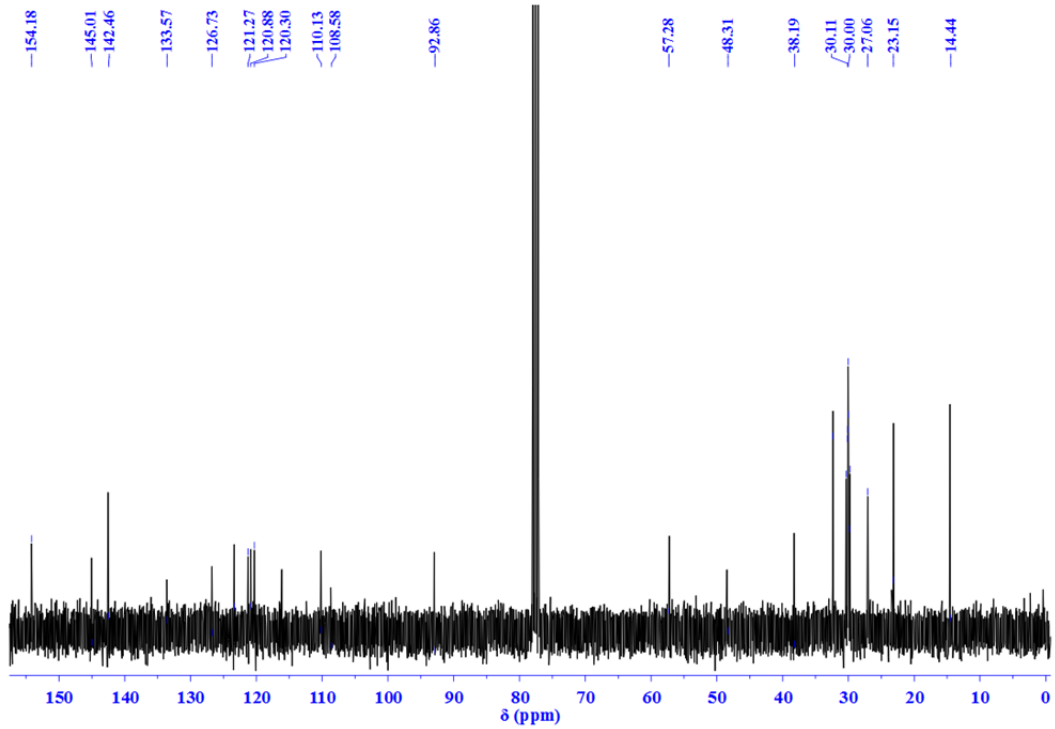


Fig. S11 ^{13}C NMR of compound **4** in $CDCl_3$.

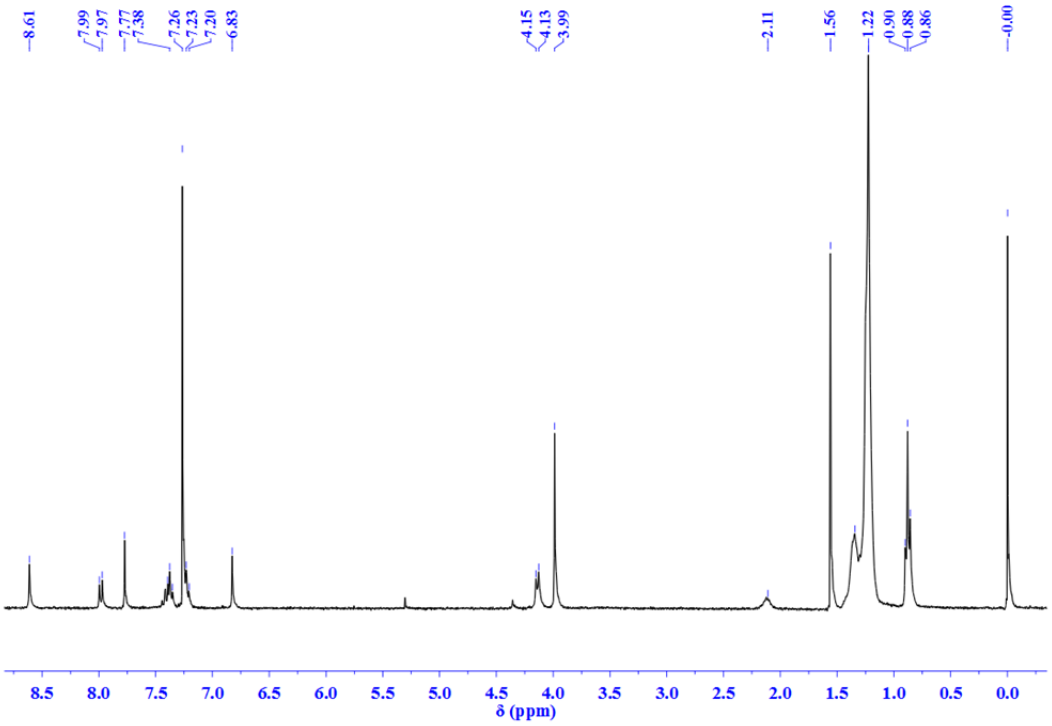


Fig. S12 ^{1}H NMR of compound **5** in $CDCl_3$.

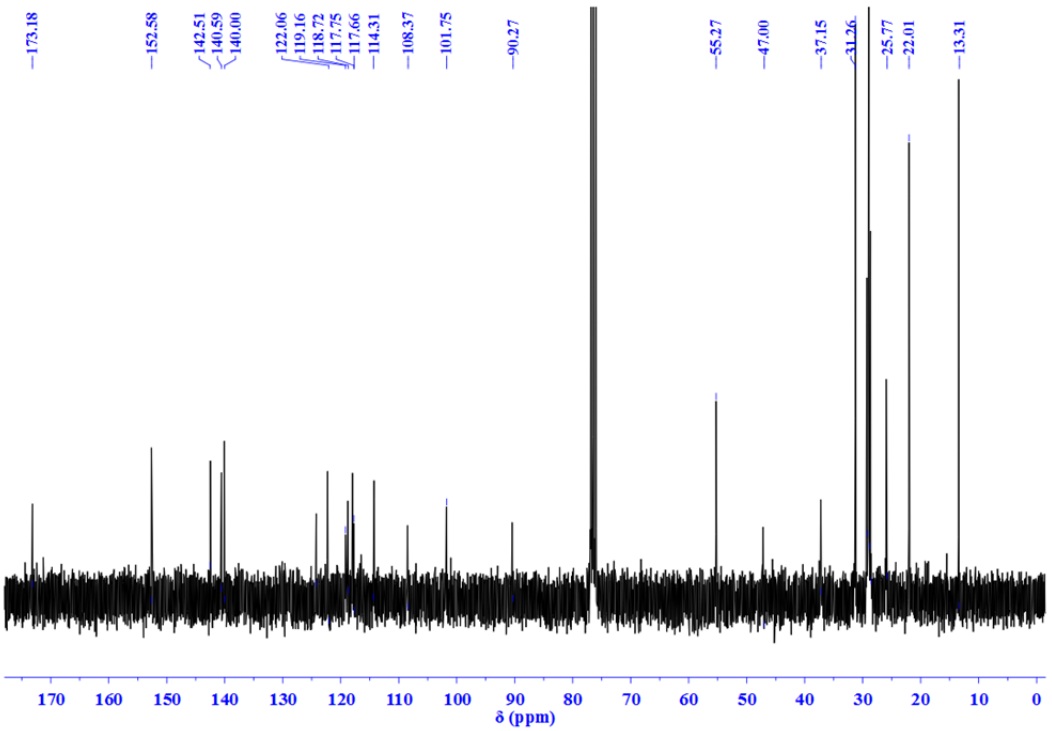


Fig. S13 ^{13}C NMR of compound **5** in $CDCl_3$.

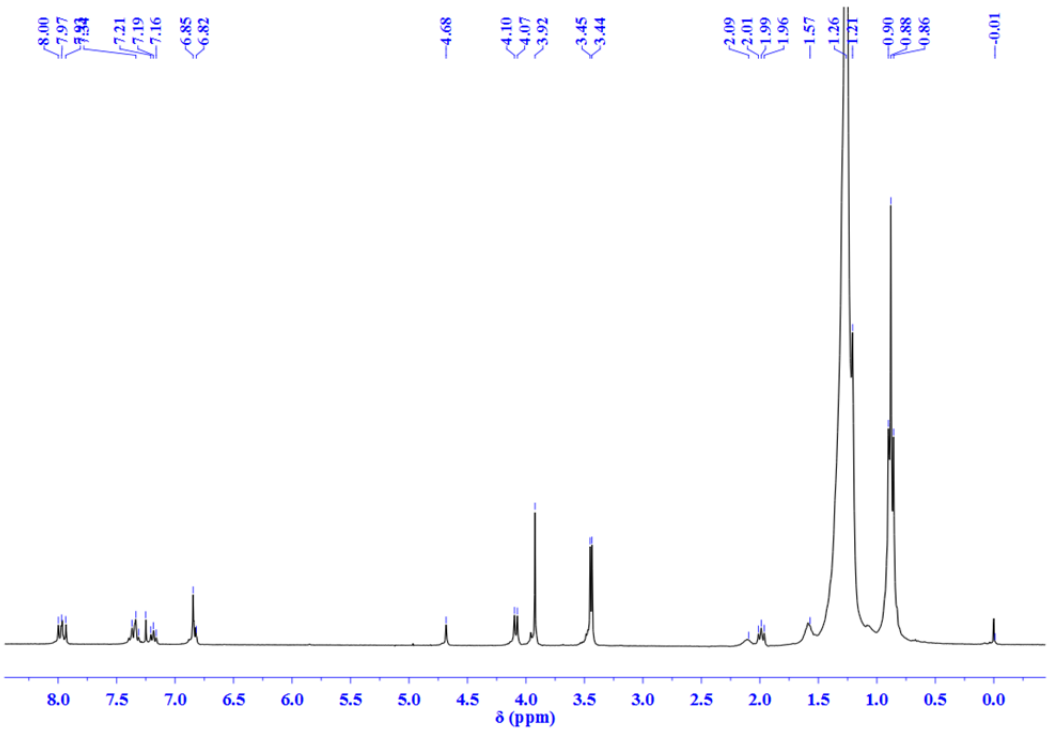


Fig. S14 ^{1}H NMR of **Lin-CZ** in $CDCl_3$.

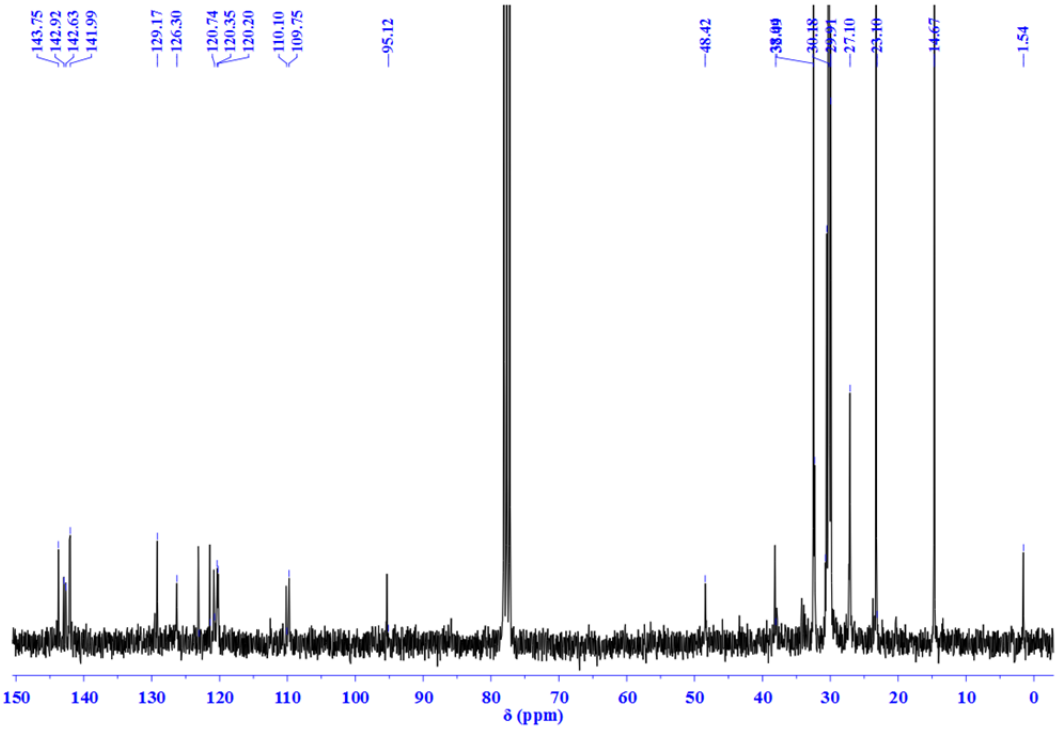


Fig. S15 ^{13}C NMR of **Lin-CZ** in $CDCl_3$.

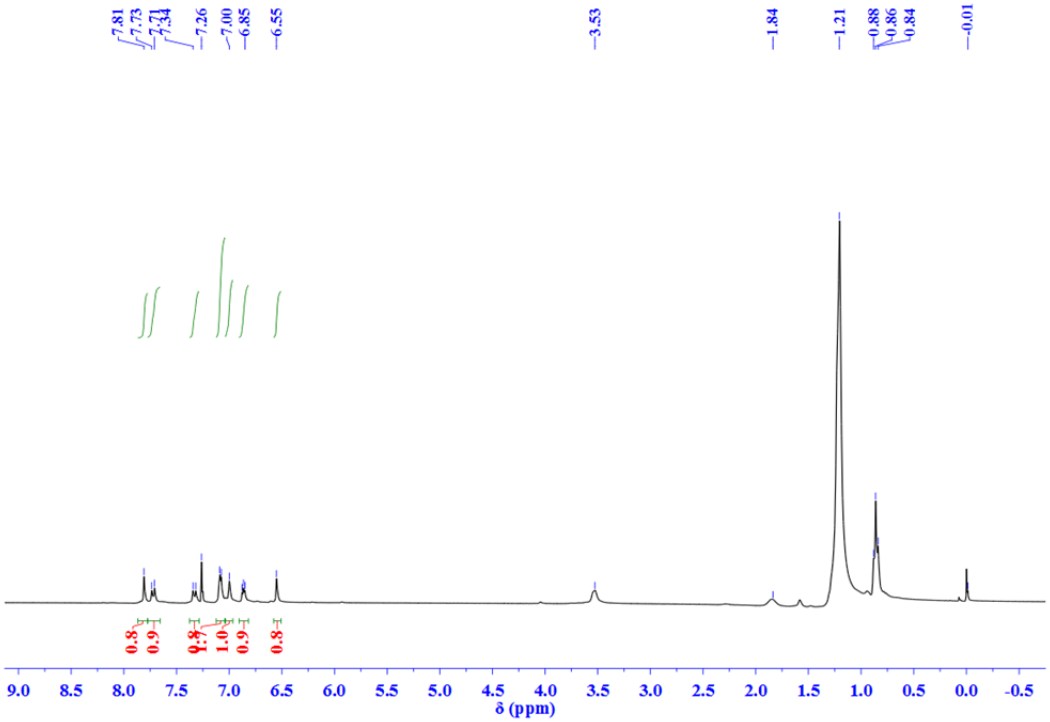


Fig. S16 ^{1}H NMR of **Lin-CZ-T** in $CDCl_3$.

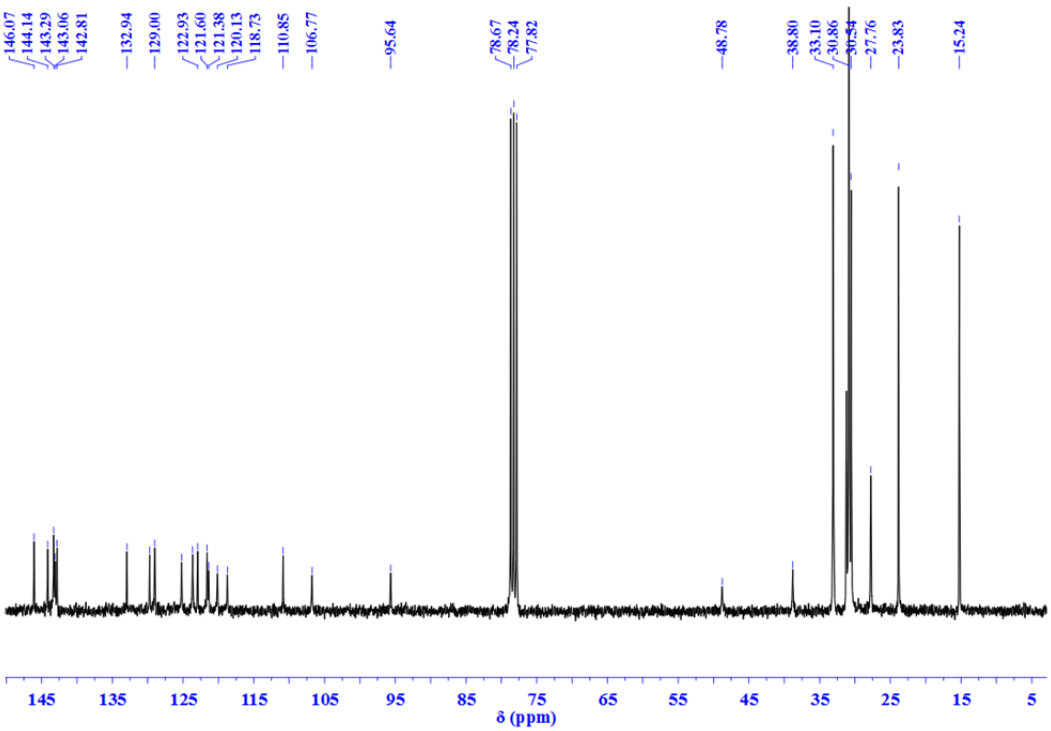


Fig. S17 ^{13}C NMR of **Lin-CZ-T** in $CDCl_3$.

11. MALDI-TOF MS spectra

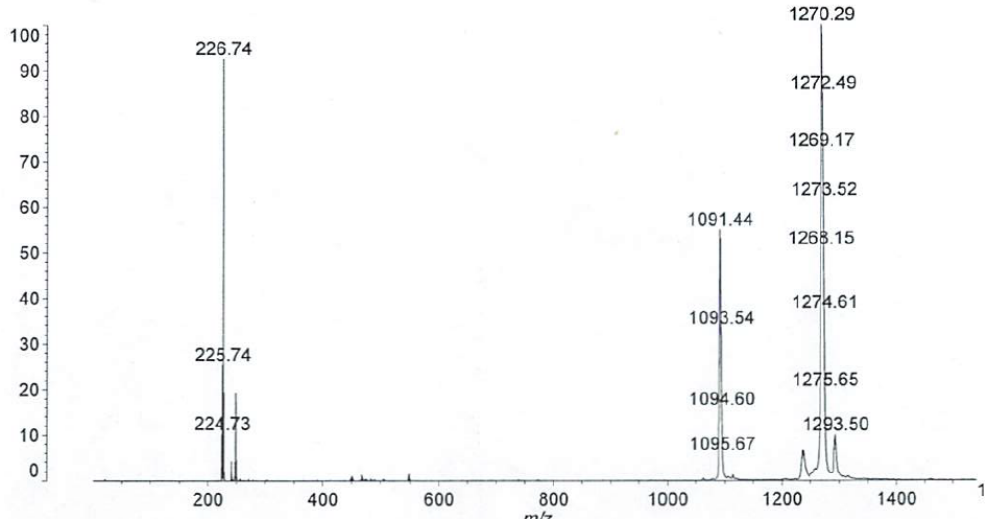


Fig. S18 MALDI-TOF MS of **5** (M_w = 1270.83): found m/z = 1270.29 [M^+], using dithranol (M_w = 226.23) as a matrix.

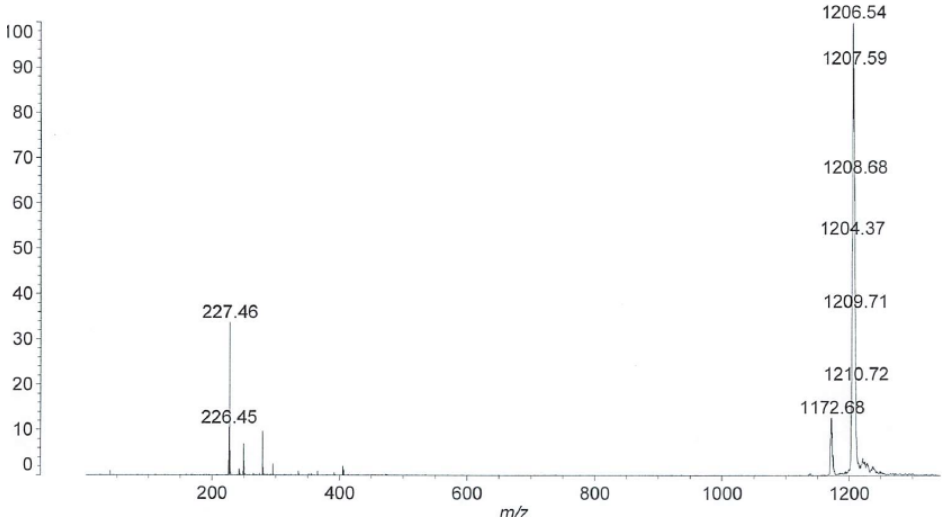


Fig. S19 MALDI-TOF MS of **Lin-CZ** (M_w = 1206.83): found m/z = 1206.54 [M^+], using dithranol (M_w = 226.23) as a matrix.

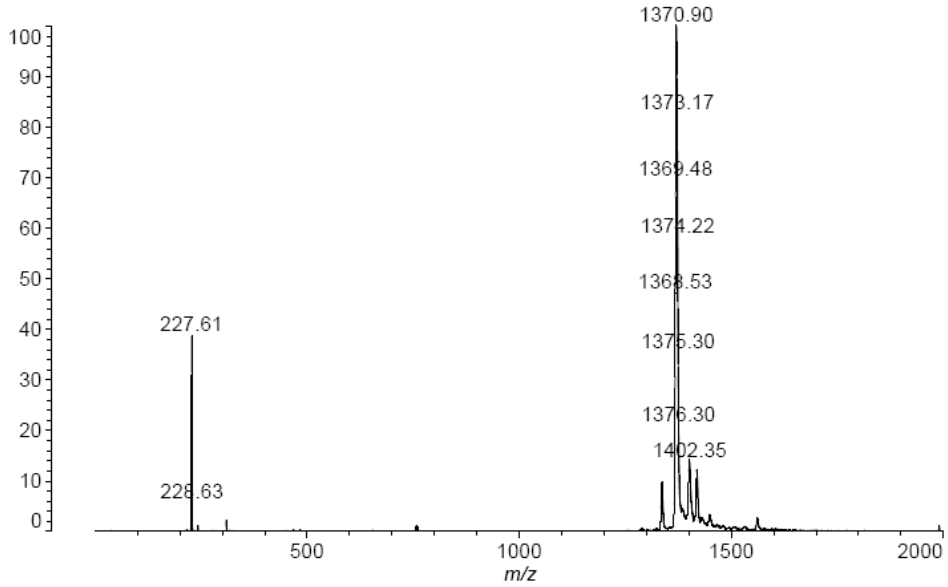


Fig. S20 MALDI-TOF MS of **Lin-CZ-T** (M_w = 1370.89): found m/z = 1370.90 [M^+], using dithranol (M_w = 226.23) as a matrix.