

Electronic supplementary information (ESI)

## Pt...Pt interaction triggered tuning of circularly polarized luminescence activity in chiral dinuclear platinum(II) complexes

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**Table S1.** Structural parameters of complexes **(-)-1**, **(+)-1** and **(-)-2-ClO<sub>4</sub>-Cl** determined by X-ray single crystal diffraction.

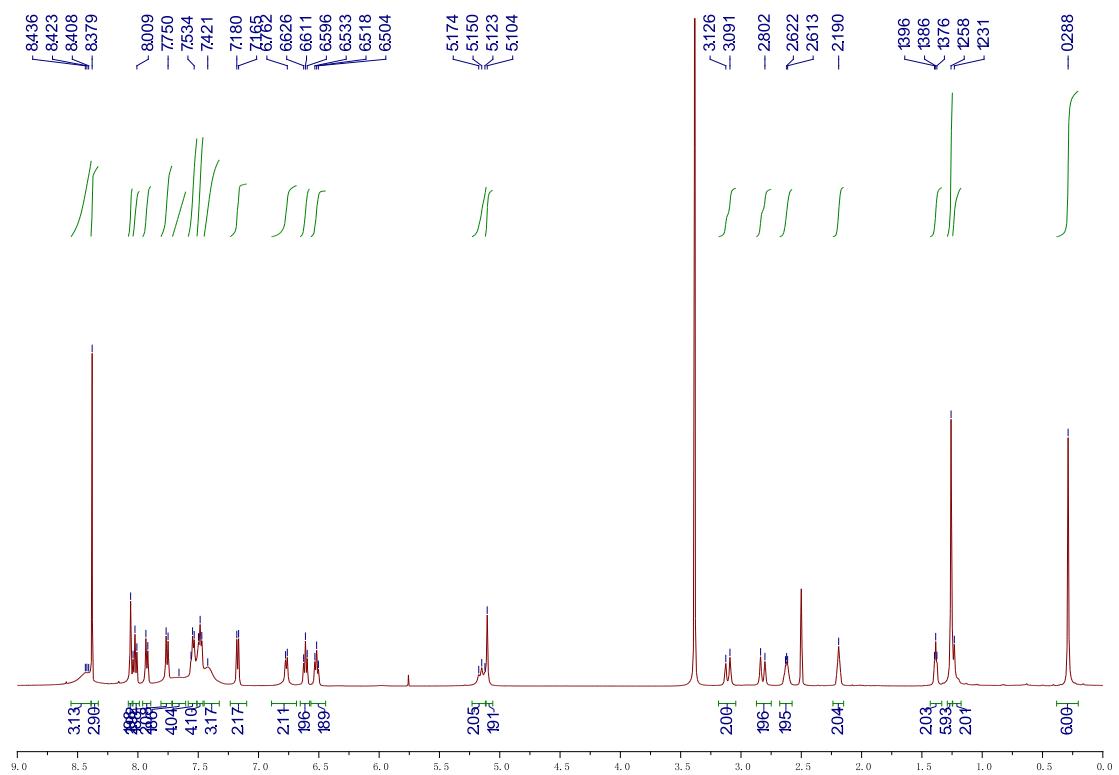
| Bond Length         | <b>(-)-1</b> | <b>(+)-1</b> | <b>(-)-2-ClO<sub>4</sub>-Cl</b> |
|---------------------|--------------|--------------|---------------------------------|
| Pt1–C1 (C1A)        | 2.023(12)    | 2.024(10)    | 2.024(10)                       |
| Pt2–C2 (C1B)        | 2.027(12)    | 2.024(11)    | 1.993(10)                       |
| Pt1–N1 (N1A)        | 2.024(9)     | 2.017(8)     | 2.020(8)                        |
| Pt1–N2 (N2A)        | 2.189(9)     | 2.190(8)     | 2.147(8)                        |
| Pt2–N3 (N1B)        | 2.027(9)     | 2.029(8)     | 2.018(8)                        |
| Pt2–N4 (N2B)        | 2.161(10)    | 2.171(8)     | 2.140(8)                        |
| Pt1–P1 (P1A)        | 2.252(3)     | 2.251(2)     | 2.250(3)                        |
| Pt2–P2 (P1B)        | 2.257(3)     | 2.259(2)     | 2.242(3)                        |
| Pt3–C1C             |              |              | 2.028(10)                       |
| Pt4–C1D             |              |              | 2.022(10)                       |
| Pt3–P1C             |              |              | 2.241(3)                        |
| Pt4–P1D             |              |              | 2.238(3)                        |
| Pt3–N1C             |              |              | 2.008(9)                        |
| Pt3–N2C             |              |              | 2.143(8)                        |
| Pt4–N1D             |              |              | 2.013(9)                        |
| Pt4–N2D             |              |              | 2.138(9)                        |
| Bond Angles         | <b>(-)-1</b> | <b>(+)-1</b> | <b>(-)-2-ClO<sub>4</sub>-Cl</b> |
| C1(C1A)–Pt1–N1(N1A) | 80.4(4)      | 80.6(4)      | 82.2(4)                         |
| C1(C1A)–Pt1–N2(N2A) | 157.8(4)     | 157.6(4)     | 158.9(4)                        |
| N1(N1A)–Pt1–N2(N2A) | 77.5(4)      | 76.9(3)      | 76.9(3)                         |
| C1(C1A)–Pt1–P1(P1A) | 96.0(3)      | 95.8(3)      | 95.3(3)                         |
| N1(N1A)–Pt1–P1(P1A) | 175.1(3)     | 174.8(3)     | 176.2(2)                        |
| N2(N2A)–Pt1–P1(P1A) | 106.1(2)     | 106.5(2)     | 105.7(2)                        |
| N3(N1B)–Pt2–C2(C1B) | 80.9(5)      | 81.0(4)      | 81.6(4)                         |
| N3(N1B)–Pt2–N4(N2B) | 76.9(4)      | 77.1(4)      | 77.8(4)                         |
| C2(C1B)–Pt2–N4(N2B) | 157.6(4)     | 157.9(4)     | 159.0(4)                        |
| N3(N1B)–Pt2–P2(P1B) | 175.5(3)     | 175.3(3)     | 172.2(2)                        |
| C2(C1B)–Pt2–P2(P1B) | 95.4(4)      | 95.3(3)      | 95.8(3)                         |
| N4(N2B)–Pt2–P2(P1B) | 106.5(3)     | 106.4(2)     | 105.1(3)                        |
| C1C–Pt3–N1C         |              |              | 81.9(4)                         |
| C1C–Pt3–N2C         |              |              | 159.6(4)                        |
| N1C–Pt3–N2C         |              |              | 77.9(3)                         |
| C1C–Pt3–P1C         |              |              | 96.6(3)                         |
| N1C–Pt3–P1C         |              |              | 173.2(2)                        |

|             |          |
|-------------|----------|
| N2C-Pt3-P1C | 103.9(2) |
| C1D-Pt4-N1D | 81.7(4)  |
| C1D-Pt4-N2D | 159.6(4) |
| N1D-Pt4-N2D | 78.1(4)  |
| C1D-Pt4-P1D | 96.5(3)  |
| N1D-Pt4-P1D | 171.8(2) |
| N2D-Pt4-P1D | 103.9(3) |

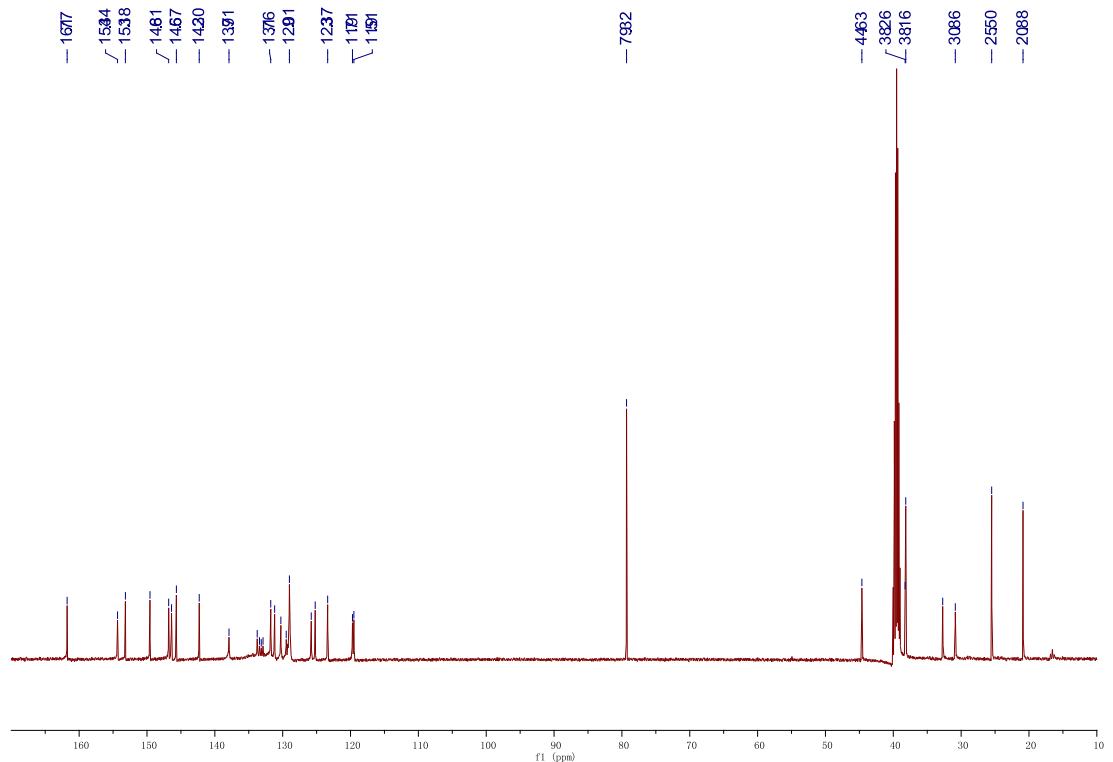
**Table S2.** Spectroscopic and photophysical data for (-)-**1** and (-)-**2** ( $5 \times 10^{-5}$  mol·L<sup>-1</sup>).

| Complex       | UV-vis <sup>a</sup><br>$\lambda_{\text{max}}$ , nm<br>( $\varepsilon$ , 10 <sup>4</sup> L·mol <sup>-1</sup> ·cm <sup>-1</sup> ) | Emission <sup>a</sup>                                     |          | Emission <sup>b</sup><br>$\lambda_{\text{max}}$ , nm at 77 K |
|---------------|---|---|----------|--|
|               |   | $\lambda_{\text{max}}$ , nm ( $\tau/\text{ns}$ , $\Phi$ ) | at 298 K |  |
| (-)- <b>1</b> | 256 (46600), 345 (16000), 423 (3300), 479 (1800), 510 (1000)  | 547, 638 (248, 0.11)                                      |          | 620  |
| (-)- <b>2</b> | 255 (60700), 273 (50800), 339 (23900), 354 (23500), 420 (1800), 475 (220), 500 (70)   | 530 (814, 0.15), 563                                      |          | 519, 559   |

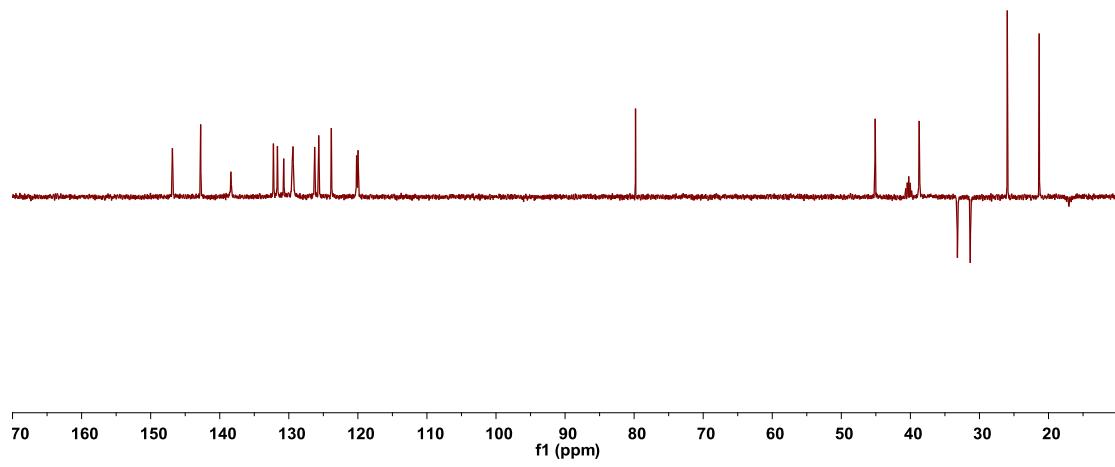
<sup>a</sup> Measured in CH<sub>2</sub>Cl<sub>2</sub> solution. <sup>b</sup> Measured in MeOH/EtOH (1/4, v/v) glassy solution.



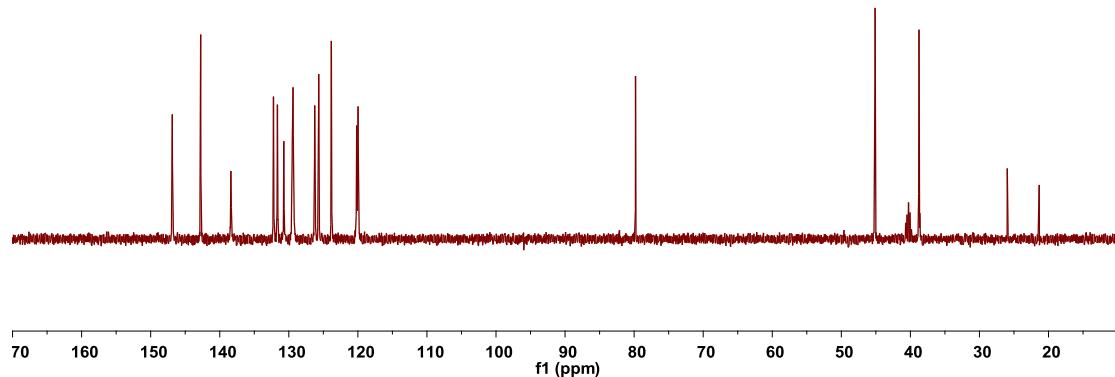
**Fig. S1** The  $^1\text{H}$  NMR spectrum of ( $-$ )-1.



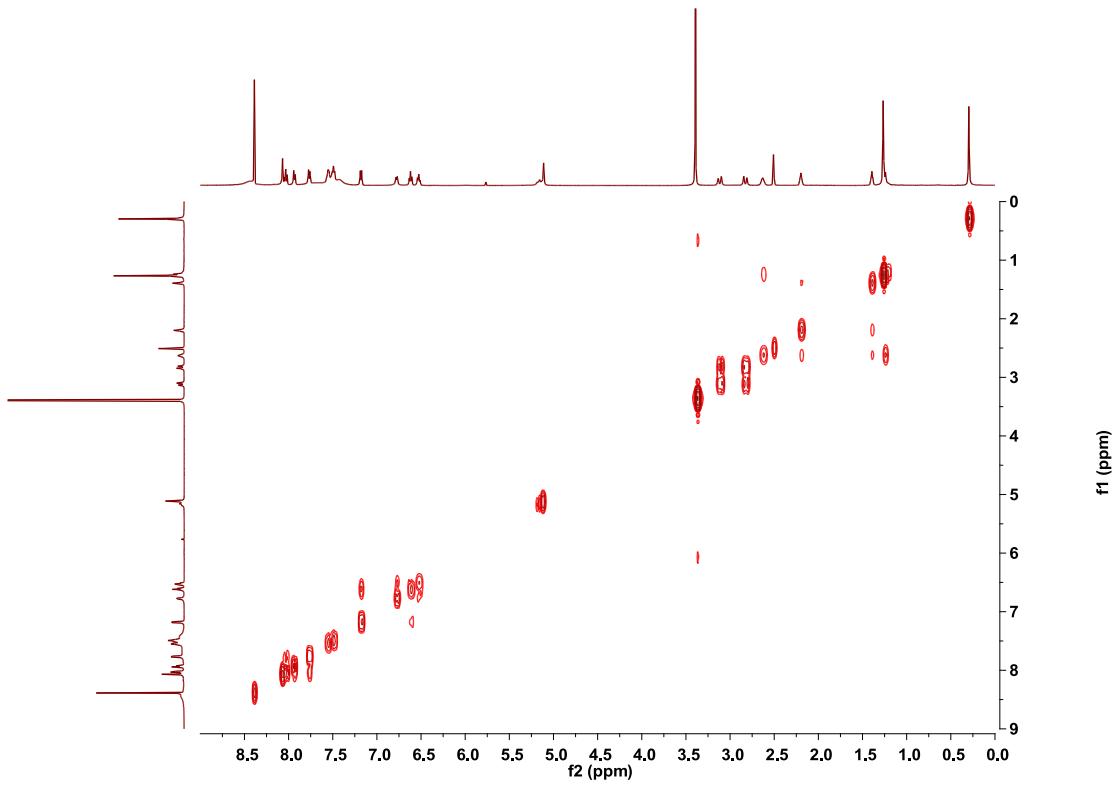
**Fig. S2** The  $^{13}\text{C}$  NMR spectrum of ( $-$ )-1.



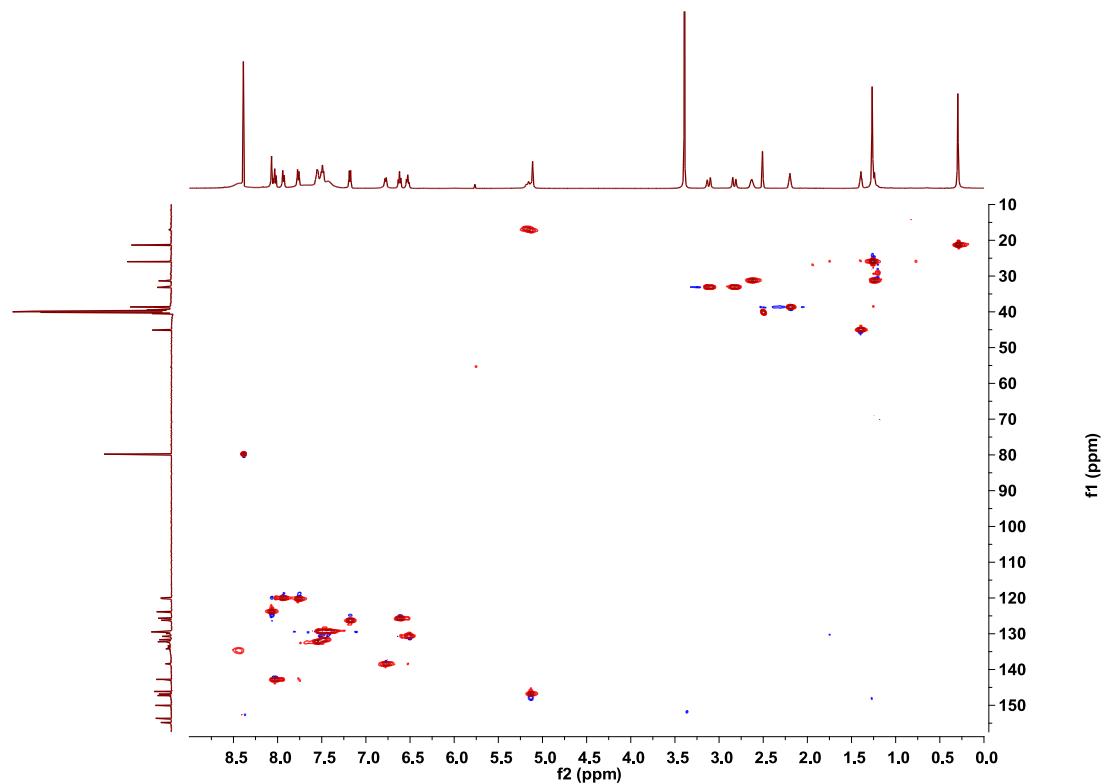
**Fig. S3** The  $^{13}\text{C}$ /DEPT 135 $^{\circ}$  NMR spectrum of (-)-1.



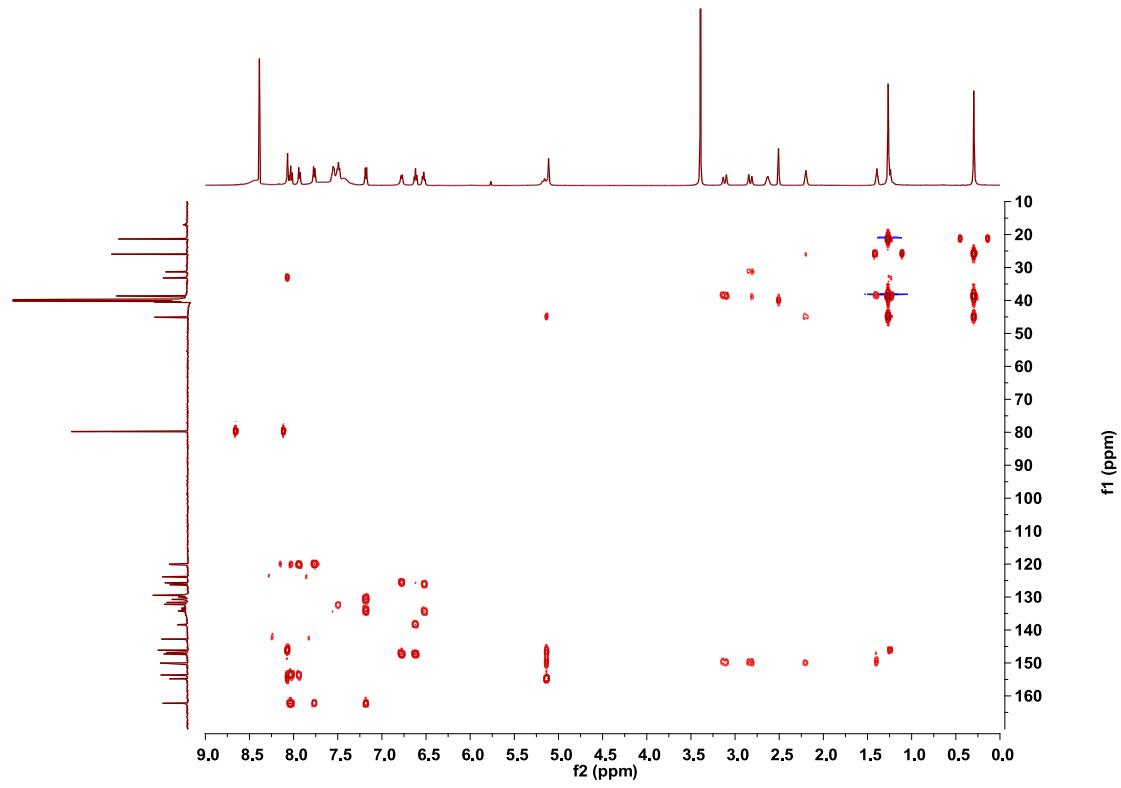
**Fig. S4** The  $^{13}\text{C}$ /DEPT 90 $^{\circ}$  NMR spectrum of (-)-1.



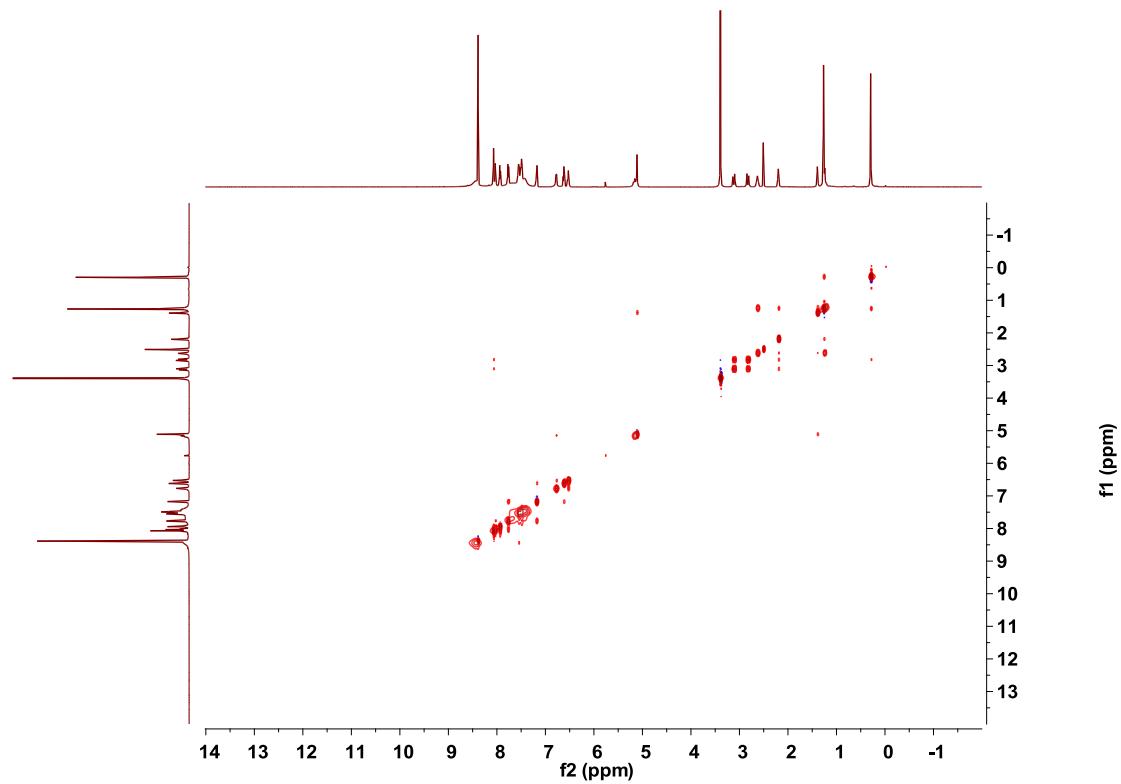
**Fig. S5** The  $^1\text{H}$  -  $^1\text{H}$  COSY NMR spectrum of ( $-$ )-1.



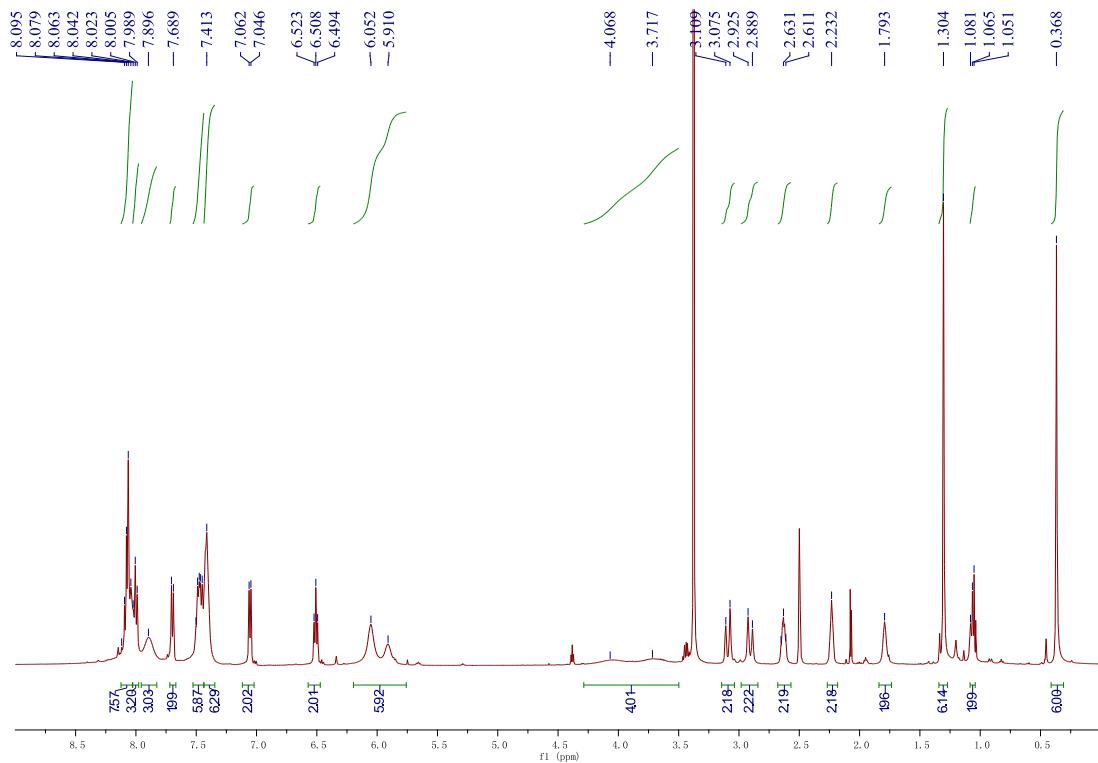
**Fig. S6** The HSQC NMR spectrum of ( $-$ )-1.



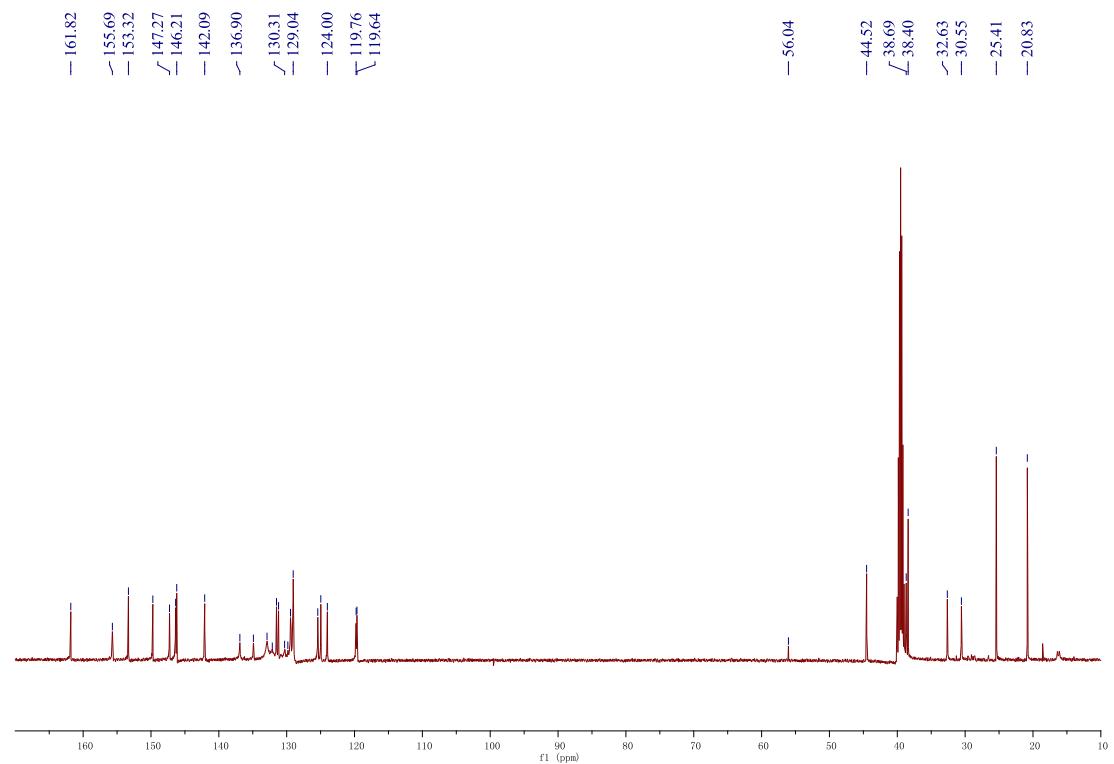
**Fig. S7** The HMBC NMR spectrum of ( $-$ )-1.



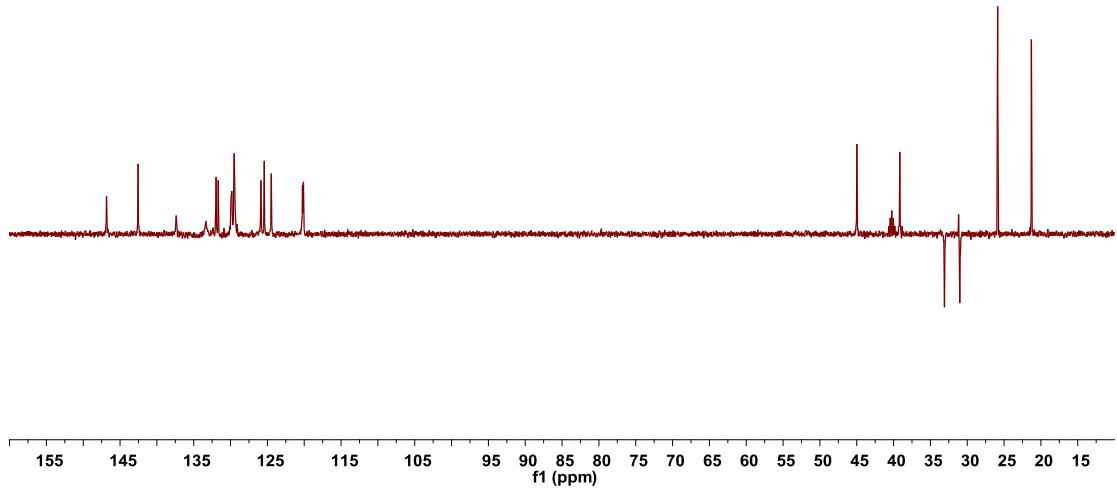
**Fig. S8** The  $^1\text{H}$  -  $^1\text{H}$  NOESY NMR spectrum of ( $-$ )-1.



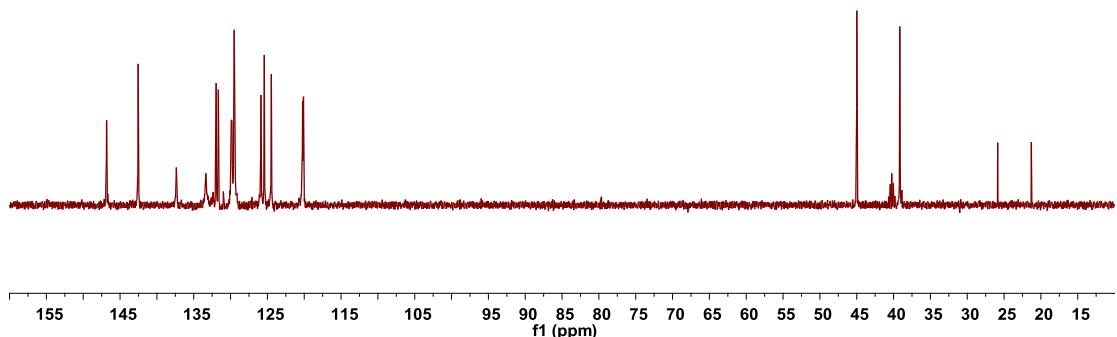
**Fig. S9** The  $^1\text{H}$  NMR spectrum of ( $-$ )-2.



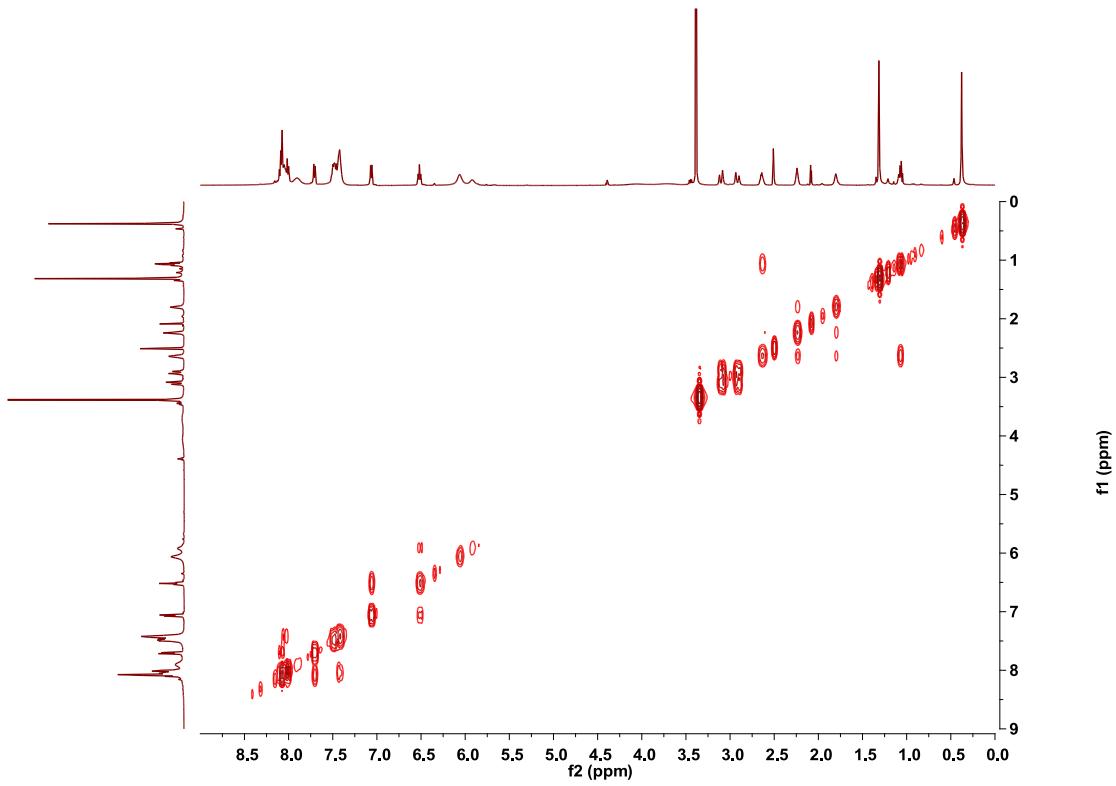
**Fig. S10** The  $^{13}\text{C}$  NMR spectrum of ( $-$ )-2.



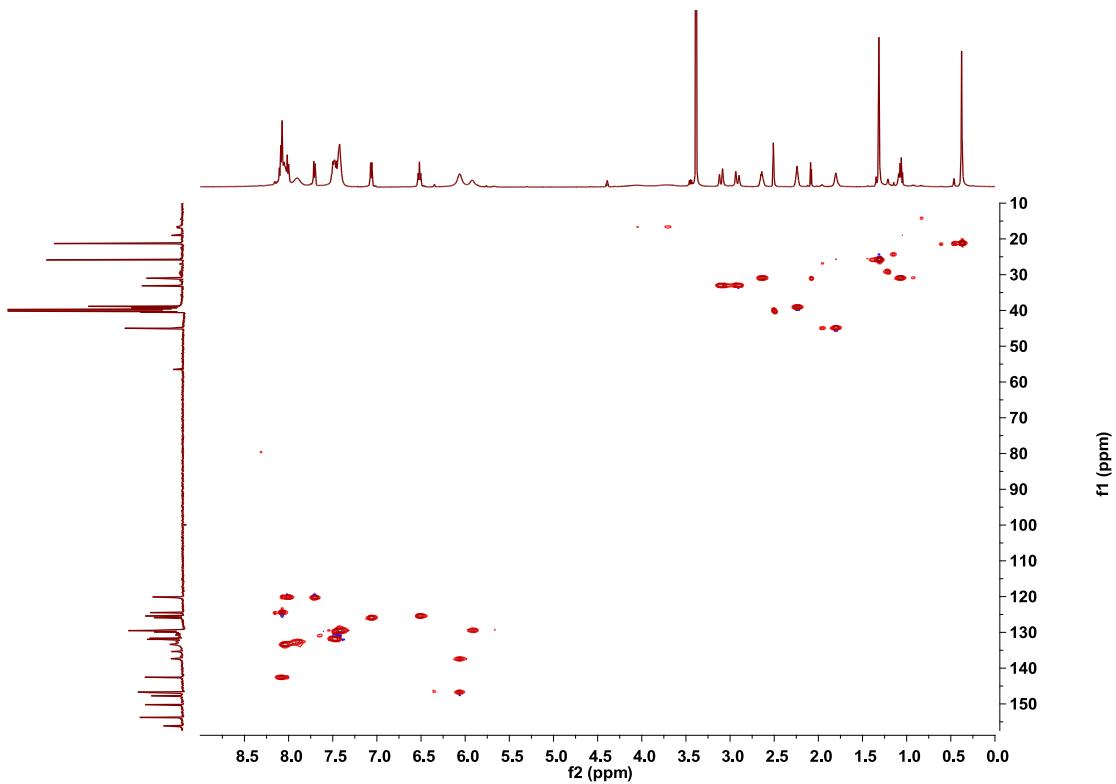
**Fig. S11** The  $^{13}\text{C}$ /DEPT 135 $^{\circ}$  NMR spectrum of (-)-2.



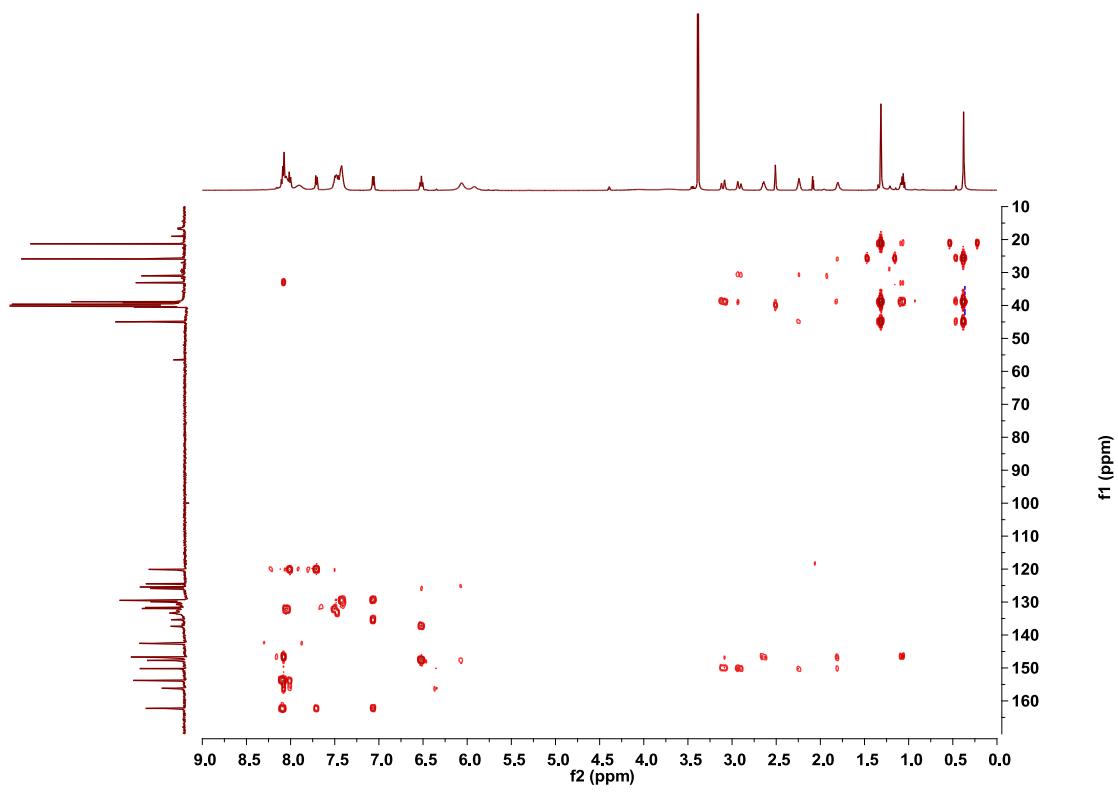
**Fig. S12** The  $^{13}\text{C}$ /DEPT 90 $^{\circ}$  NMR spectrum of (-)-2.



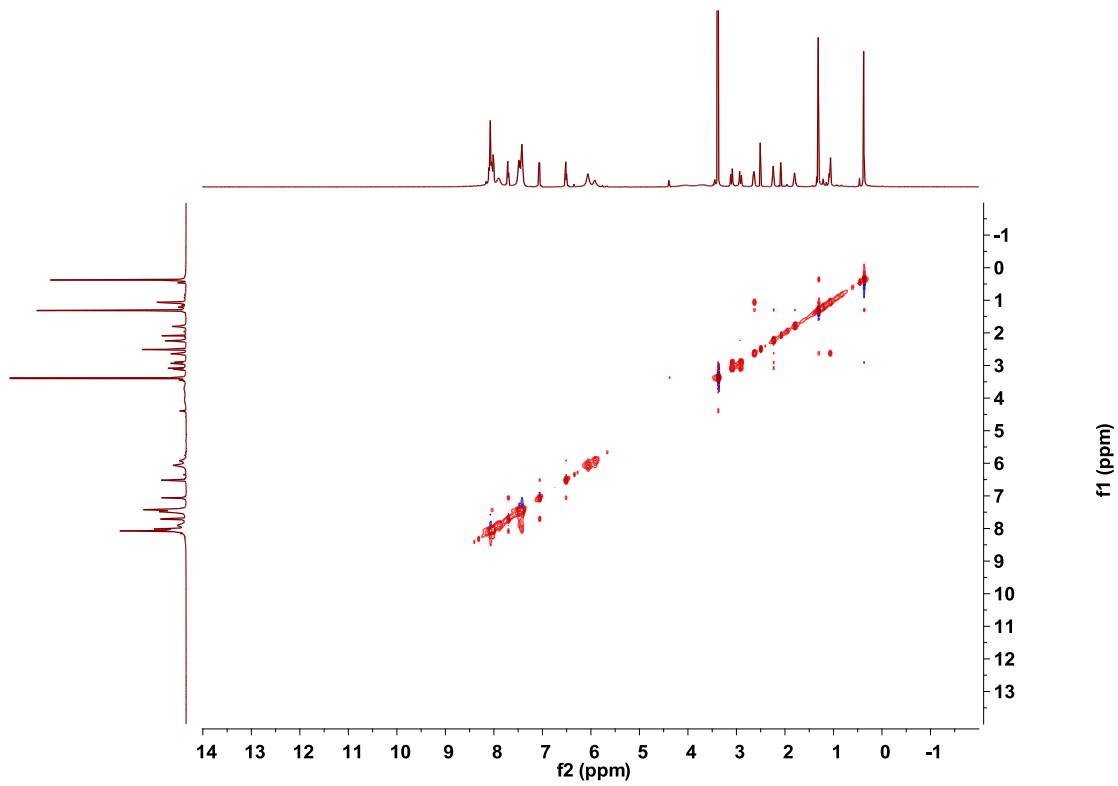
**Fig. S13** The  $^1\text{H}$  –  $^1\text{H}$  COSY NMR spectrum of ( $-$ )-2.



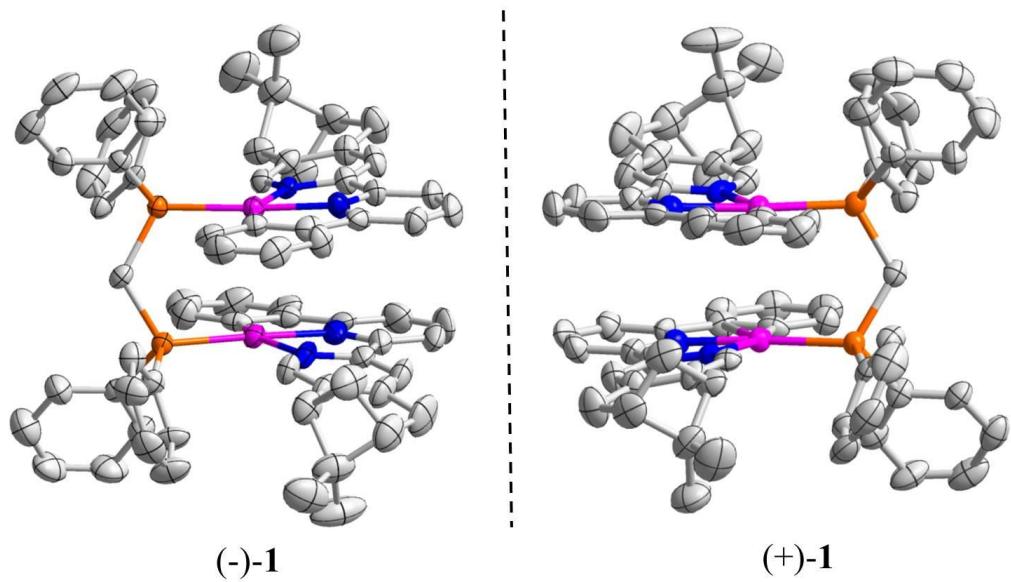
**Fig. S14** The HSQC NMR spectrum of ( $-$ )-2.



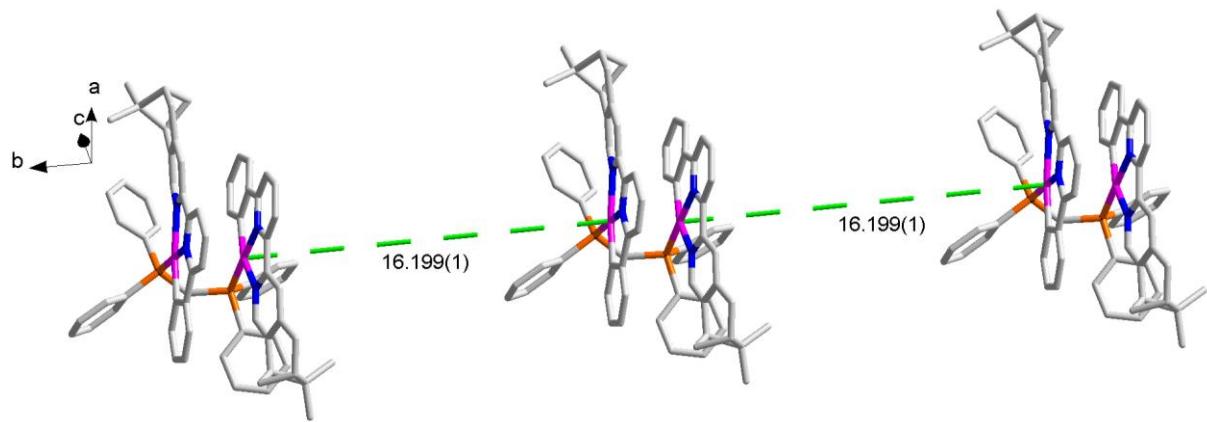
**Fig. S15** The HMBC NMR spectrum of (*-*)-2.



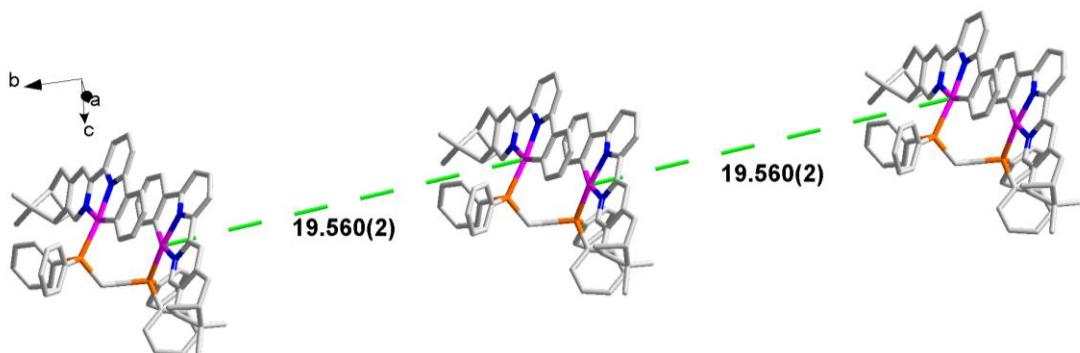
**Fig. S16** The  $^1\text{H}$  –  $^1\text{H}$  NOESY NMR spectrum of (*-*)-2.



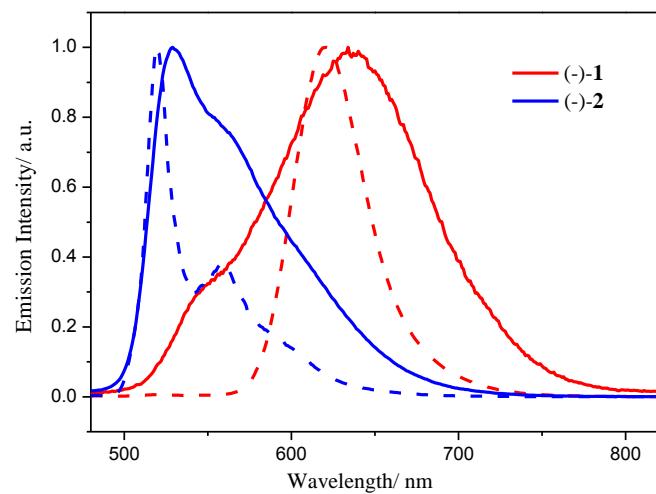
**Fig. S17** X-ray crystal structures of ( $-$ )-**1** and ( $+$ )-**1**. H atoms, solvent molecules as well as anions are omitted for clarity.



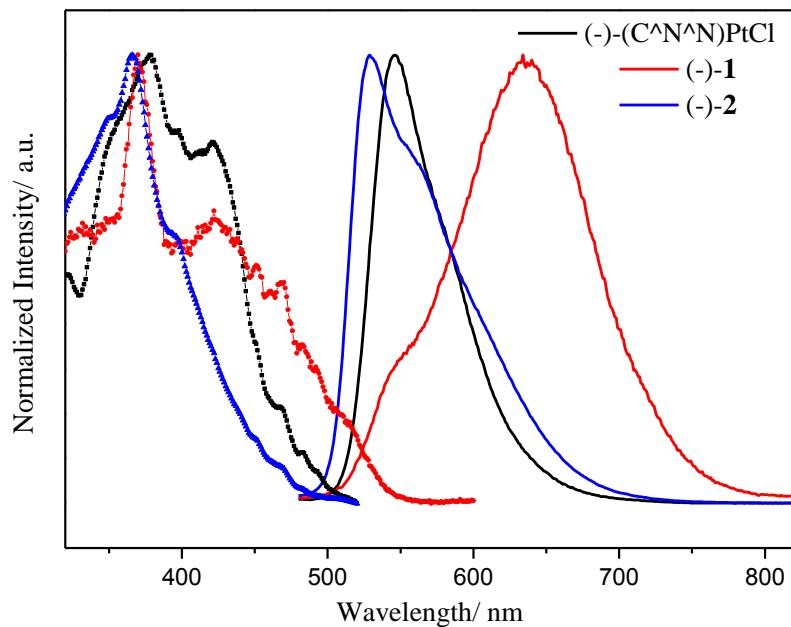
**Fig. S18** Intermolecular Pt···Pt separation between the nearest discrete  $[(-)-(C^N N^N)Pt]_2 dppm^{2+}$  units of **(-)-1**.



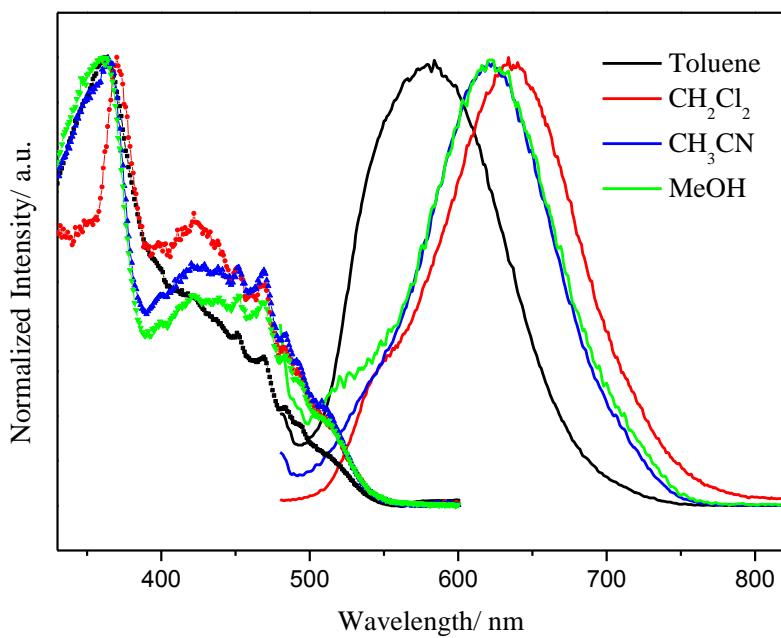
**Fig. S19** Intermolecular Pt...Pt separation between the nearest discrete  $[(-)(C^N^N)Pt]_2dppe^{2+}$  units of  $(-)\text{-2-ClO}_4\text{-Cl}$ .



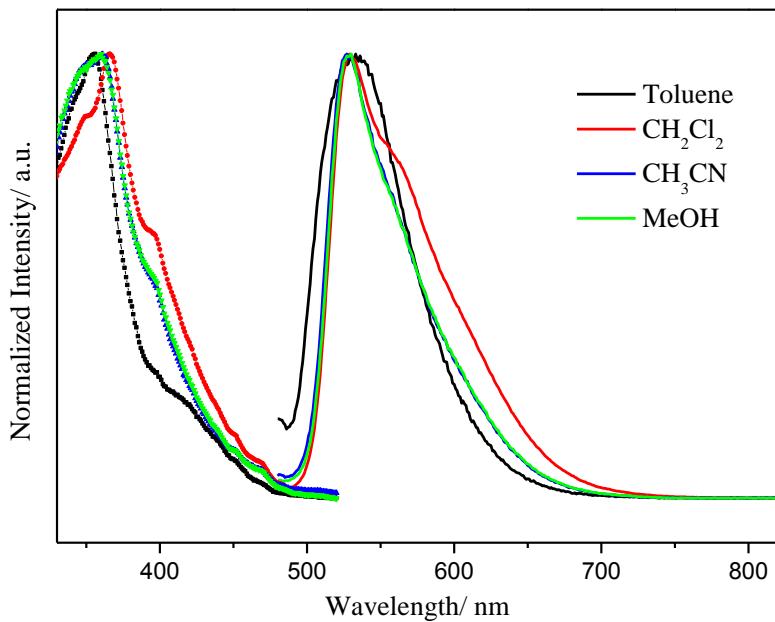
**Fig. S20** Emission spectra of **(-)-1** and **(-)-2** at 298 (solid line) and 77 K (dash line) ( $\lambda_{\text{ex}} = 420 \text{ nm}$ )



**Fig. S21** Normalized emission (line,  $\lambda_{\text{ex}} = 420 \text{ nm}$ ) and excitation (symbol + line, monitored at emission maximum) of **(-)-(C<sup>N</sup><sup>N</sup>)PtCl**, **(-)-1** and **(-)-2** in dichloromethane.



**Fig. S22** Normalized emission (line,  $\lambda_{\text{ex}} = 420 \text{ nm}$ ) and excitation (symbol + line, monitored at emission maximum) of  $(-)\text{-1}$  in different solvents.



**Fig. S23** Normalized emission (line,  $\lambda_{\text{ex}} = 420 \text{ nm}$ ) and excitation (symbol + line, monitored at emission maximum) of  $(-)\text{-2}$  in different solvents.