Electronic Supplementary Information

An insight into of transition metal ions by picolinamides associated with intramolecular hydrogen bonding and rotational isomerization

Yan Li,[a] Yiming Jia,[a] Zhenwen Wang,[a] Xianghui Li,[a] Wen Feng,[a] Pengchi Deng,*[b]

Lihua Yuan*[a]

[a] *College of Chemistry, Key Laboratory for Radiation Physics and Technology of Ministry of Education, Institute of Nuclear Science and Technology, Sichuan University, Chengdu 610064, China.* lhyuan@scu.edu.cn

[b] *Analytical & Testing Center, Sichuan University, Chengdu 610064, China.* pcdeng@yahoo.com

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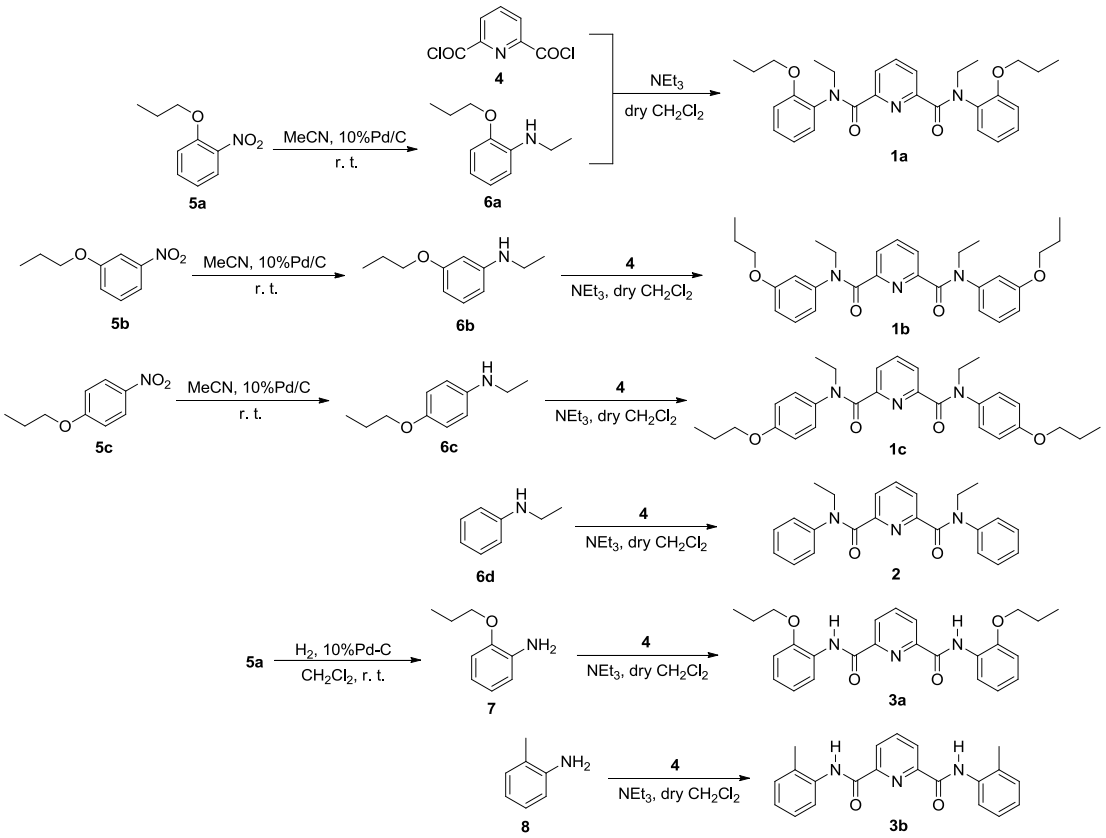
1. General Information

The ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AVANCE AV Ⅱ- 400 MHz (^{1}H: 400 MHz; ^{13}C: 100 MHz). Chemical shifts are reported in δ values in ppm and coupling constants (J) are denoted in Hz. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, and m = multiplet. High resolution mass spectrometric (HRMS) data were collected by WATERS Q-TOF Premier. $CDCl_3$, DMSO-d_6 and CD_3CN were from Cambridge Isotope Laboratories (CIL).

Crystallographic studies were performed on compounds **1a** and **3a**. The X-ray quality crystals of ligands **1a** and **3a** were obtained by slow evaporation of a solution of CH_2Cl_2/n-hexane and ethyl acetate/n-hexane at room temperature, respectively. Molecular diagrams are shown in Fig. S22 and Fig. S23. Crystal data and refinementdetails are presented in Table S1 and S2. Crystals were mounted in inert oil and transferred to the cold gas stream of the diffractometer. Data were collected on a Xcalibur E diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.7107 Å).

2. Synthesis and Characterization of Compounds **1-3**



Scheme 1. Synthesis of pyridine-based 2,6-dicarboxyamides **1a**-**1c**, **2**,[1] **3a** and **3b**. Compound **4**, **5a**-**5c** and **6d** were synthesized following the same procedures of literatures.[2-4]

Compound 6a. **6a** was synthesized following the reported procedure.[5] After two vacuum/H_2 cycles to remove air from the reaction, the stirred mixture of the nitropropoxybenzene **5a** (1.00 g, 5.52 mmol), 100 mg 10% Pd/C and 50 mL acetonitrile was hydrogenated at ordinary pressure and at room temperature for 48 h. The reaction mixture was filtrated and the filtrate was concentrated under reduced pressure. The crude mixture was purified by flash silica gel column chromatography (petroleum ether/ethyl acetate=5:1, v/v). The product was provided as light yellow oil (780 mg, yield 79 %), which was used for the immediate coupling reaction.

Compound 6b. **6b** was synthesized following the route used for **6a** using **5b** (1.00 g, 5.52 mmol). The light yellow oil was isolated in 81 % yield (800 mg).

Compound 6c. **6c** was synthesized by the same route as **6a** using **5c** (1.00 g, 5.52 mmol). The light yellow oil was isolated in 73 % yield (720 mg).

Compound 7. 1-Nitro-2-propoxybenzene **5a** (4.0 g, 22.08 mmol) was dissolved in dichloromethane (150 mL). A catalytic amount of Pd/C (10% ~ 15%) was added to the solution, and hydrogenation was carried out at room temperature under 0.3 MPa for 24 hours. The solution was filtered in darkness as fast as possible followed immediately removal of the solvent to give the amine as yellow oil **7**, which was used for the immediate coupling reaction.

Compound 1a. Triethylamine (660 mg, 6.54 mmol) was added to a solution of the above amine **6a** (780 mg, 4.36 mmol) in 100 mL of dry dichloromethane at 0 ℃ under N_2. Pyridine-2,6-dicarbonyl dichloride **4** (364 mg, 2.18 mmol) was dissolved in 50 mL of dichloromethane and added dropwise to the above mixture. The solution was stirred at room temperature under N_2 for 4 h. The organic layer was washed with 10 % HCl aqueous and water, respectively, and dried over anhydrous Na_2SO_4 and evaporated to afford the crude product. The crude product was dissolved in hot ethyl acetate and cooled to room temperature and then refrigerated overnight, affording a white crystalline compound that was collected by filtration (875 mg, 82 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35-6.68 (m, 11H, ArH), 4.10-3.95 (m, 2H, OCH_2), 3.88-3.70 (m, 4H, NCH_2), 3.66-3.54 (m, 2H, OCH_2), 1.83-1.68 (m, 4H, CH_2), 1.16-1.12 (m, 6H, CH_3), 1.04-0.96 (m, 6H, CH_3). ^{13}C NMR(100 MHz, $CDCl_3$) δ: 168.14, 167.78, 154.26, 154.22, 153.25, 152.67, 135.42, 135.28, 131.24, 131.09, 130.95, 130.41, 128.49, 128.44, 122.84, 122.37, 120.06, 119.98, 112.01, 111.76, 69.57, 69.50, 43.88, 43.58, 22.59, 12.58, 12.50, 10.71, 10.65. ESI-HRMS (m/z) calcd. for $C_{29}H_{35}N_3O_4$ $[M+H]^+$ 490.2706, $[M+Na]^+$ 512.2525, $[M+K]^+$ 528.2265; found $[M+H]^+$ 490.2701, $[M+Na]^+$ 512.2532, $[M+K]^+$ 528.2272.

Compound 1b. **1b** was synthesized by the same route as **1a** using triethylamine (679 mg, 6.72 mmol), **6b** (800 mg, 4.47 mmol) and **4** (373 mg, 2.24 mmol). The crude mixture was purified by flash silica gel column chromatography (petroleum ether/ethyl acetate=5:1, v/v) to give colourless oil which was dried under vacuum to afford a white solid (985 mg, 92 % yield). ^{1}H NMR (400 MHz, CD_3COCD_3) δ: 7.62

(br s, 1H, PyH), 7.32 (br s, 2H, PyH), 7.10 (s, 2H, ArH), 6.78 (s, 2H, ArH), 6.76 (d, J=8.4 Hz, 2H, ArH), 6.41 (br s, 2H, ArH), 3.90 (t, J=6.4 Hz, 4H, OCH_2), 3.85 (br s, 4H, NCH_2), 1.74 (m, J=6.8 Hz, 4H, CH_2), 1.13 (br s, 6H, NCH_2CH_3), 1.00 (t, J=7.4 Hz, 6H, CH_3) ^{13}C NMR(100 MHz, $CDCl_3$) δ: 167.25, 159.56, 153.11, 143.57, 136.12, 129.36, 123.53, 120.50, 114.00, 112.94, 69.60, 45.02, 22.50, 12.80, 10.50. ESI-HRMS (m/z) calcd. for $C_{29}H_{35}N_3O_4$ $[M+H]^+$ 490.2706, $[M+Na]^+$ 512.2525, $[M+K]^+$ 528.2265; found $[M+H]^+$ 490.2699, $[M+Na]^+$ 512.2533, $[M+K]^+$ 528.2267.

Compound 1c. **1c** was synthesized following the route used for **1a** using triethylamine (609 mg, 6.03 mmol), **6c** (720 mg, 4.02 mmol) and **4** (335 mg, 2.01 mmol). The compound was purified by crystallization with petroleum ether/ethyl acetate, to yield **1c** as a white solid (940 mg, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32 (t, J=8.0 Hz, 1H, PyH), 7.06 (d, J=8.0 Hz, 2H, PyH), 6.79(d, J=8.8 Hz, 4H, ArH), 6.69 (d, J=8.4 Hz, 4H, ArH), 3.87 (q, J=7.2 Hz, 4H, NCH_2), 3.83 (t, J=6.4 Hz, 4H, OCH_2), 1.76 (m, J=6.8 Hz, 4H, CH_2), 1.17 (t, J=7.0 Hz, 6H, NCH_2CH_3), 1.00 (t, J=7.4Hz, 6H, CH_3). ^{13}C NMR(100 MHz, $CDCl_3$) δ: 167.35, 157.61, 153.46, 135.67, 134.74, 129.18, 122.99, 114.30, 69.43, 44.77, 22.38, 12.47, 10.35. ESI-HRMS (m/z) calcd. for $C_{29}H_{35}N_3O_4$ $[M+H]^+$ 490.2706, $[M+Na]^+$ 512.2525, $[M+K]^+$ 528.2265; found $[M+H]^+$ 490.2699, $[M+Na]^+$ 512.2528, $[M+K]^+$ 528.2269.

Compound 2. The synthetic route of **2** was the same as that of **1a** by using triethylamine (838 mg，8.28 mmol) , **6d** (669 mg, 5.52 mmol) and **4** (563 mg, 2.76 mmol). The crude mixture was isolated by recrystallization with ethyl acetate to give white solid **2** (855 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36 (br s, 2H), 7.18 (br s, 8H), 6.87 (br s, 3H), 3.92 (br s, 4H), 1.82 (br, s, 6H). ^{13}C NMR(100 MHz, $CDCl_3$) δ: 167.28, 153.09, 142.55, 136.04, 128.86, 127.99, 126.80, 123.66, 45.06, 12.77. ESI-HRMS (m/z) calcd. for $C_{23}H_{23}N_3O_2$ $[M+H]^+$ 374.1869, $[M+Na]^+$ 396.1688, $[M+K]^+$ 412.1427; found $[M+H]^+$ 374.1872, $[M+Na]^+$ 396.1690, $[M+K]^+$ 412.1436.

Compound 3a. 3a was synthesized by a similar procedure to that used for **1a** using triethylamine (3.35 g, 33.12 mmol), **7** (3.32 g, 22.0 mmol) and **4** (2.24 g, 11.0 mmol). The crude product was purified by crystallization with methanol/ dichloromethane to give **3a** as a white solid (3.86 g, yield 81 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.20 (s, 2H, NH), 8.45 (d, J=7.6 Hz, 2H, ArH), 8.40 (d, J=8 Hz, 2H, PyH), 8.09-8.05 (t, J=8

Hz, 1H, PyH), 7.06-7.03 (t, J=7.2 Hz, 2H, ArH), 7.00-6.96 (t, J=7.6 Hz, 2H, ArH), 6.85 (d, J=8 Hz, 2H, ArH), 3.90-3.87 (t, J=6.4 Hz, 4H, OCH_2), 1.63-1.54 (m, 4H, CH_2), 0.75-0.71(t, J=7.6 Hz, 6H, CH_3). ^{13}C NMR(100 MHz, $CDCl_3$) δ: 160.15, 148.56, 147.25, 138.43, 126.07, 124.05, 123.48, 119.94, 119.14, 109.97, 69.03, 21.20, 9.12. ESI-HRMS (m/z) calcd. for $C_{25}H_{27}N_3O_4$ $[M+H]^+$ 434.2080, $[M+Na]^+$ 456.1899, $[M+K]^+$ 472.1639; found $[M+H]^+$ 434.2082, $[M+Na]^+$ 456.1894, $[M+K]^+$ 472.1647.

Compound 3b. The synthetic route of **3b** was the same as that of **1a** by using triethylamine (418 mg, 4.14 mmol) , **8** (296 mg, 2.76 mmol) and **4** (282 mg, 1.38 mmol). The crude product was purified by crystallization with petroleum ether/ dichloromethane, to provide white solid **3b** (536 mg, 89% yield). ^1H NMR (400 MHz, $CDCl_3$) δ: 9.45 (s, 2H, NH), 8.55 (d, J=7.6 Hz, 2H, PyH), 8.20-8.16 (t, J=7.6 Hz, 1H, PyH), 8.16 (d, J=8.0 Hz, 2H, ArH), 7.34-7.30 (t, J=7.6 Hz, 2H, ArH), 7.27 (d, J=7.6 Hz, 2H, ArH), 7.18-7.14 (t, J=7.6 Hz, 2H, ArH), 2.44 (s, 6H, CH_3). ^{13}C NMR(100 MHz, $CDCl_3$) δ: 160.20, 148.14, 138.56, 129.58, 127.82, 126.00, 124.53, 121.68, 16.96. ESI-HRMS (m/z) calcd. for $C_{21}H_{19}N_3O_2$ $[M+H]^+$ 346.1556, $[M+Na]^+$ 368.1375, $[M+K]^+$ 384.1114; found $[M+H]^+$ 346.1554, $[M+Na]^+$ 368.1375, $[M+K]^+$ 384.1110.

3. NMR and ESI-HRMS Spectra of Compounds **1-3**

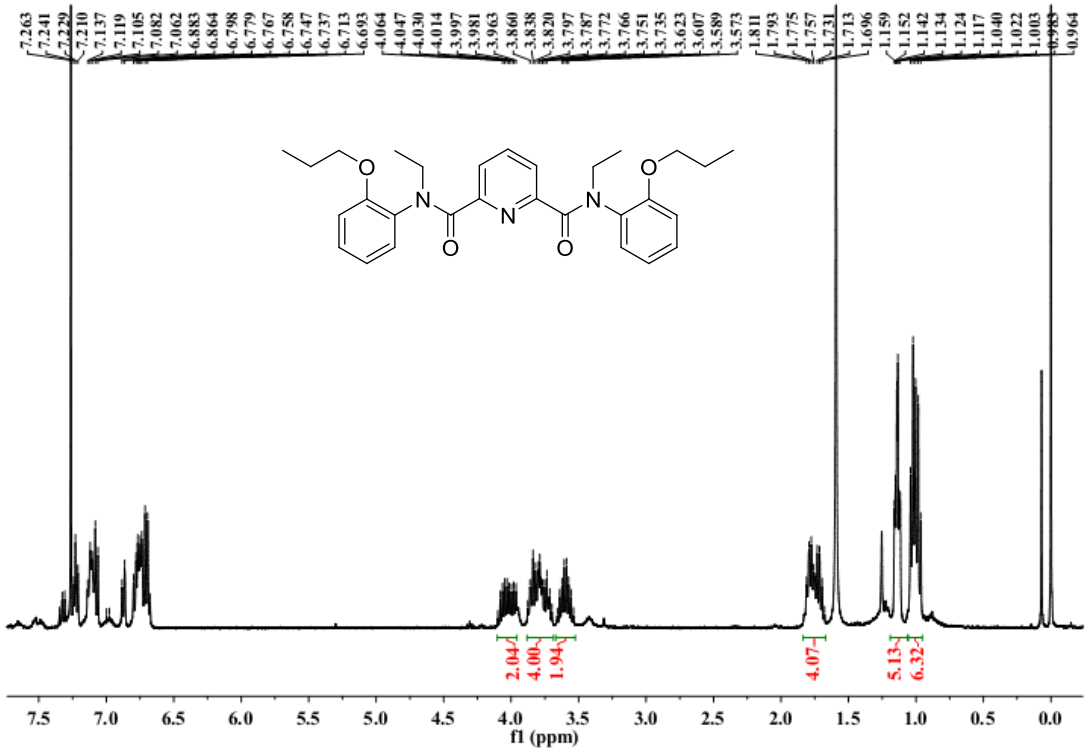


Fig. S1 ^{1}H NMR spectrum of **1a** ($CDCl_3$, 400 MHz, 298 K)

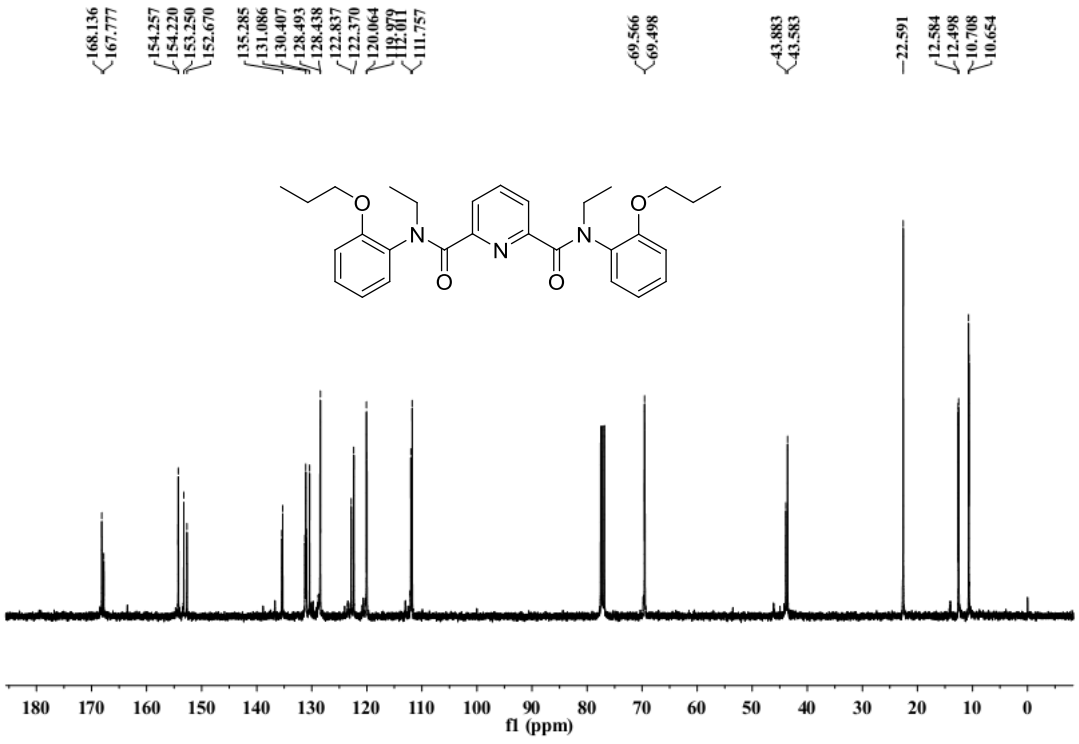


Fig. S2 ^{13}C NMR spectrum of **1a** ($CDCl_3$, 100 MHz, 298 K)

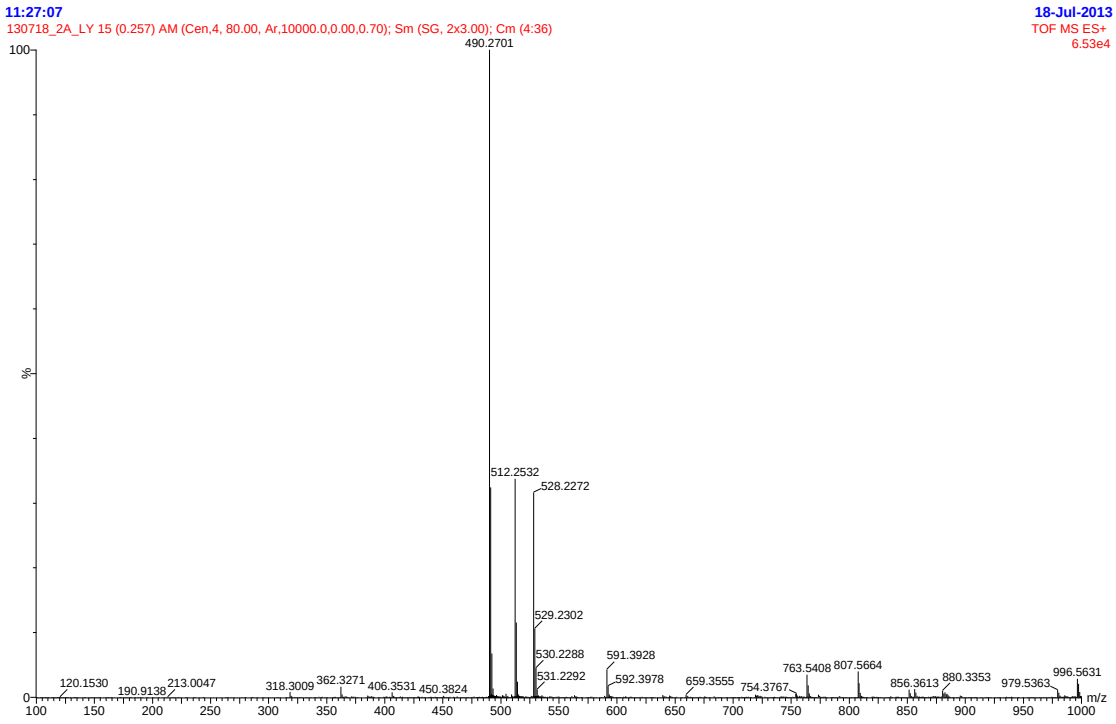


Fig. S3 ESI-HRMS spectrum of **1a.**

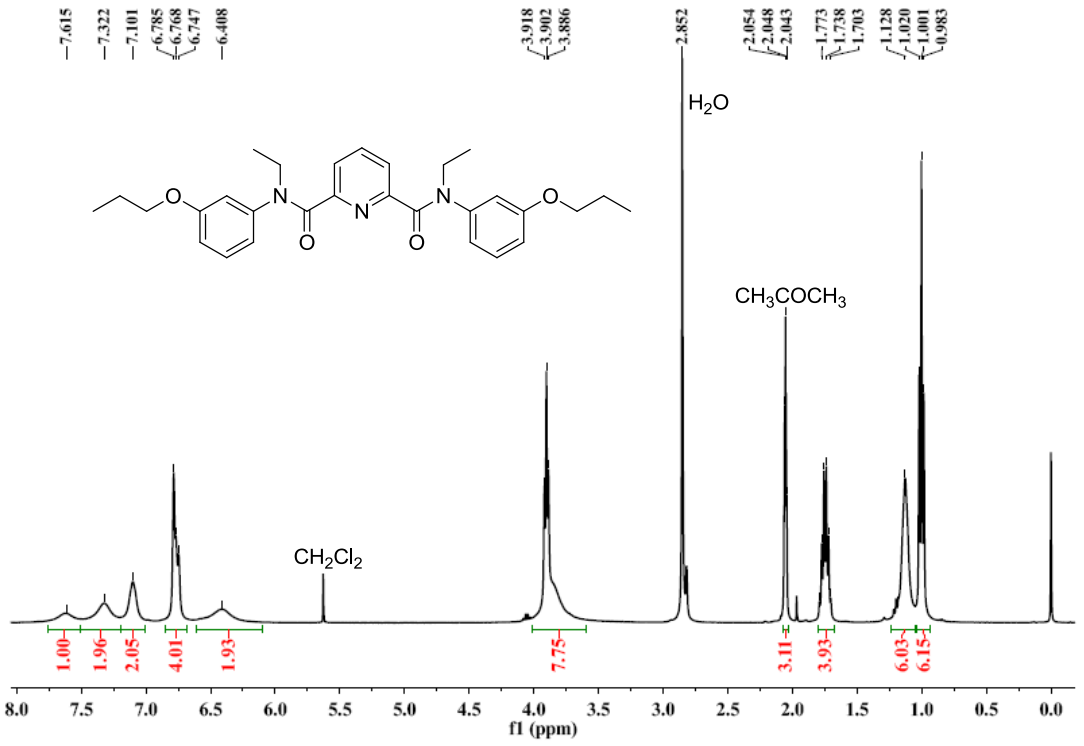


Fig. S4 ^{1}H NMR spectrum of **1b** (CD_3COCD_3, 400 MHz, 298 K)

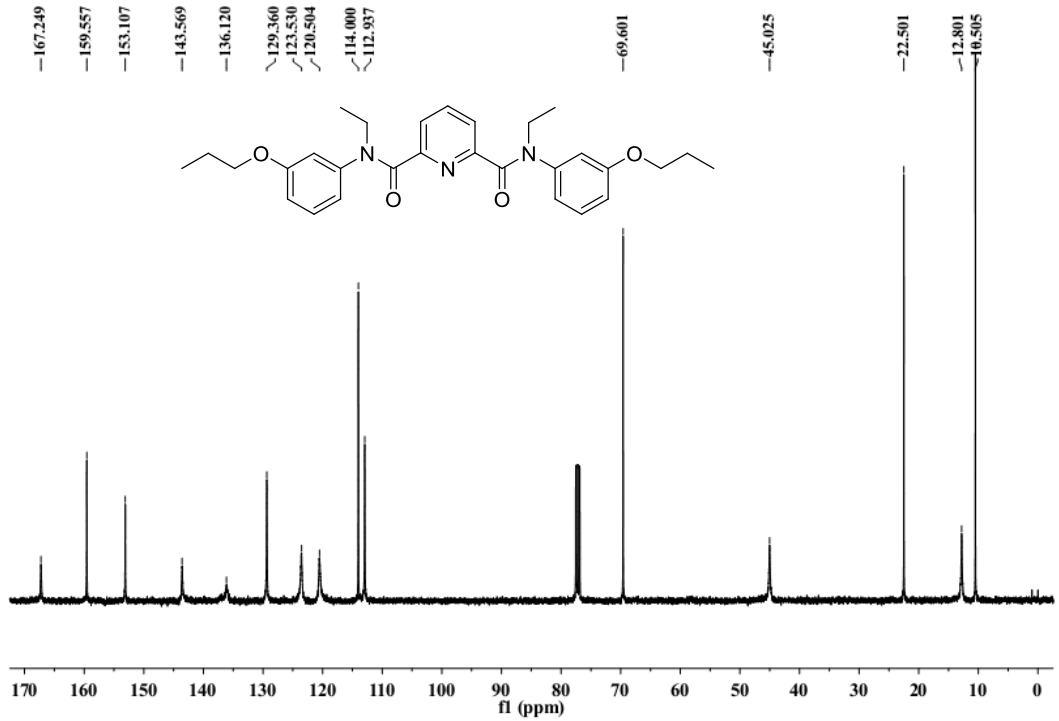


Fig. S5 ^{13}C NMR spectrum of **1b** ($CDCl_3$, 100 MHz, 298 K)

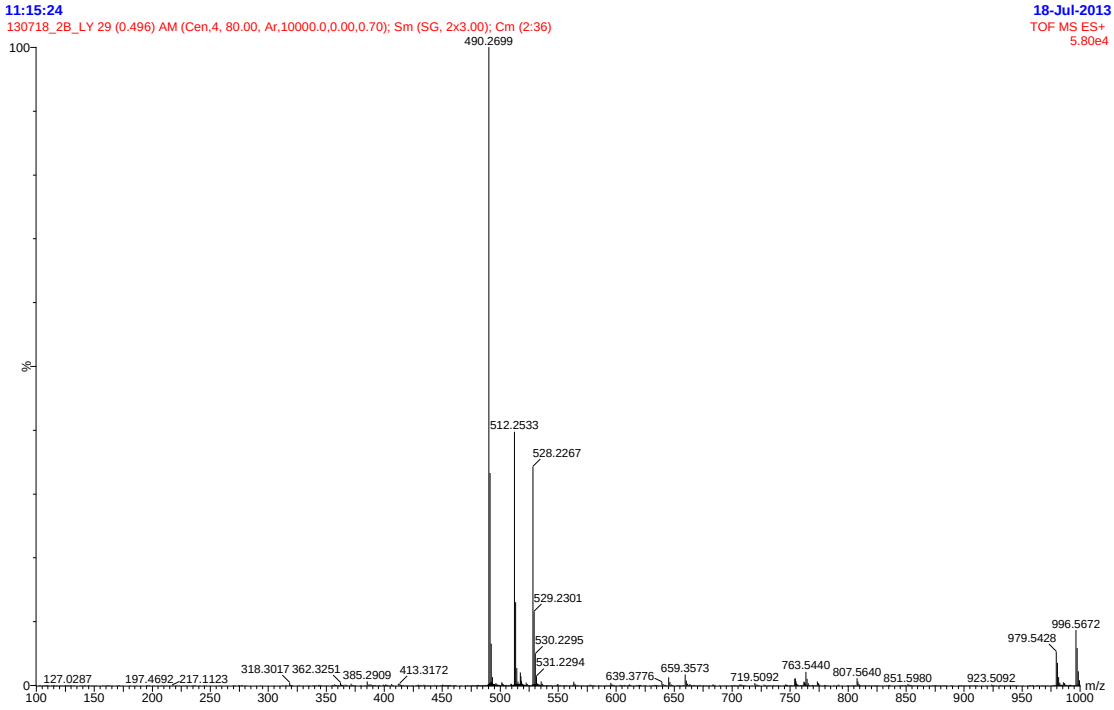


Fig. S6 ESI-HRMS spectrum of **1b.**

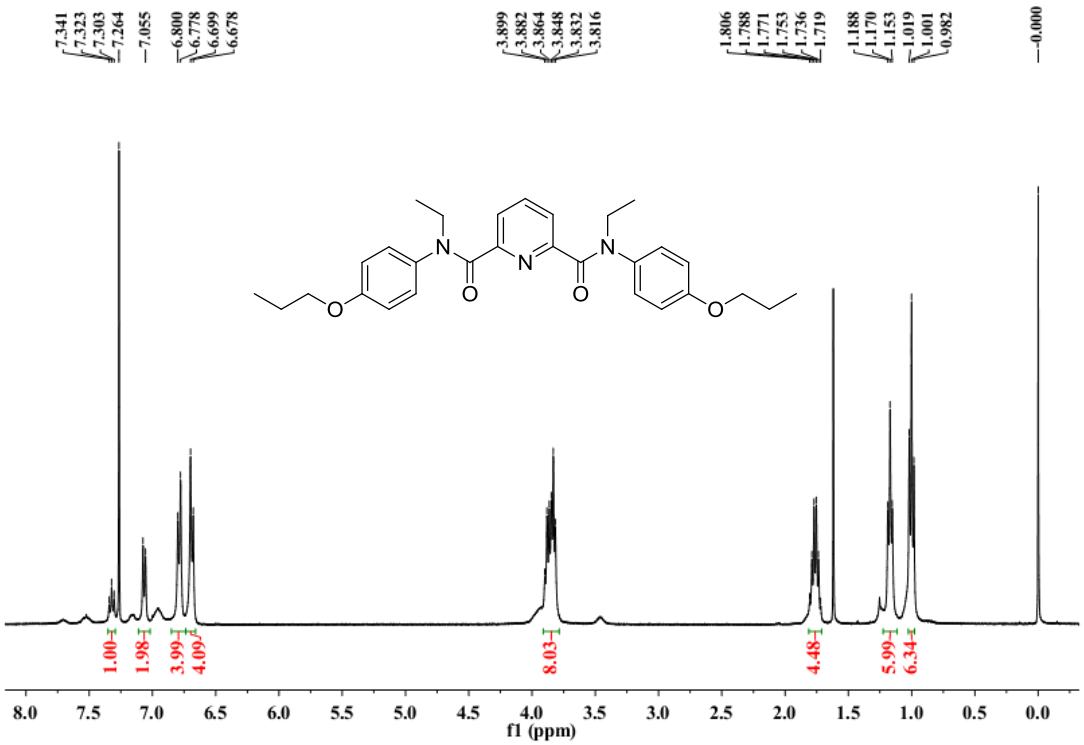


Fig. S7 ^{1}H NMR spectrum of **1c** ($CDCl_3$, 400 MHz, 298 K)

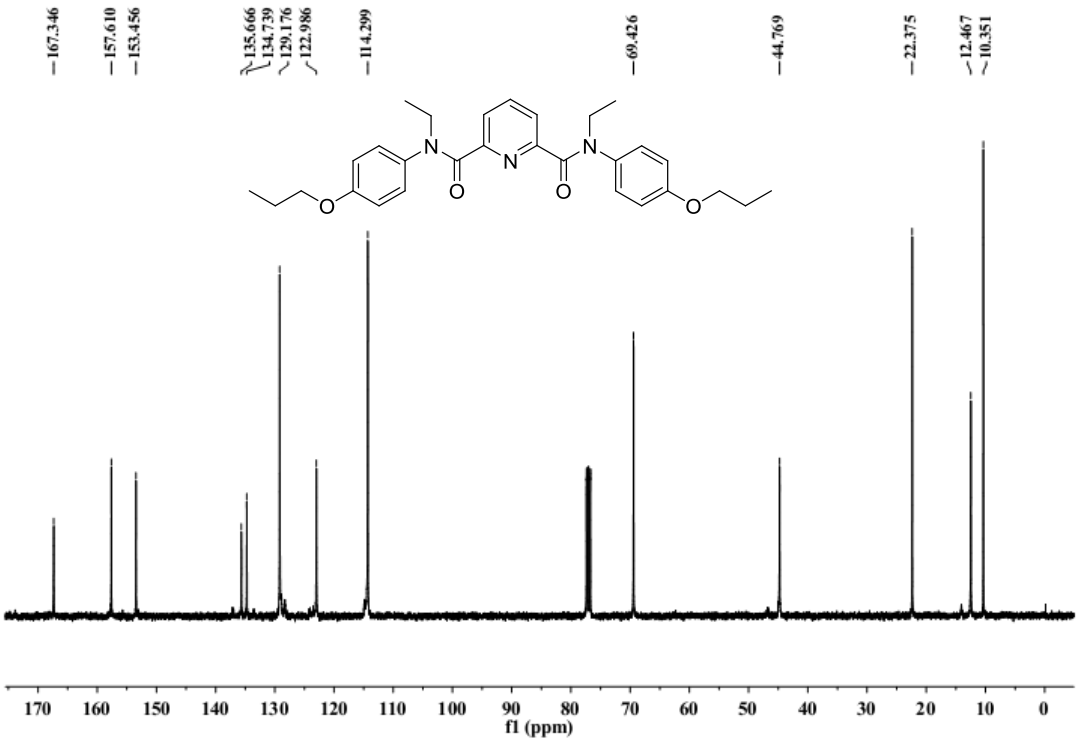


Fig. S8 ^{13}C NMR spectrum of **1c** ($CDCl_3$, 100 MHz, 298 K)

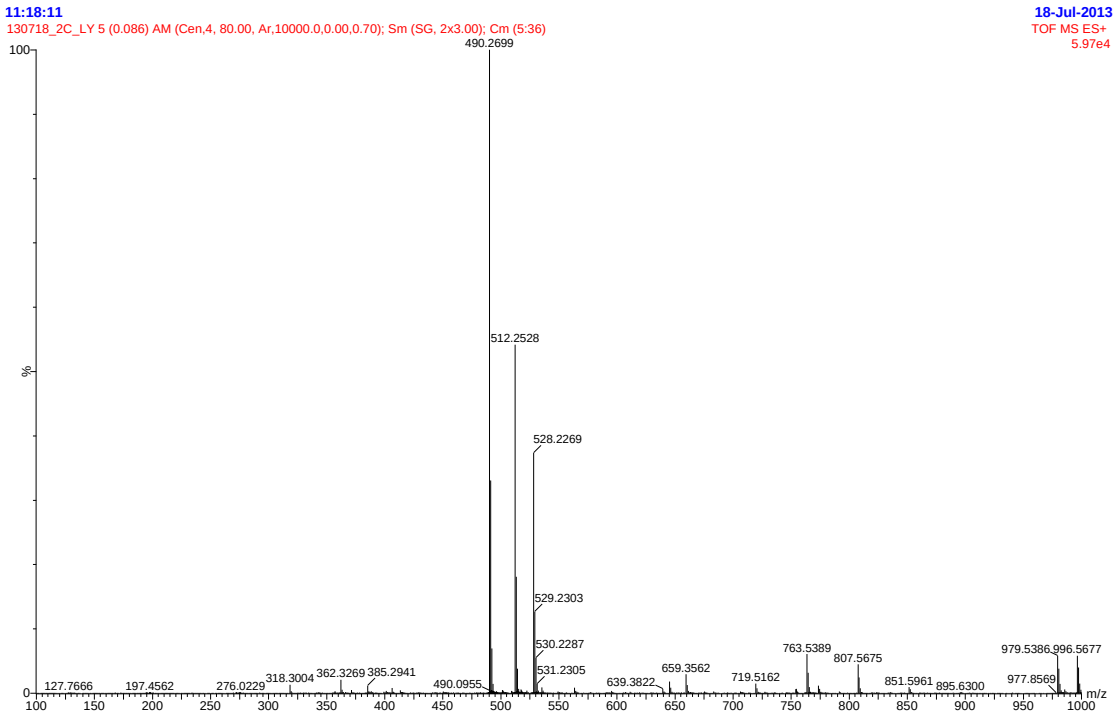


Fig. S9 ESI-HRMS spectrum of **1c.**

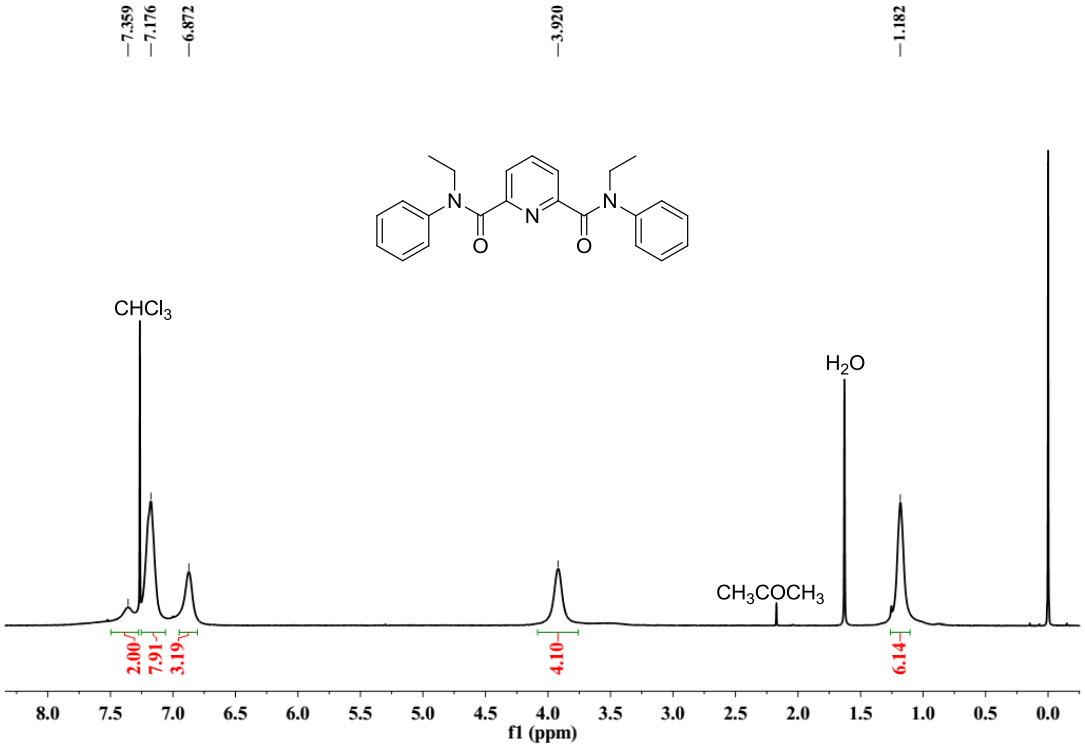


Fig. S10 ^{1}H NMR spectrum of **2** ($CDCl_3$, 400 MHz, 298 K)

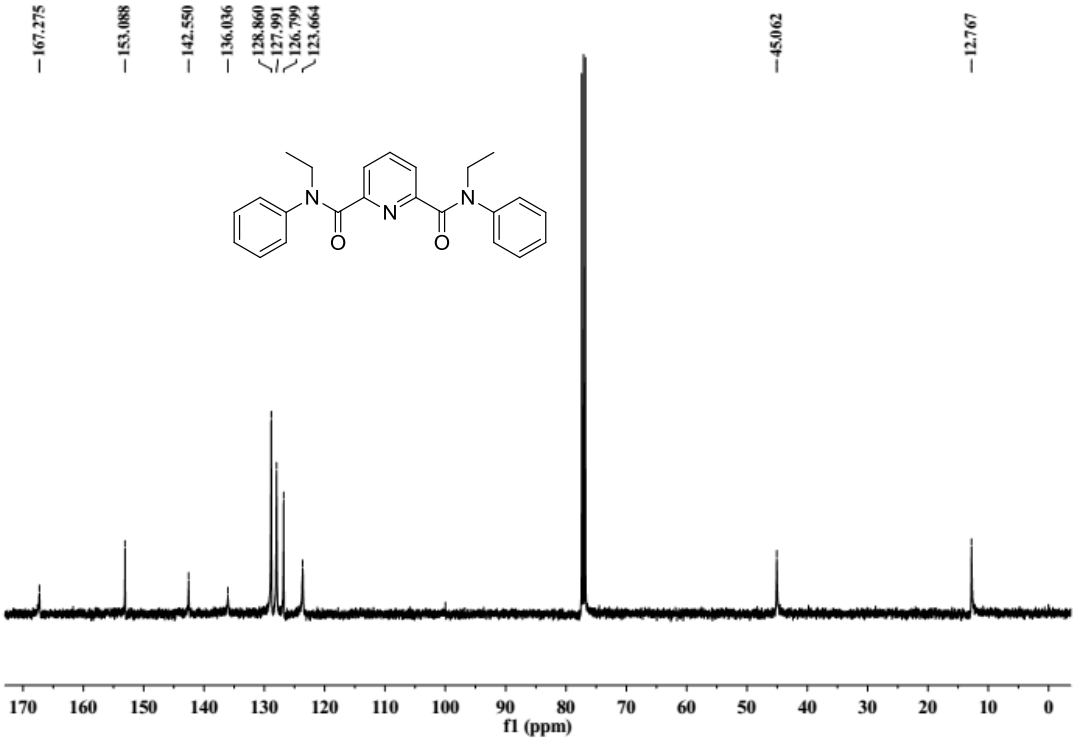


Fig. S11 ^{13}C NMR spectrum of **2** ($CDCl_3$, 100 MHz, 298 K)

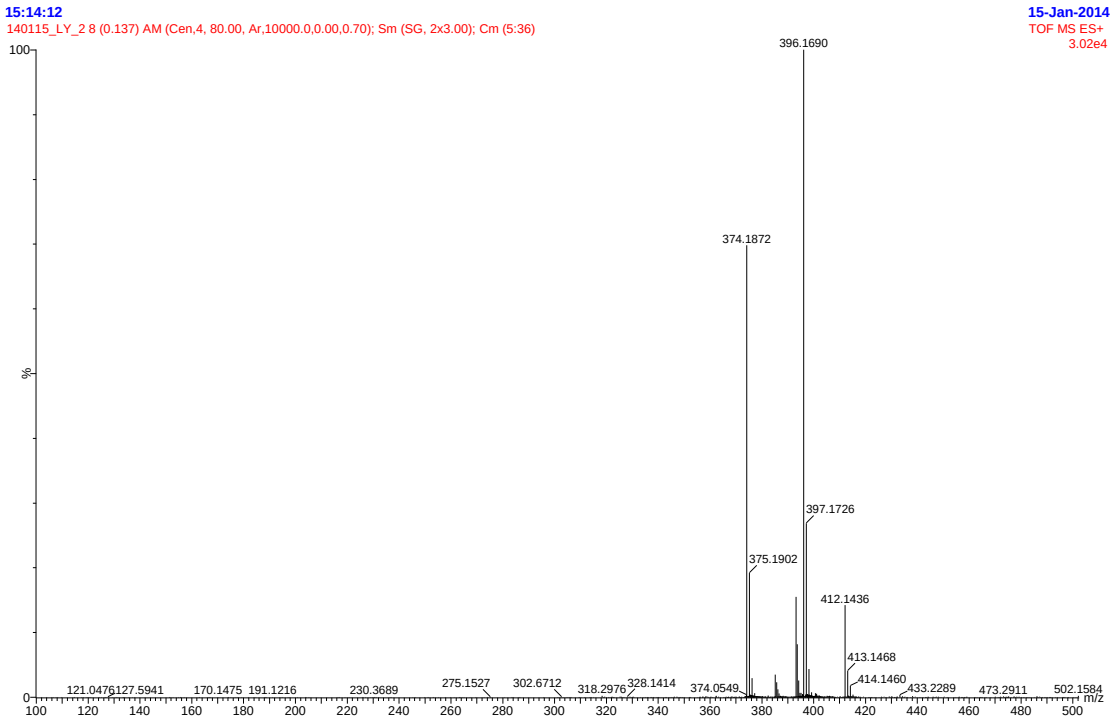


Fig. S12 ESI-HRMS spectrum of **2.**

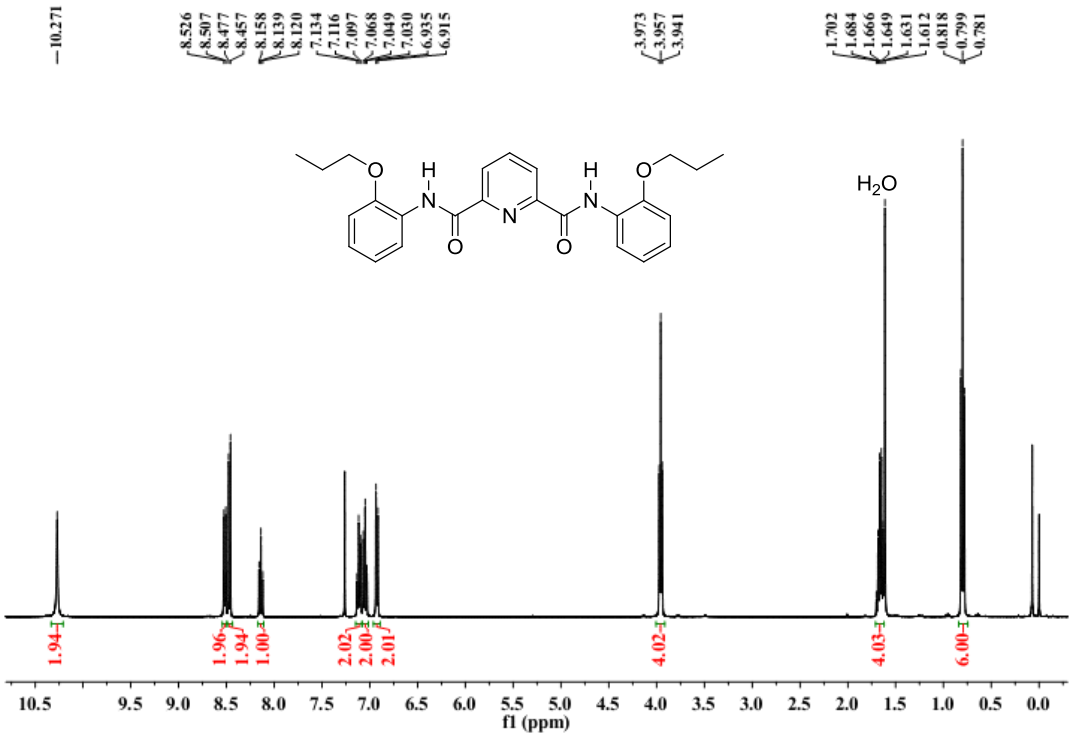


Fig. S13 ^{1}H NMR spectrum of **3a** ($CDCl_3$, 400 MHz, 298 K)

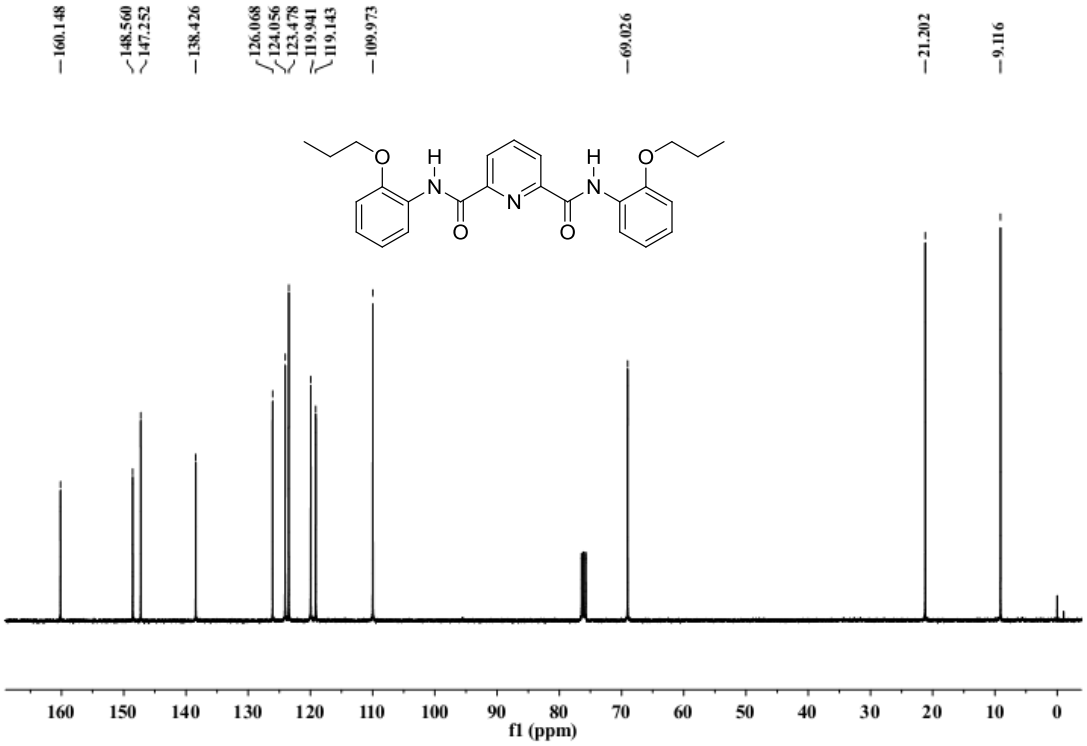


Fig. S14 ^{13}C NMR spectrum of **3a** ($CDCl_3$, 100 MHz, 298 K)

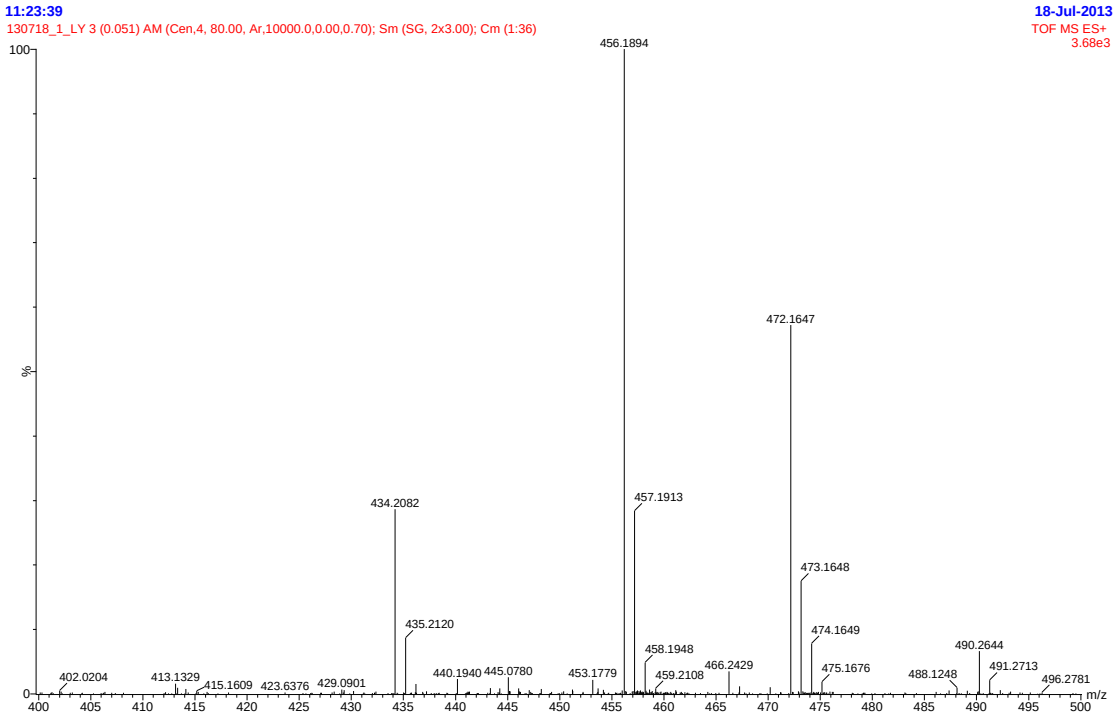


Fig. S15 ESI-HRMS spectrum of **3a**.

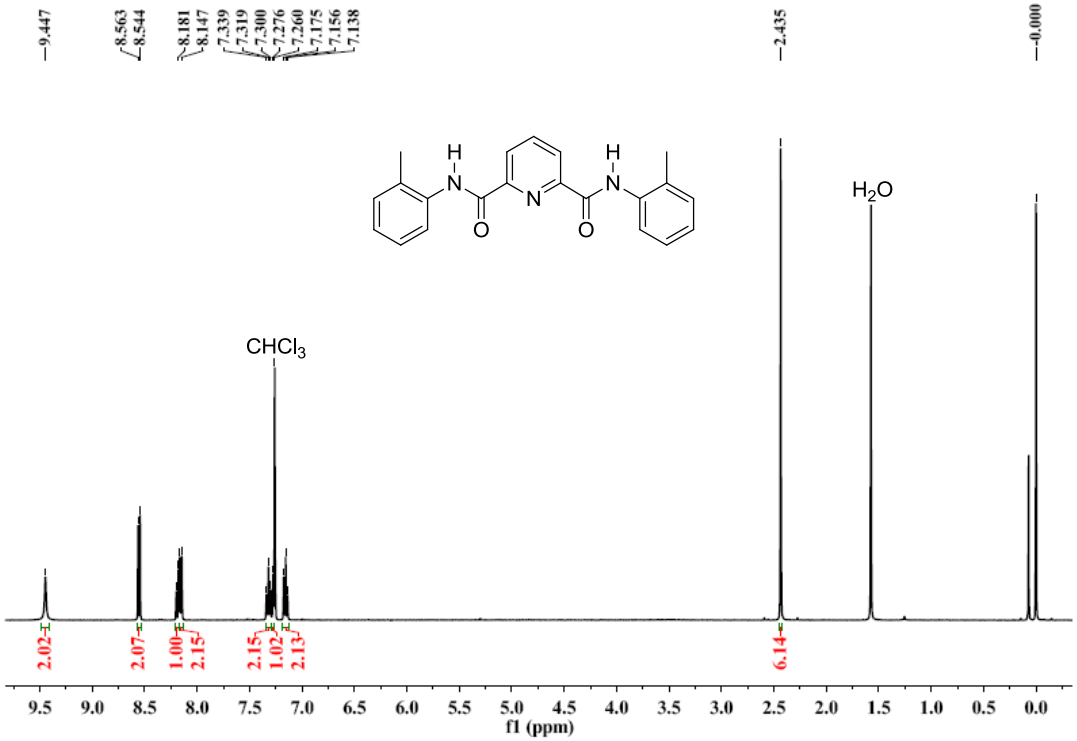


Fig. S16 ^{1}H NMR spectrum of **3b** ($CDCl_3$, 400 MHz, 298 K)

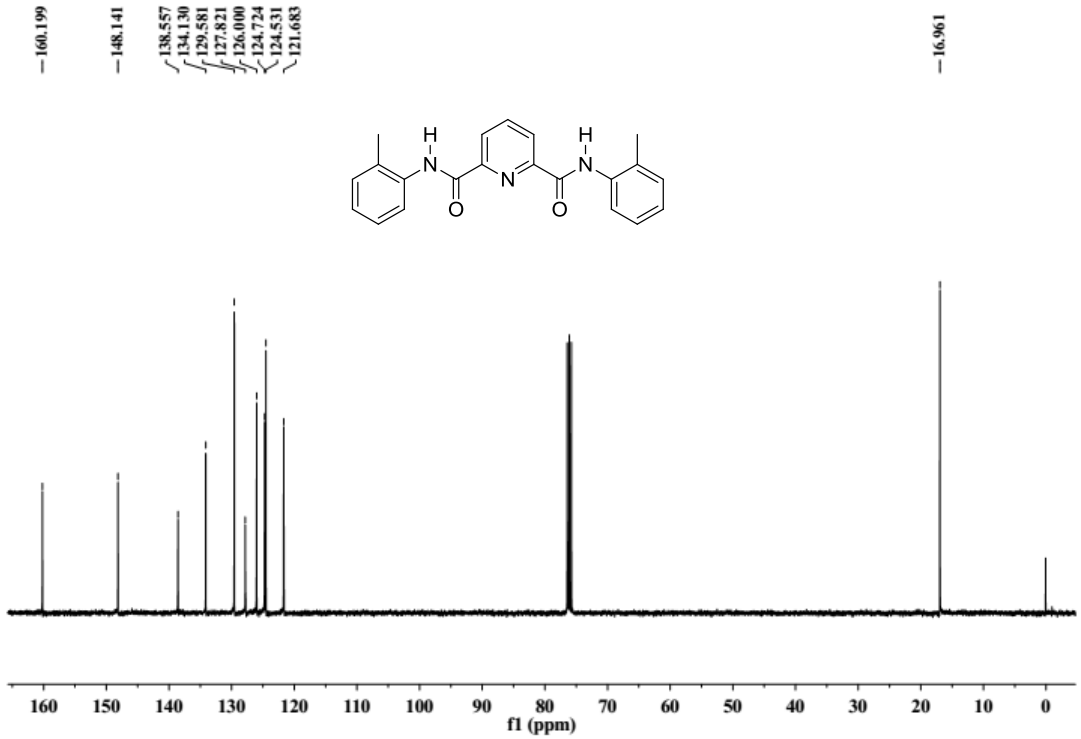


Fig. S17 ^{13}C NMR spectrum of **3b** ($CDCl_3$, 100 MHz, 298 K)

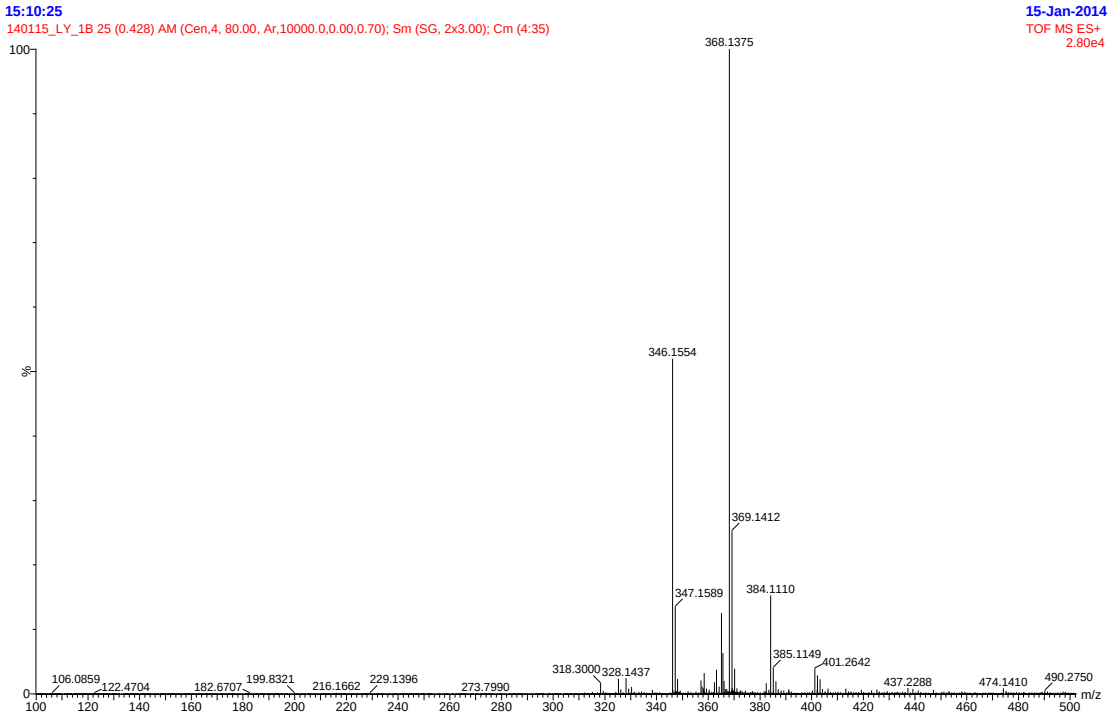


Fig. S18 ESI-HRMS spectrum of **3b.**

4. HPLC Profiles of Compounds **1a-1c.**

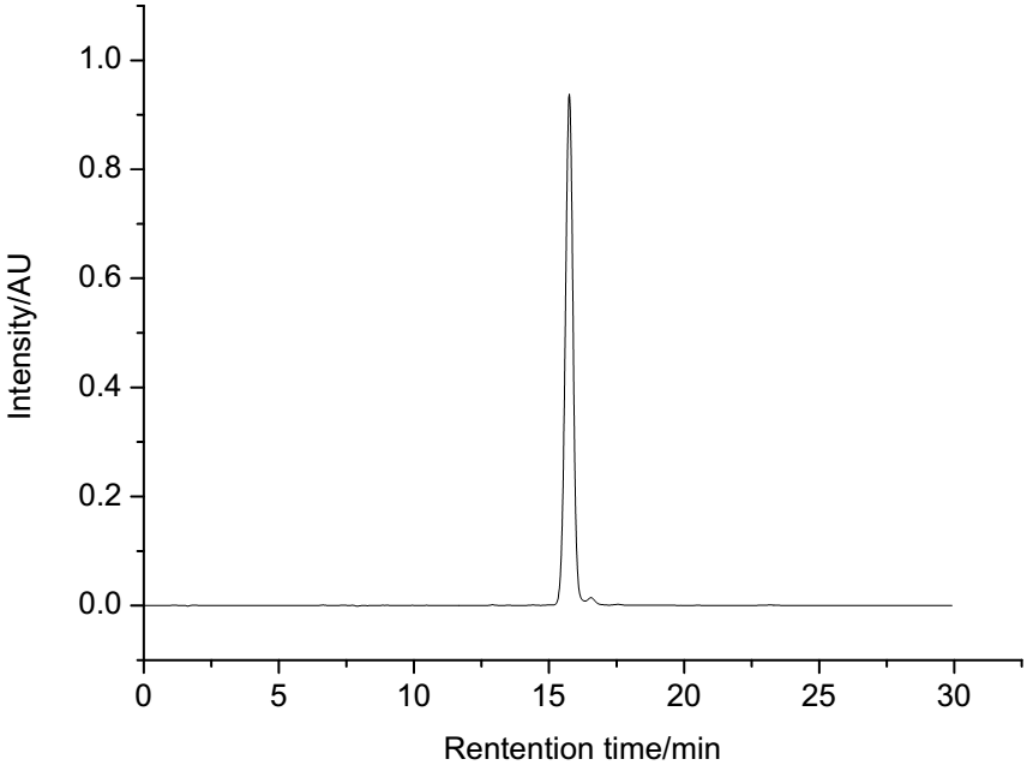


Fig. S19 HPLC profile of compound **1a**

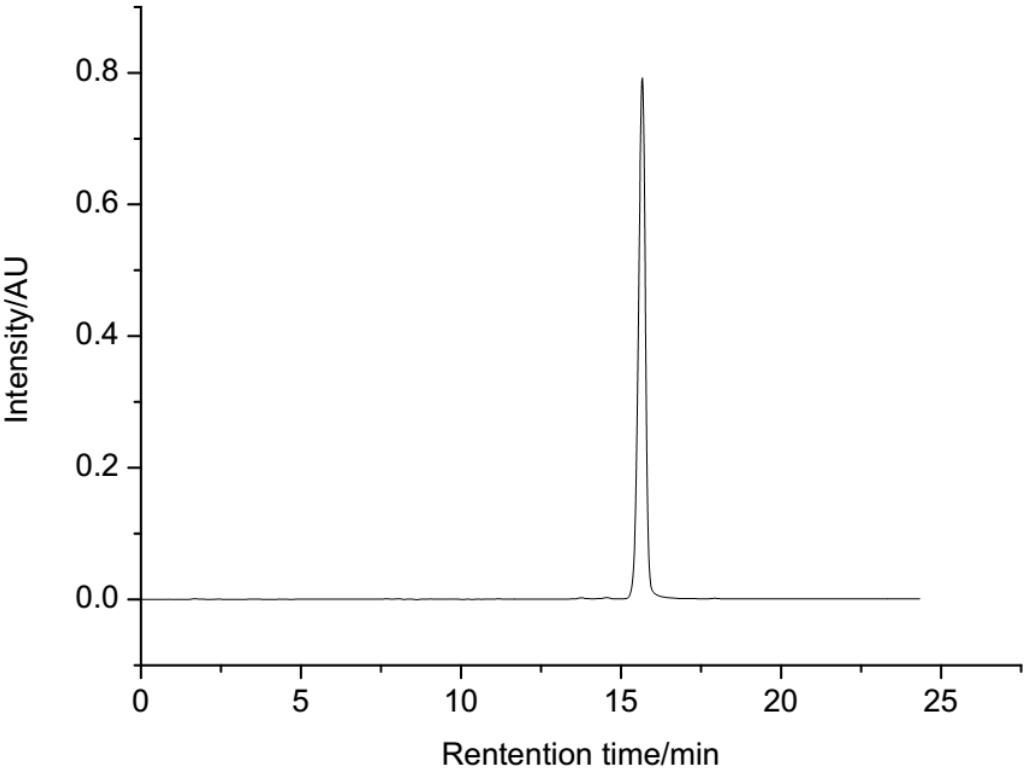


Fig. S20 HPLC profile of compound **1b**

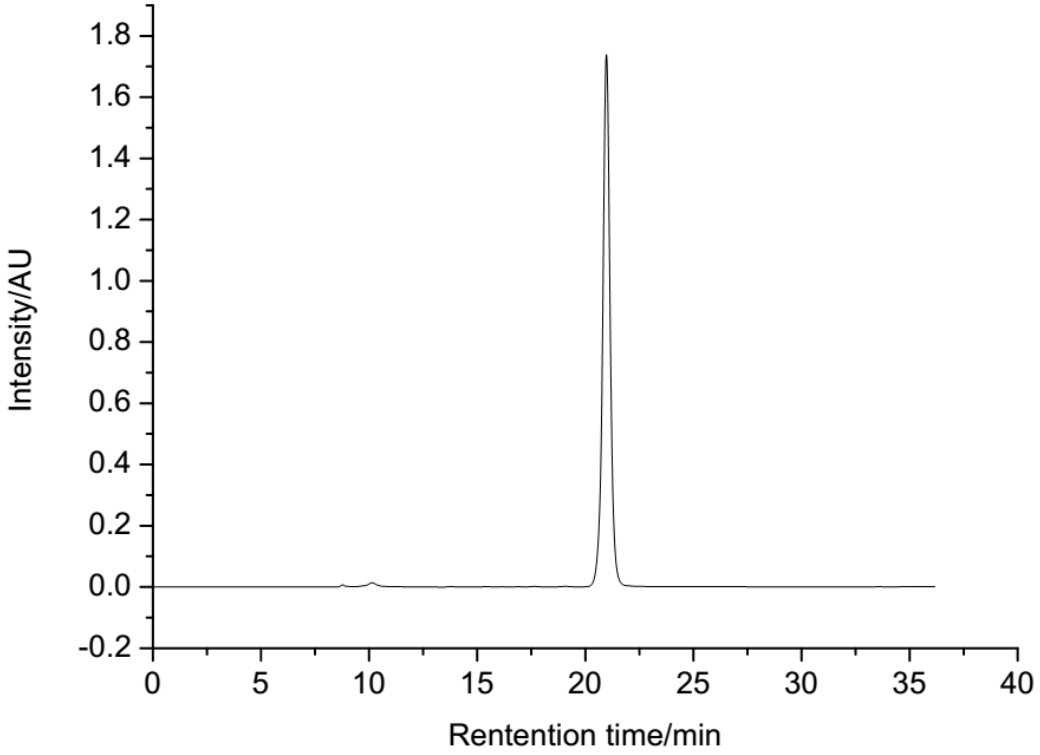


Fig. S21 HPLC profile of compound **1c**

5. X-ray Structures and Data of Compounds **1a** and **3a**

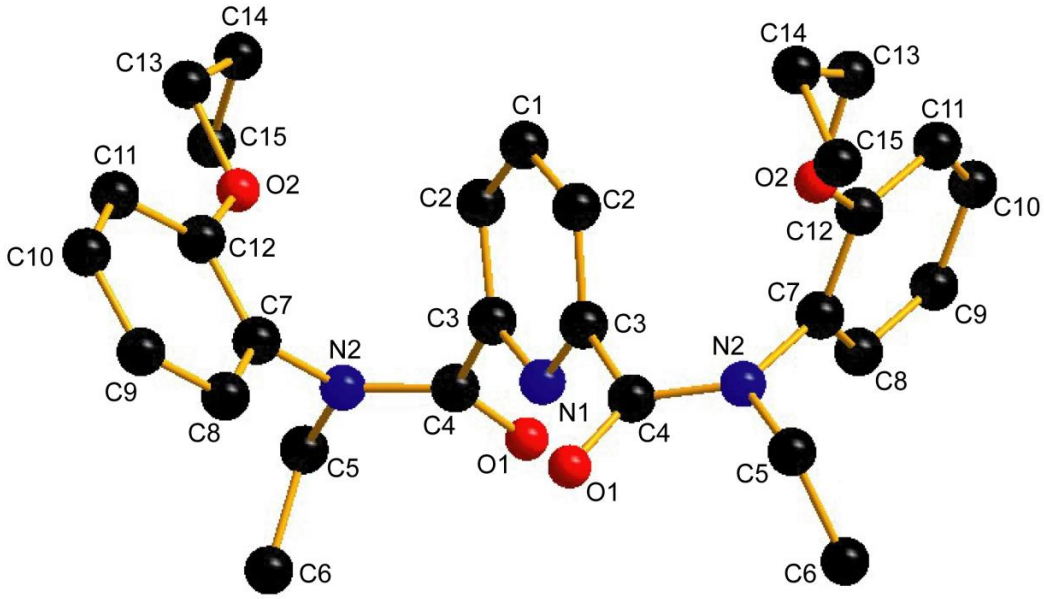


Fig. S22 The X-ray structure of compound **1a**. The total hydrogen atoms were omitted for the sake of clarity.

Table S1. Crystal data and structure refinement for compound **1a.**

Identification code	1a
Empirical formula	$C_{29}H_{35}N_3O_4$
Formula weight	489.60
Temperature/K	296.2 K
wavelength	0.71073 A
Crystal system	Orthorhombic
Space group	F dd2
a/Å, b/Å, c/Å	14.033(3), 38.450(8), 10.289(2)
α/°, β/°, γ/°	90.00, 90.00, 90.00
Volume/$Å^3$	5551.7(19)
Z	8
$\rho_{calc}mg/mm^3$	1.172
m/mm^{-1}	0.078
F(000)	2096
Crystal size/mm^3	0.34 x 0.26 x 0.23
2Θ range for data collection	3.09 to 27.48 °
Index ranges	-18<=h<=18, -49<=k<=49, -13<=l<=12
Reflections collected	13153
Independent reflections	3098 [R(int) = 0.0589]
Data/restraints/parameters	3098 / 1 / 166
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0452, wR_2 = 0.1045
Final R indexes [all data]	R_1 = 0.0631, wR_2 = 0.1133
Largest diff. peak/hole / e $Å^{-3}$	0.135 d -0.117

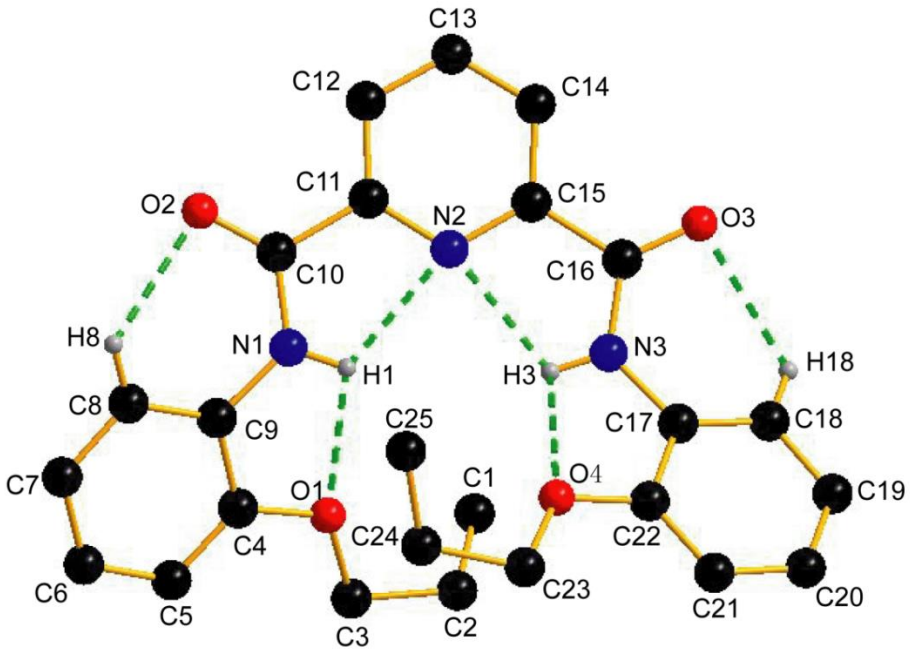


Fig. S23 The X-ray structure of compound **3a**. Hydrogen atoms were omitted except for those forming hydrogen bonds.

Table S2. Crystal data and structure refinement for compound **3a.**

Identification code	3a
Empirical formula	$C_{25}H_{27}N_3O_4$
Formula weight	433.50
Temperature/K	293.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å, b/Å, c/Å	15.0617(7), 8.8547(6), 17.7386(10)
α/°, β/°, γ/°	90.00, 97.110(4), 90.00
Volume/$Å^3$	2347.6(2)
Z	4
$\rho_{calc}mg/mm^3$	1.227
m/mm^{-1}	0.084
F(000)	920
Crystal size/mm^3	0.38 × 0.35 × 0.35
2Θ range for data collection	5.96 to 50 °
Index ranges	$-17 \leq h \leq 17$, $-10 \leq k \leq 10$, $-17 \leq l \leq 21$
Reflections collected	9186
Independent reflections	4124[R(int) = 0.0268]
Data/restraints/parameters	4124/0/291
Goodness-of-fit on F^2	1.058
Final R indexes [I>=2σ (I)]	R_1 = 0.0753, wR_2 = 0.1992
Final R indexes [all data]	R_1 = 0.1052, wR_2 = 0.2198
Largest diff. peak/hole / e $Å^{-3}$	0.250/-0.241
Flack Parameter	N/A

6. Variable-temperature ^{1}H NMR and IR spectra of **3a** and **3b**

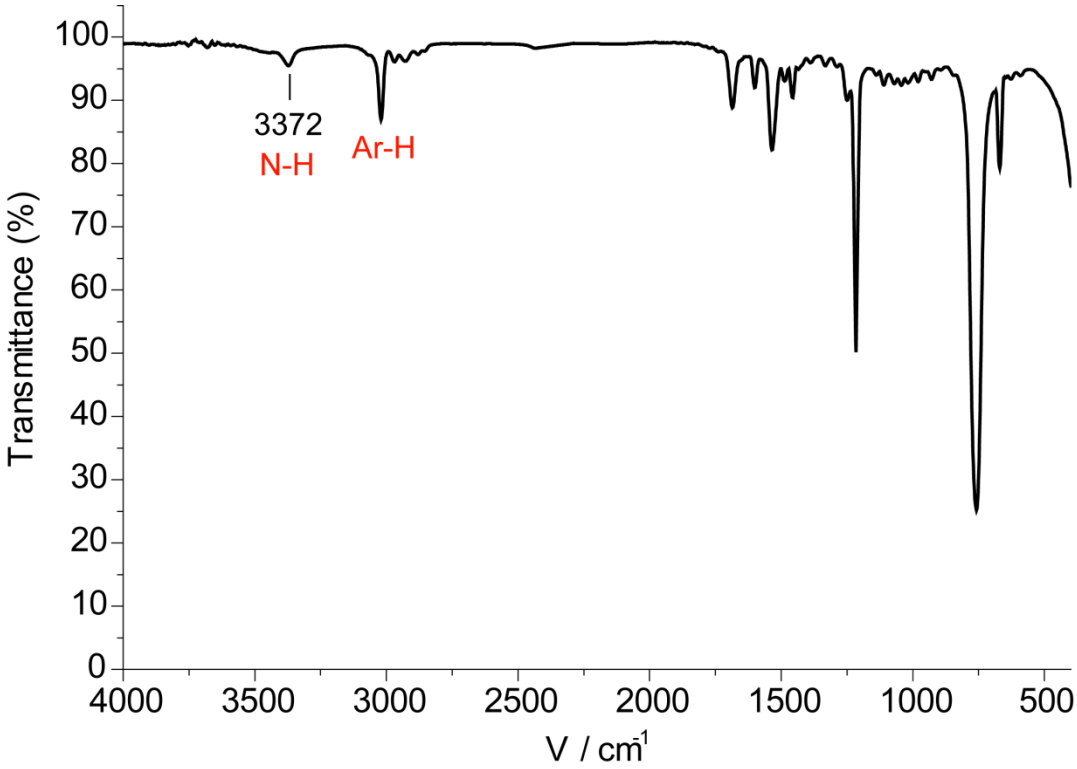


Fig. S24 Infrared spectrum of **3a** in $CHCl_3$.

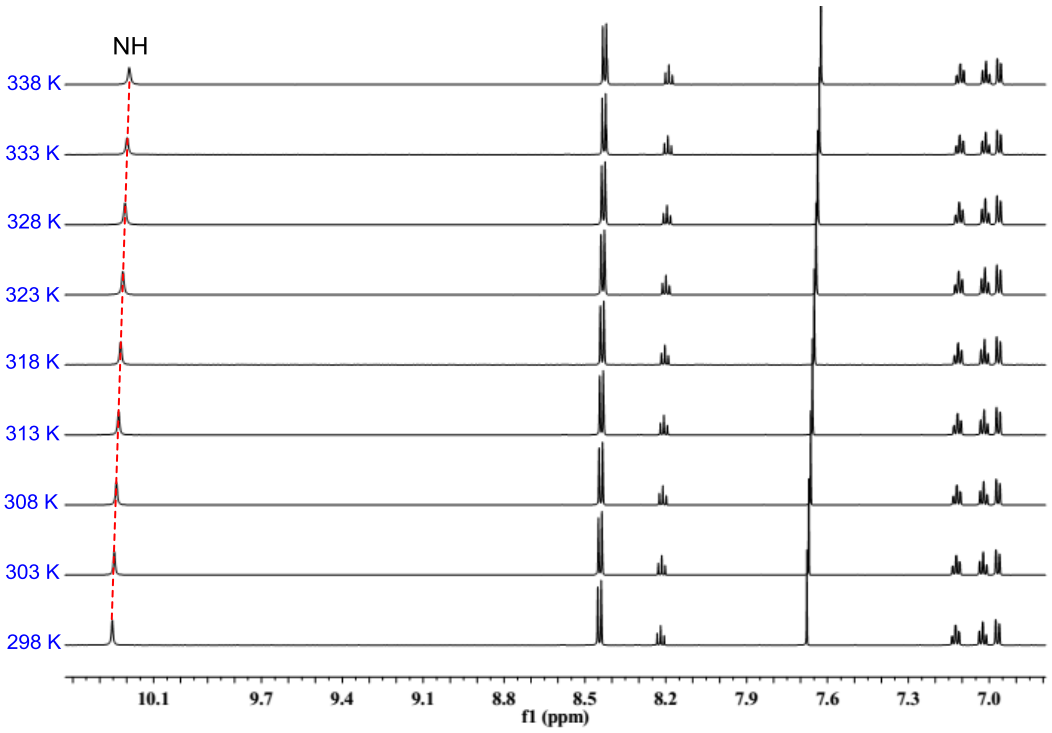


Fig. S25 Temperature dependence of the patial ^{1}H NMR of **3a** in DMSO-d_6/$CDCl_3$ (2/8, v/v).

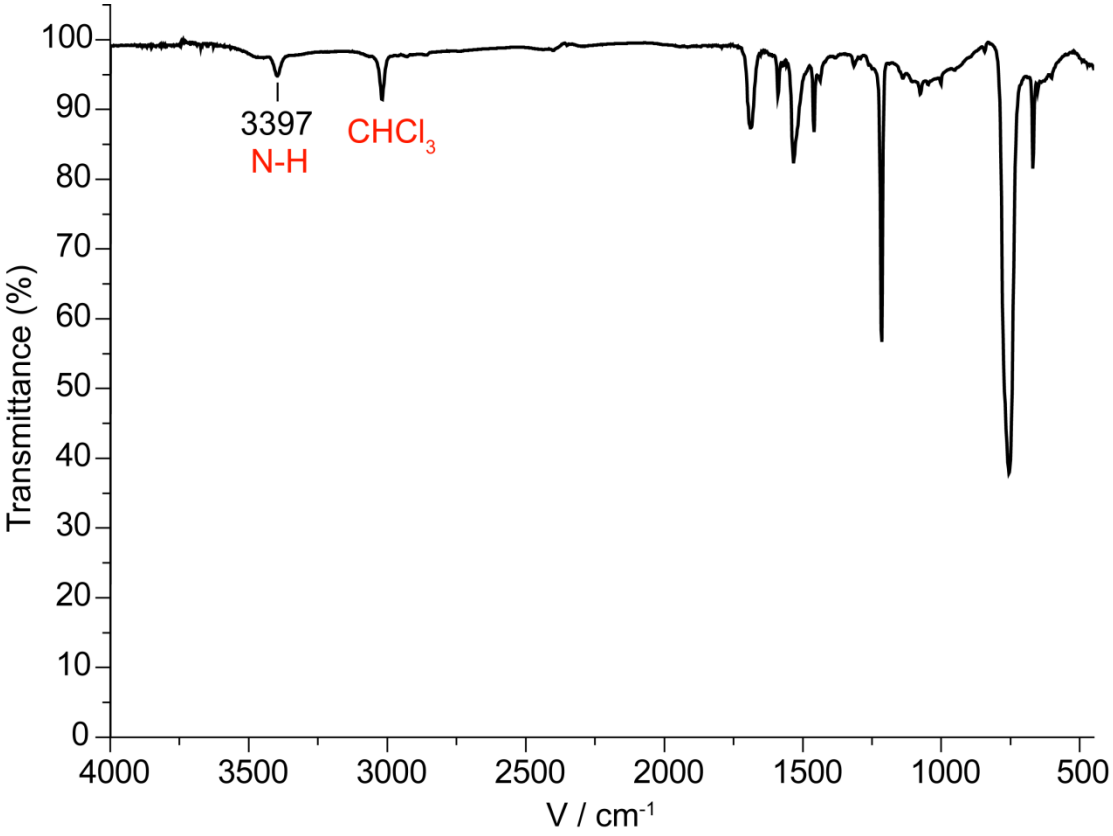


Fig. S26 Infrared spectrum of **3b** in $CHCl_3$.

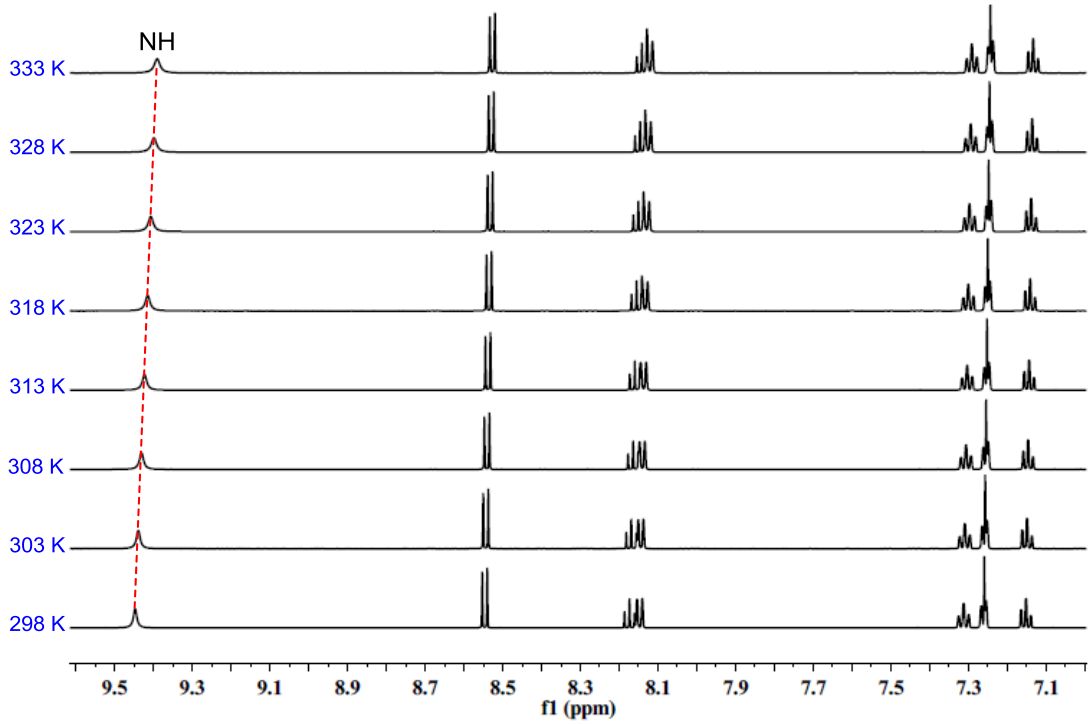


Fig. S27 Temperature dependence of the patial ^{1}H NMR of **3b** in $CHCl_3$.

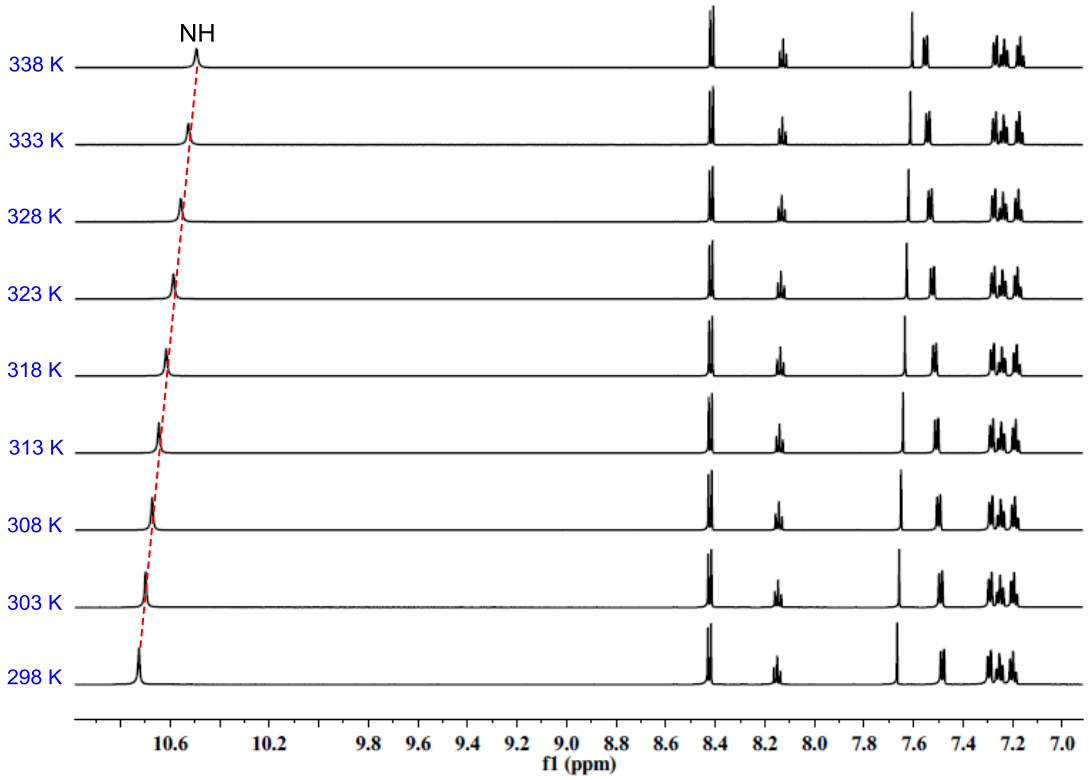


Fig. S28 Temperature dependence of the patial ^{1}H NMR of **3b** in DMSO-d_6/$CDCl_3$ (2/8, v/v).

7. Titration curves and nonlinear curve fitting of **1a-1c** upon addition of Hg^{2+}

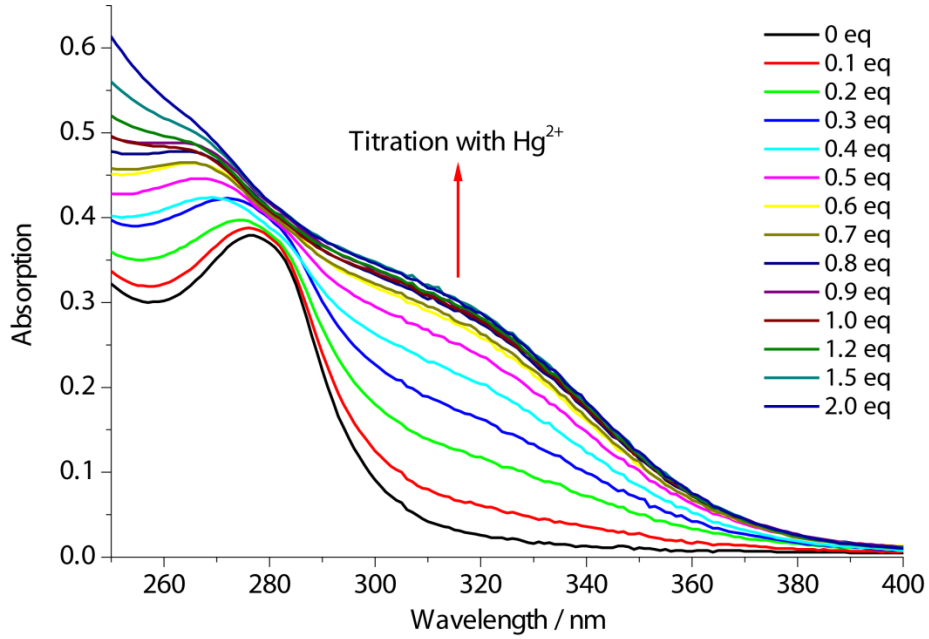


Fig. S29 Titration curves of **1a** (4.0×10^{-5} M) upon addition of $Hg(NO_3)_2$ at 0, 0.4, 0.8, 1.2, 1.6, 2.0, 2.4, 2.8, 3.2, 3.6, 4.0, 4.8, 6.0, 8.0×10^{-5} M in CH_3CN.

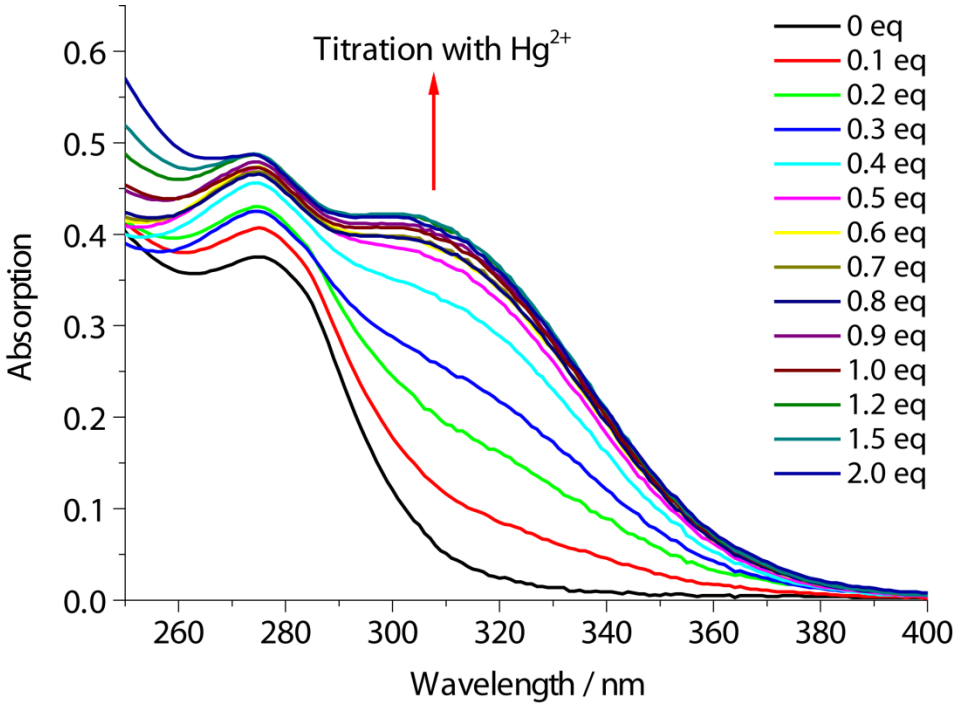


Fig. S30 Titration curves of **1b** (4.0×10^{-5} M) upon addition of $Hg(NO_3)_2$ at 0, 0.4, 0.8, 1.2, 1.6, 2.0, 2.4, 2.8, 3.2, 3.6, 4.0, 4.8, 6.0, 8.0×10^{-5} M in CH_3CN.

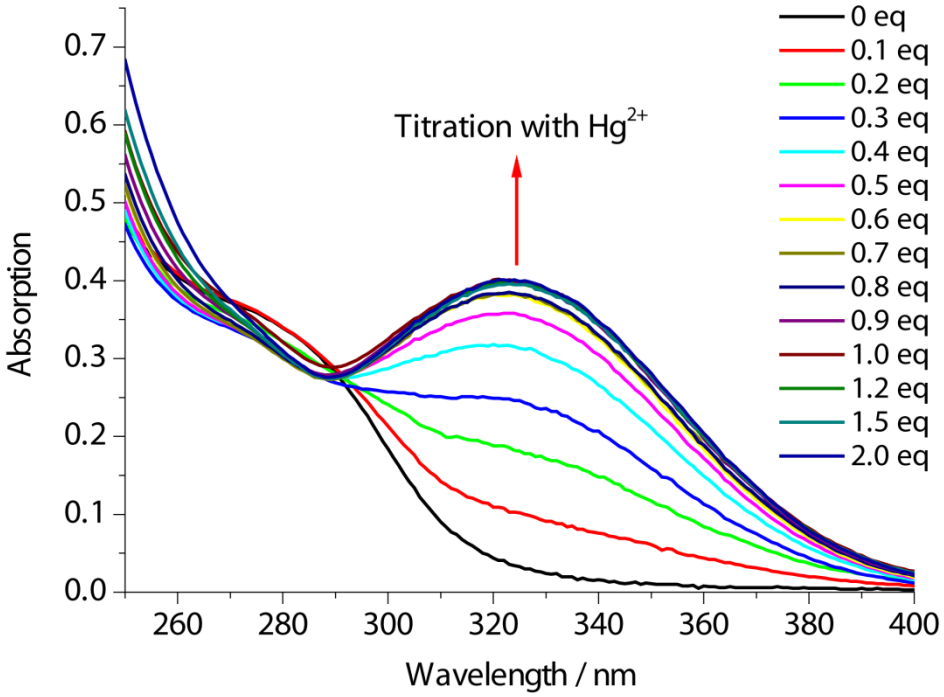


Fig. S31 Titration curves of **1c** (4.0×10^{-5} M) upon addition of $Hg(NO_3)_2$ at 0, 0.4, 0.8, 1.2, 1.6, 2.0, 2.4, 2.8, 3.2, 3.6, 4.0, 4.8, 6.0, 8.0 $\times 10^{-5}$ M in CH_3CN.

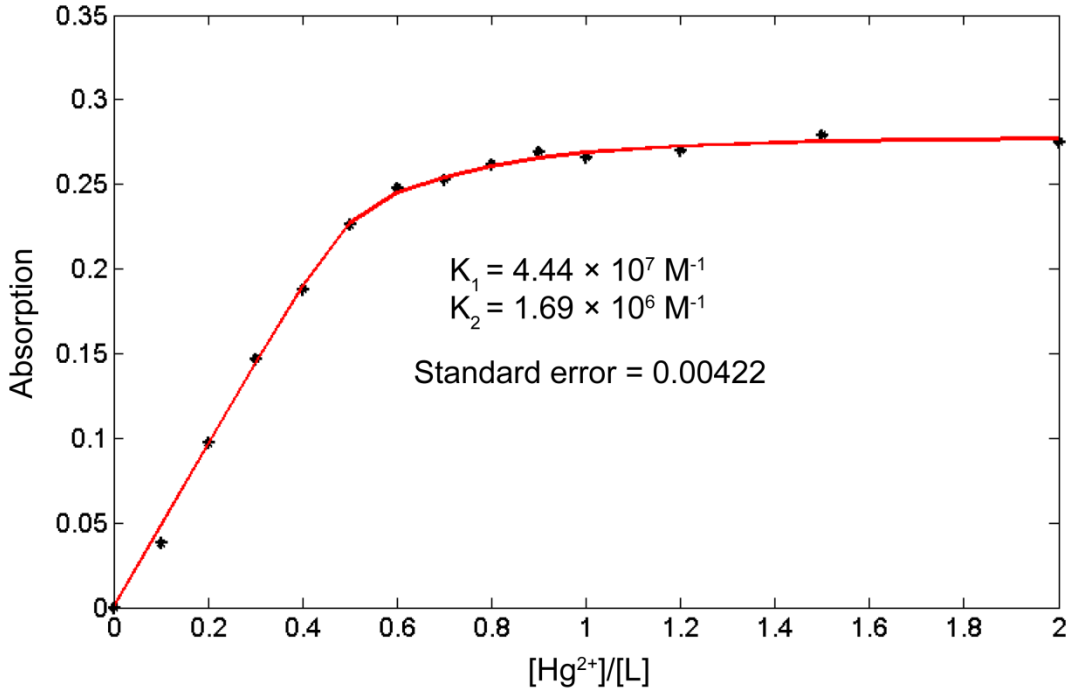


Fig. S32 Curve-fitting analysis for the complexation of **1b** with Hg^{2+} in CH_3CN.

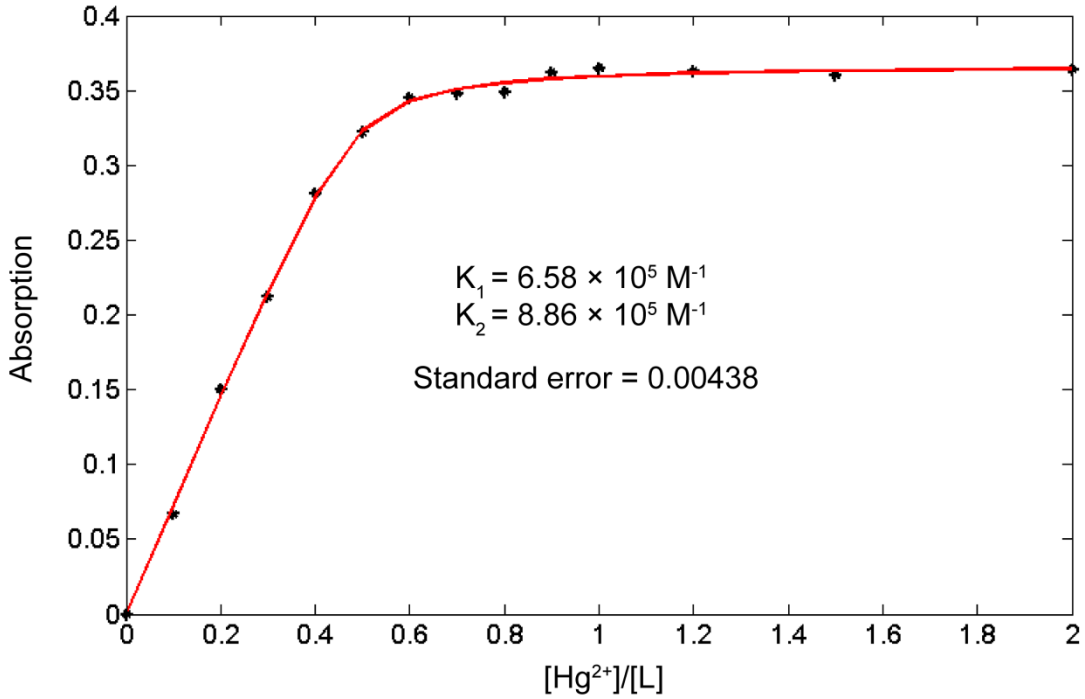
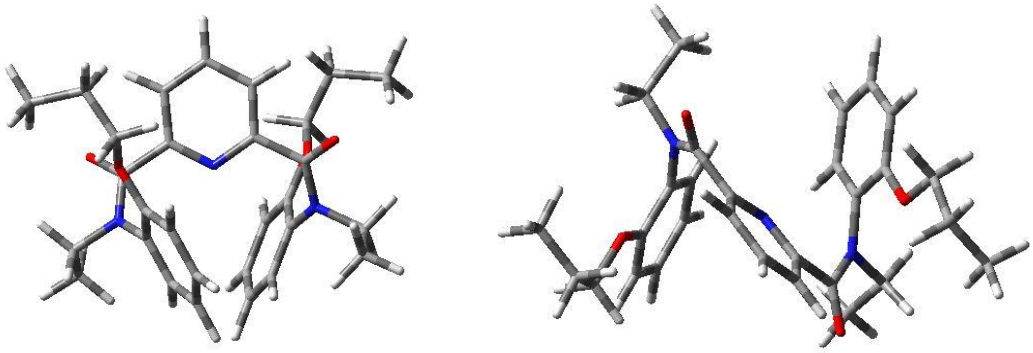


Fig. S33 Curve-fitting analysis for the complexation of **1c** with Hg^{2+} in CH_3CN.

8. Computer Modeling of Different Rotamers of **1a**[6]



Top views Side views

Fig. S34 Optimized rotational structure *E-syn-syn-E* of **1a** obtained by DFT calculation at the B3LYP/6-31G(d) level.

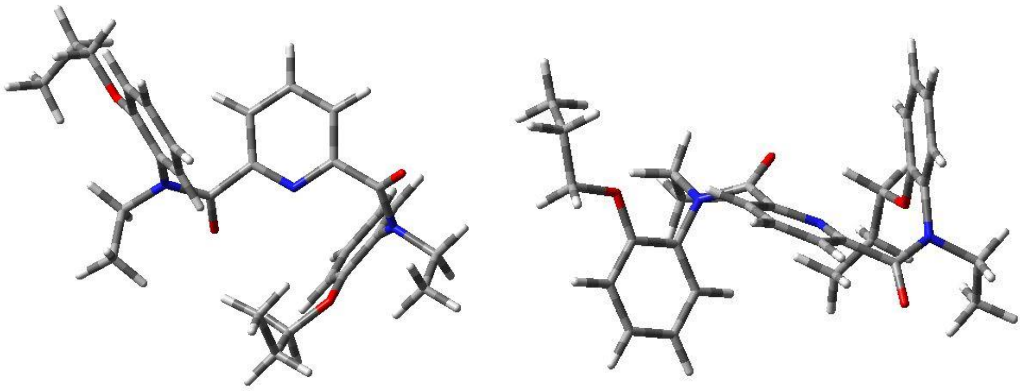
Table S3. Atomic coordinates for the optimized structure of *E-syn-syn-E*.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000054	3.306414	-0.000127
2	6	0	-0.842273	2.597626	-0.852868
3	6	0	-0.830051	1.198236	-0.792477

4	6	0	-1.746872	0.459185	-1.739672
5	6	0	-3.043885	-1.468069	-2.422368
6	6	0	-2.186124	-2.130328	-3.501809
7	6	0	-2.312790	-1.274050	-0.051086
8	6	0	-1.804701	-2.536782	0.250512
9	6	0	-1.946998	-3.087160	1.525874
10	6	0	-2.599716	-2.356317	2.515852
11	6	0	-3.123051	-1.091850	2.234031
12	6	0	-2.998509	-0.548488	0.950353
13	6	0	-4.191933	1.458770	1.537915
14	6	0	-4.624065	2.749941	0.853737
15	6	0	-5.592376	2.532026	-0.313103
16	7	0	-0.000021	0.509130	-0.000029
17	7	0	-2.242339	-0.775061	-1.388828
18	8	0	-2.002492	0.968610	-2.831111
19	8	0	-3.501813	0.660512	0.575622
20	1	0	0.000084	4.393201	-0.000166
21	1	0	-1.503569	3.089876	-1.556454
22	1	0	-3.711120	-0.731770	-2.881415
23	1	0	-3.655525	-2.209720	-1.903338
24	1	0	-1.589893	-1.378929	-4.025743
25	1	0	-2.829569	-2.631357	-4.234933
26	1	0	-1.508064	-2.876083	-3.072553
27	1	0	-1.278798	-3.077604	-0.529610
28	1	0	-1.546470	-4.073531	1.741495
29	1	0	-2.711549	-2.765108	3.516348
30	1	0	-3.637611	-0.541722	3.013165
31	1	0	-3.527146	1.671905	2.386459
32	1	0	-5.065659	0.907487	1.916808
33	1	0	-3.725498	3.274340	0.506055
34	1	0	-5.087296	3.387746	1.618468
35	1	0	-5.129733	1.923304	-1.095561
36	1	0	-5.889176	3.488172	-0.757734
37	1	0	-6.504166	2.020434	0.020038
38	6	0	0.842341	2.597641	0.852665
39	6	0	0.830045	1.198248	0.792374
40	6	0	1.746832	0.459217	1.739618
41	6	0	3.043822	-1.468016	2.422408
42	6	0	2.186034	-2.130247	3.501845
43	6	0	2.312810	-1.274063	0.051099
44	6	0	1.804744	-2.536806	-0.250494
45	6	0	1.947107	-3.087210	-1.525836
46	6	0	2.599862	-2.356381	-2.515801
47	6	0	3.123167	-1.091900	-2.233986

48	6	0	2.998561	-0.548513	-0.950325
49	6	0	4.191959	1.458769	-1.537868
50	6	0	4.624004	2.749972	-0.853695
51	6	0	5.592251	2.532121	0.313210
52	7	0	2.242304	-0.775043	1.388827
53	8	0	2.002386	0.968650	2.831068
54	8	0	3.501804	0.660515	-0.575598
55	1	0	1.503665	3.089906	1.556215
56	1	0	3.655479	-2.209681	1.903418
57	1	0	3.711043	-0.731701	2.881453
58	1	0	1.589790	-1.378836	4.025745
59	1	0	2.829462	-2.631256	4.234998
60	1	0	1.507986	-2.876014	3.072591
61	1	0	1.278811	-3.077614	0.529617
62	1	0	1.546601	-4.073591	-1.741455
63	1	0	2.711744	-2.765192	-3.516283
64	1	0	3.637750	-0.541780	-3.013111
65	1	0	3.527218	1.671864	-2.386459
66	1	0	5.065725	0.907505	-1.916694
67	1	0	3.725397	3.274348	-0.506080
68	1	0	5.087259	3.387775	-1.618414
69	1	0	5.129582	1.923402	1.095655
70	1	0	5.888989	3.488289	0.757835
71	1	0	6.504080	2.020554	-0.019862

The total electronic energy is calculated to be -1591.30518845 hartree.



Top views Side views

Fig. S35 Optimized rotational structure *E-anti-syn-E* of **1a** obtained by DFT calculation at the B3LYP/6-31G(d) level.

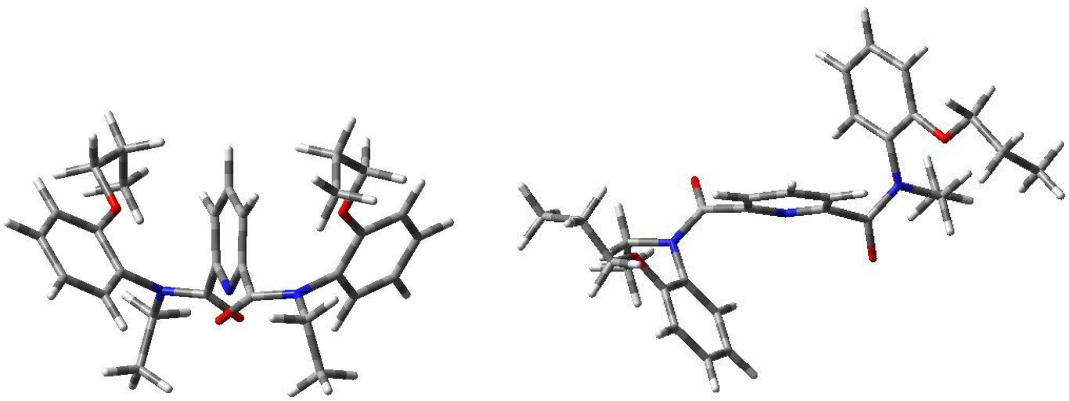
Table S4. Atomic coordinates for the optimized structure of *E-anti-syn-E*.

Center	Atomic	Atomic	Coordinates (Angstroms)		

Number	Number	Type	X	Y	Z
1	6	0	-0.520064	-2.691694	1.471423
2	6	0	0.786337	-2.925149	1.052691
3	6	0	1.478039	-1.883418	0.422415
4	6	0	2.883416	-2.147699	-0.076201
5	6	0	5.169289	-1.418000	-0.461299
6	6	0	5.219699	-1.137656	-1.964083
7	6	0	3.685784	-0.150268	1.112091
8	6	0	3.800974	-0.467252	2.466179
9	6	0	3.666833	0.513061	3.451445
10	6	0	3.417234	1.827888	3.064966
11	6	0	3.306036	2.166378	1.714999
12	6	0	3.444205	1.185570	0.724838
13	6	0	2.835695	2.685222	-1.045222
14	6	0	2.686547	2.619394	-2.560636
15	6	0	1.652187	1.589965	-3.026947
16	7	0	0.925950	-0.694091	0.158214
17	7	0	3.835126	-1.183537	0.128253
18	8	0	3.122536	-3.204275	-0.660832
19	8	0	3.370423	1.430864	-0.606141
20	1	0	-1.078534	-3.461999	1.996440
21	1	0	1.277301	-3.880346	1.203531
22	1	0	5.868187	-0.771944	0.075979
23	1	0	5.445783	-2.460070	-0.266576
24	1	0	4.532339	-1.801145	-2.495988
25	1	0	6.232831	-1.318498	-2.343272
26	1	0	4.944174	-0.100260	-2.171233
27	1	0	3.992130	-1.501979	2.738120
28	1	0	3.753600	0.249469	4.501323
29	1	0	3.303380	2.605909	3.815291
30	1	0	3.096439	3.192372	1.438013
31	1	0	3.522160	3.497735	-0.765235
32	1	0	1.867621	2.852296	-0.557127
33	1	0	3.668063	2.395274	-2.998414
34	1	0	2.408841	3.622550	-2.911744
35	1	0	1.890863	0.597635	-2.634246
36	1	0	1.617401	1.535641	-4.121037
37	1	0	0.651042	1.857727	-2.668051
38	6	0	-1.106857	-1.457244	1.195360
39	6	0	-0.349865	-0.497074	0.513271
40	6	0	-0.901175	0.886750	0.230919
41	6	0	-2.797082	2.300275	-0.378598
42	6	0	-2.447253	3.045703	-1.668055

43	6	0	-2.796834	-0.099441	-1.016595
44	6	0	-2.221069	-0.591878	-2.189379
45	6	0	-2.834934	-1.611060	-2.921157
46	6	0	-4.052643	-2.125178	-2.484344
47	6	0	-4.651102	-1.643888	-1.315782
48	6	0	-4.025631	-0.639618	-0.569707
49	6	0	-5.746758	-0.641851	1.112721
50	6	0	-6.043191	0.060576	2.431861
51	6	0	-6.249164	1.572279	2.296513
52	7	0	-2.178537	0.963657	-0.287684
53	8	0	-0.258490	1.889965	0.524223
54	8	0	-4.507192	-0.139840	0.605635
55	1	0	-2.124565	-1.235040	1.498453
56	1	0	-2.451875	2.867989	0.488120
57	1	0	-3.877779	2.160648	-0.290381
58	1	0	-1.369485	3.224419	-1.723360
59	1	0	-2.957830	4.015745	-1.691555
60	1	0	-2.757346	2.479015	-2.552969
61	1	0	-1.276874	-0.167896	-2.518266
62	1	0	-2.367520	-1.987423	-3.825760
63	1	0	-4.549208	-2.910475	-3.047619
64	1	0	-5.594242	-2.065077	-0.988003
65	1	0	-5.670131	-1.727949	1.262053
66	1	0	-6.547052	-0.453529	0.382029
67	1	0	-5.223796	-0.147907	3.131180
68	1	0	-6.943359	-0.405859	2.853927
69	1	0	-5.346746	2.059032	1.914719
70	1	0	-6.490370	2.020746	3.266234
71	1	0	-7.073354	1.799114	1.608740

The total electronic energy is calculated to be -1591.30362942 hartree.



Top views Side views

Fig. S36 Optimized rotational structure *E-anti-anti-E* of **1a** obtained by DFT calculation at the

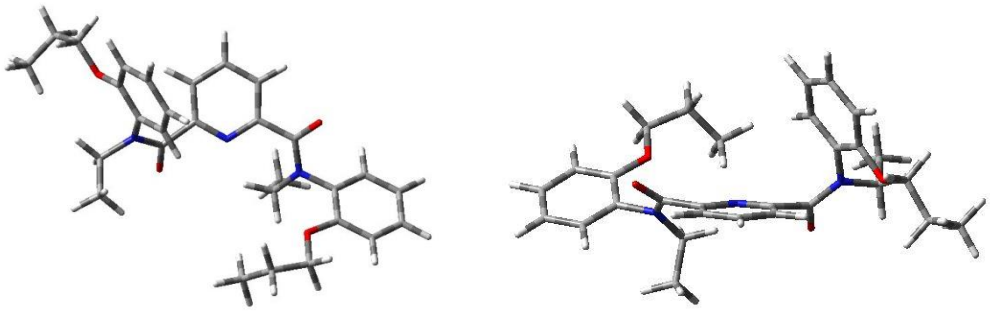
B3LYP/6-31G(d) level.

Table S5. Atomic coordinates for the optimized structure of *E-anti-anti-E*.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000815	-1.748334	0.154465
2	6	0	-1.115512	-1.010568	0.542756
3	6	0	-1.063365	0.383226	0.426961
4	6	0	-2.184609	1.245958	0.971798
5	6	0	-4.545166	1.866794	0.959087
6	6	0	-4.656171	3.291795	0.412993
7	6	0	-3.606045	0.490475	-0.895028
8	6	0	-3.020954	1.019577	-2.046801
9	6	0	-3.217731	0.420377	-3.293269
10	6	0	-4.027984	-0.707595	-3.387514
11	6	0	-4.625324	-1.254105	-2.247166
12	6	0	-4.409865	-0.669100	-0.994917
13	6	0	-5.735430	-2.320359	0.146320
14	6	0	-6.142488	-2.656098	1.575793
15	6	0	-7.009826	-1.583036	2.240721
16	7	0	-0.008030	1.041929	-0.066736
17	7	0	-3.418680	1.115034	0.376591
18	8	0	-1.987849	1.975851	1.936033
19	8	0	-4.912839	-1.152320	0.178526
20	1	0	0.004180	-2.831820	0.240224
21	1	0	-2.010177	-1.491067	0.926607
22	1	0	-4.386235	1.889047	2.039541
23	1	0	-5.455461	1.296439	0.755927
24	1	0	-3.758841	3.864964	0.663966
25	1	0	-5.523310	3.798189	0.853405
26	1	0	-4.780632	3.290883	-0.675625
27	1	0	-2.392336	1.899517	-1.950159
28	1	0	-2.745819	0.839383	-4.176471
29	1	0	-4.200328	-1.178981	-4.351334
30	1	0	-5.243079	-2.139603	-2.341267
31	1	0	-5.175418	-3.153455	-0.301542
32	1	0	-6.621881	-2.132080	-0.477371
33	1	0	-5.233297	-2.825576	2.166336
34	1	0	-6.681985	-3.612218	1.546484
35	1	0	-6.476691	-0.629584	2.300734
36	1	0	-7.286556	-1.880462	3.257954
37	1	0	-7.936494	-1.417880	1.676885

38	6	0	1.112797	-1.073992	-0.345601
39	6	0	1.051914	0.320397	-0.450809
40	6	0	2.166096	1.093048	-1.128758
41	6	0	4.528899	1.691873	-1.247911
42	6	0	4.644787	3.186028	-0.939275
43	6	0	3.614583	0.624839	0.810335
44	6	0	3.042119	1.326234	1.873040
45	6	0	3.256007	0.928745	3.195068
46	6	0	4.069948	-0.170601	3.453482
47	6	0	4.654038	-0.887909	2.404629
48	6	0	4.421350	-0.505438	1.079372
49	6	0	5.734721	-2.315129	0.190998
50	6	0	6.124894	-2.867689	-1.174309
51	6	0	6.999795	-1.918796	-1.999116
52	7	0	3.409702	1.043265	-0.540448
53	8	0	1.956880	1.675062	-2.186424
54	8	0	4.909320	-1.166226	-0.011011
55	1	0	2.010203	-1.603275	-0.650752
56	1	0	4.358452	1.540997	-2.316301
57	1	0	5.441825	1.160651	-0.966047
58	1	0	3.743199	3.711471	-1.267303
59	1	0	5.505001	3.614748	-1.467095
60	1	0	4.784057	3.360281	0.133503
61	1	0	2.410182	2.180044	1.648280
62	1	0	2.794130	1.479849	4.008262
63	1	0	4.255252	-0.486135	4.476687
64	1	0	5.274641	-1.747826	2.627739
65	1	0	5.182313	-3.069247	0.769213
66	1	0	6.628808	-2.032505	0.766306
67	1	0	5.208780	-3.112489	-1.726381
68	1	0	6.653189	-3.815377	-1.004336
69	1	0	6.473939	-0.982489	-2.208633
70	1	0	7.273703	-2.374354	-2.956840
71	1	0	7.927877	-1.674286	-1.467494

The total electronic energy is calculated to be -1591.30014508 hartree.



Top views Side views

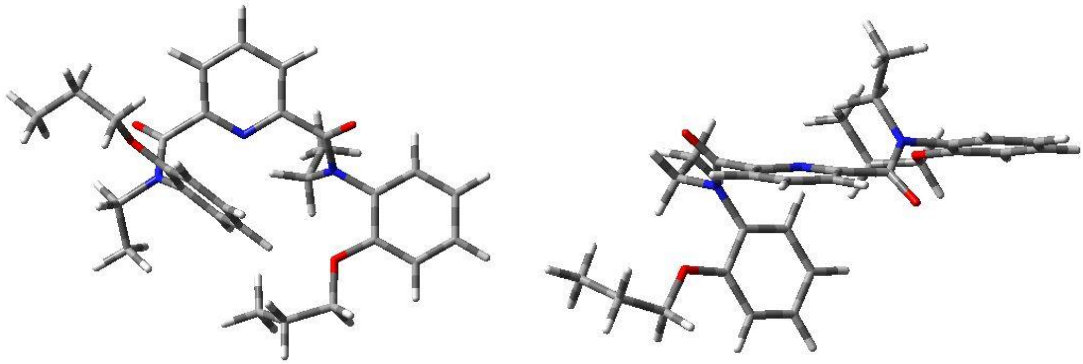
Fig. S37 Optimized rotational structure *E-anti-syn-Z* of **1a** obtained by DFT calculation at the B3LYP/6-31G(d) level.

Table S6. Atomic coordinates for the optimized structure of *E-anti-syn-Z*.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.115834	-3.010763	0.482888
2	6	0	-0.260478	-2.898972	0.652974
3	6	0	-0.898966	-1.733144	0.204784
4	6	0	-2.391666	-1.624180	0.467583
5	6	0	-2.825060	-0.452465	-1.751267
6	6	0	-3.044170	-1.505837	-2.840566
7	6	0	-4.597886	-0.850187	-0.076518
8	6	0	-5.422782	-1.972863	-0.106861
9	6	0	-6.785900	-1.871351	0.178650
10	6	0	-7.325493	-0.626866	0.494682
11	6	0	-6.515351	0.510686	0.535696
12	6	0	-5.146173	0.406747	0.260064
13	6	0	-4.755445	2.743878	0.661956
14	6	0	-3.574691	3.707454	0.664170
15	6	0	-2.923473	3.887821	-0.710458
16	7	0	-0.231849	-0.717260	-0.352905
17	7	0	-3.202866	-0.938266	-0.404405
18	8	0	-2.827154	-2.175824	1.477577
19	8	0	-4.274962	1.454415	0.284616
20	1	0	1.639115	-3.909137	0.799147
21	1	0	-0.849038	-3.675970	1.126133
22	1	0	-3.440702	0.429746	-1.946542
23	1	0	-1.787498	-0.125717	-1.727633
24	1	0	-2.403526	-2.379821	-2.675774
25	1	0	-2.794229	-1.085693	-3.821831
26	1	0	-4.086151	-1.843730	-2.869163
27	1	0	-4.978366	-2.933445	-0.345858

28	1	0	-7.414927	-2.756133	0.152975
29	1	0	-8.385210	-0.529667	0.715491
30	1	0	-6.953346	1.469268	0.788206
31	1	0	-5.212392	2.690524	1.660249
32	1	0	-5.526869	3.077588	-0.048714
33	1	0	-2.833380	3.346278	1.387749
34	1	0	-3.940278	4.672730	1.039899
35	1	0	-2.520276	2.940234	-1.079128
36	1	0	-2.100781	4.609570	-0.661197
37	1	0	-3.648693	4.257695	-1.446342
38	6	0	1.816170	-1.950249	-0.091870
39	6	0	1.096317	-0.818267	-0.487303
40	6	0	1.754363	0.322800	-1.236173
41	6	0	3.629045	1.861438	-1.500186
42	6	0	3.086978	3.282314	-1.331526
43	6	0	3.240296	0.747560	0.689431
44	6	0	2.395926	1.253101	1.679852
45	6	0	2.734158	1.160153	3.031907
46	6	0	3.944503	0.574664	3.392783
47	6	0	4.809037	0.066428	2.418334
48	6	0	4.460443	0.138191	1.065463
49	6	0	6.465773	-0.988164	0.356012
50	6	0	7.094112	-1.467924	-0.946478
51	6	0	7.446145	-0.337679	-1.918431
52	7	0	2.900778	0.863605	-0.693675
53	8	0	1.304734	0.685021	-2.317388
54	8	0	5.214080	-0.368861	0.047369
55	1	0	2.890318	-1.993108	-0.240009
56	1	0	3.543587	1.548912	-2.543191
57	1	0	4.681187	1.805439	-1.208647
58	1	0	2.046187	3.331984	-1.664313
59	1	0	3.675506	3.983750	-1.934649
60	1	0	3.140633	3.607162	-0.286414
61	1	0	1.462035	1.715674	1.374510
62	1	0	2.060926	1.550636	3.788724
63	1	0	4.227770	0.503747	4.439350
64	1	0	5.741573	-0.395038	2.721576
65	1	0	6.299851	-1.832714	1.039402
66	1	0	7.121170	-0.263647	0.861247
67	1	0	6.407336	-2.177348	-1.424945
68	1	0	7.997996	-2.033409	-0.683438
69	1	0	6.551312	0.215151	-2.219760
70	1	0	7.917880	-0.735416	-2.823381
71	1	0	8.145869	0.373418	-1.461777

The total electronic energy is calculated to be -1591.29983413 hartree.



Top views Side views

Fig. S38 Optimized rotational structure *E-syn-syn-Z* of **1a** obtained by DFT calculation at the B3LYP/6-31G(d) level.

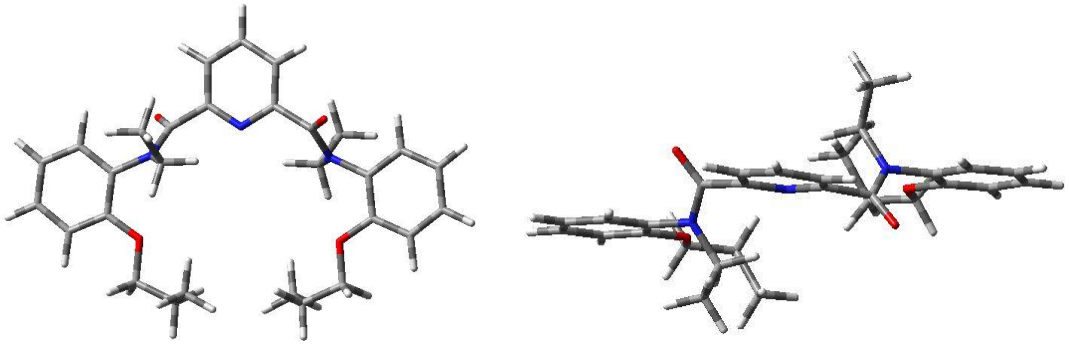
Table S7. Atomic coordinates for the optimized structure of *E-syn-syn-Z*.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.312355	-3.851537	0.241055
2	6	0	-0.020303	-3.526385	-0.165717
3	6	0	0.448619	-2.227258	0.068270
4	6	0	1.835564	-1.881363	-0.443953
5	6	0	2.438263	-0.760355	1.733840
6	6	0	2.962176	-1.867457	2.652698
7	6	0	3.941961	-0.721399	-0.230806
8	6	0	4.867312	-1.709940	-0.567948
9	6	0	6.128829	-1.378348	-1.064025
10	6	0	6.471125	-0.037601	-1.218667
11	6	0	5.561260	0.968697	-0.887092
12	6	0	4.290029	0.638100	-0.400377
13	6	0	3.658739	2.946807	-0.199049
14	6	0	2.463871	3.769191	0.267476
15	6	0	2.131384	3.591917	1.752254
16	7	0	-0.316022	-1.270433	0.610364
17	7	0	2.652420	-1.058531	0.300777
18	8	0	2.171153	-2.354948	-1.526895
19	8	0	3.340923	1.560933	-0.061162
20	1	0	-1.697996	-4.857396	0.098841
21	1	0	0.624333	-4.243981	-0.660086
22	1	0	1.375632	-0.585485	1.893164

23	1	0	2.953801	0.180169	1.938574
24	1	0	2.420356	-2.805922	2.488528
25	1	0	2.829446	-1.580670	3.702613
26	1	0	4.028498	-2.052641	2.482335
27	1	0	4.578650	-2.748330	-0.452023
28	1	0	6.833244	-2.162626	-1.324383
29	1	0	7.450119	0.238722	-1.601014
30	1	0	5.845043	2.005845	-1.019346
31	1	0	3.892889	3.167666	-1.250052
32	1	0	4.547279	3.186148	0.404172
33	1	0	1.593840	3.511137	-0.349055
34	1	0	2.693302	4.822689	0.058330
35	1	0	1.874275	2.552362	1.977265
36	1	0	1.281280	4.219901	2.040184
37	1	0	2.983601	3.872311	2.383972
38	6	0	-2.103343	-2.866443	0.828724
39	6	0	-1.571664	-1.579557	0.960402
40	6	0	-2.404559	-0.511593	1.634001
41	6	0	-3.203255	1.797638	1.729177
42	6	0	-2.332845	2.976226	2.166965
43	6	0	-2.110021	0.952189	-0.325988
44	6	0	-0.878134	1.470528	-0.720005
45	6	0	-0.602420	1.714563	-2.066972
46	6	0	-1.575208	1.438509	-3.025435
47	6	0	-2.816102	0.915356	-2.653337
48	6	0	-3.090529	0.666077	-1.303090
49	6	0	-5.284780	-0.205891	-1.767806
50	6	0	-6.462331	-0.771048	-0.982766
51	6	0	-7.111782	0.241821	-0.035043
52	7	0	-2.427602	0.738862	1.057766
53	8	0	-2.991947	-0.788683	2.676630
54	8	0	-4.261516	0.148290	-0.835850
55	1	0	-3.108266	-3.069376	1.182126
56	1	0	-3.990804	2.134563	1.045121
57	1	0	-3.682619	1.328469	2.590049
58	1	0	-1.568710	2.650797	2.881020
59	1	0	-2.952733	3.739774	2.651703
60	1	0	-1.829979	3.442355	1.312476
61	1	0	-0.124542	1.640858	0.040328
62	1	0	0.369919	2.097199	-2.361550
63	1	0	-1.372322	1.619455	-4.077572
64	1	0	-3.556620	0.699773	-3.414747
65	1	0	-4.895591	-0.950143	-2.476803
66	1	0	-5.589799	0.683269	-2.339517

67	1	0	-6.116316	-1.646374	-0.419102
68	1	0	-7.199150	-1.134655	-1.711447
69	1	0	-6.393398	0.593946	0.711086
70	1	0	-7.958560	-0.206971	0.495320
71	1	0	-7.485600	1.114462	-0.585357

The total electronic energy is calculated to be -1591.29959671 hartree.



Top views Side views

Fig. S39 Optimized rotational structure *Z-syn-syn-Z* of **1a** obtained by DFT calculation at the B3LYP/6-31G(d) level.

Table S8. Atomic coordinates for the optimized structure of *Z-syn-syn-Z*.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.000091	-4.598562	-0.000163
2	6	0	-1.156494	-3.889565	0.313156
3	6	0	-1.119850	-2.490549	0.262400
4	6	0	-2.399244	-1.760841	0.635656
5	6	0	-2.386161	-0.607136	-1.595695
6	6	0	-2.938276	-1.596330	-2.625652
7	6	0	-4.210142	-0.273042	0.058825
8	6	0	-5.314555	-1.101297	0.267306
9	6	0	-6.575971	-0.571376	0.538304
10	6	0	-6.737762	0.810594	0.594656
11	6	0	-5.649014	1.658786	0.384906
12	6	0	-4.378879	1.128446	0.122326
13	6	0	-3.392121	3.312162	-0.036812
14	6	0	-2.036431	3.927035	-0.358863
15	6	0	-1.561862	3.661223	-1.790935
16	7	0	0.000037	-1.798576	0.000091
17	7	0	-2.921285	-0.832584	-0.235768
18	8	0	-2.940434	-2.076720	1.691658

19	8	0	-3.266839	1.890645	-0.091779
20	1	0	-0.000154	-5.685087	-0.000262
21	1	0	-2.076161	-4.390865	0.593433
22	1	0	-1.298421	-0.653121	-1.546133
23	1	0	-2.649011	0.415812	-1.870473
24	1	0	-2.638682	-2.623488	-2.389150
25	1	0	-2.554787	-1.354215	-3.623711
26	1	0	-4.032552	-1.557552	-2.662376
27	1	0	-5.168863	-2.174998	0.232009
28	1	0	-7.419766	-1.234818	0.702146
29	1	0	-7.713058	1.241797	0.803734
30	1	0	-5.793594	2.731144	0.437033
31	1	0	-3.726523	3.612605	0.966220
32	1	0	-4.147518	3.648317	-0.762678
33	1	0	-1.301654	3.546537	0.360898
34	1	0	-2.119692	5.008522	-0.186110
35	1	0	-1.424969	2.590359	-1.968190
36	1	0	-0.605486	4.158987	-1.985463
37	1	0	-2.287173	4.036273	-2.523906
38	6	0	1.156371	-3.889628	-0.313358
39	6	0	1.119861	-2.490608	-0.262342
40	6	0	2.399355	-1.761006	-0.635496
41	6	0	2.386127	-0.606873	1.595664
42	6	0	2.938269	-1.595843	2.625818
43	6	0	4.210154	-0.273039	-0.058819
44	6	0	5.314616	-1.101281	-0.267065
45	6	0	6.576027	-0.571341	-0.538057
46	6	0	6.737754	0.810627	-0.594640
47	6	0	5.648952	1.658804	-0.385106
48	6	0	4.378828	1.128444	-0.122521
49	6	0	3.392021	3.312133	0.036612
50	6	0	2.036348	3.926958	0.358827
51	6	0	1.561946	3.661048	1.790934
52	7	0	2.921270	-0.832536	0.235779
53	8	0	2.940732	-2.077130	-1.691334
54	8	0	3.266749	1.890611	0.091475
55	1	0	2.075987	-4.390946	-0.593763
56	1	0	1.298388	-0.652896	1.546117
57	1	0	2.648943	0.416136	1.870246
58	1	0	2.638796	-2.623067	2.389456
59	1	0	2.554667	-1.353605	3.623805
60	1	0	4.032538	-1.556951	2.662631
61	1	0	5.168972	-2.174982	-0.231603
62	1	0	7.419867	-1.234771	-0.701722

63	1	0	7.713046	1.241839	-0.803722
64	1	0	5.793485	2.731161	-0.437395
65	1	0	3.726348	3.612655	-0.966425
66	1	0	4.147469	3.648237	0.762449
67	1	0	1.301508	3.546476	-0.360884
68	1	0	2.119564	5.008455	0.186119
69	1	0	1.425083	2.590171	1.968132
70	1	0	0.605591	4.158794	1.985615
71	1	0	2.287344	4.036050	2.523844

The total electronic energy is calculated to be -1591.29308507 hartree.

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