

## Molecular structure and ultrasound-assisted synthesis of the diazacrown derivative containing 2,3,4,6-tetraaryl- $\gamma$ -piperidone

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### 1. Experimental Data

#### Chemicals and solvents

All organic reagents and solvents were purchased from commercial sources (Merck, Sigma-Aldrich) and used without any additional purification.

#### Synthesis

15-Tosyl-30,32-diphenyl-12,18-dioxa-15,33-diazahehexacyclo[27.3.1.0<sup>2,11</sup>.0<sup>3,8</sup>.0<sup>19,28</sup>.0<sup>22,27</sup>]-tritricon-2,4,6,8,10,19(20),21,23,25,27-decaen-31-one (2<sup>3</sup>,2<sup>5</sup>-diphenyl-7-tosyl-4,10-dioxa-7-aza-2(2,6)-piperidina-1(2,1),3(1,2)-dinaphthalenacyclodecaphan-2<sup>4</sup>-one) **2**. In a round bottom flask were placed 1,5-bis(1-formylnaphthalen-2-yloxy)-3-tosyl-3-azapentane (0.5 g, 0.88 mmol), dibenzyl ketone (0.18 g, 0.88 mmol), ammonium acetate (1.35 g, 17.6 mmol), MeCN (7 ml) and acetic acid (1.5 ml). This mixture was heated at 50 °C using ultrasonic bath for 2.5 h. After the reaction was finished, dilute solution of K<sub>2</sub>CO<sub>3</sub> (5%, w/v) was added to neutralize the reaction mixture affording a yellowish sticky residue. This residue was separated by decanting, then dissolved and extracted with DCM (3×10 ml). Removing solvent *in vacuo* afforded a crude product which was purified by column chromatography using ethyl acetate/hexane (1:1, v/v) as eluent. The desired solids were collected and recrystallized in CH<sub>2</sub>Cl<sub>2</sub>/methanol solvents giving white precipitates in the yield of 0.30 g (45%); R<sub>f</sub> = 0.4 (ethyl acetate/hexane (1:1, v/v); mp = 292–294 °C (lit.<sup>10</sup> mp 293–295 °C).

<sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 298 K),  $\delta_{\text{H}}$ , ppm: 2.48 (3H, s, CH<sub>3</sub>), 3.39–3.43 (2H, m, 2xH-16), 3.99 – 4.04 (2H,m, 2xH-14), 4.57 (2H t,  $J$ = 8.8 Hz, 2xH-13), 4.64 – 4.67 (2H,m, 2xH-19), 4.75 (1H, t,  $J$ = 12.4 Hz, NH-33), 5.32 (2H, d,  $J$ = 10.9 Hz, H-30, H-32,), 5.79 (2H,t, H-1, H-29,  $J$ = 11.8 Hz), 6.84 (2H, t,  $J$ = 7.4 Hz, ArH), 6.96 (4H, t,  $J$ = 7.5 Hz, ArH), 7.23 (2H,t,  $J$ = 7.4 Hz, ArH,), 7.29 (4H, d,  $J$ = 7.6 Hz, ArH), 7.40 (2H, ddd,  $J$ = 8.5, 6.8 & 1.3 Hz, H-6, H-24), 7.47 (2H, d,  $J$ = 9.1 Hz, 2xH $\beta$ ), 7.56 (2H, d,  $J$ = 7.9 Hz, H-10, H-20), 7.65 (2H, d,  $J$ = 8.1 Hz, H-9, H-21), 7.70 (2H, d,  $J$ = 9.1 Hz, 2xH $\alpha$ ), 7.94 (2H, d,  $J$ = 8.0 Hz, H-7, H-23,), 8.8 (2H, d,  $J$ = 8.9 Hz, H-4, H-26,). <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>)  $\delta_{\text{C}}$  ppm: 154.07, 144.71, 132.40, 130.11, 129.59, 129.51, 128.18, 127.87, 127.47, 126.43, 126.28, 123.57, 123.07, 114.05, 67.67, 62.31, 61.81, 51.99, 21.54, 13.82.  $m/z$  (ESI) (%), Found,  $m/z$ : 759.2892 (100) [M+H]<sup>+</sup>. C<sub>48</sub>H<sub>43</sub>N<sub>2</sub>O<sub>5</sub>S, Calculated,  $m/z$ : 759.2887 and Found,  $m/z$ : 791.2799 [M+CH<sub>3</sub>OH+H]<sup>+</sup> (15). C<sub>49</sub>H<sub>47</sub>N<sub>2</sub>O<sub>6</sub>S. Calculated,  $m/z$ : 791.3149.

#### Instruments and methods

TLC analysis was performed on commercially prepared silica gel plates (Merck, F254) and visualized by either UV irradiation or staining with I<sub>2</sub>. Silica gel (0.063–0.2 mm) was used for column chromatography. Melting point of the synthetic molecule was determined in capillary tubes on a digital Stuart SMP3 apparatus. Elemental analysis was conducted on Euro Vector EA-3000 analyzer. The LC/MS analysis was performed using an Agilent LC/MSD VL mass spectrometer (ionization in ESI mode). <sup>1</sup>H NMR spectra were recorded on a Bruker Advance 500 spectrometer (500 MHz) in DMSO at 25 °C with TMS used as internal standard.

Single crystal X-ray diffraction data for compound **2** were collected on Bruker D8 QUEST instrument at 100 K with Mo- K $\alpha$  radiation ( $\lambda=0.71073$  Å) using a TRIUMPH monochromator. Structure solution and refinement were performed with the SHELXT and SHELXL 2014/7 programs. The colorless prismatic crystal of **2** (C<sub>48</sub>H<sub>42</sub>N<sub>2</sub>O<sub>5</sub>S,  $M = 758.90$ ) is triclinic, space group  $P-1$ , at  $T = 100$  K:  $a = 11.9057(10)$  Å,  $b = 14.2125(14)$  Å,  $c = 14.2658(13)$  Å,  $\alpha = 62.714(5)^\circ$ ,  $\beta = 74.391(5)^\circ$ ,  $\gamma = 68.364(5)^\circ$ ,  $V = 1979.5(3)$  Å<sup>3</sup>,  $Z = 2$ ,  $d_{\text{calc}} = 1.273$  g cm<sup>-3</sup>,  $F(000) = 800$ ,  $\mu = 0.133$  mm<sup>-1</sup>. A total of 92037 reflection intensities (12149 independent reflections,  $R_{\text{int}} = 0.0658$ ) were measured using a Bruker D8 QUEST diffractometer ( $\lambda(\text{MoK}\alpha)$ -radiation, graphite monochromator,  $\omega$  and  $\varphi$  scanning mode) and corrected for absorption using the SADABS program ( $T_{\text{min}} = 0.953$ ;  $T_{\text{max}} = 0.986$ ). The structure was determined by direct methods and refined by a full-matrix least squares technique on  $F^2$  with anisotropic displacement parameters for non-hydrogen atoms. The carbonyl, tolyl and one of the two phenyl substituents are disordered over two sites each with the occupancies of 0.857(6)/0.143(6), 0.647(5)/0.353(5), and 0.726(16)/0.274(16), respectively. The crystal contained two solvate water molecules, which were strongly disordered. Unfortunately, all attempts to model and refine positions of the solvate molecules were unsuccessful. Therefore, their contribution to the total scattering pattern was removed by use of the utility SQUEEZE in PLATON15. The hydrogen atom of the NH-group was localized in the difference-Fourier map and included into the refinement with fixed positional and isotropic displacement parameters [ $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ ]. The other hydrogen atoms were placed in calculated positions and refined within riding model with fixed isotropic displacement parameters [ $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ ]. The final divergence factors were  $R_1 = 0.0655$  for 7285 independent reflections with  $I > 2\sigma(I)$  and  $wR_2 = 0.1525$  for all independent reflections,  $S = 1.030$ . Crystallographic data for **2** have been deposited with the Cambridge Crystallographic Data Center. CCDC 2213231 contains supplementary crystallographic data for this paper. These data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or [www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

## 2. Spectral data of compound 2

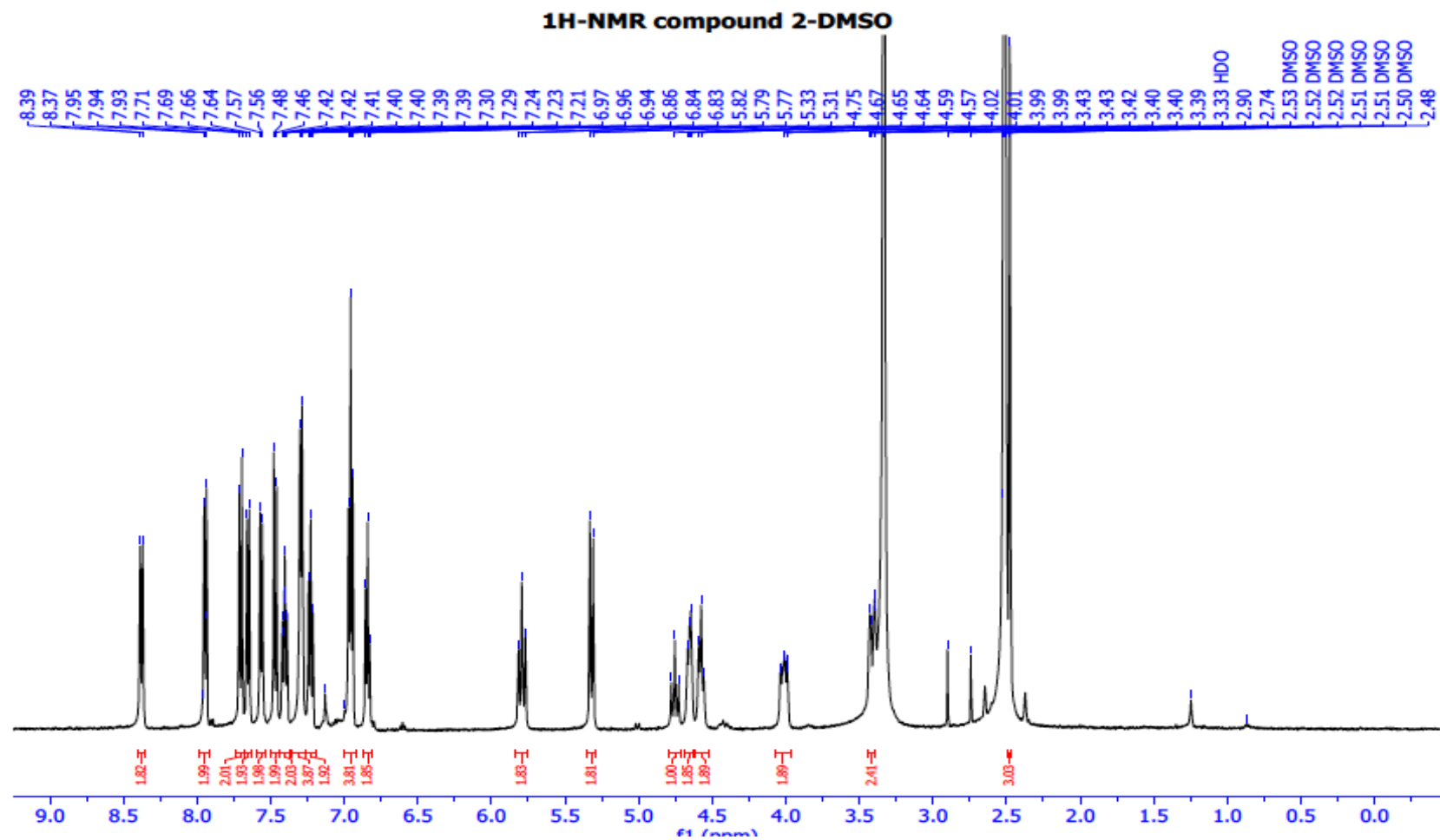


Figure S1. <sup>1</sup>H-NMR of compound 2

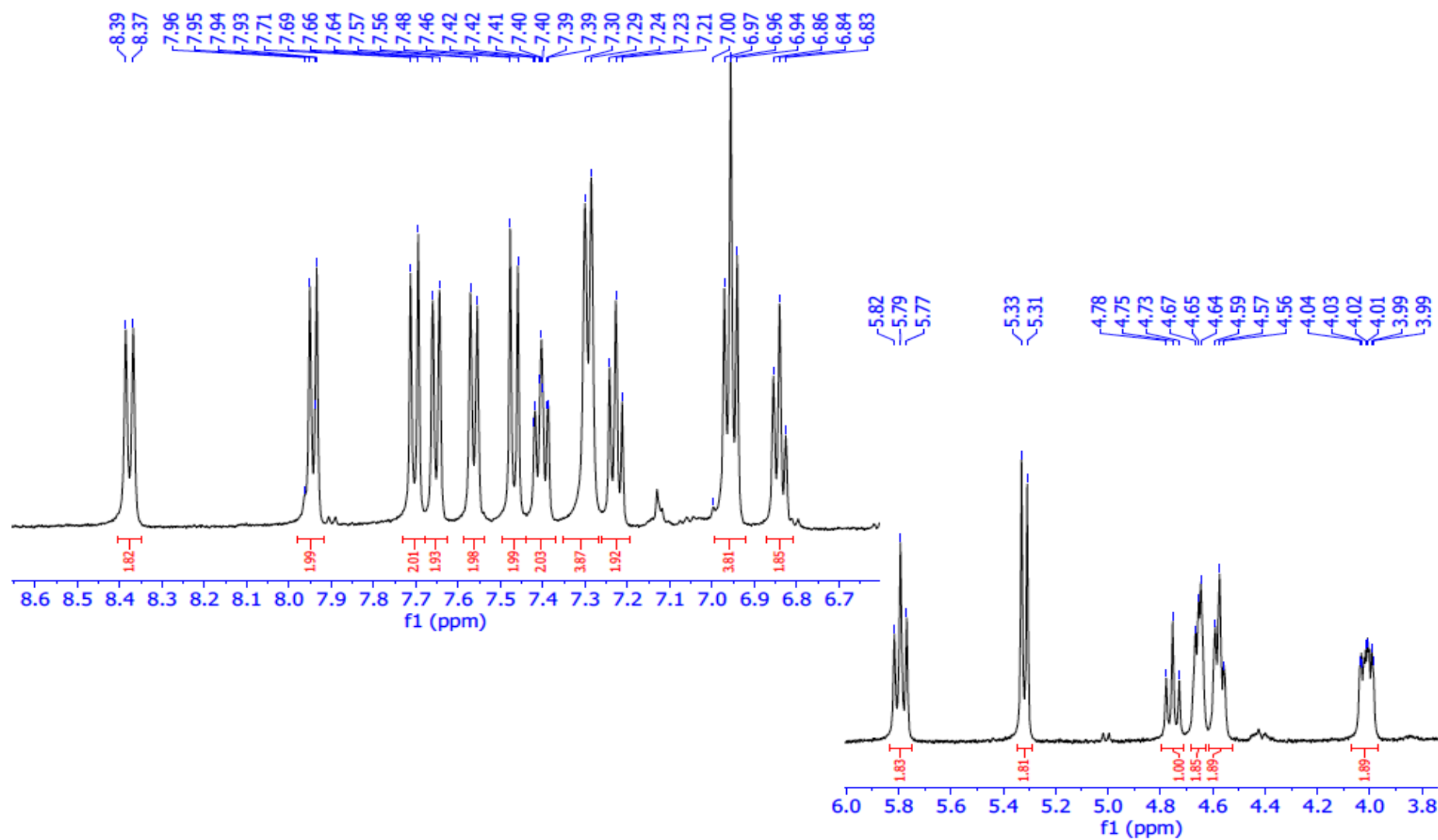


Figure S2.  $^1\text{H}$ -NMR of compound 2 (continued)

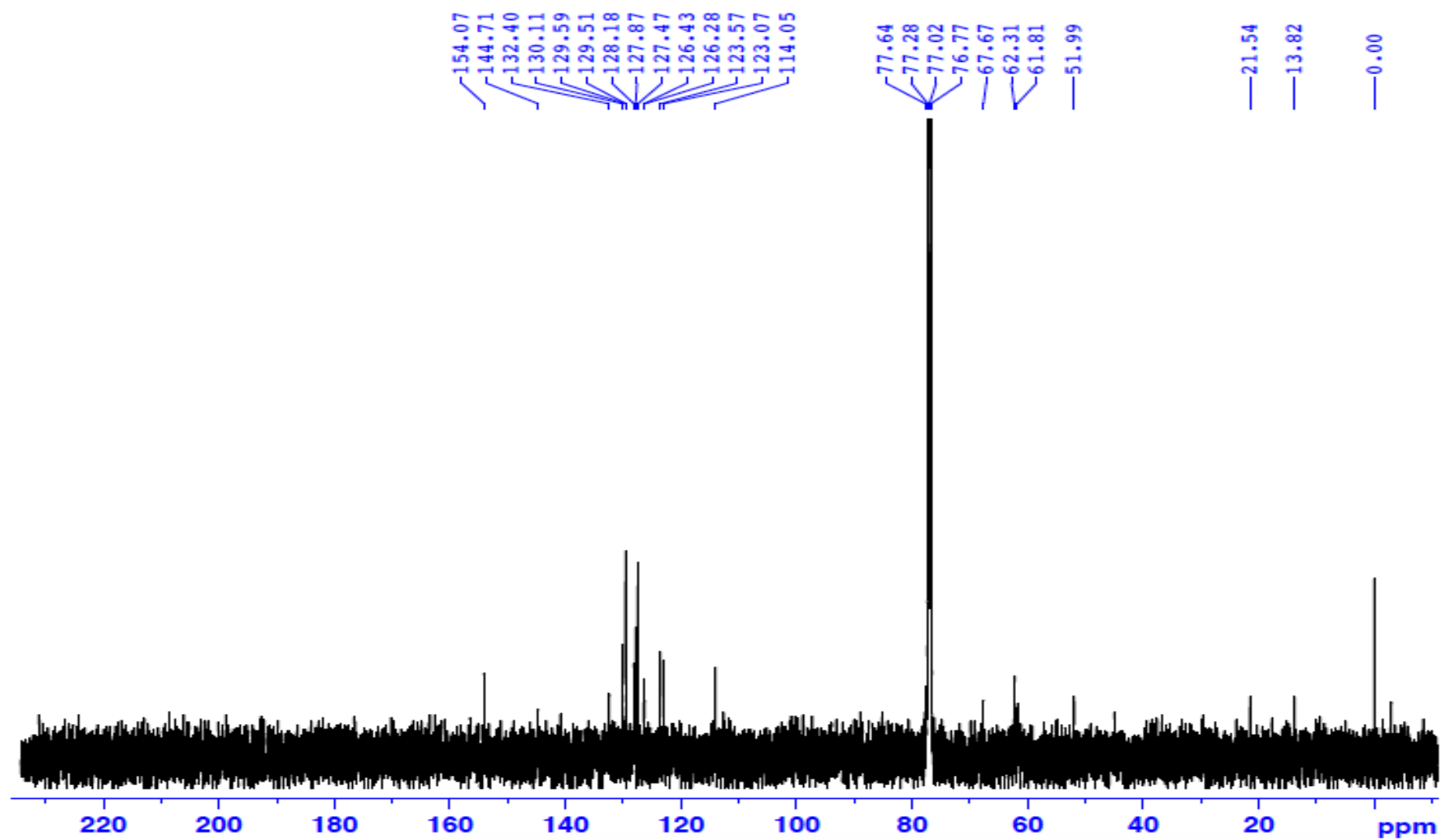
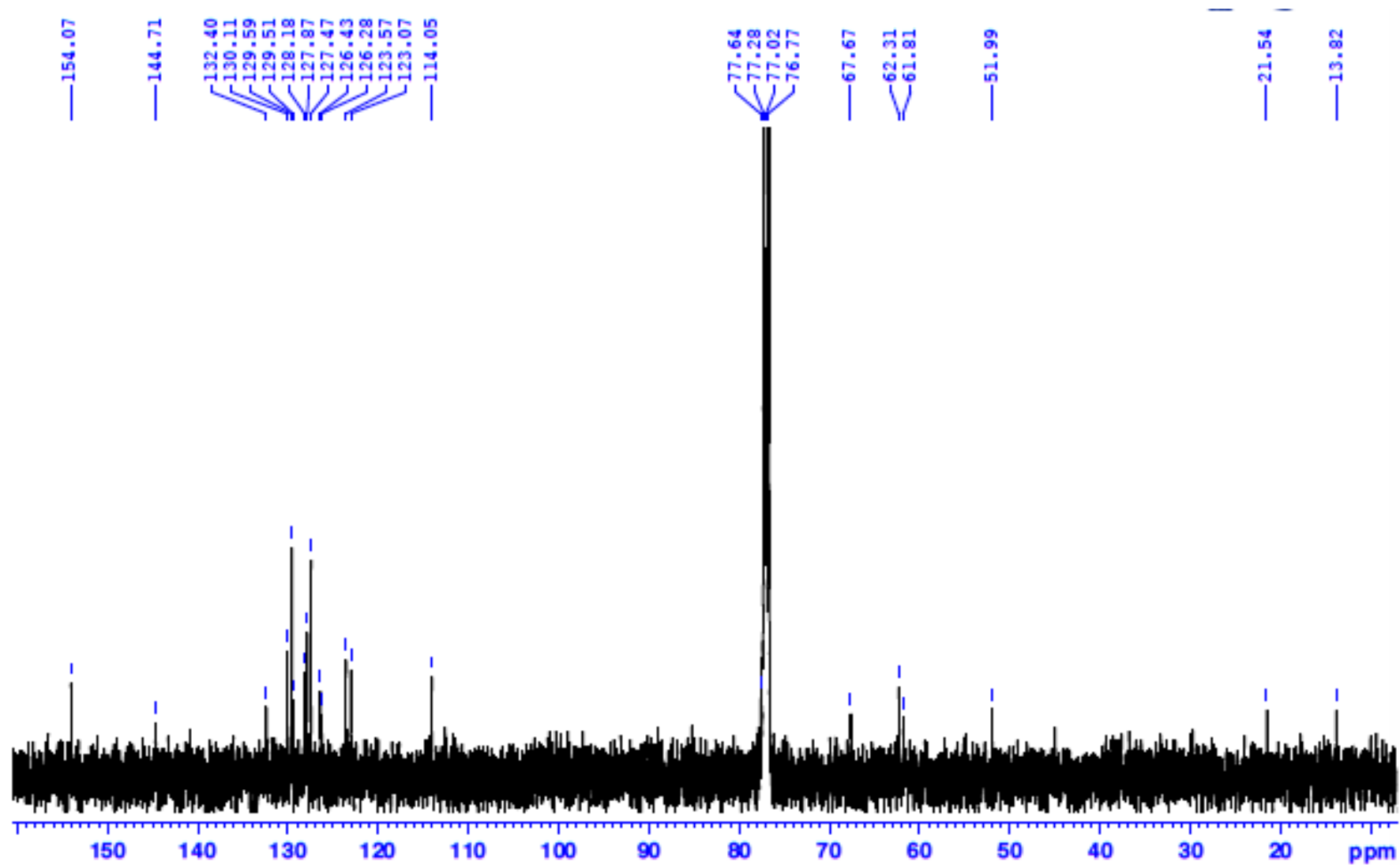


Figure S3.  $^{13}\text{C}$ -NMR of compound 2



**Figure S4.**  $^{13}\text{C}$ -NMR of compound 2 (continued)

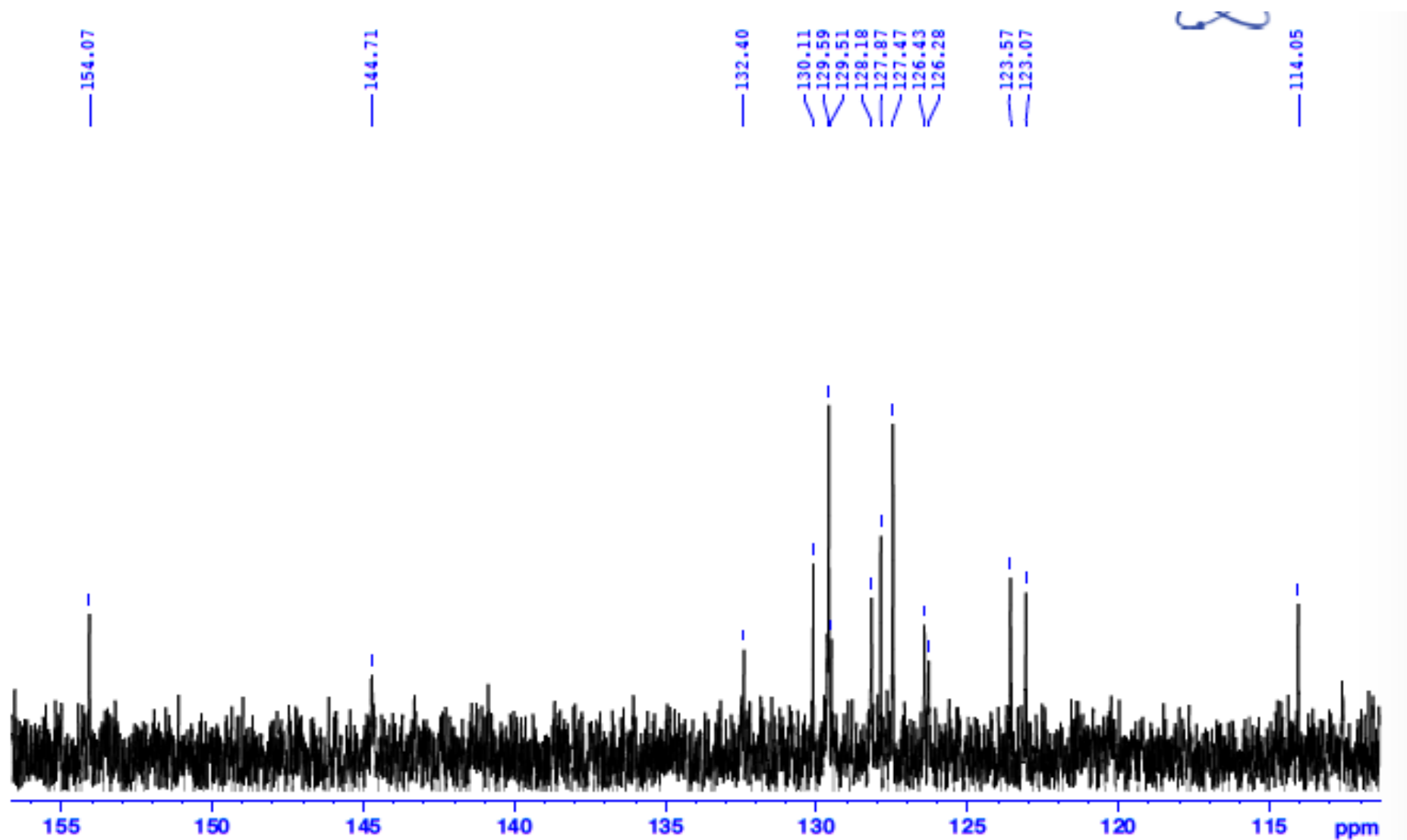


Figure S5.  $^{13}\text{C}$ -NMR of compound 2 (continued)

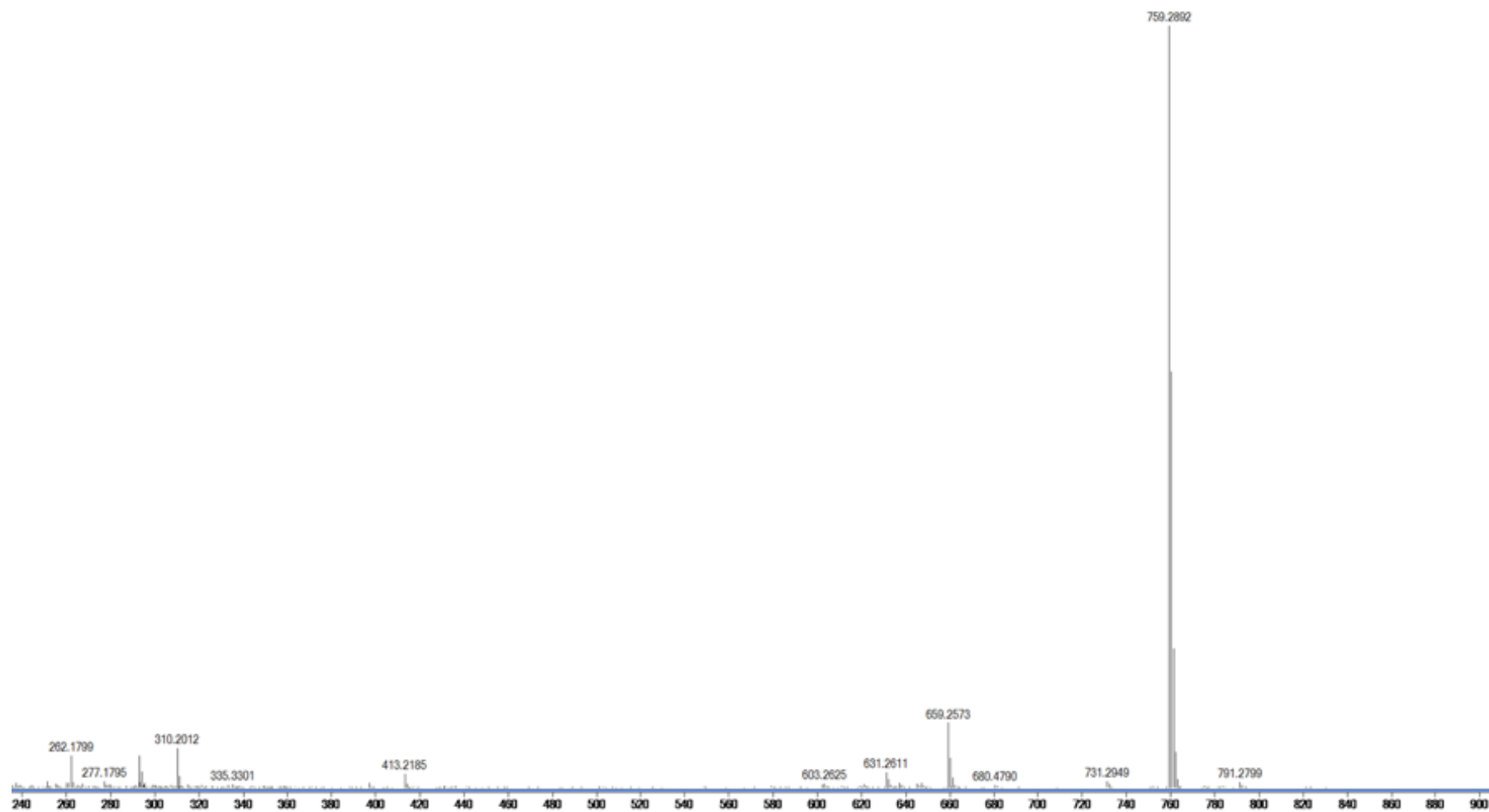


Figure S6. HRMS of compound 2



### 3. X-ray crystallographic data of compound 2

**Table S1.** Experimental details

|                                                                                                                |                                                                 |
|----------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------|
| Crystal data of diazacrown 2                                                                                   |                                                                 |
| Chemical formula                                                                                               | C <sub>48</sub> H <sub>43</sub> N <sub>2</sub> O <sub>5</sub> S |
| <i>M<sub>r</sub></i>                                                                                           | 759.90                                                          |
| Crystal system, space group                                                                                    | Triclinic, <i>P</i> <sup>−</sup> 1                              |
| Temperature (K)                                                                                                | 273                                                             |
| <i>a</i> , <i>b</i> , <i>c</i> (Å)                                                                             | 11.906 (2), 14.212 (2), 14.266 (2)                              |
| α, β, γ (°)                                                                                                    | 62.714 (5), 74.391 (5), 68.364 (5)                              |
| <i>V</i> (Å <sup>3</sup> )                                                                                     | 1979.5 (6)                                                      |
| <i>Z</i>                                                                                                       | 2                                                               |
| Radiation type                                                                                                 | Mo <i>K</i> α                                                   |
| μ (mm <sup>−1</sup> )                                                                                          | 0.13                                                            |
| Crystal size (mm)                                                                                              | 0.25 × 0.17 × 0.05                                              |
| Data collection                                                                                                |                                                                 |
| Diffractometer                                                                                                 | Bruker APEX-II CCD                                              |
| Absorption correction                                                                                          | —                                                               |
| No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections                             | 92071, 12157, 7293                                              |
| <i>R</i> <sub>int</sub>                                                                                        | 0.066                                                           |
| (sin θ/λ) <sub>max</sub> (Å <sup>−1</sup> )                                                                    | 0.716                                                           |
| Refinement                                                                                                     |                                                                 |
| <i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i> | 0.070, 0.177, 1.03                                              |
| No. of reflections                                                                                             | 12157                                                           |
| No. of parameters                                                                                              | 626                                                             |
| No. of restraints                                                                                              | 127                                                             |
| H-atom treatment                                                                                               | H-atom parameters constrained                                   |
| Δ <sub>max</sub> , Δ <sub>min</sub> (e Å <sup>−3</sup> )                                                       | 0.84, −0.72                                                     |

**Table S2.** Crystal data

|                                |                                                         |
|--------------------------------|---------------------------------------------------------|
| $C_{48}H_{43}N_2O_5S$          | $Z = 2$                                                 |
| $M_r = 759.90$                 | $F(000) = 802$                                          |
| Triclinic, $P\bar{1}$          | $D_x = 1.275 \text{ Mg m}^{-3}$                         |
| $a = 11.906 (2) \text{ \AA}$   | Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$ |
| $b = 14.212 (2) \text{ \AA}$   | Cell parameters from 9814 reflections                   |
| $c = 14.266 (2) \text{ \AA}$   | $\theta = 2.6\text{--}30.0^\circ$                       |
| $\alpha = 62.714 (5)^\circ$    | $\mu = 0.13 \text{ mm}^{-1}$                            |
| $\beta = 74.391 (5)^\circ$     | $T = 273 \text{ K}$                                     |
| $\gamma = 68.364 (5)^\circ$    | Block, colourless                                       |
| $V = 1979.5 (6) \text{ \AA}^3$ | $0.25 \times 0.17 \times 0.05 \text{ mm}$               |

**Data collection**

|                                        |                                                                        |
|----------------------------------------|------------------------------------------------------------------------|
| Bruker APEX-II CCD diffractometer      | $R_{\text{int}} = 0.066$                                               |
| $\phi$ and $\omega$ scans              | $\theta_{\text{max}} = 30.6^\circ$ , $\theta_{\text{min}} = 2.6^\circ$ |
| 92071 measured reflections             | $h = -17 \rightarrow 17$                                               |
| 12157 independent reflections          | $k = -20 \rightarrow 20$                                               |
| 7293 reflections with $I > 2\sigma(I)$ | $l = -20 \rightarrow 20$                                               |

**Refinement**

|                                 |                                                                                  |
|---------------------------------|----------------------------------------------------------------------------------|
| Refinement on $F^2$             | 127 restraints                                                                   |
| Least-squares matrix: full      | Hydrogen site location: inferred from neighbouring sites                         |
| $R[F^2 > 2\sigma(F^2)] = 0.070$ | H-atom parameters constrained                                                    |
| $wR(F^2) = 0.177$               | $w = 1/[\sigma^2(F_o^2) + (0.0616P)^2 + 1.6369P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.03$                      | $(\Delta/\sigma)_{\text{max}} < 0.001$                                           |
| 12157 reflections               | $\Delta_{\text{max}} = 0.84 \text{ e \AA}^{-3}$                                  |
| 626 parameters                  | $\Delta_{\text{min}} = -0.72 \text{ e \AA}^{-3}$                                 |

**Table S3.** Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for compound 2

|      | x            | y            | z             | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1)  |
|------|--------------|--------------|---------------|----------------------------------|------------|
| S01  | 0.25628 (6)  | 0.98256 (4)  | 0.47531 (4)   | 0.03962 (16)                     |            |
| O002 | 0.48982 (13) | 0.83103 (11) | 0.25948 (11)  | 0.0297 (3)                       |            |
| O003 | 0.19781 (12) | 0.78298 (13) | 0.34277 (12)  | 0.0338 (3)                       |            |
| O004 | 0.34111 (16) | 1.04590 (12) | 0.41926 (12)  | 0.0434 (4)                       |            |
| N005 | 0.38779 (14) | 0.72606 (13) | 0.19275 (12)  | 0.0238 (3)                       |            |
| H00A | 0.368402     | 0.763476     | 0.233383      | 0.029*                           |            |
| H00B | 0.363544     | 0.773415     | 0.129419      | 0.029*                           |            |
| N006 | 0.30528 (15) | 0.87572 (13) | 0.44378 (13)  | 0.0278 (4)                       |            |
| O007 | 0.13109 (17) | 1.03200 (14) | 0.45974 (17)  | 0.0627 (6)                       |            |
| O008 | 0.53682 (16) | 0.43083 (16) | 0.42985 (16)  | 0.0685 (7)                       |            |
| C009 | 0.57875 (16) | 0.77220 (15) | 0.12012 (14)  | 0.0222 (4)                       |            |
| C00A | 0.55867 (17) | 0.84877 (16) | 0.16174 (15)  | 0.0250 (4)                       |            |
| C00B | 0.32388 (16) | 0.64156 (15) | 0.24068 (15)  | 0.0234 (4)                       |            |
| H00C | 0.349125     | 0.600653     | 0.195246      | 0.028*                           |            |
| C00C | 0.64588 (17) | 0.78972 (16) | 0.01660 (15)  | 0.0262 (4)                       |            |
| C00D | 0.18747 (17) | 0.69634 (16) | 0.23921 (15)  | 0.0262 (4)                       |            |
| C00E | 0.35694 (17) | 0.55625 (15) | 0.35354 (15)  | 0.0245 (4)                       |            |
| H00E | 0.317627     | 0.594144     | 0.401647      | 0.029*                           |            |
| C00F | 0.52015 (16) | 0.67843 (15) | 0.18010 (14)  | 0.0219 (4)                       |            |
| H00F | 0.538298     | 0.638430     | 0.134725      | 0.026*                           |            |
| C00G | 0.57199 (16) | 0.59332 (15) | 0.28690 (15)  | 0.0235 (4)                       |            |
| H00G | 0.579580     | 0.633801     | 0.323902      | 0.028*                           | 0.200 (14) |
| H00D | 0.570662     | 0.637071     | 0.324141      | 0.028*                           | 0.800 (14) |
| C00H | 0.60119 (18) | 0.94342 (16) | 0.10467 (17)  | 0.0311 (4)                       |            |
| H00H | 0.587842     | 0.992907     | 0.134910      | 0.037*                           |            |
| C00I | 0.30314 (17) | 0.46152 (16) | 0.39103 (16)  | 0.0277 (4)                       |            |
| C00J | 0.12873 (17) | 0.76856 (17) | 0.28886 (16)  | 0.0303 (4)                       |            |
| C00K | 0.68663 (17) | 0.88643 (17) | -0.04143 (15) | 0.0301 (4)                       |            |
| C00L | 0.11953 (18) | 0.68038 (17) | 0.18147 (16)  | 0.0305 (4)                       |            |
| C00M | 0.66200 (19) | 0.96141 (17) | 0.00481 (17)  | 0.0339 (5)                       |            |
| H00M | 0.687633     | 1.024801     | -0.033364     | 0.041*                           |            |
| C00N | 0.43964 (19) | 0.82819 (17) | 0.43370 (16)  | 0.0303 (4)                       |            |
| H00I | 0.458958     | 0.749473     | 0.453258      | 0.036*                           |            |
| H00J | 0.471789     | 0.837741     | 0.483420      | 0.036*                           |            |
| C00O | 0.67629 (19) | 0.71442 (19) | -0.03222 (17) | 0.0344 (5)                       |            |
| H00O | 0.652300     | 0.650069     | 0.004093      | 0.041*                           |            |
| C00P | 0.49285 (19) | 0.51767 (17) | 0.36042 (17)  | 0.0331 (5)                       |            |
| C14  | 0.708 (4)    | 0.516 (3)    | 0.261 (3)     | 0.046 (5)                        | 0.200 (14) |
| C00R | 0.50210 (19) | 0.87991 (17) | 0.32302 (16)  | 0.0304 (4)                       |            |
| H00K | 0.464608     | 0.959145     | 0.292861      | 0.037*                           |            |
| H00L | 0.587483     | 0.866337     | 0.325585      | 0.037*                           |            |
| C00S | 0.2287 (2)   | 0.79914 (18) | 0.49287 (16)  | 0.0337 (5)                       |            |
| H00N | 0.186264     | 0.803346     | 0.559800      | 0.040*                           |            |
| H00P | 0.281310     | 0.724257     | 0.508468      | 0.040*                           |            |
| C00T | 0.1690 (2)   | 0.60473 (19) | 0.13134 (18)  | 0.0369 (5)                       |            |
| H00T | 0.248297     | 0.558962     | 0.139707      | 0.044*                           |            |
| C00U | 0.13596 (19) | 0.8222 (2)   | 0.42481 (18)  | 0.0378 (5)                       |            |
| H00Q | 0.074507     | 0.784797     | 0.467910      | 0.045*                           |            |
| H00R | 0.096061     | 0.900912     | 0.393588      | 0.045*                           |            |
| C00V | 0.3551 (2)   | 0.37842 (18) | 0.35374 (19)  | 0.0412 (5)                       |            |
| H00V | 0.426939     | 0.378493     | 0.307381      | 0.049*                           |            |
| C00W | 0.7402 (2)   | 0.7346 (2)   | -0.13162 (18) | 0.0447 (6)                       |            |
| H00W | 0.757975     | 0.684235     | -0.161813     | 0.054*                           |            |
| C00X | 0.00429 (19) | 0.8279 (2)   | 0.2824 (2)    | 0.0421 (5)                       |            |
| H00X | -0.033955    | 0.874939     | 0.317516      | 0.051*                           |            |
| C00Y | -0.0051 (2)  | 0.7436 (2)   | 0.1723 (2)    | 0.0406 (5)                       |            |

|      |             |             |               |             |            |
|------|-------------|-------------|---------------|-------------|------------|
| C00Z | 0.7791 (2)  | 0.8303 (2)  | -0.18854 (18) | 0.0472 (6)  |            |
| H00Z | 0.822737    | 0.842969    | -0.255789     | 0.057*      |            |
| C010 | 0.7527 (2)  | 0.9039 (2)  | -0.14470 (17) | 0.0430 (6)  |            |
| H010 | 0.778158    | 0.967316    | -0.182867     | 0.052*      |            |
| C011 | 0.1026 (2)  | 0.5978 (2)  | 0.0711 (2)    | 0.0458 (6)  |            |
| H011 | 0.137997    | 0.548814    | 0.037902      | 0.055*      |            |
| C012 | -0.0594 (2) | 0.8154 (2)  | 0.2243 (2)    | 0.0484 (6)  |            |
| H012 | -0.140874   | 0.855734    | 0.219102      | 0.058*      |            |
| C2   | 0.2408 (15) | 0.9373 (16) | 0.6117 (8)    | 0.048 (3)   | 0.429 (13) |
| C014 | -0.0186 (2) | 0.6640 (2)  | 0.0588 (2)    | 0.0534 (7)  |            |
| H014 | -0.062482   | 0.660311    | 0.016220      | 0.064*      |            |
| C015 | 0.1961 (2)  | 0.4599 (2)  | 0.4583 (2)    | 0.0559 (8)  |            |
| H015 | 0.158265    | 0.515812    | 0.482909      | 0.067*      |            |
| C016 | -0.0706 (2) | 0.7329 (2)  | 0.1096 (2)    | 0.0532 (7)  |            |
| H016 | -0.151588   | 0.774492    | 0.103280      | 0.064*      |            |
| C017 | 0.3019 (3)  | 0.2952 (2)  | 0.3842 (2)    | 0.0541 (7)  |            |
| H017 | 0.337395    | 0.240755    | 0.357565      | 0.065*      |            |
| C15  | 0.803 (2)   | 0.523 (2)   | 0.2797 (19)   | 0.053 (4)   | 0.200 (14) |
| H15  | 0.797506    | 0.574472    | 0.305141      | 0.064*      | 0.200 (14) |
| C19  | 0.6978 (17) | 0.4498 (18) | 0.2178 (18)   | 0.044 (4)   | 0.200 (14) |
| H19  | 0.624348    | 0.452282    | 0.204365      | 0.053*      | 0.200 (14) |
| C5   | 0.3368 (17) | 0.9318 (12) | 0.6466 (10)   | 0.066 (4)   | 0.429 (13) |
| H5   | 0.405523    | 0.947322    | 0.600113      | 0.079*      | 0.429 (13) |
| C01B | 0.1972 (3)  | 0.2933 (2)  | 0.4536 (3)    | 0.0690 (10) |            |
| H01B | 0.162521    | 0.236382    | 0.475803      | 0.083*      |            |
| C18  | 0.8077 (18) | 0.3804 (15) | 0.1978 (16)   | 0.055 (4)   | 0.200 (14) |
| H18  | 0.810282    | 0.331606    | 0.170261      | 0.066*      | 0.200 (14) |
| C01D | 0.1438 (3)  | 0.3752 (3)  | 0.4901 (3)    | 0.0824 (12) |            |
| H01D | 0.072015    | 0.374487    | 0.536554      | 0.099*      |            |
| C0   | 0.1346 (12) | 0.9192 (7)  | 0.6727 (7)    | 0.048 (2)   | 0.429 (13) |
| H0   | 0.069631    | 0.925140    | 0.643884      | 0.057*      | 0.429 (13) |
| C17  | 0.915 (2)   | 0.381 (2)   | 0.217 (2)     | 0.058 (5)   | 0.200 (14) |
| H17  | 0.988942    | 0.334197    | 0.201284      | 0.069*      | 0.200 (14) |
| C4   | 0.3312 (19) | 0.9014 (13) | 0.7566 (7)    | 0.093 (5)   | 0.429 (13) |
| H4   | 0.398286    | 0.892558    | 0.784588      | 0.112*      | 0.429 (13) |
| C16  | 0.9137 (17) | 0.451 (2)   | 0.2614 (18)   | 0.057 (5)   | 0.200 (14) |
| H16  | 0.984887    | 0.449926    | 0.277817      | 0.068*      | 0.200 (14) |
| C1   | 0.1295 (16) | 0.8912 (8)  | 0.7807 (7)    | 0.068 (3)   | 0.429 (13) |
| H1   | 0.059874    | 0.876359    | 0.825898      | 0.082*      | 0.429 (13) |
| C3   | 0.225 (2)   | 0.8851 (11) | 0.8219 (7)    | 0.082 (5)   | 0.429 (13) |
| C6   | 0.214 (2)   | 0.8641 (13) | 0.9382 (6)    | 0.135 (9)   | 0.429 (13) |
| H6A  | 0.292774    | 0.828257    | 0.962185      | 0.202*      | 0.429 (13) |
| H6B  | 0.161520    | 0.817542    | 0.979762      | 0.202*      | 0.429 (13) |
| H6C  | 0.179752    | 0.933113    | 0.945917      | 0.202*      | 0.429 (13) |
| C7   | 0.1854 (6)  | 0.9008 (6)  | 0.6938 (6)    | 0.0385 (14) | 0.571 (13) |
| H7   | 0.111500    | 0.908773    | 0.676561      | 0.046*      | 0.571 (13) |
| C8   | 0.2016 (8)  | 0.8588 (6)  | 0.8002 (5)    | 0.0472 (16) | 0.571 (13) |
| H8   | 0.137399    | 0.841530    | 0.852543      | 0.057*      | 0.571 (13) |
| C9   | 0.3117 (8)  | 0.8421 (6)  | 0.8296 (4)    | 0.0480 (16) | 0.571 (13) |
| C10  | 0.4054 (7)  | 0.8712 (5)  | 0.7490 (5)    | 0.0450 (14) | 0.571 (13) |
| H10  | 0.479901    | 0.860746    | 0.767040      | 0.054*      | 0.571 (13) |
| C11  | 0.3897 (6)  | 0.9154 (8)  | 0.6426 (6)    | 0.0365 (14) | 0.571 (13) |
| H11  | 0.453557    | 0.934682    | 0.590873      | 0.044*      | 0.571 (13) |
| C12  | 0.3306 (10) | 0.7950 (8)  | 0.9454 (4)    | 0.080 (3)   | 0.571 (13) |
| H12A | 0.253986    | 0.813218    | 0.986606      | 0.119*      | 0.571 (13) |
| H12B | 0.386035    | 0.825907    | 0.951923      | 0.119*      | 0.571 (13) |
| H12C | 0.363719    | 0.716143    | 0.970875      | 0.119*      | 0.571 (13) |
| C13  | 0.2790 (8)  | 0.9317 (12) | 0.6113 (6)    | 0.0338 (17) | 0.571 (13) |
| C1A  | 0.7010 (8)  | 0.5282 (5)  | 0.2740 (5)    | 0.0282 (11) | 0.800 (14) |

|     |            |            |            |             |            |
|-----|------------|------------|------------|-------------|------------|
| C1B | 0.7907 (5) | 0.5393 (4) | 0.3118 (5) | 0.0474 (12) | 0.800 (14) |
| H1B | 0.769029   | 0.590899   | 0.341213   | 0.057*      | 0.800 (14) |
| C1C | 0.9115 (4) | 0.4750 (4) | 0.3066 (6) | 0.0699 (17) | 0.800 (14) |
| H1C | 0.969043   | 0.482837   | 0.333475   | 0.084*      | 0.800 (14) |
| C1D | 0.9453 (5) | 0.3994 (4) | 0.2611 (6) | 0.068 (2)   | 0.800 (14) |
| H1D | 1.025801   | 0.356603   | 0.257131   | 0.082*      | 0.800 (14) |
| C1E | 0.8606 (7) | 0.3874 (3) | 0.2218 (4) | 0.0605 (19) | 0.800 (14) |
| H1E | 0.883562   | 0.336938   | 0.190926   | 0.073*      | 0.800 (14) |
| C1F | 0.7403 (6) | 0.4510 (4) | 0.2285 (4) | 0.0469 (12) | 0.800 (14) |
| H1F | 0.683721   | 0.441976   | 0.201630   | 0.056*      | 0.800 (14) |

**Table S4** Atomic displacement parameters ( $\text{\AA}^2$ ) for compound 2

|      | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$     | $U^{13}$     | $U^{23}$     |
|------|-------------|-------------|-------------|--------------|--------------|--------------|
| S01  | 0.0504 (3)  | 0.0212 (2)  | 0.0334 (3)  | -0.0074 (2)  | 0.0077 (2)   | -0.0088 (2)  |
| O002 | 0.0338 (8)  | 0.0316 (7)  | 0.0293 (7)  | -0.0180 (6)  | 0.0066 (6)   | -0.0157 (6)  |
| O003 | 0.0227 (7)  | 0.0438 (9)  | 0.0404 (8)  | -0.0078 (6)  | -0.0020 (6)  | -0.0237 (7)  |
| O004 | 0.0648 (11) | 0.0277 (8)  | 0.0335 (8)  | -0.0194 (8)  | 0.0045 (7)   | -0.0096 (7)  |
| N005 | 0.0213 (8)  | 0.0221 (7)  | 0.0229 (8)  | -0.0080 (6)  | -0.0058 (6)  | -0.0019 (6)  |
| N006 | 0.0331 (9)  | 0.0226 (8)  | 0.0238 (8)  | -0.0078 (7)  | -0.0006 (7)  | -0.0078 (6)  |
| O007 | 0.0461 (11) | 0.0295 (9)  | 0.0743 (13) | 0.0005 (8)   | 0.0101 (9)   | -0.0077 (9)  |
| O008 | 0.0384 (10) | 0.0531 (11) | 0.0681 (13) | -0.0176 (9)  | -0.0232 (9)  | 0.0258 (10)  |
| C009 | 0.0176 (8)  | 0.0242 (9)  | 0.0210 (8)  | -0.0060 (7)  | -0.0025 (7)  | -0.0058 (7)  |
| C00A | 0.0212 (9)  | 0.0258 (9)  | 0.0243 (9)  | -0.0088 (7)  | -0.0002 (7)  | -0.0069 (7)  |
| C00B | 0.0189 (8)  | 0.0239 (9)  | 0.0260 (9)  | -0.0079 (7)  | -0.0047 (7)  | -0.0064 (7)  |
| C00C | 0.0190 (9)  | 0.0329 (10) | 0.0213 (9)  | -0.0075 (8)  | -0.0029 (7)  | -0.0061 (8)  |
| C00D | 0.0191 (9)  | 0.0249 (9)  | 0.0285 (10) | -0.0079 (7)  | -0.0057 (7)  | -0.0030 (8)  |
| C00E | 0.0210 (9)  | 0.0222 (9)  | 0.0261 (9)  | -0.0073 (7)  | -0.0024 (7)  | -0.0058 (7)  |
| C00F | 0.0203 (8)  | 0.0226 (9)  | 0.0217 (8)  | -0.0076 (7)  | -0.0016 (7)  | -0.0074 (7)  |
| C00G | 0.0196 (9)  | 0.0227 (9)  | 0.0262 (9)  | -0.0053 (7)  | -0.0044 (7)  | -0.0079 (7)  |
| C00H | 0.0280 (10) | 0.0243 (10) | 0.0388 (11) | -0.0094 (8)  | -0.0033 (8)  | -0.0097 (8)  |
| C00I | 0.0233 (9)  | 0.0215 (9)  | 0.0316 (10) | -0.0064 (7)  | -0.0042 (8)  | -0.0047 (8)  |
| C00J | 0.0210 (9)  | 0.0324 (10) | 0.0337 (11) | -0.0080 (8)  | -0.0042 (8)  | -0.0095 (9)  |
| C00K | 0.0218 (9)  | 0.0310 (10) | 0.0248 (9)  | -0.0063 (8)  | -0.0041 (7)  | -0.0009 (8)  |
| C00L | 0.0249 (10) | 0.0325 (10) | 0.0313 (10) | -0.0120 (8)  | -0.0080 (8)  | -0.0051 (8)  |
| C00M | 0.0285 (10) | 0.0278 (10) | 0.0334 (11) | -0.0137 (8)  | -0.0038 (8)  | 0.0019 (8)   |
| C00N | 0.0338 (11) | 0.0278 (10) | 0.0284 (10) | -0.0068 (8)  | -0.0065 (8)  | -0.0105 (8)  |
| C00O | 0.0313 (11) | 0.0447 (12) | 0.0286 (10) | -0.0127 (9)  | -0.0003 (8)  | -0.0162 (9)  |
| C00P | 0.0278 (10) | 0.0308 (11) | 0.0307 (10) | -0.0102 (8)  | -0.0086 (8)  | 0.0001 (8)   |
| C14  | 0.025 (5)   | 0.044 (6)   | 0.051 (6)   | -0.001 (5)   | 0.008 (5)    | -0.018 (5)   |
| C00R | 0.0330 (11) | 0.0313 (10) | 0.0333 (11) | -0.0134 (9)  | 0.0003 (8)   | -0.0173 (9)  |
| C00S | 0.0406 (12) | 0.0335 (11) | 0.0260 (10) | -0.0154 (9)  | 0.0016 (9)   | -0.0105 (9)  |
| C00T | 0.0321 (11) | 0.0366 (12) | 0.0440 (12) | -0.0126 (9)  | -0.0118 (9)  | -0.0119 (10) |
| C00U | 0.0278 (11) | 0.0457 (13) | 0.0403 (12) | -0.0090 (9)  | 0.0040 (9)   | -0.0232 (11) |
| C00V | 0.0468 (13) | 0.0271 (11) | 0.0423 (13) | -0.0101 (10) | 0.0010 (10)  | -0.0118 (10) |
| C00W | 0.0403 (13) | 0.0626 (16) | 0.0303 (11) | -0.0112 (12) | 0.0007 (10)  | -0.0233 (11) |
| C00X | 0.0225 (10) | 0.0474 (14) | 0.0539 (14) | -0.0012 (9)  | -0.0051 (10) | -0.0248 (12) |
| C00Y | 0.0261 (11) | 0.0460 (13) | 0.0474 (13) | -0.0088 (10) | -0.0127 (10) | -0.0136 (11) |
| C00Z | 0.0378 (13) | 0.0647 (17) | 0.0218 (10) | -0.0097 (12) | 0.0037 (9)   | -0.0112 (11) |
| C010 | 0.0326 (12) | 0.0467 (13) | 0.0271 (11) | -0.0124 (10) | -0.0003 (9)  | 0.0027 (10)  |
| C011 | 0.0460 (14) | 0.0493 (14) | 0.0514 (15) | -0.0180 (12) | -0.0153 (11) | -0.0195 (12) |
| C012 | 0.0197 (10) | 0.0565 (15) | 0.0633 (16) | -0.0007 (10) | -0.0128 (10) | -0.0231 (13) |
| C2   | 0.087 (9)   | 0.031 (5)   | 0.032 (4)   | -0.037 (7)   | 0.027 (4)    | -0.020 (3)   |
| C014 | 0.0472 (15) | 0.0663 (18) | 0.0568 (16) | -0.0205 (13) | -0.0248 (13) | -0.0197 (14) |
| C015 | 0.0430 (14) | 0.0356 (13) | 0.0770 (19) | -0.0189 (11) | 0.0230 (13)  | -0.0233 (13) |
| C016 | 0.0318 (12) | 0.0654 (17) | 0.0644 (17) | -0.0083 (12) | -0.0252 (12) | -0.0214 (15) |
| C017 | 0.0719 (19) | 0.0271 (12) | 0.0665 (18) | -0.0121 (12) | -0.0212 (15) | -0.0158 (12) |
| C15  | 0.031 (5)   | 0.050 (6)   | 0.055 (6)   | -0.001 (5)   | 0.007 (5)    | -0.018 (5)   |
| C19  | 0.028 (5)   | 0.041 (5)   | 0.047 (6)   | 0.002 (5)    | 0.009 (5)    | -0.021 (4)   |

|      |             |             |             |              |              |              |
|------|-------------|-------------|-------------|--------------|--------------|--------------|
| C5   | 0.121 (10)  | 0.063 (8)   | 0.037 (4)   | -0.069 (9)   | 0.014 (6)    | -0.018 (4)   |
| C01B | 0.0492 (16) | 0.0326 (14) | 0.120 (3)   | -0.0220 (12) | -0.0158 (17) | -0.0158 (16) |
| C18  | 0.029 (5)   | 0.049 (5)   | 0.053 (6)   | 0.006 (4)    | 0.011 (4)    | -0.015 (4)   |
| C01D | 0.0435 (16) | 0.0468 (17) | 0.134 (3)   | -0.0284 (14) | 0.0276 (18)  | -0.0266 (19) |
| C0   | 0.070 (6)   | 0.025 (3)   | 0.035 (4)   | -0.010 (4)   | 0.016 (4)    | -0.016 (3)   |
| C17  | 0.027 (5)   | 0.055 (5)   | 0.056 (6)   | 0.005 (5)    | 0.012 (5)    | -0.016 (5)   |
| C4   | 0.186 (13)  | 0.112 (10)  | 0.035 (4)   | -0.117 (11)  | 0.001 (6)    | -0.023 (5)   |
| C16  | 0.028 (5)   | 0.054 (6)   | 0.058 (6)   | 0.005 (5)    | 0.009 (5)    | -0.018 (5)   |
| C1   | 0.126 (10)  | 0.040 (4)   | 0.038 (4)   | -0.039 (6)   | 0.021 (5)    | -0.020 (3)   |
| C3   | 0.182 (14)  | 0.066 (7)   | 0.031 (4)   | -0.084 (9)   | 0.007 (5)    | -0.019 (4)   |
| C6   | 0.31 (3)    | 0.120 (11)  | 0.026 (3)   | -0.152 (15)  | 0.013 (7)    | -0.017 (5)   |
| C7   | 0.041 (3)   | 0.036 (3)   | 0.043 (3)   | -0.014 (3)   | 0.002 (2)    | -0.021 (2)   |
| C8   | 0.068 (4)   | 0.050 (4)   | 0.032 (2)   | -0.036 (3)   | 0.012 (2)    | -0.019 (2)   |
| C9   | 0.083 (4)   | 0.051 (3)   | 0.027 (2)   | -0.044 (3)   | 0.002 (2)    | -0.015 (2)   |
| C10  | 0.065 (3)   | 0.048 (3)   | 0.034 (2)   | -0.036 (3)   | 0.001 (2)    | -0.014 (2)   |
| C11  | 0.048 (3)   | 0.041 (3)   | 0.030 (2)   | -0.024 (3)   | 0.004 (2)    | -0.018 (2)   |
| C12  | 0.138 (8)   | 0.093 (6)   | 0.028 (2)   | -0.080 (6)   | -0.005 (3)   | -0.007 (3)   |
| C13  | 0.041 (4)   | 0.031 (3)   | 0.035 (3)   | -0.017 (3)   | 0.010 (2)    | -0.021 (2)   |
| C1A  | 0.025 (2)   | 0.0163 (17) | 0.026 (2)   | -0.0006 (14) | 0.0022 (15)  | -0.0023 (12) |
| C1B  | 0.0206 (18) | 0.044 (2)   | 0.071 (3)   | -0.0020 (14) | -0.0104 (19) | -0.0206 (19) |
| C1C  | 0.0232 (18) | 0.074 (3)   | 0.098 (4)   | -0.0073 (18) | -0.008 (2)   | -0.027 (3)   |
| C1D  | 0.034 (2)   | 0.048 (2)   | 0.077 (4)   | 0.0066 (18)  | 0.015 (2)    | -0.014 (2)   |
| C1E  | 0.052 (4)   | 0.041 (2)   | 0.052 (2)   | 0.006 (2)    | 0.009 (3)    | -0.0126 (17) |
| C1F  | 0.047 (3)   | 0.0342 (17) | 0.0460 (19) | 0.005 (2)    | -0.007 (2)   | -0.0171 (15) |

**Table S5** Geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for compound **2**

|           |             |           |            |
|-----------|-------------|-----------|------------|
| S01—O004  | 1.4303 (17) | C00X—C012 | 1.366 (4)  |
| S01—N006  | 1.6371 (17) | C00Y—C012 | 1.400 (4)  |
| S01—O007  | 1.424 (2)   | C00Y—C016 | 1.420 (3)  |
| S01—C2    | 1.726 (10)  | C00Z—H00Z | 0.9300     |
| S01—C13   | 1.792 (8)   | C00Z—C010 | 1.355 (4)  |
| O002—C00A | 1.377 (2)   | C010—H010 | 0.9300     |
| O002—C00R | 1.431 (2)   | C011—H011 | 0.9300     |
| O003—C00J | 1.385 (3)   | C011—C014 | 1.408 (4)  |
| O003—C00U | 1.433 (3)   | C012—H012 | 0.9300     |
| N005—H00A | 0.8900      | C2—C5     | 1.328 (15) |
| N005—H00B | 0.8900      | C2—C0     | 1.366 (13) |
| N005—C00B | 1.459 (2)   | C014—H014 | 0.9300     |
| N005—C00F | 1.465 (2)   | C014—C016 | 1.353 (4)  |
| N006—C00N | 1.485 (3)   | C015—H015 | 0.9300     |
| N006—C00S | 1.482 (3)   | C015—C01D | 1.394 (4)  |
| O008—C00P | 1.208 (3)   | C016—H016 | 0.9300     |
| C009—C00A | 1.385 (3)   | C017—H017 | 0.9300     |
| C009—C00C | 1.434 (3)   | C017—C01B | 1.368 (4)  |
| C009—C00F | 1.521 (2)   | C15—H15   | 0.9300     |
| C00A—C00H | 1.416 (3)   | C15—C16   | 1.39 (3)   |
| C00B—H00C | 0.9800      | C19—H19   | 0.9300     |
| C00B—C00D | 1.522 (3)   | C19—C18   | 1.37 (2)   |
| C00B—C00E | 1.554 (3)   | C5—H5     | 0.9300     |
| C00C—C00K | 1.429 (3)   | C5—C4     | 1.414 (16) |
| C00C—C00O | 1.422 (3)   | C01B—H01B | 0.9300     |
| C00D—C00J | 1.384 (3)   | C01B—C01D | 1.365 (5)  |
| C00D—C00L | 1.432 (3)   | C18—H18   | 0.9300     |
| C00E—H00E | 0.9800      | C18—C17   | 1.39 (3)   |
| C00E—C00I | 1.517 (3)   | C01D—H01D | 0.9300     |
| C00E—C00P | 1.520 (3)   | C0—H0     | 0.9300     |
| C00F—H00F | 0.9800      | C0—C1     | 1.393 (11) |
| C00F—C00G | 1.559 (3)   | C17—H17   | 0.9300     |
| C00G—H00G | 0.9800      | C17—C16   | 1.39 (4)   |

|                |             |                |            |
|----------------|-------------|----------------|------------|
| C00G—H00D      | 0.9800      | C4—H4          | 0.9300     |
| C00G—C00P      | 1.525 (3)   | C4—C3          | 1.376 (16) |
| C00G—C14       | 1.65 (4)    | C16—H16        | 0.9300     |
| C00G—C1A       | 1.485 (7)   | C1—H1          | 0.9300     |
| C00H—H00H      | 0.9300      | C1—C3          | 1.377 (17) |
| C00H—C00M      | 1.366 (3)   | C3—C6          | 1.520 (11) |
| C00I—C00V      | 1.386 (3)   | C6—H6A         | 0.9600     |
| C00I—C015      | 1.374 (3)   | C6—H6B         | 0.9600     |
| C00J—C00X      | 1.413 (3)   | C6—H6C         | 0.9600     |
| C00K—C00M      | 1.402 (3)   | C7—H7          | 0.9300     |
| C00K—C010      | 1.427 (3)   | C7—C8          | 1.393 (9)  |
| C00L—C00T      | 1.423 (3)   | C7—C13         | 1.414 (9)  |
| C00L—C00Y      | 1.429 (3)   | C8—H8          | 0.9300     |
| C00M—H00M      | 0.9300      | C8—C9          | 1.388 (9)  |
| C00N—H00I      | 0.9700      | C9—C10         | 1.397 (8)  |
| C00N—H00J      | 0.9700      | C9—C12         | 1.518 (7)  |
| C00N—C00R      | 1.514 (3)   | C10—H10        | 0.9300     |
| C00O—H00O      | 0.9300      | C10—C11        | 1.387 (10) |
| C00O—C00W      | 1.371 (3)   | C11—H11        | 0.9300     |
| C14—C15        | 1.27 (5)    | C11—C13        | 1.409 (9)  |
| C14—C19        | 1.39 (4)    | C12—H12A       | 0.9600     |
| C00R—H00K      | 0.9700      | C12—H12B       | 0.9600     |
| C00R—H00L      | 0.9700      | C12—H12C       | 0.9600     |
| C00S—H00N      | 0.9700      | C1A—C1B        | 1.403 (9)  |
| C00S—H00P      | 0.9700      | C1A—C1F        | 1.398 (7)  |
| C00S—C00U      | 1.513 (3)   | C1B—H1B        | 0.9300     |
| C00T—H00T      | 0.9300      | C1B—C1C        | 1.394 (5)  |
| C00T—C011      | 1.369 (3)   | C1C—H1C        | 0.9300     |
| C00U—H00Q      | 0.9700      | C1C—C1D        | 1.385 (8)  |
| C00U—H00R      | 0.9700      | C1D—H1D        | 0.9300     |
| C00V—H00V      | 0.9300      | C1D—C1E        | 1.370 (8)  |
| C00V—C017      | 1.386 (3)   | C1E—H1E        | 0.9300     |
| C00W—H00W      | 0.9300      | C1E—C1F        | 1.389 (6)  |
| C00W—C00Z      | 1.404 (4)   | C1F—H1F        | 0.9300     |
| C00X—H00X      | 0.9300      |                |            |
| O004—S01—N006  | 106.54 (9)  | C00O—C00W—C00Z | 121.0 (2)  |
| O004—S01—C2    | 114.3 (6)   | C00Z—C00W—H00W | 119.5      |
| O004—S01—C13   | 102.9 (4)   | C00J—C00X—H00X | 120.3      |
| N006—S01—C2    | 109.3 (7)   | C012—C00X—C00J | 119.4 (2)  |
| N006—S01—C13   | 106.9 (5)   | C012—C00X—H00X | 120.3      |
| O007—S01—O004  | 119.96 (11) | C012—C00Y—C00L | 119.2 (2)  |
| O007—S01—N006  | 107.37 (11) | C012—C00Y—C016 | 121.7 (2)  |
| O007—S01—C2    | 98.9 (6)    | C016—C00Y—C00L | 119.1 (2)  |
| O007—S01—C13   | 112.4 (3)   | C00W—C00Z—H00Z | 120.3      |
| C00A—O002—C00R | 118.47 (15) | C010—C00Z—C00W | 119.5 (2)  |
| C00J—O003—C00U | 118.10 (16) | C010—C00Z—H00Z | 120.3      |
| H00A—N005—H00B | 107.9       | C00K—C010—H010 | 119.2      |
| C00B—N005—H00A | 109.2       | C00Z—C010—C00K | 121.6 (2)  |
| C00B—N005—H00B | 109.2       | C00Z—C010—H010 | 119.2      |
| C00B—N005—C00F | 112.07 (14) | C00T—C011—H011 | 119.6      |
| C00F—N005—H00A | 109.2       | C00T—C011—C014 | 120.7 (3)  |
| C00F—N005—H00B | 109.2       | C014—C011—H011 | 119.6      |
| C00N—N006—S01  | 114.46 (14) | C00X—C012—C00Y | 121.7 (2)  |
| C00S—N006—S01  | 115.37 (14) | C00X—C012—H012 | 119.1      |
| C00S—N006—C00N | 118.42 (16) | C00Y—C012—H012 | 119.1      |
| C00A—C009—C00C | 118.39 (17) | C5—C2—S01      | 113.1 (9)  |
| C00A—C009—C00F | 119.60 (16) | C5—C2—C0       | 125.6 (10) |
| C00C—C009—C00F | 121.78 (17) | C0—C2—S01      | 121.1 (9)  |
| O002—C00A—C009 | 116.44 (16) | C011—C014—H014 | 120.3      |
| O002—C00A—C00H | 121.54 (18) | C016—C014—C011 | 119.4 (2)  |
| C009—C00A—C00H | 121.94 (18) | C016—C014—H014 | 120.3      |
| N005—C00B—H00C | 107.0       | C00I—C015—H015 | 119.7      |

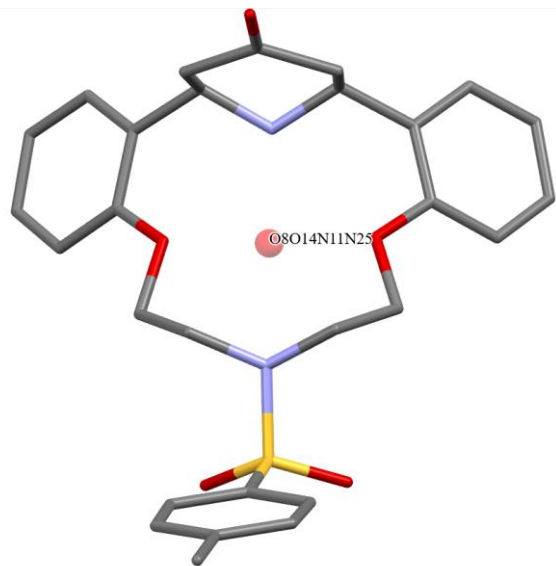
|                |             |                |            |
|----------------|-------------|----------------|------------|
| N005—C00B—C00D | 109.69 (15) | C00I—C015—C01D | 120.7 (3)  |
| N005—C00B—C00E | 113.37 (15) | C01D—C015—H015 | 119.7      |
| C00D—C00B—H00C | 107.0       | C00Y—C016—H016 | 119.0      |
| C00D—C00B—C00E | 112.30 (15) | C014—C016—C00Y | 121.9 (2)  |
| C00E—C00B—H00C | 107.0       | C014—C016—H016 | 119.0      |
| C00K—C00C—C009 | 119.41 (18) | C00V—C017—H017 | 120.0      |
| C00O—C00C—C009 | 123.33 (18) | C01B—C017—C00V | 120.0 (3)  |
| C00O—C00C—C00K | 117.26 (18) | C01B—C017—H017 | 120.0      |
| C00J—C00D—C00B | 119.66 (17) | C14—C15—H15    | 121.2      |
| C00J—C00D—C00L | 118.94 (17) | C14—C15—C16    | 118 (2)    |
| C00L—C00D—C00B | 121.28 (18) | C16—C15—H15    | 121.2      |
| C00B—C00E—H00E | 106.8       | C14—C19—H19    | 123.8      |
| C00I—C00E—C00B | 110.37 (16) | C18—C19—C14    | 112 (2)    |
| C00I—C00E—H00E | 106.8       | C18—C19—H19    | 123.8      |
| C00I—C00E—C00P | 112.94 (16) | C2—C5—H5       | 121.1      |
| C00P—C00E—C00B | 112.63 (15) | C2—C5—C4       | 117.9 (10) |
| C00P—C00E—H00E | 106.8       | C4—C5—H5       | 121.1      |
| N005—C00F—C009 | 108.59 (14) | C017—C01B—H01B | 120.2      |
| N005—C00F—H00F | 107.0       | C01D—C01B—C017 | 119.7 (2)  |
| N005—C00F—C00G | 113.28 (14) | C01D—C01B—H01B | 120.2      |
| C009—C00F—H00F | 107.0       | C19—C18—H18    | 119.1      |
| C009—C00F—C00G | 113.45 (15) | C19—C18—C17    | 122 (2)    |
| C00G—C00F—H00F | 107.0       | C17—C18—H18    | 119.1      |
| C00F—C00G—H00G | 108.6       | C015—C01D—H01D | 119.8      |
| C00F—C00G—H00D | 105.9       | C01B—C01D—C015 | 120.5 (3)  |
| C00F—C00G—C14  | 108.8 (14)  | C01B—C01D—H01D | 119.8      |
| C00P—C00G—C00F | 113.50 (15) | C2—C0—H0       | 122.0      |
| C00P—C00G—H00G | 108.6       | C2—C0—C1       | 115.9 (10) |
| C00P—C00G—H00D | 105.9       | C1—C0—H0       | 122.0      |
| C00P—C00G—C14  | 108.5 (14)  | C18—C17—H17    | 119.9      |
| C14—C00G—H00G  | 108.6       | C18—C17—C16    | 120.3 (17) |
| C1A—C00G—C00F  | 114.1 (3)   | C16—C17—H17    | 119.9      |
| C1A—C00G—H00D  | 105.9       | C5—C4—H4       | 120.3      |
| C1A—C00G—C00P  | 110.9 (3)   | C3—C4—C5       | 119.3 (11) |
| C00A—C00H—H00H | 120.3       | C3—C4—H4       | 120.3      |
| C00M—C00H—C00A | 119.4 (2)   | C15—C16—C17    | 118 (2)    |
| C00M—C00H—H00H | 120.3       | C15—C16—H16    | 121.0      |
| C00V—C00I—C00E | 121.59 (18) | C17—C16—H16    | 121.0      |
| C015—C00I—C00E | 120.31 (19) | C0—C1—H1       | 119.3      |
| C015—C00I—C00V | 118.0 (2)   | C3—C1—C0       | 121.5 (9)  |
| O003—C00J—C00X | 121.10 (19) | C3—C1—H1       | 119.3      |
| C00D—C00J—O003 | 117.28 (17) | C4—C3—C1       | 119.7 (8)  |
| C00D—C00J—C00X | 121.6 (2)   | C4—C3—C6       | 119.7 (12) |
| C00M—C00K—C00C | 119.31 (18) | C1—C3—C6       | 120.5 (11) |
| C00M—C00K—C010 | 121.5 (2)   | C3—C6—H6A      | 109.5      |
| C010—C00K—C00C | 119.2 (2)   | C3—C6—H6B      | 109.5      |
| C00T—C00L—C00D | 123.79 (18) | C3—C6—H6C      | 109.5      |
| C00T—C00L—C00Y | 117.18 (19) | H6A—C6—H6B     | 109.5      |
| C00Y—C00L—C00D | 119.0 (2)   | H6A—C6—H6C     | 109.5      |
| C00H—C00M—C00K | 121.48 (19) | H6B—C6—H6C     | 109.5      |
| C00H—C00M—H00M | 119.3       | C8—C7—H7       | 119.3      |
| C00K—C00M—H00M | 119.3       | C8—C7—C13      | 121.4 (6)  |
| N006—C00N—H00I | 108.8       | C13—C7—H7      | 119.3      |
| N006—C00N—H00J | 108.8       | C7—C8—H8       | 119.4      |
| N006—C00N—C00R | 113.61 (17) | C9—C8—C7       | 121.2 (5)  |
| H00I—C00N—H00J | 107.7       | C9—C8—H8       | 119.4      |
| C00R—C00N—H00I | 108.8       | C8—C9—C10      | 118.0 (5)  |
| C00R—C00N—H00J | 108.8       | C8—C9—C12      | 121.6 (5)  |
| C00C—C00O—H00O | 119.3       | C10—C9—C12     | 120.4 (6)  |
| C00W—C00O—C00C | 121.4 (2)   | C9—C10—H10     | 119.3      |
| C00W—C00O—H00O | 119.3       | C11—C10—C9     | 121.3 (6)  |
| O008—C00P—C00E | 120.04 (19) | C11—C10—H10    | 119.3      |



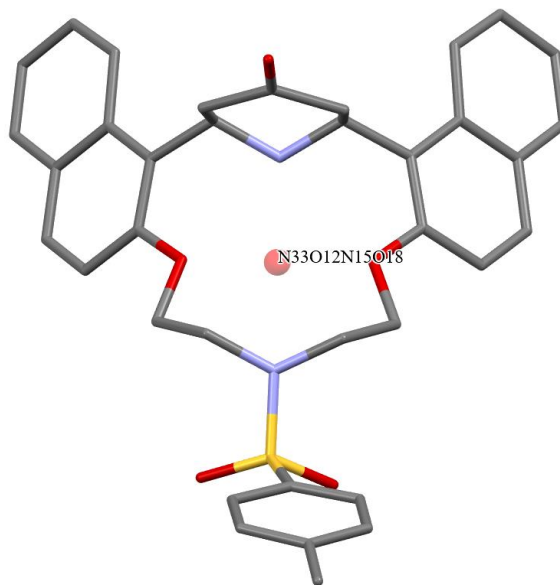
|                     |              |                     |              |
|---------------------|--------------|---------------------|--------------|
| O008—C00P—C00G      | 119.55 (18)  | C10—C11—H11         | 119.3        |
| C00E—C00P—C00G      | 120.13 (16)  | C10—C11—C13         | 121.5 (6)    |
| C15—C14—C00G        | 121 (3)      | C13—C11—H11         | 119.3        |
| C15—C14—C19         | 130 (3)      | C9—C12—H12A         | 109.5        |
| C19—C14—C00G        | 109 (3)      | C9—C12—H12B         | 109.5        |
| O002—C00R—C00N      | 107.71 (16)  | C9—C12—H12C         | 109.5        |
| O002—C00R—H00K      | 110.2        | H12A—C12—H12B       | 109.5        |
| O002—C00R—H00L      | 110.2        | H12A—C12—H12C       | 109.5        |
| C00N—C00R—H00K      | 110.2        | H12B—C12—H12C       | 109.5        |
| C00N—C00R—H00L      | 110.2        | C7—C13—S01          | 120.2 (6)    |
| H00K—C00R—H00L      | 108.5        | C11—C13—S01         | 123.2 (6)    |
| N006—C00S—H00N      | 108.7        | C11—C13—C7          | 116.5 (6)    |
| N006—C00S—H00P      | 108.7        | C1B—C1A—C00G        | 120.2 (4)    |
| N006—C00S—C00U      | 114.32 (18)  | C1F—C1A—C00G        | 123.6 (7)    |
| H00N—C00S—H00P      | 107.6        | C1F—C1A—C1B         | 116.2 (6)    |
| C00U—C00S—H00N      | 108.7        | C1A—C1B—H1B         | 119.1        |
| C00U—C00S—H00P      | 108.7        | C1C—C1B—C1A         | 121.8 (4)    |
| C00L—C00T—H00T      | 119.2        | C1C—C1B—H1B         | 119.1        |
| C011—C00T—C00L      | 121.5 (2)    | C1B—C1C—H1C         | 120.2        |
| C011—C00T—H00T      | 119.2        | C1D—C1C—C1B         | 119.5 (4)    |
| O003—C00U—C00S      | 108.40 (17)  | C1D—C1C—H1C         | 120.2        |
| O003—C00U—H00Q      | 110.0        | C1C—C1D—H1D         | 119.8        |
| O003—C00U—H00R      | 110.0        | C1E—C1D—C1C         | 120.3 (4)    |
| C00S—C00U—H00Q      | 110.0        | C1E—C1D—H1D         | 119.8        |
| C00S—C00U—H00R      | 110.0        | C1D—C1E—H1E         | 120.2        |
| H00Q—C00U—H00R      | 108.4        | C1D—C1E—C1F         | 119.7 (5)    |
| C00I—C00V—H00V      | 119.4        | C1F—C1E—H1E         | 120.2        |
| C017—C00V—C00I      | 121.2 (2)    | C1A—C1F—H1F         | 118.8        |
| C017—C00V—H00V      | 119.4        | C1E—C1F—C1A         | 122.5 (6)    |
| C00O—C00W—H00W      | 119.5        | C1E—C1F—H1F         | 118.8        |
| S01—N006—C00N—C00R  | -89.12 (18)  | C00G—C14—C19—C18    | -177.7 (18)  |
| S01—N006—C00S—C00U  | 93.84 (19)   | C00G—C1A—C1B—C1C    | 176.3 (4)    |
| S01—C2—C5—C4        | 176.6 (12)   | C00G—C1A—C1F—C1E    | -176.9 (4)   |
| S01—C2—C0—C1        | -175.1 (10)  | C00I—C00E—C00P—O008 | -32.2 (3)    |
| O002—C00A—C00H—C00M | -175.49 (18) | C00I—C00E—C00P—C00G | 153.87 (19)  |
| O003—C00J—C00X—C012 | 176.8 (2)    | C00I—C00V—C017—C01B | -1.0 (4)     |
| O004—S01—N006—C00N  | 38.16 (16)   | C00I—C015—C01D—C01B | -1.0 (6)     |
| O004—S01—N006—C00S  | -179.25 (15) | C00J—O003—C00U—C00S | 163.24 (17)  |
| O004—S01—C2—C5      | -23.1 (16)   | C00J—C00D—C00L—C00T | -177.14 (19) |
| O004—S01—C2—C0      | 151.8 (12)   | C00J—C00D—C00L—C00Y | 3.2 (3)      |
| O004—S01—C13—C7     | 156.4 (10)   | C00J—C00X—C012—C00Y | 1.3 (4)      |
| O004—S01—C13—C11    | -26.6 (12)   | C00K—C00C—C00O—C00W | -1.1 (3)     |
| N005—C00B—C00D—C00J | -58.1 (2)    | C00L—C00D—C00J—O003 | -179.16 (17) |
| N005—C00B—C00D—C00L | 117.77 (19)  | C00L—C00D—C00J—C00X | -1.0 (3)     |
| N005—C00B—C00E—C00I | -171.11 (15) | C00L—C00T—C011—C014 | -1.5 (4)     |
| N005—C00B—C00E—C00P | -43.9 (2)    | C00L—C00Y—C012—C00X | 1.0 (4)      |
| N005—C00F—C00G—C00P | 40.4 (2)     | C00L—C00Y—C016—C014 | 0.4 (4)      |
| N005—C00F—C00G—C14  | 161.3 (17)   | C00M—C00K—C010—C00Z | 178.4 (2)    |
| N005—C00F—C00G—C1A  | 168.7 (3)    | C00N—N006—C00S—C00U | -125.12 (19) |
| N006—S01—C2—C5      | 96.1 (13)    | C00O—C00C—C00K—C00M | -178.10 (18) |
| N006—S01—C2—C0      | -88.9 (14)   | C00O—C00C—C00K—C010 | 1.2 (3)      |
| N006—S01—C13—C7     | -91.6 (10)   | C00O—C00W—C00Z—C010 | -0.3 (4)     |
| N006—S01—C13—C11    | 85.4 (11)    | C00P—C00E—C00I—C00V | -50.0 (3)    |
| N006—C00N—C00R—O002 | -79.9 (2)    | C00P—C00E—C00I—C015 | 134.2 (2)    |
| N006—C00S—C00U—O003 | 76.2 (2)     | C00P—C00G—C14—C15   | -124 (3)     |
| O007—S01—N006—C00N  | 167.85 (14)  | C00P—C00G—C14—C19   | 56 (3)       |
| O007—S01—N006—C00S  | -49.56 (17)  | C00P—C00G—C1A—C1B   | -115.0 (5)   |
| O007—S01—C2—C5      | -151.8 (12)  | C00P—C00G—C1A—C1F   | 62.6 (6)     |
| O007—S01—C2—C0      | 23.1 (15)    | C14—C00G—C00P—O008  | 38.4 (17)    |
| O007—S01—C13—C7     | 26.0 (12)    | C14—C00G—C00P—C00E  | -147.6 (17)  |
| O007—S01—C13—C11    | -157.0 (9)   | C14—C15—C16—C17     | 4 (3)        |
| C009—C00A—C00H—C00M | 1.2 (3)      | C14—C19—C18—C17     | -1 (3)       |

|                     |              |                     |              |
|---------------------|--------------|---------------------|--------------|
| C009—C00C—C00K—C00M | 1.1 (3)      | C00R—O002—C00A—C009 | 157.55 (17)  |
| C009—C00C—C00K—C010 | -179.57 (18) | C00R—O002—C00A—C00H | -25.6 (3)    |
| C009—C00C—C00O—C00W | 179.7 (2)    | C00S—N006—C00N—C00R | 129.50 (18)  |
| C009—C00F—C00G—C00P | 164.76 (16)  | C00T—C00L—C00Y—C012 | 177.1 (2)    |
| C009—C00F—C00G—C14  | -74.3 (17)   | C00T—C00L—C00Y—C016 | -3.5 (3)     |
| C009—C00F—C00G—C1A  | -66.9 (4)    | C00T—C011—C014—C016 | -1.8 (4)     |
| C00A—O002—C00R—C00N | -167.75 (16) | C00U—O003—C00J—C00D | -157.49 (19) |
| C00A—C009—C00C—C00K | -1.8 (3)     | C00U—O003—C00J—C00X | 24.3 (3)     |
| C00A—C009—C00C—C00O | 177.32 (18)  | C00V—C00I—C015—C01D | 1.8 (4)      |
| C00A—C009—C00F—N005 | 59.1 (2)     | C00V—C017—C01B—C01D | 1.8 (5)      |
| C00A—C009—C00F—C00G | -67.8 (2)    | C00W—C00Z—C010—C00K | 0.4 (4)      |
| C00A—C00H—C00M—C00K | -2.0 (3)     | C00Y—C00L—C00T—C011 | 4.1 (3)      |
| C00B—N005—C00F—C009 | 174.52 (15)  | C010—C00K—C00M—C00H | -178.5 (2)   |
| C00B—N005—C00F—C00G | -58.5 (2)    | C011—C014—C016—C00Y | 2.3 (4)      |
| C00B—C00D—C00J—O003 | -3.2 (3)     | C012—C00Y—C016—C014 | 179.8 (3)    |
| C00B—C00D—C00J—C00X | 174.97 (19)  | C2—S01—N006—C00N    | -85.8 (6)    |
| C00B—C00D—C00L—C00T | 7.0 (3)      | C2—S01—N006—C00S    | 56.8 (6)     |
| C00B—C00D—C00L—C00Y | -172.71 (18) | C2—C5—C4—C3         | -4 (2)       |
| C00B—C00E—C00I—C00V | 77.0 (2)     | C2—C0—C1—C3         | 1.5 (15)     |
| C00B—C00E—C00I—C015 | -98.7 (3)    | C015—C00I—C00V—C017 | -0.8 (4)     |
| C00B—C00E—C00P—O008 | -158.1 (2)   | C016—C00Y—C012—C00X | -178.4 (3)   |
| C00B—C00E—C00P—C00G | 28.0 (3)     | C017—C01B—C01D—C015 | -0.9 (6)     |
| C00C—C009—C00A—O002 | 177.55 (16)  | C15—C14—C19—C18     | 2 (5)        |
| C00C—C009—C00A—C00H | 0.7 (3)      | C19—C14—C15—C16     | -4 (5)       |
| C00C—C009—C00F—N005 | -115.27 (18) | C19—C18—C17—C16     | 2 (3)        |
| C00C—C009—C00F—C00G | 117.83 (19)  | C5—C2—C0—C1         | -1 (2)       |
| C00C—C00K—C00M—C00H | 0.8 (3)      | C5—C4—C3—C1         | 4.4 (17)     |
| C00C—C00K—C010—C00Z | -0.9 (3)     | C5—C4—C3—C6         | -173.8 (12)  |
| C00C—C00O—C00W—C00Z | 0.7 (4)      | C18—C17—C16—C15     | -3 (3)       |
| C00D—C00B—C00E—C00I | 63.9 (2)     | C0—C2—C5—C4         | 2 (3)        |
| C00D—C00B—C00E—C00P | -168.90 (17) | C0—C1—C3—C4         | -3.3 (15)    |
| C00D—C00J—C00X—C012 | -1.2 (4)     | C0—C1—C3—C6         | 174.8 (9)    |
| C00D—C00L—C00T—C011 | -175.6 (2)   | C7—C8—C9—C10        | 1.5 (9)      |
| C00D—C00L—C00Y—C012 | -3.2 (3)     | C7—C8—C9—C12        | -179.3 (6)   |
| C00D—C00L—C00Y—C016 | 176.2 (2)    | C8—C7—C13—S01       | 178.5 (7)    |
| C00E—C00B—C00D—C00J | 68.9 (2)     | C8—C7—C13—C11       | 1.4 (15)     |
| C00E—C00B—C00D—C00L | -115.2 (2)   | C8—C9—C10—C11       | -0.1 (10)    |
| C00E—C00I—C00V—C017 | -176.7 (2)   | C9—C10—C11—C13      | -0.7 (13)    |
| C00E—C00I—C015—C01D | 177.7 (3)    | C10—C11—C13—S01     | -177.1 (9)   |
| C00F—N005—C00B—C00D | -172.99 (15) | C10—C11—C13—C7      | 0.0 (16)     |
| C00F—N005—C00B—C00E | 60.6 (2)     | C12—C9—C10—C11      | -179.3 (7)   |
| C00F—C009—C00A—O002 | 3.0 (2)      | C13—S01—N006—C00N   | -71.4 (3)    |
| C00F—C009—C00A—C00H | -173.85 (17) | C13—S01—N006—C00S   | 71.2 (3)     |
| C00F—C009—C00C—C00K | 172.60 (16)  | C13—C7—C8—C9        | -2.2 (12)    |
| C00F—C009—C00C—C00O | -8.2 (3)     | C1A—C00G—C00P—O008  | 29.5 (4)     |
| C00F—C00G—C00P—O008 | 159.5 (2)    | C1A—C00G—C00P—C00E  | -156.5 (3)   |
| C00F—C00G—C00P—C00E | -26.6 (3)    | C1A—C1B—C1C—C1D     | 1.3 (7)      |
| C00F—C00G—C14—C15   | 112 (3)      | C1B—C1A—C1F—C1E     | 0.8 (7)      |
| C00F—C00G—C14—C19   | -68 (2)      | C1B—C1C—C1D—C1E     | -0.3 (7)     |
| C00F—C00G—C1A—C1B   | 115.4 (5)    | C1C—C1D—C1E—C1F     | -0.4 (7)     |
| C00F—C00G—C1A—C1F   | -67.0 (6)    | C1D—C1E—C1F—C1A     | 0.1 (7)      |
| C00G—C14—C15—C16    | 176 (2)      | C1F—C1A—C1B—C1C     | -1.5 (7)     |

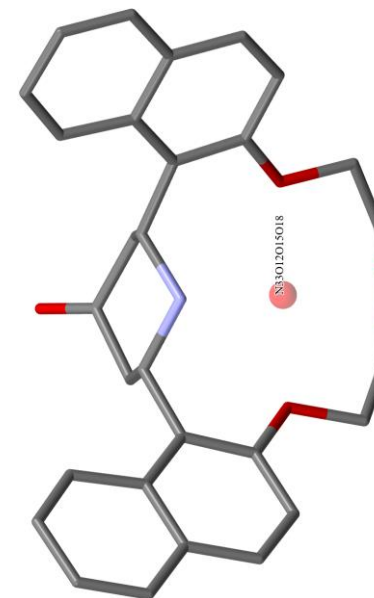
4. Table S6. The internal cavity of similar azacrown ethers



(1*RS*,21*SR*,22*RS*,24*SR*)-22,24-Diphenyl-11-tosyl-8,14-dioxo-11,25-diazatetracyclo[19.3.1.0<sup>2,7</sup>.0<sup>15,20</sup>]-pentacos-2,4,6,15(20),16,18-hexaen-23-one – Internal cavity of centroid = 4.24 Å<sup>[10]</sup>



23,25-Diphenyl-7-tosyl-4,10-dioxo-7-aza-2(2,6)-piperidina-1(2,1),3(1,2)-dinaphthalenacyclodecaphan-24-one – Internal cavity of centroid = 4.16 Å.  
Compound (2)



2<sup>3</sup>,2<sup>5</sup>-Diphenyl-4,7,10-trioxo-2(2,6)-piperidina-1,3(1,2) dinaphthalenacyclodecaphan-2<sup>4</sup>-one - Internal cavity of centroid = 4.051 Å<sup>[9,18]</sup>

Note. Reference numbers relate to those of the main text.