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Stereochemical outcome of perhydro hexaazadibenzotetracene formation from *trans*-1,2-diaminocyclohexane

Elena B. Rakhimova, Victor Yu. Kirsanov, Ekaterina S. Mescheryakova, Askhat G. Ibragimov and Usein M. Dzhemilev

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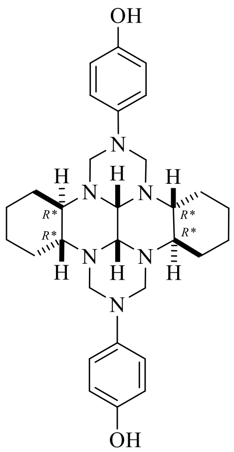
General information

The NMR spectra, including two-dimensional homo- (COSY) and heteronuclear (HSQC, HMBC) spectra, were recorded on a Bruker Avance 500 spectrometer at 500.17 MHz for ^{1}H and 125.78 MHz for ^{13}C according to standard Bruker procedures. $CDCl_3$ or DMSO-d_6 was used as the solvent, and tetramethylsilane, as the internal standard. The MALDI TOF/TOF mass spectra (positive ion detection, sinapinic acid matrix) were obtained on a Bruker AutoflexTM III Smartbeam mass spectrometer. Samples were prepared by the dried drop technique. Solutions of a matrix and analyte were mixed at a ratio of 50: 1 to 100: 1, and a drop of the resulting mixture was applied to a target and dried in a stream of warm air. The sample was transferred from the target to the gas phase by laser pulses (200 pulses at a frequency of 100 Hz) using a solid state UV laser (λ 355 nm). The elemental analyses were obtained on a Carlo Erba 1106 analyzer. The melting points were determined on a PHMK 80/2617 melting point apparatus. The reagents used in the work were acquired by Sigma-Aldrich and Acros Organics.

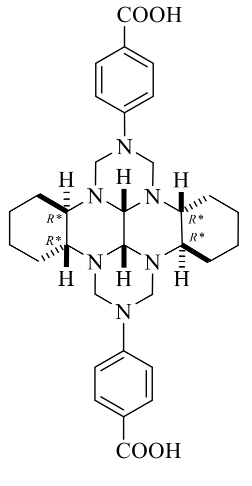
Cyclocondensation reaction of *trans*-1,6,7,12-tetraazaperhydrotetracene with formaldehyde and (het)arylamines (general synthesis procedure). A round-bottom flask equipped with a magnetic stirrer bar was charged with (±)-*trans*-cyclohexane-1,2-diamine (0.23 g, 2.00 mmol) in MeOH (5 ml) and 40 wt% aq glyoxal (0.14 g, 1.00 mmol) in MeOH (5 ml). The mixture was stirred at 70 °C for 3 h and cooled to room temperature. Then 37 wt% aq formaldehyde (0.45 ml, 4.00 mmol) in MeOH (5 ml) and $YbCl_3\cdot6H_2O$ (0.019 g, 0.05 mmol) were added. The mixture was stirred at room temperature for 30 min. Next, appropriate (het)arylamine (2.00 mmol) in MeOH (5 ml) was added, and the resultant mixture was stirred at 20 °C for 2.5 h. The mixture was then concentrated, and the residue was collected by filtration and washed twice with MeOH (2×10 ml). Compounds **2a-f** were obtained as powdery substances. The final products **2a-f** were identified by spectroscopic methods.

Analytical data for perhydro hexaazadibenzo[*fg,op*]tetracenes 2a-f and 2′a



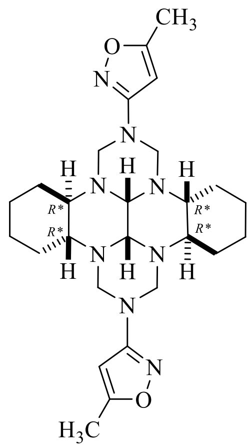
2a

(3b*R,7a*R**,10b*R**,14a*R**-*cis*-14c,14d)-2,9-Bis(4-hydroxyphenyl)octadecahydro-1*H*,8*H*-2,3a,7b,9,10a,14b-hexaazadibenzo[*fg,op*]tetracene (2a).** Yellow powder, yield 0.30 g (58%), mp 251-253 ºC, R_f 0.61 (MeOH). ^{1}H NMR (500.17 MHz, DMSO-d_6): δ = 0.79 br.s (4H, CH_2, H_a-4,7,11,14), 0.97–1.13 m (4H, CH_2, H_a-5,6,12,13), 1.52 br.s (2H, CH_2, H_b-4,11), 1.60–1.70 m (2H, CH_2, H_b-5,12; 2H, CH, H-7a,14a), 1.85 br.s (2H, CH_2, H_b-7,14), 2.09 br.s (2H, CH_2, H_b-6,13), 3.00–3.20 m (2H, CH_2, H_a-1,8; 2H, CH, H-3b,10b), 3.29 br.s (2H, CH, H-14c,14d), 3.69 d (2H, CH2, H_a-3,10, $^2J_{ab}$ = 12 Hz), 4.64 br.s (4H, CH2, H_b-1,3,8,10), 6.45 br.s (4H, CH, H-2′,2″,6′,6″), 6.45 br.s (4H, CH, H-3′,3″,5′,5″), 8.82 br.s (1H, OH). ^{13}C NMR (125.78 MHz, DMSO-d_6): δ = 24.59 (C-4,11), 24.75 (C-5,12), 27.23 (C-6,13), 28.43 (C-7,14), 55.42 (C-3b,10b), 63.45 (C-7a,14a), 67.28 (C-3,10), 70.45 (C-1,8), 77.73 (C-14c,14d), 115.85 (C-2′,2″,6′,6″), 119.24 (C-3′,3″,5′,5″), 142.65 (C-1′,1″), 151.47 (C-4′,4″). MALDI TOF/TOF, m/z: (%) = 515 $[M–H]^+$ (100). Anal. Calcd. for $C_{30}H_{40}N_6O_2$: C 69.74; H 7.80; N 16.27; O 6.19. Found: C 69.67; H 7.76; N 16.22.



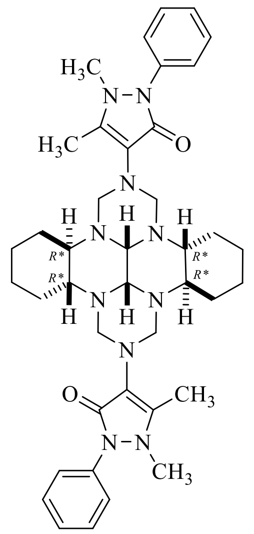
2b

(3b*R,7a*R**,10b*R**,14a*R**-*cis*-14c,14d)-2,9-Bis(4-carboxyphenyl)octadecahydro-1*H*,8*H*-2,3a,7b,9,10a,14b-hexaazadibenzo[*fg*,*op*]tetracene (2b).** Pale yellow powder, yield 0.29 g (51%), mp 250–252 ºC, R_f 0.64 (MeOH). ^{1}H NMR (500.17 MHz, DMSO-d_6): δ = 0.52–0.59 m (2H, CH_2, H_a-4,11), 0.78–0.86 m (2H, CH_2, H_a-7,14), 0.95–1.10 m (4H, CH_2, H_a-5,6,12,13), 1.52 br.s (4H, CH_2, H_b-4,5,11,12), 1.60–1.70 m (2H, CH_2, H_b-7,14; 2H, CH, H-7a,14a), 2.02–2.07 m (2H, CH_2, H_b-6,13), 2.77–2.82 м (2H, CH, H-3b,10b), 3.19 d (2H, CH_2, H_a-1,8, $^2J_{ab}$ = 11 Hz), 3.37 br.s (2H, CH, H 14c,14d), 3.80 d (2H, CH_2, H_a-3,10, $^2J_{ab}$ = 13.5 Hz), 4.80 d (2H, CH_2, H_b-1,8, $^2J_{ba}$ = 11 Hz), 4.95 d (2H, CH_2, H_b-3,10, $^2J_{ba}$ = 13.5 Hz), 6.90 d (4H, CH, H-2′,2″,6′,6″, ^3J = 8.5 Hz), 7.66 d (4H, CH, H 3′,3″,5′,5″, ^3J = 8 Hz). ^{13}C NMR (125.78 MHz, DMSO-d_6): δ = 24.03 (C-4,11), 24.12 (C-5,12), 26.61 (C-6,13), 28.07 (C-7,14), 54.87 (C-3b,10b), 62.96 (C-7a,14a), 64.57 (C-3,10), 67.86 (C-1,8), 76.86 (C-14c,14d), 115.26 (C-2′,2″,6′,6″), 128.47 (C-4′,4″), 130.80 (C-3′,3″,5′,5″), 150.75 (C-1′,1″), 173.24 (COOH). MALDI TOF/TOF, m/z: (%) = 571 $[M–H]^+$ (60), 595 $[M+Na]^+$ (100). Anal. Calcd. for $C_{32}H_{40}N_6O_4$: C 67.11; H 7.05; N 14.67; O 11.17. Found: C 67.05; H 7.01; N 14.60.



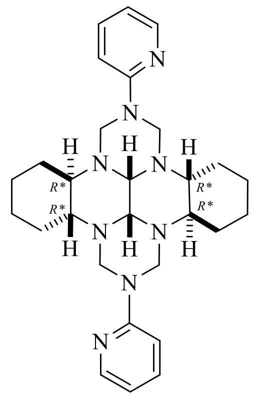
2c

(3b*R,7a*R**,10b*R**,14a*R**-*cis*-14c,14d)-2,9-Bis(5-methyl-isoxazol-3-yl)-octadecahydro-1*H*,8*H*-2,3a,7b,9,10a,14b-hexaazadibenzo[*fg*,*op*]tetracene (2c).** White powder, yield 0.27 g (56%), mp 244–246 ºC, R_f 0.60 (MeOH). ^{1}H NMR (500.17 MHz $CDCl_3$): δ = 0.95–1.02 m (2H, CH_2, H_a-7,14), 1.15–1.30 m (6H, CH_2, H_a-4,5,11,12,13), 1.74 br.s (4H, CH_2, H_b-4,5,11,12), 1.82–1.89 m (2H, CH, H-7a,14a), 2.03 d (2H, CH_2, H_b-6,13, $^2J_{ba}$ = 10 Hz), 2.23-2.29 m (2H, CH_2, H_b-7,14), 2.30 br.s (6H, CH_3, H-6′,6″), 3.08–3.13 m (2H, CH, H-3b,10b), 3.20 d (2H, CH_2, H_a-1,8, $^2J_{ab}$ = 10 Hz), 3.50 br.s (2H, CH, H-14c,14d), 3.86 d (2H, CH_2, H_a-3,10, $^2J_{ab}$ = 13.5 Hz), 4.80 d (2H, CH_2, H_b-1,8, $^2J_{ba}$ = 9.5 Hz), 4.97 d (2H, CH_2, H_b-3,10, $^2J_{ba}$ = 13 Hz), 5.62 br.s (2H, CH, H-4′,4″). ^{13}C NMR (125.78 MHz, $CDCl_3$): δ = 12.61 (C-6′,6″), 24.26 (C-4,11), 24.59 (C-5,12), 27.06 (C-6,13), 28.59 (C-7,14), 54.64 (C-3b,10b), 63.23 (C-3,10), 63.55 (C-7a,14a), 68.19 (C-1,8), 77.50 (C-14c,14d), 92.10 (C-4′,4″), 165.06 (C-3′,3″), 169.28 (C-5′,5″). MALDI TOF/TOF, m/z: (%) = 493 $[M–H]^+$ (100). Anal. Calcd. for $C_{26}H_{38}N_8O_2$: C 63.13; H 7.75; N 22.65; O 6.47. Found: C 63.05; H 7.70; N 22.59.



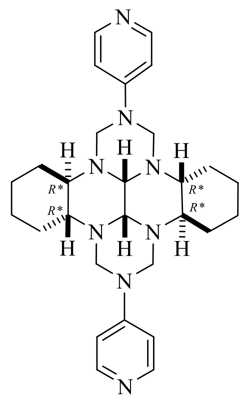
2d

(3b*R**,7a*R**,10b*R**,14a*R**-*cis*-14c,14d)-2,9-Bis(1,5-dimethyl-3-oxo-2-phenyl-pyrazol-4-yl)octadecahydro-1*H*,8*H*-2,3a,7b,9,10a,14b-hexaazadibenzo-[*fg,op*]tetracene (2d). Orange powder, yield 0.37 g (52%), mp 240–242 ºC, R_f 0.68 (MeOH). ^{1}H NMR (500.17 MHz $CDCl_3$): δ = 0.93–1.02 m (2H, CH_2, H_a-7,14), 1.15–1.35 m (6H, CH_2, H_a-4,5,6,11,12,13), 1.74 br.s (4H, CH_2, H_b-4,5,11,12), 1.90–2.08 m (4H, CH_2, H_b-6,7,13,14; 2H, CH, H-7a,14a), 2.33 br.s (6H, CH_3, H-13′,13″), 2.99 br.s (6H, CH_3, H-12′,12″), 3.54 br.s (4H, CH, H-3b,10b, H-14c,14d), 3.77 d (2H, CH_2, H_a-1,8, $^2J_{ab}$ = 8.4 Hz), 4.20 d (2H, CH_2, H_a-3,10, $^2J_{ab}$ = 12.4 Hz), 4.28 d (2H, CH_2, H_b-1,8, $^2J_{ba}$ = 8.8 Hz), 4.35 d (2H, CH_2, H_b-3,10, $^2J_{ba}$ = 12.4 Hz), 7.28 br.s (2H, CH, H-9′,9″), 7.35-7.50 m (8H, CH, H-7′,7″,8′,8″,10′,10″,11′,11″). ^{13}C NMR (125.78 MHz, $CDCl_3$): δ = 10.45 (C-13′,13″), 24.51 (C-4,11), 24.76 (C-5,12), 27.05 (C-6,13), 28.44 (C-7,14), 36.72 (C-12′,12″), 54.84 (C-3b,10b), 63.84 (C-7a,14a), 66.46 (C-3,10), 71.48 (C-1,8), 77.42 (C-14c,14d), 120.02 (C-4′,4″), 123.22 (C-8′,8″,10′,10″), 126.11 (C-9′,9″), 129.00 (C-7′,7″,11′,11″), 135.14 (C-5′,5″), 150.01 (C-6′,6″), 163.77 (C-3′,3″). MALDI TOF/TOF, m/z: (%) = 703 $[M–H]^+$ (100). Anal. Calcd. for $C_{40}H_{52}N_{10}O_2$: C 68.15; H 7.44; N 19.87; O 4.54. Found: C 68.06; H 7.40; N 19.81.



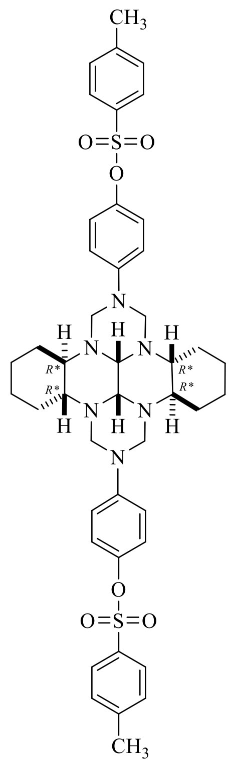
2e

(3b*R**,7a*R**,10b*R**,14a*R**-*cis*-14c,14d)-2,9-Di(pyridin-2-yl)octadecahydro-1*H*,8*H*-2,3a,7b,9,10a,14b-hexaazadibenzo[*fg,op*]tetracene (2e). Pale yellow powder, yield 0.27 g (55%), mp 263–265 ºC, R_f 0.69 (MeOH). ^{1}H NMR (500.17 MHz $CDCl_3$): δ = 0.86–1.02 m (4H, CH_2, H_a-4,7,11,14), 1.19–1.29 m (4H, CH_2, H_a-5,6,12,13), 1.64 d (2H, CH_2, H_b-4,11, $^2J_{ba}$ 12 Hz), 1.71 br.s (2H, CH_2, H_b-5,12), 1.80–1.90 m (2H, CH, H-7a,14a), 2.12 br.s (2H, CH_2, H_b-6,13), 2.33 d (2H, CH_2, H_b-7,14, $^2J_{ba}$ = 10.5 Hz), 2.80–2.90 m (2H, CH, H-3b,10b), 3.29 d (2H, CH_2, H_a-1,8, $^2J_{ba}$ = 11 Hz), 3.59 br.s (2H, CH, H-14c,14d), 3.94 d (2H, CH_2, H_a-3,10, $^2J_{ab}$ = 13.5 Hz), 5.24 d (2H, CH_2, H_b-1,8, $^2J_{ba}$ = 11 Hz), 5.75 d (2H, CH_2, H_b-3,10, $^2J_{ba}$ = 13.5 Hz), 6.61–6.67 m (2H, CH, H-5′,5″), 6.70 d (2H, CH, H-3′,3″, ^3J = 8 Hz), 7.45–7.51 m (2H, CH, H-4′,4″), 8.16 br.s (2H, CH, H-6′,6″). ^{13}C NMR (125.78 MHz, $CDCl_3$): δ = 24.19 (C-4,11), 24.75 (C-5,12), 27.17 (C-6,13), 28.89 (C-7,14), 55.00 (C-3b,10b), 62.03 (C-3,10), 63.63 (C-7a,14a), 66.16 (C-1,8), 78.44 (C-14c,14d), 106.80 (C-3′,3″), 113.78 (C-5′,5″), 137.78 (C-4′,4″), 147.92 (C-6′,6″), 158.36 (C-2′,2″). MALDI TOF/TOF, m/z: (%) = 485 $[M–H]^+$ (100). Anal. Calcd. for $C_{28}H_{38}N_8$: C 69.10; H 7.87; N 23.03. Found: C 69.02; H 7.81; N 22.97.



2f

(3b*R**,7a*R**,10b*R**,14a*R**-*cis*-14c,14d)-2,9-Di(pyridin-4-yl)-octadecahydro-1*H*,8*H*-2,3a,7b,9,10a,14b-hexaazadibenzo[*fg,op*]tetracene (2f). Pale yellow powder, yield 0.21 g (48%), mp 262–264 °C, R_f 0.62 (MeOH). ^{1}H NMR (500.17 MHz $CDCl_3$): δ = 0.82–1.02 m (4H, CH_2, H_a-4,7,11,14), 1.15–1.27 m (4H, CH_2, H_a-5,6,12,13), 1.61 d (2H, CH_2, H_b-4,11, $^2J_{ba}$ = 13 Hz), 1.71 d (2H, CH_2, H_b-5,12, $^2J_{ba}$ = 11 Hz), 1.78–1.88 m (2H, CH, H-7a,14a), 1.95 d (2H, CH_2, H_b-6,13, $^2J_{ba}$ = 10 Hz), 2.09 d (2H, CH_2, H_b-7,14, $^2J_{ba}$ = 10 Hz), 2.82–2.92 m (2H, CH, H-3b,10b), 3.25 d (2H, CH_2, H_a-1,8, $^2J_{ab}$ = 11 Hz), 3.52 br.s (2H, CH, H-14c,14d), 3.98 д (2H, CH_2, H_a-3,10, $^2J_{ab}$ = 13.5 Hz), 4.97 d (2H, CH_2, H_b-1,8, $^2J_{ba}$ = 11 Hz), 5.05 d (2H, CH_2, H_b-3,10, $^2J_{ba}$ = 13.5 Hz), 6.72 d (4H, CH, H-3′,3″,5′,5″, ^3J = 5.5 Hz), 8.28 d (4H, CH, H-2′,2″,6′,6″, ^3J = 5.5 Hz). ^{13}C NMR (125.78 MHz, $CDCl_3$): δ = 24.07 (C-4,11), 24.44 (C-5,12), 27.06 (C-6,13), 28.79 (C-7,14), 54.74 (C-3b,10b), 63.41 (C-7a,14a), 63.77 (C-3,10), 66.94 (C-1,8), 77.90 (C-14c,14d), 109.46 (C-3′,3″,5′,5″), 150.38 (C-2′,2″,6′,6″), 154.11 (C-4′,4″). Anal. Calcd. for $C_{28}H_{38}N_8$: C 69.10; H 7.87; N 23.03. Found: C 69.04; H 7.83; N 22.95.

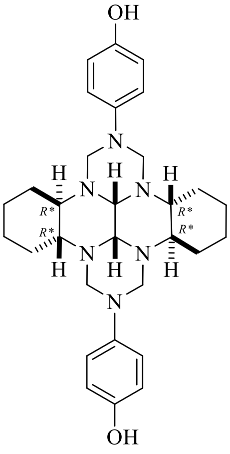


2'a

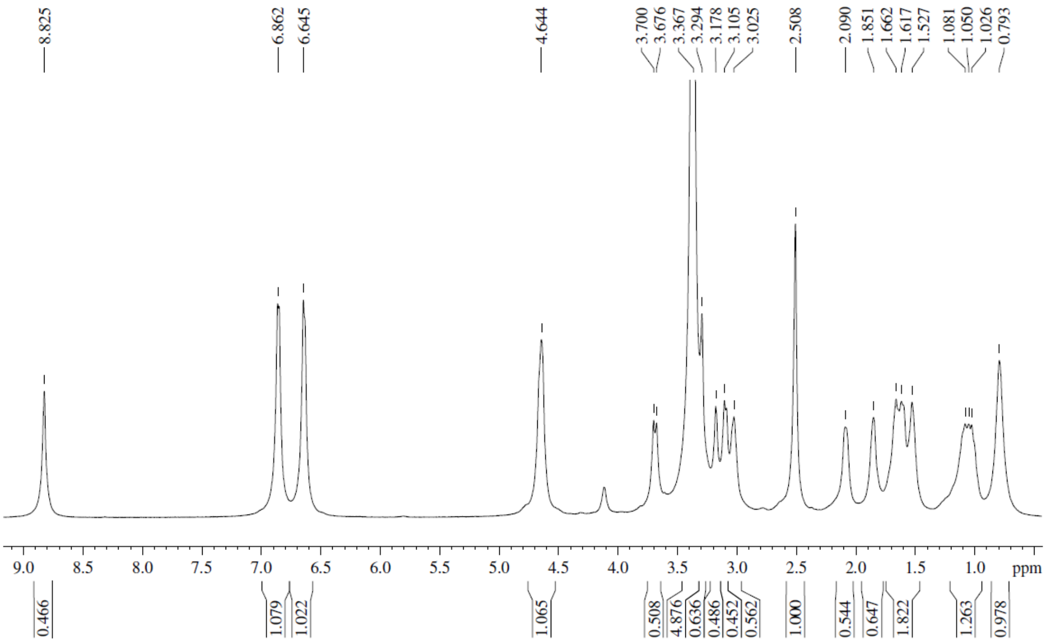
(3b*R**,7a*R**,10b*R**,14a*R**-*cis*-14c,14d)-2,9-Bis(4-tosyloxyphenyl)octadecahydro-1*H*,8*H*-2,3a,7b,9,10a,14b-hexaazadibenzo[*fg,op*]tetracene (2′a). Bis-tosyl derivative **2′a** was obtained via the reaction of compound **2a** with *p*-toluenesulfonyl chloride as described [X. Lei, A. Jalla, MhdA. A. Shama, J. M. Stafford, B. Cao, *Synthesis*, 2015, **47**, 2578]. Pale yellow crystals, yield 0.43 g (52%), mp 242–244 °C, R_f 0.57 (MeOH). ^{1}H NMR (500.17 MHz $CDCl_3$): δ = 0.75–0.82 m (2H, CH_2, H_a-4,11), 0.84–0.95 m (2H, CH_2, H_a-7,14), 1.12–1.21 m (4H, CH_2, H_a-5,6,12,13), 1.58 d (2H, CH_2, H_b-5,12, $^2J_{ba}$ = 12.5 Hz), 1.66–1.71 m (2H, CH, H_b-4,11), 1.75–1.84 m (2H, CH_2, H_b-7,14; 2H, CH, H-7a,14a), 2.06 br.s (2H, CH_2, H_b-6,13), 2.47 br.s (6H, CH_3, H-17′,17″), 2.98–3.07 m (2H, CH, H-3b,10b), 3.27 d (2H, CH_2, H_a-1,8, $^2J_{ab}$ = 11 Hz), 3.49 br.s (2H, CH, H-14c,14d), 3.93 d (2H, CH_2, H_a-3,10, $^2J_{ab}$ = 13.5 Hz), 4.80 d (2H, CH_2, H_b-1,8, $^2J_{ba}$ = 9.5 Hz), 4.83 d (2H, CH_2, H_b-3,10, $^2J_{ba}$ = 12.5 Hz), 6.85 d (4H, CH, H-3′,3″,5′,5″, ^3J = 9 Hz), 6.90 d (4H, CH, H-2′,2″,6′,6″, ^3J = 9 Hz), 7.32 d (4H, CH, H-13′,13″,15′,15″, ^3J = 8.5 Hz), 7.72 d (4H, CH, H-12′,12″,16′,16″, ^3J = 8 Hz). ^{13}C NMR (125.78 MHz, $CDCl_3$): δ = 21.75 (C-17′,17″), 24.25 (C-5,12), 24.54 (C-4,11), 27.17 (C-6,13), 28.49 (C-7,14), 55.21 (C-3b,10b), 63.45 (C-7a,14a), 66.54 (C-3,10), 69.49 (C-1,8), 77.90 (C-14c,14d), 118.01 (C-2′,2″,6′,6″),122.95 (C-3′,3″,5′,5″), 128.54 (C-12′,12″,16′,16″), 129.69 (C-13,13″,15′,15″), 132.59 (C-11′,11″), 142.79 (C-4′,4″), 145.14 (C-14′,14″), 148.77 (C-1′,1″). Anal. Calcd. for $C_{44}H_{56}N_6O_6S_2$: C 64.05; H 6.35; N 10.19; O 11.64; S 7.77. Found: C 64.01; H 6.33; N 10.12; S 7.71.

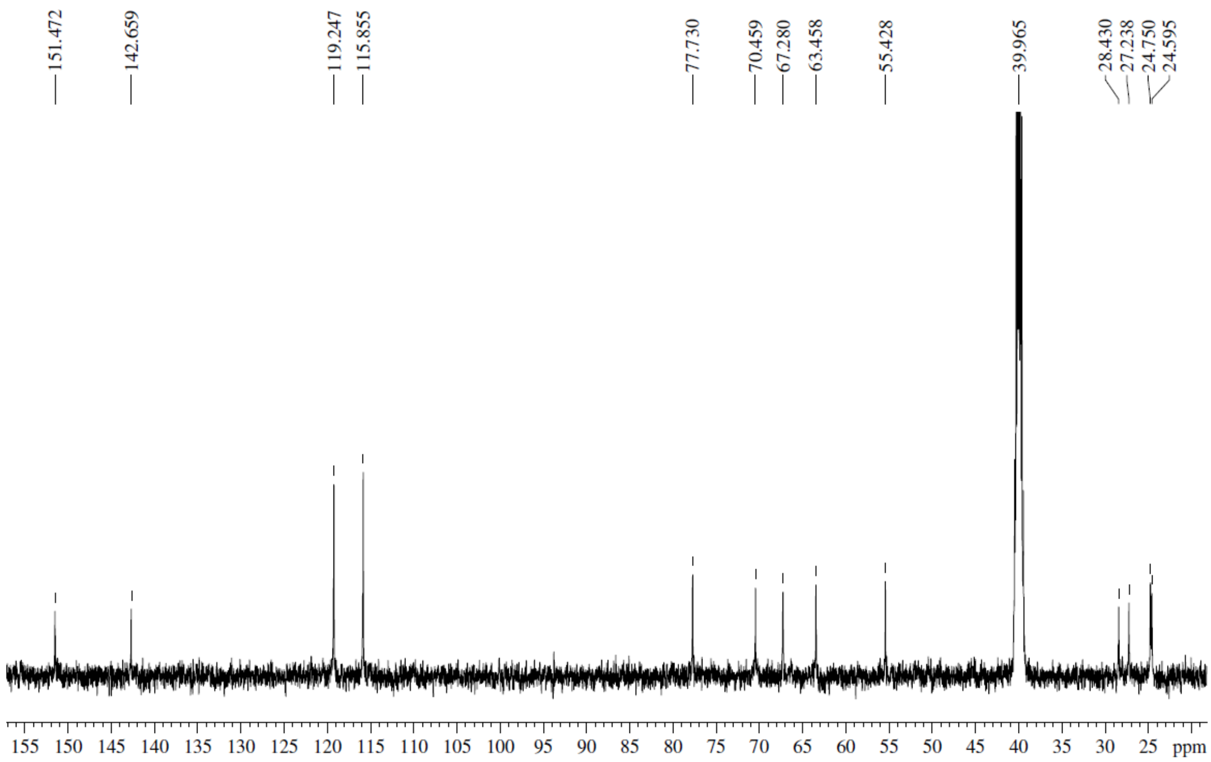
NMR and MS spectra for compounds 2a-f and 2′a

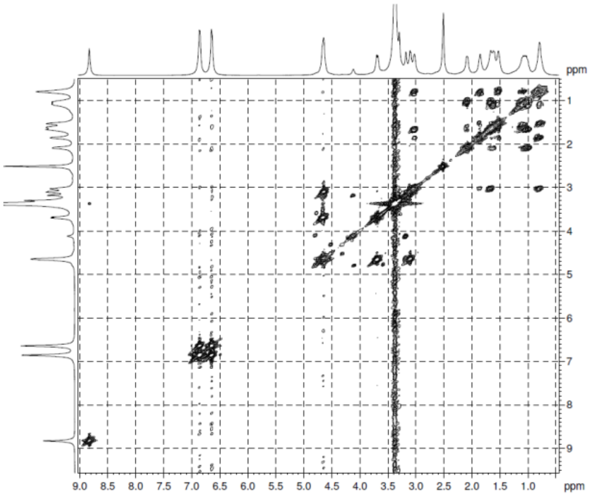
Figure S1. NMR and MS spectra of compound **2a**

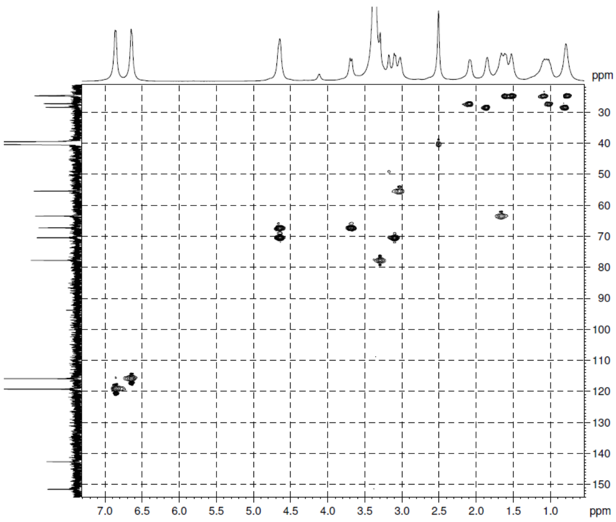


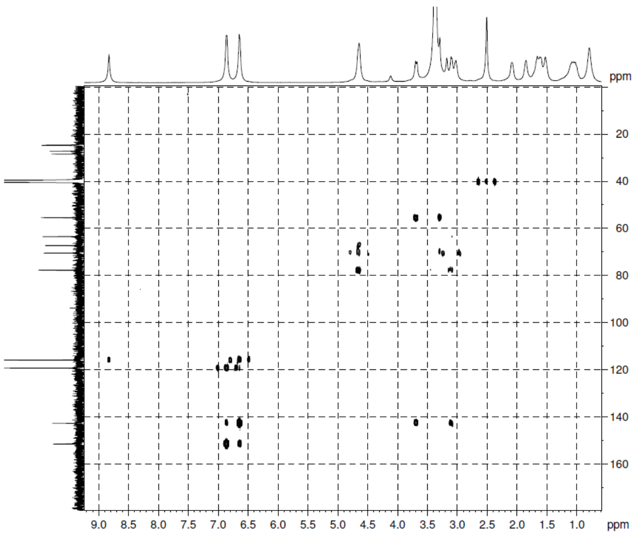
2a

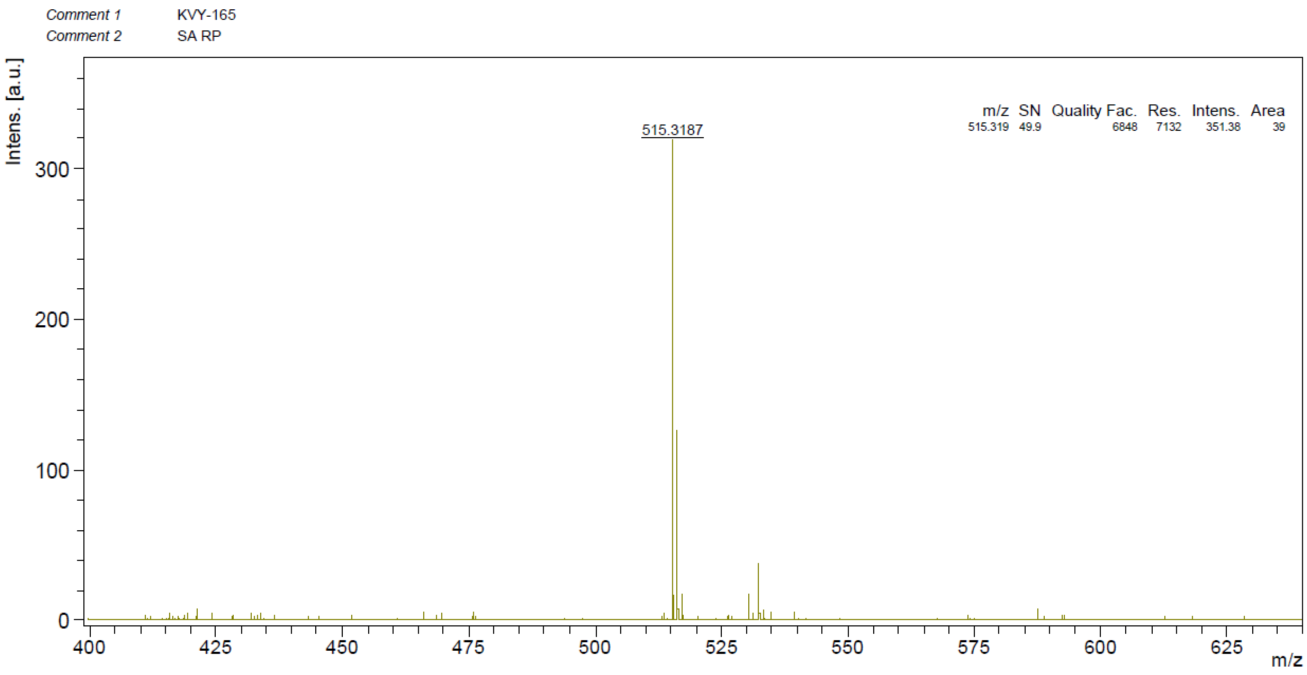








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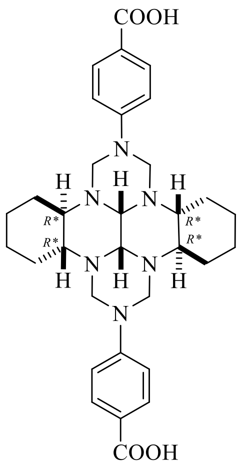
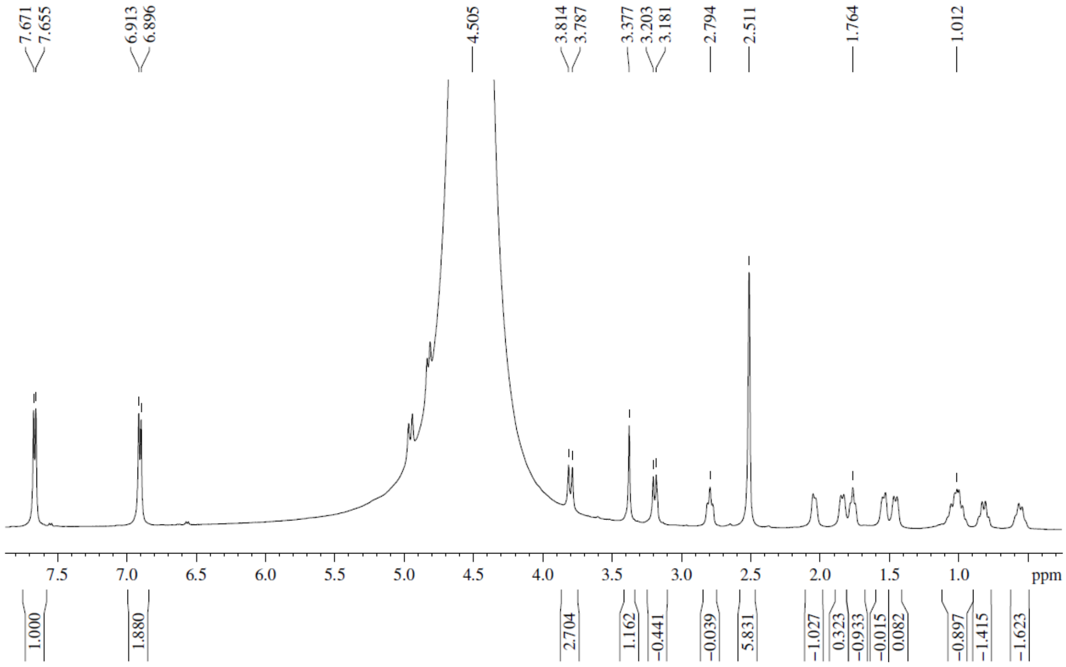
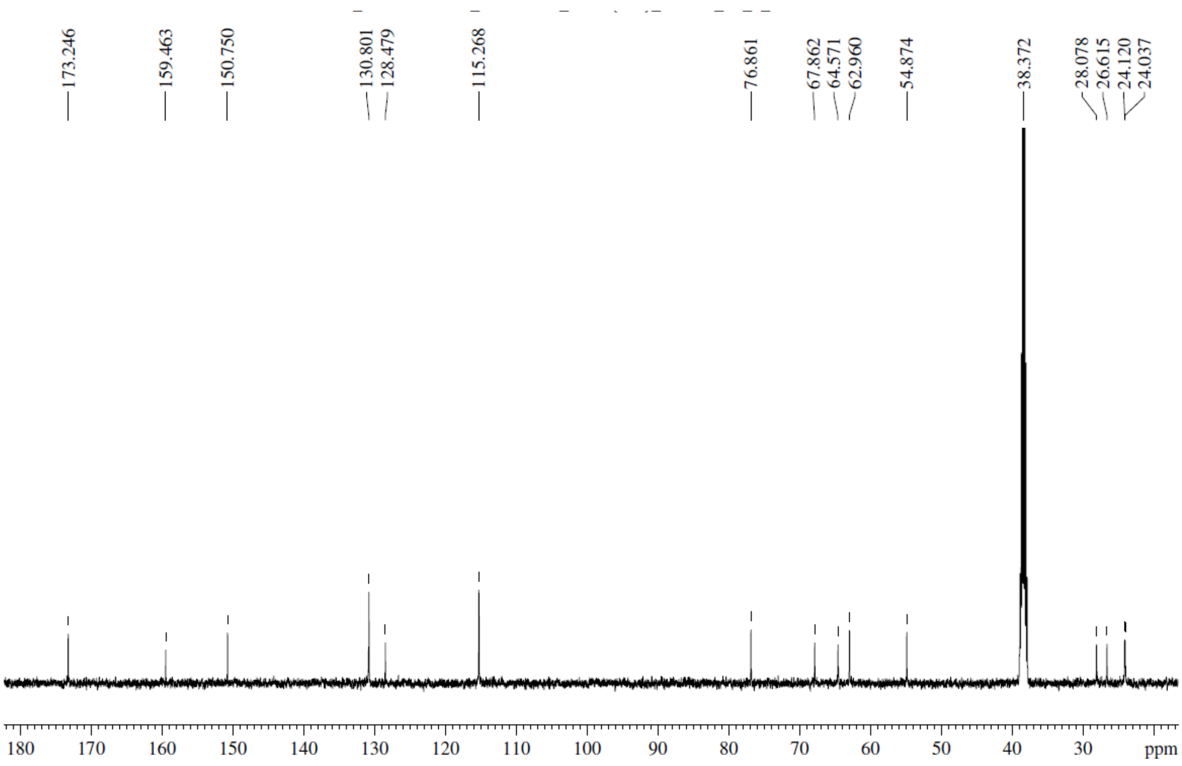
m/z

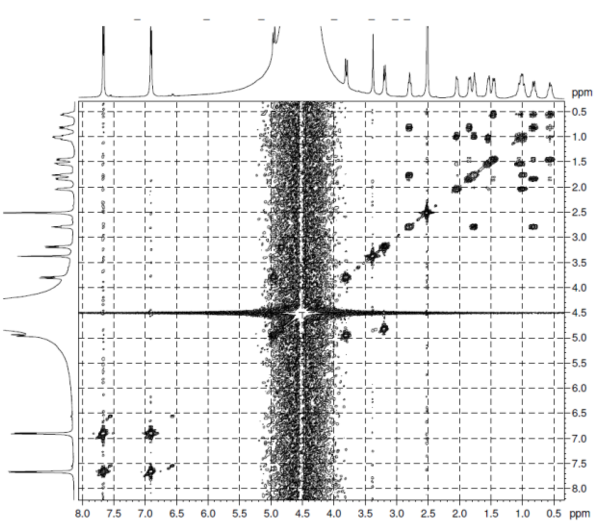
Figure S2. NMR and MS spectra of compound **2b**

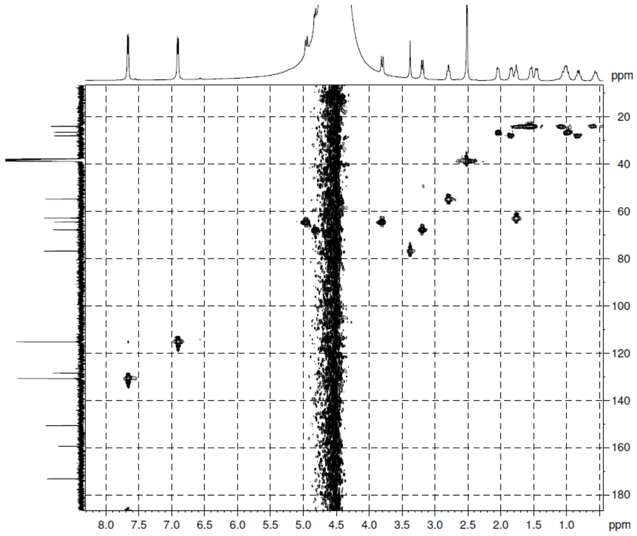


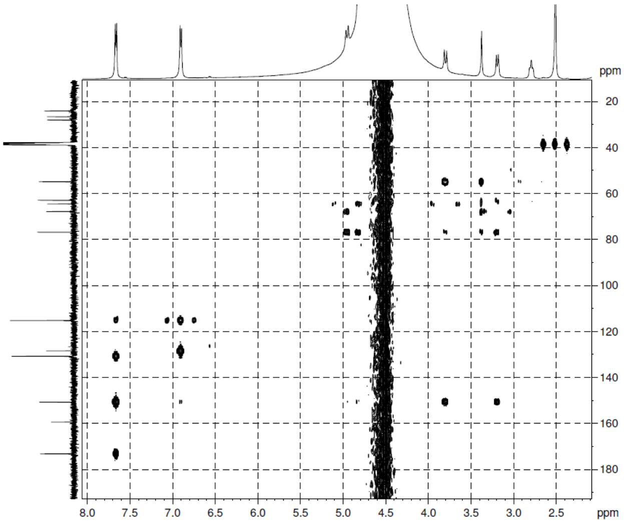
2b

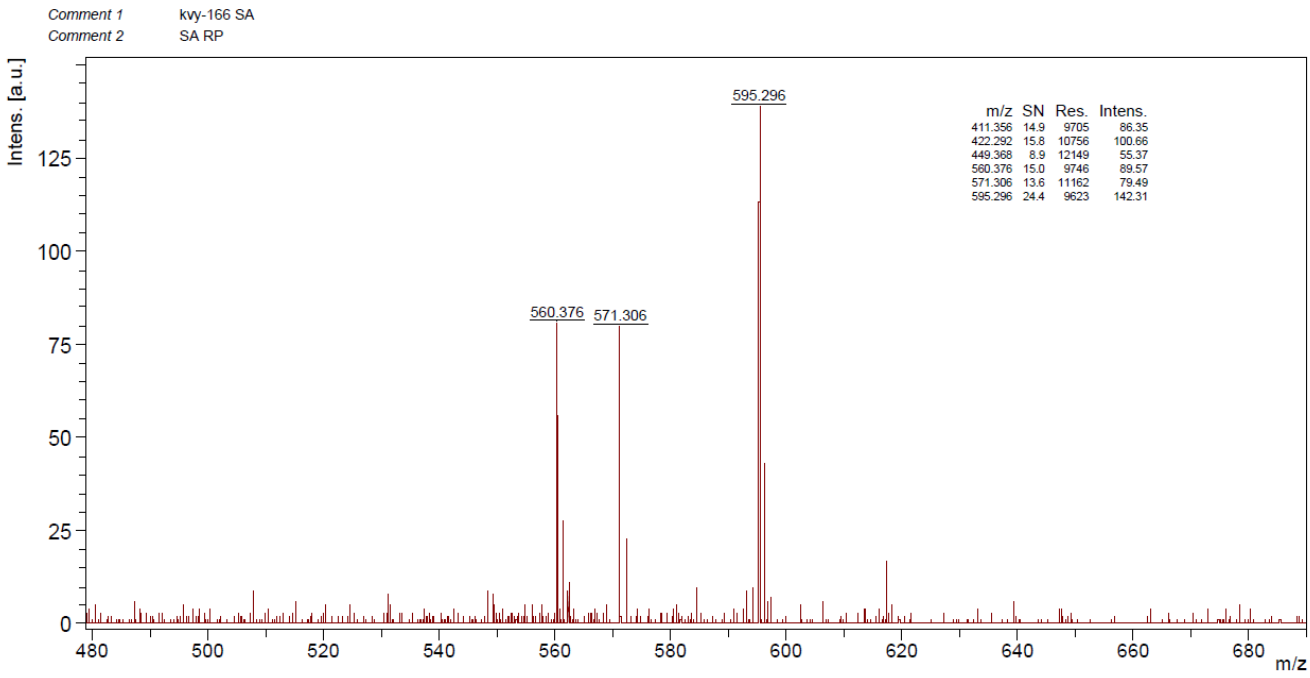












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Comment 2 SA RP
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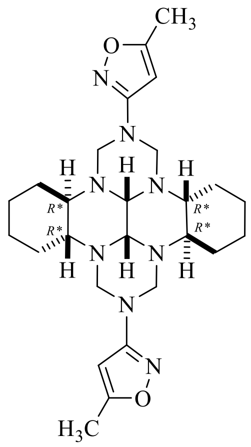
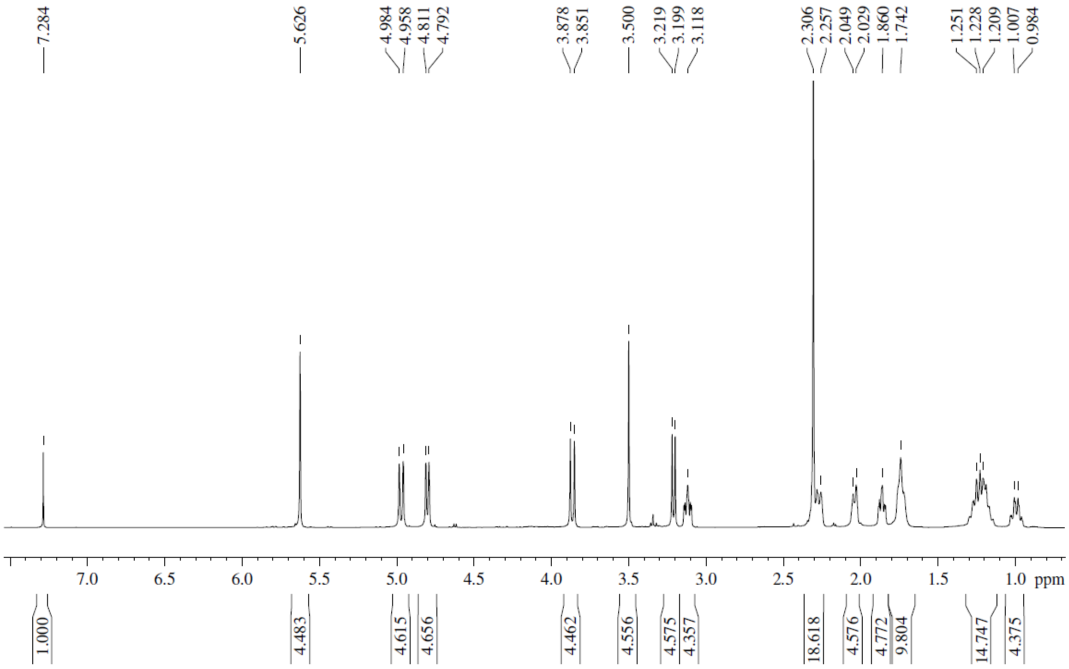
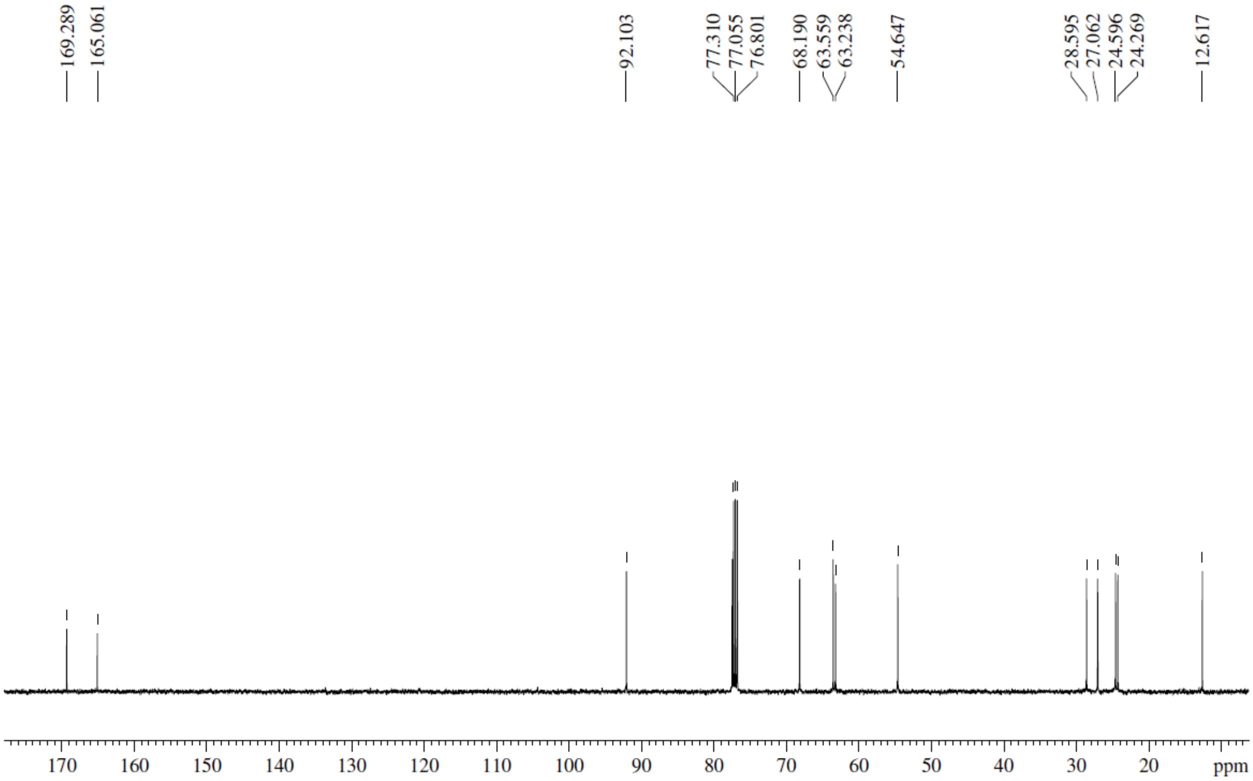
595.296
560.376
571.306
m/z SN Res. Intens.
411.356 14.9 9705 86.35
422.292 15.8 10756 100.66
449.368 8.9 12149 55.37
560.376 15.0 9746 89.57
571.306 13.6 11162 79.49
595.296 24.4 9623 142.31
m/z

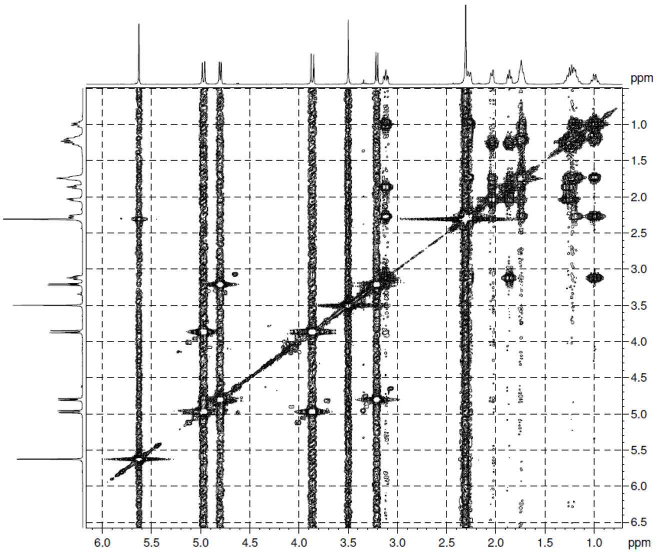
Figure S3. NMR and MS spectra of compound **2c**

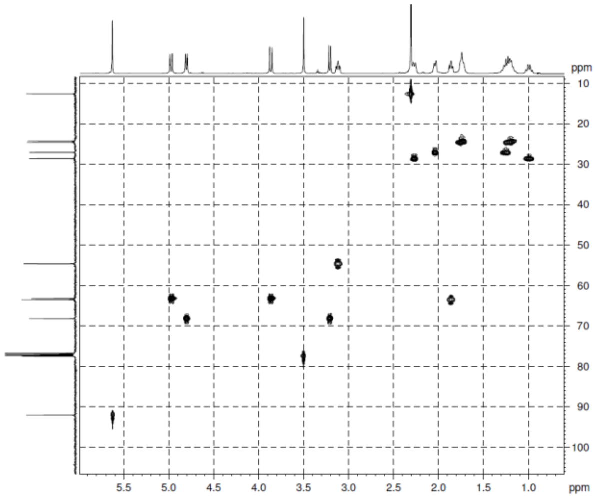


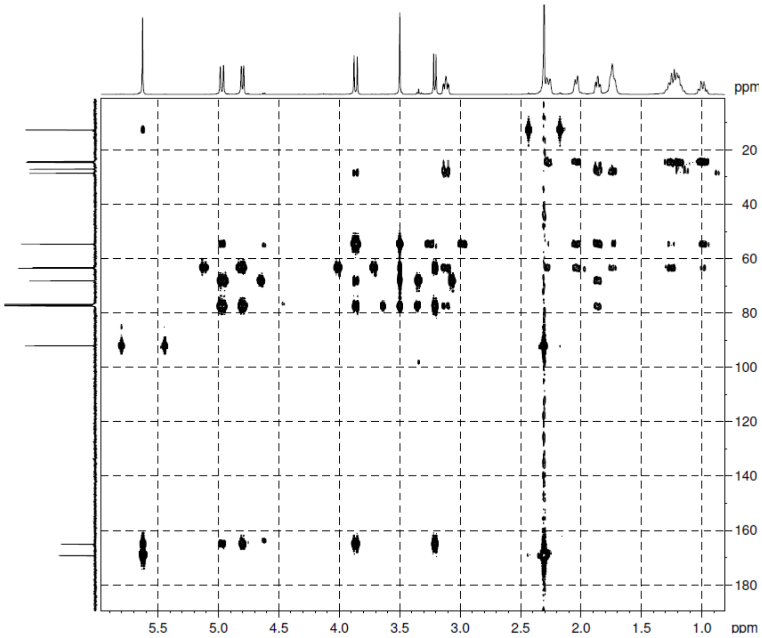
2c











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Comment 2 SA RP

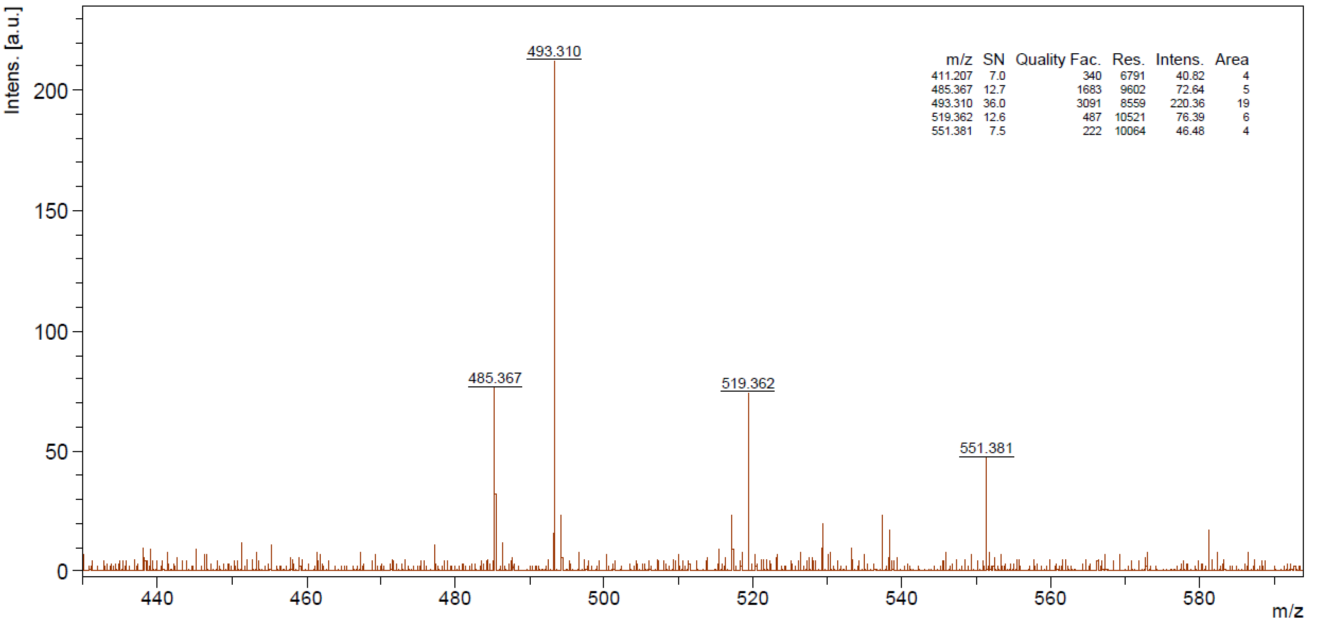
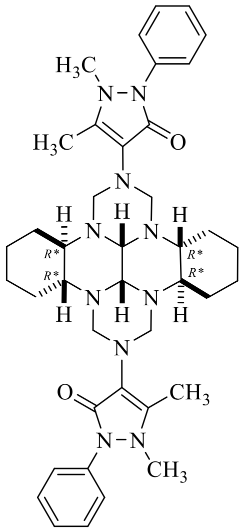
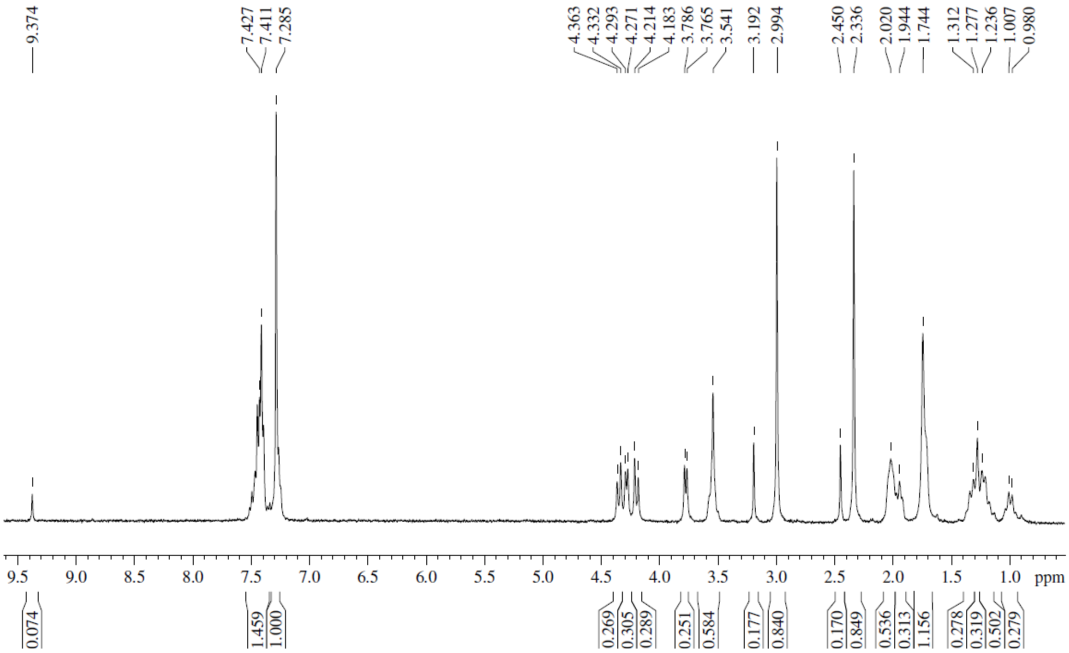
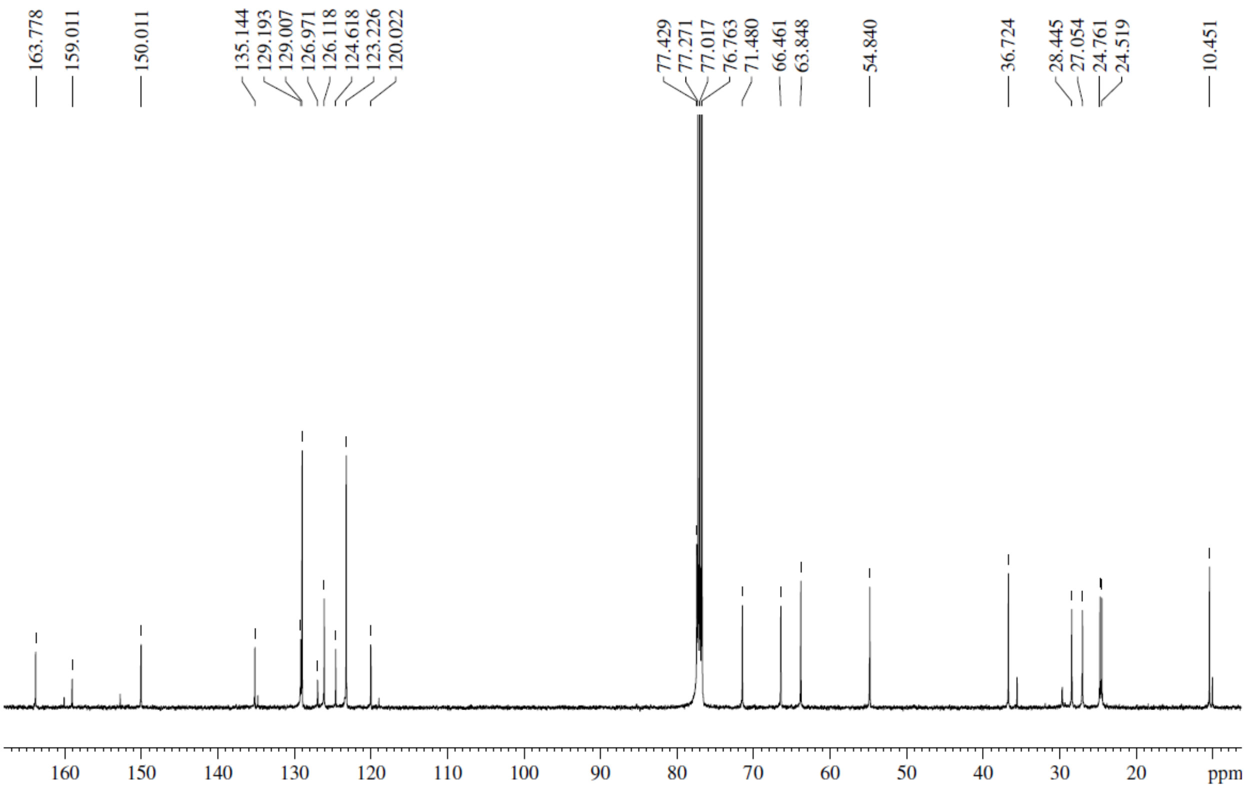


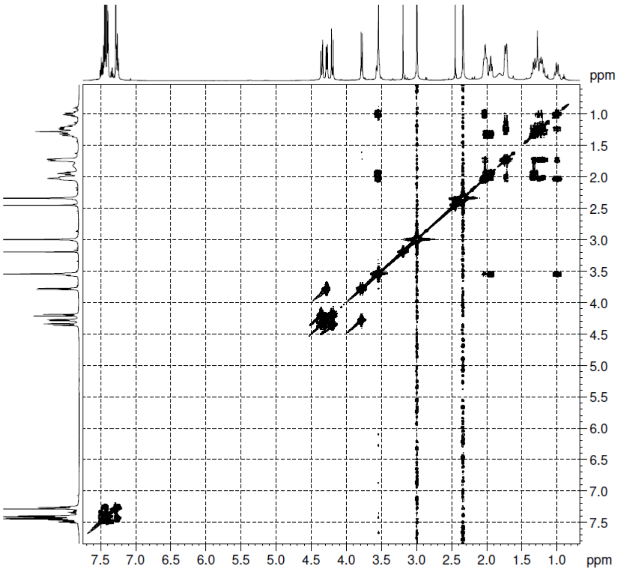
Figure S4. NMR and MS spectra of compound **2d**



2d



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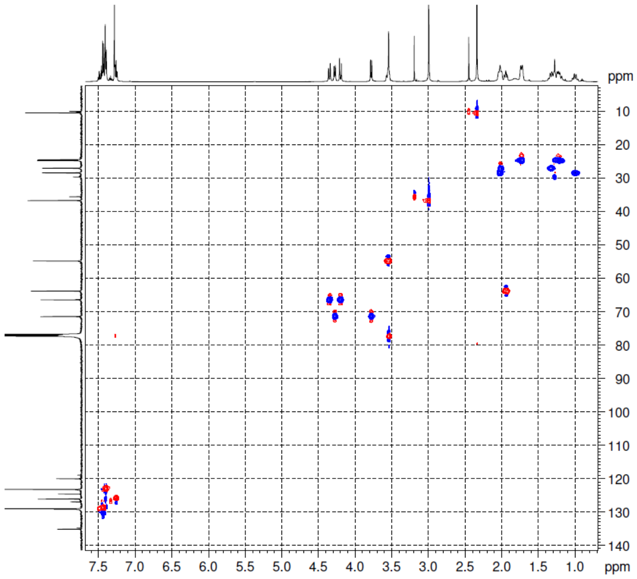
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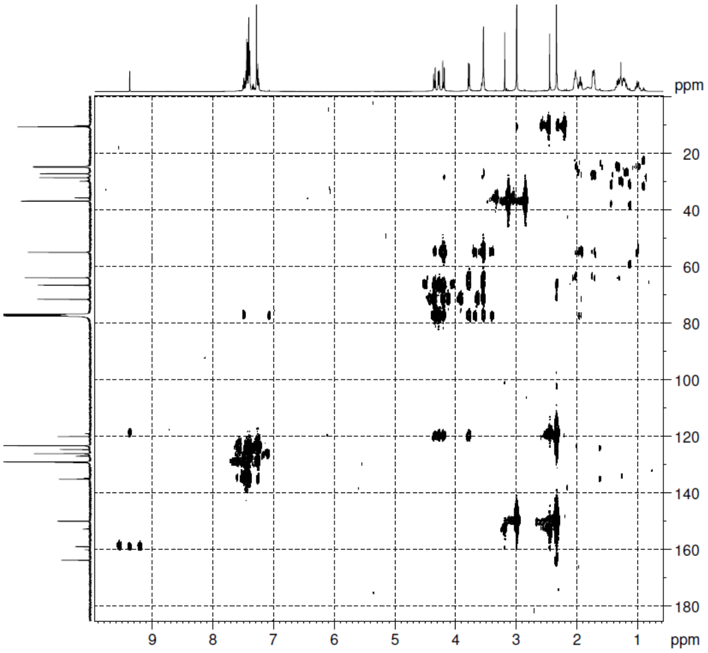
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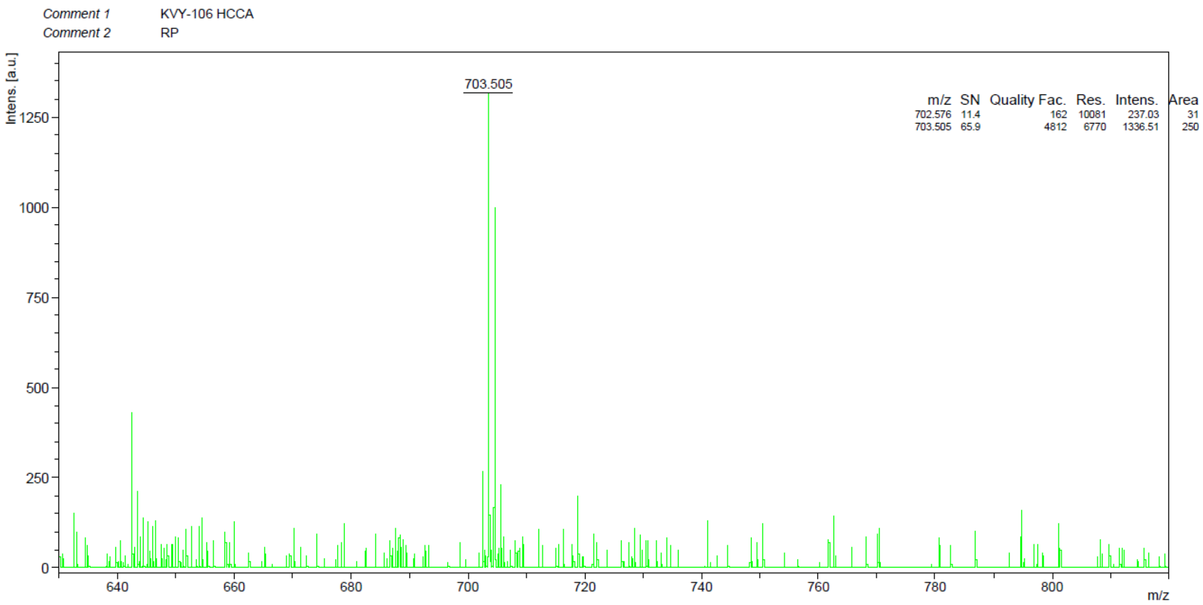
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Comment 2 RP
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m/z SN Quality Fac. Res. Intens. Area
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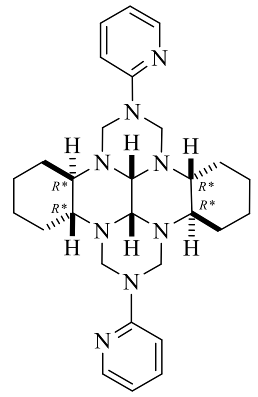
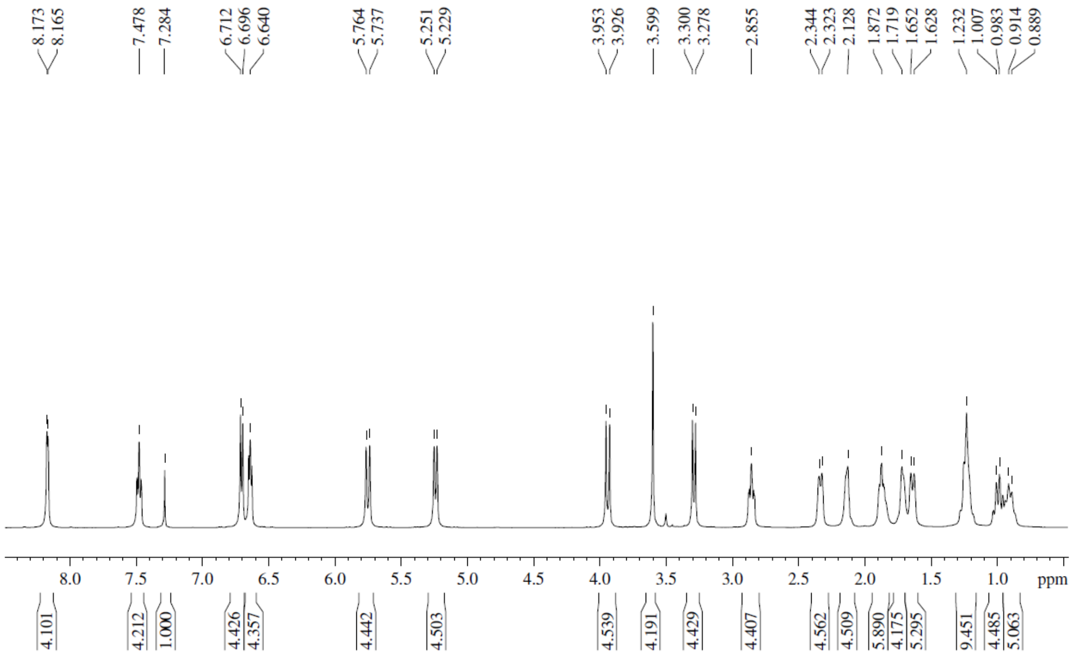
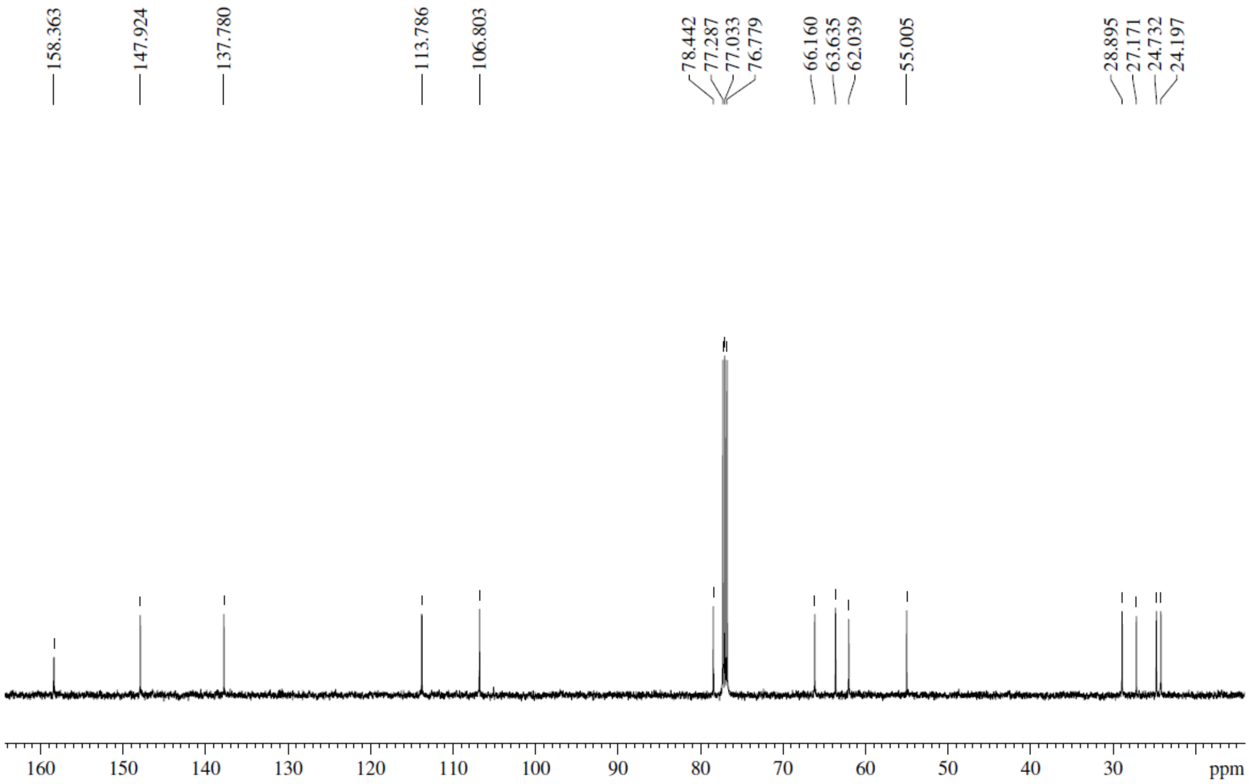
703.505 65.9 4812 6770 1336.51 250
m/z

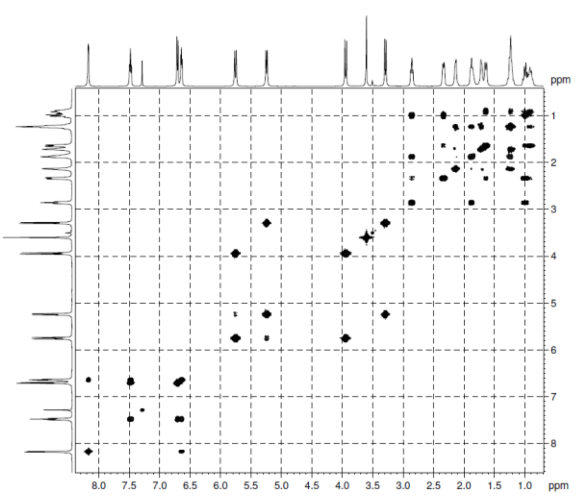
Figure S5. NMR and MS spectra of compound **2e**

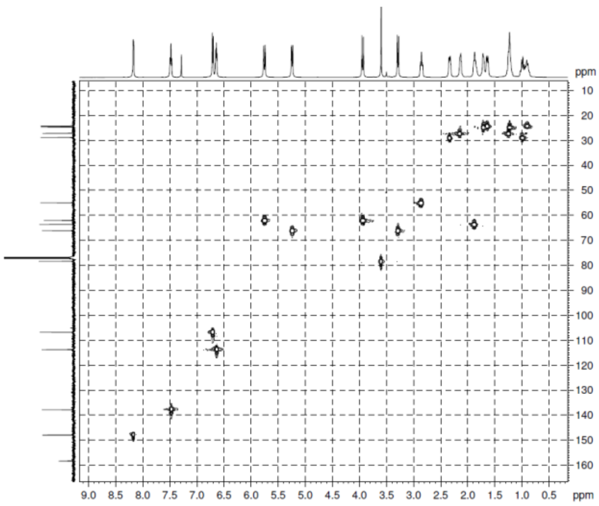


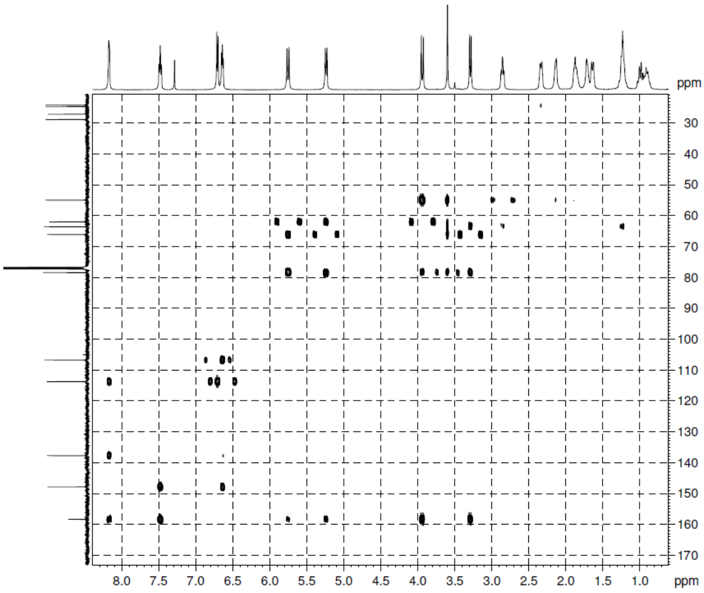
2e

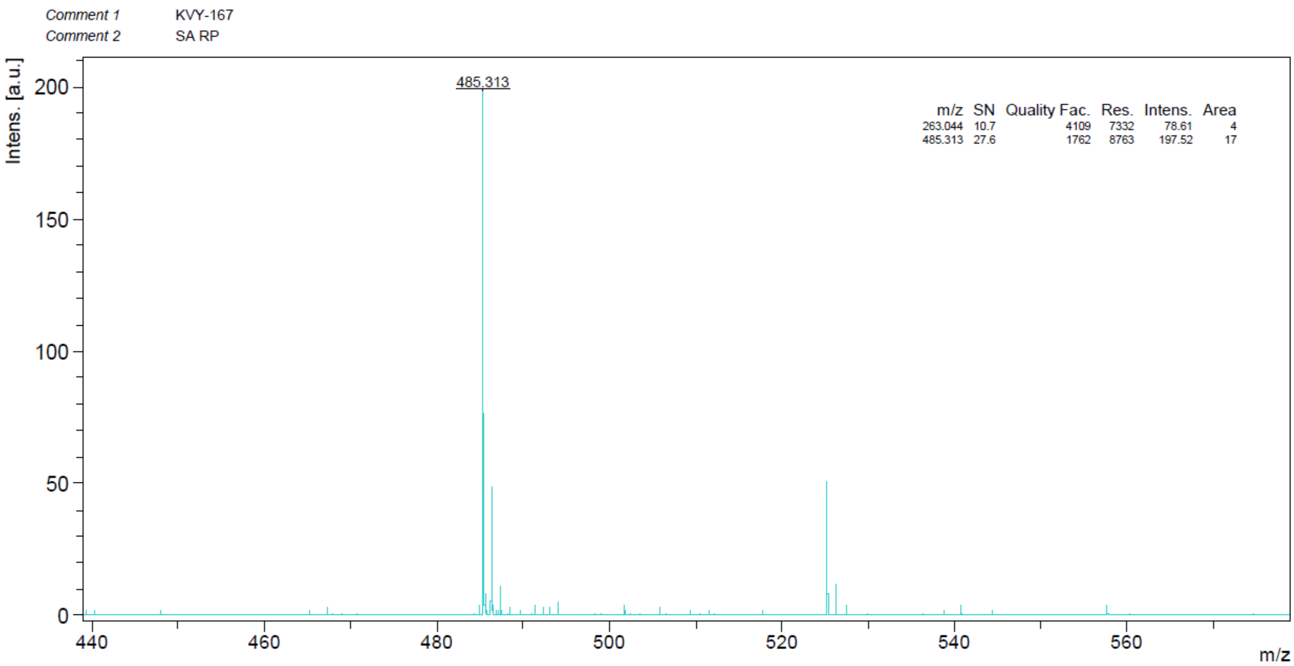











Comment 1 KVY-167
Comment 2 SA RP
Intens. [a.u.]
485.313
m/z SN Quality Fac. Res. Intens. Area
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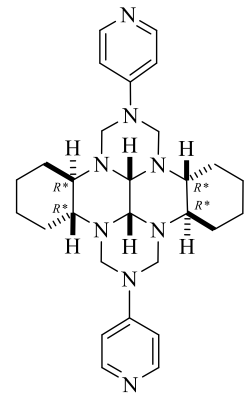
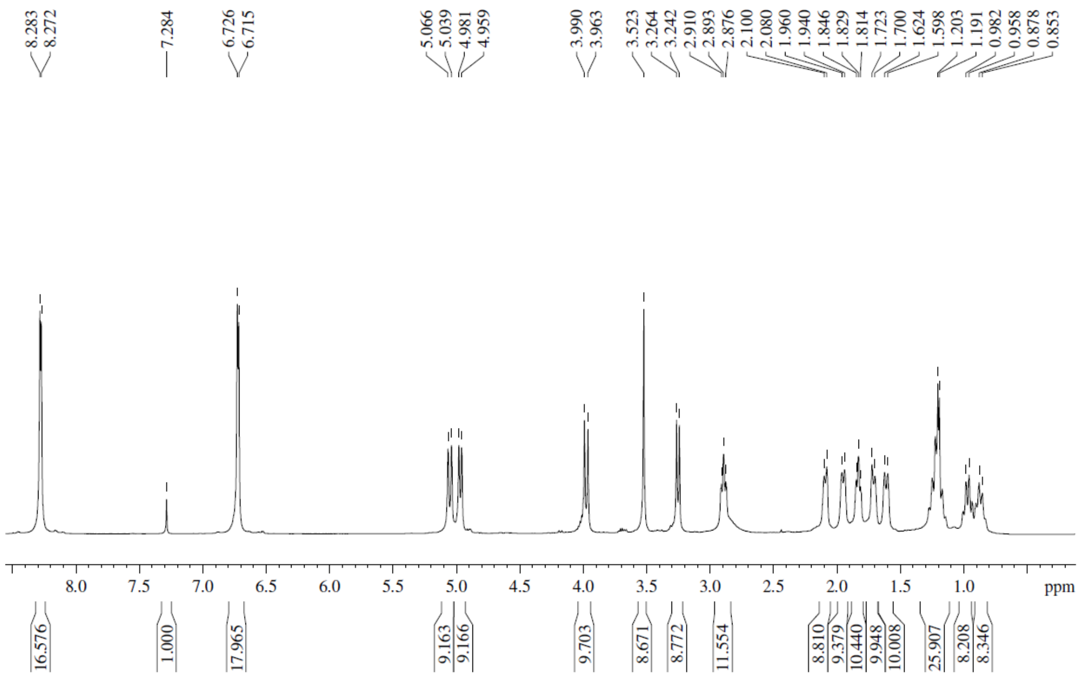
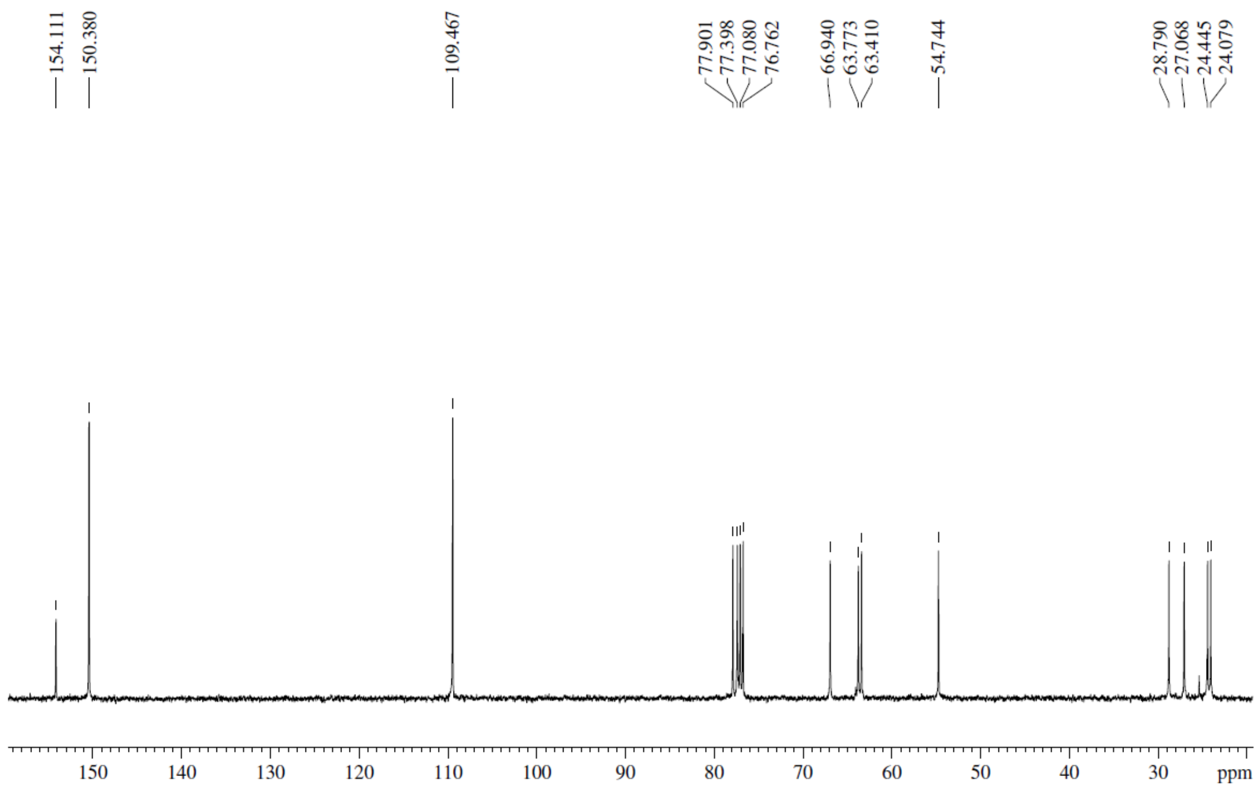
485.313 27.6 1762 8763 197.52 17
m/z

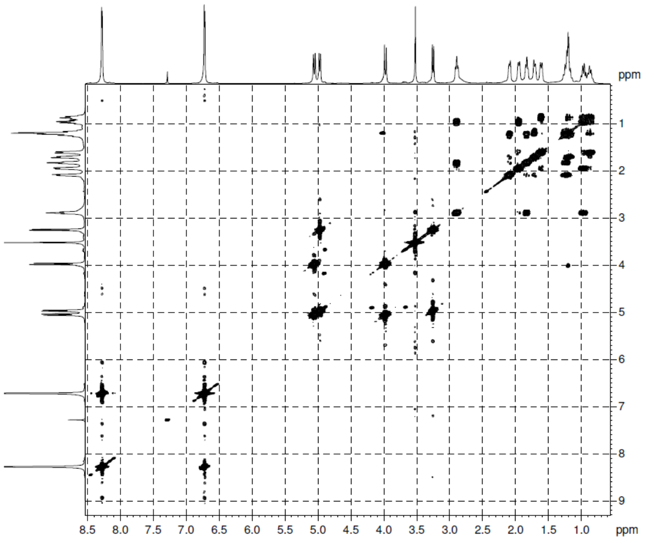
Figure S6. NMR spectra of compound **2f**



2f



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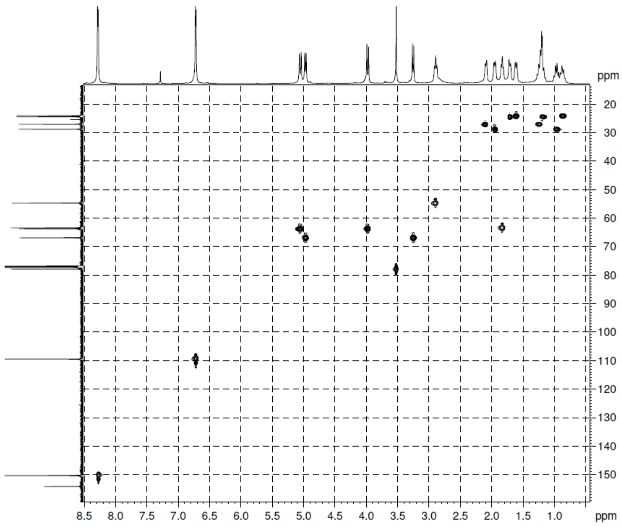
ppm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130
140
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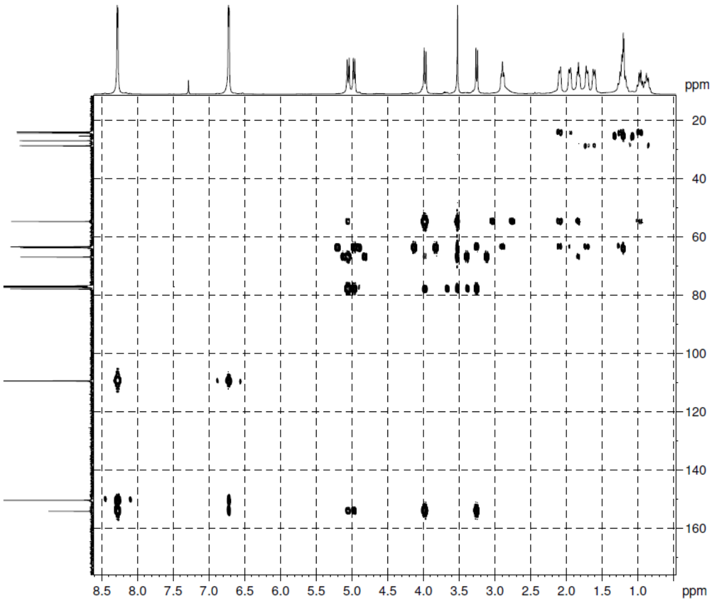
ppm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80
100
120
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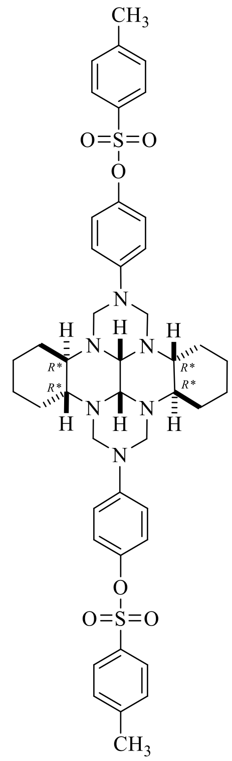
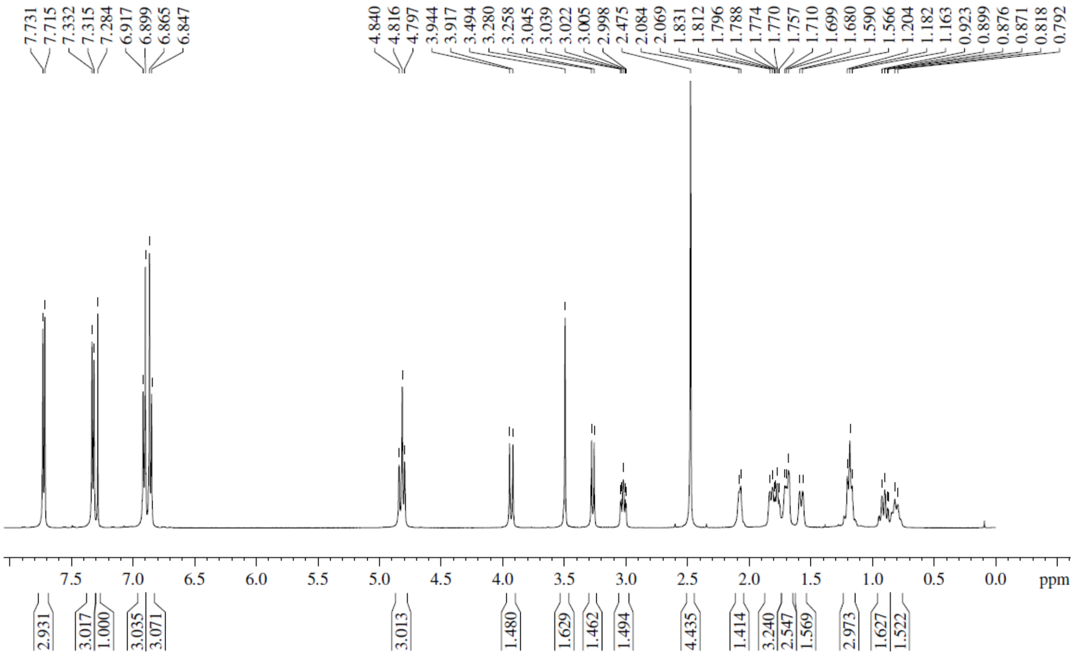
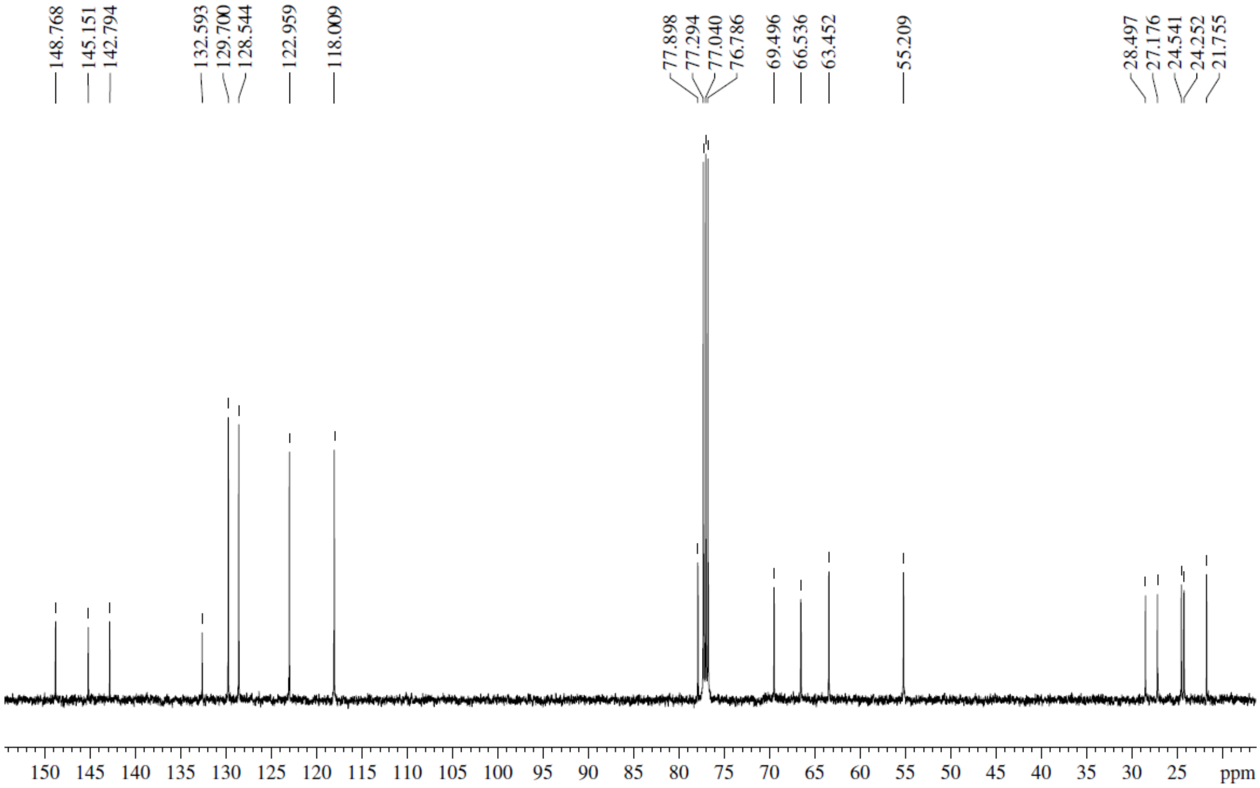
ppm

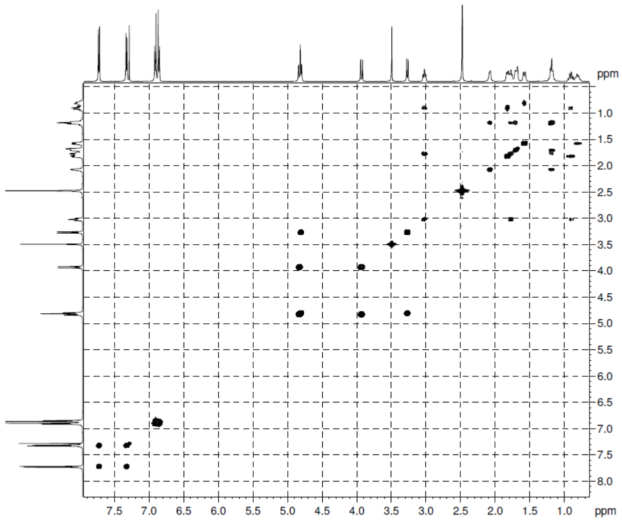
Figure S7. NMR spectra of compound **2′a**



2'a



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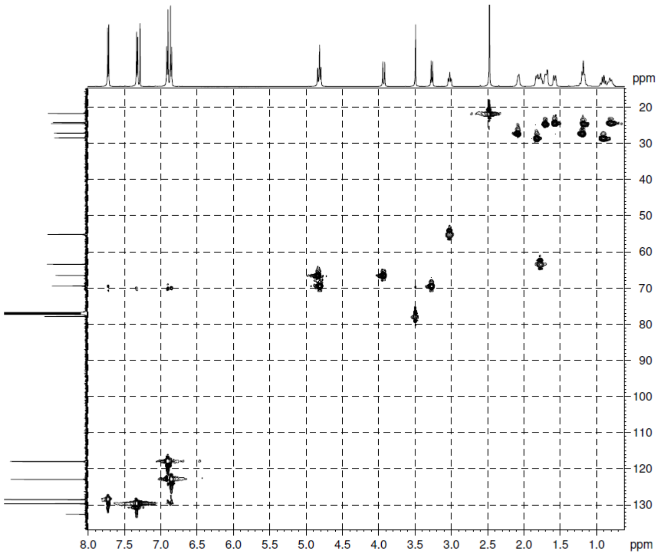
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm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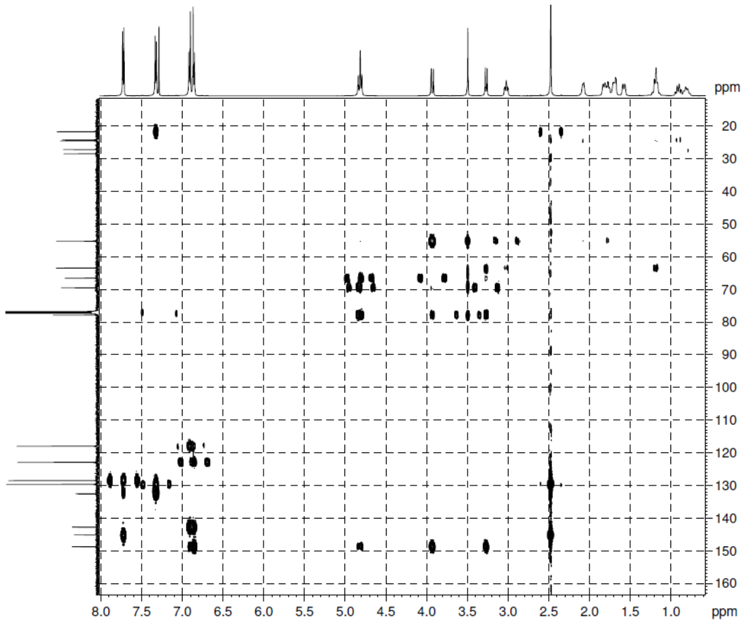
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm


ppm
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120
130
140
150
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X-ray data for compound 2′a

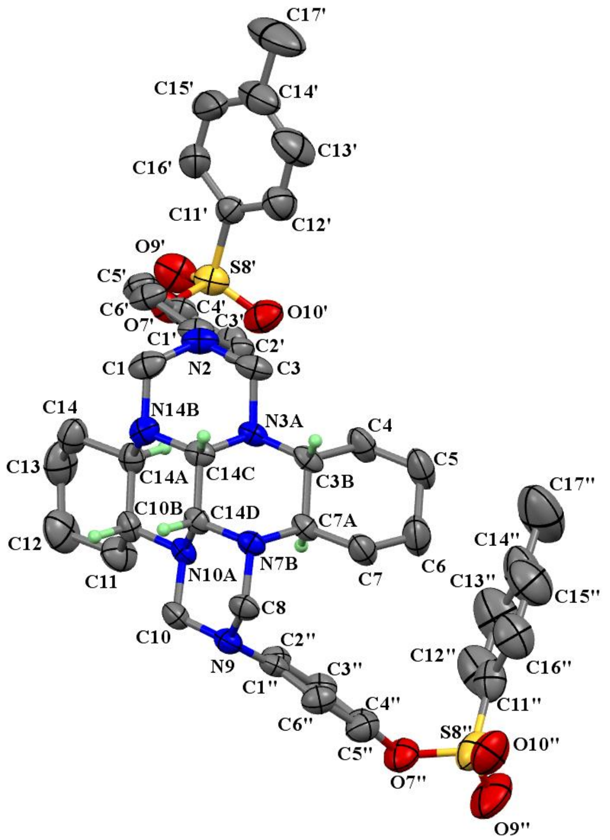

Figure S8. Molecular structure of compound **2′a** with atomic numbering according to X-ray data. Thermal displasement ellipsoids are shown at 30% probability level. The hydrogen atoms of the carbon atoms C3b, C7a, C10b, C14a, C14c, C14d show the type of ring couplingand the other hydrogen atoms are omittted for clarity.

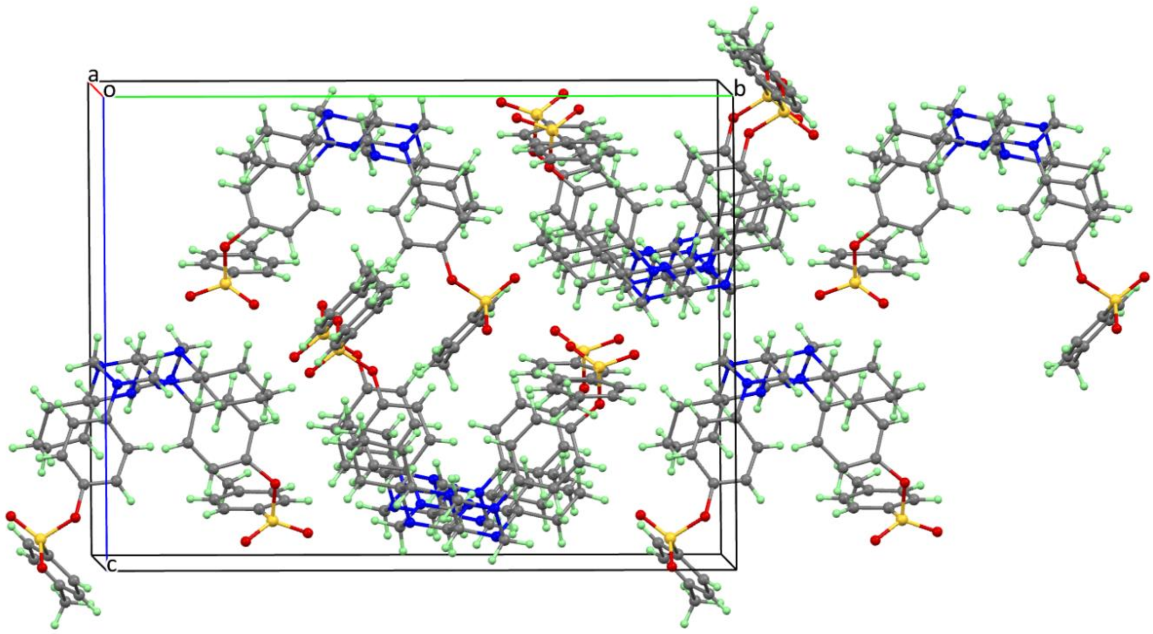

Figure S9. Packing of molecules in **2′a**,view along *a* axis.

Table S1. Crystal data and structure refinement for compound **2′a.**

CCDC	1957459
Empirical formula	$C_{44}H_{52}N_6O_6S_2$
Formula weight	825.04
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.6826(4)
b/Å	23.7412(9)
c/Å	17.9380(5)
α/°	90
β/°	98.760(3)
γ/°	90
Volume/Å^3	4075.4(3)
Z	4
ρ_{calc} /g cm^{-3}	1.345
μ/mm^{-1}	0.188
F(000)	1752.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.596 to 58.522
Index ranges	$-12 \leq h \leq 9$, $-29 \leq k \leq 32$, $-21 \leq l \leq 23$
Reflections collected	19531
Independent reflections	9426 (R_{int} = 0.0248)
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0542, wR_2 = 0.1294
Final R indexes [all data]	R_1 = 0.1048, wR_2 = 0.1515
Largest diff. peak/hole / e Å^{-3}	0.51/-0.35

Table S2. Bond Lengths for compound **2′a**, Å.

Bond	value	Bond	value
S8'–O7'	1.5826(15)	C10B–C14A	1.527(3)
S8'–O10'	1.4106(18)	C10B–C11	1.525(3)
S8'–O9'	1.4114(17)	C11'–C16'	1.378(3)
S8'–C11'	1.733(2)	C11'–C12'	1.362(3)
S8''–O7''	1.5943(18)	C1''–C2''	1.391(3)
S8''–O10''	1.4119(19)	C1''–C6''	1.388(3)
S8''–O9''	1.415(2)	C14A–C14	1.529(3)
S8''–C11''	1.733(3)	C4'–C5'	1.362(3)
O7'–C4'	1.424(3)	C4'–C3'	1.373(3)
N10A–C14D	1.473(2)	C2''–C3''	1.379(3)
N10A–C10B	1.471(3)	C4''–C3''	1.361(3)
N10A–C10	1.476(3)	C4''–C5''	1.375(3)
N7B–C14D	1.451(2)	C2'–C3'	1.383(3)
N7B–C7A	1.484(2)	C5'–C6'	1.383(3)
N7B–C8	1.456(2)	C7–C6	1.521(3)

N3A–C3B	1.469(3)	C6''–C5''	1.368(3)
N3A–C14C	1.477(2)	C4–C5	1.513(3)
N3A–C3	1.483(3)	C14–C13	1.512(4)
O7''–C4''	1.415(3)	C11–C12	1.515(4)
N9–C1''	1.410(3)	C11''–C16''	1.369(4)
N9–C8	1.460(3)	C11''–C12''	1.368(4)
N9–C10	1.438(3)	C16'–C15'	1.379(4)
N14B–C14C	1.449(3)	C12'–C13'	1.380(4)
N14B–C14A	1.477(3)	C5–C6	1.522(4)
N14B–C1	1.467(3)	C13–C12	1.510(4)
N2–C1'	1.406(3)	C14'–C15'	1.362(5)
N2–C3	1.439(3)	C14'–C13'	1.364(5)
N2–C1	1.466(3)	C14'–C17'	1.488(4)
C14D–C14C	1.504(3)	C16''–C15''	1.378(5)
C7A–C3B	1.528(3)	C14''–C15''	1.385(5)
C7A–C7	1.520(3)	C14''–C13''	1.357(5)
C3B–C4	1.538(3)	C14''–C17''	1.514(5)
C1'–C2'	1.388(3)	C12''–C13''	1.382(5)
C1'–C6'	1.387(3)		

Table S3. Bond angles for compound **2′a**, °

Angle	value	Angle	value
O7'–S8'–C11'	103.37(9)	C12'–C11'–S8'	120.4(2)
O10'–S8'–O7'	109.42(10)	C12'–C11'–C16'	120.0(3)
O10'–S8'–O9'	119.63(11)	C2''–C1''–N9	123.1(2)
O10–S8'–C11'	109.70(12)	C6''–C1''–N9	119.05(19)
O9'–S8'–O7'	103.17(10)	C6''–C1''–C2''	117.7(2)
O9'–S8'–C11'	110.16(11)	N14B–C14A–C10B	110.03(16)
O7''–S8''–C11''	104.49(11)	N14B–C14A–C14	111.67(18)
O10''–S8''–O7''	109.51(11)	C10B–C14A–C14	108.72(18)
O10''–S8''–O9''	121.15(15)	N7B–C8–N9	113.15(16)
O10''–S8''–C11''	109.35(14)	C5'–C4'–O7'	115.6(2)
O9''–S8''–O7''	101.70(12)	C5'–C4'–C3'	121.1(2)
O9''–S8''–C11''	109.22(15)	C3'–C4'–O7'	123.1(2)
C4'–O7'–S8'	121.71(14)	N9–C10–N10A	112.22(16)
C14D–N10A–C10	106.66(15)	C3''–C2''–C1''	120.2(2)
C10B–N10A–C14D	110.97(15)	C3''–C4''–O7''	117.3(2)
C10B–N10A–C10	110.83(15)	C3''–C4''–C5''	120.6(2)
C14D–N7B–C7A	110.97(14)	C5''–C4''–O7''	121.7(2)
C14D–N7B–C8	108.53(16)	N2–C3–N3A	112.55(18)
C8–N7B–C7A	114.48(16)	C4''–C3''–C2''	120.5(2)
C3B–N3A–C14C	110.76(15)	N2–C1–N14B	113.31(17)
C3B–N3A–C3	110.61(16)	C3'–C2'–C1'	121.0(2)
C14C–N3A–C3	106.42(16)	C4'–C5'–C6'	119.5(2)
C4''–O7''–S8''	123.02(14)	C4'–C3'–C2'	119.1(2)
C1''–N9–C8	119.35(17)	C7A–C7–C6	110.63(18)
C1''–N9–C10	119.60(17)	C5''–C6''–C1''	122.0(2)

C10–N9–C8	110.42(17)	C6''–C5''–C4''	119.0(2)
C14C–N14B–C14A	111.36(16)	C5–C4–C3B	112.88(18)
C14C–N14B–C1	107.88(18)	C13–C14–C14A	111.3(2)
C1–N14B–C14A	115.62(16)	C5'–C6'–C1'	120.8(2)
C1'–N2–C3	119.44(18)	C12–C11–C10B	112.0(2)
C1'–N2–C1	118.4(2)	C16''–C11''–S8''	121.5(2)
C3–N2–C1	109.85(17)	C12''–C11''–S8''	118.2(3)
N10A–C14D–C14C	112.61(15)	C12''–C11''–C16''	120.2(3)
N7B–C14D–N10A	112.12(16)	C11'–C16'–C15'	119.6(3)
N7B–C14D–C14C	110.32(16)	C11'–C12'–C13'	118.9(3)
N7B–C7A–C3B	109.40(16)	C4–C5–C6	110.9(2)
N7B–C7A–C7	111.60(16)	C7–C6–C5	111.3(2)
C7–C7A–C3B	109.17(17)	C12–C13–C14	111.9(2)
N3A–C3B–C7A	112.15(16)	C13–C12–C11	111.0(2)
N3A–C3B–C4	110.06(16)	C15'–C14'–C13'	118.0(3)
C7A–C3B–C4	107.56(18)	C15'–C14'–C17'	120.8(4)
C2'–C1'–N2	122.9(2)	C13'–C14'–C17'	121.2(4)
C6'–C1'–N2	118.97(19)	C14'–C15'–C16'	121.3(3)
C6'–C1'–C2'	118.1(2)	C11''–C16''–C15''	119.5(3)
N3A–C14C–C14D	112.36(16)	C14'–C13'–C12'	122.3(3)
N14B–C14C–N3A	111.95(16)	C15''–C14''–C17''	121.5(4)
N14B–C14C–C14D	110.30(17)	C13''–C14''–C15''	117.2(4)
N10A–C10B–C14A	112.01(16)	C13''–C14''–C17''	121.3(4)
N10A–C10B–C11	110.84(18)	C11''–C12''–C13''	118.9(3)
C11–C10B–C14A	109.10(18)	C16''–C15''–C14''	121.5(4)
C16'–C11'–S8'	119.6(2)	C14''–C13''–C12''	122.6(3)