

Diels–Alder trapping vs. amidoalkylation of cyclopentadiene with polychloroacetaldehyde sulfonylimines

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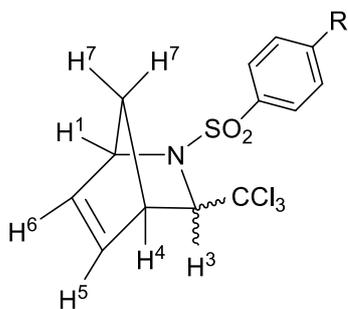
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Experimental part

General details. ^1H (400.13 MHz), ^{13}C (100.61 MHz) and ^{15}N (40.55 MHz) NMR spectra were recorded on a Bruker AV400 instrument in CDCl_3 or DMSO-d_6 at room temperature. Chemical shifts δ are quoted in parts per million (ppm). The residual solvent peak δ_{H} 7.27 and δ_{C} 77.1 (CDCl_3) and δ_{H} 2.50 and δ_{C} 39.5 (DMSO-d_6) were used as a reference. The assignment of signals in the ^1H NMR spectra was made using COSY and NOESY 2D experiments. Resonance signals of carbon atoms were assigned based on 2D ^1H - ^{13}C HSQC and ^1H - ^{13}C HMBC experiments. The values of the δ ^{15}N were measured through the 2D ^1H - ^{15}N HMBC experiment and were referenced to CH_3NO_2 (0.0 ppm). The IR spectra were measured on a Bruker IFS-25 spectrometer from samples pelleted with KBr. MW irradiation (a monomode microwave cavity Anton Paar ‘Monowave 300’). Elemental analysis was performed on a Thermo Finnigan Flash series 1112 Elemental analyzer.

2-Phenylsulfonyl-3-trichloromethyl-2-azabicyclo[2.2.1]hept-5-ene 2a (general procedure). *N,N*-Dichlorobenzenesulfonamide $\text{PhSO}_2\text{NCl}_2$ (30 mmol, 6.78 g) was refluxed in trichloroethylene (278 mmol, 25 ml) under argon for the time when chlorine was produced (12–14 h). The mixture containing *N*-(2,2,2-trichloroethylidene)benzenesulfonamide **1a** (yield 100%, 30 mmol, 8.61 g) was cooled to room temperature. Freshly distilled cyclopentadiene (40 mmol, 2.64 g) was added, and the mixture was stirred at 50°C for 5 h. The solvent was removed under vacuum, the residue of the product **2a** was recrystallized from methanol.

2-Arylsulfonyl-3-trichloromethyl-2-azabicyclo[2.2.1]hept-5-enes 2b,c were obtained in the same manner from *N,N*-dichloro-4-chlorobenzenesulfonamide $4\text{-ClC}_6\text{H}_4\text{SO}_2\text{NCl}_2$ (30 mmol, 7.82 g) and *N,N*-dichloro-4-toluenesulfonamide $4\text{-MeC}_6\text{H}_4\text{SO}_2\text{NCl}_2$ (30 mmol, 7.20 g) respectively.



2-Phenylsulfonyl-3-trichloromethyl-2-azabicyclo[2.2.1]hept-5-ene (2a) was obtained as *exo*-isomer. Yield 8.67 g (82%), m.p. 115-117°C (m.p. 115-117°C [S1]).

$^1\text{H NMR}$ (*exo*-**2a**) (CDCl_3 , 400.13 MHz): δ 7.92-7.86 (m, 2H, C_6H_5), 7.60-7.40 (m, 3H, C_6H_5), 6.79 (dd, 1H, H^6 , $^3J_{\text{H}5\text{H}6} = 5.5$ Hz, $^3J_{\text{H}1\text{H}6} = 2.4$ Hz), 6.62 (dd, 1H, H^5 , $^3J_{\text{H}5\text{H}6} = 5.5$ Hz, $^3J_{\text{H}5\text{H}4} = 1.9$ Hz), 4.93 (d, 1H, H^1 , $^3J_{\text{H}1\text{H}6} = 2.4$ Hz), 4.09 (s, 1H, H^3), 3.71 (d, 1H, H^4 , $^3J_{\text{H}4\text{H}5} = 1.9$ Hz), 2.72 (d, 1H, H^7 , $^2J_{\text{H}7\text{H}7'} = 9.5$ Hz), 1.52 (d, 1H, $\text{H}^{7'}$, $^2J_{\text{H}7\text{H}7'} = 9.5$ Hz) ppm.

$^{13}\text{C NMR}$ (*exo*-**2a**) (CDCl_3 , 100.61 MHz): δ 142.22 (C^i), 139.85 (C^6), 137.68 (C^5), 132.46 (C^p), 128.61 (C^m), 126.71 (C^o), 100.71 (CCl_3), 75.46 (C^3), 69.77 (C^1), 50.49 (C^4), 44.50 (C^7) ppm.

IR spectrum, ν , cm^{-1} : 1374, 1184 (SO_2).

Found, %: C 44.41; H 3.48; Cl 30.37; N 3.88; S 9.01 $\text{C}_{13}\text{H}_{12}\text{Cl}_3\text{NO}_2\text{S}$. Calculated, %: C 44.27; H 3.43; Cl 30.16; N 3.97; S 9.09.

2-(4-Chlorophenyl)sulfonyl-3-trichloromethyl-2-azabicyclo[2.2.1]hept-5-ene (2b) was isolated as *exo*-isomer. Yield 9.87 g (85%), m.p. 121-123°C (m.p. 120-125°C [S1]). *endo*-Isomer of **2b** was proved by NMR. According to NMR ^1H data for reaction mixture before recrystallization, ratio of *exo*-**2b**/*endo*-**2b** was 9 : 1.

$^1\text{H NMR}$ (*exo*-**2b**) (CDCl_3 , 400.13 MHz): δ 7.74-7.73 (m, 2H, $\text{C}_6\text{H}_4\text{Cl}$), 7.35-7.32 (m, 2H, $\text{C}_6\text{H}_4\text{Cl}$), 6.78 (dd, 1H, H^6 , $^3J_{\text{H}5\text{H}6} = 5.5$ Hz, $^3J_{\text{H}1\text{H}6} = 2.0$ Hz), 6.57 (dd, 1H, H^5 , $^3J_{\text{H}5\text{H}6} = 5.5$ Hz, $^3J_{\text{H}5\text{H}4} = 2.2$ Hz), 4.90 (d, 1H, H^1 , $^3J_{\text{H}1\text{H}6} = 2.0$ Hz), 4.05 (s, 1H, H^3), 3.69 (d, 1H, H^4 , $^3J_{\text{H}4\text{H}5} = 2.2$ Hz), 2.68 (d, 1H, H^7 , $^2J_{\text{H}7\text{H}7'} = 9.5$ Hz), 1.48 (d, 1H, $\text{H}^{7'}$, $^2J_{\text{H}7\text{H}7'} = 9.5$ Hz) ppm.

$^1\text{H NMR}$ (*endo*-**2b**) (CDCl_3 , 400.13 MHz): δ 7.75-7.74 (m, 2H, $\text{C}_6\text{H}_4\text{Cl}$), 7.33-7.30 (m, 2H, $\text{C}_6\text{H}_4\text{Cl}$), 6.53 (dd, 1H, H^6 , $^3J_{\text{H}5\text{H}6} = 5.5$ Hz, $^3J_{\text{H}1\text{H}6} = 2.8$ Hz), 6.46 (dd, 1H, H^5 , $^3J_{\text{H}5\text{H}6} = 5.5$ Hz, $^3J_{\text{H}5\text{H}4} = 2.7$ Hz), 5.15 (d, 1H, H^1 , $^3J_{\text{H}1\text{H}6} = 2.8$ Hz), 4.88 (s, 1H, H^3), 3.86 (d, 1H, H^4 , $^3J_{\text{H}4\text{H}5} = 2.7$ Hz), 1.69-1.66 (m, 2H, H^7 , $\text{H}^{7'}$) ppm.

$^{13}\text{C NMR}$ (*exo*-**2b**) (CDCl_3 , 100.61 MHz): δ 140.90 (C^i), 139.87 (C^6), 138.85 (C^p), 137.84 (C^5), 128.94 (C^m), 128.28 (C^o), 100.71 (CCl_3), 75.56 (C^3), 69.96 (C^1), 50.57 (C^4), 44.55 (C^7) ppm.

$^{13}\text{C NMR}$ (*endo*-**2b**) (CDCl_3 , 100.61 MHz): δ 139.35 (C^i), 139.05 (C^p), 138.26 (C^5), 136.72 (C^6), 129.21 (C^m), 128.98 (C^o), 100.63 (CCl_3), 73.59 (C^3), 70.75 (C^1), 51.66 (C^4), 50.79 (C^7) ppm.

$^{15}\text{N NMR}$ (*exo*-**2b**) (CDCl_3 , 40.55 MHz): δ -258.8 ppm.

^{15}N NMR (*endo*-**2b**) (CDCl_3 , 40.55 MHz): δ -257.3 ppm.

IR spectrum (*exo*-**2b**), ν , cm^{-1} : 1345, 1163 (SO_2).

Found, %: C 40.39; H 2.85; Cl 36.67; N 3.65; S 8.18 $\text{C}_{13}\text{H}_{11}\text{Cl}_4\text{NO}_2\text{S}$. Calculated, %: C 40.33; H 2.86; Cl 36.63; N 3.62; S 8.28.

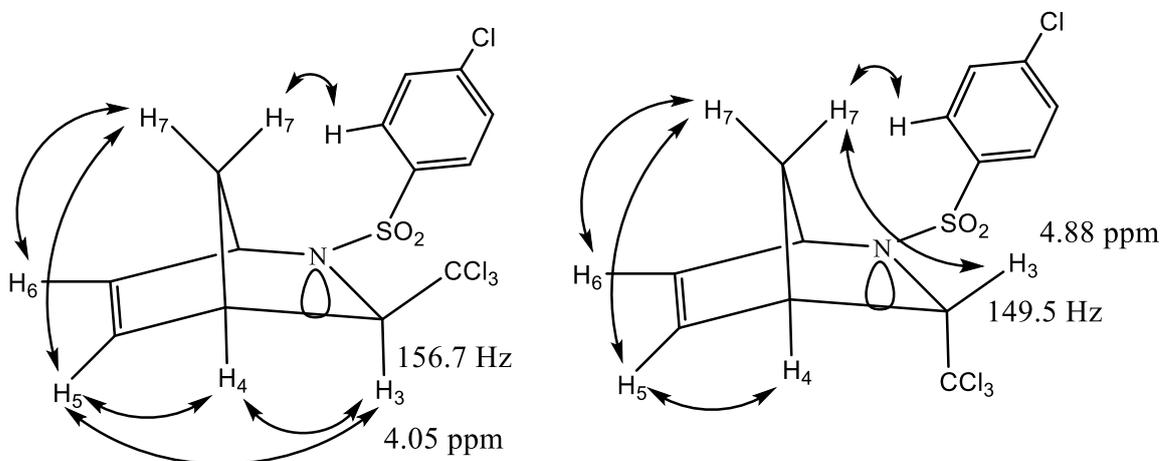


Figure S1. Key NOE interactions, chemical shifts and coupling constants for compound **2b**

2-(4-Methylphenyl)sulfonyl-3-trichloromethyl-2-azabicyclo[2.2.1]hept-5-ene (2c) was obtained as an *exo*-isomer. Yield 8.91 g (81%), m.p. 111-113°C (m.p. 111-113°C [S1]).

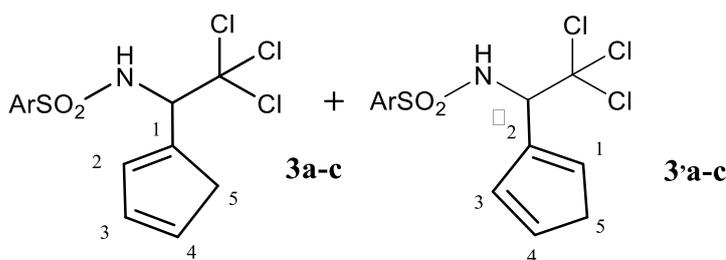
^1H NMR (*exo*-**2c**) (CDCl_3 , 400.13 MHz): δ 7.76-7.70 (m, 2H, C_6H_4), 7.40-7.32 (m, 2H, C_6H_4), 6.70 (dd, 1H, H^6 , $^3J_{\text{H}^5\text{H}^6} = 5.5$ Hz, $^3J_{\text{H}^1\text{H}^6} = 2.0$ Hz), 6.54 (dd, 1H, H^5 , $^3J_{\text{H}^5\text{H}^6} = 5.5$ Hz, $^3J_{\text{H}^5\text{H}^4} = 2.2$ Hz), 4.86 (d, 1H, H^1 , $^3J_{\text{H}^1\text{H}^6} = 2.0$ Hz), 4.00 (s, 1H, H^3), 3.64 (d, 1H, H^4 , $^3J_{\text{H}^4\text{H}^5} = 2.2$ Hz), 2.65 (d, 1H, H^7 , $^2J_{\text{H}^7\text{H}^7'} = 9.5$ Hz), 2.38 (s, 3H, CH_3), 1.44 (d, 1H, H^7' , $^2J_{\text{H}^7\text{H}^7'} = 9.5$ Hz) ppm.

^{13}C NMR (*exo*-**2c**) (CDCl_3 , 100.61 MHz): δ 140.92 (C^i), 139.88 (C^6), 138.79 (C^p), 137.86 (C^5), 128.95 (C^m), 128.29 (C^o), 100.73 (CCl_3), 75.58 (C^3), 69.97 (C^1), 50.58 (C^4), 44.52 (C^7), 21.50 (CH_3) ppm.

IR spectrum, ν , cm^{-1} : 1330, 1136 (SO_2).

Found, %: C 45.91; H 3.81; Cl 29.67; N 3.45; S 8.51 $\text{C}_{14}\text{H}_{14}\text{Cl}_3\text{NO}_2\text{S}$. Calculated, %: C 45.86; H 3.85; Cl 29.01; N 3.82; S 8.74.

***N*-[2,2,2-Trichloro-1-(cyclopentadienyl)ethyl]arenesulfonamides 3a-c and 3'a-c (general procedure).** Freshly distilled cyclopentadiene (40 mmol, 2.64 g) was added to a mixture containing imines **1a-c** obtained from trichloroethylene (278 mmol, 25 ml) and *N,N*-dichloroarenesulfonamide (30 mmol) as described above. The mixture was stirred at 80-90°C for 5 h. The solvent was evaporated in vacuum. The residue of the products **3a-c/3'a-c** was recrystallized from 1:1 methanol/hexane mixture.



***N*-[2,2,2-Trichloro-1-(cyclopenta-1,3-diene-1-yl)ethyl]benzenesulfonamide (3a) and *N*-[2,2,2-trichloro-1-(cyclopenta-1,4-diene-2-yl)ethyl]benzenesulfonamide (3'a)** were obtained as 1 : 1 mixture in total yield 8.88 g (84%).

^1H NMR (**3a**) (DMSO- d_6 , 400.13 MHz): δ 8.75 (d, 1H, NH, $^3J_{\text{CHNH}} = 10.0$ Hz), 7.70-7.65 (m, 2H, C_6H_5), 7.52-7.40 (m, 3H, C_6H_5), 6.44-6.43 (m, 1H, H^2), 6.24-6.23 (m, 1H, H^4), 6.19-6.18 (m, 1H, H^3), 5.00 (d, 1H, CHN, $^3J_{\text{CHNH}} = 10.0$ Hz), 3.03 (d, 1H, CH_2 , $^2J = 24.5$ Hz), 2.80 (d, 1H, CH_2 , $^2J = 24.5$ Hz) ppm.

^{13}C NMR (**3a**) (DMSO- d_6 , 100.61 MHz): δ 140.70 (C^i), 139.37 (C^1), 135.37 (C^2), 134.42 (C^4), 132.22 (C^p), 130.79 (C^3), 128.48 (C^m), 126.45 (C^o), 101.27 (CCl_3), 68.48 (CHN), 42.15 (CH_2) ppm.

^{15}N NMR (**3a**) (DMSO- d_6 , 40.55 MHz): δ -274.7 ppm.

^1H NMR (**3'a**) (DMSO- d_6 , 400.13 MHz): δ 8.82 (d, 1H, NH, $^3J_{\text{CHNH}} = 10.0$ Hz), 7.73-7.72 (m, 2H, C_6H_5), 7.47-7.35 (m, 3H, C_6H_5), 6.58 (d, 1H, H^3 , $^3J = 5.5$ Hz), 6.34-6.32 (m, 1H, H^1), 6.16-6.13 (m, 1H, H^4), 4.98 (d, 1H, CHN, $^3J_{\text{CHNH}} = 10.0$ Hz), 2.69 (d, 1H, CH_2 , $^2J = 24.0$ Hz), 2.61 (d, 1H, CH_2 , $^2J = 24.0$ Hz) ppm.

^{13}C NMR (**3'a**) (DMSO- d_6 , 100.61 MHz): δ 140.90 (C^i), 139.07 (C^2), 135.36 (C^1), 132.70 (C^4), 132.22 (C^p), 132.18 (C^3), 128.65 (C^m), 126.45 (C^o), 101.70 (CCl_3), 67.96 (CHN), 40.88 (CH_2) ppm.

^{15}N NMR (**3'a**) (DMSO- d_6 , 40.55 MHz): δ -272.4 ppm.

Found, %: C 44.71; H 3.61; Cl 30.27; N 3.84; S 9.11 $\text{C}_{26}\text{H}_{24}\text{Cl}_6\text{N}_2\text{O}_4\text{S}_2$. Calculated, %: C 44.27; H 3.43; Cl 30.16; N 3.97; S 9.09.

4-Chloro-*N*-[2,2,2-trichloro-1-(cyclopenta-1,3-diene-1-yl)ethyl]benzenesulfonamide (3b) and 4-chloro-*N*-[2,2,2-trichloro-1-(cyclopenta-1,4-diene-2-yl)ethyl]benzenesulfonamide (3'b) were obtained as 1 : 1 mixture in total yield 9.99 g (86%).

^1H NMR (**3b**) (DMSO- d_6 , 400.13 MHz): δ 8.93 (d, 1H, NH, $^3J_{\text{CHNH}} = 10.0$ Hz), 7.74-7.72 (m, 2H, 4- ClC_6H_4), 7.49-7.47 (m, 2H, 4- ClC_6H_4), 6.45-6.41 (m, 1H, H^2), 6.29-6.27 (m, 1H, H^4), 6.21-6.19 (m, 1H, H^3), 5.03 (d, 1H, CHN, $^3J_{\text{CHNH}} = 10.0$ Hz), 3.03 (d, 1H, CH_2 , $^2J = 24.5$ Hz), 2.85 (d, 1H, CH_2 , $^2J = 24.5$ Hz) ppm.

^{13}C NMR (**3b**) (DMSO- d_6 , 100.61 MHz): δ 139.42 (C^i), 139.21 (C^1), 137.23 (C^p), 135.75 (C^2), 134.74 (C^4), 130.81 (C^3), 128.90 (C^m), 128.56 (C^o), 101.13 (CCl_3), 68.41 (CHN), 42.03 (CH_2) ppm.

^{15}N NMR (**3b**) (DMSO- d_6 , 40.55 MHz): δ -279.9 ppm.

¹H NMR (**3'b**) (DMSO-d₆, 400.13 MHz): δ 9.02 (d, 1H, NH, ³J_{CHNH} = 10.0 Hz), 7.69-7.67 (m, 2H, 4-ClC₆H₄), 7.50-7.49 (m, 2H, 4-ClC₆H₄), 6.57 (d, 1H, H³, ³J = 5.5 Hz), 6.40-6.39 (m, 1H, H¹), 6.15-6.13 (m, 1H, H⁴), 5.00 (d, 1H, CHN, ³J_{CHNH} = 10.0 Hz), 2.78 (d, 1H, CH₂, ²J = 24.6 Hz), 2.63 (d, 1H, CH₂, ²J = 24.6 Hz) ppm.

¹³C NMR (**3'b**) (DMSO-d₆, 100.61 MHz): δ 139.67 (Cⁱ), 139.04 (C²), 137.26 (C^p), 135.75 (C¹), 132.94 (C⁴), 132.38 (C³), 128.50 (C^m), 128.73 (C^o), 101.55 (CCl₃), 67.80 (CHN), 40.97 (CH₂) ppm.

¹⁵N NMR (**3'b**) (DMSO-d₆, 40.55 MHz): δ -273.9 ppm.

Found, %: C 40.65; H 2.89; Cl 36.87; N 3.71; S 8.31 C₂₆H₂₂Cl₈N₂O₄S₂. Calculated, %: C 40.33; H 2.86; Cl 36.63; N 3.62; S 8.28.

4-Methyl-N-[2,2,2-trichloro-1-(cyclopenta-1,3-diene-1-yl)ethyl]benzenesulfonamide (3c) and 4-methyl-N-[2,2,2-trichloro-1-(cyclopenta-1,4-diene-2-yl)ethyl]benzenesulfonamide (3'c) were obtained as 1 : 1 mixture in total yield 9.09 g (82%).

¹H NMR (**3c**) (DMSO-d₆, 400.13 MHz): δ 8.88 (d, 1H, NH, ³J_{CHNH} = 10.0 Hz), 7.72-7.70 (m, 2H, 4-MeC₆H₄), 7.33-7.32 (m, 2H, 4-MeC₆H₄), 6.45-6.44 (m, 1H, H²), 6.29-6.28 (m, 1H, H⁴), 6.21-6.19 (m, 1H, H³), 5.01 (d, 1H, CHN, ³J_{CHNH} = 10.0 Hz), 3.03 (d, 1H, CH₂, ²J = 24.5 Hz), 2.82 (d, 1H, CH₂, ²J = 24.5 Hz), 2.21 (s, 3H, Me) ppm.

¹³C NMR (**3c**) (DMSO-d₆, 100.61 MHz): δ 141.61 (C^p), 139.72 (Cⁱ), 139.20 (C¹), 135.70 (C²), 134.52 (C⁴), 130.83 (C³), 129.25 (C^m), 127.71 (C^o), 101.17 (CCl₃), 68.43 (CHN), 42.07 (CH₂), 21.27 (Me) ppm.

¹H NMR (**3'c**) (DMSO-d₆, 400.13 MHz): δ 8.97 (d, 1H, NH, ³J_{CHNH} = 10.0 Hz), 7.69-7.67 (m, 2H, 4-MeC₆H₄), 7.30-7.28 (m, 2H, 4-MeC₆H₄), 6.57 (d, 1H, H³, ³J = 5.5 Hz), 6.36-6.35 (m, 1H, H¹), 6.15-6.13 (m, 1H, H⁴), 4.99 (d, 1H, CHN, ³J_{CHNH} = 10.0 Hz), 2.69 (d, 1H, CH₂, ²J = 24.5 Hz), 2.63 (d, 1H, CH₂, ²J = 24.5 Hz), 2.21 (s, 3H, Me) ppm.

¹³C NMR (**3'c**) (DMSO-d₆, 100.61 MHz): δ 141.62 (C^p), 139.93 (Cⁱ), 139.05 (C²), 135.65 (C¹), 133.02 (C⁴), 132.35 (C³), 129.22 (C^m), 127.63 (C^o), 101.61 (CCl₃), 67.84 (CHN), 40.95 (CH₂), 21.27 (Me) ppm.

Found, %: C 45.92; H 3.89; Cl 29.18; N 3.86; S 8.88 C₂₈H₂₈Cl₆N₂O₄S₂. Calculated, %: C 45.86; H 3.85; Cl 29.01; N 3.82; S 8.74.

2-Arylsulfonyl-3-dichloro(phenyl)methyl-2-azabicyclo[2.2.1]hept-5-enes 2d-f.

Procedure 1. Imine **1d-f** (6 mmol) [S2] and freshly distilled cyclopentadiene (9 mmol, 0.59 g) were stirred in toluene (10 mL) at 55-60°C for 8 h. The reaction mass was evaporated in vacuum, the rest was recrystallized from hexane.

Procedure 2. Imine **1d-f** (8 mmol) [S2] and freshly distilled cyclopentadiene (9 mmol, 0.59 g) were kept in toluene at MW irradiation (300W, 80°C) for 2 h. A precipitate was filtered out and recrystallized from hexane.

2-Phenylsulfonyl-3-dichloro(phenyl)methyl-2-azabicyclo[2.2.1]hept-5-ene (2d) was obtained as an *exo*-isomer. Yield 2.04 g (86%) in the procedure 1, 2.90 g (92%) in the procedure 2, m.p. 112-113°C.

¹H NMR (*exo*-**2d**) ([DMSO-d₆, 400.13 MHz): δ 7.90-7.83 (m, 2H, Ph), 7.72-7.60 (m, 4H, Ph), 7.40-7.27 (m, 4H, Ph), 6.54-6.52 (m, 2H, H⁵, H⁶), 4.73 (m, 1H, H¹), 3.96 (s, 1H, H³), 3.24-3.22 (m, 1H, H⁴), 0.93 (d, 1H, H⁷, ²J_{H⁷H^{7'}} = 9.3 Hz), 0.62 (d, 1H, H⁷, ²J_{H⁷H^{7'}} = 9.3 Hz) ppm.

¹³C NMR (*exo*-**2d**) (DMSO-d₆, 100.61 MHz): δ 142.76 (Cⁱ), 140.54 (Cⁱ), 139.32 (C⁶), 138.11 (C⁵), 132.34 (C^p), 129.48 (C^p), 128.96 (C^m), 128.47 (C^m), 127.63 (C^o), 127.17 (C^o), 94.35 (CCl₂), 74.91 (C³), 69.50 (C¹), 50.06 (C⁴), 44.12 (C⁷) ppm.

IR spectrum, ν, cm⁻¹: 1325, 1159 (SO₂).

Found, %: C 57.60, H 4.21, Cl 17.36, N 3.17, S 7.91. C₁₉H₁₇Cl₂NO₂S. Calculated, %: C 57.87, H 4.35, Cl 17.98, N 3.55, S 8.13.

2-(4-Chlorophenyl)sulfonyl-3-dichloro(phenyl)methyl-2-azabicyclo[2.2.1]hept-5-ene (2e) was obtained as an *exo*-isomer. Yield 2.26 g (88%) in the procedure 1, 3.23 g (94%) in the procedure 2, m.p. 165-166°C.

¹H NMR (*exo*-**2e**) (CDCl₃, 400.13 MHz): δ 7.80-7.78 (m, 2H, C₆H₄Cl), 7.50-7.45 (m, 4H, Ph, C₆H₄Cl), 7.36-7.27 (m, 3H, Ph), 6.65 (dd, 1H, H⁶, ³J_{H⁵H⁶} = 5.4 Hz, ³J_{H¹H⁶} = 2.0 Hz), 6.47 (dd, 1H, H⁵, ³J_{H⁵H⁶} = 5.4 Hz, ³J_{H⁵H⁴} = 2.2 Hz), 4.74-4.73 (m, 1H, H¹), 4.16 (s, 1H, H³), 3.23-3.22 (m, 1H, H⁴), 1.30 (d, 1H, H⁷, ²J_{H⁷H^{7'}} = 9.4 Hz), 1.10 (d, 1H, H⁷, ²J_{H⁷H^{7'}} = 9.4 Hz) ppm.

¹³C NMR (*exo*-**2e**) (CDCl₃, 100.61 MHz): δ 140.76 (Cⁱ), 139.40 (Cⁱ), 139.22 (C⁶), 138.62 (C^p), 137.61 (C⁵), 129.37 (C^p), 128.70 (C^m), 128.52 (C^o), 127.98 (C^m), 127.84 (C^o), 93.99 (CCl₂), 73.95 (C³), 69.67 (C¹), 49.45 (C⁴), 43.80 (C⁷) ppm.

¹⁵N NMR (*exo*-**2e**) (CDCl₃, 40.55 MHz): δ -259.5 ppm.

IR spectrum, ν, cm⁻¹: 1326, 1151 (SO₂).

Found, %: C 53.13, H 3.26, Cl 24.43, N 3.16, S 7.36. C₁₉H₁₆Cl₃NO₂S. Calculated, %: C 53.22, H 3.76, Cl 24.81, N 3.27, S 7.48.

2-(4-Methylphenyl)sulfonyl-3-dichloro(phenyl)methyl-2-azabicyclo[2.2.1]hept-5-ene (2f) was obtained as an *exo*-isomer. Yield 2.18 g (89%) in the procedure 1, m.p. 155-156°C.

¹H NMR (*exo*-**2f**) (CDCl₃, 400.13 MHz): δ 7.76-7.72 (m, 2H, C₆H₄), 7.48-7.43 (m, 2H, C₆H₅), 7.32-7.23 (m, 5H, C₆H₅), 6.62 (dd, 1H, H⁶, ³J_{H⁵H⁶} = 5.5 Hz, ³J_{H¹H⁶} = 2.0 Hz), 6.43 (dd, 1H, H⁵, ³J_{H⁵H⁶} = 5.5 Hz, ³J_{H¹H⁶} = 2.0 Hz), 4.16 (s, 1H, H³), 3.23-3.22 (m, 1H, H⁴), 1.30 (d, 1H, H⁷, ²J_{H⁷H^{7'}} = 9.4 Hz), 1.10 (d, 1H, H⁷, ²J_{H⁷H^{7'}} = 9.4 Hz) ppm.

$H^5H^6 = 5.5$ Hz, $^3J_{H^5H^4} = 2.2$ Hz), 4.67 (d, 1H, H^1 , $^3J_{H^1H^6} = 2.0$ Hz), 4.13 (s, 1H, H^3), 3.21 (d, 1H, H^4 , $^3J_{H^4H^5} = 2.2$ Hz), 2.44 (s, 3H, CH_3) 1.01 (s, 2H, $H^{7'}$, H^7) ppm.

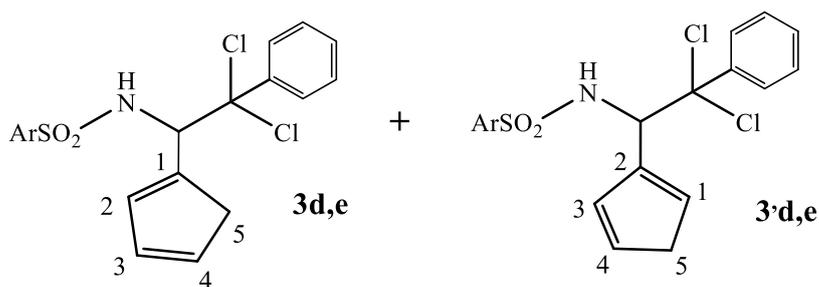
^{13}C NMR (*exo-2f*) ($CDCl_3$, 100.61 MHz): δ 142.97 (C^p), 139.27 (C^i , C^6), 137.25 (C^5), 129.23 (C^p), 128.98 (C^m), 128.03 (C^m), 127.84 (C^o), 127.17 (C^o), 94.05 (CCl_2), 73.97 (C^3), 69.35 (C^1), 49.35 (C^4), 43.65 (C^7), 21.58 (CH_3) ppm.

IR spectrum, ν , cm^{-1} : 1325, 1158 (SO_2).

Found, %: C 58.62, H 4.41, Cl 17.26, N 3.50, S 7.47. $C_{20}H_{19}Cl_2NO_2S$. Calculated, %: C 58.83, H 4.69, Cl 17.36, N 3.43, S 7.85.

General procedure for the synthesis of *N*-[2,2-dichloro-2-phenyl-1-(cyclopenta-1,4-diene-2-yl)ethyl]arenesulfonamides **3d,e** and **3'd,e**.

Imines **1d,e** (30 mmol) [S2] and freshly distilled cyclopentadiene (40 mmol, 2.64 g) were refluxed in $CHBr_3$ (15 mL) for 72 h. The reaction mass was cooled, mixed with CCl_4 (20 mL). A precipitate of the product was filtered out and purified by column chromatography (CCl_4 : CH_3OH as 97.5 : 2.5).



N-[2,2-Dichloro-2-phenyl-1-(cyclopenta-1,4-dien-1-yl)ethyl]benzenesulfonamide (**3d**) and *N*-[2,2-dichloro-2-phenyl-1-(cyclopenta-1,4-dien-2-yl)ethyl]benzenesulfonamide (**3'd**) were obtained as 1 : 1 mixture from imine **1d** (8.60 g, 30 mmol) with total yield 9.36 g (79%).

1H NMR (**3d**) ($DMSO-d_6$, 400.13 MHz): δ 8.92 (d, 1H, NH, $^3J_{CHNH} = 10.0$ Hz), 7.88-7.80 (m, 2H, C_6H_5), 7.70-7.55 (m, 5H, C_6H_5), 7.50-7.46 (m, 3H, C_6H_5), 6.46-6.45 (m, 1H, H^2), 6.29-6.28 (m, 1H, H^4), 6.21-6.120 (m, 1H, H^3), 5.03 (d, 1H, CHN, $^3J_{CHNH} = 10.0$ Hz), 3.03 (d, 1H, CH_2 , $^2J = 24.5$ Hz), 2.86 (d, 1H, CH_2 , $^2J = 24.5$ Hz) ppm.

^{13}C NMR (**3d**) ($DMSO-d_6$, 100.61 MHz): δ 140.18 (C^i), 139.55 (C^1), 137.71 (C^i), 135.23 (C^2), 133.42 (C^4), 131.30 (C^p), 129.60 (C^3), 129.20 (C^p), 128.40 (C^m), 128.66 (C^o), 101.64 (CCl_2), 68.89 (CHN), 42.53 (CH_2) ppm.

1H NMR (**3'd**) ($DMSO-d_6$, 400.13 MHz): δ 9.03 (d, 1H, NH, $^3J_{CHNH} = 10.0$ Hz), 7.88-7.80 (m, 2H, C_6H_5), 7.70-7.55 (m, 5H, C_6H_5), 7.50-7.46 (m, 3H, C_6H_5), 6.57 (d, 1H, H^3 , $^3J = 5.5$ Hz), 6.40-6.39 (m, 1H, H^1), 6.18-6.16 (m, 1H, H^4), 5.01 (d, 1H, CHN, $^3J_{CHNH} = 10.0$ Hz), 2.77 (d, 1H, CH_2 , $^2J = 24.0$ Hz), 2.63 (d, 1H, CH_2 , $^2J = 24.0$ Hz), ppm.

^{13}C NMR (**3'd**) (DMSO- d_6 , 100.61 MHz): δ 139.94 (C^i), 139.72 (C^2), 137.71 (C^i), 136.23 (C^1), 132.89 (C^4), 132.89 (C^3), 131.30 (C^p), 129.40 (C^m), 129.20 (C^p), 128.99 (C^o), 102.06 (CCl_2), 68.28 (CHN), 41.46 (CH_2) ppm.

Found, %: C 57.78; H 4.33; Cl 17.78; N 3.48; S 8.11 $\text{C}_{38}\text{H}_{34}\text{Cl}_4\text{N}_2\text{O}_4\text{S}_2$. Calculated, %: C 57.87; H 4.35; Cl 17.98; N 3.55; S 8.13.

***N*-[2,2-Dichloro-2-phenyl-1-(cyclopenta-1,4-dien-1-yl)ethyl]-4-chlorobenzenesulfonamide (3e) and *N*-[2,2-dichloro-2-phenyl-1-(cyclopenta-1,4-dien-2-yl)ethyl]-4-chlorobenzenesulfonamide (3'e)** were obtained as 1 : 1 mixture from imine **1e** (9.63 g, 30 mmol) with total yield 10.93 g (85%).

^1H NMR (**3e**) (DMSO- d_6 , 400.13 MHz): δ 8.81 (d, 1H, NH, $^3J_{\text{CHNH}} = 10.0$ Hz), 7.73-7.71 (m, 2H, 4-ClC $_6$ H $_4$), 7.60-7.55 (m, 4H, C $_6$ H $_5$), 7.43-7.35 (m, 3H, C $_6$ H $_5$), 6.45-6.44 (m, 1H, H 2), 6.25-6.24 (m, 1H, H 4), 6.19-6.17 (m, 1H, H 3), 5.01 (d, 1H, CHN, $^3J_{\text{CHNH}} = 10.0$ Hz), 3.03 (d, 1H, CH $_2$, $^2J = 24.5$ Hz), 2.80 (d, 1H, CH $_2$, $^2J = 24.5$ Hz) ppm.

^{13}C NMR (**3e**) (DMSO- d_6 , 100.61 MHz): δ 140.58 (C^i), 139.42 (C^p , C^1), 137.38 (C^i), 135.76 (C^2), 134.75 (C^4), 130.79 (C^3), 129.05 (C^p), 129.05 (C^m), 128.56 (C^o), 101.14 (CCl_2), 68.40 (CHN), 42.03 (CH_2) ppm.

^1H NMR (**3'e**) (DMSO- d_6 , 400.13 MHz): δ 8.92 (d, 1H, NH, $^3J_{\text{CHNH}} = 10.0$ Hz), 7.70-7.65 (m, 2H, 4-ClC $_6$ H $_4$), 7.60-7.55 (m, 4H, C $_6$ H $_5$), 7.43-7.35 (m, 3H, C $_6$ H $_5$), 6.60 (d, 1H, H 3 , $^3J = 5.5$ Hz), 6.36-6.35 (m, 1H, H 1), 6.16-6.15 (m, 1H, H 4), 5.01 (d, 1H, CHN, $^3J_{\text{CHNH}} = 10.0$ Hz), 2.72 (d, 1H, CH $_2$, $^2J = 24.0$ Hz), 2.61 (d, 1H, CH $_2$, $^2J = 24.0$ Hz) ppm.

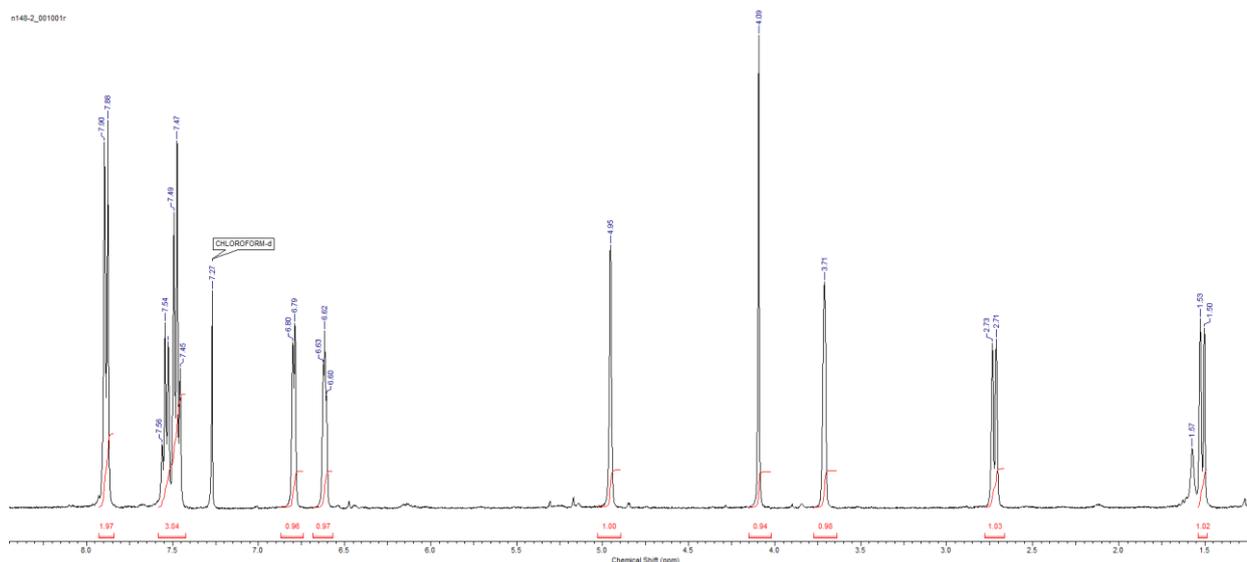
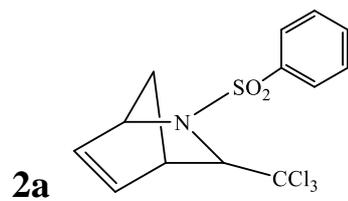
^{13}C NMR (**3'e**) (DMSO- d_6 , 100.61 MHz): δ 139.67 (C^p , C^i), 139.01 (C^2), 137.23 (C^i), 135.85 (C^1), 132.91 (C^4), 132.43 (C^3), 129.05 (C^p), 128.89 (C^m), 128.73 (C^o), 101.56 (CCl_2), 67.78 (CHN), 40.97 (CH_2) ppm.

Found, %: C 53.18; H 3.72; Cl 24.78; N 3.19; S 7.35 $\text{C}_{38}\text{H}_{32}\text{Cl}_6\text{N}_2\text{O}_4\text{S}_2$. Calculated, %: C 53.22; H 3.76; Cl 24.81; N 3.27; S 7.48.

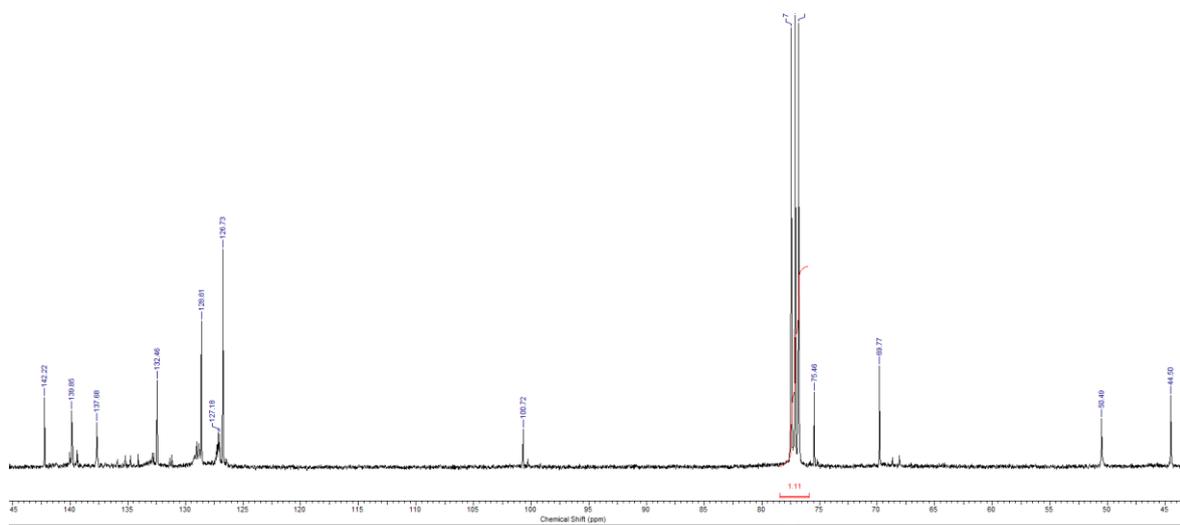
References

- [S1] A. N. Mirskova, I. T. Gogoberidze, G. G. Levkovskaya, I. D. Kalikhman, O. B. Bannikova, A. S. Kisin and M. G. Voronkov, *Zh. Org. Khim.*, 1983, **19**, 1744.
[S2] I. B. Rozentsveig, V. Yu. Serykh, G. N. Chernysheva, E. V. Kondrashov, A. I. Fedotova, I. A. Ushakov, E. V. Tretyakov and G. V. Romanenko, *Eur. J. Org. Chem.*, 2014, **29**, 6547.

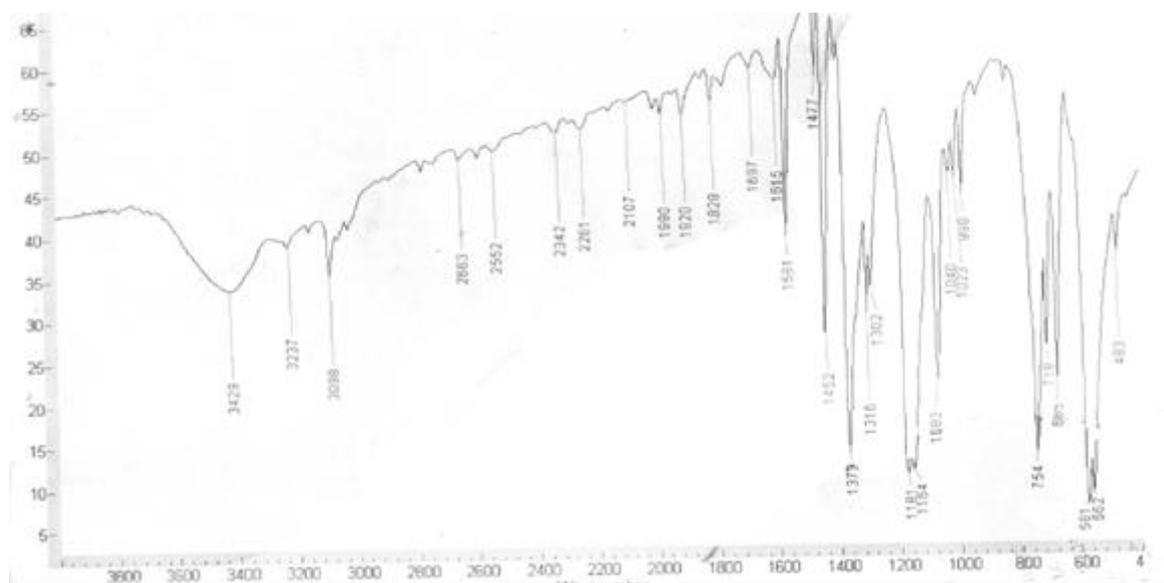
NMR and IR spectra of synthesized compounds



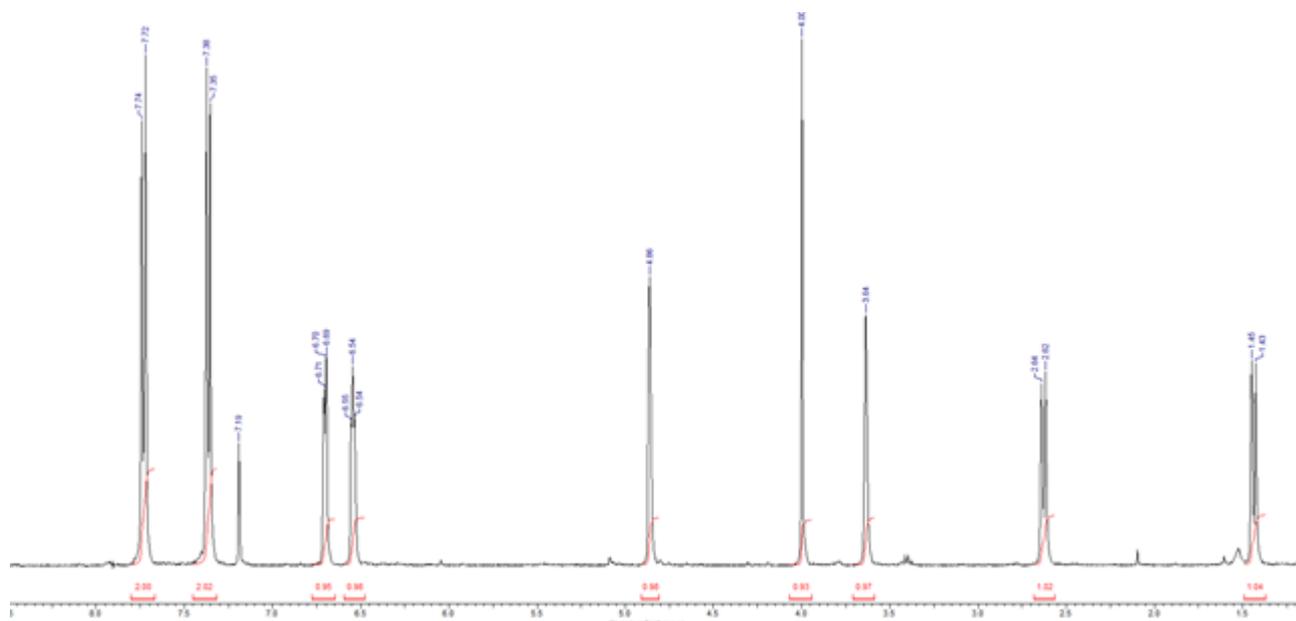
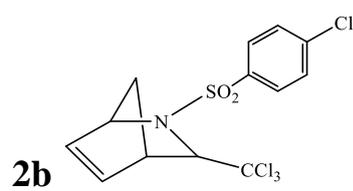
¹H NMR spectrum of **2a** (CDCl₃)



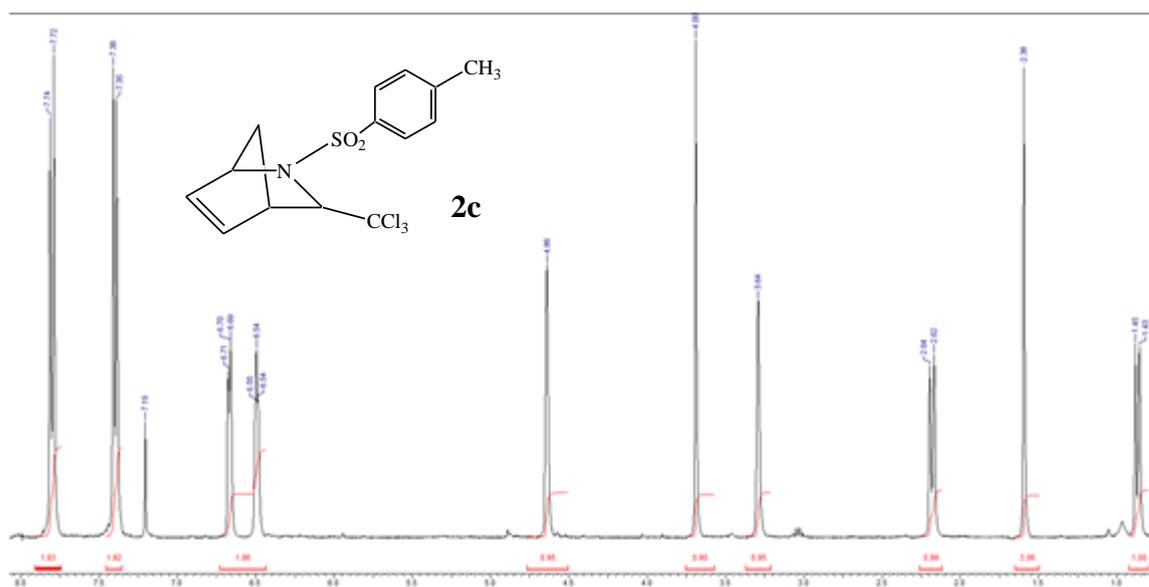
¹³C NMR spectrum of **2a** (CDCl₃)



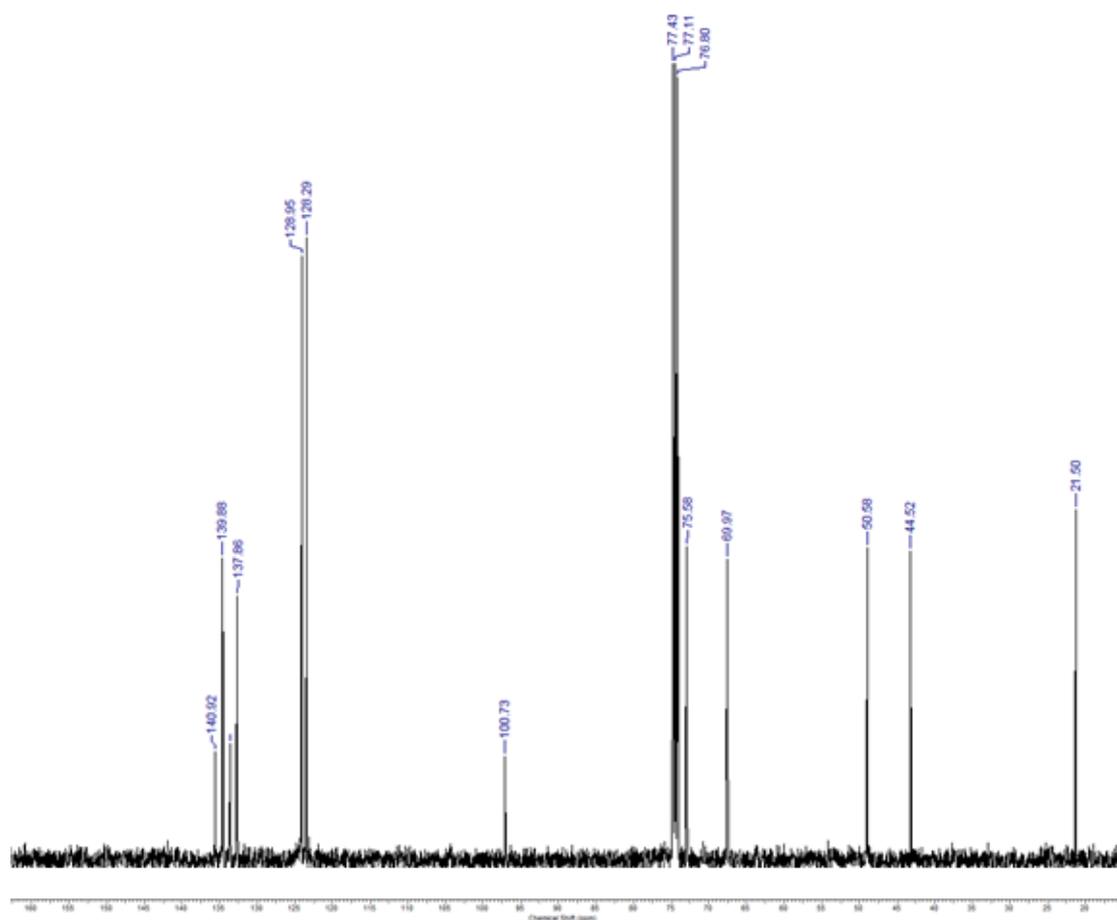
IR spectrum of **2a**



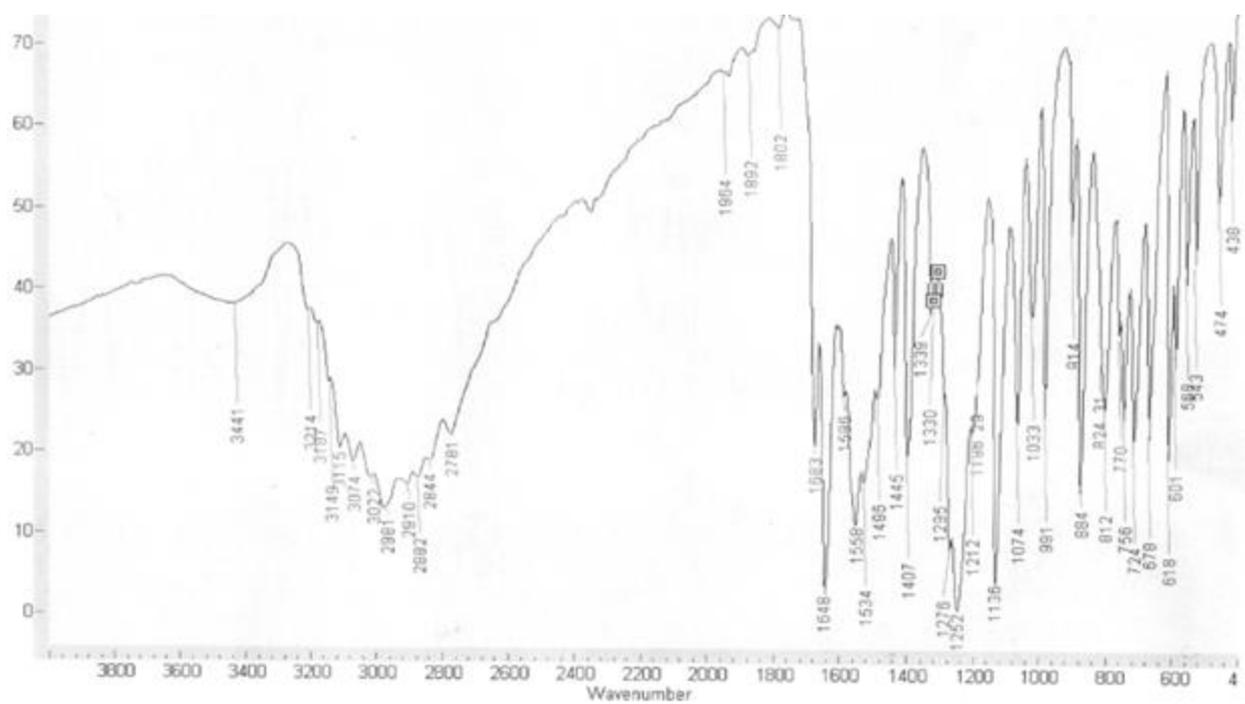
^1H NMR spectrum of **2b** (CDCl_3)



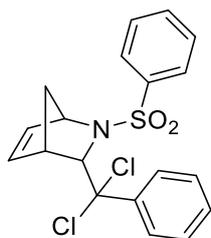
¹H NMR spectrum of **2c** (CDCl₃)



¹³C NMR spectrum of **2c** (CDCl₃)

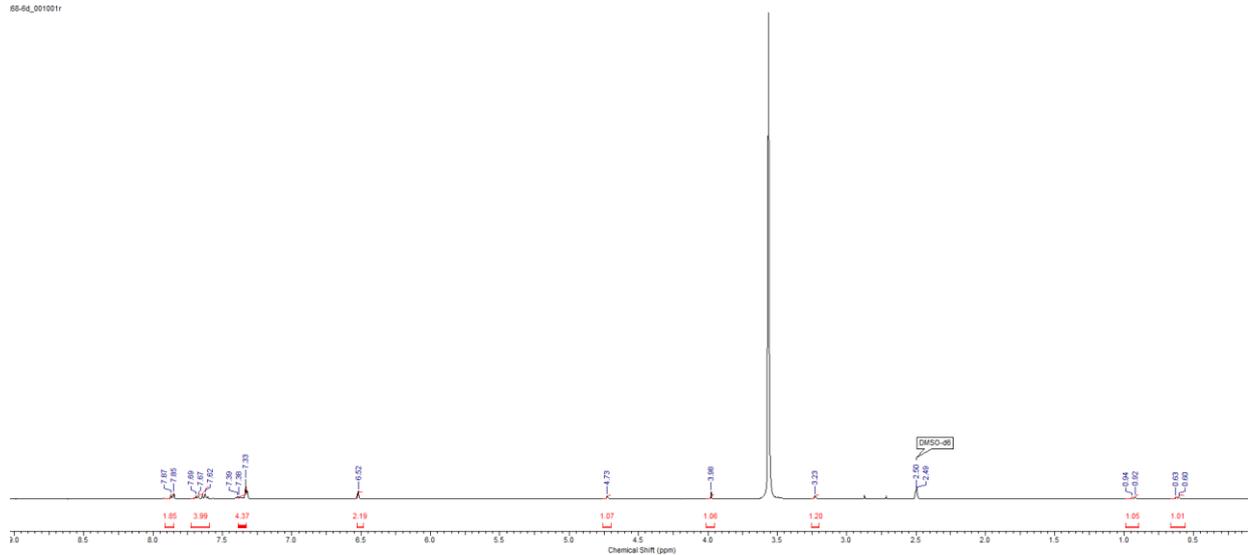


IR spectrum of **2c**

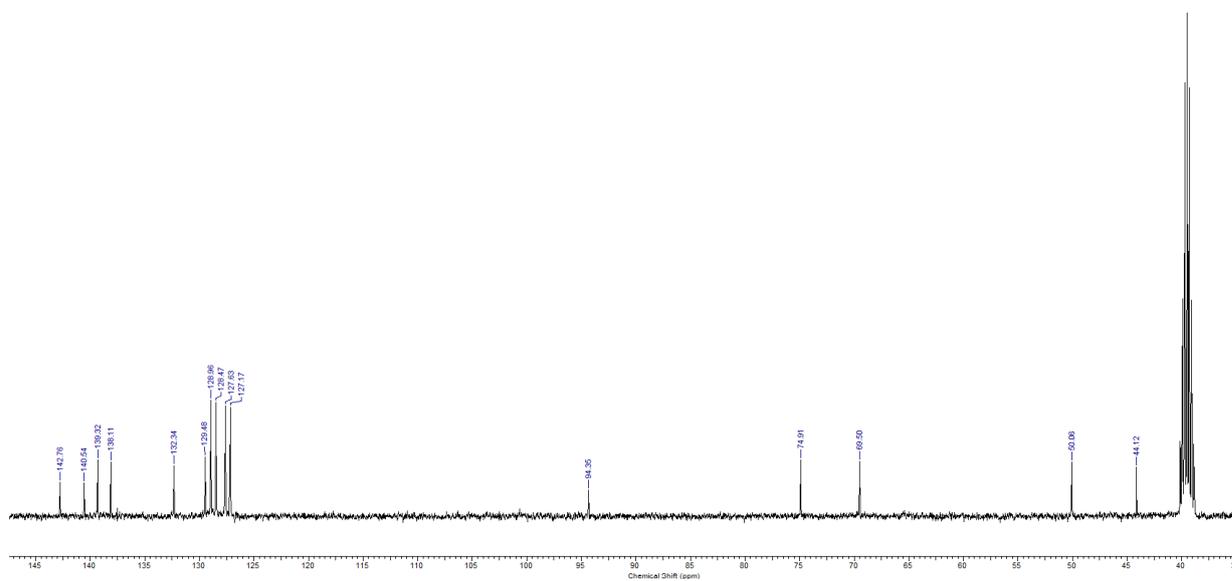


2d

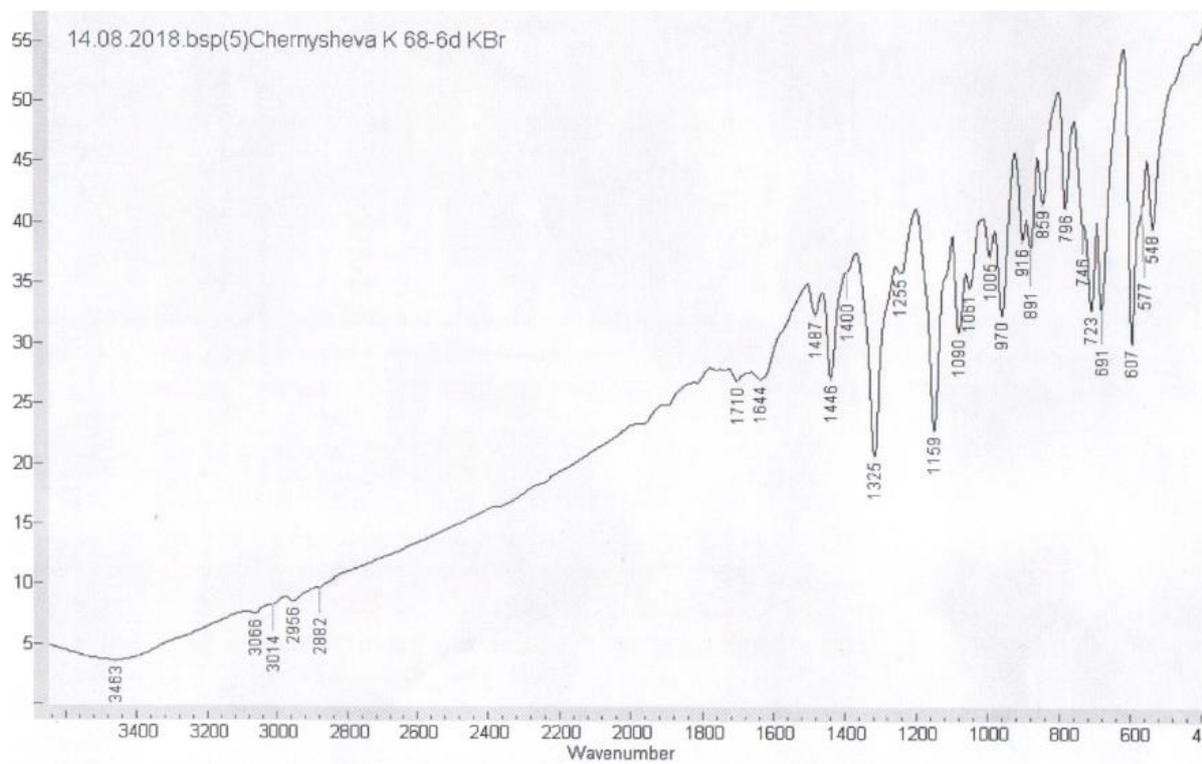
66-64_001001r



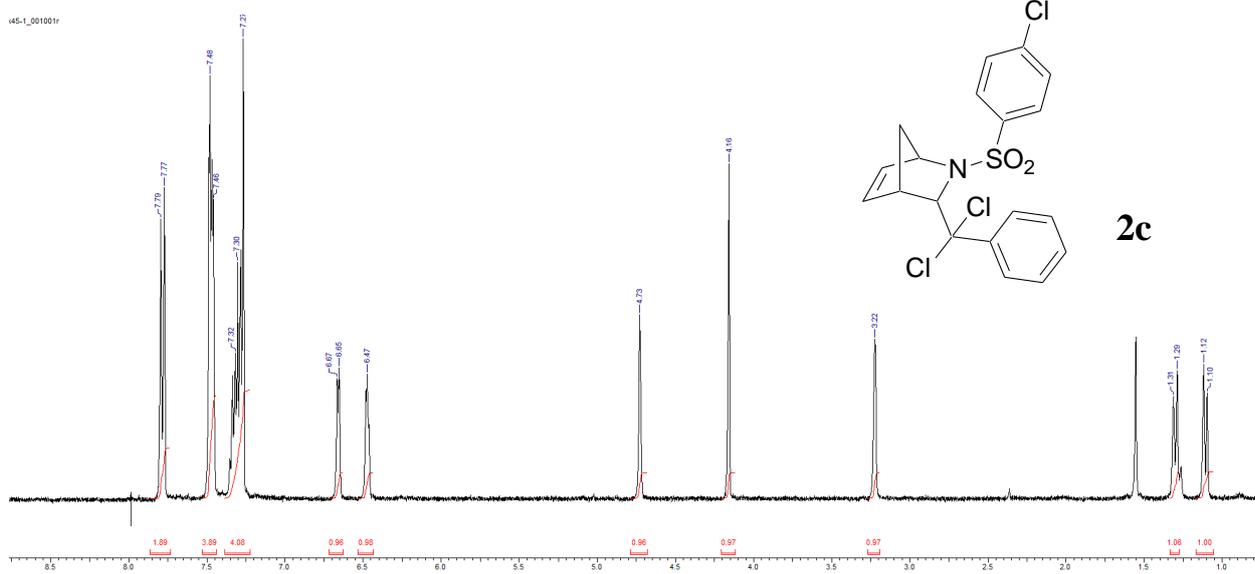
¹H NMR spectrum of **2d** (DMSO-d₆)



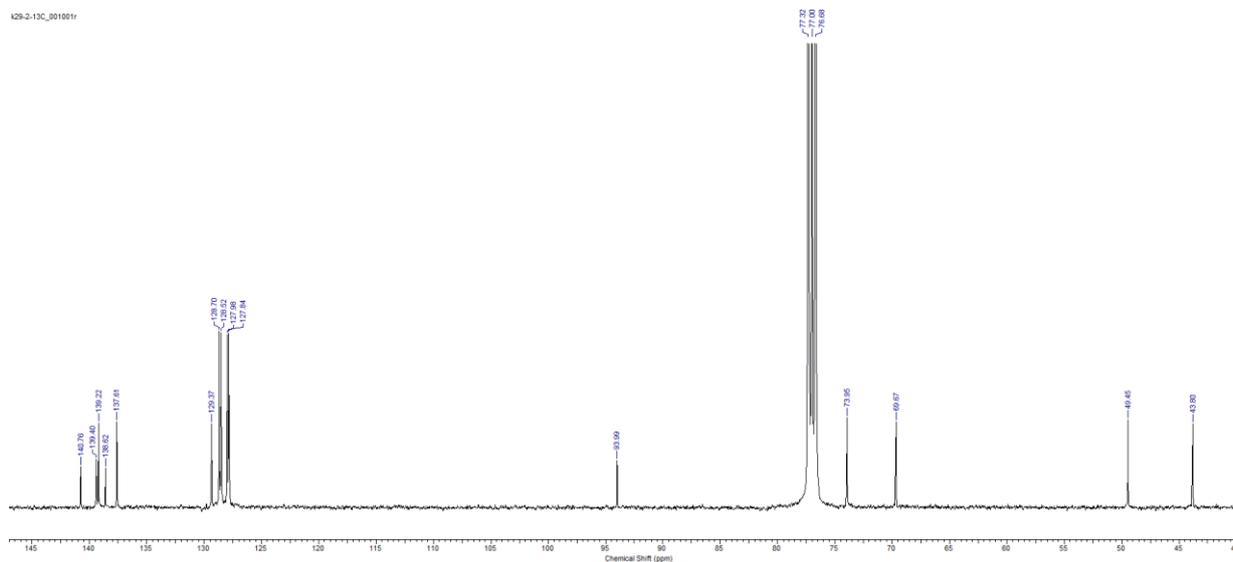
¹³C NMR spectrum of **2d** (DMSO-d₆)



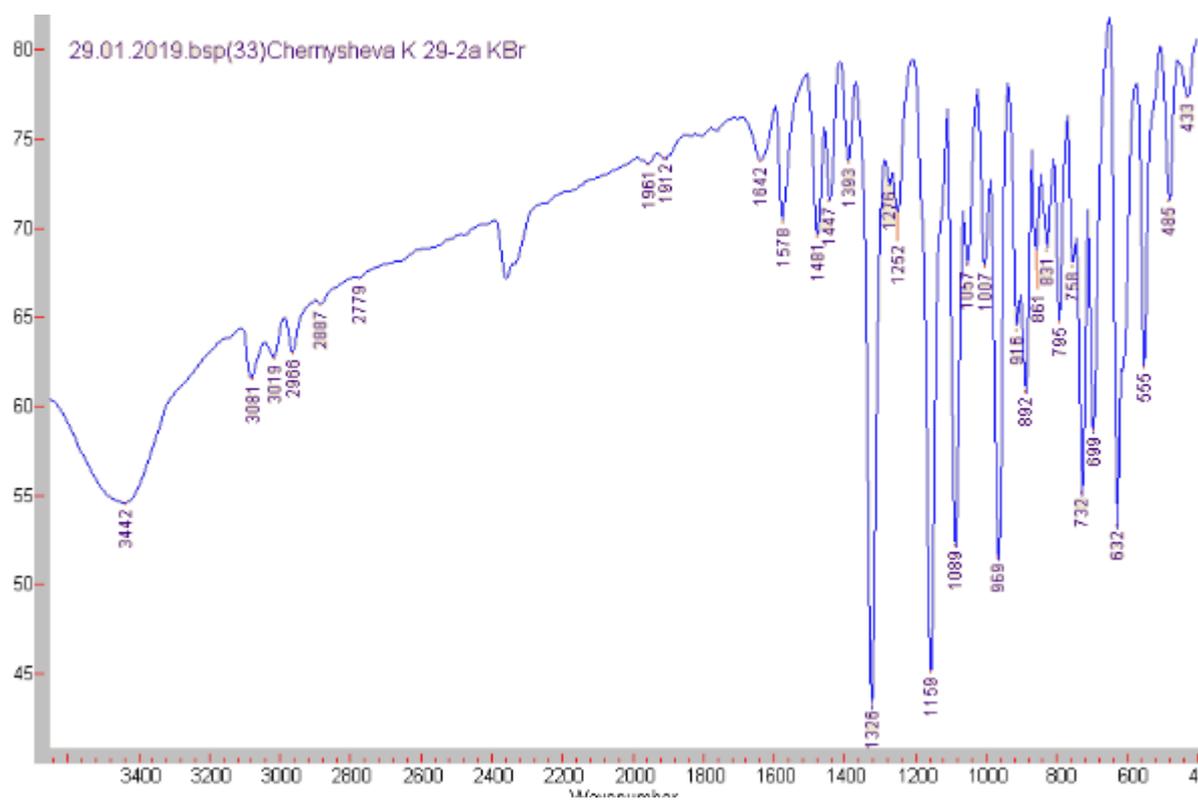
IR spectrum of **2d**



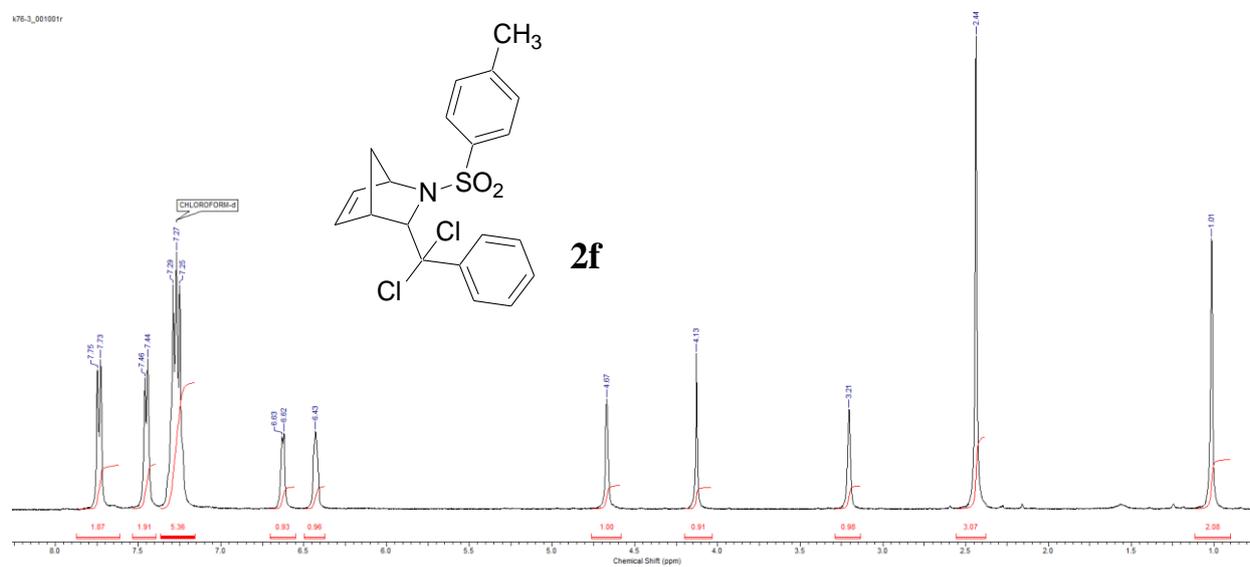
^1H NMR spectrum of **2c** (CDCl_3)



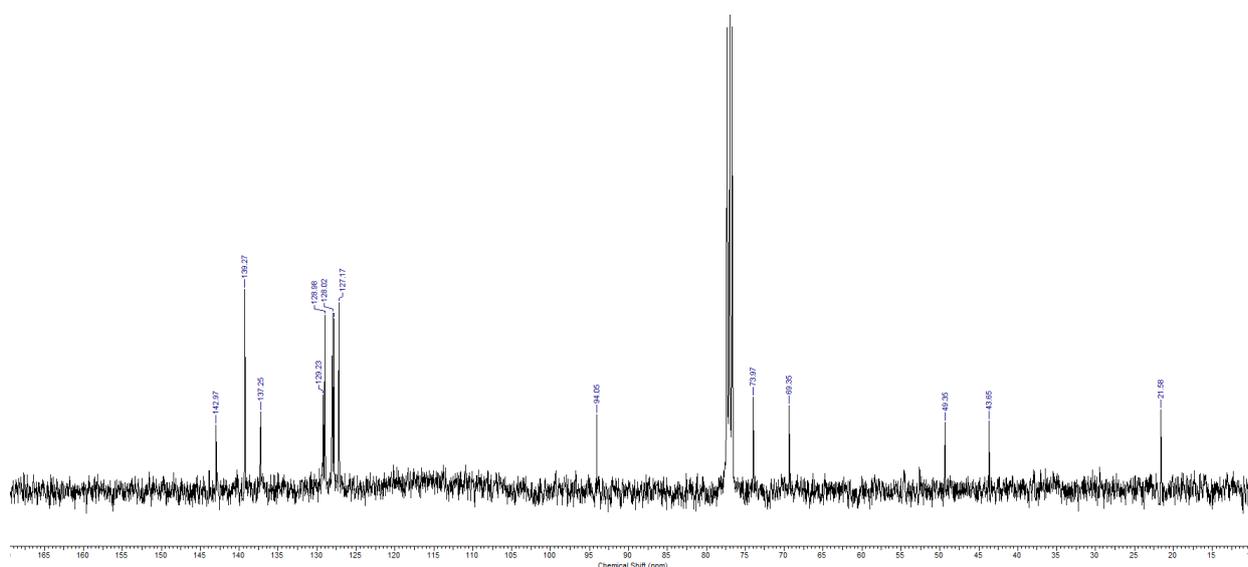
^{13}C NMR spectrum of **2c** (CDCl_3)



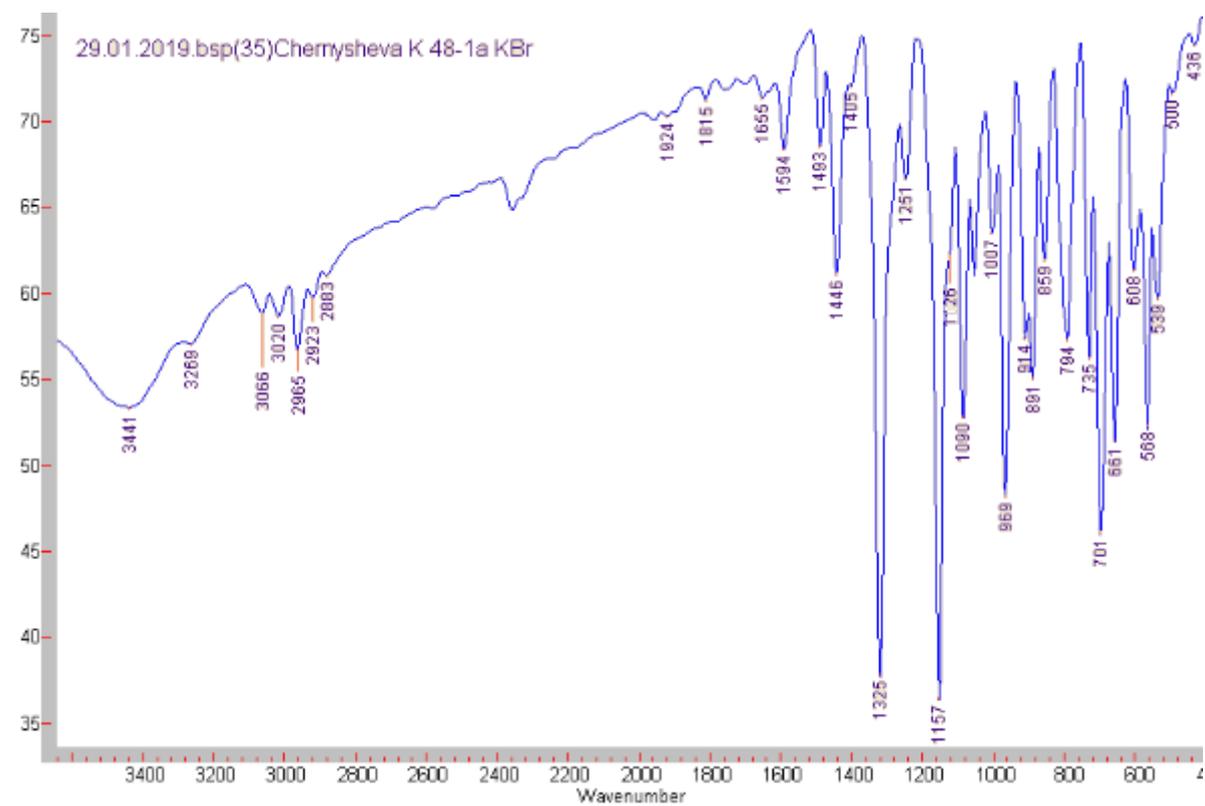
IR spectrum of **2c**



^1H NMR spectrum of **2f** (CDCl_3)

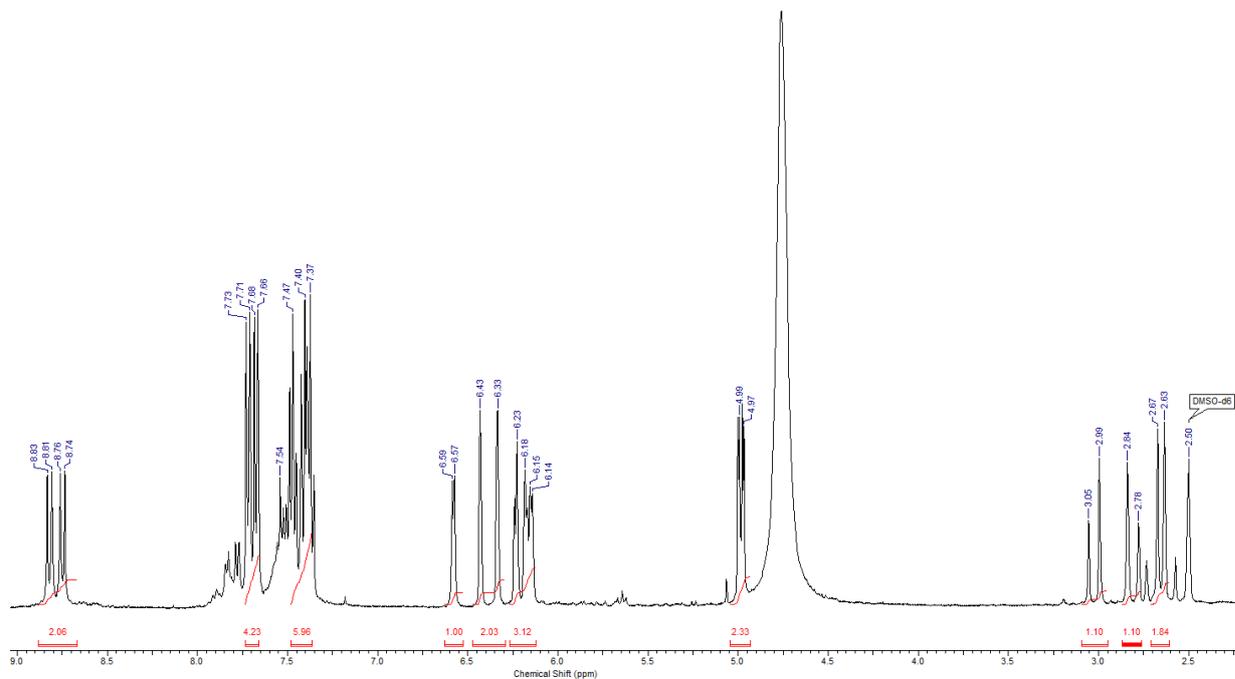
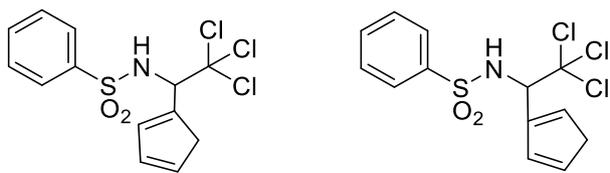


^{13}C NMR spectrum of **2f** (CDCl_3)



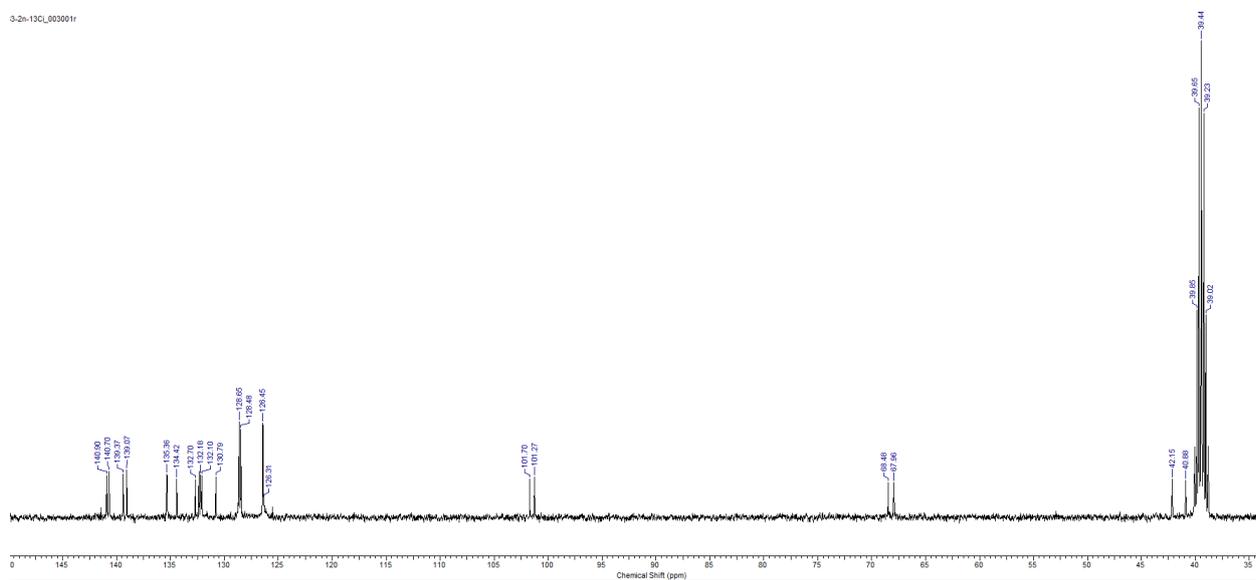
IR spectrum of **2f**

3a and 3'a



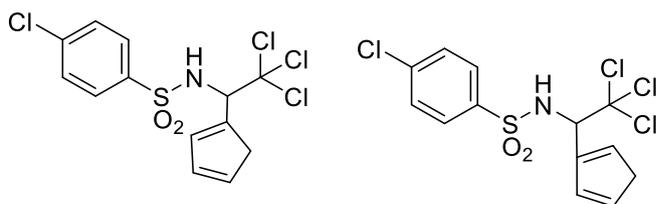
¹H NMR spectrum of mixture 3a and 3'a (DMSO-d₆)

3-2h-13C_003001r

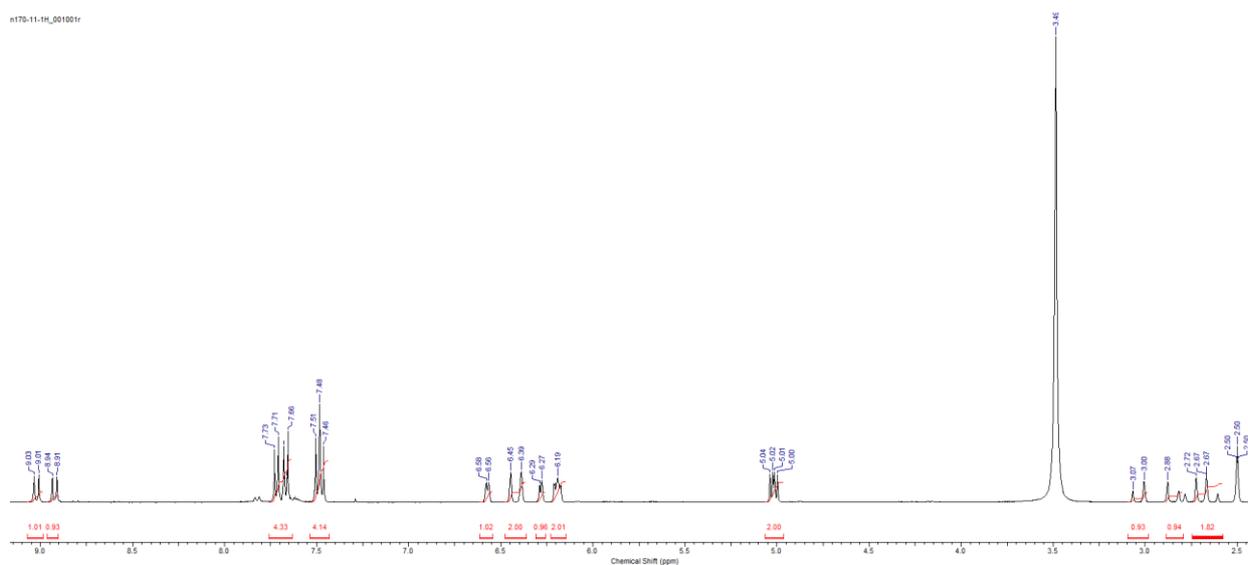


¹³C NMR spectrum of mixture 3a and 3'a (DMSO-d₆)

3b and 3'b

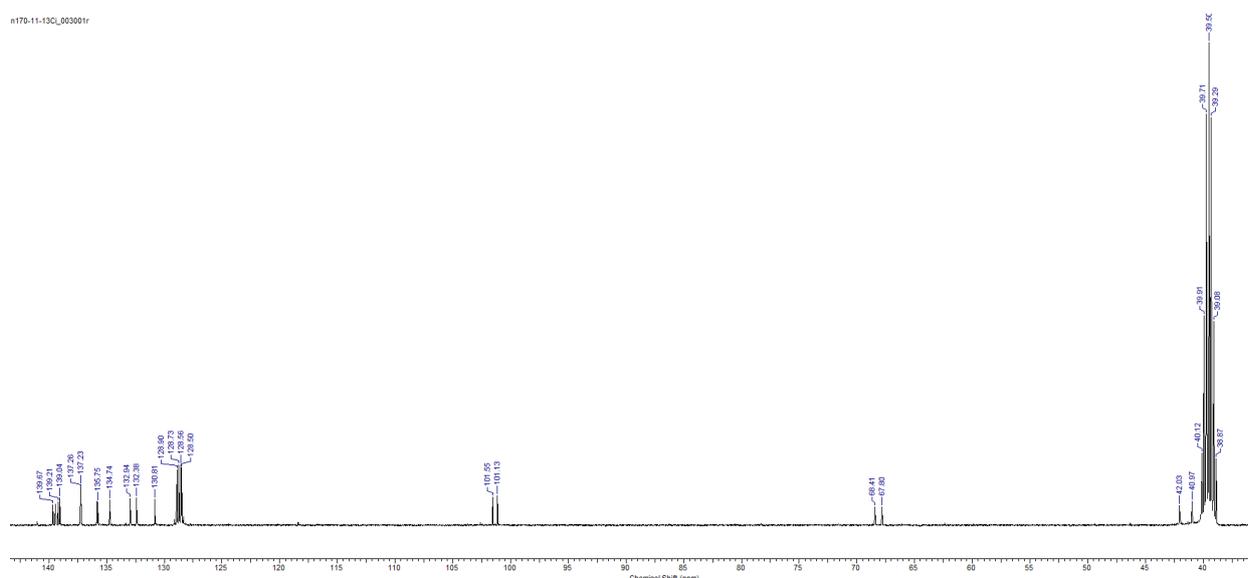


n170-11-1H_001001r



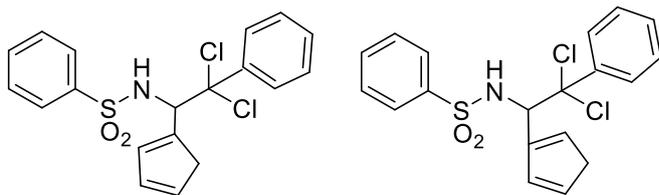
^1H NMR spectrum of mixture 3b and 3'b (DMSO- d_6)

n170-11-13C_003001r

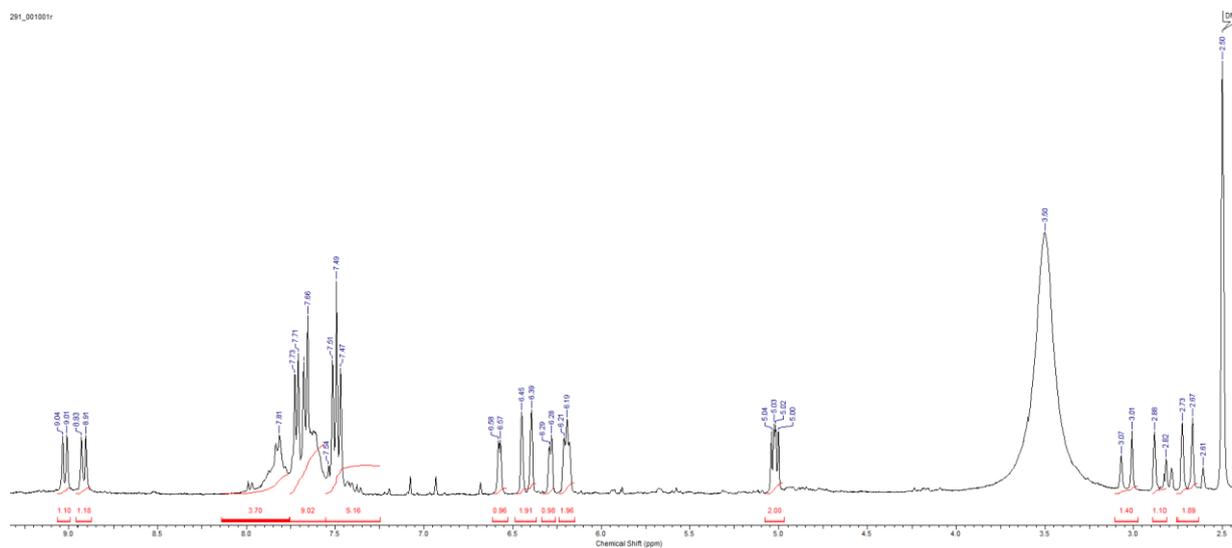


^{13}C NMR spectrum of mixture 3b and 3'b (DMSO- d_6)

3d and 3'd

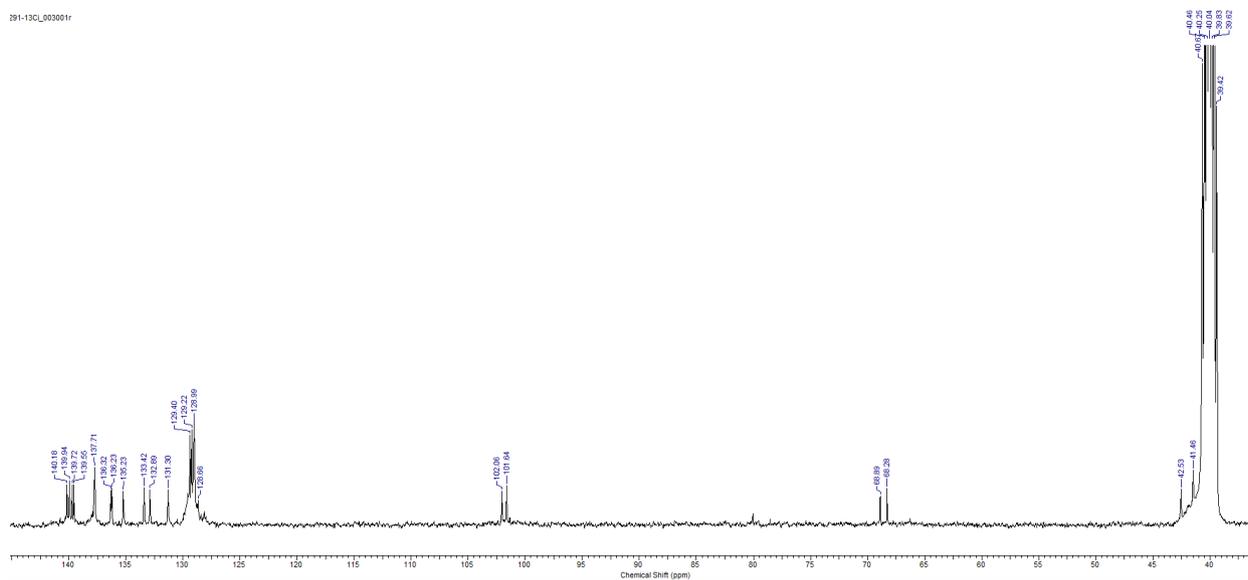


29f_001001r



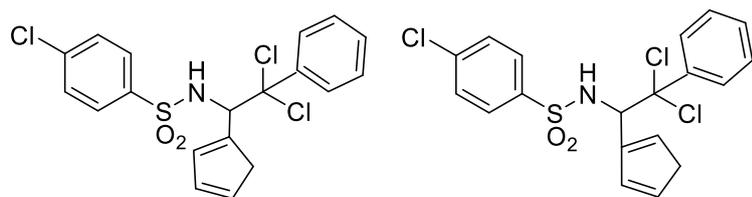
¹H NMR Spectrum of mixture 3d and 3'd (DMSO-d₆)

29f-13C_003001r

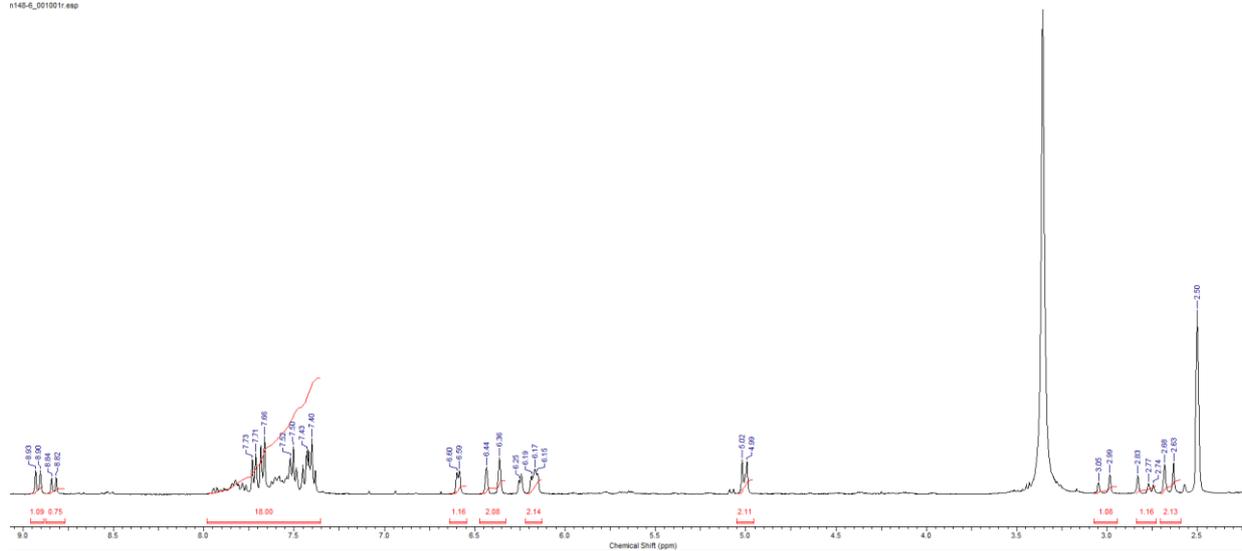


¹³C NMR spectrum of mixture 3d and 3'd (DMSO-d₆)

3e and 3'e

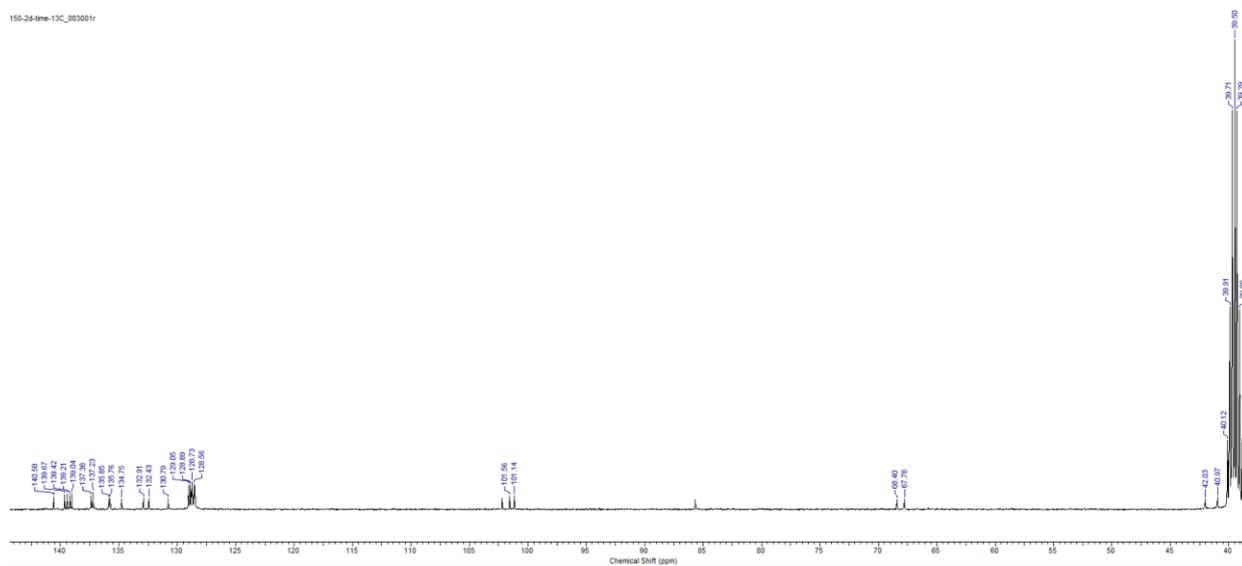


n148-6_001001r.esp



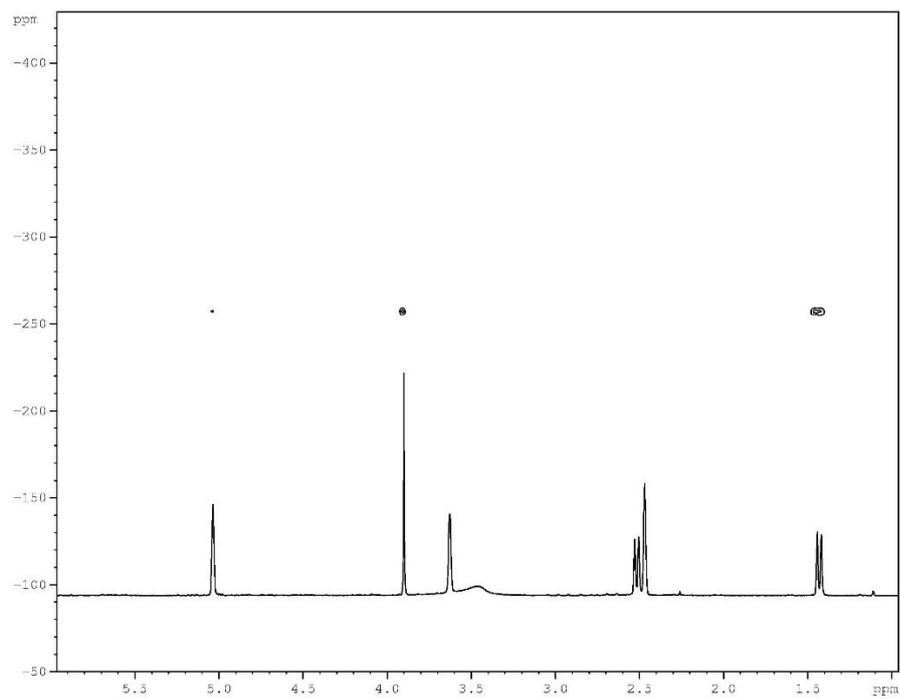
¹H NMR spectrum of mixture 3e and 3'e (DMSO-d₆)

156-26-ime-13C_003001r

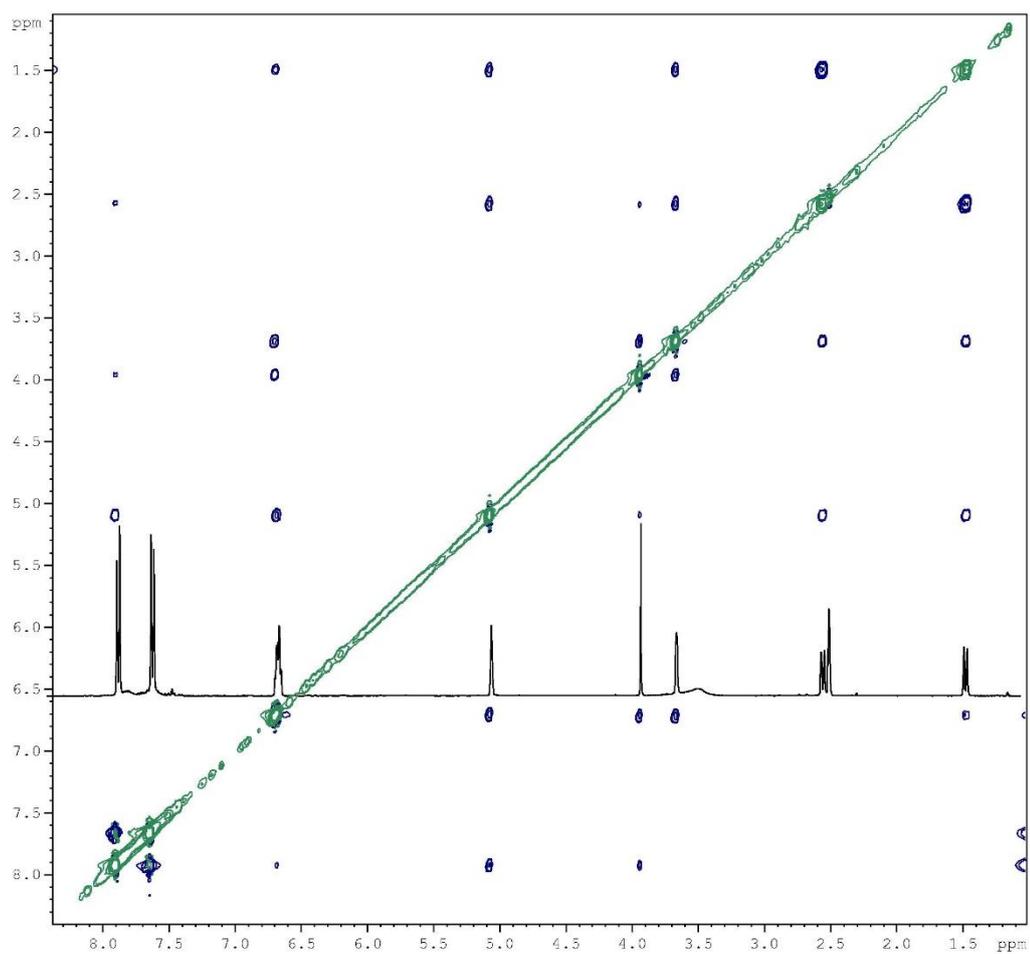


¹³C NMR spectrum of mixture 3e and 3'e (DMSO-d₆)

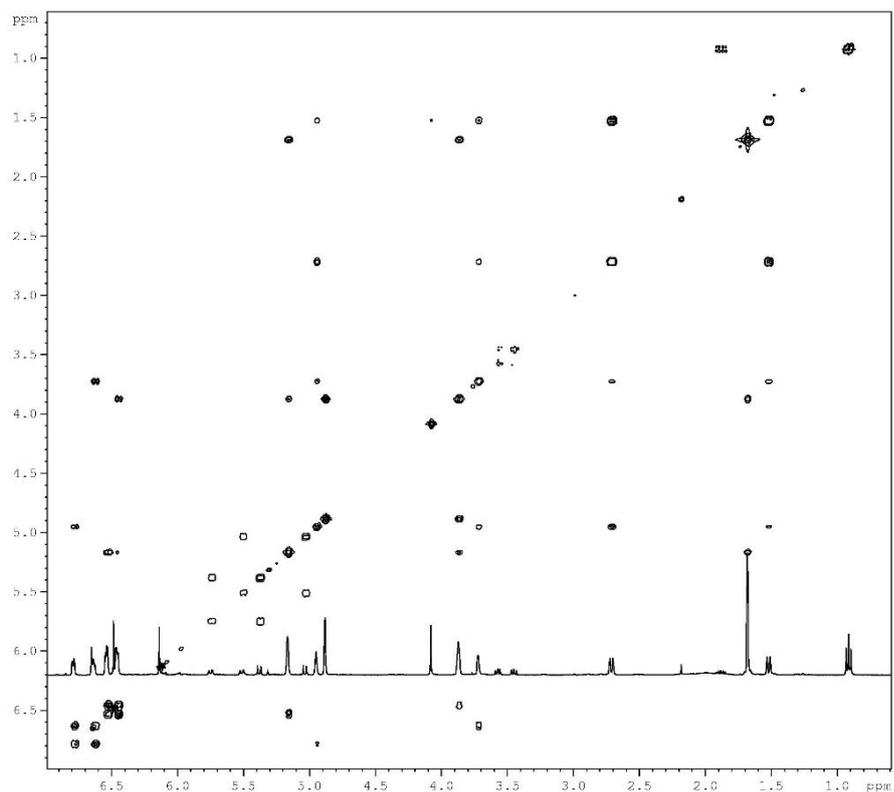
Selected 2D NMR spectra



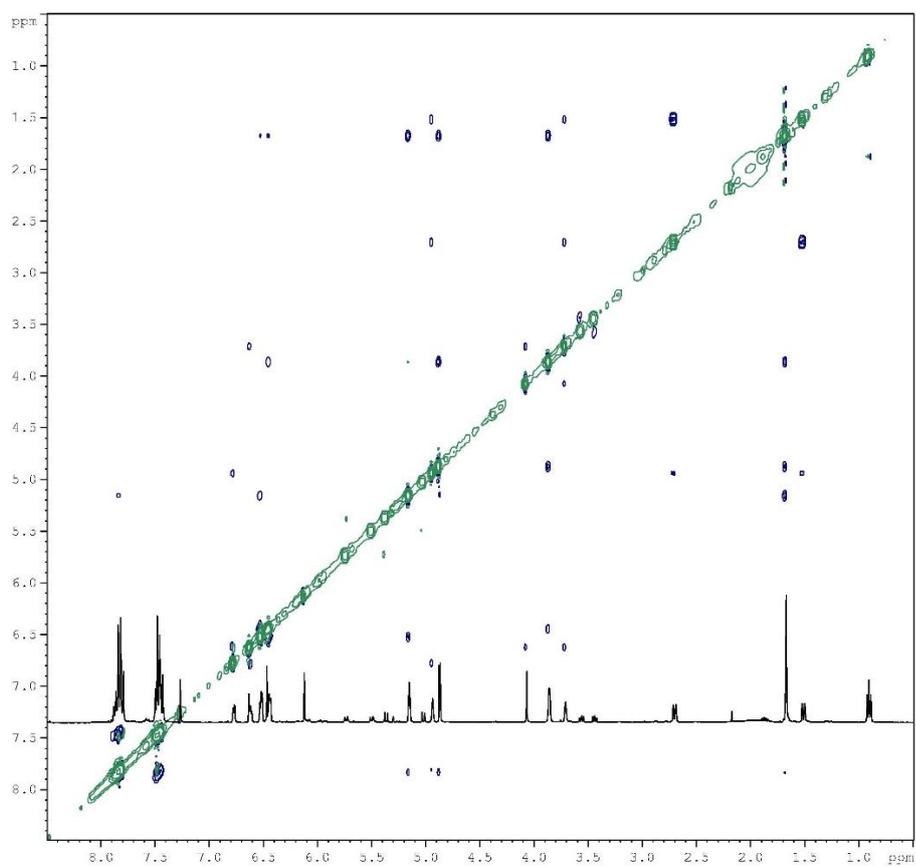
2D ^1H - ^{15}N HMBC NMR spectrum of **2b** (DMSO-d_6)



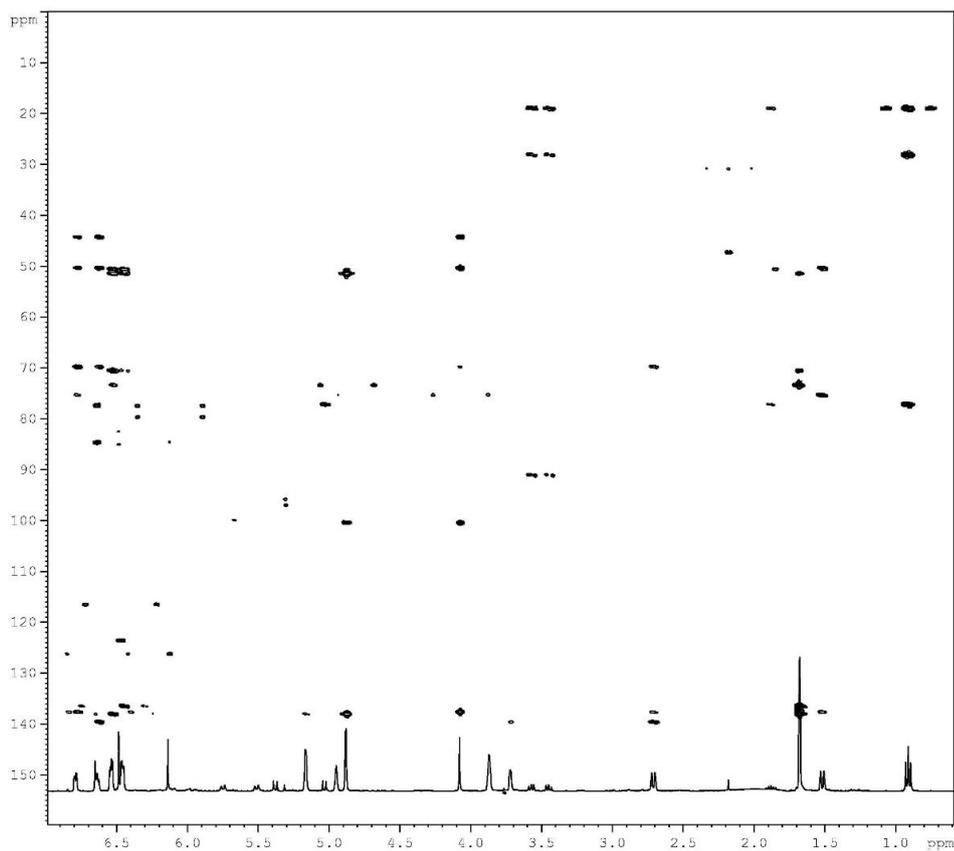
2D NOESY NMR spectrum of **2b** (DMSO-d_6)



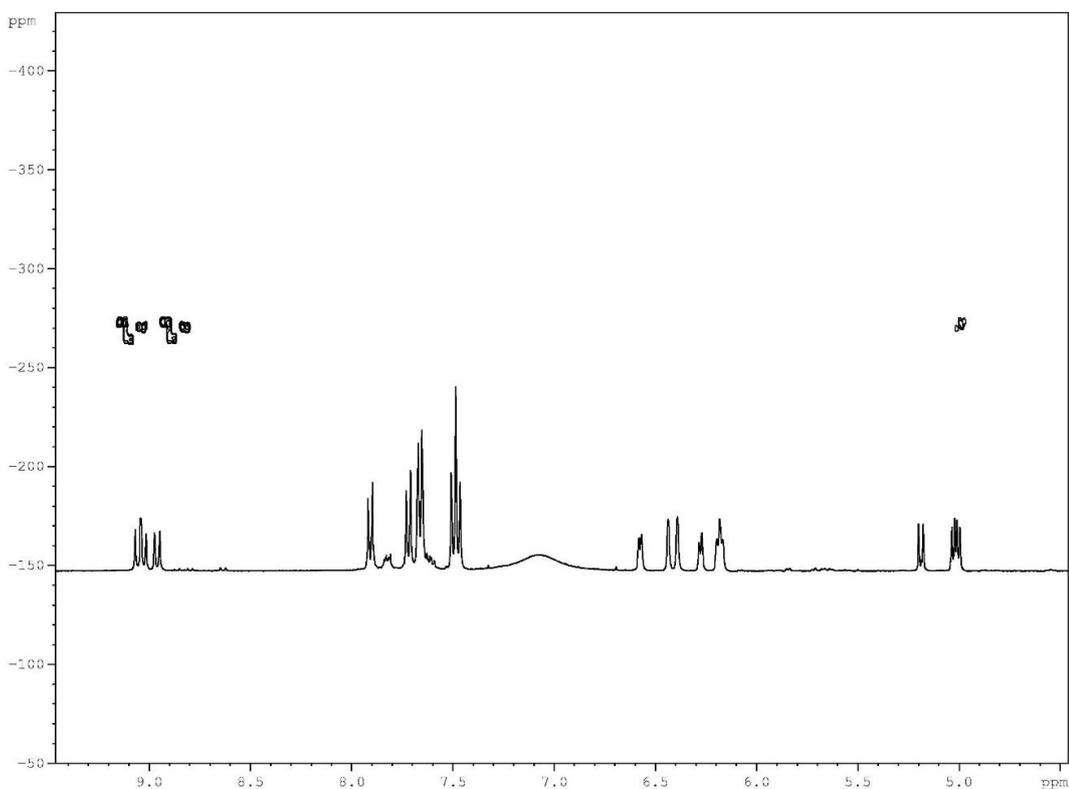
2D COSY NMR spectrum of mixture *exo-2b* and *endo-2b* (CDCl₃)



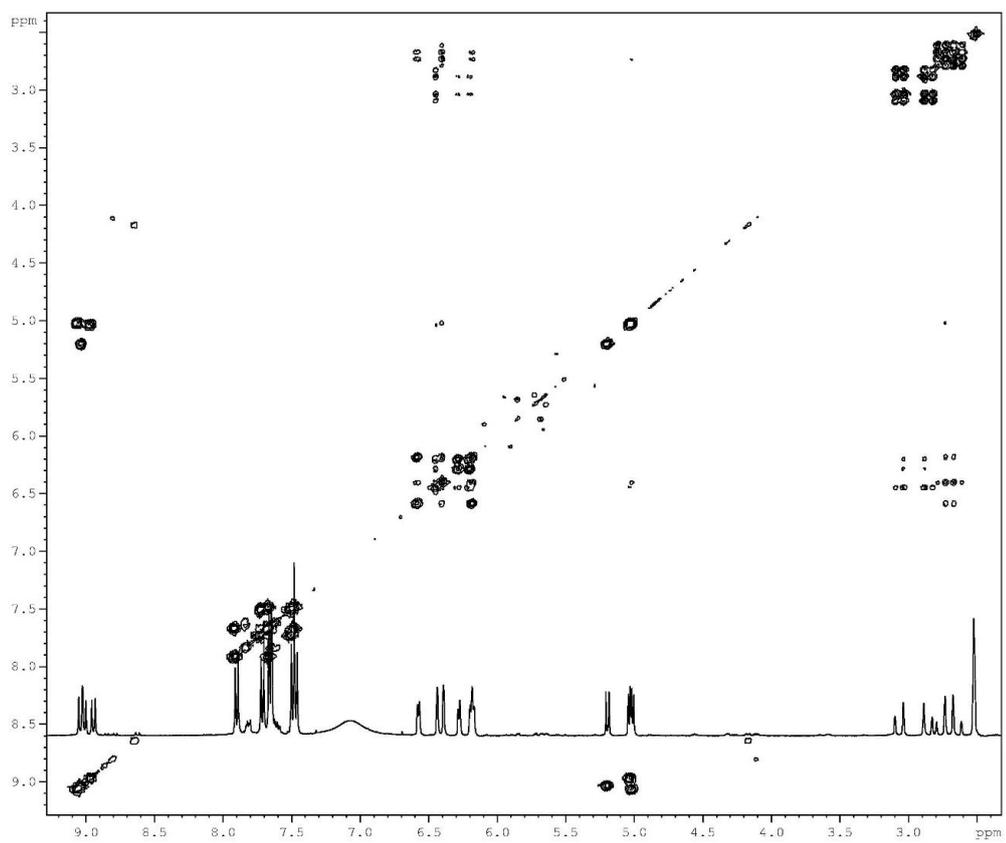
2D NOESY NMR spectrum of mixture *exo-2b* and *endo-2b* (CDCl₃)



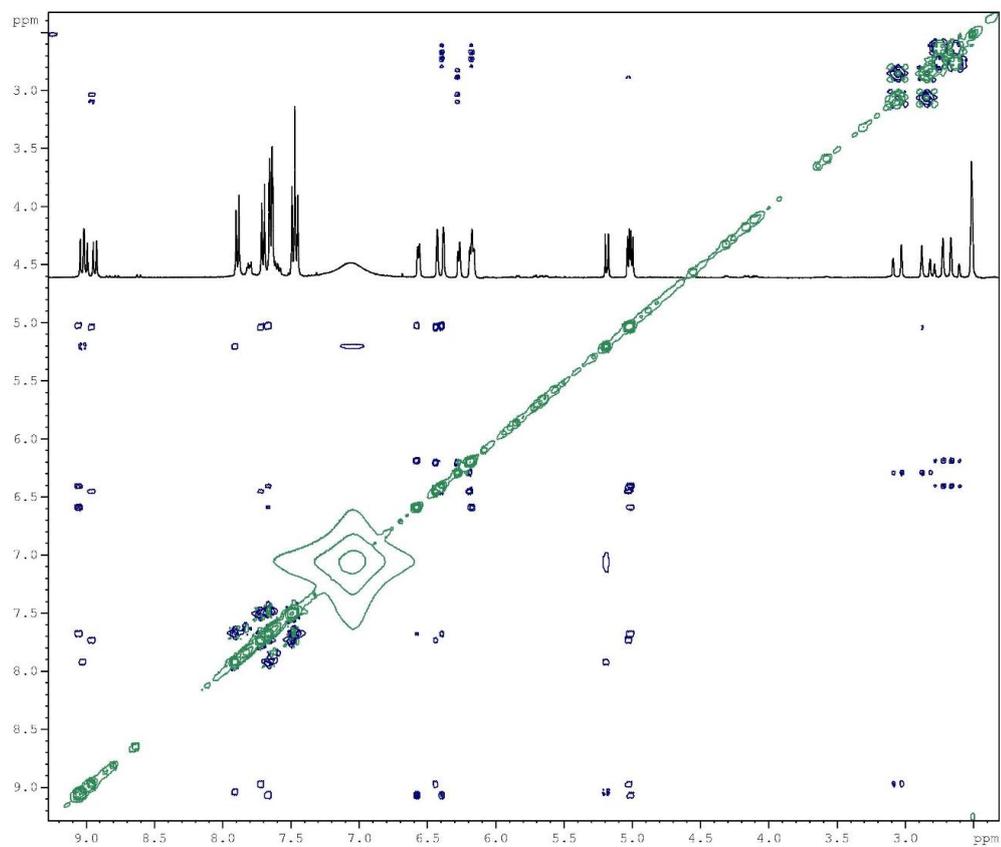
2D ^1H - ^{13}C HMBC NMR spectrum of mixture *exo*-**2b** and *endo*-**2b** (CDCl_3)



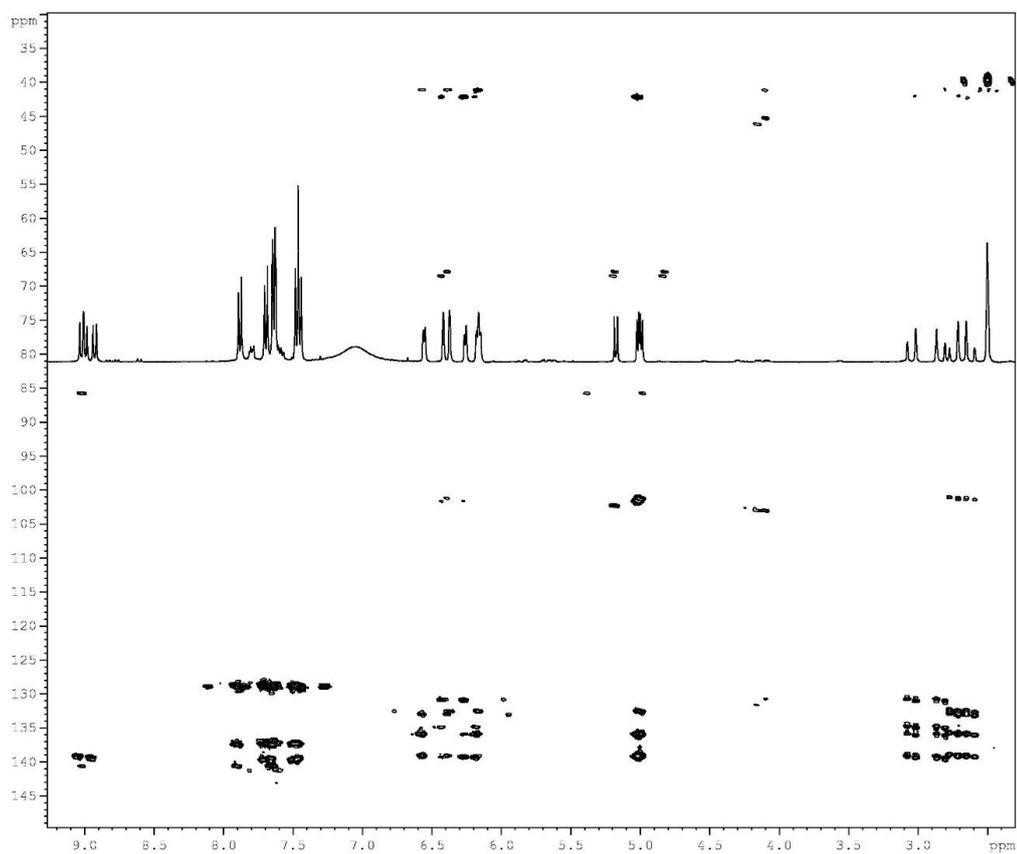
2D ^1H - ^{15}N HMBC NMR spectrum of mixture **3b** and **3'b** (DMSO-d_6)



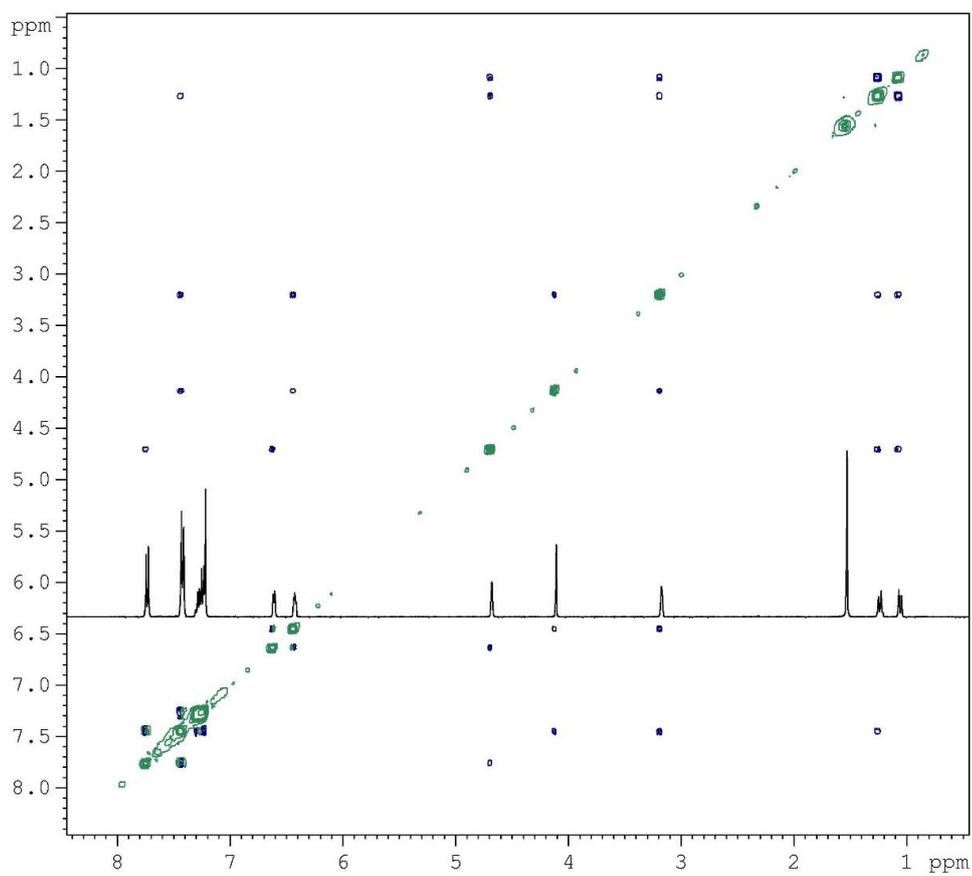
2D COSY NMR spectrum of mixture **3b** and **3'b** (DMSO-d₆)



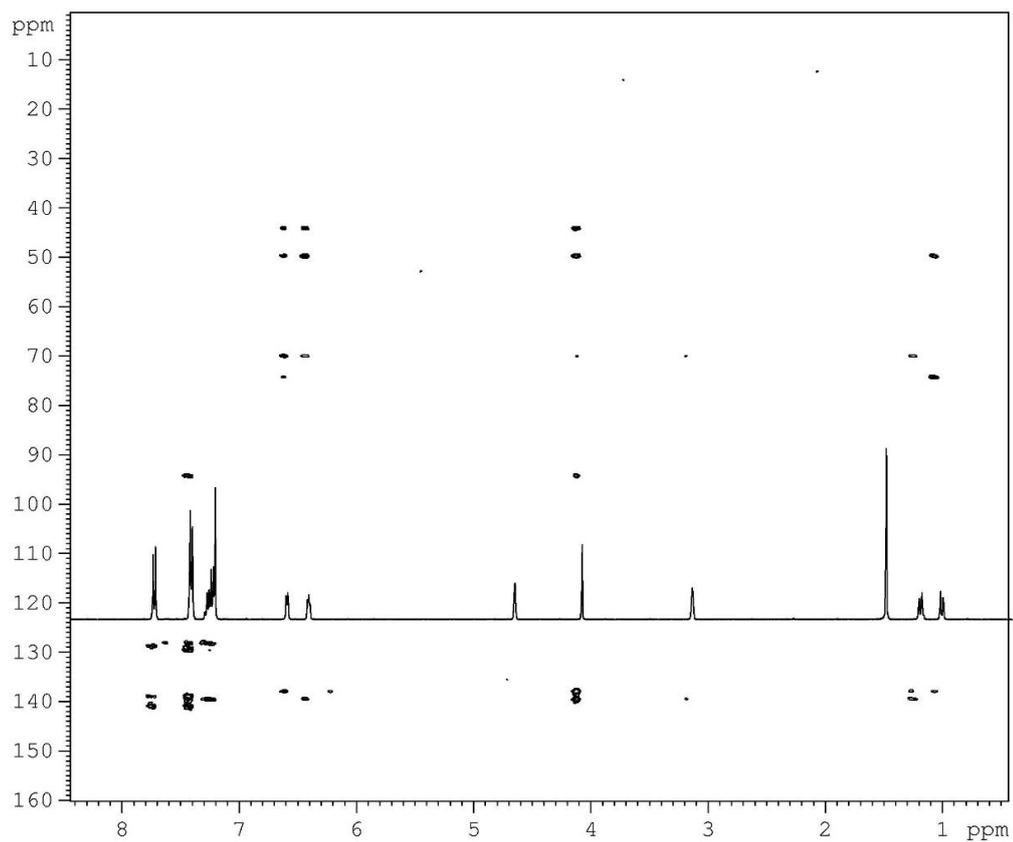
2D NOESY NMR spectrum of mixture **3b** and **3'b** (DMSO-d₆)



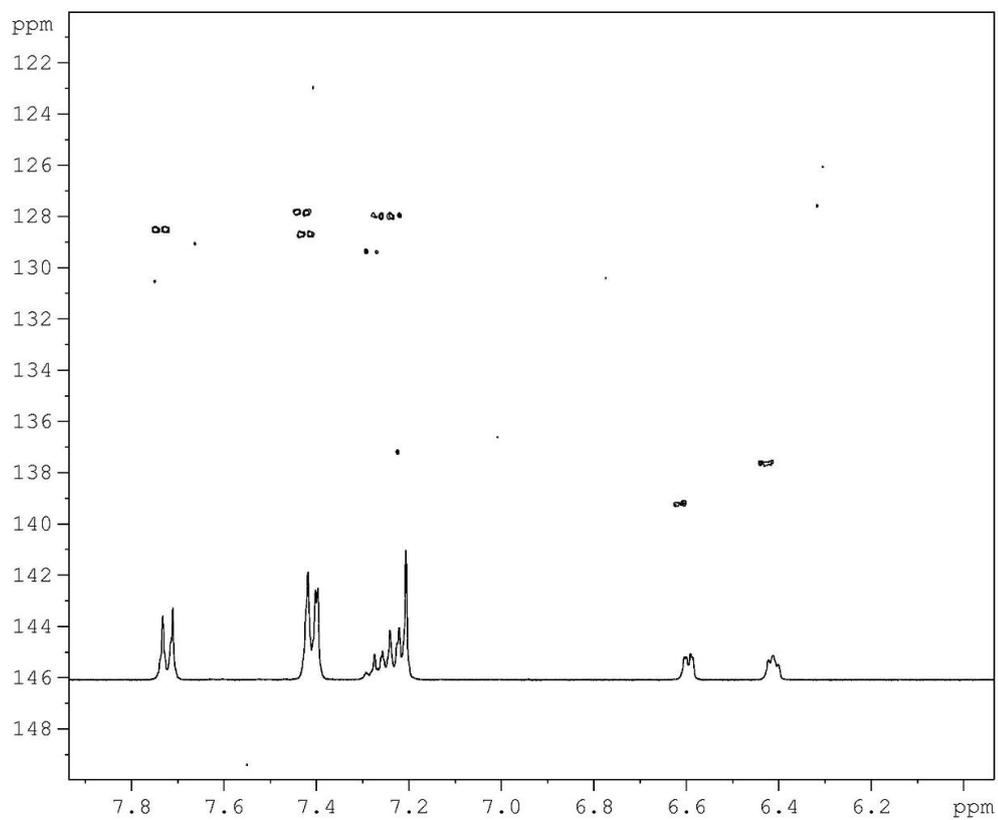
2D ^1H - ^{13}C HMBC NMR spectrum of mixture **3b** and **3'b** (DMSO- d_6)



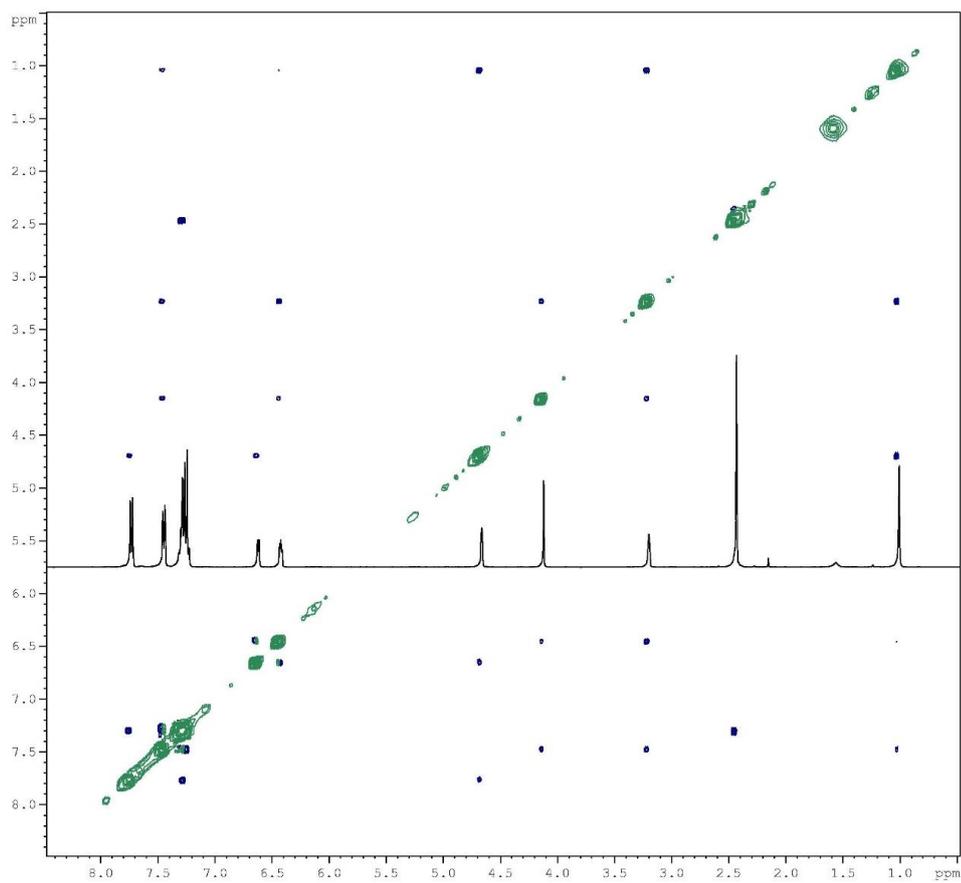
2D NOESY NMR spectrum of *exo*-**2c** (CDCl_3)



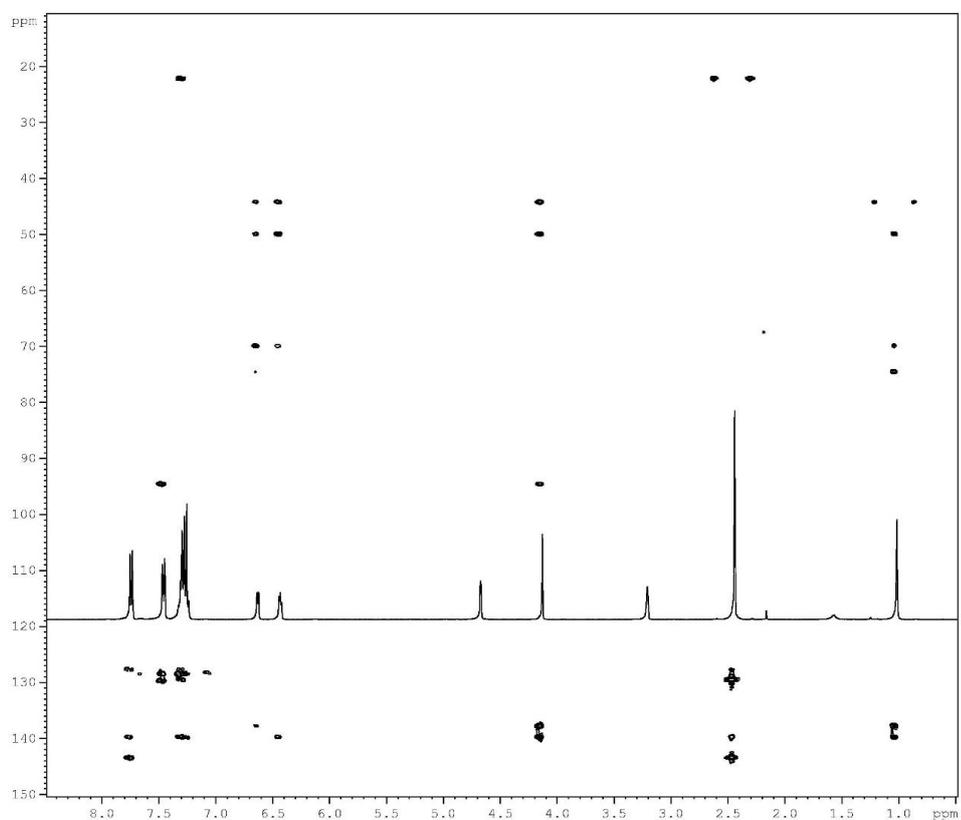
2D ^1H - ^{13}C HMBC NMR spectrum of *exo*-**2c** (CDCl_3)



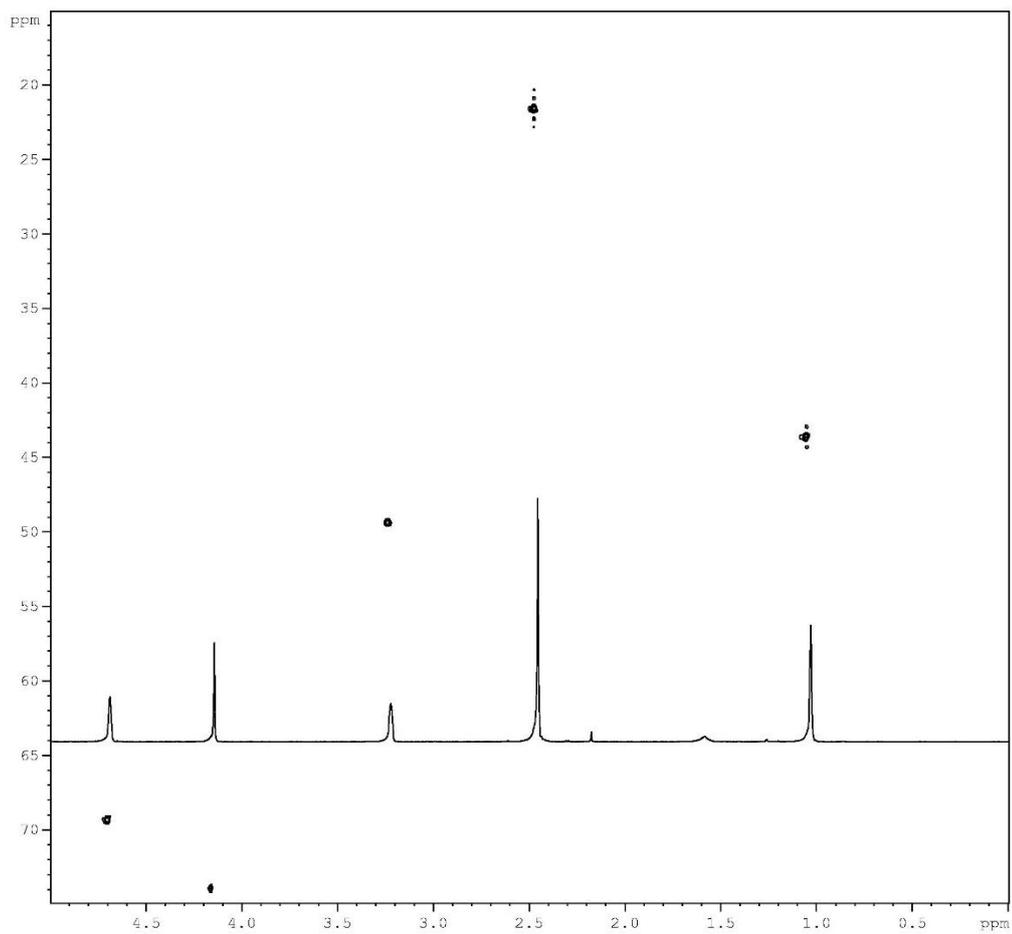
2D ^1H - ^{13}C HSQC NMR spectrum of *exo*-**2c** (aromatic part, CDCl_3)



2D NOESY NMR spectrum of *exo-2f* (CDCl₃)



2D ¹H-¹³C HMBC NMR spectrum of *exo-2f* (CDCl₃)



2D ^1H - ^{13}C HSQC NMR spectrum of *exo*-**2f** (CDCl_3)