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Palladium-catalyzed amination in the synthesis of novel fluorescent sensors based on 3,3′-diamino substituted 1,1′-bi(2-naphthol)

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General

The ^{1}H and ^{13}C NMR spectra were recorded at 298 K on a Bruker Avance-400 spectrometer operating at 400 MHz with Me_4Si as the internal standard. Positive ion MALDI mass spectra were obtained on a Bruker Ultraflex-II mass spectrometer using 1,8,9-trihydroxyanthracene as a matrix and polyethylene glycols as internal standards. Preparative column chromatography was performed using Interchim PuriFlash 4250/250 UPFP machine equipped with dry load cartridges with Merck irregular silica gel (40/60) or SepaFlash spherical silica gel (40/75). Electronic absorption spectra were registered with a Hitachi U-2900 device in a quartz cuvette (Hellma, l = 10.00 mm). Fluorescence spectra were registered with a Horiba Jobin Yvon Fluoromax-2 spectrofluorometer in a quartz cuvette (Hellma, l = 10.00 mm). Commercially available compounds (*R*-BINOL, sodium hydride, chloromethyl methyl ether, *n*-butyllithium, BINAP, sodium *tert*-butoxide, amines **2a-d**, 10% Pd/C catalyst and metal salts were purchased from Sigma-Aldrich) and acetonitrile of UHPLC grade (Fluka) were used without further purification. $Pd(dba)_2$ was synthesized by a known method.[S1] Dioxane was successively distilled over alkali and sodium metal and stored under dry argon. THF was distilled over alkali, then over sodium metal and used immediately. Dichloromethane was distilled over calcium hydride. Bromine and methanol were distilled.

[S1] T. Ukai, H. Kawazura, Y. Ishii, J. J. Bonnet and J. A. Ibers, *J. Organomet. Chem*., 1974, **65**, 253; https://doi.org/10.1016/S0022-328X(00)91277-4.

General procedure A for Pd-catalyzed amination of 3,3′-dibromo BINOL (**1**):

3,3′-Dibromo BINOL **1** (133 mg, 0.25 mmol), $Pd(dba)_2$ (12 mg, 8 mol.%), and BINAP (14 mg, 9 mol.%) were placed in a Schlenk tube (or two-necked flask) equipped with a magnetic stirrer bar and a reflux condenser and purged with dry argon. Dry dioxane (2.5 ml for compounds **3a-c**, 12 ml for compound **5**) was added to the flask under a dry argon flow, the mixture was stirred for 3 min, and then amine and sodium *tert*-butoxide (72 mg, 0.75 mmol) were added. The reaction mixture was refluxed for 36 h. After the completion of the reaction, the solvent was evaporated and the resulting dark viscous oily residue was chromatographed on silica gel using CH_2Cl_2-MeOH mixtures (0→30% MeOH) as the eluents. After evaporation of the solvents target compounds were obtained as light yellow viscous oils.

*General procedure **B*** for removing methoxymethyl group from BINOL derivatives:

MOM-protected compound was placed into a one-necked flask equipped with a magnetic stirrer bar and a reflux condenser, then methanol (C = 0.05M) and concentrated HCl (2 mL per 1 mmol of compound) were added. The mixture was heated at 60°C and maintained at this temperature for 2 hours. After the completion of the reaction, the solvent was evaporated to give the target products as solids.

N^3,$N^{3'}$-Bis(2-methoxyethyl)-2,2′-bis(methoxymethoxy)-[1,1′-binaphthalene]-3,3′-diamine 3a

was synthesized according to general procedure ***A*** from 3,3′-dibromo BINOL **1** (0.126 mmol, 67 mg), methoxyethylamine **2a** (0.378 mmol, 33 μL), $Pd(dba)_2$ (6 mg, 8 mol.%), BINAP (7 mg, 9 mol.%), Bu^tONa (36 mg, 0.378 mmol). Eluent 1 % of MeOH in DCM. Yield 66 mg (71%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.10 (s, 6H, OCH_3), 3.43 (s, 6H, CH_2–CH_2–OCH_3), 3.48 (t, 4H, NH–CH_2, ^3J 5.4 Hz), 3.75 (t, 4H, CH_2–CH_2–OMe, ^3J 5.4 Hz), 4.53 (d, 2H, O–CH_2–OMe, ^2J 5.8 Hz), 4.58 (d, 2H, O–CH_2–OMe, ^2J 5.8 Hz), 6.97 (s, 2H, $H^{4,4'}$-BINOL), 6.98 – 7.02 (m, 2H, $H^{7,7'}$-BINOL), 7.08 (d, 2H, ^3J 8.3 Hz, $H^{8,8'}$-BINOL), 7.30 (ddd, ^3J 8.2 Hz, ^3J 6.7 Hz, ^4J 1.3 Hz, 2H, $H^{6,6'}$-BINOL), 7.68 (d, 2H, $H^{5,5'}$-BINOL, ^3J 8.2 Hz).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 43.1 (2C, $NHCH_2$), 57.0 (2C, OCH_3), 58.8 (2C, OCH_3), 70.9 (2C, $NHCH_2CH_2O$), 99.0 (2C, OCH_2O), 104.8 (2C, CH-BINOL), 122.3 (2C, CH-BINOL), 125.0 ($2C^{quat}$), 125.3 (2C, CH-BINOL), 125.7 (2C, CH-BINOL), 126.1 (2C, CH-BINOL), 127.0 ($2C^{quat}$), 132.5 ($2C^{quat}$), 141.2 (2C, $C^{3(3')}$), 144.8 (2C, $C^{2(2')}$).
MALDI MS (PEG 600): found m/z 521.2631 $[M + H]^+$; calculated for $C_{30}H_{37}N_2O_6$ 521.2647.

2,2′-Bis(methoxymethoxy)-N^3,$N^{3'}$-bis((tetrahydrofuran-2-yl)methyl)-[1,1′-binaphthalene]-3,3′-diamine 3b

was synthesized according to general procedure ***A*** from 3,3′-dibromo BINOL **1** (0.25 mmol, 133 mg), tetrahydrofurfuryl amine **2b** (0.75 mmol, 77 μL), $Pd(dba)_2$ (12 mg, 8 mol.%), BINAP (14 mg, 9 mol.%), t-BuONa (72 mg, 0.75 mmol). Eluent 7 % of MeOH in DCM. Yield 132 mg (92%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.71 – 1.82 (m, 2H, CH_2), 1.89 – 2.05 (m, 4H, CH_2), 2.05 – 2.18 (m, 2H, CH_2), 3.08 (s, 6H, O–CH_3), 3.30 (dd, 2H, NH–CH_2, ^2J 12.2 Hz, ^3J 7.2 Hz), 3.43 (dd, 2H, NH–CH_2, ^2J 12.2 Hz, ^3J 4.3 Hz), 3.76 – 3.86 (m, 2H, CH_2–CH_2O), 3.88 – 3.97 (m, 2H, CH_2–CH_2O), 4.24 – 4.34 (m, 2H, –C*H*O–), 4.54 (d, O–CH_2–OMe, 2H, ^2J 5.8 Hz), 4.57 (d, O–CH_2–OMe, 2H, ^2J 5.8 Hz), 6.97 – 7.03 (m, 2H, $H^{7,7'}$-BINOL), 7.04 – 7.11 (m, 4H, $H^{4,4'}$-BINOL, $H^{8,8'}$-BINOL), 7.30 (ddd, ^3J 8.2 Hz, ^3J 6.7 Hz, ^4J 1.3 Hz, 2H, $H^{6,6'}$-BINOL), 7.68 (d, 2H, $H^{5,5'}$-BINOL, ^3J 8.2 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 25.8 (2C, CH_2–CH_2), 29.3 (2C, CH_2–CH_2), 48.3 (br.s, 2C, $NHCH_2$), 57.1 (2C, OCH_3), 68.1 (2C, OCH_2–CH_2), 77.2 (2C, CHO), 99.0 (2C, OCH_2O), 105.7 (br.s, 2C, CH-BINOL), 122.6 (2C, CH-BINOL), 125.0 ($2C^{quat}$), 125.4 (2C, CH-BINOL), 125.8 (2C, CH-BINOL), 126.0 (2C, CH-BINOL), 127.3 ($2C^{quat}$), 132.4 ($2C^{quat}$), 140.7 (2C, $C^{3(3')}$), 144.8 (2C, $C^{2(2')}$).

MALDI MS (PEG 600): found m/z 573.2978 $[M + H]^+$; calculated for $C_{34}H_{41}N_2O_6$ 573.2960.

2,2′-Bis(methoxymethoxy)-N^3,$N^{3'}$-bis(2-(benzyloxy)cyclopentyl)-[1,1′-binaphthalene]-3,3′-diamine 3c

was synthesized according to general procedure ***A*** from 3,3′-dibromo BINOL **1** (0.25 mmol, 133 mg), 2-(benzyloxy)cyclopentane amine **2c** (75 mmol, 146 μL), $Pd(dba)_2$ (12 mg, 8 mol.%), BINAP (14 mg, 9 mol.%), t-BuONa (72 mg, 0.75 mmol). Eluent 7 % of MeOH in DCM. Yield 99 mg (53%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.52 –1.66 (m, 2H, CH_2), 1.75 – 1.86 (m, 2H, CH_2), 1.86 – 2.00 (m, 6H, CH_2), 2.30 – 2.47 (m, 2H, CH_2), 3.03 (s, 6H, OCH_3), 3.92 – 4.07 (m, 4H, C*H*–NH, C*H*–O), 4.49 (d, 2H, O–CH_2–OMe, ^2J 5.9 Hz), 4.53 (d, 2H, O–CH_2–OMe, ^2J 5.9 Hz), 4.61 (d, 2H, CH_2–Ph, ^2J 11.7 Hz), 4.69 (d, 2H, CH_2–Ph, ^2J 11.7 Hz), 4.87 (br. s, 2H, N*H*), 7.01 (ddd, 2H, $H^{7,7'}$-BINOL ^3J 8.2 Hz, ^3J 6.7 Hz, ^4J 1.3 Hz), 7.07 – 7.16 (m, 4H, $H^{8,8'}$-BINOL, $H^{4,4'}$-BINOL), 7.28 – 7.36 (m, 4H, H^4-Ph, $H^{6,6'}$-BINOL), 7.40 (t, 4H, $H^{3,5}$-Ph, $^3J_{obs}$ 7.2 Hz), 7.47 (d, 4H, $H^{2,6}$-Ph, ^3J 7.1 Hz), 7.64 (d, 2H, $H^{5,5'}$-BINOL, ^3J 8.2 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 22.3 (2C, CH_2–*C*H_2–CH_2), 30.4 (2C, CH–*C*H_2), 31.9 (2C, CH–*C*H_2), 57.1 (2C, OCH_3), 59.9 (2C, CHNH), 71.2 (2C, OCH_2Ph), 85.1 (2C, CHO), 99.1 (2C, OCH_2O), 105.6

(2C, CH-BINOL), 122.2 (2C, CH-BINOL), 124.8 (2C^{quat}), 125.3 (2C, CH-BINOL), 125.8 (2C, CH-BINOL), 126.0 (2C, CH-BINOL), 126.8 (2C^{quat}), 127.6 (2C, CH-Ph), 127.8 (4C, CH-Ph), 128.4 (4C, CH-Ph), 132.5 (2C^{quat}), 138.6 (2C^{quat}), 140.4 (2C^{quat}), 144.5 (2C^{quat}).
MALDI MS (PEG 600): found m/z 753.3917 $[M + H]^+$; calculated for $C_{48}H_{53}N_2O_6$ 753.3899.

3,3′-Bis{[(tetrahydrofuran-2-yl)methyl]amino}[1,1′-binaphthalene]-2,2′-diol 4b

was synthesized according to general procedure ***B*** from compound **3b** (0.112 mmol, 64 mg) and concentrated HCl (0.223 mL). Yield 51 mg (94%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.63 – 1.76 (m, 2H, CH_2), 1.81 – 1.96 (m, 4H, CH_2), 1.96 – 2.08 (m, 2H, CH_2), 3.27 (dd, 2H, NH–CH_2, ^2J 12.6 Hz, ^3J 7.4 Hz), 3.39 (dd, 2H, NH–CH_2, ^2J 12.6 Hz, ^3J 3.9 Hz), 3.62 – 3.71 (m, 2H, CH_2O), 3.73 – 3.83 (m, 2H, CH_2O), 4.09 – 4.20 (m, 2H, CHO), 6.97 –7.03 (m, 6H, $H^{4,4'}$-BINOL, $H^{7,7'}$-BINOL, $H^{8,8'}$-BINOL), 7.23 – 7.30 (m, 2H, $H^{6,6'}$-BINOL), 7.68 (d, 2H, $H^{5,5'}$-BINOL, ^3J 8.1 Hz).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 25.5 (2C, CH_2–CH_2), 29.1 (2C, CH_2–CH_2), 47.5 (2C, $NHCH_2$), 67.7 (2C, OCH_2–CH_2), 76.9 (2C, CHO), 104.7 (2C, CH-BINOL), 111.0 (2C^{quat}), 122.7 (2C, CH-BINOL), 124.0 (2C, CH-BINOL), 124.3 (2C, CH-BINOL), 125.6 (2C, CH-BINOL), 126.4 (2C^{quat}), 130.6 (2C^{quat}), 137.7 (2C, $C^{3(3')}$), 143.7 (2C, $C^{2(2')}$).
MALDI MS (PEG 400): found m/z 485.2418 $[M + H]^+$; calculated for $C_{30}H_{33}N_2O_4$ 485.2435.

3,3′-Bis[(2-benzyloxycyclopentyl)amino][1,1′-binaphthalene]-2,2′-diol 4c

was synthesized according to general procedure ***B*** from compound **3c** (0.076 mmol, 57 mg) and concentrated HCl (0.151 mL). Yield 50 mg (80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.53 – 1.68 (m, 2H, CH_2), 1.75 – 2.04 (m, 8H, CH_2), 2.31 – 2.50 (m, 2H, CH_2), 3.94 – 4.08 (m, 4H, CH–NH, CH–O), 4.59 (d, 2H, CH_2–Ph, ^2J 11.7 Hz), 4.69 (d, 2H, CH_2–Ph, ^2J 11.7 Hz), 5.18 (br. s, 4H, OH, NH), 7.03 – 7.11 (m, 4H, $H^{8,8'}$-BINOL, $H^{7,7'}$-BINOL), 7.19 (s, 2H, $H^{4,4'}$-BINOL), 7.27 – 7.35 (m, 4H, H^4-Ph, $H^{6,6'}$-BINOL), 7.39 (dd, 4H, $H^{3,5}$-Ph, ^3J 8.3 Hz, ^3J 7.1 Hz), 7.46 (d, 4H, $H^{2,6}$-Ph, ^3J 7.1 Hz), 7.68 (d, 2H, $H^{5,5'}$-BINOL, ^3J 8.1 Hz).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 22.3 (2C, CH_2–CH_2–CH_2), 30.4 (2C, CH–CH_2), 32.0 (2C, CH–CH_2), 60.3 (2C, CHNH), 71.3 (2C, OCH_2Ph), 85.3 (2C, CHO), 106.4 (2C, CH-BINOL), 110.4 (2C^{quat}), 123.0 (2C, CH-BINOL), 124.1 (2C, CH-BINOL), 124.4 (2C, CH-BINOL), 125.8 (2C^{quat}), 126.1 (2C, CH-BINOL), 127.7 (2C, CH-Ph), 127.8 (4C, CH-Ph), 128.5 (4C, CH-Ph), 131.0 (2C^{quat}), 136.7 (2C^{quat}), 138.5 (2C^{quat}), 143.0 (2C^{quat}).
MALDI MS (PEG 600): found m/z 665.3354 $[M + H]^+$; calculated for $C_{44}H_{45}N_2O_4$ 665.3374.

30,31-Bis(methoxymethoxy)-7,8,9,10,12,13,15,16,18,19,20,21-dodecahydro-6,29:28,22-dimethenodibenzo[*n*,*r*][1,4,7,11,22]trioxadiazacyclopentacosine 5

was synthesized according to general procedure ***A*** from 3,3′-dibromo BINOL **1** (0.25 mmol, 133 mg), trioxadiamine **2d** (0.25 mmol, 55 μL) $Pd(dba)_2$ (24 mg, 16 mol.%), BINAP (28 mg, 18 mol.%), t-BuONa (72 mg, 0.75 mmol) in dry dioxane (12.5 mL, C=0.02M). Eluent 2 % of MeOH in DCM. Yield 20 mg (14%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.81 – 2.24 (m, 4H, CH_2–CH_2–CH_2), 2.88 (s, 6H, O–CH_3), 3.22 – 3.29 (m, 2H, CH_2–NH), 3.33 – 3.74 (m, 8H, CH_2–NH, CH_2–O), 3.73 – 3.90 (m, 6H, CH_2NH, CH_2–O), 4.22 (d, 2H, O–CH_2–OMe, ^2J 5.3 Hz), 4.49 (d, 2H, O–CH_2–OMe, ^2J 5.3 Hz), 5.83 (br. s, 2H, NH), 6.96 (br.s, 2H, $H^{4,4'}$-BINOL), 7.06 (t, 2H, $H^{7,7'}$-BINOL, $^3J_{obs}$ 8.5 Hz), 7.26 – 7.37 (m, 4H, $H^{6,6'}$-BINOL, $H^{8,8'}$-BINOL), 7.70 (d, 2H, $H^{5,5'}$-BINOL, ^3J 8.2 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 27.7 (2C, $CH_2CH_2CH_2$), 45.0 (2C, $NHCH_2$), 56.7 (2C, OCH_3), 70.1 (2C, OCH_2–CH_2), 70.4 (2C, OCH_2–CH_2), 72.5 (2C, OCH_2–CH_2), 98.3 (2C, OCH_2O), 105.0 (br.s, 2C, CH-BINOL), 122.3 (2C, CH-BINOL), 124.4 (2C^{quat}), 125.1 (2C, CH-BINOL), 125.8 (2C, CH-BINOL), 126.1 (2C, CH-BINOL), 127.2 (2C^{quat}), 132.4 (2C^{quat}), 142.2 (2C, C$^{3(3')}$), 144.7 (2C, C$^{2(2')}$).
MALDI MS (PEG 600): found m/z 591.3083 $[M + H]^+$; calculated for $C_{34}H_{43}N_2O_7$ 591.3065.

7,8,9,10,12,13,15,16,18,19,20,21-Dodecahydro-6,29:28,22-dimethenodibenzo[*n*,*r*][1,4,7,11,22]trioxadiazacyclopentacosine-30,31-diol 6

was synthesized according to general procedure ***B*** from compound **5** (0.027 mmol, 16 mg) and concentrated HCl (0.054 mL). Yield 9 mg (66%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.82 – 1.99 (m, 2H, CH_2–CH_2–CH_2), 2.00 – 2.12 (m, 2H, CH_2–CH_2–CH_2), 3.37 – 3.62 (m, 14H, CH_2–NH, CH_2–O), 3.75 – 3.65 (m, 2H, CH_2–NH, CH_2–O), 5.40 (br. s, 4H, NH, OH), 7.00 (s, 2H, $H^{4,4'}$-BINOL), 7.05 (t, 2H, $H^{7,7'}$-BINOL, $^3J_{obs}$ 7.2 Hz), 7.15 (d, 2H, $H^{8,8'}$-BINOL, ^3J 8.2 Hz), 7.29 (t, 2H, $H^{6,6'}$-BINOL, $^3J_{obs}$ 7.5 Hz), 7.71 (d, 2H, $H^{5,5'}$-BINOL, ^3J 8.2 Hz).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 27.4 (2C, $CH_2CH_2CH_2$), 44.3 (2C, $NHCH_2$), 69.7 (2C, OCH_2–CH_2), 70.4 (2C, OCH_2–CH_2), 72.0 (2C, OCH_2–CH_2), 106.0 (2C, CH-BINOL), 111.3 (2C^{quat}), 122.8 (2C, CH-BINOL), 124.3 (2C, CH-BINOL), 124.7 (2C, CH-BINOL), 125.8 (2C, CH-BINOL), 126.4 (2C^{quat}), 131.0 (2C^{quat}), 138.2 (2C, C$^{3(3')}$), 143.3 (2C, C$^{2(2')}$).
MALDI MS (PEG 600): found m/z 503.2566 $[M + H]^+$; calculated for $C_{30}H_{35}N_2O_5$ 503.2541.

3,3′-Bis[(2-hydroxycyclopentyl)amino][1,1′-binaphthalene]-2,2′-diol (compound **7**):

Compound **4c** (0,08 mmol, 55 mg), 10% Pd-C catalyst (55 mg) and MeOH (2.5 ml, 0.03M) were placed into two-necked flask equipped with a magnetic stirrer bar, a reflux condenser and a capillary tube almost reaching the bottom of the flask. The mixture was heated at 60°C and hydrogen flow was constantly bubbled through capillary tube for 2 hours. After the completion of the reaction, the catalyst was filtered off and solvent was evaporated to give the target product as light yellow viscous oil (40 mg, 99%).

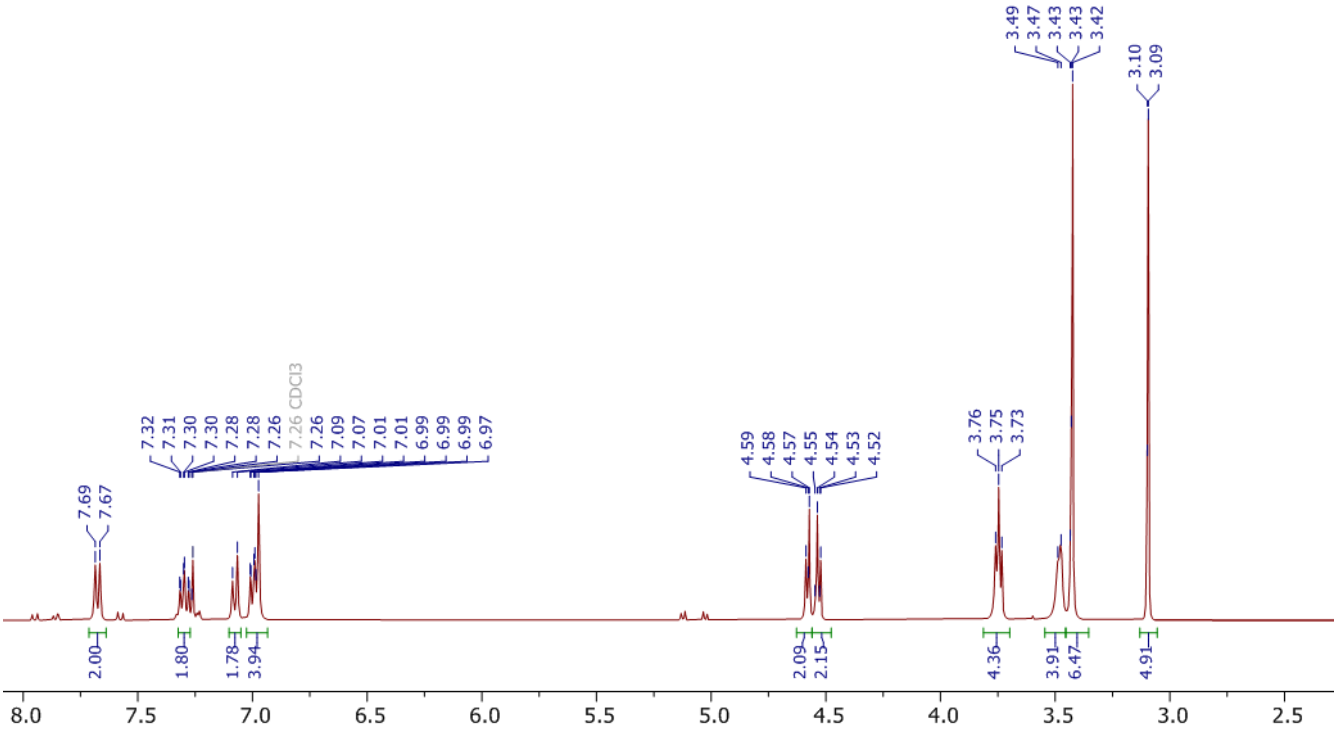
^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.42 – 1.56 (m, 2H, CH_2), 1.59 – 1.69 (m, 2H, CH_2), 1.69 – 1.78 (m, 2H, CH_2), 1.78 – 1.90 (m, 2H, CH_2), 1.90 – 2.05 (m, 2H, CH_2), 2.27 – 2.43 (m, 2H, CH_2), 3.59 – 3.77 (m, 2H, CH–NH), 4.06 – 4.21 (m, 2H, CH–O), 6.90 – 7.02 (m, 4H, $H^{7,7'}$-BINOL, $H^{8,8'}$-BINOL), 7.07 (s, 2H, $H^{4,4'}$-BINOL), 7.18 – 7.25 (m, 2H, $H^{6,6'}$-BINOL), 7.68 (d, 2H, $H^{5,5'}$-BINOL, ^3J 8.1 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 21.1 (2C, CH_2–CH_2–CH_2), 30.9 (2C, CH–CH_2), 32.7 (2C, CH–CH_2), 61.5 (2C, CHNH), 77.5 (2C, CHO), 105.5 (2C, CH-BINOL), 111.4 (2C^{quat}), 122.8 (2C, CH-BINOL), 124.1 (4C, CH-BINOL), 125.8 (2C, CH-BINOL), 126.4 (2C^{quat}), 130.5 (2C^{quat}), 137.2 (2C, C$^{3(3')}$), 143.3 (2C, C$^{2(2')}$).
MALDI MS (PEG 400): found m/z 485.2449 $[M + H]^+$; calculated for $C_{30}H_{33}N_2O_4$ 485.2435.

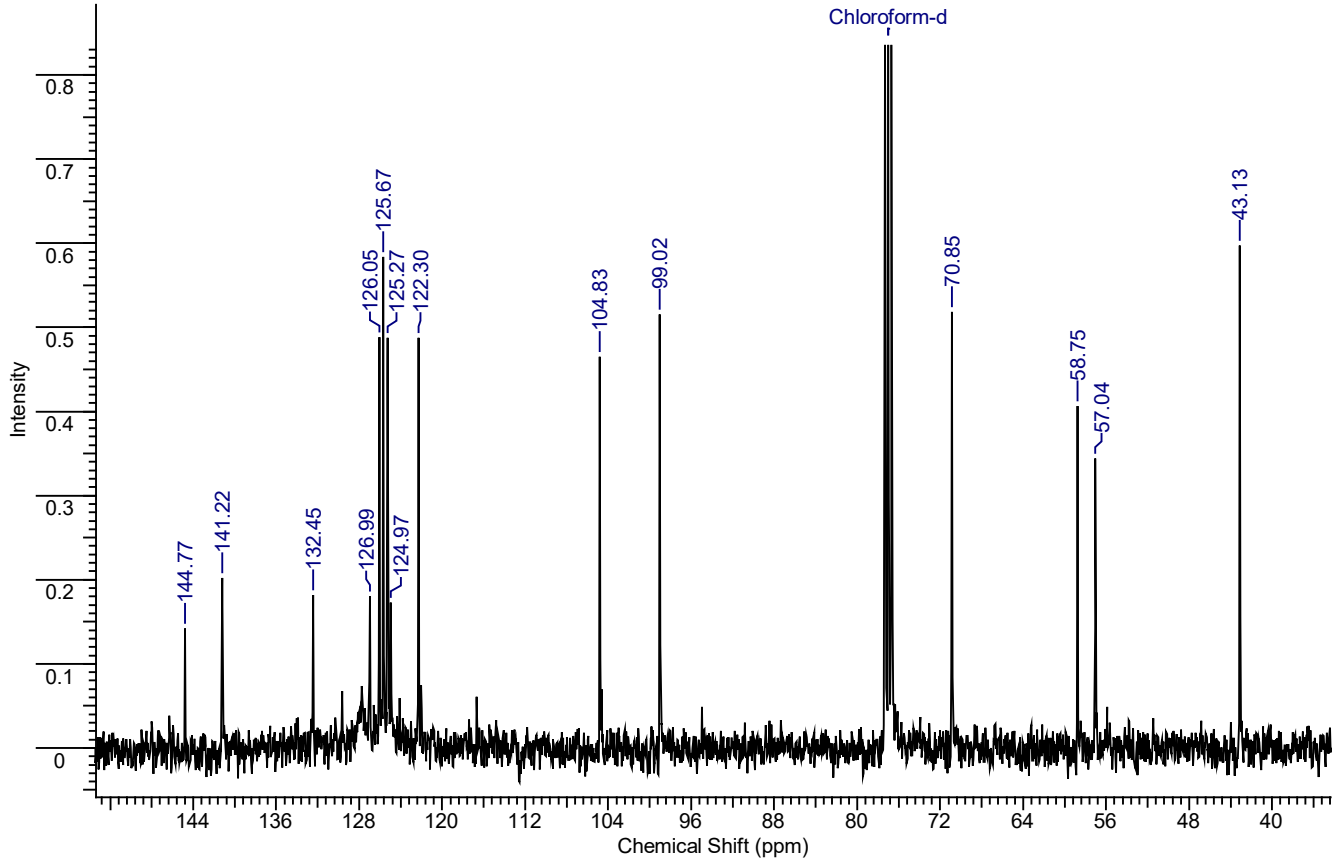
Procedure for the spectrophotometric and fluorescence detection of metal cations. Solutions of compounds **4b,c, 5, 6, 7** in UHPLC grade acetonitrile were placed in spectrofluorimetric cuvette and UV and fluorescence spectra were registered. Then an acetonitrile solution of a metal perchlorate (Li^I, Na^I, Mg^{II}, Ca^{II}, Ba^{II}, Al^{III}, Mn^{II}, Fe^{II}, Cr^{III}, Ni^{II}, Co^{II}, Cu^{II}, Zn^{II}, Cd^{II}, Pb^{II}, Ag^I, Hg^{II}) or nitrate (Ga^{III}, In^{III}, Y^{III}) or acetate (K^I) (C = 0.01 M) was added stepwise (to make 1, 2, 5, and 10 equiv.) and UV and fluorescence spectra were registered after each addition.

Experimental spectra

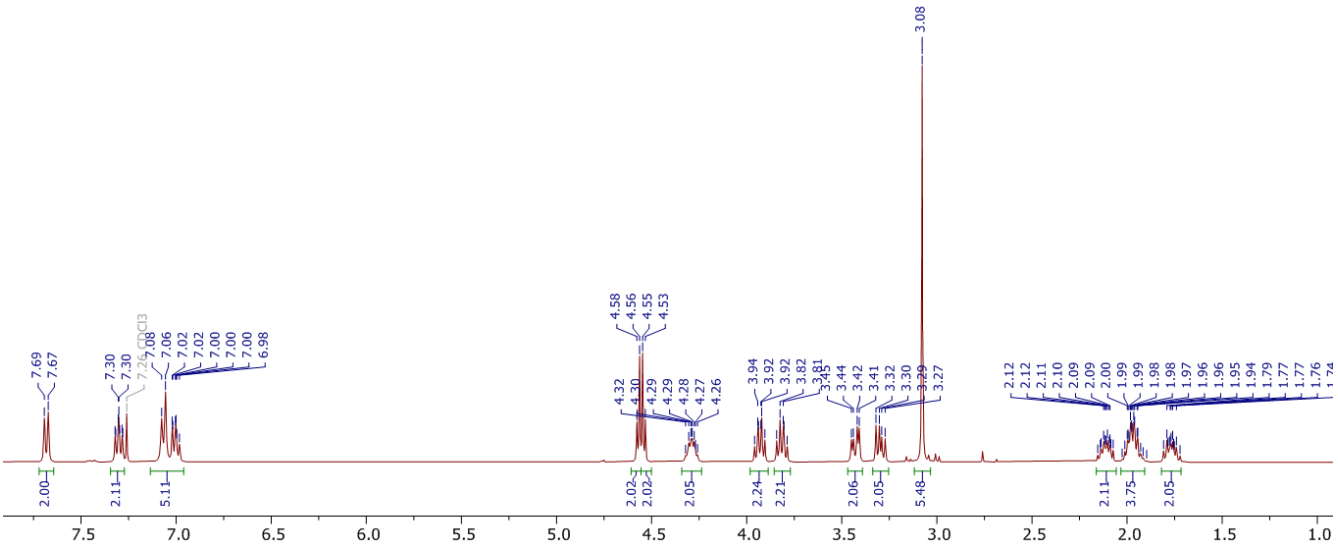
Compound **3a**, ^{1}H NMR (400 MHz, $CDCl_3$)



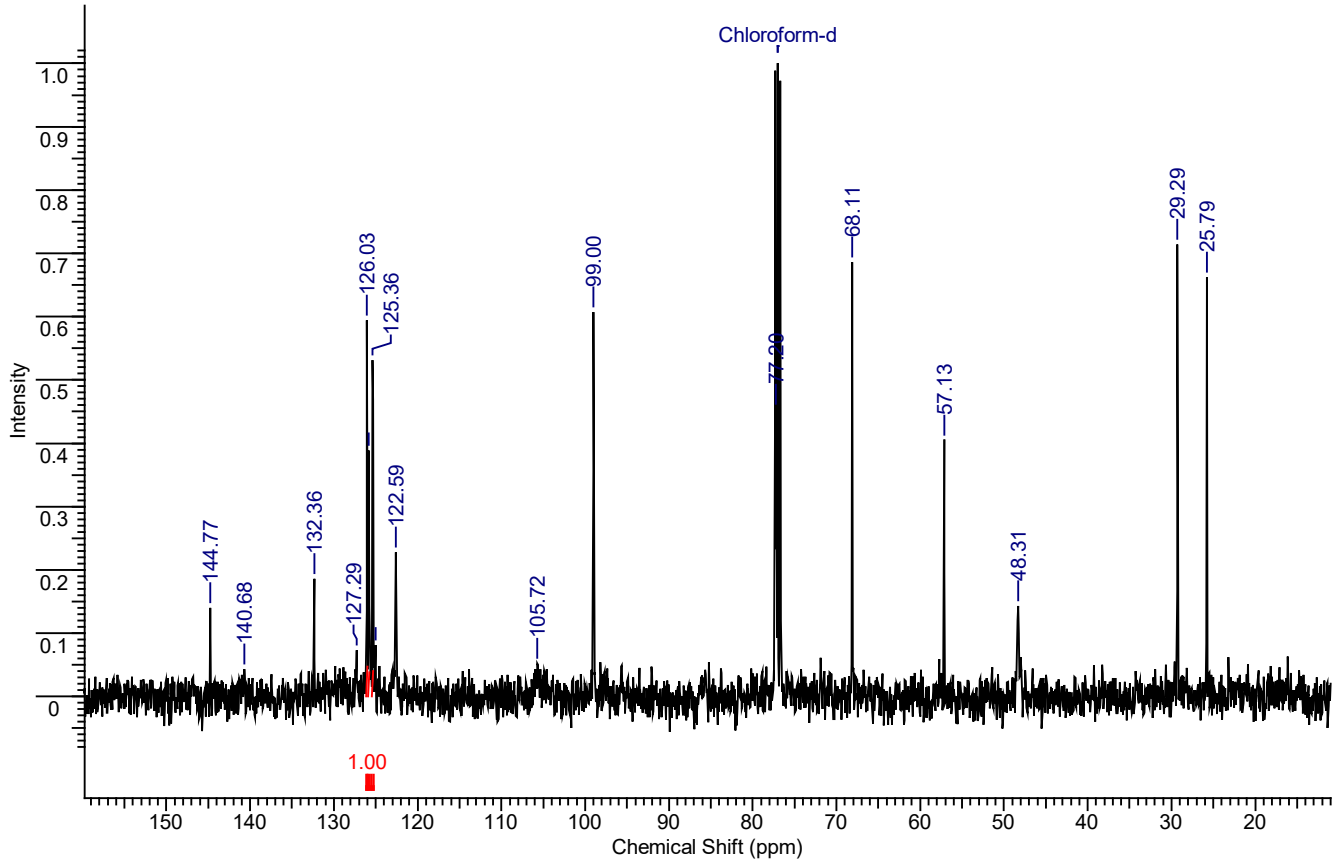
Compound **3a**, ^{13}C NMR (101 MHz, $CDCl_3$)



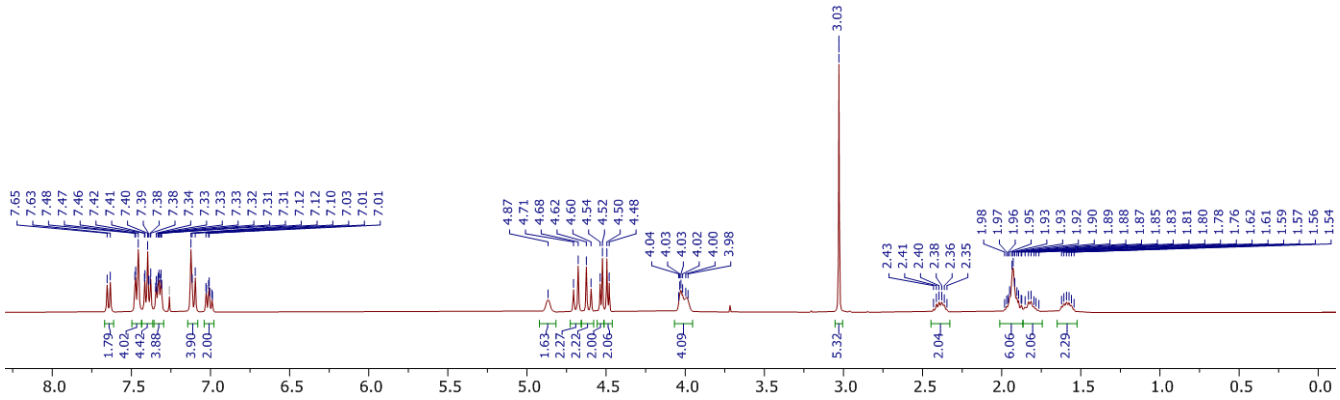
Compound **3b**, ^{1}H NMR (400 MHz, $CDCl_3$)



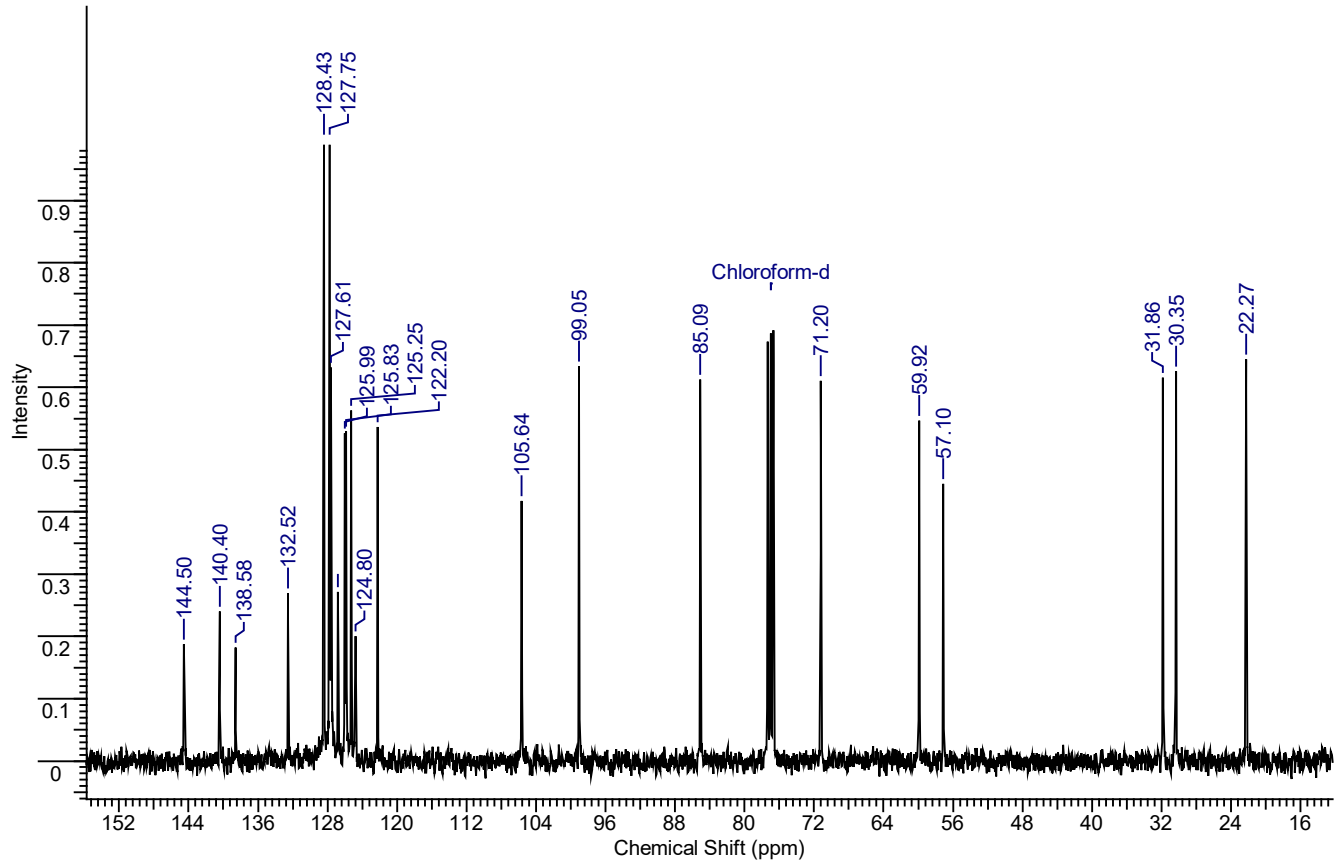
Compound **3b**, ^{13}C NMR (101 MHz, $CDCl_3$)



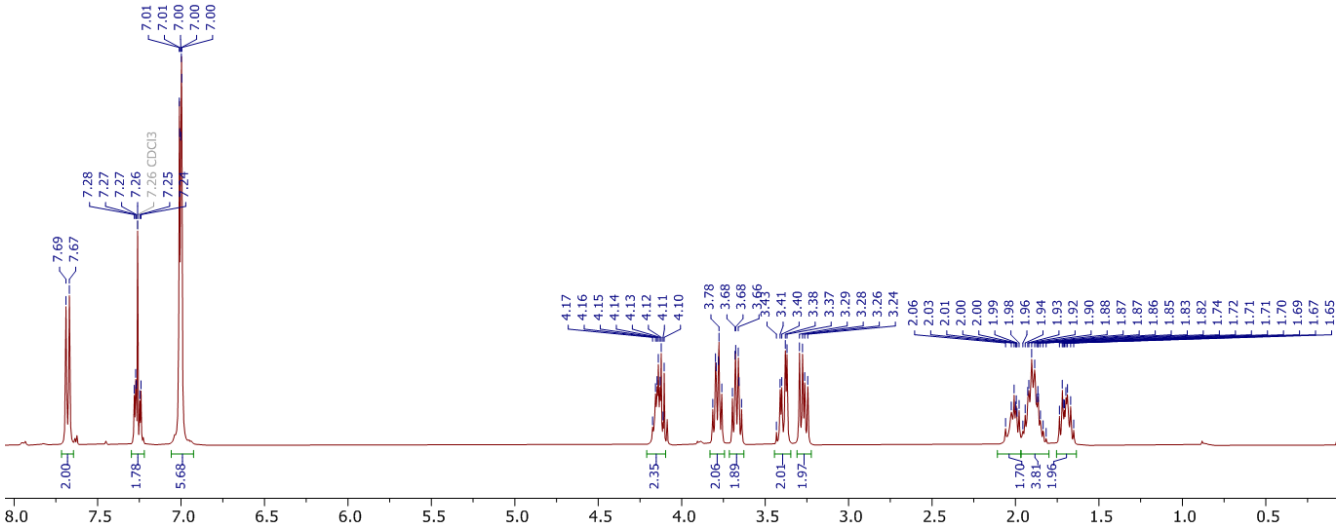
Compound **3c**, ^{1}H NMR (400 MHz, $CDCl_3$)



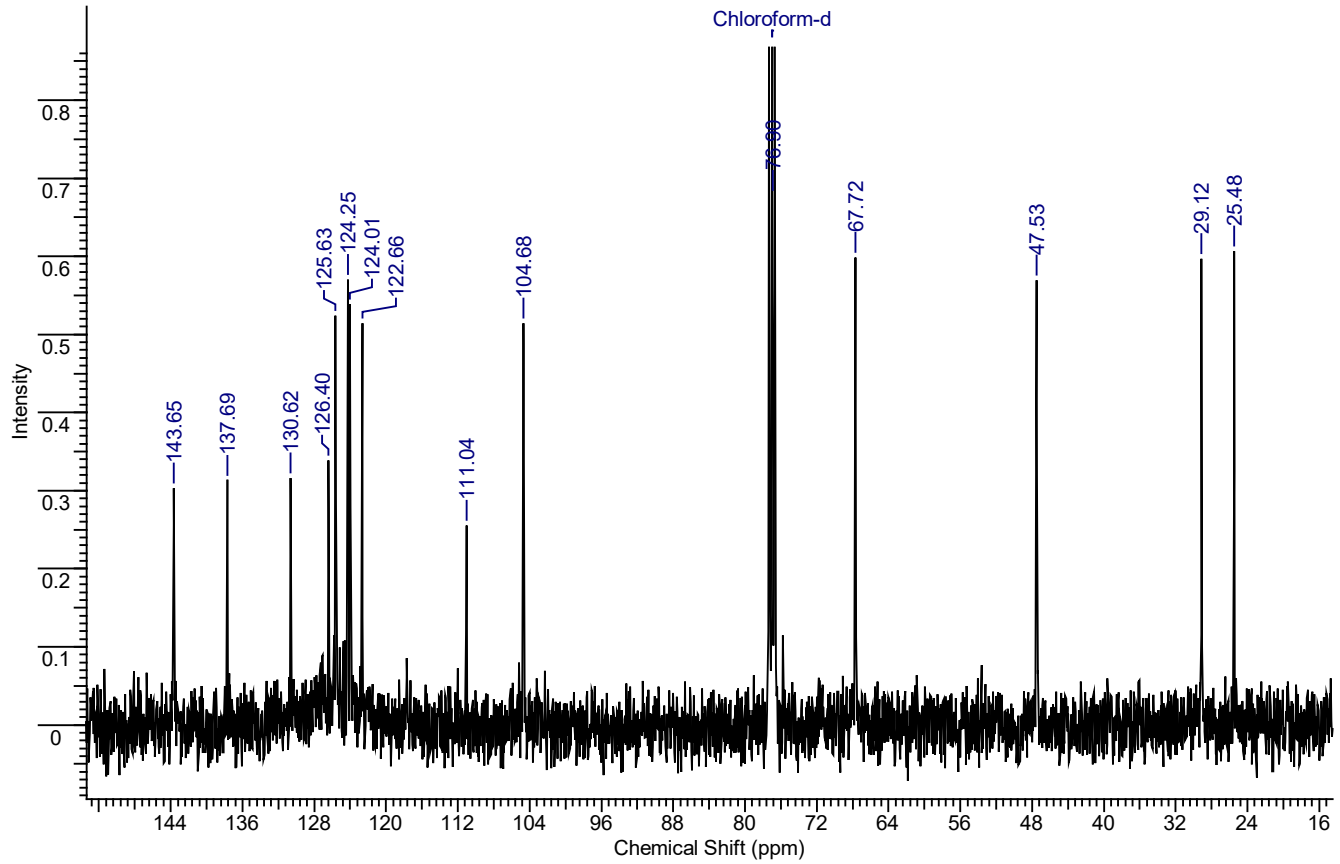
Compound **3c**, ^{13}C NMR (101 MHz, $CDCl_3$)



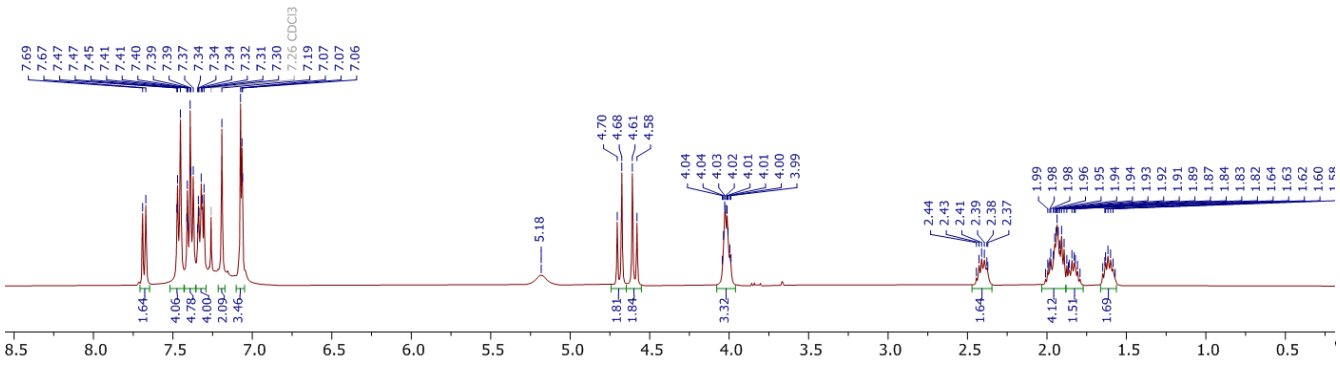
Compound **4b**, ^{1}H NMR (400 MHz, $CDCl_3$)



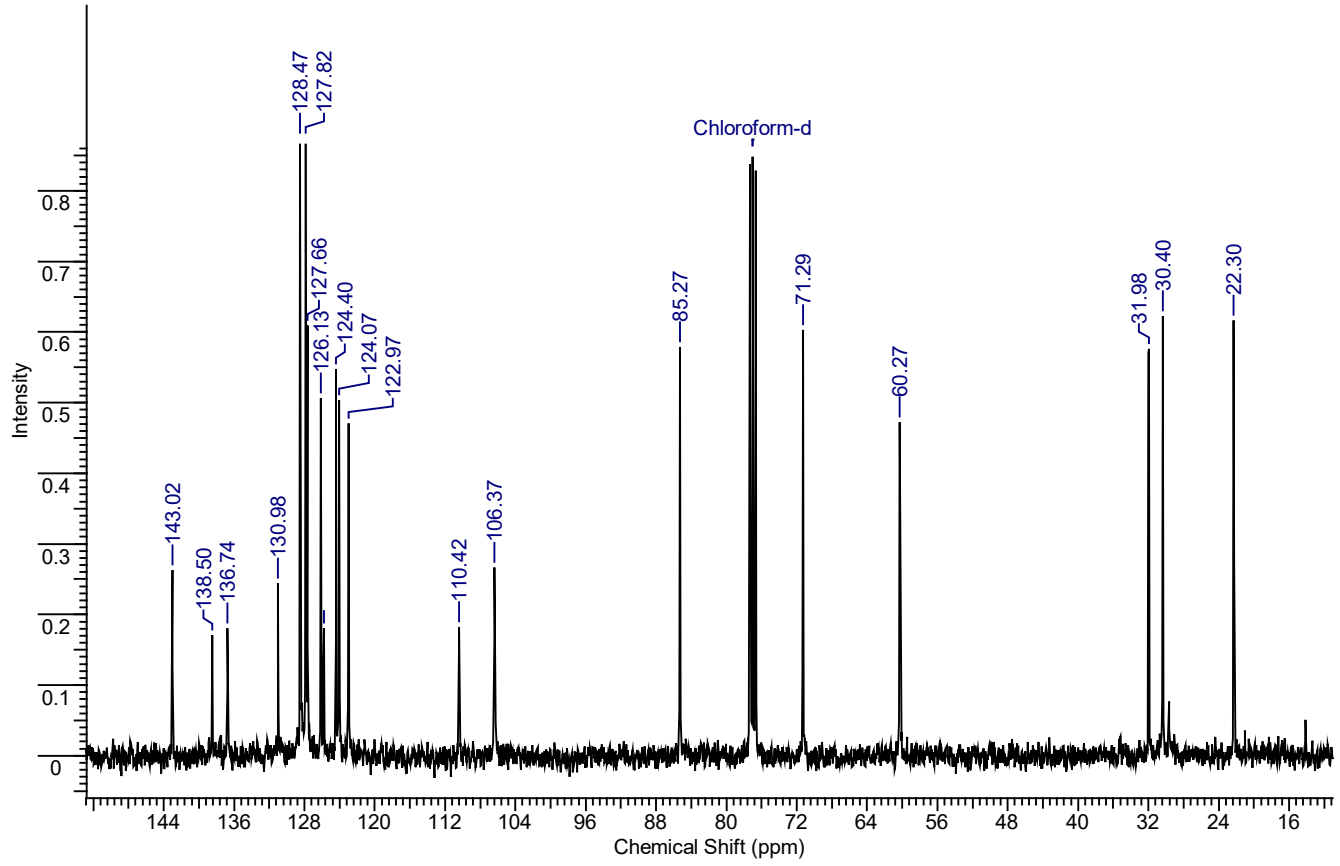
Compound **4b**, ^{13}C NMR (101 MHz, $CDCl_3$)



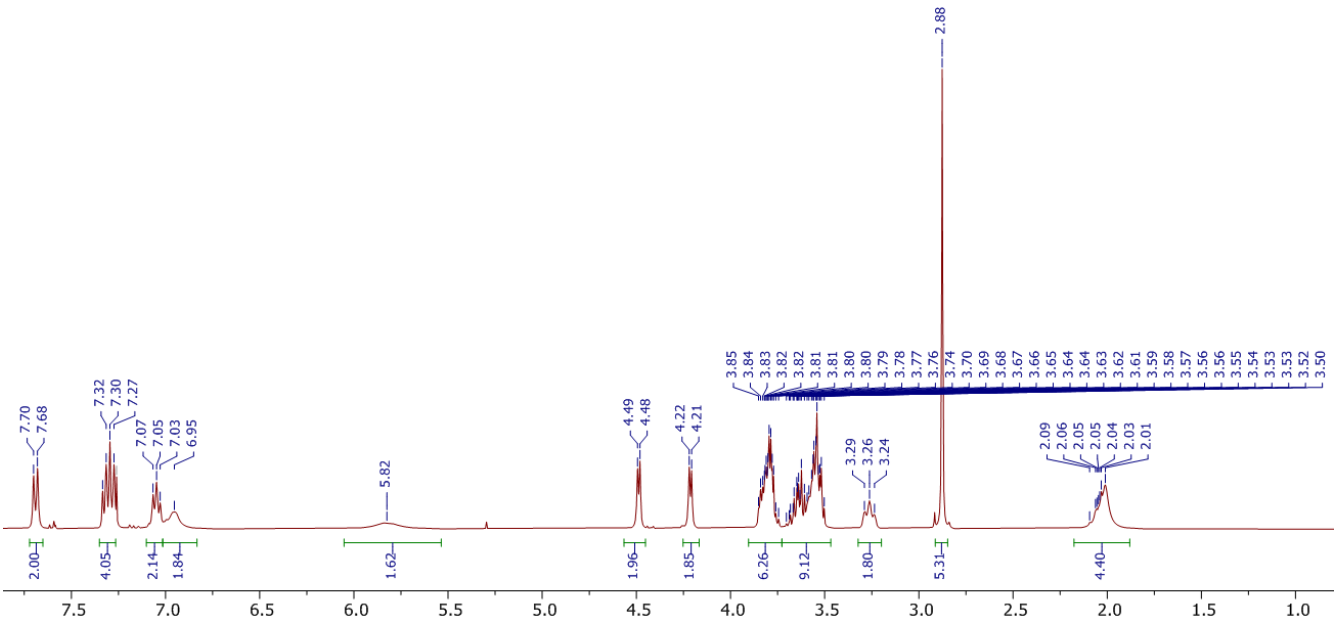
Compound **4c**, ^{1}H NMR (400 MHz, $CDCl_3$)



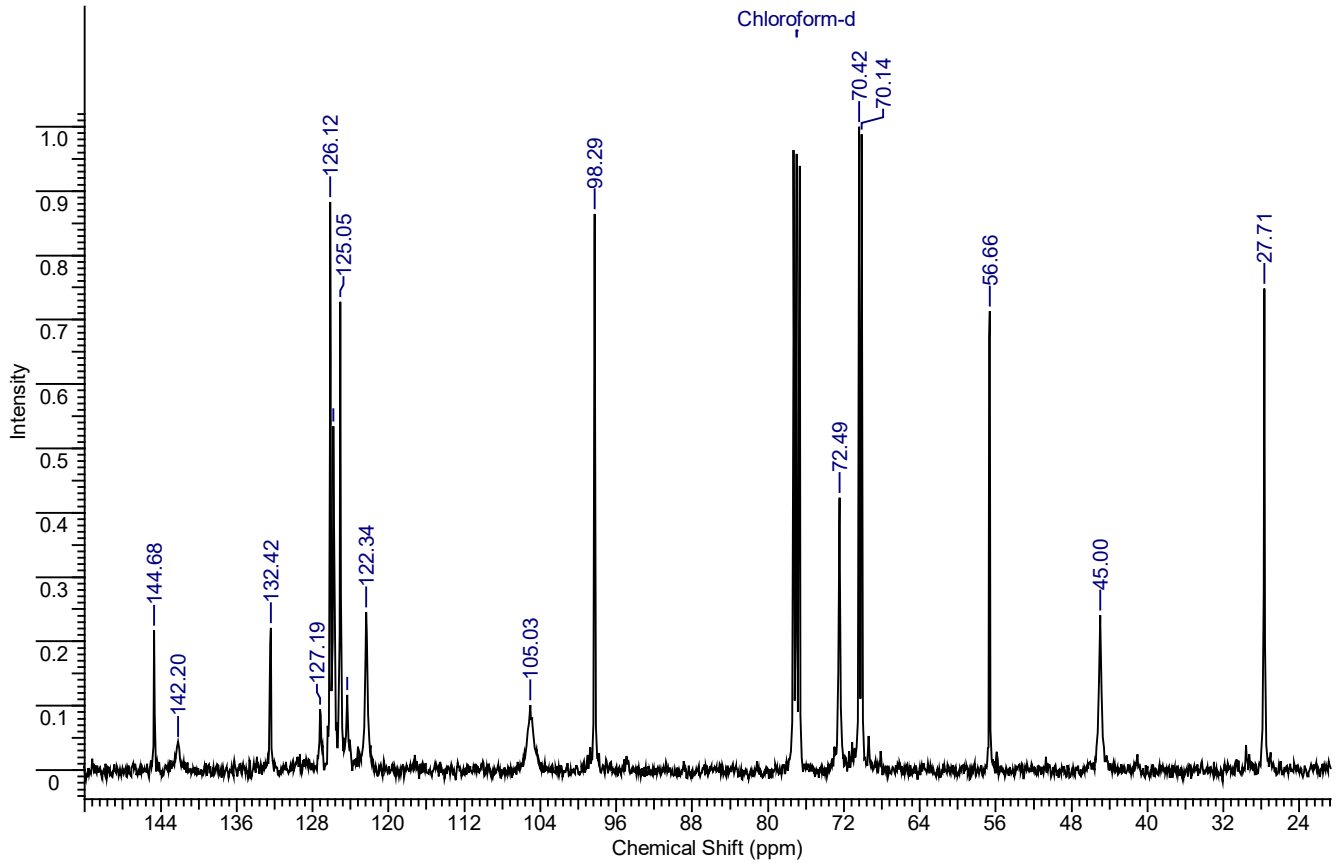
Compound **4c**, ^{13}C NMR (101 MHz, $CDCl_3$)



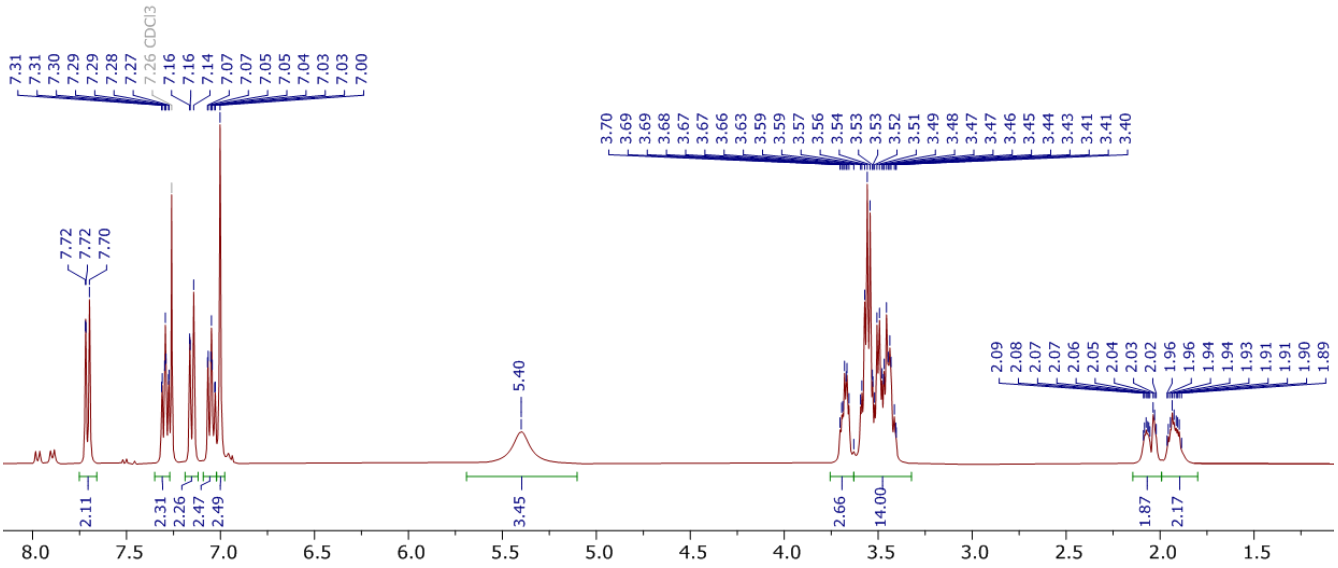
Compound **5**, ^{1}H NMR (400 MHz, $CDCl_3$)



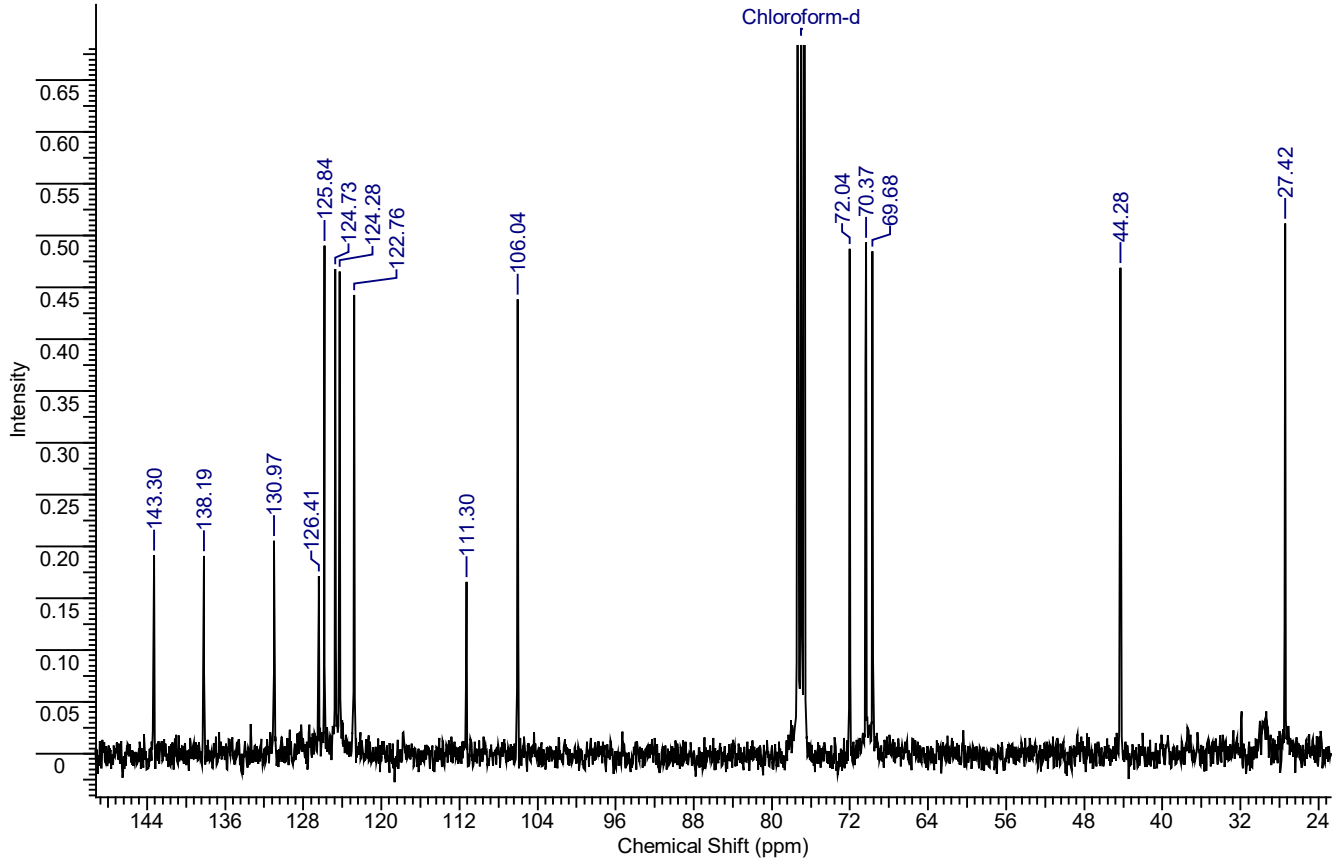
Compound **5**, ^{13}C NMR (101 MHz, $CDCl_3$)



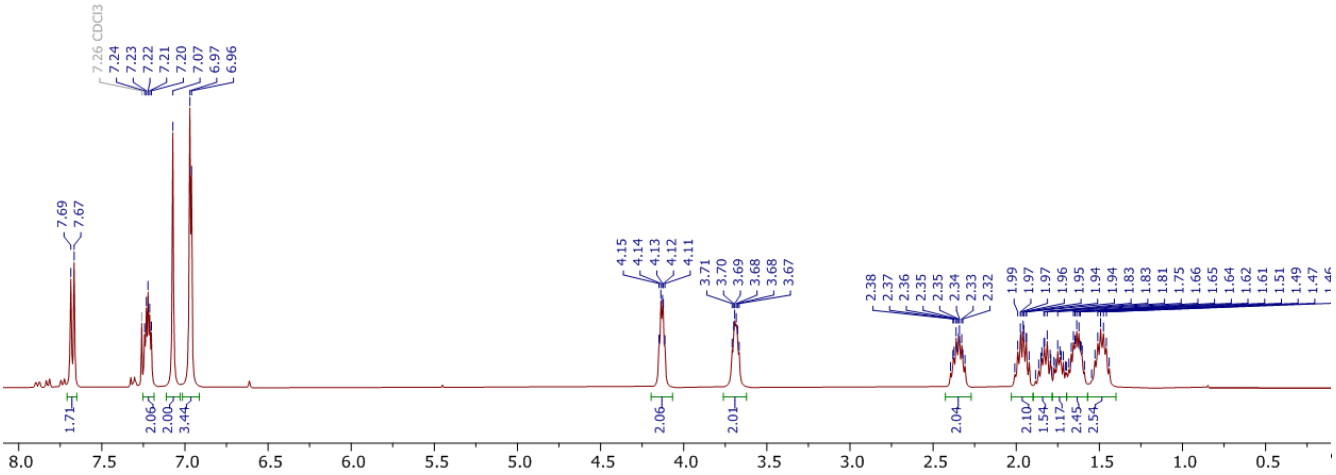
Compound **6**, ^{1}H NMR (400 MHz, $CDCl_3$)



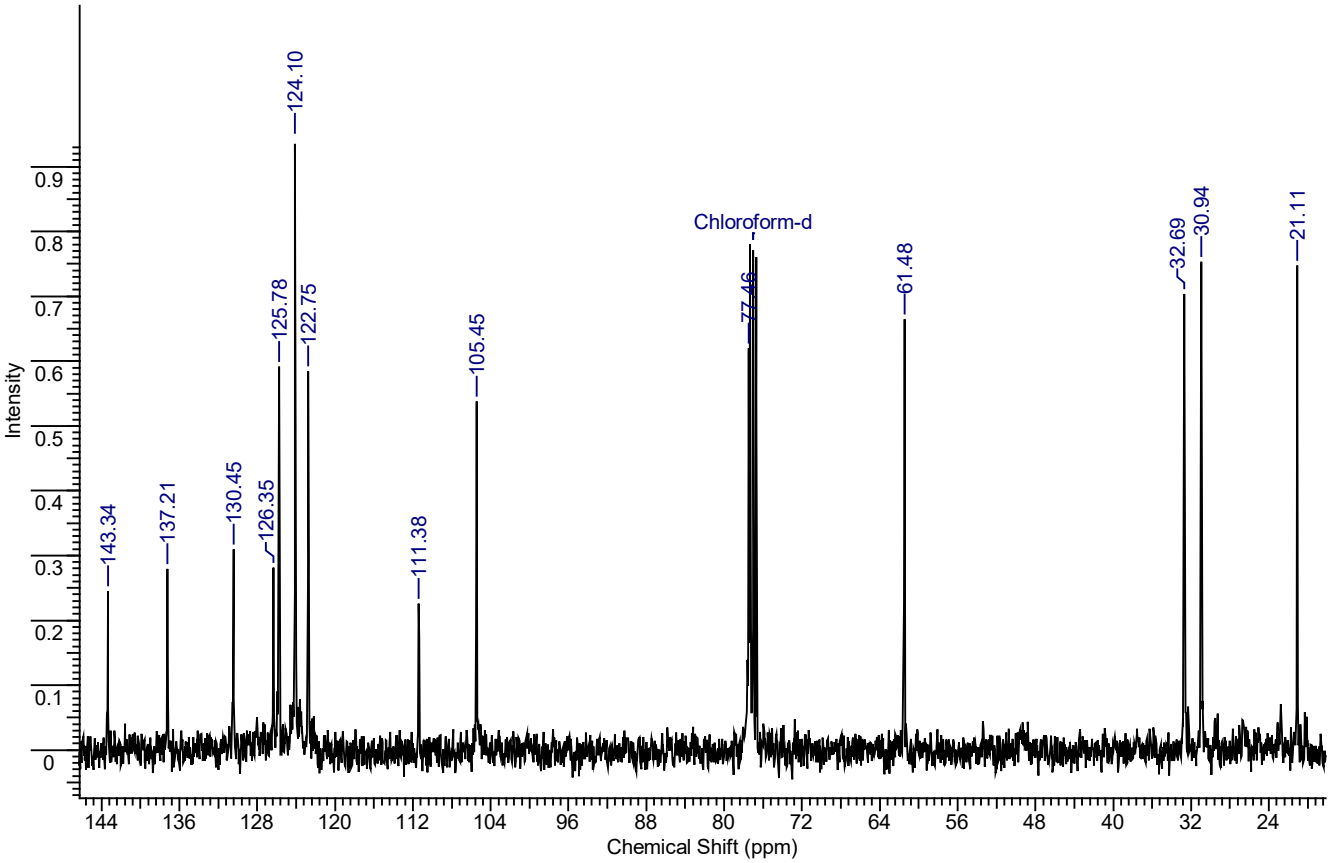
Compound **6**, ^{13}C NMR (101 MHz, $CDCl_3$)



Compound **7**, ^{1}H NMR (400 MHz, $CDCl_3$)

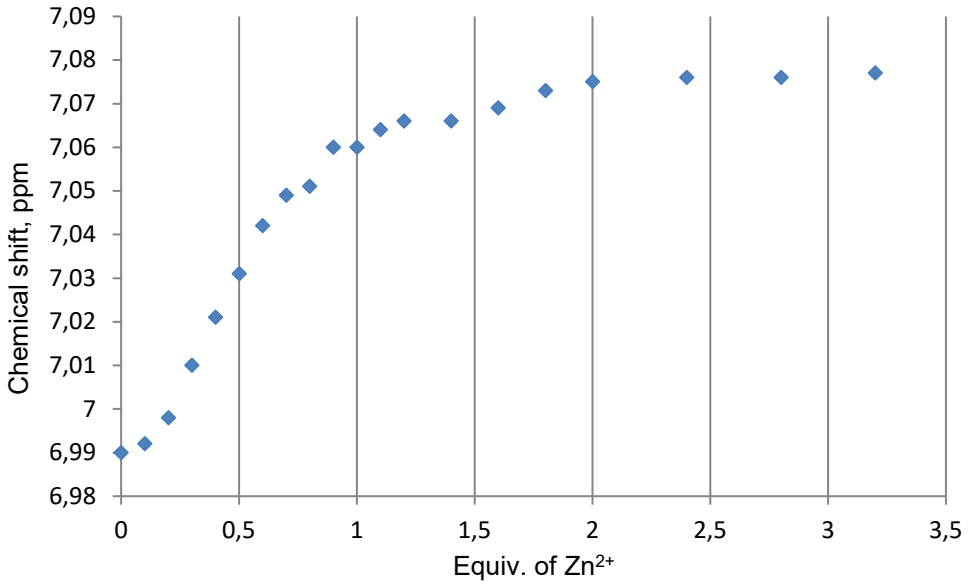


Compound **7**, ^{13}C NMR (101 MHz, $CDCl_3$)

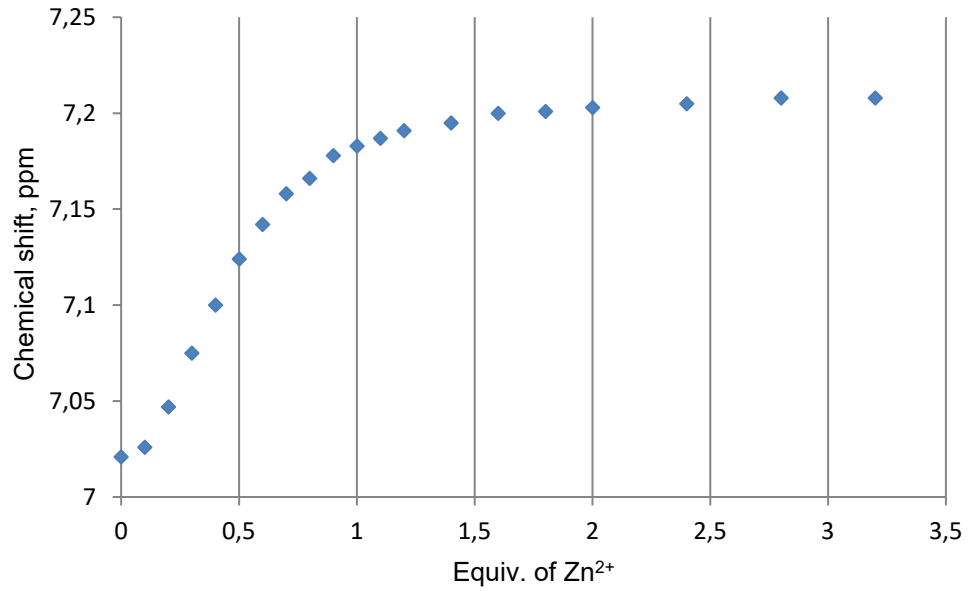


NMR-titration of compound **6** with $Zn(ClO_4)_2*6H_2O$ ($CD_3CN/CDCl_3$, $C_L=1.99*10^{-2}$M, increment 0.1-0.4 equiv., range 0-3.2 equiv. Zn^{II}).

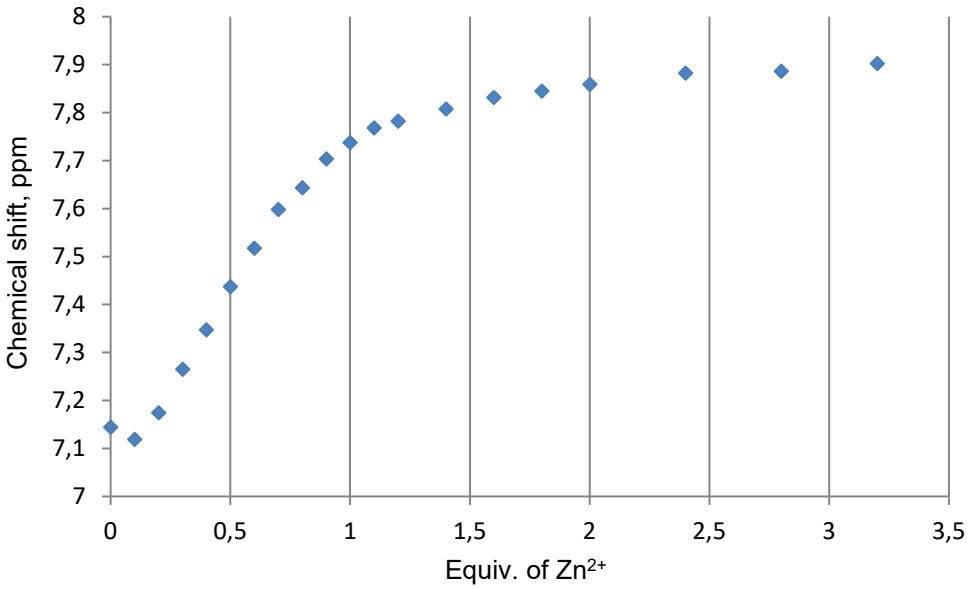
Chemical shift of protons H4, H4' (BINOL) *vs* equiv. of Zn^{2+}



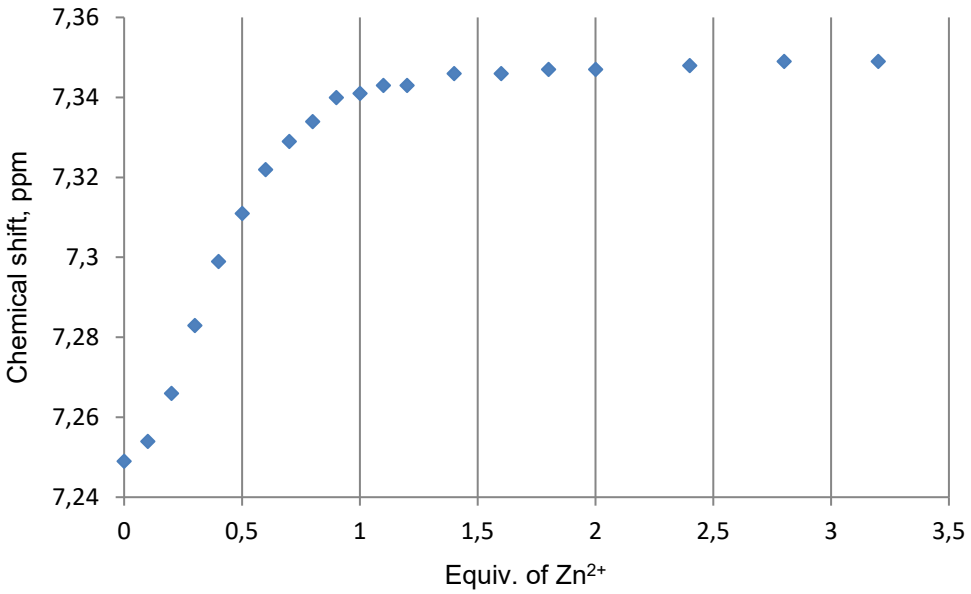
Chemical shift of protons H7, H7' (BINOL) *vs* equiv. of Zn^{2+}



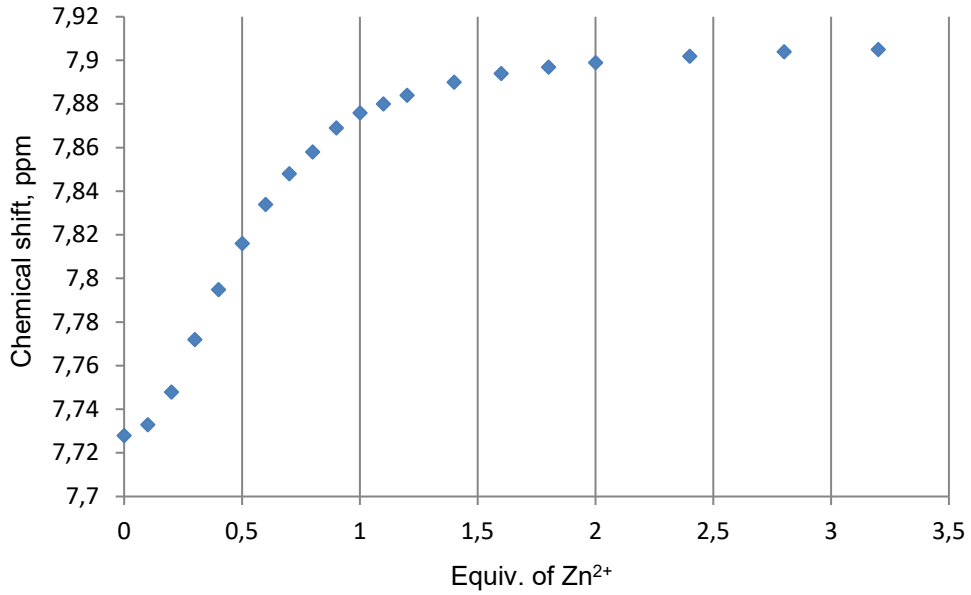
Chemical shift of protons H8, H8’ (BINOL) *vs* equiv. of Zn^{2+}



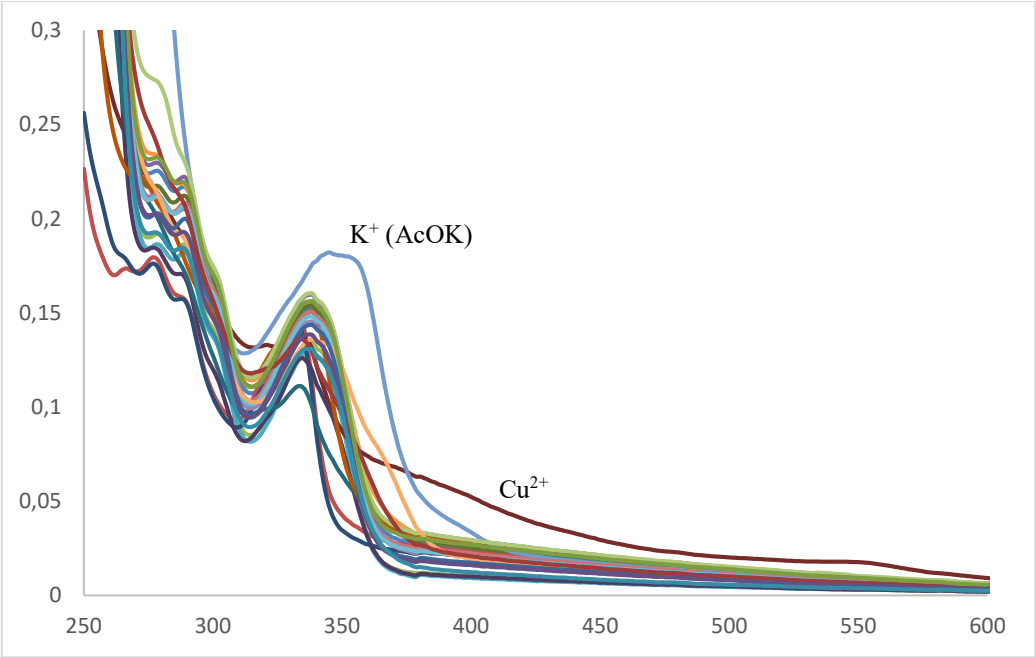
Chemical shift of protons H6, H6’ (BINOL) *vs* equiv. of Zn^{2+}



Chemical shift of protons H5, H5' (BINOL) *vs* equiv. of Zn^{2+}

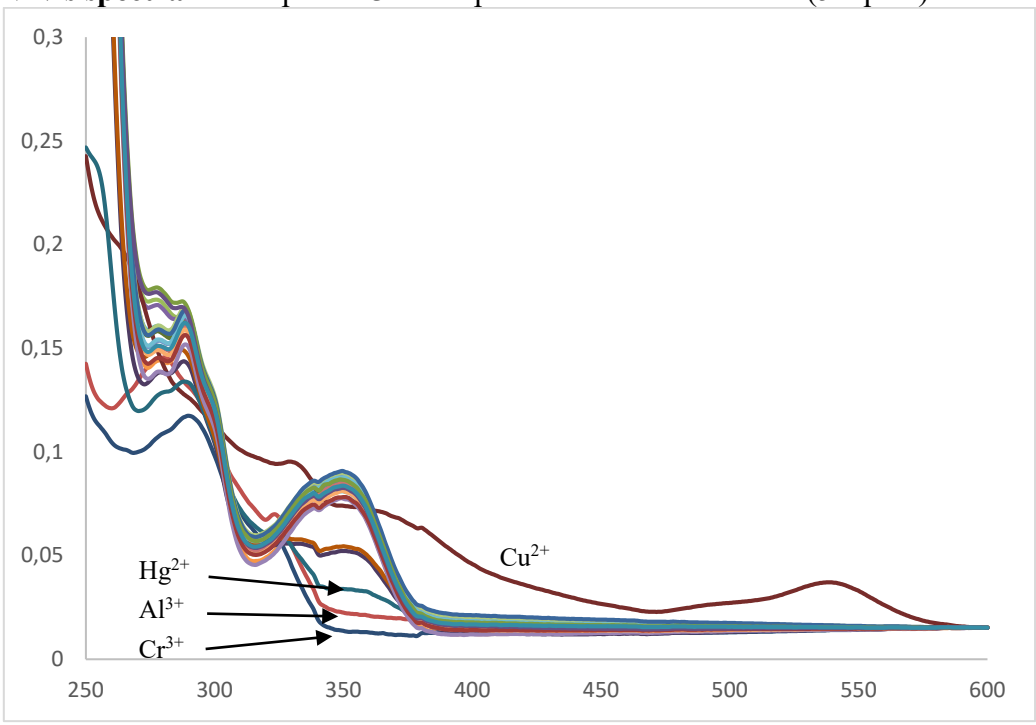


UV-vis spectra of compound **4b** in the presence of metal cations (5 equiv.) in MeCN



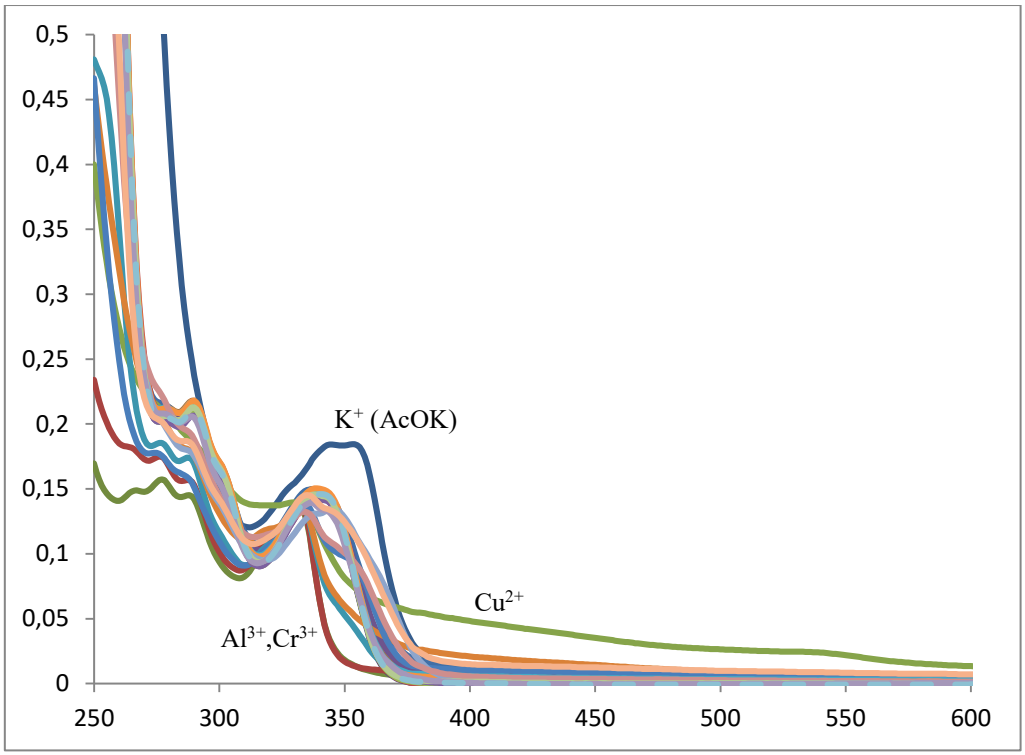
The addition of Cu^{II} cations leads to an increase of absorbance in 350-450 nm region without notable maximum. Other cations do not notably affect the absorbance spectrum.

UV-vis spectra of compound **5** in the presence of metal cations (5 equiv.) in MeCN



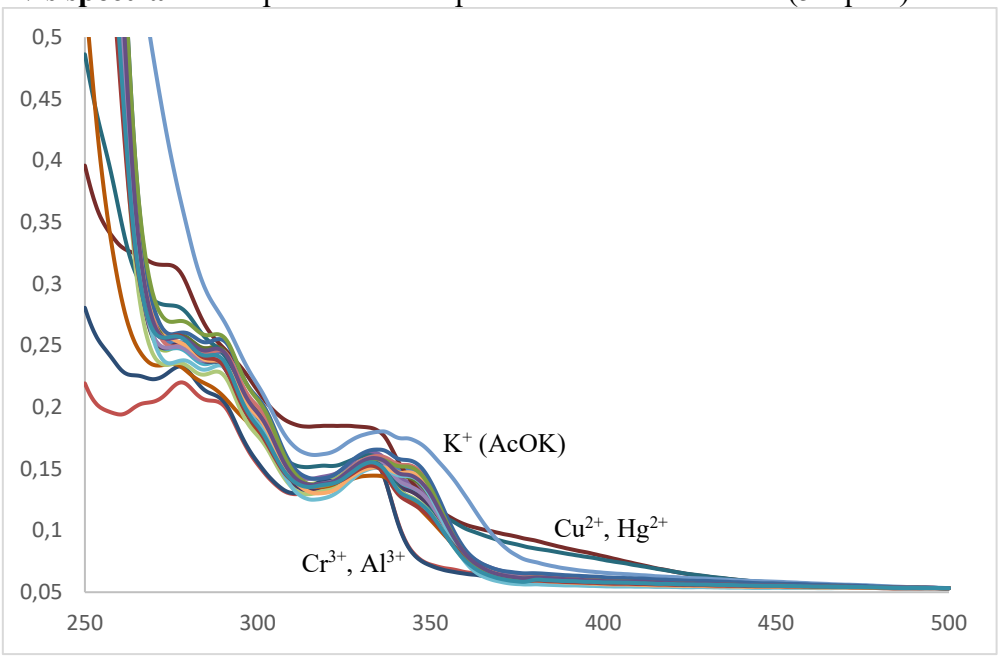
The addition of Cu^{II} cations leads to an increase of absorbance in 350-450 nm region without notable maximum and formation of a new maximum at 540 nm. In the presence of Al^{III}, Cr^{III} and Hg^{II} maximum at 350 nm fully disappears while the addition of In^{III} and Ga^{III} leads to partial decrease of the maximum intensity.

UV-vis spectra of compound **6** in the presence of metal cations (5 equiv.) in MeCN



The addition of Cu^{II} cations leads to an increase of absorbance in 350-450 nm region without notable maximum. In the presence of Al^{III} and Cr^{III} the peak at 340 nm is sharpened.

UV-vis spectra of compound **7** in the presence of metal cations (5 equiv.) in MeCN



The addition of Cu^{II} and Hg^{II} cations leads to an increase of absorbance in 350-450 nm region without notable maximum. Additionally, in the case of Cu^{II} absorbance in 310-340 nm region increases. In the presence of Al^{III} and Cr^{III} the peak at 350 nm is sharpened.