SUPPORTING INFORMATION:

A Practical Approach to Structurally Diverse Monoimine Salts and Nonsymmetrical Metallosalphen Complexes

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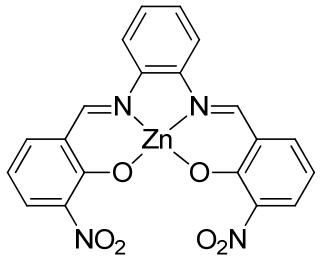
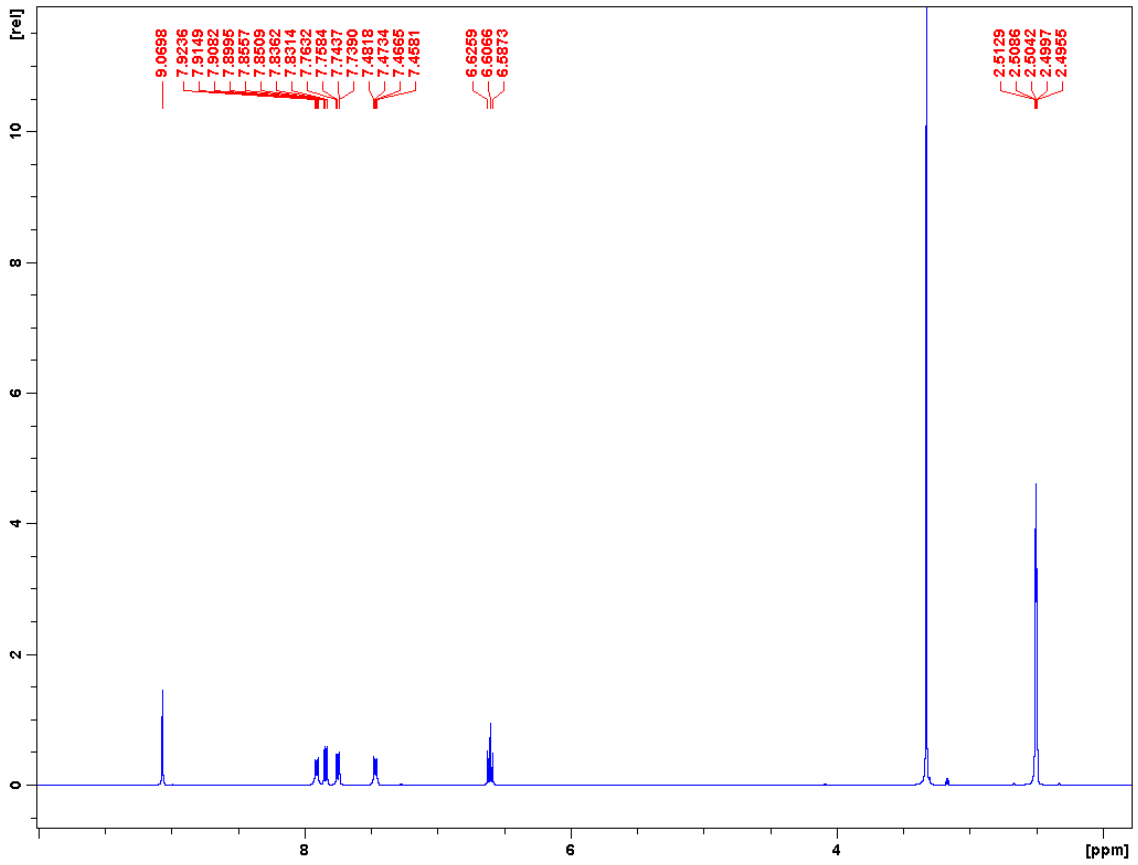
Contents:

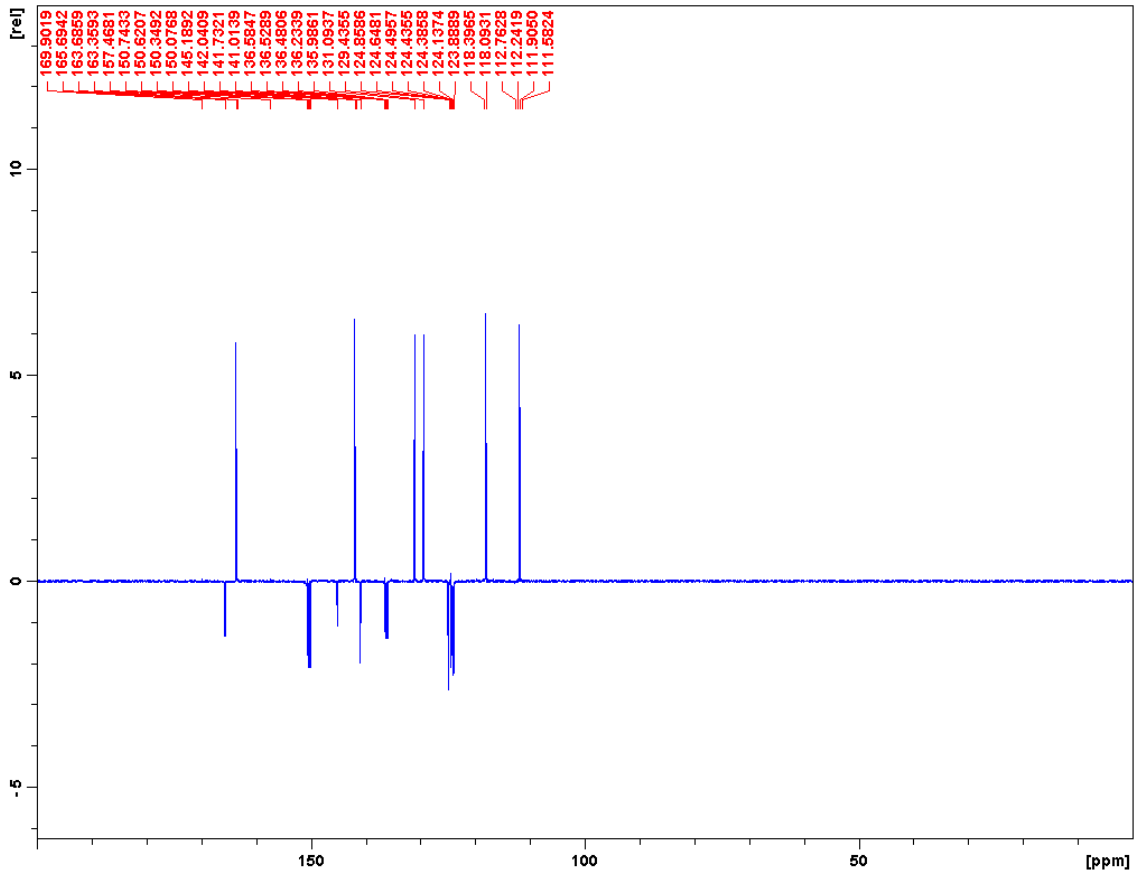
Synthesis of Zn(salphen) complexes **1a-12a**



1a

To a solution of 1,2-phenylenediamine (0.48 g, 4.44 mmol) and 3-nitro-salicylaldehyde (1.40 mg, 8.38 mmol) in MeOH (100 mL) was added solid $Zn(OAc)_2 \cdot 2H_2O$ (1.18 g, 5.38 mmol) in MeOH . The reaction mixture was stirred for 18 h and filtered to yield the product as a yellow solid (1.95 g, 4.15 mmol, 93%). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.07 (s, 2H, CH=N), 7.90-7.92 (m, 2H, ArH), 7.84 (d, ^3J = 7.8 Hz, ^4J = 1.9 Hz, 2H, ArH), 7.75 (d, ^3J = 7.8 Hz, ^4J = 1.9 Hz, 2H, ArH), 7.46-7.48 (m, 2H, ArH), 6.61 (t, ^3J = 7.7 Hz, 2H, ArH). ^{13}C {^{1}H} NMR (100 MHz, pyridine-d_5): δ = 165.69, 163.69, 145.19, 142.04, 141.01, 131.09, 129.44, 124.86, 118.09, 111.91. MS (MALDI+, dctb): *m/z* = 468.0 $(M)^+$ (calcd. 468.0), 938.1 $(2M)^+$ (calcd. 938.1). Anal. calcd. for $C_{20}H_{12}N_4O_6Zn \cdot 2H_2O$: C 47.50, H 3.19, N 11.08; Found: C 47.39, H 3.02, N 10.76.

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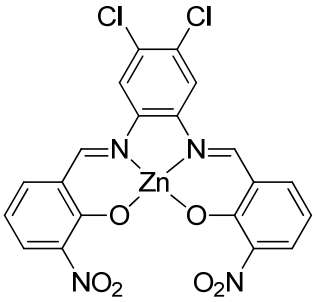
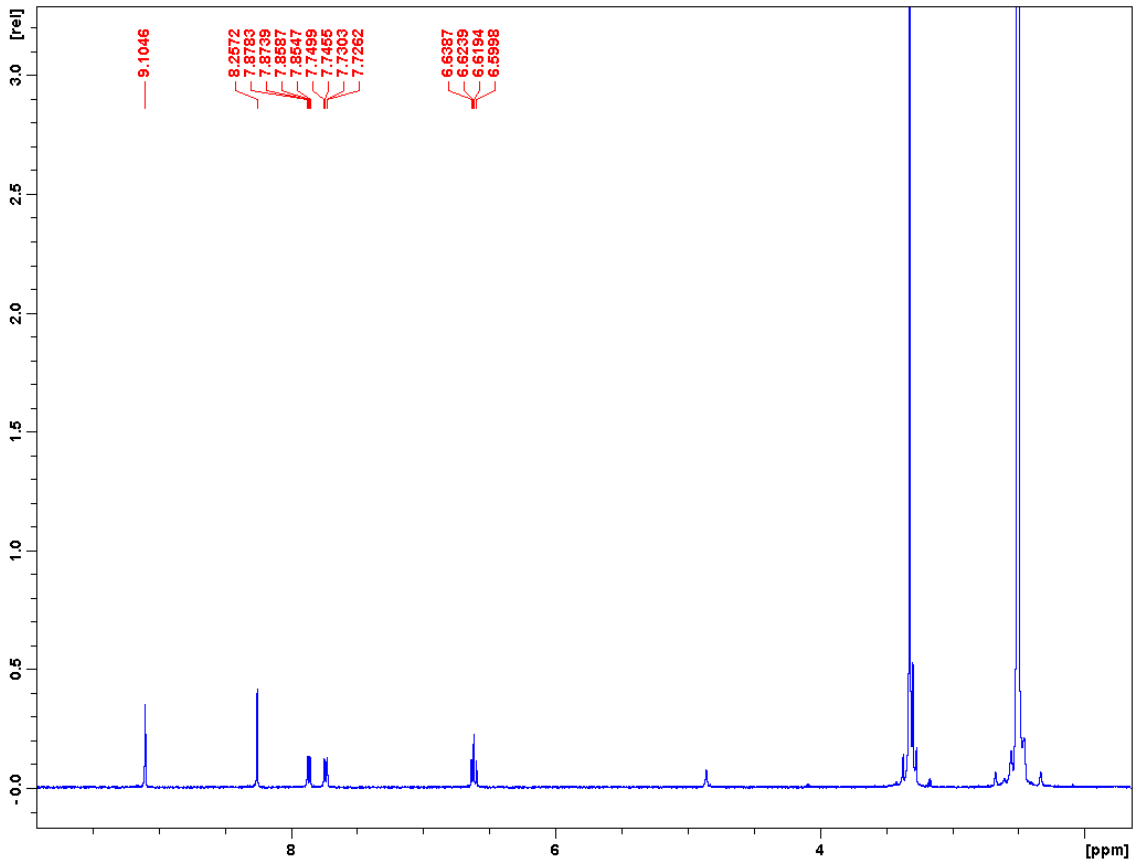
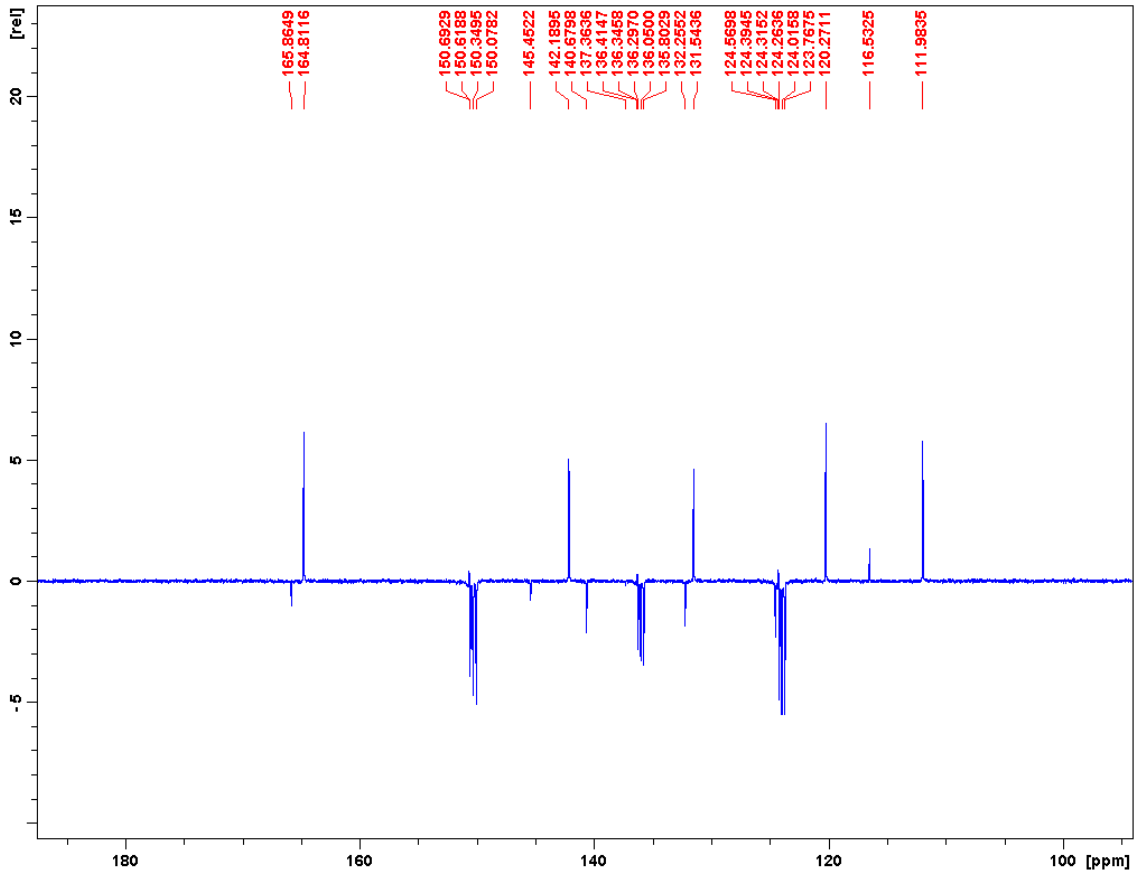


2a

To a solution of 4,5-dichloro-1,2-phenylenediamine (0.24 g, 1.35 mmol) and $Zn(OAc)_2 \cdot 2H_2O$ (0.41 g, 1.87 mmol) in MeOH (40 mL) was added 3-nitro-salicylaldehyde (0.52 g, 3.11 mmol). The reaction mixture was filtered after 1 h yielding a yellow solid (659.9 mg, 1.23 mmol, 91%). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.10 (s, 2H, CH=N), 8.26 (s, 2H, ArH), 7.86 (d, ^3J = 7.8 Hz, ^4J = 1.8 Hz, 2H, ArH), 7.74 (d, ^3J = 7.8 Hz, ^4J = 1.8 Hz, 2H, ArH), 6.62 (t, ^3J = 7.8 Hz, 2H, ArH). ^{13}C {^{1}H} NMR (100 MHz, pyridine-d_5): δ = 165.86, 164.81, 145.45, 142.19, 140.68, 132.26, 131.54, 124.57, 120.27, 116.53, 111.98. MS (MALDI+, dctb): *m/z* = 538.0 $(M+H)^+$ (calcd. 537.9), 1076.0 $(2M)^+$ (calcd 1075.8). Anal. calcd. for $C_{20}H_{10}Cl_2N_4O_6Zn \cdot H_2O$: C 43.16, H 2.17, N 10.07; Found: C 42.97, H 2.16, N 10.35.

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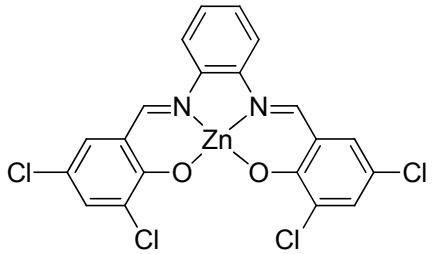
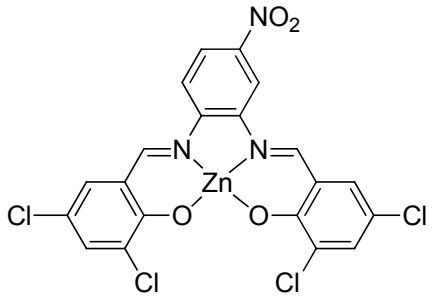


3a

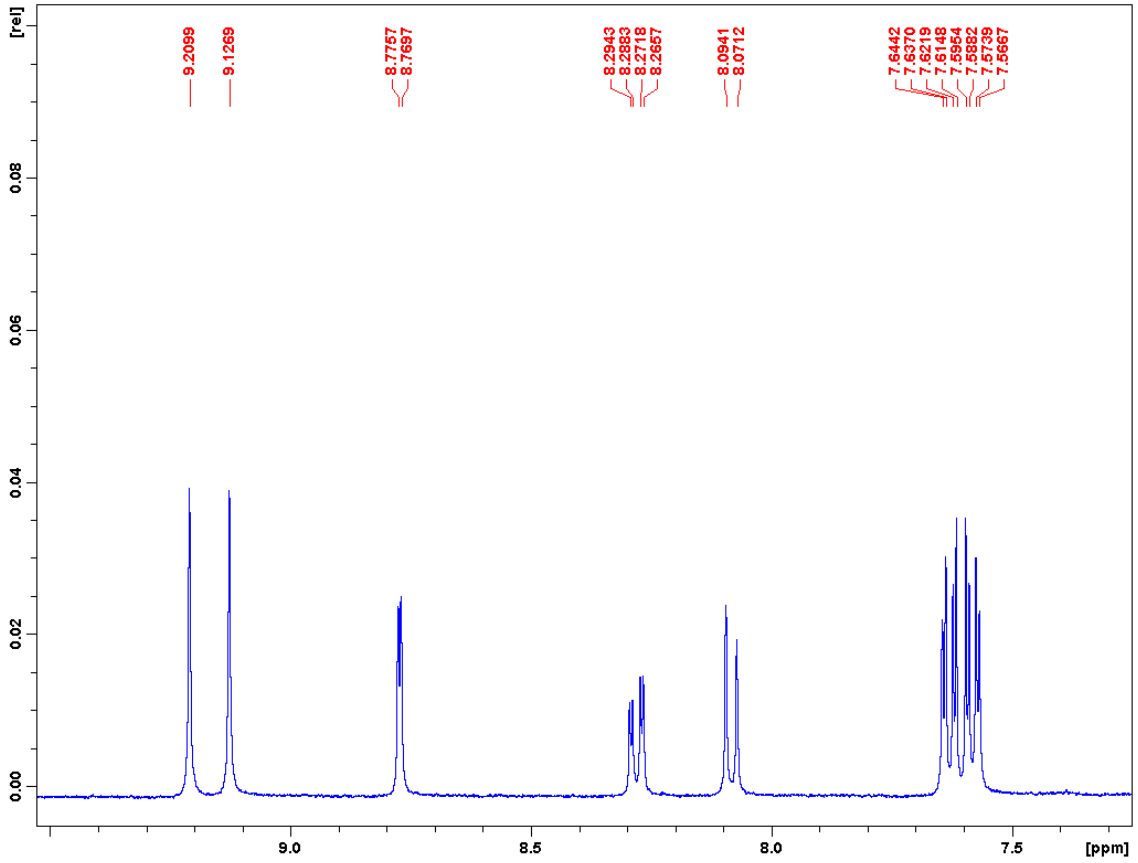
This compound was prepared according to a previously reported procedure.[1]

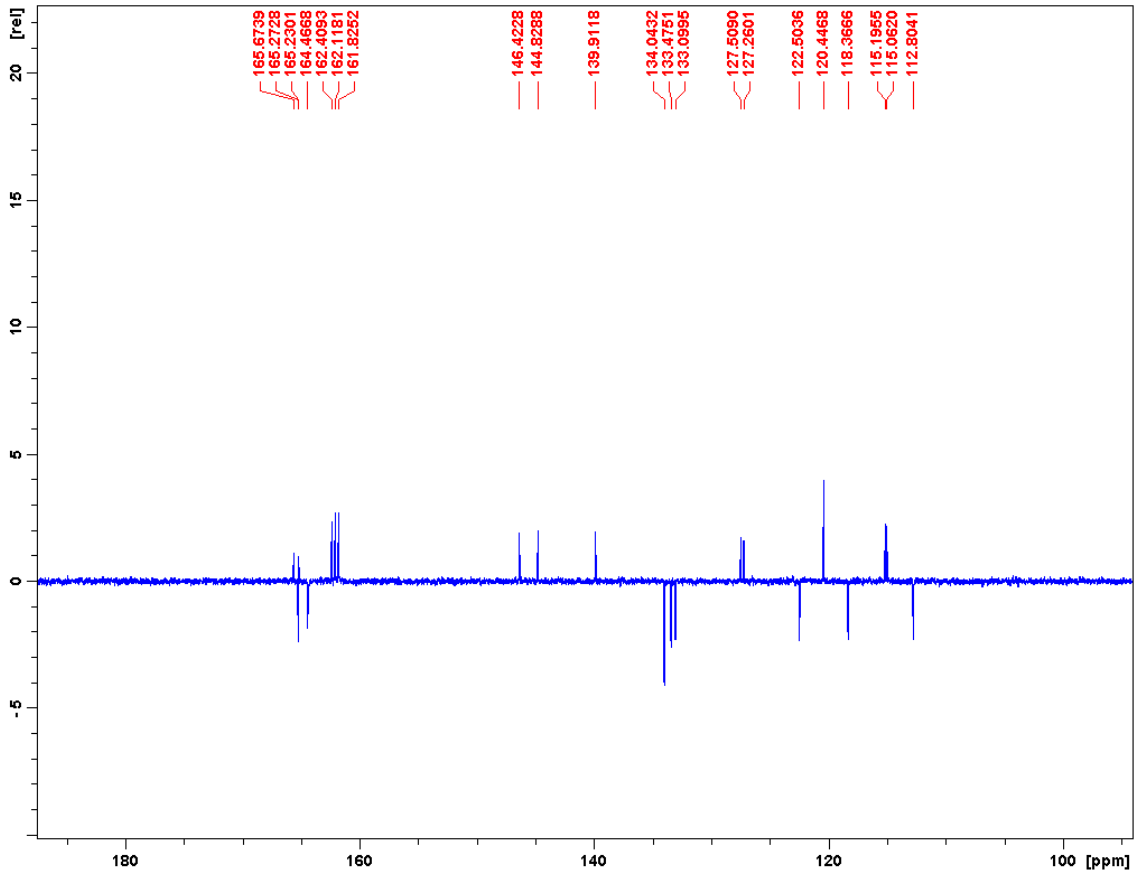
[1] See: Kleij, A. W.; Kuil, M.; Lutz, M.; Tooke, D. M.; Spek, A. L.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Reek, J. N. H. *Inorg. Chim. Acta* **2006**, *359*, 1807-1814.



4a

A mixture of 4-nitro-1,2-phenylenediamine (164.7 mg, 1.08 mmol), $Zn(OAc)_2 \cdot 2H_2O$ (342.4 mg, 1.56 mmol) and 3,5-dichloro-salicylaldehyde (545.1 mg, 2.85 mmol) in MeOH (60 mL) was stirred for 0.5 h during which a precipitate was formed. The reaction mixture was filtered yielding a red solid (591.1 mg, 1.05 mmol, 97%). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.21 (s, 1H, CH=N), 9.13 (s, 1H, CH=N), 8.77 (d, ^4J = 2.4 Hz, 1H, ArH), 8.27 (d, ^3J = 9.0 Hz, ^4J = 2.4 Hz, 1H, ArH), 8.08 (d, ^3J = 9.2 Hz, 1H, ArH), 7.64 (d, ^4J = 2.9 Hz, 1H, ArH), 7.62 (d, ^4J = 2.8 Hz, 1H, ArH), 7.59 (d, ^4J = 2.9 Hz, 1H, ArH), 7.57 (d, ^4J = 2.9 Hz, 1H, ArH). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6 + 20% DMF-d_7): δ = 165.67, 165.27, 165.23, 164.47, 146.42, 144.83, 139.91, 134.04, 133.48, 133.10, 127.51, 127.26, 122.50, 120.45, 118.37, 115.20, 115.06, 112.80. MS (MALDI+, dctb): *m/z* = 560.9 $(M+H)^+$ (calcd. 560.9). Anal. calcd. for $C_{20}H_9Cl_4N_3O_4Zn \cdot H_2O$: C 41.38, H 1.91, N 7.24; Found: C 41.31, H 1.92, N 7.11.

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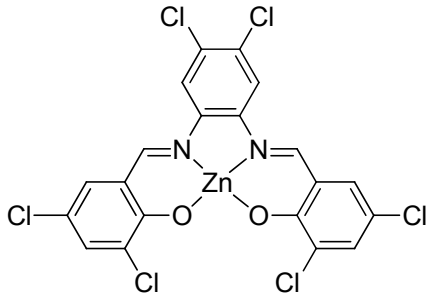
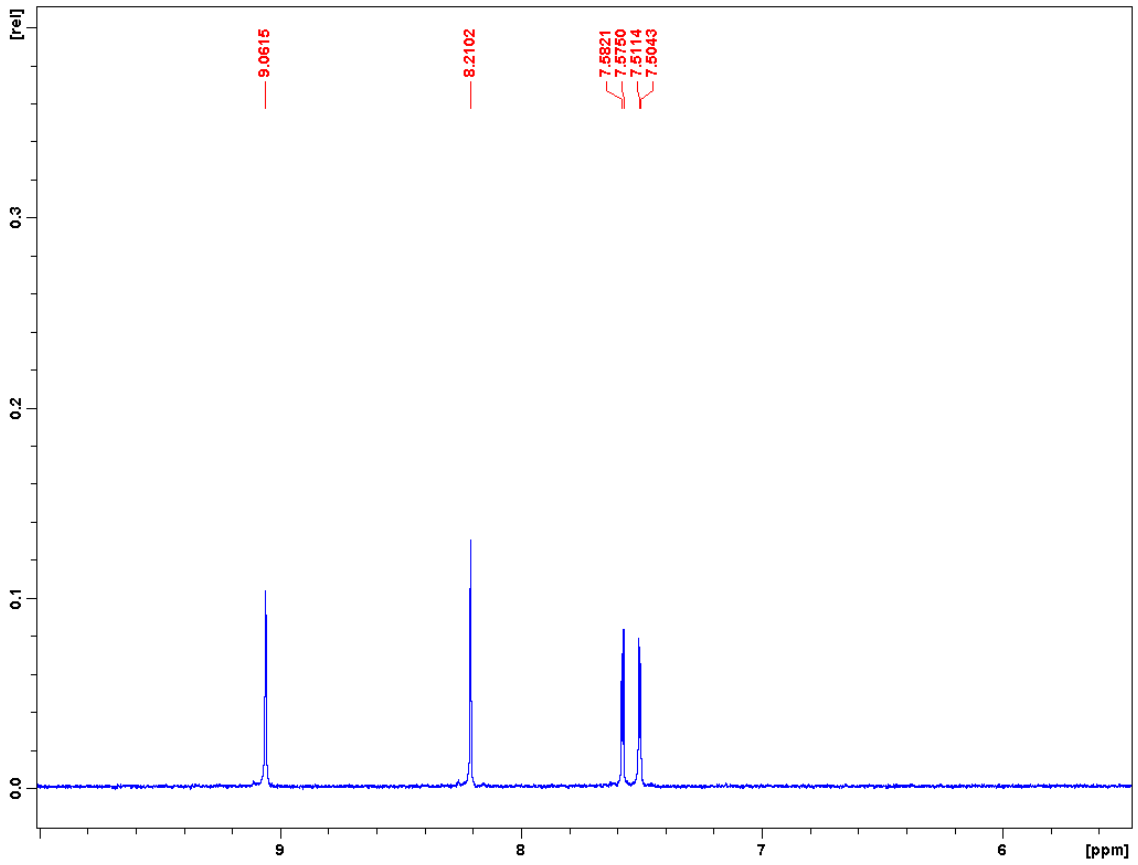
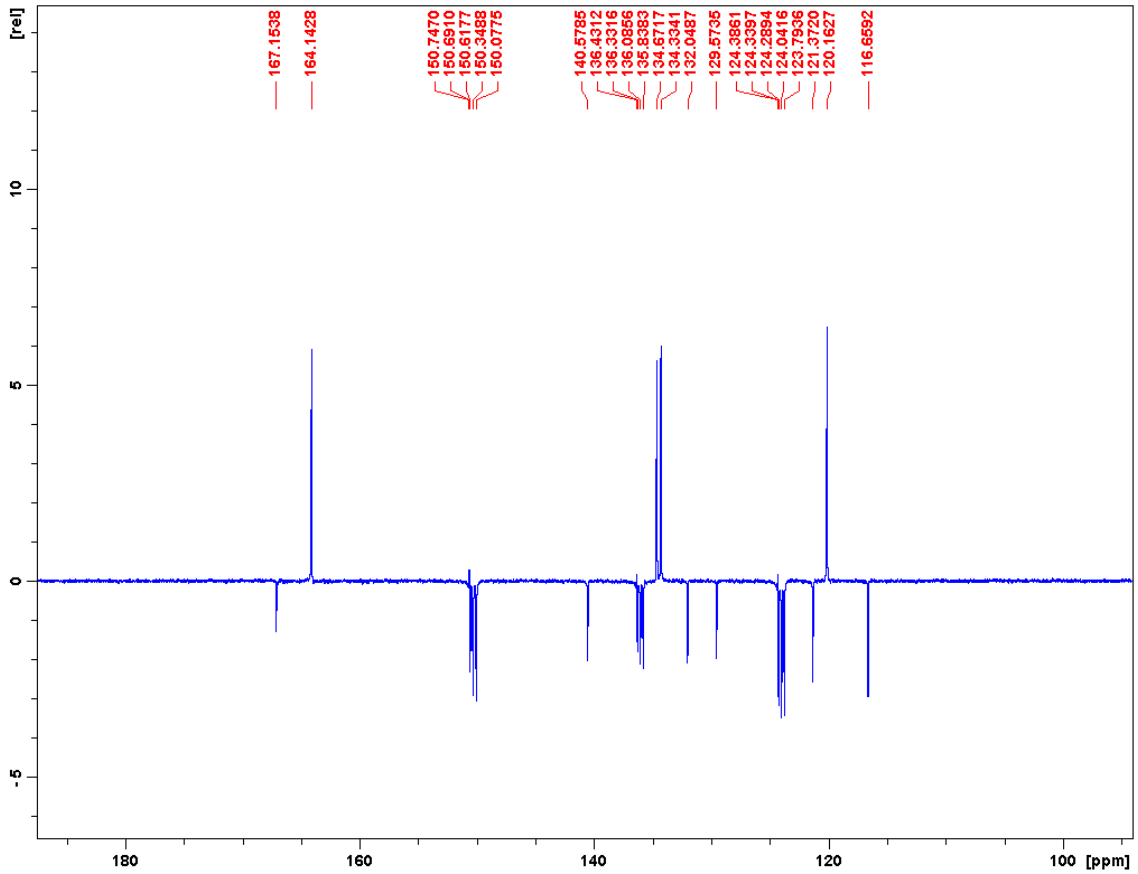


5a

To a solution of 4,5-dichloro-1,2-phenylenediamine (153.6 mg, 0.868 mmol) and 3,5-di-chloro-salicylaldehyde (340.5 mg, 1.78 mmol) in THF/MeOH (75:25 mL) was added $Zn(OAc)_2 \cdot 2H_2O$ (240.1 mg, 1.09 mmol). The reaction mixture was filtered after 1.5 h yielding a yellow to orange solid (409.3 mg). A second fraction (49.2 mg) was obtained by further stirring the mother liquor for 16 h, cooling to -30ºC and filtration. Total yield: 458.5 mg (0.782 mmol, 90%). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.06 (s, 2H, CH=N), 8.21 (s, 2H, ArH), 7.58 (d, ^4J = 2.8 Hz, 2H, ArH), 7.51 (d, ^4J = 2.8 Hz, 2H, ArH). ^{13}C {^{1}H} NMR (100 MHz, pyridine-d_5): δ = 167.15, 164.14, 140.58, 134.67, 134.33, 132.05, 129.57, 121.37, 120.16, 116.67. MS (MALDI+, dctb): *m/z* = 585.8 $(M)^+$ (calcd. 585.8), 1171.6 $(2M)^+$ (calcd 1171.6). Anal. calcd. for $C_{20}H_8Cl_6N_2O_2Zn \cdot H_2O$: C 39.74, H 1.67, N 4.63; Found: C 39.83, H 1.66, N 4.56.

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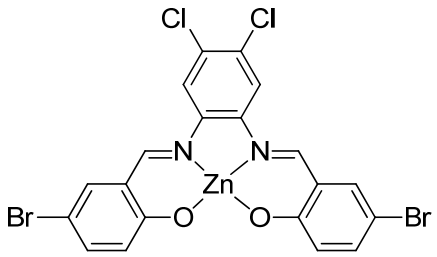
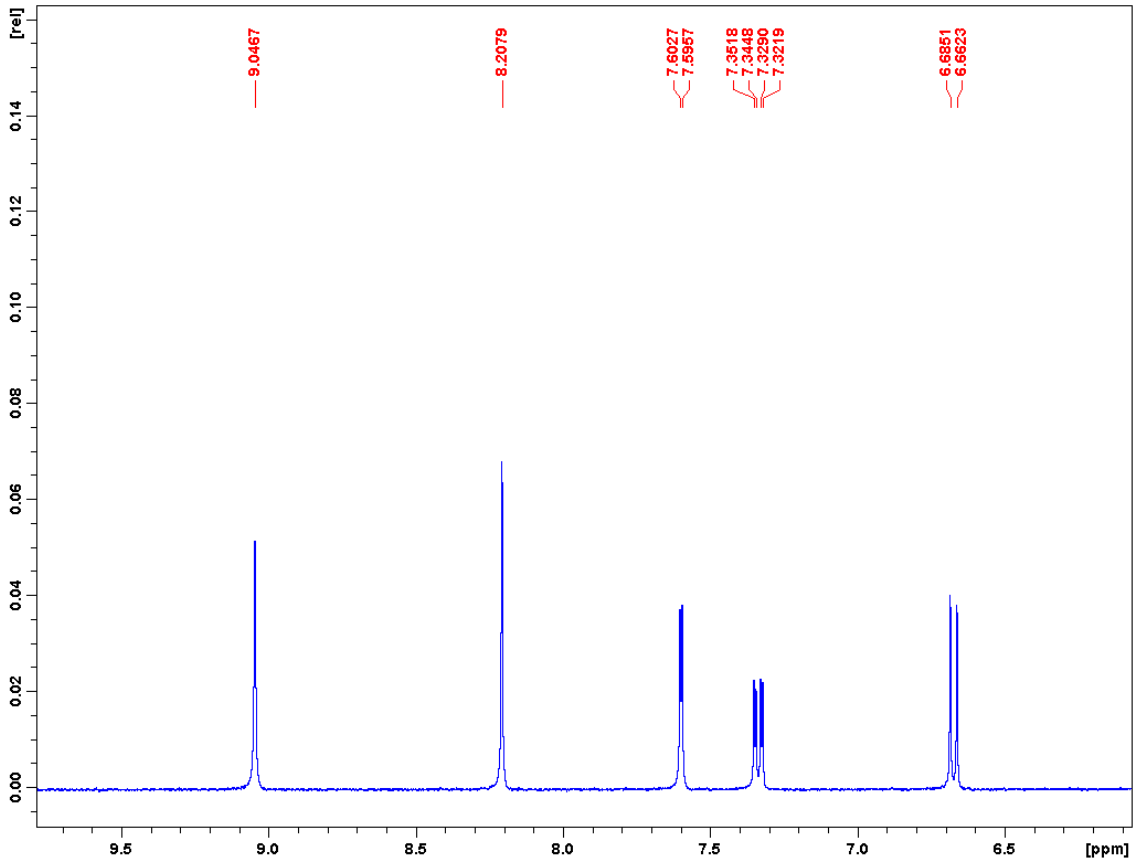
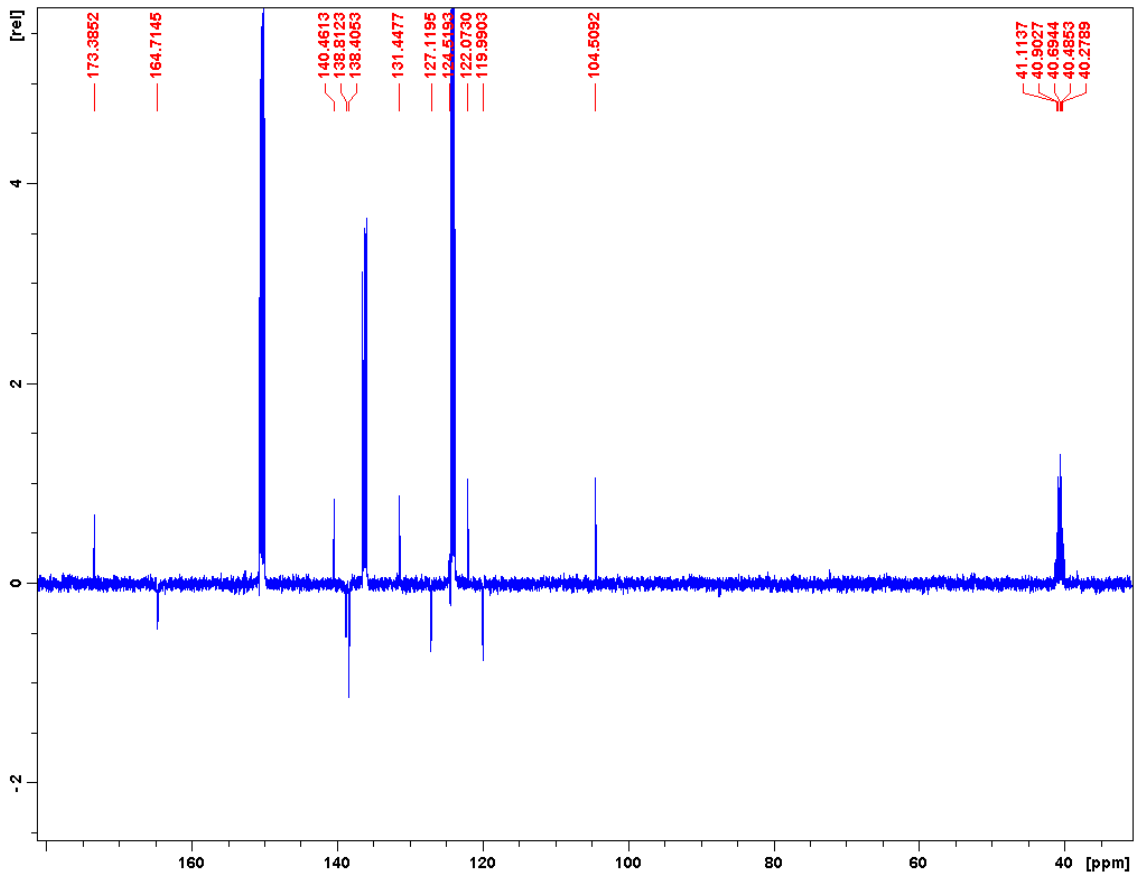


6a

To a solution of 4,5-dichloro-1,2-phenylenediamine (174.9 mg, 0.988 mmol) and 5-bromo-salicylaldehyde (0.40 g, 1.99 mmol) in MeOH (50 mL) was added $Zn(OAc)_2 \cdot 2H_2O$ (0.37 g, 1.69 mmol). The reaction mixture was filtered after 1 h yielding a yellow to orange solid (483.4 mg). A second fraction (114.9 mg) was obtained by further stirring the mother liquor for 16 h, cooling to -30ºC and filtration. Total yield: 598.3 mg (0.987 mmol, 99%). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.05 (s, 2H, CH=N), 8.21 (s, 2H, ArH), 7.60 (d, ^4J = 2.8 Hz, 2H, ArH), 7.33 (d, ^3J = 9.1 Hz, ^4J = 2.8 Hz, 2H, ArH), 6.67 (d, ^3J = 9.1 Hz, 2H, ArH). ^{13}C {^{1}H} NMR (100 MHz, pyridine-d_5): δ = 173.39, 164.71, 140.46, 138.81, 138.41, 131.44, 127.12, 122.07, 119.99, 104.51. MS (MALDI+, dctb): *m/z* = 605.8 $(M)^+$ (calcd. 605.8), 1212.6 $(2M+H)^+$ (calcd 1212.6). Anal. calcd. for $C_{20}H_{10}Cl_2Br_2N_2O_2Zn \cdot 2.5H_2O$: C 36.87, H 2.32, N 4.30; Found: C 36.78, H 1.82, N 4.24.

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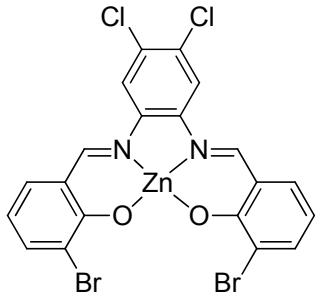
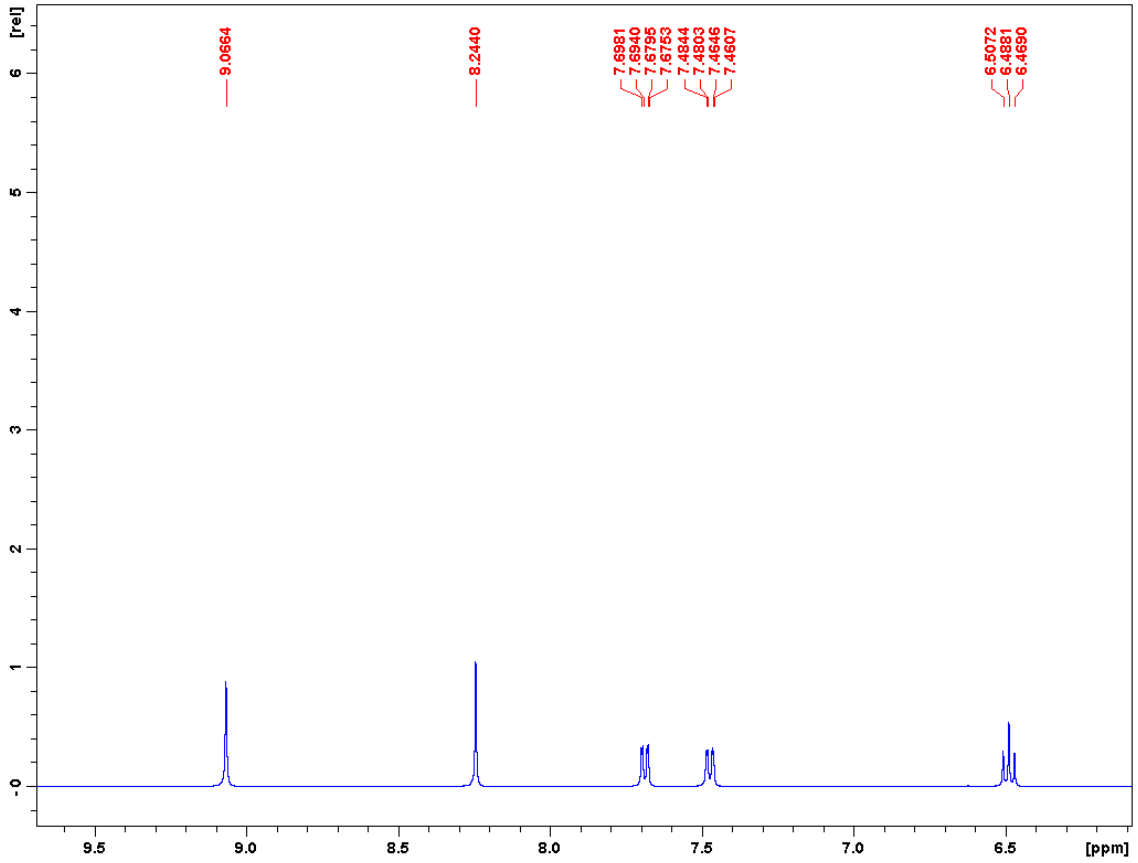
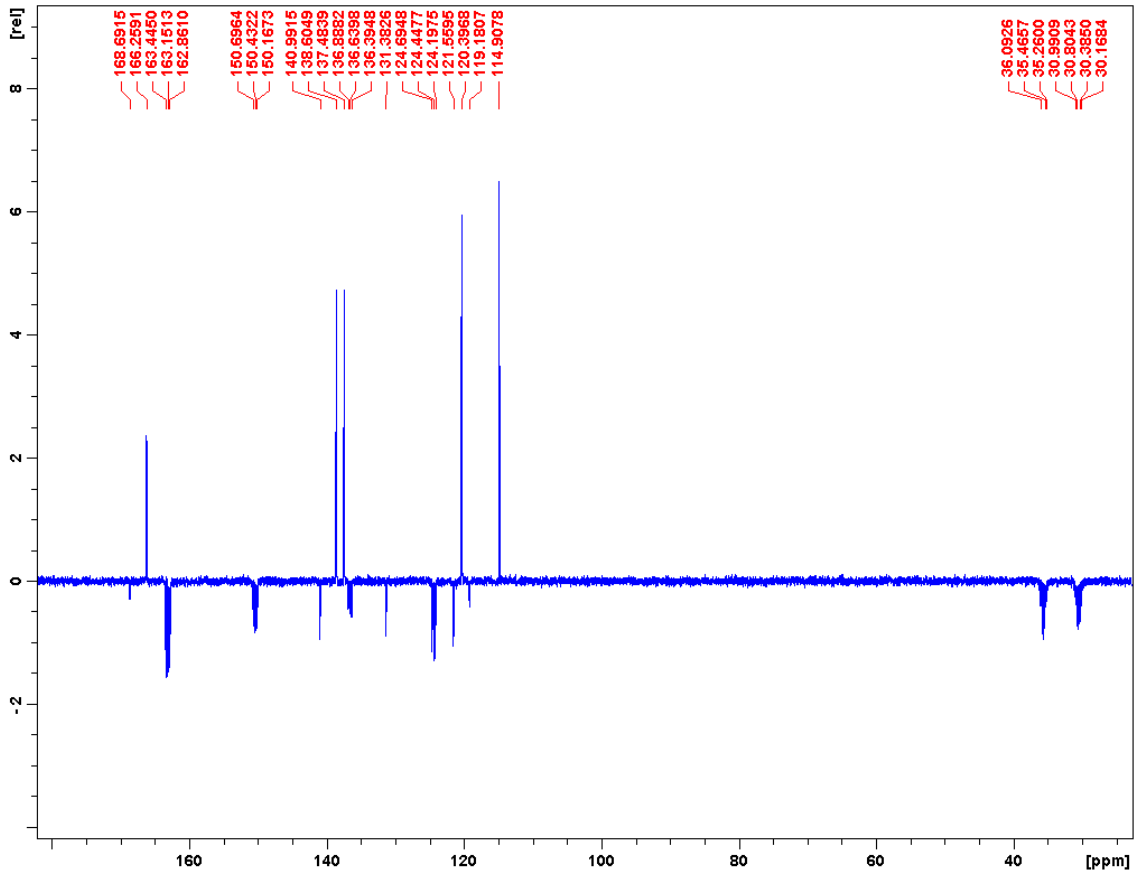


7a

To a solution of 4,5-dichloro-1,2-phenylenediamine (85.4 mg, 0.482 mmol) and 3-bromo-salicylaldehyde (197.0 mg, 0.980 mmol) in MeOH (30 mL) was added $Zn(OAc)_2 \cdot 2H_2O$ (198.8 mg, 0.906 mmol). The reaction mixture was filtered after 2 h yielding a yellow to orange solid (248.5 mg). A second fraction (29.0 mg) was obtained by further stirring the mother liquor for 16 h, cooling to -30ºC and filtration. Total yield: 277.5 mg (0.458 mmol, 95%). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.07 (s, 2H, CH=N), 8.24 (s, 2H, ArH), 7.68 (d, ^3J = 7.5 Hz, ^4J = 1.6 Hz, 2H, ArH), 7.47 (d, ^3J = 7.9 Hz, ^4J = 1.6 Hz, 2H, ArH), 6.49 (t, ^3J = 7.6 Hz, 2H, ArH). ^{13}C {^{1}H} NMR (100 MHz, 20% pyridine-d_5 + 80% DMF-d_7): δ = 168.69, 166.26, 140.99, 138.60, 137.48, 131.38, 121.56, 120.40, 119.18, 114.91. MS (MALDI+, dctb): *m/z* = 605.8 $(M)^+$ (calcd. 605.8), 1211.5 $(2M)^+$ (calcd 1211.5). Anal. calcd. for $C_{20}H_{10}Cl_2Br_2N_2O_2Zn \cdot H_2O$: C 38.47, H 1.94, N 4.49; Found: C 38.21, H 1.91, N 4.38.

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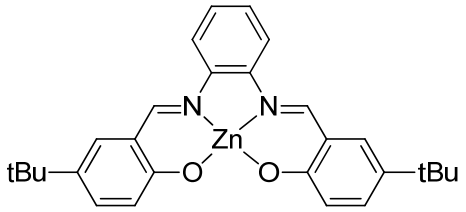
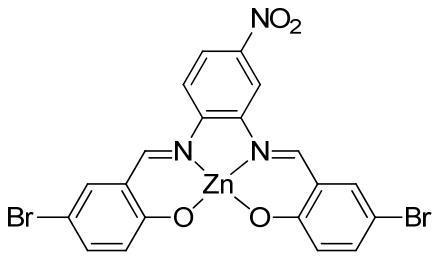


8a

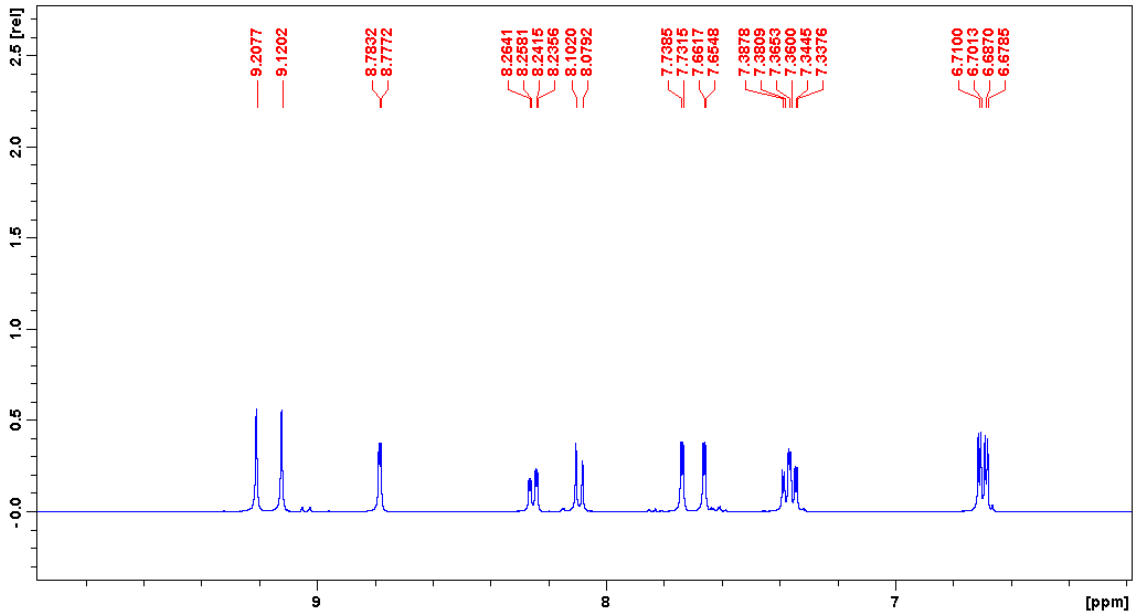
This compound was prepared according to a previously reported procedure.[2]

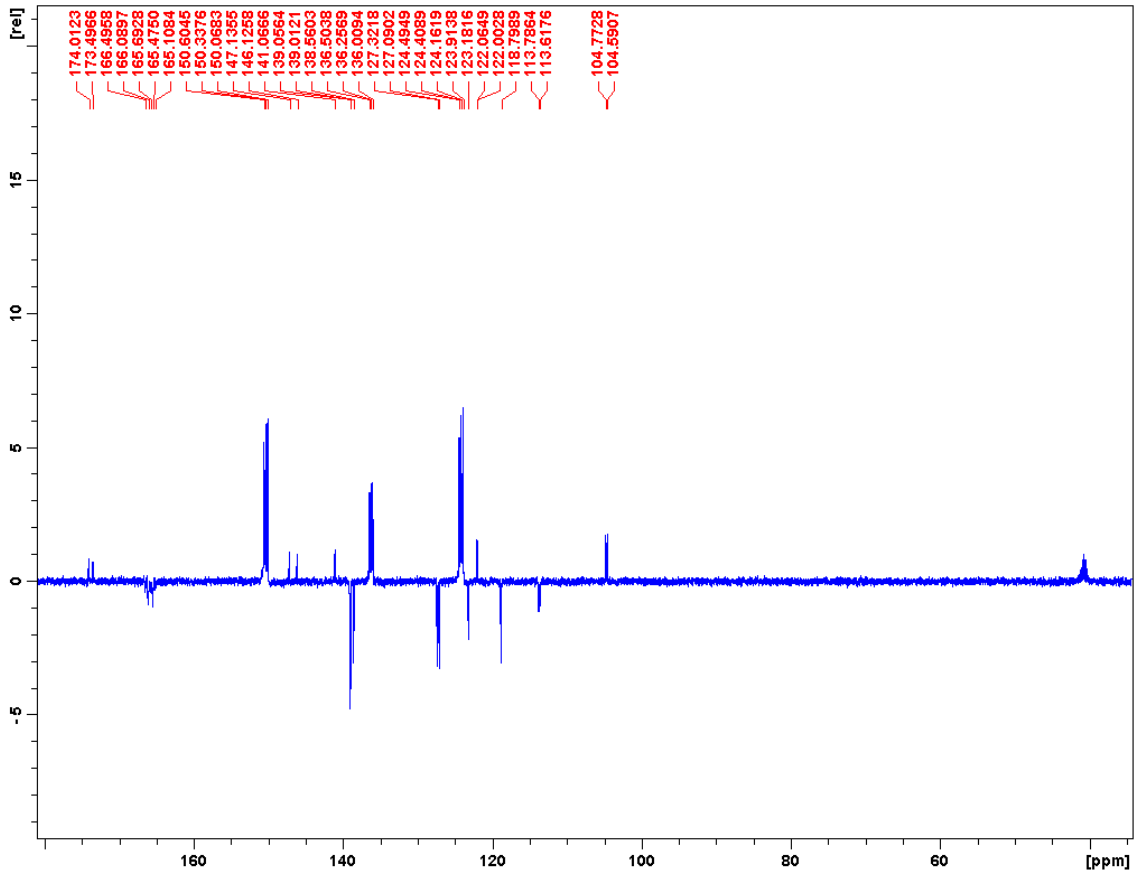
[2] Escudero-Adán, E. C.; Benet-Buchholz, J.; Kleij, A. *Inorg. Chem.* **2007**, *46*, 7265–7267.



9a

To a warm solution of 4-nitro-1,2-phenylenediamine (0.21 g, 1.37 mmol) and $Zn(OAc)_2 \cdot 2H_2O$ (0.40 g, 1.82 mmol) in MeOH (50 mL) was added 5-bromo-salicylaldehyde (0.57 g, 2.84 mmol) dissolved in MeOH (20 mL). The reaction mixture was filtered after 1 h yielding a red solid (510.9 mg). A second fraction (210.6 mg) was obtained by further stirring the mother liquor for 16 h, cooling to -30ºC and filtration. Total yield: 721.5 mg (1.24 mmol, 90%). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.21 (s, 1H, CH=N), 9.12 (s, 1H, CH=N), 8.78 (d, ^4J = 2.4 Hz, 1H, ArH), 8.25 (d, ^3J = 9.0 Hz, ^4J = 2.4 Hz, 1H, ArH), 8.09 (d, ^3J = 9.1 Hz, 1H, ArH), 7.73 (d, ^4J = 2.8 Hz, 1H, ArH), 7.66 (d, ^4J = 2.8 Hz, 1H, ArH), 7.34-7.39 (m, 2H, ArH), 6.68-6.71 (m, 2H, ArH). ^{13}C {^{1}H} NMR (100 MHz, pyridine-d_5): δ = 174.01, 173.50, 166.09, 165.48, 147.14, 146.13, 141.07, 139.06, 139.01, 138.56, 127.32, 127.09, 123.18, 122.06, 122.0, 118.80, 113.78, 113.62, 104.77, 104.59. MS (MALDI+, pyrene): *m/z* = 580.8 $(M)^+$ (calcd. 580.7). Anal. calcd. for $C_{20}H_{11}CBr_2N_3O_4Zn \cdot 1.5H_2O$: C 39.41, H 2.32, N 6.89; Found: C 39.44, H 2.09, N 6.73.

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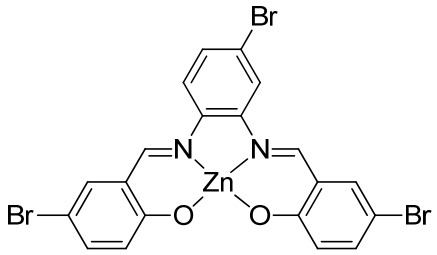
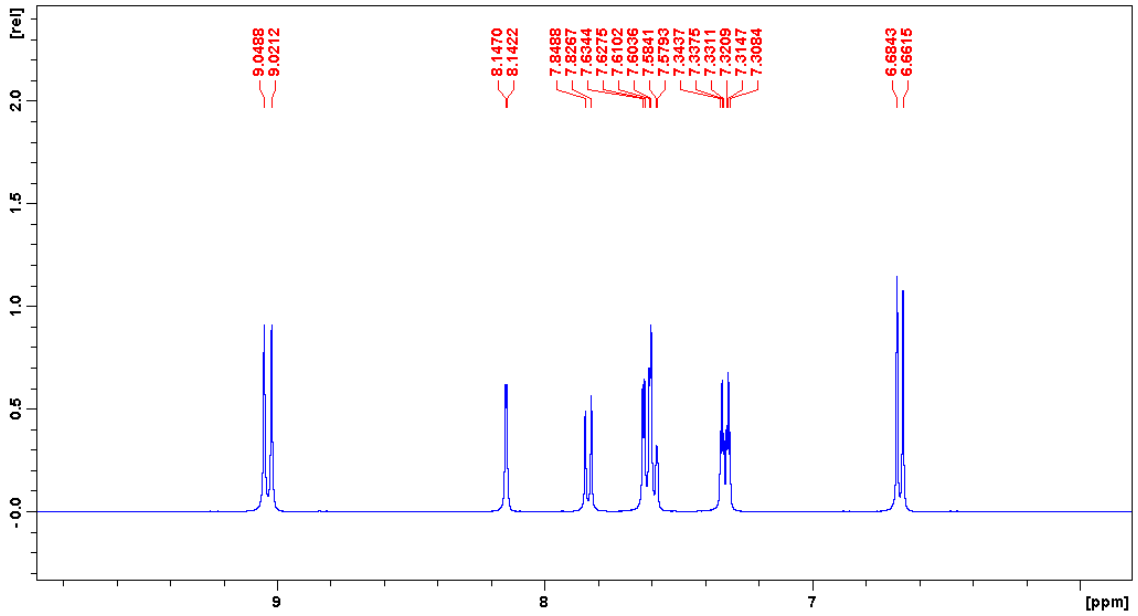
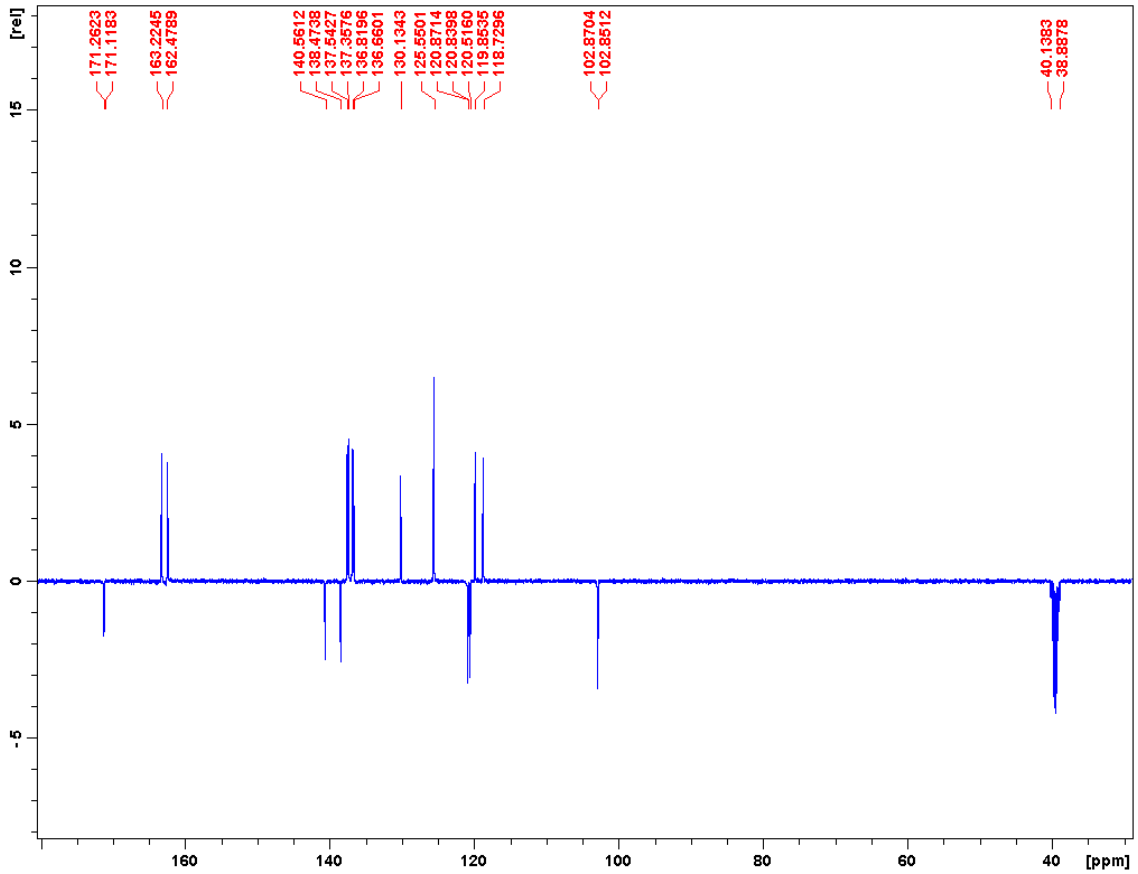


10a

To a solution of 4-bromo-1,2-phenylenediamine (0.14 g, 0.749 mmol) and $Zn(OAc)_2 \cdot 2H_2O$ (0.26 g, 1.18 mmol) in MeOH (40 mL) was added 5-bromo-salicylaldehyde (0.32 g, 1.59 mmol) dissolved in MeOH (10 mL). The reaction mixture was filtered after 1 h yielding a yellow solid (336.8 mg). A second fraction (58.9 mg) was obtained by further stirring the mother liquor for 16 h, cooling to -30ºC and filtration. Total yield: 395.7 mg (0.642 mmol, 86%). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.05 (s, 1H, CH=N), 9.02 (s, 1H, CH=N), 8.14 (d, ^4J = 1.9 Hz, 1H, ArH), 7.83 (d, ^3J = 8.8 Hz, 1H, ArH), 7.58-7.63 (m, 3H, ArH), 7.31-7.34 (m, 2H, ArH), 6.67 (d, ^3J = 9.1 Hz, 2H, ArH). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ = 171.26, 171.11, 163.22, 162.48, 140.56, 138.47, 137.54, 137.36, 136.82, 136.66, 130.13, 125.55, 120.87, 120.84, 120.52, 119.85, 118.73, 102.87, 102.85. MS (MALDI+, dctb): *m/z* = 615.8 $(M)^+$ (calcd. 615.8), 1231.5 $(2M)^+$ (calcd 1231.5). Anal. calcd. for $C_{20}H_{11}Br_3N_2O_2Zn \cdot 1.5H_2O$: C 37.33, H 2.19, N 4.35; Found: C 36.99, H 2.12, N 4.23.

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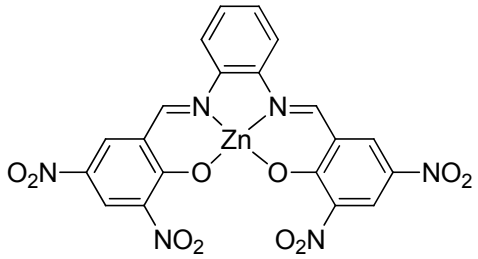
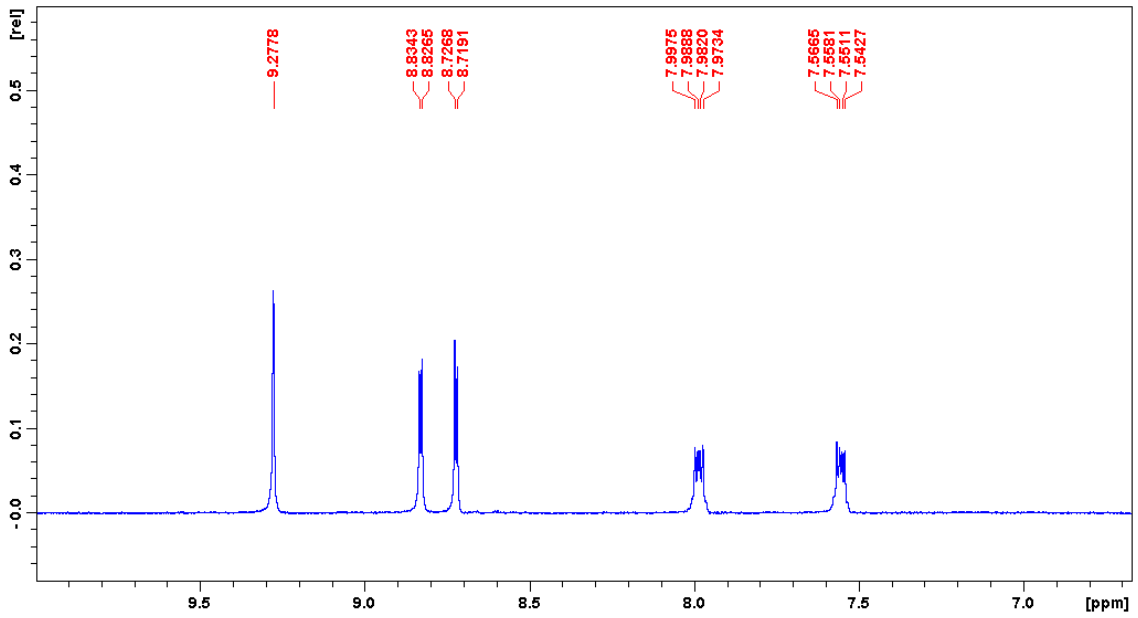
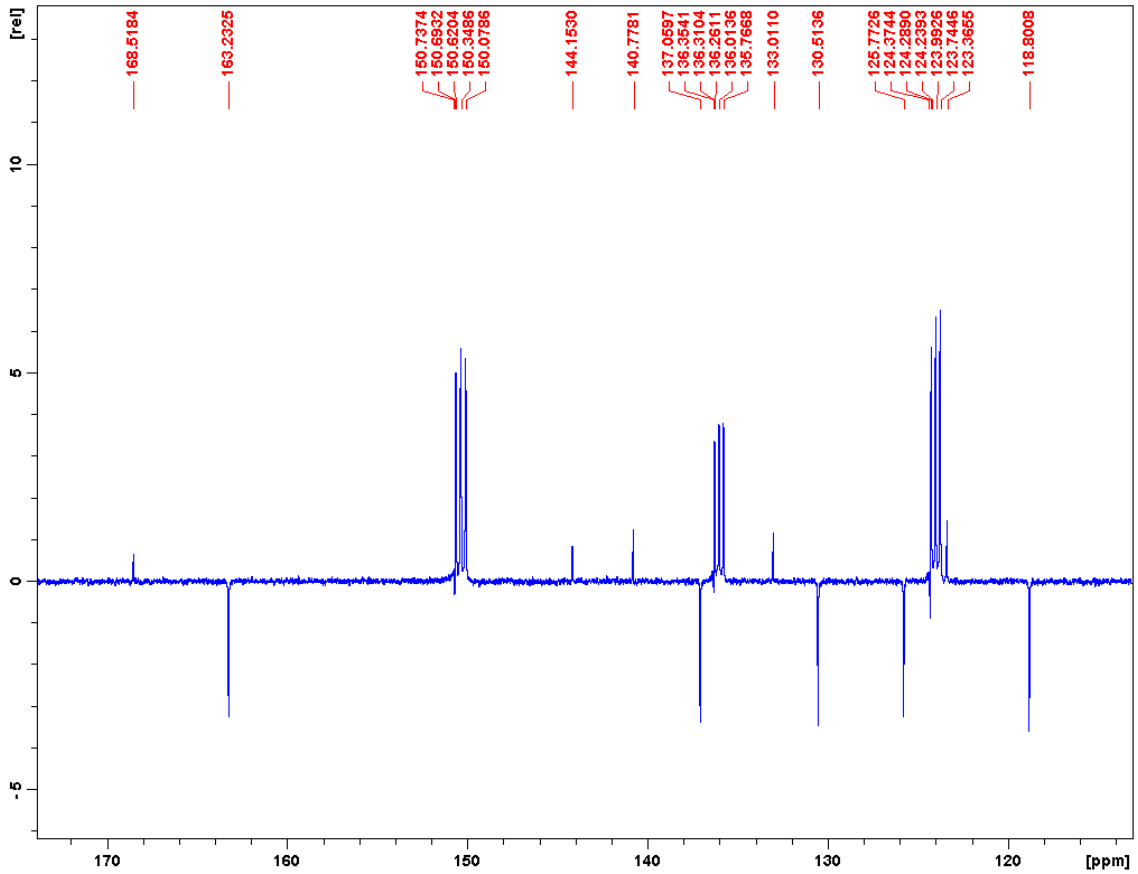


11a

To a solution of 1,2-phenylenediamine (86.3 mg, 0.80 mmol) and $Zn(OAc)_2 \cdot 2H_2O$ (285.4 mg, 1.30 mmol) in MeOH (40 mL) was added 3,5-dinitro-salicylaldehyde (348.3 mg, 1.64 mmol) dissolved in MeOH (15 mL). The reaction mixture was filtered after 15 min yielding a yellow solid (276.5 mg). A second fraction (63.4 mg) was obtained by further stirring the mother liquor for 16 h, cooling to -30ºC and filtration. Total yield: 339.9 mg (0.607 mmol, 76%). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.23 (s, 2H, CH=N), 8.83 (d, ^4J = 3.1 Hz, 2H, ArH), 8.72 (d, ^4J = 3.1 Hz, 2H, ArH), 7.97-7.98 (m, 2H, ArH), 7.54-7.57 (m, 2H, ArH). ^{13}C {^{1}H} NMR (100 MHz, pyridine-d_6): δ = 168.52, 163.23, 144.15, 140.78, 137.06, 133.01, 130.51, 125.77, 123.37, 118.80. MS (MALDI–, dctb): m/z = 558.0 $(M)^+$ (calcd. 558.0). Anal. calcd. for $C_{20}H_{10}N_6O_{10}Zn \cdot H_2O$: C 41.58, H 2.09, N 14.55; Found: C 41.33, H 2.09, N 14.04.

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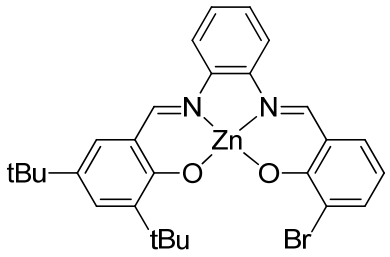
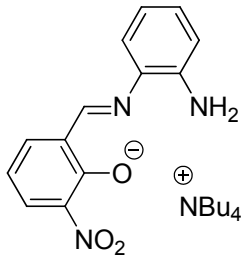


12a

This compound was prepared according to a previously reported procedure.[3]

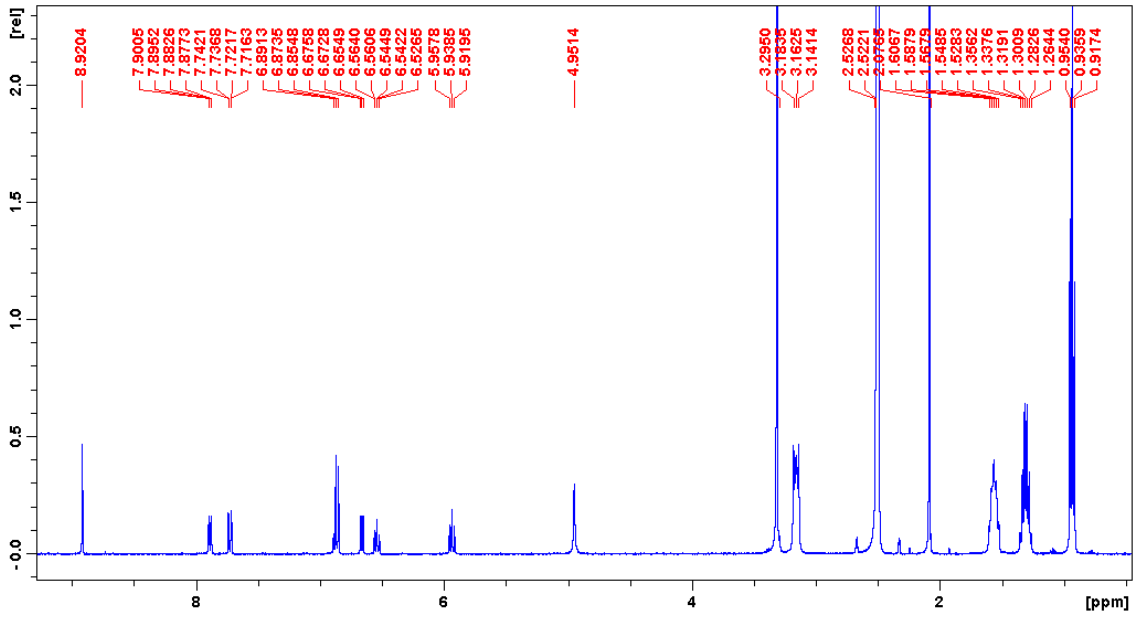
[3] Martínez Belmonte, M.; Wezenberg, S. J.; Haak, R. M.; Anselmo, D.; Escudero-Adán, E. C.; Benet-Buchholz, J.; Kleij, A. W. *Dalton Trans*. **2010**, *39*, 4541-4550.

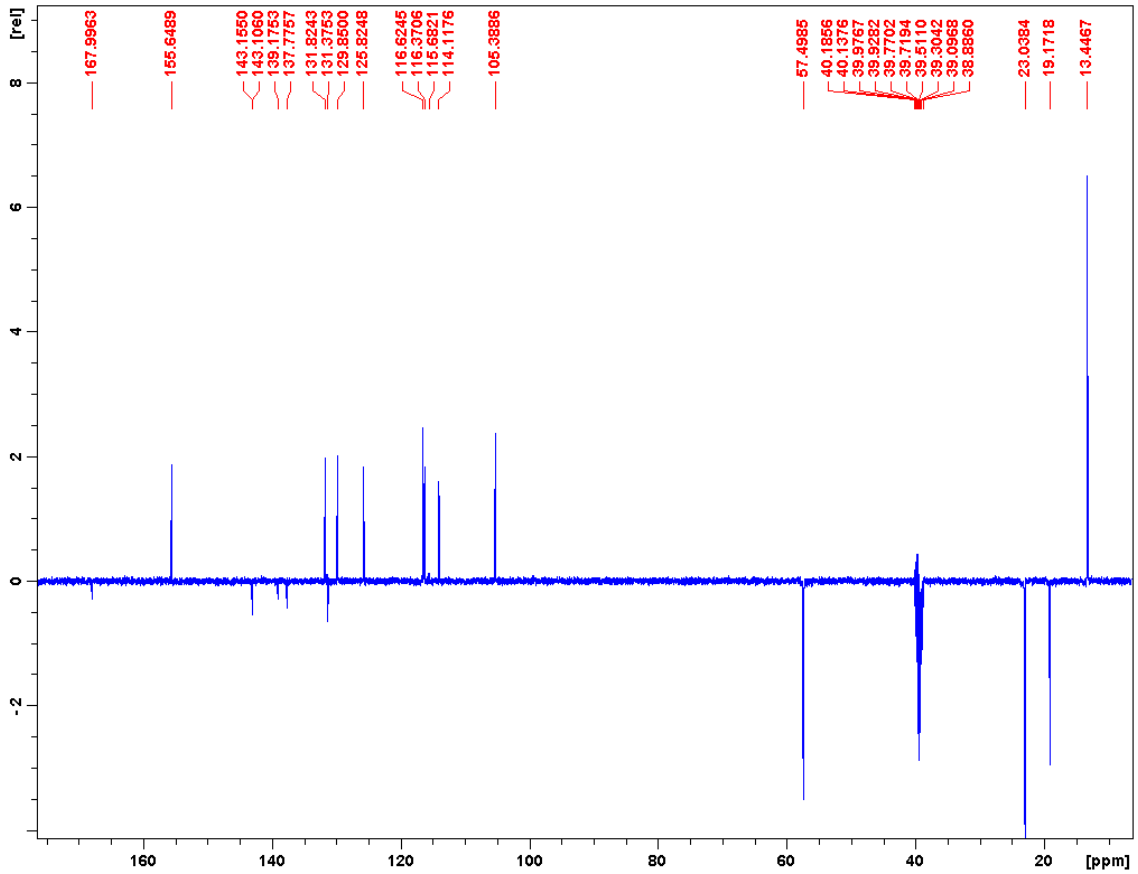
Synthesis of monoimine NBu_4 salts **1b-12b**.



1b

To a suspension of Zn(salphen) **1a** (286.8 mg, 0.611 mmol) in CH_3CN (10 mL) was added a solution of NBu_4OH (1 M in MeOH) until full dissolution of the solid material occurred. The colour of the mixture turned deep red and was filtered after 5 min. Then the filtrate was concentrated and cooled to -30ºC to give the product as red crystals (155.3 mg, 0.312 mmol, 51% based on **1a**). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.92 (s, 1H, CH=N), 7.89 (d, ^3J = 7.2 Hz, ^4J = 2.1 Hz, 1H, ArH), 7.73 (d, ^3J = 8.2 Hz, ^4J = 2.1 Hz, 1H, ArH), 6.85-6.89 (m, 2H, ArH), 6.66 (d, ^3J = 7.8 Hz, ^4J = 1.2 Hz, 1H, ArH), 6.54 (t, ^3J = 7.5 Hz, ^4J = 1.4 Hz, 1H, ArH), 5.93 (t, ^3J = 7.7 Hz, 1H, ArH), 4.95 (br s, 2H, NH_2), 3.14-3.18 (m, 8H, NBu), 1.53-1.60 (m, 8H, NBu), 1.26-1.36 (m, 8H, NBu), 0.94 (t, ^3J = 7.3 Hz, 12H, NBu). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ = 168.00, 155.65, 143.16, 139.18, 137.78, 131.82, 131.38, 129.85, 125.82, 116.62, 116.37, 114.12, 105.39, 57.50, 23.04, 19.17, 13.45. MS (ESI+, MeOH): *m/z* = 242.3 (M – anion)$^+$ (calcd. 242.3). Anal. calcd. for $C_{29}H_{46}N_4O_3 \cdot H_2O$: C 67.41, H 9.36, N 10.84; Found: C 67.64, H 9.50, N 10.97.

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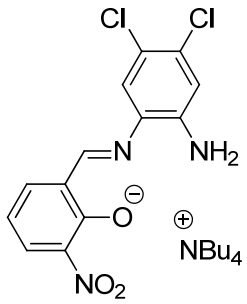
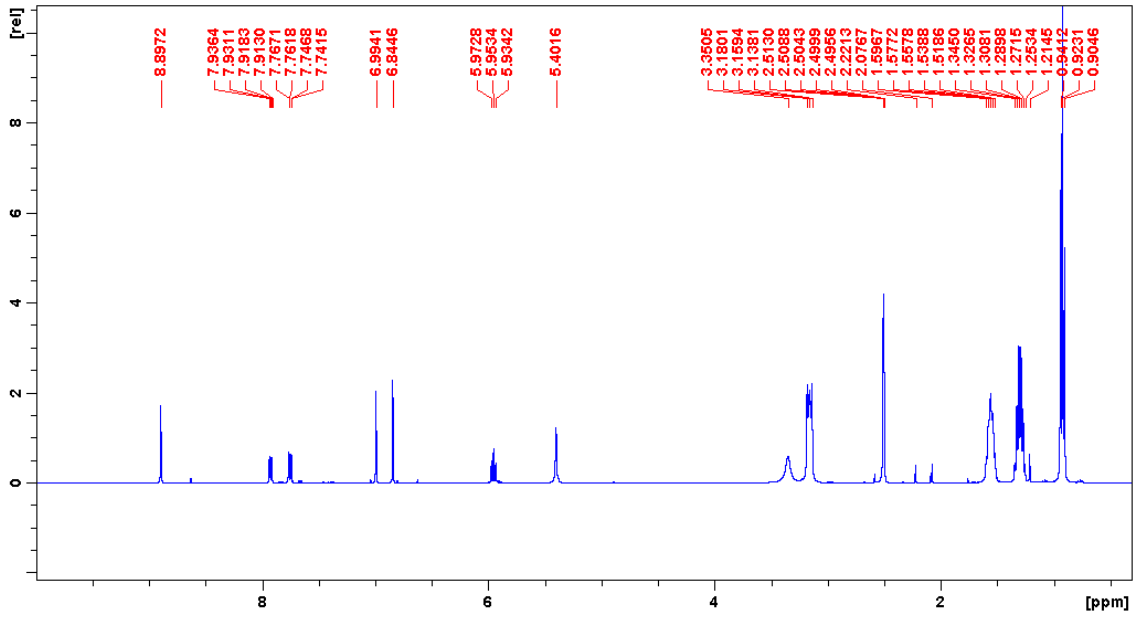
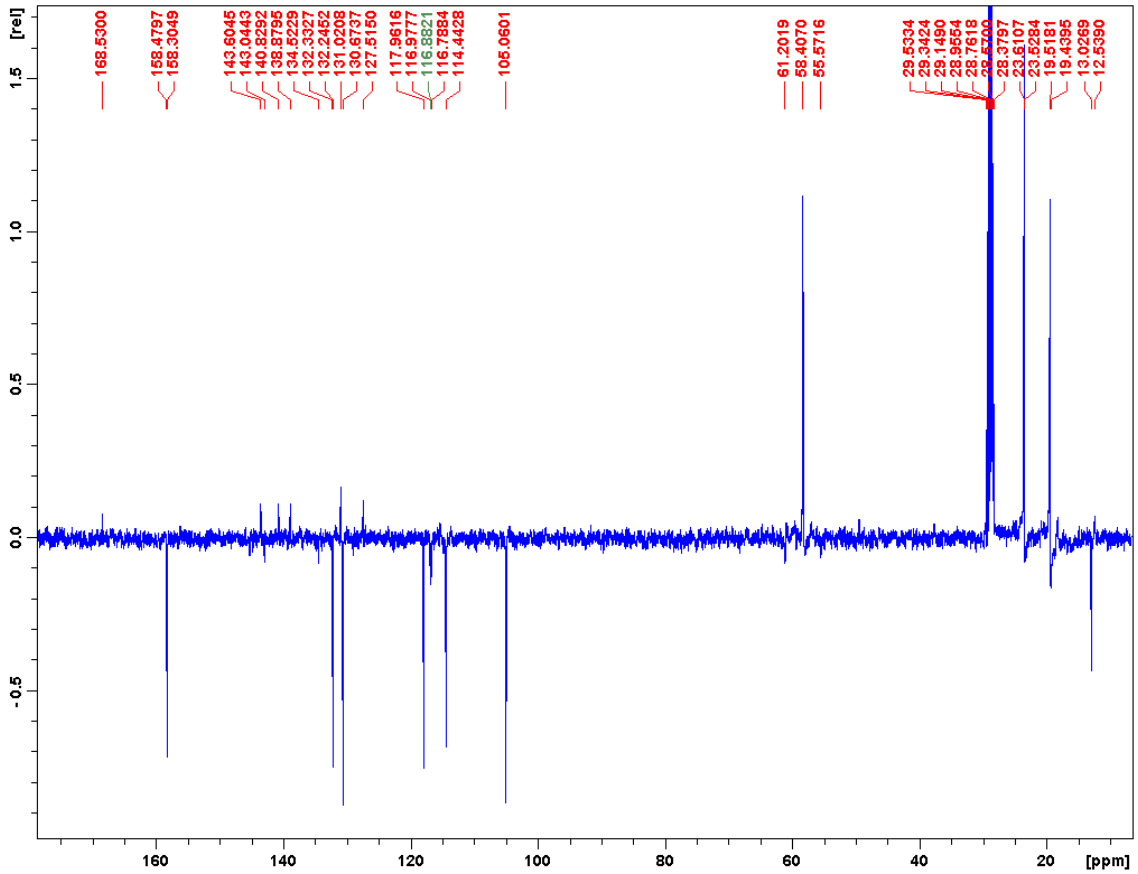


2b

To a suspension of Zn(salphen) **2a** (177.6 mg, 0.330 mmol) in CH_3CN (8 mL) was added a solution of NBu_4OH (1 M in MeOH) until full dissolution of the solid material occurred. The colour of the mixture turned red and was filtered after 5 min. Then the filtrate was concentrated and cooled to -30ºC to give the product as red crystals (108.4 mg, 0.191 mmol, 58% based on **2a**). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.89 (s, 1H, CH=N), 7.92 (d, ^3J = 7.2 Hz, ^4J = 2.1 Hz, 1H, ArH), 7.75 (d, ^3J = 8.1 Hz, ^4J = 2.1 Hz, 1H, ArH), 6.99 (s, 1H, ArH), 6.84 (s, 1H, ArH), 5.95 (t, ^3J = 7.7 Hz, 1H, ArH), 5.40 (br s, 2H, NH_2), 3.14-3.18 (m, 8H, NBu), 1.52-1.60 (m, 8H, NBu), 1.25-1.35 (m, 8H, NBu), 0.92 (t, ^3J = 7.3 Hz, 12H, NBu). ^{13}C {^{1}H} NMR (100 MHz, acetone-d_6): δ = 168.53, 158.30, 143.60, 140.83, 138.88, 132.25, 131.02, 130.67, 127.52, 117.96, 116.88, 114.44, 105.06, 58.41, 23.61, 19.52, 13.03. MS (ESI–, MeOH): *m/z* = 323.9 (M – NBu_4)$^-$ (calcd. 324.0). Anal. calcd. for $C_{29}H_{44}Cl_2N_4O_3 \cdot H_2O$: C 61.37, H 7.81, N 9.87; Found: C 61.75, H 8.30, N 9.43.

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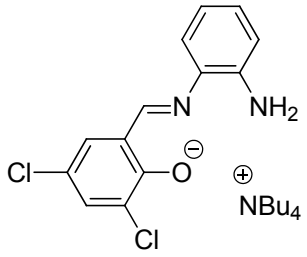
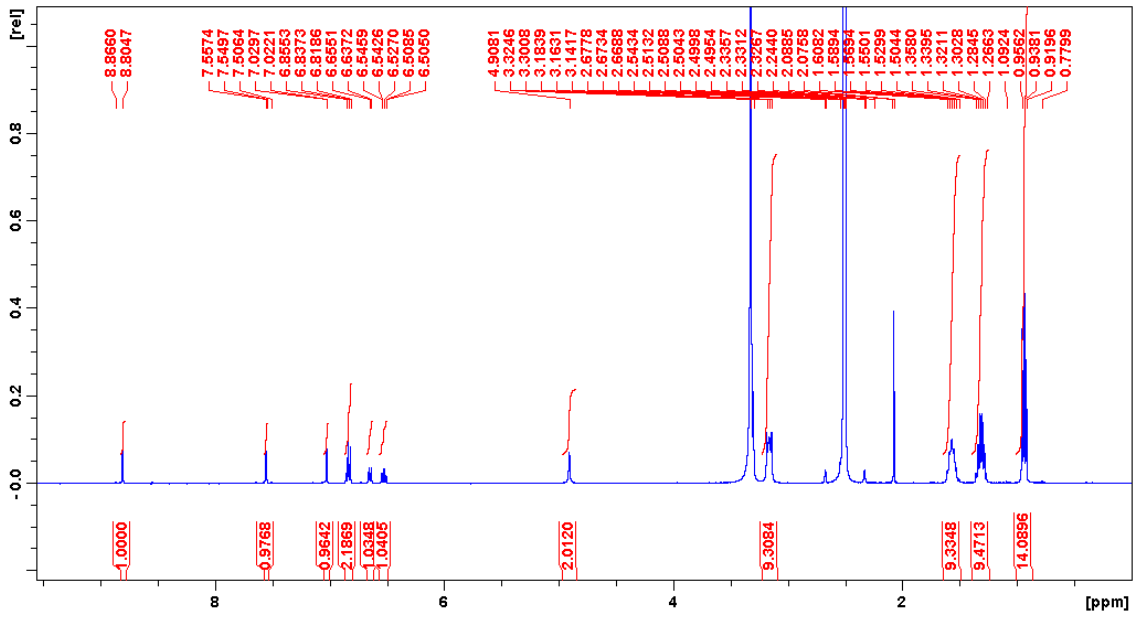
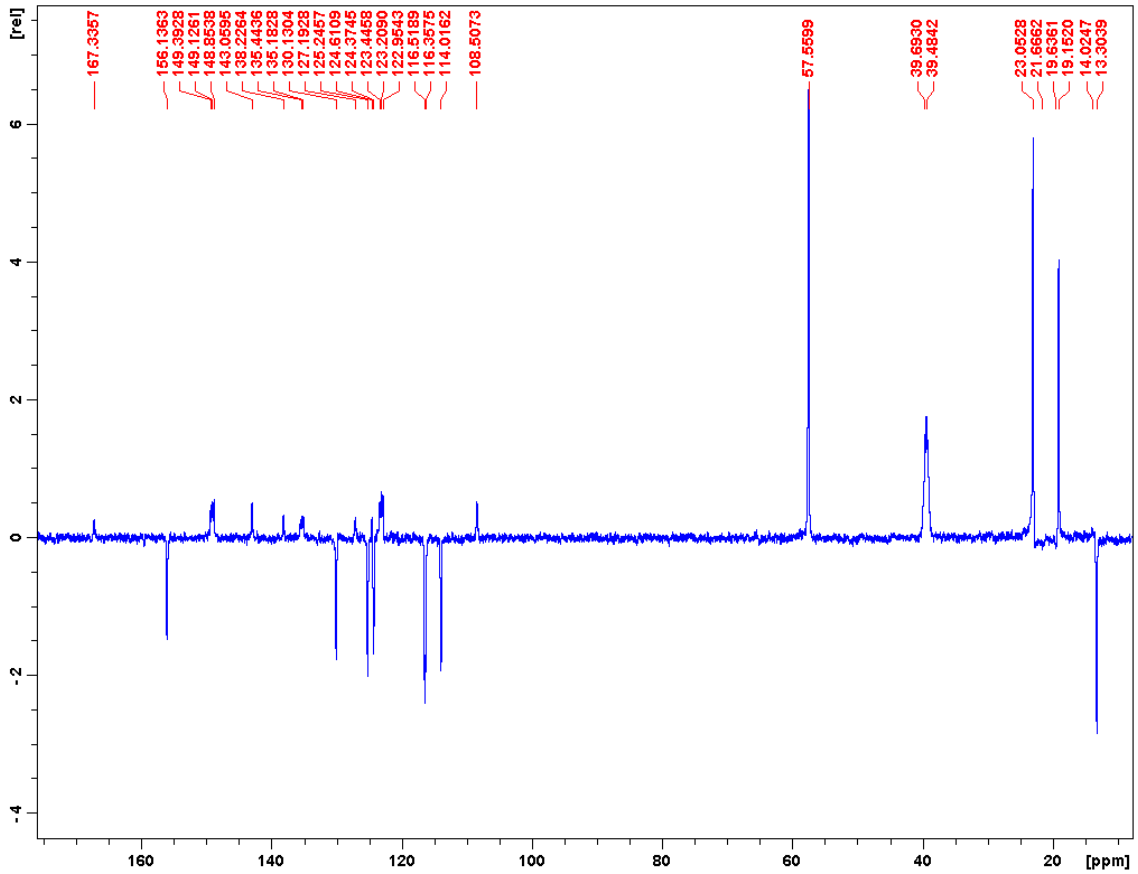


3b

To a suspension of Zn(salphen) **3a** (208.6 mg, 0.403 mmol) in CH_3CN (8 mL) was added a solution of NBu_4OH (0.7 mL of a 1 M solution in MeOH) and the mixture shortly shaken at rt. The yellow reaction mixture was then filtered after 10 min. Then the filtrate was concentrated and cooled to -30ºC to give the product as orange crystals (84.5 mg, 0.162 mmol, 40% based on **3a**). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.80 (s, 1H, CH=N), 7.55 (d, ^4J = 3.1 Hz, 1H, ArH), 7.03 (d, ^4J = 3.0 Hz, 1H, ArH), 6.82-6.86 (m, 2H, ArH), 6.64 (d, ^3J = 7.2 Hz, 1H, ArH), 6.53 (t, ^3J = 7.5 Hz, ^4J = 1.3 Hz, 1H, ArH), 4.91 (br s, 2H, NH_2), 3.14-3.18 (m, 8H, NBu), 1.50-1.61 (m, 8H, NBu), 1.27-1.36 (m, 8H, NBu), 0.94 (t, ^3J = 7.3 Hz, 12H, NBu). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6 + 10% pyridine-d_5): δ = 167.34, 156.14, 143.06, 138.23, 130.13, 127.19, 125.25, 124.61, 124.37, 116.52, 116.36, 114.02, 108.51, 57.56, 23.05, 19.15, 13.30. MS (ESI–, MeOH): *m/z* = 279.0 $(M - NBu_4)^-$ (calcd. 279.0). Anal. calcd. for $C_{29}H_{45}Cl_2N_3O{\cdot}1/3H_2O$: C 65.89, H 8.71, N 7.95; Found: C 65.93, H 8.79, N 7.91.

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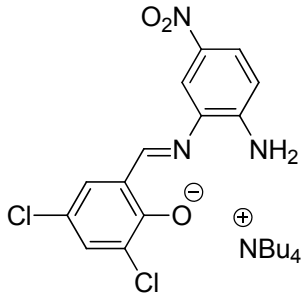
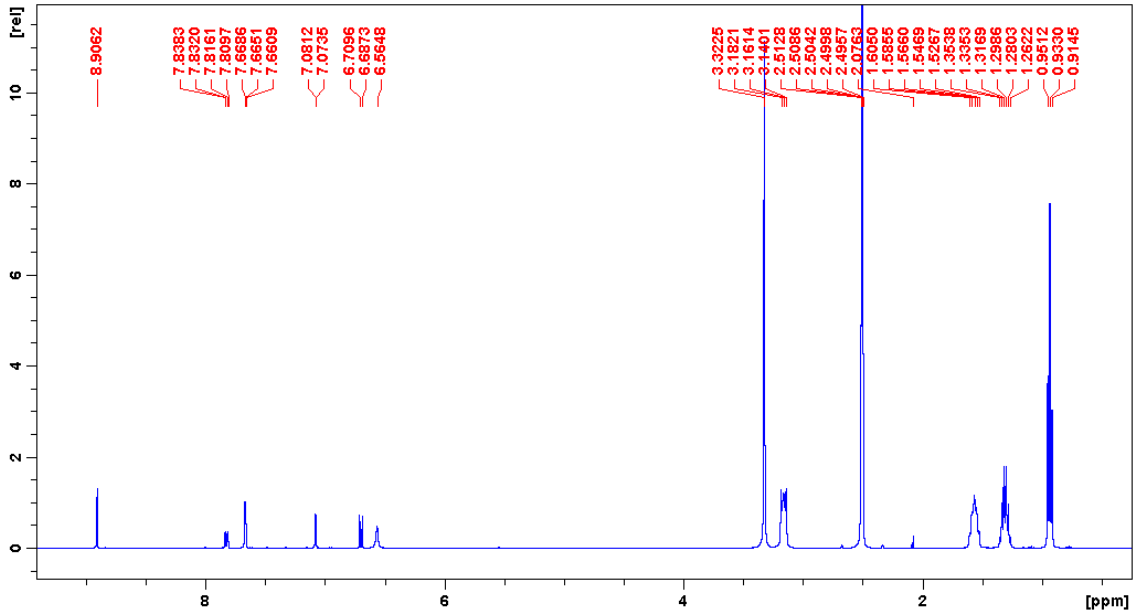
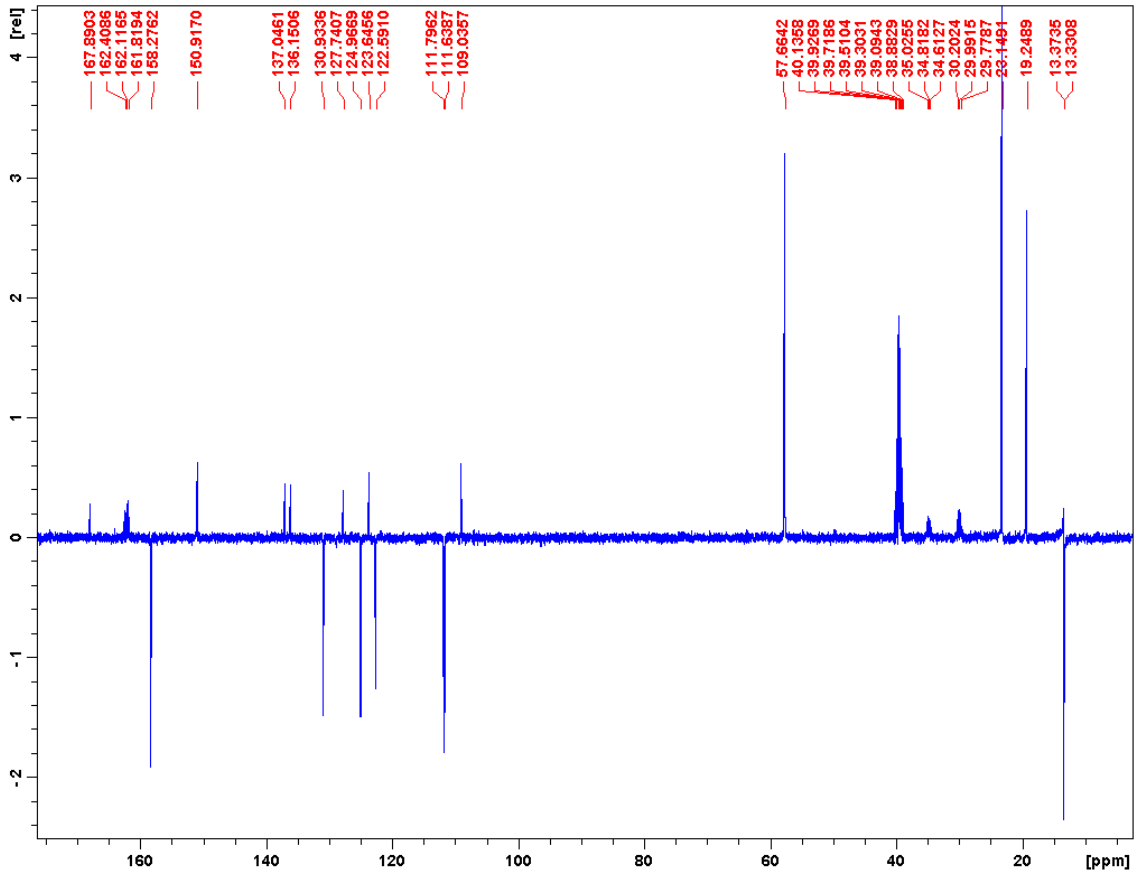


4b

To a suspension of Zn(salphen) **4a** (171.1 mg, 0.304 mmol) in CH_3CN (5 mL) was added a solution of NBu_4OH (0.6 mL of a 1 M solution in MeOH) and the mixture shortly shaken at rt. The red reaction mixture was then filtered after 10 min. and the filtrate first kept at rt to give a first fraction of red crystals (48.0 mg). From the mother liquor another crop was obtained (36.2 mg) by cooling to -30ºC. Total yield: 84.2 mg (0.148 mmol, 49% based on **4a**). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.91 (s, 1H, CH=N), 7.82 (d, ^3J = 8.9 Hz, ^4J = 2.5 Hz, 1H, ArH), 7.66-7.67 (m, 2H, ArH), 7.08 (d, ^4J = 3.1 Hz, 1H, ArH), 6.89 (d, ^3J = 8.9 Hz, 1H, ArH), 6.56 (br s, 2H, NH_2), 3.14-3.18 (m, 8H, NBu), 1.53-1.61 (m, 8H, NBu), 1.26-1.35 (m, 8H, NBu), 0.93 (t, ^3J = 7.3 Hz, 12H, NBu). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6 + 10% DMF-d_7): δ = 167.89, 158.28, 150.92, 137.05, 136.15, 130.93, 127.74, 124.97, 123.65, 122.59, 111.79, 111.64, 109.04, 57.66, 23.15, 19.25, 13.33. MS (ESI−, MeOH): *m/z* = 323.9 $(M - NBu_4)^-$ (calcd. 324.0). Anal. calcd. for $C_{29}H_{44}Cl_2N_4O_3 \cdot 2/3H_2O$: C 60.09, H 7.88, N 9.67; Found: C 60.02, H 7.73, N 9.91.

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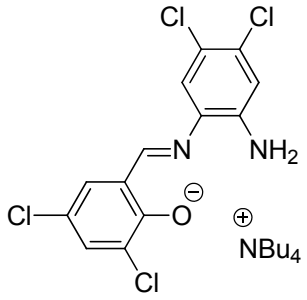
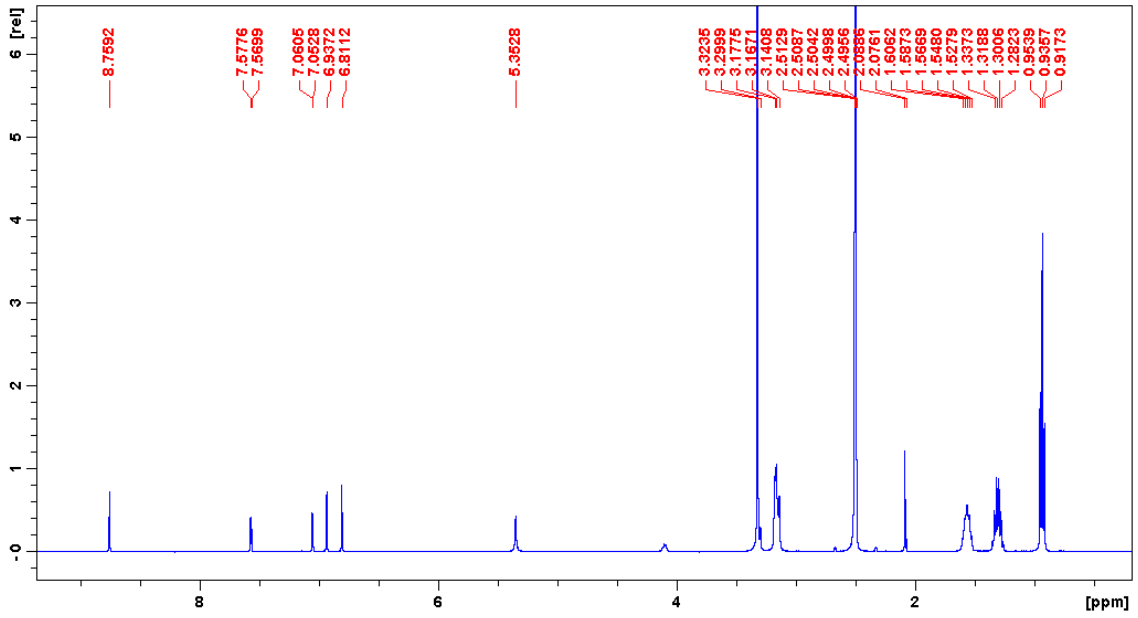
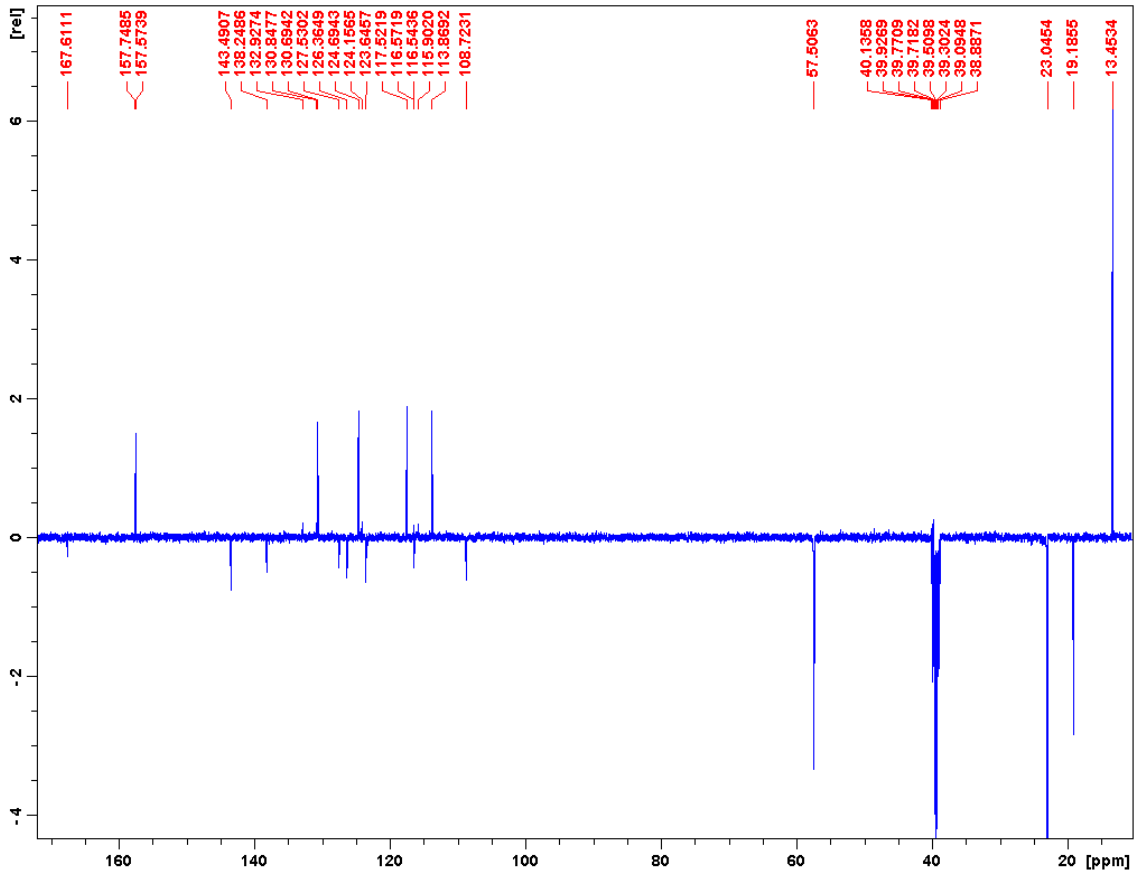


5b

To a suspension of Zn(salphen) **5a** (147.8 mg, 0.252 mmol) in CH_3CN (7 mL) was added a solution of NBu_4OH (0.5 mL of a 1 M solution in MeOH) and the mixture shortly shaken at rt. The yellow reaction mixture was then filtered after 10 min. and the filtrate concentrated and cooled to -30ºC to yield 114.0 mg of orange crystals (0.193 mmol, 76% based on **5a**). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.76 (s, 1H, CH=N), 7.57 (d, ^4J = 3.1 Hz, 1H, ArH), 7.06 (d, ^4J = 3.1 Hz, 1H, ArH), 6.94 (s, 1H, ArH), 6.81 (s, 1H, ArH), 5.35 (br s, 2H, NH_2), 3.14-3.18 (m, 8H, NBu), 1.53-1.61 (m, 8H, NBu), 1.27-1.36 (m, 8H, NBu), 0.94 (t, ^3J = 7.3 Hz, 12H, NBu). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ = 167.61, 157.57, 143.49, 138.25, 130.69, 127.53, 126.36, 124.69, 123.65, 117.52, 116.54, 113.89, 108.72, 57.51, 23.04, 19.19, 13.45. MS (ESI–, MeOH): *m/z* = 348.9 $(M - NBu_4)^-$ (calcd. 348.9). Anal. calcd. for $C_{29}H_{44}Cl_4N_3O$: C 58.89, H 7.33, N 7.10; Found: C 58.87, H 7.57, N 7.08.

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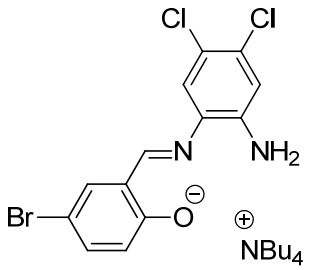
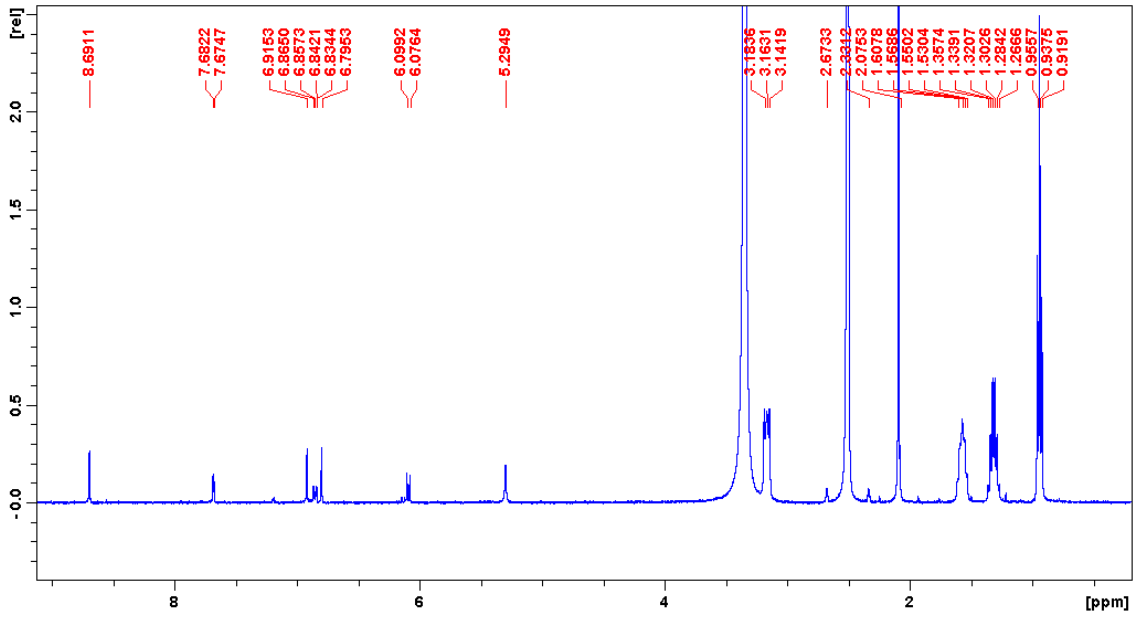
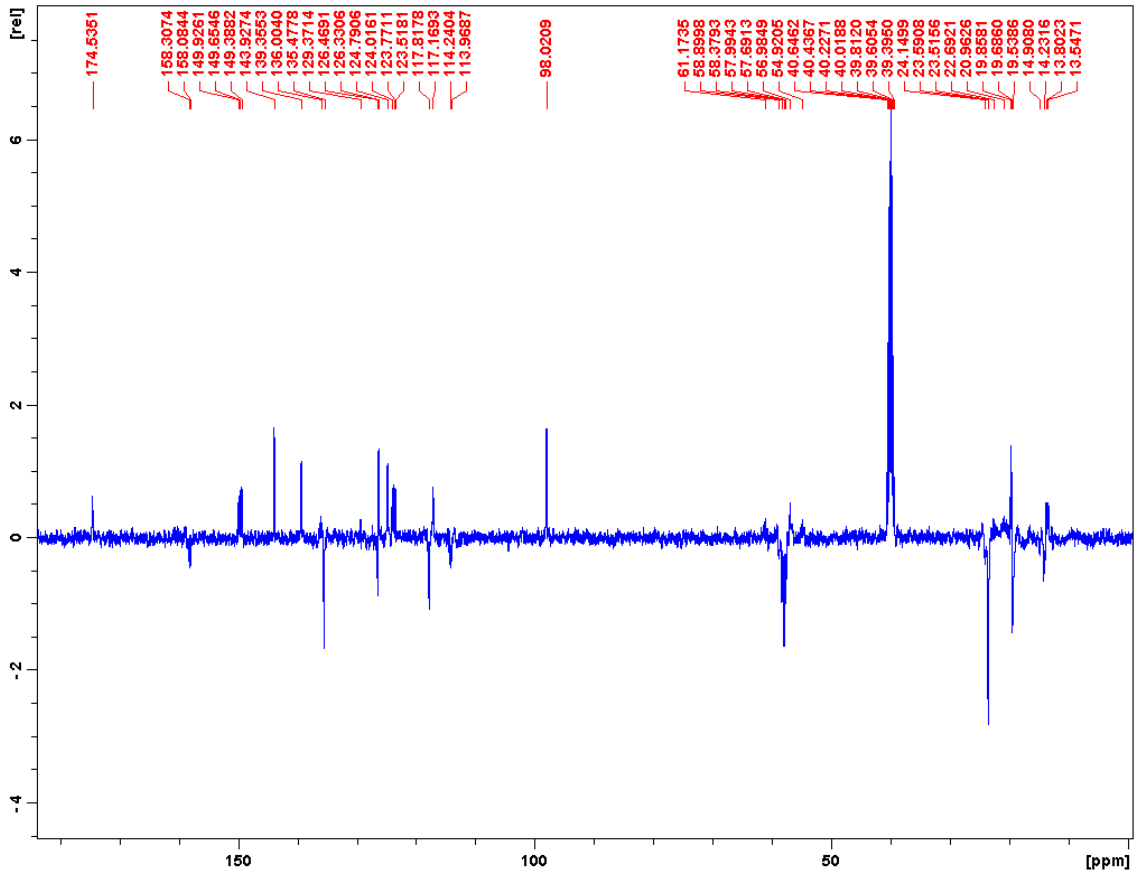


6b

To a suspension of Zn(salphen) **6a** (156.7 mg, 0.258 mmol) in CH_3CN (8 mL) was added a solution of NBu_4OH (0.6 mL of a 1 M solution in MeOH) and the mixture shortly shaken at rt. The yellow reaction mixture was then filtered after 10 min. and the orange filtrate concentrated and cooled to -30ºC to yield 90.9 mg of orange crystals (0.151 mmol, 59% based on **6a**). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.69 (s, 1H, CH=N), 7.68 (d, ^4J = 3.0 Hz, 1H, ArH), 6.92 (s, 1H, ArH), 6.85 (d, ^3J = 9.2 Hz, ^4J = 3.1 Hz, 1H, ArH), 6.80 (s, 1H, ArH), 6.08 (d, ^3J = 9.1 Hz, 1H, ArH), 5.29 (br s, 2H, NH_2), 3.14-3.18 (m, 8H, NBu), 1.53-1.61 (m, 8H, NBu), 1.27-1.36 (m, 8H, NBu), 0.94 (t, ^3J = 7.3 Hz, 12H, NBu). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ = 173.93, 157.67, 143.27, 138.84, 134.95, 128.83, 125.87, 124.31, 118.00, 117.43, 116.69, 114.00, 113.70, 97.61, 57.53, 23.05, 19.20, 13.44. MS (ESI–, MeOH): *m/z* = 358.9 $(M - NBu_4)^-$ (calcd. 358.9). Anal. calcd. for $C_{29}H_{44}Cl_2BrN_3O{\cdot}½H_2O$: C 57.05, H 7.43, N 6.88; Found: C 57.15, H 7.59, N 6.84.

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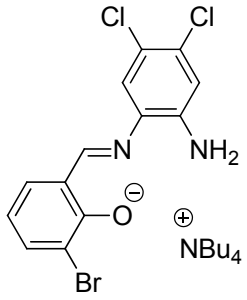
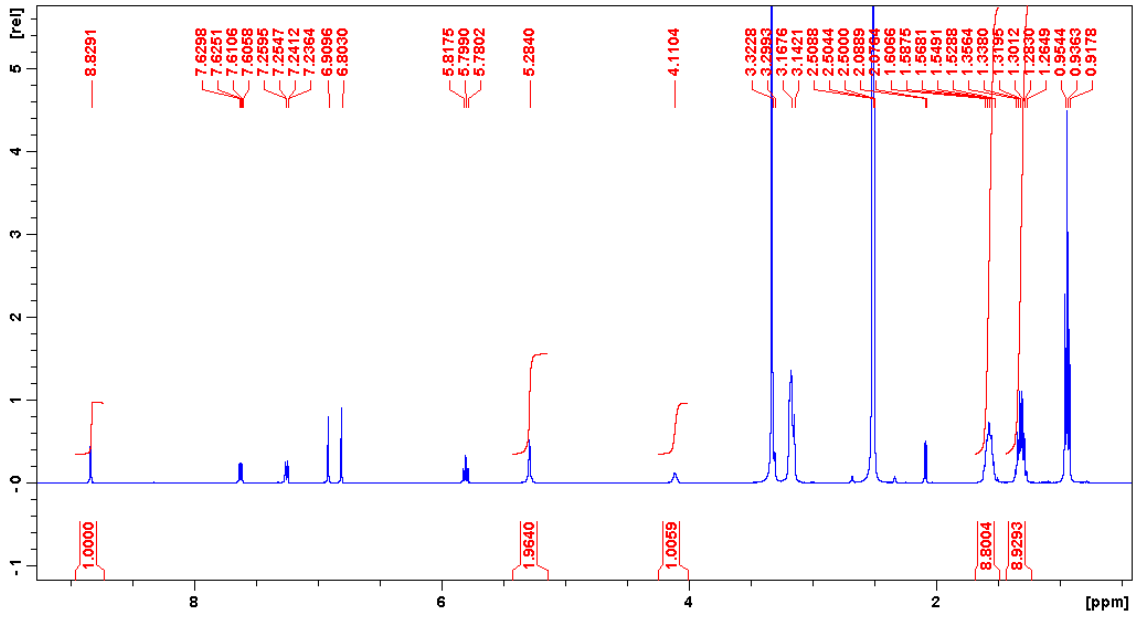
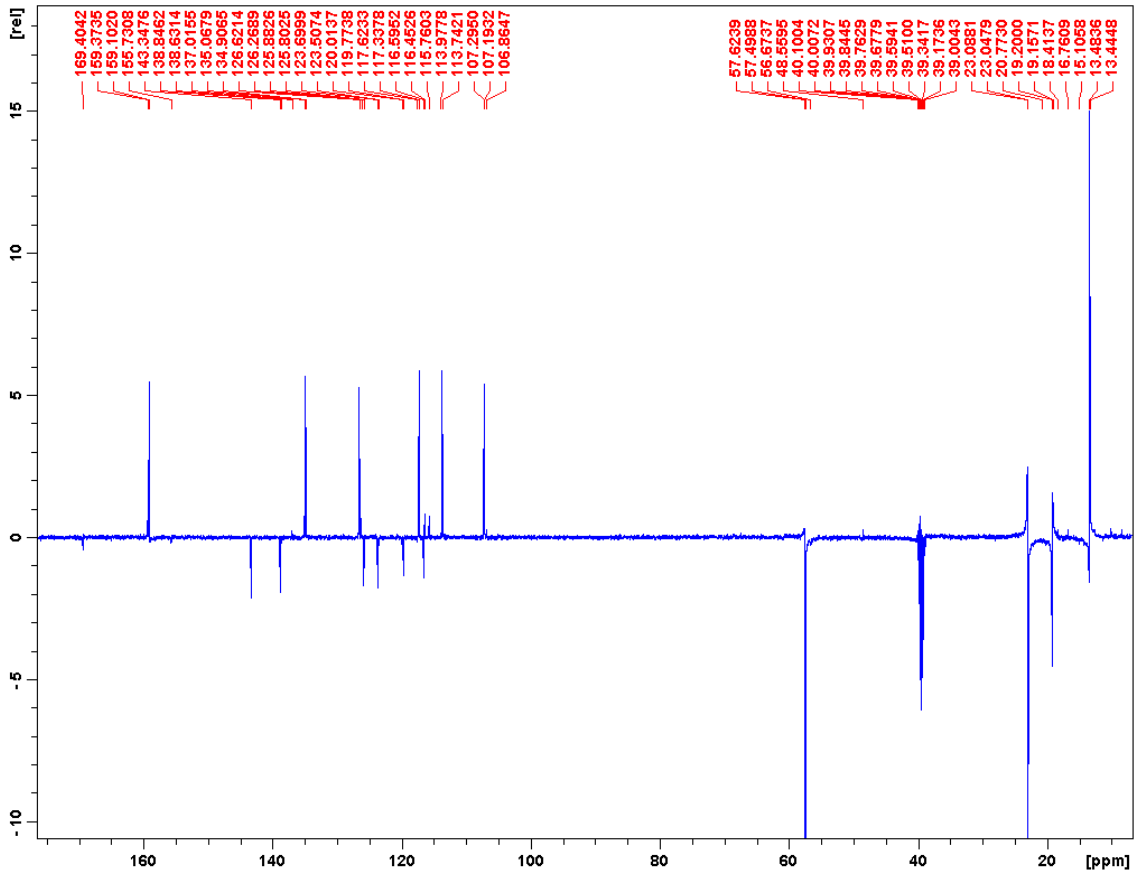


7b

To a suspension of Zn(salphen) **7a** (154.7 mg, 0.255 mmol) in CH_3CN (6 mL) was added a solution of NBu_4OH (0.5 mL of a 1 M solution in MeOH) and the mixture shortly shaken at rt. The yellow reaction mixture was then filtered after 10 min. and the orange filtrate concentrated and cooled to -30ºC to yield 102.2 mg of orange crystals (0.170 mmol, 67% based on **7a**). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.83 (s, 1H, CH=N), 7.62 (d, ^3J = 7.7 Hz, ^4J = 1.9 Hz, 1H, ArH), 7.25 (d, ^3J = 7.3 Hz, ^4J = 1.9 Hz, 1H, ArH), 6.91 (s, 1H, ArH), 6.80 (s, 1H, ArH), 5.80 (t, ^3J = 7.5 Hz, 1H, ArH), 5.28 (br s, 2H, NH_2), 3.14-3.17 (m, 8H, NBu), 1.53-1.61 (m, 8H, NBu), 1.26-1.36 (m, 8H, NBu), 0.94 (t, ^3J = 7.3 Hz, 12H, NBu). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ = 169.40, 159.10, 143.35, 134.90, 126.62, 125.80, 123.70, 119.77, 117.34, 116.60, 115.76, 113.74, 107.19, 57.50, 23.05, 19.16, 13.44. MS (ESI–, MeOH): *m/z* = 358.9 $(M - NBu_4)^-$ (calcd. 358.9). Anal. calcd. for $C_{29}H_{44}Cl_2BrN_3O$: C 57.91, H 7.37, N 6.99; Found: C 57.44, H 7.70, N 6.86.

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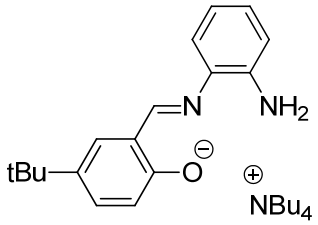
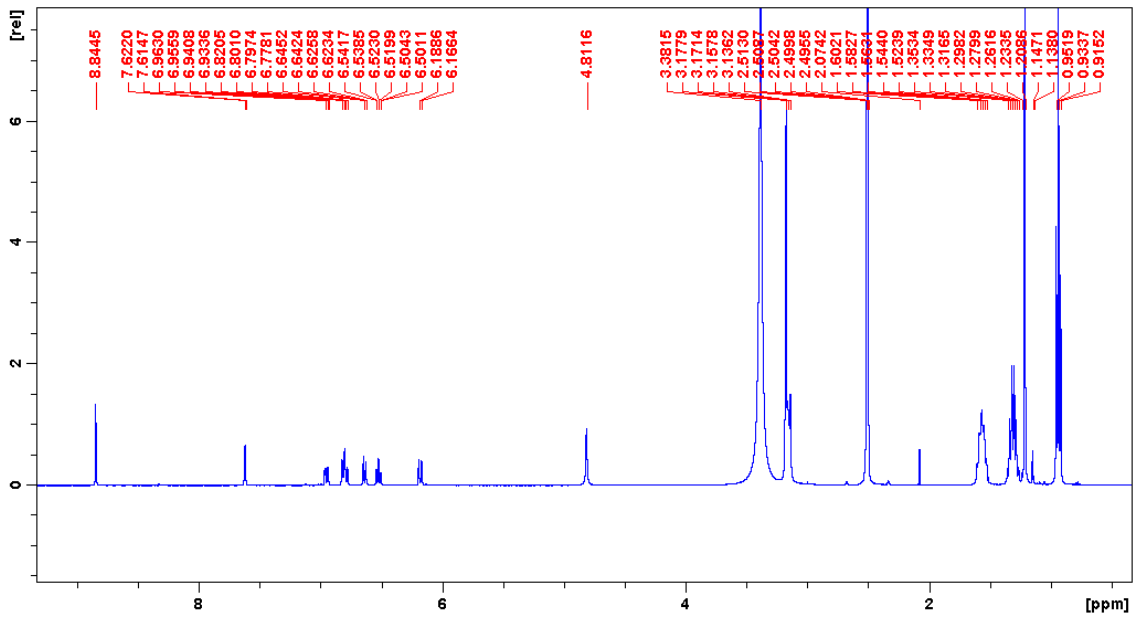
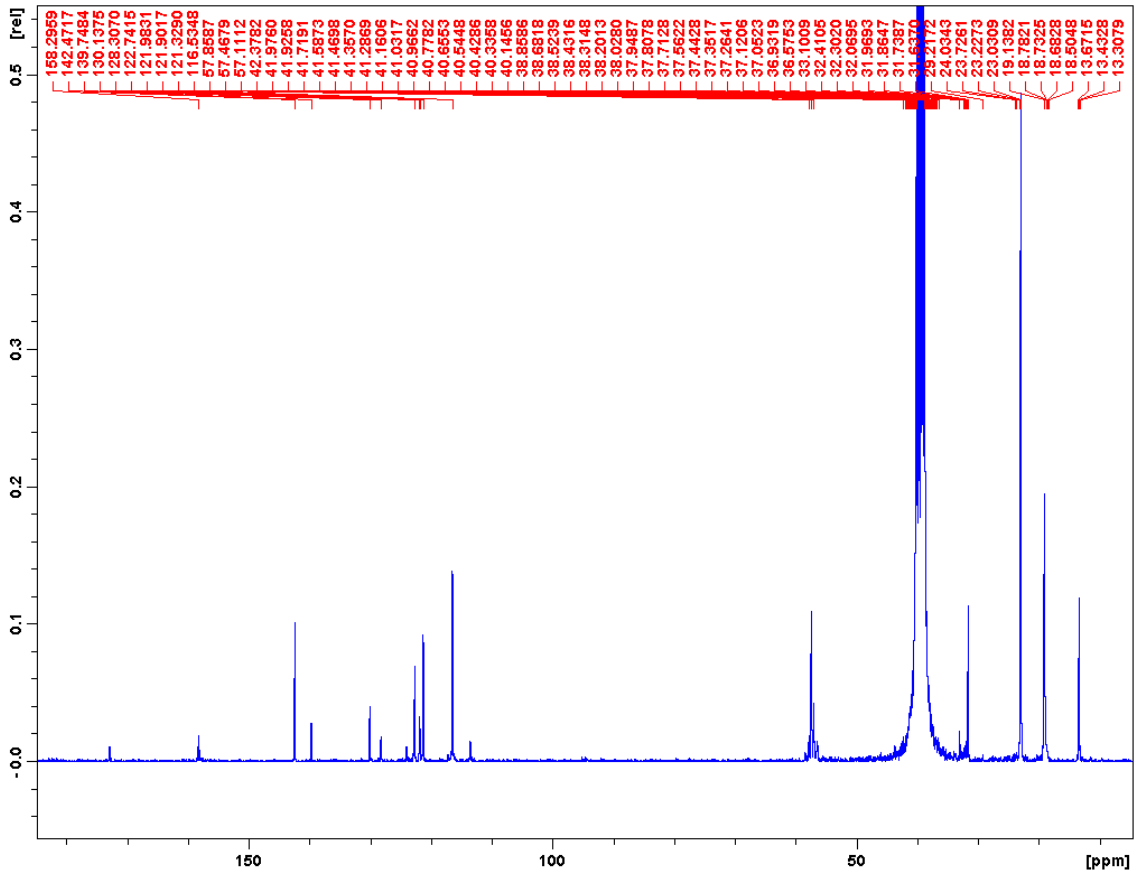


8b

To a suspension of Zn(salphen) **8a** (0.41 g, 0.833 mmol) in CH_3CN (10 mL) was added a solution of NBu_4OH (1.0 mL of a 1 M solution in MeOH) and the mixture shortly shaken at rt. Then another portion of NBu_4OH was added (1.5 mL) and the mixture shortly warmed. The yellow reaction mixture was filtered after 15 min. and the yellow/orange filtrate concentrated and cooled to -30ºC to yield 187.3 mg of orange crystals (0.367 mmol, 44% based on **8a**). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.84 (s, 1H, CH=N), 7.62 (d, ^4J = 2.9 Hz, 1H, ArH), 6.94 (d, ^3J = 8.9 Hz, ^4J = 2.8 Hz, 1H, ArH), 6.80 (m, 2H, ArH), 6.63 (d, ^3J = 7.7 Hz, ^4J = 1.1 Hz, 1H, ArH), 6.52 (t, ^3J = 7.5 Hz, ^4J = 1.3 Hz, 1H, ArH), 6.17 (d, ^3J = 8.9 Hz, 1H, ArH), 4.81 (br s, 2H, NH_2), 3.14-3.18 (m, 8H, NBu), 1.52-1.60 (m, 8H, NBu), 1.26-1.35 (m, 8H, NBu), 1.21 (s, 9H, $C(CH_3)_3$), 0.93 (t, ^3J = 7.3 Hz, 12H, NBu). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ = 172.93, 158.30, 142.47, 139.75, 130.14, 128.31, 124.07, 122.74, 121.98, 121.90, 121.33, 116.53, 113.60, 57.47, 31.64, 23.03, 19.14, 13.43. MS (ESI–, MeOH): *m/z* = 267.1 (M – NBu_4)$^-$ (calcd. 267.1). Anal. calcd. for $C_{33}H_{55}N_3O{\cdot}H_2O$: C 75.09, H 10.88, N 7.96; Found: C 74.79, H 10.73, N 7.85.

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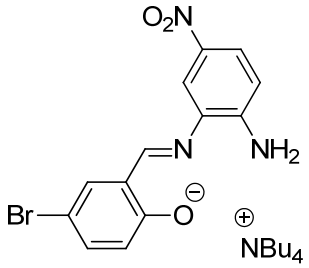
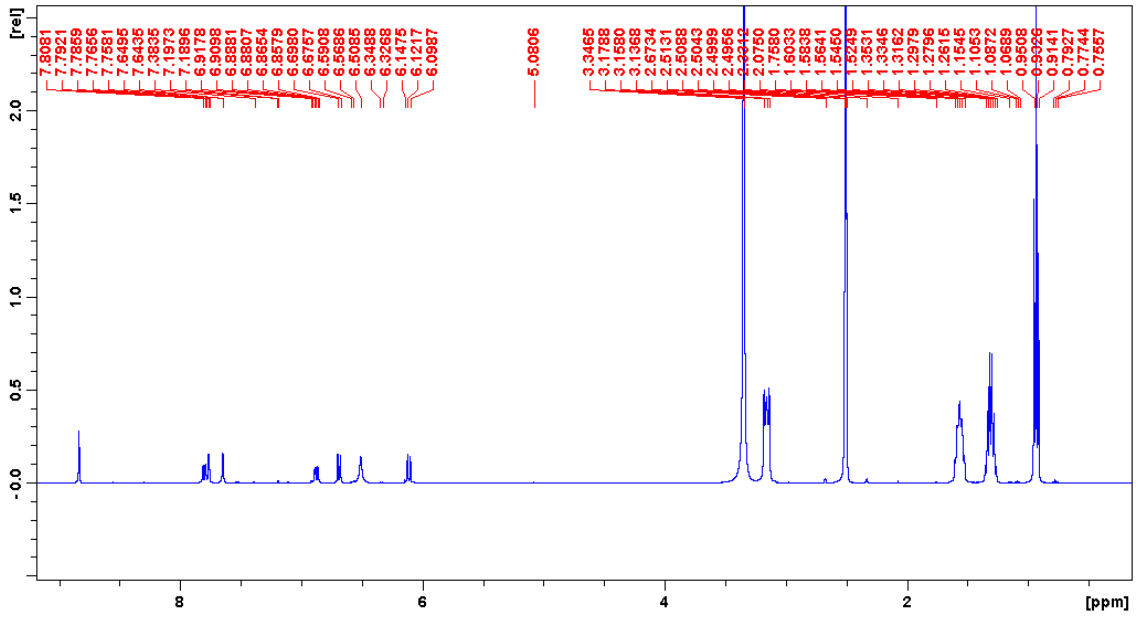
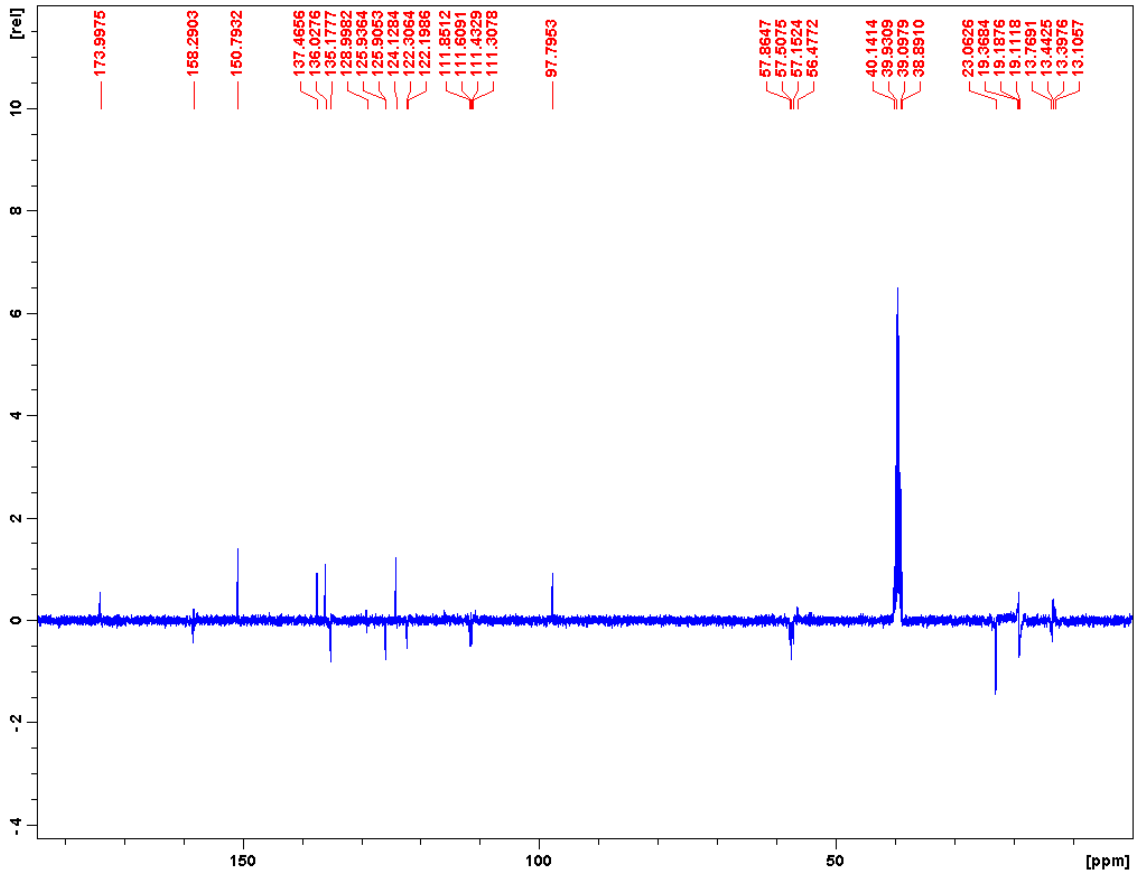


9b

To a suspension of Zn(salphen) **9a** (142.2 mg, 0.244 mmol) in CH_3CN (6 mL) was added a solution of NBu_4OH (0.6 mL of a 1 M solution in MeOH) and the mixture shortly shaken at rt. Then the red-brown mixture was filtered after 10 min. and the filtrate concentrated and cooled to -30ºC to yield 75.2 mg of red/brown crystals (0.130 mmol, 53% based on **9a**). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.83 (s, 1H, CH=N), 7.80 (d, ^3J = 8.9 Hz, ^4J = 2.5 Hz, 1H, ArH), 7.76 (d, ^4J = 3.0 Hz, 1H, ArH), 7.65 (d, ^4J = 2.4 Hz, 1H, ArH), 6.87 (d, ^3J = 9.1 Hz, ^4J = 3.0 Hz, 1H, ArH), 6.68 (d, ^3J = 8.9 Hz, 1H, ArH), 6.51 (br s, 2H, NH_2), 6.11 (d, ^3J = 9.2 Hz, 1H, ArH), 3.14-3.18 (m, 8H, NBu), 1.52-1.60 (m, 8H, NBu), 1.26-1.35 (m, 8H, NBu), 0.93 (t, ^3J = 7.3 Hz, 12H, NBu). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ = 173.80, 158.29, 150.79, 137.47, 136.03, 135.18, 128.30, 125.93, 125.91, 124.13, 122.31, 111.43, 97.80, 57.51, 23.06, 19.11, 13.44. MS (ESI–, MeOH): *m/z* = 335.9 $(M - NBu_4)^-$ (calcd. 336.0). Anal. calcd. for $C_{29}H_{45}BrN_4O_3 \cdot 1.5H2O$: C 57.61, H 8.00, N 9.27; Found: C 57.38, H 7.75, N 8.75.

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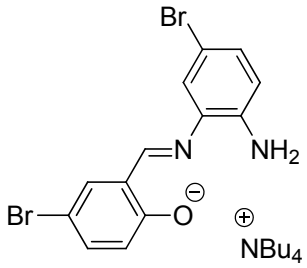
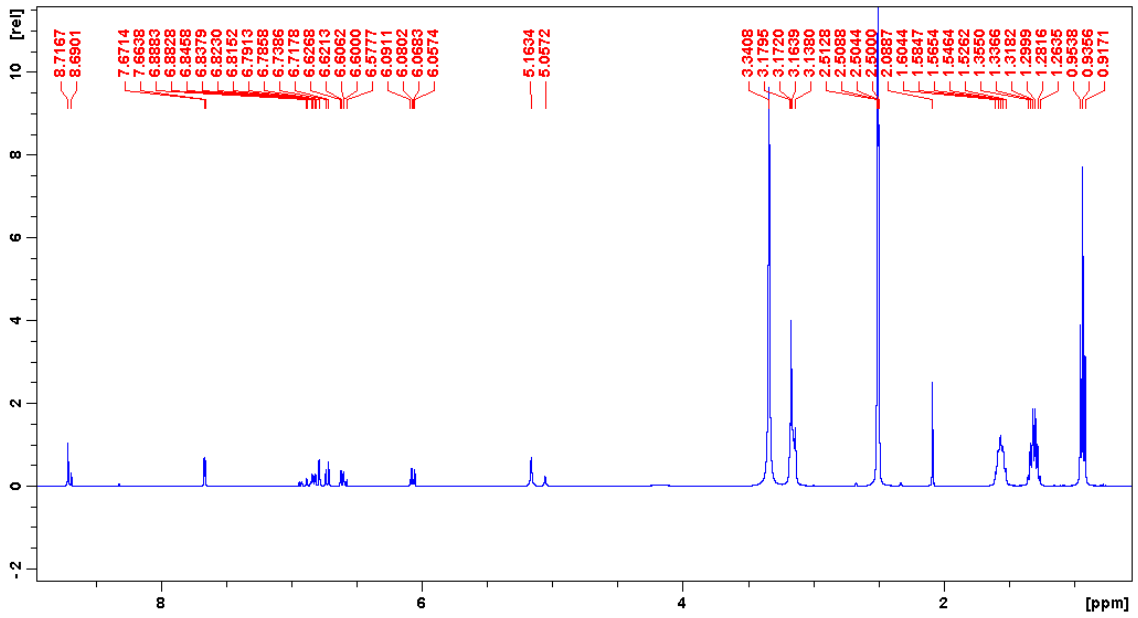
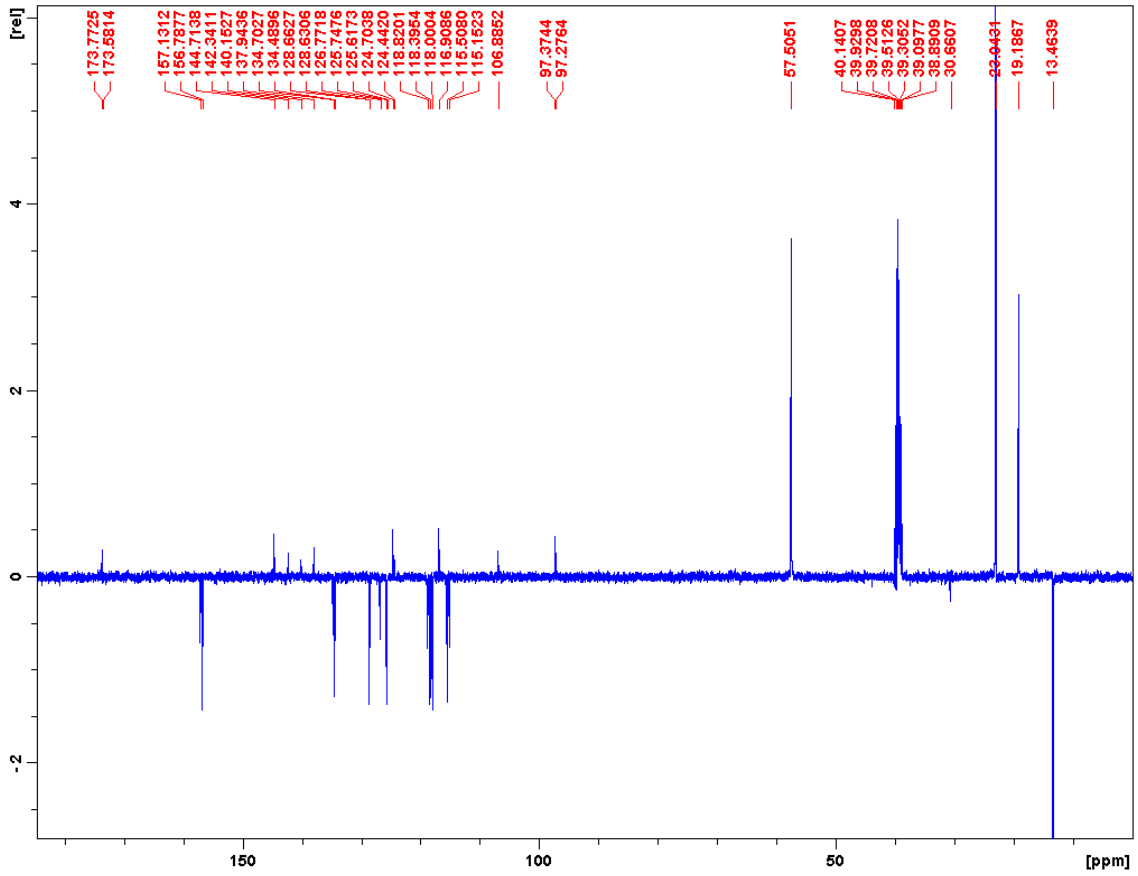


10b

To a suspension of Zn(salphen) **10a** (148.7 mg, 0.241 mmol) in CH_3CN (5 mL) was added a solution of NBu_4OH (0.6 mL of a 1 M solution in MeOH) and the mixture shortly shaken at rt. Then the yellow/orange mixture was filtered after 5 min. and the filtrate concentrated and cooled to -30ºC to yield 61.1 mg of yellow/orange crystals (0.0999 mmol, 41% based on **10a**). The compound is isolated as a mixture of isomers where the position of the bromine atom in the aromatic bridging fragment is either *meta* or *para* with respect to the imine N. The NMR data for the major isomer is reported. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.72 (s, 1H, CH=N), 7.67 (d, ^4J = 3.0 Hz, 1H, ArH), 6.81 (d, ^3J = 9.1 Hz, ^4J = 3.2 Hz, 1H, ArH), 6.79 (d, ^4J = 2.2 Hz, 1H, ArH), 6.72 (d, ^3J = 8.3 Hz, 1H, ArH), 6.61 (d, ^3J = 8.4 Hz, ^4J = 2.2 Hz, 1H, ArH), 6.07 (d, ^3J = 9.1 Hz, 1H, ArH), 5.16 (br s, 2H, NH_2), 3.14-3.18 (m, 8H, NBu), 1.53-1.60 (m, 8H, NBu), 1.26-1.36 (m, 8H, NBu), 0.94 (t, ^3J = 7.3 Hz, 12H, NBu). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ = 173.58, 156.79, 144.71, 137.94, 134.49, 128.63, 125.62, 124.70, 118.40, 118.00, 115.51, 106.89, 97.28, 57.51, 23.04, 19.19, 13.46. HRMS (ESI–, MeOH): calcd for $C_{29}H_{45}Br_2N_3O$: 366.9082; found: 366.9094. MS (ESI–, MeOH): *m/z* = 368.8 $(M - NBu_4)^-$ (calcd. 368.9). Anal. calcd. for $C_{29}H_{45}Br_2N_3O{\cdot}H_2O$: C 55.33, H 7.53, N 6.68; Found: C 54.98, H 7.28, N 6.55.

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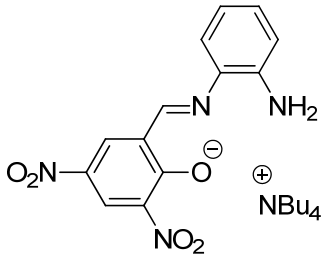
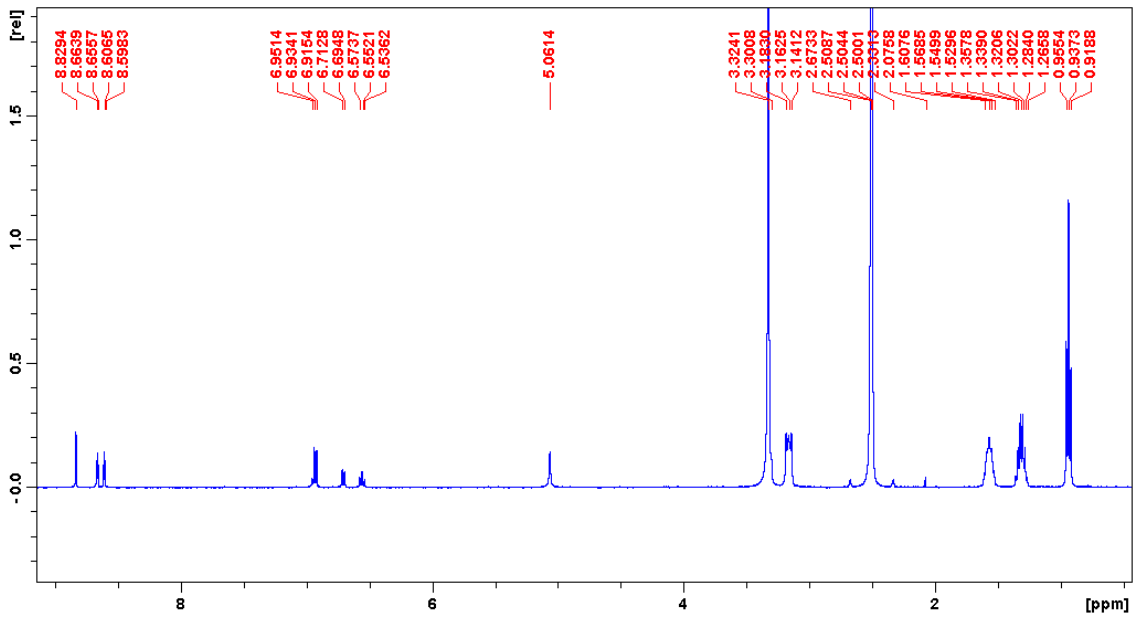
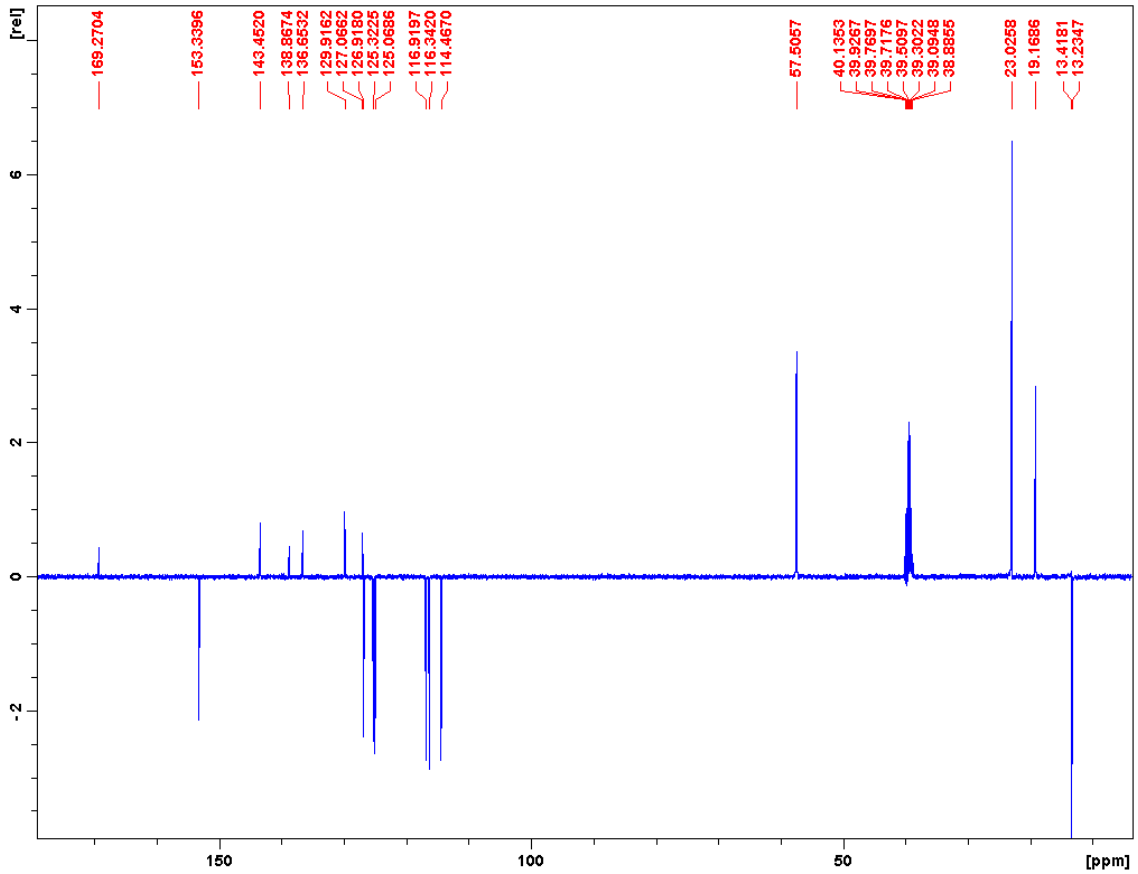


11b

To a suspension of Zn(salphen) **11a** (139.3 mg, 0.249 mmol) in CH_3CN (8 mL) was added a solution of NBu_4OH (0.5 mL of a 1 M solution in MeOH) and the mixture shortly shaken at rt. Then the dark reddish mixture was filtered after 10 min. and the filtrate concentrated and cooled to -30ºC to yield in due course 74.1 mg of dark red-brown crystals (0.136 mmol, 55% based on **11a**). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.83 (s, 1H, CH=N), 8.66 (d, ^4J = 3.3 Hz, 1H, ArH), 8.60 (d, ^4J = 3.3 Hz, 1H, ArH), 6.92-6.95 (m, 2H, ArH), 6.70 (d, ^3J = 7.2 Hz, 1H, ArH), 6.55 (t, ^3J = 7.5 Hz, ^4J = 1.3 Hz, 1H, ArH), 5.06 (br s, 2H, NH_2), 3.14-3.18 (m, 8H, NBu), 1.53-1.61 (m, 8H, NBu), 1.27-1.36 (m, 8H, NBu), 0.94 (t, ^3J = 7.3 Hz, 12H, NBu). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ = 169.27, 153.34, 143.45, 138.87, 136.65, 129.92, 127.07, 126.92, 125.32, 125.07, 116.92, 116.34, 114.47, 57.51, 23.03, 19.17, 13.42. MS (ESI–, MeOH): *m/z* = 301.0 $(M - NBu_4)^-$ (calcd. 301.1). HRMS (ESI–, MeOH): calcd for $C_{29}H_{45}N_5O_5$: 301.0573; found: 301.0584. Anal. calcd. for $C_{29}H_{45}N_5O_5 \cdot 1/3H_2O$: C 63.36, H 8.37, N 12.74; Found: C 63.55, H 8.75, N 12.73.

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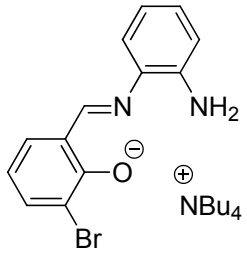
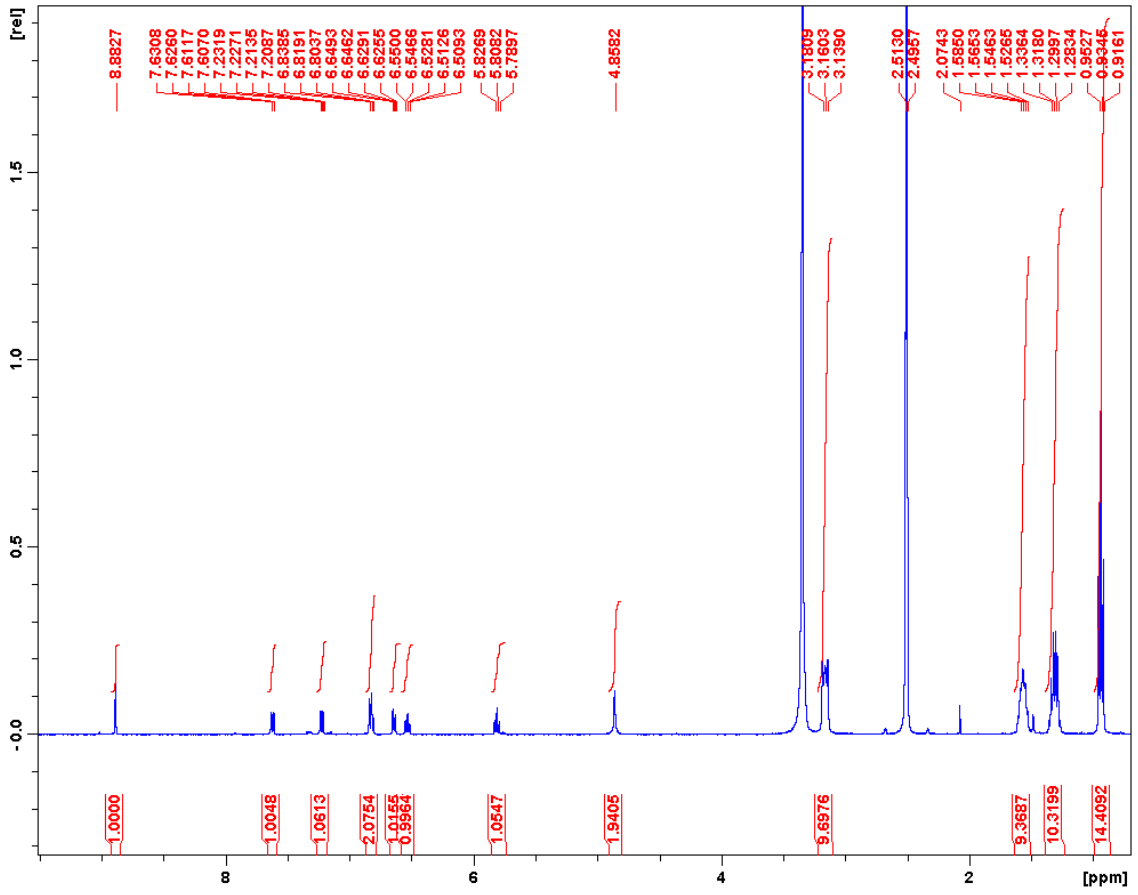


12b

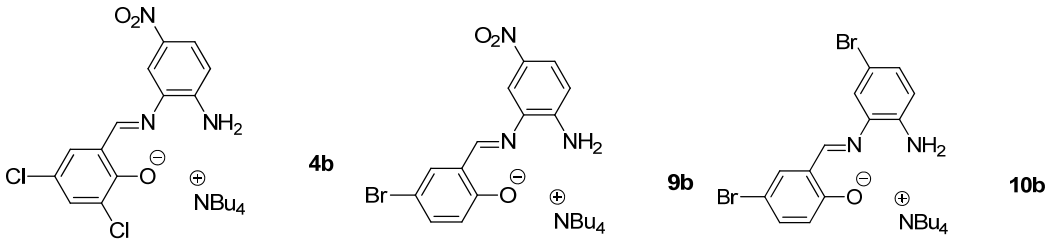
To a suspension of Zn(salphen) **12a** (165.6 mg, 0.290 mmol) in CH_3CN (8 mL) was added a solution of NBu_4OH (0.6 mL of a 1 M solution in MeOH) and the mixture shortly shaken at rt. Then the yellow/orange mixture was filtered after 10 min. and the filtrate concentrated and cooled to -30ºC to yield a first fraction (12.7 mg) of yellow/orange crystals. This fraction was identified as pure **12b**. Hereafter, 2 subsequent fractions were collected and analyzed by 1H NMR but proved to be a mixture of the two possible monoimine salts. Yield of **12b**: 0.0238 mmol (8%). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.88 (s, 1H, CH=N), 7.62 (d, ^3J = 7.6 Hz, ^4J = 1.9 Hz, 1H, ArH), 7.22 (d, ^3J = 7.4 Hz, ^4J = 1.9 Hz, 1H, ArH), 6.80-6.84 (m, 2H, ArH), 6.63 (d, ^3J = 8.2 Hz, ^4J = 1.2 Hz, 1H, ArH), 6.53 (t, ^3J = 7.5 Hz, ^4J = 1.4 Hz, 1H, ArH), 5.81 (t, ^3J = 7.4 Hz, 1H, ArH). MS (ESI−, MeOH): *m/z* = 291.0 $(M - NBu_4)^-$ (calcd. 291.0). Anal. calcd. for $C_{29}H_{46}BrN_3O{\cdot}½H_2O$: C 64.31, H 8.75, N 7.76; Found: C 64.54, H 9.22, N 7.58.[4]

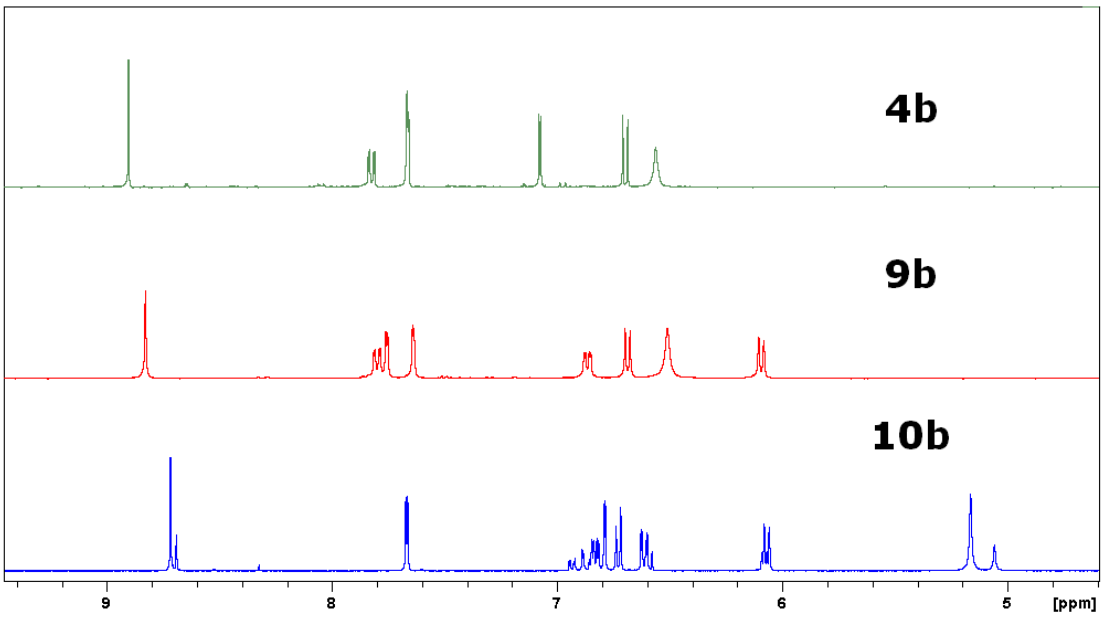


[4] There was not enough material available for a ^{13}C NMR.

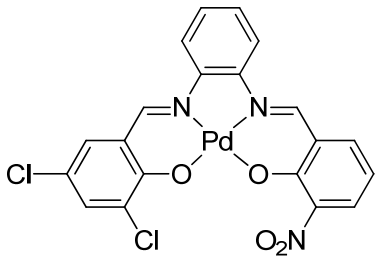
NMR comparison between compounds **4b**, **9b** and **10b**.

In the case of **4b** and **9b** exclusive isolation of one isomer is observed while for **10b** two isomers in an approximate 3:1 ratio is noted; see spectra below. All spectra recorded in DMSO-d_6, only the aromatic region is shown here.



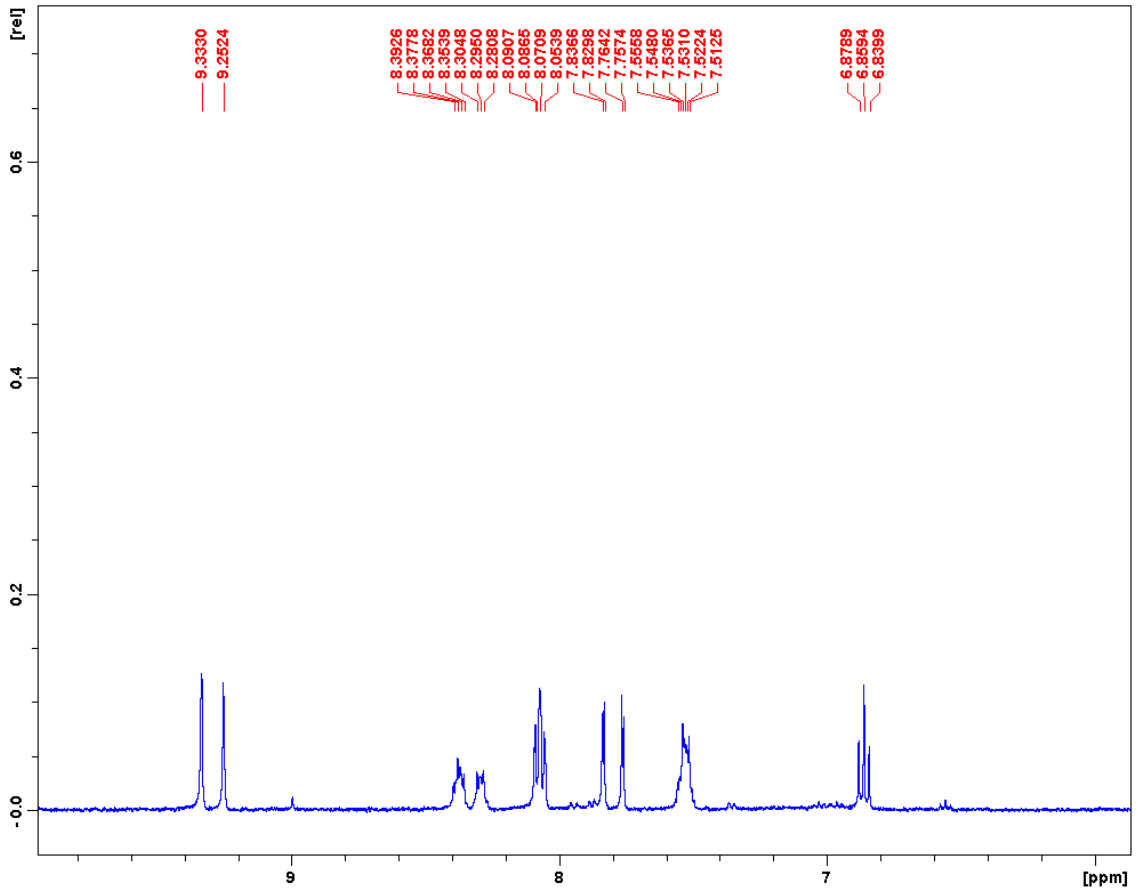


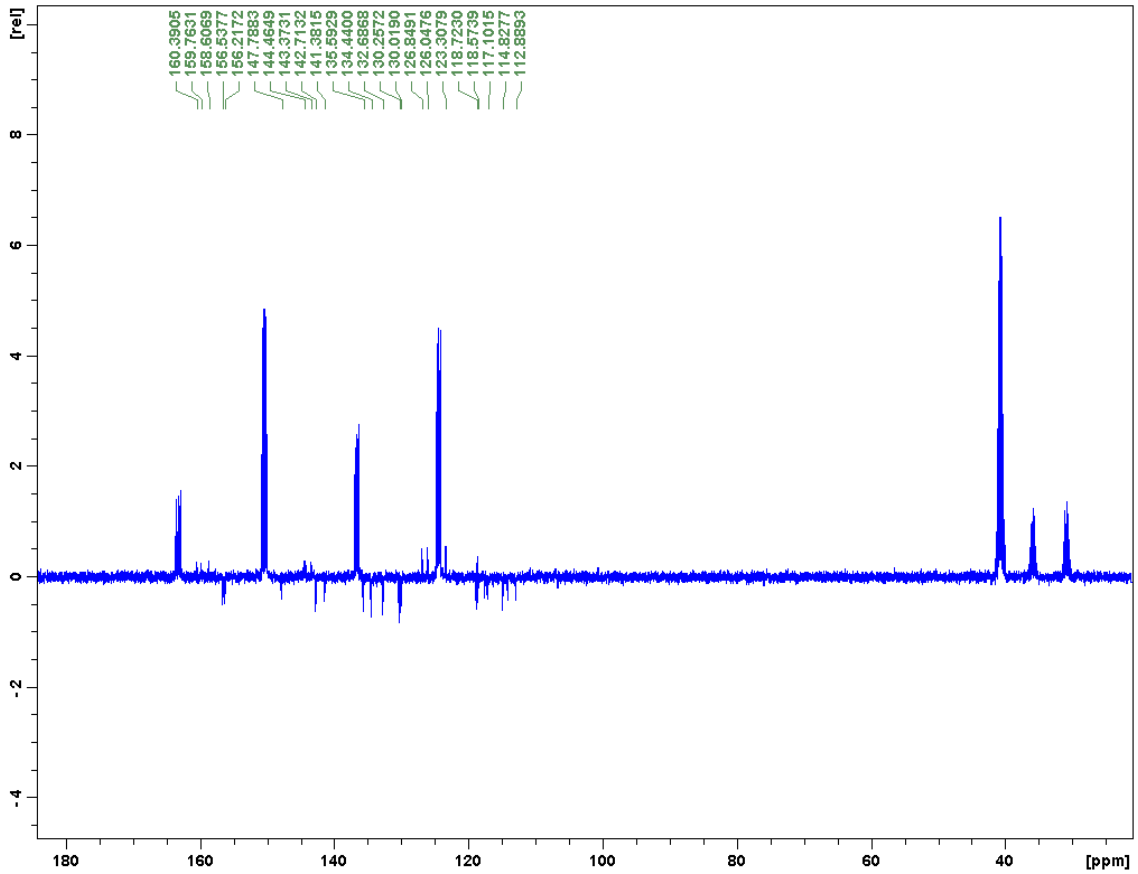
Synthesis of complexes **13-17**.



13

Monoimine salt **1b** (38.9 mg, 0.0780 mmol) was combined with 3,5-dichlorosalicylaldehyde (18.5 mg, 0.0969 mmol) in MeOH (15 mL). Then $Pd(OAc)_2$ (19.6 mg, 0.0873 mmol) disolved in MeOH (5 ml) was added and almost immediately a suspension was obtained. After 1 h, the reaction mixture was filtered yielding an orange/brown solid (29.7 mg, 0.0556 mmol, 71%). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.33 (s, 1H, CH=N), 9.25 (s, 1H, CH=N), 8.35-8.39 (m, 1H, ArH), 8.28-8.30 (m, 1H, ArH), 8.05-8.09 (m, 2H, ArH), 7.83 (d, ^4J = 2.7 Hz, 1H, ArH), 7.76 (d, ^4J = 2.7 Hz, 1H, ArH), 7.51-7.56 (m, 2H, ArH), 6.86 (t, ^3J = 7.8 Hz, 1H, ArH). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6 + 20% pyridine-d_5 + 10% DMF-d_7): δ = 160.39, 159.76, 156.54, 156.22, 147.79, 142.71, 141.38, 135.59, 134.44, 132.69, 130.26, 130.02, 126.85, 126.05, 123.31, 118.72, 118.57, 117.10, 114.83, 112.89. MS (MALDI+, dctb): *m/z* = 535.0 $(M)^+$ (calcd. 535.0). Anal. calcd. for $C_{20}H_{11}Cl_2N_3O_4Pd{\cdot}2H_2O$: C 42.09, H 2.65, N 7.36; Found: C 41.69, H 2.23, N 7.82.

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134.4400
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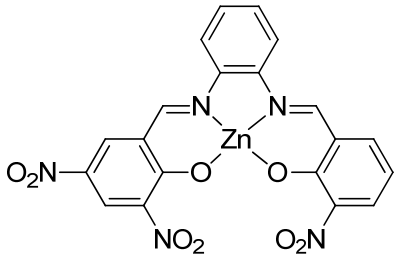
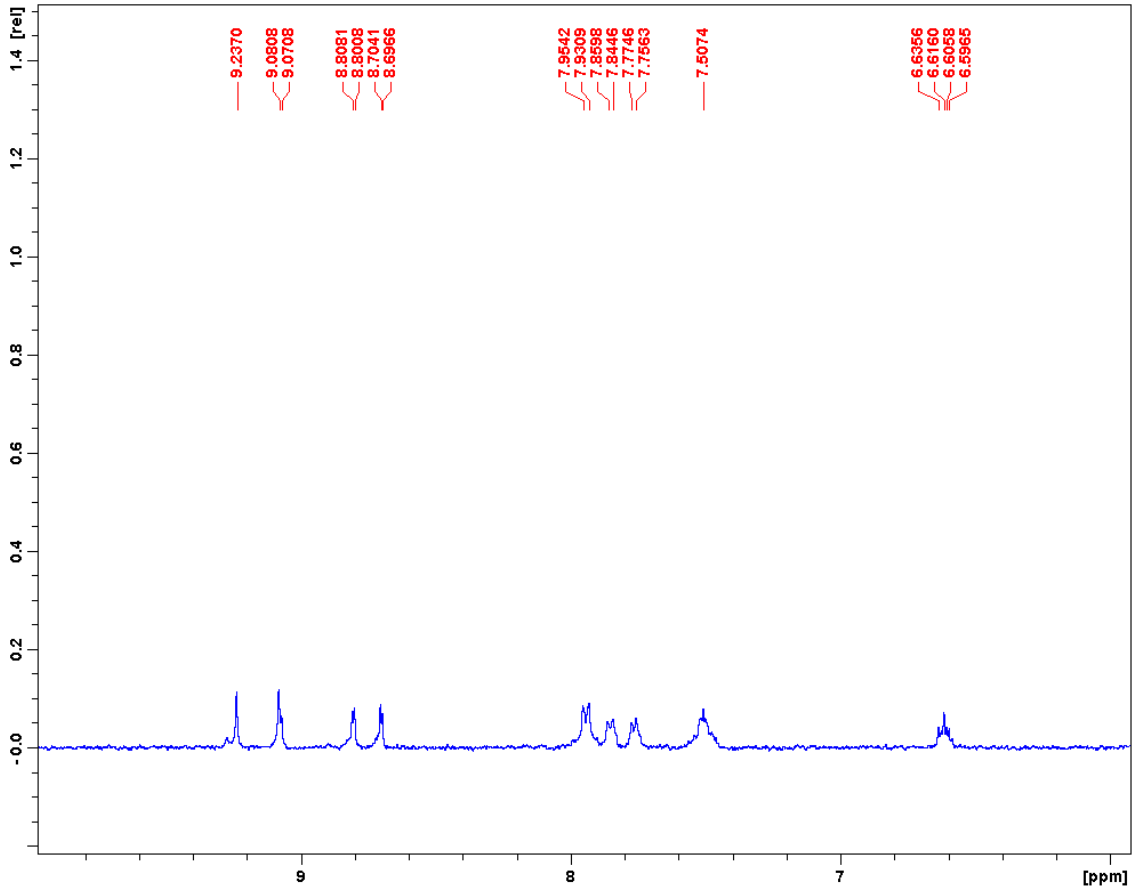
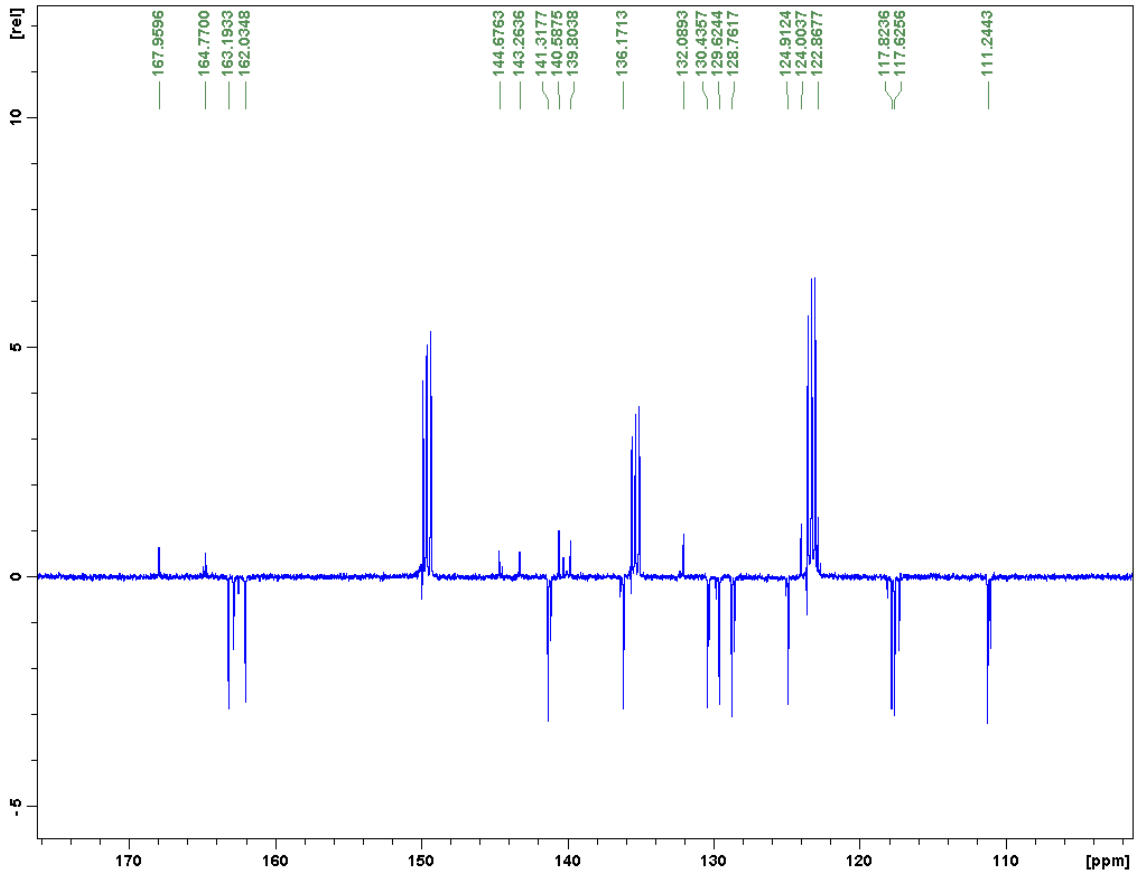


14

Monoimine salt **1b** (60.5 mg, 0.121 mmol) was combined with 3,5-di-nitro-salicylaldehyde (31.7 mg, 0.149 mmol) in MeOH (15 mL). Then $Zn(OAc)_2 \cdot 2H_2O$ (39.3 mg, 0.179 mmol) disolved in MeOH (5 ml) was added and almost immediately an orange suspension was obtained. After 1 h, the reaction mixture was filtered yielding a yellow solid (52.7 mg, 0.102 mmol, 85%). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.24 (s, 1H, CH=N), 9.08 (s, 1H, CH=N), 8.80 (d, ^4J = 2.9 Hz, 1H, ArH), 8.70 (d, ^4J = 2.9 Hz, 1H, ArH), 7.94 (d, ^3J = 9.3 Hz, 2H, ArH), 7.84-7.86 (m, 1H, ArH), 7.74-7.77 (m, 1H, ArH), 7.51 (m, 2H, ArH), 6.62 (t, ^3J = 7.8 Hz, 1H, ArH). ^{13}C {^{1}H} NMR (100 MHz, pyrdine-d_5): δ = 167.96, 164.77, 163.19, 162.03, 144.68, 143.26, 141.32, 140.59, 139.80, 136.17, 132.09, 130.44, 129.62, 128.76, 124.91, 124.00, 122.87, 117.82, 117.63, 111.24. MS (MALDI+, dctb): *m/z* = 513.0 $(M)^+$ (calcd. 513.0), 1028.1 $(2M)^+$ (calcd. 1028.0). HRMS (MALDI+, dctb): calcd for $C_{20}H_{11}N_5O_8Zn$: 512.9905; found: 512.9950. Anal. calcd. for $C_{20}H_{11}N_5O_8Zn \cdot 1.5H_2O$: C 44.34, H 2.60, N 12.93; Found: C 44.33, H 2.54, N 12.14.

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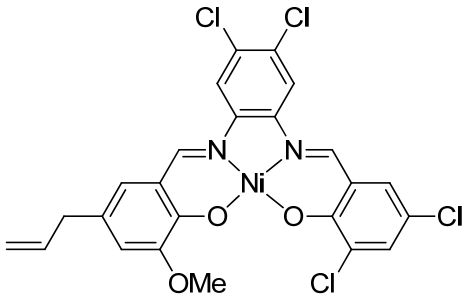
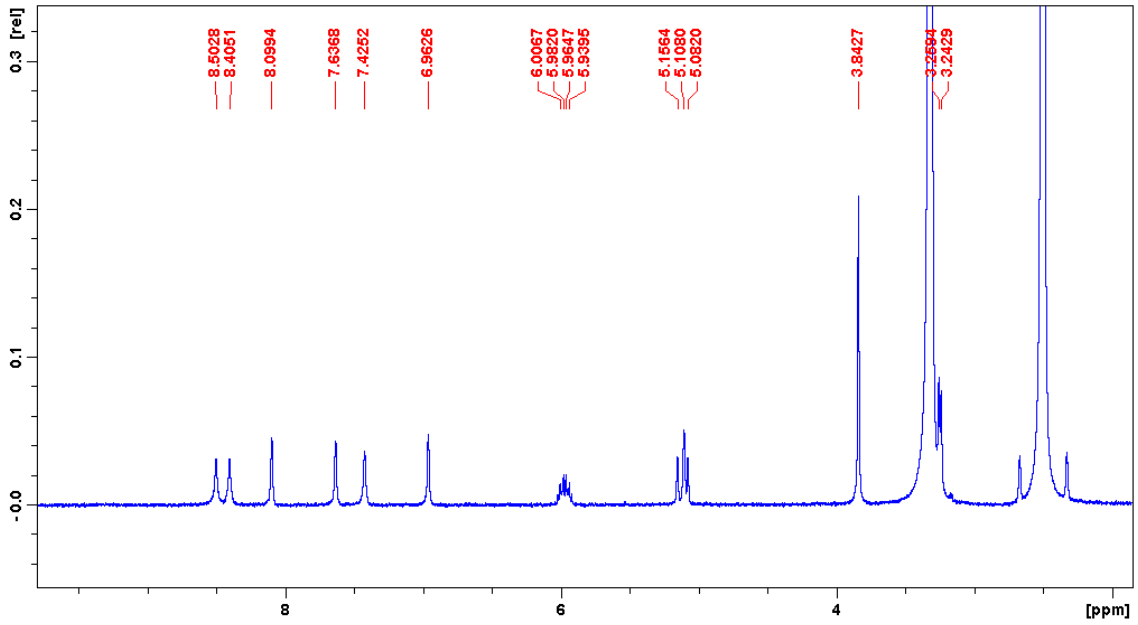
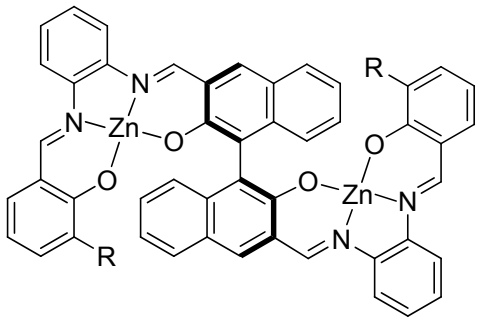


15

Monoimine salt **5b** (41.9 mg, 0.0708 mmol) was combined with 3-methoxy-5-allyl-salicylaldehyde[5] (20.1 mg, 0.105 mmol) in MeOH (20 mL). Then $Ni(OAc)_2 \cdot 4H_2O$ (23.6 mg, 0.0948 mmol) disolved in MeOH (10 ml) was added. In due course a brownish suspension was obtained which was filtered after 45 min to yield a brown solid (30.2 mg, 0.0520 mmol, 73%). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.50 (s, 1H, CH=N), 8.41 (s, 1H, CH=N), 8.10 (s, 1H, ArH), 7.64 (s, 1H, ArH), 7.43 (s, 1H, ArH), 6.96 (s, 1H, ArH), 5.92-6.03 (m, 1H, allyl), 5.08-5.16 (m, 2H, allyl), 3.84 (s, 3H, OMe), 3.25 (d, ^3J = 6.6 Hz, 2H, allyl). A proper ^{13}C NMR could not be obtained because the compound was too insoluble. MS (MALDI+, dctb): *m/z* = 579.9 $(M)^+$ (calcd. 597.9). Anal. calcd. for $C_{24}H_{16}Cl_4N_2O_3Ni \cdot \frac{2}{3}H_2O$: C 48.62, H 2.95, N 4.72; Found: C 48.54, H 3.05, N 4.60.



[5] This reagent is commercially available through ACROS organics.

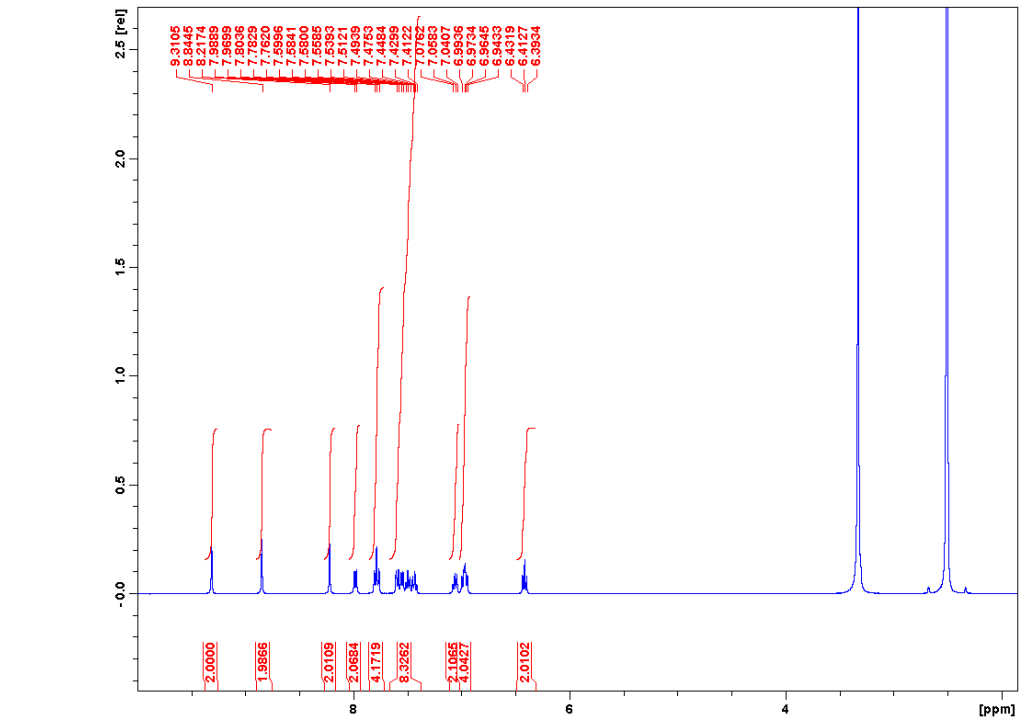


16

R = NO_2

Monoimine salt **1b** (85.1 mg, 0.171 mmol) was combined with (*S*)-3,3′-diformyl-2,2′-dihydroxy-1,10-binaphthalene[6] (27.5 mg, 0.0803 mmol) in MeOH/THF (20/20 mL). Then $Zn(OAc)_2 \cdot 2H_2O$ (46.8 mg, 0.213 mmol) disolved in MeOH (10 ml) was added. In due course an orange suspension was obtained which was filtered after 18 h to yield a red/brown solid (26.3 mg). As second fraction was obtained by concentration and cooling of the mother liquor affording another 24.0 mg of product. Total yield: 50.3 mg (0.0531 mmol, 66% based on the bis-aldehyde reagent). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.31 (s, 2H, CH=N), 8.84 (s, 2H, CH=N), 8.22 (s, 2H, ArH), 7.97 (d, ^3J = 7.6 Hz, 2H, ArH), 7.78 (t, ^3J = 8.3 Hz, 2H, ArH), 7.59 (d, ^3J = 7.9 Hz, ^4J = 1.7 Hz, 2H, ArH), 7.54 (d, ^3J = 7.7 Hz, ^4J = 1.5 Hz, 2H, ArH), 7.49 (t, ^3J = 7.4 Hz, 2H, ArH), 7.43 (t, ^3J = 7.2 Hz, 2H, ArH), 7.04-7.08 (m, 2H, ArH), 6.94-6.99 (m, 4H, ArH), 6.41 (t, ^3J = 7.7 Hz, 2H, ArH). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ = 165.24, 164.85, 163.57, 162.59, 141.56, 141.24, 139.86, 139.60, 137.78, 137.61, 129.63, 129.41, 129.04, 128.24, 127.88, 127.25, 124.85, 124.35, 123.37, 123.23, 119.74, 116.97, 111.08, 110.72. MS (MALDI+, dctb): *m/z* = 947.1 $(M+H)^+$ (calcd. 947.1), 1895.2 $(2M+H)^+$ (calcd. 1895.1). Anal. calcd. for $C_{48}H_{28}N_6O_8Zn_2 \cdot 6H_2O$: C 54.61, H 3.82, N 7.96; Found: C 54.26, H 3.25, N 7.78.

[6] See: Belokon, Y. N.; Chusov, D.; Borkin, D. A.; Yashkina, L. V.; Bolotov, P.; Skrupskaya, T.; North, M. *Tetrahedron Asymm*. **2008**, *19*, 459. Note that we used the (*S*)-isomer of BINOL instead in the synthetic protocol.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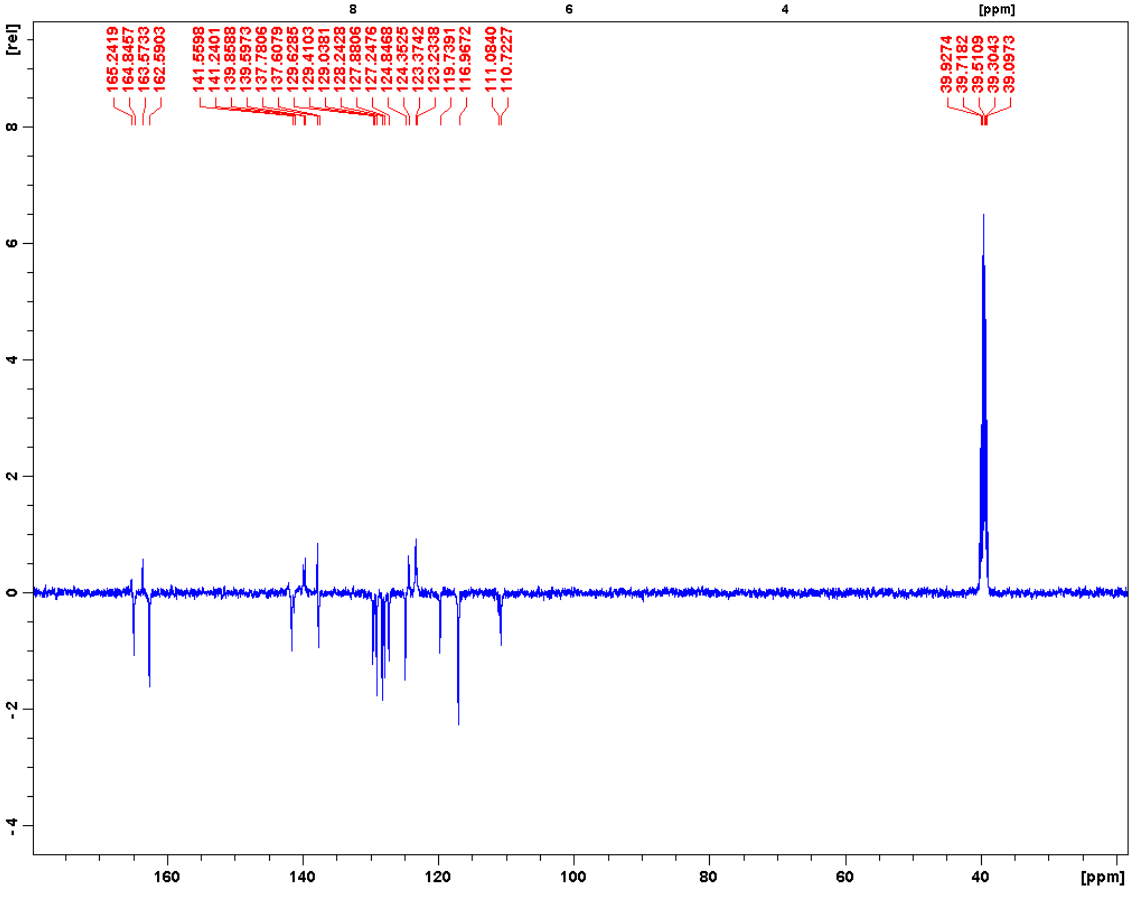
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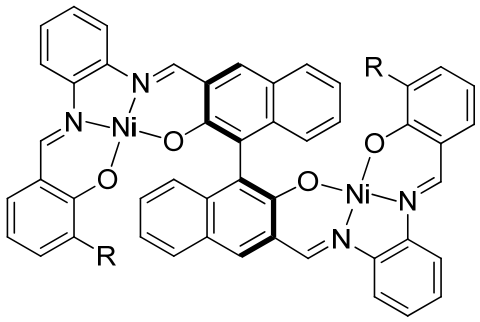
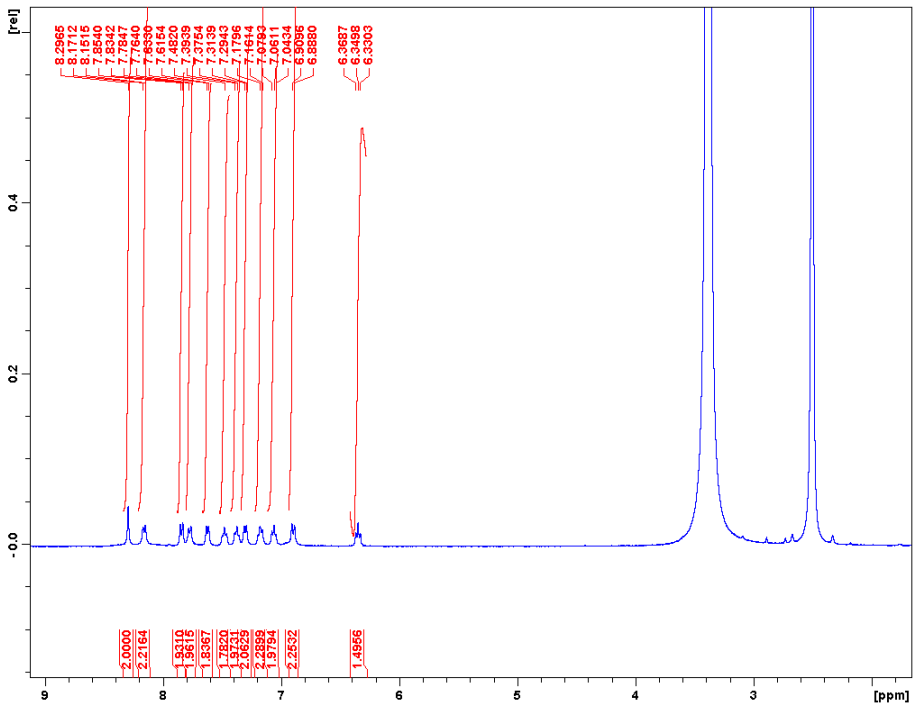


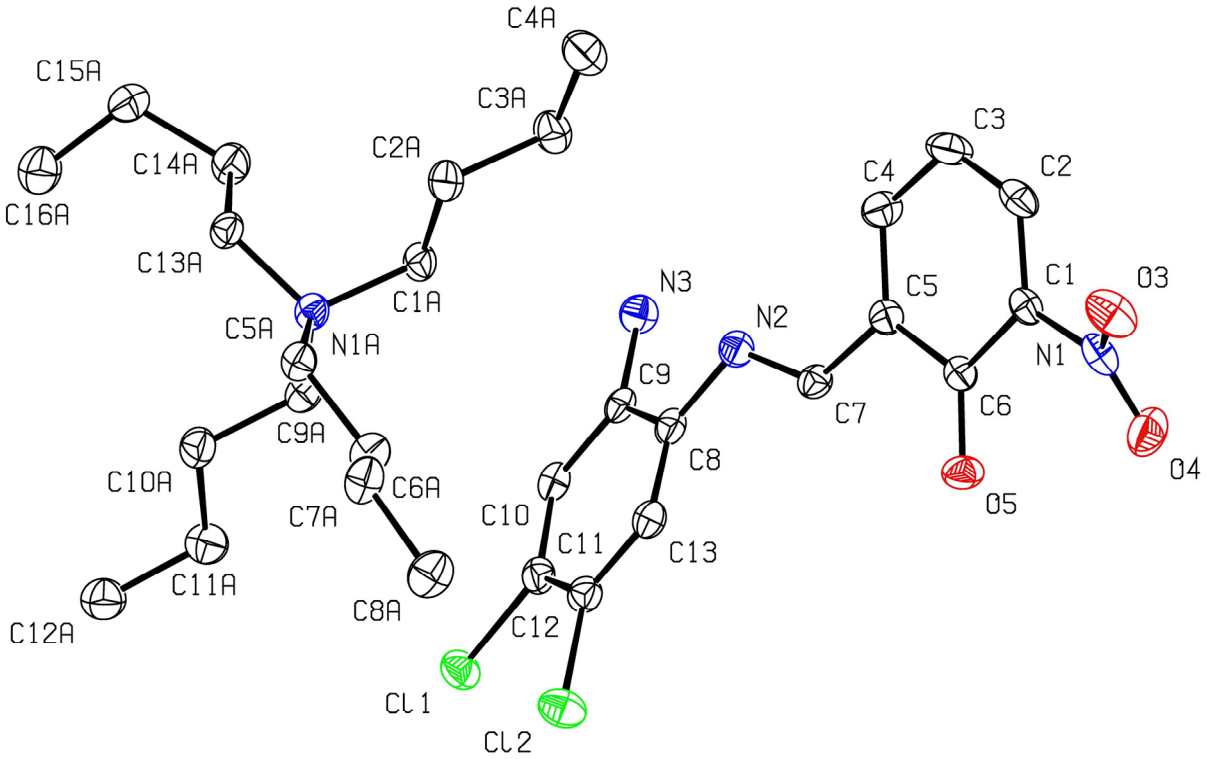
17

Monoimine salt **1b** (79.5 mg, 0.159 mmol) was combined with (*S*)-3,3′-diformyl-2,2′-dihydroxy-1,10-binaphthalene[7] (26.6 mg, 0.0777 mmol) in MeOH/THF (30/20 mL). Then $Ni(OAc)_2 \cdot 4H_2O$ (39.5 mg, 0.159 mmol) disolved in MeOH (10 ml) was added. In due course a precipitate was formed. After 1 h this was collected and analyzed by ^1H NMR. This fraction (16.2 mg) turned out to be a mixture of components, viz. the mono-Ni and bis-Ni complex. The mother liquor was then further stirred for 18 h, to yield a second fraction as a dark brown solid, which turned out to be the desired bis-Ni complex. Yield: 30.5 mg (0.0326 mmol, 42%). ^1H NMR (400 MHz, DMSO-d_6): δ = 8.30 (s, 2H, ArH), 8.17 (s, 2H, CH=N), 8.15 (s, 2H, CH=N), 7.84 (d, ^3J = 7.9 Hz, 2H, ArH), 7.77 (d, ^3J = 8.3 Hz, 2H, ArH), 7.62 (d, ^3J = 7.0 Hz, 2H, ArH), 7.48 (t, ^3J = 7.2 Hz, 2H, ArH), 7.38 (t, ^3J = 7.1 Hz, 2H, ArH), 7.30 (d, ^3J = 7.8 Hz, 2H, ArH), 7.18 (t, ^3J = 7.2 Hz, 2H, ArH), 7.06 (t, ^3J = 7.2 Hz, 2H, ArH), 6.89 (d, ^3J = 8.6 Hz, 2H, ArH), 6.35 (t, ^3J = 7.7 Hz, 2H, ArH). The compound was too insoluble for a proper ^{13}C {^1H} NMR measurement. MS (MALDI+, dctb): *m/z* = 934.0 $(M)^+$ (calcd. 934.1). Anal. calcd. for $C_{48}H_{28}N_6O_8Ni_2 \cdot 2H_2O$: C 59.42, H 3.32, N 8.66; Found: C 59.87, H 3.02, N 8.11.

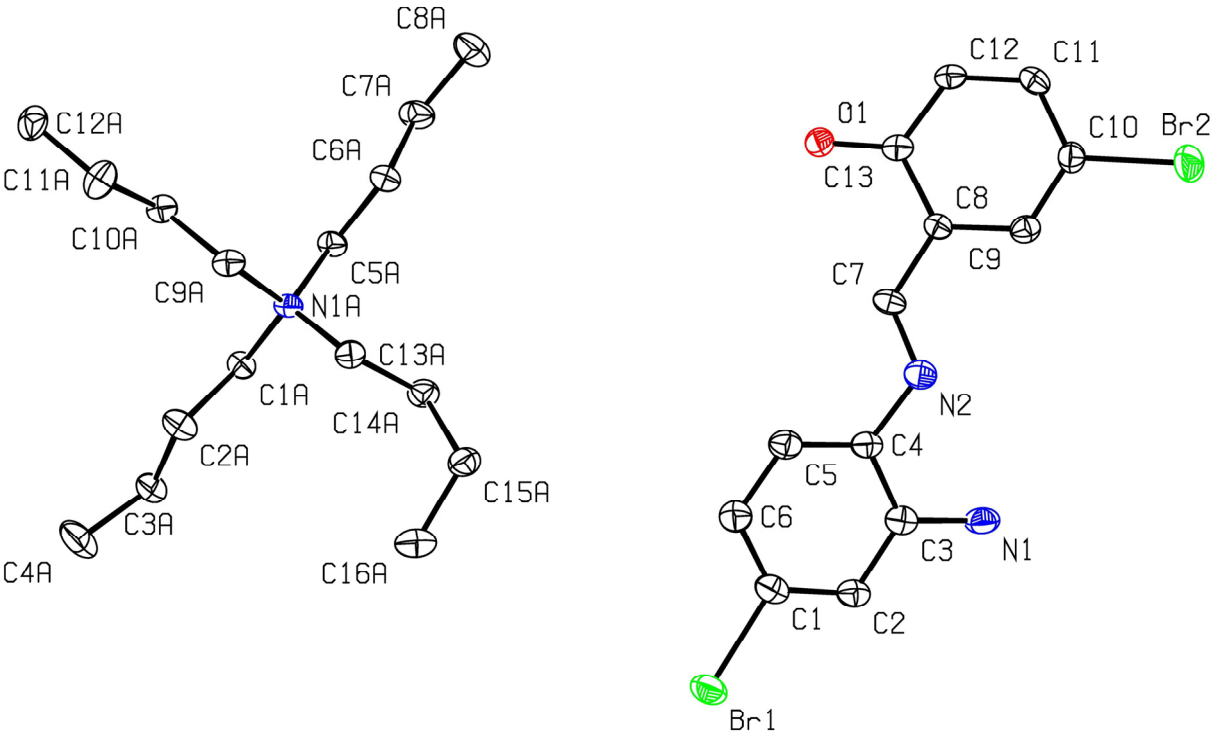


[7] See: Belokon, Y. N.; Chusov, D.; Borkin, D. A.; Yashkina, L. V.; Bolotov, P.; Skrupskaya, T.; North, M. *Tetrahedron Asymm*. **2008**, *19*, 459. Note that we used the (*S*)-isomer of BINOL instead in the synthetic protocol.

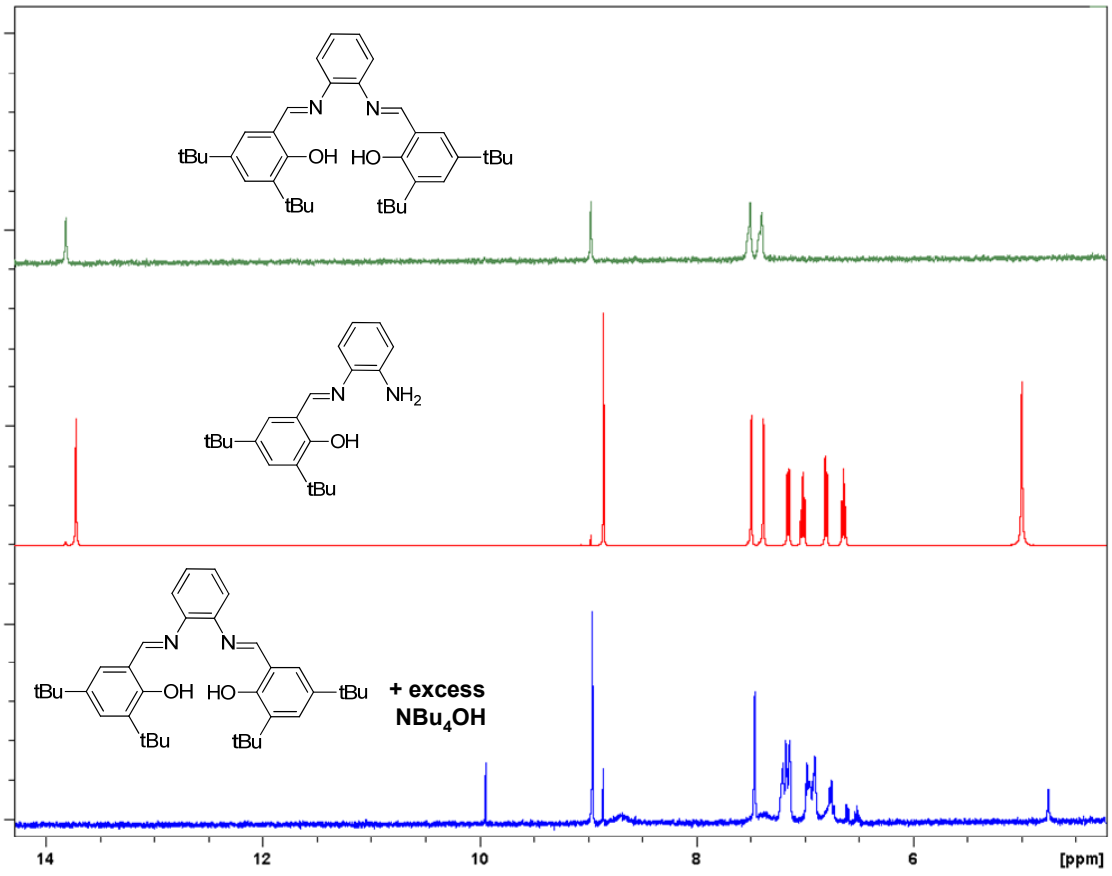
Displacement ellipsoid plot for **2b**.



Displacement ellipsoid plot for **10b**.



NMR investigation of the use of a salphen ligand as substrate.



Solvent used in each case: DMSO-d_6.

The reaction of the salphen ligand with NBu_4OH was carried out as follows: to a mixture of the salphen ligand (153.0 mg, 0.283 mmol) in CH_3CN (5 mL) was added 0.5 mL of NBu_4OH (1M solution in MeOH). A clear red-orange solution was obtained from which some crystalline material separated in due course (an approximate 20 mg). Further cooling did not lead to more crystallization. The solid material was isolated by filtration, dried and subjected to ^1H NMR analysis (see above). The recorded NMR trace was compared with authentic samples of the bis-imine and mono-imine compounds.

Observation:

1. The major component in the reaction product is the starting bis-imine (i.e., the salphen-H_2 ligand).
2. Indication of the formation of some aldehyde is noted (at δ = 10 ppm).
3. Indication of some mono-imine formation (see peak around 4.7 ppm).
4. The isolated product is far from pure and contains (at least) 3 different co-crystallized species.