Electronic Supplementary Material (ESI) for Dalton Transactions


# Supporting Information

# Ligand dissociation/recoordination in fluorescent ionic zinc–salicylideneimine compounds: synthesis, characterization, photophysical properties, and $^{1}$H NMR studies

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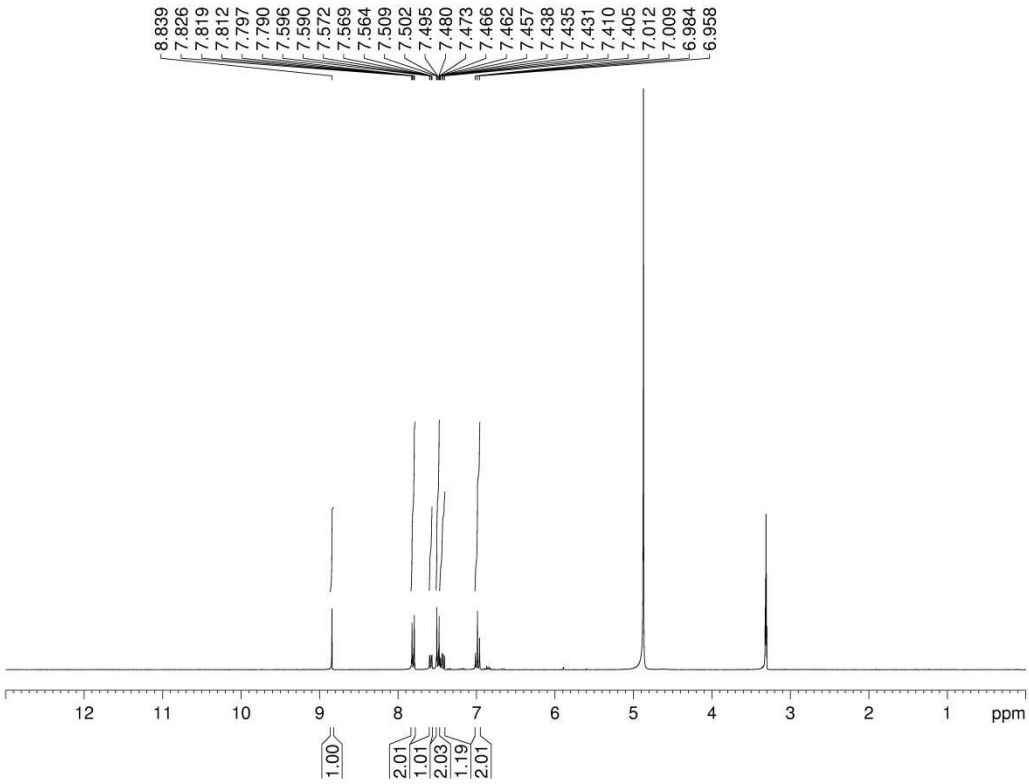
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7.410
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10
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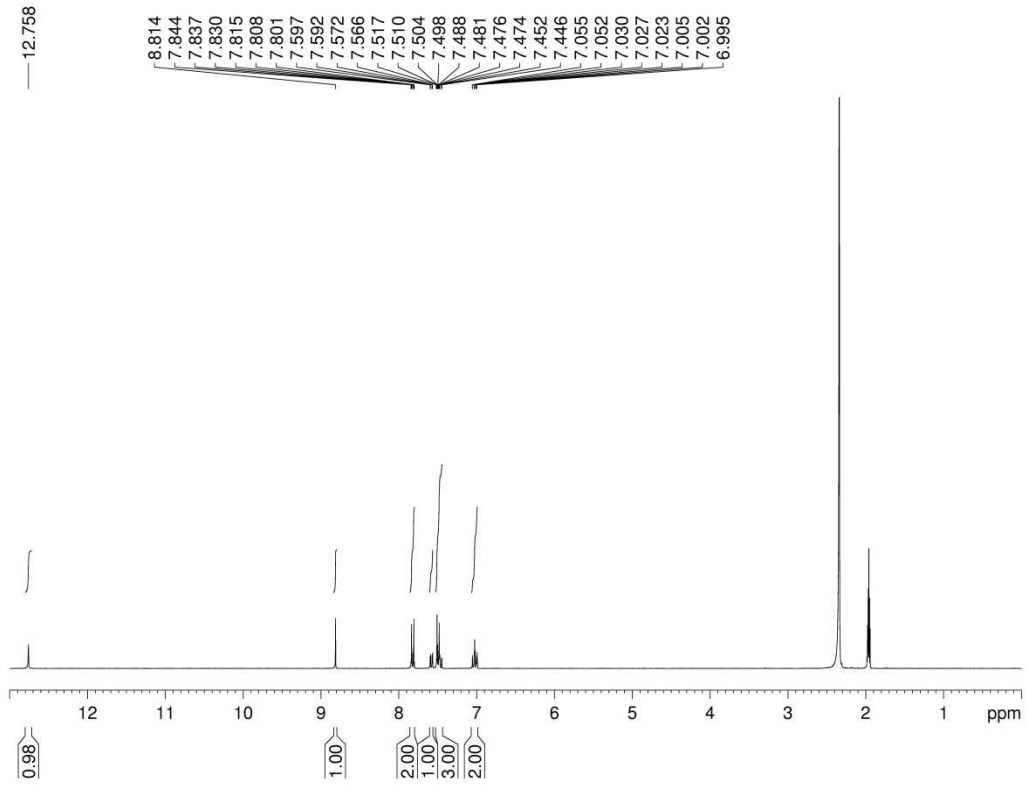
1.01
2.03
1.19
2.01

**(b)**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7.446
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7.030
7.027
7.023
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2.00

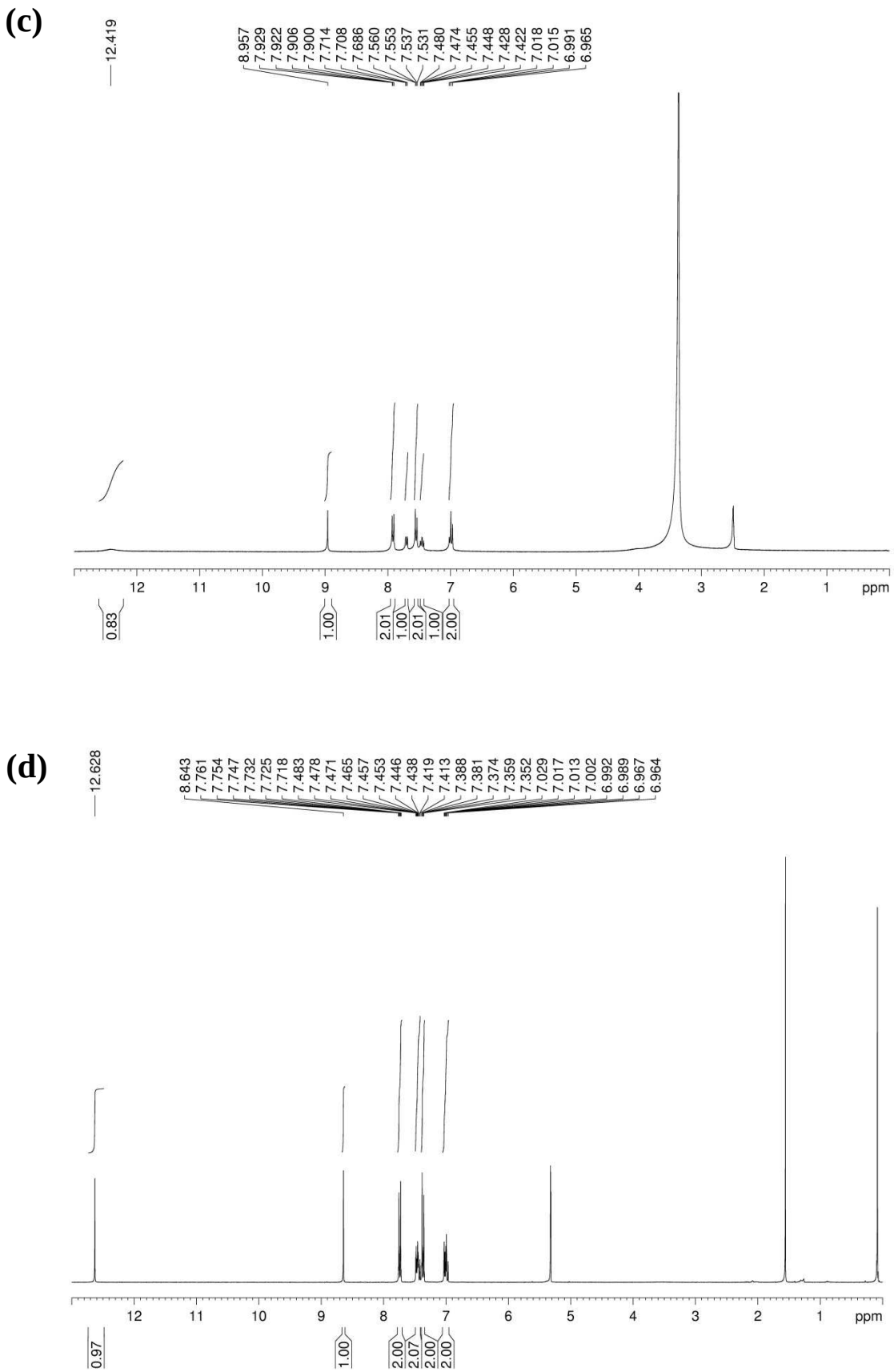
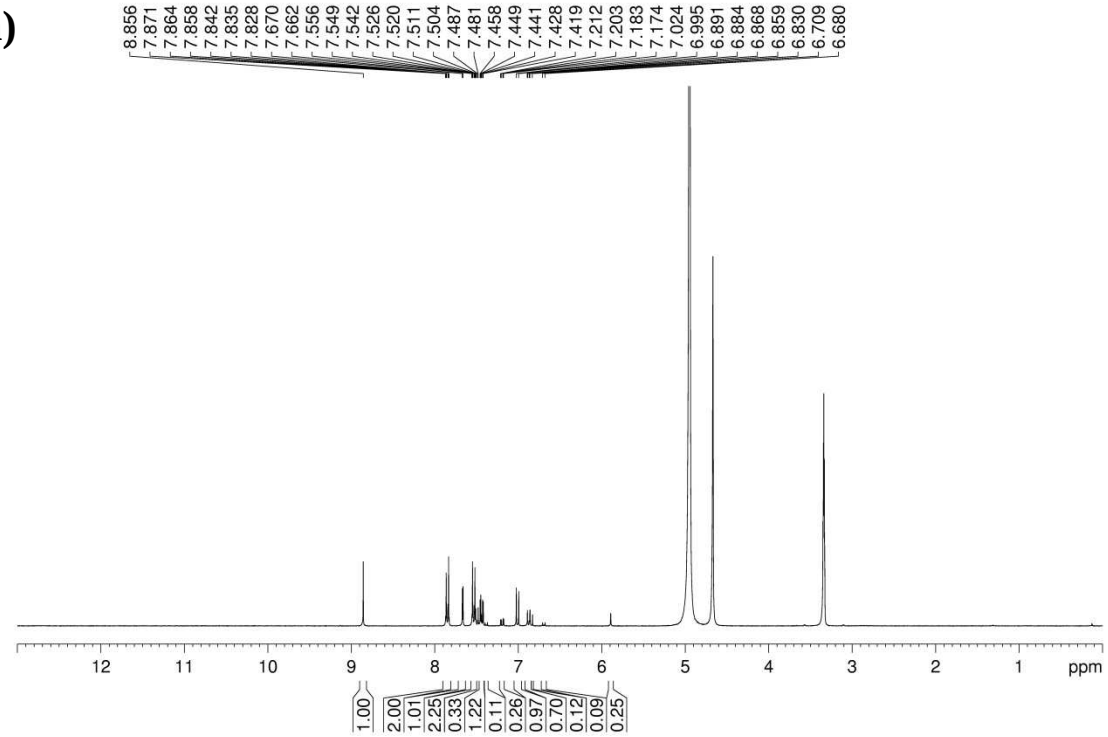



**Fig. S1** $^{1}$H NMR spectra of 4-(salicylideneimino)benzonitrile (Hsal$^{H}$-4-CN) in (a) MeOH-$d_4$, (b) ACN-$d_3$, (c) DMSO-$d_6$, and (d) DCM-$d_2$.

**(a)**

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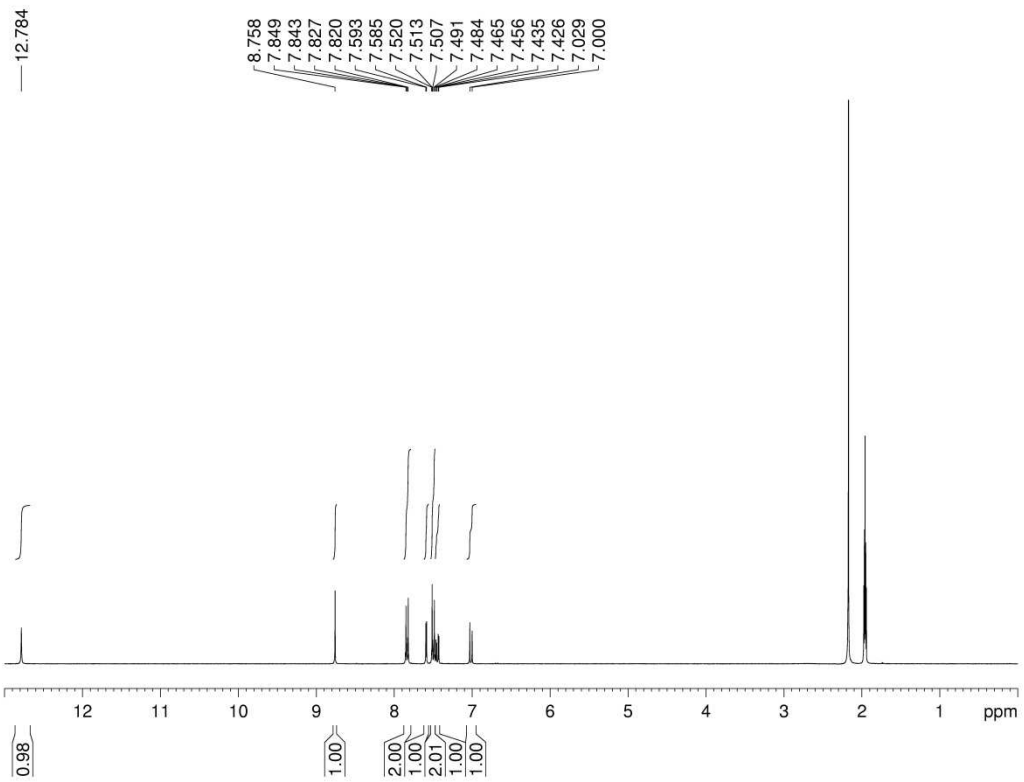


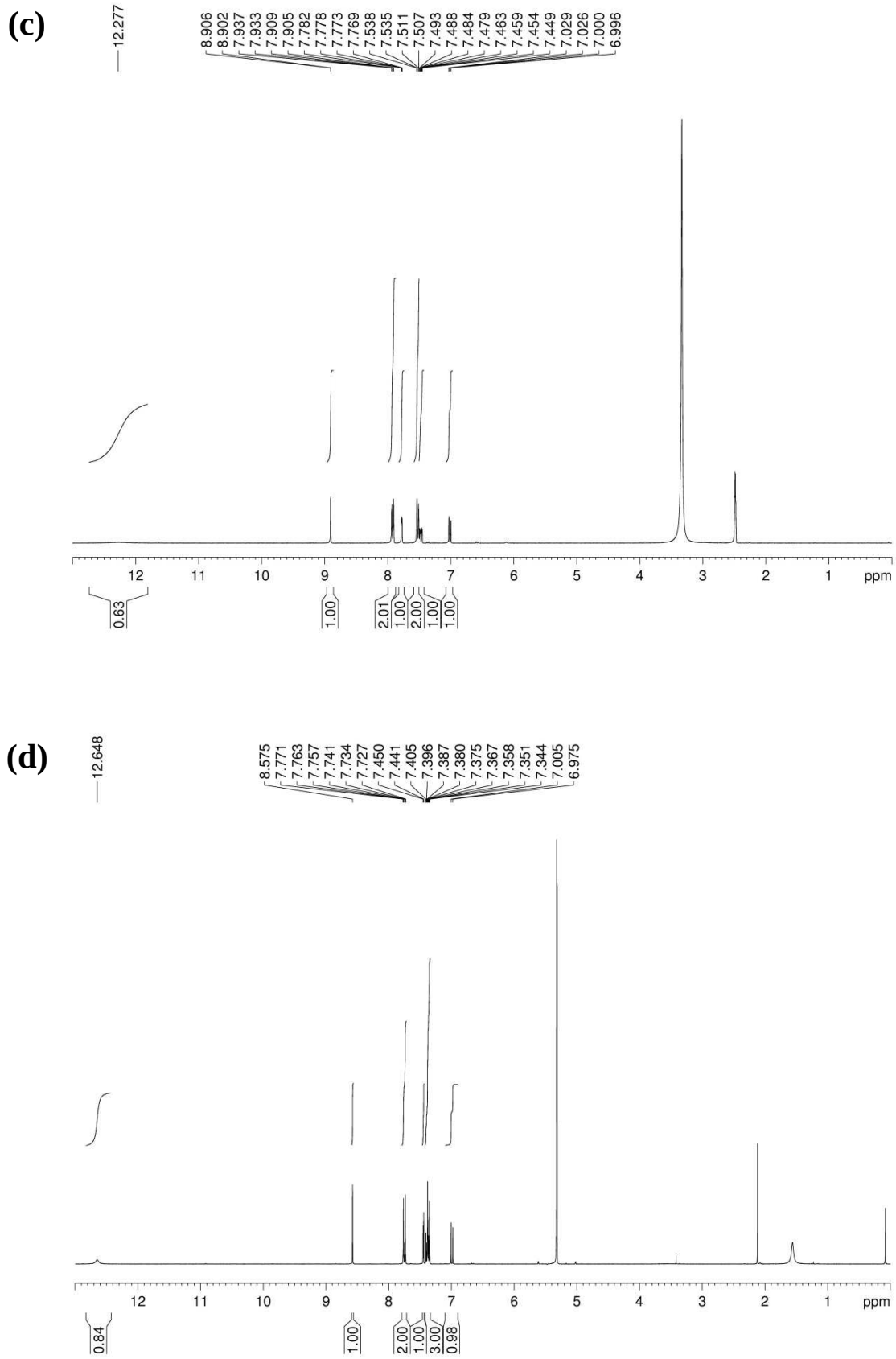
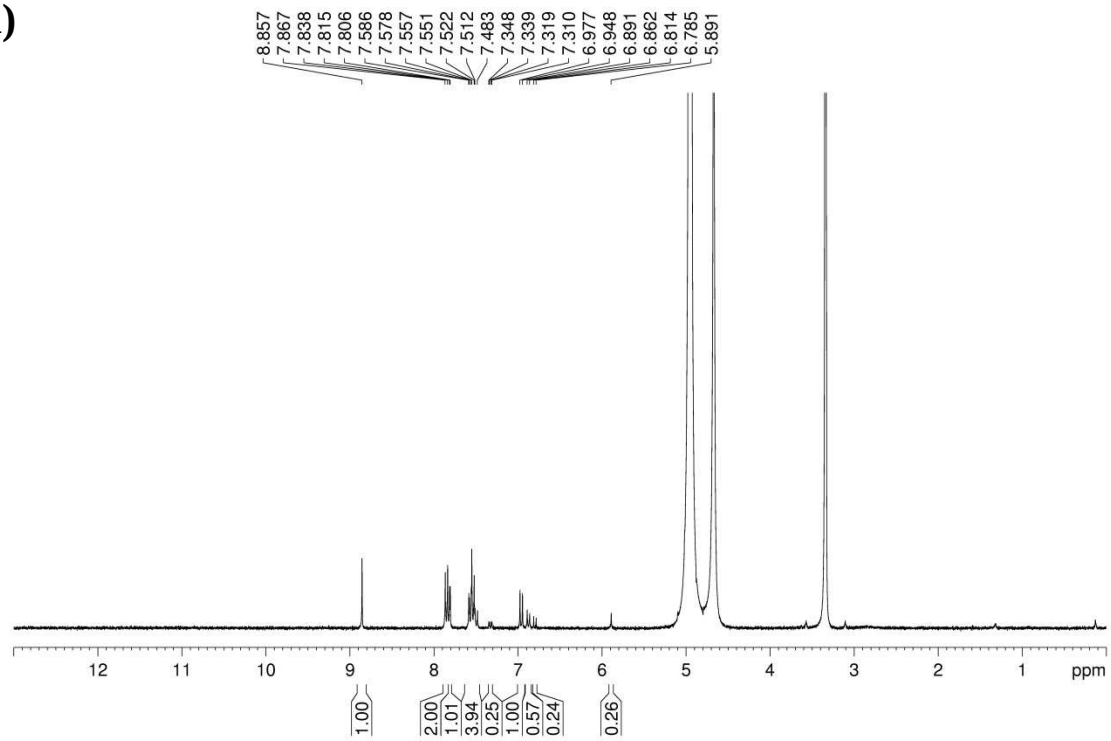



**Fig. S2** $^{1}$H NMR spectra of 4-(5′-chlorosalicylideneimino)benzonitrile (Hsal$^{Cl}$-4-CN) in (a) MeOH-$d_4$, (b) ACN-$d_3$, (c) DMSO-$d_6$, and (d) DCM-$d_2$.

**(a)**

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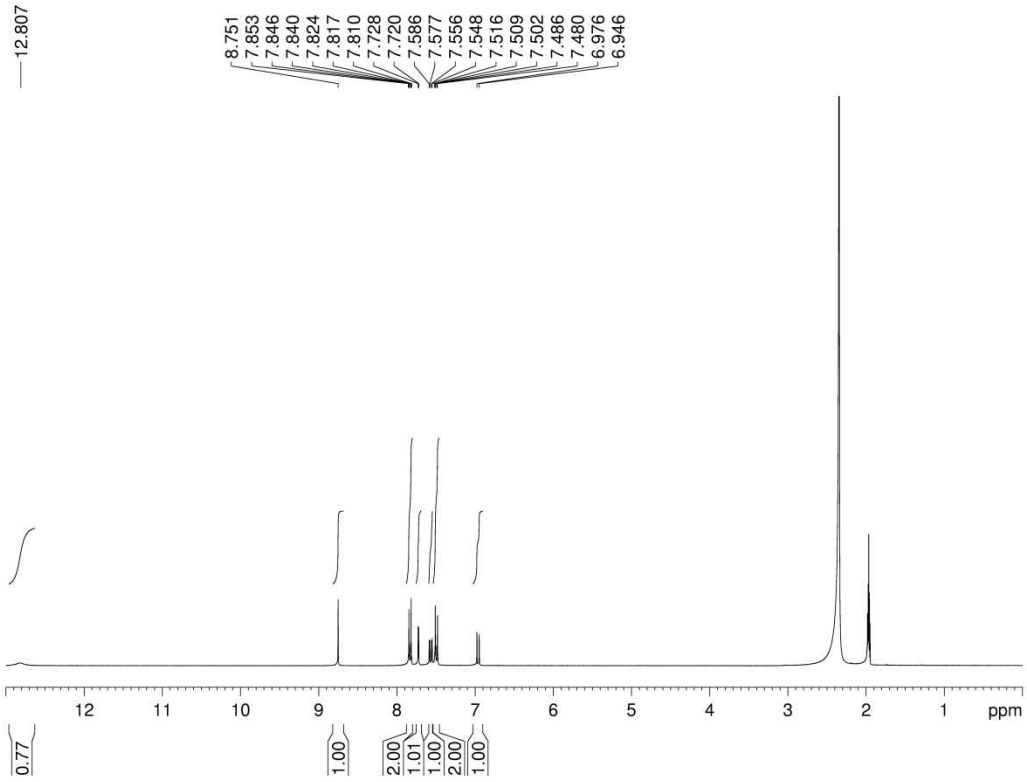


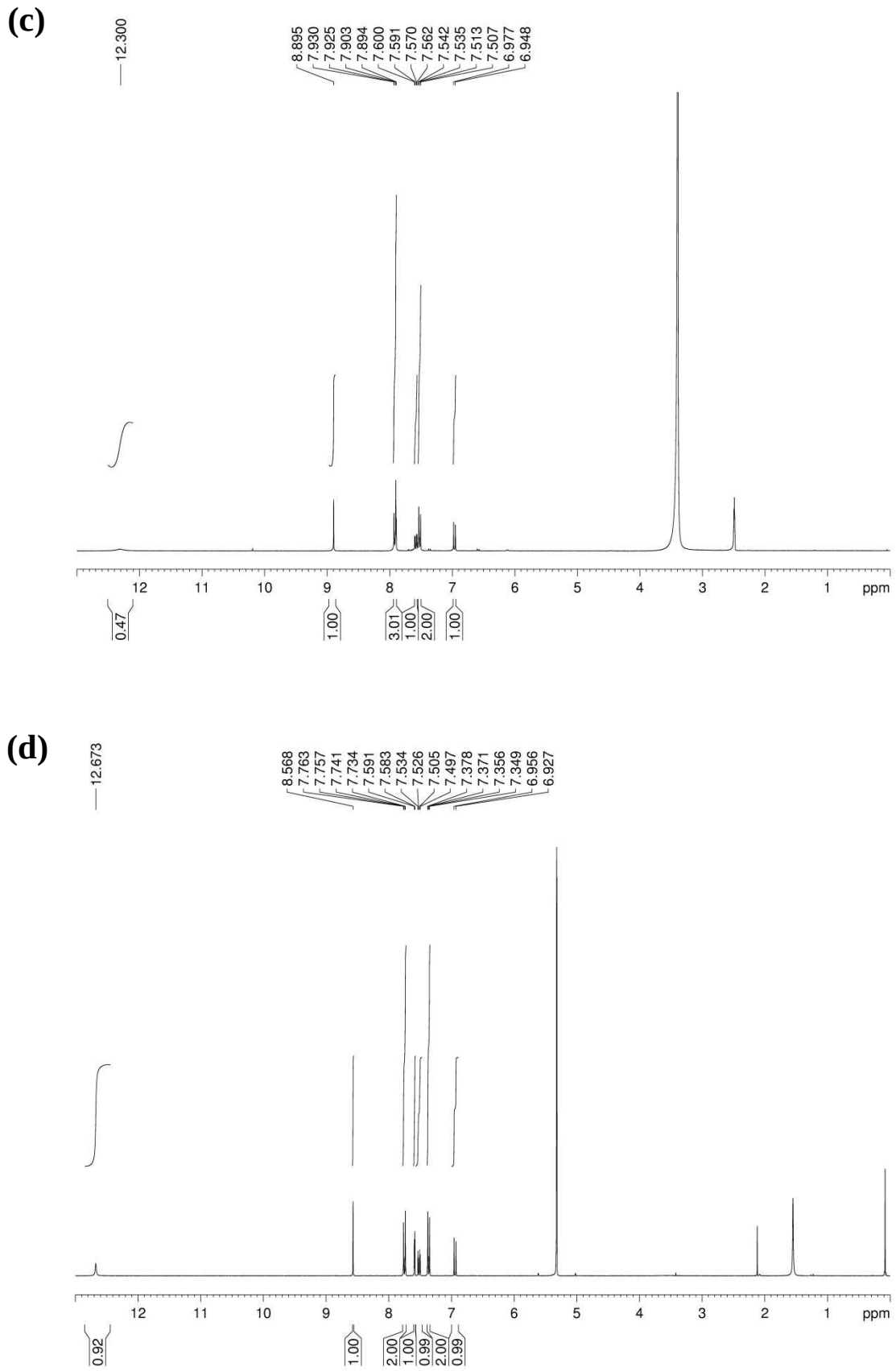
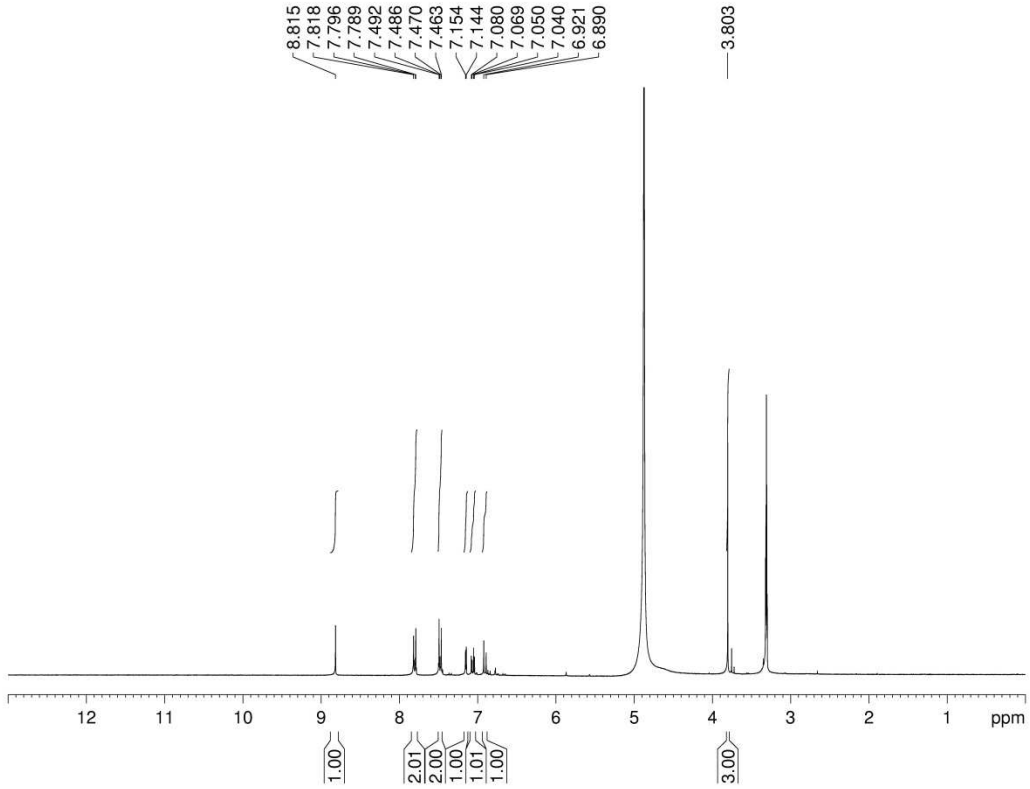



**Fig. S3** $^{1}$H NMR spectra of 4-(5′-bromorosalicylideneimino)benzonitrile (Hsal$^{Br}$-4-CN) in (a) MeOH-$d_4$, (b) ACN-$d_3$, (c) DMSO-$d_6$, and (d) DCM-$d_2$.

**(a)**

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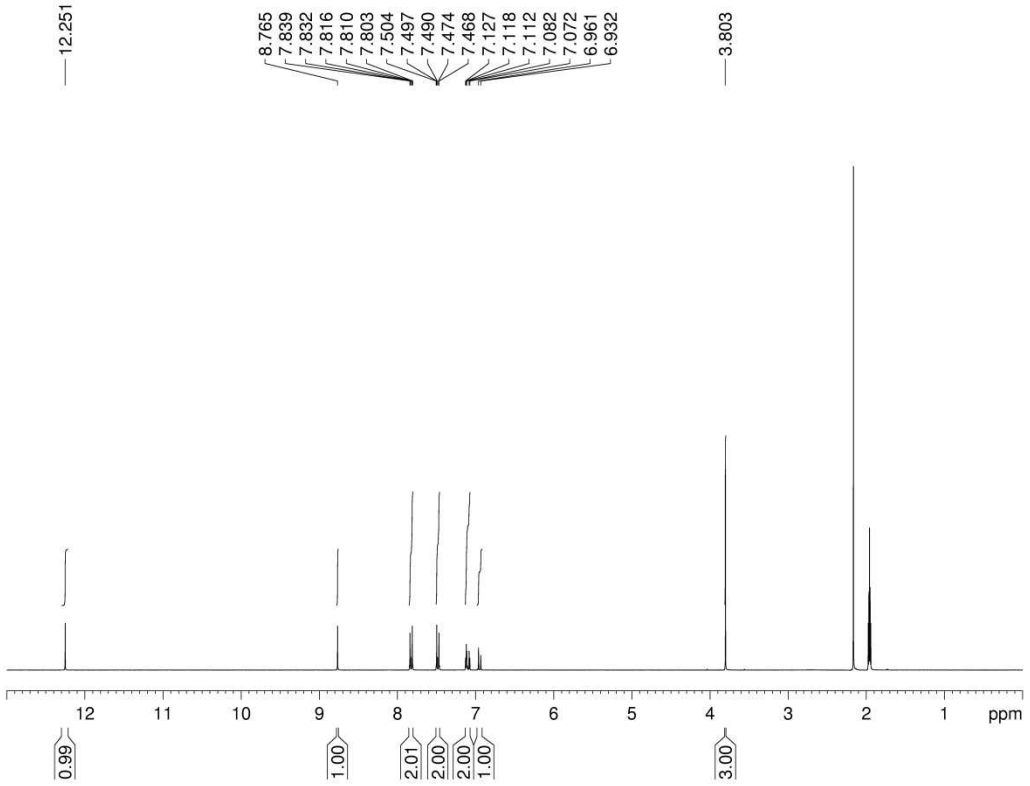


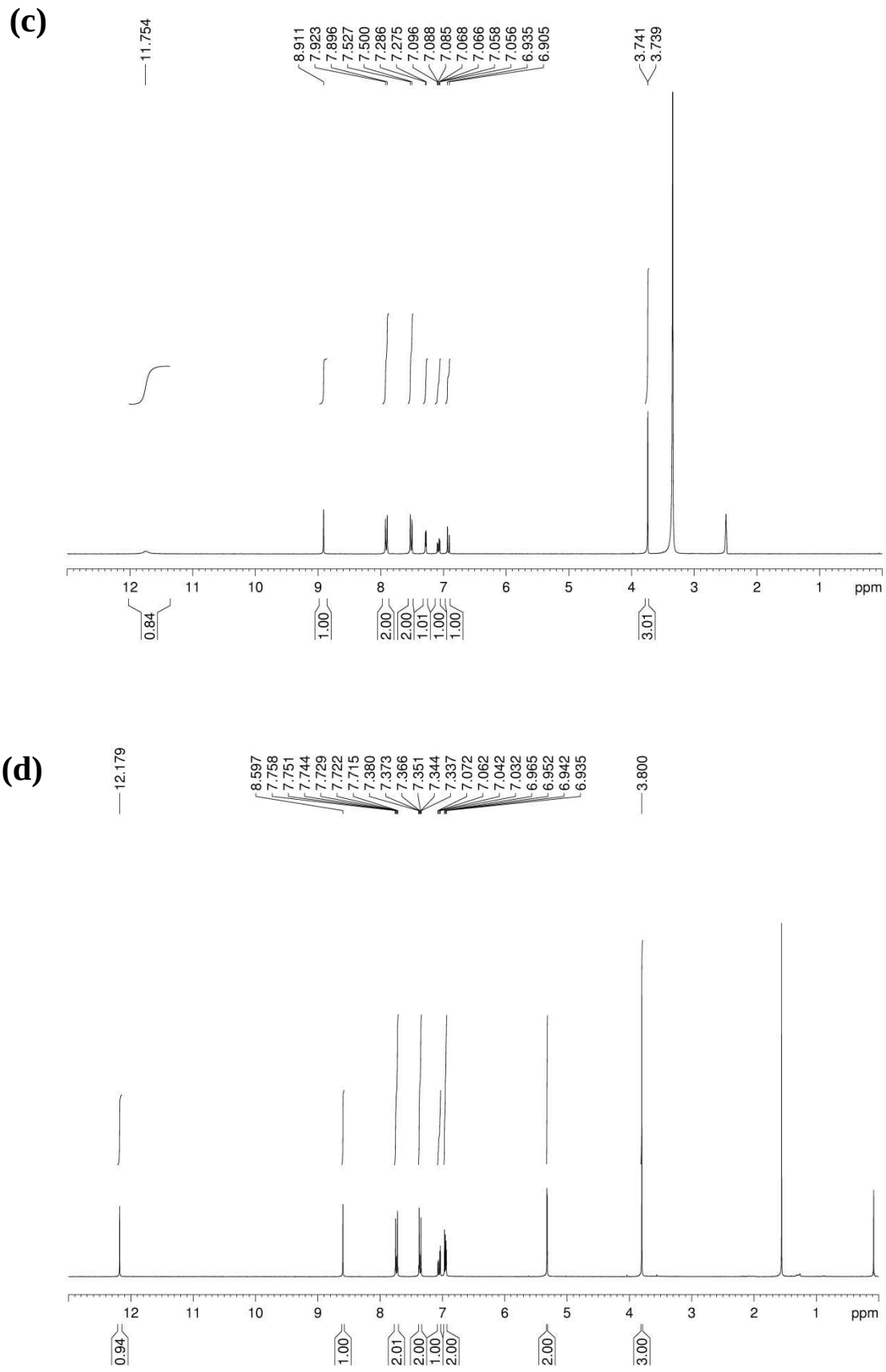
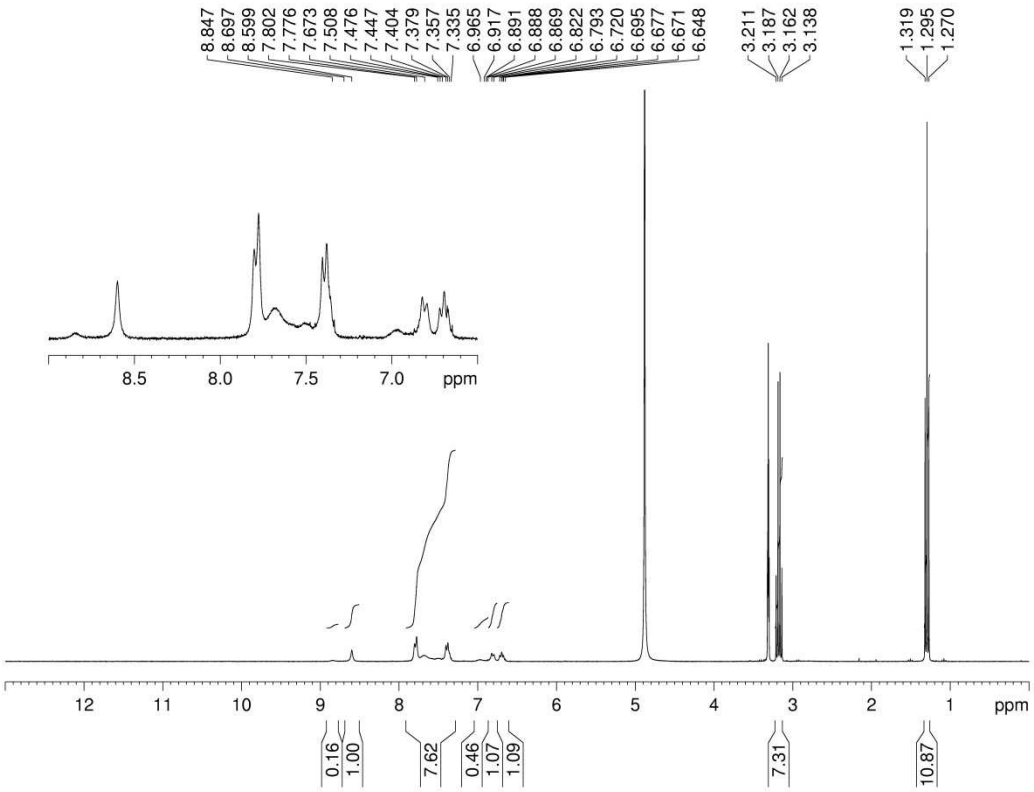



**Fig. S4** $^{1}$H NMR spectra of 4-(5′-methoxysalicylideneimino)benzonitrile (Hsal$^{OMe}$-4-CN) in (a) MeOH-$d_4$, (b) ACN-$d_3$, (c) DMSO-$d_6$, and (d) DCM-$d_2$.

**(a)**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6.917
6.891
6.888
6.869
6.822
6.793
6.720
6.695
6.677
6.671
6.648
3.211
3.187
3.162
3.138
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1.295
1.270
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7.0
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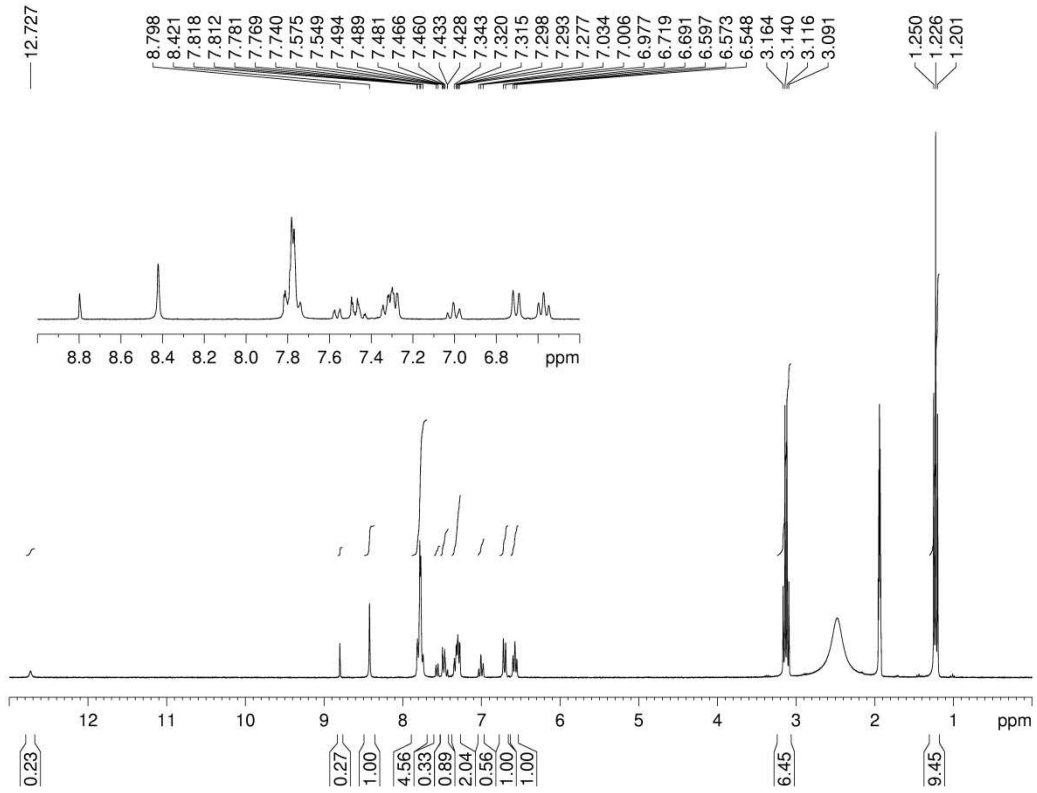
**(b)**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7.293
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7.6
7.4
7.2
7.0
6.8
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12
11
10
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8
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6
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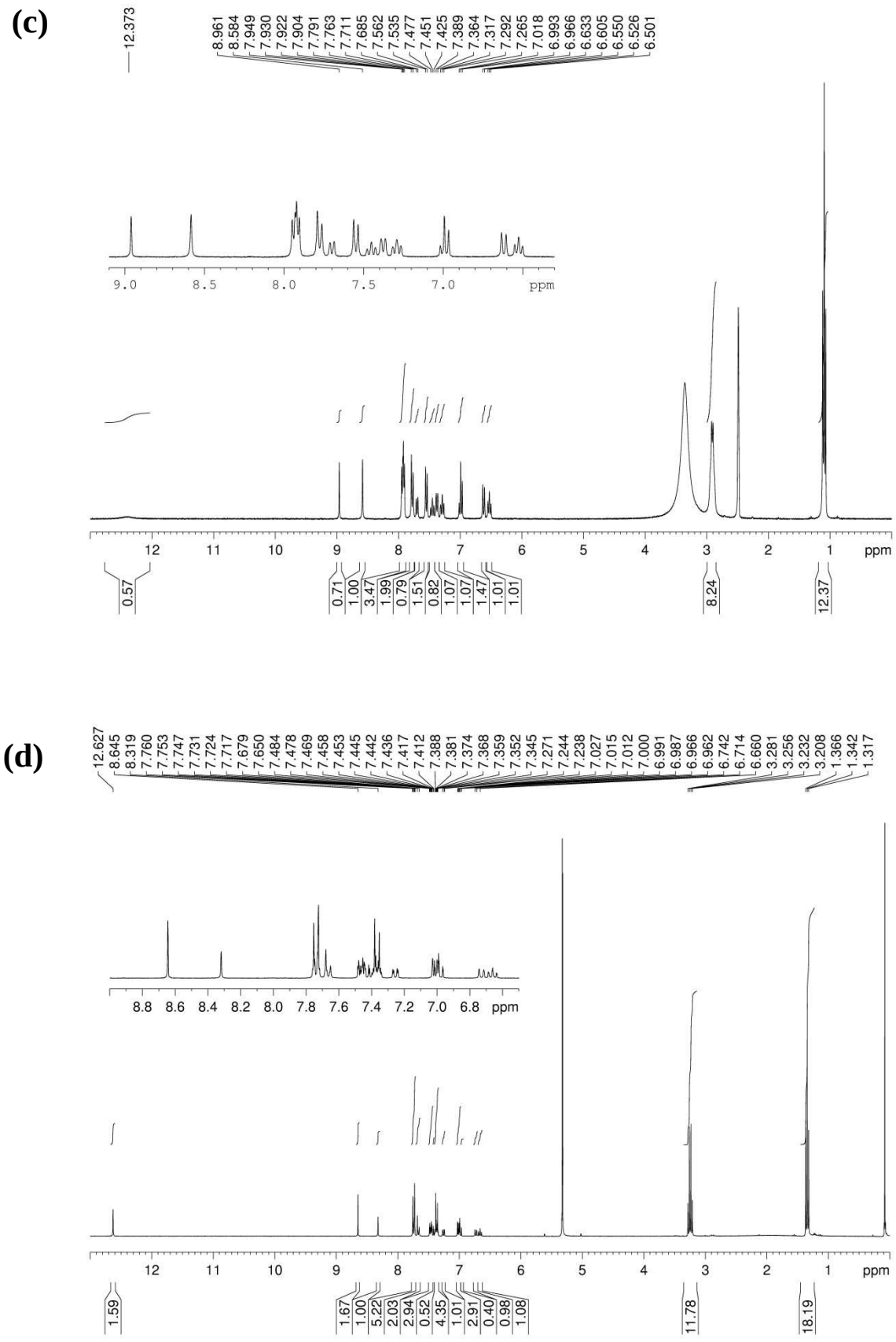
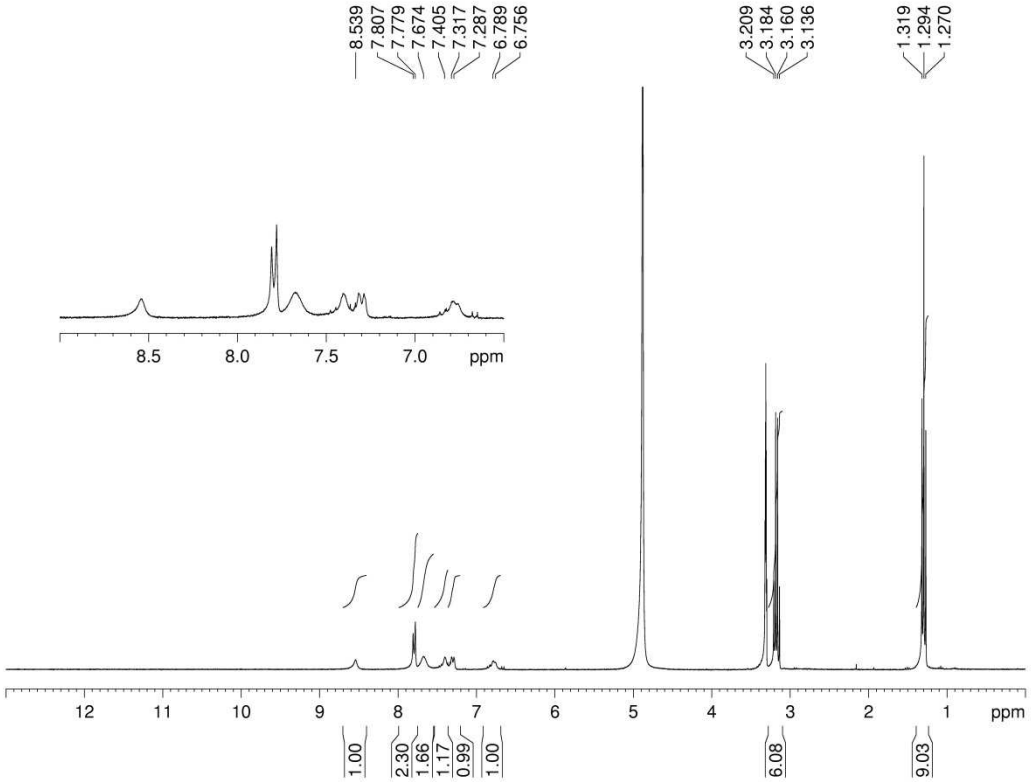



**Fig. S5** $^{1}$H NMR spectra of [HNEt$_3$][Zn(sal$^{H}$-4-CN)Cl$_2$] (**1**) in (a) MeOH-$d_4$, (b) ACN-$d_3$, (c) DMSO-$d_6$, and (d) DCM-$d_2$.

**(a)**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7.0
ppm
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11
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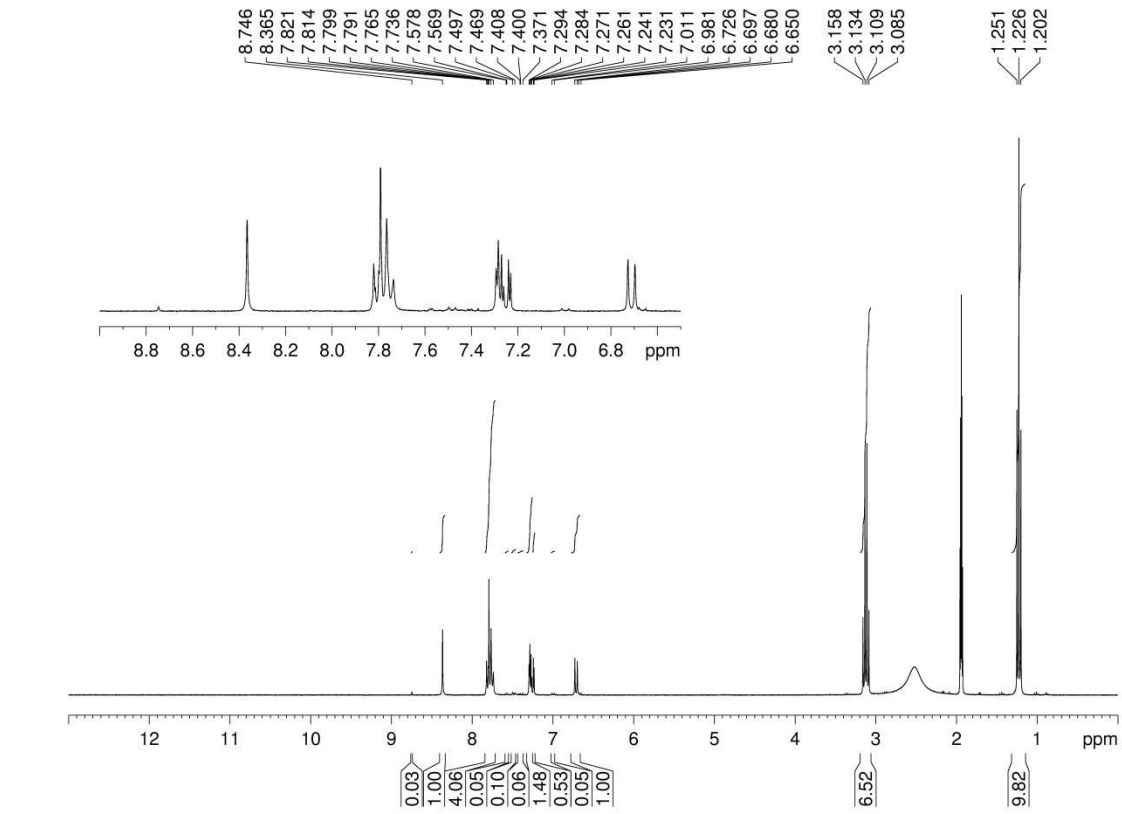
**(b)**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7.400
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7.271
7.261
7.241
7.231
7.011
6.981
6.726
6.697
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3.134
3.109
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8.4
8.2
8.0
7.8
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7.4
7.2
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ppm
12
11
10
9
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6
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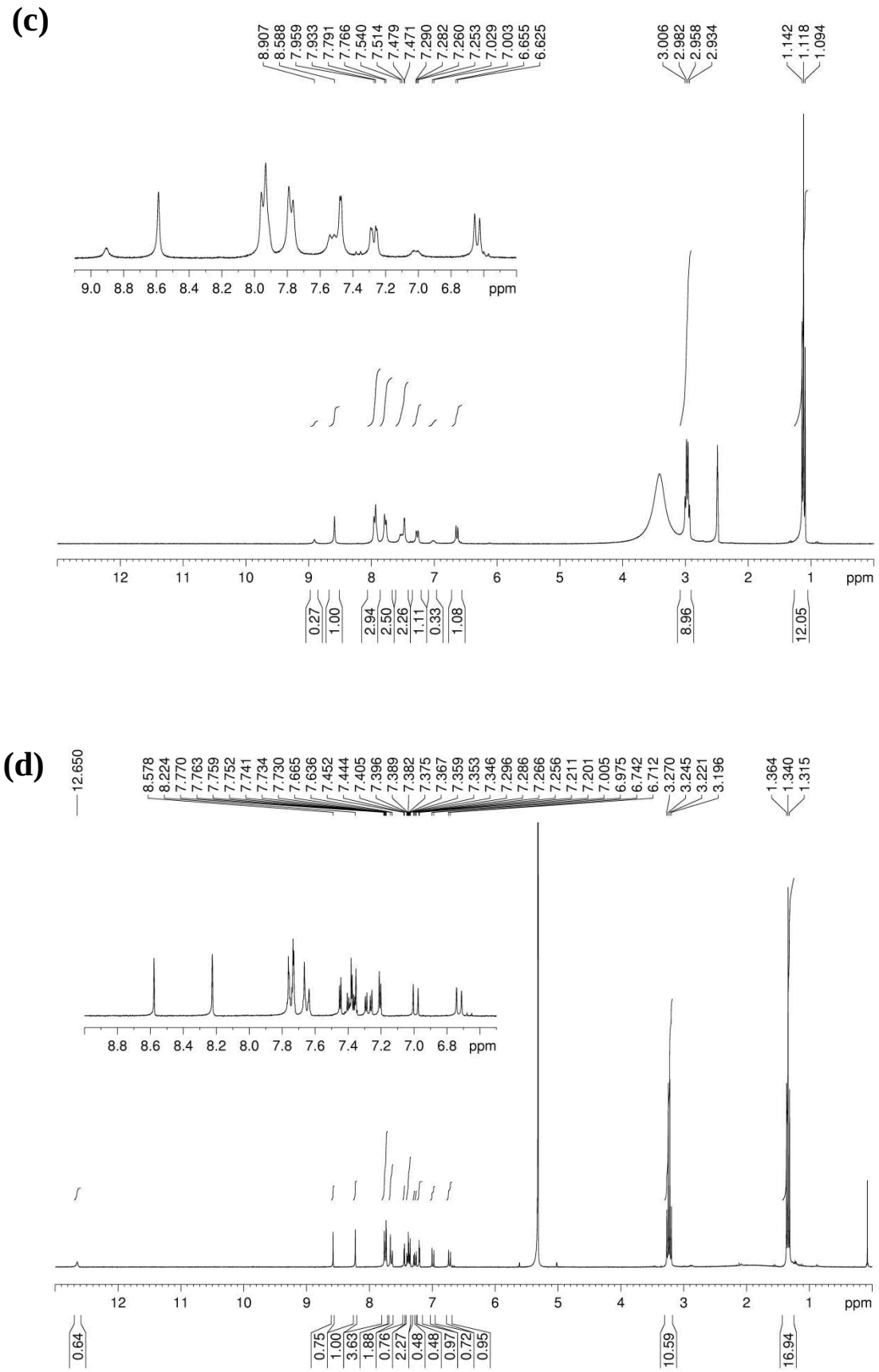
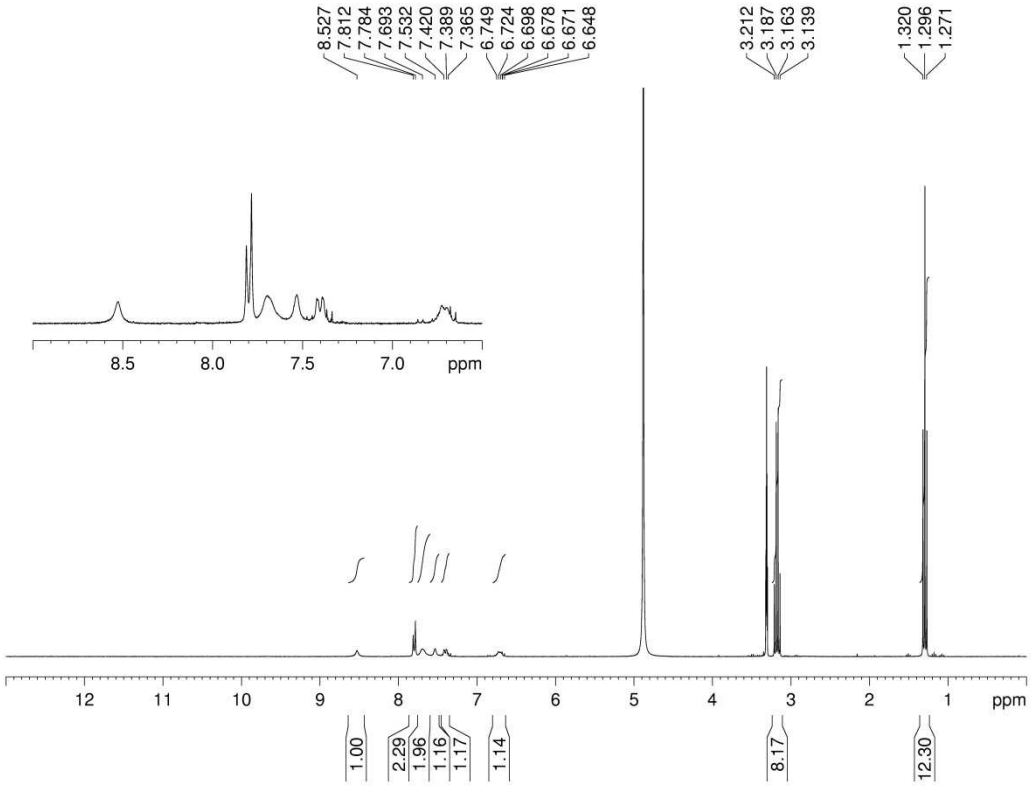



**Fig. S6** $^{1}$H NMR spectra of [HNEt$_3$][Zn(sal$^{Cl}$-4-CN)Cl$_2$] (**2**) in (a) MeOH-$d_4$, (b) ACN-$d_3$, (c) DMSO-$d_6$, and (d) DCM-$d_2$.

**(a)**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6.671
6.648
3.212
3.187
3.163
3.139
1.320
1.296
1.271
8.5
8.0
7.5
7.0
ppm
12
11
10
9
8
7
6
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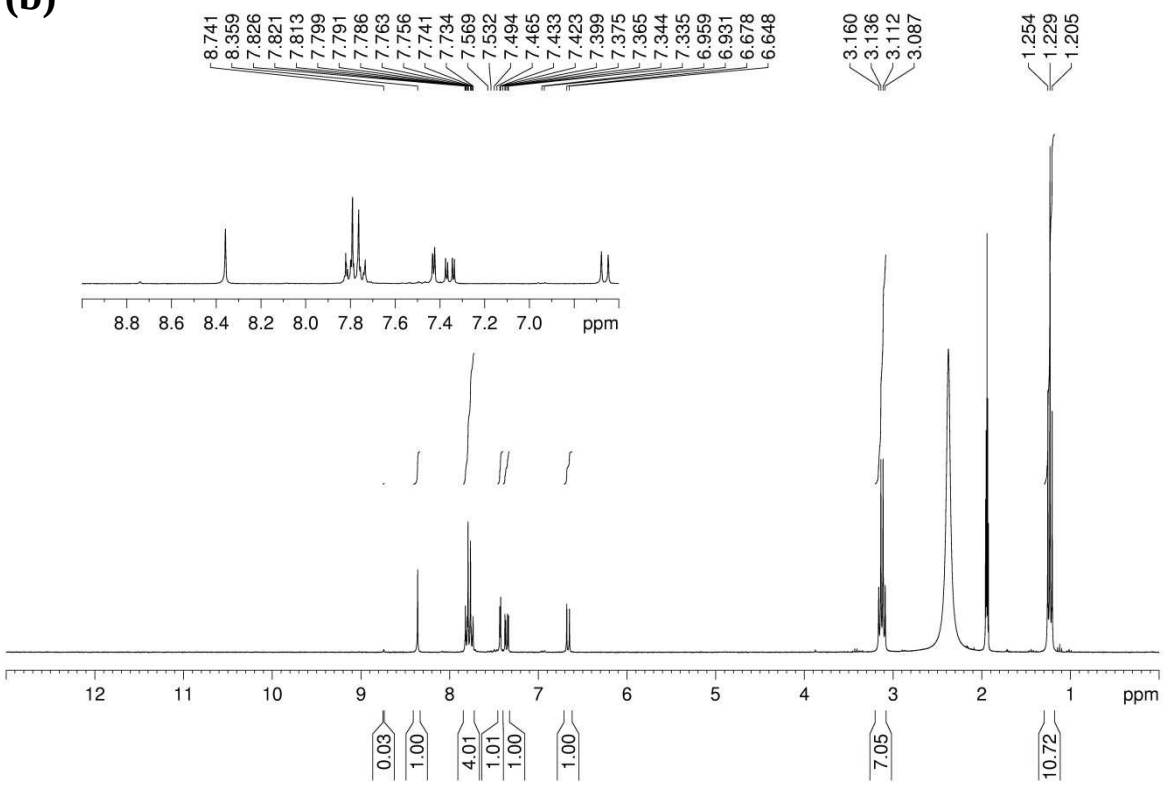
12.30

**(b)**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7.532
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7.423
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7.365
7.344
7.335
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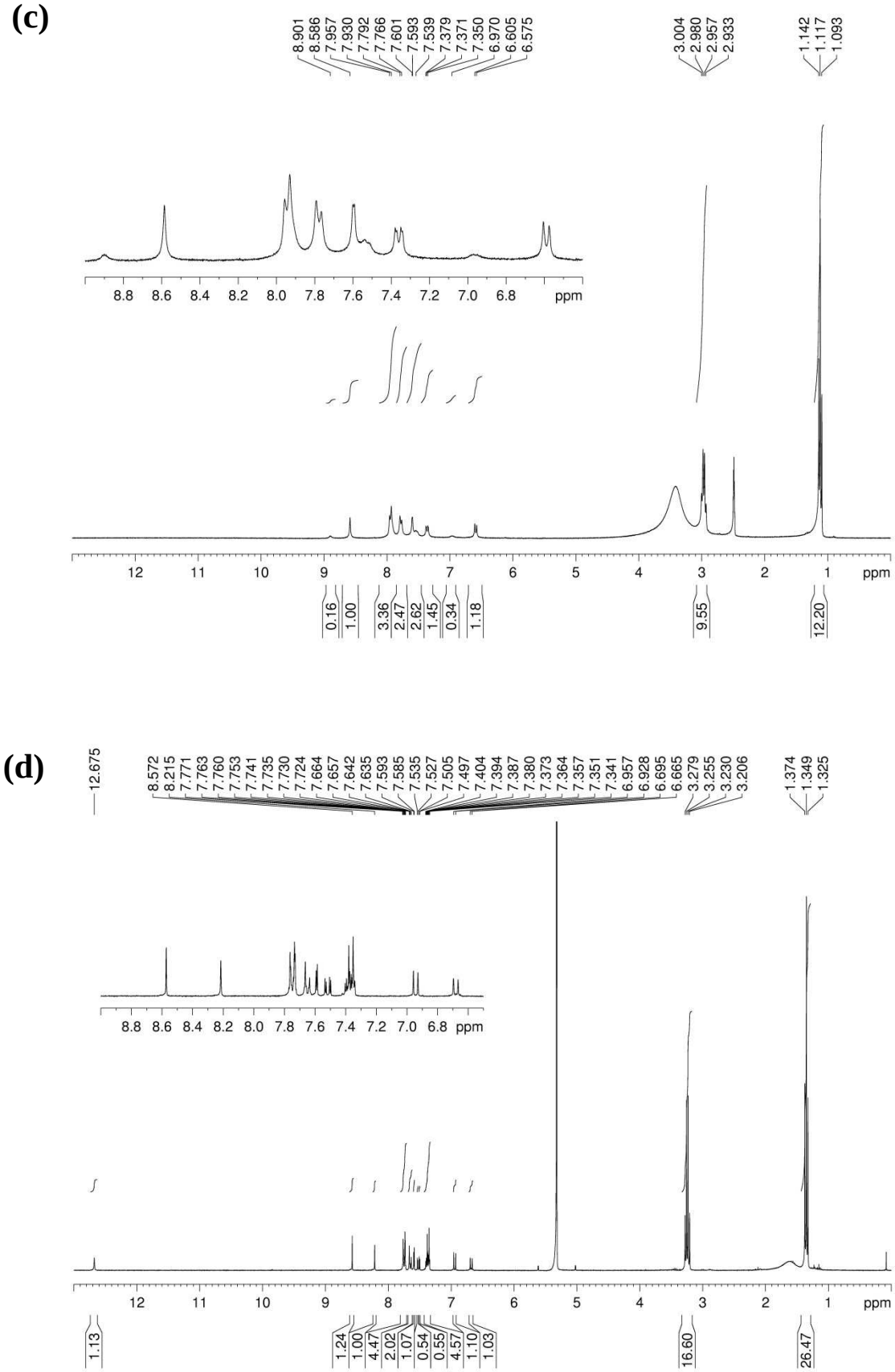
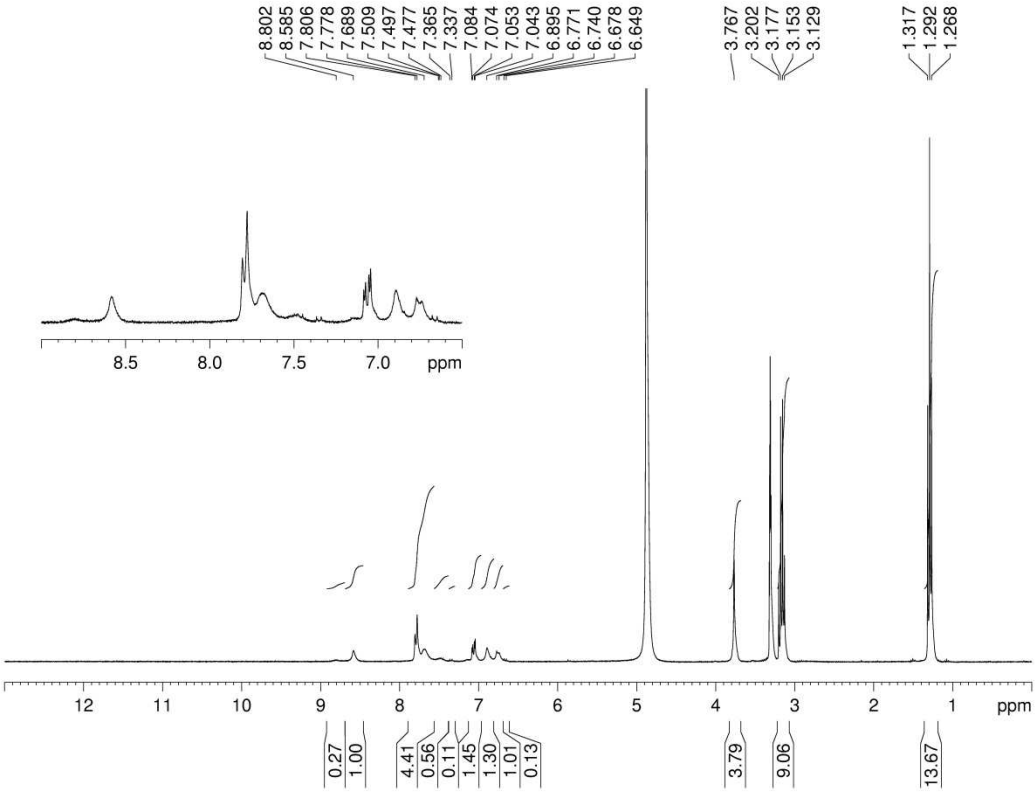



**Fig. S7** $^{1}$H NMR spectra of [HNEt$_3$][Zn(sal$^{Br}$-4-CN)Cl$_2$] (**3**) in (a) MeOH-$d_4$, (b) ACN-$d_3$, (c) DMSO-$d_6$, and (d) DCM-$d_2$.

**(a)**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6.895
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6.649
3.767
3.202
3.177
3.153
3.129
1.317
1.292
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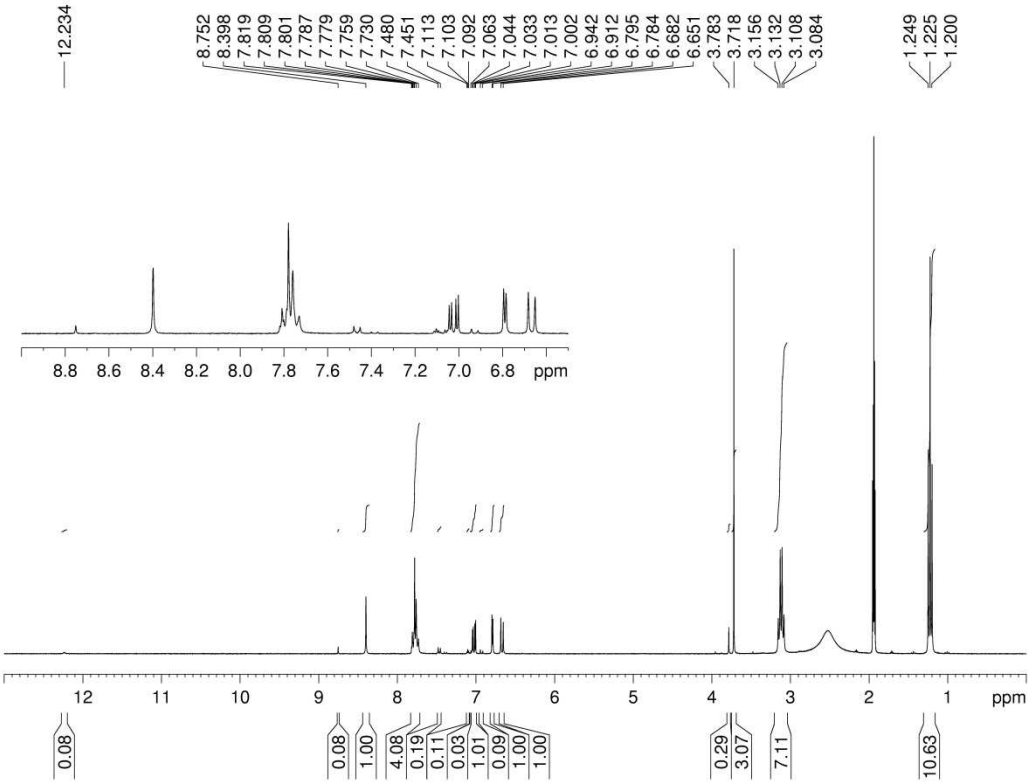
**(b)**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7.103
7.092
7.063
7.044
7.033
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6.795
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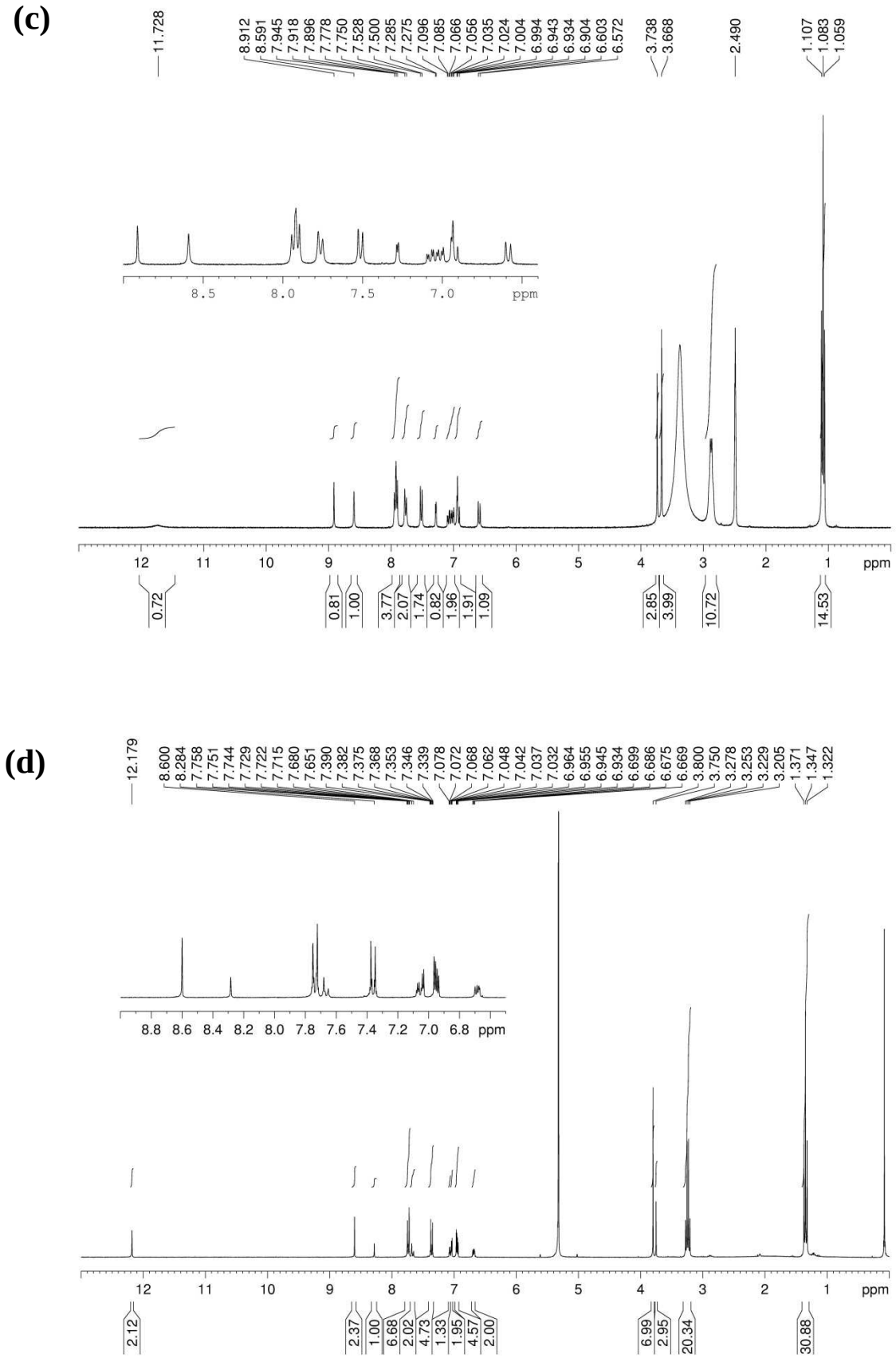


**Fig. S8** $^{1}$H NMR spectra of [HNEt$_3$][Zn(sal$^{OMe}$-4-CN)Cl$_2$] (**4**) in (a) MeOH-$d_4$, (b) ACN-$d_3$, (c) DMSO-$d_6$, and (d) DCM-$d_2$.

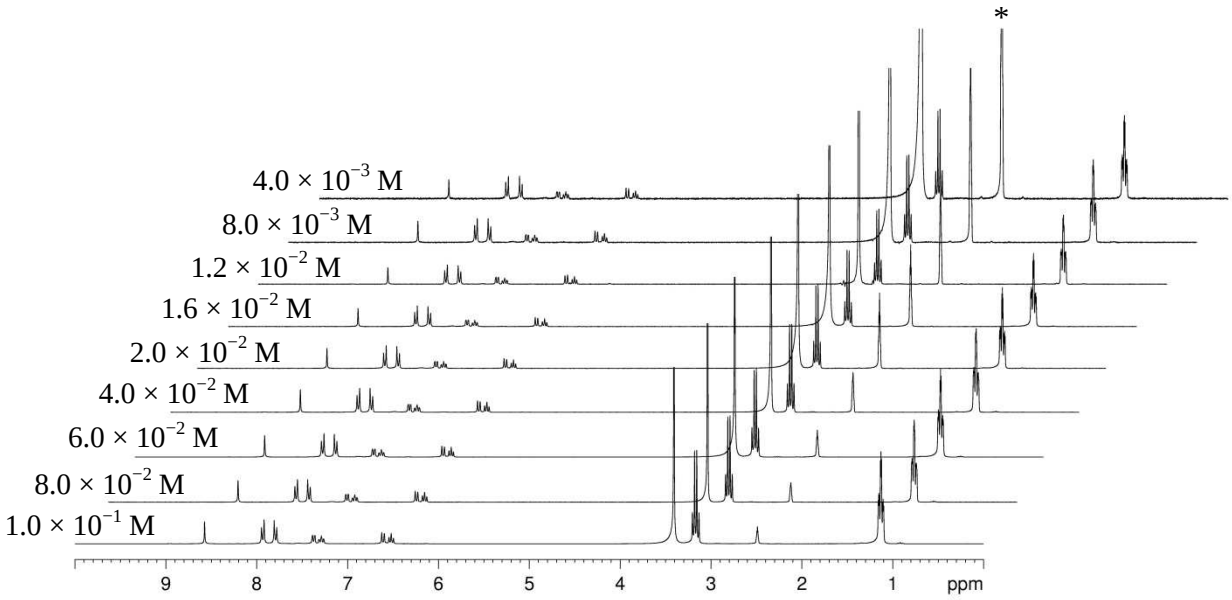


**Fig. S9** Concentration independence of $^{1}$H NMR spectra of [$NEt_4$][Zn($sal^{H}$-4-CN)$Cl_2$] (**5**) in DMSO-$d_6$ at room temperature.

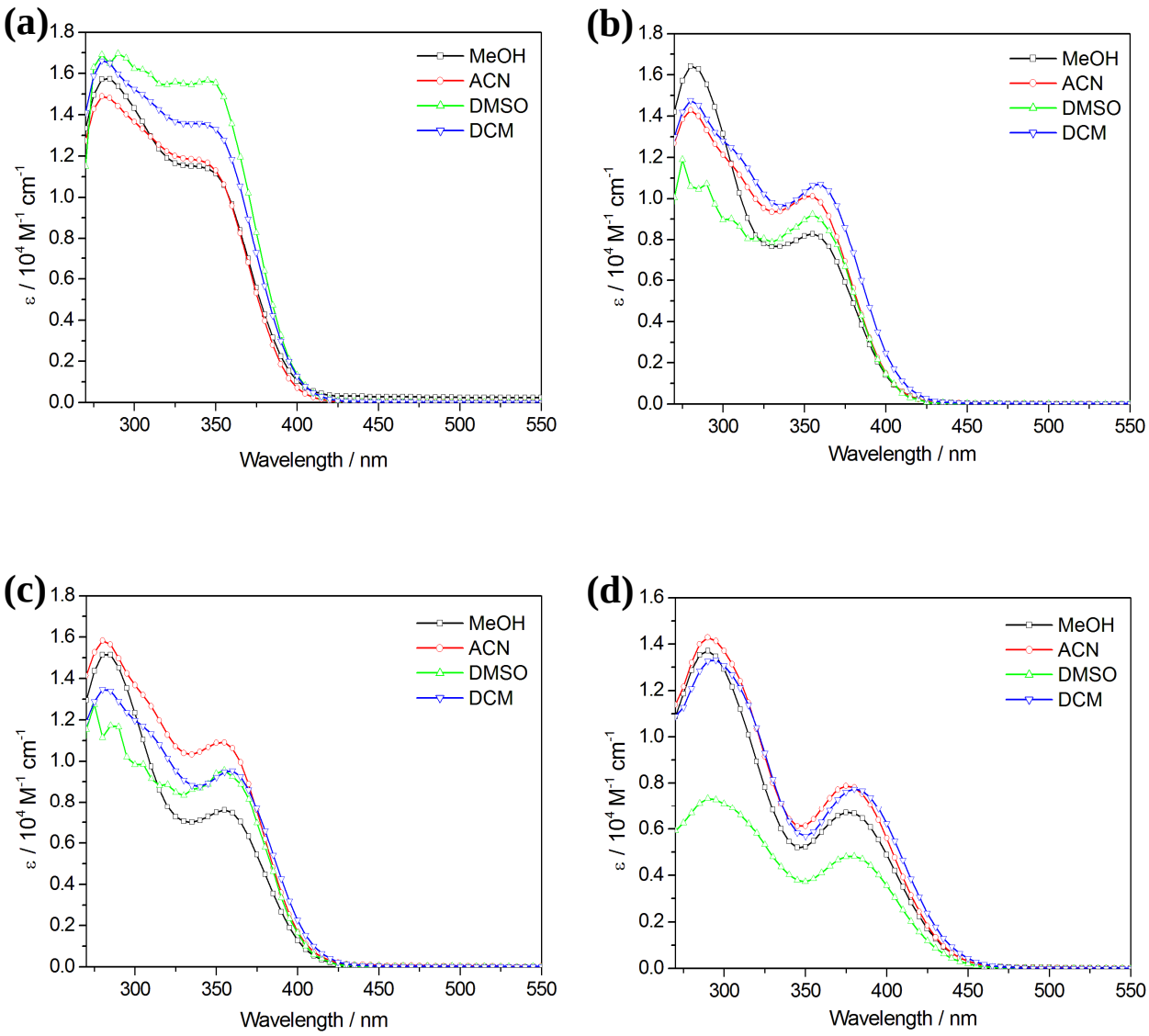


**Fig. S10** UV–vis absorption spectra of (a) $Hsal^{H}$-4-CN, (b) $Hsal^{Cl}$-4-CN, (c) $Hsal^{Br}$-4-CN, and (d) $Hsal^{OMe}$-4-CN in various solvents (100 $\mu$M) at room temperature.

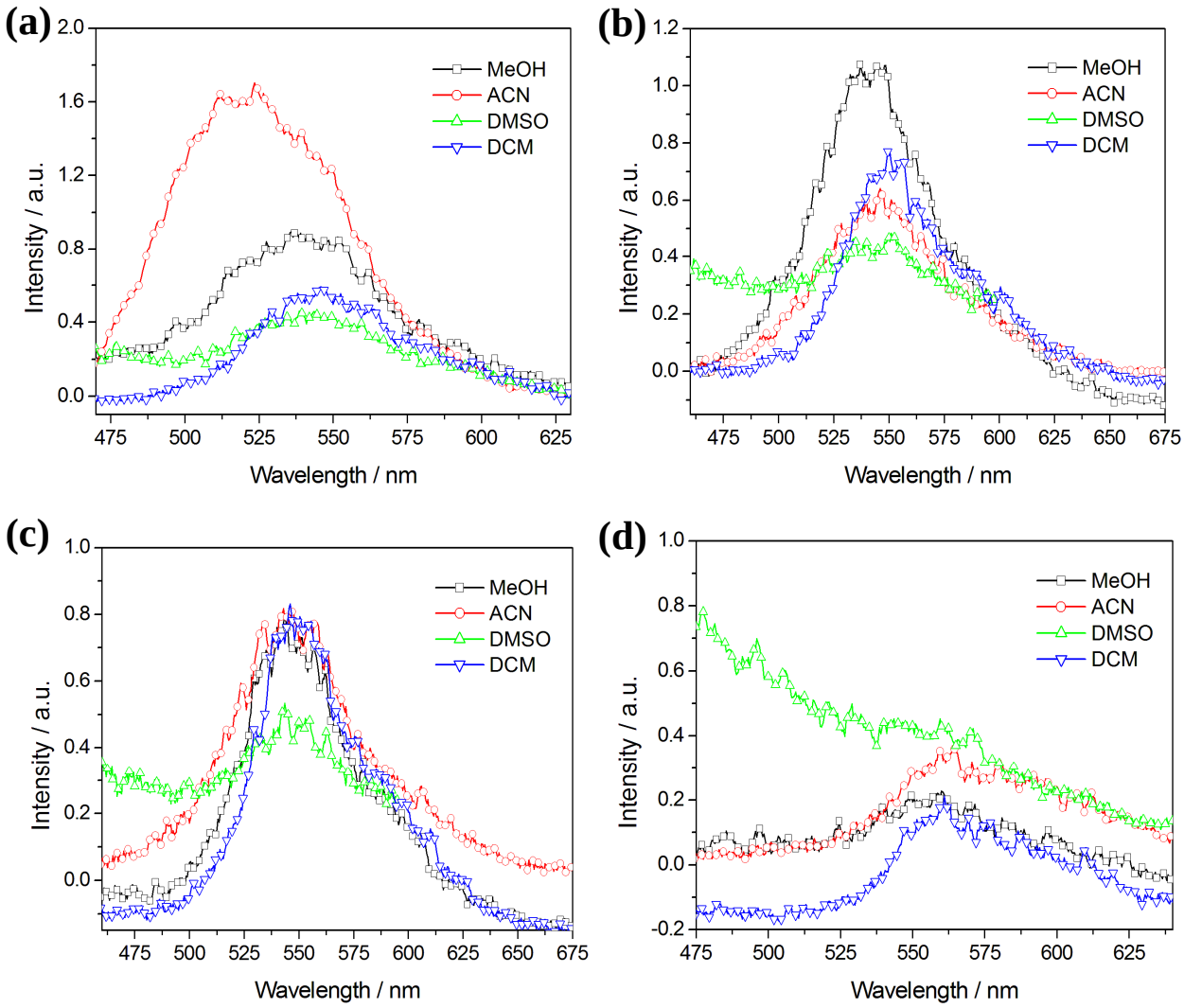


**Fig. S11** Fluorescence spectra of (a) $Hsal^{H}$-4-CN, (b) $Hsal^{Cl}$-4-CN, (c) $Hsal^{Br}$-4-CN, and (d) $Hsal^{OMe}$-4-CN in various solvents (100 $\mu$M) at room temperature.

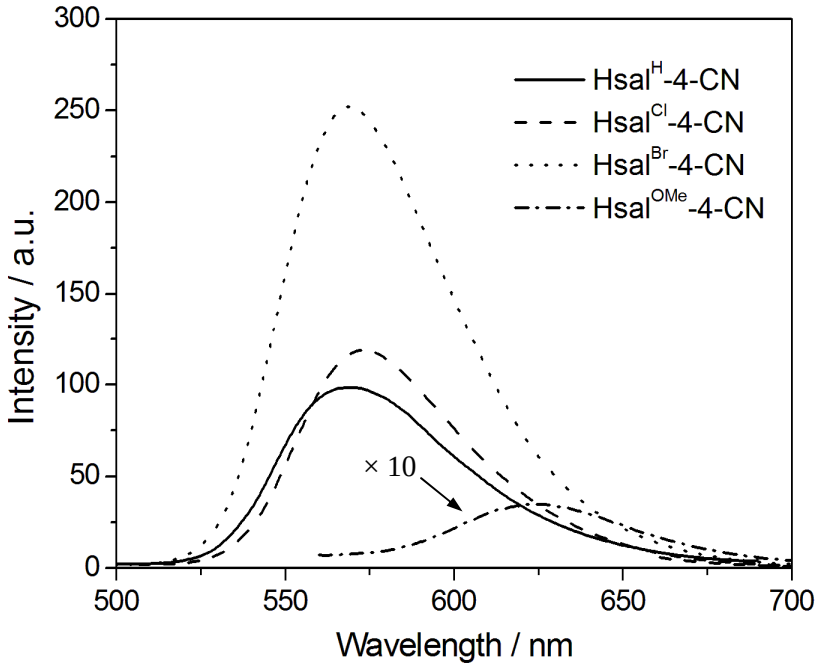


**Fig. S12** Solid-state fluorescence spectra of Hsal$^{R}$-4-CN (R = H, Cl, Br, and OMe) ligands at room temperature.

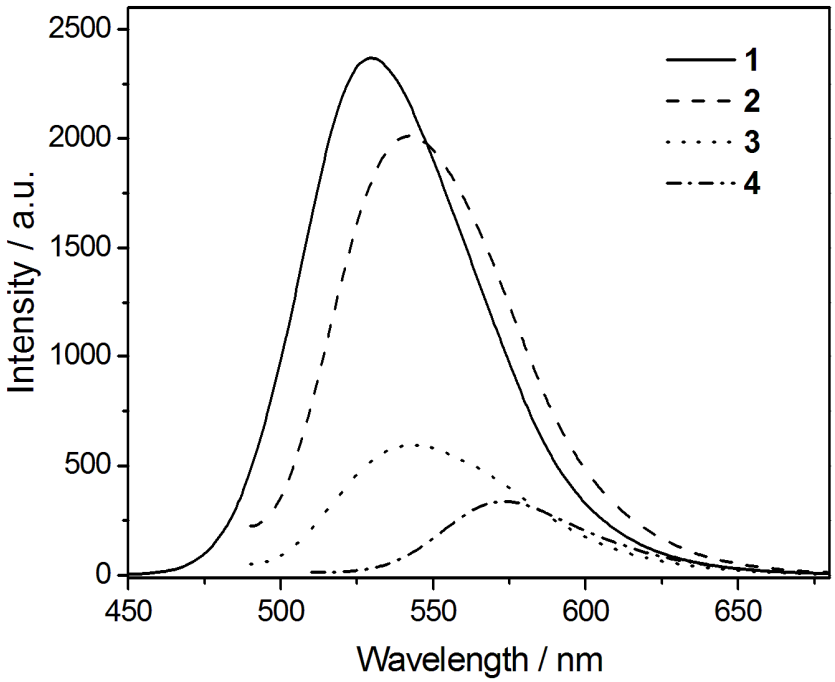


**Fig. S13** Solid-state fluorescence spectra of compounds **1**–**4** at room temperature.

**Table S1** Selected bond lengths (å) and angles (°) and dihedral angle $\theta$ (°) between the salicylideneimine phenyl ring and the benzonitrile phenyl ring for zinc–salicylideneimine compounds **1**–**5**

| Compound | | | | **4** | | |
|---|---|---|---|---|---|---|
| | **1** | **2** | **3** | Molecule I | Molecule II | **5** |
| Zn1/2–O1/3 | 1.9598(11) | 1.9551(12) | 1.9555(15) | 1.956(4) | 1.950(4) | 1.9345(16) |
| Zn1/2–N1/4 | 2.0471(13) | 2.0473(13) | 2.0393(17) | 2.031(5) | 2.054(5) | 2.0360(19) |
| Zn1/2–Cl1/3 | 2.2452(4) | 2.2287(5) | 2.2293(8) | 2.241(2) | 2.244(2) | 2.2646(6) |
| Zn1/2–Cl2/4 | 2.2300(4) | 2.2313(6) | 2.2233(8) | 2.232(2) | 2.233(2) | 2.2418(7) |
| O1/3–Zn1/2–N1/4 | 94.00(5) | 95.50(5) | 95.50(5) | 95.7(2) | 93.6(2) | 95.42(7) |
| O1/3–Zn1/2–Cl1/3 | 114.73(4) | 110.15(4) | 108.52(5) | 112.43(17) | 115.91(17) | 111.87(5) |
| O1/3–Zn1/2–Cl2/4 | 111.68(3) | 108.50(4) | 109.91(5) | 107.42(14 | 106.15(15) | 112.47(5) |
| N1/4–Zn1/2–Cl1/3 | 106.93(4) | 118.18(4) | 106.55(5) | 106.63(17) | 105.46(17) | 102.96(6) |
| N1/4–Zn1/2–Cl2/4 | 115.45(4) | 106.83(4) | 118.21(6) | 118.00(18) | 121.81(18) | 119.33(5) |
| Cl1/3–Zn1/2–Cl2/4 | 112.728(16) | 115.60(2) | 115.92(3) | 115.15(8) | 112.95(8) | 113.28(3) |
| $\theta$ | 26.5 | 1.9 | 2.2 | 36.5 | 6.3 | 22.5 |

**Table S2** Dissociation ratio ($R_D$) of **1** in DMSO-$d_6$ with different concentrations at room temperature[a]

| Concentration (M) | Dissociation Ratio ($R_D$) |
|---|---|
| $4.0 \times 10^{-3}$ | 52.2 |
| $8.0 \times 10^{-3}$ | 43.8 |
| $1.2 \times 10^{-2}$ | 40.5 |
| $1.6 \times 10^{-2}$ | 36.7 |
| $2.0 \times 10^{-2}$ | 32.4 |
| $4.0 \times 10^{-2}$ | 29.1 |
| $6.0 \times 10^{-2}$ | 25.4 |
| $8.0 \times 10^{-2}$ | 21.9 |
| $1.0 \times 10^{-1}$ | 18.0 |

[a] $R_D = I_{CH=N}(HL)/\{I_{CH=N}(HL) + I_{CH=N}([Zn(L)Cl_2]^-)\} \times 100$, where $I_{CH=N}(HL)$ = relative integrated area of the azomethine proton (C*H*=N) signal of free ligand form and $I_{CH=N}([Zn(L)Cl_2]^-)$ = relative integrated area of the azomethine proton (C*H*=N) signal of complex form.