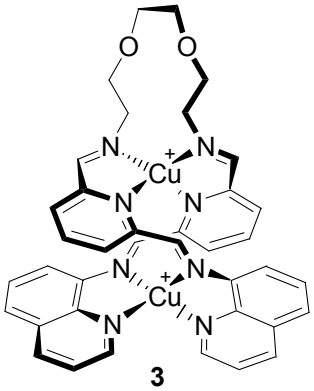
Supporting Text

General: All manipulations were carried out in degassed solvents using reagents of the highest commercially available purity. The ^{1}H NMR spectra were assigned with the help of COSY, NOESY, HSQC and HMBC measurements. NMR spectra were referenced to the residual ^{1}H or ^{13}C signal of the solvent. All mass spectra were taken in degassed methanol.

General procedure for the preparation of dimeric structures (Scheme 4) incorporating diamines C-E (Table 1): Into an NMR tube with a Teflon screw cap were added diamine **C**, **D** or **E** (1 eq., 0.02 mmol), diformylpyridine **A** (2 eq., 0.04 mmol), 8-aminoquinoline **B** (2 eq., 0.04 mmol), $Cu(NCMe)_4BF_4$ (2 eq., 0.04 mmol) and CD_3CN (in the cases of **C** and **E**) or CD_3OD (in the case of **D**) (0.5 ml). The brown solution obtained were deoxygenated by three vacuum / argon fill cycles and heated overnight at 50°C.

Characterization data for product complexes

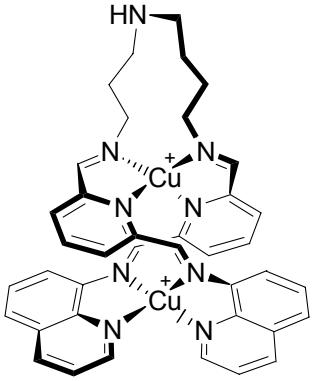
Amine **C** (product **3**):



3

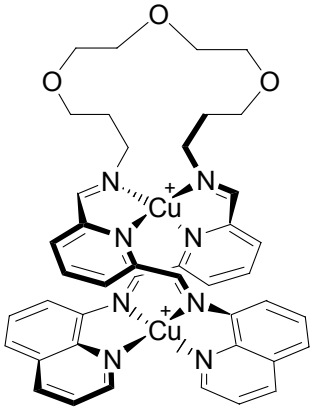
When this complex was prepared in an NMR tube following the general procedure detailed above, the ^{1}H and ^{13}C spectra were the same as reported in the Materials and Methods section of the main text.

Amine **D**:



^{1}H NMR (400 MHz, 298 K, CD_3OD): δ = 9.51 (s, 2H, quinoline imine), 8.37 (d, J = 8.0 Hz, 2H, 4-aminoquinoline), 8.17 (br s, 2H, 2-aminoquinoline), 8.00-8.20 (m, 8H, diamine imine, 5-aminoquinoline, 7-aminoquinoline, 3-pyridinedicarboxaldehyde next to the aminoquinoline), 7.94 (t, J = 8.0 Hz, 2H, 4-pyridinedicarboxaldehyde), 7.81 (t, J = 8.5 Hz, 2H, 6-aminoquinoline), 7.41 (br s, 2H, 3-aminoquinoline), 7.35 (d, J = 7.5 Hz, 2H, 5-pyridinedicarboxaldehyde next to the diamine), 2.7-4.0 (m, 12H, diamine). ESI-MS: *m/z* = 379.0 ([**M**]$^{2+}$), 758.3 ([**M** – Cu + 2 MeOH]$^+$), 845.8 ([**M** + BF_4]$^+$).

Amine **E**:



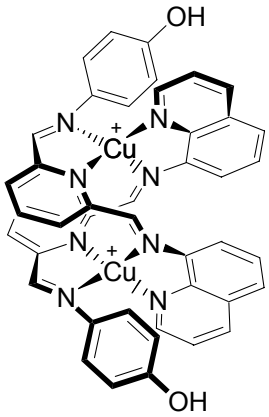
^{1}H NMR (400 MHz, 298 K, CD_3CN): δ = 9.30 (s, 2H, quinoline imine), 8.37 (dd, J = 8.5 Hz, J' = 1.0 Hz, 2H, 4-aminoquinoline), 8.23 (dd, J = 4.5 Hz, J' = 1.0 Hz, 2H, 2-aminoquinoline), 8.02 (m, 8H, diamine imine, 5-aminoquinoline, 7-aminoquinoline, 3-pyridinedicarboxaldehyde next to the aminoquinoline), 7.88 (t, J = 8.0 Hz, 2H, 4-pyridinedicarboxaldehyde), 7.79 (t, J = 8.0 Hz, 2H, 6-aminoquinoline), 7.41 (dd, J = 8.5 Hz, J' = 4.5 Hz, 2H, 3-aminoquinoline), 7.28 (d, J = 7.5 Hz, 2H, 5-pyridinedicarboxaldehyde, next to the diamine), 3.00-3.60 (m, 16H, diamine), 1.40-1.60 (m, 4H, diamine). ESI-MS: *m/z* = 416.1 ([**M**]$^{2+}$), 833.5 ([**M** - Cu + 2 MeOH]$^+$), 919.7 ([**M** + BF_4]$^+$).

General procedure for the preparation of dimeric structures (Scheme 4) incorporating anilines F-J (Table 1):

Into an NMR tube with a Teflon screw cap were added **F, G, H, I,** or **J** (1 eq., 0.02 mmol), 8-aminoquinoline **C** (1 eq.), $Cu(NCMe)_4BF_4$ (1eq.), diformylpyridine **A** (1eq.) and solvent (0.5 ml) (CD_3CN gave the best results with amines **F** and **G**, CD_3OD with **H**, **I** and **J**). The brown homogeneous solution thus obtained was deoxygenated by three vacuum / argon fill cycles and

heated overnight at 50°C. The next morning a brown precipitate was observed to have formed. The supernatant was removed by filtration through a glass fiber plug in a Pasteur pipette and the precipitate was washed with freshly distilled dichloromethane (2 × 2 ml) (no washing was carried out in the case of **I**). The brown microcrystalline product was dried under vacuum.

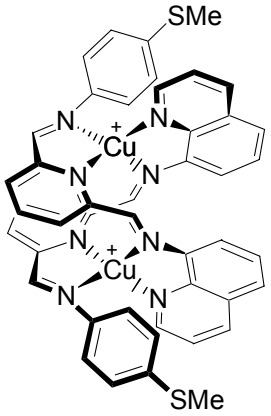
Amine **F**:



(+ Head to Head isomer)

Head-to-tail: ^{1}H NMR (500 MHz, 298 K, DMSO): δ =9.95 (s, 2H, -OH), 9.09 (s, 2H, quinoline imine), 8.86 (s, 2H, aniline imine), 8.52 (d, J = 8.0 Hz, 2H, 4-aminoquinoline), 8.41 (d, J = 4.0 Hz, 2H, 2-aminoquinoline), 8.04 (t, J = 8.0 Hz, 2H, 4-pyridinedicarboxaldehyde), 7.97 (d, J = 7.5 Hz, 2H, 3-pyridinedicarboxaldehyde next to the aniline), 7.74 (d, J = 8.0 Hz, 2H, 5-aminoquinoline), 7.66 (dd, J = 8.0 Hz, J' = 4.5 Hz, 2H, 3-aminoquinoline), 7.43 (d, J = 7.5 Hz, 2H, 3-pyridinedicarboxaldehyde next to the quinoline), 7.25 (t, J = 7.50 Hz, 2H, 6-aminoquinoline), 7.11 (d, J = 7.5 Hz, 2H, 7-aminoquinoline), 6.84 (d, J = 8.5 Hz, 4H, aniline next to the -OH), 6.67 (d, J = 8.0 Hz, 4H, aniline next to the imine). ^{13}C NMR (125.77 MHz, 298 K, DMSO): δ = 158.78, 155.98, 154.34, 150.37, 149.93, 149.19, 141.39, 140.22, 138.32, 137.51, 136.82, 129.05, 128.93, 128.58, 128.06, 126.96, 123.96, 123.73, 117.18, 115.93. **Head-to-head**: ^{1}H NMR (500 MHz, 298 K, DMSO): δ = 10.05 (s, 2H, -OH), 9.20 (s, 2H, quinoline imine), 8.66 (s, 2H, aniline imine), 8.53 (d, J = 8.50 Hz, 2H, 4-aminoquinoline), 8.33 (d, J = 4.0 Hz, 2H, 2-aminoquinoline), 8.16 (d, J = 8.0 Hz, 2H, 5-aminoquinoline), 8.00 (overlapping signals, 2H, 4-pyridinedicarboxaldehyde, 2H, 3-pyridinedicarboxaldehyde next to the aminoquinoline), 7.84 (t, J = 8.0 Hz, 2H, 6-aminoquinoline), 7.68 (overlapping signal, 2H, 7-aminoquinoline), 7.53 (d, J = 6.5 Hz, 2H, 3-aminoquinoline), 6.90 (d, J = 8.0 Hz, 4H, aniline next to the -OH), 6.67 (overlapping signal, 4H, aniline next to the imine). ESI-MS: *m/z* = 415.4 ($[\mathbf{M}]^{2+}$), 831.3 ($[\mathbf{M}$ - Cu + 2 MeOH$]^{+}$), 919.5 ($[\mathbf{M} + BF_4]^{+}$).

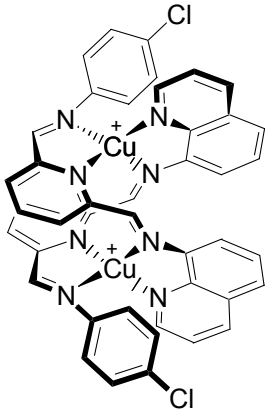
Amine **G**:



(+ Head to Head isomer)

When this complex was prepared in an NMR tube following the general procedure detailed above, the ^{1}H and ^{13}C spectra were the same as reported in the Materials and Methods section of the main text.

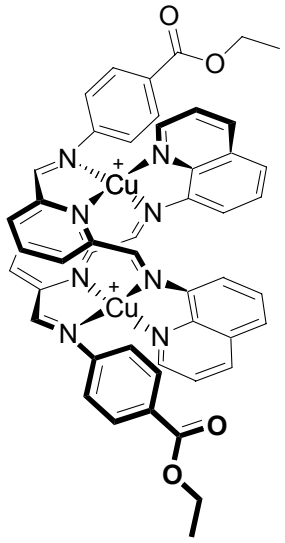
Amine **H**:



(+ Head to Head isomer)

^{1}H NMR (400 MHz, 298 K, DMSO) **Head-to-tail**: δ = 9.14 (s, 2H, quinoline imine), 9.00 (s, 2H, aniline imine), 8.46 (d, J = 8.5 Hz, 2H, 4-aminoquinoline), 8.38 (d, J = 3.5 Hz, 2H, 2-aminoquinoline), 7.16 (t, J = 8.0 Hz, 2H, 4-pyridinedicarboxaldehyde), 8.08 (d, J = 7.0 Hz, 2H, 3-pyridinedicarboxaldehyde next to the aniline), 7.76 (d, J = 8.0 Hz, 2H, 5-aminoquinoline), 7.67 (dd, J = 8.5 Hz, J' = 4.5 Hz, 2H, 3-aminoquinoline), 7.55 (d, J = 7.5 Hz, 2H, 3-pyridinedicarboxaldehyde next to the quinoline), 7.37 (d, J = 8.5 Hz, 4H, aniline next to the -Cl), 7.27 (t, J = 8.0 Hz, 2H, 6-aminoquinoline), 7.13 (d, J = 7.5 Hz, 2H, 7-aminoquinoline), 6.92 (d, J = 9.0 Hz, 4H, aniline next to the imine). **Head-to-head**: δ = 9.31 (s, 2H, quinoline imine), 8.90 (s, 2H, aniline imine), 8.55 (d, J = 9.0 Hz, 2H, 4-aminoquinoline), 8.38 (overlapping signal, 2H, 2-aminoquinoline), 8.18 (d, J = 8.0 Hz, 2H, 5-aminoquinoline), 8.05 (overlapping signal, 2H, 4-pyridinedicarboxaldehyde, 2H, 3-pyridinecarboxaldehyde next to the quinoline), 7.86 (m, 2H, 6- aminoquinoline), 7.78 (overlapping signal, 2H, 7-aminoquinoline), 7.66 (overlapping signal, 2H, 3-pyridinedicarboxaldehyde next to the quinoline), 7.48 (dd, J = 8.5 Hz, J' = 4.5 Hz, 2H, 2-aminoquinoline), 7.38 (overlapping signal, 4H, aniline next to the -Cl), 7.01 (d, J = 8.5 Hz, 4H, aniline next to the imine). ESI-MS: *m/z* = 434.0 ($[\mathbf{M}]^{2+}$), 803.0 ($[\mathbf{M} - Cu]^{+}$), 955.7 ($[\mathbf{M} + BF_4]^{+}$).

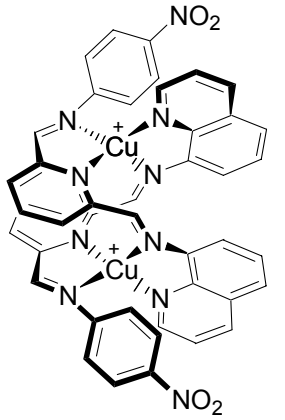
Amine **I**:



(+ Head to Head isomer)

^{1}H NMR (400 MHz, 298 K, DMSO) **Head-to-tail**: δ = 9.14 (s, 2H, quinoline imine), 9.07 (s, 2H, aniline imine), 8.47 (d, J = 7.5 Hz, 2H, 4-aminoquinoline), 8.38 (d, J = 4.0 Hz, 2H, 2-aminoquinoline), 8.13 (t, J = 7.0 Hz, 2H, 4-pyridinedicarboxaldehyde), 8.09 (d, J = 8.0 Hz, 2H, 3-pyridinedicarboxaldehyde next to the aniline), 7.87 (d, J = 8.5 Hz, 4H, aniline next to $–CO_2Et$), 7.77 (d, J = 8.0 Hz, 2H, 5-aminoquinoline), 7.67 (dd, J = 8.5 Hz, J' = 5 Hz, 2H, 3-aminoquinoline), 7.49 (d, J = 7.5 Hz, 2H, 3-pyridinedicarboxaldehyde next to the quinoline), 7.28 (t, J = 8.0 Hz, 2H, 6-aminoquinoline), 7.14 (d, J = 7.5 Hz, 2H, 7-aminoquinoline), 7.0 (d, J = 8.5 Hz, 4H, aniline next to the imine), 4.32 (dd, J = 13.5 Hz, J' = 7.0 Hz, 4H, -$COOC\underline{H}_2CH_3$), 1.34 (t, J = 7.0 Hz, 6H, -$COOCH_2C\underline{H}_3$). **Head-to-head**: δ = 9.31 (s, 2H, quinoline imine), 8.95 (s, 2H, aniline imine), 4.18 (dd, J = 13.5 Hz, J' = 7.0 Hz, 4H, -$COOC\underline{H}_2CH_3$), 1.26 (t, J = 7.0 Hz, 6H, -$COOCH_2C\underline{H}_3$). Aromatic signals were obscured by noise and peaks corresponding to the head-to-tail isomer. ESI-MS: *m/z* = 471.1 ($[\mathbf{M}]^{2+}$), 943.5 ($[\mathbf{M}$ - Cu + 2 MeOH$]^+$), 1030.8 ($[\mathbf{M} + BF_4]^+$).

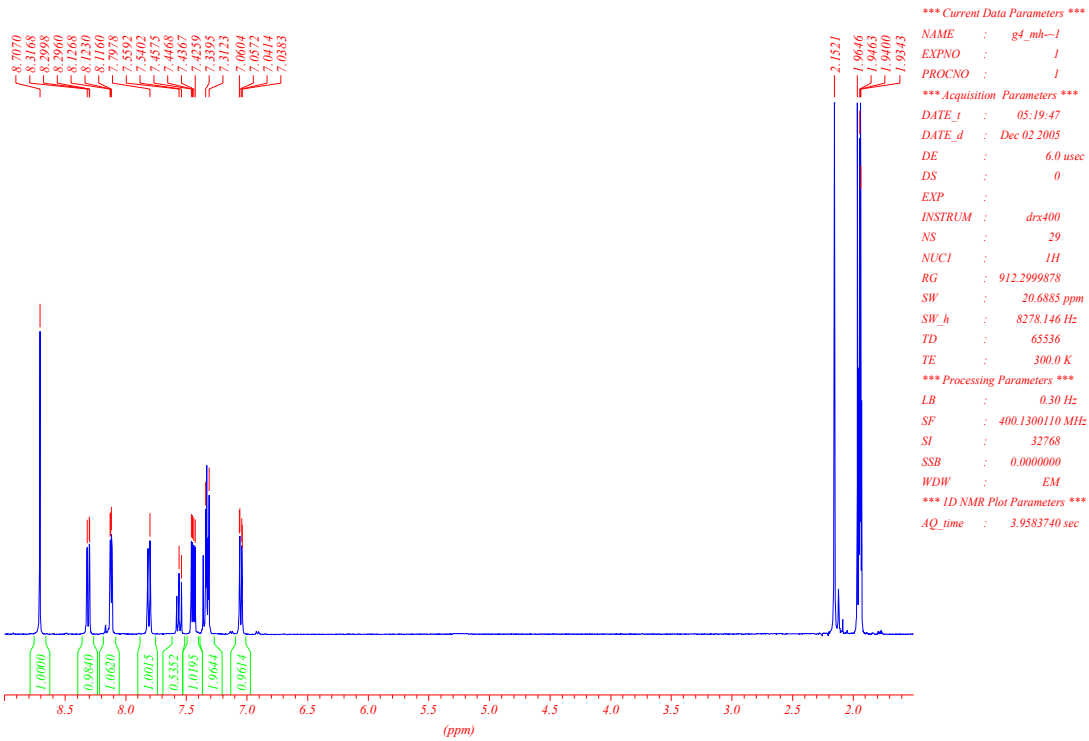
Amine **J**:

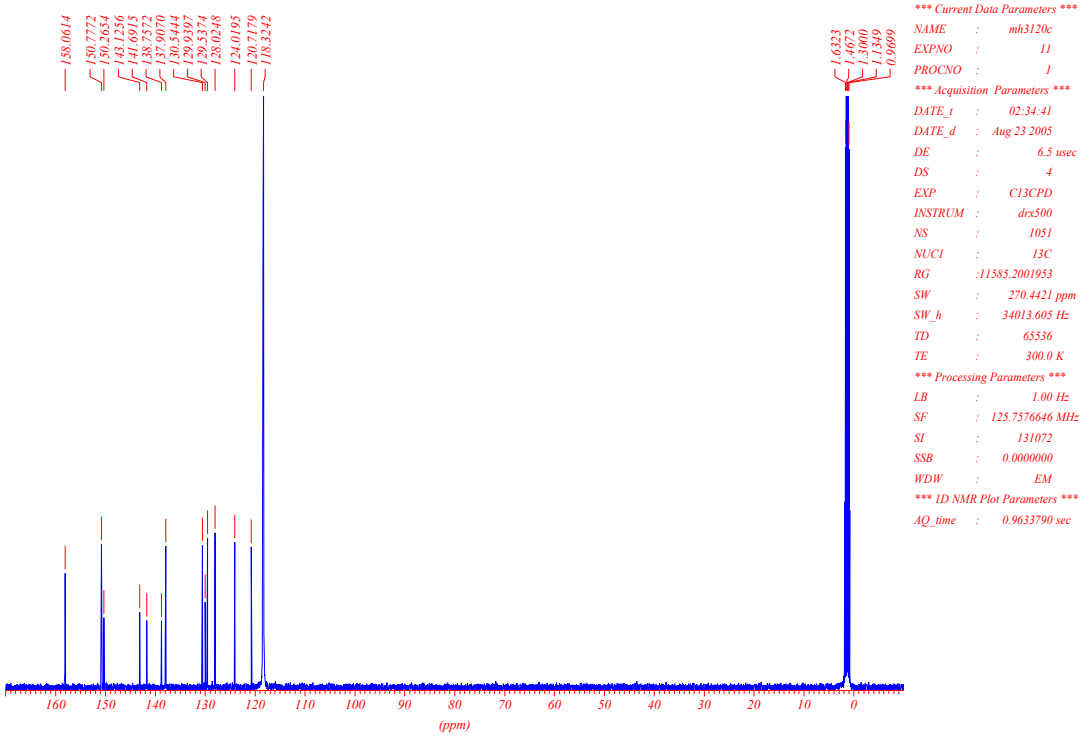


(+ Head to Head isomer)

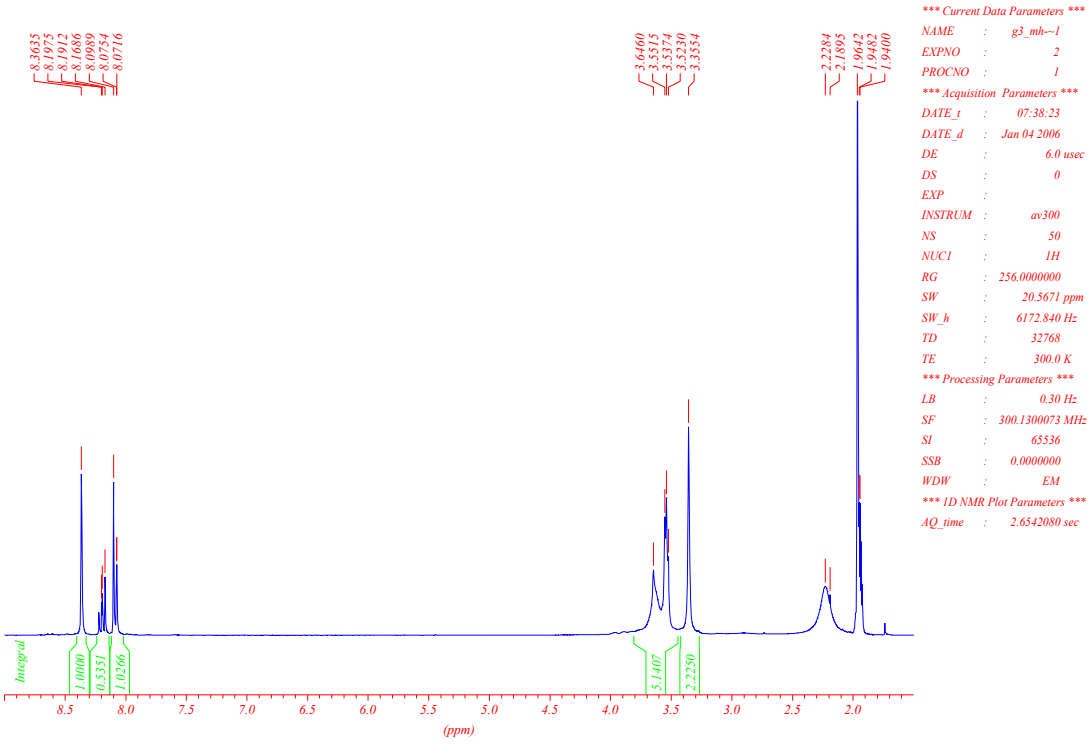
^{1}H NMR (400 MHz, 298 K, DMSO) **Head-to-tail**: δ = 9.10 (s, 2H, quinoline imine), 9.09 (s, 2H, aniline imine), 8.47 (d, J = 8.0 Hz, 2H, 4-aminoquinoline), 8.37 (d, J = 4.5 Hz, 2H, 2-aminoquinoline), 8.14 (m, 2H, 4-pyridinedicarboxaldehyde, 2H, 3-pyridinedicarboxakdehyde next to the aniline, 4H, aniline next to the nitro), 7.77 (d, J = 8.0 Hz, 2H, 5-aminoquinoline), 7.67 (dd, J = 8.0 Hz, J' = 4.5 Hz, 2H, 3-aminoquinoline), 7.59 (d, J = 7.5 Hz, 2H, 3-pyridinedicarboxaldehyde next to the quinoline), 7.28 (t, J = 8.0 Hz, 2H, 6-aminoquinoline), 7.14 (d, J = 7.5 Hz, 2H, 7-aminoquinoline), 7.07 (d, J = 9.0 Hz, 4H, aniline next to the imine). **Head-to-head**: δ = 9.24 (s, 2H, quinoline imine), 8.97 (s, 2H, aniline imine). Aromatic signals were obscured by noise and peaks corresponding to the head-to-tail isomer.

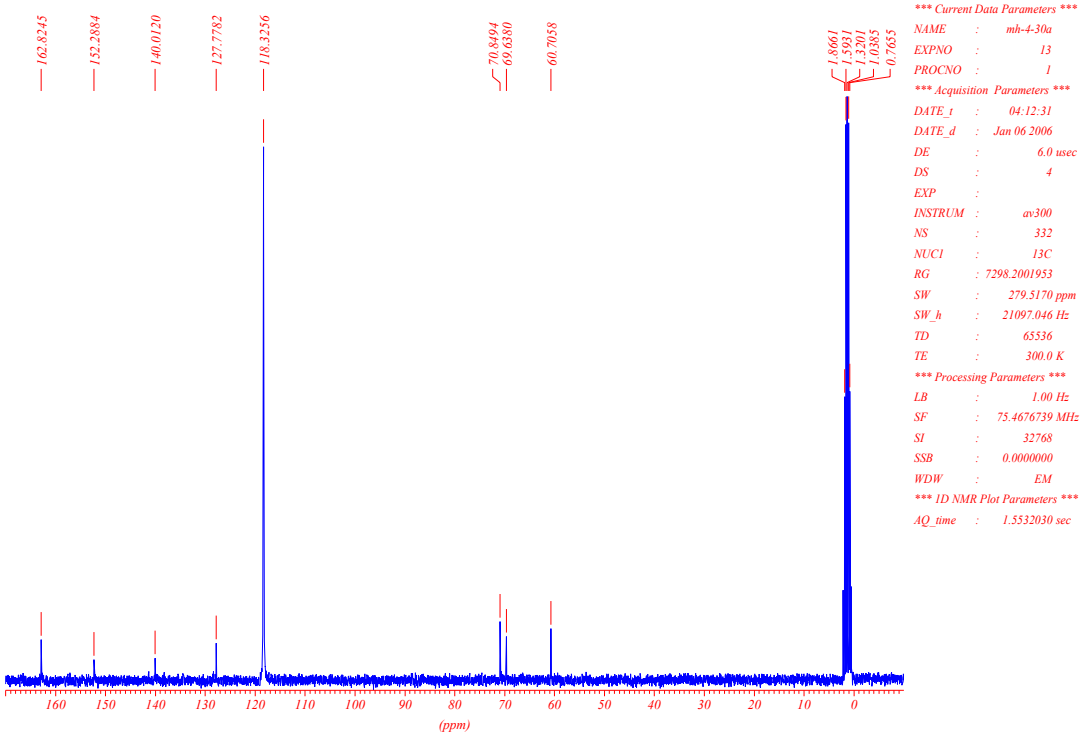
Supplementary NMR Spectra of Key Compounds



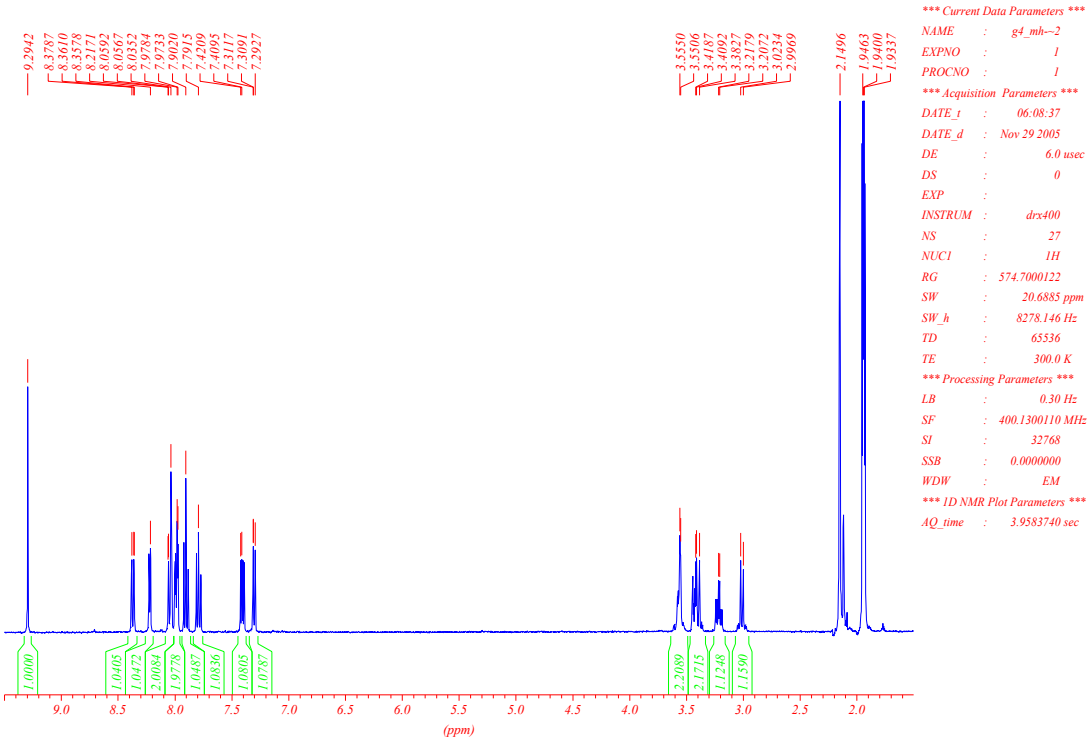


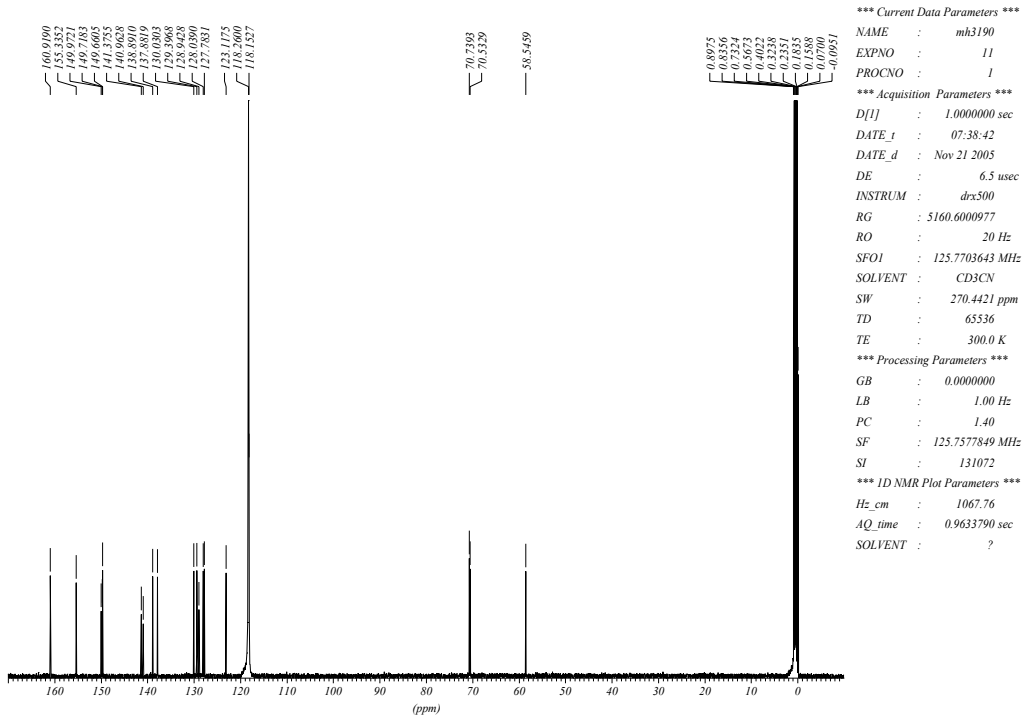
^{1}H and ^{13}C NMR spectra of **1** in CD_3CN



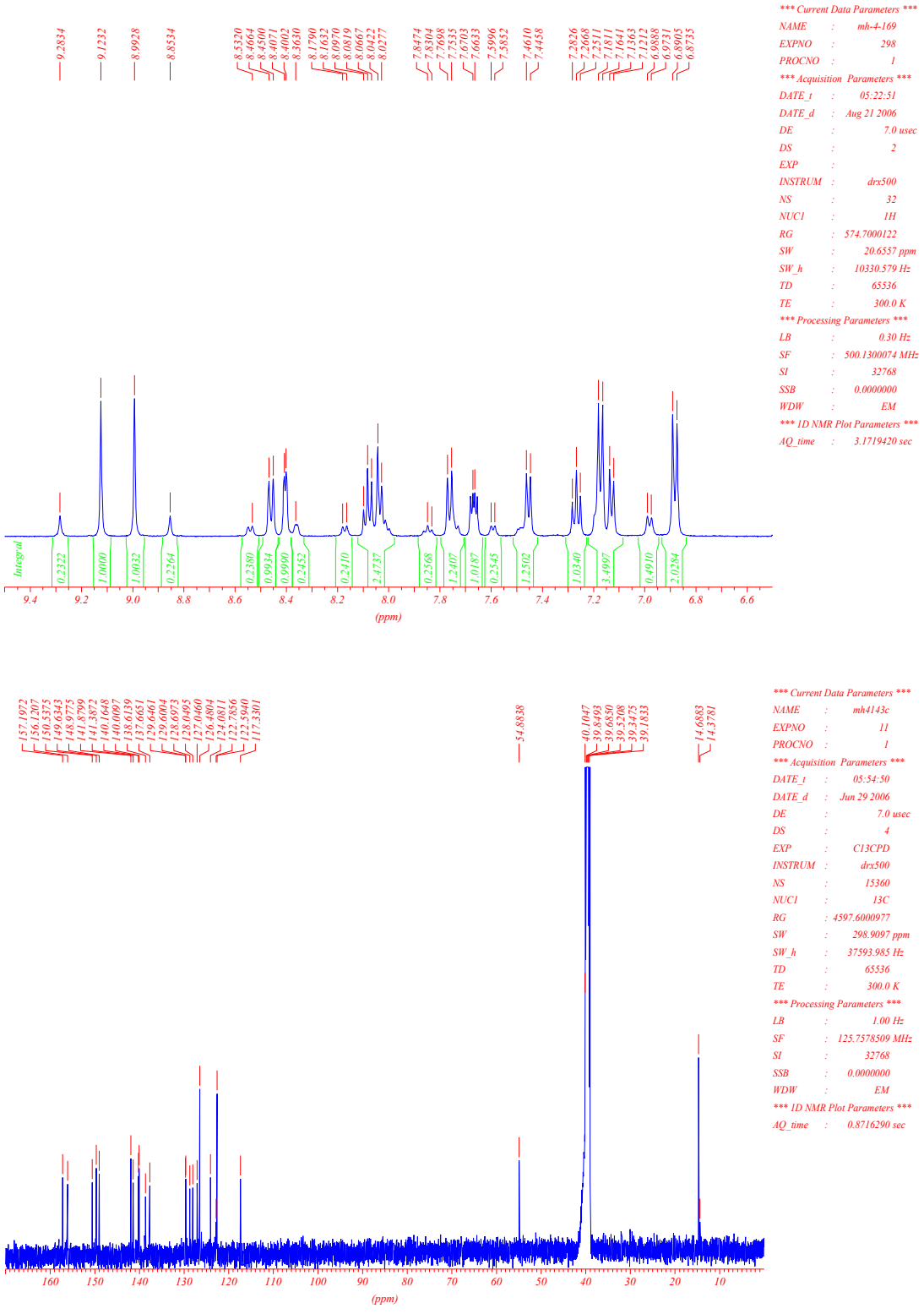


^{1}H and ^{13}C NMR spectra of **2** in CD_3CN

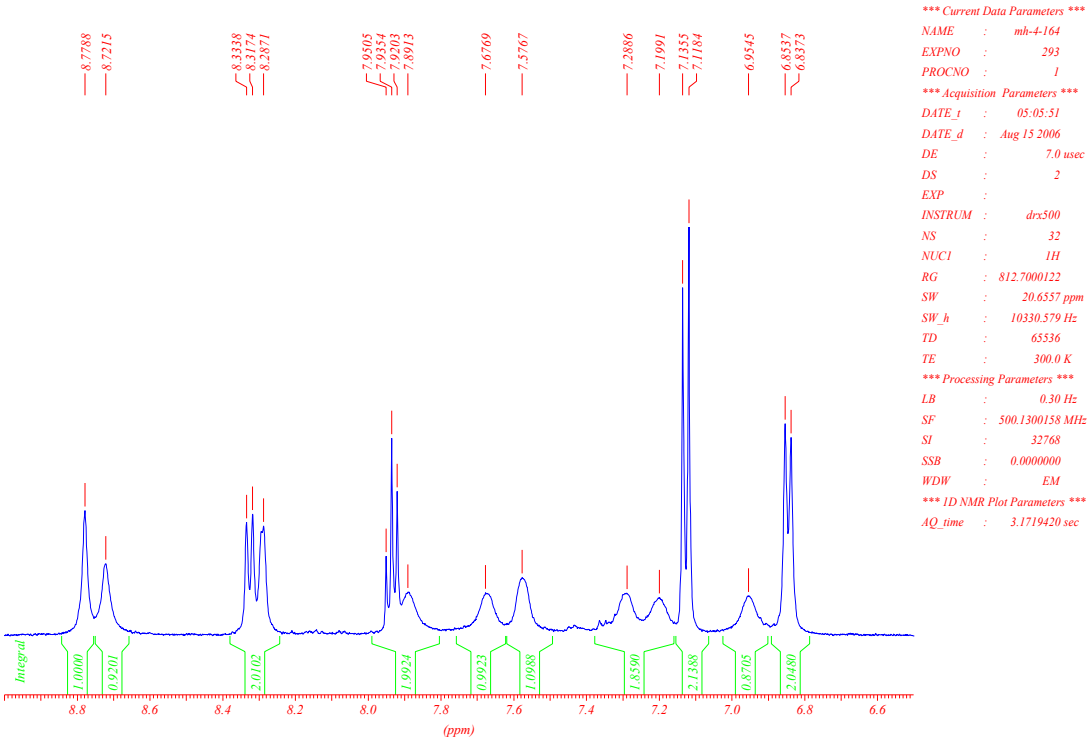




^{1}H and ^{13}C NMR spectra of **3** in CD_3CN



^{1}H and ^{13}C NMR spectra of the heterocomplex incorporating aniline **G** in DMSO at 298K



^{1}H NMR spectrum of the heterocomplex incorporating aniline **G** in CD_3CN