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Theoretical Studies of the Tautomerism in 3-(2-R-Phenylhydrazono)-naphthalene-1,2,4-triones: Synthesis of Copper(II) Complexes and Studies of Antibacterial and Antitumor Activities

Acácio I. Francisco,[a] Maria D. Vargas,*[,a] Thaís P. Fragoso,[a] J. Walkimar de M. Carneiro,[a] Annelise Casellato,[b] Fernando de C. da Silva,[a] Vitor F. Ferreira,[a] Jussara P. Barbosa,[c] Claudia Pessoa,[d] Letícia V. Costa-Lotufo,[d] José D. B. Marinho Filho,[d] Manoel O. de Moraes[d] and Antonio S. Mangrich[e]

[a]*Instituto de Química, Universidade Federal Fluminense, Campus do Valonguinho, Centro, 24020-150 Niterói-RJ, Brazil*

[b]*Instituto de Química, Universidade Federal do Rio de Janeiro, Ilha do Fundão, 21945-970 Rio de Janeiro-RJ, Brazil*

[c]*Instituto Oswaldo Cruz, FIOCRUZ, CP 926, 21045-900 Rio de Janeiro-RJ, Brazil*

[d]*Universidade Federal do Ceará, Depto de Fisiologia e Farmacologia, Campus do Porangabussu, 60430-270 Fortaleza-CE, Brazil*

[e]*Departamento de Química da Universidade Federal do Paraná, 81531-990 Curitiba-PR, Brazil*

Synthesis and characterization of the hydrazone compounds ***HL1-HL13***

Syntheses

A mixture of the respective arylamine (6.63 mmol), water (3.5 mL) and concentrated HCl (3.5 mL) was stirred until dissolution. The solution was then cooled by addition of crushed ice (1.00 g). When the temperature reached 0 ºC, $NaNO_2$ (4.39 mmol, 0.303 g) in cold water (2 mL) was added to the mixture. The solution was stirred at 0 ºC for 20 min and then added dropwise to a stirred solution of 2-hydroxy-1,4 naphthoquinone (3.65 mmol, 0.635 g) and sodium hydroxide (10.95 mmol, 0.438 g) in ethanol (28 mL) kept at 0 ºC. The resulting orange solids were filtered, washed with cold water and ethanol and dried under vacuum.

Analytical and spectroscopic data for ***HL1-HL13***

*3-[2-(4-methoxy)phenylhydrazono]-naphthalene-1,2,4-trione (**HL1**)*

From 0.815 g of 4-methoxyaniline. Yield: 0.922 g, 82%, mp 229-230 ºC. Anal. Calcd. for $C_{17}H_{12}N_2O_4$: C 66.04; H 4.29; N 8.76%. Found: C 66.06; H 4.32; N 8.67%. IR (KBr, ν_{max}/cm^{-1}): 3435 (N-H), 3078 (C-H arom.), 2847 (C-H alif.), 1678 (C=O/C=N), 1587 (C=C), 1260 (C-O), 972 (C-N=N-C). ^{1}H NMR (dmso-d_6, 300 MHz): δ 8.33 (bd, *J* 7.74 Hz, 1H), 8.21 (dd, *J* 7.74, 0.48 Hz, 1H), 8.06 (td, *J* 7.74, 7.74, 0.48 Hz, 1H), 7.98 (td, *J* 7.74, 7.74, 0.48 Hz, 1H), 7.87 (bd, *J* 6.42 Hz, 2H), 7.23 (bd, *J* 6.42 Hz, 2H), 3.94 (s, 3H). ^{13}C NMR (dmso-d_6, 75 MHz): δ 160.0, 136.1, 135.4, 135.1, 134.4, 128.2, 127.9, 120.7, 116.0, 56.3. UV-Vis [dmso; λ/nm (log ε)]: 276 (4.51), 473 (3.52).

*3-[2-(4-benzoyl)phenylhydrazono]-naphthalene-1,2,4-trione (**HL2**)*

From 1.306 g of 4-aminoazobenzol. Yield: 1.101 g, 79%, mp 290-292 ºC. Anal. Calcd. for $C_{22}H_{14}N_4O_3$: C 69.10; H 3.69; N 14.65%. Found: C 69.05; H 3.73; N 14.69%. IR (KBr, ν_{max}/cm^{-1}): 3439 (N-H), 3062, 3102 (C-H arom.), 1688 (C=O/C=N), 1590 (C=C), 1255 (C-O), 974 (C-N=N-C). ^{1}H NMR (dmso-d_6, 300 MHz): δ 8.36 (bd, *J* 7.38 Hz, 1H), 8.24 (dd, *J* 7.38, 1.48 Hz, 1H), 8.15 (bd, *J* 8.85 Hz, 2H), 8.12-7.98 (m, 6H), 7.76-7.67 (m, 3H). ^{13}C NMR (dmso-d_6, 75 MHz): δ 175.8, 152.4, 150.4, 144.1, 135.4, 131.9, 129.8, 127.5, 124.7, 118.8. UV-Vis [dmso; λ/nm (log ε)]: 257 (4.73), 459 (3.79).

*3-[2-(4-chloro)phenylhydrazono]-naphthalene-1,2,4-trione (**HL3**)*

From 0.842 g of 4-chloroaniline. Yield: 0.945 g, 83%, mp 215-217 ºC. Anal. Calcd. for $C_{16}H_9ClN_2O_3$: C 61.45; H 2.90; N 8.96%. Found: C 61.65; H 3.10; N 9.07%. IR (KBr, ν_{max}/cm^{-1}): 3428 (N-H), 3083 (C-H arom.), 1695 (C=O/C=N) and 1669 (C=O), 1594 (C=C), 1255 (C-O), 969 (C-N=N-C). ^{1}H NMR (dmso-d_6, 300 MHz): δ 8.34 (bd, *J* 7.28 Hz, 1H), 8.24 (dd, *J* 7.28, 1.81 Hz, 1H), 8.07 (td, *J* 7.28, 7.28, 1.81 Hz, 1H), 8.01 (td, *J* 7.28, 7.28, 1.81 Hz,

*e-mail: mdvargas@vm.uff.br

1H), 7.92 (bd, *J* 8.80 Hz, 2H), 7.69 (bd, *J* 8.80 Hz, 2H). ^{13}C NMR (dmso-d_6, 75 MHz): δ 140.6, 135.1, 129.7, 127.1, 119.4. UV-Vis [dmso; λ/nm (log ε)]: 266 (4.33), 431 (3.48).

3-[2-(4-iodo)phenylhydrazono]-naphthalene-1,2,4-trione ***(HL4)***

From 1.452 g of 4-iodoaniline. Yield: 1.179 g, 80%, mp 201-202 ºC. Anal. Calcd. for $C_{16}H_9IN_2O_3$: C 47.55; H 2.24; N 6.93%. Found: C 47.57; H 2.34; N 7.04%. IR (KBr, ν_{max}/cm^{-1}): 3438 (N-H), 3084 (C-H arom.), 1690 (C=O/C=N) and 1663 (C=O), 1599 (C=C), 1257 (C-O), 969 (C-N=N-C). ^{1}H NMR (dmso-d_6, 300 MHz): δ 8.32 (dd, *J* 7.31, 1.55 Hz, 1H), 8.22 (dd, *J* 7.31, 1.55 Hz, 1H), 8.10-8.02 (m, 2H), 7.97 (bd, *J* 8.86 Hz, 2H), 7.69 (bd, *J* 8.86 Hz, 2H). ^{13}C NMR (dmso-d_6, 75 MHz): δ 175.9, 141.9, 139.0, 135.6, 134.7, 133.9, 128.1, 127.7, 120.4. UV-Vis [dmso; λ/nm (log ε)]: 298 (4.57), 438 (3.61).

3-[2-(3-iodo)phenylhydrazono]-naphthalene-1,2,4-trione ***(HL5)***

From 1.452 g of 3-iodoaniline. Yield: 1.135 g, 77%, mp 216-218 ºC. Anal. Calcd. for $C_{16}H_9IN_2O_3$: C 47.55; H 2.24; N 6.93%. Found: C 47.53; H 2.21; N 6.90%. IR (KBr, ν_{max}/cm^{-1}): 3438 (N-H), 3087 (C-H arom.), 1688 (C=O/C=N), 1600 (C=C), 1261 (C-O), 969 (C-N=N-C). ^{1}H NMR (dmso-d_6, 300 MHz): δ 8.35 (dd, *J* 7.35, 1.49 Hz, 1H), 8.29-8.21 (m, 2H), 8.07 (td, *J* 7.35, 7.35, 1.49 Hz, 1H), 8.01 (td, *J* 7.35, 7.35, 1.49 Hz, 1H), 7.90 (dd, *J* 7.35, 1.57 Hz, 1H), 7.79 (dl, *J* 7.35 Hz, 1H), 7.42 (bt, *J* 7.35 Hz, 1H). ^{13}C NMR (dmso-d_6, 75 MHz): δ 175.3, 142.7, 135.4, 134.4, 135.0, 131.5, 127.1, 125.7, 117.2, 95.2. UV-Vis [dmso; λ/nm (log ε)]: 270 (4.61), 425 (3.32).

3-[2-(2-iodo)phenylhydrazono]-naphthalene-1,2,4-trione ***(HL6)***

From 1.452 g of 2-iodoaniline. Yield: 1.297 g, 88%, mp 230-232 ºC. Anal. Calcd. for $C_{16}H_9IN_2O_3$: C 47.55; H 2.24; N 6.93%. Found: C 47.55; H 2.24; N 6.93%. IR (KBr, ν_{max}/cm^{-1}): 3438 (N-H), 3087 (C-H arom.), 1688 (C=O/C=N), 1601 (C=C), 1259 (C-O), 969 (C-N=N-C). ^{1}H NMR (dmso-d_6, 300 MHz): δ 8.37 (bd, *J* 7.33 Hz, 1H), 8.26 (bd, *J* 7.33 Hz, 1H), 8.12-7.91 (m, 4H), 7.70 (bt, *J* 7.63 Hz, 1H), 7.23 (bt, *J* 7.63 Hz, 1H). ^{13}C NMR (dmso-d_6, 75 MHz): δ 178.9, 141.5, 139.6, 135.0, 134.5, 134.0, 133.4, 133.1, 132.5, 129.9, 128.6, 127.7, 127.2, 117.6, 117.4, 87.5. UV-Vis [dmso; λ/nm (log ε)]: 276 (4.44), 434 (3.33).

3-[2-(4-carboxy)phenylhydrazono]-naphthalene-1,2,4-trione ***(HL7)***

From 0.908 g of 4-carboxyaniline. Yield: 1.046 g, 89%, mp 235-237 ºC. Anal. Calcd. for $C_{17}H_{10}N_2O_5$: C 62.66; H 3.22; N 8.65%. Found: C 62.55; H 3.25; N 8.67%. IR (KBr, ν_{max}/cm^{-1}): 3451-2700 (O-H COOH/N-H), 3068 (C-H arom.), 1689 (C=O/C=N), 1598 (C=C), 1263 (C-O), 968 (C-N=N-C). ^{1}H NMR (dmso-d_6, 300 MHz): δ 8.35 (bd, *J* 8.41 Hz, 1H), 8.24 (dd, *J* 8.41, 1.53 Hz, 1H), 8.17 (bd, *J* 7.44 Hz, 2H), 8.08 (td, *J* 8.41, 8.41, 1.53 Hz, 1H), 8.02 (td, *J* 8.41, 8.41, 1.53 Hz, 1H), 7.96 (bd, *J* 7.44 Hz, 2H). ^{13}C NMR (dmso-d_6, 75 MHz): δ 175.5, 166.5, 144.8, 135.0, 131.0, 128.6, 127.1, 117.4. UV-Vis [dmso; λ/nm (log ε)]: 277 (4.49), 424 (3.67).

3-[2-(3-carboxy)phenylhydrazono]-naphthalene-1,2,4-trione ***(HL8)***

From 0.908 g of 3-carboxyaniline. Yield: 0.834 g, 71%, mp 270-272 ºC. Anal. Calcd. for $C_{17}H_{10}N_2O_5$: C 62.66; H 3.22; N 8.65%. Found: C 62.67; H 3.20; N 8.64%. IR (KBr, ν_{max}/cm^{-1}): 3449-2600 (O-H COOH/N-H), 3051 (C-H arom.), 1689 (C=O/C=N), 1605 (C=C), 1251 (C-O), 968 (C-N=N-C). ^{1}H NMR (dmso-d_6, 300 MHz): δ 8.36 (m, 1H), 8.31 (dd, *J* 7.42, 1.45 Hz, 1H), 8.13 (dd, *J* 7.42, 1.45 Hz, 1H), 8.05-7.95 (m, 3H), 7.90 (td, *J* 7.42, 7.42, 1.45 Hz, 1H), 7.71 (bt, *J* 7.51 Hz, 1H). ^{13}C NMR (dmso-d_6, 75 MHz): δ 179.1, 172.0, 167.7, 147.8, 135.4, 134.0, 133.5, 133.1, 130.0, 128.3, 127.4, 127.2, 124.0, 120.0. UV-Vis [dmso; λ/nm (log ε)]: 271 (4.63), 441 (3.63).

3-[2-(4-ciano)phenylhydrazono]-naphthalene-1,2,4-trione ***(HL9)***

From 0.782 g of 4-cianoaniline. Yield: 0.929 g, 84%, mp 255-259 ºC. Anal. Calcd. for $C_{17}H_9N_3O_3$: C 67.33; H 2.99; N 13.86%. Found: C 67.69; H 3.01; N 13.88%. IR (KBr, ν_{max}/cm^{-1}): 3426 (N-H), 3070 (C-H arom.), 2220 (CN), 1695 (C=O/C=N), 1607 (C=C), 1260 (C-O), 967 (C-N=N-C). ^{1}H NMR (dmso-d_6, 300 MHz): δ 8.34 (dd, *J* 6.93, 1.65 Hz, 1H), 8.24 (dd, *J* 6.93, 1.65 Hz, 1H), 8.10-7.99 (m, 6H). ^{13}C NMR (dmso-d_6, 75 MHz): δ 179.4, 176.0, 135.6, 134.8, 134.4, 128.0, 127.7, 119.1, 118.6, 108.7. UV-Vis [dmso; λ/nm (log ε)]: 282 (4.77), 425 (3.42).

3-[2-(3-ciano)phenylhydrazono]-naphthalene-1,2,4-trione ***(HL10)***

From 0.782 g of 3-cianoaniline. Yield: 0.818 g, 74%, mp 280-281 ºC. Anal. Calcd. for $C_{17}H_9N_3O_3$: C 67.33; H 2.99; N 13.86%. Found: C 67.30; H 2.96; N 13.87%. IR (KBr, ν_{max}/cm^{-1}): 3431 (N-H), 3080 (C-H arom.), 2231 (CN), 1692 (C=O/C=N) and 1655 (C=O), 1600 (C=C), 1261 (C-O), 972 (C-N=N-C). ^{1}H NMR (dmso-d_6, 300 MHz): δ 8.38-8.17 (m, 4H), 8.12-7.98 (m, 2H), 7.90-7.80 (m, 2H). ^{13}C NMR (dmso-d_6, 75 MHz): δ 179.3, 176.1, 143.2, 135.7, 135.3, 134.3, 131.7, 130.5, 128.4, 127.8, 122.5, 121.6, 118.9, 113.1. UV-Vis [dmso; λ/nm (log ε)]: 278 (4.63), 417 (3.41).

*3-[2-(4-nitro)phenylhydrazono]-naphthalene-1,2,4-trione (**HL11**)*

From 0.915 g of 4-nitroaniline. Yield: 1.084 g, 92%, mp 275-276 ºC. Anal. Calcd. for $C_{16}H_9N_3O_5$: C 59.45; H 2.81; N 13.00%. Found: C 59.33; H 2.87; N 13.05%. IR (KBr, ν_{max}/cm^{-1}): 3452 (N-H), 3084 (C-H arom.), 1686 (C=O/C=N), 1512 and 1316 (NO_2), 1264 (C-O), 968 (C-N=N-C). ^{1}H NMR (dmso-d_6, 300 MHz): δ 8.48 (bd, *J* 8.51 Hz, 2H), 8.34 (dd, *J* 7.07, 1.64 Hz, 1H), 8.25 (dd, *J* 7.07, 1.64 Hz, 1H), 8.11-7.99 (m, 4H). ^{13}C NMR (dmso-d_6, 75 MHz): δ 184.1, 181.1, 152.5, 150.1, 140.4, 139.0, 133.0, 132.7, 131.1, 123.2. UV-Vis [dmso; λ/nm (log ε)]: 290 (4.55), 429 (3.71).

*3-[2-(3-nitro)phenylhydrazono]-naphthalene-1,2,4-trione (**HL12**)*

From 0.915 g of 3-nitroaniline. Yield: 0.955 g, 81%, mp 167-168 ºC. Anal. Calcd. for $C_{16}H_9N_3O_5$: C 59.45; H 2.81; N 13.00%. Found: C 59.28; H 2.97; N 12.99%. IR (KBr, ν_{max}/cm^{-1}): 3445 (N-H), 3090 (C-H arom.), 1675 (C=O/C=N), 1496 and 1315 (NO_2), 1261 (C-O), 973 (C-N=N-C). ^{1}H NMR (dmso-d_6, 300 MHz): δ 8.71 (m, 1H), 8.35 (dd, *J* 7.97, 1.93 Hz, 1H), 8.31 (dd, *J* 7.97, 1.93 Hz, 1H), 8.22 (m, 2H), 8.07 (td, *J* 7.97, 7.97, 1.93 Hz, 1H), 8.01 (td, *J* 7.97, 7.97, 1.93 Hz, 1H), 7.90 (bt, 7.54 Hz, 1H). ^{13}C NMR (dmso-d_6, 75 MHz): δ 184.1, 181.1, 153.7, 150.0, 141.2, 133.7, 131.3, 123.5. UV-Vis [dmso; λ/nm (log ε)]: 293 (4.57), 416 (3.68).

*3-[2-(2-nitro)phenylhydrazono]-naphthalene-1,2,4-trione (**HL13**)*

From 0.915 g of 2-nitroaniline. Yield: 1.297 g, 78%, mp 249-250 ºC. Anal. Calcd. for $C_{16}H_9N_3O_5$: C 59.45; H 2.81; N 13.00%. Found: C 59.52; H 2.89; N 12.95%. IR (KBr, ν_{max}/cm^{-1}): 3455 (N-H), 3090 (C-H arom.), 1683 (C=O/C=N), 1600 (C=C), 1457 and 1332 (NO_2), 1271 (C-O), 982 (C-N=N-C). ^{1}H NMR (dmso-d_6, 300 MHz): δ 8.37 (bd, *J* 7.33 Hz, 1H), 8.26 (bd, *J* 7.33 Hz, 1H), 8.12-7.91 (m, 4H), 7.70 (bt, *J* 7.63 Hz, 1H), 7.23 (bt, *J* 7.63 Hz, 1H). ^{13}C NMR (dmso-d_6, 75 MHz): δ 178.9, 141.5, 139.6, 135.0, 134.5, 134.0, 133.4, 133.1, 132.5, 129.9, 128.6, 127.7, 127.2, 117.6, 117.4, 87.5. UV-Vis [dmso; λ/nm (log ε)]: 278 (4.52), 440 (3.74).

*^{1}H and ^{13}C NMR spectra of compounds **HL1**-**HL13***

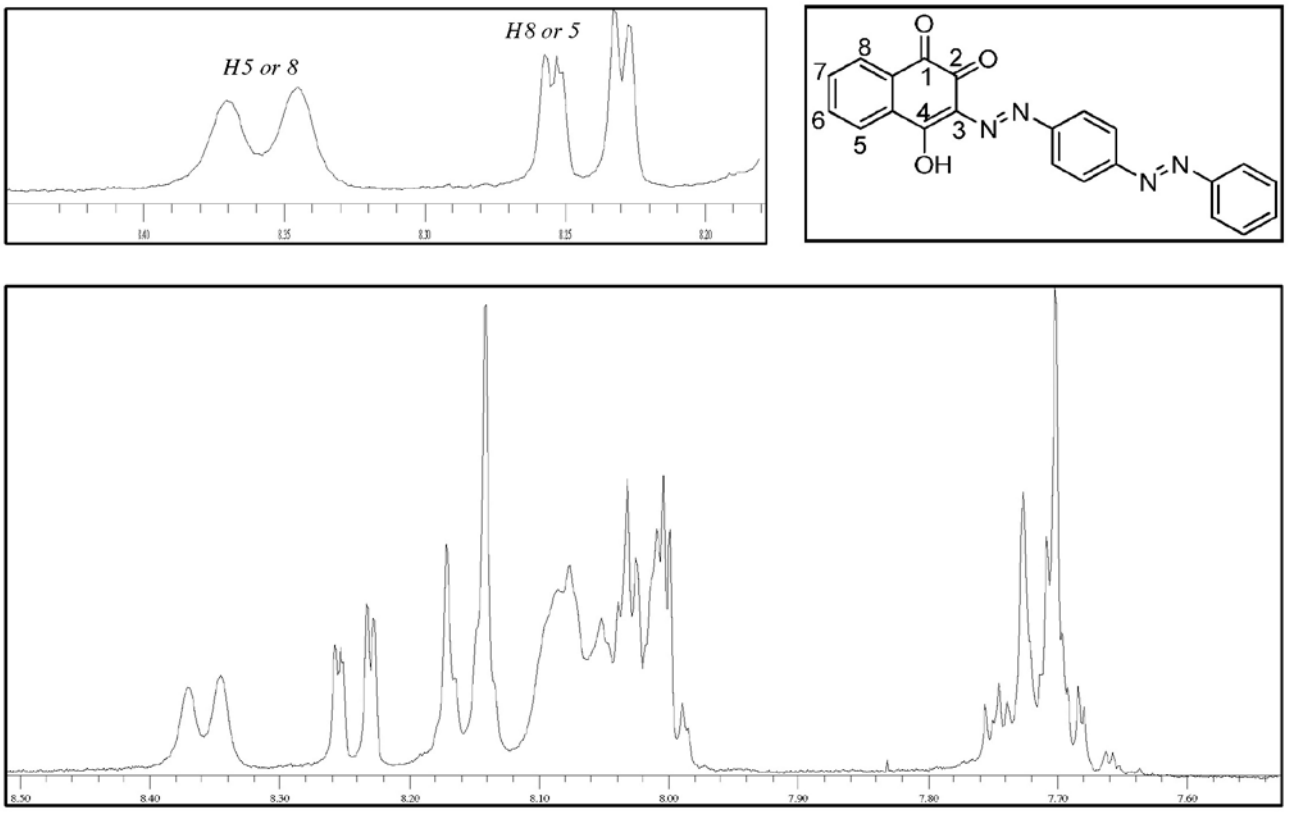


Figure S1. ^{1}H NMR spectrum of 3-[2-(4-benzoyl)phenylhydrazono]-naphthalene-1,2,4-trione (**HL2**).

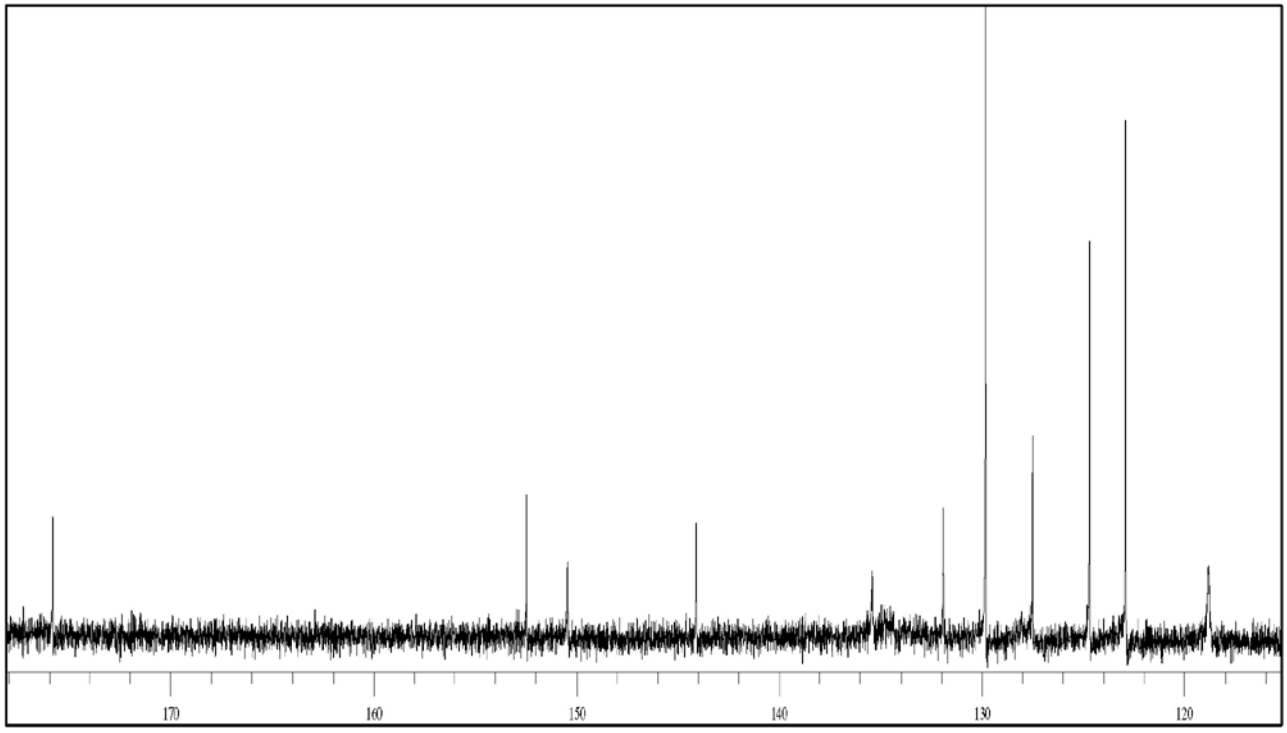


Figure S2. ^{13}C NMR spectrum of 3-[2-(4-benzoyl)phenylhydrazono]-naphthalene-1,2,4-trione (**HL2**).

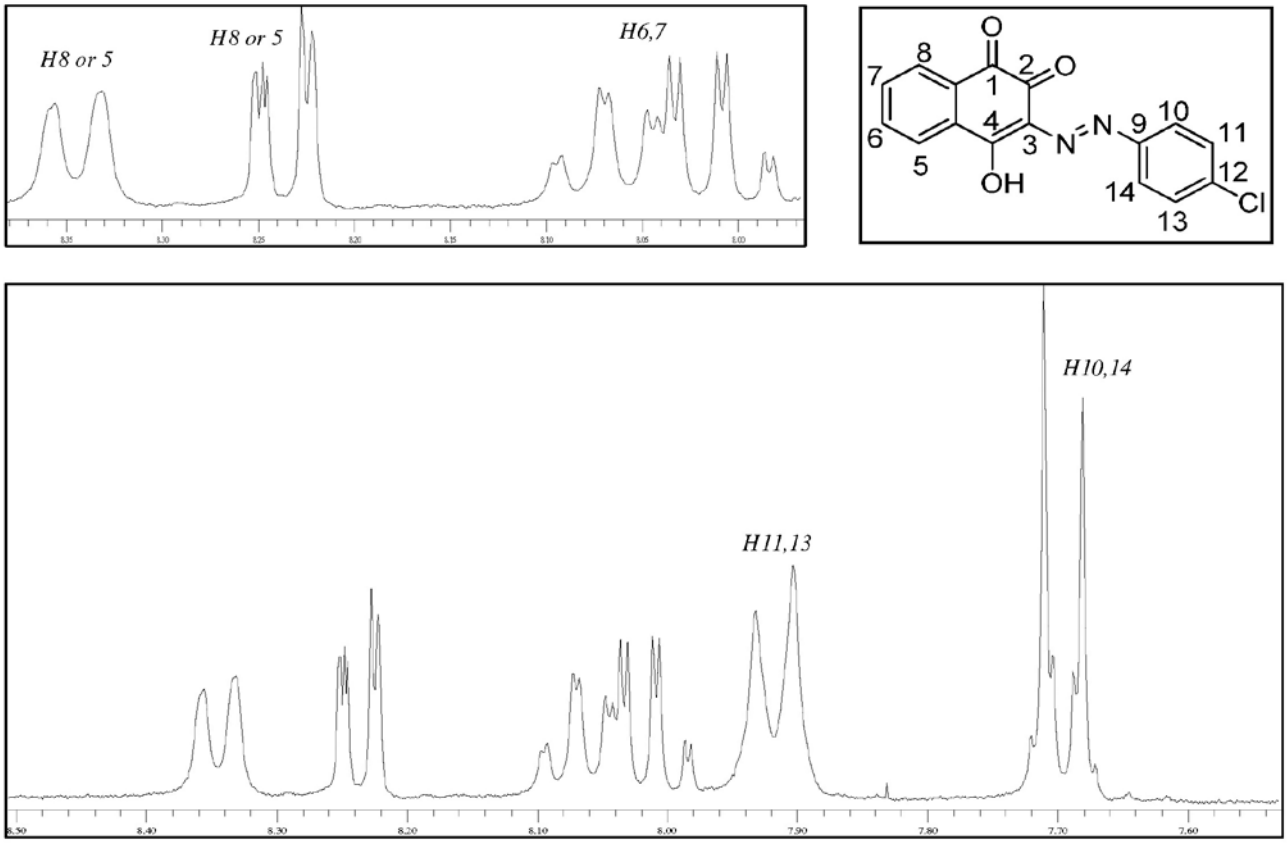


Figure S3. ^{1}H NMR spectrum of 3-[2-(4-chloro)phenylhydrazono]-naphthalene-1,2,4-trione (**HL3**).

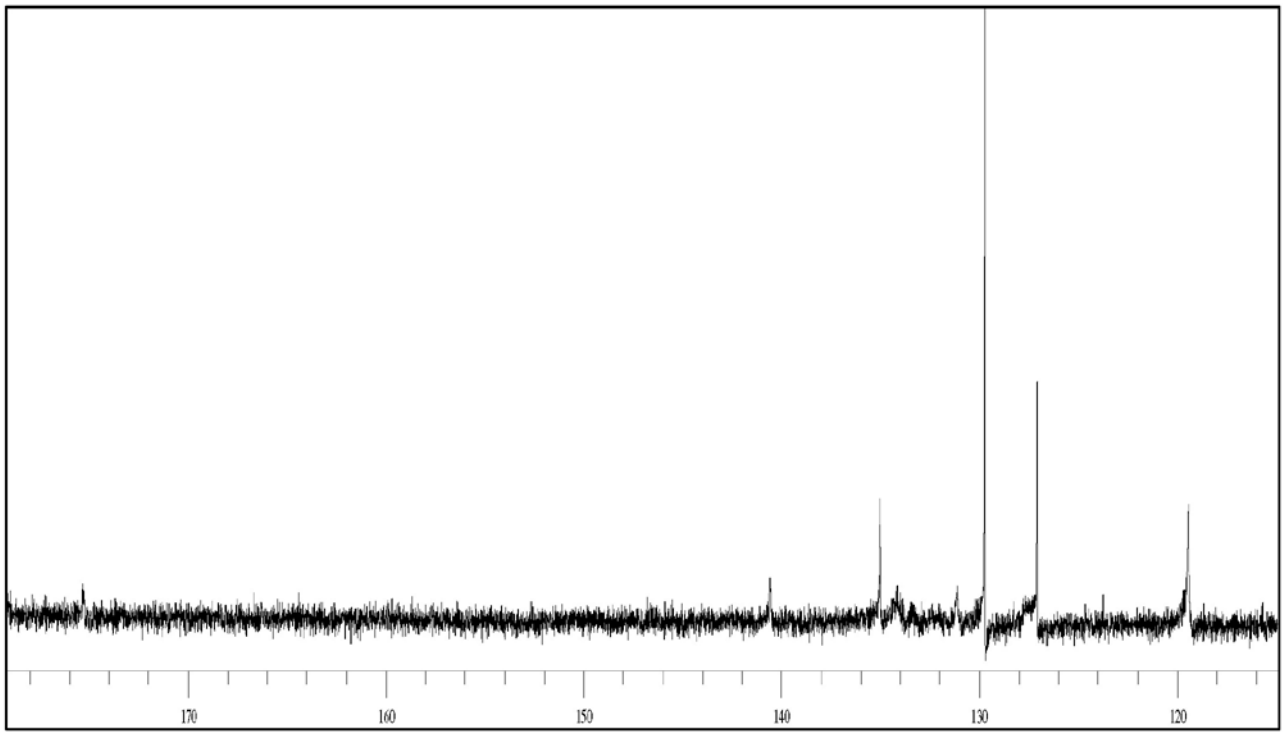


Figure S4. ^{13}C NMR spectrum of 3-[2-(4-chloro)phenylhydrazono]-naphthalene-1,2,4-trione (**HL3**).

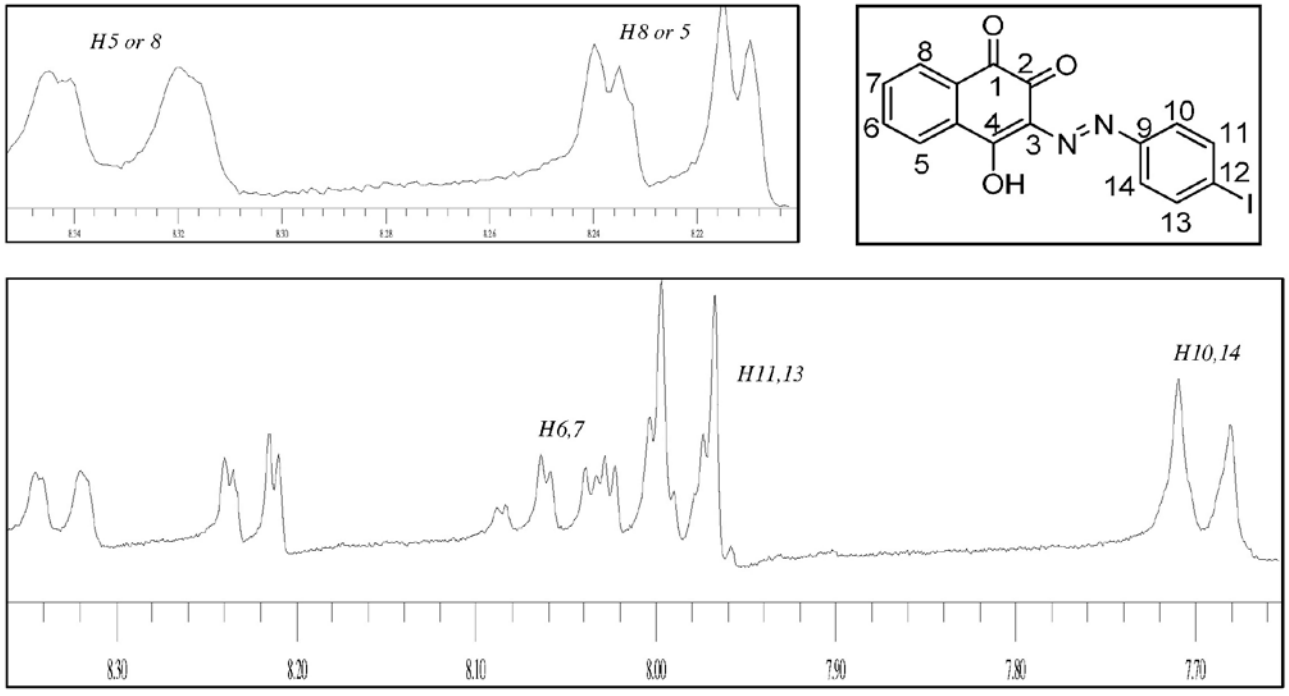


Figure S5. ^{1}H NMR spectrum of 3-[2-(4-iodo)phenylhydrazono]-naphthalene-1,2,4-trione (**HL4**).

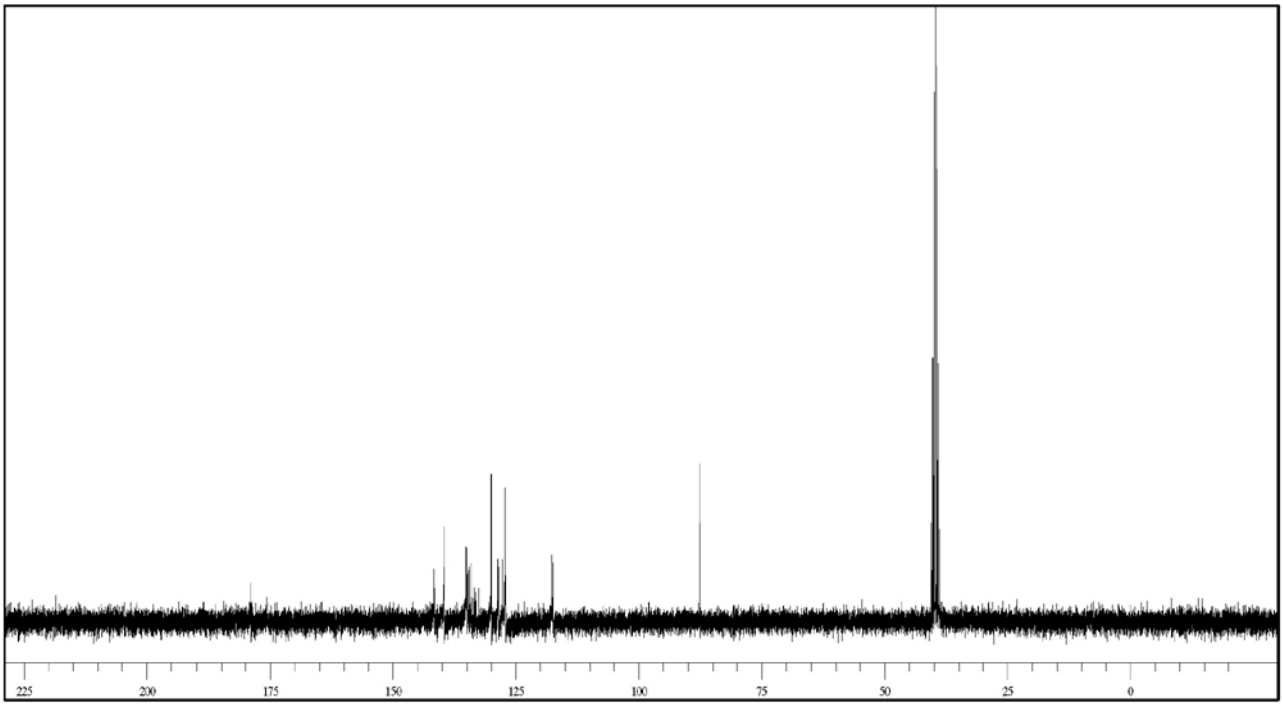


Figure S6. ^{13}C NMR spectra of 3-[2-(4-iodo)phenylhydrazono]-naphthalene-1,2,4-trione (**HL4**).

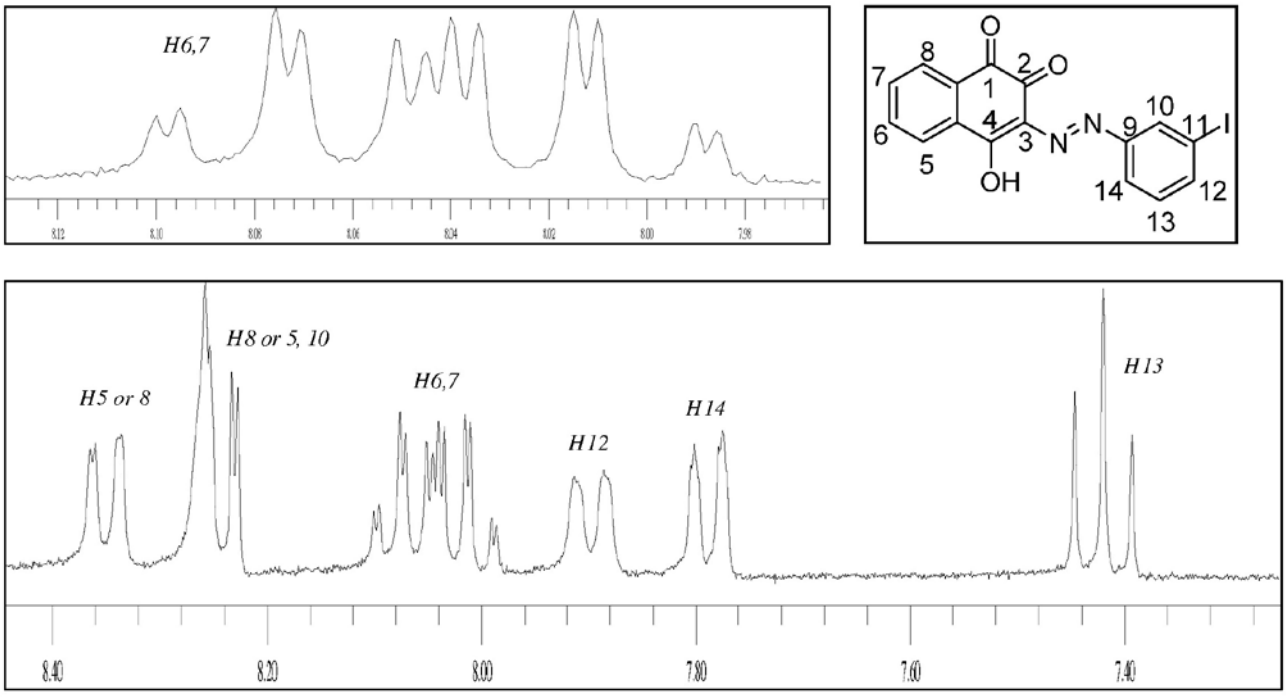


Figure S7. ^{1}H NMR spectrum of 3-[2-(3-iodo)phenylhydrazono]-naphthalene-1,2,4-trione (**HL5**).

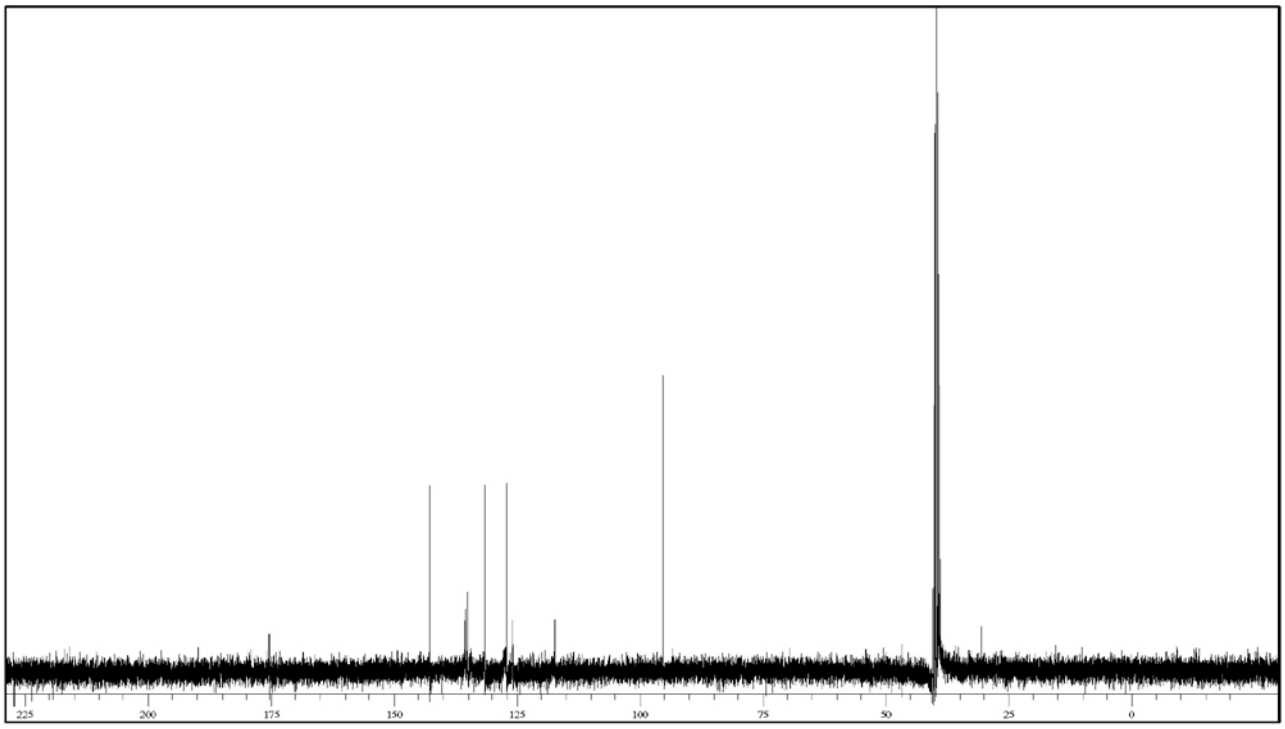
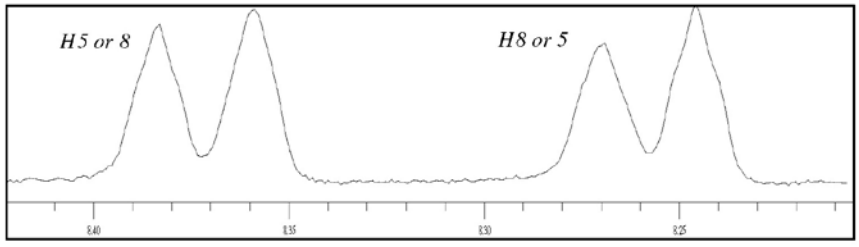
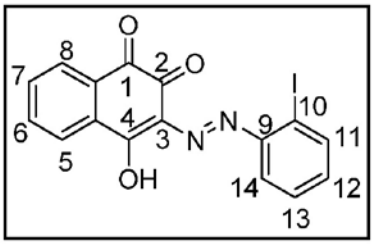


Figure S8. ^{13}C NMR spectrum of 3-[2-(3-iodo)phenylhydrazono]-naphthalene-1,2,4-trione (**HL5**).





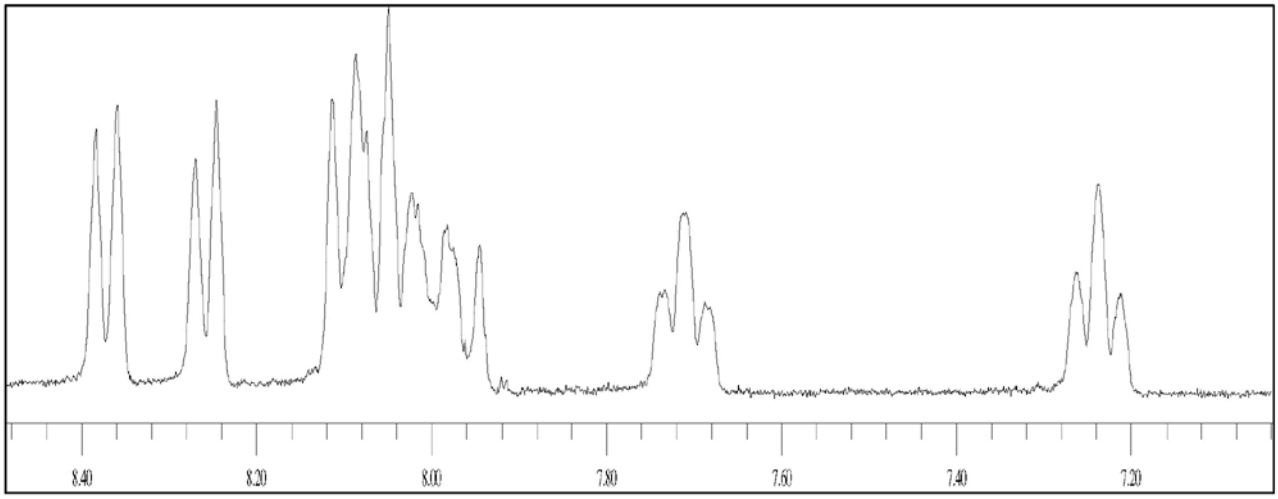


Figure S9. ^{1}H NMR spectrum of 3-[2-(2-iodo)phenylhydrazono]-naphthalene-1,2,4-trione (**HL6**).

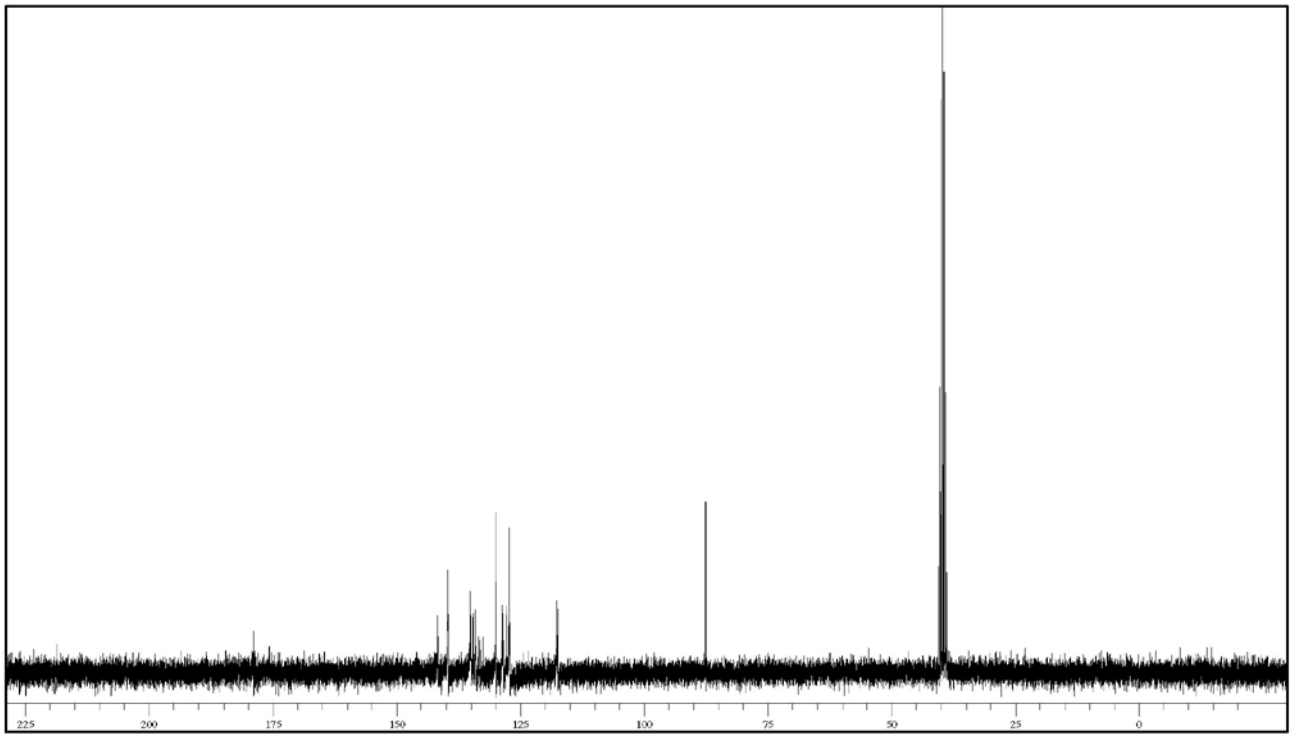


Figure S10. ^{13}C NMR spectrum of 3-[2-(2-iodo)phenylhydrazono]-naphthalene-1,2,4-trione (**HL6**).

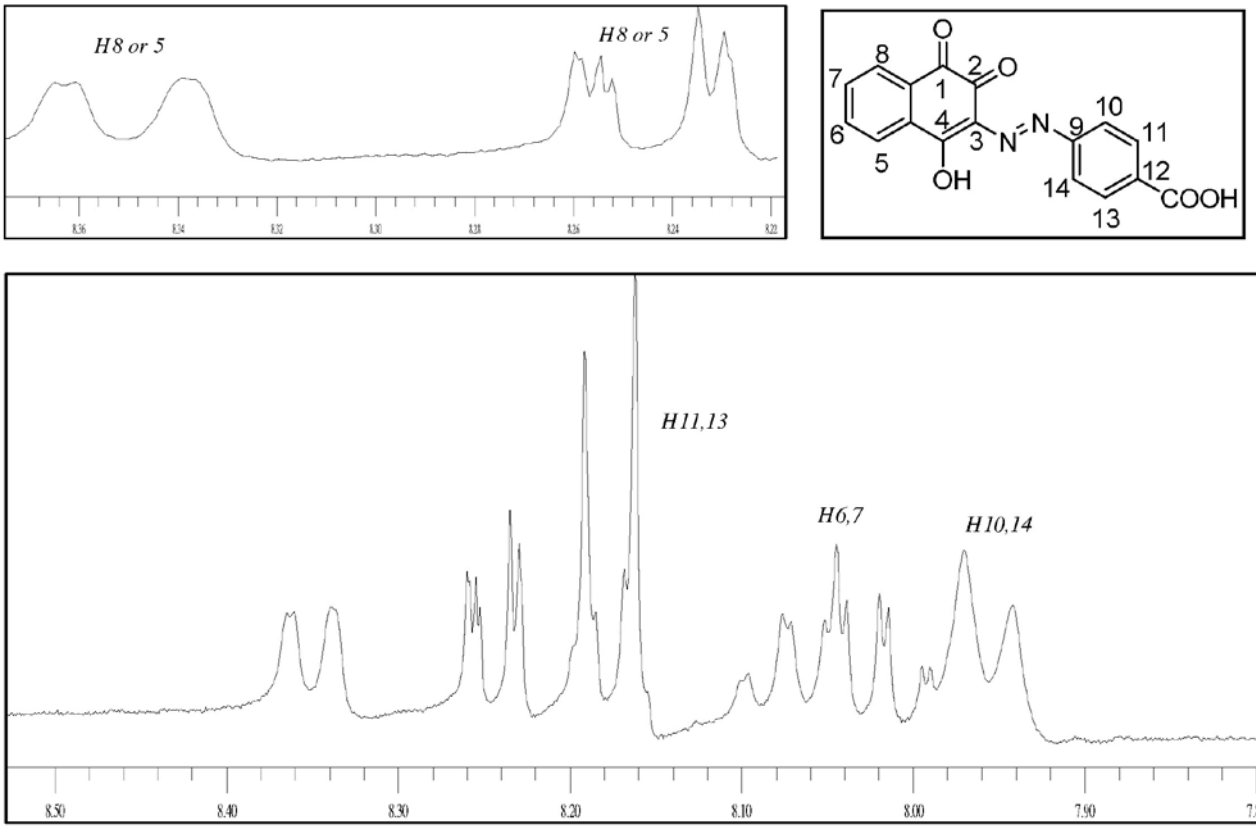


Figure S11. ^{1}H NMR spectrum of 3-[2-(4-carboxy)phenylhydrazono]-naphthalene-1,2,4-trione (**HL7**).

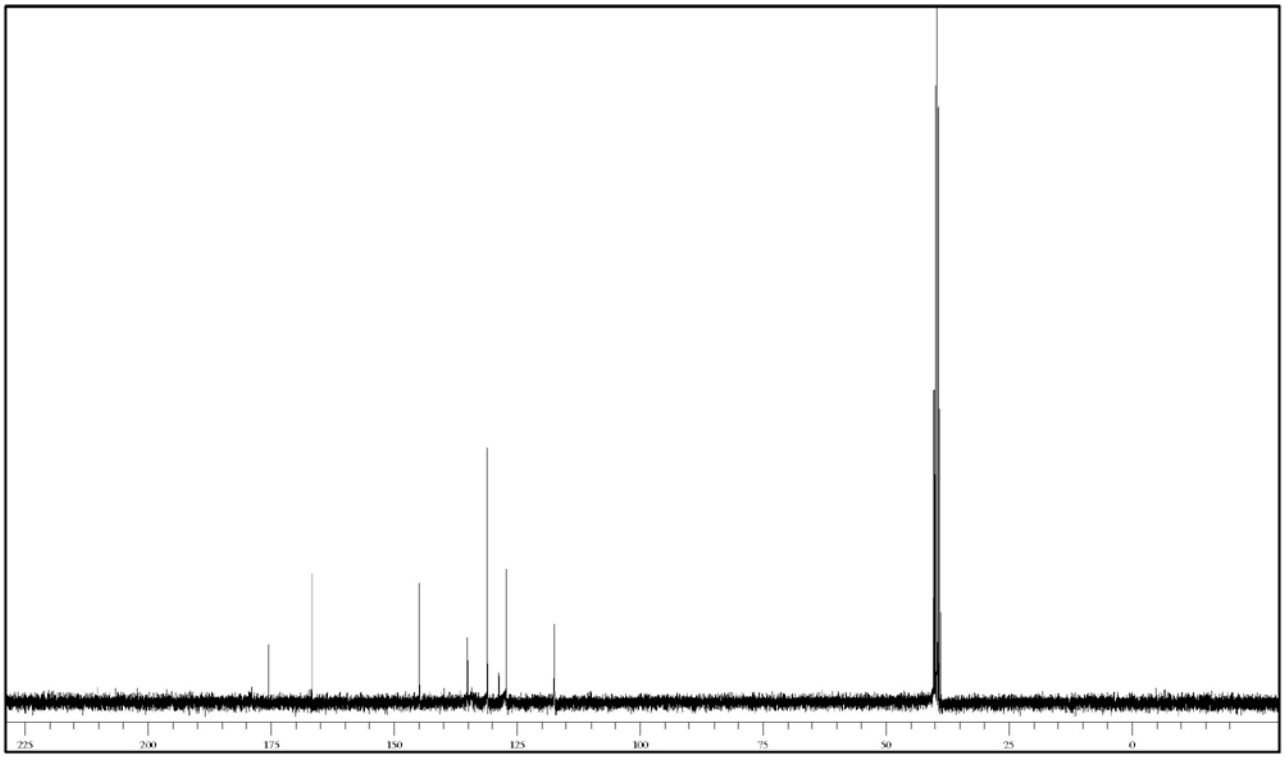


Figure S12. ^{13}C NMR spectrum of 3-[2-(4-carboxy)phenylhydrazono]-naphthalene-1,2,4-trione (**HL7**).

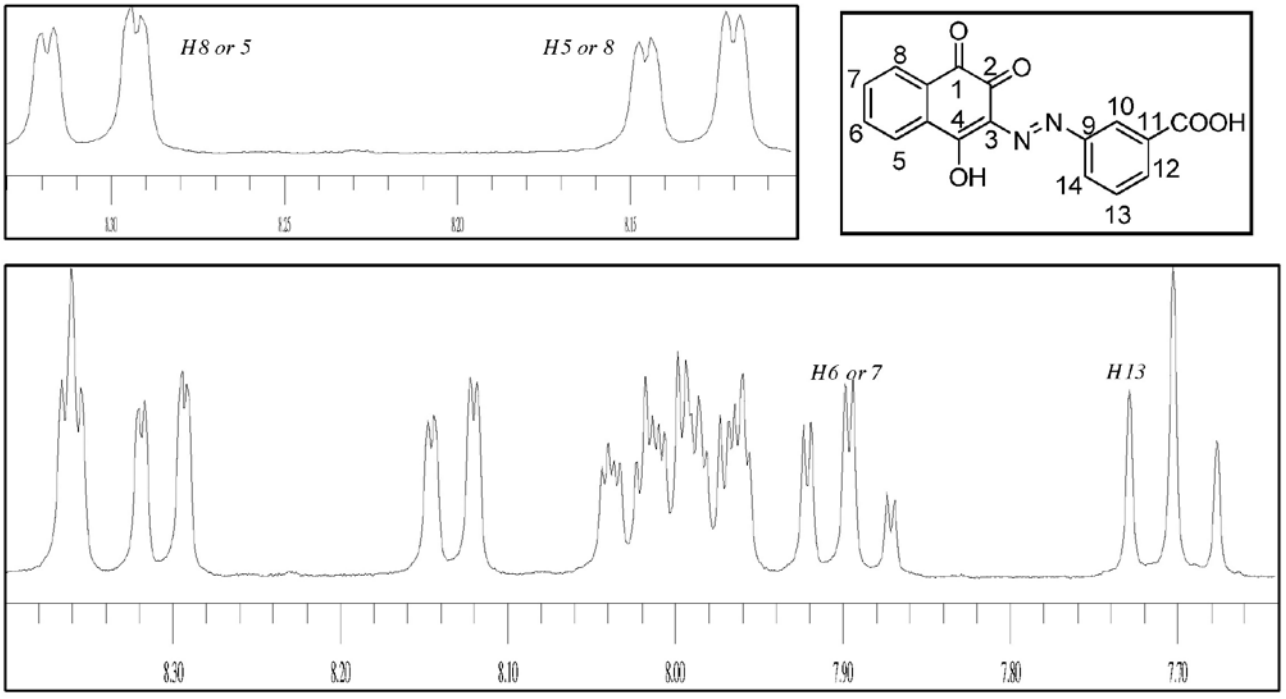


Figure S13. ^{1}H NMR spectrum of 3-[2-(3-carboxy)phenylhydrazono]-naphthalene-1,2,4-trione (**HL8**).

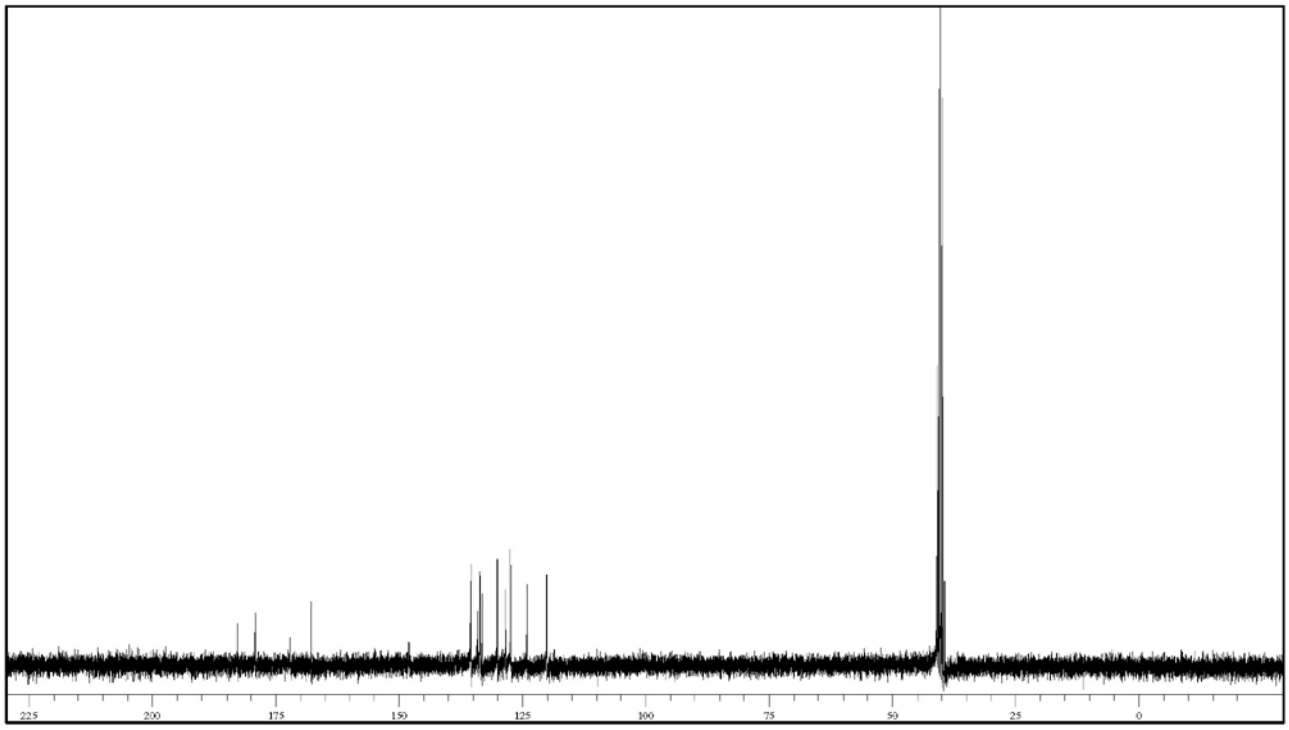


Figure S14. ^{13}C NMR spectrum of 3-[2-(3-carboxy)phenylhydrazono]-naphthalene-1,2,4-trione (**HL8**).

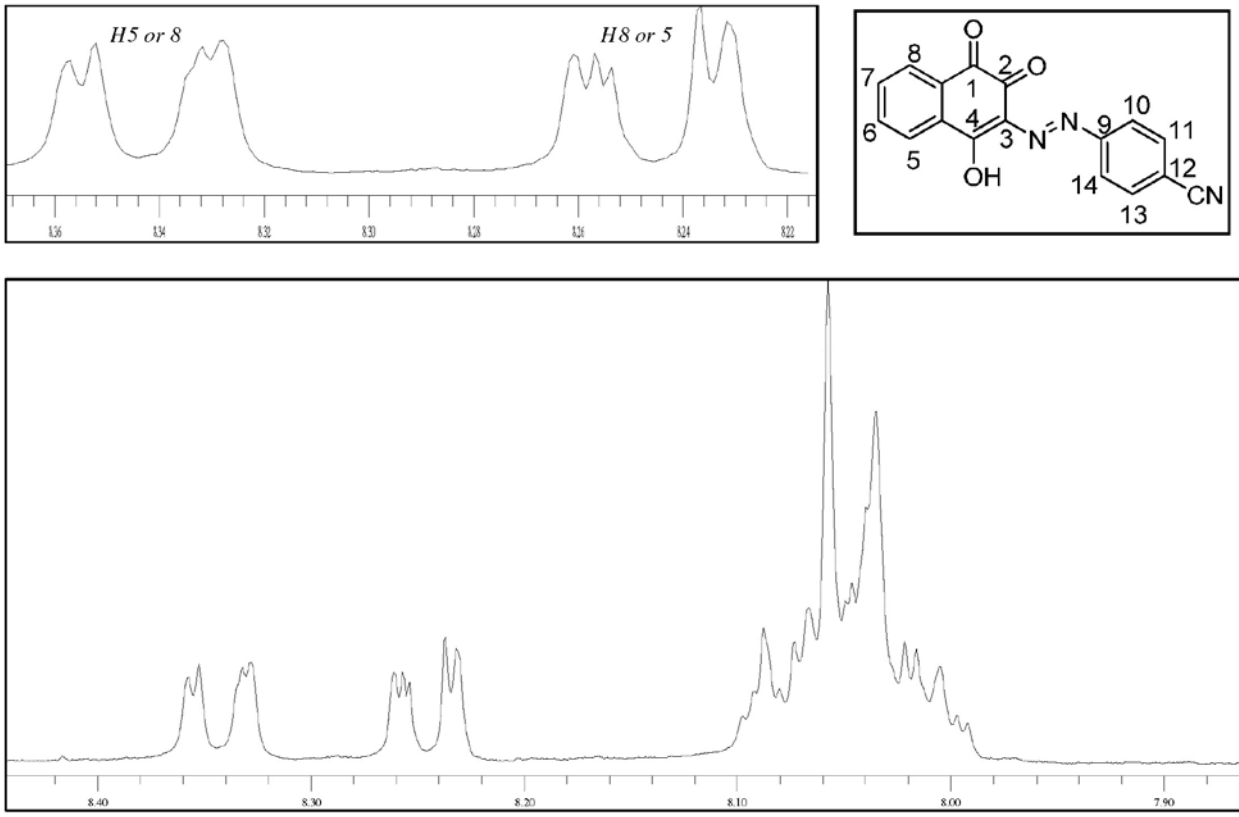


Figure S15. ^{1}H NMR spectrum of 3-[2-(4-ciano)phenylhydrazono]-naphthalene-1,2,4-trione (**HL9**).

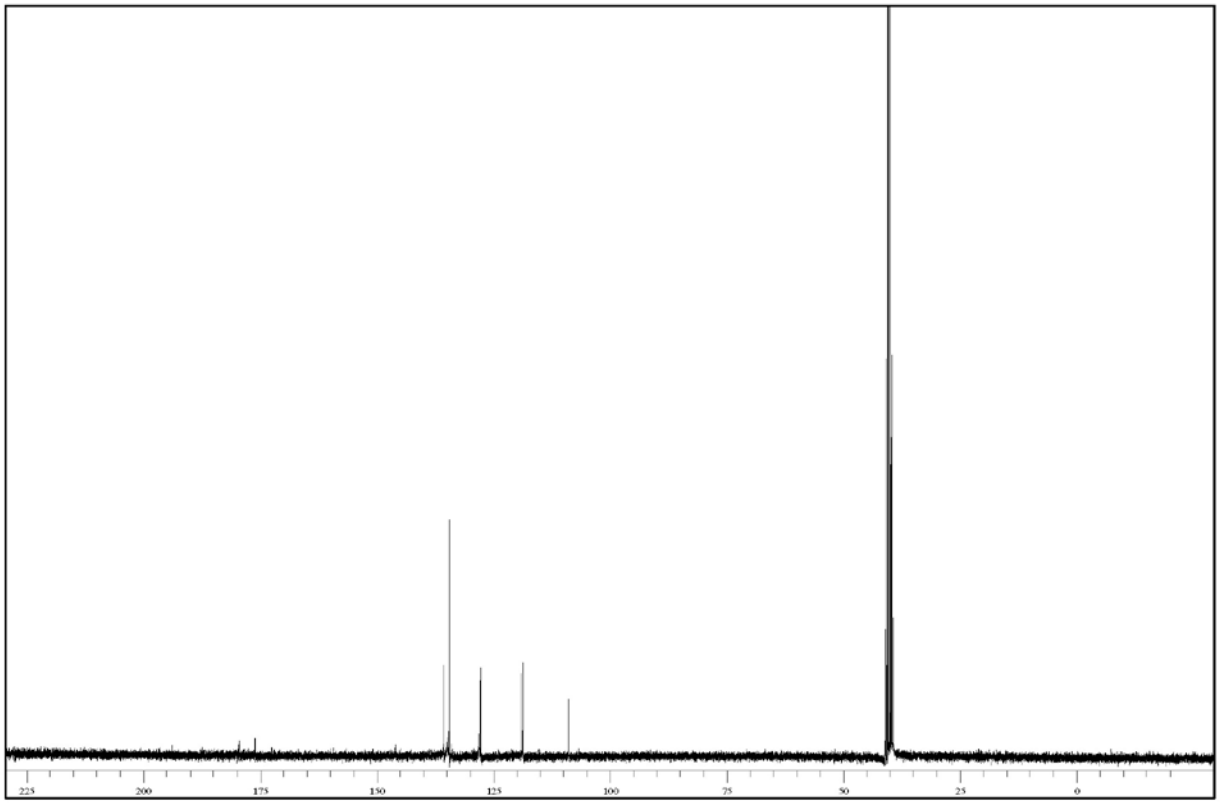


Figure S16. [13]C NMR spectrum of 3-[2-(4-ciano)phenylhydrazono]-naphthalene-1,2,4-trione (**HL9**).

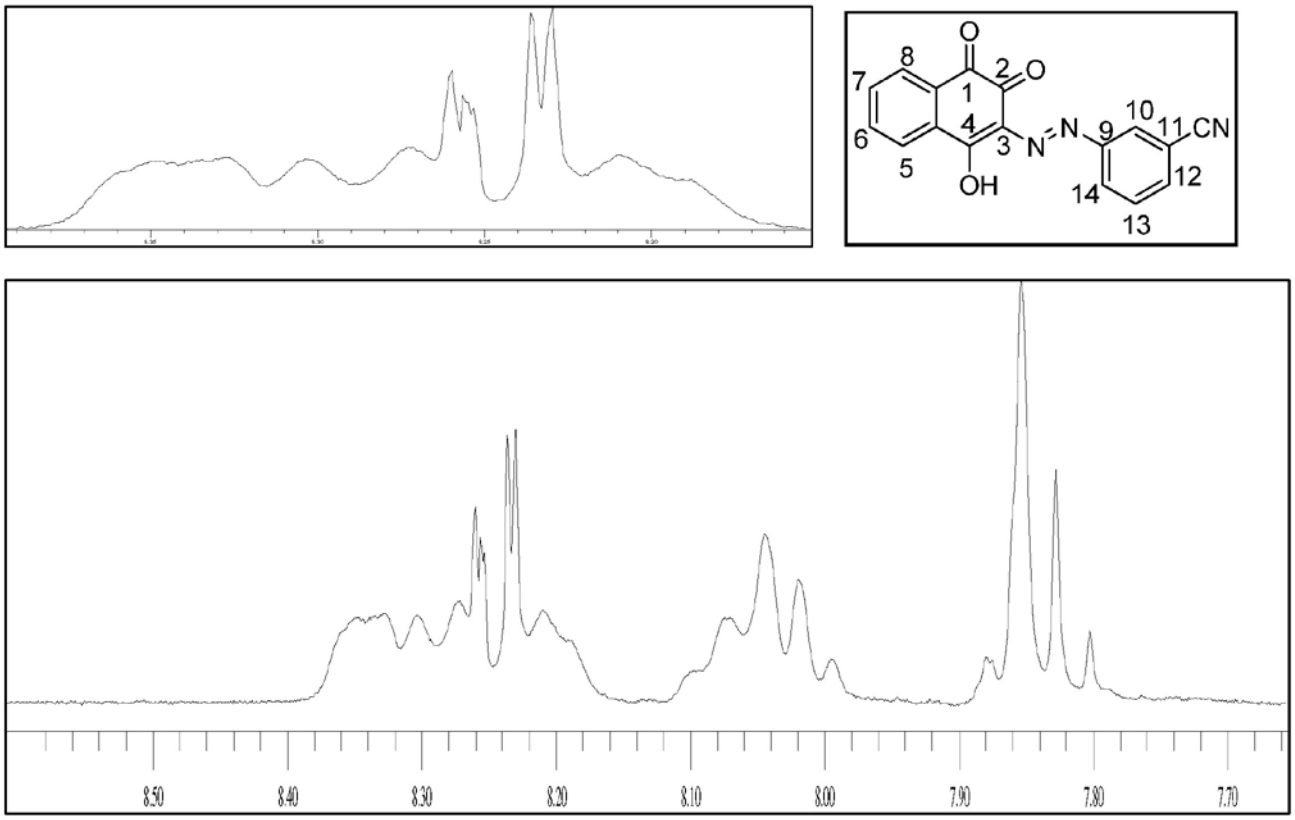


Figure S17. [1]H NMR spectrum of 3-[2-(3-ciano)phenylhydrazono]-naphthalene-1,2,4-trione (**HL10**).

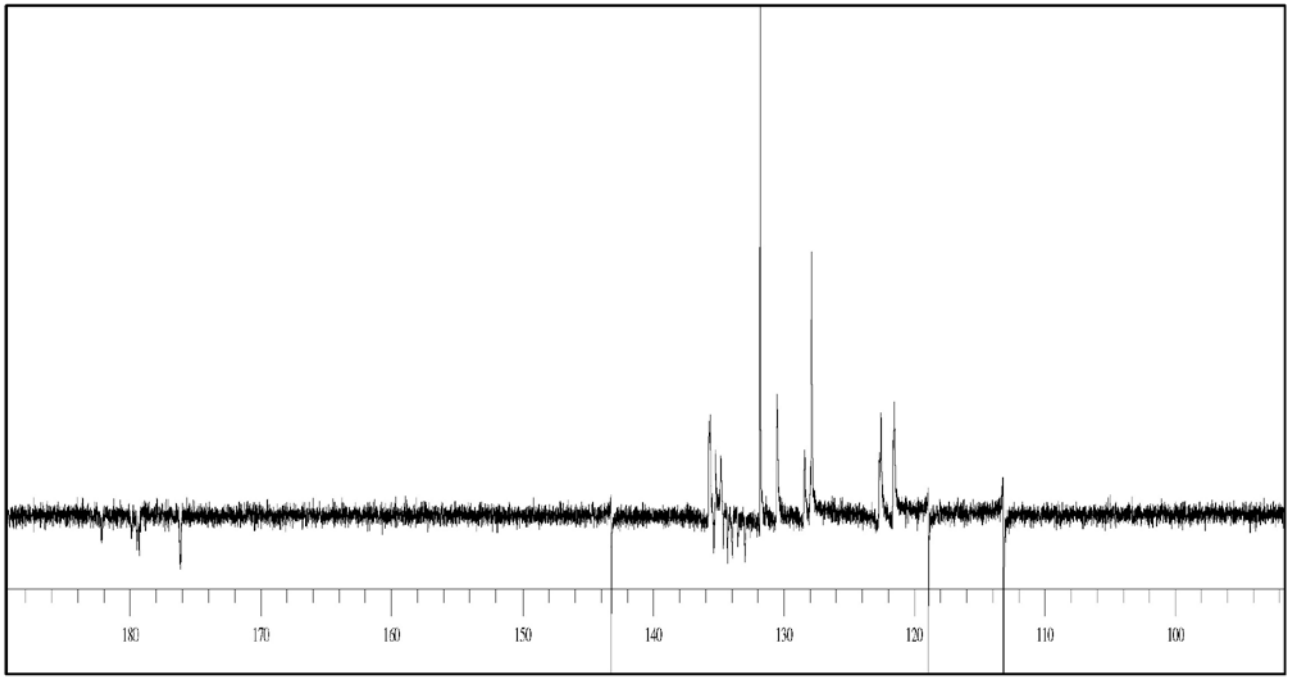


Figure S18. ^{13}C NMR spectrum of 3-[2-(3-ciano)phenylhydrazono]-naphthalene-1,2,4-trione (**HL10**).

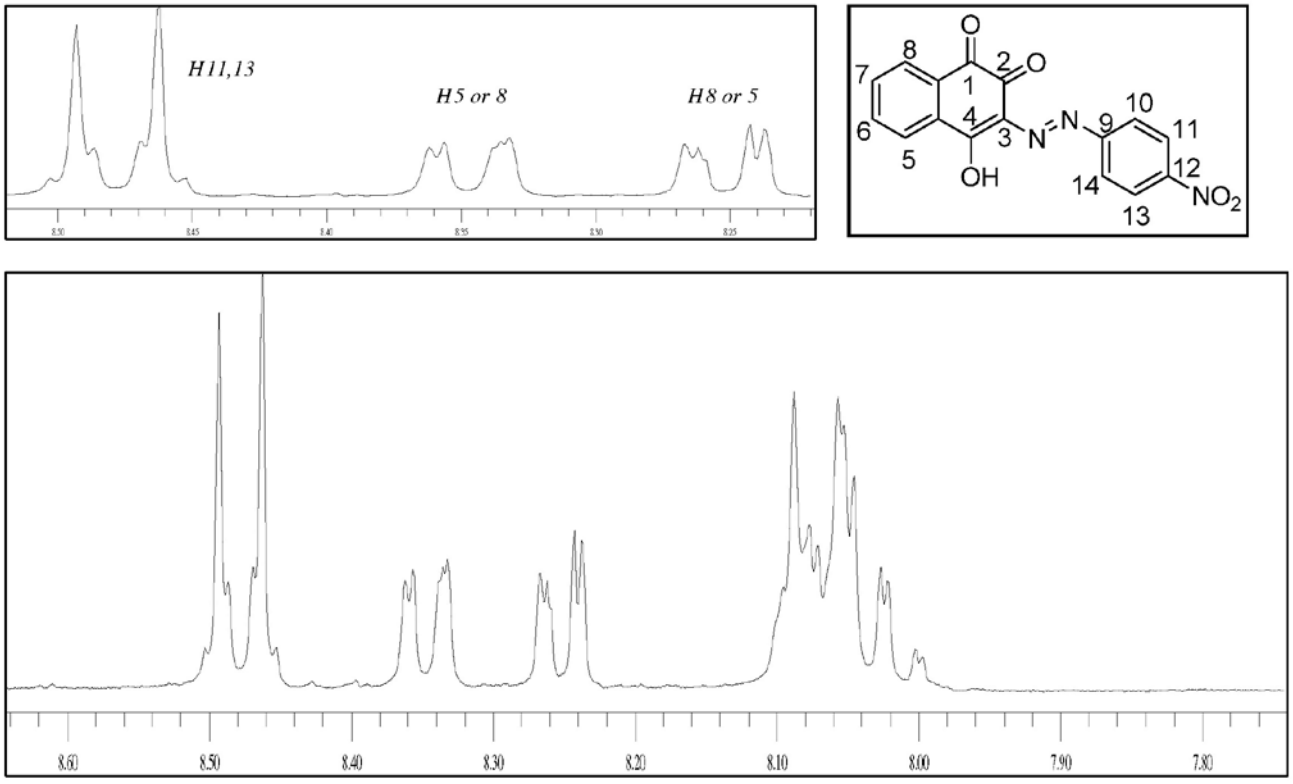


Figure S19. ^{1}H NMR spectrum of 3-[2-(4-nitro)phenylhydrazono]-naphthalene-1,2,4-trione (**HL11**) .

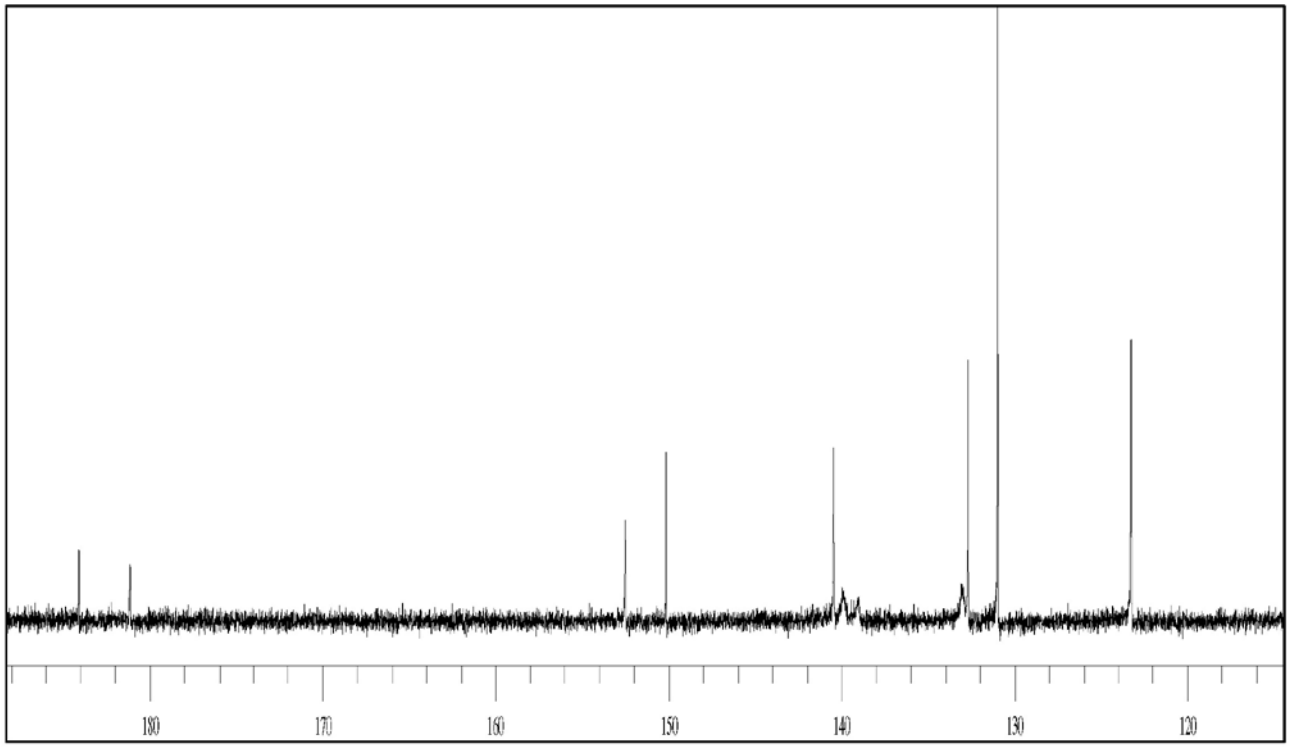


Figure S20. ^{13}C NMR spectrum of 3-[2-(4-nitro)phenylhydrazono]-naphthalene-1,2,4-trione (**HL11**).

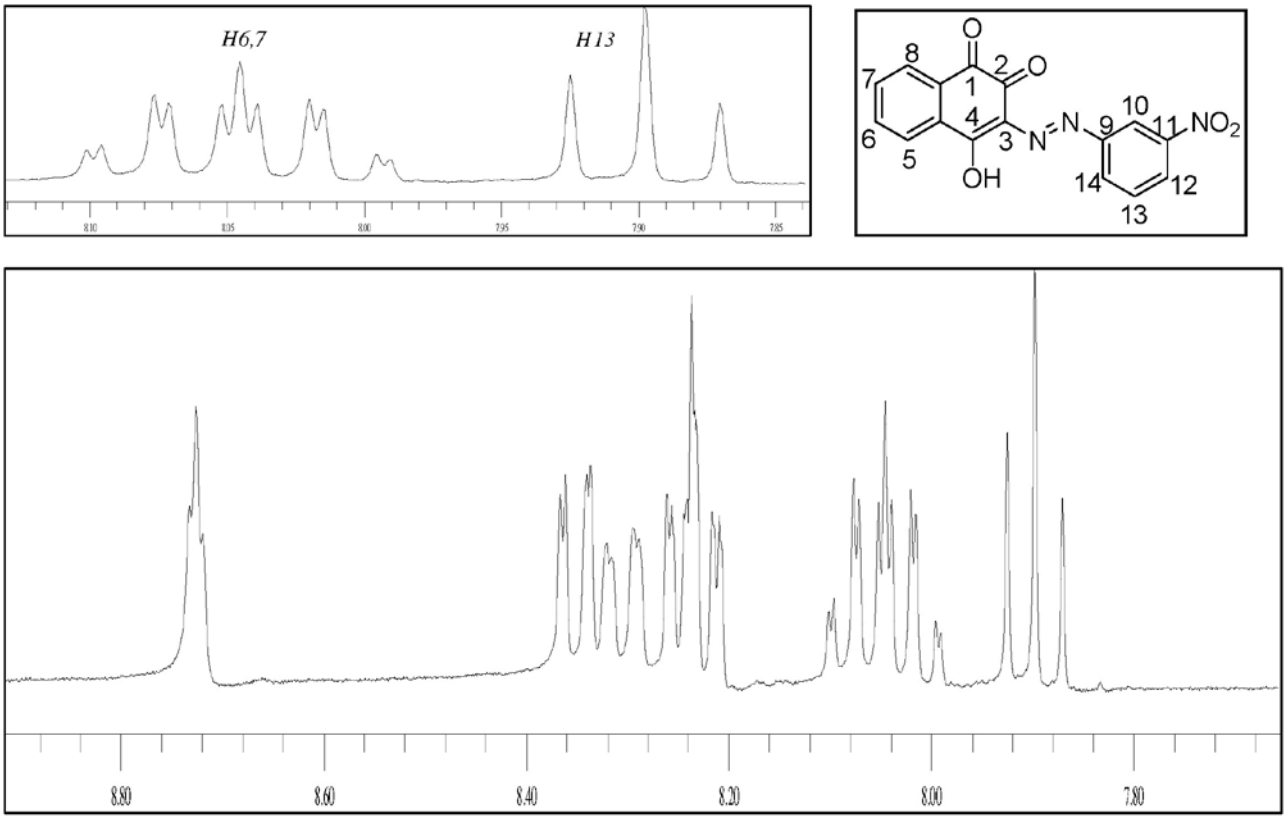


Figure S21. ^{1}H NMR spectrum of 3-[2-(3-nitro)phenylhydrazono]-naphthalene-1,2,4-trione (**HL12**).

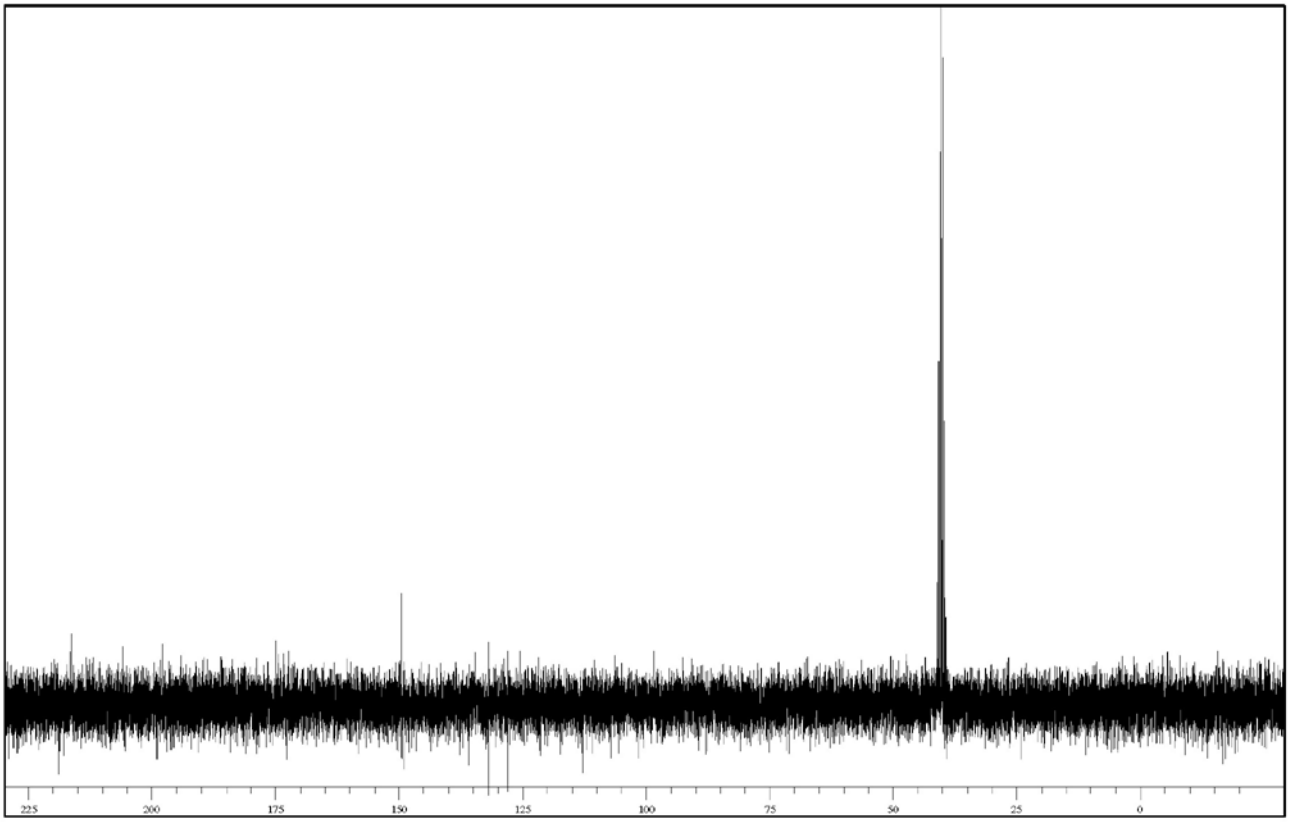


Figure S22. ^{13}C NMR spectrum of 3-[2-(3-nitro)phenylhydrazono]-naphthalene-1,2,4-trione (**HL12**).

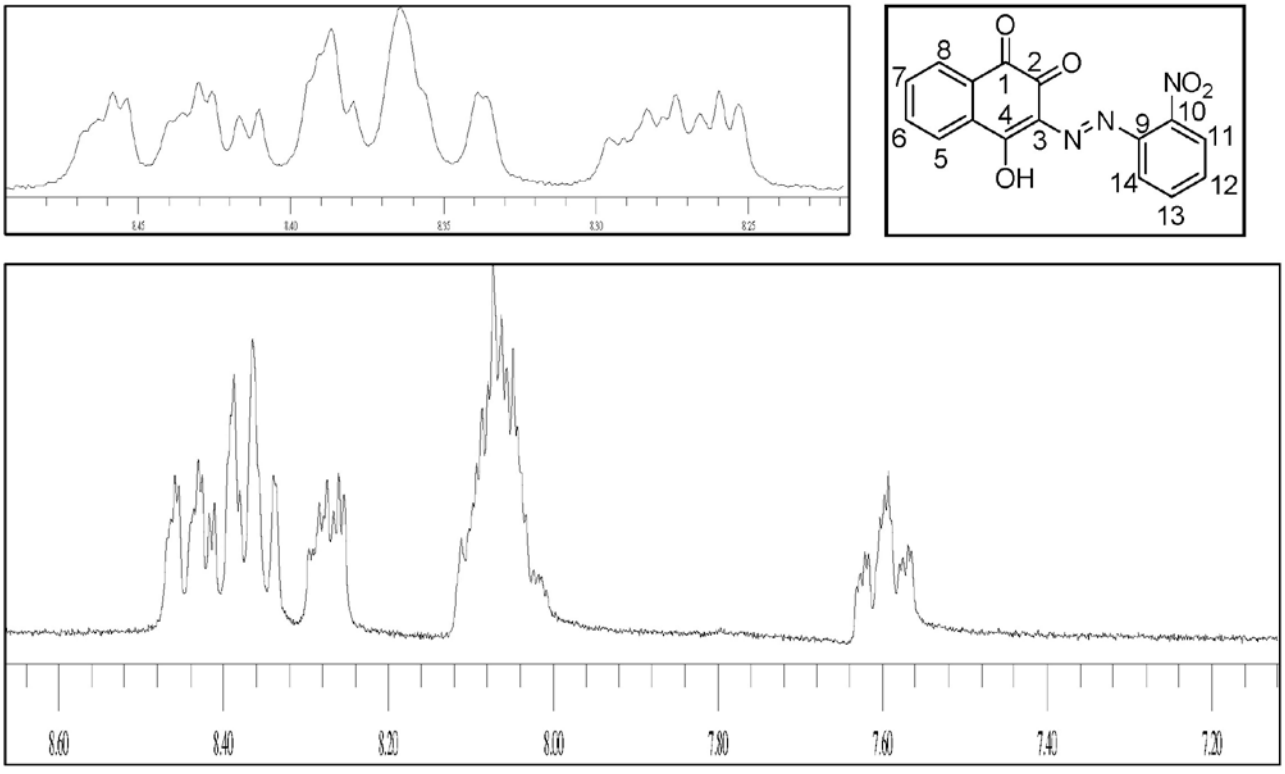


Figure S23. ^{1}H NMR spectrum of 3-[2-(2-nitro)phenylhydrazono]-naphthalene-1,2,4-trione (**HL13**).

Theoretical calculations

Relative energies of tautomers

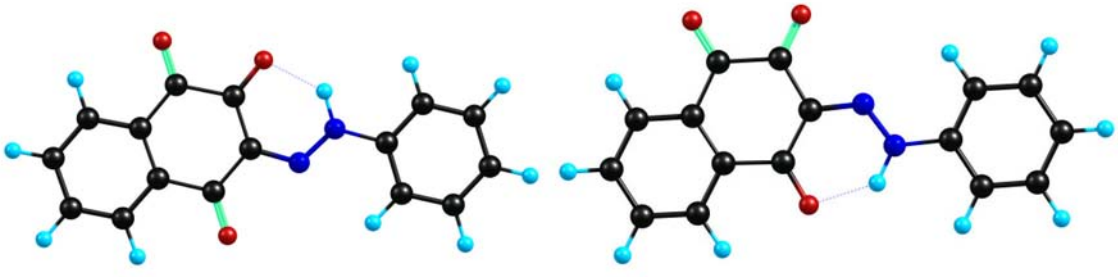
The table below presents absolute (hartree) and relative energies (kcal mol^{-1}) of tautomers **Ia**, **Ib**, **IIa** and **III** with different substituents. In the first entry B3LYP/6-31G(d) results are given. The second entry refers to PBE1PBE/6-311+G(2d,p) results, including solvent effect (dmso).

Table S1. Absolute and relative energies (kcal mol^{-1}) of tautomers **Ia**, **Ib**, **IIa** and **IIb** with different substituents

R	**Ia**	**Ib**	**IIa**	**III**
H	–950.86824	–950.86902	–950.84219	–950.85681
	0.49	0.0	16.84	7.66
	–950.07927	–950.07963	–950.05670	–950.06850
	0.23	0.0	14.39	6.98
CN	–1043.11014	–1043.11068	–1043.08445	–1043.09815
	0.34	0.0	16.46	7.86
	–1042.24636	–1042.24634	–1042.22382	–1042.23440
	-0.01	0.0	14.13	7.49
NO_2	–1155.36828	–1155.36875	–1155.34229	–1155.35575
	0.29	0.0	16.60	8.16
	–1154.44761	–1154.44757	–1154.42494	–1154.43524
	-0.03	0.0	14.20	7.74
NH_2	–1006.22180	–1006.22287	–1006.19911	
	0.67	0.0	14.91	
	–1005.40727	–1005.40819	–1005.38686	
	0.58	0.0	13.38	
OCH_3	–1065.39115	–1065.39216	–1065.36720	–1065.38181
	0.63	0.0	15.66	6.49
	–1064.51448	–1064.51505	–1064.49338	–1064.50567
	0.36	0.0	13.60	5.89

*Electronic spectra of tautomers **Ia** and **Ib***

The electronic spectra of the hydrazono compounds were calculated with the RPBE/6-311+G(2d,p) method with inclusion of solvent effects using the CPCM approach and dmso as solvent. The geometries were optimized at the B3LYP/6-31G(d) level. These compounds may exist as a set of tautomers of which the two rotamers **Ia** and **Ib** are the most stable (Figure S24). For each tautomer two high intensity bands were calculated. In each case they correspond to transitions of the type HOMO → LUMO and HOMO → LUMO+1. HOMO is one of the π orbitals of the phenyl ring (Figures S25 and S28) while LUMO and LUMO+1 both are π* orbitals of the quinone ring (Figures S26 and S29, respectively).



Ia **Ib**

Figure S24. Hydrazono compounds **Ia** and **Ib**.

Table S2. Theoretical electronic spectra of tautomers **Ia** and **Ib**(*)

	Ib	**Ia**
	R = H	
λ1 (HOMO → LUMO)	449 (0.13)	457 (0.34)
λ2 (HOMO → LUMO+1)	407 (0.81)	387 (0.60)
	R = CN	
λ1 (HOMO → LUMO)	426 (0.42)	438 (0.58)
λ2 (HOMO → LUMO+1)	399 (0.75)	375 (0.59)
	R = NO_2	
λ1 (HOMO → LUMO)	424 (0.87)	435 (0.77)
λ2 (HOMO → LUMO+1)	398 (0.39)	377 (0.47)
	R = NH_2	
λ1 (HOMO → LUMO)	598 (0.11)	598 (0.30)
λ2 (HOMO → LUMO+1)	505 (0.91)	483 (0.72)
	R = OCH_3	
λ1 (HOMO → LUMO)		508 (0.37)
λ2 (HOMO → LUMO+1)		423 (0.64)

(*) λ is given in nm. The oscillator strength is given in parenthesis. Spectra are calculated at the RPBE/6-311+G(2d,p) level with inclusion of solvent effects (dmso).

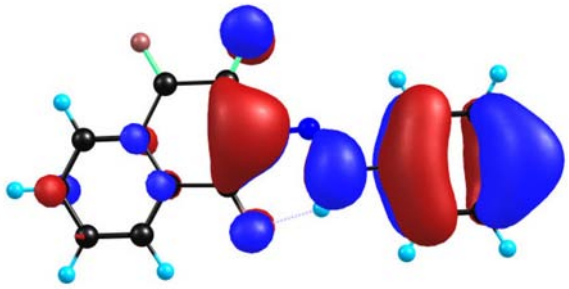


Figure S25. HOMO of rotamer **Ib** (R = H).

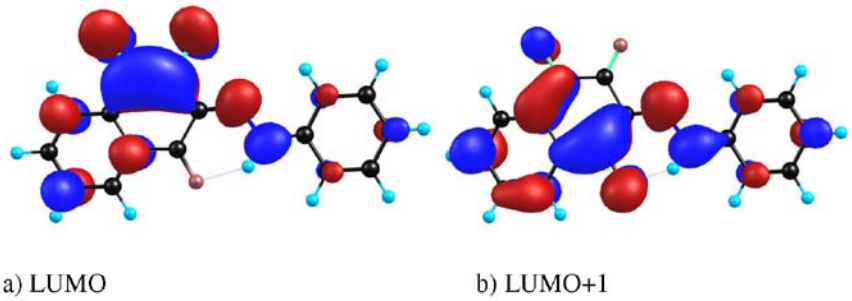


Figure S26. a) LUMO and b) LUMO+1 of rotamer **Ib** (R = H).

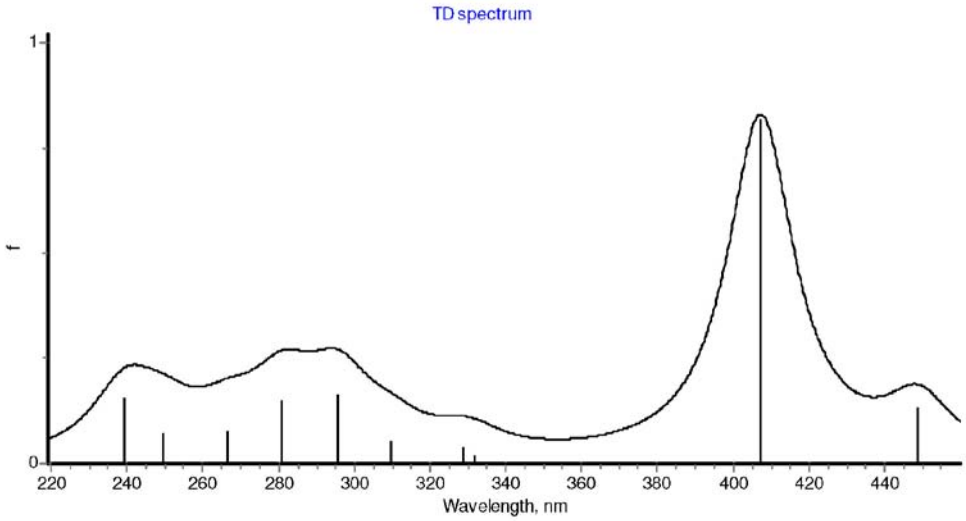


Figure S27. TDDFT spectrum of rotamer **Ib** (R = H).

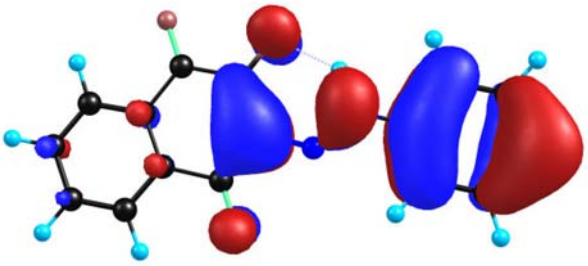


Figure S28. HOMO of rotamer **Ia** (R = H).

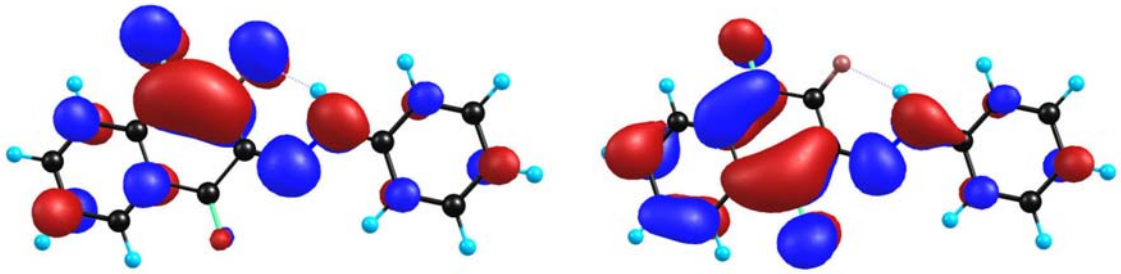


Figure S29. a) LUMO and b) LUMO+1 of rotamer **Ia** (R = H).

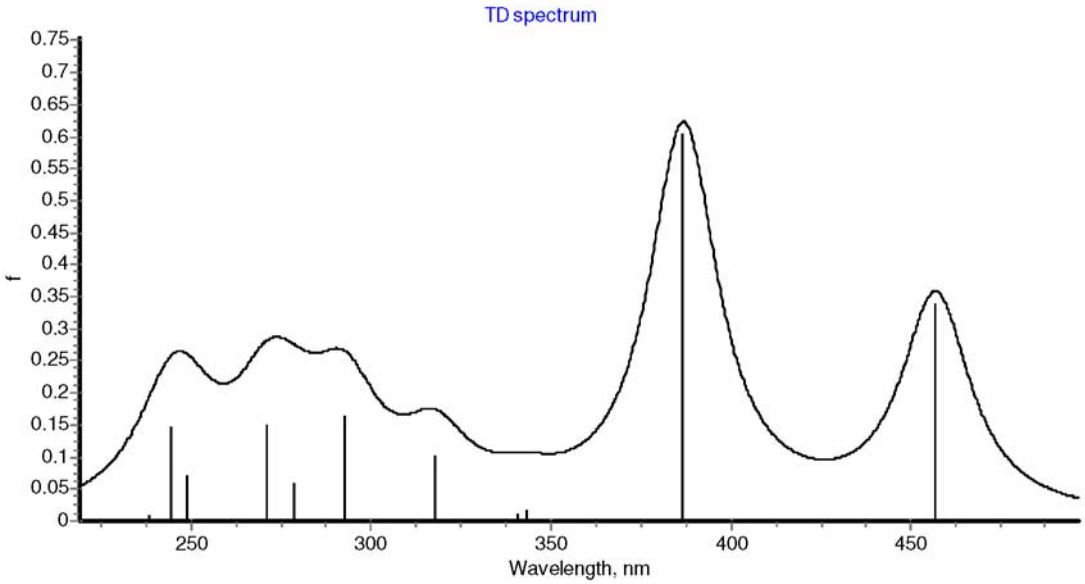


Figure S30. TDDFT spectrum of rotamer **Ia** (R = H).

Theoretical ^{13}C and ^{1}H chemical shifts (ppm)

Table S3. B3LYP/6-31G(d,p) relative ^{13}C and ^{1}H chemical shifts (ppm) for the unsubstituted derivatives **Ia**, **Ib, IIb**, and **III**. Me_4Si (tms) was used as reference. Absolute ^{13}C and ^{1}H chemical shifts of tms are 191.61 and 31.71 ppm, respectively

Atom	**Ia**	**Ib**	**IIb**	**III**
C1	175.72	173.33	172.68	177.99
C2	170.76	168.59	167.83	148.26
C3	130.42	129.69	129.12	129.11
C4	172.53	176.96	160.21	174.61
C4a	130.72	130.41	127.36	127.72
C5	124.72	124.48	123.58	123.89
C6	129.16	128.57	128.50	129.07
C7	127.16	128.12	127.55	126.96
C8	124.85	125.92	126.28	122.96
C8a	128.66	129.26	128.41	127.44
C9	136.45	136.45	144.91	145.91
C10	113.69	111.77	111.91	125.54
C11	123.80	125.40	124.44	123.72
C12	122.15	121.88	125.59	126.64
C13	125.28	123.57	123.43	124.45
C14	111.88	111.35	123.85	111.79
H5	8.54	8.48	8.25	8.47
H6	7.79	7.76	7.67	7.78
H7	7.73	7.75	7.68	7.72
H8	8.42	8.44	8.37	8.31
H10	7.04	8.36	8.42	7.71
H11	7.43	7.56	7.54	7.58
H12	7.31	7.29	7.45	7.51
H13	7.56	7.43	7.54	7.55
H14	8.38	6.99	7.57	8.40

*Analytical and spectroscopic data for complexes **1-13***

*[Cu(**L1**)$_2$] **(1)***

From 308 mg of **HL1**. Yield: 481 mg, 71%; mp 297-300 ºC with decomposition. Anal. calcd. for $C_{34}H_{22}CuN_4O_8 \cdot 0.8H_2O$: C 49.54; H 4.89; N 6.80%. Found: C 49.52; H 4.79; N 6.74%. IR (KBr, ν_{max}/cm^{-1}): 3445 (O-H), 3088 (C-H arom.), 1683 and 1658 (C=O), 1600 (C=C), 1270 (C-O), 975 (C-N=N-C). UV-Vis [dmso; λ/nm (log ε)]: 279 (4.59), 459 (3.51). Diffuse reflectance [λ/nm]: 586.

*[Cu(**L2**)$_2$] **(2)***

From 382 mg of **HL2**. Yield: 668 mg, 81%; mp 275-277 ºC with decomposition. Anal. calcd. for $C_{44}H_{26}CuN_8O_6 \cdot 0.2H_2O$: C 61.14; H 3.73; N 12.96%. Found: C 61.07; H 3.69; N 12.93%. IR (KBr, ν_{max}/cm^{-1}): 3447 (O-H), 3090 (C-H arom.), 1685 and 1663 (C=O), 1595 (C=C), 1277 (C-O), 975 (C-N=N-C). UV-Vis [dmso; λ/nm (log ε)]: 256 (4.64), 457 (3.74), 581 (2.33).

*[Cu(**L3**)$_2$] **(3)***

From 312 mg of **HL3**. Yield: 603 mg, 88%; mp 237-239 ºC with decomposition. Anal. calcd. for $C_{32}H_{16}Cl_2CuN_4O_6 \cdot 0.5H_2O$: C 49.34; H 3.62; N 7.19%. Found: C 49.24; H 3.59; N 7.09%. IR (KBr, ν_{max}/cm^{-1}): 3448 (O-H), 3097 (C-H arom.), 1675 (C=O), 1585 (C=C), 1278 (C-O), 976 (C-N=N-C). UV-Vis [dmso; λ/nm (log ε)]: 277 (4.37), 431 (3.34). Diffuse reflectance [λ/nm]: 629.

*[Cu(**L4**)$_2$] **(4)***

From 404 mg of **HL4**. Yield: 634 mg, 73%; mp 210-213 ºC with decomposition. Anal. calcd. for $C_{32}H_{16}CuI_2N_4O_6 \cdot 0.4H_2O$: C 40.72; H 2.78; N 5.94%. Found: C 40.69; H 2.75; N 5.90%. IR (KBr, ν_{max}/cm^{-1}): 3419 (O-H),

3099 (C-H arom.), 1691 and 1640 (C=O), 1599 (C=C), 1273 (C-O), 1001 (C-N=N-C). UV-Vis [dmso; λ/nm (log ε)]: 281 (4.61), 437 (3.57). Diffuse reflectance [λ/nm]: 636.

*[Cu(**L5**)$_2$] (**5**)*

From 404 mg of **HL5**. Yield: 730 mg, 84%; mp 224-226 ºC, with decomposition. Anal. calcd. for $C_{32}H_{16}CuI_2N_4O_6 \cdot 0.3H_2O$: C 41.51; H 2.61; N 6.05%. Found: C 41.49; H 2.57; N 6.00%. IR (KBr, ν_{max}/cm^{-1}): 3430 (O-H), 3066 (C-H arom.), 1690 and 1640 (C=O), 1585 (C=C), 1273 (C-O), 1001 (C-N=N-C). UV-Vis [dmso; λ/nm (log ε)]: 271 (4.63), 460 (3.27), 582 (2.17).

*[Cu(**L6**)$_2$] (**6**)*

From 404 mg of **HL6**. Yield: 617 mg, 71%; mp 205-207 ºC, with decomposition. Anal. calcd. for $C_{32}H_{16}CuI_2N_4O_6 \cdot 0.3H_2O$: C 41.51; H 2.61; N 6.05%. Found: C 41.45; H 2.59; N 5.97%. IR (KBr, ν_{max}/cm^{-1}): 3431 (O-H), 3067 (C-H arom.), 1690 and 1640 (C=O), 1585 (C=C), 1274 (C-O), 1001 (C-N=N-C). UV-Vis [dmso; λ/nm (log ε)]: 270 (4.49), 423 (3.36), 583 (2.25).

*[Cu(**L7**)$_2$] (**7**)*

From 322 mg of **HL7**. Yield: 444 mg, 63%; mp 231-232 ºC, with decomposition. Anal. calcd. for $C_{34}H_{18}CuN_4O_{10} \cdot 0.1H_2O$: C 56.24; H 3.05; N 7.72%. Found: C 56.20; H 3.01; N 7.69%. IR (KBr, ν_{max}/cm^{-1}): 3400-2700 (O-H), 3069 (C-H arom.), 1688 and 1639 (C=O), 1586 (C=C), 1271 (C-O), 1001 (C-N=N-C). UV-Vis [dmso; λ/nm (log ε)]: 271 (4.51), 422 (3.64), 584 (2.02).

*[Cu(**L8**)$_2$] (**8**)*

From 322 mg of **HL8**. Yield: 451 mg, 64%; mp 280-282 ºC, with decomposition. Anal. calcd. for $C_{34}H_{18}CuN_4O_{10} \cdot 0.1H_2O$: C 56.24; H 3.05; N 7.72%. Found: C 56.21; H 3.04; N 7.64%. IR (KBr, ν_{max}/cm^{-1}): 3420-2669 (O-H), 3081 (C-H arom.), 1690 and 1640 (C=O), 1591 (C=C), 1280 (C-O), 1001 (C-N=N-C). UV-Vis [dmso; λ/nm (log ε)]: 269 (4.67), 406 (3.68), 584 (2.13).

*[Cu(**L9**)$_2$] (**9**)*

From 303 mg of **HL9**. Yield: 607 mg, 91%; mp 269-272 ºC, with decomposition. Anal. calcd. for $C_{35}H_{20}CuN_6O_6 \cdot 0.2H_2O$: C 57.83; H 3.14; N 11.90%. Found: C 57.74; H 3.11; N 11.85%. IR (KBr, ν_{max}/cm^{-1}): 3430 (O-H), 3090 (C-H arom.), 1689 and 1650 (C=O), 1585 (C=C), 1261 (C-O), 975 (C-N=N-C). UV-Vis [dmso; λ/nm (log ε)]: 272 (4.82), 419 (3.44). Diffuse reflectance [λ/nm]: 635.

*[Cu(**L10**)$_2$] (**10**)*

From 303 mg of **HL10**. Yield: 594 mg, 89%; mp 207-208 ºC, with decomposition. Anal. calcd. for $C_{35}H_{20}CuN_6O_6 \cdot 0.8H_2O$: C 50.15; H 4.21; N 10.32%. Found: C 50.13; H 4.17; N 10.28%. IR (KBr, ν_{max}/cm^{-1}): 3455 (O-H), 3090 (C-H arom.), 1693 and 1647 (C=O), 1598 (C=C), 1264 (C-O), 972 (C-N=N-C). UV-Vis [dmso; λ/nm (log ε)]: 277 (4.68), 415 (3.38). Diffuse reflectance [λ/nm]: 609.

*[Cu(**L11**)$_2$] (**11**)*

From 323 mg of **HL10**. Yield: 544 mg, 77%; mp 291-292 ºC, with decomposition. Anal. calcd. for $C_{32}H_{18}CuN_6O_{10} \cdot 0.4H_2O$: C 49.14; H 3.35; N 10.75%. Found: C 49.11; H 3.30; N 10.71%. IR (KBr, ν_{max}/cm^{-1}): 3443 (O-H), 3075 (C-H arom.), 1668 (C=O), 1607 (C=C), 1245 (C-O), 975 (C-N=N-C). UV-Vis [dmso; λ/nm (log ε)]: 280 (4.58), 499 (3.65).

*[Cu(**L12**)$_2$] (**12**)*

From 323 mg of **HL12**. Yield: 558 mg, 79%; mp 244-246 ºC, with decomposition. Anal. calcd. for $C_{32}H_{18}CuN_6O_{10} \cdot 0.2H_2O$: C 51.51; H 2.97; N 11.26%. Found: C 51.49; H 2.95; N 11.21%. IR (KBr, ν_{max}/cm^{-1}): 3443 (O-H), 3077 (C-H arom.), 1672 (C=O), 1607 (C=C), 1242 (C-O), 976 (C-N=N-C). UV-Vis [dmso; λ/nm (log ε)]: 275 (4.64), 506 (3.63). Diffuse reflectance [λ/nm]: 637.

*[Cu(**L13**)$_2$] (**13**)*

From 323 mg of **HL13**. Yield: 587 mg, 83%; mp 257-259 ºC, with decomposition. Anal. calcd. for $C_{32}H_{18}CuN_6O_{10} \cdot 0.6H_2O$: C 46.98; H 3.70; N 10.27%. Found: C 46.90; H 3.66; N 10.24%. IR (KBr, ν_{max}/cm^{-1}): 3457 (O-H), 3073 (C-H arom.), 1675 (C=O), 1603 (C=C), 1235 (C-O), 987 (C-N=N-C). UV-Vis [dmso; λ/nm (log ε)]: 277 (4.54), 439 (3.77). Diffuse reflectance [λ/nm]: 620.

*Antibacterial activity of compounds **HL1-HL13** and complexes **1-13***

Experimental

The cultures were maintained on Mueller Hinton agar at 8 °C. The inoculum suspension of each strain, in Mueller Hinton broth, was prepared to attain a final inoculum of 108 CFU mL^{-1} (OD = 0.08-0.1 at λ = 625 nm, ThermoSpectronic Genesys 10UV) and diluted 1:10 by the broth micro-dilution procedure according to the M7-A6 document (National Committee for Clinical Laboratory Standards Methods for Dilution Antimicrobial Susceptibility Tests for Bacteria that Grow Aerobically, 6th ed.; Approved Standard NCCLS Document M7-A6: Wayne, PA, 2003). Minimum inhibitory concentration was determined using 96-well microtitre plates filled with Mueller Hinton broth (100 µL *per* well). All samples were dissolved in dmso/

Mueller Hinton broth and tested in eight concentrations (3×10^{-3}-0.02 mmol mL^{-1}). Chloramphenicol (Aldrich) was used as positive control. For sterility and growth control, a culture medium without compounds was used. The inoculum suspension (5 µL) was applied into the wells and the microplates were incubated at 37 °C overnight. Afterwards, 20 µL of 0.2 mg mL^{-1} of *p*-iodonitrotetrazolium chloride (p-INT) (Sigma) aqueous solution was added and once more incubated for 1 h at 37 °C. The MIC was defined as the lowest concentration of the compounds that inhibited the antibacterial visible growth as indicated by the p-INT colorimetric reagent.

The antibacterial activity of the *hydrazono compounds* **HL1-HL13** and their respective copper(II) complexes **1-13** was evaluated against seven strains of bacteria: *Bacillus cereus*, *Bacillus subtilis*, *Escherichia coli*, *Enterococcus faecalis*, *Klebsiella pneumoniae*, *Pseudomonas aeruginosa* and *Staphylococcus aureus*. The results are reported in Table S4 below, where the MIC values are expressed in µmol L^{-1}. Chloramphenicol was used as a positive control in all tests. Compounds 2-hydroxy-1,4-naphthoquinone (lawsone) and $CuCl_2{\cdot}2H_2O$ were also tested for comparison.

Results

Table S4. Antibacterial activity data of compounds ***HL1-HL13***, complexes **1-13**, lawsone and $CuCl_2{\cdot}2H_2O$

Compound	Entry	BC	BS	EC	EF	KP	PA	SA
HL1 (R = OMe)	1	> 200	> 200	> 200	> 200	> 200	> 200	> 200
HL2 (R = N_2-C_6H_5)	2	> 200	> 200	> 200	> 200	> 200	> 200	> 200
HL3 (R = 4-Cl)	3	> 200	> 200	> 200	> 200	> 200	> 200	> 200
HL4 (R = 4-I)	4	> 200	> 200	> 200	> 200	> 200	> 200	> 200
HL5 (R = 3-I)	5	90	90	20	180	> 200	> 200	> 200
HL6 (R = 2-I)	6	> 200	> 200	> 200	> 200	> 200	> 200	> 200
HL7 (R = 4-OOH)	7	> 200	> 200	> 200	> 200	> 200	> 200	> 200
HL8 (R = 3-OOH)	8	> 200	> 200	> 200	> 200	> 200	> 200	> 200
HL9 (R = 4-CN)	9	> 200	> 200	> 200	> 200	> 200	> 200	> 200
HL10 (R = 3-CN)	10	> 200	> 200	> 200	> 200	> 200	> 200	> 200
HL11 (R = 4-NO_2)	11	> 200	> 200	> 200	> 200	> 200	> 200	> 200
HL12 (R = 3-NO_2)	12	> 200	> 200	> 200	> 200	> 200	> 200	> 200
HL13 (R = 2-NO_2)	13	180	> 200	> 200	> 200	> 200	> 200	> 200
Lawsone	14	> 200	> 200	> 200	> 200	> 200	> 200	> 200
Chloramphenicol	15	40-90	20-40	90	90	40-90	40	40-90
1 (R = OMe)	18	> 200	> 200	> 200	> 200	> 200	> 200	> 200
2 (R = N_2-C_6H_5)	19	> 200	> 200	> 200	> 200	> 200	> 200	> 200
3 (R = 4-Cl)	20	> 200	> 200	> 200	> 200	> 200	> 200	> 200
4 (R = 4-I)	21	> 200	> 200	180	> 200	> 200	> 200	> 200
5 (R = 3-I)	22	> 200	> 200	> 200	> 200	> 200	> 200	> 200
6 (R = 2-I)	23	> 200	> 200	> 200	> 200	> 200	> 200	> 200
7 (R = 4-COOH)	24	> 200	> 200	> 200	> 200	> 200	> 200	> 200
8 (R = 3-COOH)	25	> 200	> 200	> 200	> 200	> 200	> 200	> 200
9 (R = 4-CN)	26	> 200	> 200	> 200	> 200	> 200	> 200	> 200
10 (R = 3-CN)	27	> 200	180	> 200	> 200	> 200	> 200	> 200
11 (R = 4-NO_2)	28	> 200	> 200	> 200	> 200	> 200	> 200	> 200
12 (R = 3-NO_2)	29	> 200	> 200	180	> 200	> 200	> 200	> 200
13 (R = 2-NO_2)	30	> 200	> 200	> 200	> 200	> 200	> 200	> 200
$CuCl_2{\cdot}2H_2O$	31	>3000	>3000	>3000	>3000	>3000	>3000	>3000

Minimum inhibitory concentrations (MICs) are reported in µmol L^{-1}.

*Antitumor activity of compounds **HL1-HL13** and complexes **1-13***

Experimental

The compounds (1-5 mg mL^{-1}) were tested for cytotoxic activity against three cancer cell lines: SF-295 (central nervous system), HCT-8 (colon), MDAMB-435 (breast) and HL-60 (human leukemia). All cell lines were maintained in RPMI 1640 medium supplemented with 10% fetal bovine serum, 2 mmol L^{-1} glutamine, 100 U mL^{-1} penicillin, and 100 μg mL^{-1} streptomycin at 37 °C with 5% CO_2. Each compound was dissolved in dmso and diluted with water to obtain a concentration of 1 mg mL^{-1}. They were incubated with the cells for 72 h. The negative control received the same amount of dmso (0.005% in the highest concentration). Doxorubicin (dox, 0.1-0.58 μg mL^{-1}) was used as a positive control. The cell viability was determined by reduction of the yellow dye 3-(4,5-dimethyl-2-thiazol)-2,5-phenyl-2H-tetrazolium bromide (MTT) to a blue formazan product as described by Mosmann.

Results

In the Table S5 below, we present the screening of the cytotoxic activity (growth inhibition %) of the synthesized compounds **HL1-HL13**, complexes **1-13** and lawsone for comparison.

Table S5. Screening of the cytotoxic activity (growth inhibition %) of **HL1-HL13**, complexes **1-13** and lawsone

Compound	Entry	SF295	GI% (SD)	HCT-8	GI% (SD)	MDA-MB435	GI% (SD)
HL1 (R = OMe)	1	0.65	1.80	6.48	5.95	11.00	6.34
HL2 (R = N_2-C_6H_5)	2	–3.30	5.20	4.74	1.01	3.92	10.49
HL3 (R = 4-Cl)	3	31.04	2.20	19.89	0.22	23.24	3.42
HL4 (R = 4-I)	4	–5.99	2.20	–11.12	0.11	13.76	0.00
HL5 (R = 3-I)	5	19.38	1.10	18.86	6.17	14.19	5.00
HL6 (R = 2-I)	6	25.45	43.27	92.23	7.85	67.40	13.17
HL7 (R = 4-COOH)	7	15.00	13.49	–8.98	6.06	22.64	2.81
HL8 (R = 3-COOH)	8	2.07	0.80	–4.07	6.95	–7.12	0.98
HL9 (R = 4-CN)	9	–7.75	9.09	7.20	0.22	–0.65	7.44
HL10 (R = 3-CN)	10	48.98	12.99	25.84	8.41	5.39	3.05
HL12 (R = 3-NO_2)	12	17.75	5.00	9.26	12.79	3.06	2.20
HL13 (R = 2-NO_2)	13	52.87	8.69	58.52	0.56	32.56	1.95
Lawsone	14	–35.56	5.29	–36.98	0.48	–54.48	0.78
dox	15	83.96	1.30	91.67	11.78	96.55	2.44
1 (R = OMe)	18	–10.51	16.79	–16.52	11.78	12.20	1.71
2 (R = N_2-C_6H_5)	19	16.13	5.30	16.64	0.11	14.36	1.34
3 (R = 4-Cl)	20	11.39	4.00	6.17	9.53	16.17	0.73
4 (R = 4-I)	21	6.80	0.90	2.44	2.02	12.55	0.24
6 (R = 2-I)	23	5.11	5.30	–5.18	3.37	25.66	14.39
9 (R = 4-CN)	26	19.87	1.40	30.28	0.11	20.14	7.32
10 (R = 3-CN)	27	–7.61	4.90	–6.68	3.25	7.89	8.29
12 (R = 3-NO_2)	29	–2.24	7.49	8.47	5.61	–3.32	10.98
13 (R = 2-NO_2)	30	69.26	29.88	96.03	7.18	54.20	1.34

*EPR spectra of the copper(II) complexes **1-13***

The X-band EPR Hamiltonian parameters of frozen solutions of copper(II) complexes in dmso are shown in Table S6 below.

Table S6. Spin-Hamiltonian parameters used in the simulated spectra of the copper(II) ion in complexes **1**-**13**

Complexes	$A_{\perp}$ ($\times 10^{-4}$ cm^{-1})	$A_{\parallel}$ ($\times 10^{-4}$ cm^{-1})	$g_{\perp}$	$g_{\parallel}$	$g_{\parallel}/A_{\parallel}$
1	25	170	2.078	2.2500	132
2	25	171	2.082	2.2420	131
3	25	120	2.075	2.4000	200
4	25	134	2.078	2.4000	185
5	25	170	2.097	2.2250	131
6	25	170	2.092	2.2240	131
7	25	170	2.090	2.2450	132
8	25	170	2.090	2.2450	132
9	25	171	2.095	2.3000	134
10	25	170	2.078	2.2530	132
11	25	135	2.060	2.4000	178
12	25	162	2.060	2.2620	140
13 (OFR)*	25	173	2.060	2.2300	129

*OFR means organic free radical, a very sharp EPR line observed over the perpendicular copper(II) spectrum of complex **13**.

*Cyclic voltammograms of compounds **HL1-L13** and [Cu(**L1**)$_2$] - [Cu(**L13**)$_2$]*

Cyclic voltammograms were obtained on an Epsilon - BAS potentiostat-galvanostat from 1×10^{-3} mol L^{-1} solutions in dmso containing 0.1 mol L^{-1} of $(Bu_4N)BF_4$ as supporting electrolyte, at room temperature and under argon atmosphere. A standard three component system was used: a carbon-glassy working electrode, a platinum wire auxiliary electrode, and an Ag/AgCl reference electrode for organic media. Ferrocene was used as an internal standard ($E_{1/2}$ 0.40 V *vs.* NHE).

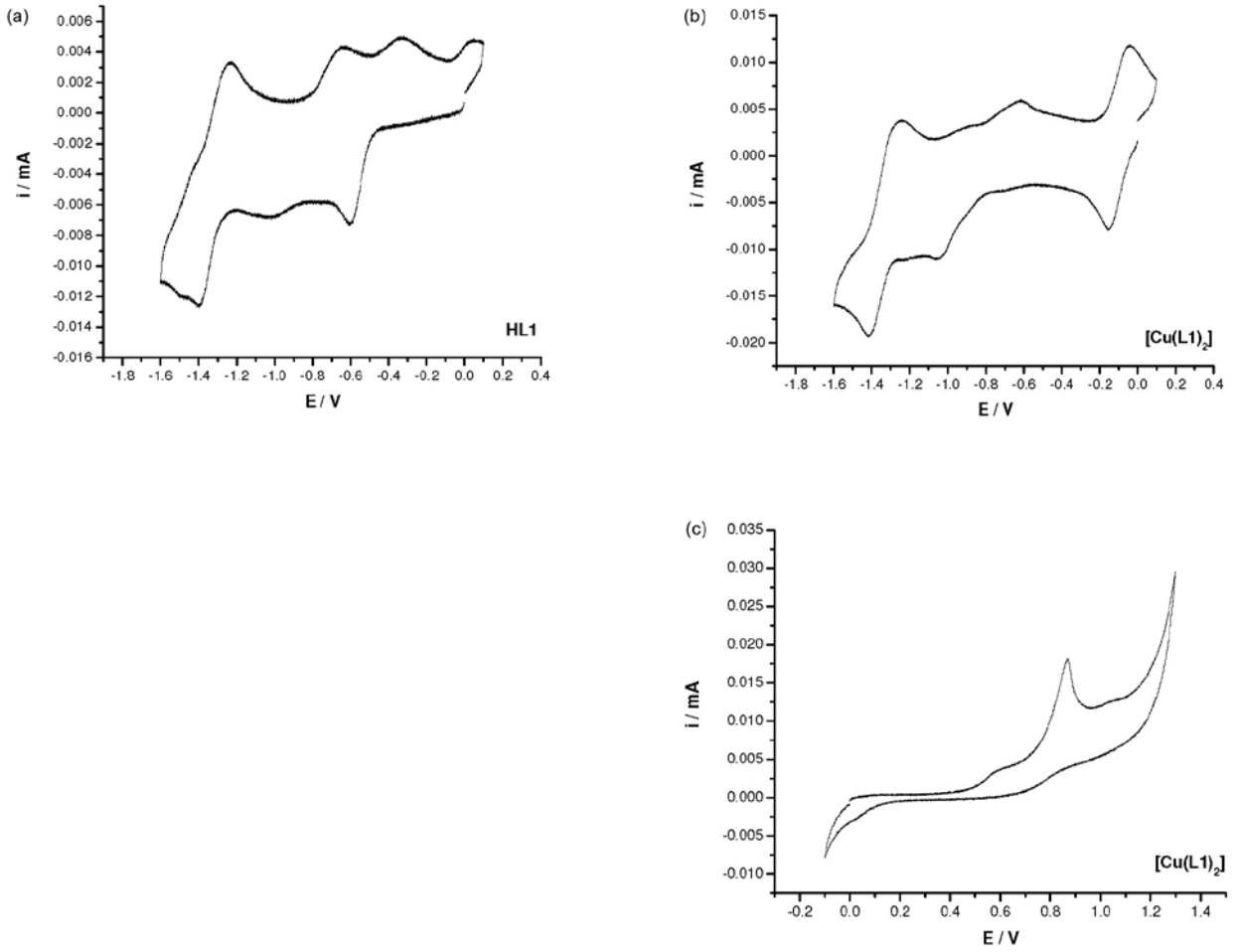


Figure S31. Cyclic voltammograms registered for **HL1** (a) and [Cu(**L1**)$_2$] (b) and (c). The process attributed the redox couple Cu/Cu^{2+} in [**Cu**(**L1**)$_2$] is not visible in the range presented in voltammogram (c), but can be seen in voltammogram (b) scan in the range from –0.4 to 1.8V.

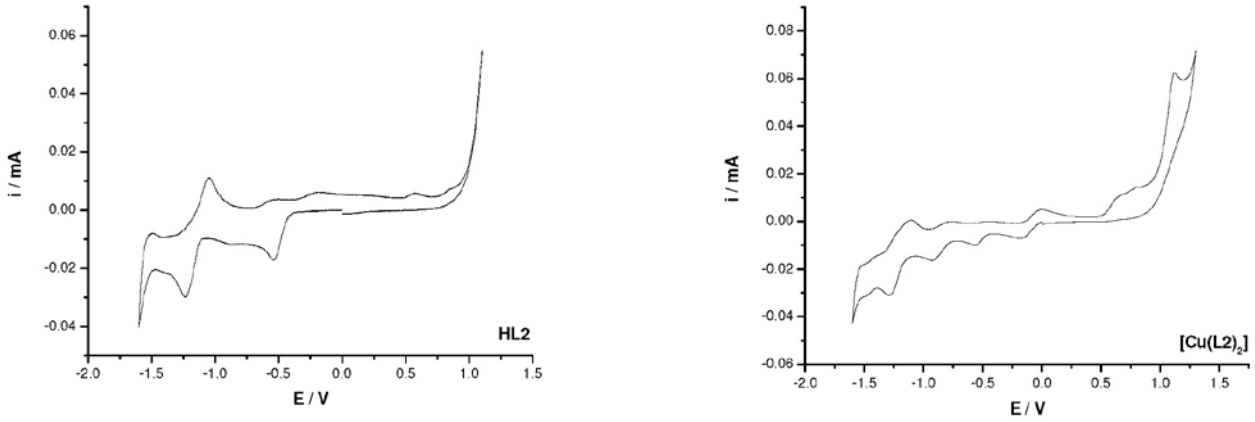


Figure S32. Cyclic voltammograms registered for **HL2** and [Cu(**L2**)$_2$].

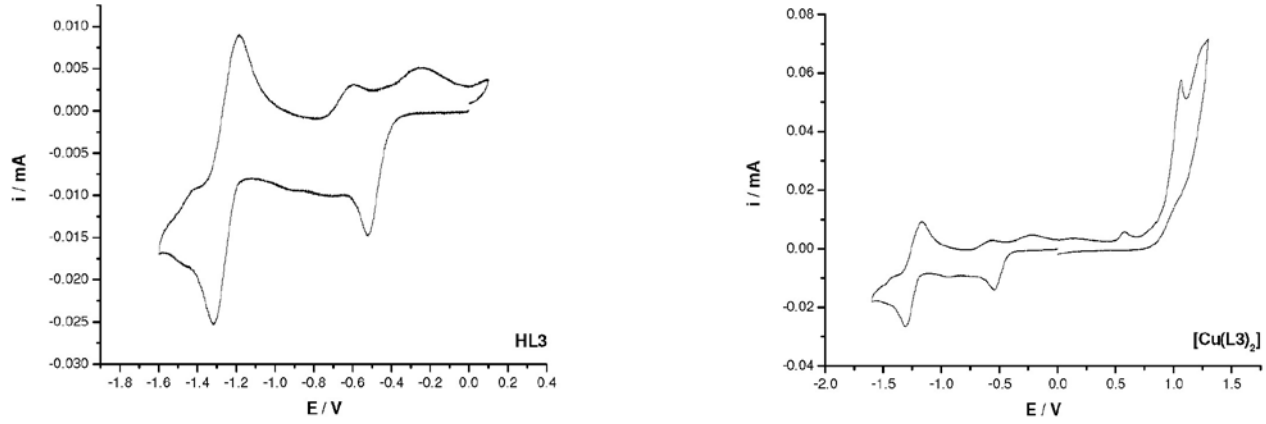


Figure S33. Cyclic voltammograms registered for **HL3** and [Cu(**L3**)$_2$].

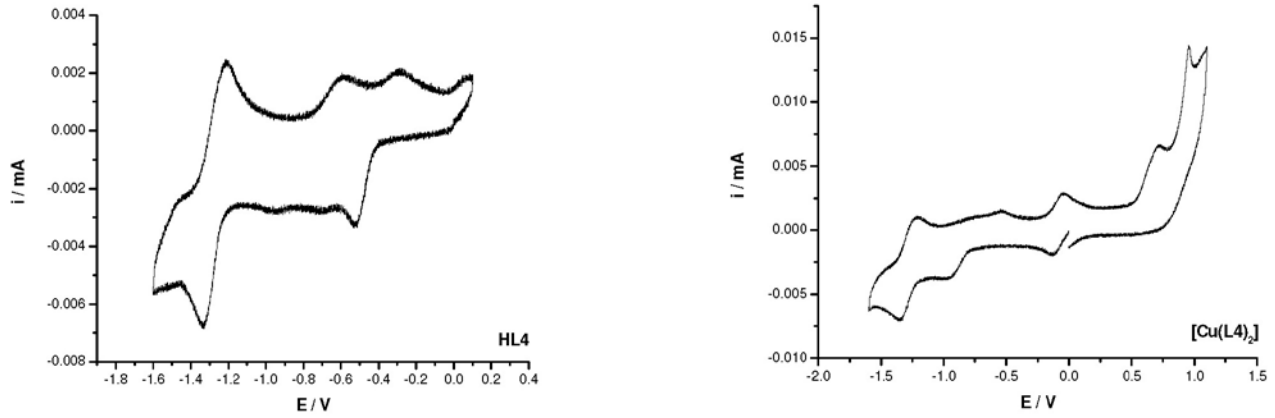


Figure S34. Cyclic voltammograms registered for **HL4** and [Cu(**L4**)$_2$].

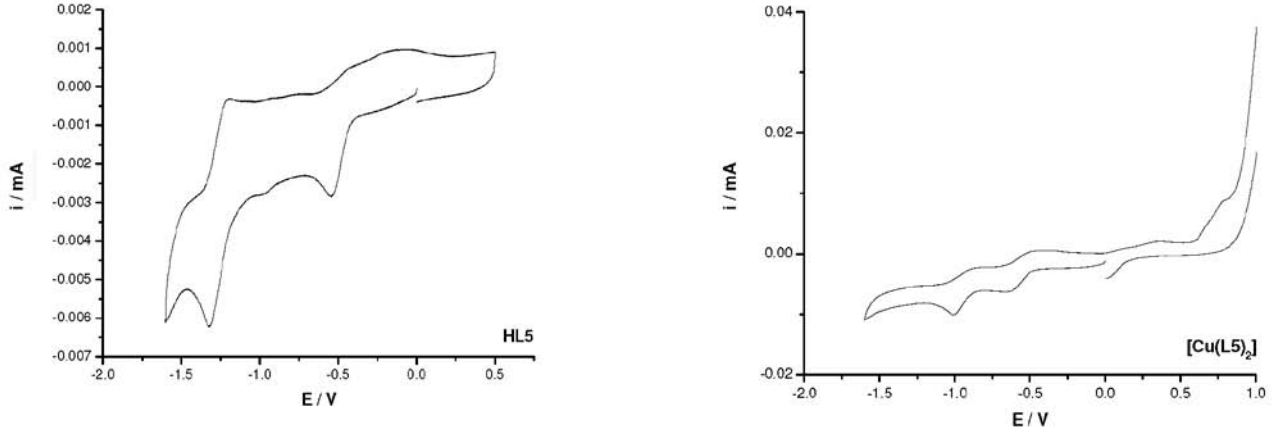


Figure S35. Cyclic voltammograms registered for **HL5** and [Cu(**L5**)$_2$].

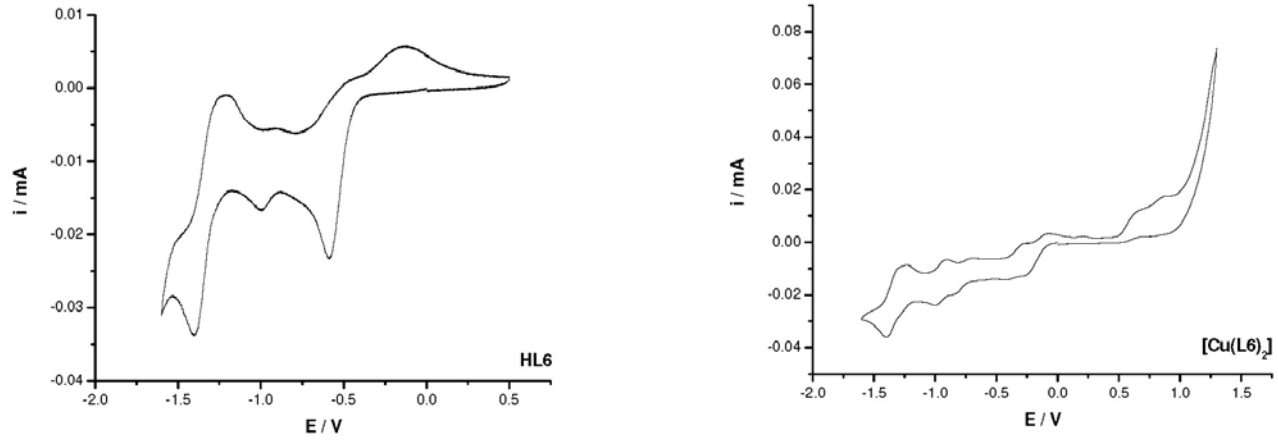


Figure S36. Cyclic voltammograms registered for **HL6** and [Cu(**L6**)$_2$].

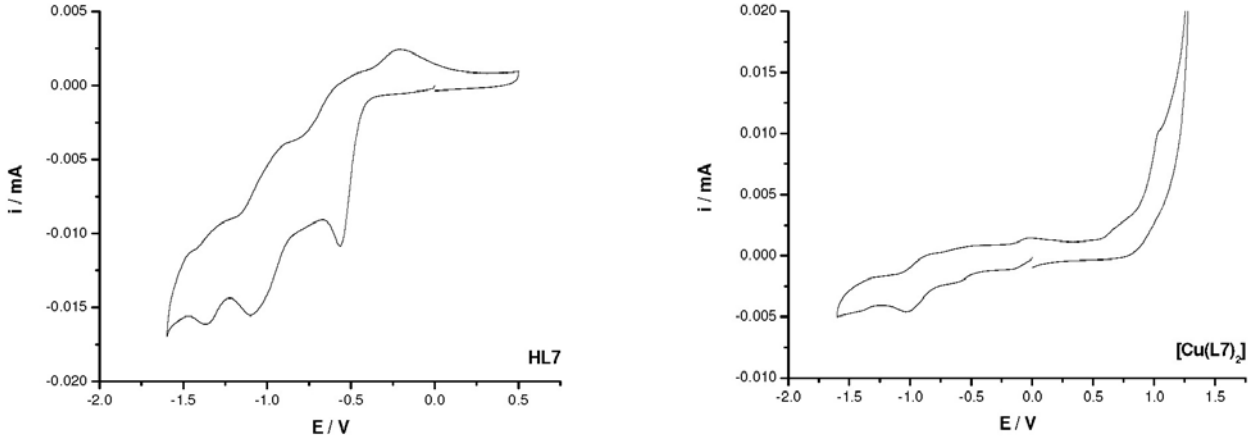


Figure S37. Cyclic voltammograms registered for **HL7** and [Cu(**L7**)$_2$].

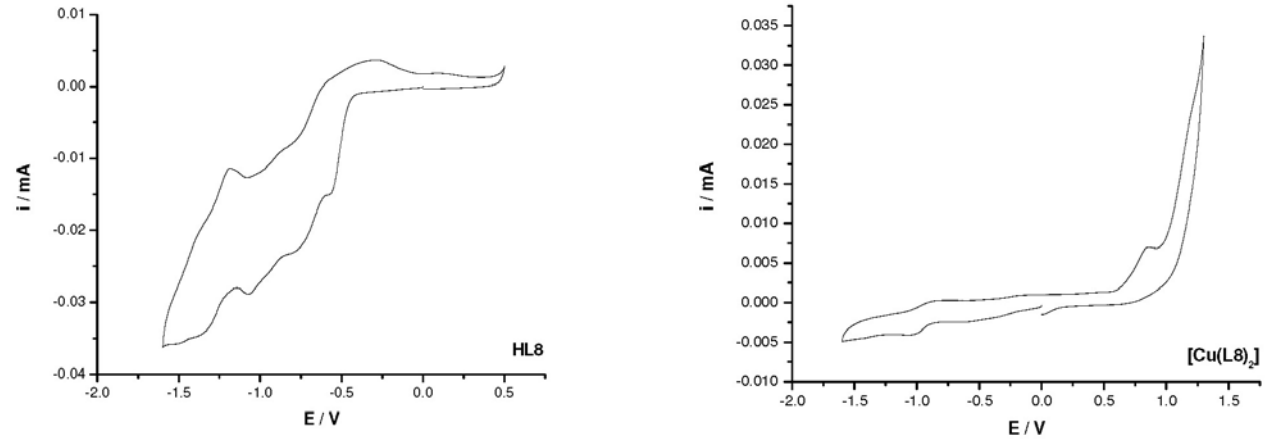


Figure S38. Cyclic voltammograms registered for **HL8** and [Cu(**L8**)$_2$].

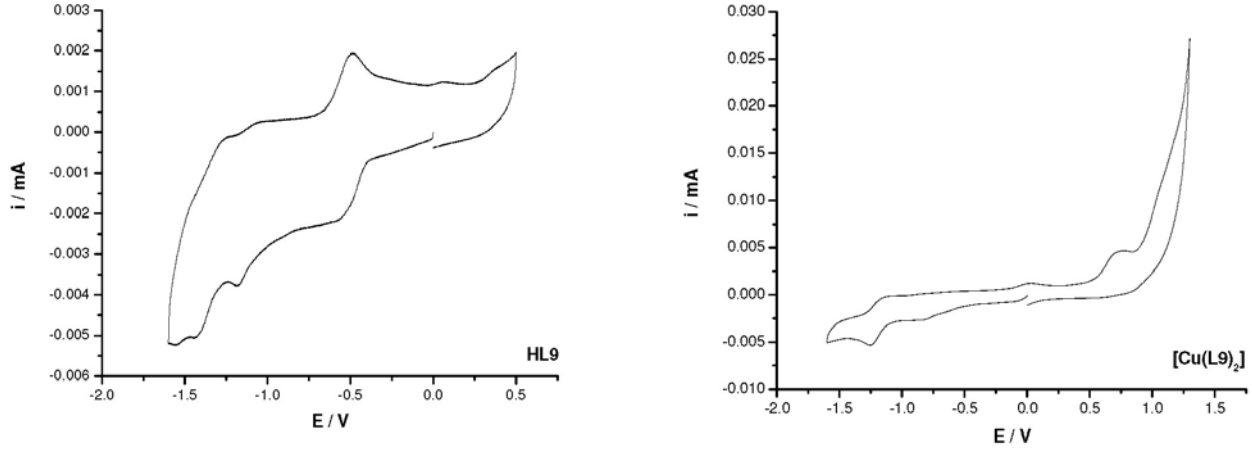


Figure S39. Cyclic voltammograms registered for **HL9** and [Cu(**L9**)$_2$].

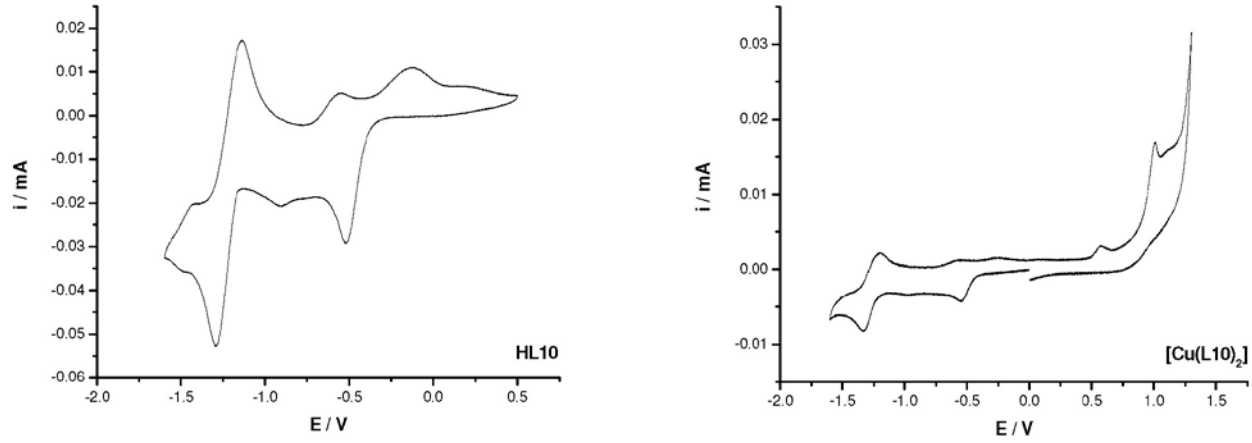


Figure S40. Cyclic voltammograms registered for **HL10** and [Cu(**L10**)$_2$].

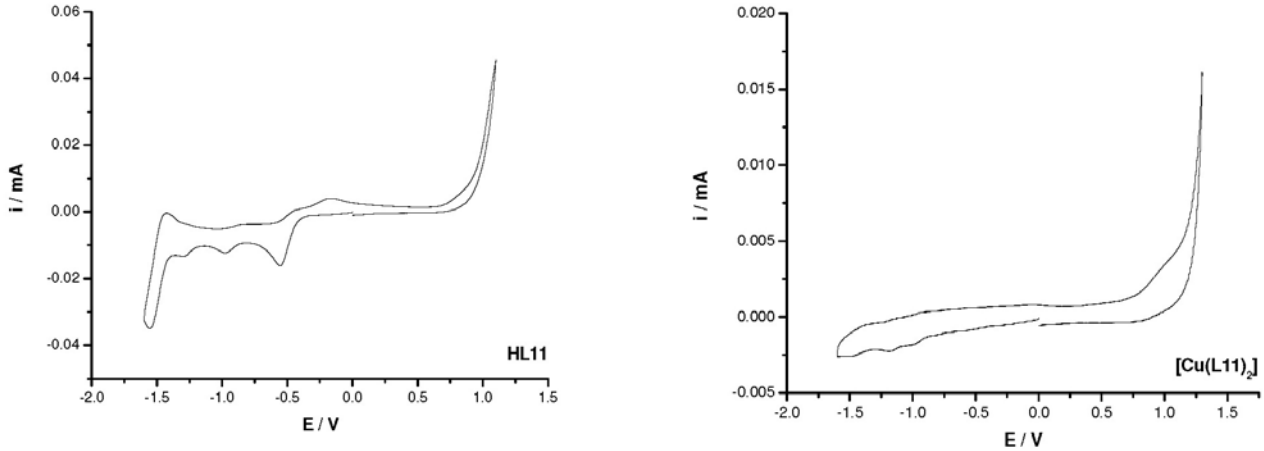


Figure S41. Cyclic voltammograms registered for **HL11** and [Cu(**L11**)$_2$].

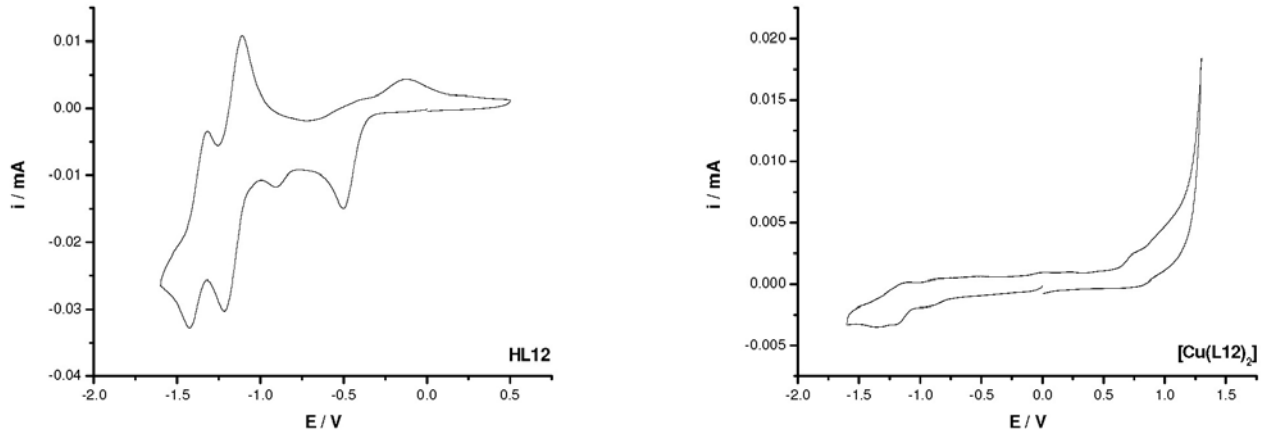


Figure S42. Cyclic voltammograms registered for **HL12** and [Cu(**L12**)$_2$].

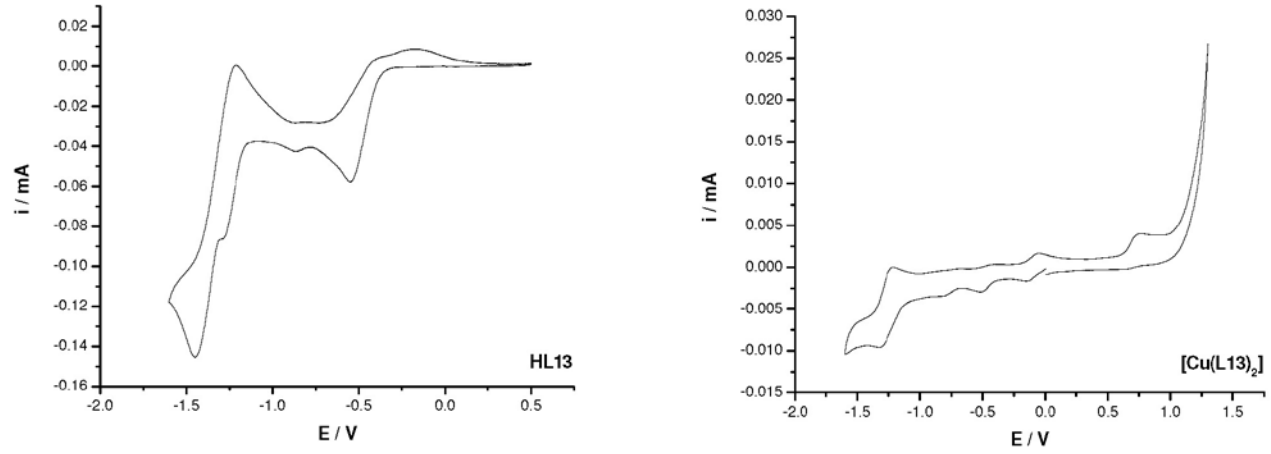


Figure S43. Cyclic voltammograms registered for **HL13** and [Cu(**L13**)$_2$].