Supporting Information (SI)

Synthesis and Reactions of Benzannulated Spiroaminals: Tetrahydrospirobiquinolines

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X-Ray Crystallography

All crystals for X-ray structural elucidation unless otherwise stated were obtained by vapor diffusion of pentane into a saturated solution of purified product in dichloromethane at room temperature from 1-4 days.

The X-ray crystal structure of Spiro-biquinoline 14a

Crystal data for **14a**: $C_{17}H_{18}N_2$, M = 250.33, tetragonal, $I\bar{4}$ (no. 82), a = b = 18.6804(6), c = 7.6330(4) Å, V = 2663.6(2) Å^3, Z = 8, D_c = 1.249 g cm^{-3}, μ(Mo-Kα) = 0.074 mm^{-1}, T = 173 K, colorless tablets, Agilent Xcalibur 3 E diffractometer; 2775 independent measured reflections (R_{int} = 0.0251), F^2 refinement,[X2] R_1(obs) = 0.0400, wR_2(all) = 0.0771, 2305 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{full}$ = 50°], 180 parameters. The absolute structure of 14a could not be unambiguously determined [Flack parameter x^+ = –1.2(10)]. CCDC 1528661.
The two N–H hydrogens in the structure of 14a were located from a ΔF map and refined freely subject to an N–H distance constraint of 0.90 Å.

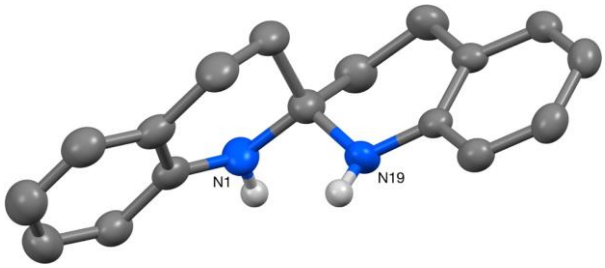
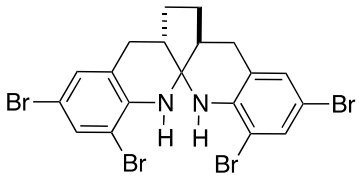


Fig. S1 The crystal structure of **14a** (50% probability ellipsoids).

The X-ray crystal structure of 1,3,10,12-tetrabromo-5,5a,6,7,7a,8,13,13,14-octahydrocyclopenta[1,2-b:1,5-b']diquinoline - 18b



Crystal data for **18b**: $C_{19}H_{16}Br_4N_2$, M = 591.98, monoclinic, $P2_1/c$ (no. 14), a = 12.6560(8), b = 8.9013(6), c = 16.6514(11) Å, β = 97.911(6)°, V = 1858.0(2) Å^3, Z = 4, D_c = 2.116 g cm^{-3}, μ(Mo-Kα) = 8.669 mm^{-1}, T = 173 K, colourless plates, Agilent Xcalibur 3 E diffractometer; 3719 independent measured reflections (R_{int} = 0.0335), F^2 refinement,[X2] R_1(obs) = 0.0436, wR_2(all) = 0.0656, 2465 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{full}$ = 50°], 235 parameters. CCDC 1539105.
The two N–H hydrogens in the structure of **18b** were located from a ΔF map and refined freely subject to an N–H distance constraint of 0.90 Å.

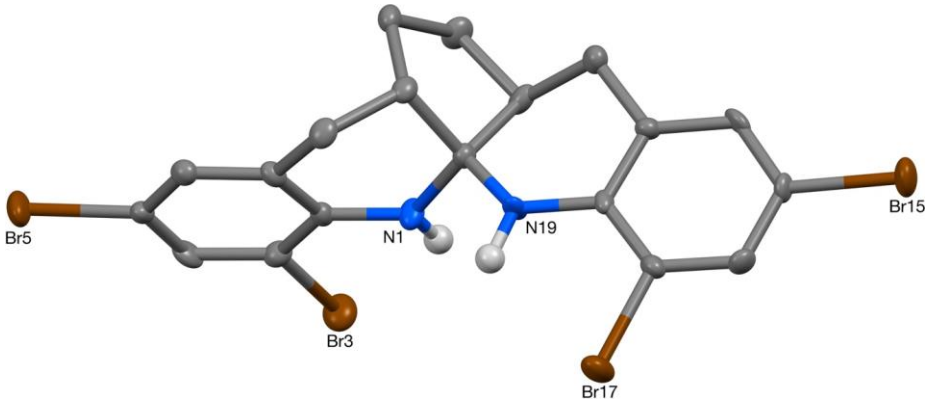
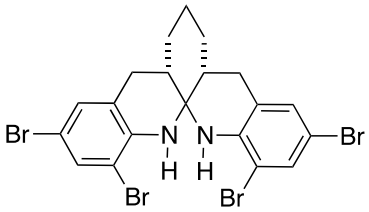


Fig. S2 The crystal structure of **18b** (50% probability ellipsoids).

The X-ray crystal structure of 1,3,11,13-tetrabromo-5a,6,7,8,8a,9,14,15-octahydro-5H-quinolino[3,2-*d*]acridine - 19b



Crystal data for **19b**: $C_{20}H_{18}Br_4N_2$, *M* = 606.00, triclinic, *P*-1 (no. 2), *a* = 8.6429(5), *b* = 9.5129(5), *c* = 12.9337(6) Å, α = 80.017(4), β = 72.909(5), γ = 77.318(5)°, *V* = 984.87(10) Å^3, *Z* = 2, D_c = 2.043 g cm^{-3}, μ(Mo-Kα) = 8.180 mm^{-1}, *T* = 173 K, colourless blocks, Agilent Xcalibur 3 E diffractometer; 3873 independent measured reflections (R_{int} = 0.0178), F^2 refinement,[X2] R_1(obs) = 0.0335, wR_2(all) = 0.0648, 3033 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{full}$ = 50°], 244 parameters. CCDC 1539106.
The two N–H hydrogens in the structure of **19b** were located from a Δ*F* map and refined freely subject to an N–H distance constraint of 0.90 Å.

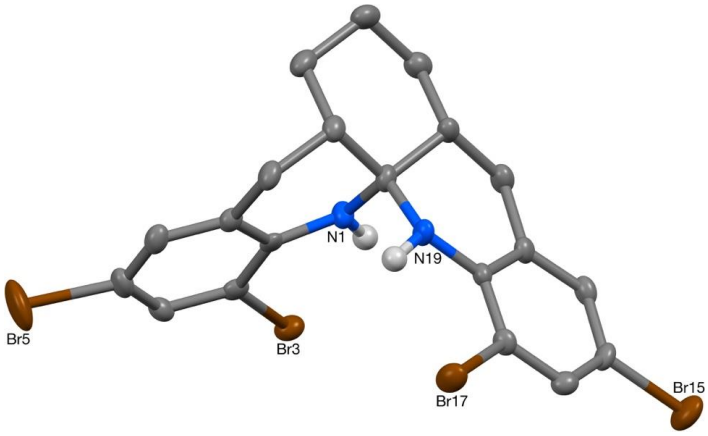


Fig. S3 The crystal structure of **19b** (50% probability ellipsoids).

The X-ray crystal structure of Spiro-biquinoline 25

Crystal data for **25**: $C_{17}H_{16}Br_2N_2$, *M* = 408.14, triclinic, *P*-1 (no. 2), *a* = 8.2840(6), *b* = 10.2385(6), *c* = 10.3631(8) Å, α = 68.118(6), β = 71.449(7), γ = 87.541(6)°, *V* = 770.38(10) Å^3, *Z* = 2, D_c = 1.759 g cm^{-3}, μ(Mo-Kα) = 5.256 mm^{-1}, *T* = 173 K, colorless blocks, Agilent Xcalibur 3 E diffractometer; 3027 independent measured reflections (R_{int} = 0.0222), F^2 refinement,[X2] R_1(obs) = 0.0305, wR_2(all) = 0.0649, 2411 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{full}$ = 50°], 199 parameters. CCDC 1528662.
The two N–H hydrogens in the structure of **25** were located from a Δ*F* map and refined freely subject to an N–H distance constraint of 0.90 Å

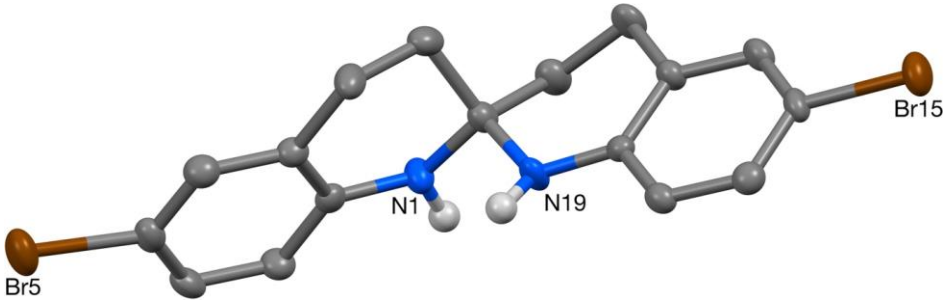


Fig. S4 The crystal structure of **25** (50% probability ellipsoids).

The X-ray crystal structure of Spiro-biquinoline 26

Crystal data for **26**: $C_{17}H_{14}Br_4N_2$, M = 565.94, monoclinic, $P2_1/c$ (no. 14), a = 8.7964(3), b = 12.5727(4), c = 15.8234(5) Å, β = 100.818(3)°, V = 1718.88(10) Å^3, Z = 4, D_c = 2.187 g cm^{-3}, μ(Cu-Kα) = 11.422 mm^{-1}, T = 173 K, colorless tablets, Agilent Xcalibur PX Ultra A diffractometer; 3310 independent measured reflections (R_{int} = 0.0295), F^2 refinement,[X2] R_1(obs) = 0.0354, wR_2(all) = 0.0846, 2760 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{full}$ = 135°], 217 parameters. CCDC 1528663.
The two N–H hydrogens in the structure of **26** were located from a ΔF map and refined freely subject to an N–H distance constraint of 0.90 Å.

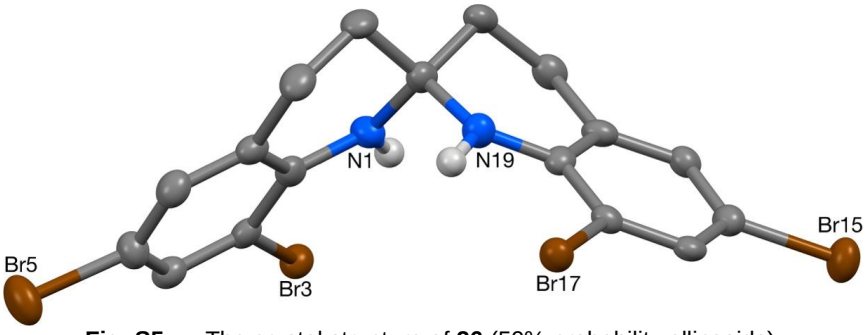


Fig. S5 The crystal structure of **26** (50% probability ellipsoids).

The X-ray crystal structure of Spiro-biquinoline 27

Crystal data for **27**: C41H34N2, M = 554.70, orthorhombic, Pbca (no. 61), a = 18.7174(5), b = 12.0319(4), c = 26.3744(7) Å, V = 5939.6(3) Å3, Z = 8, Dc = 1.241 g cm–3, μ(Mo-Kα) = 0.072 mm–1, T = 173 K, pale yellow blocks, Agilent Xcalibur 3 E diffractometer; 6138 independent measured reflections (Rint = 0.0221), F2 refinement,[X2] R1(obs) = 0.0439, wR2(all) = 0.0992, 4594 independent observed absorption-corrected reflections [|Fo| > 4σ(|Fo|), 2θfull = 50°], 397 parameters. CCDC 1528664.
The two N–H hydrogens in the structure of **27** were located from a ΔF map and refined freely subject to an N–H distance constraint of 0.90 Å.

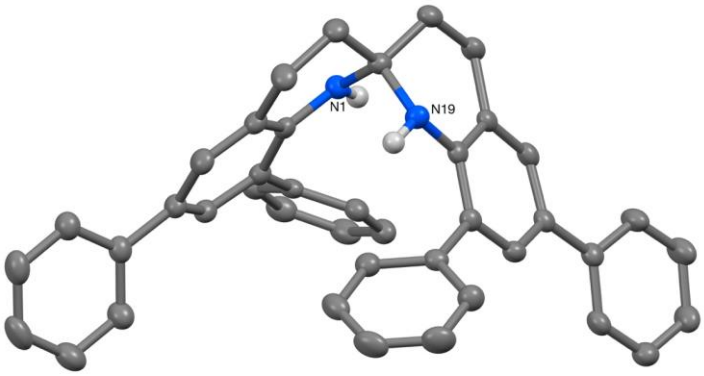


Fig. S6 The crystal structure of **27** (50% probability ellipsoids).

The X-ray crystal structure of Spiro-biquinoline 29

Crystal data for 25: $C_{21}H_{22}N_2$, M = 302.40, monoclinic, $P2_1/n$ (no. 14), a = 8.4668(4), b = 8.8098(4), c = 20.8081(9) Å, β = 91.110(4)°, V = 1551.81(12) Å^3, Z = 4, D_c = 1.294 g cm^{-3}, μ(Mo-Kα) = 0.076 mm^{-1}, T = 173 K, pale yellow blocks, Agilent Xcalibur 3 E diffractometer; 3097 independent measured reflections (R_{int} = 0.0185), F^2 refinement,[X2] R_1(obs) = 0.0427, wR_2(all) = 0.1009, 2549 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{full}$ = 50°], 209 parameters. CCDC 1528665**.**

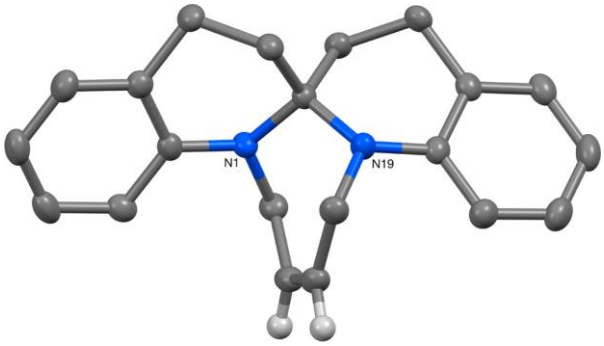


Fig. S7 The crystal structure of **29** (50% probability ellipsoids).

References

[X1] G. Zhou, K. Emerson, E. Majusiak, C. Anderson, O. Sudah, *Org. Process Res. Dev.* **2012**, *16*, 204–213.

[X5] (a) SHELXTL, Bruker AXS, Madison, WI; (b) SHELX-2013, G.M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8.

Fig S8 - ^{1}H NMR Spectra (400 MHz) – 8-Azidoquinoline-7-carbaldehyde – **15c**

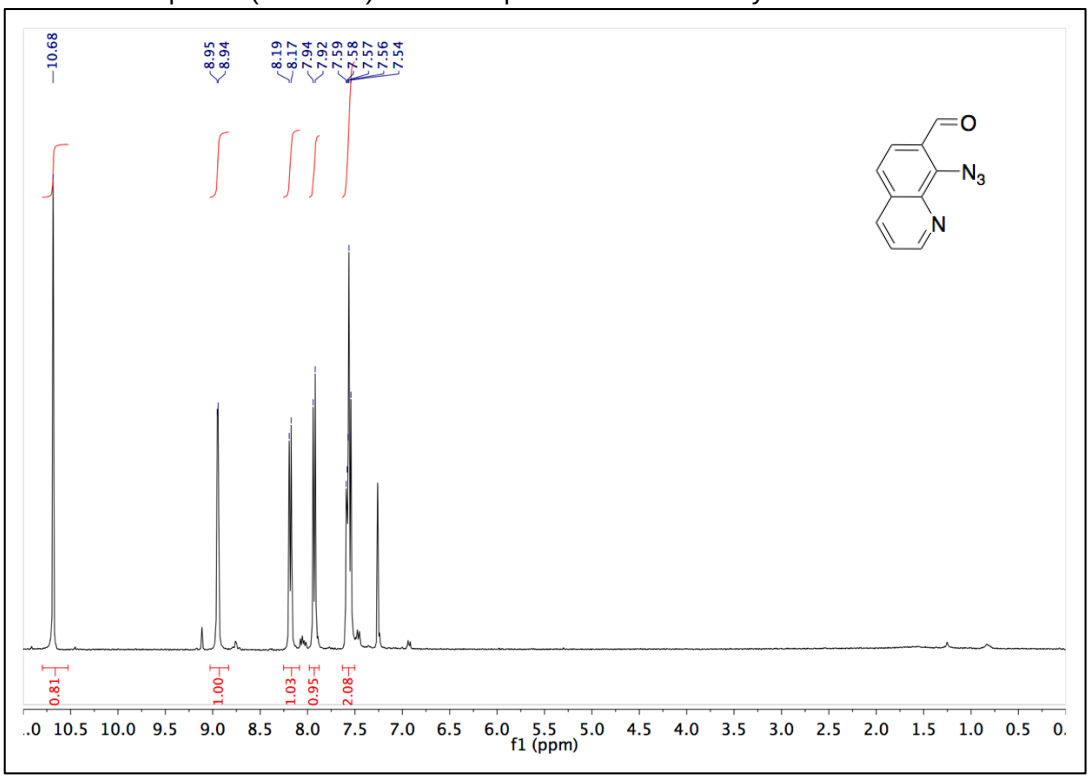


Fig S9 - ^{13}C NMR Spectra (101 MHz) – 8-Azidoquinoline-7-carbaldehyde – **15c**

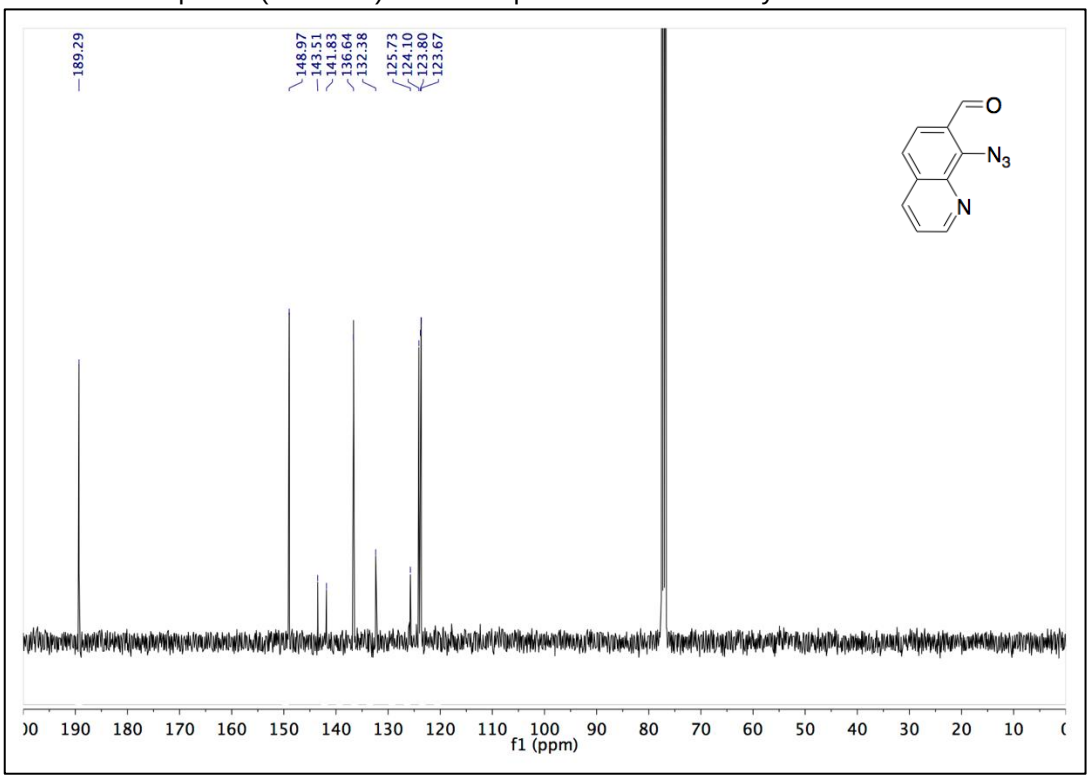


Fig S10 - ^{1}H NMR Spectra (400 MHz) - 3,3',4,4'-Tetrahydro-1H,1'H-2,2'-spirobi[quinoline] – **14a**

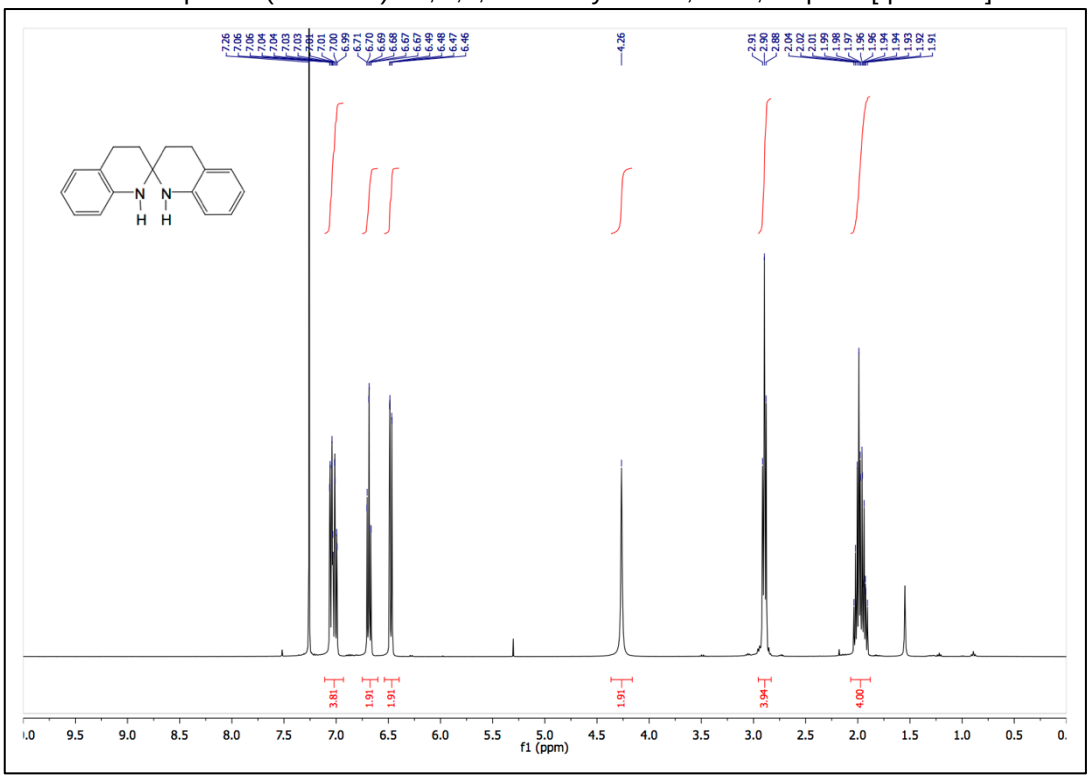


Fig S11 - ^{13}C NMR Spectra (101 MHz) - 3,3',4,4'-Tetrahydro-1H,1'H-2,2'-spirobi[quinoline] – **14a**

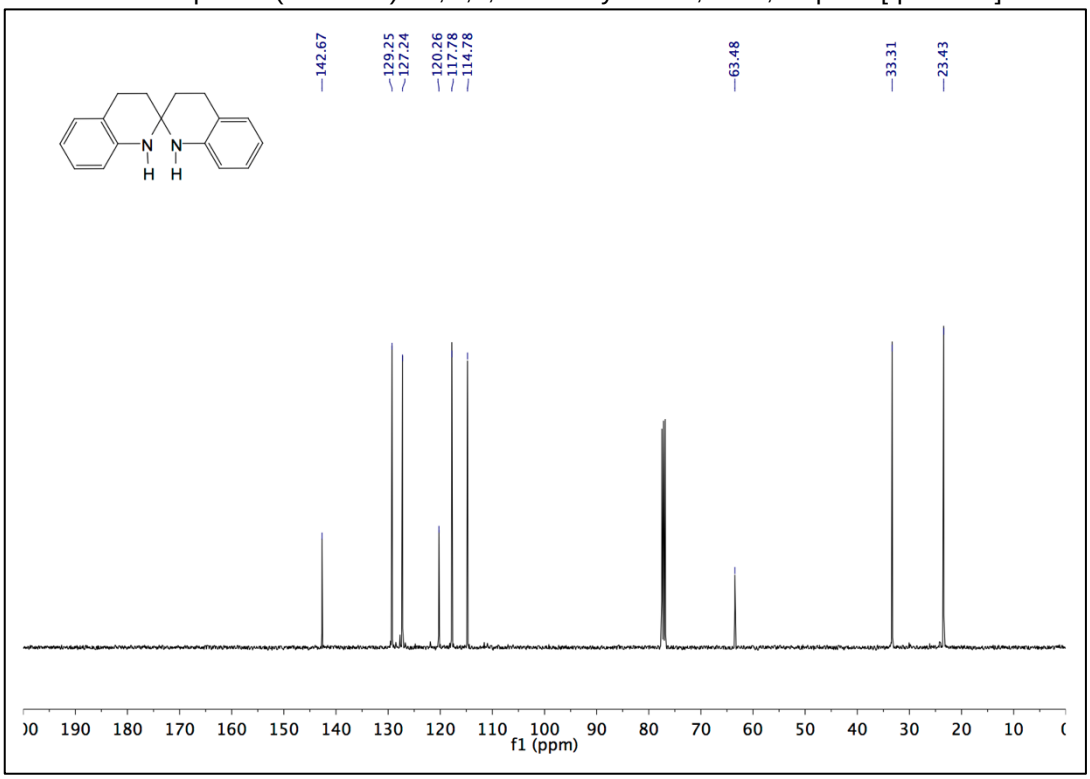


Fig S12 - COSY Spectrum - 3,3',4,4'-Tetrahydro-1H,1'H-2,2'-spirobi[quinoline] – **14a**

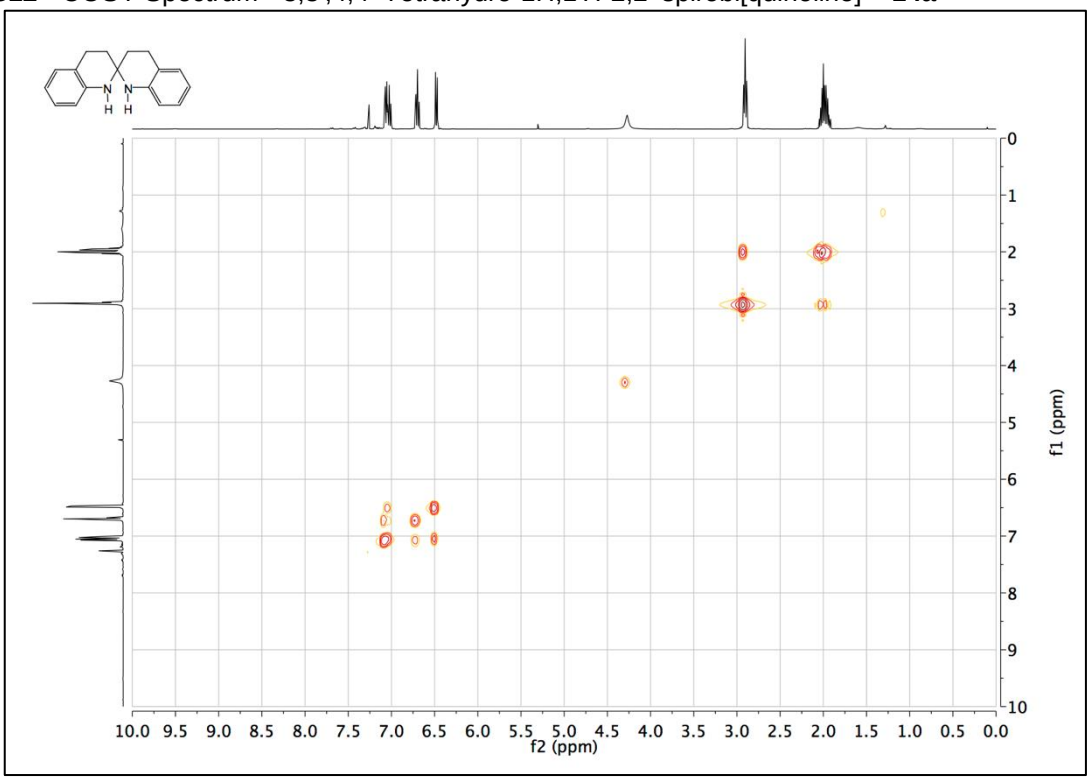


Fig S13 - HMBC Spectrum - 3,3',4,4'-Tetrahydro-1H,1'H-2,2'-spirobi[quinoline] – **14a**

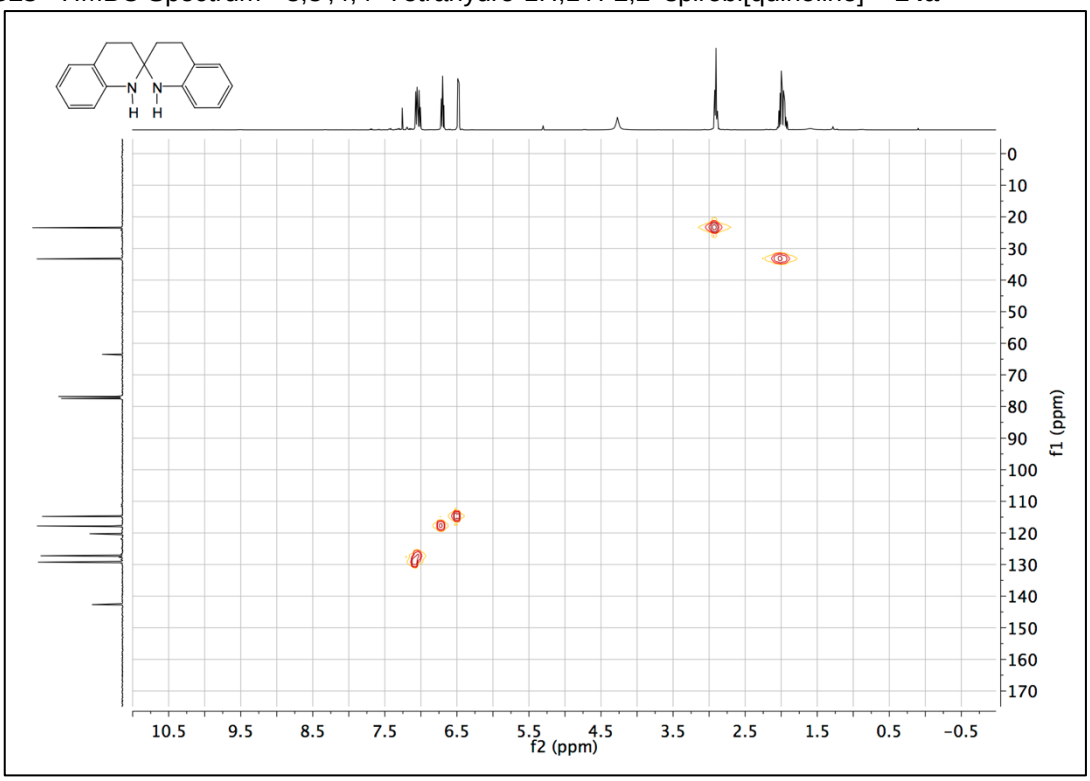


Fig S14 - HMQC Spectrum - 3,3',4,4'-Tetrahydro-1H,1'H-2,2'-spirobi[quinoline] – **14a**

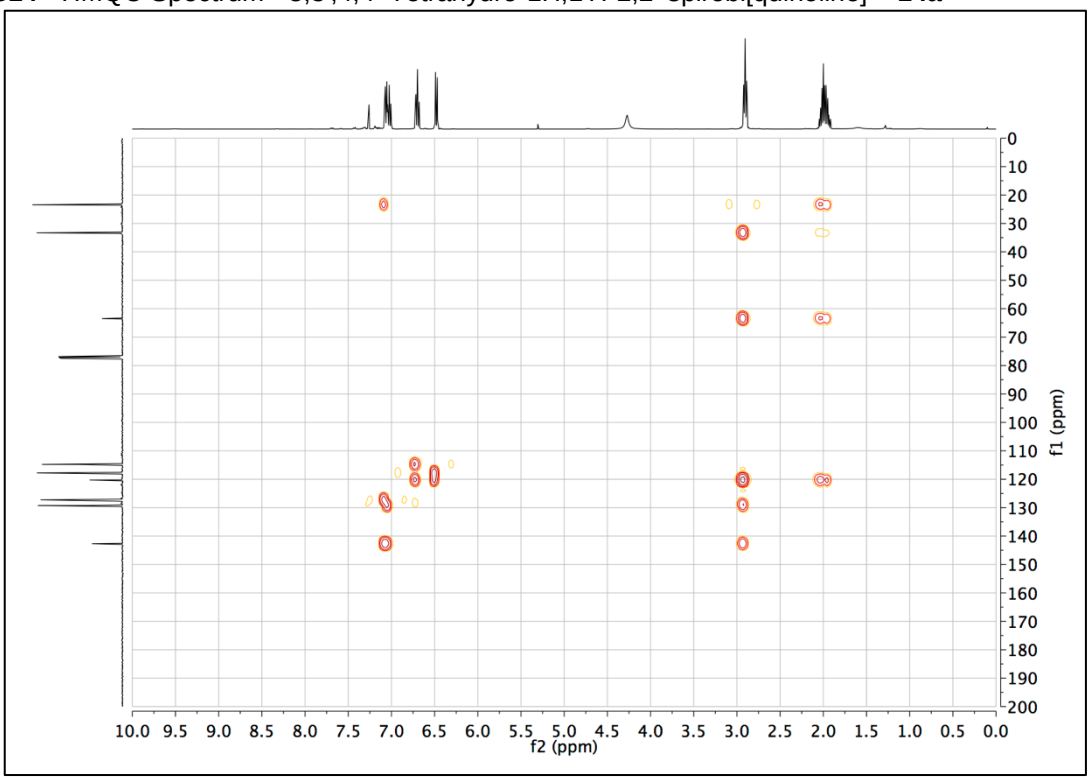


Fig S15 - ^{1}H NMR Spectra (400 MHz) - 3,3',4,4'-Tetrahydro-1H,1'H-2,2'-spirobi[benzo[h]quinoline] – **14b**

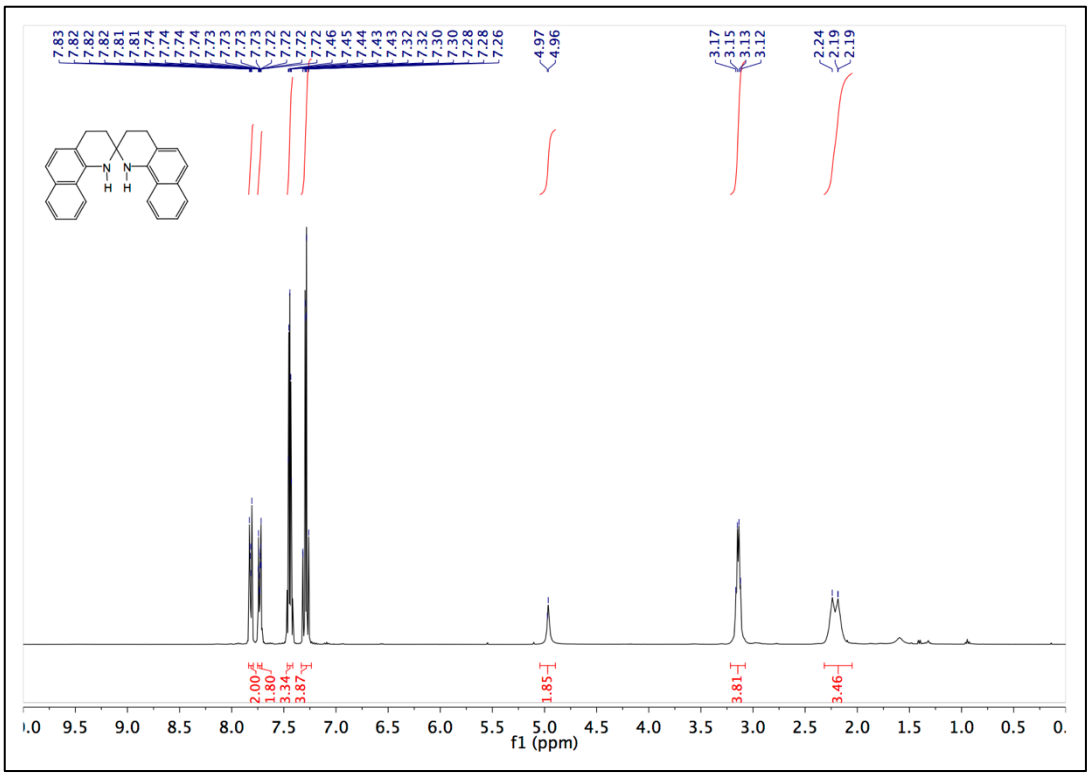


Fig S16 - ^{13}C NMR Spectra (101 MHz) 3,3',4,4'-Tetrahydro-1H,1'H-2,2'-spirobi[benzo[h]quinoline] – **14b**

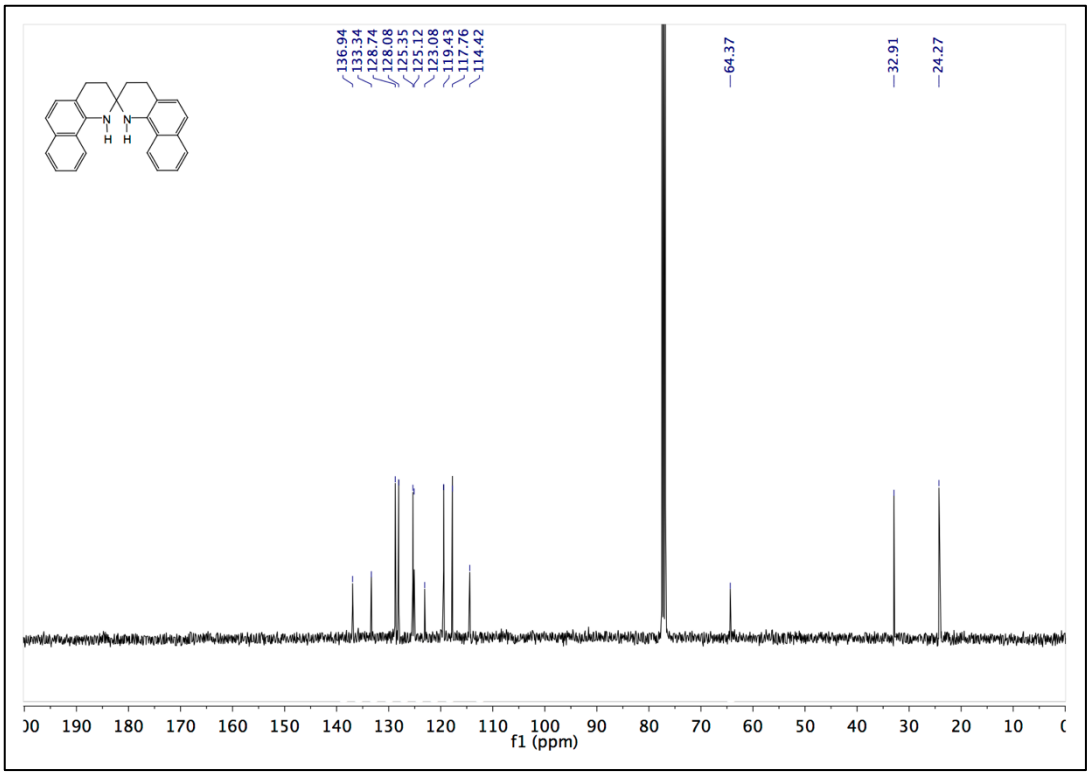


Fig S17 - ^{1}H NMR Spectra (400 MHz) - 3,3',4,4'-Tetrahydro-1H,1'H-2,2'-spirobi[[1,10]phenanthroline] – **14c**

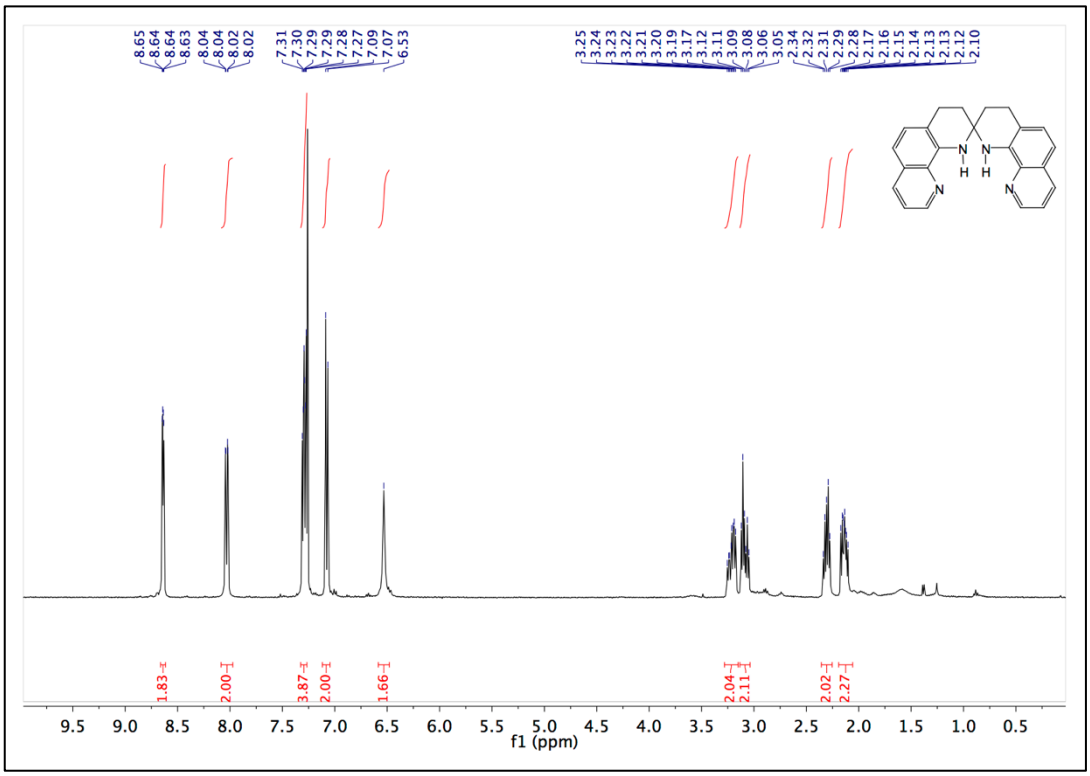


Fig S18 - ^{13}C NMR Spectra (101 MHz) - 3,3',4,4'-Tetrahydro-1H,1'H-2,2'-spirobi[[1,10]phenanthroline] – **14c**

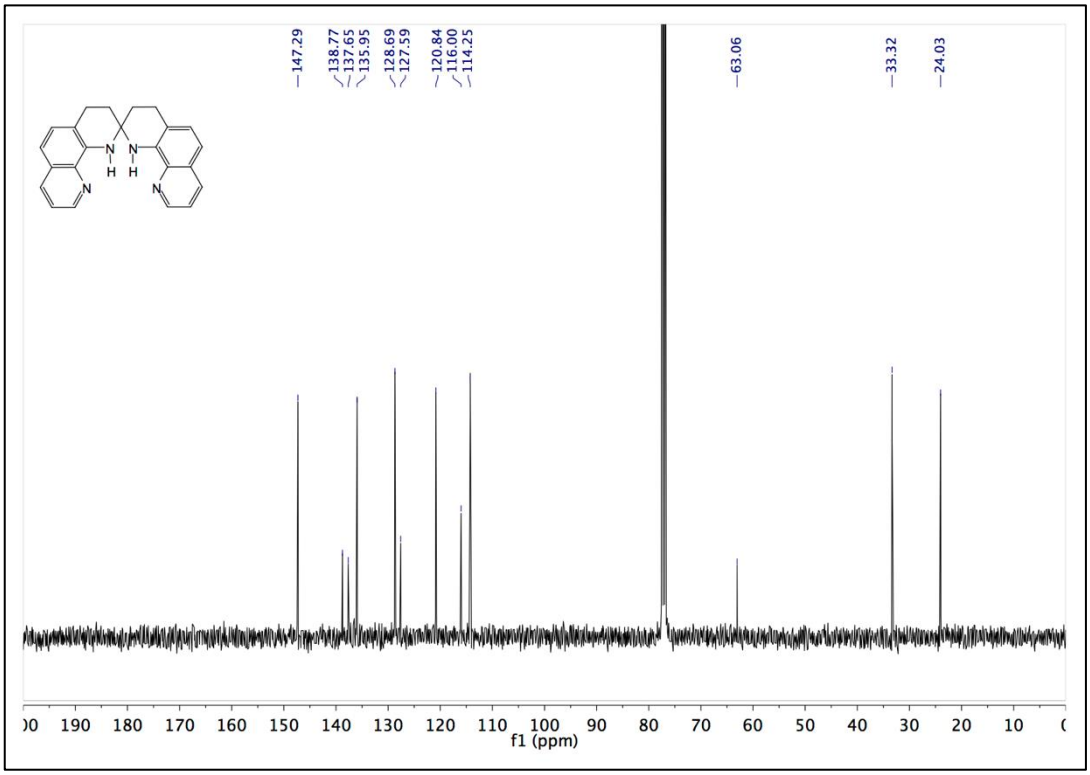


Fig S19 - ^{1}H NMR Spectra (400 MHz) - 8,8'-Dimethyl-3,3',4,4'-tetrahydro-1H,1'H-2,2'-spirobi[quinoline] – **14d**

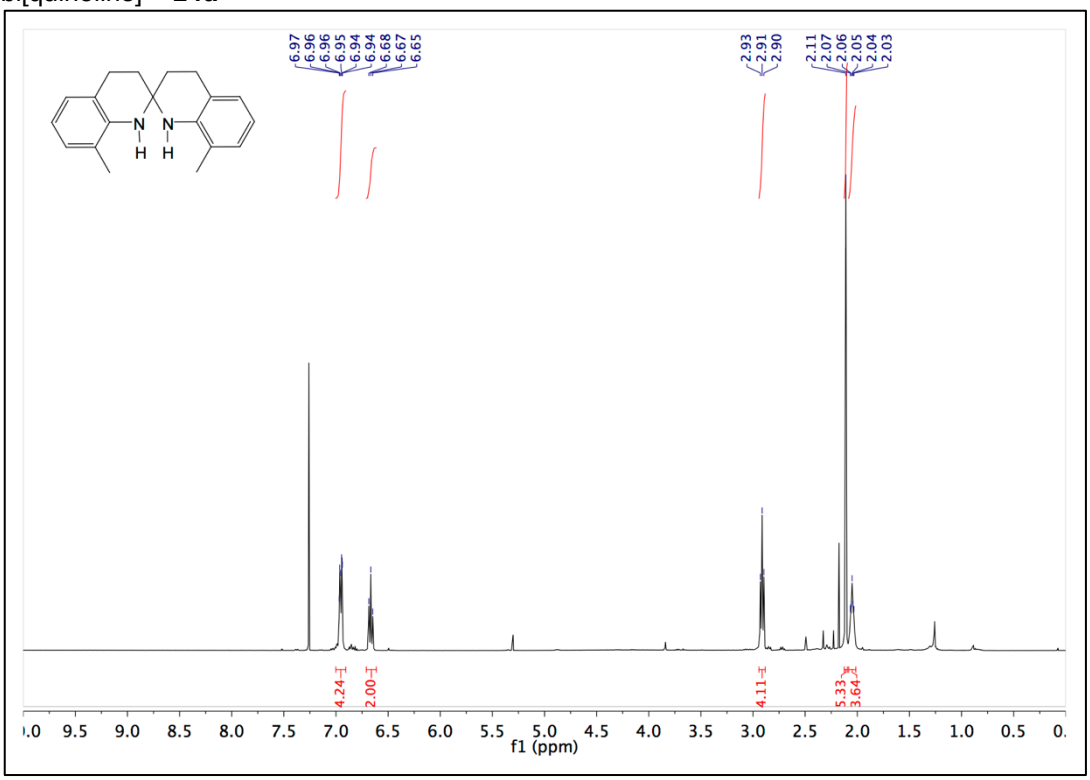


Fig S20 - ^{13}C NMR Spectra (101 MHz) - 8,8'-Dimethyl-3,3',4,4'-tetrahydro-1H,1'H-2,2'-spirobi[quinoline] – **14d**

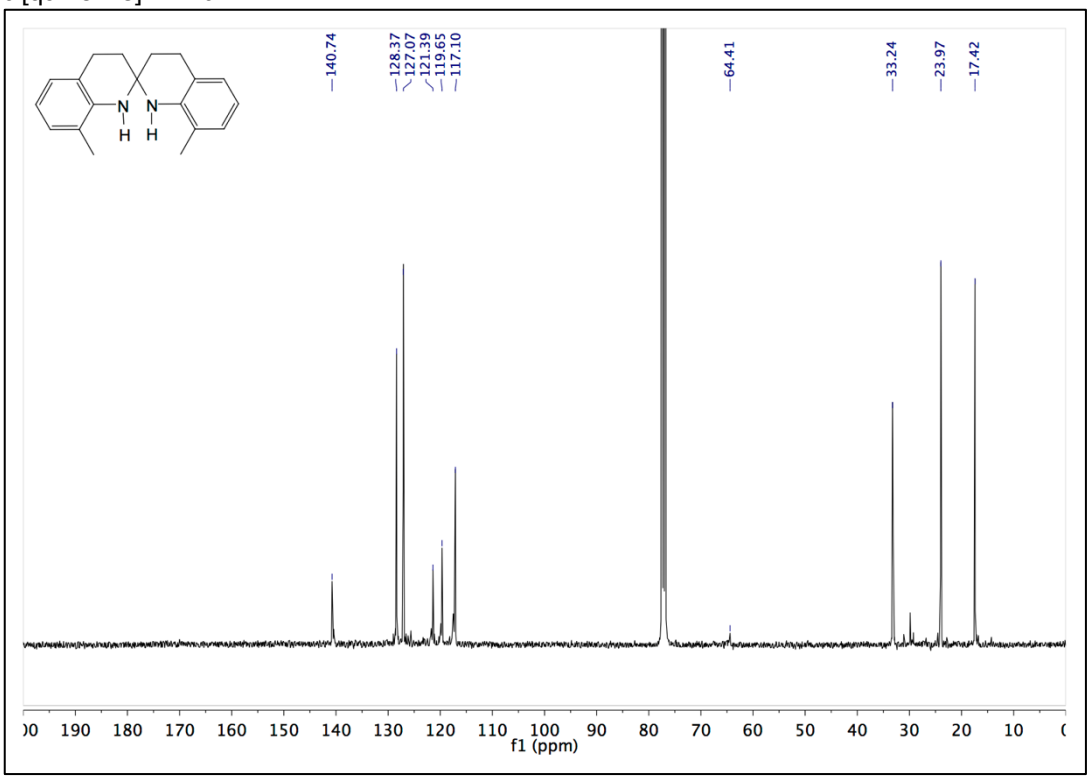


Fig S21 - ^{1}H NMR Spectra (400 MHz) - 7,7'-Bis(trifluoromethyl)-3,3',4,4'-tetrahydro-1H,1'H-2,2'-spirobi[quinoline] – **14e**

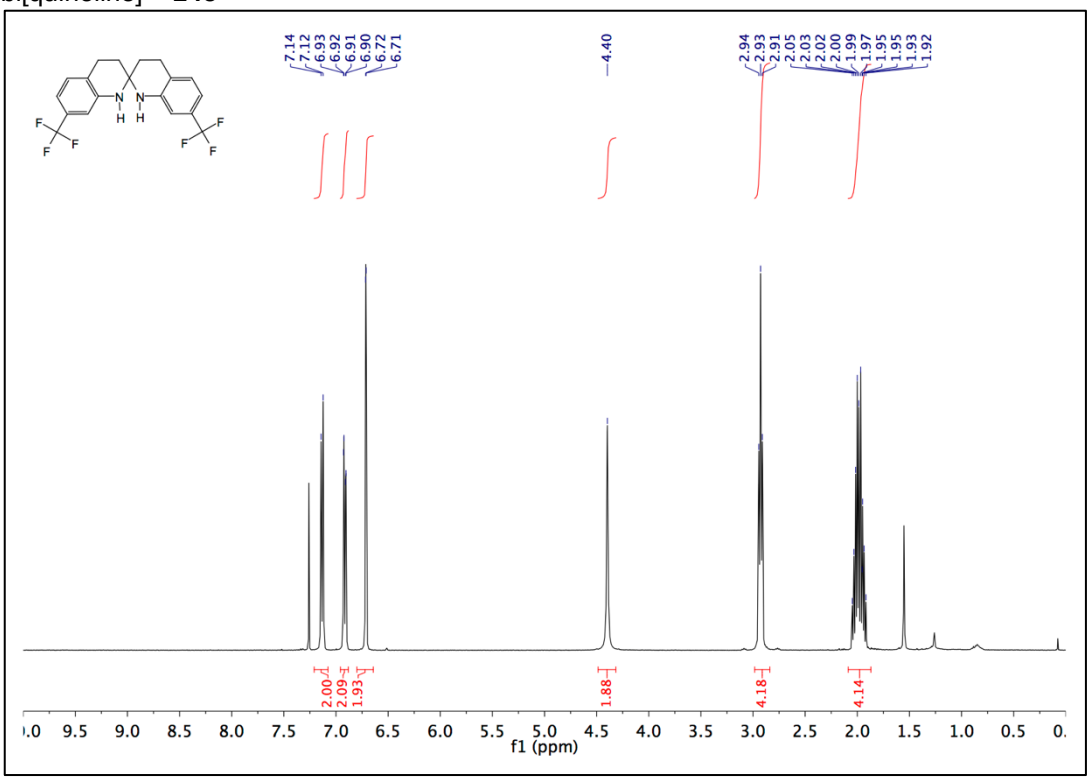


Fig S22 - ^{13}C NMR Spectra (101 MHz) - 7,7'-Bis(trifluoromethyl)-3,3',4,4'-tetrahydro-1H,1'H-2,2'-spirobi[quinoline] – **14e**

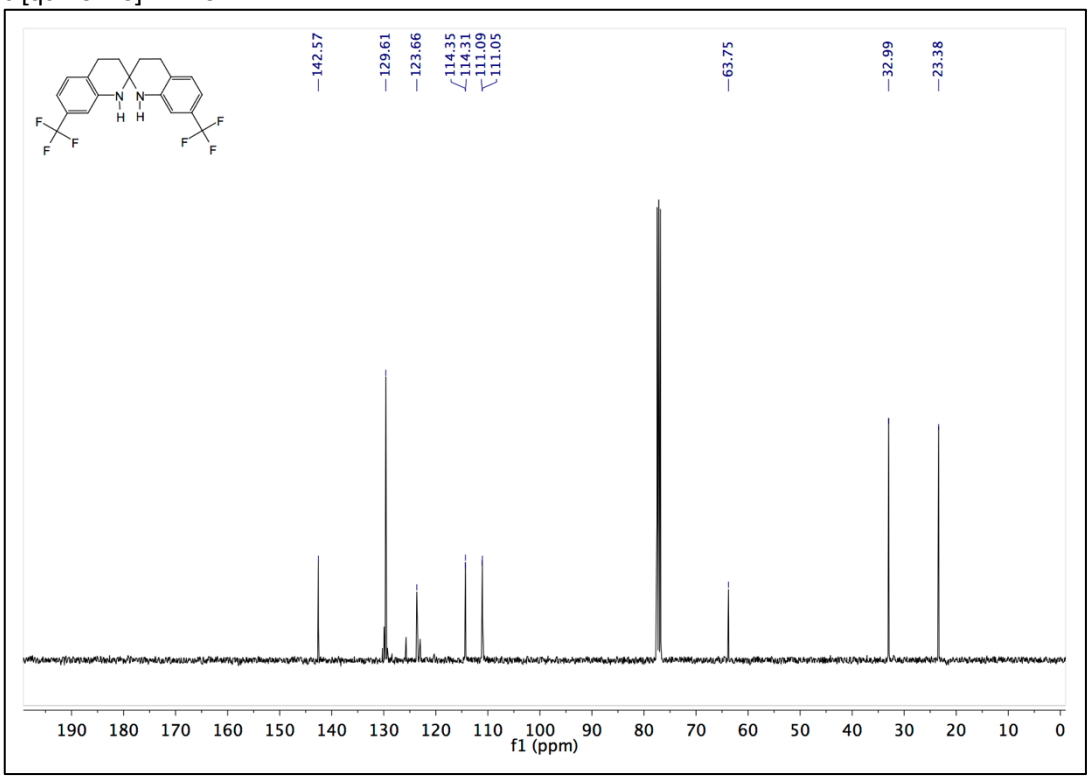


Fig S23 - ^{1}H NMR Spectra (400 MHz) - 7,7'-Dimethoxy-3,3',4,4'-tetrahydro-1H,1'H-2,2'-spirobi[quinoline] – **14f**

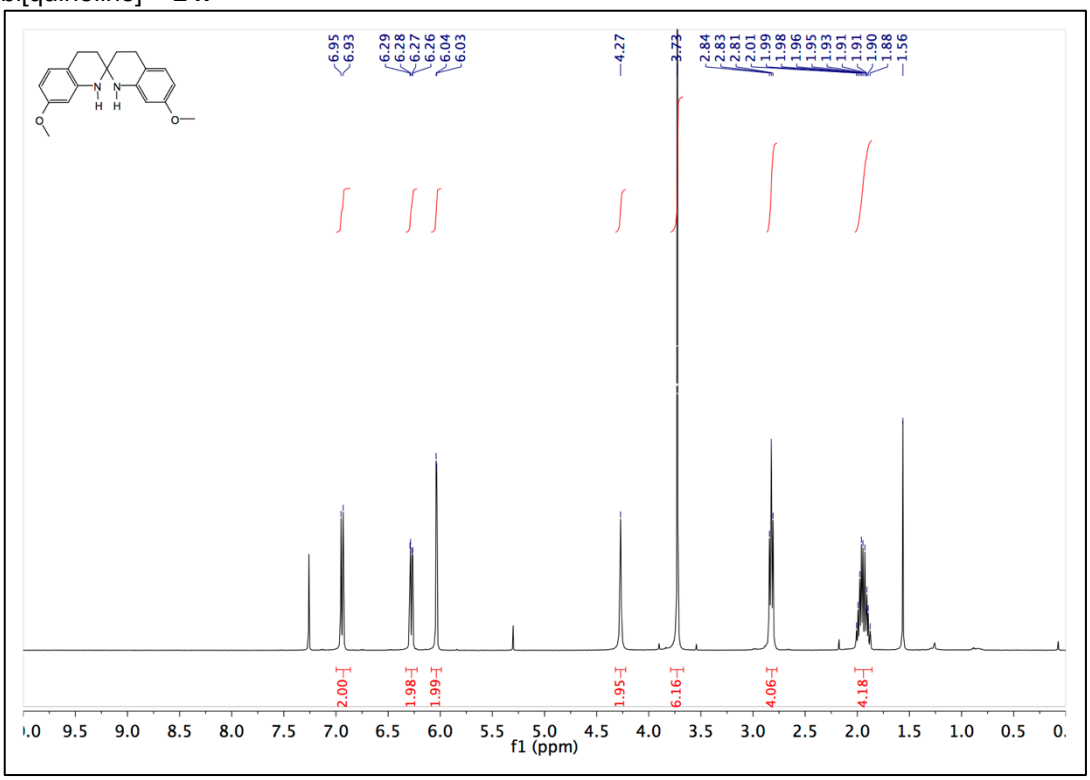


Fig S24 - ^{13}C NMR Spectra (101 MHz) - 7,7'-Dimethoxy-3,3',4,4'-tetrahydro-1H,1'H-2,2'-spirobi[quinoline] – **14f**

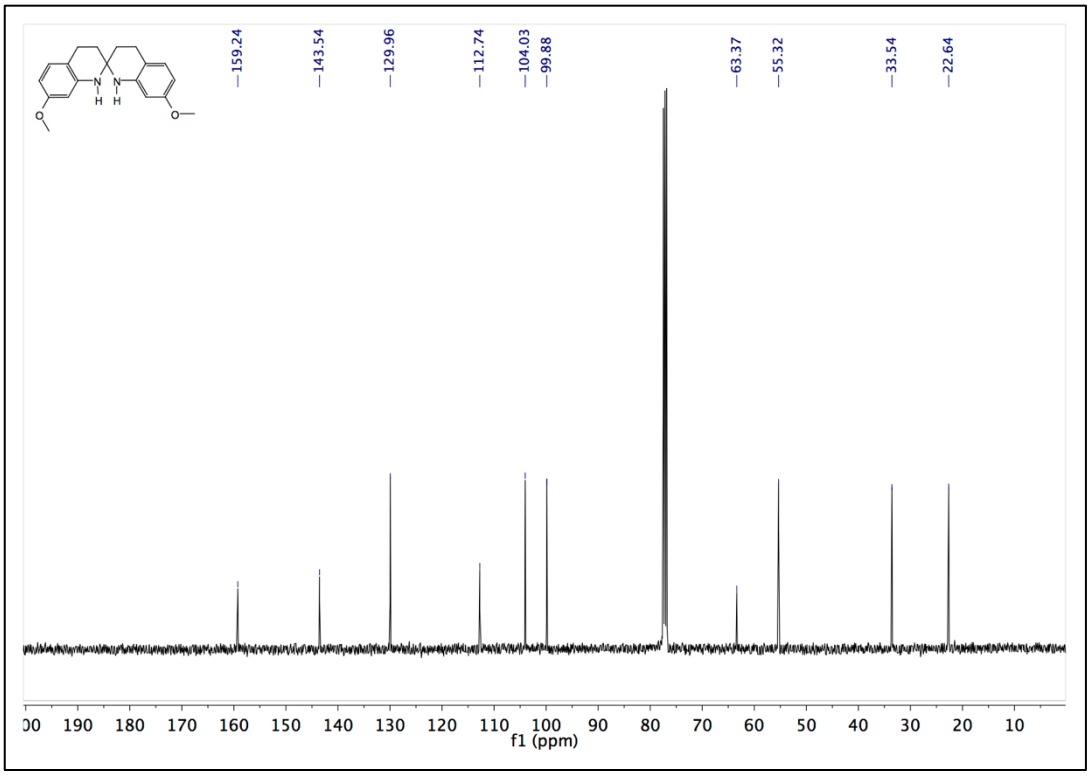


Fig S25 - ^{1}H NMR Spectra (400 MHz) - 6,6'-Dichloro-3,3',4,4'-tetrahydro-1H,1'H-2,2'-spirobi[quinoline] – **14g**

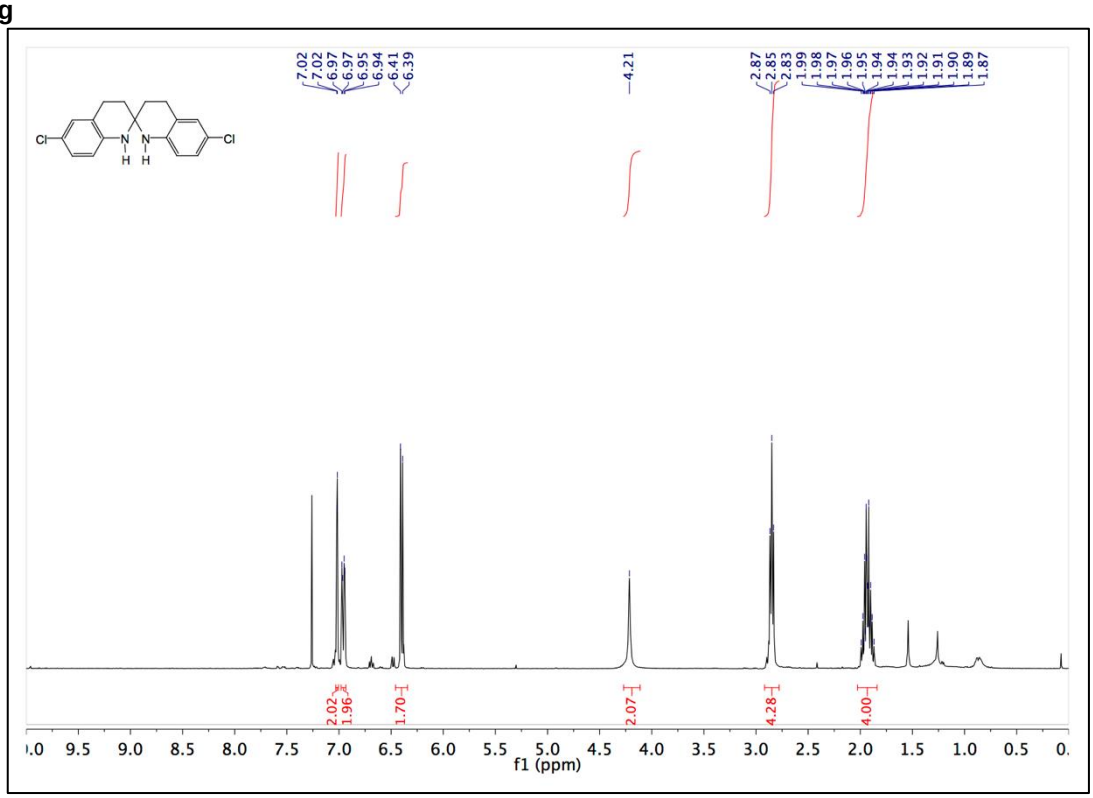


Fig S26 - ^{13}C NMR Spectra (101 MHz) - 6,6'-Dichloro-3,3',4,4'-tetrahydro-1H,1'H-2,2'-spirobi[quinoline] – **14g**

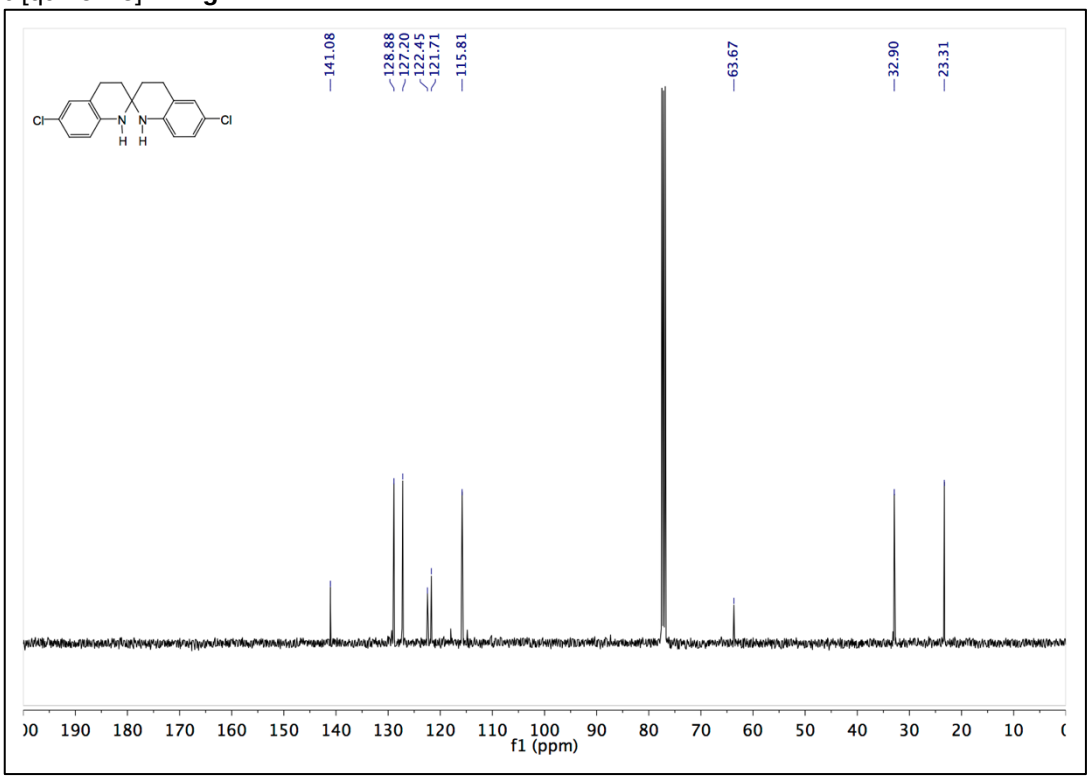


Fig S27 - ^{1}H NMR Spectra (400 MHz) - 5,5a,6,7,7a,8,13,14-Octahydrocyclopenta[1,2-b:1,5-b']diquinoline - **18**

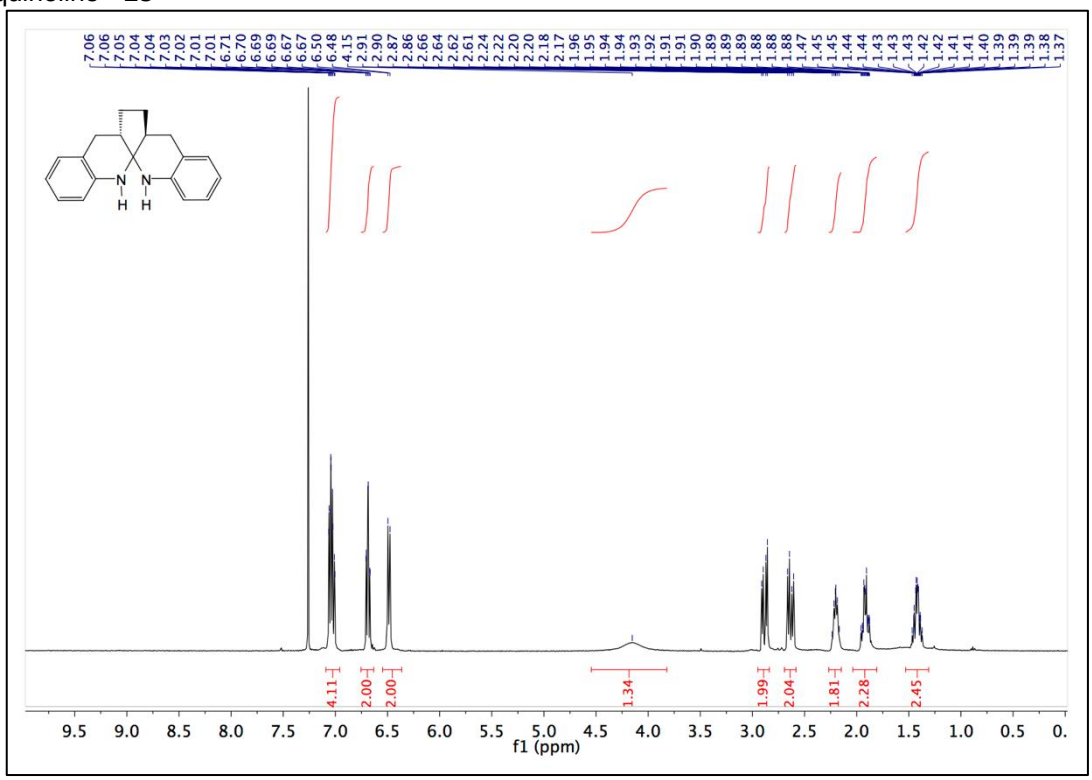


Fig S28 - ^{13}C NMR Spectra (101 MHz) - 5,5a,6,7,7a,8,13,14-Octahydrocyclopenta[1,2-b:1,5-b']diquinoline - **18**

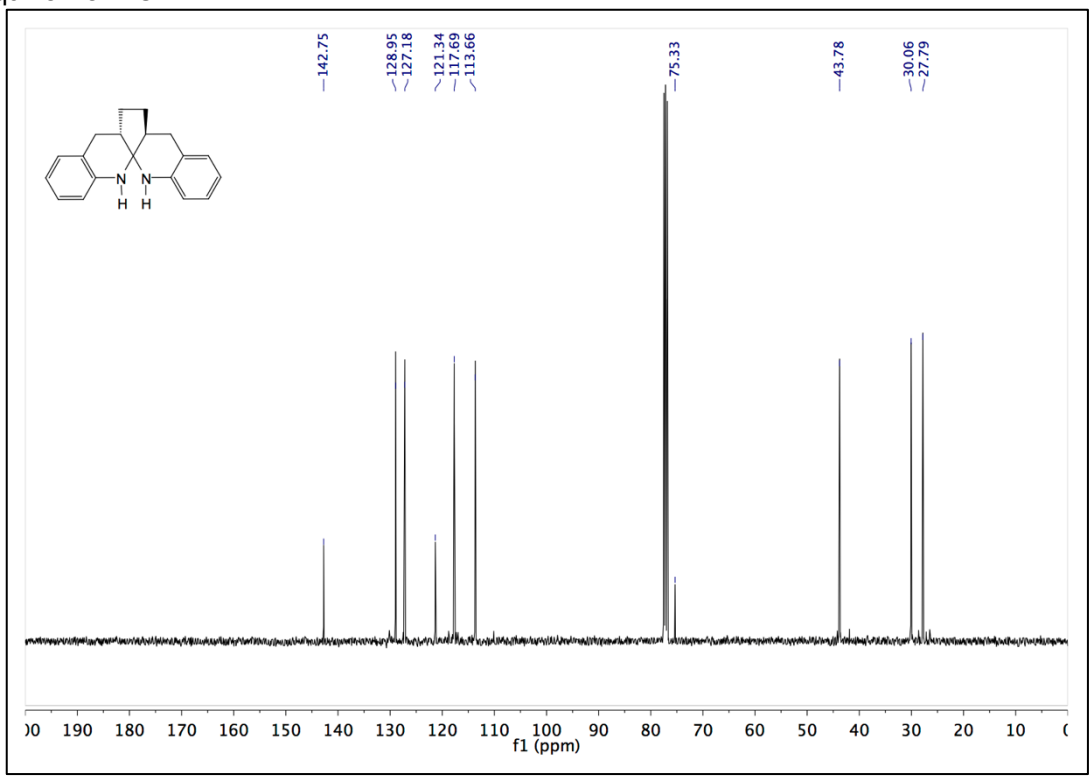


Fig S29 - ^{1}H NMR Spectra (400 MHz) - 1,3,10,12-tetrabromo-5,5a,6,7,7a,8,13,14-octahydrocyclopenta[1,2-*b*:1,5-*b'*]diquinoline – **18b**

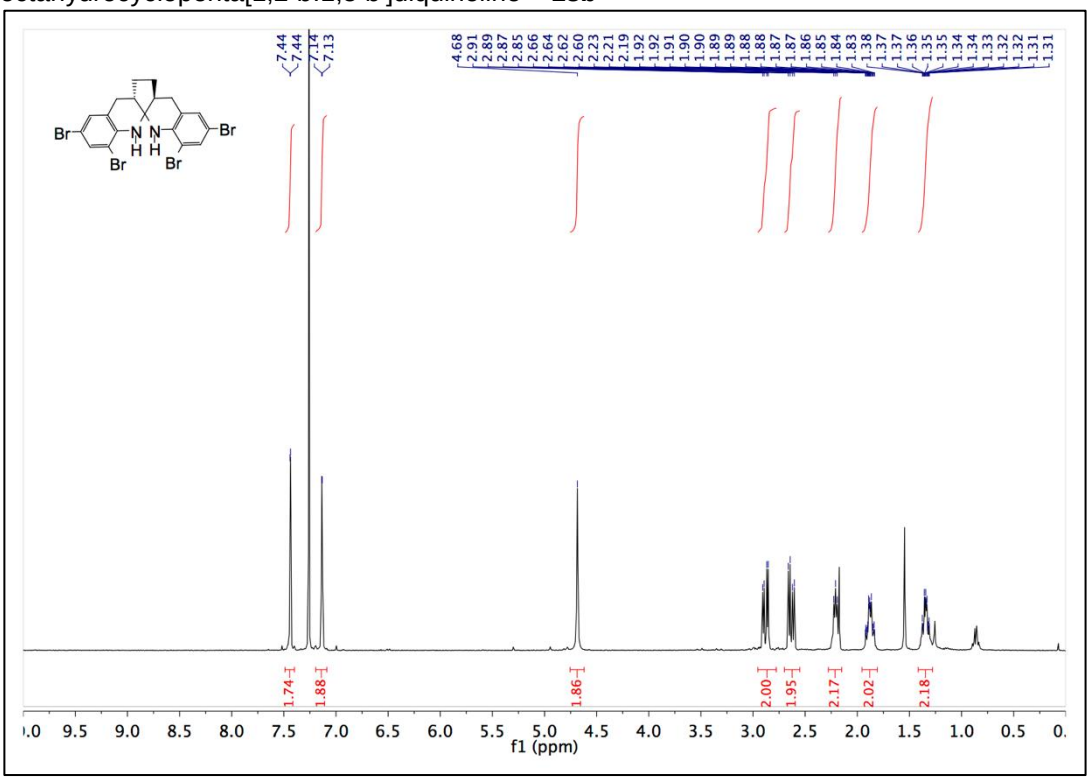


Fig S30 - ^{13}C NMR Spectra (101 MHz)- 1,3,10,12-tetrabromo-5,5a,6,7,7a,8,13,14-octahydrocyclopenta[1,2-*b*:1,5-*b'*]diquinoline – **18b**

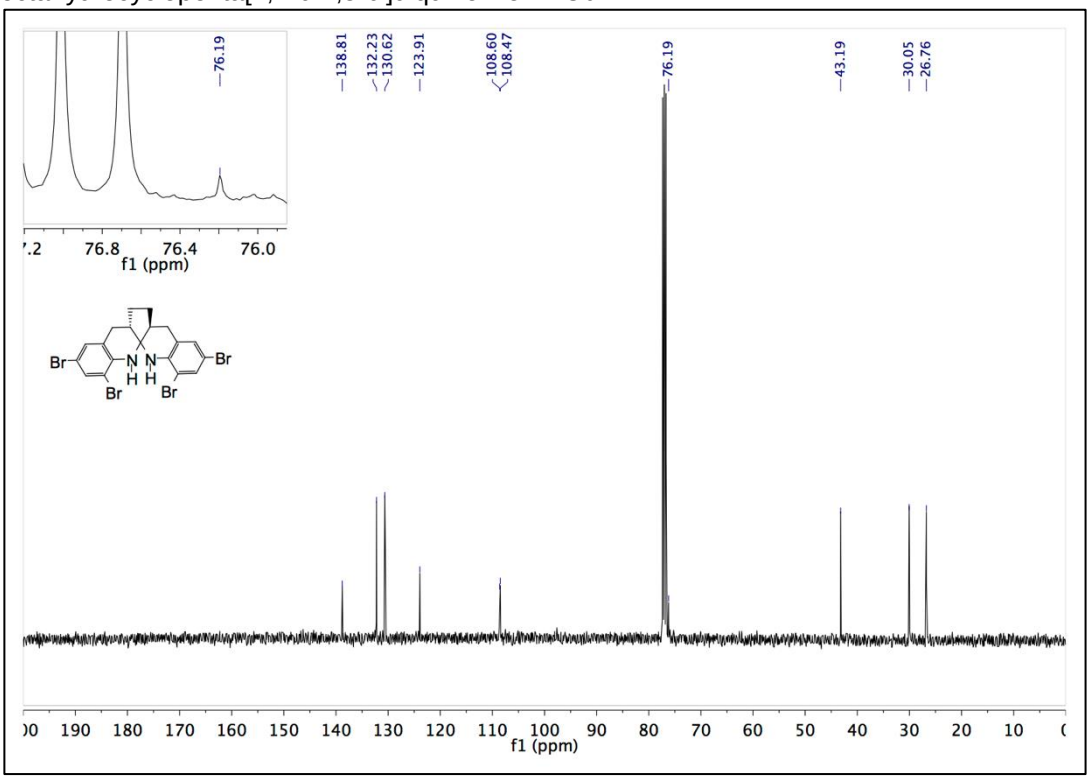


Fig S31 - ^{1}H NMR Spectra (400 MHz) - 5a,6,7,8,8a,9,14,15-Octahydro-5H-quinolino[3,2-d]acridine - **19**

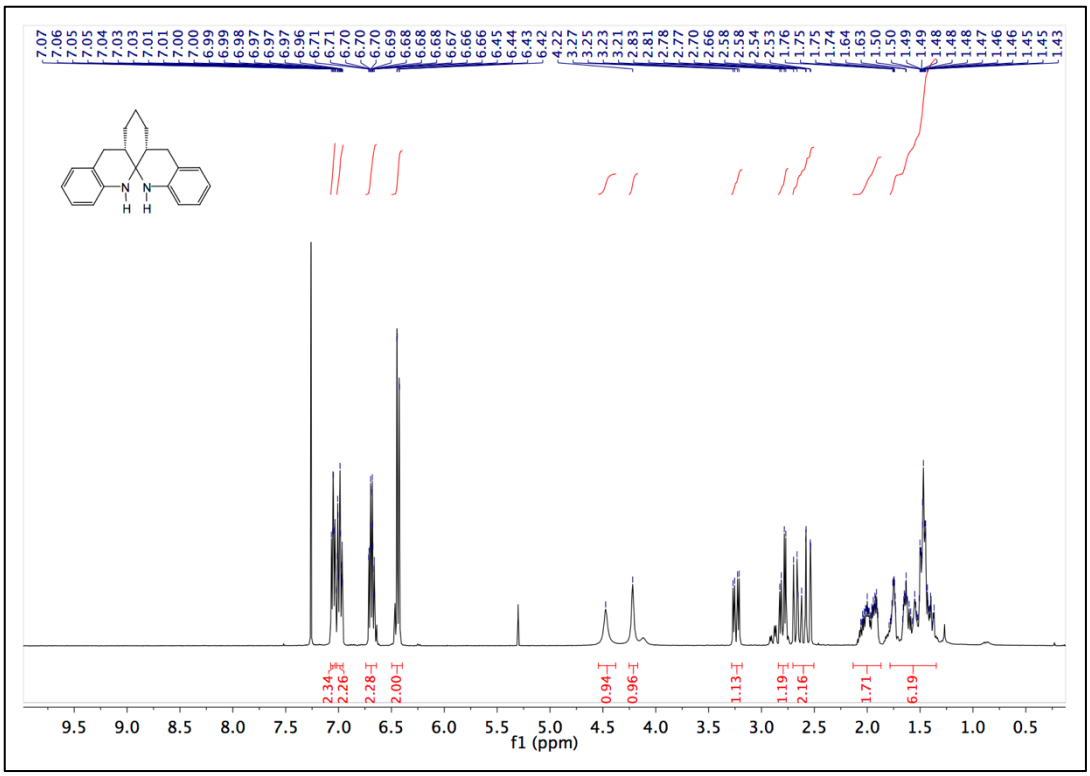


Fig S32 - ^{13}C NMR Spectra (101 MHz) - 5a,6,7,8,8a,9,14,15-Octahydro-5H-quinolino[3,2-d]acridine – **19**

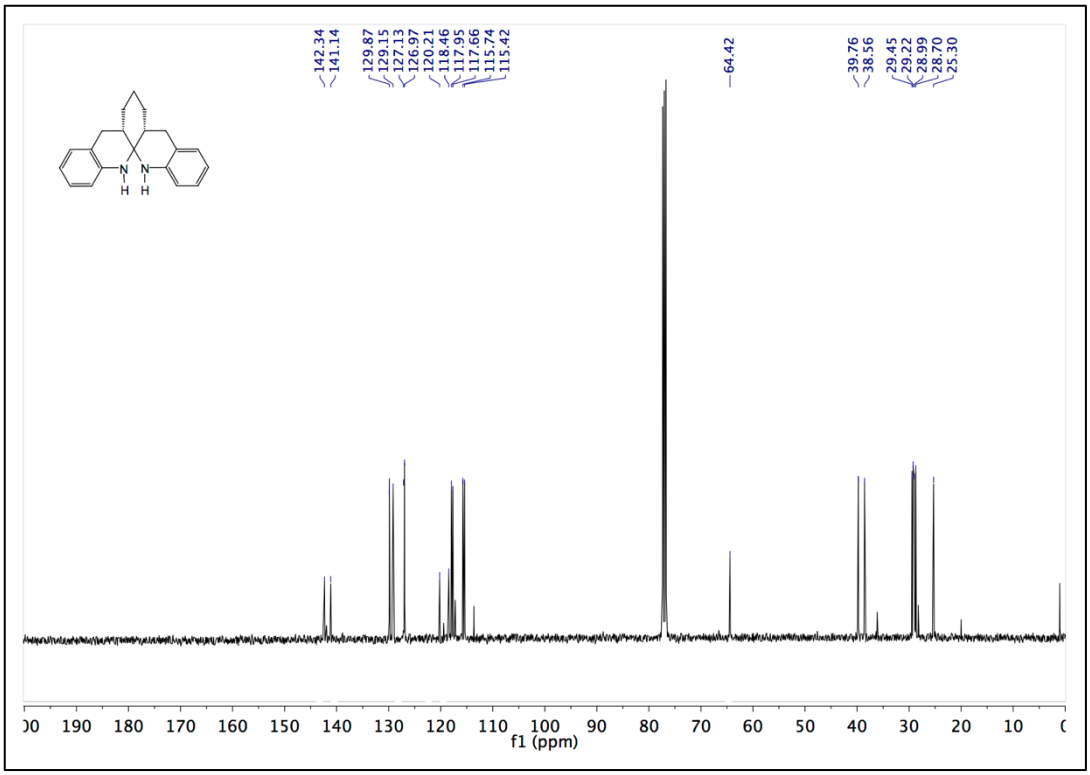


Fig S33 - [1]H NMR Spectra (400 MHz) - 1,3,11,13-tetrabromo-5a,6,7,8,8a,9,14,15-octahydro-5*H*-quinolino[3,2-*d*]acridine – **19b**

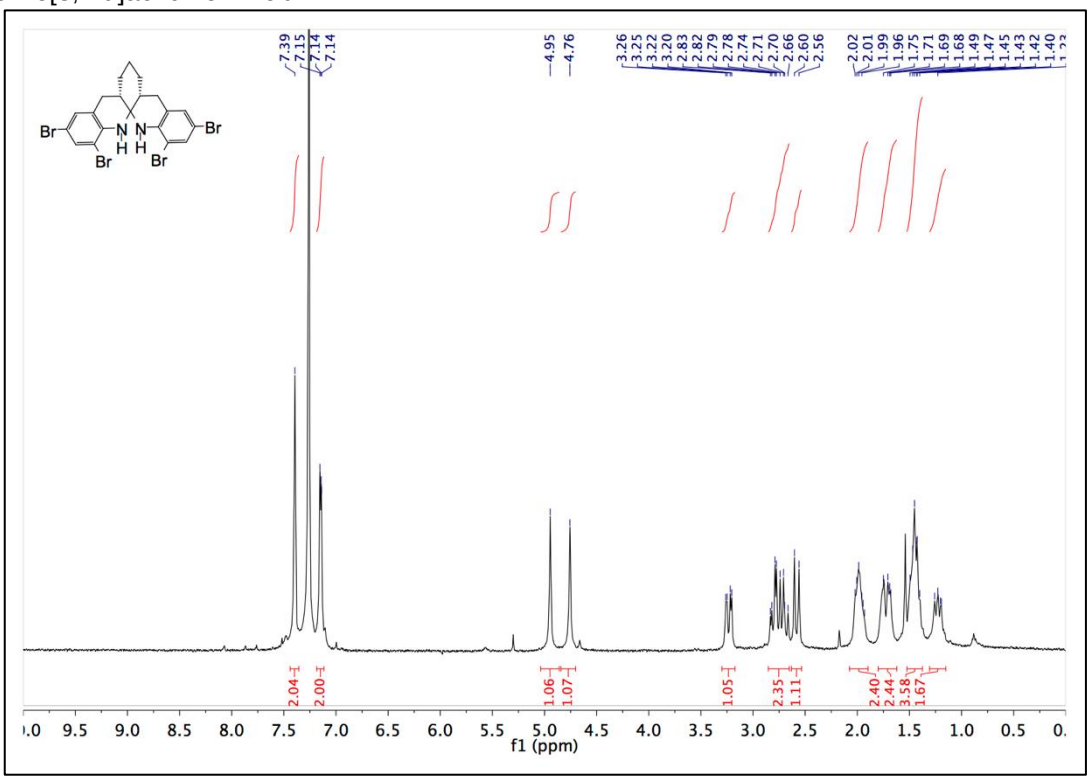


Fig S34 - [13]C NMR Spectra (101 MHz) - 1,3,11,13-tetrabromo-5a,6,7,8,8a,9,14,15-octahydro-5*H*-quinolino[3,2-*d*]acridine – **19b**

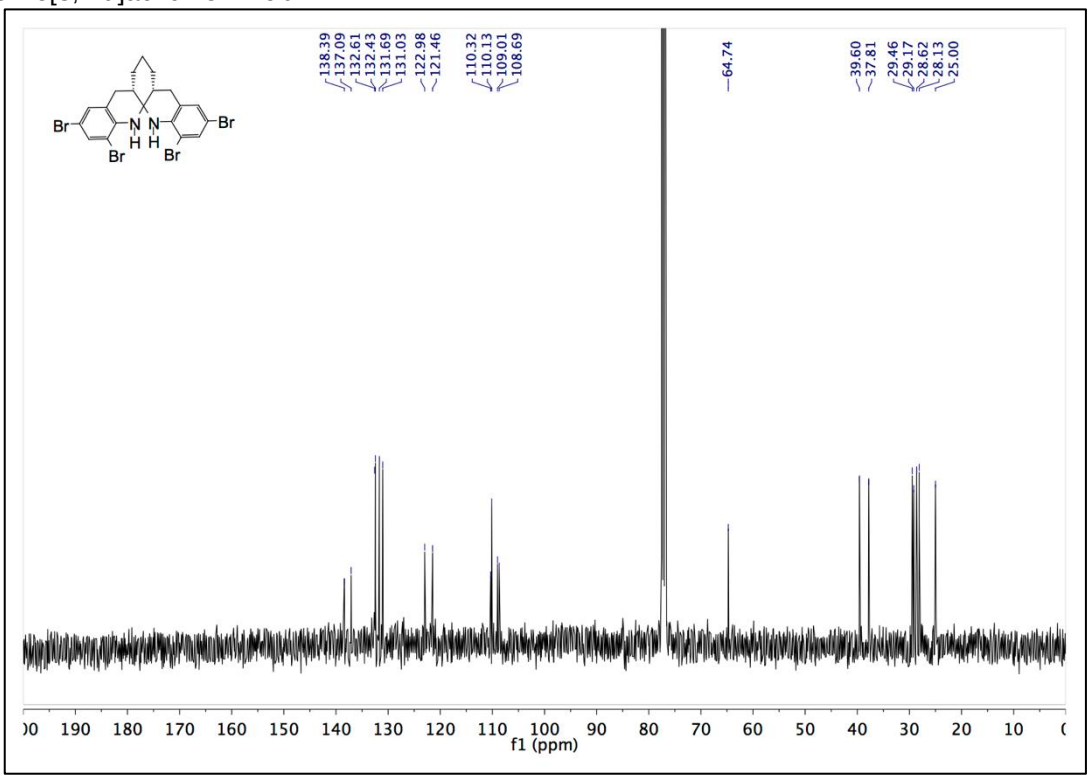


Fig S35 - ^{1}H NMR Spectra (400 MHz) - 3,3',4,4'-Tetrahydro-1H,1'H-spiro[benzo[h]quinoline-2,2'-quinoline] – **24a**

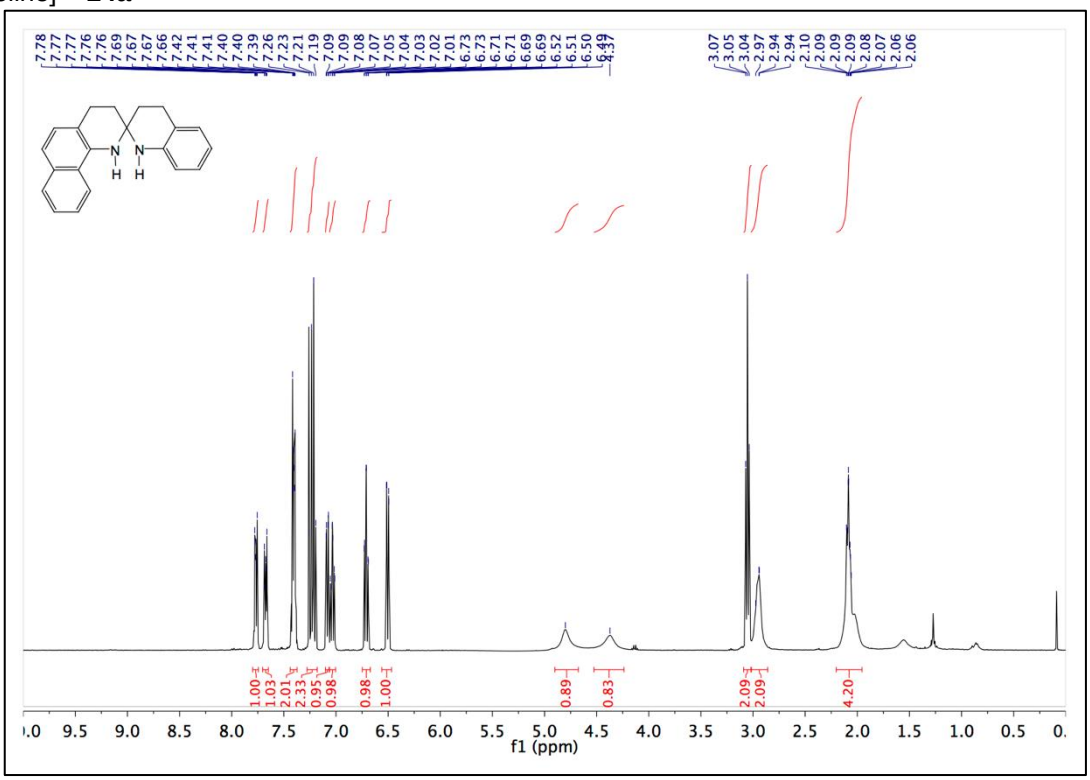


Fig S36 - ^{13}C NMR Spectra (101 MHz) - 3,3',4,4'-Tetrahydro-1H,1'H-spiro[benzo[h]quinoline-2,2'-quinoline] – **24a**

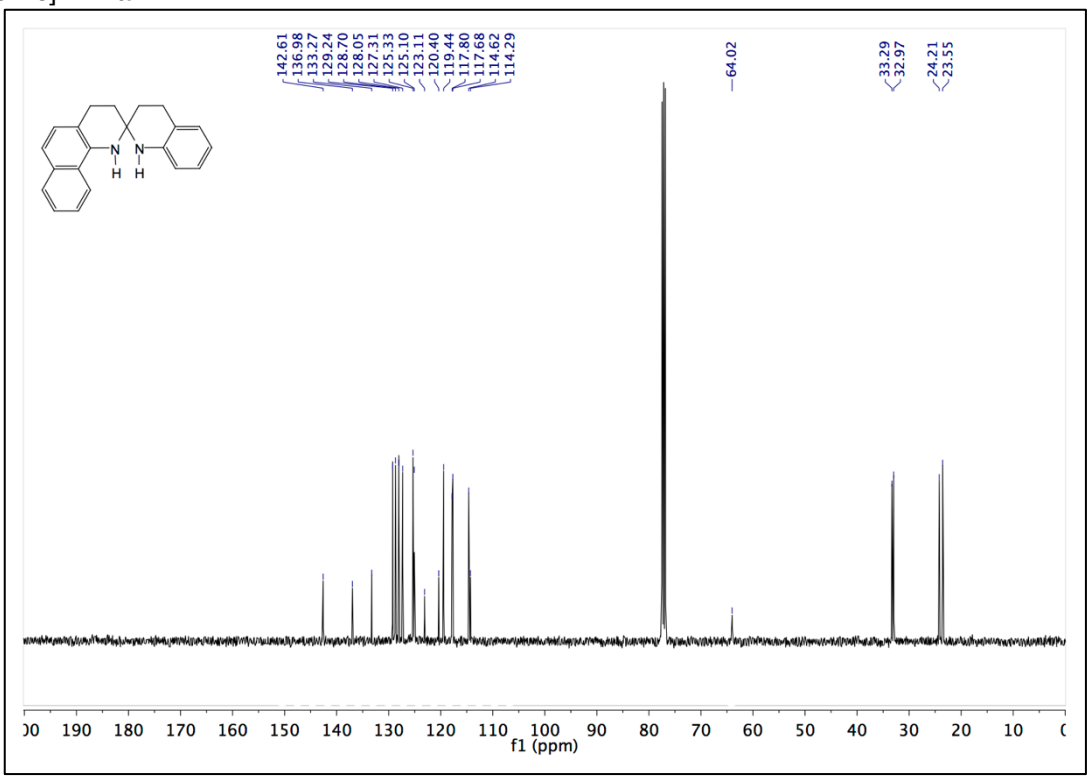


Fig S37 - ^{1}H NMR Spectra (400 MHz) - 7'-(Trifluoromethyl)-3,3',4,4'-tetrahydro-1H,1'H-spiro[benzo[h]quinoline-2,2'-quinoline] – **24b**

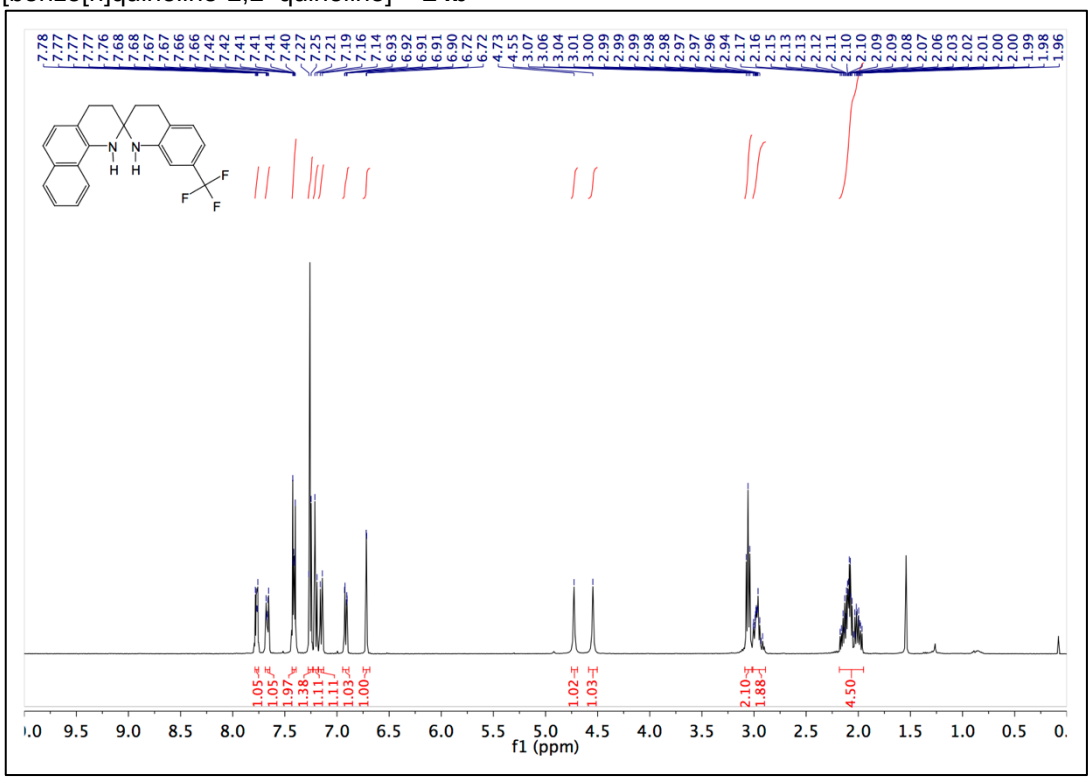


Fig S38 - ^{13}C NMR Spectra (101 MHz) - 7'-(Trifluoromethyl)-3,3',4,4'-tetrahydro-1H,1'H-spiro[benzo[h]quinoline-2,2'-quinoline] – **24b**

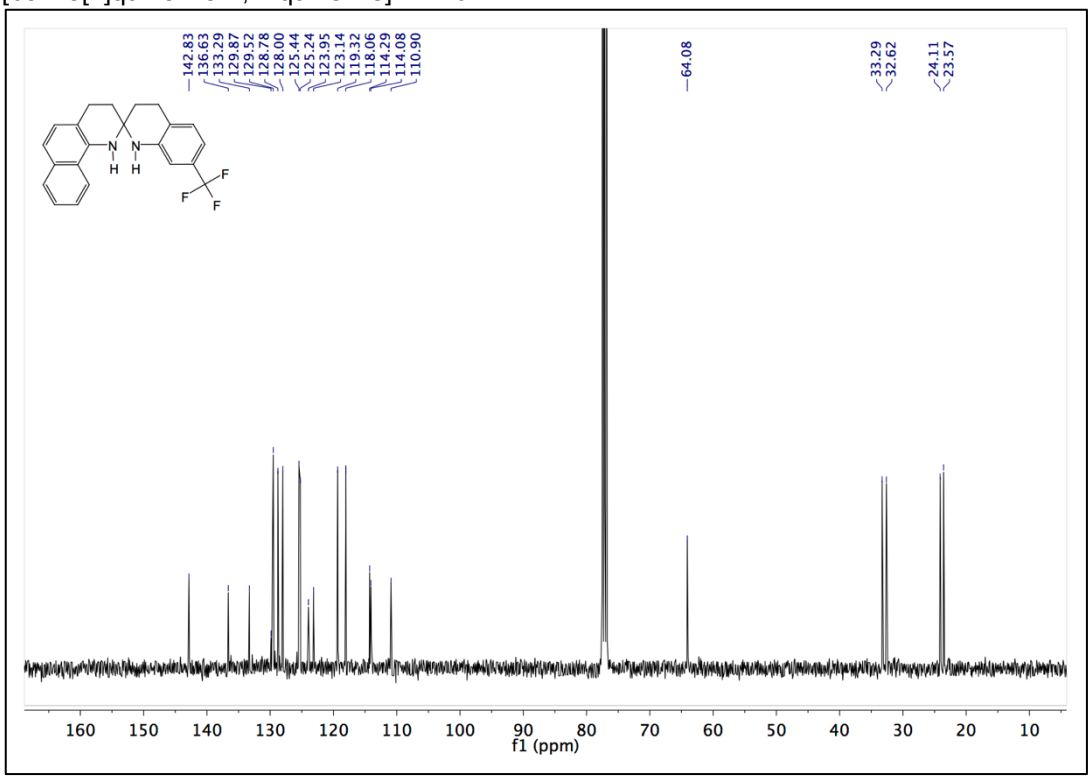


Fig S9 - ^{1}H NMR Spectra (400 MHz) - 6,6'-Dibromo-3,3',4,4'-tetrahydro-1H,1'H-2,2'-spirobi[quinoline] – **25**

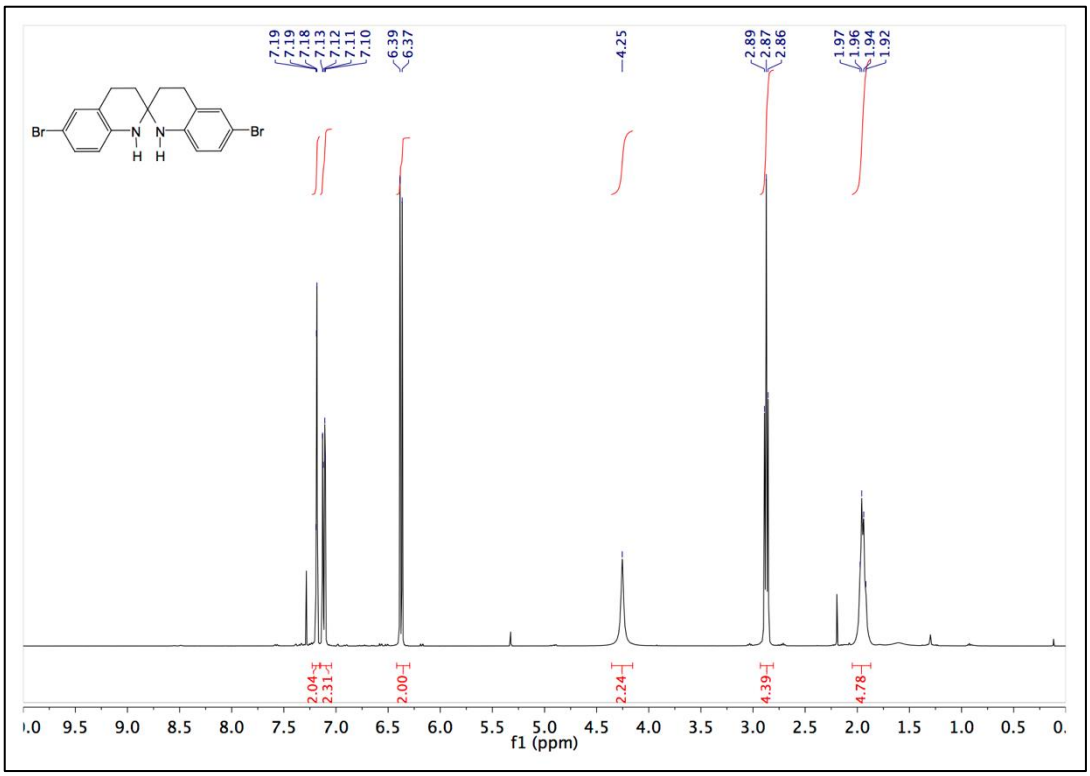


Fig S40 - ^{13}C NMR Spectra (101 MHz) - 6,6'-Dibromo-3,3',4,4'-tetrahydro-1H,1'H-2,2'-spirobi[quinoline] – **25**

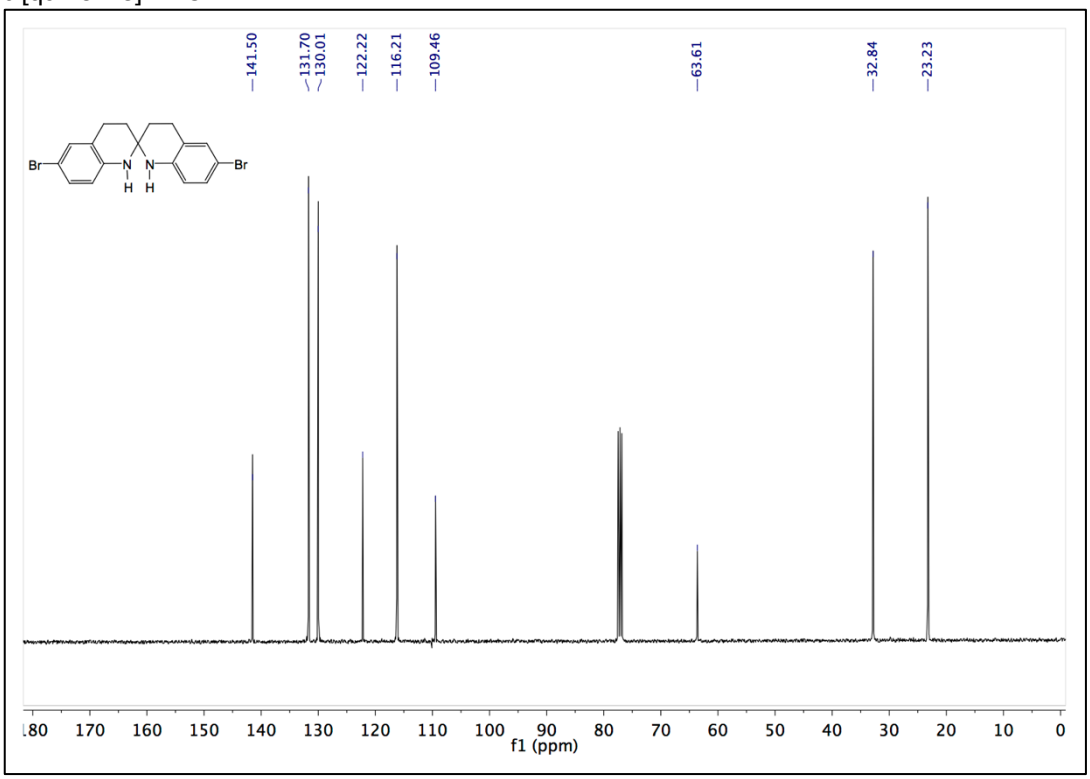


Fig S41 - ^{1}H NMR Spectra (400 MHz) - 6,6',8,8'-Tetrabromo-3,3',4,4'-tetrahydro-1H,1'H-2,2'-spirobi[quinoline] – **26**

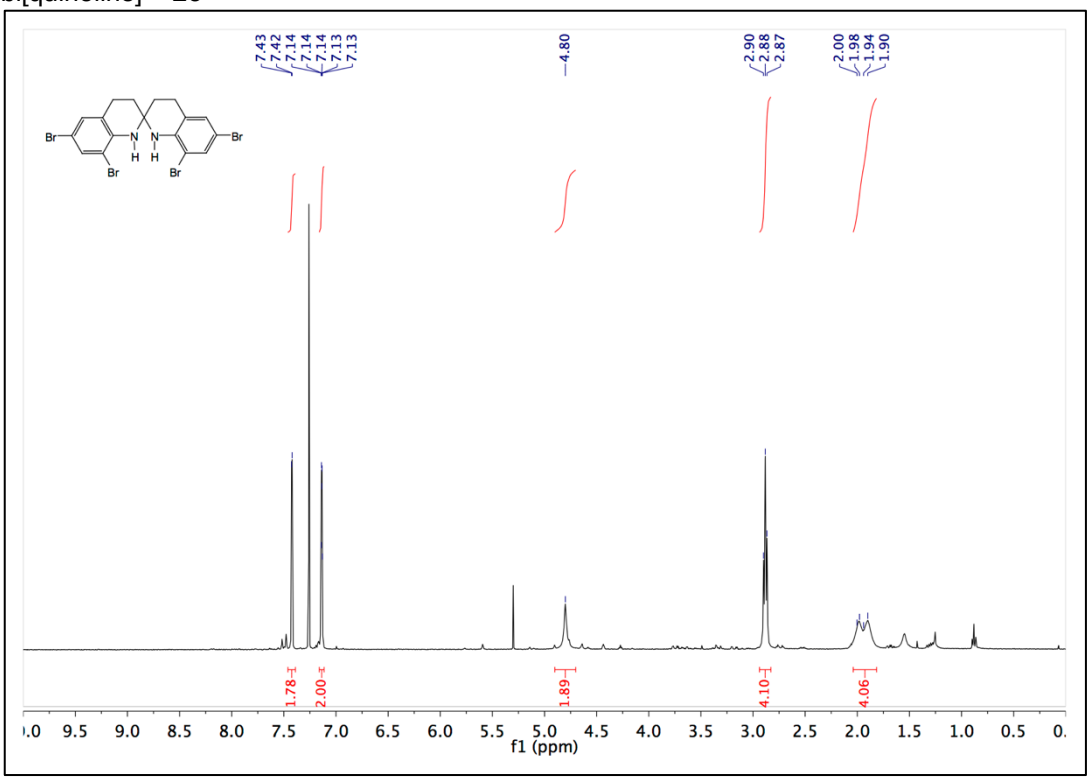


Fig S42 - ^{13}C NMR Spectra (101 MHz) - 6,6',8,8'-Tetrabromo-3,3',4,4'-tetrahydro-1H,1'H-2,2'-spirobi[quinoline] – **26**

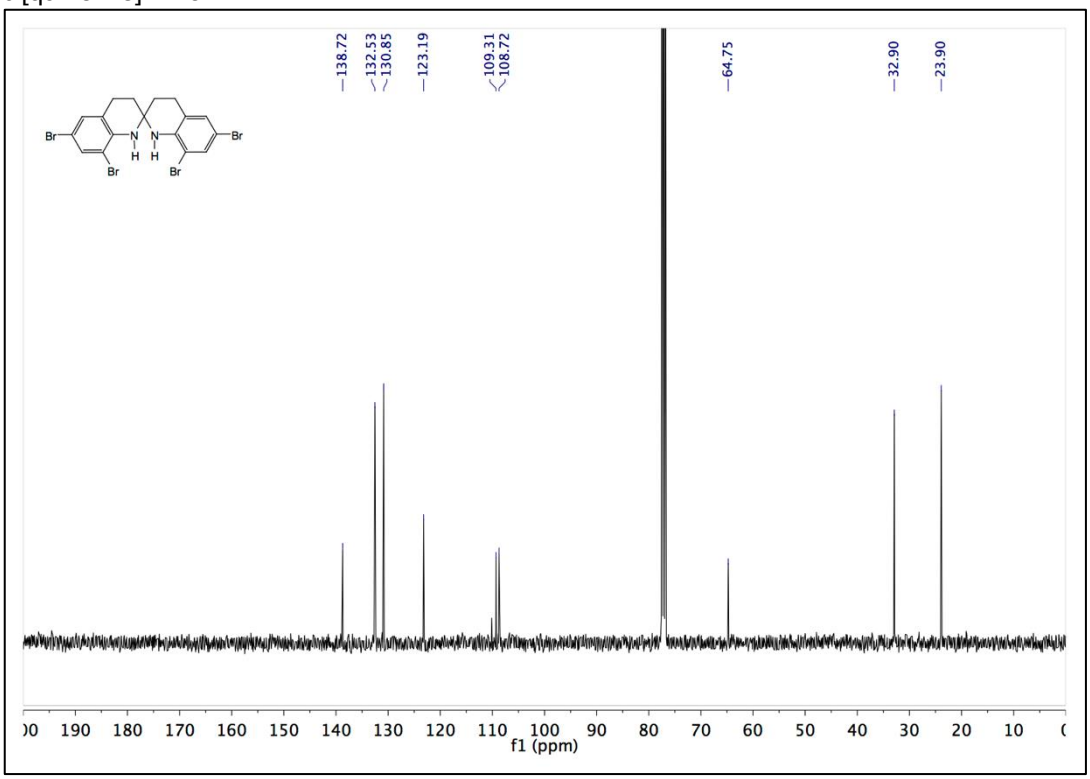


Fig S44 - ^{1}H NMR Spectra (400 MHz) - 6,6',8,8'-Tetraphenyl-3,3',4,4'-tetrahydro-1H,1'H-2,2'-spirobi[quinoline] – **27**

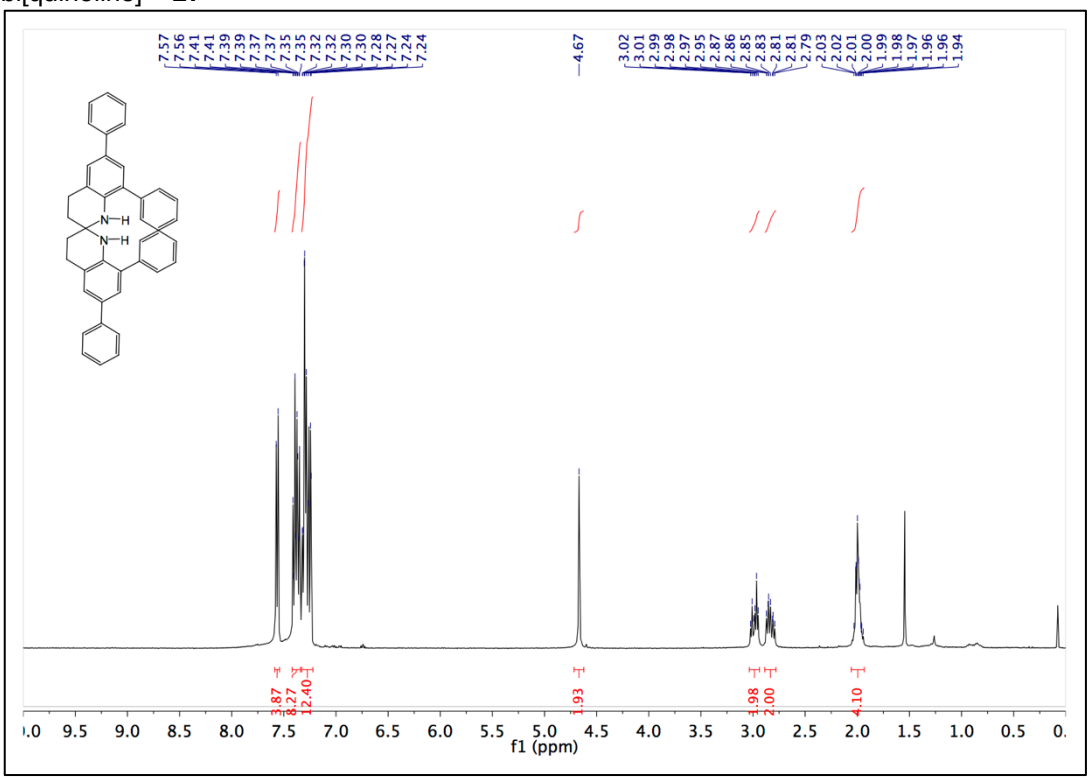


Fig S45 - ^{13}C NMR Spectra (101 MHz) - 6,6',8,8'-Tetraphenyl-3,3',4,4'-tetrahydro-1H,1'H-2,2'-spirobi[quinoline] – **27**

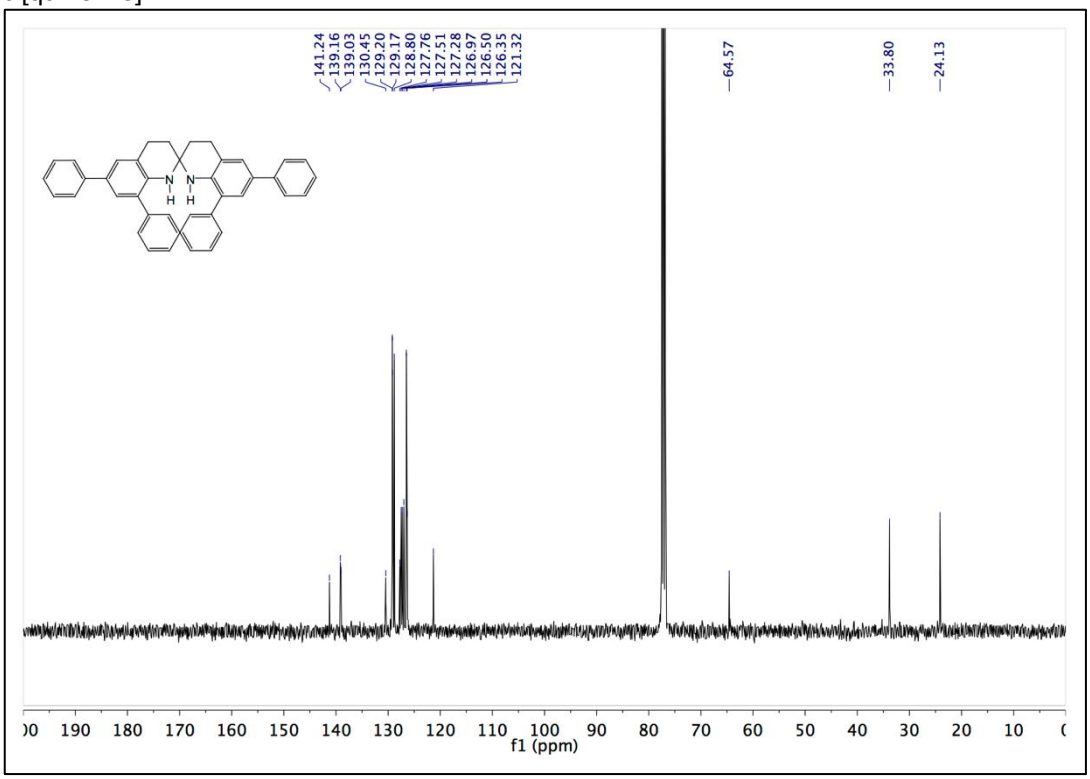


Fig S46 - ^{1}H NMR Spectra (400 MHz) - 1,1'-Dimethyl-3,3',4,4'-tetrahydro-1H,1'H-2,2'-spirobi[quinoline] – **28a**

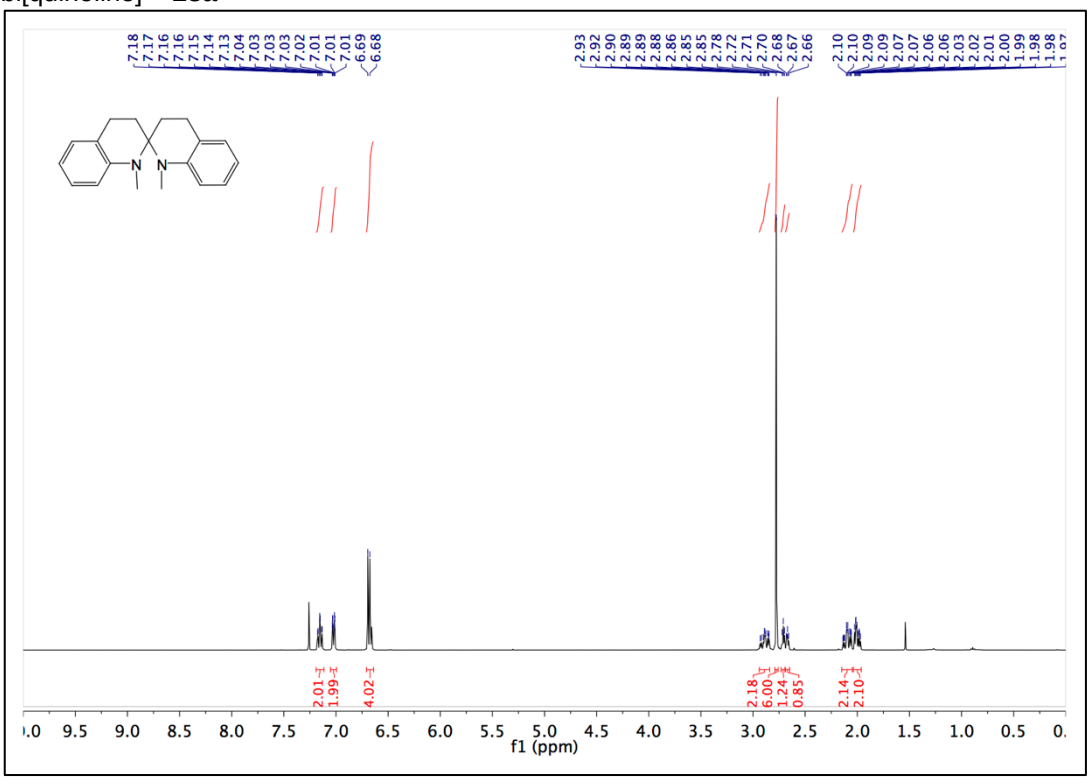


Fig S47 - ^{13}C NMR Spectra (101 MHz) 1,1'-Dimethyl-3,3',4,4'-tetrahydro-1H,1'H-2,2'-spirobi[quinoline] – **28a**

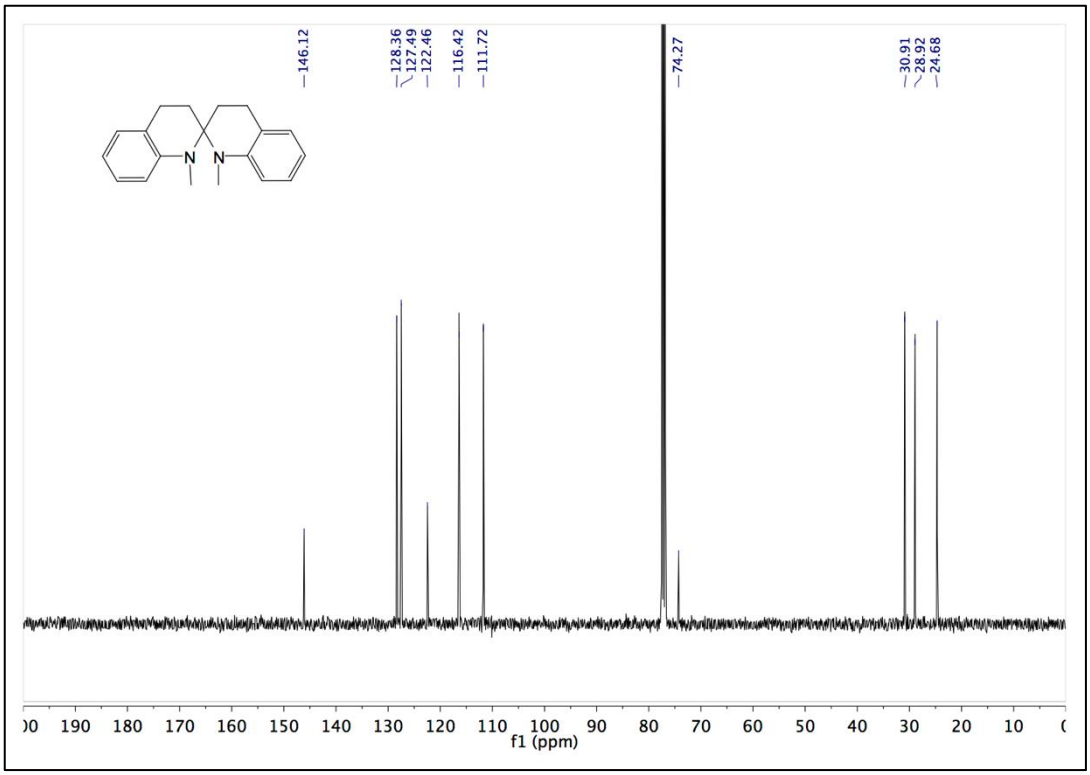


Fig S48 - ^{1}H NMR Spectra (400 MHz) - 1,1'-Diallyl-3,3',4,4'-tetrahydro-1H,1'H-2,2'-spirobi[quinoline] – **28b**

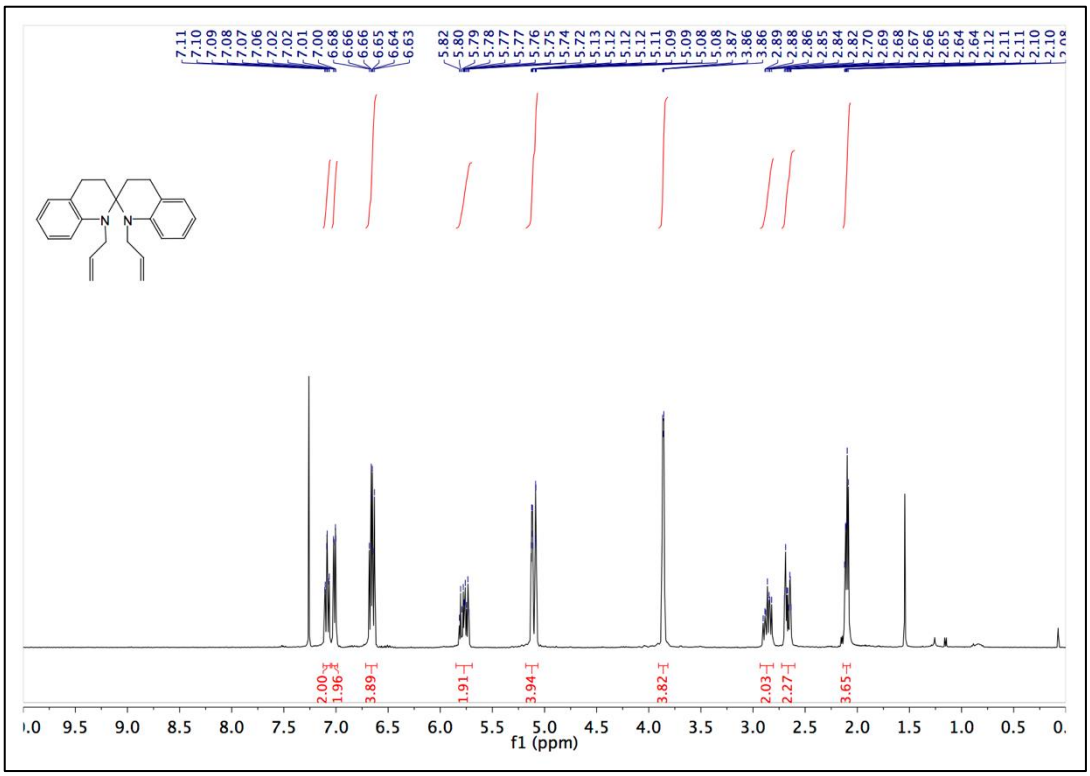


Fig S49 - ^{13}C NMR Spectra (101 MHz) - 1,1'-Diallyl-3,3',4,4'-tetrahydro-1H,1'H-2,2'-spirobi[quinoline] – **28b**

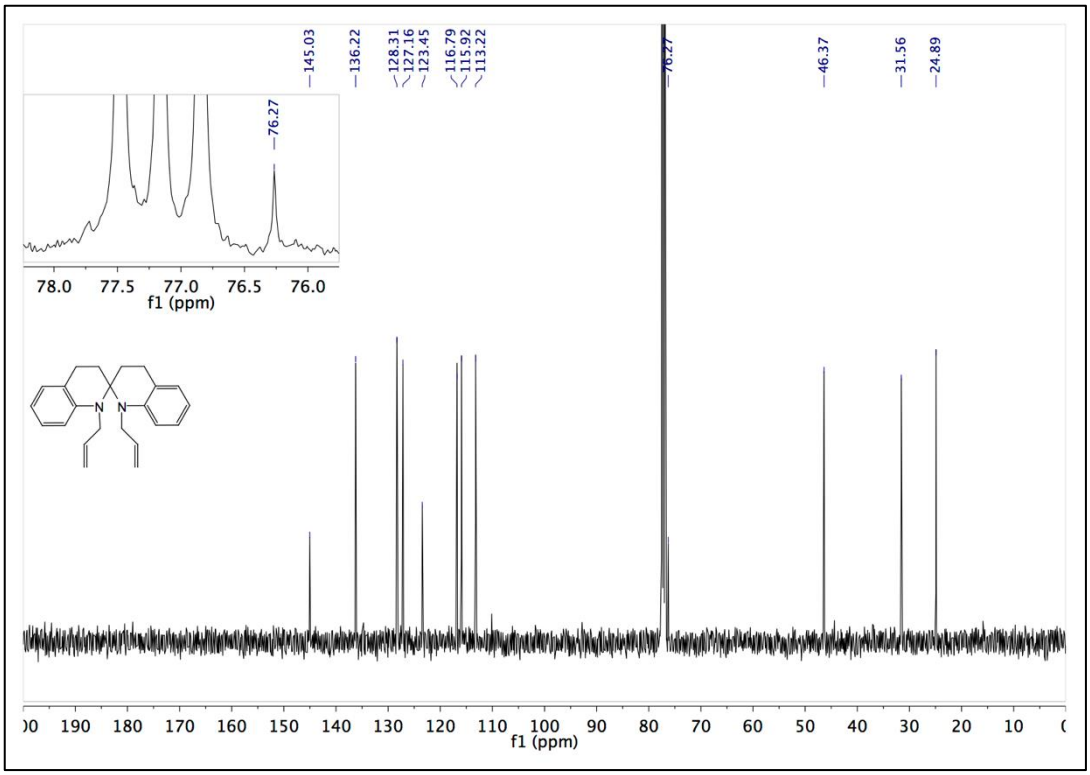


Fig S50 - ^{1}H NMR Spectra (400 MHz) - 1,4,10,11,12,13-Hexahydro-[1,3]diazepino[1,2-a:3,2-a']diquinoline - **29**

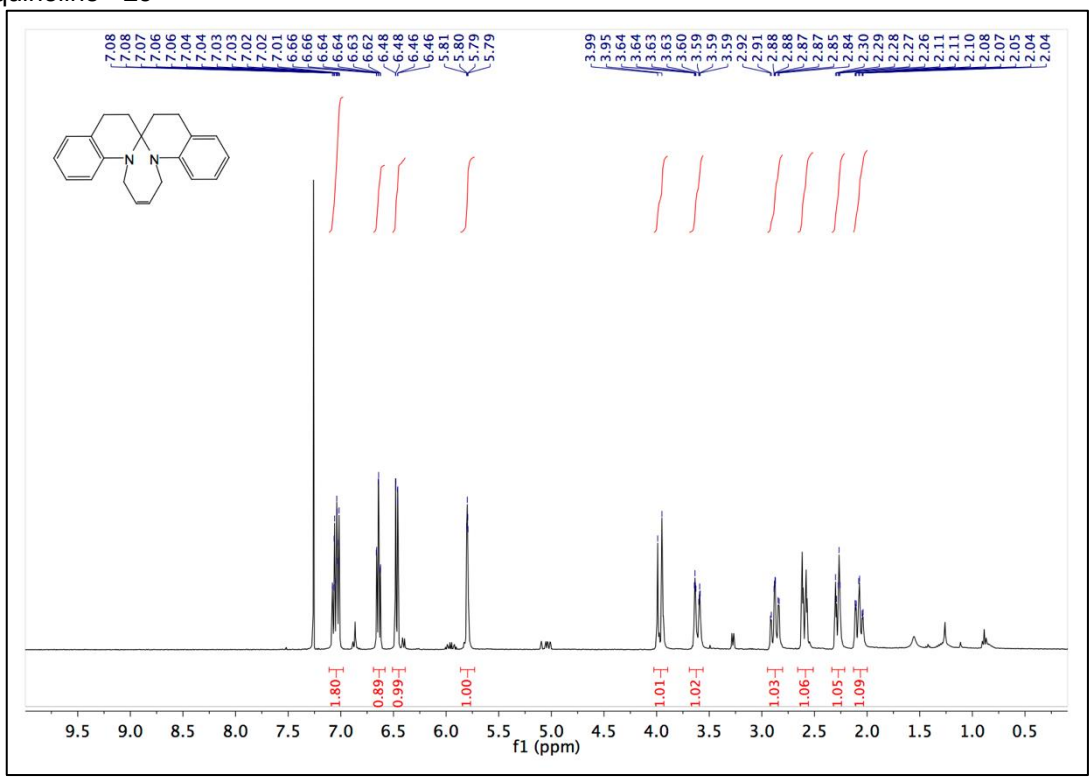


Fig S51 - ^{13}C NMR Spectra (101 MHz) - 1,4,10,11,12,13-Hexahydro-[1,3]diazepino[1,2-a:3,2-a']diquinoline - **29**