Supplementary Information for

Diastereoselective Generation of Triple-Stranded Helicates Induced by a Quaternary Carbon Linker

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Contents

Ⅰ Experimental

All the starting materials and solvents were purchased from commercial suppliers and used without further purification. TLC analyses were performed using commercial pre-coated alumina or silica gel plates. Column chromatography was carried out using silica gel (particle size: 0.040-0.063 mm, 230-400 mesh) or alumina (particle size: 60-325 mesh, neutral, 6% H_2O added for brockman activity III). The mass spectrum and high-resolution mass spectrum (HRMS) of the ligand were performed on a Kratos MS50 (EI). The mass spectra of the metal complexes were measured using MALDI-TOF in the presence of DCTB as matrix on a Bruker Biflex IV. Elemental analysis was performed on a Carlo Erba Elemental Analyzer EA 1108. ^{1}HNMR and ^{13}CNMR spectra were recorded with Bruker 300 spectrometers and chemical shifts are reported in ppm using the residual non-deuterated solvent as reference standard (CDCl$_3$: ^{1}H 7.27ppm, ^{13}C 77.00ppm; CD$_3$CN: ^{1}H 1.94ppm; CD$_2$Cl$_2$: ^{1}H 5.32 ppm, ^{13}C 54.00 ppm). X-ray crystallographic analyses were carried out on a Bruker X8 APEX diffractometer with graphite monochromated Mo-K radiation. Data were collected and integrated using the Bruker SAINT software package.[S1] The structures were solved by direct methods.[S2] All refinements were performed using the SHELXTL[S3] crystallographic software package of Bruker-AXS.

(4,4'-(propane-2,2-diyl)bis(1H-pyrrole-4,2-diyl))bis(phenylmethanone) (4). To an acetonitrile solution (50mL) of 2-benzoylpyrrole (3.4g, 20mmol) and acetone dimethyl acetal (12mmol) were added boron trifluoride diethyl etherate (20mmol) at r. t. The reaction mixture was then heated at 80 ^{o}C for 1h before being quenched with NEt$_3$. The reaction mixture was separated on silica gel using ethyl acetate and hexanes (1 : 3) as eluent. **4** (0.84g. 2.2mmol) was obtained in a 22% yield. White crystals (mp: 213-214 ^{o}C). R$_f$ (silica; ethyl acetate/hexanes, 1 : 2) 0.33. ^{1}H NMR (300 MHz, CDCl$_3$) δ = 9.91 (br s, 2H, NH), 7.89-7.86 (m, 4H, Ph-H), 7.59-7.45 (m, 6H, Ph-H), 6.98-6.96 (dd, J = 2.8 Hz, J' = 1.7 Hz, 2H, pyrrole-H), 6.77-6.76 (dd, J = 2.6 Hz, J' = 1.8 Hz, 2H, pyrrole-H), 1.63 (s, 6H, CH$_3$). ^{13}C NMR (75 MHz, CDCl$_3$) δ = 184.5, 138.4, 137.2, 131.7, 130.8, 128.9, 128.3, 122.4, 117.4, 33.7, 31.5. MS (EI) m/z 382 (M$^+$). HRMS (EI) Calcd for C$_{25}$H$_{22}$N$_2$O$_2$ (M$^+$): 382.16813. Found: 382.16784. Elemental Anal. Calcd for C$_{25}$H$_{22}$N$_2$O$_2$: C, 78.51; H, 5.80; N, 7.32. Found: C, 77.84; H, 5.81; N, 7.23.

4,4'-(propane-2,2-diyl)bis(2-(phenyl(1H-pyrrol-2-yl)methyl)-1H-pyrrole) (5). **4** (2.0g, 5.2mmol) in MeOH/THF (1 : 1, 50mL) was treated with excess NaBH$_4$ in several portions at r.t. The solution was stirred for 6h to get all the starting material reduced. The solvent was then removed and the organic compounds were extracted with H$_2$O and CH$_2$Cl$_2$. After evaporation of the solvent, the organic residue was dissolved in pyrrole (50mL) and treated with TFA (1mmol) at 0 ^{o}C. The reaction mixture was stirred for 30 min at this temperature and quenched with aqueous NaOH. After the reaction mixture was washed and dried, pyrrole was removed by distillation and the residue was separated on silica gel. **5** (2.1g, 4.3mmol) was obtained as a viscous oil in an 83% yield. R$_f$ (silica; CH$_2$Cl$_2$) 0.45. ^{1}H NMR (300 MHz, CD$_3$CN) δ

= 8.83 (br s, 2H, NH), 8.45 (br s, 2H, NH), 7.31-7.19 (m, 10H, Ph-H), 6.64-6.62 (dd, J = 4.4 Hz, J' = 2.6 Hz, 2H, pyrrole-H), 6.37-6.36 (m, 2H, pyrrole-H), 6.02-6.00 (dd, J = 5.9 Hz, J' = 2.9 Hz, 2H, pyrrole-H), 5.78-5.77 (m, 2H, pyrrole-H), 5.70-5.68 (t, J = 1.8 Hz, 2H, pyrrole-H), 5.34 (s, 2H, CH)1.44 (s, 6H, CH$_3$). ^{13}C NMR (75 MHz, CDCl$_3$) δ = 142.2, 135.4, 132.7, 131.9, 128.4, 128.4, 126.7, 117.2, 112.8, 108.1, 107.2, 106.3, 44.1, 33.6, 31.2. MS (EI) m/z 484 (M$^+$). HRMS (EI) Calcd for C$_{33}$H$_{32}$N$_4$ (M$^+$): 484.26270. Found: 484.26347.

4,4'-(propane-2,2-diyl)bis(2-(phenyl(2H-pyrrol-2-ylidene)methyl)-1H-pyrrole) (3-H$_2$). Tetrapyrrole **5** (2.1g, 4.3mmol) in acetonitrile was treated with chloranil (2.45g, 10mmol) at r.t. ant the reaction mixture was stirred overnight. After the solvent was removed, the product was isolated on silica gel using hexanes and CH$_2$Cl$_2$ (1 : 1) as eluents. **3**-H$_2$ (1.8g) was obtained in an 87% yield. Red solid (mp: 89-91 ^{o}C). R$_f$ (silica; ethyl acetate/hexanes, 1 : 4) 0.64.^{1}H NMR (300 MHz, CD$_2$Cl$_2$) δ = 12.56 (br s, 2H, NH), 7.71 (d, J = 1.1 Hz, 2H, pyrrole-H), 7.51-7.43 (m, 10H, Ph-H), 7.35-7.34 (m, 2H, pyrrole-H), 6.42 (d, J = 1.1 Hz, 2H, pyrrole-H), 6.37-6.35 (dd, J = 3.8 Hz, J' = 1.3 Hz, 2H, pyrrole-H), 6.29-6.28 (dd, J = 3.8 Hz, J' = 2.0 Hz, 2H, pyrrole-H), 1.46 (s, 6H, CH$_3$). ^{13}C NMR (75 MHz, CD$_2$Cl$_2$) δ = 153.6, 146.8, 146.4, 141.1, 137.9, 136.7, 133.8, 131.3, 129.3, 128.2, 126.8, 124.2, 113.7, 34.6, 29.6. MS (EI) m/z 480 (M$^+$). HRMS (EI) Calcd for C$_{33}$H$_{28}$N$_4$ (M$^+$): 480.23140. Found: 480.23120.

General procedure for the synthesis of M$_2$3$_3$ helicates. 3-H$_2$ (50mg, 0.10mmol) was placed into a 100mL flask. To the flask was added a small amount of chloroform (1mL) to dissolve the proligand and then methanol (50mL). The solution was heated to reflux and a trivalent metal (FeCl$_3$ or Na$_3$[Co(NO$_2$)$_6$] or Mn(OAc)$_3$ or Ga(NO$_3$)$_3$ or InCl$_3$) dissolved in methanol (2mL) was added, followed by the addition of a few drops of NEt$_3$. The mixture was allowed to proceed at reflux for 2h. After chromatography on alumina gel, M$_2$3$_3$ complexes were isolated as a diastereomeric mixture.

Fe$_2$3$_3$ helicate (6). A diastereomeric mixture was obtained in 52% yield. Recrystallization by vapour diffusion of hexanes into a CH$_2$Cl$_2$ solution provided **6** as red crystals. R$_f$ (alumina; CH$_2$Cl$_2$/hexanes, 1 : 1) 0.86. MS (MALDI-TOF) m/z 1547.6 (M$^+$). HRMS (ESI) Calcd for C$_{99}$H$_{79}$N$_{12}$^{56}Fe$_2$ ([M + H]$^+$): 1547.5249. Found: 1547.5215.

Co$_2$3$_3$ helicate (7). A diastereomeric mixture was obtained in a 28% yield. The ratio of helicate to mesocate is roughly 14 : 1. Recrystallization provided **7** as red crystals. R$_f$ (alumina; CH$_2$Cl$_2$/hexanes, 1 : 1) 0.86. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$) δ = 7.55-7.35 (m, 30H, Ph-H), 6.64-6.62 (dd, J = 4.2 Hz, J' = 1.3 Hz, 6H, pyrrole-H), 6.49-6.48 (d, J = 1.8 Hz, 6H, pyrrole-H), 6.32 (m, 6H, pyrrole-H), 6.29-6.27 (dd, J = 4.2 Hz, J' = 1.6 Hz, 6H, pyrrole-H), 6.14 (d, J = 1.4 Hz, 6H, pyrrole-H), 1.12 (s, 18H, CH$_3$). ^{13}C NMR (75 MHz, CD$_2$Cl$_2$) δ = 153.0, 150.4, 145.7, 141.2, 138.8, 135.6,
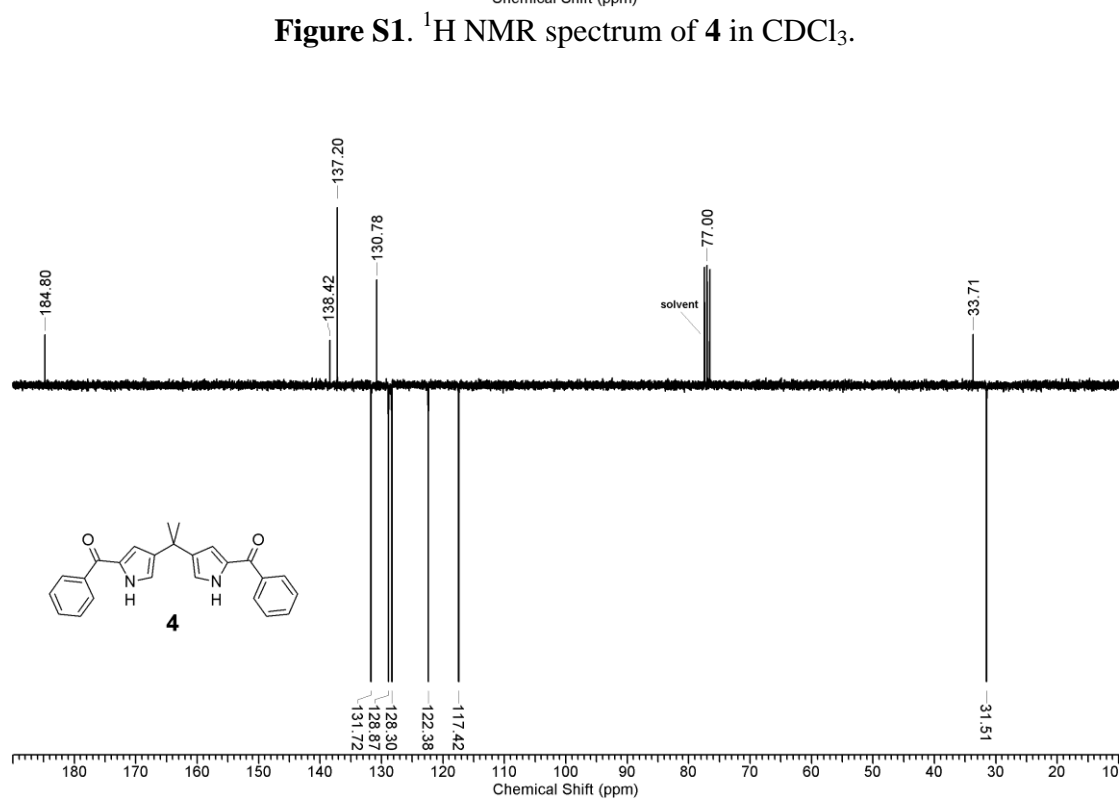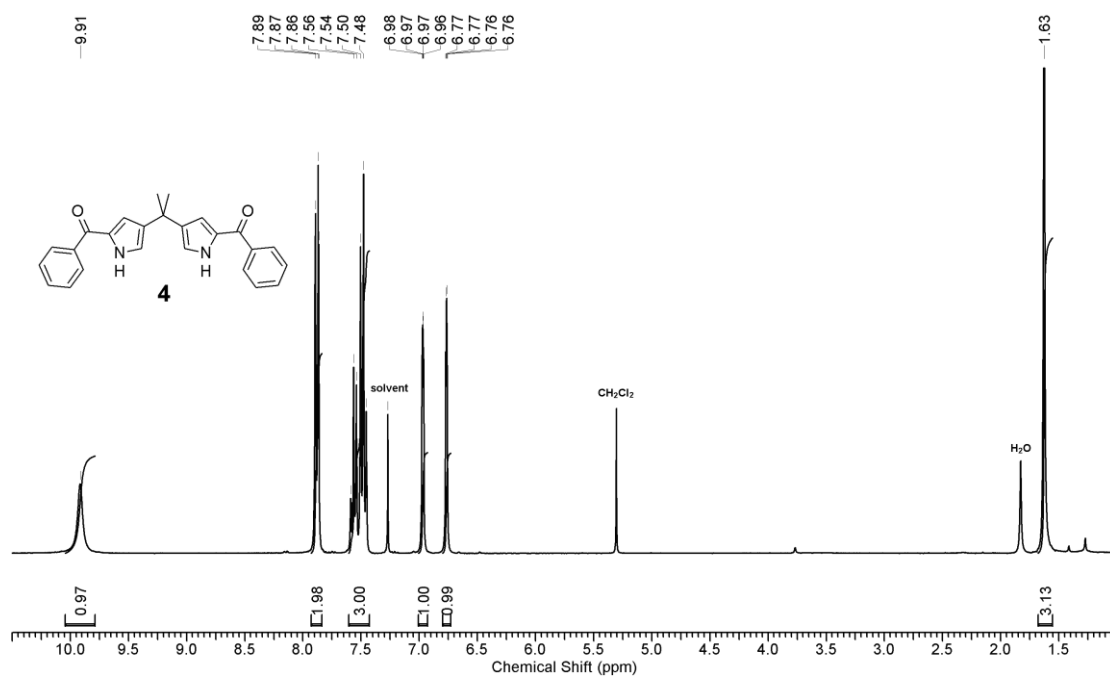
135.2, 132.3, 131.1, 130.9, 129.0, 127.9, 127.5, 118.1, 34.7, 30.6. MS (MALDI-TOF) m/z 1553.6 (M$^+$). HRMS (ESI) Calcd for $C_{99}H_{79}N_{12}{}^{59}Co_2$ ([M + H]$^+$): 1553.5215. Found: 1553.5247.

Mn$_2$3$_3$ helicate (8). A diastereomeric mixture was obtained in a 58% yield. Recrystallization provided **8** as dark red crystals. R_f (alumina; CH_2Cl_2/hexanes, 1 : 1) 0.86. MS (MALDI-TOF) m/z 1545.3 (M$^+$). HRMS (ESI) Calcd for $C_{99}H_{79}N_{12}{}^{55}Mn_2$ ([M + H]$^+$): 1545.5312. Found: 1545.5298.

Ga$_2$3$_3$ helicate (9). A diastereomeric mixture was obtained in a 70% yield. The ratio of helicate to mesocate is roughly 8 : 1. Recrystallization provided **9** as red crystals. R_f (alumina; CH_2Cl_2/hexanes, 1 : 1) 0.86. ^{1}H NMR (300 MHz, CD_2Cl_2) δ = 7.53-7.33 (m, 30H, Ph-H), 6.90 (m, 6H, pyrrole-H), 6.64 (d, J = 1.4 Hz, 6H, pyrrole-H), 6.51-6.50 (dd, J = 4.0 Hz, J' = 1.1 Hz, 6H, pyrrole-H), 6.41 (d, J = 1.5 Hz, 6H, pyrrole-H), 6.22-6.20 (dd, J = 4.0 Hz, J' = 1.5 Hz, 6H, pyrrole-H), 1.16 (s, 18H, CH$_3$). ^{13}C NMR (75 MHz, CD_2Cl_2) δ = 149.4, 147.7, 146.9, 142.9, 139.4, 139.3, 132.2, 131.2, 131.0, 128.9, 127.8, 127.5, 115.9, 34.2, 31.3. MS (MALDI-TOF) m/z 1575.8 (M$^+$). HRMS (ESI) Calcd for $C_{99}H_{79}N_{12}{}^{69}Ga_2$ ([M + H]$^+$): 1573.5062. Found: 1573.5035.

In$_2$3$_3$ complexes (10). A diastereomeric mixture was obtained in a 29% yield. The ratio of helicate to mesocate is roughly 8 : 1. Attempted Recrystallization failed. Red powder. R_f (alumina; CH_2Cl_2/hexanes, 1 : 1) 0.86. ^{1}H NMR (300 MHz, CD_2Cl_2, peaks for the helicate) δ = 7.49-7.33 (m, 30H, Ph-H), 7.24 (s, 6H, pyrrole-H), 6.85 (s, 6H, pyrrole-H), 6.51-6.50 (d, J = 3.3 Hz, 6H, pyrrole-H), 6.43 (s, 6H, pyrrole-H), 6.31-6.29 (m, 6H, pyrrole-H), 1.19 (s, 18H, CH$_3$). ^{13}C NMR (75 MHz, CD_2Cl_2, peaks for the helicate) δ = 150.0, 148.8, 148.1, 143.0, 141.1, 140.9, 140.1, 133.5, 131.2, 131.1, 129.2, 128.8, 127.7, 116.4, 34.3, 31.8. MS (MALDI-TOF) m/z 1665.4 (M$^+$). HRMS (ESI) Calcd for $C_{99}H_{79}N_{12}{}^{155}In_2$ ([M + H]$^+$): 1665.4628. Found: 1665.4596.
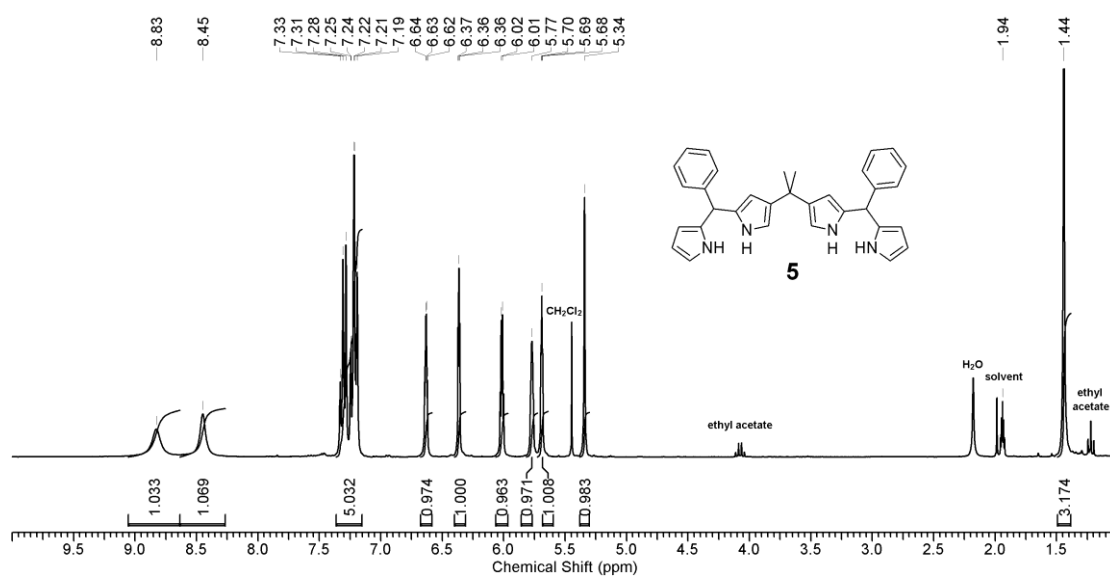
II NMR Spectra

Figure S1. ^{1}H NMR spectrum of **4** in CDCl$_3$.

Figure S2. ^{13}C NMR spectrum of **4** in CDCl$_3$.

Figure S3. ^{1}H NMR spectrum of **5** in CD$_3$CN.
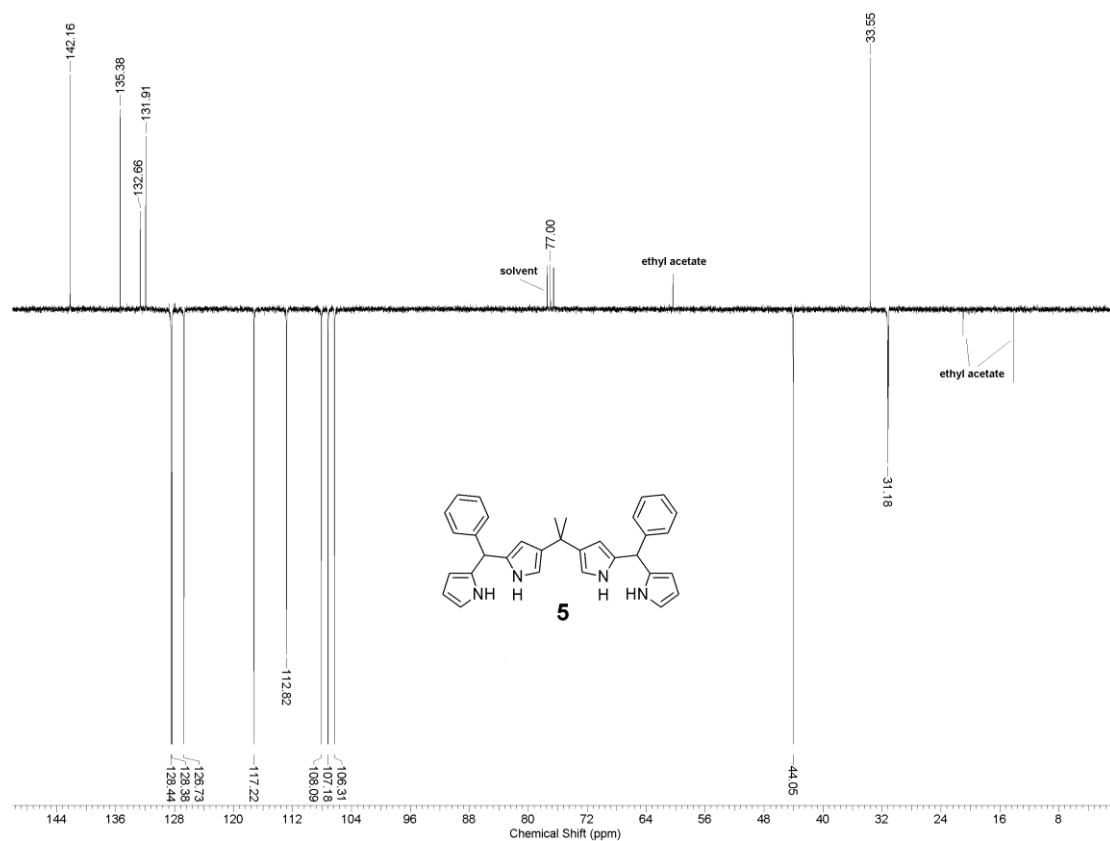
Figure S4. ^{13}C NMR spectrum of **5** in CDCl$_3$.
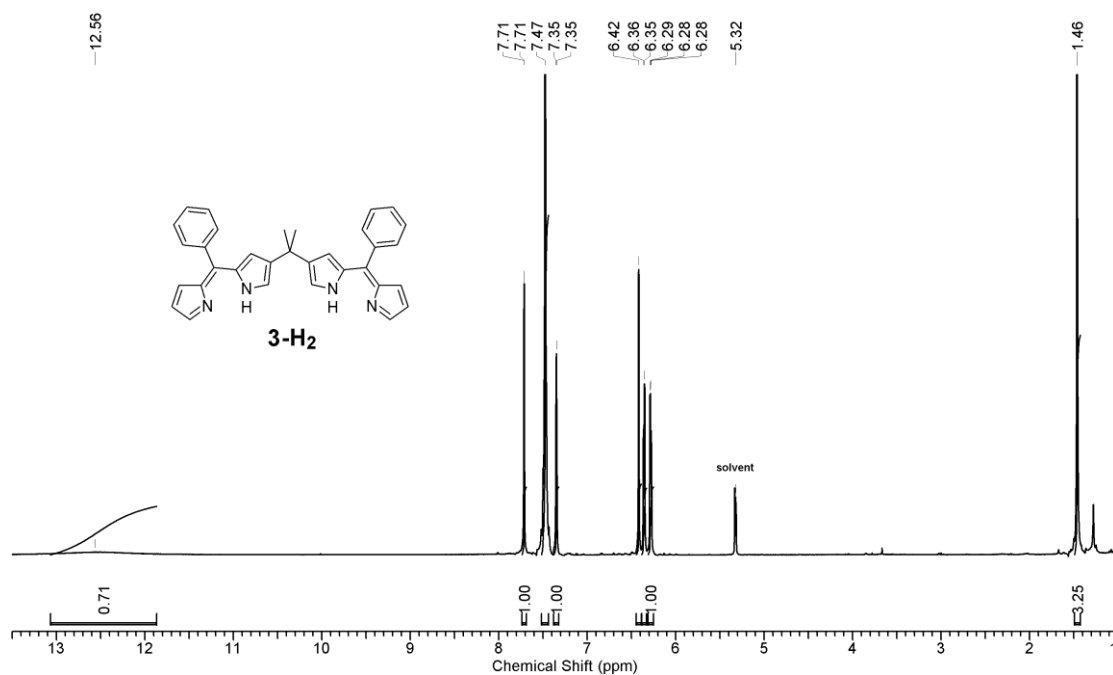
Figure S5. ^{1}H NMR spectrum of **3-H$_2$** in CD$_2$Cl$_2$.
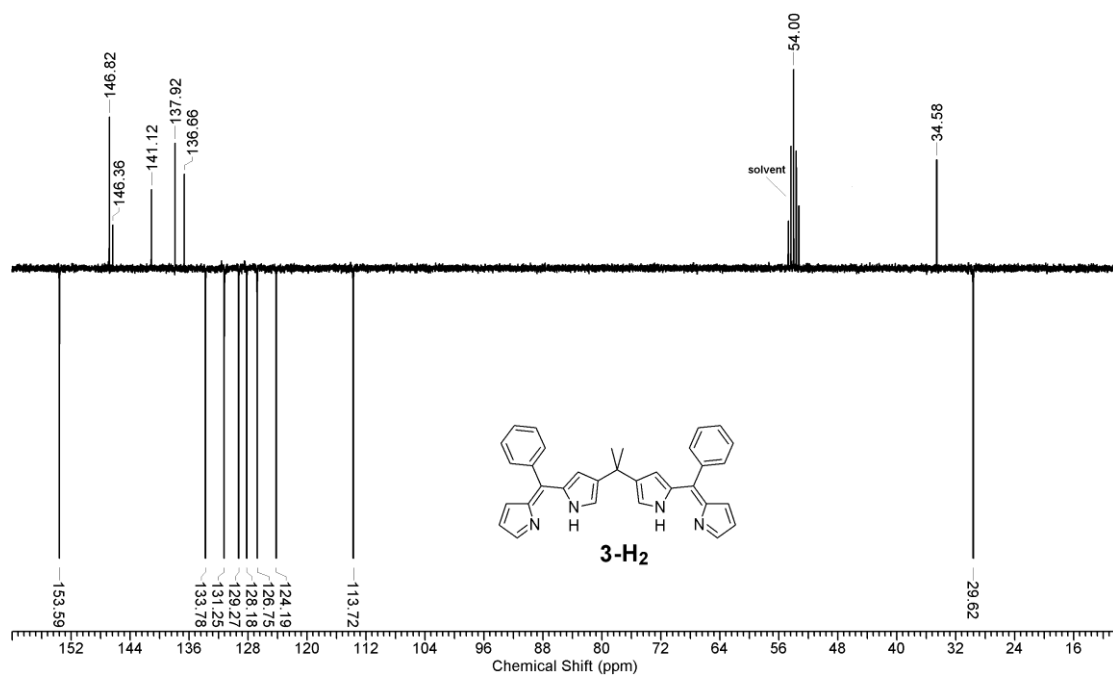
Figure S6. ^{13}C NMR spectrum of **3-H$_2$** in CD$_2$Cl$_2$.

Co$_2$3$_3$ Helicate
(7)

solvent

H$_2$O

7.55 7.48 7.37 7.35 · 6.64 6.63 6.62 6.62 6.49 6.48 6.32 6.29 6.28 6.27 · 6.14 6.14 · 5.32 · 1.52 · 1.12

5.11 · 1.00 1.01 1.98 0.98 · 2.96
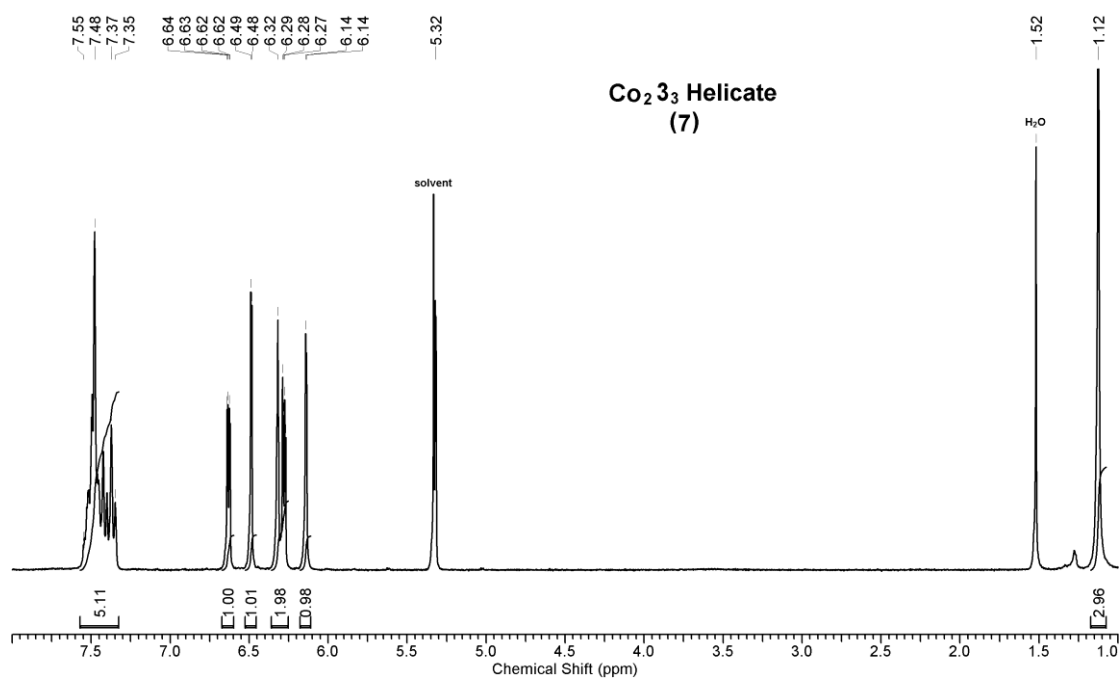
Figure S7. ^{1}H NMR spectrum of Co$_2$3$_3$ helicate in CD$_2$Cl$_2$.

Co$_2$3$_3$ Helicate
(7)

solvent

145.71 145.23 · 138.75 135.55 135.20 · 54.00 · 34.71

150.38 152.98 · 132.34 131.12 128.95 127.90 127.48 · 118.13 · 30.64
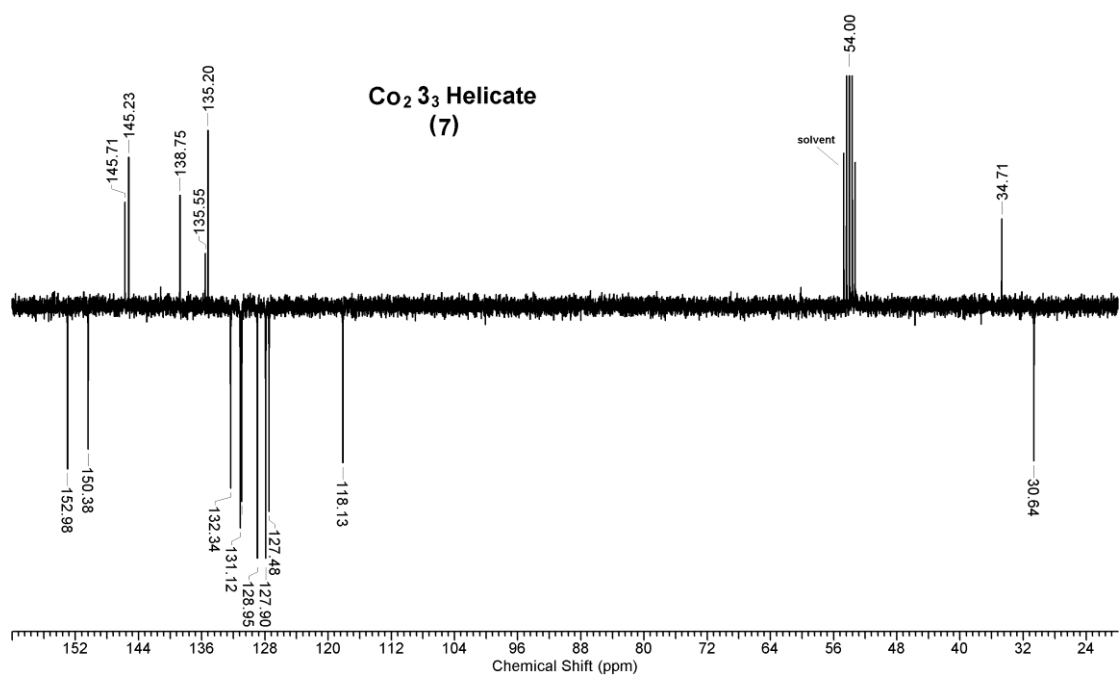
Figure S8. ^{13}C NMR spectrum of Co$_2$3$_3$ helicate in CD$_2$Cl$_2$.
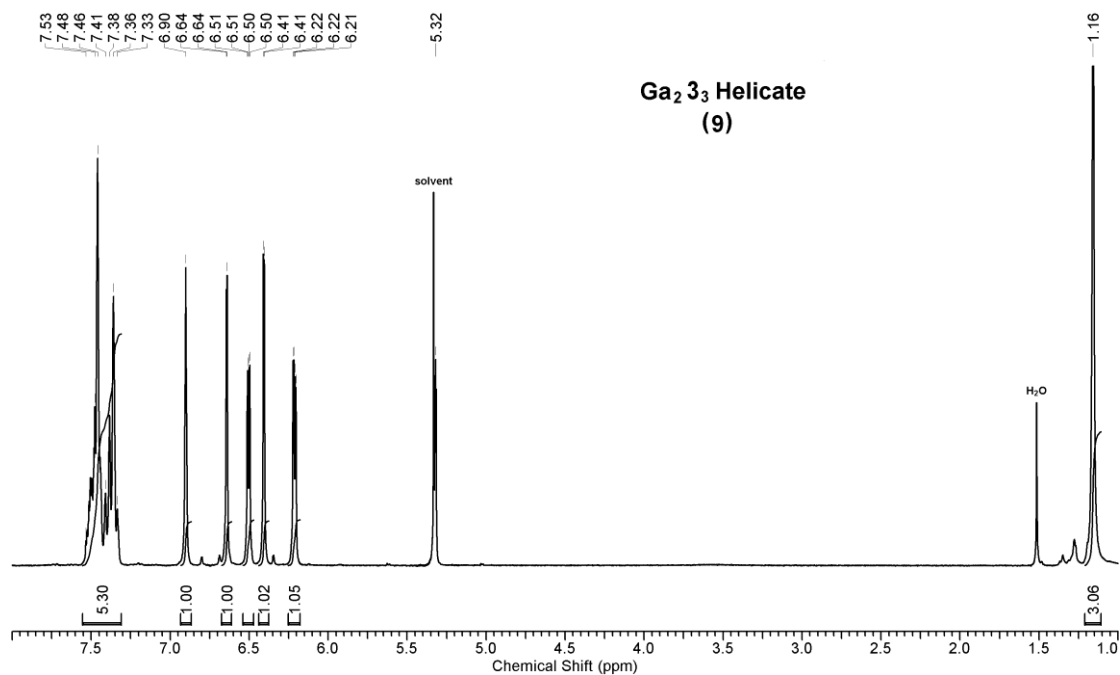
Figure S9. ^{1}H NMR spectrum of Ga$_2$**3**$_3$ helicate in CD$_2$Cl$_2$.
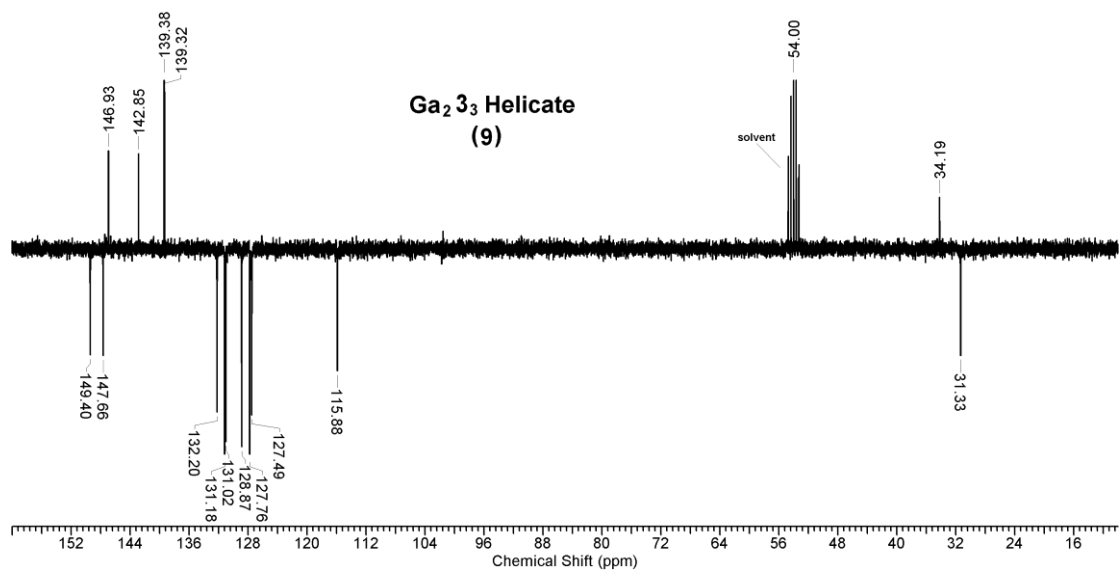
Figure S10. ^{13}C NMR spectrum of Ga$_2$**3**$_3$ helicate in CD$_2$Cl$_2$.
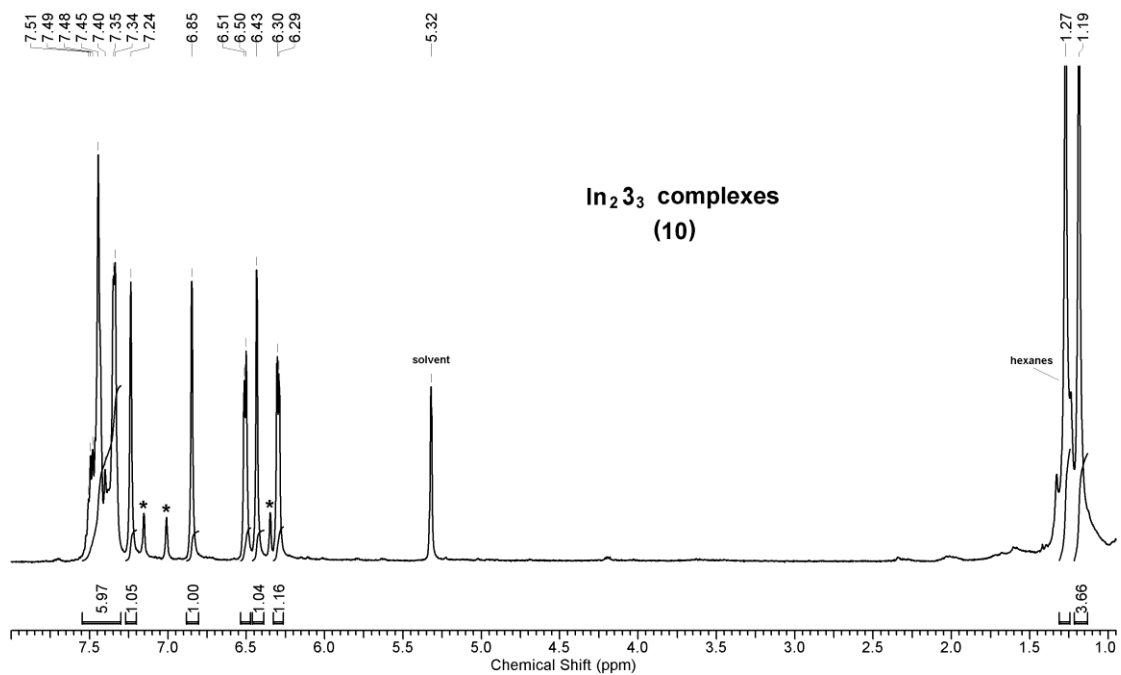
Figure S11. ^{1}H NMR spectrum of In$_2$3$_3$ complexes in CD$_2$Cl$_2$.
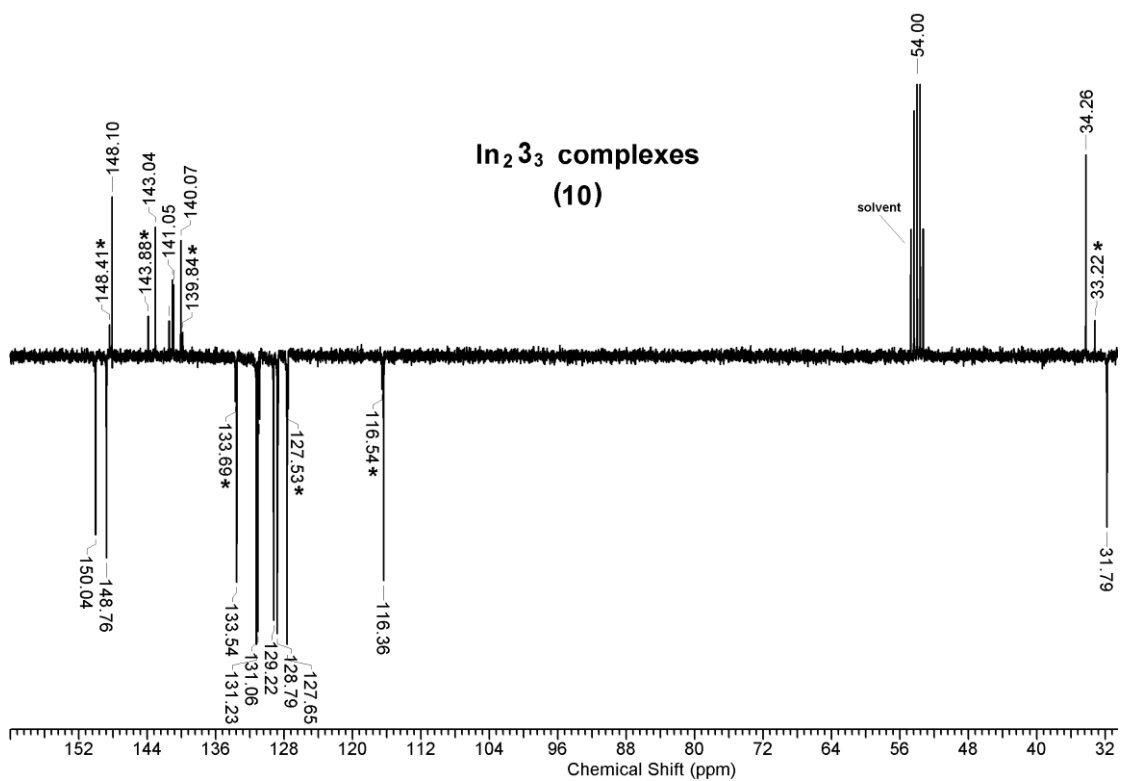
Figure S12. ^{13}C NMR spectrum of In$_2$3$_3$ complexes in CD$_2$Cl$_2$.

* The peaks belong to the In$_2$3$_3$ mesocate.

III   UV Spectra
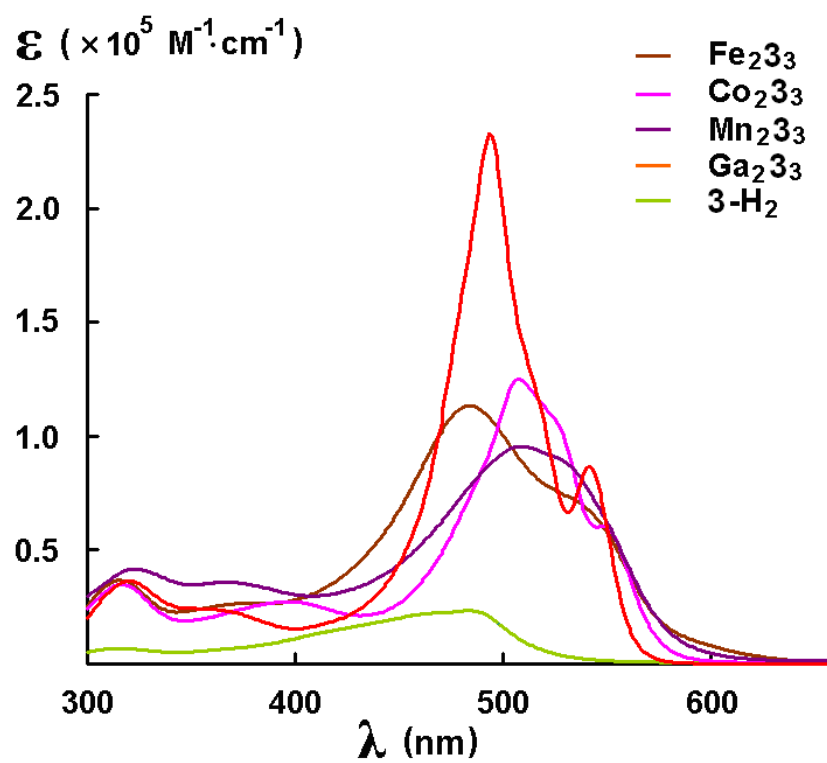
Figure S13. Optical absorption spectra of $M_2 3_3$ helicates and proligand **3**-H_2.

IV **Crystallographic Data**

Single crystals of **6-9** suitable for X-ray crystallography were grown by vapor diffusion of hexane into a CH_2Cl_2 solution. X-ray crystallographic analyses were carried out on a Bruker X8 APEX diffractometer with graphite monochromated Mo-K radiation. Data were collected and integrated using the Bruker SAINT software package.[S1] The structures were solved by direct methods.[S2] All refinements were performed using the SHELXTL[S3] crystallographic software package of Bruker-AXS.

Table S1. Crystallographic Data of **6-9**.

	6	7	8	9
Formula	$C_{101}H_{80}N_{12}Fe_2Cl_6$	$C_{101}H_{82}N_{12}Co_2Cl_4$	$C_{100}H_{80}N_{12}Mn_2Cl_2$	$C_{99}H_{78}N_{12}Ga_2$
Mw	1786.17	1723.45	1630.54	1575.17
cryst. syst.	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$C\,2/c$ (#15)	$C\,2/c$ (#15)	$C\,2/c$ (#15)	$C\,2/c$ (#15)
a/Å	28.2832(19)	28.2196(9)	30.649(5)	28.1300(7)
b/Å	12.7319(8)	12.5132(4)	11.690(2)	12.8500(3)
c/Å	24.0914(14)	23.8825(7)	25.147(3)	24.1340(5)
α/deg	90.0	90.0	90.0	90.0
β/deg	95.252(3)	96.244(2)	109.172(5)	94.951(1)
γ/deg	90.0	90.0	90.0	90.0
V/Å^3	8638.9(9)	8383.3(5)	8510(2)	4774.6(5)
Z	4	4	4	4
D_c/g cm^{-3}	1.373	1.366	1.273	1.204
μ(MoKα) cm^{-1}	5.79	5.81	4.15	6.73
No. of obsd data ($I>0.00\sigma(I)$)	7772	10170	6927	8504
R_{int}	0.034	0.053	0.058	0.042
$R1^a$; $wR2^b$ (all data)	0.058; 0.127	0.072; 0.113	0.105; 0.149	0.061; 0.114
GOF	1.10	1.00	1.11	1.11
No. of obsd data ($I>2\sigma(I)$)	6148	7448	5125	6463
($R1$; $wR2$)^c	(0.046; 0.119)	(0.043; 0.098)	(0.064; 0.132)	(0.042; 0.106)

^{a} $R1 = \Sigma\omega||Fo|-|Fc|| / \Sigma\omega|Fo|,$ ^{b} $wR2 = \sqrt{\Sigma^1 / \Sigma\omega(Fo^2)^2}$ ^{c} refined on F, $I>2\sigma(I)$

Crystallographic data of 6

A green hexagon crystal of $C_{99}H_{78}N_{12}Fe_2 \cdot 2CHCl_3$ having approximate dimensions of 0.10 x 0.20 x 0.35 mm was mounted on a glass fiber. All measurements were made on a Bruker X8 APEX II diffractometer with graphite monochromated Mo-Kα radiation. The data were collected at a temperature of -100.0 ± 0.1°C to a maximum 2θ value of 55.6°. Data were collected in a series of ϕ and ω scans in 0.50° oscillations with 10.0 second exposures. The crystal-to-detector distance was 36.00 mm.

Of the 53355 reflections that were collected, 7772 were unique (R_{int} = 0.034); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT[S1] software package. The linear absorption coefficient, μ, for Mo-Kα radiation is 5.79 cm^{-1}. Data were corrected for absorption effects using the multi-scan technique (SADABS[S4]), with minimum and maximum transmission coefficients of 0.861 and 0.944, respectively. The data were corrected for Lorentz and polarization effects.

Figure S14. ORTEP structure of **6**. Phenyl rings and hydrogen atoms were omitted for clarity. Ellipsoids scaled to the 50% probability level. Symmetry operator (-x,y,3/2-z) is used to generate the atoms flagged with a * character.

The structure was solved by direct methods.[S2] The material crystallizes with one half-molecule residing on two-fold rotation axis. C43 is on the twofold axis. Additionally the material crystallizes with one badly disordered molecule of CHCl$_3$ solvent in the asymmetric unit. The PLATON/SQUEEZE[S5] program was used to generate a solvent-free data set. The program removed electron density equivalent to 476 electrons in the unit cell, or roughly 8 CHCl$_3$ molecules. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions but were not refined. The final cycle of full-matrix least-squares refinement[S6] on F^2 was based on 7772 reflections and 516 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors (R1 = 0.058; wR2 = 0.127).

The standard deviation of an observation of unit weight[S7] was 1.10. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.87 and -0.44 e$^-$/Å^3, respectively.

Neutral atom scattering factors were taken from Cromer and Waber.[S8] Anomalous dispersion effects were included in Fcalc;[S9] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[S10] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[S11] All refinements were performed using the SHELXTL[S3] crystallographic software package of Bruker-AXS.

Crystallographic data of 7
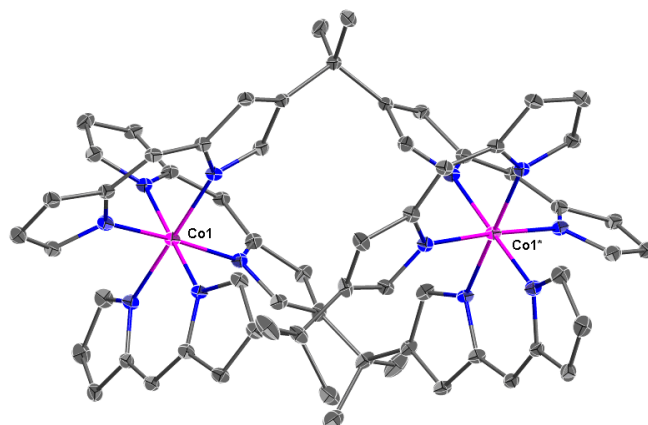
Figure S15. ORTEP structure of **7**. Phenyl rings and hydrogen atoms were omitted for clarity. Ellipsoids scaled to the 50% probability level. Symmetry operator (-x,y,1/2-z) is used to generate the atoms flagged with a * character.

A red plate crystal of $C_{99}H_{78}N_{12}Co_2 \cdot 2CH_2Cl_2$ having approximate dimensions of 0.10 x 0.40 x 0.55 mm was mounted on a glass fiber. All measurements were made on a Bruker APEX II diffractometer with graphite monochromated Mo-Kα radiation. The data were collected at a temperature of -100.0 ± 0.1°C to a maximum 2θ value of 55.4°. Data were collected in a series of ϕ and ω scans in 0.50° oscillations with 20.0-second exposures. The crystal-to-detector distance was 40.00 mm.

Of the 61786 reflections that were collected, 10170 were unique (R_{int} = 0.053); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT[S1] software package. The linear absorption coefficient, μ, for Mo-Kα radiation is 5.81 cm^{-1}. Data were corrected for absorption effects using the multi-scan technique (SADABS[S4]), with minimum and maximum transmission coefficients of 0.845 and 0.944, respectively. The data were corrected for Lorentz and polarization effects.
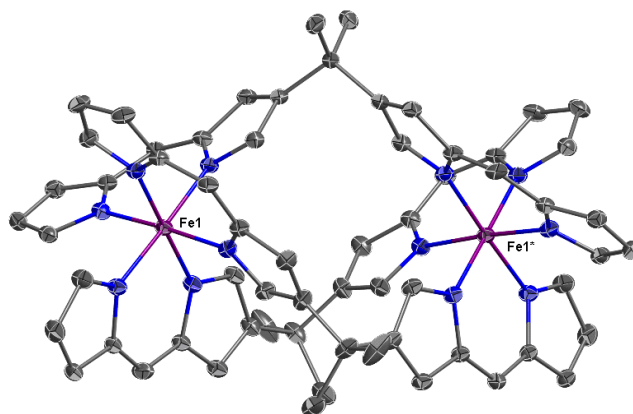
The structure was solved by direct methods.[S2] The material crystallizes residing on a two-fold axis. C43 is on the twofold axis. The material crystallizes with one molecule of CH_2Cl_2 in the asymmetric unit. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. The final cycle of full-matrix least-squares refinement[S6] on F^2 was based on 10170 reflections and 540 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors (R1 = 0.072; wR2 = 0.113). Compounds 7 and 6 are isomorphous. The standard deviation of an observation of

unit weight[S7] was 1.00. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.57 and –0.63 e⁻/Å³, respectively.

Neutral atom scattering factors were taken from Cromer and Waber.[S8] Anomalous dispersion effects were included in Fcalc;[S9] the values for Δf' and Δf'' were those of Creagh and McAuley.[S10] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[S11] All refinements were performed using the SHELXL[S3] via the WinGX[S12] interface.

Crystallographic data of 8

Figure S16. ORTEP structure of **8**. Phenyl rings and hydrogen atoms were omitted for clarity. Ellipsoids scaled to the 50% probability level. Symmetry operator (-x,y,1/2-z) is used to generate the atoms flagged with a * character.

A red plate crystal of $C_{99}H_{78}N_{12}Mn_2 \cdot CH_2Cl_2$ having approximate dimensions of 0.03 x 0.25 x 0.60 mm was mounted on a glass fiber. All measurements were made on a Bruker X8 APEX II diffractometer with graphite monochromated Mo-Kα radiation. The data were collected at a temperature of -100.0 ± 0.1°C to a maximum 2θ value of 48.2°. Data were collected in a series of φ and ω scans in 0.50 oscillations with 25.0-second exposures. The crystal-to-detector distance was 40.00 mm.

The material crystallizes as a two-component split crystal with the two components related by a 6.7° rotation about the (-0.51 1 0.37) reciprocal 'axis'. Data were integrated for both twin components, including both overlapped and non-overlapped reflections. In total 33266 reflections were integrated (11003 from component one only, 10764 from component two only, 11499 overlapped). Data were collected and integrated using the Bruker SAINT[S1] software packages. The linear absorption coefficient, μ, for Mo-Kα radiation is 4.15 cm⁻¹. Data were corrected for absorption effects using the multi-scan technique (TWINABS[S13]), with minimum and maximum transmission coefficients of 0.685 and 0.988, respectively. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods[S2] using non-overlapped data from the major twin component. The material crystallizes residing on a two-fold axis. C43 is on the twofold axis. Subsequent refinements were carried out using an HKLF 5 format data set containing complete data from component 1 and any overlapped reflections from component 2. All hydrogen atoms were included in calculated positions but not refined. The batch scale refinement showed a roughly 60:40 ratio between the major and minor twin components. The material crystallizes with one-half molecule of disordered CH_2Cl_2 in the asymmetric unit. The final cycle of full-matrix least-squares refinement[S6] on F^2 was based on 6927 reflections and 563 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors (R1 = 0.105; wR2 = 0.149). Compounds 8, 7 and 6 are isomorphous.

The standard deviation of an observation of unit weight[S7] was 1.11. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.43 and –0.42 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber.[S8] Anomalous dispersion effects were included in Fcalc;[S9] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[S10] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[S11] All refinements were performed using the SHELXTL[S3] crystallographic software package of Bruker-AXS.
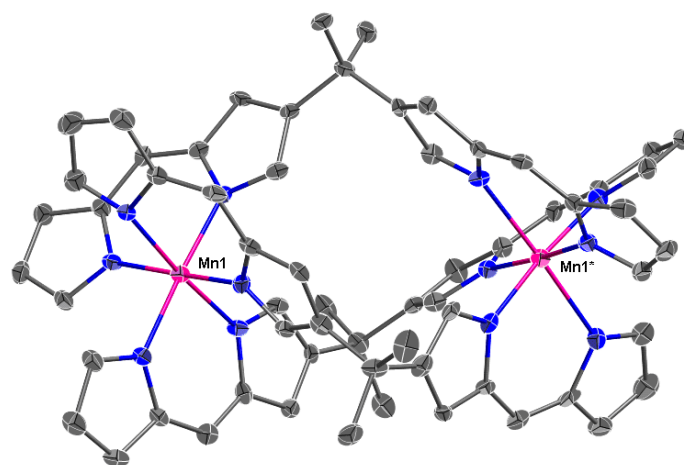
Crystallographic data of 9

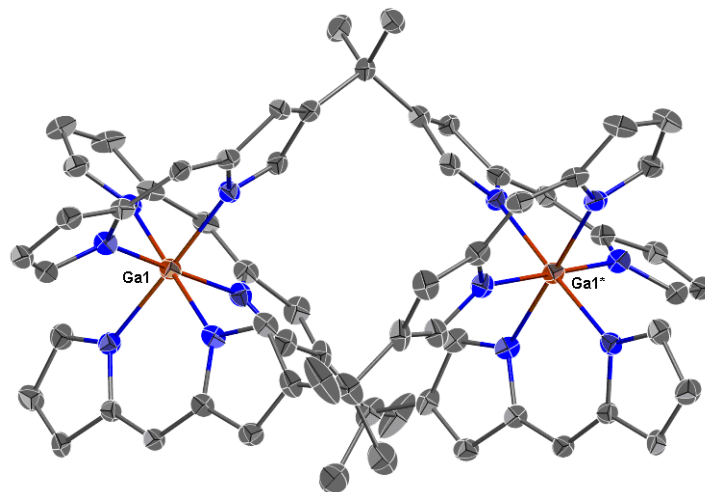**Figure S17.** ORTEP structure of **9**. Phenyl rings and hydrogen atoms were omitted for clarity. Ellipsoids scaled to the 50% probability level. Symmetry operator (-x,y,1/2-z) is used to generate the atoms flagged with a * character.

A red plate crystal of $C_{99}H_{78}N_{12}Ga_2$ having approximate dimensions of 0.10 x 0.24 x 0.30 mm was mounted on a glass fiber. All measurements were made on a

Bruker APEX II diffractometer with graphite monochromated Mo-Kα radiation. The data were collected at a temperature of -100.0 ± 0.1°C to a maximum 2θ value of 52.0°. Data were collected in a series of φ and ω scans in 0.50° oscillations with 20.0-second exposures. The crystal-to-detector distance was 40.00 mm.

Of the 62051 reflections that were collected, 8504 were unique (R_{int} = 0.049); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT[S1] software package. The linear absorption coefficient, μ, for Mo-Kα radiation is 6.73 cm^{-1}. Data were corrected for absorption effects using the multi-scan technique (SADABS[S4]), with minimum and maximum transmission coefficients of 0.852 and 0.935, respectively. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods.[S2] The molecule crystallizes with one half-molecule residing on a two-fold rotation axis. C43 is on the twofold axis. The material crystallizes with a mixture of disordered solvent occupying one site in the asymmetric unit. The mixture appears to contain both CH_2Cl_2 and $CHCl_3$ however no reasonable model for each fragment was obtained. As a result the PLATON/SQUEEZE[S5] program was used to generate a 'solvent-free' data set. Additionally, one phenyl ring (C45 – C50) is disordered in two orientations, using restraints on bond lengths and angles on the minor fragment. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. The final cycle of full-matrix least-squares refinement[S6] on F^2 was based on 8504 reflections and 548 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors (R1 = 0.061; wR2 = 0.114). Compounds 9, 8, 7 and 6 are isomorphous.

The standard deviation of an observation of unit weight[S7] was 1.11. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.72 and –0.34 e$^-$/Å^3, respectively.

Neutral atom scattering factors were taken from Cromer and Waber.[S8] Anomalous dispersion effects were included in Fcalc;[S9] the values for Δf' and Δf" were those of Creagh and McAuley.[S10] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[S11] All refinements were performed using the SHELXL[S3] via the WinGX[S12] interface.

V   Calculation

The geometries of **2**-H$_2$ and **3**-H$_2$ were fully optimized using the Gaussian 03 package.[S14] All-electron density functional theory calculations were carried out employing Becke's three-parameter hybrid exchange functional in combination with the correlation functional.[S15,S16] The Pople's 6-311+g(d, p) basis set was chosen to expand the wavefunction.[S17,S18] The harmonic vibrational analysis indicates that our optimized results are equilibrium structures. The total electronic energies of **2**-H$_2$ and **3**-H$_2$, after geometry optimization, are -1415.07159671 and -1493.71111776 Hartree; the linker C-C-C bond angles of **2**-H$_2$ and **3**-H$_2$ are 113.6^{o} and 108.7^{o}; and the average lengths of the linker C-C bonds are 1.51 and 1.52 Å, respectively. The Cartesian coordinates of each optimized structure are shown below.

In order to gain more insight into the effect of the germ-dimethyl groups, theoretical calculations were carried out at the B3LYP/6-31+G(2df,2pd) level of theory using the Gaussian 03 package[S14, S15,S16,S17,S18]. The Cartesian coordinates of each optimized structure are shown in the following section. After geometry optimization, the calculated linker C-C-C bond angles of the "S" conformers of proligands **2**-H$_2$ and **3**-H$_2$ are 113.6 and 108.7 degrees, and the average lengths of the linker C-C bonds are 1.51 and 1.52 Å, respectively. These calculated data are in good agreement with those determined from X-ray diffraction experiments.19 The "C" conformers of proligands **2**-H$_2$ and **3**-H$_2$ were also optimized at the same level of theory. Thermodynamically, the "C" conformer of proligand **2**-H$_2$ is less stable than the "S" one by 1.095 kcal/mol, while the energy difference is 1.786 kcal/mol for **3**-H$_2$, again with "S" conformer being more stable. This indicates that, at the same temperature, "S" conformer is more populated for **3**-H$_2$ compared to **2**-H$_2$. We suggest the different population of the "S" conformers might be responsible for the distinct helicate/mesocate ratios. However, this complicated multi-step self-assembly is still not well-understood.

Table S2. Optimized Cartesian coordinates of **2**-H$_2$ (in angstrom)

atom	X	Y	Z

Optimized Cartesian coordinates of the proligand of **2**-H$_2$ (in angstrom)

atom	X	Y	Z
C	-5.479510	3.041206	2.451614
C	-0.010368	-0.168651	-1.973484
C	1.280264	-1.545498	-0.134331
C	1.203971	-0.515037	-1.153181
C	2.447903	0.053104	-1.180835
C	3.250582	-0.639991	-0.193849
C	4.566657	-0.399957	0.160552
C	5.244745	-1.098274	1.212529
C	6.583420	-1.034743	1.634445

C	6.742609	-1.946306	2.691504
C	5.507089	-2.554689	2.896081
C	-6.697300	2.366849	2.426523
C	-5.366132	-0.693658	-0.430386
C	-5.043310	-2.030901	-0.165725
C	-5.798918	-3.064642	-0.715082
C	-6.881466	-2.777597	-1.544440
C	-7.208670	-1.449823	-1.816715
C	-6.462140	-0.415162	-1.258383
C	5.346337	0.636290	-0.576243
C	5.846420	1.763109	0.090605
C	6.562974	2.735877	-0.602112
C	6.804714	2.590218	-1.967566
C	-6.546005	1.274854	1.555654
C	6.320505	1.468228	-2.637487
C	5.592268	0.500441	-1.948717
C	-5.232769	1.303961	1.056904
C	-4.558031	0.412099	0.160038
C	-3.220405	0.529891	-0.174416
C	-2.460661	-0.256600	-1.125339
C	-1.193983	0.259167	-1.146126
C	-1.214146	1.354860	-0.194992
H	-5.183065	3.923049	2.997658
H	0.259051	0.628848	-2.675639
H	-0.303951	-1.027731	-2.587608
H	0.470483	-2.200732	0.167744
H	2.776915	0.872771	-1.801641
H	7.343668	-0.402128	1.205956
H	7.645285	-2.148509	3.246053
H	5.212500	-3.310674	3.606993
H	-3.627730	2.580136	1.442159
H	-7.581989	2.640552	2.979364
H	-4.205803	-2.255533	0.484244
H	-5.541775	-4.094312	-0.492857
H	-7.466680	-3.582242	-1.975127
H	-8.045559	-1.218123	-2.466065
H	-6.716560	0.615633	-1.475939
H	5.657113	1.881689	1.151110
H	6.931063	3.608804	-0.074659
H	7.367363	3.345306	-2.504863
H	-7.290040	0.533883	1.312489
H	6.510427	1.343533	-3.697713
H	5.221331	-0.374127	-2.470053
H	3.645596	-2.284444	1.837284

H	-2.841073	-1.076009	-1.716527
H	-0.373907	1.993371	0.054897
N	-4.616945	2.401083	1.629251
N	-2.385848	1.522894	0.369667
N	2.462716	-1.625931	0.427659
N	4.622576	-2.038724	2.012071

Optimized Cartesian coordinates of the proligand of **3**-H$_2$ (in angstrom)

atom	X	Y	Z
C	5.224174	2.721278	3.032836
C	-0.005156	-1.955657	-0.254008
C	-1.140827	0.167118	-1.331256
C	-1.174174	-1.010511	-0.479351
C	-2.450380	-1.053420	0.013602
C	-3.158584	0.081351	-0.544582
C	-4.484496	0.433230	-0.365752
C	-5.110428	1.534961	-1.036730
C	-6.403702	2.067280	-0.904049
C	-6.504496	3.168078	-1.771500
C	-5.276504	3.295311	-2.414722
C	6.489009	2.658699	2.454771
C	0.330700	-2.669859	-1.583210
C	-0.362001	-3.027038	0.801702
C	5.341416	-0.253915	-0.629257
C	5.861526	0.587650	-1.622100
C	6.647525	0.070099	-2.648729
C	6.939009	-1.292767	-2.690969
C	6.434534	-2.136486	-1.703162
C	5.637657	-1.622342	-0.682525
C	-5.334417	-0.358696	0.569938
C	-5.029415	-0.413620	1.936099
C	6.413147	1.739067	1.395144
C	-5.824075	-1.151554	2.811017
C	-6.929251	-1.852596	2.332217
C	-7.239784	-1.806103	0.973722
C	-6.453685	-1.059029	0.099940
C	5.094479	1.257610	1.339853
C	4.490691	0.293668	0.466456
C	3.183706	-0.142307	0.595140
C	2.449504	-1.040612	-0.273419
C	1.184970	-1.149295	0.239428
C	1.184199	-0.297057	1.417244
H	-3.471511	2.134964	-2.180286
H	3.426332	1.635476	2.534868
H	4.868937	3.301594	3.869904
H	-0.279476	0.526782	-1.882871
H	-2.877567	-1.789872	0.675377
H	-7.167769	1.693641	-0.241932
H	-7.363069	3.803980	-1.918813
H	-4.945685	4.013884	-3.148123
H	7.356587	3.215137	2.772436

H	-0.535807	-3.236703	-1.931738
H	1.164381	-3.365225	-1.449505
H	0.603331	-1.957294	-2.365116
H	-0.631548	-2.575122	1.759051
H	0.493477	-3.685657	0.969517
H	-1.203648	-3.638962	0.464687
H	5.633869	1.646865	-1.594902
H	7.031122	0.732160	-3.416988
H	7.555745	-1.693524	-3.487494
H	6.662385	-3.196362	-1.724287
H	5.251550	-2.278503	0.088587
H	-4.174305	0.136468	2.310986
H	7.215577	1.439446	0.740878
H	-5.579975	-1.175941	3.867204
H	-7.545222	-2.429890	3.012450
H	-8.094662	-2.353350	0.592367
H	-6.695737	-1.028643	-0.956019
H	2.843076	-1.508677	-1.161580
H	0.340214	-0.124679	2.075678
N	4.401681	1.885568	2.357716
N	2.335934	0.291229	1.629873
N	-2.285708	0.803377	-1.377993
N	-4.456169	2.314510	-1.972035

Optimized Cartesian coordinates of "C" conformer of the proligand of **2**-H$_2$
(in angstrom)

atom	X	Y	Z
C	6.057077	-3.051118	-1.402419
C	-6.057295	-3.051041	-1.402136
C	-0.000003	-0.511315	2.687693
C	6.899483	-2.037996	-1.852471
C	-6.899637	-2.037902	-1.852268
C	6.351214	-0.821009	-1.414474
C	-6.351282	-0.820914	-1.414384
C	5.173750	-1.112559	-0.705283
C	-5.173830	-1.112481	-0.705179
C	4.251372	-0.243356	-0.035783
C	-4.251387	-0.243283	-0.035762
C	3.170356	-0.695403	0.700822
C	-3.170399	-0.695344	0.700877
C	2.132592	0.085678	1.342004
C	-2.132568	0.085716	1.341973
C	1.263726	-0.800472	1.917019
C	-1.263764	-0.800447	1.917064
C	1.802621	-2.111227	1.608172
C	-1.802766	-2.111189	1.608351
H	6.127824	-4.120676	-1.523794
H	-6.128116	-4.120606	-1.523416
H	0.000015	0.539108	2.989654
H	0.000008	-1.098943	3.614705
H	2.058687	1.162636	1.339785
H	-2.058578	1.162668	1.339651
H	1.378194	-3.063084	1.910157
H	-1.378413	-3.063049	1.910429
N	5.031412	-2.487357	-0.724198
N	-5.031584	-2.487290	-0.723976
N	2.906172	-2.062105	0.900778
N	-2.906320	-2.062048	0.900961
H	-6.754931	0.165410	-1.575537
H	-7.802139	-2.175808	-2.426451
H	7.801970	-2.175912	-2.426675
H	6.754928	0.165301	-1.575544
H	-4.262190	-2.923160	-0.210779
H	4.261991	-2.923222	-0.211040
C	4.495600	1.222952	-0.155150
C	4.768626	1.993032	0.982931
C	4.459996	1.855423	-1.405432
C	5.001874	3.362210	0.873070

H	4.811303	1.510481	1.952255
C	4.681112	3.226275	-1.511776
H	4.242257	1.271002	-2.291711
C	4.956004	3.983307	-0.373636
H	5.221664	3.942370	1.762340
H	4.636925	3.703210	-2.484528
H	5.133821	5.049442	-0.458392
C	-4.495513	1.223031	-0.155253
C	-4.459896	1.855393	-1.405589
C	-4.768461	1.993227	0.982770
C	-4.680922	3.226251	-1.512044
H	-4.242216	1.270882	-2.291822
C	-5.001620	3.362411	0.872797
H	-4.811151	1.510761	1.952135
C	-4.955737	3.983399	-0.373963
H	-4.636725	3.703100	-2.484838
H	-5.221350	3.942661	1.762023
H	-5.133484	5.049538	-0.458806

Optimized Cartesian coordinates of "C" conformer of the proligand of **3**-H$_2$

(in angstrom)

atom	X	Y	Z
C	5.871960	-3.215920	-1.533006
C	-5.872171	-3.215836	-1.532754
C	0.000006	-0.192174	2.539566
C	6.764439	-2.268551	-2.026882
C	-6.764571	-2.268446	-2.026731
C	6.286962	-1.007303	-1.632726
C	-6.287017	-1.007198	-1.632667
C	5.101377	-1.206443	-0.905543
C	-5.101465	-1.206361	-0.905436
C	4.234678	-0.262874	-0.261884
C	-4.234713	-0.262801	-0.261836
C	3.137951	-0.627153	0.499570
C	-3.138031	-0.627097	0.499677
C	2.158433	0.234118	1.128308
C	-2.158470	0.234158	1.128367
C	1.242812	-0.576177	1.744863
C	-1.242870	-0.576147	1.744946
C	1.700865	-1.928383	1.466135
C	-1.701082	-1.928341	1.466418
H	5.883046	-4.291607	-1.613367
H	-5.883329	-4.291529	-1.613026
H	2.161854	1.311375	1.088401
H	-2.161828	1.311410	1.088374
H	1.230076	-2.847440	1.795348
H	-1.230372	-2.847405	1.795724
N	4.884274	-2.571032	-0.870334
N	-4.884454	-2.570962	-0.870113
N	2.794890	-1.967774	0.744910
N	-2.795078	-1.967720	0.745146
H	-6.742783	-0.051570	-1.834686
H	-7.653521	-2.477394	-2.600619
H	7.653389	-2.477513	-2.600763
H	6.742800	-0.051689	-1.834654
H	-4.095719	-2.944183	-0.337472
H	4.095498	-2.944244	-0.337745
C	4.558587	1.182177	-0.438495
C	4.882146	1.979253	0.667231
C	4.547682	1.767479	-1.711971
C	5.187809	3.328679	0.503500
H	4.906688	1.532345	1.654092
C	4.841943	3.119234	-1.872406

H	4.291350	1.162257	-2.573619
C	5.165869	3.903297	-0.765936
H	5.445596	3.929630	1.368448
H	4.816320	3.560176	-2.862663
H	5.400509	4.954148	-0.892837
C	-4.558507	1.182259	-0.438581
C	-4.547549	1.767447	-1.712109
C	-4.882011	1.979459	0.667073
C	-4.841707	3.119210	-1.872666
H	-4.291256	1.162129	-2.573701
C	-5.187570	3.328893	0.503219
H	-4.906590	1.532642	1.653974
C	-5.165581	3.903396	-0.766268
H	-4.816042	3.560062	-2.862962
H	-5.445316	3.929941	1.368112
H	-5.400140	4.954254	-0.893265
C	0.000062	1.319031	2.830827
H	-0.000320	1.909874	1.912459
H	-0.884920	1.594125	3.409859
H	0.885483	1.594201	3.409151
C	0.000051	-0.944944	3.895455
H	0.887969	-0.679121	4.475817
H	-0.887800	-0.679079	4.475896
H	0.000021	-2.029028	3.764921

VI   References

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S2.   **SIR97.** Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori G.; Spagna, R. *J. Appl. Cryst.* **1999**, *32*, 115-119.

S3.   **SHELXTL.** Version 5.1, Bruker AXS Inc., Madison, Wisconsin, USA. (1997).

S4.   **SADABS.** Bruker Nonius area detector scaling and absorption correction – V2.10, Bruker AXS Inc., Madison, Wisconsin, USA. (2003).

S5.   **SQUEEZE.** Sluis, P.; Spek, A. L. *Acta Crystallogr., Sect A* **1990**, *46*, 194-201.

S6.   Least Squares function minimized: $\Sigma w(F_o^2 - F_c^2)^2$

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