Supplementary Information

Supramolecular chiroptical switching of helical-sense preferences through the two-way intramolecular transmission of a single chiral source associated with a dynamic helical loop

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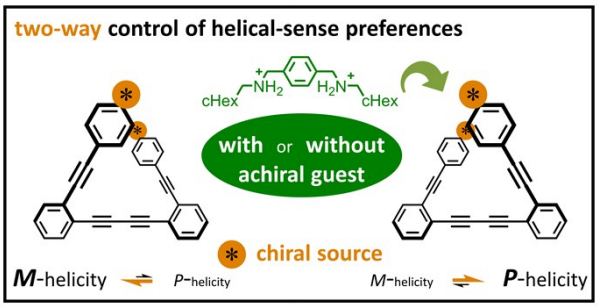

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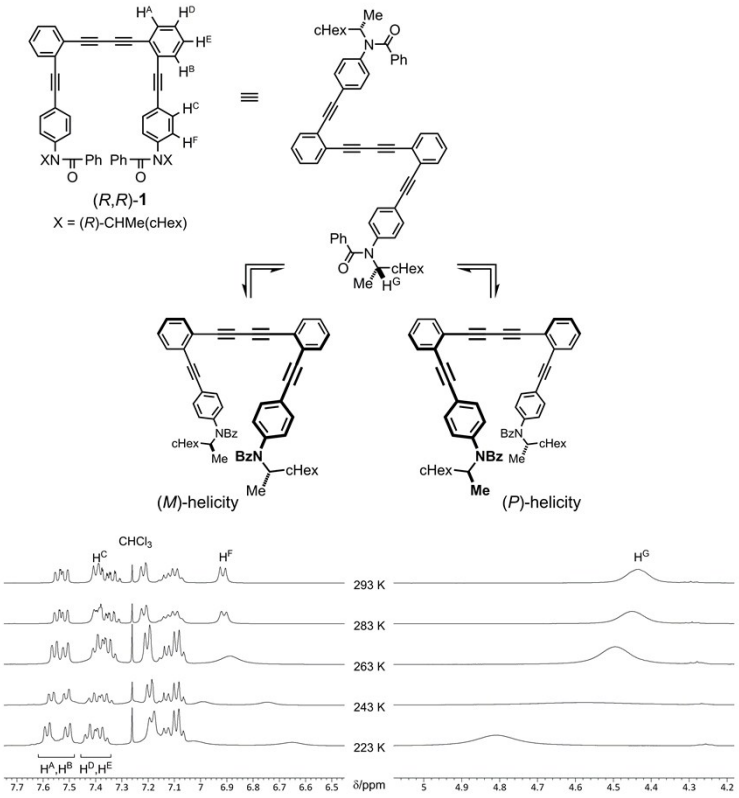


Fig. S1 Partial ^{1}H NMR spectra (400 MHz) of (*R*,*R*)-**1**,[1] measured in chloroform-*d* at 223-293 K.

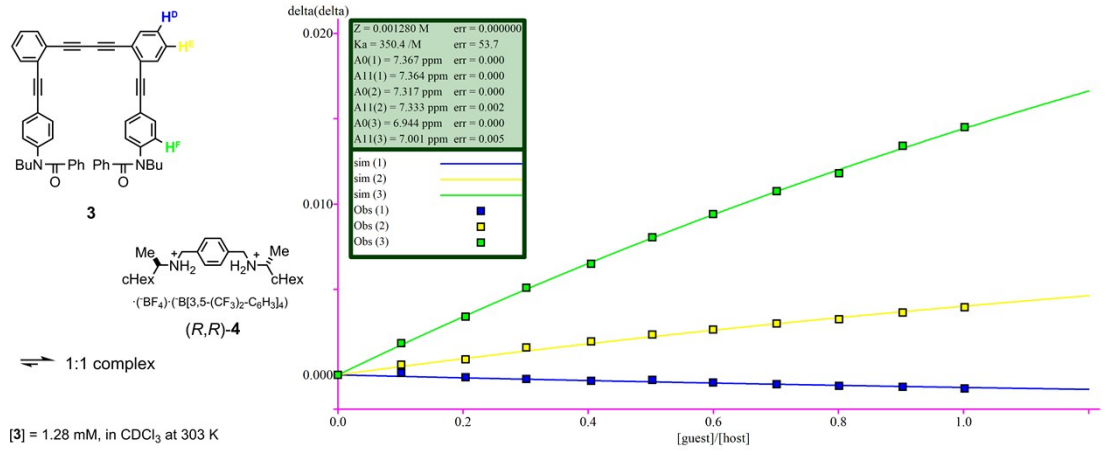


Fig. S2a Titration curves for the complexation of **3** with (*R*,*R*)-**4** and the 1:1 binding constant, obtained by a curve fitting method,[2] based on changes in the chemical shift for protons H^{D} (blue), H^{E} (yellow) and H^{F} (green) upon complexation.

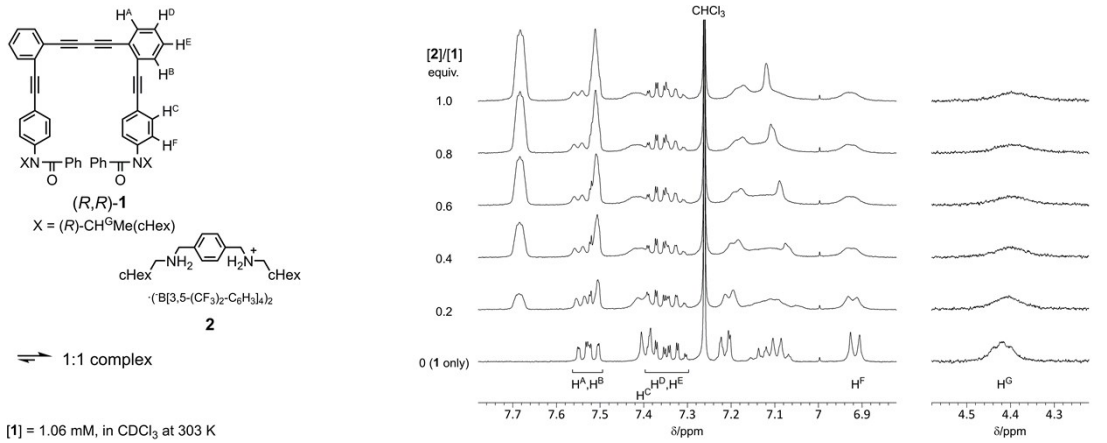


Fig. S2b Partial ^{1}H NMR spectra (400 MHz) of (*R*,*R*)-**1** ([**1**] = 1.06 mM) in the presence of **2**[3] [0 (**1** only)-3 equiv.], measured in chloroform-*d* at 303 K.

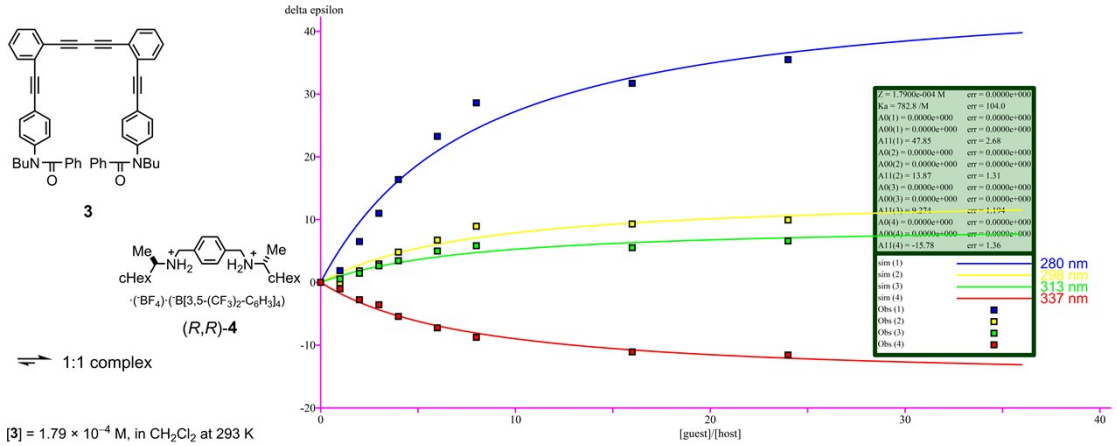


Fig. S3 Titration curves for the complexation of **3** with (*R*,*R*)-**4** and the 1:1 binding constant, obtained by a curve fitting method,[2] based on changes in the induced CD ($\Delta\varepsilon$) at 280 (blue), 298 (yellow), 313 (green) and 337 (red) nm upon complexation.

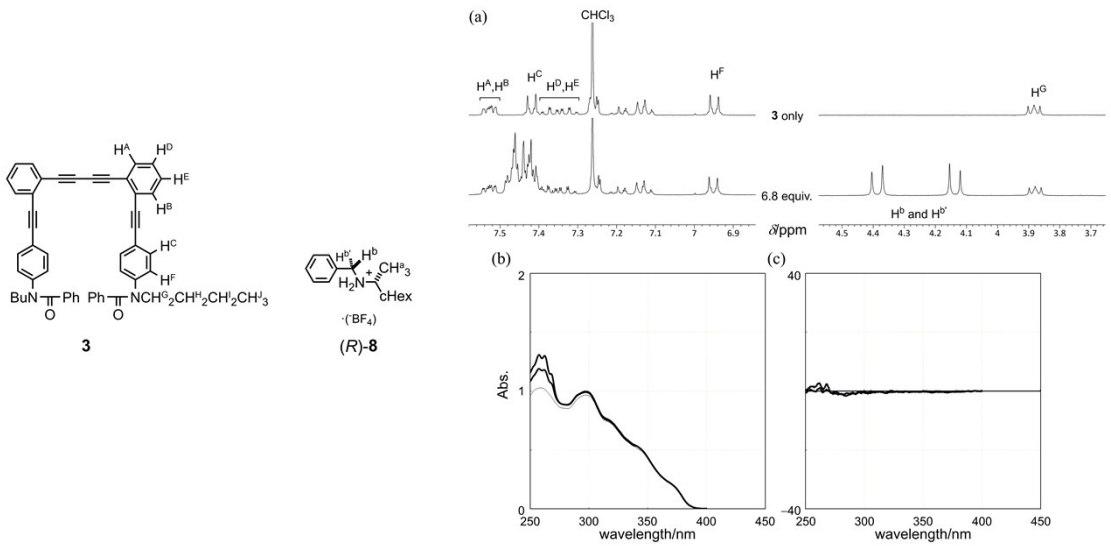
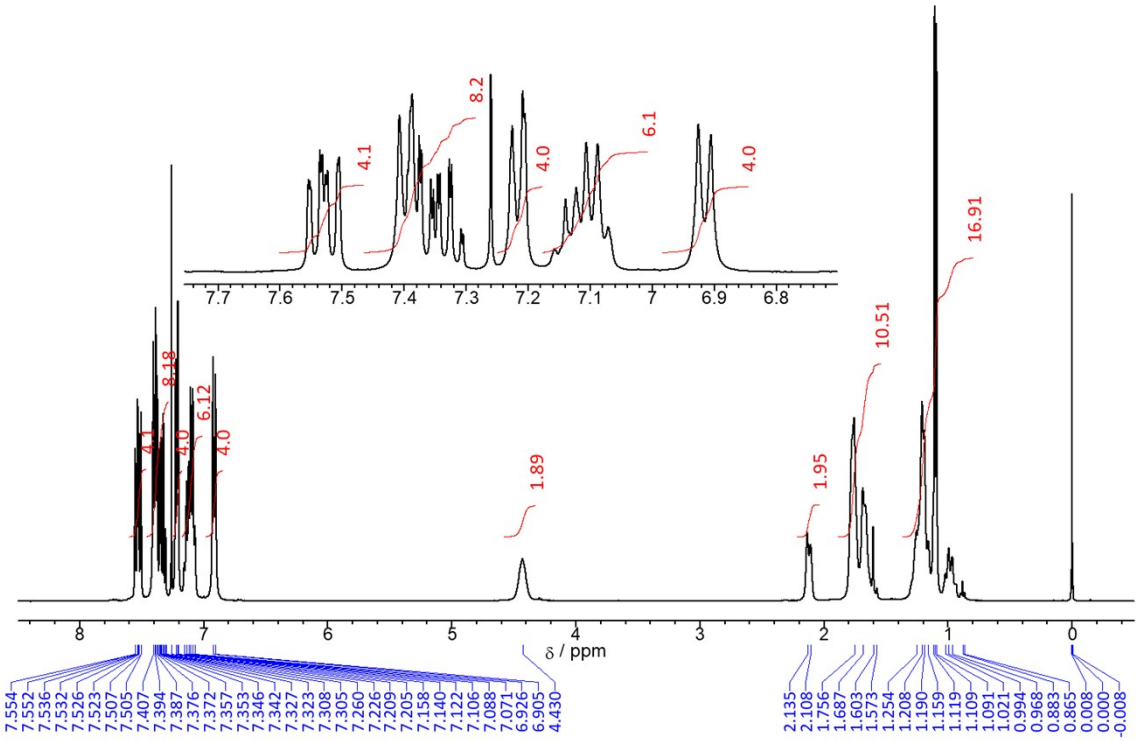


Fig. S4 (a) Partial ^{1}H NMR spectra (400 MHz) of **3** in the presence of a monotopic guest (*R*)-**8**[4] [0 (**3** only) and 6.8 equiv.], measured in chloroform-*d* at 303 K; (b) UV spectrum of **3** (1.79×10^{-4} M) in the presence of (*R*)-**8** [0 (**3** only, thin line), 8 and 16 (bold lines) equiv.]; (c) CD spectra of **3** (1.79×10^{-4} M) in the presence of (*R*)-**8** (8 and 16 equiv.). UV and CD spectra were measured in dichloromethane at room temperature.

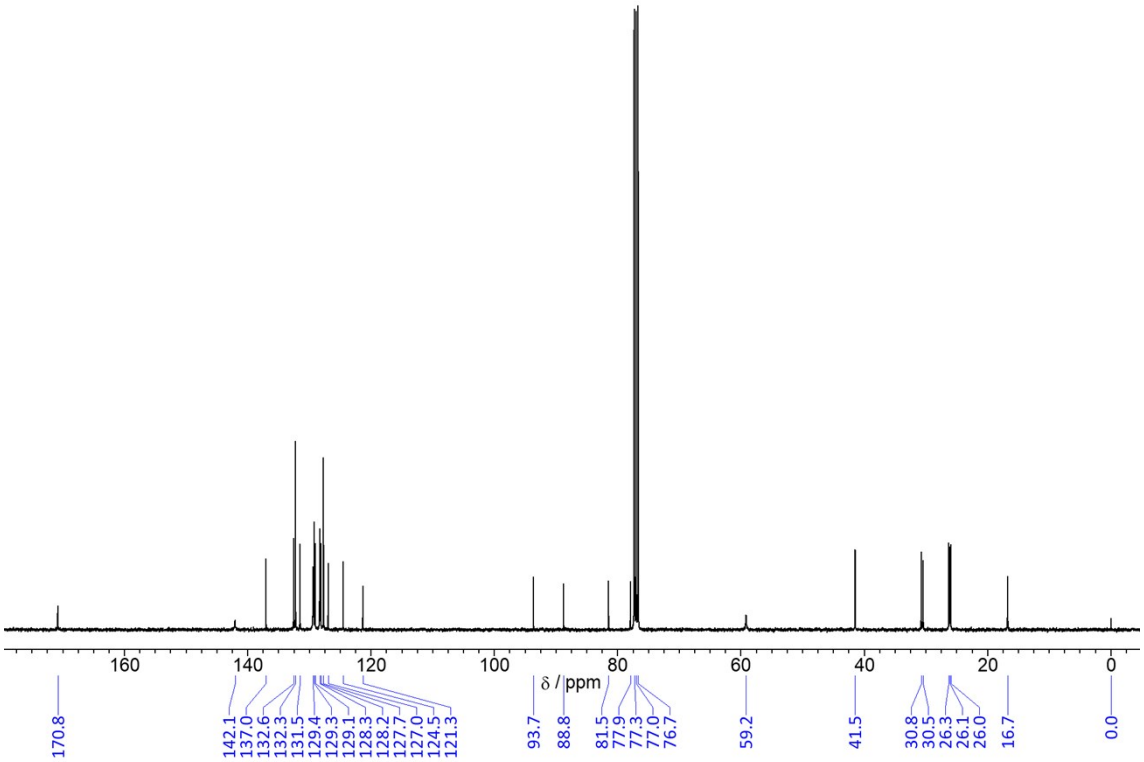
Experimental

Preparation of **3**

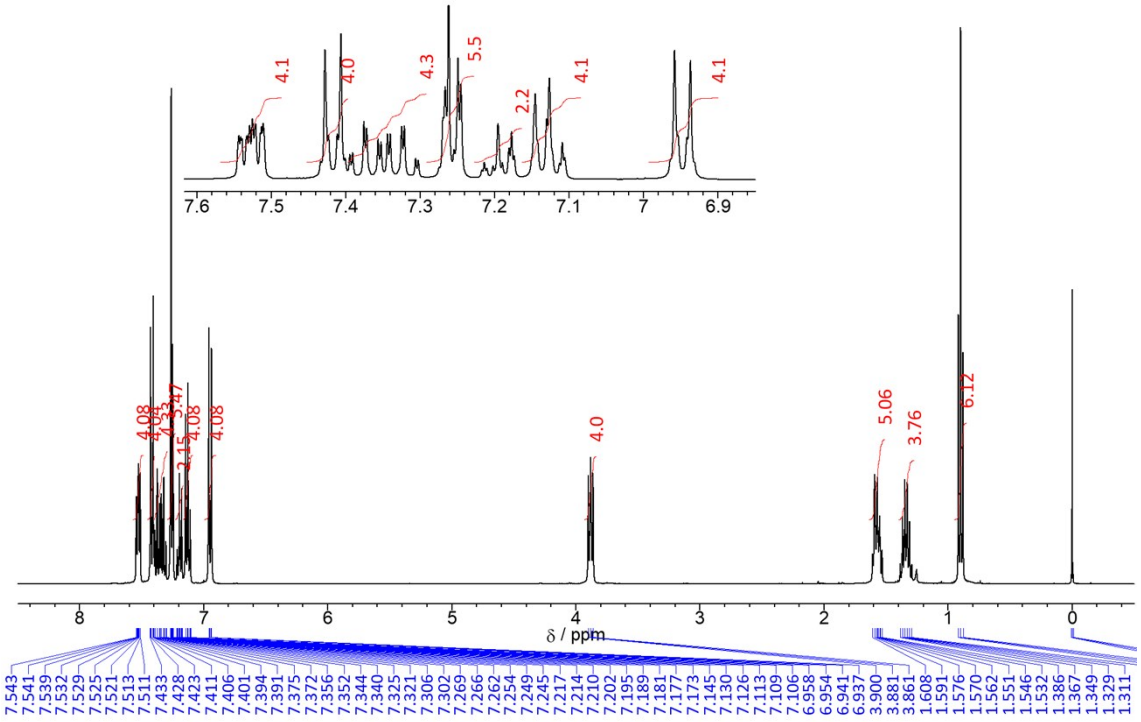
To a solution of **6**[1] (183 mg, 0.731 mmol) and **7b**[5] (824 mg, 1.90 mmol) in THF/Et_3N (7 mL/7 mL) were added $Pd(PPh_3)_4$ (45 mg, 0.039 mmol) and CuI (13 mg, 0.068 mmol) at room temperature under an argon atmosphere, and the mixture was stirred at 50 °C for 20 hours. After removal of a solid by filtration, the filtrate was concentrated and purified by column chromatography on SiO_2 (ethyl acetate/dichloromethane/hexane), followed by GPC (chloroform) to give **3** (470 mg) as a yellow solid in 75% yield. An analytical sample was obtained as a white solid by recrystallization from ethanol. **3**: mp 139-140 °C; elemental analyses Found: C, 86.11; H, 6.10; N, 3.69. Calc. for $C_{54}H_{44}N_2O_2$: C, 86.14; H, 5.89; N 3.72%; IR (KBr) ν_{max}/cm^{-1} 3059, 2959, 2928, 2860, 2215, 1644, 1599, 1510; ^{1}H NMR δ_H(400 MHz, $CDCl_3$, Me_4Si)/ppm 7.54-7.51 (4H, m), 7.42 (4H, d, J = 8.8 Hz), 7.37 (2H, dt, J = 1.2, 7.6 Hz), 7.32 (2H, dt, J = 1.6, 7.6 Hz), 7.27-7.25 (4H, m), 7.22-7.17 (2H, m), 7.15-7.11 (4H, m), 6.95 (4H, d, J = 8.8 Hz), 3.88 (4H, t, J = 7.6 Hz), 1.61-1.53 (4H, m), 1.39-1.29 (4H, m), 0.90 (6H, t, J = 7.6 Hz); ^{13}C NMR δ_C(100 MHz, $CDCl_3$)/ppm 170.1, 143.7, 136.0, 132.6, 132.6, 131.6, 129.6, 129.0, 128.6, 128.1, 127.8, 127.4, 126.8, 124.4, 120.9, 93.5, 88.5, 81.4, 77.8, 50.1, 29.8, 20.1, 13.8; FD-LRMS m/z 755.3 ([M+3]$^+$, 4%), 754.2 ([M+2]$^+$, 19), 753.2 ([M+1]$^+$, 61), 752.2 (M$^+$, 100); UV $\lambda_{max}(CH_2Cl_2)$/nm (log ε) 372 (sh, 4.03), 346 (sh, 4.42), 319 (sh, 4.60), 297 (4.73), 259 (4.76).



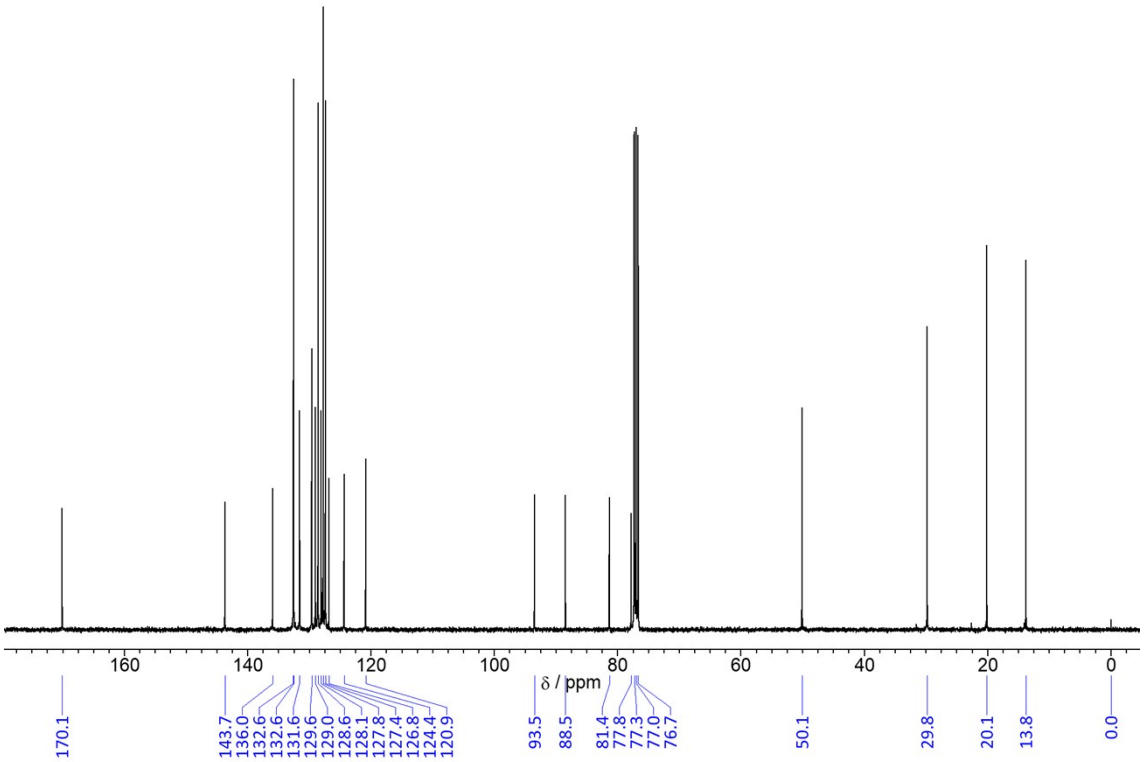
[1]H NMR (400 MHz) spectrum of (*R*,*R*)-**1**, measured in chloroform-*d* at room temperature.[1]



[13]C NMR (100 MHz) spectrum of (*R*,*R*)-**1**, measured in chloroform-*d* at room temperature.[1]



^{1}H NMR (400 MHz) spectrum of **3**, measured in chloroform-*d* at room temperature.



^{13}C NMR (100 MHz) spectrum of **3**, measured in chloroform-*d* at room temperature.

References and note

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