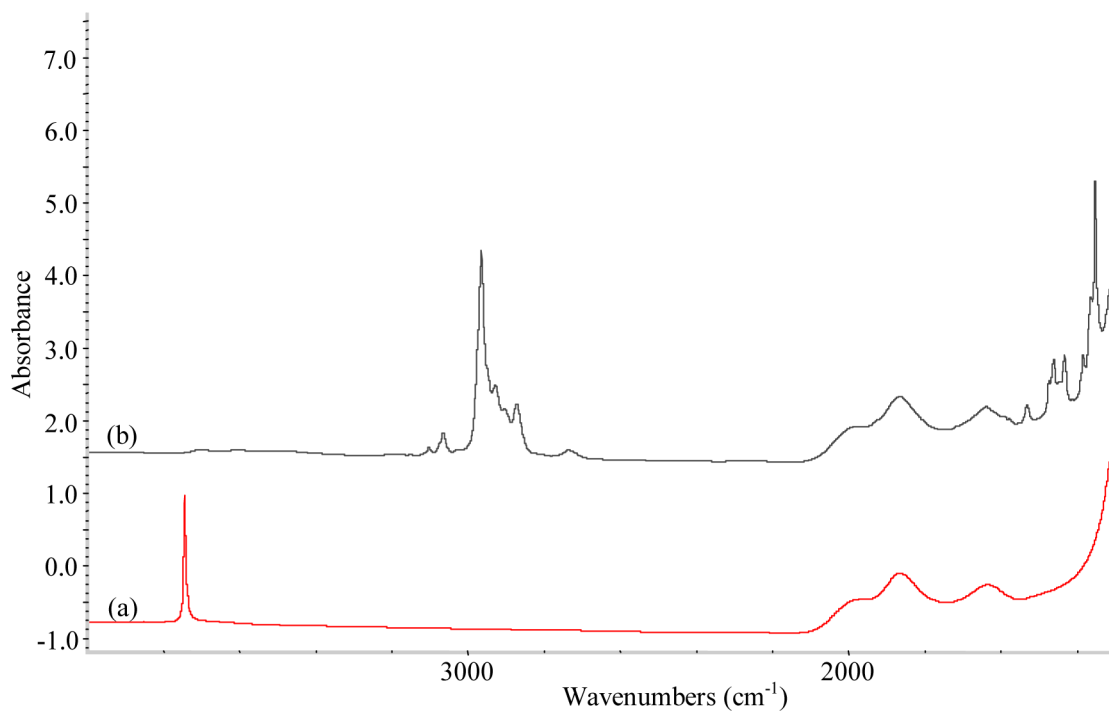
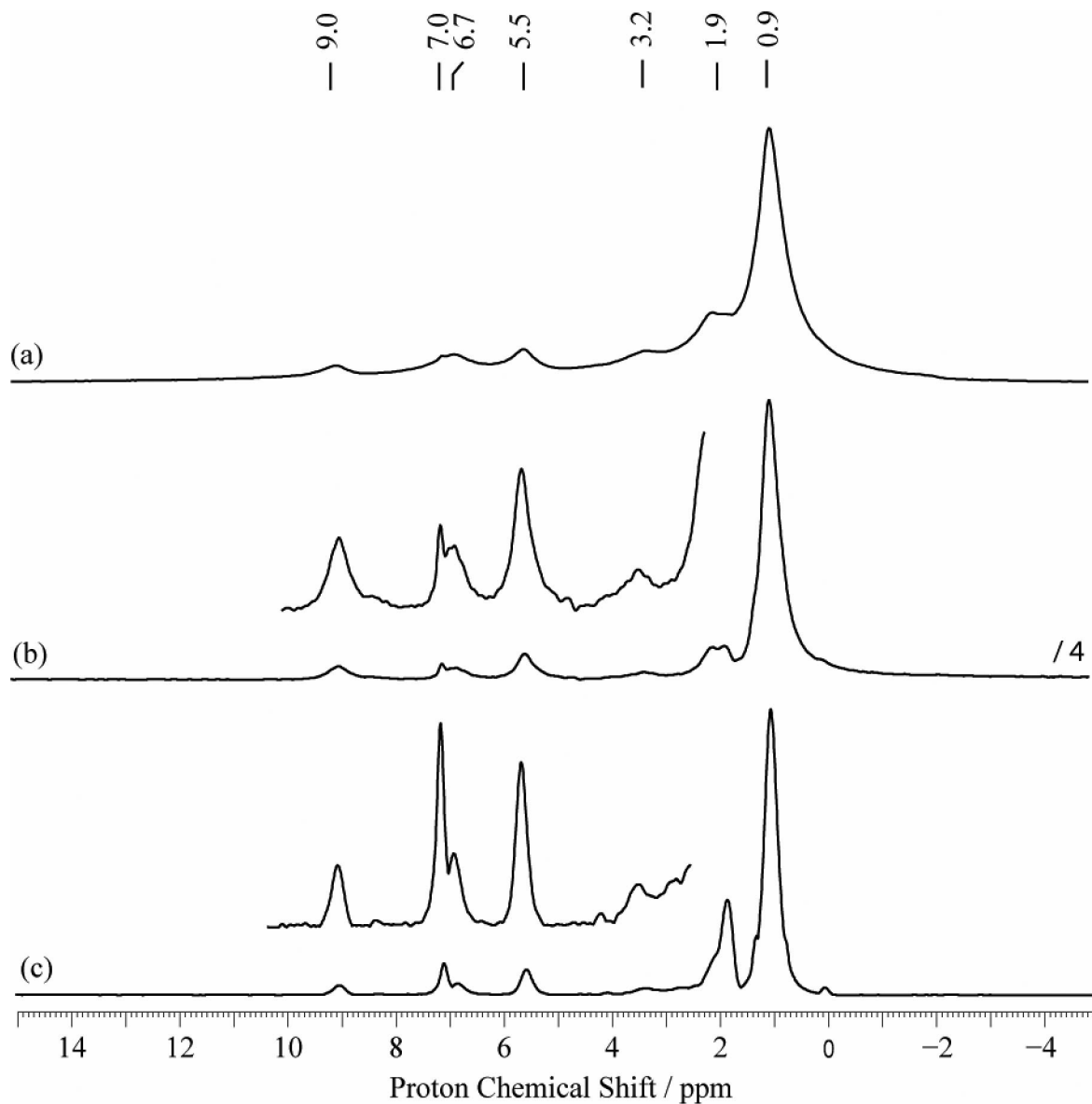


# Supporting Information

Blanc et al. 10.1073/pnas.0802147105

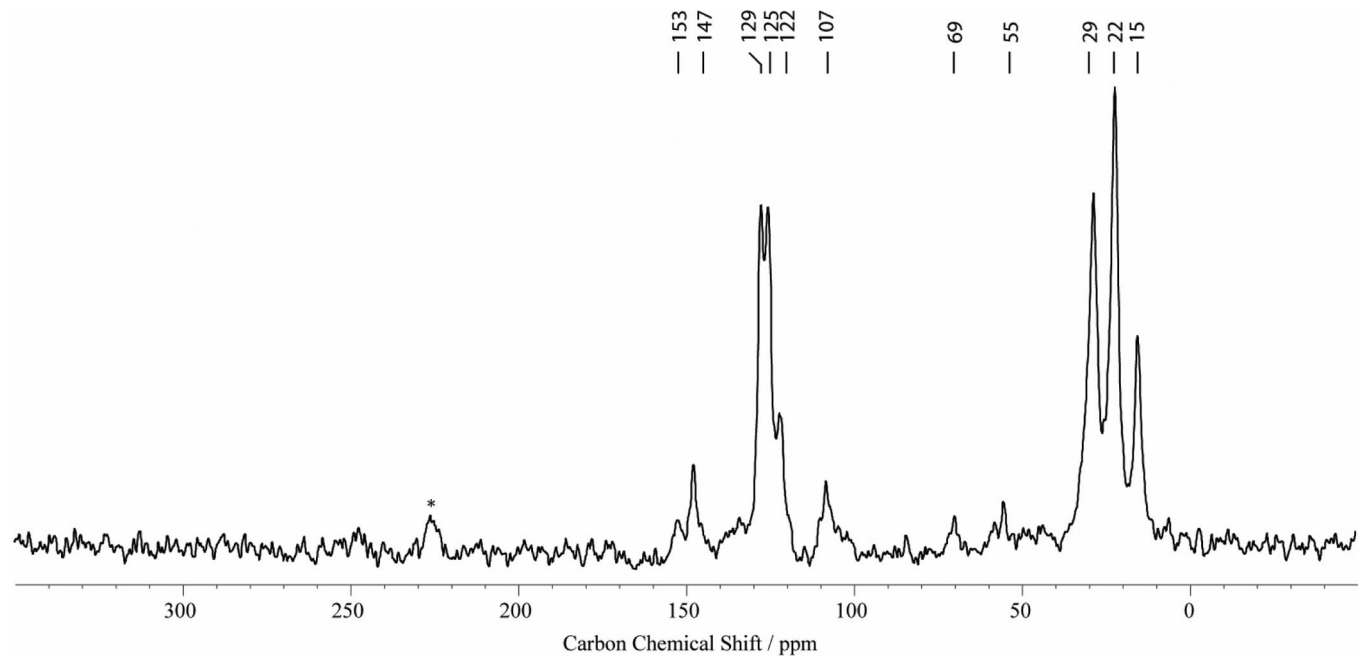


**Fig. S1.** Grafting of  $[W(\equiv NAr)(=CHtBu)(2,5-Me_2NC_4H_2)_2]$ , (compound 2) [Kreickmann T, Arndt S, Schrock RR, Muller P (2007) *Organometallics* 26:5702–5711], on a silica partially dehydroxylated at 700°C,  $SiO_2$ -<sub>(700)</sub>, monitored by IR spectroscopy. (A)  $SiO_2$ -<sub>(700)</sub> pellet (55 mg). (B) Impregnation of the silica pellet with 2 (28 mg) in benzene (10 ml) (12 h, 25°C) was followed by three washes (30 min, 25°C) in benzene and a drying step under vacuum (1.34 Pa, 2 h, 25°C).

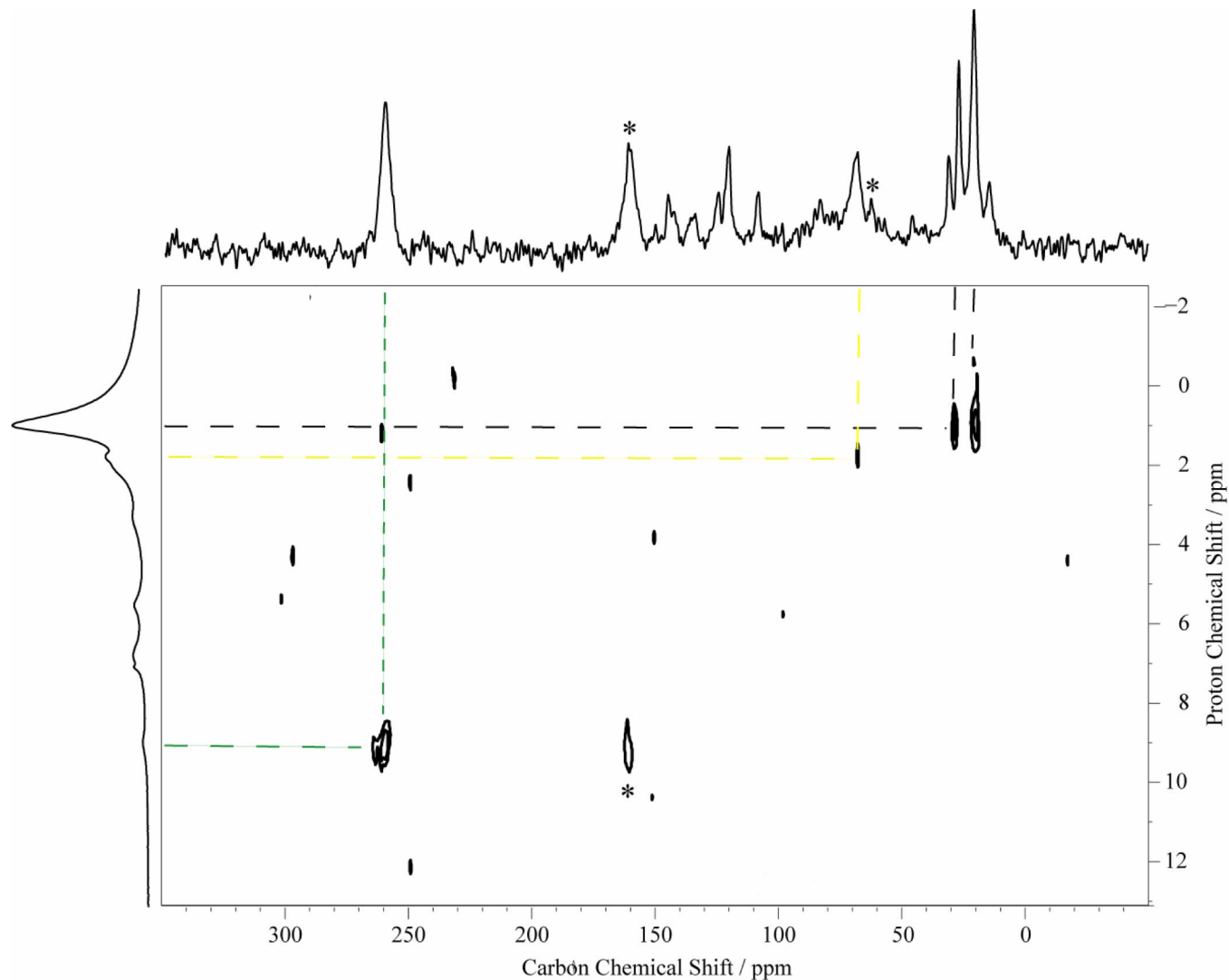


**Fig. S2.** One-dimensional proton solid state MAS spectra of  $[2/\text{SiO}_2]$ . (A) Single pulse spectrum (eight scans) at a recycle delay of 16 s. (B) Delayed acquisition spectrum (64 scans) acquired with an echo period  $2\tau$  of 2 ms. (C) Constant-time proton spectrum (1, 2). This spectrum has been constructed from a 2D spectrum by summing  $\omega_1$  traces extracted along  $\omega_2$  at the relevant proton frequencies (2, 3). The constant time T was set to 10 ms. A total of 196  $t_1$  points with 16 scans each were collected. (Inset) Magnification of the [10–2 ppm] region.

1. Lesage A, Duma L, Sakellariou D, Emsley L (2001) *J Am Chem Soc* 123:5747–5752.
2. Blanc F, et al. (2006) *Inorg Chem* 45:9587–9592.
3. Fung BM, Khitrin AK, Ermolaev K (2000) *J Magn Reson* 142:97–101.

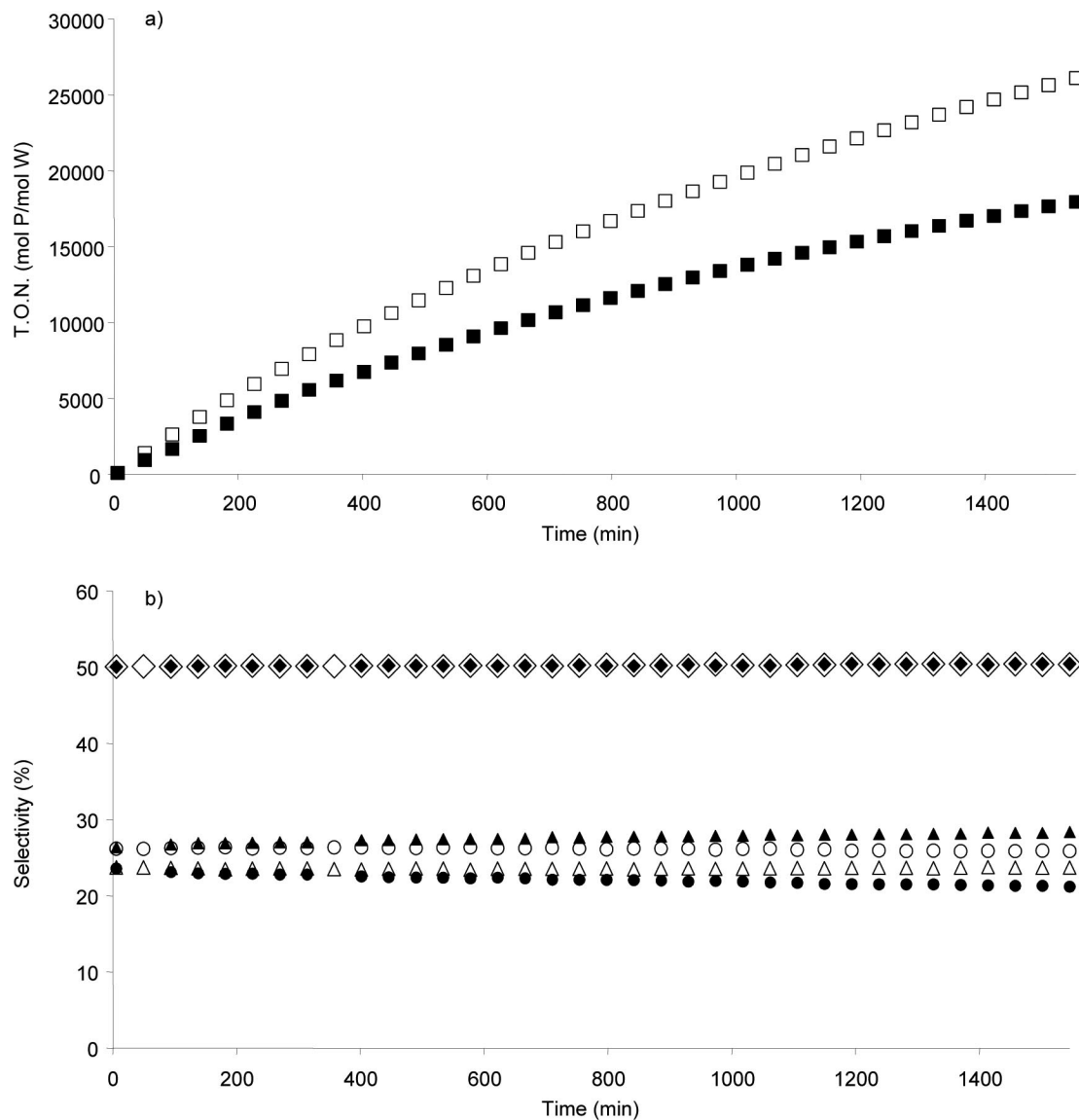


**Fig. S3.**  $^{13}\text{C}$  CP solid state NMR spectra of  $[\text{Z}/\text{SiO}_2]$  acquired under SPINAL-64  $^1\text{H}$  [Fung BM, Khitrin AK, Ermolaev K (2000) *J Magn Reson* 142:97–101] decoupling at  $\nu_{\text{H}}^{\text{H}} = 83$  kHz. The contact time for CP and the recycle delay were 1 s and 1 ms, respectively. A total of 105,000 scans were collected. An exponential line broadening of 80 Hz was applied before Fourier transform. Asterisks indicate spinning side bands.



**Fig. S4.** 2D  $^1\text{H}$ - $^{13}\text{C}$  HETCOR solid state NMR spectra of  $[2^*/\text{SiO}_2]$  acquired under SPINAL-64  $^1\text{H}$  [Fung BM, Khitrin AK, Ermolaev K (2000) *J Magn Reson* 142:97–101] decoupling at  $\nu_1^{\text{H}} = 83$  kHz. The contact time for CP and the recycle delay were 1 ms and 1 s, respectively. A total of 32  $t_1$  points with 512 scans each were collected. Asterisks indicate spinning side bands of the alkydine resonance. Above the graph is indicated the  $^{13}\text{C}$  CP MAS spectrum (10,240 scans) recorded with a CP step of 1 ms and a recycle delay of 2 s. To the left of the graph is indicated the  $^1\text{H}$  single pulse spectrum (eight scans). Green and yellow correlations correspond to the alkydine  $[W] = \text{CHtBu}$  and methylene  $[W]-\text{CH}_2\text{tBu}$  moieties, respectively.





**Fig. S6.** Comparison of the metathesis activity, expressed in Turn over numbers vs. time, in the metathesis of propene in a flow reactor with  $[2/\text{SiO}_2]$   $\{[(\equiv\text{SiO})\text{W}(\equiv\text{NAr})(=\text{CHtBu})(2,5\text{-Me}_2\text{NC}_4\text{H}_2)]$  (compound 1) (■) vs. the mixture of tungsten methylidene  $[(\equiv\text{SiO})\text{W}(\equiv\text{NAr})(=\text{CH}_2)(2,5\text{-Me}_2\text{NC}_4\text{H}_2)]$  (compound 4) and metallacyclobutane  $[(\equiv\text{SiO})\text{W}(\equiv\text{NAr})(\text{CH}_2\text{CH}_2\text{CH}_2)(2,5\text{-Me}_2\text{NC}_4\text{H}_2)]$  (compound 5) (□) (products obtained by contacting  $[2/\text{SiO}_2]$  with ethylene).

**Table S1. Discernable  $^{13}\text{C}$  NMR signals of  $[(=\text{SiO})\text{W}(=\text{NAr})(=\text{CHtBu})(2,5\text{-Me}_2\text{NC}_4\text{H}_2)]$  (compound 1) and  $[(=\text{SiO})\text{W}(=\text{NAr})(\text{CH}_2\text{tBu})(2,5\text{-Me}_2\text{NC}_4\text{H}_2)_2]$  (compound 3) in the  $^{13}\text{C}$  CP MAS solid-state NMR data**

| Complexes        | $^{13}\text{C}$ NMR, ppm | Assignment  |
|------------------|--------------------------|---|
| 1 + 3            | 15                       | 2,5-Me <sub>2</sub> C <sub>4</sub> H <sub>2</sub>                       |
|                  | 22                       | CH <sub>3</sub> , <i>i</i> Pr   |
|                  | 29                       | C(CH <sub>3</sub> ) <sub>3</sub>  |
|                  | 29                       | CH, <i>i</i> Pr   |
|                  | 55                       | =CHC(CH <sub>3</sub> ) <sub>3</sub>                                     |
|                  | 69 <sup>†</sup>          | CH <sub>2</sub> tBu   |
|                  | 107                      | C <sub>ortho</sub> (2,5-Me <sub>2</sub> C <sub>4</sub> H <sub>2</sub> ) |
|                  | 125                      | C <sub>meta</sub> (2,5-Me <sub>2</sub> C <sub>4</sub> H <sub>2</sub> )  |
|                  | 122–153                  | ArC   |
| 260 <sup>‡</sup> | =CHtBu                   |   |

<sup>†</sup>This signal belongs to  $[(=\text{SiO})\text{W}(=\text{NAr})(\text{CH}_2\text{tBu})(2,5\text{-Me}_2\text{NC}_4\text{H}_2)_2]$  (compound 3).

<sup>‡</sup>Only observed when using 33%  $^{13}\text{C}$ -labeled on the  $\alpha$  carbons  $[(=\text{SiO})\text{W}(=\text{NAr})(=\text{*CHtBu})(2,5\text{-Me}_2\text{NC}_4\text{H}_2)]$  (compound 1\*).