Supplementary Information

Influence of Functional Groups on Ethylene Polymerization Performance of Silsesquioxane-Supported Phillips-Type Catalyst

Ryuki Baba, Ashutosh Thakur, Patchanee Chammingkwan, Minoru Terano and Toshiaki Taniike*

Graduate School of Advanced Science and Technology, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan

* Corresponding Author:

Tel: +81-761-51-1630; Fax: +81-761-51-1635; E-mail: taniike@jaist.ac.jp

Contents

A. NMR spectra of modified POSS (**1a-1d**)

(^{i}Bu)$_7$Si$_7$O$_9$(OH)$_2$(OSiMe$_3$) (**1a**)

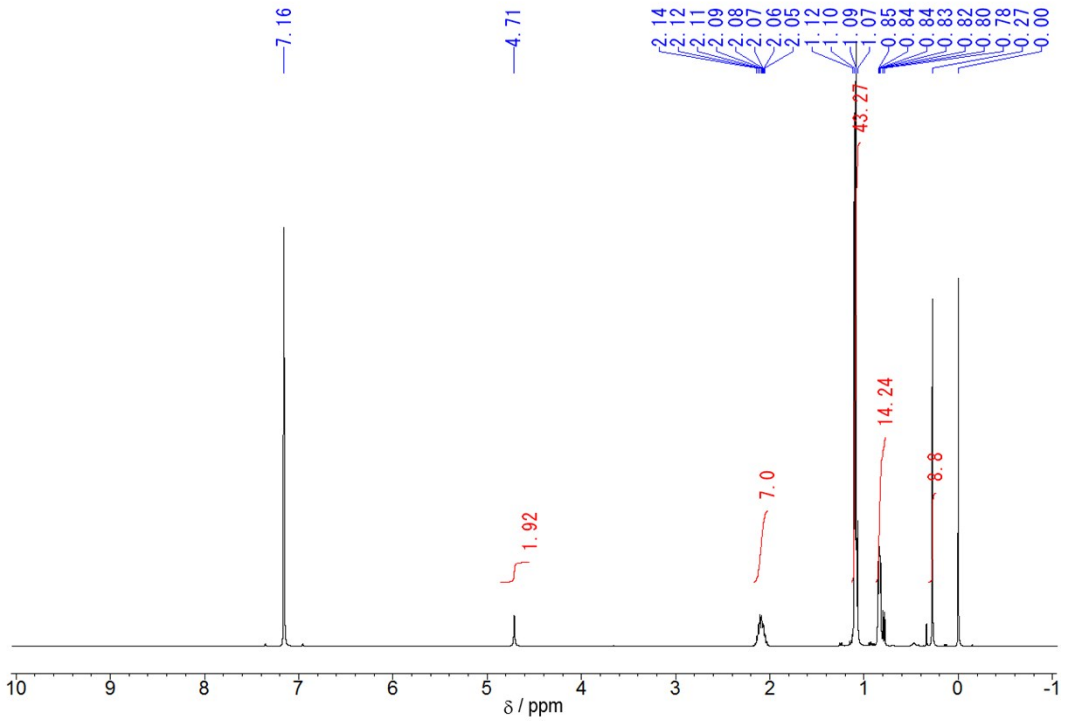

Figure S1.1. ^{1}H NMR spectrum of **1a** in benzene-d_6 at r.t. (400 MHz).

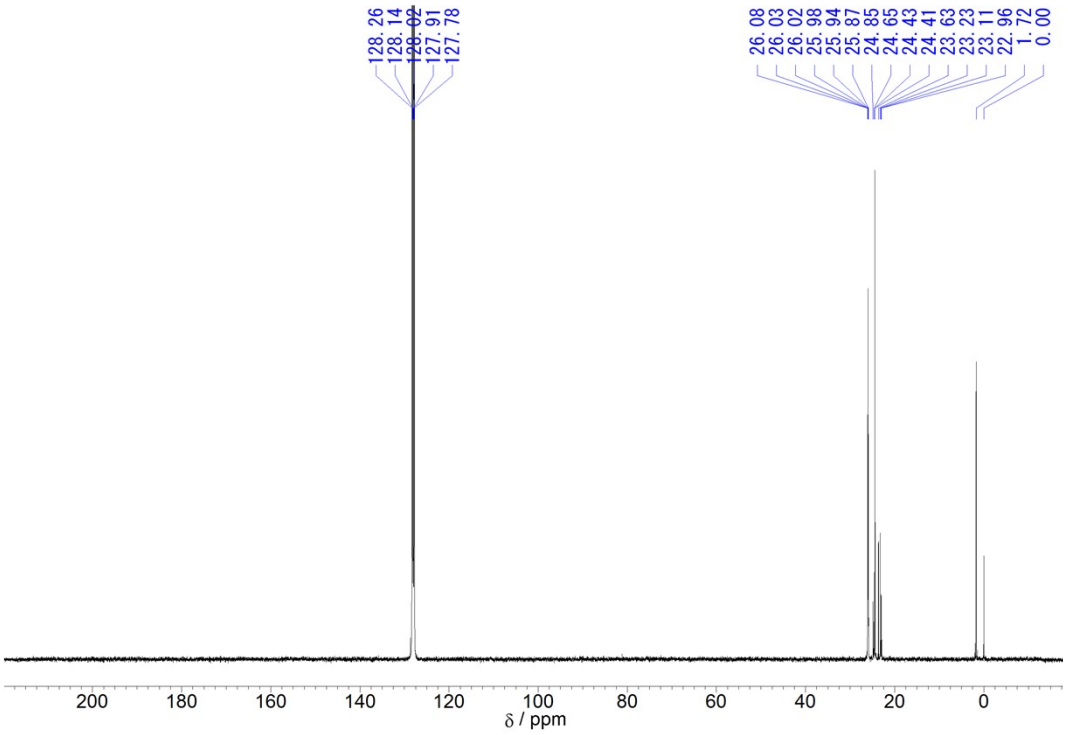

Figure S1.2. ^{13}C{^{1}H} NMR spectrum of **1a** in benzene-d_6 at r.t. (100 MHz).

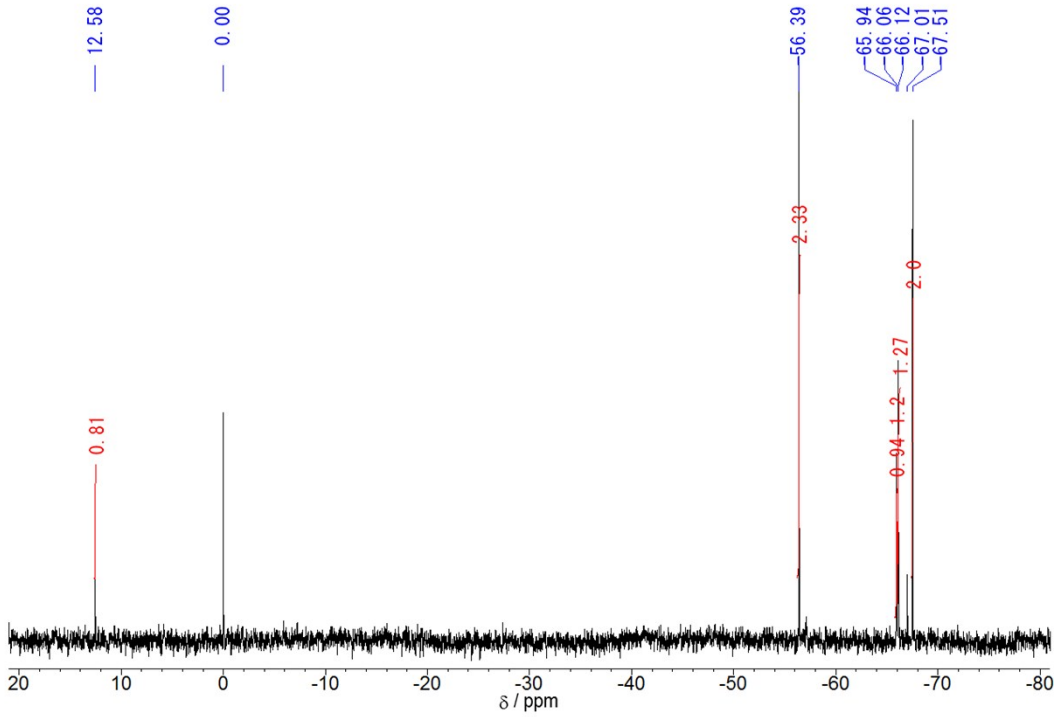

Figure S1.3. $^{29}Si\{^{1}H\}$ NMR spectrum of **1a** in benzene-d_6 at r.t. (79 MHz).

(^{t}Bu)$_7$Si$_7$O$_9$(OH)$_2$(OSiMe$_2$Ph) (**1b**)

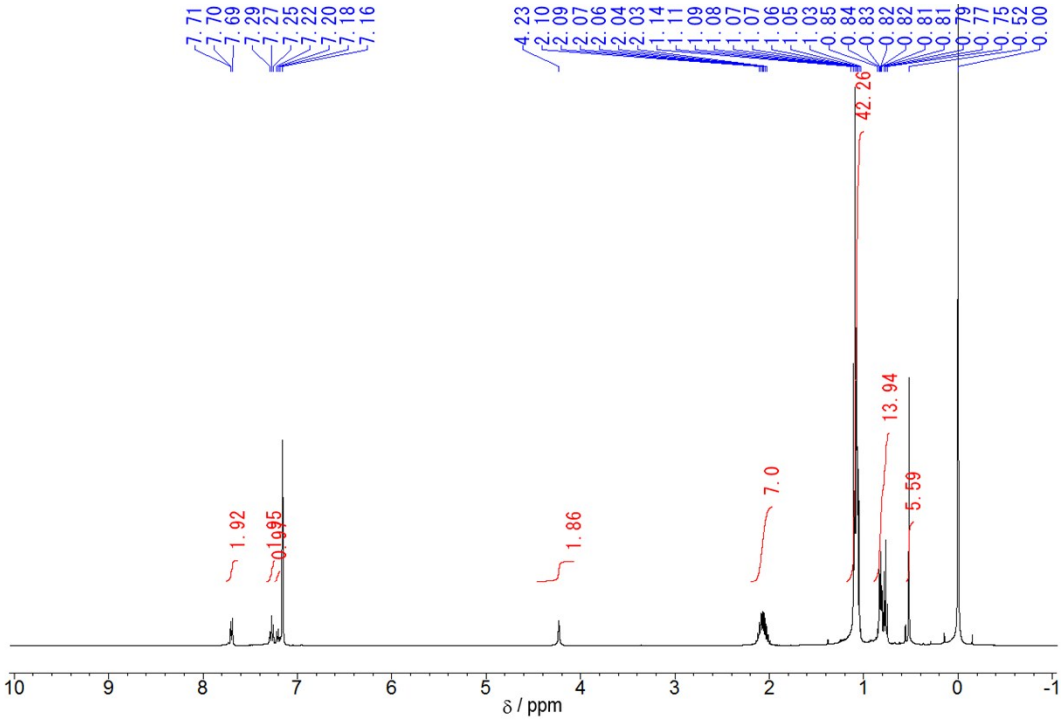

Figure S2.1. ^{1}H NMR spectrum of **1b** in benzene-d_6 at r.t. (400 MHz).

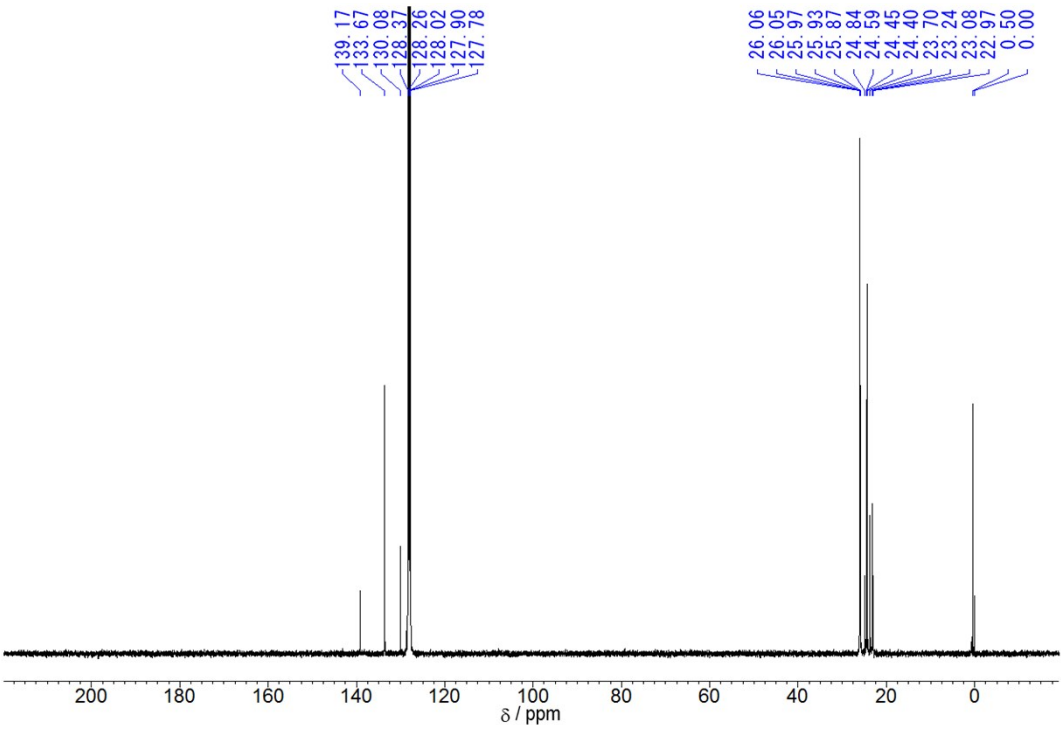

Figure S2.2. $^{13}C\{^{1}H\}$ NMR spectrum of **1b** in benzene-d_6 at r.t. (100 MHz).

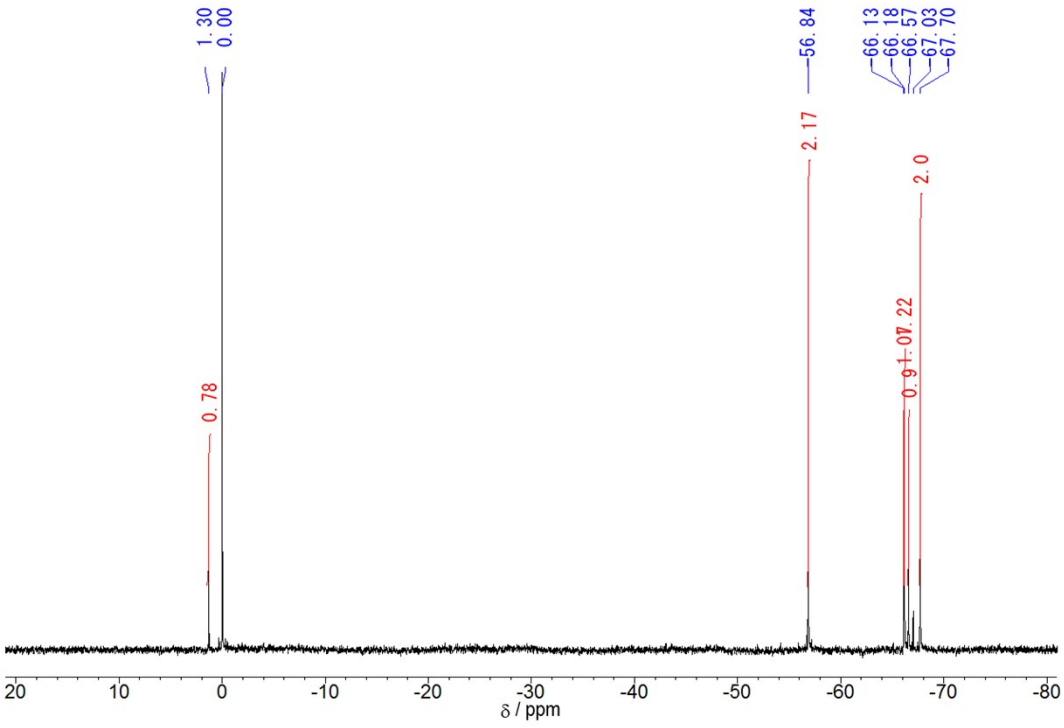

Figure S2.3. $^{29}Si\{^{1}H\}$ NMR spectrum of **1b** in benzene-d_6 at r.t. (79 MHz).

(^{i}Bu)$_7$Si$_7$O$_9$(OH)$_2$[OSiMe$_2$C$_6$H$_4$(OMe-2)] (**1c**)

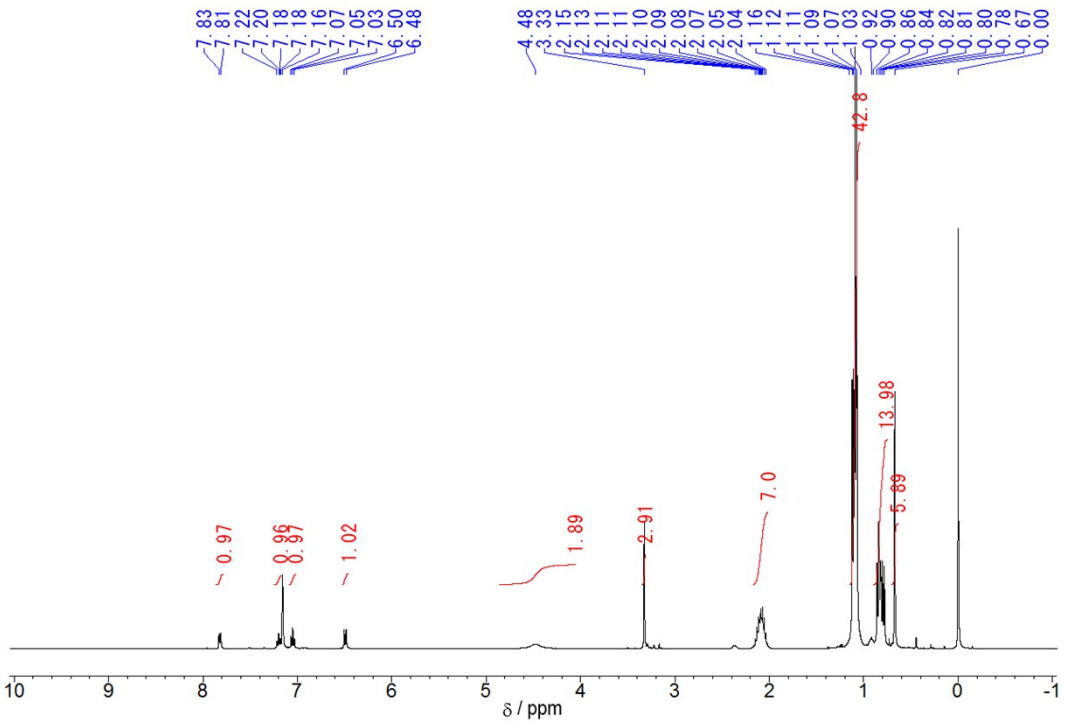

Figure S3.1. ^{1}H NMR spectrum of **1c** in benzene-d_6 at r.t. (400 MHz).

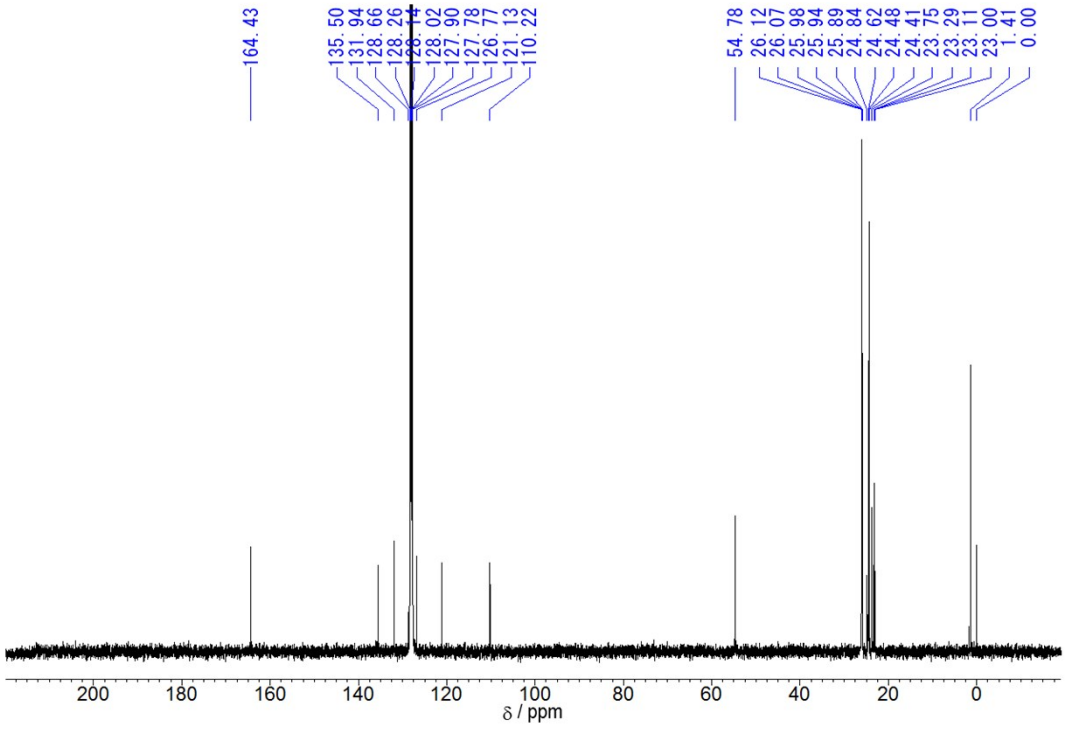

Figure S3.2. $^{13}C\{^{1}H\}$ NMR spectrum of **1c** in benzene-d_6 at r.t. (100 MHz).

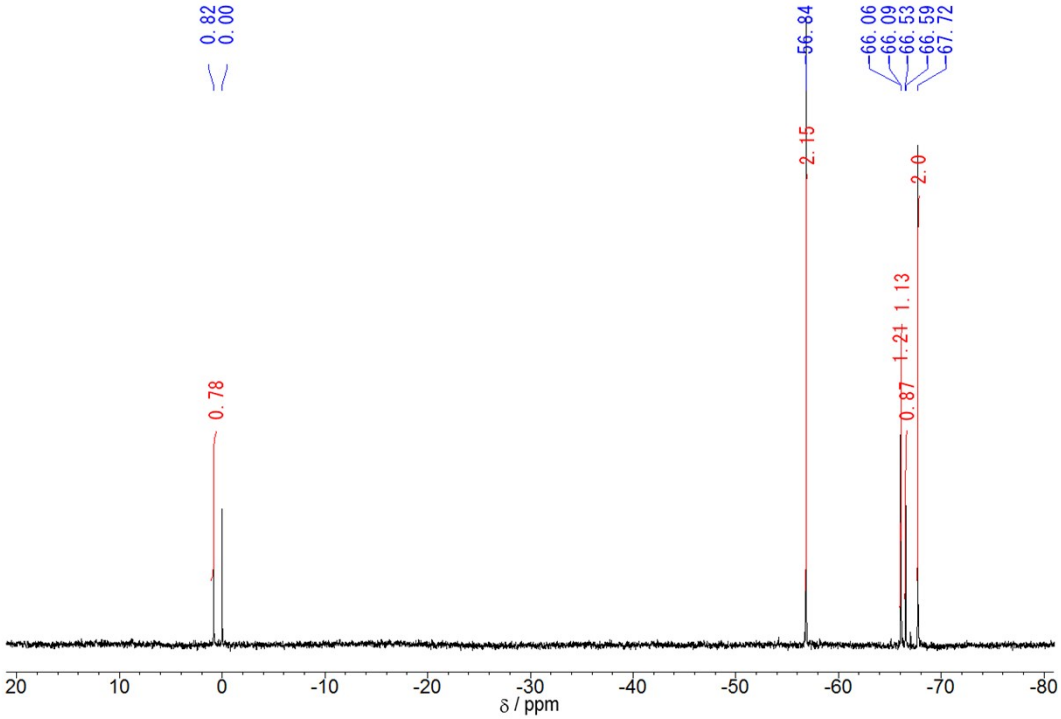

Figure S3.3. $^{29}Si\{^{1}H\}$ NMR spectrum of **1c** in benzene-d_6 at r.t. (79 MHz).

(^{t}Bu)$_7$Si$_7$O$_9$(OH)$_2$[OSiMe$_2$C$_6$H$_4$(PPh$_2$-2)] (**1d**)

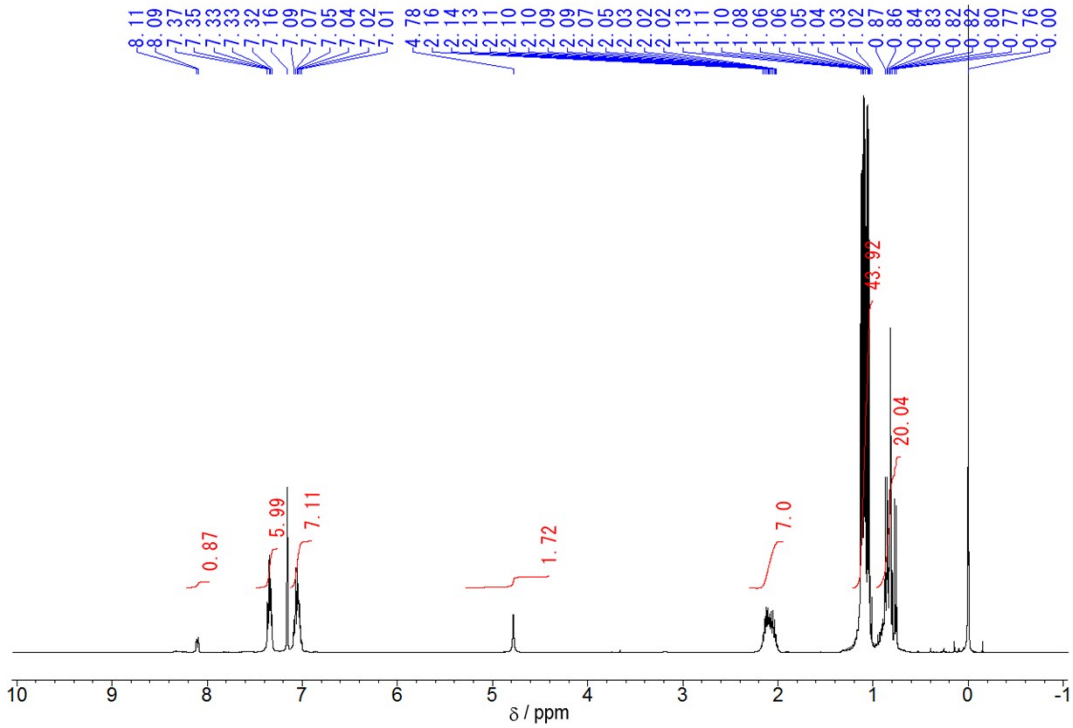

Figure S4.1. ^{1}H NMR spectrum of **1d** in benzene-d_6 at r.t. (400 MHz).

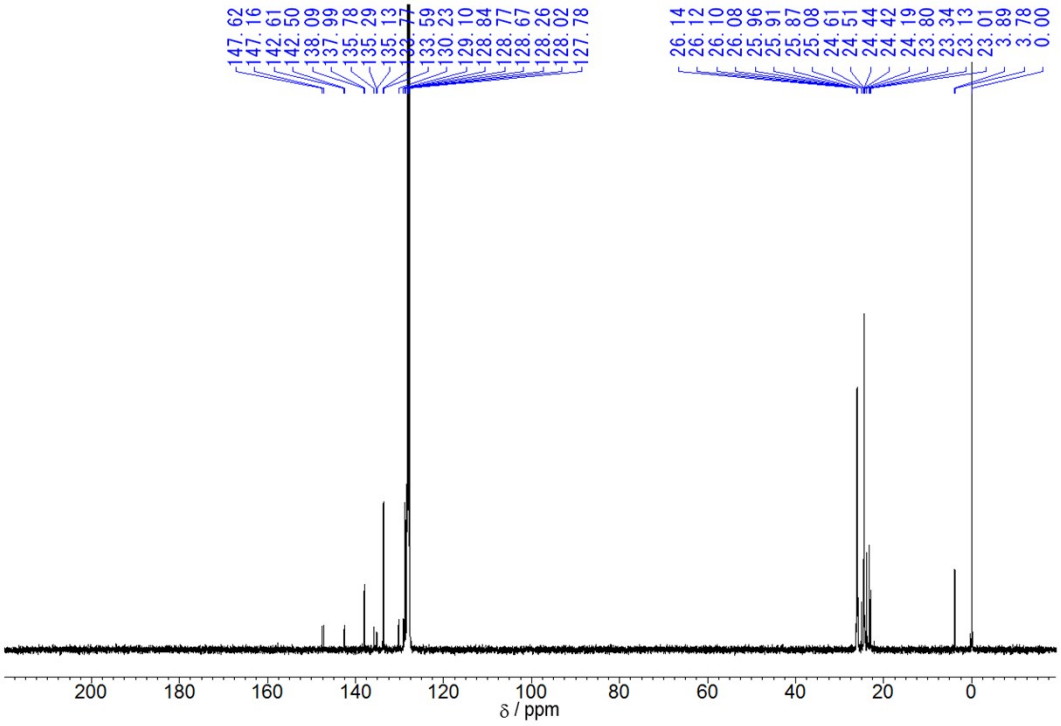

Figure S4.2. ^{13}C{^{1}H} NMR spectrum of **1d** in benzene-d_6 at r.t. (100 MHz).

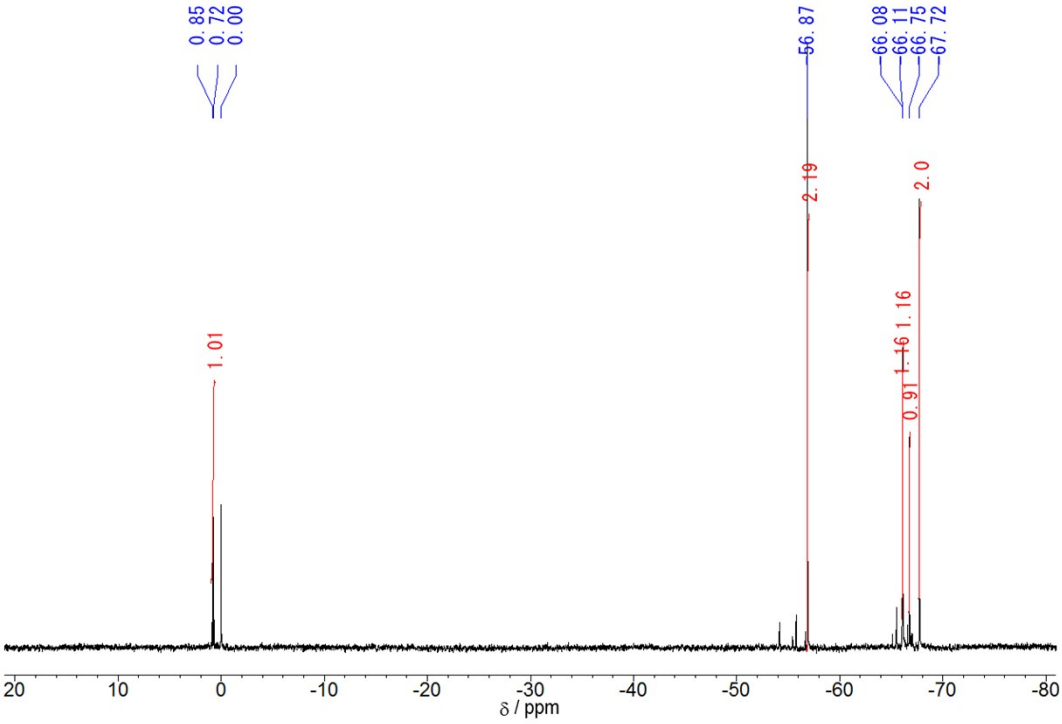

Figure S4.3. ^{29}Si{^{1}H} NMR spectrum of **1d** in benzene-d_6 at r.t. (79 MHz).

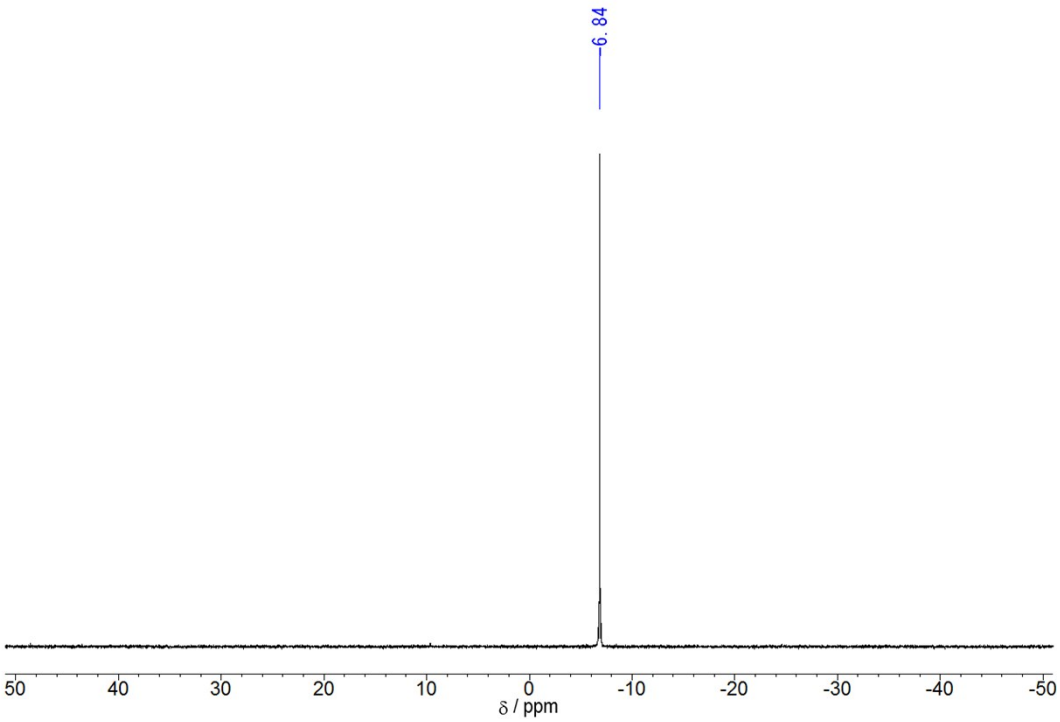

Figure S4.4. $^{31}P\{^{1}H\}$ NMR spectrum of **1d** in benzene-d_6 at r.t. (162 MHz).

B. NMR spectra of POSS supported chromium catalysts (**2a**-**2d**)

[(^{i}Bu)$_7$Si$_7$O$_{11}$(OSiMe$_3$)]CrCH(SiMe$_3$)$_2$ (**2a**)

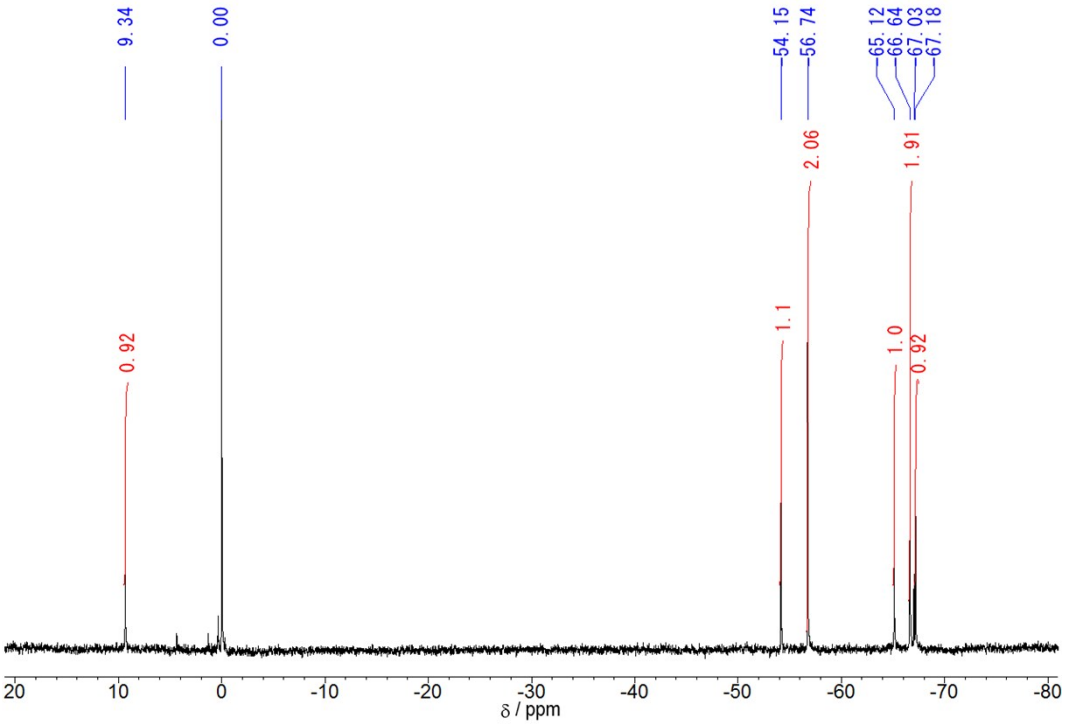

Figure S5.1. ^{29}Si{^{1}H} NMR spectrum of **2a** in benzene-d_6 at r.t. (79 MHz).

(^{i}Bu)$_7$Si$_7$O$_{11}$(OSiMe$_2$Ph)]CrCH(SiMe$_3$)$_2$ (**2b**)

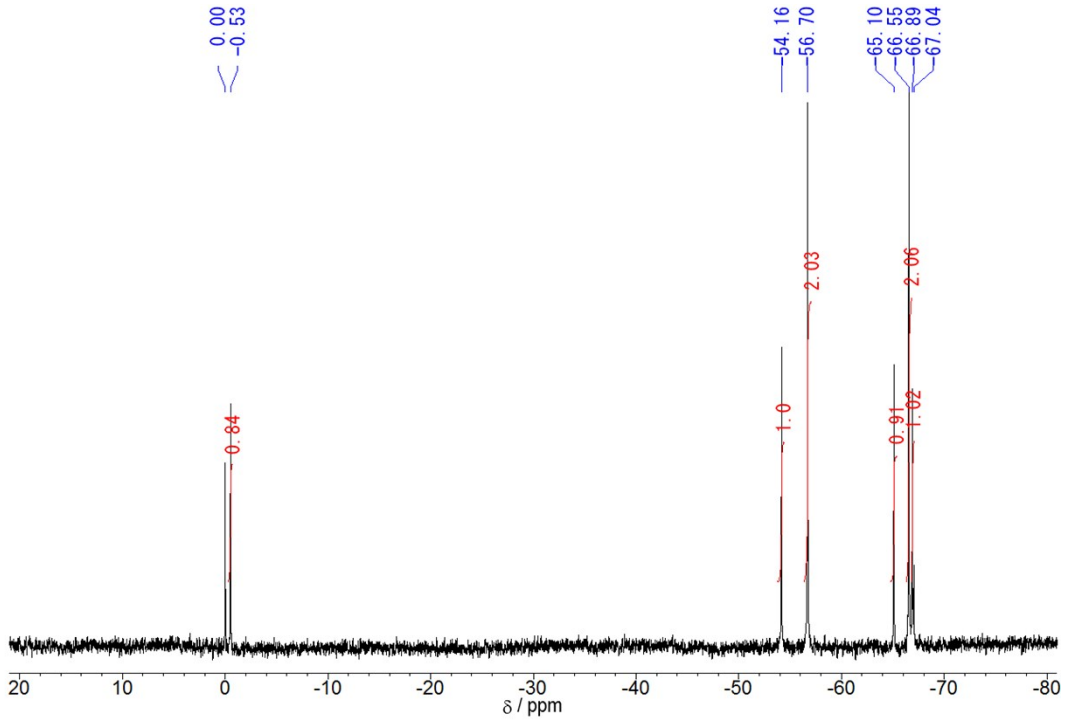

Figure S6. ^{29}Si{^{1}H} NMR spectrum of **2b** in benzene-d_6 at r.t. (79 MHz).

{(^{t}Bu)$_7$Si$_7$O$_{11}$[OSiMe$_2$C$_6$H$_4$(OMe-2)]}CrCH(SiMe$_3$)$_2$ (**2c**)

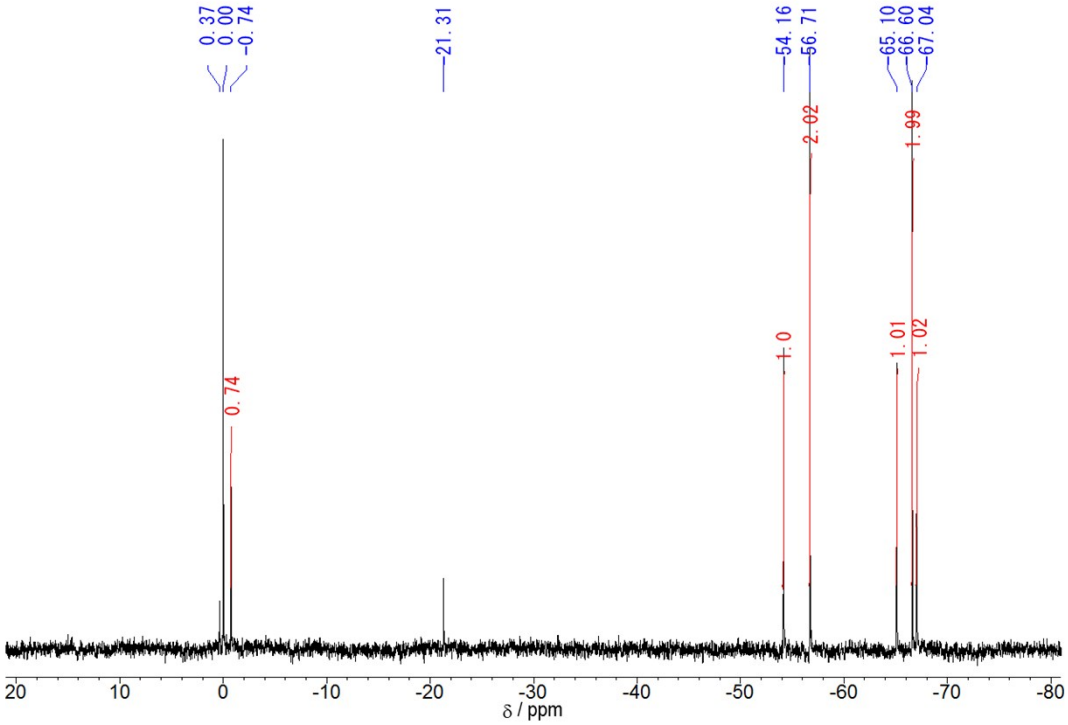

Figure S7. ^{29}Si{^{1}H} NMR spectrum of **2c** in benzene-d_6 at r.t. (79 MHz).

{(^{t}Bu)$_7$Si$_7$O$_{11}$[OSiMe$_2$C$_6$H$_4$(PPh$_2$-2)]}CrCH(SiMe$_3$)$_2$ (**2d**)

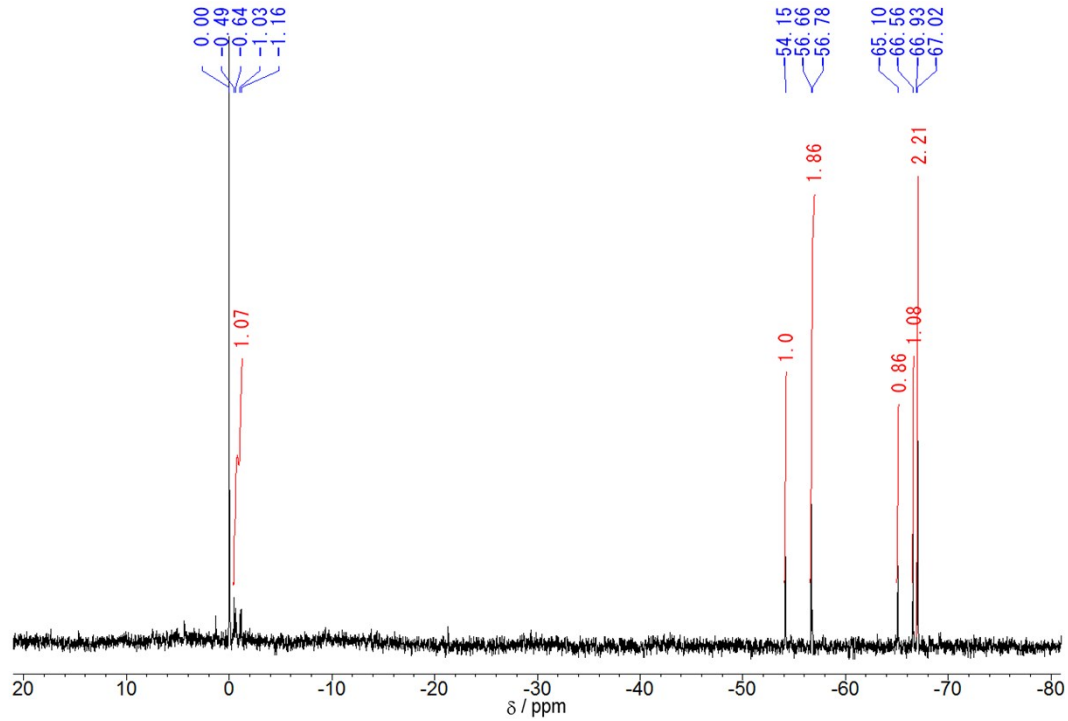

Figure S8.1. ^{29}Si{^{1}H} NMR spectrum of **2d** in benzene-d_6 at r.t. (79 MHz).

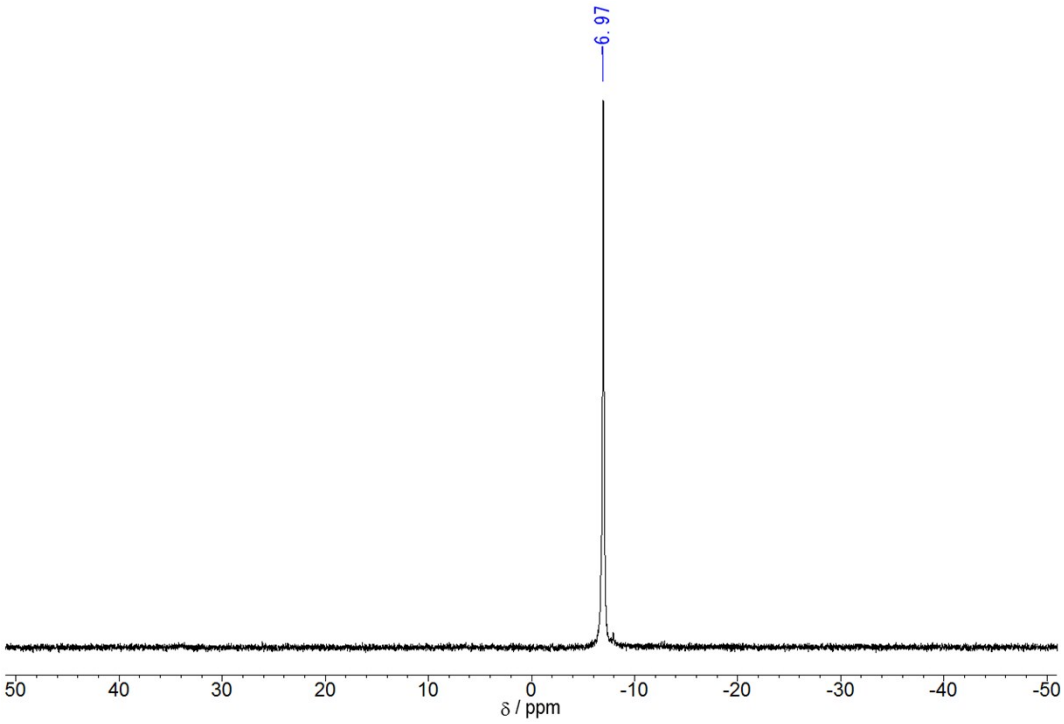

Figure S8.2. ^{31}P NMR spectrum of **2d** in benzene-d_6 at r.t. (162 MHz).

C. UV/vis spectra measurement

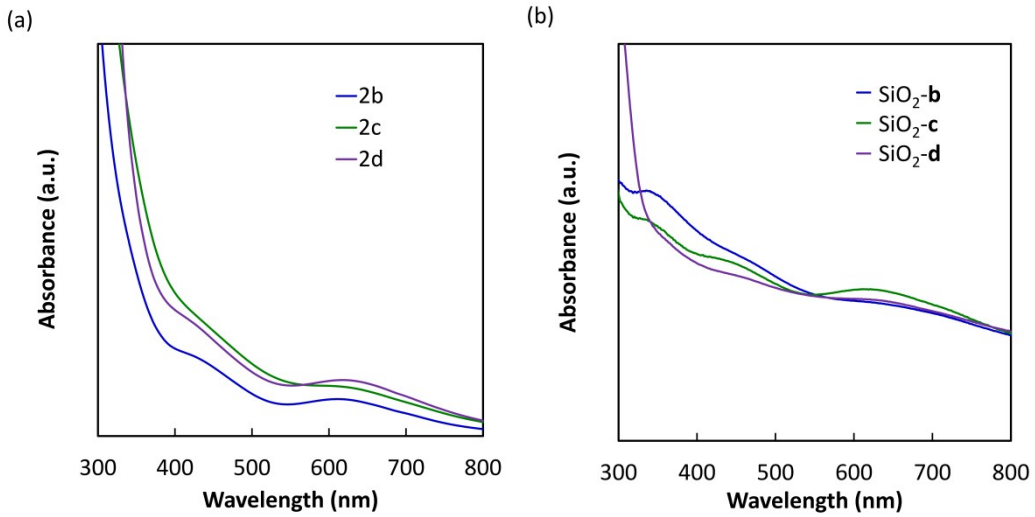

Figure S9. UV/vis (DRS) spectra of a) POSS-supported catalysts (**2a**-**2d**) and b) SiO_2-supported catalysts (SiO_2-**b**-**d**).

D. Assignment and analytical method in NMR for polyethylene

Figure S10 reports typical $^{13}C\{^{1}H\}$ and ^{1}H NMR spectra of the obtained PE (entries 3 and 5 in **Table 1**). The chemical shift was referenced to methyl carbon (1.98 ppm) and methyl proton (0.09 ppm) of hexamethyldisiloxane (HMDS) in $^{13}C\{^{1}H\}$ and ^{1}H NMR, respectively. The peak assignments have been done based on Refs. [1] and [2]. The fractions of methyl branches and the saturated ends were determined from $^{13}C\{^{1}H\}$ NMR based on the following equations.

Eq. (1) $$\text{Fraction } of\ methyl\ branch\ (/1000C) = I_{B1}/I_{totalC} \times 1000$$

Eq. (2) $$\text{Fraction } of\ saturated\ end\ (/1000C) = I_{S}/I_{totalC} \times 1000$$

Eq. (3) $$I_{B1} = (I_{1B1} + I_{brB1} + I_{\alpha B1})/4$$

Eq. (4) $$I_{S} = (I_{1S} + I_{2S} + I_{3S})/3$$

Eq. (5) $$I_{totalC} = I_{Main\ chain}$$

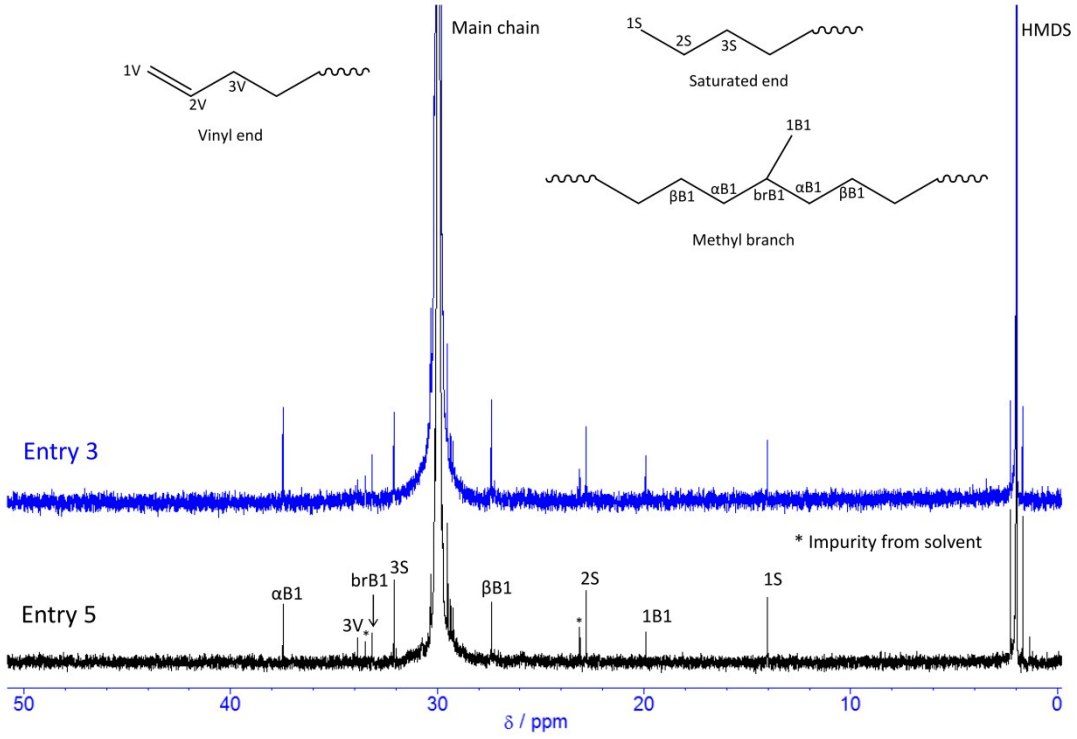

Figure S10.1. $^{13}C\{^{1}H\}$ NMR spectra of typical PE (100 MHz).

The fraction of the vinyl ends were determined from ^{1}H NMR based on the following equations.

Eq. (6) $$Fraction\ of\ vinyl\ end\ (/1000C)\ =\ {}^{I_{Vi}}/_{I_{total}} \times 1000$$

Eq. (7) $$I_{Vi} = (I_{1V} + I_{2V})/3$$

Eq. (8) $$I_{total} = (I_{Main\ chain})/2$$

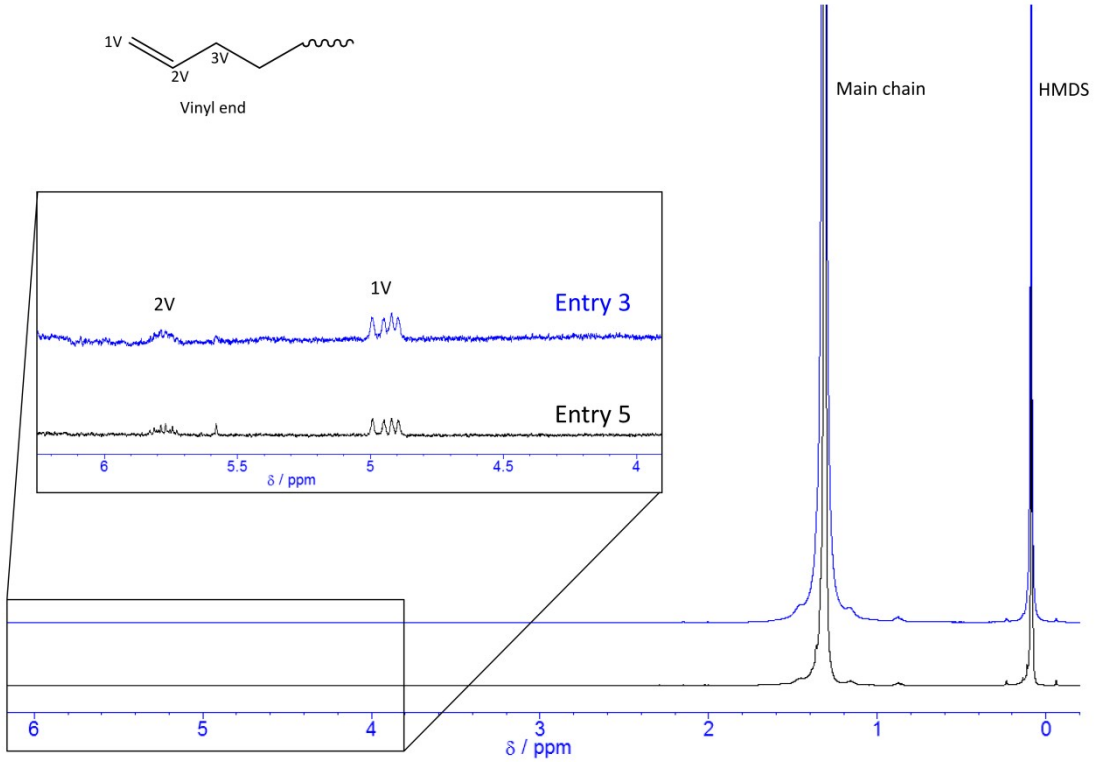

Figure S10.2. ^{1}H NMR spectra of typical PE (400 MHz).

References

[1] B. Qu, X. Qu, Y. Xu, U. Jacobsson, B. Rånby, K. E. Russell and W. E. Baker, *Macromolecules*, 1997, **30**, 1408.

[2] E. W. Hansen, R. Blom and O. M. Bade, *Polymer*, 1997, **38**, 4295.