# Supporting Information for

## Controlled synthesis cyclosiloxanes by NHC-catalyzed hydrolytic oxidation of dihydrosilanes

Guoping Qin, Chunming Cui*

*State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071; Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), 300072, Tianjin, China*

E-mail: cmcui@nankai.edu.cn

**Contents**

**General Conditions.** $CH_3CN$ was dried over $P_2O_5$ and distilled prior to use. Commercial hydrosilanes were purchased from alpha and purified by distillation. The N-heterocyclic carbene 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (I*i*Pr) was prepared according to literature.[S1] The other hydrosilanes used in this work were prepared according to literature[S2] or by modified procedures. Elemental analysis was carried out on an Elemental Vario EL analyzer. The $^1H$, $^{13}C$ and $^{29}Si$ spectra were recorded on a Bruker Mercury Plus 400 NMR spectrometers. Chemical shifts are referenced against external $Me_4Si$ ($^1H$, $^{13}C$).

**Solvent effects for the hydrolysis of $Ph_3SiH$**

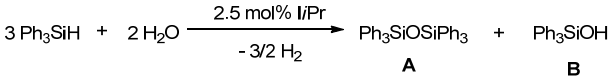



**Table S1** Solvent effects for the hydrolysis of $Ph_3SiH$

| Entry | solvent | Time (h) | product ( **A**:**B**) |
|---|---|---|---|
| 1 | THF | 3 | 30:70 |
| 2 | THF | 5 | 98:2 |
| 3 | $CH_3CN$ | 2 | >99:0 (not detected) |

Conditions: 0 °C, reactions with 6 equivalents of water, proton NMR ratio

**General Procedure for Catalytic Hydrolysis of Hydrosilanes in $CH_3CN$.** In a glovebox, I*i*Pr (0.1%, 0.9 mg, 0.005 mmol) and a hydrosilane (5 mmol) were added into a Schlenk tube. The Schlenk tube was removed from the glove box and was placed in an oil bath at a specified temperature for a specific time. To this mixture was added 1 mL of $CH_3CN$ containing water (5.0 M of $H_2O$ in $CH_3CN$) by syringe. In most cases, vigorous evolution of $H_2$ was noted. The reaction was monitored by thin layer chromatography (TLC). After the reaction was completed, the solvent was removed under vacuum and the product was purified by flash column chromatography on neutral $Al_2O_3$ using *n*-hexane/ethyl acetate (10:1) as eluent or was washed with *n*-hexane.

**General Procedure for Catalytic Hydrolysis of Hydrosilanes under Solvent-Free Conditions.** I*i*Pr (2.5%, 0.0072 g, 0.04 mmol) and a hydrosilane (1.6 mmol) were added into a Schlenk tube. Then the Schlenk tube was placed in an oil bath at a specified temperature. Then $H_2O$ (16 mmol) was added to the solution by syringe. The mixture was heated to 60 or 90 °C for a specific time. In most cases, vigorous evolution of $H_2$ was noted. The reaction was monitored by TLC. After the reaction was completed, the product was purified by flash column chromatography on neutral $Al_2O_3$ using *n*-hexane/ethyl acetate (10:1) as eluent or was washed with *n*-hexane.

**Reactions in $CH_3CN$ and Spectroscopic Data for the Si–O Coupling Products**

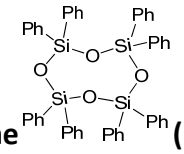
**$Et_3SiOSiEt_3$.**[S3] 3 h at room temperature, colorless oil, 90% yield. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 0.94 (t, $J$ = 8.0 Hz , 18H, $CH_2CH_3$), 0.52 (q, $J$ = 8.0 Hz, 12H, $CH_2CH_3$); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta$ 6.95 ($CH_2CH_3$), 6.58 ($CH_2CH_3$); $^{29}Si$ NMR (79 MHz, $CDCl_3$): $\delta$

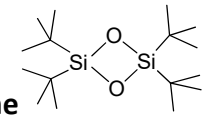
78.8 (s).

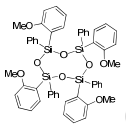
**$Ph_3SiOSiPh_3$.**[S4] 1 h at room temperature, white solid, 98% yield. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.51-7.49 (m, 12H, *o*-$C_6H_5$), 7.42-7.38 (m, 6H, *p*-$C_6H_5$), 7.31-7.27 (m, 12H, *m*-$C_6H_5$); $^{13}C\{^1H\}$ NMR (101MHz, $CDCl_3$): $\delta$ 135.48, 135.23, 129.83, 127.74; $^{29}$Si NMR (79 MHz, $CDCl_3$): $\delta$ -18.57 (s) .

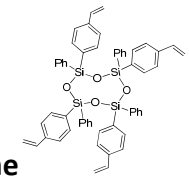
**$(EtO)_3SiOSi(OEt)_3$.**[S3] 2 h at room temperature, colorless oil, 88% yield. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 3.64 (q, $J$ = 7.1 Hz, 12H, $CH_2CH_3$), 1.20 (t, $J$ = 7.1 Hz, 18H, $CH_2CH_3$); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$):$\delta$ 57.31 ($CH_2CH_3$), 17.98 ($CH_2CH_3$); $^{29}$Si NMR (79 MHz, $CDCl_3$): $\delta$ 8.87 (s).

**$PhMe_2SiOSiPhMe_2$.**[S4] 1 h at room temperature, colorless oil, 95% yield. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.62-7.60 (m, 4H, *o*-$C_6H_5$), 7.43-7.38 (m, 6H, *m, p*- $C_6H_5$), 0.38 (s, 12H, *Me*); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta$ 139.96, 133.15, 129.40, 127.86, ($C_6H_5$), 1.01 ($Me_2$); $^{29}$Si NMR (79 MHz, $CDCl_3$): $\delta$ 1.17 (s).

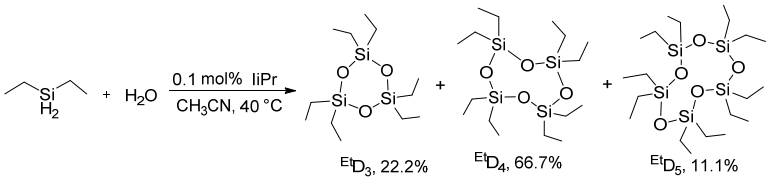
**Hydrolysis of Diphenylsilane**  **($D_4$).**[S5] 5 min at room temperature, white solid, 91% yield. $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ 7.72-7.70 (d, $J$ = 8 Hz, 16H, *o*-$C_6H_5$), 7.13-7.09 (t, $J$ = 8.0 Hz, 8H, *p*-$C_6H_5$), 7.05-7.01 (t, $J$ = 8 Hz, 16H, *m*-$C_6H_5$); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta$ 134.49, 134.45, 130.12, 127.70, ($C_6H_5$); $^{29}$Si NMR (79 MHz, $C_6D_6$): $\delta$ -42.82 (s, *Si*).

**Hydrolysis of Di(*tert*)butylsilane**  **($^{tBu}D_2$).** 12 h at 40°C, white solid, 83 % yield. $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ 1.05 (s, 36H, $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR (101 MHz, $C_6D_6$): $\delta$ 27.31 ($C(CH_3)_3$), 19.79 ($C(CH_3)_3$); $^{29}$Si NMR (79 MHz, $CDCl_3$): $\delta$ -7.19 (s, *Si*); MS (EI): *m/z* 176.1 $[^{tBu}D_2/2+H_2O]^+$. The NMR spectra are given in Figures S1-S3.

**Hydrolysis of *o*-methoxy-phenylphenylsilane**  **($^{OMe}D_4$).** 6 min at room temperature, white solid, 92% yield. $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ 7.92-7.89 (2H), 7.83-7.81 (2H), 7.57-7.54 (4H), 7.50-7.46 (2H), 7.42-7.32 (5H), 7.29-7.27 (2H), 7.25-7.04 (11H), 6.77-6.52 (6H), 6.28-6.22 (2H), 3.37 (s, 3H), 3.30 (s, 3H), 2.98 (s, 3H), 2.84 (s, 3H). $^{13}C\{^1H\}$ NMR (101MHz, $CDCl_3$): $\delta$ 139.00, 136.88, 134.61, 134.45, 134.30, 133.92, 130.09, 127.69, 125.42, 114.60 (*o*-$OCH_3$-$C_6H_4$,$C_6H_5$), 53.88 (O*Me*); $^{29}$Si NMR (79 MHz, $C_6D_6$): $\delta$ -42.82 (s, *Si*); MS (ESI): *m/z* 930.2736 $[^{OMe}D_4+H_2O]^+$. The NMR spectra are given in Figures S4-S6.

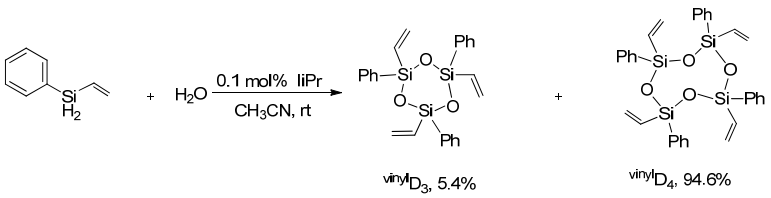
**Hydrolysis of *p*-vinyl-phenylphenylsilane**  **($^{p\text{-viny}}D_4$).** 7 min at room temperature, white solid, 90% yield. $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ 7.80-7.77 (m, 8H ), 7.69-7.65 (m, 8H), 7.13-7.07 (m, 20H, $C_6H_5$), 6.53-6.45 (dd, $J$ = 12 Hz, 4H, C$H$CH$_2$), 5.59-5.54 (d, $J$ = 12 Hz, 4H, CHC$H_2$), 5.07-5.02 (d, $J$ = 12 Hz, 4H, CHC$H_2$); $^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$): $\delta$ 139.00, 136.88, 134.61, 134.45, 134.30, 133.92, 130.09, 127.69 (*p*-$C_2H_3C_6H_4$, $C_6H_5$), 125.42 ($C$HCH$_2$), 114.60 (CH$C$H$_2$); $^{29}$Si NMR (79 MHz, $CDCl_3$): $\delta$ -42.94 (s, *Si*); MS (ESI): *m/z* 914.2942 [$^{p\text{-viny}}D_4$+$H_2O$]$^+$. The NMR spectra are given in Figures S7-S9.

**Hydrolysis of Diethylsilane.**[S6]



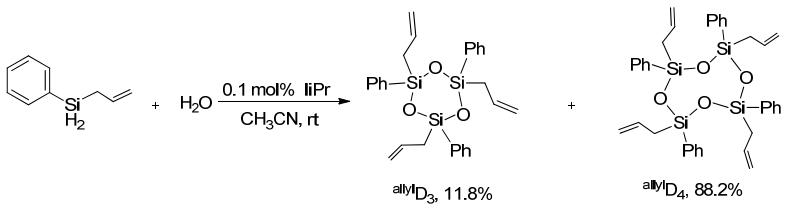

12 h at 40°C, colorless oil, 83% yield. A mixture containing $^{Et}D_3$, $^{Et}D_4$and $^{Et}D_5$ were obtained, the ratio of $^{Et}D_3$/$^{Et}D_4$/$^{Et}D_5$ = 22 /67/11 estimated by GC-MS. $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ 1.10-1.06 (t, $J$ = 8 Hz, $CH_2CH_3$), 0.66-0.64 (q, $J$ = 8 Hz, $CH_2CH_3$). GC-MS: *m/z* 481.2 [$D_5$-$C_2H_5$]$^+$, 379.0 [$D_4$-$C_2H_5$]$^+$, 277.0 [$D_3$-$C_2H_5$]$^+$. The $^1$H NMR spectrum and GC-MS spectra are given in Figures S10-S14.

**Hydrolysis of Vinylphenylsilane.**[S7]



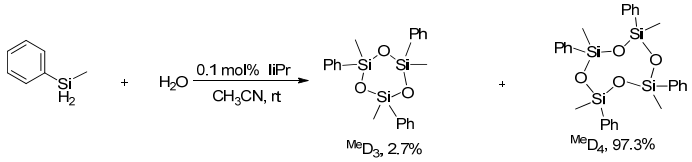

12 min at room temperature, colorless oil, 88% yield. A mixture containing $^{viny}D_3$ and $^{viny}D_4$ were obtained, the ratio of $^{viny}D_3$ and $^{viny}D_4$ = 5/95 estimated by GC-MS. $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ 7.93-7.62, 7.25-7.02 ($C_6H_5$), 6.39-5.75 ($C_2H_3$). MS (EI): *m/z* 714.0 [$^{viny}D_5$-$C_2H_3$]$^+$, 565.1 [$^{viny}D_4$-$C_2H_3$]$^+$. The $^1$H NMR spectrum and GC-MS spectra are given in Figures S15-S18.

**Hydrolysis of Allylphenylsilane.**




16 min at room temperature. Colorless oil. 85% yield. A mixture containing $^{ally}D_3$ and $^{ally}D_4$ were obtained, the ratio of $^{ally}D_3$ and $^{ally}D_4$ = 12/88 estimated by GC-MS. $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ 7.90-7.47, 7.29-6.98 (m, $C_6H_5$), 6.09-5.55 ($CH_2CH$=$CH_2$), 5.15-4.64 ($CH_2CH$=C$H_2$), 2.09-1.69 (C$H_2$CH=$CH_2$). MS (EI): *m/z* 649.2 $[^{allyl}D_4]^+$, 607.2 $[^{ally}D_4\text{-}C_3H_5]^+$, 571.2 $[^{ally}D_4\text{-}C_6H_5]^+$, 549.1 $[^{ally}D_4\text{-}C_6H_5\text{-}C_3H_5\text{+}H_2O]^+$, 487.1 $[^{allyl}D_3]^+$, 447.1 $[^{ally}D_3\text{-}C_3H_5]^+$, 409.0 $[^{ally}D_3\text{-}C_6H_5]^+$. The $^1$H NMR spectrum and GC-MS spectra are given in Figures S19-S22.

**Hydrolysis of Methylphenylsilane.**[S8]




6 min at room temperature, colorless oil, 92% yield. A mixture containing $^{CH3}D_3$ and $^{CH3}D_4$ were obtained, the ratio of $^{CH3}D_3$ and $^{CH3}D_4$ = 3/97 estimated by GC-MS. $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ 7.84-7.49, 7.27-7.04 (m, $C_6H_5$), 0.56-0.26 (*Me*). MS (EI): *m/z* 529.2 $[^{CH3}D_4\text{-}CH_3]^+$, 451.1 $[^{CH3}D_4\text{-}C_6H_5\text{-}CH_3]^+$, 393.2 $[^{CH3}D_3\text{-}CH_3]^+$, 315.1 $[^{CH3}D_3\text{-}C_6H_5\text{-}CH_3]^+$. The $^1$H NMR spectrum and GC-MS spectra are given in Figures S23-S26.

## 3. Reactions under solvent-free conditions and spectroscopic data for the Si–O coupling products

**Hydrolysis of Diphenylsilane ($D_4$).**[5] 10 h at 90 °C, white solid, 90% yield. Spectroscopic data are the same as those obtained in $CH_3CN$.

**Hydrolysis of Di(*tert*)butylsilane($^{tBu}D_2$).** 5 h at 60 °C, white solid, 83% yield. Spectroscopic data are the same as those obtained in $CH_3CN$.

**Hydrolysis of *o*-methoxy-phenylphenylsilane($^{OMe}D_4$).** 12 h at 60 °C, white solid, 95% yield. Spectroscopic data are the same as those obtained in $CH_3CN$.

**Hydrolysis of *p*-vinyl-phenylphenylsilane($^{p\text{-}vinyl}D_4$).** 10 h at 90 °C, white solid, 90% yield. Spectroscopic data are the same as those obtained in $CH_3CN$.

**Hydrolysis of Diethylsilane.** 6 h at 60 °C, colorless oil, 90% yield. A mixture containing $^{Et}D_3$,$^{Et}D_4$ and $^{Et}D_5$ were obtained, the ratio of $^{Et}D_3$/$^{Et}D_4$/$^{Et}D_5$ = 7/56/37 estimated by GC-MS. $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ 1.10-1.06 (t, *J* = 8 Hz, $CH_2CH_3$), 0.66-0.64 (q, *J* = 8 Hz, C$H_2$CH$_3$); GC-MS: *m/z* 481.2 $[D_5\text{-}C_2H_5]^+$, 379.0 $[D_4\text{-}C_2H_5]^+$, 277.0

$[D_3\text{-}C_2H_5]^+$. The $^1$H NMR spectrum and GC-MS spectra are given in Figures S10-S14.

**Hydrolysis of Vinylphenylsilane.**[7] 5 h at 60 °C, colorless oil, 80% yield. A mixture containing $^{vinyl}D_4$ and $^{vinyl}D_5$ were obtained, the ratio of $^{vinyl}D_4$ and $^{vinyl}D_5$ = 5/95 estimated by GC-MS. $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ 7.93-7.62, 7.25-7.02 (m, $C_6H_5$), 6.39-5.75 ($C_2H_3$); MS (EI): *m/z* 714.0 $[^{vinyl}D_5\text{-}C_2H_3]^+$, 565.1 $[^{vinyl}D_4\text{-}C_2H_3]^+$. The $^1$H NMR spectrum and GC-MS spectra are given in Figures S15-S18.

**Hydrolysis of Allylphenylsilane.** 8 h at 60 °C, colorless oil, 95% yield. A mixture containing $^{allyl}D_3$ and $^{allyl}D_4$ were obtained, the ratio of $^{allyl}D_3$ and $^{allyl}D_4$ = 12/88 estimated by GC-MS. $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ 7.90-7.47, 7.29-6.98 (m, $C_6H_5$), 6.09-5.55 ($CH_2CH$=$CH_2$), 5.15-4.64 ($CH_2CH$=C$H_2$), 2.09-1.69 (C$H_2$CH=$CH_2$). MS (EI): *m/z* 649.2 $[^{ally}D_4]^+$, 607.2 $[^{ally}D_4\text{-}C_3H_5]^+$, 571.2 $[^{ally}D_4\text{-}C_6H_5]^+$, 549.1 $[^{ally}D_4\text{-}C_6H_5\text{-}C_3H_5\text{+}H_2O]^+$, 487.1 $[^{ally}D_3]^+$, 447.1 $[^{ally}D_3\text{-}C_3H_5]^+$, 409.0 $[^{ally}D_3\text{-}C_6H_5]^+$. The $^1$H NMR spectrum and GC-MS spectra are given in Figures S19-S22.

**Hydrolysis of Methylphenylsilane.**[8] 10 h at 60 °C, colorless oil, 92% yield. A mixture containing$^{Me}D_3$ and $^{Me}D_4$ were obtained, the ratio of $^{Me}D_3$ and $^{Me}D_4$ = 3/97 estimated by GC-MS. $^1$H NMR (400 MHz, $C_6D_6$): $\delta$ 7.84-7.49, 7.27-7.04 (m, $C_6H_5$), 0.56-0.26 (*Me*); MS(EI): *m/z* 529.2 $[^{CH3}D_4\text{-}CH_3]^+$, 451.1 $[^{CH3}D_4\text{-}C_6H_5\text{-}CH_3]^+$, 393.2 $[^{CH3}D_3\text{-}CH_3]^+$, 315.1 $[^{CH3}D_3\text{-}C_6H_5\text{-}CH_3]^+$. The $^1$H NMR spectrum and GC-MS spectra are given in Figures S23-S26.

## 4. NMR and GC-MS Spectra for the Resulting Cyclosiloxanes

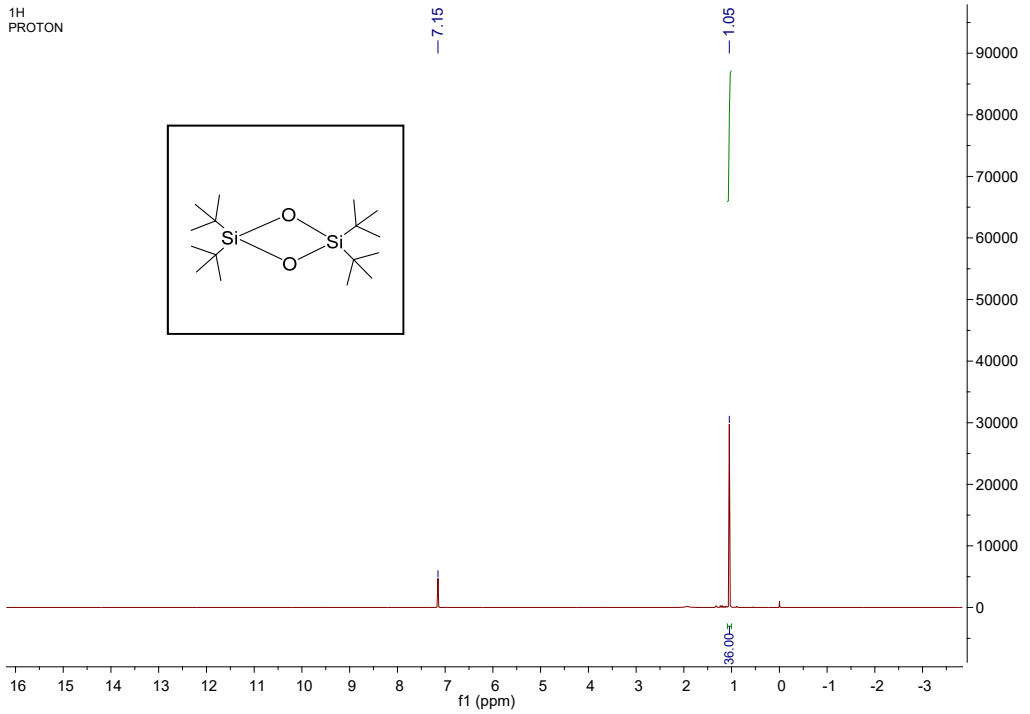



**Figure S1.** $^{1}H$ NMR spectrum of $^{tBu}D_2$ in $C_6D_6$.

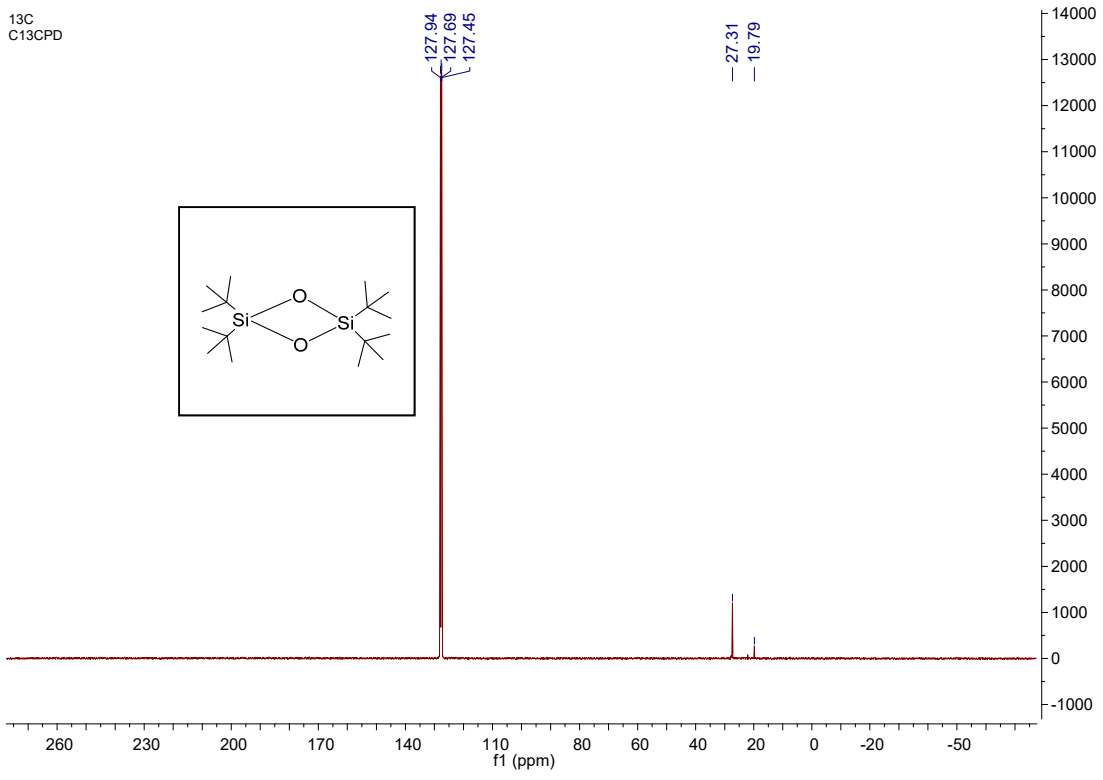



**Figure S2.** $^{13}C$ NMR spectrum of $^{tBu}D_2$ in $C_6D_6$

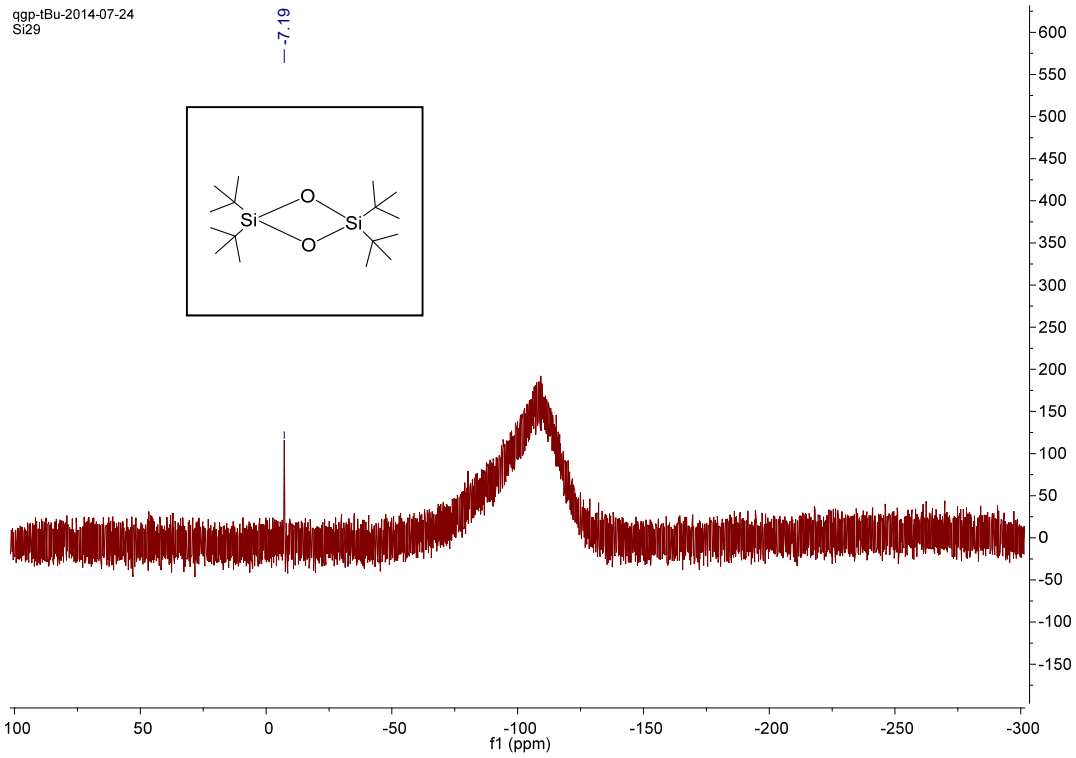



**Figure S3.** $^{29}$Si NMR spectrum of $^{tBu}D_2$ in $CDCl_3$

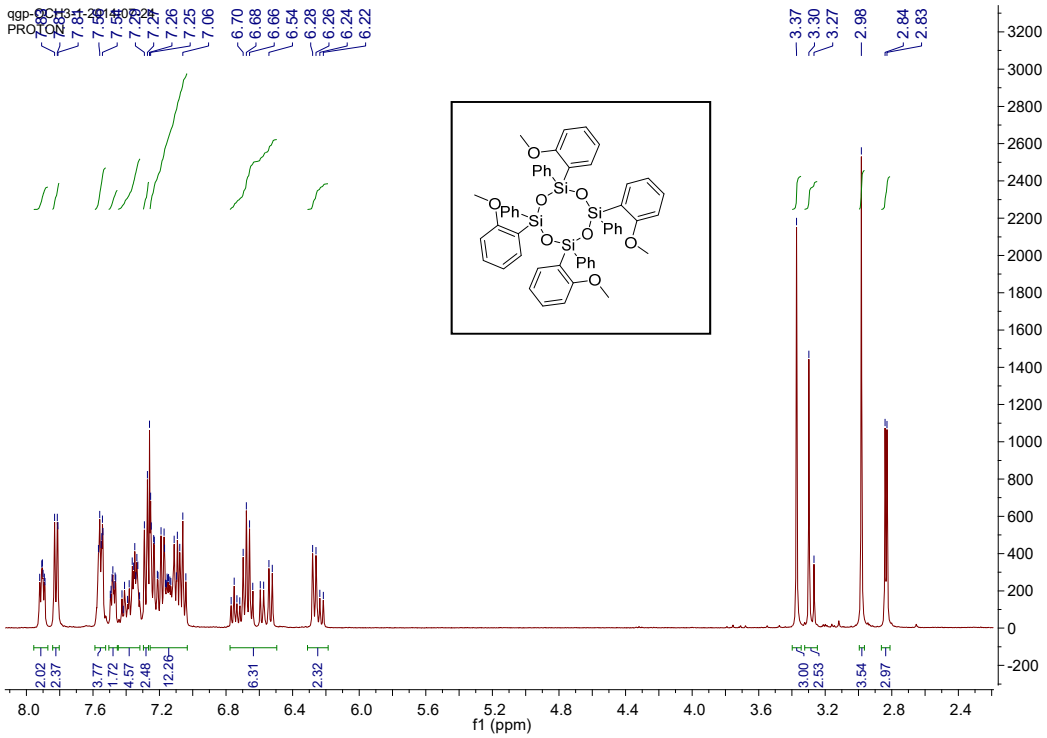



**Figure S4.** $^{1}$H NMR spectrum of $^{OMe}D_4$ in $C_6D_6$

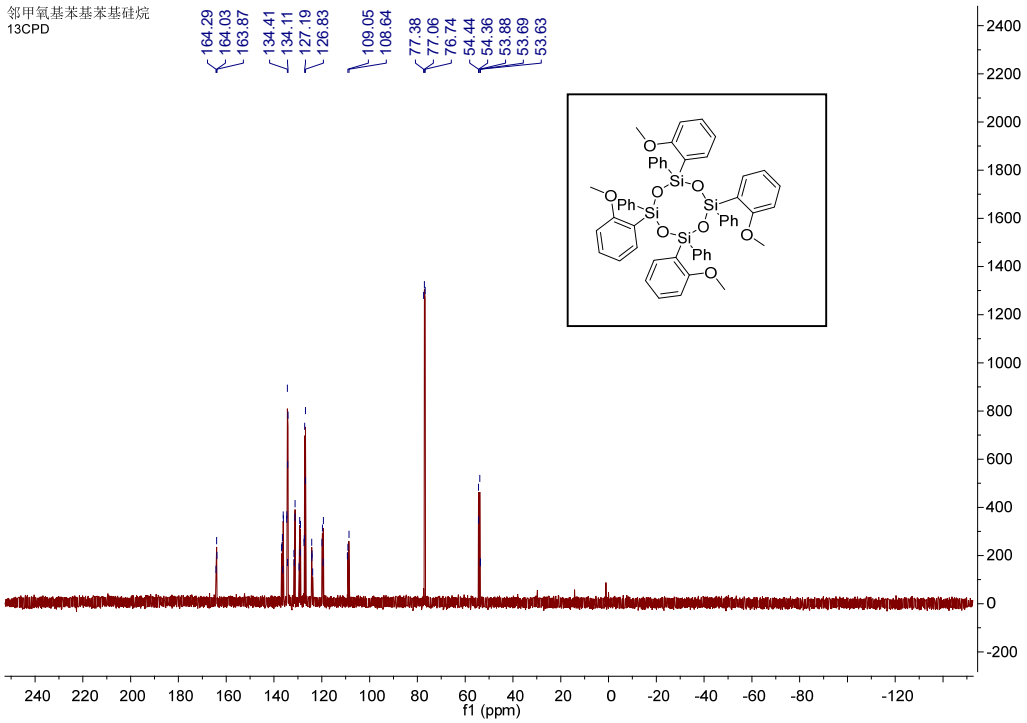



**Figure S5.** $^{13}$C NMR spectrum of $^{OMe}D_4$ in $CDCl_3$.

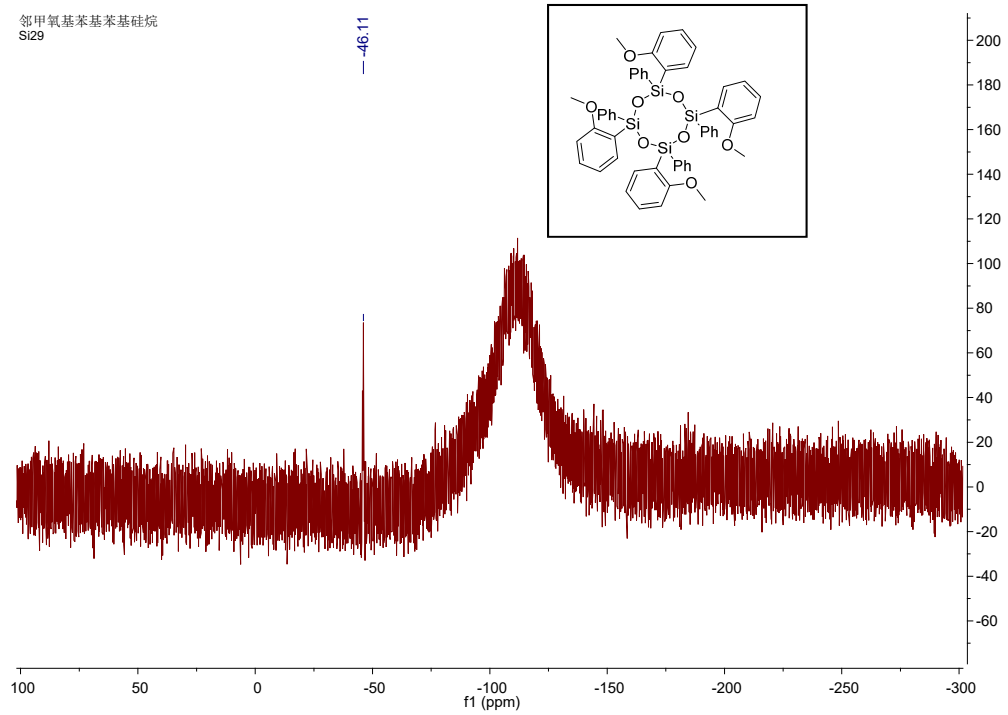



**Figure S6.** $^{29}$Si NMR spectrum of $^{OMe}D_4$ in $CDCl_3$.

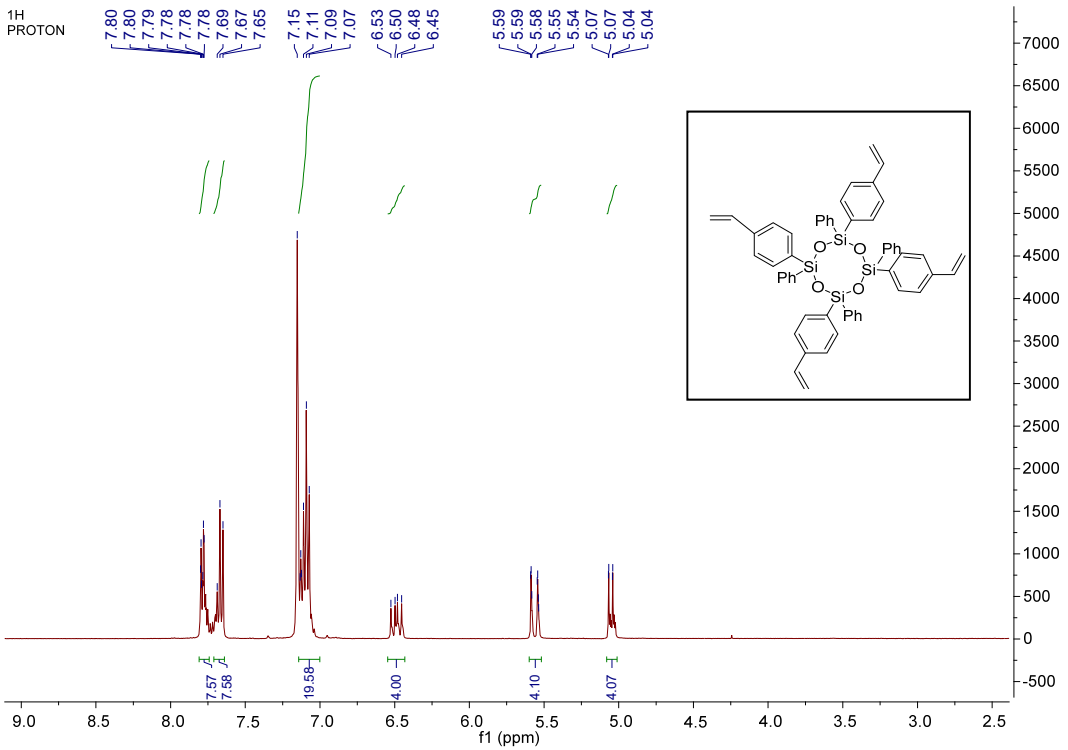



**Figure S7.** $^{1}$H NMR spectrum of $^{p\text{-viny}}D_4$ in $C_6D_6$

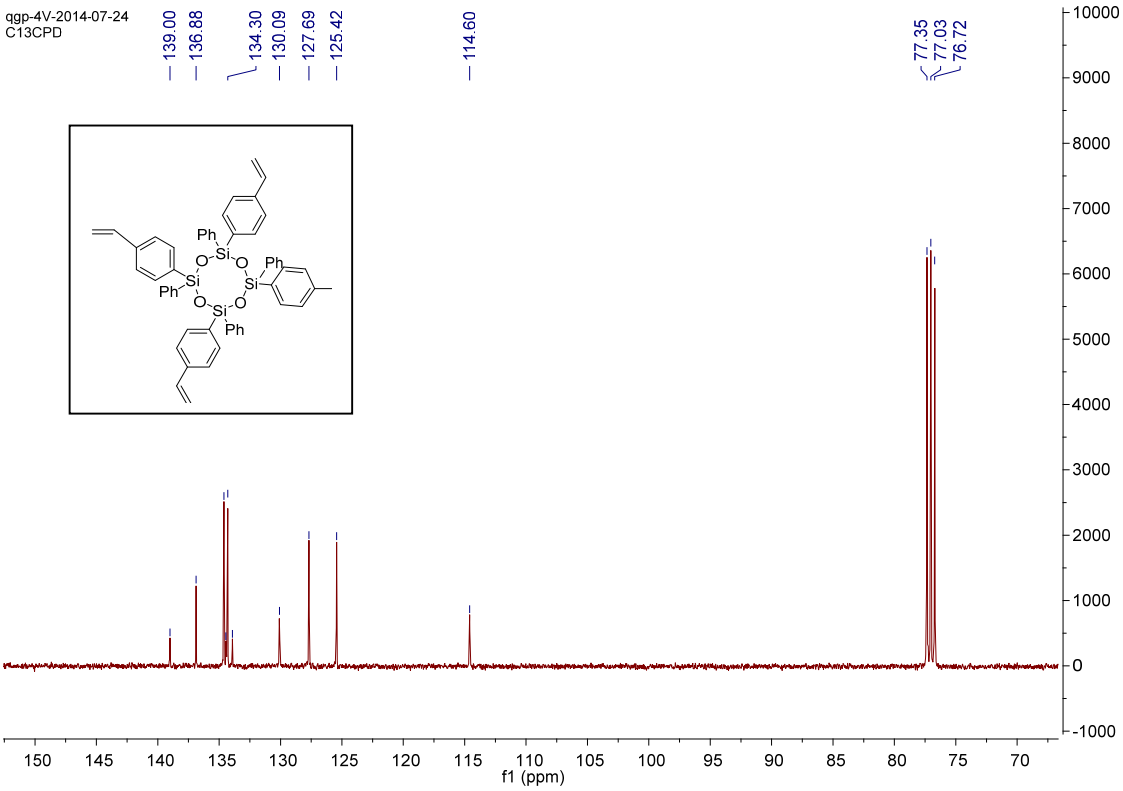



**Figure S8.** $^{13}$C NMR spectrum of $^{p\text{-vinyl}}D_4$ in $CDCl_3$.

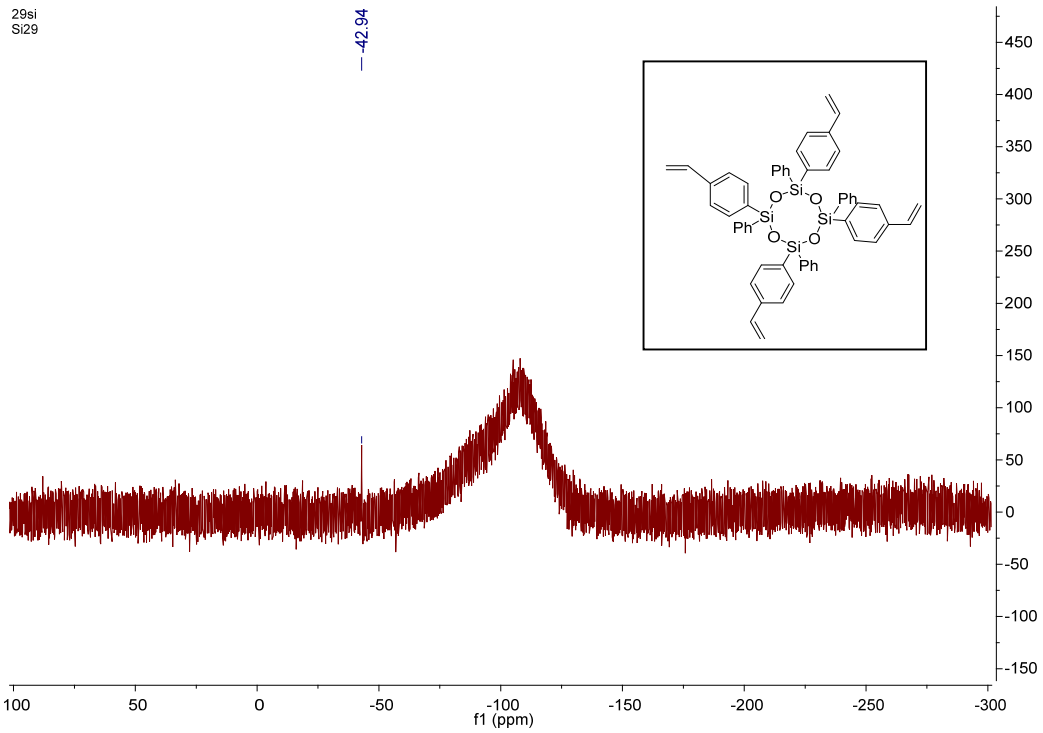



**Figure S9.** $^{29}$Si NMR spectrum of $^{p\text{-vinyl}}D_4$ in $CDCl_3$.

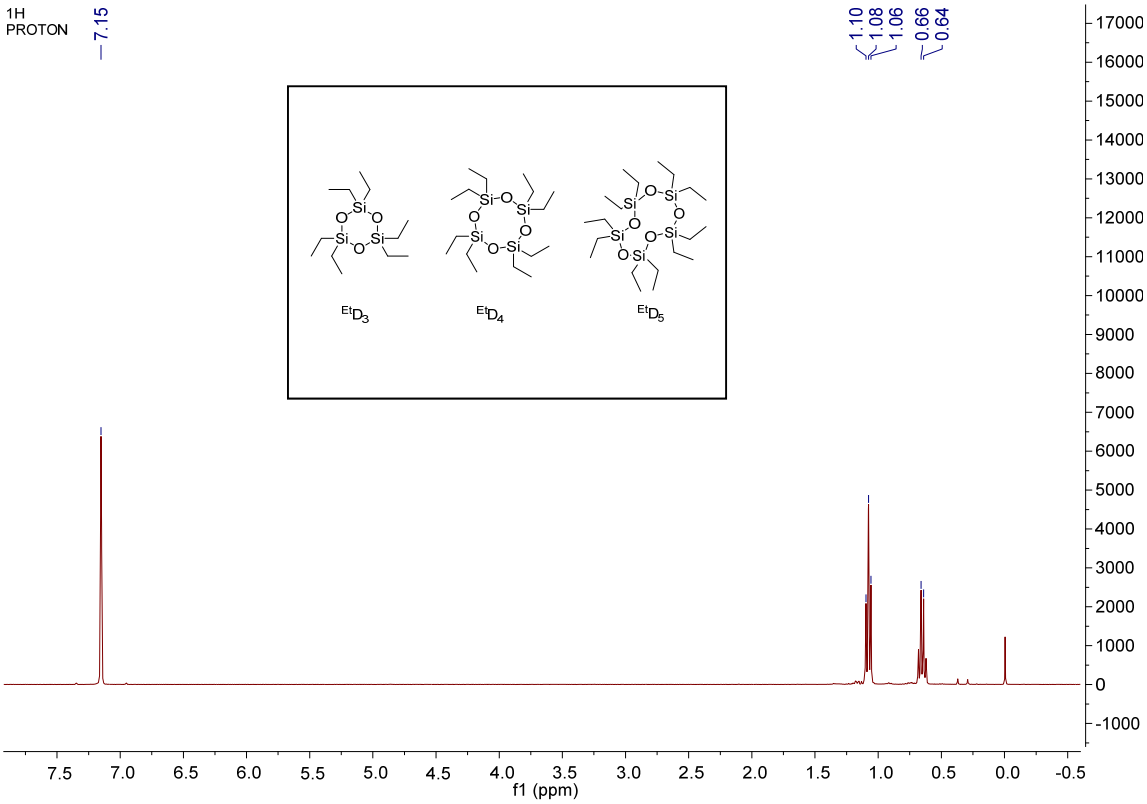



**Figure S10.** $^{1}$H NMR spectrum of $^{Et}D_3$ , $^{Et}D_4$, $^{Et}D_5$ .

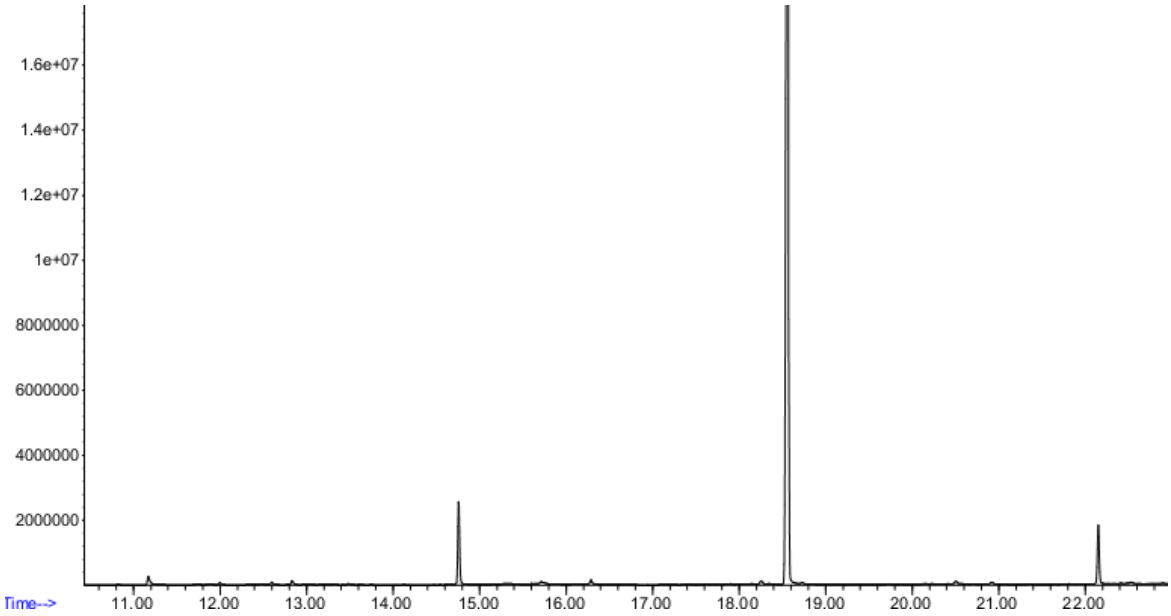



**Figure S11.** GC-MS spectrum of $^{Et}D_3$ , $^{Et}D_4$, $^{Et}D_5$ .

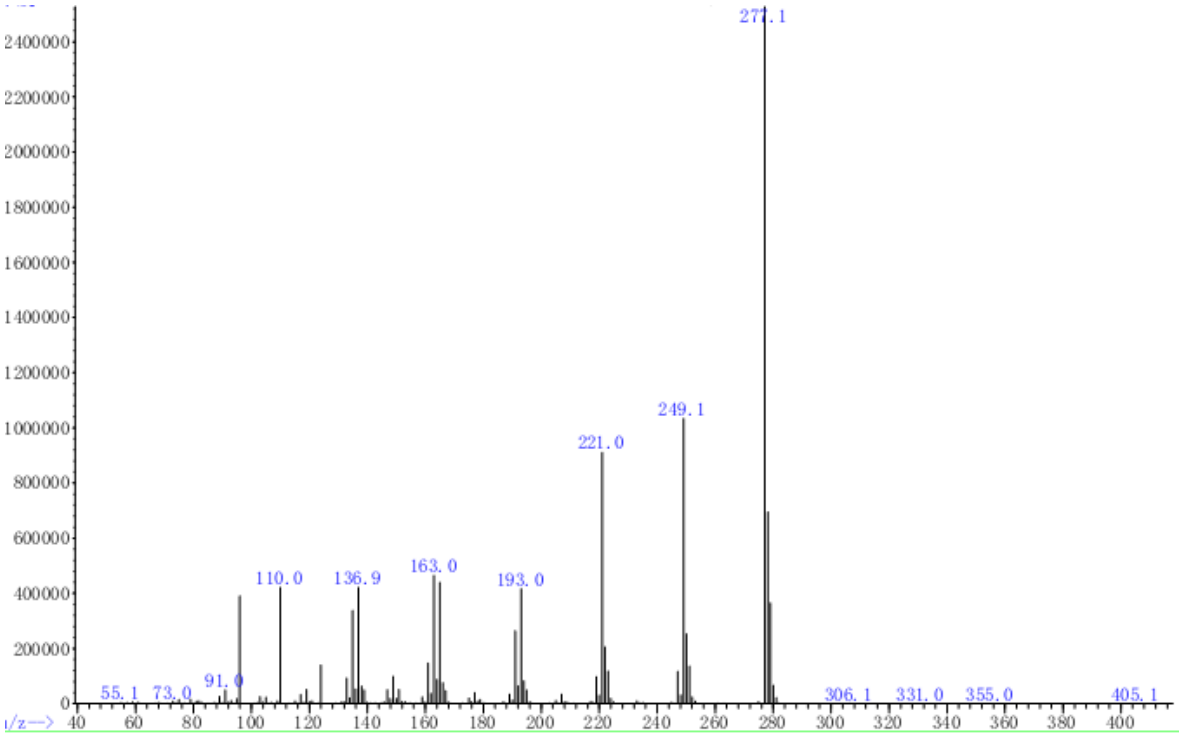



**Figure S12.** GC-MS spectrum of $^{Et}D_3$ .

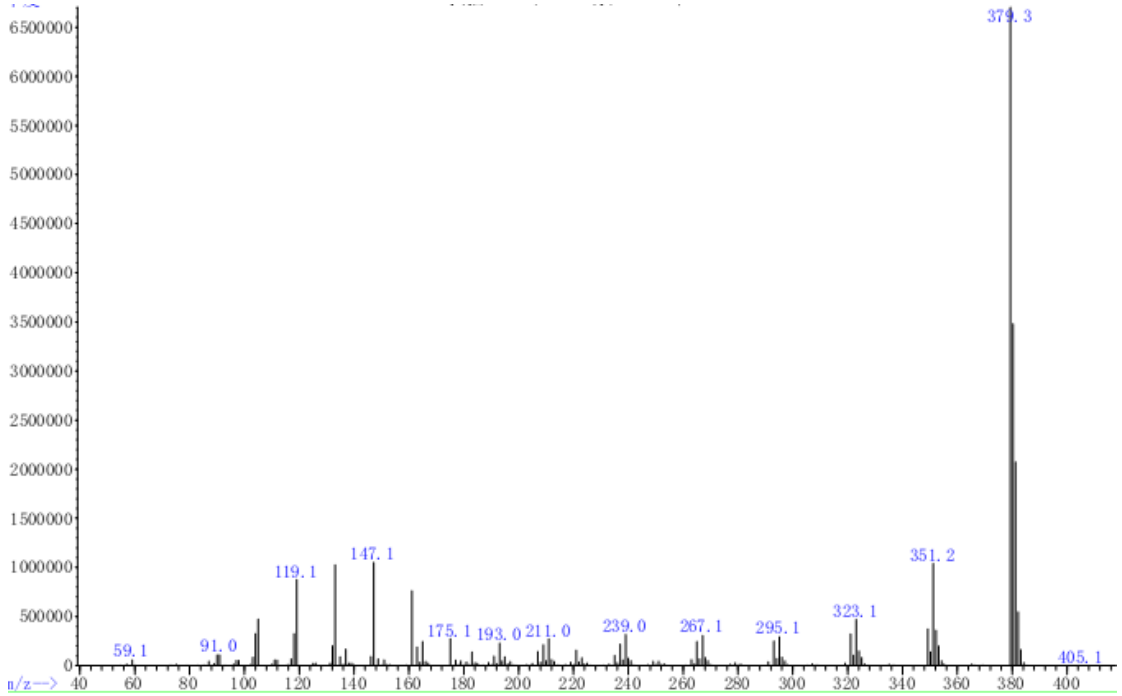



**Figure S13.** GC-MS spectrum of $^{Et}D_4$.

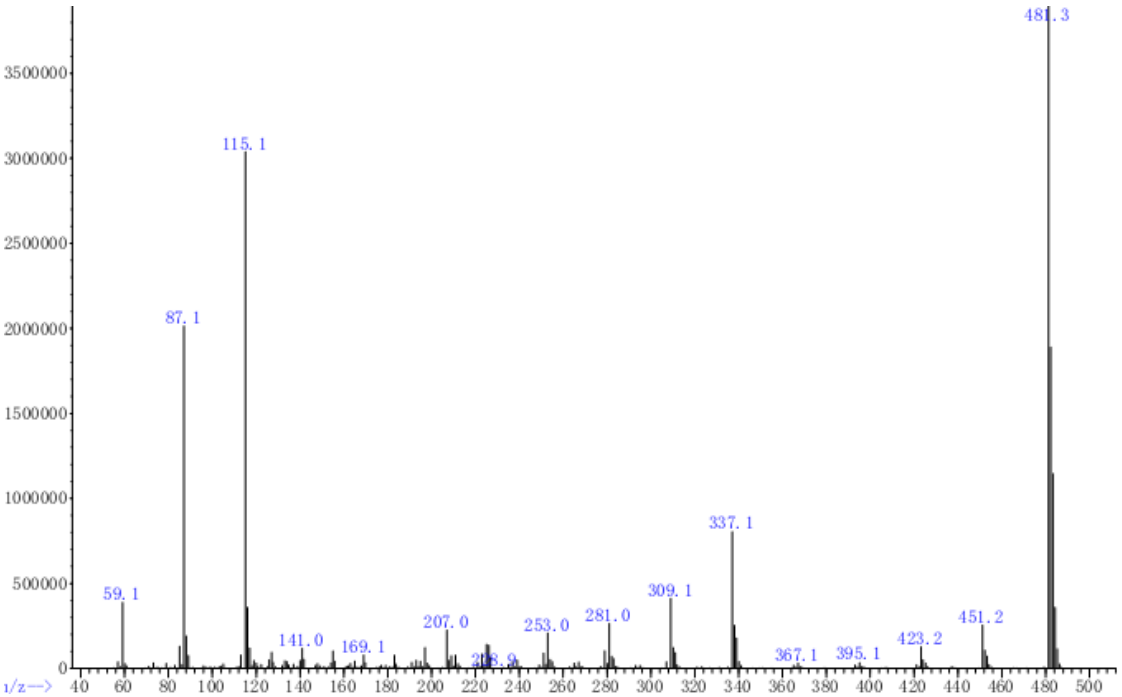



**Figure S14.** GC-MS spectrum of $^{Et}D_5$.

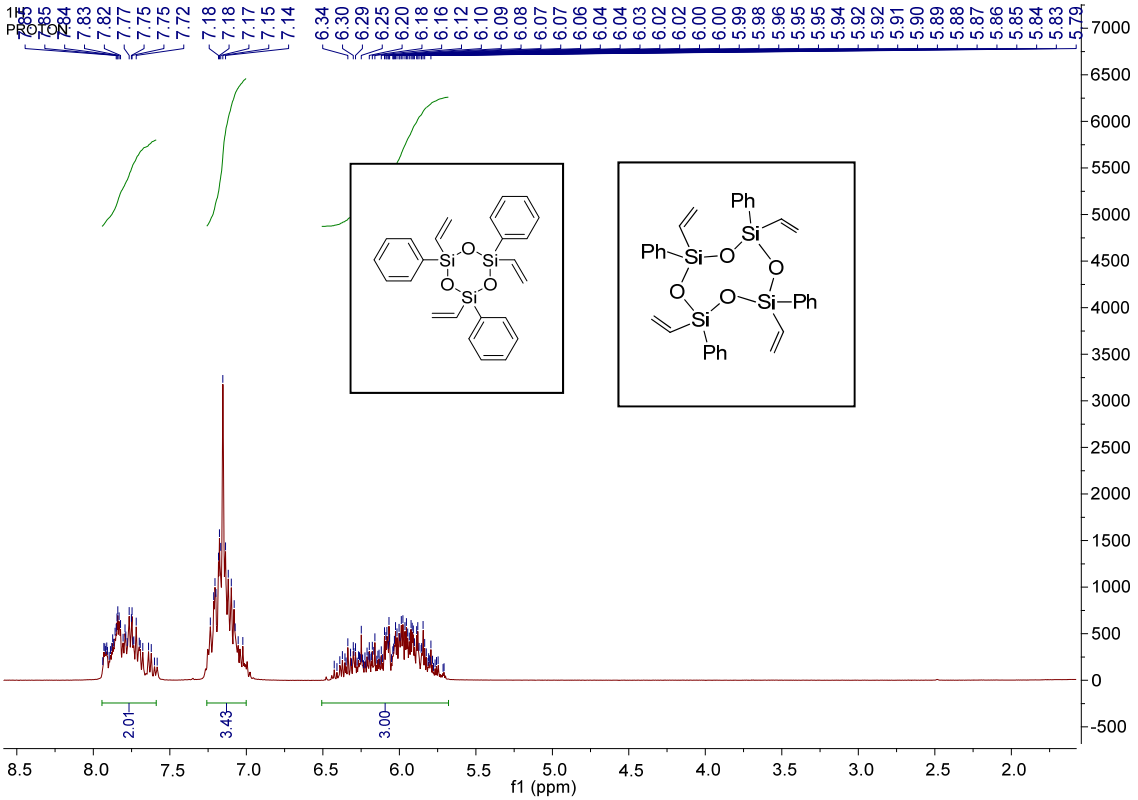



**Figure S15.** $^{1H}$ NMR spectrum of $^{vinyl}D_3$ and $^{vinyl}D_4$ in $C_6D_6$.

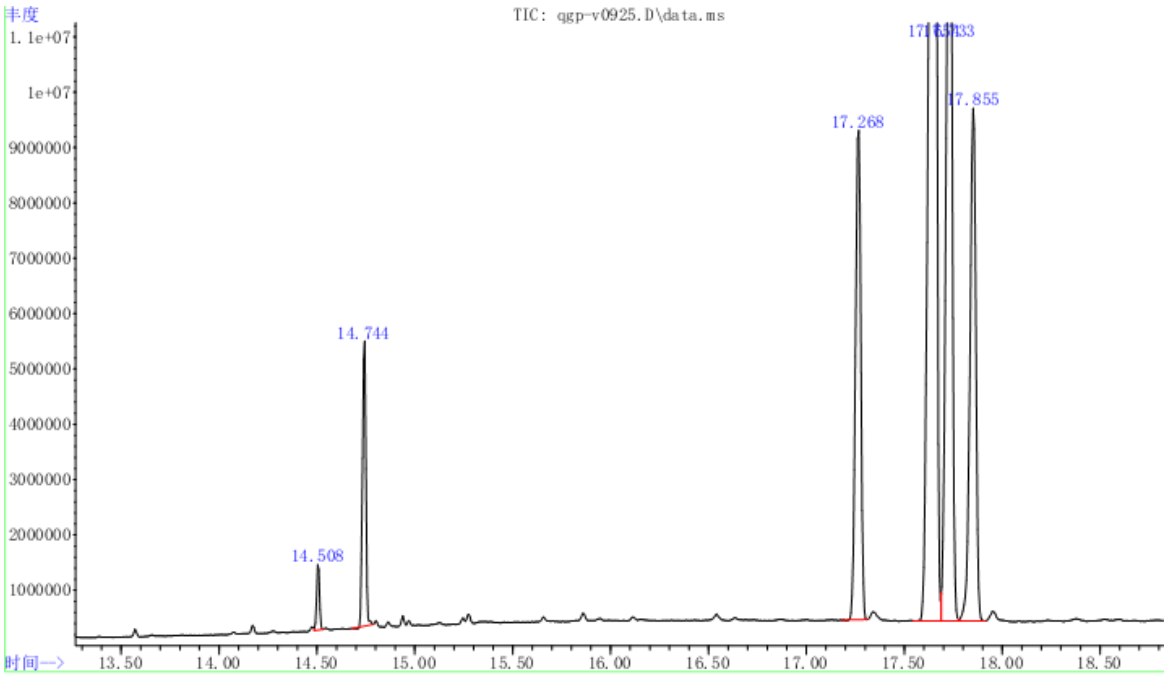



**Figure S16.** GC-MS spectrum of $^{vinyl}D_3$ and $^{vinyl}D_4$.

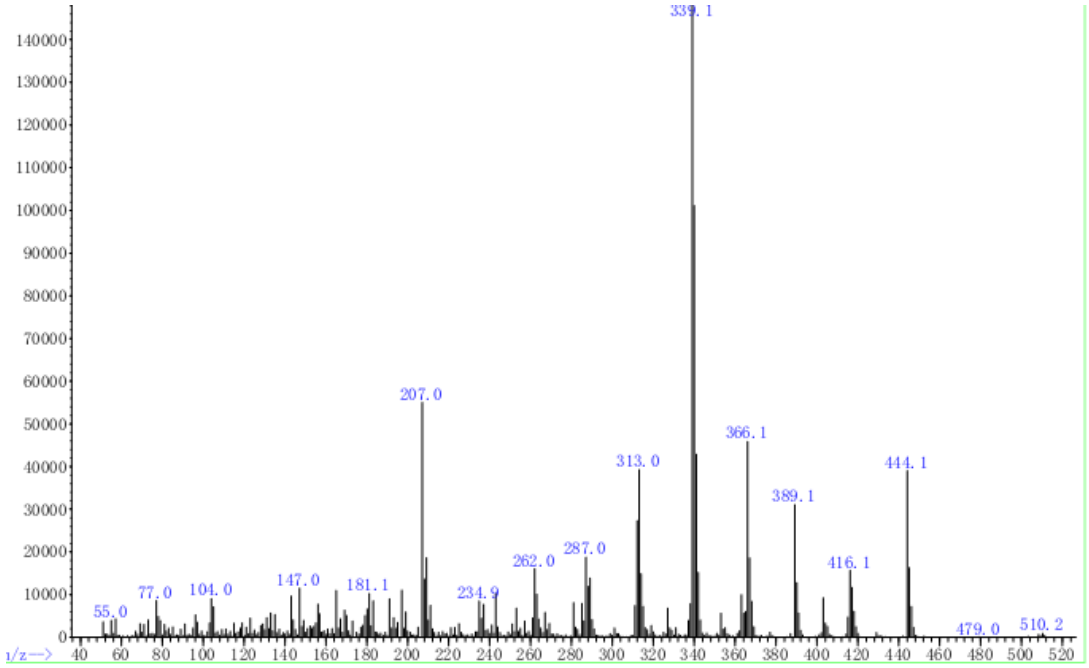



**Figure S17.** GC-MS spectrum of $^{vinyl}D_3$.

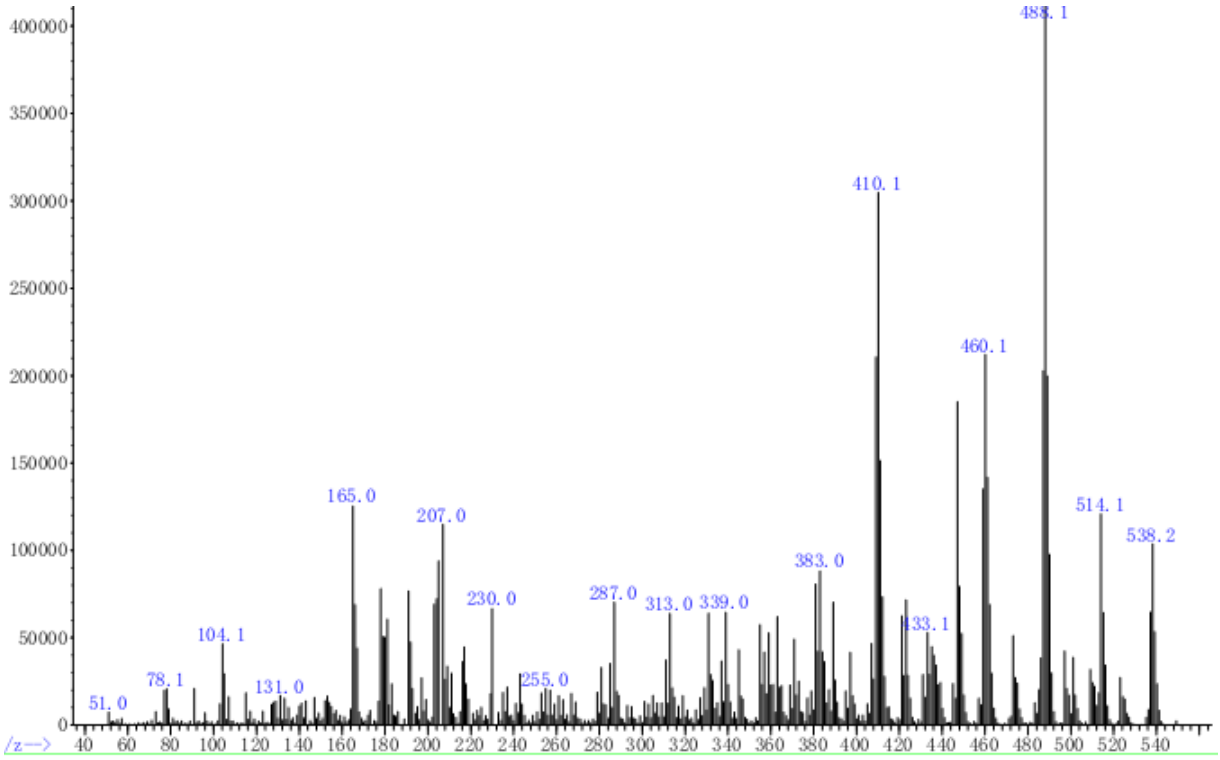



**Figure S18.** GC-MS spectrum of $^{vinyl}D_4$.

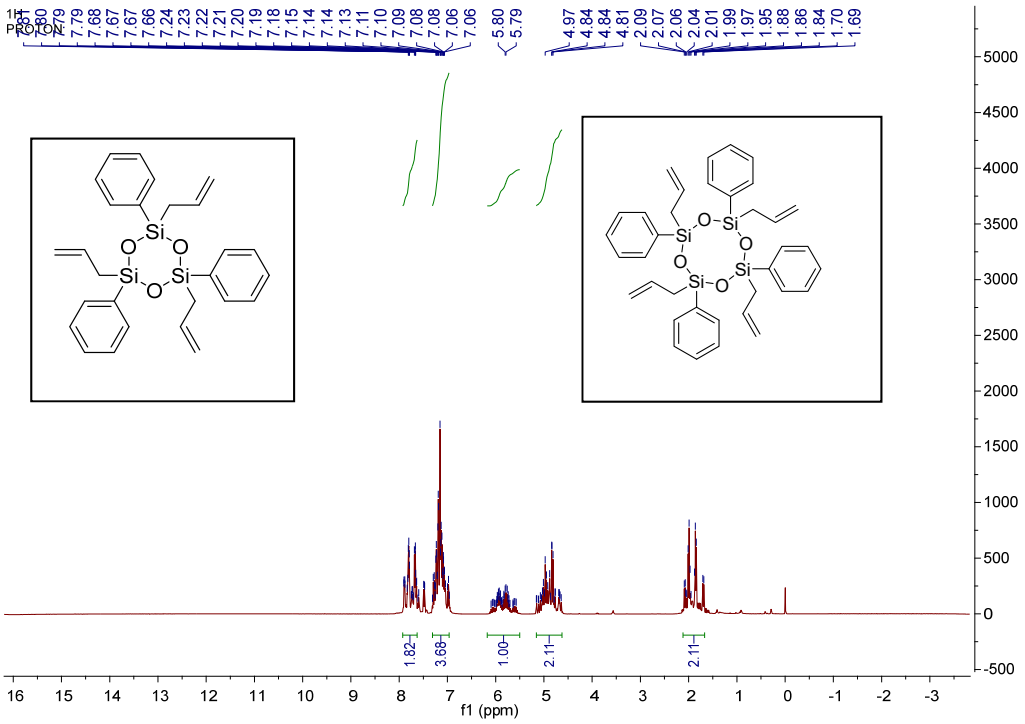



**Figure S19.** $^{1H}$ NMR spectrum of $^{allyl}D_3$, $^{allyl}D_4$ in $C_6D_6$

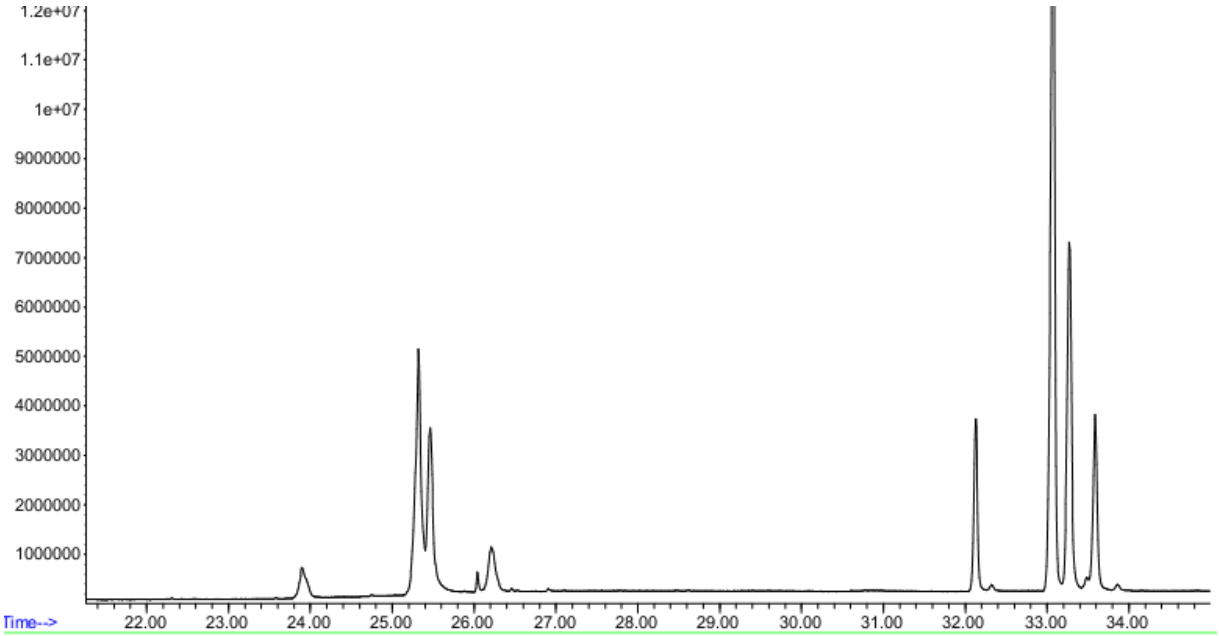



**Figure S20.** GC-MS spectrum of $^{allyl}D_3$ and $^{allyl}D_4$.

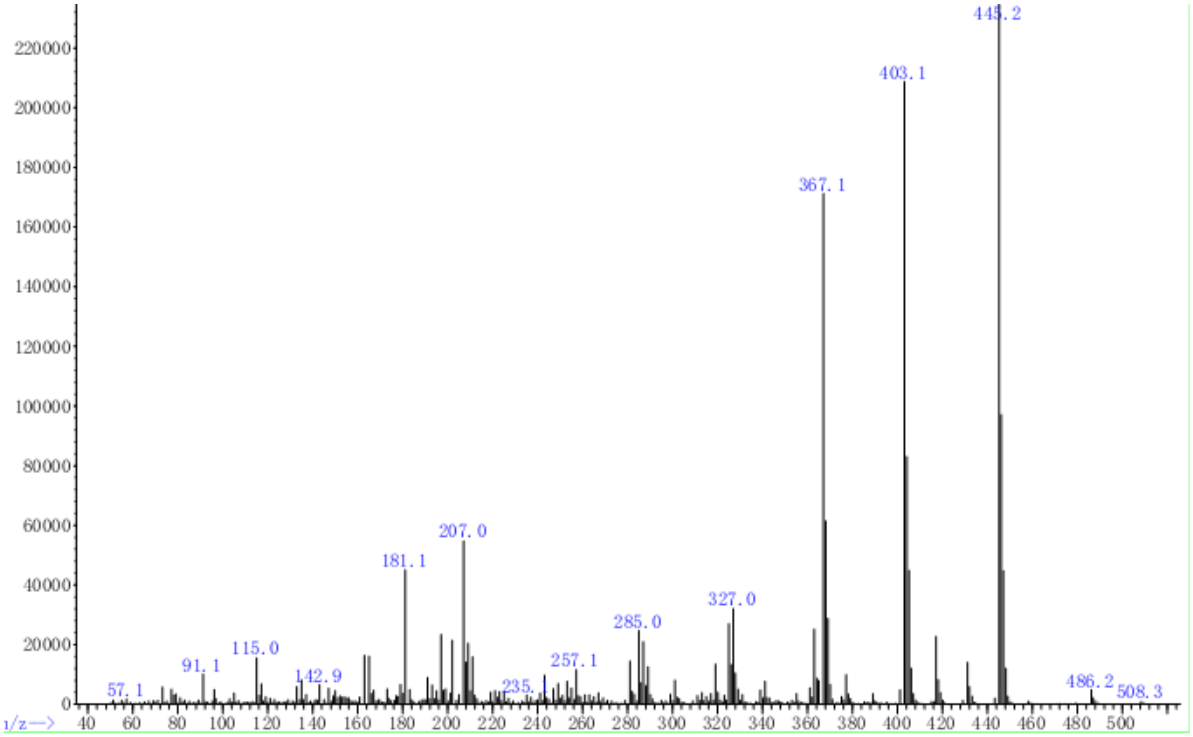



**Figure S21.** GC-MS spectrum of $^{allyl}D_3$.

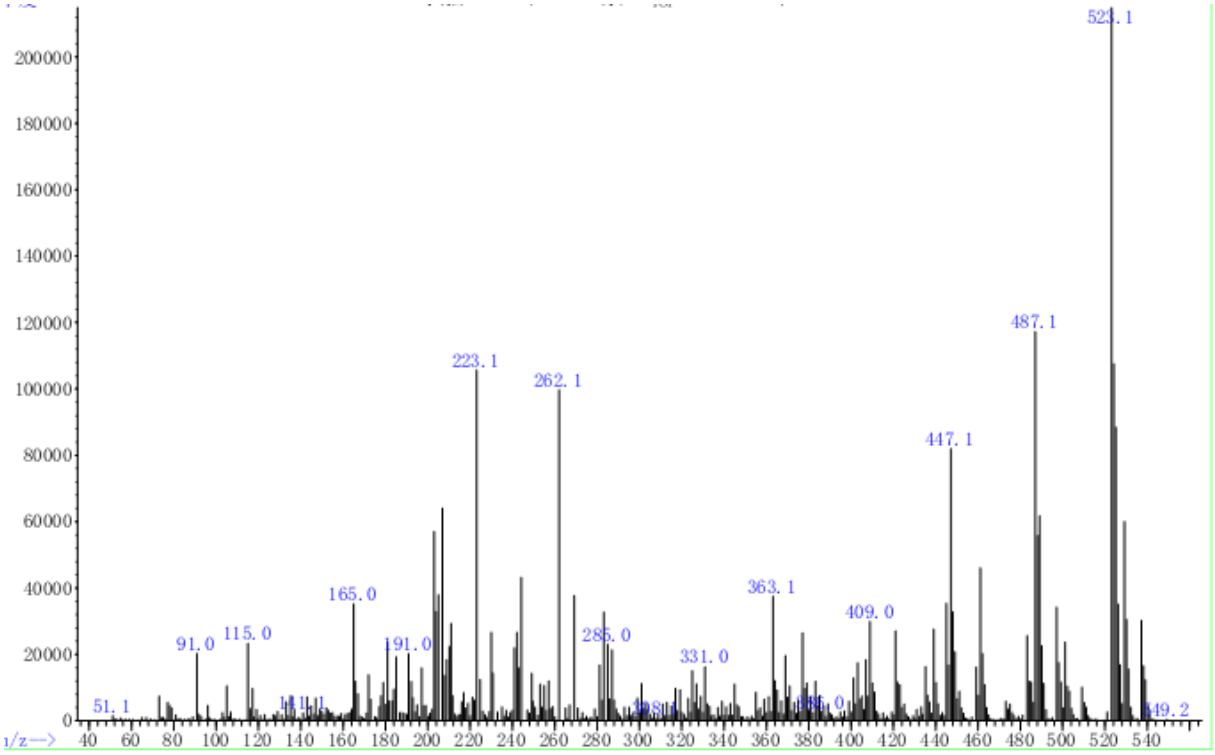



**Figure S22 .**GC-MS spectrum of $^{allyl}D_4$.

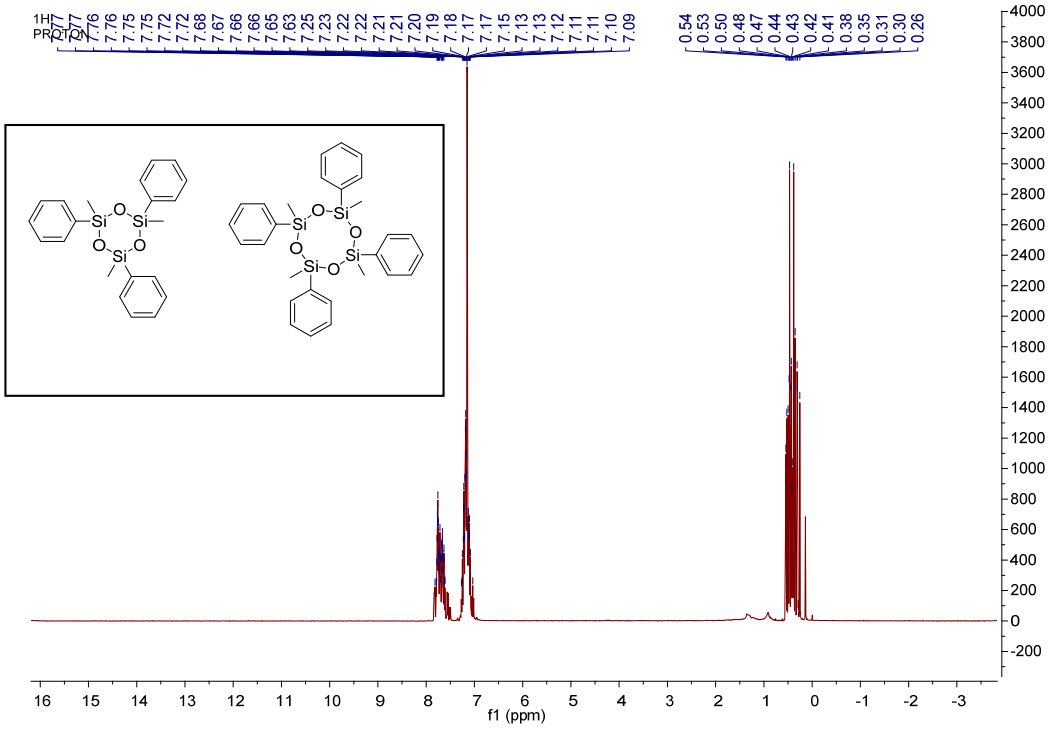



**Figure S23.** $^{1}$H NMR spectrum of $^{Me}D_3$ and $^{Me}D_4$ in $C_6D_6$

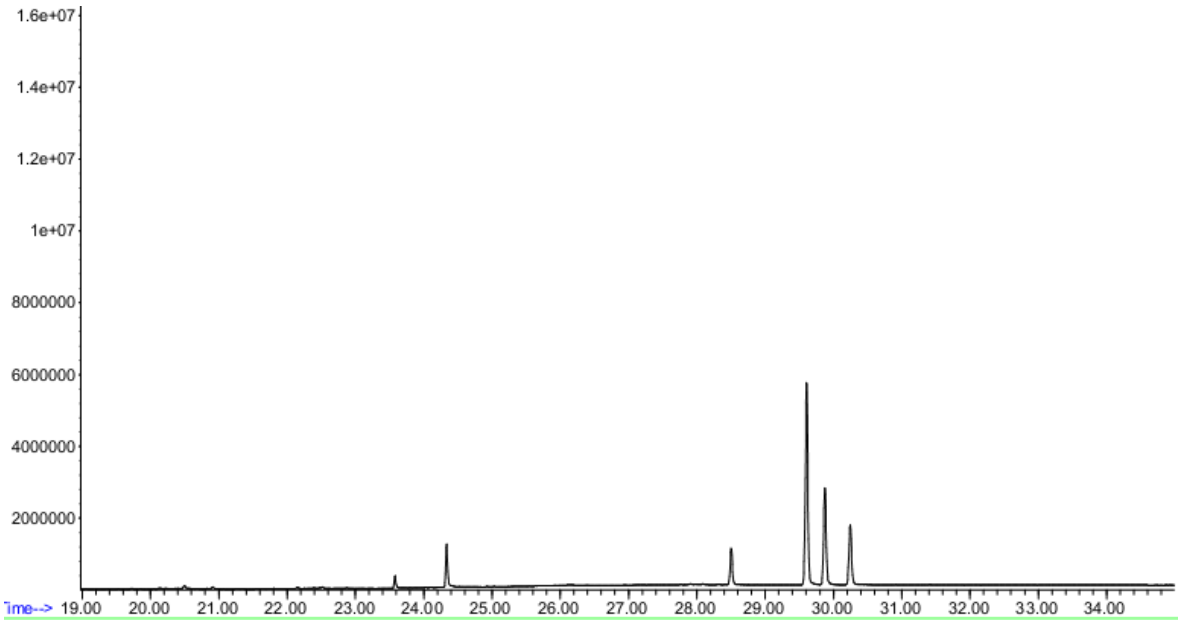



**Figure S24.** GC-MS spectrum of $^{Me}D_3$ and $^{Me}D_4$.

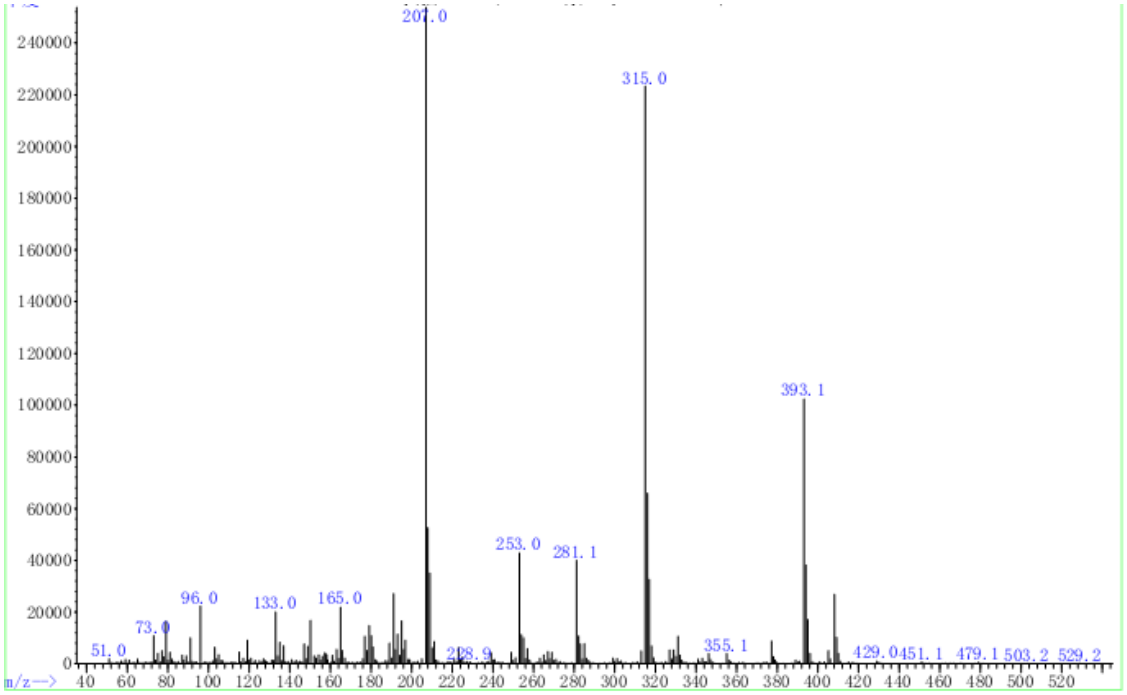



**Figure S25.** GC-MS spectrum of $^{Me}D_3$.

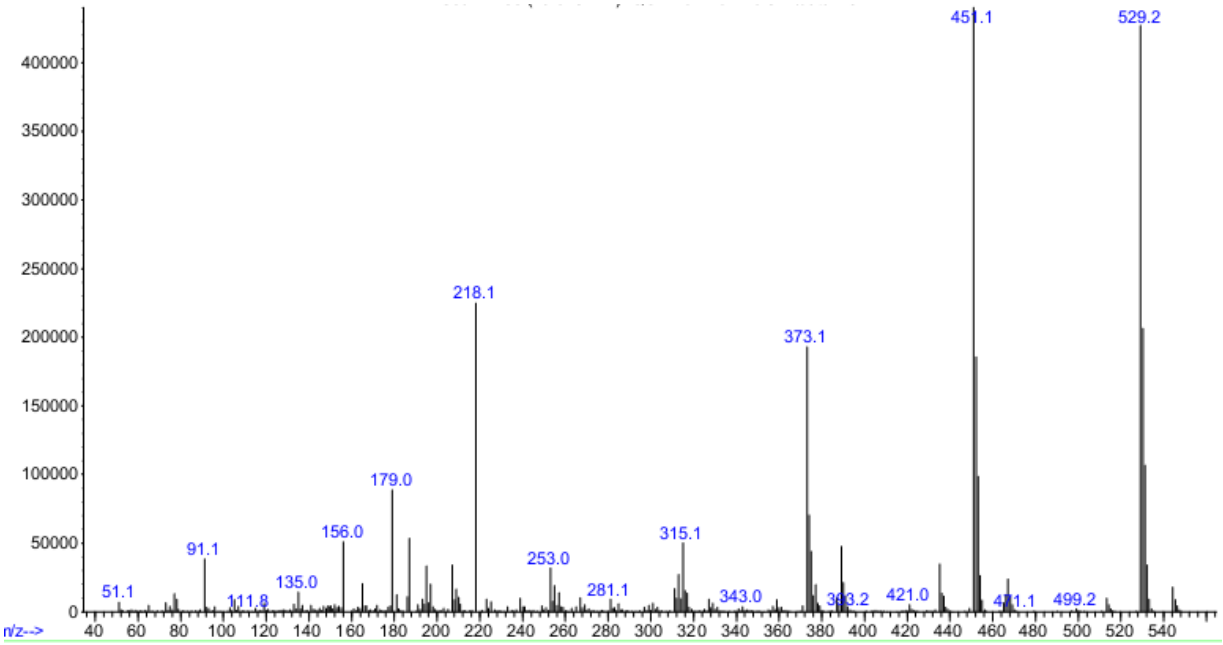



**Figure S26.** GC-MS spectrum of $^{Me}D_4$.

**References**


S1 (a) A. J. Arduengo, H. V. R. Dias, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* 1992, **114**, 5530; (b) R. A. Kunetskiy, I. Cisarova, D. Saman, I. M. Lyapkalo, *Chem. Eur. J.* 2009, **15**, 9477; (c) F. Hanasaka, K. –I. Fujita, R. Yamaguchi, *Organometallics* 2005, **24**, 3422.

S2 N. Hirone, H. Sanjiki, R. Tanaka, T. Hata, H. Urabe, *Angew. Chem. Int. Ed.* 2010, **49**, 7762.

S3 A. Berkefeld, W. E. Piers, M. Parvez, *J. Am. Chem. Soc.* 2010, **132**, 10660.

S4 Y. R. Jorapur, T. Shimada, *Synlett* 2012, **23**, 1633.

S5 A. Albright, R. E. Gawley, *Tetrahedron Lett.* 2011, **52**, 6130.

S6 (a) D. S. Fattakhova, V. V. Jouikov, M. G. Voronkov, *J. Organomet. Chem.* 2000, **613**, 170; (b) T. L. Krasnova, *Zh. ObshcheiKhim.* 1985, **55**, 1528.

S7 P. Zak, C. Pietraszuk, B. Marciniec, *J. Mol. Catal. A: Chem.* 2008, **289**, 1.

S8 (a) V. V. Zuev, Z. V. Kalinin, *Phosphorus, Sulfur and Silicon and the Related Elements* 2003, **178**, 1289; (b) M.-H. Yang, H.-W. Liu, H. –T. Lin, *J. Chin. Chem. Soc.* 2004, **51**, 791; (c) R. K. Harris, B. J. Kimber, M. D. Wood, A. Holt, *J. Organomet. Chem.* 1976, **116**, 291; (d) A. A. Bychkova, F. V. Soskov, A. I .Demchenko, P. A. Storozhenko, A. M. Muzafarov, *Russ. Chem. Bull. Int. Ed.* 2011, **60**, 2384.