Supporting Information for:

Rh(III)-Catalysed Solvent-Free Hydrodehalogenation of Alkyl Halides by Tertiary Silanes

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Dehalogenation of $CDCl_3$ using different silanes

To a solution of **1** (4.2mg, 0.0025 mmol) in $CDCl_3$ (0.5 mL) charged in a J. Young NMR tube was added a hydrosilane (Et_3SiH 40 µL, 0.25 mmol; Me_2PhSiH, 40 µL, 0.25 mmol; $MePh_2SiH$ 51 µL, 0.25 mmol; Ph_3SiH, 65.1 mg, 0.25 mmol). The solution was monitored by ^1H NMR at 50 ºC, following the disappearance of the hydrosilane resonance and the appearance of new chlorosilane and $CHDCl_2$.

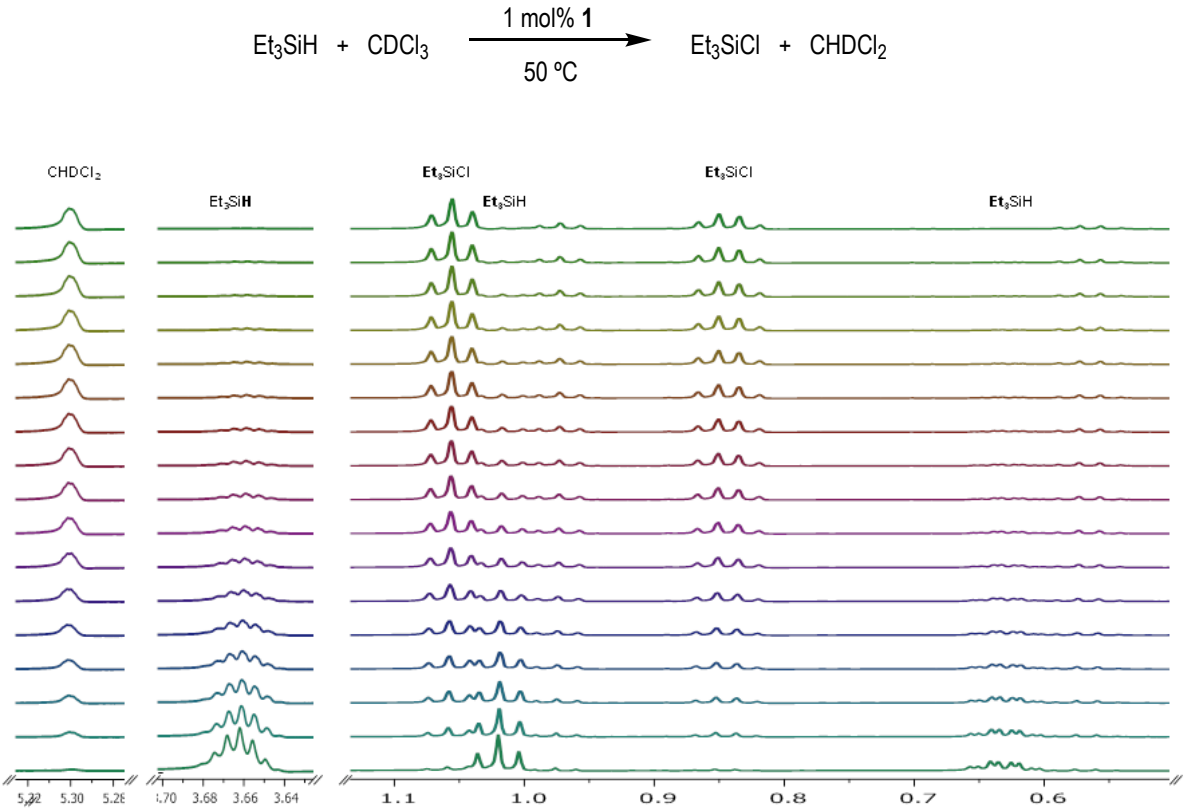


Figure 1. Dechlorination of $CDCl_3$ using Et_3SiH. Reaction monitoring by ^1H NMR at 50 ºC.

Triethylchlorosilane: ^1H NMR (500 MHz, $CDCl_3$): δ 1.06 (t, J = 7.8 Hz, 9H), 0.84 (q, J = 7.9 Hz, 6H).

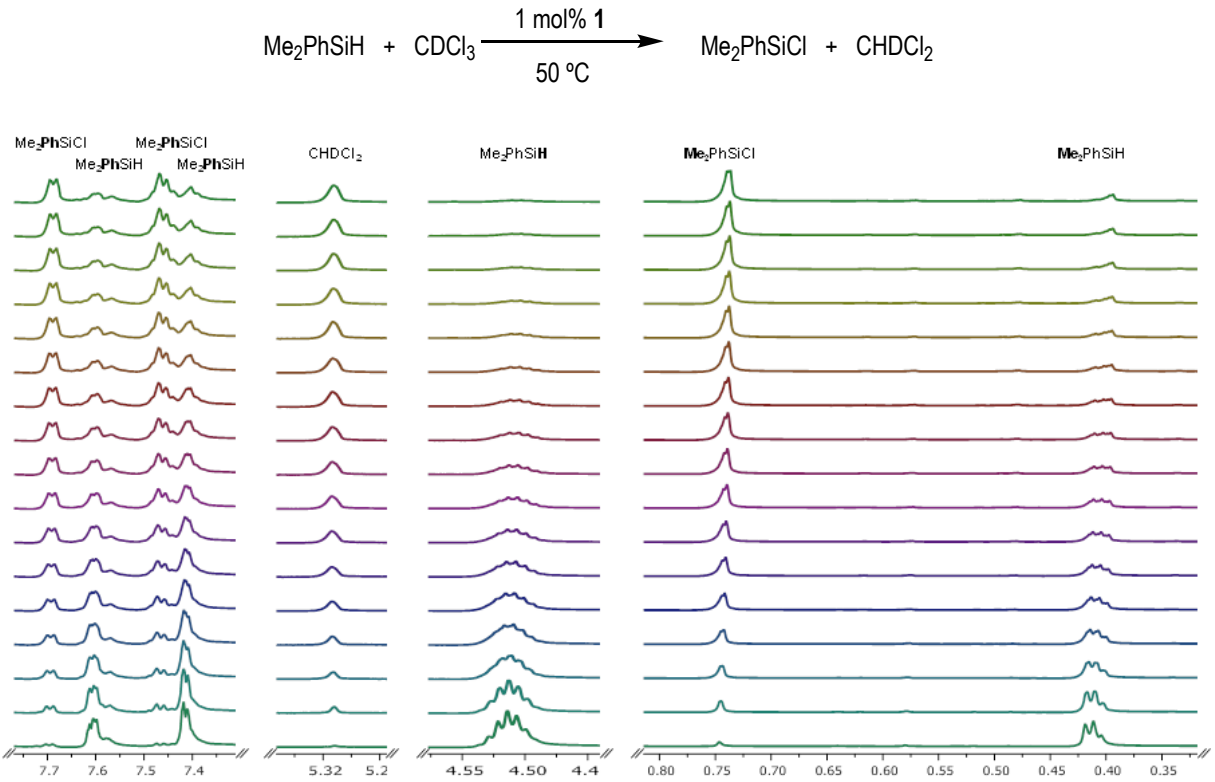


Figure 2. Dechlorination of $CDCl_3$ using Me_2PhSiH. Reaction monitoring by ^1H NMR at 50 ºC.

Dimethylphenylchlorosilane: **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.61 (m, 2H), 7.42 (m, 3H), 0.74 (t, d = 1.5 Hz, 6H).

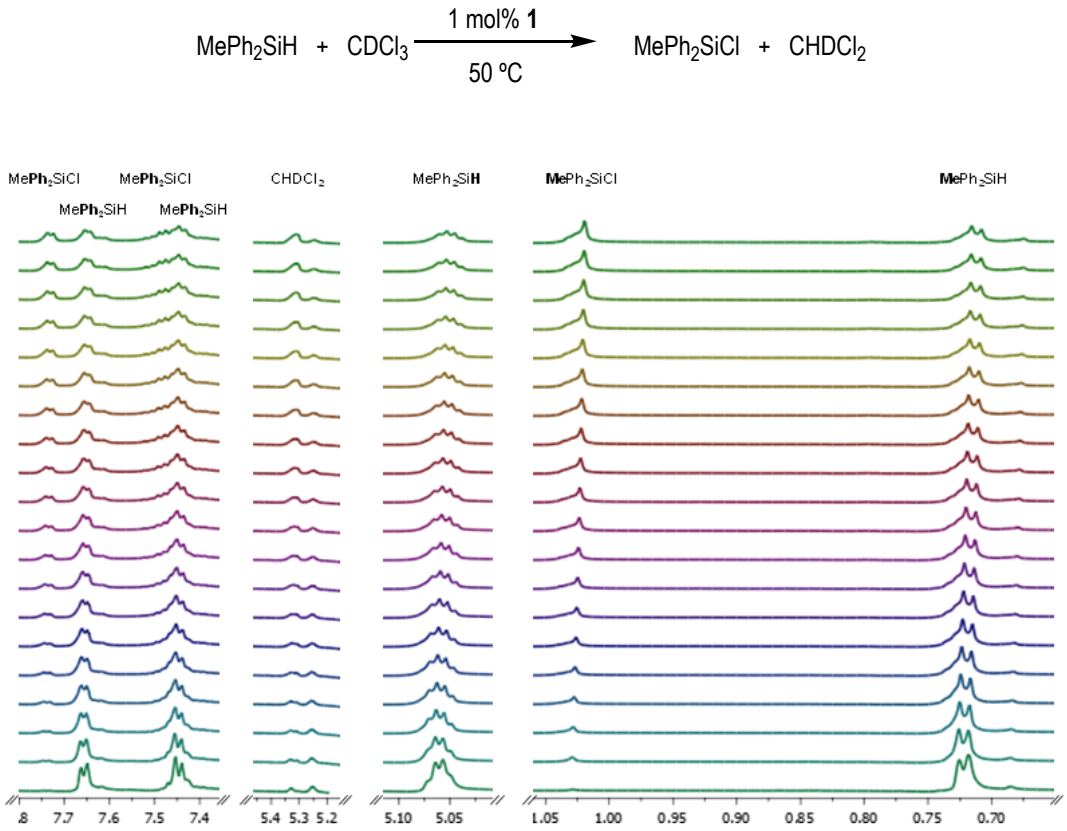


Figure 3. Dechlorination of $CDCl_3$ using $MePh_2SiH$. Reaction monitoring by ^1H NMR at 50 °C

Methyldiphenylchlorosilane: **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.73 (m, 4H), 7.48 (m, 6H), 1.02 (s, 3H).

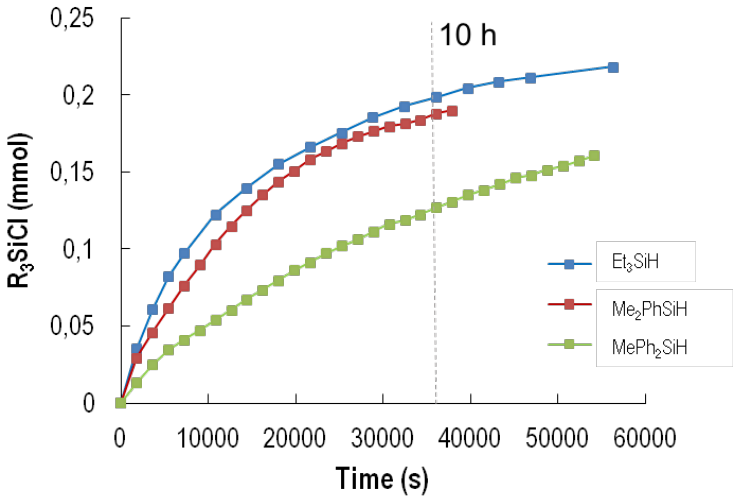
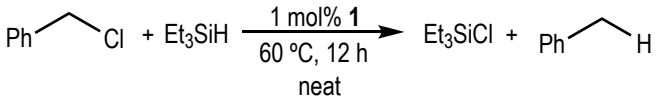


Figure 4. Reaction of R_3SiH with $CDCl_3$ catalysed by **1**. Concentration of R_3SiCl *vs* time.

Dehalogenation of different alkyl halides using Et_3SiH

A Young flask charged with **1** (8.4 mg, 0.05 mmol), Et_3SiH (80 µL, 0.5 mmol) and the alkyl halides (benzylchloride, 57 µL, 0.5 mmol; benzylbromide, 60 µL, 0.5 mmol; tritylchloride, 189 mg, 0.5 mmol; tert-pentylchloride, 61 µL, 0.5 mmol; tetrachloroethane, 53 µL, 0.5 mmol) was stirred during 12 h at 60 ºC. After this time, $CDCl_3$ and dichloroethane (10 µL, 0.0126 mmol, Internal Standard) were added and a ^1H NMR spectra was carried out at room temperature to calculate the conversion.



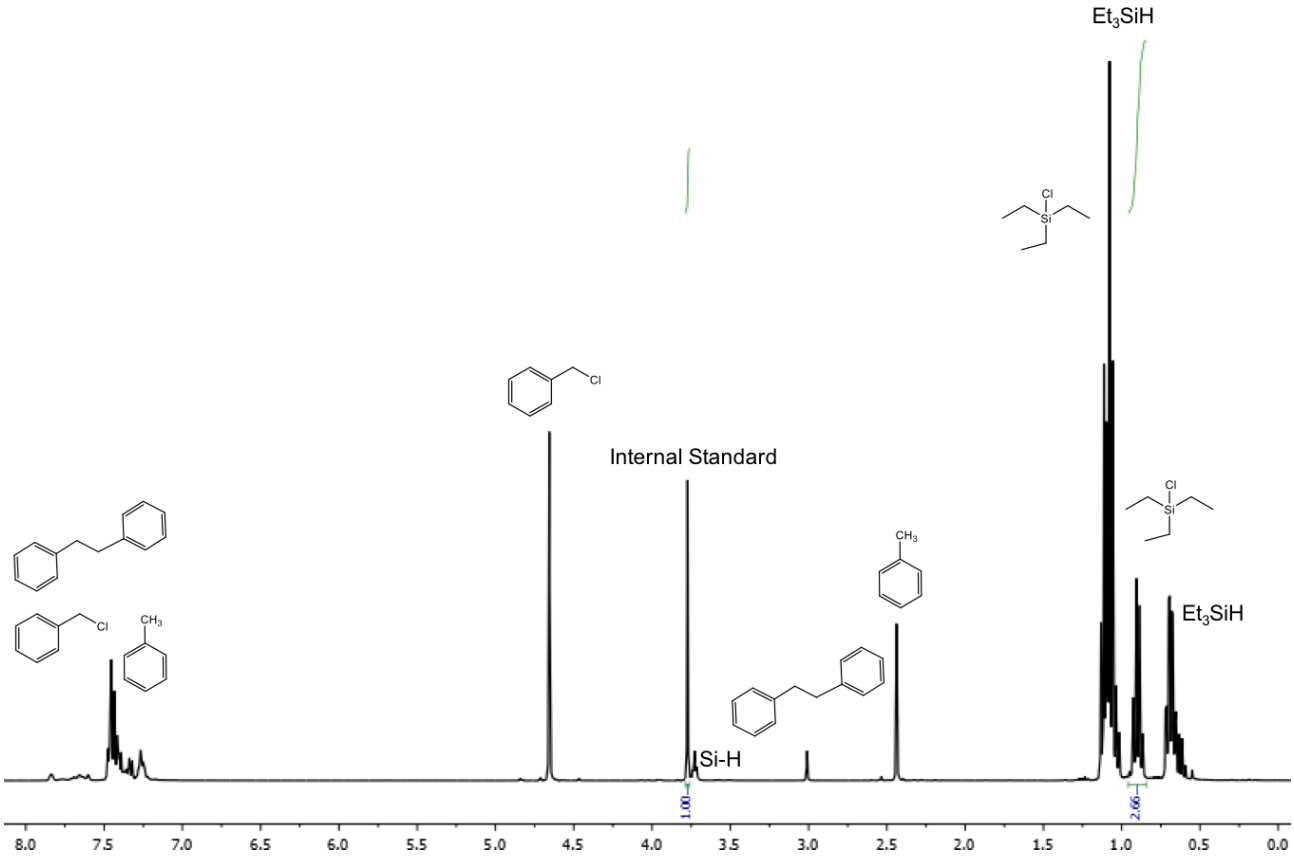
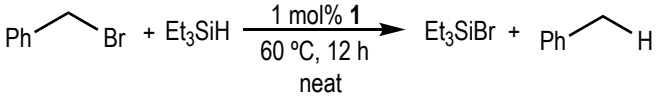


Figure 5. ^1H NMR spectrum for the reaction of dechlorination of benzyl chloride using Et_3SiH.



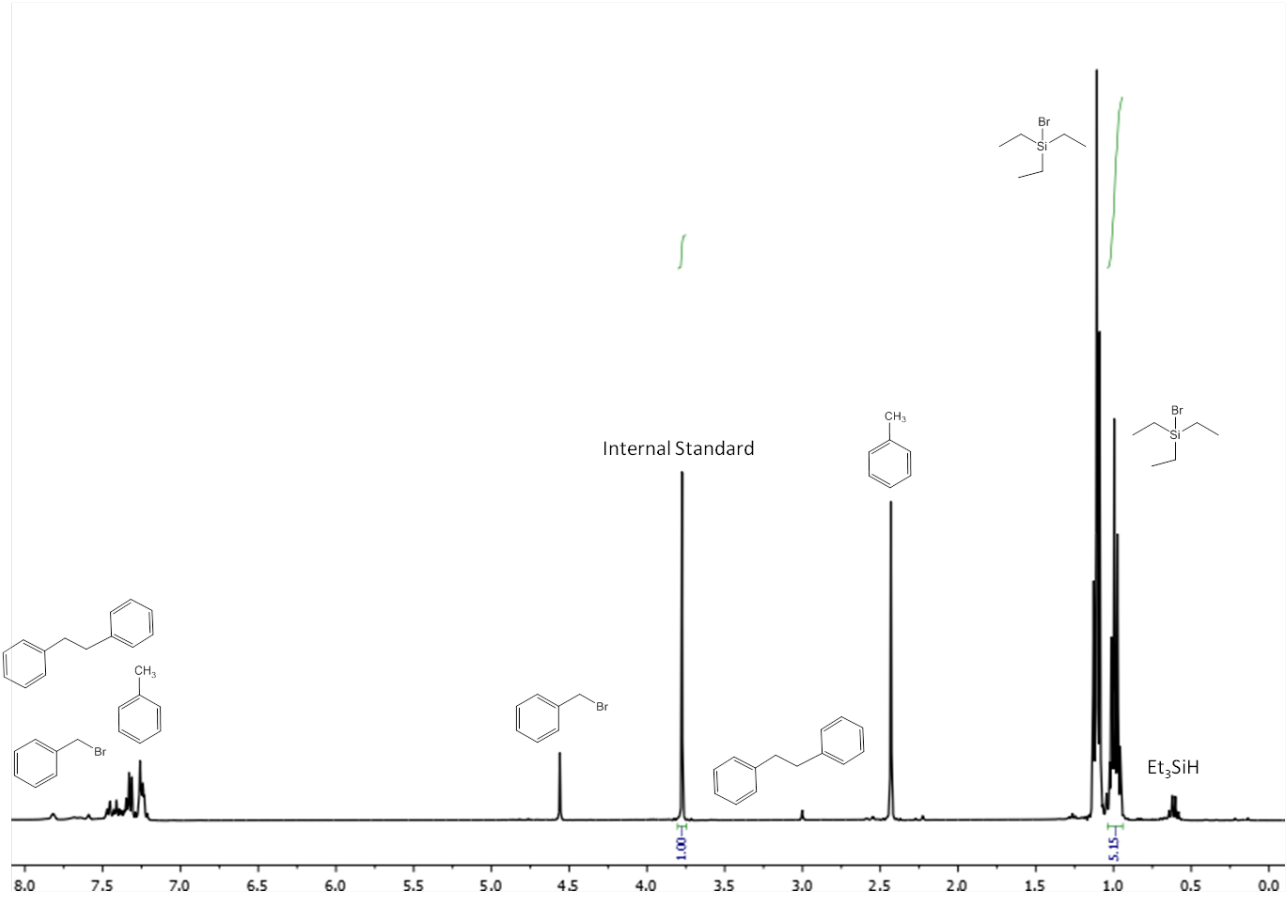
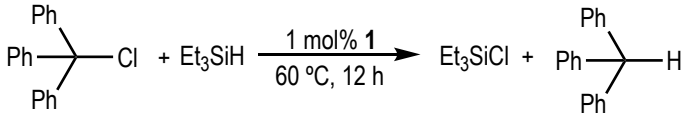


Figure 6. ^{1}H NMR spectrum for the reaction of debromination of benzyl bromide using Et_3SiH.



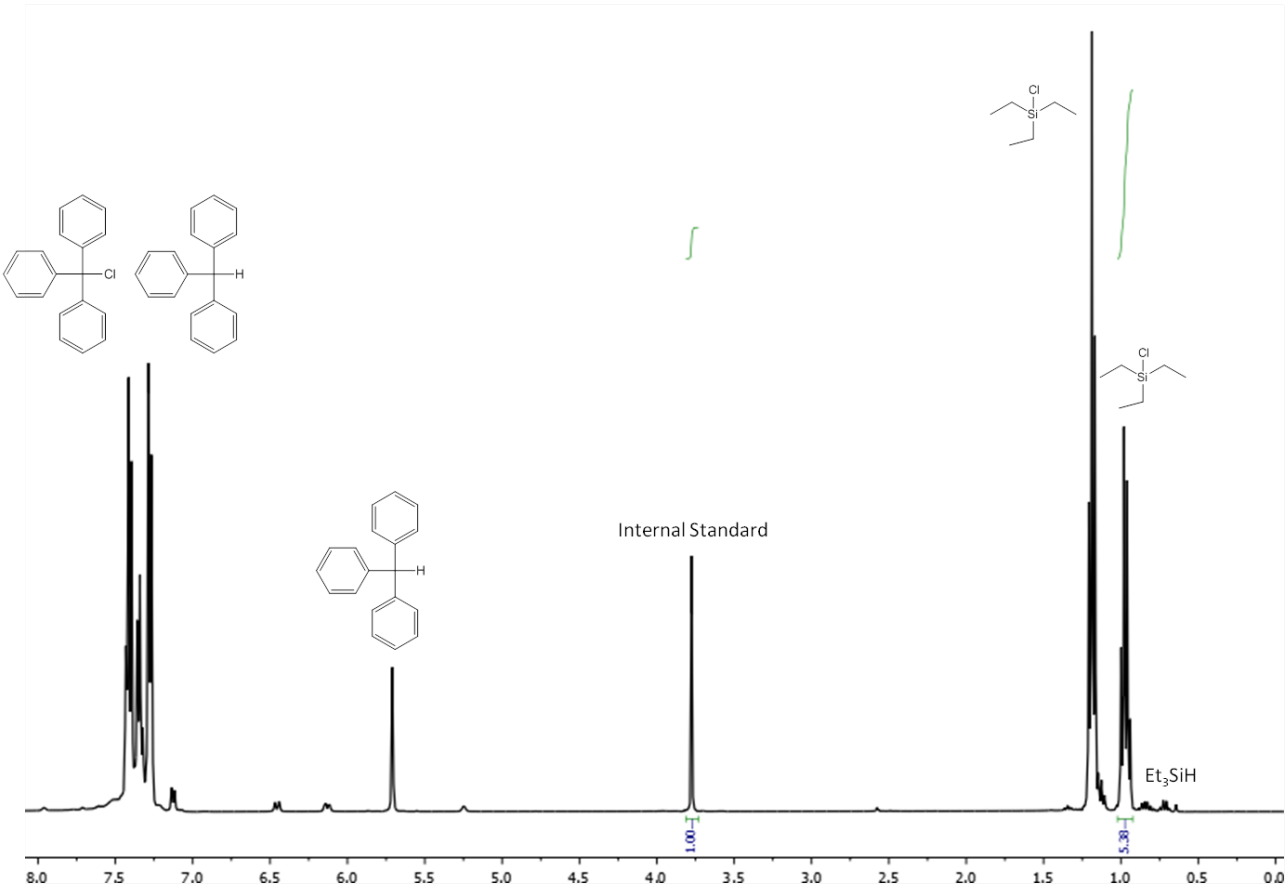
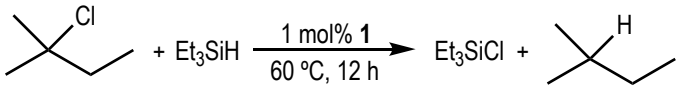


Figure 7. ^{1}H NMR spectrum for the reaction of dechlorination of trityl chloride using Et_3SiH.



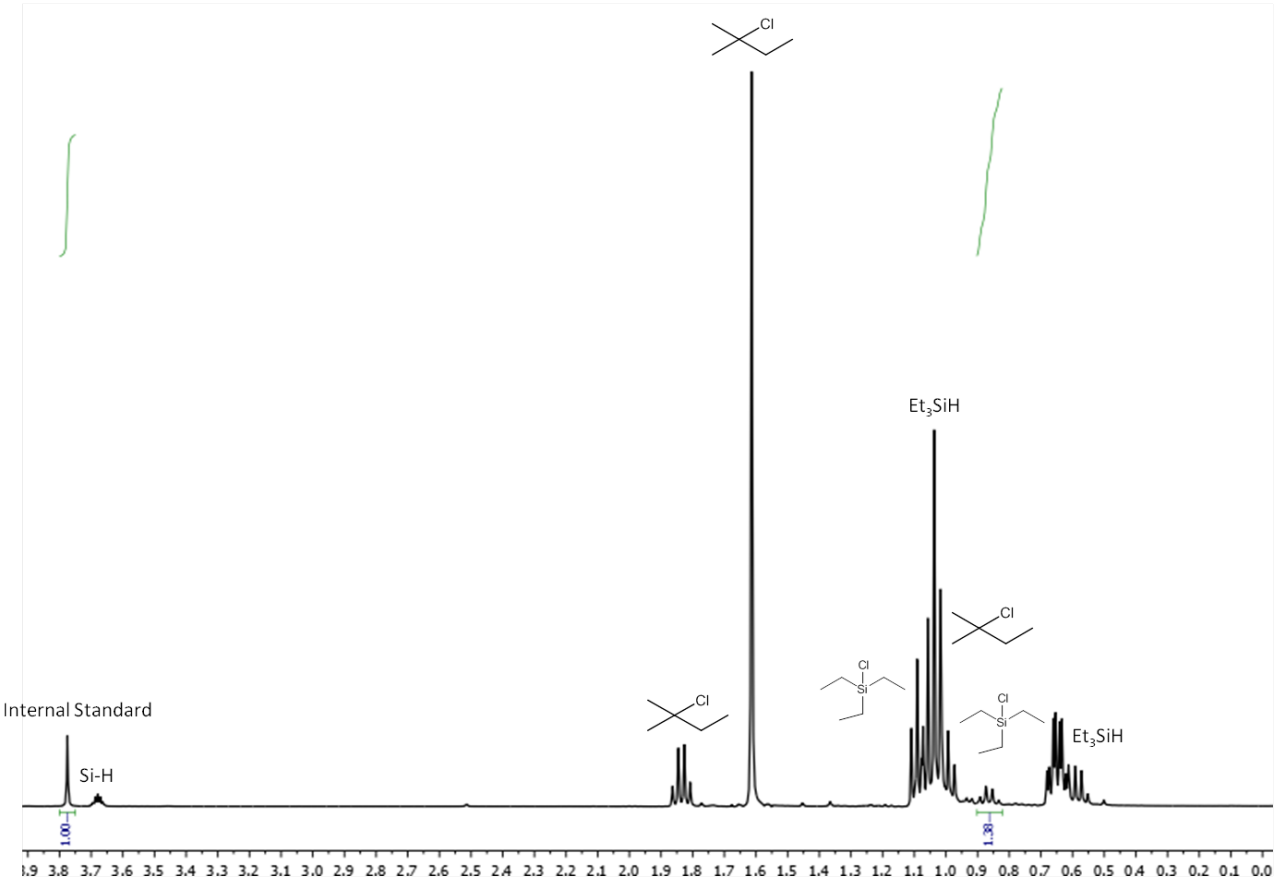
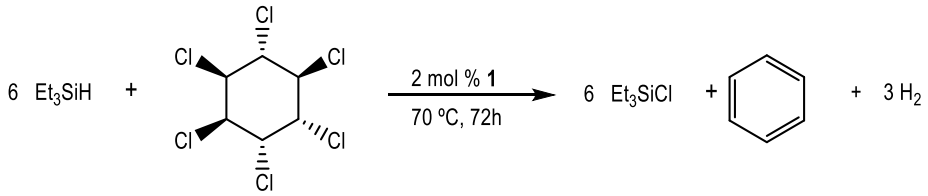


Figure 8. ^{1}H NMR spectrum for the reaction of dechlorination of *tert*-pentyl chloride using Et_3SiH.

Dehalogenation of polychlorinated pesticides using Et_3SiH

A Young flask charged with **1,** Et_3SiH and 10 mg of the organochlorines (hexachlorocyclohexane isomers α-, β-, δ-, γ-HCH, 0.035 mmol); dichlorodiphenyldichloroethane isomers (2,4'- and 4,4'-DDD, 0.031 mmol); 4,4'-dichlorodiphenyltrichloroethane (DDT, 0.028 mmol); and methoxychlor, 0.29 mmol) was stirred up to 72 h at temperatures between 70 - 80 ºC. After this time, 0.5 mL of $CDCl_3$ and 2 equivalents of dichloroethane (Internal Standard) were added and a ^1H NMR spectra was carried out at room temperature to calculate the conversion.



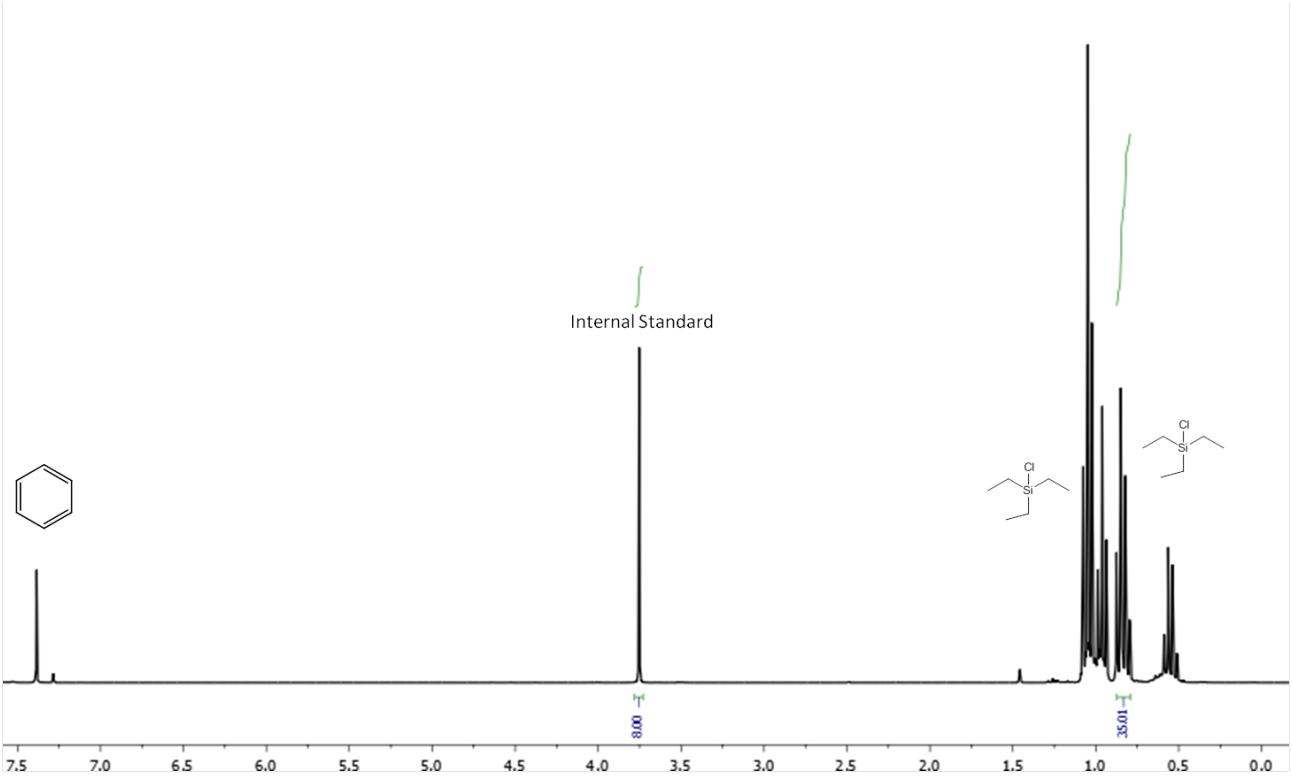
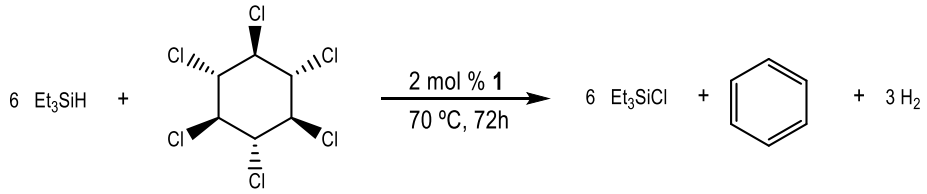


Figure 9. ^1H NMR spectrum for the reaction of dechlorination of α-1,2,3,4,5,6-hexachlorocyclohexane using Et_3SiH (50 µL, 0,31 mmol) and **1** with a catalyst charge of 2 mol % (1,16 mg, $6.95 \cdot 10^{-4}$ mmol) at 70 ºC.



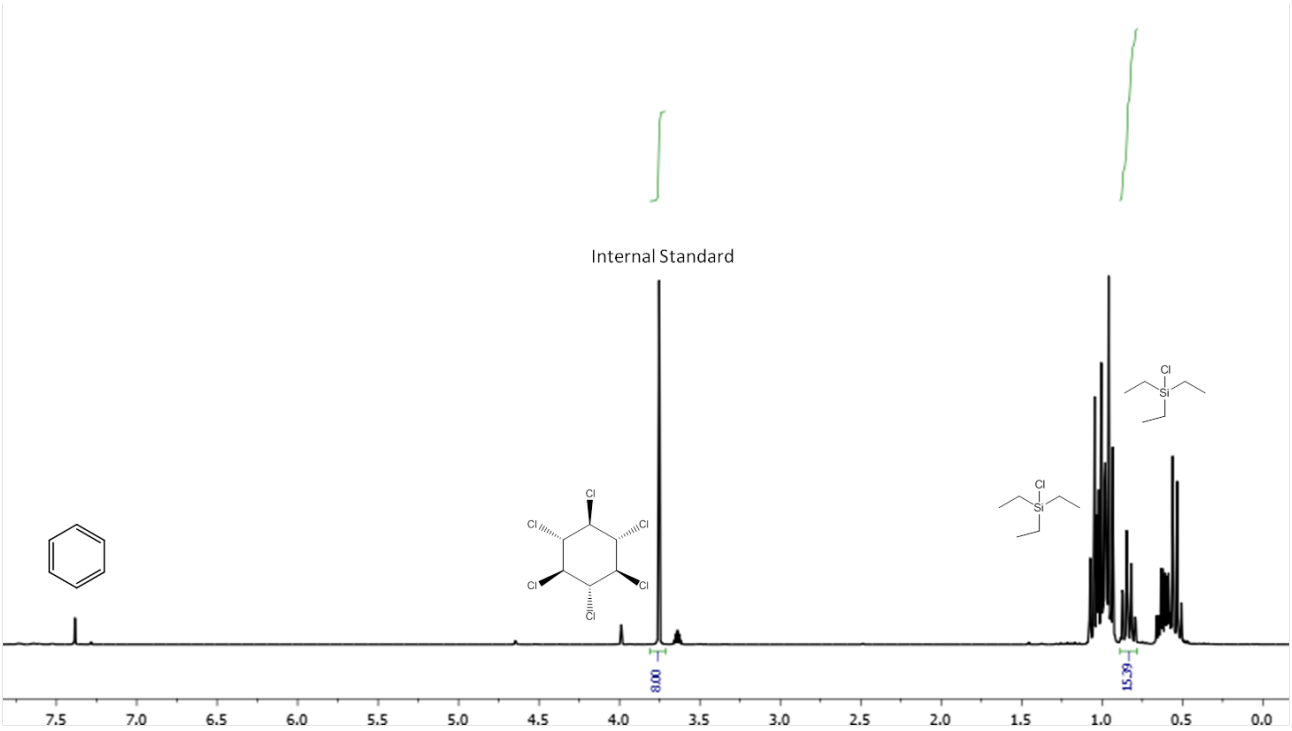
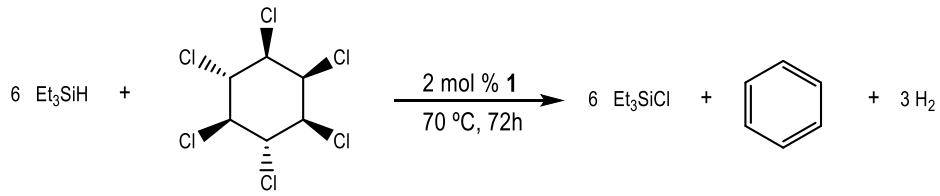


Figure 10. ^{1}H NMR spectrum for the reaction of dechlorination of β-1,2,3,4,5,6-hexachlorocyclohexane using Et_3SiH (50 µL, 0,31 mmol) and **1** with a catalyst charge of 2 mol % (1,16 mg, $6.95 \cdot 10^{-4}$ mmol) at 70 ºC.



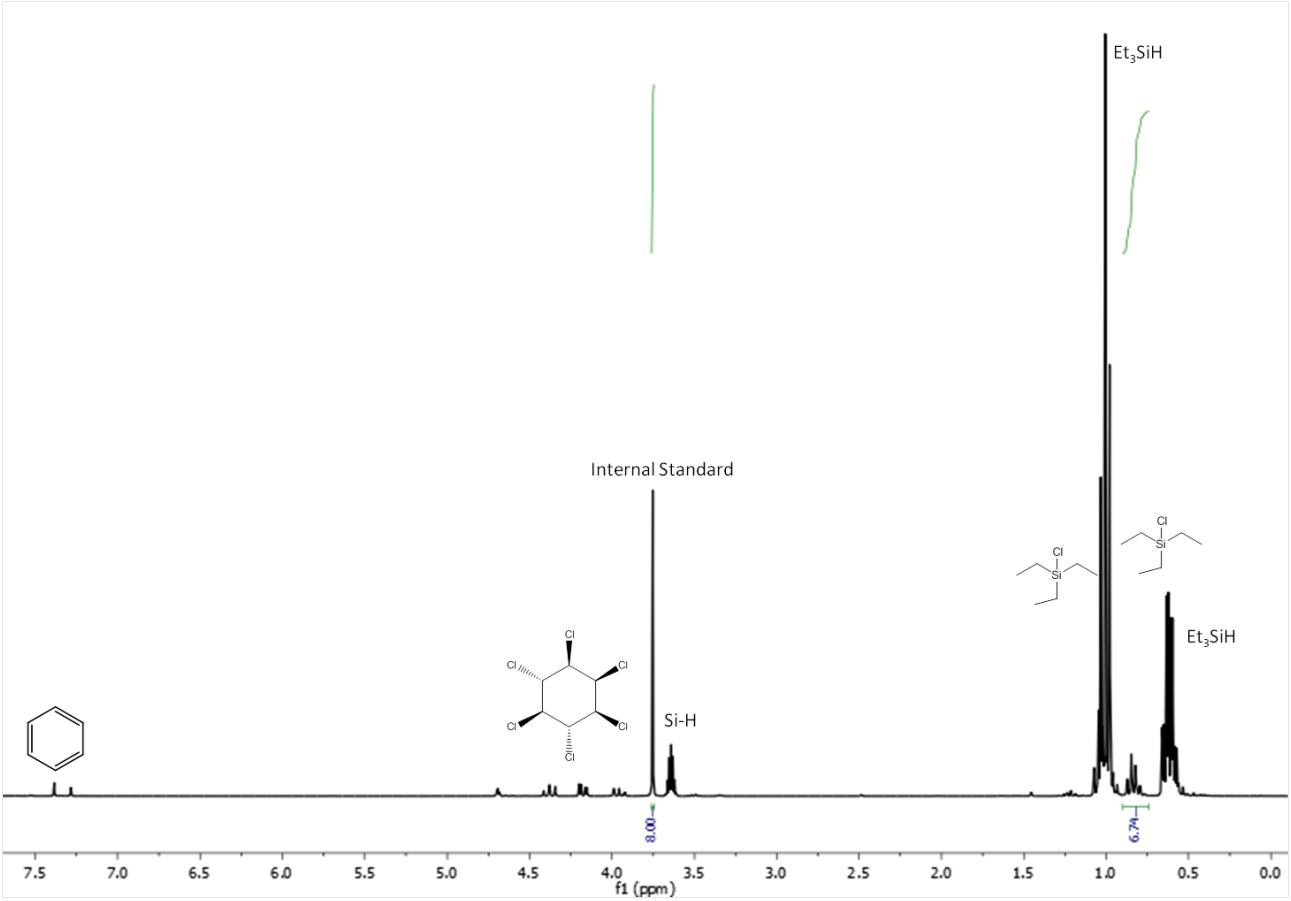
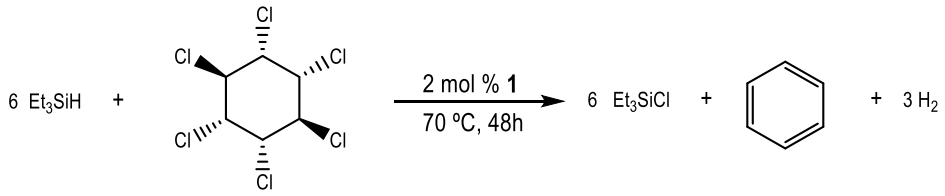


Figure 11. ^{1}H NMR spectrum for the reaction of dechlorination of δ-1,2,3,4,5,6-hexachlorocyclohexane using Et_3SiH (50 µL, 0,31 mmol) and **1** with a catalyst charge of 2 mol % (1,16 mg, $6.95 \cdot 10^{-4}$ mmol) at 70 ºC.



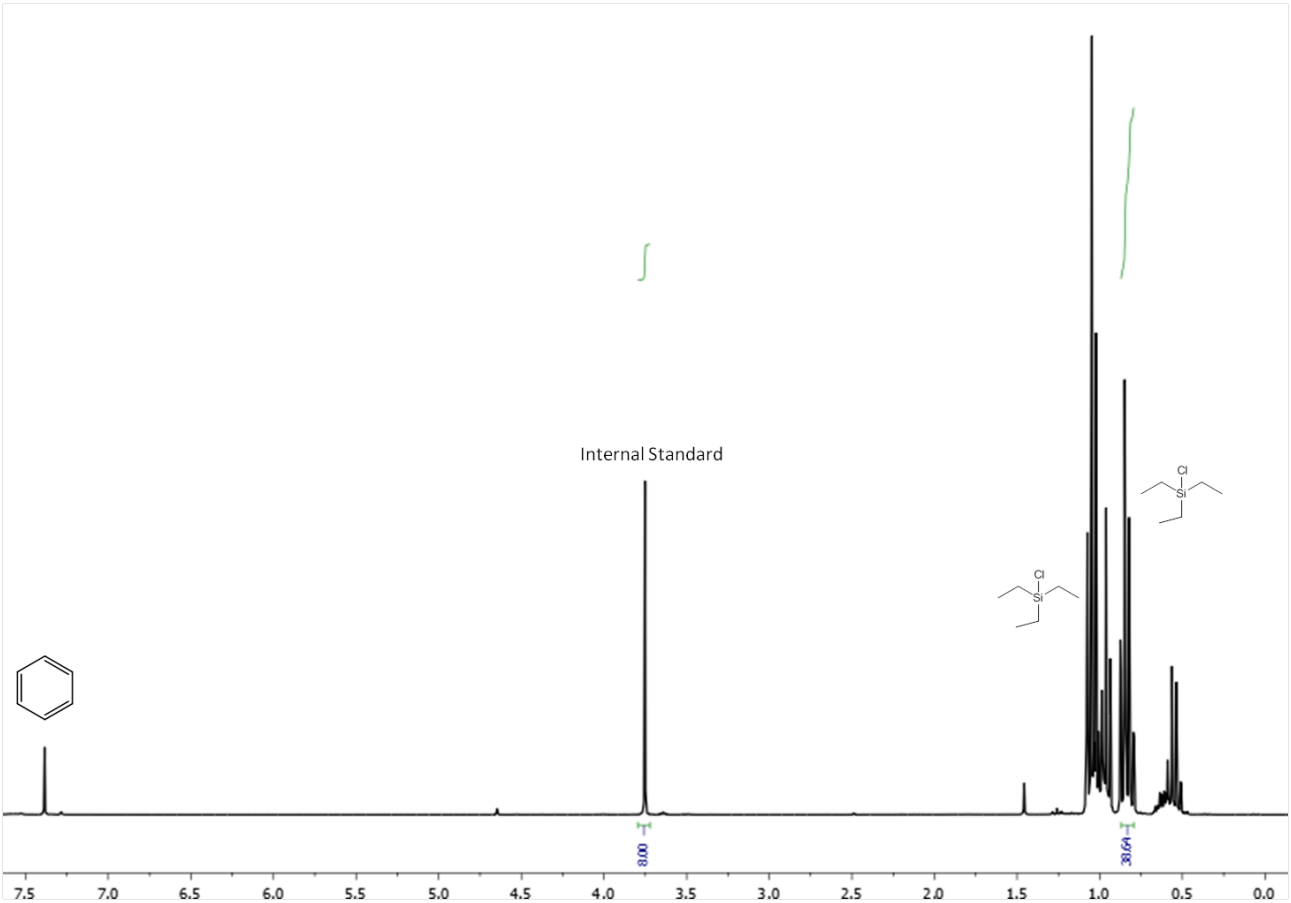
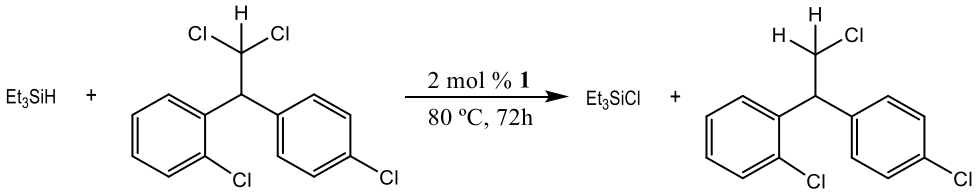


Figure 12. ^{1}H NMR spectrum for the reaction of dechlorination of γ-1,2,3,4,5,6-hexachlorocyclohexane using Et_3SiH (50 µL, 0,31 mmol) and **1** with a catalyst charge of 2 mol % (1,16 mg, $6.95 \cdot 10^{-4}$ mmol) at 70 ºC.



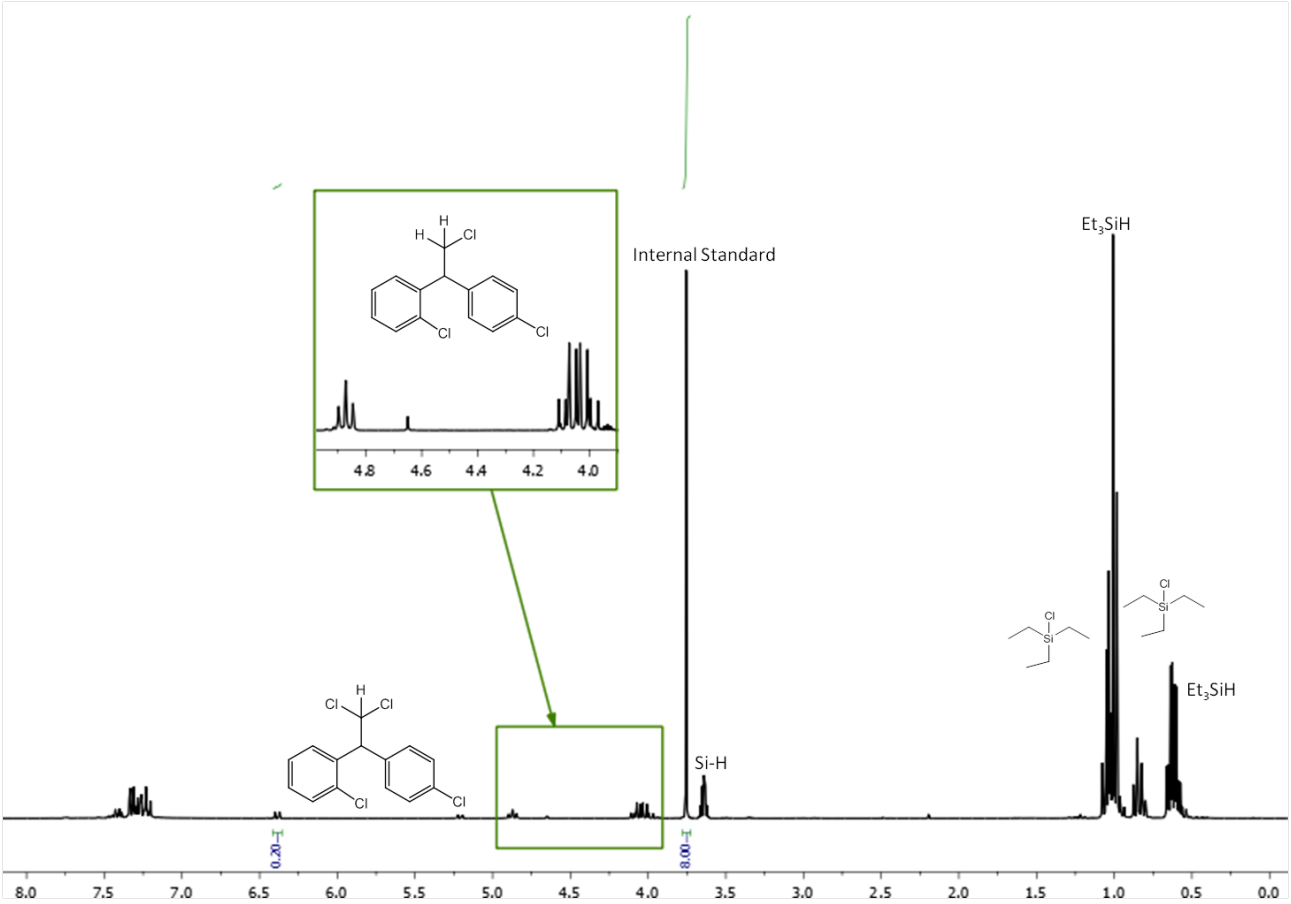
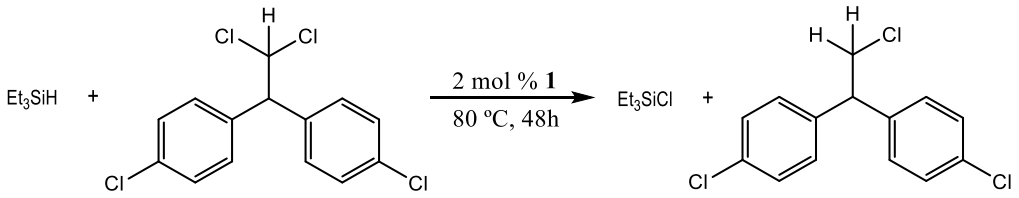


Figure 13. ^{1}H NMR spectrum for the reaction of dechlorination of 2,4'-dichlorodiphenyldichloroethane (2,4'-DDD) using Et_3SiH (26 µL, 0,16 mmol) and **1** with a catalyst charge of 2 mol % (1,05 mg, $6.29 \cdot 10^{-4}$ mmol) at 80 ºC.



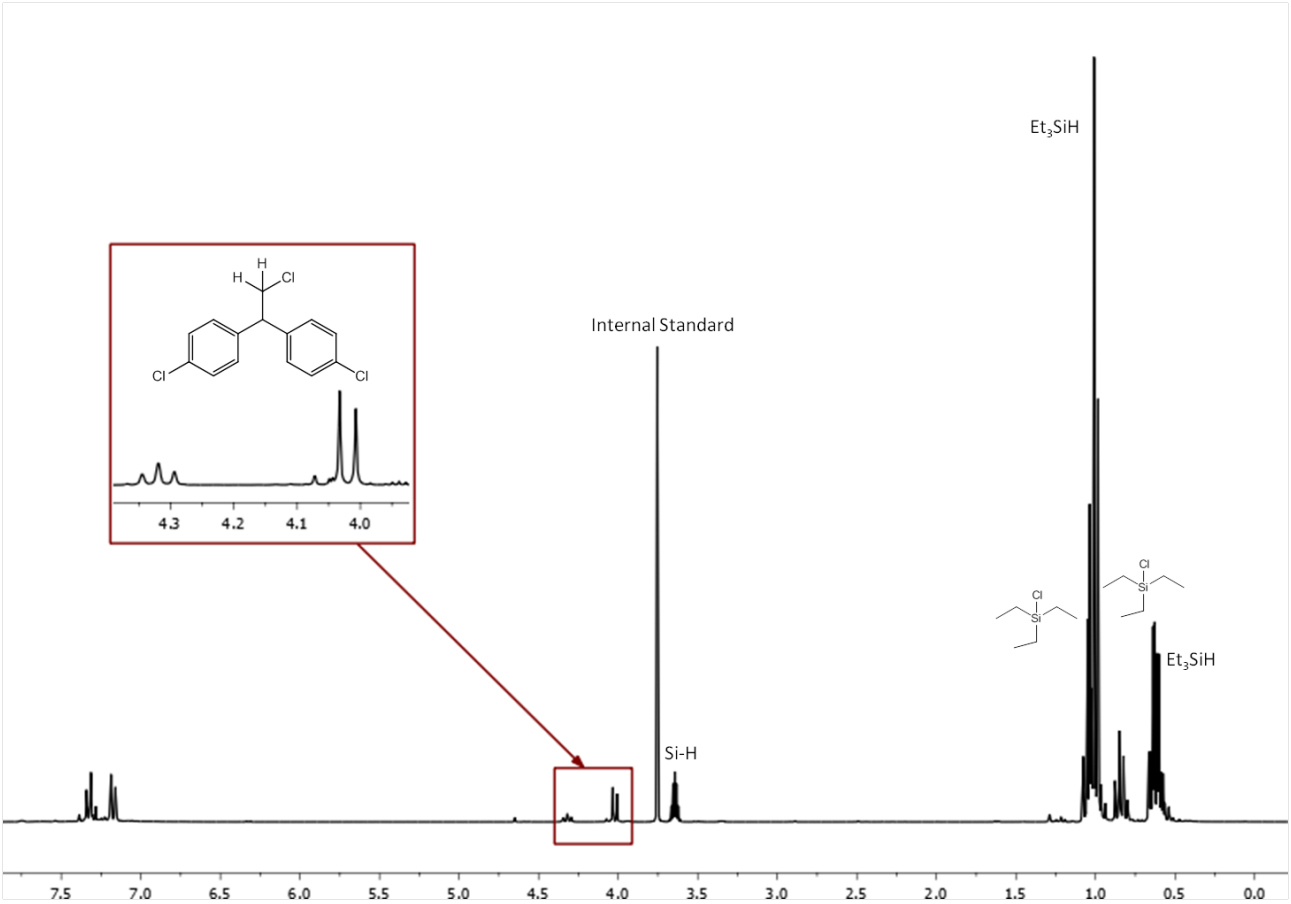
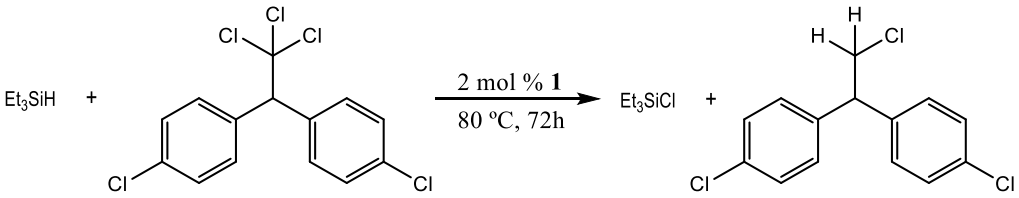


Figure 14. ^{1}H NMR spectrum for the reaction of dechlorination of 4,4'-dichlorodiphenyldichloroethane (4,4'-DDD) using Et_3SiH (26 µL, 0,16 mmol) and **1** with a catalyst charge of 2 mol % (1,05 mg, $6.29 \cdot 10^{-4}$ mmol) at 80 ºC.



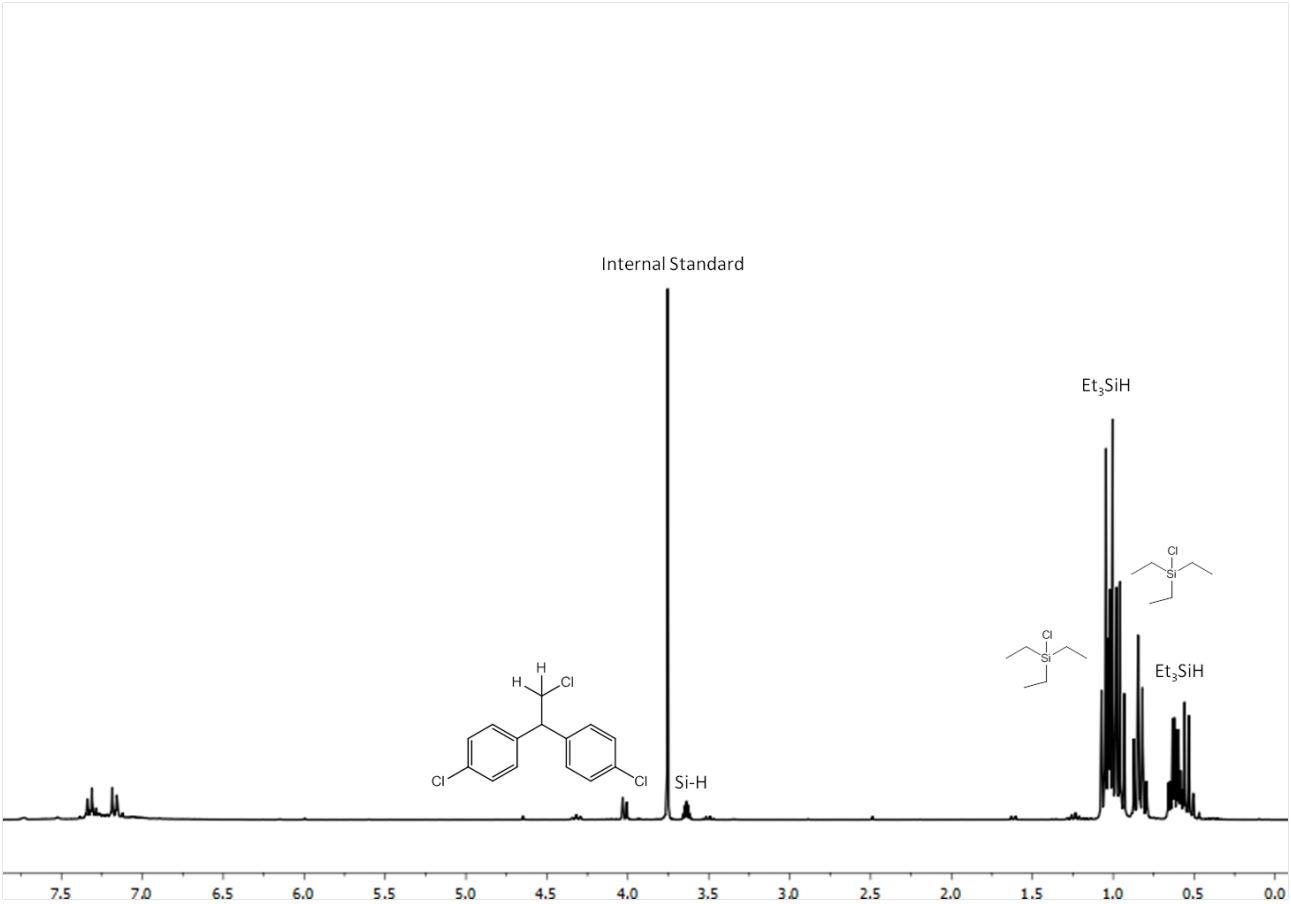
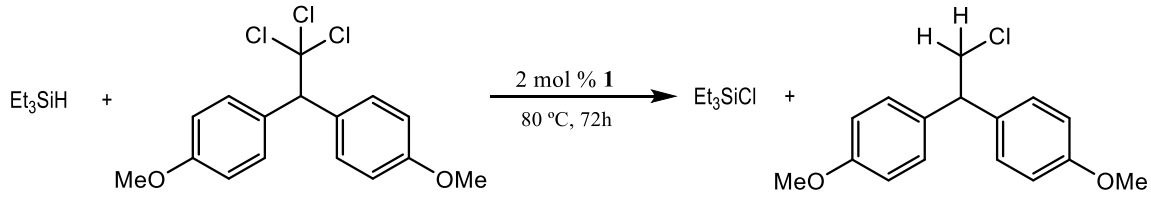


Figure 15. ^{1}H NMR spectrum for the reaction of dechlorination of 4,4'-dichlorodiphenyltrichloroethane (DDT) using Et_3SiH (27 µL, 0,17 mmol) and **1** with a catalyst charge of 2 mol % (0,94 mg, $5.64 \cdot 10^{-4}$ mmol) at 80 ºC.



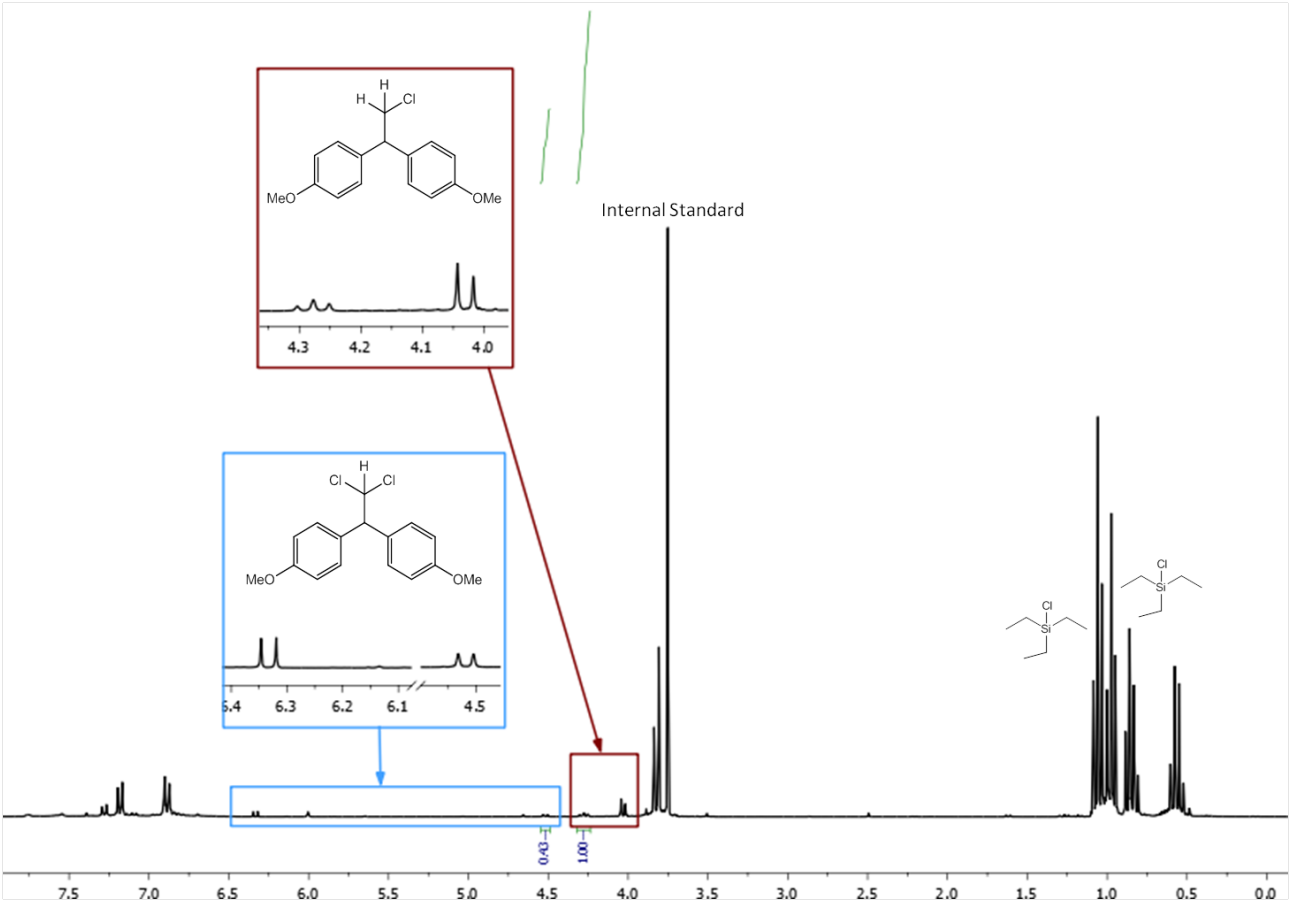


Figure 16. ^{1}H NMR spectrum for the reaction of dechlorination of methoxychlor using Et_3SiH (19 µL, 0,12 mmol) and **1** with a catalyst charge of 2 mol % (0,97 mg, $5.79 \cdot 10^{-4}$ mmol) at 80 ºC.

Dehalogenation of $CDCl_3$ using Et_3SiH at different temperatures

To a solution of **1** (4.2mg, 0.0025 mmol) in $CDCl_3$ (0.5 mL) charged in a J. Young NMR tube was added triethylsilane (Et_3SiH 40 µL, 0.25 mmol). The solution was monitored by ^1H NMR at 40ºC, following the disappearance of the hydrosilane resonance and the appearance of new chlorosilane and $CHDCl_2$. This experiment was repeated at different temperatures (45 ºC, 50 ºC and 55 ºC).

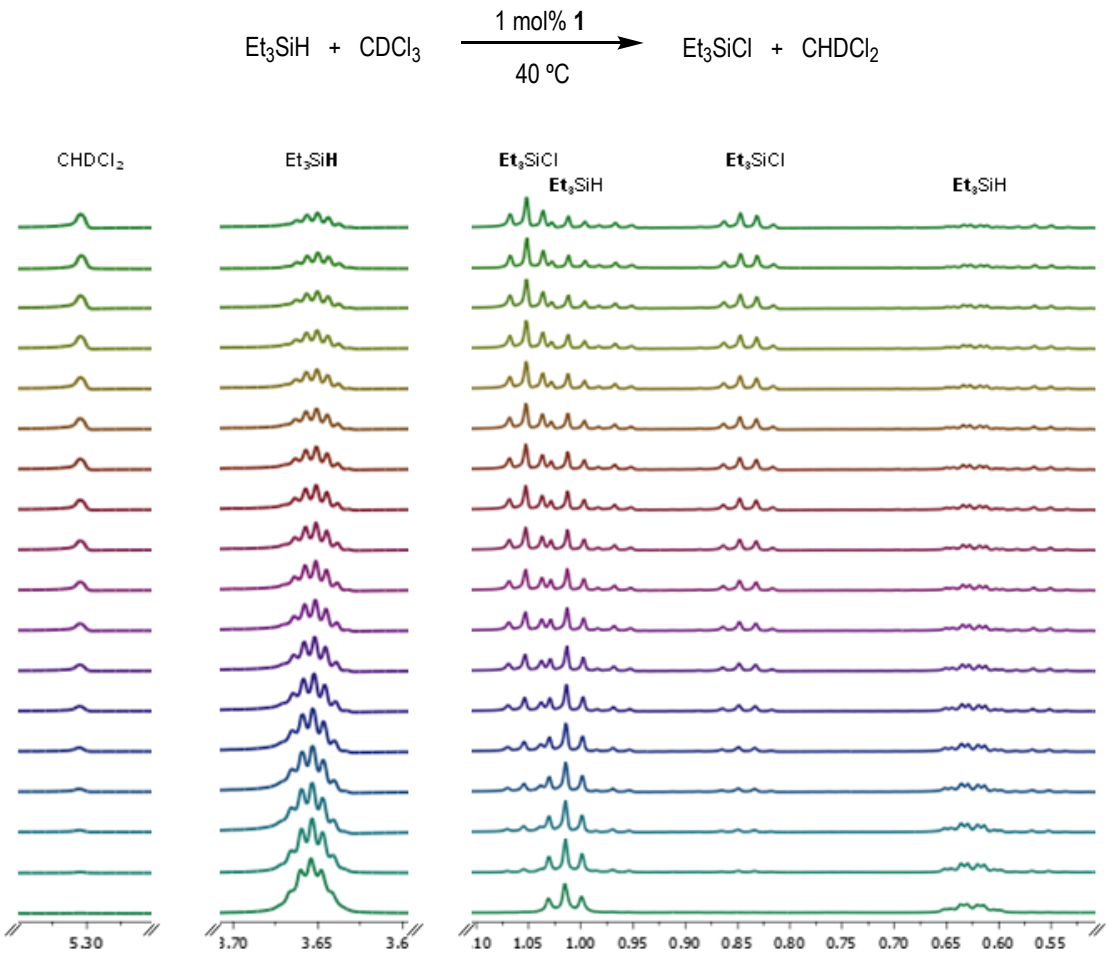


Figure 17. Dechlorination of $CDCl_3$ using Et_3SiH. Reaction monitoring by ^1H NMR at 40 ºC.

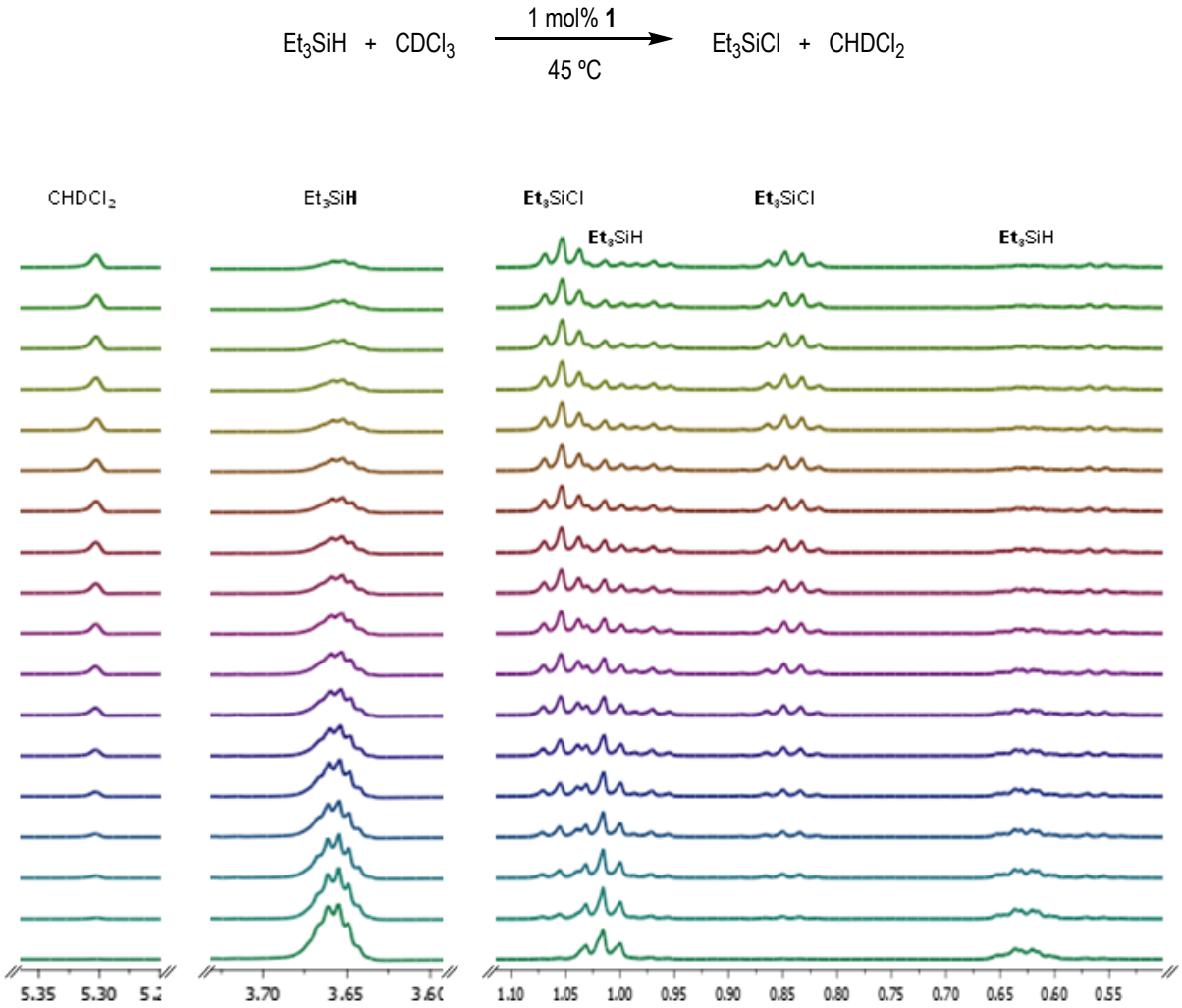


Figure 18. Dechlorination of $CDCl_3$ using Et_3SiH. Reaction monitoring by ^1H NMR at 45 ºC.

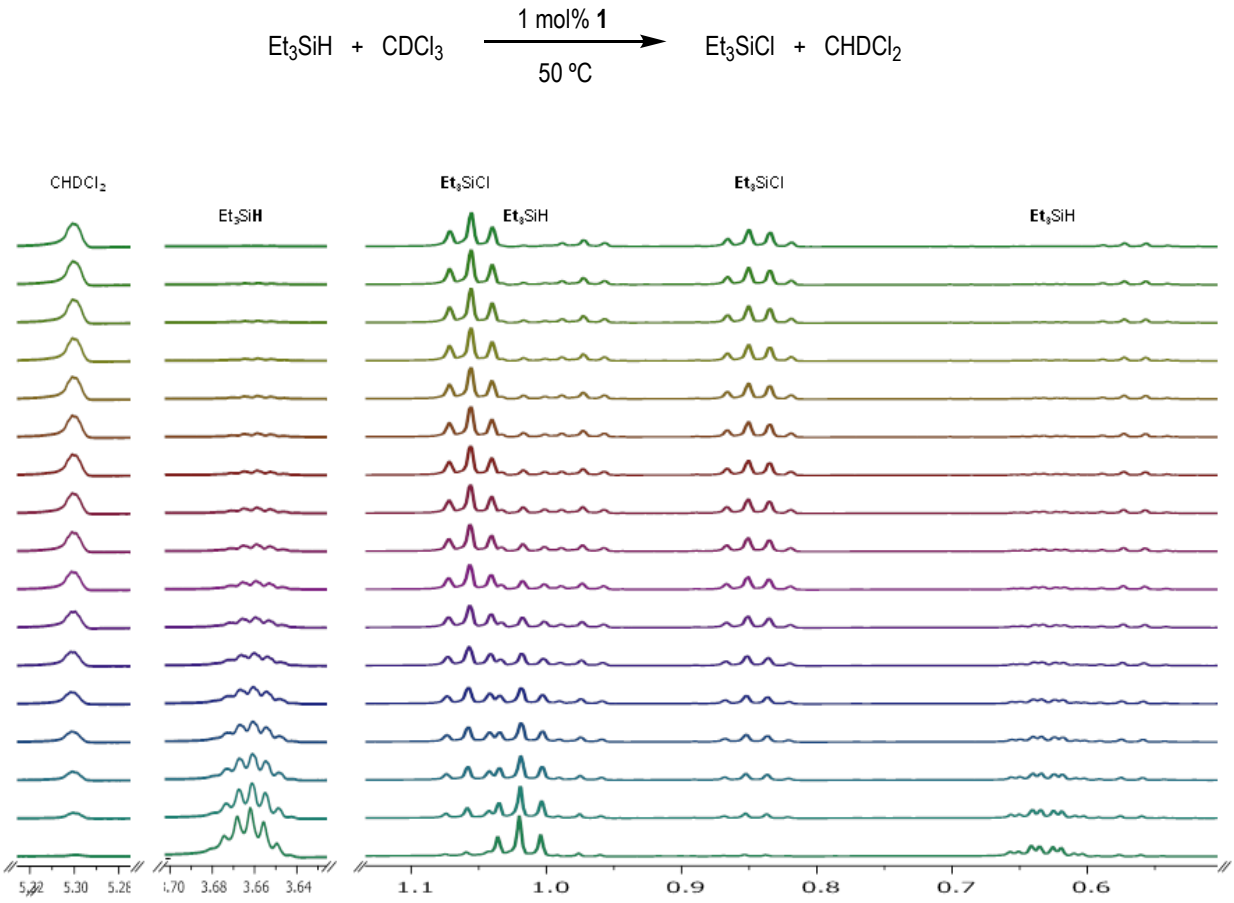


Figure 19. Dechlorination of $CDCl_3$ using Et_3SiH. Reaction monitoring by ^1H NMR at 50 °C.

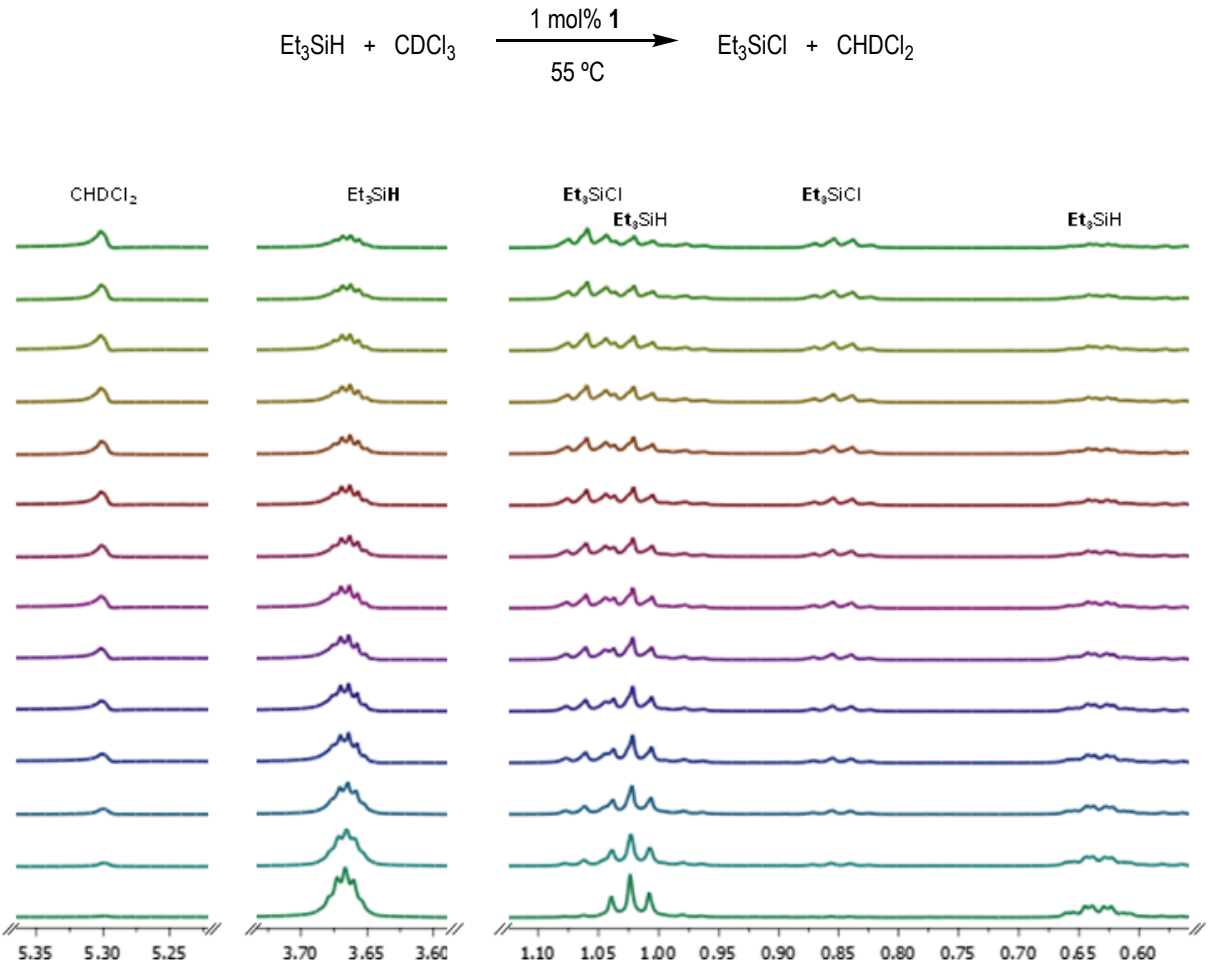


Figure 20. Dechlorination of $CDCl_3$ using Et_3SiH. Reaction monitoring by ^1H NMR at 55 ºC.

Dehalogenation of $CDCl_3$ using Et_3SiD (KIE)

To a solution of **1** (4.2mg, 0.0025 mmol) in $CDCl_3$ (0.5 mL) charged in a J. Young NMR tube was added Et_3SiD (40 µL, 0.25 mmol). The solution was monitored by ^1H NMR at 40ºC, following the disappearance of the hydrosilane resonance and the appearance of new chlorosilane

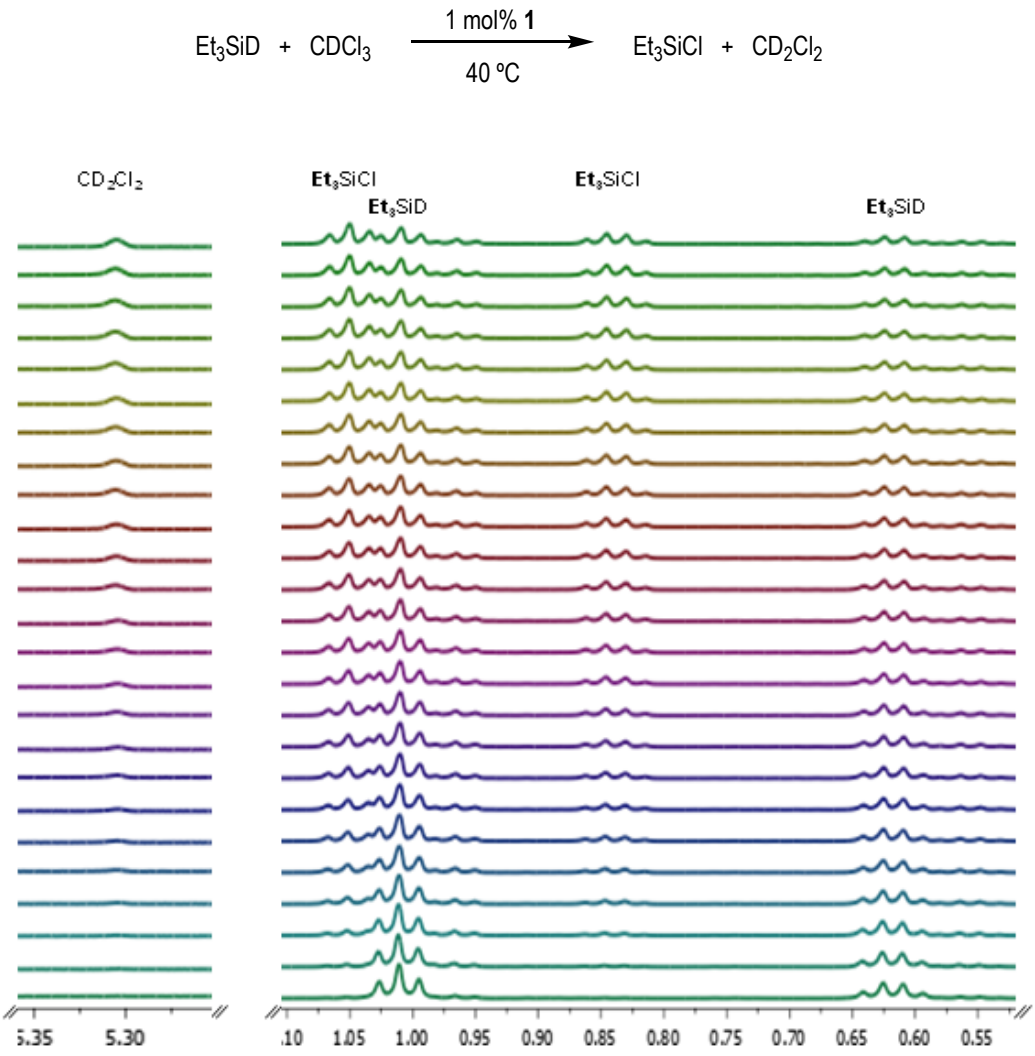


Figure 21. Dechlorination of $CDCl_3$ using Et_3SiD. Reaction monitoring by ^1H NMR at 40 ºC.

Dehalogenation of $CDBr_3$ using Et_3SiH

To a solution of **1** (4.2mg, 0.0025 mmol) in $CDBrI_3$ (0.5 mL) charged in a J. Young NMR tube was added a triethylsilane (Et_3SiH 40 µL, 0.25 mmol). The solution was monitored by ^1H NMR at 40ºC, following the disappearance of the hydrosilane resonance and the appearance of new bromosilane.

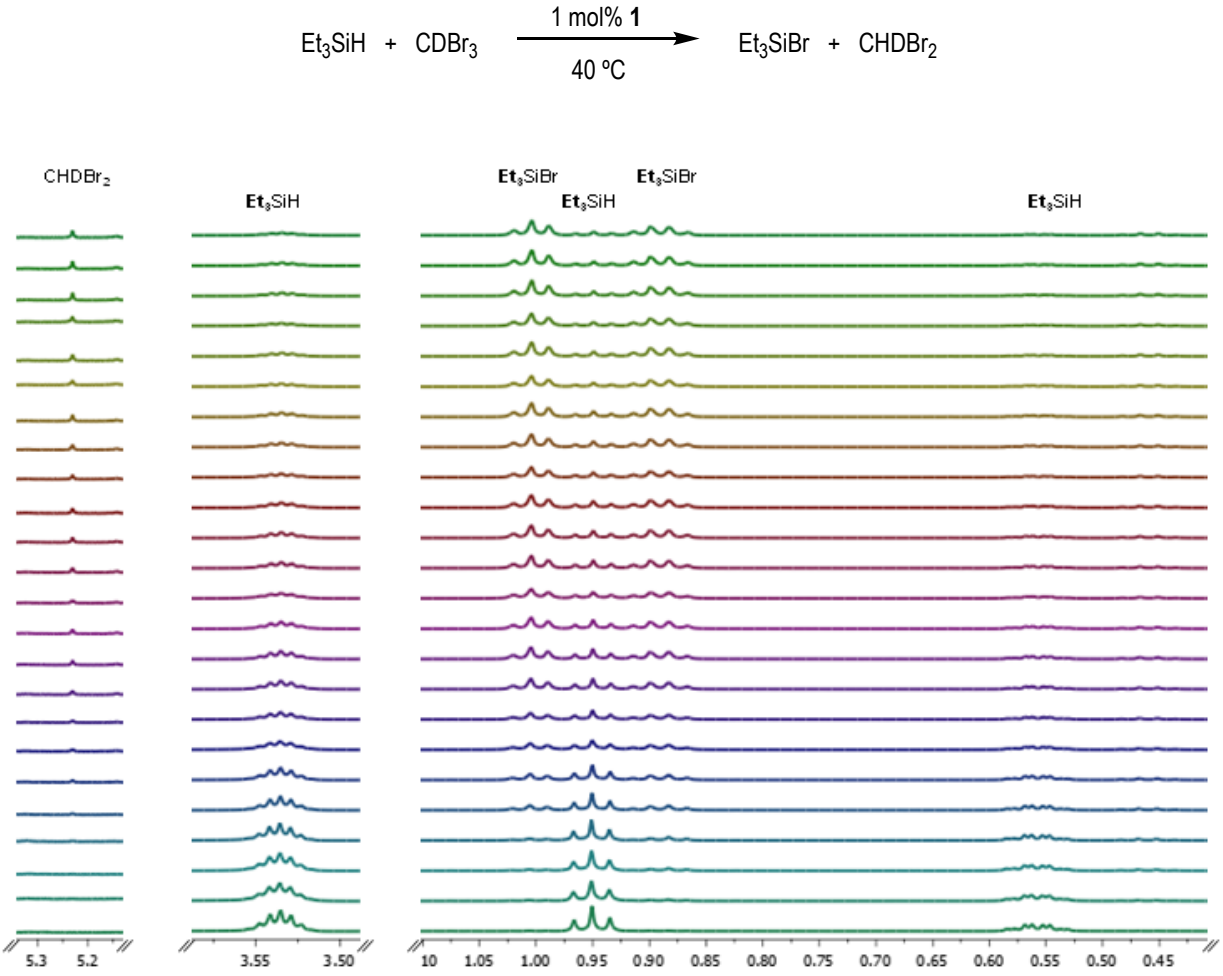


Figure 22. Debromination of $CDBr_3$ using Et_3SiH. Reaction monitoring by ^1H NMR at 40 ºC.

Triethylbromosilane: **^1H NMR (500 MHz, $CDCl_3$):** δ 1.00 (t, J= 7.6 Hz, 9H), 0.89 (q, J = 8.7, 7.7 Hz, 6H).

Dehalogenation of $CDCl_3$ using Et_3SiH and PPh_3

To a solution of **1** (4.2 mg, 0.0025 mmol) and PPh_3 (1 mg, 0.0038 mmol) in $CDCl_3$ (0.5 mL) charged in a J. Young NMR tube was added Et_3SiH (40 µL, 0.25 mmol). The solution was monitored by ^1H NMR at 50ºC, following the disappearance of the hydrosilane resonance and the appearance of new chlorosilane.

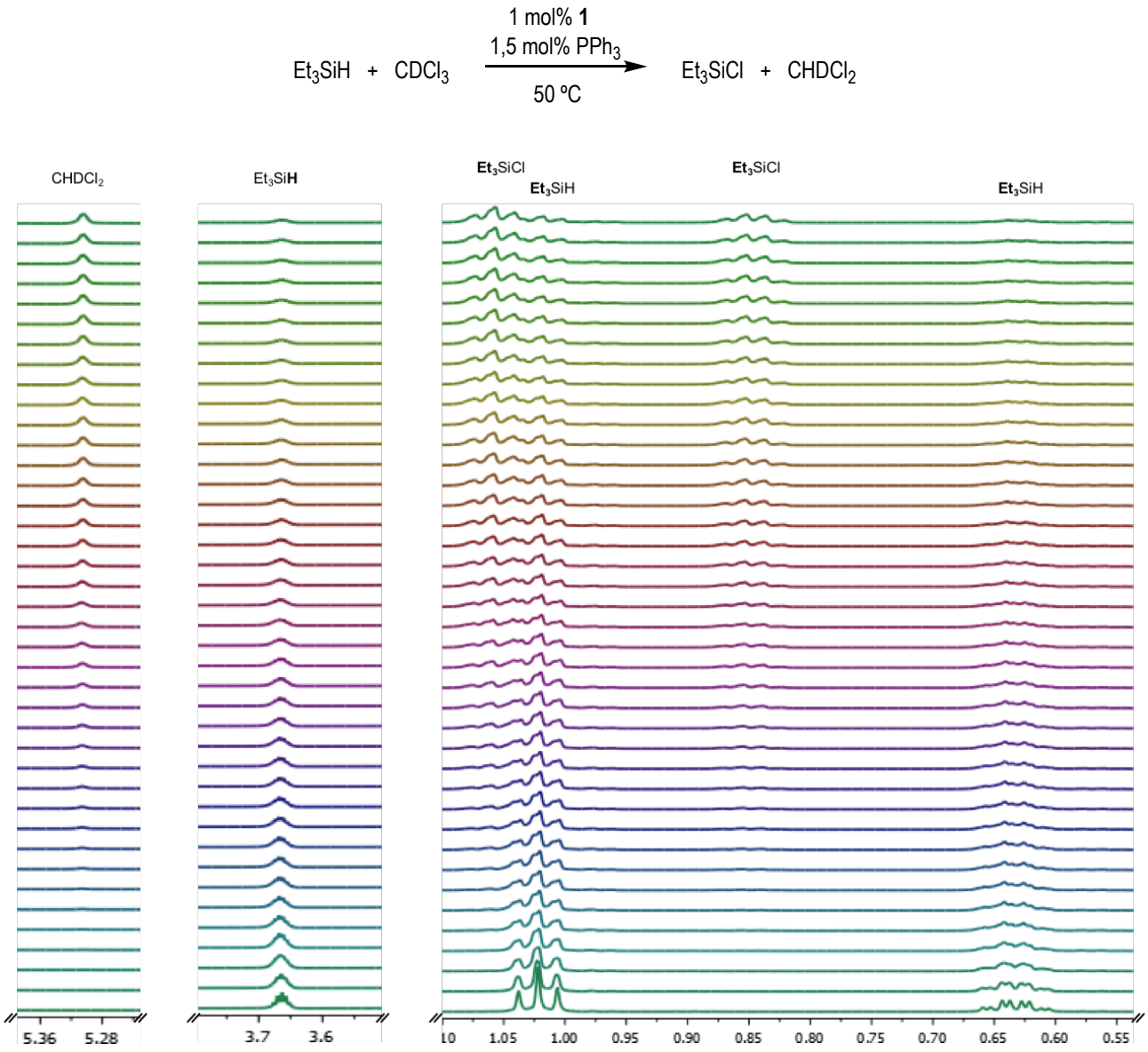


Figure 23. Dechlorination of $CDCl_3$ using Et_3SiH and 1.5 mol% of PPh_3. Reaction monitoring by ^1H NMR at 50 ºC.

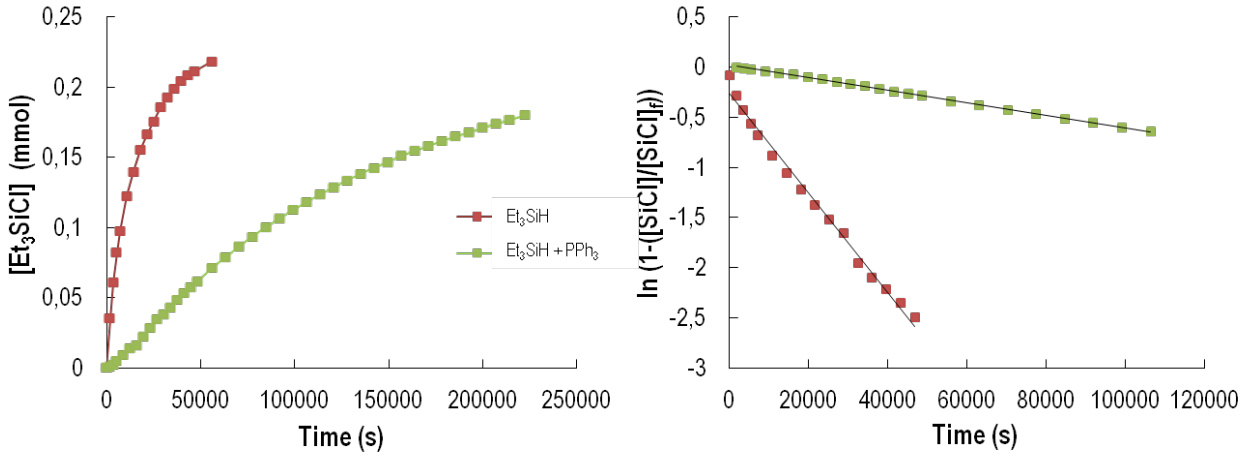
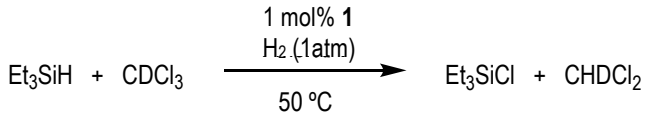


Figure 24. Concentration of Et_3SiCl *vs* time and first order plots for the dechlorination of $CDCl_3$ using Et_3SiH with and without PPh_3.

Dehalogenation of $CDCl_3$ using Et_3SiH under H_2 atmosphere.

A J. Young NMR tube charged with **1** (4.2 mg, 0.0025 mmol), $CDCl_3$ (0.5 mL) and Et_3SiH (40 µL, 0.25 mmol) was placed under 1 atm. of H_2. The solution was monitored by ^1H NMR at 50ºC, following the disappearance of the hydrosilane resonance and the appearance of new chlorosilane.



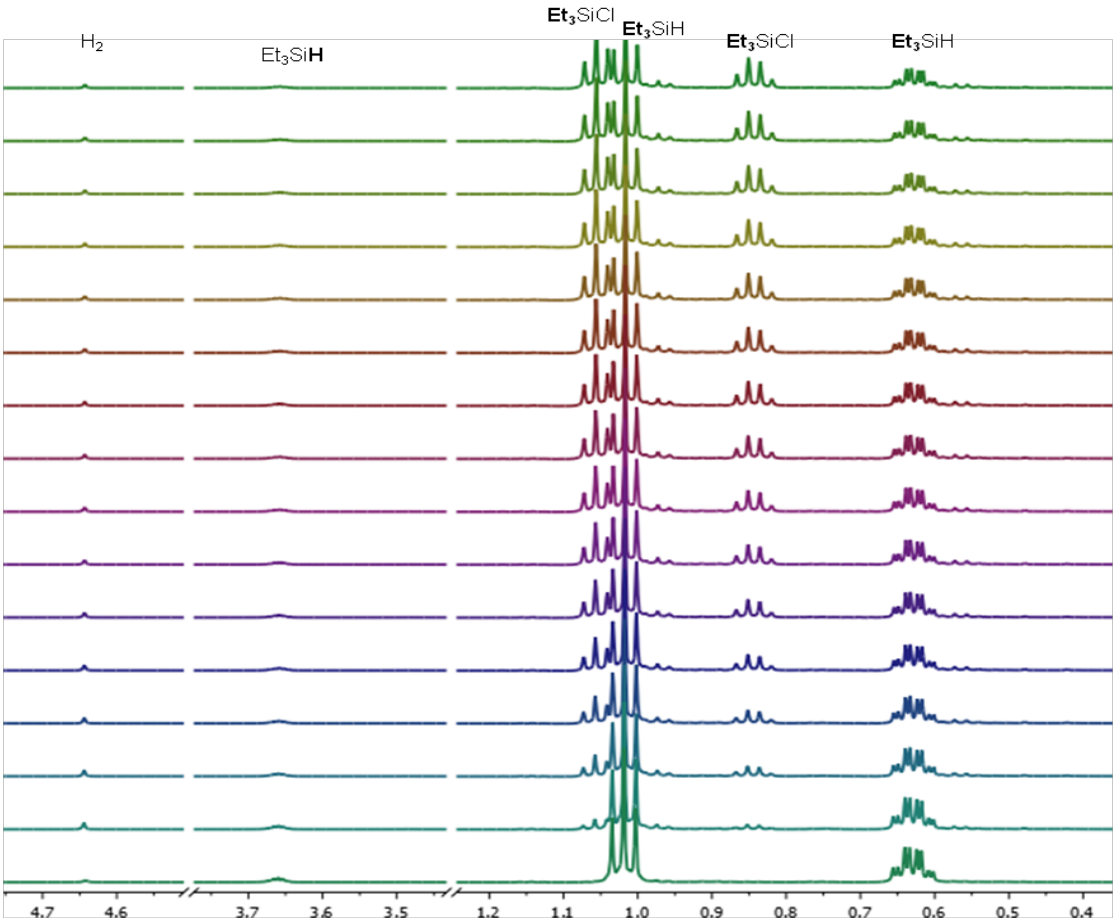


Figure 25. Dechlorination of $CDCl_3$ using Et_3SiH under 1 atm of H_2. Reaction monitoring by ^1H NMR at 50 ºC.

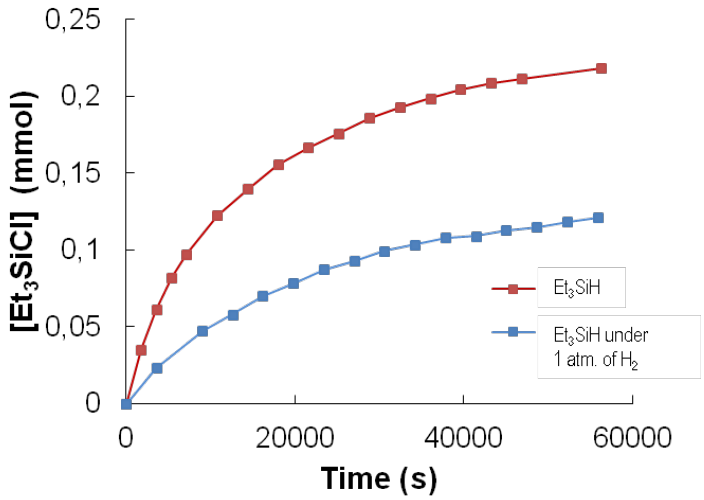
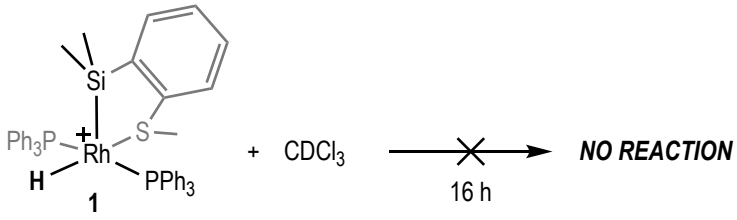


Figure 26. Concentration of Et_3SiCl *vs* time for the dechlorination of $CDCl_3$ using Et_3SiH and under H_2 atmosphere.

Control experiment

A solution of **1** (20 mg, 0.012 mmol) in $CDCl_3$ (5 mL) in a J. Young NMR tube was monitored by ^1H NMR observing that after 16 h *NO REACTION* was observed.



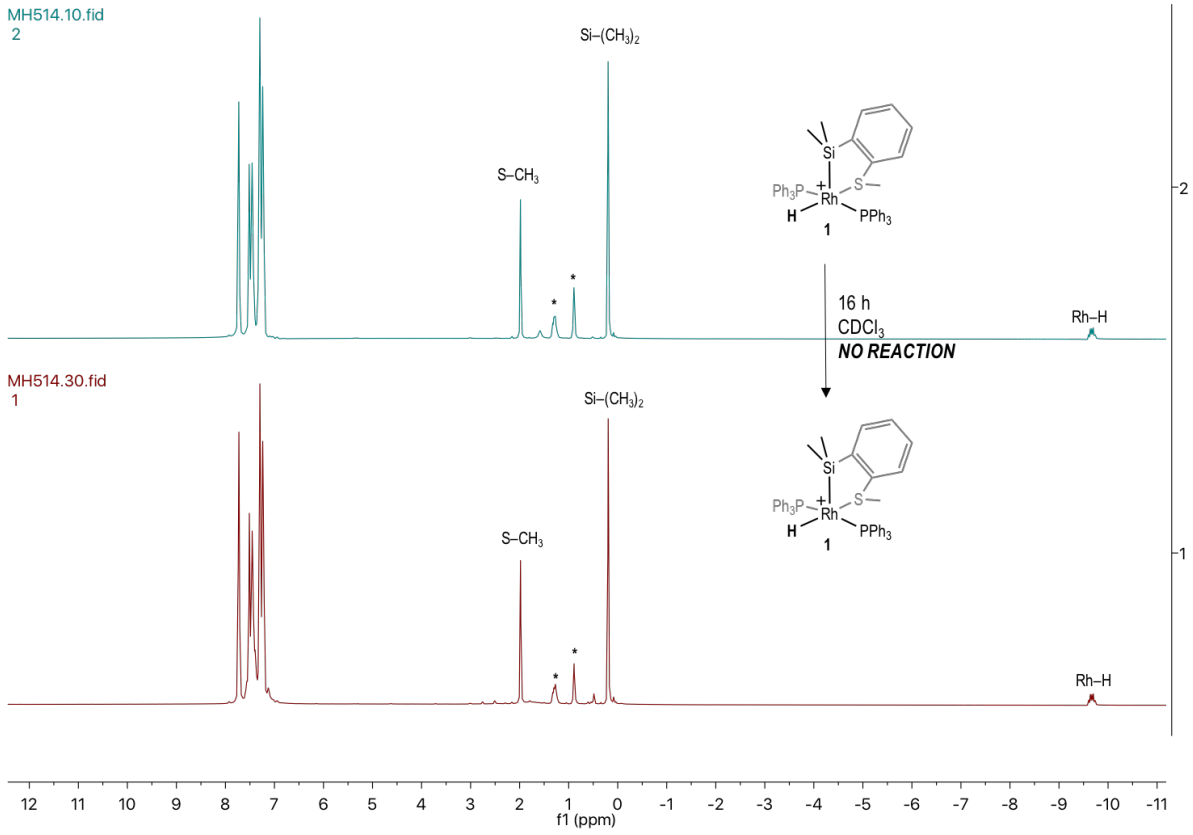
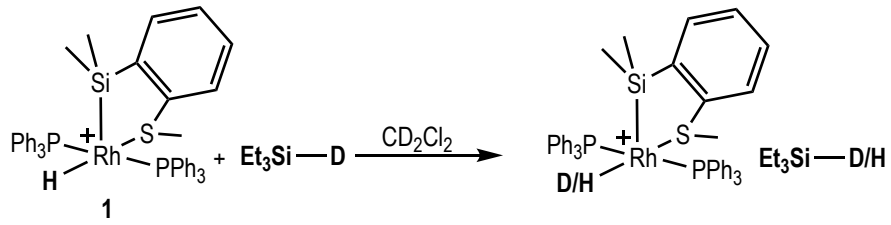


Figure 27. ^1H NMR spectrum of **1** in $CDCl_3$ after 10 minutes (top) and after 16 hours (bottom). (*) pentane

H/D Exchange experiment

A solution of **1** (20 mg, 0.012 mmol) in CD_2Cl_2 (5 mL) in a J. Young NMR tube was added Et_3SiD (2 µL, 0.012 mmol), after 15 minutes of reaction the ^1H NMR shows the formation of a 20 % of Et_3SiH demonstrating the H/D interchange.



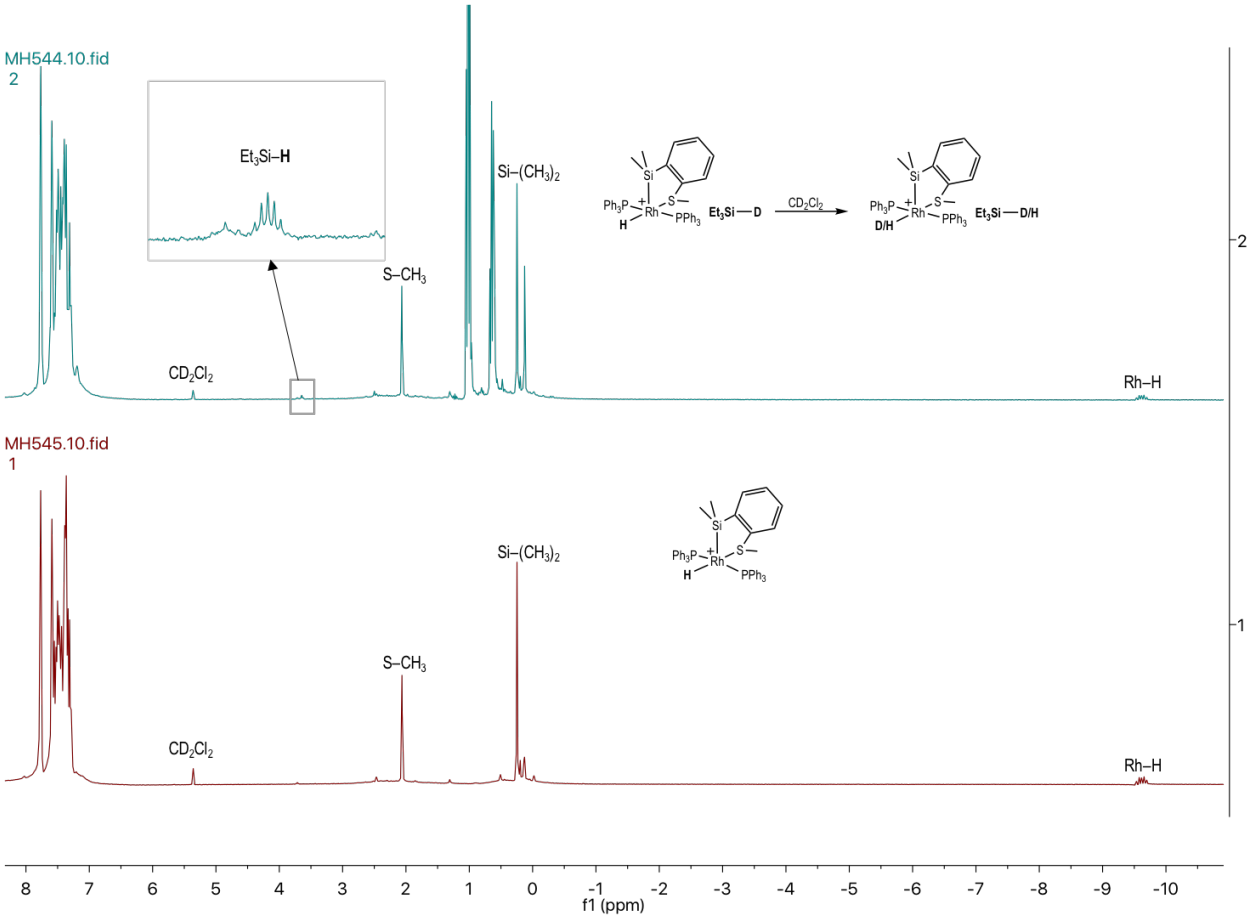


Figure 28. ^1H NMR spectrum (CD_2Cl_2) of **1** in presence of an equivalent of Et_3SiD after 10 minutes to has been prepared (top). ^1H NMR spectrum (CD_2Cl_2) of **1** (bottom).

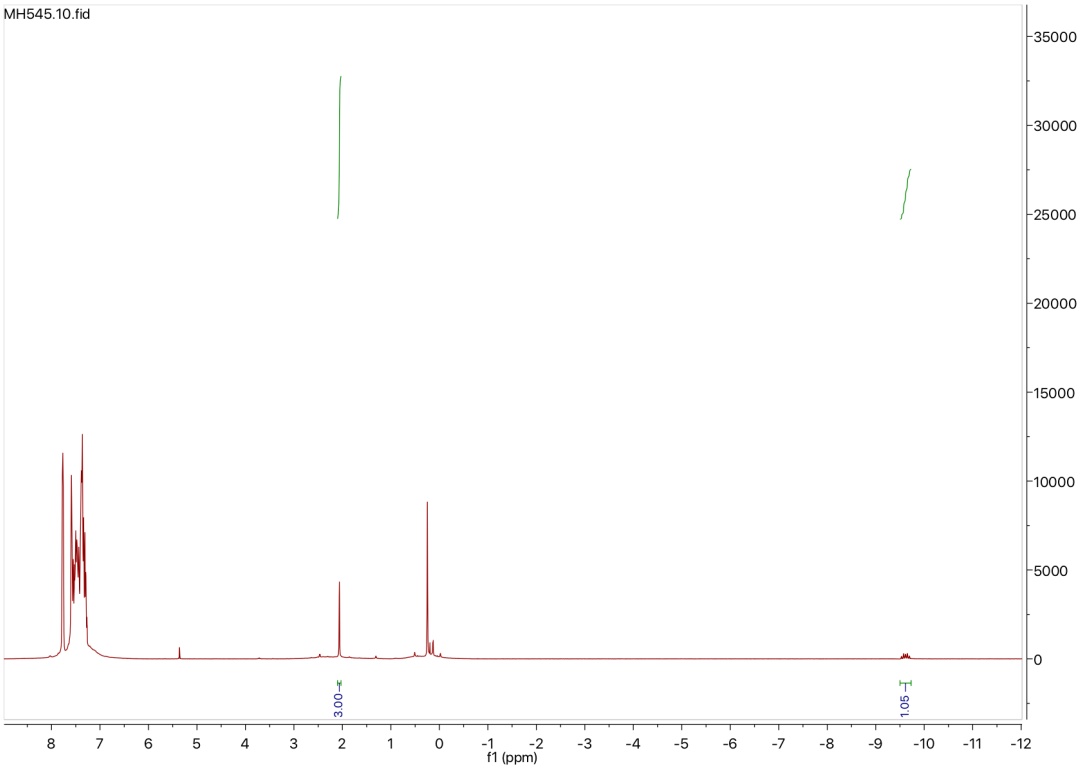


Figure 29. ^{1}H NMR spectrum (CD_2Cl_2) of **1**.

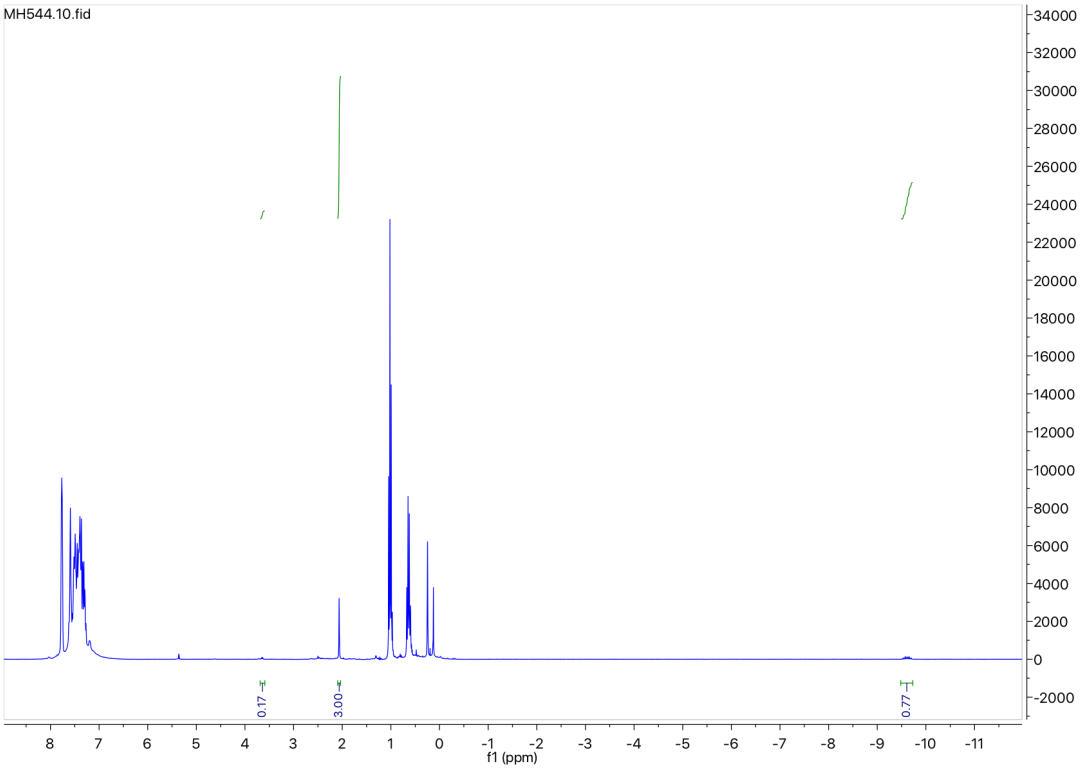


Figure 30. ^{1}H NMR spectrum (CD_2Cl_2) of **1** in presence of an equivalent of Et_3SiD after 10 minutes to has been prepared.

References

1. S. Azpeitia, M. A. Garralda and M. A. Huertos *ChemCatChem,* 2017, **9**, 1901-1905.