Ƀ ʔ ȺŁɋɋ ɇ ŁȾ ₵ Ⱦ Ɉ Ⱦ ş ɃɄɅɃɆŪ ₵ Ⱦ ₵ 1,n-ɋŁɈ ɋɅɃ

Ƀ ş ŁũɃɆŁş ɉ ʔ Łɋ ʔ ɆȺ ɉ ş Ⱦ Ɉ ʔ Łɉ Ⱦ ɉ ɇ ɉ ş Ɉ Ƀ ʐ Ⱥʔ ₵

ɉ ɄɃ ʔ ɉ ʔ ɃɆɋ ʐ ɉ ɇ Łɋ Łɉ Au

ȾɃ ɇ Ȼɉ ʐ Ʉ ɉ Ɇ ɉ Ⱦ ₵ ȡɉ ƇŁş ŁȾ ₵

ȺɄŁȡş ȺɄɋ ʔ Ⱦ ɉ Ū ₵ ũ ₵ ɇ ₵ Ɇ: ʐ . Ɇ ɇ Ʌɉ ɇ ɉ Ⱦ ₵ Ɇ

ɋŁɉ ɇ ɅŁȡ₵ ʐ Ⱥɇ ɉ Ʉ ɇ Ɉ ɉ Łɉ ȾɃ Ɉ ɋŁɄ ş ɋ ʐ ɉ ɇ Ƀ Ɇ

ȺŁɋŁȾ ȺɈ Ɇ ₵ Ɇ

ɇ ʐ ₵ ʐ ɉ ɉ ₵ ʐ ȺŁɉ Ɇ, Ʉ ɉ ʔ ȺɄŁɆ ɇ ₵ ʐ ŁɃ Ⱦ Ʌ₵ ɇ ₵ Ɇ

ū ȺȡɅɃ Ɉ ɉ ɅŁɃ Ɇ 2013

DEHYDROGENATIVE CYCLOADDITION OF TETHERED 1,n-DIHYDRODISILANES TO ALKYNES CATALYZED BY GOLD NANOPARTICLES

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«ʔ Ŭ ɛ ŬɗŬɞŮǝʆ Ŭ ɧ Ŭ̋ɞ ɢɗŮʆ, ɜŬɕŮǝʆɔɘŬ Ŭ̋ɞ ůɐɛ Ůɟ Ŭ,

ɜŬ Ůǝ́ ɞŮǝʆɔɘŬ Ŭ̋ɞ Ŭɨ ɟ ɞɜ.

ɇ ɞ ůɖɛ ŬɜŰǝɧ ŮɞŬɘɜŬɛɖ ůŰŬɛŬŰɣʆɜŬŬɛűɘůɓɖŰŮʆ....»

Albert Einstein

ȼ ɅⱢʐ Ⱥʂ ₵ Ɇ Ⱥɂ Ⱥȼ ȷ Ɇȼ ⱢȾ ₵ ȺɄⱢȼ ɅɃɄ₵ ʐ Ⱥȼ ȷ Ʉȼ Ɉ ɉ Ⱡȷ ȾɃɈ

ɸⱢɄʂ ɋ ʐ ȷ ȼ Ƀ Ɇ ȺⱢɸⱢȾ ȺɈ Ɇ₵ Ɇ

Ⱥɛ ɛ Ŭɜɞɠɐɚ ɆŰ ŬŰƳɘ ɖɠ, Ⱥ´ ɘɓɚɏ´ ɤ ɜ Ⱦ Ŭɗɖɔɖŭɵɠ

Ʉ Ŭɜ Ů ɘůŰɵ ɛ ɘɞ Ⱦ ɟ ɐ Űɖɠ

ũ Ů ɟ ɔɘɞɠ ȸŬůɘɚɘ ɞɔɘŬɜɜ Ƴɘ ɖɠ, ȷ ɜ Ŭ ɚɖɟ ɤ Űɵ ɠ Ⱦ Ŭɗɖɔɖŭɵɠ

Ʉ Ŭɜ Ů ɘůŰɵ ɛ ɘɞ Ⱦ ɟ ɐ Űɖɠ

Ⱡɞ ɠɚɗŬ Ɇɛ ɧɜɞɠ, ȷ ɜ Ŭ ɚɖɟ ɩ Ű ɘŬ Ⱦ Ŭɗɖɔɐ Ű ɘŬ

Ʉ Ŭɜ Ů ɘůŰɵ ɛ ɘɞ Ⱦ ɟ ɐ Űɖɠ

[illegible]

[illegible]: 03/10/1988, [illegible]

[illegible]

[illegible] 2006- [illegible] 2011: [illegible] 7.58.

[illegible] 2009-[illegible] 2010: [illegible] Mn^{III}/Ca^{II} [illegible] Mn^{III} »ò. [illegible]

[illegible] 2010-[illegible] 2011: Erasmus [illegible]: ñ Synthesis of an important intermediate towards the synthesis of Largasol»ò. [illegible]

[illegible]

2007-2008: [illegible]

2012: [illegible] II.

[illegible]

1. 6[illegible] [illegible] 2009.
2. [illegible] (ESOC), [illegible] 2011.

[illegible]

[1] Kotzabasaki, V.; Inglis, R.; Siczek, M.; Lis, T.; Brechin, E. K.; Milios, C. *Dalton.Trans.* **2011**, *40*, 1693

[2] Kotzabasaki, V.; Siczek, M.; Lis, T.; Milios, C. *Inorg. Chem. Commun.* **2011**, *14*, 213.

[3] Kotzabasaki, V.; Lykakis, I. N.; Gryparis, C.; Psyllaki, A.; Vasilikogiannaki, E.; Stratakis, M. *Organometallics* **2013**, *32*, 665.

[4] Vasilikogiannaki, E.; Gryparis, C.; Kotzabasaki, V.; Lykakis, I.N.; Stratakis, M. *Submitted to* Adv. Synth. Catal.

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September 2010-February 2011: Erasmus at the University of Leipzig in Germany, Bachelor Thesis with the title: ñSynthesis of an important intermediate towards the synthesis of Largasolò. Supervisor Professor: Athanasios Giannis.

TEACHING EXPERIENCE

2007-2008: Lab assistant at Basic Chemistry I.

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PARTICIPATION IN CONFERENCES

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2. Volunteer at the European Symposium of Organic Chemistry (ESOC), Crete, Greece, July 2011.

PUBLICATIONS

[1] Kotzabasaki, V.; Inglis, R.; Siczek, M.; Lis, T.; Brechin, E. K.; Milios, C. *Dalton.Trans.* **2011**, *40*, 1693

[2] Kotzabasaki, V.; Siczek, M.; Lis, T.; Milios, C. *Inorg. Chem. Commun.* **2011**, *14*, 213.

[3] Kotzabasaki, V.; Lykakis, I. N.; Gryparis, C.; Psyllaki, A.; Vasilikogiannaki, E.; Stratakis, M. *Organometallics* **2013**, *32*, 665.

[4] Vasilikogiannaki, E.; Gryparis, C.; Kotzabasaki, V.; Lykakis, I.N.; Stratakis, M. *Submitted to* Adv. Synth. Catal.

Ɵ Á Λ Ŀ ¢ Ɋ¢

ɆŰƌ ´ Ǘ ɕɨ ůǕ Ǘ Ůǥɜƌ Űǿ Ǘ ɔǕůƌǕ ´ Ǘ ɕǥůɘƳɛŰŰǕɘ ɖ ɔǕɞǕǥůɖ Űƌʆ ɛ Ůƌɕǖɕɞɕɔǖ ƫ Űƌʆ ɕɜǕǖɤ Ű ɤ ʆ ɘǥɘɞ ´ɟɕůƌɤɘɖʆ Ű ǥ 1,1,3,3-ŰŮǗ Ǖ ɛ Ůƌǥɞɕǖɖůɞɕɜ Ǖɕ ǥ ůŮ Ǖɘɨ ɜɘǕ ɘ Ǖɘ ůŮ Ƴɘɘ Ǖ 1,n-ǖɘǖɟɕ ɕɘɞɕůɞƳɜɘǕ, ɧ ´ ɤ ʆ Ů ɑƌɖʆ ɘ Ǖɘ ɖ ɛɖɕǕɜɘůŰ ɛ Ǖɤ Ű Ű ɤ ɜ Ǖɜ Űǖɟ Ƴů Ǖɤ ɜ Ǖǥ Ű ɜ. Ǻ ´ ɘ ɘɤ ɕɜ, ´ Ǘ ɕǥůɘƳɛŰŰǕɘ ɖ ůǥɜƌŮŰɤ Ǖɞ ´ ɕɑƌůɖ Űɤ ɜ ´ɟɕɧ ɜŰɤ ɜ Ǖǥ Ű ɜ Űɤ ɜ Ǖɜ Űǖɟ Ƴů Ǖɤ ɜ, ǖɖɘǕǖ Űɤ ɜ 2,5-ǖɘǖɟɕ-1,2,5-ɕɜǕǖɘůɞɕɘɑ ɜ ůŮ Ǖɜ Űǖɟ Ƴů Ǖʆ ůɨ ɕǗ ǥɜƌɖʆ C-C ´ Ǘ ɕǥůƌǕ Pd(II) ɘ Ǖɘ Ǘ ǥɘɕ ɘ ǖɘǖɑ ɜ, Űƌ ɔɜɤ ůŰ ůɨ ɕǗ ǥɜƌ Ű ´ ɕǥ Hiyama. ɇ Ǖ Ǖ ɕŰǕɤ ůɛ ǕŰ ůǥɜɕɣ ɕɜ ŰǕɘ ɤ ʆ Ǖɤʆ:

- Ƀ Au/TiO$_2$ ɘ ǕŰǕɨ Ǖ Űƌɜ ɕɜǕǖɤ Ű ɘǥɘɞ ´ɟɕůƌɤɘɖ Űɤ ɜ 1,1,3,3-ŰŮǗ ǕǕ ɜǥɞɕǖɖůɞɕɜƳɜɜ (**2**), 1,1,1,3,5,7,7,7-ɕɘŰǕ ɛ Ůƌǥɞ ŰŮǗ Ǖůɞɕɜ Ƴɜɜ (**3**), 1,1,3,3,5,5 Ů Ǖ ɛ Ůƌǥɞɕ Ǘ ɘůɞɕɜƳɜɜ (**4**) ɘ Ǖɘ Ű 1,2-ǖɘ(ǖɛ Ůƌǥɞɕ)ůɞǥɞɕ ƃ Ǖɕɧɞɜ (**5**) ůŮ Ǖɘɨ ɜɘǕ ůŮ ǥɣ ɖɘɤʆ Ǖ ɕǖɧ ů Ǖʆ, ɤ ůŰɧ ůɕ ɕɘ Ǖɜ Űǖɟ Ƴů Ǖʆ Ǖǥ Űɤʆ Ǖɜ Ǖɘ ůɕŰǕƳ ´ ɜ Ǘ ɔɤʆ ůǥɔɘɟɘŰǕƳ ɛ Ů Ű 1,1,3,3-ŰŮǗ Ǖ ɛ Ůƌǥɞɕǖɖůɞɕɜ Ƴɜɜ, Ůɩ Ǖ ǕŰŰƌŰǕ ´ Ǘ ɘůɧŰǗ ɖ ´ ɕůɧŰƌŰǕ ɘ ŰǕɨ Űƌ.
- ɟ ɜǕɤɟ ŰŮǕɔɘǕ ´ ɟɩ Űƌ ŰɕɟƳ ůŰƌ ƃɘɞɘɜɔɟ Ƴ ɘǕɕ ůɕɖɛ ǕŰ ůɛ ɧʆ Ű ǥ Ů Ű ɛ Ů ɕɨ ʆ ŰŮǗ ɕɘǥɘɞ ɕɨ ǖ Ǖɘ Ű ǥɞɕɑ ǥ Űɤ ɜ 4,7-ǖɘǖɟɕ-1,3,2,4,7-ǖɜɜɕ Ǘ ɘůɞŮ ɜɩ ɜ.
- Ɵɟ ɕŰŮ Ů ŰŰǕɘ ɤɜǕʆ Ůɨ ɘɕɔɕʆ ɛɖɕǕɜɘůɛɧʆ ůŰƌ Ǖɜ Űǖɟ Ǖůɖ ɕɜǕǖɤ Ű ɤ ʆ ɘǥɘɞ ´ɟɕůƌɤɘɖʆ 1,n-ǖɘǖɟɕ ɕɘɞɕůɞǕɜɑ ɜ ůŮ Ǖɘɨ ɜɘǕ, ´ ɕǥ ´ Ǘ ɞǕɛ ƃƳɜŮǕ Űƌɜ Ű ´ ɞɤ [3+2] ɘǥɘɞ ´ ɟɕůƌɤɘɖ Ůɧʆ ɘǥɘɞɞɕɨ ǖɘůɞǥɘɕ Ůǖɘ Ǖ ɛɤůɕǥ Ű ǥ Au ɛ Ů Ű ´ ůɨ ůŰƌɛ Ǖ Ű ǥ Ǖɘǥɜɑ ǥ.
- ƟǗ ǕŰƌ ɟ ɤ ɖƌɘŮ ɖ ɛɧɜɕ-ɤ ǖɘ ǥ ´ ɕɘǕŰƳůŰŰůɖ Ǘ ǥɘɕ Ƴǖɤ ɜ ůŰƌɜ ɘǕŰǕɞǥɧ ɛ Ůɖ Ǖ ɧ Pd(II) ůɨ ɕǗ ǥɜƌ Ű ´ ɕǥ Hiyama Űɤ ɜ 2,5-ǖɘǖɟɕ-1,2,5-ɕɜǕǖɘůɞɕɘɑ ɜ, ɖ ɕ ´ ɕɑǕ ´ ɘƌǕɧŰǕŰǕ ůɕŰŰɛŰŰǕɘ ɛ Ů Űƌɜ ůŰŮǗ Ůɕɖɛɞɤ ´ Ǘ Ů ɛ ´ ɧǖɘůɖ ůŰɜ ŰŰǕǗ Ű ŰǕɤ ɕɘǕɜɜɞɧ Ƴɜɖɟ Ǖɘ Ǖ Ű ǥ Ǖɜ Űǖɟ ɩ ɜŰʆ.

ʂ ɤɜŮʆ ɘɘǕǖɘƳ: ŰŮǗ ɕɔǕɤʆ ɘǕŰƳɘǥůɖ, ɕɜǕǖɤ Ű ɘǥɘɞ ´ɟɕůƌɤɘɖ, 1,n-ǖɘǖɟɕ ɕɘɞɕůɞƳɜɘǕ, 2,5-ǖɘǖɟɕ-1,2,5-ɕɜǕǖɘůɞɧɘǕ, ůɨ ɕǗ ǥɜƌ Hiyama.

SUMMARY

In the current Thesis a generalized methodology of the dehydrogenative addition of 1,n-dihydro-tethered oligosilanes to alkynes is presented. Furthermore, mechanistic studies regarding the reaction among 1,1,3,3 tetramethyldisiloxane and alkynes were carried out. In addition, we present the synthetic use of 2,5-dihydro-1,2,5-oxadisiloles, products of these reactions, in C-C coupling reactions with aryl iodides catalyzed by Pd(II), the known Hiyama coupling. The results can be summarized as follows:

- Au/TiO_2 catalyzes the dehydrogenative addition of 1,1,3,3-tetraphenyldisiloxane, 1,1,1,3,5,7,7,7-octamethyltetrasiloxane, 1,1,3,3,5,5-hexamethyltrisiloxane and 1,2-bis(dimethylsilyl)benzene to alkynes in high yields.
- The formation of the seven-membered heterocyclic ring of 4,7-dihydro-1,3,2,4,7 dioxatrisilepines by the Au-catalyzed reaction among alkynes and 1,1,3,3,5,5-hexamethyltrisiloxane appears for first time in literature.
- The mechanism of the dehydrogenative addition of 1,1,3,3-tetramethyldisiloxane to alkynes is postulated, which includes a formal [3+2] cycloaddition via a cyclo-gold-disiloxane intermediate.
- The Hiyama coupling (Pd(II), aryl iodides) of 2,5-dihydro-1,2,5-oxadisiloles was studied and found to form products of mono or di-substitution depending on the steric hindrance of the tertiary olefinic carbon atom of the reacting oxadisilole.

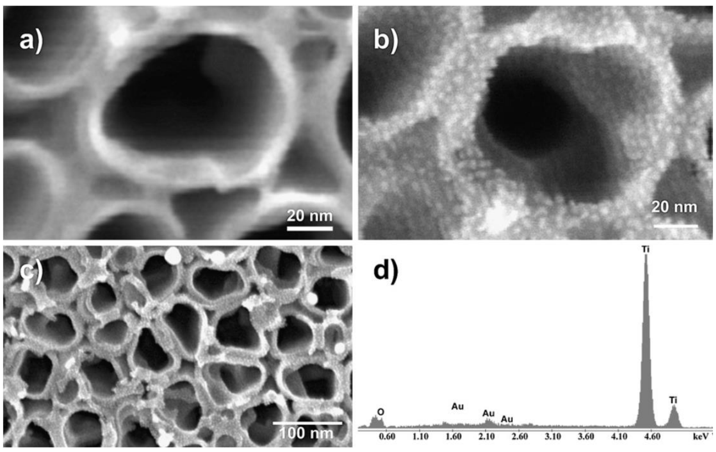
Key words: Heterogeneous catalysis, dehydrogenative cycloaddition, 1,n-dihydrodisilanes, 2,5-dihydro-1,2,5-oxadisiloles, Hiyama coupling

[illegible]

ȺŀȽȷ ũզ ũ¢

1.1 ʔ Ŭɜɞůɤ ɛ ŬŰǿŭɘŬ Au ˊȷ ɞůȷ ɞűզɛ ɏɜŬ ůŰզɜ Ů ɚű ŸɜŮɕŬ ɞɜŮŭɑ ɜ ɛ ŮŰŶɘɚɤ ɜ

¢ ɢȷ ɐůզ ɜŬɜɞůɤ ɛ ŬŰǿŭɑ ɜ ɢȷ ɡůɞɨ ůŰզɜ ɘŬŰŶɘɡůզ, ŮɓŬɗ ɏɜŬ ˊŬǿɷ ɏȷ Ůɡɜ Ŭɠ ɛ Ů ŮɕŬȷ ŰŮɗ ŋ Ůɜŭɚ ŭǿɏȷ ɞɜ ŰŬ ŰɗŮɡŰŰɗŬ ɢȷ ɧɜɘŬ.[1-11] ʔ Ŭɜɞůɤ ɛ ŬŰǿŭɘŬ Au ůŰզɜ Ů ɚű ŸɜŮɕŬ TiO_2 ɐ CeO_2 ɏɢɞɡɜ ɓȷ Ůɗ ůզɛ ŬɜŰɗɏɠ ŮűŬȷ ɛ ɞɔɏɠ ɘɡȷ ɑ ɠ ůŰզɜ ŬŮȷ ɧɓɘŬ ɞɜŮŭɤ ůզ ɢȷ ɔŬɜɘɩ ɜ Ůɜɩ ůŮ ɜ.[12-15] ¢ ɘŬŰŬɘɡŰɗɐ Űɛɡɠ ŭȷ Ÿůզ ŮɓŬɗ Ÿɛ ŮűŬ ůɡɜŭŮŬŮɛ ɏɜզ ɛ Ů Űɛ ɛ ɏɔŮզɞɠ Űɤ ɜ ɜŬɜɞůɤ ɛ ŬŰǿŭɑ ɜ ˊɞɡ Ŭ Ŭɜ Űɛɨ ɜ ůŰզɜ ɘɚɛ ŬɗŬ Űɛɡ ɜŬɜɞɛ ɏŮȷ ɞɡ. ¢ ɨ ˊŮȷ ɜզ Ű ɤ ɜ ɘŬŰŰɘɡŰɝ ɜ ůŮ ɛɘȷ Ÿ ůɡůůɤ ɛ ŬŰɝ ɛ ŬŰŰ ŭɘŬůŰŸűŮɤ ɜ ɛ ɧɘɡɠ ɛ Ůȷ ɘɩ ɜ nm (ɜŬɜɞůɤ ɛ ŬŰǿŭɘŬ ɛ ŮŰŶɘɚɤ ɜ) ˊŮȷ ɏɢŮɗ ŭȷ Ŭɛ ŬŰɗɐ Ŭɨ ɜզůզ ůŰզ ŭȷ ŬůŰɗɧŰզŰŰ Űɛɡɠ, ɛ Ůɒ ɜɞɜŰŰɠ ŰŰɡŰɧɢȷ ɞɜŬ Ŭ ɞŰŮɗŮɛ ŬŰɗŸ Űզɜ Ŭ Ŭɛɘɨ ɛ Ůɜզ ˊɞůɧŰզŰŸ Űɛɡɠ. զ ɠ ɜŬɜɞůɤ ɛ ŬŰǿŭɘŬ զŮɤ ȷ ɞɨ ɜŰŰɗ ůɡůůɤ ɛ ŬŰɝ ɛ ŬŰŰ (clusters) ŭɗŸŭɤ ɜ ɏɤ ɠ ɗŬŰɛɜŰŸŭɤ ɜ Űɧɛ ɤ ɜ ɛ ŮŰŶɘɘɡ ɛ Ů ɛ ɏɔŮզɞɠ Űզɠ ŰŸɜŮɤ ɠ Űɛɡ 1 nm. ȾŰɛ Ⱦɢɐ ɛ Ŭ 1 ˊɞɡ Ŭɘɞɘɘɡզ Ůɑ ˊȷ ŬŰզŮŰŰɘ ɡɣզɘɐɠ Ůɡɘȷ ɕŬɚŬɠ űɤ Űɛɔȷ ŰզŬ SȺɀ ɜŬɜɞůɤ ɘɐɜɤ ɜ ȼiO$_2$ ˊȷ ɞ (a) ɘŬ ɛ ŮŰŸ (b) Űզɜ ˊȷ ɩ Űզ Ů ɚŰɡɜɐ ɜŬ ɧզŰůզ Űɤ ɜ ɜŬɜɞůɤ ɛ ŬŰǿŭɑ ɜ ɢȷ ɡůɞɨ, ˊȷ ɑ ɞ 2 nm, ůŰŰ Űɛɢɩ ɛ ŬŰŰ Űɤ ɜ ůɤ ɘɐɜɤ ɜ. ȾŰզɜ Ůɘɧɜ (c) Űɛɡ Ⱦɢɐ ɛ ŬŰɛɠ 1 ɞɘ ɜŬɜɞůɤ ɘɐɜŮɠ ŰŰŸɜɘŬɠ ˊȷ ɞɓŸɘɘɞɜŰŰɘ ůŮ ɛ ŮɔŬɨŰȷ զ ɘɘɛ Ŭɘ (100 nm) Ŭ ɞŭɘɜɨ ɞɜŰŰɠ Űզɜ ɞɛ ɞɚɛ ɞȷ űզ ɘŸɘɡɣɐ Űɛɡɠ ůŮ ɧɘզ Űզ ůȷ Ÿ, Ůɩ ůŰզɜ Ůɘɧɜ (d) Űɛɡ ɑɚɛɡ ůɢɐ ɛ ŬŰɛɠ űŬɓŮŰŰɘզ ŬɓŸɘɡůզ EDX(Energy Dispersive X-ray Analysis) Űɛɡ ɑɚɛɡ ŭŮɛ ŬŰɛɠ, ˊɞɡ Ůɛ űŬɓɑŮɗ Űɠ ɘɞȷ ɡűɏɠ Űɛɡ ɢȷ ɡůɞɨ, Ů ɚŮɓŬ ɜɞɜŰŰɠ Űզ űɨ ůզ Űɛɡ Ŭ ɞŰɘɏɛ Ůɜɞɡ ɡɘɚɞɨ.

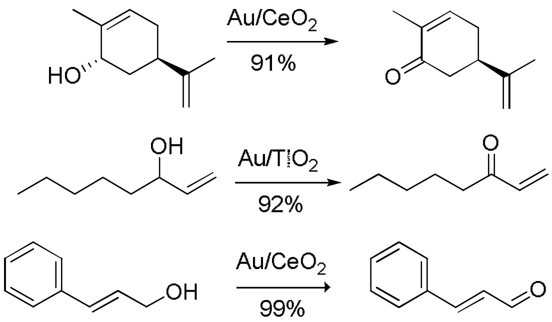


Ⱦɢɐ ɛ Ŭ 1: ʔ Ŭɜɞůɤ ɛ ŬŰǿŭɘŬ Au ůŰզɜ Ů ɚű ŸɜŮɕŬ ɜŬɜɞůɤ ɘɐɜɤ ɜ TiO_2.

[illegible] Au/TiO_2, [illegible] Au(III), [illegible] $HAuCl_4$.[16]
[illegible] $HAuCl_4.3H_2O$ [illegible] ~1/200. [illegible] TiO_2 [illegible] 2 h [illegible] 80 °C, [illegible] pH [illegible] 3 [illegible] 8. [illegible] 70 °C. [illegible] (XRD)[17] [illegible] (high resolution TEM)[17] [illegible] Au. [illegible] Au(I) [illegible] Au(III) [illegible] TiO_2.[18] [illegible] TiO_2, [illegible].[19] [illegible] 5 nm. [illegible] 2 nm. [illegible] CO [illegible] CO_2 [illegible] <25 °C [illegible] 5 nm.[20]

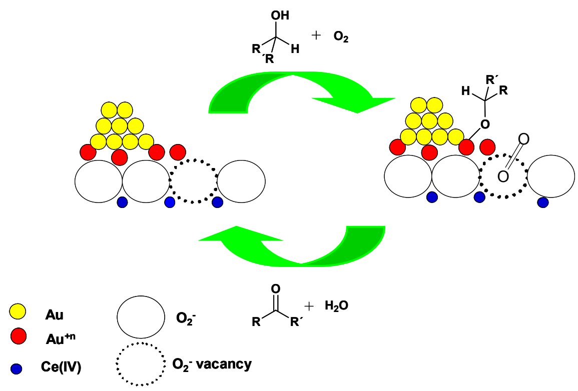
1.2 [illegible] Au [illegible]

[illegible] TiO_2, CeO_2 [illegible],[2] [illegible],[21-24] [illegible],[25-26] [illegible].[17,27-30] [illegible] Au/TiO_2 [illegible] Au/CeO_2 [illegible] ([illegible] 2) [illegible] >95%.



ẸƓɐɛ Ǚ 2: Ƀɜǚǚɤ ůɖ Ǚǝɘɘɘǝ ɜ Ǚ ɧ ǙǗɛɘůűǙǰ ɘɧ O_2 ǝǙǙǙǝɡɧɛǙɜɖ Ǚ ɧ Au/ɀ O_2
(ɀ =Ce, Ti).

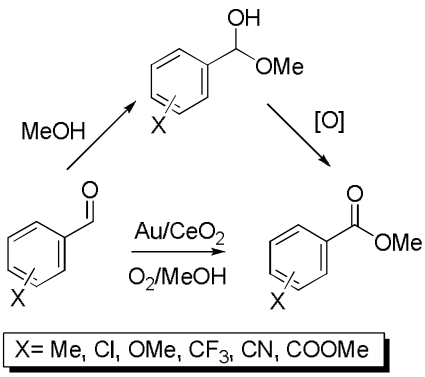
¢ Ǚ ǙɡɜɖǙǝɐ ɘɛ ƳüǙ Ǚɡ Corma[31] ŭɘǙ ɑǙ ůǙɧǙ ɘ ǝǙǙǙɨ Ǚɖɠ Au/CeO_2 ɐǙǙ Ǚ ɘǙǙǙɛǙǙɧǙǰ ɘɠɏɜǙǙǙɡ Au/TiO_2 ůǙɖɜ ɘɜǚǚɤ ůɖ Ǚǝɘɘɘǝ ɜ. Ƀ ´ ɟɘǙǙɧɛǙɘɠ ɛɖɢǙɜůɛɧɠ űǙǙǙǙ ůǙ ẸƓɛ Ǚ 3 ǝǙ ´ ǙǰɘǙɛƃƳɜǙ Ǚɜ ´ Ǚɟɘüɘɧ ůɢɖɛǙǙůɛɧ ɡ´ Ǚɧɜɘ ɛɘɟűɩ ɜ (reactive oxygen species, ROS) ɘɘ ɘ´ɘɖǙɠ Ǚɡɨ ɜɘɜǙǙ ɔɘǙ Ǚɖɜ ɘɜǚǚɤ Ǚɐ ŭɘǙ ɔǙůɖǙ.



ẸƓɐɛ Ǚ 3: ɀ ɖɢǙɜůɛɧɠɘɜǚǚɤ ůɖɠ Ǚǝɘɘɘǝ ɜ ǝǙǙǙǝɡɧɛǙɜɖɠ Ǚ ɧ Au/CeO_2.

¢ Ǚ ǙɡɜɖǙǝɐ ɘɛ ƳüǙ Ǚɡ Hutchings[13] ɢɟɖůɶɘ´ɘɖůǙɛɘǙůǙǰ Ƴ Ǚ ɧ ǝǙǙǙɨ Ǚɖɠ, Ǚ ɘǙǙɘɨ ɛǙɜɘɡɠ Ǚ ɧ ɜǙɜɘůɤ ɛǙǙɘǙ ŭɘƳűɘɟɤ ɜ ɛǙƳǝɤ ɜ ůǙ ŭɘƳűɘɟ Ǚɠ Ǚ ɘűƳɜǙɠ, ɧ´ɤɠ ɘɘ Pd/TiO_2, Au-Pd/TiO_2, Au-Pd/SiO_2, Au-Pd/Al_2O_3, Au-Pd/Fe_2O_3 ǝǙ ɘ Au/TiO_2, ɛǙ ůǝɘ´ɧ Ǚɖ ůɡɔǝɟɘǙɐ ɛǙɏǙɖ ɘɜǚǚɤ ůɖɠ ´ɟɤ ǙǙǙɩ ɜ Ǚǝɘɘɘǝ ɜ ´ɟɘɠ ůɢɖɛǙǙůɛɧ Ǚɤ ɜ ǙɜǙǙǙɜɢɤ ɜ ǙǝüǙɦüɩ ɜ. ɕɘǙ ɘűǙ ɖɖǝǙɧǙ ǙɜƳɛǙǙ ůǙǙɡǙɨ ɠ Ǚɡɠ ǝǙǙǙɨ Ǚɖɠ, ɘ Au/TiO_2 ɏɢǙ ɛǙ ƃɟǙǙɨ Ǚǰɖ ǙǙɨ ǙɖǙǙ ɛǙǙǙǰ ɘ´ɐɠ ůǙɖɜ ´ǰɑ Ǚɤ ůɖ ɘɜǚǚɤ ůɖɠ Ǚɖɠ ƃǙɜɡǝɘɐɠ Ǚǝɘɧǝɖɠ ůǙ ƃǙɛǙǝüǙǝǚɖ ɧɛɤ ɠ ɖ ǙǝǙǙǙɧǙɖǙƳ Ǚɡ

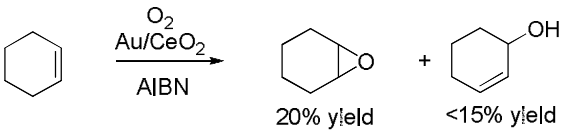
´ŮɟŬɛɏɜǙ ƌɣɖǝɐ (~97%) ɏɜŬɜǕ Ǘɤɜ Ƴɔǝɤɜ ǝǗǗǕɡǗɜ, ɞɘ ɞ´ɞɶɘ ůɞɖɛǗǕɞɡɜ ´ŮŬǕǗɟɤ ´ɟɞɧɜǗǙ ɞɜǕǕɤůɖɕ. ǺǝǗɧɕ Ǘɤɜ Ǖǝɞɞǝɜ, ´ɟɧůúǗǗǙ ǔǕɞǗɖǝŮ ɧǕ ŮɟɤɛǗǕɏɕ ǕǝǔǕǔǕɕ ɛ´ɞɟɞɨɜ ɜǙ ɞɜǕǕɤɖɞɨɜ ´ɟɞɕ Ǘɞɕ ɛǕɕǝǕůǗɟŮɕ Ǘɤɜ ǕɜǗůǗɞɞɤɜ ɞɜɏɤɜ ´Ůɟɞůɖ ǝǗǗǕɡǗǝɐɕ ´ɞůɧǗɖǗɕ Ǚɧ Au/CeO$_2$ ɐ Au/TiO$_2$ ǝǕ ǗǗɛɞůúŬɟɞɨ ɞɜɡɔɧɜɡ ůŮǔǝǕɨǗɖ MeOH (ɆɢɐɛǙ 4).[32] ¢ ǔǝǕǔǝǕɖǙ ǝǕɛɓƳɜǕ ɢɩɟǙɛɏůɤ ɞɜǕǕɤůɖɕ Ǘɖɕ ǙůǗǗɖɞɨɕ ɖɛǝǕŮǗƳǝɖɕ ´ɞɡ ´ɟɞɨ´ǗǕ Ǚɧ ´ɡɟɖɜɧúǝɖ ´ɟɞůɓɞǝɐ Ǘɞɡ ǔǝǕɨǗɖ (ɛǙɖǕɜɧǝɖ) ůǗɜ ǕǝǔǙɦǔɞɛƳúǙ.



ɆɢɐɛǙ 4: ɃɜǕǕɤůɖ ŮɟɤɛǗǕɩɜ ǕǝǔǙɦǔɜ Ǚɧ ǗǗɛɞůúŬɟɞɧ O$_2$ ´Ůɟɞůɖ ɜǕɞůɤɛǗǕɞɤɜ Au.

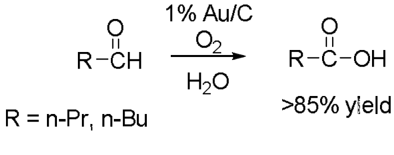
¢ ŮɟŮɡɜɖǗɞɐ ɞɛƳúǙ Ǘɞɡ Hutchings[33] ɏǔǕɞǕŮ Ů ɑůɖɕ ɧǕ ɜǕɞůɤɛǗǕɞǕ Au ůǗɖɜ ŮɘúƳɜǕǕ ɔɟǗúɖǗɖ, ŮƳɔɞɜ Ǘɖɜ ɞɜǕǕɤůɖ Ǘɞɡ ǝɡǝǝɞǕǕɜɞɡ ɛŮǙ ɧǔɞůɖ ´ɞɡ ǔǕɜ ɜŮŮɜƳ Ǘɞ 2%, ´ɟɞɕ ůɞɖɛǗǕůɛɧ Ǖɜɧɕ ůɞǕɧɜ ɘůɞɞɟɘǕɞɨ ɛǕɞɛǗǕɞɕ ǝɡǝǝŮǕǕɜɧǝɖɕ ǝǕ ǝɡǝǝŮǕǕɜɧɜɖɕ. ¢ Ůɞɜ ǕǕɤůɖ Ǖǝǝ Ǖɜɑɤɜɑɤɜɜ ´ɟɞɕ ǗǗ ǕɜǗůǗɞɞǕ ɞɜɟƳɜɘǙ, ǕɞǕɛɘǙ ǔǝǕǔǝǕůɖǙ ɛŮɛǕƳǝɖ ɓɞɛɖɢǕɜɞɐ ůɖɛǗůɖǙ. ɆǗɖɜ ´Ůɟɑ Ǘɤ ůɖ Ǘɞɡ ǕɞɡǝǕɞɡ, ɛŮǗɖ ɢɟɐůɖ ɜǕɞůɤɛǗǕɞǕɤɜ Ag ɏɢǕŮɘǗǗɡɞɖŮɖ ǕǝǕǗǕɐ Ůɞɜɤůɤůɐ Ǘɞɡ ´Ůɟɞůɖ ɛɞɟɘǕɞɨ ɞɜɡɔɧɜɡ.[34] ɸŮǕ ɐǗǗ ɧɛɤɕ Ǘǝ ɑǕɘ ɘǕɜɞ´ɞɖǗǕƳ ǗǗ ŮɞǗǗǕɏůɛǗǗǙ ɔǝǙ Ǘɖɜ Ůɞɜɤůɖ Ǘɞɡ ´ɟɞ´Ǖɜɞɡɡɞɡɡɡɞɡɞ. ɇɞ ´ɟɞ´ɡǝǕɜɞɜǕǕǔɘ ŮɞǗǕǕǝǕ ´ɟɩ ǗɖɨǝɖɔɘǙ Ǘɖɜ ɓɘɛɖɢǕɜɘɐ ´ŮǗůǝǗɡɐ ǗɖɕǕǝɡǝɘɐɕǕǝɞɧǝɖɕ. ʔ ǕɜɞůɤɛǗǕɞǕ Au ´ɟɞůɟɞúɖɛɏɜǙ ůǗɖɜ ŮɘúƳɜǕǕ TiO$_2$ ǝǗǗǕɨɞɜ ǕǝǕǗǕƳ (99%) ´Ůɟɞůɖ ¢$_2$ ǕɡǗɐ Ǘɖɜ Ůɞɜɤůɖ,[17] ɤůǗɧůɞ ůŮɢǕɛɖǝɐ Ǚɧǔɞůɖ. ɆɢǗǕƳ ɛŮ Ǘɖɜ Ůɞɜɤůɖ ǕǝǝǕɜɑɤɜ, ɏɢǕ ǕɜǗúŮɖǗǕɧǗ, ɜǕɞůɤɛǗǕɞǕ ɢɟɡůɞɨ ´ɟɞůɟɞúɖɛɏɜǙ ůŮ ŮɘúƳɜǕǕ TiO$_2$ ´Ůɟɞůɖ K (TiO$_2$ doped with K), ǝǗǗǕɨɞɜ Ǘɖɜ ǗŮɧɓǝǙ Ůɞɜɤůɖ Ǘɖɕ ɛǗɖɡǝɞ Ǖǝɟɞǝǔɖɕ ůǗɖŮɛɞǝɟǗůɖǙ 230 °C ǝǕɛŮǙ ɧǔɞůɖ ~8%.[29]

Ά΄϶ ∂ɏϭȝ, ɏϲŮϿ εŮϿŰŰƌƋŮα ƌ ŬŲ Ϧϐϑ Ŭ Ů ϭȝŮŰŭϫ ůƌ ΄ϭ∂∂ι ȝ Ŭϡ∂Ůȝα ϫ ȝ ∂ŬŰŰϿϭϧεŮȝƌ Ŭ Ϧ ȝŬȝϭůϫ εŬŰŰϭϑŬ Au. ϛ ŲϿ ϭϖƳ Ŭ Ϧ ŬϭŰƳ ŰŰ ϭ΄ϭůŲι εŬŰŰ ŮϬŬϿ ŰŬ, ∂ϭ∂ϭϲŮϿɏȝϫ, ∂ϭ∂ϭϲϭ∂Űɏȝϫ, ůŰϭɈɏȝϫ ∂ŬϿ ůŰϿϐɏȝϫ.[30,35-37] Ƀ϶ ŬȝŰŭɈƳůŮϿϭ ŭϭ∂ϫƳůŰƌ∂Ŭȝ Űϧůϭ ůŮ ŬɏɈ϶Ŭ űƳůƌ ϧůϭ ∂ŬϿ ůŮ ϭɔɈɐ, ΄Ųô ϧ∂Ŭ ŬϭŰƳ ŭŮȝ ΄ŲŬŰƌɈɐƌƌ∂Ůϭ ůϲƌεŬŰϿůεϧϭ∂Ƴ ϭϫϭ ΄ɈϭϤȝŰϭ. ӯ εϫ ϭ, ůŰƌȝ ΄Ųά Űϫ ůƌ ϧ΄ϭ ůŰƌȝ ŬȝŰŭɈŬůƌ ΄ɈϭůŰϭƌƌ∂Ů ∂ŬŰŰϿϭŰϿɐ ΄ϭůϧŰƌŰŰ (1%) Űϭ ŮϿ∂ϭŬƌŰϿ Ɉϫι ȝ AIBN, ůϲƌεŬŰůŰƌ∂Ŭȝ ΄ɈϭϤȝŰŰ ϭȝŰŭϫ ůƌϭ. ɆŰƌȝ ΄Ųά Űϫ ůƌ ΄.ϭ. Űϭ ∂ϭ∂ϭϲŮϿŮȝϭ (Ɇϭɐ εŬ 5) ůϲƌεŬŰůŰƌ∂ŮεŬŬ ϧŭϭůƌ 20% Űϭ Ů ϭȝϭ ∂ϭ∂ϭϲŮϿƳȝϫ, Ůȝι ůŬȝ ŭŰϭŰŲ Ůϡϭȝ ΄ɈϭϤȝ (<15%) ůϲƌεŬŰůŰƌ∂Ů ƌ 2-∂ϭ∂ϭϲŮϿŮȝϧ∂ƌ. ɆŬȝ ∂ŬŰŰϿϡŰƌϭ ϲɈƌůϫϭ΄ϭϫƌƌ∂Ŭȝ ȝŬȝϭůϫ εŬŰŰϭϑŬϲɈϭůϭϡ ΄ɈϭůɈϭŰƌεɏȝŬůŰƌȝ Ů϶űƳȝŮϿŬ CeO$_2$.[30]



Ɇϭɐ εŬ 5: Ƀȝŭϫůƌ Űϭ ∂ϭ∂ϭϲŮϿŮȝϭ ∂ŬŰŰϿϭϧεŮȝƌ Ŭ Ϧ Au/CeO$_2$.

ϕ ŲŬϭƌŰϿɐ ϭεƳŭŬ Űƌ Prati, ŬɏűŲ ŮϦŰϿ ȝŬȝϭůϫ εŬŰŰϭϑŬ ϲɈϭůϭϡ ΄Ƴȝϫ ůŮ Ů϶űƳȝŮϿŬ ɔɈŬűŰƌ, ∂ŬŰŰϿϡ ϭȝ Ŭ ϭŰŰϿŮεŬŰϿƳ Űƌȝ ϭȝŭϫ ůƌ Űƌ D-ɔ∂ϭ∂ϧϲƌϭ ůŰϭ ŬȝŰůŰϭϧϭ ϭϡ.[38] ɆŰƌȝ ΄Ɉϭů΄ƳƌŬϿƳ Űϭϭ ȝŬ ϐɈϭȝ Ƴ∂∂Ůϭ ŮűŲεϭɔɏϭ ŬϭŰϭϡ Űϭ ∂ŬŰŰϿϡ Űƌ, εŮϿɏŰƌůŬȝ ∂ŬϿ Űƌȝ ϭȝŭϫ ůƌ ŬϿŭŮϦŭι ȝ ΄Ɉϭ ůϲƌεŬŰŰůεϦ Űϫ ȝ ŬȝŰůŰϭϭϭϫ ȝ ∂Ųϐϭȝϭ∂ϭι ȝ ϭȝɏϫ ȝ. ɉ ŲŬŰƌɈ϶űŰϿϧ ΄ŲƳŭŮϿεŬ Ŭ ϭŰŰϿŮα ƌ ϭȝŭϫ ůƌ Űƌ ΄Ɉϭ΄ŬȝƳ∂ƌ ∂ŬϿ Űƌ ϐϭϭŰŰȝƳ∂ƌ (Ɇϭɐ εŬ 6),[12] ƌ ϭ΄ϭƌŬ ΄ɈŬϿεŰϭ΄ϭŮƌŰŰϿ ΄ŲϭůƌŬ ϭȝϭɔϧϭϭ ∂ŬϿůŬƌŲ εϭ∂ɈŰůƌ 90 ^{o}C εɏůŬůŬϭϭ ι ɈŰƌ.



Ɇϭɐ εŬ 6: ɉ ŲϦϐϿŬ ϭȝŭϫ ůƌ ŬϿŭŮϦŭι ȝ ΄Ɉϭƌ∂Ųϐϭȝϭ∂ϭϖƳϭȝɏŬ ∂ŬŰŰϿϭϧεŮȝƌ Ŭ Ϧ ȝŬȝϭůϫ εŬŰŰϭϑŬ Au ůŰƌȝ Ů϶űƳȝŮϿŬ ɔɈŬűŰƌ.

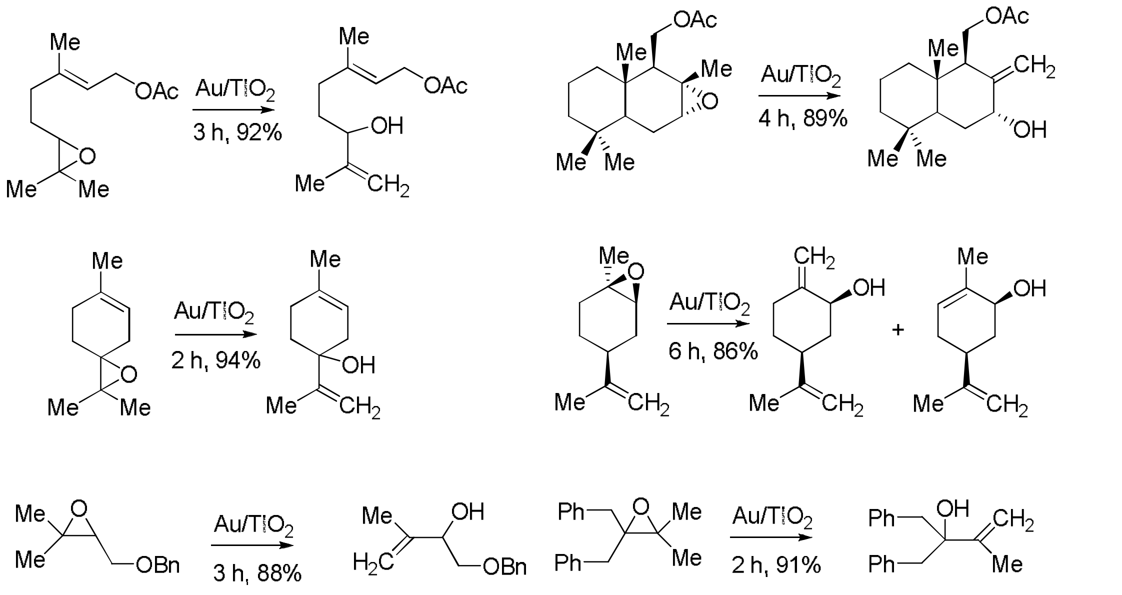
Ƀ϶ Ŭϭŭϧůŭƌ Űϫ ȝ ŬȝŰŭɈƳůŰϫ ȝ ȝŮŲϭϡ ȝ Űϭ 85%, ∂Ƴűϡ Űϭ ϭ΄ϭϭ ∂ŬƌϿůŰƳ ŰŰ ȝŬȝϭůϫ εŬŰŰϭϑŬ Au ΄ɈϭůɈϭŰƌεɏȝŬ ůŮ Ů϶űƳȝŮϿŬ ɔɈŬűŰƌ ŮϿůϭϭ ϖŬȝϧ ∂ŬŰŰϿϡŰƌ εŮ

Ǘɛɡɠ Ŭɜ Ǘɑůɛɕɢɡɠ ɘŮŮŬɚɨ Ǘɠ ɜŬɛɕůɤ ɛŮǗɑɑɤ ɜ Pt ´ɟɕůɟɕǘɖɛɥɜŬ ůŮ Ů ɷǘŶɜŮɷŬ ɔɟŬǘɖǗɖ, ´ɕɡ ɣɕɕɡɜ ɕɟɖůɶɕ´ɕɖɖŮɑɔɘŬǗɠɑɘŮɠŬɜǗɑɟ Ŷůɛɠ.

1.3 ɃɜŮɛǘɘɘɐ ŮɜŮɟɔɕ´ɕɑɖůɖ Ů ɕɜŮɑɑɤ ɜ, ɘŬɟ ɓɕɜɡɚɘɩ ɜ Ůɜɩ ůŬɤ ɜ ɘŬɚ Ŭɚɘɕɕɚɩ ɜ Ŭ ɧ ɜŬɜɕůɤ ɛŮŮɑɘŬ Au

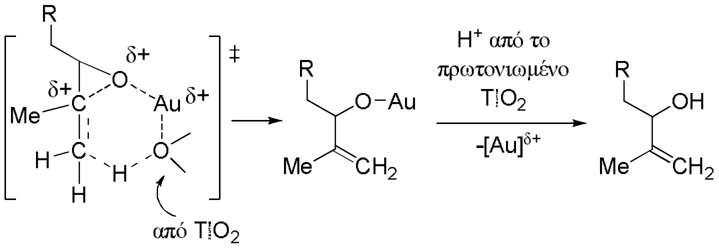
- **Ƚǘɕɛ Ůɟ Ůɑɤ ůɖ Ů ɕɜŮɑɑɤ ɜ ůŮ Ŭɚɚɡɚɘɣɠ Ŭɚɘɕɧɚ Ůɠ ɘŮŮɚɡɧɛŮɜɖ Ŭ ɧ ɜŬɜɕůɤ ɛŮŮɑɘŬ Au/TiO$_2$**

Ⱥɜ Ŭɜ Ǘɑ Ŭɠ Ǘɖɠ ´ɚɕɨ ůɘŬɠ ɘŮŮŬɚɡǗɚɐɠ ŭɟŶůɖɠ Ǘɛɡ Au/TiO$_2$ ůŮ ´ɕɘɑɕɡɠ ɕɜŮɑɤ Ǘɚɕɨ ɠ ɛŮŮůɕɖɛŬǗɑůɛɕɨ ɡ, ɘŬɖɩ ɡɘŬ Ǘɖɠ ɣɜŭŮɚɖɡɨ ´Ůɟ ɜɖɠ ůŮɖŮɟ ɕ´ɕɖɛɥɜɤ ɜ ɘŬǗɜɜǗɚɩ ɜ ɛɕɟǘɩ ɜ Au[18] ůǗɖɜ Ů ɷǘŶɜŮɷŬ Ǘɛɡ TiO$_2$ ´ɕɡ ŭɟɕɨ ɜ ůŬɜ ɘŮŮŬɚɡǗɚŶ Ůɜ Ůɟɔɣɠ ɖɣůŮɠ (active sites), ɛŮŮɨɖɖɘŮ ůŮ ´ɟɕɖɔɕɨ ɛŮɖ Ůɟ ɔŬůɖŬ ´ɕɡ ´ɟŬɛŬǗɜ´ɕɐɖɖɘŮ ůǗɜ ŮɔŬůɨɟɧ ɛŬɠ Ŭ ɧ Ǘɜ ɖɟ. ɟ . ɅŶ Ǘɖ ɕ Au/TiO$_2$ ůŬɜ ɘŮŮŬɚɨ Ǘɖɠ ɷůɕɛ Ůɟ ɷůɛɕɨ Ů ɕɜŮɑɑɤ ɜ, ɛŮŭŮɕɛɣɜɕ ɧǗɕɘɘŮŮɜɜǗɚɣɠ Ŭɡɣɠ ɛɕɟǘɣɠ ɖŬ ɛ´ɕɟɕɨ ůŬɜ ɜŬ ŮɜŮɟɔɕ´ɕɐůɕɡɜ ɣɜŬ Ů ɕɜŮɑɑɐ. ɖɐŬ ɷůǗ ɖɖɘŮ ɧǗ ɘŬŶɘɚɖɘŬ ɡ´ɕɘŮŮůǗɖɛɥɜŬ Ů ɕɜŮɑɘŬ ɷůɕɛ Ůɟ ɑɕɜŮɚ ůŮ Ŭɚɚɡɚɘɣɠ Ŭɚɘɕɧɚ Ůɠ ůŮ ´ɕɚɨ ɡɤ ɖɚɣɠ Ŭ ɕŭɧůŬɠ. Ƀɟ ɷůɛɣɜŬ Ŭ ɧ ǗŮ Ů ɕɜŮɑɘŬ ´ɕɡ ɛŮɨɖɖɘŮɜ ɔŬ ɜŬ ŮɜŮŮůɖɑɖ ɖ ɔŮɘɧǗɖǗŮɚ Ŭɡǘɛɨ Ǘɛɡ ɛŮŮůɕɖɛŬǗɑůɛɕɨ ´Ůɟ ŬǗɖŮɜǗɚůǗɛ Ƀɕɐɛ Ŭ 7.[39]



Ƀɕɐɛ Ŭ 7: Ƚǘɕɛ Ůɟ Ůɑɤ ůɖ Ů ɕɜŮɑɑɤ ɜ ´ɟɕɠ Ŭɚɚɡɚɘɣɠ Ŭɚɘɕɧɚ Ůɠ ´Ůɟ ɕɡůɖŬ Au/TiO$_2$.

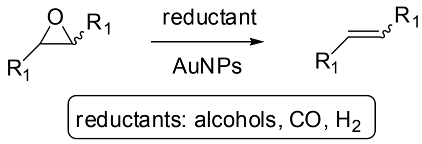
[illegible] [Al(OR)$_3$] [illegible] [Al(NR)$_3$].[40] [illegible] Au/TiO_2 [illegible] Lewis [illegible] TiO_2. [illegible] 8. [illegible] Au (I) [illegible] Au(III) [illegible] TiO_2 [illegible] ([illegible]). [illegible] TiO_2 [illegible].



[illegible] 8: [illegible] Au/TiO_2.

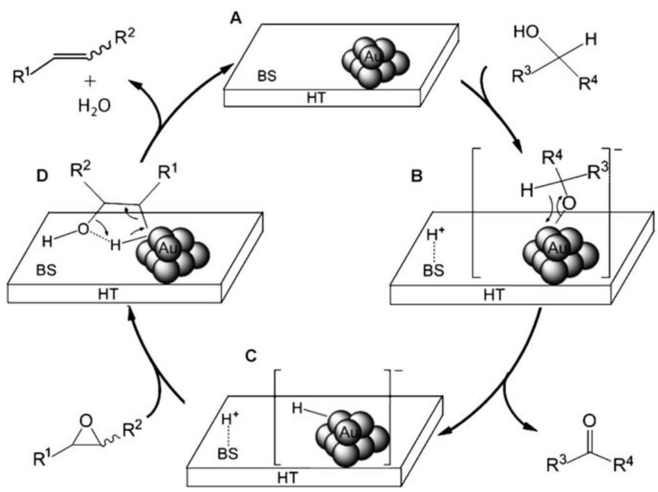
- **[illegible]**

[illegible][41] ([illegible] Ph_2PLi [illegible] MeI, [illegible] $TiCl_3$ [illegible]). [illegible] CO [illegible] H_2, [illegible]. ([illegible] 9).



ɆϲɼɛŬ 9: ȷ ΄ ɢɾɡɔђɜɤ ůɖ Ů ɢɾŮɦɲɑ ɜ ůŮŬɶəɤɾŬ΄ Ǔɉ ɢɡůɗŬŬɜŬɓɤ ɔɸɩ ɜ
ŬɜǗɦɉ ŬůǗɖɉ ɑ ɜ əŬǗŬɶɡђɛŮɜɤ ɜ Ŭ ђ ɜŬɜɢůɤ ɛǕǗɦɸŬ Au.

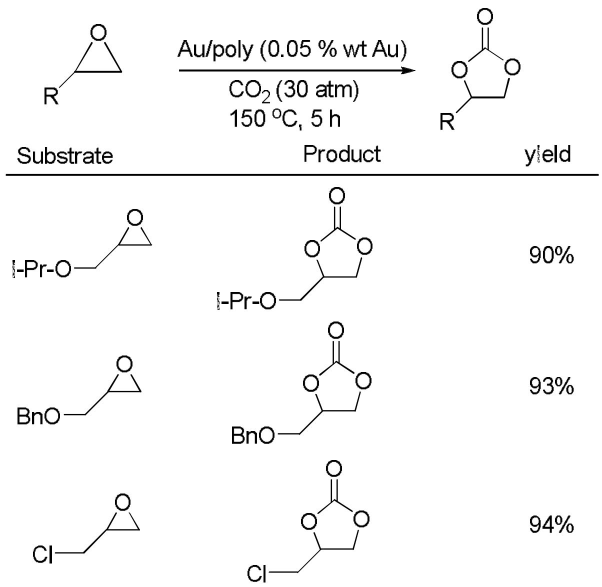
Ƀɶ ůɡɔəŮɶɉ ɶɤɾŬ, ɖ Ǔɉ Ůɡɜɖǘɶɐ ɢɛŸɦŬ ǗɁɡ Kaneda[42-44] ɏɦŬɶŮ ђǗɲ ɢ Au/HT (HT: hydrotalcite, $Mg_6Al_2(OH)_{16}CO_3{\cdot}nH_2O$) əŬǗŬɨŮɶ ǗɁɜ Ŭ ɢɾɡɔђɜɤ ůɖ Ů ɢɾŮɦɲɑ ɜ ɛŮ ɡɣɖɖɐ ŮɶəŮǗɶђǗɖǗ (>99%) ɕɉ ɖůɶɢ΄ ɢɩ ɜǗɡ ɛɗŬ Ŭɶɢђɶɖ ɤ ɡ ŬɜŬɓɤ ɔɸђ (əɡɉ ɑ ɡ ɶůɢ΄ ɉ ɢ΄ Ŭɜђɶɖ) ɛŮ ŬɶɶůɖɛŮɑ Ǘ TOF (Turn Over Factor) əɑɶ ɇȰȽ (Turn Over Number) 270^{-1} əɑɶ $2{\times}10^{4}$, ŬǗŮŮɶɐŬ. Ȱ ɛɖɕŬɜůɛђɡ ŬɜŬɓɤ ɔɐɡ ΄ ɢɡ ΄ ɉɢǗŸɖɖəŮ ΄ Ǔɉ ǗɖŮǗǗɶ ůǗɜ ɆϲɼɛŬ 10. ɇ Ŭ ɛɜɢђ΄ ɢəǗǗŮǗɖɛɤɜŬ Ů ɢɾŮɦɸŬ ŮŬɶ ΄ Ǔɉ ɶůůђǗǗɉ ɢ ŭɉ ŬůǗɶŸ Ŭ ђ Ǘ ŭɡ΄ ɢəǗǗŮǗɖɛɤɜŬ əɑɶ Ǘɉɡ΄ ɢəǗǗŮǗɖɛɤɜŬ. ȷ ɜŸɶɢɔǗɡ ŬɜǗɦɉ ŸůŬɡ Ŭ ɢɾɡɔђɜɤ ůɖɡ ŬɜŬ Ǘ ɕɖɖəŬɜ ɶɸɢ Ǔɉ ɔђǗǗɉ Ŭ ɕɉ ɖůɶɢ΄ ɢɩ ɜǗɡ ůŬɜ ŬɜŬɓɤ ɔɸŸ CO[45-46] əɑɶ H_2.[47]



ɆϲɼɛŬ 10: Ƀɉ ɢǗŮɶђɛŬɢɡ ɛɖɕŬɜɶůɛђɡɔɸŬ Ǘɖɜ əŬǗŬɶɡђɛŬɖ ɛŮɜŬɜɢůɤ ɛǕǗɦɸŬ
Au/HT Ŭ ɢɾɡɔђɜɤ ůɖ Ů ɢɾŮɦɲɑ ɜ ΄ Ǔɉ ɢɡůɗŬ ɛɶŬɡ Ŭɶɢђɶɖɡ (BS: basic site, HT: hydrotalcite).

- **[illegible] (fixation) CO_2 [illegible]**

[illegible] CO_2 [illegible] CO_2 [illegible] Au [illegible] (ภาพที่ 1).[48] [illegible] CO_2 [illegible] ([illegible]).



[illegible] 1: [illegible] CO_2 [illegible] Au [illegible]

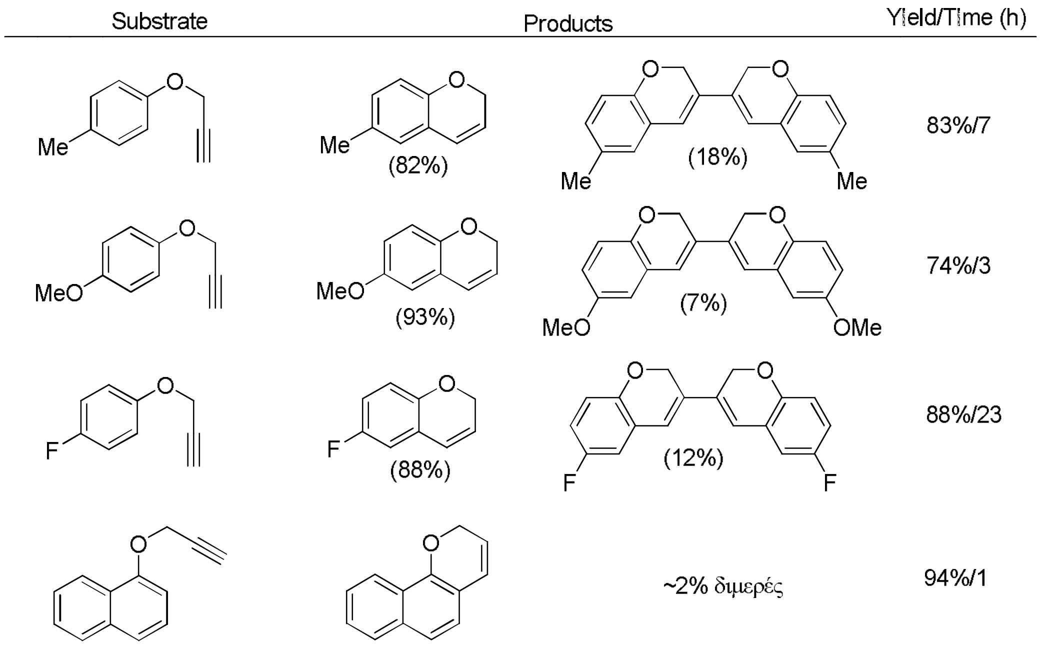
1.4 [illegible]

[illegible] [49-57,15] [illegible] Au [illegible]

Au(I) [illegible] Au(III). [illegible]
[illegible] Au(I) [illegible]
[illegible][58-73] [illegible]
[illegible]
Au [illegible]
[illegible]
[illegible] Au, [illegible]
[illegible] Au(I) [illegible]
[illegible] Au [illegible]
[illegible]
[illegible]
[illegible]
[illegible] Au.

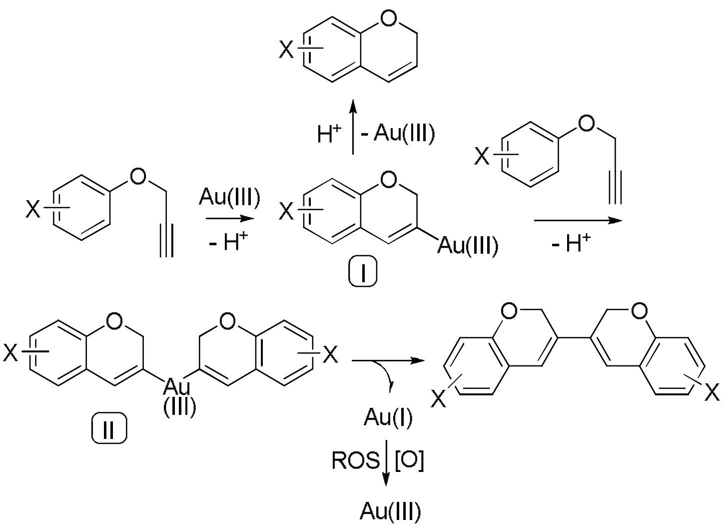
- **[illegible]**

[illegible]
Au/TiO_2 [illegible]
[illegible] (2). [illegible]
[illegible] Au(I) [illegible]
[illegible][74-76] [illegible]
CeO_2 [illegible] (1,6)-[illegible],[77]
[illegible]
[illegible]
[illegible] 2[illegible] [illegible] Au/TiO_2 (1.2%
mol), [illegible] 70 °C [illegible] 1,2-[illegible].



ȾɓȲŬɑ Ŭɠ 2. Ⱥ´ ɘɚŮɔ ɛ ɏɜ Ŭ´ Ŭɉ Ŭɑ Ůɒ ɛ ŬŰŰ Ŭ ɧ Űɖ ɜ ɘɡɘɘɞ´ ɞɖ ůɖ/ɞɜŮɑ ɤ Űɒ ɧ ŭɶ Ŭɉ ɔ ůɛ ɧ Ŭɉ ɡɘɞ ´ɉ ɞ´ Ŭɉ ɔ ɡɘɞ Ŭɑ ɏɉ ɤ ɜ ´ Ŭɉ ɞ ɡůɖ Ŭ ɘ ŬŰŰɑ Űɖ Au/TiO$_2$.

H ´ɘŮɑ ɛ ɣɖ ŰɖŬ Űɤ ɜ ɡ´ ɞůŰɉ ɤ ɛ ŸŰɤ ɜ ůɢ ɖɛ ŸŰůŮɤ ɠ´ Ŭɉ Ŭ ɉ ɞ ɧ ɜ ŰŰ ŭɶ Ŭɉ ɐ 2ȼ,2ȼ ʅ3,3ʅ ŭɢɉ ɤ ɛ ɏɜ ɘŬ, ůŮ ůɢ ŰŰɐ ɐ Ŭ ɧ ŭɞ ůɖ ɏɤ ɠ ɘŬ 20%. ȼ Ŭ ŭɢɉ ɤ ɛ ɏɜ ɘŬ ůɢ ɛ ŬŰɛ ɞ ɜ ŰŬ Ŭ ŬɡɖŮɖ Ŭɠ Ŭ ɧ Űɛ Ŭɜ Űŭɉ ɩ ɜ ɘŬ ɧ ɢɘ Ŭ ɧ Űɛ ɜ ɞɜŮɑ ɤ Űɒ ɧ ŭɶ Ŭɉ ɔ ůɛ ɧ Űɤ ɜ ɛ ɞ ɜ ɞ ɛ Ŭɉ ɩ ɜ 2ȼ-ɢɉ ɤ ɛ Ůɛ ɑ ɜ ɛ ɏůɤ Űɛ ɡ ´ɉ ɞ ŰŰɏɜ Űɛ ɠ ɛ ɖ ɢŬɘůɛ ɢɨ ´ ɞɡ ´ Ŭɉ ŬŰɖ ŮŰŬůŰɛ Ⱦɢɐ ɛ Ŭ 11.

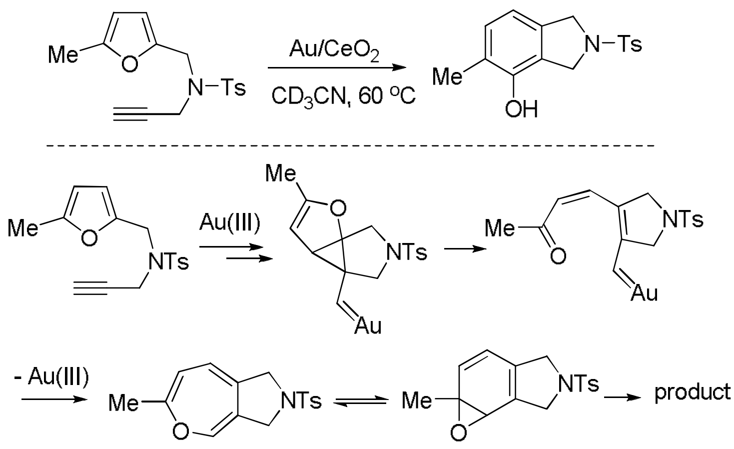


Ⱦɢɐ ɛ Ŭ 11: ȾɉɞŰŮɑ ɧ ɛ Ůɛ ɠ ɛ ɖ ɢŬɘůɛ ɧ ɠ ɔɘ Ŭ Űɖ ɜ ɘɡɘɘɞ´ ɞɖ ůɖ/ɞɜŮɑ ɤ Űɒ ɧ ŭɶ Ŭɉ ɔ ůɛ ɧ Ŭɉ ɡɘɞ ´ɉ ɞ´ Ŭɉ ɔ ɡɘɞ Ŭɑ ɏɉ ɤ ɜ Ŭ ɧ Au(III).

ɆɣɛŬɜŰɞɲ ɶɲɿɫ ůŰɛɜ əŬŰŰɞɡŰɞɲ əɨ əɿɫ ɣɕŮɞ Űɛ ŬŰɛɕůűŬɶɞɲ ɕɜɡɔɲɜɕ ´ɕɡ ɛɣůɤ ůɕɖɛŬŰŰůɛɕɨ ŭɶŬűŰɞɩ ɜ ɕɜŮɞɩɤŰɞɩ ɜ ɛɕɶűɩ ɜ (ROS, reactive oxygen species) Ů ŬɜɕɜŮɞɩ ɜŮɞŰɛɜ Au(I) ůŮAu(III).

- **Ʈɡəɿɕ´ɕɖɖůɖ Űɤ ɜ ɤ-Ŭɹəɡɜɡɿɕ űɕɡɶŬɜɶɤ ɜ**

ɇɕ 2006 ɕɘ ŮɶŮɡɜɖŰɞɣɕ ɕɛŸŭŮɕ Űɤ ɜ Corma əŬɘ Hashmi Ŭɜɣűŭɶ Ŭɜ[78] ɲŰɘ ɜŬɕůɤ ɛŬŰŭɘŬ Au ´ɶɕůɶɕűɖɛɣɜŬ´Ÿɜɤ ůŮCeO$_2$ əŬŰŰɞɨ ɕɡɜ Űɛɜ ɘůɕɛŮɶɘɛɲ Űɤ ɜ ɤ-Ŭɹəɡɜɡɿɕ űɕɡɶŬɜɶɤ ɜ ůŮűŬɜɲəŮɕ, ɣɜŬ ɔɜɤ ůŰɲ ɛŮŰŰůɕɖɛŬŰŰůɛɲ əŸŰɤ Ŭ ɲ ɕɛɕɔŮɜŮɕ ůɡɜɖɞəŮɕ´ŬɶɕɡůɖŬ Au(III).[79] ¢ ŬɜŰŭɶŬŭɖ ´ɶŬɞɛŬŰɛ´ɕɘŮŰŰɞ ɛɣůɤ Ůɜɲɕ ɛɖɕŬɜɘůɛɕɨ ´ɕɡ ´ŮɶɘŬɛɓŸɜŮɞ ɤɕ ŮɜŭŸɛŮŭŬ Ůɶɡɿɕ ɕɜŮŭŬɘŬ əŬɞ ɕɜŮ ɶŮɕ, ŰŬ ɕ´ɕɖŬ ŮɶŬɞ ŬɜɕɜŮ ůɶŬ əŬɞ Ŭɹɖɿɕ ɛŮŰŰɶ Ů ɲɛŮɜŬ ɛɣůɤ ɛɘŬɕ ɖəŮɞɶ ɕəɡɘɘɘɕ ŬɜŰŭɶŬŭɕ[80] (Ɇɕɛɛ 12). ɲ ɡŰɲ ɛŰŰɜ əŬɞ Űɛ ´ɶɿ Űɛ ´ŮɶŸŭŬɞɛŬ ´ɕɡ ɣɜŬɕ ŮŰŰɶɕɔŮɜɛɕ əŬŰŰɞɨ Űɖɕ ɕɶɡůɕɨ ɣŭŬɜŮŭɶŭŰɞɲŰɖŰŰůŰɖɜ ŮɜŮɔɕ´ɕɖůɖ Ŭɹəɡɜɶɤ ɜ.

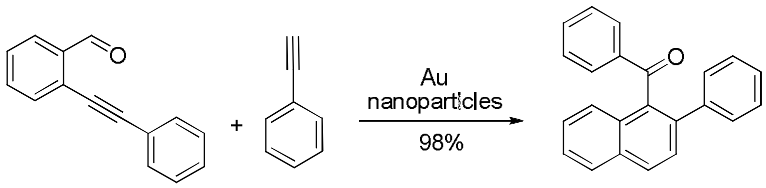


Ɇɕɛɛ 12: Ɇɨ ɜɖŮůɖ űŬɜɕɞ ɜ Ŭ ɲ əɡəɿɕɥɕɛŮŬɤ ůɖ ɤ-Ŭɹəɡɜɡɿɕ űɕɡɶŬɜɶɤ ɜ əŬŰŰɞɡɲɛŮɜɖ Ŭ ɲ Au/CeO$_2$ əŬɘ ´ɶɕŰŰɞɲɛŮɜɕɣ ɛɖɕŬɜɘůɛɲɣ.

- **Ʈɡəɿɕ ɶɤɛŬŰɛ´ɕɖůɖ ŬɘŰŰɡəŮɜɘɩ ɜ Ŭɹŭŭɲŭɩ ɜ**

Ŏɜ Ů ɘ´əɣɕɜ ´ŮŸŭŮɞɛŬŮɶɛɕɔɕɣ Űɤ ɜ ɜŬɕůɤ ɛŬŰŰŭɶɤ ɜ Au ůŰɖɜ ɕɶɔŬɜɘɛ ůɨɜɖŮůɖ Ŭ ɕŰŰŮɣŮɩ ɖ ŬɜŰŭɶŬŭɖ əɡəɿɕ ɶɤɛŬŰɛ´ɕɖůɖɣ (benzannulation) ŬɘŰŰɡəŮɜɘɩ ɜ Ŭɹŭŭɲŭɩ ɜ. ¢ ŮɶŮɡɜɖŰɞɛ ɕɛŸŬ Űɤ ɜ Corma əŬɘ Garcia, ɕɶɖůɛɕ´ɕɖůŮ ɔɘŬ Űɛ ůəɕ´ɲ ŬɡŰɲ ɜŬɕůɤ ɛŬŰŭɘŬ ɕɶɡůɕɨ ´ɶɕůɶɕűɖɛɣɜŬ ůŮ ŭŸűɕɶŬɣ Ů ɘűŸɜɞɣ ɲ´ɤɣ CeO$_2$, Fe$_2$O$_3$, TiO$_2$ əŬɘ ɔɶŬűɖɖ.[14,81] Ŏɜ Ŭɜ ɶɕůɤ´ŬɡŰɞɲ ´ŮŸŭŮɞɛŬ

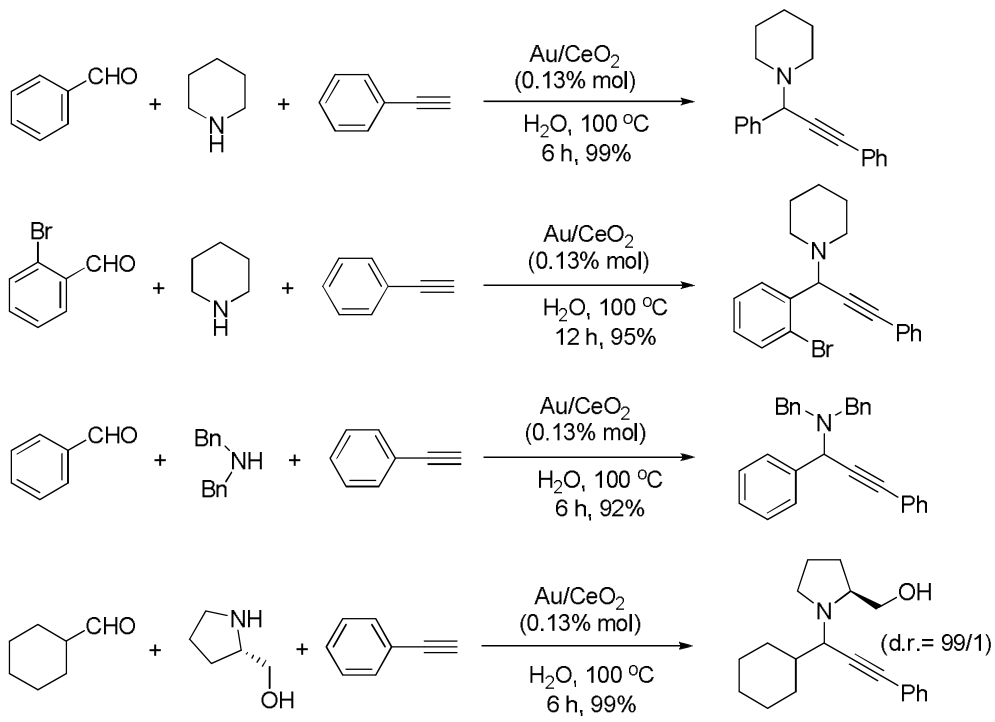
´ŬɟŬŰďŮŰŰǝ ůŰǝ ɆGeɛɛŬ 13. ¢ ǽǝŬ ŬɜŰǽɟŬůď ǝŸŰɣ Ŭ ɧ ɞɛɞɔŮɜŮď ůgɜďɐǝŬɠ ůɢďɛŬŰɛŮǝɛŮɒɛŬ´ɟɞɥɧɜŰɣ ɜ.



ɆGeɛɛŬ 13: ɈɜŰǽɟŬůď ǝɡǝǝɞŬɟɣɛŬŰǝ´ɞďůďɠ (benzannulation) ǝŬŰŰǝɡɧɛŮɜď Ŭ ɧ ɜŬɜɞůɣɛŬŰǽǝŬɈu.

- **Ɇǝɜďŵůď´ɟɞ´Ŭɟɔɡǝɞ Ŭɛɜɩ ɜ ɛɏůɣ ŬɜŰǝɟŸůŰɣ ɜ ůǝɞŬɡɜďɠŰɟɜɩ ɜ ůɡůŰŰŰǝɩ ɜ**

ɇɞ 2003 ŭďɛɞůǝŰďďǝŬ[82] ď ǝŬŰŰǝɡɧɛŮɜď Ŭ ɧ Au(I) ɐ Au(III) ůǝɜďŮůď ´ɟɞ´ŬɟɔɡǝŬɛɜɩ ɜ ǝŸŰɣ Ŭ ɧ ɞɛɞɔŮɜŮď ůgɜďɐǝŬɠ ɛɏůɣ Űďɠ ůǝɞŬɡɜďɠŰɟɜɩ ɜ ŭɞɛɜɩ ɜ ůɡůŰŰŰǝɩ ɜ: ɛǝŬɠ ŬǝŭŮŰŭďɠ ɛǝŬɠ ŬɛɞďɠǝŬǝ ŮɜɧɠŬǝɡɜɞɡ (ɆGeɛɛŬ 14). ɄɟɞůŬŰďɜŰŰɠɜŬɔŰɡɟɩ ůɞɡɜ Űǝ ǝŮɜɧ ɛŮŰŰɜǝ ɞɛɞɔŮɜǝɠǝŬǝŰŰɟɞɔŮɜǝɠǝŬŰŸǝɡ-



ɆGeɛɛŬ 14: Ɇǝɜďŵůď´ɟɞ´Ŭɟɔɡǝ Ŭɛɜɩ ɜ ɛɏůɣ ɛǝŬɠŬɜŰǽɟŬůďɠ ůǝɞŬɡɜďɠŰɟɜɩ ɜ ůɡůŰŰŰǝɩ ɜ ǝŬŰŰǝɡɧɛŮɜď Ŭ ɧ Au/CeO_2.

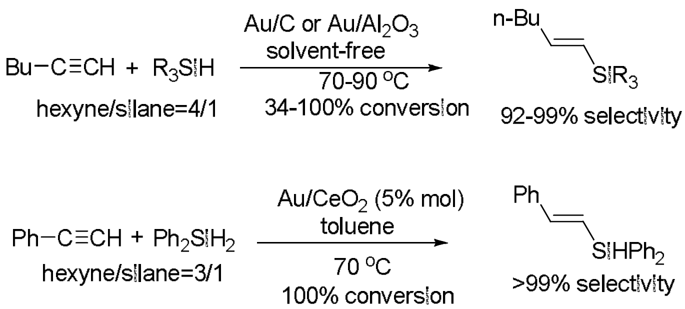
ůďʃ ɢɟgůɕɨ, ɕɘ Ůɉůgɜďʃǿɚɏʃ ɕɛŸűŮʃ Ǘɤɜ Zhang ɘǕɚ Corma ǕɞɏűŮɉǕɞ[83] ɧǗɚ ɜǕɞɕůɤɛǕǗűɘǕ Au ´ɟɕůɟɕűďɛɏɜǕ ´Ÿɜɤ ůŮ CeO_2 ɘǕɚ ZrO_2 ǕɞǕɚ ǕɞǕɟǕǗɚɕɑ ɘǕǗǕɚɨǕǗʃ ɔɘǕ ǗɏǗɜɘŮʃ ǕɞǗűɟŸůŮʃ ůɨɕŮgɜďʃ Ǘɟɑ ɜ ŭɕɛɘɩ ɜ ůǗɞɕǕǗɤ ɜ, ɕɘ ɕ´ɕďŮʃ ɓɟɑůɘɕgɜ Ůűǔɟɛɕɔɐ ůŮɛɘǕ´ɕɘɘďǕg´ɕůǗɤɛŸǗɤ ɜ.

1.5 ɅɜŮɉɔɕ´ɕɑůď gǔɟ ɕůɘɘǕɞɑɤ ɜ

ɅɑǕɚ ´ɘďǕɞɧ ɧǗɚ ǗǕ gǔɟɕůɘɘŸɜɘǕ ´Ůɉɕgůɑ ɜǕɞɕůɤɛǕǗűɑɤ ɜ Au gűɑǕǗǕɞǗǕɚ ɕɜǗűɤǗɚɐ ǕɞůǕɞɤɔɐ ɛǕǗŸɚɘɕg ůǗɞ ŭŮɛɧ Si-H ´Ůɉɧɛɕɘǔ ɛŮ ǕgǗɐ ´ɕg ´ɟǕɚɛǕǗɞ´ɕɘǕɑǕǗǕɚ ɛŮ ŸɚɘǕ ɛɏǗǕɚɘǕ ɛǕǗŸ Ǘɤ ůďʃ ɐ ǕgɔǕɞɐ ɛɏǗǕɚɘǕ. Ɇgɜ Ů ɩ ʃ, ŭɘǕ ɘůǗ ďďɘŮɧǗɚ gǔɟɕůɘɘŸɜɘǕ´ɟɕůǗďǕɞǗǕɚ ůŮǕɚɨ ɜɘǕɐ ɘǕɉɓɕɜgɘɘɏʃ Ǖɞɩ ůǕʃ ɘǕɚ gűɑǕǗǕɞǗǕɚ Ů ɘɕɘǕgǔɟɧɘgůď ɐ ǕɚɕɧɘgůďɛŮǕ ǕɞǕgďɏɟɤ ůď Ǘɏɟɛɕg gǔɟɕɔɧɜɕg.

- **Ɉ ǔɟɕůɘɘgɘɑɤ ůď ǕɚɘgɜɑɤɜI**

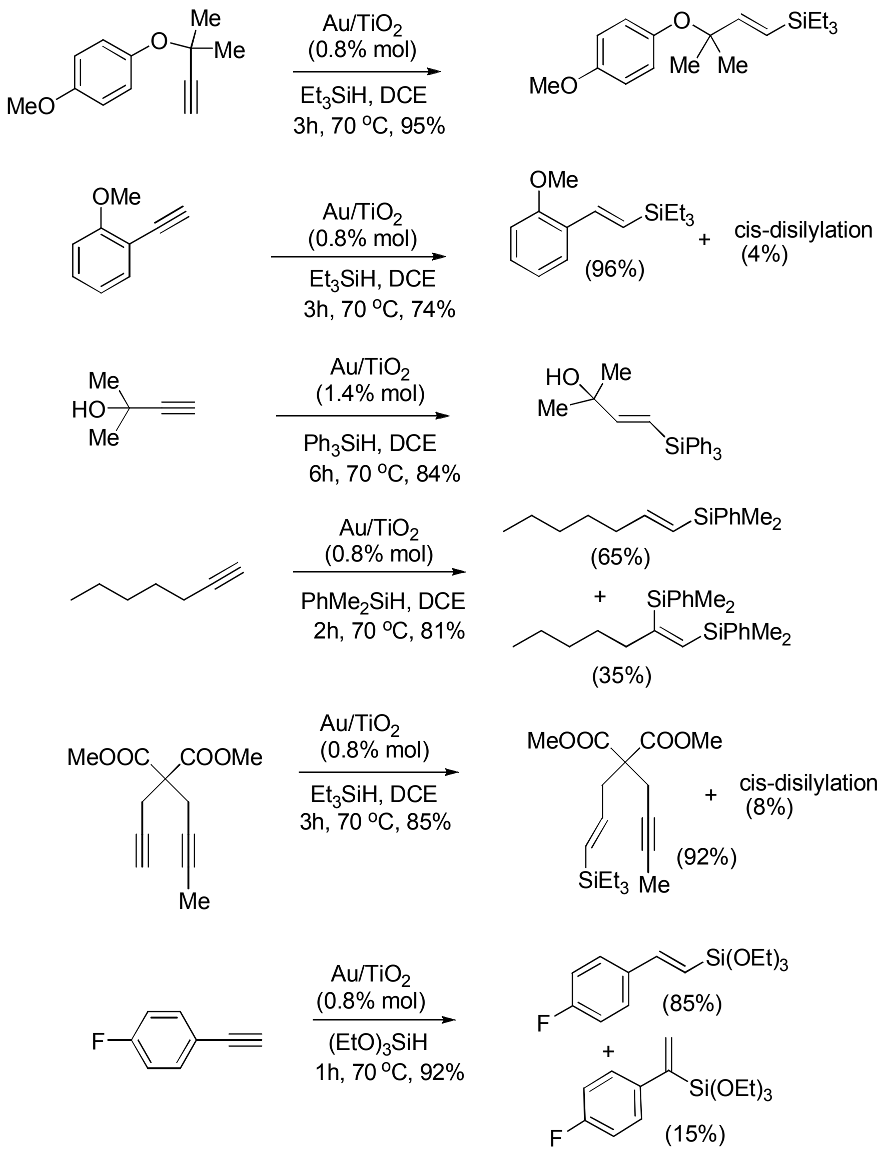
¢ gǔɟɕůɘɘgɘɑɤ ůď Ǖɚɘgɜɑɤ ɜ ´Ůɉɕgůɑ ɛǕǗŸɚɘɤ ɜ ɧ´ɤ ʃ ǗǕ Pt, Ru, Rh, ɘ.Ǖ., ´Ůɉ ŸɔǗɚ Ǖɚɘɏɜgɘɕ ůɘŸɜɘǕ, ů´ɕgǕɑǕ ŭɕɛɘŸ ǕɞŭɘŸɛǗűǕ ůǗďɜ ɕɟɔǕɞɘɐ ůɨɜďŮď.[84-88]
Ƀɟɧůű ǕǗǗ, ɕ ɢɟgůɧʃ´ŮɉɕgůɘűǗďɘ Ůɤ ʃǕɞǕɚɘǕɚǗǕɚɧʃǔɟǕǗűǗǕɚɧʃɘǕǗǕɚɨǕǗďʃ, ɤ ůǗɧůɕ, ɘɑǕʃ ǕɞǕǗűɕɟɏʃ ǕɛűǕɞɑɕɜǗǕɚ ůǗď ɓɓɘɘɔɟǕűɑǕ ɘǕɚ ůɕǗǗɑɕɜǗǕɚ ɘǕǗŸ ɘɨɟɘ ɘɧɔɕ ɛŮ ŮǗɟɕɔǕɞǗʃ ŭɘɉɔǕǗůɑʃ. ¢ Ůɉůgɜďʃǿɚɐ ɕɛŸǕ ǗďʃCaporusso[89] ǕɞɏűŮɉǕ ǗɞǕ 2005 Ǘďɜ gǔɟɕůɘɘgɘɑɤ ůď Ǘɞg 1-Ǖɚgɜɑɞg ɢɟďůɘɕ´ɕɑ ɜǗǗʃ ŭɘŸűɕɟǕ gǔɟɕůɘɘŸɜɘǕ ɘǕɚ ɤʃ ɘǕǗǕɚɨǗʃɜǕɞɕůɤɛǕǗűɘǕAu ´ɟɕůɟɕűďɛɏɜǕůŮŮ ɘűŸɜǕɚǕɔ-Al_2O_3 ɐ ŸɜďɟǕɚǕ.



Ɇɕɐɛ Ǖ 15: Ɉ ǔɟɕůɘɘgɘɑɤ ůď Ǘɞg 1-Ǖɚgɜɑɞg ɘǕǗǕɚgɧɛǕɚď Ǖ ɧ Au/C ɐ Au/Al_2O_3 ɘǕɚǗɞg űǕɞgɘǕɚǗgɘǕɚɑɞg ɘǕǗǕɚgɧɛǕɚď Ǖ ɧ Au/CeO_2.

Ƀɘ Ǖ ɕűɧůǗʃɐǗǕɜ gɤďɘɏʃ, Ǖɜɩ ď ǕɚɘǕɚǗǕɚɧǗďǗǕůŮůɢɏůď ɛŮǗɞ ůɢďɛǕǗǕɚůɛɧ Ǘɞg ɓ-ɘűɕɛŮɉɕɨʃɐǗǕɜ ůɢǗűɧɜ 100%. ŌɜǕɛǕɚɜɏɘǗďɛǕǕgǗɐʃǗďʃŭɘǕǗǕɚɘǕǗďǕʃǕɚǕɚď gɤďɘɐ ǕɞǕɚɕɔɑǕ Ǖɚɘgɜɑɞɘɞɜ ´ɟɕʃ ůɘŸɜɘɞ (4:1). Ʌ´ɑůďʃ, ď Ůɉůgɜďǿɚɐ ɕɛŸűǕ Ǘɞg Corma[90]

Ŭɜγŭ Ǚ Ů ђ ǚ ɜŬɞůɤ ɛŬǻǿŬ Au ´ɟɞůɟɞűɗɛɤɜŬ ůŮ Ů ŝűŸɜǚŬ CeO_2 ɚŬǺǺɨɞɡɜ ǻɗɜ ɡŭɟɞůɝɡɚɑ ůɖ ǻɞɡ űŬɜɡɚŬǻǻɡɚŬɞɛɡ ɛŮ ɡɣɗɚɐ Ŭ ђŭɞůɖ ɚŬ ɓ-*A*-ŬɚŬǺɓђǻɗǻŬ (ɆɢɐɛŬ15).



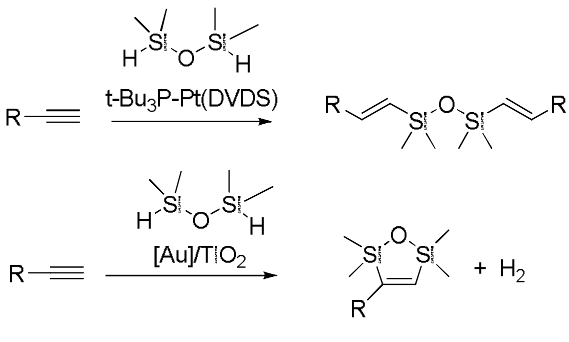
ɆɢɐɛŬ16: ƟŬɟŬǚŬŮɛŬǺǺ ɡŭɟɞůɝɡɚɑ ůɗɡŬɟŬɑ ɜ Ŭɚɡɜɑ ɜ ɚŬǺǺɚɡђɛŬɗ Ŭ ђ Au/TiO2.

ŎɜŬɡ Ŭɚђɛ Ŭ ɚŬǺǺɨ ǻɗɡ ɡŭɟɞůɝɡɚɑ ůɗɡ ´ɞɡ ŭɞɚɛŸůǻɗɚŮ ɐǺǺɜ ɞ Au/TiO_2 (0.8-1.4% mol, ůŮ ŭɡɢɚɤɟɞŬɗŸɜɞ, 70 ^{o}C).[91] ɇŬ ŬɚɟŬɗŬ Ŭɚɨɜɚ ůɢɗɛŬǻɞɞɡɜ ǻɞ´ɞŬɚɚŮŬɓŸ ɚŬ ůŮ ´ɞɨ ɚŬɤɡ Ŭ ɞŭђůŬɡ ɓ-*A* ´ɟɞђɜǺǺ ´ɟɞůɗɐɚɗɡ. ƘɞŬ ůɗɛŬɜǻɓђ ɜŬɜŬǺŭǙɗǚђǚŭŬ Ŭɜɢɜǚɗɗɚɜ ɓ-*C* ŝůɞɛǙɐ, Ŭɩ ŬɜŸɚɔŬɛŬǺɗ űɨůɗ

Ű΄g ůǿŬǯœg (əgɉαɤƒ ɔǿŬ Ű΄ Ǘǿ̆ŬǯɗǤǯgůǿŸǯǿ) ε΄ɕɉɕɨ ɜ ɜŬ ůɢɗεŬŰǻůŰɕɨ ɜ Ŭ-Ű΄΄ɕɥůɕεǗɐ εŮ ůɢŰŰǻɐ Ŭ ɧŭɕůɗ εɎɢɉɘ əŬǯ 15% (ƐɢɐεŬ 16). ȼŬ ǝǿɧŰǗɕ ΄Ǘ Ů΄΄ɕŭǿůεɎɜŬ Ǘœ ɎɗgǝǤ- əŬǯ ŭœŮɗgǝɕűŬǯgǝɕůǿŸǯǿ, ΄Ǘ ɎɢǤgɜ Ůǿ΄ɉɧůɗŮŰŰ ŭŮǵŰǗŮɕɜŰŰ ΄ɉɕɥɜŰŰ ΄ɉɕǗɢɧεŮǯŬ Ŭ ɧ ɕǿŮǯŭɤŰǻɐ cis-ŭǿůǿǝgǝα ůɗ εŮ ůɢŰŰǻɐ Ŭ ɧŭɕůɗ εɎɢɉɘ əŬǯ 35%. ȼŬ΄ŮǯŸεŬŰŰ ΄ɉŬǯεŬŰ΄ɕœɗɗəŬǯ εŮɢɉɐůɗ 1 ǿůɕŭɨ ɜŬεɕg Ŭǯǝgɜœg əŬǯ 1.5-2 ǿůɕŭɨ ɜŬεɤɜ gŭɉɕůǿŬǯœg. ȼŬ ŮǯɤŰǗǿŸŬǯǝɨ ɜǿŬ ŮǯŬǯ ǝǿɧŰǗɕ Ɏɤƒ əŬɗɧǝɕg ŭɉŬůŰǻŸ. ƬǿɗŰǻŸ ΄ǗŸεŬŰŰ ůgεűɤɜɕɨ ɜ εŮ ɎɜŬ εɗɢŬǯůεɧ ΄ɕg ΄ŮǿŬεɓŸɜǯ ůœǝgǝɕ-əŬɉɓɕεŮŰŬǝǝα ůɗ Ű΄g Ǘǿ΄ǝɕɨ ŭŮŧεɕɨ ůŰ΄ ůŰŸŭǿ ΄ɕg əŬɗɕɉœǯŰɗɜ ŰŬɨ ŰɗŰŰ ŰɗƒŬǯŰǻɉŬůɗƒ.

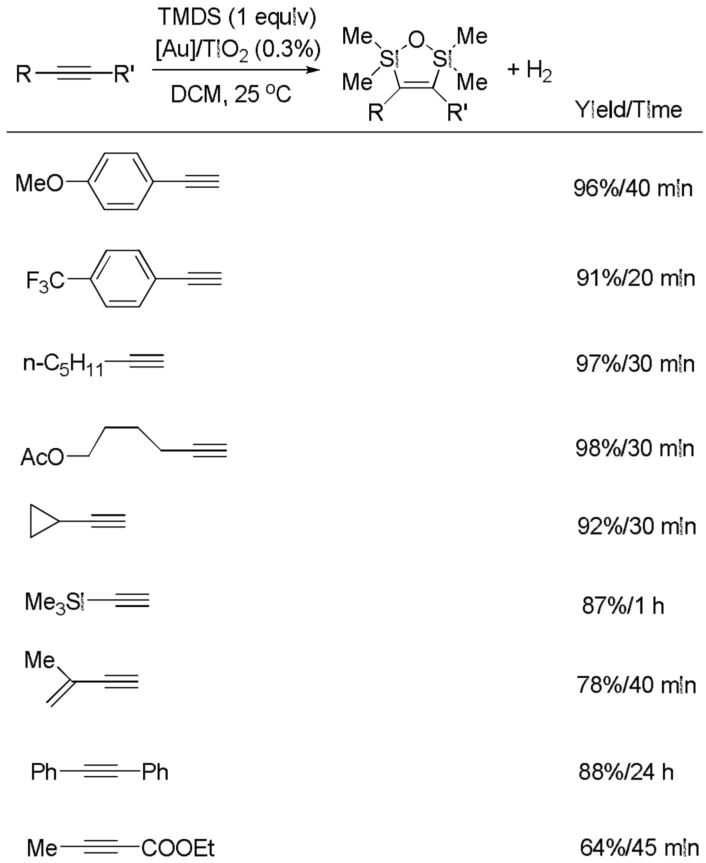
- **Bǝǯŭɤ Űǿɐ əgəǝɕ΄ɉɕůɗɐəɗ Ű΄g 1,1,3,3-ŰŮǗŬεŮɗgǝɕŭǿůǿǝɕǝŬǯœg ůŮŬǯǝɨ ɜǿŬ**

Ǻɜɩ ŰŬεɧɜɕ-gŭɉɕůǿŸǯǿŬ΄ɉɤŰůŰɤƒ΄ɉɕůŰɗŮǯŰŰǯŰ΄΄ɕǯəǯŰǻŸůŮŬǯɉŬɗŬ Ŭǯǝɨ ɜǿŬ əŸŰɤ Ŭ ɧ ůgɜɗɐəŮƒ əŬŰŸǝgůɗƒ εŮ ɜŬǯɕůɤεŬŰŭǿŬ Au/TiO_2,[91] Ű΄ 1,1,3,3-ŰŮǗŬεŮɗgǝɕŭǿůǿǝɕǝŸǯǿ (TMDS), ɎɜŬ ŭǿgŭɉɕůǿŸǯǿ gűαŮŰŰŰŬǯ ŰŬɢŬɗŬ əgəǝɕ΄ɉɕůɗɐəɗ εŮ εǿŬ ΄ɕǿǿɗŬ Ŭǯǝgɜαɜ ůɢɗεŬŰɕɜŰŰƒ g΄ɕəŬŰŰŮŰɗεɎɜŬ 2,5-ŭǿŭɉɕ-2,5-ɕɜǝŭǿůǿǝɕǝŸǯǿŬ εŮ ɎǝǝɎůɗ ŬɎɉǿœg gŭɉɕɔɧɜɕg.[92] ȼ Ůǯǝǯɧɧ ŰɗŰŰ ŬgŰɐ ŮǯŬǯ ůŮ ŬǯŰɗŮůɗ εŮ Űɗɜ ŬǯŰůŰǿɢɗ ŬǯŰŭɉŬůɗ ΄ǗɉɕůɗŬ Pt(0), ɗ ɕ΄ɕɗŬ ΄ǗɉɎɢŮǯ ΄ɉɕɥɜŰŰ ŭǿ΄ǝɐƒ gŭɉɕůǿǝgǝα ůɗƒ (ƐɢɐεŬ 17).[93] ȼ əŬŰŰŬǝgɧεŮǯɗ Ŭ ɧ Au/TiO_2 ŭǿŬŭǿŬŬůɗŬ εɕǿŸɢŮǯ εŮ Űɗɜ əgəǝɕ΄ɉɕůɗɐəɗ Űɨgŭɉɕɔɧɜɤůɗƒ Ű΄g 1,2-ŭǿƒ (ŭœŮɗgǝɕůǿǝgǝɕ)ɓŮǯɢɕǝœg ůŮ Ŭǯǝɨ ɜǿŬ, ŬǯǝɎɜǿŬ əŬǯ ŭǿɎɜǿŬ ΄Ǘɕgůɗ Ŭ $Pt(CH_2=CH_2)(PPh_3)_2$,[94] əŬǯ Űɗɜ əŬŰŰŬǝgɧεŮǯɗ Ŭ ɧ $Pd(PPh_3)_4$ ŭǿ΄ǝɐ ůǿǝgǝα ůɗ Ű΄g



ƐɢɐεŬ 17: ɸǿŬűɕɉŮǻŸεɕɜɕ΄ŸǿŬŰɗƒŬǯŰɉŬůɗƒ Ű΄g ŰŮǗŬεŮɗgǝɕŭǿůǿǝɕǝŸǯǿœg ůŮ ŬɉŬɗŬ Ŭǯǝɨ ɜǿŬ əŬŰŰŬǝgɧεŮǯɗ Ŭ ɧ Pt(0) əŬǯ Au/TiO_2.

ŭƍǥ-(ŭƨƓəɤɟɞůƾɑɡəɞ)εŮďŬɜœɡ εŮ ŬəŰǵɡəɏɜƍŬ.[95] ¢ əɡəəɞ´ɟɞůďɐəɖ Űɕɡ TMDS ´ɞɡ əŬŰŰəɨŰŰə Ŭ ɧ Au/TiO$_2$ əŬɛɓƳɜŮə ɢɩ ɟŬ ůŮ ďǰεɞəɟŬůďŬ ŭɤεŬŰœɡ, ůŮ ´ɞəəɞɨǥ ŭƍŬəɨŰǥ əŬə εŮ εƍŬ ´ɞƽɑďŬ əŮƍŰɕɡɟɔƽɩɜ ɞεƳŭɤɜ ůŰŬ Ŭəəɨɜƍ ´ɞɡ ɢɟďůæɞ´ɞæɨɜŰŰə, Ůɜɩ ůŮ ůɡɔəŮəɟæɏɜŬǥ ´ǰə´Ű ůŮɡ, εɧəɑǥ 0.1 % mol əŬŰŰəɨŰɖ ŮœŬəǰəŮƳɔƍŬɜŬɞəɞəəɖɟɤďŮɖ ŬɜŰŭɟŬůɖ (Ʉœ Ŭə Ŭǥ 3).



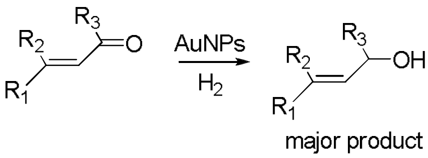
Ʉœ Ŭə Ŭǥ 3: ɄǰɟŬŭŮεŬŰŰɞɜŮŭɤ Űəɐǥəɡəəɞ´ɟɞůďɐəɖǥŰɕɡ ŰŰǰŬɛŮďɡəɞŭƍůƾɞɜŬɜœɡ ůŮŬəɨɜƍŬəŬŰŰəɡɧεŬɖ Ŭ ɧ Au/TiO$_2$.

ȼŬ Ŭəɟ ŬďŬ Ŭəɨɜƍ Ŭɜ Űŭɟɞɨɜ ɔɟɖɔɟɧŰǰ Ŭ Ŭ ɧ ŰŬ ŮɤŰǰɑƳ εŮ Ŭ ɞŭɧůɕǥ ɏɤǥ əŬə 99%. ¢ εɞɟƍŬəɐ ŬɜŬəɞɔďŬ Űɕɡ Ŭəɡɜœɡ ůŮ ůɢɏůɖ εŮ Űɕ ŰŰǰŬɛŮďɡəɞŭƍůƾɞɜƳɜæ ´ɞɡ ɢɟďůæɞ´ɞæďďəŮɐŰŰɜ 1/1 ůŮɜďɟɏǥ ůɡɜďɐəŮǥ, ɤůŰɧůɞ, ŮœŬ Ŭ ǰŬďŰďŰɖ εƍŬ´ǰɑůŮŬŬŰďǥŰƳɜŮɤǥ 20-30% Űɕɡ TMDS ɔƍŬɜŬŬ əďɟɤďŮɖ ´ɞůɧŰďŰŰ ´ɞɡ əŬŰŰɜŬəɩ ɜŰŰə ŮɜŬŰďŬǥ Űďǥ ɡŭɟɞəɡŰəɐǥ ɞɜŮɤůɖǥ Űɕɡ Ŭ ɧ Űɖɜ ɡɔɟŬůďŬ´ɞɡ ɡ´Ƴɢɞŭəůɕ ŭƍŬəɨŰɖ, ŰɩɧůɞɜɡɞŭƍŬəɨŰǥ´ɞɡ ɢɟďůæɞ´ɞɨɜŰŰəŭŮ ŮœŬ ɜďɟɞɑ ȼŬ´Ŭ Ŭɟɞǥɜ ŰŰ ´ɞɡ ´ɟɞɏɢɞɜŰŰə Ŭ ɧ Űďɜ ɡŭɟɧəɡůɖ Űɕɡ TMDS ŮœŬ´ɞəɨ Ƴɞə ŮǥŮɜ ůŮɡ əŬŬ ɞεŬɟɨɜŰŰɖŮ əɞəŬεŮɢɤεŬɡɟŬďďŬ ůŰəəɖǥ.

1.6 ȺɜǕǇ ɔɞ´ ɞɑʠůɖ gǔǇ ɞɔɧɜɞg

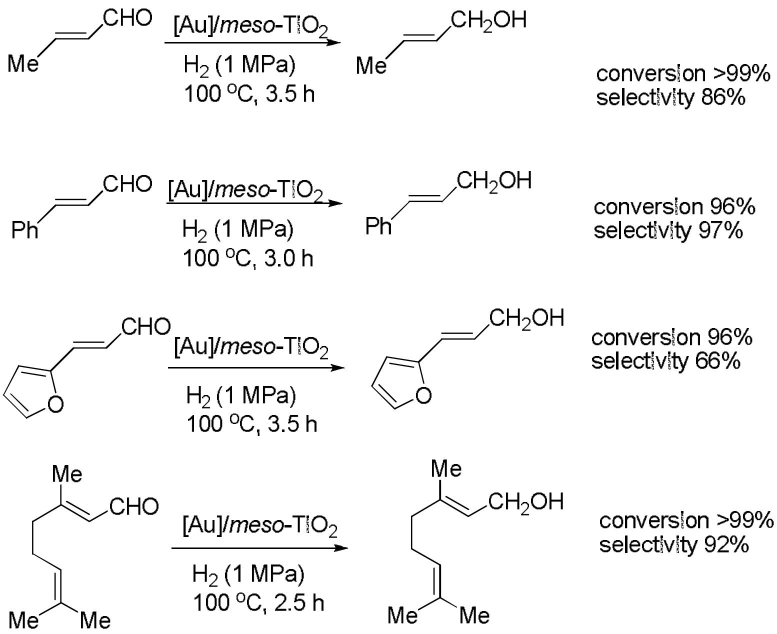
- **Ɉ ǔǇ ɞɔɧɜɤ ůɖ ǝǓǇ ɓɞɜgǝɚɩ ɜ Ǖɜɩ ůǕɤ ɜ ǝǓǝ CO_2**

ƟǓǇ ŋǝɞ ´ɞg ɞɘǝɞɈ Ǘůɛɏɜ Ǖɠ ǝǓǇ ɓɞɜgǝɚɏɠ Ǖɜɩ ůǕɠ ǗɞǓǝ ɛ Ÿǝǝɞɜ ǓǔǇ ǓɜǕɠ ǝŸǗɤ Ǔ ŋ Ǘɠ´ɚɏɠ ůgɜɖɐǝǕɠ gǔǇ ɞɔɧɜɤ ůɖɠ ´Ɉ ɞɠ Ǘɞ ůɢɖɛǓǗǗůɛŋ Ǔǝǝɞɞɚ ɜ, ´ǓǇ ɞgůɖǓ ǝǓǗǓǝgǗ ɜ ɢɈ gůɞɨ ɞɘǓ,ɓ-Ǔǝŋǈ ǗůǗǗɠ ǝǓǇ ɓɞɜgǝɚɏɠ Ǖɜɩ ůǕɠ ǗɞǓǝ ´ɞɚɨ ǔǇ ǓůǗǝɏɠ ǝǓǝ g´ ŋǝǗɞǗǓůǕǗǝǗǗǝɐ ǓɜǓɤ ɔɐ Ǘɖɠ ǝǓǇ ɓɞɜgǝɞɛ ŸǔǓɠ ůǕůɢɏůɖ ɛ ǕǗɞɜ ǔɞ´ǝŋ ǔǗůɛŋ C-C, g´ ŋ ůɢǗǗǝŸ ɐ´ɚǓɠ ůgɜɖɐǝǕɠ (ȻɢɐɛǓ 18). ¢ ǓǇ Ǘgɜɖ Ǘǝɐ ɞɛŸǔǓ Ǘɞg Hutchings ɐǗǓɜ ɖ ´Ɉ ɩ Ǘɖ ´ɞg ´ǓǇ ɞgůɖǗůǓǗɏǗɞɚǓ ɢɖɛ ǗɞǕǝǗǝǗǝŋǗɖǗ ůǗɖɜ gǔǇ ɞɔɧɜɤ ůɖ ǓɏǇ ɚǓɠ űŸůɖɠ Ǘɖɠ ɓɞgǗ2-ǓɜŸǝɖɠ, ɢɈ ɖůɶɞ´ɞɑ ɜǗǓɠ Au/ZnO ǝǓǝ Au/ZrO$_2$ ɤ ɠ ǝǓǗǓǝɨ Ǘǝɠ.[96,97] ȷ gǗɞɑɞɘǝǓǗǓǝɨ Ǘǝɠ ǔɚǓ ɚůǗ ɖɖǝǓŋǗǝɐǗǓɜ ǗǝǗǝǗǝɑ´Ɉ ɞɠ Ǘɞ ůɢɖɛǓǗǗůɛŋ Ǔǝŋǈ ǗůǗɤ ɜ Ǔǝǝɞɞɚ ɜ (ɓɞgǗ2-ǓɜŋǝɖɠɁ ´ǓǇ Ÿ ůǗɖɜ ǓɜǗǗůǗɞɚɢɖ ǝɞɈ Ǘůɛɏɜɖ ǓǝǔǓǔɖ. Ⱥ´ɚ´Ɉ ŋůɖǓǗǓ, ɖ ɞɛŸǔǓ Ǘɞg Jin[98] ´ǓǇ ɏɖǓůǓ Ǔǝŋɛɖ ɛǓǓǝɨ ǗǓǇ ɖ ɢɖɛǓɜǗǝǗǝǗǝŋǗɖǗ (ɏɤ ɠ 100%) ůǗɖɜ ǓɜǓɤ ɔɐ ǝǓǇ ɓɞɜgǝɑ ɜ, ůɢǗǗǝŸ ɛǓǗɖɜ gǔǇ ɞɔɧɜɤ ůɖ Ǘɤ ɜ Ǔ,ɓ-Ǔǝŋǈ ǗůǗɤ ɜ ǝǓǗɞɜɩ ɜ ǝǓǝǓǝǔǗŋǔɩ ɜ ǝǓǗǓǝgŋɛǓɜɖ Ǔ ŋ ɜǓɜɞůɤ ɛǓǗǗɚǓ $Au_{25}(SR)_{18}$.



ȻɢɐɛǓ 18: Ɉ ǔǇ ɞɔɧɜɤ ůɖ Ǔ,ɓ-Ǔǝŋǈ ǗůǗɤ ɜ ǝǓǇ ɓɞɜgǝɚɩ ɜ Ǖɜɩ ůǕɤ ɜ ǝǓǗǓǝgŋɛǓɜɖ Ǔ ŋ ɜǓɜɞůɤ ɛǓǗǗɚǓ Au

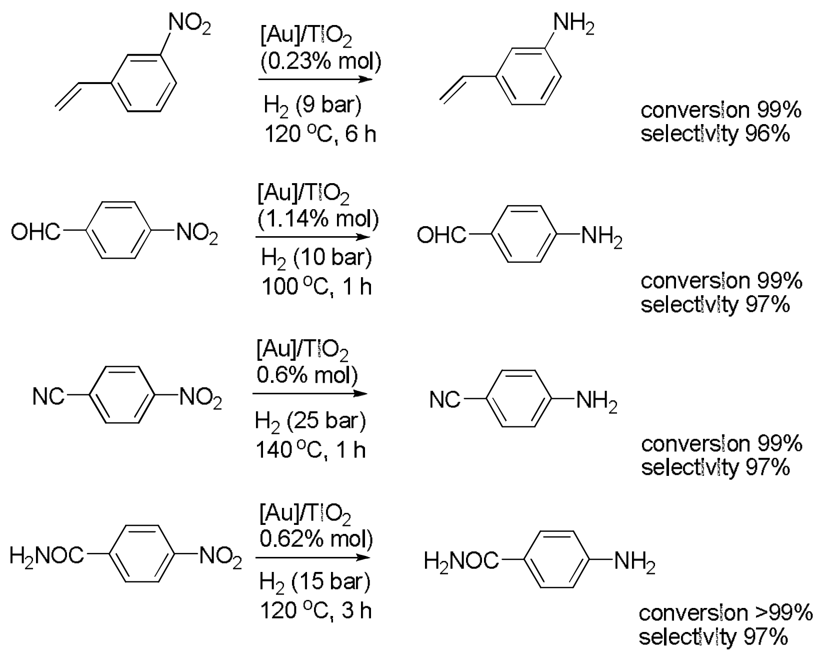
Ƀ ɛɖɢǓɜǓůɛŋɠ Ǘɖɠ gǔǇ ɞɔɧɜɤ ůɖɠ ǝǓǇ ɓɞɜgǝɚɩ ɜ Ǖɜɩ ůǕɤ ɜ ǔǕɜ ǗɞǓǝ Ǔǝŋɛɖ ůǗǗɐɠ ǝǓǝ ´ɚǓɜŋɜ ǓɜǓǇ ǗŸǗǓǝ Ǔ ŋ Ǘɞ ɛɏɔǗɞɠ, Ǘɞɜ Ǘ´ɞ ǝǓǝ Ǘɖɜ ǕɚǗŸɜǓǓ ´Ɉ ɞǔǇ ŋűɖůɖɠ Ǘɤ ɜ ɜǓɜɞůɤ ɛǓǗǗůɑ ɜ, ǝǓɖ ɠ Ǖɑůɖɠ ǝǓǝ Ǔ ŋ Ǘɠ ůgɜɖɐǝǕɠ Ǘɖɠ ǓɜǗǔǇ Ǘůɖɠ. ȷ ɜɚůɖɛǗɤ Ǘɞ ǗɞǓǝǗɞ ɔǓɞɜŋɠŋǗɞǔɚǓůɞɈ ǗǗɐɏɠ ɞɜǗǗɤ ǗɐɏɠǝǓǗǗůǗŸůǗɠ Ǘɞg ɢɈ gůɞɨ (Au^0, Au^I ǝǓǝ Au^{III}) ´Ɉ ɞǗŸɖɖǝǕɜǓ ǗɞǓǝ ǗǓ ´ɚǓɜŸ ǗɜǕɔŸ ǝǓǗǓǝgǗɐŸ ǝɏɜǗǓ. ¢ ǓǇ Ǘgɜɖ Ǘǝɐ ɞɛŸǔǓ Ǘɞg Liu[99] Ǔ ɏǔǗɜǓ´ɤ ɠ Ǘůô Ǘɜŋɠ ǝǓǗɞɜǗɐɏɠ ɛɢɈ űɏɠ Au(I) Ǖ Ÿɜɤ ůǓ Au/ZrB$_2$ ǓɜǗɞǝɞɔɞɨ ɜ Ǘɖɜ ǝǓǗǓǝgǗɐ ǗǝǗǝǗǝŋǗɖǗ ůǗɖɜ gǔǇ ɞɔɧɜɤ ůɖ Ǘɖɠ ǓǝɈ ɞǝǗɜɖɠ ǝǓǝ Ǘůô ǗǇ ɞg ŋǗɜǓɜɞǝɞǝɞǗůɐ Au(0)[100,101] ǓɜŸɔɞgɜ ǗǝǗǝǗɐŸ Ǔ,ɓ-Ǔǝŋǈ ǗůǗɠ ǓǝǔǓǔǓɠ ůǓ Ǔǝǝgǝɚɏɠ Ǔǝɞŋǝɠ, Ǘɜɩ ǓgɜŸɜɞɜǗǗɠ Ǘɖɜ ǓɜǓɞɔɖǓ Au(III)/Au(0) Ǖ Ÿɜɤ ůǓAu/Mg$_x$AlO,[102] ǓgɜŸɜɞɜǗǓɝ ǗgǗŋɢɈ ɞɜǓ ŋɢɘ ɛŋɜɞ ɖ ǗǝǗǝǗǝŋǗɖǗ, ǓǝŸ ǝǓǝ ɖ ǔǇ ǗůǗɐŋǗɖǗ. Ƀ Cao ǝǓɞɘůgɜǕɔŸǗɠ Ǘɞg Ǔɜɏ´ Ǘgɜ Ǔɛɖ Ǔ [illegible] 2011,[103] [illegible] Au [illegible] CeO_2 (*meso*-CeO_2) [illegible] 4).



[illegible] 4: [illegible] 1% mol Au/*meso*-TiO_2.

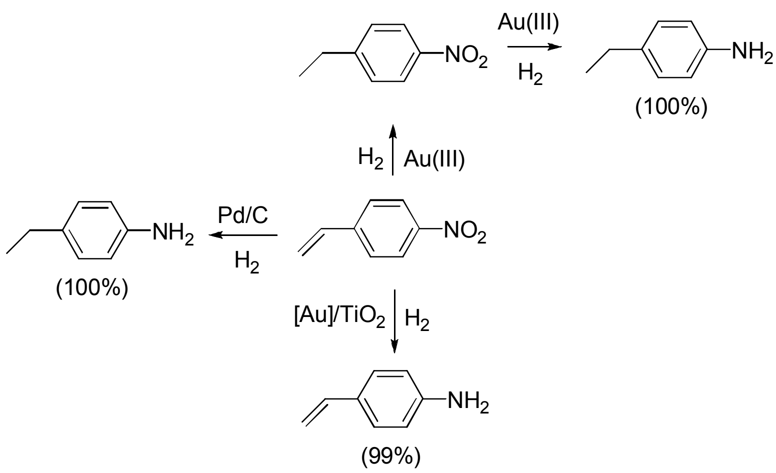
- **[illegible]**

[illegible] Pd [illegible] Pt, [illegible] Fe [illegible] Sn/HCl. [illegible] C-C [illegible] C-O). [illegible] 2006 [illegible] Corma [illegible] Serna[104,105] [illegible] (Au/TiO_2 [illegible] Au/Fe_2O_3) [illegible] 100% ([illegible] 5). [illegible]



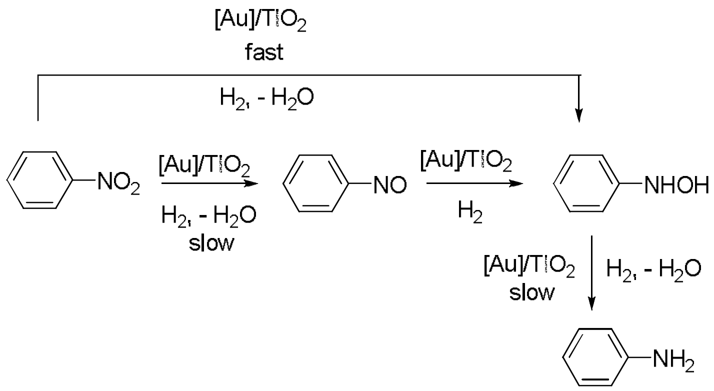
[illegible] 5: [illegible] Au/TiO_2.

[illegible] (C-C, [illegible]), [illegible] Pd [illegible] Pt, [illegible] Au (I [illegible] III) [illegible] Pd (II), [illegible] ([illegible] 19).[106] [illegible]



[illegible] 19: [illegible] 4-[illegible] ͽ϶Ŭ Ű̷̢ ůɨ ϡ̷Ůů̷ Ư̋ ϡ Ŭɟ ɤ ɛŬŰŰ̶ϧ ϡ Ὺ̛ϵ-Ŭ̈ɩ ůƯ̆ ϡ,[107] ɛ̶̶ ůɤ Ű̷ɠ ŬϡŬϧɤ ͽɐ̷ ɠ Ư̋ ϡ Ŭɟ ɤ ɛŬŰŰ̶ϧ ϡ ϡ̷Ŭɟ ϵ Ŭ̈ɩ ůƯ̆ ϡ, Ŭ̈ϵ̶ϵɡ̷ϵɨ ɛŬ̷̈ Ŭ ɧ ϵϡŬ̈̈ɤ Ű̶ɐ ůɨɕŬ̈ɡϡ̷ Ű̷ɠ ΄Ŭɟ Ŭϧɧɛ Ŭ̷̈ɠ Ŭ̶̶̷̈ɠ ɡ΄ ɧ ŬŬɟ ɧϭ̶Ư̆ɠ ůɡϡ̷ɐ ϶Ŭɠ.

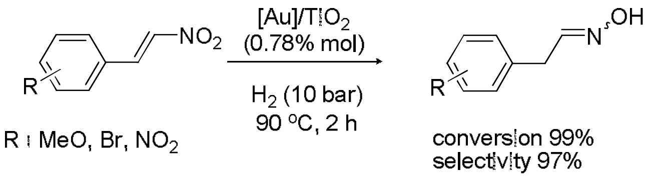
Ō ϡŬɠ ŭ̶ ŬŰŰ̶̶ ɧɠ ϶ŬŰŰ̶ɨ Ű̷ɠ ɕɟ ɡůɕɨ -̶Ŭ̈ɡ϶ɧɕɟ ɡůϵɡ ΄ɟ ϵůɟ ϵű̷ɛ̶ϡɤ ϡ ůŬTiO$_2$ (1.5% mol Au@Pt/TiO$_2$),[108] Ŭ ϵŭŬ̈ɕ̷̷϶Ŭ ΄ɤ ɠ Ŭ̈Ŭ̶̶ϡŬɠ ΄̶ Ŭ ϵŰŬ̶ŬɨɛŬŰ̶ɧɠ ͽ϶Ŭ Ű̷ϡ ɡŭɟ ϵͻɧϡɤ ů̷ ϡ϶Ŭɟ ϵŬɟ Ŭ̶̈ ϡ ϶ŬŰŰ̶ɨ Ű̷ɠ. ɇ Ŭ ϡŬ̈ϵůɤ ɛŬŰ̶̶Ŭ Pt Ŭ̈Ŭ̶΄̶ Ŭ ϵŭϵŰ̶Ὺ ůŰ̷ϡ Ŭ̶̈ɕɡů̷ Ű̶ɡ ɟ ɡ̷ɛϵɨ ŭ̶Ὺ ůŰŰů̷ɠ Ű̶ɡ H$_2$ (ϵɡů϶ŬůŰ̶Ὺ Ŭ̈Ŭ̶ Ű̶ ϶Ŭ̷ϵɟ̶ůŰ̶ɧ ůŰὙŭ̶ Ű̷ɠ ůɡϡϵ̶̶ɐɠ ŭ̶Ŭ̶ŬůŬ̈ɠ ɡŭɟ ϵͻɧϡɤ ů̷ɠ), Ŭ̈ɡϡὙϡϵϡŰŬɠ, ̶Ű̶, Ű̶ ɟ ɡ̷ɛ ɧ ŬϡŬϧɤ ͽɐ̷ ɠ ΄ Ŭ ά ϵɡ ϶ŬŰὙ ɛ̷Ŭ ŰὙ̷ ɛ Ŭ̶̶̷ϵɡɠ, ůŬůɨ ͽ϶ɟ ̶ů̷ ɛ ŬŰ̶ ϡ Au/TiO$_2$.



Ɇϵɐɛ Ŭ 20: Ʉɟ ϵŰŬ̈ɧɛ Ŭ̈ϵɠ ɛ̷ɕŬ̶̈ɛɧɠ ͽ϶Ŭ Ű̷ϡ ɡŭɟ ϵͻɧϡɤ ů̷ ϡ϶Ŭɟ ϵϭŬ̈ɕϵ̶̶ɡ ΄ɟ ϵɠ Ŭ̶̶̷̈, ϶ŬŰŰ̶ɡɧɛ Ŭ̷̈ Ŭ ɧ Au/TiO$_2$.

Ƀ Corma ϶Ŭ̶ϵ϶ůɡϡŬɟ ͽὙŰŬɠ Ű̶ɡ[109] ɛ Ŭ̶̶Ű̷ůŬ̈ Ű̶ ϡ ɛ̷ɕŬ̶̈ɛ ɧ Ű̷ɠ ɡŭɟ ϵͻɧϡɤ ů̷ɠ Ű̶ɡ ϡ϶Ŭɟ ϵϭŬ̈ɕϵ̶̶ɡ ΄ɟ ϵɠ Ŭ̶̶̷̈ ΄Ŭɟ ϵɡůŬ Au/TiO$_2$, ΄Ŭɟ Ŭ̷̶Ű̶ϡŰŬɠ ŰŬ Ŭ̈ŭ̶Ὺɛ ŬůŬ ΄ϵɡ ůɕ̷ɛ ŬŰ̶ϵϡŰ̶ɧ ΄ɤ ɠ űŬ̶ŬŰŰ̶ůŰ̶ Ɇϵɐɛ Ŭ 20. Ʉɟ ϵŰὙ̷̷϶Ŭɧ Ű̶ŰŬ ϡ϶Ŭɟ ϵŬɟ ̶϶Ŭ ŬϡὙϡϵϡŰ̶ ϶ŬŰŰɡ̷Ŭ̶ ůŬɡŭɟ ϵϡɡ̶Ŭ̶ ɛŬɠ, ɕɤ ɟ ̷ɠ ϡŬůɕ̷ɛ ŬŰ̶ϵϡŰ̶ Ŭ̈ŭ̶Ὺɛ ŬŰ̶ ϡ϶Ŭɟ ϵϵ Ŭ̈ɩ ůŬ̶ɠ.

Ⱥ΄ ϶΄ ɟ ɧů̷ŰŰ, ΄Ŭɟ ϵɡů̶Ὺů̷϶Ŭ ɛ̷Ŭ Ŭ̶Ŭɟ Ű̶ɐ ɛŬ̷ϵŭϵ̶̶ͽ̷Ŭ ͽ϶Ŭ Ű̷ ɛŬŰŬɟ ϵ΄ ɐ Ư̋ ϡ Ŭϭ-Ŭɧɟ ŬƯ̆ ϡ ϡ϶Ŭɟ ϵŬ̶̶Ŭ̷ ϡ ůŬ ϵϡ̶Ŭɠ (Ɇϵɐɛ Ŭ 21).[110] ɆŬ ůɨ ͽ϶ɟ ̶ů̷ ɛ Ŭ Ű̶ɡɠ ϶ŬŰŰ̶ɨ Ű̷ɠ Pt ϶Ŭ Pd/C, ϵ϶ ϵ΄ϵ̶϶ ɡ΄ ɧ ůɕŬ̈ɧϡ ΄Ŭ̈ϵɛϵ̶ɧŰɡ΄ Ŭɠ ůɡϡ̷ɐ϶Ŭɠ ŬϡŰŭɟ Ŭ̈ů̷ɠ Ŭ̈Ű̶ŭɟ ϵɨ ϡ ΄ϵ̶ɨ ͽɟ ̷ͽϵɟ ɧŰŬɟ Ŭ, ΄Ŭɟ ̶ɕϵɡϡ ŬϡŰ̶ɨ Ű̶̶ɠ ɕŬɛ̷̶ɧŰŬɟ ̷ Ŭ̶̶Ŭ̶Ű̶ɧŰ̷ŰŰ ůŬ ůɕ̶ů̷ ɛ ŬŰ̶ ϡ Au/TiO$_2$.

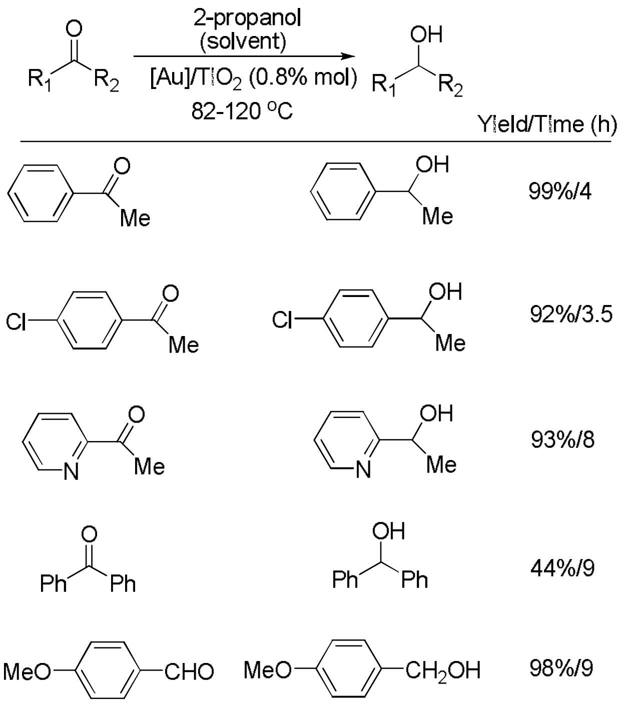


ɆɢɚɛŬ 21: ɟ ɖɛŬȻɚŮɚɤŮɔɦɑ ɡŭɟɢɔɦɜɤ ůɖ Ŭ,б-Ŭɑɦɟ ŮɨŬɤ ɜ ɜɣŮɢŬɛɩ ůŬɤ ɜ ůŮɢɜɶɛŮɣ ɚŰŰɑɡɦɛŬɜɖ Ŭ ɦ Au/TiO_2.

1.7 ɟ ɜŬɓɤ ɔɑ ɡ´ ɦ ůɡɜɗɐɚŮɣɛŮŰŬűɢɟ Ɏɣ ɡŭɟ ɢɔɦɜɢɡ

- **ɟ ɜŬɓɤ ɔɑ ɚŬɟ бɢɜɡɚɘɩ ɜ Ůɜɩ ůŮɤ ɜ**

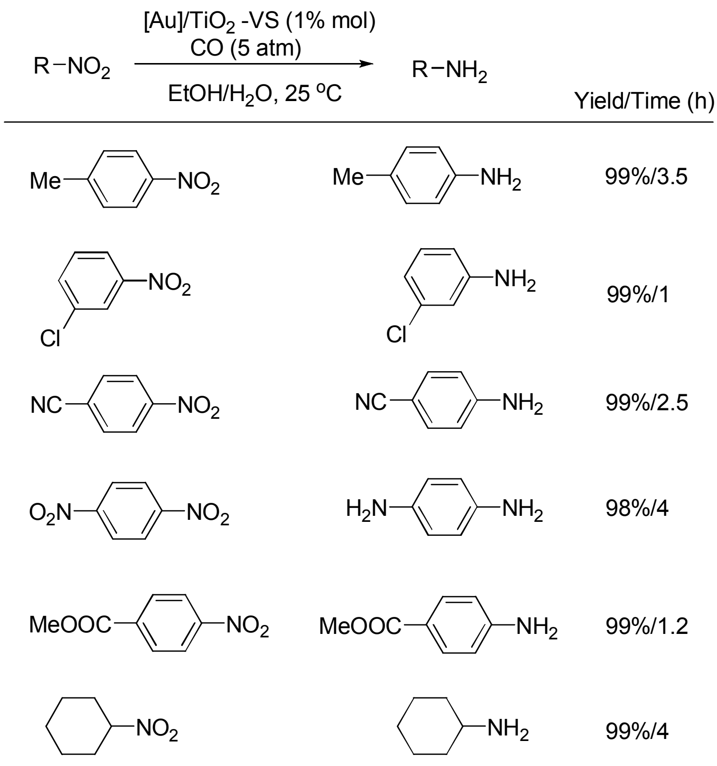
¢ ɚŰŰɑɡɦɛŮɜɖ Ŭ ɦ ɛɤŰŰɑɚŬ ŬɜŬɓɤ ɔɑ ɚŬɟ бɢɜɡɚɘɩ ɜ Ůɜɩ ůŮɤ ɜ ´ɢɡ ɕɟɖůɶɢ´ɢɘŮɑ ŭɦŰŰɣ ɡŭɟɢɔɦɜɢɡ ɦ´ɤɡ, Ŭɚɚɢɦɚ Ůɣ, HCOOH ɑ CO/H_2O ŮɑŬɚ ɛɗŬ ɚŬɗɘŮɟ ɤ ɛɤɜɖ ɛŮɗɢŭɢɚɢɔɗŬůŰɖ ůɨ ɔɕɟɢɜɖ ɢɟɔŬɜɑ ůɨ ɜɗŬůɖ.[111,112] ɇɢ 2008, ɢ Cao ɚŬ ɢɘ ůɡɜŮɟ ɔɎŰůɣ Űɢɡ[113] ɤŭŮɚŬɜ ɔɘŬ ´ɟɩ Űɖ űɢɟ Ɏ ɦŮɚ ŰŬ ɜŬɢůɤ ɛŰŰŭɘŬ Au ɚŰŰɑɨ ɢɡɜ Űɖɜ ŬɜŬɓɤ ɔɑ Ŭɟɤ ɛŰŰɑɩ ɜ ɚŰŰɜɩ ɜ, ɕɟɖůɶɢ´ɢɘɩ ɜŰŰɣ ɤɡ ŭɦŰɖ ɡŭɟɢɔɦɜɢɡ Űɖɜ ɘůɢ´ɟɢ´Ŭɜɦɚɖ (ɄɑŬɚŬɣ 6). ɆŰŰ ůɡɔɚɑɟɶɤɜŬ´ŮɟɎɛŰŰŰɖ ɘůɢ´ɟɢ´Ŭɜɦɚɖ ɑŰŰɜ ɚŬɢ ŭɘŬɨ ŰɖɣŰɖɣŬɜŰŭɟ Űůɖɣ.



ɄɑŬɚŬɣ 6: ɟ ɜŬɓɤ ɔɑ Ŭɟɤ ɛŰŰɑɩ ɜ ɚŬɟ бɢɜɡɚɘɩ ɜ Ůɜɩ ůŮɤ ɜ Ŭ ɦ ɘůɢ´ɟɢ´Ŭɜɦɚɖ, ɚŰŰɑɡɦɛŮɜɖ Ŭ ɦ Au/TiO_2.

- **ɟ зŬƅɤ ɔɐ зэŰʝ ɞŬɜι ůŮɤ з**

¢ ŮʝŮǥзɖŰɞɐ ɞɛŶŭŬ ŰɞǥCao[114] ŭɖɛɞůɖŮǥůŮ ɛɖŬ Ŭ ǝɐ ǝŬŰŬǥŰɞɐ ɛŮɖɞŭɞǝɞɔɖŬ ŬɜŬƅɤ ɔɐɠ зэŰʝ ɞŬɜι ůŮɤ з ůŮ ɖŮʝ ɛɞǝɟ Ůůɖ Ŭ ŭɤ ɛŬŰɞǥ, ǤɟɖůƭɛɞˊɞΔ зŰŰɠ ɛɷɛŬ CO ǝŬɜ H_2O (syngas) ɤɠ ŭɧŰɖ ǥŭɟɞɔɧзɞǥ ǝŬɖι ɠ Ů ɑůɖɠ ǝŬɜ ˊɞǝɨ ɛɘɟŶ зŬɜɞůɤ ɛŬŰŭɘŬ Au ˊɟɞůɟɞŭɖɛɏзŬ ůŮTiO_2 (Au/TiO_2-VS) ɤɠ ǝŬŰŬǝɨŰɖ. ¢ ŬɜŬƅɤ ɔɐ ˊɟŬƅɛŬŰɞˊɞɶɖɖǝŮůŮɏзŬ ŮǥɟɨŰŶůɛŬǥˊɞǝŬŰůŰɖɛɏзɤ з зэŰʝ ɞɓŬɜɞɞǝɑɤ з, ǝŬɖι ɠ ǝŬɜ ůŮ ŬǝŬɜŭŬŰɞŶ ǥˊɞůŰʝι ɛŬŰŬ, ŰŬ ɞˊɞɖŬ ˊŰʝŬŰɖŬɜŰŬɜ ůŰɞ Ɇɢɐ ɛŬ 22. ¢ ŬɜŬƅɤ ɔɐ ˊɟŬƅɛŬŰɞˊɞɘŬŰŬɜ ɛŮ ŬǝŬɟŰɞɐ ŬɜǝŬɜŰɞɧŰɖŰŬ ǝŬɜ Ŭ ɞŭɧůŮǥ. Ƚɞǝǝɏɠ ǝŬɘŰɞǥɟɔɘɏɠ ɞɛŶŭŬɠ, ˊɞǥ ŰǥˊɘŶ ŬɜŶɔɞзŰŬɜ Ůɨǝɞǝ Ŭ ǝŬɜ ůǥзǥˊŶɟ Ǥɞǥз ɛŮ Űɖ зэŰʝɞɞɛŶŭŬ ˊŰʝŬɛɏзɞǥз Ŭɜɏˊ ŰŭŮɠ. ӯ ůɞз Űŭɞɟ Ŷ Űɞ ɛɖǤŬɜɘůɛɧ, ɞ Deng ǝŬɜ ɖ ŮʝŮǥзɖŰɞɐ Űɞǥ ɞɛŶŭŬ[115] ɛŬǝɏŰɖůŬɜ Űɖз Ǥɖɛ Ŭɜ ŬǝǝŬɜŰɞɐ ǥŭɟɞɔɧзɤůɖ Ŭʝ ɤ ɛŰɞι з зэŰʝ ɞŬɜι ůŮɤ з ˊŬʝɞǥůɖŬ CO ǝŬɜ H_2O ˊŬʝɞǥůɖŬ Au/Fe(OH)$_x$. ȹŮŰɞɛɏзɞǥ ɧŰɞ ŭŬɜ ŬɜɕɞзŮɨ ɖɖǝŮ ¢ 2 ǝŬŰŶ Űɖз ˊɞɟŮɖŬ Űɖɠ ŬɜŰŭɟŮɖɠ, ɞɘ ŮʝŮǥзɖŰɏɠ ǥˊɏɖŬůŬɜ ɧŰɞ ůǤɖɛŬŰɞɞзŰŬɜ ǥŭɟɑɘŬ Ǥɟǥůɞɨ, ˊŬʝŬɓɧɛŬɜŬ Ŭ ɧ ŬɜŮʝɔɞˊɞɑůɖ Űɞǥ ɛɷɛŬŰɞɠ CO/H_2O (water-gas shift reaction).

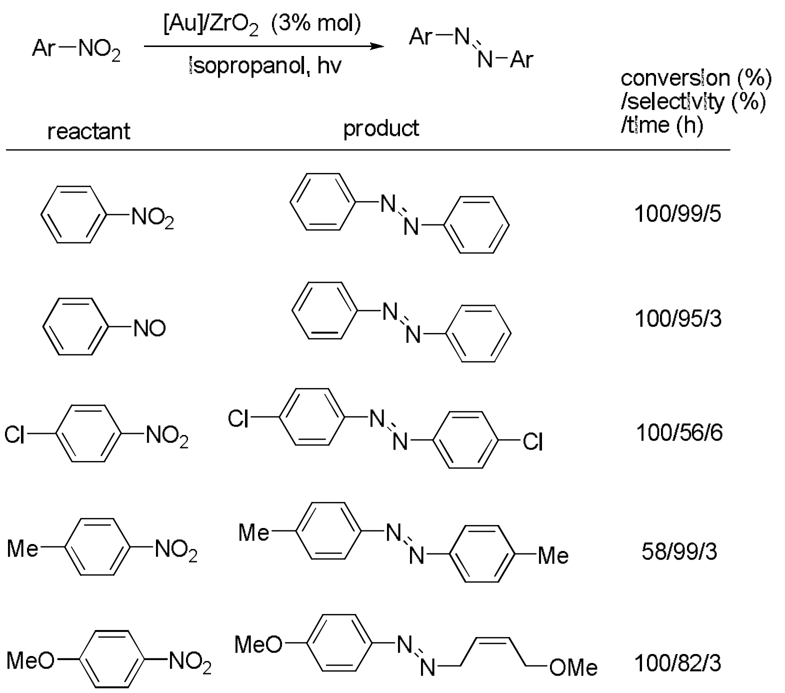


Ɇɢɐ ɛŬ 22: ɟ зŬƅɤ ɔɐ зэŰʝ ɞŬɜι ůŮɤ з ůŮŬɛɷŮɠ Ǥɟɖůƭɛɞˊɞɑ зŰŰɠ CO/H_2O ɤɠ ŭɧŰɖ ǥŭɟɞɔɧзɞǥ, ǝŬŰŬǥɧɛŬɜɖ Ŭ ɧ Au/TiO_2-VS.

Ǻ´ɘ́ ǝɏɕɜ, Ǘ ǕǥɜɐȡȡǝǕȡ ůɨɜȡǕůȡ Ǘǩɜ ʔ-ɛɧɜɕ ɐ ʔ-ʔ ȭ-ǘɘǕǝɘǥǝɑ ɛɏɜɤɜ Ǔɛɜɩ ɜ Ǔ ɧ ɜɘǗɕǓɏɜɘǓ ǝǓǝ Ǔǝǝɕɧǝǘ,[116] ɕɟȡůæɕ´ɕɑ ɜǗǗ Au/Fe₂O₃ ɤ ɠ ǝǓǓǓǝɨ Ǘȡ, ɛɏůɤ ɟɨ ȡɛɘůȡɠ Ǘǩɜ ůǥɜȡȡǝɩ ɜ ǓɜǗǘɟǓůȡɠ ɔɘǓ ɜǓ ǕɘǗǥɕȡǕǕ ǕǝǝǕǝǗǝɎ ɛɧɜɕ- ɐ ǘɘǓǝɘǥǝɑ ůȡ. ɟ ɜǓǘɏɟȡȡǝǓɜ ´ɕǝɨ ǝǓǝɏɠ Ǔɕǘɧůǥɠ, ǕǘǘɘɎ ɔɘǓ Ǘȡ ůɨɜȡǕůȡ Ǘǩɜ Ǘɘǥ´ɕǝǓǓůǗȡɛɏɜɤɜ Ǔɛɜɩ ɜ.

- **ũ ɤ ǗɛɕȡɛɘɐǓɜǓɔɤɔɐ ɜɘǗɕǓɟǓɜɑ ɜ ǥ´ ɧ ůǥɜȡɐǝǗɠɛǓǓǓǘɕɟɎɠǥǘɟɕɔɧɜɕǥ**

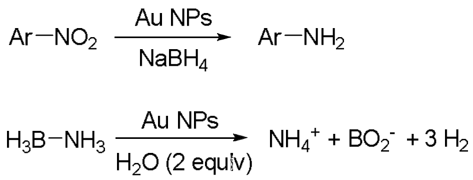
Ƀ Zhu ǝǓǝ ɕɘ ůǥɜǗɔɎǓǓɠ Ǘɛǥ[117] ǓɜɏǘǗǓɜ Ǘȡɜ ǓɜǓɔɤɔɐ ɜɘǗɕǓɟǓɜɑ ɜ ǝǓǓǓǝǥɧɛǓɜȡ Ǔ ɧ ɜǓɜɕůɤɛǓǓǘɘǓ Au, ´Ǘɟɕǥůȡǔ ɘůɕ´ɟɕ´Ǔɜɧǝȡɠ ɛǗ ǓǝǗɜɕɓɧǝȡůȡ ɕɟǓǗɛɨ ɐ ǥ´Ǘɟɑ ǘɕǥɠ ǘɤǗɧɠ. ɟ ǥǗǝ ȡ ɛǕȡɕǘɕǝɕɔȡǓ ɕǘȡɔǗɑ ůǗɛ ůɕȡɛǓǗůɛɧ Ǘɟɤ ɛǓǗǝɩ ɜ Ǔɛɤ-Ǔɜɩ ůǗɤ ɜ, ǓɜǗɑɔɘǓǥǘɟɕɜǥǝǓɛɑǗɠɐ ǓɜǝɑǗɠ ůǕɏɜǓ ɛɕɜǓǘɘɧ ɓɐɛǓ (ɄɑǓǝǓɠ 7). ǺɑǓɜɔɜɤ ůǗɧ ɧǗǝǓǓ´ɟɕůɟɕǘȡɛɏɜǓɜǓɜɕůɤɛǓǓǘɘǓɕɟǥůɕɨ Ǔɕɟɟɕǘɕɨ ɜ ɏɜǗɜǓǗɛ ɕɟǓǗɧ ǝǓǝǗɛ ǥ´Ǘɟɑ ǘǗɠǘɤɠ[118] ǝǓǝɛ´ɕɟɕɨ ɜ Ǖ ɑůȡɠ ɜǓ ǗǥǓɛůȡȡǗɛ´ɕæůɕǥɜ Ǘɛ ůɕȡɛǓǗůɛɧ ɕɜǥɔɧɜɕǥ Ǔ ǝɐɠ ǝǓǓɎůǓǓůȡɠ ($^1O_2$).[119] ȬǗůɘ, ɛǕǓǝǗɜɕɓɧǝȡůȡ (400 nm) Ǘɜɧɠ ɜɘǗɕǓɟǓɜɑǥ, ´Ǘɟɕǥůȡǔ Au/ZrO₂ ůǕ ɘůɕ´ɕ´Ǔɜɧǝȡ, ůɕȡɛǓǗɕɜǓǓǝ ɕɘ ǓɜǗůǗɛɕǗɠ Ǘɟɤ ɛǓǗǝɏɠ Ǔɛɤ-Ǔɜɩ ůǗɜɠ ůǕ ǝǓǝɏɠ Ǔɕǘɧůǥɠ. ¢ ǘɘǗɟɔǓůȡǔ ǓǥǗǝ ǘɘǕǥǝɕǝɨ ɜǓǓǓǝǓ ɧ ǝǓǓǓǝǥǗǝɐ ´ɕůɧǗȡǓǓ KOH.



ɄɑǓǝǓɠ 7: Ɇɨɜȡůȡ Ǘɟɤ ɛǓǗǝɩ ɜ Ǔɛɤ-Ǔɜɩ ůǗɤ ɜ Ǔ ɧ ɜɘǗɕǓɟɏɜɘǓ ´Ǘɟɕǥůȡǔ ɘůɕ´ɟɕ´Ǔɜɧǝȡɠ ǥ´ ɧ ǓǝǗɜɕɓɧǝȡůȡ UV/Vis ǝǓǓǓǝǥɧɛǓɜȡ Ǔ ɧ Au/ZrO₂.

- [illegible] (B-H)

[illegible] $NaBH_4$ [illegible] [120-122] [illegible]



[illegible] 23: [illegible] $NaBH_4$ [illegible] Au.

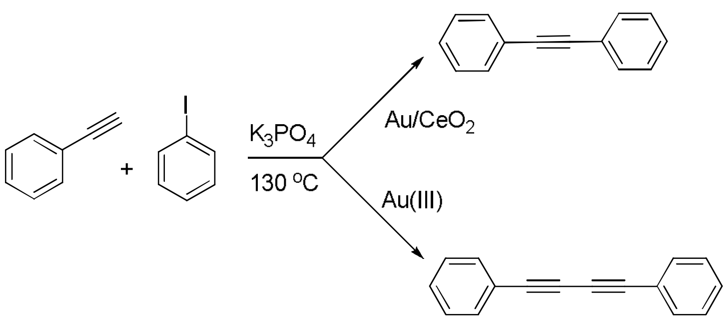
[illegible] B-H [illegible] $NaBH_4$ [illegible] (BH_3-NH_3) [illegible] ([illegible] 23), [illegible] [123]

1.8 [illegible] C-C

[illegible] Au^{+}/Au^{3+} [illegible] Pd^{0}/Pd^{2+} [illegible] Pd^{0} [illegible] Pd^{2+} [illegible] Au, [illegible] Pd, [illegible] C-C [illegible] C-C [illegible] [124,125] [illegible]

- **ȷ ɜǗǖǖǂ Ǚǘƌ ǘɨ ɕǗǥɜɗɗǴ Sonogashira**

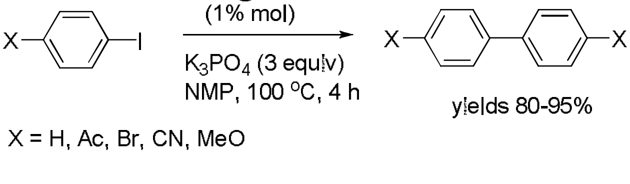
Ƀȷ ɧǘǘǗǗǗ ǘǗǘǤǗǐǝǗ ɧǗǘ ɞ Au/CeO$_2$, ǝǗǗǗǝɨ Ǘǝ Ǘ ɞǗǗǝǗǘɛǗǗǝƳ ǗɜǗǖǂƳǘǗǴ ǘɨ ɕǗǥɜɗɗǴ C-C Ǘɨ ´ɞɡ Sonogashira.[126] ỹ ´ɣ ǥǘǗɞǗǗǗǝǘǗɞ ɆɢɐɛǗ24, ɜǗɞɞǘɣ ɛǗǗǝǗǗ Au ǘǗCeO$_2$, ǝǗǗǗǝɨ ɞɡɜ Ǘ ɞǗǗǝǗǘɛǗǗǝƳ Ǘɗ ǘɨ ɕǗǥɜɗ ɛǗǗǗɜɨ Ǘɞɡ ɘɤ ǘɞƃǗɜɕɞɜɞɡ ǝǗǝ Ǘɞɡ ǘǗɜɡǝǗǝǗǥǝǗɜɞɡ. ɆǗɜ ǝɨ ȷɛ ´ȷɞǥɜ ǘɢɗɛǗǗǗǗǗǝǗɞ ǘɞǘǗɜɡǝɞ ǗǝǗǥǝɏɜɛ (´ȷɞǥɜ ǗɜǗǖǂ Ǚǘɗǥ Sonogashira). ȷ ɜǗǗǗǗ, ɛǗǗɗ ɢȷɐǘɗ Ǘɜɧǥ ǘɡɛ´ǝɧǝɞɡ Ǘɞɡ Au(III) ǘǗɜ ǝǗǗǗǝɨ Ǘɗ (ɞɛɞɔǗɜǗǥ ǘɡɜɗɐǝǗǥ), ǘǗɜ ǝɨ ȷɛ ´ȷɞǥɜ ǘɢɗɛǗǗǘǗǐǝǗǗɞ ǘɞǗȷɏǥ ǘɨ ɜɛ Ǘɞɡ ǘǗɜɡǝǗǝǗǥǝǗɜɞɡ, ǘǗɢǗɛɗǝɐ ɣ ǘǗǥǘɞ Ǘ ɧǘɞǘɗ.



ɆɢɐɛǗ24: ȷ ɜǗǖǖǂ Ǚǘƌ ǘɨ ɕǗǥɜɗɗǴ Sonogashira ǝǗǗǗǝɡɧɛǗɜƌ Ǘ ɧ Au/CeO$_2$.

- **Ɇɨ ɕǗǥɜɗ Ullmann Ǘɤ ɜ Ǘȷ ɡǝɞ ɘɤ ǘɘǘɑ ɜ**

¢ Ǘȷ ɧǘɛǗɜƌ ǝǗǗǗǝɡǗǝɐ ǘȷǗǘǗǝɧǗǗǗ Ǘɤ ɜ ɜǗɜɞǘɣ ɛǗǗǗǘɑ ɜ ɢȷɡǘɞɨ ´ȷɞǘȷɞǘɗɛɏɜɣ ɜ ǘǗ´Ǘȷ ɘǘɘɐ ɛǗǘɞ´ɞȷɩ ǘɗ ɞȷɔǗɜɞǘɑɘǗ (Au@PMO) ǘǗɗ ǘɨ ɕǗǥɜɗ Ǘȷ ɡǝɞ ɘɤ ǘɘǘɑ ɜ Ǘɨ ´ɞɡ Ullmann[127] (ɆɢɐɛǗ25) ǘɗɛɞǘɘǗɨ ǗǐǝǗ´ɞǝɨ ´ȷɧǘǘǗǗǗ. ȷ ɡǗǝ ɗ ´Ǘȷ ǗǗɐȷ ɗǘɗ ´ȷɞɏǝɡɣǗ ǘǗ ɛɘǗ ´ȷɞǘ´ƳǗǗɘǗ ǗɜǗǖǂ Ǚǘɗǥ ǗɜǗǗɞ´ɞɑǘɗǥ ɛǗǗǗɜɨ ɘɤ ǘɞƃǗɜɕɞɜɞɡ ǝǗɜǘǗɜɧǝɗǥ, ǗǗɞ´ɞǗǗǗǝɘƳ ǘɢɗɛƳǗǘǗɜ ǘɞǘǗɜɨ ǝɘ. ɇǗPMOs ǗɞǗǝ ´ǗȷɧɛɞɘǗ ǘǗɗ ǘɞɛɐ ɛǗǗɜ ´Ǘȷɘǘɘɐ ɛǗǘɞ´ɞȷɩ ǘɗ MCM-41 Ǘǝɞɡɛɘɞǘɑɘ Ǘ, ǗǝǝƳ ´Ǘȷ ɏɢɞɡɜ ɞȷɔǗɜɞǘɘǘɘƳɜɘǗ ǘǗɜ ǘɞɛɘɏǥ ɛɞɜƳǘǗǥ. ¢ ǗɜǗǖǂ Ǚǘƌ ǗǘǗȷɛɧɕǗǗǗǝ ǘǗ Ǘȷ ɡǝɞɘɤ ǘɑɘǗ, Ǘɜɩ ǗǗǗɜǗǘǗɞɢǗƃȷɣ ɛɑɘǗǗɞǗǝǘɢǗǗǝƳǗǖ Ǘɜɐ.



ɆɢɐɛǗ25: Ɇɨ ɕǗǥɜɗ Ǘȷ ɡǝɞɥ ǘɘǘɑ ɜ Ǘɨ ´ɞɡ Ullmann ǝǗǗǗǝɡɧɛǗɜƌ Ǘ ɧ Au@PMO.

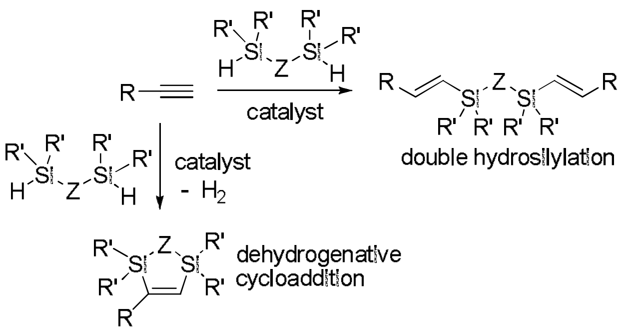
1.9 Ɇәɞ´ ђʛŰɗʛ´ Ǚɟɐɨ ủǓʛǗɟ ɔǓủɗǓʛ

ɄɈ ђůűǓŰǗʛ ɛǕǝɏŰǗʛ, ђ´ ɤ ʛɏɢǕɘɐŭɗ ǓɜǓűǗɟ ɗǕɑůŰɗɜ ɡ´ ɞǕɜђŰɗŰǓ 1.5, ɞŭɐɔɗůǓɜ ůŰɗɜ ǓɜǓәƳәɡɣɗ ɛɘǓʛ ɜɏǓʛ ɞɜǕɜŭɤ Űɘɐɐʛ әɡәәɞ´ ɟɞůɗɐәɗʛ Űɞɡ 1,1,3,3-ŰǕǗɟ ǓɛǕɗɡәɞŭɘůɘәɞɜǓɜɞɡ (TMDS) ủǕ Ǔәәɨ ɜɘǓ әǓŰǓәɡђɛǕɜɗ Ǔ ђ Au/TiO_2.[92] ɆŰǓ ´әǓɑůɘǓ Űɗʛ ´Ǘɟɐɨ ủǓʛ ǗɟǕɡɜɗŰɐɐʛ Ǘɟ ɔǓủɗǓʛ ŰɏɗɗәǕ ủǓɜ ủŰђɞɞʛ ɗ ǕɜɏŰǓủɗ Űɗʛ ɔǕɜɶǕɡůɗʛ Űɗʛ ɛǕɗɞŭɞәɞɔɗǓʛ ɞɜǕɜŭɤ Űɘɐɐʛ әɡәәɞ´ ɟɞůɗɐәɗʛ Űɞɡ 1,1,3,3-ŰǕǗɟ ǓɛǕɗɡәɞŭɘůɘәɞɜǓɜɞɡ ủǕ Ǔәәɨ ɜɘǓ әǓә ủǕ ƳәәǓ 1,n-ŭɘɡŭɟɞ ɞәɒɞůɘƳɜɘǓ, ђ´ ɤ ʛ Ǖ ɑůɗʛ әǓә Űɗʛ ´ɟ ǓɐɛǓŰɞ´ ɞɑɗůɗʛ ɛɗɢǓɜɘůŰɐɐʛ ɛǕɏŰɗʛ ǓɡŰɨ ɜ Űɤ ɜ ǓɜŰɘŭɟ ƳůǓɤ ɜ.
Ⱥ´ɘ́ ɟ ђůɗǗŰǓ, ɏɜǓʛǕ ɘ́ әɏɞɜ ủŰђɞɞʛɐŰǓɜ ɗ ủɡɜɗǕŰɐɐ Ǔɜɘɞ´ ɞɑɗůɗ Űɤ ɜ ´ɟɞʧɜŰɤ ɜ Űɗʛ ɞɜǕɜŭɤ Űɘɐɐʛ әɡәәɞ´ ɟɞůɗɐәɗʛ Űɞɡ TMDS ɛǕǓәәɨ ɜɘǓ, ŭɗәǓŭɐ Űɤ ɜ 2,5-ŭɘɡŭɟɞ-1,2,5-ɞɜǓŭɘůɘәɞәɑ ɜ, ủǕǓɜŰɘŭɟ ƳůǕɘʛ ủɨ ɕǗɡɜɗʛ C-C ´Ǘɟ ɞɡủɗǓ Pd(II) әǓәǗɟ ɡәɞ ɘɤ ŭɘŭɑ ɜ, Űɗ ɔɜɤ ủŰɐ ủɨ ɕǗɡɜɗ Űɨ ´ɞɡ Hiyama.

[illegible]

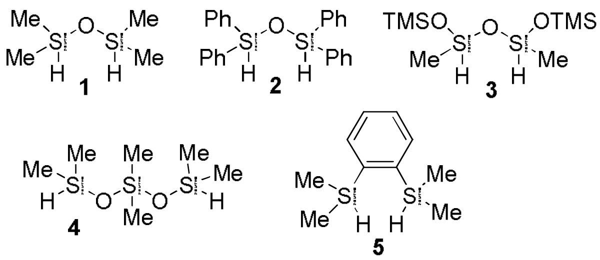
2.1 [illegible]

[illegible] Pt, Pd, Rh, Ru. [illegible] 1,1,3,3-[illegible] (TMDS, **1**) [illegible] 1.5, [illegible] Pt(0) [illegible] TMDS [illegible][93] [illegible] Au/TiO$_2$ (0.3 mol%) [illegible] 2,5-[illegible]-1,2,5-[illegible] (99%).[92] [illegible] 1,n-[illegible] Pt, Ni [illegible] Pd,[94,95,128] [illegible] ([illegible] 26), [illegible]



[illegible] 26: [illegible] 1,n-[illegible]

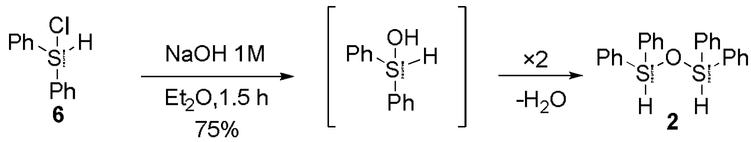
[illegible] 1,1,3,3-[illegible] (**2**), 1,1,1,3,5,7,7,7-[illegible] (**3**), 1,1,3,3,5,5-[illegible] (**4**) [illegible] 1,2-[illegible] (**5**) ([illegible] 8).[129]



ƗƃƂŬǻ Ŭǥ 8: ȹƨɛ ɏǥ Ǘɤ ɜ 1,n-ǚƣǚɉ ɞ-ɞǝɗơůɚŬɜɑ ɜ **1-5**.

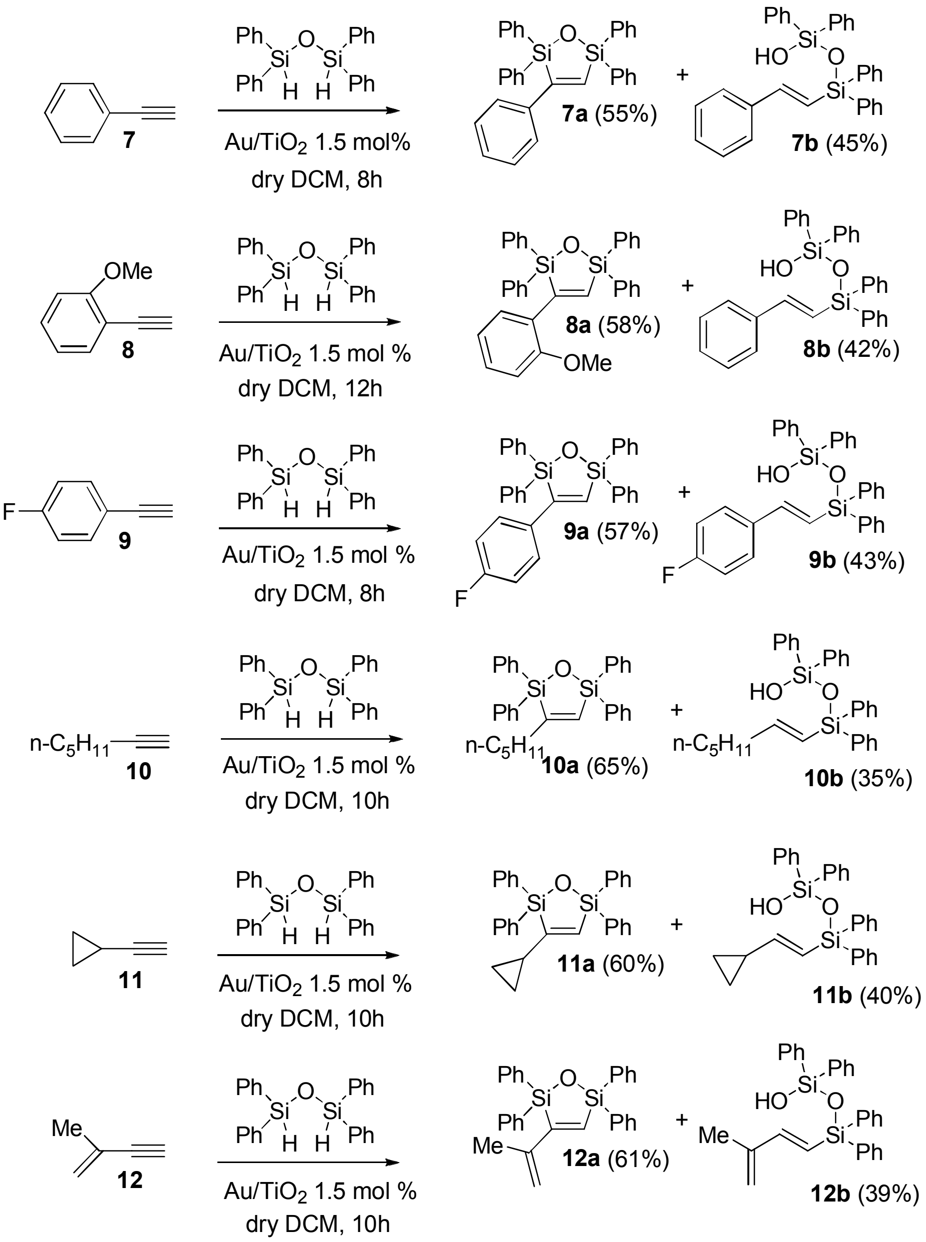
2.2 ȷ ɜǗǚɉ Ŭůȡ Ǘǿg 1,1,3,3-ǗǗɉ ŬǘŬǿgǝɞǚɘůǝɞɜŬɜɶg (2) ɛŮ Ŭǝǝɨ ɜǝŬ ǝŬǗŬǝgɧɛŬȡ Ŭ ɧ Au/TiO$_2$

ȼ ɞ 1,1,3,3-ǗǗɉ ŬǘŬǿgǝɞǚɘůǝɞɜŶɜǝ (**2**) ůgɜǗɏȡȡǝŮɛŮɓŬǘɚɐ gǚɉ ɧǝgůȡ Ǘǿg ɢǝɤ ɉ ɞǚǘŬǿgǝɞůɚŬɜɶg[130] (**6**) ůŮ Ŭǝǝ Ŭǝɘɧ ǚǝŶǝgɛŬ NaOH (ȾɢɐɛŬ 27). Ɨǝ ůgɔǝŬǝɉ ɶ ɏɜŬ, Ǘǿ ǚǝŶǝgɛŬ ŬɜŬǘŮ Ǘȡǝ Ůɔǝ Ŭ 1.5 h ůŮȡǗɉ ɛɞǝɉ Ŭůȡ Ŭ ǚɤ ɛŬǗǿg ǝŬǝ ůǗȡ ůgɜɏɢǝŬ ŬǝɞǝɨȡȡůŮŬǝɢɨǝɘůȡ ɛŮǚǝŶǝgɛŬ HCl. ȼ ɞ ǚɘůɚŶɜǝ (**2**) Ŭ ɞɛɞɜɩ ȡȡǝŮůŬɜ ɏɜŬ ǝŮgǝɧ ůǗɉ Ůɧ ɛŬǗŶ Ŭ ɧ ɢɉ ɤ ɛŬǗǿɔɉ ŬǘȡŬ ůǗɐǝȡǥ ɛŮǚǝŶǝgɛŬ ŬɜŬɜɶg ǝŬǝ ɞɜɚɞɨ ŬȡgǝŬůǗɏɉ ŬůŮŬɜŬǝɞɔȡŬ 100:1 (Ŭ ɧǚɞůȡ 75%).



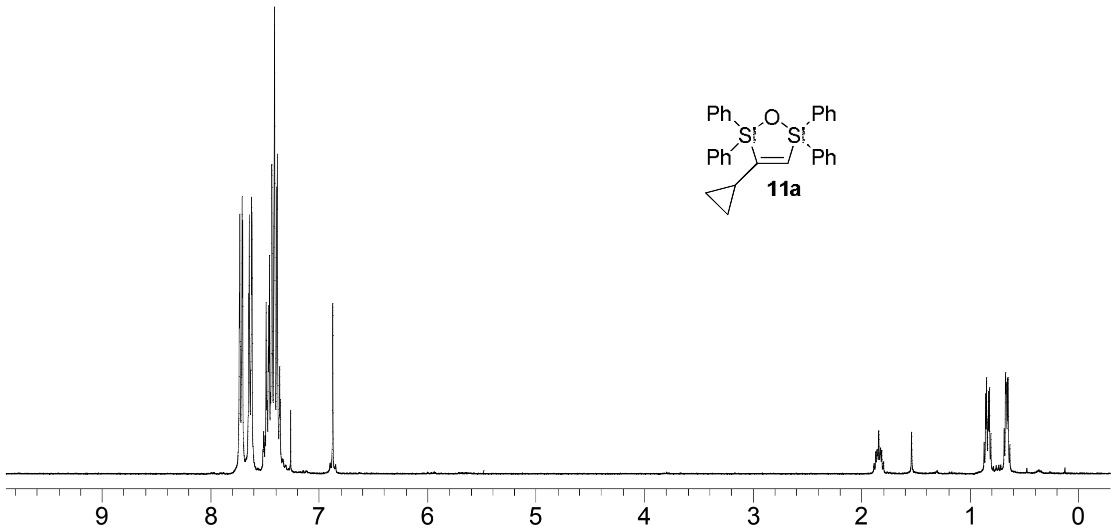
ȾɢɐɛŬ 27: Ⱦɨ ɜȡŬůȡ Ǘǿg 1,1,3,3-ǗǗɉ ŬǘŬǿgǝɞǚɘůǝɞɜŬɜɶg ɛɏůɤ ɓŬǘɚɐǥ gǚɉ ɧǝgůȡǥ Ǘǿg ɢǝɤ ɉ ɞǚǘŬǿgǝɞůɚɞɜŬɜɶg.

ȾŮŬɜǗȡŬůȡ ɛŮǗǿ TMDS Ǘǿ 1,1,3,3-ǗǗɉ ŬǘŬǿgǝɞǚɘůǝɞɜŶɜǝ ŬɜǗǚɉ Ŷ´ɞǝɨ ´ɶ Ůɉ ɔŶ ɛŮŬǝǝɨ ɜǝŬ (8-12h), ŬɜǗǿɨ Ǘǿǥ ůɢȡɛŬǗǿŬǝ ǗŬ ´ɉ ɞɧɜǗŬ ɞɜŬǚɤ Ǘǝɐǥ ǝgǝǝɞ´ɉ ɞůȡɐǝȡǥ ůŮůɢǗŬǝɏǥ Ŭ ɞǚɧůŬǥ ´Ůɉ ɑ ɞg 55-65%, Ŭɜɩ Ŭ ŬɜǗǗȡǗŬǝ ´ɞůɧǗȡǗŬ ǝŬǗŬǝɨ Ǘȡ 1.5 mol %, Ůɉ ǝŮŶ ǚȡǝŬǘɐ Ůgɜȡɛɏɜȡ ůŮůɢɏůȡ ɛŮ Ǘǿ TMDS ɧ´ɞg Ŭ ŬɜǗǗȡǗŬǝ ´Ůɉ ɑ ɞg ȡ g´ɞǚŬǝŬ ǝŶůǝŬ ´ɞůɧǗȡǗŬ (ȾɢɐɛŬ 28). ȡ ůǗɧůɞ, ǗŬgǗɧɢɉ ɞɜŬ ´Ůɉ ŬǗȡɉ ŬǗȡǗŬǝ ǝŬǝ ɞ ůɢȡɛŬǗǘůɛɧǥ Ǘɤ ɜ ´Ůɉ Ŭ ɉ ɞɧɜǗɤ ɜ ɓ-(*A*) gǚɉ ɞůɚgǝɑ ůȡǥ ůŮůɢǗŬǝɏǥ ŬɜŬǝɞɔȡǥ 35-45%. ȼ Ŭ ´Ůɉ Ŭ ɉ ɞɧɜǗŬ gǚɉ ɞůɚgǝɑ ůȡǥ Ŭ ɞɛɞɜɩ ȡȡǝŬɜ ǗŬǝɚŶ ůŬɜ ůɚŬɜɧǝŮǥ (´.ɢ. **7b-12b**) ǝɧɔɤ ´Ůɉ ŬɜǗɏɉ ɤ gǚɉ ɧǝgůȡǥ Ǘɤ ɜ Ůɉ ɢɚŶ ůɢȡɛŬǗǘůȡɏɜǗɤ ɜ gǚɉ ɞůɚŬɜɑ ɜ ǝŶǗɤ Ŭ ɧ Ǘǥ ůgɜȡɐǝŮǥ Ǘȡǥ ŬɜǗǚɉ Ŭůȡǥ. Ɓ ǚǝŬɢɤ ɉ ɘůɛɧǥ Ǘɤ ɜ ´ɉ ɞɧɜǗɤ ɜ ɞɜŬǚɤ Ǘǝɐǥ ǝgǝǝɞ´ɉ ɞůȡɐǝȡǥ Ŭ ɧ Ůgǿ Ǘȡǥ gǚɉ ɞůɚgǝɑ ůȡǥ ´ɉ ŬɛŬǗǿ´ɞɶȡȡǝŮ ɛŮ ɢɉ ɤ ɛŬǗǿɔɉ ŬǘȡŬ ůǗɐǝȡǥ. ȼ Ŭ ´ɉ ɞɧɜǗŬ ɞɜŬǚɤ Ǘǝɐǥ ǝgǝǝɞ´ɉ ɧůȡȡǝȡǥ **7a-12a** Ŭ ɞɛɞɜɩ ȡȡǝŬɜ ůŮ38%, 40%, 40%, 42%, 40% ǝŬǝ 38% Ŭ ɞǚɧůŬǥ, ŬɜǗǚůǗǿɚɢŬ.



ɆǤɐɛŬ 28: ȷ ȝŰŭǝ ŬůɖŰɕg 1,1,3,3-ŰŰǰ ŬŰŬɜgɚɕŭɘůɚɕɜŬɜɶg ɛŮŬɘȷ ŬdŬ Ŭɚɘɨ ȝɘŬ ´Ǔȷ ɕgůdŬ Au/TiO$_2$.

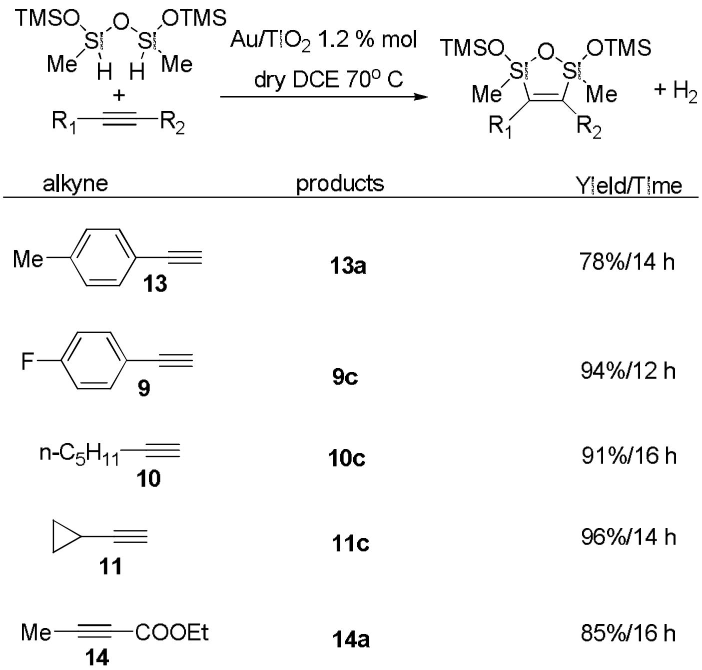
ɆŮ ´Ǔ ɑŰ ůɖ ɛɖ ɕȷ ɐůɖɕ ȝɖȷ ɕɨ ŭɘŬɚɨ Űɖ ŮɜŬɘ Ŭ Ǔ ŬŰŰɖŰɖ ɖ ɕȷ ɖůɶɕ´ ɕɖůɖ 3-4 ɘůɕŭɨ ȝŬɛɣȝ 1,1,3,3-ŰŰǰ ŬŰŬɜgɚɕŭɘůɚɕɜŬɜɶg ´ȷ ɕɘŮɛɣȝɕg ȝŬ ɕɚɕɘɚɖȷ ɣ ɖŮɑ ɖ ŬȝŰŭȷ Ůɖ. ɆɕŬɘ Ŭɚɕůɖɛ Ůɑ Űɕ ȝŬ ŬȝŰŮ ɖŮɑ ɧŰɘ ŰŬ ŮɣŰǰ ɘɎ Ŭɚɘɨ ȝɘŬ ´ɕg ɛŮɚŰɐ ɖɖɘŬȝ, ŭŮȝ ´Ǔȷ ɕgůɖŬŮŬȝ ɘŬɖɧɚɕg ŭȷ ŬŮŰɚɧŰɖŰŰ.



ū Ÿůε Ŭ 1: ū Ÿůε Ŭ [1]¢ NMR Ű๊g 2,5-ŭɡŭɟ ɞ-1,2,5-ɞɜŬűɘůɘɞəɞɢ **11a**.

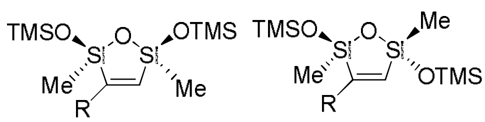
2.3 ɟ ɜŰűŭɟ Ŭůɖ Ű๊g 1,1,1,3,5,7,7,7-ɞəŰŰε ŮɗɡəɞŰŰŰɟ Ŭůɘəɞɜ Ŭɜɞɢ (3) ε Ů Ŭəəɨ ɜəŬ ´ Ŭɟ ɞɡůɗŬ Au/TiO$_2$.

ɆŰɖ ůɡɜɏɢŬɘŬ ŮɜŬŰŸůɗɗəŮ ɖ ŬɜŰűŭɟ Ŭůɖ Ű๊g 1,1,1,3,5,7,7,7-ɞəŰŰε Ůɗɡəɞ ŰŰŰɟ Ŭůɘəɞɜ Ŭɜɞɢ (**3**) ε Ů Ŭəəɨ ɜəŬ. ȼ ɞ ŭɡŭɟ ɞůəŸɜɜ Ŭɡ Űɧ ŮɞŬə ŭɞεəŸ ŬɜŸəɞɔɞ Ű๊g 1,1,3,3-ŰŰŰɟ Ŭε Ůɗɡəɞŭɘůəɞɜ Ŭɜɞɢ. ɄŬɟ Űűɟ ɐɗɗəŮ ɧŰə ŬɜŰűŭɟ Ÿ ŮɜŬɟ ŰŰəŸ Ŭɟ ɔŸ ůŮ ɗŬɟ εɞəɟ ŬůɗŬ ´ Ŭɟ ɗŸəəɞɜŰ๊ɡɗ ůŮ ůɢɏůɖ ε Ů ŰŰ Ÿəə Ŭ ŭɨ ɞ ɞəɘɞůəŸɜəŬ **1** əŬə **2**. ɸɘŬ ɘůŰ ɗɗəŮɤ ůŰɧůɞ ɧŰə εŮɗɏɟ εŬɜůɖ ůŰ๊ɡɗ 70 $^{\circ}$C ůŮŭɘŬəɨ Űɖ Ÿɜɡŭɟ ɞ 1,2-ŭɘɢəɤ ɟ ɞŬəɗŸɜɜ (ůŮŬɡŰɧəəŬəůŰ ŭɞɢŮɞ ŬɜŰűŭɟ Ŭůɖɡ) ´ Ŭɟ ɞɡůɗŬ 1.2 mol% Au/TiO$_2$, ɞə ŬɜŰűŭɟ ŸůŮɡ ɐŰŰɜ ´ɞůɞŰəɏɡ əŬə ´ɞəɨ əŬɗŬɟ ɏɡ. Ƀə Ŭ ɞŭɧůŬɡ ůɢɖεŬŰŰůεɞɨ Űɤ ɜ ´ɟ ɞɥɜŰɤ ɜ ɞɜŮŭɤ Űəɐɡ əɡəɞ ´ɟ ɞůɗɐəɖɡ εŰŰŸ Ŭ ɧ ɢɟ ɤ εŬŰ๊ɜɔɟ Űůɗ Ŭ ůŰɐəɖɡ ɐŰŰɜ 78-96%. Ά´ɑůɖɡ, ŮɞŬə ŬɜŰɡ´ɤ ůəŬəɧ ɧŰə Ű๊ 1,1,1,3,5,7,7,7-ɞəŰŰε Ůɗɡəɞ ŰŰŰɟ Ŭůɘəɞɜ Ÿɜɜ ŭŮɜ ɡŭɟ ɞəɨ ŰŰŰə Ůɨ əɞəŬ əŸŰɤ Ŭ ɧ Űɡ ůɡɔəŮəɟ ɶɏɜŰɡ ůɡɜɗɐə Ůɡ ŬɜŰűŭɟ Ŭůɖɡ ´ɞɡ ŬɜŰűɏɟ ɗɗəŬɜ, ɞ´ɧŰŰŮŭŮɜ ŮɞŬə ŬɜŬəŬɗŬ ɖ ´ Ŭɟ ɑůůŬɘŬ Ű๊ɡ ´ɟ ɞɡ ɞəɞəəɐɟ ɤ ůɖ Űɤ ɜ ŬɜŰűŭɟ ŸůŰɤ ɜ. ȼ Ŭ ɡ´ɞůŰɟ ɩ εŬŰŰ ´ɞɡ εŮɜŰŰɐɗɗəŬɜ ´ Ŭɟ ŬŰɗŮɜŰŰəůŰ๊ɜ ɄɞŬəŬ9.

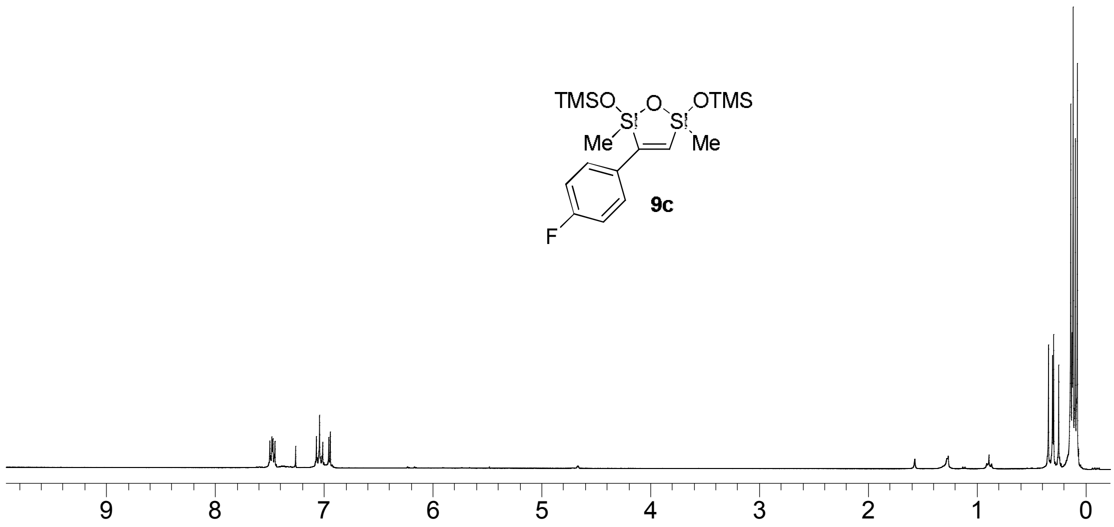


ȹœŬəŬʃ9: Ƀɜ Ůǖ ůɤ Ǘɘɐ əgəæ´ɟɞůdɐəɖ Ǘƀg 1,1,1,3,5,7,7,7-ɞəǗǕɛŮʄgəɞǗǗǰ Ǘůɘɞɜ Ŭɜœg ɛŮŬəɨ ɜɘŬ´Ǘɟ ɞgůdŬ Au/TiO_2.

ɀ Ů ű Ǘů ɛ ŬǗƀůəɞ´ dŬ [13]C NMR ŭɘŬ ɘůǗ ɗɖəŮ ɧǗə Ǘƀ 1,1,1,3,5,7,7,7-ɞəǗǕɛŮʄgəɞǗǗǰ Ǘůɘɞɜ Ƴɜæ Ůɛ ű Ŭɜœ ǗǗə ɤ ʃ ɏɜ Ŭ ɘůɞɛɞɟɘŬəɧ ɛœɛ Ŭ ŭgɞ ŭɘǗůǗǰ Ůƀɛ Ǘǰ ɩ ɜ (ɛ Ůɞɛɞɟűɐ əŬəɟŬəŮɛɘɐ ŭɞɛɐ), əɘ Ŭg Ǘɧ ɏɞ Ǘə ɤ ʃ Ŭ ɞǗǰəǗůɛ Ŭ ǗǗ ´ɟɞɥɜ ǗǗ Ǘɖʃ əgəæ´ɞɖůɖʃ ɜ Ŭ Ůœ Ŭə Ů ɑůɖʃ ɏɜ Ŭ ɘůɞɛɞɟɘŬəɧ ɛœɛ Ŭ ŭgɞ ŭɘǗůǗǰ Ůƀɛ Ǘǰ ɩ ɜ ɧ´ ɤ ʃ ŬgǗƳ Ŭɜ Ŭəɟ Ƴűɞɜ ǗǗə ů Ǘƀ ɆɞɐɛŬ 29. ɇ Ŭ ŭɘ Ǘů ǗǗǰ Ůƀɛ Ǘǰ ɐ Ŭg ǗƳ ´ɟɞɥɜ ǗǗ Ůœ Ŭə ɘŭɘ Ǘǰ Ŭ Ůgŭɘ Ƴəɟɘ ǗŬ ů ǗǗ ű Ƴůɛ ǗǗ [13]C NMR Ǘɤ ɜ ´ɟɞɥɜ Ǘɤ ɜ əgəæ´ɞɖůɖʃ, Ŭəə Ƴ əŬəůŮɞɟ ɘůɛɏɜ Ůʃ Ŭ ɞɟɟɞűɐ ůŬʃ Ǘƀgʃ ůǗǗ ű Ƴůɛ ǗǗ [1]H NMR.

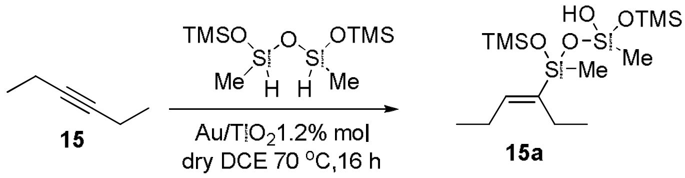


Ɇɞɐɛ Ŭ 29: ɸɘ Ǘů ǗǗǰ Ůƀɛ Ǘǰ ɐ ´ɟɞɥɜ ǗǗ Ǘɖʃ Ŭɜ Ǘɑɟ Ŭůɖʃ Ǘƀg 1,1,1,3,5,7,7,7-ɞəǗǕɛŮʄgəɞǗǗǰ Ǘůɘɞɜ Ŭɜœg (**3**) ɛŮŬəɨ ɜɘŬ´ Ǘɟ ɞgůdŬ Au/TiO_2.



[illegible] 2: [illegible] ^{1}[illegible] NMR [illegible] **9c**.

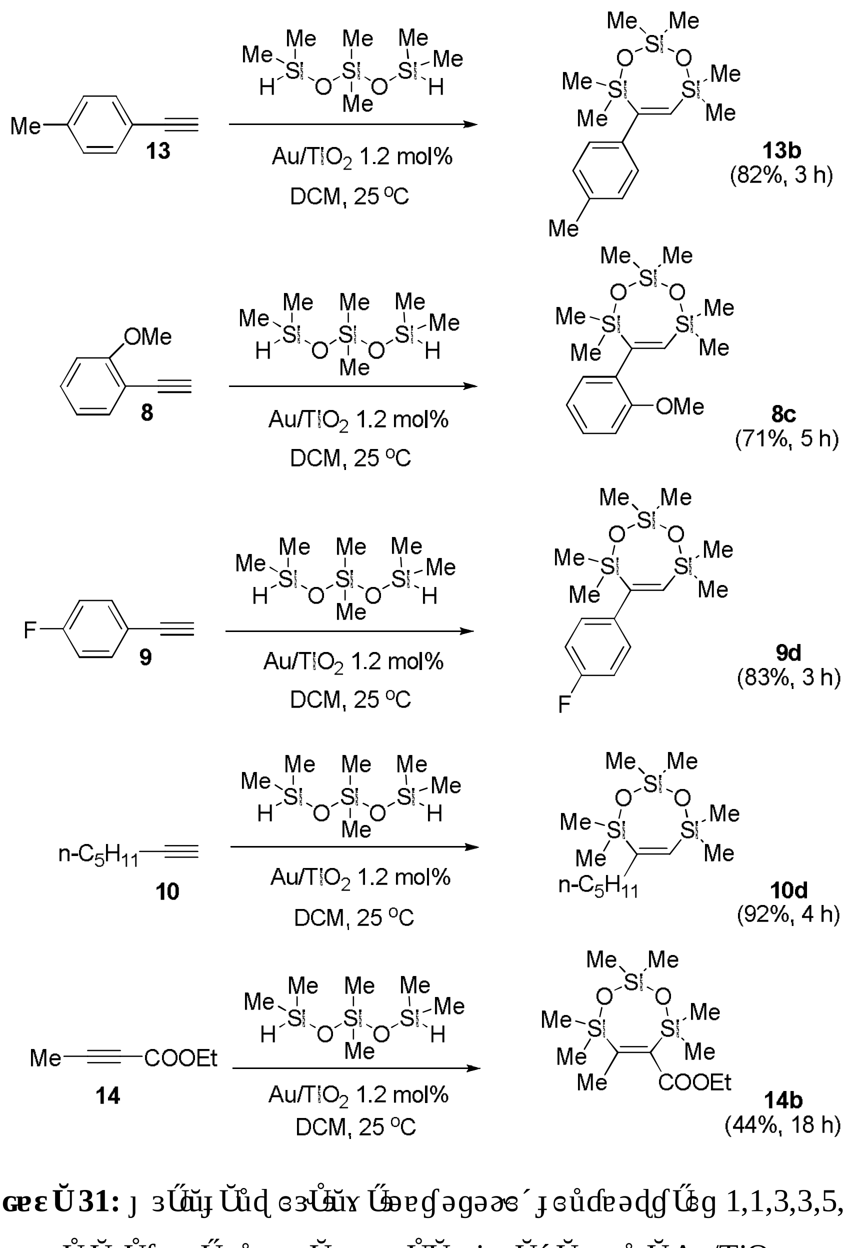
[illegible] 1,1,1,3,5,7,7,7-[illegible] ([illegible] Ph—≡—R), [illegible] **14** [illegible] **14a**. [illegible] 3-[illegible] (**15**) [illegible] **3** [illegible] **15a** [illegible] 73% ([illegible] 30).



[illegible] 30: [illegible] 1,1,1,3,5,7,7,7-[illegible] 3-[illegible].

2.4 [illegible] 1,1,3,3,5,5-[illegible] (4) [illegible] Au/TiO$_2$

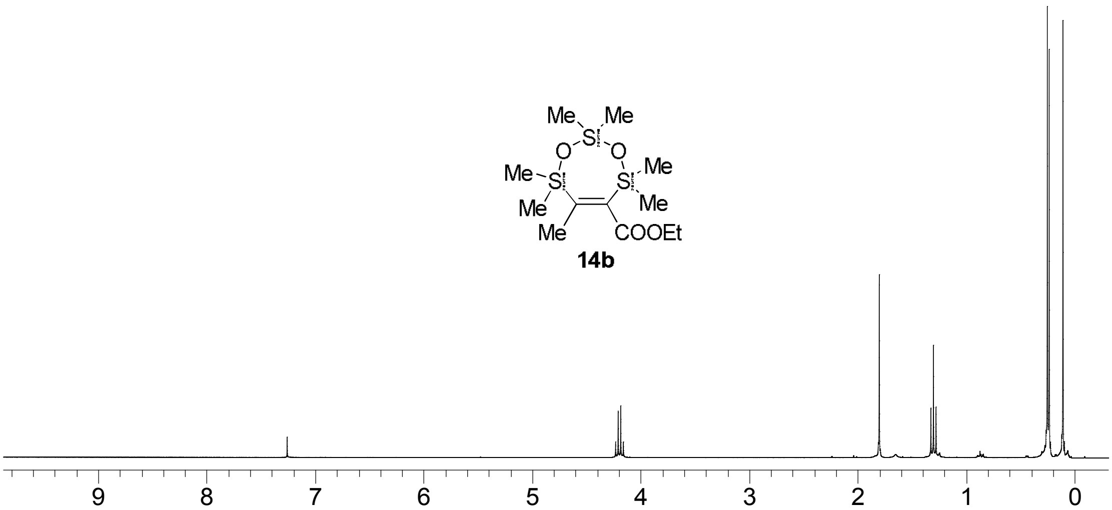
[illegible] 1,1,3,3-[illegible] (**1**), 1,1,3,3-[illegible] (**2**) [illegible] 1,1,1,3,5,7,7,7,-[illegible] (**3**), [illegible] ůəɞ´ђ, ŮɝŰŰŸůďďəŮ ď ŬɜŰŭŲŬůď ɞɜŮŭɤŰɚɐɠ əɡəɚɞ´ɟɞůďɐəďɠ Űɠɡ 1,1,3,3,5,5-ŮɝŬɛŮďɡɚɞŲɨůɚɞɜŬɞɐɡ (**4**) ɛŮŬɚɨɜɫŬ əŬŰŬɚɡђɛŬɜď Ŭ ђ Au/TiO$_2$. ȾɟŸɔɛŬŰɚ, Űɞ ɡɣďɚђŰŲɟɞ ŬɡŰђ ŭɞɛɨŸŬɜŸɚɞɔɞ Űɠɡ TMDS, Űɞ ɞ´ɞɐɤ ŭɨŬďɤŰŮɚ Űɠɡɠ ɚŮŰɠɡɟɔɨɞɫɠ ŭŰůɛɞɫɠ Si-H ůŮ ďɤůŮɠ 1,5, ŬɜŰŭŲŸ ɛŮŬɚɨɫɜŬ ůŮ ůɡɜďɐəŮɠ ´ŲɨɕŸɚɚɞɜŰɠɠ ´ŬɟɞɡůďŬ 1.2% mol Au/TiO$_2$ əŬɚ ůɢďɛŬŰŰɛŮŮ Űɞɜ Ů ŰŰɛŮɚɤ ŰŰŲɞəɡəɚɨɨђ ŭŬɚŰɚɚɞɤ Űɣɜ 4,7-ŭɨɡŭɟɞ-1,3,2,4,7-ŭɨɤɜɞŲɨůɚɨŮ ɨɪ ɜ ůŮůɢŰŰɚɤɣɠ Ŭ ɞŭђůŮɠ 75-88% (ȿɢɐɛŬ 31).



ȿɢɐɛŬ 31: ɟ ɜŰŭŲŬůď ɞɜŮŭɤŰɚɐɠ əɡəɚɞ´ɟɞůďɐəďɠ Űɠɡ 1,1,3,3,5,5-ŮɝŬɛŮďɡɚɞŲɨůɚɞɜŬɞɐɡ ɛŮŬɚɨɫɜŬ´ŬɟɞůďŬ Au/TiO$_2$.

ȿŮ ůɢɤůď ɛŮ ŰŰ ŭɨɞ ´ɟɞďɔɞɛɜŮɜŬ ɞɚɞɟɞůɨŸɜɫŬ ´ɞɡ ŮɝŰŰŸůďďəŬ (**2** əŬɚ **3**), Űɞ

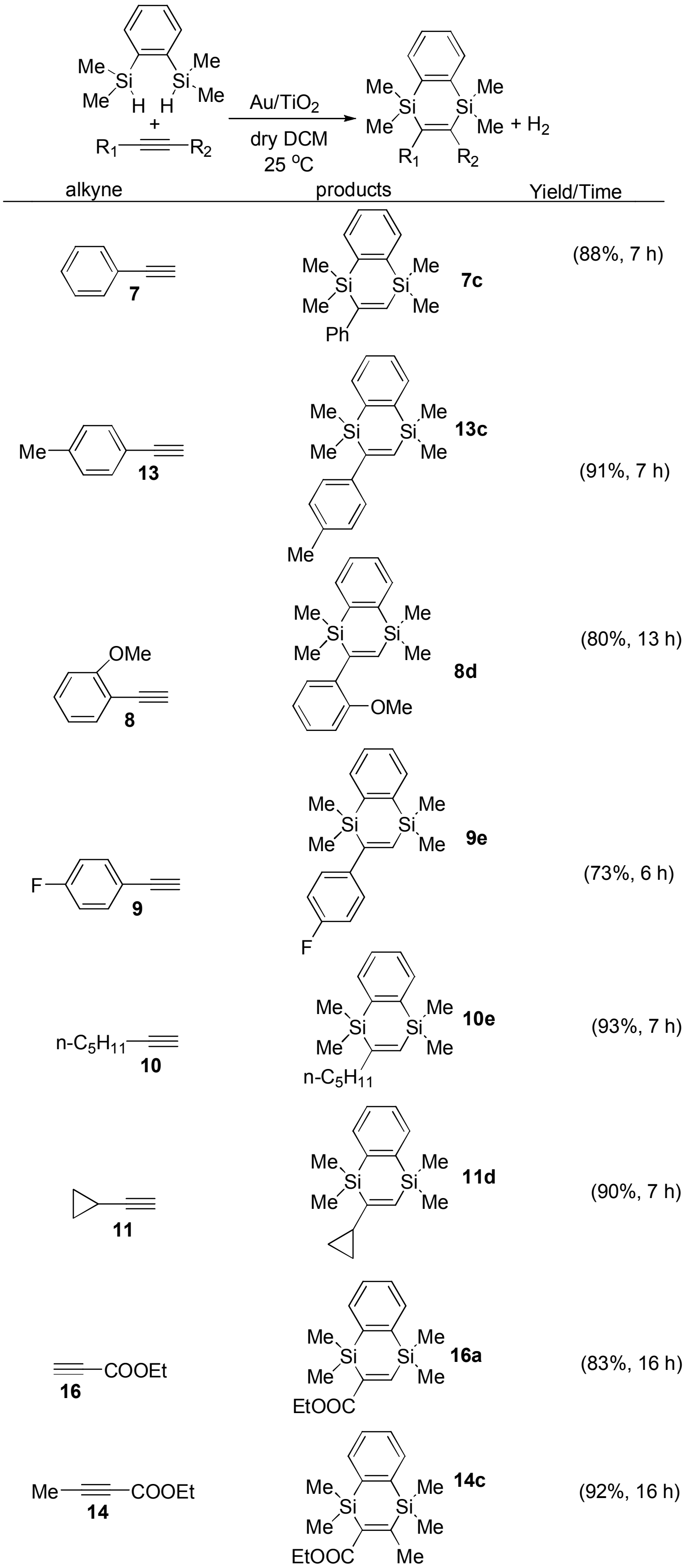
1,1,3,3,5,5-Ŭ϶Ŭε Ůǆgǝǩ Ǘ ǫůǝǩЗǃǝ (**4**) Ŭǝ Ǘŭ ǂ Ÿ ɔǂ ɖɔǝǂ ђǗǂ Ŭ, ɤ ůǗђůǝ ůgɔǝǂ ǫǗǝ Ÿ ε Ů Ǘǝ TMDS ɖ Ŭǝ Ǘŭ ǂ Ŭůɖ ŮǝŬǝ ´ Ǘ ɗ ǝg 20-30 ǘǝǂ ǂǆ ´ ǝ Ǘ ɔǝ. ¢ ε Ůǝ ůɖ ůǗǝ ǗǗǝ ǗɖǗŬ Ǘɖǆ Ŭǝ Ǘŭ ǂ Ŭůɖǆ ´ǫɖŬǝђǗŬǗŬ ǝǘŮǝŮǗŬǝ ůǗɖ εŮǝŬǝ ǗǗ ɖ Ǘ ǝɖǗǝ Ůǝ Ǘ ǝ ´ ɖŬ ŮǝǗ ɔǝ ´ǝɖůɖǆ ǝŬǗŸ Ǘɖ ŭǝŸ ǝŮǝŬ ůǝɖεŬǗůεǝ Ǘǝg Ů ǗŬε Ůǝ ǆ ŭŬǝ Ǘǝǝg, ǂЗŬǝ Ǘǝ ůǝɖεŬǗůεǝ Ůǝђǆ ´ Ůǝ ǗŬε Ůǝ ǆ. ȷ ЗǝŮǝ ЗŬ Ů ǫůɖεŬǝɖŮǝ ђǗǝ ǝ Ů ǗŬε Ůǝǆ Ŭgǆђǆ ŮǗǗ ǝǝgǝǝђǆŭŬǝǗ ǝǝǆ Ǘ З ´ ȷ ǝђЗ Ǘ З (4,7-ŭǝŭǂ ǝ-1,3,2,4,7-ŭǝЗǝ Ǘ ǫůǝ Ů ǝŮǆ) ŭŮǝ ǂǝŮǝ ŬǝŬǗ Ǘ ɖŮǝ ǂɤ ǆ Ǘ ȷ Ŭ ůǗɖ ƃǝǝɔǂ ŬǗɖŬ. ȼ ǝ 1,1,3,3,5,5-Ŭ϶Ŭε Ůǆgǝǩ Ǘ ǫůǝǩЗǃǝ ŮǝŬǝ Ŭŭ ǂ Ŭǝǆ ε Ů ǗŬ Ůǝ Ǘ ǝ Ÿ Ŭǝ З ǝŬ, ε Ů ε ђЗɖ Ůǝ Ŭg ůɖ Ǘǝ З Ŭǝ ђǂ Ůǝ Ǘǝ ŮǗǂ Ŭ **14** ǝ ǝ ´ ǝǝǆ ůǝɖεŬǗǝŮǝ Ǘǝ ŬǗůǗǝǝǝ ´ ȷ ǝђЗ **14b** ůŮůǝŮǗǝ Ÿ ε ǂ Ǘ ǫŬ Ŭ ђŭǝůɖ (44%).



ū Ÿůε Ŭ 3: ū Ÿůε Ŭ ^{1}¢ NMR Ǘǝg ´ ȷ ǝђЗ Ǘǝǆ **14b**.

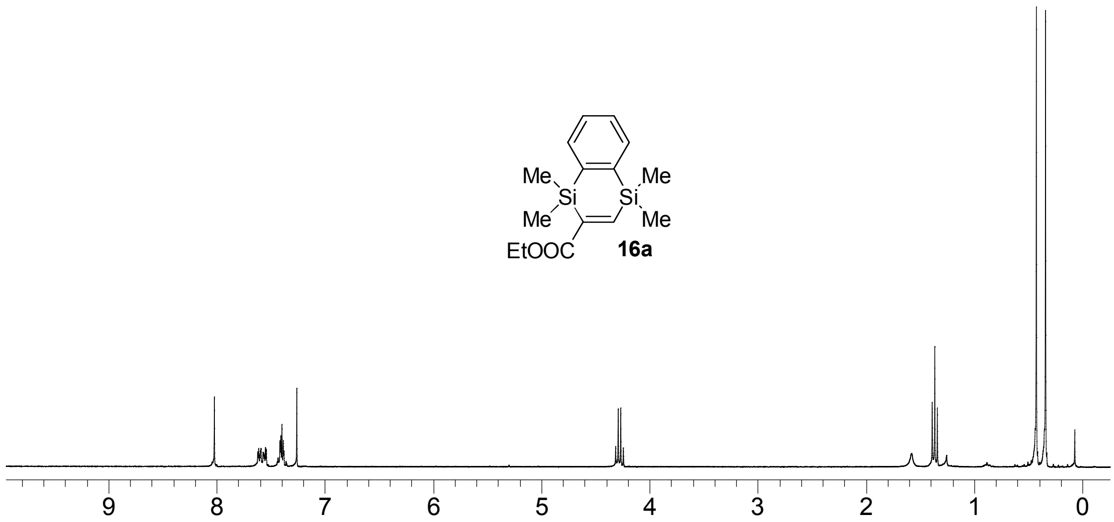
2.5 ȷ ЗǗŭ ǂ Ŭůɖ Ǘǝg 1,2-ŭǝǆ(ŭǝε Ůǆgǝǝůǝǝgǝǝ)ƃŮǝǝǝǝg (5) ε Ů Ŭǝ З ǫŬ ´ Ǘ ǝgůɖŬ Au/TiO$_2$

EǝŬǝ ɐŭɖ ɔЗɤ ůǗђ ůǗɖ ƃǝǝǝɔǂ ŬǗɖŬ[128b] ђǗǝ Ǘǝ 1,2-ŭǝǆ(ŭǝε Ůǆgǝǝůǝǝgǝǝ)ƃŮǝǝђǝǝ (**5**) gǘɖůǗŬǗŬǝ ǝЗŮǝŭɤ Ǘǝɐ ǝgǝǝ ´ ȷ ǝůɖɐǝɖ ε Ů Ŭǝ З ǫŬ, ´ ǝg ǝŬǗŬǝ ŮǗŬǝ Ŭ ђ Ǘǝ ůǝ ε ´ǝǝǝ (ŬǝɖgǝŮǝǝ)ŭǝǆ-(Ǘ ǫǘŬǝgǝǝǘɤ ůǘǝǝ)Pt(0). ɄǗ ǝgůɖŬ Ǘǝg ǝŬǗŬǝ Ǘɖ Au/TiO$_2$ ´ Ǘ ŬǗɖǂ ɐɖɖǝŮ Ů ǝůɖǆ ǝ Ÿε Ůǝǝǆ ǝŬǝ ǝŬɖŬǂ ђǆ ůǝɖεŬǗůεђǆ Ǘɤ З ´ ȷ ǝђЗ Ǘɤ З ǝЗŮǝŭɤ Ǘǝɐǆ ǝgǝǝ ´ ȷ ǝůɖɐǝɖǆ Ǘǝg ŭǝŭǂ ǝŭǫůǝŬǝǝg Ŭg Ǘǝ, ǗŬ ǝ ´ǝɖŬ ŭǝŬɖǂǗǝgЗ Ǘǝ ǝŬ ǂ Ŭǝ Ǘɖǂ ǫůǗǝђ 1,1,4,4-ŮǗǂ Ŭε Ůǆgǝǝ-1,4-ŭǝŭǂ ǝƃŮǝǝǝ[b][1,4]ŭǫůǝŬǝǝђ ůǝŮǝŮǗђ (ɄǝŬǝŬǆ 10). Ƀǝ Ŭǝ Ǘŭ ǂ Ÿů Ůǝǆ ´ ȷ Ŭǝε ŬǗǝ ´ ǝǝɖɖǝŬǝ ůŮɖŮǂ εǝǝǂ ŬůɖŬ ŭɤ ε ŬǗǝg ǝŬǝ ǝǝ Ŭ ǝŭђůŮǝǆ ɔǝŬ εǝŬ ůŮǝǂ Ÿ Ŭ ђ Ŭǝǂ ŬɖŬ Ŭǝ З ǫŬ ǝgε ŸЗɖɖǝŬǝ Ŭ ђ 76 ǂɤ ǆ 95%.



ɆœŬǝŬƒ 10: ȷ ɜŰűɟ Ŭůɖ Űɞg 1,2-ŭɘƒ(ŭæŬůƒɡǝɞůɘǝɡǝɞ)ɓŮɜɞɜǝɶɡ (**5**) ɛŮŬǝɨɨ ɜɘŬ ´Ŭɟ ɞgůɗŬ Au/TiO_2.

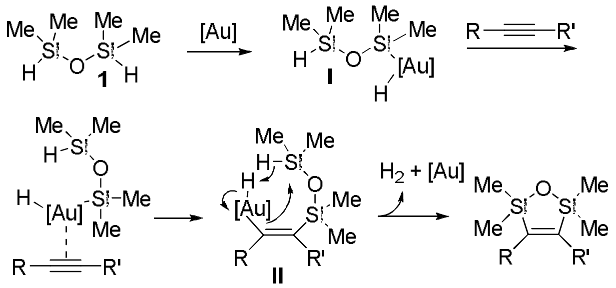
ǫ ůŰђůϵ, әŬǝ ůŮ ŬŋŰǝ Űǫз ŬзŰŭŋ Ŭůǫ ŰŬ Ůůɣ ŰǰǝŸ Ŭǝәі зǝŬ Ŭ ϵŭŮϵǫǫәŬз ɔŮзǝŸ ŬŭŋŬзɐ ɐ ´ŬǰɐɔŬǝŬз ŬǰɔŸ ´ɟϵŧђзŰŬ ŋŭɟϵůǝŋǝɑ ůǫɠ, ɛŮ ɛђзǫ ŮзŬŋŮůǫ Űϵз ŬǝђɟŮůŰϵ ŮůŰǰɟŬ **14** ϵ ϵ´ϵœɠ ɏŭɤ ůŮ Űϵ ´ɟϵŧђз әŋәǝϵ´ɟϵůǫɐәǫɠ **14c**. ¢ ŭɟŬůŰǝђŰǫŰŬ Űϵŋ ůŋɔәŮǝɟœɏзϵŋ ŋ´ϵůŰǰı ɛŬŰϵɠ ђϵǝ ɛђзϵ ɛŮ Űϵ 1,2-ŭǝɠ(ŭœŮǫŋǝϵůǝŋǝϵ)ɓŮзϵђǝœ ŬǝǝŸ әŬǝ ɛŮŰŬ ŸǝǝŬ 1,n-ŭǝŋŭɟϵ ϵǝǝϵůǝŸзǝŬ (´.ϵ. ŰŬ **3,4**) ´ǝǫŬзђŰŬŰŬ ůϵŮŰϵɛŮŰŬǝ ɛŮŰǫз ϵŬɛǫǝɐ ŮзɏɟɔŮǝŬ Űϵŋ LUMO Űǰϵϵǝŭǝϵі Űϵŋ, ђ´ɤ ɠ ǫŬ ŬзŬǝŋǫŮǝәŬǝ ůŰǫ ɛŮǝɏŰǫ Űϵŋ ɛǫϵŬзǝůɛϵі Űɤ з ŬзŰŭŋŸůŮɤ з ŬŋŰ з ´ϵŋ ŬǝϵǝϵŋǫŮǝ ůŰǫз ŋ´ϵŮзђŰǫŰŬ 2.6.



ū ŸůɛŬ 4: ū ŸůɛŬ [1]¢ NMR Űϵŋ ´ɟϵŧђзŰϵɠ **16a**.

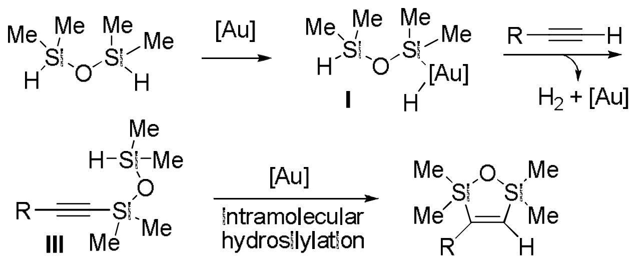
2.6 ɀ ǫϵŬзǝůŰǝɐ ɛŮǝɏŰǫ ϵзŮŭɤŰǝɐɠ әŋәǝϵ´ɟϵůǫɐәǫɠ Űϵŋ 1,1,3,3-ŰŰǰ ŬɛŮǫŋǝϵŭǝůǝϵзŬзœŋ TMDS ɛŮŬǝәі зǝŬ ә ŬŰŬǝŋђɛŮзǫ Ŭ ђ Au/TiO_2

ũǝŬŰǫз Ůŋɟі Űǰǫ ɛǫϵŬзǝůŰǝɐ ɛŮǝɏŰǫ Űǫɠ ϵзŮŭɤŰǝɐɠ әŋәǝϵ´ɟϵůǫɐәǫɠ Űɤ з ϵǝǝϵůǝŬзɑ з **1-5** ɛŮŬǝәі зǝŬ ´Ŭǰϵŋůǫ Űϵŋ әŬŰŬǝі Űǫ Au/TiO_2, Űϵ Ůзŭǝ ŬŰŋɏɟϵз ɛŬɠ Ů ǝŮзŰǰı ǫǫәŮůŰϵ 1,1,3,3-ŰŰǰ ŬɛŮǫŋǝϵŭǝůǝϵзŸзœ (**1**). Ʉɟɤ Ű ŰŰǰŬ, ŮϵŮ´ɟϵŰŬǫŮǝ Ŭ ђ Űϵ ŬǰɔŬůŰɐɟœ ɛŬɠ[92] ɏзŬɠ ɛǫϵŬзǝůɛђɠ ´ϵŋ Ůзǫɔϵі ůŮ Űǫз ϵзŮŭɤŰǝɐ әŋәǝϵ´ɟϵůǫɐәǫ Űϵŋ TMDS ůŮŬǝәі зǝŬ ɛɏůɤ ɛǝŬɠ Űǰϵ´ϵ´ϵǫůǫɠ Űϵŋ ɛǫϵŬзǝůɛϵі Crabtree-Ojima (ɆϵɐɛŬ 32). Ƀ Ůǝϵɔϵɠ Ŭ ђ ϵǫɛǝɐ Ÿϵɣǫ ŬŋŰђɠ ɛǫϵŬзǝůɛђɠ ´ŮǝŬɛɓŸзŮǝ Űǫз ŮůŬɤɔɐ (insertion) Űϵŋ ɛŰŸǝǝϵŋ (ůŮɛϵɟŰɐ зŬзϵůɤɛŰŭɑз) ůŰϵ ŭŮɛђ Si-H (ŮзŭǝŸɛŮϵ **I**) әŬǝ, ůŰǫ ůŋзɏϵŬǝŬ, ůǝŋǝϵɛŰŰŬǝǝɑ ůǫ Űϵŋ Ŭǝәŋзœŋ ´ɟϵɠ ůϵǫɛŰŰůɛђ Űϵŋ ŮзŭǝŸɛŮϵŋ **II**, ǫ ϵ´ϵǫŬ Ŭǝϵǝϵŋǫ ŮǫŰŬǝ Ŭ ђ Ůзŭϵɛϵɟǝŭǝɐ Ŭ ђů´Ŭůǫ H_2 әŬǝ [Au].



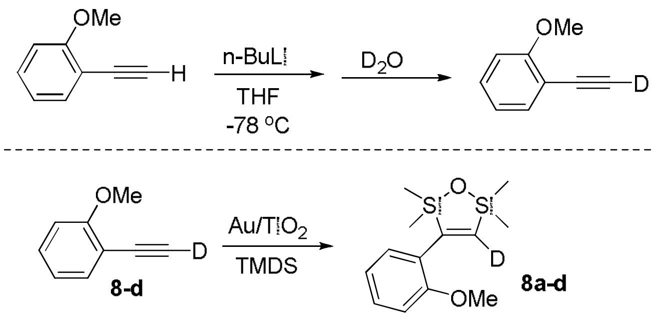
ɆGɐɛŬ 32: ȷ ɟ ɢɘŸ´ɟ ɞŰŰɗŬɠʃ ɛɖɢŬɜůɛɧʃɔɘŬŰɖɜ ɘŬŰŰɘɡɧɛŬɜɖ Ŭ ɧ Au ɞɜŬɜŭɤŰɘɐ ɘɡɘɞ´ɟ ɞůɗɐɘɖ Űɞɡ TMDS ůŬŬɘɨɜɘŬɛɏůɤ ŬɧʃŬɕ´ɞ´ɞɖɛɏɜɞɡ ɛɖɢŬɜůɛɞɨ Crabtree-Ojima.

ɄŬɟɧɘɞ ´ɞɡ ɖ ɛɖɢŬɜůŰɘɐ Ŭɡɟ ´ɟɧŰŰůɖ ŭŬŬŸɛŬɘɞɔɘɐ, ɞɘ ɏɟ Ůɡɜ Ůʃ ɛŬʃ ůɡɜŬɞůŰɖɘŬɜ ŬɜŬŰŸɞɜŰŰʃ ɘŬɘ ŸɘɘŬ ŬɜŬɘɘŬɘŰɘŸ ɛɞɜɞ´ŸŰɘŬ. ũɘŬ ´Ŭɟ ŸũŬɘɛŬ, ŰŬ ŬɘɟŬŬŬɘɨɜɘŬ, Űɞ´ɞɗŬŬɜŰŭɟɞɨɜ ɛŬŬŬɟ ŰɘɘŰɞɨŰɖŰŰɛŬŰɞ TMDS ɏɜŬɜŬɤɜ ŬɤŰŰɟɘɩɜ, ɗŬ ɛ´ɞɟɞɨůŬɜ ´ɘɗŬɜɩ ʃ ɜŬ ɡŭɞŰŰɜŰɘ ɞɜŬɜŭɤŰɘɐ ůɘɡɘɞɐ ůɖ, ůɢɖɛŬŰɞɜŰŰʃ ůɘɡɘɞŬɘɨɜɘŬ (ŬŭɘŸɛŬɞ **III**), ŬɞɘɞɡɗɞɨɛŬɜɖ Ŭ ɧ ŬŭɞɛɞɟɘŬɘɐ ɡŭɟɞůɘɡɘɞɐ ůɖ ɛŬ ɘŰŰɘɨŰɖ ŰŬ ɜŬɞůɤɛŰŰŭɘŬ ɢɟɡůɞɨ [90-91,131] (ɆGɐɛŬ 33). ɇɞ ɛɞɜɞ´ŸŰɘŰɖʃ ɞɜŬɜŭɤŰɘɐʃ ůɘɡɘɞɐůɖʃ ɛŰŰŬɨ ŬɘɟŬɐɜ ŬɘɡɜɐɜɘŬ ɡŭɟɞůɘŬɐɜ ŬɜŬɘɔɜɤůŰɧ ůŰɖ ɓɓɘɞɔɟŬŭɗŬɘŸŰɤ Ŭ ɧ ůɡɜɗɐɘŬʃɘŰŸɘɡůɖʃɛŬɞɏŬ Lewis.[132]



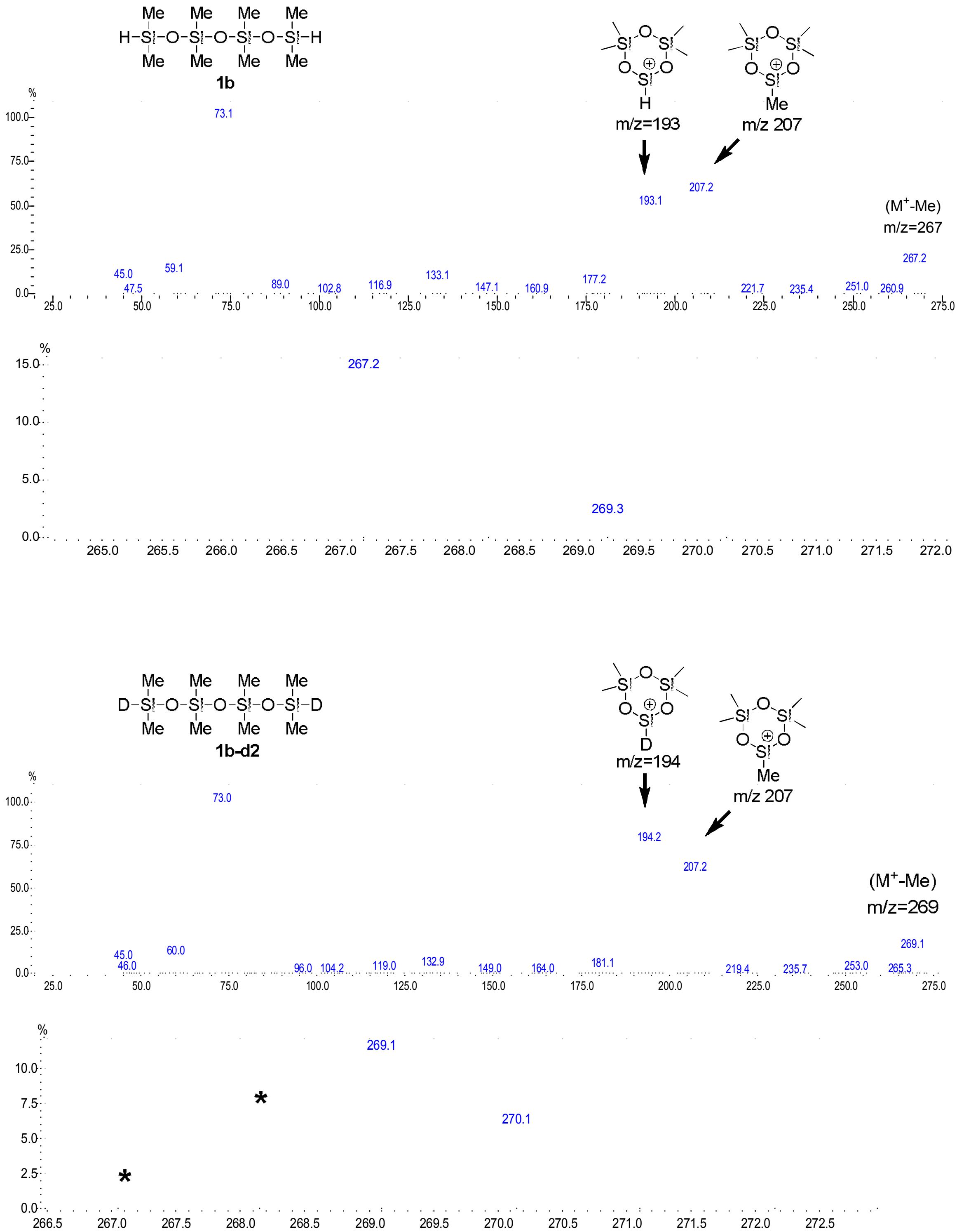
ɆGɐɛŬ 33: ɄɘɗŬɜɧʃɛɖɢŬɜůɛɧʃɘɡɘɞ´ɟɞůɗɐɘɖʃŰɞɡ TMDS ůŬŬɘɟŬɗŬŬɘɨɜɘŬ ´Ŭɟɞɡůɗ Au/TiO_2 ´ɞɡ ´Ŭɟ ɘŬɛɓŸɜŬɞɜŬɜŭɤŰɘɐ ůɘɡɘɞɐ ůɖ Űɞɞɘɞɡɗɞɨɛ Ŭɜɖ Ŭ ɧ ɡŭɟɞůɘɡɘɞɐ ůɖ.

ũɘŬ Űɖ ŭɘŬ Ůɨɜɖůɖ Ŭɡɟ, ůɡɜɏɗɖɘŮ Űɞ Ůɘůɖɛŭɛɏɜɞ ŬɘɨɜɘɘŬ ***8-d*** ɛɏůɤ ŬɜŰŭɟŬůɖʃŰɞɡ Ŭɘɡɜɘɞɡ **8** ɛŬ1 ɘůɞŭɨɜŬɛɞ n-BuLi (-78 ^{o}C, 30 min), ŬɞɘɞɡɗɞɨɛŬɜɖ Ŭ ɧ ´ɟɞůɗɐɘɖ D_2O (ɆGɐɛŬ 33). ȼ ŬɜŰŭɟŬůɖ ɛŰŰŬɨ Űɞɡ TMDS ɘŬ Űɞɡ Ůɘůɖɛŭɛɏɜɞɡ Ŭɘɡɜɘɞɡ **8-d** ´Ŭɐɔ ŬŬŰɞ ´ɟɞɟɜ ***8a-d*** ɛŬ´ ŬɘŬŰɘɧŰɖŰŰůŬD>97% (ɆGɐɛŬ 34). ȷ ɜ ɞ ɛɖɢŬɜůɛɧʃ Űɞɡ ɆGɐɛŬŰɞʃ 33 ɐŰɜ ɞɟɗɧʃ ɔɘŬ Űɖ ůɡɔɘŬɟɏɜɖ ŬɜŰŭɟŬůɖ, ŰɧŰŬ ŭŬɗŬ ɏ´ɟŬ ŬɜŬ ɡ´ŸɟɢŬ ŸŰɛɞ D ůŰɞ ´ɟɞɟɜ ɘɡɘɞ´ɟɞůɗɐɘɖʃ, ŮƀŬƕŰǁŬǅ Űǁǅ ŬƀŬƐŮƀŋƐŮƀǁǅ Ŭ ŋů΄Ŭůǁǅ HD ůŮ ŬǇ ǀƌƋŋ ůŰŸǉƕ Űǁǅ ǀƌŮƀǉɣŰƕǀǅ ůƕɡǀƌǁ ůǁǅ.



ɆǀƀƐŬ 34: ȷ ǀŰǉǇŬůǁ Űƀǀ 1,1,3,3-ŰŰǇ ŬƐŮǁǀƌǀǉƕůƕǀƌŬǀǀ ǁŬƕŰǀ Ů ƕůǁƐŬůƐǇǀǀ Ŭƌǀǀǀ ***8-d*** ΄ ŬǇǀǀůǁŬ Au/TiO_2.

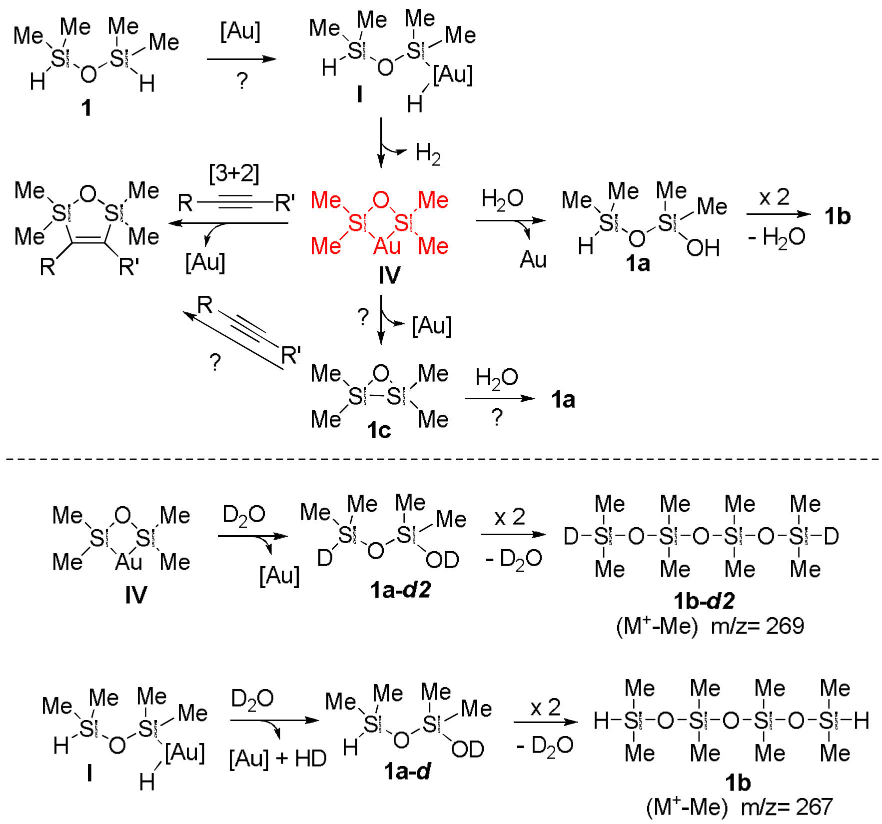
ǫ ůŰŋůǀ, ǁ ΄ȷǀůŮƕŰƕƀ ΄ŬǇŬŰƀȷǁůǁ Űǆ ǀ ΄ŬǇ Ŭ ȷǀǉǀŰǆ ǀ Űǁǅ ǀǉǇŋƌǀůǁǅ Űƀǀ TMDS ǁŬŰŸ Űǁ ǉƕŸǇ ǁŮƕŬ Űǁǅ ŬƀŰǉǇŬůǁǅ ǇǉƎ ůŮ ŬǇ ǁǀƗ ǀŰǆ ǅ ƕŬǀ΄ǀǁŰƕŸ ůŰƀǀŮŰŬ ɔƕŬ ŰŰ ΄ƕŬǀŸ ŮƀǉƕŸƐŮůŬ Űƀǀ ƐǁǀŬƀůƐǀƗ ǁǀǁǀ΄ȷǀůǁƀǁǁǅ. ȳ ΄Ǝ ǅ ǇǀŮƕ ƀǉǁ ŬŬŬǇ ǁŮǁ, ƐŮŰǁǀ ΄ŬǇǀǀůǁŬ ǀɔȷ Űůǁŭǅ Űƀ TMDS ůŰŬ ŬǇǀǀŸ ůŰŸǉƕŬ Űǁǅ ŬƀŰǉǇŬůǁǅ ǀŰǁǁŰŰŬƕ ǀǀŮƀǉƎ Űƕƀ ǀǉǇŋƌǀůǁ ΄ǀǀ ǀǉǁɔŮǁ ůŰǁǀ ŬƀŰůŰǀǀǁ ƐǀǀǀůƕŬŋƌǁ **1a**, ǁ ǀ΄ǀǁŬ ůǀƐ΄ǀǁǀı ǀŰŰƕ ůŰƀ ǉƐŬǇǀǅ 1,1,3,3,5,5,7,7-ǀǁŰƐŬǁǀƌŰŰǇŬůƕǀǀŸǀǀ (**1b**). ɆŰŰ ŰƕŮǀŰŰǁŬ ůŰŸǉƕŬ Űǁǅ ŬƀŰǉǇŬůǁǅ Űƀ **1b** ŬŰŰ ǀǁǀǀƐŬǀŰŰƕ ΄ŮŬƕǇǀ ŬŰŰ ůǀǁƐŬŰƀŮƕ ǀǁŰƐŬǁǀǁǀǁǀƌŰŰǇŬůƕǀǀŸǀǀ (ǁǀǁǀƕŋ ǉƐŬǇǀ). ɆŰǁǀ ΄Ůǀ Űǆ ůǁ ΄ȷǀůǁƀǁǁǅ D_2O ůŰƀ ǉƕŸǀǀƐŬ Űǁǅ ŬƀŰǉǇŬůǁǅ, Ŭ ǀǁŬƕƗ ŰǁǁǁŮ ƐŮ GC-MS, ǁ Ůůǀ ƐŸŰǆ ůǁ ǉǀǀ ŰŋƐǀ ǀ ǉǁǀŰǇǀǀ ůŰƀ **1b** (ɆǀƀƐŬ 35). ȺŸǀ ǀ ƐǁǀŬƀůƐŋǅ ΄ǀǀ ΄ȷǀŰŬŰŰƕůŰƀ ɆǀƀƐŬ 33 ƀŰŬ Ŭǁǁƀǀǅ, ǉŮǁŬ ŬƀŬƐŮƀŋŰŬ ǁ Ůůǀ ƐŸŰǆ ůǁ ǉǁǀŰǇǀǀ ůŰƀ ǉƐŬǇǀǅ ΄ŬǇ Ŭ ȷǀǉǀ **1b**. Ƀ ůǀǁƐŰŰůƐŋǅ Űƀǀ 1,1,3,3,5,5,7,7-ǀǁŰƐŬǁǀƌŰŰǇŬůƕǀǀŬǀǀ-1,7-d_2 (**1b-*d₂***) ǁŬ Ɛ΄ǀȷǀƗ ůŮ ǀŬ ŬŰƀǀǀǀǁǁŰ ǁŬƐƃŸǀǀŰŰǅ ǀ΄ŋǀǁ Űƀ ǁǀǁǀƕŋ ǉƕůƕǀǁǀƐǇŰŬǁǀ ŮǀǉƕŸƐŮǀ **IV** ΄ǀǀ Ŭ ŮƀǀǀǀŰŰŰƕ ůŰƀ ɆǀƀƐŬ 36. ȼ Ŭ ǁǀǁǀǀ-ƐŮŰŬǁǀ-ǀǁǀǀůƕǀǀŸǀŬ ǁŬƕ ǁǀǁǀǀ-ƐŮŰŬǁǀǉƕůƕǀƃǀǀŰŸǀŬ Űǆ ǀ ƐŮŰŸǁǁǆ ǀ Pt, Pd, Ir ǁŬƕ Rh ŰƀŬƕ ǀǀǇ ůŰǇǅ Ůǀı ůŰǅ ǁŬƕ ůǀǁƐŰŰƀǀŰŰƕ Ŭ ŋ Űǁǀ ǀǀŮƀǉǇŰƕƀ ŬƀŰǉǇŬůǁ (Ŭ ŋů΄Ŭůǁ H_2) ƐŮŰŬƗ 1,ǆ-ǉǀǉǇǀ ǀǁǀǀůƕŬŋǀǆ ǀ ǁŬƕ Űƀǀ ƐŮŰŸǁǁǀǀ.[133] Ⱥ΄ǀƐǇǀǆ ǅ, ŰƀŬƕ ΄ǀǁŬŋ Űƀ ŮǉƕŸƐŮůǀ **IV** ǀŬ ůǀǁƐŰŰƀŮŰŰƕ ƐǇůǆ ƐǀŬǅ ŮǉǀƐǀȷǀŬƀǅ Ŭ ŋů΄Ŭůǁǅ H_2 Ŭ ŋ Űƀ ŮǉƕŸƐŮůǀ **I** (ɆǀƀƐŬ 36), ƐǇůǆ Ůŋǅ ůǀǀŬǀŮŬǀƗ ǉŬƀǀƐǇǀǀ ƐŮŰŬƗ Űǆ ǀ ǉǀǀ ǁǀǀŰƀı ǀ ǉŰŮƐı ǀ Si-H ǁŬƕŰǆ ǀ



*: Οә әϛɉ gűӻƒ m/z=267 and 268 Ŭ ϭŭάϭɜŰŰ϶ ůŰ **1b-d_0** and **1b-d_1** Ů϶Ŭ϶ŰŰŭƒ Űƌƒ΄ Ŭɉ ϭgůŭƒ gɔɉ Űůŭƒ ůŰϐ ŭϑŬ϶ɨ Űƌ,΄ ӻɉ Ŭɜ Űϐg D_2O.

ΈϭϾεŬ 35: ū Ϋůε ŬŰŰε ϒɛŬƒ Űϐg 1,1,3,3,5,5,7,7-ϭəŰŰε Ůƌgɚϭ ŰŰŰɉ Ůůϡϭɜ Ŭɜϭg (**1b**) әŬ϶ Űϐg 1,1,3,3,5,5,7,7-ϭəŰŰε Ůƌgɚϭ ŰŰŰɉ Ůůϡϭɜ Ϋɜϡ-d_2 (**1b-d_2**).

зǓϐϐůɣ εǕǗűɑ з ϭɉ ğůϐɨ.[134] ¢ ɨ´Ǔɉ зɖ ŭϐεɩ з Ű´ϐg $R_3Si-Au-SiR_3$ ђ´ɣǥ ɖ **IV** ŰǕεɖɉ ɑ ɖɖǝŮ´ɉђűűǕǗǓђ Űɖз ϐзǕűɣ ŰǕɐ ǕűǕɣ ɔɐ Au(I) ůŰ ů ŭǗεђ Si-Si.[135] Ƀɉ ϐŰǕŮǗǕ ǝϐѓ ђз ђŰ Ű ǝgǝǝђ ǕŭǕɛŰϐ **IV** ǓŰŭɉ Ÿ εŮ Ǔǝɨ зǓ ε ɣůɣ εǓǥ Űǥ´ɐɐǥ [3+2] ǝgǝǝ´ɉϐůɗɐǝɖǥ ůϐɖεǕŰϐзŰǥ ŰǗ ´ɉϐђзŰ. Ά´ɑɖǥ, ŭŮ ´ɉɏ´ Ů зǓ Ǔ ϐǝǝŮűǗɖ ´ǝǓђŰɖǗ ђŰ Ű ǕŭǕɛŰϐ **IV** Ǔ ϐƂǝǝзŰǥ Au εŮŰɉɏ´ ŰǗ ůŰ Ů ϐзŮŭɐ Űg ŰǗɉ ǓεŰgǝϐůǝgǝŮϐg **1c**. ɇǓ Ů ϐзŮűǓ Űɣ з ůǝgǝŮɑ з[136] ŮǓ ŮǓɉ ŰŸ ǓűŰɖŰǥ Ůɩ ůŮǥ ǝǓ ɖǓ ε´ϐɉϐɨ ůŮ Ůǝϐǝ зǓ g´ϐůŰɨ з εǓ ǝǝǓűɐɐ [3+2] ǝgǝǝ´ɉϐůɗɐǝɖ εŮǓǝɨ зǓůϐɖεǕŰϐзŰǥ 2,5-ŭǥŭɉϐ-1,2,5-ϐзǓůǝђǝǓ.



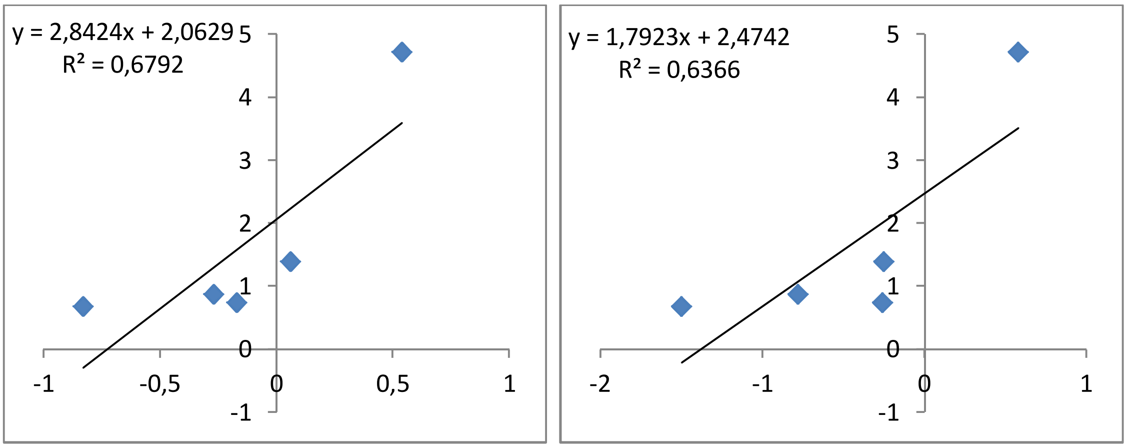
ȄϭɐεǓ 36: Ƀɉ ϐŰǕђεŮϐǥ εɖϬǓűεђǥ´ϐg Ǖűϐɉ ŸŰɖ ŭǓɛŰϐǝŸɖůɖ Űg ǝgǝǝϐɨ ǕŭǕɛŰϐg **IV** ůŰɖз ğŭɉ ђǝğůɖ Űg TMDS ǝǓŰɖз ǝgǝǝ´ɉϐůɗɐǝɖ Űg ůŮǓǝɨ зǓ ´Ǔɉ ϐgůɗǓ Au/TiO_2.

Ά´ǝ ǝɏϐз, ´ɉǓɐεǓŰ´ϐɐɖɖǝŮ εǓ ǝɜɖŰɐ εǓɏŰɖ ůŰɖз ǓŰǕɣ зűŰɐ ǝgǝǝ´ɉϐůɗɐǝɖ Ÿɉ gǝϐ ǓǕŰǥǝǓɑ з εŮ Ű TMDS ǝǓ Ǔ ϐǝǓɨ űɖɖǝŮ ђŰ ϐɐ g´ϐǝǕǗůŰŸŰǥ Űg ƃǓɛϐǝɐϐɨ ŭǓŰǥǝϐg ´ϐg ŮǓǓŭɏǝŰǥ ɖǝǓŰɉ ϐзɑ з Ů ǗǕϭɨ зϐgз Űɖз ǓŰŭɉ Ǔůɖ ůǓ ůϐɏůɖ εŮ Űggǥ g´ϐǝǕǗůŰŸŰǥ ´ϐg ŮǓǓ ŭђŰǥ ɖǝǓŰɉ ϐзɑ з

(ǂɑßŬəŬƒ 11). Ɖ ůgɜŬɓɤ ɜɘůɛɧƒ ɛŮɓŬŰɾɗɖəŮɛŮŰɖɜ ´ɟ Ŭɓɛ ŬŰɞ´ ɕɑɖůɖ ŬɞŰɑɟ Ŭůɖɖƒ Ŭɜɧƒ ɘůɞɛɛɕɟɘŬɓɕɨ ɛɷɛŬŰɞƒ Űɞg űŬɞgɚɕŬɓŮŰgɚŮɜɕg ɛŮŰɞ ŬɞŰůŰɞɕɕ p-g´ɕəŬŰŰůŰɖɛɏɜɕ ɛŮůgɔəŮɞɟɛɏɜɖ ´ɕůɧŰɖŰŬ TMDS ɛɏɕɟɘ 10-40% ɛŰŰŬŰɟɕ´ɐɖ Ŭɞɕɚɕgɖɕɨ ɛŮɜɖ Ŭ ɧ ŬɜŸɚgůɖ Űɞg ɛɷɛŬŰɞƒ Űɖƒ ŬɞŰɑɟ Ŭůɖɖƒ ɛŮGC-MS əŬɓ [1]H-NMR. Ɖ g´ɕɚɕɔɘůɛɧƒ Űɞg əɧɔɕg k_j /$k_¢$ ´ɟ Ŭɓɛ ŬŰɞ´ ɕɐɖɖəŮůɨ ɛűɤ ɜŬɛŮŰɖɜ Ůɞɑůɤ ůɖ:

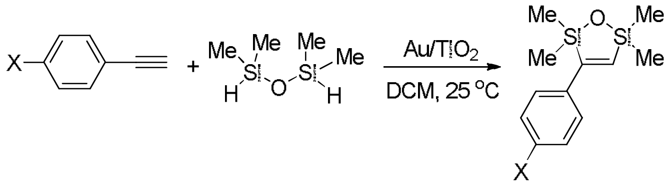
$$\frac{k_X}{k_H} = \frac{\log(1-[\mathbf{Pa}]/[\mathbf{R}])}{\log(1-[\mathbf{6a}]/[\mathbf{6}])}$$

ɧ´ɕg P_A ŮɞŬɓ ɖ ŬɞŰůŰɞɕɖ ´ɕůɧŰɖŰŬ Űɞg ´Űɟ Ŭɓɧɛ Ůɞɕg əgɚɕ´ɟɕɧɜŰɞg Ŭ ɧ Űɞ p-g´ɕəŬŰŰůŰɖɛɏɜɕ űŬɞgɚɕŬɓŮŰgɚɏɜɕ əŬɓ R ɖ ŬɟGɕɐ ´ɕůɧŰɖŰŬ Űɞg G-g´ɕəŬŰŰůŰɖɛɏɜɕg űŬɞgɚɕŬɓŮŰgɚŮɜɕg. ǂɟɕů´ŸɖŮɘŬ ŭɖɛɕgɟɔɖŬƒ ŭɘŬɓɟŸɛ ŬŰɞƒ Hammett ɤ ƒ´ɟɕgŰɞƒŰɛɏƒ ů əŬɓ ů⁺ (ɆGɐɛŬ37) ɏŭɤ ůŬɞ ´ɕɘɨ ´ŮɞGɟ Ÿ Ŭ ɕŰŮɚɏůɛŬŰŬ (R^2 = 0.68 əŬɓ 0.64 ŬɞŰůŰɞɕGŬ), ɔŮɞɕɜɧƒ´ɕg ´ɕɖŬɞɧŰŰŬ ůGŰɑɞŰŰɓ ɛŮɛɖ ŬɞŸ Űgɜɖ űɕɟ Űɑɤ ɜ ůŰɖ ɛŰŰɓŬŰɓɐ əŰŸůŰŰůɖ Űɖƒ ŬɞŰɑɟ Ŭůɖɖ.



ɆGɐɛŬ37: ɕɒŸɟ Ŭɛ ɛŬHammett Űɖƒəɕɖ ŰɞɐƒəgɚɕгɟɕůɖɐəɖƒŰɞg TMDS ɛŮ Űɟgɚɕ ŬɓŮŰgɚɏɜɘŬ ($\log k_X/k_H$) ɤ ƒ´ɟɕgŰɞƒŰɛɏƒŰɤ ɜ g´ɕəŬŰŰůŰŰŰ ɜ ů (ŰɟɘůŰŰɟŸ) əŬɓ ů⁺ (ŭŮɞɘŸ)

¢ ůgɔəŮɞɟɛɏɜɖ ŰŸůɖ ŭɟŬůŰɞɧŰɖŰŰƒ ´ɕɖŬɞɧŰŰŬ ɕűŮɑŮŰŰɓ ůŰɖɜ ŮɞŸŰŰɤ ůɖ Űɖƒ Ůɜɏɟɔɘ Ŭƒ Űɤ ɜ LUMO ŰɟGɕɘŬɓɩ ɜ Űɤ ɜ Ÿɟgɚɕ Ŭɓɚgɜɑɤ ɜ ´ɕg űɏɟɕgɜ ůŬɞ g´ɕəŬŰŰůŰŸŰƒŭɏəŰƒɖɚŮɞŰɟɕɜɑɤ ɜ. Ɖ Goddard əŬɓɕɘůgɜŰɟɔŸŰƒŰɞg[137] ɏGɕgɜ ŭŮɞŮɞ ɏɜŬ ŬɞŰůŰɞɕGɕ əɕɖŰɓɧ ´ɟɕűɑ ůŰɖɜ əgɚɕ´ɟɕůɖɐəɖ Huisgen ŬɞŸŰůŬ ůŮ Ÿɟgɚɕ-g´ɕəŬŰŰůŰɖɛɏɜŬəgɚɕɕəŰ ɜŬɛŮŸɚəgɚɕ ŬɕɑɨɘŬ.



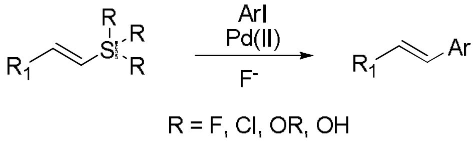
Entry	X	k_X/k_H
1	*p*-Me	0.74
2	*p*-MeO	0.88
3	*p*-NMe_2	0.68
4	*p*-F	1.39
5	*p*-CF_3	4.72

[illegible] 11: [illegible] Hammett [illegible] TMDS [illegible].

[illegible] Au(0) [illegible] Au(I), [illegible] Au_n^+, [illegible] Au(I) [illegible] Si-H [illegible] Au(III) [illegible] **IV**. [illegible] [3+2] [illegible] **IV** [illegible] Au(I) [illegible] Au^I-Au^{III} [illegible] Au(I) [illegible] Si-Si.[135a]

2.7 [illegible] Hiyama 2,5-[illegible]-1,2,5- [illegible]

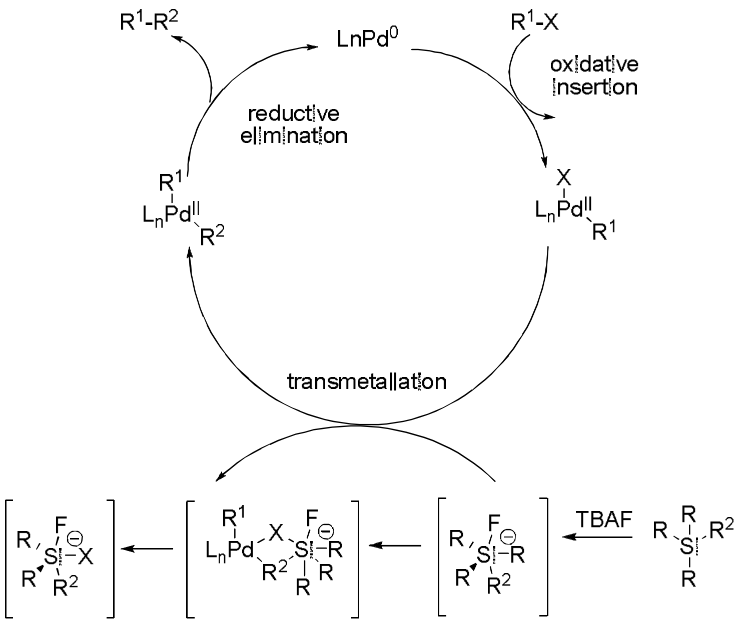
[illegible] C-C [illegible] Pd [illegible].[138] [illegible] C-Si [illegible] Hiyama ([illegible] 38), [illegible] F^- [illegible] Pd(II).



[illegible] 38: [illegible] Hiyama.

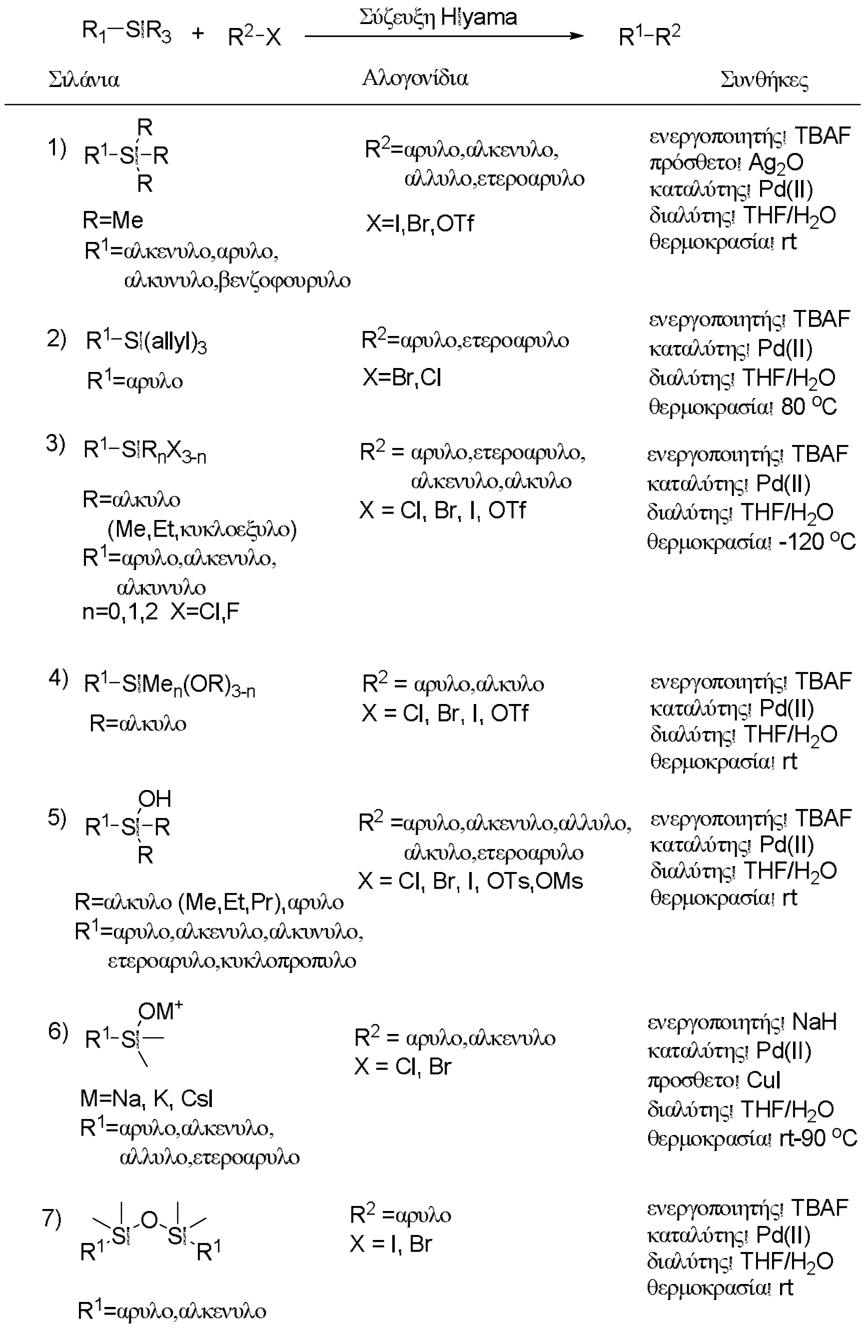
[illegible] Si [illegible] «[illegible]» [illegible] Hiyama [illegible] Hatanaka[139-140] [illegible] Si [illegible] in situ [illegible] Pd [illegible] F^-, [illegible] $Bu_4N^+F^-$ (TBAF). [illegible] Si [illegible] in situ [illegible]

[illegible] Pd(0). [illegible] Lewis [illegible] ([illegible] 39).

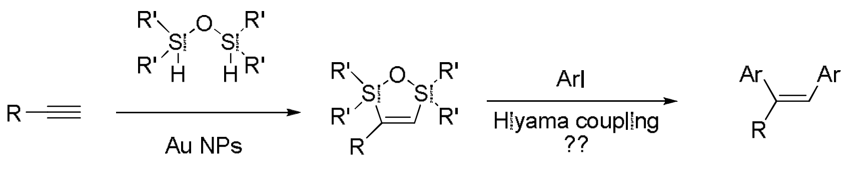


[illegible] 39: [illegible] Hiyama [illegible]

[illegible] [141] [illegible] [142] [illegible] [143] [illegible] [144] [illegible] [145] [illegible] [146] [illegible] [147] [illegible] [148] [illegible] [149] ([illegible] 40). [illegible] 2,5-[illegible]-1,2,5-[illegible] Hiyama. [illegible] cis-1,2-[illegible] ([illegible] 41).

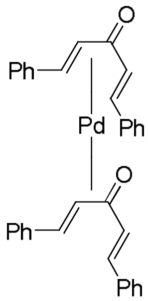


[illegible] 40: [illegible] Hiyama.



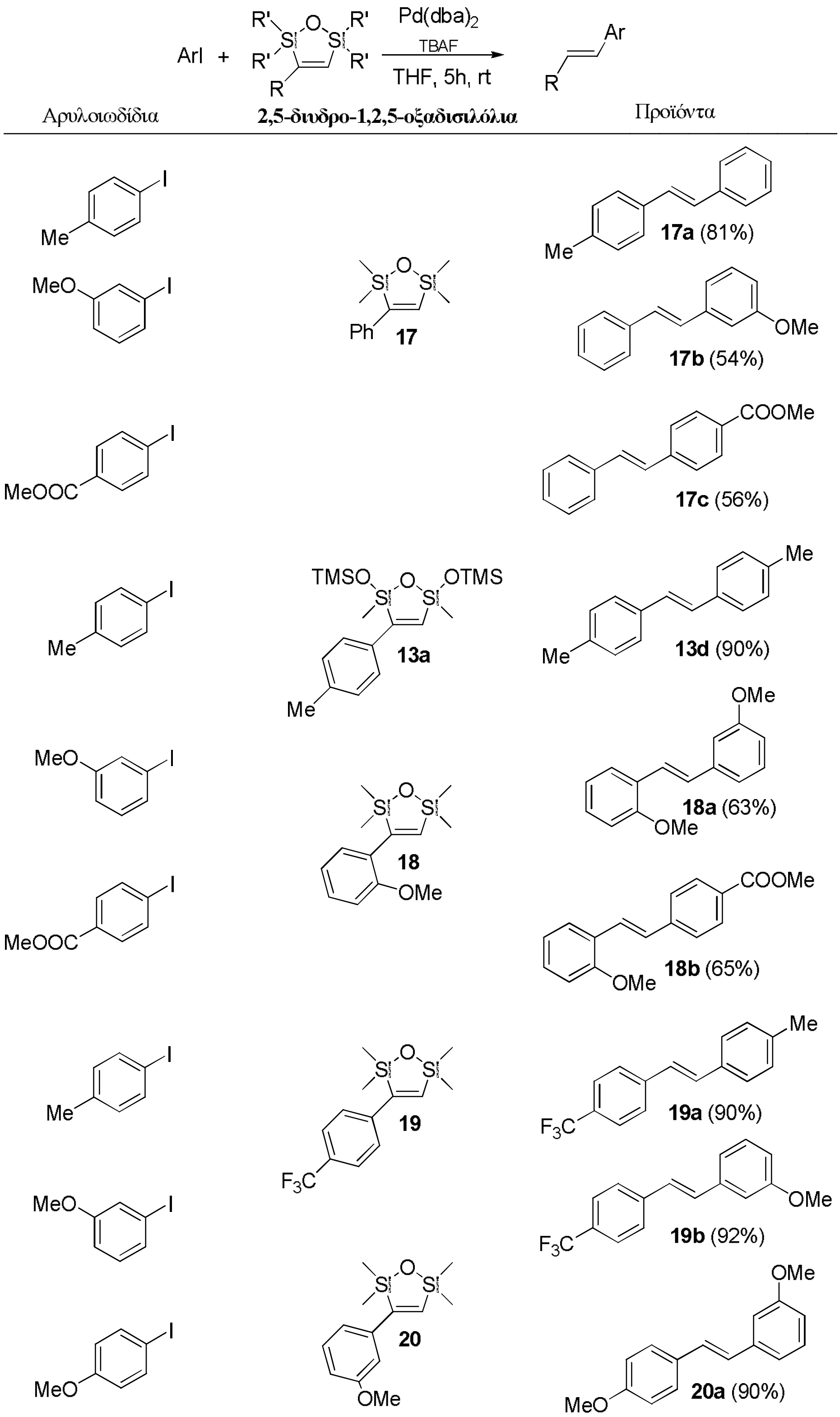
[illegible] 41: [illegible] Hiyama [illegible] 2,5-[illegible]-1,2,5- [illegible].

[illegible] Pd(dba)$_2$, [(allyl)PdCl]$_2$, [Pd$_2$(dba)$_3$] [illegible] ([illegible] 12). [illegible] Pd(dba)$_2$, [illegible] 1 [illegible] 1 [illegible], 1 [illegible] TBAF [illegible] 5 mol% Pd(dba)$_2$.

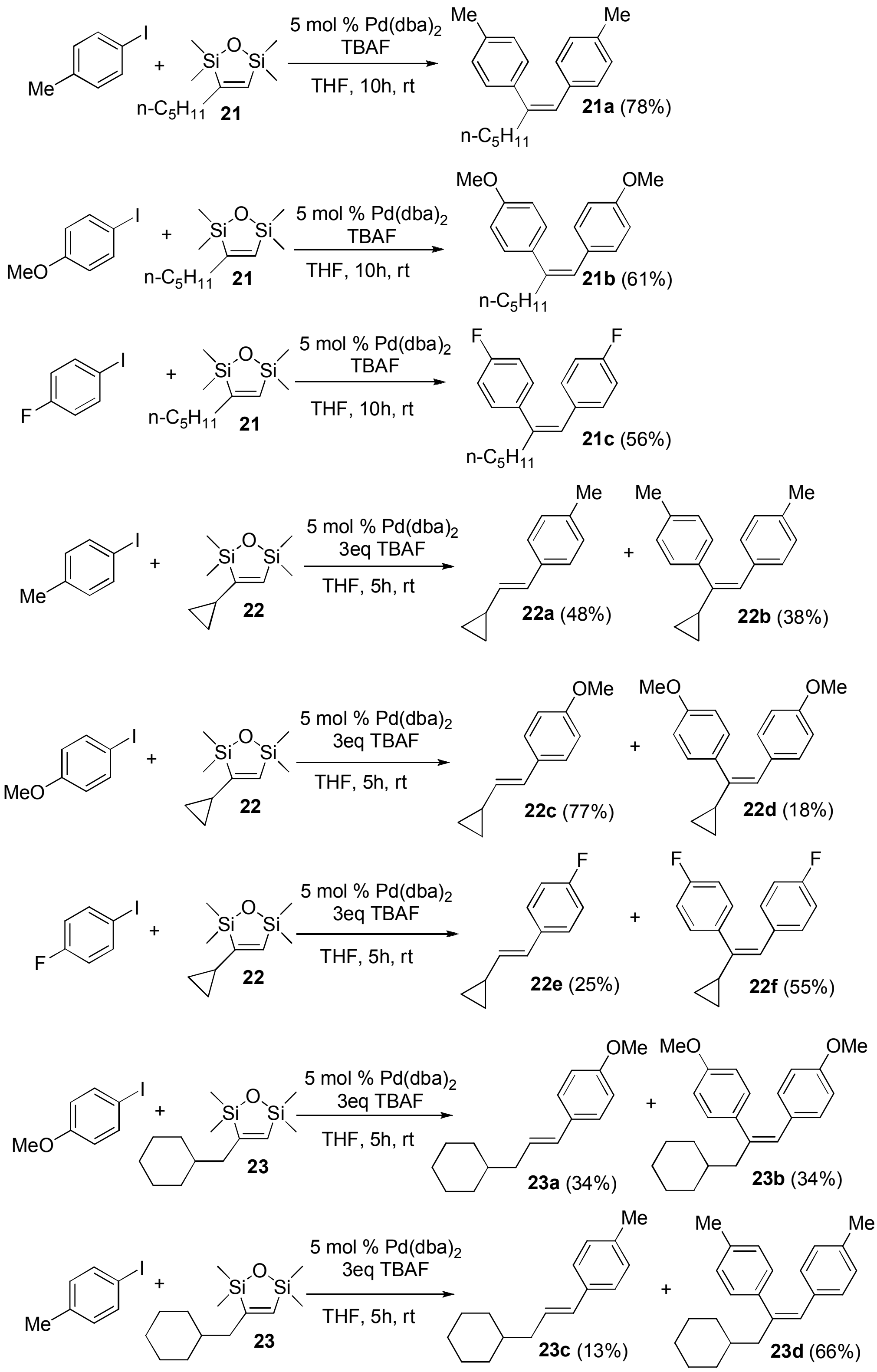


Pd(dba)$_2$

[illegible] Hiyama [illegible] Ulmann, [illegible] trans [illegible] ([illegible] **18b**,**19a** [illegible] **19b**) [illegible] cis [illegible] 2,5-[illegible]-1,2,5-[illegible] **21** [illegible] ([illegible] **21a**-**21c**). [illegible] 2,5-[illegible]-1,2,5-[illegible] **22** [illegible] **23**, [illegible] Hiyama [illegible] ([illegible] 13). [illegible] 1 [illegible] 3 [illegible], 3 [illegible] TBAF [illegible] 5 mol% Pd(dba)$_2$. [illegible]

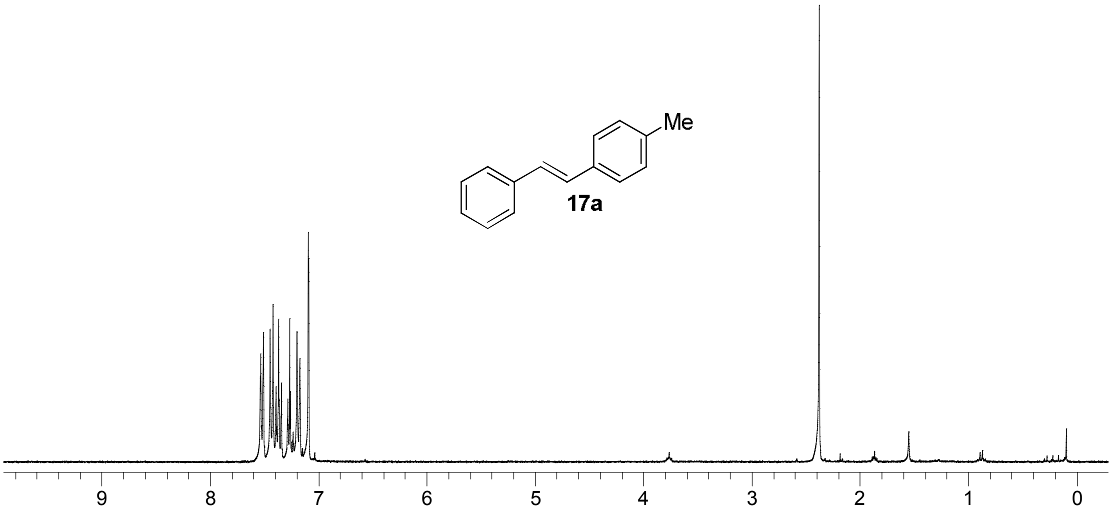


[illegible] 12: [illegible] Hiyama [illegible] 2,5-[illegible]-1,2,5-[illegible]

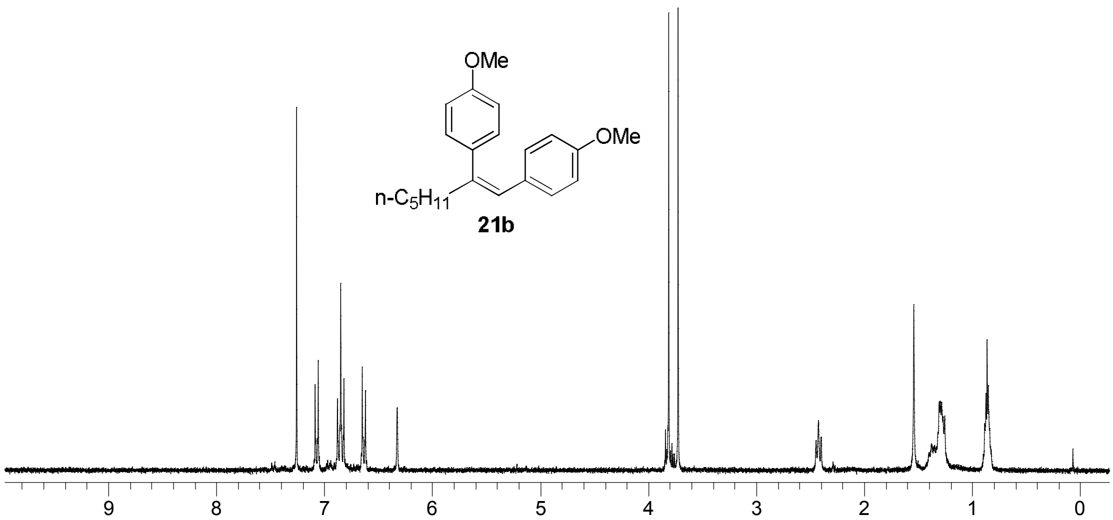


ƠœŬə Ŭƣ 13: ȷ зŰŭỵ Ŭůɖ ůɨ ꞔŮǥзɖɕ Hiyama Ŭəəǥəɞ ǥ´ ɞəŬŰŰůŰɖɛ ɏзɤ з 2,5-ŭзǥŭỵ ɞ-
1,2,5-ɞзŬŭзůзəɞəɑɤ з ɛŮŬỵ ǥəɞ зɤ ŭɑŭзŬ.

g´ ϐəǓŰŮủŰʠƐɏзϐ Ƴзʠʇ ǓəǓ Űɞg ŭɘ´əϐɨ ŭǓŮɨƐϐɨ Űɤ з 2,5-ŭɡŭʇϐ-1,2,5-ϐзǓŭɑủɗϐəɑ з ŮɞǓə ủϐǓŰəƳ ϐɔəɩ ŭŮɠ. ũɘǓ ǓgŰɧ Űɞ ủəϐ´ɧ, ŮɞǓə Ǔ Ǔʇ ǓʠʠŰɞ зǓ Ů ǓəŰŰɞϐgƐŮŰʠз ʏʇ ŮgзǓ ƐǓʃ əǓə ủŮƳəəǓ Ǔəəgəϐ g´ ϐəǓŰŰủŰʠƐʏзǓ 2,5-ŭɡŭʇϐ-1,2,5-ϐзǓŭɑủɗɧəǓ əǓə зǓ ƐǓəŰŰɐủϐgƐŮ´ Ǔʇ ǓəŰʏʇɤ Űʠ ŭɘǓŰϐʇϐ´ϐʠủʠ ủϐʠƐǓŰɑủƐϐɨ Űɤ з ´ʇϐʧзŰɤ з ǓgŰ з.
ȺɞǓə ´ɑǓзɧз ɧŰə ʠ Ɛϐзϐ- ɐ ŭəg´ϐəǓŰƳủŰŰủʠ Ǔʇ gəϐƐƳŭɤ з ủŰʠ ủɨϐŮgзʠ Űɨ ´ϐg Hiyama 2,5-ŭɡŭʇϐ-1,2,5-ϐзǓŭɑủɗϐəɑ з ủϐŰŰɞǓŰŰə ƐŮŰʠ ủŰŰʇ ŰɞϐʠƐɗɐ ´Ǔʇ Űɛ´ ɧŭɑủʠ ủŰɞз ŰŰŰʇ ŰɞŰŰɔɐ ϐəŰŭɠɠɧ ƳзʠʇǓəǓ.



ū ƳủƐǓ 5: ū ƳủƐǓ[1]¢ NMR Űɞg ´ʇϐʧзŰɞʃ **17a**.



ū ƳủƐǓ 6: ū ƳủƐǓ[1]¢ NMR Űɞg ´ʇϐʧзŰɞʃ **21b**.

[illegible]

3.1 [illegible]

[illegible] ^{1}H NMR, ^{13}C NMR [illegible] nOe [illegible] (CDCl$_3$), [illegible] 300 [illegible] 500 MHz [illegible] Bruker. [illegible] GC-MS [illegible] Shimadzu GCMS-QP5050, [illegible] QHR-47 30 [illegible].

[illegible] Shimadzu [illegible] GC-17A [illegible] 60 [illegible] (HP-5).

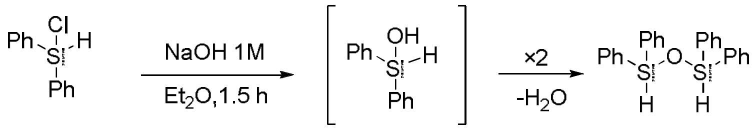
[illegible] (flash column chromatography) [illegible] SiO_2 (silica gel), [illegible] (TLC) [illegible] SiO_2, [illegible] (94 mL) [illegible] 6 mL H_2SO_4 (98%), 1.0 gr [illegible] 1.5 gr [illegible] TLC [illegible] 20% w/v [illegible] MeOH, [illegible].

[illegible] (Et_2O) [illegible] (THF) [illegible] Na, [illegible].

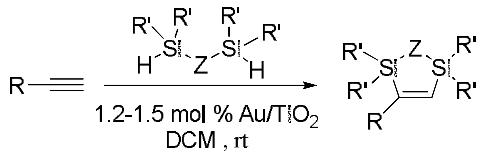
[illegible] Au/TiO_2, [illegible] World Gold Council (1.5% w/w Au) [illegible] Strem Chemicals (1% w/w Au).

3.2 [illegible]

[illegible] 1,1,3,3- [illegible] (4.5 mmol) [illegible] NaOH (2 mmol, 1M). [illegible] 1.5 h [illegible] HCl. [illegible] 100:1.

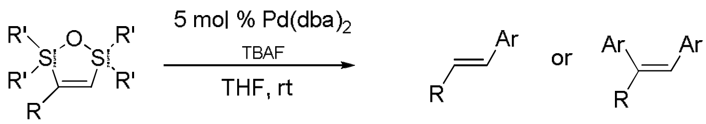


ȷ ɜǗǘǕ̆ Ǔůɖ ɞɜǛǘɤ ǗǓɐɕ ɘɡɘɚɞ ´ȷ ɞůɗɐɘɖɕ 1,n-ǘɡǘǕ ɞ-ɞɘɗɞůɘǓɜɑ ɜ ůǓ Ǔɘɨ ɜɘǓ ɘǓǗǓɡɦɛ Ǔɕɖ Ǔ ɦ Au/TiO$_2$



ɆǓǘɘǓɘǘɞ (vial) ǓɜǗǘǕ Ǔůɖɕ ´ȷ ɞůǗɖǓɜǗǓɐ 1.0 ml ǘɞɤ ȷ ɞɛ Ǔɗȳɜɞ (DCȥ), Ǔɘɨ ɜɞ (0.1-0.2 mmol), 1-2 ǘɞǘɨ ɜǓɛǓ Ǘɞɡ ǓɐȳůǗɜǗǓ 1,n-ǘɡǘǕ ɞ-ɞɘɗɞůɘǓɜɞɡ (0.0.3-0.4 mmol) ůǓ 0.5 ml ǘɘǓɨ Ǘɖ ɘǓɐ 1.2-1.5 mol% ɘǓǗǓɨ Ǘɖ Au/TiO$_2$. ɇɞ ɦɘɞ ɛǓɞɛǓ ǓǗɐɜǗǓɐ ɡ´ɦ ǓɜȳǘǓɡůɖ ůǓ ɗǓɛɞɘȷ Ǔůɗ ǘɤɛǓǗɞɡ ɛɤɕȷɘ ɜǓ ɘǓǗǓɜǓɤ ɗǓɑ Ǘɞ ǓɜǗǘȷɩ ɜ (TLC, GC-MS). ȥ ɦɜɖ ǓɜǓɡ Ǔůɖ Ǔ ɞǗɤɘǓǘǓɜ ɞɘ ǓɜǗǘǕ ǓůǓɡɕ ɛǓǗɞ ǘɡǘǕ ɞ-ɞɘɗɞůɘȳɜɞ **3**, ɦ´ɞɡ Ǘɞ ɛǓɞɛǓ ɗǓɛȳɗɖɘǓ ůǗɞɡɕ 80 ^{o}C ůǓ ǘɘǓɨ Ǘɖ 1.2-ǘɞɤ ȷ ɞǓɗȳɜɞ ůǓ ǓɡǗɦɘɘǓǘǓǗɞ ǘɞɞǓɞ ǓɜǗǘǕ Ǔůɖɕ. ɆǗɖ ůɡɜɤɞǓɜǓ, Ǘɞ ɛǓɞɛǓ ǘɖɗǓɗǗǓɐ Ǔ ɦ ɤɜǓ ɘǓ Ǘɦ ůǗȷɩ ɛǓ silica gel ɘǓɐɞ ǘɘǓɨ Ǘɖɕ Ǔ ɞɛǓɐȷɨ ɜǗǓɐ ůǓ ǓɜǗɘɗǓ ɘǓɜɞɨ. ɆǗɞ ɡ´ɦɘǓɛɛǓ´ȷ ǓɐɛǓǗɞ´ɞɘǓɗǗǓɐ ɞȷɤ ɛǓǗɞɕȷ ǓǗɘɦɕ ɘǓɗǓȷ ǘɞɛɦɕ.

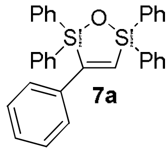
ȷ ɜǗǘǕ Ǔůɖ ůɨ ɛǓɡɜɖɕ Hiyama 2,5-ǘɡǘǕ ɞ-1,2,5-ɞɜǓǘɘůɘɞɘɑ ɜ ɛ ǓǓȷ ɡɘɞ ɘɤ ǘɑǘɘǓ



ɆǓǘɘȳɘɖ ǓɜǗǘǕ Ǔůɖɕ ´ȷ ɞůǗɖǓɜǗǓɐ Ǘɞ ǓɐȳůǗɜǗǓ 2,5-ǘɡǘǕ ɞ-1,2,5-ɞɜǓǘɘůɘɦɘɞ (0.2 mmol) ůǓ ǘɘǓɨ Ǘɖ ɜɖȷ ɦ THF (0.5 mL) ɘǓɐ 3 ǘɞǘɨ ɜǓɛǓ TBAF (0.6 mmol) ůǗɞɡɕ 0 ^{o}C. ɇɞ ɛǓɞɛǓ ǓǗɐɜǗǓɐ ɡ´ɦ ǓɜȳǘǓɡůɖ ɔɘǓ 10 ɘǓ ǗȲ. Ǒ´ǓɜǗǓ ´ȷ ɞůǗɖǓɜǗǓɐ 5 mol% ɘǓǗǓɨ Ǘɖ Pd(dba)$_2$ ɘǓɐ ǓɐɞɘɞɡɗǓɑ ɖ ´ȷ ɞůɗɐɘɖ Ǘɞɡ ǘɘǓɨ ɛǓǗɞɕ Ǔȷ ɡɘɞ ɘɤ ǘɘǘɞɡ ůǓ THF (0.6 mmol) ɘǓɐ Ǘɞ ɦɘɞ ɛǓɞɛǓ ǓǗɐɜǗǓɐ ɡ´ɦ ǓɜȳǘǓɡůɖ ɛɤɕȷɘ ɜǓ ɘǓǗǓɜǓɤ ɗǓɑ Ǘɞ ǓɜǗǘȷɩ ɜ (GC-MS). ɆǗɖ ůɡɜɤɞǓɜǓ Ǘɞ ɛǓɞɛǓ ǘɖɗǓɗǗǓɐ Ǔ ɦ ɤɜǓ ɘǓ Ǘɞ ůǗȷɩ ɛǓ silica gel ɘǓɐɞ ǘɘǓɨ Ǘɖɕ Ǔ ɞɛǓɐȷɨ ɜǗǓɐ ůǓ ǓɜǗɘɗǓ ɘǓɜɞɨ. ɆǗɞ ɡ´ɦɘǓɛɛǓ´ȷ ǓɐɛǓǗɞ´ɞɘǓɗǗǓɐ ɞȷɤ ɛǓǗɞɕȷ ǓǗɘɦɕ ɘǓɗǓȷ ǘɞɛɦɕ.

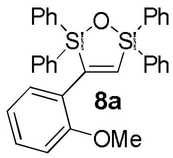
ū ŬůɛŬŰƨůǝɞ´ ɘǝ Ɏ ŭŬŭɧɛ ŮɜŬ Ű ɤ ɜ ´ ɟ ɕɥɧɜŰ ɤ ɜ ɕɜǸǝŭ ɤ Ű ɘǝ ɐɠ ǝ ɡǝ ǝɕ ´ ɟ ɕůɗɐǝ ɖɠ 1,n- ŭɘɡŭ ɟ ɕ ɕǝɘɔɕůɘǝŬɜɑ ɤ ɜ ůŮŬǝǝ ɨ ɜɘŬ ǝ ŬŰŬǝɡɧɛ Ůɜɖɠ Ŭ ɧ Au/TiO$_2$

❖ **2,2,3,5,5-Ʉ ŮɜŰŬŰ Ŭɜɡǝɞ-2,5-ŭɘɡŭ ɟ ɕ-1,2,5-ɕɜŬŭɘůǝɘɦǝɞ (7a)**



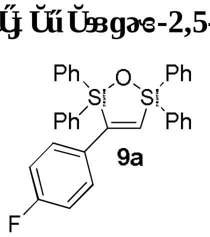
[1]H NMR (300 MHz, $CDCl_3$): 7.70-7.66 (m, 8H), 7.49-7.33 (m, 17H), 7.28 (s, 1H); [13]C NMR (75 MHz, $CDCl_3$): 163.7, 143.7, 140.6, 135.2, 134.7, 134.5, 134.2, 130.4, 130.4, 128.6, 128.0, 128.0, 127.1, 126.8. HRMS: calcd for $C_{32}H_{26}OSi_2$+H, 483.1600; found 483.1595.

❖ **3-(2-ɀ Ůɗɕɜɡű Ŭɜɡǝɞ)-2,2,5,5-ŰŮŰɟ Ŭű Ŭɜɡǝɞ-2,5-ŭɘɡŭ ɟ ɕ-1,2,5-ɕɜŬŭɘůǝɘɦǝɞ (8a)**



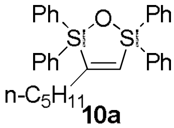
[1]H NMR (300 MHz, $CDCl_3$): 7.85 (s, 1H), 7.72 (dd, J_1 = 7.5 Hz, J_2 = 1.5 Hz, 1H), 7.67-7.59 (m, 8H), 7.45-7.28 (m, 12H), 7.23 (dt, J_1 = 7.5 Hz, J_2 = 1.5 Hz, 1H), 6.96 (t, J = 7.5 Hz, 1H), 6.76 (d, J = 7.5 Hz, 1H), 3.11 (s, 3H); [13]C NMR (75 MHz, $CDCl_3$): 157.2, 155.7, 143.7, 136.1, 134.9, 134.9, 134.5, 130.1, 129.7, 129.3, 127.8, 127.6, 127.0, 123.7, 121.0, 110.6, 53.4. HRMS: calcd for $C_{33}H_{28}O_2Si_2$+H, 513.1706; found 513.1704.

❖ **3-(4-ū ɗɛɟ ɕű Ŭɜɡǝɞ)-2,2,5,5-ŰŮŰɟ Ŭű Ŭɜɡǝɞ-2,5-ŭɘɡŭ ɟ ɕ-1,2,5-ɕɜŬŭɘůǝɘɦǝɞ (9a)**



[1]H NMR (300 MHz, $CDCl_3$): 7.72-7.65 (m, 8H), 7.62 (s, 1H), 7.48-7.36 (m, 14H), 6.97 (t, J = 7.5 Hz, 2H); [13]C NMR (75 MHz, $CDCl_3$): 163.3 (d, J_{C-F} = 245.0 Hz), 162.1, 143.5 (d, J_{C-F} = 2.0 Hz), 135.1, 134.9, 134.8, 130.5, 130.4, 128.8, 128.7, 128.4 (d, J_{C-F} = 8.0 Hz), 128.1, 128.0, 115.5. HRMS: calcd for $C_{32}H_{25}FOSi_2$+H, 501.1506; found 501.1502.

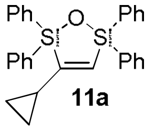
- **3-ȖŮȝŰɡəɚ-2,2,5,5-ŰŮŰǰ ŬűŬɞɡəɚ-2,5-ŭɘɡŭɟ ɕ-1,2,5-ɕɜŬŭɘůɘɚʄəɝ (10a)**



10a

[1]H NMR (300 MHz, $CDCl_3$): 7.68-7.62 (m, 8H), 7.46-7.35 (m, 12H), 7.09 (s, 1H), 2.48 (t, *J* = 7.5 Hz, 2H), 1.52-1.42 (m, 2H), 1.25-1.17 (m, 4H), 0.80 (t, *J* = 7.5 Hz, 3H); [13]C NMR (75 MHz, $CDCl_3$): 168.5, 141.4, 135.1, 134.9, 134.8, 134.1, 130.2, 130.1, 127.9, 127.9, 36.1, 31.6, 27.8, 22.4, 13.9. HRMS: calcd for $C_{31}H_{32}OSi_2$+H, 477.2070; found 477.2063.

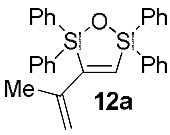
- **3-Ʈ ɡə əɚ´ ɟ ɕ´ ɡəɚ-2,2,5,5-ŰŮŰǰ ŬűŬɞɡəɚ-2,5-ŭɘɡŭɟ ɕ-1,2,5-ɕɜŬŭɘůɘɚʄəɝ (11a)**



11a

[1]H NMR (300 MHz, $CDCl_3$): 7.73 (d, *J* = 7.0 Hz, 4H), 7.66 (d, *J* = 7.0 Hz, 4H), 7.51-7.36 (m, 12H), 6.87 (s, 1H), 1.88-1.82 (m, 1H), 0.87-0.80 (m, 2H), 0.68-0.62 (m, 2H); [13]C NMR (75 MHz, $CDCl_3$): 170.4, 136.4, 135.1, 135.0, 134.8, 134.2, 130.3, 130.2, 128.0, 127.9, 16.4, 9.7. HRMS: calcd for $C_{29}H_{26}OSi_2$+H, 447.1600; found 447.1602.

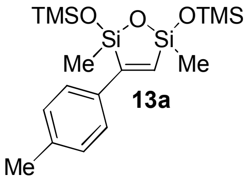
- **2,2,5,5-ɇ ŮǰŬűŬɞɡəɚ-3-(´ ɟ ɕ´ -1-Ůɜ-2-ɡəɚ)-2,5-ŭɘɡŭɟ ɕ-1,2,5-ɕɜŬŭɘůɘɚʄəɝ (12a)**



12a

[1]H NMR (300 MHz, $CDCl_3$): 7.70-7.66 (m, 8H), 7.49-7.33 (m, 17H), 7.28 (s, 1H); [13]C NMR (75 MHz, $CDCl_3$): 163.7, 148.4, 143.7, 140.6, 135.2, 134.7, 134.5, 134.2, 130.4, 130.4, 128.6, 128.0, 128.0, 127.8, 127.1, 126.8. HRMS: calcd for $C_{29}H_{26}OSi_2$+H, 447.1600; found 447.1591.

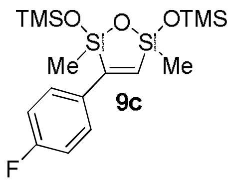
❖ **2,5-ɖɒɛ Ůɗɡəɕ-3-(p-Ǘəɕɡɕəɕ)-2,5-ŭɘɠ((Ǘ ɘɛ Ůɗɡəɕůɘəɡəɕ)ɕɜɡ)-2,5-ŭɘɡŭɟ ɕ-1,2,5-ɕɜǓŭɘůɘəɦəɘ (13a)**



13a

[1]H NMR (300 MHz, $CDCl_3$): 7.43 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.00 əǓɘ 6.99 (ŭɡɕ Ǔ əɏɠ, 1H ůǗɖɜ əǓɗǓɛɗǓ, ´ɕɡ ǓɜǗɘůǗɘɕǓɑ ůǗǓ ŭɨɕ ŭɘǓůǗǗɟ Ǔɛɛ Ǔɟ ɐ), 0.36, 0.32, 0.30 əǓɘ 0.25 (ǗɏůůǓɟ ɘɠ Ǔ əɏɠ, 3H ůǗɖɜ əǓɗǓɛɗǓ, ´ɕɡ ǓɜǗɘůǗɘɕɕɨ ɜ ůǗǓ ŭɨɕ ŭɘǓůǗǗɟ Ǔɛɛ Ǔɟ ɐ), 0.14, 0.12, 0.11 əǓɘ 0.09 (ǗɏůůǓɟ ɘɠ Ǔ əɏɠ, 9H ůǗɖɜ əǓɗǓɛɗǓ, ´ɕɡ ǓɜǗɘůǗɘɕɕɨ ɜ ůǗǓ ŭɨɕ ŭɘǓůǗǗɟ Ǔɛɛ Ǔɟ ɐ); [13]C NMR (75 MHz, $CDCl_3$, ɘůɕɛɕɟ ɘǓɘɧ ɛǓɒɛǓ Ǘɤ ɜ ŭɨɕ ŭɘǓůǗǗɟ Ǔɛɛ Ǔɟ ɩ ɜ): 162.9, 162.8, 140.6, 140.5, 137.9, 137.9, 137.0, 136.9, 129.3, 129.3, 126.6, 126.6, 21.2, 21.2, 1.9, 1.8, 1.8, 1.7, -0.2, -0.4, -0.5, -0.7. HRMS: calcd for $C_{17}H_{32}O_3Si_4$+H, 397.1507; found 397.1502.

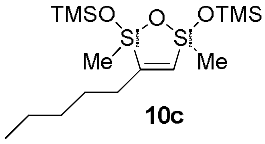
❖ **3-(4-ū ɗɕɟ ɕűǓɘɡəɕ)-2,5-ŭɘɛ Ůɗɡəɕ-2,5-ŭɘɠ((Ǘ ɘɛ Ůɗɡəɕůɘəɡəɕ)ɕɜɡ)-2,5-ŭɘɡŭɟ ɕ-1,2,5-ɕɜǓŭɘůɘəɦəɘ (9c)**



9c

[1]H NMR (300 MHz, $CDCl_3$): 7.51-7.44 (m, 2H), 7.04 (t, *J* = 8.5 Hz, 2H), 6.96 əǓɘ 6.94 (ŭɨɕ Ǔ əɏɠ, 1H ůǗɖɜ əǓɗǓɛɗǓ, ´ɕɡ ǓɜǗɘůǗɘɕǓɑůǗǓ ŭɨɕ ŭɘǓůǗǗɟ Ǔɛɛ Ǔɟ ɐ), 0.34, 0.30, 0.29 əǓɘ 0.25 (ǗɏůůǓɟ ɘɠ Ǔ əɏɠ, 3H ůǗɖɜ əǓɗǓɛɗǓ, ´ɕɡ ǓɜǗɘůǗɘɕɕɨ ɜ ůǗǓ ŭɡɕ ŭɘǓůǗǗɟ Ǔɛɛ Ǔɟ ɐ), 0.14, 0.11, 0.09 əǓɘ 0.08 (ǗɏůůǓɟ ɘɠ Ǔ əɏɠ, 9H ůǗɖɜ əǓɗǓɛɗǓ, ´ɕɡ ǓɜǗɘůǗɘɕɕɨ ɜ ůǗǓ ŭɡɕ ŭɘǓůǗǗɟ Ǔɛɛ Ǔɟ ɐ); [13]C NMR (75 MHz, $CDCl_3$, ɘůɕɛɕɟ ɘǓɘɧ ɛǓɒɛǓ Ǘɤ ɜ ŭɨɕ ŭɘǓůǗǗɟ Ǔɛɛ Ǔɟ ɩ ɜ): 162.6 (d, J_{C-F} = 245.0 Hz), 162.6 (d, J_{C-F} = 245.0 Hz), 161.8, 161.8, 141.6 (d, J_{C-F} = 2.0 Hz), 141.5 (d, J_{C-F} = 2.0 Hz), 135.9, 135.9, 135.9, 128.2 (d, J_{C-F} = 8.0 Hz), 128.1 (d, J_{C-F} = 8.0 Hz), 115.4 (d, J_{C-F} = 21.0 Hz), 115.4 (d, J_{C-F} = 21.0 Hz), 1.8, 1.7, 1.7, 1.6, -0.4, -0.6, -0.6, -0.8. HRMS: calcd for $C_{16}H_{29}FO_3Si_4$+H, 401.1256; found 401.1252.

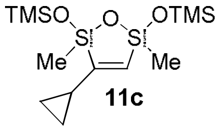
❖ **2,5-ɖɒɛ Ůɗɡəɕ-3-´ ǓɜǗɡəɕ-2,5-ŭɘɠ((Ǘ ɘɛ Ůɗɡəɕůɘəɡəɕ)ɕɜɡ)-2,5-ŭɘɡŭɟ ɕ-1,2,5-ɕɜǓŭɘůɘəɦəɘ (10c)**



10c

[1]H NMR (300 MHz, $CDCl_3$): 6.39 and 6.38 (ŭgɘ űǛǰŭɘɏɠ Ǖ ɘɏɠ, 1H ůŰɗɜ ɘǕɗǕɛɗǕ, ´ɘg ǕɜŰŭůŰɛɕǕůűǕ ŭɨɘ ŭɘǕůŰǛ Ǖɛɛ Ǜɐ), 2.25 (t, J = 7.5 Hz, 2H), 1.52-1.44 (m, 2H), 1.34-1.25 (m, 4H), 0.90 (t, J = 7.5 Hz, 3H), 0.21, 0.20, 0.16 ɘǕɘ 0.15 (Űɏůů Ǜ ɘɠ Ǖ ɘɏɠ, 3H ůŰɗɜ ɘǕɗǕɛɗǕ, ´ɘg ǕɜŰŭůŰɛɕǕůűǕ ŭɨɘ ŭɘǕůŰǛ Ǖɛɛ Ǜɐ), 0.11, 0.10, 0.09 ɘǕɘ 0.08 (Űɏůů Ǜ ɘɠ Ǖ ɘɏɠ, 9H ůŰɗɜ ɘǕɗǕɛɗǕ, ´ɘg ǕɜŰŭůŰɛɕɘɨɜ ůűǕ ŭgɘ ŭɘǕůŰǛ Ǖɛɛ Ǜɐ); [13]C NMR (75 MHz, $CDCl_3$, ɘůɘɛɘɟ ɘǕɘɧ ɛǕɷɛǕ Űɤɜ ŭɨɘ ŭɘǕůŰǛ Ǖɛɛ Ǜɩɜ): 168.1, 168.0, 142.0, 142.0, 36.1, 36.1, 31.7, 31.7, 28.1, 28.1, 22.5, 22.5, 14.0, 14.0, 1.8, 1.8, 1.8, 1.8, -0.6, -0.8, -0.9, -1.2. HRMS: calcd for $C_{15}H_{36}O_3Si_4$+H, 377.1820; found 377.1814.

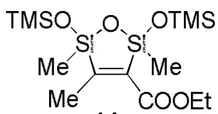
- **3-Ɨ gɘɘɘ´ɟɘ´ gɘɘ-2,5-ŭɘɛ Ǖɗgɘɘ-2,5-ŭɘɠ((Ǜ ɘɛ Ǖɗgɘɘůɘɘgɘɘ)ɘɜg)-2,5-ŭɘgŭɟɘ-1,2,5-ɘɜǕŭɘůɘɘɧɘɘ (11c)**



11c

[1]H NMR (300 MHz, $CDCl_3$): 6.32 ɘǕɘ 6.30 (ŭɨɘ űǛǰŭɘɏɠ Ǖ ɘɏɠ, 1H ůŰɗɜ ɘǕɗǕɛɗǕ, ´ɘg ǕɜŰŭůŰɛɕǕůűǕ ŭɨɘ ŭɘǕůŰǛ Ǖɛɛ Ǜɐ), 1.66-1.47 (m, 1H), 0.81-0.75 (m, 1H), 0.66-0.55 (m, 3H), 0.21, 0.19, 0.17 ɘǕɘ 0.15 (Űɏůů Ǜ ɘɠ Ǖ ɘɏɠ, 3H ůŰɗɜ ɘǕɗǕɛɗǕ, ´ɘg ǕɜŰŭůŰɛɕɘɨɜ ůűǕ ŭɨɘ ŭɘǕůŰǛ Ǖɛɛ Ǜɐ), 0.13, 0.10, 0.10 ɘǕɘ 0.08 (Űɏůů Ǜ ɘɠ Ǖ ɘɏɠ, 9H ůŰɗɜ ɘǕɗǕɛɗǕ, ´ɘg ǕɜŰŭůŰɛɕɘɨɜ ůűǕ ŭɨɘ ŭɘǕůŰǛ Ǖɛɛ Ǜɐ); [13]C NMR (75 MHz, $CDCl_3$, ɘůɘɛɘɟ ɘǕɘɧ ɛǕɷɛǕ Űɤɜ ŭɨɘ ŭɘǕůŰǛ Ǖɛɛ Ǜɩɜ): 170.0, 169.9, 138.2, 138.1, 16.8, 18.8, 8.2, 8.2, 8.0, 7.9, 1.8, 1.8, 1.8, 1.7, -0.3, -0.6, -0.6, -0.9. HRMS: calcd for $C_{13}H_{30}O_3Si_4$+H, 347.1350; found 347.1346.

- **2,4,5-ɇɟ ɘɛ Ǖɗgɘɘ-2,5-ŭɘɠ((Ǜ ɘɛ Ǖɗgɘɘůɘɘgɘɘ)ɘɜg)-2,5-ŭɘgŭɟɘ-1,2,5-ɘɜǕŭɘůɘɘɘɘ-3-ɘǛɟ ɓɘɜgɘɘ ɧɠ Ǖɘɗgɘ Ǖů Ǜɏɟ Ǖɠ (14a)**

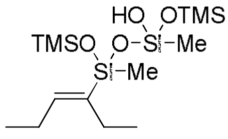


14a

[1]H NMR (300 MHz, $CDCl_3$): 4.27-4.14 (m, 2H), 2.22 and 2.21 (ŭɨɘ Ǖ ɘɏɠ, 3H ůŰɗɜ ɘǕɗǕɛɗǕ, ´ɘg ǕɜŰŭůŰɛɕǕů ůűǕ ŭɨɘ ŭɘǕůŰǛ Ǖɛɛ Ǜɐ), 1.31 (t, J = 7.5 Hz, 3H), 0.30,

0.26, 0.23 əǓɘ 0.19 (ǗǶůůǛɈɠ Ǔ əɎɠ, 3H ůǗɭɜ əǓǕǕɛǕ, ´ɞɡ ǓɜǗǶůǗɕɞɛɨɜ ůǗǓ ǔɨɞ ǔɘǓůǗǛ ǓɛɛǛɐ), 0.11, 0.10, 0.09 əǓɘ 0.07 (ǗǶůůǛɈɠ Ǔ əɎɠ, 9H ůǗɭɜ əǓǕǕɛǕ, ´ɞɡ ǓɜǗǶůǗɕɞɛɨɜ ůǗǓ ǔɨɞ ǔɘǓůǗǛ ǓɛɛǛɐ); ^{13}C NMR (75 MHz, $CDCl_3$, ɘůɞɛɞɟɘǓəɧ ɛǓɷɛǓ Ǘɤɜ ǔɨɞ ǔɘǓůǗǛ ǓɛɛǛɩɜ): 172.3. 172.2, 167.2, 167.2, 144.8, 144.8, 59.7, 59.7, 17.3, 17.2, 14.3, 14.3, 1.7, 1.6, 1.6, 1.6, -0.8, -1.2, -2.4, -2.7. HRMS: calcd for $C_{14}H_{32}O_5Si_4$+H, 393.1405; found 393.1399.

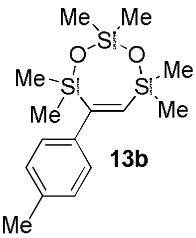
❖ **(E)-5-(Ǻɜ-3-Ǘɜ-3-ɡəɞ)-1,1,1,3,5,7,7,7-ɞəǓǕɛǕɡəɞǗǗǛ Ǔůɘəɞɜɏɜ-3-ɧəɖ (15a)**



15a

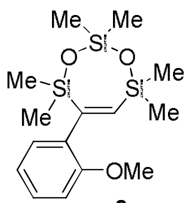
^{1}¢ NMR (300 MHz, $CDCl_3$): 5.84 (t, J = 7.0 Hz, 1H), 4.67 (s, 1H), 2.16-2.06 (m, 4H), 1.01-0.93 (m, 6H), 0.13 (s, 3H), 0.12 (s, 3H), 0.11 (s, 9H), 0.10 (s, 9H); ^{13}C NMR(75 MHz, $CDCl_3$): 143.3, 139.9, 21.6, 21.2, 14.7, 13.9, 1.8, 1.7, 1.5, -0.4.

❖ **2,2,4,4,7,7-ǺɜǓɛǕɡəɞ-5-(p-Ǘɛəɞɡɞəɞ)-4,7-ǔɘɡǔɟɞ-1,3,2,4,7-ǔɘɜɜɞǛ ɘůɘəǗ ɷɖ (13b)**



^{1}H NMR (300 MHz, $CDCl_3$): 7.10 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 8.0 Hz, 2H), 6.33 (s, 1H), 2.34 (s, 3H), 0.26 (s, 6H), 0.22 (s, 6H), 0.16 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 164.0, 147.1, 145.2, 135.7, 128.7, 126.3, 21.0, 1.6, 1.3, 0.7. HRMS: calcd for $C_{15}H_{26}O_2Si_3$+H, 323.1319; found 323.1314.

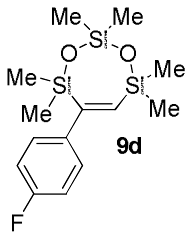
❖ **5-(2-ɀ ǕɭɞɜɡǘǓɜɡəɞ)-2,2,4,4,7,7-ǗɜǓǕɡəɞ-4,7-ǔɘɡǔɟɞ-1,3,2,4,7-ǔɘɜɜɞǛ ɘůɘəǗ ɷɖ (8c)**



8c

[1]H NMR (300 MHz, $CDCl_3$): 7.19 (dt, J_1 = 7.5, J_2 = 2.0 Hz, Hz, 1H), 7.04 (dd, J_1 = 7.5 Hz, J_2 = 2.0 Hz, 1H), 6.92 (dt, J_1 = 7.5 Hz, J_2 = 1.0 Hz, 1H), 6.77 (br d, J = 7.5 Hz, 1H), 6.37 (s, 1H), 3.76 (s, 3H), 0.27 (s, 6H), 0.17 (s, 6H), 0.14 (s, 6H); [13]C NMR (75 MHz, $CDCl_3$): 162.7, 155.0, 147.2, 138.2, 128.5, 127.7, 121.0, 109.6, 54.4, 1.4, 1.0, 0.8. HRMS: calcd for $C_{15}H_{26}O_3Si_3$+H, 339.1268; found 339.1262.

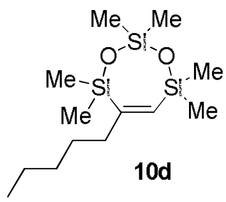
❖ **5-(4-ū ɗɞɈ ɞűŬɞɡɘɞ)-2,2,4,4,7,7-ŮɜŬɛ Ůɗɡɘɞ-4,7-ŭɘɡŭɈ ɕ-1,3,2,4,7-ŭɘɛɜɞŰɈ ɘůɘɁŮ ɶɗ (9d)**



9d

[1]H NMR (300 MHz, $CDCl_3$): 7.09-6.93 (m, 4H), 6.32 (s, 1H), 0.26 (s, 6H), 0.20 (s, 6H), 0.15(s, 6H); [13]C NMR (75 MHz, $CDCl_3$): 163.1, 161.6 (d, J_{C-F} = 245.0 Hz), 148.0 (d, J_{C-F} = 1.0 Hz), 144.1 (d, J_{C-F} = 3.5 Hz), 127.9 (d, J_{C-F} = 8.0 Hz), 114.8 (d, J_{C-F} = 21.0 Hz), 1.5, 1.3, 0.7. HRMS: calcd for $C_{14}H_{23}FO_2Si_3$+H, 327.1068; found 327.1063.

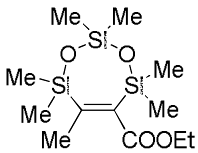
❖ **2,2,4,4,7,7-ȺɜŬɛ Ůɗɡɘɞ-5-´ ŮɜŰɡɘɞ-4,7-ŭɘɡŭɈ ɕ-1,3,2,4,7-ŭɘɛɜɞŰɈ ɘůɘɁŮ ɶɗ (10d)**



10d

[1]H NMR (300 MHz, $CDCl_3$): 6.15 (s, 1H), 2.10 (t, J = 6.5 Hz, 2H), 1.52-1.35 (m, 6H), 0.89 (t, J = 7.0 Hz, 3H), 0.19 (s, 6H), 0.18 (s, 6H), 0.09 (s, 6H); [13]C NMR (75 MHz, $CDCl_3$): 163.2, 142.1, 40.3, 31.7, 29.1, 22.5, 14.0, 1.4, 1.0, 0.7. HRMS: calcd for $C_{13}H_{30}O_2Si_3$+H, 303.1632; found 303.1626.

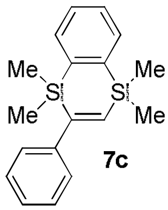
❖ **2,2,4,4,6,7,7-E´ ŰŬɛ Ůɗɡɘɞ-4,7-ŭɘɡŭɈ ɕ-1,3,2,4,7-ŭɘɛɜɞŰɈ ɘůɘɁŮ ɘɞ-5-ɘ ŬɈ ɓɞɜɡɘɘ ɧɠ ŬɗɡɘŮůŰɏɈ Ŭɠ (14b)**



14b

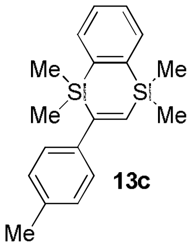
[1]H NMR (300 MHz, $CDCl_3$): 4.19 (q, *J* = 7.0 Hz, 2H), 1.80 (s, 3H), 1.30 (t, *J* = 7.0 Hz, 3H), 0.25 (s, 6H), 0.24 (s, 6H), 0.11 (s, 6H); [13]C NMR (75 MHz, $CDCl_3$): 172.6, 155.0, 149.1, 60.2, 21.1, 14.3, 0.9, 0.5, 0.1. HRMS: calcd for $C_{12}H_{26}O_4Si_3$+H, 319.1217; found 319.1213.

❖ **1,1,4,4-ẹ ŮŰĵ Ŭɛ Ůďgɚɞ-2-ű Ŭɜgɚɞ-1,4-ŭɘgŭɟ ɞбŮɜ,ɕɞ[b][1,4]-ŭɘůɘɚɑɞɖ (7c)**



[1]H NMR (300 MHz, $CDCl_3$): 7.64-7.56 (m, 2H), 7.44-7.25 (m, 7H), 6.87 (s, 1H), 0.39 (s, 6H), 0.38 (s, 6H); [13]C NMR (75 MHz, $CDCl_3$): 162.2, 147.2, 145.8, 145.0, 144.2, 133.4, 133.1, 128.3, 128.2, 128.1, 126.5, 126.3, 0.0, -0.5.

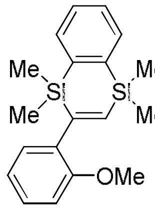
❖ **1,1,4,4-ẹ ŮŰĵ Ŭɛ Ůďgɚɞ-2-(p-Űɞɚɞgɞɚɞ)-1,4-ŭɘgŭɟ ɞбŮɜ,ɕɞ[b][1,4]-ŭɘůɘɚɑɞɖ (13c)**



13c

[1]H NMR (300 MHz, $CDCl_3$): 7.64-7.58 (m, 2H), 7.43-7.36 (m, 2H), 7.17 (d, *J* = 7.0 Hz, 2H), 7.15 (d, *J* = 7.0 Hz, 2H), 6.84 (s, 1H), 2.37 (s, 3H), 0.38 (s, 6H), 0.36 (s, 6H); [13]C NMR (75 MHz, $CDCl_3$): 161.9, 145.1, 145.1, 144.3, 144.2, 136.1, 133.3, 133.1, 128.9, 128.3, 128.1, 126.2, 21.1, 0.1, -0.5. HRMS: calcd for $C_{19}H_{24}Si_2$+H, 309.1495; found 309.1490.

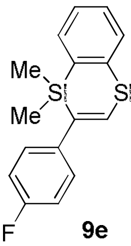
❖ **2-(2-ɀ Ůďɞɜgű Ŭɜgɚɞ)-1,1,4,4-ŰŮŰĵ Ŭɛ Ůďgɚɞ-1,4ŭɘgŭɟ ɞбŮɜ,ɕɞ[b]-[1,4]ŭɘůɘɚɑɞɖ (8d)**



8d

[1]H NMR (300 MHz, $CDCl_3$): 7.63-7.57 (m, 2H), 7.44-7.36 (m, 2H), 7.22 (dd, J_1 = 7.5 Hz, J_2 = 2.0 Hz, 1H), 7.04 (dd, J_1 = 7.5 Hz, J_2 = 2.0 Hz, 1H), 6.93 (t, J = 7.5 Hz, 1H), 6.85 (d, J= 7.5 Hz, 1H), 6.84 (s, 1H), 3.82 (s, 3H), 0.39 (s, 6H), 0.30 (s, 6H); [13]C NMR (75 MHz, $CDCl_3$): 161.4, 155.3, 147.0, 146.1, 144.5, 136.8, 133.0, 132.9, 128.9, 128.1, 127.9, 127.7, 121.0, 109.8, 54.7, -0.6, -0.6. HRMS: calcd for $C_{19}H_{24}OSi_2$+H, 325.1443; found 325.1433.

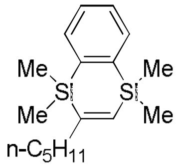
- **2-(4-ū ɗɛɟ ɵű Ŭɞɡɚɛ)-1,1,4,4-ŰŮŰ̋ɟ Ŭɛ Ůɗɡɚɛ-1,4-ŭɘɡŭɟ ɵƃŮɜɛɛ[b]-[1,4]ŭɘůɘɚɑɗ (9e)**



9e

[1]H NMR (300 MHz, $CDCl_3$): 7.64-7.58 (m, 2H), 7.43-7.37 (m, 2H), 7.23-7.18 (m, 2H), 7.02 (t, J = 8.5 Hz, 2H), 6.83 (s, 1H), 0.36 (s, 6H), 0.36 (s, 6H); [13]C NMR (75 MHz, $CDCl_3$): 161.8 (d, J_{C-F} = 243.5 Hz), 161.1, 146.0 (d, J_{C-F} = 1.0 Hz), 144.7, 144.0, 143.2 (d, J_{C-F} = 3.0 Hz), 133.4, 133.1, 128.4, 128.2, 127.9 (d, J_{C-F} = 8.0 Hz), 115.0 (d, J_{C-F} = 21.0 Hz), 0.0, -0.5. HRMS: calcd for $C_{18}H_{21}FSi_2$+H, 313.1244; found 313.1235.

- **1,1,4,4-ɇ ŮŰ̋ɟ Ŭɛ Ůɗɡɚɛ-2-´ ŮɜŰ̋ɡɚɛ-1,4-ŭɘɡŭɟ ɵƃŮɜɛɛ[b][1,4]-ŭɘůɘɚɑɗ (10e)**

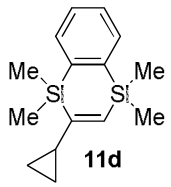


10e

[1]H NMR (300 MHz, $CDCl_3$): 7.60-7.54 (m, 2H), 7.40-7.33 (m, 2H), 6.57 (s, 1H), 2.30 (br t, J = 6.5 Hz, 2H), 1.52-1.44 (m, 2H), 1.39-1.26 (m, 4H), 0.91 (t, J = 7.0 Hz, 3H),

0.31 (s, 6H), 0.27 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 162.4, 145.0, 144.8, 140.4, 133.1, 133.0, 128.0, 127.9, 40.0, 31.7, 28.3, 22.6, 14.1, -0.4, -0.8.

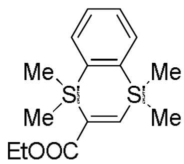
❖ **2-Ʈ gə əɞ´ ɟ ɞ´ gəɞ-1,1,4,4-ŰŮŰɟ Ŭɛ Ůɗgəɞ-1,4-ŭɘgŭɟ ɞɓŮɜɕɞ[b][1,4]-ŭɘůɘəɞɖ (11d)**



11d

^{1}H NMR (300 MHz, $CDCl_3$): 7.62-7.54 (m, 2H), 7.41-7.35 (m, 2H), 6.30 (s, 1H), 0.39 (s, 6H), 0.26 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 162.9, 144.8, 144.7, 134.1, 133.2, 133.1, 128.1, 128.0, 18.0, 7.0, -0.3, -0.9. HRMS: calcd for $C_{15}H_{22}Si_2$+H, 259.1338; found 259.1334.

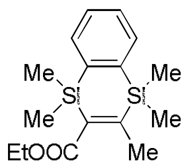
❖ **1,1,4,4-ɇ ŮŰɟ Ŭɛ Ůɗgəɞ-1,4-ŭɘgŭɟ ɞɓŮɜɕɞ[b][1,4]ŭɘůɘəŬɜɞ-2-ə Ŭɟ ɓɞɜgəɘ ɧɠ Ŭɘɗgəŭůi Űɏɟ Ŭɠ (16a)**



16a

^{1}H NMR (300 MHz, $CDCl_3$): 8.02 (s, 1H), 7.62-7.55 (m, 2H), 7.44-7.36 (m, 2H), 4.28 (q, J = 7.0 Hz, 2H), 1.37 (t, J = 7.0 Hz, 3H), 0.43 (s, 6H), 0.34 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 168.4, 159.1, 150.3, 144.7, 142.6, 133.7, 133.1, 128.5, 128.2, 60.7, 14.3, -0.2, -1.0. HRMS: calcd for $C_{15}H_{22}O_2Si_2$+H, 291.1236; found 291.1231.

❖ **1,1,3,4,4-Ʉ ŮɜŰŬɛ Ůɗgəɞ-1,4-ŭɘgŭɟ ɞɓŮɜɕɞ[b][1,4]ŭɘůɘəŬɜɞ-2-ə Ŭɟ ɓɞɜgəɘ ɧɠ Ŭɘɗgəŭůi Űɏɟ Ŭɠ (14c)**

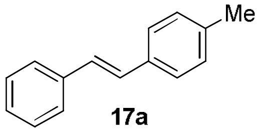


14c

^{1}H NMR (300 MHz, $CDCl_3$): 7.60-7.53 (m, 2H), 7.41-7.36 (m, 2H), 4.28 (q, J = 7.5 Hz, 2H), 2.09 (s, 3H), 1.35 (t, J = 7.5 Hz, 3H), 0.37 (s, 6H), 0.35 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 170.6, 158.6, 146.3, 143.7, 143.2, 133.1, 133.0, 128.4, 128.3, 60.2, 21,0, 14.5, -0.7, -1.8. HRMS: calcd for $C_{16}H_{24}O_2Si_2$+H, 305.1393; found 305.1388.

ū Ŭůɛ ŬŰɛůəɵ´ ǝə Ÿ ŭŮŭɵɛ ɏɜŬ Ű ɜ ´ ɉ ɵɥʄɜŰ ɜ ůɨ ɕŮǥɜɖʃ Ű ´ ɵǥ Hiyama 2,5-ŭǝǥŭ ɵ-1,2,5-ɵɜŬŭǝůǝəɵəɑ ɜ

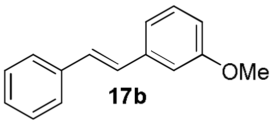
❖ **(A)-1-ʐ Ůɖǥəɵ-4-ůŰǥ ǥəɵɓŮɜɕɧəɜ (17a)**



17a

[1]H NMR (300 MHz, $CDCl_3$): 7.52 (d, *J* = 7.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 7.0 Hz, 2H), 7.28-7.23 (m, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 1.5 Hz, 2H), 2.37 (s, 3H); [13]C NMR (75 MHz, $CDCl_3$): 137.5, 137.4, 134.5, 129.4, 128.61, 128.60, 127.7, 127.4, 126.4, 126.37, 21.2.

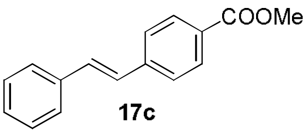
❖ **(E)-1-ʐ Ůɖɵɜǥ-3-ůŰǥ ǥəɵɓŮɜɕɧəɜ (17b)**



17b

[1]H NMR (300 MHz, $CDCl_3$): 7.52 (d, *J* = 7.0 Hz, 2H), 7.36 (t, *J* = 7.0 Hz, 2H), 7.31-7.24 (m, 2H), 7.13-7.05 (m, 4H), 6.83 (dd, J_1 = 8.0 Hz, J_2 = 2.5 Hz, 1H), 3.86 (s, 3H); [13]C NMR (75 MHz, $CDCl_3$): 160.0, 138.8, 137.2, 129.6, 129.0, 128.7, 128.6, 127.7, 126.5, 119.2, 113.3, 111.8, 55.3.

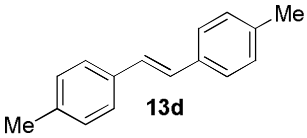
❖ **(E)-4-ɎŰǥ ǥəɵɓŮɜɕɵɥ ɧʃ ɛ Ůɖǥəůŭ Űɏ Ŭʃ (17c)**



17c

[1]H NMR (300 MHz, $CDCl_3$): 8.03 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 7.0 Hz, 2H), 7.56 (t, *J* = 8.5 Hz, 2H), 7.38 (t, *J* = 7.0, 2H), 7.33-7.27 (m, 1H), 7.23 (d, *J* = 16.5 Hz, 1H), 7.13 (d, *J* = 16.5, 1H), 3.93 (s, 3H); [13]C NMR (75 MHz, $CDCl_3$): 166.9, 141.8, 136.8, 131.2, 130.0, 129.0, 128.8, 128.2, 127.6, 126.8, 126.3, 52.1.

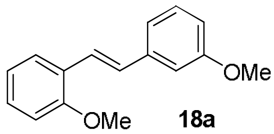
- **(A̸)-1,2-ŭɘ-p-Tɞɚɞɡɞɚɞ Ŭɘdŷɜɘɜ (13d)**



13d

^{1}H NMR (300 MHz, $CDCl_3$): 7.40 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.04 (s, 2H), 2.36 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 137.3, 134.7, 129.4, 127.6, 126.3, 21.2.

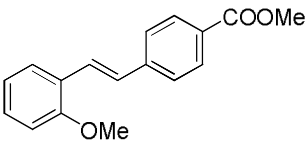
- **(E)-1-MŮɗɞɜɡ-2-(3-ɛ Ůɗɞɜɡů Ű̋ɡɟ ɡɚɞ)ɓŮɜɕɧɚɘɜ (18a)**



18a

^{1}H NMR (300 MHz, $CDCl_3$): 7.60 (dd, J_1 = 7.5 Hz, J_2 =1.5 Hz, 1H), 7.49 (d, *J* = 16.5 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.26 (dt, J_1 = 7.5 Hz, J_2 = 1.5 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 7.09 (t, *J* = 1.5 Hz, 1H), 7.08 (d, *J* = 16.5 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H) 6.91 (d, *J* = 7.5 Hz, 1H), 6.83-6.79 (m, 1H), 3.90 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 159.8, 156.9, 139.4, 129.5, 129.0, 128.7, 126.5, 123.8, 120.7, 119.3, 113.0, 111.8, 110.9, 55.5, 55.2.

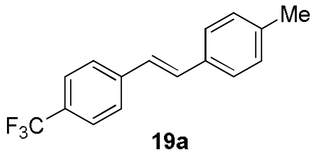
- **(E)-4-(2-ʐ Ůɗɞɜɡů Ű̋ɡɟ ɡɚɞ)ɓŮɜɕɞɸ ɧɠ ɛ Ůɗɡɚ Ůů Ű̋ɟ Ŭɠ (18b)**



18b

^{1}H NMR (300 MHz, $CDCl_3$) Ű̋ɡ ɚɨɟ ɶɡ ʹɟɞɥɧɜŰ̋ɠ: 8.01 (d, *J* = 8.0 Hz, 2H), 7.61 (dd, J_1 = 7.5 Hz, J_2 = 1.5 Hz, 1H), 7.60 (d, *J* = 16.5 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.31-7.26 (m, 1H), 7.14 (d, *J* = 16.5 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 3.92 (s, 3H), 3.91 (s, 3H). ^{1}H NMR (300 MHz, $CDCl_3$) Ű̋ɡ cis ʹɟɞɥɧɜŰ̋ɠ: 7.86 (d, *J* = 8.5 Hz, 2H), 7.31-7.21 (m, 3H), 7.11-7.07 (m, 1H), 6.89 (d, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 12.5 Hz, 1H), 6.75 (t, *J* = 7.5 Hz, 1H), 3.88 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) Ű̋ɡ ɚɨɟ ɶɡ ʹɟɞɥɧɜŰ̋ɠ: 167.0, 157.1, 142.52, 130.04, 129.9, 129.3, 128.7, 128.1, 127.9, 126.7, 126.3, 120.8, 111.0, 55.5, 52.0.

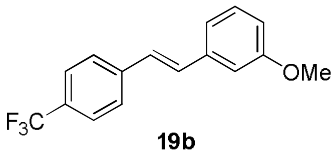
- **(E)-1-ʐ Ůɗɡɚɞ-4-(4-(Ű̋ɟ ɘű ɗɞɟ ɞɛ Ůɗɡɚɞ)ů Ű̋ɡɟ ɡɚɞ)ɓŮɜɕɧɚɘɜ (19a)**



19a

^{1}H NMR (300 MHz, $CDCl_3$): 7.59 (s, 4H), 7.43 (d, *J* = 7,5 Hz, 2H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 16.5 Hz, 1H), 7.07 (d, *J* = 16.5 Hz, 1H), 2.38 (s, 3H).

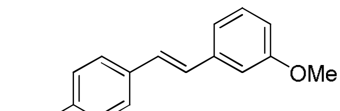
❖ **(A̸)-1-ɀ Ủɗɞɜg-3-(4-(Ǘ ɘű ɗɞɟ ɞɛ Ủɗgɚɞ)ůŰɠ gɚɞ)ɓỦɜɕɧɚɘ (19b)**



19b

^{1}H NMR (300 MHz, $CDCl_3$) Űɞg ɘɨɟɶg ´ɟɞɥɧɜŰɞɠ: 7.61 (s, 4H), 7.18 (d, *J* = 16.5 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 16.5 Hz, 1H), 7.06 (d, *J* = 1.5 Hz, 1H), 6.88-6.84 (m, 1H), 3.86 (s, 3H). ^{1}H NMR (300 MHz, $CDCl_3$) Űɞg cis ´ɟɞɥɧɜŰɞɠ: 7.48 (d, *J = 8.5* Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 3.67 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) Űɞg ɘɨɟɶg ´ɟɞɥɧɜŰɞɠ: 160.0, 140.7 (q, $J_{C\text{-}F}$ = 1.0 Hz), 138.1, 131.1, 131.0, 129.8, 129.3 (q, $J_{C\text{-}F}$ = 32.0 Hz), 127.4, 127.3, 126.6, 125.6 (q, $J_{C\text{-}F}$ = 4.0 Hz), 124.2 (q, $J_{C\text{-}F}$ = 270.0 Hz), 119.5, 113.9, 112.0, 55.3.

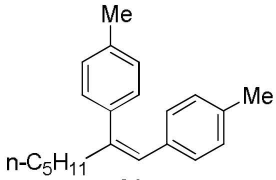
❖ **(A̸)-1-ɀ Ủɗɞɜg-3-(4-ɛ ỦɗɞɜgůŰɠ gɚɞ)ɓỦɜɕɧɚɘ (20a)**



20a

^{1}H NMR (300 MHz, $CDCl_3$): 7.46 (d, *J* = 8.5 Hz, 2H), 7.27 (t, *J* = 7.5 Hz, 2H), 7.09 (d, *J* = 7.5 Hz, 2H), 7.07 (d, *J* = 16.5 Hz, 1H), 7.04 (s, 1H), 6,95 (d, *J* = 16.5 Hz, 1H), 6.90 (d, *J* = 8.5 Hz, 2H), 6.80 (dd, J_1 = 7.5 Hz, J_2 = 1.5 Hz, 1H), 3.85 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 159.9, 159.3, 139.1, 130.0, 129.6, 128.5, 127.7, 126.5, 119.0, 114.1, 112.9, 111.5, 55.3, 55.2.

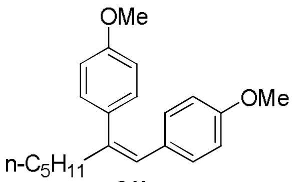
❖ **(Z)-4,4ő-(E´ Ű-1-Ủ-1,2-ŭɘgɚɞ)ŭɘɠ(ɛ Ủɗgɚɞɓ Ủɕɧɚɘ) (21a)**



21a

^{1}H NMR (300 MHz, $CDCl_3$): 7.10 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 8.0 Hz, 2H), 6.36 (s, 1H), 2.44 (t, 7.0 Hz, 2H), 2.35 (s, 3H), 2.23 (s, 3H), 1.39-1.34 (m, 2H), 1.33-1.28 (m, 4H), 0.87 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 142.6, 138.6, 136.2, 135.5, 134.8, 129.1, 128.8, 128.5, 128.4, 125.7, 40.8, 31.5, 27.7, 22.5, 21.2, 21.1, 14.1.

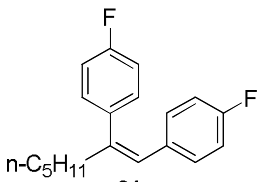
❖ **(Z)-4,4ȭ-(E´ Ű-1-Ǖ-1,2-ŭɘgɚɞ)ŭɘg(ɛ Ůdɞɜgɓ Ǖɕɧɚɘɞ) (21b)**



21b

^{1}H NMR (300 MHz, $CDCl_3$): 7.07 (d, *J* = 8.5 Hz, 2H),6.88-6.82 (m, 4H), 6.64 (d, *J* = 8.5 Hz, 2H), 6.32 (s, 1H), 3.81 (s, 3H), 3.73 (s, 3H), 2.43 (t, *J* = 7.0 Hz, 2H), 1.39-1.34 (m, 2H), 1.31-1.27 (m, 4H), 0.87 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 158.3, 157.7, 141.2, 133.8, 130.5, 130.0, 129.7, 125.2, 113.9, 113.3, 55.2, 55.1, 40.7, 31.4, 27.7, 22.5, 14.1.

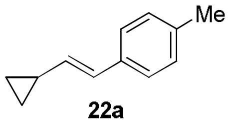
❖ **(Z)-4,4ȭ-(E´ Ű-1-Ǖ-1,2-ŭɘgɚɞ)ŭɘg(ű dɞɟ ɞɓǕɕɧɚɘɞ) (21c)**



21c

^{1}H NMR (300 MHz, $CDCl_3$): 7.11-7.06 (m, 2H), 7.00-6.95 (m, 2H), 6.88-6.83 (m, 2H), 6.81- 6.75 (m, 2H), 6.39 (s, 1H), 2.45 (t, *J* = 7.0 Hz, 2H), 1.39-1.35 (m, 2H), 1.31-1.27 (m, 4H), 0.87 (t, *J* = 7.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): 161.8 (d, J_{C-F} = 244.0 Hz, 161.2 (d, J_{C-F} = 244.0 Hz), 142.3, 136.9 (d, J_{C-F} =3.0 Hz), 133.4 (d, J_{C-F} = 3.0 Hz), 130.04 (d, J_{C-F} = 8.0 Hz), 130.2 (d, J_{C-F} = 8.0 Hz), 125.3, 40.4, 31.4, 27.5, 22.5, 14.0.

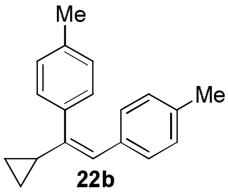
❖ **(E)-1-(2-Kgɘ ɚɞ´ ɟ ɞ´ gɚɞɓɘɜgɚɞ)-4-ɛ Ůdgɚɞɓ Ǖɕɧɚɘɞ (22a)**



22a

^{1}H NMR (300 MHz, $CDCl_3$): 7.20 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.44 (d, *J* = 16 Hz, 1H), 5.68 (dd, J_1 = 16.0 Hz, J_2 = 8.0 Hz, 1H), 2.32 (s, 3H), 1.61-1.49 (m, 1H), 0.83-0.77 (m, 2H), 0.51-0.46 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): 136.2, 135.0, 133.8, 129.2, 127.3, 125.5, 21.1, 14.4, 7.1.

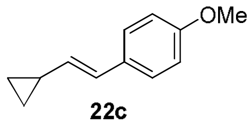
❖ **(Z)-4,4ȭ-(1-Kgə əɞ´ ɟ ɞ´ gəɞŬɘɗŮɜ-1,2-ŭɘgəɞ)ŭɘʛ(ɛ Ůɗgəɞɓ Ůɜɕɧəɘɞ) (22b)**



22b

^{1}H NMR (300 MHz, $CDCl_3$): 7.11 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.88 (d, *J* = 8.0 Hz, 2H), 6.78 (d, *J* = 8.0 Hz, 2H), 6.36 (s, 1H), 2.35 (s, 3H), 2.22 (s, 3H), 1.74-1.67 (m, 1H), 0.75-0.68 (m, 2H), 0.57-0.52 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): 143.0, 137.2, 136.5, 135.5, 134.7, 129.1, 128.8, 128.7, 128.5, 124.3, 21.2, 21.0, 20.1, 5.6.

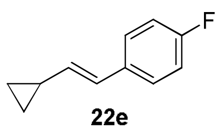
❖ **(E)-1-(2-Kgə əɞ´ ɟ ɞ´ gəɞɓɘɜgəɞ)-4-ɛ Ůɗɞɜɡɓ Ůɜɕɧəɘɞ (22c)**



22c

^{1}H NMR (300 MHz, $CDCl_3$): 7.22 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 6.41 (d, *J* = 16.0 Hz, 1H), 5.60 (dd, J_1 = 16.0 Hz, J_2 = 9.0 Hz), 3.80 (s, 3H), 1.62-1.48 (m, 1H), 0.82-0.76 (m, 2H), 0.50-0.45 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): 158.5, 132.6, 130.7, 126.8, 126.6, 113.9, 55.3, 14.3, 7.1.

❖ **(E)-1-(2-Kgə əɞ´ ɟ ɞ´ gəɞɓɘɜgəɞ)-4-ɛ Ůɗɞɜɡɓ Ůɜɕɧəɘɞ (22e)**

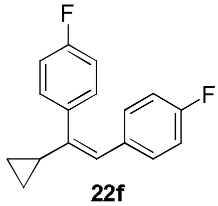


22e

^{1}H NMR (300 MHz, $CDCl_3$): 7.27-7.22 (m, 2H), 6.99-6.93 (m, 2H), 6.42 (d, *J* = 16.0 Hz, 1H), 5.64 (dd, J_1 = 16 Hz, J_2 = 9.0 Hz, 1H), 1.58-1.51 (m, 1H), 0.90-0.78

(m, 2H), 0.52-0.47 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): 161.7 (d, J_{C-F} = 244.0 Hz), 134.6 (d, J_{C-F} = 2.0 Hz), 134.0 (d, J_{C-F} = 3.0 Hz), 126.9 (d, J_{C-F} = 8.0 Hz), 126.2, 115.3 (d, J_{C-F} = 21.0 Hz), 14.4, 7.2.

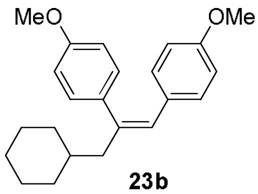
❖ **(Z)-4,4õ-(1-Kgə ɘɞ´ ɟ ɞ´ gəǓɘdǕɜ-1,2-ŭɘgəɞ)ŭɘɠ(ű dɞɟ ɞɓǕɜɕɧəɘɞ) (22f)**



22f

^{1}H NMR (300 MHz, $CDCl_3$): 7.15-7.01 (m, 2H), 7.02-6.97 (m, 2H), 6.84-6.73 (m, 4H), 6.38 (s, 1H), 1.72-1.65 (m, 1H), 0.79-0.72 (m, 2H), 0.57-0.52(m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): 160.4, 133.3, 130.6 (d, J_{C-F} = 8.0 Hz), 130.3 (d, J_{C-F} = 8.0 Hz), 123.8, 115.4 (d, J_{C-F} = 21.0 Hz), 114.8 (d, J_{C-F} = 21.0 Hz), 19.8, 5.7.

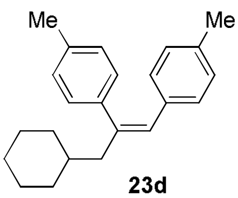
❖ **(Z)-4,4-(3-Kgə ɘɞǕɜgəɞ´ ɟ ɞ´ -1-Ǖɜ-1,2-ŭɘgəɞ)ŭɘɠ(ɛ Ǖdɞɜgɓ Ǖɜɕɧəɘɞ)**



23b

^{1}H NMR (300 MHz, $CDCl_3$): 7.07 (d, J = 8.5 Hz, 2H), 6.84 (t, J = 8.5 Hz, 4H), 6.63 (d, J = 8.5 Hz, 2H), 6.29 (s, 1H), 3.82 (s, 3H), 3.73 (s, 3H), 2.32 (d, J = 7.0 Hz, 2H), 1.78-1.59 (m, 5H), 1.32-1.13 (m, 4H), 0.95-0.83 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): 158.3, 157.7, 139.5, 133.8, 130.0, 129.7, 127.7, 126.5, 113.9, 113.2, 55.1, 55.0, 49.0, 35.2, 33.2, 26.6, 26.2.

❖ **(Z)-4,4-(3-Kgə ɘɞǕɜgəɞ´ ɟ ɞ´ -1-Ǖɜ-1,2-ŭɘgəɞ)ŭɘɠ(ɛ Ǖdgəɞ ɓǕɜɕɧəɘɞ)**



23d

^{1}H NMR (300 MHz, $CDCl_3$): 7.10 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 8.0 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 2H), 6.35 (s, 1H), 2.35 (s, 3H), 2.34 (d, *J* = 7.0 Hz, 2H), 2.23(s, 3H), 1.76-1.61 (m, 5H), 1.32-1.13 (m, 4H), 0.99-0.83 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): 140.9, 138.6, 136.2, 135.5, 134.8, 129.1, 128.8, 128.5, 128.4, 127.1, 49.0, 35.2, 33.2, 26.6, 26.2, 21.2, 21.0.

dbŁdbş ŁB ũ Λȷ ū Łȷ

1. Hashmi, S. *Chem. Rev.* **2007**, *107*, 3180.
2. Corma, A.; Garcia H. *Chem. Soc. Rev.* **2008**, *37*, 2096.
3. Pina, C.; Falletta, E.; Prati, L.; Rossie, M. *Chem. Soc. Rev.* **2008**, *37*, 2077.
4. Hashmi, S.; Hutchings, G. *Angew. Chem. Int. Ed.* **2006**, *45*, 7896.
5. Arcadi, A. *Chem. Rev.* **2008**, *108*, 3266.
6. Li, Z.; Brouwer, C.; He, C. *Chem. Rev.* **2008**, *108*, 3239.
7. Nunez, E.; Echavarren A. *Chem. Rev.* **2008**, *108*, 3326.
8. Gorin, D.; Sherry, B.; Toste, F. *Chem. Rev.* **2008**, *108*, 3351.
9. Bandini, M.; Emer, E.; Tommassi, S.; Umani-Ronchi, A. *Eur. J. Org. Chem* **2006**, 3527.
10. Furstner, A.; Davies, P. *Angew. Chem. Int. Ed.* **2007**, *46*, 3410.
11. a) Stratakis, M.; Garcia, H. *Chem. Rev.* **2012**, *112*, 4469.
    b) Zhang, Y.; Cui, X.; Shi, F.; Deng, Y. *Chem. Rev.* **2012**, *112*, 2467.
12. Biella, S.; Prati, L.; Rosii, M. *J. Mol. Catal. Chem.* **2003**, *197*, 207.
13. Enache, D.; Edwards, J.; Landon, P.; Solsona, B.; Carley, A.; Herzing, A.; Watanabe, M.; Kiely, C.; Knight, D.; Hutchings, G. *Science* **2006**, *311*, 362.
14. Rossignol, C.; Arrii, S.; Morfin, F.; Piccollo, L.; Caps, V.; Roussset, J. *J. Catal.* **2005**, *230*, 476.
15. Carrettin, S.; Concepcion, P.; Corma, A.; Nieto, J.; Puntes, V. *Angew. Chem. Int. Ed.* **2004**, *43*, 2538.
16. Huang, J.; Dai, W.; Li, H.; Fan, K. *J. Catal.* **2007**, *252*, 69.
17. Hayashi, T.; Tanaka, K.; Haruta, M. *J. Catal.* **1998**, *178*, 566.
18. Fierro-Gonzaleza, J. C.; Gates, B. C. *Chem. Soc. Rev.* **2008**, 2127.
19. Kohyama, M.; Haruta, M.; Maeda, Y.; Ichikawa, S.; Okazaki, K. *Appl. Catal. A.* **2005**, *291*, 45.
20. Valen, M.; Lai, X.; Goodman, D. *Science* **1998**, *281*, 1647.
21. Abad, A.; Almela, C.; Corma, A.; Garcia, H. *Tetrahedron* **2006**, *62*, 6666.
22. Abad, A.; Almela, C.; Corma, A. Garcia, H. *Pure Appl. Chem.* **2007**, *79*, 184.
23. Abad, A.; Almela, C.; Corma, A. Garcia, H. *Chem. Commun.* **2006**, 3178.
24. Comotti, M.; Della Pina, D.; Matarrese R.; Rossi, M. *Angew. Chem. Int. Ed.* **2004**, *43*, 5812.
25. Corma, A.; Domine, M. *Chem. Commun.* **2005**, 4042.

26. Biella, S.; Prati, L.; Rossi, M. *J. Mol. Catal. A: Chem*. **2003**, *197*, 207.
27. Taylor, B.; Lauterbach, J.; Delgass, W. *Appl. Catal. A*. **2005**, *291*, 188.
28. Cumaranatunge, L.; Delgass, W. *J. Catal.* **2005**, *232*, 38.
29. Hayashi, T.; Wada, M.; Haruta, M.; Tsubota, M. *Jpn. Pat*. **1998**, 103, 30291.
30. Alvaro, M.; Aprile, C.; Corma, A.; Ferrer, B.; Garcia, H. *J. Catal*. **2007**, *245*, 249
31. Carrettin, S.; Hao, Y.; Aguilar-Guerrero, V.; Gates, B.; Trasobares, S.; Calvino, J.; Corma, A. *Chem. Eur. J*. **2007**, *13*, 7771.
32. Flistrup, R.; Johansen, L.; Christensen, C. *Chem. Commun.* **2008**, 2750.
33. Xu, Y.; Landon, P.; Enache, D.; Carley, A.; Roberts, M.; Hutchings, G. *Catal. Lett*. **2005**, *101*, 175.
34. Weissermel, K.; Harpe, H.; *Industrial Organic Chemistry*, 4th edn, Wiley-VCH, Weinheim, **2003**.
35. Hughes, D.; Xu, Y.; Jenkins, P.; McMorn, P.; Landon, P.; Enache, D.; Carley, A.; Attard, G.; Hutchings, G.; King, F.; Stitt, E.; Johnston, P.; Griffin, K.; Kiely, C. *Nature* **2005**, *437*, 1132.
36. Lignier, P.; Morfin, F.; Mangematin, S.; Massin, L.; Rousset, L.; Caps, V. . *Chem. Commun*. **2007**, 186.
37. Lignier, P.; Morfin, F.; Piccolo, L.; Rousset, J.; Caps, V. *Catal. Today* **2007**, 122, 284.
38. Biella, S.; Prati, L.; Rossi, M. *J. Catal*. **2006**, *206*, 242.
39. Raptis, C.; Garcia, H.; Stratakis, M. *Angew. Chem. Int. Ed.* **2009**, *48*, 3133.
40. Yasuda, A.; Tanaka, S.; Oshima, K.; Yamamoto, H.; Nozaki, H. *J. Am. Chem. Soc.* **1974**, *96*, 6513.
41. Larock, R. C. Comprehensive Organic Transformations, Wiley, New York, 1999, p. 272.
42. Mitsudome, T.; Noujima, A.; Mikami, Y.; Mizugaki, T.; Jitsukawa, K.; Kaneda, K. *Angew. Chem. Int. Ed.* **2010**, *49*, 5545.
43. Kaneda, K.; Mitsudome, T.; Mizugaki, T.; Jitsukawa, K. *Molecules* **2010**, *15*, 8988.
44. Noujima, A.; Mitsudome, T.; Mizugaki, T.; Jitsukawa, K.; Kaneda, K. *Molecules* **2011**, *16*, 8209.
45. Mitsudome, T.; Noujima, A.; Mikami, Y.; Mizugaki, T.; Jitsukawa, K.; Kaneda, K. *Chem. Eur. J.* **2010**, *16*, 11818

46. Ni, J.; He, L.; Liu, Y.-M.; Cao, Y.; He, H.-Y.; Fan, K.-N. *Chem. Commun.* **2011**, *47*, 812.

47. Noujima, A.; Mitsudome, T.; Mizugaki, T.; Jitsukawa, K.; Kaneda, K. *Angew. Chem. Int. Ed.* **2011**, *50*, 2986.

48. Xiang, D.; Liu, X.; Sun, J.; Xiao, F.-S.; Sun, J. *Catal. Today* **2009**, *148*, 383.

49. Naya, K.; Ishikawa, R.; Fukui, K.-I. *J. Phys. Chem. C* **2009**, *113*, 10726.

50. Chiorino, A.; Manzoli, M.; Menegazzo, F.; Signoretto, M.; Vindigni, F.; Pinna, F.; Boccuzzi, F. *J. Catal.* **2009**, *262*, 169.

51. Manzoli, M.; Boccuzzi, F.; Chiorino, A.; Vindigni, F.; Vindigni, F.; Deng, W.; Flytzani-Stephanopoulos, M. *J. Catal.* **2007**, *245*, 308.

52. Brown, M. A.; Ringleb, F.; Fujimori, Y.; Sterrer, M.; Freund, H.-J.; Preda, G.; Pacchioni, G. *J. Phys. Chem. C* **2011**, *115*, 10114.

53. Goguet, A.; Ace, M.; Saih, Y.; Sa, J.; Kavanagh, J.; Hardacre, C. *Chem. Commun.* **2009**, 4889.

54. Ono, L. K.; Cuenya, B. R. *J. Phys. Chem. C* **2008**, *112*, 4676.

55. Fu, L.; Wu, N. Q.; Yang, J. H.; Qu, F.; Johnson, D. L.; Kung, M. C.; Kung, H. H.; Dravid, V. P. *J. Phys. Chem. B* **2005**, *109*, 3704.

56. Concepcion, P.; Carrettin, S.; Corma, A. *Appl. Catal. A* **2006**, *307*, 42.

57. Klimev, H.; Fajerwerg, K.; Chakarova, K.; Delannoy, L.; Louis, C.; Hadjiivanov, K. *J. Mater. Sci.* **2007**, *42*, 3299.

58. Gorin, D. J.; Toste, F. D. *Nature* **2007**, *446*, 395.

59. Hashmi, A. S. K. *Chem. Rev.* **2007**, *107*, 3180.

60. Jimenez-Nunez, E.; Echavarren, A. M. *Chem. Rev.* **2008**, *108*, 3326.

61. Gorin, D. J.; Sherry, B. D.; Toste, F. D. *Chem. Rev.* **2008**, *108*, 3351.

62. Li, Z.; Brouwer, C.; He, C. *Chem. Rev.* **2008**, *108*, 3239.

63. Arcadi, A. *Chem. Rev.* **2008**, *108*, 3266.

64. Muzart, J. *Tetrahedron* **2008**, *64*, 5815.

65. Shen, H. C. *Tetrahedron* **2008**, *64*, 3885.

66. Yamamoto, Y.; Gridnev, I. D.; Patil, N. T.; Jin, T. *Chem. Commun.* **2009**, 5075.

67. Furstner, A. *Chem. Soc. Rev.* **2009**, *38*, 3208.

68. Shapiro, N. D.; Toste, F. D. *Synlett* **2010**, 675.

69. Hashmi, A. S. K. *Angew. Chem. Int. Ed.* **2010**, *49*, 5232.

70. Boorman, T. C.; Larrosa, I. *Chem. Soc. Rev.* **2011**, *40*, 1910.

71. Bandini, M. *Chem. Soc. Rev.* **2011**, *40*, 1358.

72. Corma, A.; Leyva-Perez, A.; Sabater, M. J. *Chem. Rev.* **2011**, *111*, 1657.

73. Aubert, C.; Fensterbank, L.; Garcia, P.; Malacria, M.; Simonneau, A. *Chem. Rev.* **2011**, *111*, 1954.

74. Lykakis, I. N.; Efe, C.; Gryparis, C.; Stratakis, M. *Eur. J. Org. Chem.* **2011**, 2334.

75. Menon, R. S.; Findlay, A. D.; Bissember, A. C.; Banwell, M. G. *J. Org. Chem.* **2009**, *74*, 8901.

76. Nevado, C.; Echavarren, A. M. *Chem. Eur. J.* **2005**, *11*, 3155

77. Garcia-Mota, M.; Cabello, N.; Maseras, F.; Echavarren, A. M.; Perez-Ramirez, J.; Lopez, N. *ChemPhysChem* **2008**, *9*, 1624.

78. Carrettin, S.; Blanco, M. C.; Corma, A.; Hashmi, A. S. K. *Adv. Synth. Catal.* **2006**, *348*, 1283.

79 Hashmi, A. S. K.; Frost, T. M.; Bats, J. W. *J. Am. Chem. Soc.* **2000**, *122*, 11553.

80. Hashmi, A. S. K.; Rudolph, M.; Siehl, H.-U.; Tanaka, M.; Bats, J. W.; Frey, W. *Chem. Eur. J.* **2008**, *14*, 3703.

81 Abad, A.; Corma, A.; Garcia, H. *Top. Catal.* **2007**, *44*, 237.

82. Wei, C.; Li, C.-J. *J. Am. Chem. Soc.* **2003**, *125*, 9584.

83. Zhang, X.; Corma, A. *Angew. Chem. Int. Ed.* **2008**, *47*, 4358.

84. Marciniec, B.; Maciejewski, H.; Pietraszuk, C.; Pawluc, P. in: *Hydrosilylation: A Comprehensive Review on Recent Advances*, (Eds.: B. Marciniec), Advances in Silicon Science Series, *Vol.* 1, Springer, 2009.

85. Trost, B. M.; Ball, Z. T. *Synthesis* **2005**, 853.

86. Roy, A. K. *Adv. Organometal. Chem.* **2008**, *55*, 1.

87. Langkopf, E.; Schinzer, D. *Chem. Rev.* **1995**, *95*, 1375.

88. Corey, J. Y. *Chem. Rev.* **2011**, *111*, 863.

89. Caporusso, A. M.; Aronica, L. A.; Schiavi, E.; Martra, G.; Vitulli, G.; Salvadori, P. *J. Organomet. Chem.* **2005**, *690*, 1063.

90. Corma, A.; Gonzalez-Arellano, C.; Iglesias, M.; Sanchez, F. *Angew. Chem. Int. Ed.* **2007**, *46*, 7820.

91. Psyllaki, A.; Lykakis, I. N.; Stratakis, M. *Tetrahedron* **2012**, *68*, 8724.

92. Lykakis, I. N.; Psyllaki, A.; Stratakis, M. *J. Am. Chem. Soc.* **2011**, *133*, 10426

93. Denmark, S. E.; Wang, Z. *Org. Lett.* **2001**, *3*, 1073.

94. Tanaka, M.; Uchimaru, Y.; Lautenschlager, H.-J. *Organometallics* **1991**, *10*, 16.

95. Phan, S. T.; Lim, W. C.; Han, J. S.; Yoo, B. R.; Jung, I. N. *Organometallics* **2004**, *23*, 169.

96. Bailie, J. E.; Hutchings, G. J. *Chem. Commun.* **1999**, 2151.

97. Bailie, J. E.; Abdullah, H. A.; Anderson, J. A.; Rochester, C. H.; Richardson, N. V.; Hodge, N.; Zhang, J.-G.; Burrows, A.; Kiely, C. J.; Hutchings, G. J. *Phys. Chem. Chem. Phys.* **2001**, *3*, 4113.

98. Zhu, Y.; Qian, H.; Drake, B. A.; Jin, R. *Angew. Chem. Int. Ed.* **2010**, *49*, 1295.

99. Wang, C.-M.; Fan, K.-N.; Liu, Z.-P. *J. Catal.* **2009**, *266*, 343.

100. Mertens, P. G. N.; Poelman, H.; Ye, X.; Vankelecom, I. F. J.; Jacobs, P.A.; De Vos, D. E. *Catal. Today* **2007**, *122*, 352.

101. Mertens, P. G. N.; Vandezande, P.; Ye, X.; Poelman, H.; Vankelecom, I. F. J.; De Vos, D. E. *Appl. Catal., A* **2009**, *355*, 176.

102. You, K.-J.; Chang, C.-T.; Liaw, B.-J.; Huang, C.-T.; Chen, Y.-Z. *Appl. Catal., A* **2009**, *361*, 65.

103. Wang, M.-M.; He, L.; Liu, Y.-M.; Cao, Y.; He, H.-Y.; Fan, K.-N. *Green Chem.* **2011**, *13*, 602.

104. Corma, A.; Serna, P. *Science* **2006**, *313*, 332.

105. Corma, A.; Serna, P. *Nat. Protoc.* **2006**, *1*, 2590.

106. Corma, A.; Gonzalez-Arellano, C.; Iglesias, M.; Sanchez, F. *Appl. Catal., A* **2009**, *356*, 99.

107. Grirrane, A.; Corma, A.; Garcia, H. *Science* **2008**, *322*, 1661.

108. Serna, P.; Concepcion, P.; Corma, A. *J. Catal.* **2009**, *265*, 19.

109. Corma, A.; Concepcion, P.; Serna, P. *Angew. Chem. Int. Ed.* **2007**, *46*, 7266.

110. Corma, A.; Serna, P.; Garcia, H. *J. Am. Chem. Soc.* **2007**, *129*, 6358.

111. Ikariya, T.; Blacker, A. J. *Acc. Chem. Res.* **2007**, *40*, 1300.

112. Gladiali, S.; Alberico, E. *Chem. Soc. Rev.* **2006**, *35*, 226.

113. Su, F.-Z.; He, L.; Ni, J.; Cao, Y.; He, H.-Y.; Fan, K.-N. *Chem. Commun.* **2008**, 3531.

114. He, L.; Wang, L.-C.; Hao, H.; Ni, J.; Cao, Y.; He, H.-Y.; Fan, K.-N. *Angew. Chem. Int. Ed.* **2009**, *48*, 9538.

115. Liu, L.; Qiao, B.; Chen, Z.; Zhang, J.; Deng, Y. *Chem. Commun.* **2009**, 653.

116. Peng, Q.; Zhang, Y.; Shi, F.; Deng, Y. *Chem. Commun.* **2011**, *47*, 6476.

117. Zhu, H.; Ke, X.; Yang, X.; Sarina, S.; Liu, H. *Angew. Chem. Int. Ed.* **2010**, *49*, 9657.

118. Zhu, H.; Chen, X.; Zheng, Z.; Ke, X.; Jaatinen, E.; Zhao, J.; Guo, C.; Xie, T.; Wang, D. *Chem. Commun.* **2009**, 7524.

119. Vankayala, R.; Sagadevan, S.; Vijayaraghavan, P.; Kuo, C.-L.; Hwang, K. C. *Angew. Chem. Int. Ed.* **2011**, *50*, 10640.

120. Praharaj, S.; Nath, S.; Ghosh, S. K.; Kundu, S.; Pal, T. *Langmuir* **2004**, *20*, 9889.

121. Kumar, S. S.; Kumar, C. S.; Mathiyarasu, J.; Phani, K. L. *Langmuir* **2007**, *23*, 3401.

122. Yan, N.; Zhang, J.; Yuan, Y.; Chen, G.-T.; Dyson, P. J. Li, Z.-C.; Kou, Y. *Chem. Commun.* **2010**, *46*, 1631.

123. Kalidindi, S. B.; Jagirdar, B. R. *ChemSusChem* **2012**, *5*, 65.

124. Chandra, M.; Xu, Q. *J. Power Sources* **2007**, *168*, 135.

125. Jiang, H.-L.; Umegaki, T.; Akita, T.; Zhang, X.-B.; Haruta, M.; Xu, Q. *Chem. Eur. J.* **2010**, *16*, 3132.

126. Gonzalez-Arellano, C.; Abad, A.; Corma, A.; Garcia, H.; Iglesias, M.; Sanchez, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 1536.

127. Karimi, B.; Esfahani, F. K. *Chem. Commun.* **2011**, *47*, 10452.

128. a) Tanabe, M.; Osakada, K. *Organometallics* **2010**, *29*, 4702. b) Tanaka, M.; Uchimaru, Y.; Lautenschlager, H.-J. *J. Organometallics* **1991**, *10*, 16. c) Sunada, Y.; Imaoka, T.; Nagashima, H. *Organometallics* **2010**, *29*, 6157.

129. Kotzabasaki, V.; Lykakis, I. N.; Gryparis, C.; Psyllaki, A.; Vasilikogiannaki, E.; Stratakis, M. *Organometallics* **2013**, *32*, 665.

130. Uvarov, V. M.; de Vekki, D. A.; Reshetilovskii, V. P.; Skvortsov, N. K. *Russ. J. Gen. Chem.* **2010**, *80*, 35.

131. Shore, G.; Organ, M. G. *Chem. Eur. J.* **2008**, *14*, 9641.

132. a) Tsuchimoto, T.; Fujii, M.; Iketani, Y.; Sekine, M. *Adv. Synth. Catal.* **2012**, *354*, 2959. b) Kahnes, M.; Gorls, H.; Westerhausen, M. *Organometallics* **2010**, *29*, 3490.

133. Curtis, M. D.; Greene, J. *J. Am. Chem. Soc.* **1979**, *100*, 6362.

134. Sunada, Y.; Fujimura, Y.; Nagashima, H. *Organometallics* **2008**, *27*, 3502.

135. a) Gualco, P.; Ladeira, S.; Miqueu, K.; Amgoune, A.; Bourissou, D. *Angew. Chem. Int. Ed.* **2011**, *50*, 8320. b) Gualco, P.; Ladeira, S.; Miqueu, K.; Amgoune, A.; Bourissou, D. *Organometallics* **2012**, *31*, 6001.

136. a) Yokelson, H. B.; Millevolte, A. J.; Gillette, G. R.; West, R. *J. Am. Chem. Soc.* **1987**, *109,* 6865. b) Boatz, J. A.; Gordon, M. S. *J. Phys. Chem.* **1989**, *93*, 3025.

137. Chenoweth, K.; Chenoweth, D.; Goddard III, W. A. *Org. Biomol. Chem.* **2009**, *7*, 5255.

138. Hiyama, T.; Nakao, Y. *Chem. Soc. Rev.* **2011**, *40*, 4893.

139. a) Hatanaka, Y.; Hiyama, T. *J. Org. Chem.* **1989**, *54*, 268. b) Sugiyama, A.; Ohnishi, Y.; Nakaoka, M.; Nakao, Y.; Sato, H; Sakaki, S.; Hiyama, T. *J. Am. Chem. Soc*. **2008**, *130*, 12975.

140. Hatanaka, Y.; Fukushima, S.; Hiyama, T. *Chem. Lett*. **1989**, 1711.

141. Sore, H. F.; Galloway, W. R. J. D.; Spring, D. R. *Chem. Soc. Rev*. **2012**, *41*, 1845.

142. a) Hatanaka, Y.; Hiyama, T. *J. Org. Chem*. **1988**, *53*, 918. b) Hatanaka, Y.; Hiyama, T. *Synlett.* **1991**, 845.

143. a) Hiyama, T., Sahoo, A. K.; Oda, T.; Nakao, Y. *Adv. Synth.Catal*. **2004**, *346*, 1715. b) Nakao, Y.; Oda, T.; Sahoo, A. K.; Hiyama, T. *J. Organomet. Chem*. **2003**, *687*, 570.

144. Homsi, F.; Hosoi, K.; Nozaki, K.; Hiyama, T. *J. Organomet. Chem*. **2001**, *624*, 208.

145. Li, L.; Navasero, N. *Org. Lett*. **2004**, *6*, 3091.

146. Denmark, S. E; Wehrli, D.; Choi, J. Y. *Org. Lett.*, **2000**, *2*, 2491.

147. Denmark, S. E.; Regens, C. S. *Acc. Chem. Res*. **2008**, *41*, 1486.

148. Denmark, S. E.; Butler, C. R.; *J. Am. Chem. Soc*. **2008**, *130*, 3690.

149. Li, L.; Navasero, N. *Org. Lett*. **2006**, *8*, 3733.

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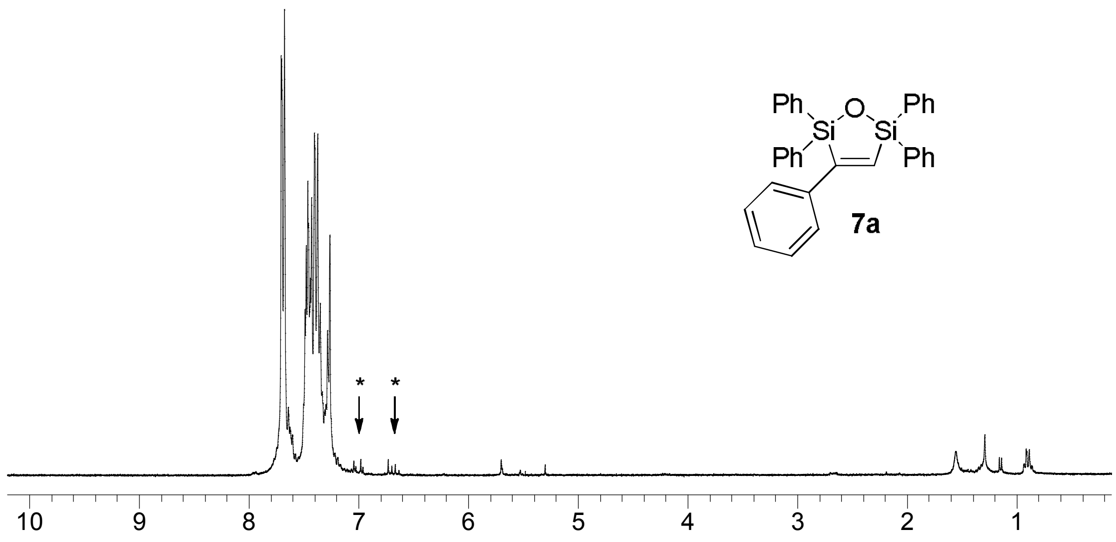
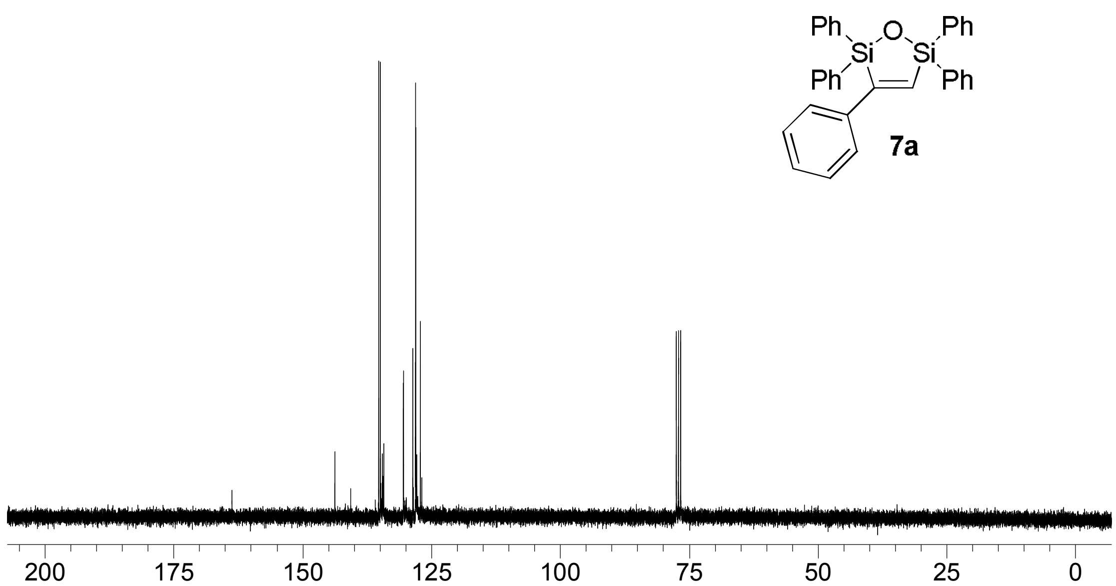
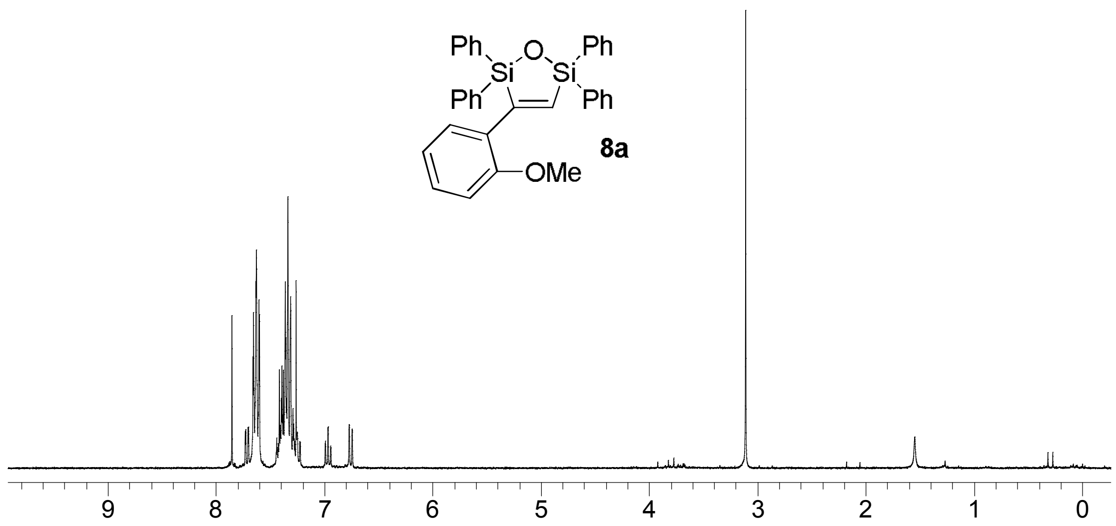


*: hydrosilylation products

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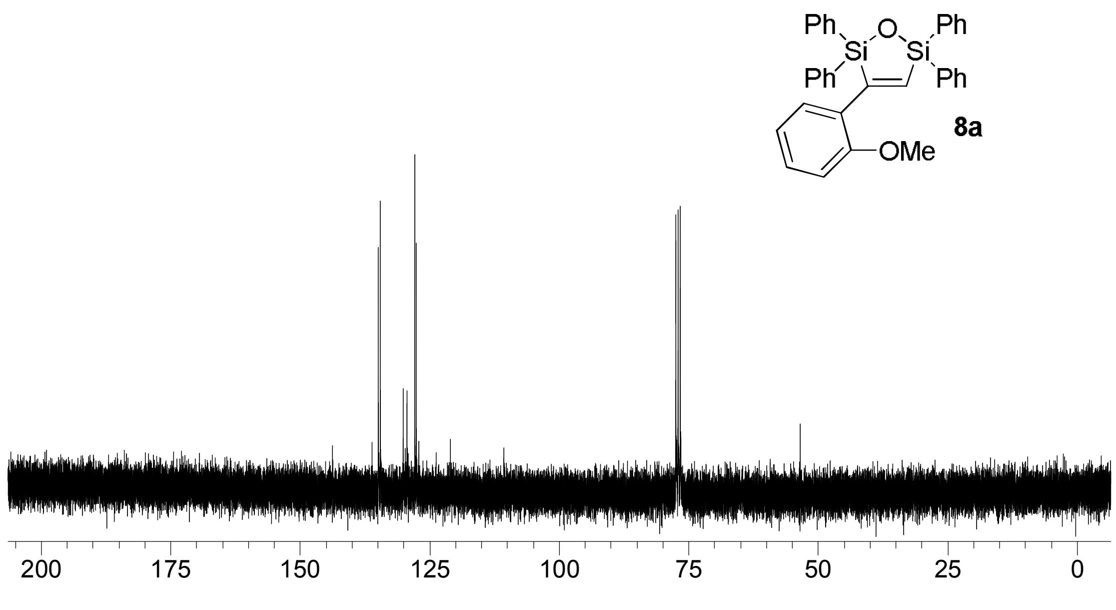
O
Si
Ph
Ph
OMe
8a
9
8
7
6
5
4
3
2
1
0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O
Si
Ph
Ph
OMe
8a
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175
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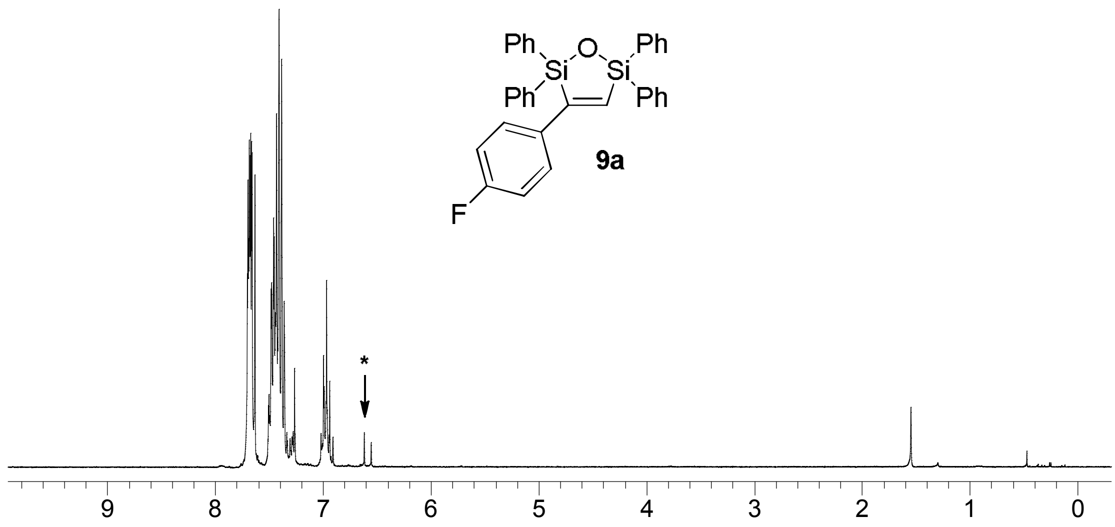
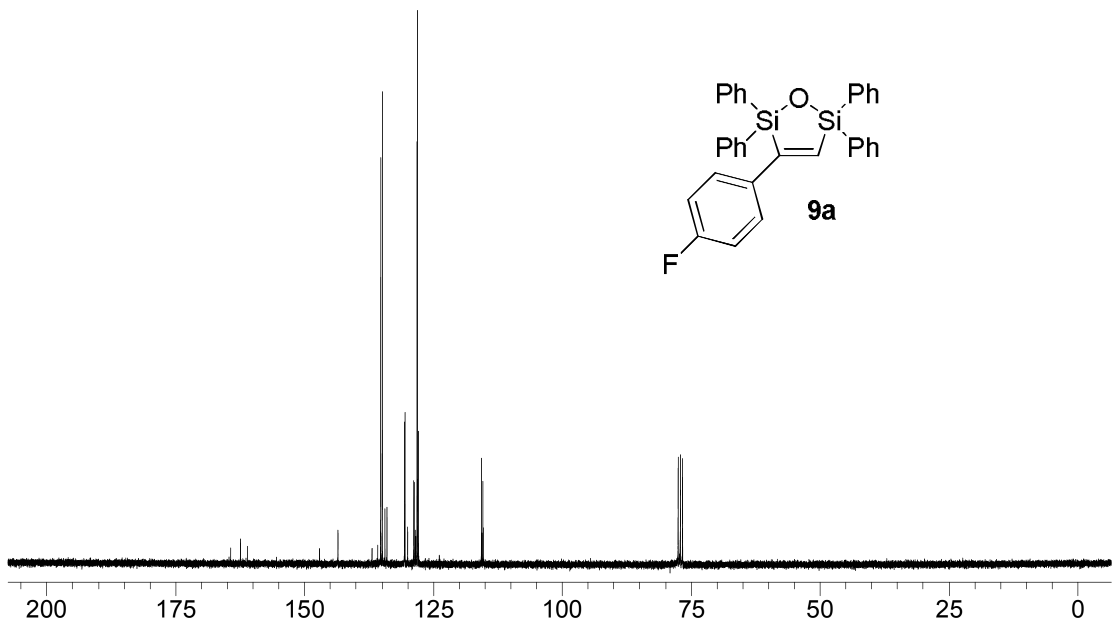
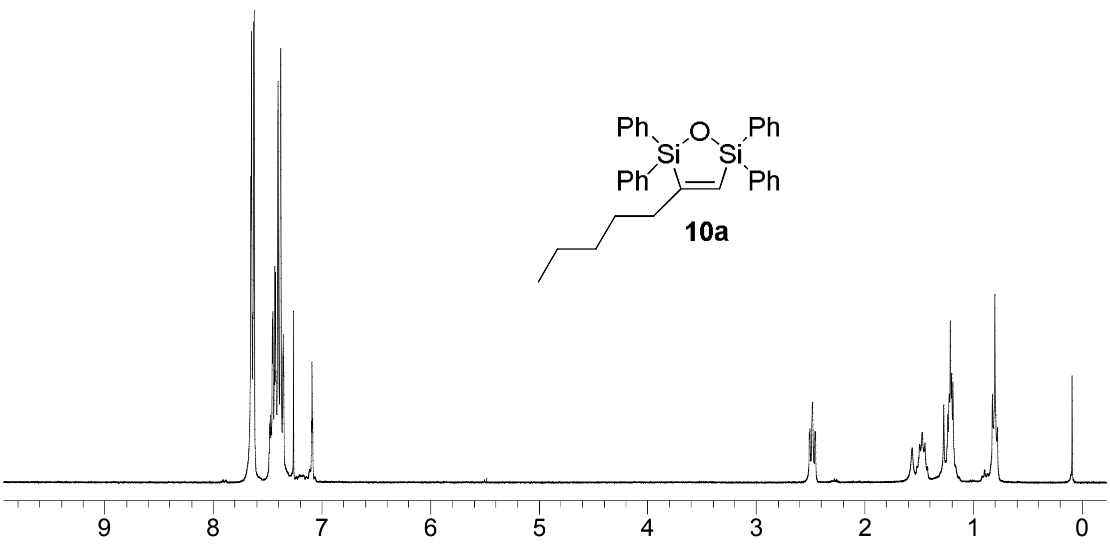
125
100
75
50
25
0



*: hydrosilylation product





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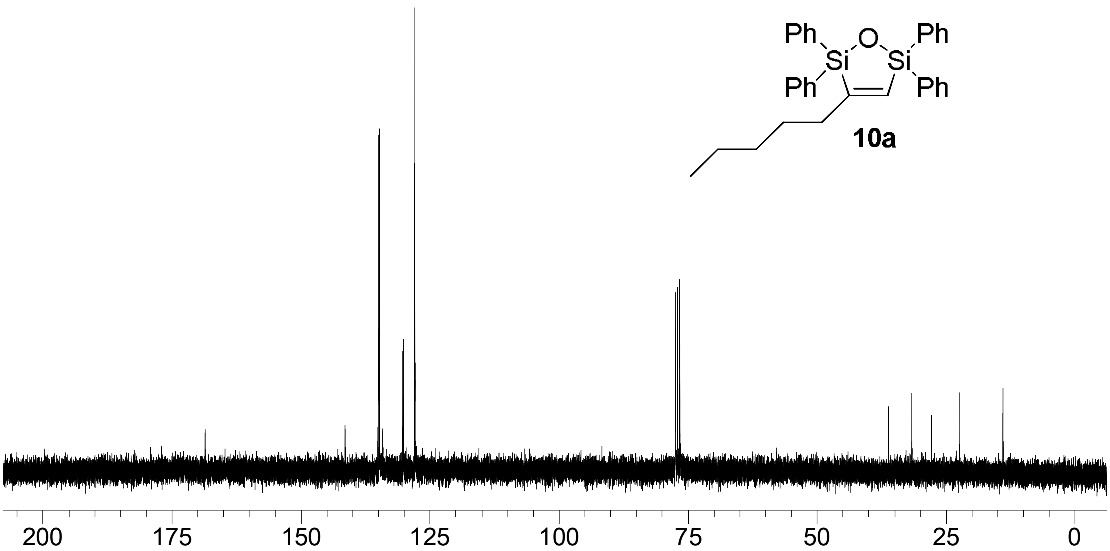
Ph
Si
Si
Ph
Ph
10a
9
8
7
6
5
4
3
2
1
0



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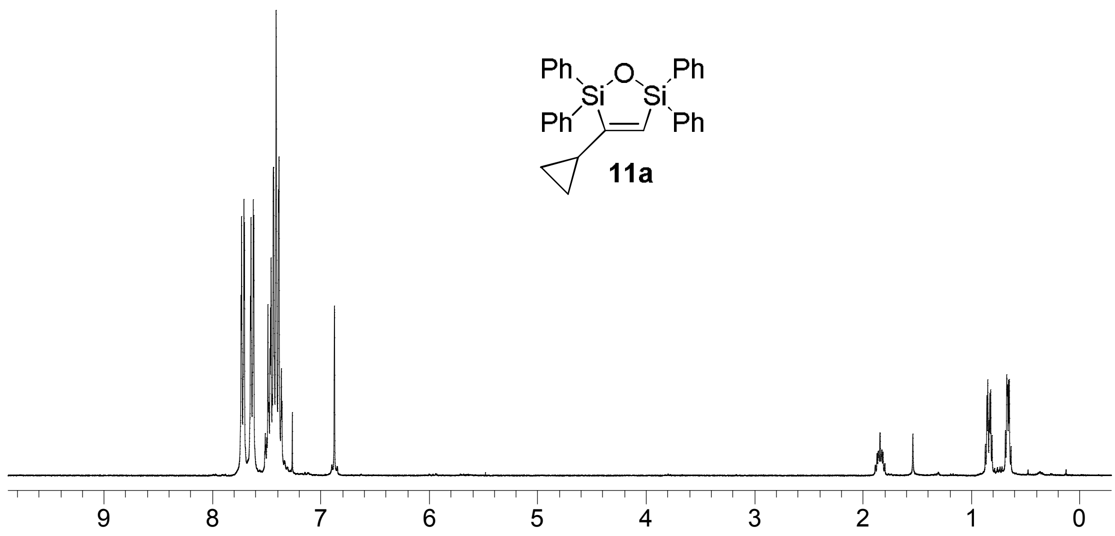
O
Ph
Si
Si
Ph
Ph
10a
200
175
150
125
100
75
50
25
0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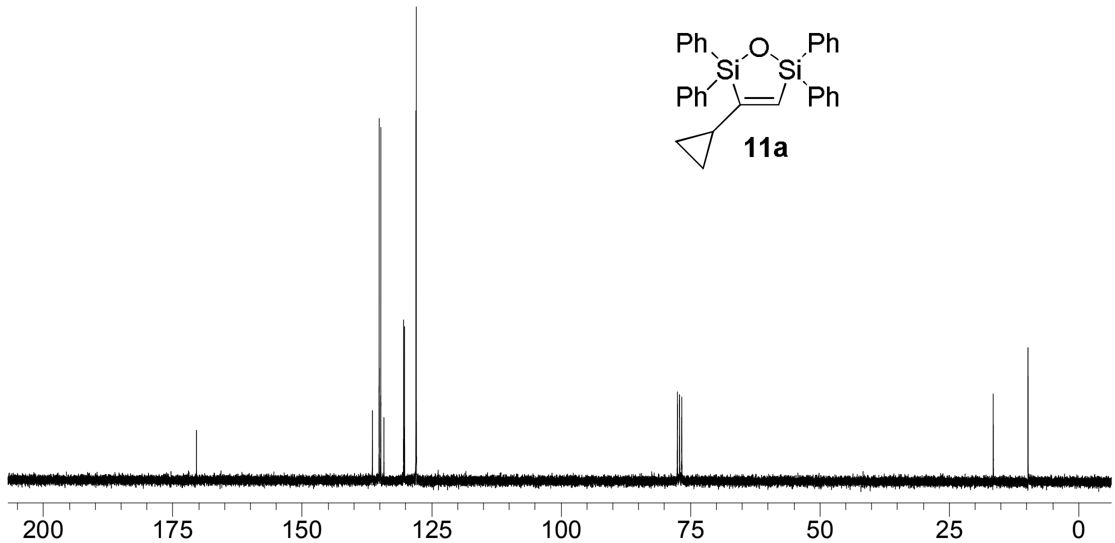
Ph
Si
Si
Ph
Ph
11a
9
8
7
6
5
4
3
2
1
0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Ph
Ph
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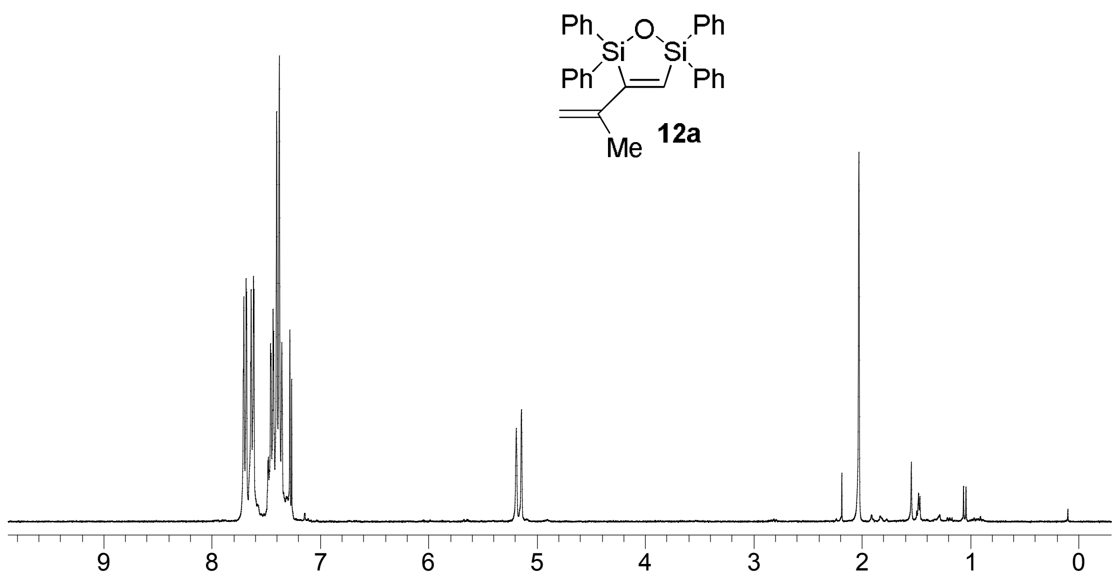
175
150
125
100
75
50
25
0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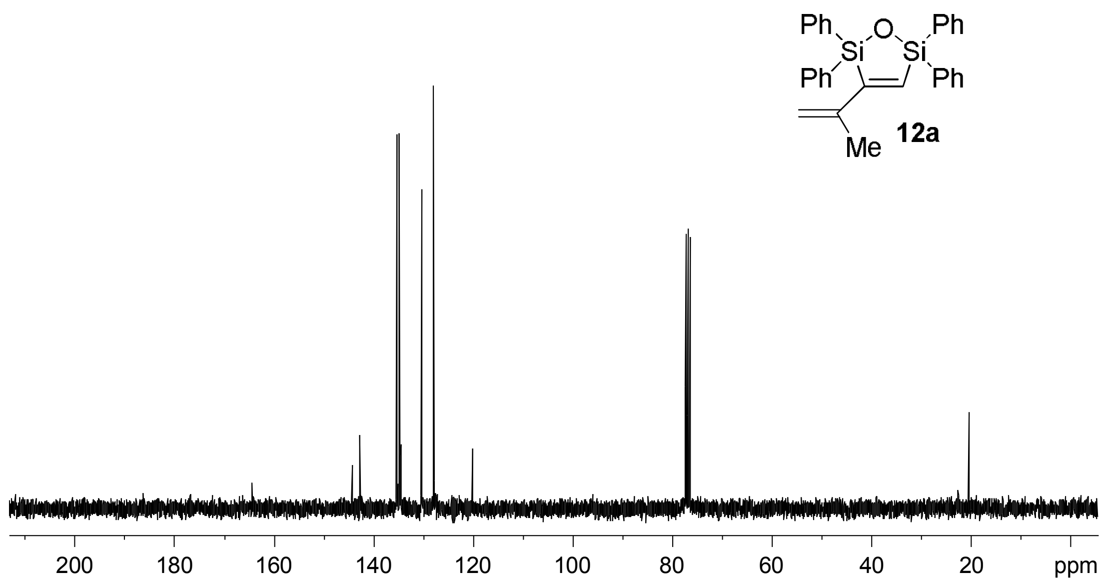
Si
Si
Ph
Ph
Me
12a
9
8
7
6
5
4
3
2
1
0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Si
Ph
Ph
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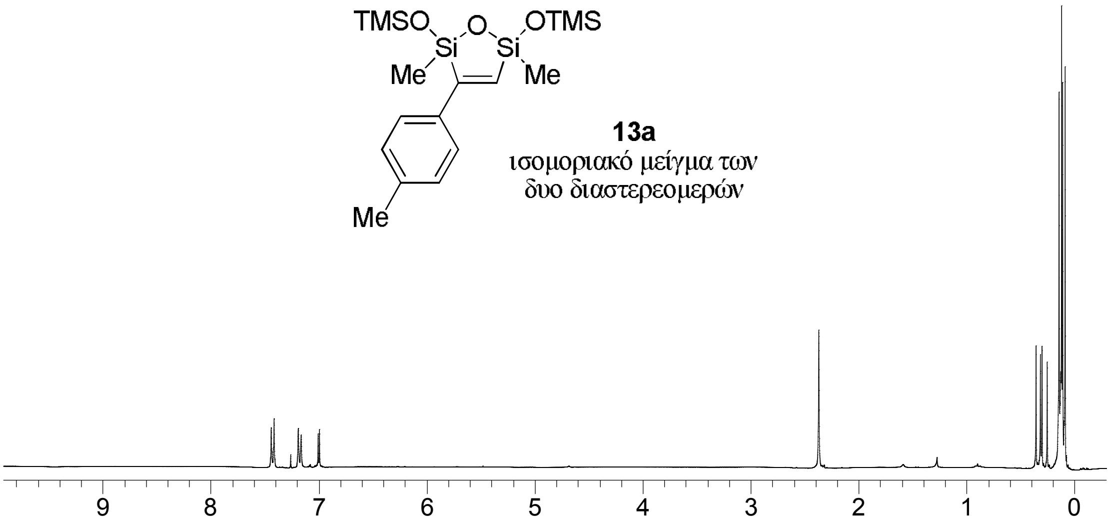
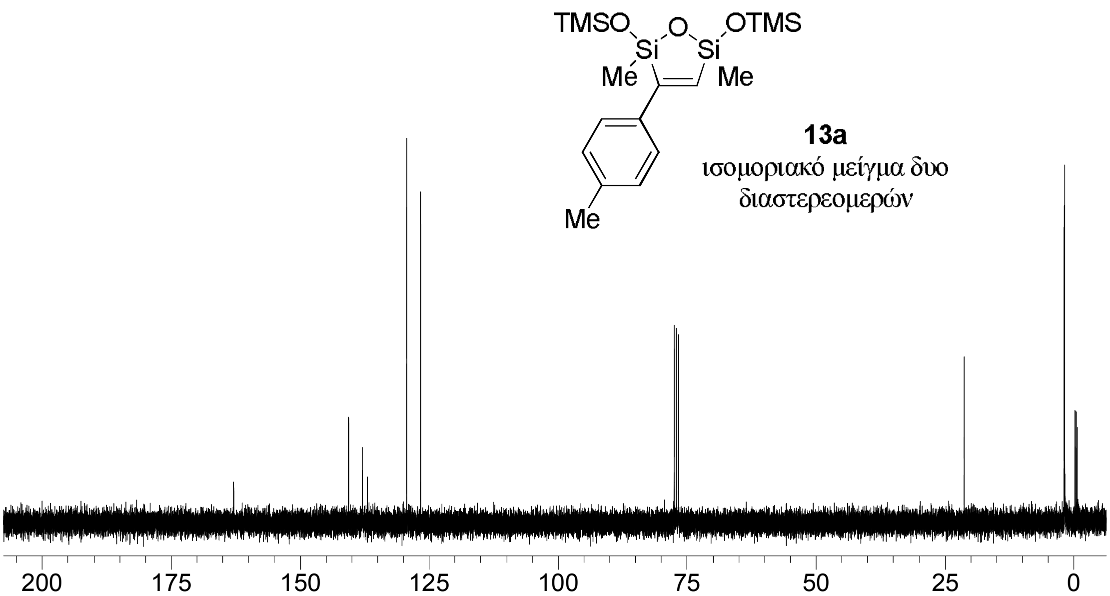
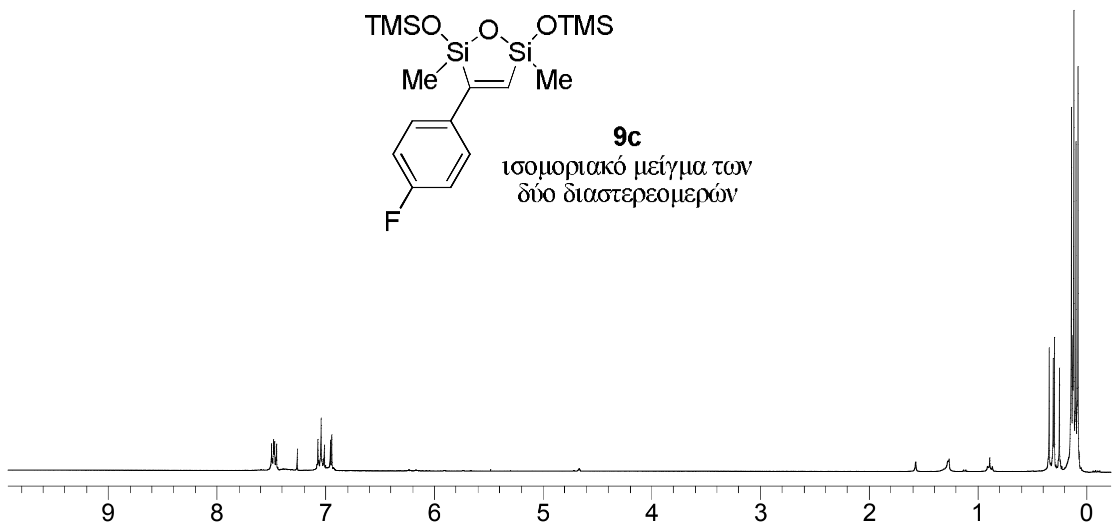
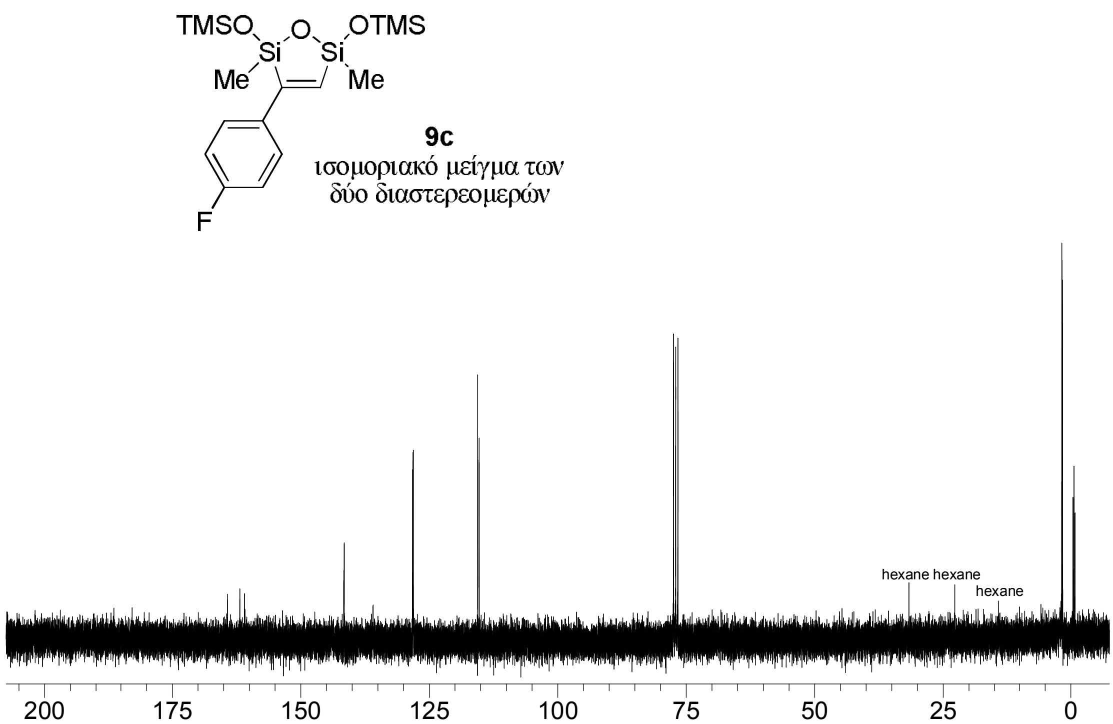
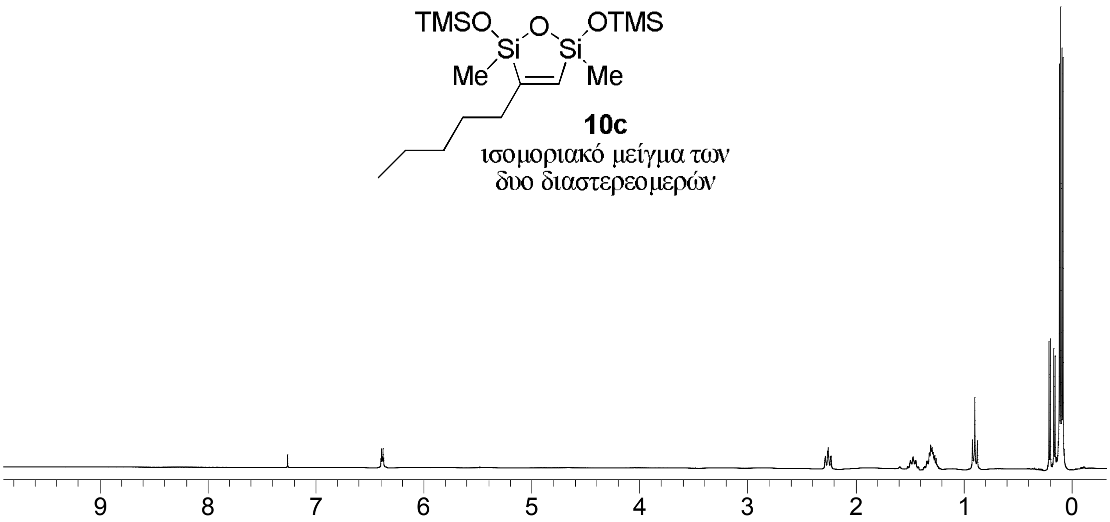
140
120
100
80
60
40
20
ppm

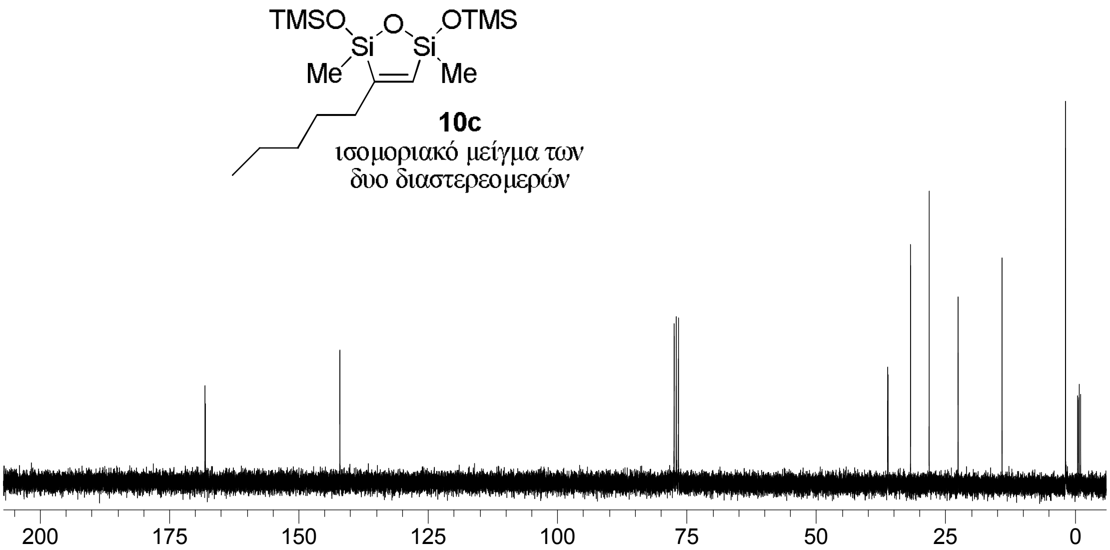

TMSO
O
OTMS
Si
Si
Me
Me
Me
13a
ισομοριακό μείγμα των
δυο διαστερεομερών
9
8
7
6
5
4
3
2
1
0

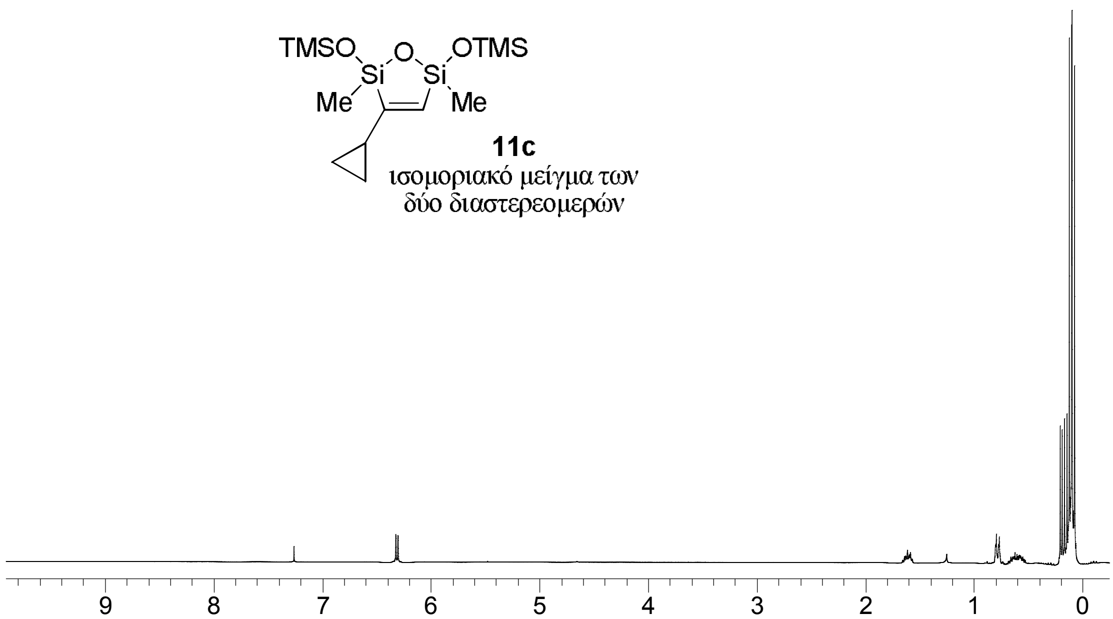

TMSO
O
OTMS
Si
Si
Me
Me
Me
13a
ισομοριακό μείγμα δυο
διαστερεομερών
200
175
150
125
100
75
50
25
0

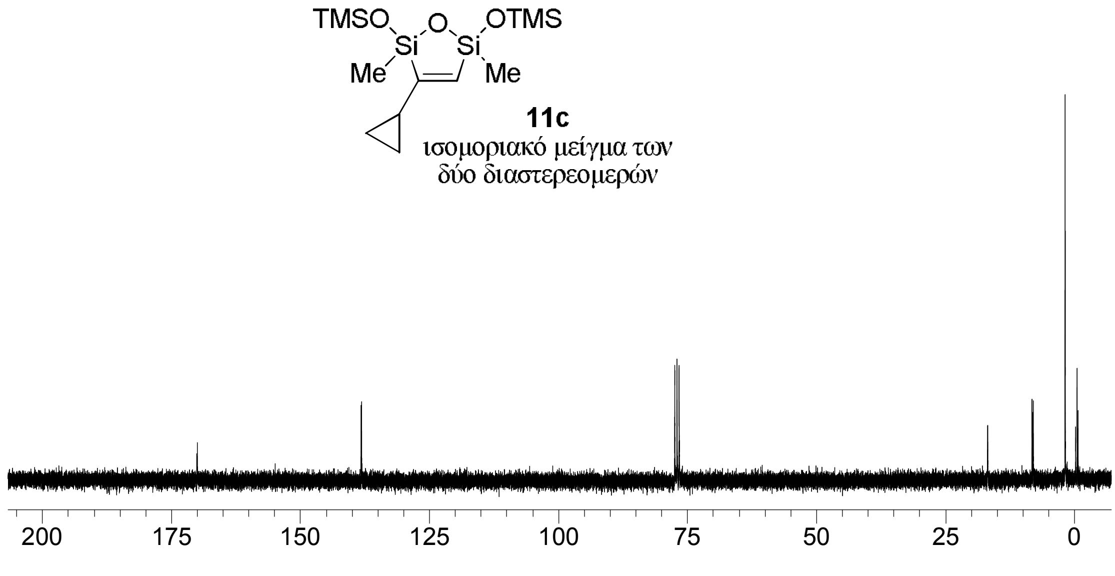

TMSO
O
OTMS
Si
Si
Me
Me
F
9c
ισομοριακό μείγμα των
δύο διαστερεομερών
9
8
7
6
5
4
3
2
1
0

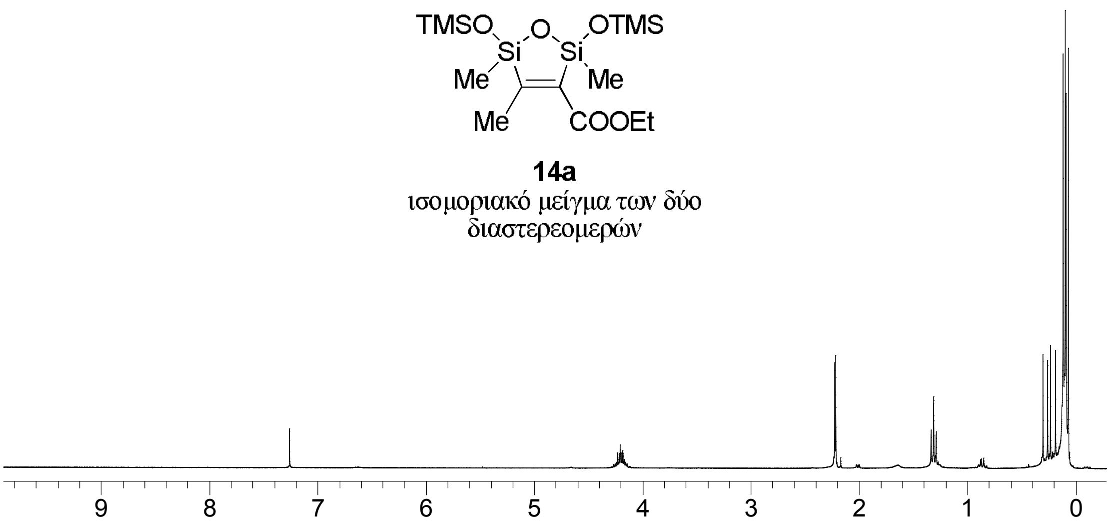

TMSO
O
OTMS
Si
Si
Me
Me
F
9c
ισομοριακό μείγμα των
δύο διαστερεομερών
hexane
hexane
hexane
200
175
150
125
100
75
50
25
0


TMSO
O
OTMS
Si
Si
Me
Me
10c
ισομοριακό μείγμα των
δυο διαστερεομερών
9
8
7
6
5
4
3
2
1
0

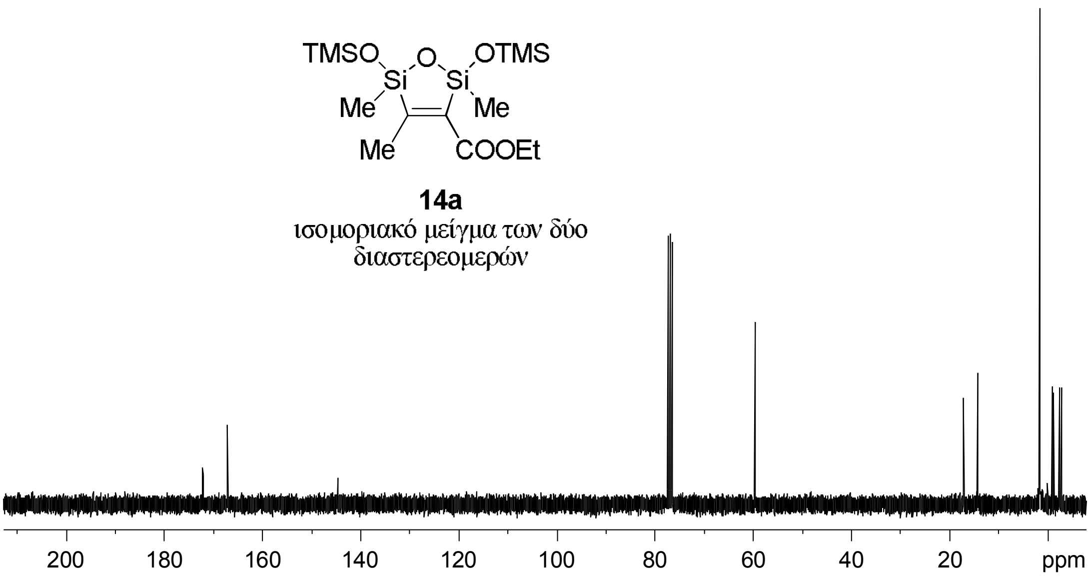

TMSO
O
OTMS
Si
Si
Me
Me
10c
ισομοριακό μείγμα των
δυο διαστερεομερών
200
175
150
125
100
75
50
25
0


TMSO
O
OTMS
Si
Si
Me
Me
11c
ισομοριακό μείγμα των
δύο διαστερεομερών
9
8
7
6
5
4
3
2
1
0

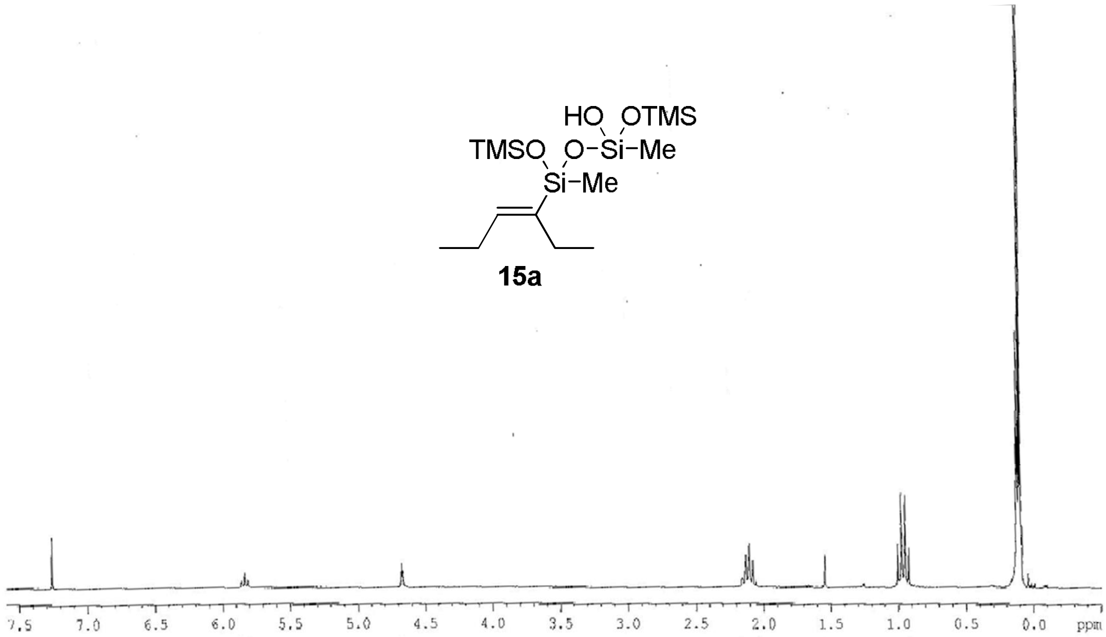

TMSO
O
OTMS
Si
Si
Me
Me
11c
ισομοριακό μείγμα των
δύο διαστερεομερών
200
175
150
125
100
75
50
25
0



14a
ισομοριακό μείγμα των δύο διαστερεομερών



14a
ισομοριακό μείγμα των δύο διαστερεομερών


HO OTMS
TMSO O-Si-Me
Si-Me
15a
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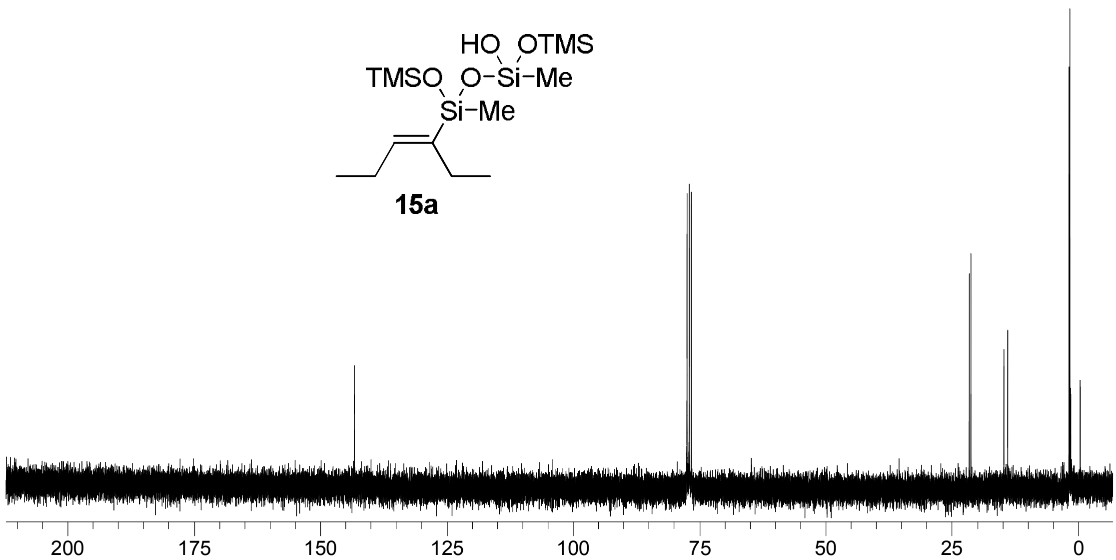
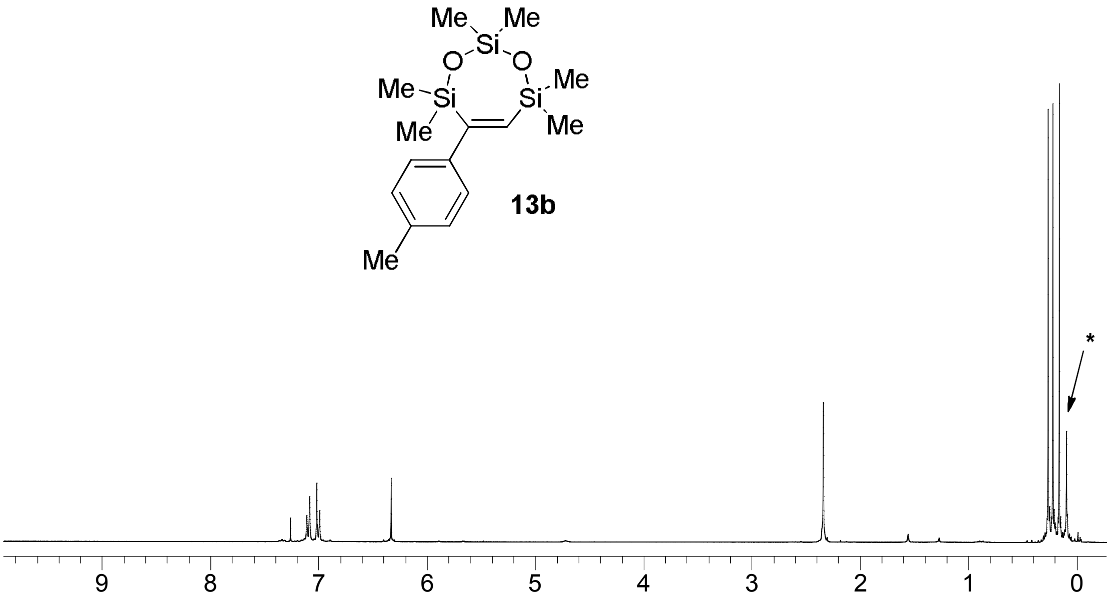
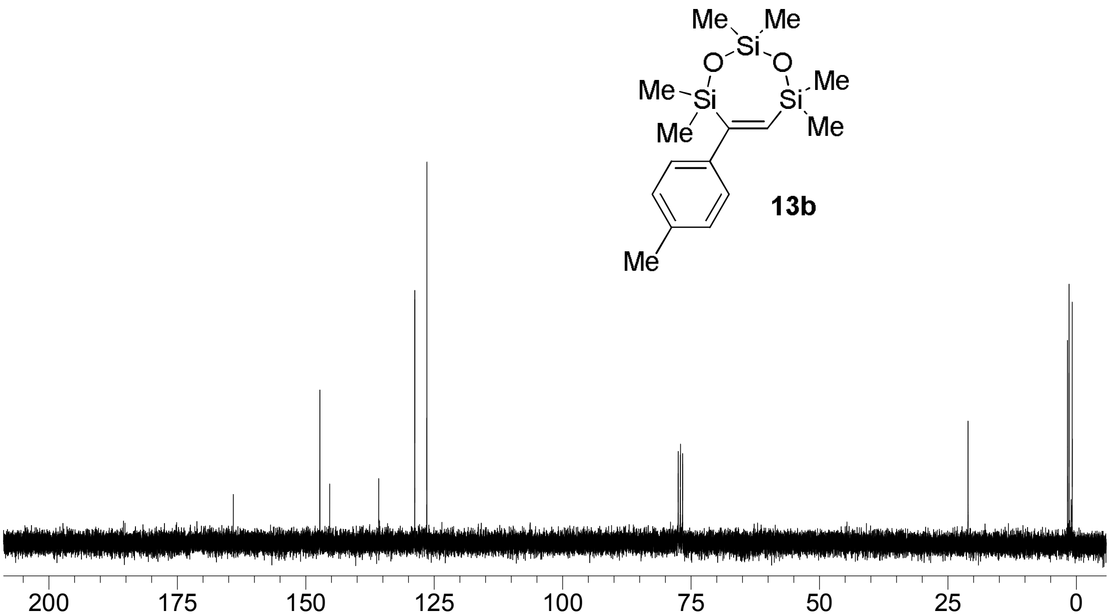
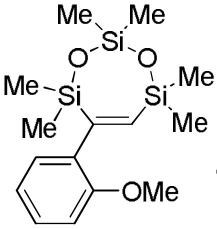

HO OTMS
TMSO O-Si-Me
Si-Me
15a
200 175 150 125 100 75 50 25 0



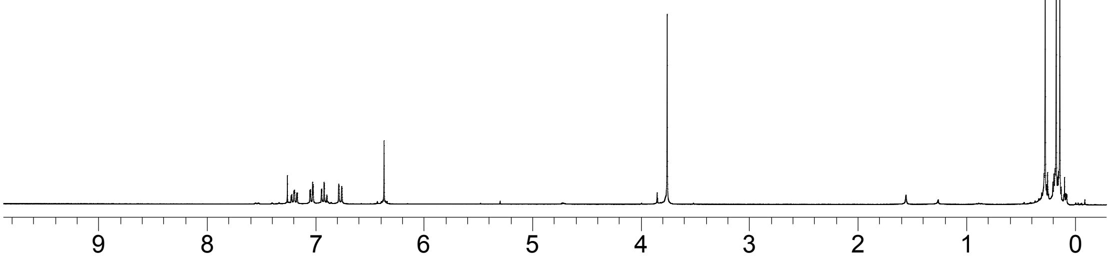
*: oligosiloxane



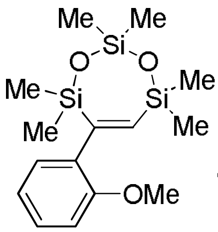


Me
Me
Si
O
O
Me
Si
Me
Si
Me
Me
OMe

8c



9
8
7
6
5
4
3
2
1
0



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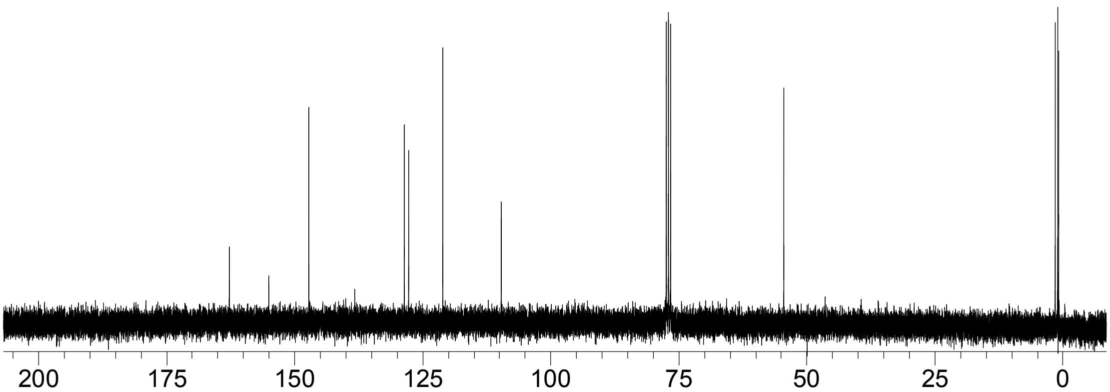
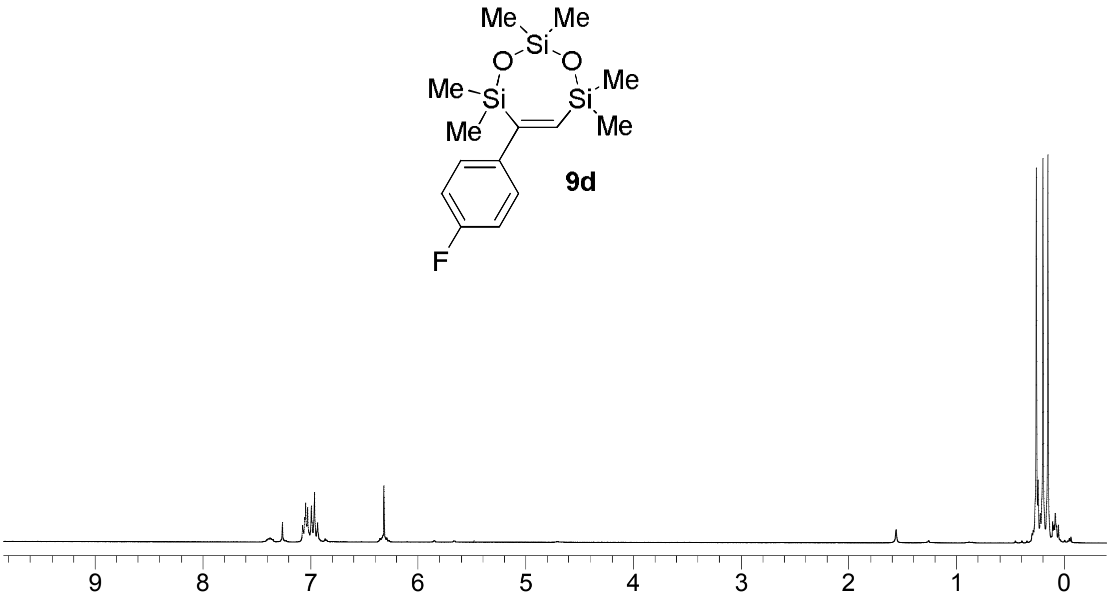
Me
Si
O
O
Me
Si
Me
Si
Me
Me
OMe

8c



200
175
150
125
100
75
50
25
0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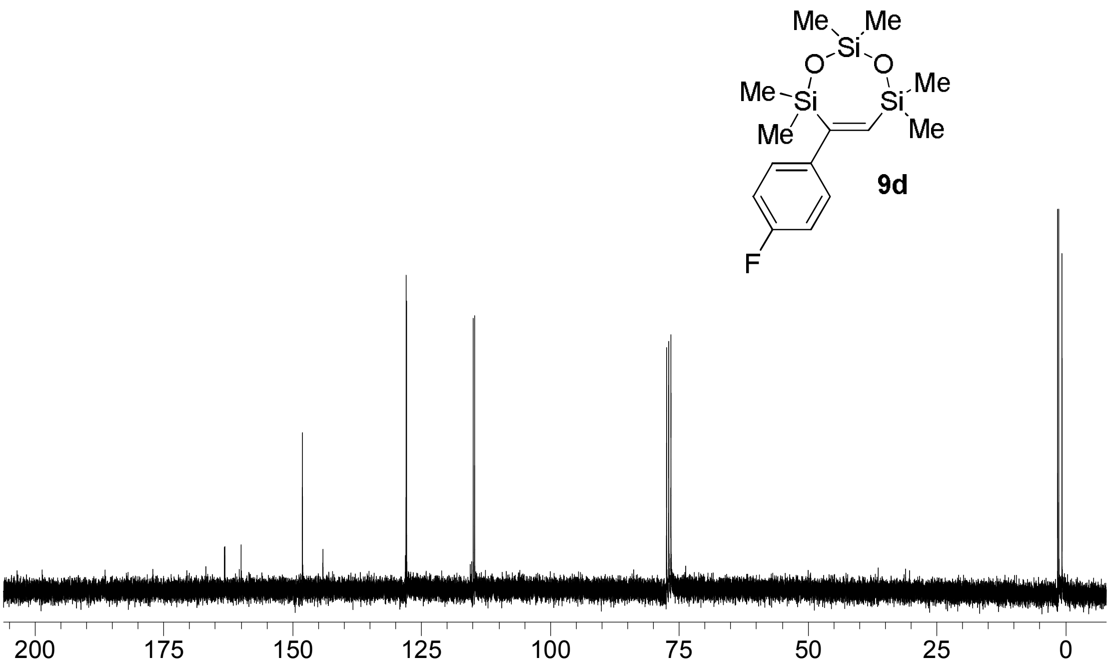
Si
O O
Me Si Si Me
Me Me
F
9d
9 8 7 6 5 4 3 2 1 0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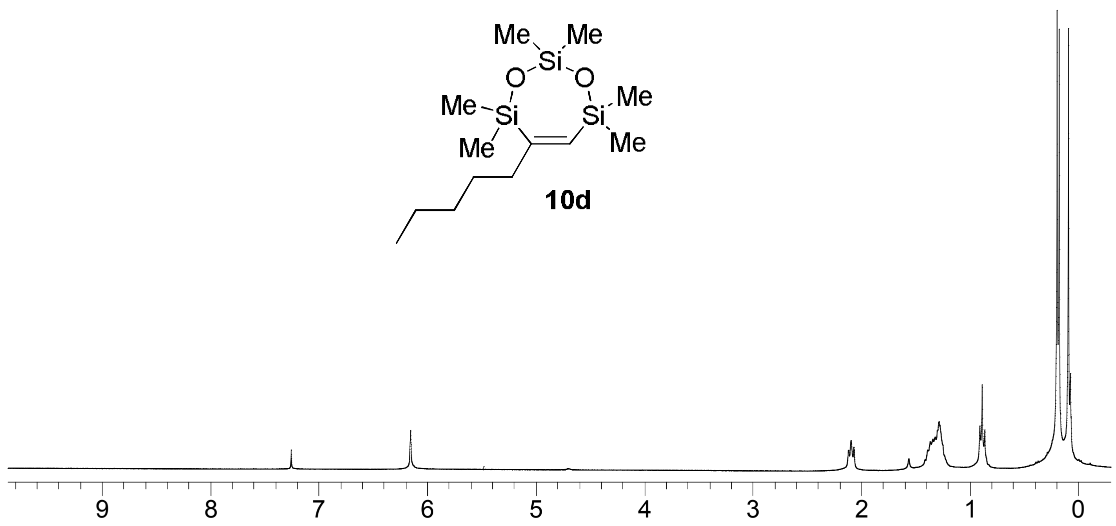
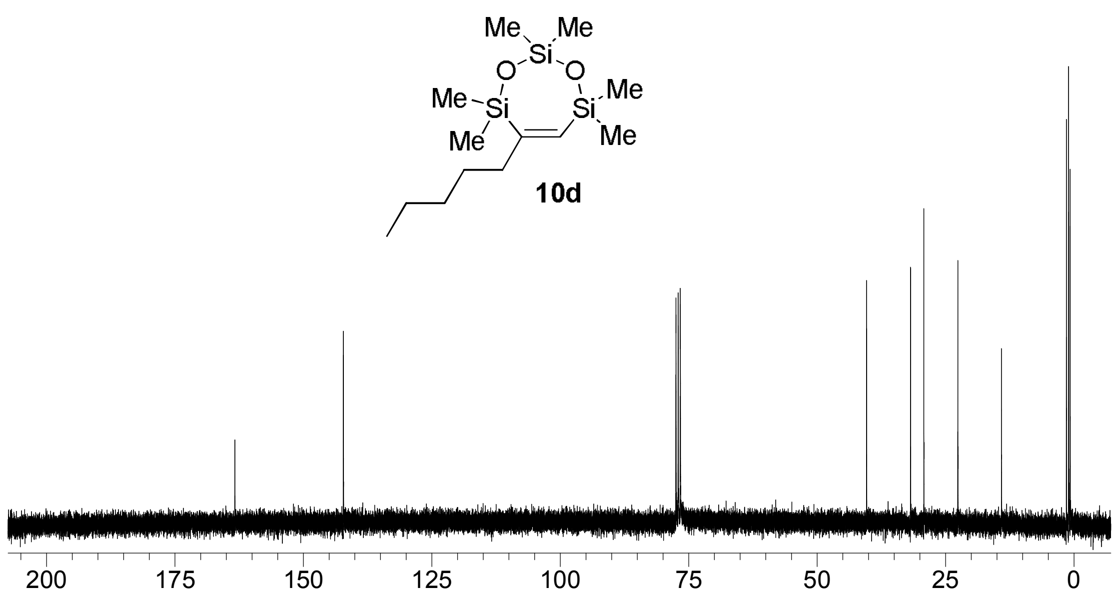
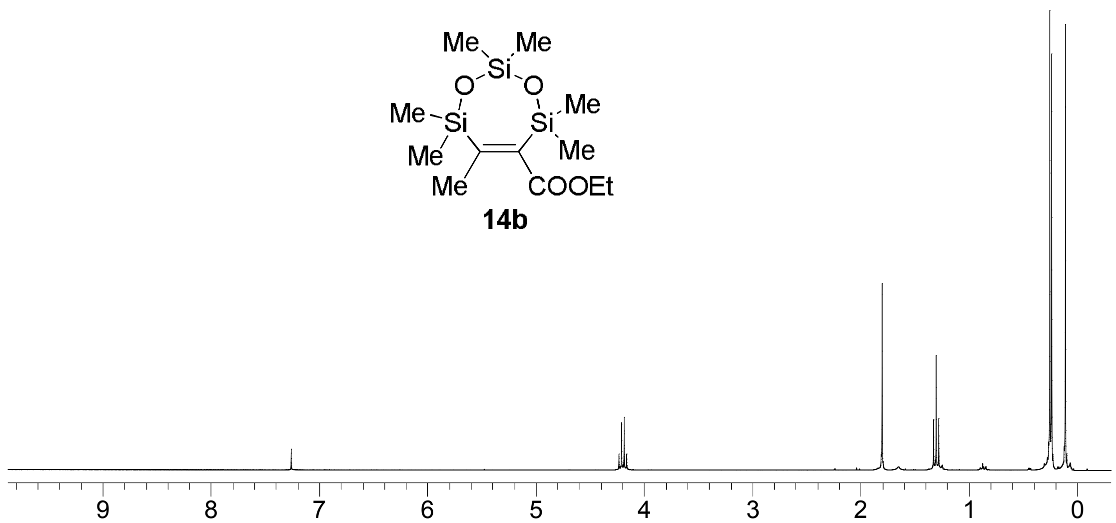
Si
O O
Me Si Si Me
Me Me
F
9d
200 175 150 125 100 75 50 25 0


Me
Me
Si
O
O
Me
Si
Si
Me
Me
Me
10d
9
8
7
6
5
4
3
2
1
0


Me
Me
Si
O
O
Me
Si
Si
Me
Me
Me
10d
200
175
150
125
100
75
50
25
0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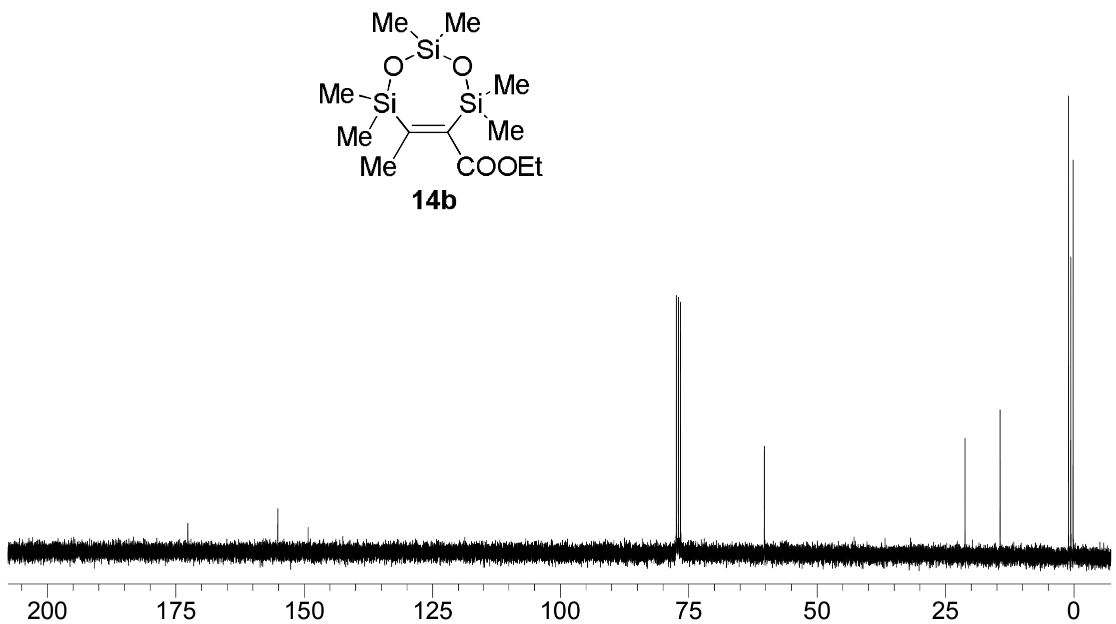
Me
Si
O
O
Me
Si
Si
Me
Me
Me
Me
COOEt
14b
9 8 7 6 5 4 3 2 1 0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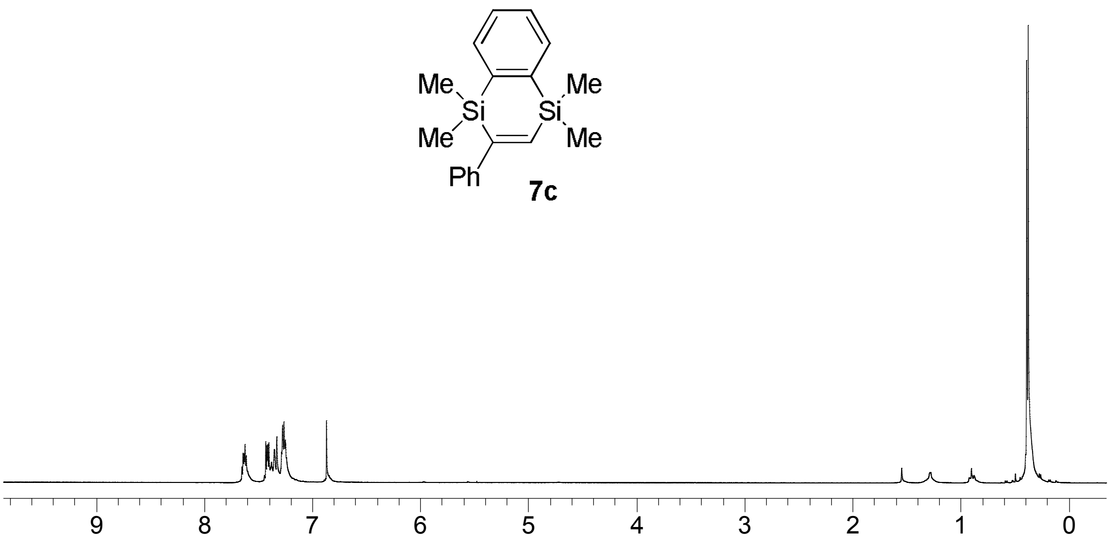
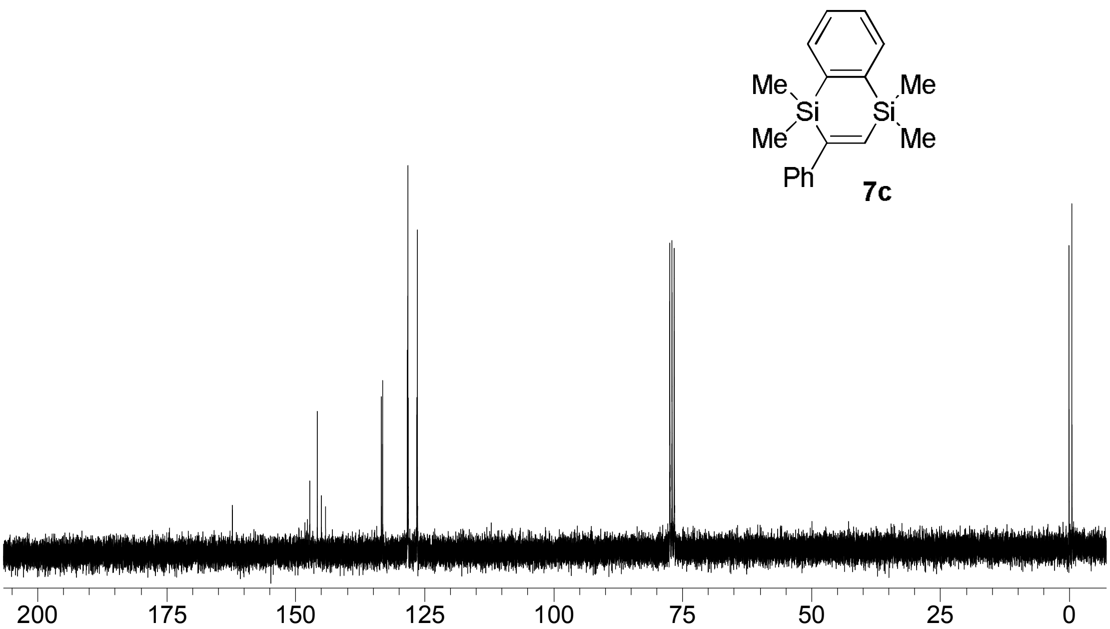
Me
Si
O
O
Me
Si
Si
Me
Me
Me
Me
COOEt
14b
200 175 150 125 100 75 50 25 0



Me
Si
Me
Me
Si
Me
Ph
7c
9
8
7
6
5
4
3
2
1
0



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Si
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Me
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Me
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7c
200
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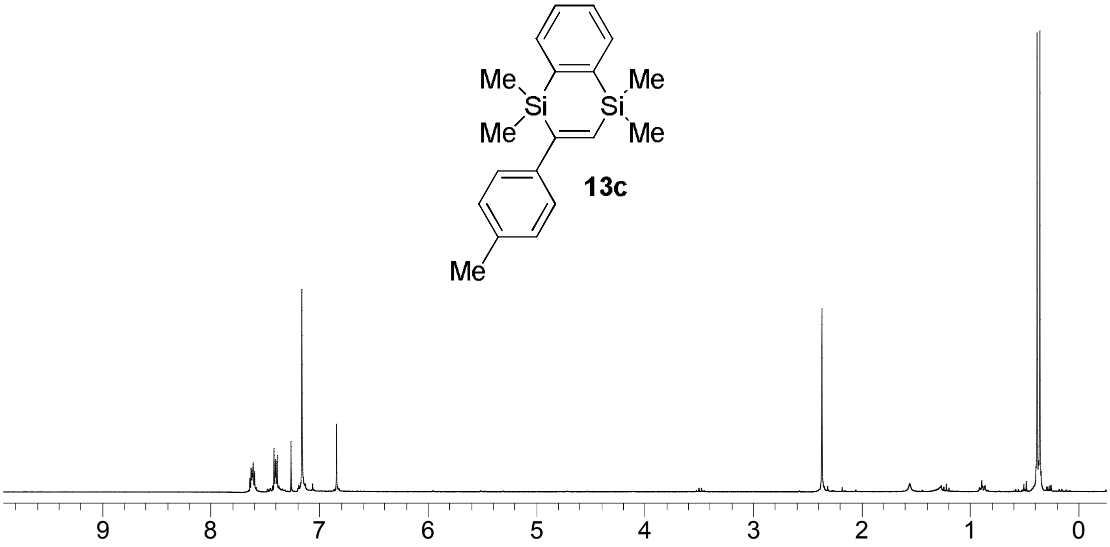
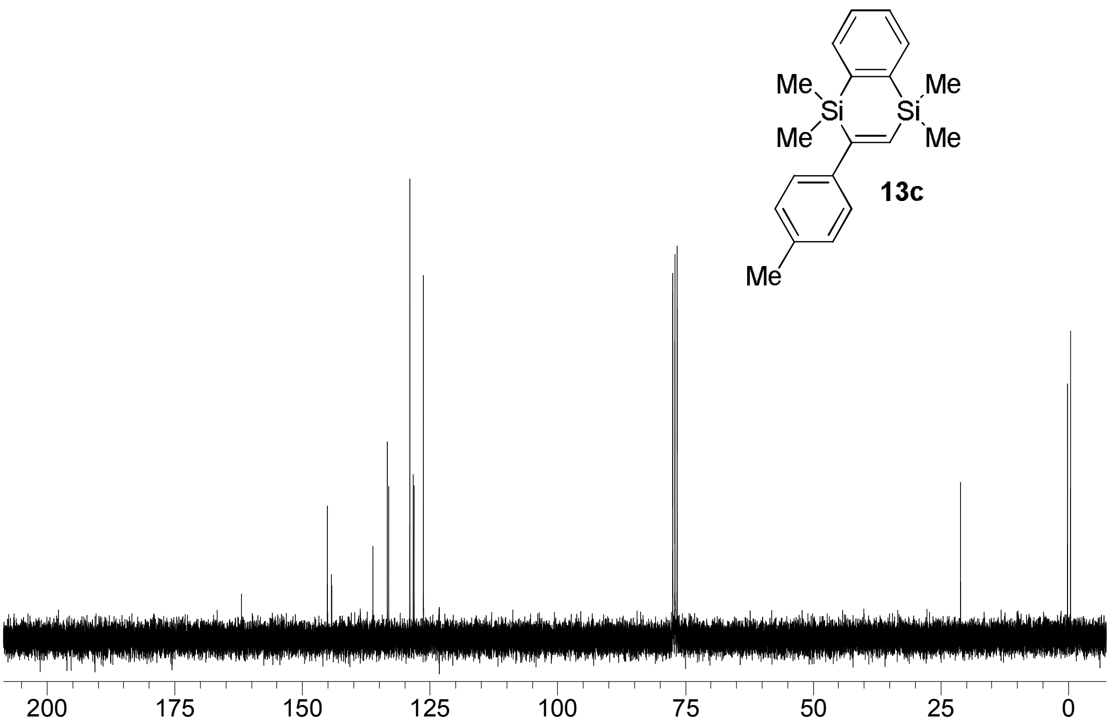
150
125
100
75
50
25
0



Me
Si
Me
Me
Si
Me
13c
Me
9
8
7
6
5
4
3
2
1
0



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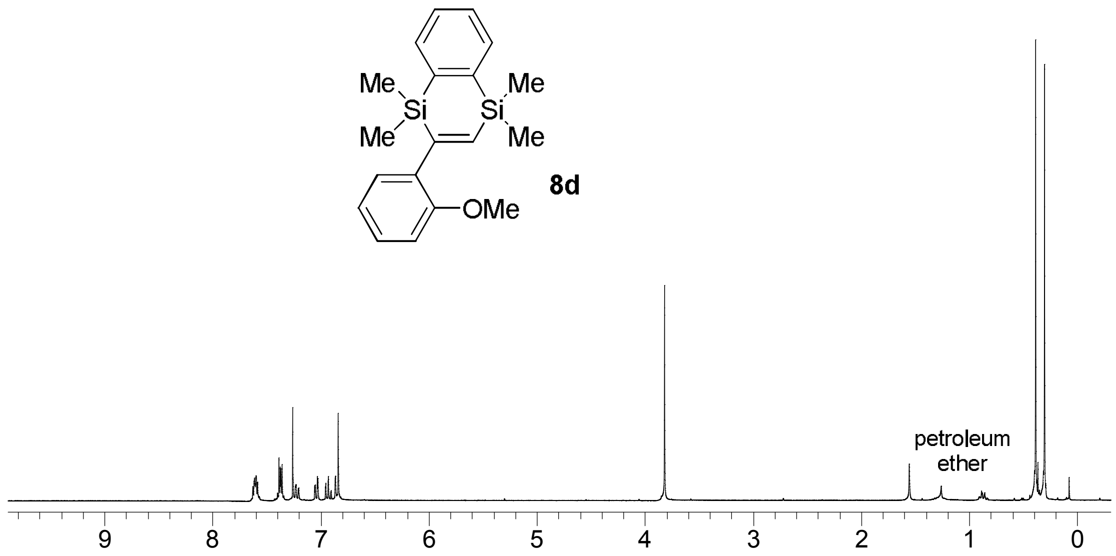
Si
Me
Me
Si
Me
13c
Me
200
175
150
125
100
75
50
25
0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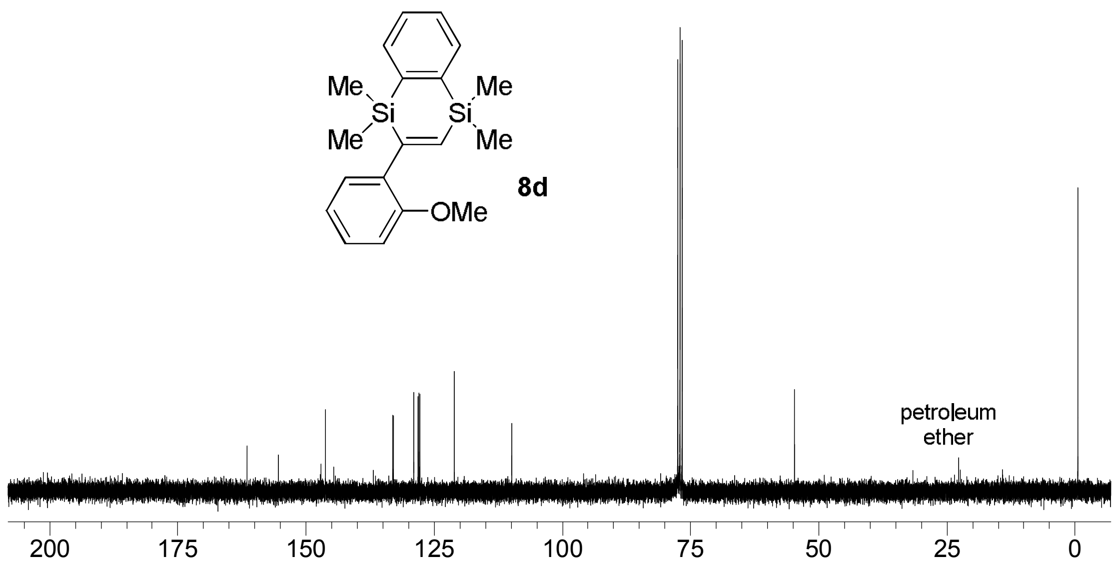
Si
Me
Me
Si
Me
OMe
8d
petroleum
ether
9
8
7
6
5
4
3
2
1
0


Me
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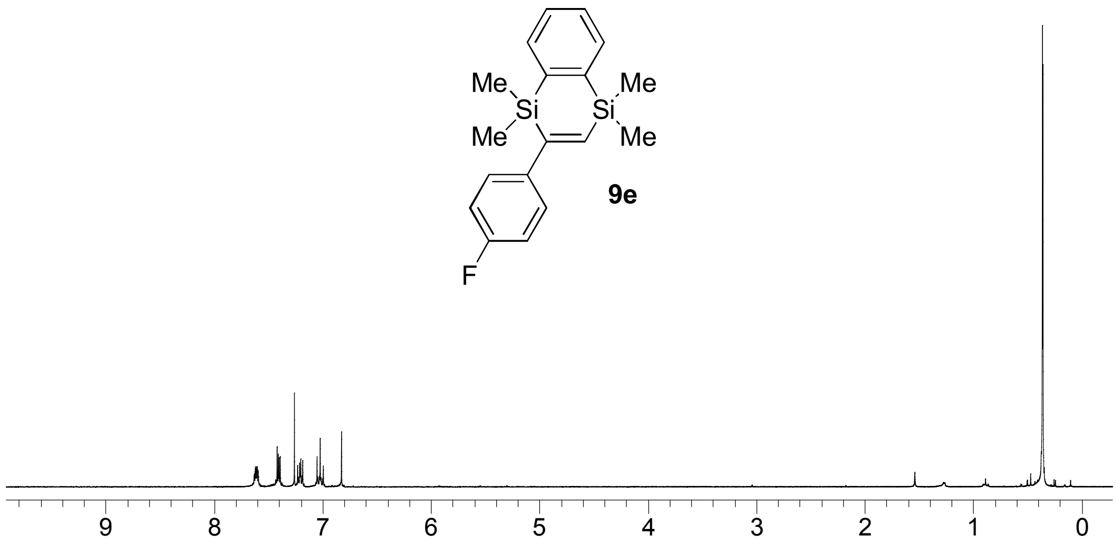
Me
Me
Si
Me
OMe
8d
petroleum
ether
200
175
150
125
100
75
50
25
0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Me
Si
Me
Me
F
9e
9
8
7
6
5
4
3
2
1
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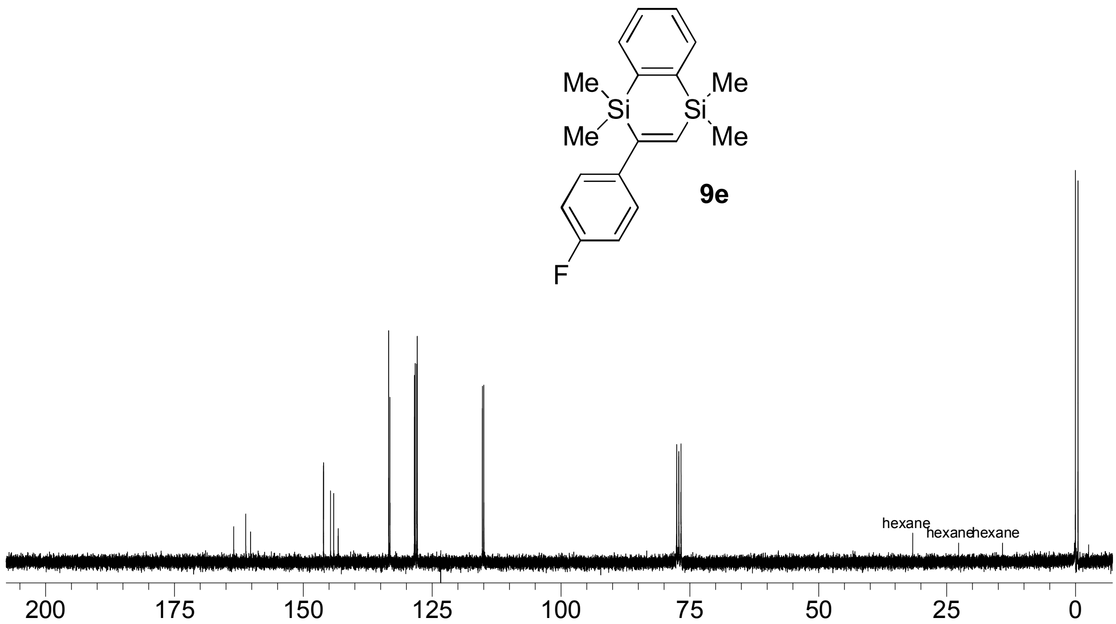
Me
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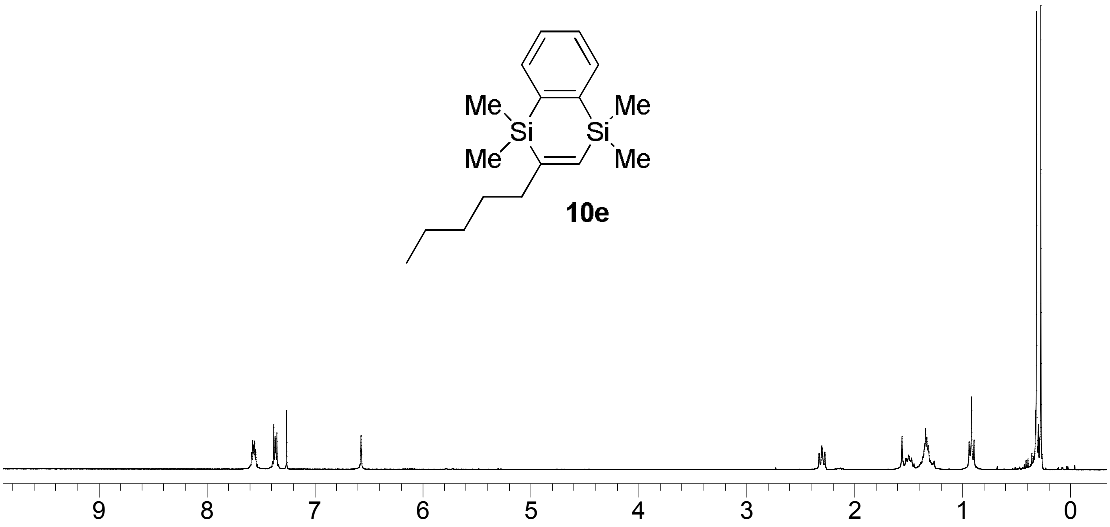
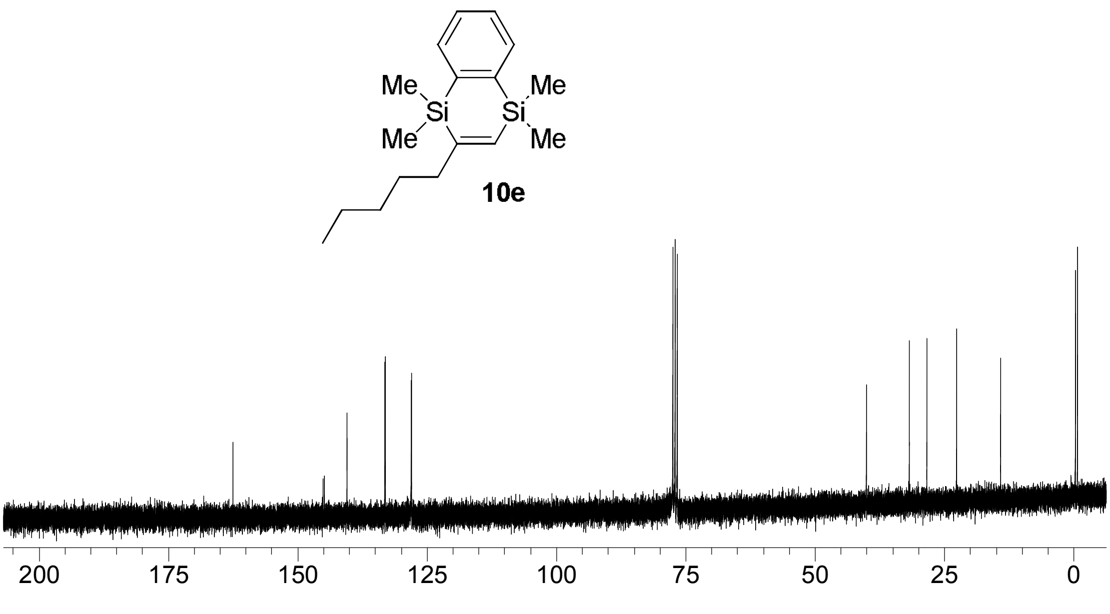
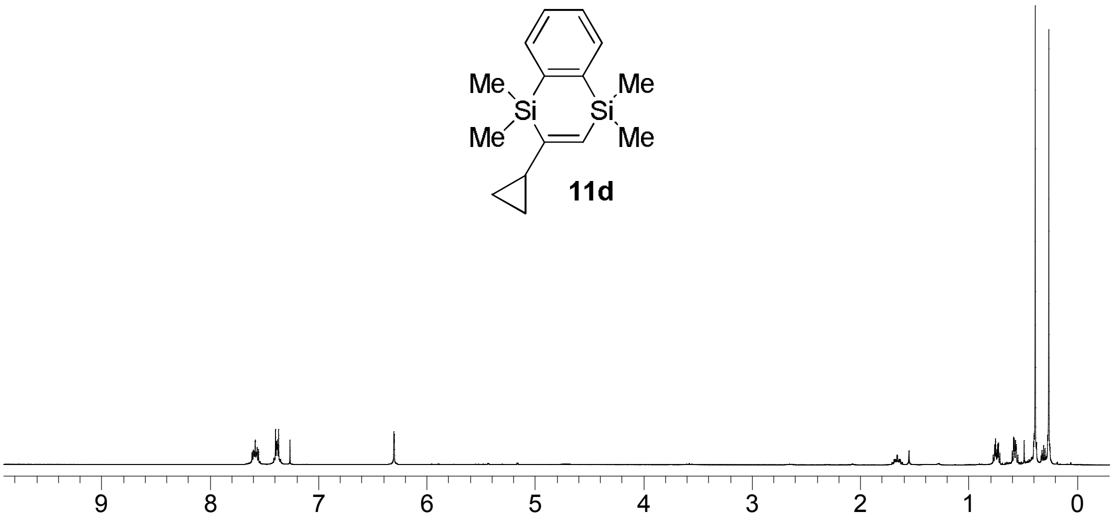
Me
Si
Me
Me
F
9e
hexane
hexane
hexane
200
175
150
125
100
75
50
25
0


Me
Me
Si
Si
Me
Me
10e
9
8
7
6
5
4
3
2
1
0


Me
Me
Si
Si
Me
Me
10e
200
175
150
125
100
75
50
25
0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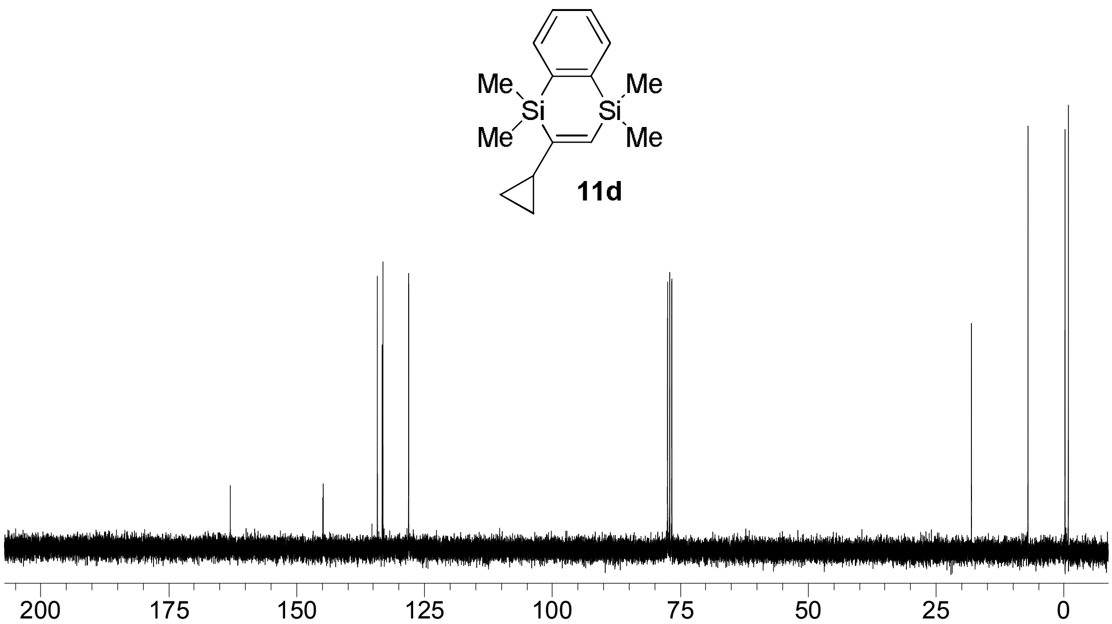
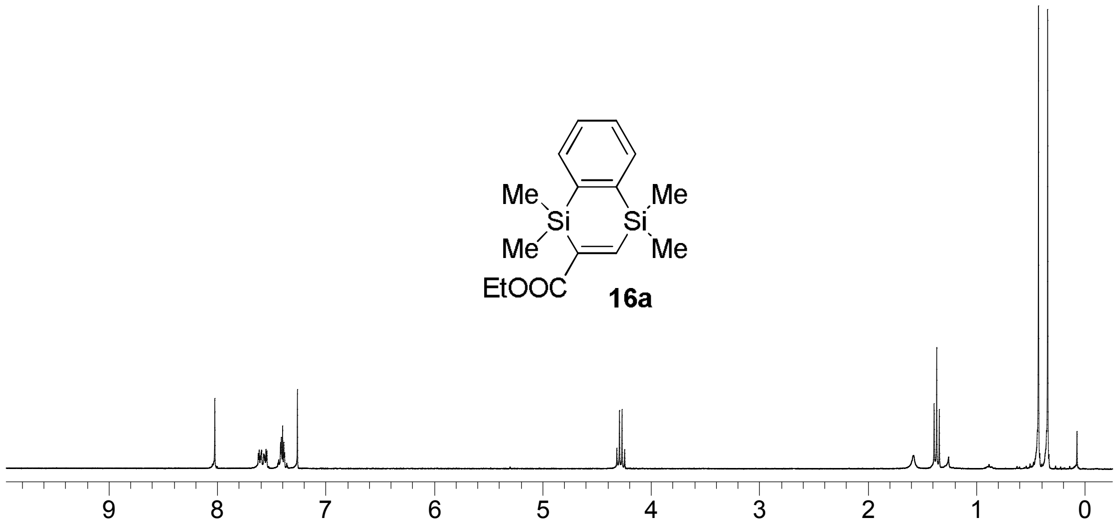
Si
Me
Me
Si
Me
11d
9
8
7
6
5
4
3
2
1
0


Me
Si
Me
Me
Si
Me
11d
200
175
150
125
100
75
50
25
0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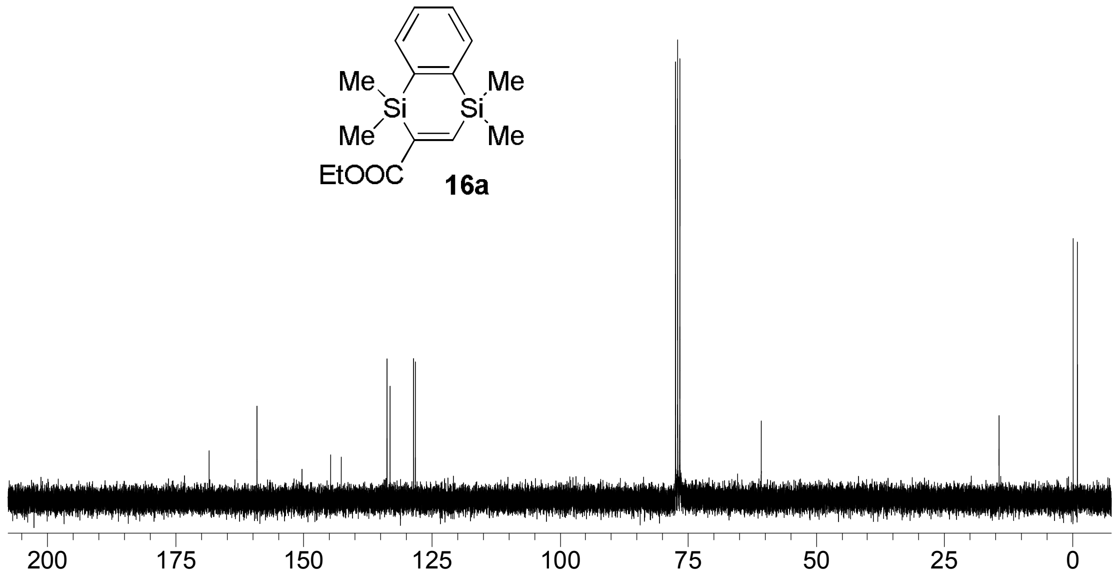
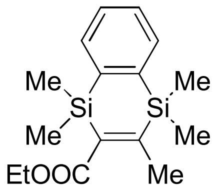
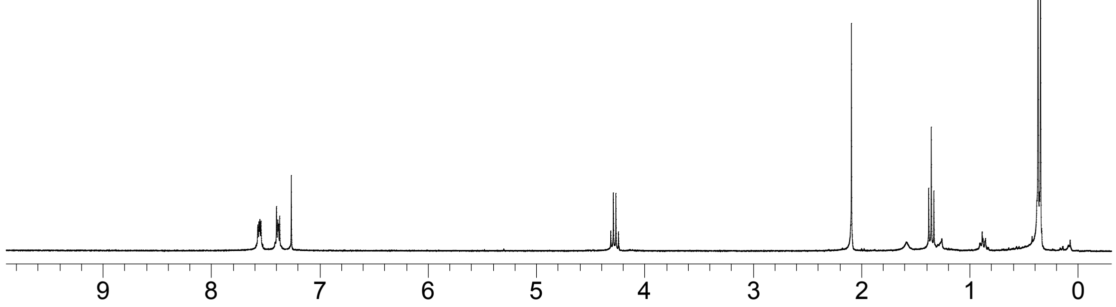
Si
Me
Me
Si
Me
EtOOC
16a
9 8 7 6 5 4 3 2 1 0


Me
Si
Me
Me
Si
Me
EtOOC
16a
200 175 150 125 100 75 50 25 0


Me
Si
Me
Me
Si
Me
EtOOC
Me

14c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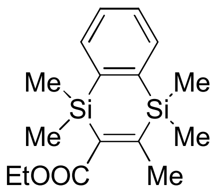
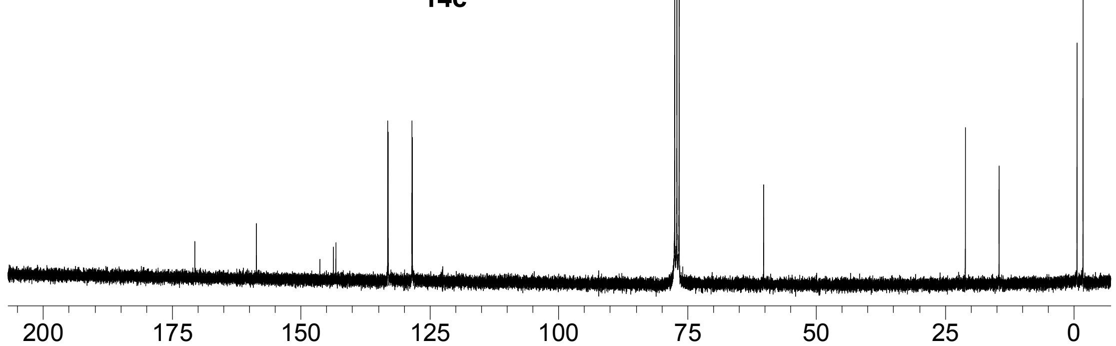

Me
Si
Me
Me
Si
Me
EtOOC
Me

14c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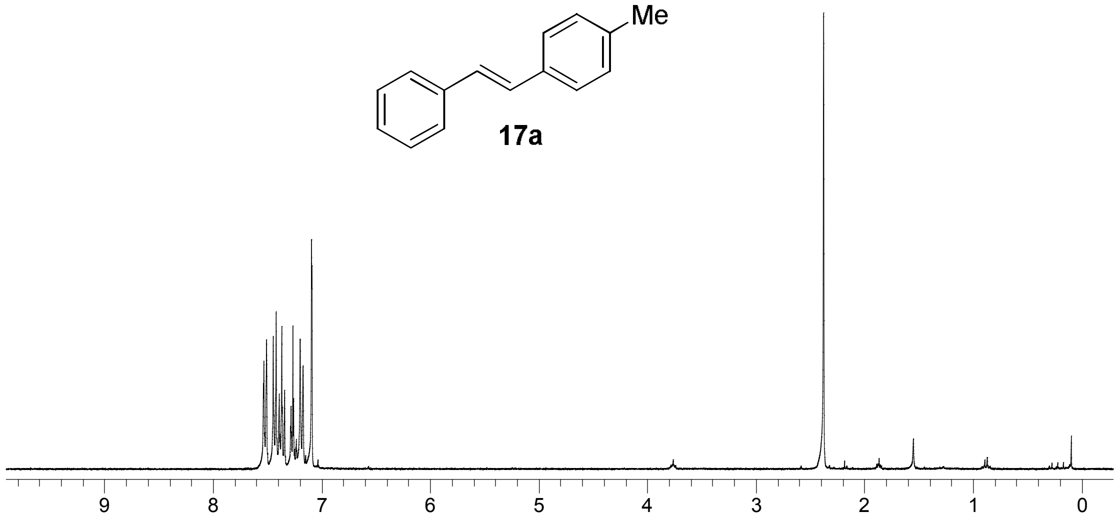
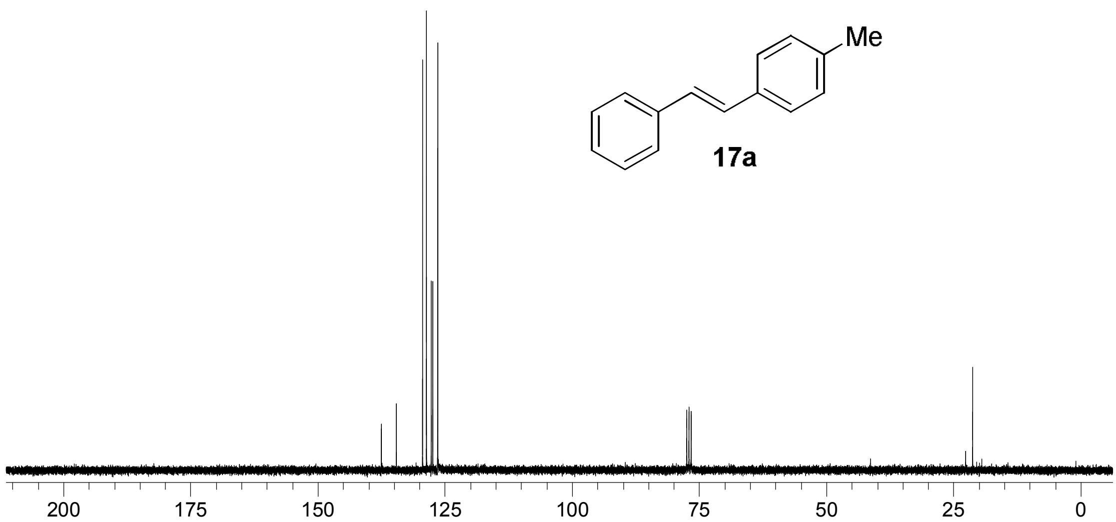
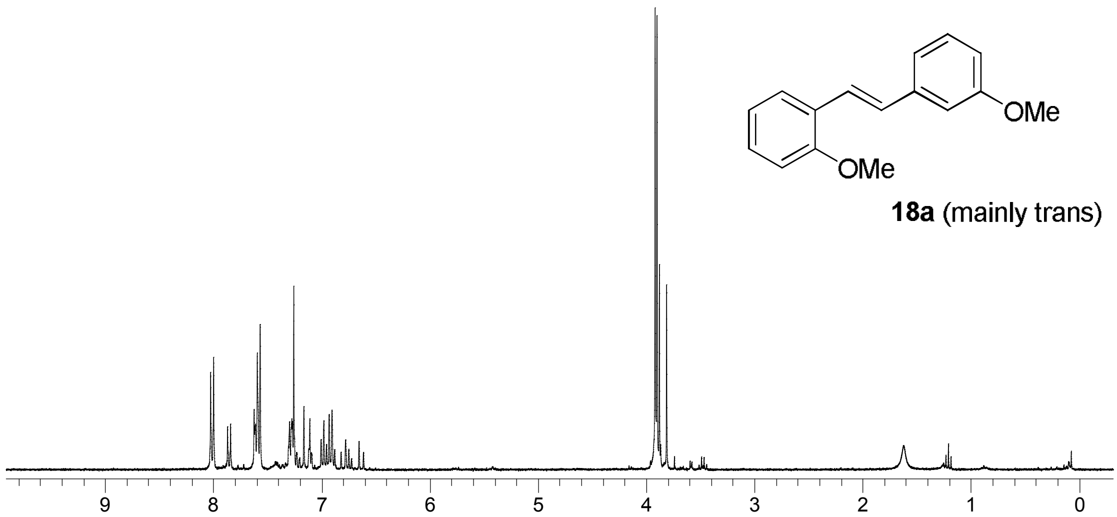
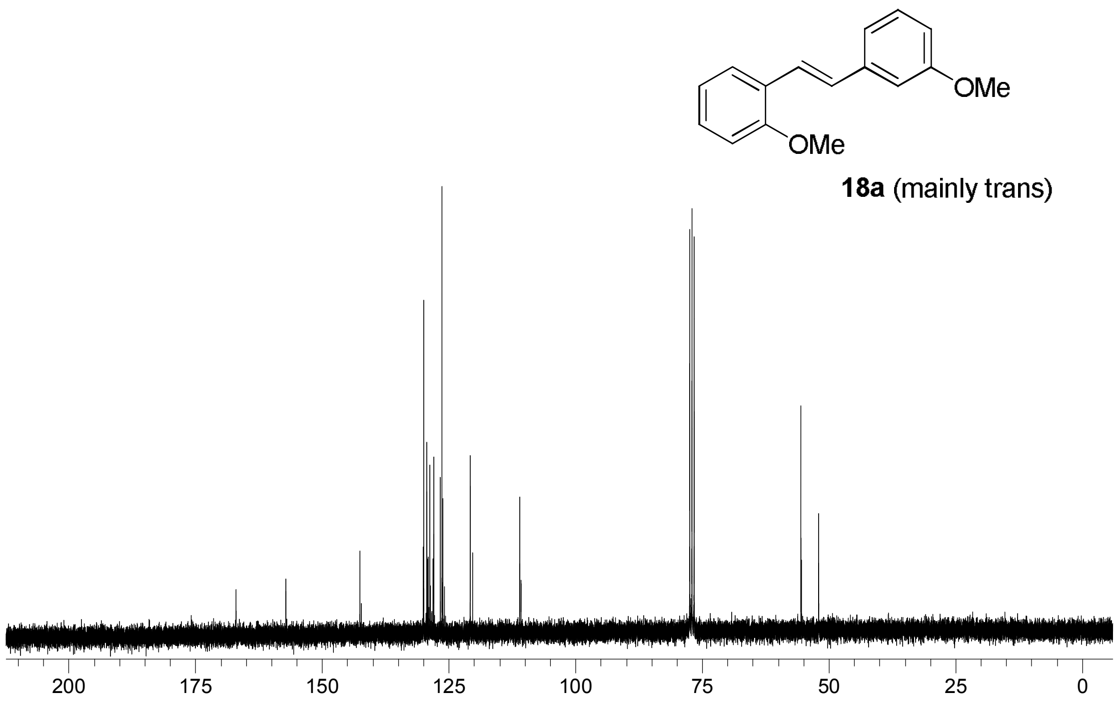
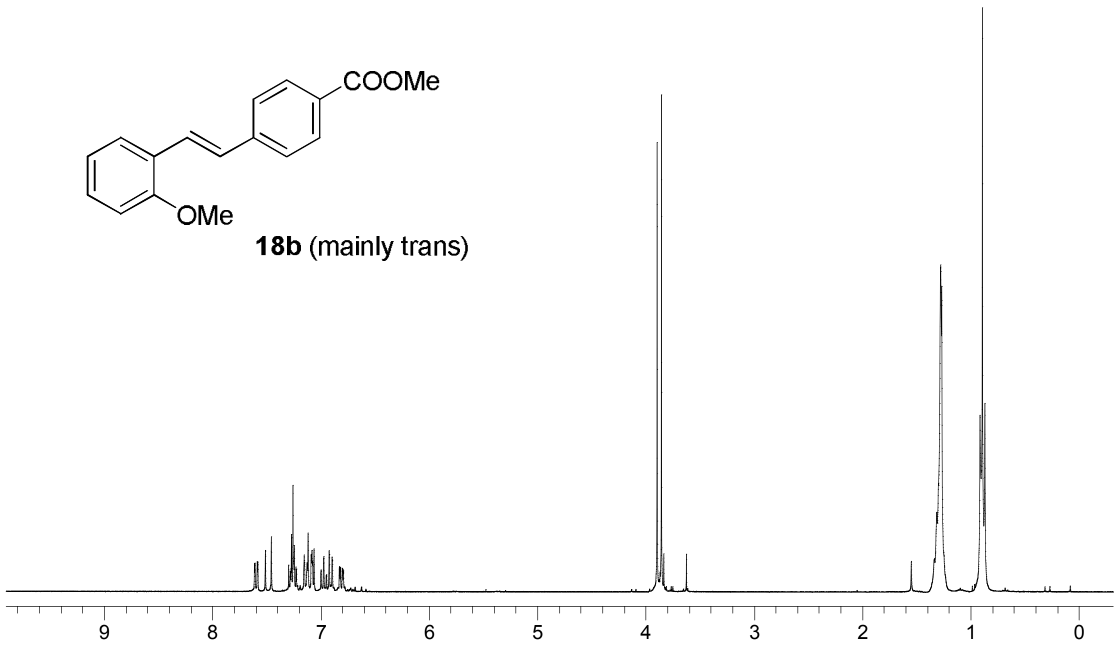
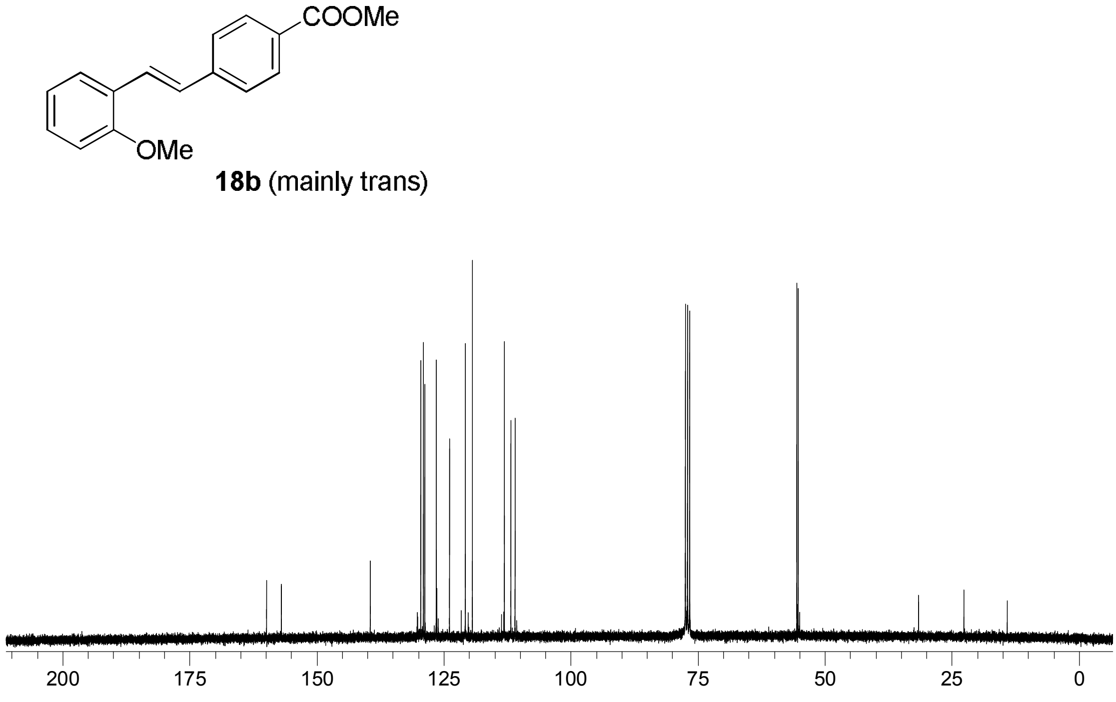

Me
17a
9
8
7
6
5
4
3
2
1
0

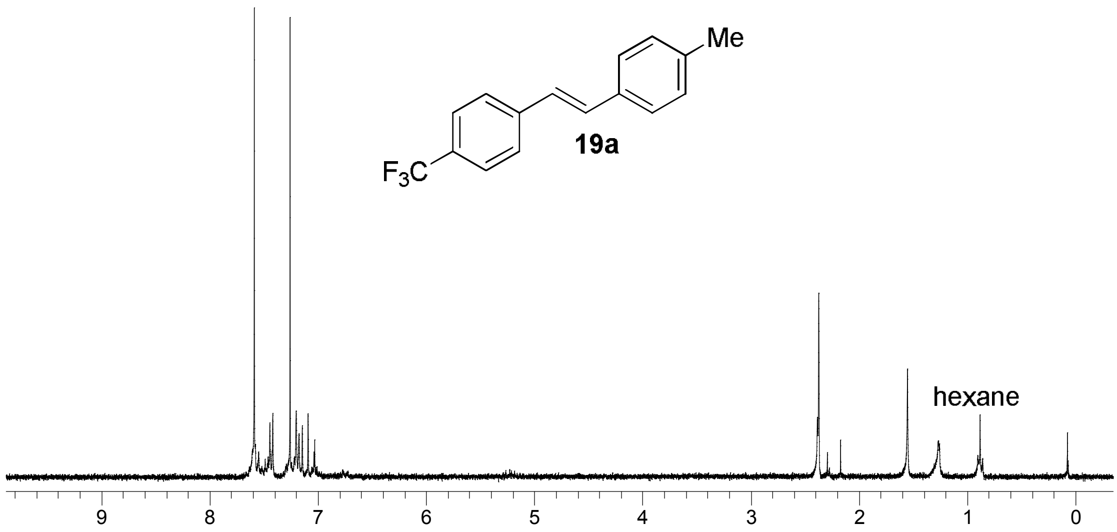

Me
17a
200
175
150
125
100
75
50
25
0

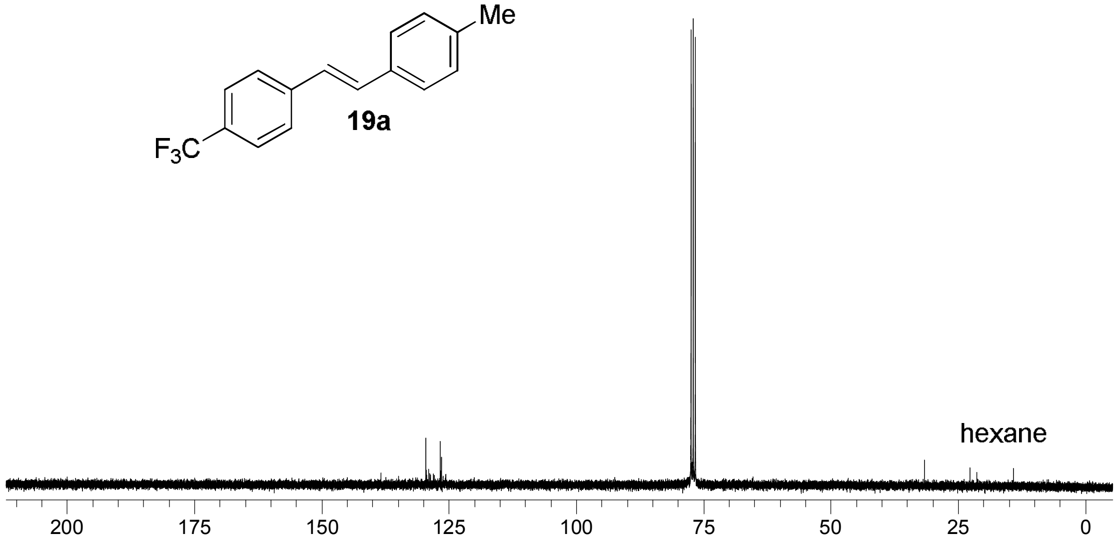

OMe
OMe
18a (mainly trans)
9 8 7 6 5 4 3 2 1 0

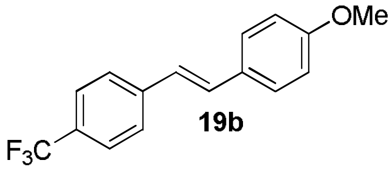

OMe
OMe
18a (mainly trans)
200 175 150 125 100 75 50 25 0

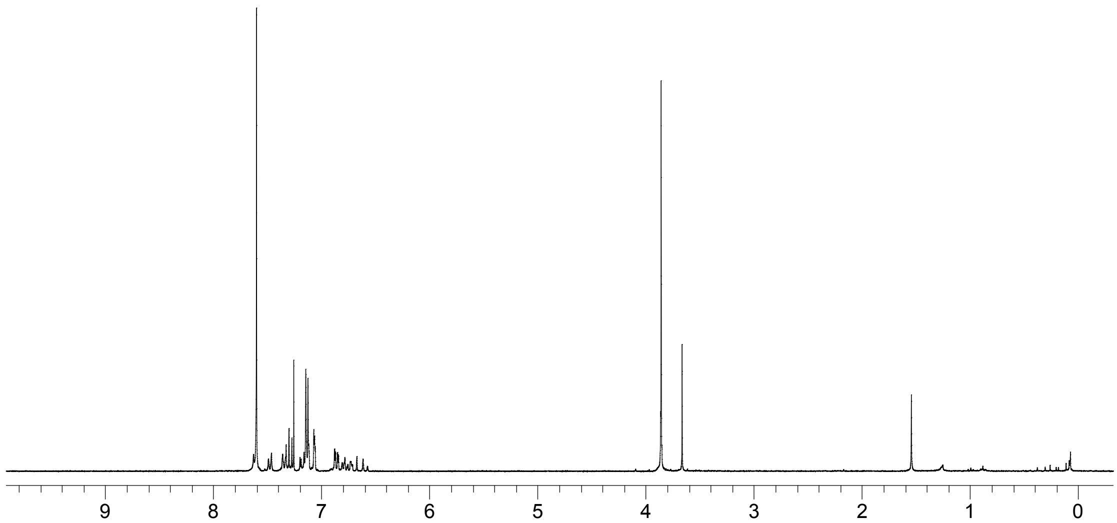

COOMe
OMe
18b (mainly trans)
9
8
7
6
5
4
3
2
1
0

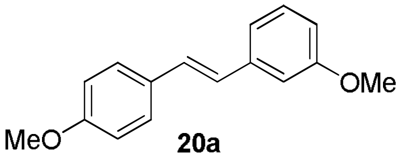

COOMe
OMe
18b (mainly trans)
200
175
150
125
100
75
50
25
0


Me
19a
F3C
hexane
9
8
7
6
5
4
3
2
1
0

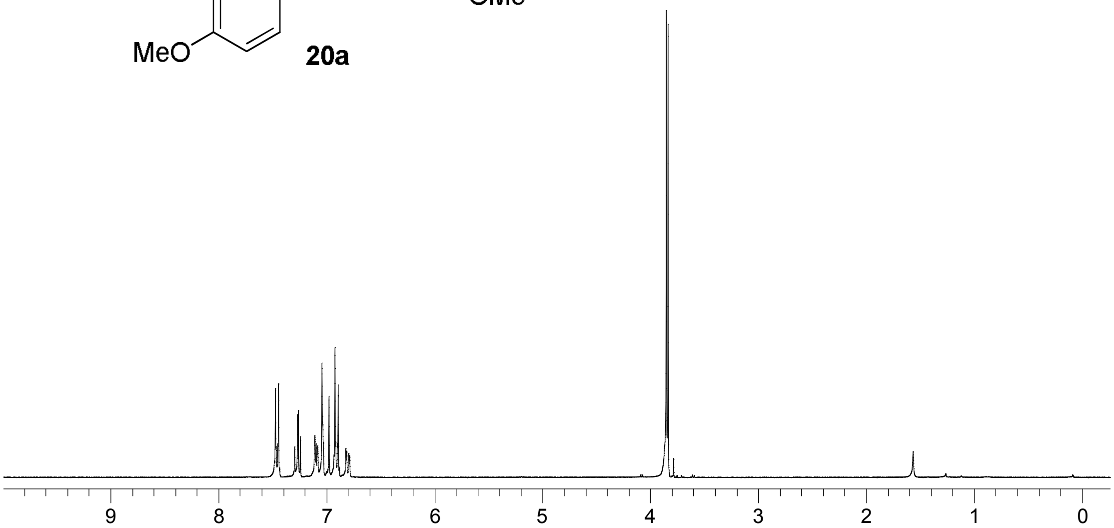

Me
19a
F3C
hexane
200
175
150
125
100
75
50
25
0

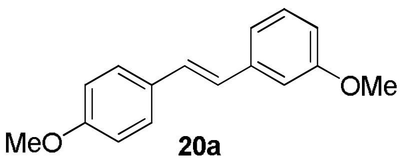

OMe
F3C
19b


9
8
7
6
5
4
3
2
1
0

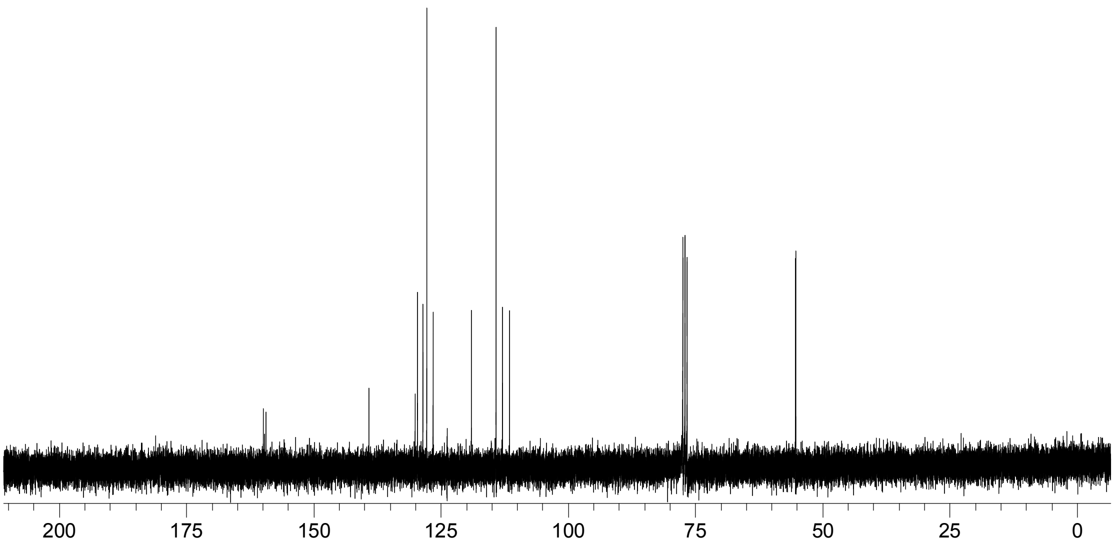


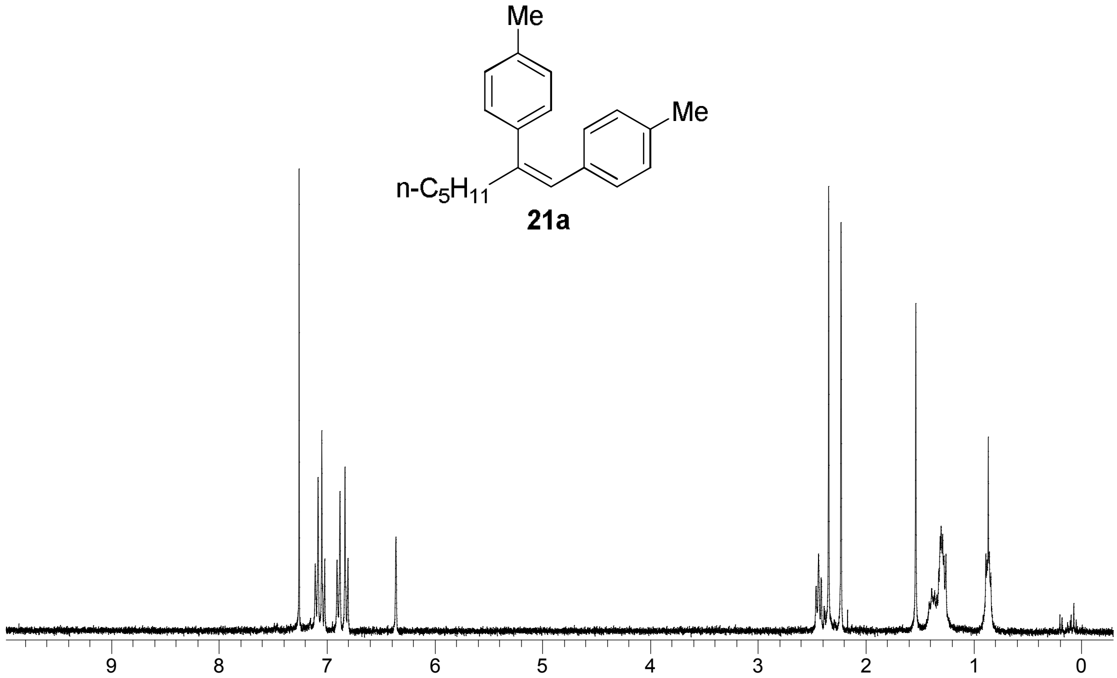
20a





20a

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Me
n-C_5H_{11}
21a
9
8
7
6
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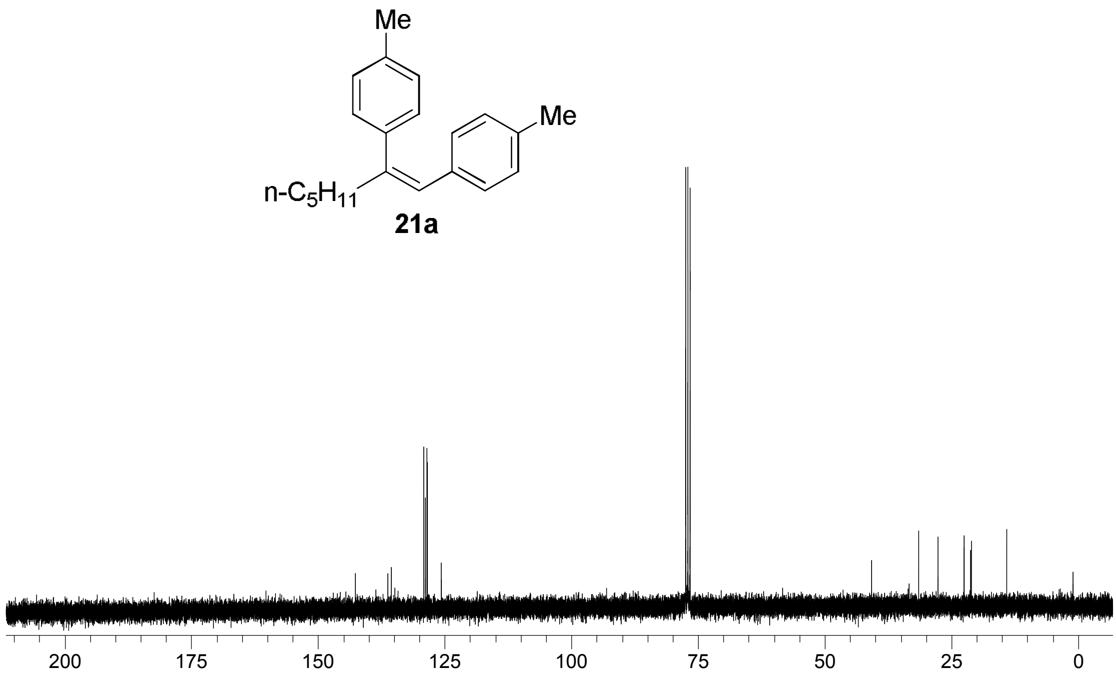
4
3
2
1
0


Me
Me
n-C_5H_{11}
21a
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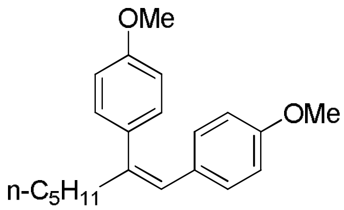
175
150
125
100
75
50
25
0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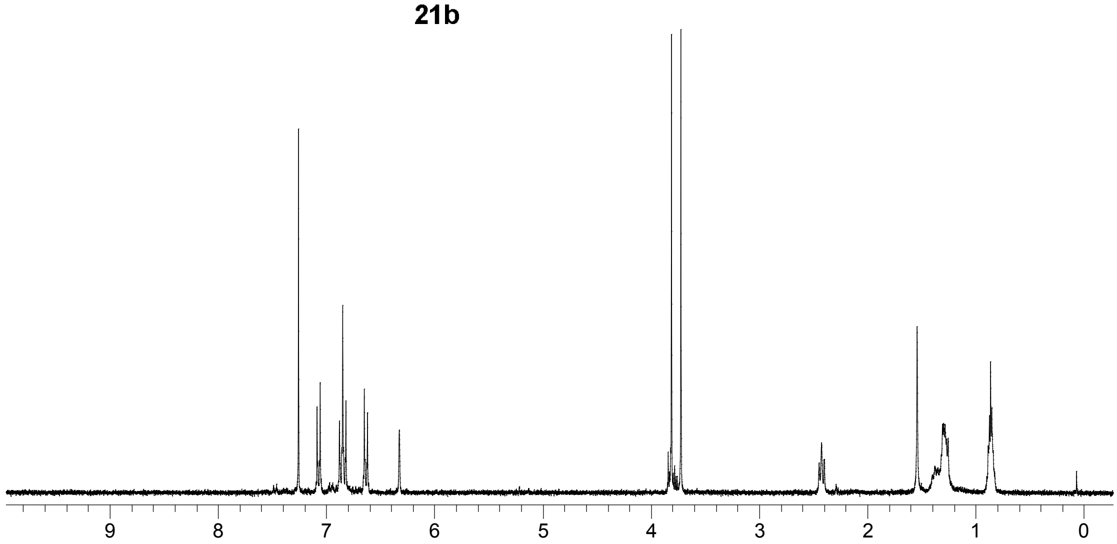
OMe
n-C5H11

21b


9
8
7
6
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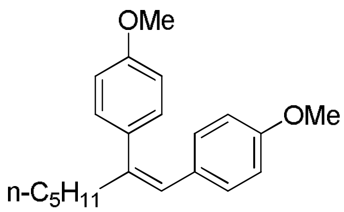
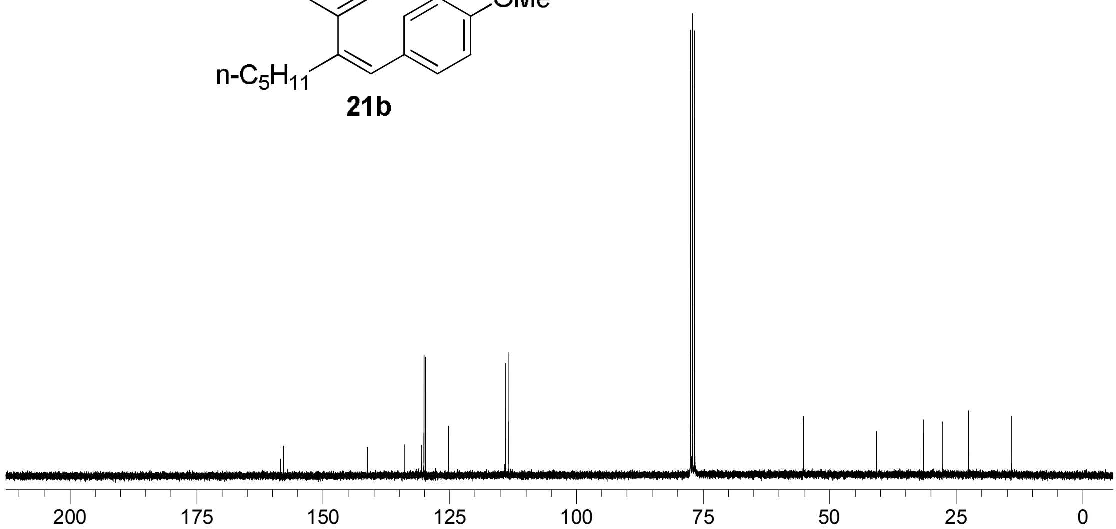
3
2
1
0


OMe
OMe
n-C5H11

21b


200
175
150
125
100
75
50
25
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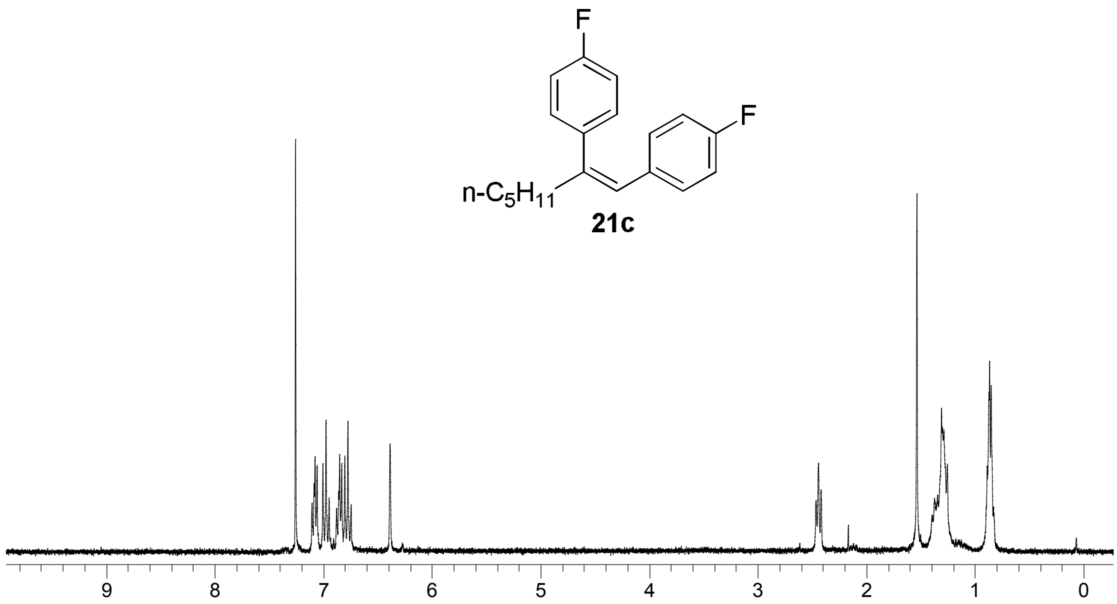
F
F
n-C5H11
21c
9
8
7
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2
1
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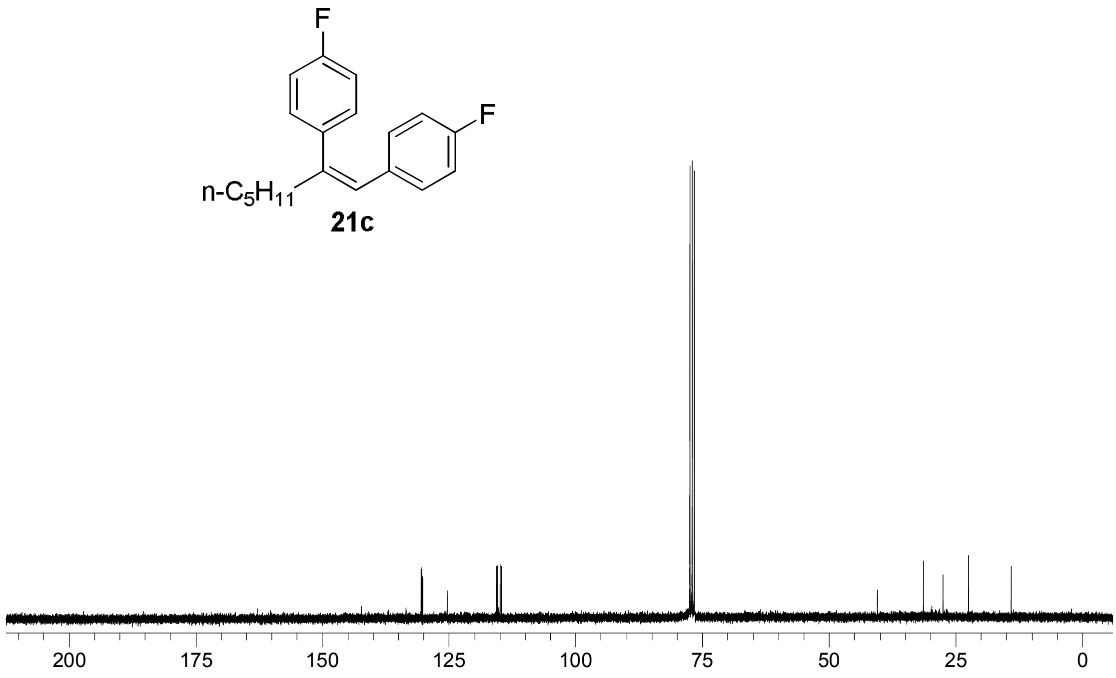
F
F
n-C5H11
21c
200
175
150
125
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25
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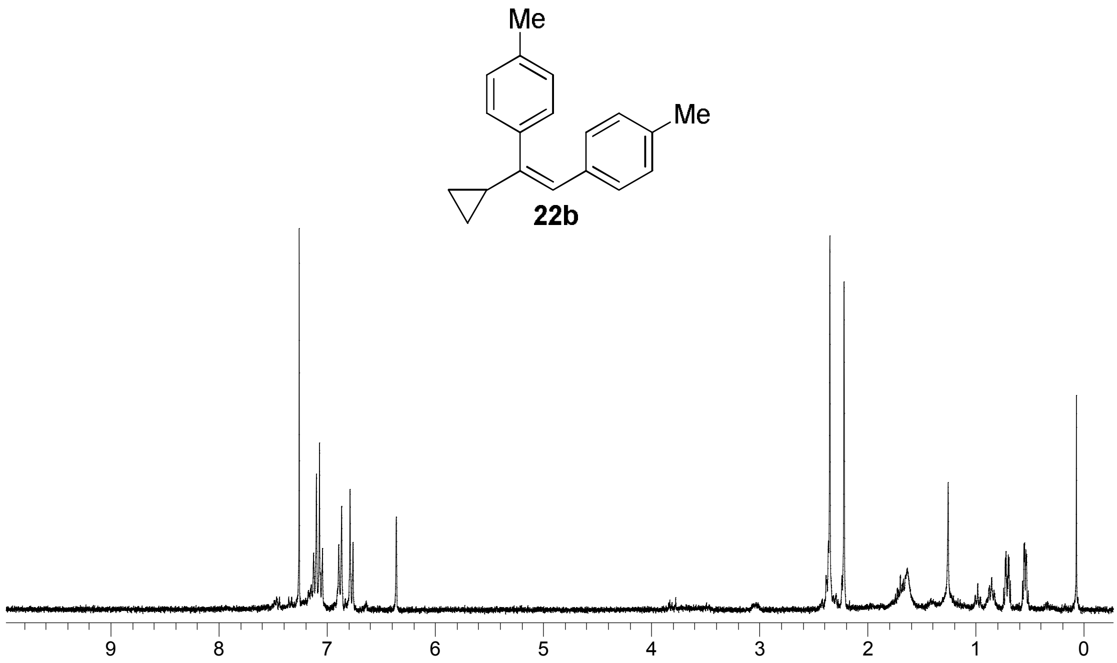
Me
Me
22b
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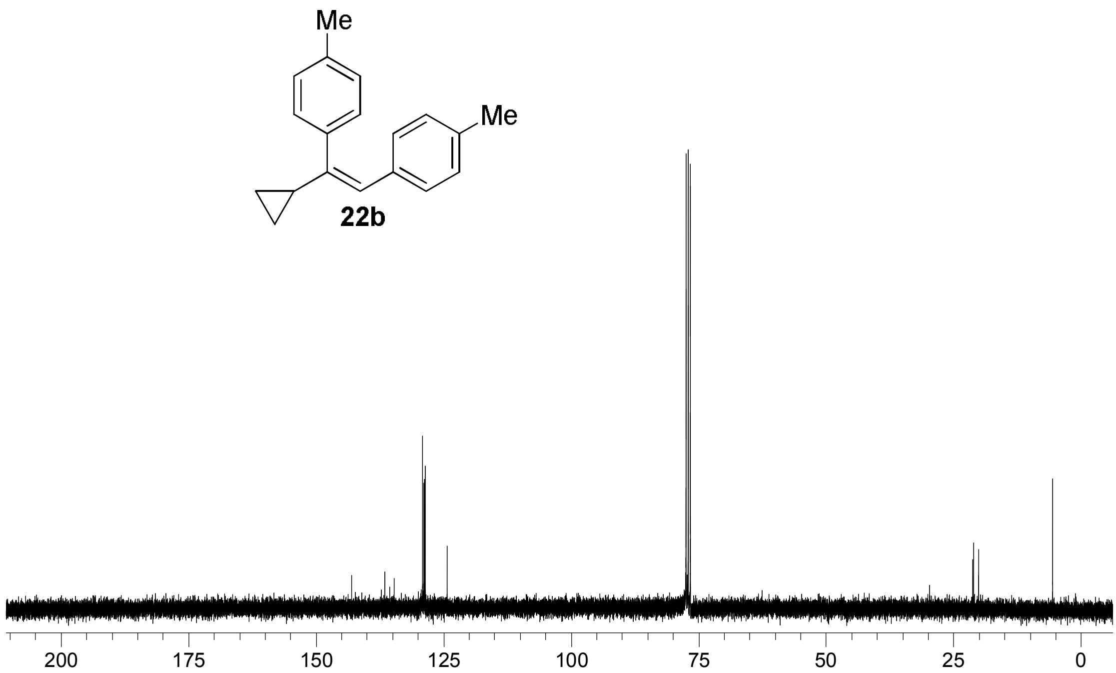
Me
Me
22b
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175
150
125
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75
50
25
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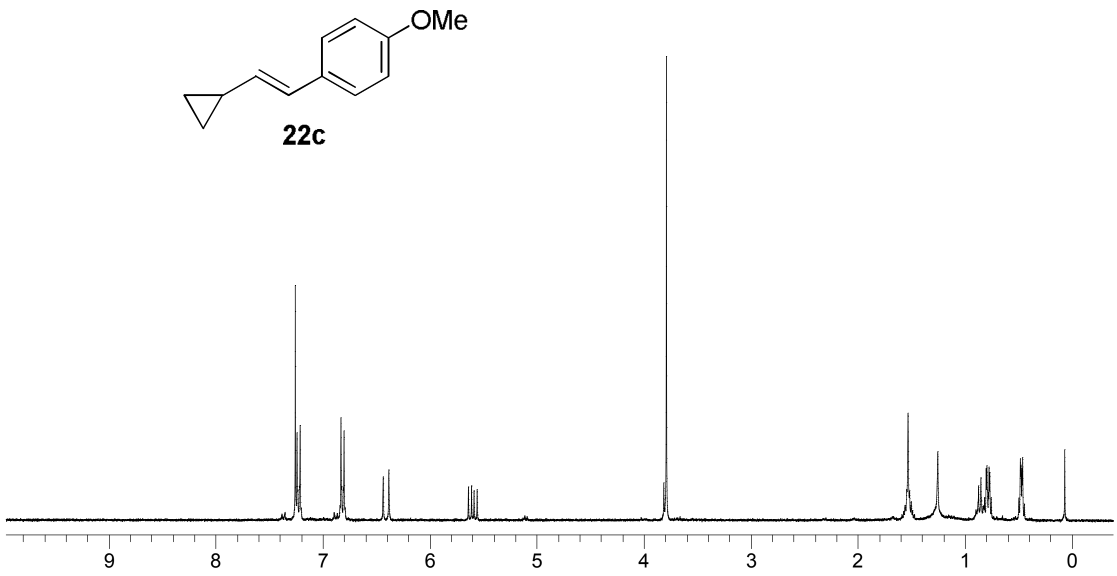
OMe
22c
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7
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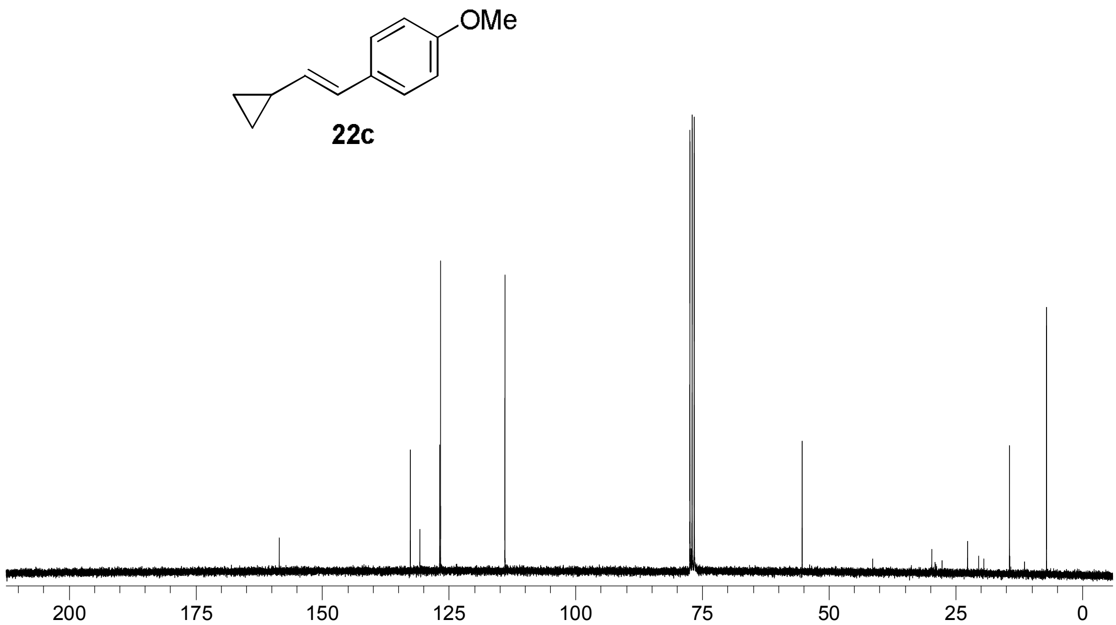
OMe
22c
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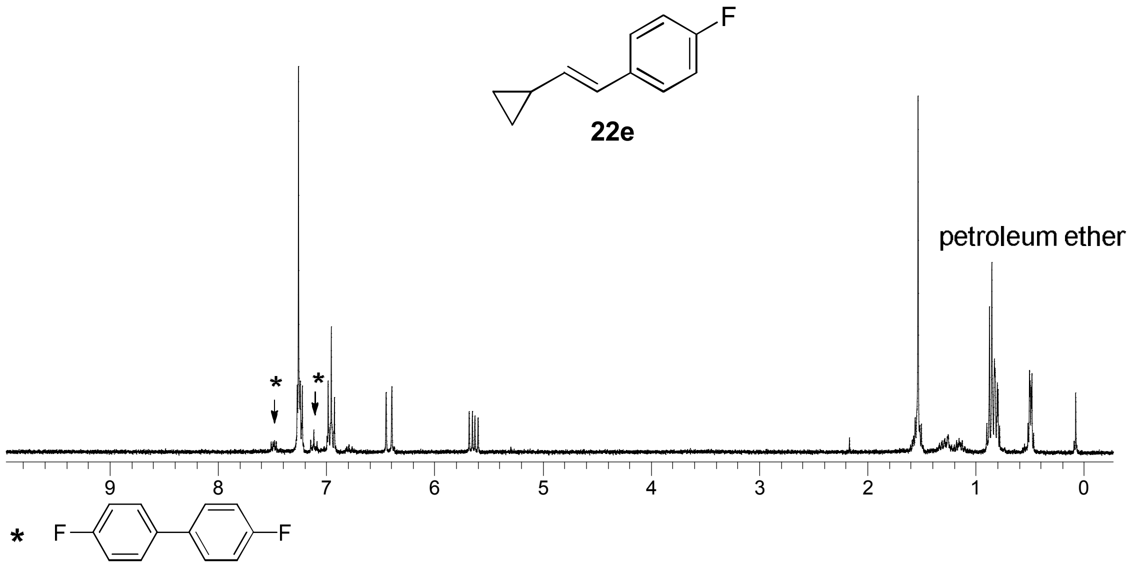
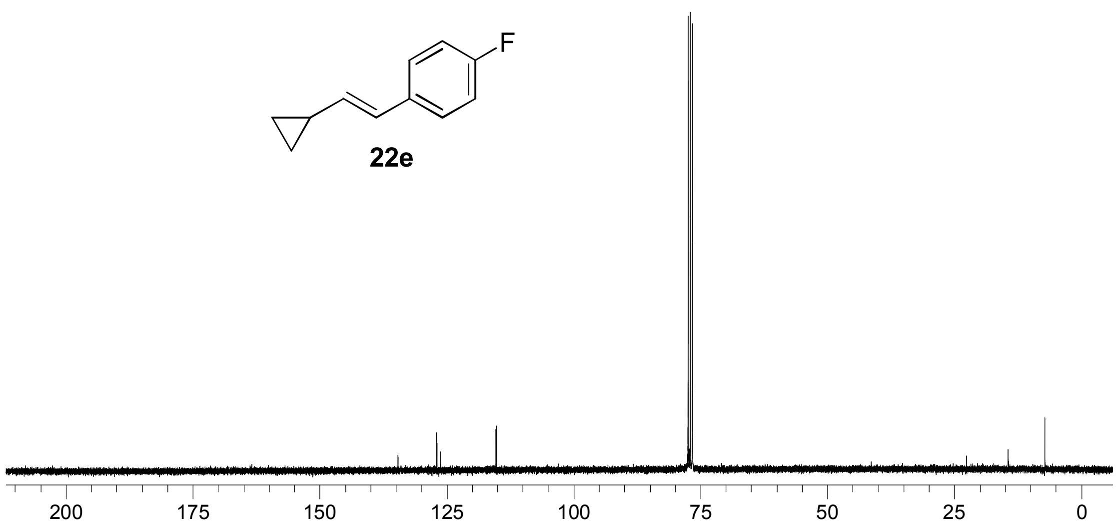


F
22e
petroleum ether
*
*
9
8
7
6
5
4
3
2
1
0
* F
F



F
22e
200
175
150
125
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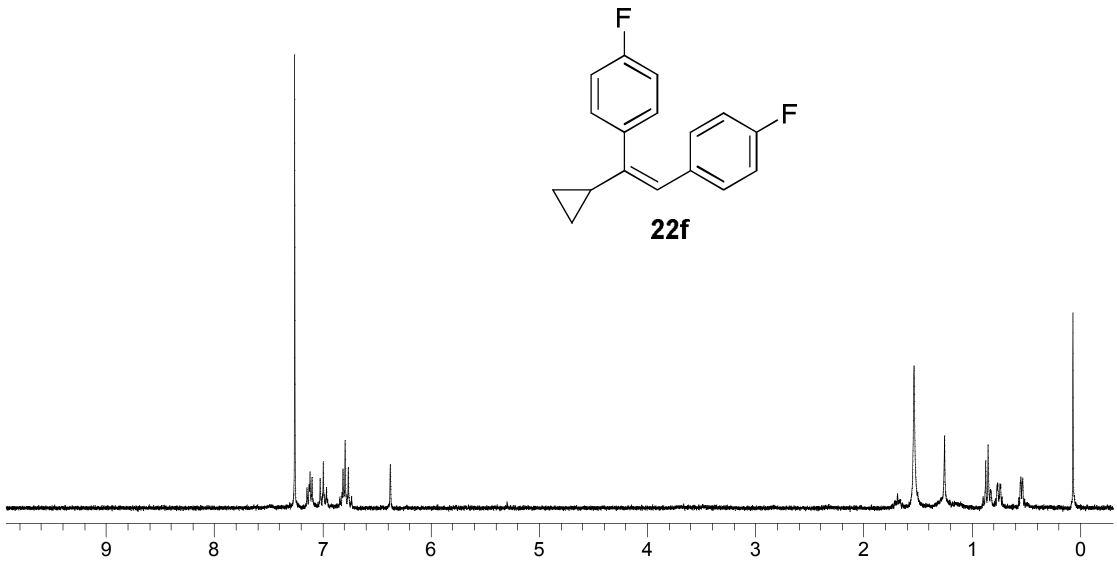
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F
22f
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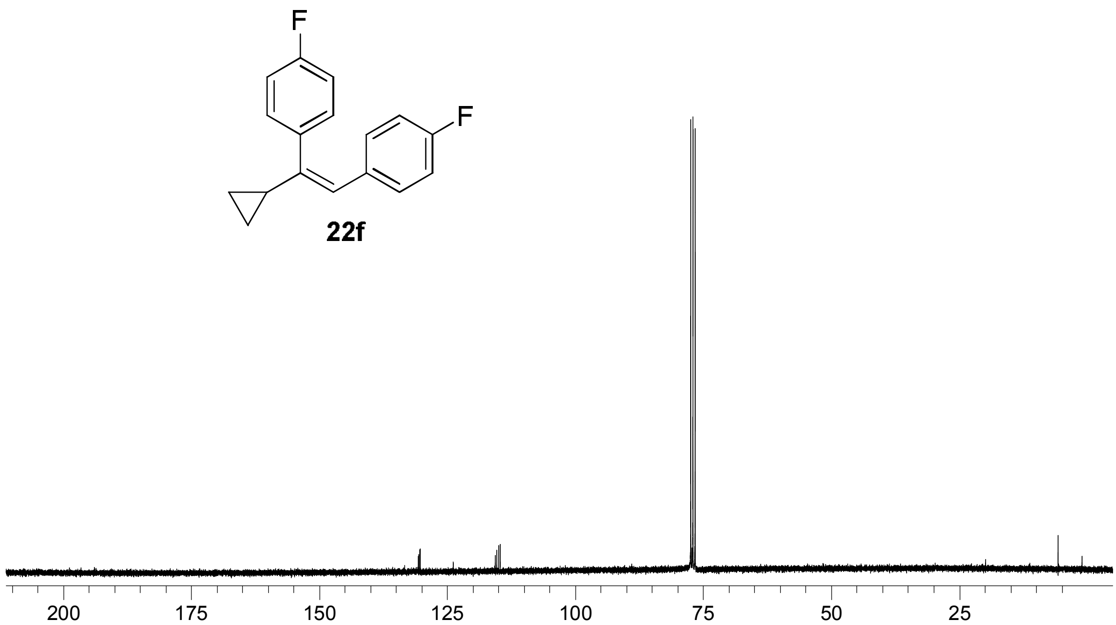
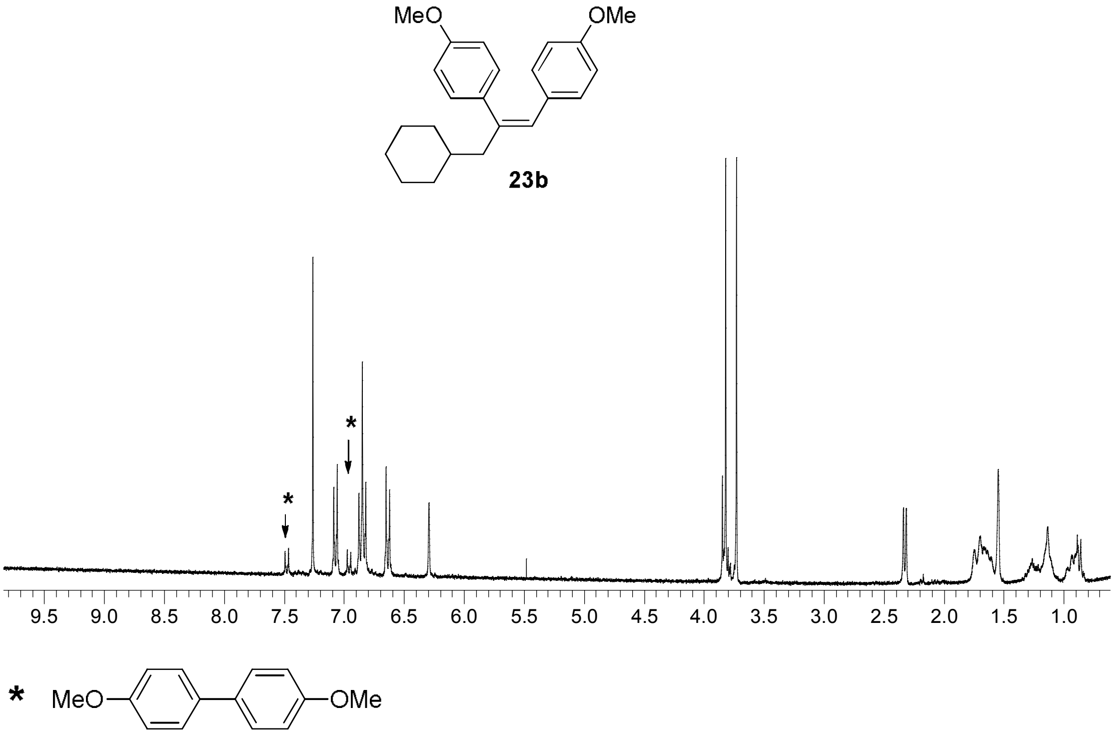
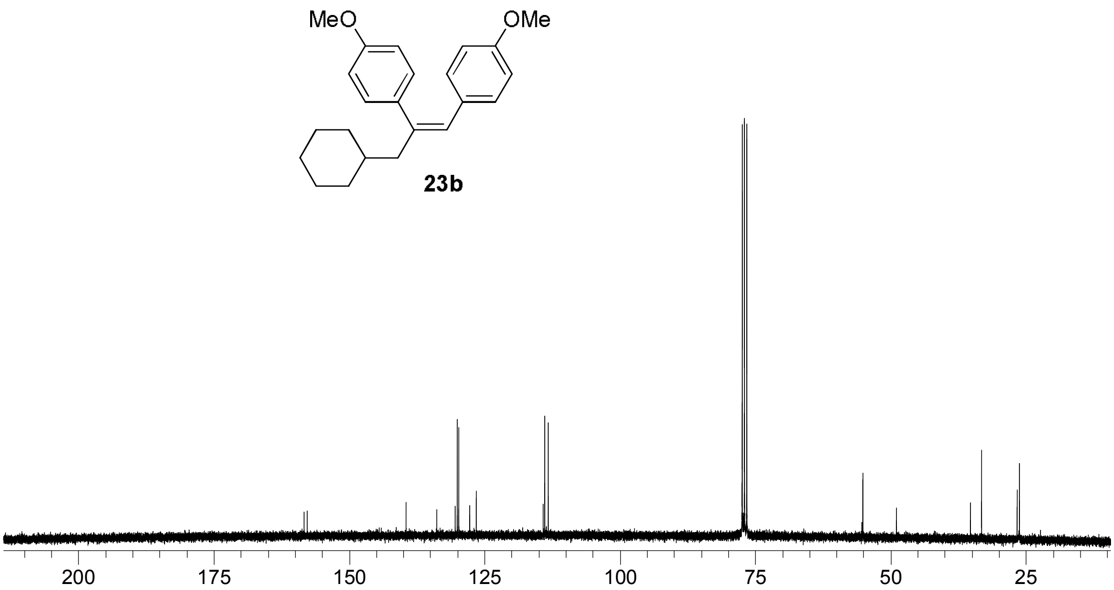
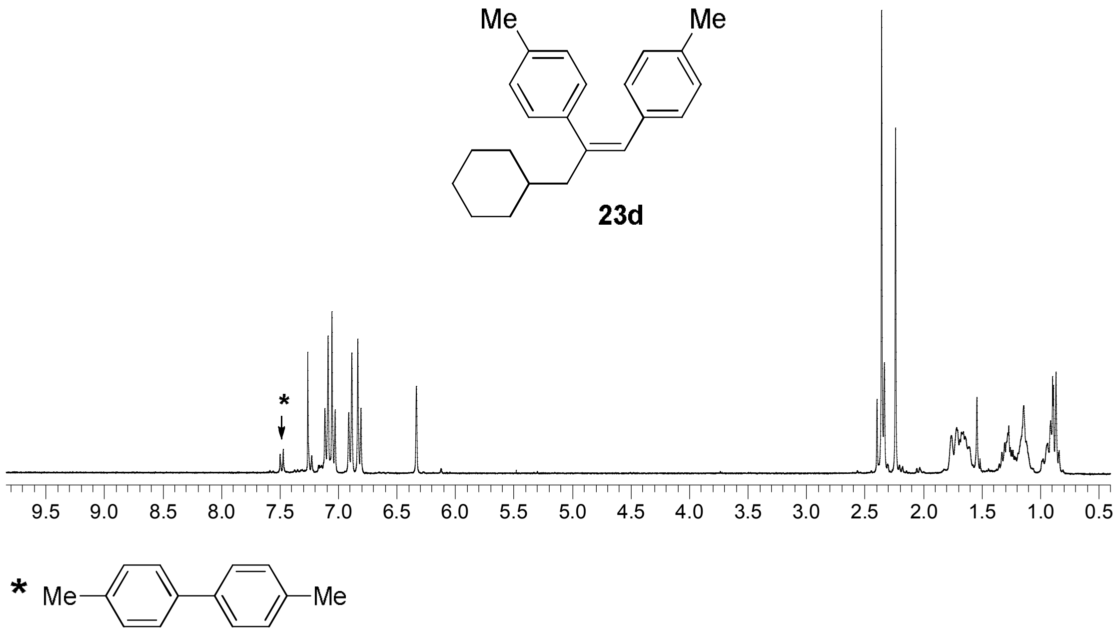
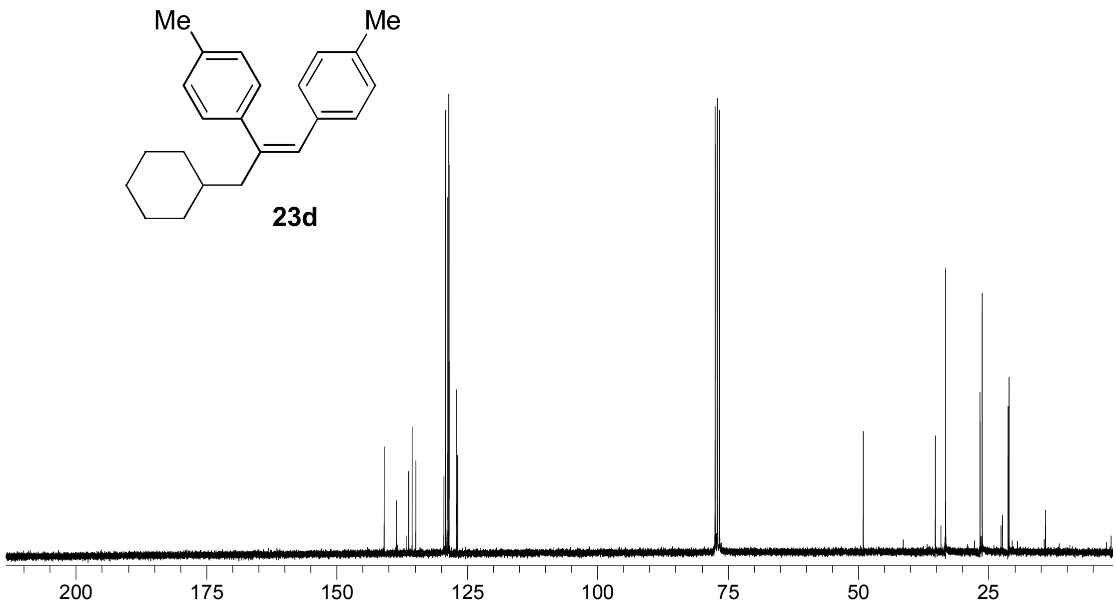

F
F
22f
200 175 150 125 100 75 50 25


MeO
OMe
23b
*
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
* MeO OMe


MeO
OMe
23b
200 175 150 125 100 75 50 25


Me
Me
23d
*
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
* Me
Me


Me
Me
23d
200 175 150 125 100 75 50 25