Supporting information

Using Light to Control the Inhibition of Karstedt's Catalyst

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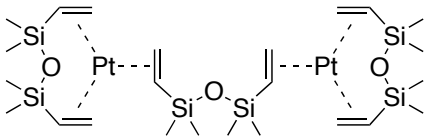
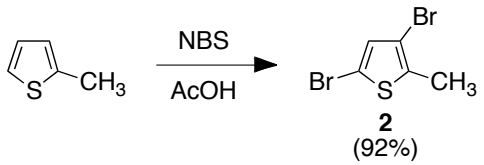
Materials and Methods

General. All solvents and reagents used for synthesis, chromatography, UV-vis spectroscopy and photochemical studies were purchased from Aldrich, Anachemia, Caledon Labs, Fisher Scientific or Alfa Aesar, and used as received. Solvents used for metal-halogen exchange reactions were dried and degassed by passing them through steel columns containing activated alumina under nitrogen using an MBraun solvent purification system. Solvents for NMR analysis were purchased from Cambridge Isotope Laboratories and used as received. Column chromatography was performed using silica gel 60 (230–400 mesh) from Silicycle Inc. Karstedt's catalyst used for all hydrosilylation experiments was purchased from Aldrich and was used as received. According to the company, it is a complex solution containing Pt(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane in xylene with *approx.* 2% metal content. The structure of complex in solution consists of both bridging and chelating divinyl ligands (shown in the figure below).

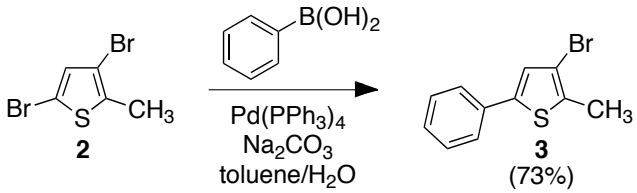


Instrumentation. ^{1}H and ^{13}C NMR characterizations were performed on a Bruker Avance-400 instrument with a 5 mm inverse probe operating at 400.13 MHz for ^{1}H NMR and 100.61 MHz for ^{13}C NMR. ^{195}Pt NMR characterizations were performed on a Bruker Avance-400 Solids and Microimaging instrument. Chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane using the residual solvent peak as a reference. Coupling constants (J) are reported in Hertz. UV-visible absorption spectra were recorded on a Varian Cary 300 Bio-spectrophotometer. High Resolution Mass Spectroscopy (HRMS) measurements were performed using an Agilent 6210 TOF LC/MS in ESI-(+) mode. Melting points were measured using a Gallenkamp melting point apparatus and are uncorrected.

Photochemistry. All the ring-closing reactions were carried out using the light source from a lamp used for visualizing TLC plates at 312 nm (Spectroline E series, 470 W/cm^2). The ring-opening reactions were carried out using the light of a 150 W halogen photo-optic source passed through a 435 nm cut-off filter to eliminate higher energy light.



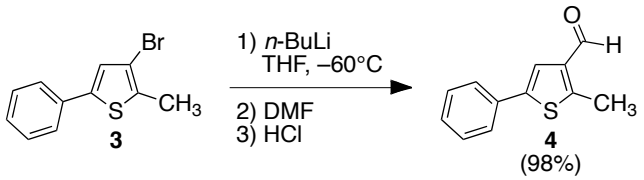
Synthesis of 3,5-dibromo-2-methylthiophene (2).[1] A solution of 2-methylthiophene (20.0 g, 0.2 mol) in glacial acetic acid (200 mL) was slowly treated with *N*-bromosuccinimide (72.5 g, 0.4 mol) while stirring at room temperature. After stirring for an additional 90 min, the reaction was neutralized by the addition of aqueous NaOH (8% w/v). The mixture was extracted with CH_2Cl_2 (3 × 100 mL), the combined organic extracts were washed with saturated aqueous sodium thiosulphate (100 mL) to remove any unreacted bromine, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. Purification by vacuum distillation afforded 18.5 g (92%) of 3,5-dibromo-2-methylthiophene (**2**) as a colourless oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.85 (s, 1H), 2.34 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 135.7, 131.7, 108.5, 108.3, 14.6.



Synthesis of 3-bromo-2-methyl-5-phenylthiophene (3).[2]

A bi-phasic mixture of a solution of 3,5-dibromo-2-methylthiophene (**2**) (15.0 g, 58.6 mmol) in toluene (100 mL) and aqueous Na_2CO_3 (100 mL, 1M) in a 250 mL 3-necked round-bottom flask equipped with a reflux condenser was deoxygenated by bubbling N_2 through it for 60 min. The mixture was then treated with a solution of phenylboronic acid (7.2 g, 58.6 mmol) in EtOH (50 mL). The resulting mixture was heated to 80°C for 30 min, followed by the addition of $Pd(PPh_3)_4$ (0.6 g, 0.5 mmol) in one portion. The reaction contents were heated at reflux for 16 h under a N_2 atmosphere. The heat source was removed and the mixture was allowed to cool to room temperature, at which time it was extracted with Et_2O (3 × 100 mL). The combined organic extracts were washed with brine (100 mL), dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. Purification by column chromatography using silica gel (hexanes) afforded 11.0 g (73%) of 3-bromo-2-methyl-5-phenylthiophene (**3**) as a white solid.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, J = 7.3 Hz, 2H), 7.38 (d, J = 7.9 Hz, 2H), 7.31 (d, J = 7.3 Hz, 1H), 7.13 (s, 1H), 2.44 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 140.9, 133.4, 133.3, 128.7, 127.5, 125.33, 125.1, 109.6, 14.6.
Melting point: 60-61 °C.

[1] S. Lee, Y. You, K. Ohkubo, S. Fukuzumi and W. Nam, W. *Chem. Sci.* 2014, **5**, 1463.
[2] D. Sud, T.J. Wigglesworth and N.R Branda, *Angew. Chem. Int. Ed.* 2007, **46**, 8017.



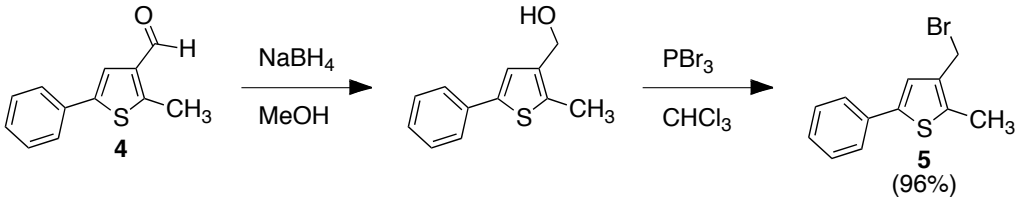
Synthesis of 2-methyl-5-phenylthiophene-3-carbaldehyde (4).[3] A solution of 3-bromo-2-methyl-5-phenylthiophene (**3**) (356 mg, 1.41 mmol) in anhydrous THF (50 mL) in a flame dried 3-necked round bottom flask equipped with a mechanical stirrer was cooled to -60°C (dry ice/acetone bath) under N_2 atmosphere. The solution was treated with *n*-BuLi (2.5 M in hexanes, 0.58 mL, 1.45 mmol) dropwise over a period of 15 min. The mixture was stirred for a further 10 min at -60°C and the reaction progress was monitored by TLC (20:1 hexanes/EtOAc). After all the starting material was consumed, dimethylformamide (0.22 mL, 2.85 mmol) was added to the reaction mixture. After stirring for 1 h at -60°C, the cooling bath was removed and the reaction contents were allowed to warm to room temperature, and was left to stir for 16 h under a N_2 atmosphere. The mixture was poured into 1M HCl (50 mL) and extracted with Et_2O. The organic layer was washed with saturated $NaHCO_3$ (2 × 50 mL), followed by brine (2 × 50 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification by column chromatography using silica gel (20:1 hexanes/EtOAc) afforded 348 mg (98%) of 2-methyl-5-phenylthiophene-3-carbaldehyde (**4**) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.01 (s, 1H), 7.55 (s, 1H), 7.54 (d, J = 7.1 Hz, 2H), 7.37 (d, J = 7.8 Hz, 2H), 7.31 (d, J = 7.8 Hz, 1H), 2.77 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 184.6, 151.4, 141.4, 138.1, 133.3, 129.2, 128.16, 125.9, 122.2, 13.8.

Melting point: 78-79 °C.

HRMS (ESI): m/z (M+H) calculated for $C_{12}H_{11}OS$: 203.052512, found: 203.052572.

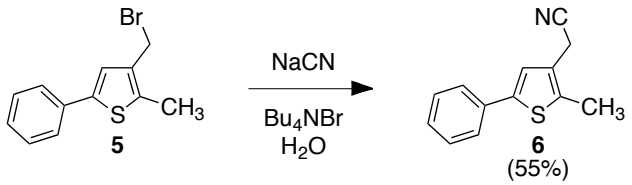


Synthesis of 3-(bromomethyl)-2-methyl-5-phenylthiophene (5).[4]

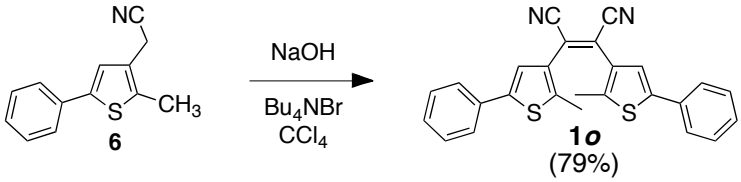
A solution of 2-methyl-5-phenylthiophene-3-carbaldehyde (**4**) (1.6 g, 7.8 mmol) in MeOH (50 mL) was cooled to 0 °C in an ice bath and treated with $NaBH_4$ (0.59 g, 15.6 mmol). The reaction was stirred at 0 °C for 1 h and the reaction progress was monitored by TLC (20:1 hexanes/EtOAc). On completion, the reaction mixture was washed with 5% HCl and extracted with Et_2O (2 × 50 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure at low temperature. The crude alcohol was dissolved in chloroform (50 mL) and slowly treated with a solution of PBr_3 (1M in CH_2Cl_2, 15.6 mL, 15.6 mmol). The reaction mixture were allowed to stir for 2.5 h at room temperature while monitoring the reaction using TLC (3:1 hexanes/EtOAc). Upon completion, the contents were washed with saturated $NaHCO_3$ (50 mL),

[3] D. Wilson, and N.R. Branda, *Angew. Chem. Int. Ed.* 2012, **51**, 5431.
[4] M. D'Auria, A. De Mico, F. D'Onofrio and G. Piancatelli, *J. Org. Chem.* 1987, **52**, 5243.

followed by brine (50 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure to afford 1.51 g (96%) of 3-(bromomethyl)-2-methyl-5-phenylthiophene (**5**) as a yellow solid, which was used without further purification.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, J = 7.1 Hz, 2H), 7.36 (d, J = 7.8 Hz, 2H), 7.28 (d, J = 7.4 Hz, 1H), 7.18 (s, 1H), 4.46 (s, 2H), 2.46 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 140.8, 137.9, 134.4, 134.1, 129.0, 127.6, 125.6, 124.6, 26.3, 13.2.
Melting point: 70-71 °C



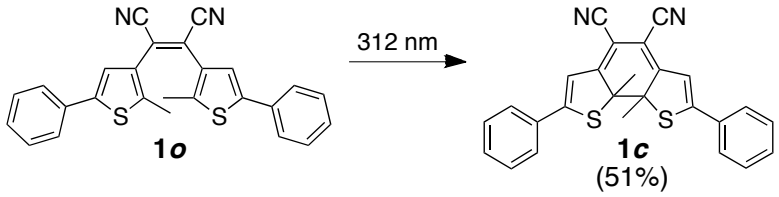
Synthesis of 2-(2-methyl-5-phenylthiophen-3-yl) acetonitrile (6).[5] A mixture of 3-(bromomethyl)-2-methyl-5-phenylthiophene (**5**) (0.53 g, 2.0 mmol), tetrabutylammonium bromide (310 mg, 1 mmol) and sodium cyanide (560 mg, 11.4 mmol) in water (10 mL) was heated at reflux for 3 h. After complete consumption of reactant **5** as monitored by TLC (4:1 hexanes/EtOAc), the reaction was cooled to room temperature and extracted with Et_2O (3 × 20 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification by column chromatography using silica gel (4:1 hexanes/EtOAc) afforded 291 mg (55%) of 2-(2-methyl-5-phenylthiophen-3-yl) acetonitrile (**6**) as a yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, J = 7.2 Hz, 3H), 7.36 (d, J = 7.8 Hz, 2H), 7.29 (d, J = 7.4 Hz, 1H), 7.15 (s, 1H), 3.59 (s, 2H), 2.43 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 141.1, 135.2, 133.6, 128.8, 127.4, 125.3, 123.5, 117.2, 16.8, 13.0.
Melting point: 58-59 °C.
HRMS (ESI): m/z (M+Na) calculated for $C_{13}H_{11}NNaS$: 236.050441, found: 236.050476.



Synthesis of 2,3-bis(2-methyl-5-phenylthiophen-3-yl) maleonitrile (1*o*).[6] A solution of 2-(2-methyl-5-phenylthiophen-3-yl) acetonitrile (**6**) (0.93 g, 2.2 mmol) in CCl_4 (5 mL) was added to a stirring solution of 50% aqueous NaOH (5 mL) containing tetrabutylammonium bromide (35 mg, 0.11 mmol) at room temperature. The mixture was stirred at 50°C for 1.5 h and the reaction progress was monitored by TLC (10:1 hexanes/EtOAc). Upon completion, the reaction mixture was poured into water and extracted with chloroform (2 × 10 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification by column chromatography using silica gel (10:1 hexanes/EtOAc) afforded 735 mg (79%) of 2,3-bis(2-methyl-5-phenylthiophen-3-yl) maleonitrile (**1*o***) as a yellow-green solid.

[5] K. Uchida, Y. Kido, T. Yamaguchi and M. Irie, *Bull. Chem. Soc. Jpn.* 1998, **71**, 1101.
[6] M. Ohsumi, T. Fukaminato and M. Irie, *Chem. Commun.* 2005, 3921.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, J = 8.1 Hz, 3H), 7.33 (d, J = 7.2 Hz, 2H), 7.29 (d, J = 7.1 Hz, 1H), 6.91 (s, 1H), 2.31 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 142.4, 133.1, 131.8, 129.4, 128.6, 127.5, 126.0, 121.1, 116.4, 15.0.
Melting point: 132-133 °C.
HRMS (ESI): m/z (M+H) calculated for $C_{26}H_{18}N_2S_2$: 423.098417, found: 423.097986.



Photochemistry of 1*o*. A $CHCl_3$ solution of **1*o*** (1.05×10^{-5} M) in a cuvette was exposed to 312 nm light until no further changes were observed in the UV-vis absorption spectrum.[7] After 120 s the photostationary state was reached (Figure S1).

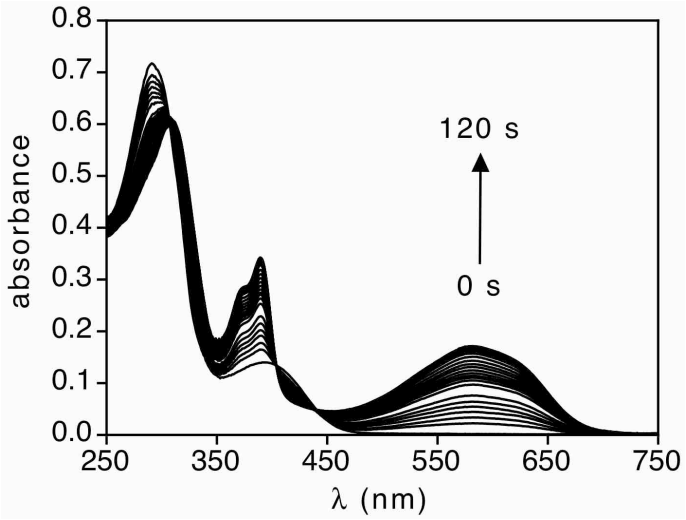


Figure S1. Changes in UV-vis absorption spectrum when a $CDCl_3$ solution of **1*o*** (1.05×10^{-5} M) was exposed to 312 nm light for 120 s.

Photochemical synthesis of 1*c*. A $CDCl_3$ solution of compound **1*o*** (5×10^{-3} M) in an NMR tube was irradiated with 312 nm light until no further changes were observed in the ^{1}H NMR spectrum (Figure S1). After 120 min the photostationary state was reached at this concentration, which contained 51% of the ring-closed isomer **1*c*** as measured by comparing relative integrals for chemical shifts for **1*o*** and **1*c*** (Figure S2). The ring-closed isomer **1*c*** was isolated by column chromatography using silica gel (2:1 CH_2Cl_2/hexanes).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, J = 6.8 Hz, 2H), 7.46 (d, J = 6.8 Hz, 2H), 7.44 (d, J = 6.7 Hz, 1H), 6.72 (s, 1H), 2.17 (s, 3H).

[7] All ring-closing reactions were carried out using the light source from a lamp used for visualizing TLC plates at 312 nm (Spectroline E series, 470 W/cm^2).

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.72, 144.69, 130.82, 129.20, 127.25, 115.62, 108.90, 99.58, 57.19, 29.87.

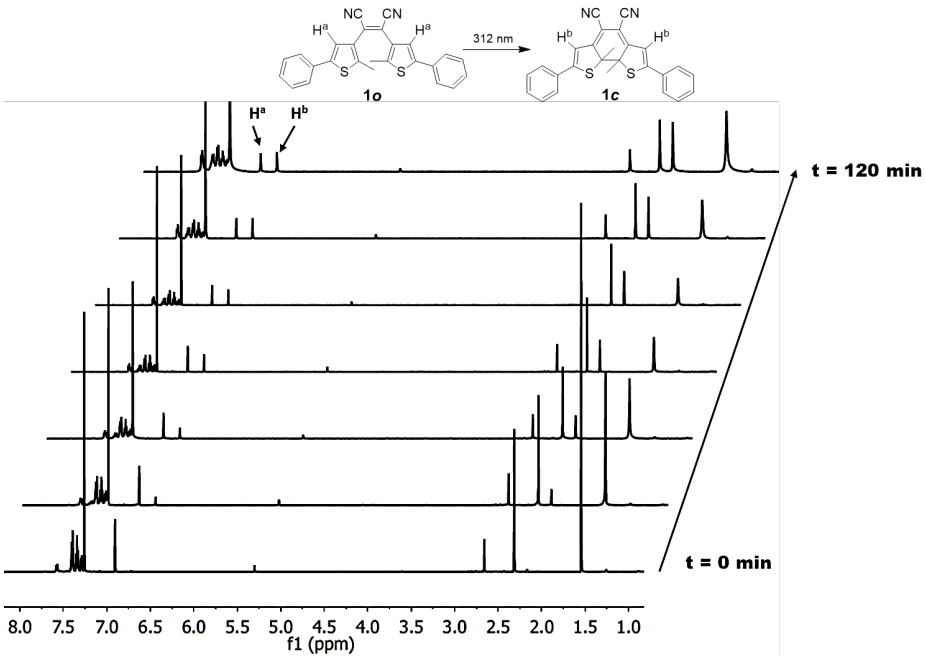


Figure S2. Changes in the ^{1}H NMR spectrum when a $CDCl_3$ of **1*o*** (5×10^{-3} M) was exposed to 312 nm light for 120 min.

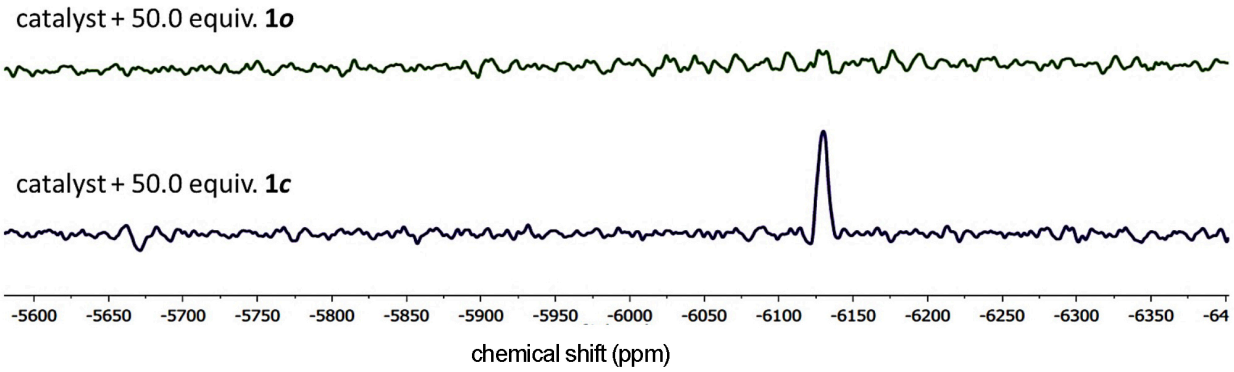
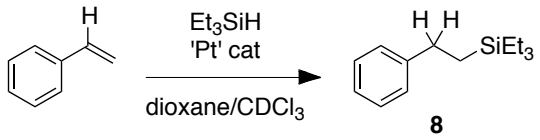


Figure S3. The ^{195}Pt-NMR spectra for solutions of Karstedt's catalyst (15 µL) in toluene-d_8 (500 µL) at 25 °C in the presence of an excess of ring-open isomer (**1*o***) (top) and ring-closed isomer (**1*c***) (bottom). The spectra acquired for pure Karstedt's catalyst has a peak at δ = -6130 ppm, which is common for low valent, platinum alkene complexes.[8,9]

[8] T.K. Meister, K. Riener, P. Gigler, J. Stohrer, W.A. Herrmann and F.E. Kühn, *ACS Catal.*, 2016, **6,** 1274.
[9] B. Marcinie and J. Chojnowski, *Progress in Organosilicon Chemistry*, Gordon and Breach Science Publishers S.A., Basel, 1995.



Model reaction 1: hydrosilylation without an inhibitor. A solution of styrene (124 µL, 1.08 mmol) and 1,4-dioxane (20 µL) as an internal standard in $CDCl_3$ (500 µL) in an NMR tube was treated with Karstedt's catalyst (15 µL solution (*approx.* 2% metal content in xylene), 1.31 µmol of Pt, 0.12% catalyst) followed by triethylsilane (172 µL, 1.08 mmol). An initial ^{1}H NMR spectrum was immediately acquired. The NMR tube was heated at 30 °C for 4 h while ^{1}H NMR spectra were recorded every hour. The areas under the peaks corresponding to styrene proton (δ = 5.82 ppm) and the protons of product **8** (δ = 2.72 ppm) were measured and compared to the internal standard to monitor the progress of the reaction. These results are shown in Figure S4 and S5.

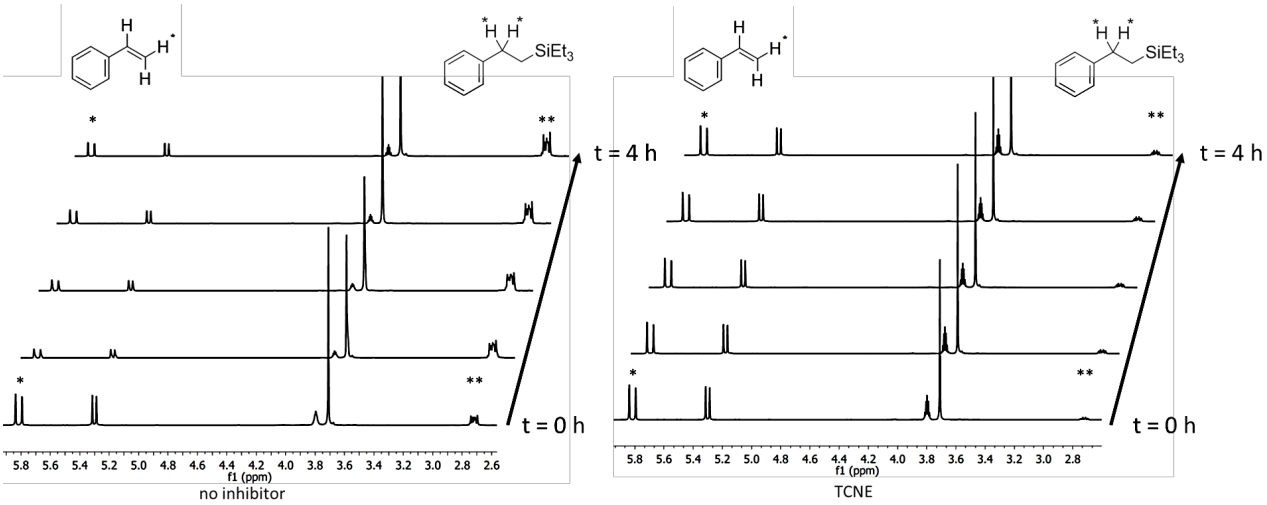


Figure S4. Changes in ^{1}H NMR spectrum corresponding to styrene proton (δ = 5.82 ppm) and the protons of product **8** (δ = 2.72 ppm) when a $CDCl_3$ solution of styrene, triethylsilane and dioxane (as an internal standard) was treated with Karstedt's catalyst for 4 h at 30°C without inhibitor (left) and with TCNE (right).

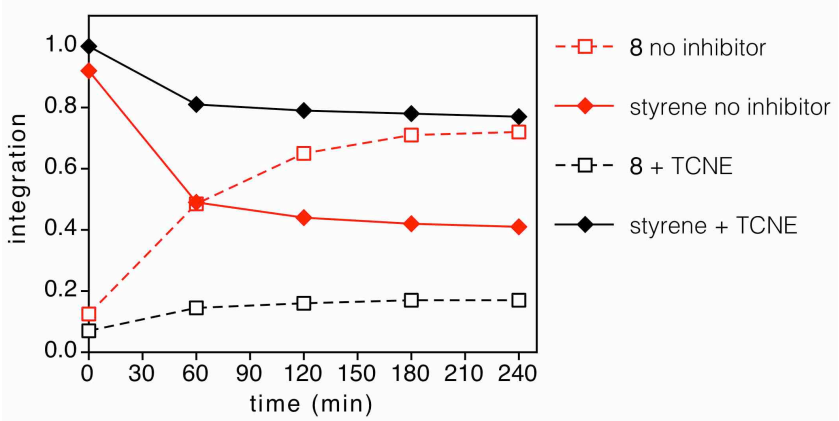


Figure S5. Changes in integration of the signals in the ^{1}H NMR spectrum corresponding to the protons highlighted in Figure S3 when a $CDCl_3$ solution of styrene, triethylsilane and dioxane (as an internal standard) was treated with Karstedt's catalyst for 4 h at 30°C without inhibitor and with TCNE.

Model reaction 2: hydrosilylation with tetracyanoethylene (TCNE) as an inhibitor. A solution of styrene (124 μL, 1.08 mmol) and 1,4-dioxane (20 μL) as an internal standard in $CDCl_3$ (500 μL) in an NMR tube was treated with Karstedt's catalyst (15 μL solution (*approx.* 2% metal content in xylene), 1.31 μmol of Pt, 0.12% catalyst) followed by TCNE (0.4 mg, 3.3 μmol, 2.5 equivalents compared to Pt) and finally triethylsilane (172 μL, 1.08 mmol). An initial ^{1}H NMR spectrum was immediately acquired. The NMR tube was heated at 30°C for 4 h while ^{1}H NMR spectra were recorded every hour. The areas under the peaks corresponding to styrene proton (δ = 5.82 ppm) and the protons of product **8** (δ = 2.72 ppm) were measured and compared to the internal standard to monitor the progress of the reaction. These results are shown in Figure S4 and S5.

Hydrosilylation with ring-open isomer 1*o* as an inhibitor. A solution of styrene (124 μL, 1.08 mmol) and 1,4-dioxane (20 μL) as an internal standard in $CDCl_3$ (500 μL) in an NMR tube was treated with Karstedt's catalyst (15 μL solution (*approx.* 2% metal content in xylene), 1.31 μmol of Pt, 0.12% catalyst) followed by compound **1*o*** (1.4 mg, 3.3 μmol, 2.5 equivalents compared to Pt) and triethylsilane (172 μL, 1.08 mmol). An initial ^{1}H NMR spectrum was immediately acquired. The NMR tube was heated at 30 °C for 4 h while ^{1}H NMR spectra were recorded every 10 min. The areas under the peaks corresponding to styrene proton (δ = 5.82 ppm) and the protons of product **8** (δ = 2.72 ppm) were measured and compared to the internal standard to monitor the progress of the reaction. These results are shown in Figure S6.

Hydrosilylation with ring-closed isomer 1*c* as an inhibitor. A solution of styrene (124 μL, 1.08 mmol) and 1,4-dioxane (20 μL) as an internal standard in $CDCl_3$ (500 μL) in an NMR tube was treated with Karstedt's catalyst (15 μL solution (*approx.* 2% metal content in xylene), 1.31 μmol of Pt, 0.12% catalyst) followed by isolated compound **1*c*** (1.4 mg, 3.3 μmol, 2.5 equivalents compared to Pt) and triethylsilane (172 μL, 1.08 mmol). An initial ^{1}H NMR spectrum was immediately acquired. The NMR tube was heated at 30°C for 4 h while ^{1}H NMR spectra were recorded every 10 min. The areas under the peaks corresponding to styrene proton (δ = 5.82 ppm) and the protons of product **8** (δ = 2.72 ppm) were measured and compared to the internal standard to monitor the progress of the reaction. These results are shown in Figure S5. The reaction was repeated at 20°C and the results are shown in Figure S6.

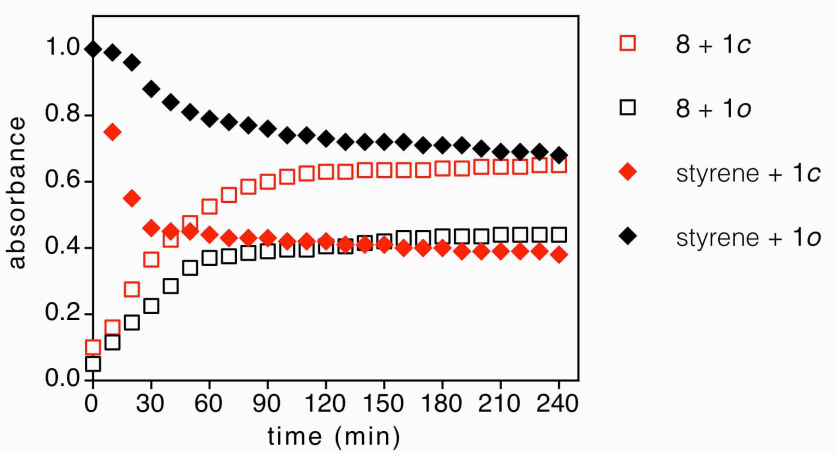


Figure S6. Changes in integration of the signals in the ^{1}H NMR spectrum corresponding to the protons shown in the reaction above when a $CDCl_3$ solution of styrene, triethylsilane, **1*o*** and dioxane (as an internal standard) was treated with Karstedt's catalyst for 4 h at 30 °C.

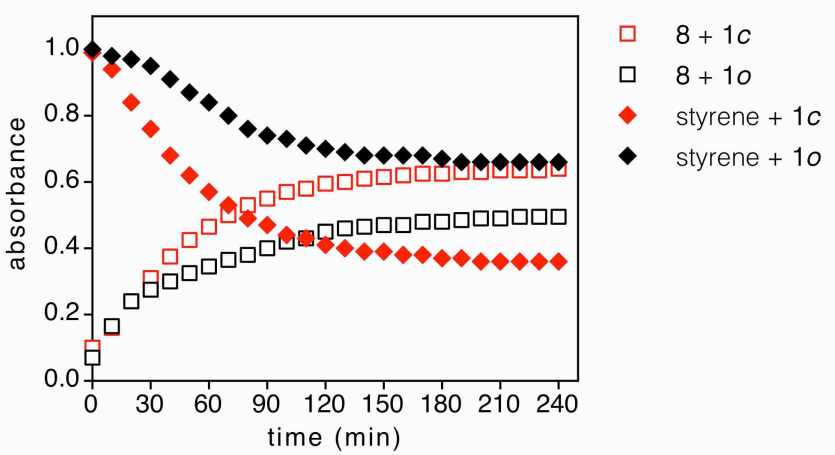


Figure S7. Changes in integration of the signals in the ^{1}H NMR spectrum corresponding to the protons shown in the reaction above when a $CDCl_3$ solution of styrene, triethylsilane, **1*c*** and dioxane (as an internal standard) was treated with Karstedt's catalyst for 4 h at 20 °C.

In situ experiments

A solution of styrene (124 µL, 1.08 mmol) and 1,4-dioxane (20 µL) as an internal standard in $CDCl_3$ (500 µL) in an NMR tube was treated with Karstedt's catalyst (15 µL solution (*approx.* 2% metal content in xylene), 1.31 µmol of Pt, 0.12% catalyst) followed by compound **1*o*** (1.4 mg, 3.3 µmol, 2.5 equivalents compared to Pt) and triethylsilane (172 µL, 1.08 mmol). An initial ^{1}H NMR spectrum was immediately acquired. The NMR tube was kept in a water bath at 20 °C for 30 min followed by the acquisition of another ^{1}H NMR spectrum. The contents of the tube were then irradiated with 312 nm light for 5 minutes to induce the ring-closing reaction. The colour changed from colourless to blue indicating the reaction was successful. A ^{1}H NMR spectrum for this coloured solution was immediately acquired. The tube was kept in a water bath at 20 °C for another

150 minutes with ^{1}H NMR spectra being acquired every 30 min. The areas under the peaks corresponding to styrene proton (δ = 5.82 ppm) were measured and compared to the internal standard to monitor the progress of the reaction before and after irradiation. These results are shown in Figure S8.

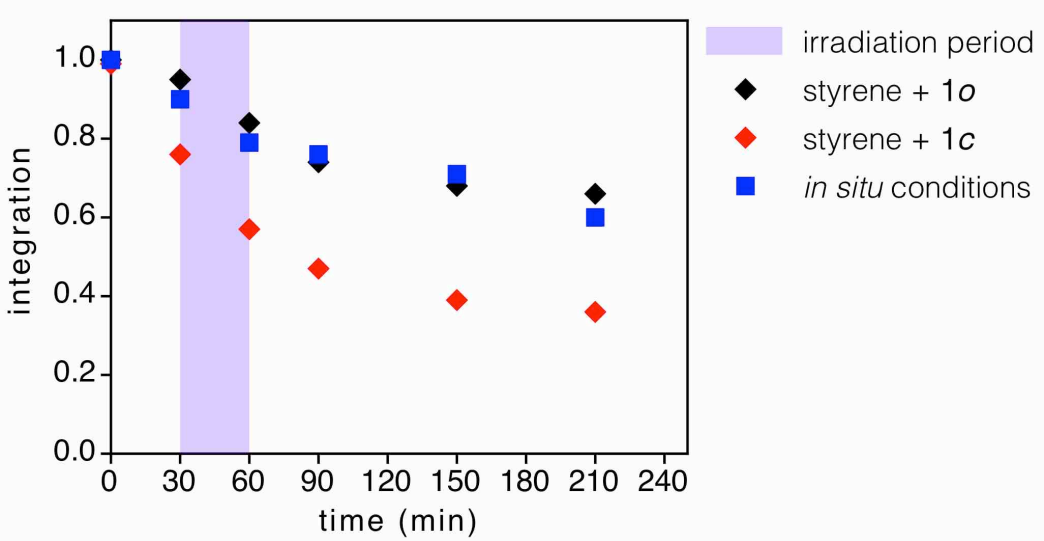


Figure S8. Changes in integration of the signals in the ^{1}H NMR spectrum corresponding to the protons shown in the Figure S3 when a $CDCl_3$ solution of styrene, triethylsilane, **1*o*** and dioxane (as an internal standard) was treated with Karstedt's catalyst at 20 °C for 30 minutes (blue squares) followed by irradiation with 312 nm UV light for 30 minutes (violet shaded area), and further incubation at 20 °C for 150 minutes. The results are compared with corresponding reactions of isolated forms **1*o*** (black diamonds) and **1*c*** (red diamonds).