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Tellurorhodamine photocatalyzed aerobic oxidation of organo-silanes and phosphines by visible-light

Irving D. Rettig, Jackson Van, Jacob Brauer, Wentai Luo, Theresa M. McCormick*

Department of Chemistry, Portland State University, Portland, Oregon, 97201, USA
*t.m.mccormick@pdx.edu

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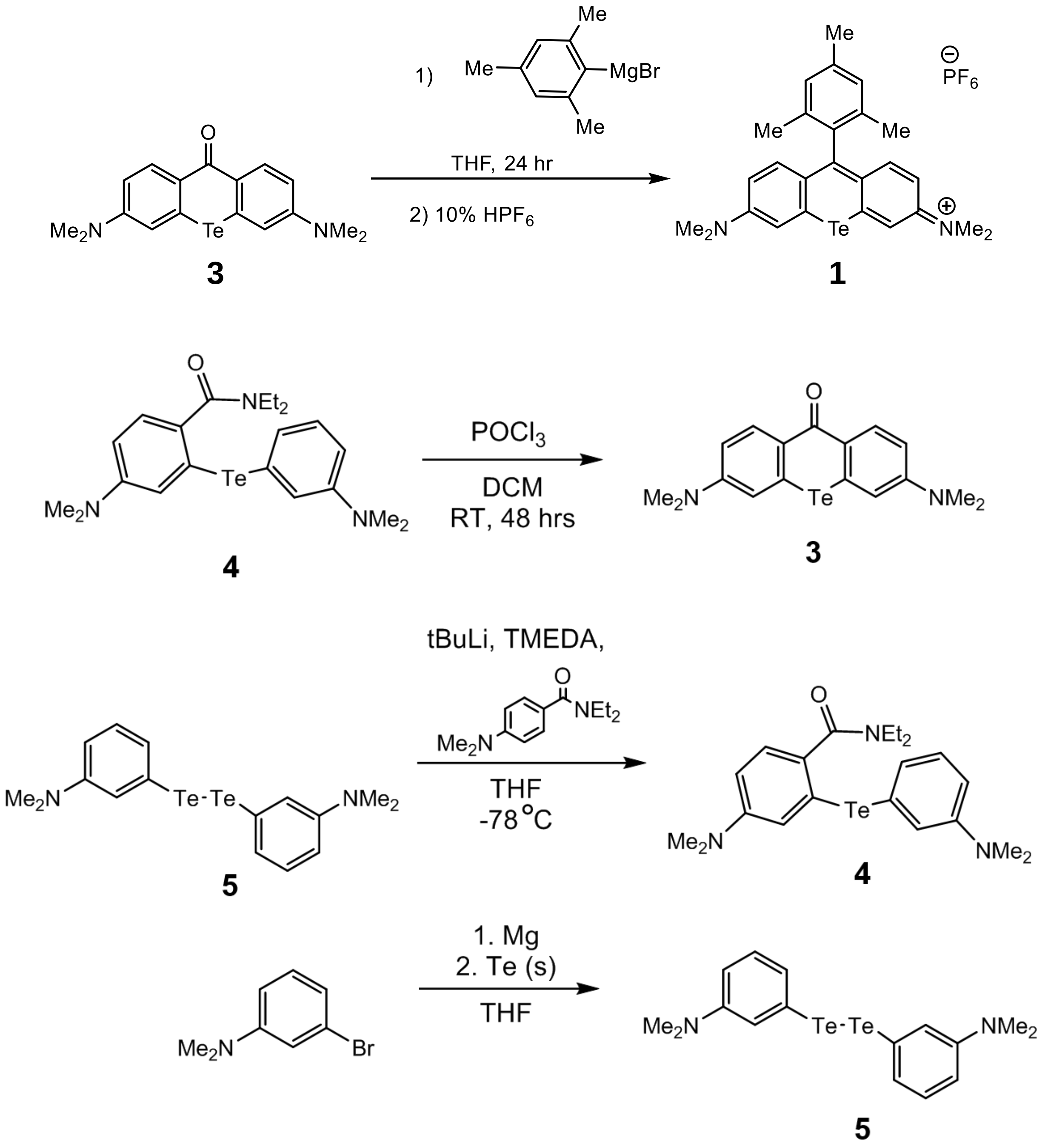

Scheme 1. Complete synthesis of **1** including intermediates **5-3**.

Preparation of the Di-3-N,N-dimethylaminophenyl Ditelluride.(5)

3-Bromo-N,N-dimethylanline (6.0 g, 30.0 mmol) was added to a stirred solution of ground magnesium turnings (14.1 g, 32.0 mmol) in 30 mL of anhydrous THF. The resulting mixture was heated at reflux for 2 h and was then cooled to ambient temperature. Ground tellurium shot (3.82 g, 30.0 mmol) was added, and the reaction mixture was heated at 40 °C for 2 h. The reaction mixture was then cooled to ambient temperature and poured over 10 g of ice. Hydrochloric acid (7.8 mL of a 20% solution) was then added, and the reaction mixture was filtered through Celite to remove unreacted magnesium turnings. Air was bubbled through the reaction mixture for 1 h. The reaction mixture was extracted with ether (3 × 50 mL), and the combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated. The crude product was recrystallized from methanol to give 5.78 g (33%) of a red crystalline solid, ^1H NMR [400 MHz, $CDCl_3$] δ 7.16 (m, 4 H), 7.00 (t, 2 H, J = 7.9), 6.58 (d×d, 2 H, J = 2.0, 7.2 Hz), 2.90 (s, 12 H).

Preparation of N,N-Diethyl 4-N,N-Dimethylamino-2- [3-(N,N-dimethylamino)phenyltelluro]benzamide. (4)

tert-Butyllithium (1.7 M in cyclohexane, 4.6 mL, 7.1 mmol) was added dropwise to a stirred solution of TMEDA (0.82 g, 7.1 mmol) and N,N-diethyl 4-N′,N′-dimethylaminobenzamide (1.9 g, 8.4 mmol) in 99 mL of THF at -78 °C. The resulting solution was stirred at -78 °C for 0.5 h. A solution of di-3- (N,N-dimethylamino)phenyl ditelluride (1.4 g, 6.4 mmol) in 23 mL of THF was then added dropwise. The resulting mixture was stirred at -78 °C for 1.0 h and was then warmed to ambient temperature for 14 h. The reaction mixture was poured into 150 mL of saturated NaCl, and the products were extracted with CH_2Cl_2 (3 × 50 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated. The resulting orange oil was purified via column chromatography on SiO_2 eluted with 30% hexanes in ethyl acetate to give 0.86 g (20.4%) as an orange oil, which was used without further purification: ^{1}H NMR [400 MHz, $CDCl_3$] δ 7.43 (d, 1 H, J = 2.1 Hz), 7.38 (br d, 1 H, J = 7.3 Hz), 7.12 (t, 1 H, J = 7.8 Hz), 6.83 (d×d, 1 H, J 2.3, 8.3 Hz), 6.78 (d, 1 H, J = 4.7 Hz), 6.65 (d×d, 1 H, J = 1.1, 7.48 Hz), 6.56 (d×d, 1 H, J = 2.4, 8.5 Hz), 3.59 (q, 4 H, J = 7.0 Hz), 3.02 (s, 6 H), 2.84 (s, 6 H), 1.35 (t, 6 H, J = 7.0 Hz).

Preparation of 2,7-Bis(N,N-dimethylamino)telluroxanthen-9-one. (3)

Phosphorus oxychloride (2.2 mL, 21.6 mmol) was added dropwise to a solution of N,N-diethyl 4-N,N- (dimethylamino)-2-(3-N,N-dimethylaminophenyltelluro)benzamide (0.85 g, 1.8 mmol) in anhydrous triethylamine (3.0 mL, 21 mmol) and anhydrous CH_2Cl_2 (36 mL) at 0 °C. After addition was complete, the reaction mixture was stirred at ambient temperature for 48 h. A solution of 3 M NaOH (36 mL) was added, and the resulting mixture was stirred for 1 h at ambient temperature. The products were extracted with CH_2Cl_2 (3 × 50 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated. The resulting yellow solid was recrystallized from acetonitrile/ether to give 0.0585 g (11%) as a yellow powder: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, 2 H, J = 9.1 Hz), 6.78 (d, 2 H, J = 2.5 Hz), 6.74 (d×d, 2 H, J = 2.6, 9.1 Hz), 3.05 (s, 12 H).

*Preparation of 3,6-Bis(dimethylamino)-9-(2,4,6-trimethylphenyl)-9H-telluroxanthen-9-ylium Hexafluorophosphate (***1)** 2-Bromomesitylene (0.3 M, 4.3 mmol) was added dropwise to a solution containing solid magnesium turnings (0.15 g, 5.0 mmol) that had been coated with liquid bromine in 10 mL of anhydrous THF. The solution was stirred for 2 hours at ambient temperature. When most of the magnesium turnings had been consumed, the reaction mixture was transferred by canula to a stirring solution of 3,6-bis(dimethylamino)-9H-telluroxanthen-9-one (**4**) (4.0 g, 7.8 mmol) in 15 mL of anhydrous THF. The resultant mixture was heated to reflux for 24 hours, then cooled to ambient temperature and quenched with 0.4 mL of glacial acetic acid. The product was allowed to precipitate for 12 hours after the addition of 10% aqueous HPF_6. The precipitate was collected and rinsed with water (10 mL x 3) and diethyl ether (10 mL x 3) to give 63.0 mg of **1** (35% yield) as a forest green solid and its spectroscopic properties were identical to those reported for **1**.[1]; ^{1}H NMR (400 MHz, methanol-d4) δ 7.89 (s, 2 H), 7.52 (d, 2 H, J = 9.70 Hz), 7.12 (s, 2 H), 6.94 (dd, 2 H, J = 1.18, 9.72 Hz), 3.25 (s, 12 H), 2.43 (s, 3 H), 1.84 (s, 6 H); ^{13}C NMR (600 MHz, methanol-d4) δ 166.2, 153.8,140.1, 139.8, 136.6, 133.0, 129.7, 122.4, 117.1, 116.6, 98.0, 40.6, 21.2,19.6; λmax in MeOH, 598 nm (8.6×10^5 $M^{-1}cm^{-1}$).

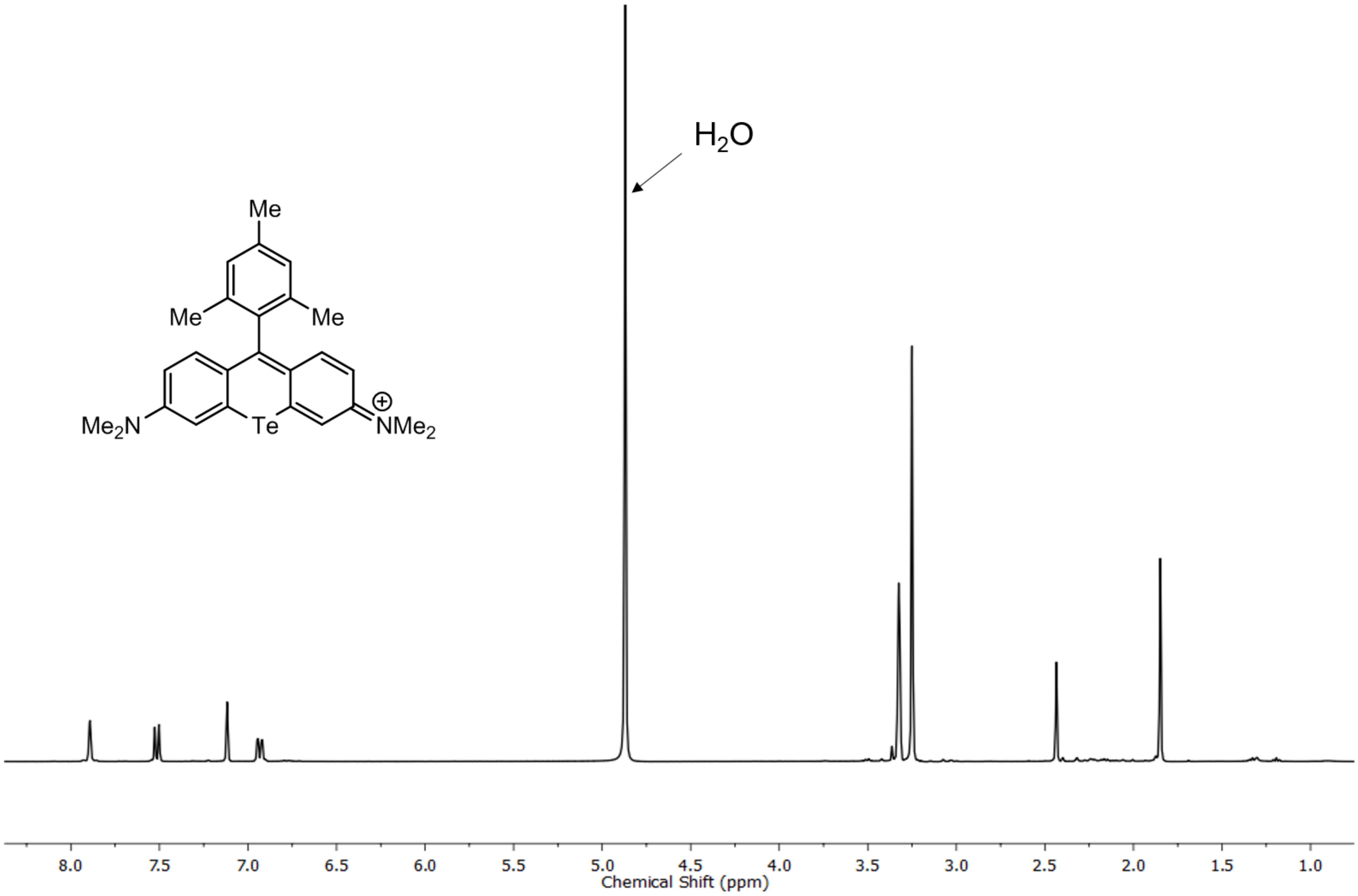

Figure S1. ^{1}H NMR spectrum of **1** in methanol-*d4*

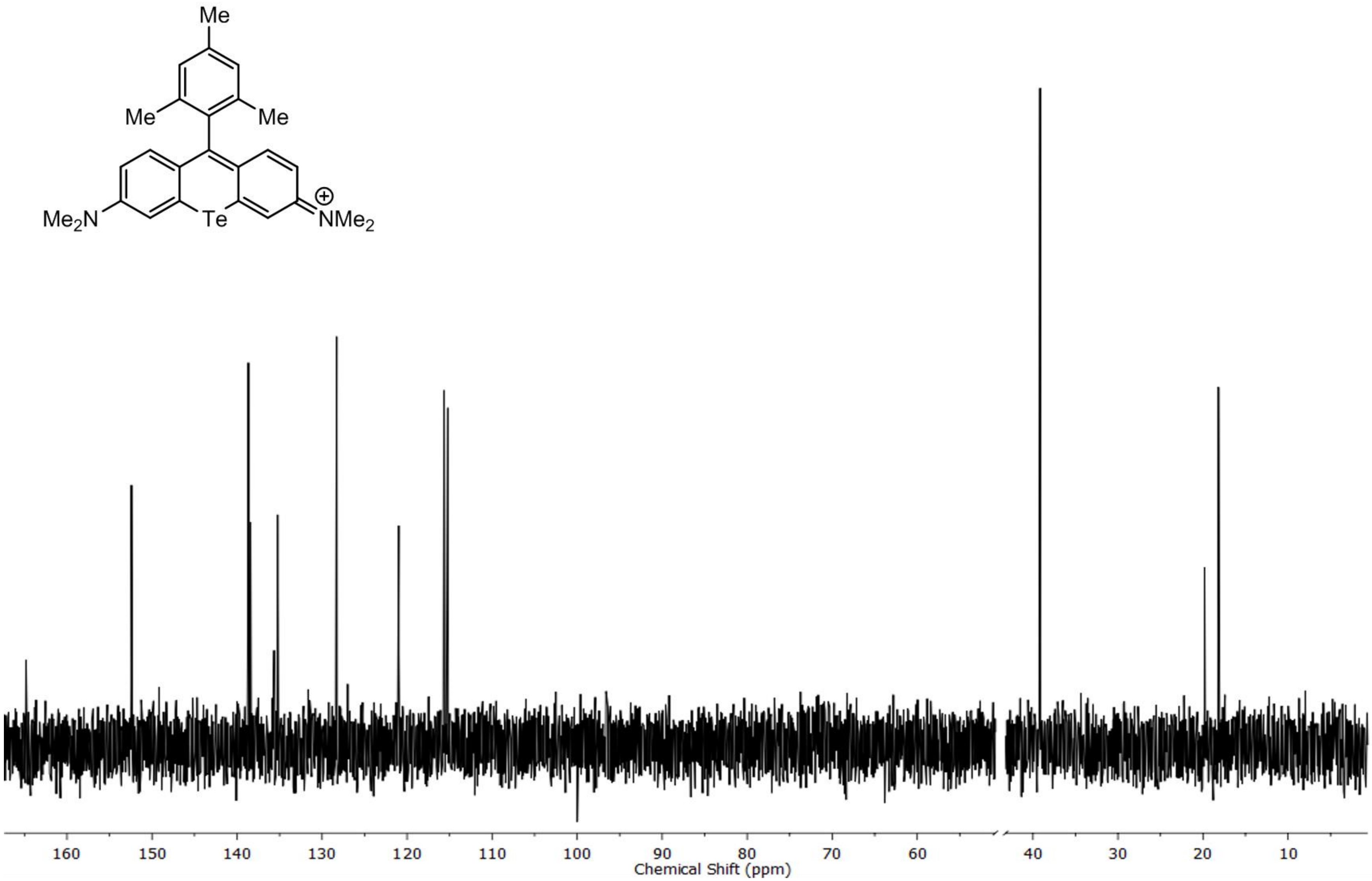

Figure S2. ^{13}C NMR spectrum of **1** in methanol-*d4*

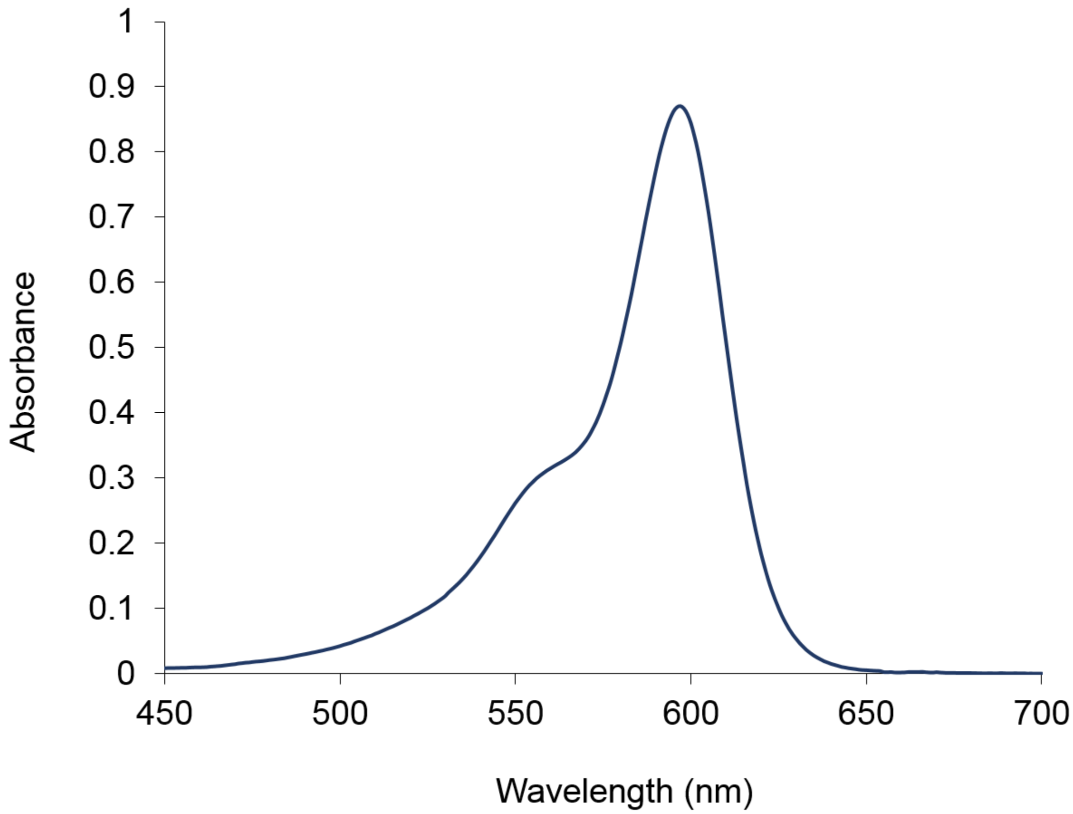

Figure S3. Uv-Vis absorbance spectrum of **1** (1.0 x 10^{-5} M) in methanol.

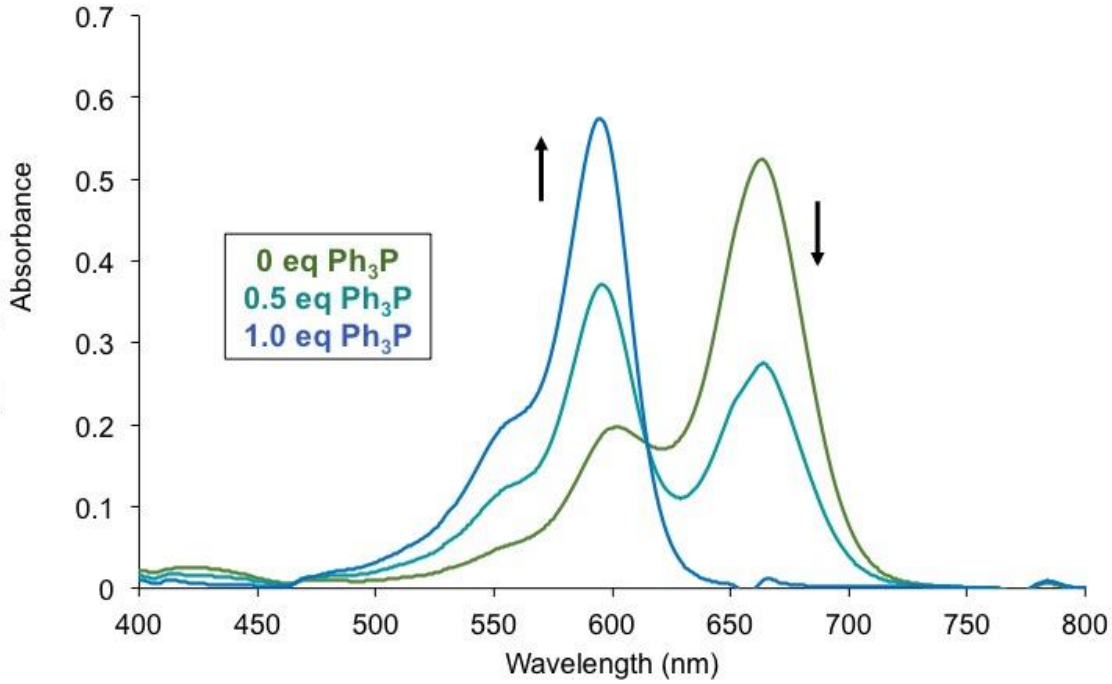

Figure S4. Titration of **2** (5.4×10^{-6} M) with half equivalents of triphenyl phosphine (Ph_3P) in 50:50 water/methanol. Samples were allowed to stir for 2 hr in the dark before spectra were obtained.

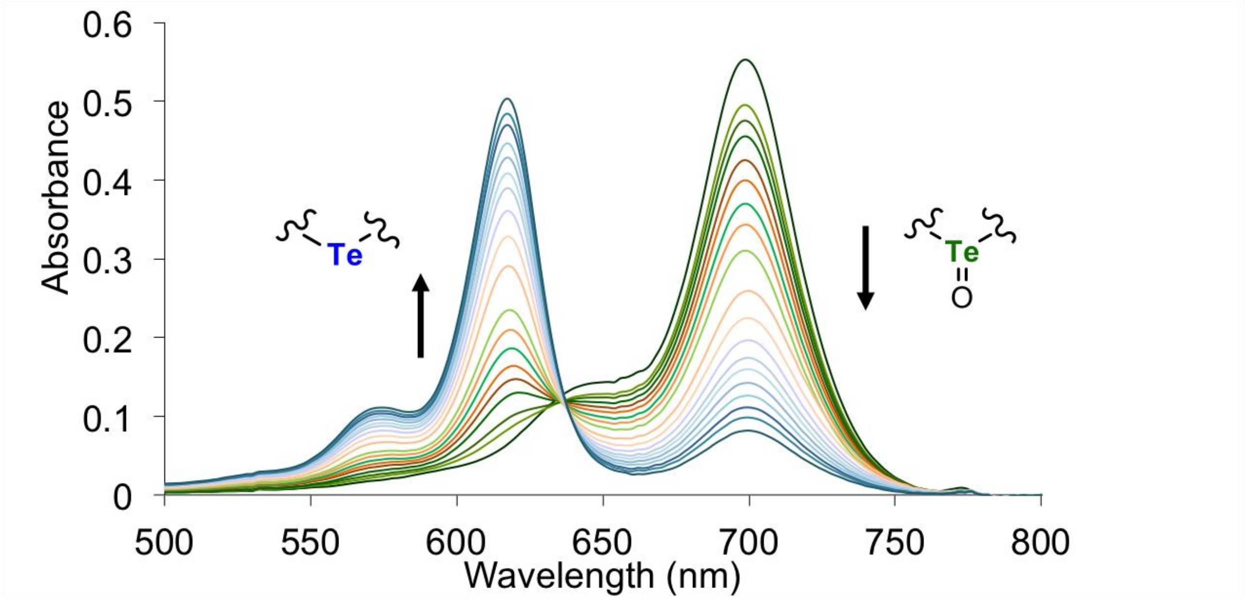

Figure S5. Absorption spectra of **2** (5.4×10^{-6} M) with 100 eq of triphenyl silane (Ph_3P) in 50:50 water/methanol. Spectra acquired every 15 min for 11 hrs and was stirred in the dark between scans.

NMR Spectroscopy and mass spectrometry general set up

Phosphines and silanes were oxidized catalytically using 5 mol % of **1** in methanol-d4. Samples were prepared under oxygen atmosphere with **1** (3.3×10^{-3} M), 20 eq of reductant (phosphine or silane) (6.6×10^{-2} M), 5% water, and cyclohexane as an internal standard. GCMS samples were prepared at the same concentrations in non-deuterated methanol with 5% **1** and 5% water. Samples were diluted to 100 ng/uL for analysis.

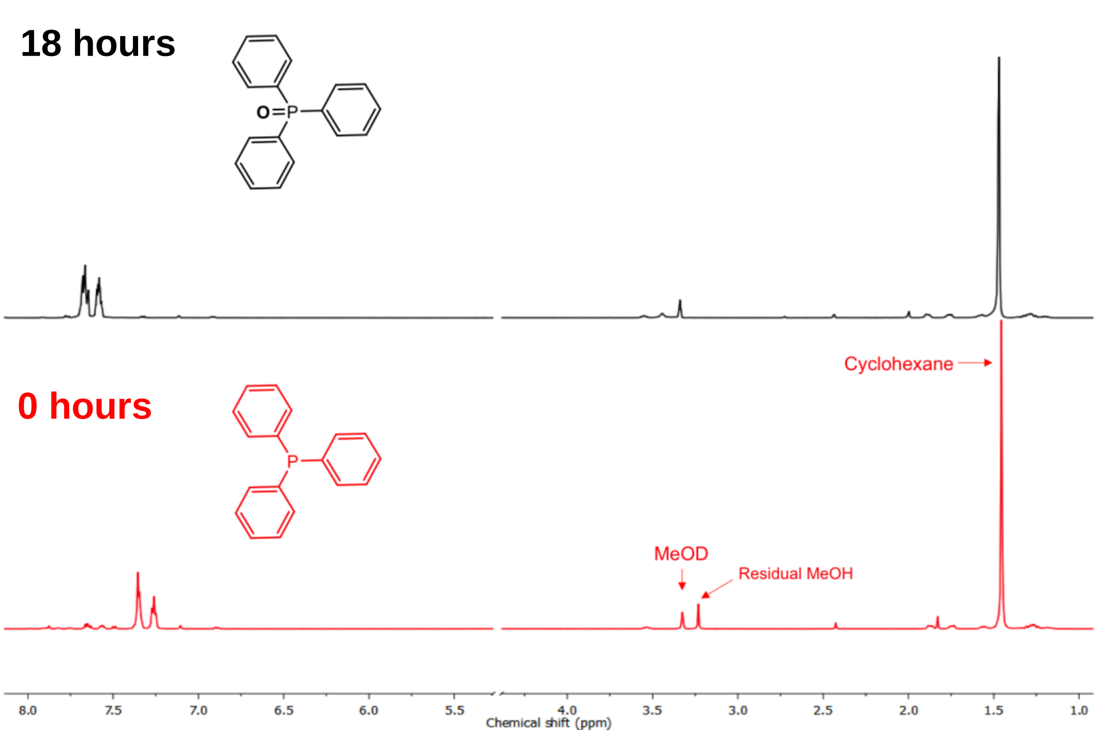

Figure S6. ^{1}H NMR spectrum of the triphenyl phosphine reaction mixture at 0 and 18 hours of irradiation.

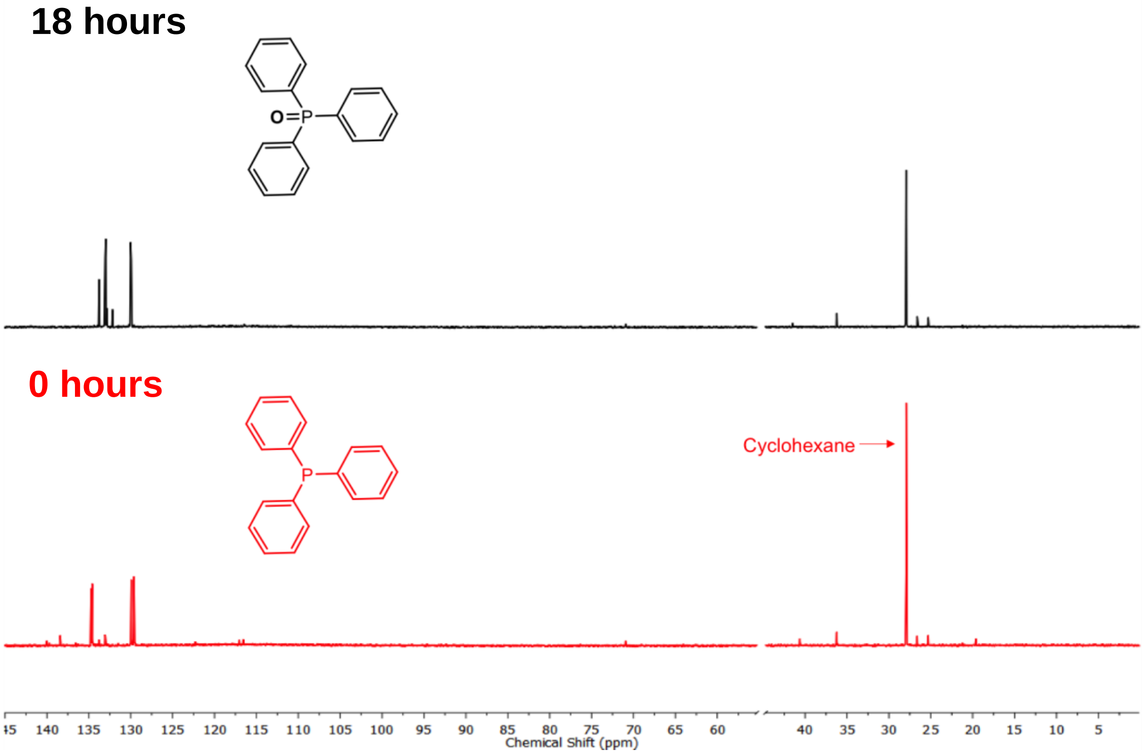

Figure S7. ^{13}C NMR spectrum of triphenyl phosphine reaction mixture at 0 and 18 hours of irradiation.

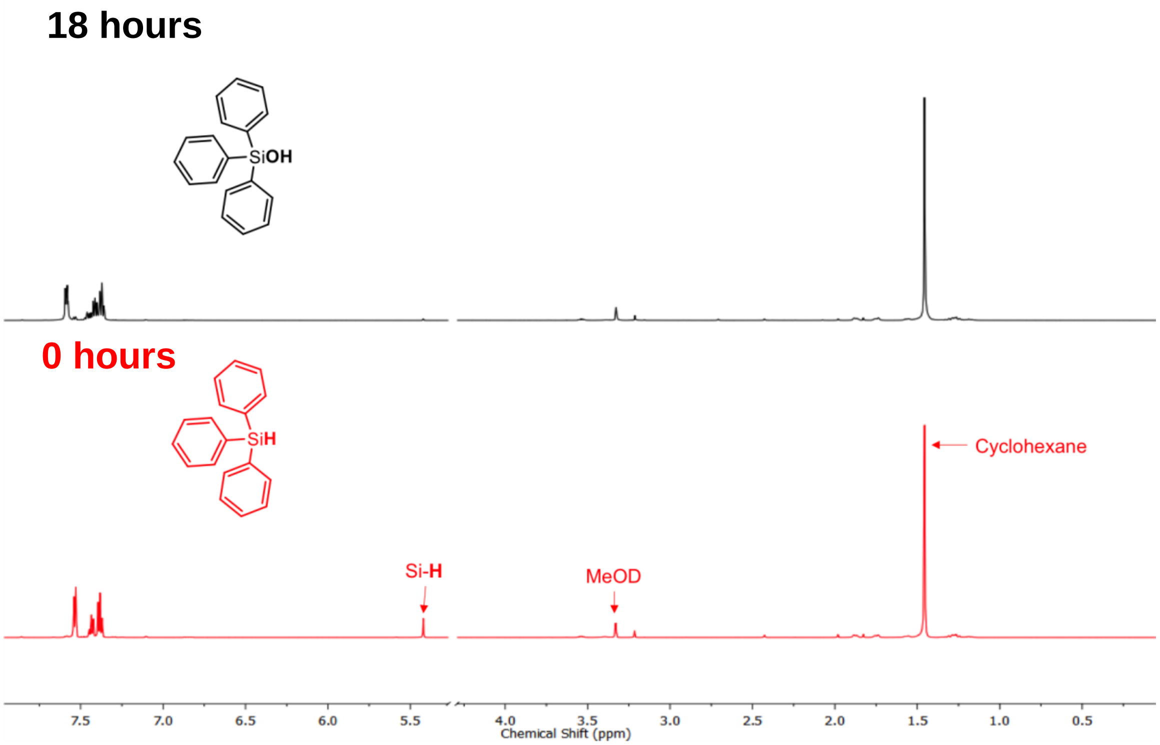

Figure S8. ^{1}H NMR spectrum of triphenyl silane reaction mixture at 0 and 18 hours of irradiation.

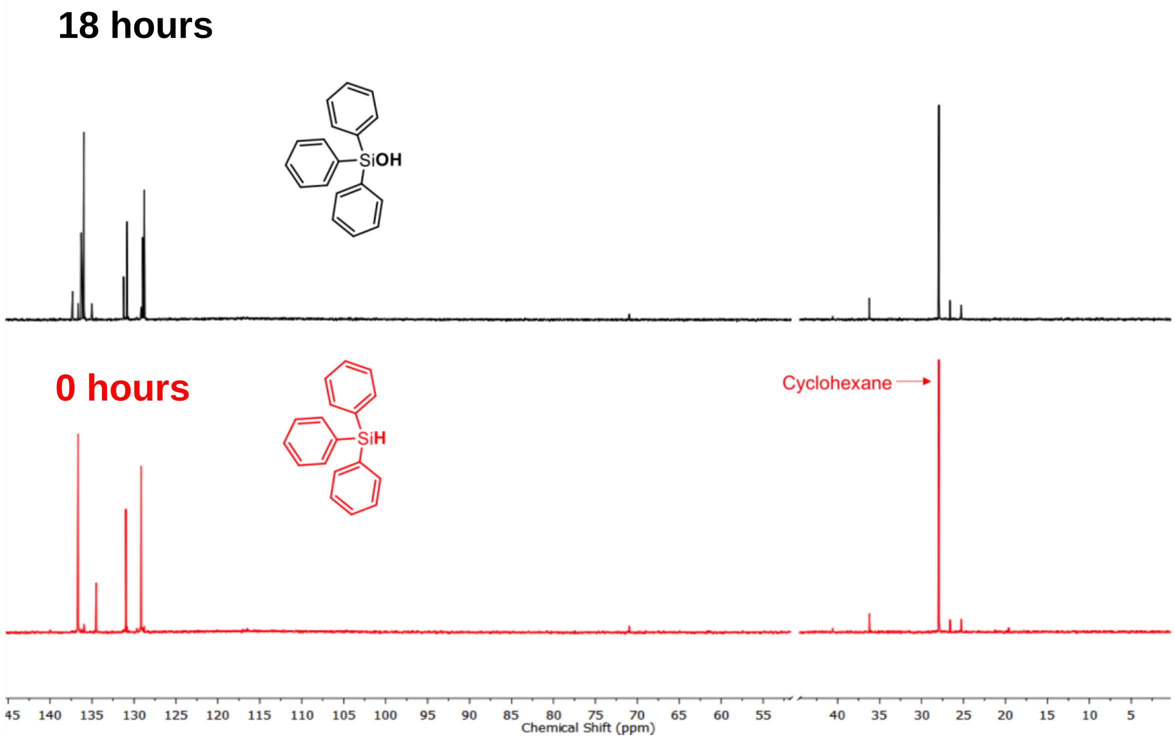

Figure S9. ^{13}C NMR spectrum of triphenyl silane reaction mixture at 0 and 24 hours of irradiation.

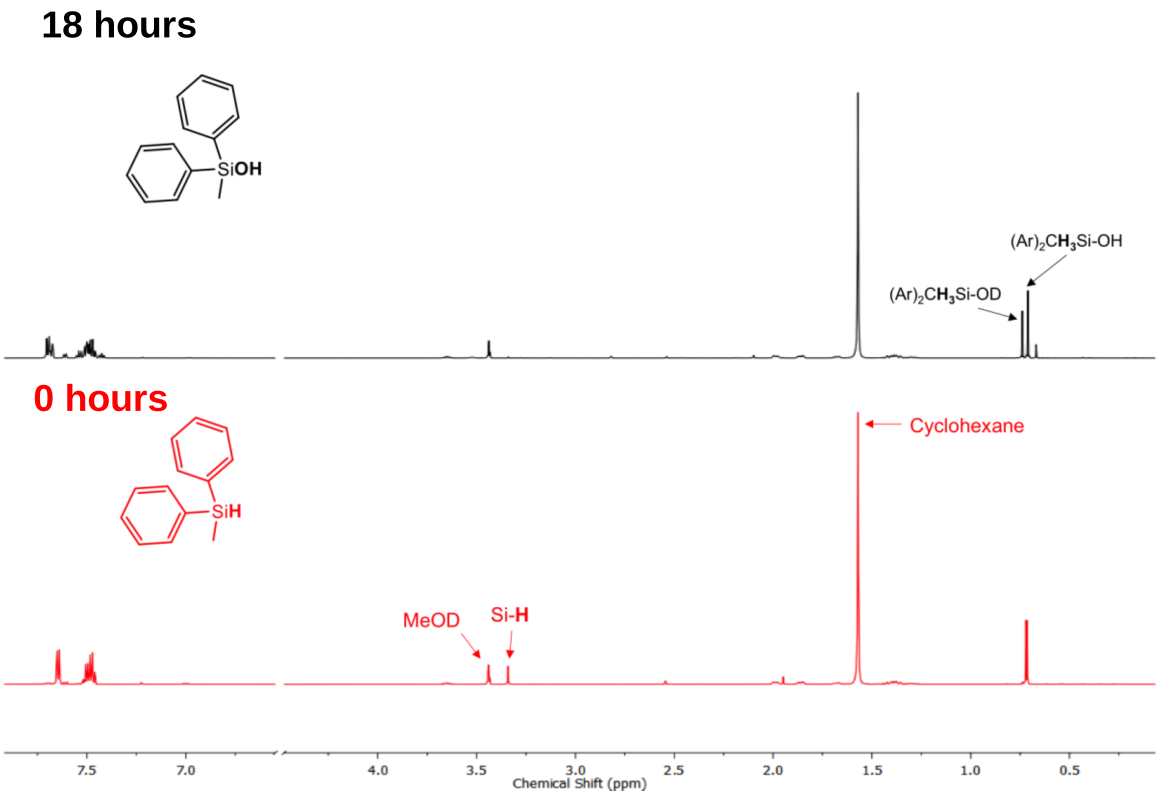

Figure S10. ^{1}H NMR spectrum of methyl diphenyl silane reaction mixture at 0 and 18 hours of irradiation.

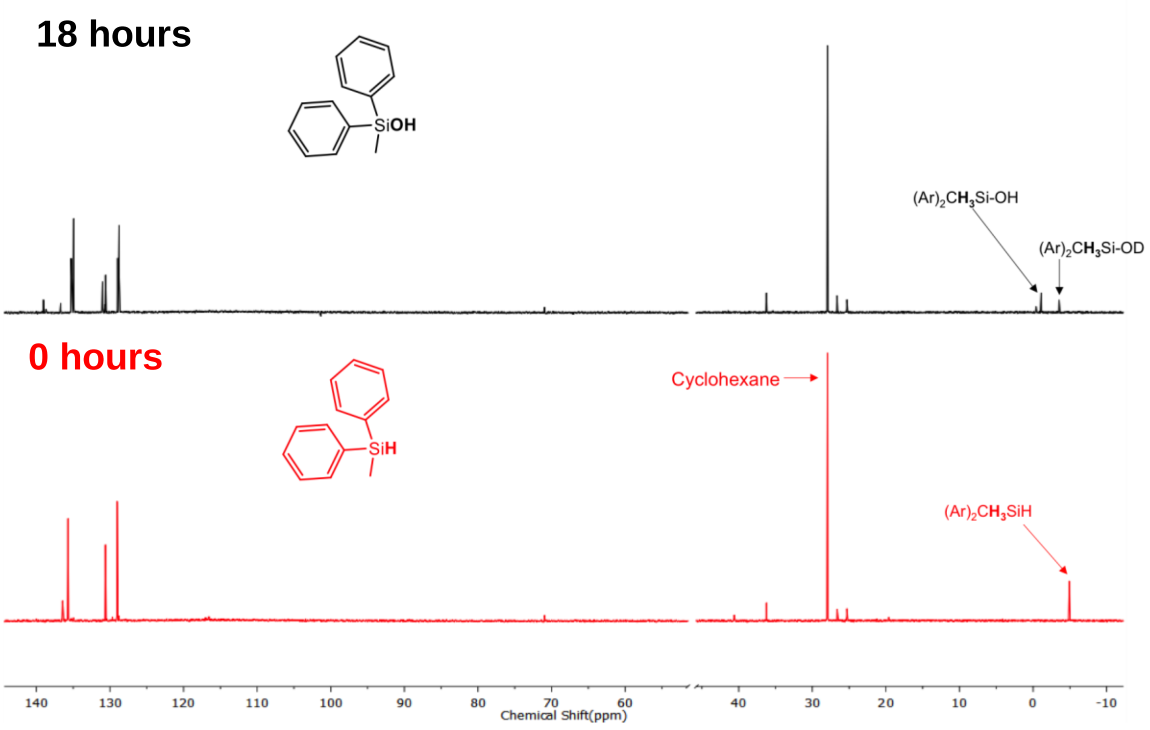

Figure S11 ^{13}C NMR spectrum of methyl diphenyl silane reaction mixture at 0 and 18 hours of irradiation.

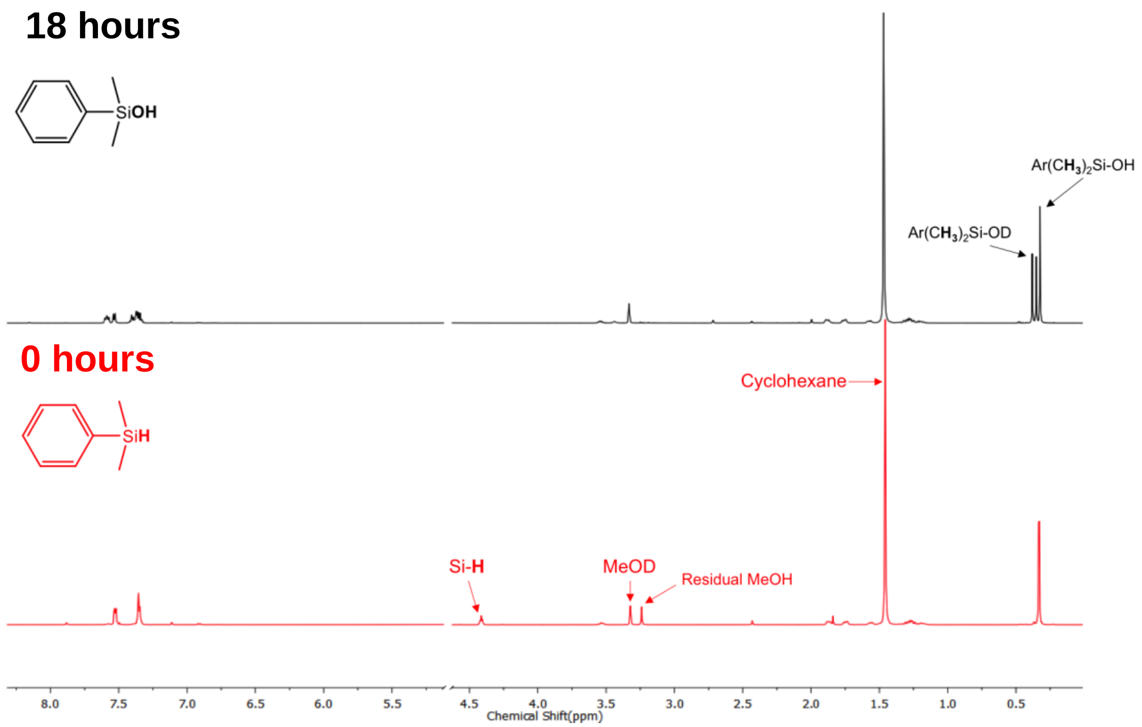

Figure S12. ^{1}H NMR spectrum of dimethyl phenyl silane reaction mixture at 0 and 18 hours of irradiation.

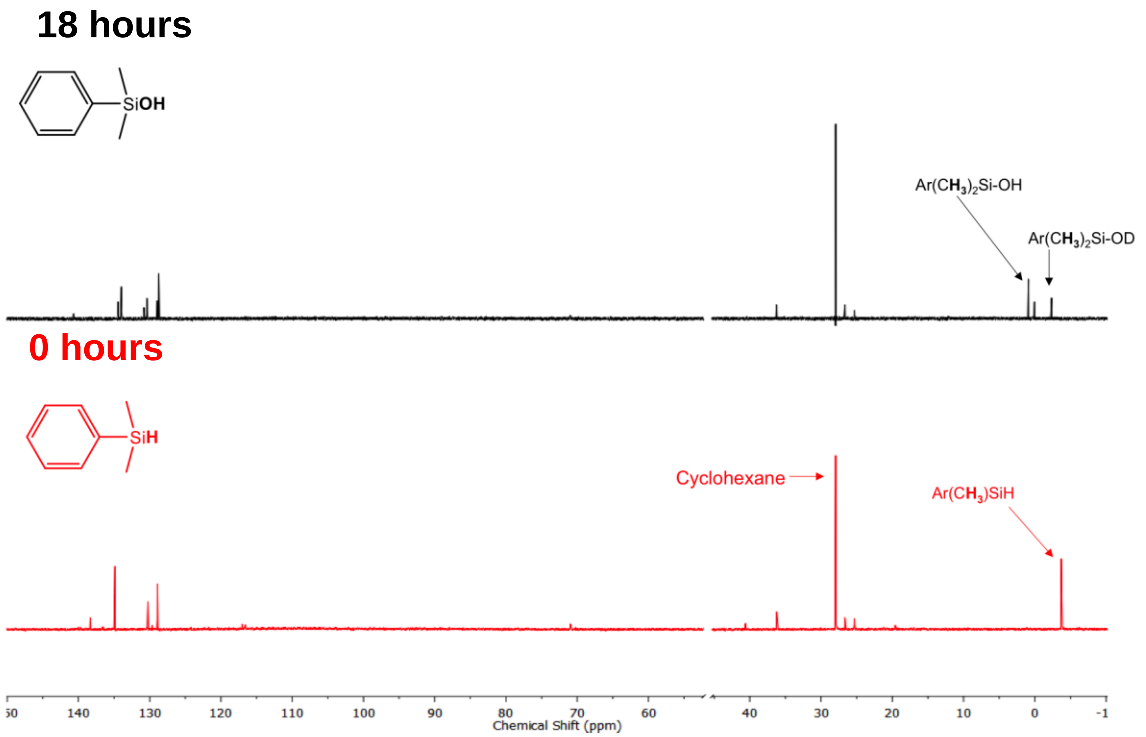

Figure S13. ^{13}C NMR spectrum of dimethyl phenyl silane reaction mixture at 0 and 18 hours of irradiation.

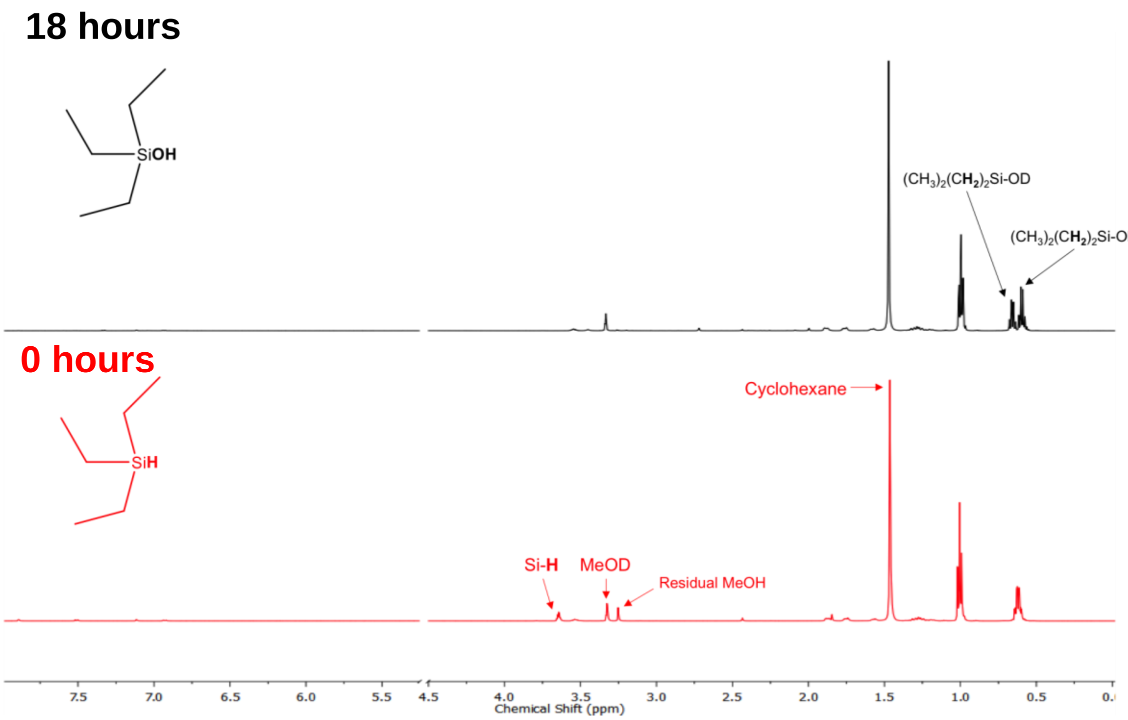

Figure S14. ^{1}H NMR spectrum of triethyl silane reaction mixture at 0 and 18 hours of irradiation.

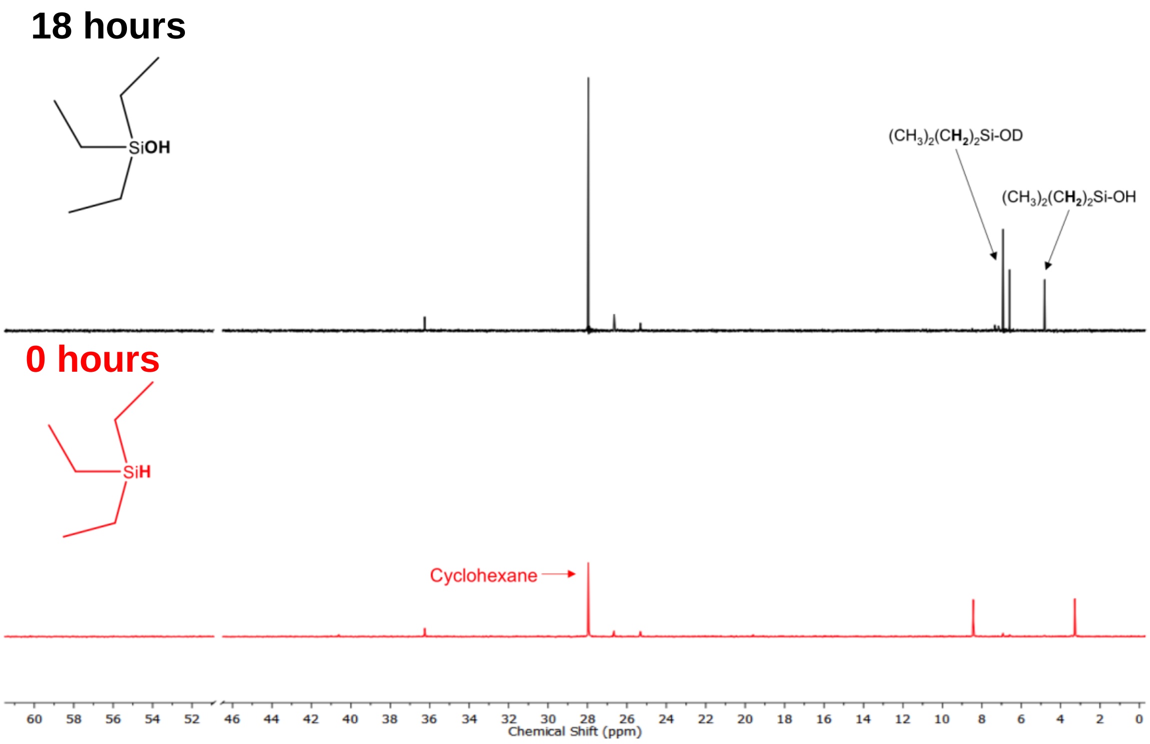

Figure S15. ^{13}C NMR spectrum of triethyl silane reaction mixture at 0 and 18 hours of irradiation.

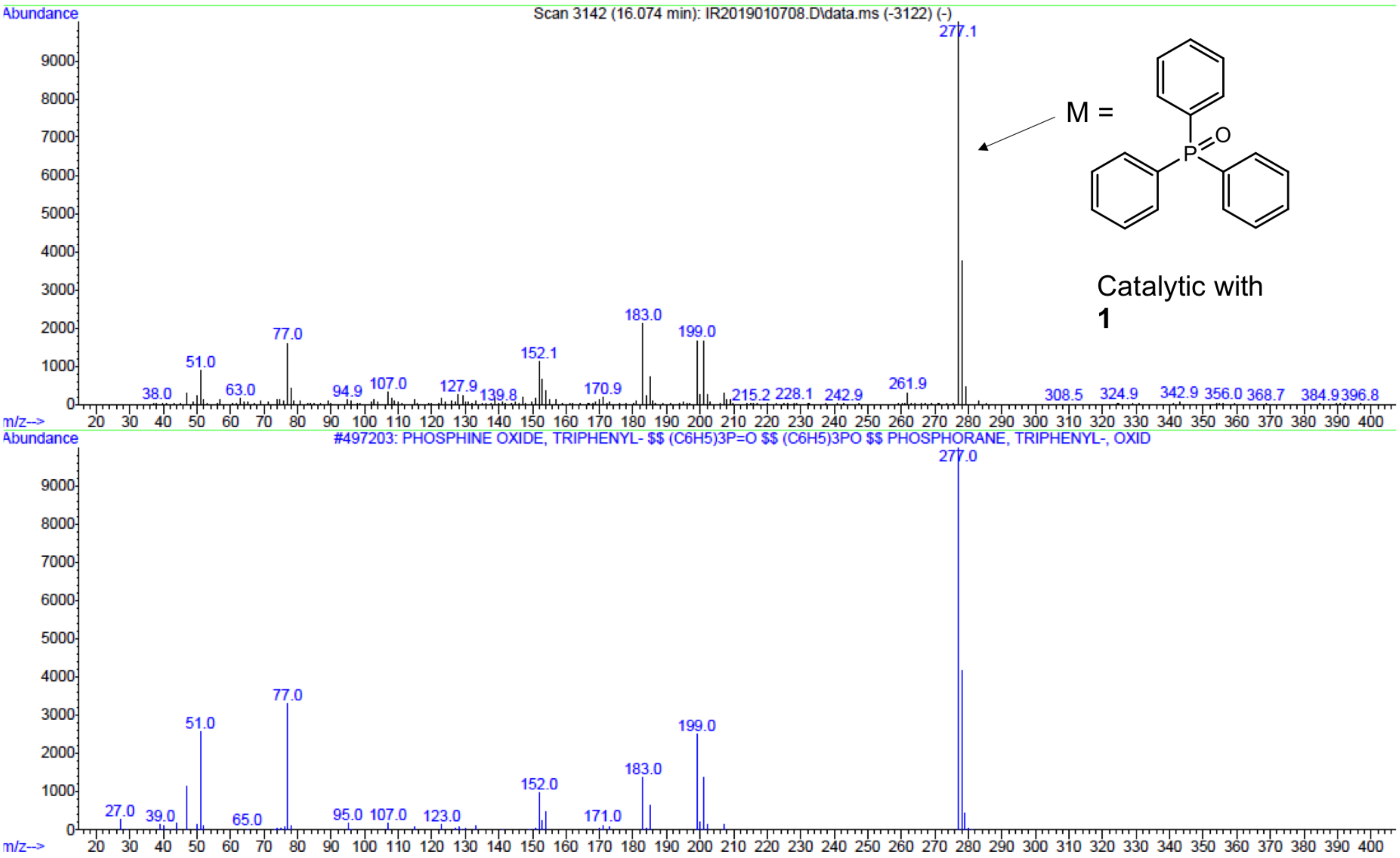

Figure S16. Mass spectrum of a) triphenyl phosphine oxide generated catalytically with 5% Rose Bengal in methanol with b) the database-matched spectrum.

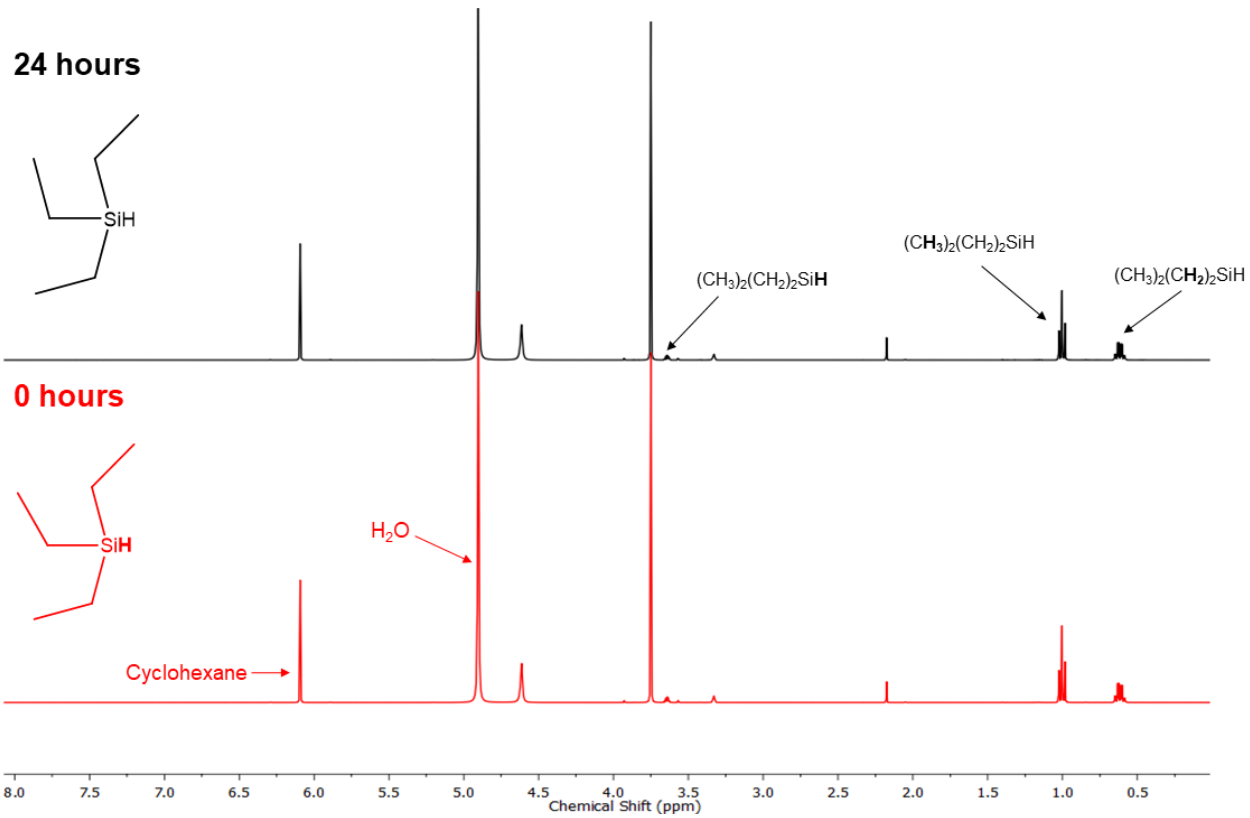

Figure S17. Control ^{1}H NMR spectrum of triethyl silane with Rose Bengal, 5% water, and cyclohexane in MeOD at 0 and 24 hours of irradiation showing no silanol formation.

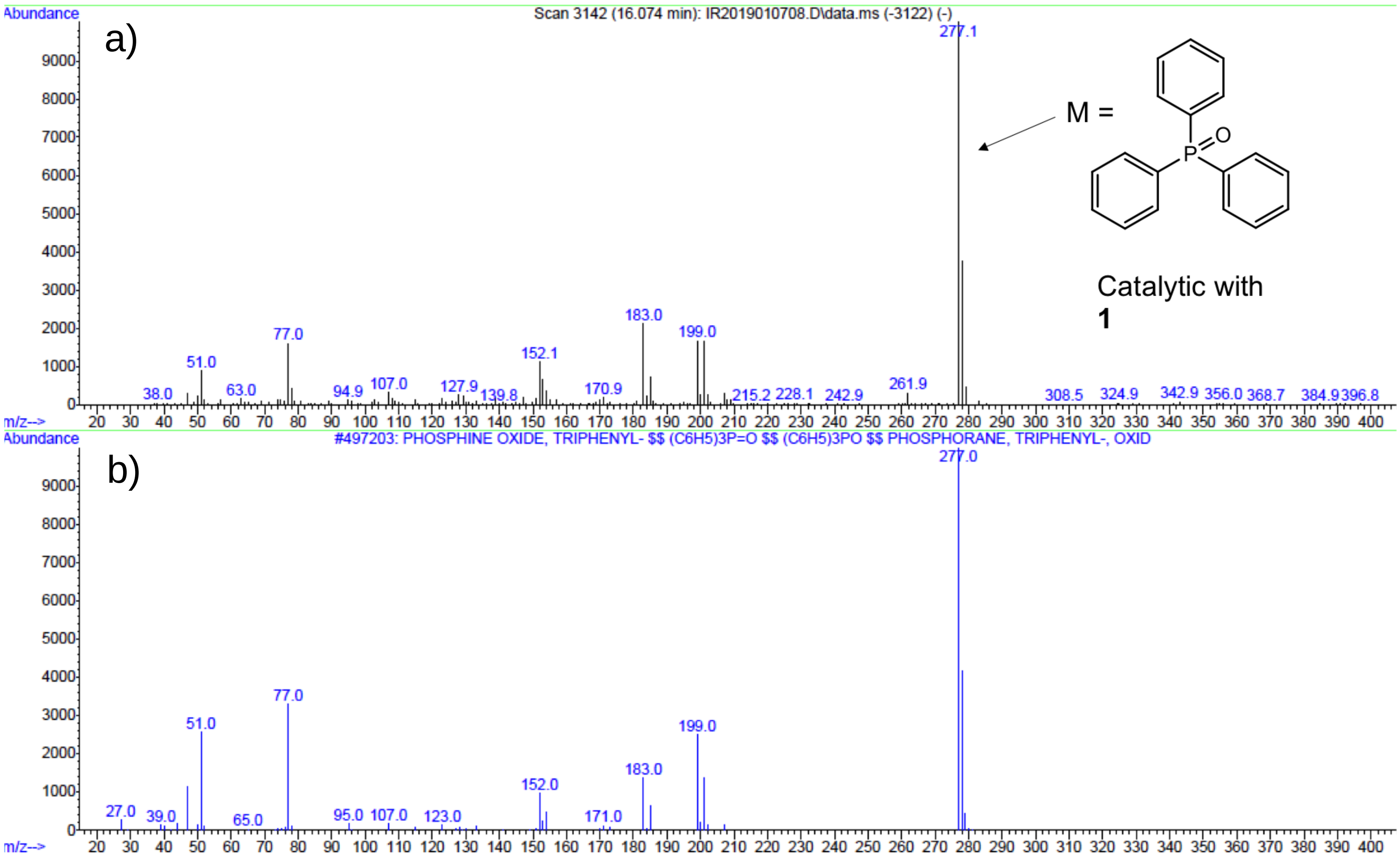

Figure S18. Mass spectrum of a) triphenyl phosphine oxide generated catalytically with 5% **1** in methanol with b) the database-matched spectrum.

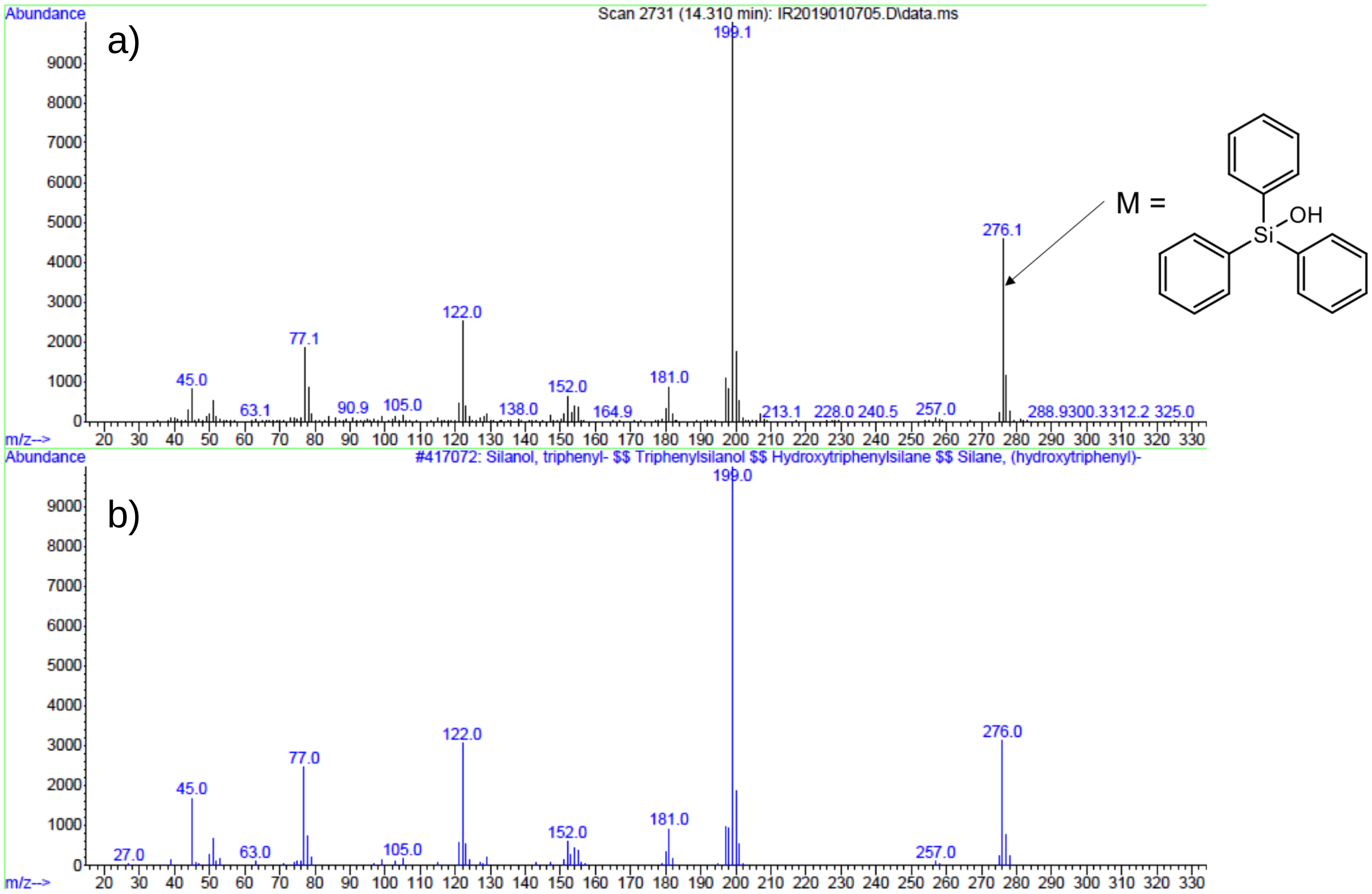

Figure S19. Mass spectrum of triphenyl silanol photocatalytically generated by **1** in methanol with b) the database matched spectrum.

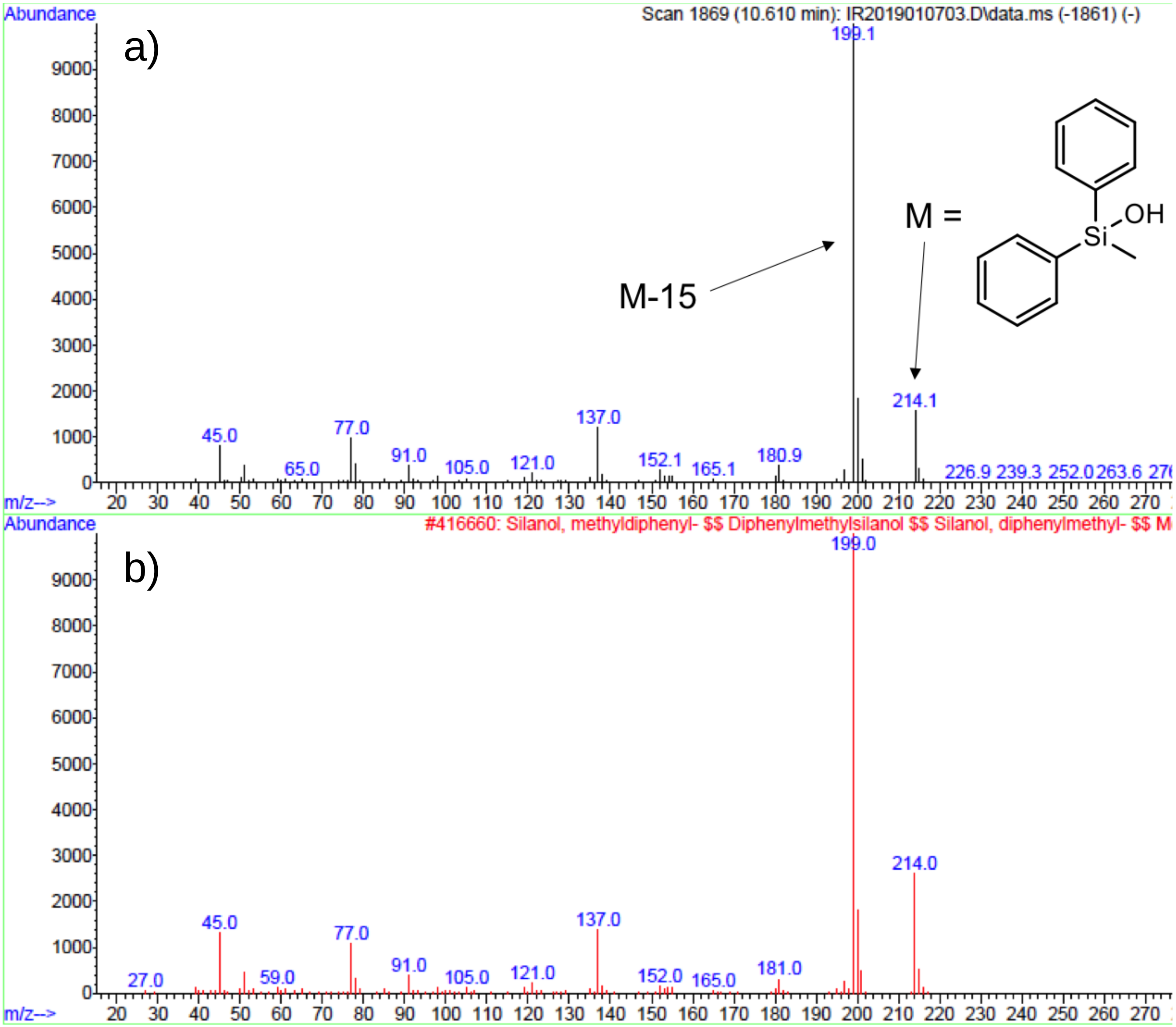

Figure S20. Mass spectrum of methyl diphenyl silanol photocatalytically generated by **1** in methanol with b) the database matched spectrum.

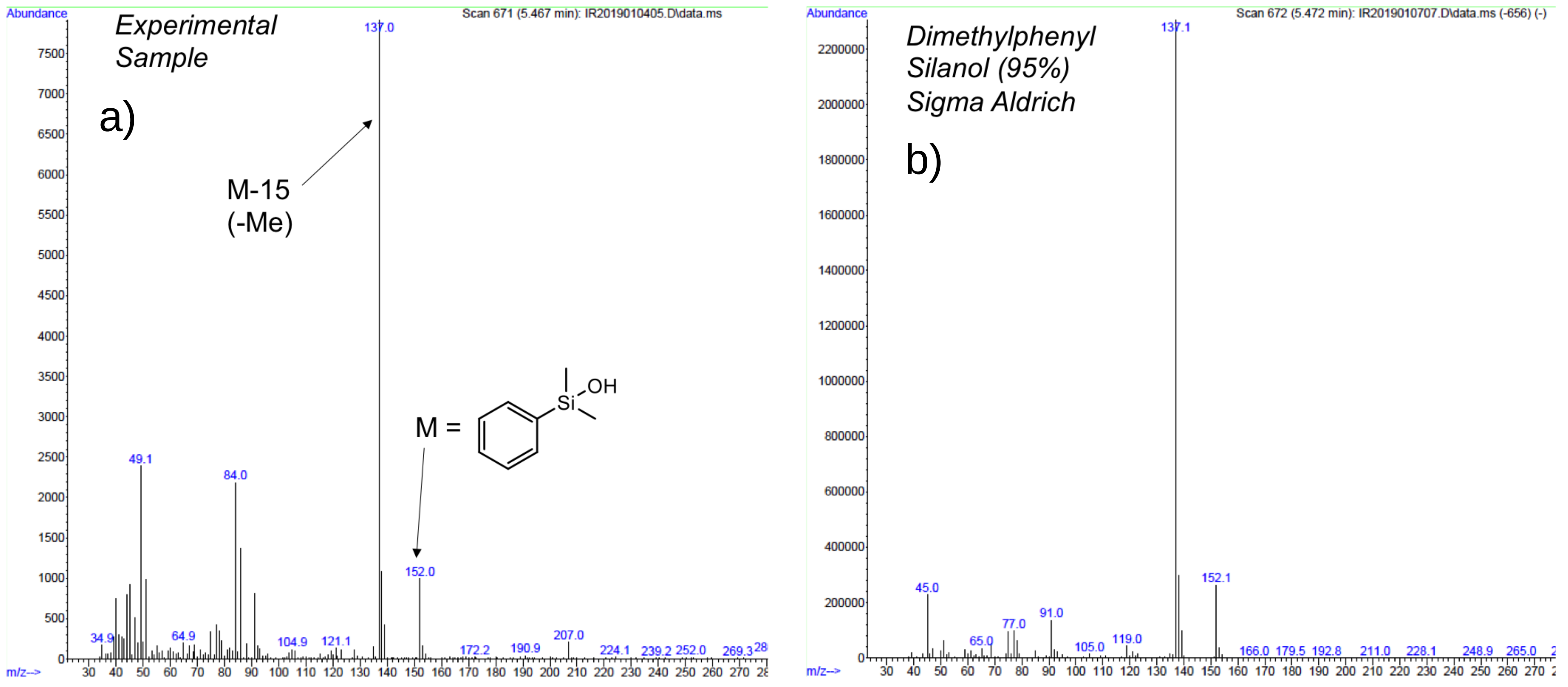

Figure S21. Mass spectrum of dimethyl phenyl silanol photocatalytically generated by **1** in methanol with b) compared to a Sigma Aldrich standard

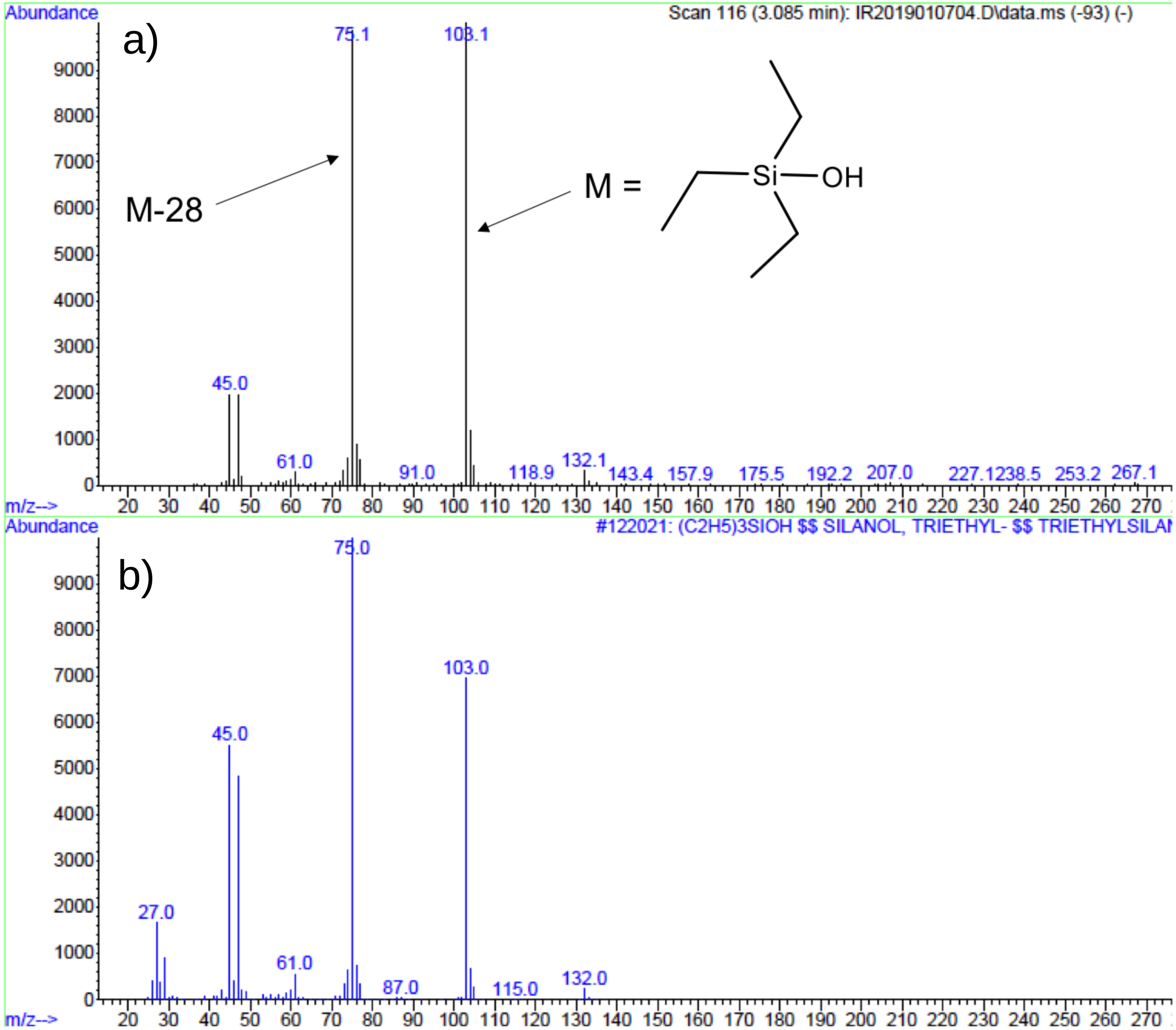

Figure S22. Mass spectrum of triethyl silanol photocatalytically generated by **1** in methanol with b) compared to a database-matched standard.

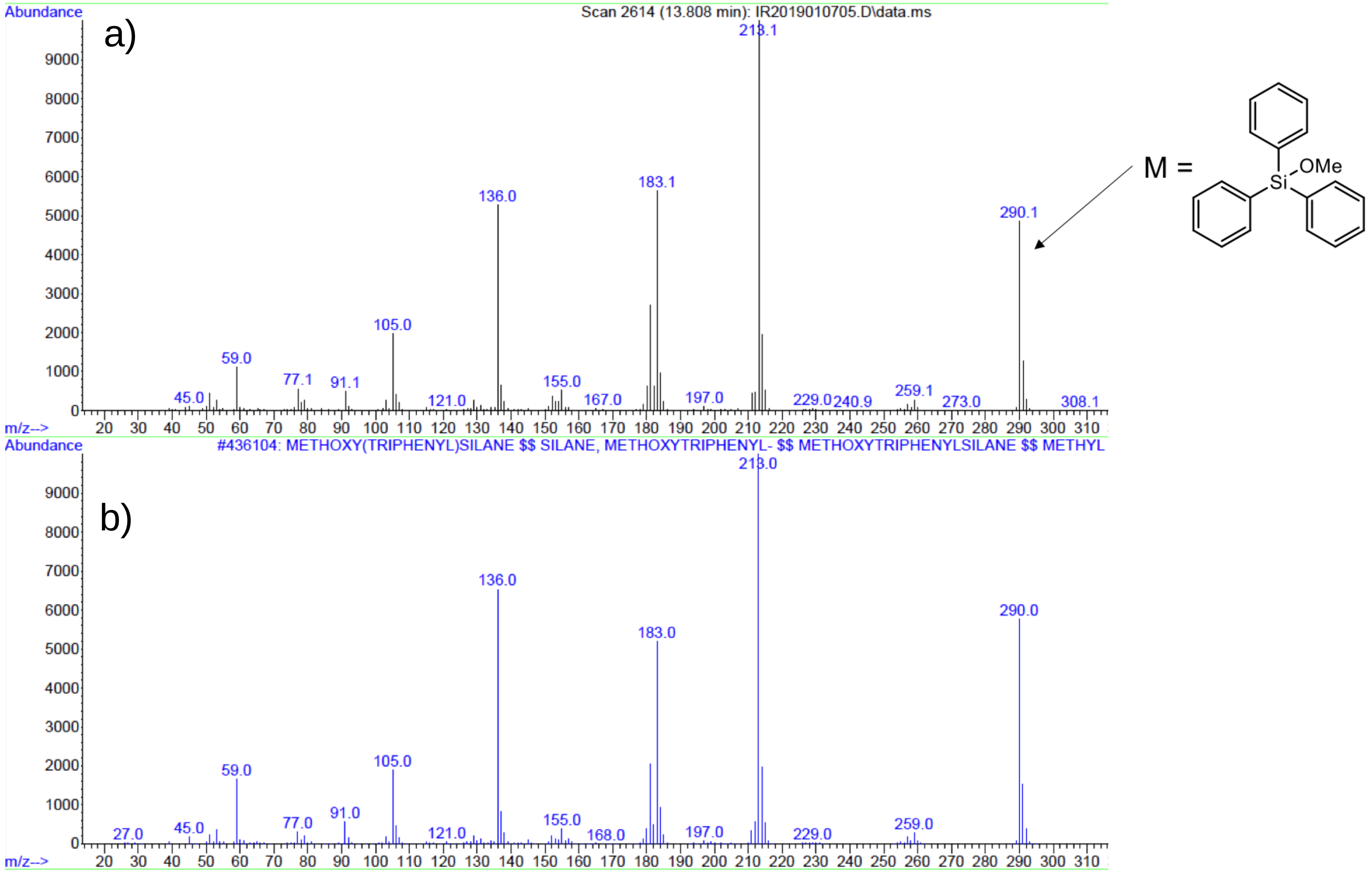

Figure S23. Mass spectrum of triphenyl methoxy silane photocatalytically generated by **1** in methanol with b) compared to a database-matched standard.

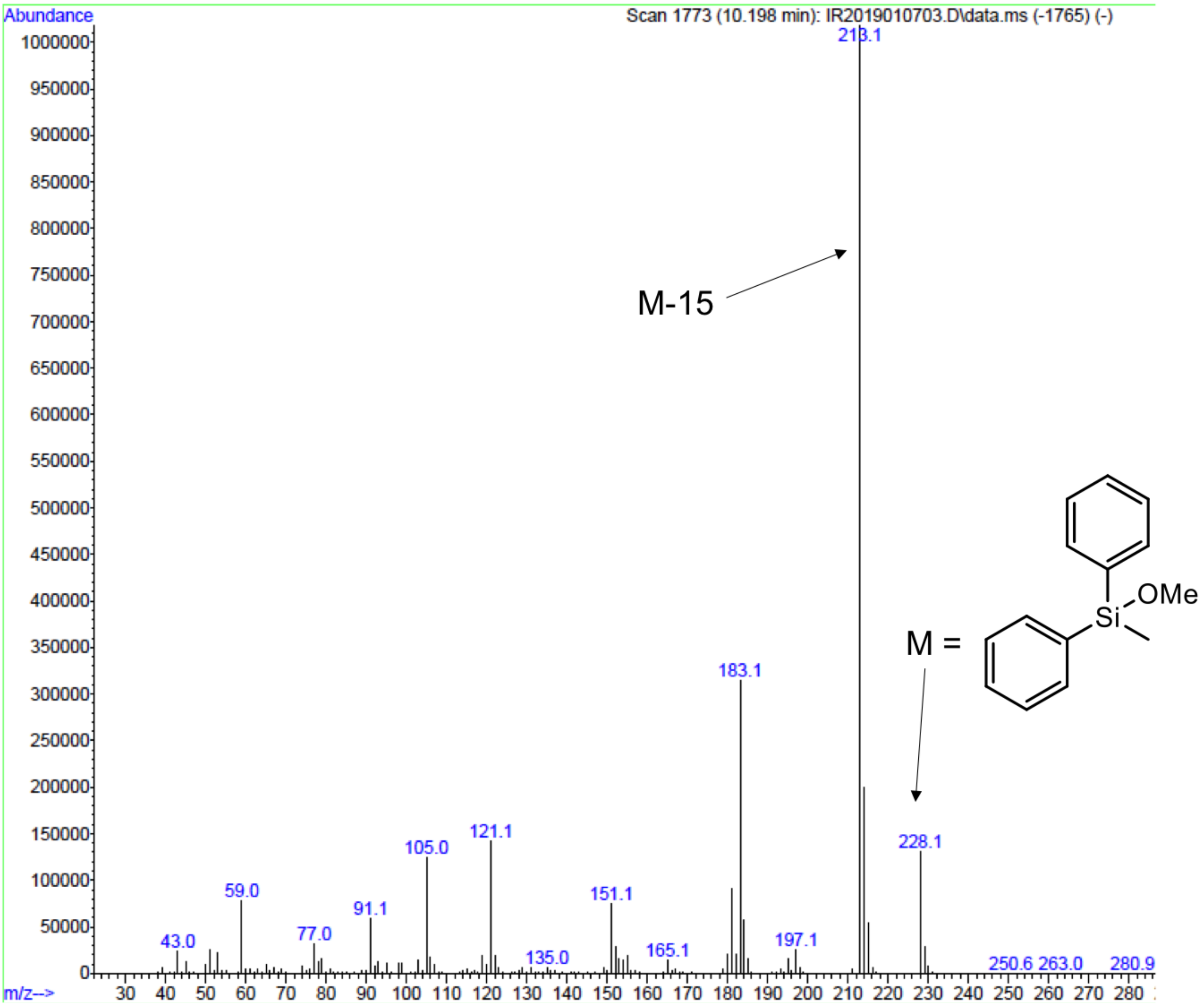

Figure S24. Mass spectrum of methyl diphenyl methoxy silane photocatalytically generated by **1** in methanol

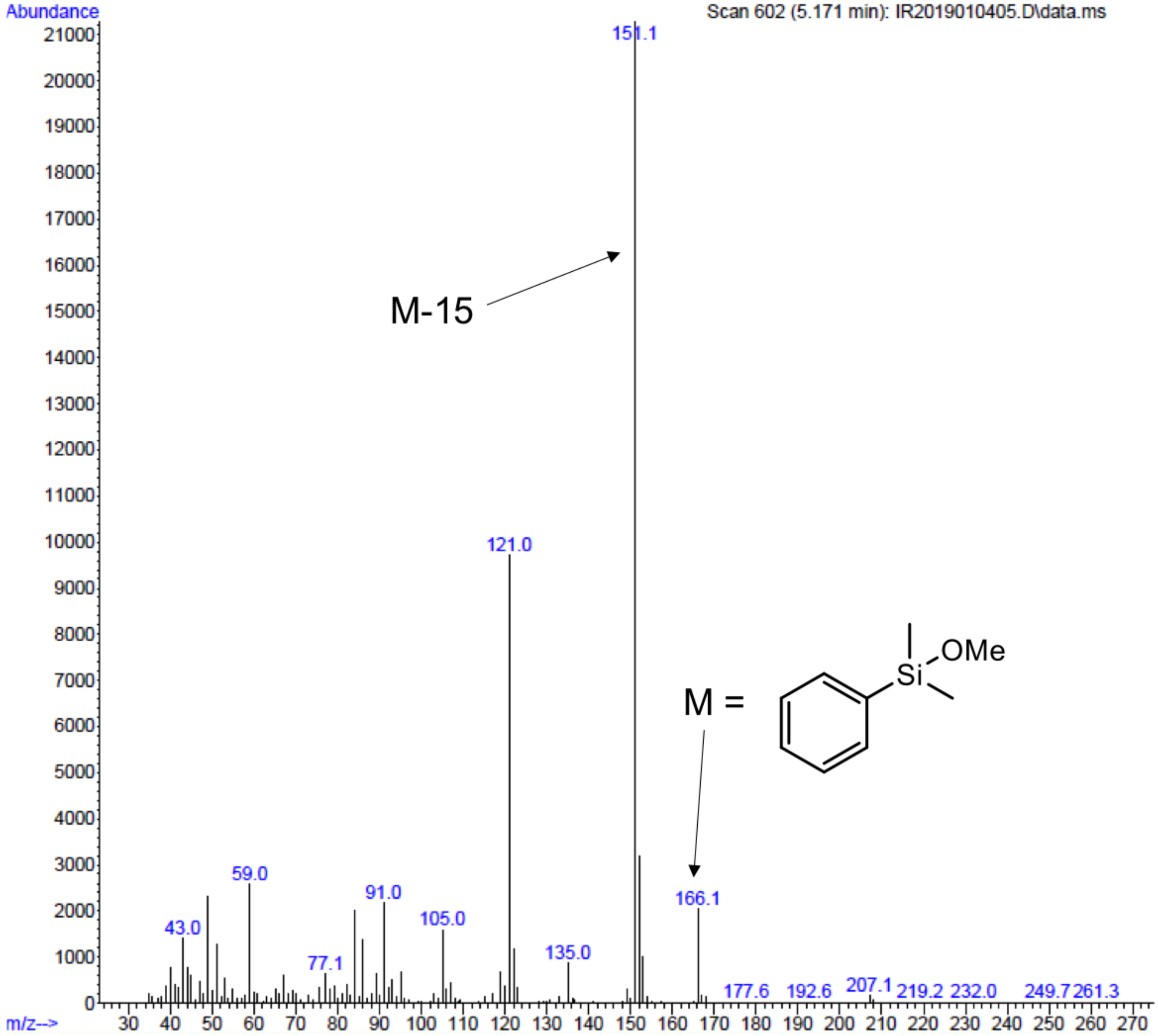

Figure S25. Mass spectrum of dimethyl phenyl methoxy silane generated photocatalytically by **1** in methanol.

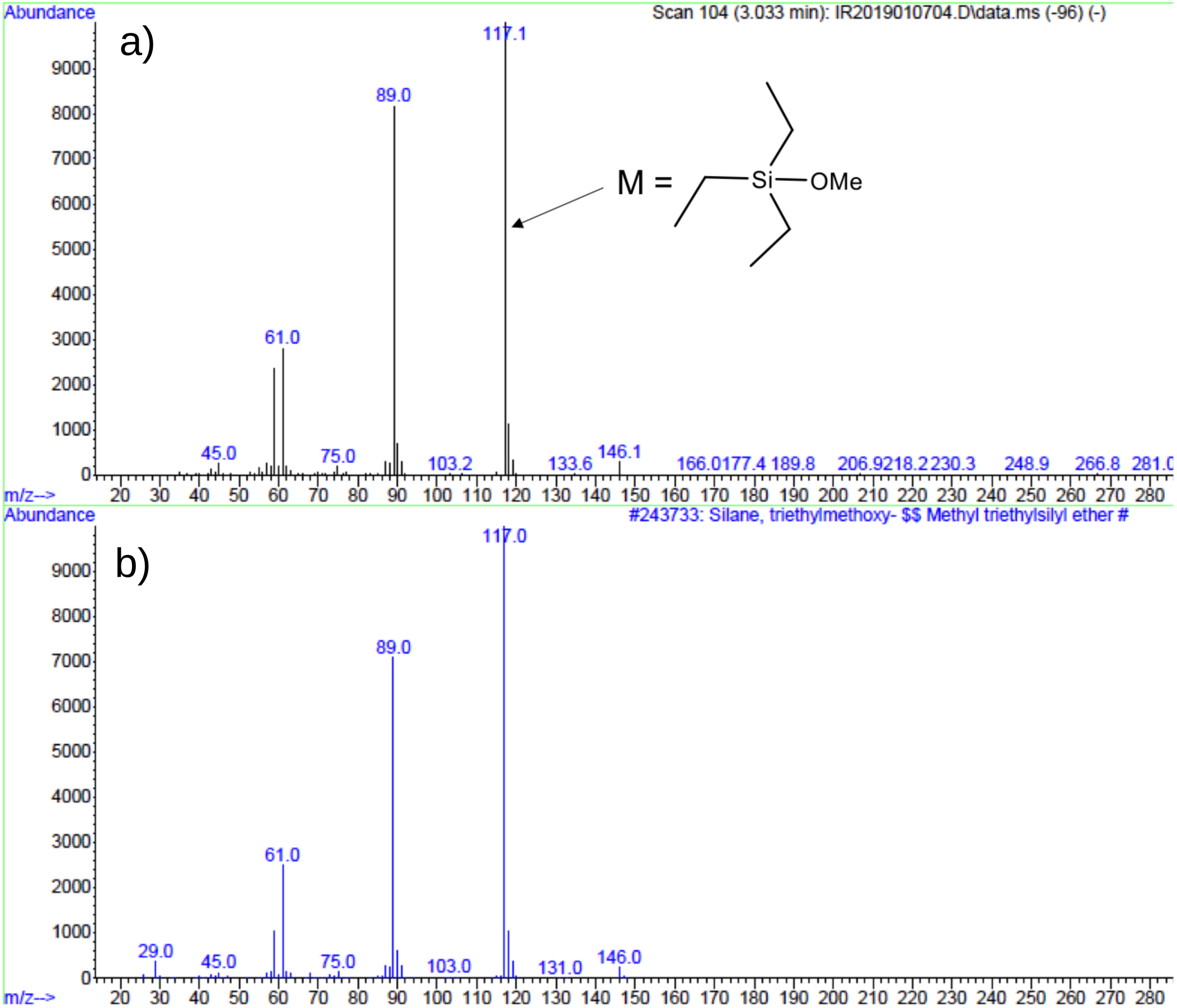

Figure S26. Mass spectrum of a) triethyl methoxy silane generated photocatalytically by **1** in methanol and b) a databased-matched spectrum.

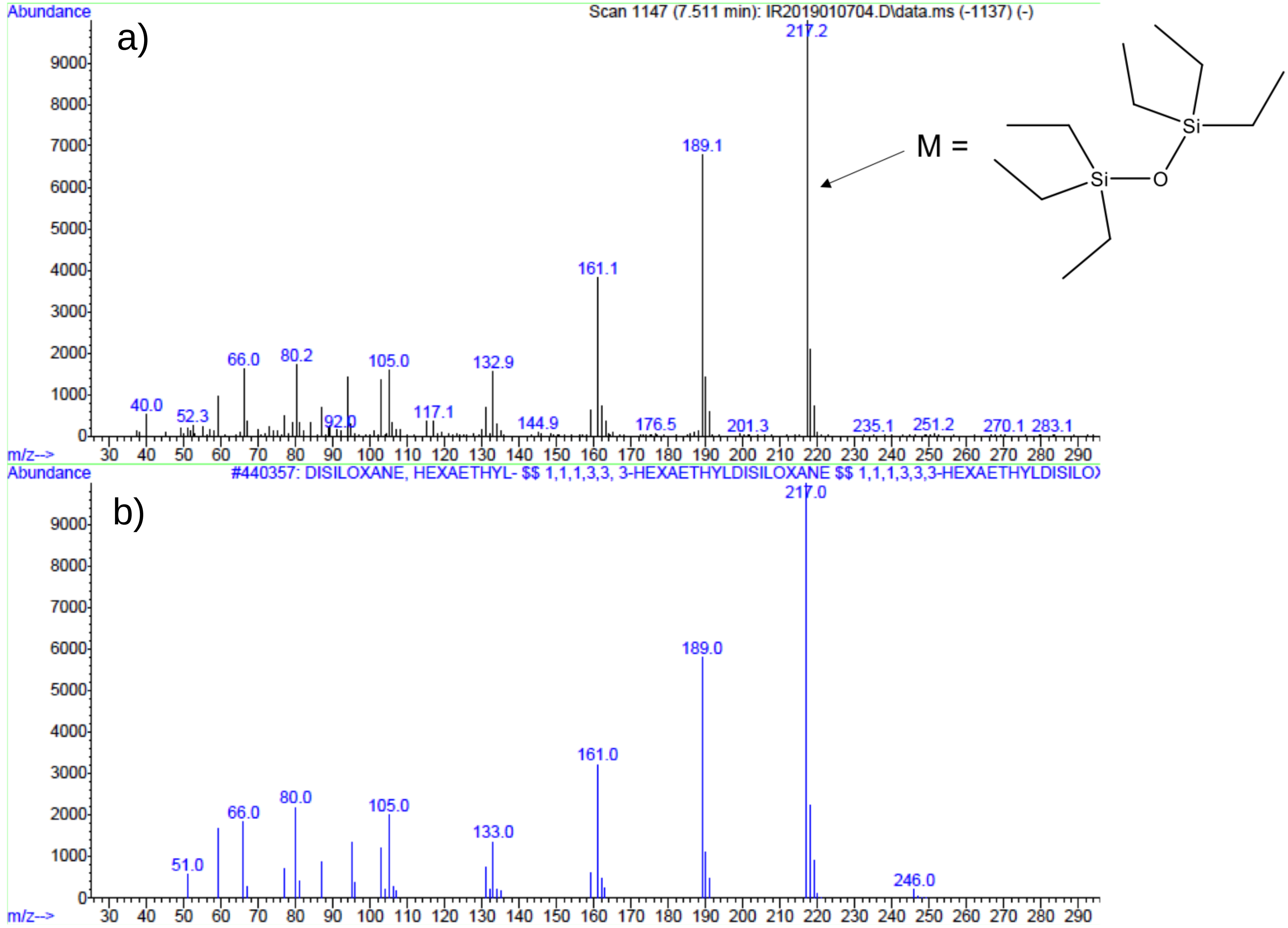

Figure S27. Mass spectrum of a) triethyl disiloxane detected in the sample mixture containing triethyl silanol and b) the database-matched spectrum.

Table S1. Relative energy of optimized reactants, intermediates and products. Energies were calculated in kcal/mol from Hartree (627.5 kcal·mol-1 /H). The energy values were taken from the free energy corrected values obtained from frequency calculations.

Compound	Compound name	Energy (Hartree)	Energy (kcal/mol)
Te-1	telluride	-1125.226	-706089.3416
Te-2	telluroxide	-1200.409	-753267.447
Te-A	dihydroxy tellurane	-1276.829	-801221.599
Te-P	(monotrimethylphospho)tellurane	-1661.41	-1042549.881
Te-Si	(monotrimethylsilyl)tellurane	-1610.171	-1010396.835
H_2O	water	-76.435	-47963.594
PMe_3	trimethylphosphine	-461.0201	-289294.401
$HSiMe_3$	trimethylsilane	-409.778	-257139.299
$OPMe_3$	trimethylphosphine oxide	-536.295	-336530.343
$HOSiMe_3$	trimethylsilanol	-485.0581	-304378.380

Table S2. Calculated Gibbs free energy (ΔG) values in kcal/mol for the balanced reaction for each step in the oxidation of silane and phosphine.

Reaction Scheme	ΔG (kcal/mol)
Te-2 + H_2O → Te-A	9.442128
Te-A + $HSiMe_3$ → Te-Si +H_2O	0.469377
Te-Si → Te + $HOSiMe_3$	-70.885927
Te-2 + PMe_3 → Te-P	11.967224
Te-P → Te + $OPMe_3$	-69.804101

1. Kryman, M. W.; Schamerhorn, G. A.; Yung, K.; Sathyamoorthy, B.; Sukumaran, D. K.; Ohulchanskyy, T. Y.; Benedict, J. B.; Detty, M. R. Organotellurium Fluorescence Probes for Redox Reactions: 9 -Aryl- 3,6-diaminotelluroxanthylium Dyes and Their Telluroxides. *Organometallics* **32,** 4321–4333 (2013).