

Practical Metal- and Additive-Free Methods for Radical-Mediated Reduction and Cyclization Reactions

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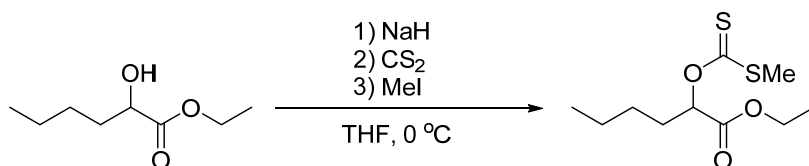
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1. General methods

NMR spectra were acquired on a Varian AS 400 spectrometer, running at 400 MHz for ^1H and 100 MHz for ^{13}C , respectively. Chemical shifts (δ) are reported in ppm relative to residual solvent signals (CHCl_3 , 7.26 ppm for ^1H -NMR, CDCl_3 , 77.0 ppm for ^{13}C -NMR). The following abbreviations are used to indicate the multiplicity in NMR spectra: s, singlet; d, doublet; t, triplet; q, quartet; quint., quintet; m, multiplet; bs, broad signal. Deuterium-exchangeable proton signals (OH signals) are omitted for clarity reasons. ^{13}C -NMR spectra were acquired on a broad band decoupled mode. Mass spectra were recorded on a micromass LCT spectrometer using electrospray (ES^+) ionization techniques. Analytical thin layer chromatography (TLC) was performed using pre-coated aluminium-backed plates (Merck Kieselgel 60 F254) and visualized by ultraviolet irradiation or KMnO_4 dip. An Osram Dulux Longlife 30W-840 bulb was employed for irradiation. Unless otherwise noted, analytical grade solvents and commercially available reagents were used without further purification. For flash chromatography (FC) silica gel (SiO_2 60, 230-400 mesh, Fluka) was used. Physical and spectroscopic data of known products were compared and found identical to literature reports (references cited for each compound). Starting materials **3g**¹ and **9a,b**² were prepared following literature procedures.

Compound **1b** was prepared by the following procedure:



To a suspension of NaH (5.4 mmol, 1.1 eq.) in THF (5 mL) at 0 °C under argon atmosphere was added a solution of ethyl 2-hydroxyhexanoate (4.9 mmol, 1 eq.) in THF (5 mL). The reaction mixture was stirred at 0 °C for 25 min, after which carbon disulfide (14.2 mmol, 3 eq.) was added. After 35 min of stirring at 0 °C, methyl iodide (29.8 mmol, 6 eq.) was added and the stirring was continued at 0 °C for another hour. The reaction was quenched with ice and NH_4Cl (sat.) and extracted with Et_2O (2 x 15 mL). The combined organic phases were washed with 1 M NaOH and brine, dried over MgSO_4 and concentrated *in vacuo* to yield **1b** as a brown oil in 85% yield. ^1H -NMR (400 MHz, CDCl_3) δ ppm 5.64 (dd, $J = 7.6, 5.1$ Hz, 1H), 4.21 (q, $J = 7.1$ Hz, 2H), 2.59 (s, 3H), 2.06-1.90 (m, 2H), 1.49-1.32 (m, 4H), 1.27 (t, $J = 7.1$ Hz, 3H), 0.92 (t, $J = 7.1$ Hz, 3H). ^{13}C -NMR (100 MHz, CDCl_3) δ ppm 215.8, 169.2, 80.3, 61.4, 31.1, 27.3, 22.2, 19.2, 14.1, 13.8. HRMS: calculated for ($\text{M}+\text{Na}^+$): 273.0590; found: 273.0579.

¹ R. M. Denton, J. T. Scragg and J. Saska, *Tetrahedron Lett.*, 2011, **52**, 2554.

² (a) A. Dahlén, A. Petersson and G. Hilmersson, *Org. Biomol. Chem.*, 2003, **1**, 2423; (b) M. Durandetti, L. Hardou, R. Lhermet, M. Rouen and J. Maddaluno, *Chem. Eur. J.*, 2011, **17**, 12773.

2. Screening and control experiments

Table S1. Screening results for a photo-initiated protocol.^a

1a $\xrightarrow[\text{Conditions, MeCN, 20 h}]{\text{30 W household bulb (compact fluorescent light)}}$ **2a**

Entry	[1a] (M)	Conditions	Yield (%) ^b
1	0.1 ^c	Ru(bpy) ₃ Cl ₂ (0.1 mol%), Et ₃ N (0.05 eq.), TTMSS (1 eq.)	>95
2	0.1 ^c	TTMSS (1 eq.)	>95
3	0.1 ^d	TTMSS (1 eq.)	>95
4	0.1 ^d	TTMSS (1 eq.), no light	<1
5	0.1 ^d	TTMSS (1 eq.), no light, 50 °C	<5
6 ^e	1 ^d	TTMSS (1 eq.)	>95

^a Performed with 0.1 mmol **1a** in MeCN. ^b NMR yield using 1,3,5-(CF₃)₃-C₆H₃ as internal standard. ^c Degassed by three cycles of freeze-pump-thaw. ^d Degassed by 1 min argon sparging. ^e Performed on 0.5 mmol scale.

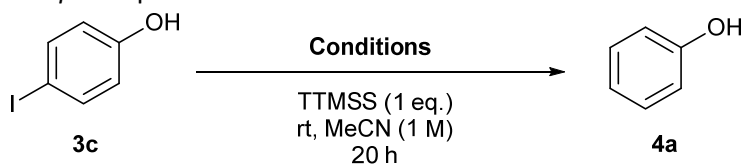
Table S2. Screening results for an oxygen-initiated protocol under air atmosphere.^a

1a $\xrightarrow[\text{TTMSS (1 eq.), Temperature, MeCN, 20 h}]{\text{Air atmosphere, no light}}$ **2a**

Entry	[1a] (M)	Temperature (°C)	Yield (%) ^b
1	1	20	<1
2	1	30	5
3	1	40	79
4	1	50	87 (>95 ^c)
5	1	60	87
6 ^d	0.2	50	80
7 ^e	2	50	90

^a Performed with 0.5 mmol **1a** in MeCN. ^b NMR yield using 1,3,5-(CF₃)₃-C₆H₃ as internal standard. ^c TTMSS (1.5 eq.) was employed. ^d Performed on 0.05 mmol scale. ^e Performed on 1 mmol scale.

Table S3. Screening results *p*-iodophenol.^a



Entry	Light	Conditions	Yield (%) ^b
1	ON ^c	Degassed by Ar-sparging	>95
2	OFF	Degassed by Ar-sparging	<1
3	OFF	Degassed by Ar-sparging, 50 °C	30
4	OFF	Degassed by 3 x FPT cycles, 50 °C	30
5	OFF	Air atmosphere	>95

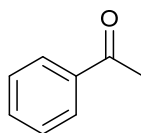
^a Performed with 0.5 mmol **3c** in MeCN at rt. ^b NMR yield using 1,3,5-(CF₃)₃-C₆H₃ as internal standard. ^c Temperature of the reaction mixture upon irradiation reaches ca. 30 °C.

3. General procedures and characterizations

General procedures

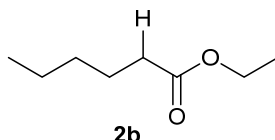
Method A (employing irradiation using a household CFL-bulb): To a Schlenk-tube (or an ordinary test tube) charged with a magnetic stirring bar was added the substrate (0.5 mmol), tris(trimethylsilyl)silane (TTMSS) (0.5 mmol or the given amount) and MeCN (0.5 mL) under a nitrogen atmosphere. The reaction mixture was then briefly degassed by nitrogen or argon sparging for 1 min. The reaction was stirred at ca. 10 cm's distance from a 30 W household compact fluorescent light bulb until completion of reaction, which was monitored by ¹H-NMR spectroscopy (usually within 24 h). Direct purification by FC on silica gel afforded the final products. For highly non-polar compounds, the crude reaction mixture was concentrated *in vacuo* in the presence of silica. The crude product, absorbed on silica, was then charged on the column and subjected to FC (gradient pentane/EtOAc or pentane/Et₂O). Due to their high volatility, the yield of some products was determined by ¹H NMR using 1,3,5-(CF₃)₃-C₆H₃ as internal standard.

Method B (employing an air atmosphere at rt or 50 °C): To an ordinary vial charged with a magnetic stirring bar was added the substrate (0.5 mmol), tris(trimethylsilyl)silane (TTMSS) (0.5 mmol or the given amount) and MeCN (0.5 mL) under air atmosphere (closed with screw cap). The reaction mixture was stirred at rt (for substrates **3a-g** and **5**) or at 50 °C (for substrates **1**, **7**) until completion of reaction, which was monitored by ¹H-NMR spectroscopy. Direct purification by FC on silica gel afforded the final products. For highly non-polar compounds, the crude reaction mixture was concentrated *in vacuo* in the presence of silica. The crude product, absorbed on silica, was then charged on the column and subjected to FC (gradient pentane/EtOAc or pentane/Et₂O). Due to their high volatility, the yield of some products was determined by ¹H NMR using 1,3,5-(CF₃)₃-C₆H₃ as internal standard.



2a

Following the general procedures (1 eq. of TTMSS, 20 h) using **1a** as substrate, compound **2a**³ was formed in 98% (Method A) and 87% (Method B) yield (by ¹H-NMR to an internal standard). ¹H-NMR (400 MHz, CDCl₃) δ ppm 7.96 (d, *J* = 7.4 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 2.61 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ ppm 198.3, 137.2, 133.2, 128.7, 128.4, 26.7. When employing **3d** as substrate, **2a** was obtained in 80% (Method A) and 53% (Method B) isolated yield. With **3h** as substrate, the reaction was much more demanding. With 2 eq. TTMSS and 7 d of reaction time, **2a** was obtained in 50% isolated yield following Method A. Method B facilitated only low conversion of the substrate.

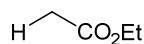


2b

Following the general procedures (1 eq. of TTMSS, 24 h), compound **2b**⁴ was formed in 91% (Method A) and 61% (Method B) yield (by ¹H-NMR to an internal standard). ¹H-NMR (400 MHz, CDCl₃) δ ppm 4.11 (q, *J* = 7.1 Hz, 2H), 2.27 (t, *J* = 7.6 Hz, 2H), 1.61 (quint., *J* = 7.5 Hz, 2H), 1.36 – 1.27 (m, 4H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.88 (t, *J* = 6.9 Hz, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ ppm 173.9, 60.2, 34.4, 31.3, 24.7, 22.3, 14.3, 13.9.

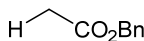
³ K. Moriyama, M. Takemura and H. Togo, *Org. Lett.*, 2012, **14**, 2414.

⁴ F. Alonso, P. Riente and M. Yus, *Tetrahedron*, 2009, **65**, 10637.



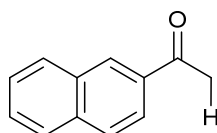
2c

Following the general procedures (1 eq. of TTMSS, 24 h), compound **2c**⁵ was formed in 98% (Method A) and 95% (Method B) yield (by ¹H-NMR to an internal standard). ¹H-NMR (400 MHz, CDCl₃) δ ppm 4.12 (q, *J* = 7.1 Hz, 2H), 2.05 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ ppm 171.4, 60.5, 21.0, 14.2.



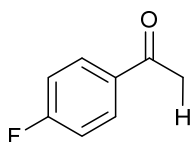
2d

Following the general procedures (1 eq. of TTMSS, 24 h), compound **2d**⁶ was obtained in 87% (Method A) and 80% (Method B) yield after purification by FC (pentane/Et₂O gradient) as a colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ ppm 7.40-7.32 (m, 5H), 5.11 (s, 2H), 2.10 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ ppm 170.8, 135.9, 128.5, 128.2, 66.2, 20.9.



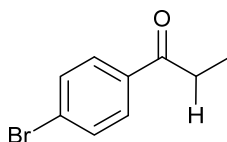
2e

Following the general procedures (1 eq. of TTMSS, 24 h), compound **2e**⁷ was obtained in 98% (Method A) and 88% (Method B) yield after purification by FC (pentane/EtOAc gradient) as a colorless solid. ¹H-NMR (CDCl₃) δ ppm 8.45 (s, 1H), 8.03 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.95 (d, *J* = 7.9 Hz, 1H), 7.92-7.81 (m, 2H), 7.65-7.50 (m, 2H), 2.72 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ ppm 197.9, 135.5, 134.5, 132.5, 130.1, 129.5, 128.4, 128.3, 127.7, 126.7, 123.8, 26.6.



2f

Following the general procedures (1 eq. of TTMSS, 24 h), compound **2f**⁷ was obtained in 89% (Method B) and 76% (Method B) yield after purification by FC (pentane/EtOAc gradient) as a colorless solid. ¹H-NMR (CDCl₃) δ ppm 8.02-7.97 (m, 2H), 7.16-7.11 (m, 2H), 2.57 (s, 3H). ¹³C-NMR (CDCl₃) δ ppm 196.4, 165.7 (d, *J* = 254.6 Hz), 133.6 (d, *J* = 3.0 Hz), 130.9 (d, *J* = 9.4 Hz), 115.6 (d, *J* = 21.9 Hz), 26.4.



2g

Following the general procedures (1 eq. of TTMSS, 24 h), compound **2g**⁸ was obtained in 93% (Method A) and 90% (Method B) yield after purification by FC (pentane/EtOAc gradient) as an off white solid. ¹H-NMR

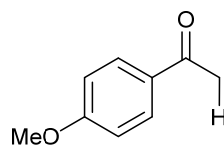
⁵ H. E. Gottlieb, V. Kotlyar and A. Nudelman, *J. Org. Chem.*, 1997, **62**, 7512.

⁶ Y.-C. Yang, D. Y. C. Leung and P. H. Toy, *Synlett*, 2013, **24**, 1870.

⁷ T. M. Gøgsig, J. Kleimark, S. O. N. Lill, S. Korsager, A. T. Lindhardt, P.-O. Norrby and T. Skrydstrup, *J. Am. Chem. Soc.*, 2012, **134**, 443.

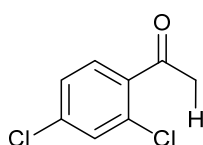
⁸ B. Scheiper, M. Bonnekessel, H. Krause and A. Fürstner, *J. Org. Chem.*, 2004, **69**, 3943.

(400 MHz, CDCl₃) δ ppm 7.86-7.70 (m, 2H), 7.59-7.47 (m, 2H), 2.93 (q, *J* = 7.2 Hz, 2H), 1.19 (t, *J* = 7.2 Hz, 3H).
¹³C-NMR (100 MHz, CDCl₃) δ ppm 199.5, 135.5, 131.7, 129.4, 127.9, 31.7, 8.0.



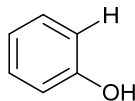
2h

Following the general procedures (1 eq. of TTMSS, 24 h), compound **2h**⁹ was obtained in 89% (Method A) and 86% (Method B) yield after purification by FC (pentane/EtOAc gradient) as a colorless solid. ¹H-NMR (400 MHz, CDCl₃) δ ppm 7.90 (d, *J* = 8.9 Hz, 2H), 6.90 (d, *J* = 8.9 Hz, 2H), 3.83 (s, 3H), 2.52 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ ppm 196.6, 163.4, 130.5, 130.2, 113.6, 55.3, 26.2.



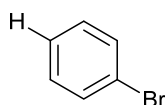
2i

Following the general procedure (1.5 eq. of TTMSS, 24 h), compound **2i**¹⁰ was obtained in 91% (Method A) after purification by FC (CH₂Cl₂/Et₂O 99:1) as an off white solid. Method B failed to provide satisfactory conversion of the substrate. ¹H-NMR (400 MHz, CDCl₃) δ ppm 7.53 (d, *J* = 8.3 Hz, 1H), 7.45 (d, *J* = 2.0 Hz, 1H), 7.31 (dd, *J* = 8.4, 2.0 Hz, 1H), 2.64 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ ppm 198.8, 137.6, 137.1, 132.4, 130.6, 130.4, 127.3, 30.6.



4a

Following the general procedures (1 eq. of TTMSS, 24 h) using **3a** as substrate, compound **4a**¹¹ was obtained in 98% yield (for both Method A and B) after purification by FC (pentane/EtOAc gradient) as a colorless solid. ¹H-NMR (400 MHz, CDCl₃) δ ppm 7.25 (t, *J* = 7.9 Hz, 2H), 6.94 (t, *J* = 7.4 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ ppm 155.5, 129.8, 121.0, 115.4. When employing **3b** as substrate, **4a** was obtained in 73%/83% yield. When employing **3c** as substrate, **4a** was obtained in 70%/79% yield.



4b

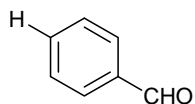
Following the general procedures (1 eq. of TTMSS, 24 h), compound **4b**¹² was formed in 93% (Method A) and 89% (Method B) yield (by ¹H-NMR to an internal standard). ¹H-NMR (400 MHz, CDCl₃) δ ppm 7.54 (d, *J* = 7.5 Hz, 2H), 7.36-7.24 (m, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ ppm 131.5, 130.0, 126.9, 122.5.

⁹ Q. Gao, S.-Y. Li, Y.-M. Pan, Y.-L. Xu and H.-S. Wang, *Tetrahedron*, 2013, **69**, 3775.

¹⁰ G.-F. Zhang, X.-W. Han, Y.-X. Luan, Y. Wang, X. Wen and C.-R. Ding, *Chem. Commun.*, 2013, **49**, 7908.

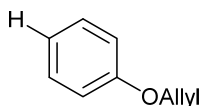
¹¹ H. Jiang, L. Lykke, S. U. Pedersen, W.-J. Xiao and K. A. Jørgensen, *Chem. Commun.*, 2012, **48**, 7203.

¹² B. Li, L.-F. Gao, F.-L. Bian and W. Yu, *Tetrahedron Lett.*, 2013, **54**, 1063.



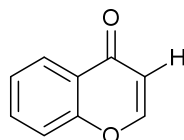
4c

Following the general procedures (1 eq. of TTMSS, 24 h), compound **4c**¹³ was obtained in 84% (Method A) and 75% yield (Method B) after purification by FC (pentane/EtOAc gradient) as a colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ ppm 10.01 (s, 1H), 7.90-7.82 (m, 2H), 7.65-7.56 (m, 1H), 7.56-7.46 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ ppm 192.3, 136.3, 134.4, 129.6, 128.9.



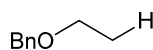
4d

Following the general procedures (1.0 eq. of TTMSS, 24 h), compound **4d**¹⁴ was obtained in 60% (Method A; contaminated with <5% of the dimeric product from radical dimerization) and 99% (Method B, 1.5 eq. of TTMSS, 24 h) yield after purification by FC (pentane/EtOAc gradient) as a pale yellow oil. ¹H-NMR (400 MHz, CDCl₃) δ ppm 7.29 (m, 2H), 6.99-6.91 (m, 3H), 6.07 (ddt, *J* = 17.3, 10.6, 5.3 Hz, 1H), 5.42 (dq, *J* = 17.3, 1.6 Hz, 1H), 5.29 (dq, *J* = 10.5, 1.4 Hz, 1H), 4.55 (dt, *J* = 5.3, 1.6 Hz, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ ppm 158.6, 133.3, 129.4, 120.8, 117.6, 114.7, 68.7.



6

Following the general procedures (1 eq. of TTMSS, 24 h), compound **6**¹⁵ was obtained in 73% (Method A) and 95% (Method B) yield after purification by FC (pentane/EtOAc gradient) as a colorless solid. ¹H-NMR (400 MHz, CDCl₃) δ ppm 8.21 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.86 (d, *J* = 6.0 Hz, 1H), 7.71-7.64 (m, 1H), 7.50-7.37 (m, 2H), 6.35 (d, *J* = 6.0 Hz, 1H). ¹³C-NMR (100 MHz, CDCl₃) δ ppm 177.8, 156.7, 155.4, 133.9, 126.0, 125.4, 125.1, 118.3, 113.2.



8

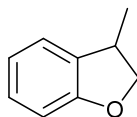
Following the general procedures (2 eq. of TTMSS, 24 h), compound **8**¹⁶ was obtained in 52% (Method A) and 95% (Method B) yield after purification by FC (pentane/EtOAc gradient) as a colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ ppm 7.39-7.27 (m, 5H), 4.52 (s, 2H), 3.55 (q, *J* = 7.0 Hz, 2H), 1.26 (t, *J* = 7.0 Hz, 3H). ¹³C-NMR (CDCl₃) δ ppm 138.7, 128.5, 127.8, 127.6, 72.9, 65.9, 15.4.

¹³ Y.-F. Wang, H.-B. Zhao, Z.-Z. Hu, M. Kimura, Z.-Q. Zhang, L. Peng and K. Hiratsuka, *Synthesis*, 2011, 287.

¹⁴ H. Noda, K. Motokura, A. Miyaji and T. Baba, *Adv. Synth. Catal.*, 2013, **355**, 973.

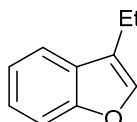
¹⁵ A. V. Dubrovskiy and R. C. Larock, *Tetrahedron*, 2013, **69**, 2789.

¹⁶ N. Sakai, T. Moriya and T. Konakahara, *J. Org. Chem.*, 2007, **72**, 5920.



10a

Following Method A (1 eq. of TTMSS, 24 h), compound **10a**¹⁷ was obtained in 62% yield after purification by FC (pentane/EtOAc 19:1) as a pale yellow oil. ¹H-NMR (400 MHz, CDCl₃) δ ppm 7.16 (d, *J* = 7.3 Hz, 1H), 7.15-7.09 (m, 1H), 6.87 (td, *J* = 7.4, 1.0 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 4.68 (t, *J* = 8.8 Hz, 1H), 4.07 (dd, *J* = 8.6, 7.5 Hz, 1H), 3.62-3.48 (m, 1H), 1.33 (d, *J* = 6.9 Hz, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ ppm 159.7, 132.2, 128.0, 123.8, 120.4, 109.4, 78.4, 36.5, 19.3.



10b

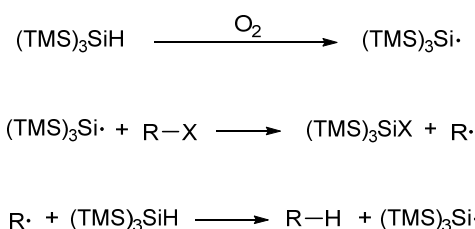
Following Method A (1 eq. of TTMSS, 24 h), compound **10b**¹⁸ was obtained in 51% yield after purification by FC (pentane/EtOAc gradient) as a colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ ppm 7.58-7.54 (m, 1H), 7.46 (dt, *J* = 8.4, 0.9 Hz, 1H), 7.40 (d, *J* = 1.2 Hz, 1H), 7.29 (ddd, *J* = 8.2, 7.7, 1.5 Hz, 1H), 7.26-7.21 (m, 1H), 2.71 (dq, *J* = 7.5, 1.2 Hz, 2H), 1.34 (t, *J* = 7.5 Hz, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ ppm 155.4, 140.5, 128.2, 124.0, 122.3, 122.1, 119.6, 111.4, 17.0, 13.5.

¹⁷ J. Barluenga, F. J. Fañanás, R. Sanz and C. Marcos, *Chem. Eur. J.*, 2005, **11**, 5397.

¹⁸ M. Durandetti, L. Hardou, M. Clémenta and J. Maddaluno, *Chem. Commun.*, 2009, 4753.

4. Mechanistic discussion

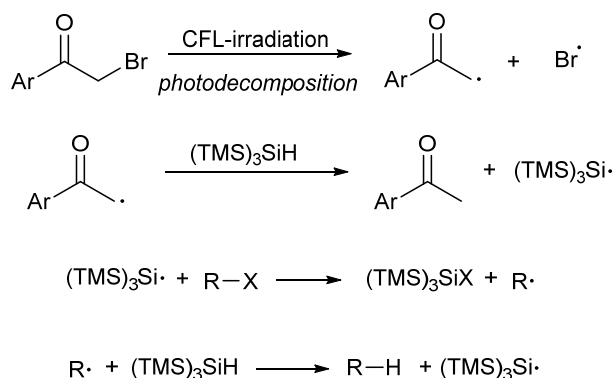
The oxygen-initiated reactions are believed to follow the general mechanism of oxygen-initiated tris(trimethylsilyl)silane-mediated radical reactions. A simplified overview of the general mechanisms is outlined in Scheme S1. Initiation by oxygen occurs with the contaminant formation of a silyl radical (and a peroxy radical). This species reacts readily with substrates such as alkyl or aryl halides to generate the corresponding alkyl or aryl radical species (R·). Propagation occurs via hydrogen abstraction from another silane molecule by R·, furnishing the desired product while regenerating a new silyl radical.



Scheme S1 Simplified mechanism of the oxygen-initiated dehalogenation reaction.

It should be noted that Scheme S1 only holds a simplified mechanistic overview. Other species, such as siloxane, different peroxy radicals and peroxide species, are formed and involved in the oxygen-mediated initiation pathway. This process has previously been studied in detail (see reference 8 in the manuscript).

For the irradiation-mediated protocol, the mechanism of initiation is more unclear. The homolytic cleavage of the Si-H bond by visible light is not very likely, since TTMSS has no significant absorbance above 210 nm.¹⁹ One possibility is that the trace amount of UV components in the emitted light is involved in the initiation process. UV irradiation at 254 nm has previously been shown to drive TTMSS-based reactions (see reference 6b in the manuscript). However, the amount, if any, of UVC emitted by CFLs is extremely limited (see reference 7 in the manuscript). The majority of the ultraviolet radiation is transmitted through the phosphor coating and the glass envelope of CFL-bulbs consists of UVA. The UVA (315-400 nm) emission of the employed light source, Osram Dulux Longlife 30W-840 bulb, has been measured by the manufacturer to 60.8 mW/m².²⁰ Substrates, such as α -bromoacetophenone **1a**, have a reasonable absorbance in the UVA region, and are known to undergo photodecomposition to a phenacyl radical and a bromine atom in alcoholic solvents.²¹ It is possible that the formation of a trace amount of the carbon-centered radical can be triggered by CFL-irradiation in MeCN. This carbon-based radical should then readily perform H-abstraction from TTMSS, which will generate the required silyl radical for chain propagation. This possible initiation route is depicted in Scheme S2.



¹⁹ H. Gilman, W. H. Atwell, P. K. Sen and C. L. Smith, *J. Organomet. Chem.*, 1965, **4**, 163.

²⁰ Compact Fluorescent Lamps OSRAM DULUX, technical guide, p. 26.

²¹ J. Renaud and J. C. Scaiano, *Can. J. Chem.*, 1996, **74**, 1724.

Scheme S2 Possible initiation route by photodecomposition induced by CFL-irradiation.

Intriguingly, several other substrates, without any significant UVA absorbance, are also able to participate in the reaction, thus complicating the attempted rationalization. It is possible that only a minimum amount of photodecomposition (which might take place even for these substrates) is necessary to trigger the initiation of the reaction. Alternatively, the initiation process for the reduction of different types of substrates may also proceed via completely different mechanisms. Nevertheless, a future full mechanistic study might be necessary to fully unveil the complexity of such mechanism.