

Supporting information available for

**Unraveling the Activity and Stability of Cationic Tellurium Activators in Ritter-Type Reactions**

*Koji Takagi,\* Shuhei Hayashi, and Souma Sugie*

Graduate School of Engineering, Nagoya Institute of Technology, Gokiso, Showa, Nagoya,  
Aichi 466-8555, Japan

## S1. General

### Materials

All materials were obtained from commercial suppliers and used without purification unless otherwise noted. Anhydrous tetrahydrofuran (THF) and dichloromethane (DCM) were purchased from Kanto Chemical Co. Other solvents were dried and distilled following to standard methods, and stored under nitrogen atmosphere.

### Instruments

Nuclear magnetic resonance spectra (NMR) were obtained on a Bruker Ascend™400 FT-NMR Spectrometer. <sup>1</sup>H- and <sup>13</sup>C-NMR signals were referenced using tetramethylsilane and residual solvent peaks as an internal standard, respectively. <sup>125</sup>Te-NMR signals were externally referenced to 1.0 M solution of K<sub>2</sub>TeO<sub>3</sub> in D<sub>2</sub>O (1737 ppm) against Me<sub>2</sub>Te. Elemental analyses (EA) were performed on an Elementar vario EL cube. High resolution electrospray ionization mass spectra (HR ESI-MS) were obtained on a Waters Synapt G2 HDMS. Ultraviolet-visible (UV-vis) and fluorescence spectra were recorded on a Shimadzu UV-1650 spectrophotometer and RF-5300 spectrofluorometer, respectively, using a 10 mm quartz cell. Controller PD3-5024-4-SI-NR (CCS) and LED light heads HLV3-22BL-2C ( $\lambda = 465$  nm, 0.7 A/2.7 W, CCS) were used as light sources and set to 25% power as the emission spectrum.

### Theoretical calculations

Calculations were performed on Gaussian 09 (Revision E.01) software package<sup>S1</sup> using computers at the Research Center for Computational Science, Okazaki, Japan. The geometries were optimized using the M06-2X functional. The DGDZVP basis set<sup>S2</sup> was used for the tellurium atom and the 6-31+G(d) basis set was used for the other atoms. Vibrational analysis was carried out demonstrating that all the optimized geometries correspond to energy minimum structures with no negative frequency. Electrostatic potential (ESP) maps were visualized by Gauss View 5 software. Local maxima of electrostatic potential ( $V_{s,max}$ ) were determined with multiwfn software<sup>S3</sup> and reported in kcal·mol<sup>-1</sup>.

## S2. Preparation

### DAnT(Me)-TfO

MeI (0.180 mL, 2.88 mmol) was added to a mixture of bis(4-methoxyphenyl)telluride (0.329 g, 0.962 mmol) and AgOTf (0.271 g, 1.06 mmol) in dichloroethane (4 mL) under dark, and the system was stirred overnight at room temperature. After the precipitate was filtered off and washed with CH<sub>3</sub>CN (2 mL), organic solvents were removed by rotary evaporator. A crude product was purified by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>:CH<sub>3</sub>OH = 95:5 in volume ratio, R<sub>f</sub> = 0.12) to obtain colorless solid (0.258 g, 53% yield). <sup>1</sup>H-NMR (400 MHz, CD<sub>3</sub>CN) δ ppm 7.55 (d, *J* = 8.9 Hz, 4H), 7.03 (d, *J* = 8.9 Hz, 4H), 3.85 (s, 6H), 2.88 (s, 3H); <sup>13</sup>C-NMR (100 MHz, CD<sub>3</sub>CN): δ ppm 163.9, 136.7, 117.4, 111.8, 56.5, 12.2; <sup>19</sup>F-NMR (376 MHz): δ ppm -79.3; <sup>125</sup>Te-NMR (126 MHz, CD<sub>3</sub>CN) δ ppm 639.2; Elemental Analysis Calcd. for C<sub>16</sub>H<sub>17</sub>F<sub>3</sub>O<sub>5</sub>STe: C, 37.98; H, 3.39; S, 6.34. Found: C, 37.58; H, 3.58; S, 5.94.

### TVio-2TfO

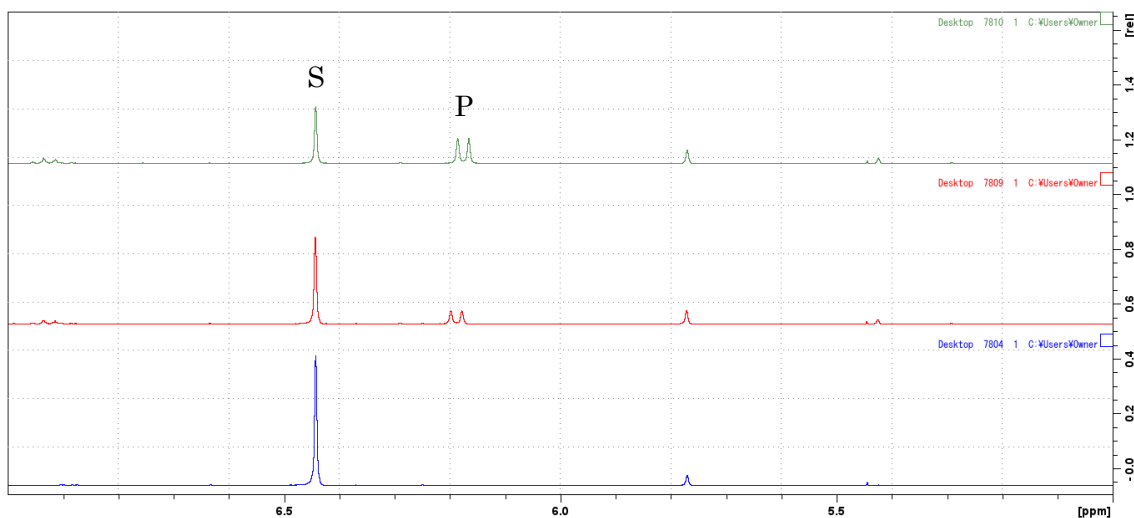
2-Ethylhexyl trifluoromethanesulfonate (221 mg, 841 μmol) was added to telluro[2,3-c:5,4-c']bipyridine (54.0 mg, 190 μmol) in DCM (5 mL) at 0 °C, and the system was stirred overnight at room temperature. After evaporating solvent, a crude product was washed with hexane and recrystallized from CHCl<sub>3</sub>/acetone (3/1) obtain yellow solid (44.2 mg, 29% yield). <sup>1</sup>H-NMR (400 MHz, CD<sub>3</sub>CN) δ ppm 9.52 (s, 2H), 8.96 (d, *J* = 8.0 Hz, 2H), 8.83 (d, *J* = 8.0 Hz, 2H), 4.60 (d, *J* = 8.0 Hz, 4H), 2.14-2.05 (m, 2H), 1.47-1.25 (m, 16H), 0.98-0.85 (m, 12H); <sup>13</sup>C-NMR (100 MHz, CD<sub>3</sub>CN): δ ppm 152.7, 150.4, 141.5, 138.7, 126.7, 66.8, 42.4, 30.4, 28.9, 23.8, 23.5, 14.2, 10.6; <sup>19</sup>F-NMR (376 MHz): δ ppm -79.3; <sup>125</sup>Te-NMR (126 MHz, CD<sub>3</sub>CN) δ ppm 878.2; Elemental Analysis Calcd. for C<sub>28</sub>H<sub>40</sub>F<sub>6</sub>N<sub>2</sub>O<sub>6</sub>S<sub>2</sub>Te: C, 41.71; H, 5.00; S, 7.95. Found: C, 41.48; H, 5.09; S, 7.87.

### TVio-2TFSI

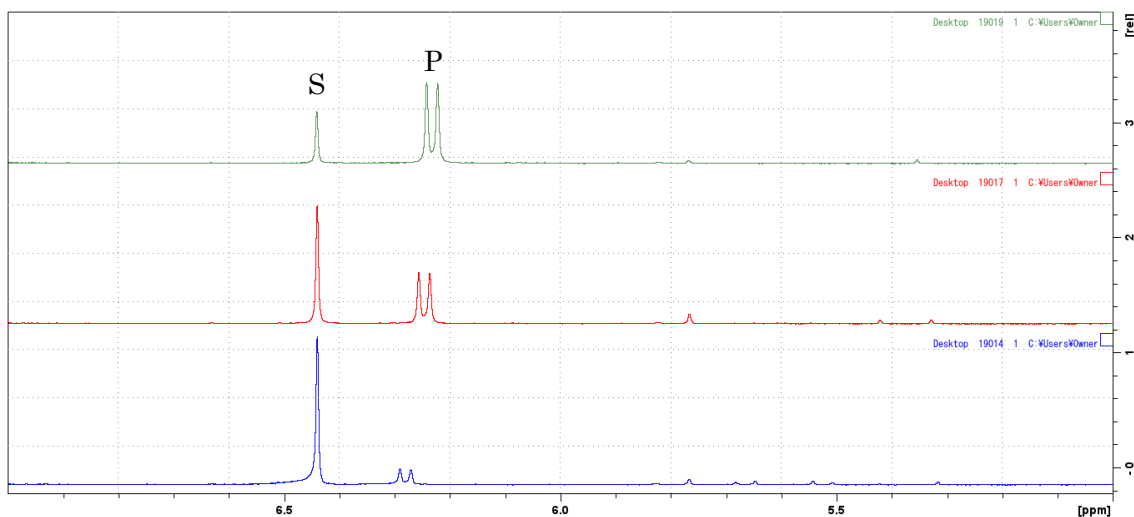
Lithium bis(trifluoromethanesulfonyl)imidate (43 mg, 150 μmol) was added to TVio-2TfO (50 mg, 62 μmol) in DCM (7 mL), and the system was stirred for 96 h at room temperature. After the mixture was washed with water (15 mL × 3) and dried over Na<sub>2</sub>SO<sub>4</sub>, solvent was evaporated to dryness and the product was dried at 50 °C under vacuum to obtain orange solid (41 mg, 61% yield). <sup>1</sup>H-NMR (400 MHz, CD<sub>3</sub>CN) δ ppm 9.40 (s, 2H), 8.93 (d, *J* = 8.0 Hz, 2H), 8.82 (d, *J* = 8.0 Hz, 2H), 4.60 (d, *J* = 8.0 Hz, 4H), 2.12-2.04 (m, 2H), 1.47-1.25 (m, 16H), 0.98-0.85 (m, 12H); <sup>13</sup>C-NMR (100 MHz, CD<sub>3</sub>CN): δ ppm 152.8, 150.2, 141.6, 138.3, 126.7, 122.6, 119.4, 66.8, 42.4, 30.3, 28.9, 23.8, 23.3, 14.3, 10.6; <sup>19</sup>F-NMR (376 MHz, CD<sub>3</sub>CN): δ ppm -80.2; <sup>125</sup>Te-NMR

(126 MHz, CD<sub>3</sub>CN)  $\delta$  ppm 872.4; Elemental Analysis Calcd. for C<sub>30</sub>H<sub>40</sub>F<sub>12</sub>N<sub>4</sub>O<sub>8</sub>S<sub>4</sub>Te: C, 33.72; H, 3.77; N, 5.24; S, 12.00. Found: C, 33.73; H, 4.25; N, 4.70; S, 10.74.

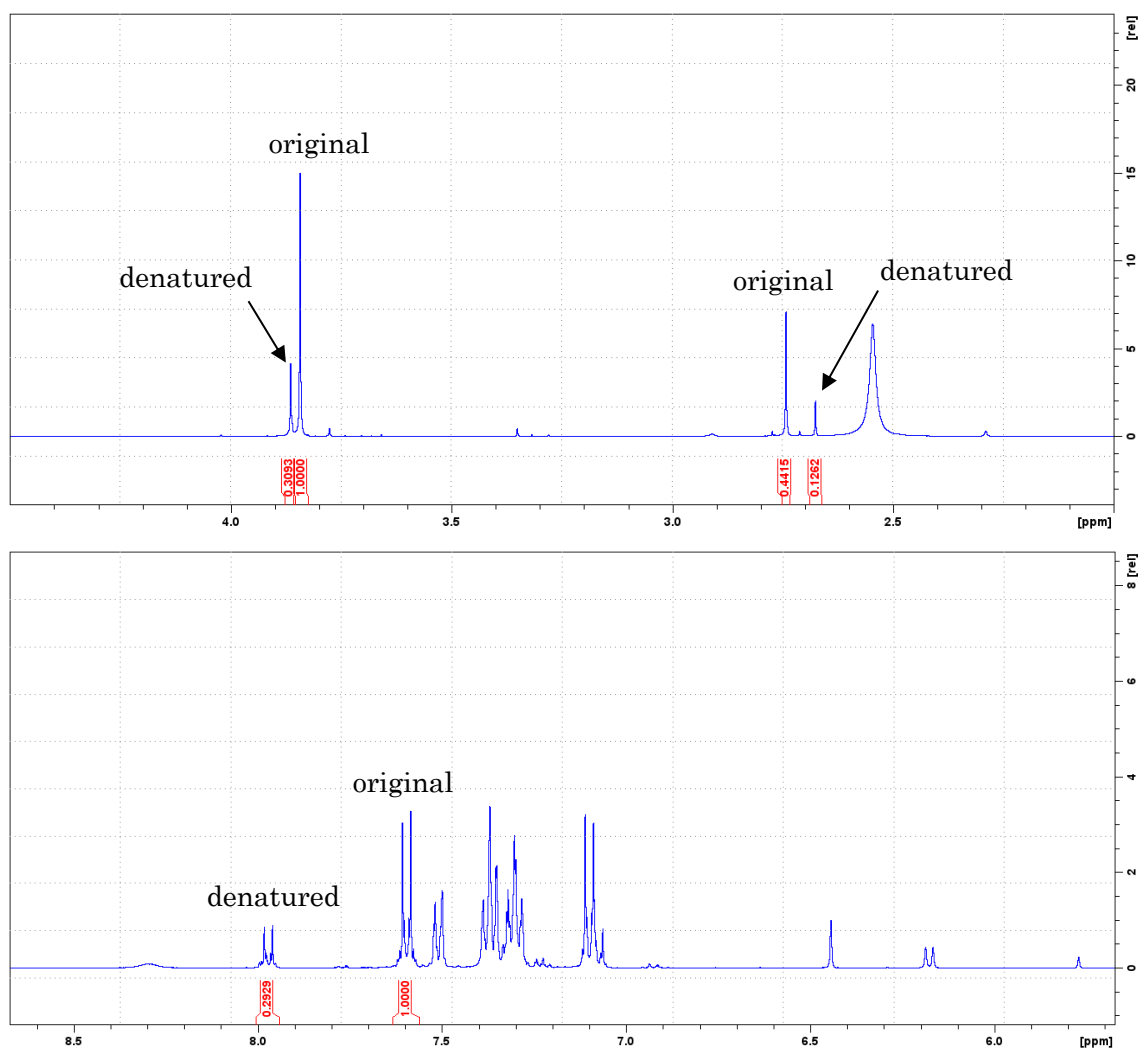
### S3. Supplementary experimental data



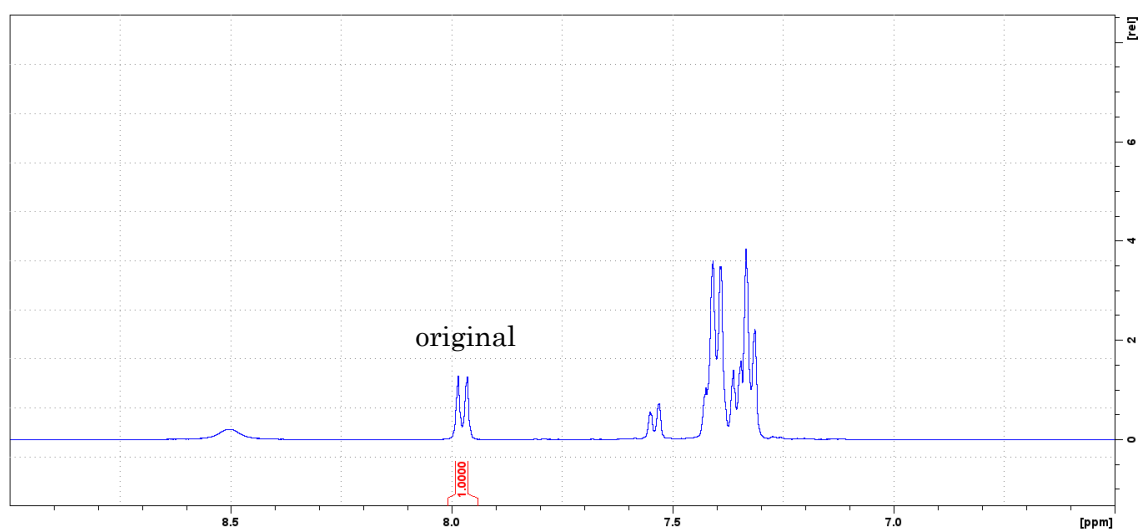
**Figure S1.** Selected  $^1\text{H}$ -NMR spectra in the Ritter-type reaction of benzhydryl bromide using **DAnT(Me)-TfO** (100 mol%) an activator. From bottom to top: 4, 48, and 96. Characters S and P denote proton signals derived from the starting material (benzhydryl bromide) and the product, respectively.



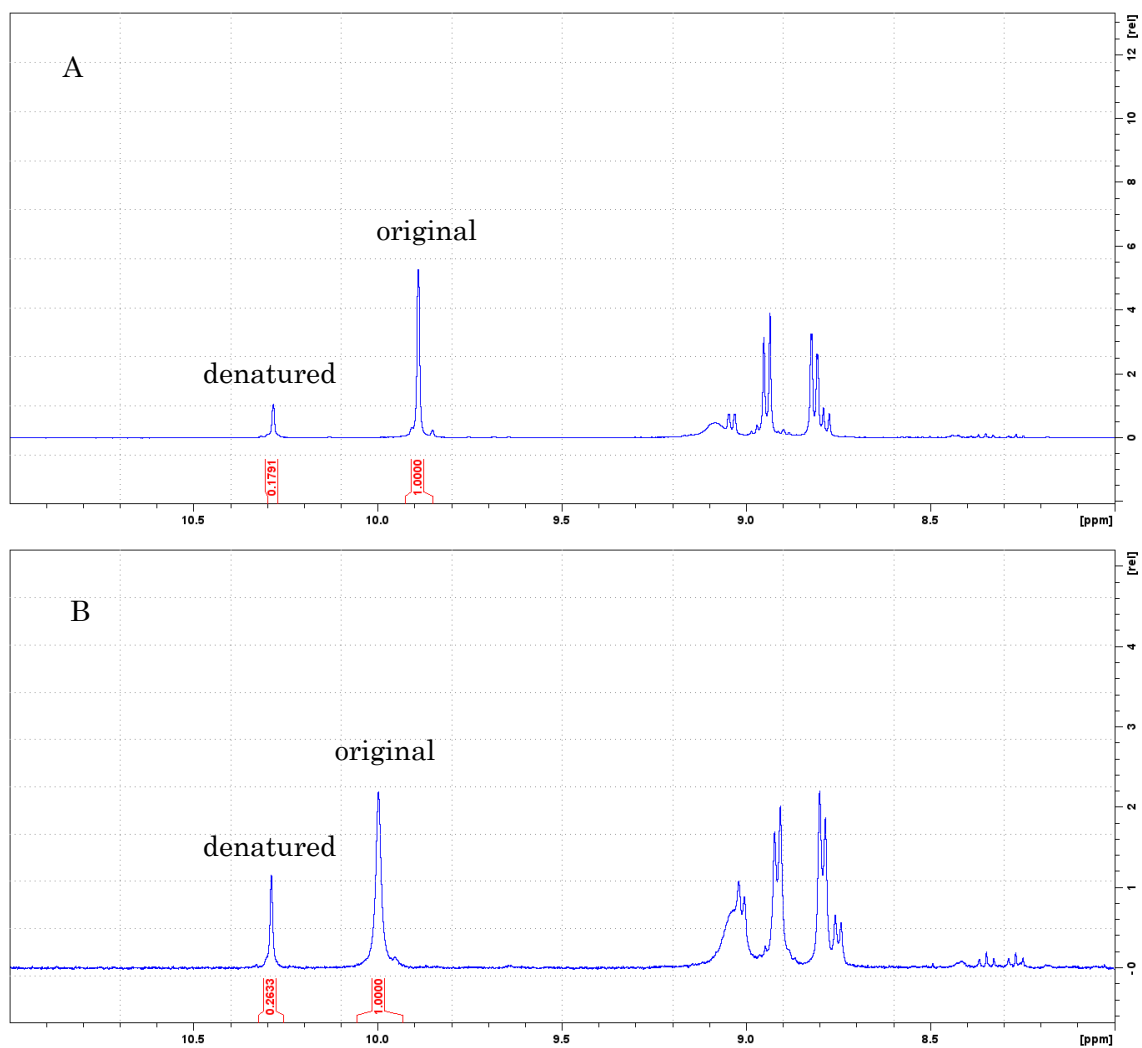
**Figure S2.** Selected  $^1\text{H}$ -NMR spectra in the Ritter-type reaction of benzhydryl bromide using **TVio-2TfO** (100 mol%) as an activator. From bottom to top: 4, 24, and 96 h. Characters S and P denote proton signals derived from the starting material (benzhydryl bromide) and the product, respectively.



**Figure S3.** <sup>1</sup>H-NMR spectra of **DANt(Me)-TfO** after 96 h of the Ritter-type reaction of benzhydryl bromide.

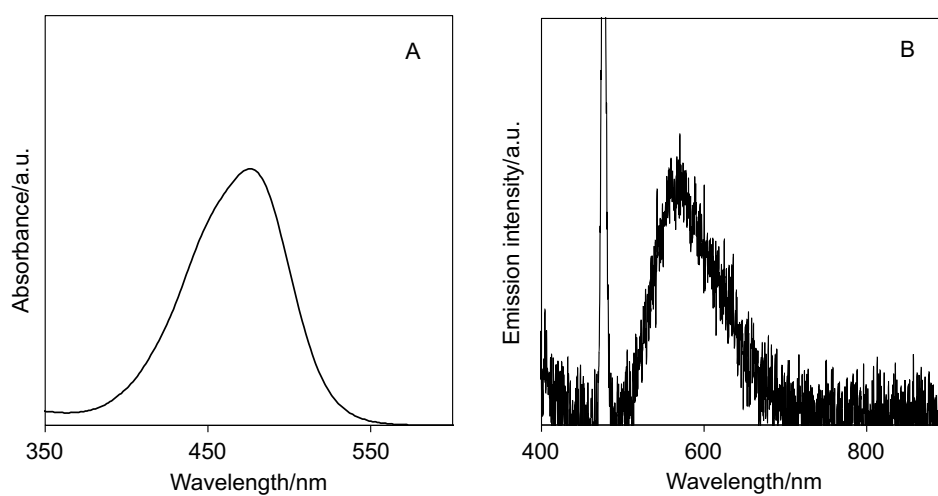


**Figure S4.**  $^1\text{H-NMR}$  spectrum of **DAnT(OH)-TfO** after 96 h of the Ritter-type reaction of benzhydryl bromide. No proton signal derived from the denatured activator was observed.

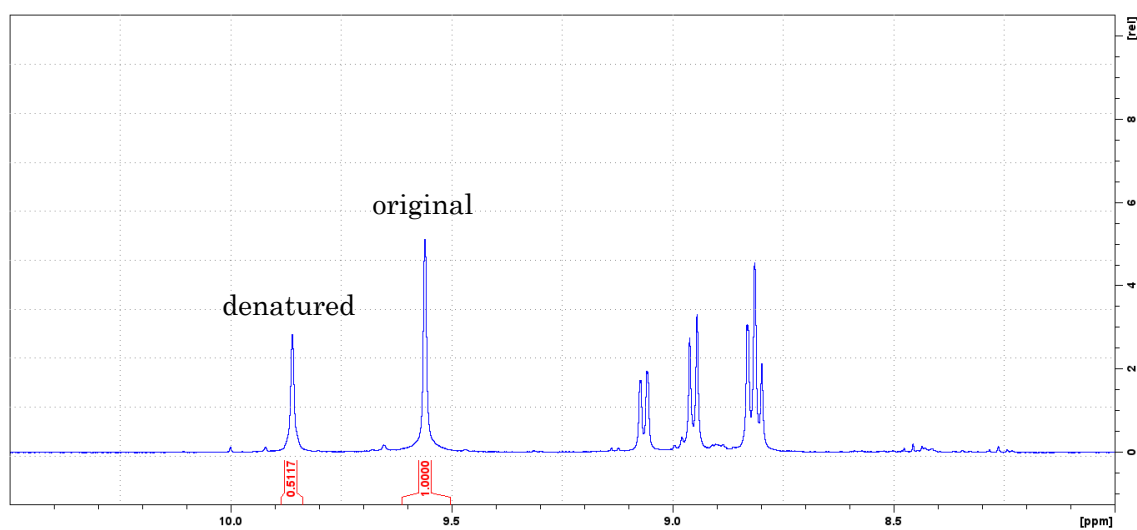


**Figure S5.**  $^1\text{H-NMR}$  spectra of TVio-2TfO after 96 h of the Ritter-type reaction of benzhydryl bromide. A: 100 mol% activator and B: 40 mol% activator..

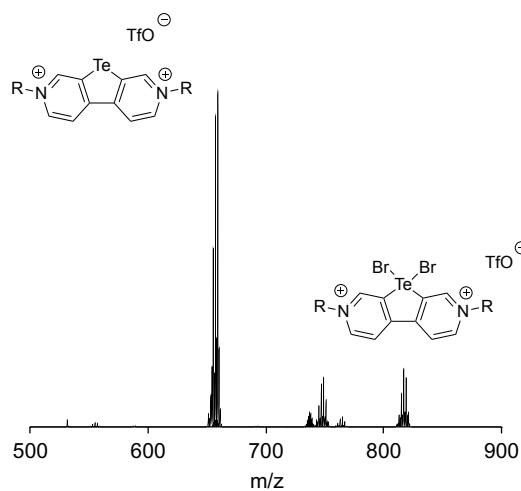




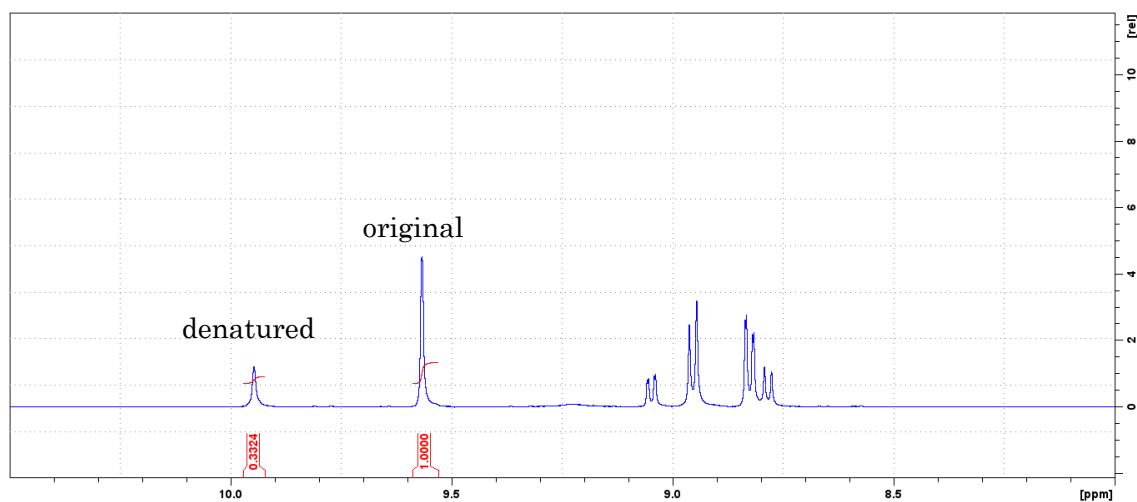
**Figure S6.** (A) UV absorption and (B) PL emission spectra of **TVio-2TfO** in 0.1 mM  $\text{CH}_3\text{CN}$  solution.



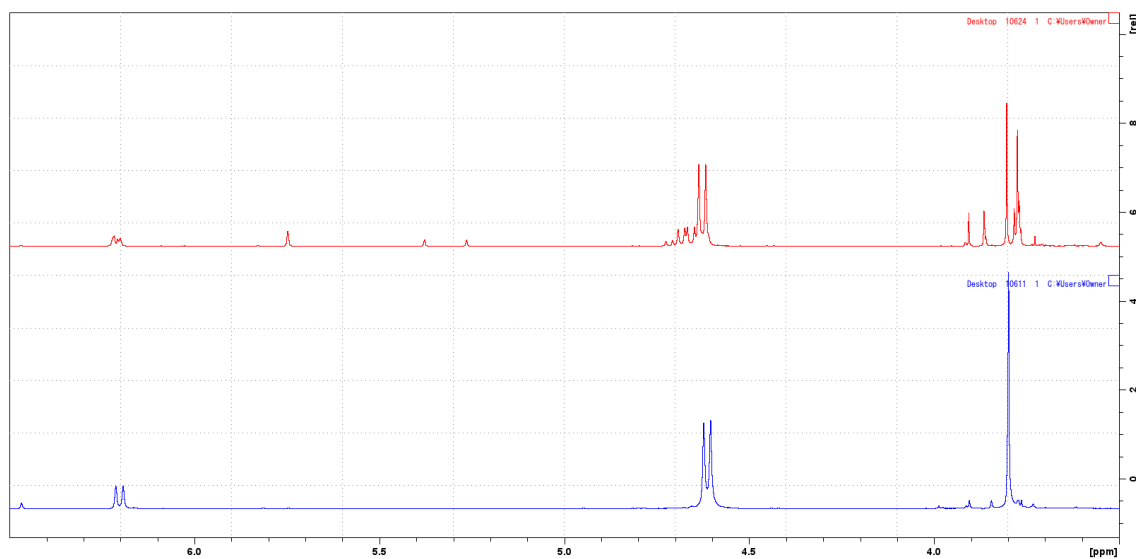
**Figure S7.**  $^1\text{H-NMR}$  spectrum of **TVio-2TfO** after 1 h of the Ritter-type reaction of benzhydryl bromide under light irradiation with 465 nm LED light.



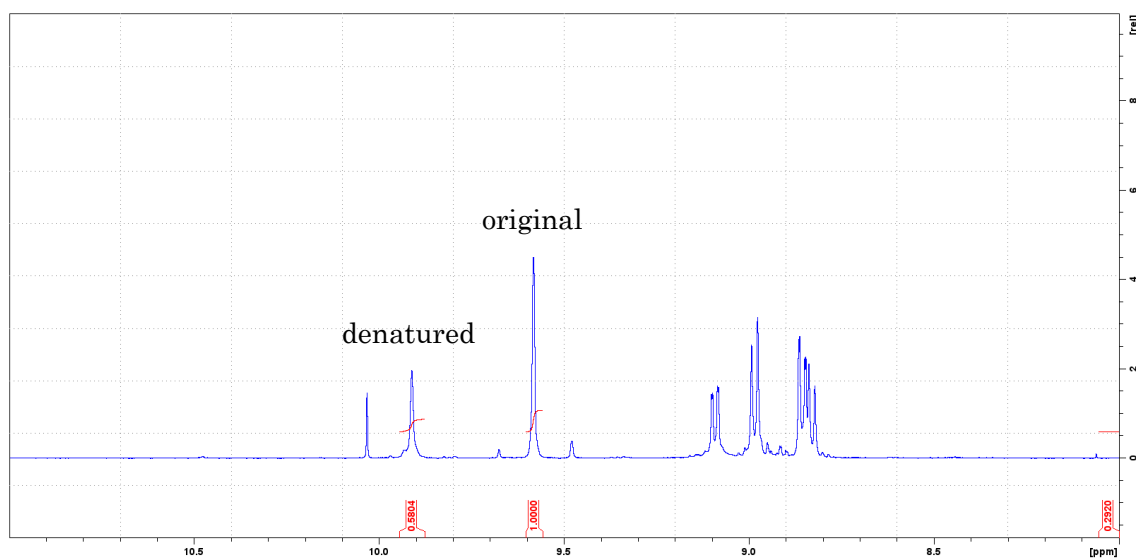
**Figure S8.** ESI-MS spectrum of the reaction mixture after 96 h of the Ritter-type reaction of benzhydryl bromide under light irradiation with 465 nm LED light.



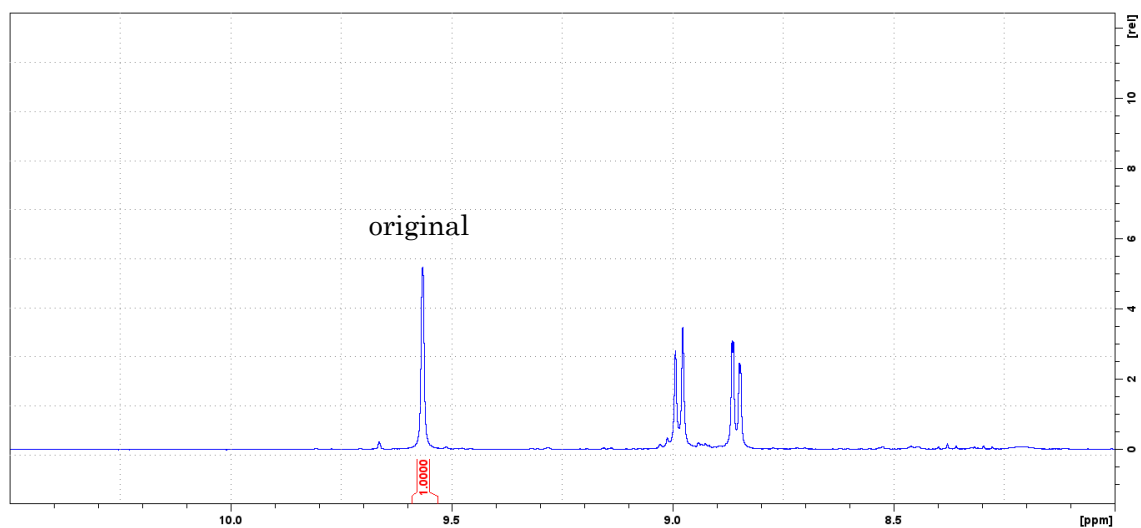
**Figure S9.**  $^1\text{H-NMR}$  spectrum of TVio-2TfO after 1 h of the Ritter-type reaction of benzhydryl bromide under light irradiation with 465 nm LED light and under nitrogen.



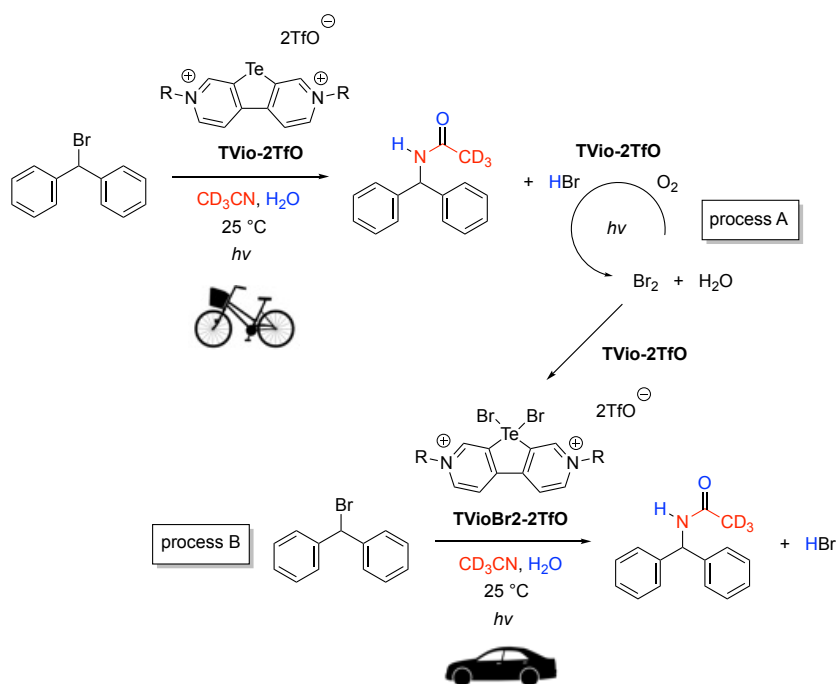
**Figure S10.**  $^1\text{H-NMR}$  spectra in the Ritter-type reaction of 4-methoxybenzhydryl bromide using **TVio-2TfO** (100 mol%) as an activator. Top: with light irradiation for 1 h. Bottom: without light irradiation for 114 h (91% yield).



**Figure S11.**  $^1\text{H-NMR}$  spectrum of **TVio-2TfO** after 1 h of the Ritter-type reaction of 4-methoxybenzhydryl bromide under light irradiation with 465 nm LED light.

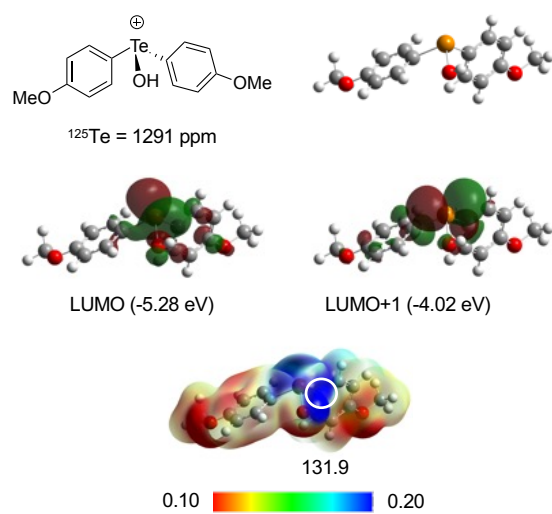


**Figure S12.**  $^1\text{H-NMR}$  spectrum of **TVio-2TfO** after 96 h of the Ritter-type reaction of benzhydryl bromide under light irradiation with 465 nm LED light. No proton signal derived from the denatured activator was observed.



**Scheme S1.** Plausible mechanism for accelerating the Ritter-type reaction using **TVio-2TfO** with 465 nm light irradiation.

## S4. DFT calculations



**Figure S13.** Chemical structure of activator **DAnT(OH)-TfO** with  $^{125}\text{Te}$ -NMR chemical shift, optimized structure, LUMO and LUMO+1 surface with potential, and ESP map with  $V_{s,\text{max}}$  value in kcal mol $^{-1}$ . Isosurface value: 0.002.

## S5. References

- S1) Gaussian 09, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.
- S2) N. Godbout, D. R. Salahub, J. Andzelm, and E. Wimmer, *Can. J. Chem.* **1992**, *70*, 560–571.
- S3) T. Lu and F. Chen, *J. Comput. Chem.* **2012**, *33*, 580–592.