

# New Synthetic Entry to OH-Functionalized Nitrile *N*-Oxide and Polyfunctional Nitrile *N*-Oxides For Click Crosslinking and Decrosslinking of Natural Rubber

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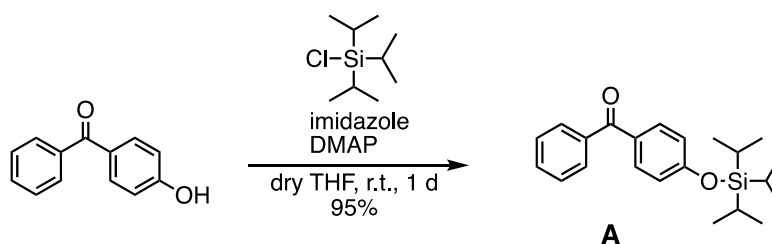
## 1. Experimental Section

### 1.1 Materials and instruments

Tetrahydrofuran (>99%, dry, Wako), *n*-butyllithium (2.6 M, hexane solution) (Kanto Chemical Co., Inc.) and other commercially available solvents were used as received. Natural rubber (NR) was kindly donated by Toyoda Gosei Co. Ltd. (Aichi, Japan) and used as received. <sup>1</sup>H NMR (400 MHz) was recorded on a JEOL AL-400 spectrometer, <sup>1</sup>H NMR (500 MHz) and <sup>13</sup>C NMR spectra (125 MHz) were recorded on a Bruker AVANCE III-HD 500 spectrometer using CDCl<sub>3</sub> as the solvent calibrated using residual undeuterated solvents or tetramethylsilane as the internal standard. FAB HR-MS were collected using a JEOL JMS700 mass spectrometer at the Center for Advanced Materials Analysis, Tokyo Institute of Technology on request. IR spectra were recorded on a JASCO FT/IR-230 spectrometer. Size exclusion chromatography (SEC) was carried out at 30 °C in CHCl<sub>3</sub> (0.85 mL/min) using a JASCO PU-2080 system equipped with a set of Shodex K-804 and Shodex K-805 columns. The number average molecular weight ( $M_n$ ), weight average molecular weight ( $M_w$ ), and polydispersity index (PDI) of the obtained polymers were calculated on the basis of a polystyrene calibration. Samples for tensile test were fabricated by using a punching blade (No. 7, Kobunshi Keiki Co., Ltd.) conformed to ISO 37-4 specimens (dumbbell shape, 12 mm×2 mm).

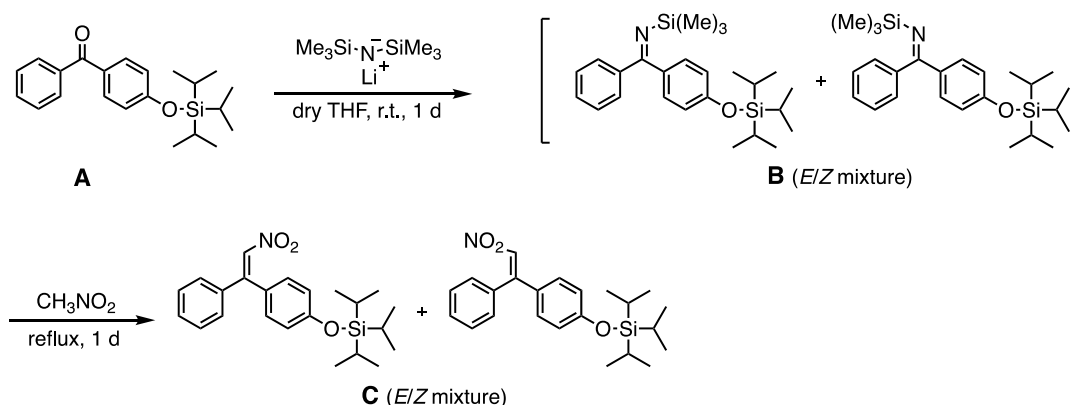
## 1.2 Chemical synthesis

### Synthesis of A



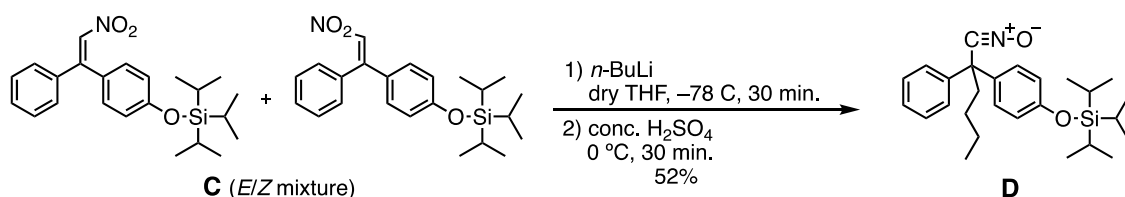
4-Hydroxybenzophenone (15 g, 75 mmol), imidazole (10 g, 0.15 mol) and DMAP (1.8 g, 15 mmol) were dissolved in dry THF (0.15 L) and cooled to 0 °C. To the reaction mixture was added triisopropylsilyl chloride (22 g, 0.11 mol) dropwise and then the reaction mixture was warmed to room temperature. After stirring for 1 d, the reaction mixture was evaporated, diluted in AcOEt, washed with water and brine. The separated organic phase was dried over anhydrous magnesium sulfate, filtered, and evaporated. The crude was purified by a silica gel column chromatography (eluent: hexane/AcOEt = 10/1) to obtain **A** in 95% yield (25 g, 71 mmol) as a colorless oil; <sup>1</sup>H NMR (500 MHz, 298 K, CDCl<sub>3</sub>): δ 7.78–7.76 (m, 4H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 6.94 (d, *J* = 8.5 Hz, 2H), 1.35–1.26 (m, 3H), 1.11 (d, *J* = 5.0 Hz, 18H) ppm; <sup>13</sup>C NMR (125 MHz, 298 K, CDCl<sub>3</sub>): δ 195.4, 160.2, 138.2, 132.4, 131.7, 130.3, 129.6, 128.0, 119.4, 17.8, 12.6 ppm; FAB-HRMS (*m/z*) calc'd for C<sub>22</sub>H<sub>31</sub>O<sub>2</sub>Si [M+H]<sup>+</sup>, 355.2093; found, 355.2101.

### Synthesis of C



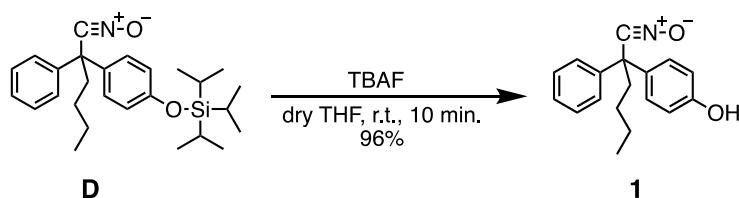
To a solution of **A** (7.3 g, 21 mmol) in dry THF (20 mL) was added LiHMDS (1.3 M in THF, 19 mL, 25 mmol) at 0 °C under Ar atmosphere. The reaction mixture was stirred at room temperature for 1 d and then evaporated. The mixture was diluted with AcOEt, washed with water and brine. The separated organic phase was dried over anhydrous magnesium sulfate, filtered, and evaporated to give the crude residue **B** (*E/Z* mixture). Nitromethane (50 mL) was added to **B** and the mixture was refluxed for 1 d. After cooling to room temperature, the mixture was evaporated to give crude residue **C** (*E/Z* mixture) as a brown oil. **C** was used for next step without further purification.

## Synthesis of **D**



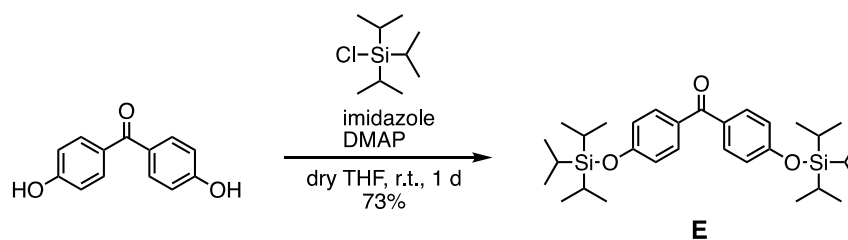
The crude of **C** (7.0 g) was dissolved in dry THF (0.20 L) under Ar atmosphere and cooled to  $-78\text{ }^\circ\text{C}$ . *n*-Butyllithium (2.6 M in hexane, 10 mL, 26 mmol) was added into the reaction solution and the mixture was stirred for 30 min at the same temperature. To the reaction mixture was added conc.  $\text{H}_2\text{SO}_4$  (>95%, 9.5 mL, 0.18 mol) at  $0\text{ }^\circ\text{C}$  and stirred for 30 min. The mixture was diluted with dichloromethane, washed with water and brine. The separated organic phase was dried over anhydrous magnesium sulfate, filtered, and evaporated. The crude was purified by a silica gel column chromatography (eluent: hexane/ $\text{CH}_2\text{Cl}_2 = 2/1$ ) to obtain **D** in 52% yield (4.6 g, 11 mmol) as a yellow oil;  $^1\text{H NMR}$  (500 MHz, 298 K,  $\text{CDCl}_3$ ):  $\delta$  7.35–7.31 (m, 2H), 7.28–7.25 (m, 3H), 7.12 (d,  $J = 8.8$  Hz, 2H), 6.83 (d,  $J = 8.8$  Hz, 2H), 2.33 (t,  $J = 7.8$  Hz, 2H), 1.37–1.29 (m, 4H), 1.27–1.20 (m, 3H), 1.08 (d,  $J = 7.6$  Hz, 18H), 0.88 (t,  $J = 7.0$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (125 MHz, 298 K,  $\text{CDCl}_3$ ):  $\delta$  155.5, 142.1, 134.0, 128.7, 127.9, 127.8, 126.8, 112.0, 52.6, 40.8, 28.0, 22.6, 17.9, 13.9, 12.6 ppm; FAB-HRMS ( $m/z$ ) calc'd for  $\text{C}_{27}\text{H}_{40}\text{NO}_2\text{Si}$  [ $\text{M}+\text{H}$ ] $^+$ , 438.2828; found, 438.2831.

## Synthesis of **1**



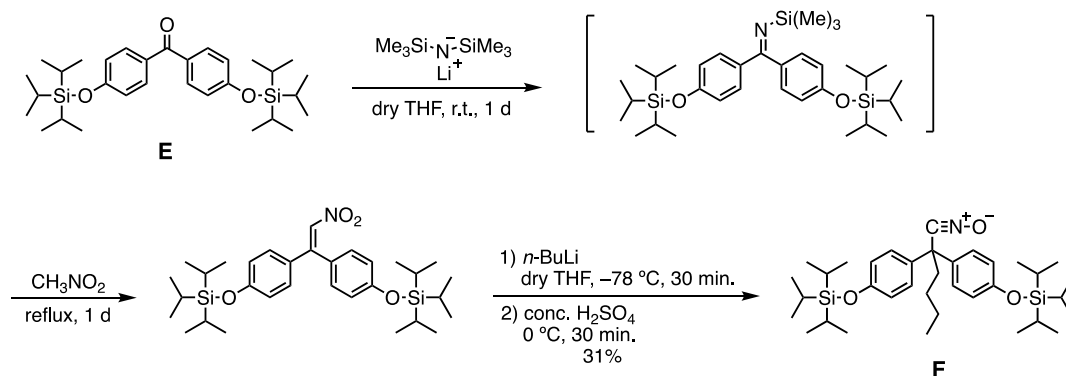
**D** (2.0 g, 4.5 mmol) was dissolved in dry THF (50 mL). To the reaction mixture was added TBAF (1.0 M in THF, 6.7 mL, 6.7 mmol). After stirring for 10 min at room temperature, the reaction mixture was diluted in  $\text{CH}_2\text{Cl}_2$ , washed with water and brine. The separated organic phase was dried over anhydrous magnesium sulfate, filtered, and evaporated. The crude was purified by a silica gel column chromatography (eluent: hexane/ $\text{CH}_2\text{Cl}_2 = 1/6$ ) to obtain nitrile *N*-oxide **1** in 96% yield (1.2 g, 4.3 mmol) as a yellow oil;  $^1\text{H NMR}$  (500 MHz, 298 K,  $\text{CDCl}_3$ ):  $\delta$  7.36–7.32 (m, 2H), 7.29–7.26 (m, 3H), 7.15 (d,  $J = 8.5$  Hz, 2H), 6.79 (d,  $J = 8.5$  Hz, 2H), 4.92 (br, 1H), 2.34 (t,  $J = 7.8$  Hz, 2H), 1.37–1.28 (m, 4H), 0.89 (t,  $J = 7.0$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (125 MHz, 298 K,  $\text{CDCl}_3$ ):  $\delta$  155.3, 141.7, 133.4, 128.7, 128.1, 127.7, 126.6, 115.5, 52.5, 40.6, 28.0, 22.5, 13.8 ppm; IR (NaCl):  $\nu$  2296 (CNO)  $\text{cm}^{-1}$ ; FAB-HRMS ( $m/z$ ) calc'd for  $\text{C}_{18}\text{H}_{20}\text{NO}_2$  [ $\text{M}+\text{H}$ ] $^+$ , 282.1494; found, 282.1499.

## Synthesis of **E**



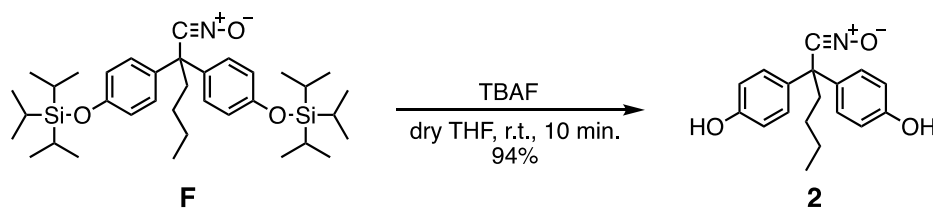
**E** was prepared according to the procedure for **A**. 4,4'-dihydroxybenzophenone (17 g, 78 mmol), imidazole (20 g, 0.30 mol), DMAP (4.1 g, 32 mmol), triisopropylsilyl chloride (33 g, 0.17 mol) and dry THF (0.20 L) were used for preparation. The resulting residue was purified by a silica gel column chromatography (eluent: hexane/ AcOEt = 20/1) to obtain **E** in 73% yield (30 g, 57 mmol) as a colorless viscous liquid;  $^1\text{H NMR}$  (500 MHz, 298 K,  $\text{CDCl}_3$ ):  $\delta$  7.72 (d,  $J = 8.8$  Hz, 4H), 6.93 (d,  $J = 8.8$  Hz, 4H), 1.36–1.27 (m, 3H), 1.14 (d,  $J = 5.0$  Hz, 18H) ppm;  $^{13}\text{C NMR}$  (125 MHz, 298 K,  $\text{CDCl}_3$ ):  $\delta$  194.7, 159.9, 132.2, 131.0, 119.4, 17.9, 12.7 ppm; FAB-HRMS ( $m/z$ ) calc'd for  $\text{C}_{31}\text{H}_{51}\text{O}_3\text{Si}_2$   $[\text{M}+\text{H}]^+$ , 527.3377; found, 527.3375.

## Synthesis of **F**



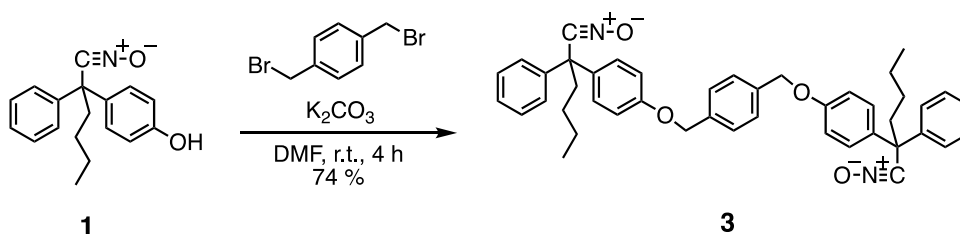
**F** was prepared according to the procedure for **C** and **D**. **E** (11 g, 20 mmol), LiHMDS (1.3 M in THF, 24 mL, 24 mmol), dry THF (20 mL) and nitromethane (20 mL) were used for preparation. **G** was obtained as a brown oil and used for next step without further purification. The crude (7.7 g),  $n$ -butyllithium (2.6 M in hexane, 7.5 mL, 20 mmol), dry THF (0.13 L) and conc.  $\text{H}_2\text{SO}_4$  (>95%, 15 mL, 0.30 mol) were used for preparation. The resulting residue was purified by a silica gel column chromatography (eluent: hexane/  $\text{CH}_2\text{Cl}_2 = 2/1$ ) to obtain **F** in 31% yield (3.8 g, 6.2 mmol) as a yellow oil;  $^1\text{H NMR}$  (500 MHz, 298 K,  $\text{CDCl}_3$ ):  $\delta$  7.10 (d,  $J = 8.8$  Hz, 4H), 6.78 (d,  $J = 8.8$  Hz, 4H), 2.27 (t,  $J = 7.8$  Hz, 2H), 1.36–1.29 (m, 4H), 1.27–1.20 (m, 3H), 1.08 (d,  $J = 5.0$  Hz, 18H), 0.87 (t,  $J = 7.0$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (125 MHz, 298 K,  $\text{CDCl}_3$ ): 155.4, 134.4, 127.9, 119.9, 51.9, 41.0, 28.1, 22.6, 17.9, 13.9, 12.6 ppm; FAB-HRMS ( $m/z$ ) calc'd for  $\text{C}_{36}\text{H}_{60}\text{O}_3\text{Si}_2$   $[\text{M}+\text{H}]^+$ , 610.4112; found, 610.4118.

## Synthesis of **2**



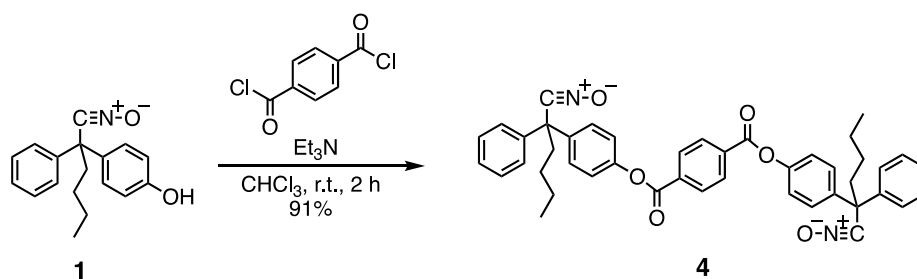
**2** was prepared according to the procedure for **1**. **F** (2.1 g, 3.5 mmol), TBAF (1.0 M in THF, 5.3 mL, 5.3 mmol) and dry THF (40 mL) were used for preparation. The resulting residue was purified by a silica gel column chromatography (eluent: hexane/AcOEt = 2/1) to obtain **2** in 94% yield (0.97 g, 3.3 mmol) as a yellow oil;  $^1\text{H NMR}$  (500 MHz, 298 K,  $\text{CDCl}_3$ ):  $\delta$  7.11 (d,  $J = 8.5$  Hz, 4H), 6.78 (d,  $J = 8.5$  Hz, 4H), 5.32 (br, 2H), 2.29 (t,  $J = 7.5$  Hz, 2H), 1.39–1.28 (m, 4H), 0.87 (t,  $J = 7.0$  Hz, 3H) ppm;  $^{13}\text{C NMR}$  (125 MHz, 298 K,  $\text{CDCl}_3$ ):  $\delta$  155.1, 133.9, 128.1, 115.6, 51.9, 40.8, 28.1, 22.6, 13.9 ppm; IR (NaCl):  $\nu$  2292 (CNO)  $\text{cm}^{-1}$ ; FAB-HRMS ( $m/z$ ) calc'd for  $\text{C}_{18}\text{H}_{20}\text{O}_3$   $[\text{M}+\text{H}]^+$ , 298.1443; found, 298.1442.

## Synthesis of **3**



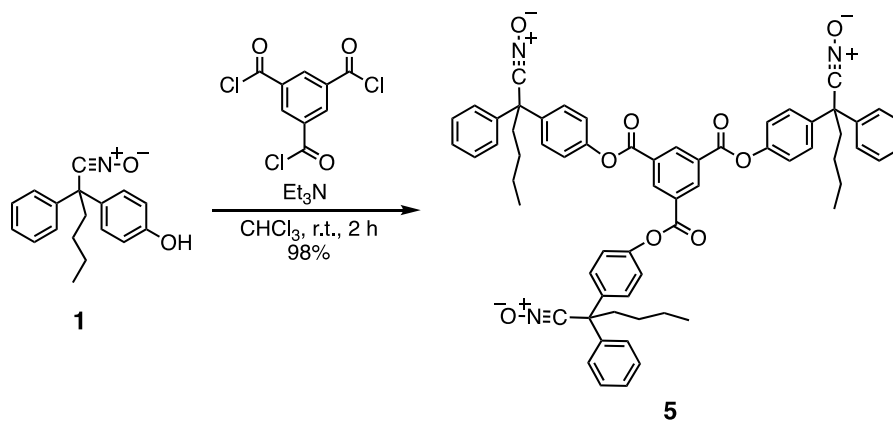
Nitrile *N*-oxide **1** (1.7 g, 6.0 mmol), 1,4-bis(bromomethyl)benzene (0.71 g, 2.7 mmol) and  $\text{K}_2\text{CO}_3$  (1.2 g, 9.0 mmol) were dissolved in DMF (20 mL) and the mixture was stirred for 4 h at room temperature. To the reaction mixture was added  $\text{H}_2\text{O}$ , following by stirring for 30 min. The reaction mixture was diluted in  $\text{CH}_2\text{Cl}_2$ , washed with water and brine. The separated organic phase was dried over anhydrous magnesium sulfate, filtered, and evaporated. The crude was purified by a silica gel column chromatography (eluent: hexane/ $\text{CH}_2\text{Cl}_2 = 1/2$ ) to obtain bifunctional nitrile *N*-oxide **3** in 74% yield (1.3 g, 2.0 mmol) as a yellow solid; m.p. 48.1–49.7  $^\circ\text{C}$ ;  $^1\text{H NMR}$  (500 MHz, 298 K,  $\text{CDCl}_3$ ):  $\delta$  7.44 (s, 4H), 7.36–7.32 (m, 4H), 7.29–7.26 (m, 6H), 7.20 (d,  $J = 8.8$  Hz, 4H), 6.93 (d,  $J = 8.8$  Hz, 4H), 5.05 (s, 4H), 2.35 (t,  $J = 7.8$  Hz, 4H), 1.40–1.29 (m, 8H), 0.89 (t,  $J = 7.0$  Hz, 6H) ppm;  $^{13}\text{C NMR}$  (125 MHz, 298 K,  $\text{CDCl}_3$ ):  $\delta$  158.0, 142.0, 136.6, 134.2, 128.8, 128.0, 127.8, 127.7, 126.7, 114.9, 69.7, 52.6, 40.8, 28.1, 22.6, 13.9 ppm; IR (NaCl):  $\nu$  2291 (CNO)  $\text{cm}^{-1}$ ; FAB-HRMS ( $m/z$ ) calc'd for  $\text{C}_{44}\text{H}_{45}\text{N}_2\text{O}_4$   $[\text{M}+\text{H}]^+$ , 665.3379; found, 665.3357.

## Synthesis of 4



Nitrile *N*-oxide **1** (2.0 g, 7.0 mmol) and trimethylamine (1.4 g, 14 mmol) were dissolved in  $\text{CHCl}_3$  (60 mL) and cooled to 0 °C. A solution of terephthaloyl dichloride (0.61 g, 3.0 mmol) in  $\text{CHCl}_3$  (10 mL) was added to the reaction mixture slowly. After stirring for 2 h at room temperature, the reaction mixture was diluted in  $\text{CHCl}_3$ , washed with water and brine. The separated organic phase was dried over anhydrous magnesium sulfate, filtered, and evaporated. The crude was purified by a silica gel column chromatography (eluent: hexane/ $\text{CH}_2\text{Cl}_2$  = 1/2) to obtain bifunctional nitrile *N*-oxide **4** in 91% yield (1.9 g, 2.7 mmol) as a white solid; m.p. 82.4–83.6 °C;  $^1\text{H}$  NMR (500 MHz, 298 K,  $\text{CDCl}_3$ ):  $\delta$  8.32 (s, 4H), 7.39–7.23 (m, 18H), 2.41 (t,  $J$  = 7.8 Hz, 4H), 1.43–1.35 (m, 8H), 0.89 (t,  $J$  = 7.0 Hz, 6H) ppm;  $^{13}\text{C}$  NMR (125 MHz, 298 K,  $\text{CDCl}_3$ ):  $\delta$  164.0, 150.0, 141.4, 139.8, 133.7, 130.3, 128.9, 128.1, 127.9, 126.8, 121.9, 52.9, 40.8, 28.0, 22.6, 13.9 ppm; IR (NaCl):  $\nu$  2291 (CNO)  $\text{cm}^{-1}$ ; FAB-HRMS ( $m/z$ ) calc'd for  $\text{C}_{44}\text{H}_{41}\text{N}_2\text{O}_6$  [ $\text{M}+\text{H}$ ] $^+$ , 693.2965; found, 693.2966.

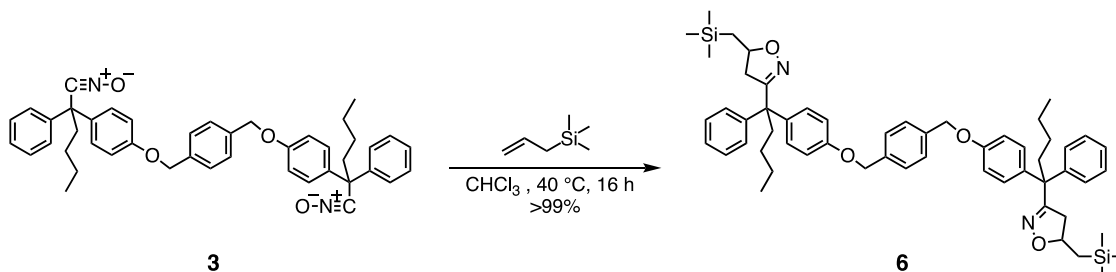
## Synthesis of 5



Nitrile *N*-oxide **1** (2.8 g, 9.9 mmol) and trimethylamine (2.0 g, 20 mmol) were dissolved in  $\text{CHCl}_3$  (90 mL) and cooled to 0 °C. A solution of 1,3,5-benzenetricarbonyl trichloride (0.8 g, 3.0 mmol) in  $\text{CHCl}_3$  (10 mL) was added to the reaction mixture slowly. After stirring for 2 h at room temperature, the reaction mixture was diluted in  $\text{CHCl}_3$ , washed with water and brine. The separated organic phase was dried over anhydrous magnesium sulfate, filtered, and evaporated. The crude was purified by a silica gel column chromatography (eluent: hexane/ $\text{CH}_2\text{Cl}_2$  = 1/2) to obtain trifunctional nitrile *N*-oxide **5** in 98% yield (2.9 g, 2.9 mmol) as a white solid; m.p. 95.3–96.8 °C;  $^1\text{H}$  NMR (500 MHz, 298

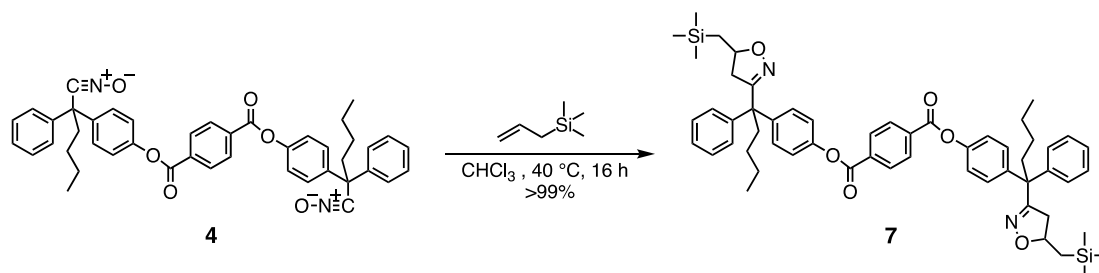
K, CDCl<sub>3</sub>): δ 9.21 (s, 3H), 7.39–7.24 (m, 27H), 2.41 (t, *J* = 7.8 Hz, 6H), 1.42–1.34 (m, 12H), 0.90 (t, *J* = 6.8 Hz, 9H) ppm; <sup>13</sup>C NMR (125 MHz, 298 K, CDCl<sub>3</sub>): δ 163.0, 149.8, 141.3, 140.1, 136.2, 131.0, 128.9, 128.2, 128.0, 126.8, 121.8, 52.9, 40.8, 28.0, 22.6, 13.9 ppm; IR (NaCl): ν 2291 (CNO) cm<sup>-1</sup>; FAB-HRMS (*m/z*) calc'd for C<sub>63</sub>H<sub>58</sub>N<sub>3</sub>O<sub>9</sub> [M+H]<sup>+</sup>, 1000.4173; found, 1000.4099.

### Synthesis of **6**



Bifunctional nitrile *N*-oxide **3** (13 mg, 19 μmol) and allyltrimethylsilane (43 mg, 0.38 mmol) were dissolved in CHCl<sub>3</sub> (0.20 mL) and stirred for 16 h at 40 °C. The reaction mixture was evaporated and dried in vacuo to obtain isoxazoline **6** in >99% yield (17 mg, 19 μmol) as a yellow oil; <sup>1</sup>H NMR (500 MHz, 298 K, CDCl<sub>3</sub>): δ 7.50 (s, 4H), 7.37–7.23 (m, 14H), 6.97–6.95 (m, 4H), 5.10 (s, 4H), 4.66–4.57 (m, 2H), 2.81–2.74 (m, 2H), 2.35 (t, *J* = 8.1 Hz, 4H), 2.28–2.20 (m, 2H), 1.30–1.25 (m, 8H), 1.11–1.00 (m, 2H), 0.87–0.84 (m, 2H), 0.83 (t, *J* = 7.3 Hz, 6H), 0.00 (s, 18H) ppm; <sup>13</sup>C NMR (125 MHz, 298 K, CDCl<sub>3</sub>): δ 163.6, 157.3, 143.0, 136.8, 135.2, 130.2, 128.9, 127.9, 126.6, 114.2, 79.2, 69.7, 53.7, 43.2, 38.5, 27.0, 23.9, 23.2, 14.0, -1.06 ppm; FAB-HRMS (*m/z*) calc'd for C<sub>56</sub>H<sub>73</sub>N<sub>2</sub>O<sub>4</sub>Si<sub>2</sub> [M+H]<sup>+</sup>, 893.5109; found, 893.5070.

### Synthesis of **7**

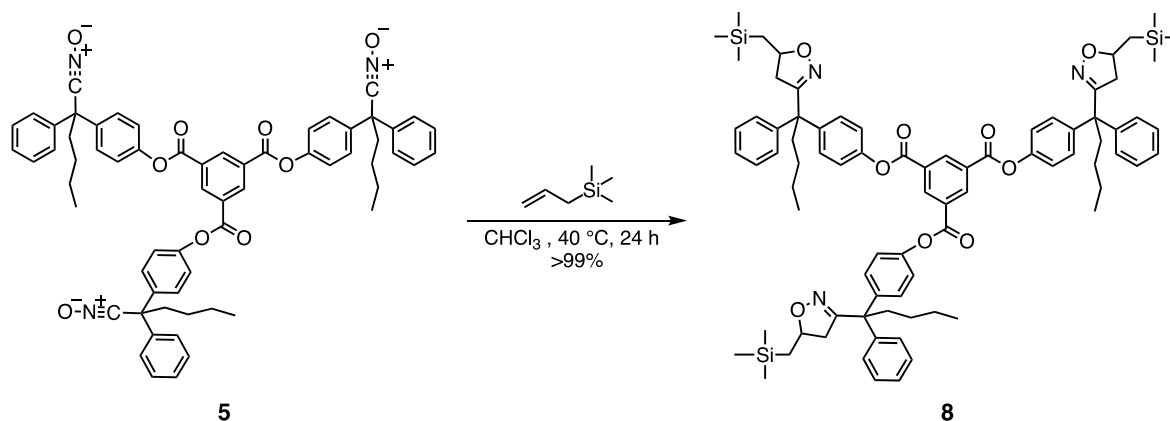


**7** was prepared according to the procedure for **6**. Bifunctional nitrile *N*-oxide **4** (32 mg, 46 μmol), allyltrimethylsilane (0.11 g, 1.0 mmol) and CHCl<sub>3</sub> (0.50 mL) were used for preparation. The reaction mixture was evaporated and dried in vacuo to obtain isoxazoline **7** in >99% yield (42 mg, 46 μmol) as a colorless oil; <sup>1</sup>H NMR (500 MHz, 298 K, CDCl<sub>3</sub>): δ 8.35 (s, 4H), 7.41–7.23 (m, 18H), 4.67–4.60 (m, 2H), 2.83–2.77 (m, 2H), 2.43 (t, *J* = 7.8 Hz, 4H), 2.30–2.23 (m, 2H), 1.34–1.25 (m, 8H), 1.13–1.07 (m, 2H), 0.89–0.85 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 6H), 0.00 (s, 18H) ppm; <sup>13</sup>C NMR (125 MHz, 298 K, CDCl<sub>3</sub>): δ 164.2, 163.1, 149.3, 142.6, 140.9, 133.9, 130.3, 128.9, 128.2, 126.9, 120.9, 79.35, 54.05, 43.2, 38.5, 27.0, 23.9, 23.1, 14.0, -1.06 ppm; FAB-HRMS (*m/z*) calc'd for C<sub>56</sub>H<sub>69</sub>N<sub>2</sub>O<sub>6</sub>Si<sub>2</sub>



$[M+H]^+$ , 921.4649; found, 921.4736.

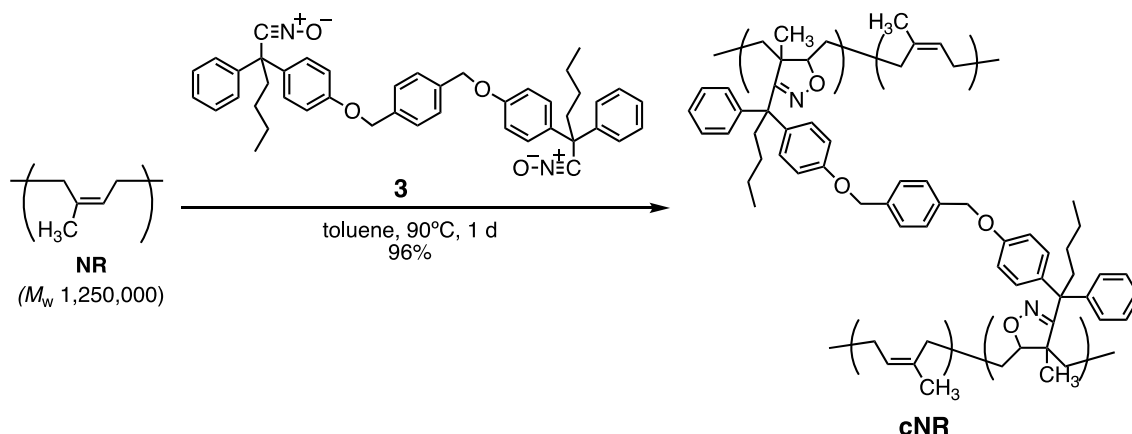
### Synthesis of **8**



**8** was prepared according to the procedure for **6**. Trifunctional nitrile *N*-oxide **5** (54 mg, 54  $\mu\text{mol}$ ), allyltrimethylsilane (0.17 g, 1.5 mmol) and  $\text{CHCl}_3$  (0.50 mL) were used for preparation. After stirring for 24 h, the reaction mixture was evaporated and dried in vacuo to obtain isoxazoline **8** in >99% yield (73 mg, 54  $\mu\text{mol}$ ) as a colorless oil;  $^1\text{H}$  NMR (500 MHz, 298 K,  $\text{CDCl}_3$ ):  $\delta$  9.25 (s, 3H), 7.42–7.14 (m, 27H), 4.67–4.60 (m, 3H), 2.84–2.77 (m, 3H), 2.48–2.38 (m, 6H), 2.30–2.23 (m, 3H), 1.34–1.26 (m, 12H), 1.13–1.28 (m, 3H), 0.87–0.84 (m, 3H), 0.90 (t,  $J = 7.3$  Hz, 12H), 0.00 (s, 27H) ppm;  $^{13}\text{C}$  NMR (125 MHz, 298 K,  $\text{CDCl}_3$ ):  $\delta$  163.2, 149.1, 142.5, 141.9, 136.1, 131.2, 130.3, 128.89, 128.14, 126.9, 120.9, 79.3, 54.0, 43.2, 38.5, 27.0, 23.9, 23.1, 14.0,  $-1.08$  ppm; FAB-HRMS ( $m/z$ ) calc'd for  $\text{C}_{81}\text{H}_{99}\text{N}_3\text{O}_9\text{Si}_3\text{Na}$   $[M+\text{Na}]^+$ , 1364.6587; found, 1364.6606.

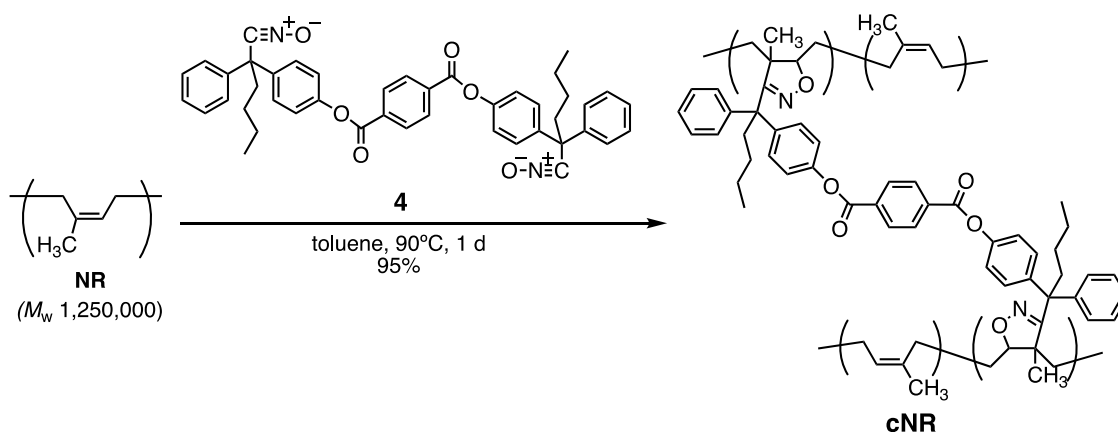
### 1-3. Catalyst-free cross-linking reaction of NR

Catalyst-free cross-linking reaction of NR using bifunctional nitrile *N*-oxide **3**.



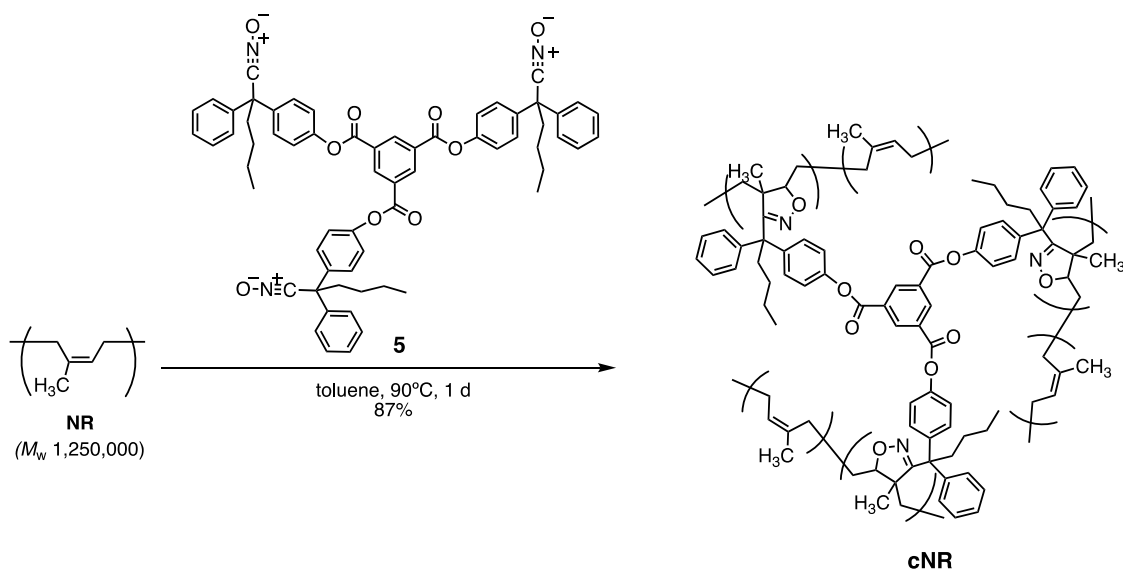
In a PTFE Petri dish (60 mm $\phi$ ) was placed NR ( $M_w$  1,250,000) (2.4 g, 35 mmol of the monomeric unit) and toluene (30 mL). After NR was dissolved, **3** (0.23 g, 0.35 mmol) in toluene (1.0 mL) was added into the reaction mixture with stirring, and then the homodispersed mixture was warmed levelly at 90 °C for 1 d. The obtained film was immersed in CHCl<sub>3</sub> (10 mL) in a closed system and then dried in vacuo at 70 °C to give cNR (2.7 g) in 96% yield as a pale-yellow film (Table 1, entry 4).

Catalyst-free cross-linking reaction of NR using bifunctional nitrile *N*-oxide **4**.



In a PTFE Petri dish (60 mm $\phi$ ) was placed NR ( $M_w$  1,250,000) (2.4 g, 35 mmol of the monomeric unit) and toluene (30 mL). After NR was dissolved, **4** (0.24 g, 0.35 mmol) in toluene (1.0 mL) was added into the reaction mixture with stirring, and then the homodispersed mixture was warmed levelly at 90 °C for 1 d. The obtained film was immersed in CHCl<sub>3</sub> (10 mL) in a closed system and then dried in vacuo at 70 °C to give cNR (2.7 g) in 95% yield as a pale-yellow film (Table 1, entry 8).

Catalyst-free cross-linking reaction of NR using trifunctional nitrile *N*-oxide **5**.



In a PTFE Petri dish (42 mm $\phi$ ) was placed NR ( $M_w$  1,250,000) (2.4 g, 35 mmol of the monomeric unit) and toluene (30 mL). After NR was dissolved, **5** (0.35 g, 0.35 mmol) in toluene (1.0 mL) was added into the reaction mixture with stirring, and then the homodispersed mixture was warmed levelly at 90 °C for 1 d. The obtained film was immersed in CHCl<sub>3</sub> (10 mL) in a closed system and then dried in vacuo at 70 °C to give **cNR** (2.4 g) in 87% yield as a pale-yellow film (Table 1, entry 12).

Evaluation of the reaction condition for crosslinking

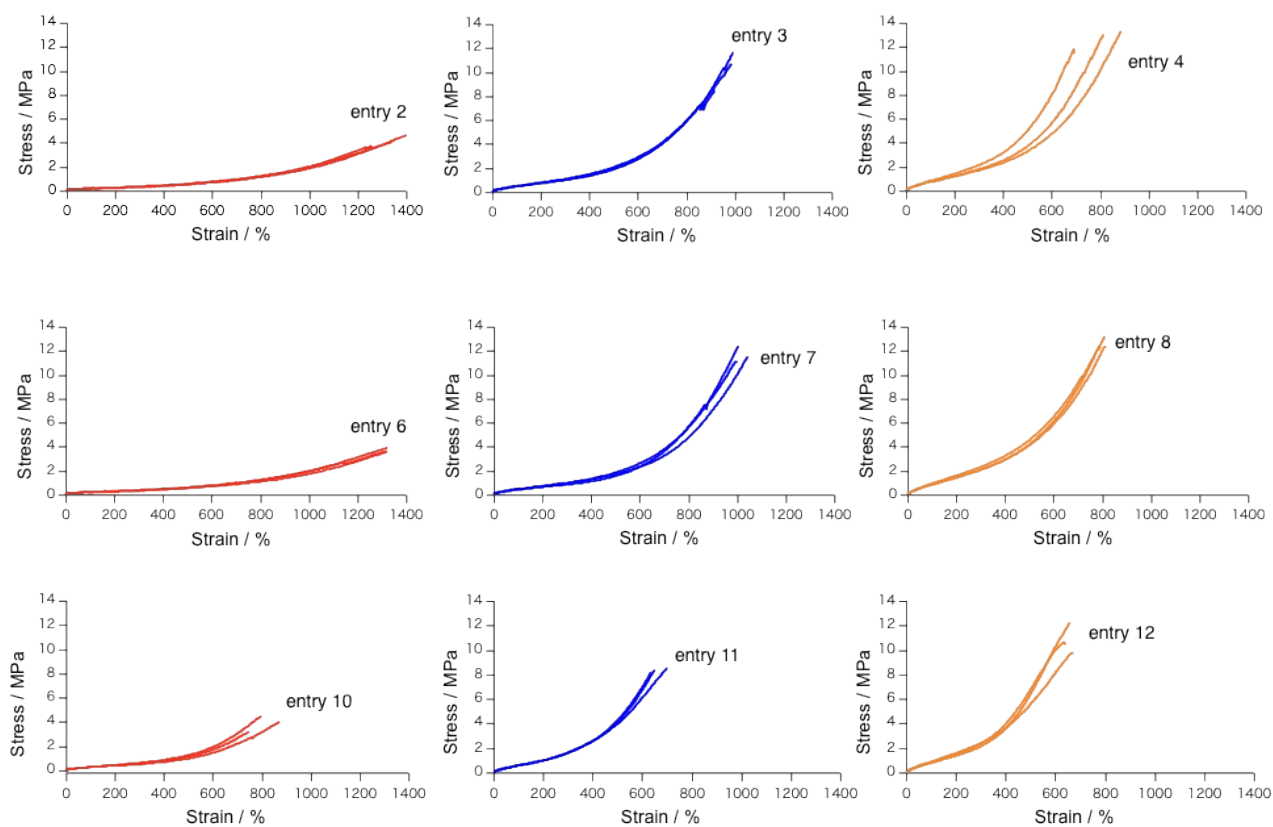
The model reaction of crosslinking reactions were carried out by dissolving NR in toluene at 90 °C with 0.5 mol% of nitrile *N*-oxide **3** for 1, 2 or 3 days, and the results are shown in Table S1. The crosslinking reaction proceed smoothly in all cases and the cross-linked NRs showed similar swelling property. This result indicates that the crosslinking reaction using nitrile *N*-oxide crosslinker **3** was completed within 1 day.

**Table S1.** Crosslinking reaction of NR with nitrile *N*-oxide **3** for different reaction time.<sup>a</sup>

Entry	Time of crosslinking reaction / day	Swelling ratio / % <sup>b</sup>
1	1	1000
2	2	1000
3	3	1100

<sup>a</sup> 0.50 mol% feed ratio of nitrile *N*-oxide **3**. <sup>b</sup> swollen in CHCl<sub>3</sub>. Calculated from  $(W_s - W_d) / W_d$ , where  $W_s$  is weight of swelling gel and  $W_d$  is weight of dry gel.





**Figure S1.** Stress-strain curves of cNR obtained using crosslinker 3–5. Elongation rate: 10mm/min. Each cNR was tested more than 3 times. Entry numbers are corresponded to the numbers in Table 1.

#### 1-4. Decrosslinking reaction of cNRs

Degradation of **cNR** (entry 2 in Table 1, the use of cross-linker **3**) in the basic condition

**cNR** (99 mg) was swollen in THF (30 mL). After that, KOH solution (3.0 M in methanol, 10 mL, 30 mmol) and H<sub>2</sub>O (10 mL) were added and the mixture was stirred at 80 °C for 24 h. After the reaction, insoluble part was collected by filtration and immersed in CHCl<sub>3</sub>.

Degradation of **cNR** (entry 6 in Table 1, the use of cross-linker **4**) in the basic condition

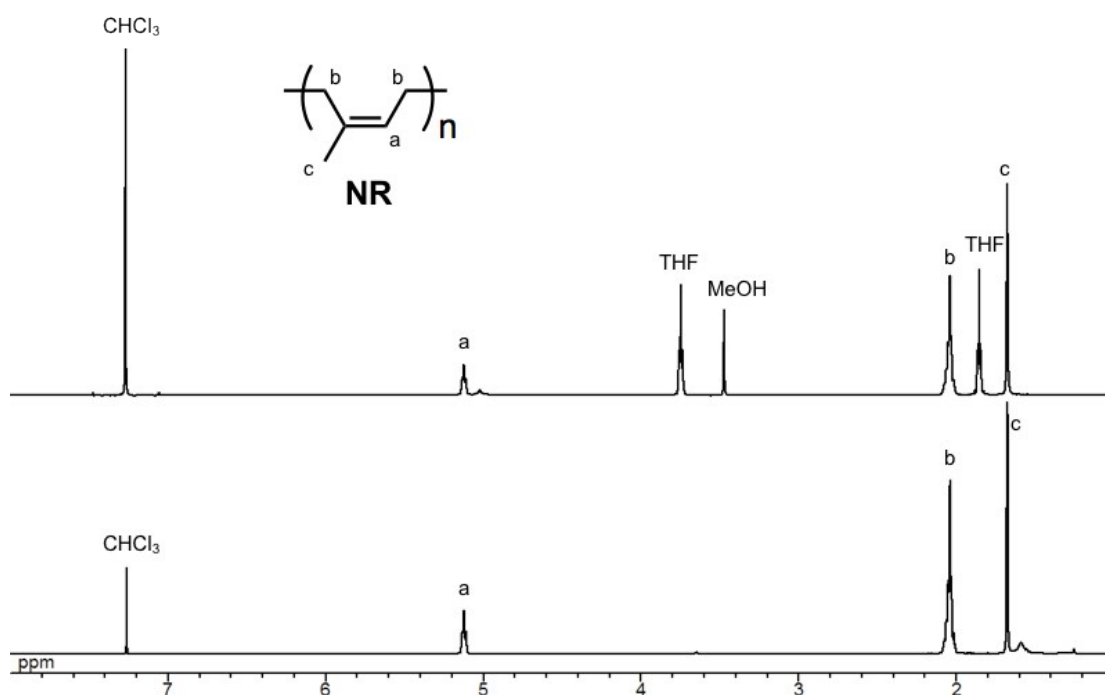
**cNR** (92 mg) was swollen in THF (30 mL). After that, KOH solution (3.0 M in methanol, 10 mL, 30 mmol) and H<sub>2</sub>O (10 mL) were added and the mixture was stirred at 80 °C for 24 h. After the reaction, insoluble part was collected by filtration and immersed in CHCl<sub>3</sub>, resulting in the complete dissolution in the solvent. In addition, CHCl<sub>3</sub> was evaporated *in vacuo* to give decrosslinked-NR in 99% yield (91 mg).

Degradation of **cNR** (entry 10 in Table 1, the use of cross-linker **5**) in the basic condition

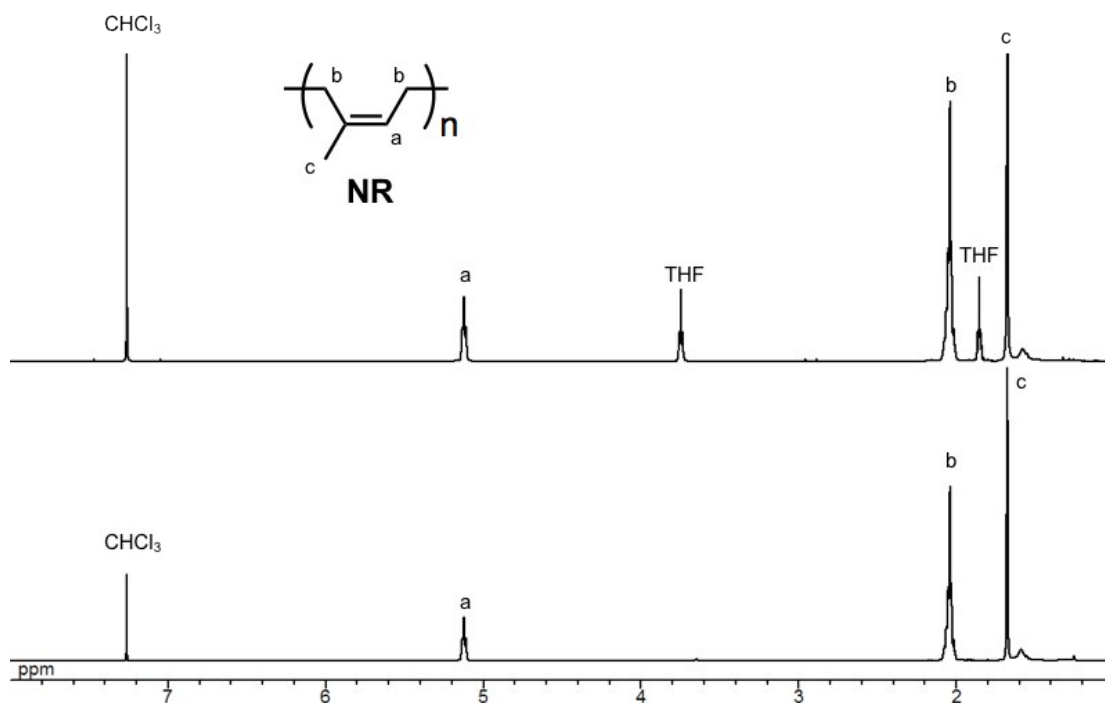
**cNR** (88 mg) was swollen in THF (30 mL). After that, KOH solution (3.0 M in methanol, 10 mL, 30 mmol) and H<sub>2</sub>O (10 mL) were added and the mixture was stirred at 80 °C for 24 h. After the reaction, insoluble part was collected by filtration and immersed in CHCl<sub>3</sub>, resulting in the complete dissolution in the solvent. In addition, CHCl<sub>3</sub> was evaporated *in vacuo* decrosslinked-NR in 96% yield (85 mg).

Degradation of **cNR** (entry 6 in Table 1, the use of cross-linker **4**) in the acidic condition

**cNR4** (99 mg) was swollen in THF (30 mL). After that, HCl aq. (3.0 M, 10 mL, 30 mmol) and methanol (10 mL) were added and the mixture was stirred at 80 °C for 24 h. After the reaction, insoluble part was collected by filtration and immersed in CHCl<sub>3</sub>.



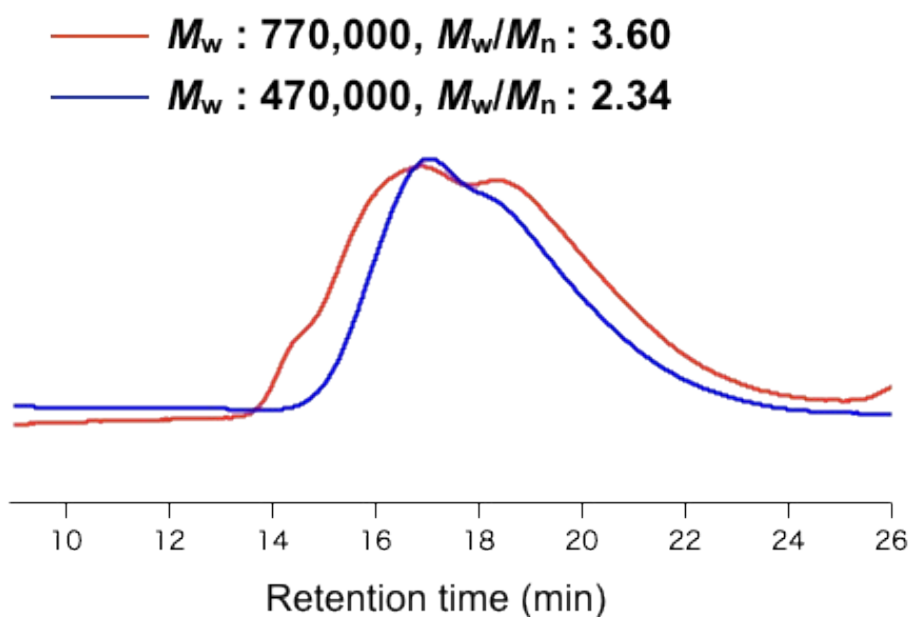
**Figure S2.**  $^1\text{H}$  NMR spectra of  $\text{CHCl}_3$ -soluble part after decrosslinking reaction of **cNR** obtained by the use of ditopic nitrile *N*-oxide **3** with ester linkage (above) and virgin NR (bottom) (500 MHz, 298 K,  $\text{CDCl}_3$ )



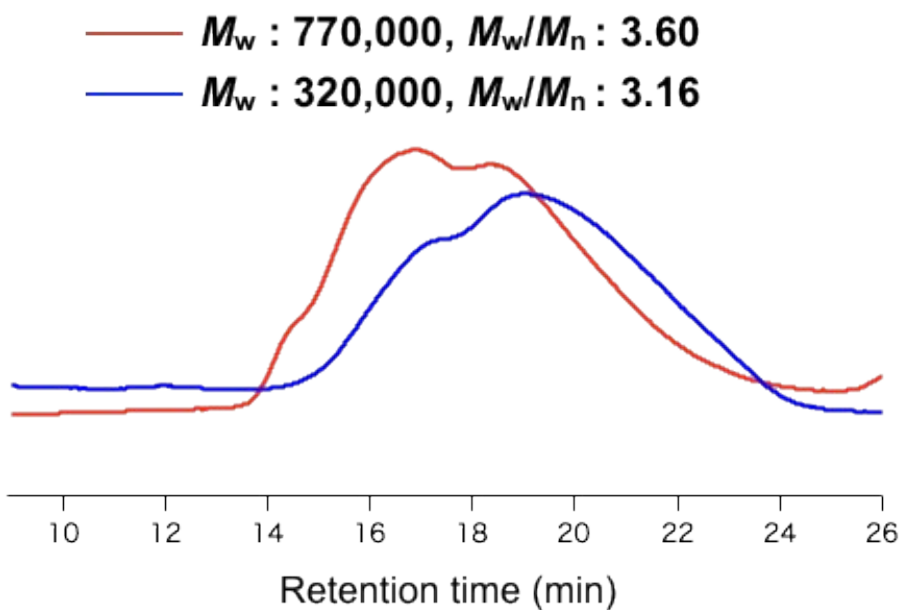
**Figure S3.**  $^1\text{H}$  NMR spectra of  $\text{CHCl}_3$ -soluble part after decrosslinking reaction of **cNR** obtained by the use of tritopic nitrile *N*-oxide **5** with ester linkage (above) and virgin NR (bottom) (500 MHz, 298 K,  $\text{CDCl}_3$ )







**Figure S4.** SEC profiles of virgin NR (red) and  $\text{CHCl}_3$ -soluble part after decrosslinking reaction of cNR obtained by the use of ditopic nitrile *N*-oxide **3** with ester linkage (blue) (Eluent:  $\text{CHCl}_3$ , detected by RI, PSt standard)



**Figure S5.** SEC profiles of virgin NR (red) and  $\text{CHCl}_3$ -soluble part after decrosslinking reaction of cNR obtained by the use of tritopic nitrile *N*-oxide **5** with ester linkage (blue) (Eluent:  $\text{CHCl}_3$ , detected by RI, PSt standard)

## 2. NMR and FT-IR spectra

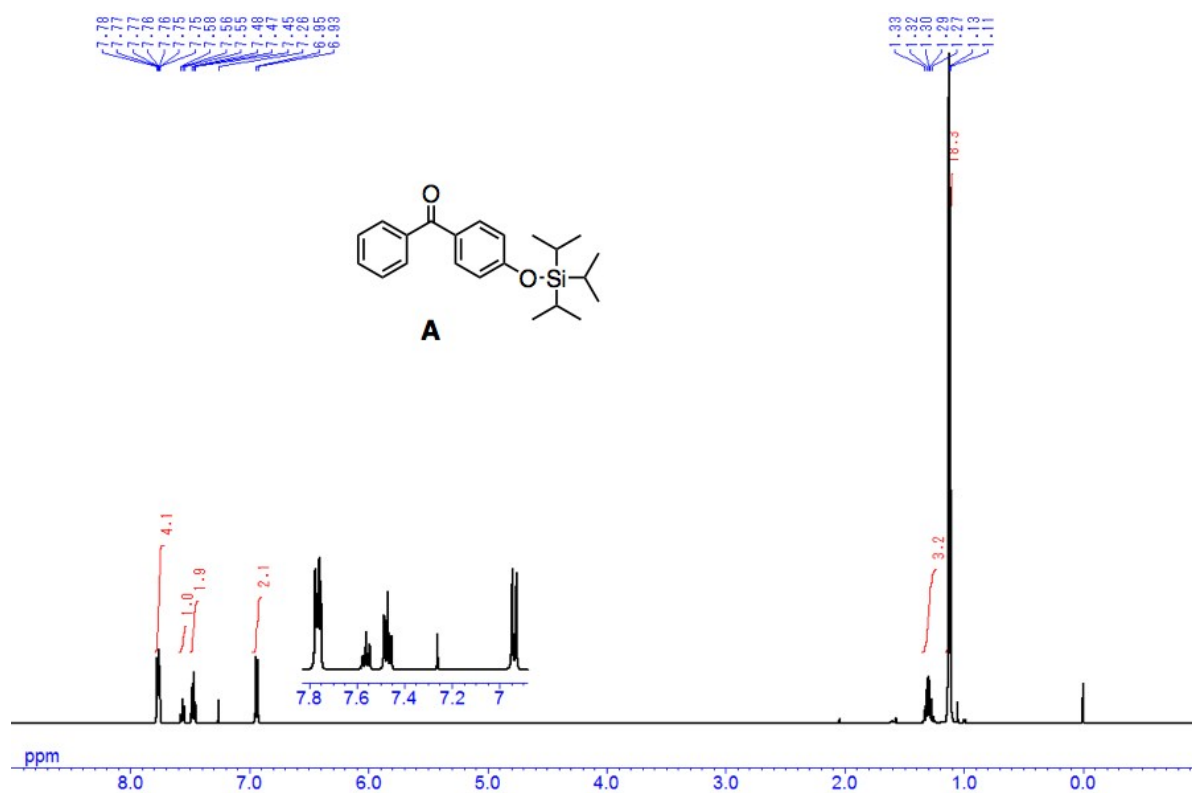


Figure S6.  $^1\text{H}$  NMR spectrum of A (500 MHz, 298 K,  $\text{CDCl}_3$ )

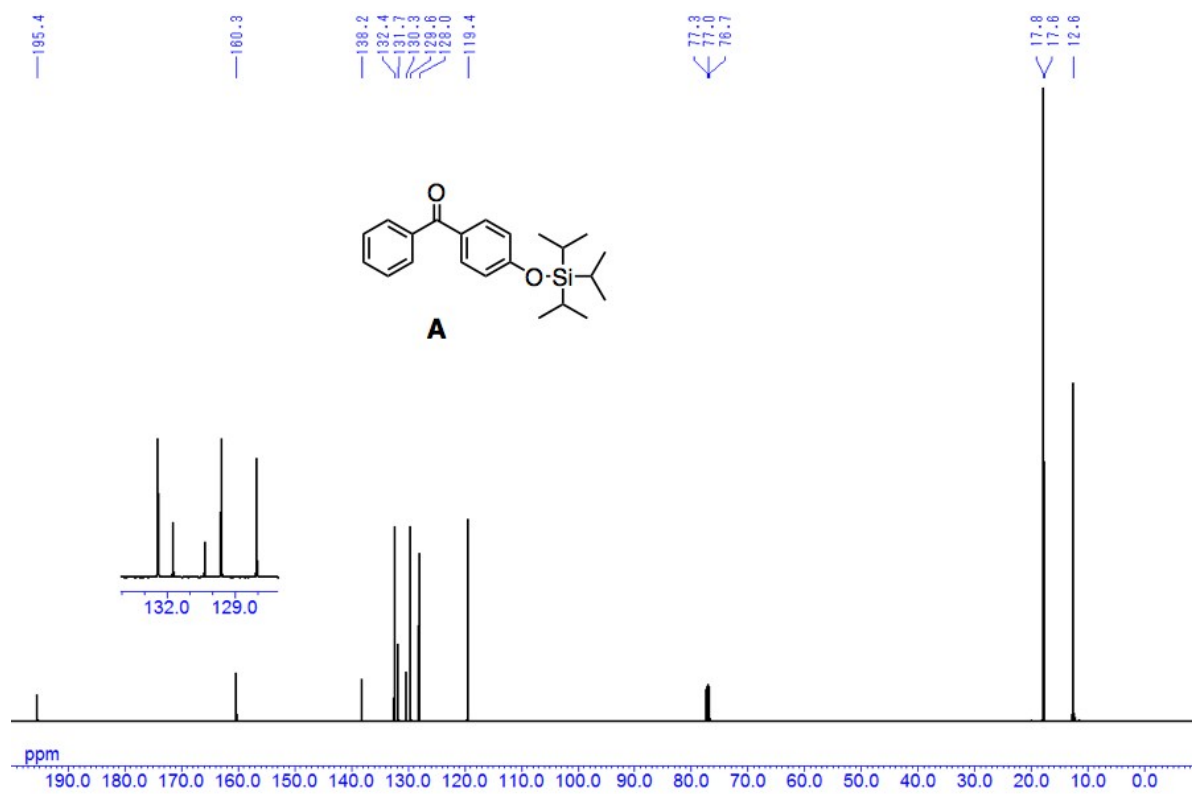
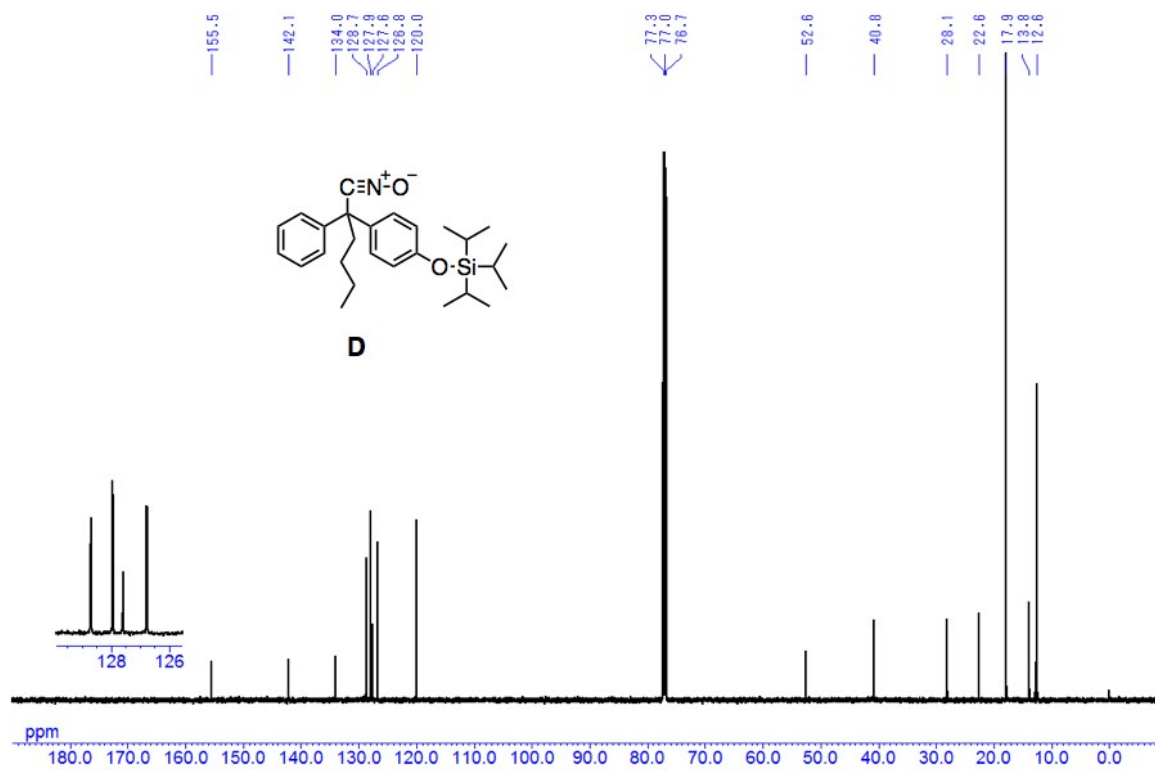
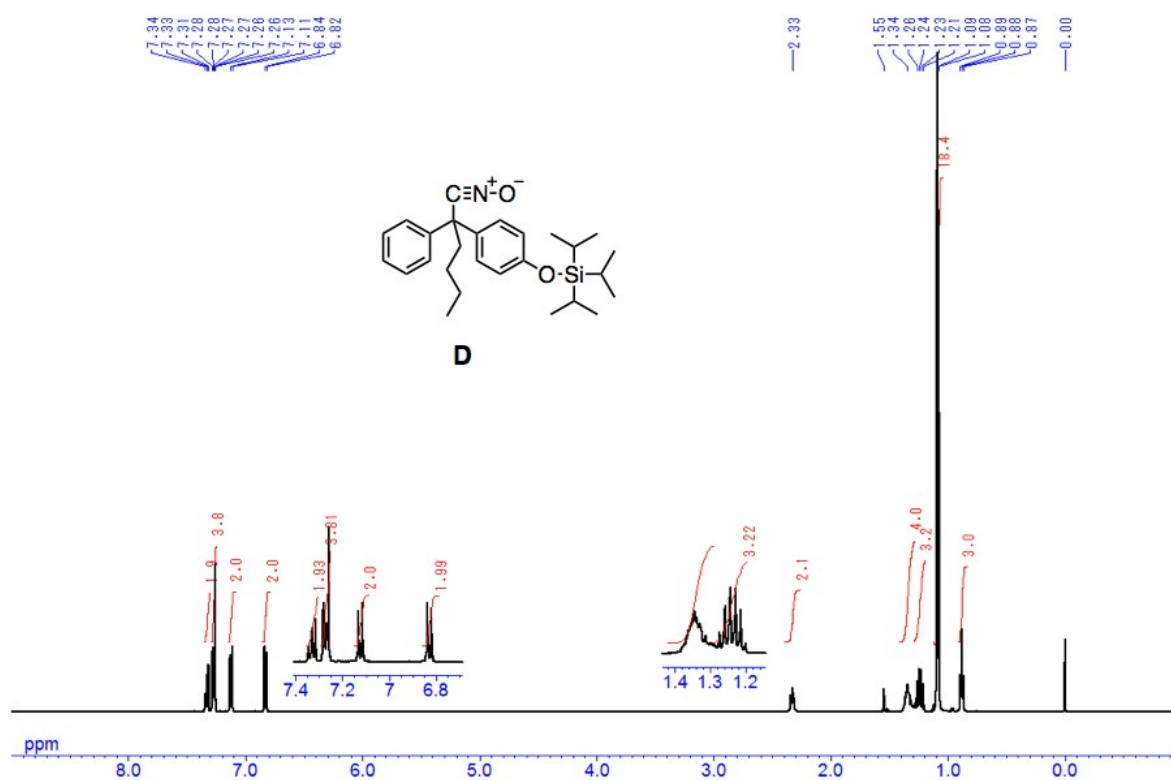
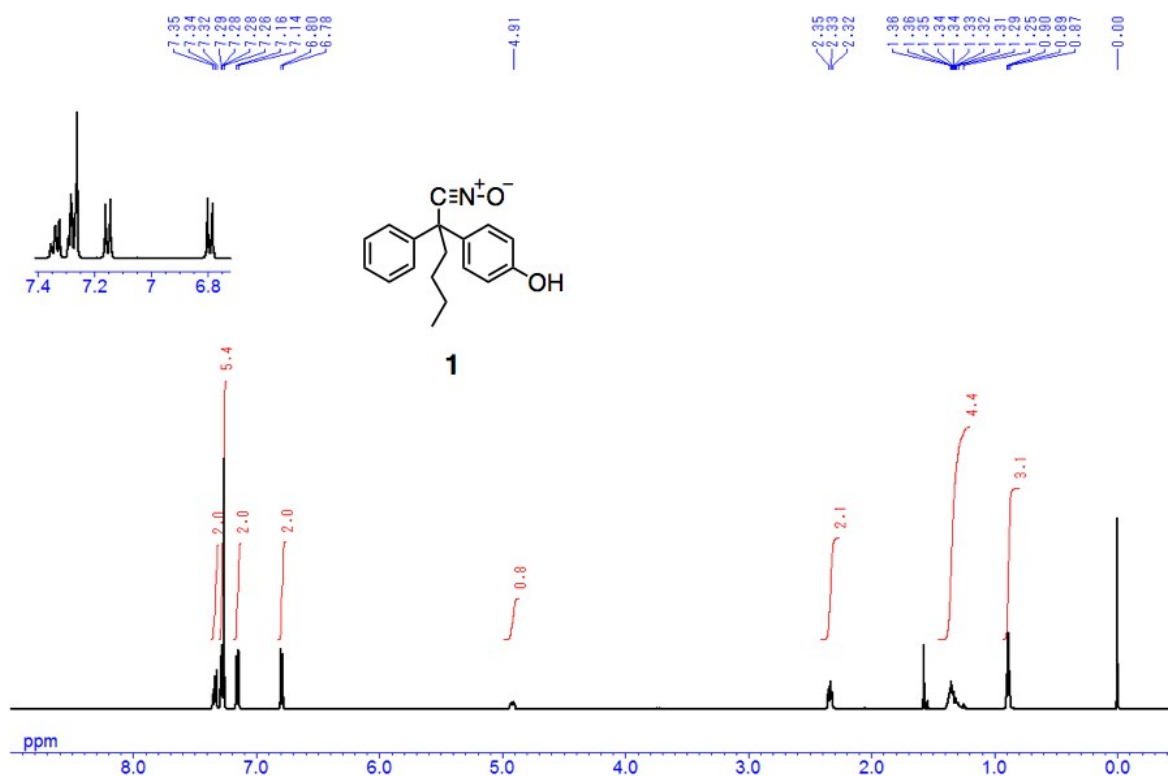
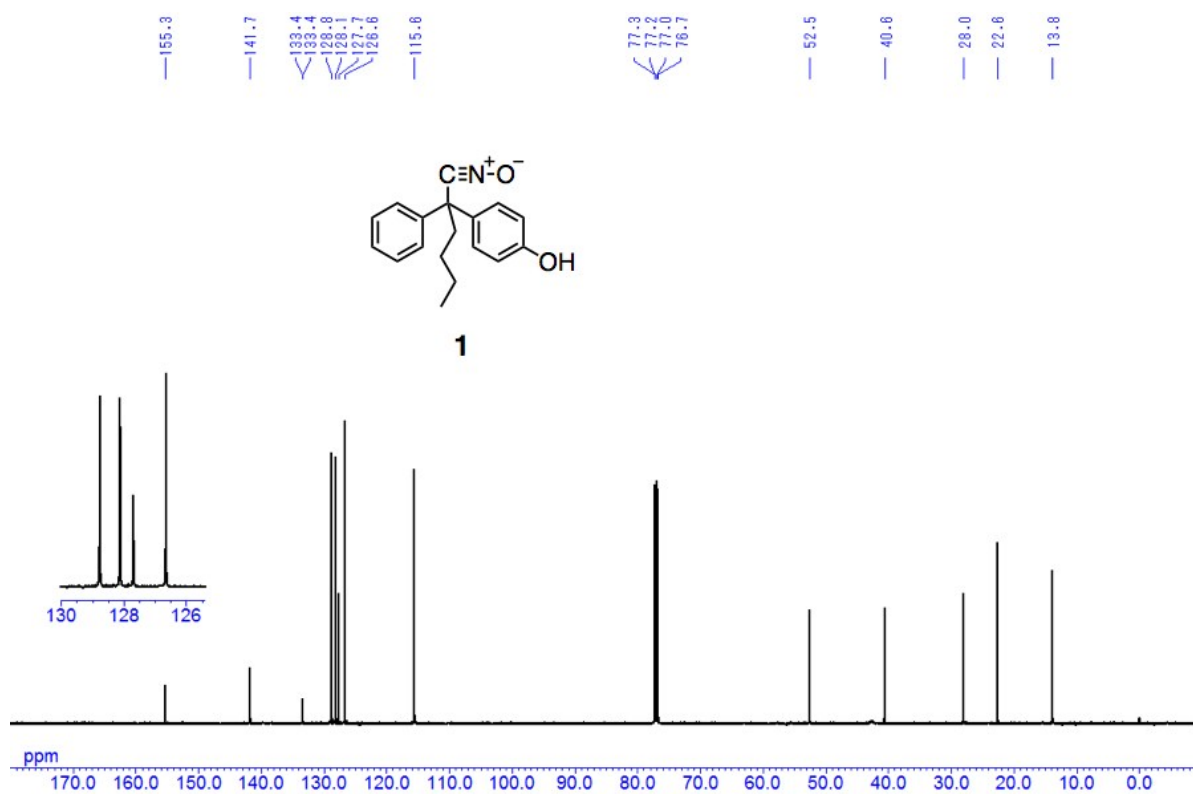


Figure S7.  $^{13}\text{C}$  NMR spectrum of A (125 MHz, 298 K,  $\text{CDCl}_3$ )

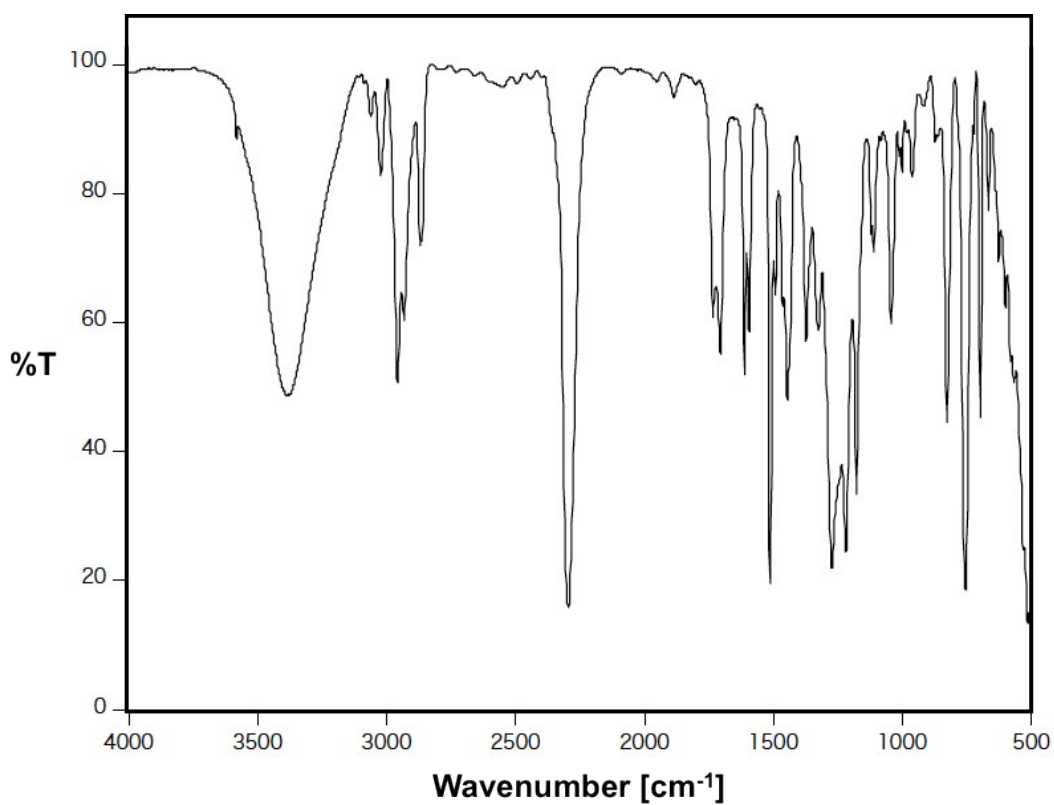




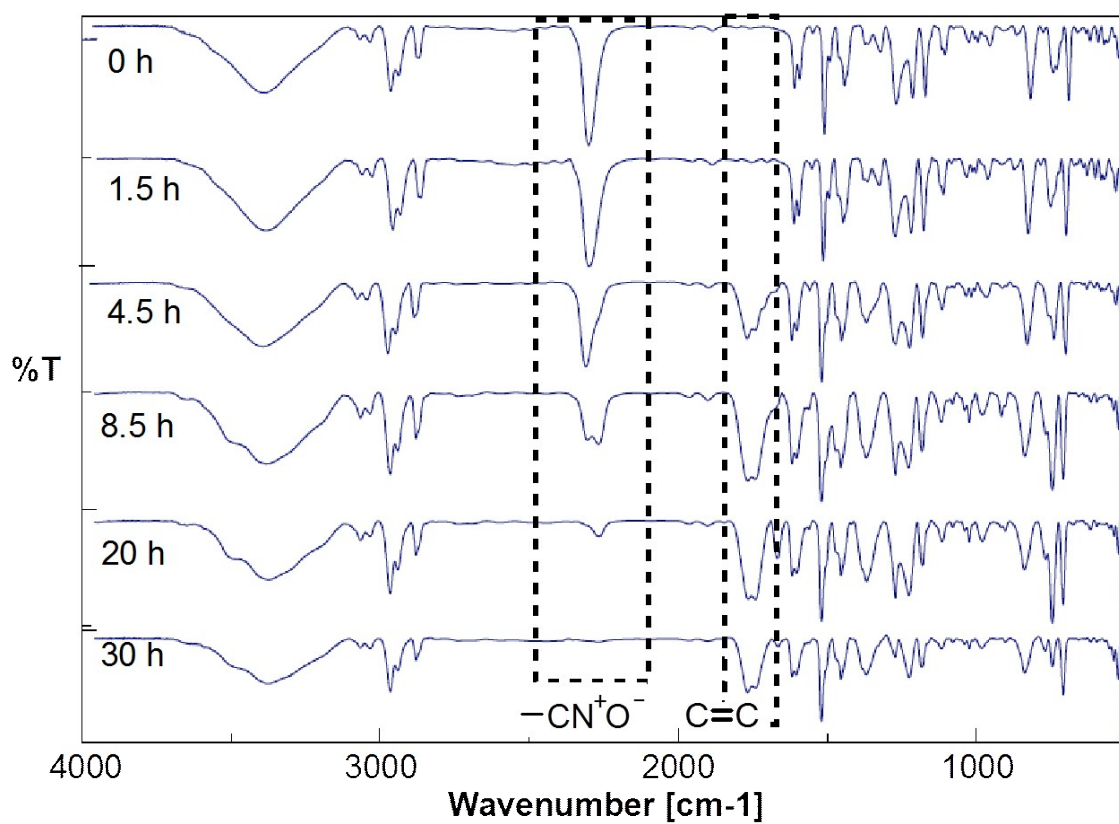
**Figure S10.** <sup>1</sup>H NMR spectrum of **1** (500 MHz, 298 K, CDCl<sub>3</sub>)



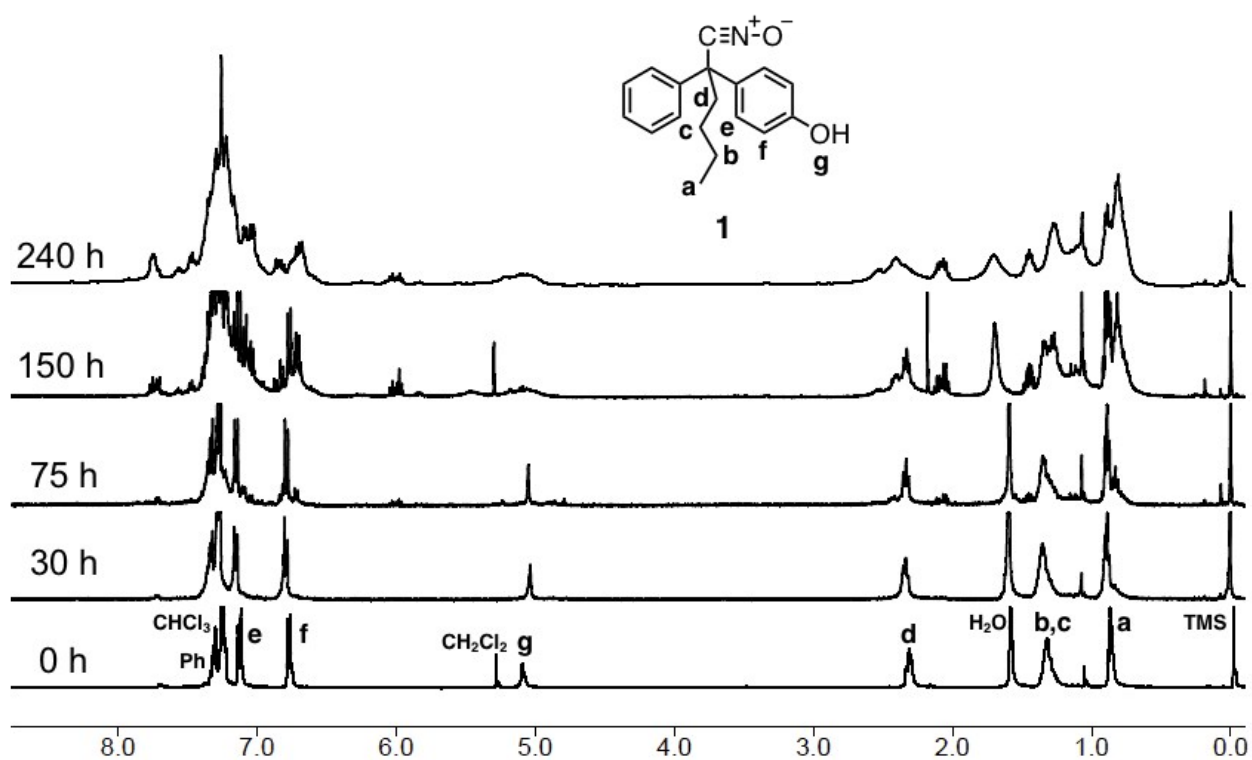
**Figure S11.** <sup>13</sup>C NMR spectrum of **1** (125 MHz, 298 K, CDCl<sub>3</sub>)



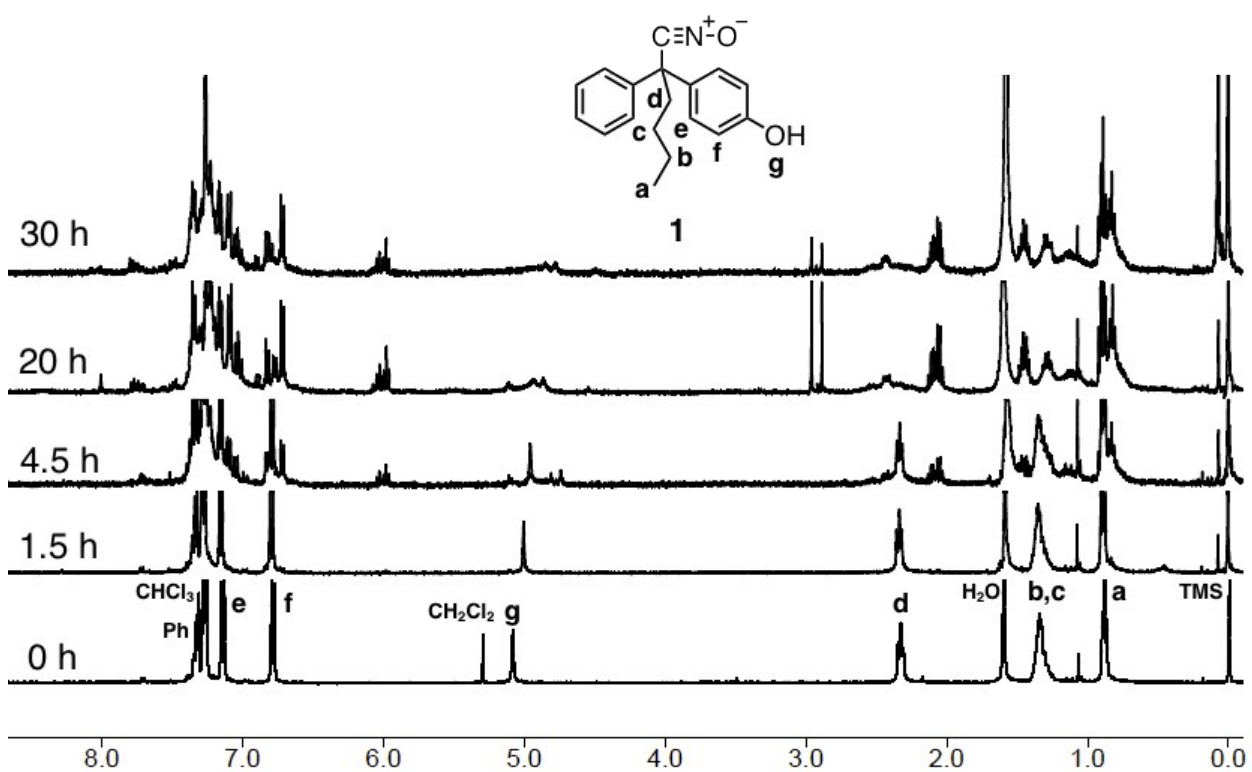
**Figure S12.** FT-IR spectrum of **1** (NaCl)



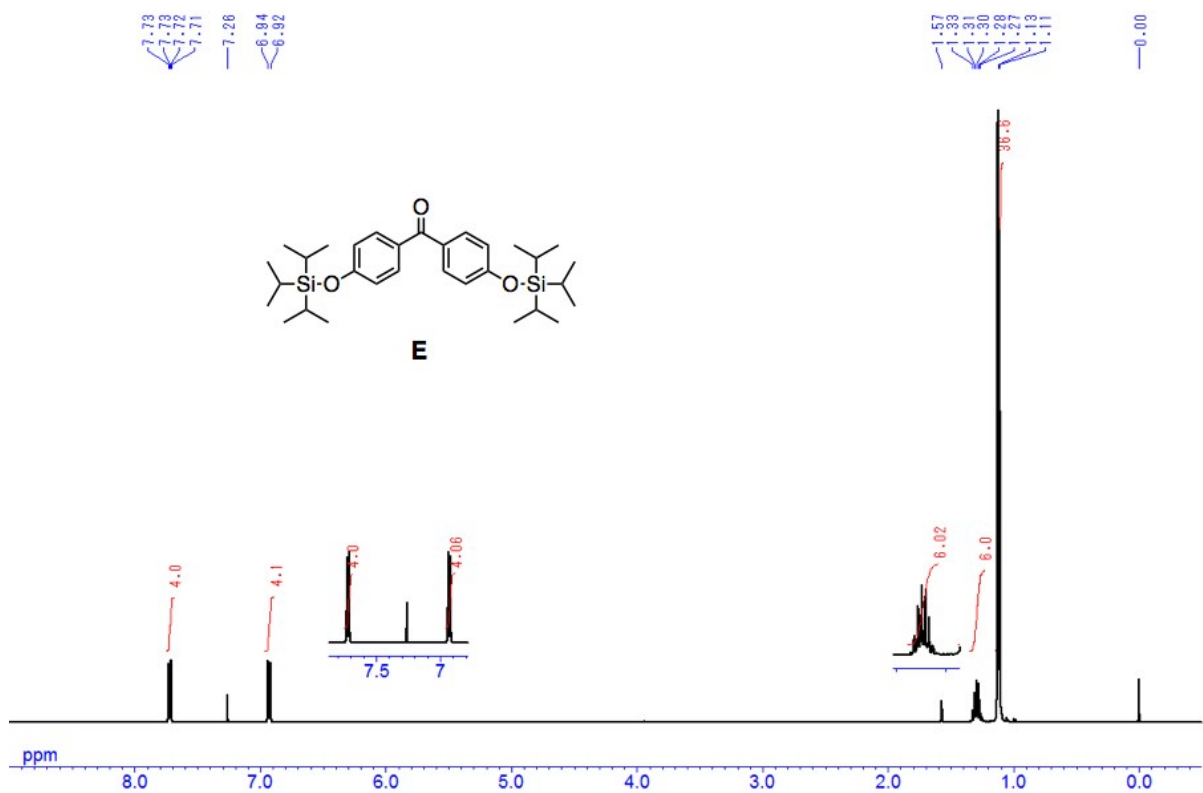
**Figure S13.** Time-dependent IR spectra of nitrile *N*-oxide **1** at 100 °C (NaCl)



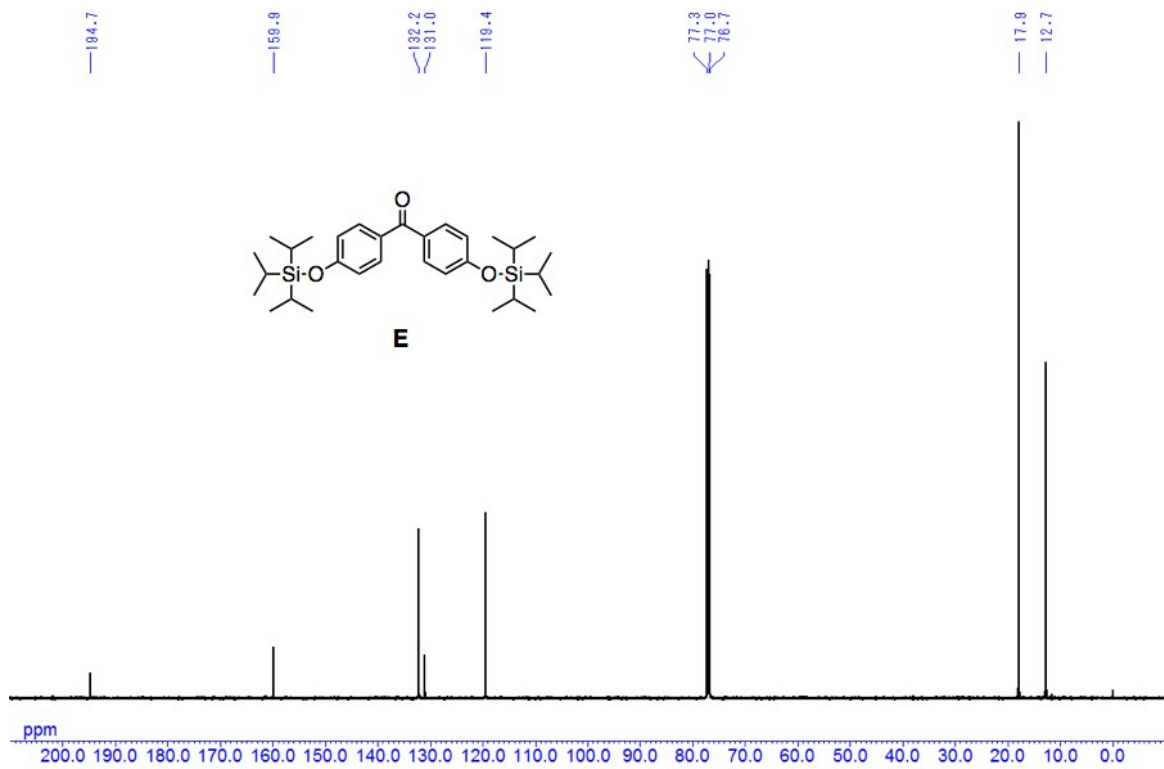
**Figure S14.** Time-dependent  $^1\text{H}$  NMR spectra of **1** at 60 °C (400 MHz, 298 K,  $\text{CDCl}_3$ )



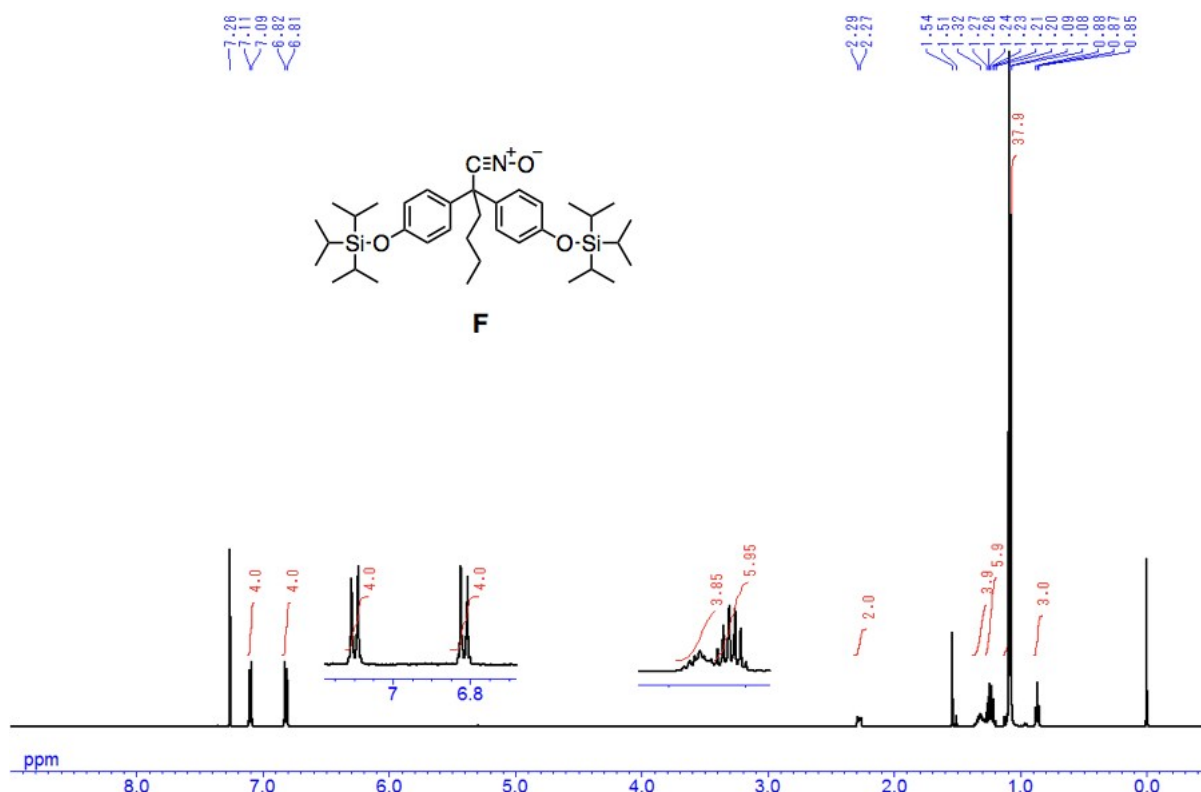
**Figure S15.** Time-dependent  $^1\text{H}$  NMR spectra of **1** at 100 °C (400 MHz, 298 K,  $\text{CDCl}_3$ )



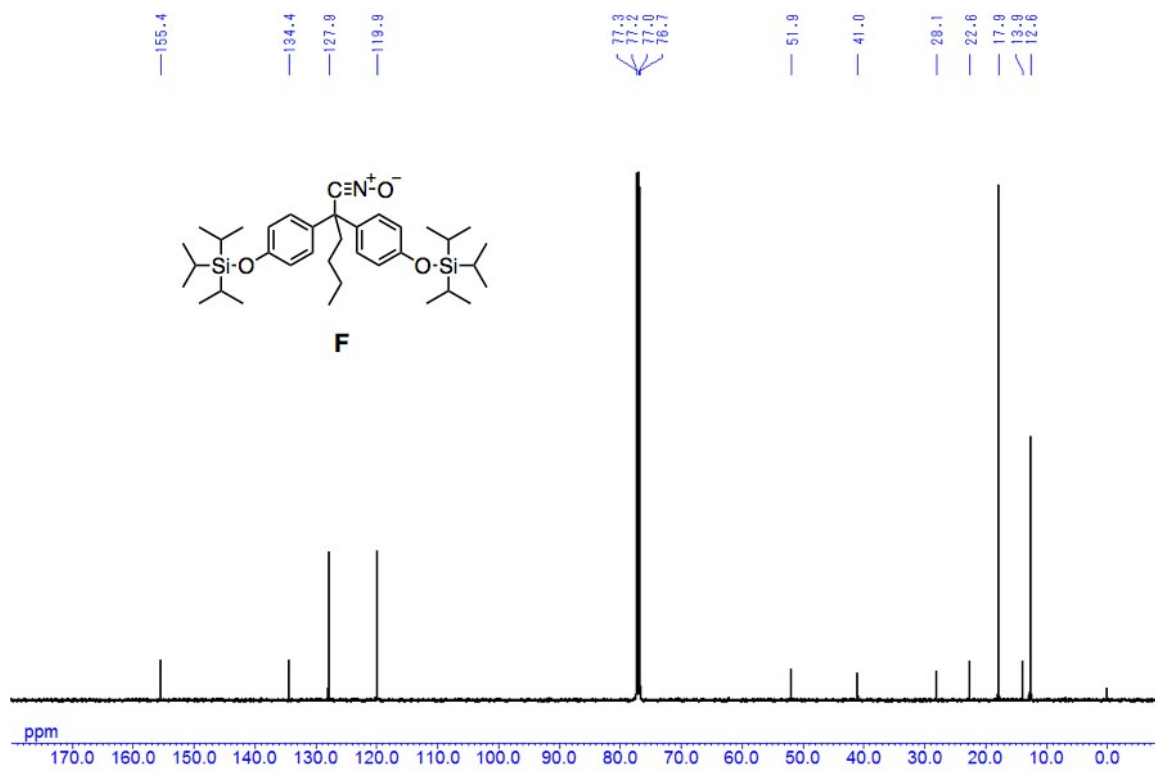
**Figure S16.**  $^1\text{H}$  NMR spectrum of **E** (500 MHz, 298 K,  $\text{CDCl}_3$ )



**Figure S17.**  $^{13}\text{C}$  NMR spectrum of **E** (125 MHz, 298 K,  $\text{CDCl}_3$ )

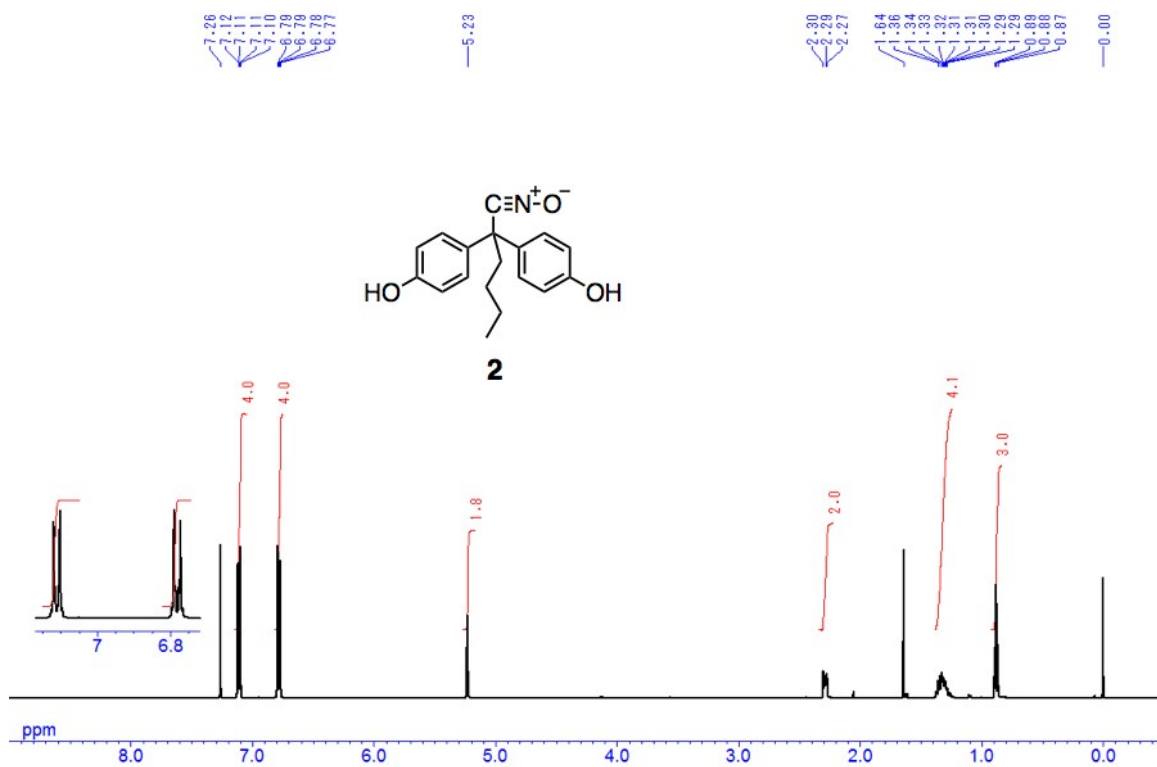


**Figure S18.** <sup>1</sup>H NMR spectrum of **F** (500 MHz, 298 K, CDCl<sub>3</sub>)

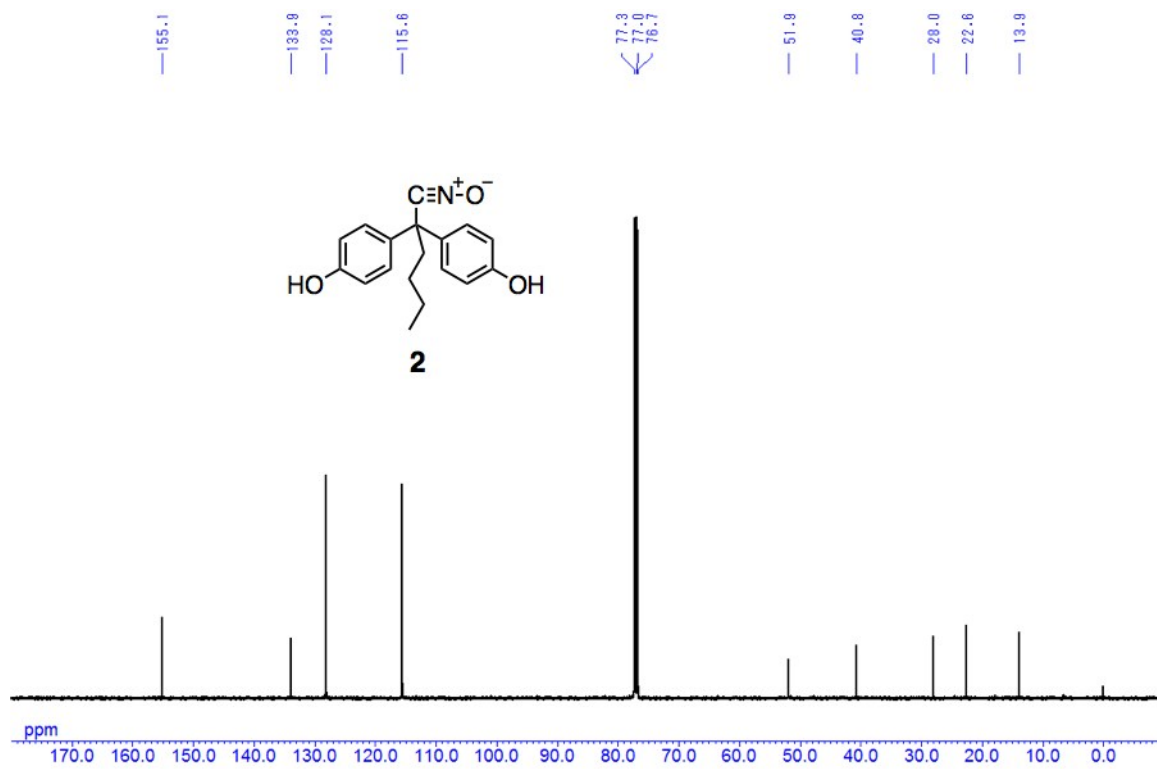


**Figure S19.** <sup>13</sup>C NMR spectrum of **F** (125 MHz, 298 K, CDCl<sub>3</sub>)





**Figure S20.** <sup>1</sup>H NMR spectrum of **2** (500 MHz, 298 K, CDCl<sub>3</sub>)



**Figure S21.** <sup>13</sup>C NMR spectrum of **2** (125 MHz, 298 K, CDCl<sub>3</sub>).

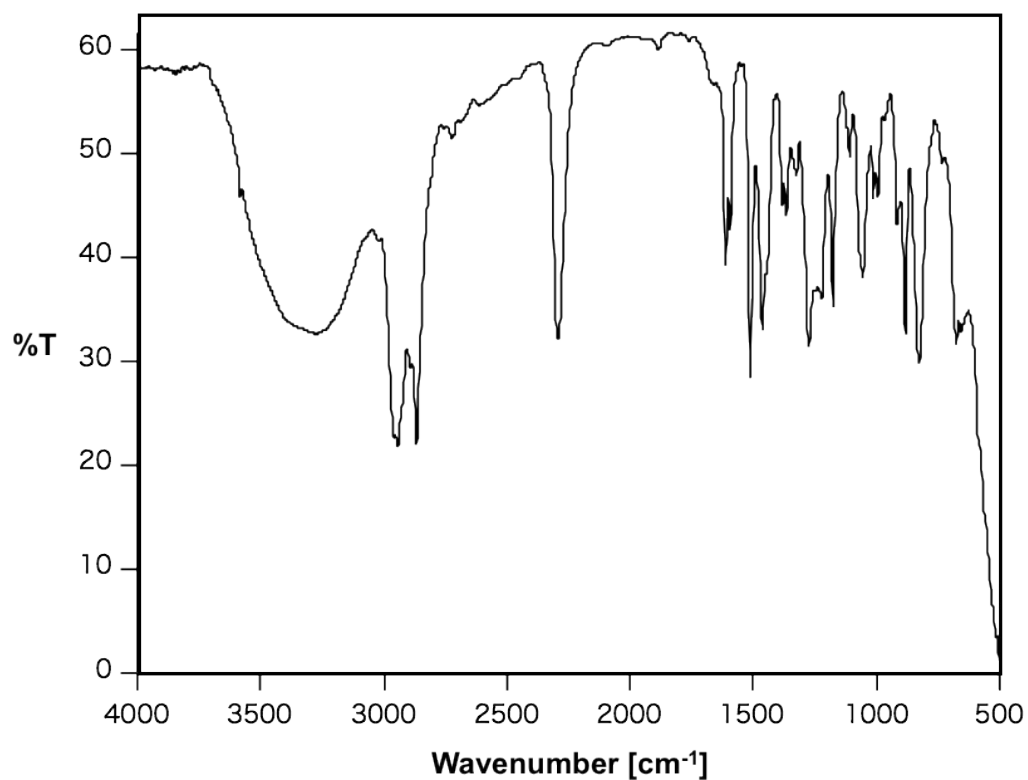


Figure S22. FT-IR spectrum of **2** (NaCl).

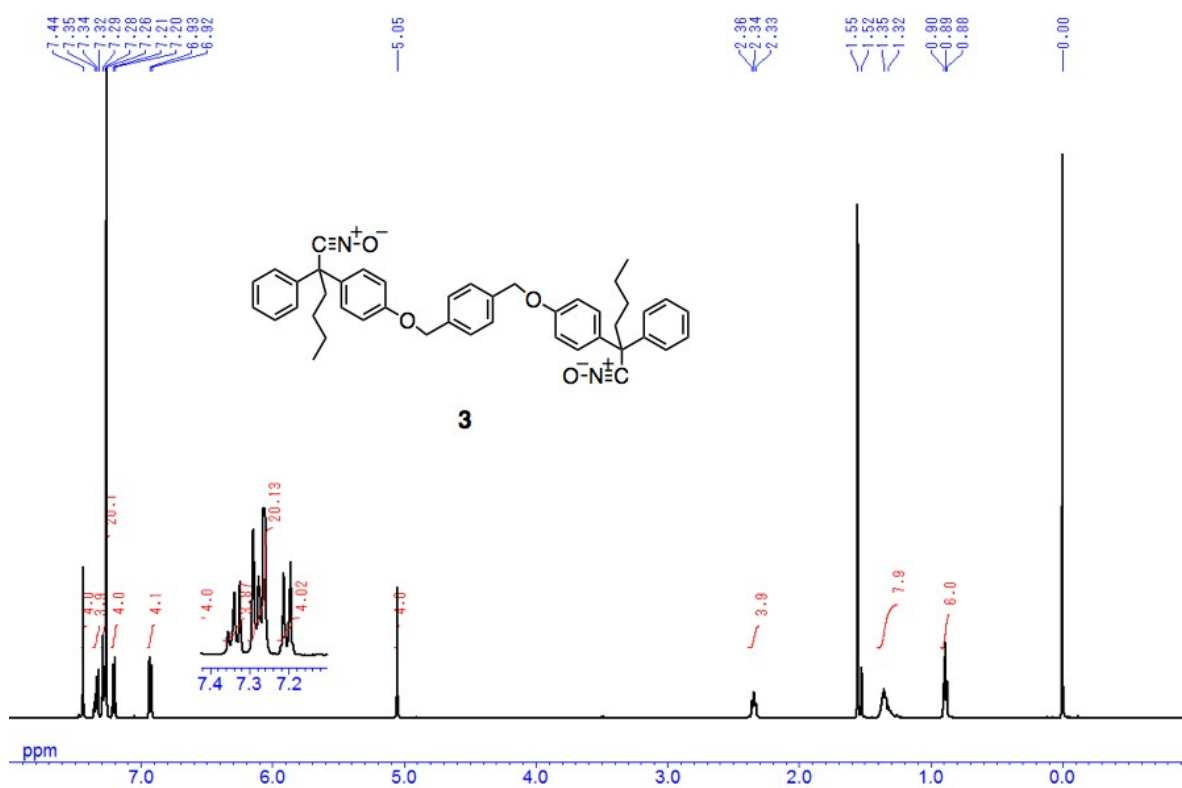
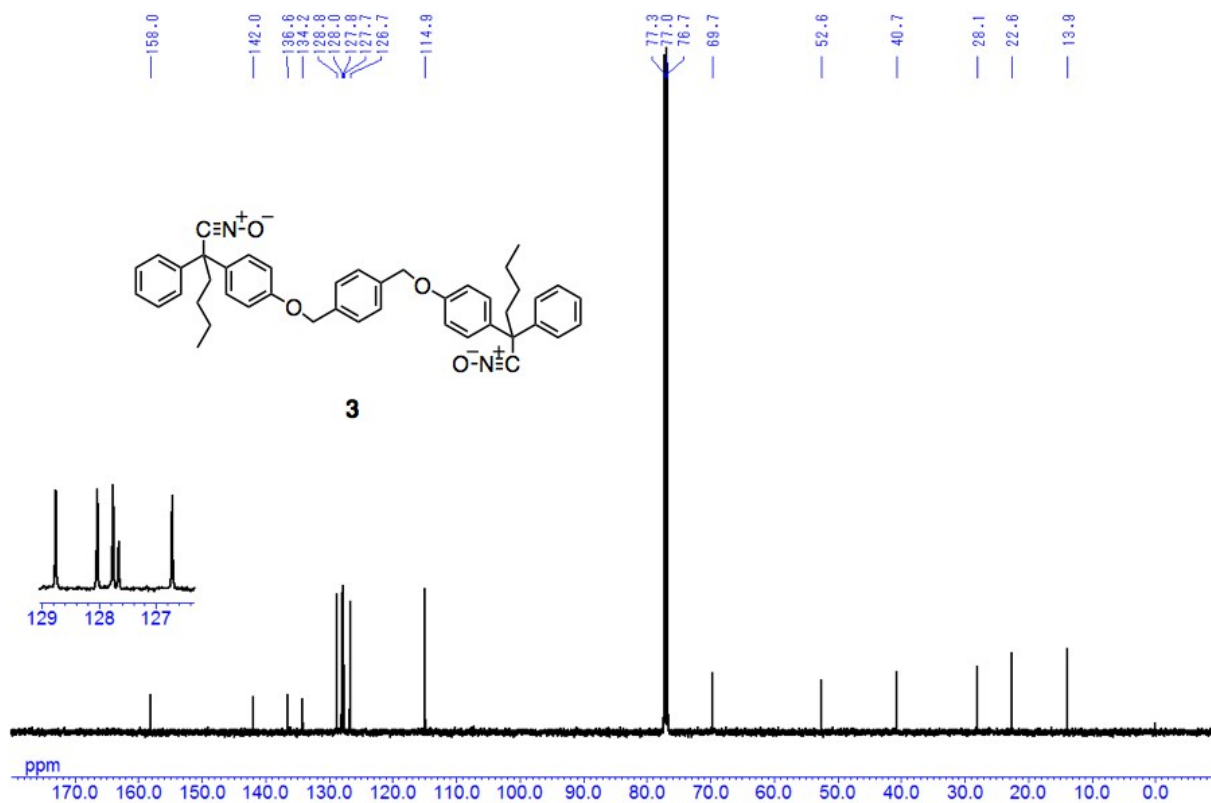
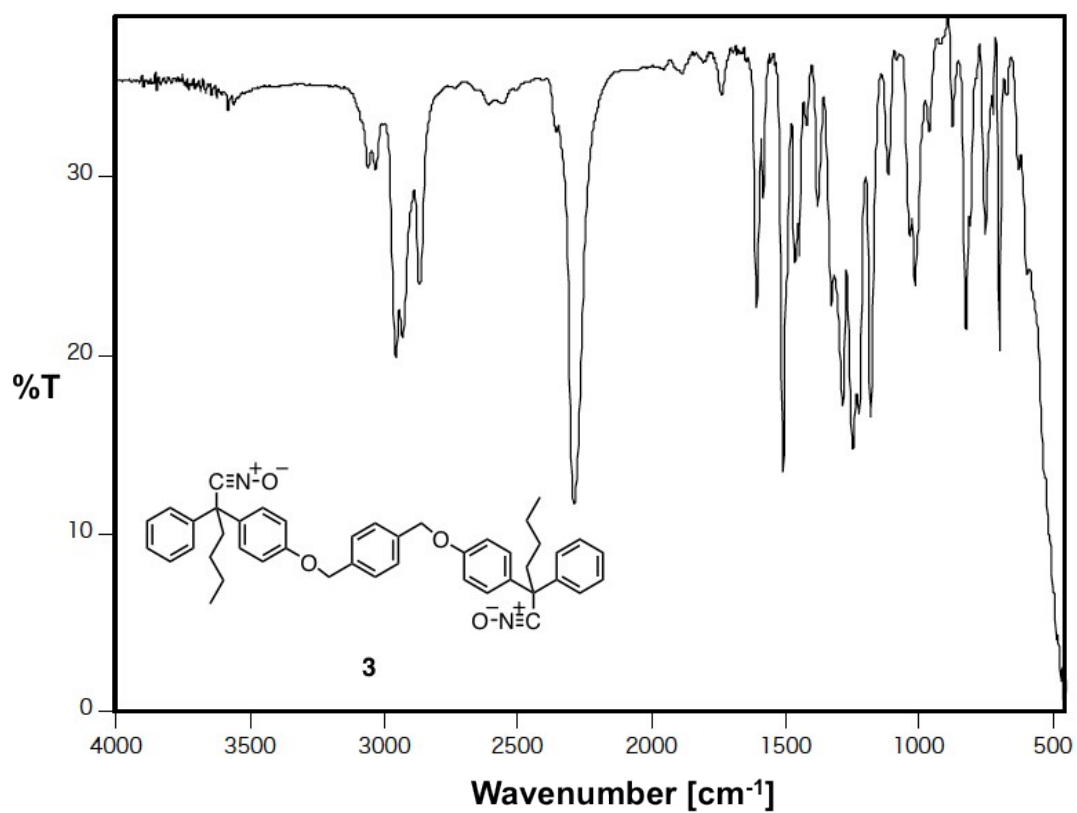


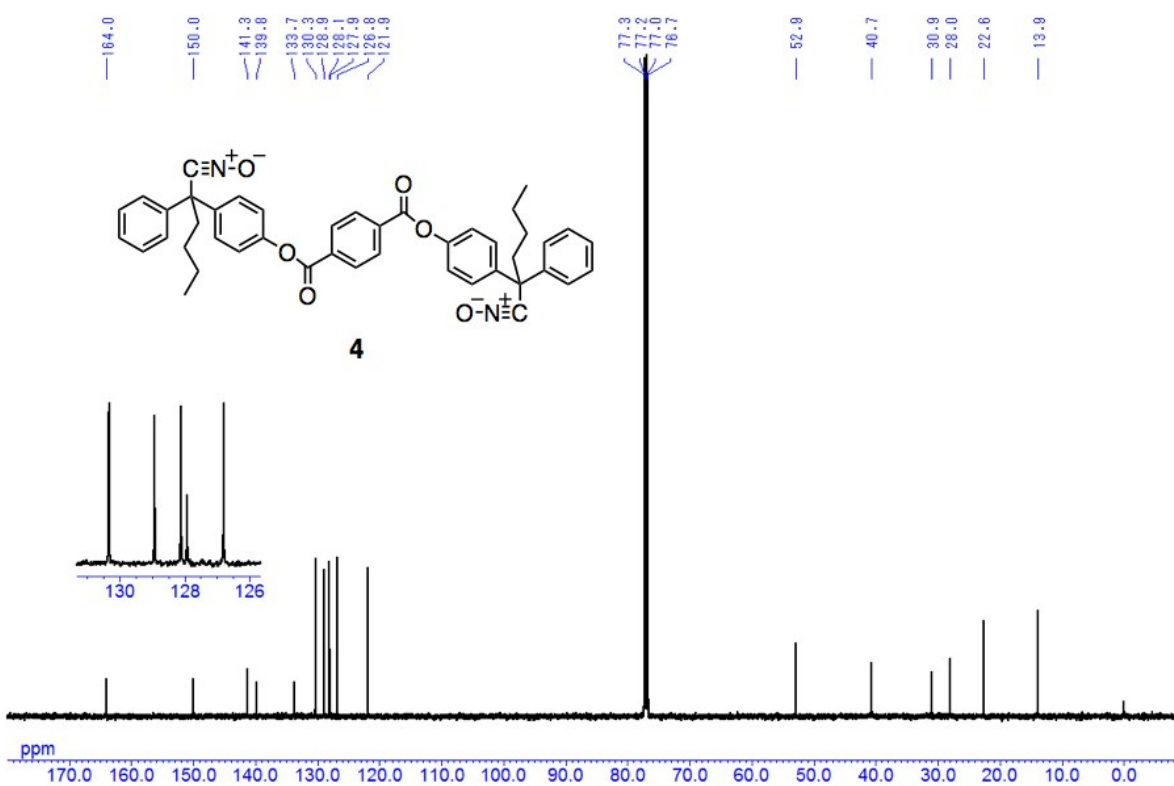
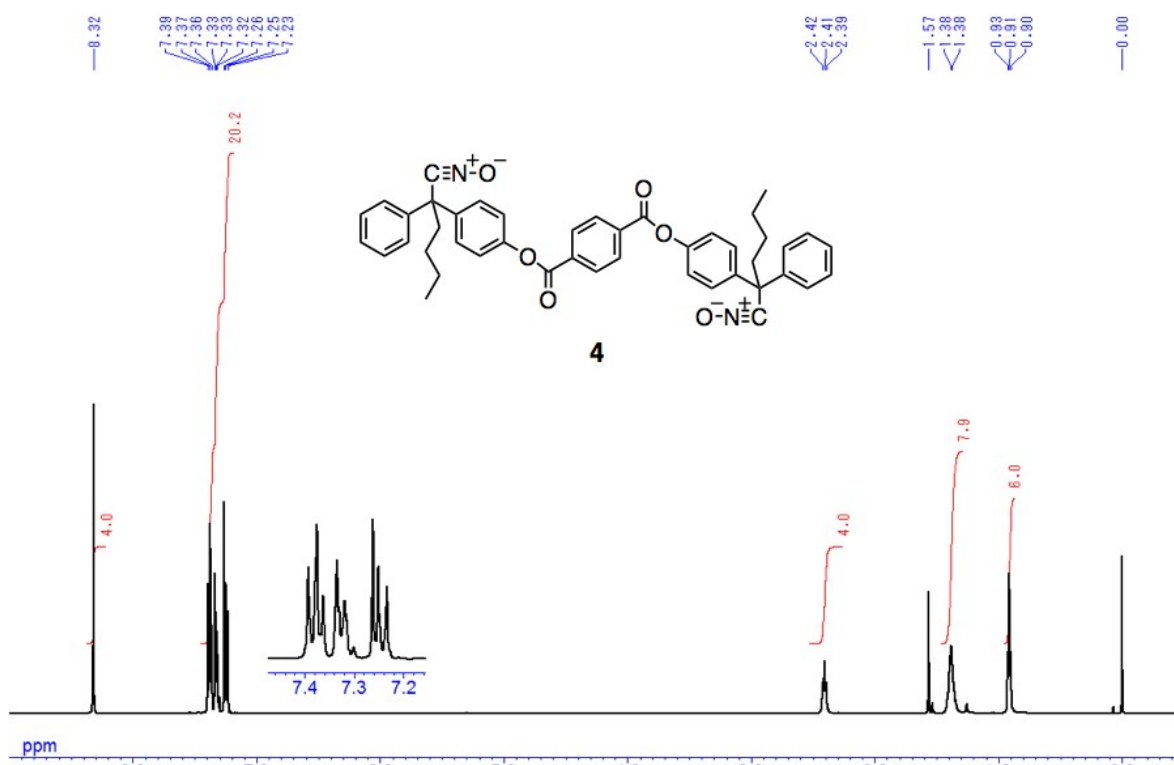
Figure S23.  $^1\text{H}$  NMR spectrum of **3** (500 MHz, 298 K,  $\text{CDCl}_3$ )



**Figure S24.** <sup>13</sup>C NMR spectrum of **3** (125 MHz, 298 K, CDCl<sub>3</sub>)



**Figure S25.** FT-IR spectrum of **3** (NaCl)



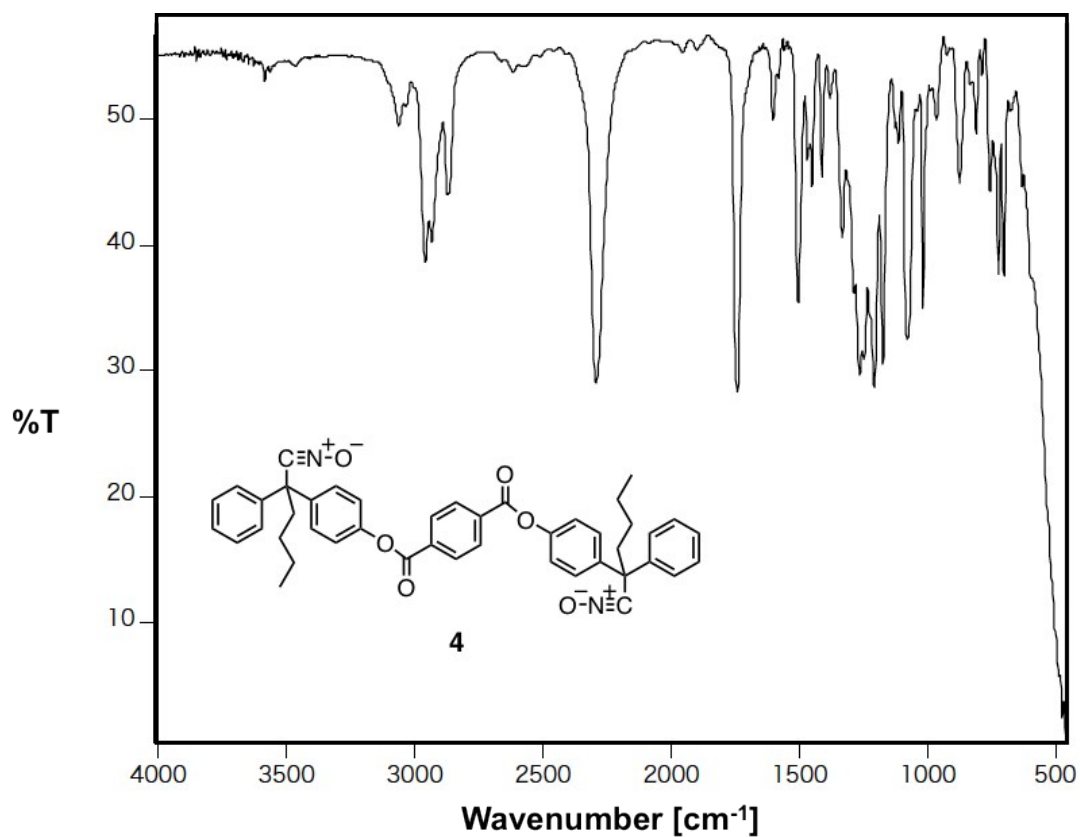


Figure S28. FT-IR spectrum of **4** (NaCl).

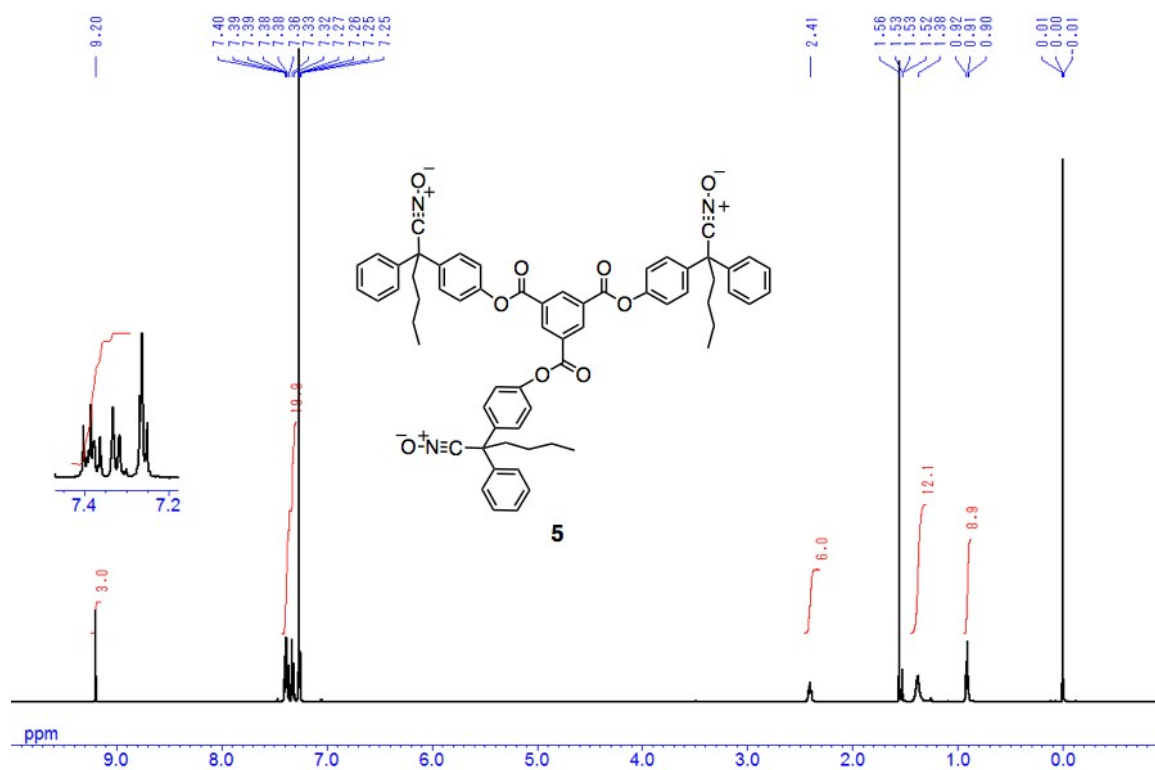
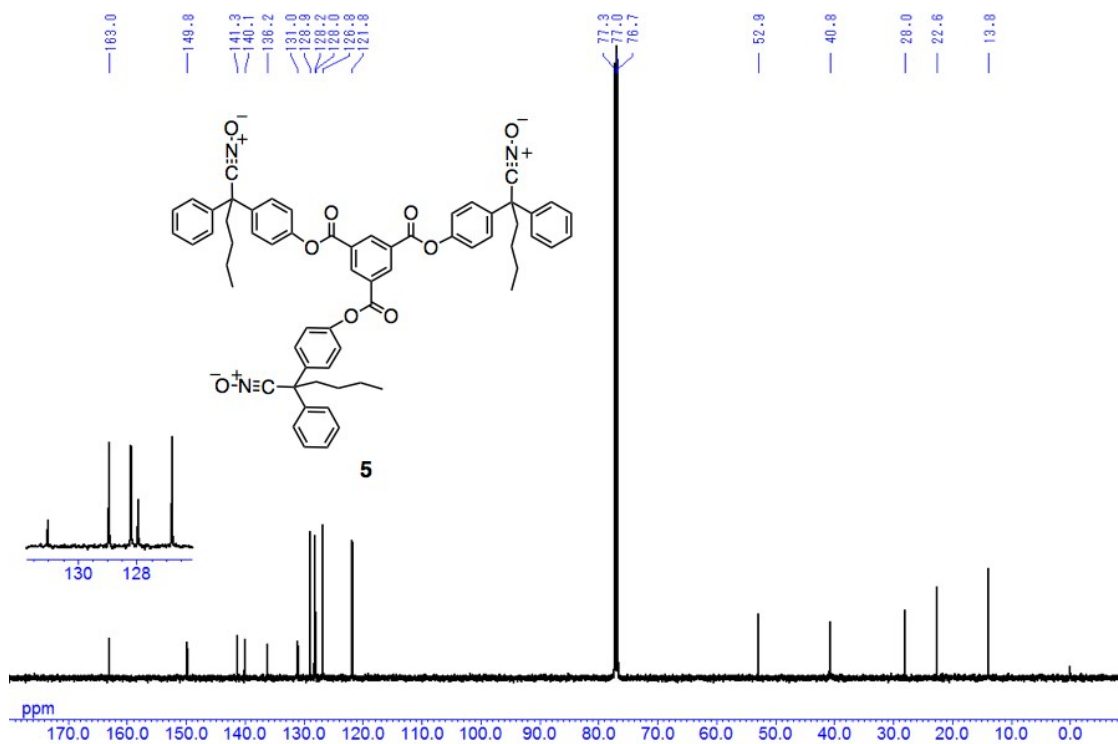
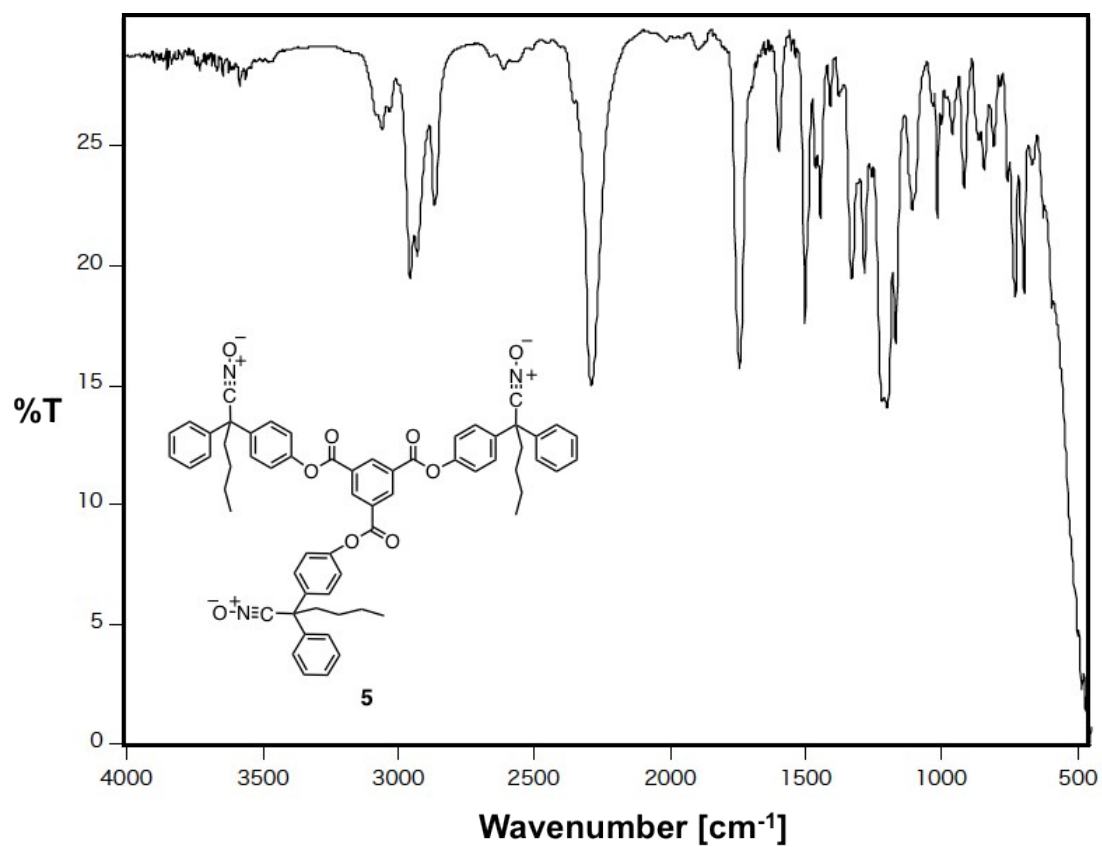


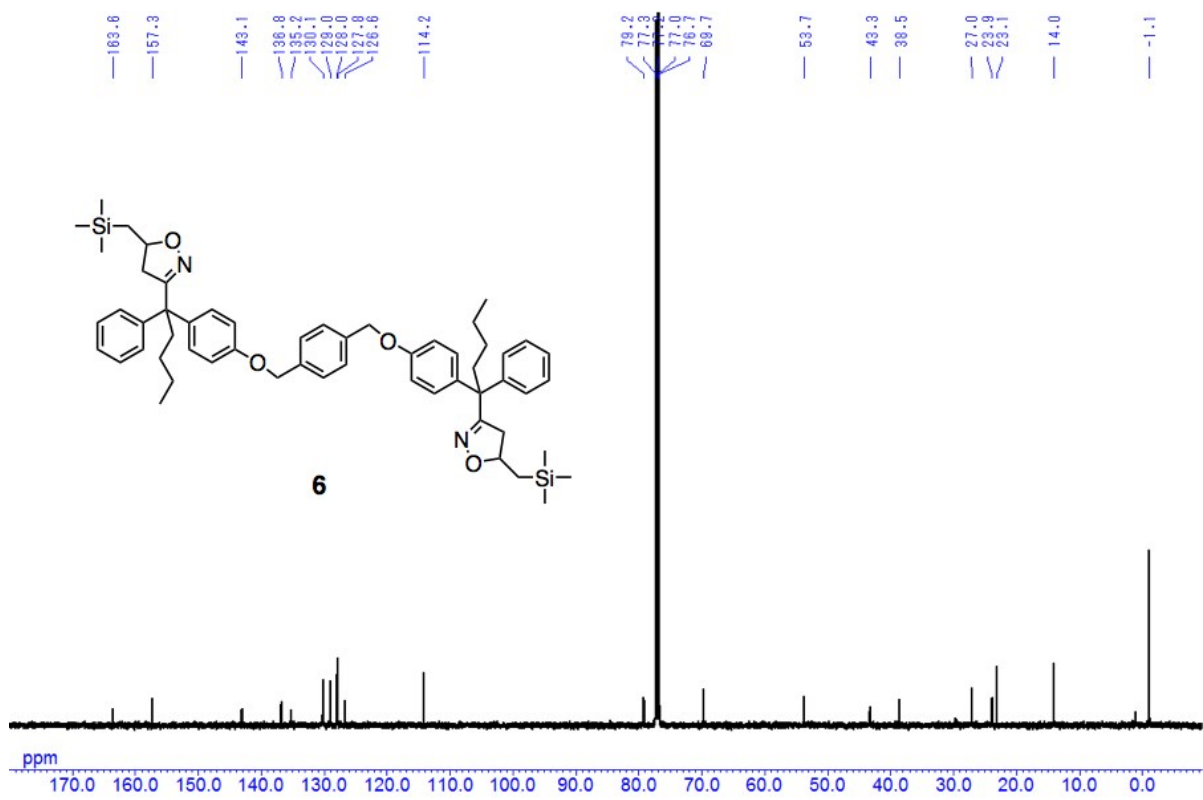
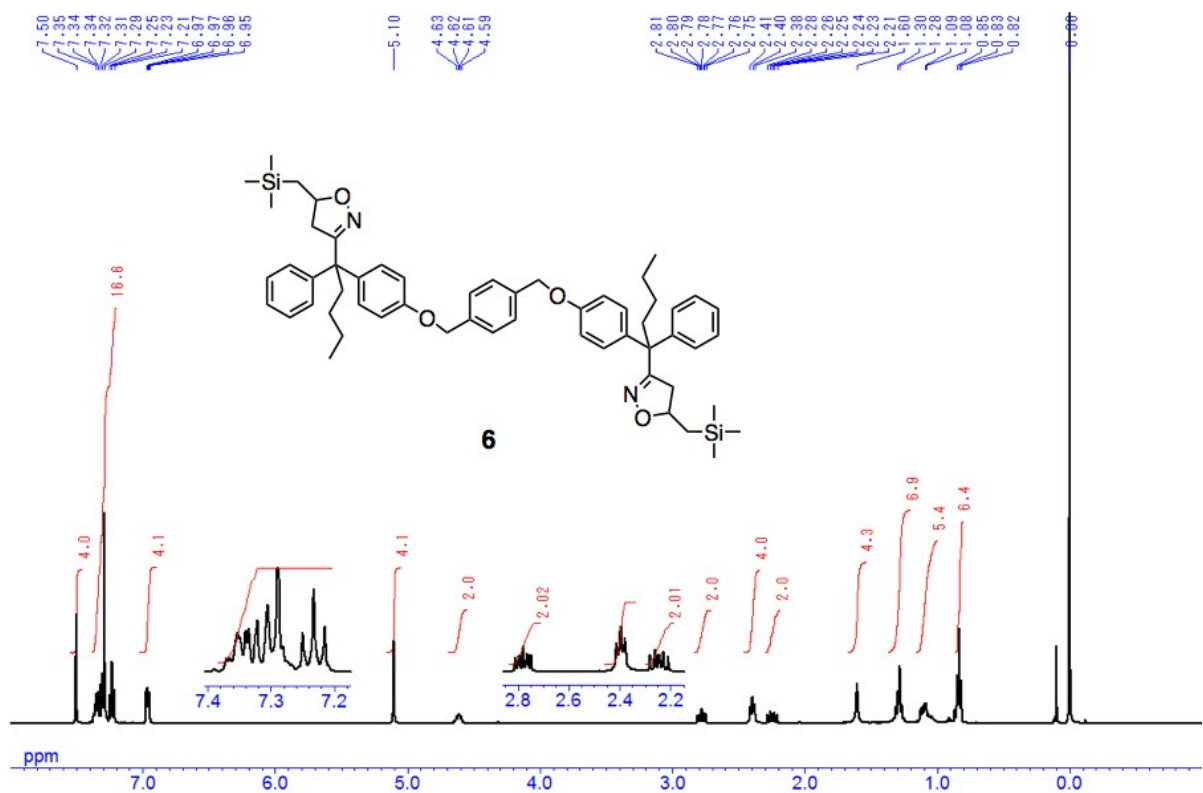
Figure S29. <sup>1</sup>H NMR spectrum of **5** (500 MHz, 298 K, CDCl<sub>3</sub>)



**Figure S30.**  $^{13}\text{C}$  NMR spectrum of **5** (125 MHz, 298 K,  $\text{CDCl}_3$ )



**Figure S31.** FT-IR spectrum of **5** (NaCl)



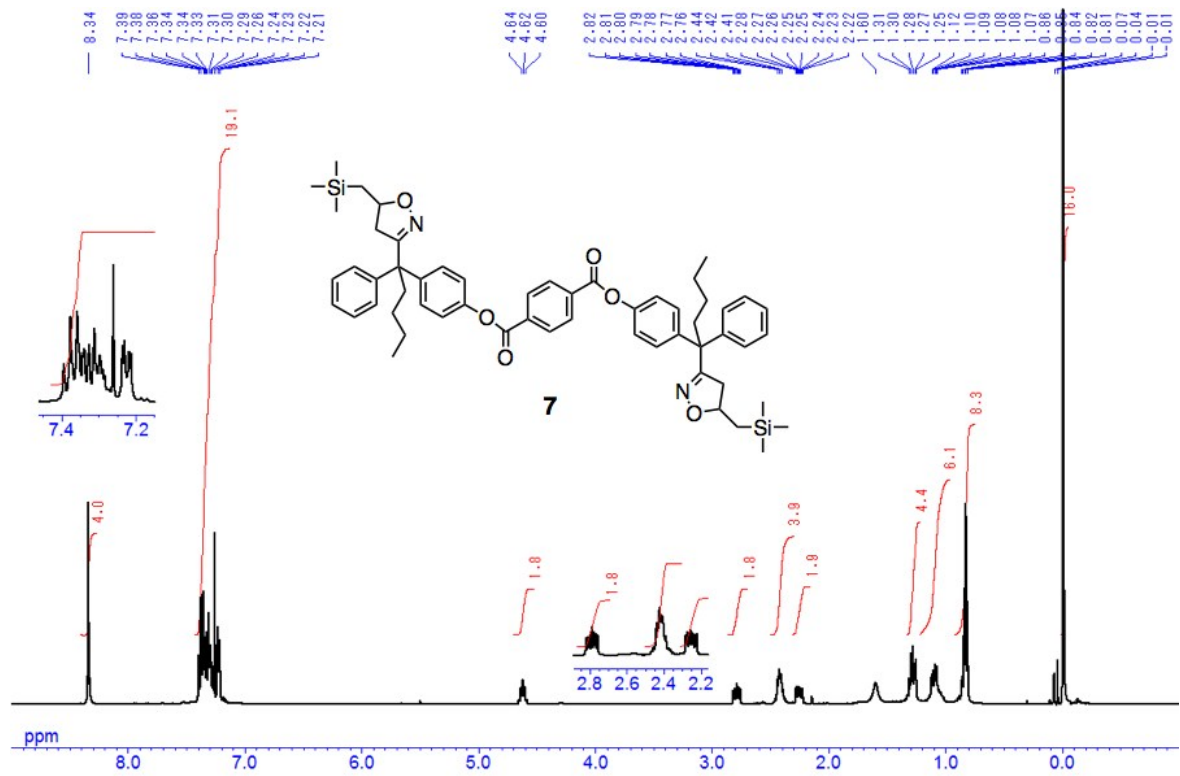


Figure S34.  $^1\text{H}$  NMR spectrum of **7** (500 MHz, 298 K,  $\text{CDCl}_3$ )

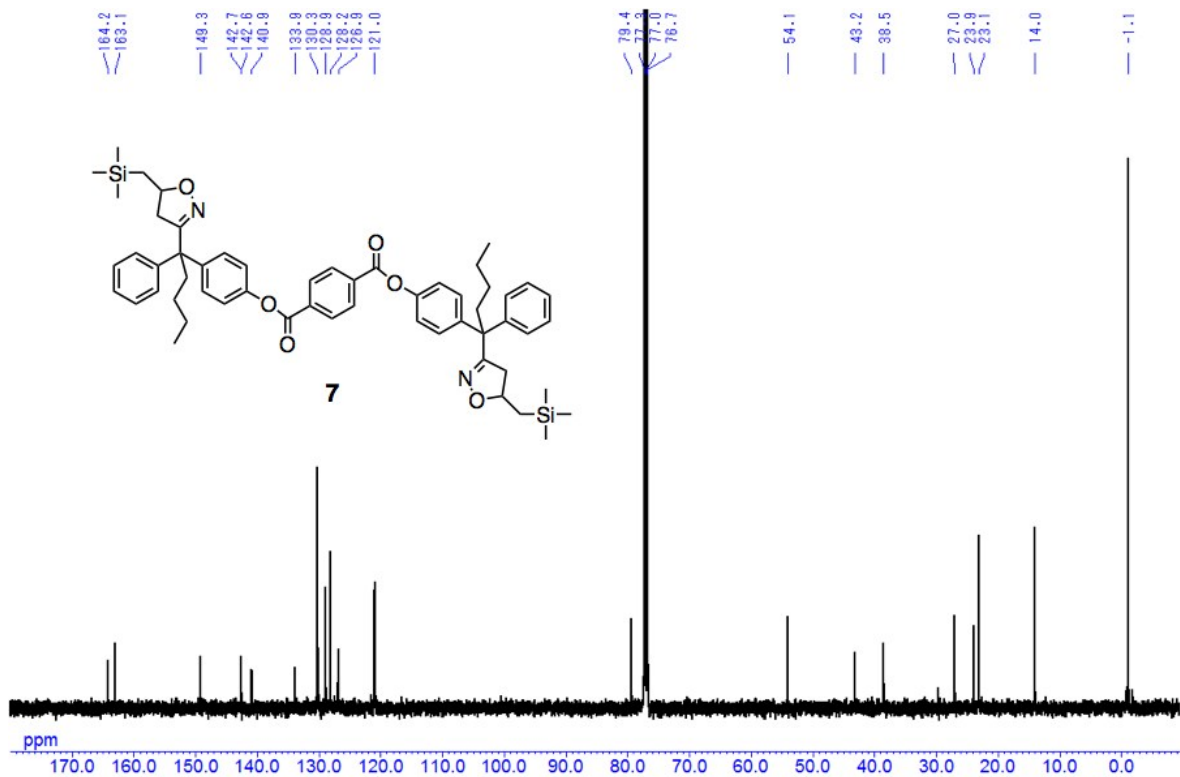
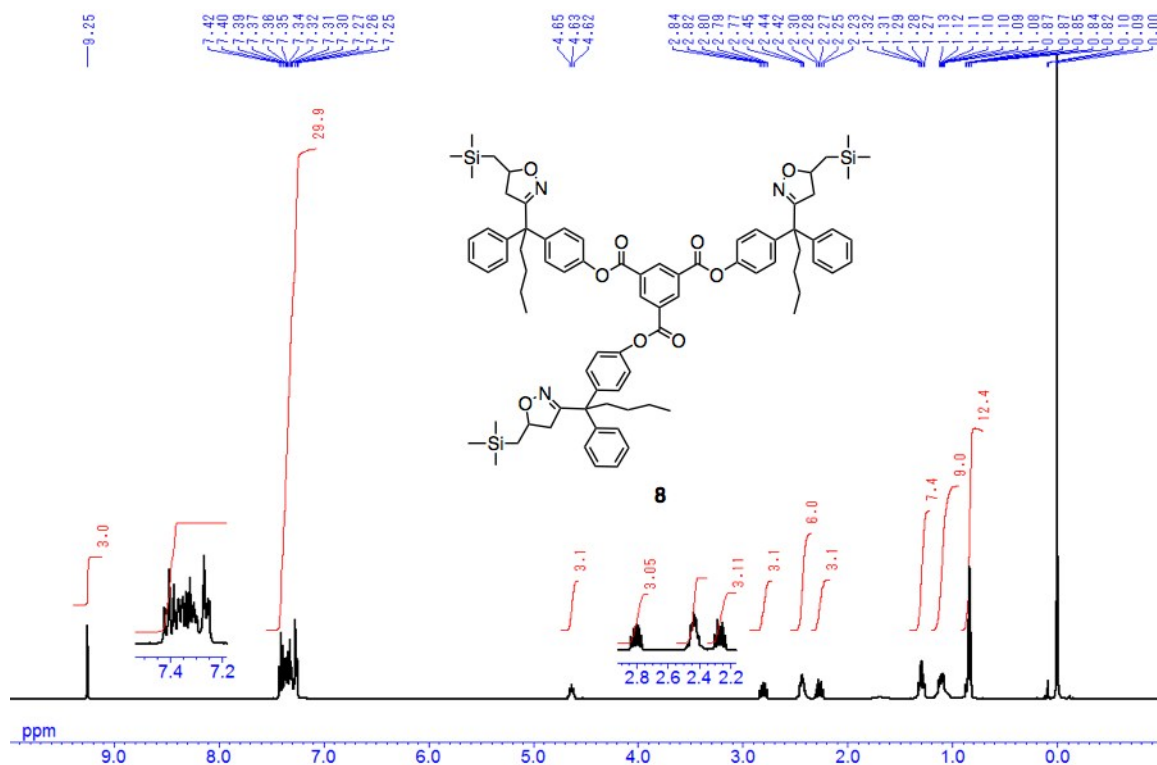
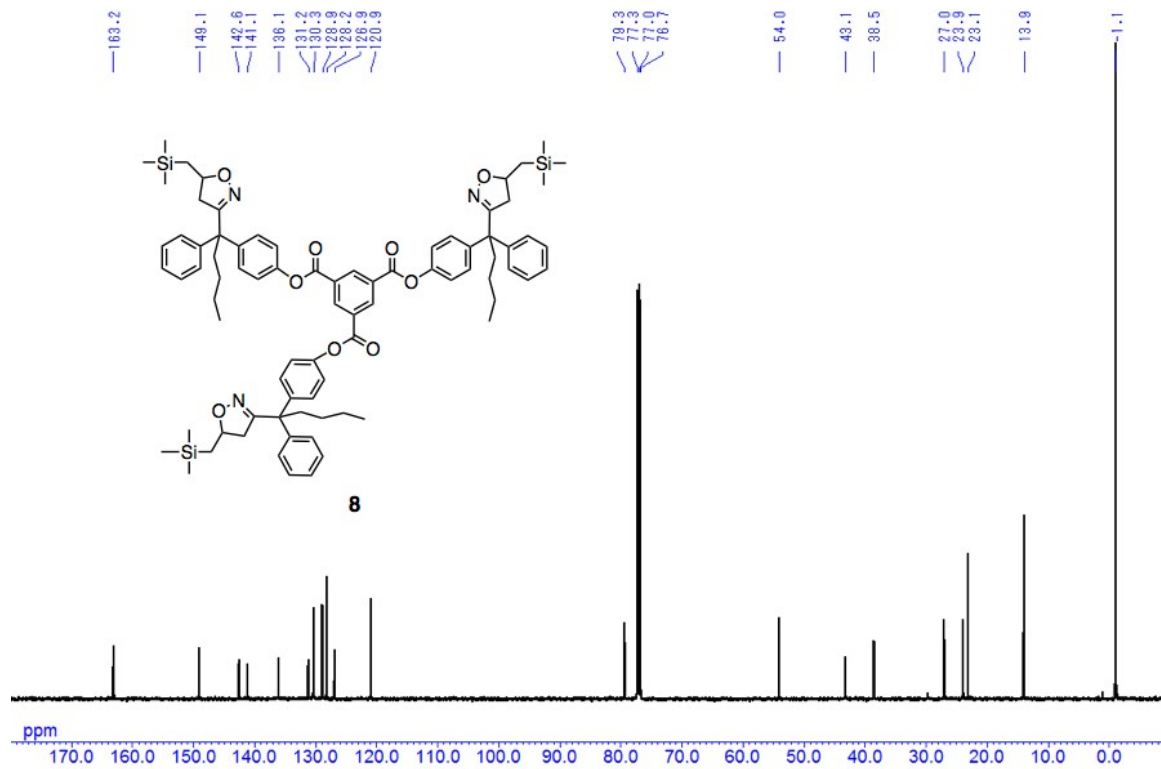


Figure S35.  $^{13}\text{C}$  NMR spectrum of **7** (125 MHz, 298 K,  $\text{CDCl}_3$ )





**Figure S36.** <sup>1</sup>H NMR spectrum of **8** (500 MHz, 298 K, CDCl<sub>3</sub>)



**Figure S37.** <sup>13</sup>C NMR spectrum of **8** (125 MHz, 298 K, CDCl<sub>3</sub>)

### 3. Reference

[1] Wang, C.-G.; Koyama, Y.; Yonekawa, M.; Uchida, S.; Takata, T. *Chem. Commun.* **2013**, *49*, 7723.