

Supporting Information for

Cascade Functionalization of Unsaturated Bond-Containing Polymers Using Ambident Agents Possessing both Nitrile *N*-Oxide and Electrophilic Functions

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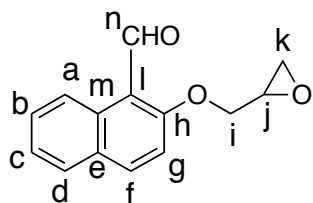
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1. General methods

Equipments. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a JEOL AL-400 spectrometers using tetramethylsilane as an internal standard. MALDI-TOF MS spectra were measured with a Shimadzu AXIMA-CFR mass spectrometer using a dithranol matrix. FAB HRMS spectra were measured with a JEOL JMS-700 mass spectrometer. Melting points were measured with a Stuart Scientific SMP3. SEC analyses were carried out on JASCO PU-2080 plus pump with a JASCO UV-1570 (UV detector) and JASCO RI-1530 (RI detector) equipped with a consecutive linear polystyrene gel columns TOSO TSK gel GMHXL and G5000HXL at 30 °C. TGA analyses were carried out on a Shimadzu TGA-50 instrument at N_2 atmosphere (flow rate of 50 mL/min) to determine 5% weight decomposition temperature (T_{d5}) at which 5% weight loss was observed. DSC analyses were carried out with a Shimadzu DSC-60 instrument at N_2 atmosphere (flow rate of 50 mL/min) with liquid N_2 as a refrigerant to determine glass transition temperature (T_g).

Materials. For NMR analyses, deuterated solvents with trimethylsilane by Across Organics Inc. were used. Wako Gel[®] C-400HG (Wako Chemical Inc.) was used for silica gel chromatography. Other reagents and solvents commercially available were used without further purification unless otherwise noted. All compounds given below bear the same formula numbers as used in the main text. Compounds unlabeled in the main text are labeled with letters [A–E].

2. Chemical Synthesis



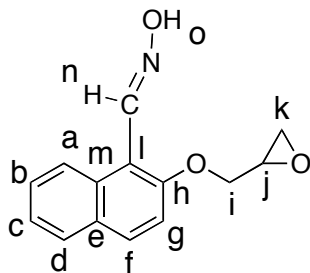
2-(Glycidyl oxy)-1-naphthaldehyde (B)

2-Hydroxy-1-naphthaldehyde (**A**) (17.1 g, 99.0 mmol) was dissolved in epichlorohydrin (196 mL, 2.47 mol). Benzyl triethylammonium chloride (2.26 g, 9.94 mmol) was added to the reaction mixture. The mixture was refluxed for 15 min. The reaction mixture was cooled to room temperature, diluted with CHCl_3 , and washed with distilled water. The organic layer was dried over MgSO_4 , filtered, and evaporated in vacuo. To the residue was added a small amount of 2-propanol to rapidly give the product as solids, which were filtered and washed with 2-propanol to yield **B** as white solids (16.1 g, 71.4%).

B: white solids, m.p. 97.4–98.9 °C (lit. 102–104 °C)¹

^1H NMR (400 MHz, CDCl_3 , 298 K) δ 10.9 (s, 1H, n), 9.24 (d, $J = 8.8$ Hz, 1H, a), 7.99 (d, $J = 7.3$ Hz, 1H, f), 7.74 (d, $J = 8.6$ Hz, 1H, d), 7.62–7.58 (m, 1H, b), 7.43–7.39 (m, 1H, c), 7.21 (d, $J = 9.3$ Hz, 1H, g), 4.46 (dd, $J_1 = 2.7$ Hz, $J_2 = 11.2$ Hz, 1H, i), 4.13 (dd, $J_1 = 5.6$ Hz, $J_2 = 11.2$

Hz, 1H, i), 3.41–3.38 (m, 1H, j), 2.93 (dd, $J_1 = 4.1$ Hz, $J_2 = 4.7$ Hz, 1H, k), 2.78 (dd, $J_1 = 2.7$ Hz, $J_2 = 4.7$ Hz, 1H, k) ppm; ^{13}C NMR (100 MHz, CDCl_3 , 298 K) δ 191.7, 162.7, 137.5, 131.3, 129.9, 128.7, 128.2, 125.0, 124.9, 117.1, 113.5, 70.2, 49.9, 44.4 ppm; IR (KBr) ν 2997 (C-H (aliphatic), epoxy), 2925 (C-H (aromatic)), 2879 (C-H (aliphatic)), 2800 (C-H, aldehyde), 1665 (C=O), 1619, 1592, 1512 (C=C), 1336 (C-H, aldehyde), 1270 (C-O, as, Ar-O-R), 1246 (C-O, s, epoxy), 1062 (C-O, s, Ar-O-R), 875 (C-O, as, epoxy), 813 (C-H) cm^{-1} .

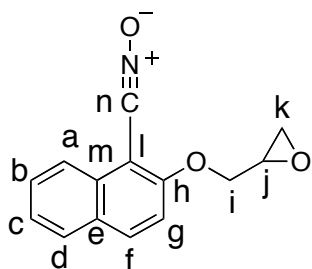


2-(Glycidyoxy)-1-naphthaldoxime (C)

Aldehyde **B** (5.03 g, 21.9 mmol) was dissolved in ethanol (110 mL). A solution of $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ (4.48 g, 32.9 mmol) and $\text{NH}_2\text{OH} \cdot \text{HCl}$ (2.29 g, 32.9 mmol) in water (110 mL) was added to the mixture at room temperature which stirred for 4 h to precipitated white products. The suspension was diluted with water. The precipitates were filtered and washed with water to give **C** as white solids (5.36 g, 100 %).

C: white solids, m.p. 102.2–103.6 °C

^1H NMR (400 MHz, CDCl_3 , 298 K) δ 8.90 (s, 1H, n), 8.77 (d, $J = 8.8$ Hz, 1H, a), 8.17 (s, 1H, o), 7.85 (d, $J = 9.3$ Hz, 1H, f), 7.78 (d, $J = 8.3$ Hz, 1H, d), 7.56–7.52 (m, 1H, b), 7.42–7.38 (m, 1H, c), 7.24 (d, $J = 8.6$ Hz, 1H, g), 4.39 (dd, $J_1 = 3.0$ Hz, $J_2 = 11.2$ Hz, 1H, i), 4.15 (dd, $J_1 = 5.6$ Hz, $J_2 = 11.2$ Hz, 1H, i), 3.44–3.40 (m, 1H, j), 2.94 (dd, $J_1 = 4.5$ Hz, $J_2 = 4.9$ Hz, 1H, k), 2.79 (dd, $J_1 = 2.7$ Hz, $J_2 = 4.9$ Hz, 1H, k) ppm; ^{13}C NMR (100 MHz, CDCl_3 , 298 K) δ 155.8, 147.5, 132.1, 131.6, 129.5, 128.3, 127.9, 125.6, 124.4, 114.5, 114.3, 70.6, 50.2, 44.7 ppm; IR (KBr) ν 3483 (O-H), 3078 (C-H (aliphatic), epoxy), 3009 (C-H (aromatic)), 2930 (C-H (aliphatic)), 1686 (C=N), 1625, 1587, 1512 (C=C), 1287 (C-O, as, Ar-O-R), 1244 (C-O, s, epoxy), 1080 (C-O, s, Ar-O-R), 863 (C-O, as, epoxy), 811 (C-H) cm^{-1} ; FAB-HRMS (m/z): calcd for $\text{C}_{19}\text{H}_{22}\text{O}_4$ $[\text{M}]^+$, 314.1518; found, 314.1517.

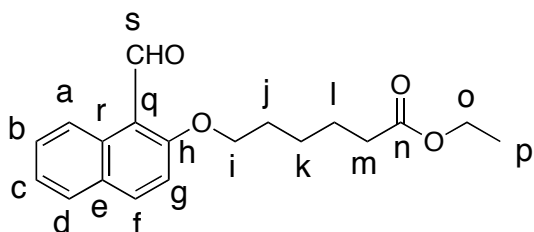


2-(Glycidyloxy)-1-naphthonitrile N-oxide (1)

Oxime **C** (3.00 g, 12.3 mmol) was dissolved in CHCl₃ (66 mL) at 0 °C. *N*-Chlorosuccinimide (NCS) (1.84 g, 13.5 mmol) and Et₃N (2.23 mL, 16.0 mmol) were added to this solution. After 6 h, the reaction was stopped by the addition of water. The organic layer was dried over MgSO₄, filtered, and evaporated in vacuo to give **C** (2.34 g, 78.8%) as yellow solids. The product was used for next reaction without further purifications.

C: yellow solids, m.p. 77.6–78.4 °C

¹H NMR (400 MHz, CDCl₃, 298 K) δ 7.99 (d, *J* = 8.5 Hz, 1H, a), 7.93 (d, *J* = 9.0 Hz, 1H, e), 7.82 (d, *J* = 8.3 Hz, 1H, d), 7.63–7.59 (m, 1H, b), 7.47–7.43 (m, 1H, c), 7.28 (d, *J* = 9.3 Hz, 1H, f), 4.50 (dd, *J*₁ = 3.0 Hz, *J*₂ = 11.5 Hz, 1H, g), 4.23 (dd, *J*₁ = 5.6 Hz, *J*₂ = 11.5 Hz, 1H, g), 3.46–3.42 (m, 1H, h), 2.97 (dd, *J*₁ = 4.7 Hz, *J*₂ = 4.4 Hz, 1H, i), 2.86 (dd, *J*₁ = 2.7 Hz, *J*₂ = 4.7 Hz, 1H, i) ppm; ¹³C NMR (100 MHz, CDCl₃, 298 K) δ 160.2, 133.9, 132.7, 128.7, 128.4, 125.1, 123.8, 120.4, 113.2, 96.9, 69.8, 49.9, 44.4 ppm; IR (NaCl) *ν* 3059 (C-H(aliphatic), epoxy), 3005 (C-H(aromatic)), 2928 (C-H(aliphatic)), 2293 (C≡N), 1622, 1589, 1510 (C=C) 1313 (C≡N⁺O⁻), 1275 (C-O, as, Ar-O-R), 1249 (C-O, s, epoxy), 1063 (C-O, s, Ar-O-R), 863 (C-O, as, epoxy), 815 (C-H) cm⁻¹; FAB-HRMS (*m/z*): calcd for C₁₄H₁₁NO₃ [M]⁺, 241.0739; found, 241.0744.



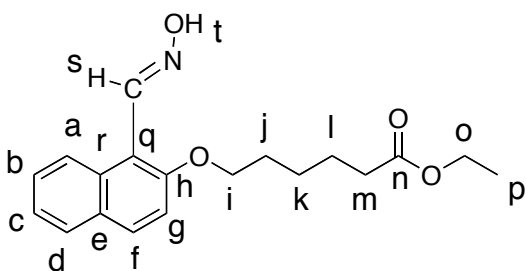
2-[5-(Ethoxycarbonyl)pentyl]oxy]-1-naphthaldehyde (D)

2-Hydroxy-1-naphthaldehyde (**1**) (5.00 g, 29.0 mmol) was dissolved in DMF (100 mL) and K₂CO₃ (6.04 g, 43.7 mmol) and ethyl 6-bromohexanoate (8.94 g, 40.1 mmol) was added to this solution. The mixture was stirred at 100 °C for 13 h. The reaction mixture was cooled to room temperature, diluted with ethylacetate and washed with distilled water and brine. The organic layer was dried

over MgSO₄, filtered, and evaporated in vacuo. The residue was recrystallized from hexane to give **D** (8.25 g, 90.4%) as colorless solids.

D: colorless solids, m.p. 65.0–66.1 °C

¹H NMR (400 MHz, CDCl₃, 298 K) δ 10.9 (s, 1H, s), 9.28 (d, *J* = 8.6 Hz, 1H, a), 8.03 (d, *J* = 9.2 Hz, 1H, f), 7.76 (d, *J* = 8.0 Hz, 1H, d), 7.63–7.59 (m, 1H, b), 7.43–7.39 (m, 1H, c), 7.26 (d, *J* = 9.2 Hz, 1H, g), 4.22 (t, *J* = 6.6 Hz, 2H, i), 4.14 (q, *J* = 7.1 Hz, 2H, o), 2.35 (t, *J* = 7.3 Hz, 2H, m), 1.94–1.87 (m, 2H, j), 1.77–1.69 (m, 2H, l), 1.60–1.53 (m, 2H, k), 1.26 (t, *J* = 7.1 Hz, 3H, p) ppm; ¹³C NMR (100 MHz, CDCl₃, 298 K) δ 191.9, 173.4, 163.5, 137.4, 131.5, 129.7, 128.3, 128.1, 124.8, 124.6, 116.6, 113.4, 69.1, 60.2, 34.1, 28.9, 25.5, 24.5, 14.2 ppm; IR (KBr) ν 2946 (C-H(aromatic)), 2861 (C-H(aliphatic)), 2803 (C-H, aldehyde), 1733 (C=O, ester), 1671 (C=O, aldehyde), 1377 (C-H, aldehyde), 1252 (C-O, as, Ar-O-R), 1178 (C-O, as, ester), 1057 (C-O, s, Ar-O-R), 825 (C-H) cm⁻¹; FAB-HRMS (*m/z*): calcd for C₁₄H₁₃NO₃ [M]⁺, 243.0895; found, 243.0896.



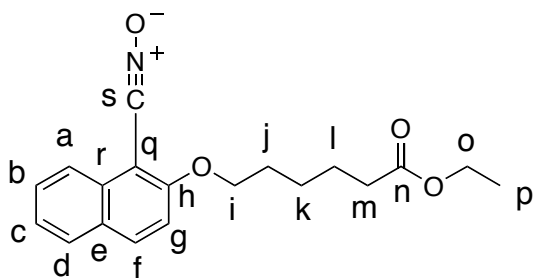
2-[5-(Ethoxycarbonyl)pentyl]oxy-1-naphthaldoxime (**E**)

Aldehyde **D** (406 mg, 1.29 mmol) was dissolved in ethanol (6 mL). A solution of CH₃COONa·3H₂O (263 mg, 1.94 mmol) and NH₂OH·HCl (146 mg, 2.10 mmol) in water (6 mL) was added to the mixture at room temperature which stirred at room temperature for 4 h to precipitate white powders. The suspension was diluted with water and the precipitates were filtered and washed with water to give **E** as white solids (404 mg, 95.0%).

E: white solids, m.p. 88.5–91.4 °C

¹H NMR (400 MHz, CDCl₃, 298 K) δ 8.87 (s, 1H, s), 8.78 (d, *J* = 8.8 Hz, 1H, a), 8.12 (s, 1H, t), 7.84 (d, *J* = 9.2 Hz, 1H, f), 7.77 (d, *J* = 8.1 Hz, 1H, d), 7.54–7.50 (m, 1H, b), 7.39–7.35 (m, 1H, c), 7.22 (d, *J* = 9.2 Hz, 1H, g), 4.17–4.10 (m, 4H, i and o), 2.36 (t, *J* = 7.3 Hz, 2H, m), 1.90–1.83 (m, 2H, j), 1.77–1.69 (m, 2H, l), 1.59–1.51 (m, 2H, k), 1.25 (t, 3H, p) ppm; ¹³C NMR (100 MHz, CDCl₃, 298 K) δ 173.8, 156.2, 147.4, 131.8, 131.6, 129.0, 128.2, 127.7, 125.4, 123.9, 113.8, 113.7, 69.2, 60.3, 34.2, 29.0, 25.6, 24.6, 14.2 ppm; IR (KBr) ν 2988

(C-H(aromatic)), 2941 (C-H(aliphatic)), 1692 (C=O, ester), 1268 (C-O, as, Ar-O-R), 1180 (C-O, as, ester), 1066 (C-O, s, Ar-O-R), 818 (C-H) cm^{-1} ; FAB-HRMS (m/z): calcd for $\text{C}_{19}\text{H}_{23}\text{NO}_4\text{Na}$ $[\text{M}+\text{Na}]^+$, 352.1525; found, 352.1519.

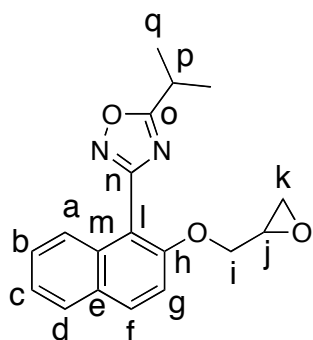


2-[5-(Ethoxycarbonyl)pentyl]oxy-1-naphthonitril N-oxide (2)

Oxime **E** (88.2 mg, 0.268 mmol) was dissolved in CHCl_3 (30 mL) at 0 °C. NCS (38.2 mg, 0.325 mmol) and Et_3N (50 μL , 0.36 mmol) were added to this solution. After 6 h, the reaction was stopped by the addition of water. The organic layer was dried over MgSO_4 , filtered, and evaporated in vacuo to give **2** (81.9 mg, 79.3%) as yellow solids. The product was used for next reaction without further purifications.

2: yellow solids, m.p. 58.9–60.0 °C

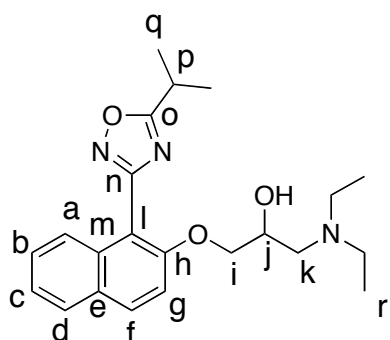
^1H NMR (400 MHz, CDCl_3 , 298 K) δ 7.97 (d, $J = 8.0$ Hz, 1H, a), 7.91 (d, $J = 8.0$ Hz, 1H, f), 7.81 (s, $J = 8.0$ Hz, 1H, d), 7.61–7.57 (m, 1H, b), 7.42 (t, 1H, c), 7.24 (t, 1H, g), 4.20 (t, $J = 8.0$ Hz 2H, i), 4.14 (q, 2H, o), 2.37 (t, $J = 8.0$ Hz 2H, m), 1.94–1.87 (m, 2H, j), 1.78–1.71 (m, 2H, l), 1.62–1.54 (m, 2H, k), 1.26 (t, 3H, p) ppm; ^{13}C NMR (100 MHz, CDCl_3 , 298 K) δ 173.6, 160.8, 134.2, 132.7, 128.7, 128.5, 128.3, 125.7, 123.9, 113.1, 69.2, 60.3, 34.1, 28.8, 25.6, 25.4, 14.2 ppm; IR (KBr) ν 2942 (C-H(aromatic)), 2871 (C-H(aliphatic)), 2291 ($\text{C}\equiv\text{N}$), 1731 (C=O, ester), 1273 (C-O, as, Ar-O-R), 1217 (C-O, as, ester), 1062 (C-O, s, Ar-O-R), 810 (C-H) cm^{-1} ; FAB-HRMS (m/z): calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_4\text{Na}$ $[\text{M}+\text{Na}]^+$, 350.1368; found, 350.1372.



Oxadiazole (3)

Nitrile *N*-oxide **1** (50.0 mg, 0.21 mmol) and isobutyronitrile (188 μ L, 2.10 mmol) were dissolved in DMF (400 μ L) and stirred at 90 °C for 4 h. The mixture was cooled to room temperature, and directly purified on alumina silica gel column chromatography (eluent: AcOEt/ CHCl₃/ hexane = 2/ 1/ 3, R_f = 0.5). **3** was obtained as a brown oil (99.0 %).

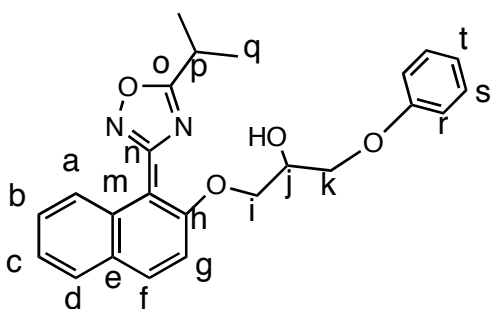
¹H NMR (400 MHz, CDCl₃, 298 K) δ 7.95 (d, J = 12 Hz, 1H, a), 7.81 (d, J = 8.0 Hz, 1H, f), 7.67 (d, J = 8.0 Hz, 1H, d), 7.48–7.44 (m, 1H, b), 7.40–7.36 (m, 1H, c), 7.33 (d, J = 8.0 Hz, 1H, g), 4.36 (dd, J_1 = 4.0 Hz, J_2 = 12 Hz, 1H, i), 4.15 (dd, J_1 = 8.0 Hz, J_2 = 12.0 Hz, 1H, i), 3.41–3.34 (m, 1H, p), 3.31–3.27 (m, 1H, j), 2.81 (t, 1H, j), 2.71 (dd, J_1 = 2.7 Hz, J_2 = 4.0 Hz, 1H, k), 1.52 (d, J = 8.0 Hz, 6H, q) ppm; ¹³C NMR (100 MHz, CDCl₃, 298 K) δ 183.7, 165.2, 155.3, 133.0, 132.4, 129.1, 128.1, 127.6, 124.4, 124.3, 115.0, 111.5, 70.5, 50.1, 44.5, 27.6, 20.3 ppm; IR (NaCl) ν 1250 (C-O, s, epoxy), 903 (C-O, as, epoxy) cm⁻¹; FAB-HRMS (m/z): calcd for C₁₈H₁₈N₂O₃Na [M+Na]⁺, 333.1215; found, 333.1220.



Oxadiazole (4a)

Oxadiazole **3** (39.8 mg, 0.128 mmol) and diethylamine (14 μ L, 0.136 mmol) was dissolved in CHCl₃ (1.3 mL) and stirred at 50 °C for 48 h. The mixture was evaporated in vacuo to give **4a** as a brown oil (quant.).

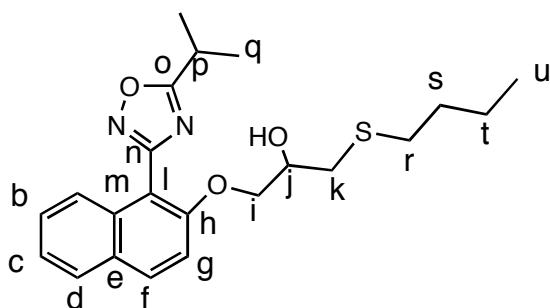
^1H NMR (400 MHz, CDCl_3 , 298 K) δ 7.98 (d, $J = 8.0$ Hz, 1H, a), 7.94 (d, $J = 8.0$ Hz, 1H, d), 7.83 (d, $J = 8.0$ Hz, 1H, d), 7.51–7.47 (m, 1H, b), 7.42–7.40 (m, 1H, c), 7.37 (d, $J = 8.0$ Hz, 1H, g), 4.36 (dd, $J_1 = 4.0$ Hz, $J_2 = 12$ Hz, 1H, i), 4.18 (dd, $J_1 = 4.0$ Hz, $J_2 = 12$ Hz, 1H, i), 4.02–3.97 (m, 1H, j), 3.41–3.34 (m, 1H, p), 2.58–2.52 (m, 6H, k), 1.52 (d, $J = 8.0$ Hz, 1H, q), 1.01 (t, 6H, r) ppm; ^{13}C NMR (100 MHz, CDCl_3 , 298 K) δ 183.6, 165.2, 155.9, 132.6, 129.0, 128.1, 127.7, 124.3, 115.1, 73.3, 67.1, 55.6, 47.6, 29.6, 27.6, 20.2, 11.7 ppm; IR (NaCl) ν 3363 (O–H), 1271 (C–N) cm^{-1} ; FAB-HRMS (m/z): calcd for $\text{C}_{22}\text{H}_{29}\text{N}_3\text{O}_3\text{Na}$ [$\text{M}+\text{Na}$] $^+$, 406.2107; found, 406.2111.



Oxadiazole (4b)

Phenol (32.7 mg, 0.347 mmol) was dissolved in DMF (1.6 mL) and K_2CO_3 (61.0 mg, 0.441 mmol) and Oxadiazole **3** (101 mg, 0.322 mmol) was added to this solution. The mixture was stirred at 120 °C overnight. The reaction mixture was cooled to room temperature, diluted with CHCl_3 and washed with distilled water and brine. The organic layer was dried over MgSO_4 , filtered, and evaporated in vacuo. The residue was purified on alumina silica gel column chromatography (eluent: $\text{AcOEt}/\text{CHCl}_3/\text{hexane} = 2/1/2$, $R_f = 0.5$) to give **4b** as a brown oil (quant.).

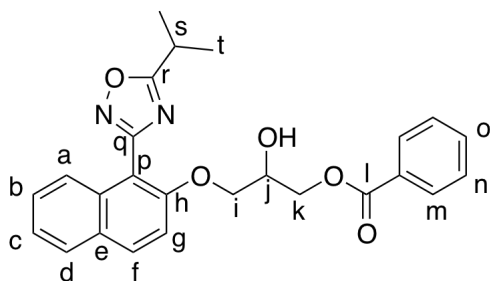
^1H NMR (400 MHz, CDCl_3 , 298 K) δ 8.15 (d, $J = 12$ Hz, 1H, a), 7.98 (d, $J = 8.0$ Hz, 1H, f), 7.83 (d, $J = 8.0$ Hz, 1H, d), 7.52–7.50 (m, 1H, b), 7.44–7.42 (m, 1H, c), 7.35 (d, $J = 8.0$ Hz, 1H, g), 7.30–7.25 (m, 2H, r), 6.98–6.90 (m, 2H, s and t), 4.57 (dd, $J_1 = 2.4$ Hz, $J_2 = 8.0$ Hz, 1H, i), 4.39–4.36 (m, 2H, i and j), 4.12–4.03 (m, 2H, k), 3.39–3.35 (m, 1H, p), 1.51 (d, $J = 4.0$ Hz, 6H, q) ppm; ^{13}C NMR (100 MHz, CDCl_3 , 298 K) δ 183.7, 165.0, 158.4, 156.2, 133.0, 132.3, 129.5, 129.3, 128.3, 128.0, 124.6, 124.5, 121.0, 115.6, 114.4, 110.8, 73.0, 68.6, 68.1, 27.6, 20.2, 20.1 ppm; IR (NaCl) ν 3359 (O–H), 1244 (O–Ar), 1063 (O–Ar) cm^{-1} ; FAB-HRMS (m/z): calcd for $\text{C}_{24}\text{H}_{24}\text{N}_2\text{O}_4\text{Na}$ [$\text{M}+\text{Na}$] $^+$, 427.1634; found, 427.1649.



Oxadiazole (4c)

Butanethiol (35 μ L, 0.327 mmol) was dissolved in DMF (1.6 mL) and K_2CO_3 (60.0 mg, 0.434 mmol) and Oxadiazole **3** (100 mg, 0.322 mmol) was added to this solution. The mixture was stirred at 120 $^\circ$ C overnight. The reaction mixture was cooled to room temperature, diluted with $CHCl_3$ and washed with distilled water and brine. The organic layer was dried over $MgSO_4$, filtered, and evaporated in vacuo. The residue was purified on alumina silica gel column chromatography (eluent: AcOEt/ $CHCl_3$ / hexane = 2/ 1/ 3, R_f = 0.5) to give **4c** as a brown oil (quant.).

1H NMR (400 MHz, $CDCl_3$, 298 K) δ 8.11 (d, J = 8.0 Hz, 1H, a), 7.99 (d, J = 8.0 Hz, 1H, f), 7.83 (d, J = 8.0 Hz, 1H, d), 7.52–7.49 (m, 1H, b), 7.44–7.42 (m, 1H, c), 7.35 (d, J = 8.0 Hz, 1H, g), 4.50 (dd, J_1 = 2.8 Hz, J_2 = 8 Hz, 1H, i), 4.26–4.22 (m, 1H, i), 4.08–4.03 (m, 1H, j), 3.40–3.37 (m, 1H, j), 3.39–3.35 (m, 1H, p), 2.74–2.66 (m, 1H, k), 2.57 (t, J = 8.0 Hz, 2H, r), 1.59–1.37 (m, 10H, q, s and t), 0.90 (t, J = 8.0 Hz, 6H, u) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 183.7, 165.1, 156.1, 133.1, 133.0, 132.4, 129.3, 128.3, 127.9, 124.6, 124.5, 124.4, 115.5, 110.9, 74.0, 69.6, 34.5, 32.6, 31.7, 27.6, 21.9, 20.2, 13.7 ppm; IR (NaCl) ν 3375 (O–H), 667 (C–S) cm^{-1} ; FAB-HRMS (m/z): calcd for $C_{22}H_{29}N_2O_3S$ [$M+Na$] $^+$, 401.1899; found, 406.1900.



Oxadiazole (4d)

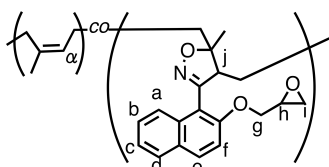
To a mixture of oxadiazole **3** (100 mg, 0.322 mmol) and benzoic acid (41.3 mg, 0.338 mmol) in CH_3CN (1.6 mL) was added Bu_4NBr (3.1 mg, 9.67 μ mol). The mixture was refluxed overnight. The reaction mixture was cooled to room temperature, diluted with $CHCl_3$ and washed with

distilled water and brine. The organic layer was dried over MgSO_4 , filtered, and evaporated in vacuo. The residue was purified on preparative silica gel column chromatography (eluent: $\text{AcOEt}/\text{CHCl}_3/\text{hexane} = 2/1/3$, $R_f = 0.5$) to give **4d** as a pale red oil (117.2 mg, 84%).

^1H NMR (400 MHz, CDCl_3 , 298 K) δ 8.05 (d, $J = 8.0$ Hz, 1H, a), 7.93 (d, $J = 8.0$ Hz, 2H, m), 7.85 (d, $J = 8.0$ Hz, 1H, f), 7.69 (d, $J = 8.0$ Hz, 1H, d), 7.44–7.38 (m, 2H, b and c), 7.32–7.27 (m, 3H, n and o), 7.16 (d, $J = 8.0$ Hz, 1H, g), 4.38–4.20 (m, 5H, i, j, and k), 3.26 (hept, $J = 8.0$ Hz, 1H, s), 1.39 (d, $J = 8.0$ Hz, 6H, t) ppm; ^{13}C NMR (100 MHz, CDCl_3 , 298 K) δ 183.7, 166.3, 164.9, 156.1, 133.01, 132.97, 132.2, 129.7, 129.5, 129.2, 128.3, 128.2, 127.9, 124.54, 124.47, 115.4, 110.8, 72.7, 68.4, 65.0, 27.5, 20.04, 19.97 ppm; IR (NaCl) ν 3364, 3062, 2978, 2940, 2879, 1722, 1716, 1622, 1598, 1568, 1505, 1463, 1393, 1347, 1270, 1112, 1071, 1026, 902, 813, 750, 712 cm^{-1} ; MALDI-TOF MS (m/z): calcd for $\text{C}_{25}\text{H}_{24}\text{N}_2\text{NaO}_5$ $[\text{M}+\text{Na}]^+$ 455.16; found 454.96.

Typical procedure for modification of natural rubber (NR)

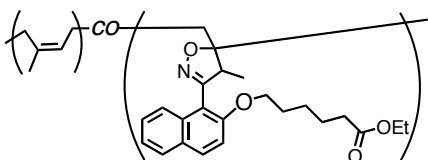
NR (50.6 mg, M_w 1250000) was dissolved in CHCl_3 (2 mL) and nitrile *N*-oxide **1** (179 mg, 0.742 mmol) was added to this solution. The solution was refluxed for 24 h. The mixture was reprecipitated from methanol (200 mL) and product was obtained (quant.).



(Table 2, entry 4)

^1H NMR (400 MHz, CDCl_3 , 298 K) δ 8.11–7.00 (m, a–f), 5.00 (s, α), 4.38–3.96 (m, g), 3.74–3.27 (m, h and j), 2.94–2.65 (m, i), 1.63–0.93 (m, CH_3 of NR) ppm; IR (NaCl) ν 1271 (C–O, s, epoxy), 898 (C–O, as, epoxy) cm^{-1} .

T_{d5} 253 $^\circ\text{C}$, T_g –19 $^\circ\text{C}$



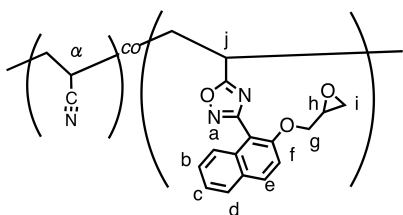
(Table 2, entry 6)

^1H NMR (400 MHz, CDCl_3 , 298 K) δ 7.97–7.33 (m, Ar of **2**), 5.13–4.90 (m, $\text{CH}=\text{C}$ of NR), 4.11 (m, $\text{O}-\text{CH}_2\text{CH}_2$ of **6**), 2.32–0.88 (m, CH_2 and CH_3 of NR, $\text{O}-\text{CH}_2\text{CH}_2$ and CH_3 of **2**) ppm; IR (KBr) ν 1739 (C=O, s, ester), 1059 (C–C(=O)–O, as, ester) cm^{-1} .

T_{d5} 323 °C, T_g 143 °C

Typical procedure for modification of polyacrylonitrile (PAN)

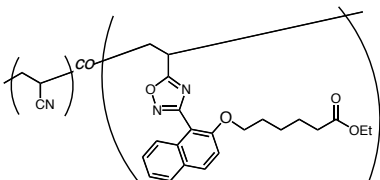
PAN (50.1 mg, M_w 150000) was dissolved in DMF (2 mL) and nitrile *N*-oxide **1** (227 mg, 0.941 mmol) was added to this solution. The solution was mixed at 90 °C for 24 h. The mixture was reprecipitated from methanol (200 mL) and product was obtained (quant.).



(Table 1, entry 3)

^1H NMR (400 MHz, DMSO- d_6 , 298 K) δ 8.12 (s, 1H, a), 7.94 (s, 1H, e), 7.54 (s, 1H, d), 7.38 (s, 3H, b,c and f), 4.44 (s, 1H, g), 4.01 (s, 1H, g), 3.64 (s, 1H, CH₂ of PAN), 3.21 (s, 3H, h and CH₂ of PAN), 2.88 (t, 1H, i), 2.73 (t, 1H, i), 2.23 (s, 4H, α), 2.00 (s, 2H, j) ppm. IR (KBr) ν 1253 (C-O, s, epoxy), 901 (C-O, as, epoxy) cm^{-1} .

T_{d5} 291 °C, T_g 146 °C



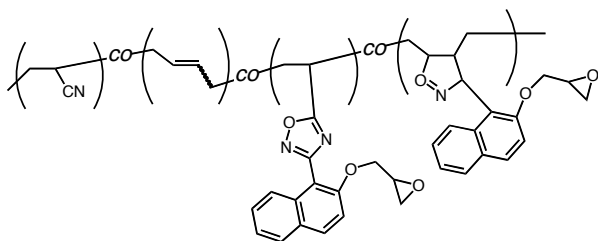
(Table 1, entry 5)

^1H NMR (400 MHz, DMSO- d_6 , 298 K) δ 8.09–7.34 (m, Ar of **2**), 3.95 (m, O-CH₂CH₂ of **2**), 3.64–1.06 (m, CH₂C≡N and CH₂ of PAN, O-CH₂CH₂ and CH₃ of **2**) ppm; IR (KBr) ν 1726 (C=O, s, ester), 1059 (C-C(=O)-O, as, ester) cm^{-1} .

T_{d5} 281 °C, T_g 145 °C

Typical procedure for modification of acrylonitrile-butadiene rubber (NBR)

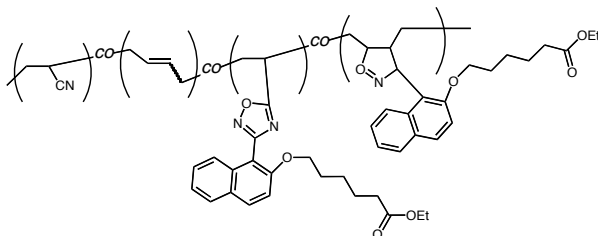
NBR (49.3 mg) was dissolved in CHCl₃ (2.0 mL) and nitrile *N*-oxide **1** (271.9 mg, 1.13 mmol) was added to this solution. The solution was refluxed for 24 h. The mixture was reprecipitated from methanol (200 mL) and product was obtained (244 mg, 91.0%).



(Table S1, entry 1)

^1H NMR (400 MHz, CDCl_3 , 298 K) δ 8.02–7.00 (m, Ar of **1**), 4.52–3.28 (m, CH_2 and CH of **1**), 2.98–1.20 (s, CH_2 of **1**, $\text{CHC}\equiv\text{N}$ and CH_2 of NBR) ppm; IR (KBr) ν 1267 (C-O, s, epoxy), 864 (C-O, as, epoxy) cm^{-1} .

$T_{\text{d}5}$ 282 °C, T_g 124 °C



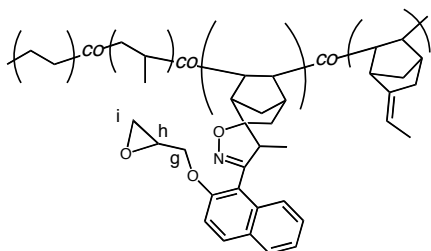
(Table S1, entry 2)

^1H NMR (400 MHz, CDCl_3 , 298 K) δ 8.00–7.31 (m, Ar of **2**), 4.25–4.04 (m, $\text{CHC}\equiv\text{N}$ of NBR, O- CH_2CH_2 of **2**), 2.36–1.06 (m, CH_2 of NBR, O- CH_2CH_2 and CH_3 of **2**) ppm; IR (KBr) ν 1721 (C=O, s, ester), 1193 (C-C(=O)-O, as, ester) cm^{-1} .

$T_{\text{d}5}$ 271 °C, T_g 140 °C

Typical procedure for modification of EPDM

EPDM (51.3 mg) was dissolved in CHCl_3 (137 μL) and nitrile *N*-oxide **1** (17.6 mg, 0.0730 mmol) was added to this solution. The solution was refluxed for 24 h. The mixture was reprecipitated from methanol (200 mL) and product was obtained (60.6 mg, 97.0%).

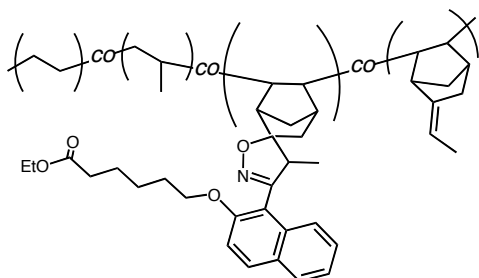


(Table S1, entry 3)

^1H NMR (400 MHz, CDCl_3 , 298 K) δ 8.09–7.26 (m, Ar of **1**), 5.23 (m, $\text{CH}_3\text{CH}=\text{C}$ of EPDM),

4.42–4.11 (m, g), 3.70–3.33 (m, h), 2.93–2.72 (m, i), 2.39–0.83 (m, EPDM) ppm; IR (NaCl) ν 1215 (C-O, s, epoxy), 979 (C-O, as, epoxy) cm^{-1} .

T_{d5} 309 °C, T_g 130 °C

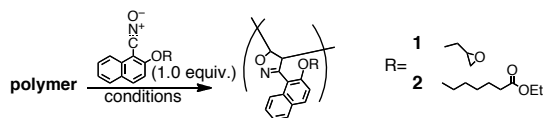


(Table S1, entry 4)

^1H NMR (400 MHz, CDCl_3 , 298 K) δ 8.10–7.29 (m, Ar of **2**), 5.20 (s, $\text{CH}_3\text{CH}=\text{C}$ of EPDM), 4.27–4.08 (m, $\text{O}-\text{CH}_2\text{CH}_2$ of **2**), 3.67–0.83 (m, EPDM, $\text{O}-\text{CH}_2\text{CH}_2$ and CH_3 of **2**) ppm; IR (NaCl) ν 1732 (C=O, s, ester), 1216 (C–C(=O)–O, as, ester) cm^{-1} .

T_{d5} 309 °C, T_g 154 °C

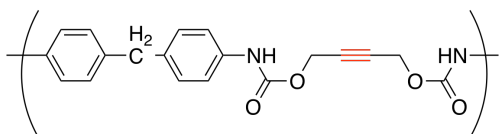
Table S1. Results of modification of polymers.



entry	polymer	reagent	solvent	temp. (°C)	time (h)	yield (%)	conversion (%) ^{a)}	T_{d5} (°C)	T_g (°C)	M_n	M_w	M_w/M_n
1		1	CHCl_3	reflux	24	91	olefine : 100 CN : 44	282	124	– ^{c)}	– ^{c)}	– ^{c)}
2	NBR	2	CHCl_3	reflux	24	71	olefine : 100 CN : 57	271	140	– ^{c)}	– ^{c)}	– ^{c)}
3		1	CHCl_3	reflux	24	97	68	309	130	59000	119000	2.03
4	EPDM	2	CHCl_3	reflux	24	83	60	309	154	79000	228000	2.88

a) Conversion ratio of unsaturated bonds. b) Not measured. c) Not estimated.

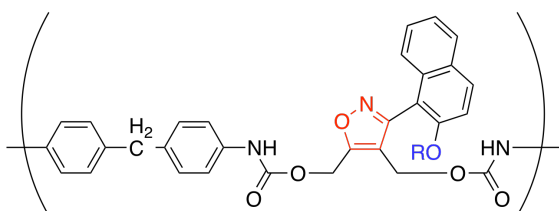
Synthesis of internal alkyne-containing polymer



To a solution of 4,4-diphenylmethane diisocyanate (MDI, 300 mg, 1.20 mmol) and 2-butyne-1,4-diol (86.0 μL , 1.20 mmol) in DMF (1.0 mL) was added dibutyltindilaurate (35.5 μL ,

0.060 mmol) and the mixture was stirred at room temperature for 1 h. The mixture was warmed to 100 °C, stirred for 1 h, warmed to 160 °C, and stirred for 1 h. The reaction mixture was cooled to room temperature and poured into MeOH to give precipitates. The resulting precipitates were filtered and dried in vacuo to give the internal alkyne-containing polyurethane (393.6 mg, 98%) as a brown solid; M_w 10000, M_w/M_n 1.8 on the basis of polystyrene standards (eluent: DMF); no T_g was observed in a range from room temperature to 220 °C; T_{d5} 272 °C; ^1H NMR (400 MHz, DMSO- d_6 , 298 K) δ 9.74 (s, 2H), 7.32 (d, J = 8.4 Hz, 4H), 7.09 (d, J = 8.4 Hz, 4H), 4.80 (s, 4H), 3.78 (s, 2H) ppm; IR (KBr) ν 3322, 3127, 3034, 2940, 1906, 1709, 1599, 1527, 1413, 1367, 1316, 1226, 1154, 1054, 1017, 914, 848, 816, 764, 616, 510 cm^{-1} .

Typical procedure for the modification of internal alkyne-containing polyurethane with 2



To a solution of internal alkyne-containing polymer (100 mg, 0.297 mmol) in DMF (0.3 mL) was added **2** (97.6 mg, 0.297 mmol) and the mixture was warmed to 90 °C and stirred for 13 h. The mixture was cooled to room temperature and poured into MeOH to give precipitates. The resulting precipitates were filtered and dried in vacuo to give the corresponding isoxazole-containing polymer (171 mg, 87%, >99% conversion) as a brown solid; no T_g was observed in a range from room temperature to 105 °C; T_{d5} 263 °C; ^1H NMR (400 MHz, CDCl_3 , 298 K) δ 7.87–6.98 (m), 5.57–4.63 (m), 4.98 (brd), 3.74 (brd), 2.20 (brd), 1.76 (brd), 1.59 (brd), 1.50 (brd), 1.20 (brd) ppm; ^{13}C NMR (100 MHz, CDCl_3 , 298 K) δ 174.6, 164.9, 160.1, 159.9, 159.6, 155.0, 153.3, 136.6, 136.3, 135.9, 133.5, 129.4, 129.0, 124.7, 124.3, 119.2, 115.4, 110.9, 69.5, 68.7, 56.1, 40.6, 34.3, 28.9, 25.6, 24.7, 14.4, 14.0 ppm; IR (KBr) ν 3319, 3055, 2942, 1733, 1597, 1538, 1457, 1435, 1414, 1373, 1311, 1221, 1151, 1055, 1018, 914, 849, 812, 736 cm^{-1} .

Modification of NR exploiting epoxy group

Epoxycontaining-NR (100 mg) and 4-(heptadecafluorooctyl)aniline (192 mg, 0.376 mmol) was dissolved in DMF (1.0 mL), and the solution was stirred at 120 °C for 24 h. The reaction mixture was cooled to room temperature and reprecipitated from water. The product was washed with hexane several times and dried in vacuo to give product (124 mg) as a brown solid.

^1H NMR (400 MHz, CDCl_3 , 298 K) δ 8.01–7.12 (m, Ar of **1** and aniline), 5.00 (s, $-\text{CH}=\text{C}(\text{CH}_3)-$ of NR), 4.27–2.61 (m, epoxy, OH, NH and CH_2 of **1** and NR), 1.63–0.93 (m, CH_3 of NR) ppm; ^{19}F NMR (400 MHz, CDCl_3 , 298 K) δ –28.8 (s, 2H, Ar– CF_2), –40.6 (s, 2H, Ar– CF_2CF_2), –41.2 (s, 8H, CF_2), –42.0 (s, 2H, $-\text{CF}_2\text{CF}_3$), –45.4 (s, 3H, $-\text{CF}_2\text{CF}_3$) ppm; IR (NaCl) ν 3376 (O–H and N–H), 1515 (N–H), 1337 (C–N), 1242 ($-\text{CF}_2-$), 754 ($-\text{CF}_3$) cm^{-1} .

Typical procedure for cross-linking of modified NR (Table 2, entry 3)

Epoxy-modified NR (Table 1, entry 4, 1.21 g, 0.332 mmol) and *N,N'*-diethyl-1,6-diaminohexane (34 μL , 0.166 mmol) were dissolved in CHCl_3 (12 mL), the solution was degassed by using diaphragm pump. The mixture was heated at 40 °C on the electrical hot plate in open for 24 h. The cross-linked NR was washed by immersion in CHCl_3 for 6 h and dried in vacuo. Finally, the cross-linked NR was yielded 709 mg (99%).

Table S2. Evaluations of cross-linked NRs.

entry	amount of linker (mol%)	swelling ratio (%) ^a	degree of cross-link (%) ^b	yield (%)	T_{d5} (°C) ^b	T_g (°C) ^b
1	5	930	0.41	87	338	– 57
2	25	540	1.2	98	340	– 57
3	50	380	2.5	99	340	– 56

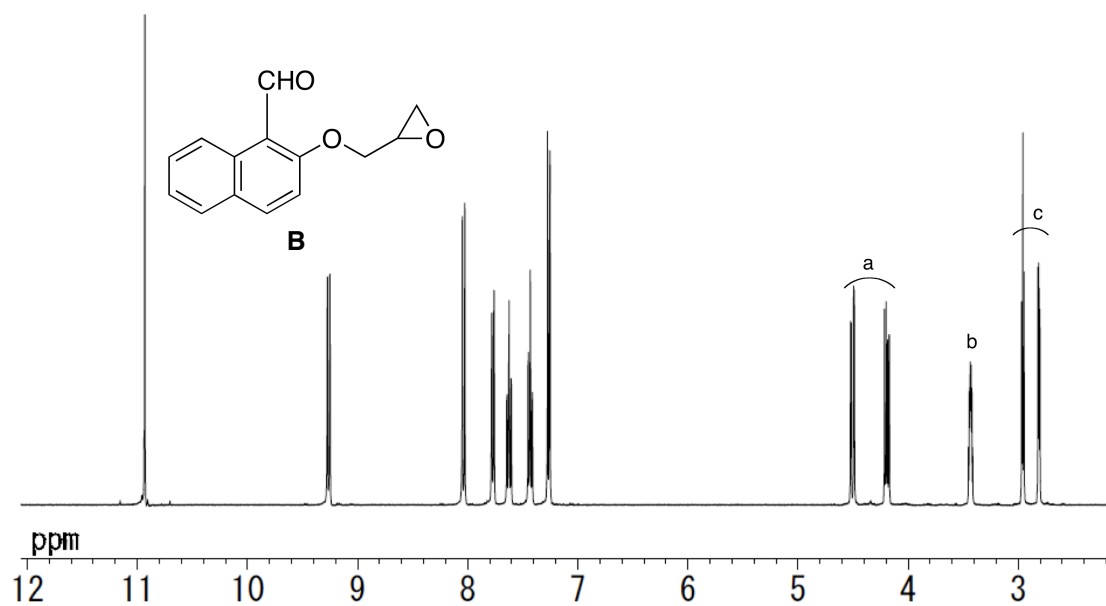
a) swollen in toluene, $(W_s - W_d) / W_d$. b) molar ratio of cross-linked alkenes / feedalkenes.

b) under N_2 , NR: $T_{d5} = 345$ °C, $T_g = -65$ °C

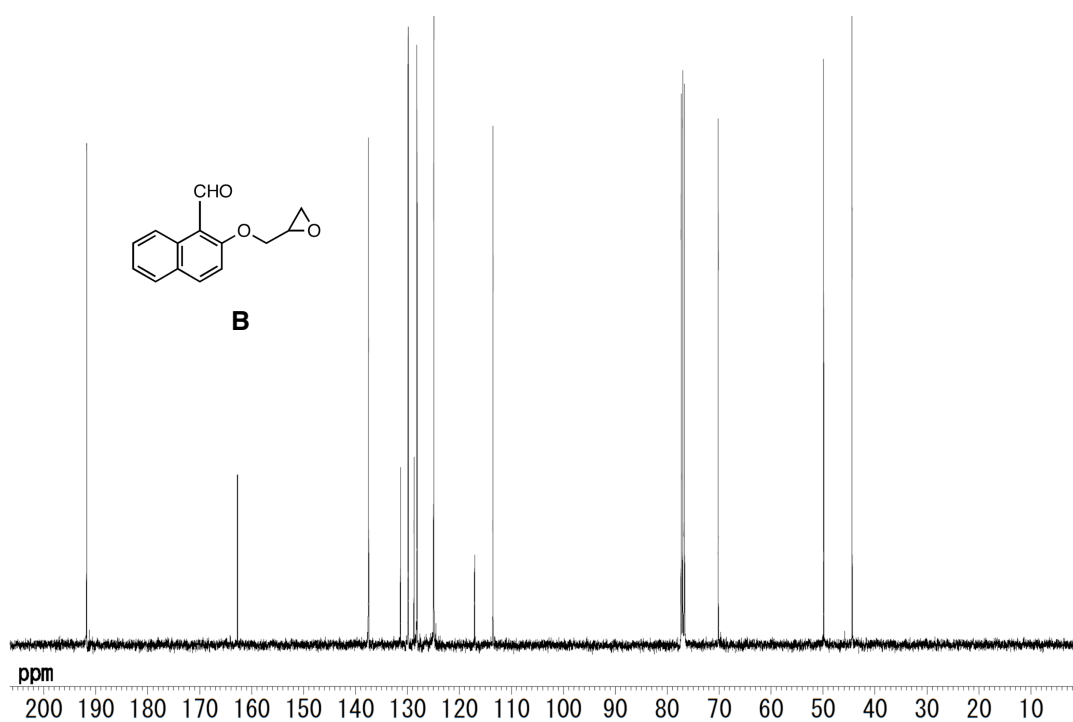
Table S3. Results of stress-strain measurement of cross-linked NRs.

entry	amount of cross-linker (mol%)	degree of cross-link (%) ^a	Young's modulus (%) ^b	tensile strength ^c (MPa)	elongation ^d (%)
ref.	–	–	0.62	6.34	1100
1	25	1.2	0.50	5.04	698
2	50	2.5	0.86	5.20	452

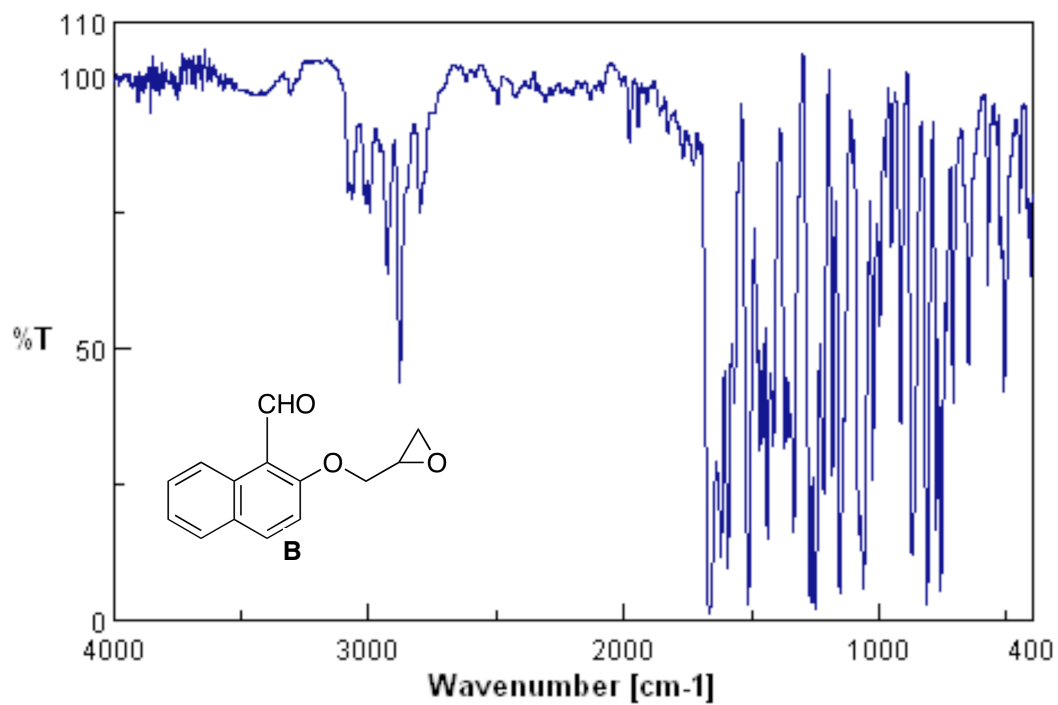
a) molar ratio of cross-linked alkenes / feedalkenes. b) stress when strain is 100%. c) maxima of the stress. d) maxima of the strain.



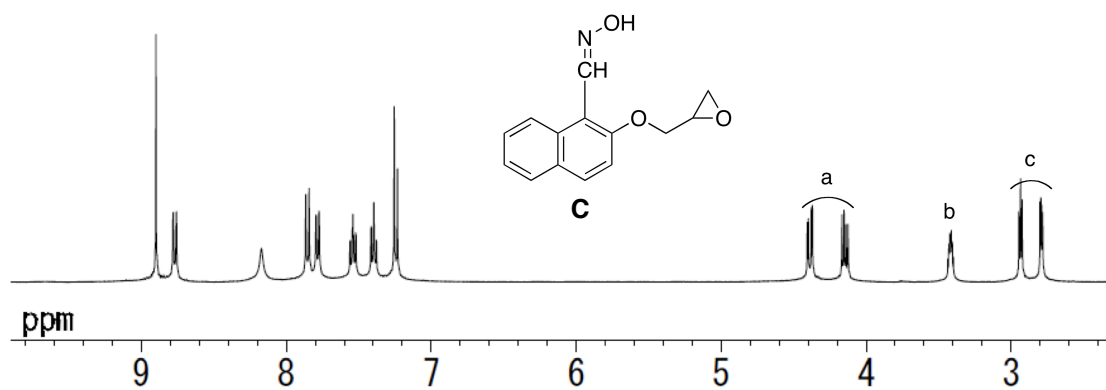
^1H NMR spectrum of **B** (400 MHz, CDCl_3 , 298 K)



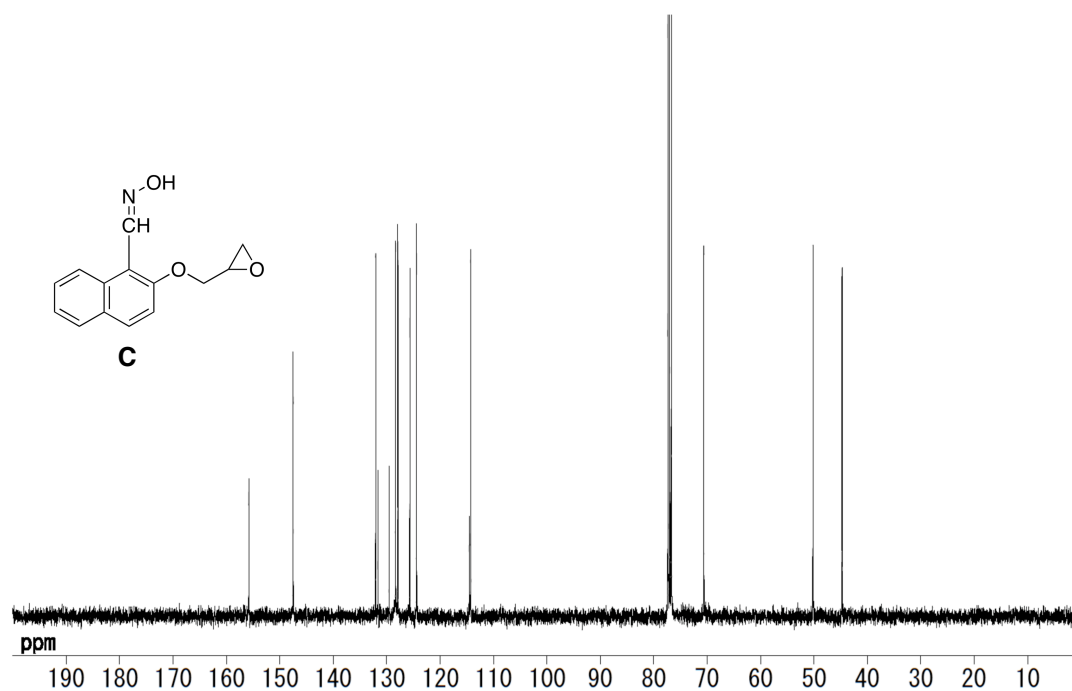
^{13}C NMR spectrum of **B** (100 MHz, CDCl_3 , 298 K)



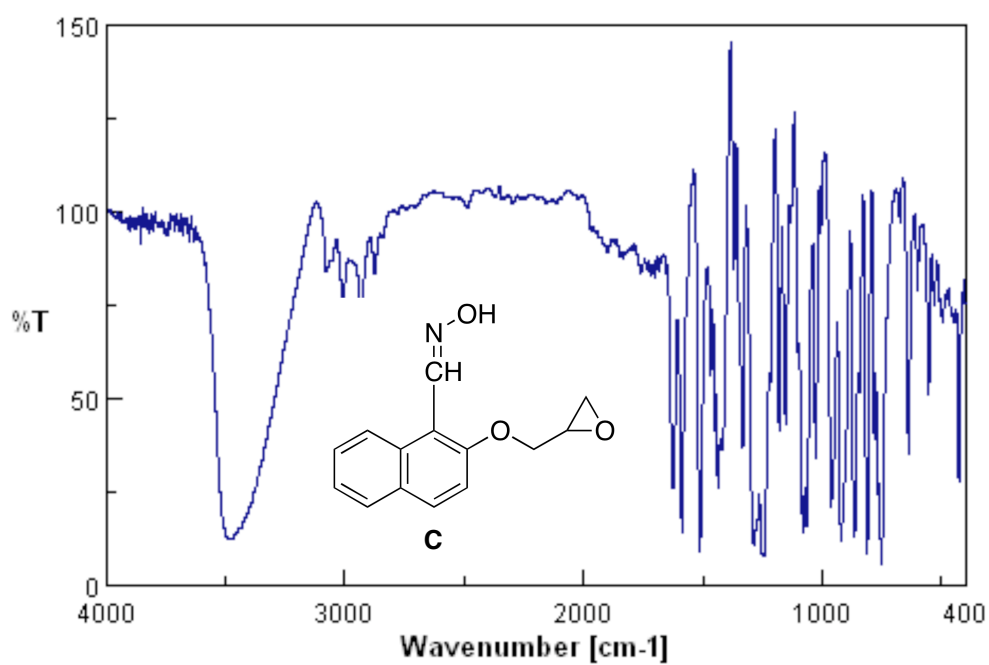
IR spectrum of **B** (KBr)



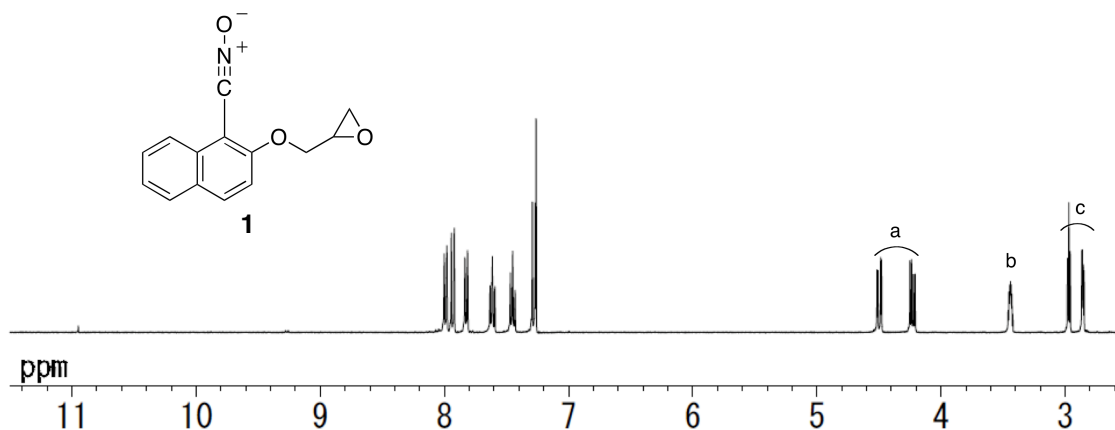
¹H NMR spectrum of **C** (400 MHz, DMSO-*d*₆, 298 K)



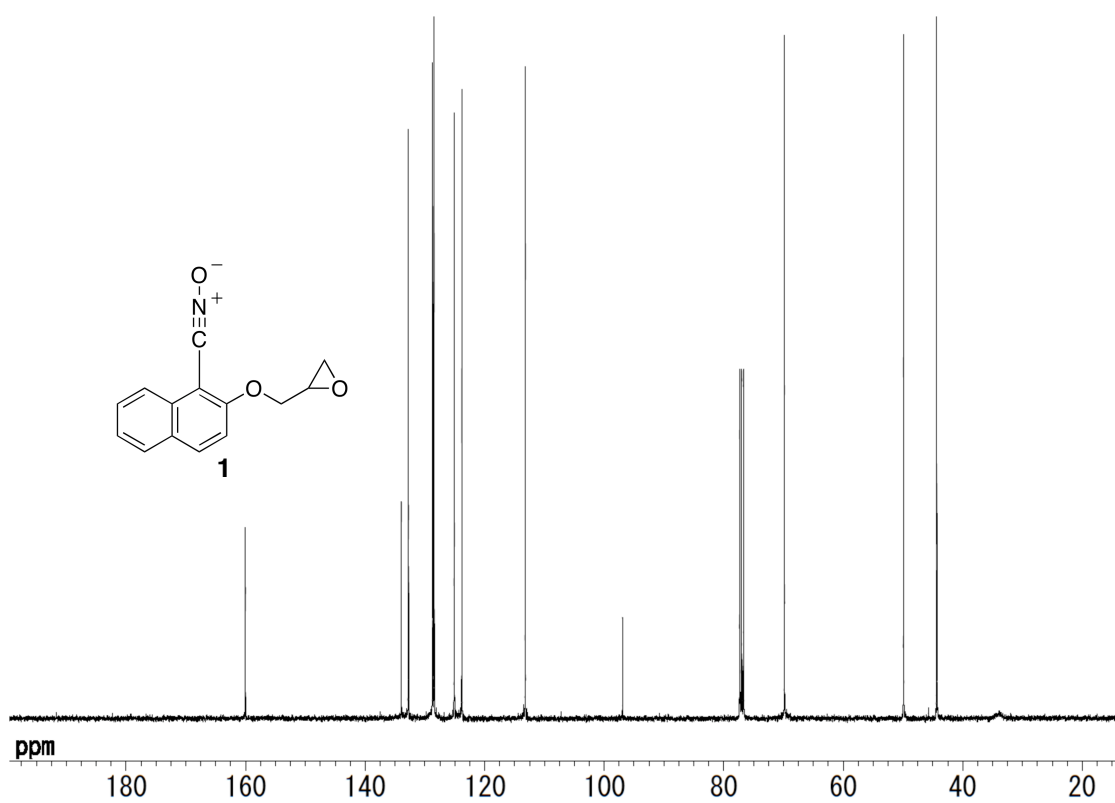
¹³C NMR spectrum of **C** (100 MHz, CDCl₃, 298 K)



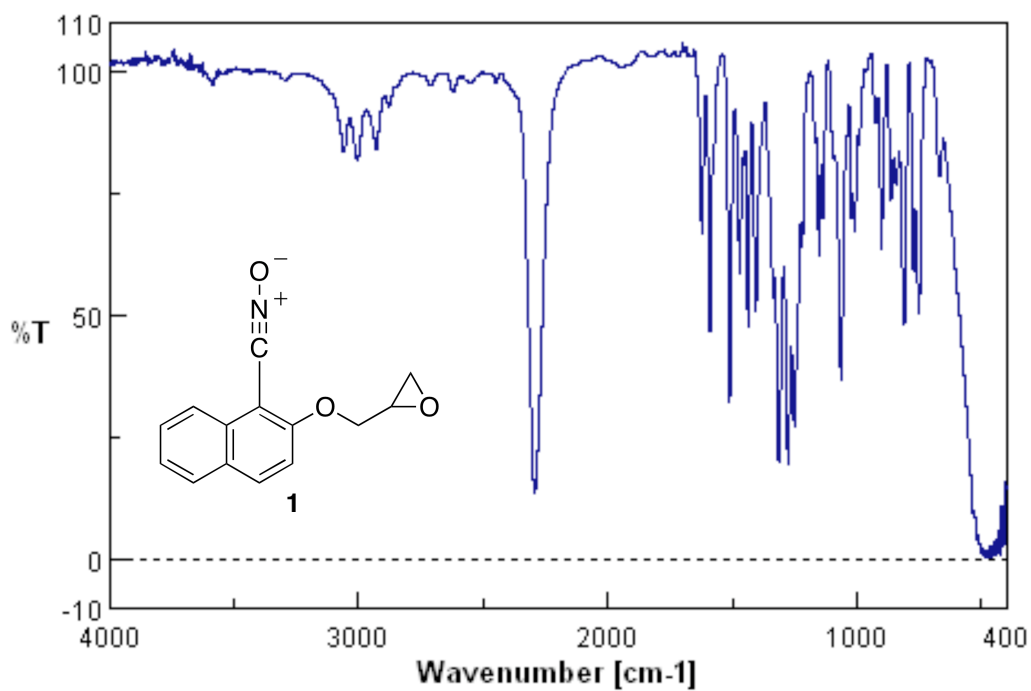
IR spectrum of **C** (KBr)



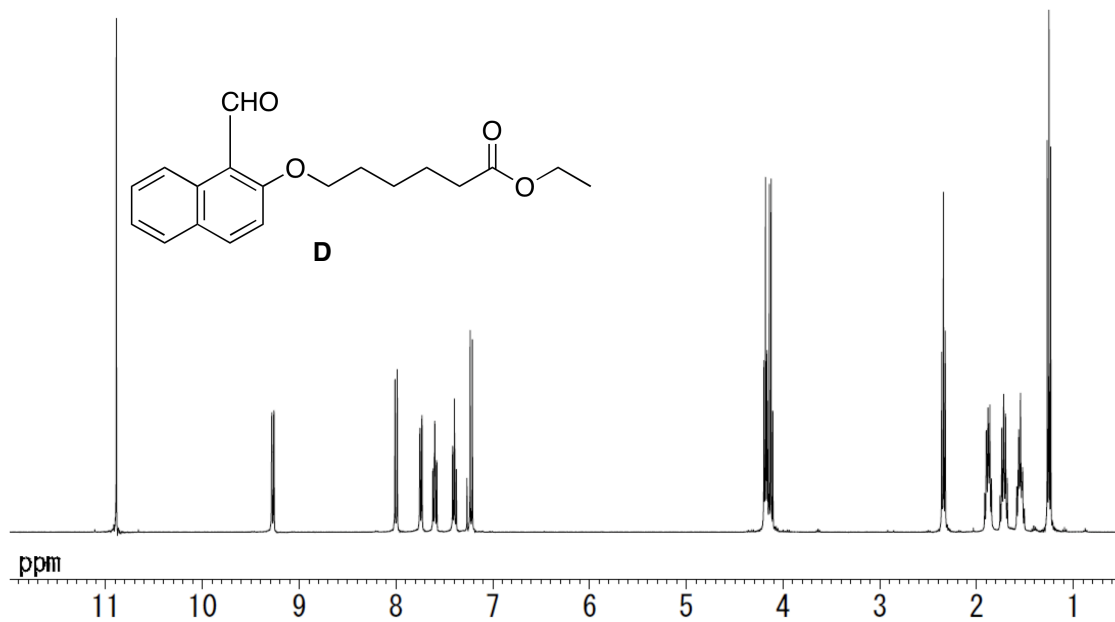
¹H NMR spectrum of **1** (400 MHz, CDCl₃, 298 K)



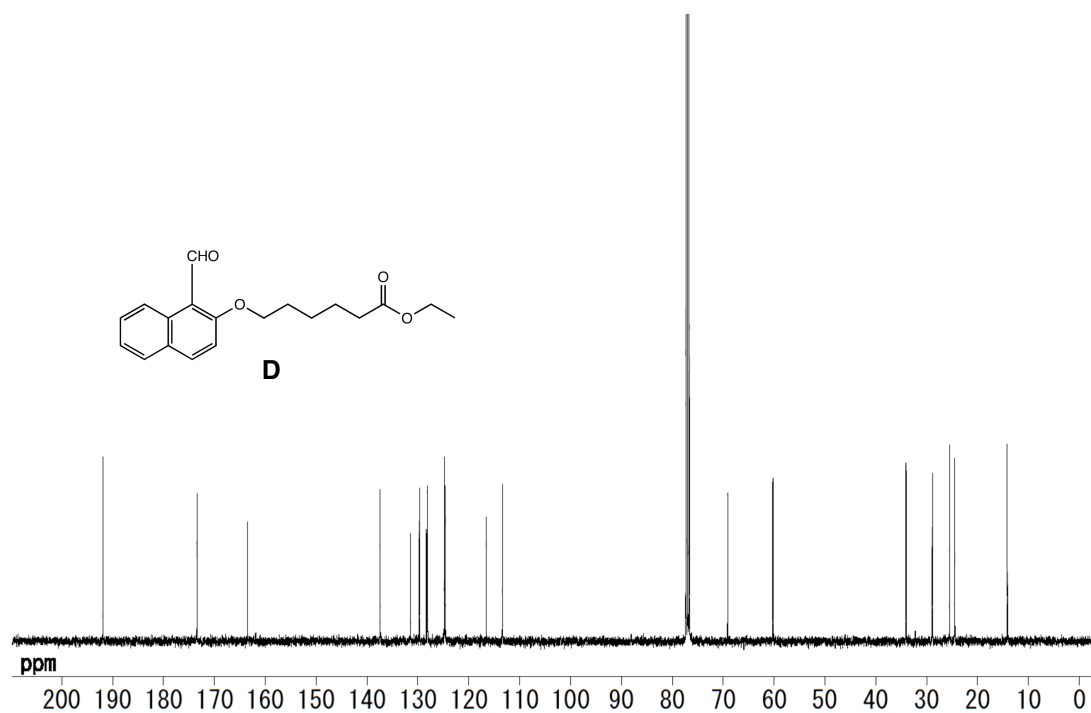
¹³C NMR spectrum of **1** (100 MHz, CDCl₃, 298 K)



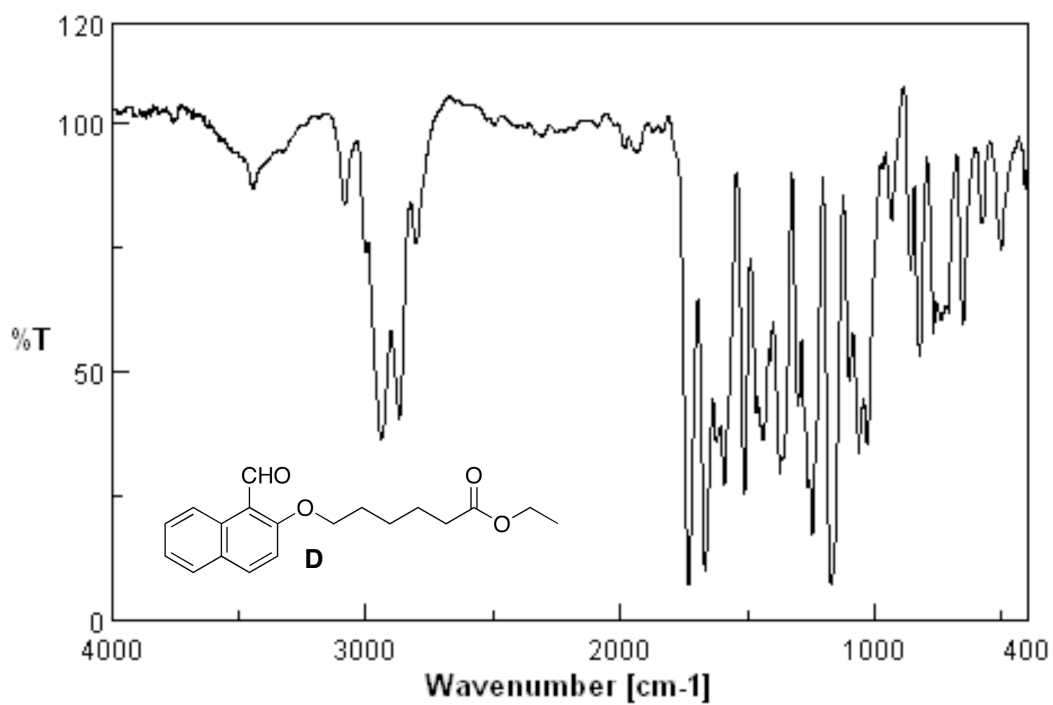
IR spectrum of **1** (KBr)



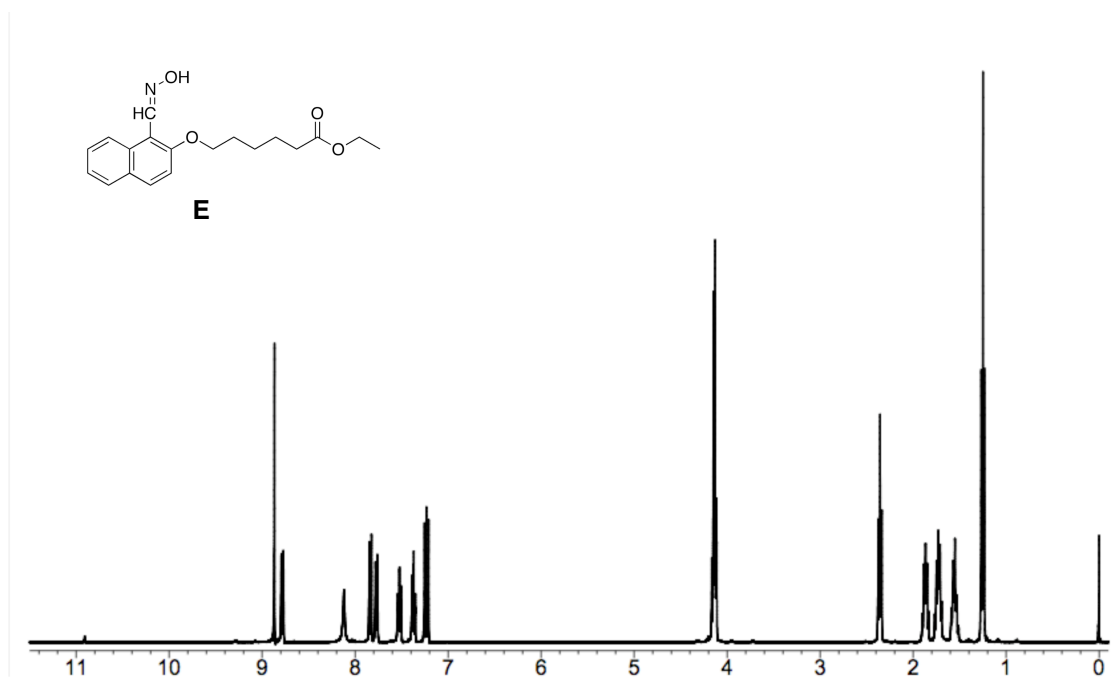
¹H NMR spectrum of **D** (400 MHz, CDCl₃, 298 K)



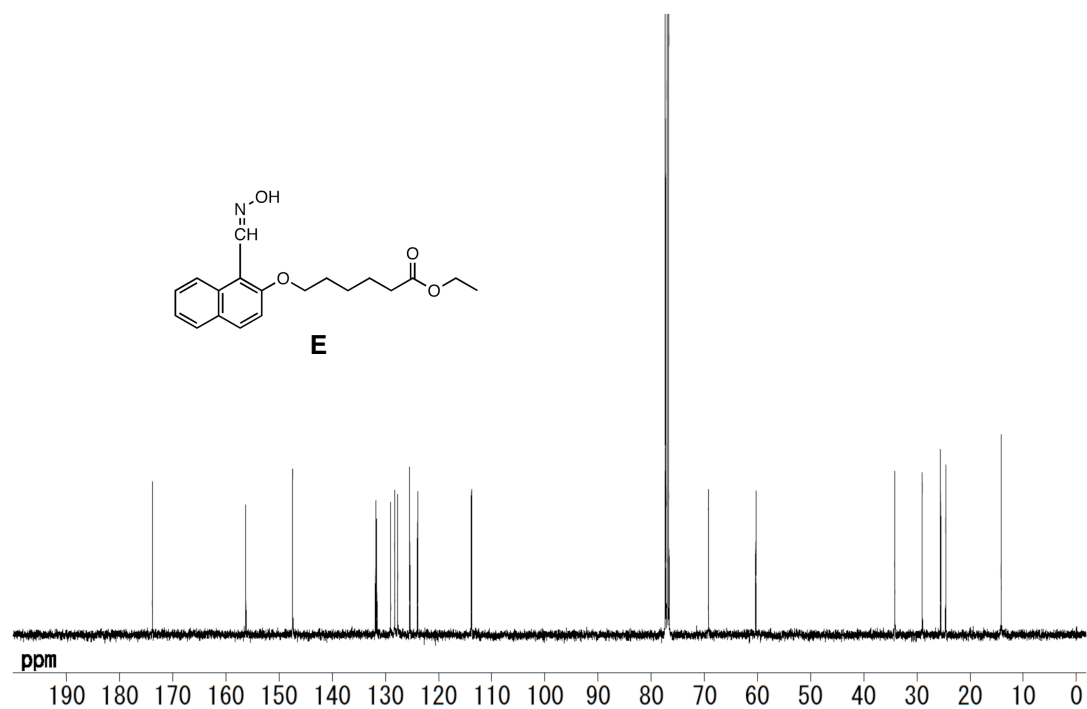
¹³C NMR spectrum of **D** (100 MHz, CDCl₃, 298 K)



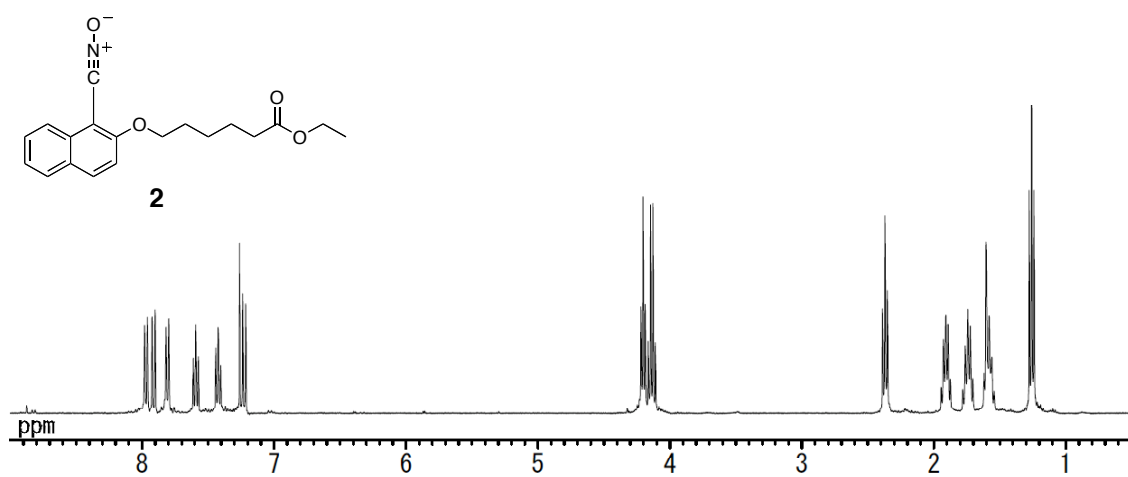
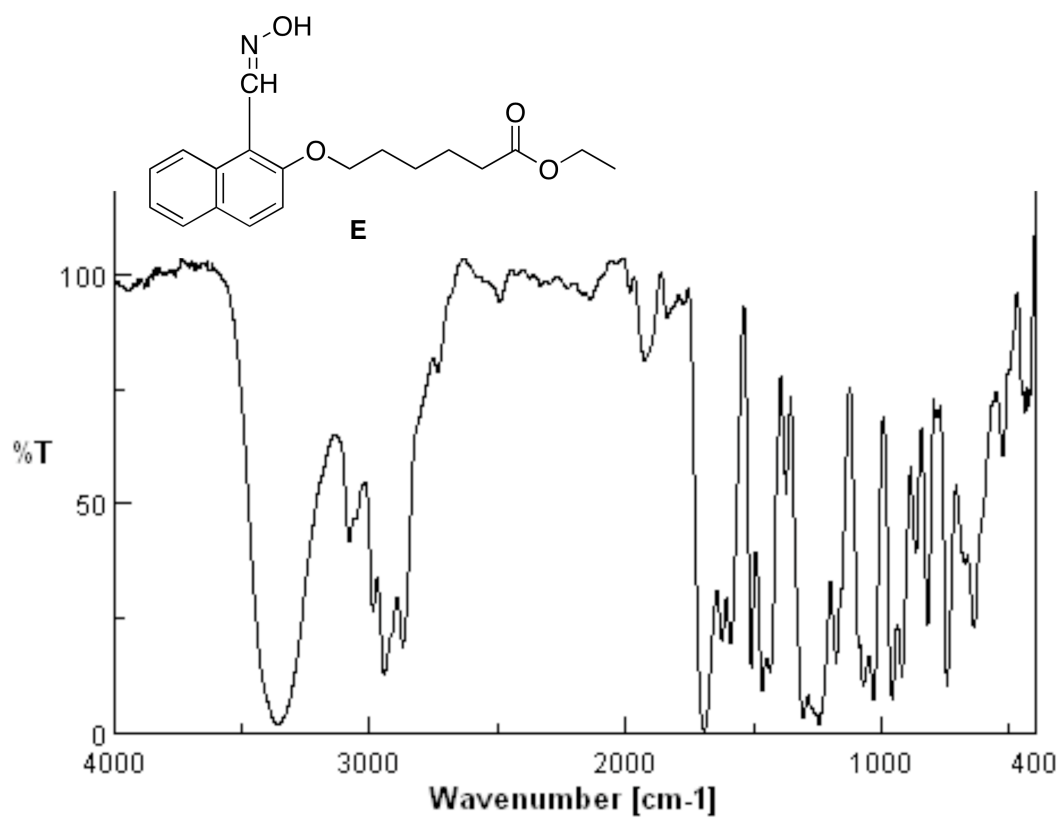
IR spectrum of **D** (KBr)

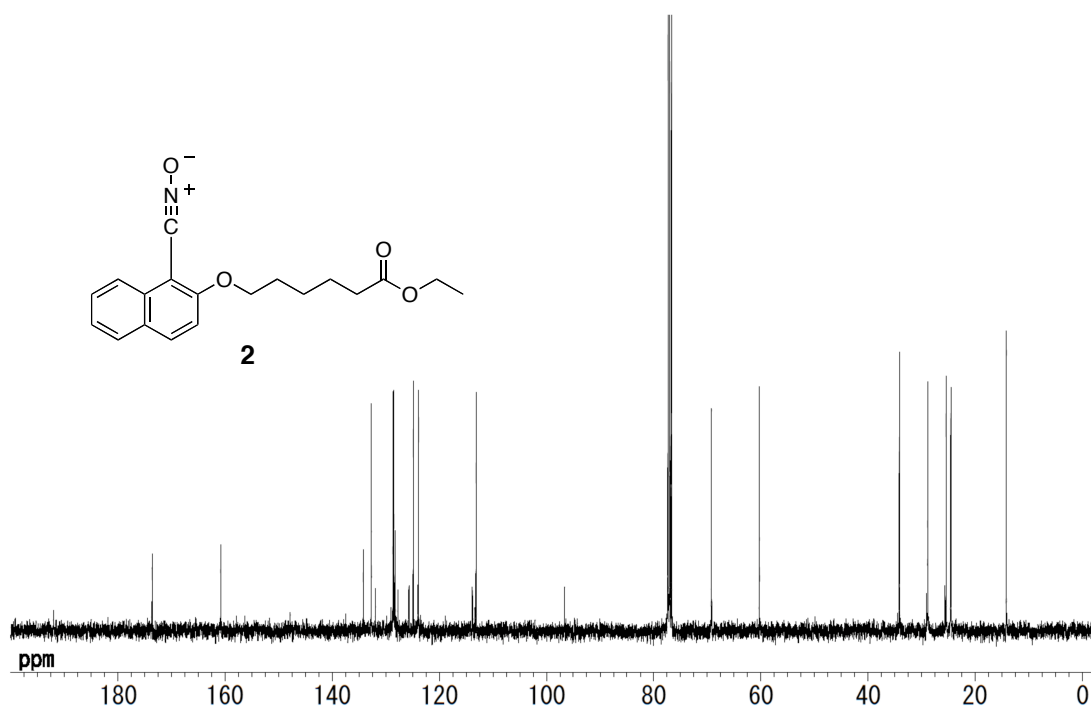


¹H NMR spectrum of **E** (400 MHz, DMSO-*d*₆, 298 K)

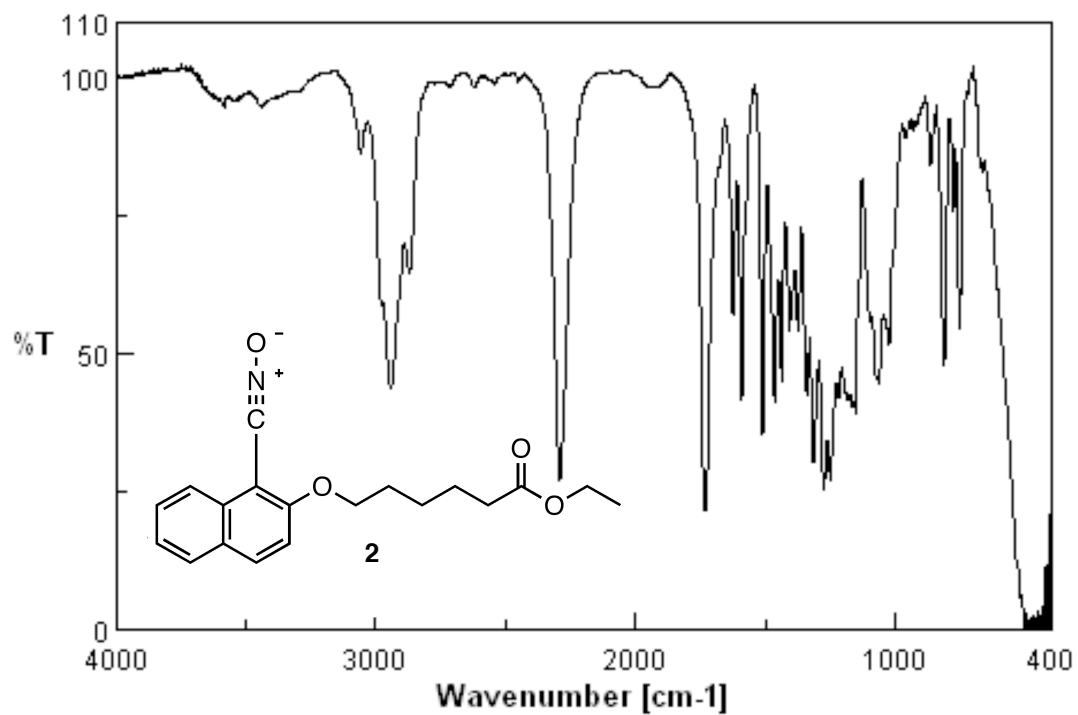


¹³C NMR spectrum of **E** (100 MHz, CDCl₃, 298 K)

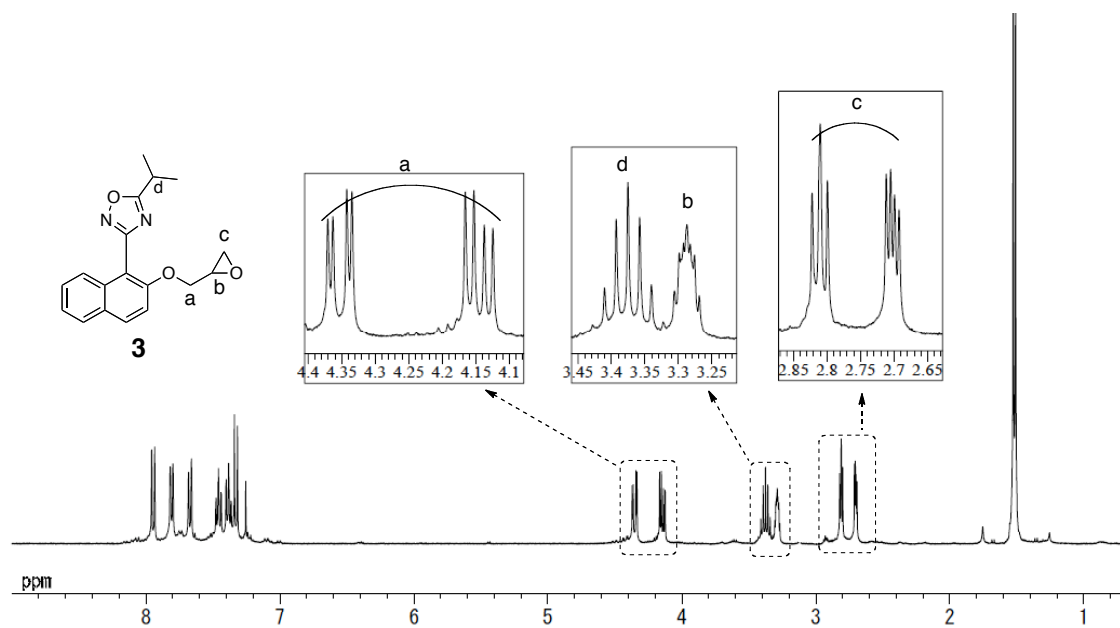




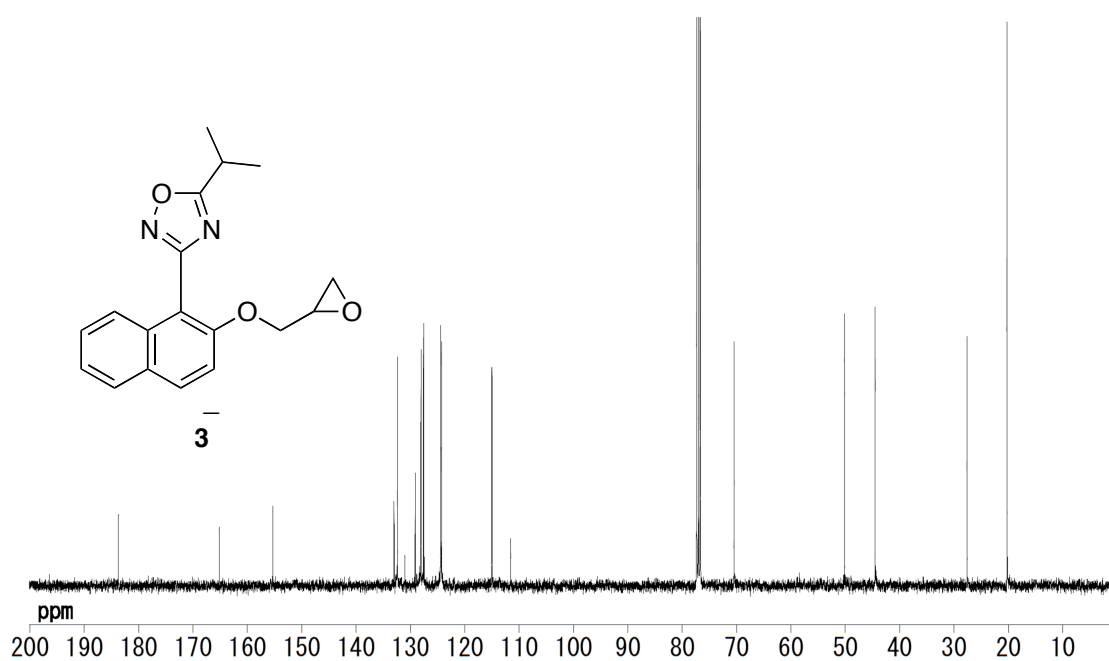
¹³C NMR spectrum of **2** (100 MHz, CDCl₃, 298 K)



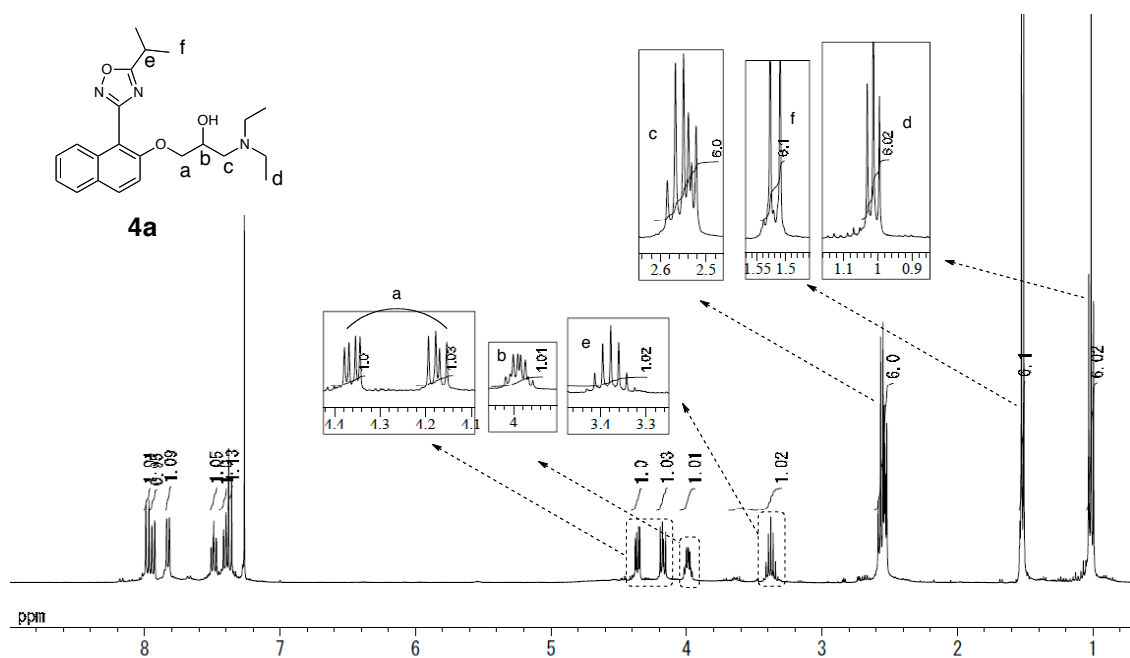
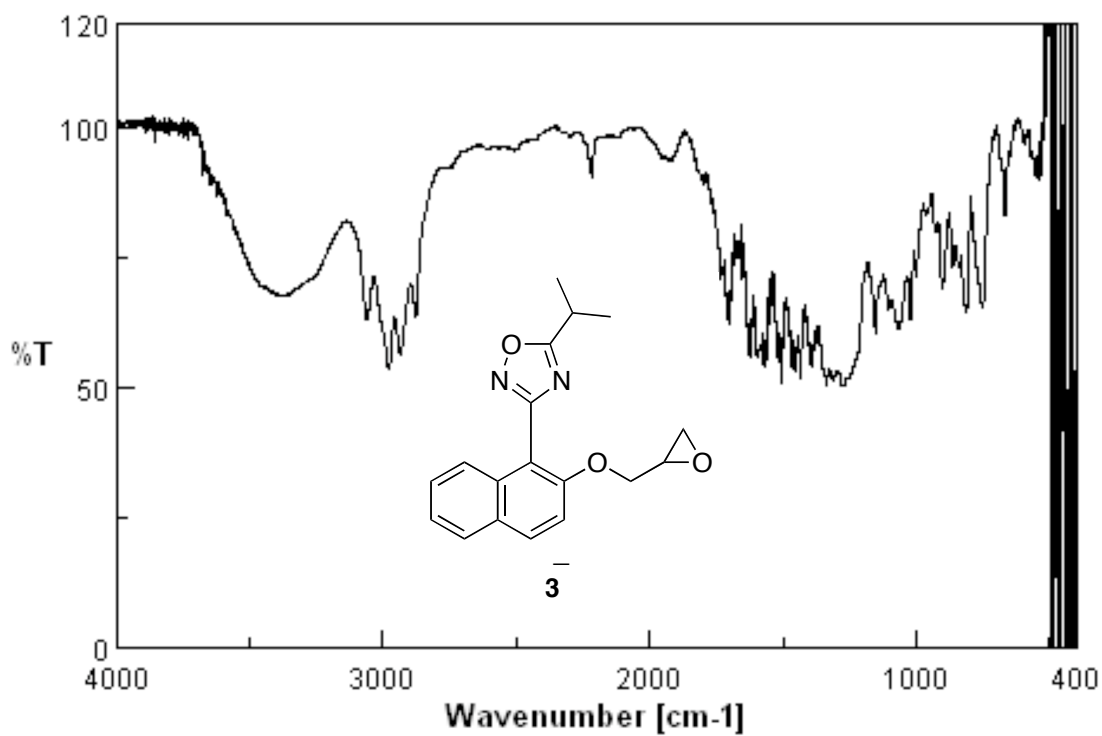
IR spectrum of **2** (KBr)



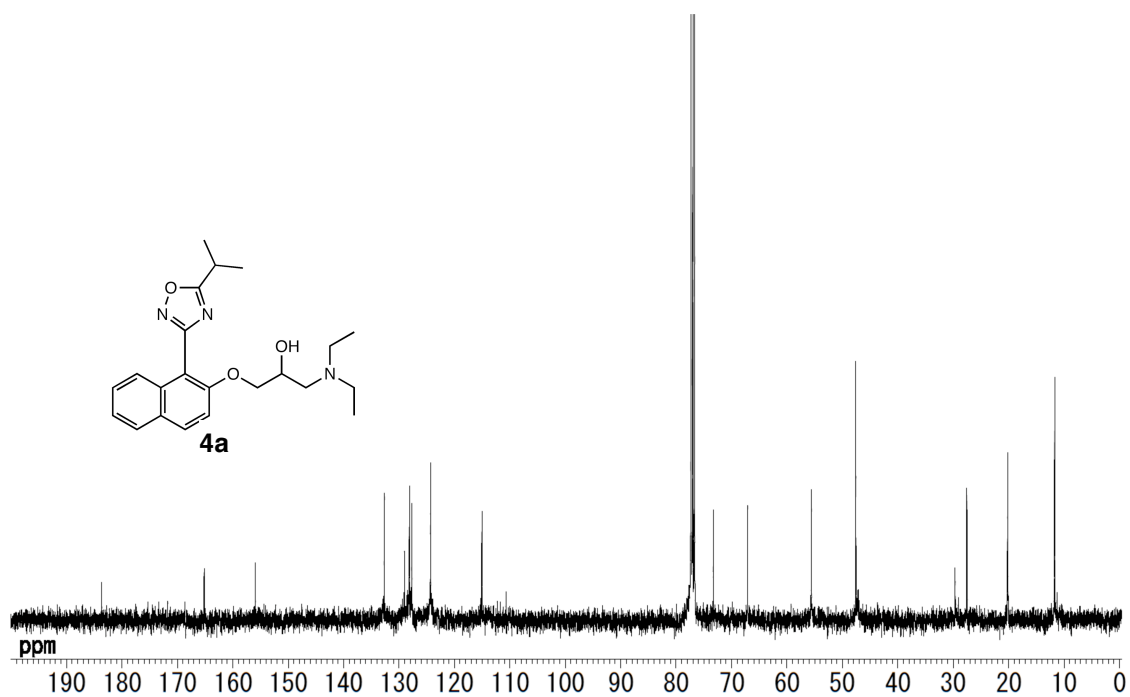
¹H NMR spectrum of **3** (400 MHz, CDCl₃, 298 K)



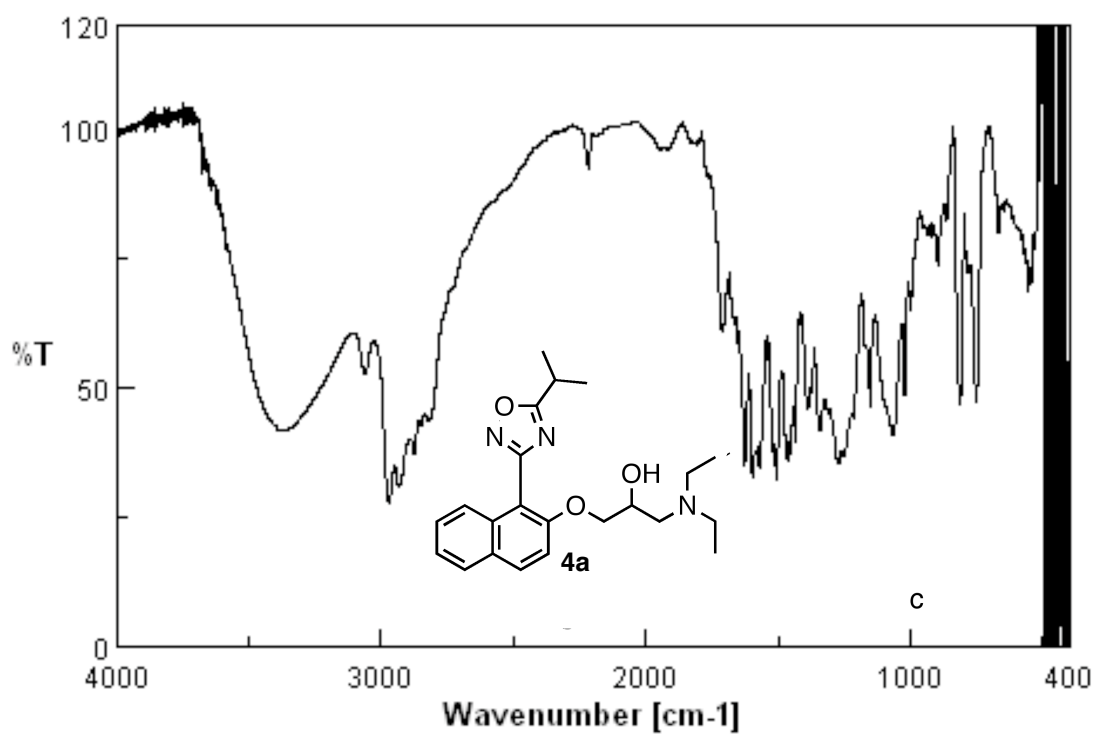
¹³C NMR spectrum of **3** (100 MHz, CDCl₃, 298 K)



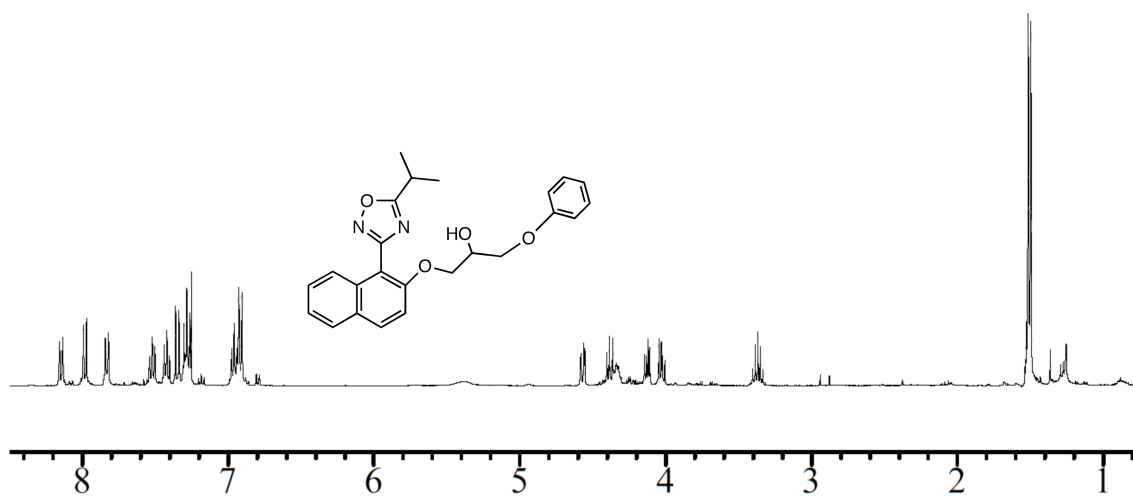
¹H NMR spectrum of **4a** (400 MHz, CDCl₃, 298 K)



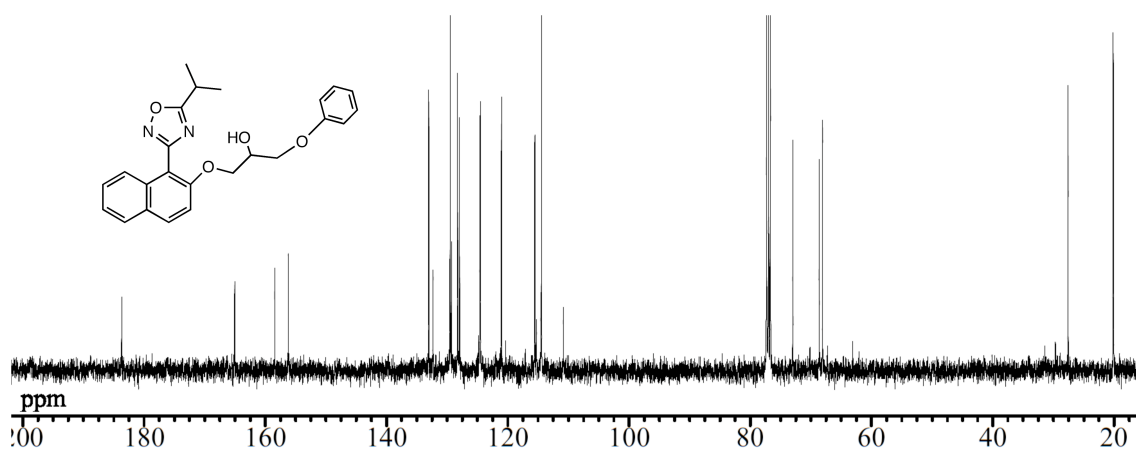
^{13}C NMR spectrum of **4a** (100 MHz, CDCl_3 , 298 K)



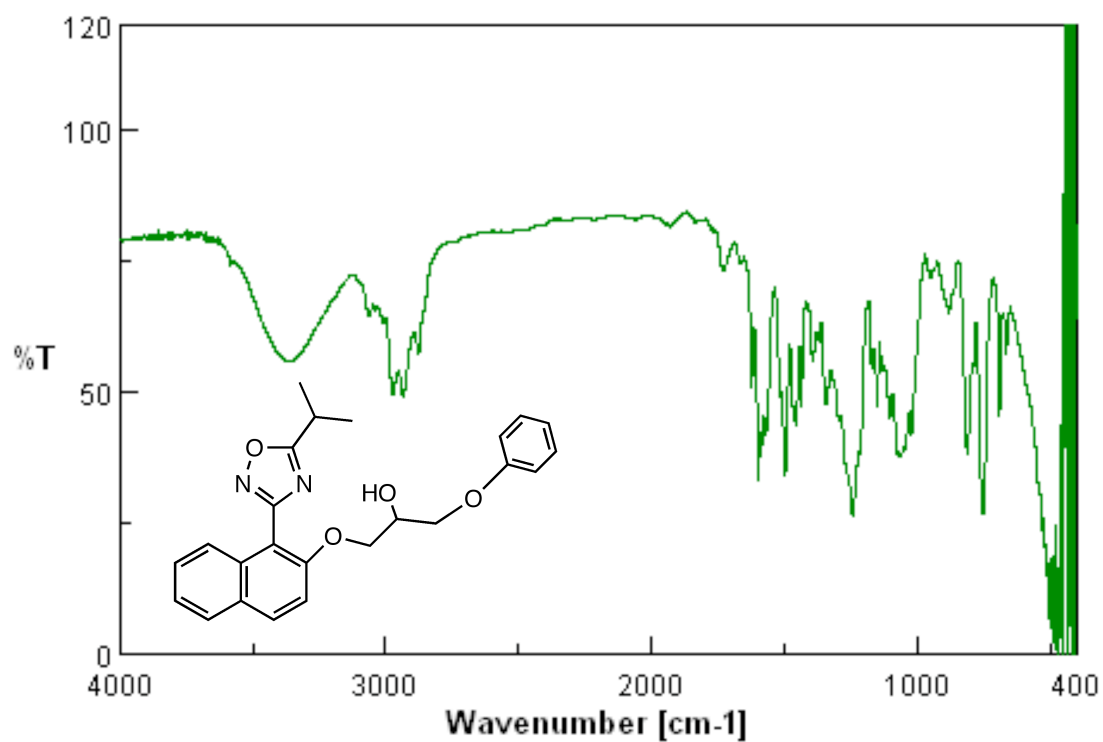
IR spectrum of **4a** (NaCl)



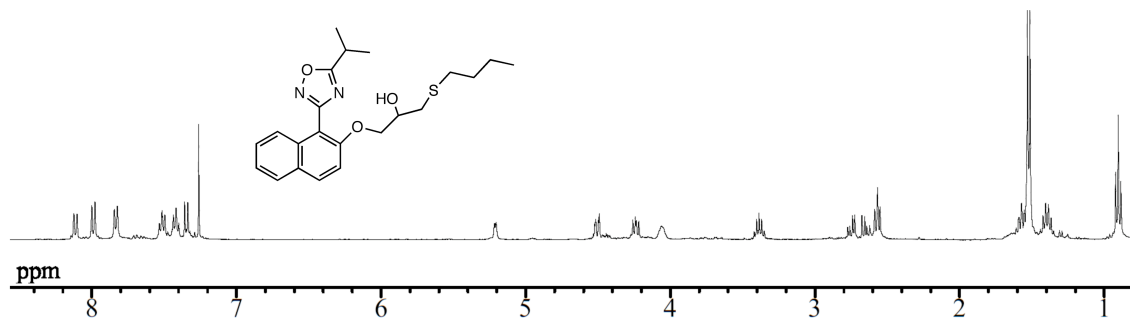
¹H NMR spectrum of **4b** (400 MHz, CDCl₃, 298 K)



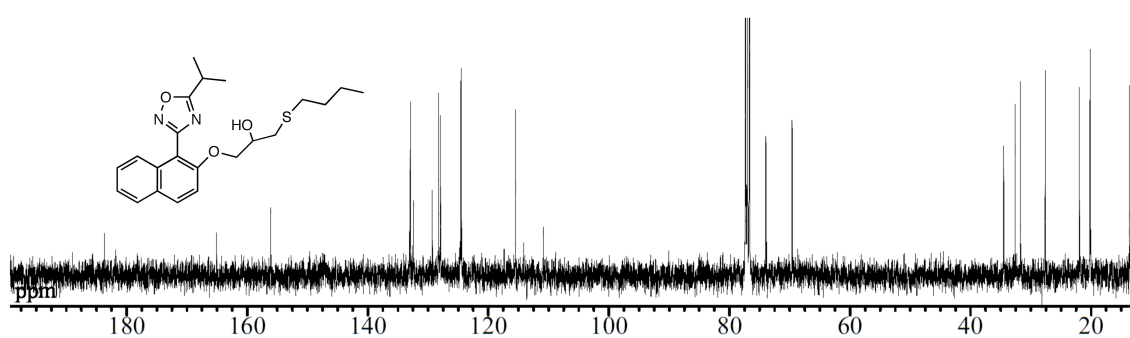
¹³C NMR spectrum of **4b** (100 MHz, CDCl₃, 298 K)



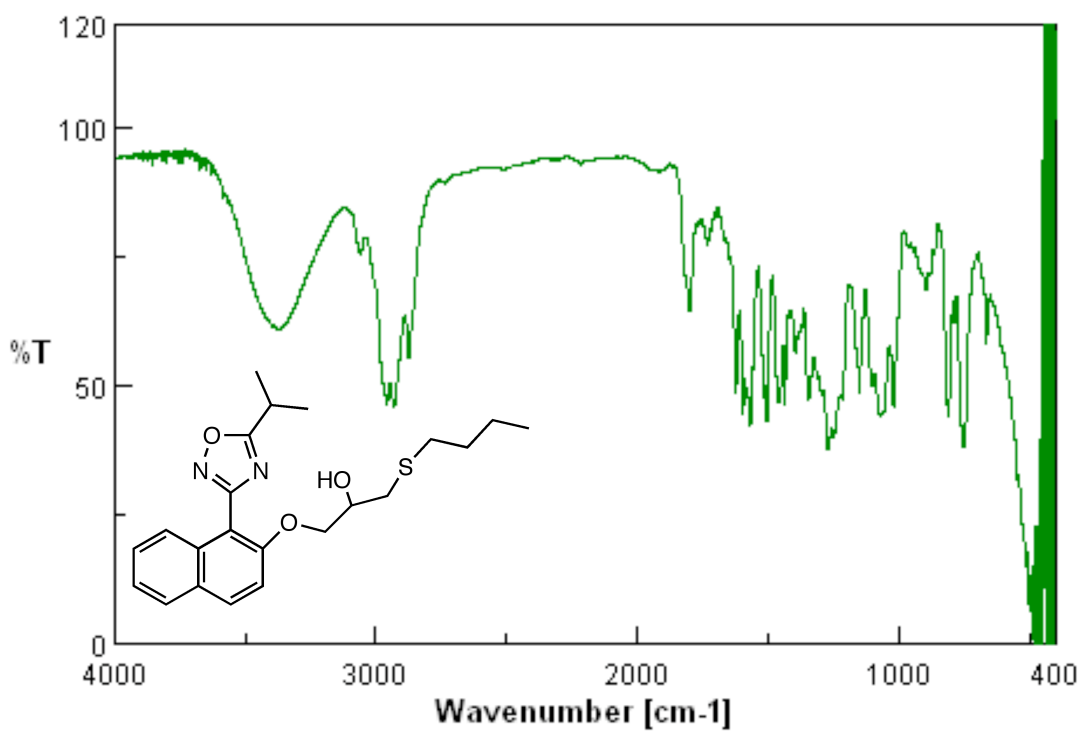
IR spectrum of **4b** (NaCl)



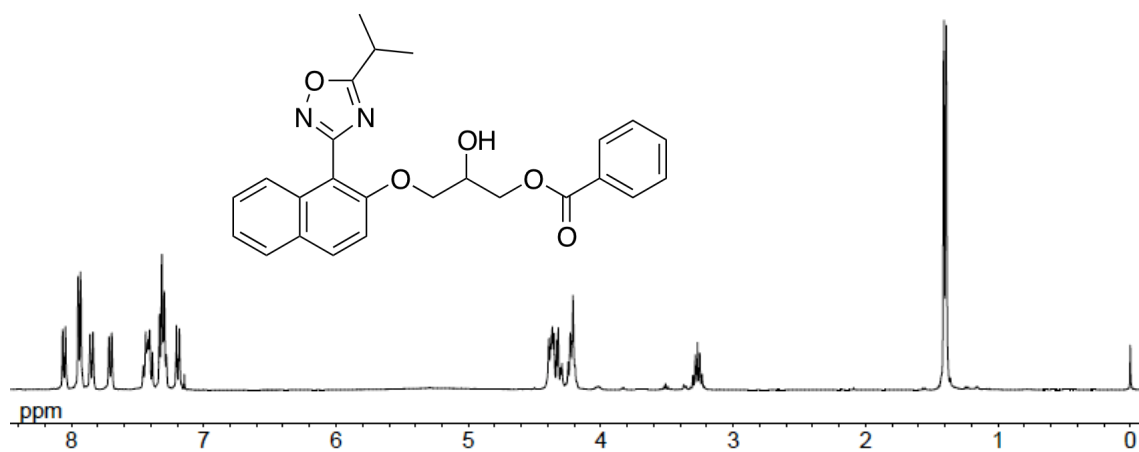
¹H NMR spectrum of **4c** (400 MHz, CDCl₃, 298 K)



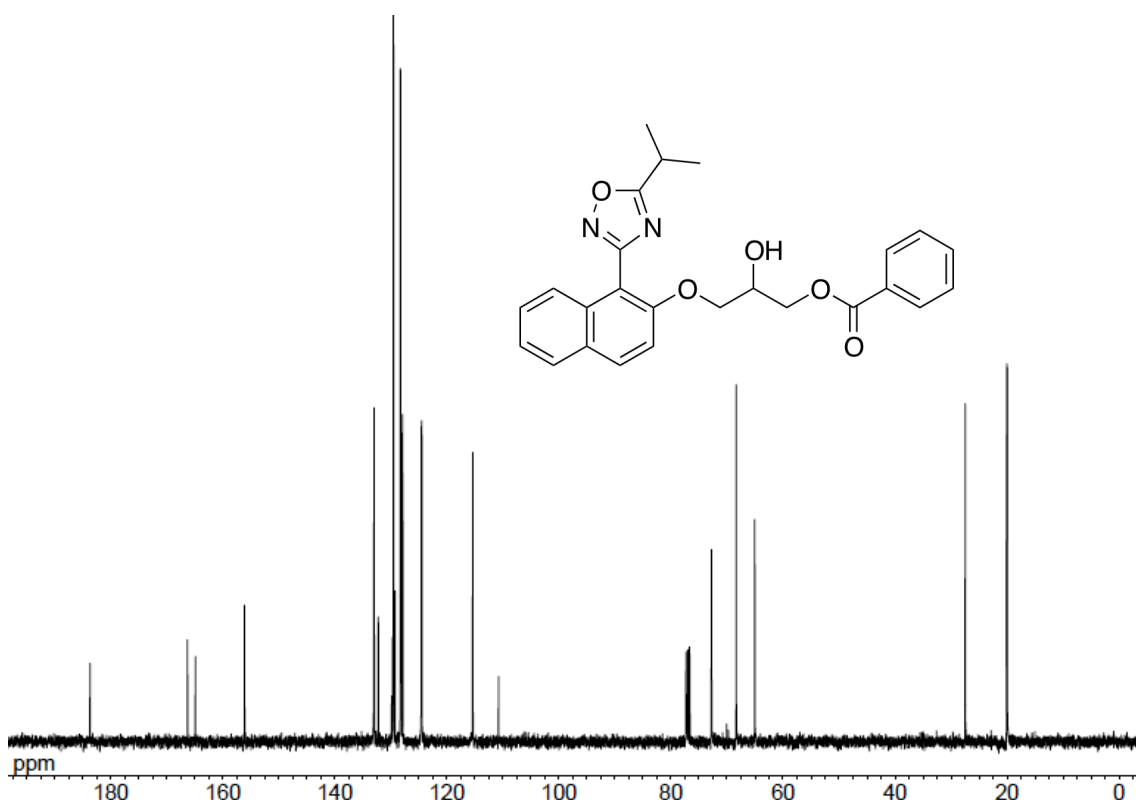
¹³C NMR spectrum of **4c** (100 MHz, CDCl₃, 298 K)



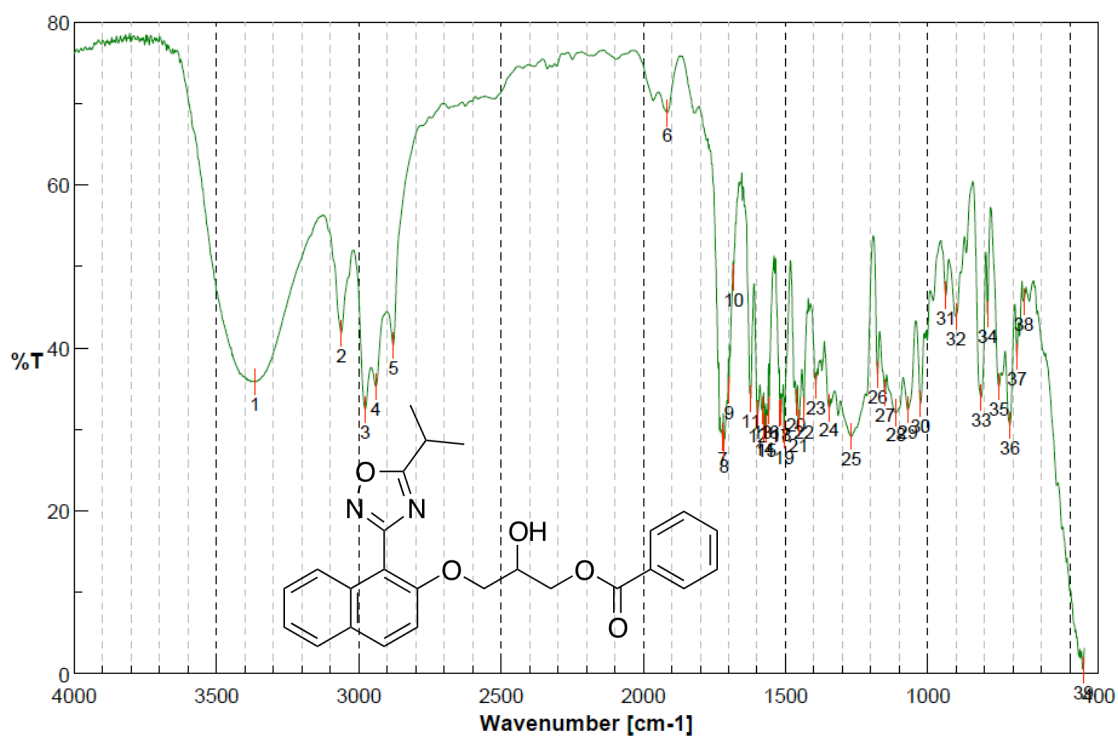
IR spectrum of **4c** (NaCl)



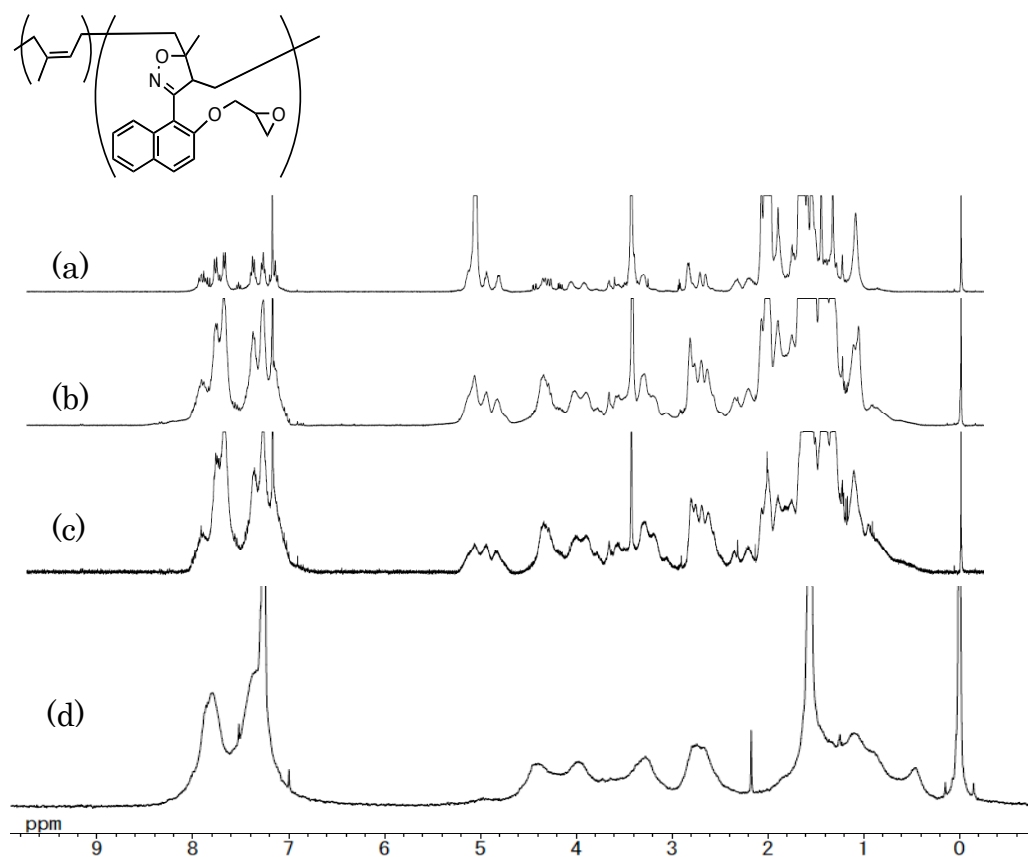
¹H NMR spectrum of **4d** (400 MHz, CDCl₃, 298 K)



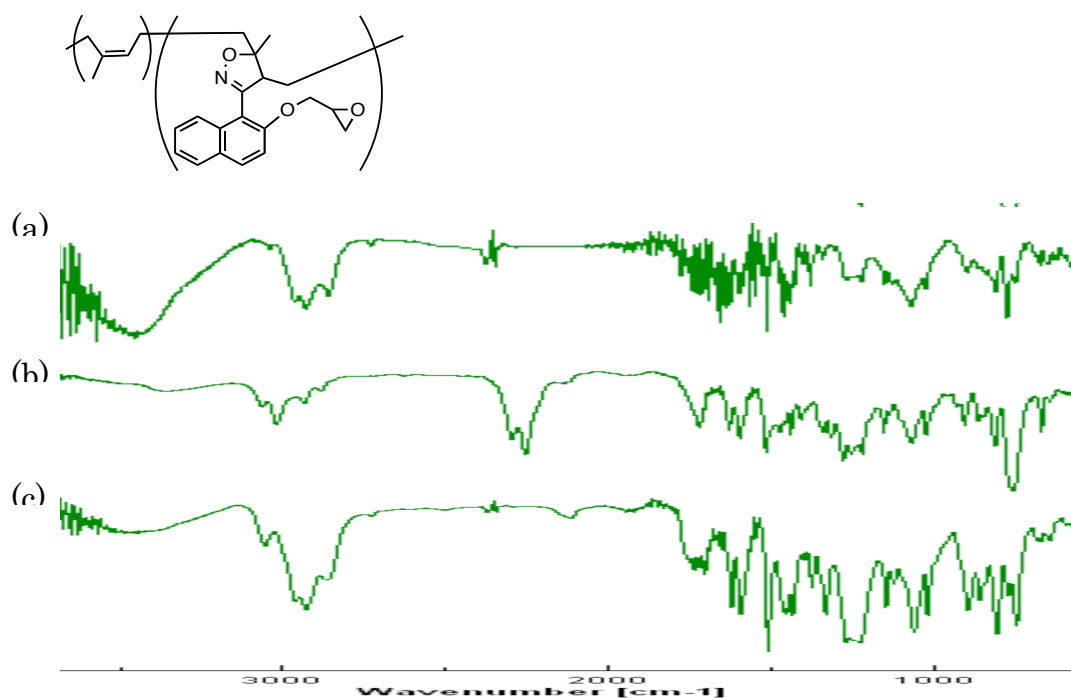
¹³C NMR spectrum of **4d** (100 MHz, CDCl₃, 298 K)



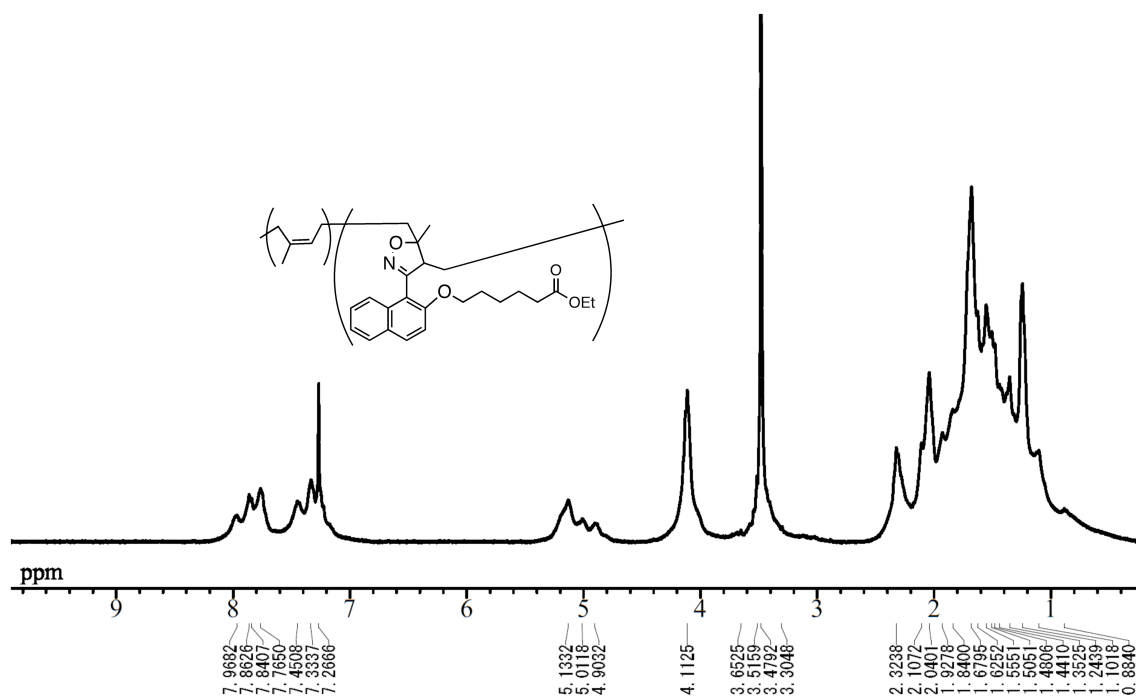
IR spectrum of **4d** (NaCl)



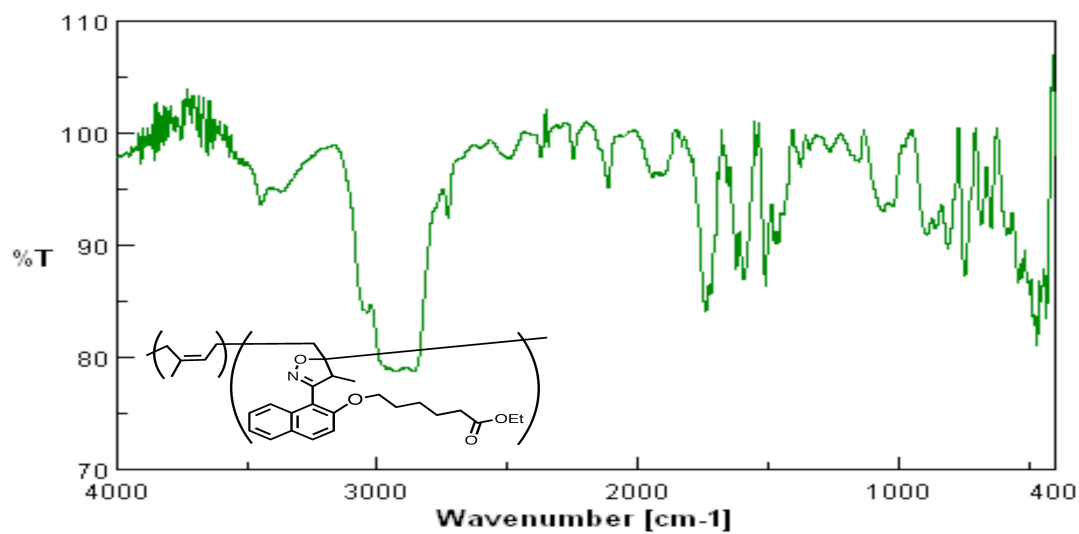
¹H NMR spectra of modified NR (with reagent **1**, (a) 2 h (Table 2, entry 2), (b) 24 h (entry 3), (c) 96 h (entry 4), and (d) 72 h (entry 5, 3.0 equiv of **1** were used for this reaction.)) (400 MHz, CDCl₃, 298 K)



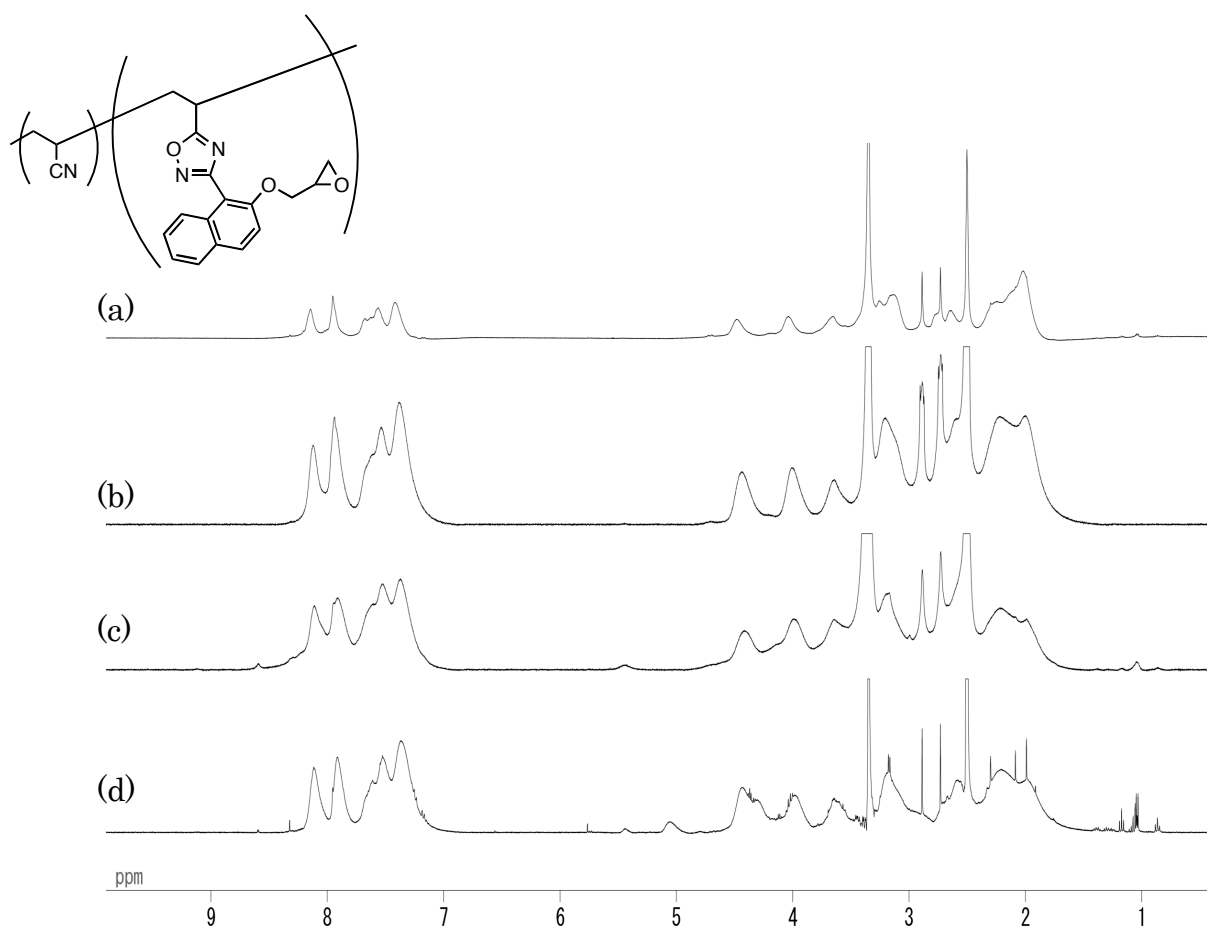
IR spectra of modified NR (with reagent **1**, (a) 2, (b) 24, and (c) 96 h)
(KBr)



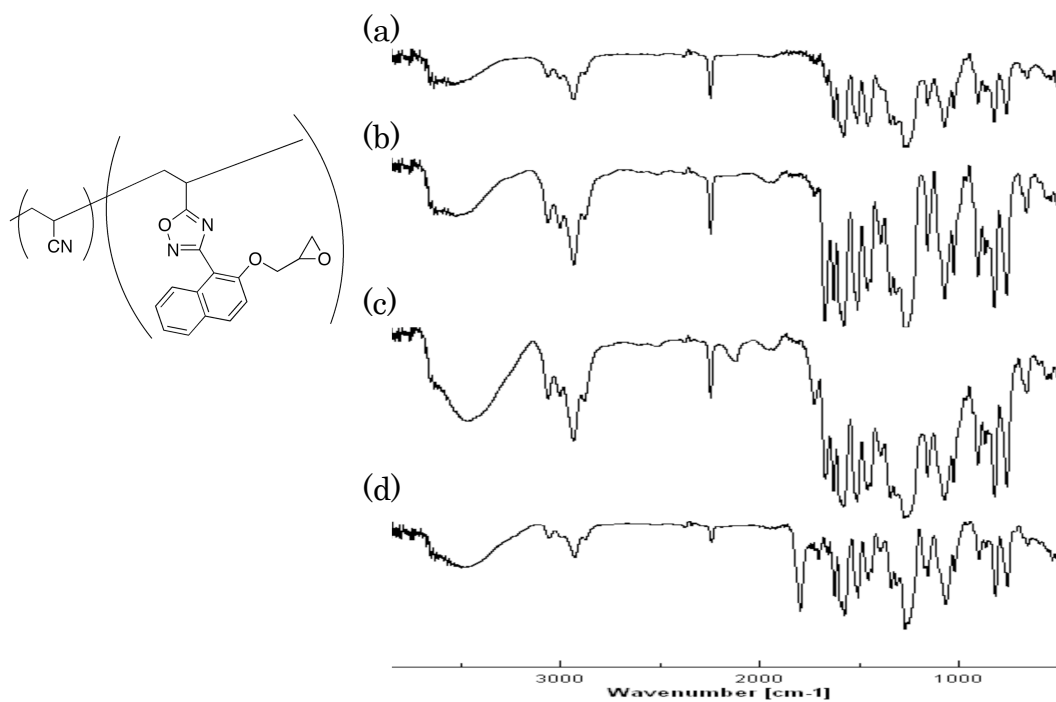
¹H NMR spectra of modified NR (with reagent **2**)(400 MHz, CDCl₃, 298 K)



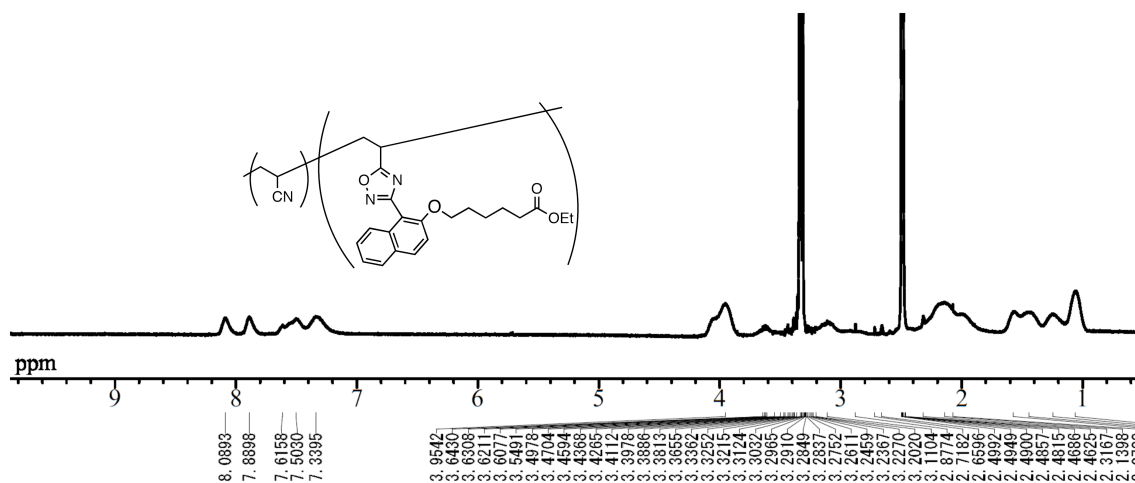
IR spectrum of modified NR (with reagent **2**) (KBr)



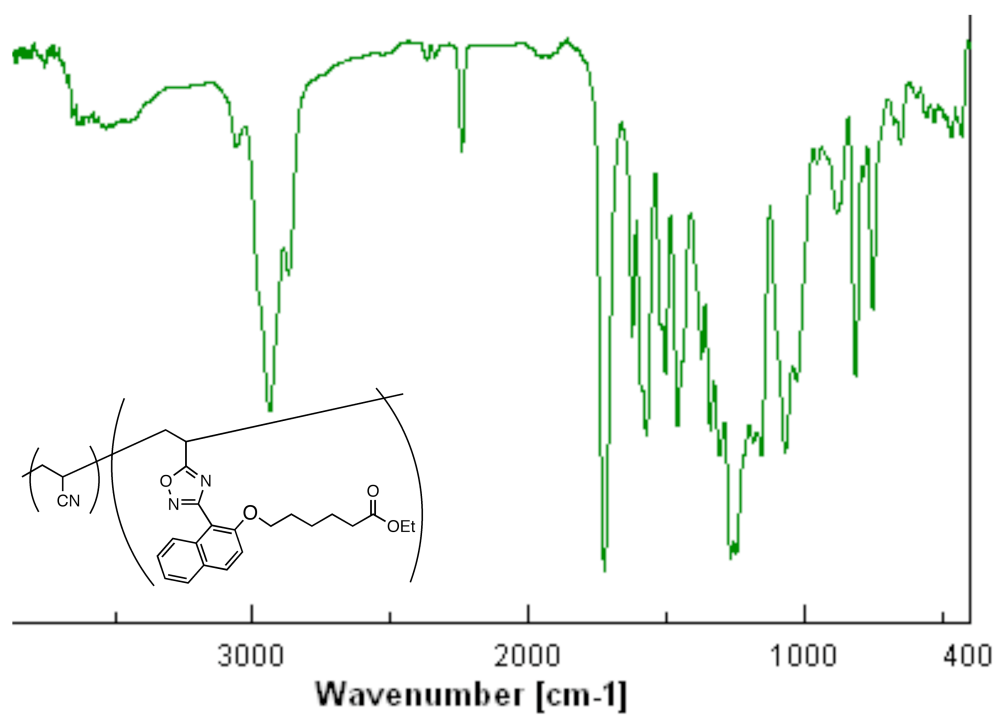
¹H NMR spectra of modified PAN (with reagent **1**, (a) 1, (b) 4, (c) 24, and (d) 96 h) (400 MHz, DMSO, 298 K)



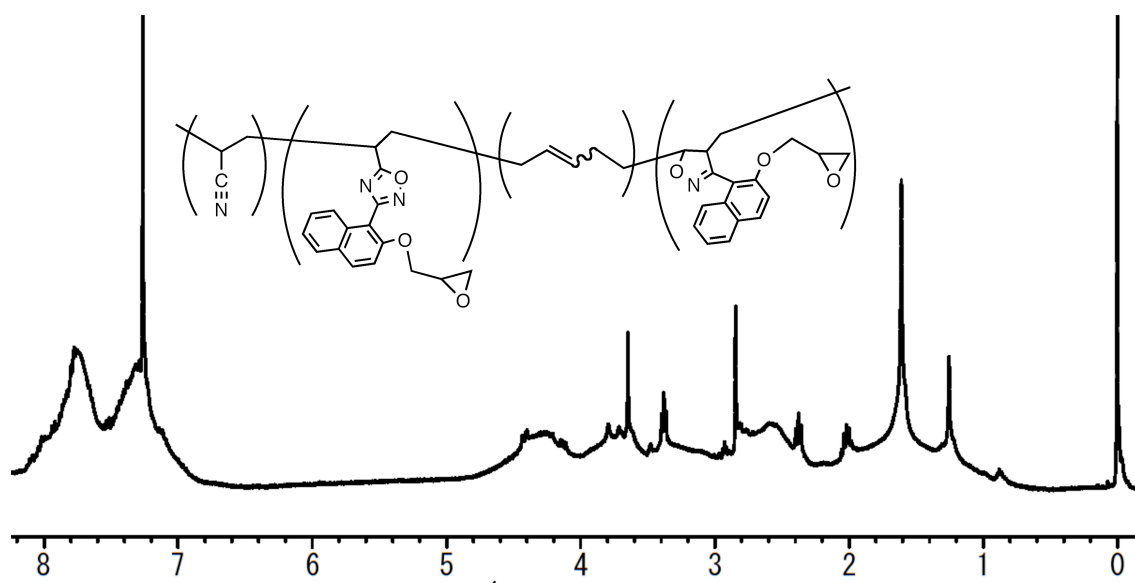
IR spectra of modified PAN (with reagent **1**, (a) 1, (b) 4, (c) 24, and (d) 96 h)
(KBr)



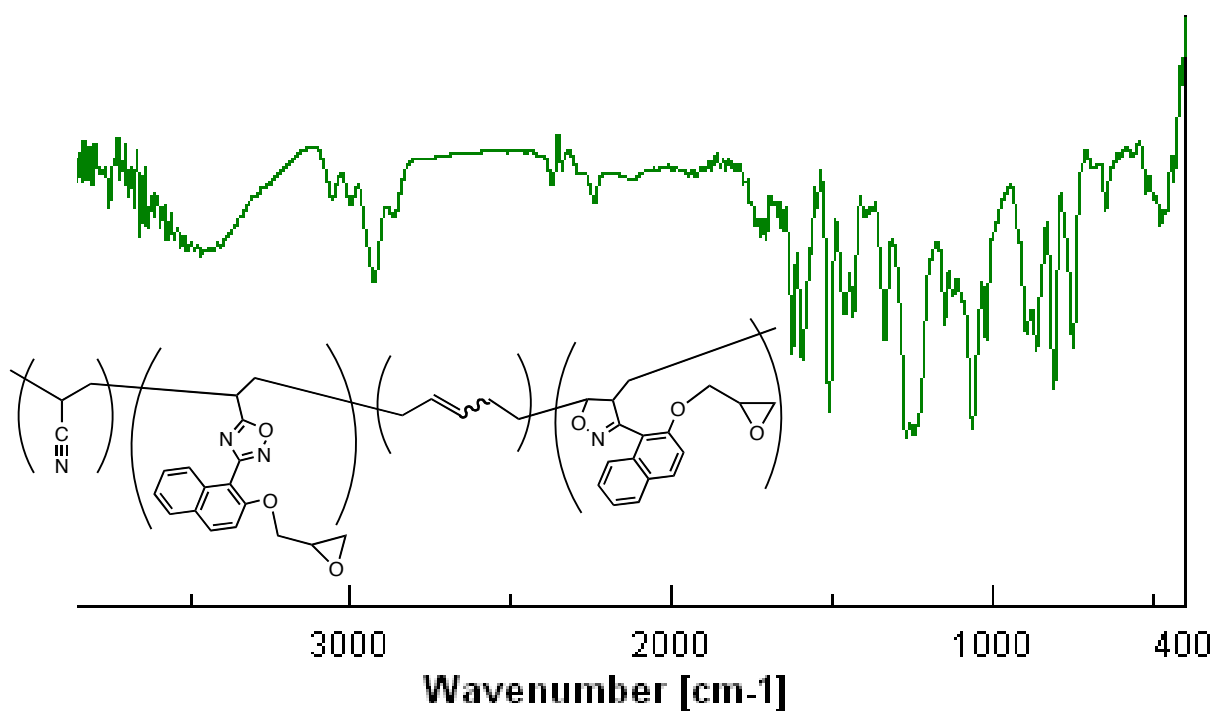
¹H NMR spectra of modified PAN (with reagent **2**)(400 MHz, DMSO-*d*₆, 298 K)



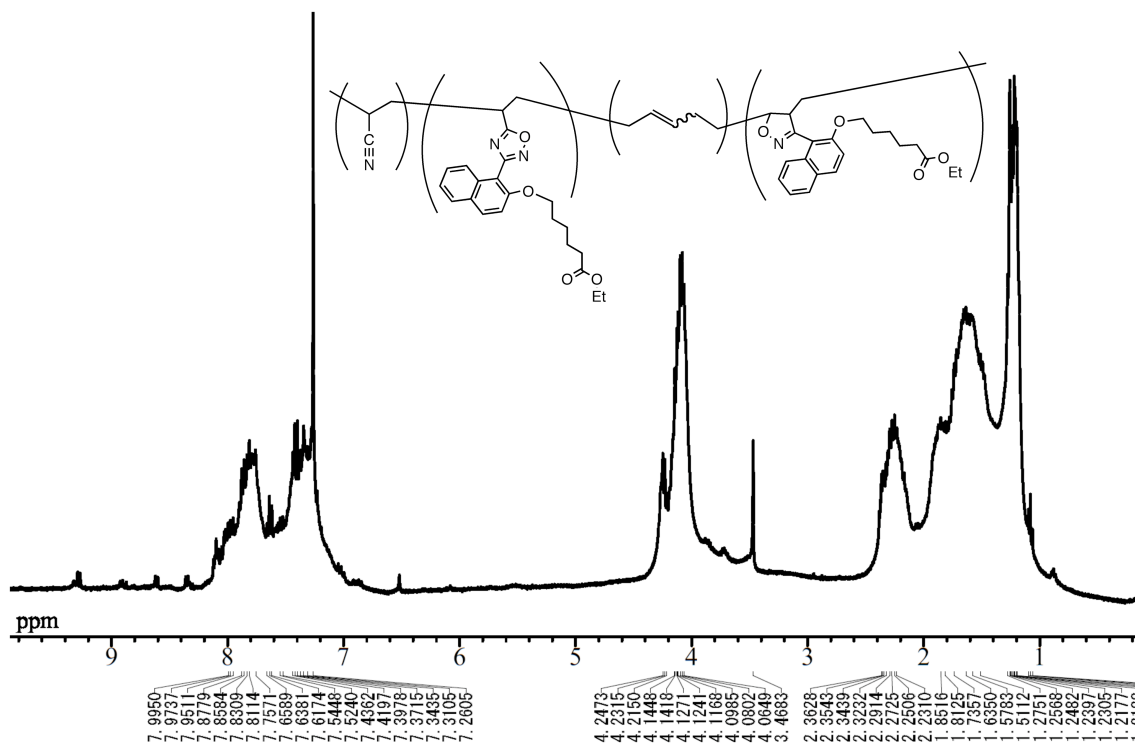
IR spectrum of modified PAN (with reagent **2**) (KBr)



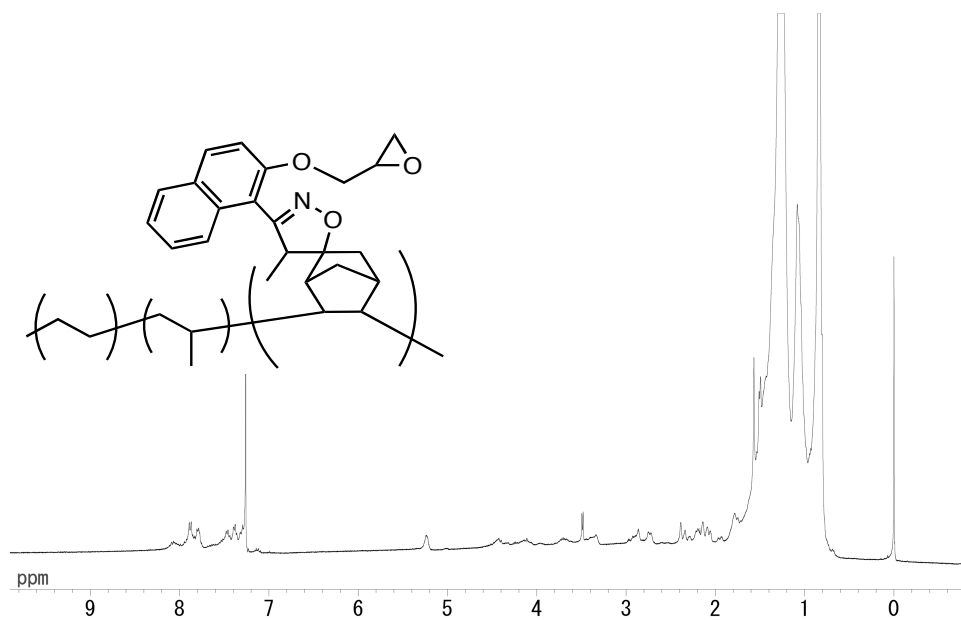
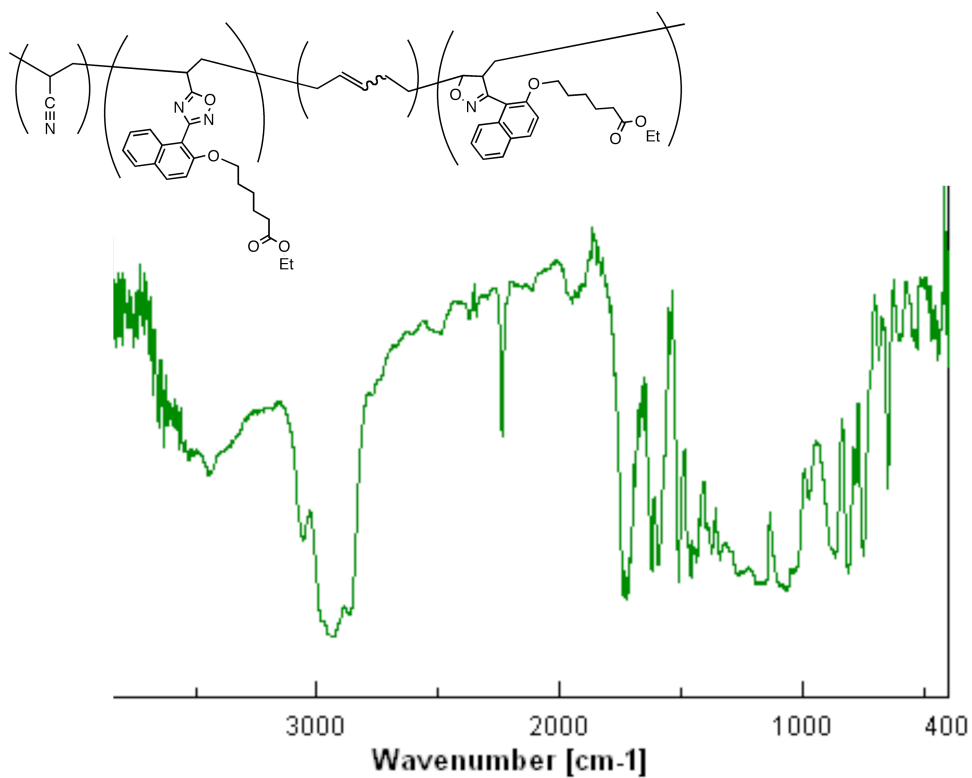
¹H NMR spectrum of modified NBR (with reagent **1**) (400 MHz, CDCl₃, 298 K)

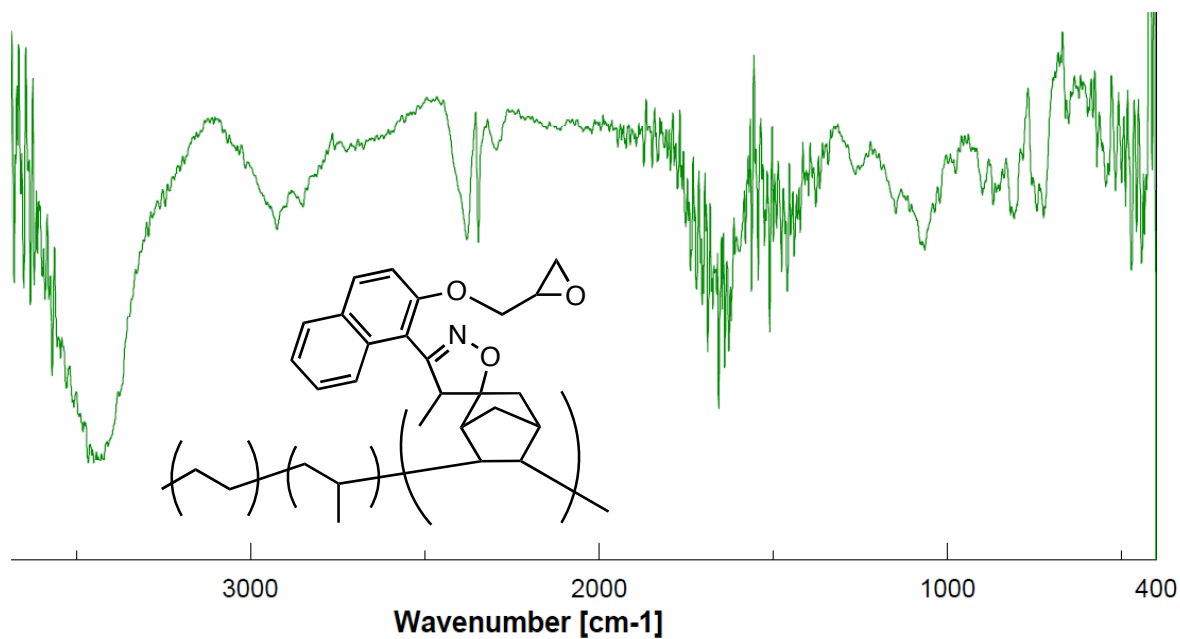


IR spectrum of modified NBR (with reagent **1**) (KBr)

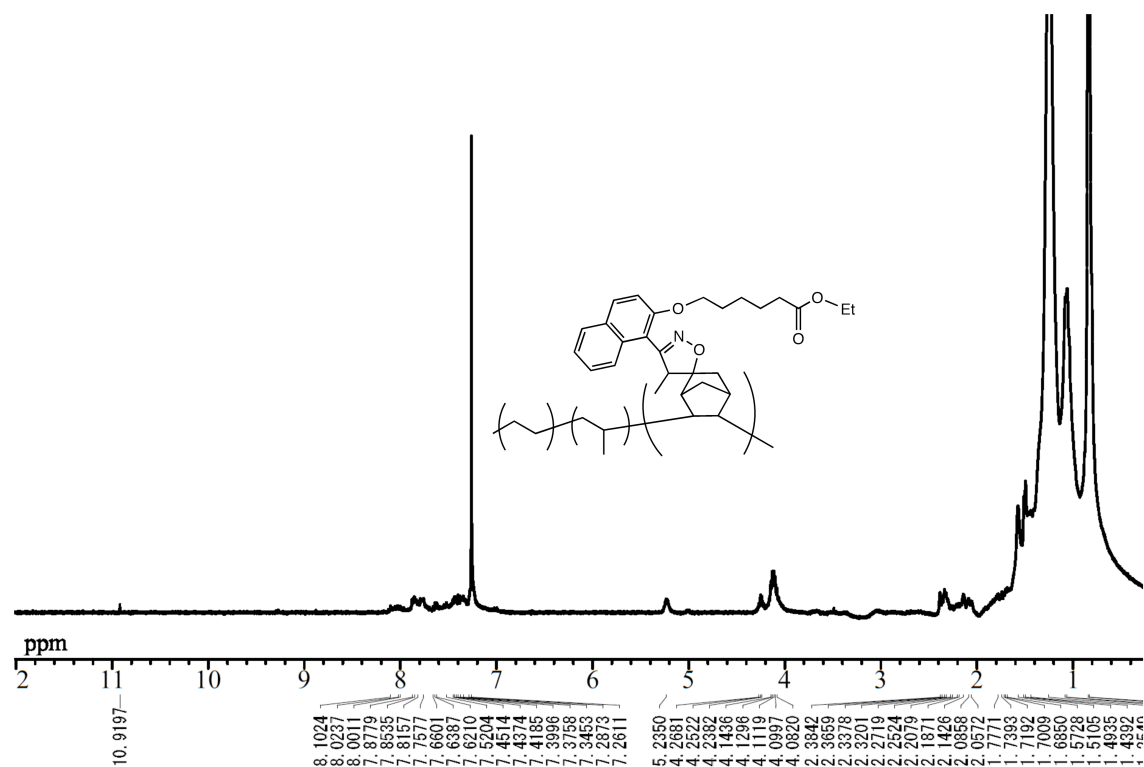


¹H NMR spectrum of modified NBR (with reagent **2**) (400 MHz, CDCl₃, 298 K)

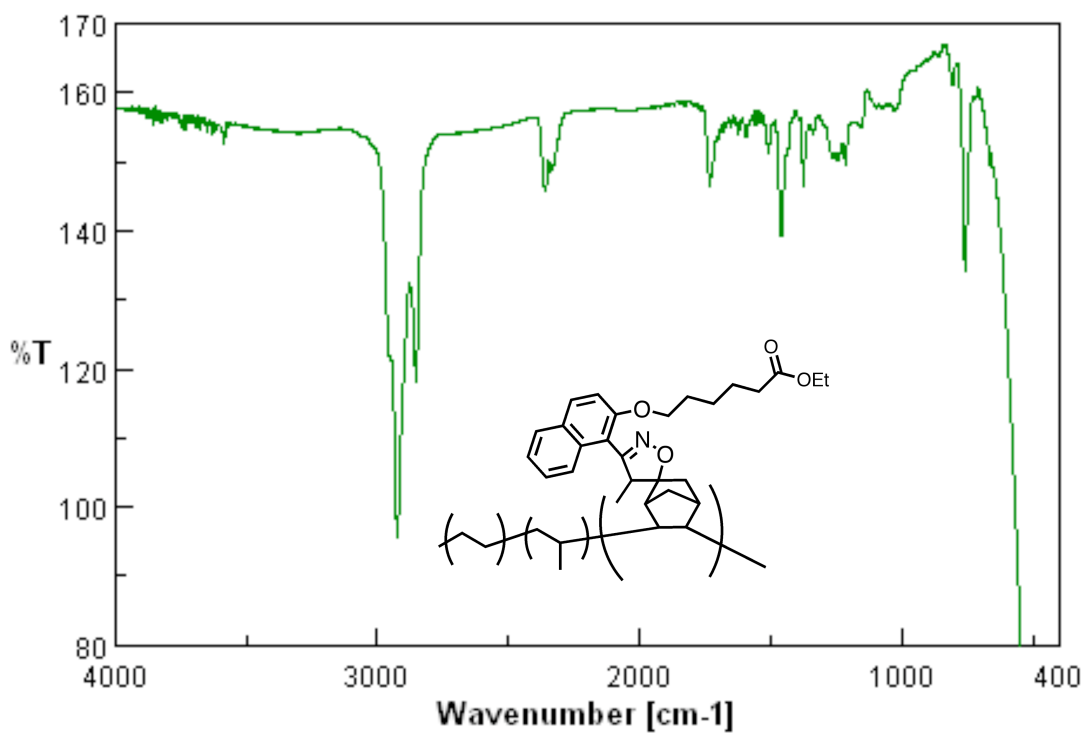




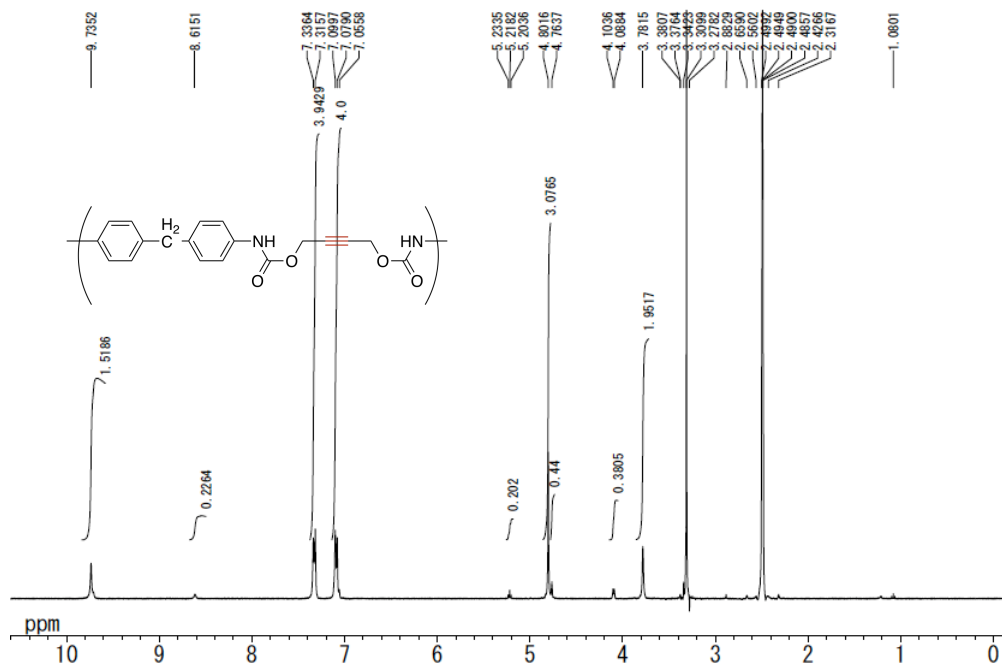
IR spectrum of modified EPDM (with reagent **1**) (KBr)



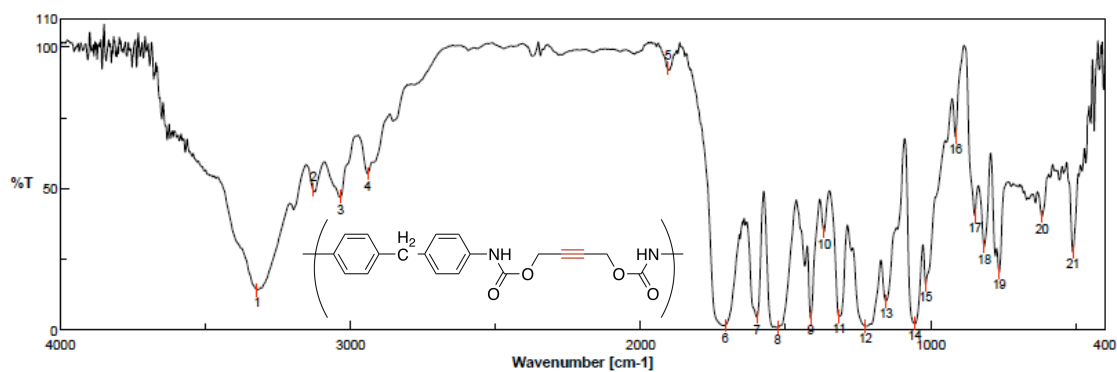
¹H NMR spectrum of modified EPDM (with reagent **2**) (400 MHz, CDCl₃, 298 K)



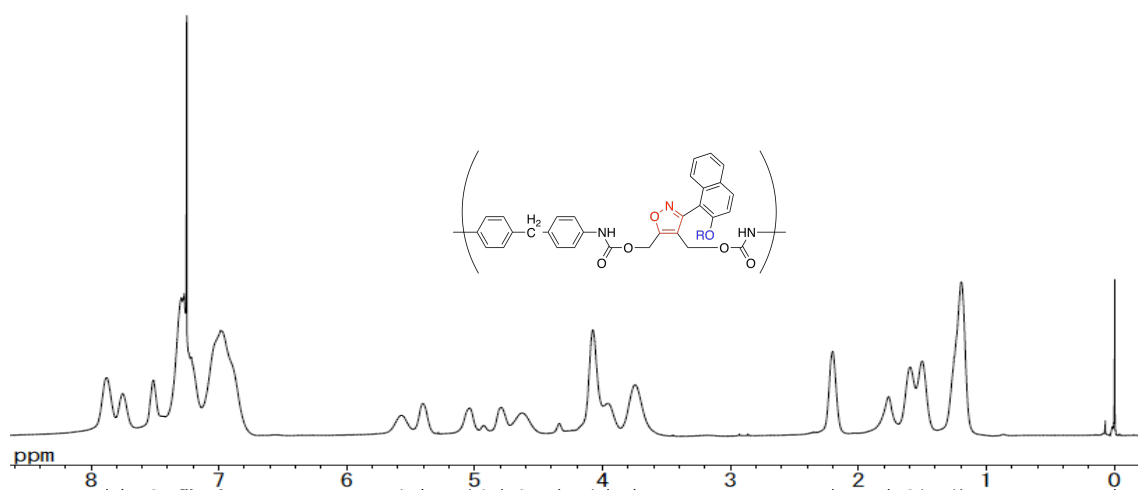
IR spectrum of modified EPDM (with reagent **2**) (KBr)



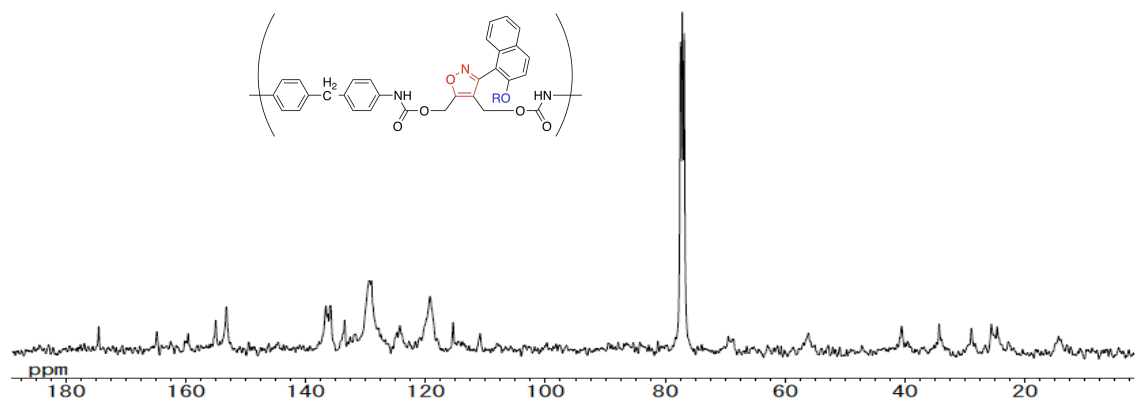
^1H NMR spectrum of internal alkyne-containing polyurethane (400 MHz, DMSO- d_6 , 298 K)



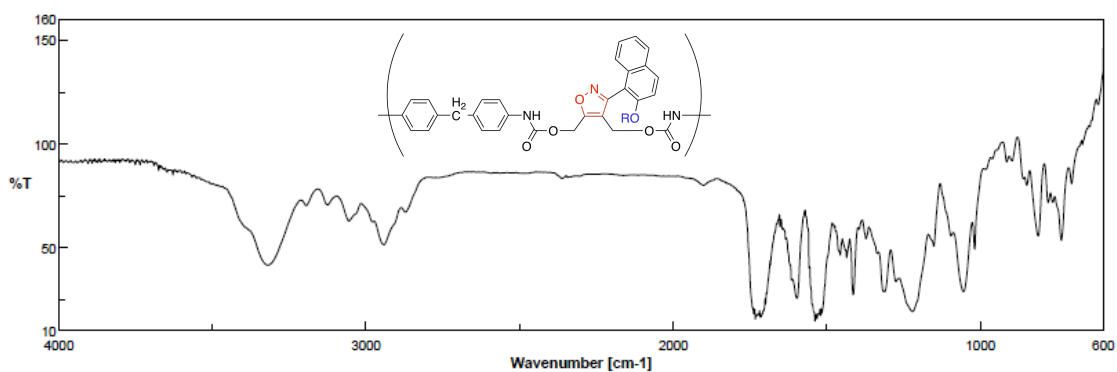
IR spectrum of internal alkyne-containing polyurethane (KBr)



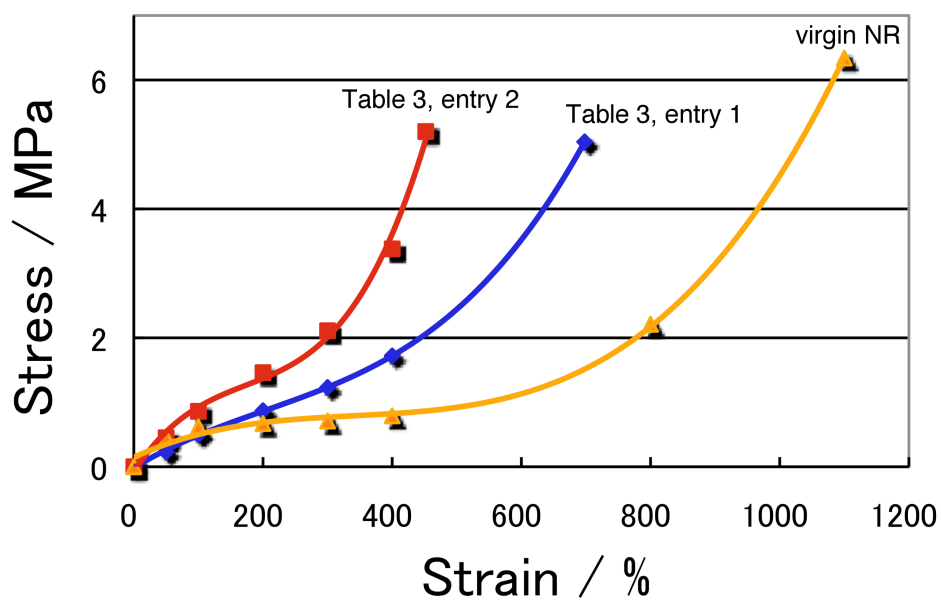
¹H NMR spectrum of modified polyurethane with **2** (400 MHz, CDCl₃, 298 K)



¹³C NMR spectrum of modified polyurethane with **2** (100 MHz, CDCl₃, 298 K)



IR spectrum of modified polyurethane with **2** (KBr)



Stress–strain curves of virgin and cross-linked NRs.

References

- (1) D. Janeliunas, M. Daskeviciene, T. Malinauskas, V. Getautis, *Tetrahedron*. **2009**, 65, 8407–8411.
- (2) D. S. Campbell, *J. Appl. Polym. Sci.*, **1970**, 14, 1409–1419.