Supporting information for

# DNP NMR Spectroscopy Enabled Direct Characterization of Polystyrene-supported Catalyst Species for Synthesis of Glycidyl Esters by Transesterification

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## 1. General

Glycidol (**GD**), methylesters (**5a-h**), ($^nC_{12}H_{25})_3$MeNCl, NaOH, $HNO_3$, $HNO_3$ ($^{15}N$ 98%), organic solvents, and alkyl amines used for the synthesis of **2-Cl**, **3-Cl**, **7**, **8** were purchased from chemical suppliers. **GD** was purified by distillation before to use. Other chemicals were used as received. Two types of Merrifield resins (A: 200-400 mesh, 1% cross-linked, Cl content: 2.2 mmol/g, Tokyo Chemical Industry, Co. Ltd., B: 200-400 mesh, 1% cross-linked, Cl content: 4.5 mmol/g, Sigma-Aldrich, Co. LLC.) were used as a starting material for preparation of **2-Cl** (A), **3-Cl** (A), **7** (B), and **8** (B). Preparation of **1-Cl** and **4-Cl** was reported in our previous study.[1] 1-nitro-2,3-propanediol was synthesized according to the reported procedure.[2] Catalytic reactions were performed using ChemiStation (Tokyo Rika Inc.) equipped with thermostated apparatus. Elemental analyses were measured with a Flash 2000 instrument (Thermo Fisher Scientific Inc.) for C, H, and N, and with ion chromatography ICS-2000 (DIONEX) for Cl. Fourier-transform Infrared spectroscopy (FT-IR) was measured using FT/IR-4100 (JASCO). Solution NMR was measured with Bruker Avance III spectrometer (600 MHz for $^1H$ nuclei) using cryo-probe. All spectra were recorded at 25 ± 1 ºC. Chemical shifts ($\delta$) are in parts per million relative to tetramethylsilane at 0 ppm for $^1H$. Conventional solid-state NMR was measured with Bruker Avance II+ or Avance NEO spectrometer (400 MHz for $^1H$ nuclei) using 3.2 mm MAS probe. Standard ramped cross polarization (CP) was used to transfer polarization from the $^1H$ nuclei to the nucleus of interest ($^{13}C$). SPINAL-64 $^1H$ heteronuclear decoupling was applied during acquisition. $^{13}C$ chemical shifts were referenced to tetramethylsilane at 0 ppm using adamantane as an external standard (38.52 ppm). Details of DNP solid-state NMR measurement were described in section 5.

## 2. Preparation of compounds

**2-Cl:** To 300 mL round-bottom flask charged with Merrifield resin (5.0 g, 11 mmol based on Cl), $CH_3CN$ (100 mL) and *N,N*-Dimethyl-n-octylamine (11 mL, 55 mmol, 5.0 eq) were added. The suspension was gently stirred at 80 $^oC$ for 43 h. The insoluble polymer beads were filtered and rinsed with toluene (30 mL x 3) acetone (30 mL x 3) and MeOH (30 mL x 3). After drying under vacuum at 80 $^oC$ for 3 hours, **2-Cl** was obtained as pale-yellow beads (7.1 g). Combustion analysis (%) H: 9.07, C: 78.70, N: 2.25. N content: 1.61 mmol/g.

**3-Cl:** To 500 mL round-bottom flask charged with Merrifield resin (14 g, 31 mmol based on Cl), $CH_3CN$ (230 mL) and *N*-Methyl-di-n-octylamine (49 mL, 0.15 mol, 5.0 eq) were added. The suspension was gently stirred at 80 $^oC$ for 67 h. The insoluble polymer beads were filtered and rinsed with toluene (100 mL x 3) acetone (100 mL x 3) and MeOH (100 mL x 3). After drying under vacuum at 80 $^oC$ for overnight, **3-Cl** was obtained as pale-yellow beads (21.7 g). Combustion analysis (%) H: 9.71, C: 80.59, N: 1.85. N content: 1.32 mmol/g. Ion chromatography (%): Cl: 4.5

**3-NO$_3$:** To 100 mL flask charged with **3-Cl** (2.0 g, 2.6 mmol based on N), 1N NaOH (52.8 mL, 20 eq) and THF (14 mL) were added. The solution with polymer beads was gently stirred for 67 hours at ambient temperature. The beads were separated by filtration and rinsed with $H_2O$ (100 mL x 3), acetone (100 mL x 3) and dried. The resulting polymer beads (1.0 g) were further treated with 1N $HNO_3$ aq (7.1 mL, 5 eq). After gentle stirring for 66 hours at ambient temperature, the beads were filtered and rinsed with water (50 mL x 3) and acetone (50 mL x 3), and dried under vacuum at ambient temperature for overnight. Pale-yellow beads were obtained (0.61 g)**.** Combustion analysis (%) H: 8.88, C: 76.17, N: 3.16. N content: 2.26 mmol/g. Ion chromatography (%): Cl: 0.7

**3-NO$_3$-$^{15}$N:** This material was prepared in similar way to **3-NO$_3$** using 98% $^{15}N$ labeled $HNO_3$. Combustion analysis (%) H: 8.95, C: 77.31, N: 3.27. N content: 2.34 mmol/g.

**3-NO$_3$-$^{15}$N-GD:** To 15 mL test tube charged with **3-NO$_3$-$^{15}$N** (37.6 mg), glycidol (6.5 μL, 0.098 mmol) was treated in hexane (0.5 mL). The suspension was gently stirred at 80 $^oC$ for 1 hour, and all volatiles were removed under reduced pressure at ambient temperature. The dried polymer beads were employed for structural analysis.

**7:** To 100 mL test tube charged with Merrifield resin (1.0 g, 4.5 mmol based on Cl) and Di-n-octylamine (6.8 mL, 23 mmol, 5.1 eq), *N,N*-diisopropyl ethylamine (3.9 mL, 23 mmol, 5.1 eq) and $CH_3CN$ (20 mL) were added. The suspension was gently stirred at 80 $^oC$ for 43 h. The polymer beads were filtered and rinsed with toluene (30 mL x 3), acetone (30 mL x 3), THF (30 mL x 3) and MeOH (30 mL x 3). After drying under reduced pressure at 80 $^oC$ for 3 hours, pale yellow beads were obtained (1.10 g). Combustion analysis (%) H: 11.13, C: 84.78, N: 2.97. N content: 2.12 mmol/g.

**8:** To 50 mL round-bottom flask charged with Merrifield resin (1.1 g, 5.0 mmol based on Cl) and *N*-Methyl-n-octylamine (3.2 g, 22 mmol, 4.5 eq), *N,N*-Diisopropyl ethylamine (1.5 mL, 8.7 mmol, 1.8 eq) and $CH_3CN$ (20 mL) were added. The suspension was gently stirred at 80 $^oC$ for 43 h. The polymer beads were filtered and rinsed with toluene (30 mL x 3) acetone (30 mL x 3) and MeOH (30 mL x 3). After drying under reduced pressure at room temperature for overnight, pale yellow beads were obtained (1.3 g). Combustion analysis (%) H: 10.50, C: 84.74, N: 3.96. N content: 2.83 mmol/g.

## 3. Characterization of PS-supported catalysts

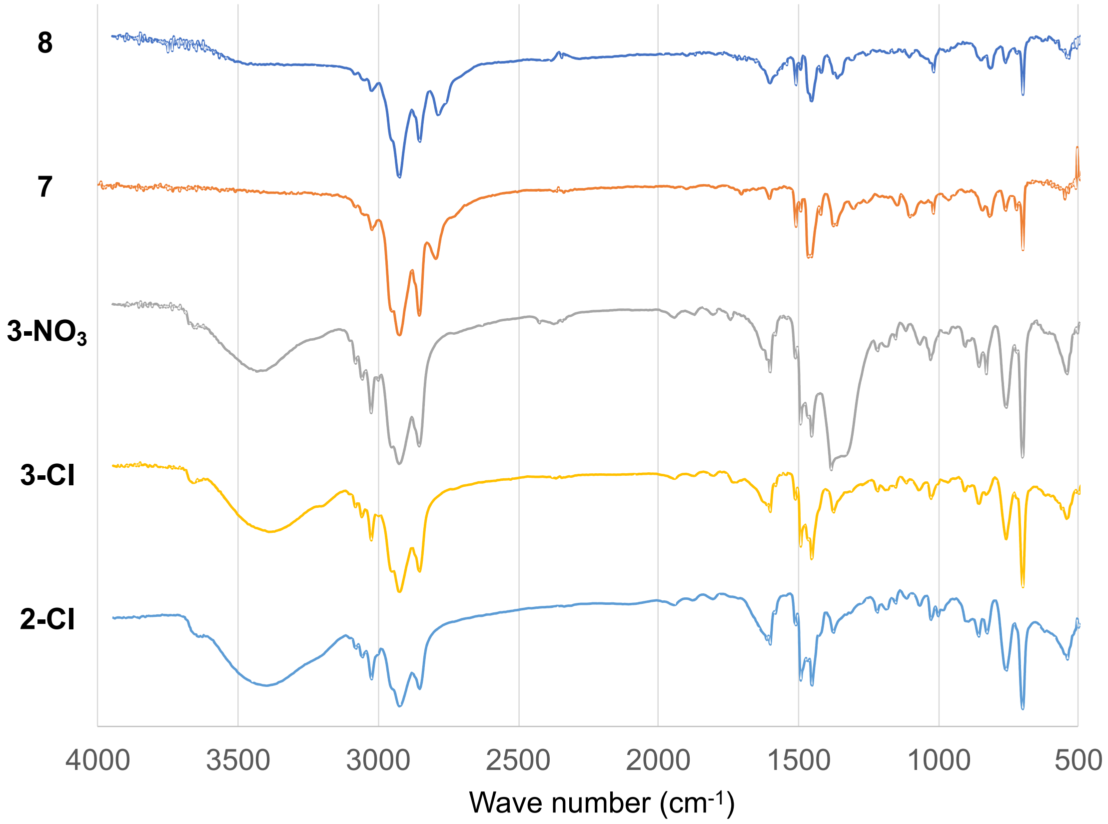

**Figure S1.** FT-IR spectra of **2-Cl**, **3-Cl**, **3-NO$_3$**, **7** and **8**. All spectra showed peaks from N-alkyl group in addition to peaks from PS. **3-NO$_3$** showed an additional peak at 1350 cm$^{-1}$ assigned to NO$_3^-$ group. A broad peak at 3100-3600 cm$^{-1}$ observed from PS-supported ammonium salts (**2-Cl**, **3-Cl**, **3-NO$_3$**) is likely due to water molecules attached to ionic moieties.

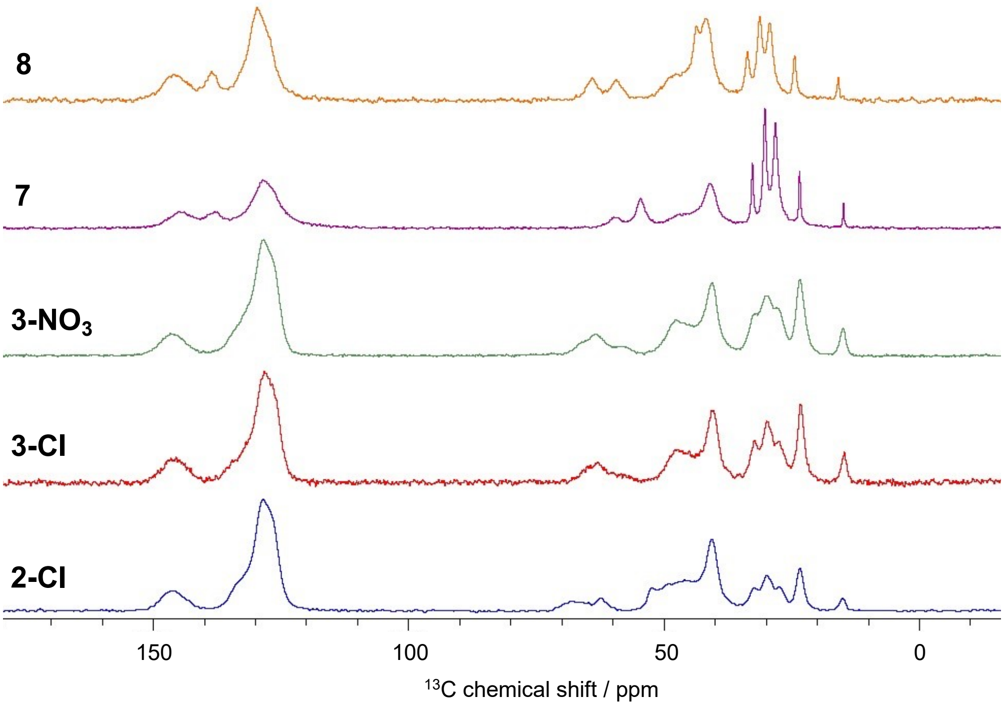

**Figure S2.** $^{13}$C CPMAS NMR of **2-Cl**, **3-Cl**, **3-NO$_3$**, **7** and **8**. MAS frequency: 16 kHz (3.2 mm rotor), CP contact time: 1 ms, recycle delay: 2 s, number scans: 4300 (**2-Cl**), 1024 (**3-Cl**), 8192 (**3-NO$_3$**), 16384 (**7**), 2048 (**8**). All spectra showed signals from PS chain (36-52 ppm for aliphatic group, 122-152 ppm for aromatic group) and *n*-octyl groups (15, 24, 28, 30, 33 ppm). Signals from carbons attached to nitrogen were observed in the region from 43 to 70 ppm. Some signals were observed with large half bandwidth due to possible conformers of alkylammonium fragments existed in polymer network.

## 4. Swelling test

Swelling property of polymers were measured by the syringe method according to the reported procedure.[1,3] A syringe (total volume: 1.0 mL) equipped with a PTFE filter (pore size: 0.22 μm) at the exit was loaded with a known amount (typically 100 mg) of polymer (**A** g), and the volume of dry polymer was recorded (**B** mL). 1,1,2,2-tetrachloroethane (TCE) or dimethyl sulfoxide (DMSO) was added to the syringe, and the mixture was let stand for overnight at room temperature to reach equilibrium. The extra solvent was removed from the syringe by using the plunger, and a volume of swollen polymer was recorded (**C** mL). The swelling volume (mL/g) was estimated as a volume of solvent in swollen polymer (**C** – **B** mL) divided by a weight of used polymer (**A** g). The swelling volume of polymers for each solvent were listed in Table S1.

**Table S1.** Swelling volume for PS-supported catalysts.

| | | **1-Cl**[1] | **2-Cl** | **3-Cl** | **3-$NO_3$** | **4-Cl**[1] | **7** | **8** |
|---|---|---|---|---|---|---|---|---|
| Swelling volume (mL/g) | TCE | 0.2 | 2.3 | 3.9 | 3.2 | 1.8 | 1.6 | 1.7 |
| | DMSO | 0.9 | 3.5 | 2.9 | 3.3 | 0.4 | 0.8 | 1.4 |

## 5. DNP solid-state NMR measurements

All experiments were performed with a Bruker Avance NEO 400 MHz/263 GHz 9.4 T DNP system using 3.2 mm H-X double channel probe or 1.9 mm H-X-Y triple channel probe. TEKPol and AMUPol were purchased from a commercial source and used as a polarizing agent (PA). Incipient wetness impregnation of polymer beads with 16 mM TEKPol in TCE or 16 mM AMUPol in DMSO-$d_6$ was performed to prepare the samples for DNP experiments. Typically, a measured amount of polymer beads (ca. 15 mg) was loaded in a microtube (ca. 1 mL), and an appropriate volume of PA solution was added over the polymer beads. The samples were mixed with a plastic spatula and the microtube was closed with a cap and let standing at room temperature for overnight. The impregnated samples were packed into sapphire rotors and sealed with teflon insert closed with a zirconia cap. The sample was frozen at ca. 100 K inside the precooled low temperature 3.2 mm MAS probe head and degassed by freeze-thaw cycles according to a literature procedure.[4] The sweep coil of the main magnetic field was tuned so that microwave irradiation occurred at the $^1$H positive DNP enhancement maximum of the nitroxide biradicals. Standard ramped cross polarization (CP) was used to transfer polarization from the $^1$H nuclei to the nucleus of interest ($^{13}$C, $^{15}$N). SPINAL-64 $^1$H heteronuclear decoupling was applied during acquisition. A recycle delay was based on DNP build-up time, $T_{DNP}$, determined by $^1$H saturation recovery experiment under microwave irradiation, and set as $T_{DNP}$ x 1.3 s. $^{13}$C chemical shifts were referenced to tetramethylsilane at 0 ppm using adamantane as an external standard (38.52 ppm). $^{15}$N chemical shifts were referenced to liq. $NH_3$ at 0 ppm using $^{15}NH_4Cl$ as an external standard (39.3 ppm).[5] DNP-enhanced heteronuclear correlation (HETCOR) experiments were performed using frequency-switched Lee-Goldburg (FSLG) homonuclear decoupling during the evolution of the chemical shift.[6] A decoupling field of 100 kHz was used. A CP contact time was 1 ms for $^{15}$N and 0.2 ms for $^{13}$C experiment, respectively. Referencing of the $^1$H chemical shift was performed using PS signals as an internal standard: set an aliphatic signal as 1.2 ppm and an aromatic signal as 7.0 ppm, respectively.

To determine $\varepsilon_H$ values, Hahn-echo experiment was applied for $^1$H. Intensities of $^1$H signal at 1-10 ppm under microwave on/off accumulated by 16 scans were utilized for the determination of $\varepsilon_H$ value. The sample spinning frequency was set to 10 kHz and a sample temperature was 102-103 K under microwave on, and 99-100 K under microwave off condition. DNP enhancement ($\varepsilon$) is defined as the ratio between the signal intensity attained from the sample under microwave irradiation condition ($I_{\text{mw, on}}$) and normal condition ($I_{\text{mw, off}}$), and calculated according to following formula (eq 1):

$$\varepsilon = \frac{I_{\text{mw on}}}{I_{\text{mw off}}} \qquad (1)$$

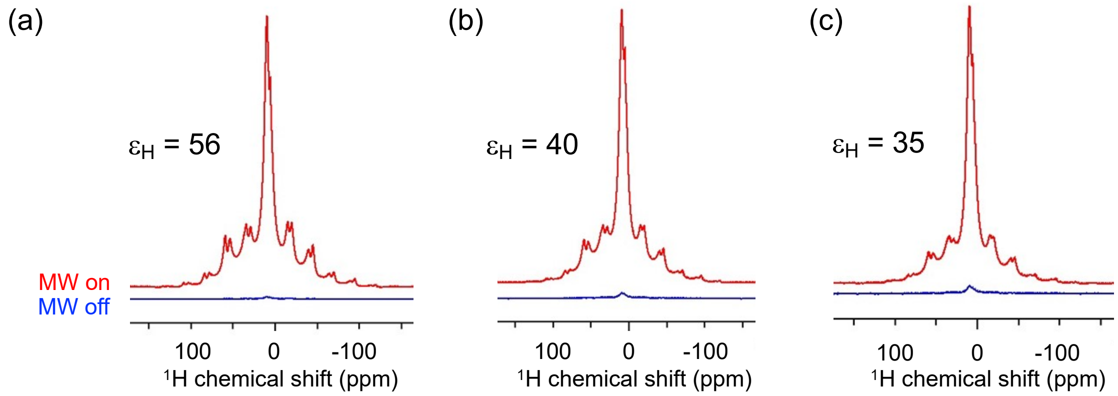

**Figure S3.** DNP $^1$H MAS NMR spectra under microwave on/off conditions of **2-Cl** (a), **3-Cl** (b), and **3-NO$_3$** (c). Small peaks observed around a central peak are spinning side band signals.

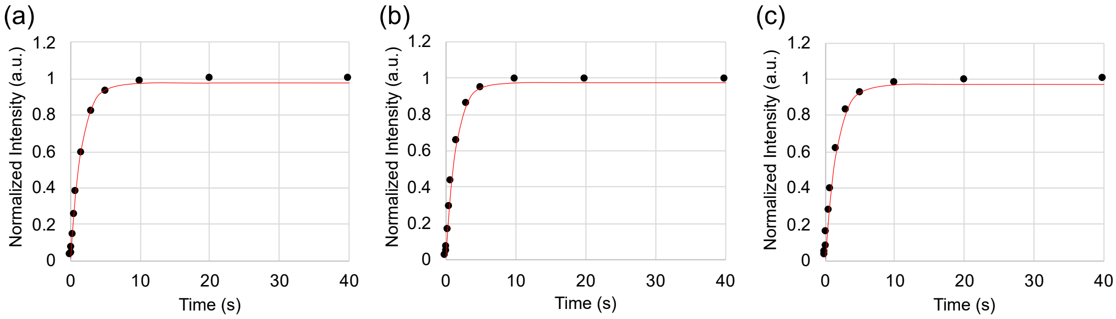

**Figure S4.** $^1$H DNP build-up curves obtained from **2-Cl** (a), **3-Cl** (b), and **3-NO$_3$** (c). All plots were fitted with a single exponential function, giving $T_{DNP}$ values of 1.6 s (**2-Cl**), 1.4 s (**3-Cl**) and 1.6 s (**3-NO$_3$**).

## 6. Procedure for the catalytic reaction

### General procedure

In the test tube (volume: 15 mL), PS-supported catalyst beads (30-50 mg, 0.050 mmol based on ammonium moiety) and methyl 4-nitrobenzoate (0.18 g, 1.0 mmol) were charged. Hexane (0.5 mL) and glycidol (90 mg, 1.2 mmol) were added in this order to give colorless suspension. The test tube was placed in the ChemiStation apparatus whose temperature setting was stabilized, and magnetically stirred for 1 h under azeotropic reflux condition (heater temp: 80 °C). Resulting reaction mixture was diluted with $CH_3CN$ (3 mL), and filtered using a syringe equipped with a PTFE filter (pore size: 0.22 μm). Extra $CH_3CN$ (3 mL) was used for a collection of residual chemicals in a test tube and filtered. To a combined solution was then added measured amount of biphenyl (as an internal standard), and an aliquot was used for $^1$H NMR measurement (600 MHz, $CDCl_3$, 298 K). Yields of glycidyl 4-nitrobenzoate was determined by comparing integrals of signals from epoxy moiety of product (4.74 ppm)[7] with that from biphenyl (7.59 ppm). For isolation of product, silica-gel column chromatography was performed using Hexane/EtOAc as an eluent.

### Procedure for reuse test of catalyst

The first catalytic reaction was performed as described above. After cooling a reaction mixture, $CH_3CN$ (1 mL) was added, and a supernatant solution was separated by decantation. The polymer beads were further extracted with THF (1 mL), hexane (1 mL), $CH_3CN$ (1 mL), THF (1 mL), and hexane (1 mL). To a combined solution was then added measured amount of biphenyl (as an internal standard), and an aliquot was used for $^1$H NMR measurement (600 MHz, $CDCl_3$, 298 K) to determine a yield of product in that run. To the test tube charged with a used catalyst, substrates and solvent were added directly, and run a catalytic reaction again. After a fifth run was performed, the polymer catalyst was dried under reduced pressure at ambient temperature and employed for structural analysis.

### Spectral data of isolated products

Glycidyl 4-nitrobenzoate (**6a**)[7]

$^1$H NMR ($CDCl_3$, 600 MHz) $\delta$ 2.74 (1 H, dd, $J$ = 4.8 Hz, 2.6 Hz, epoxide C$H_2$), 2.93 (1 H, dd, $J$ = 4.8 Hz, 4.2 Hz, epoxide C$H_2$), 3.35-3.38 (1 H, m, epoxide C$H$), 4.19 (1 H, dd, $J$ = 12.3 Hz, 6.6 Hz, C$H_2$-OCO), 4.74 (1 H, dd, $J$ = 12.4 Hz, 3.0 Hz, C$H_2$-OCO), 8.25 (2 H, d like, $J$ = 9.0 Hz, Ar$H$), 8.30 (2 H, d like, $J$ = 9.0 Hz, Ar$H$); $^{13}$C{$^1$H}NMR ($CDCl_3$, 150 MHz) $\delta$ 44.7, 49.2, 66.4, 123.6, 130.9, 135.0, 150.7, 164.4.

Glycidyl 4-cyanobenzoate (**6b**)[7]

$^1$H NMR ($CDCl_3$, 600 MHz) $\delta$ 2.73 (1 H, dd, $J$ = 4.9 Hz, 2.6 Hz, epoxide C$H_2$), 2.92 (1 H, dd, $J$ = 4.7 Hz, 4.1 Hz, epoxide C$H_2$), 3.34-3.36 (1 H, m, epoxide C$H$), 4.17 (1 H, dd, $J$ = 12.3 Hz, 6.6 Hz, C*H*$_2$-OCO), 4.72 (1 H, dd, *J* = 12.4 Hz, 2.9 Hz, C*H*$_2$-OCO), 7.76 (2 H, d like, *J* = 8.7 Hz, Ar*H*), 8.17 (2 H, d, *J* = 8.7 Hz, Ar*H*); $^{13}$C{$^1$H}NMR (CDCl$_3$, 150 MHz) $\delta$ 44.6, 49.2, 66.3, 116.7, 117.8, 130.2, 132.3, 133.4, 164.6

Glycidyl 3-nitrobenzoate (**6c**)

$^1$H NMR (CDCl$_3$, 600 MHz) $\delta$ 2.75 (1 H, dd, *J* = 4.9 Hz, 2.6 Hz, epoxide C*H*$_2$), 2.94 (1 H, t, *J* = 4.5 Hz, epoxide C*H*$_2$), 3.37-3.39 (1 H, m, epoxide C*H*), 4.22 (1 H, dd, *J* = 12.4 Hz, 6.5 Hz, C*H*$_2$-OCO), 4.74 (1 H, dd, *J* = 12.2 Hz, 3.0 Hz, C*H*$_2$-OCO), 7.68 (1 H, t, J = 8.0 Hz, Ar*H*), 8.40 (1 H, d like, *J* = 7.6 Hz, Ar*H*), 8.44 (1 H, d like, *J* = 8.3 Hz, Ar*H*), 8.90 (1 H, s, Ar*H*); $^{13}$C{$^1$H}NMR (CDCl$_3$, 150 MHz) $\delta$ 44.7, 49.2, 66.5, 124.7, 127.7, 129.7, 131.4, 135.4, 148.3, 164.2.

Glycidyl 2-nitrobenzoate (**6d**)

$^1$H NMR (CDCl$_3$, 600 MHz) $\delta$ 2.70 (1 H, dd, *J* = 4.7 Hz, 2.5 Hz, epoxide C*H*$_2$), 2.90 (1 H, t, *J* = 4.4 Hz, epoxide C*H*$_2$), 3.30-3.33 (1 H, m, epoxide C*H*), 4.20 (1 H, dd, *J* = 12.0 Hz, 6.1 Hz, C*H*$_2$-OCO), 4.64 (1 H, dd, *J* = 12.2 Hz, 3.3 Hz, C*H*$_2$-OCO), 7.67 (1 H, t like, J = 7.7 Hz, Ar*H*), 7.70 (1 H, t like, *J* = 7.5 Hz, Ar*H*), 7.76 (1 H, d like, *J* = 7.7 Hz, Ar*H*), 7.95 (1 H, d like, *J* = 7.9 Hz, Ar*H*); $^{13}$C{$^1$H}NMR (CDCl$_3$, 150 MHz) $\delta$ 44.8, 48.8, 66.8, 124.0, 127.3, 129.9, 131.9, 133.0, 148.1, 165.2.

Glycidyl 2-pyridinecarboxylate (**6e**)[7]

$^1$H NMR (CDCl$_3$, 600 MHz) $\delta$ 2.75 (1 H, dd, *J* = 5.0 Hz, 2.6 Hz, epoxide C*H*$_2$), 2.90 (1 H, dd, *J* = 4.9 Hz, 4.2 Hz, epoxide C*H*$_2$), 3.38-3.42 (1 H, m, epoxide C*H*), 4.33 (1 H, dd, *J* = 12.2 Hz, 6.1 Hz, C*H*$_2$-OCO), 4.66 (1 H, dd, *J* = 12.1 Hz, 3.6 Hz, C*H*$_2$-OCO), 7.50 (1 H, ddd, *J* = 7.7 Hz, 4.7 Hz, 1.2 Hz, Py*H*), 7.86 (1 H, td, *J* = 7.7 Hz, 1.7 Hz, Py*H*), 8.16 (1 H, dt, *J* = 7.8 Hz, 1.1 Hz, Py*H*), 8.78 (1 H, ddd, *J* = 4.7 Hz, 1.8 Hz, 1.1 Hz, Py*H*); $^{13}$C{$^1$H}NMR (CDCl$_3$, 150 MHz) $\delta$ 45.0, 49.2, 66.3, 125.4, 127.1, 137.1, 147.5, 150.0, 164.8.

Glycidyl 2-thiophenecarboxylate (**6f**)[7]

$^1$H NMR (CDCl$_3$, 600 MHz) $\delta$ 2.73 (1 H, dd, *J* = 4.9 Hz, 2.6 Hz, epoxide C*H*$_2$), 2.89 (1 H, dd, *J* = 5.2 Hz, 4.2 Hz, epoxide C*H*$_2$), 3.31-3.34 (1 H, m, epoxide C*H*), 4.16 (1 H, dd, *J* = 12.3 Hz, 6.2 Hz, C*H*$_2$-OCO), 4.62 (1 H, dd, *J* = 12.2 Hz, 3.2 Hz, C*H*$_2$-OCO), 7.12 (1 H, dd, *J* = 5.0 Hz, 3.7 Hz, thiophene*H*), 7.59 (1 H, dd, *J* = 5.0 Hz, 1.2 Hz, thiophene*H*), 7.84 (1 H, dd, *J* = 3.7 Hz, 1.2 Hz, thiophene*H*); $^{13}$C{$^1$H}NMR (CDCl$_3$, 150 MHz) $\delta$ 44.7, 49.4, 65.4, 127.8, 132.8, 133.1, 133.9, 161.9.

Glycidyl 2-furancarboxylate (**6g**)[7]

$^1$H NMR (CDCl$_3$, 600 MHz) $\delta$ 2.72 (1 H, dd, *J* = 4.8 Hz, 2.6 Hz, epoxide C*H*$_2$), 2.89 (1 H, *J* = 4.8 Hz, 4.2 Hz, epoxide C*H*$_2$), 3.31-3.33 (1 H, m, epoxide C*H*), 4.16 (1 H, dd, *J* = 11.8 Hz, 6.2 Hz, C*H*$_2$-OCO), 4.62 (1 H, dd, *J* = 12.3 Hz, 3.2 Hz, C*H*$_2$-OCO), 6.52 (1 H, dd, *J* = 3.5 Hz, 1.8 Hz, furan*H*), 7.23 (1 H, dd, *J* = 3.5 Hz, 0.9 Hz, furan*H*), 7.60 (1 H, dd, *J* = 1.7 Hz, 0.9 Hz, furan*H*); $^{13}$C{$^1$H}NMR (CDCl$_3$, 150 MHz) $\delta$ 44.7, 49.3, 65.3, 111.9, 118.5, 144.1, 146.6, 158.3.

Diglycidyl 2,4-furandicarboxylate (**6h**)[8]

$^1$H NMR (CDCl$_3$, 600 MHz) $\delta$ 2.73 (2 H, dd, *J* = 4.9 Hz, 2.6 Hz, epoxide C*H*$_2$), 2.90 (2 H, *J* = 4.8

Hz, 4.2 Hz, epoxide C$H_2$), 3.32-3.35 (2 H, m, epoxide C$H$), 4.19 (2 H, dd, $J$ = 12.2 Hz, 6.3 Hz, C$H_2$-OCO), 4.65 (2 H, dd, $J$ = 12.3 Hz, 3.2 Hz, C$H_2$-OCO), 7.27 (2 H, s, furan$H$); $^{13}C\{^1H\}$NMR ($CDCl_3$, 150 MHz) $\delta$ 44.8, 49.1, 66.0, 119.0, 146.5, 146.6, 157.5.

### 7. DNP NMR spectra of tertiary amines

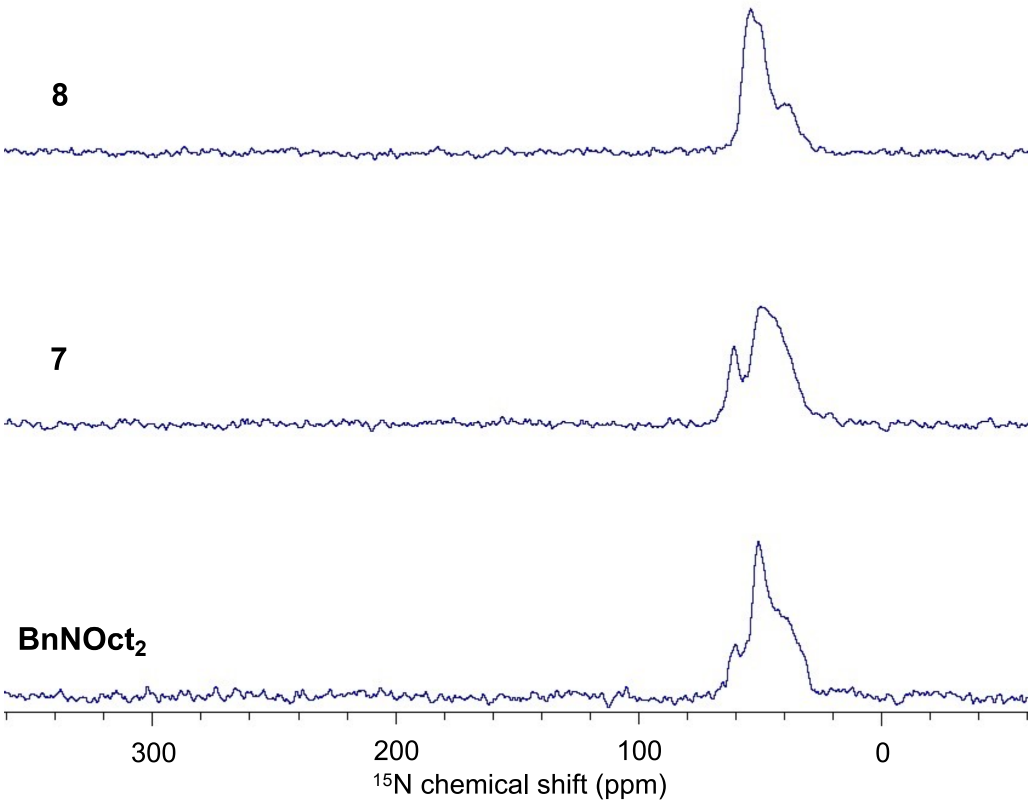

**Figure S5.** DNP $^{15}$N CPMAS NMR spectra of **7** and **8** with TEKPol/TCE (16 mM) as a polarizing agent. To confirm the signals observed from **7**, BnNOct$_2$ was synthesized as a model molecule from benzyl chloride and di(*n*-octyl)amine, and used for DNP $^{15}$N CPMAS NMR measurement under same conditions. All spectra displayed overlapped signals at 25-60 ppm due to conformers of bulky tertiary amines which possibly exist at cryogenic temperature.[9] Temperature: 102 K, MAS frequency: 10 kHz (3.2 mm rotor), CP contact time: 3 ms, recycle delay: 4.3 s (BnNOct$_2$), 7.3 s (**7**), 4.4 s (**8**), number of scans: 4096 (BnNOct$_2$), 2250 (**7**), 1024 (**8**).

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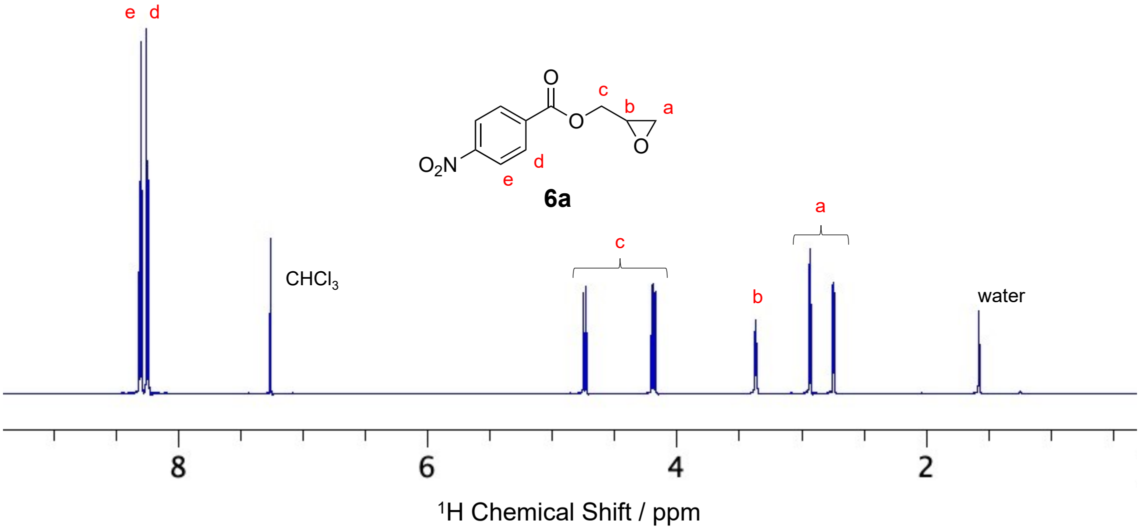
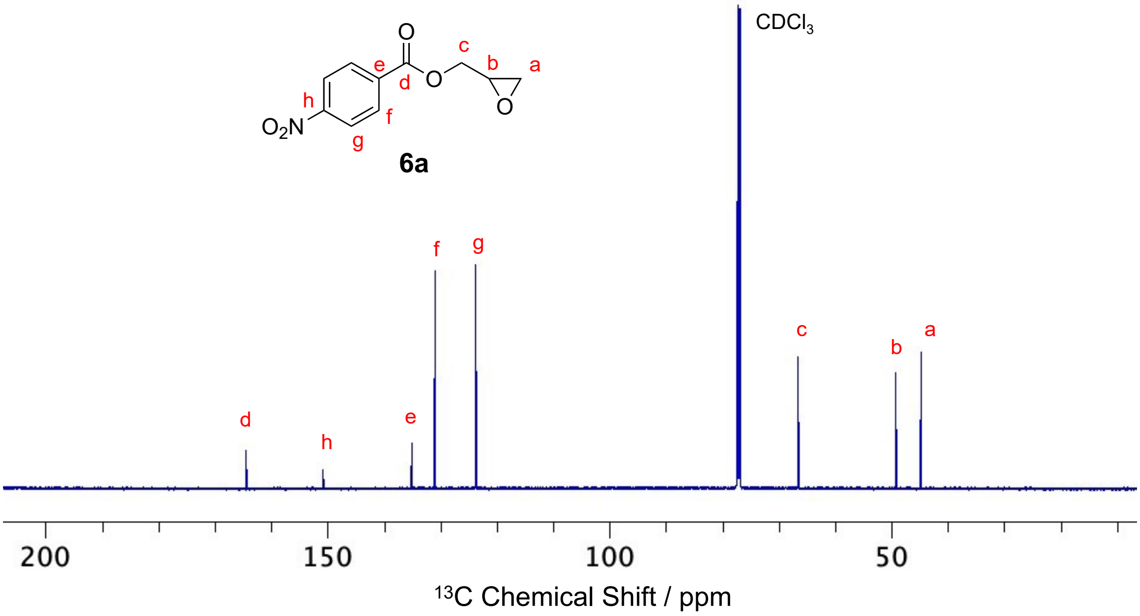
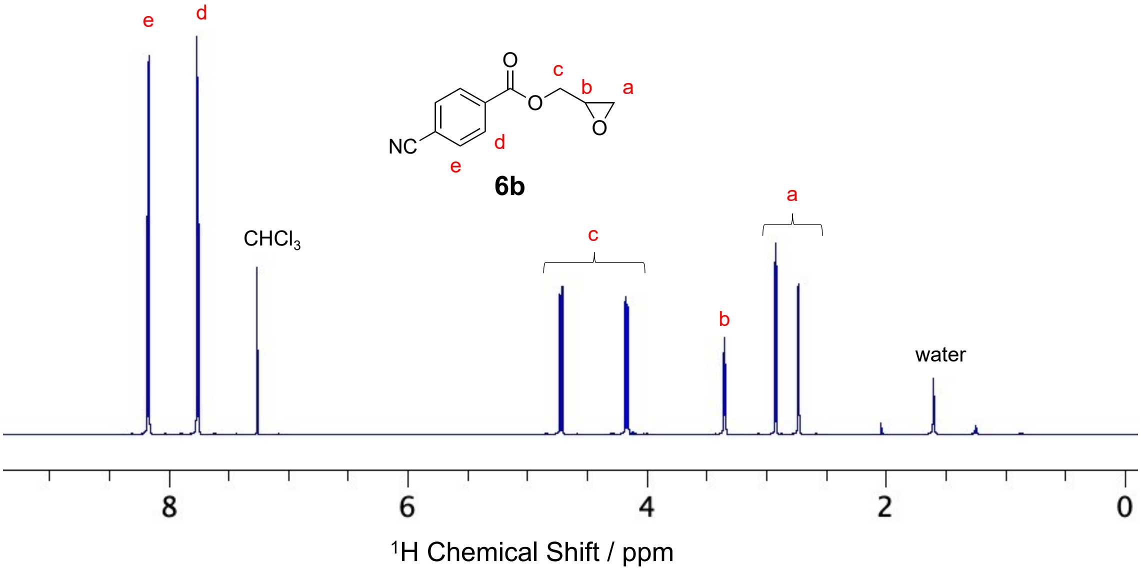
## 9. $^1$H, $^{13}$C NMR spectra of isolated products

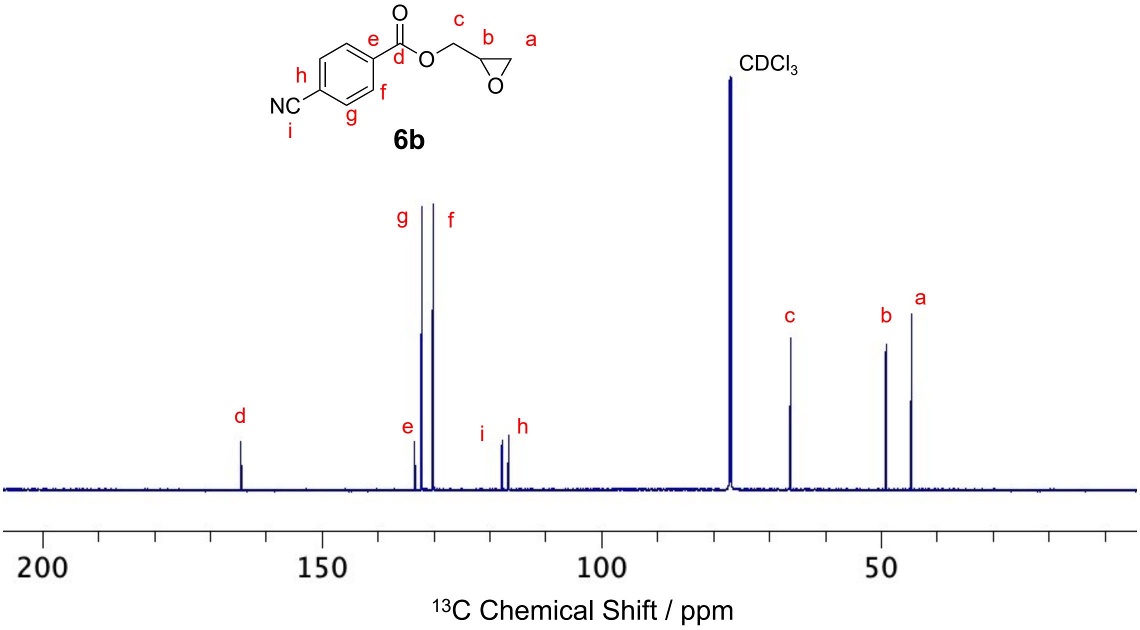
Glycidyl 4-nitrobenzoate (**6a**)



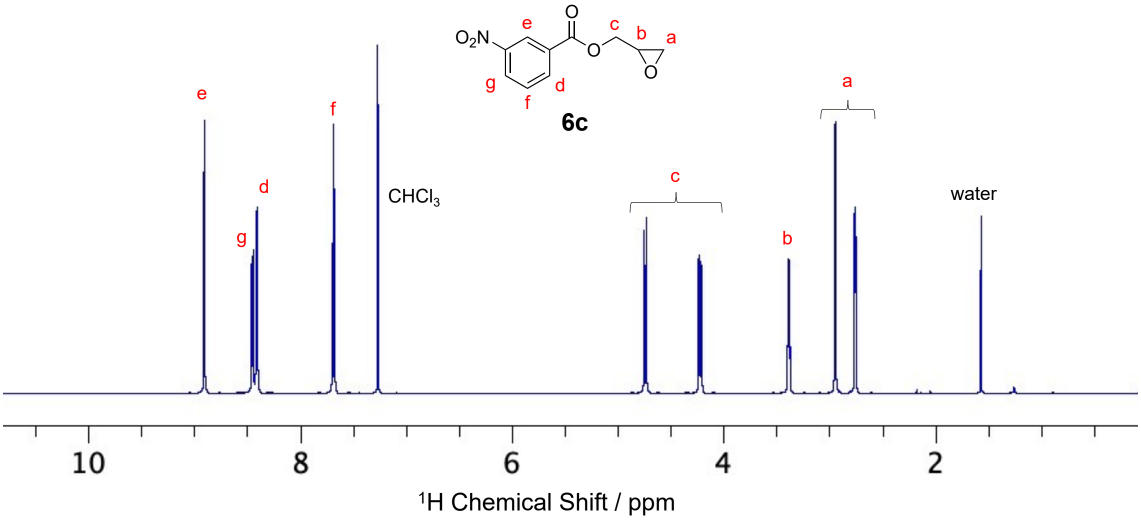


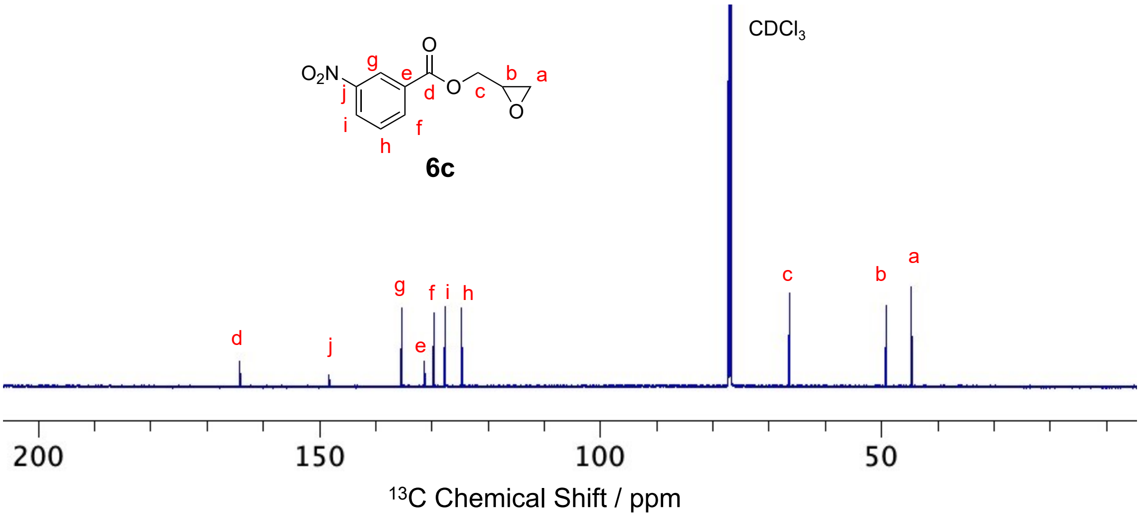
Glycidyl 4-cyanobenzoate (**6b**)



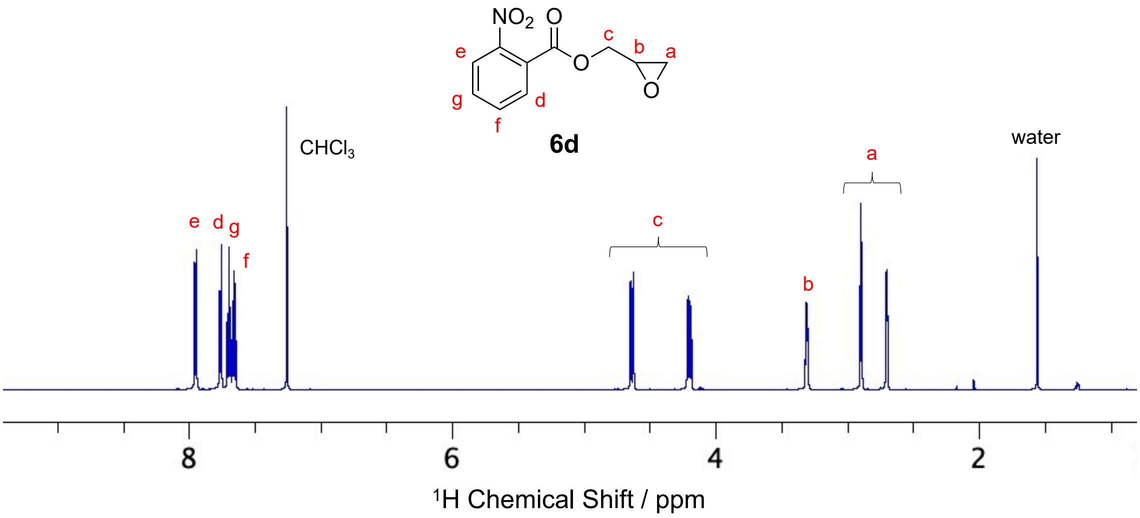


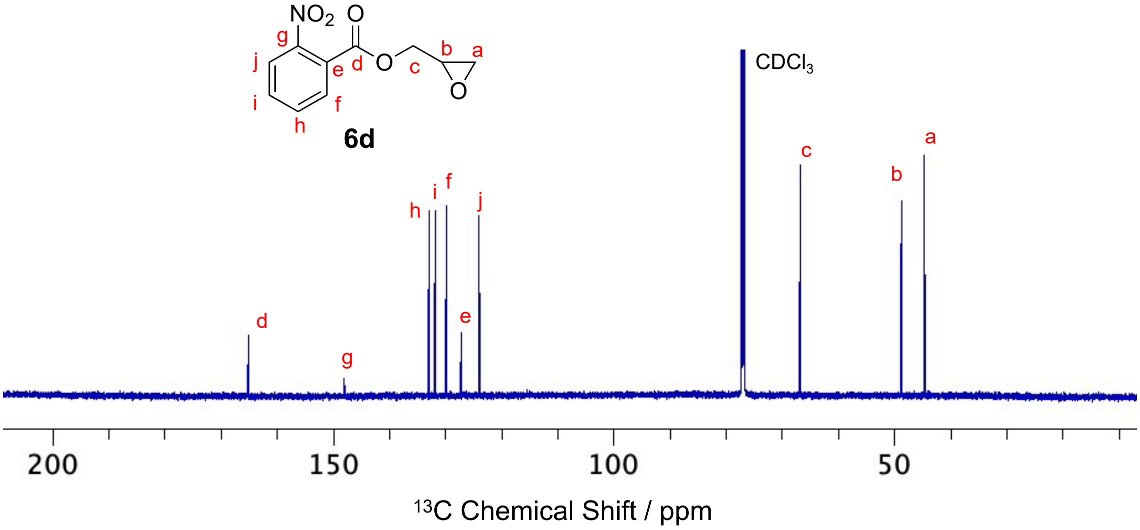
Glycidyl 3-nitrobenzoate (**6c**)



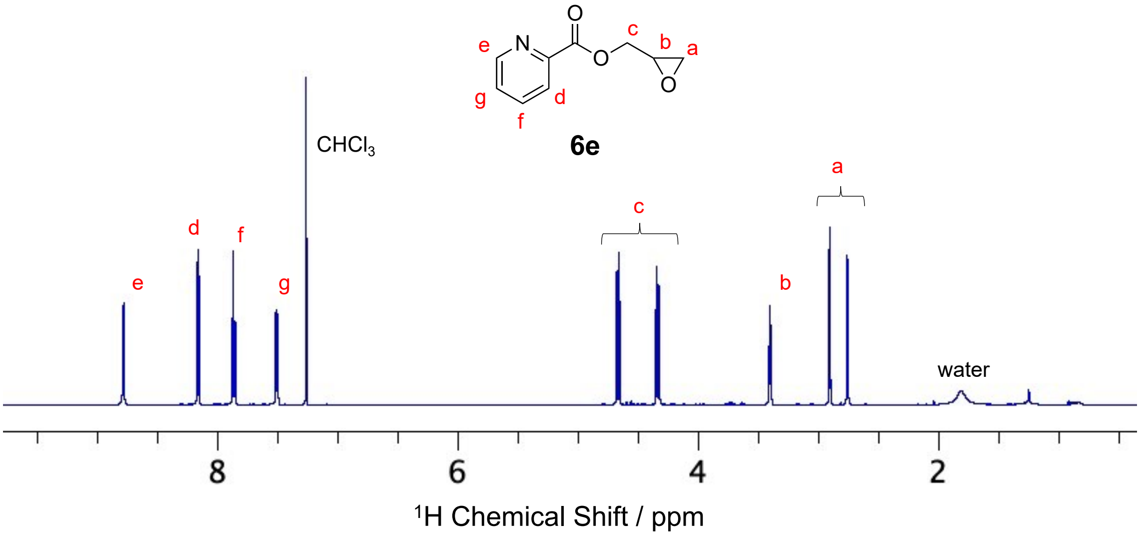


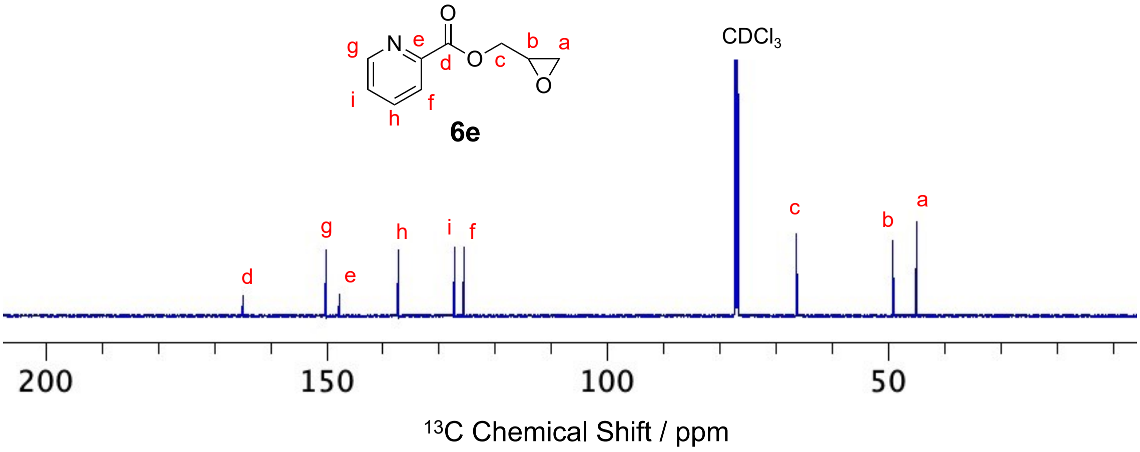
Glycidyl 2-nitrobenzoate (**6d**)



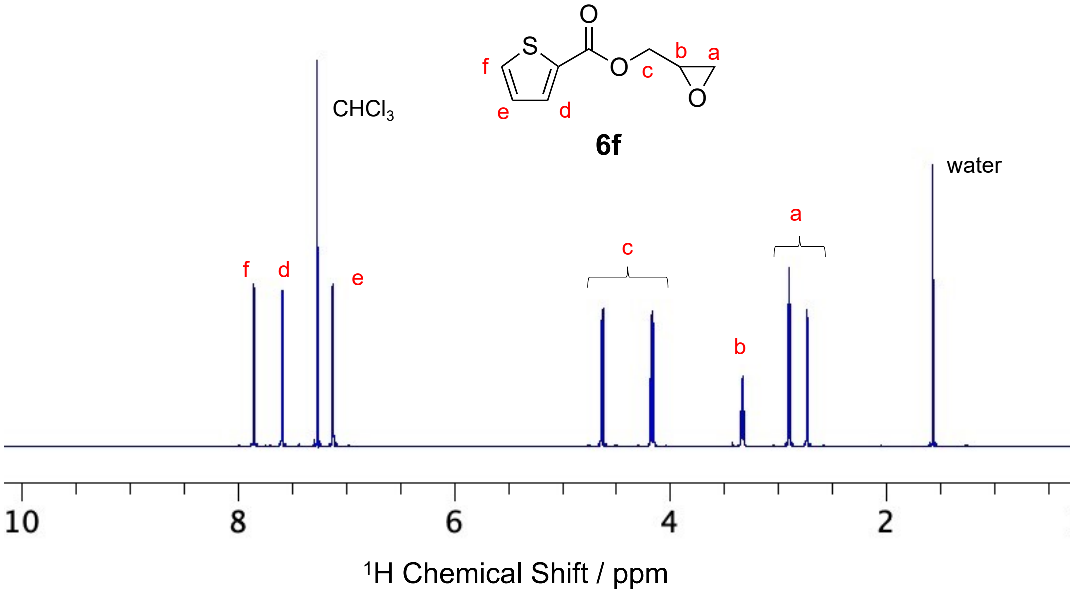


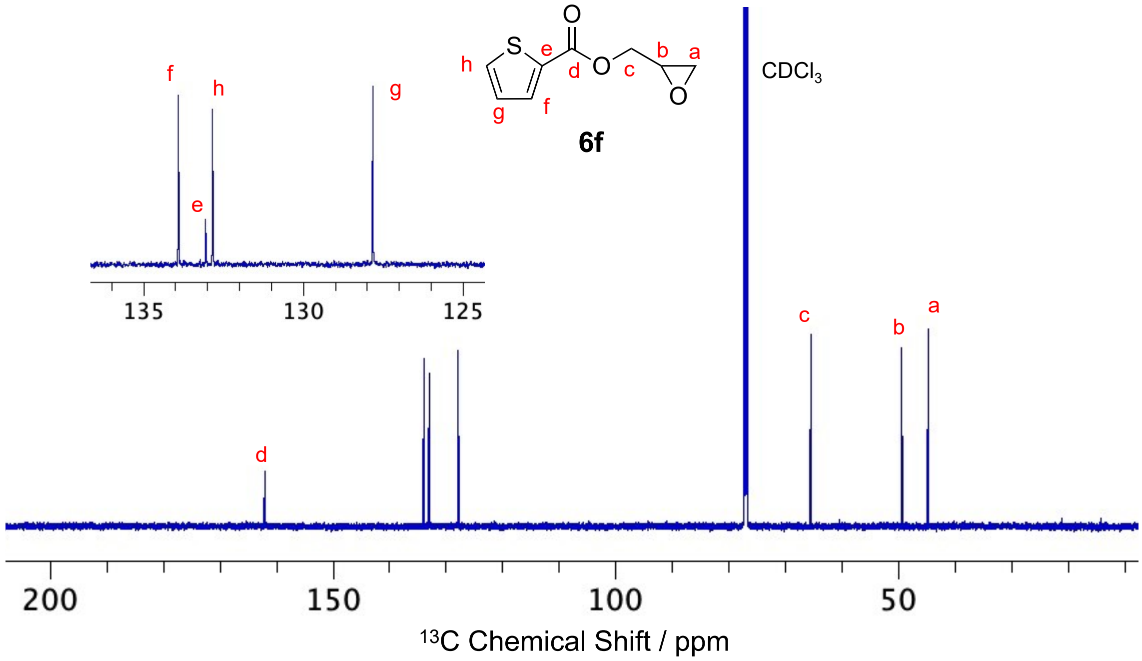
Glycidyl 2-pyridinecarboxylate (**6e**)



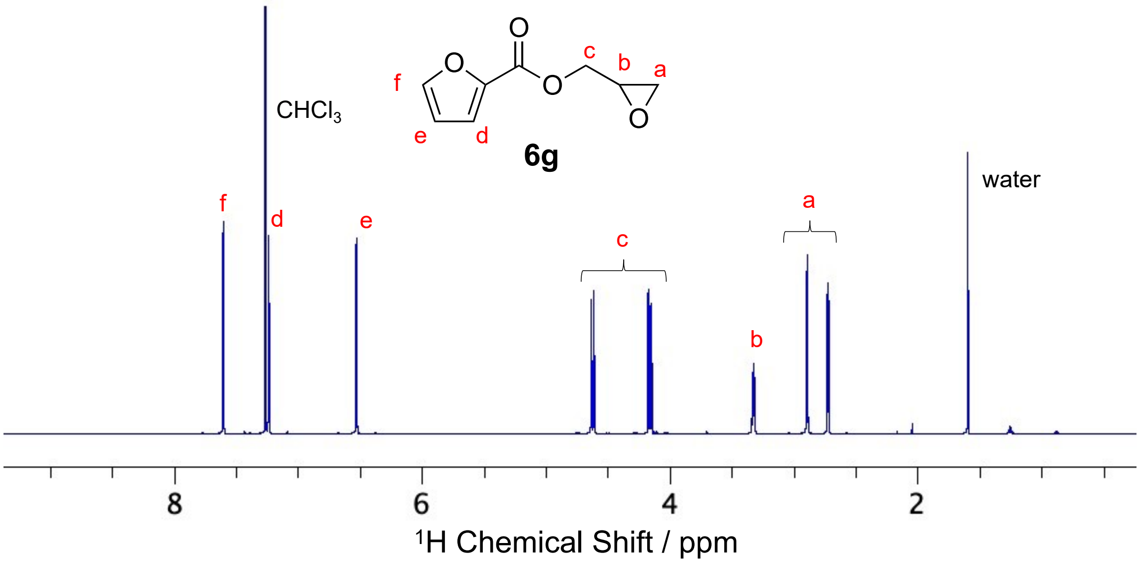


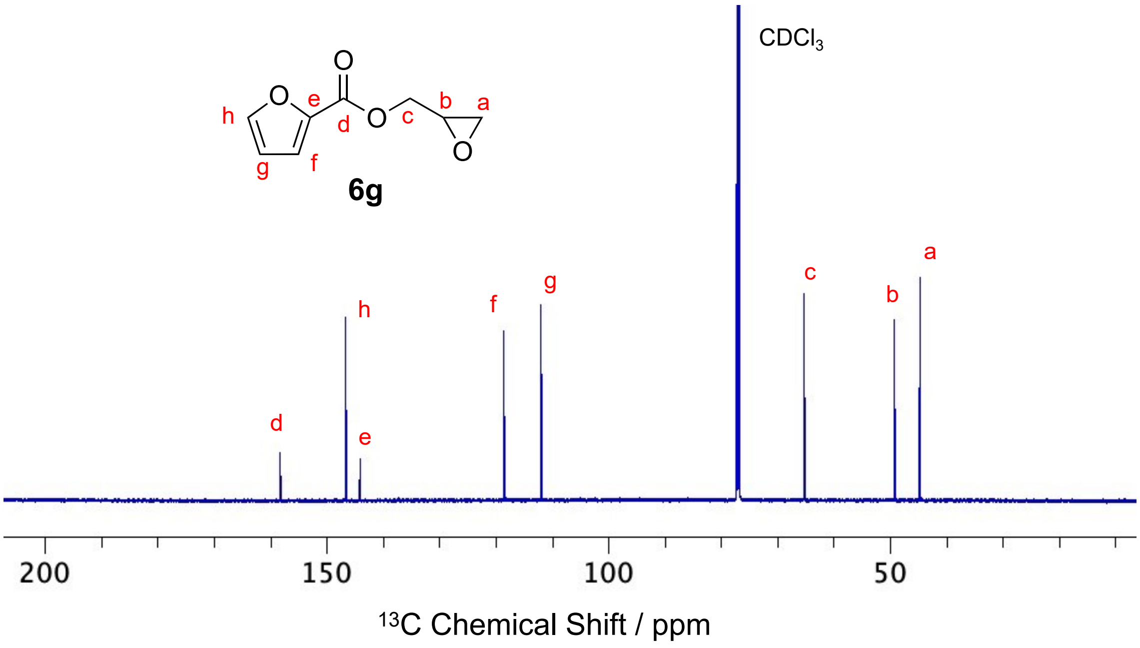
Glycidyl 2-thiophenecarboxylate (**6f**)





Glycidyl 2-furancarboxylate (**6g**)





Diglycidyl 2,4-furandicarboxylate (**6h**)