Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information

Specific Lift-Up Behavior of Acetate-Intercalated Layered Yttrium Hydroxide Interlayer in Water: Application for Heterogeneous Brønsted Base Catalysts toward Knoevenagel Reactions

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General

All chemical compounds were purified by standard procedures before use.[S1] X-Ray diffraction (XRD) measurements were performed on a Rigaku MiniFlex 600 using monochromatic Cu *K*α radiation (λ = 0.15418 nm), and the diffraction data were collected with D/teX Ultra 250 1D detector. The XRD was operated at 40 kV and 15 mA with divergence slit of 0.625°, scattering slit of 1.25°, and receiving slit of 0.30 mm, a step width of 0.02° and a scan speed of 10°/min. Catalytic activity was determined by gas chromatography with a flame ionization detector (FID) equipped with Shimadzu CPB-20 widebore-capillary column (25 m×0.53 mm×1 μm). GC analysis was also performed by GC-2010 with a flame ionization detector equipped with a Shimazu Rtx-5MS capillary column (30 m×0.25 mm×0.25 μm). Gas chromatograph-mass spectroscopy (GC-MS) was performed by Shimadzu GCMS-QP2010 Plus with a thermal conductivity detector equipped with a RESTEK Rtx®-5MS capillary column (30 m×0.25 mm×0.25 μm), and ionizing by electron impact. Products were confirmed by use of GC-MS, FT-IR, and ^{1}H and ^{13}C NMR. ^{1}H and ^{13}C NMR spectroscopy were performed using a JNM-AL400 spectrometer at 400 MHz in $CDCl_3$ with TMS as an internal standard. Fourier transform infrared (FT-IR) analysis was conducted using Shimadzu IRAffinity-1S, equipped with the diffuse reflectance measurement instrument DRS-8000. The sample was diluted with KBr powder and measured at room temperature. TG-DTA was performed using a Rigaku Thermo plus EVOII TG8120 and STAR System TGA/DSC 2 under air flow. Ion chromatography was performed by ICA-2000 (DKK-TOA) equipped with PCI-230 column (DKK-TOA) and chemical suppressor system (SeQuant® SAMS^{TM} Standard Suppressor). 3.2 mM of Na_2CO_3 and 1.0 mM of $NaHCO_3$ was selected for the eluent. 10 mM of H_2SO_4 was also used for the eluent of chemical suppressor.

Gram-scale Knoevenagel reaction between ethylcyanoacetate (1) and benzaldehyde (2)

CH_3COO^-/Y-LRH catalyst (0.05 g) was placed in a reaction vessel, followed by addition of **1** (10 mmol), **2** (10 mmol), acetonitrile (2 mL), and H_2O (8 mL). The reaction mixture was stirred at 333 K. After 3 h, CH_3COO^-/Y-LRH was separated from the reaction mixture by a centrifugation. The supernatant was extracted with diethyl ether and then dried over $MgSO_4$. Removal of diethyl ether under the reduced pressure, followed by recrystallization with *n*-hexane and ethyl acetate, afforded analytically pure (2*E*)-2-

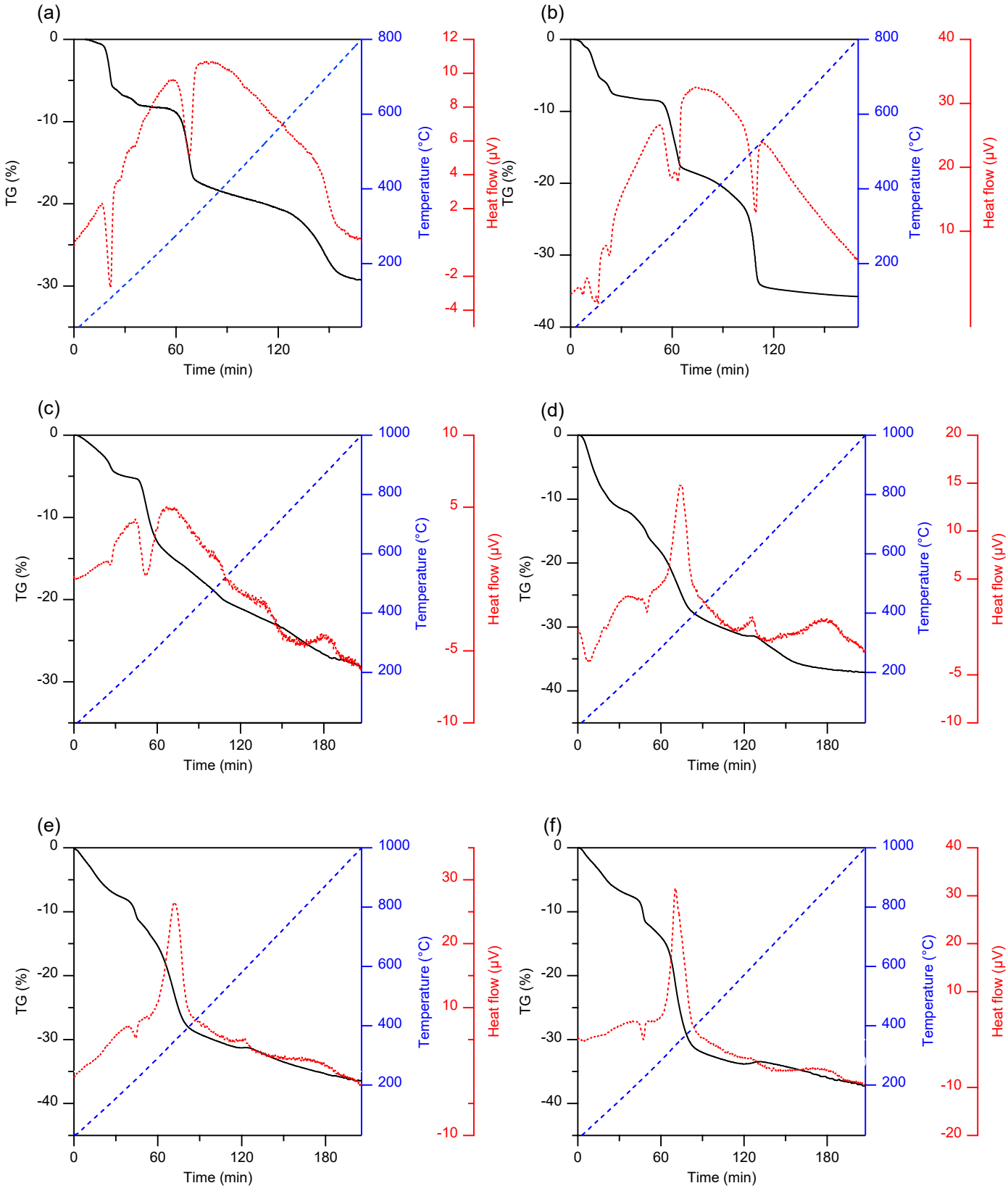
cyano-3-phenyl- 2-propenoic acid ethyl ester (**3**) as a white powder (93% isolated yield): CAS registry number [2025-40-3]; mp 52 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.45 (t, 3H, *J* = 7.1 Hz), 4.42 (q, 2H, *J* = 7.1 Hz), 7.48-7.64 (m, 3H), 8.02 (m, 2H), 7.98-8.08 (s, 1H); ^{13}C NMR (105 MHz, $CDCl_3$) δ 14.2, 62.9, 103.7, 115.3, 128.3, 130.3, 132.3, 132.7, 153.6, 162.3; IR (KBr) 1200, 1610, 2240 cm^{-1}.

Recycling test

After the Knoevenagel reaction, acetonitrile (3 mL) was added to the reaction mixture, then, all of the reaction mixture was transferred into 10 mL of sample tube. The liquid phase and the solid catalyst were separated by simple centrifugation (3500 rpm for 5 min). By use of the same procedure, the solid catalyst was washed with 3 mL of acetonitrile 3-5 times and dried under vacuum overnight. For the next catalytic reaction, the water solvent (5 mL) was added to this sample tube, and all of the aqueous dispersion containing the recovered catalyst was moved into Schlenk tube.

References

S1) W. L. F. Armarego and C. L. L. Chai, *Purification of Laboratory Chemicals*, Elsevier, 2003.


(a)
TG (%)
Temperature (°C)
Heat flow (μV)
Time (min)
(b)
TG (%)
Temperature (°C)
Heat flow (μV)
Time (min)
(c)
TG (%)
Temperature (°C)
Heat flow (μV)
Time (min)
(d)
TG (%)
Temperature (°C)
Heat flow (μV)
Time (min)
(e)
TG (%)
Temperature (°C)
Heat flow (μV)
Time (min)
(f)
TG (%)
Temperature (°C)
Heat flow (μV)
Time (min)

(*Continued*)

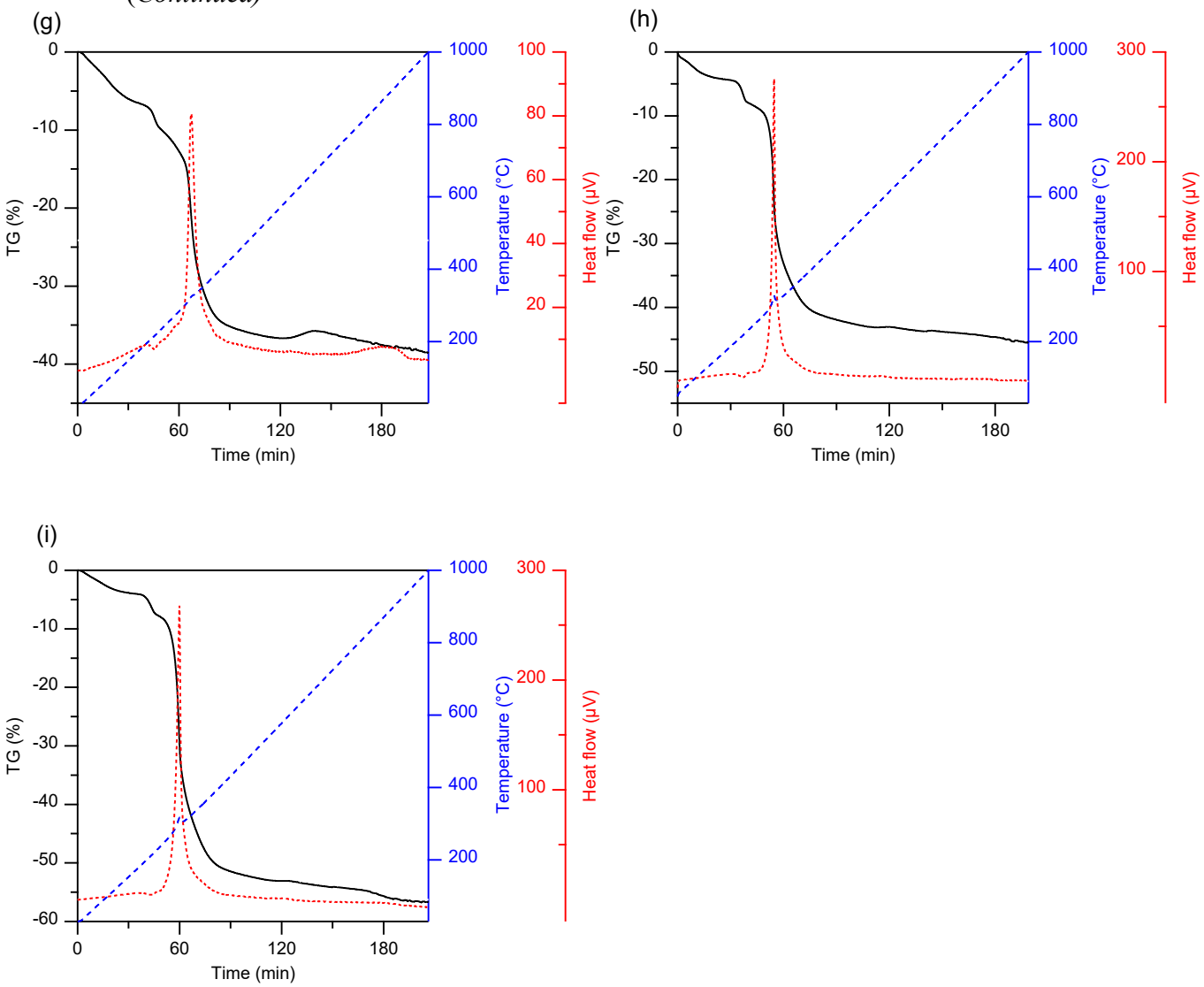


Fig. S1 Thermogravimetric-differential thermal analysis (TG-DTA) for (a) Cl^-/Y-LRH, (b) NO_3^-/Y-LRH, (c) $HCOO^-$/Y-LRH, (d) CH_3COO^-/Y-LRH, (e) $C_2H_5COO^-$/Y-LRH, (f) $C_3H_7COO^-$/Y-LRH, (g) $C_5H_{11}COO^-$/Y-LRH, (h) $C_7H_{15}COO^-$/Y-LRH, and (i) $C_9H_{19}COO^-$/Y-LRH catalyst.
Black curve: TG line, blue line: temperature, and red curve: DTA line.

Table S1. The *n* value and Y^{3+} amount in various Anion/Y-LRH, $Y_2(OH)_5(Anion)\cdot nH_2O$

Entry	Anion	*n*	Y^{3+} amount in 0.05 g (10^{-2} mmol)
1	Cl^-	1.43	7.71
2	NO_3^-	1.60	7.07
3	$HCOO^-$	1.35	7.53
4	CH_3COO^-	1.40	7.20
5	$C_2H_5COO^-$	1.56	6.87
6	$C_3H_7COO^-$	1.30	6.70
7	$C_5H_{11}COO^-$	1.44	6.41
8	$C_7H_{15}COO^-$	1.22	6.25
9	$C_9H_{19}COO^-$	1.04	6.09

[a] Determined by TG-DTA and ion-chromatography

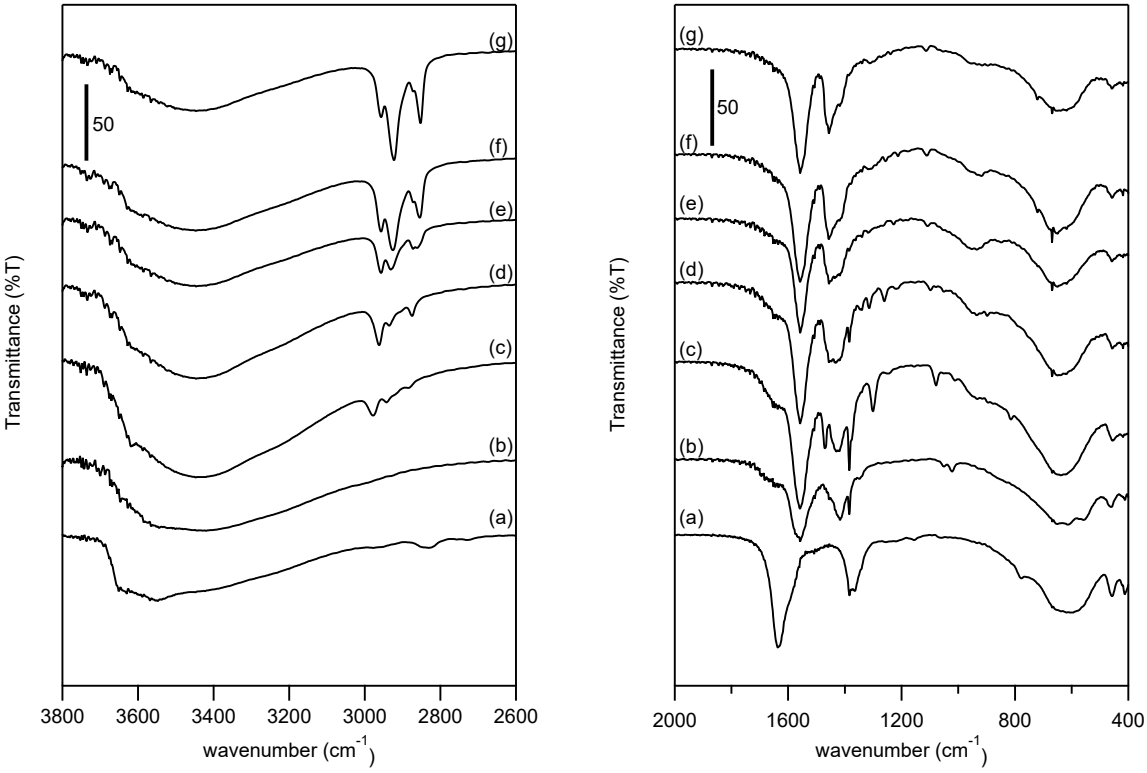


Fig. S2 FT-IR spectra for (a) $HCOO^-$/Y-LRH, (b) CH_3COO^-/Y-LRH, (c) $C_2H_5COO^-$/Y-LRH, (d) $C_3H_7COO^-$/Y-LRH, (e) $C_5H_{11}COO^-$/Y-LRH, (f) $C_7H_{15}COO^-$/Y-LRH, and (g) $C_9H_{19}COO^-$/Y-LRH catalyst.

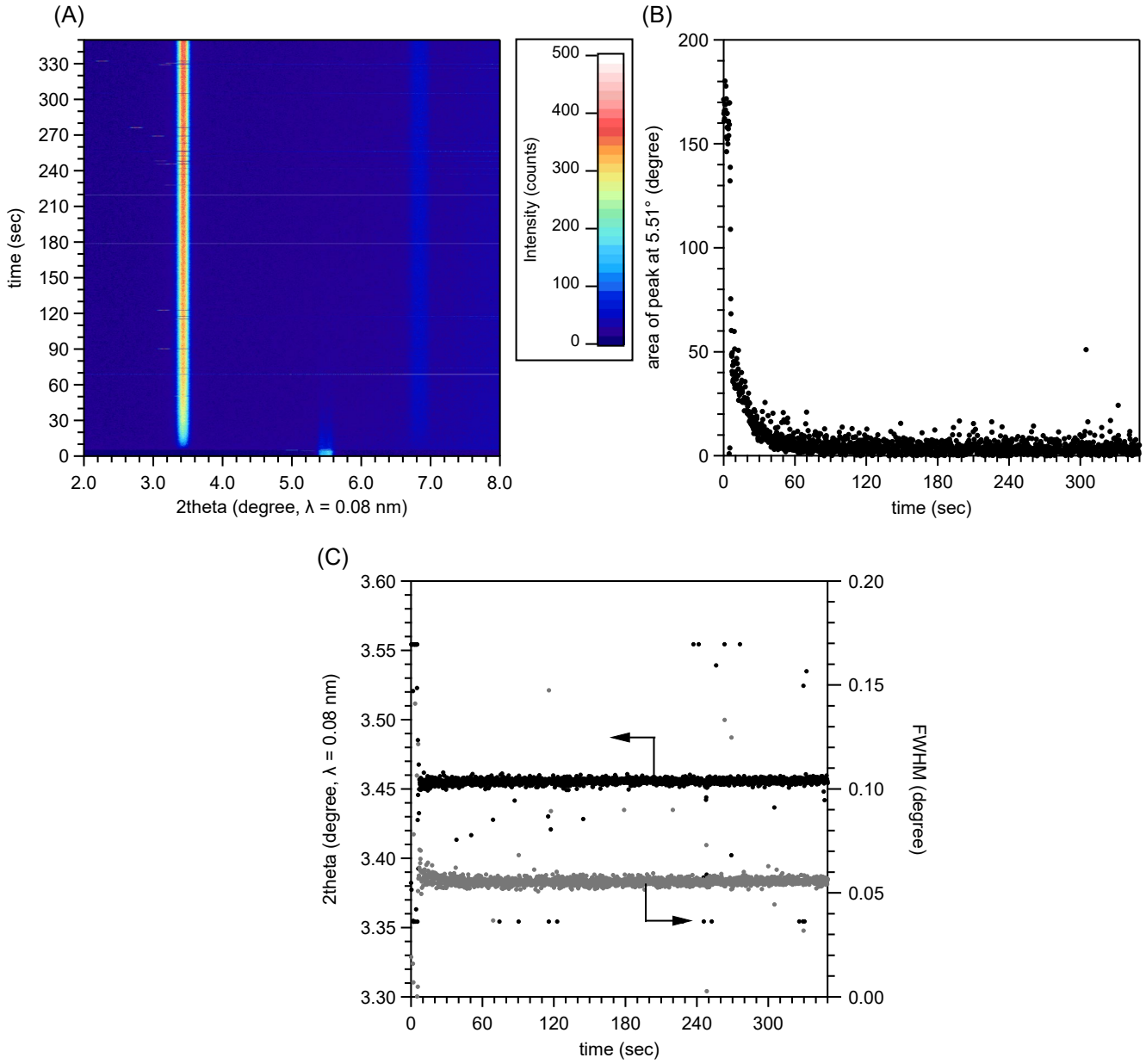


Fig. S3 (A) 2D mapping plots of the *t*-SXRD patterns of Y-LRH during anion-exchange reaction from Cl^- into CH_3COO^-. (B) Time profile of the disappeared peak area at 5.51° in *t*-SXRD. (C) The peak position and FWHM values of newly appeared peak at 3.45°.

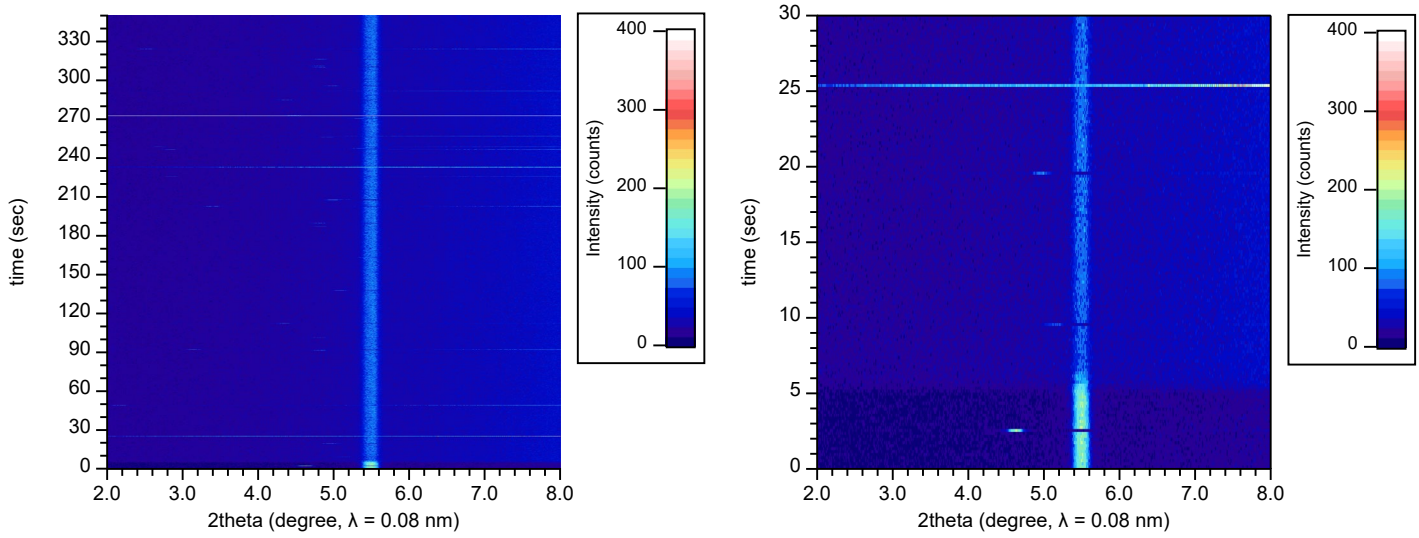


Fig. S4 2D mapping plots of the *t*-SXRD patterns of Cl^{-}/Y-LRH. After 5 sec, 2 mL of water was added in the slurry of Cl^{-}/Y-LRH (0.05 g) and water (0.5 mL).

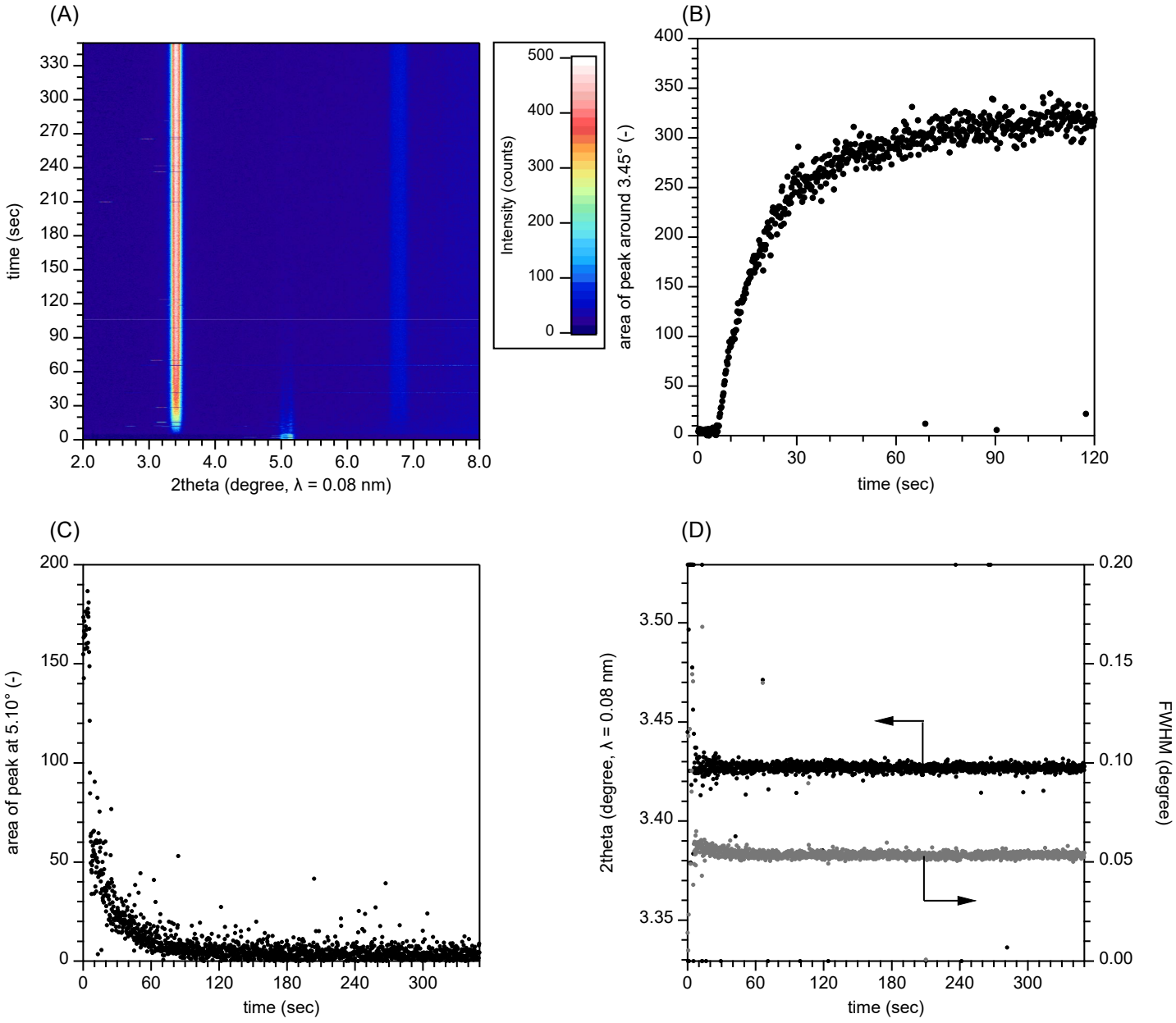


Fig. S5 (A) 2D mapping plots of the *t*-SXRD patterns of Y-LRH during anion-exchange reaction from NO_3^- into CH_3COO^-. (B) Time profile of the newly appeared peak area at 3.43° in *t*-SXRD. (C) Time profile of the disappeared peak area at 5.10° in *t*-SXRD. (D) The peak position and FWHM values of newly appeared peak at 3.43°.

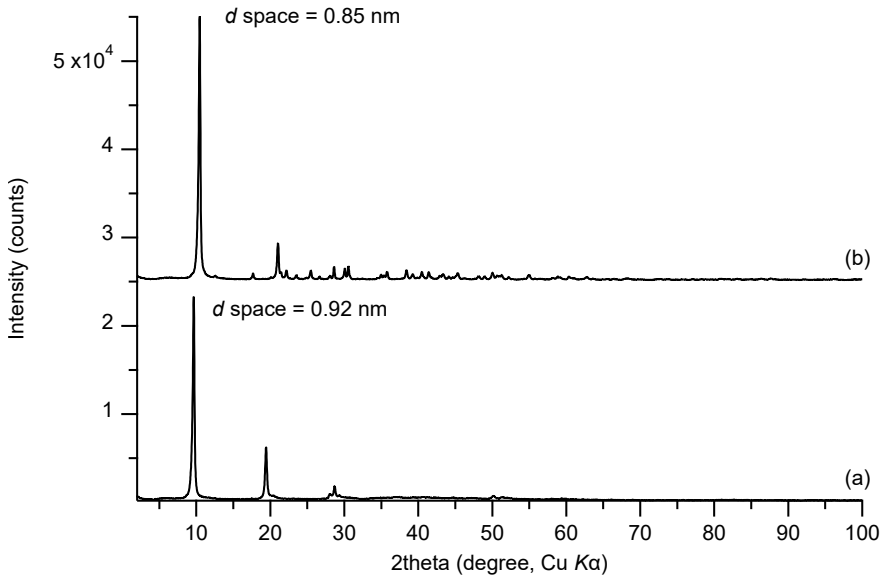


Fig. S6 XRD profiles for (a) NO_3^-/Y-LRH and (b) Cl^-/Y-LRH catalyst

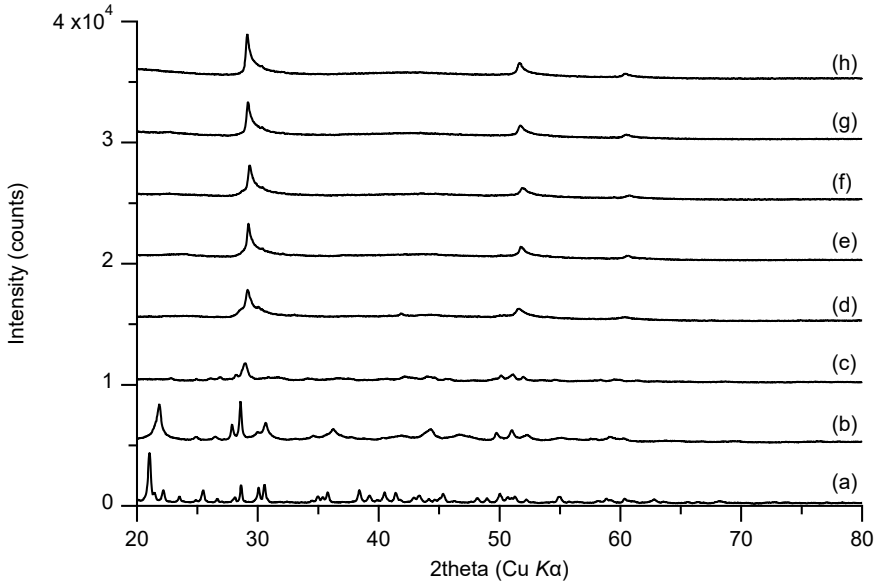


Fig. S7 XRD profiles for (a) Cl^-/Y-LRH, (b) $HCOO^-$/Y-LRH, (c) CH_3COO^-/Y-LRH, (d) $C_2H_5COO^-$/Y-LRH, (e) $C_3H_7COO^-$/Y-LRH, (f) $C_5H_{11}COO^-$/Y-LRH, (g) $C_7H_{15}COO^-$/Y-LRH, and (h) $C_9H_{19}COO^-$/Y-LRH catalyst.

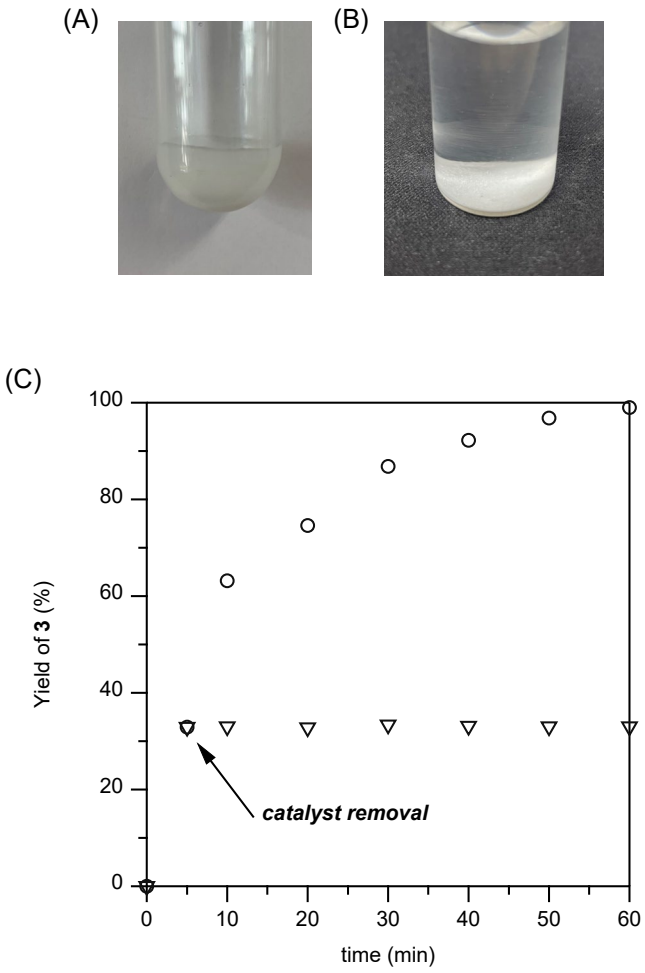


Fig. S8 (A) Photoimages of CH_3COO^-/Y-LRH catalyst: (A) during reaction and (B) after centrifugation. (C) Hot filtration experiment. reaction conditions were as follows: CH_3COO^-/Y-LRH catalyst (0.05 g), **1** (1.5 mmol), **2** (1 mmol), H_2O (5 mL), 303 K. Yield was based on **2**, determined by GC.

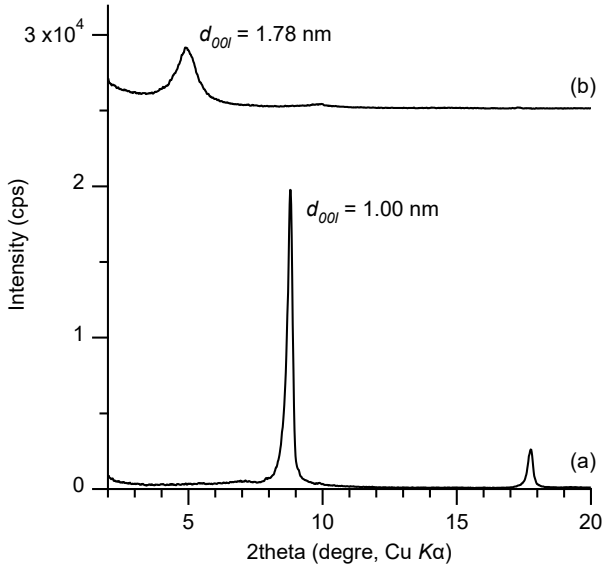


Fig. S9 XRD profiles for (a) fresh CH_3COO^-/Y-LRH in dry state and (b) recovered CH_3COO^-/Y-LRH in dry state. Values in graph were d_{00l} space, calculated by the Bragg equation

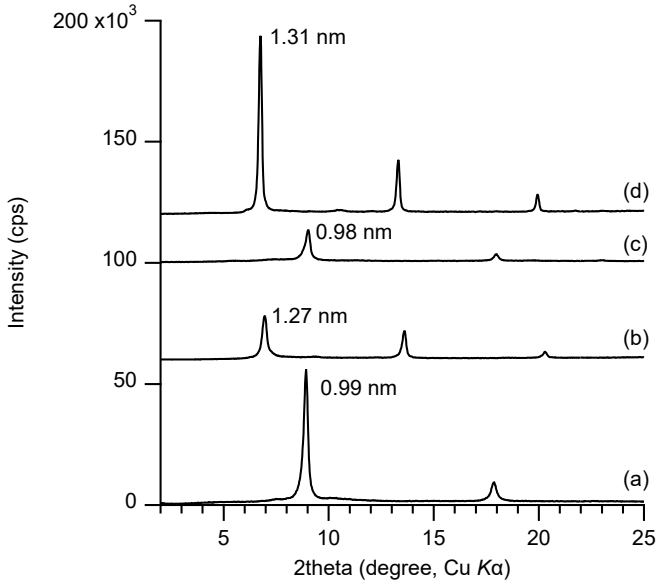


Fig. S10 XRD profiles for (a) dry CH_3COO^-/Gd-LRH, (b) wet CH_3COO^-/Gd-LRH, (c) dry CH_3COO^-/Yb-LRH, and (d) wet CH_3COO^-/Yb-LRH. Values in graph were d_{00l} space, calculated by the Bragg equation.

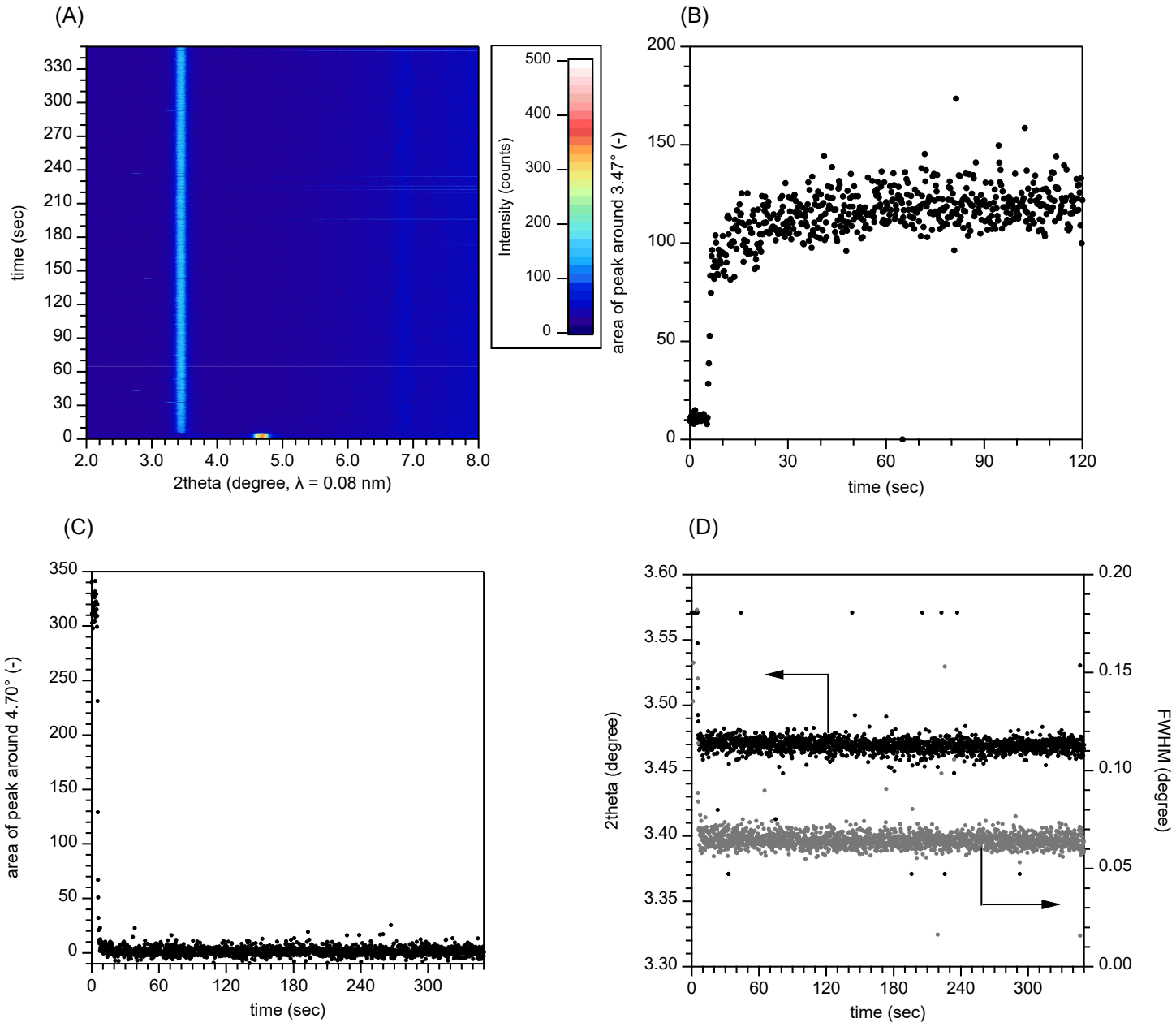


Fig. S11 (A) 2D mapping plots of the *t*-SXRD patterns of CH_3COO^-/Y-LRH during the interlayer lift-up process. Arrows indicated the start point of addition of water into solid dispersion in acetonitrile solution. (B) Time profile of the newly appeared peak area at 3.47° in *t*-SXRD. (C) Time profile of the disappeared peak area at 4.70° in *t*-SXRD. (D) The peak position and FWHM values of newly appeared peak at 3.47°.

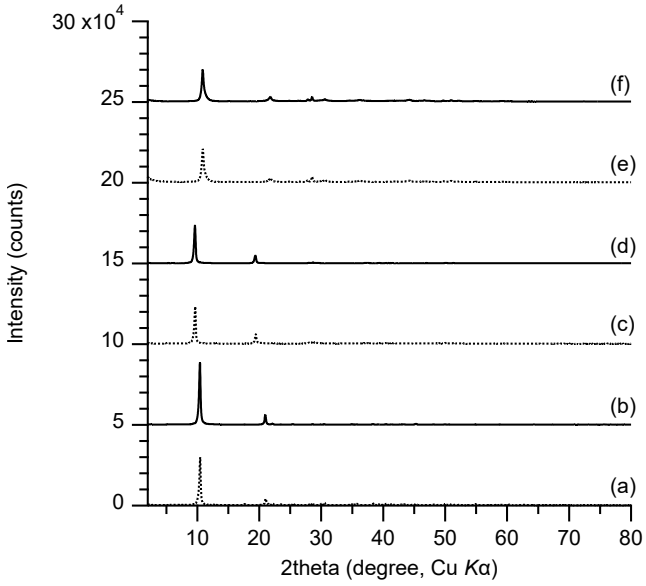


Fig. S12 XRD profiles for (a) dry Cl^-/Y-LRH, (b) wet Cl^-/Y-LRH, (c) dry NO_3^-/Y-LRH, (d) wet NO_3^-/Y-LRH, (e) dry $HCOO^-$/Y-LRH, and (f) wet $HCOO^-$/Y-LRH,

Table S2. Kinetic rate constants for the Knoevenagel condensation with CH_3COO^-/Y-LRH catalyst[a]

T (K)	T^{-1} (10^{-3} K^{-1})	k (M^{-1}·min^{-1})	ln k (-)
303	3.300	0.2547	-1.3677
313	3.195	0.3220	-1.1332
323	3.096	0.3947	-0.9296
333	3.003	0.4987	-0.7160
343	2.915	0.5947	-0.5197

[a] CH_3COO^-/Y-LRH catalyst (0.01 g), **1** (1 mmol), **2** (1 mmol), H_2O (5 mL), 5 min.

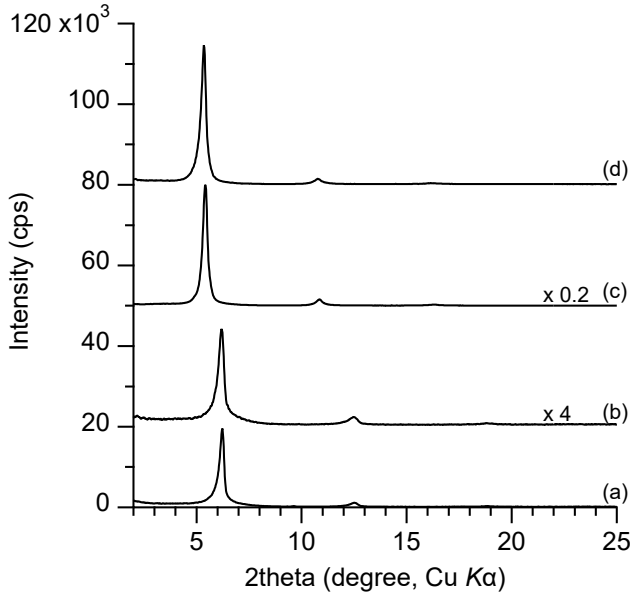
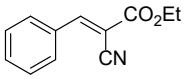
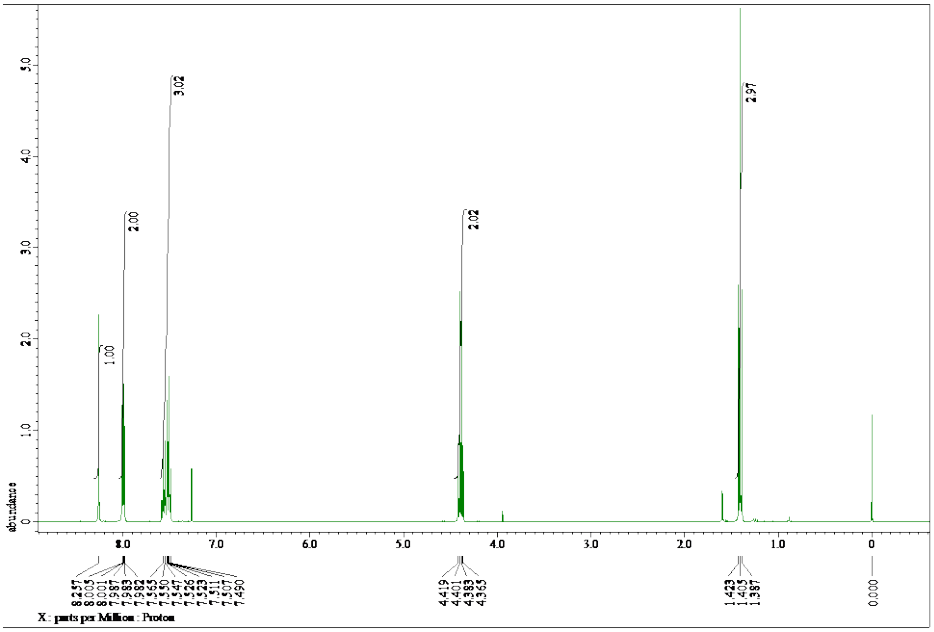


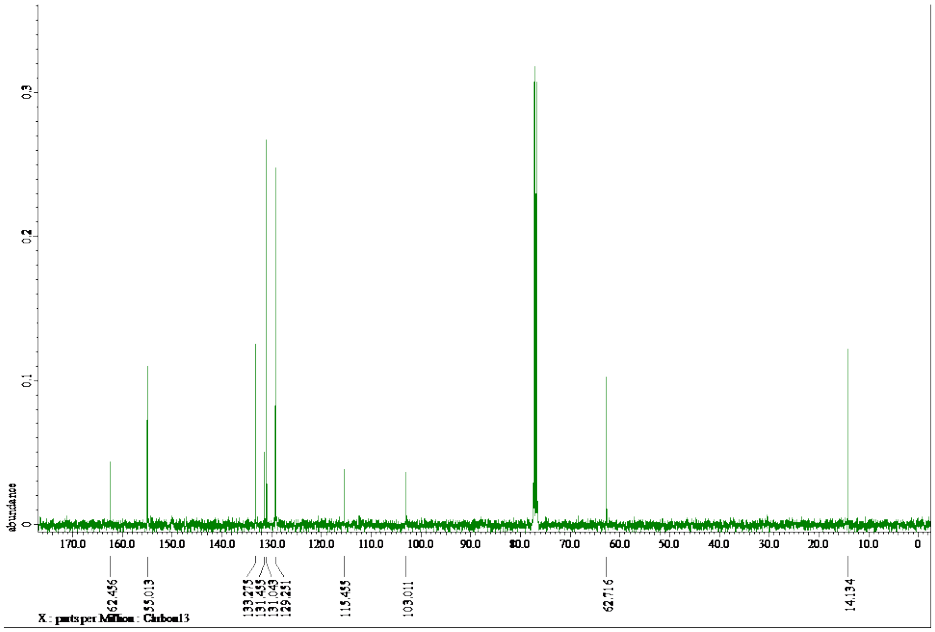
Fig. S13 XRD profiles for (a) dry $C_2H_5COO^-$/Y-LRH, (b) wet $C_2H_5COO^-$/Y-LRH, (c) dry $C_3H_7COO^-$/Y-LRH and (d) wet $C_3H_7COO^-$/Y-LRH catalyst

Ethyl (*E*)-2-cyano-3-phenyl-2-propenoate (CAS: 2169-69-9)

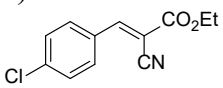


A white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 1.41 (t, J = 7.2 Hz, 3H), 4.39 (q, J = 7.2 Hz, 2H), 7.49-7.57 (m, 3H), 8.00 (d, J = 7.2 Hz, 2H), 8.26 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δppm: 14.1, 62.7, 103.0, 115.5, 129.3, 131.0, 131.5, 133.3, 155.0, 162.5.



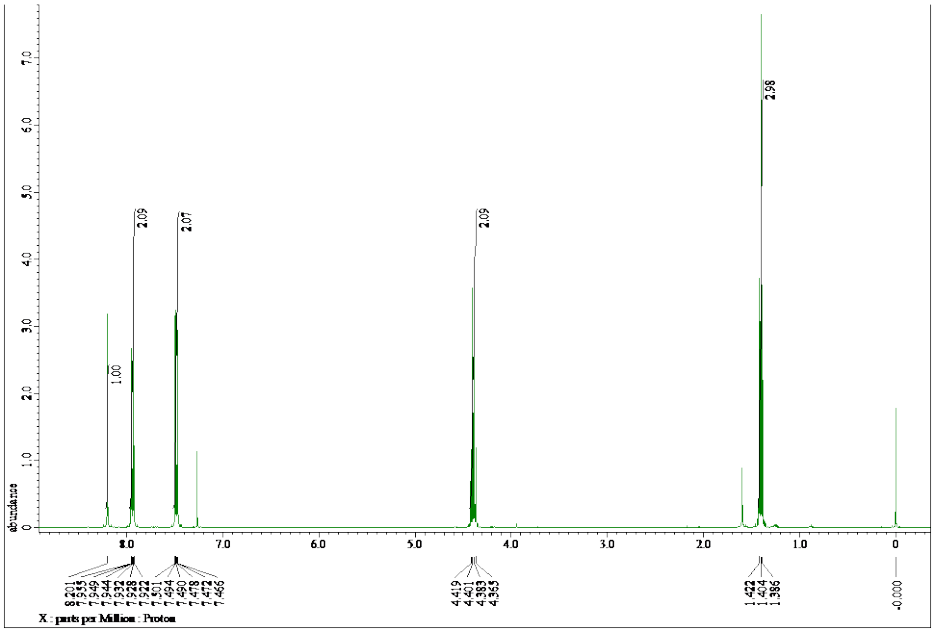


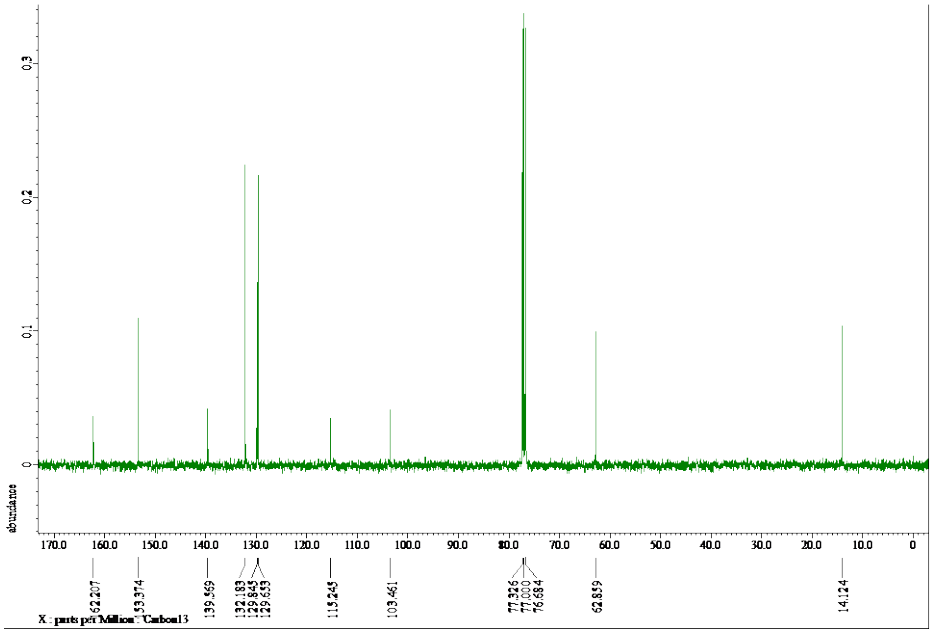
Ethyl (*E*)-2-cyano-3-(4-chlorophenyl)-2-propenoate (CAS: 2169-68-8)



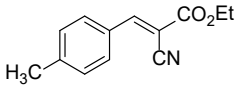
A white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 1.40 (t, J = 7.2 Hz, 3H), 4.39 (q, J = 7.2 Hz, 2H), 7.48 (d, J = 8.8 Hz, 2H), 7.94 (d, J = 8.4 Hz, 2H), 8.20 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δppm: 14.1, 62.6, 103.5, 115.2, 129.7, 129.8, 132.2, 139.6, 153.4, 162.2.



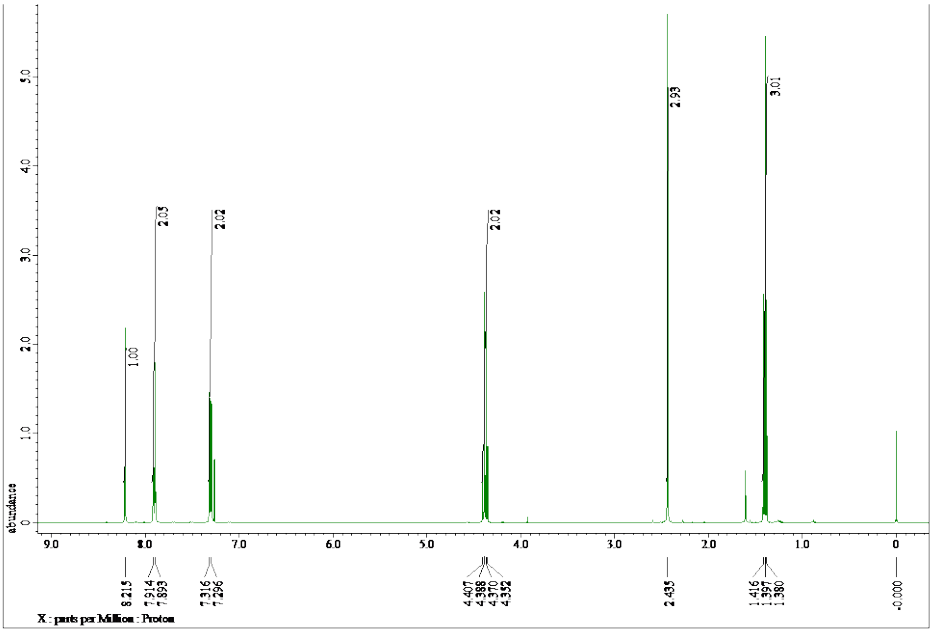


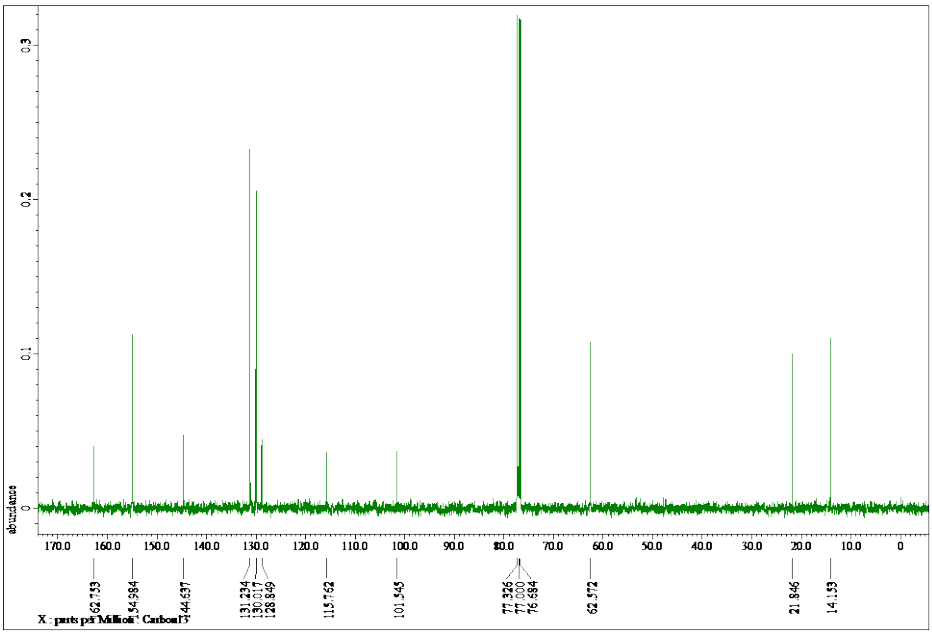
Ethyl (*E*)-2-cyano-3-(4-methylphenyl)-2-propenoate (CAS: 2017-88-1)



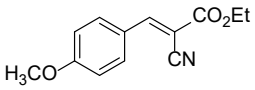
A white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 1.40 (t, J = 7.6 Hz, 3H), 2.44 (s, 3H), 4.38 (q, J = 7.6 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.90 (d, J = 8.4 Hz, 2H), 8.22 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 14.2, 21.8, 62.6, 101.5, 115.8, 128.8, 130.0, 131.2, 144.6, 155.0, 162.8.



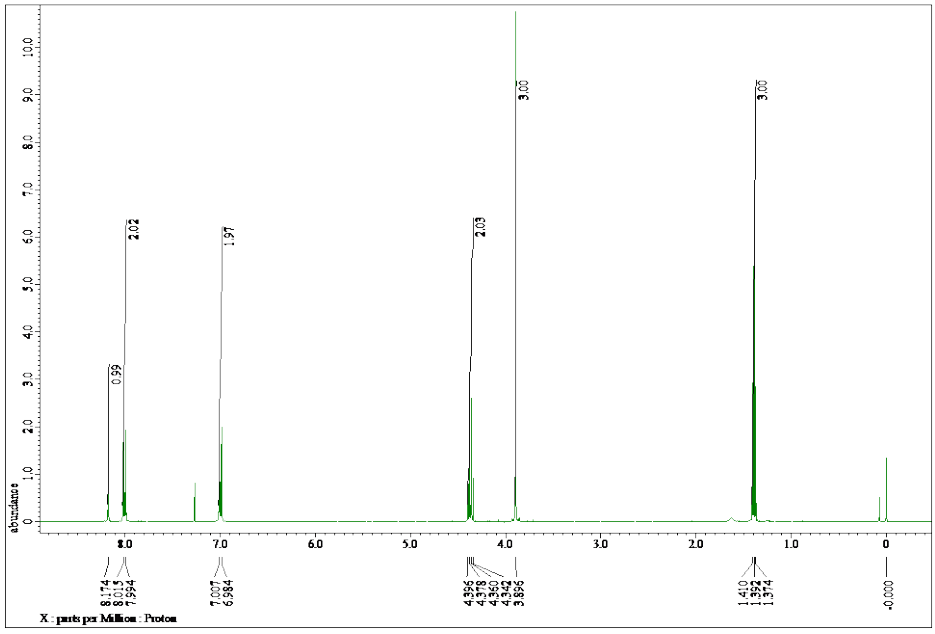


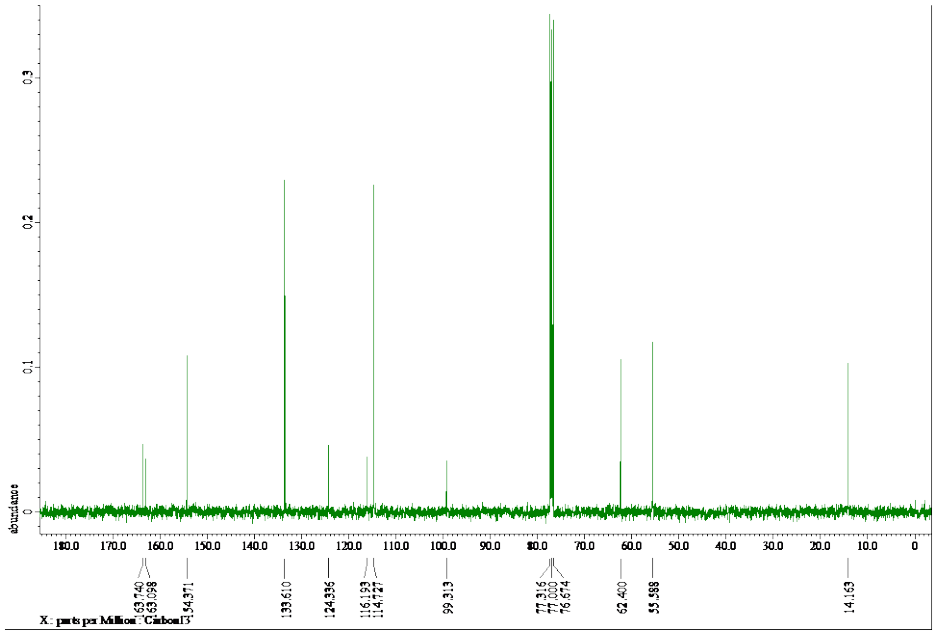
Ethyl (*E*)-2-cyano-3-(4-methoxyphenyl)-2-propenoate (CAS: 2017-87-0)



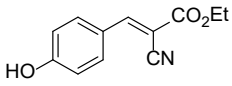
A yellow crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 1.39 (t, *J* = 8.0 Hz, 3H), 3.90 (s, 3H), 4.37 (q, *J* = 7.2 Hz, 2H), 7.00 (d, *J* = 9.2 Hz, 2H), 8.00 (d, *J* = 8.4 Hz, 2H), 8.17 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 14.2, 55.6, 62.4, 99.3, 114.7, 116.2, 124.3, 133.6, 154.4, 163.1, 163.7.



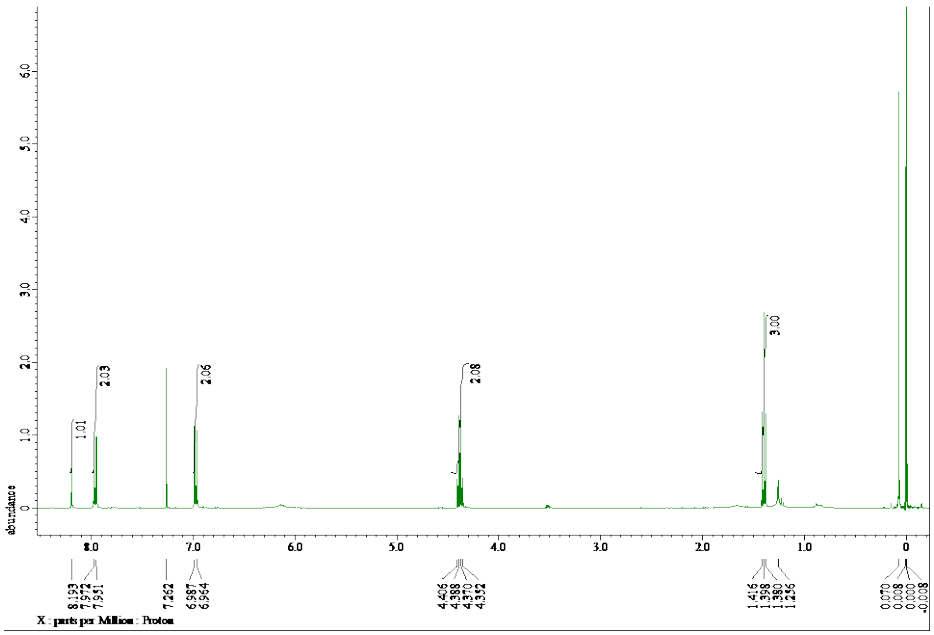


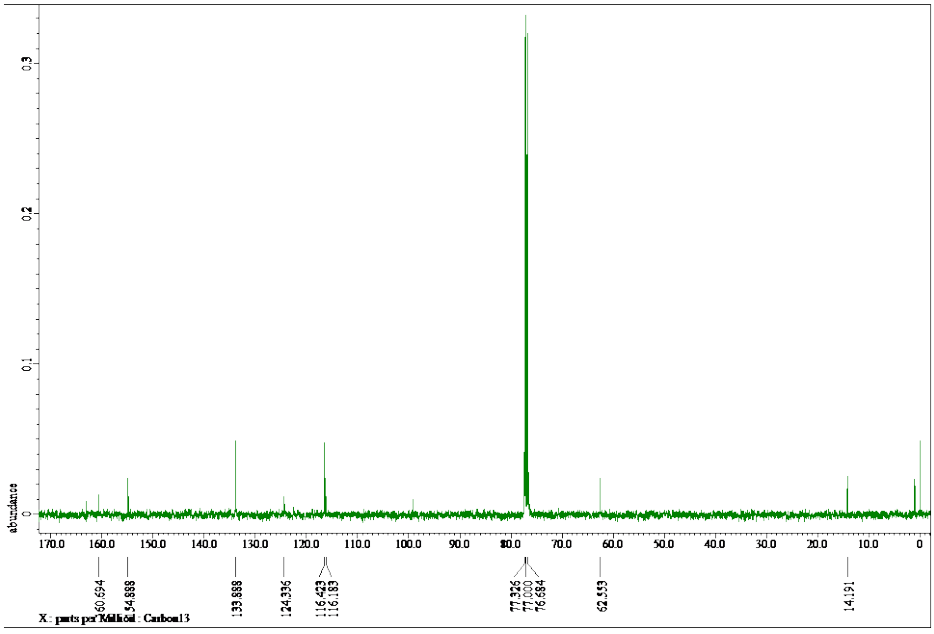
Ethyl (*E*)-2-cyano-3-(4-hydroxyphenyl)-2-propenoate (CAS: 42205-38-9)



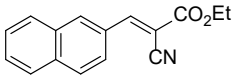
A yellow crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 1.39 (t, *J* = 7.2 Hz, 3H), 4.38 (q, *J* = 7.2 Hz, 2H), 6.98 (d, *J* = 9.2 Hz, 2H), 7.96 (d, *J* = 8.4 Hz, 2H), 8.19 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 14.2, 62.6, 99.2, 116.2, 116.4, 124.3, 133.9, 154.9, 160.7.



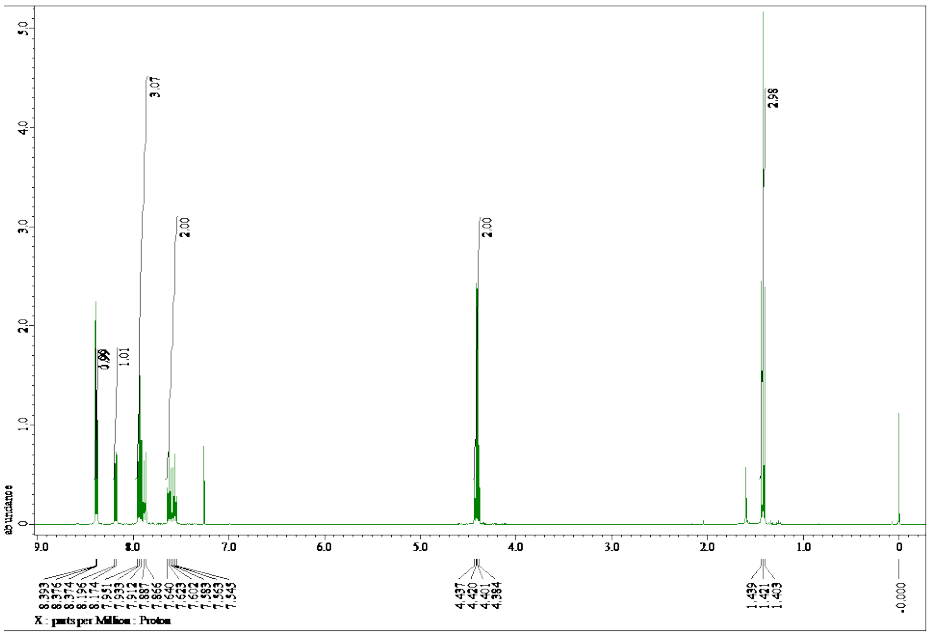


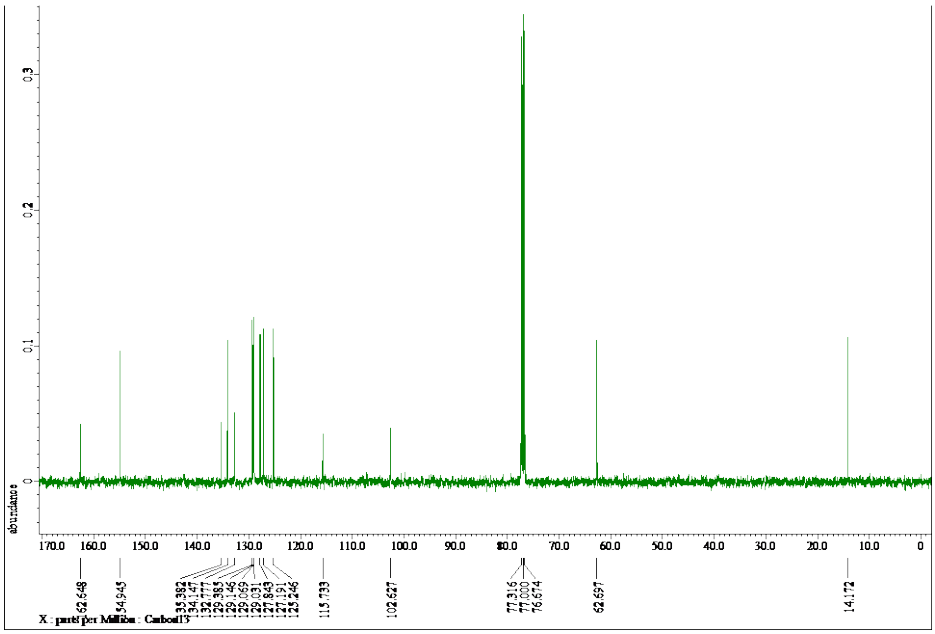
Ethyl (*E*)-2-cyano-3-(1-naphthyl)-2-propenoate (CAS: 29708-01-8)



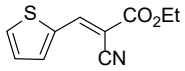
A light yellow needle. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 1.42 (t, *J* = 7.2 Hz, 3H), 4.41 (q, *J* = 6.8 Hz, 2H), 7.55-7.64 (m, 2H), 7.87-7.95 (m, 3H), 8.17-8.20 (m, 1H), 8.37-8.38 (m, 1H), 8.39 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 14.2, 62.7, 102.6, 115.7, 125.2, 127.2, 127.8, 129.0, 129.1, 129.1, 129.4, 132.8, 134.1, 135.4, 154.9, 162.6.



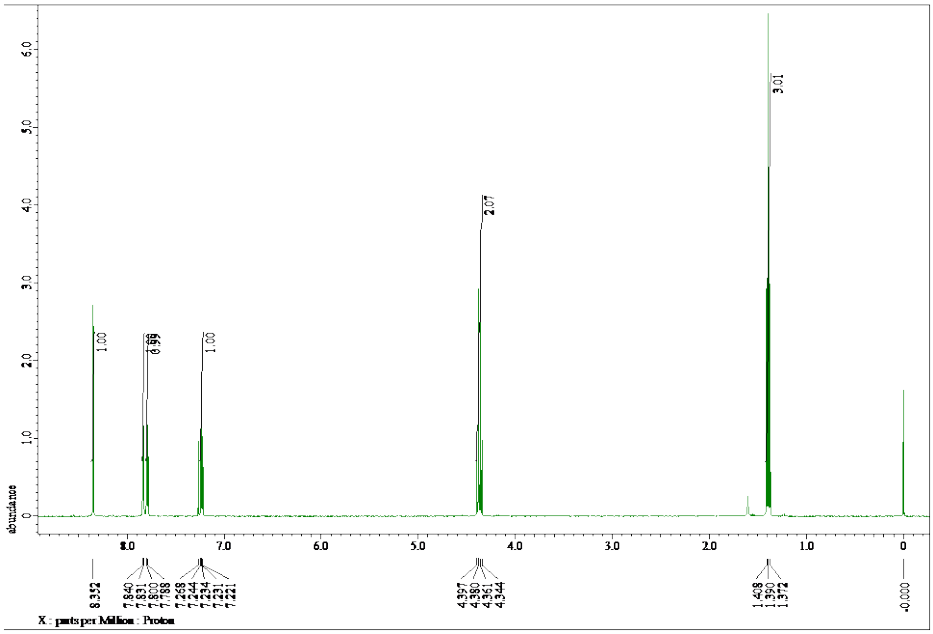


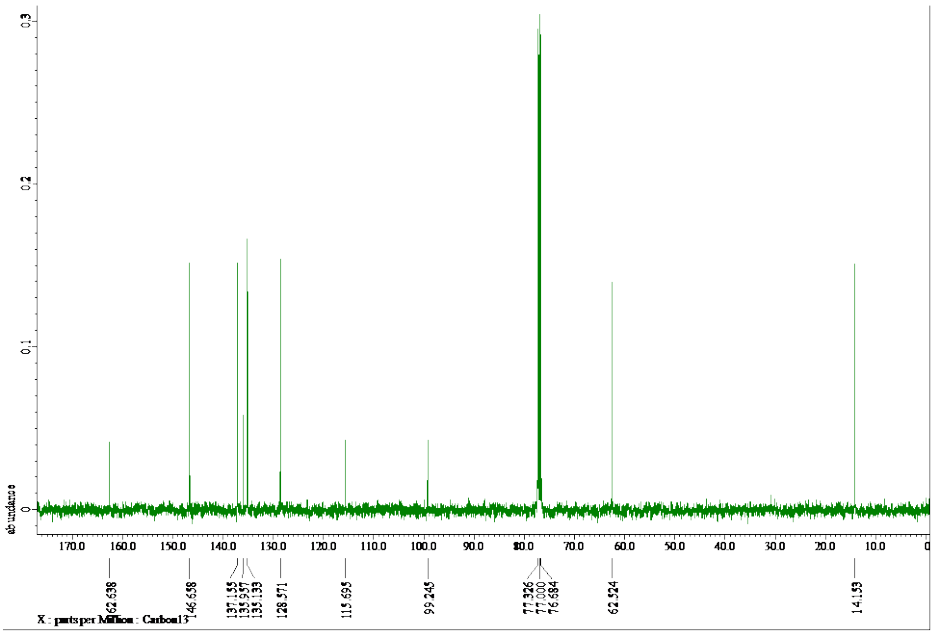
Ethyl (*E*)-2-cyano-3-(2-thienyl)-2-propenoate (CAS: 62309-97-1)



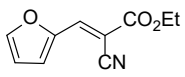
A pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 1.39 (t, *J* = 7.2 Hz, 3H), 4.37 (q, *J* = 6.8 Hz, 2H), 7.22-7.24 (m, 1H), 7.79 (d, *J* = 4.8 Hz, 1H), 7.84 (d, *J* = 3.6 Hz, 1H), 8.35 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 14.2, 62.5, 99.2, 115.7, 128.6, 135.1, 136.0, 137.2, 146.7, 162.7.



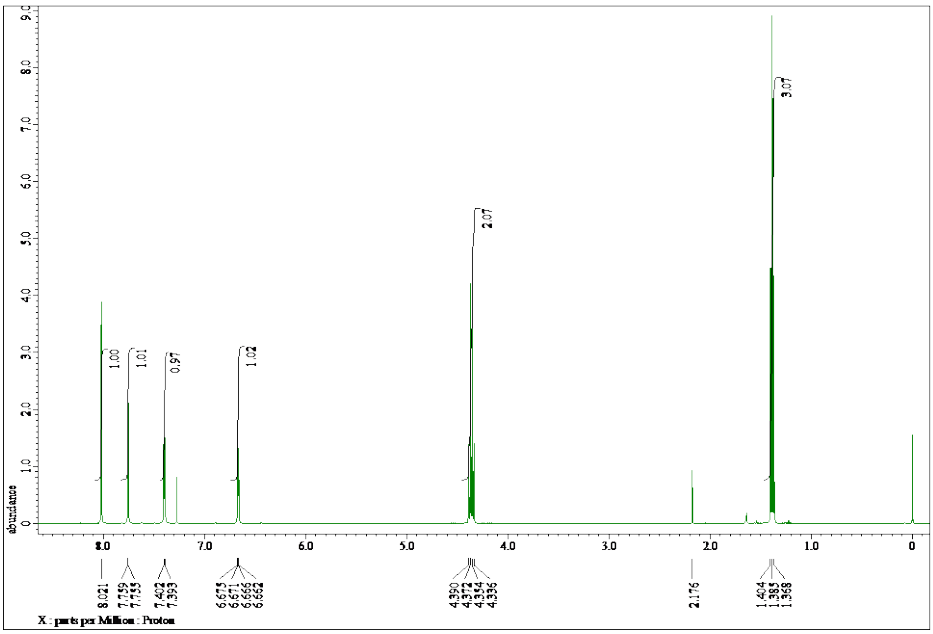


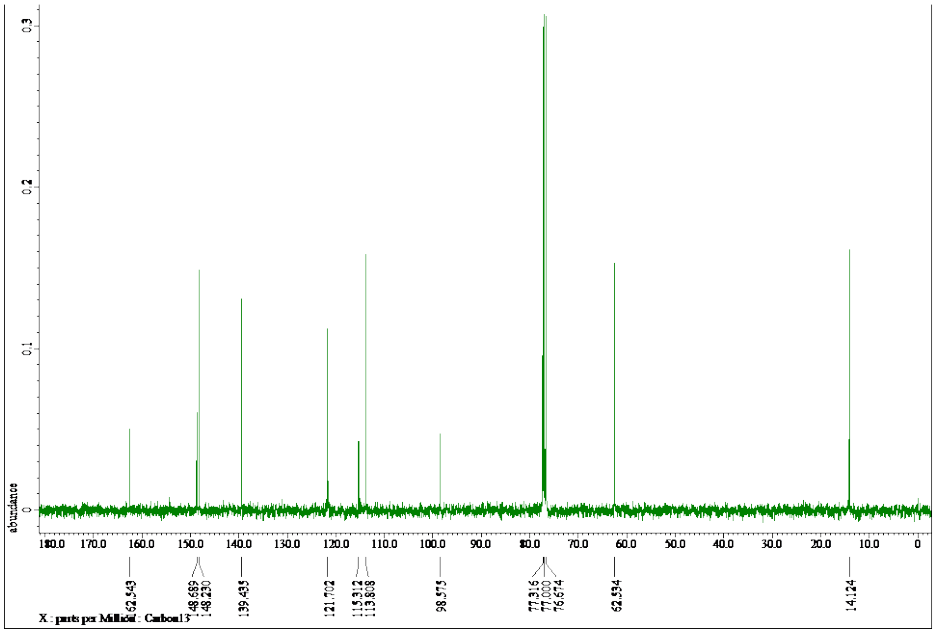
Ethyl (*E*)-2-cyano-3-(2-furanyl)-2-propenoate (CAS: 67449-75-6)



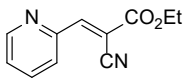
An orange pillar. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 1.39 (t, J = 7.6 Hz, 3H), 4.36 (q, J = 7.2 Hz, 2H), 6.66-6.68 (m, 1H), 7.40 (d, J = 3.6 Hz, 1H), 7.77 (d, J = 1.6 Hz, 1H), 8.02 (s, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 14.1, 62.5, 98.6, 113.8, 115.3, 121.7, 139.4, 148.2, 148.7, 162.5.



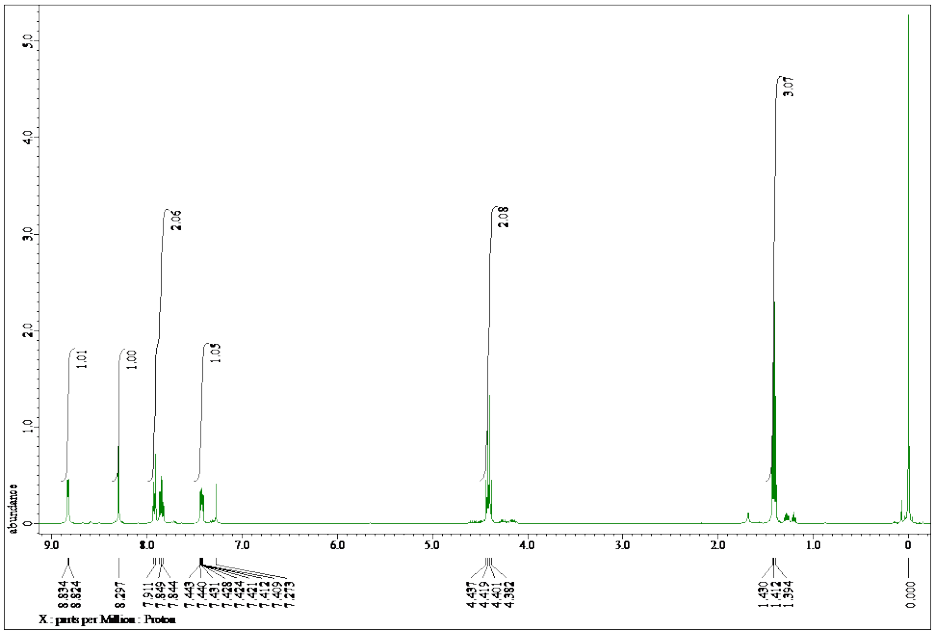


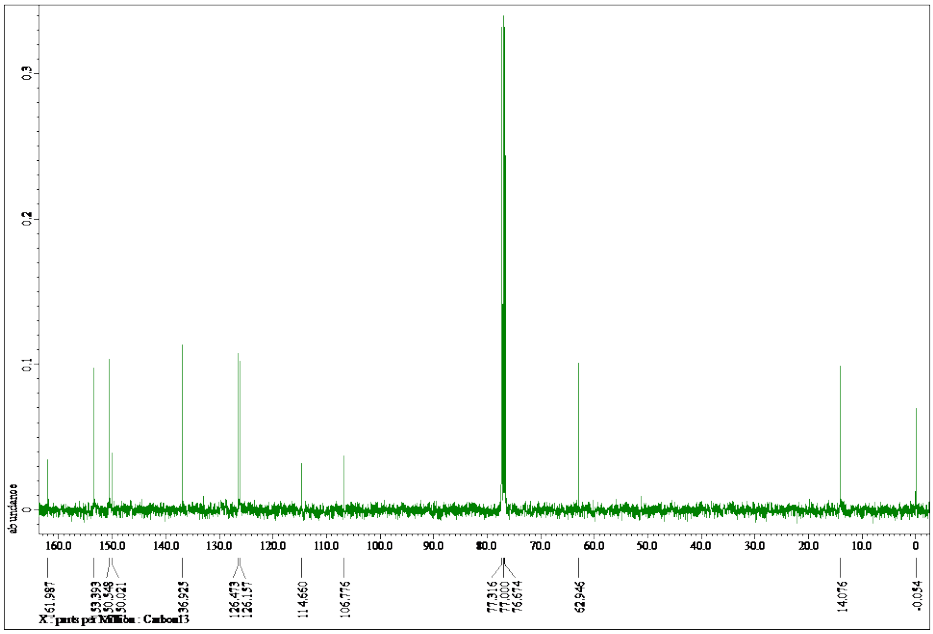
Ethyl (*E*)-2-cyano-3-(pyridin-2-yl)2-propenoate (CAS: 68752-87-4)



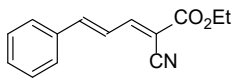
A yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 1.41 (t, *J* = 7.2 Hz, 3H), 4.41 (q, *J* = 7.2 Hz, 2H), 7.41-7.44 (m, 1H), 7.84-7.91 (m, 2H), 8.30 (s, 1H), 8.83 (d, *J* = 4.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 14.1, 62.9, 106.8, 114.7, 126.2, 126.5, 136.9, 150.0, 150.5, 153.4, 162.0.



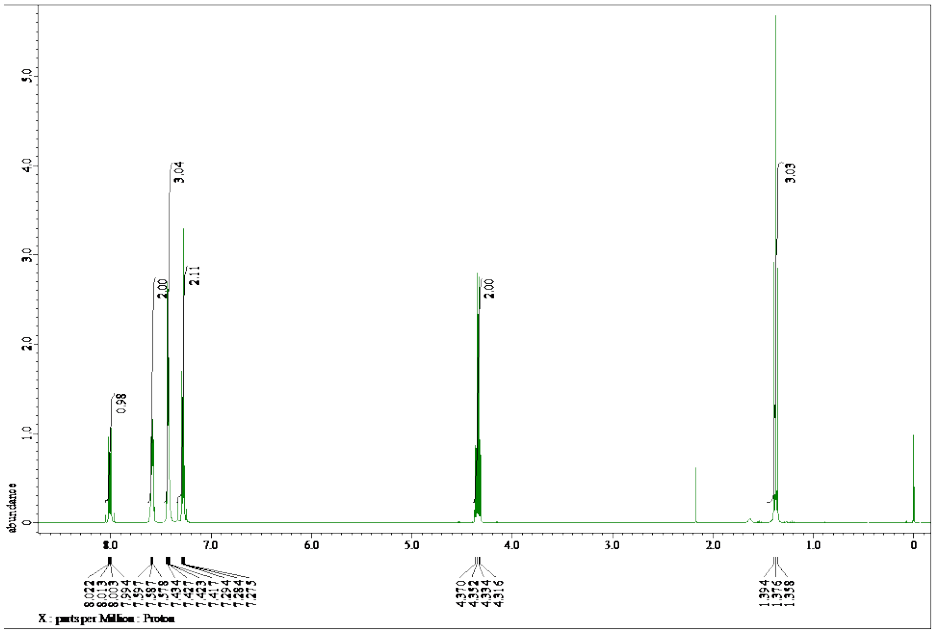


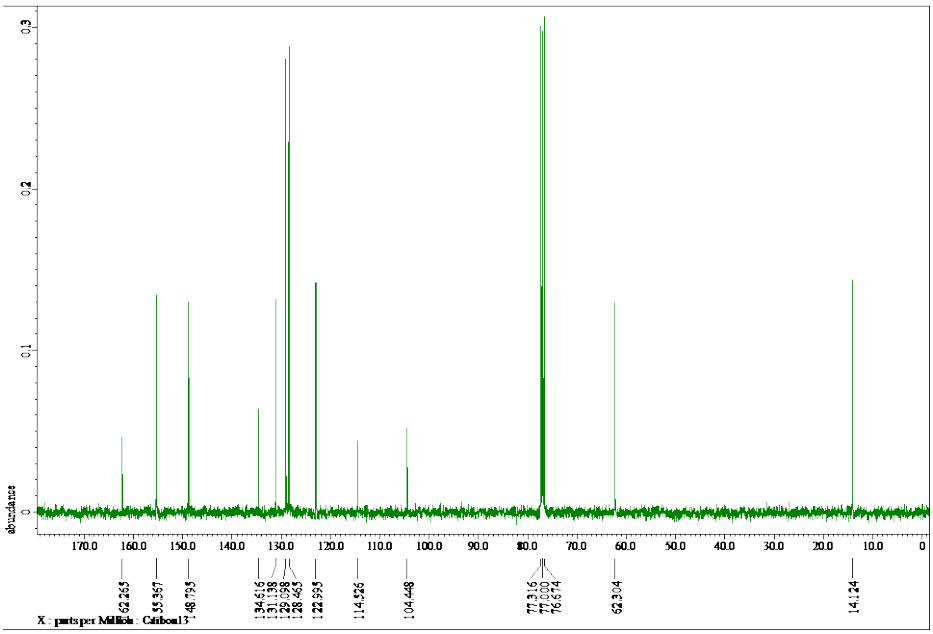
Ethyl 2-cyano-5-phenyl-(2*E*, 4*E*)-pentadienoate (CAS: 41109-95-9)



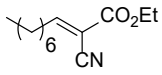
A pale yellow pillar. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 1.38 (t, *J* = 7.2 Hz, 3H), 4.34 (q, *J* = 7.2 Hz, 2H), 7.26-7.29 (m, 2H), 7.41-7.44 (m, 3H), 7.58-7.60 (m, 2H), 7.99-8.02 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 14.1, 62.3, 104.4, 114.5, 123.0, 128.5, 129.1, 131.1, 134.6, 148.8, 155.4, 162.3.



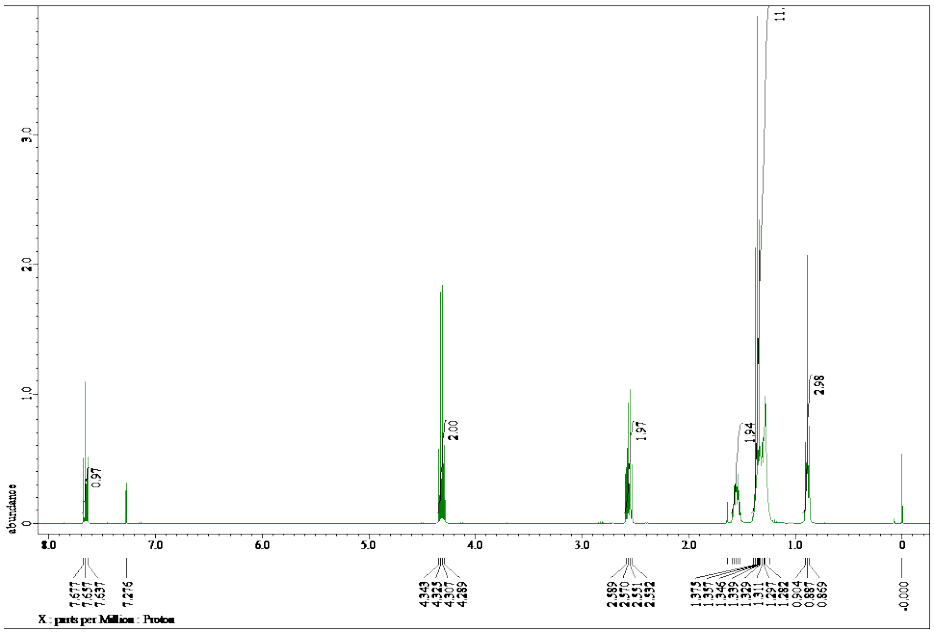


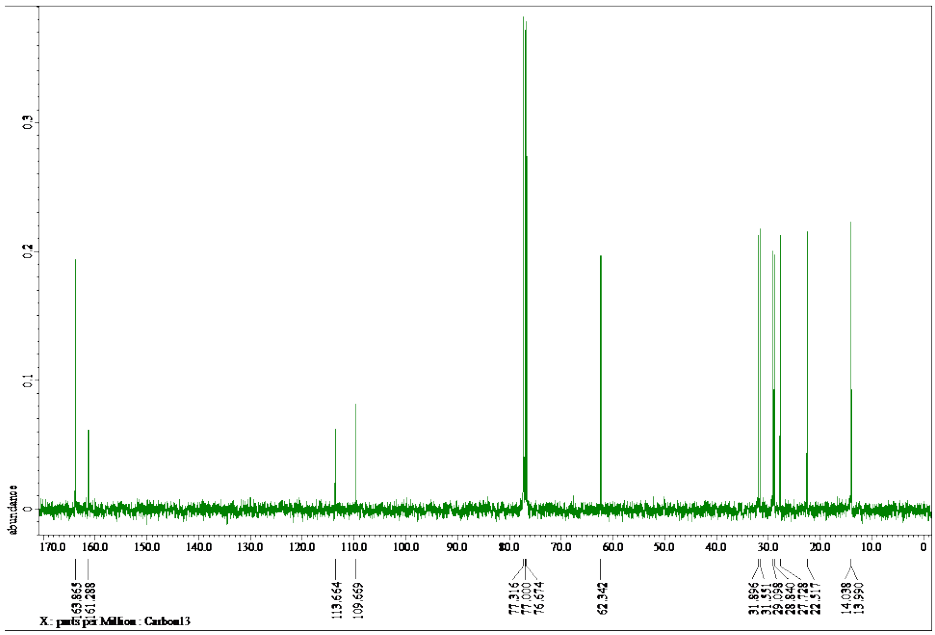
Ethyl (*E*)-2-cyano-2-decenoate (CAS: 879496-08-9)



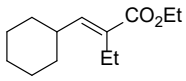
A colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 0.89 (t, J = 6.8 Hz, 3H), 1.24-1.39 (m, 11H), 1.52-1.59 (m, 2H), 2.56 (q, J = 7.6 Hz, 2H), 4.32 (q, J = 7.2 Hz, 2H), 7.66 (t, J = 8.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 14.0, 14.0, 22.5, 27.7, 28.8, 29.1, 31.5, 31.9, 62.3, 109.7, 113.7, 161.3, 163.9.



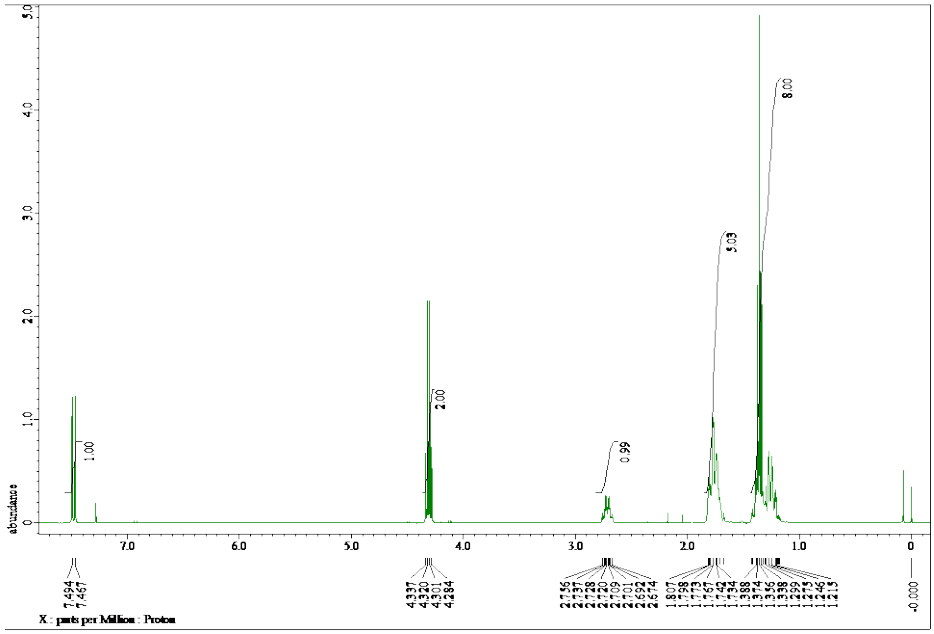


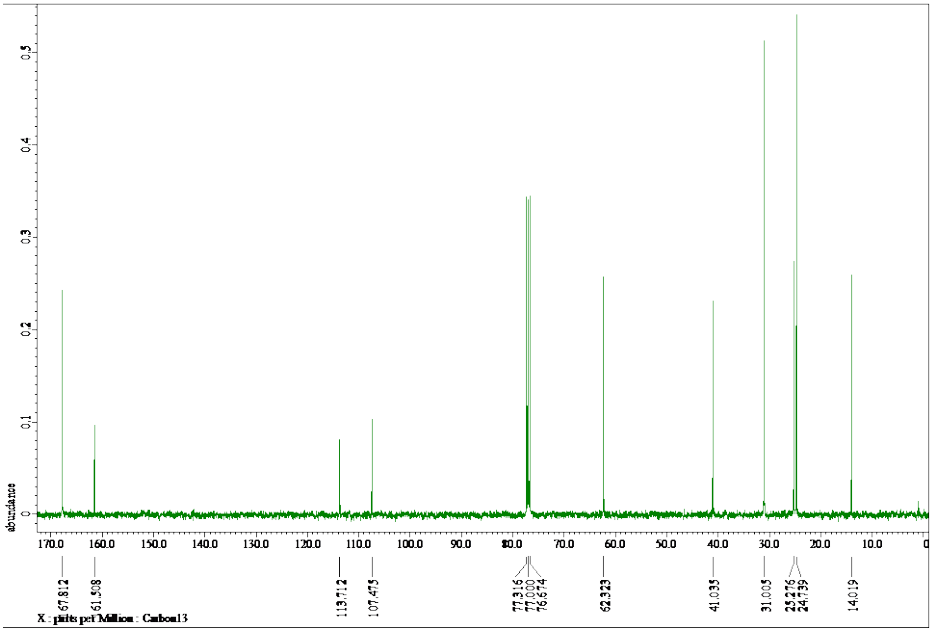
Ethyl (*E*)-2-cyano-3-cyclohexylacrylate (CAS: 90913-43-2)



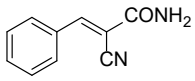
A colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 1.18-1.42 (m, 8H), 1.68-1.82 (m, 5H), 2.67-2.76 (m, 1H), 4.31 (q, *J* = 6.8 Hz, 2H), 7.48 (d, *J* = 10.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 14.0, 24.7, 25.3, 31.0, 41.0, 62.3, 107.5, 113.7, 161.5, 167.8.





(*E*)-2-Cyano-3-phenyl-2-propenamide (CAS: 15795-18-3)



A white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 6.40 (d, J = 15.6 Hz, 2H), 7.49-7.58 (m, 3H), 7.94-7.98 (m, 2H), 8.35 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 103.1, 117.0, 129.3, 130.8, 131.5, 133.1, 154.0, 162.1.