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Physically Mixed Catalytic System of Amino and Sulfo-functional Porous Organic Polymers as Efficiently Synergistic Co-catalysts for One-pot Cascade Reactions

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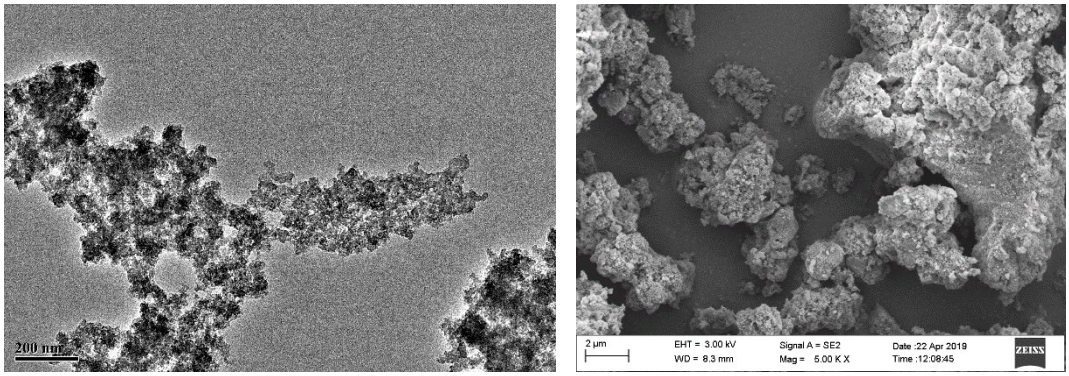


Figure S1 TEM and SEM image of the recycled co-catalyst system P(DVB-0.2-VBS)/P(DVB-0.2-VBA)

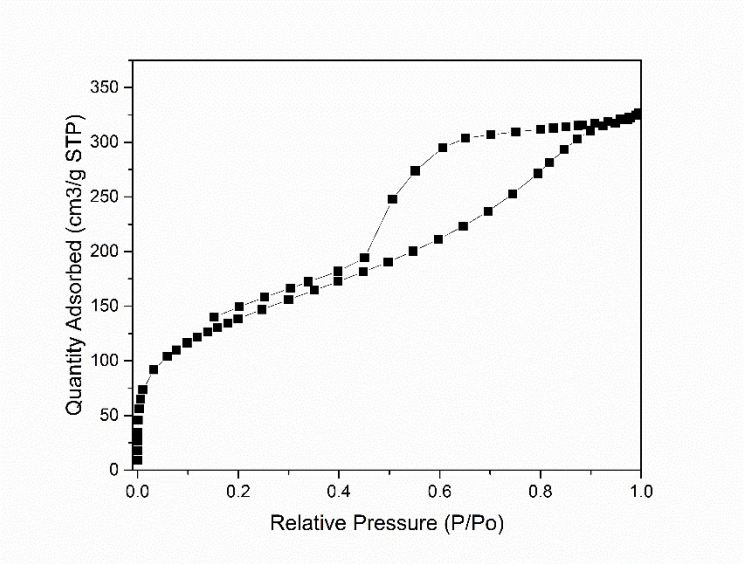


Figure S2 N_2 sorption isotherm of the recycled co-catalyst system P(DVB-0.2-VBS)/P(DVB-0.2-VBA)

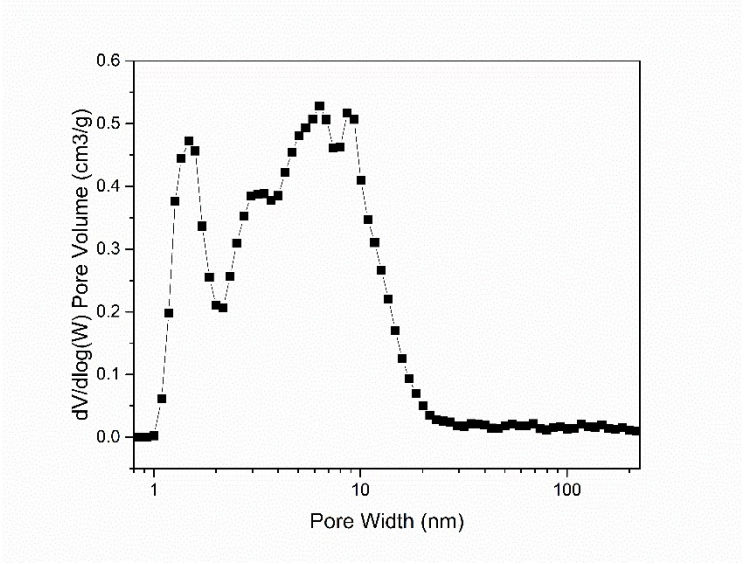


Figure S3 pore size distribution of the recycled co-catalyst system P(DVB-0.2-VBS)/P(DVB-0.2-VBA)

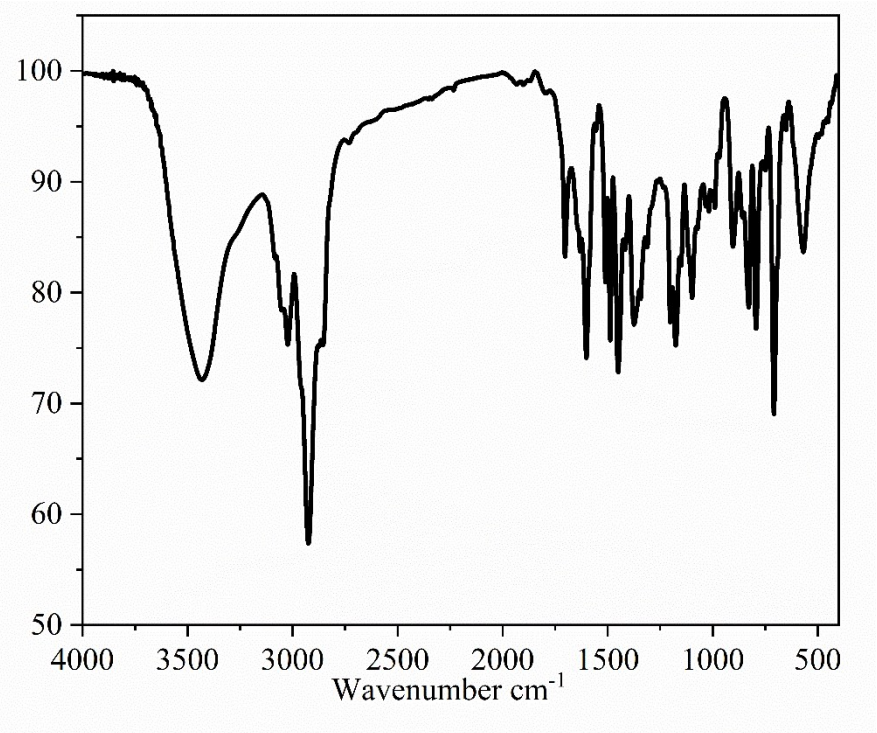


Figure S4 FT-IR spectra of the recycled co-catalyst system P(DVB-0.2-VBS)/P(DVB-0.2-VBA)

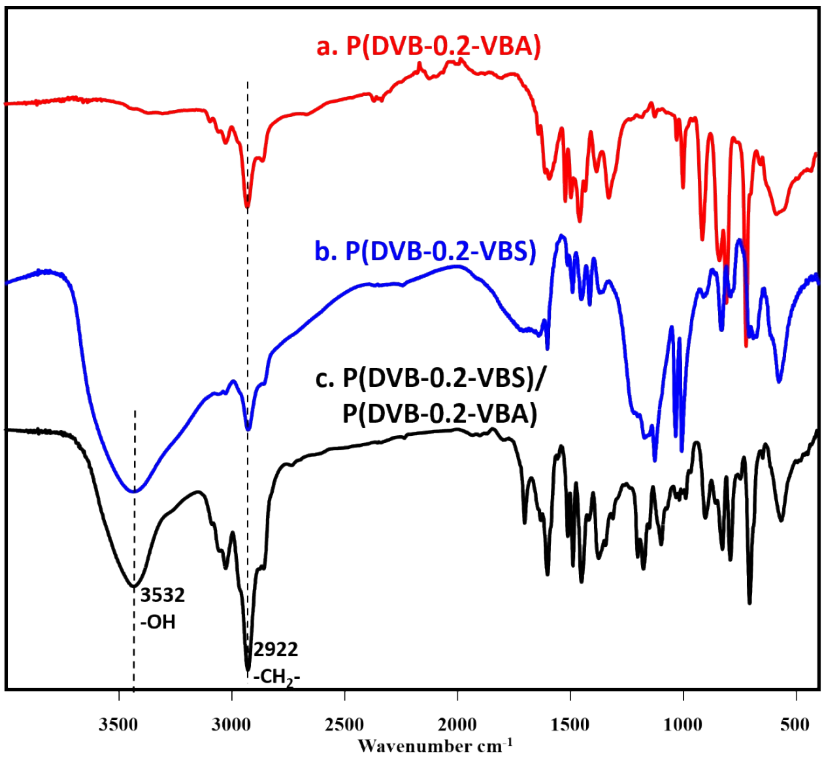


Figure S5 FT-IR spectra of P(DVB-0.2-VBA)(a), P(DVB-0.2-VBS)(b) and the recycled co-catalyst system P(DVB-0.2-VBS)/P(DVB-0.2-VBA)(c)

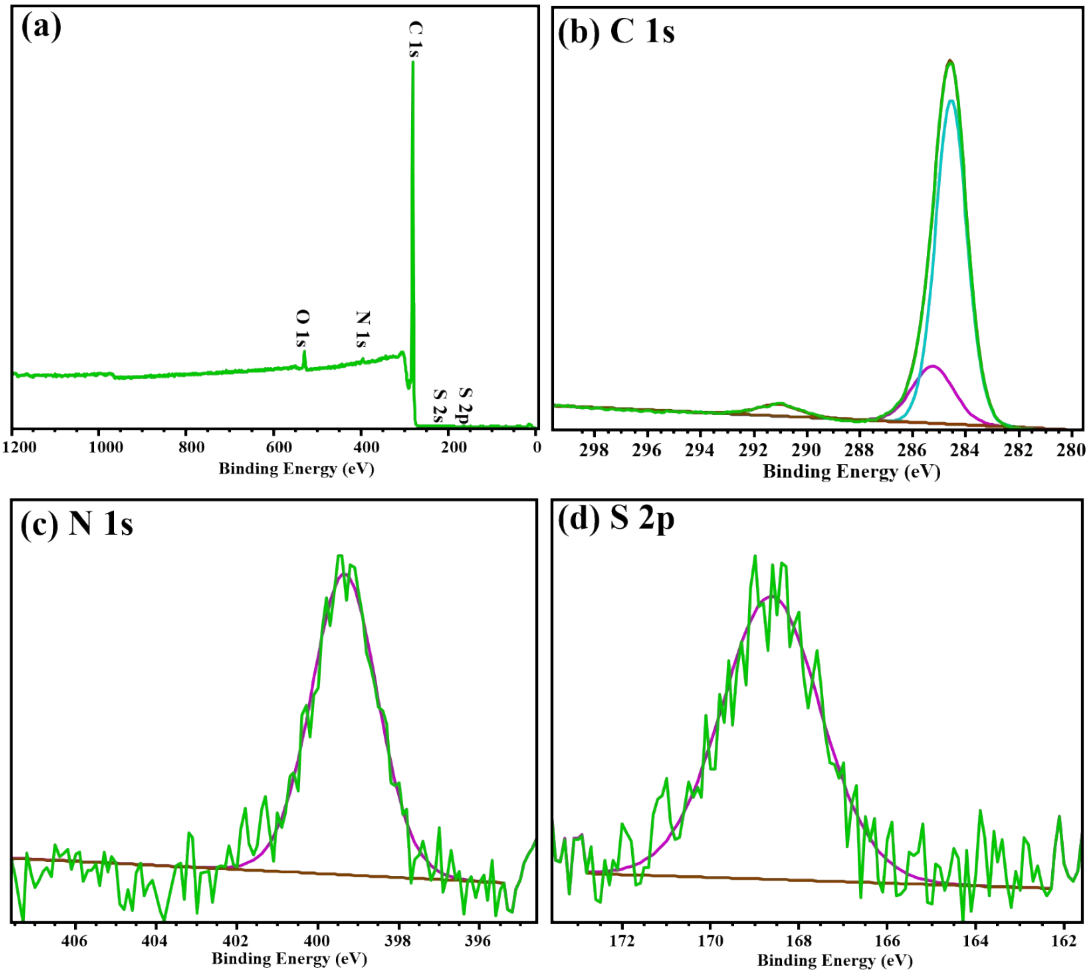


Figure S6 XPS spectra of the recycled co-catalyst system P(DVB-0.2-VBS)/P(DVB-0.2-VBA)

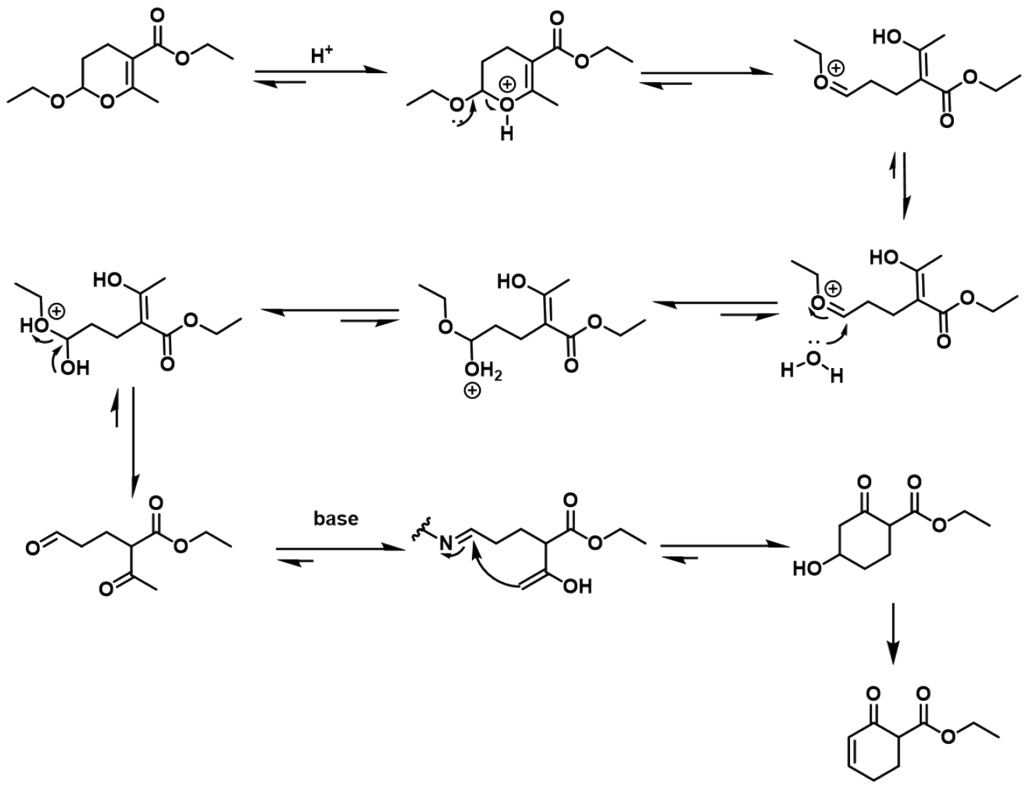
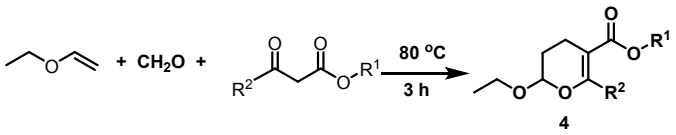


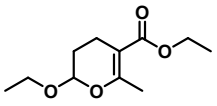
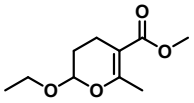
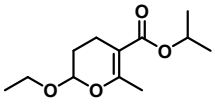
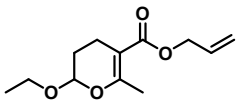
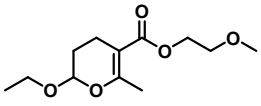
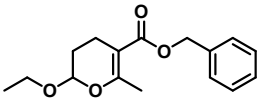
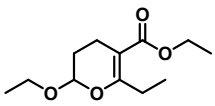
Figure S7 the plausible mechanism of reaction.

General procedure for preparing substrates 4a–4g

The procedure for preparing substrates **4a-4g** were according to the reported method.[1] In a typical procedure, aqueous formaldehyde (0.203 g, 2.5 mmol, 37 wt% in H_2O) was mixed with vinyl ethyl ether (0.072 g, 1.0 mmol) and ethyl acetoacetate (0.260mg, 2.0 mmol) under air. The mixture was then stirred for 3 hours at 80 °C. After reaction completion, the products were extracted from water with a solution of ethyl acetate and heptane (1:4 v/v, 6 mL × 2). After concentration of the organic phases, the crude compound **4a** were purified by flash chromatography over silica gel (eluting solvent: ethyl acetate/petroether = 1/8 (v/v)).The synthesis procedure of **4b-4g** are similar to this method. The yields of **4a-4g** are listed in **Table S1**.

Table S1 summary of substrates **4a-4g.**



entry	substrate		isolated yield
1		4a	88
2		4b	85
3		4c	83
4		4d	78
5		4e	80
6		4f	70
7		4g	89

1. Y. Gu, R. De Sousa, G. Frapper, C. Bachmann, J. Barrault and F. Jérôme, *Green Chem.*, 2009, **11**, 1968-1972.

Spectroscopic data of compounds

phenyl 4-vinylbenzenesulfonate (PVBS): yellow crystals. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.77 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.26 (dq, *J* = 14.3, 7.0 Hz, 3H), 6.99 (d, *J* = 7.8 Hz, 2H), 6.75 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.91 (d, *J* = 17.6 Hz, 1H), 5.48 (d, *J* = 10.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 149.66, 143.32, 135.16, 134.12, 129.69, 128.90, 127.20, 126.71, 122.41, 118.13 ppm.

2-(4-vinylbenzyl)isoindoline-1,3-dione: write solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.84 (dt, *J* = 7.0, 3.5 Hz, 2H), 7.78 – 7.61 (m, 2H), 7.37 (q, *J* = 8.2 Hz, 4H), 6.67 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.71 (d, *J* = 17.6 Hz, 1H), 5.22 (d, *J* = 10.9 Hz, 1H), 4.83 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 168.13, 137.31, 136.42, 135.96, 134.10, 132.22, 128.98, 126.60, 123.46, 114.27, 41.45 ppm.

(4-vinylphenyl)methanamine: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.38 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 2H), 6.71 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.73 (d, *J* = 17.6 Hz, 1H), 5.22 (d, *J* = 10.9 Hz, 1H), 3.85 (s, 2H).

4-Vinylbenzylamine hydrochloride (VBAH): write solid. ^{1}H NMR (400 MHz, D_2O, 25 °C): δ = 7.62 (d, *J* = 7.8 Hz, 2H), 7.46 (dd, *J* = 17.9, 9.0 Hz, 2H), 6.87 (dd, *J* = 17.7, 11.0 Hz, 1H), 5.95 (d, *J* = 17.7 Hz, 1H), 5.42 (d, *J* = 10.9 Hz, 1H), 4.21 (d, *J* = 11.1 Hz, 2H), 1.52 (s, 1H).

(E)-(2-nitrovinyl)benzene: colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.01 (d, *J* = 13.7 Hz, 1H), 7.59 (d, *J* = 13.7 Hz, 1H), 7.56 (d, *J* = 6.9 Hz, 2H), 7.53 – 7.42 (m, 3H).

ethyl (E)-2-cyano-3-phenylacrylate: yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.25 (s, 1H), 7.99 (d, *J* = 7.4 Hz, 2H), 7.52 (dt, *J* = 14.6, 7.1 Hz, 3H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H).

ethyl (E)-3-(4-bromophenyl)-2-cyanoacrylate: colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 8.18 (s, 1H), 7.85 (d, *J* = 8.5 Hz, 2H), 7.65 (d, *J* = 8.6 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H).

ethyl (E)-2-cyano-3-(4-nitrophenyl)acrylate: colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 8.35 (d, *J* = 8.6 Hz, 2H), 8.30 (s, 1H), 8.13 (d, *J* = 8.6 Hz, 2H), 4.43 (q, *J* = 7.2 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H).

ethyl (E)-2-cyano-3-(2-methoxyphenyl)acrylate: colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 8.76 (s, 1H), 8.29 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.52 (s, 1H), 7.06 (s, 1H), 6.96 (d, *J* = 8.3 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 3.91 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H).

ethyl (E)-2-cyano-3-(2-nitrophenyl)acrylate: colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 8.72 (s, 1H), 8.28 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.81 (t, *J* = 7.5 Hz, 1H), 7.72 (t, *J* = 7.8 Hz, 1H), 4.43 (q, *J* = 7.2 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H).

2-benzylidenemalononitrile: yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.91 (dd, *J* = 8.2, 0.8 Hz, 2H), 7.78 (s, 1H), 7.67 – 7.60 (m, 1H), 7.55 (t, *J* = 7.6 Hz, 2H).

methyl 2-ethoxy-6-methyl-3,4-dihydro-2H-pyran-5-carboxylate: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 5.03 (dd, *J* = 4.2, 2.6 Hz, 1H), 3.85 (dq, *J* = 9.7, 7.1 Hz, 1H), 3.76 – 3.63 (m, 3H), 3.59 (dq, *J* = 9.7, 7.1 Hz, 1H), 2.44 – 2.25 (m, 2H), 2.23 (dd, *J* = 4.5, 3.0 Hz, 3H), 1.94 – 1.79 (m, 1H), 1.79 – 1.67 (m, 1H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 168.71, 161.86, 101.84, 97.82, 64.15, 50.94, 26.14, 19.89, 17.86, 15.11 ppm.

ethyl 2-ethoxy-6-methyl-3,4-dihydro-2H-pyran-5-carboxylate: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 5.03 (dd, *J* = 4.3, 2.7 Hz, 1H), 4.17 (dq, *J* = 14.2, 7.1 Hz, 2H), 3.86 (dq, *J* = 9.7, 7.1 Hz, 1H), 3.60 (dq, *J* = 9.7, 7.1 Hz, 1H), 2.46 – 2.27 (m, 2H), 2.24 (dd, *J* = 4.0, 2.6 Hz, 3H), 1.91 – 1.69 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 168.36, 161.57, 102.16, 97.89, 64.19, 59.64, 26.25, 19.94, 17.98, 15.17, 14.44 ppm.

allyl 2-ethoxy-6-methyl-3,4-dihydro-2H-pyran-5-carboxylate: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 5.95 (ddt, *J* = 17.1, 10.8, 5.5 Hz, 1H), 5.31 (ddd, *J* = 17.2, 3.2, 1.6 Hz, 1H), 5.21 (ddd, *J* = 10.5, 2.7, 1.3 Hz, 1H), 5.04 (dd, *J* = 4.2, 2.6 Hz, 1H), 4.61 (dt, *J* = 5.5, 1.5 Hz, 2H), 3.86 (dq, *J* = 9.7, 7.1 Hz, 1H), 3.60 (dq, *J* =

9.7, 7.1 Hz, 1H), 2.47 – 2.28 (m, 2H), 2.25 (dd, *J* = 3.6, 2.2 Hz, 3H), 1.94 – 1.83 (m, 1H), 1.83 – 1.69 (m, 1H), 1.23 (q, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 167.87, 162.16, 132.98, 117.30, 101.83, 97.89, 64.41, 64.20, 26.17, 20.00, 17.88, 15.14 ppm.

isopropyl 2-ethoxy-6-methyl-3,4-dihydro-2H-pyran-5-carboxylate: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 5.26 – 4.85 (m, 2H), 3.86 (dq, *J* = 14.2, 7.1 Hz, 1H), 3.59 (dq, *J* = 14.3, 7.1 Hz, 1H), 2.45 – 2.24 (m, 2H), 2.24 (d, *J* = 16.9 Hz, 3H), 1.93 – 1.66 (m, 2H), 1.25 (t, *J* = 7.5 Hz, 6H), 1.21 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 167.92, 161.24, 102.42, 97.86, 66.76, 64.19, 26.23, 22.09, 21.71, 21.58, 19.95, 18.00, 15.16 ppm.

2-methoxyethyl 2-ethoxy-6-methyl-3,4-dihydro-2H-pyran-5-carboxylate: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 5.02 (dd, *J* = 4.2, 2.7 Hz, 1H), 4.30 – 4.14 (m, 2H), 3.84 (dd, *J* = 9.6, 7.1 Hz, 1H), 3.59 (ddd, *J* = 9.7, 7.1, 3.7 Hz, 3H), 3.36 (d, *J* = 10.2 Hz, 3H), 2.46 – 2.27 (m, 2H), 2.24 (d, *J* = 10.7 Hz, 3H), 1.90 – 1.68 (m, 2H), 1.21 (q, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 168.17, 162.09, 101.80, 97.88, 70.72, 64.17, 62.83, 58.91, 26.10, 19.96, 17.88, 15.27, 15.11 ppm.

benzyl 2-ethoxy-6-methyl-3,4-dihydro-2H-pyran-5-carboxylate: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.50 – 7.21 (m, 5H), 5.16 (t, *J* = 4.0 Hz, 2H), 5.04 (d, *J* = 2.3 Hz, 1H), 3.98 – 3.75 (m, 1H), 3.73 – 3.42 (m, 1H), 2.38 (s, 2H), 2.24 (t, *J* = 11.6 Hz, 3H), 1.81 (dd, *J* = 26.8, 3.7 Hz, 2H), 1.23 (dt, *J* = 10.6, 5.8 Hz, 3H), 0.86 (dd, *J* = 6.6, 3.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 168.09, 162.41, 136.88, 128.53, 127.95, 101.86, 97.99, 65.57, 64.30, 26.22, 20.14, 18.00, 15.22 ppm.

ethyl 2-ethoxy-6-ethyl-3,4-dihydro-2H-pyran-5-carboxylate: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 5.04 (dd, *J* = 4.0, 2.6 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.87 (dq, *J* = 9.6, 7.1 Hz, 1H), 3.60 (dq, *J* = 9.6, 7.1 Hz, 1H), 2.74 (dt, *J* = 14.8, 7.3 Hz, 1H), 2.66 – 2.47 (m, 1H), 2.45 – 2.23 (m, 2H), 1.84 (ddd, *J* = 10.3, 7.1, 5.1 Hz, 1H), 1.76 (ddd, *J* = 10.5, 6.6, 3.2 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz,

3H), 1.17 – 1.02 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 168.25, 166.29, 101.44, 97.70, 64.12, 59.74, 26.52, 26.26, 18.03, 15.23, 14.46, 12.22 ppm.

ethyl 2-oxocyclohex-3-ene-1-carboxylate: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 6.99 (dt, *J* = 10.1, 3.6 Hz, 1H), 6.06 (dt, *J* = 10.2, 1.9 Hz, 1H), 4.25 – 4.16 (m, 2H), 3.39 (dd, *J* = 9.9, 4.9 Hz, 1H), 2.59 – 2.43 (m, 1H), 2.43 – 2.29 (m, 2H), 2.29 – 2.20 (m, 1H), 1.28 (dd, *J* = 9.5, 4.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 194.03, 170.01, 150.72, 129.06, 61.21, 53.43, 25.62, 24.32, 14.13 ppm.

methyl 2-oxocyclohex-3-ene-1-carboxylate: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.11 – 6.94 (m, 1H), 6.08 (d, *J* = 10.2 Hz, 1H), 3.76 (s, 3H), 3.52 – 3.25 (m, 1H), 2.59 – 2.44 (m, 2H), 2.39 (dd, *J* = 9.7, 7.0 Hz, 3H), 2.32 – 2.20 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 193.87, 170.44, 150.80, 129.06, 53.32, 52.33, 25.60, 24.33 ppm.

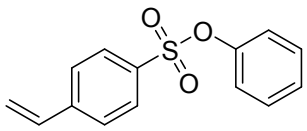
allyl 2-oxocyclohex-3-ene-1-carboxylate: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.13 – 6.91 (m, 1H), 6.08 (dd, *J* = 10.1, 1.9 Hz, 1H), 5.99 – 5.79 (m, 1H), 5.34 (dd, *J* = 17.2, 1.4 Hz, 1H), 5.24 (dd, *J* = 10.4, 1.2 Hz, 1H), 4.79 – 4.53 (m, 2H), 3.45 (dd, *J* = 9.8, 4.6 Hz, 1H), 2.62 – 2.32 (m, 3H), 2.31 – 2.19 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 193.81, 169.69, 150.71, 131.76, 129.09, 118.47, 65.75, 53.44, 25.65, 24.34 ppm.

isopropyl 2-oxocyclohex-3-ene-1-carboxylate: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.10 – 6.89 (m, 1H), 6.05 (d, *J* = 10.1 Hz, 1H), 5.06 (td, *J* = 12.5, 6.3 Hz, 1H), 3.35 (dd, *J* = 9.6, 5.0 Hz, 1H), 2.55 – 2.44 (m, 1H), 2.37 (dd, *J* = 10.6, 7.6 Hz, 2H), 2.26 – 2.18 (m, 1H), 1.25 (t, *J* = 6.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 194.25, 169.99, 150.54, 129.31, 68.89, 53.70, 25.77, 24.43, 21.88, 21.81 ppm.

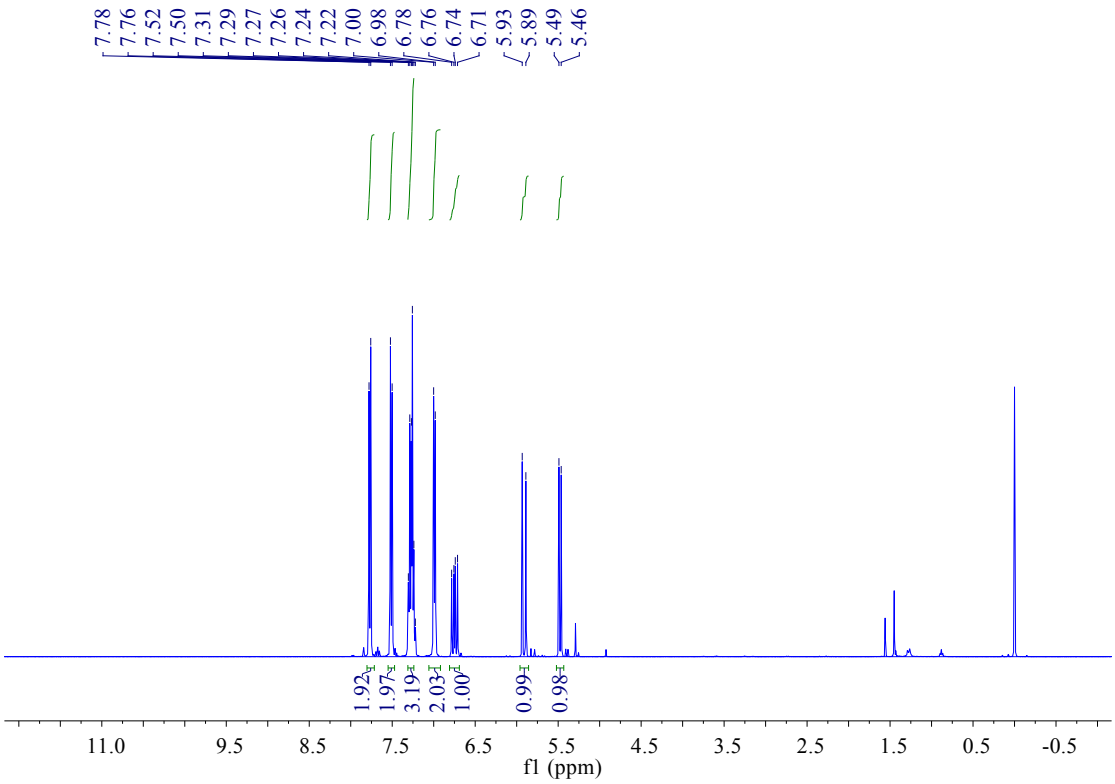
benzyl 2-oxocyclohex-3-ene-1-carboxylate: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.45 – 7.27 (m, 5H), 7.00 (dt, *J* = 9.9, 3.7 Hz, 1H), 6.07 (dd, *J* = 10.1, 1.9 Hz, 1H), 5.30 – 5.07 (m, 2H), 3.57 – 3.28 (m, 1H), 2.53 – 2.30 (m, 3H), 2.29 – 2.13 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 193.83, 169.97, 150.76, 135.72, 129.19, 128.64, 128.34, 128.19, 66.97, 53.58, 25.74, 24.44 ppm.

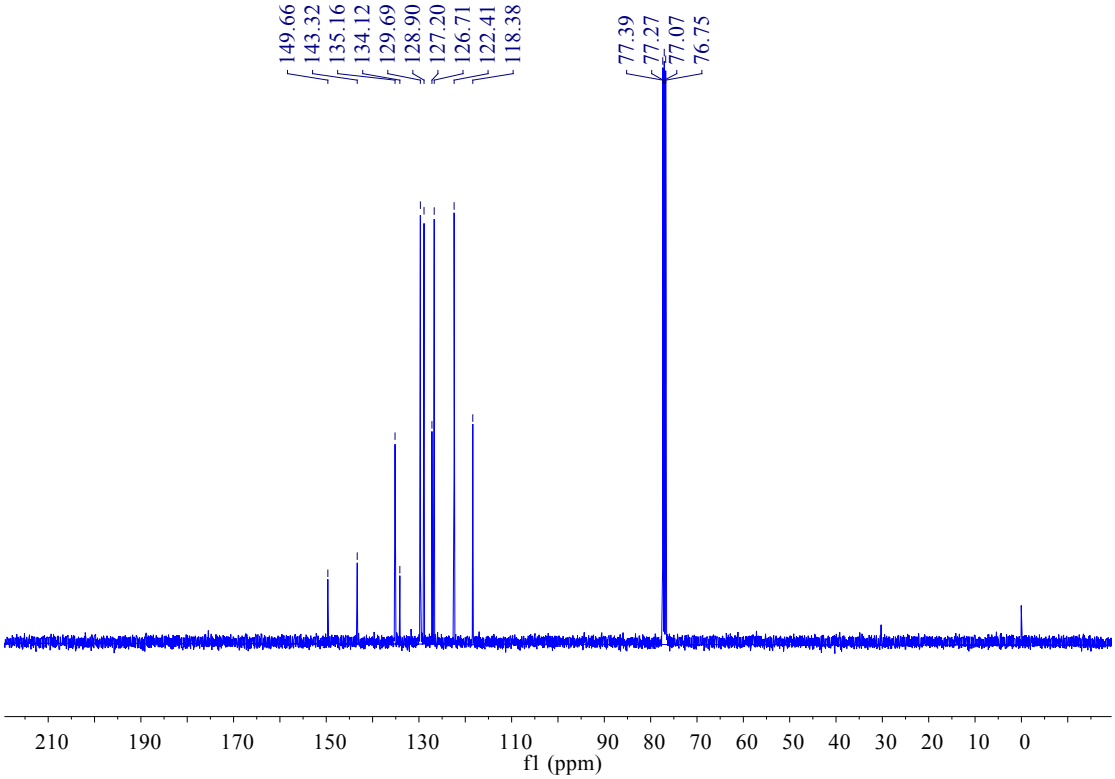
2-methoxyethyl 2-oxocyclohex-3-ene-1-carboxylate: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.06 – 6.95 (m, 1H), 6.12 – 6.04 (m, 1H), 4.32 (ddd, *J* = 6.1, 4.0, 2.3 Hz, 2H), 3.74 – 3.53 (m, 2H), 3.47 (dd, *J* = 10.5, 4.9 Hz, 1H), 3.39 (d, *J* = 7.7 Hz, 3H), 2.58 – 2.44 (m, 1H), 2.39 (ddd, *J* = 11.8, 7.2, 2.3 Hz, 2H), 2.24 (dd, *J* = 9.9, 7.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 193.94, 170.20, 150.77, 129.19, 70.41, 64.23, 59.09, 53.52, 25.75, 24.51 ppm.

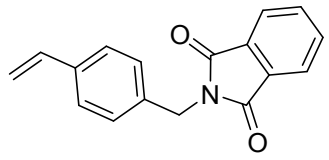
ethyl 3-methyl-2-oxocyclohex-3-ene-1-carboxylate: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ = 6.74 (d, *J* = 1.3 Hz, 1H), 4.20 (qdd, *J* = 14.2, 9.0, 5.4 Hz, 2H), 3.42 – 3.34 (m, 1H), 2.53 – 2.28 (m, 3H), 2.23 – 2.11 (m, 1H), 1.79 (d, *J* = 1.4 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C): δ = 194.72, 170.45, 145.50, 135.26, 61.16, 53.72, 26.21, 24.48, 16.09, 14.22 ppm.



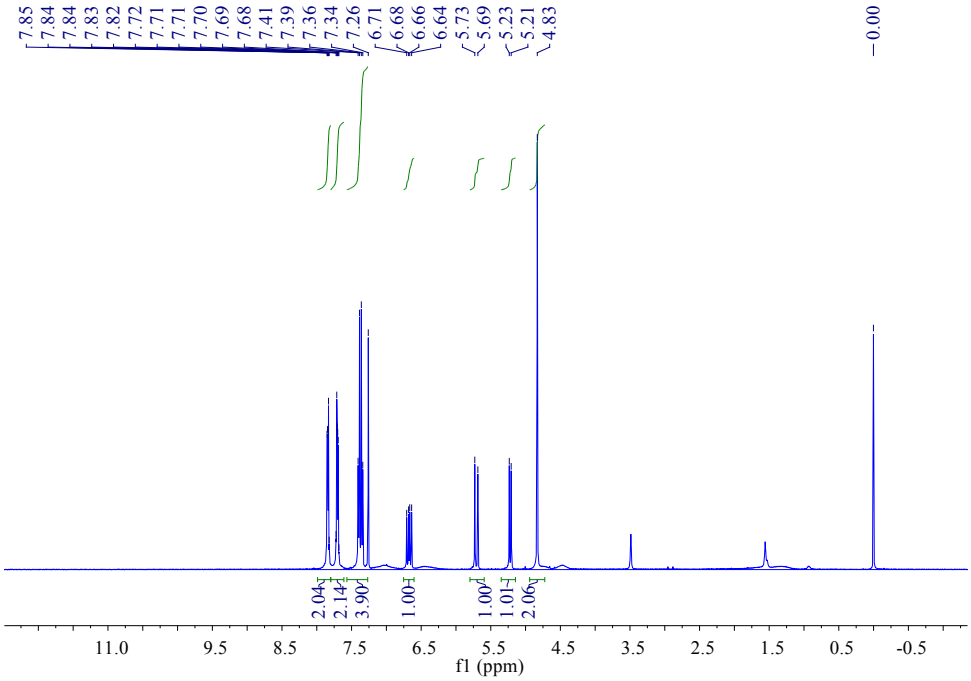
phenyl 4-vinylbenzenesulfonate

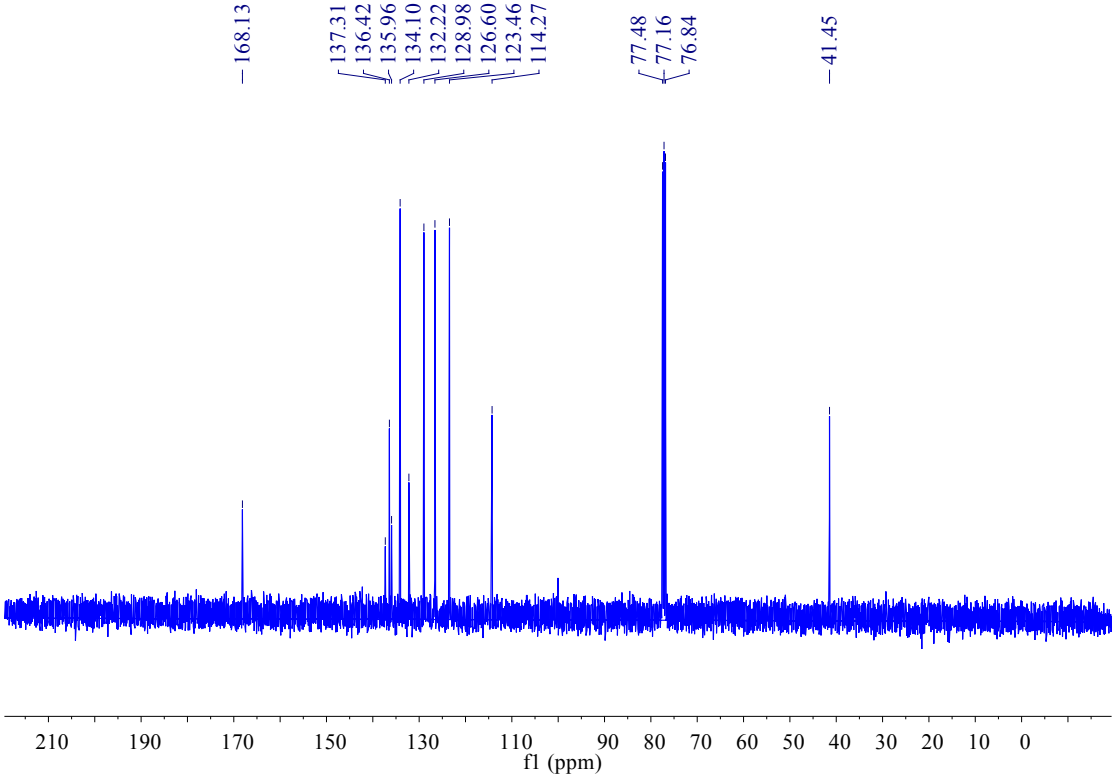


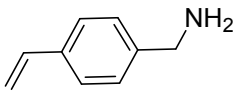




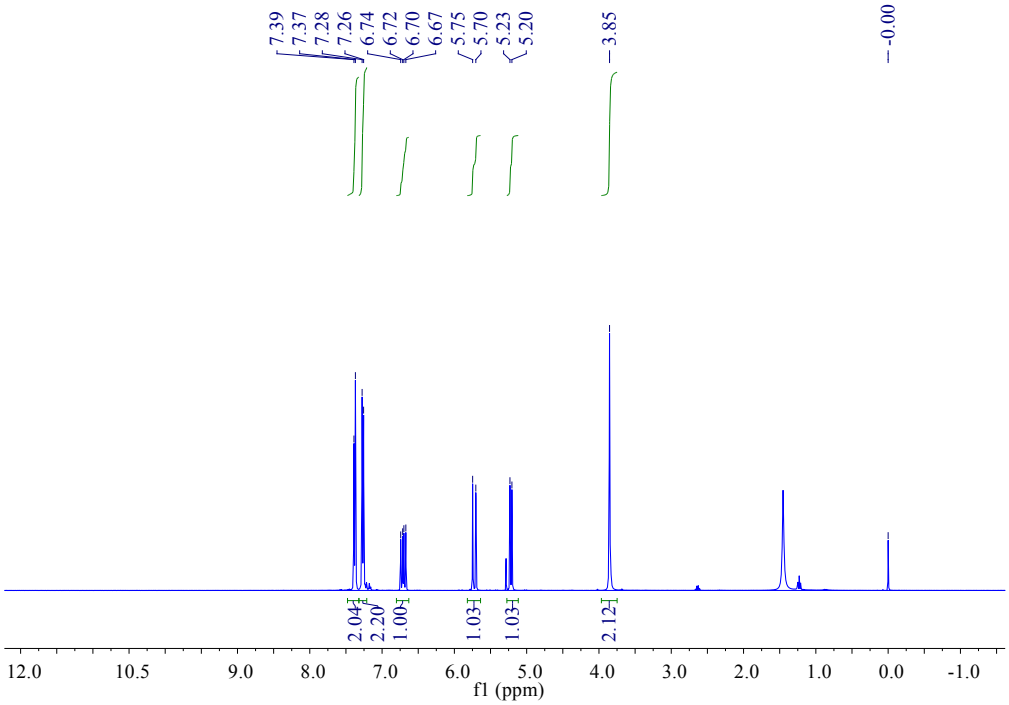
2-(4-vinylbenzyl)isoindoline-1,3-dione

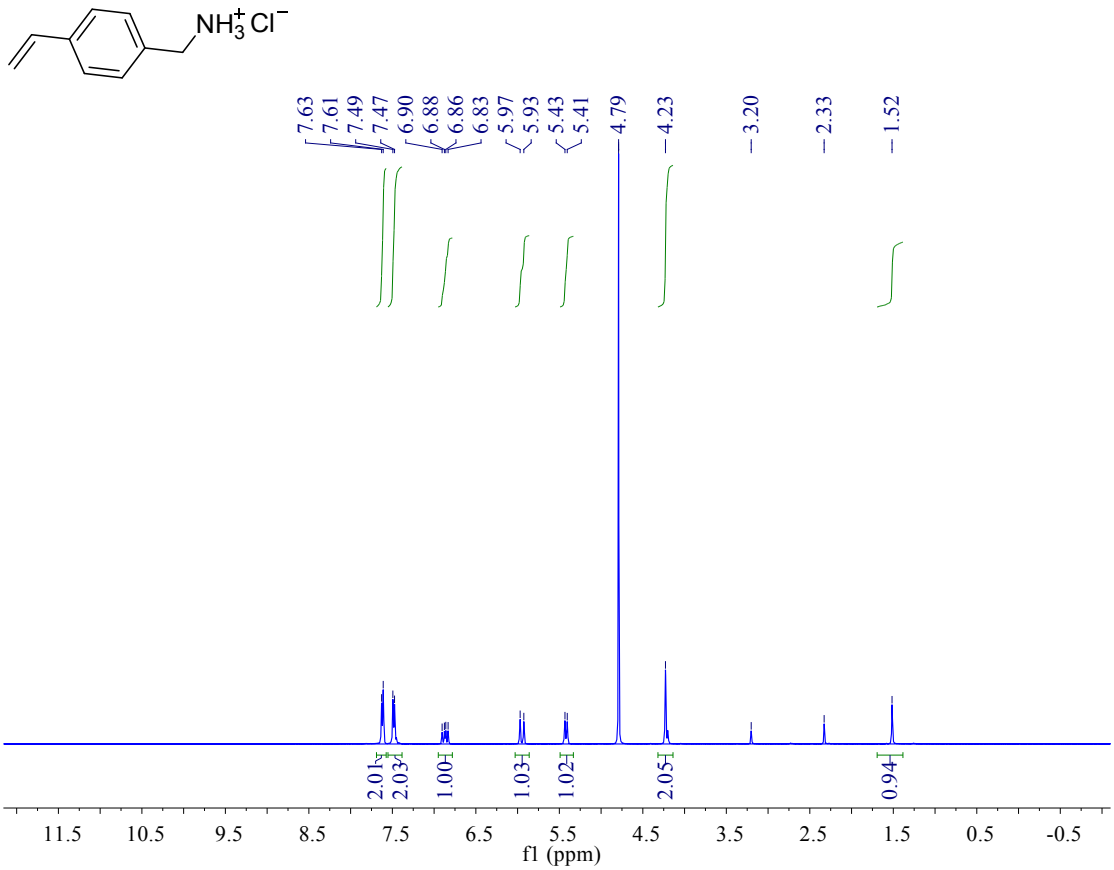


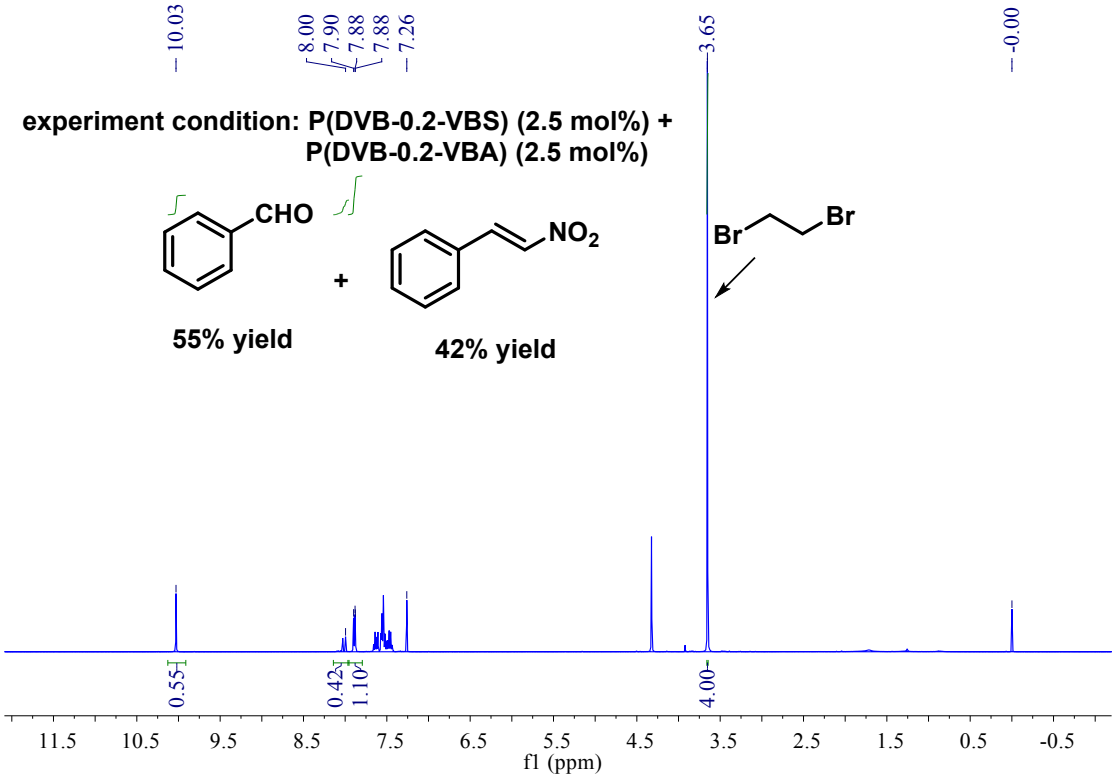


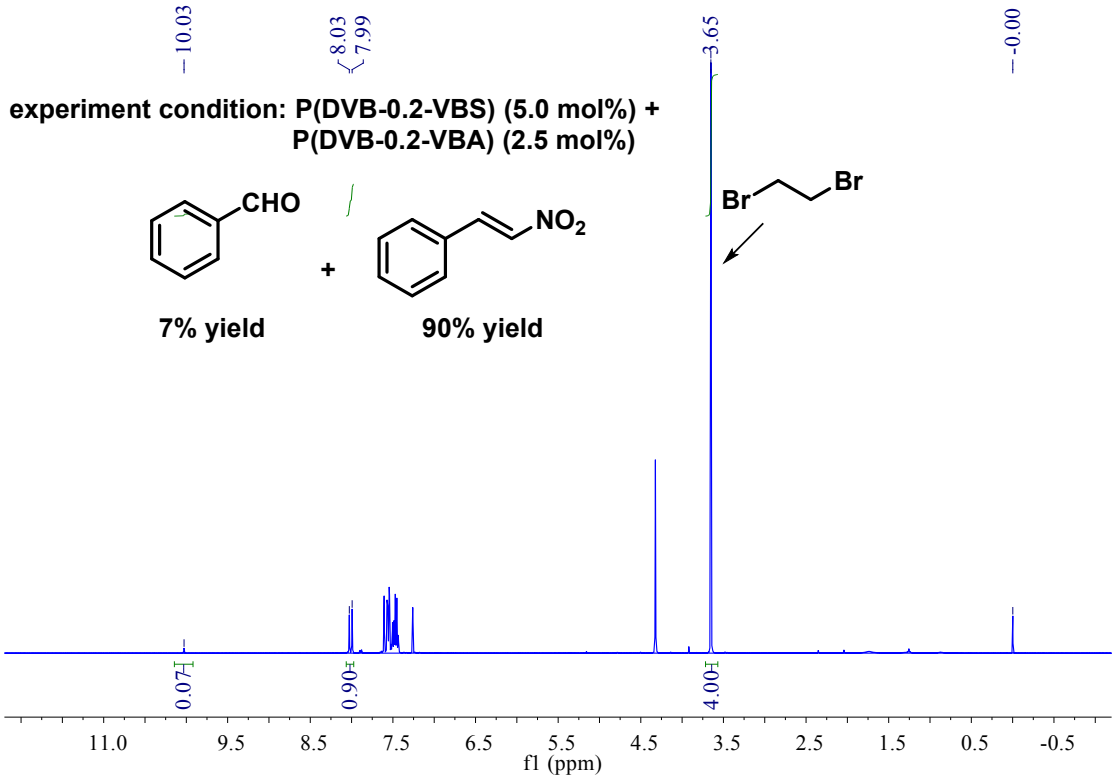


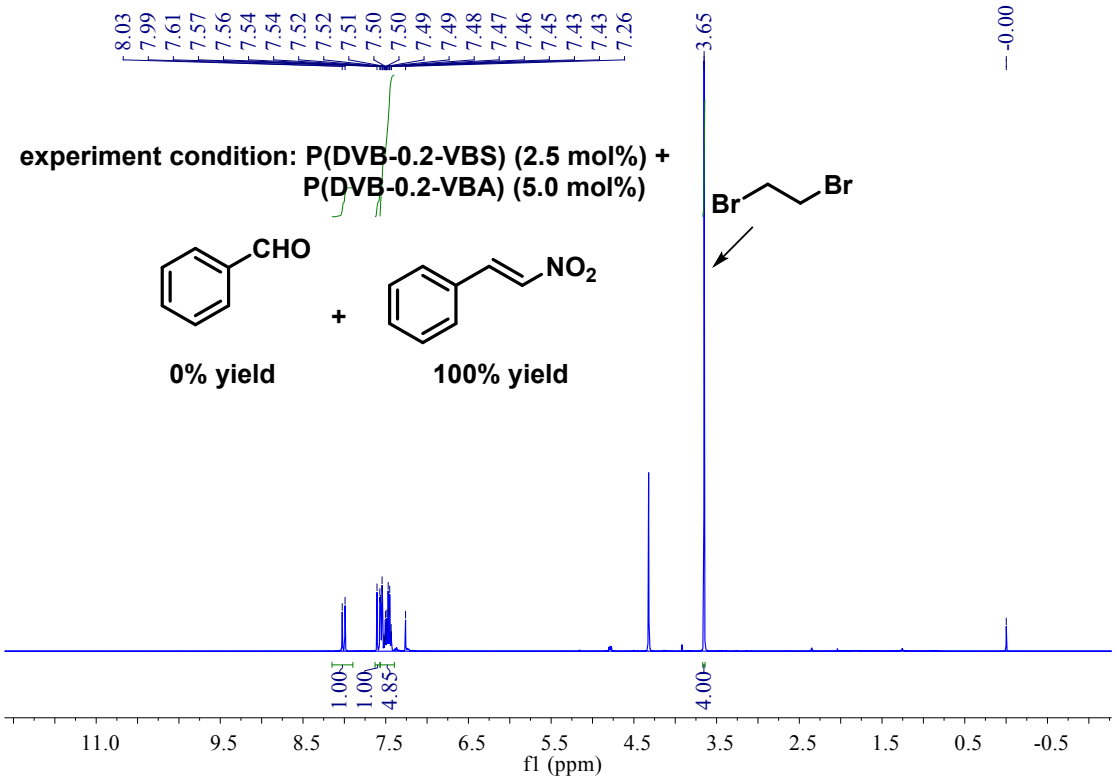
(4-vinylphenyl)methanamine

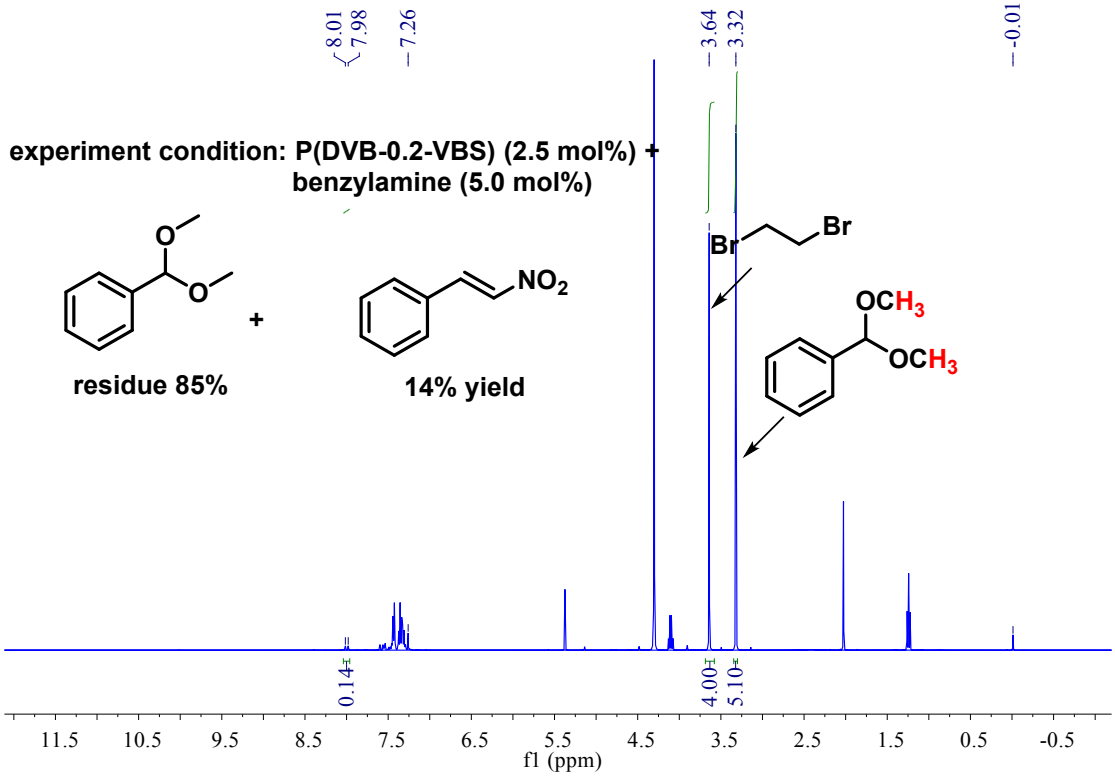


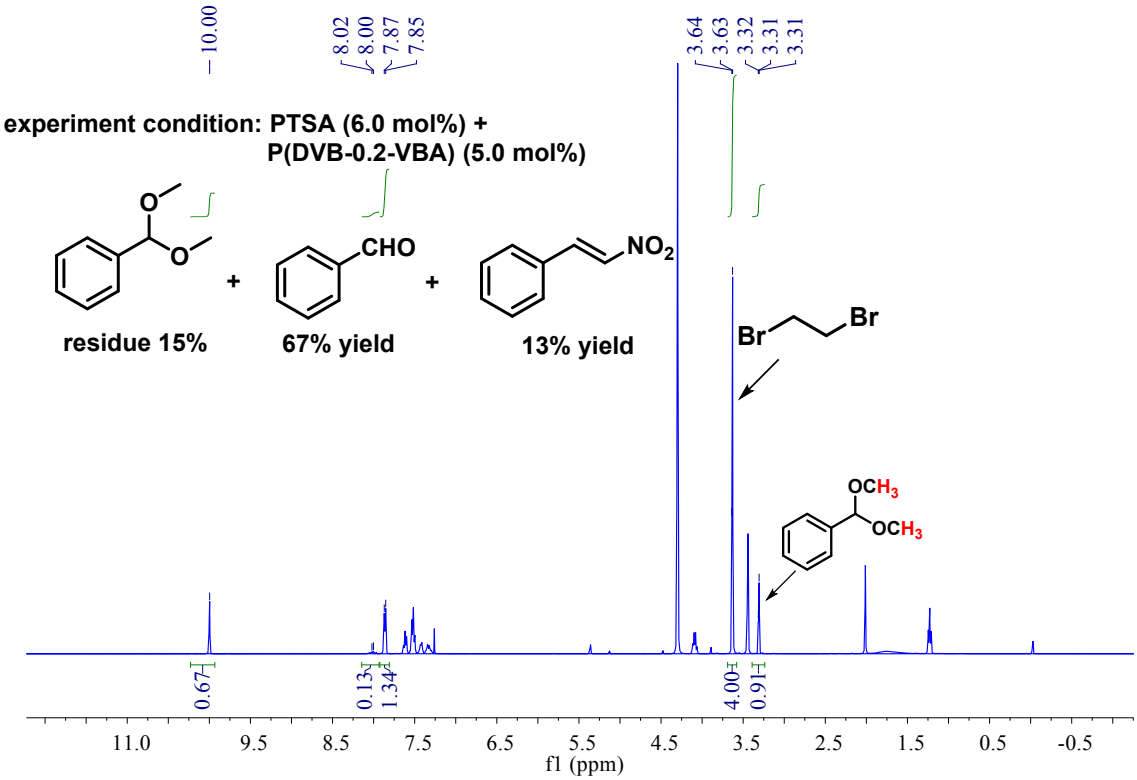

NH3+ Cl−
7.63
7.61
7.49
7.47
6.90
6.88
6.86
6.83
5.97
5.93
5.43
5.41
4.79
4.23
3.20
2.33
1.52
2.01
2.03
1.00
1.03
1.02
2.05
0.94
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

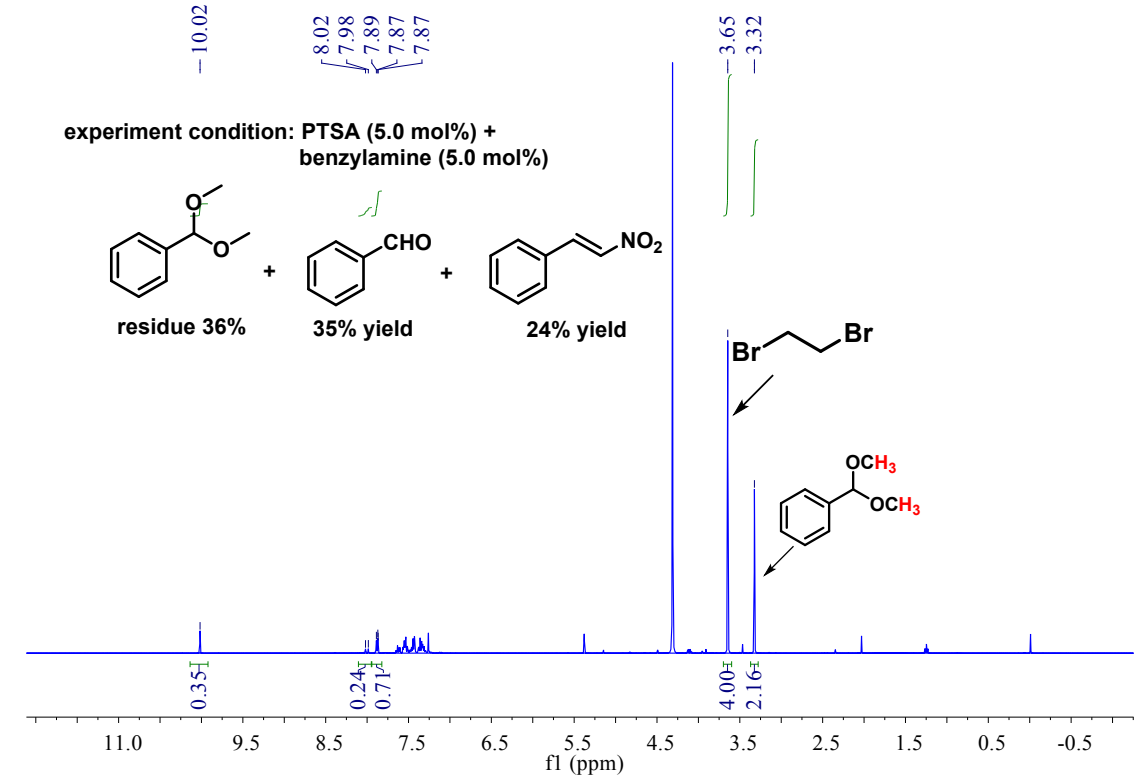

10.03
8.00
7.90
7.88
7.88
7.26
3.65
-0.00
experiment condition: P(DVB-0.2-VBS) (2.5 mol%) +
P(DVB-0.2-VBA) (2.5 mol%)
CHO
NO2
+
Br
Br
55% yield
42% yield
0.55
0.42
1.10
4.00
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

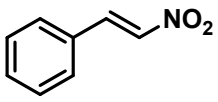

10.03
8.03
7.99
3.65
-0.00
experiment condition: P(DVB-0.2-VBS) (5.0 mol%) +
P(DVB-0.2-VBA) (2.5 mol%)
CHO
NO2
+
Br
Br
7% yield
90% yield
0.07
0.90
4.00
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


8.03
7.99
7.61
7.57
7.56
7.54
7.54
7.52
7.52
7.51
7.50
7.50
7.49
7.49
7.48
7.47
7.46
7.45
7.43
7.43
7.26
3.65
-0.00
experiment condition: P(DVB-0.2-VBS) (2.5 mol%) +
P(DVB-0.2-VBA) (5.0 mol%)
CHO
+
NO2
Br
Br
0% yield
100% yield
1.00
1.00
4.85
4.00
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

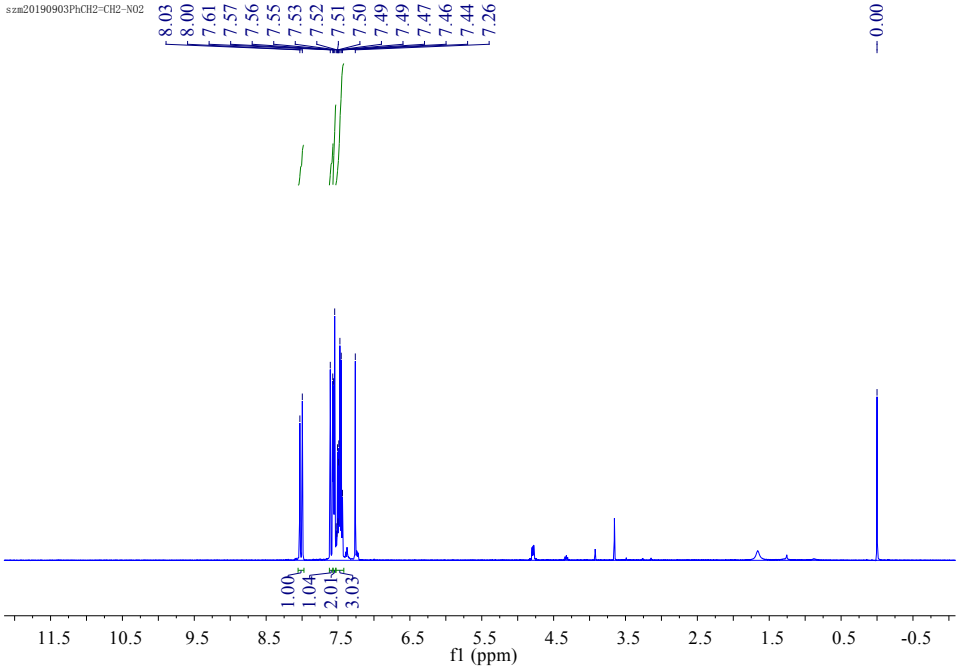

8.01
7.98
7.26
3.64
3.32
-0.01
experiment condition: P(DVB-0.2-VBS) (2.5 mol%) +
benzylamine (5.0 mol%)
O
O
+
NO2
Br
Br
OCH3
OCH3
residue 85%
14% yield
0.14
4.00
5.10
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

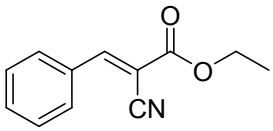

10.00
8.02
8.00
7.87
7.85
3.64
3.63
3.32
3.31
3.31
experiment condition: PTSA (6.0 mol%) +
P(DVB-0.2-VBA) (5.0 mol%)
O
O
+
CHO
+
NO2
residue 15%
67% yield
13% yield
Br
Br
OCH3
OCH3
0.67
0.13
1.34
4.00
0.91
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


10.02
8.02
7.98
7.89
7.87
7.87
3.65
3.32
experiment condition: PTSA (5.0 mol%) +
benzylamine (5.0 mol%)
O
O
+
CHO
+
NO2
residue 36%
35% yield
24% yield
Br
Br
OCH3
OCH3
0.35
0.24
0.71
4.00
2.16
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

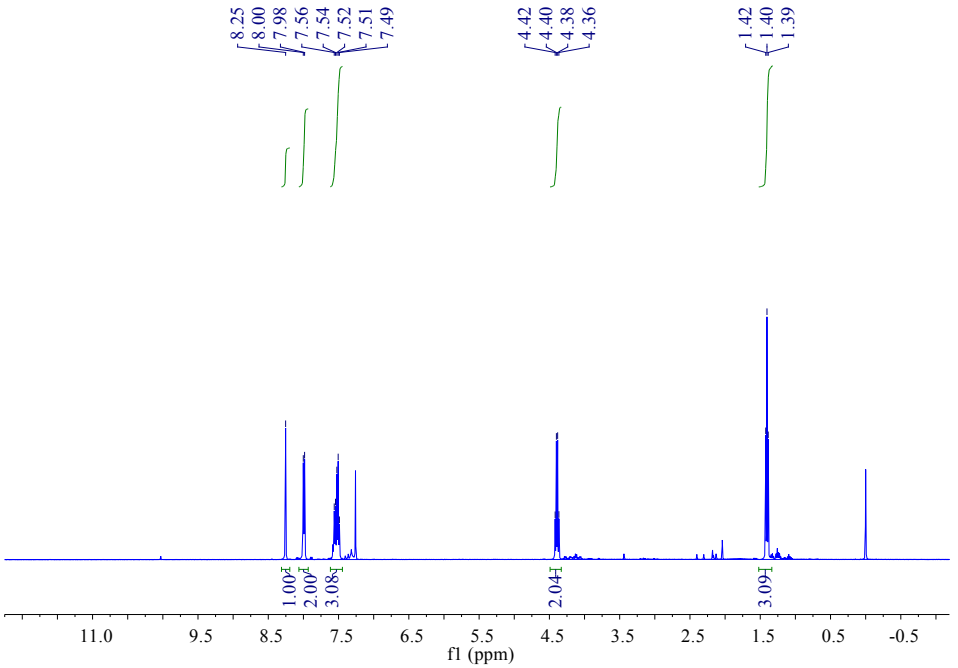


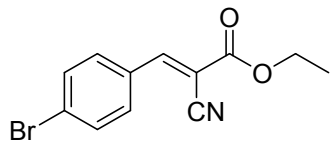
(*E*)-(2-nitrovinyl)benzene



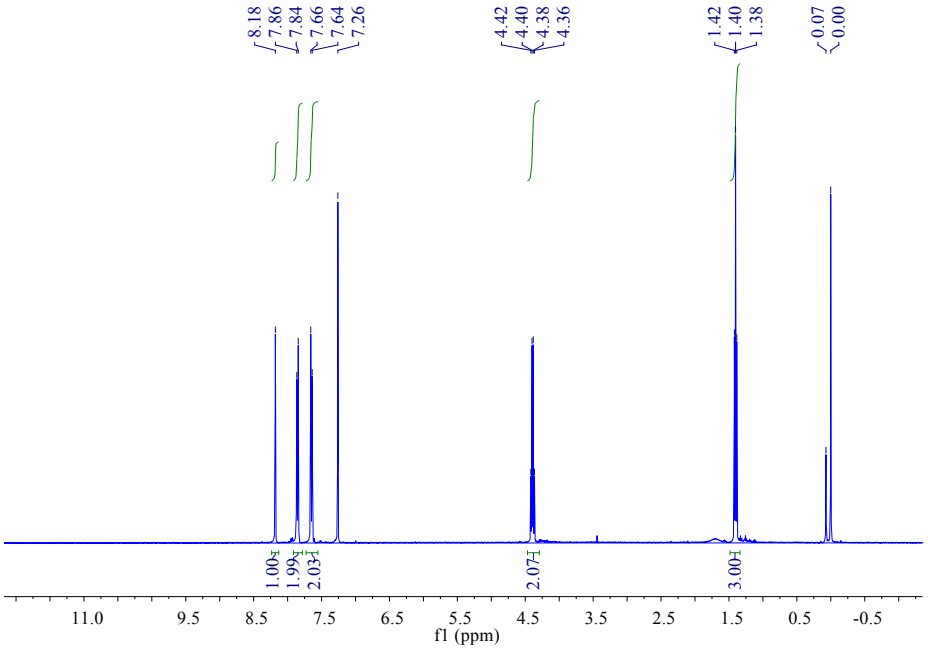


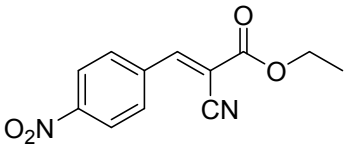
ethyl (*E*)-2-cyano-3-phenylacrylate



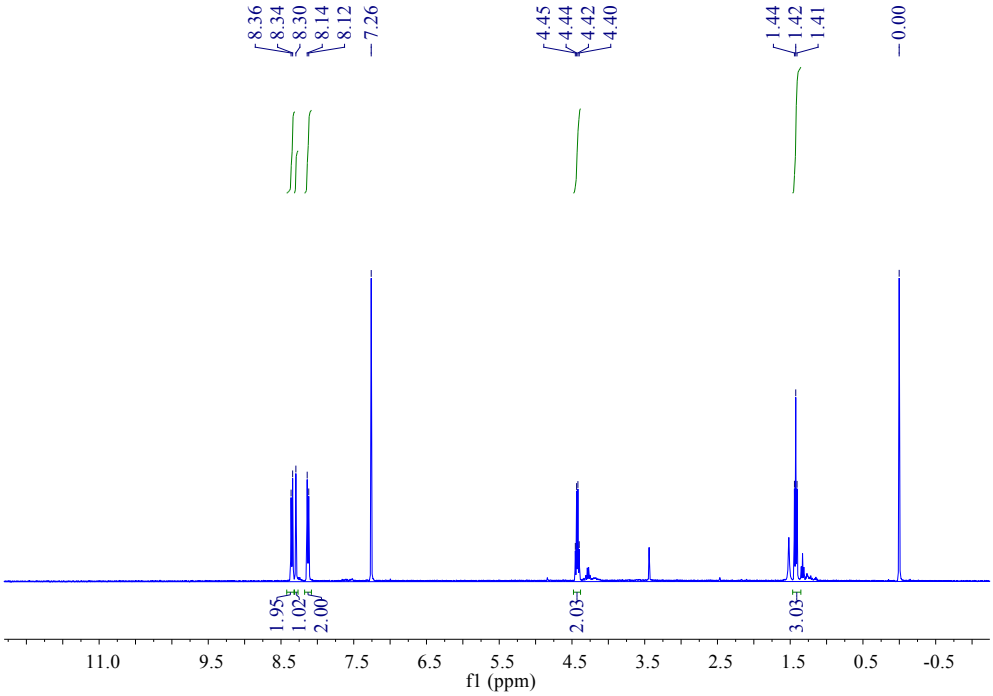


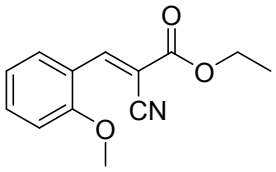
ethyl (*E*)-3-(4-bromophenyl)-2-cyanoacrylate



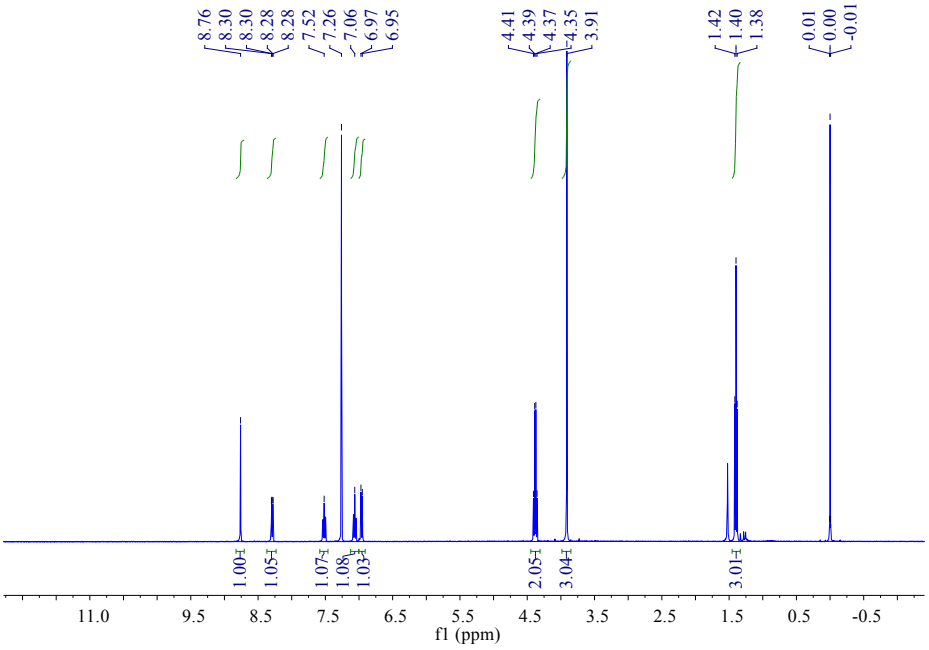


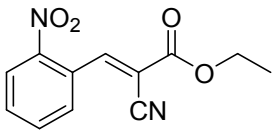
ethyl (*E*)-2-cyano-3-(4-nitrophenyl)acrylate



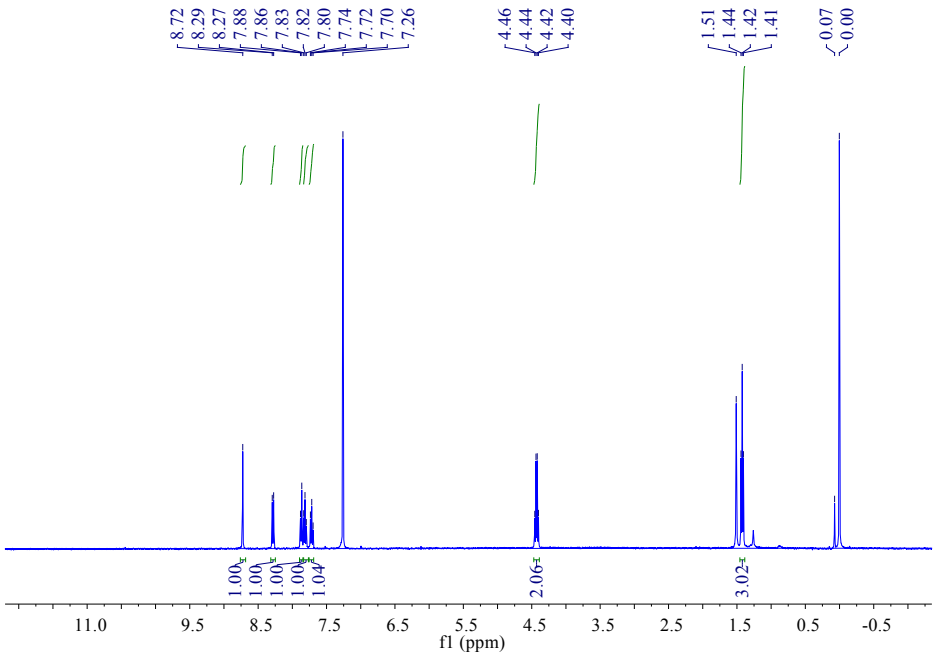


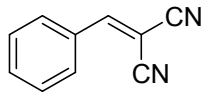
ethyl (*E*)-2-cyano-3-(2-methoxyphenyl)acrylate



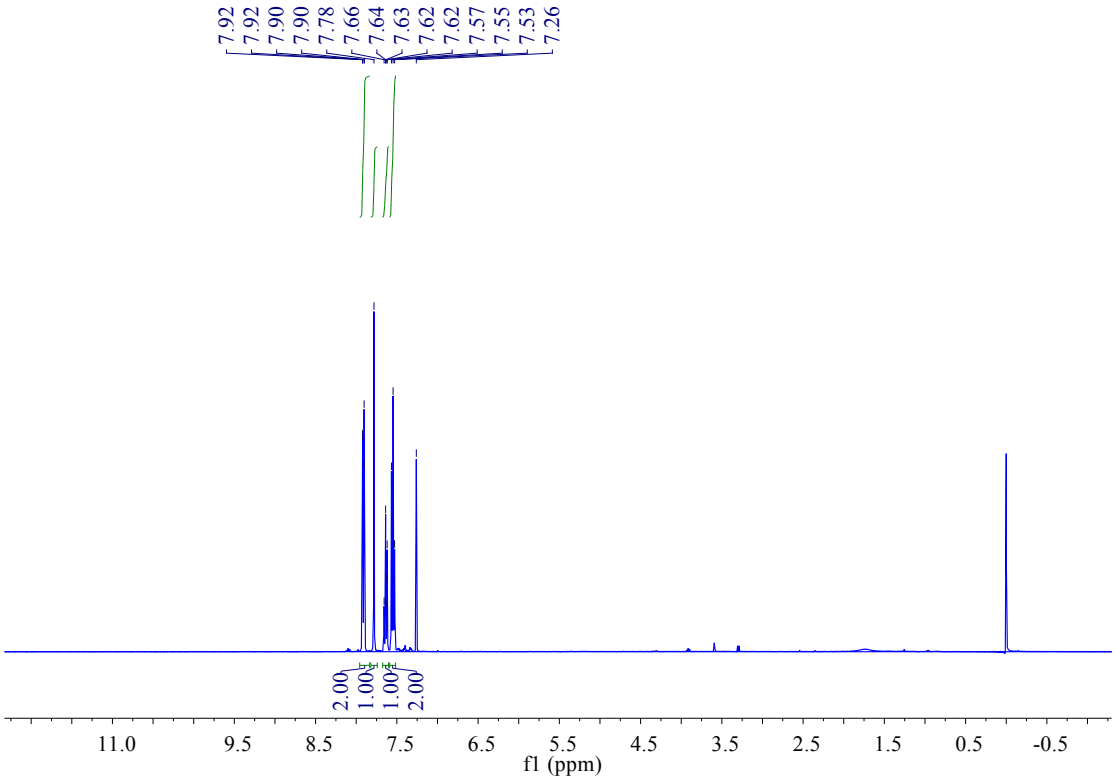


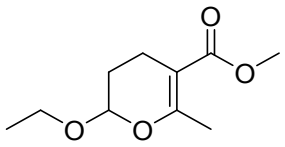
ethyl (*E*)-2-cyano-3-(2-nitrophenyl)acrylate



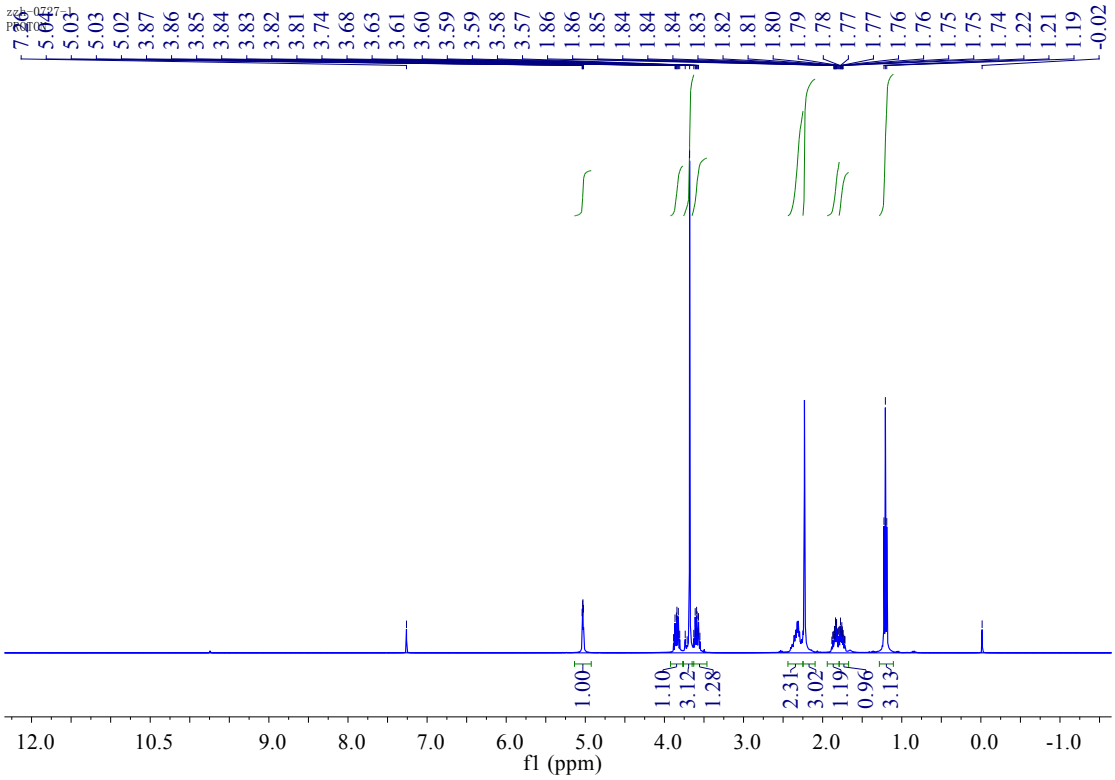


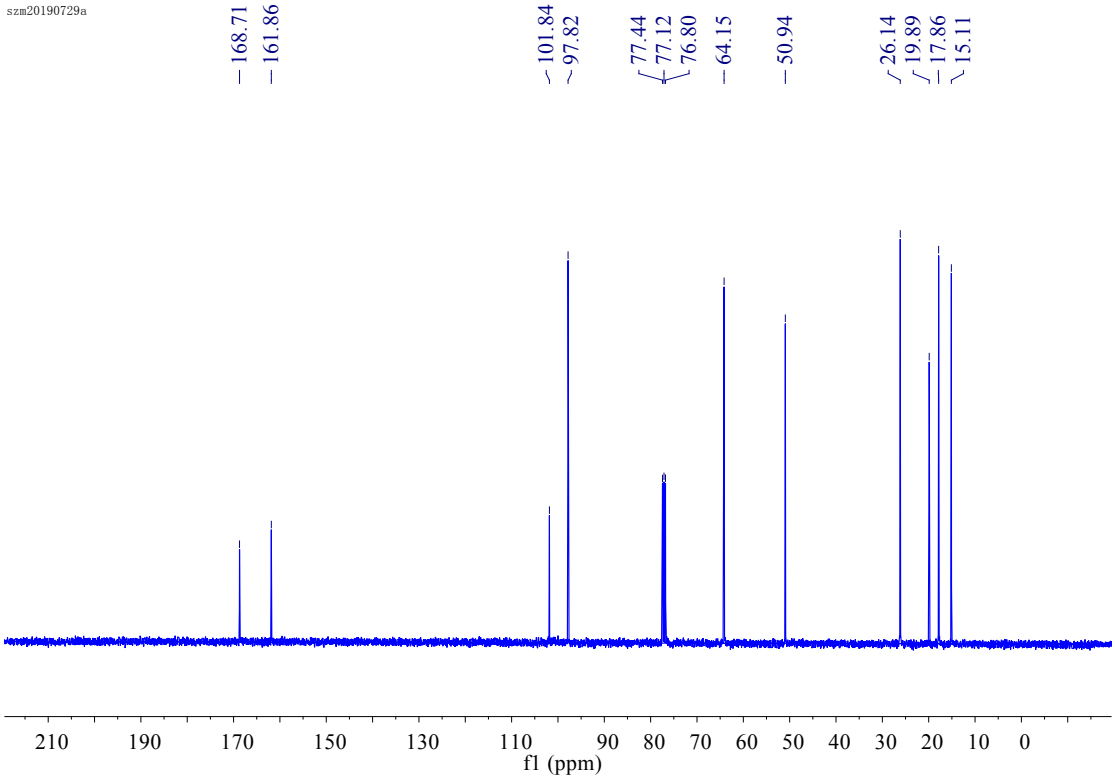
2-benzylidenemalononitrile

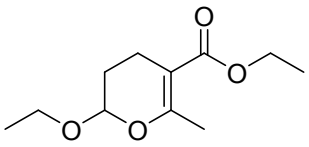




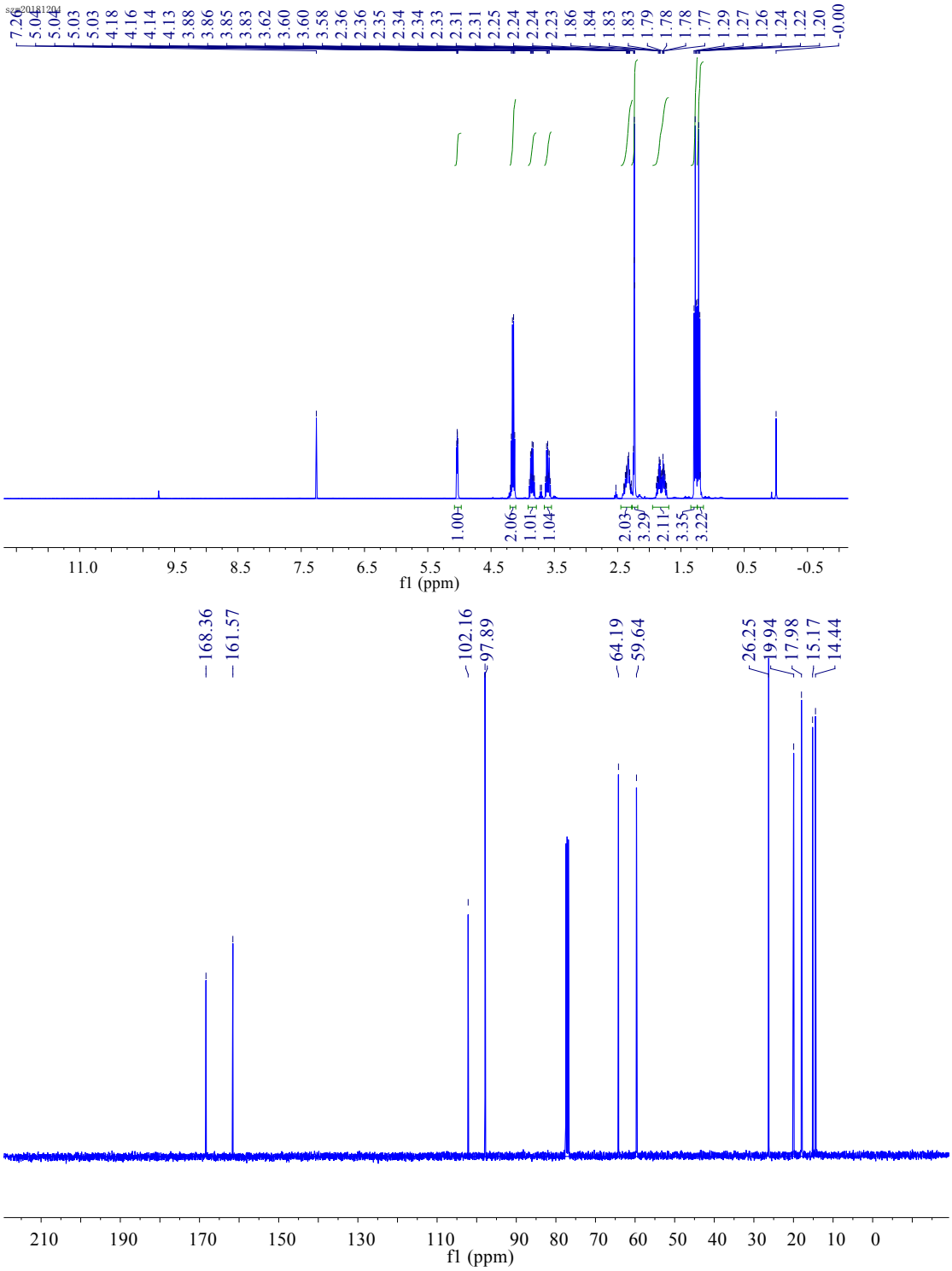
methyl 2-ethoxy-6-methyl-3,4-dihydro-2*H*-pyran-5-carboxylate

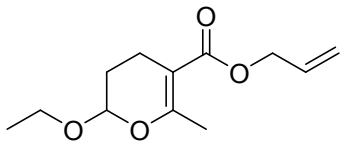




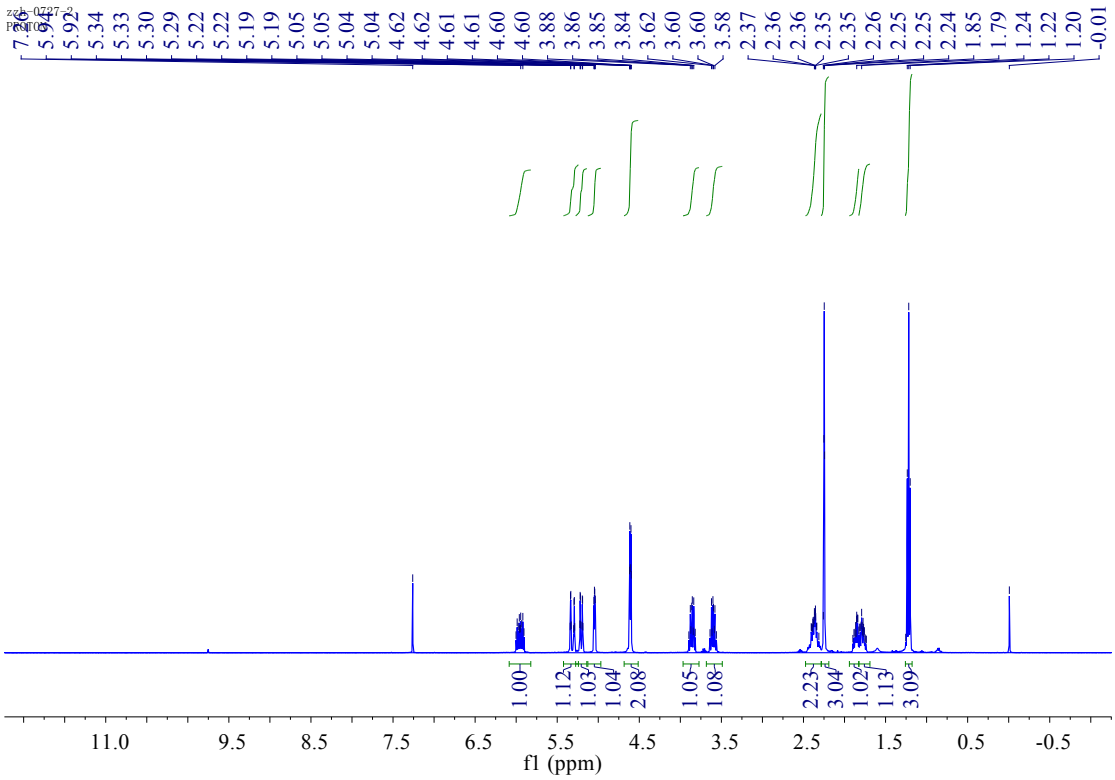


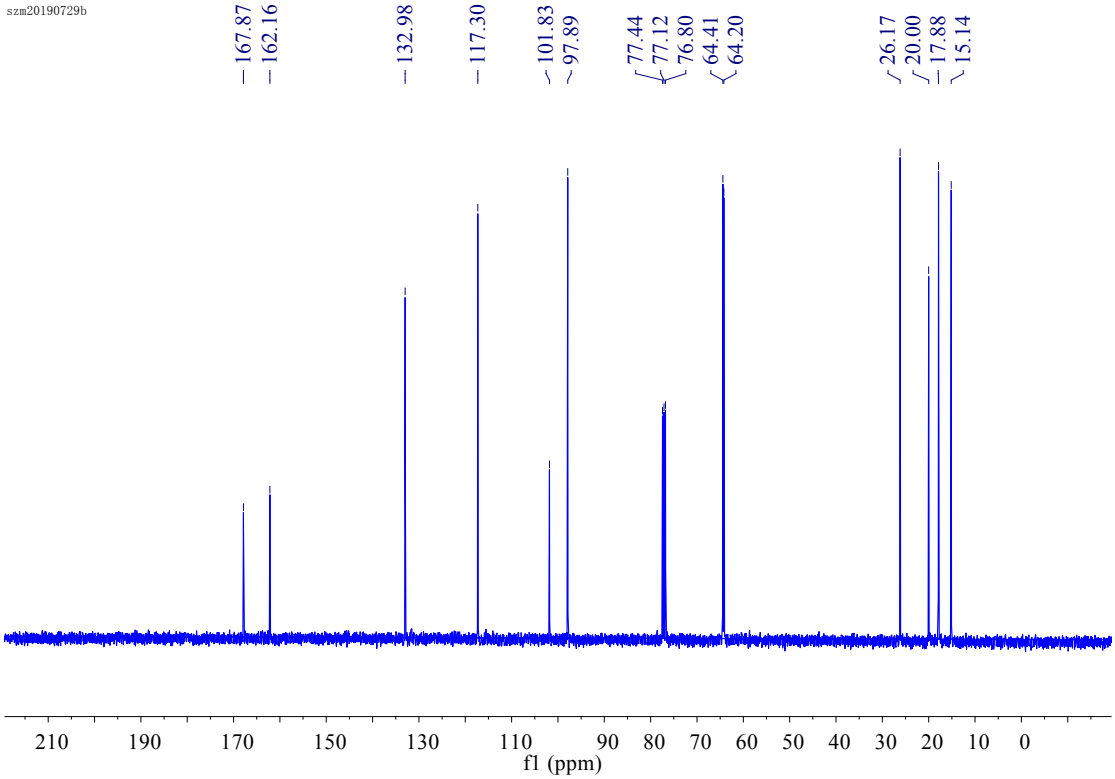
ethyl 2-ethoxy-6-methyl-3,4-dihydro-2*H*-pyran-5-carboxylate

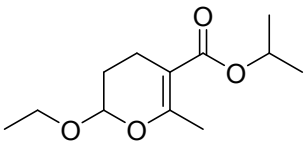




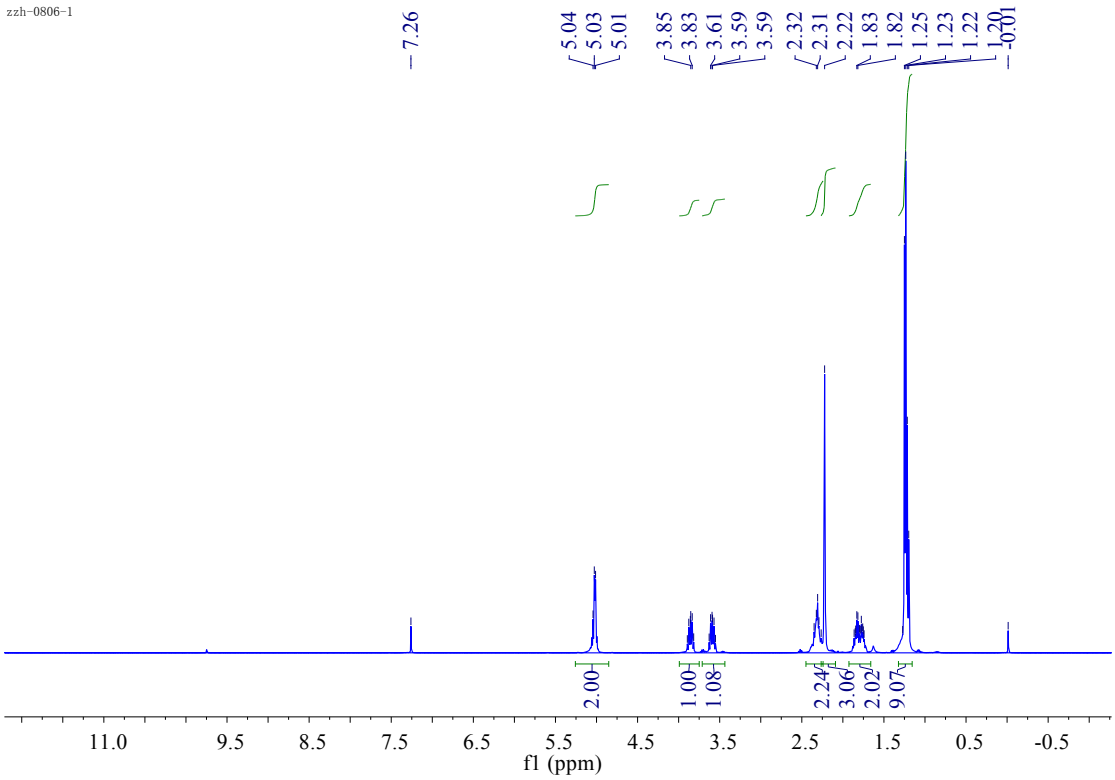
allyl 2-ethoxy-6-methyl-3,4-dihydro-2*H*-pyran-5-carboxylate

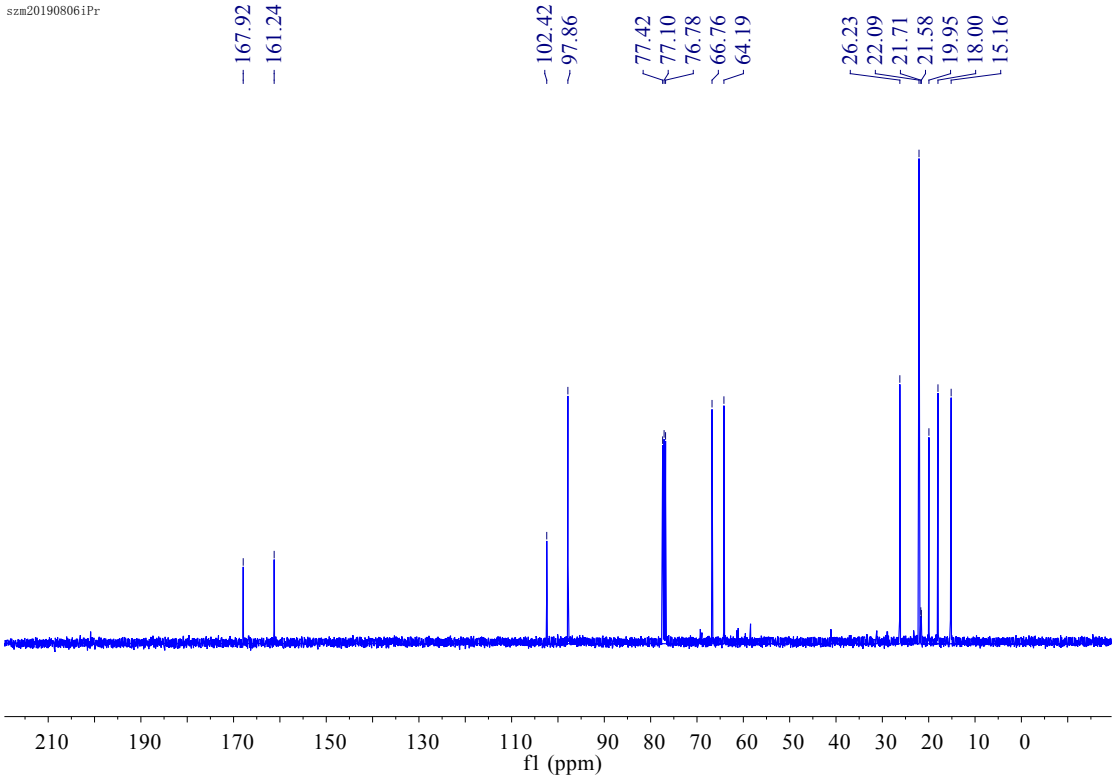


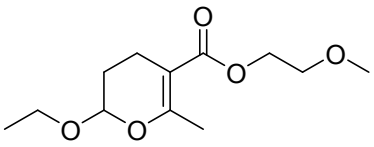




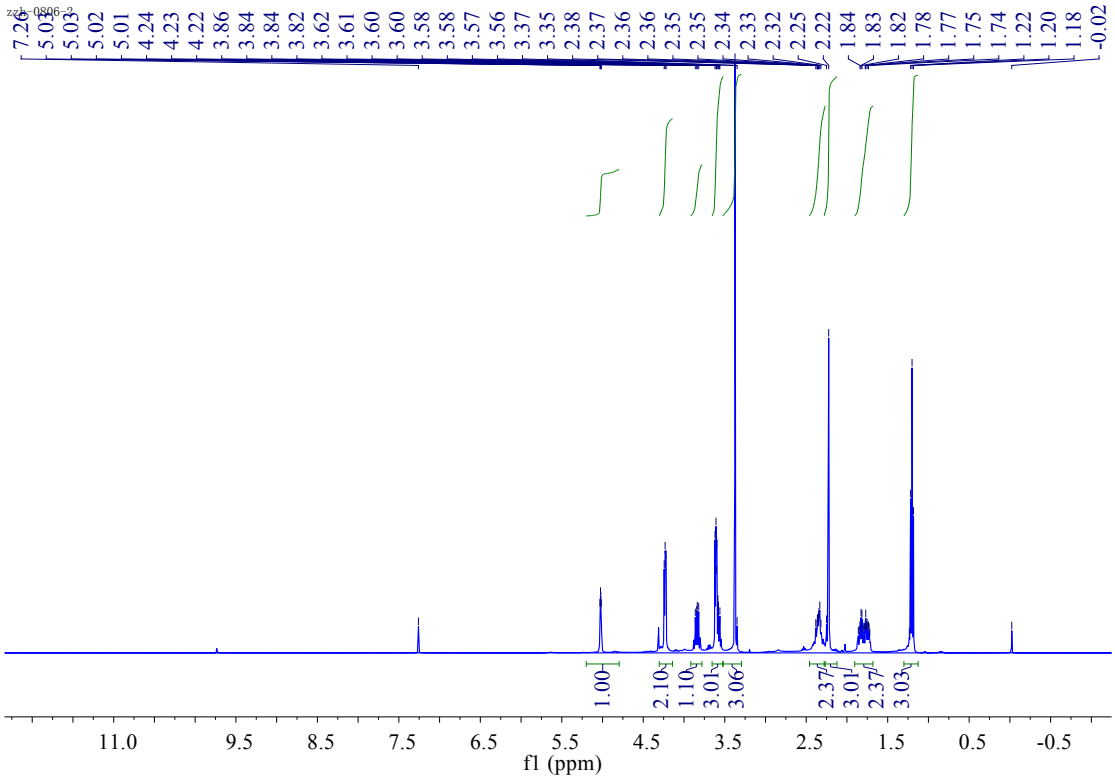
isopropyl 2-ethoxy-6-methyl-3,4-dihydro-2*H*-pyran-5-carboxylate

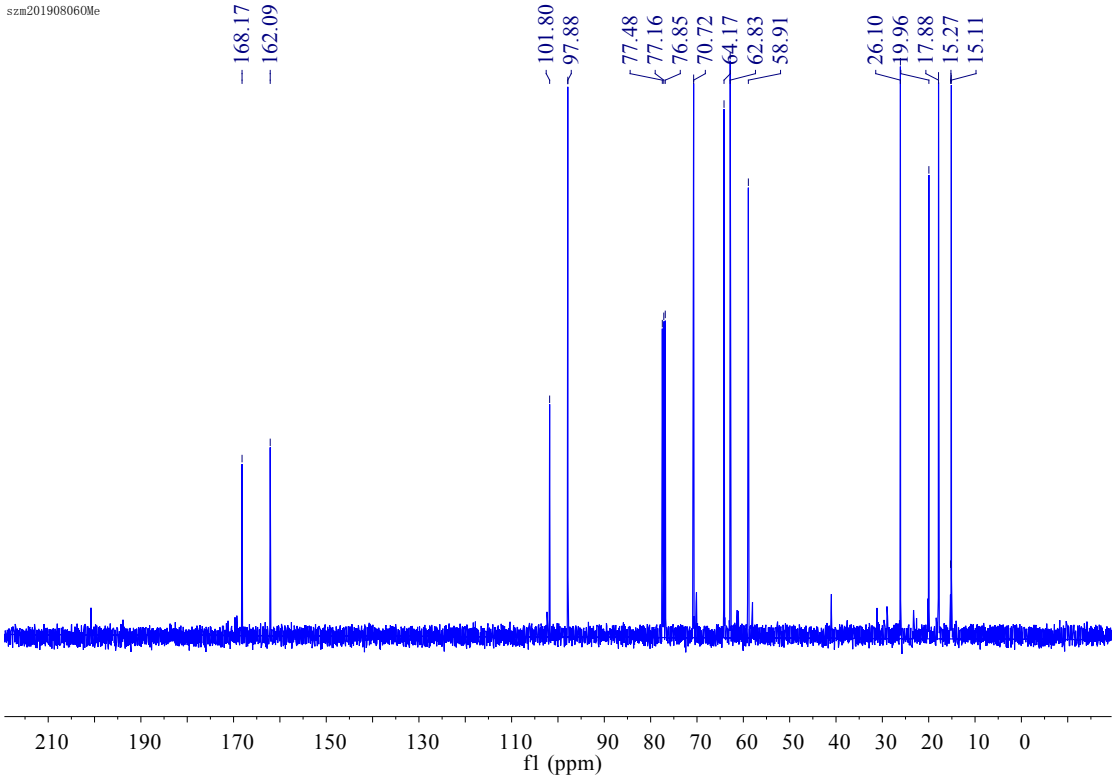


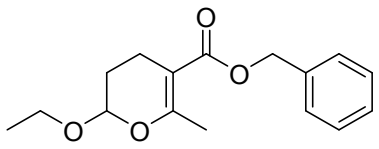




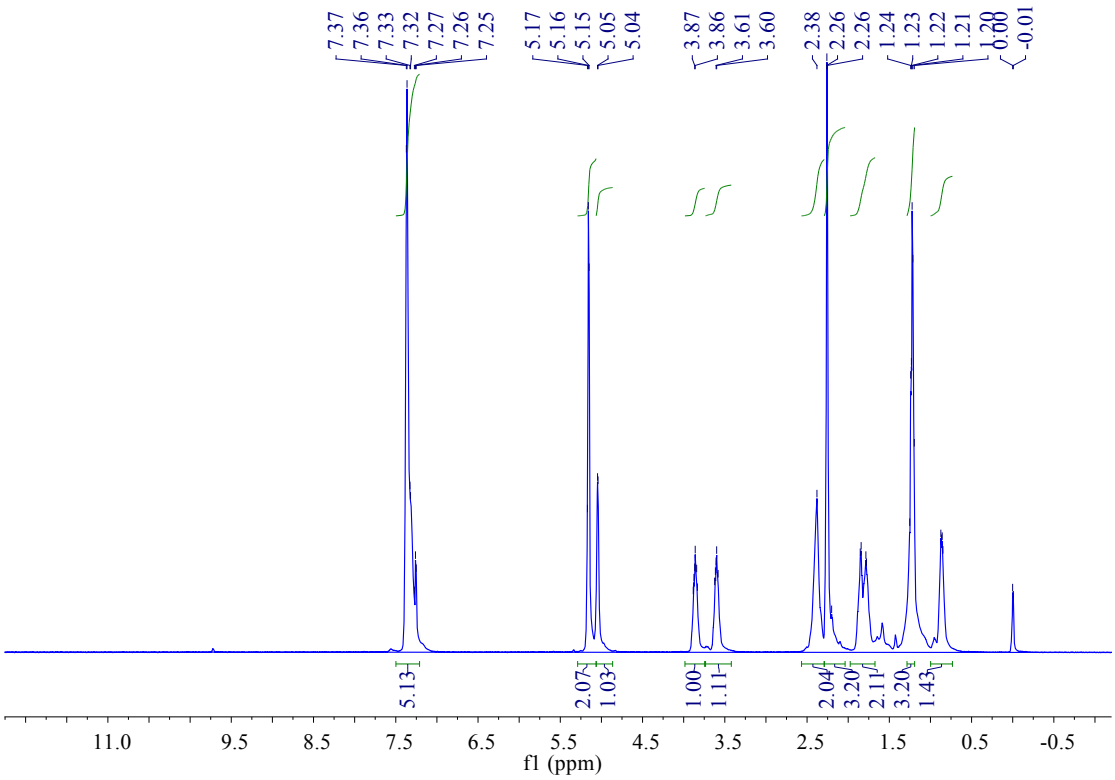
2-methoxyethyl 2-ethoxy-6-methyl-3,4-dihydro-2*H*-pyran-5-carboxylate

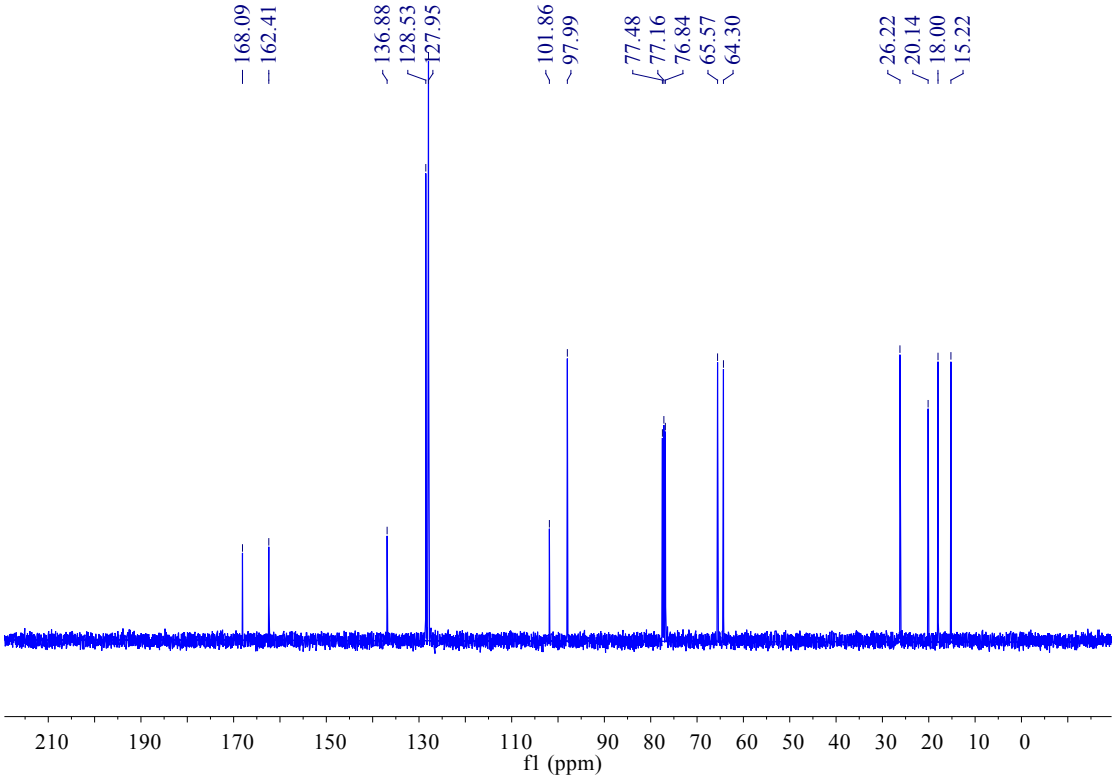


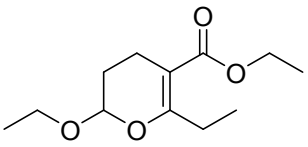




benzyl 2-ethoxy-6-methyl-3,4-dihydro-2*H*-pyran-5-carboxylate







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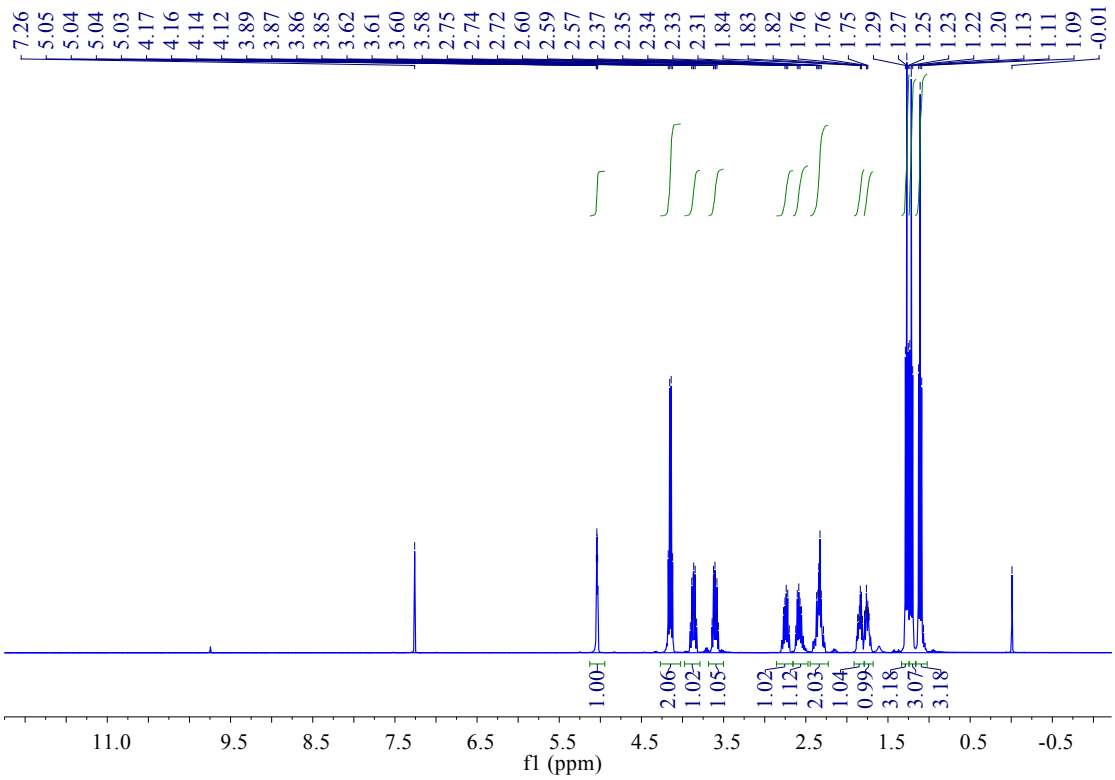
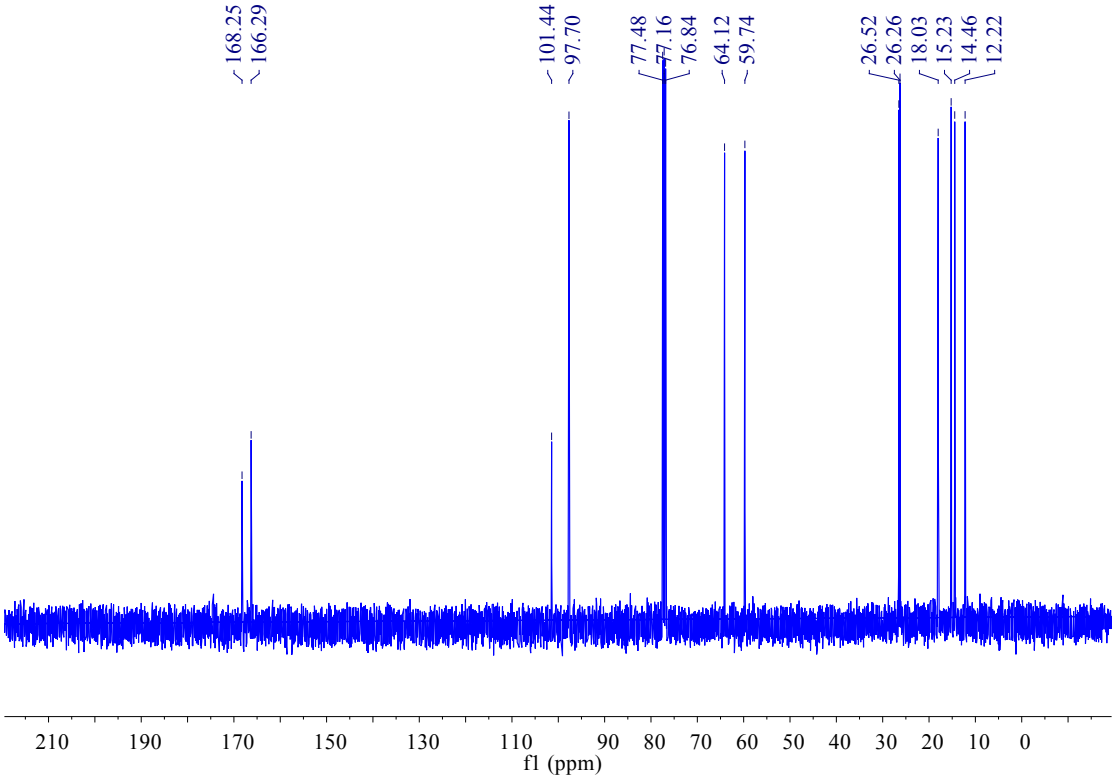
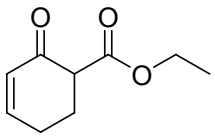
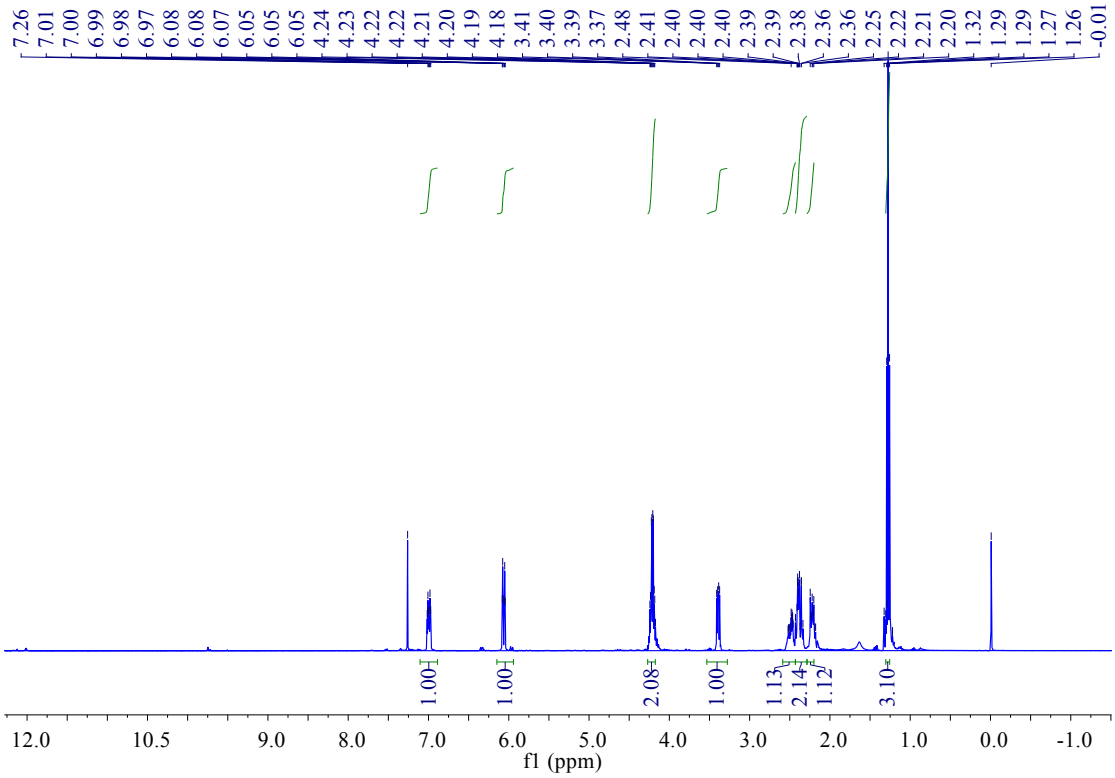
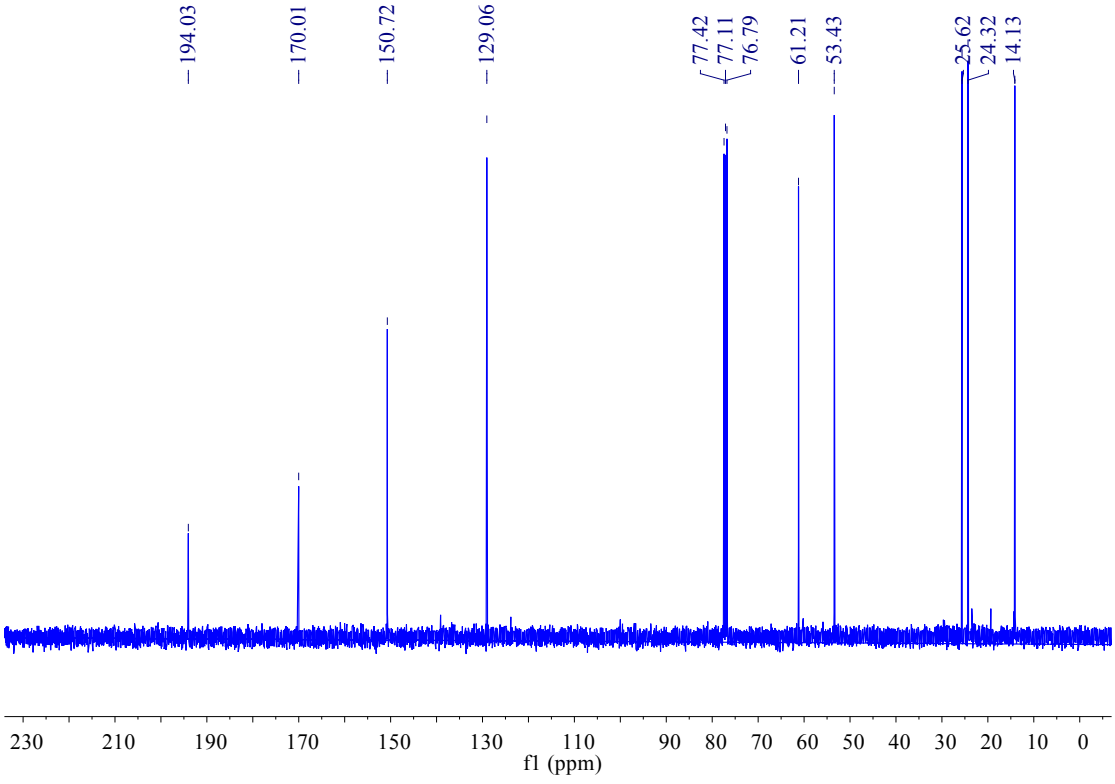


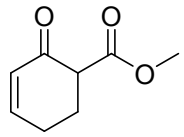




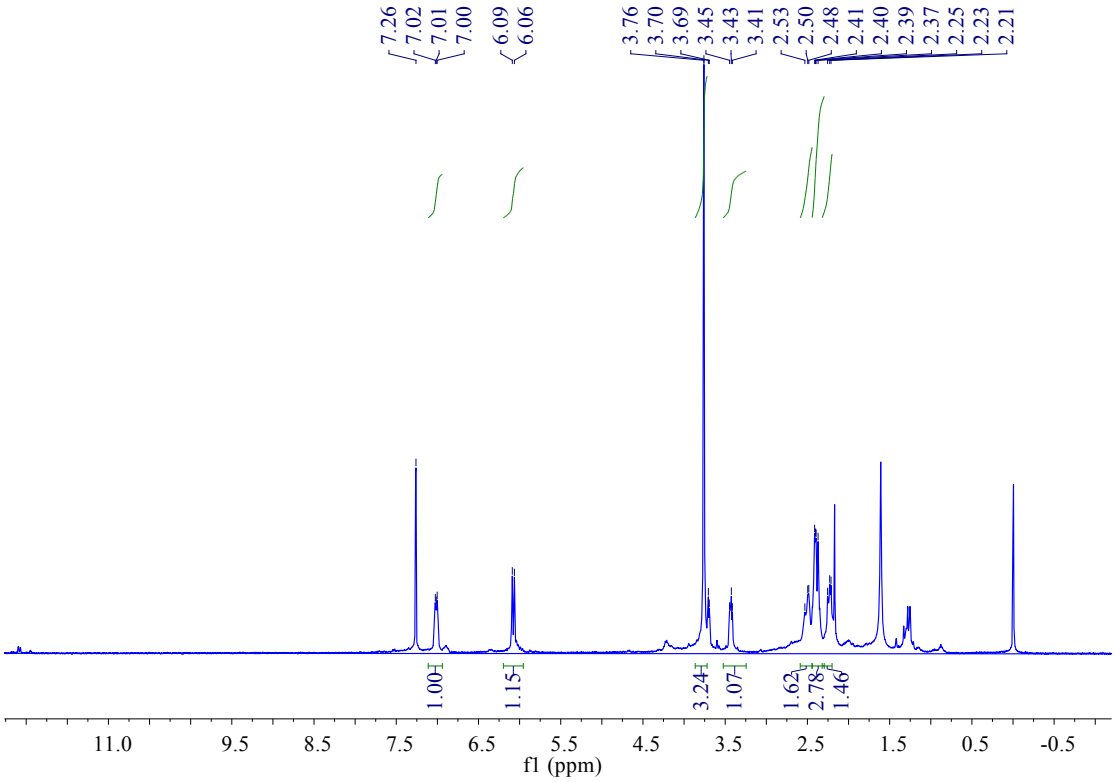
ethyl 2-oxocyclohex-3-ene-1-carboxylate

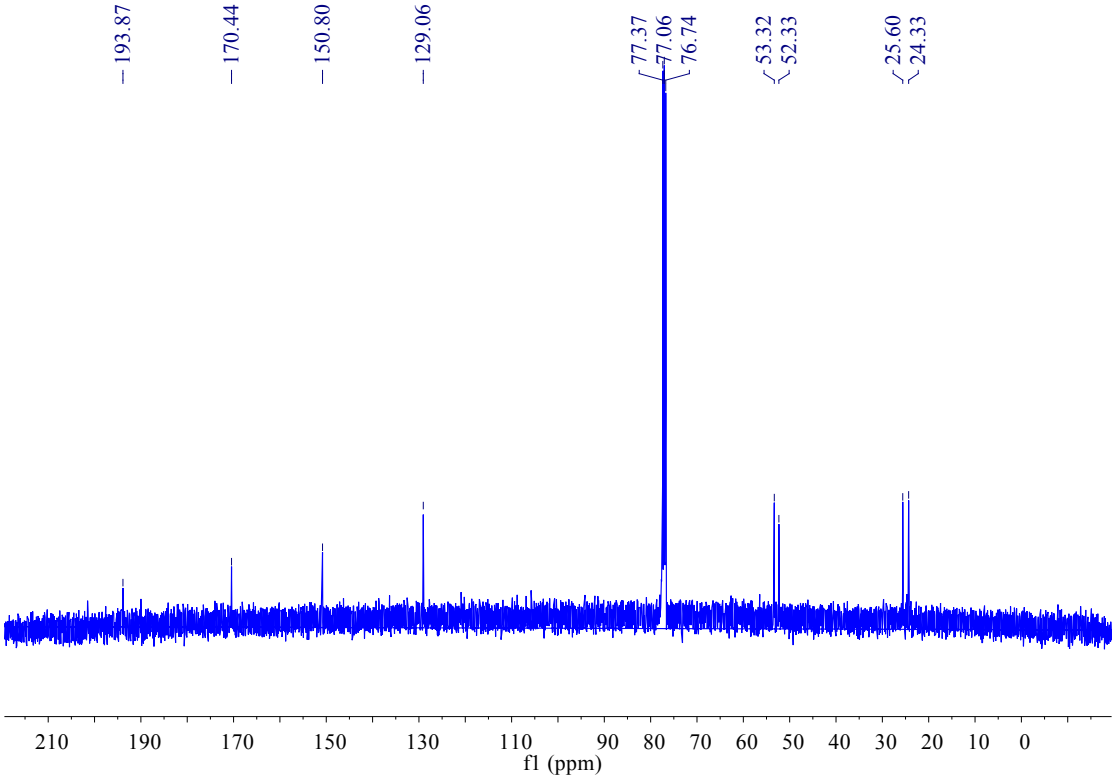


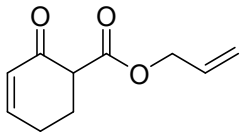




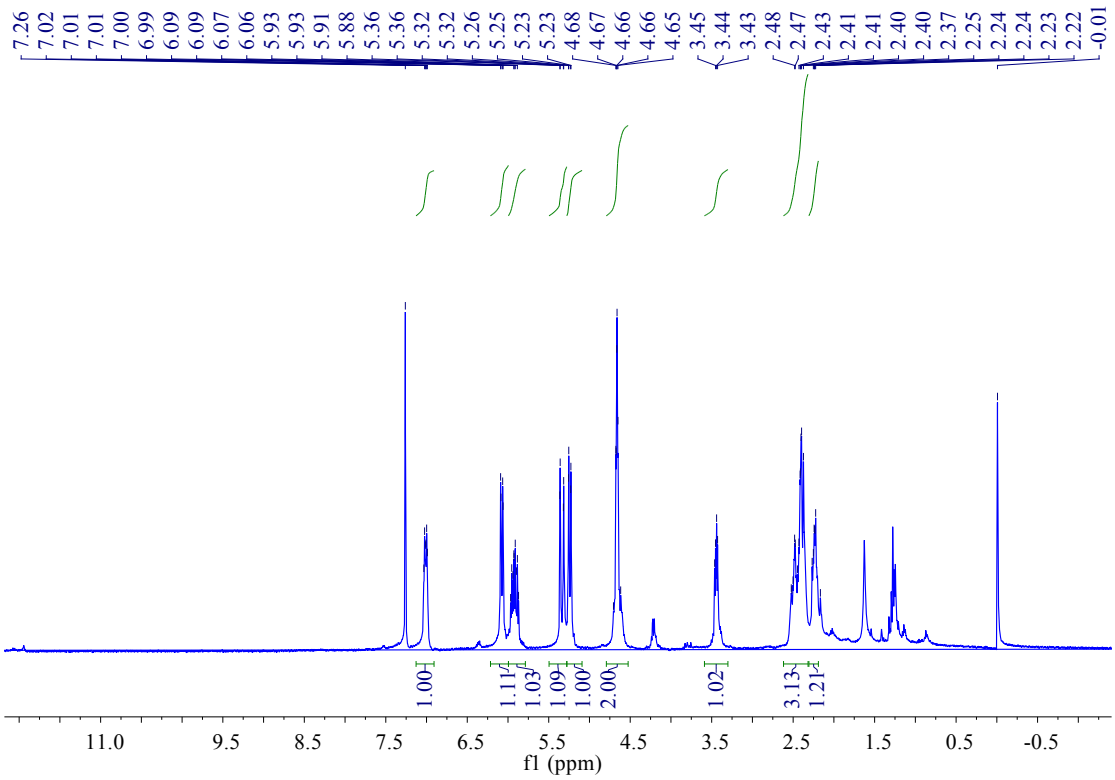
methyl 2-oxocyclohex-3-ene-1-carboxylate

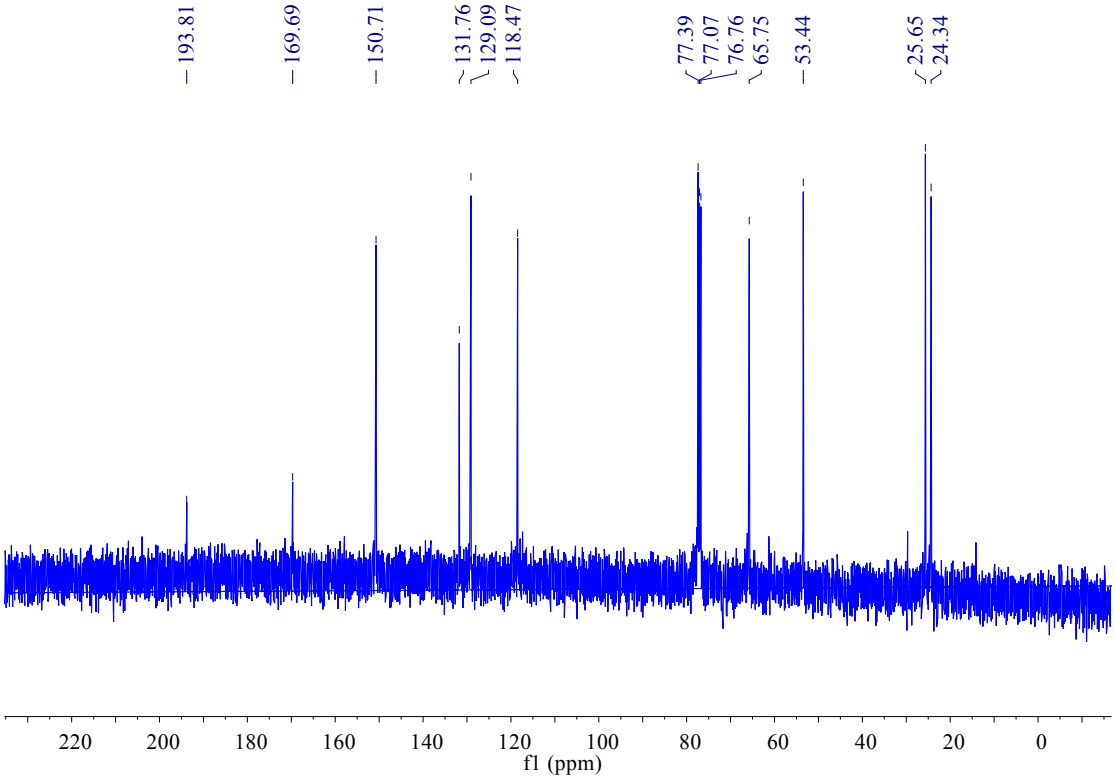


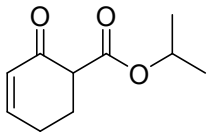




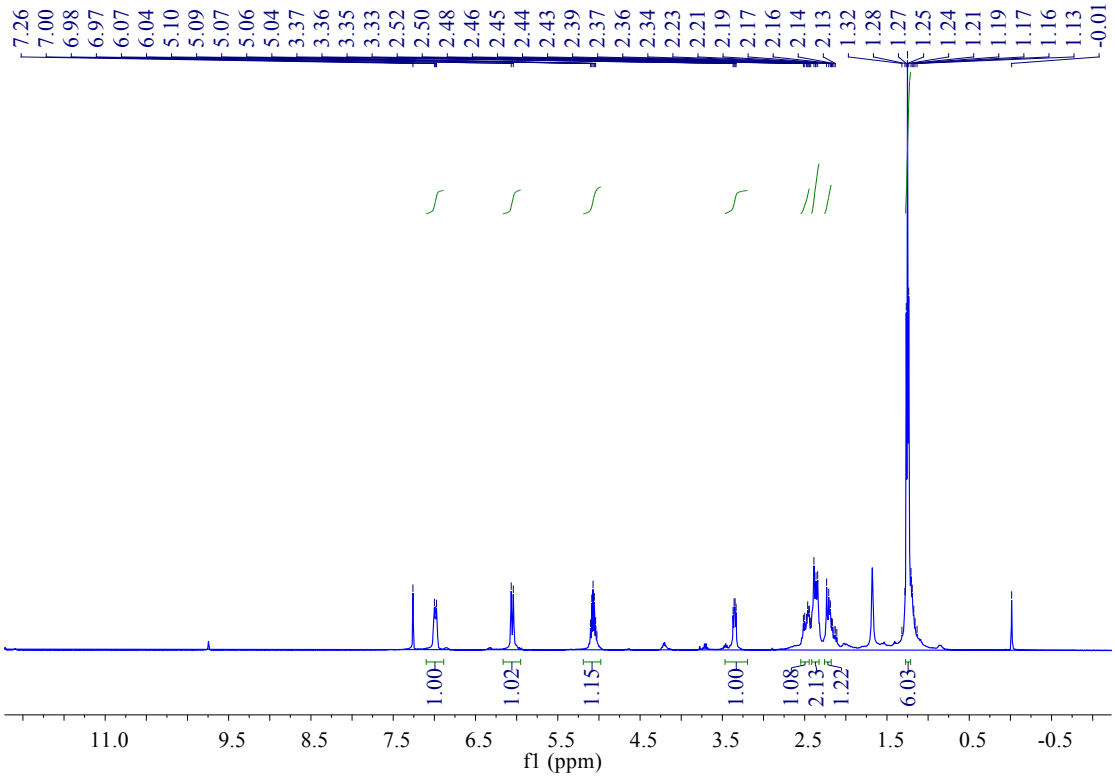
allyl 2-oxocyclohex-3-ene-1-carboxylate

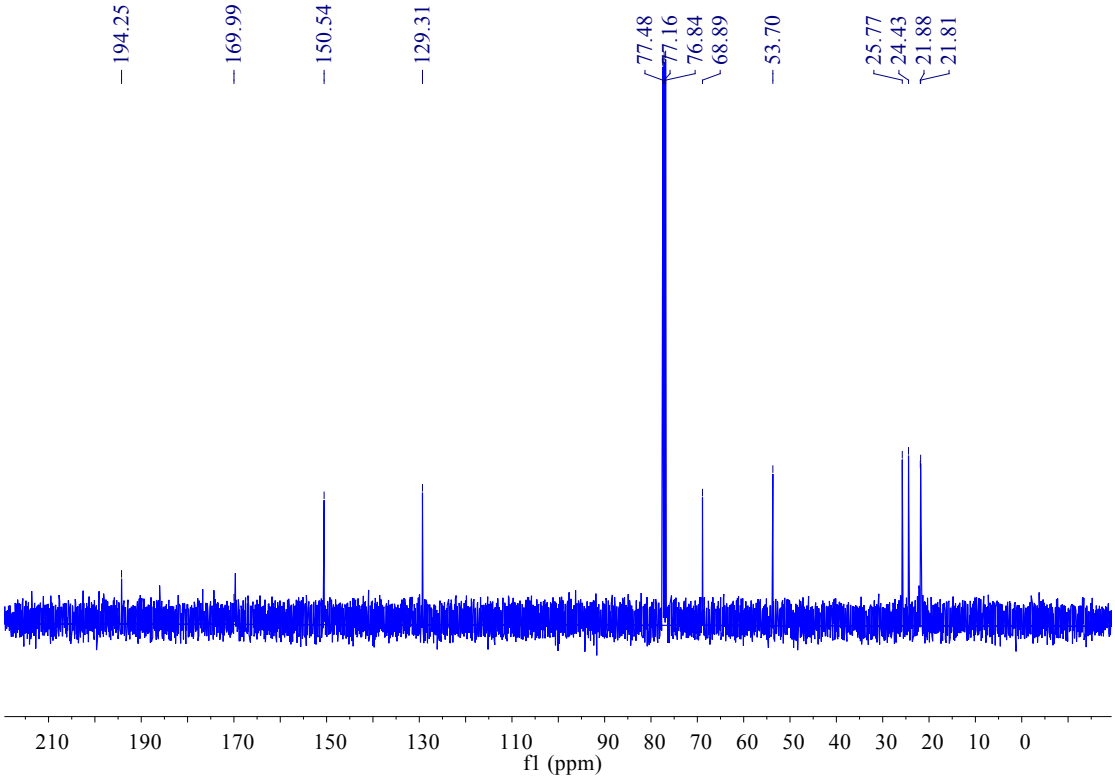


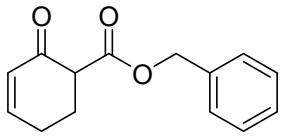




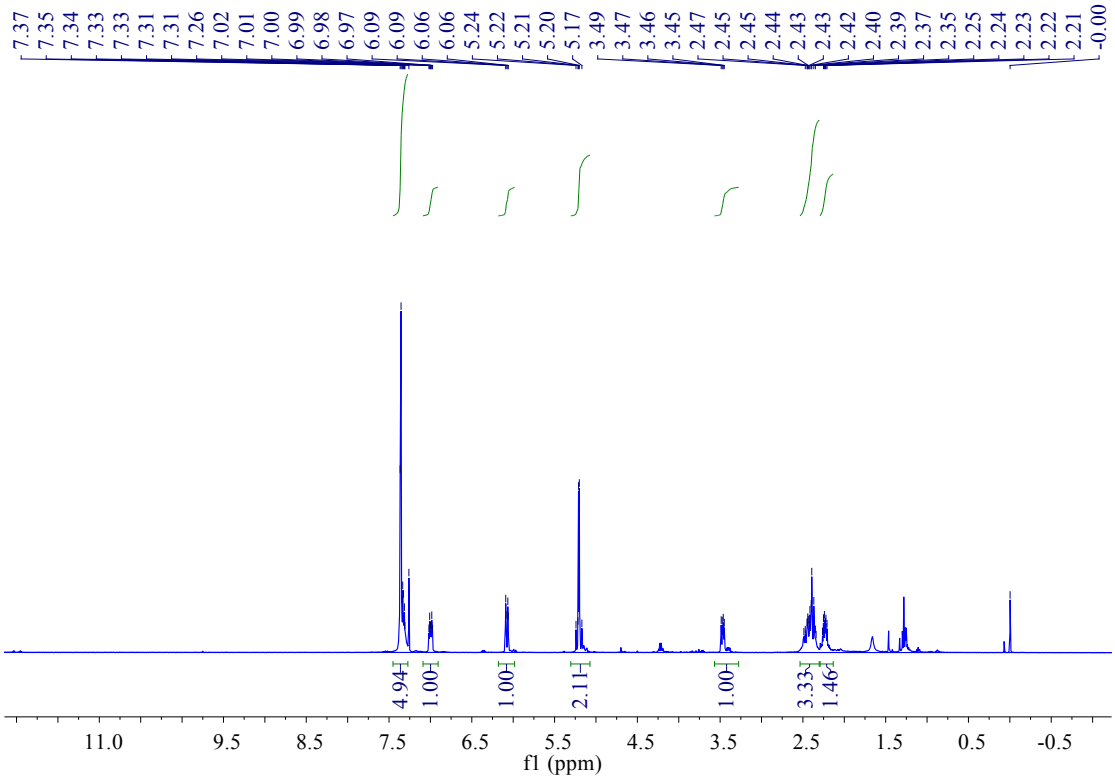
isopropyl 2-oxocyclohex-3-ene-1-carboxylate

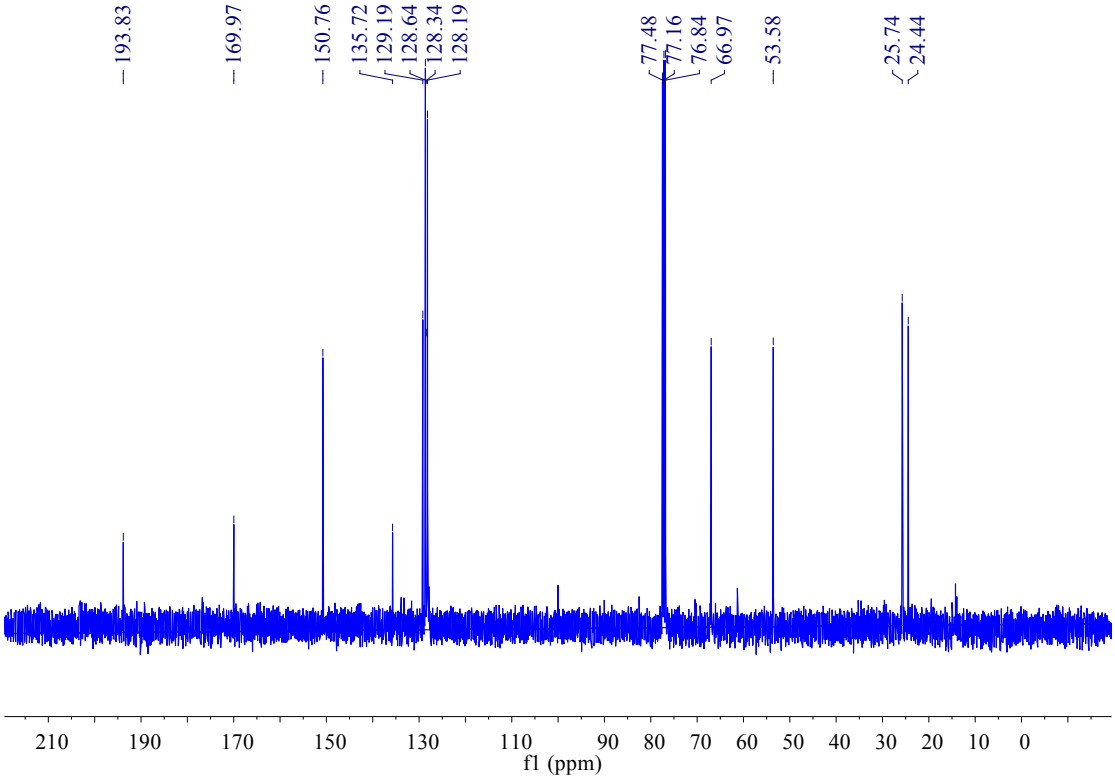


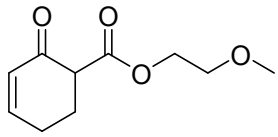




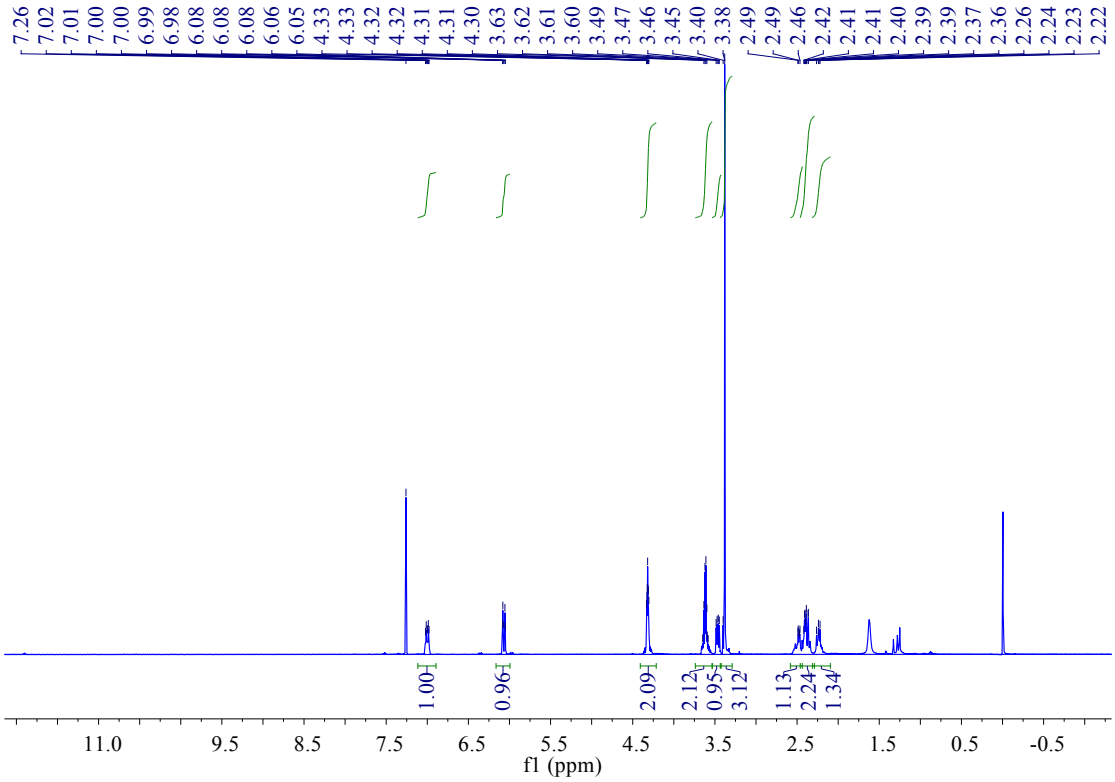
benzyl 2-oxocyclohex-3-ene-1-carboxylate

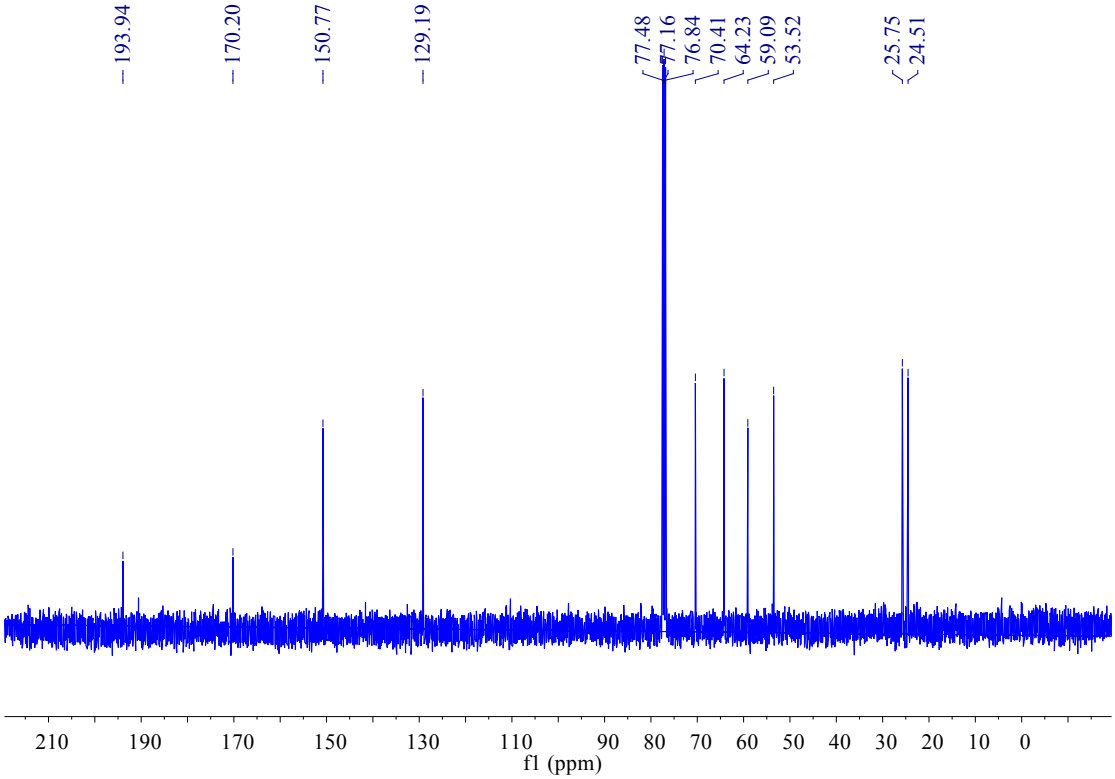


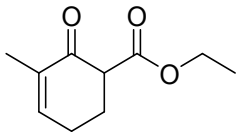




2-methoxyethyl 2-oxocyclohex-3-ene-1-carboxylate







ethyl 3-methyl-2-oxocyclohex-3-ene-1-carboxylate