Supporting Information

Palladium-Catalyzed C–H Monoalkoxylation of α,β-Unsaturated Carbonyl Compounds

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1. General

The ^{1}H NMR and ^{13}C NMR spectra were recorded by a JEOL JNM ECA-500 (500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR), ECS-400 (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR), or AL-400 (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR) spectrometer. $CDCl_3$, CD_2Cl_2 or DMSO-d_6 was used as the solvent for the NMR measurements. The chemical shifts (δ) are expressed in part per million and internally referenced (^{1}H NMR: δ= 0.00; ^{13}C NMR; δ= 77.0 for $CDCl_3$; ^{1}H NMR: δ = 5.32; ^{13}C NMR: δ = 53.3 for CD_2Cl_2; ^{1}H NMR: δ = 2.49; ^{13}C NMR: δ = 39.5 for DMSO-d_6). The mass spectra (EI) were taken by a JEOL JMS Q1000GC Mk II Quad GC/MS. The IR spectra were recorded by a Brucker FT-IR ALPHA. The ESI high resolution mass spectra (HRMS) were measured by a Shimazu hybrid IT-TOF mass spectrometer.

2. Typical procedures to prepare the substrates

Procedure A: To a solution of acrylic acid (216 mg, 3.00 mmol) in DMF (5 mL) in a 50-mL round bottom flask equipped with a reflux condenser at 0 °C was added K_2CO_3 (415 mg, 3.00 mmol). After 45 minutes, the alkyl chloride or alkyl bromide (2.50 mmol) was dropwise added, and the reaction mixture under an Ar atmosphere was stirred at 100 °C for 24 hours. The reaction mixture was cooled to room temperature, quenched with water (20 mL), and extracted with Et_2O (20 mL × 2). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by silica-gel column chromatography using hexane–EtOAc or hexane–Et_2O as the eluent to give the corresponding alkyl acrylate.

Procedure B: To a solution of acrylic acid (288 mg, 4.00 mmol), *N*,*N*'-dicyclohexylcarbodiimide (DCC, 1.03 g, 5.00 mmol), and the phenol derivative (4.00 mmol) in CH_2Cl_2 (20 mL) in a 50-mL round bottom flask was added *N*,*N*-dimethyl-4-aminopyridine (DMAP, 50.0 mg, 409 μmol) at room temperature. The mixture was sitirred under an Ar atmosphere for 24 hours, quenched with water (20 mL), and extracted with Et_2O (20 mL × 2). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by silica-gel column chromatography using hexane–EtOAc as the eluent to give the corresponding alkyl acrylate.

4-Nitrobenzyl Acrylate[1]

The reaction was carried out using 4-nitrobenzyl bromide (540 mg, 2.50 mmol) according to typical procedure A. 4-Nitrobenzyl acrylate was obtained in 82% yield (425 mg, 2.05 mmol) after purification by silica-gel column chromatography (Hexane/EtOAc = 10/1).

Analytical TLC, 10:1 Hexane/EtOAc, R_f = 0.15; Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (2H, d, J = 8.3 Hz), 7.55 (2H,

d, J = 8.3 Hz), 6.50 (1H, dd, J = 17.0, 2.5 Hz), 6.21 (1H, dd, J = 17.0, 10.5 Hz), 5.94 (1H, dd, J = 10.5, 2.5 Hz), 5.31 (2H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.5, 147.6, 143.1, 131.9, 128.3, 127.6, 123.7, 64.7; ESI-HRMS m/z: 208.0625 ($[M+H]^+$); Calcd for $C_{10}H_{10}NO_4$: 208.0604.

4-Bromobenzyl Acrylate

The reaction was carried out using 4-bromobenzyl bromide (630 mg, 2.52 mmol) according to typical procedure A. 4-Bromobenzyl acrylate was obtained in 56% yield (338 mg, 1.41 mmol) after purification by silica-gel column chromatography (Hexane/Et_2O = 20/1).

Analytical TLC, 10:1 Hexane/EtOAc, R_f = 0.47; Colorless oil; IR (ATR) cm^{-1}: 2954, 1721, 1634, 1596, 1489, 1451, 1403, 1368, 1293, 1265, 1170, 1108, 1069, 1048, 1012; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (2H, d, J = 8.3 Hz), 7.26 (2H, d, J = 8.3 Hz), 6.45 (1H, dd, J = 17.5, 1.3 Hz), 6.16 (1H, dd, J = 17.5, 10.5 Hz), 5.87 (1H, dd, J = 10.5, 1.3 Hz), 5.15 (2H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.7, 134.8, 131.6, 131.2, 129.8, 128.0, 122.1, 65.3; ESI-HRMS m/z: 262.9681 ($[M+Na]^+$); Calcd for $C_{10}H_9O_2BrNa$: 262.9678.

4-Methoxybenzyl Acrylate[2]

The reaction was carried out using 4-methoxybenzyl chloride (392 mg, 2.50 mmol) according to typical procedure A. 4-Methoxybenzyl acrylate was obtained in 71% yield (341 mg, 1.78 mmol) after purification by silica-gel column chromatography (Hexane/Et_2O = 10/1).

Analytical TLC, 10:1 Hexane/EtOAc, R_f = 0.43; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (2H, d, J = 8.8 Hz), 6.88 (2H, d, J = 8.8 Hz), 6.42 (1H, dd, J = 17.5, 1.3 Hz), 6.13 (1H, dd, J = 17.5, 10.5 Hz), 5.81 (1H, dd, J = 10.5, 1.3 Hz), 5.12 (2H, s), 3.78 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 159.5, 130.8, 130.0, 128.3, 127.8, 113.8, 66.0, 55.1; MS (EI) m/z (%) 192 (M^+, 48), 121 (100).

4-Methylbenzyl Acrylate[2]

The reaction was carried out using 4-methylbenzyl bromide (462 mg, 2.50 mmol) according to typical procedure A. 4-Methylbenzyl acrylate was obtained in 87% yield (383 mg, 2.18 mmol) after purification by silica-gel column chromatography (Hexane/Et_2O = 15/1).

Analytical TLC, 10:1 Hexane/EtOAc, R_f = 0.54; Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (2H, d, J = 8.0 Hz), 7.18 (2H, d, J = 8.0 Hz), 6.43 (1H, dd, J = 17.5, 1.5 Hz), 6.15 (1H, dd, J = 17.5, 10.5 Hz), 5.83 (1H, dd, J = 10.5, 1.5 Hz), 5.16 (2H, s), 2.35 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.1, 138.1, 132.8, 130.9, 129.2, 128.4, 128.4, 66.3, 21.2; MS (EI) m/z (%) 176 (M^+, 89), 105 (100).

2-Methylbenzyl Acrylate

The reaction was carried out using 2-methylbenzyl bromide (462 mg, 2.50 mmol) according to typical procedure A. 2-Methylbenzyl acrylate was obtained in 82% yield (361 mg, 2.05 mmol) after purification by silica-gel column chromatography (Hexane/Et_2O = 15/1).

Analytical TLC, 10:1 Hexane/EtOAc, R_f = 0.35; Colorless oil; IR (ATR) cm^{-1}: 3026, 2957, 1721, 1634, 1494, 1462, 1405, 1370, 1294, 1265, 1174, 1044; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (1H, d, J = 7.5 Hz), 7.24 (1H, m), 7.20–7.18 (2H, m), 6.43 (1H, dd, J = 17.5, 1.5 Hz), 6.15 (1H, dd, J = 17.5, 10.5 Hz), 5.82 (1H, dd, J = 10.5, 1.5 Hz), 5.20 (2H, s), 2.35 (3H, s); ^{13}C NMR (125

MHz, $CDCl_3$) δ 165.9, 136.9, 133.7, 131.0, 130.3, 129.2, 128.5, 128.2, 125.9, 64.7, 18.8; ESI-HRMS m/z: 199.0744 ($[M+Na]^+$); Calcd for $C_{11}H_{12}O_2Na$: 199.0730.

2-Naphthylmethyl Acrylate[3]

The reaction was carried out using 2-bromomethylnaphthalene (570 mg, 2.58 mmol) according to typical procedure A. 2-Naphthylmethyl acrylate was obtained in 44% yield (241 mg, 1.14 mmol) after purification by silica-gel column chromatography (Hexane/Et_2O = 10/1).

Analytical TLC, 10:1 Hexane/EtOAc, R_f = 0.34; White solid; ^1H NMR (500 MHz, DMSO-d_6) δ 7.94–7.91 (4H, m), 7.54–7.51 (3H, m), 6.39 (1H, dd, *J* = 17.3, 1.5 Hz), 6.26 (1H, dd, *J* = 17.3, 10.0 Hz), 5.98 (1H, dd, *J* = 10.0, 1.5 Hz), 5.34 (2H, s); ^{13}C NMR (125 MHz, DMSO-d_6) δ 165.4, 133.6, 132.7, 132.6, 132.0, 128.2, 128.2, 127.8, 127.6, 126.9, 126.4, 126.3, 126.0, 65.8; MS (EI) m/z (%) 212 (M^+, 79), 158 (100).

1-Decyl Acrylate[1]

The reaction was carried out using 1-bromodecane (556 mg, 2.51 mmol) according to typical procedure A. 1-Decyl acrylate was obtained in 90% yield (477 mg, 2.26 mmol) after purification by silica-gel column chromatography (Hexane/Et_2O = 20/1).

Analytical TLC, 10:1 Hexane/EtOAc, R_f = 0.67; Colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 6.40 (1H, dd, *J* = 17.3, 1.0 Hz), 6.12 (1H, dd, *J* = 17.3, 10.5 Hz), 5.82 (1H, dd, *J* = 10.5, 1.0 Hz), 4.15 (2H, t, *J* = 7.0 Hz), 1.67 (2H, quin, *J* = 7.0 Hz), 1.38–1.27 (14H, m), 0.88 (3H, t, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.4, 130.4, 128.6, 64.7, 31.9, 29.5, 29.3, 29.2, 28.6, 25.9, 22.7, 14.1 (one signal could not be located because of its overlap with another signal); ESI-HRMS m/z: 235.1648 ($[M+Na]^+$); Calcd for $C_{13}H_{24}O_2Na$: 235.1669.

Phenyl Acrylate[4]

The reaction was carried out using phenol (378 mg, 4.02 mmol) according to typical procedure B. Phenyl acrylate was obtained in 65% yield (383 mg, 2.61 mmol) after purification by silica-gel column chromatography (Hexane/EtOAc = 30/1).

Analytical TLC, 10:1 Hexane/EtOAc, R_f = 0.58; Colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.38 (2H, t, *J* = 8.0 Hz), 7.23 (1H, t, *J* = 8.0 Hz), 7.12 (2H, d, *J* = 8.0 Hz), 6.59 (1H, dd, *J* = 17.3, 1.0 Hz), 6.31 (1H, dd, *J* = 17.3, 10.3 Hz), 5.99 (1H, dd, *J* = 10.3, 1.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.5, 150.5, 132.5, 129.4, 127.8, 125.8, 121.4; MS (EI) m/z (%) 148 (M^+, 67), 55 (100).

4-Methoxyphenyl Acrylate[4]

The reaction was carried out using 4-methoxyphenol (512 mg, 4.12 mmol) according to typical procedure B. 4-Methoxyphenyl acrylate was obtained in 70% yield (517 mg, 2.88 mmol) after purification by silica-gel column chromatography (Hexane/EtOAc = 20/1).

Analytical TLC, 20:1 Hexane/EtOAc, R_f = 0.29; Colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.04 (2H, d, *J* = 8.8 Hz), 6.90 (2H, d, *J* = 8.8 Hz), 6.58 (1H, dd, *J* = 17.8, 1.0 Hz), 6.30 (1H, dd, *J* = 17.8, 10.5 Hz), 5.98 (1H, dd, *J* = 10.5, 1.0 Hz), 3.79 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.9, 157.2, 143.9, 132.3, 127.9, 122.2, 114.4, 55.5; MS (EI) m/z (%) 178 (M^+, 52), 55 (100).

4-Nitrophenyl Acrylate[4]

The reaction was carried out using 4-nitrophenol (500 mg, 3.59 mmol) according to typical procedure B. 4-Nitrophenyl acrylate

was obtained in 85% yield (655 mg, 3.05 mmol) after purification by silica-gel column chromatography (Hexane/EtOAc = 10/1).

Analytical TLC, 10:1 Hexane/EtOAc, R_f = 0.21; White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (2H, d, J = 9.3 Hz), 7.34 (2H, d, J = 9.3 Hz), 6.67 (1H, dd, J = 17.3, 1.3 Hz), 6.34 (1H, dd, J = 17.3, 10.3 Hz), 6.11 (1H, dd, J = 10.3, 1.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.4, 155.3, 145.3, 134.0, 127.0, 125.2, 122.4; MS (EI) m/z (%) 193 (M^+, 3), 55 (100).

(*E*)-Benzyl But-2-enoate[5]

The reaction was carried out using benzyl bromide (431 mg, 2.52 mmol) according to typical procedure A. Crotonic acid (259 mg, 3.00 mmol) was used instead of acrylic acid. (*E*)-Benzyl but-2-enoate was obtained in 84% yield (374 mg, 2.12 mmol) after purification by silica-gel column chromatography (Hexane/Et_2O = 20/1).

Analytical TLC, 10:1 Hexane/EtOAc, R_f = 0.50; Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.30 (5H, m), 7.03 (1H, dq, J = 15.5, 7.0 Hz), 5.90 (1H, dq, J = 15.5, 1.8 Hz), 5.17 (2H, s), 1.88 (3H, dd, J = 7.0, 1.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.3, 145.2, 136.1, 128.5, 128.1, 122.4, 65.9, 18.0 (one signal could not be located because of its overlap with another signal); MS (EI) m/z (%) 176 (M^+, 7), 69 (100).

***N*-Methoxy-*N*-methyl-3-phenylpropanamide[6]**

To a 50-mL round bottom flask were placed 3-phenylpropionyl chloride (683 mg, 4.05 mmol), dry CH_2Cl_2 (8 mL), and then *N*,*O*-dimethylhydroxylamine hydrochloride (414 mg, 4.25 mmol) under an Ar atmosphere. The flask was cooled to 0 °C in an ice bath for 5 minutes. Pyridine (664 mg, 8.40 mmol) was added dropwise to the flask over 5 minutes. The reaction flask was warmed to room temperature, a white precipitate formed. The reaction mixture was stirred at room pemperature overnight, concentrated in vacuo, and diluted with Et_2O (20 mL) and H_2O (20 mL). 1M HCl (5 mL, 5 mmol) was added. The layers were separated, and the organic layer was washed with saturated aqueous $NaHCO_3$ (20 mL) and brine (20 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo, to give the pure *N*-methoxy-*N*-methyl-3-phenylpropanamide (761 mg, 97%).

Analytical TLC, 10:1 Hexane/EtOAc, R_f = 0.91; Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (2H, t, J = 7.5 Hz), 7.22 (2H, d, J = 7.5 Hz), 7.19 (1H, t, J = 7.5 Hz), 3.58 (3H, s), 3.16 (3H, s), 2.96 (2H, t, J = 7.8 Hz), 2.74 (2H, t, J = 7.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.4, 141.1, 128.2, 128.1, 125.8, 60.9, 33.5, 31.9, 30.4; MS (EI) m/z (%) 193 (M^+, 17), 91 (100).

5-Phenyl-1-penten-3-one[7]

To a solution of *N*-methoxy-*N*-methyl-3-phenylpropanamide (967 mg, 5.00 mmol) in dry THF (30 mL) at 0 ^{o}C under an Ar atmosphere was slowly added vinyl magnesium bromide (5.5 mL, 5.5 mmol, 1 M solution in THF), and the mixture was gradually warmed to room temperature and stirred for 24 hours. The reaction was quenched with saturated aqueous NH_4Cl (10 mL), and Et_2O (20 mL) and H_2O (20 mL) were added. The layers were separated, and the aqueous layer was extracted with Et_2O (20 mL × 2), and the combined organic layers were washed with brine (20 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by silica-gel column chromatography (Hexane/EtOAc = 10/1) as the eluent to give the 5-phenyl-1-penten-3-one (152 mg, 19%).

Analytical TLC, 10:1 Hexane/EtOAc, R_f = 0.38; Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (2H, m), 7.21–7.18 (3H, m), 6.35 (1H, dd, J = 17.8, 10.5 Hz), 6.21 (1H, dd, J = 17.8, 1.0 Hz), 5.82 (1H, dd, J = 10.5, 1.0 Hz), 2.97–2.89 (4H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.7, 141.0, 136.4, 128.4, 128.3, 128.2, 126.1, 41.1, 29.7; MS (EI) m/z (%) 160 (M^+, 76), 55 (100).

3. Typical procedure for the preparation of enol ether derivatives

In a test tube were placed the substrate (250 μmol), $Pd(OAc)_2$ (11.2 mg, 50.0 μmol), AgOAc (91.8 mg, 550 μmol), $NaNO_2$ (3.5 mg, 50.0 μmol), and alcohol (1 mL). The mixture was stirred at room temperature under an Ar atmosphere. After a specific time, the mixture was diluted with Et_2O (5 mL) and water (5 mL). After filtration through a celite pad, the pad was washed with Et_2O (10 mL) and H_2O (10 mL), and the filtrate were separated into the organic and aqueous layers. The aqueous layer was extracted with Et_2O (10 mL × 2), and the combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by silica-gel column chromatography using hexane–EtOAc or hexane–Et_2O as the eluent to give the corresponding enol ethers.

Benzyl 3-Methoxyacrylate (2a)

Obtained in 70% yield (34.2 mg, 175 μmol) from benzyl acrylate (41.2 mg, 254 μmol) and methanol (1.00 mL, 24.7 mmol) after purification by silica-gel column chromatography (Hexane/Et_2O = 10/1 → 5/1).

Analytical TLC, 10:1 Hexane/EtOAc, R_f = 0.29; Colorless oil; IR (ATR) cm^{-1}: 1705, 1623, 1454, 1324, 1217, 1188, 1119, 1018; ^1H NMR [400 MHz (ECS-400), $CDCl_3$] δ 7.67 (1H, d, J = 12.8 Hz), 7.36–7.31 (5H, m), 5.24 (1H, d, J = 12.8 Hz), 5.16 (2H, s), 3.68 (3H, s); ^{13}C NMR [100 MHz (ECS-400), $CDCl_3$] δ 167.4, 163.5, 136.4, 128.5, 128.1, 128.0, 95.7, 65.6, 57.2; ESI-HRMS m/z: 215.0684 ($[M+Na]^+$); Calcd for $C_{11}H_{12}O_3Na$: 215.0679.

Benzyl 3-Ethoxyacrylate (2b)

Obtained in 71% yield (37.3 mg, 178 μmol) from benzyl acrylate (41.2 mg, 254 μmol) and ethanol (1.00 mL, 17.1 mmol) after purification by silica-gel column chromatography (Hexane/Et_2O = 10/1 → 5/1).

Analytical TLC, 10:1 Hexane/EtOAc, R_f = 0.32; Colorless oil; IR (ATR) cm^{-1}: 2983, 1705, 1621, 1454, 1396, 1324, 1279, 1204, 1105, 1012; ^1H NMR [400 MHz (AL-400), $CDCl_3$] δ 7.64 (1H, d, J = 12.8 Hz), 7.34–7.31 (5H, m), 5.24 (1H, d, J = 12.8 Hz), 5.16 (2H, s), 3.91 (2H, q, J = 7.2 Hz), 1.34 (3H, t, J = 7.2 Hz); ^{13}C NMR [100 MHz (AL-400), $CDCl_3$] δ 167.7, 162.8, 136.4, 128.5, 128.1, 128.0, 96.1, 66.7, 65.6, 14.4; ESI-HRMS m/z: 229.0838 ($[M+Na]^+$); Calcd for $C_{12}H_{14}O_3Na$: 229.0835.

Benzyl 3-*n*-Propoxyacrylate (2c)

Obtained in 72% yield (41.3 mg, 180 μmol) from benzyl acrylate (40.8 mg, 252 μmol) and 1-propanol (1.00 mL, 13.4 mmol) after purification by silica-gel column chromatography (Hexane/Et_2O = 10/1 → 5/1).

Analytical TLC, 10:1 Hexane/EtOAc, R_f = 0.29; Colorless oil; IR (ATR) cm^{-1}: 2967, 2880, 1706, 1621, 1497, 1456, 1392, 1325, 1277, 1236, 1206, 1112, 1019; ^1H NMR (500 MHz, $CDCl_3$) δ 7.65 (1H, d, J = 12.5 Hz), 7.38–7.29 (5H, m), 5.24 (1H, d, J = 12.5 Hz), 5.16 (2H, s), 3.79 (2H, t, J = 7.5 Hz), 1.72 (2H, sext, J = 7.5 Hz), 0.96 (3H, t, J = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.7, 163.0, 136.4, 128.5, 128.1, 128.0, 95.9, 72.6, 65.5, 22.1, 10.2; ESI-HRMS m/z: 221.1190 ($[M+H]^+$); Calcd for $C_{13}H_{17}O_3$: 221.1172.

Benzyl 3-*i*-Propoxyacrylate (2d)

Obtained in 44% yield (24.4 mg, 110 μmol) from benzyl acrylate (40.3 mg, 248 μmol) and 2-propanol (1.00 mL, 13.0 mmol) after purification by silica-gel column chromatography (Hexane/Et_2O = 10/1 → 5/1).

Analytical TLC, 10:1 Hexane/EtOAc, R_f = 0.24; Colorless oil; IR (ATR) cm^{-1}: 2979, 1705, 1639, 1619, 1454, 1377, 1325, 1278, 1234, 1205, 1125, 1097, 1018; ^1H NMR [400 MHz (ECS-400), $CDCl_3$] δ 7.57 (1H, d, J = 12.4 Hz), 7.38–7.29 (5H, m), 5.28 (1H, d, J = 12.4 Hz), 5.15 (2H, s), 4.22 (1H, sep, J = 6.0 Hz), 1.29 (6H, d, J = 6.0 Hz); ^{13}C NMR [100 MHz (ECS-400), $CDCl_3$]

δ 168.0, 162.0, 136.5, 128.5, 128.1, 128.0, 96.9, 75.7, 65.5, 22.0; ESI-HRMS m/z: 221.1167 ($[M+H]^+$); Calcd for $C_{13}H_{17}O_3$: 221.1172.

Benzyl 3-*t*-Buthoxyacrylate (2e)

Obtained in 33% yield (19.4 mg, 83.0 μmol) from benzyl acrylate (41.1 mg, 253 μmol) and t-buthanol (1.00 mL, 10.5 mmol) after purification by silica-gel column chromatography (Hexane/Et_2O = 10/1 → 5/1).

Analytical TLC, 10:1 Hexane/EtOAc, R_f = 0.33; Yellow oil; IR (ATR) cm^{-1}: 2978, 1704, 1632, 1456, 1372, 1329, 1269, 1212, 1151, 1104, 1017; ^1H NMR (500 MHz, $CDCl_3$) δ 7.23 (1H, d, *J* = 12.0 Hz), 7.37–7.30 (5H, m), 5.36 (1H, d, *J* = 12.0 Hz), 5.15 (2H, s), 1.35 (9H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.2, 158.5, 136.6, 128.4, 128.0, 127.9, 98.2, 79.9, 65.4, 28.1; ESI-HRMS m/z: 235.1351 ($[M+H]^+$); Calcd for $C_{14}H_{19}O_3$: 235.1329.

4-Nitrobenzyl 3-Methoxyacrylate (2f)

Obtained in 70% yield (41.4 mg, 174 μmol) from 4-nitrobenzyl acrylate (51.6 mg, 249 μmol) and methanol (1.00 mL, 24.7 mmol) after purification by silica-gel column chromatography (Hexane/EtOAc = 3/1).

Analytical TLC, 2:1 Hexane/EtOAc, R_f = 0.53; White solid; M.p. 64–66 °C; IR (ATR) cm^{-1}: 3386, 3070, 2942, 2842, 2445, 2139, 1925, 1698, 1625, 1601, 1514, 1492, 1453, 1376, 1343, 1282, 1217, 1168, 1111, 1063, 1041, 1009; ^1H NMR (500 MHz, $CDCl_3$) δ 8.22 (2H, d, *J* = 8.5 Hz), 7.70 (1H, d, *J* = 12.5 Hz), 7.52 (2H, d, *J* = 8.5 Hz), 5.27 (1H, d, *J* = 12.5 Hz), 5.26 (2H, s), 3.73 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1, 164.1, 147.5, 143.8, 128.1, 123.7, 95.1, 64.1, 57.4; ESI-HRMS m/z: 260.0530 ($[M+Na]^+$); Calcd for $C_{11}H_{11}NO_5Na$: 260.0529.

4-Bromobenzyl 3-Methoxyacrylate (2g)

Obtained in 67% yield (45.6 mg, 170 μmol) from 4-bromobenzyl acrylate (60.9 mg, 253 μmol) and methanol (1.00 mL, 24.7 mmol) after purification by silica-gel column chromatography (Hexane/Et_2O = 15/1 → 10/1).

Analytical TLC, 10:1 Hexane/EtOAc, R_f = 0.24; Yellow solid; M.p. 34–35 °C; IR (ATR) cm^{-1}: 2938, 1706, 1622, 1488, 1439, 1373, 1324, 1280, 1245, 1217, 1188, 1119, 1069, 1025, 1009; ^1H NMR (500 MHz, $CDCl_3$) δ 7.67 (1H, d, *J* = 12.5 Hz), 7.48 (2H, d, *J* = 8.0 Hz), 7.24 (2H, d, *J* = 8.0 Hz), 5.23 (1H, d, *J* = 12.5 Hz), 5.10 (2H, s), 3.69 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.3, 163.6, 135.3, 131.6, 129.7, 122.0, 95.4, 64.8, 57.3; ESI-HRMS m/z: 292.9765 ($[M+Na]^+$); Calcd for $C_{11}H_{11}O_3BrNa$: 292.9784.

4-Methoxybenzyl 3-Methoxyacrylate (2h)

Obtained in 79% yield (43.7 mg, 198 μmol) from 4-methoxybenzyl acrylate (48.0 mg, 250 μmol) and methanol (1.00 mL, 24.7 mmol) after purification by silica-gel column chromatography (Hexane/Et_2O = 3/1).

Analytical TLC, 3:1 Hexane/EtOAc, R_f = 0.26; Yellow oil; IR (ATR) cm^{-1}: 2935, 2839, 1704, 1623, 1513, 1457, 1376, 1324, 1303, 1282, 1244, 1216, 1175, 1118, 1019; ^1H NMR (500 MHz, $CDCl_3$) δ 7.65 (1H, d, *J* = 12.5 Hz), 7.31 (2H, d, *J* = 8.5 Hz), 6.89 (2H, d, *J* = 8.5 Hz), 5.22 (1H, d, *J* = 12.5 Hz), 5.09 (2H, s), 3.80 (3H, s), 3.67 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.5, 163.3, 159.5, 129.9, 128.4, 113.9, 95.8, 65.4, 57.2, 55.2; ESI-HRMS m/z: 245.0776 ($[M+Na]^+$); Calcd for $C_{12}H_{14}O_4Na$: 245.0784.

4-Methylbenzyl 3-Methoxyacrylate (2i)

Obtained in 74% yield (38.2 mg, 184 μmol) from 4-methylbenzyl acrylate (43.9 mg, 249 μmol) and methanol (1.00 mL, 24.7 mmol) after purification by silica-gel column chromatography (Hexane/Et_2O = 10/1 → 5/1).

Analytical TLC, 10:1 Hexane/EtOAc, R_f = 0.23; Colorless oil; IR (ATR) cm^{-1}: 2938, 1706, 1624, 1517, 1452, 1376, 1324, 1281, 1245, 1217, 1188, 1118, 1017; ^1H NMR (500 MHz, $CDCl_3$) δ 7.66 (1H, d, *J* = 12.5 Hz), 7.26 (2H, d, *J* = 8.0 Hz), 7.17 (2H, d, *J* = 8.0 Hz), 5.23 (1H, d, *J* = 12.5 Hz), 5.12 (2H, s), 3.67 (3H, s), 2.35 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.5, 163.4, 137.9, 133.3, 129.2, 128.3, 95.7, 65.6, 57.2, 21.2; ESI-HRMS m/z: 229.0841 ($[M+Na]^+$); Calcd for $C_{12}H_{14}O_3Na$: 229.0835.

2-Methylbenzyl 3-Methoxyacrylate (2j)

Obtained in 71% yield (36.6 mg, 178 μmol) from 2-methylbenzyl acrylate (44.2 mg, 251 μmol) and methanol (1.00 mL, 24.7 mmol) after purification by silica-gel column chromatography (Hexane/Et_2O = 10/1 → 5/1).

Analytical TLC, 10:1 Hexane/EtOAc, R_f = 0.21; Colorless oil; IR (ATR) cm^{-1}: 2938, 1705, 1624, 1494, 1457, 1376, 1323, 1280, 1245, 1217, 1189, 1119, 1014; ^1H NMR (500 MHz, $CDCl_3$) δ 7.67 (1H, d, *J* = 12.5 Hz), 7.33 (1H, d, *J* = 7.0 Hz), 7.24 (1H, m), 7.20–7.18 (2H, m), 5.23 (1H, d, *J* = 12.5 Hz), 5.17 (2H, s), 3.67 (3H, s), 2.35 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.5, 163.4, 136.9, 134.2, 130.3, 129.1, 128.3, 125.9, 95.6, 64.1, 57.2, 18.9; ESI-HRMS m/z: 229.0846 ($[M+Na]^+$); Calcd for $C_{12}H_{14}O_3Na$: 229.0835.

2-Naphthylmethyl 3-Methoxyacrylate (2k)

Obtained in 74% yield (44.4 mg, 184 μmol) from 2-naphthylmethyl acrylate (52.8 mg, 249 μmol) and methanol (1.00 mL, 24.7 mmol) after purification by silica-gel column chromatography (Hexane/Et_2O = 10/1 → 5/1).

Analytical TLC, 10:1 Hexane/EtOAc, R_f = 0.24; Yellow oil; IR (ATR) cm^{-1}: 3056, 2938, 1704, 1623, 1510, 1439, 1320, 1281, 1245, 1217, 1187, 1118, 1025; ^1H NMR (500 MHz, $CDCl_3$) δ 7.84–7.82 (4H, m), 7.69 (1H, d, *J* = 12.5 Hz), 7.48–7.46 (3H, m), 5.32 (2H, s), 5.27 (1H, d, *J* = 12.5 Hz), 3.67 (3H, s); ^{13}C NMR (500 MHz, $CDCl_3$) δ 167.5, 163.5, 133.8, 133.2, 133.0, 128.3, 127.9, 127.6, 127.1, 126.2, 126.1, 125.9, 95.7, 65.8, 57.2; ESI-HRMS m/z: 265.0847 ($[M+Na]^+$); Calcd for $C_{15}H_{14}O_3Na$: 265.0835.

1-Decyl 3-Methoxyacrylate (2l)

Obtained in 77% yield (46.5 mg, 193 μmol) from 1-decyl acrylate (53.1 mg, 250 μmol) and methanol (1.00 mL, 24.7 mmol) after purification by silica-gel column chromatography (Hexane/Et_2O = 15/1 → 10/1).

Analytical TLC, 10:1 Hexane/EtOAc, R_f = 0.36; Yellow oil; IR (ATR) cm^{-1}: 2924, 2854, 1710, 1627, 1458, 1325, 1219, 1190, 1127; ^1H NMR (500 MHz, $CDCl_3$) δ 7.63 (1H, d, *J* = 12.5 Hz), 5.19 (1H, d, *J* = 12.5 Hz), 4.10 (2H, t, *J* = 7.0 Hz), 3.69 (3H, s), 1.64 (2H, quin, *J* = 7.0 Hz), 1.37–1.26 (14H, m), 0.88 (3H, t, *J* = 6.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.8, 163.0, 95.9, 64.0, 57.1, 31.9, 29.5, 29.3, 29.3, 28.7, 25.9, 22.6, 14.1 (one signal could not be located because of its overlap with another signal); ESI-HRMS m/z: 243.1966 ($[M+H]^+$); Calcd for $C_{14}H_{27}O_3$: 243.1955.

Phenyl 3-Methoxyacrylate (2m)

Obtained in 73% yield (32.5 mg, 183 μmol) from phenyl acrylate (37.0 mg, 250 μmol) and methanol (1.00 mL, 24.7 mmol) after purification by sSilica-gel column chromatography (Hexane/Et_2O = 20/1 → 10/1).

Analytical TLC, 10:1 Hexane/EtOAc, R_f = 0.38; White solid; M.p. 64–65 °C; IR (ATR) cm^{-1}: 2923, 2854, 1721, 1622, 1585, 1478, 1453, 1434, 1327, 1245, 1197, 1184, 1162, 1100, 1067, 1021; ^1H NMR (500 MHz, $CDCl_3$) δ 7.81 (1H, d, *J* = 12.5 Hz),

7.38 (2H, t, J = 7.5 Hz), 7.22 (1H, t, J = 7.5 Hz), 7.11 (2H, d, J = 7.5 Hz), 5.39 (1H, d, J = 12.5 Hz), 3.77 (3H, s); ^{13}C NMR (500 MHz, $CDCl_3$) δ 166.1, 164.6, 150.7, 129.3, 125.5, 121.8, 95.3, 57.5; ESI-HRMS m/z: 201.0532 ($[M+Na]^+$); Calcd for $C_{10}H_{10}O_3Na$: 201.0522.

4-Methoxyphenyl 3-Methoxyacrylate (2n)

Obtained in 74% yield (38.3 mg, 185 μmol) from 4-methoxyphenyl acrylate (44.5 mg, 250 μmol) and methanol (1.00 mL, 24.7 mmol) after purification by silica-gel column chromatography (Hexane/Et_2O = 15/1 → 5/1).

Analytical TLC, 10:1 Hexane/EtOAc, R_f = 0.18; Yellow oil; IR (ATR) cm^{-1}: 2938, 2838, 1721, 1623, 1503, 1440, 1329, 1282, 1246, 1221, 1190, 1099, 1032; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (1H, d, J = 12.8 Hz), 7.02 (2H, d, J = 9.0 Hz), 6.89 (2H, d, J = 9.0 Hz), 5.37 (1H, d, J = 12.8 Hz), 3.79 (3H, s), 3.76 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.5, 164.5, 157.0, 144.1, 122.5, 114.3, 95.3, 57.5, 55.5; ESI-HRMS m/z: 231.0627 ($[M+Na]^+$); Calcd for $C_{11}H_{12}O_4Na$: 231.0628.

4-Nitrophenyl 3-Methoxyacrylate (2o)

Obtained in 56% yield (34.4 mg, 140 μmol) from 4-nitrophenyl acrylate (48.3 mg, 250 μmol) and methanol (1.00 mL, 24.7 mmol) after purification by silica-gel column chromatography (Hexane/Et_2O = 5/1).

Analytical TLC, 3:1 Hexane/EtOAc, R_f = 0.47; White solid; M.p. 110–111 °C; IR (ATR) cm^{-1}: 2921, 2851, 1724, 1630, 1588, 1490, 1444, 1354, 1321, 1252, 1207, 1190, 1168, 1105; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (2H, d, J = 9.3 Hz), 7.85 (1H, d, J = 12.5 Hz), 7.31 (2H, d, J = 9.3 Hz), 5.39 (1H, d, J = 12.5 Hz), 3.81 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.7, 165.0, 155.6, 145.0, 125.1, 122.5, 94.6, 57.9; ESI-HRMS m/z: 246.0378 ($[M+Na]^+$); Calcd for $C_{10}H_9NO_5Na$: 246.0373.

1-Methoxy-5-phenyl-1-pentene-3-on (2p)

Obtained in 29% yield (13.8 mg, 73 μmol) from 5-phenyl-1-pentene-3-on (40.1 mg, 250μmol) and (1.00 mL, 24.7 mmol) after purification by silica-gel column chromatography (Hexane/Et_2O = 3/1).

Analytical TLC, 10:1 Hexane/EtOAc, R_f = 0.15; Colorless oil; IR (ATR) cm^{-1}: 3026, 2934, 2843, 1684, 1654, 1619, 1590, 1495, 1452, 1410, 1341, 1310, 1238, 1186, 1139, 1088, 1067, 1012; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (1H, d, J = 13.0 Hz), 7.30–7.27 (2H, m), 7.21–7.18 (3H, m), 5.58 (1H, d, J = 13.0 Hz), 3.69 (3H, s) , 2.95 (2H, t, J = 7.8 Hz) , 2.78 (2H, t, J = 7.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.5, 162.7, 141.3, 128.4, 128.3, 126.0, 105.5, 57.4, 42.7, 30.3; ESI-HRMS m/z: 213.0906 ($[M+Na]^+$); Calcd for $C_{12}H_{14}O_2Na$: 213.0886.

(*E*)-Benzyl 3-Methoxybut-2-enoate (2q)[8]

Obtained in 38% yield (19.6 mg, 95.4 μmol) from (*E*)-benzyl but-2-enoate (44.2 mg, 251 μmol) and methanol (1.00 mL, 24.7 mmol) after purification by silica-gel column chromatography (Hexane/EtOAc = 50/1 → 25/1).

Analytical TLC, 10:1 Hexane/EtOAc, R_f = 0.46; Yellow oil; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.37–7.29 (5H, m), 5.10 (2H, s), 5.09 (1H, s), 3.63 (3H, s), 2.28 (3H, s); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 173.4, 167.2, 136.9, 127.8, 127.7, 90.2, 64.9, 55.4, 18.5; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.32 (5H, m), 5.13 (2H, s), 5.09 (1H, s), 3.63 (3H, s), 2.31 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.6, 167.7, 136.6, 128.5, 128.2, 128.0, 90.5, 65.3, 55.5, 19.0; ESI-HRMS m/z: 229.0839 ($[M+Na]^+$); Calcd for $C_{12}H_{14}O_3Na$: 229.0835.

Benzyl 3,3-Dimethoxypropionate (3)

Silica-gel column chromatography (Hexane/Et_2O = 10/1 → 5/1). Analytical TLC, 10:1 Hexane/EtOAc, R_f = 0.21; Colorless oil; IR (ATR) cm^{-1}: 2938, 2833, 1735, 1498, 1455, 1393, 1311, 1260, 1211, 1191, 1166, 1114, 1076, 1053, 1020; ^1H NMR (500 MHz, $CDCl_3$) δ 7.36–7.32 (5H, m), 5.15 (2H, s), 4.86 (1H, t, *J* = 6.5 Hz), 3.35 (6H, s), 2.71 (2H, d, *J* = 6.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.6, 135.7, 128.5, 128.2, 128.1, 101.1, 66.3, 53.4, 38.8; ESI-HRMS m/z: 247.0949 ($[M+Na]^+$); Calcd for $C_{12}H_{16}O_4Na$: 247.0941.

Benzyl Methyl Malonate (4)

Silica-gel column chromatography (Hexane/Et_2O = 10/1 → 5/1). Analytical TLC, 10:1 Hexane/EtOAc, R_f = 0.14; Colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.38–7.31 (5H, m), 5.18 (2H, s), 3.72 (3H, s), 3.43 (2H,s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.7, 166.2, 135.1, 128.5, 128.3, 128.2, 67.1, 52.4, 41.2; MS (EI) m/z (%) 208 (M^+, 7), 91 (100).

4. Typical procedure for the introduction of amine substituent to the acrylic acid derivatives

In a test tube were placed benzyl acrylate (122 mg, 750 μmol), *N*,*N*-diphenylamine (42.3 mg, 250 μmol), $Pd(OAc)_2$ (11.2 mg, 50.0 μmol), AgOAc (91.8 mg, 550 μmol), $NaNO_2$ (3.5 mg, 50.0 μmol), and 1,2-dichloroethane (1 mL). The mixture was stirred at room temperature under an Ar atmosphere for 24 hours. The mixture was diluted with Et_2O (5 mL) and water (5 mL). After filtration through a celite pad, the pad was washed with Et_2O (10 mL) and H_2O (10 mL), and the filtrate were separated into the organic and aqueous layers. The aqueous layer was extracted with Et_2O (10 mL × 2), and the combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by silica-gel column chromatography using hexane–EtOAc (15 : 1) as the eluent to give benzyl 3-diphenylaminoacrylate in 84% yield (69.0 mg, 209 μmol).

Benzyl 3-Diphenylaminoacrylate

Analytical TLC, 10:1 Hexane/EtOAc, R_f = 0.26; Yellow solid; M.p. 105–107 °C; IR (ATR) cm^{-1}: 3029, 2957, 1678, 1610, 1579, 1489, 1455, 1388, 1344, 1326, 1281, 1241, 1184, 1151, 1123, 1019; ^1H NMR (500 MHz, $CDCl_3$) δ 8.19 (1H, d, *J* = 13.0 Hz), 7.36–7.26 (9H, m), 7.20 (2H, t, *J* = 7.0 Hz), 7.09 (4H, d, *J* = 7.0 Hz), 5.14 (2H, s), 4.90 (1H, d, *J* = 13.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.8, 147.5, 143.6, 136.7, 129.7, 128.4, 128.1, 127.8, 125.8, 124.1, 93.8, 65.3; ESI-HRMS m/z: 352.1305 ($[M+Na]^+$); Calcd for $C_{22}H_{19}NO_2Na$: 352.1308.

5. Typical procedure for the introduction of phenyl substituent to the acrylic acid derivatives

In a test tube were placed benzyl acrylate (40.5 mg, 250 μmol), phenylboronic acid (30.5 mg, 250 μmol), $Pd(OAc)_2$ (11.2 mg, 50.0 μmol), AgOAc (91.8 mg, 550 μmol), $NaNO_2$ (3.5 mg, 50.0 μmol), and 1,2-dichloroethane–H_2O (1 mL, 100 : 1). The mixture was stirred at room temperature under an Ar atmosphere for 24 hours. The mixture was diluted with Et_2O (5 mL) and water (5 mL). After the filtration through a celite pad, the pad was washed with Et_2O (10 mL) and H_2O (10 mL), and the filtrate were separated into organic and aqueous layers. The aqueous layer was extracted with Et_2O (10 mL × 2), and the combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by silica-gel column chromatography using hexane–EtOAc (15 : 1) as the eluent to give benzyl (*E*)-cinnamate in 89% yield (52.8 mg, 222 μmol).

(*E*)-Benzyl Cinnamate[9]

Analytical TLC, 10:1 Hexane/EtOAc, R_f = 0.38; Yellow solid; ^1H NMR (500 MHz, $CDCl_3$) δ 7.73 (1H, d, *J* = 16.0 Hz), 7.52–7.50 (2H, m), 7.42–7.33 (8H, m), 6.49 (1H, d, *J* = 16.0 Hz), 5.35 (2H, s); ^{13}C NMR (125 MHz, $CDCl_3$)δ 166.7, 145.1,

136.0, 134.2, 130.3, 128.8, 128.5, 128.2, 128.2, 128.0, 117.8, 66.3; ESI-HRMS m/z: 261.0915 ($[M+Na]^+$); Calcd for $C_{16}H_{14}O_2Na$: 261.0886.

6. References

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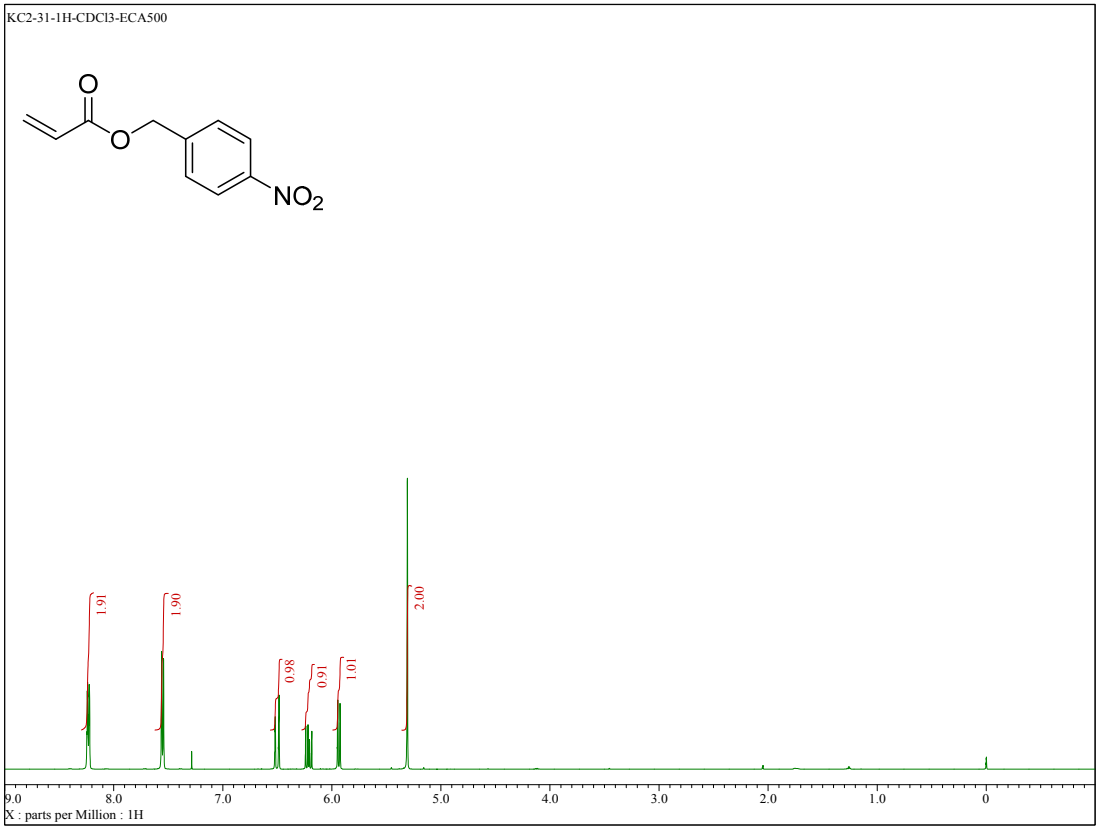
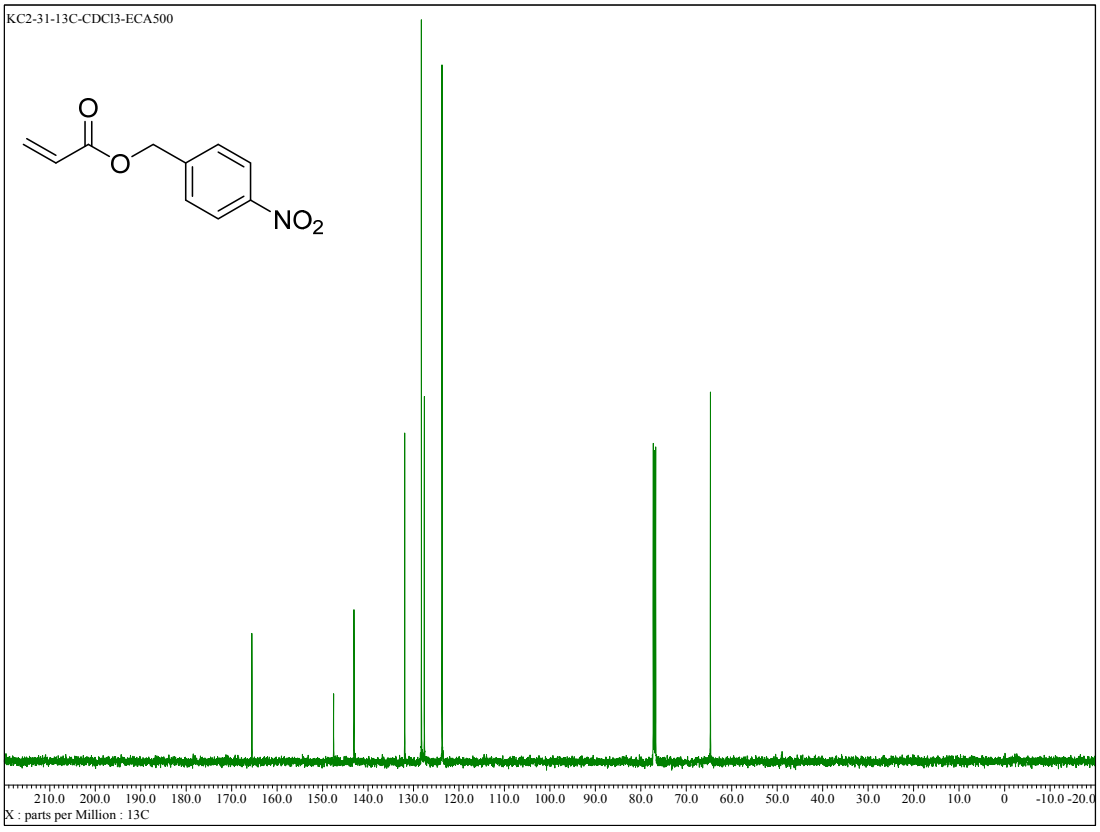
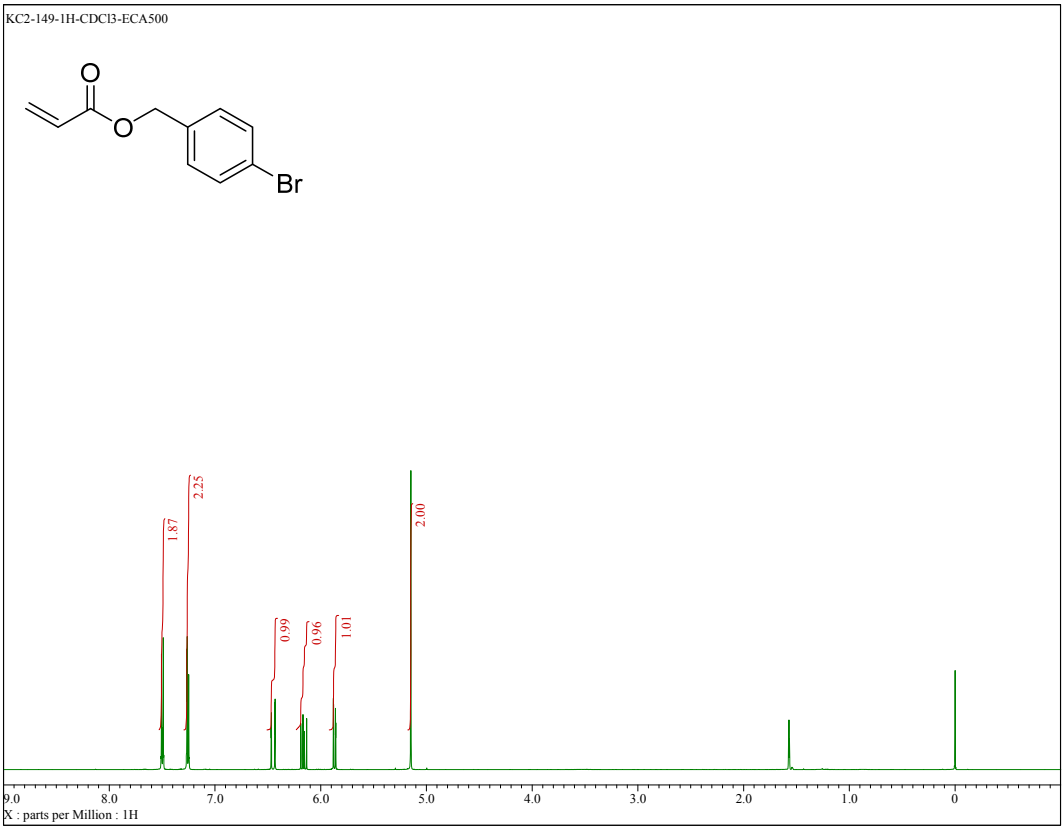
7. NMR spectra of starting materials

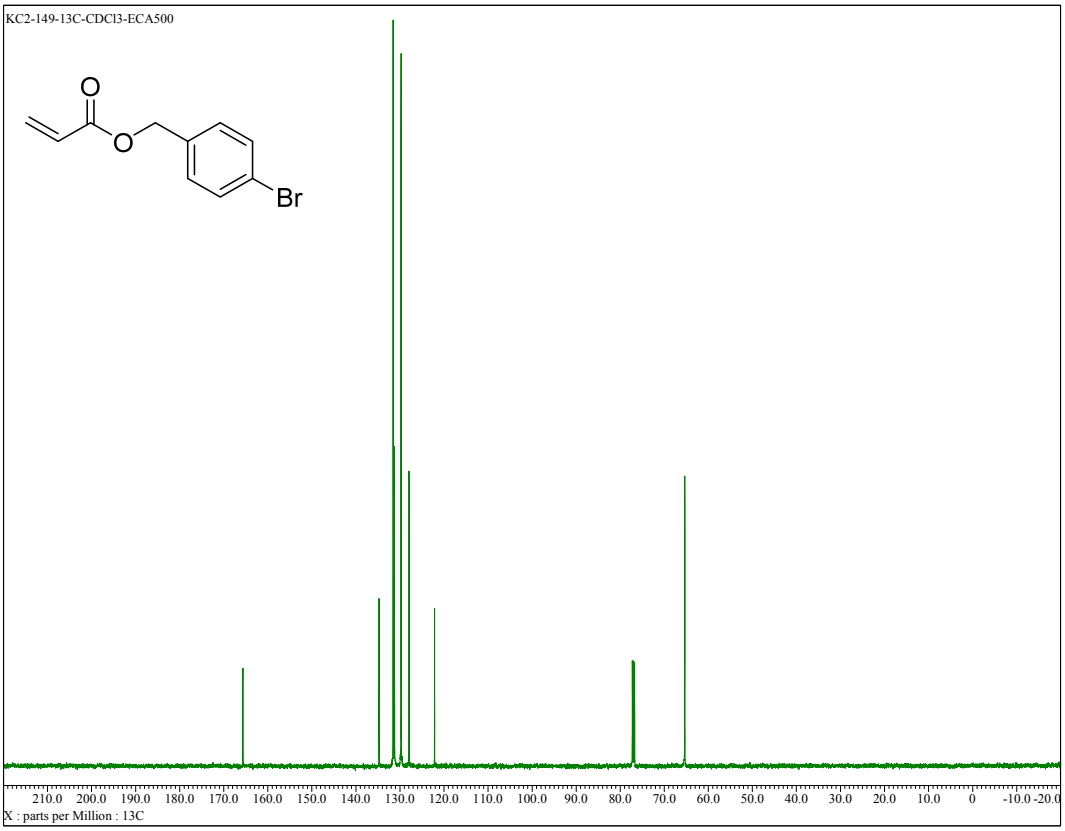
4-Nitrobenzyl acrylate



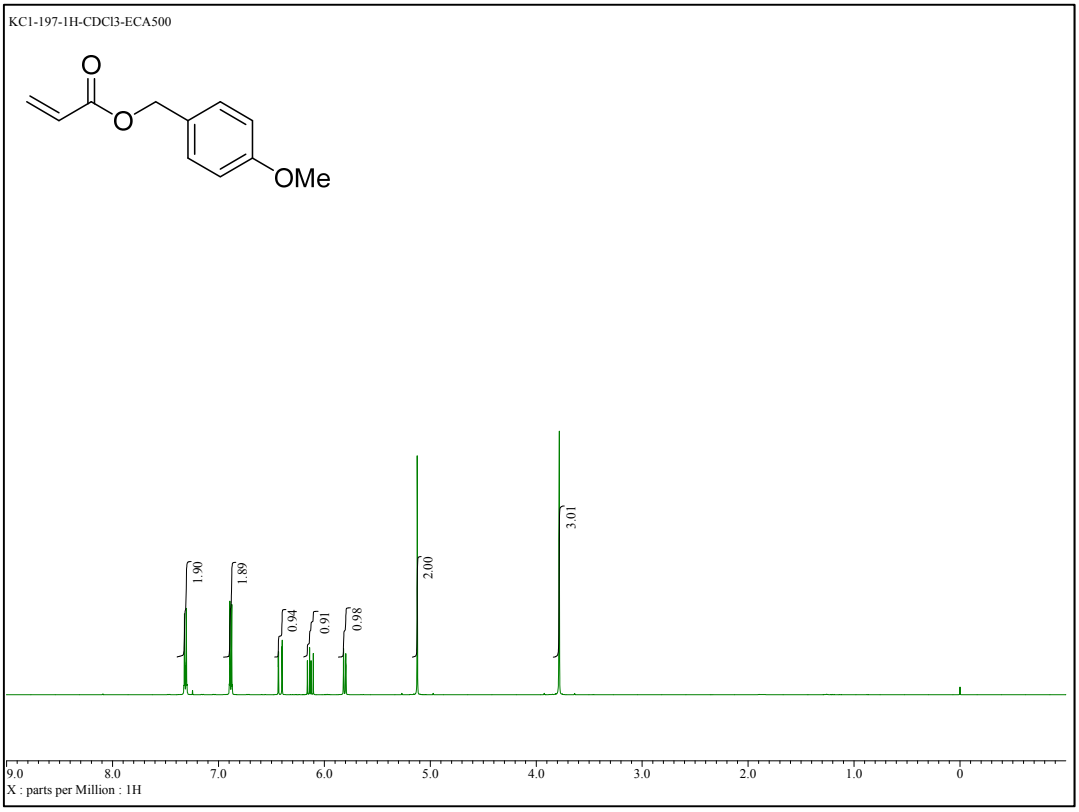


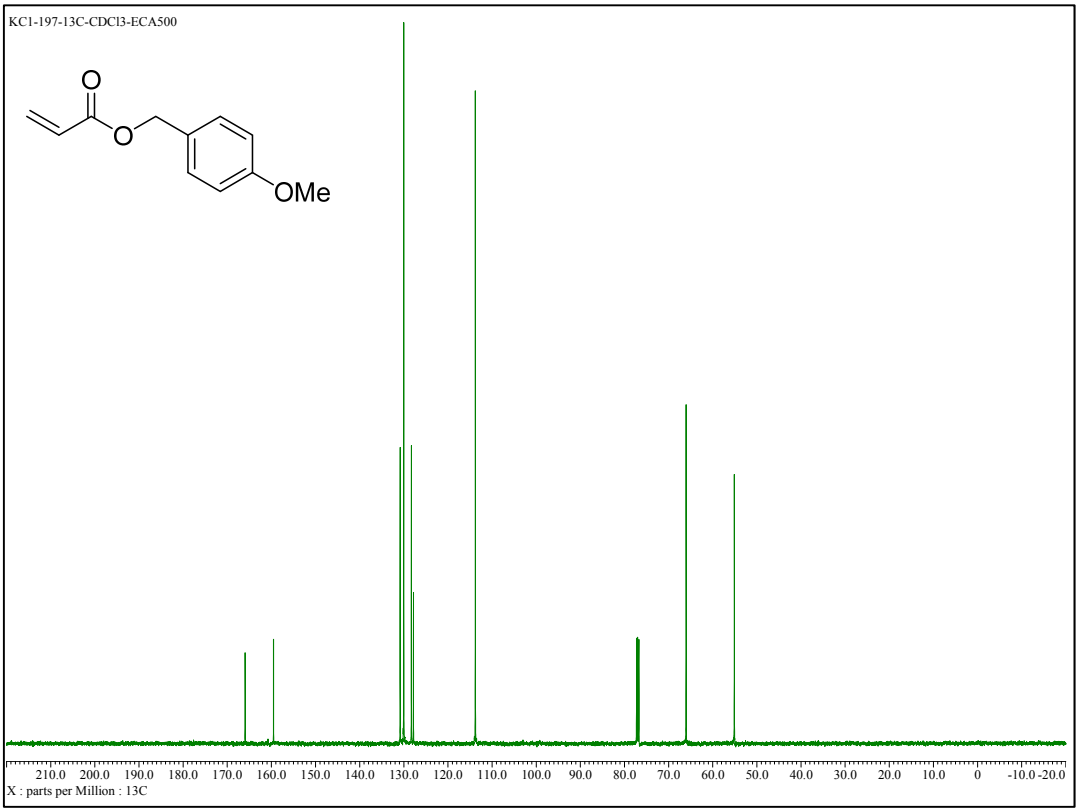
4-Bromobenzyl acrylate



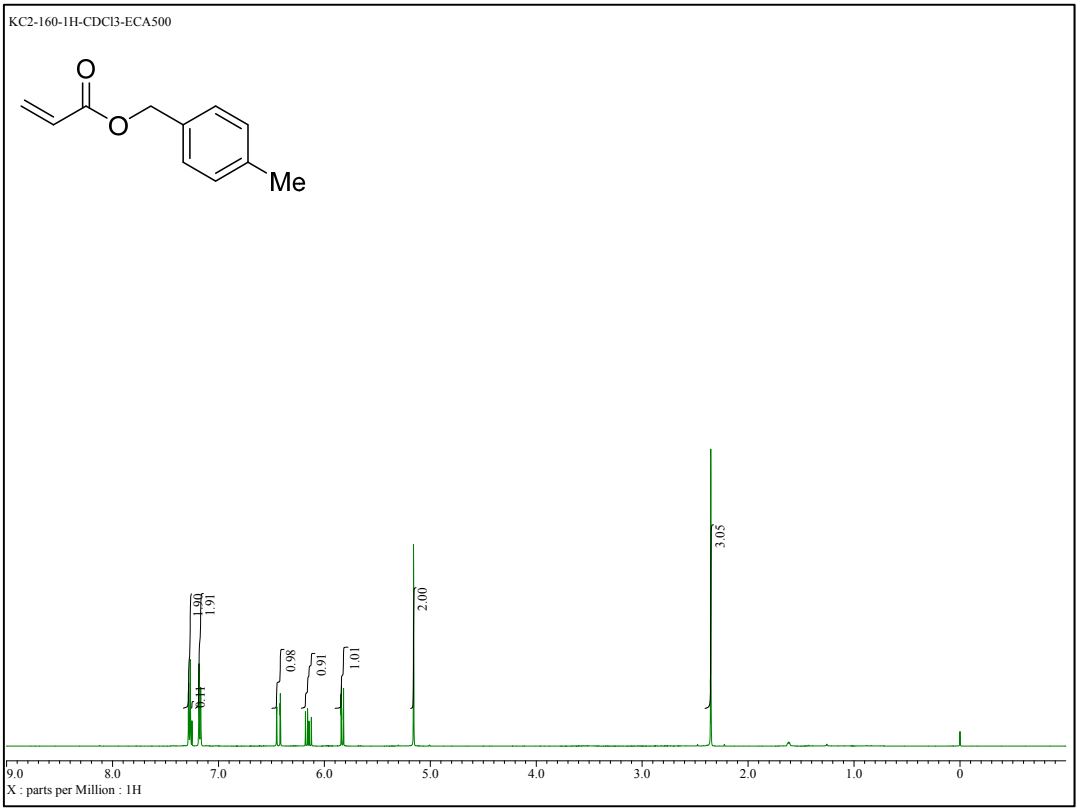


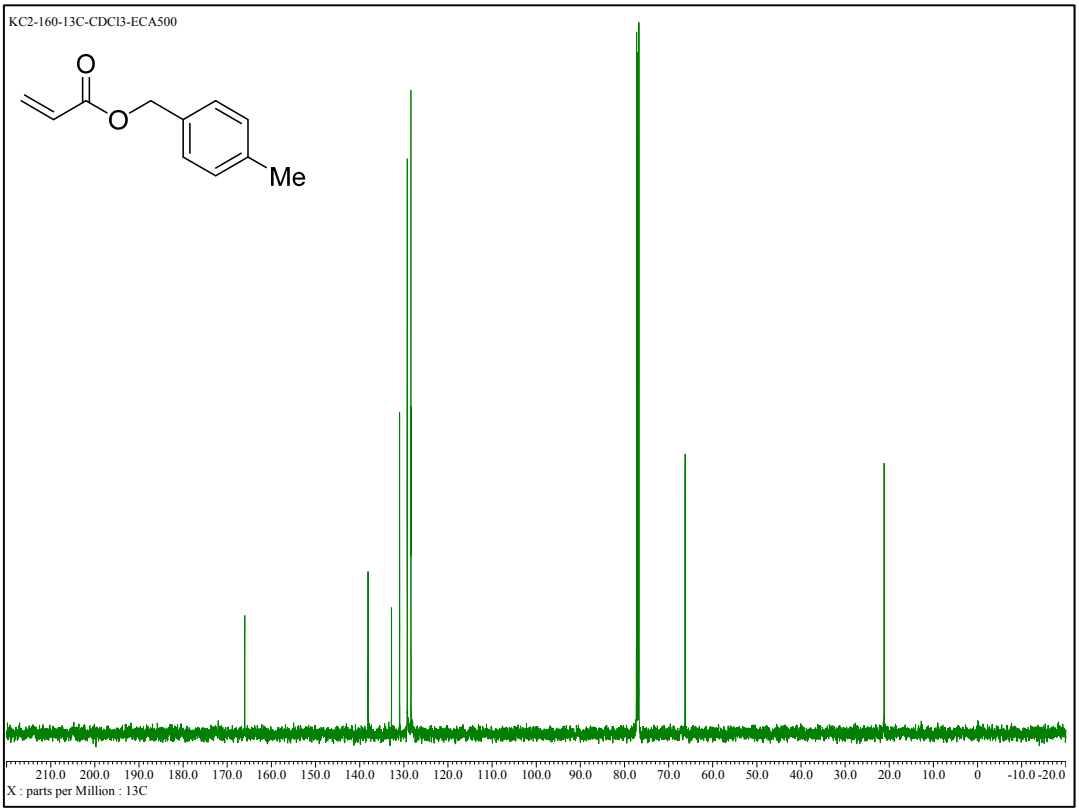
4-Methoxybenzyl acrylate



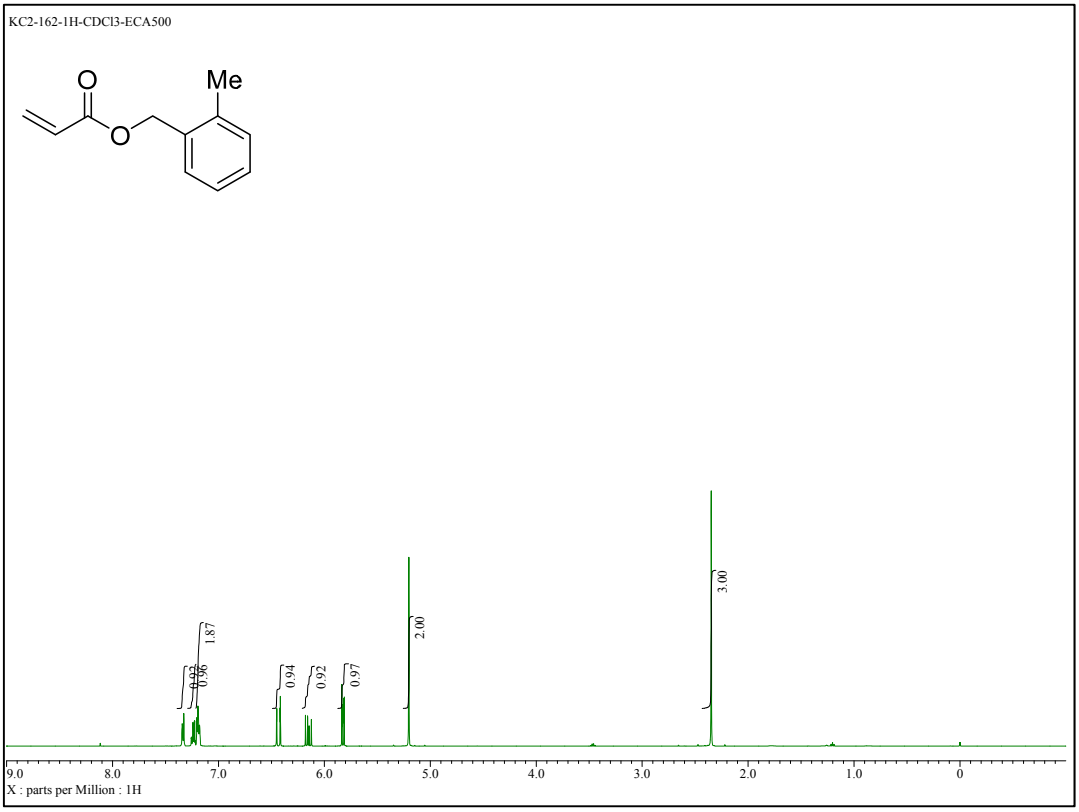


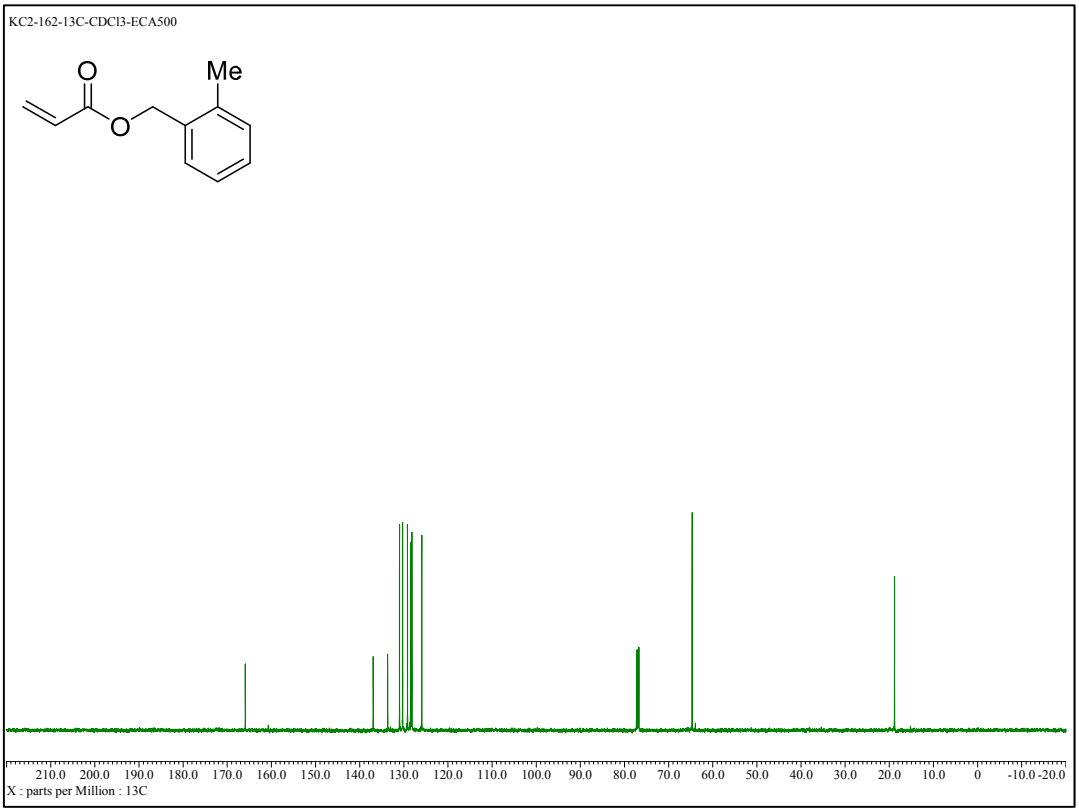
4-Methylbenzyl acrylate



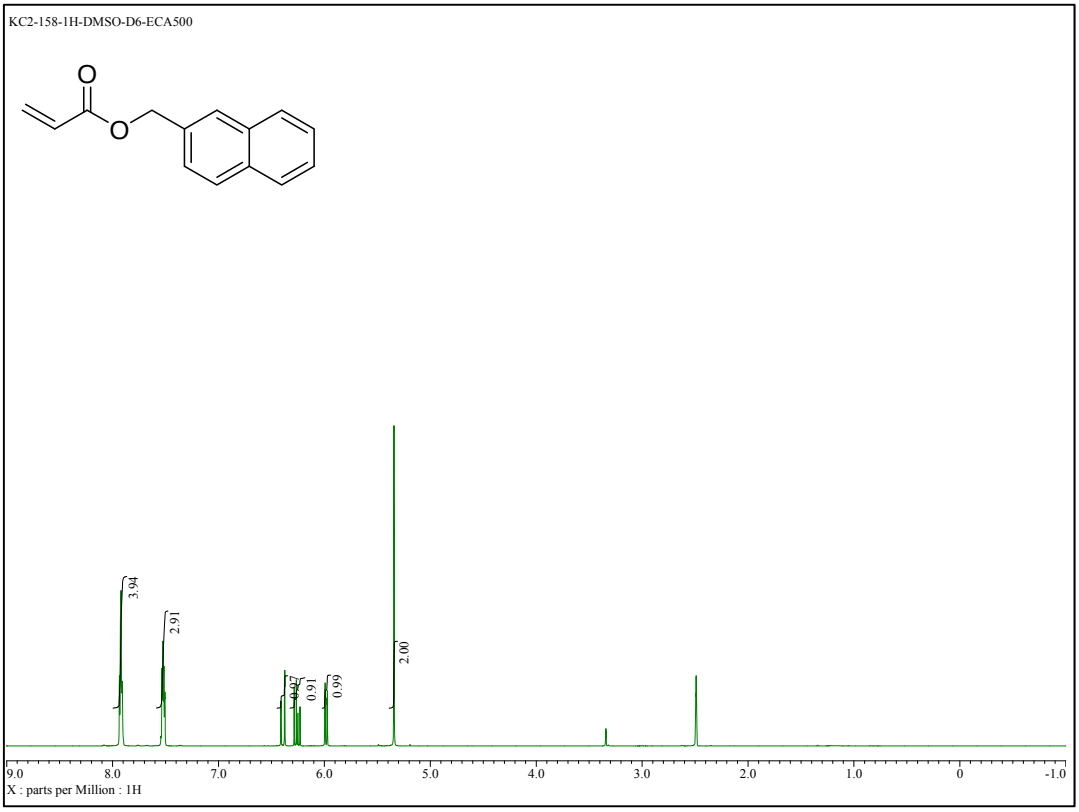


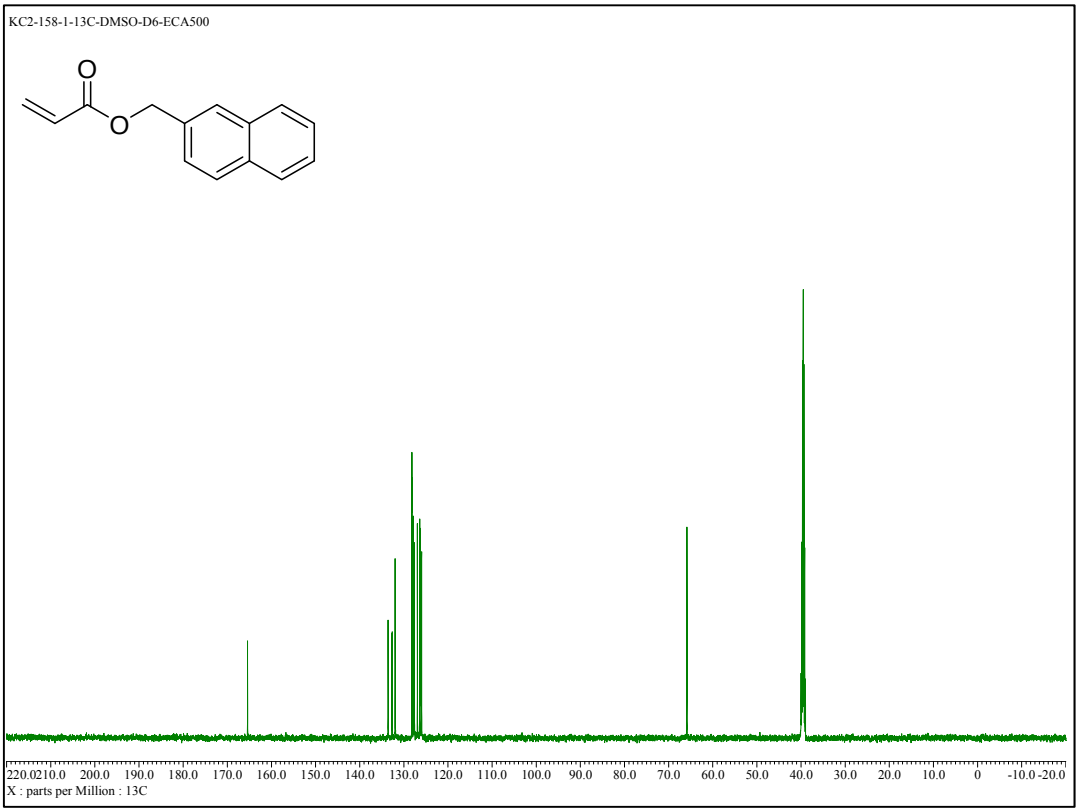
2-Methylbenzyl acrylate



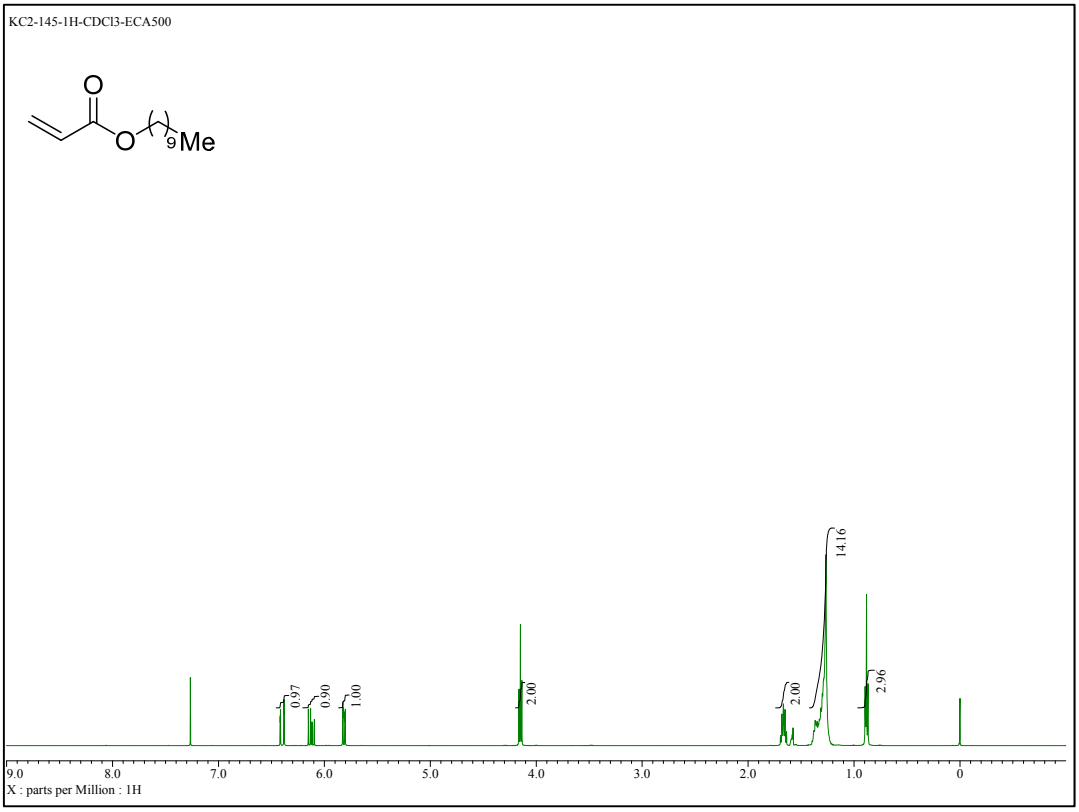


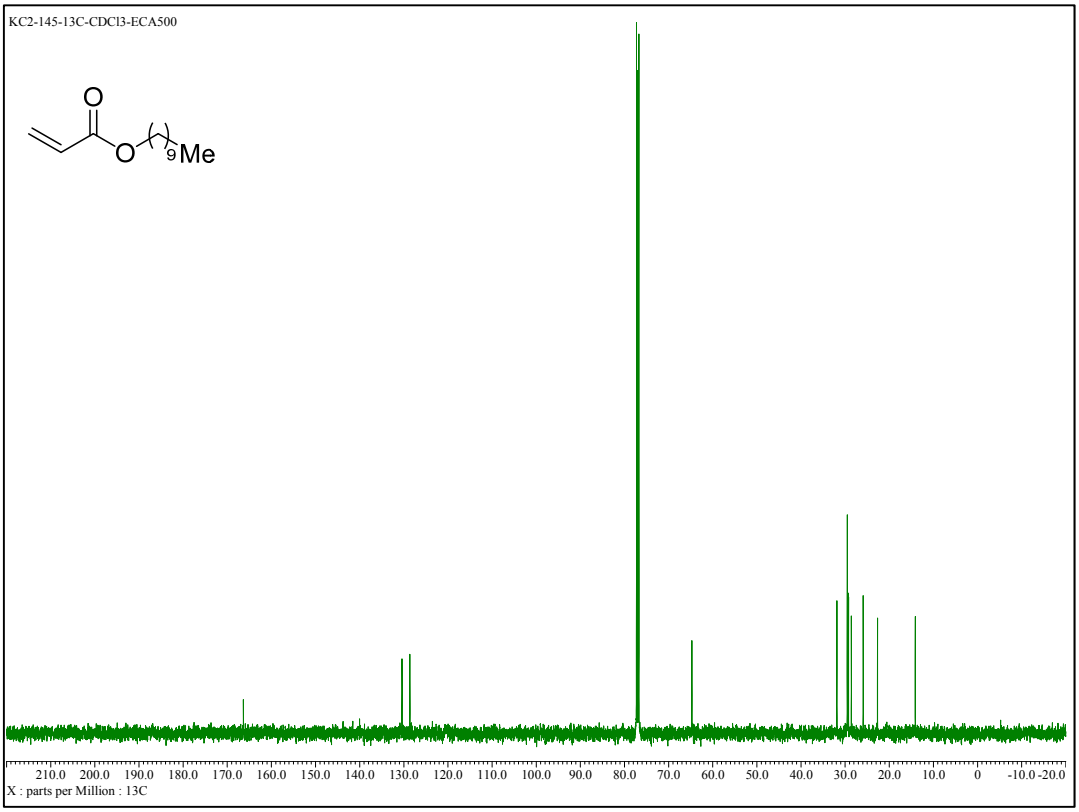
2-Naphthylmethyl acrylate



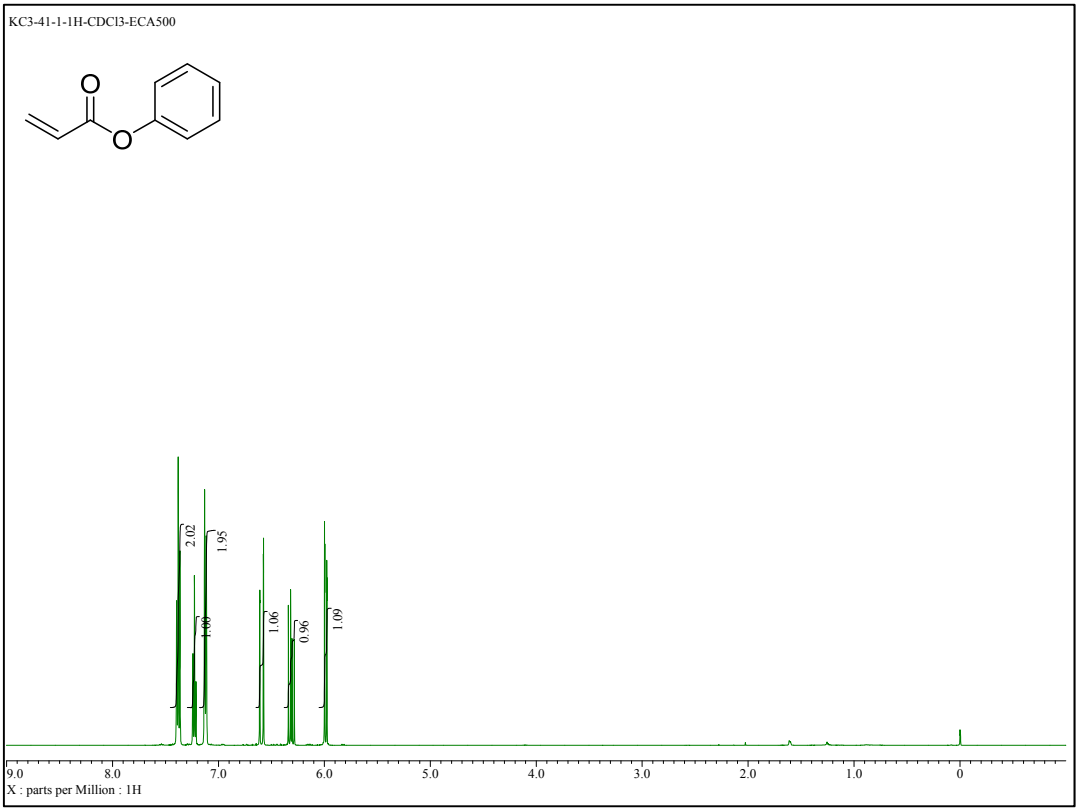


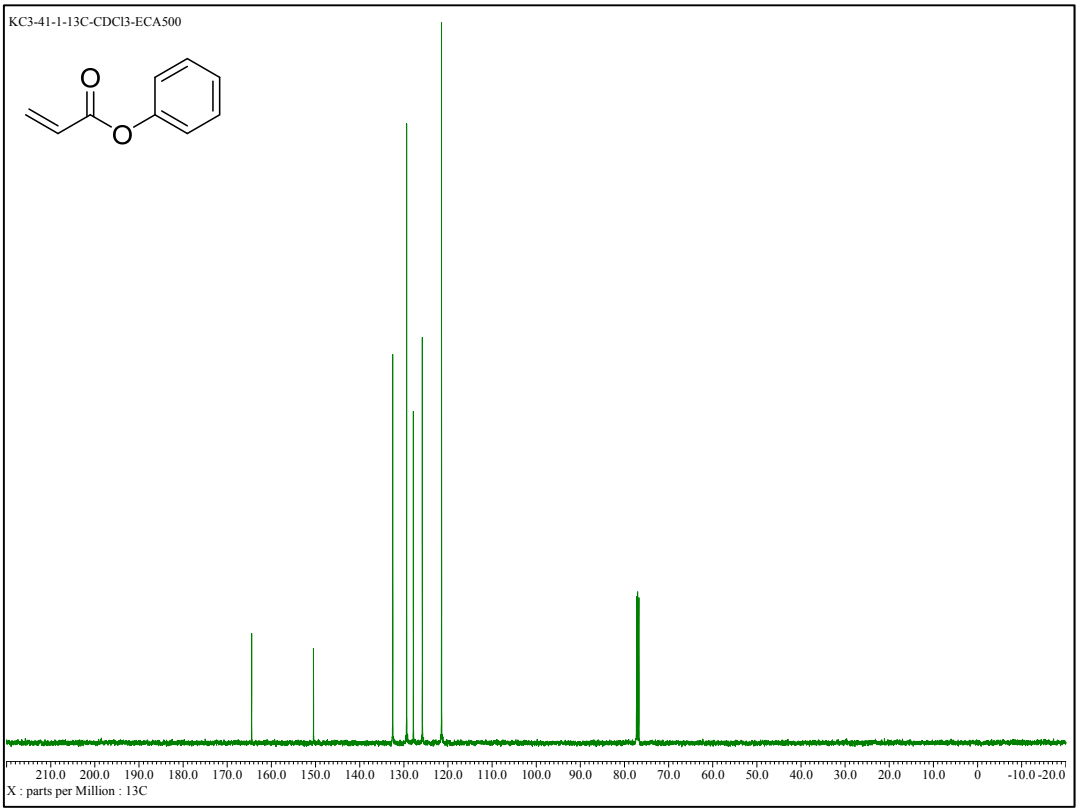
1-Decyl acrylate



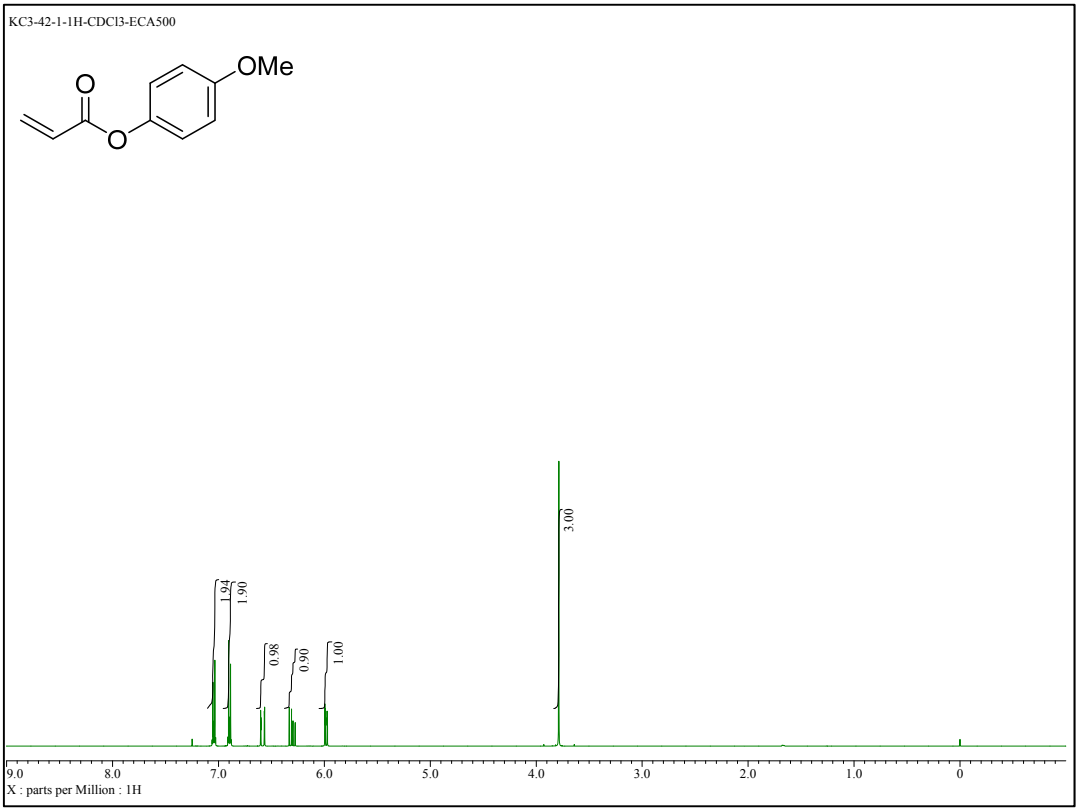


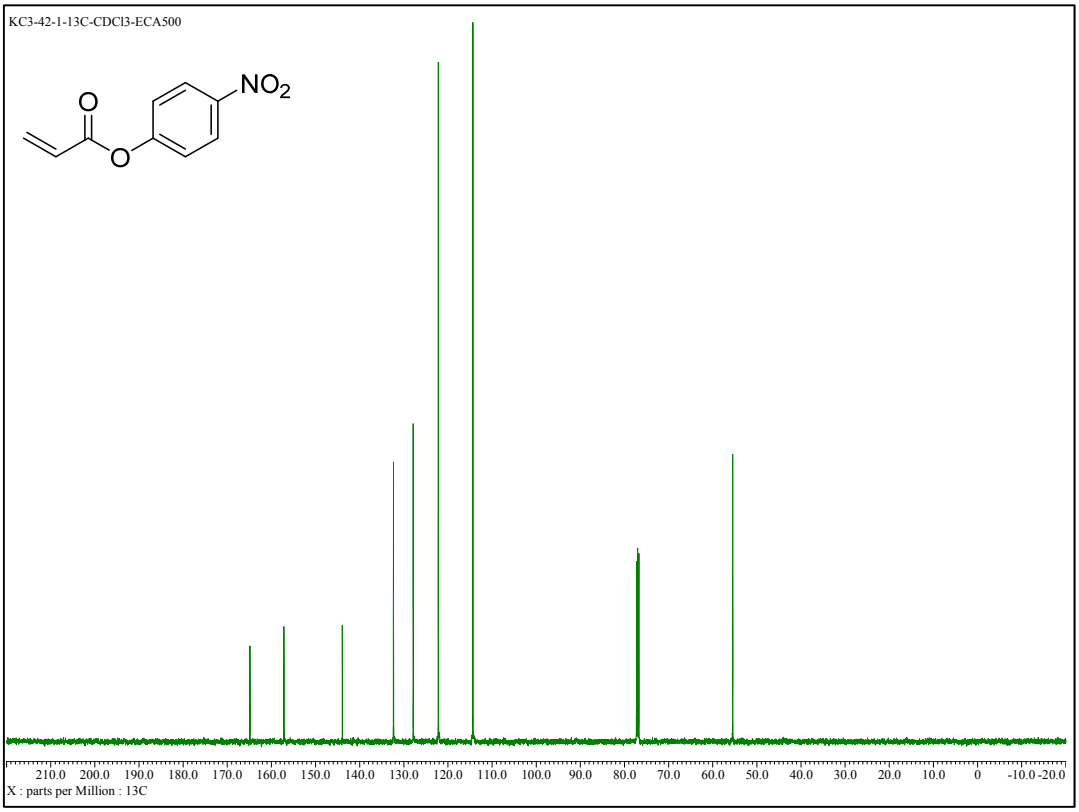
Phenyl acrylate



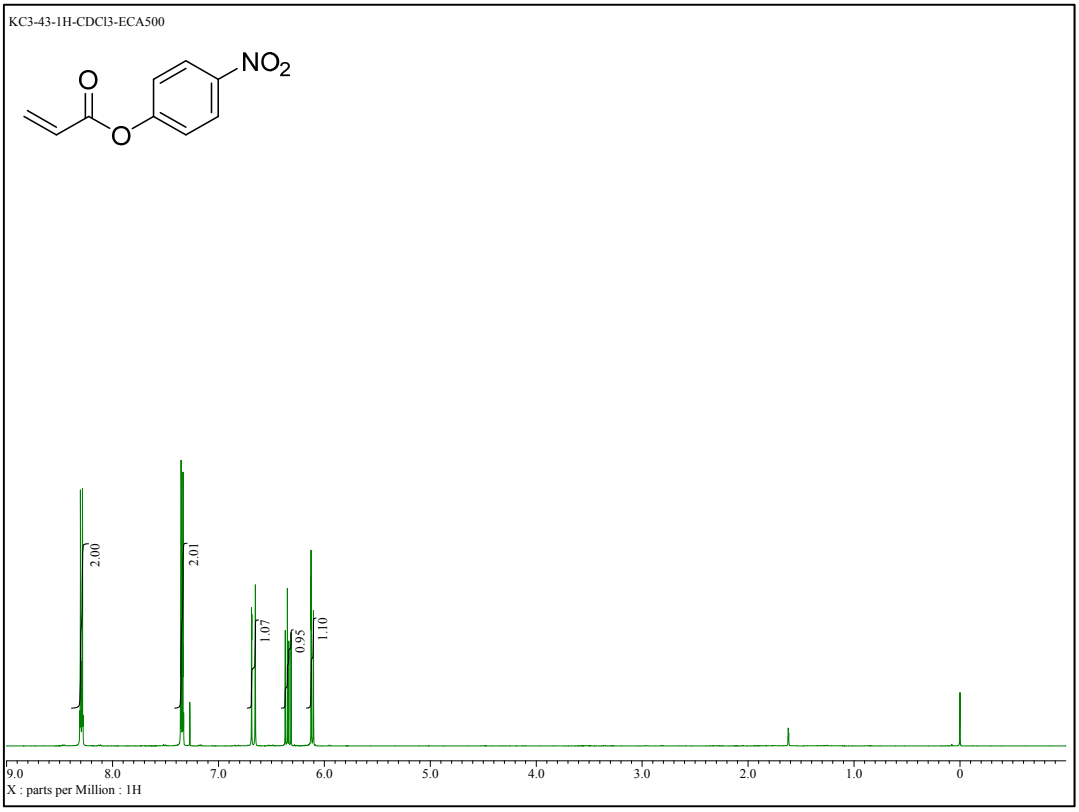


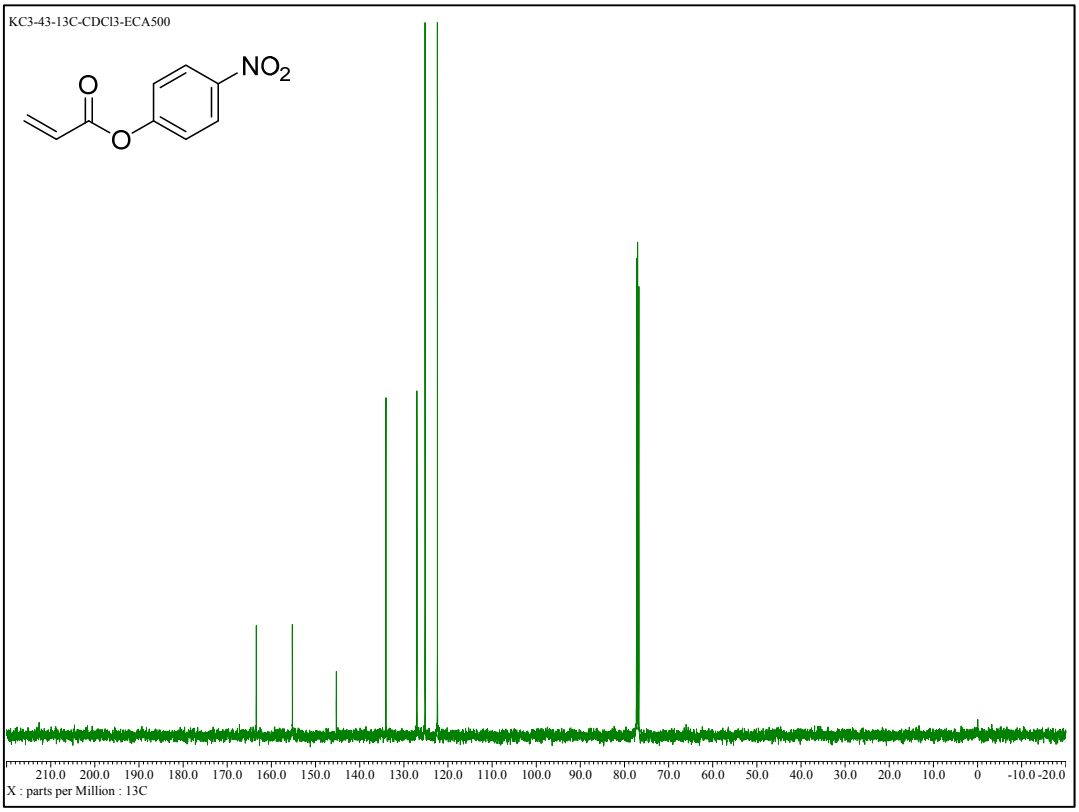
4-Methoxyphenyl acrylate



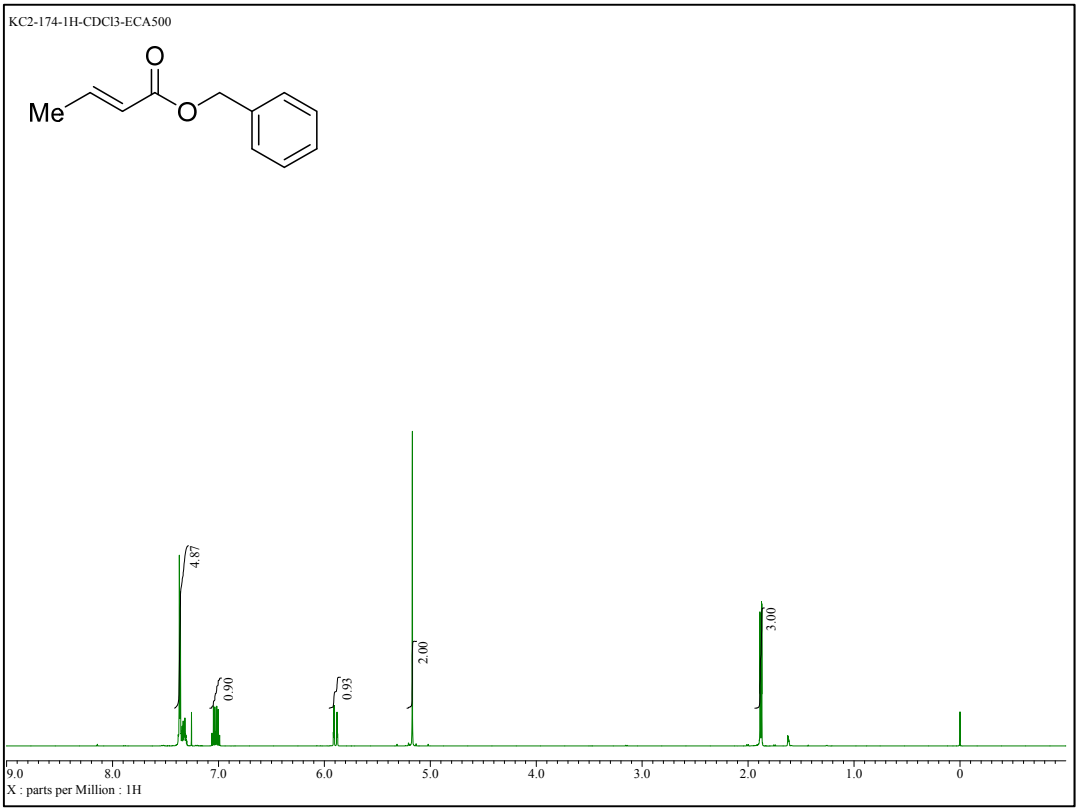


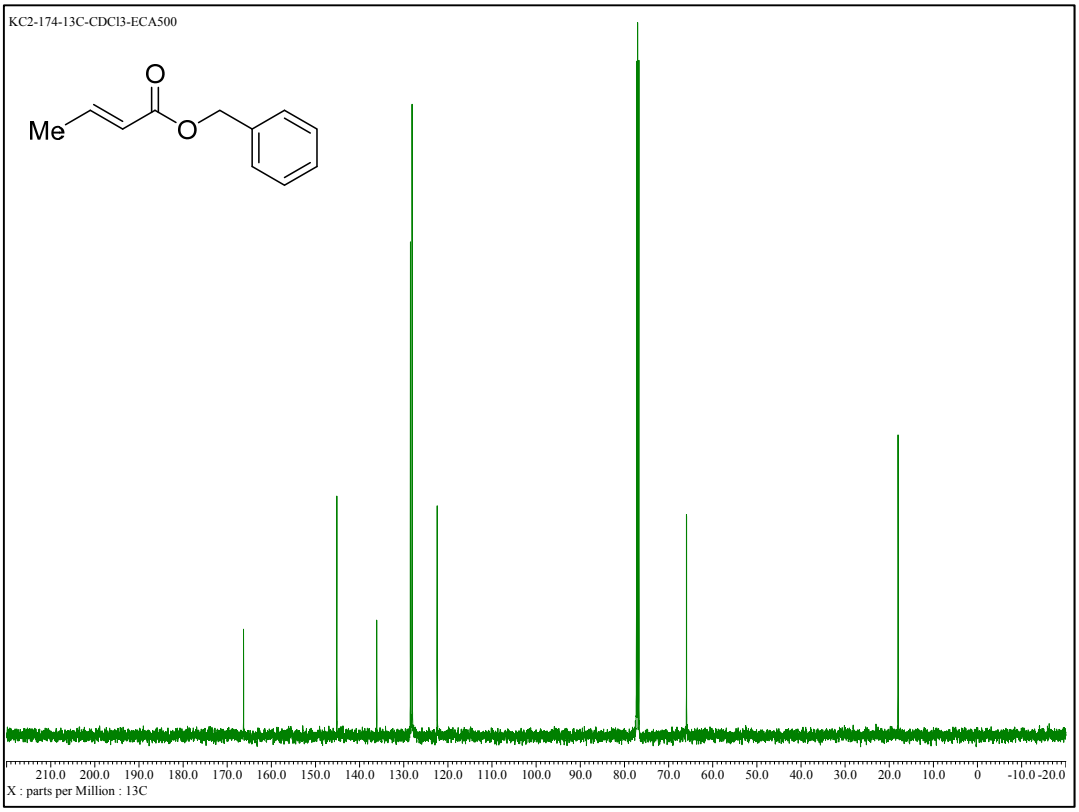
4-Nitrophenyl acrylate



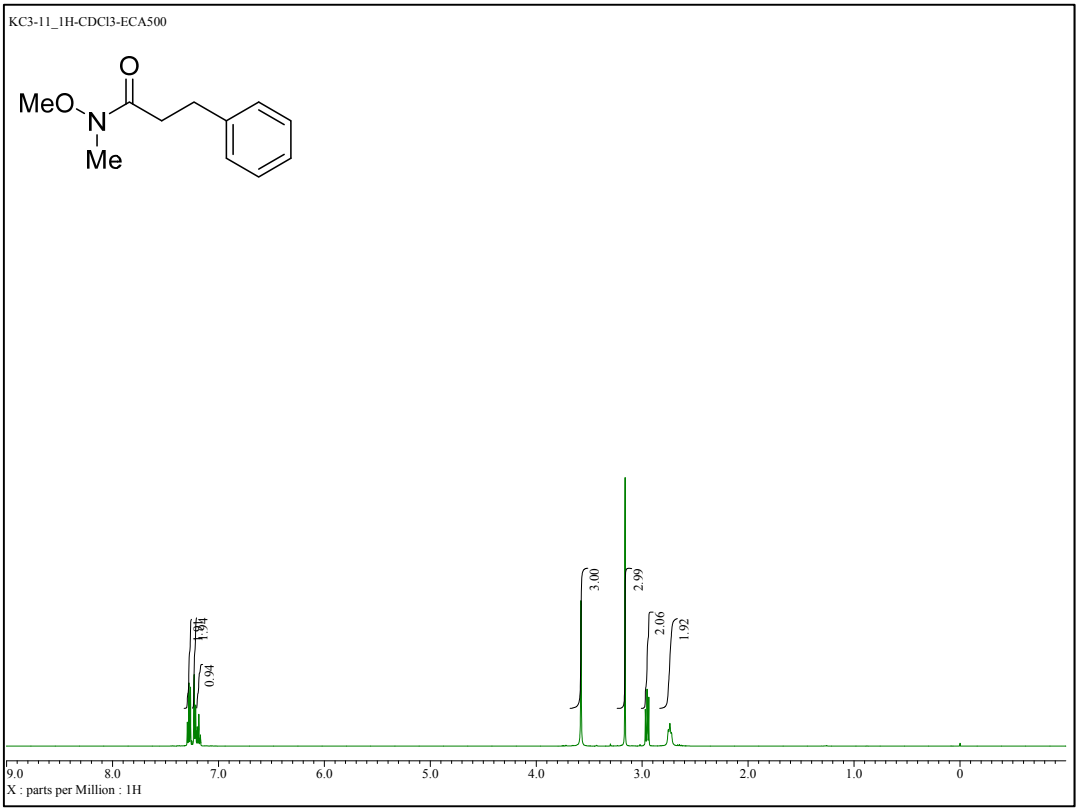


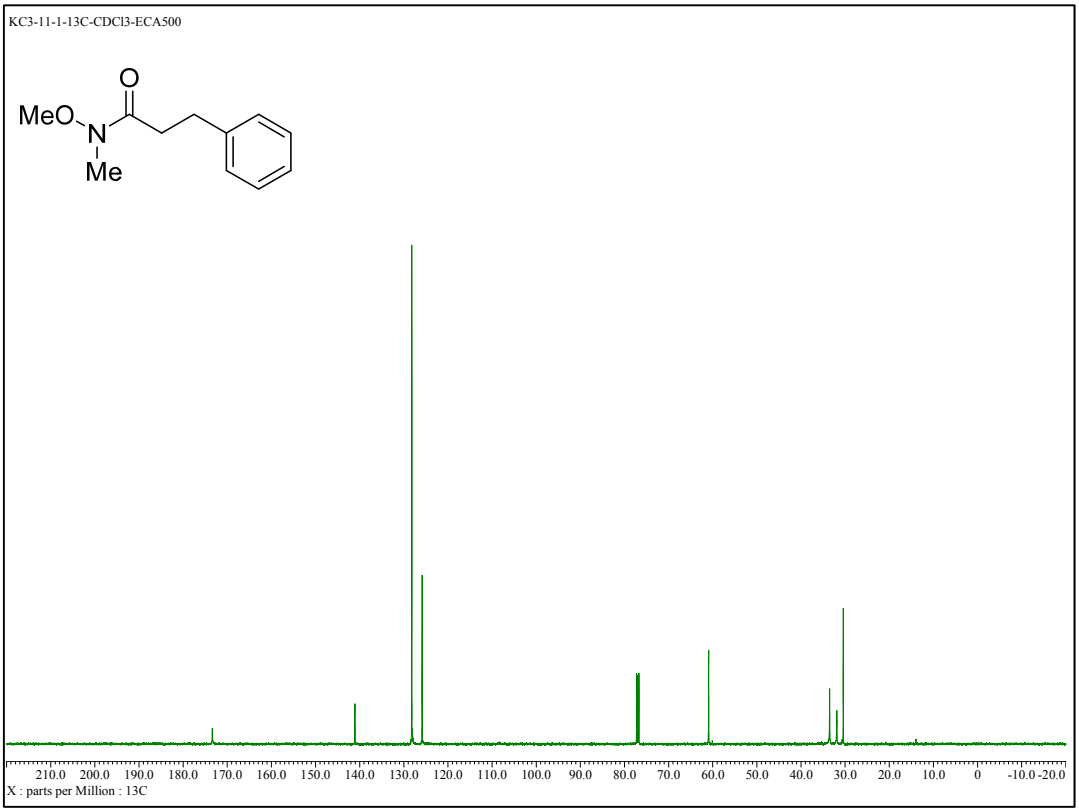
(*E*)-Benzyl but-2-enoate



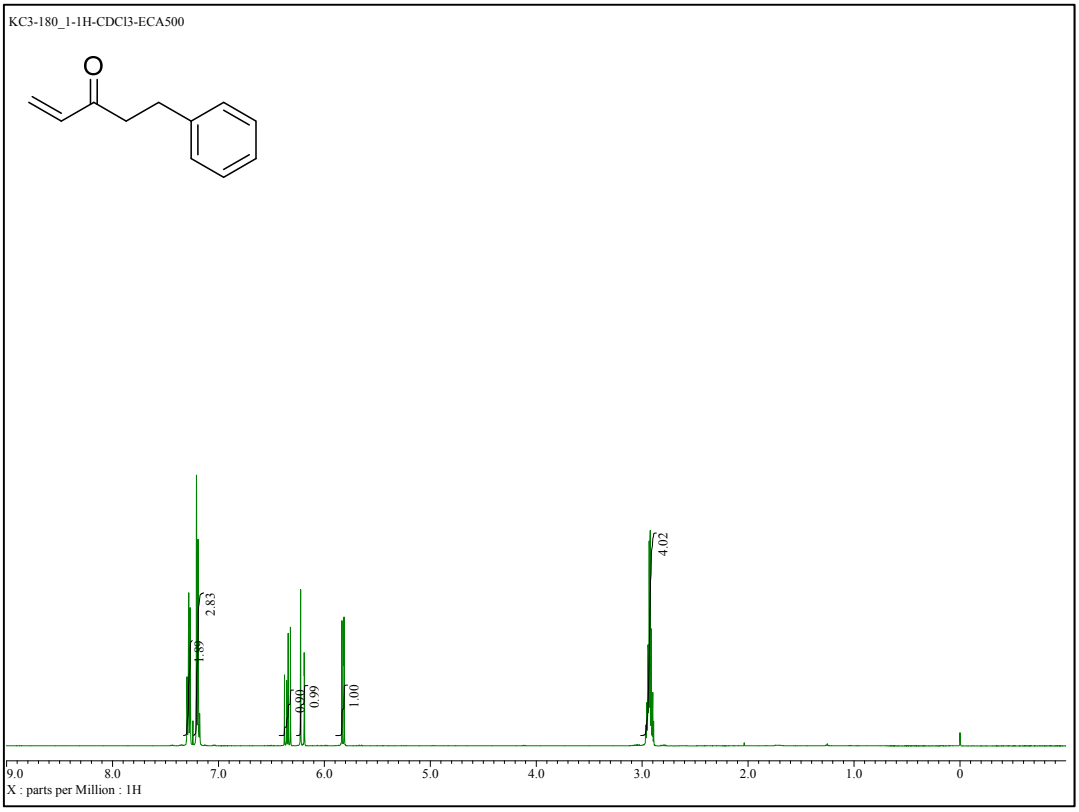


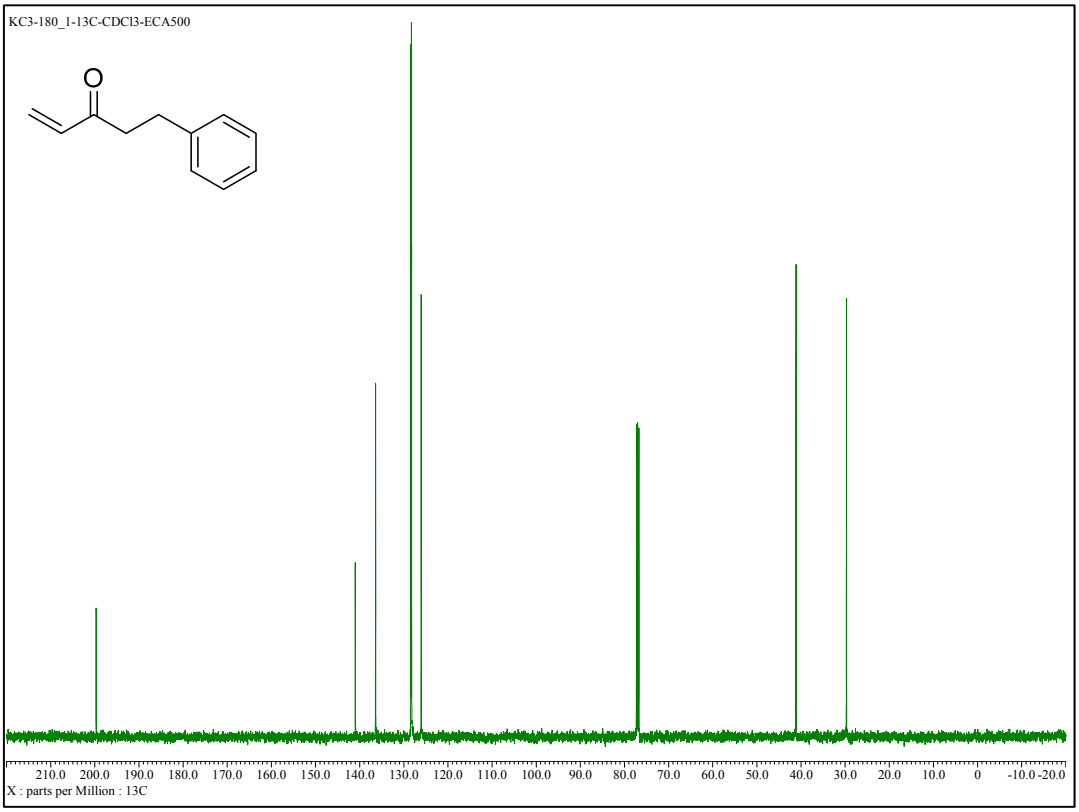
***N*-Methoxy-*N*-methyl-3-phenylpropanamide**





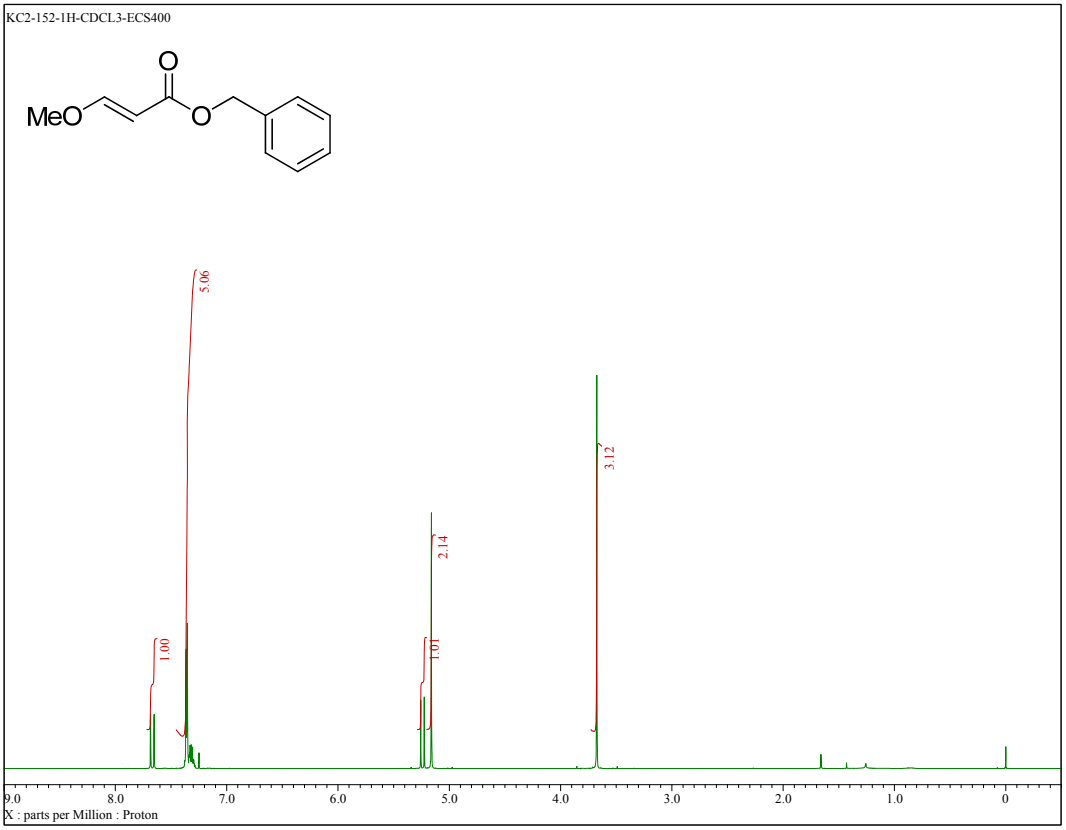
5-Phenyl-1-penten-3-one

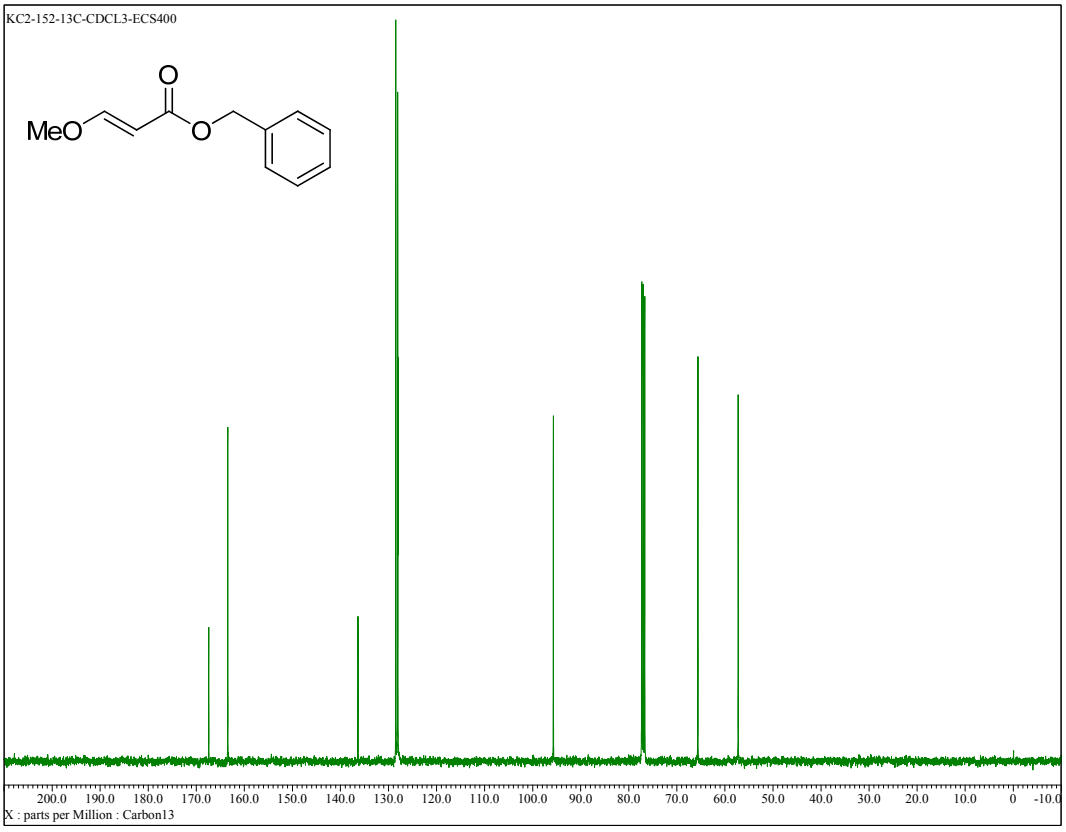




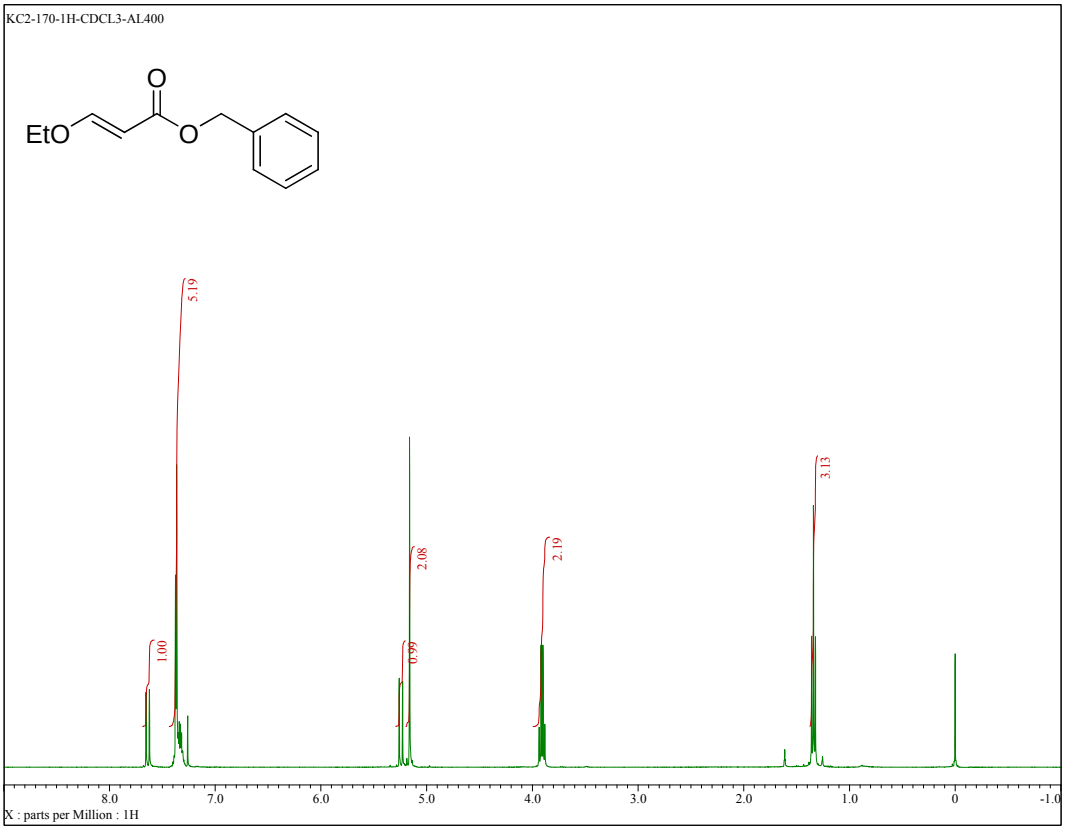
8. NMR spectra of products

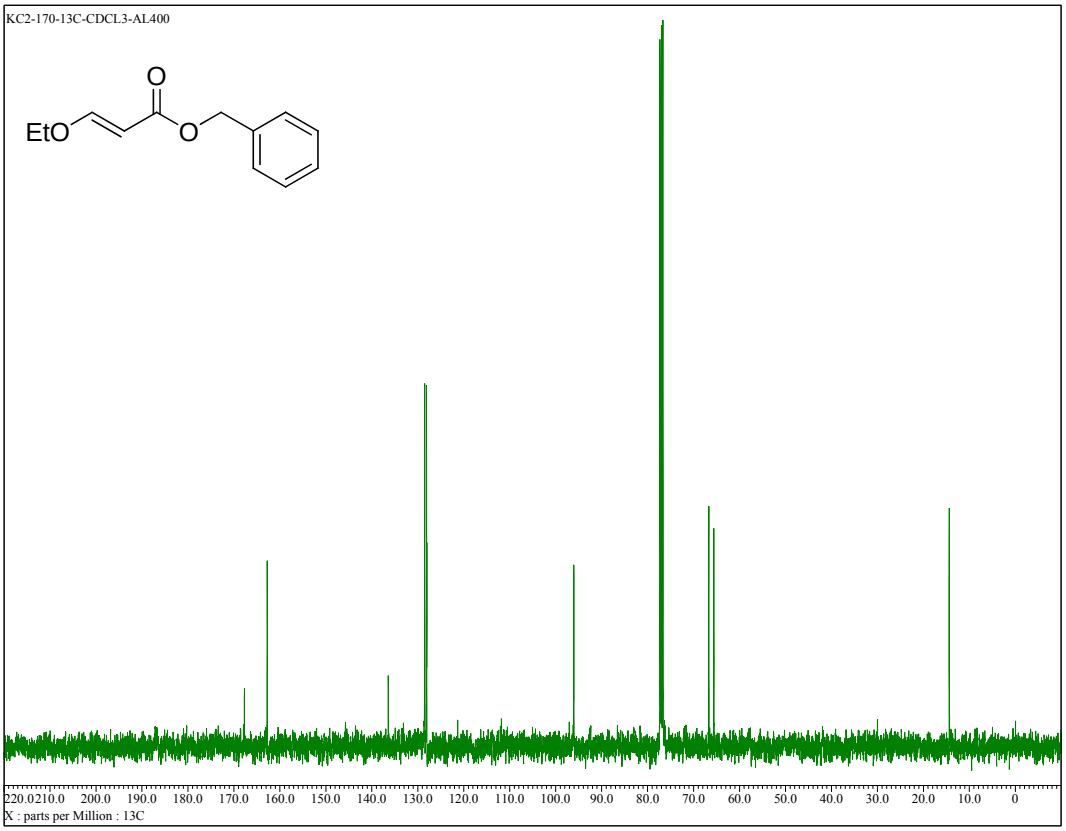
Benzyl 3-Methoxyacrylate (2a)



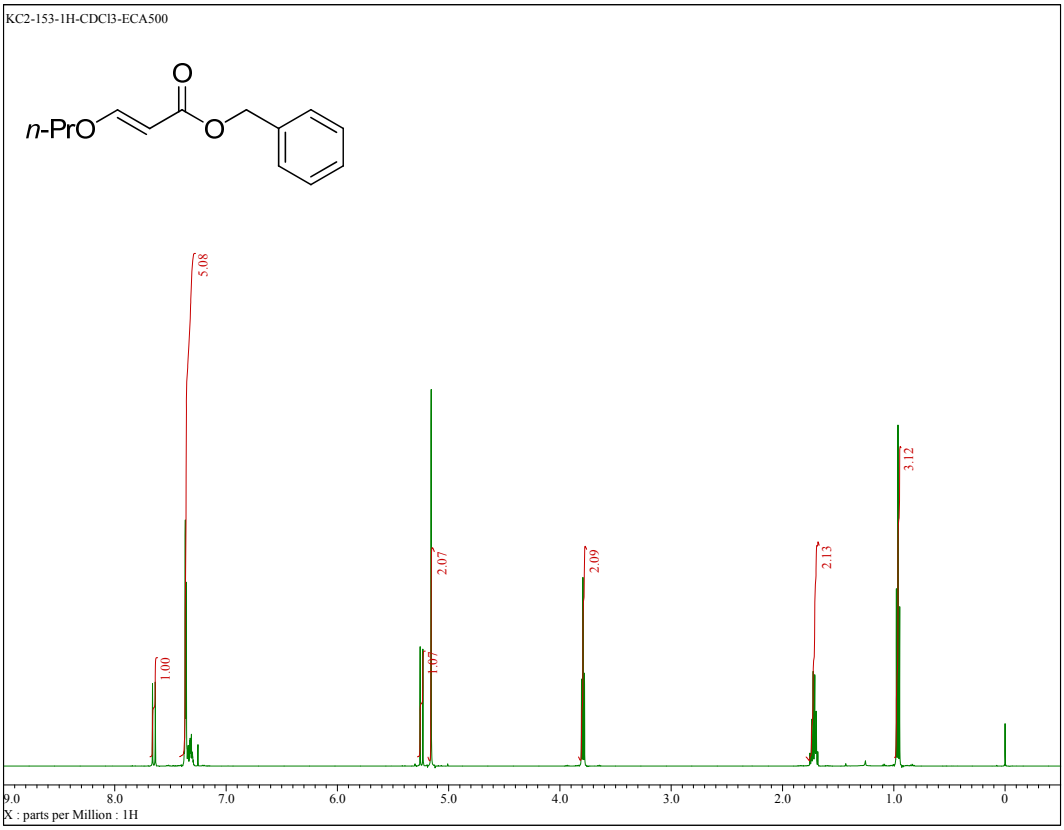


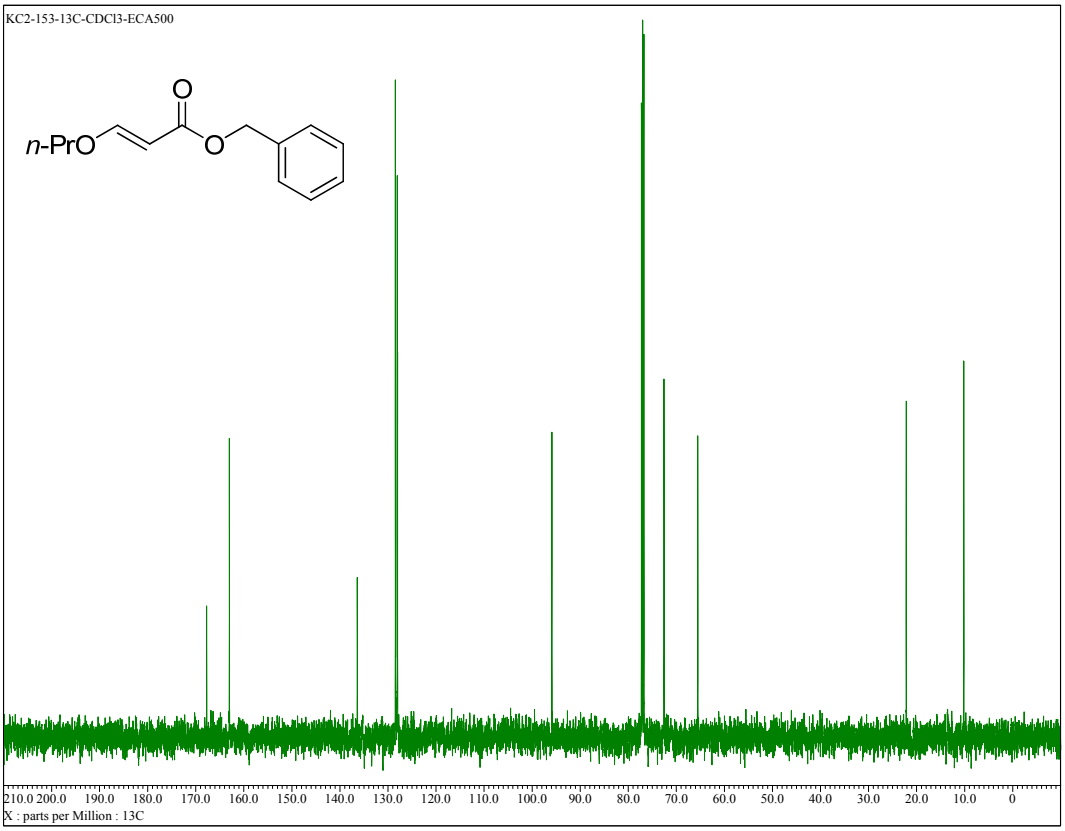
Benzyl 3-Ethoxyacrylate (2b)



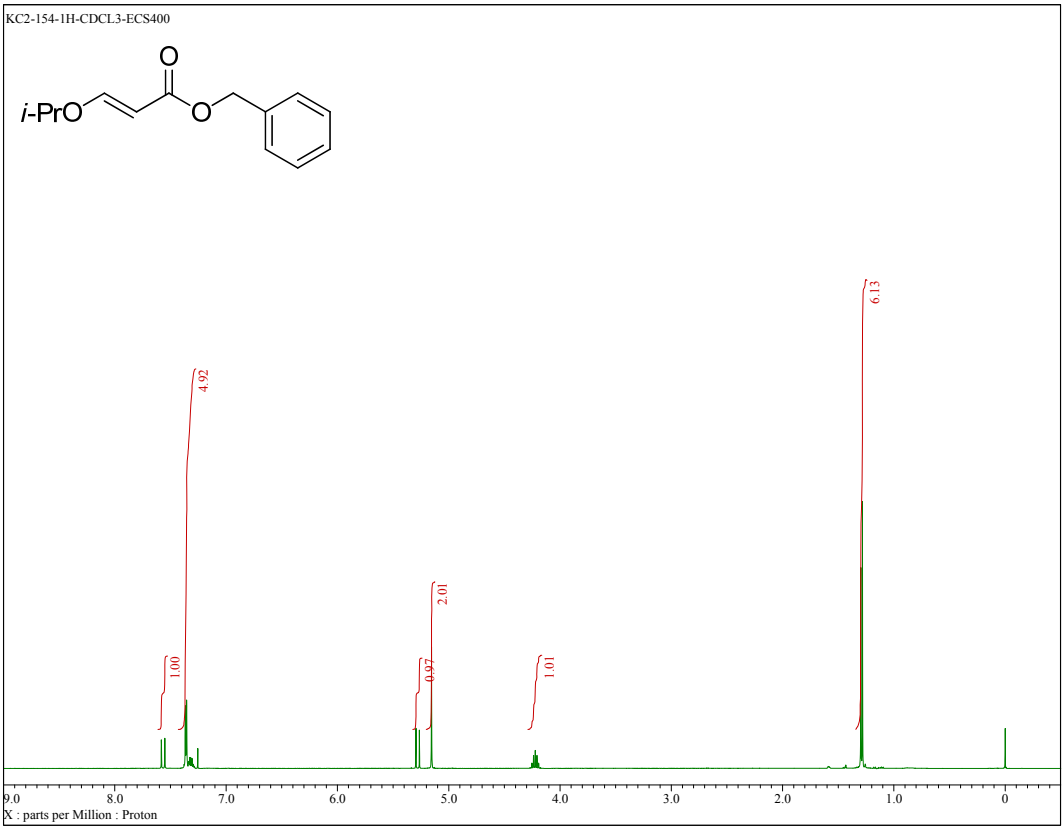


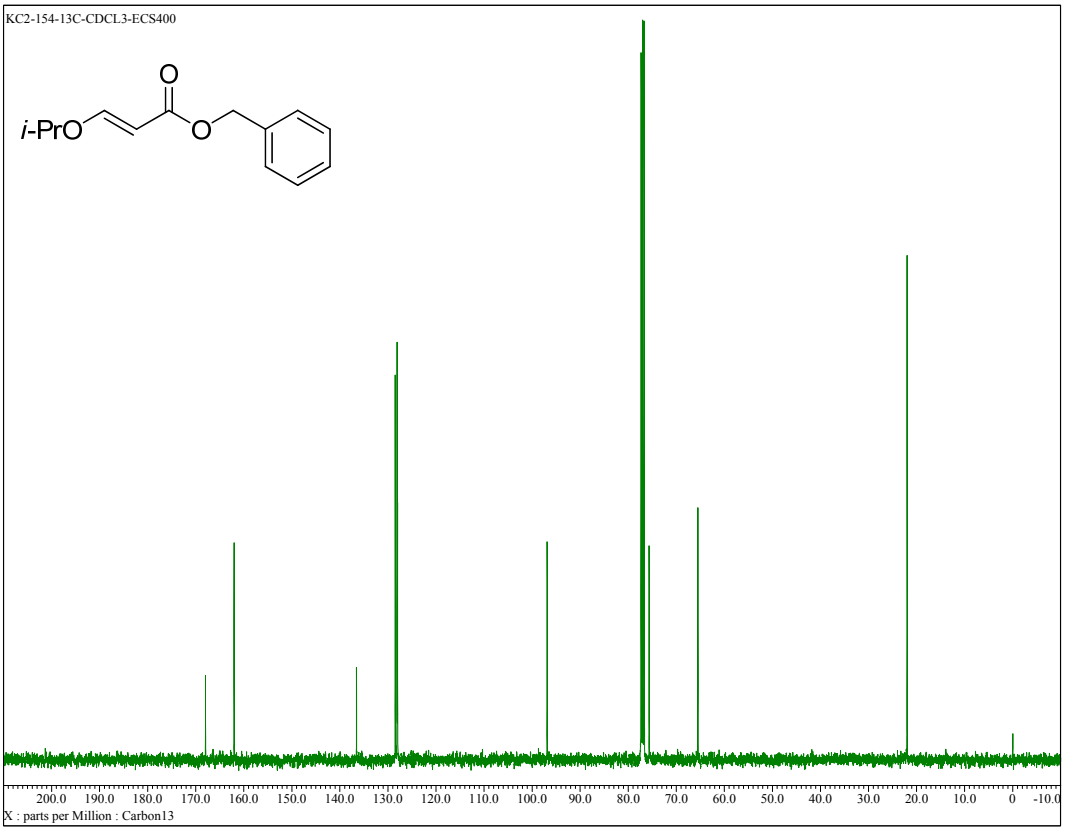
Benzyl 3-*n*-Propoxyacrylate (2c)



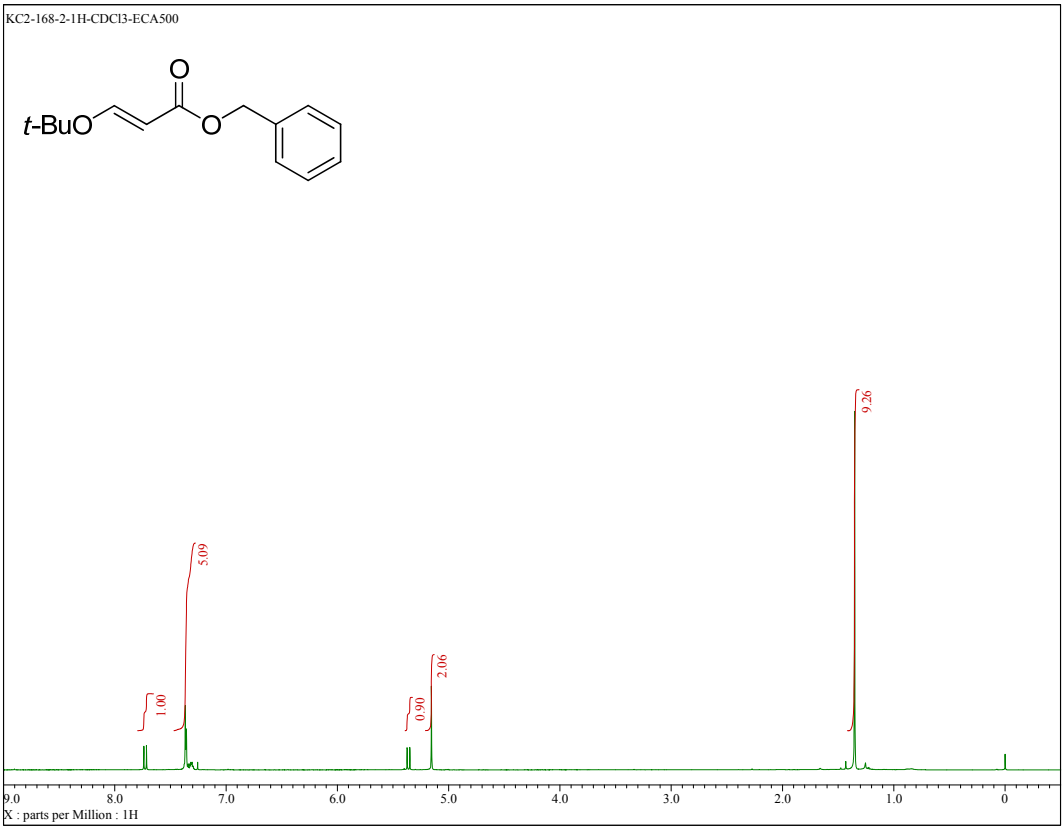


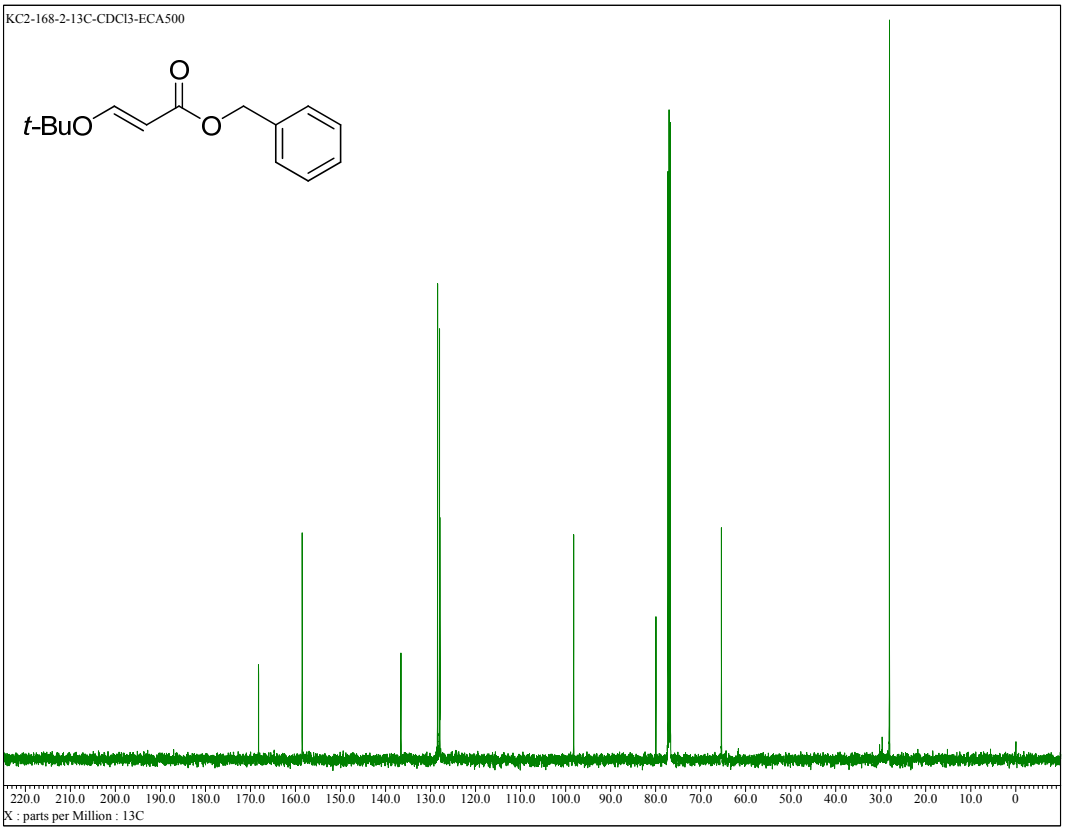
Benzyl 3-*i*-Propoxyacrylate (2d)



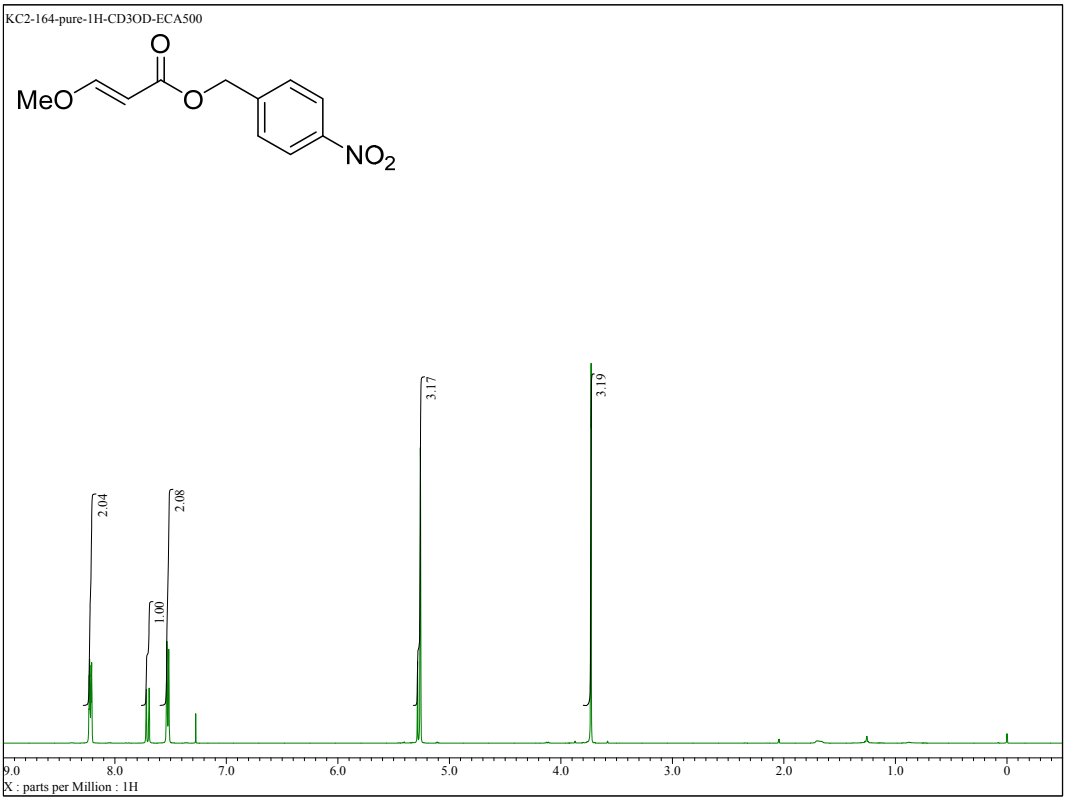


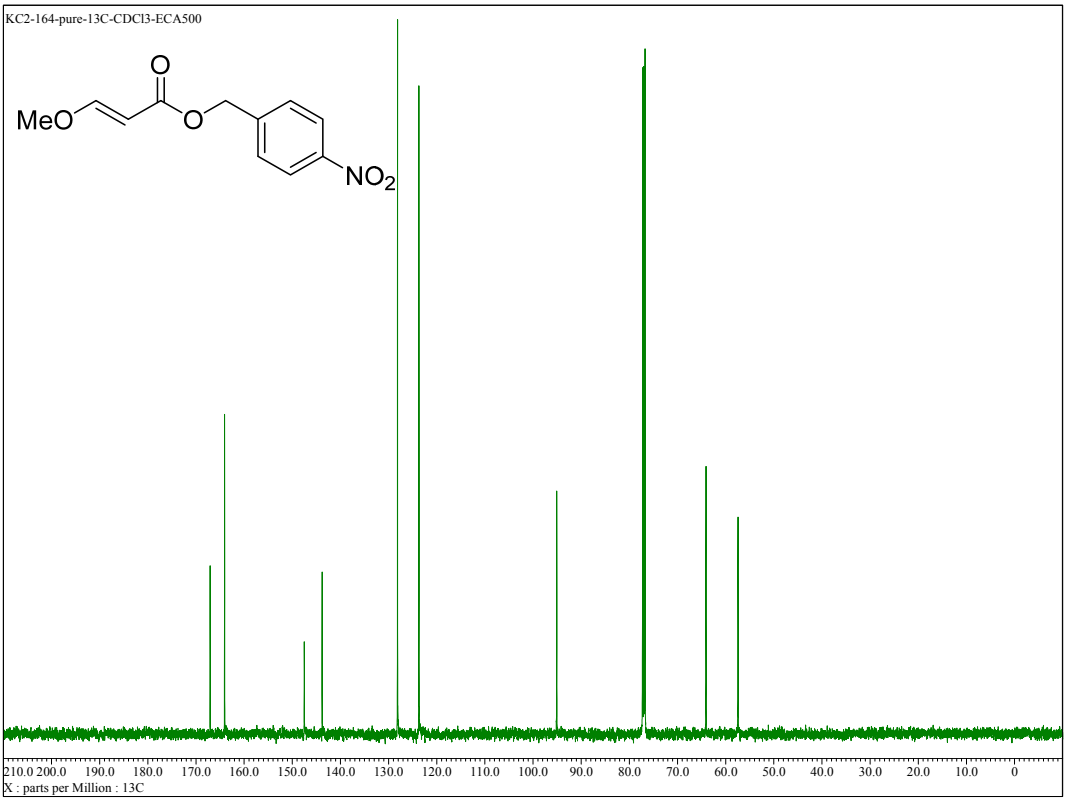
Benzyl 3-*t*-Buthoxyacrylate (2e)



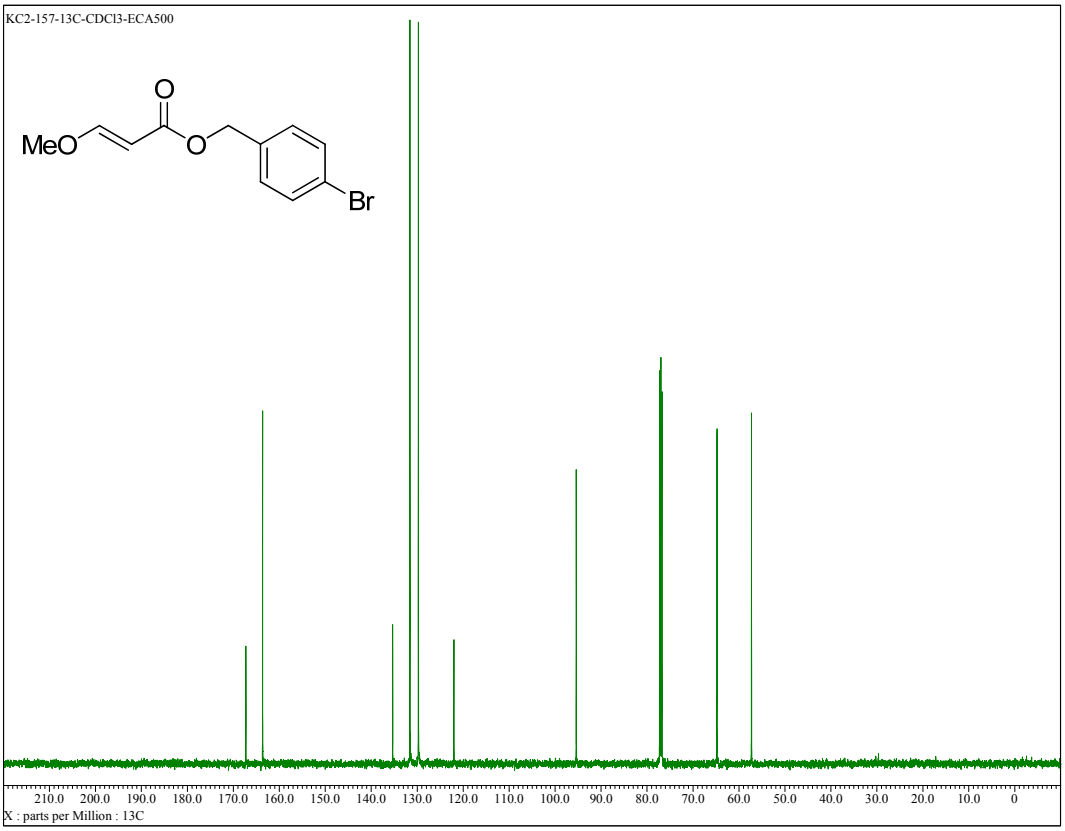


4-Nitrobenzyl 3-Methoxyacrylate (2f)

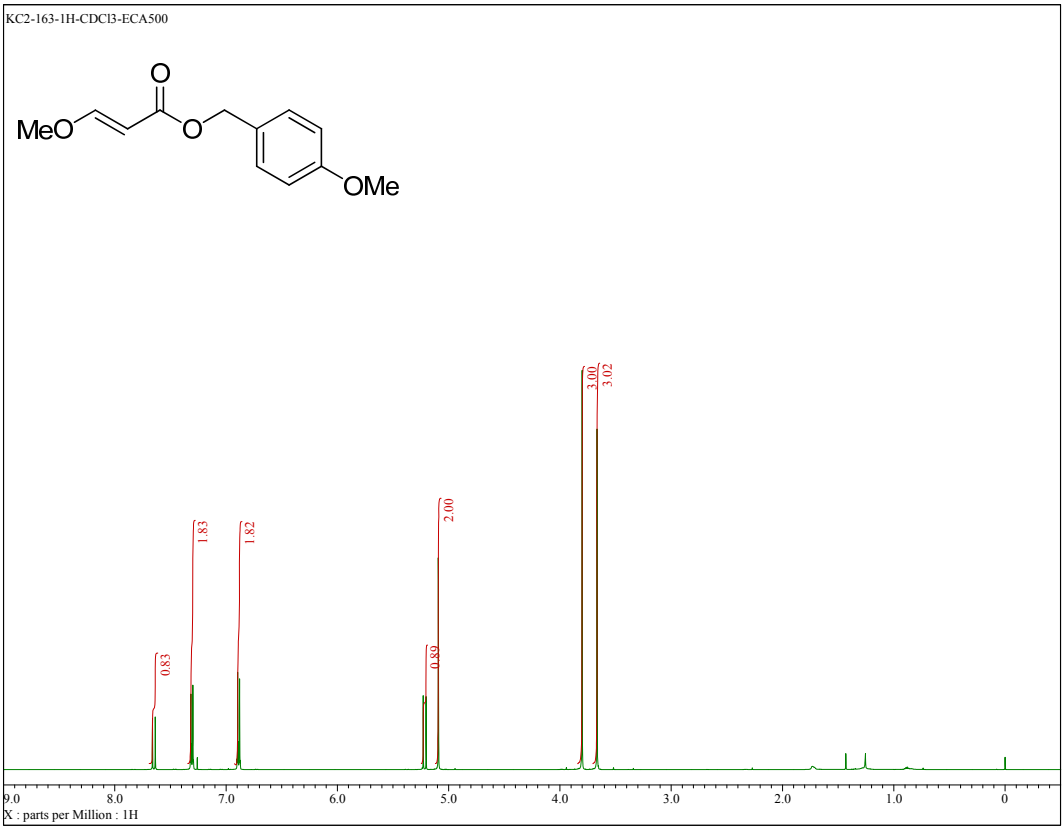


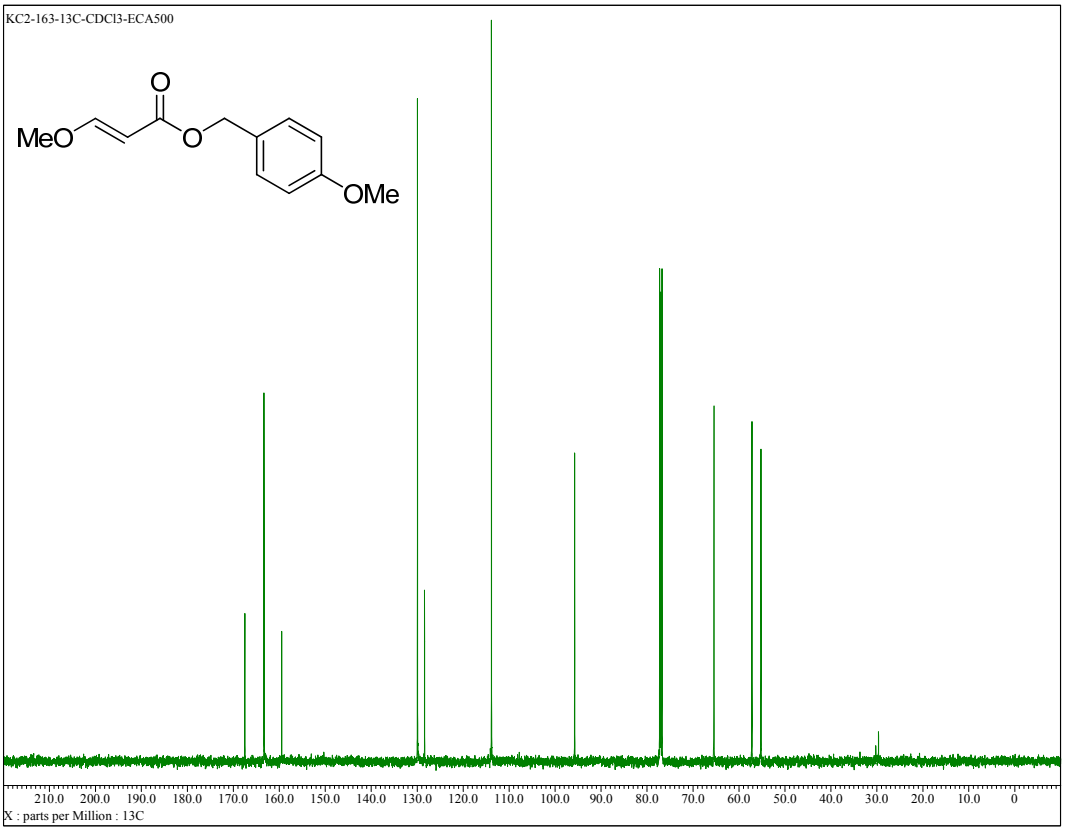


4-Bromobenzyl 3-Methoxyacrylate (2g)

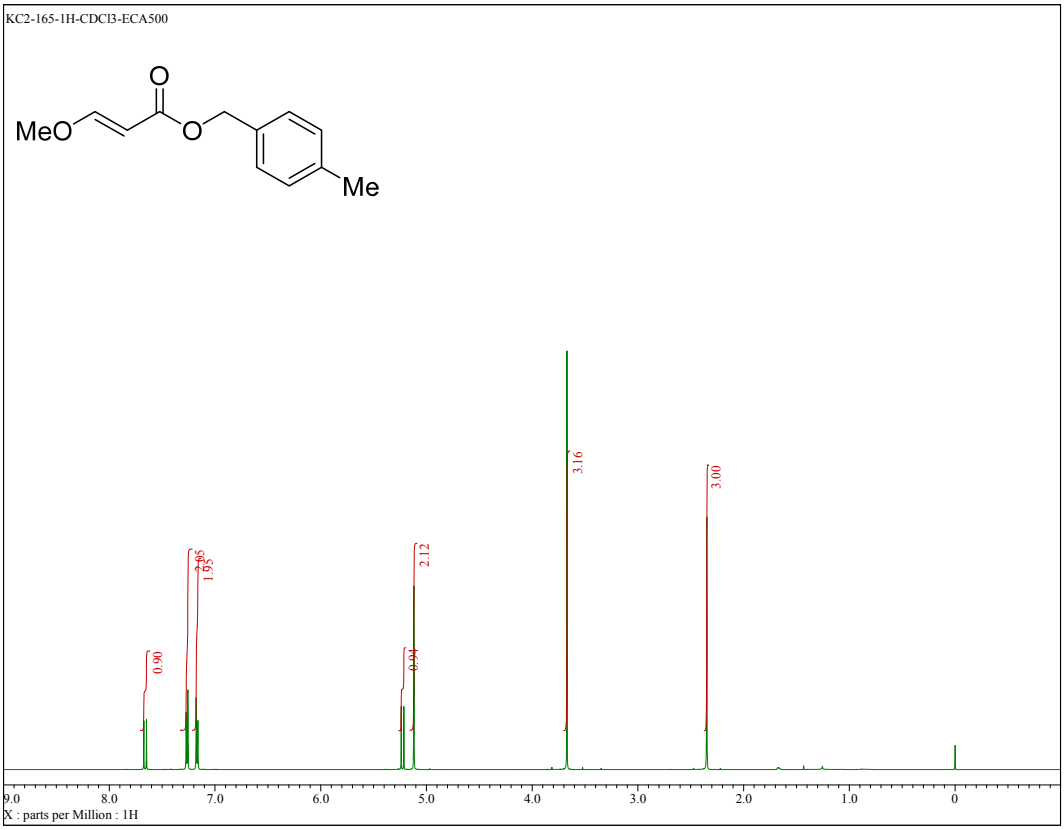


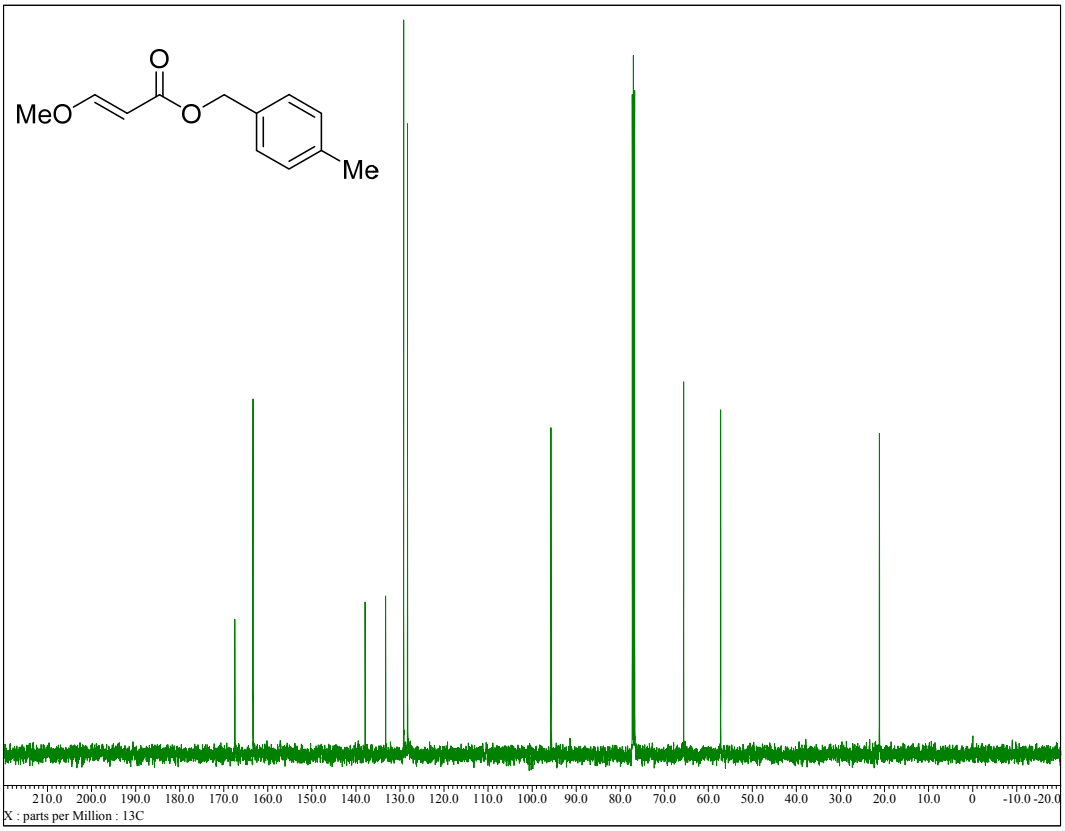
4-Methoxybenzyl 3-Methoxyacrylate (2h)



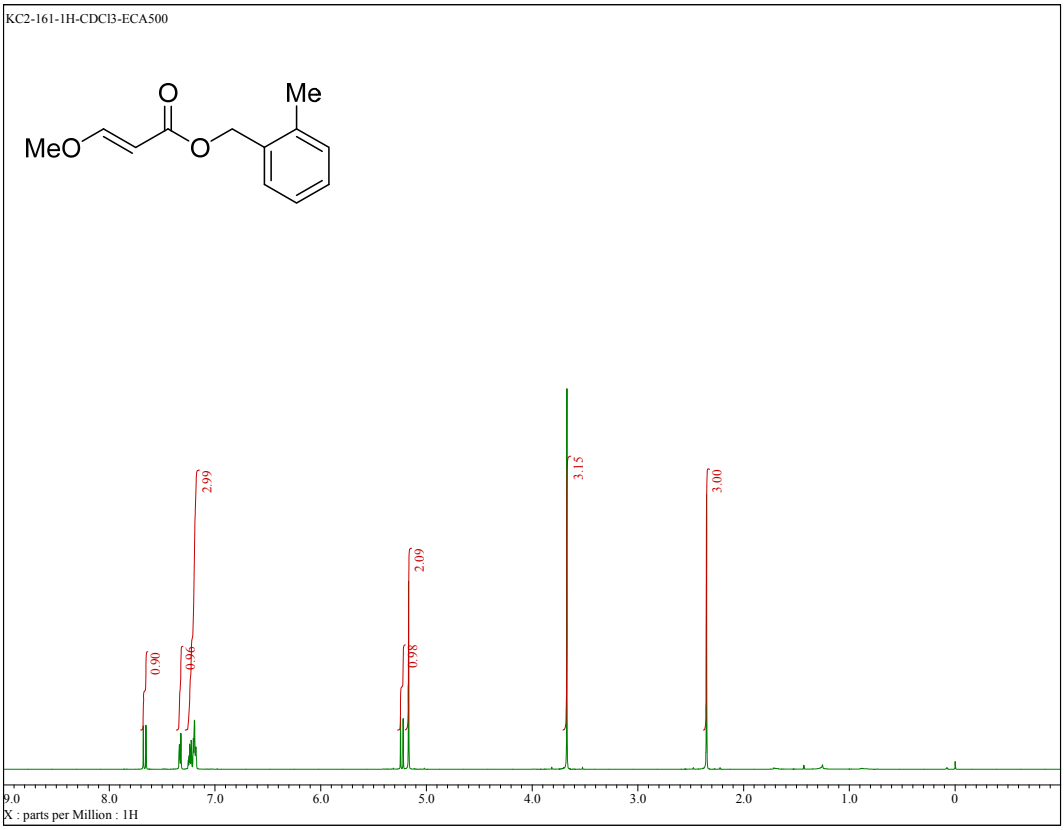


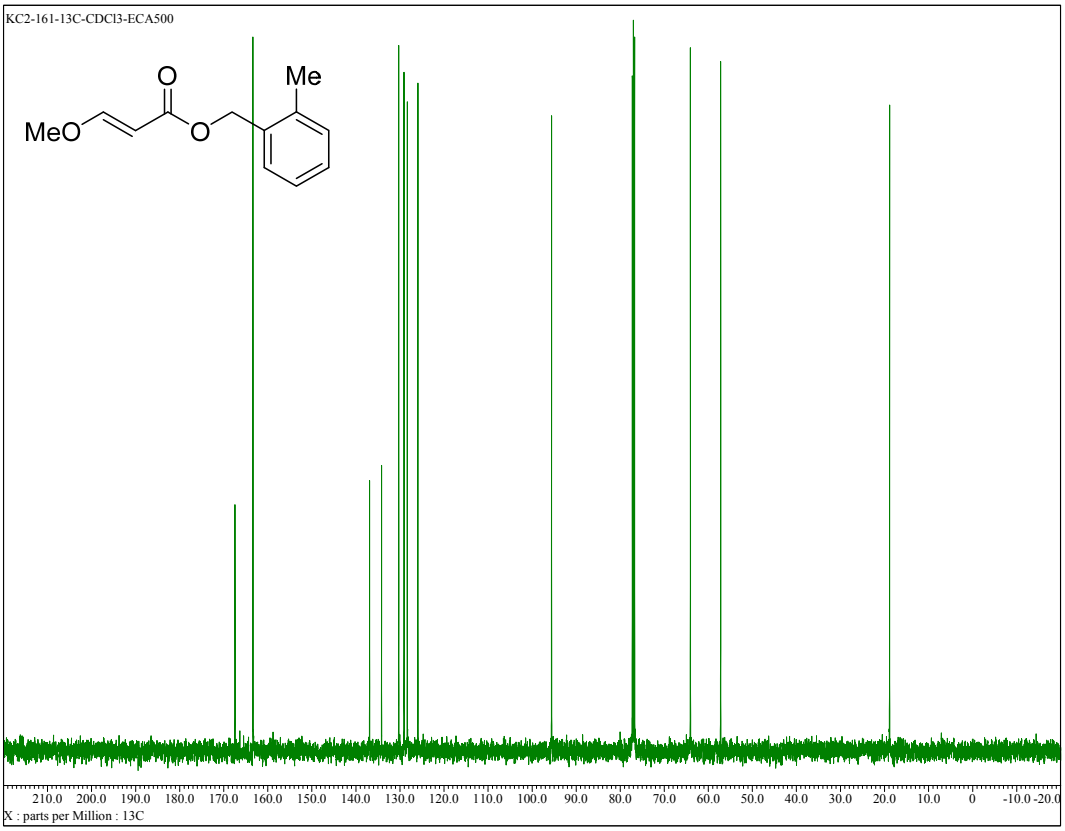
4-Methylbenzyl 3-Methoxyacrylate (2i)



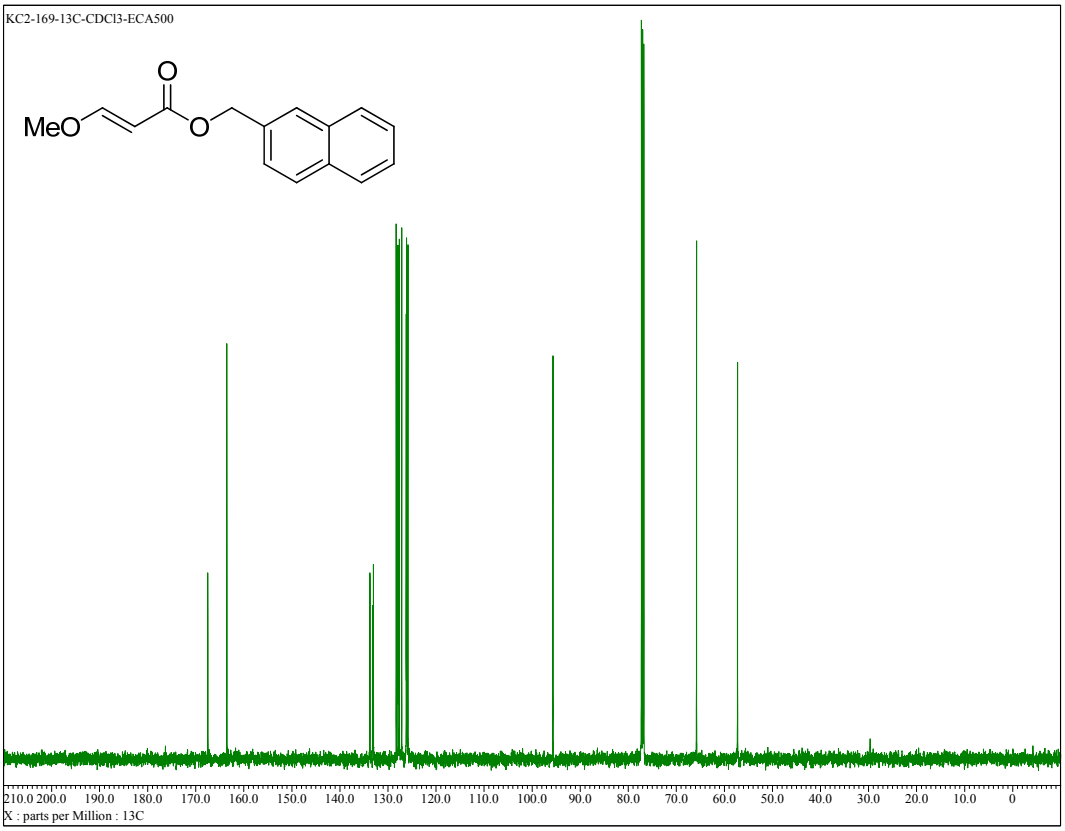


2-Methylbenzyl 3-Methoxyacrylate (2j)

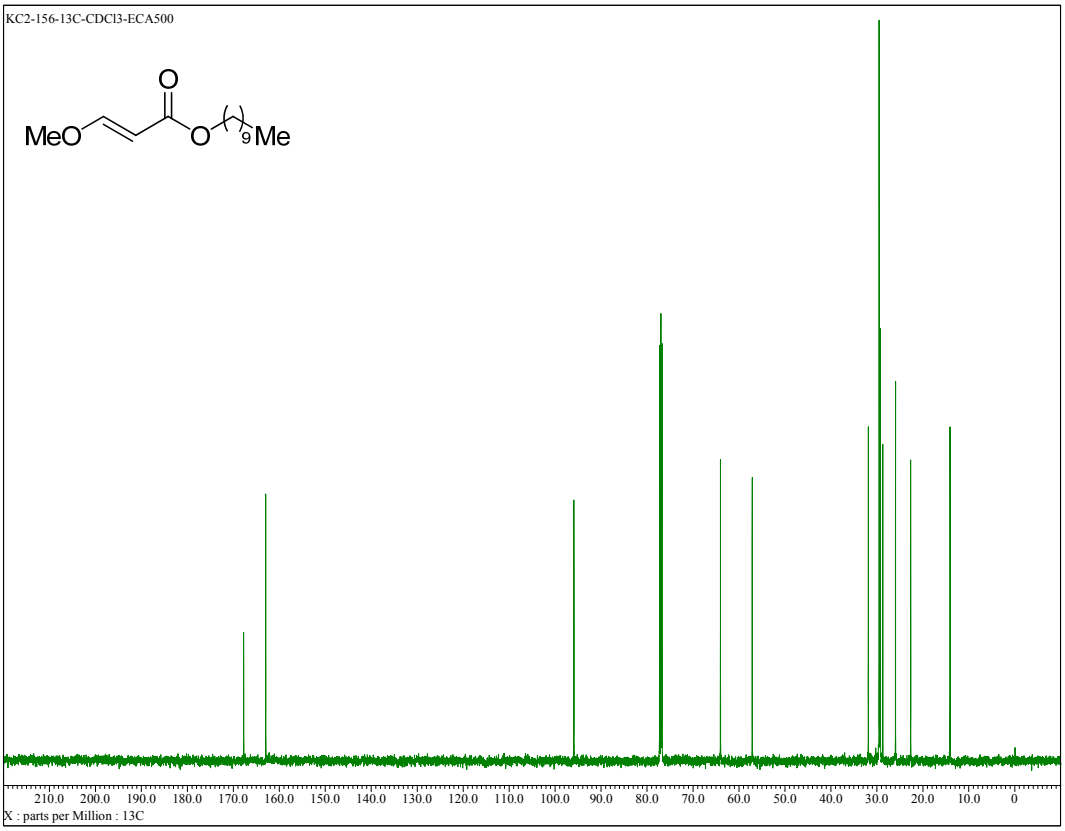




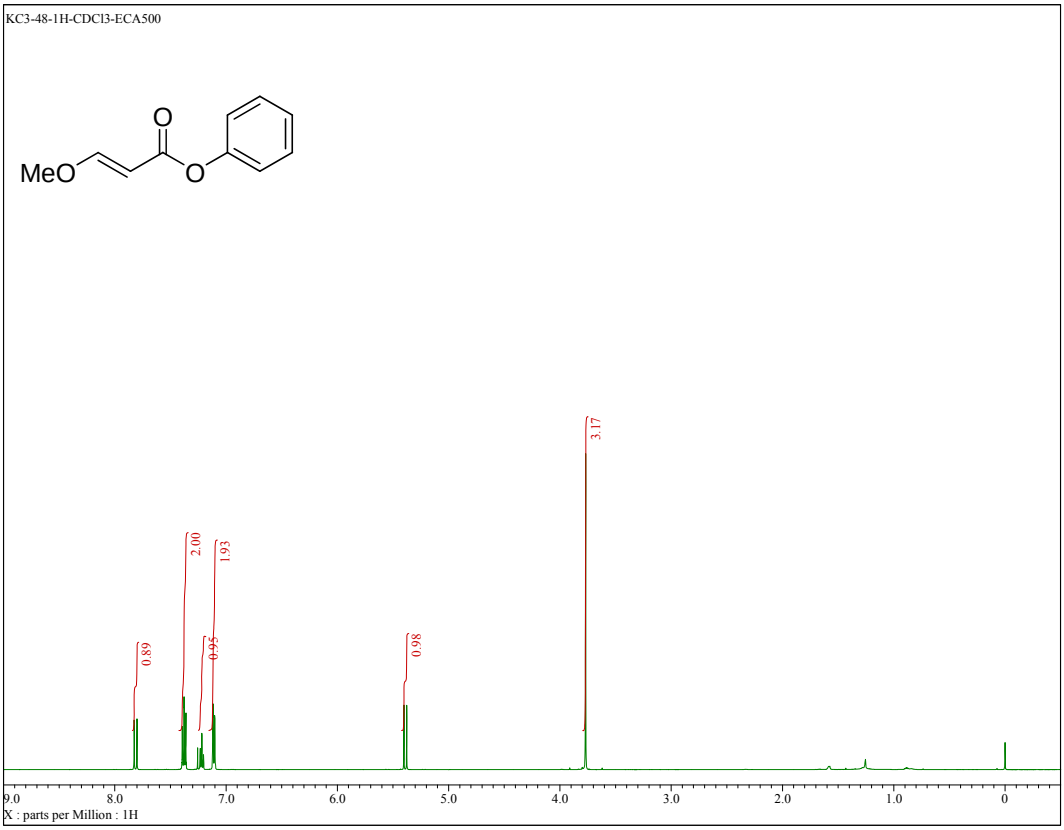
2-Naphthyl 3-Methoxyacrylate (2k)

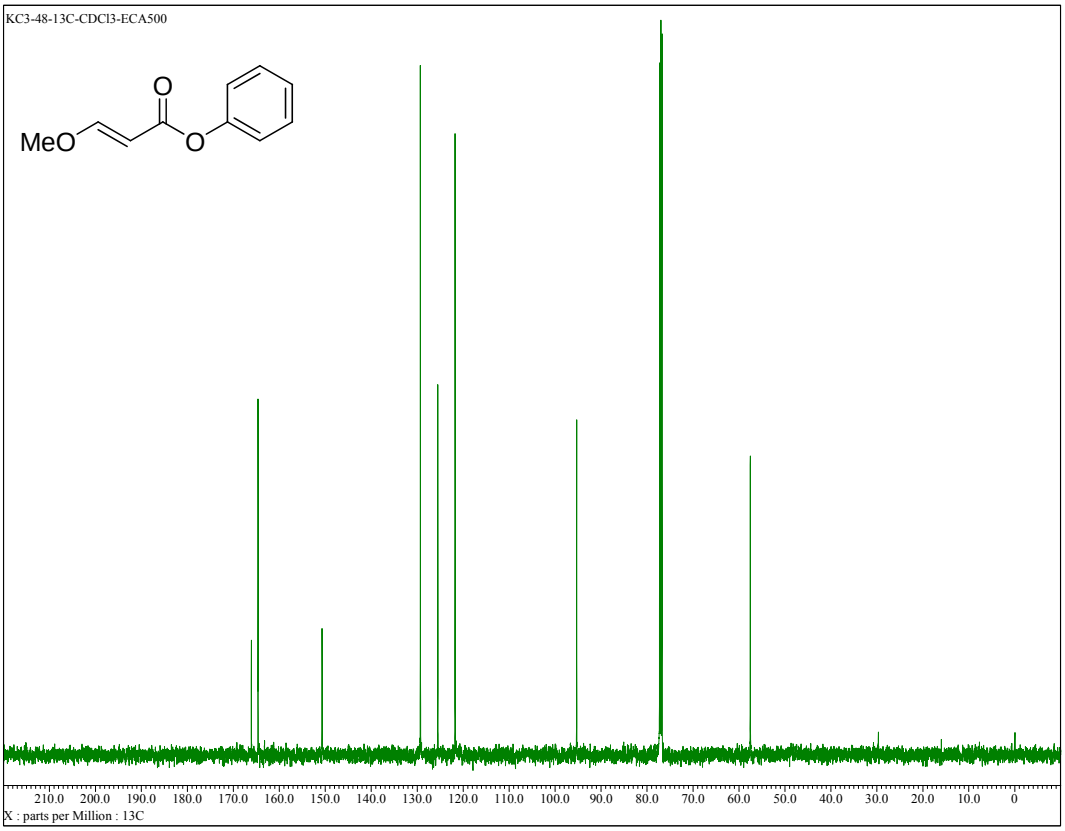


1-Decyl 3-Methoxyacrylate (2l)

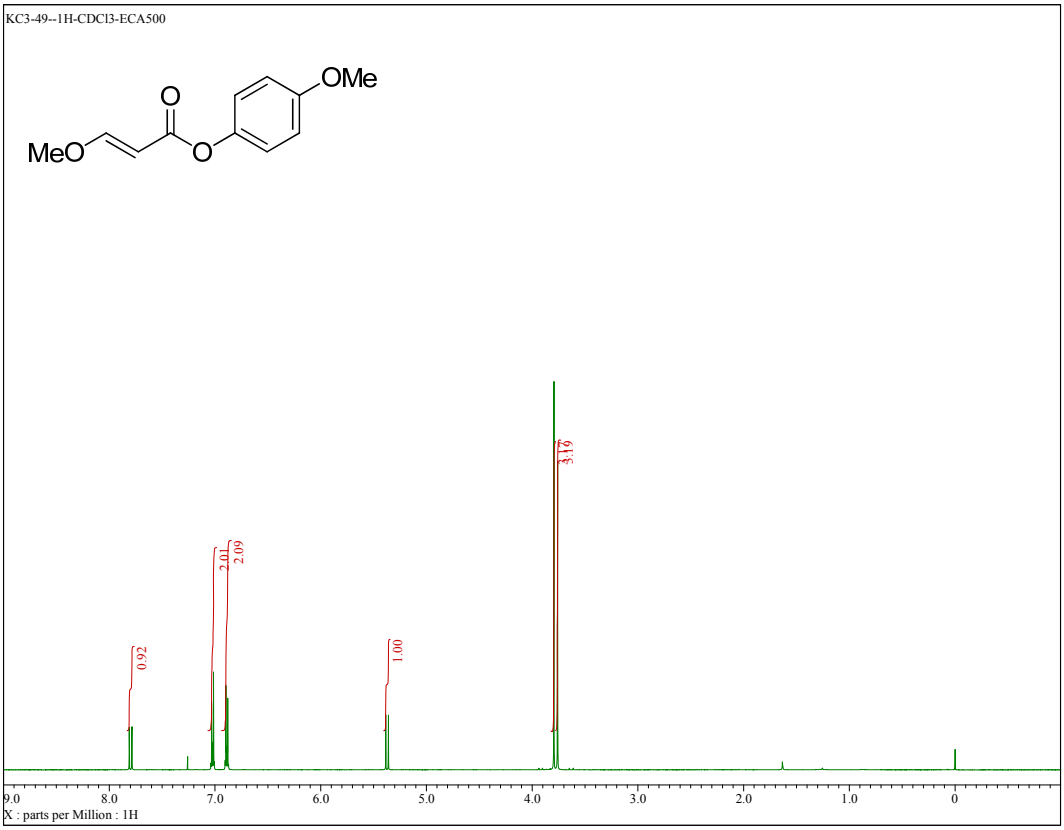


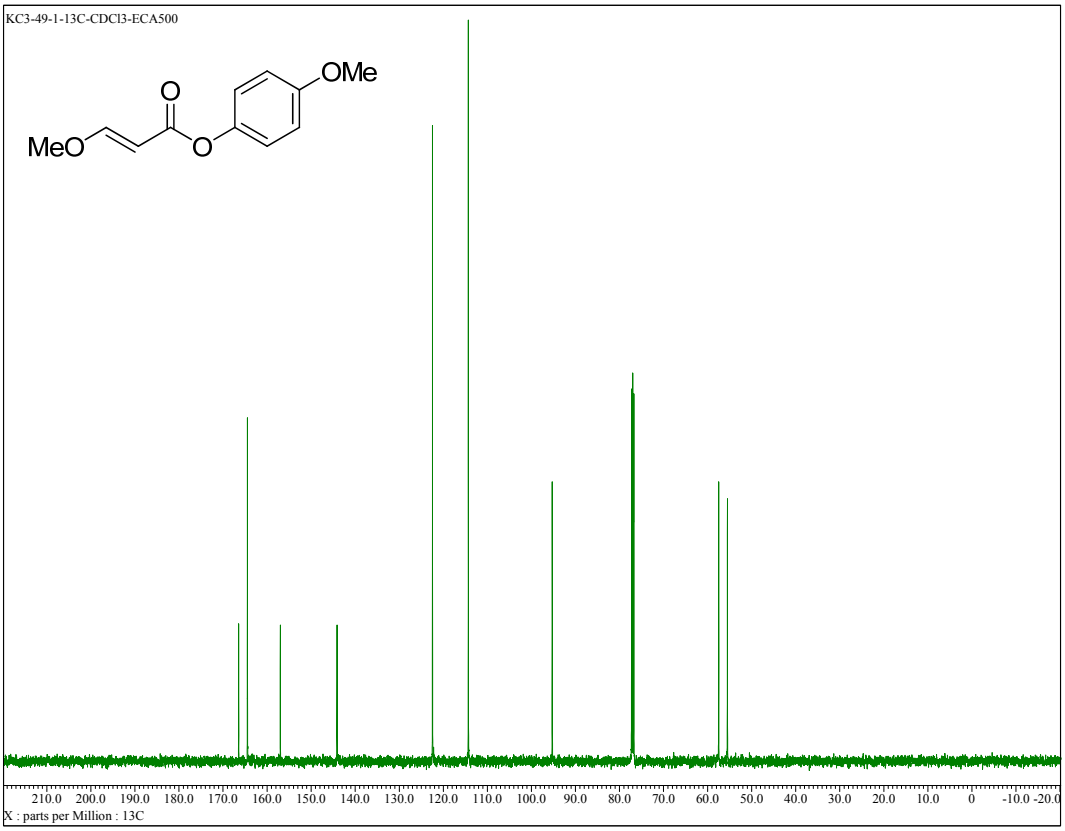
Phenyl 3-Methoxyacrylate (2m)



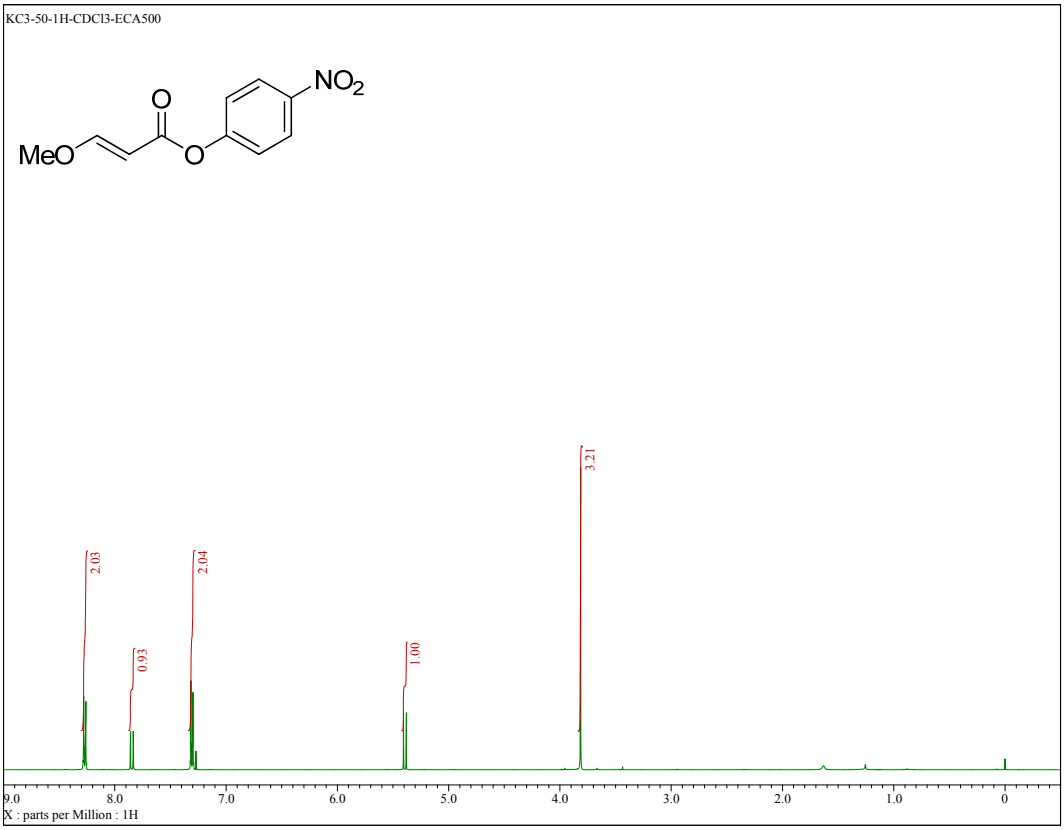


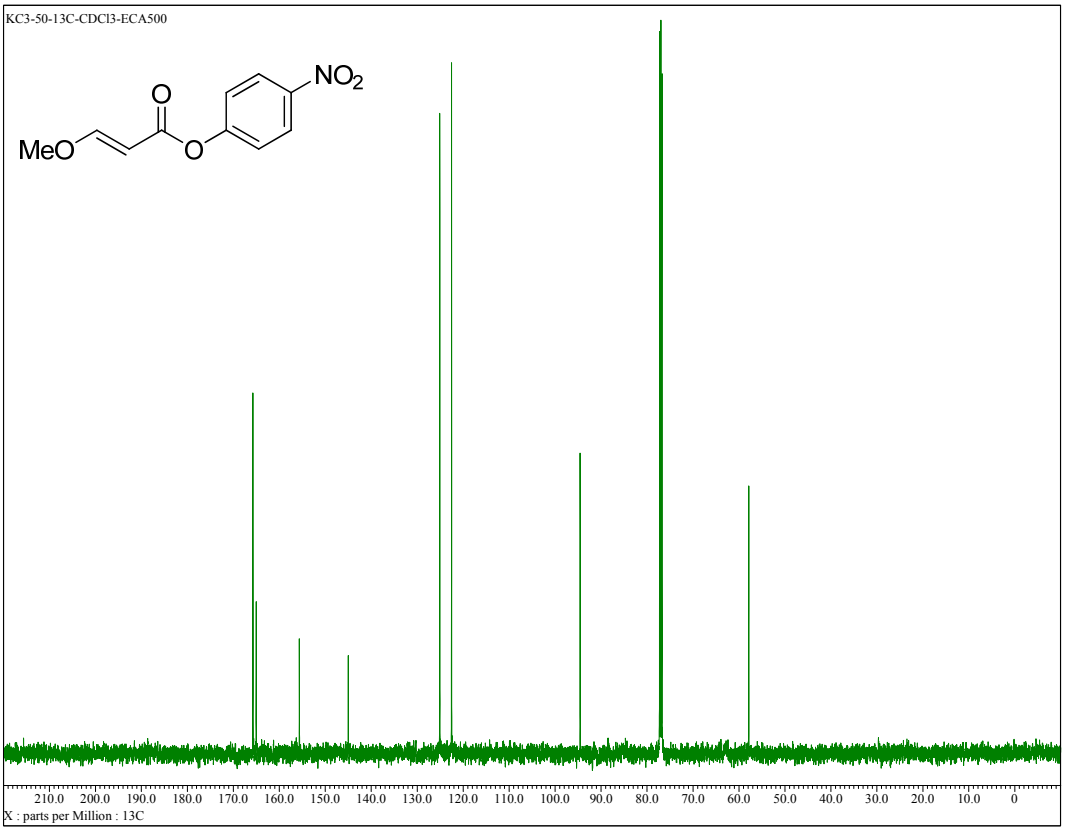
4-Methoxyphenyl 3-Methoxyacrylate (2n)



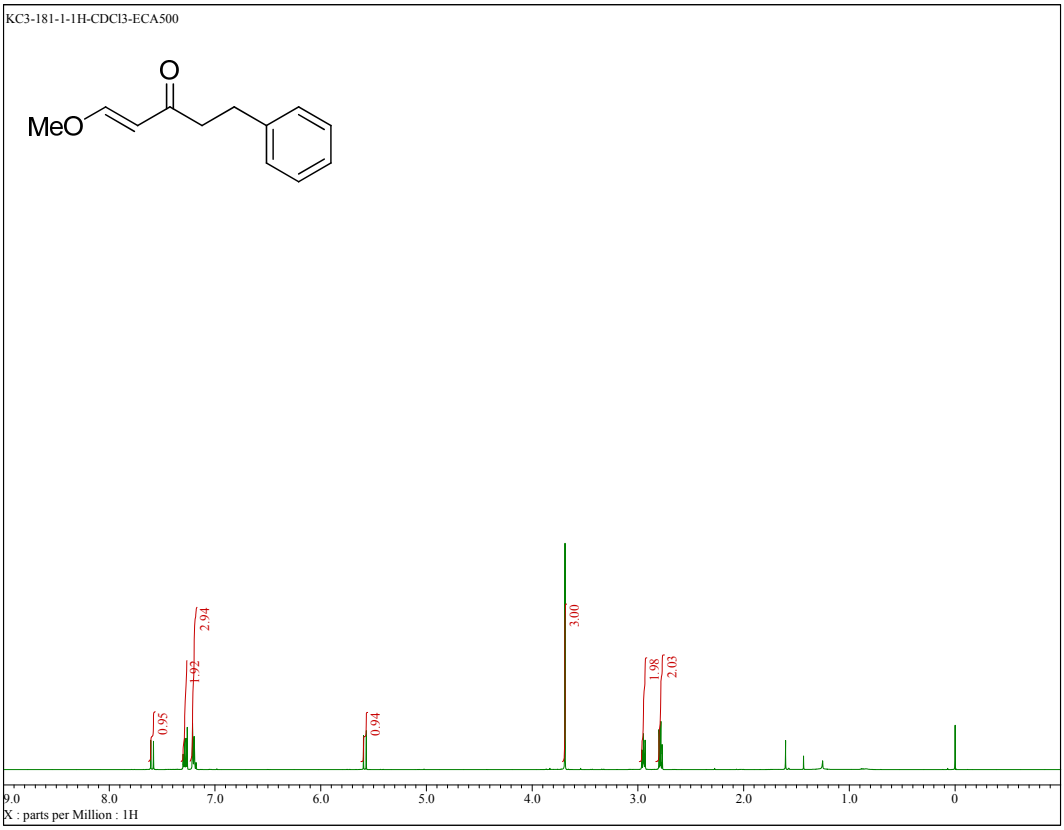


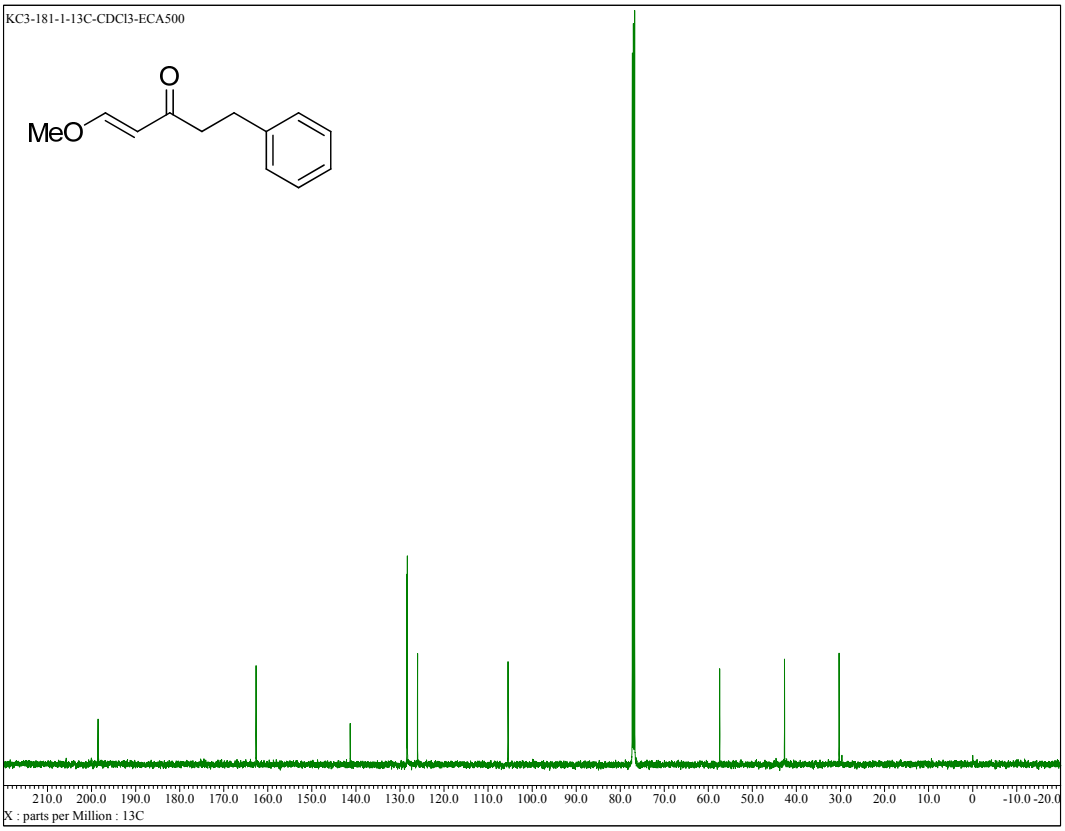
4-Nitrophenyl 3-Methoxyacrylate (2o)



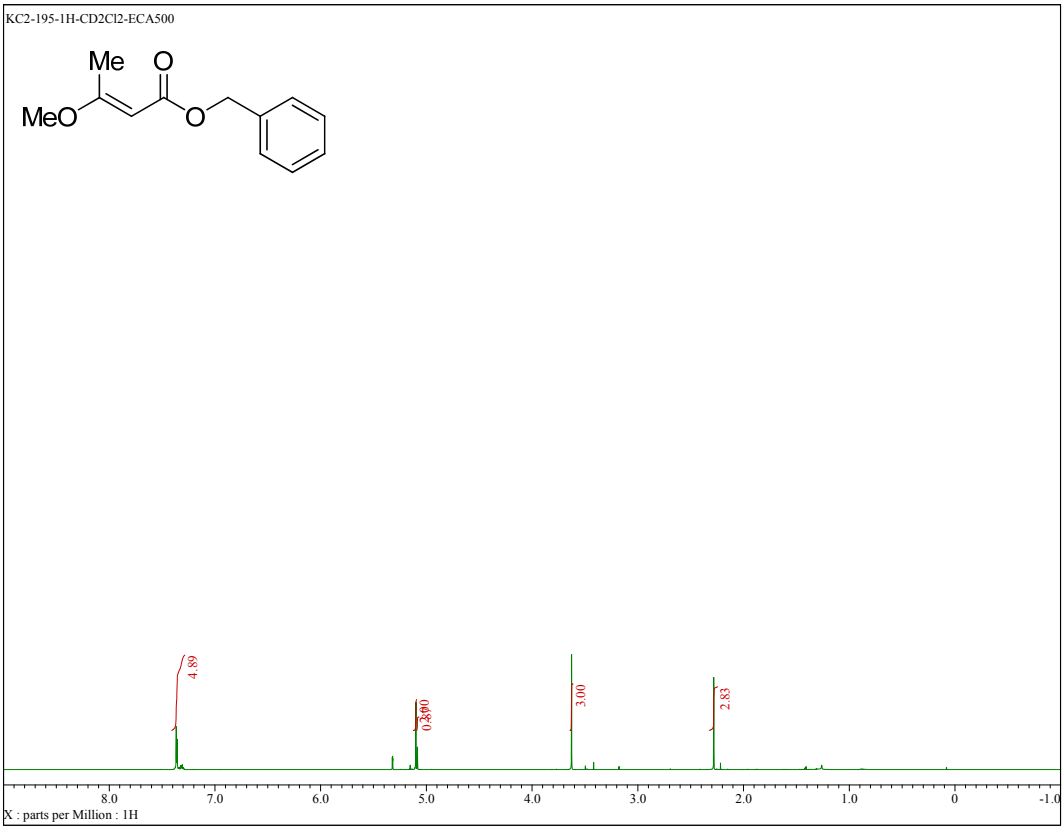


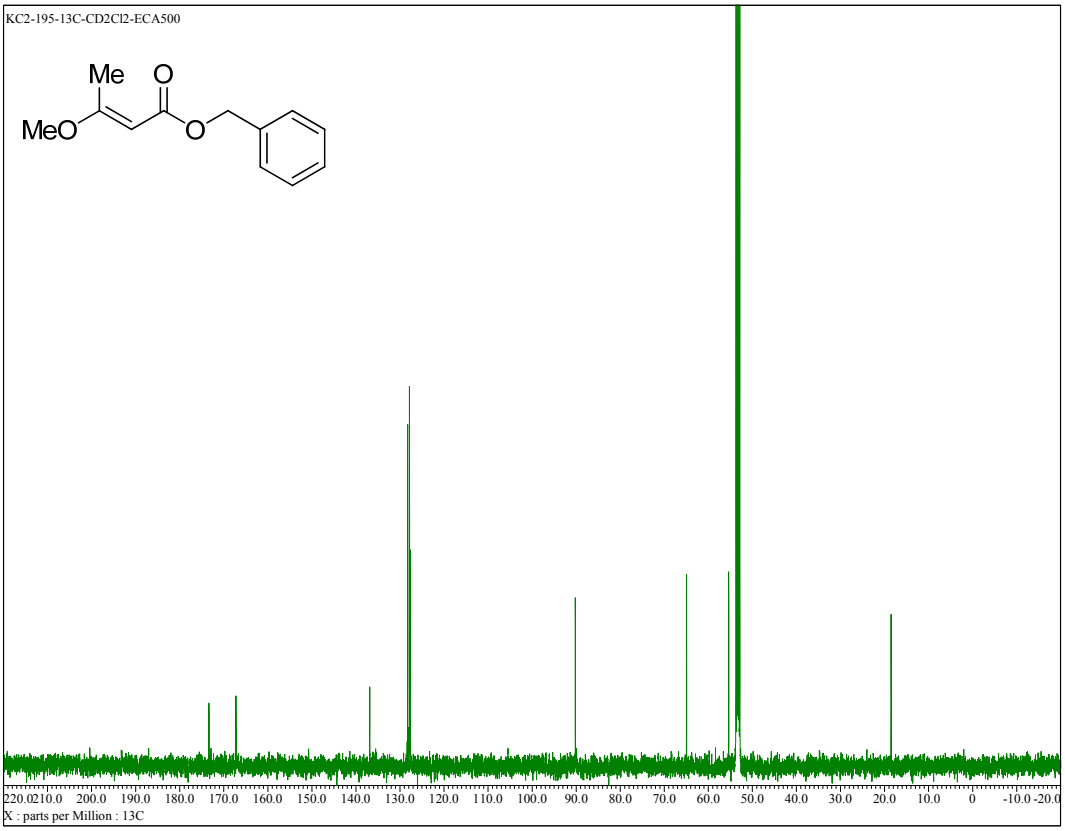
1-Methoxy-5-phenyl-1-pentene-3-on (2p)

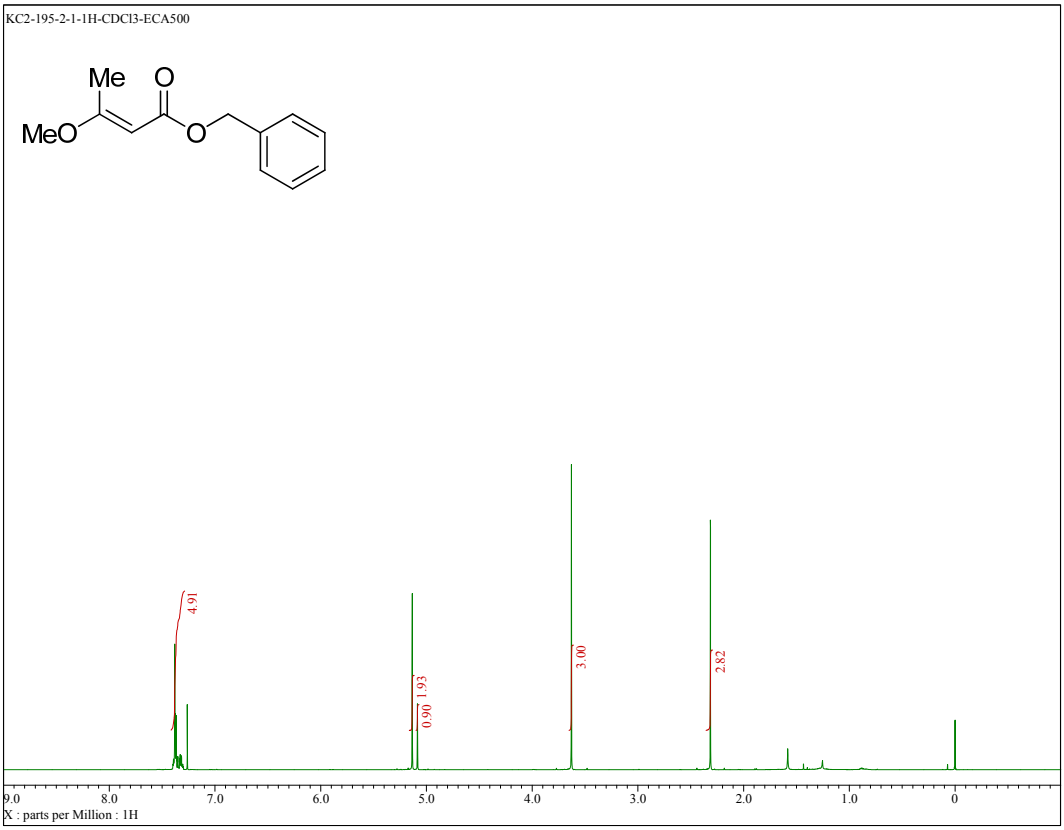


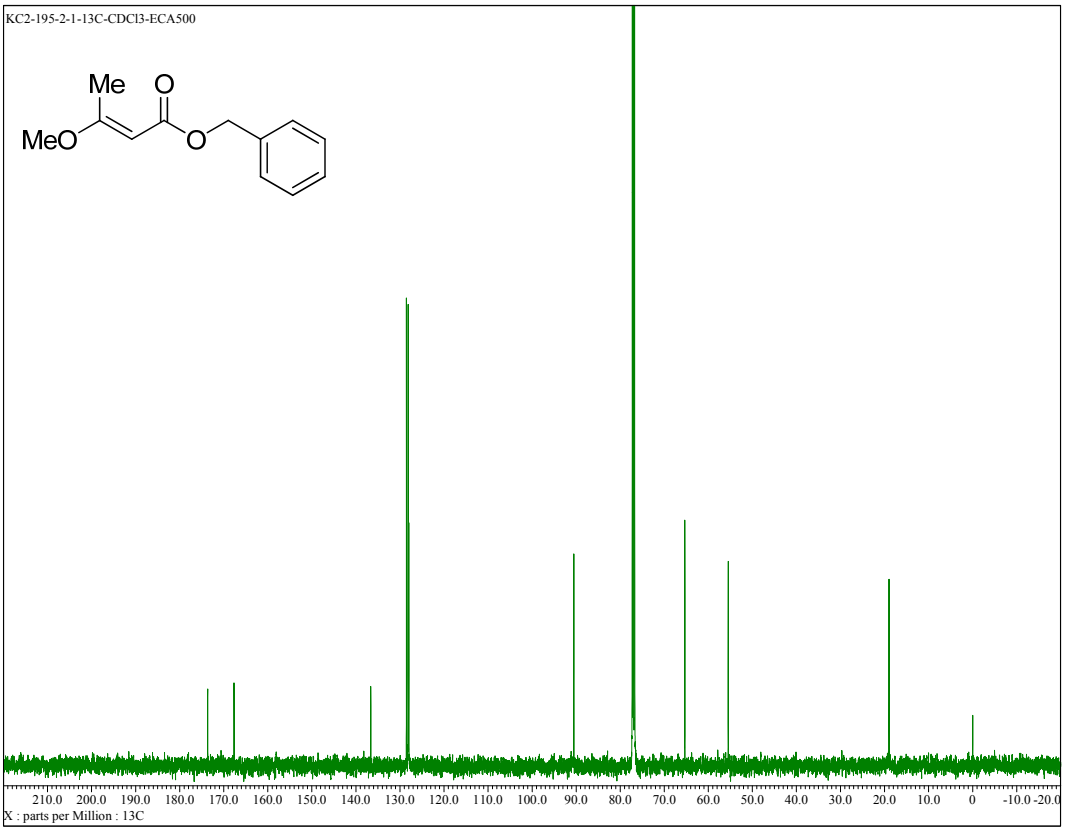


Benzyl 3-Methoxybut-2-enoate (2q)

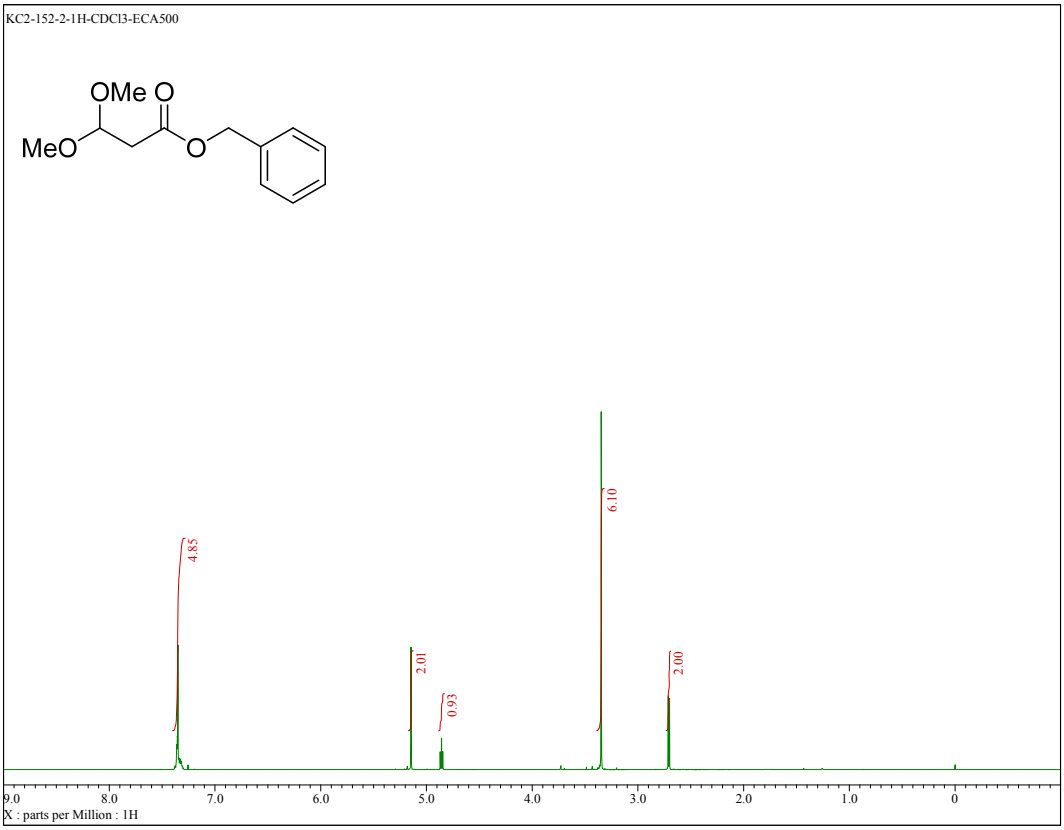


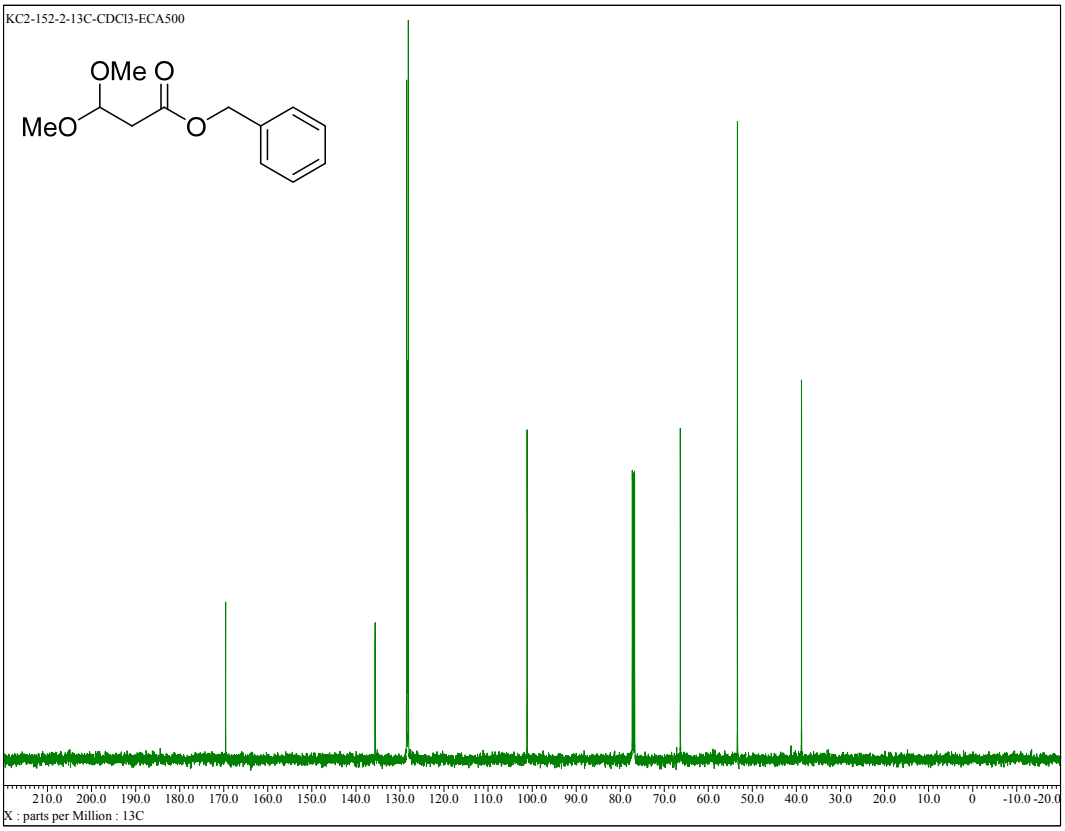



KC2-195-2-1-1H-CDCl3-ECA500
Me
O
MeO
O
4.91
0.90
1.93
3.00
2.82
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H

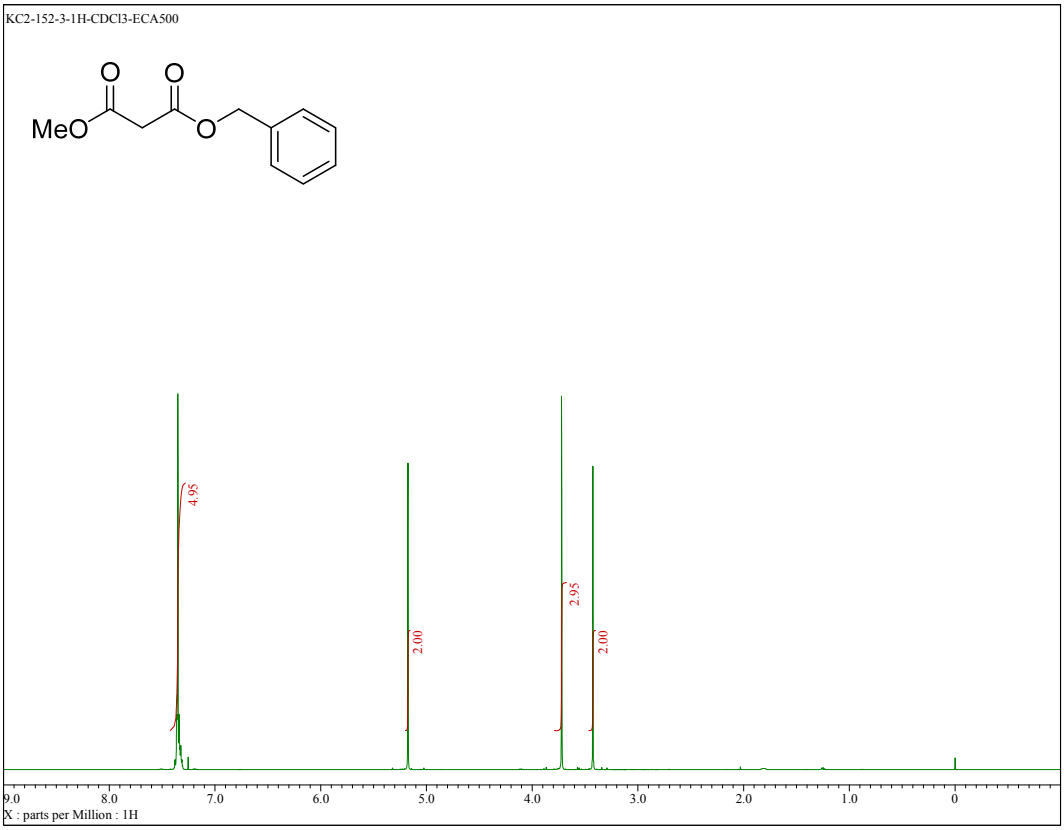

KC2-195-2-1-13C-CDCl3-ECA500
Me
O
MeO
O
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
X : parts per Million : 13C

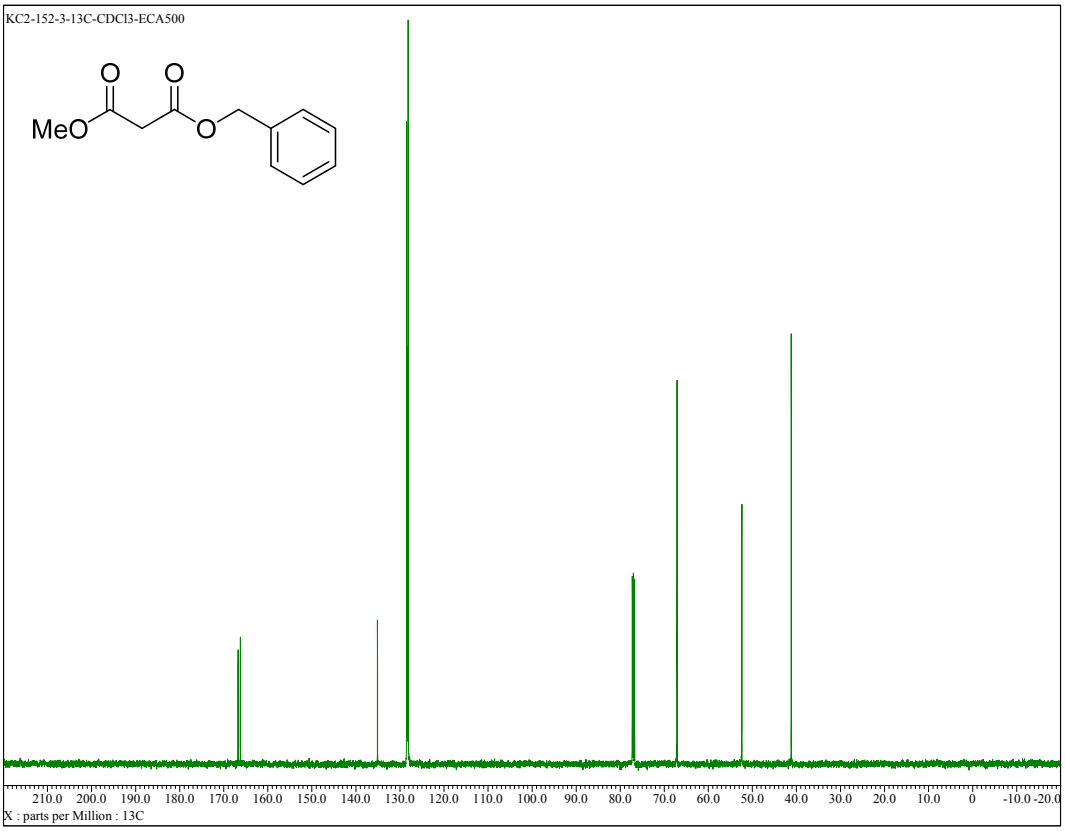
Benzyl 3,3-Dimethoxypropionate (3)



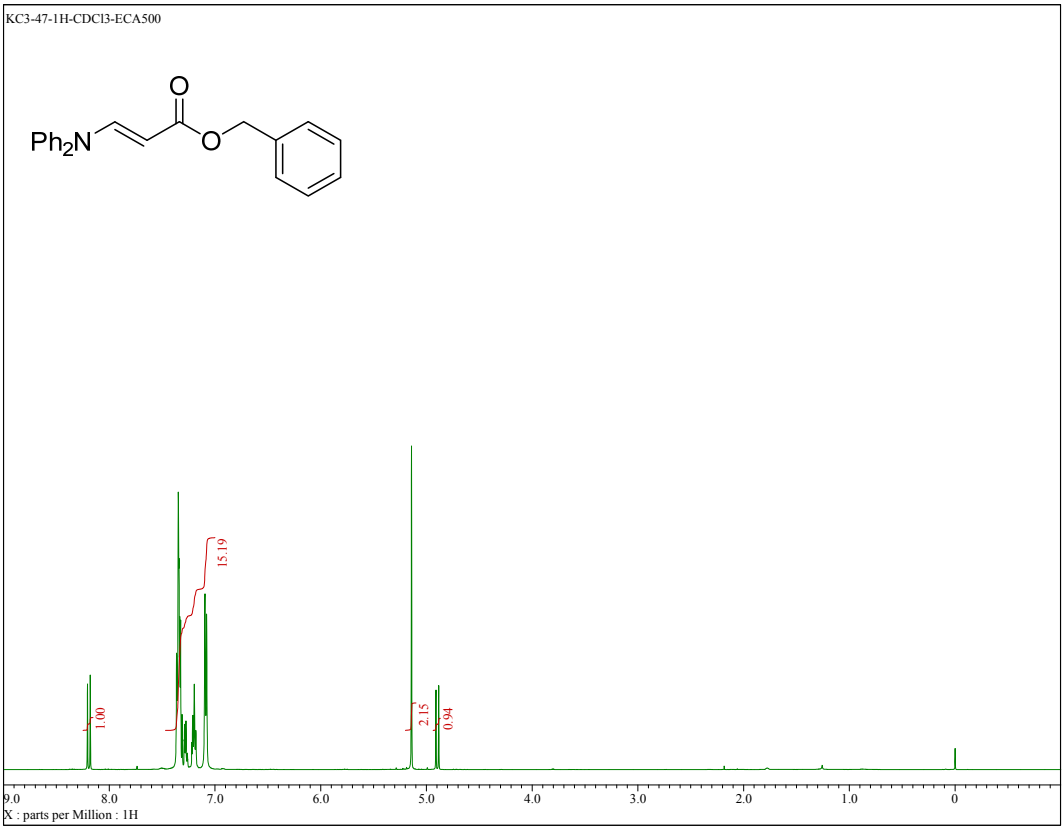


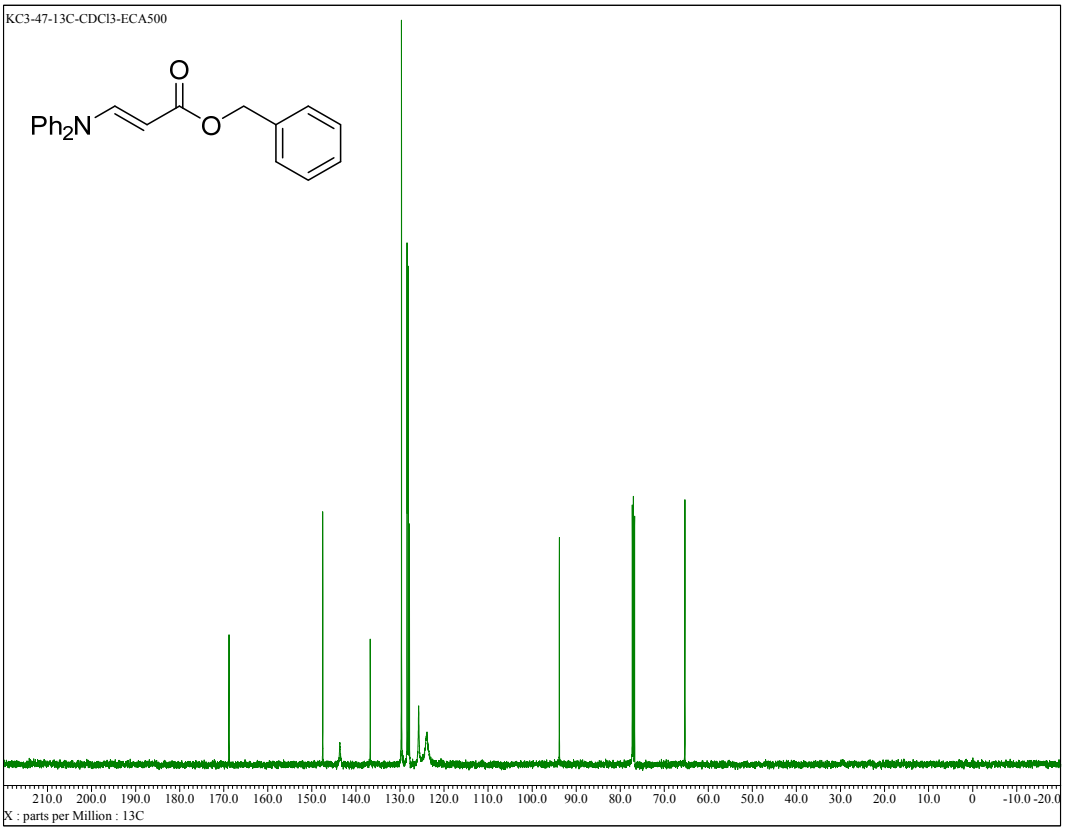
Benzyl Methyl Malonate (4)





Benzyl 3-Diphenylaminoacrylate





(*E*)-Benzyl Cinnamate