Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

Metal free stereoselective synthesis of functionalized enamides

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A. General procedure for the synthesis of α-halo-β- amidoalkenes. N-halosuccinimide (2.0 mmol) and DABCO (134.6 mg, 1.2 mmol) were added to a solution of acrylonitrile (66.3 μl, 1.0 mmol) or ester (1.0 mmol) in acetonitrile (2-3 ml) and the reaction mixture was stirred for 12 h at room temperature. The reaction mixture was partitioned between water and ethylacetate (3×10ml). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude products obtained were subjected to column chromatography (ethylacetate / hexane; 10:90, v/v) to afford the pure products (**2a -2t**).

(*E*)-2-bromo-3-(2,5-dioxopyrrolidin-1-yl)acrylonitrile (2a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (s, 1H), 2.9 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4 (2C), 132.7, 113.1, 86.3, 28.2 (2C); IR (KBr) 3049, 2227, 1729, 1625, 1353, 1323 cm^{-1}; HRMS (ESI+) calcd. for $C_7H_5BrN_2O_2$ $[M]^+$ 229.0308, found 229.0301.

(*E*)-2-chloro-3-(2, 5-dioxopyrrolidin-1-yl)acrylonitrile (2b). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.9 (s, 1H), 2.75 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.0 (2C), 142.2, 114.2, 89.0, 29.4 (2C); IR (KBr) 3055, 2222, 1726, 1619, 1412, 1364, 1299, 843 cm^{-1}; HRMS (ESI+) calcd. for $C_7H_5ClN_2O_2$ $[M]^+$ 184.5798, found 184.5793.

(*E*)-3-(2,5-dioxopyrrolidin-1-yl)-2-iodoacrylonitrile (2c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.3 (s, 1H), 2.79 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.4 (2C), 139.4, 115.0, 89.7, 29.7 (2C); IR (KBr) 3054, 2232, 1741, 1623, 1362 cm^{-1}; HRMS (ESI+) calcd. for $C_7H_5IN_2O_2$ $[M]^+$ 276.0313, found 276.0311.

(*E*)-methyl-2-bromo-3-(2,5-dioxopyrrolidin-1-yl)acrylate (2d). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 3.85 (s, 3H), 2.84 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1(2C), 161.8, 131.3, 116.8, 53.6, 28.7 (2C); IR (KBr) 3480, 3452, 3067, 1772, 1721, 1619, 1434, 1378 cm^{-1}; HRMS (ESI+) calcd. for $C_8H_8BrNO_4$ $[M]^+$ 262.0574, found 262.0571.

(*E*)-methyl 2-chloro-3-(2,5-dioxopyrrolidin-1-yl)acrylate (2e). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 3.84 (s, 3H), 2.84 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3 (2C), 161.6, 127.7, 124.7, 53.6, 28.6 (2C); IR (KBr) 3473, 3446, 3036, 1769, 1735, 1622, 1435, 1233 cm^{-1}; HRMS (ESI+) calcd. for $C_8H_8ClNO_4$ $[M]^+$ 217.6064, found217.6058.

(*E*)-methyl-3-(2,5-dioxopyrrolidin-1-yl)-2-iodoacrylate (2f). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 3.76 (s, 3H), 2.82 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4 (2C), 167.2, 131.1, 110.2, 51.9, 27.7 (2C); IR (KBr) 3397, 3077, 2951, 1767, 1713, 1636, 1427, 1221 cm^{-1}; HRMS (ESI+) calcd. for $C_8H_8INO_4$ $[M]^+$ 309.0579, found 309.0571.

(*E*)-ethyl-2-bromo-3-(2,5-dioxopyrrolidin-1-yl)acrylate (2g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 4.32 (q, 2H, J = 8.0 Hz), 2.89 (s, 4H), 1.3 (t, 3H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2 (2C), 161.0, 131.4, 116.8, 63.1, 28.7 (2C), 13.9; IR (KBr) 3373, 3176, 1756, 1723, 1622, 1412, 1372 cm^{-1}; HRMS (ESI+) calcd. for $C_9H_{10}BrNO_4$ $[M]^+$ 276.0840, found 276.0821.

(*E*)-tert-butyl 2-bromo-3-(2,5-dioxopyrrolidin-1-yl)acrylate (2h). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.9 (s, 1H), 2.75 (s, 4H), 1.24 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.1(2C), 172.8, 138.8, 115.9, 83.0, 29.3 (3C), 28.1; IR (KBr) 3053, 1723, 1752, 1645, 1431, 1372, 1332, 1243 cm^{-1}; HRMS (ESI+) calcd. for $C_{11}H_{14}BrNO_4$ $[M]^+$ 304.1372, found 304.1361.

(*E*)-butyl 2-bromo-3-(2,5-dioxopyrrolidin-1-yl)acrylate (2i). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.6 (s, 1H), 4.21 (t, 2H, *J* = 8.2 Hz), 2.9 (s, 4H), 1.5 (m, 2H), 1.3 (m, 2H), 0.98 (t, 3H, *J* = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9 (2C), 170.4, 153.3, 130.8, 66.7, 31.2, 28.5 (2C), 21.9, 13.7; IR (KBr) 3397, 3077, 2951, 1761, 1732, 1622, 1618 cm^{-1}; HRMS (ESI+) calcd. for $C_{11}H_{14}BrNO_4$ $[M]^+$ 304.1373, found 304.1353.

(*E*)-hexyl 2-bromo-3-(2,5-dioxopyrrolidin-1-yl)acrylate (2j). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 4.16 (t, 2H, *J* = 8.0 Hz), 2.95 (s, 4H), 1.6 (m, 2H), 1.3 (m, 6H), 0.99 (t, 3H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0 (2C), 172.9, 154.2, 132.0, 68.3, 31.5, 29.3 (2C), 29.1, 26.3, 23.3,14.8; IR (KBr) 3086, 1760, 1747,1627, 1213, 1121 cm^{-1}; HRMS (ESI+) calcd. for $C_{13}H_{18}BrNO_4$ $[M]^+$ 332.1903, found 332.1891.

(*E*)-octyl 2-bromo-3-(2,5-dioxopyrrolidin-1-yl)acrylate (2k). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 4.26 (t, 2H, *J* = 8.0 Hz), 2.8 (s, 4H), 1.73-1.67 (m, 2H), 1.40-1.29 (m, 10H), 0.88 (t, 3H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.0 (2C), 172.6, 152.8, 130.9, 67.4, 31.4, 28.9 (2C), 28.7 (2C), 28.4, 25.9, 22.7, 14.1; IR (KBr) 2947, 2863, 1737,1624, 1452, 1371, 1232, 1223 cm^{-1}; HRMS (ESI+) calcd. for $C_{15}H_{22}BrNO_4$ $[M]^+$ 360.2435, found 360.2416.

(*E*)-benzyl 2-bromo-3-(2,5-dioxopyrrolidin-1-yl)acrylate (2l). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.38 (m, 5H), 5.28 (s, 2H), 2.85 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7 (2C), 172.8, 160.7, 134.4, 131.4 (2C), 128.5 (3C), 116.9, 68.9, 28.3(2C); IR (KBr) 3160, 3076, 3035, 2951, 1782, 1717, 1624, 1494, 1457, 1373, 1123, 843 cm^{-1}; HRMS (ESI+) calcd. for $C_{14}H_{12}BrNO_4$ $[M]^+$ 338.1534, found 338.1517.

(*E*)-cyclopentyl 2-bromo-3-(2,5-dioxopyrrolidin-1-yl)acrylate (2m). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 4.92 (m, 1H), 2.93 (s, 4H), 1.89 (m, 2H), 1.5 (m, 4H), 1.2 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9 (2C), 160.2, 130.5, 117.8, 75.5, 31.0 (2C), 28.7 (2C), 23.3 (2C); IR (KBr) 3337, 2942, 2863, 1783, 1723, 1631, 1526 cm^{-1}; HRMS (ESI+) calcd. for $C_{12}H_{14}BrNO_4$ $[M]^+$ 316.1479, found 316.1453.

(*E*)-cyclohexyl 2-bromo-3-(2,5-dioxopyrrolidin-1-yl)acrylate (2n). ^{1}H NMR **(**400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 4.94 - 4.90 (m, 1H), 2.87 (s, 4H), 1.89-1.75 (m, 2H), 1.75 (m, 2H), 1.53 (m, 3H), 1.39-1.35 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1 (2C), 160.4, 130.8, 118.6, 75.8, 31.2 (2C), 28.7 (2C), 24.9, 23.3 (2C); IR (KBr) 3332, 2937, 2858, 1786, 1721, 1628, 1573, 1378 cm^{-1}; HRMS (ESI+) calcd. for $C_{13}H_{16}BrNO_4$ $[M]^+$ 330.1744, found 330.1720.

(*E*)-4-bromophenyl 2-bromo-3-(2,5-dioxopyrrolidin-1-yl)acrylate (2o). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.53 (d, 2H, *J* = 8.0 Hz), 7.07 (d, 2H, *J* = 8.0 Hz), 2.91 (s, 4H); ^{13}C NMR

(100 MHz, $CDCl_3$) δ 172.8 (2C), 159.6, 149.5, 132.9, 132.7 (2C), 122.9 (2C), 119.7, 115.8, 28.7(2C); FT-IR (KBr) 3090, 3030, 2947, 1898, 1740, 1712, 1624, 1480, 1392, 1239,1223, 862 cm^{-1}; HRMS (ESI+) calcd. for $C_{13}H_9Br_2NO_4$ $[M]^+$ 403.0229, found 403.0225.

(*E*)-2-chlorophenyl 2-bromo-3-(2,5-dioxopyrrolidin-1-yl)acrylate (2p). ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.45 (m, 1H), 7.30 (m, 1H), 7.24 (m, 2H), 2.88 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7 (2C), 159.3, 146.8, 133.3, 130.4, 127.9, 127.7, 126.6, 123.1, 114.7, 28.6 (2C); IR (KBr) 3453, 3342, 3052, 2929, 2827, 1753, 1714, 1681, 1633, 1604, 1432, 1134, 843, 826 cm^{-1}; HRMS (ESI+) calcd. for $C_{13}H_9BrClNO_4$ $[M]^+$ 358.5719, found 358.5703.

(*E*)-naphthalen-1-yl 2-bromo-3-(2,5-dioxopyrrolidin-1-yl)acrylate (2q). ^1H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.93 (m, 2H), 7.89 (m, 1H), 7.57 (m, 3H), 7.39 (m, 1H), 2.92 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7 (2C), 159.8, 146.1,134.2, 132.9 (2C), 127.9, 126.9 (2C), 126.6, 125.3,121.0, 117.6, 115.7, 28.3 (2C); IR (KBr) 3058, 1786, 1726, 1624, 1592, 1223, 862. cm^{-1}; HRMS (ESI+) calcd. for $C_{17}H_{12}BrNO_4$ $[M]^+$ 374.1855, found 374.1850.

(*E*)-2-nitrophenyl 2-bromo-3-(2,5-dioxopyrrolidin-1-yl)acrylate (2r). ^1H NMR (400 MHz, $CDCl_3$) δ 8.81 (s, 1H), 8.41 (m, 2H), 8.63 (m, 2H), 2.65 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2 (2C), 157.4, 150.9, 146.2, 139.4, 134.3, 127.9 (2C), 118.2 (2C), 112.0, 28.4(2C); IR (KBr) 3429, 3086, 2928, 2854, 1726, 1719, 1531, 1429, 1378, 1346, 866, 853 cm^{-1}; HRMS (ESI+) calcd. for $C_{13}H_9BrN_2O_6$ $[M]^+$ 369.1244, found 369.1224.

(*E*)-2-acetylphenyl 2-bromo-3-(2,5-dioxopyrrolidin-1-yl)acrylate (2s). ^1H NMR **(**400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.89 (m, 1H), 7.60 (m, 1H), 7.41 (m, 1H), 7.28 (m, 1H), 2.93 (s, 4H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 172.4 (2C), 160.1, 148.5, 133.6, 133.1, 130.3, 130.0, 126.7, 123.5, 115.1, 29.3, 28.7 (2C); IR (KBr) 3492, 3355, 3053, 2933, 2854, 1796, 1717, 1684, 1629, 1601, 1387, 1121, 856, 863 cm^{-1}; HRMS (ESI+) calcd. for $C_{15}H_{12}BrNO_5$ $[M]^+$ 366.1665, found 366.1611.

(*E*)-17-(5-ethyl-6-methylheptan-2-yl)-10,13-dimethylhexadeca- hydro-1H-cyclopenta[a]-phenanthren-3-yl 2-bromo-3-(2,5-dioxopyrrolidin-1-yl)acrylate (2t). ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 4.84 (m, 1H), 2.87 (s, 4H),1.9-1.7 (m, 4H), 1.6 (m, 4H), 1.5 (m, 4H), 1.4-1.1 (m, 11H), 1.00 (m, 2H), 0.92 (m, 5H), 0.83 (m, 4H), 0.75 (m, 10H), 0.66 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8 (2C), 160.3, 130.8, 118.5, 77.2, 56.4, 56.1, 54.1, 45.8, 44.5, 42.5, 39.9, 36.6, 36.1 (2C), 35.4, 33.9, 33.7, 31.9, 29.1, 28.7, 28.5 (2C), 28.2, 27.3, 26.1, 24.2, 23.0, 21.2, 19.7, 19.0,18.7,12.2, 12.0, 11.9; IR (KBr) 2947, 2863, 1750,1721,1633, 1466, 1387, 1242, 1213, 1121 cm^{-1}; HRMS (ESI+) calcd. for$C_{36}H_{56}BrNO_4$ $[M]^+$ 646.7381, found 646.7352.

General procedure for Sonogoshira coupling reaction. An alkyne solution (1.2 mmol) in 1,4-dioxane (0.5 mL) was added to a stirred solution of **2a** (229 mg, 1.0 mmol) or **2c** (276 mg, 1.0 mmol), CuI (19.4 mg, 0.1 mmol), $Pd(PPh_3)_4$ (23 mg, 0.02 mmol) and triethylamine (418 µl, 3 mmol) in 1,4-dioxane (5.0 ml) under nitrogen atmosphere. After completion of the reaction (2-3h), the reaction mixture was quenched by adding saturated solution of sodium bicarbonate and

extracted with ethyl acetate (3×10ml). The combined organic layer was dried over sodium sulphate, concentrated under reduced pressure and subjected to silica gel (60-120 mesh) column chromatography (ethyl acetate/hexane; 10:90, v/v) to afford pure products (**5a-5f**) in 81-85% yield.

(*Z*)-2-(2,5-dioxopyrrolidin-1-yl)methylene)-4-(4-methoxyphenyl)but-3-ynenitrile (5a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.49 (d, 2H, J = 8.0 Hz), 6.87 (d, 2H, J = 8.0 Hz), 3.84 (s, 3H), 3.09 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1 (2C), 160.2, 150.7, 134.0 (2C), 115.5, 114.1(2C), 113.9, 113.0, 90.8, 81.0, 55.3, 27.4 (2C); IR (KBr) 2225, 2215, 1736,1591, 1463, 823 cm^{-1}; HRMS (ESI+) calcd. for $C_{16}H_{12}N_2O_3$ $[M]^+$ 280.2781, found 280.2769.

(*Z*)-2-(2,5-dioxopyrrolidin-1-yl)methylene)-4-phenylbut-3-ynenitrile (5b). ^{1}H NMR **(**400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.55 (m, 2H), 7.35 (m, 3H), 2.84 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3 (2C), 153.5, 132.4 (2C), 129.3, 128.4 (2C), 127.1, 121.6, 114.7, 81.5, 73.7, 29.8 (2C); IR (KBr) 2236, 2133, 1734,1651, 1499, 812 cm^{-1}; HRMS (ESI+) calcd. for $C_{15}H_{10}N_2O_2$ $[M]^+$ 250.2521, found 250.2512.

(*Z*)-2-(2,5-dioxopyrrolidin-1-yl)methylene)-4-p-tolylbut-3-ynenitrile (5c). ^{1}H NMR **(**400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.44 (d, 2H, J = 8.0 Hz), 7.16 (d, 2H, J = 8.0 Hz), 2.93 (s, 4H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0 (2C), 148.2, 139.4, 132.4(2C), 129.2 (2C), 124.0, 118.8, 115.0, 88.8, 81.3, 29.7 (2C), 21.5; IR (KBr) 2236, 2133, 1734,1651, 1499, 812 cm^{-1}; HRMS (ESI+) calcd. for $C_{16}H_{12}N_2O_2$ $[M]^+$ 264.2787, found 264.2780.

(*Z*)-2-(2,5-dioxopyrrolidin-1-yl)methylene)-4-(3-fluorophenyl)but-3-ynenitrile (5d). ^{1}H NMR **(**400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.31 (m, 2H), 7.23 (m, 1H), 7.11 (m, 1H), 3.09 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8 (2C), 163.5, 161.0, 130.1, 128.5, 123.4, 119.1, 116.8 (2C), 115.1, 80.6, 74.4, 29.7 (2C); IR (KBr) 2237, 2155, 1731,1623, 832 cm^{-1}; HRMS (ESI+) calcd. for $C_{15}H_9FN_2O_2$ $[M]^+$ 268.2426, found 268.2420.

(*Z*)-4-cyclohexyl-2-((2,5-dioxopyrrolidin-1-yl)methylene)but-3-ynenitrile (5e). ^{1}H NMR **(**400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 2.91 (s, 4H), 2.44 (m, 1H), 1.81-1.71 (m, 4H), 1.47 (m, 2H), 1.27 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2 (2C), 150.2, 128.3, 115.0, 89.1, 82.8, 32.2 (2C), 29.4, 28.3 (2C), 25.7 (2C), 24.7; IR (KBr) 2243, 2201, 2130, 1743, 1633, 826 cm^{-1}; HRMS (ESI+) calcd. for $C_{15}H_{16}N_2O_2$ $[M]^+$ 256.2997, found 256.2991.

(*Z*)-2-(2,5-dioxopyrrolidin-1-yl)methylene)-4-(4-phenoxyphenyl)but-3-ynenitrile (5f). ^{1}H NMR **(**400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.51 (m, 2H), 7.42 (m, 2H), 7.38 (m, 1H), 7.17 (m, 2H), 6.98 (m, 2H), 2.96 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.1 (2C), 158.5, 155.8, 137.2, 133.9 (2C), 129.9 (2C), 123.9, 119.7 (2C), 118.0 (2C), 116.0, 114.0, 112.0, 99.0, 84.7, 28.6 (2C); IR (KBr) 2260, 2229, 1745,1633, 1724, 1512 cm^{-1}; HRMS (ESI+) calcd. for $C_{21}H_{14}N_2O_3$ $[M]^+$ 342.3475, found 342.3469.

General procedure for Suzuki coupling reaction. Phenyl boronic acid (1.1 mmol) in degassed 1,4-dioxane (0.5 mL) was added to a stirred solution of **2a** (229 mg, 1.0 mmol) or **2c**

(276 mg, 1.0 mmol), K_3PO_4 (636.3 mg, 3 mmol), $Pd(PPh_3)_4$ (57.8 mg, 0.05 mmol) and triethylamine (279 µl, 2 mmol) in 1,4-dioxane (5.0 ml) at 70 °C under nitrogen atmosphere. After 3h, the reaction mixture was subjected to normal workup, purified through column chromatography to result the desired products in 82-85% yield.

(*Z*)-3-(2,5-dioxopyrrolidin-1-yl)-2-phenylacrylonitrile (6a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.36 (m, 2H), 7.29-7.20 (m, 3H), 2.99 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1 (2C), 158.1, 148.2, 130.6 (2C), 126.3, 121.3 (2C), 115.7, 113.6, 28.6 (2C); IR (KBr) 3144, 3025, 2239, 1749, 1624, 1619, 845 cm^{-1}; HRMS (ESI+) calcd. for $C_{13}H_{10}N_2O_2$ $[M]^+$ 226.2307, found 226.2269.

(*Z*)-3-(2,5-dioxopyrrolidin-1-yl)-2-(2-(trifluoromethyl)phe- nyl)acrylonitrile (6b). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.67 (m, 1H), 7.35-7.24 (m, 2H), 7.11 (m, 1H), 3.12 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5(2C), 159.1, 151.7, 133.1, 128.2, 125.3, 124.0, 119.5, 117.7, 116.1, 112.7, 30.3(2C); IR (KBr) 3089, 3078, 2245, 1729, 1665, 1619,1187 cm^{-1}; HRMS (ESI+) calcd. for $C_{14}H_9F_3N_2O_2$ $[M]^+$ 294.2287, found 294.2252.

(*Z*)-3-(2,5-dioxopyrrolidin-1-yl)-2-(4-methyl-3-nitrophenyl)- acrylonitrile (6c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.50 (s, 1H), 7.23 (d, 1H, J = 8.0 Hz), 7.04 (d, 1H, J = 8.0 Hz), 3.01 (s, 4H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1 (2C), 154.1, 133.7, 131.1, 125.7, 120.6, 119.0, 118.0 113.2, 111.4, 29.7 (2C), 19.7; IR (KBr) 3163, 3076, 2243, 1738, 1656, 1523, 1357, 1155 cm^{-1}; HRMS (ESI+) calcd. for $C_{14}H_{11}N_3O_4$ $[M]^+$ 285.2548, found 285.2534.

(*Z*)-3-(2,5-dioxopyrrolidin-1-yl)-2-(4-fluoro-3-methylphenyl)- acrylonitrile (6d). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.33 (m, 2H), 7.22 (m, 1H), 3.20 (s, 4H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1 (2C), 158.1, 148.2, 130.6, 126.3, 121.3, 120.3, 115.7, 113.6, 112.0, 28.6 (2C), 16.9; IR (KBr) 3103, 3045, 2246, 1731, 1642, 1187, 1054 cm^{-1}; HRMS (ESI+) calcd. for $C_{14}H_{11}FN_2O_2$ $[M]^+$ 258.2477, found 258.2473.

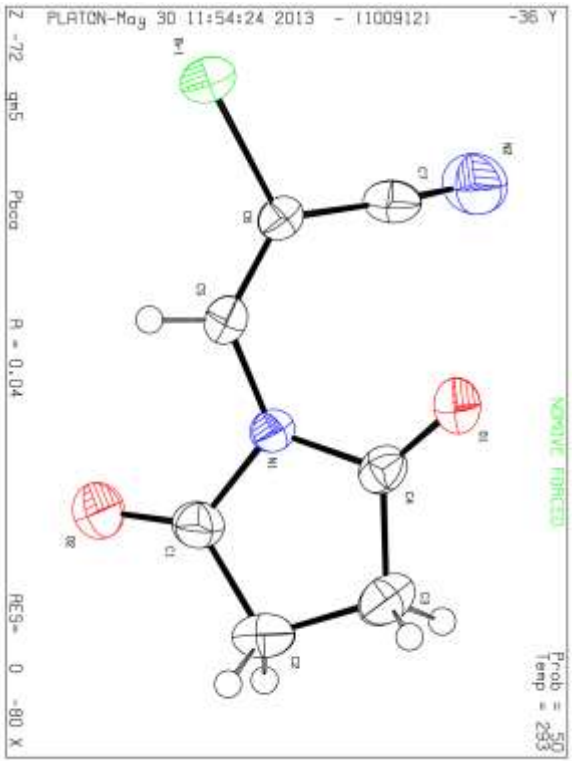


Figure: ORTEP structure of **2a**

Table: Crystal data and structure refinement of 2a.

Identification code	gm5		
CCDC:	942083		
Bond precision:	C-C = 0.0056 A	Wavelength = 0.71073	
Cell:	a =12.8346 (13)	b =7.4175 (9)	c =17.3968 (16)
	Alpha = 90	beta = 90	gamma = 90
Temperature:	293 K		

	Calculated	Reported

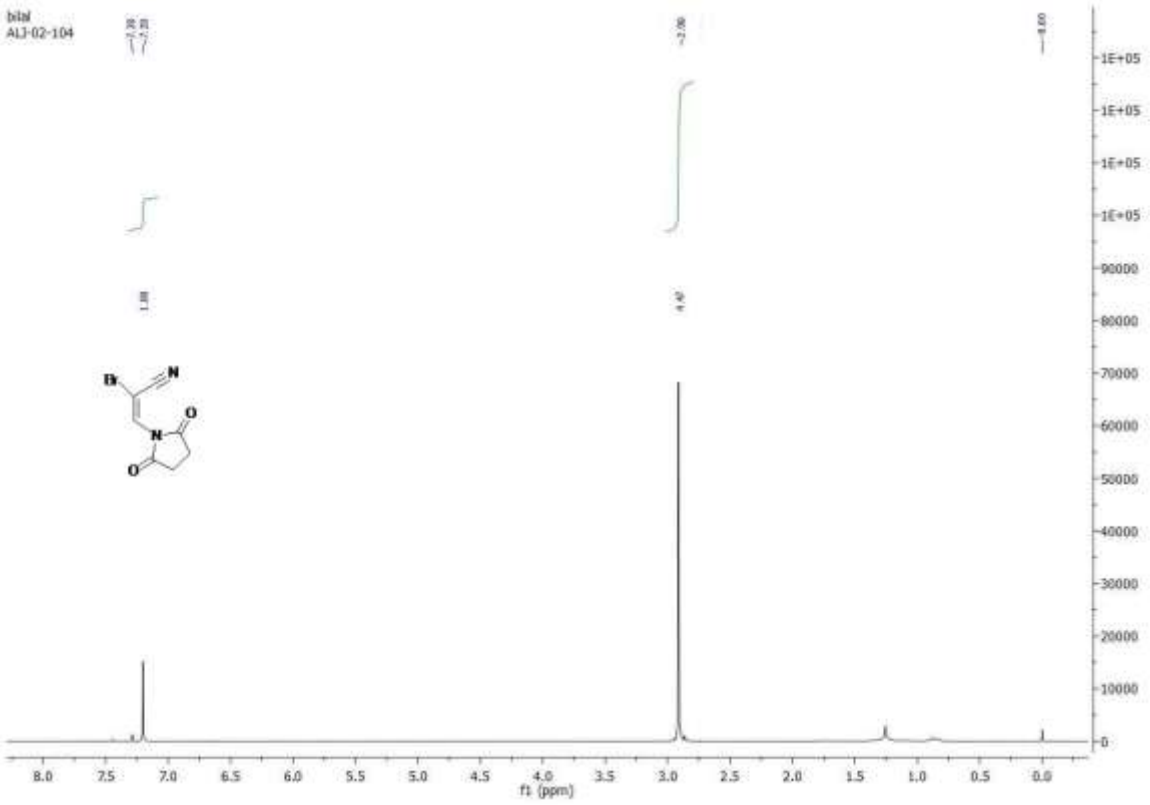
Volume	1656.2 (3)	1656.2 (3)
Space group	P b c a	Pbca
Hall group	-P 2ac 2ab	-
Moiety formula	C7 H5 Br N2 O2	-
Sum formula	C7 H5 Br N2 O2	C7 H5 Br N2 O2
Mr	229.03	229.04
Dx, g cm-3	1.837	1.837
Z	8	8
Mu (mm-1)	4.921	4.921
F000	896.0	896.0
F000’	894.16	
h, k, l max	17, 10, 23	17, 9, 23
Nref	2205	1921
Tmin, Tmax	0.389, 0.374	0.469, 1.000
Tmin’	0.359	

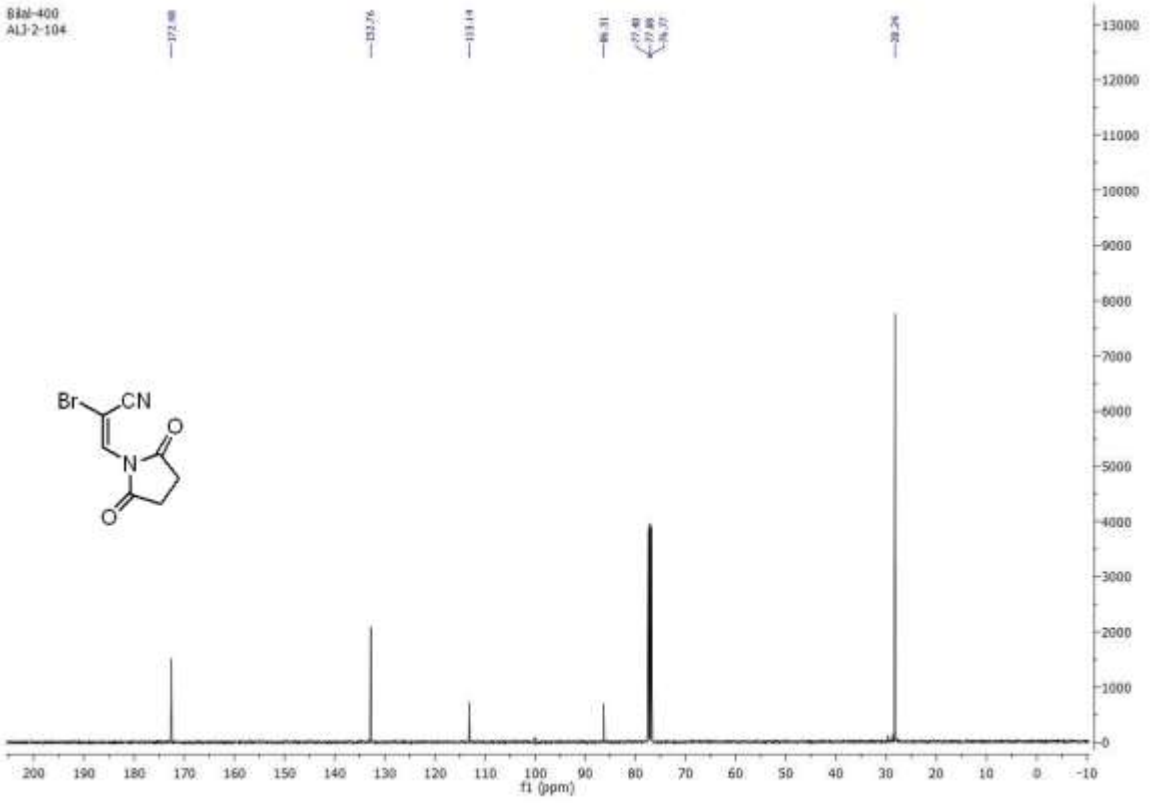
Correction method = MULTI-SCAN

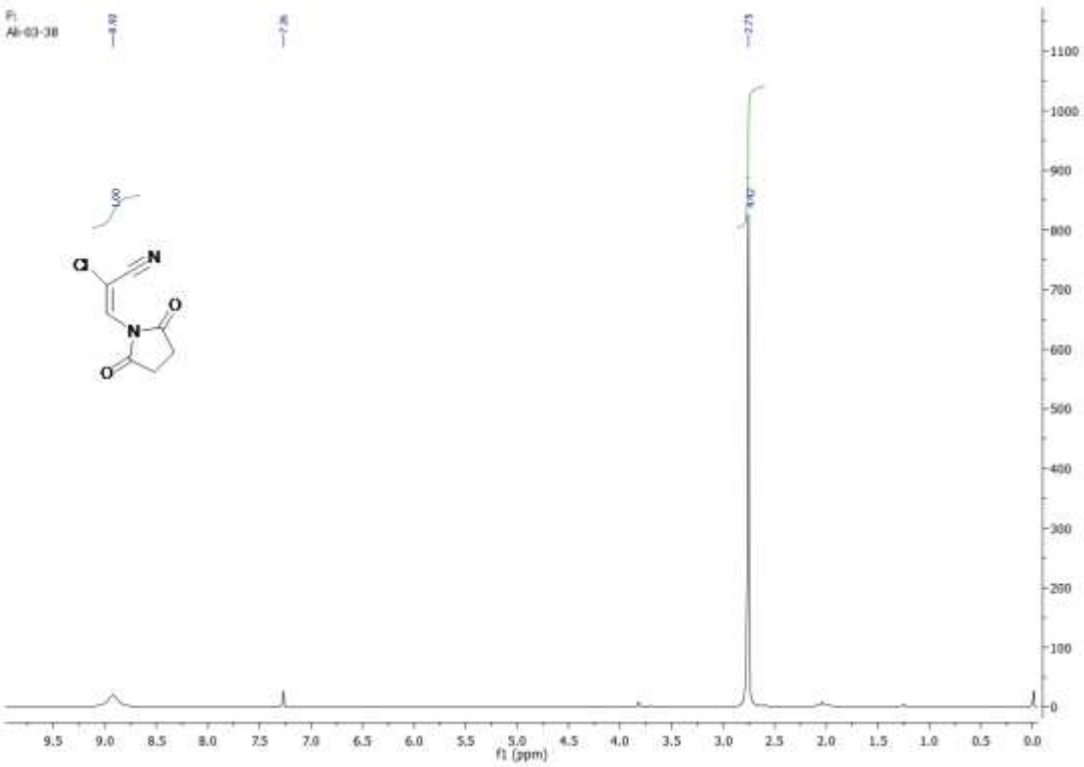
Data completeness = 0.871 Theta (max) = 29.020

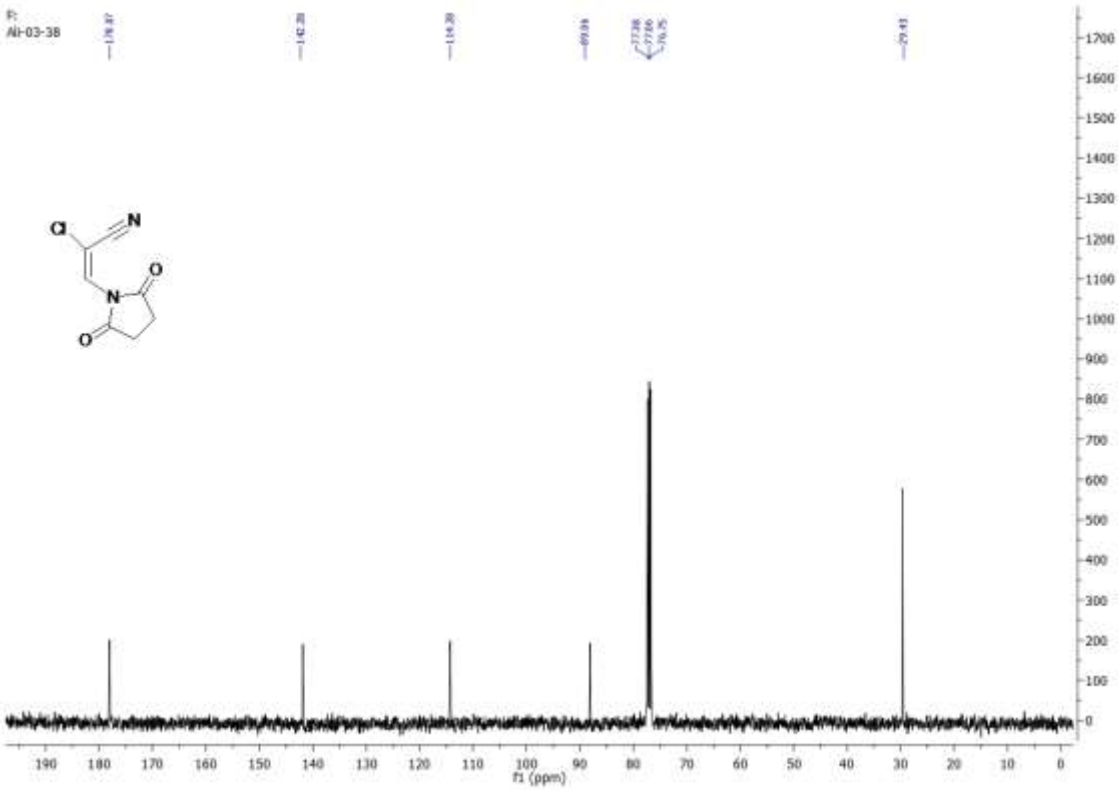
R (reflections) = 0.0437(1324) wR2 (reflections) = 0.1071(1921)

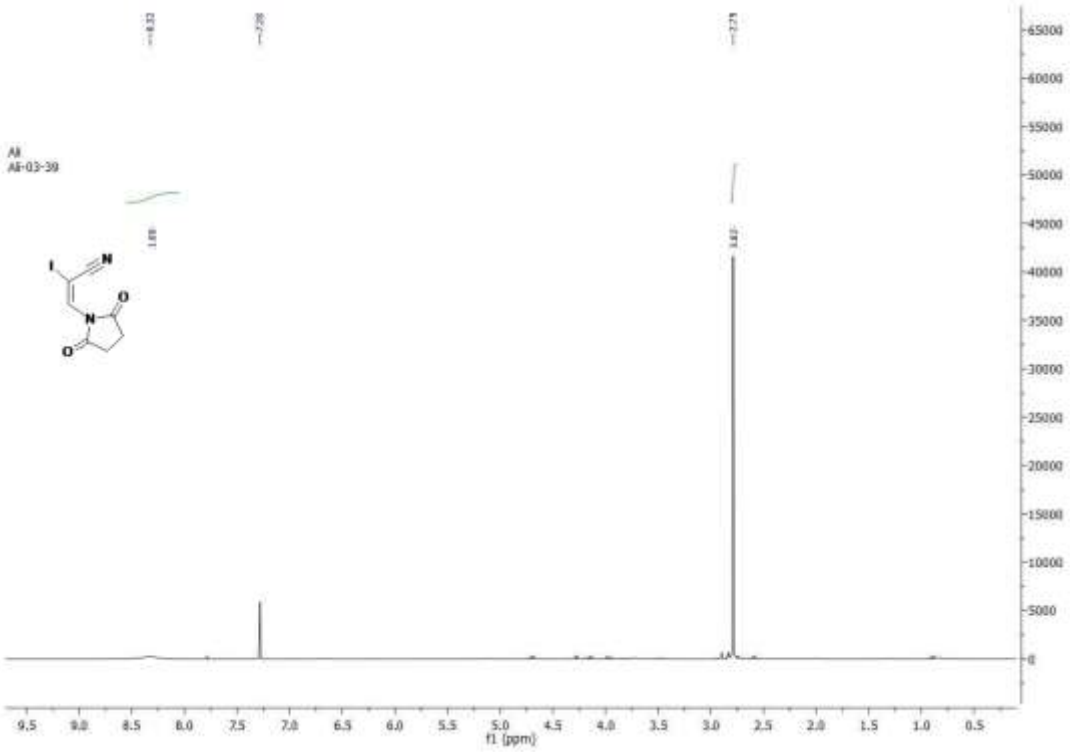
S = 1.051 Npar = 113

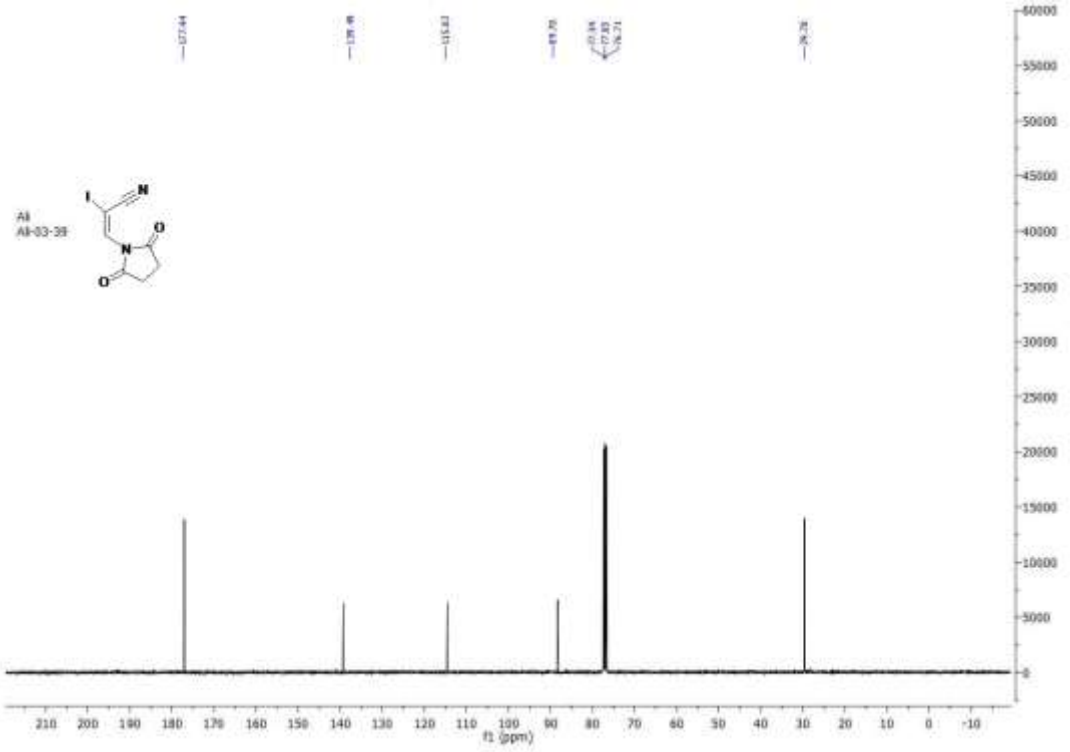


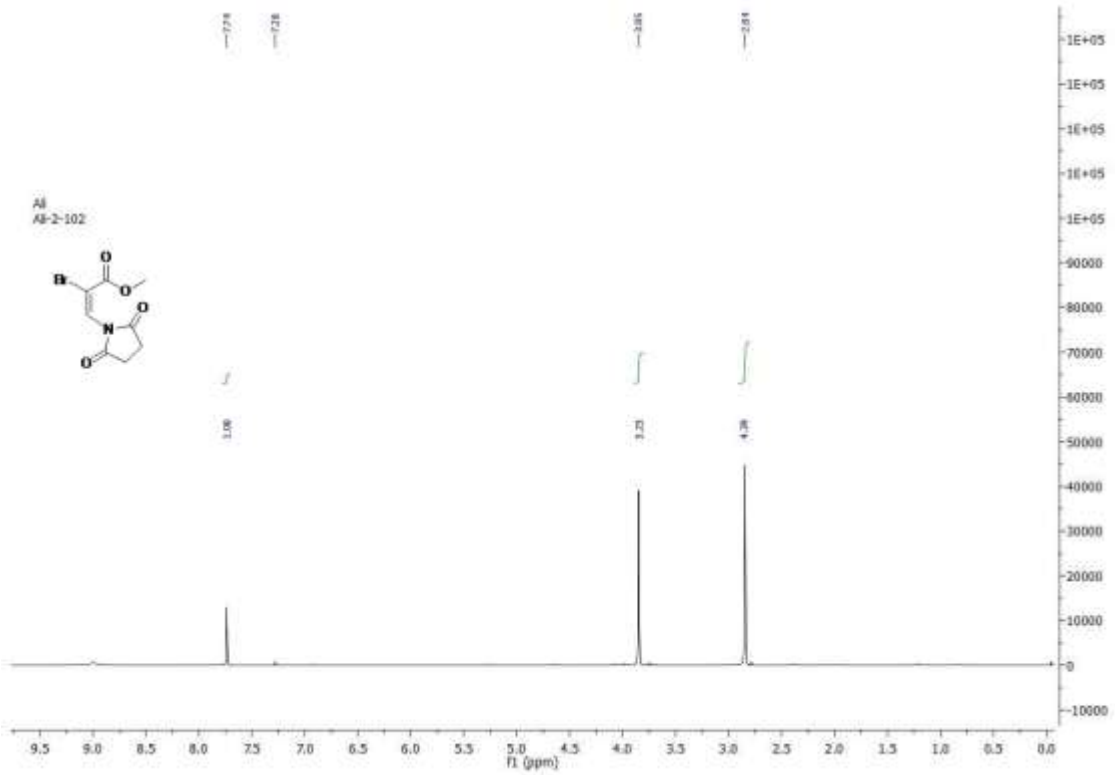


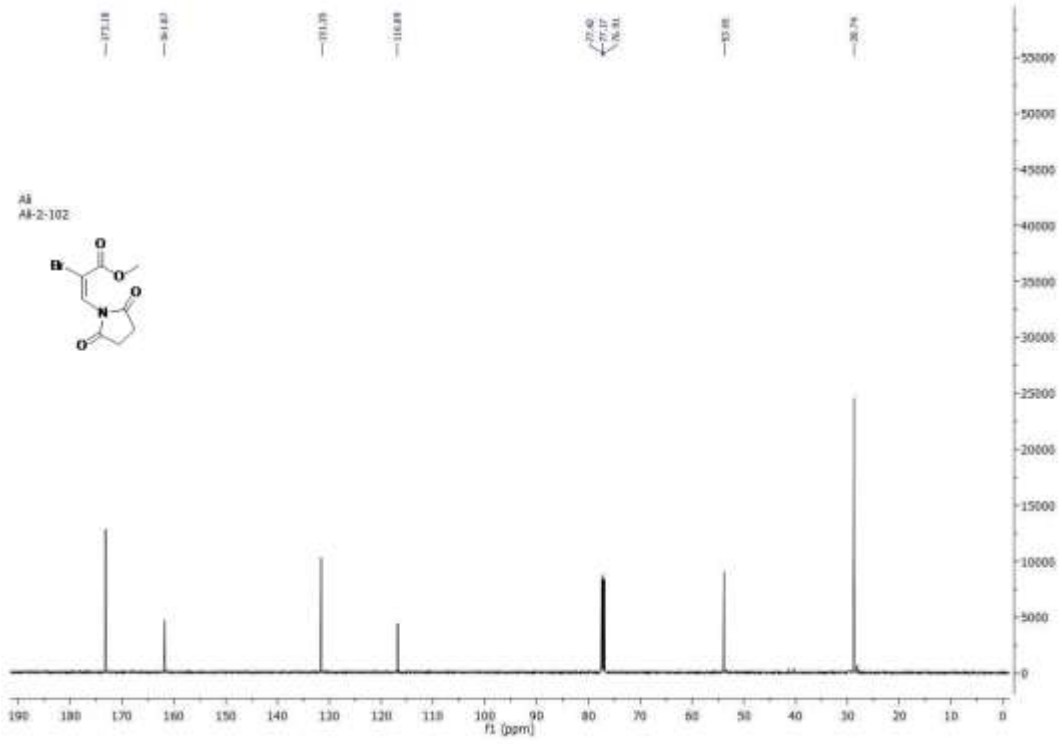


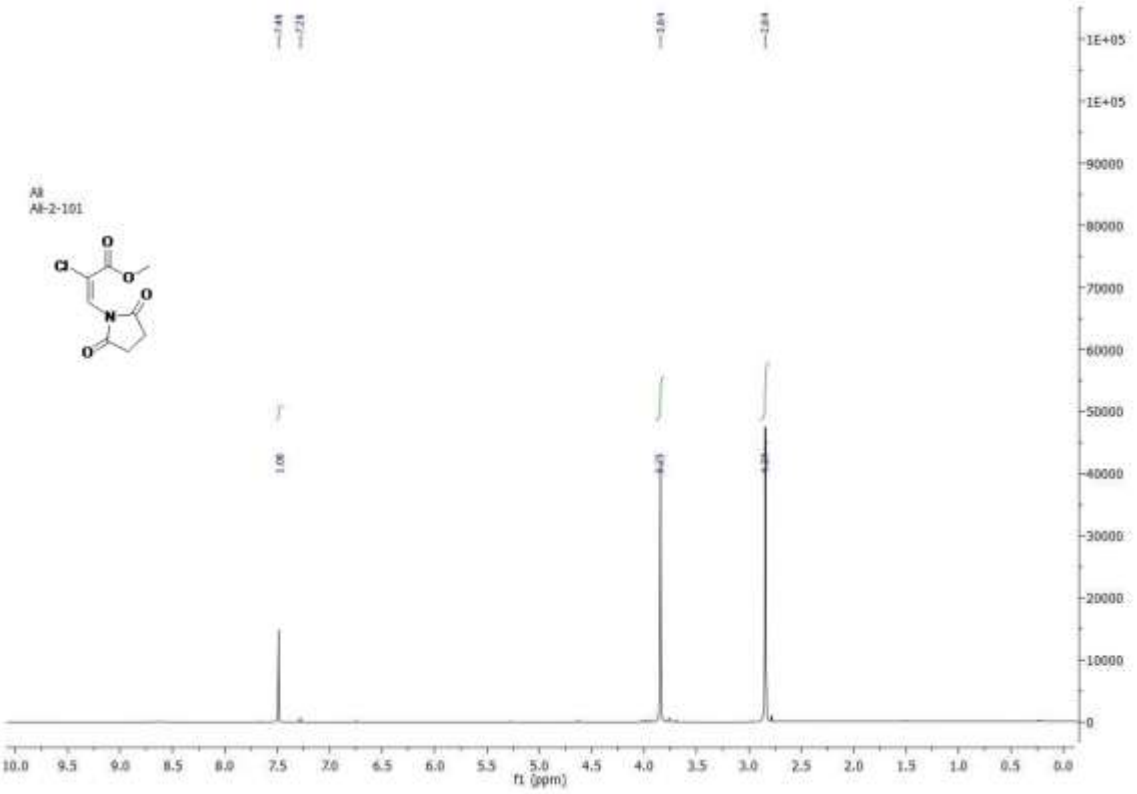


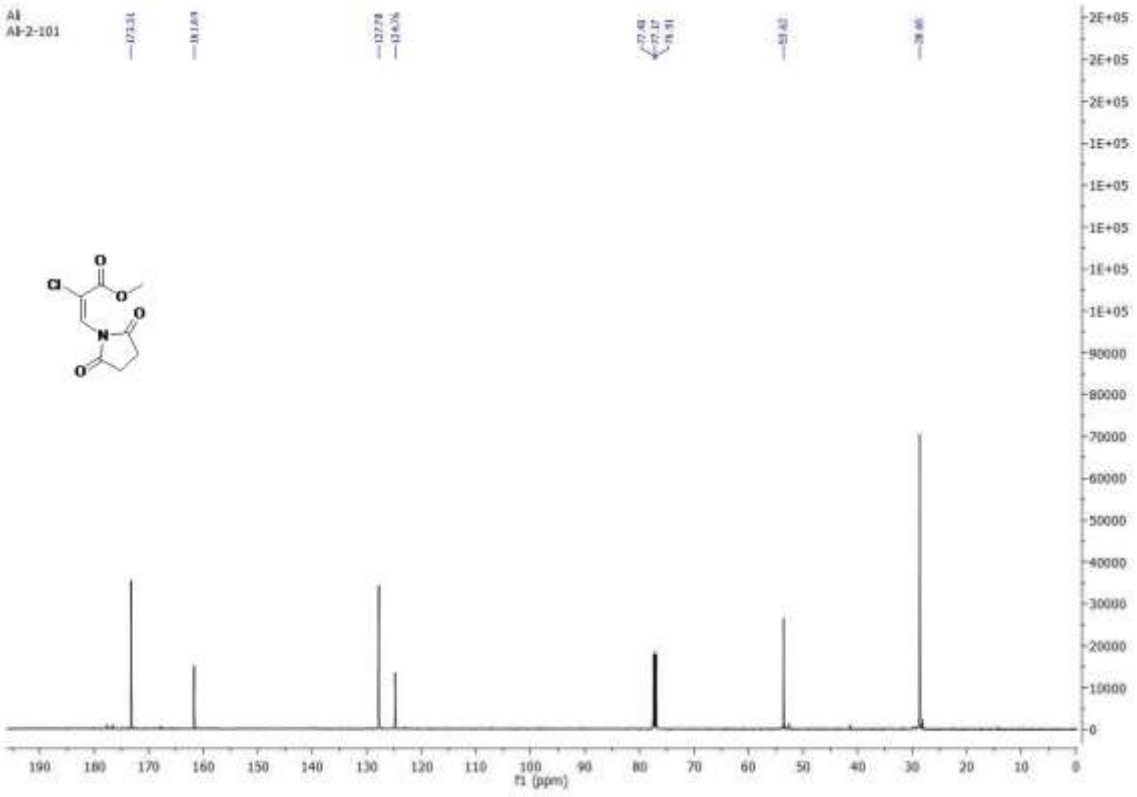


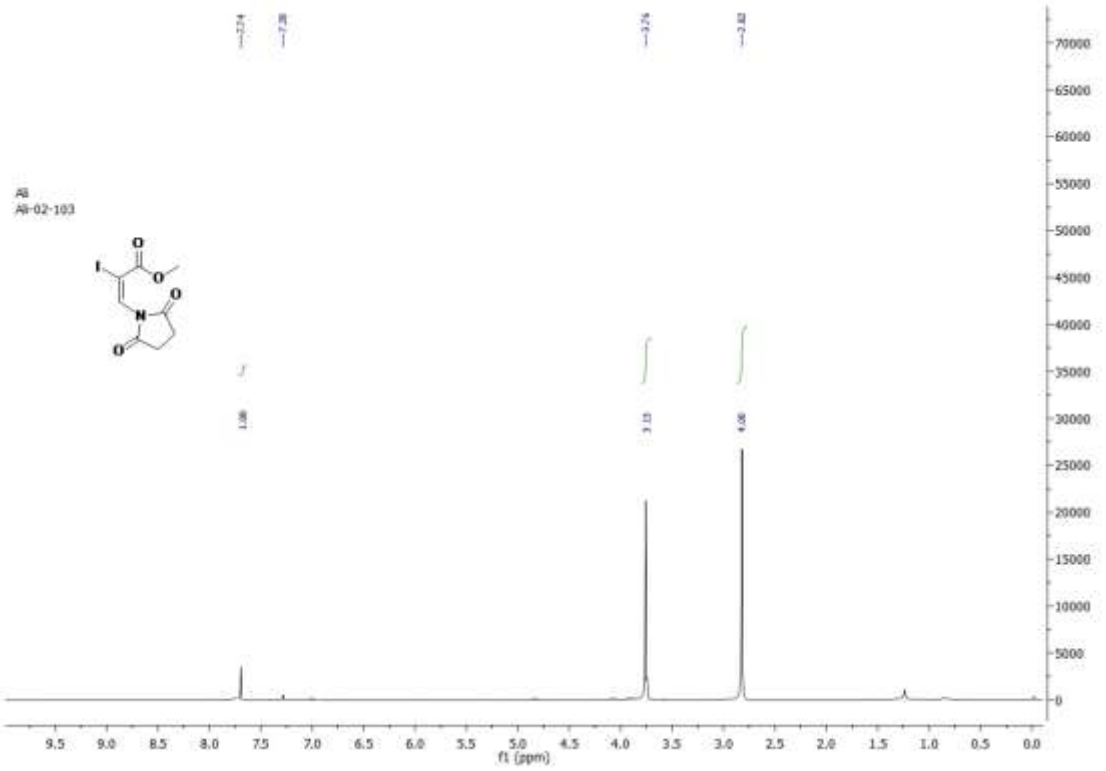


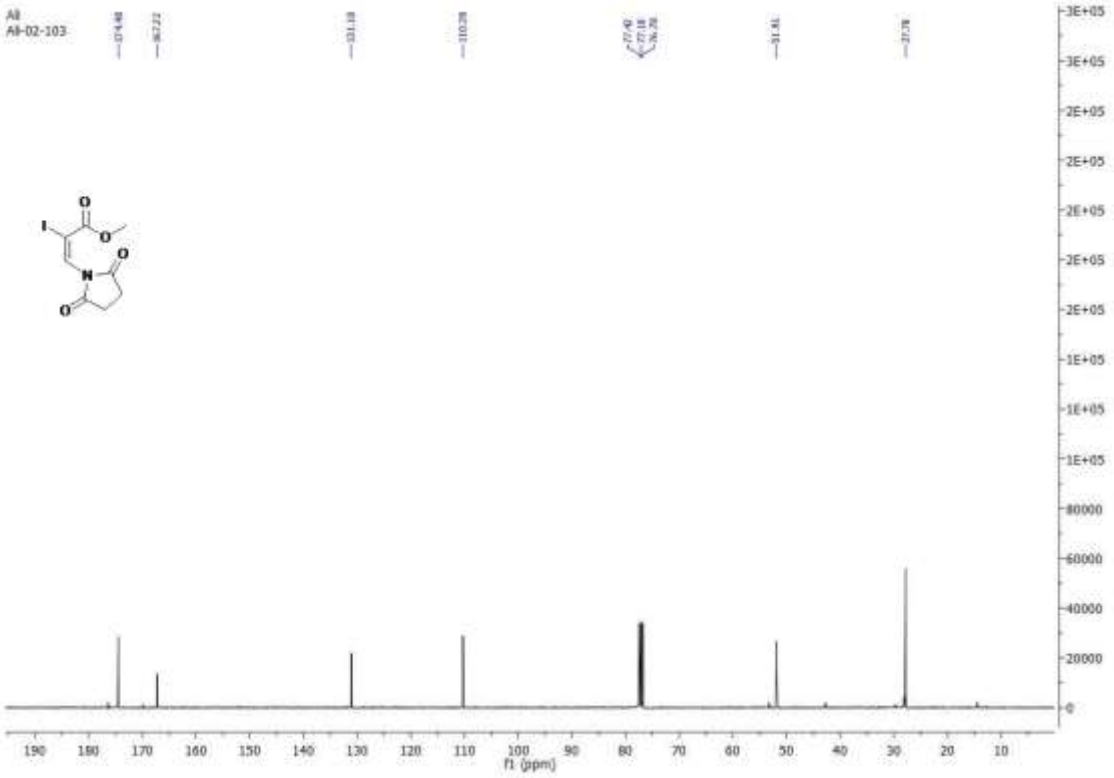


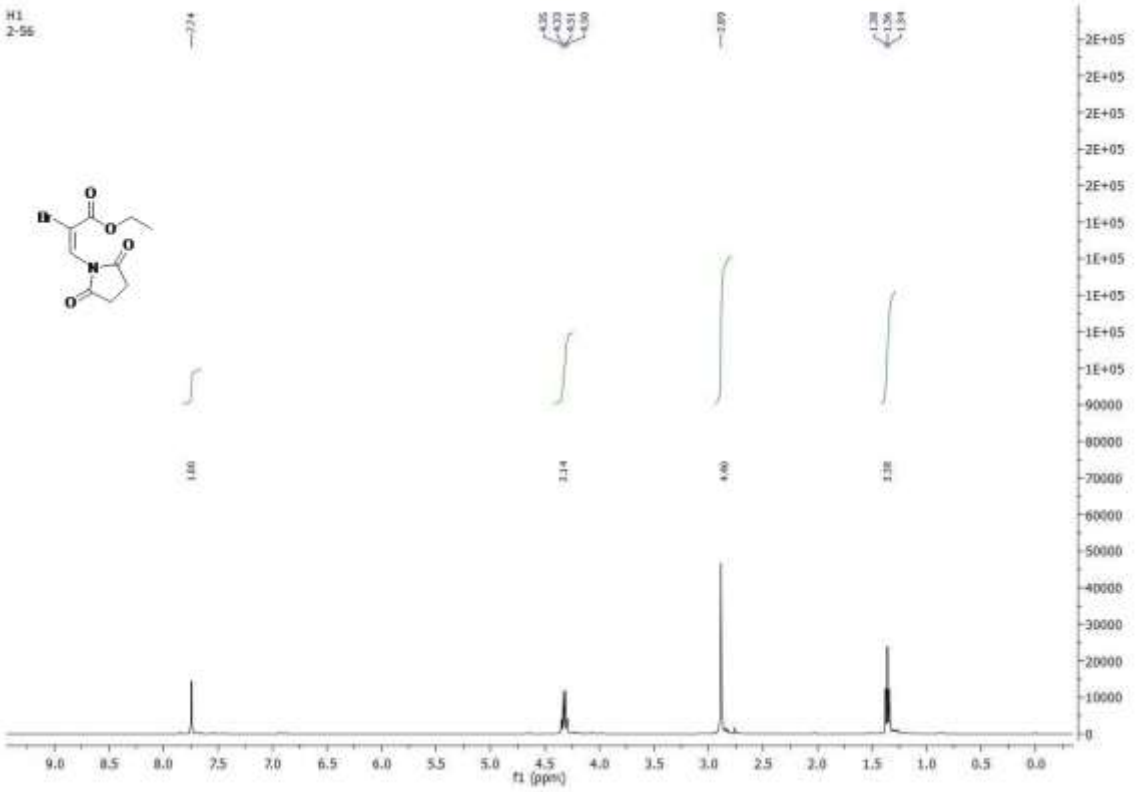


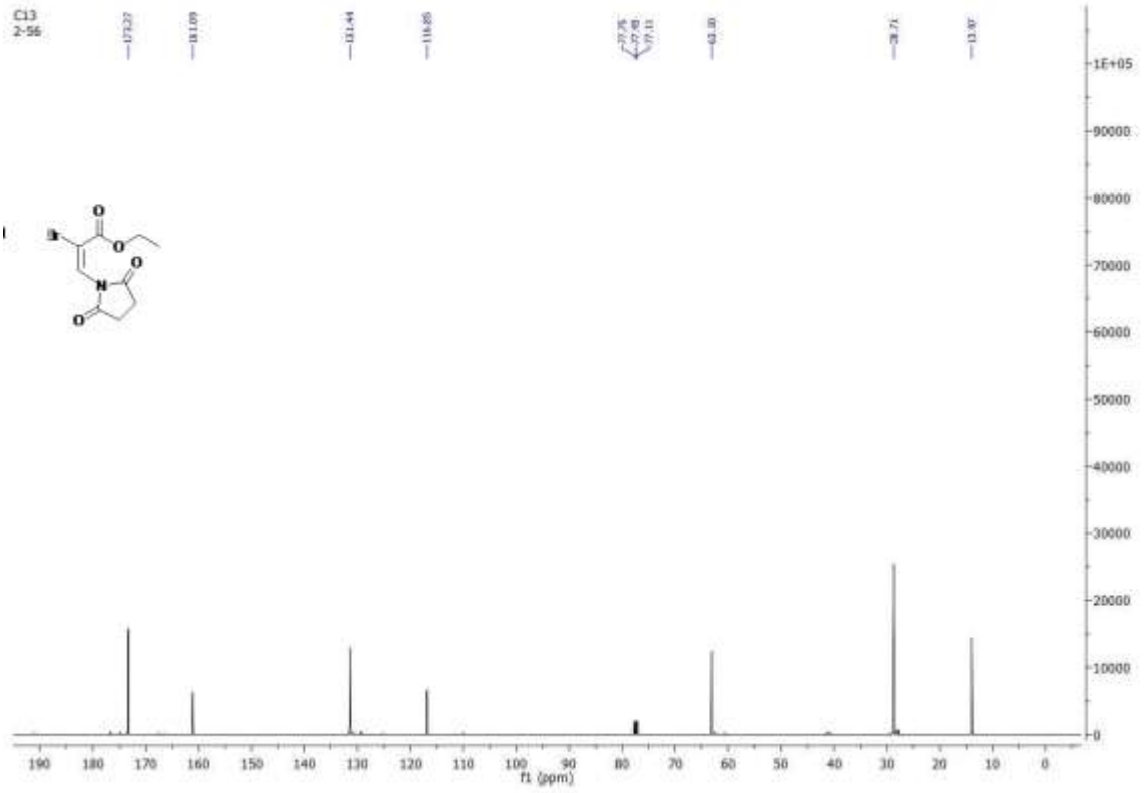

Ali
Ali-2-101
f1 (ppm)

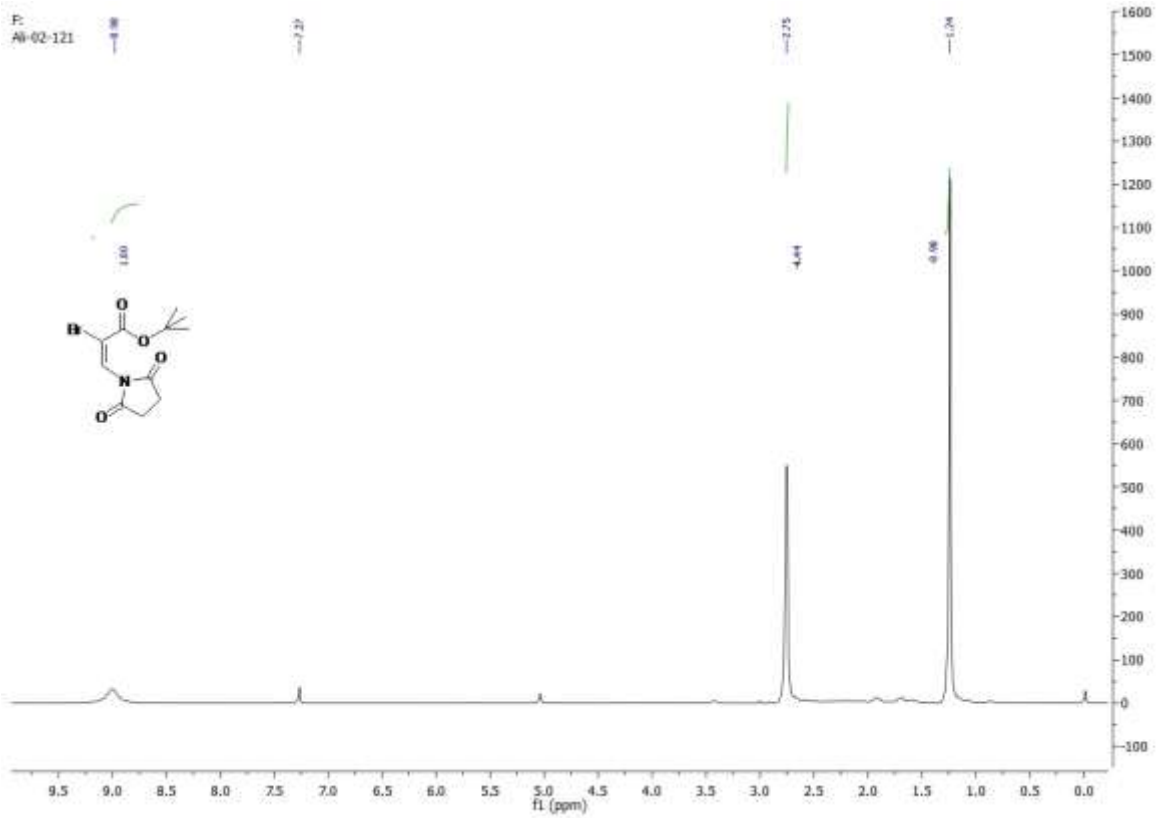

Ali
Ali-2-101
f1 (ppm)

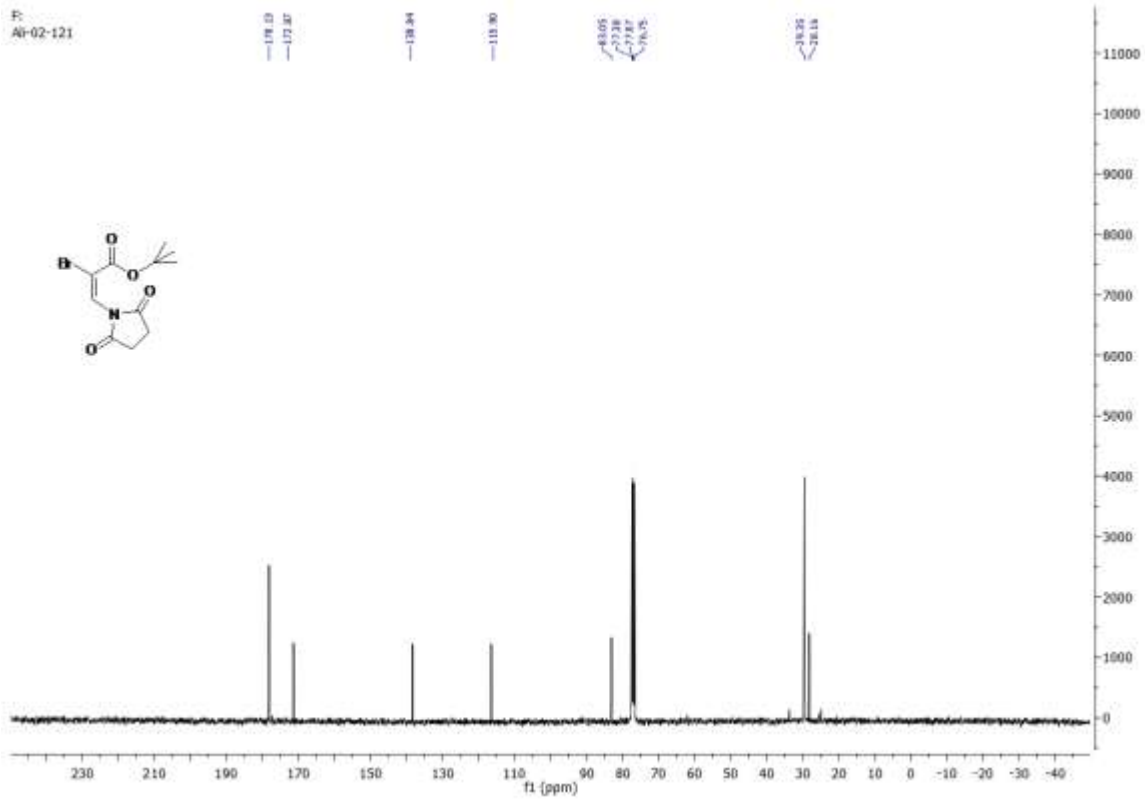


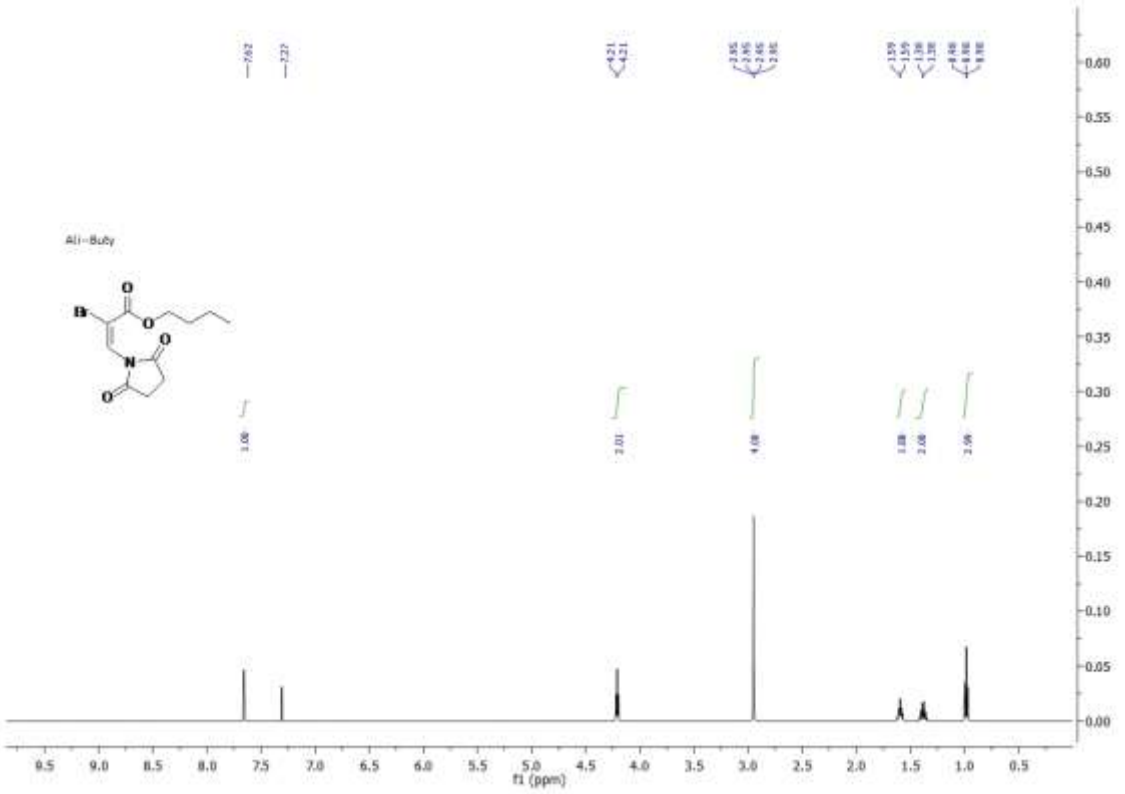


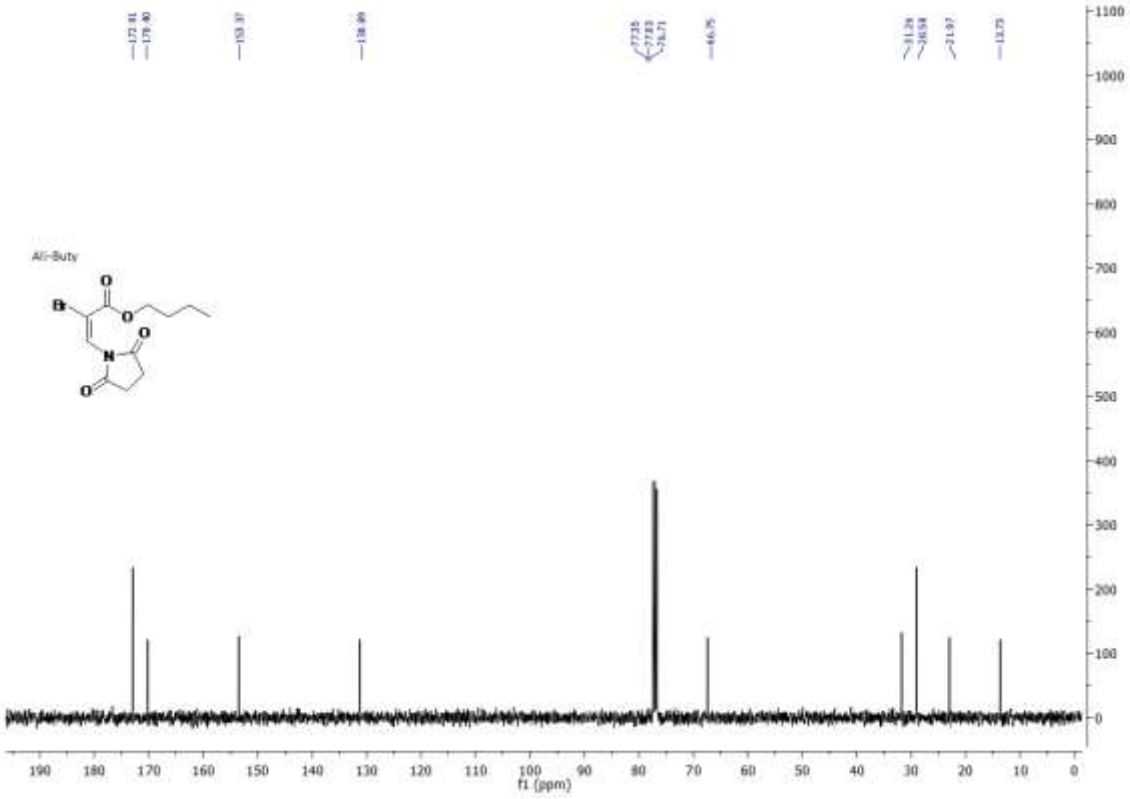

H1
2-56
f1 (ppm)

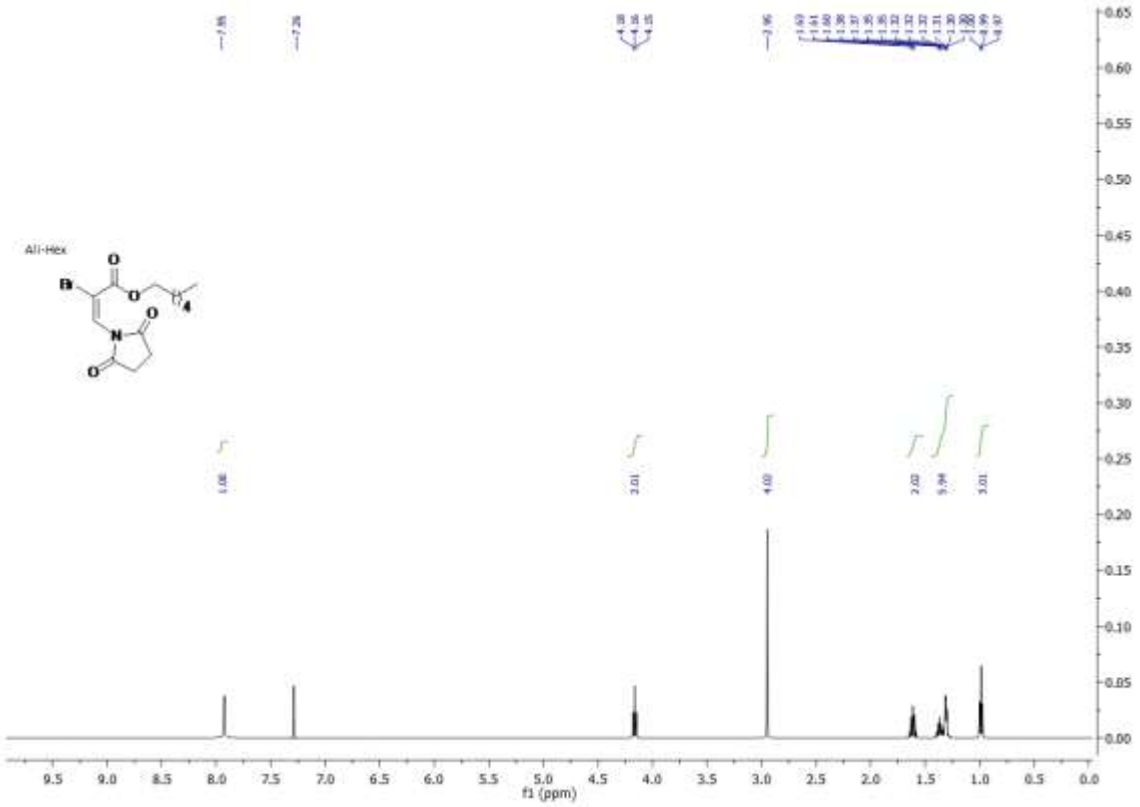

C13
2-56
f1 (ppm)

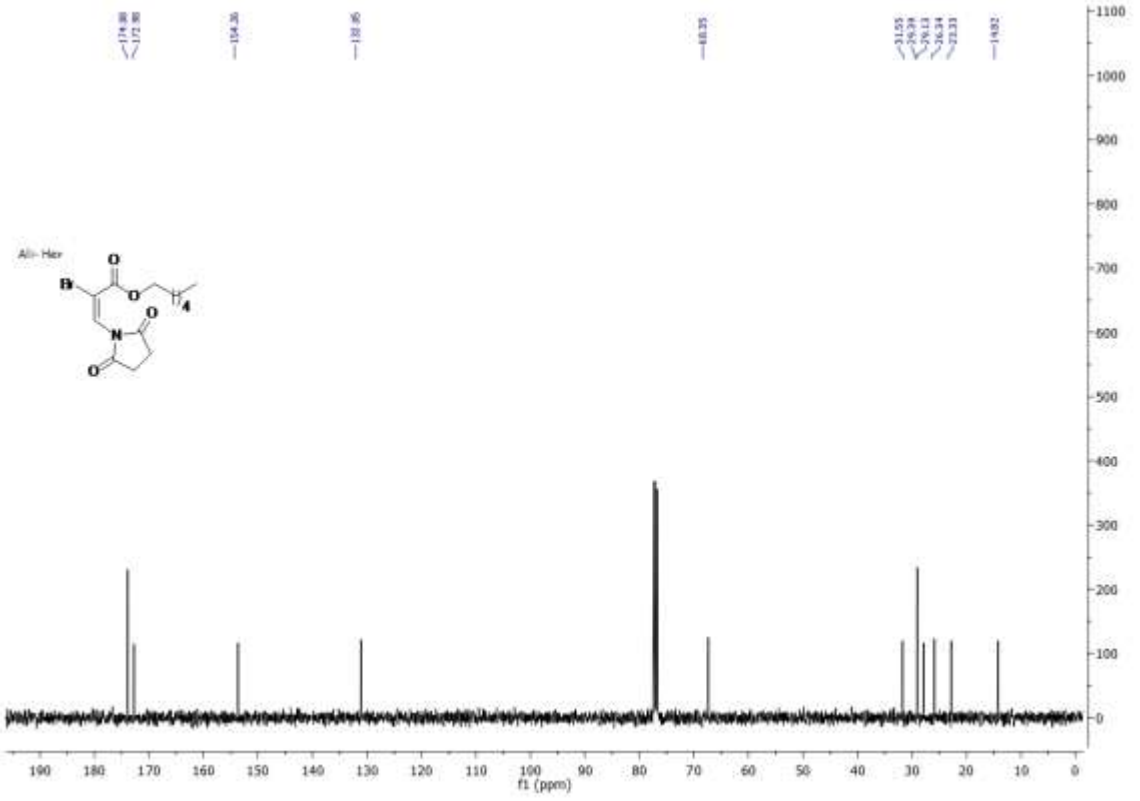


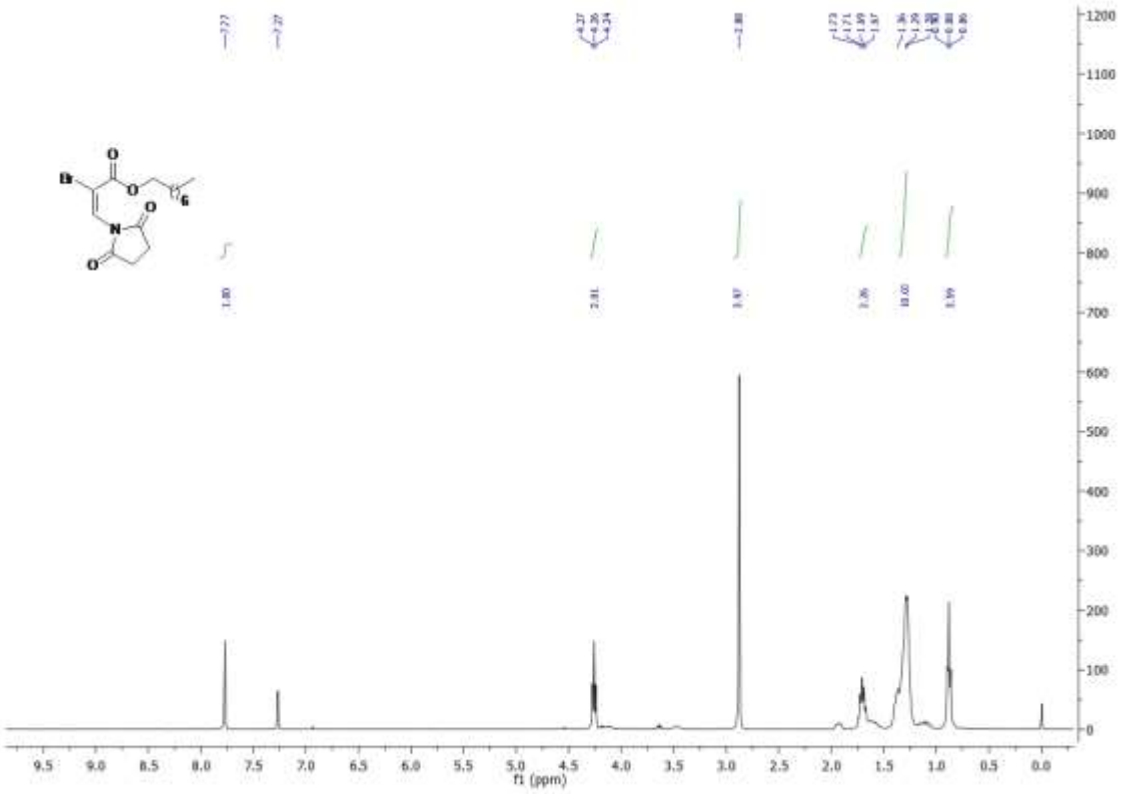


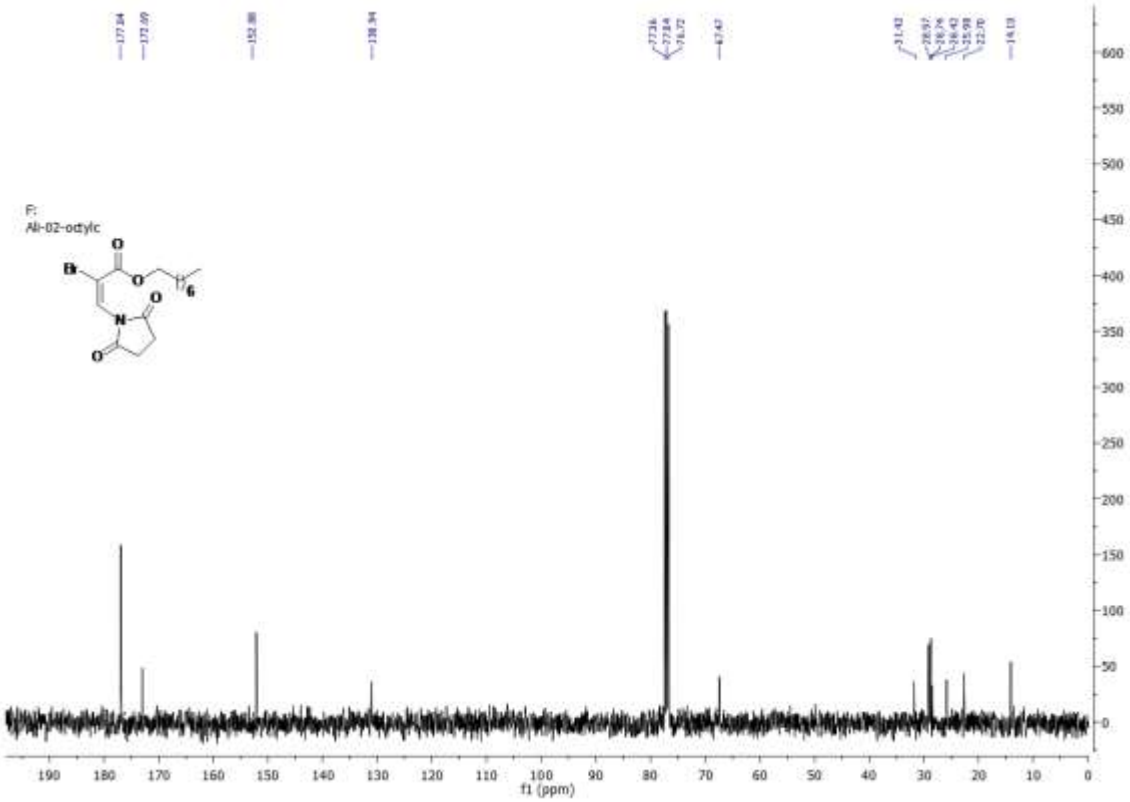


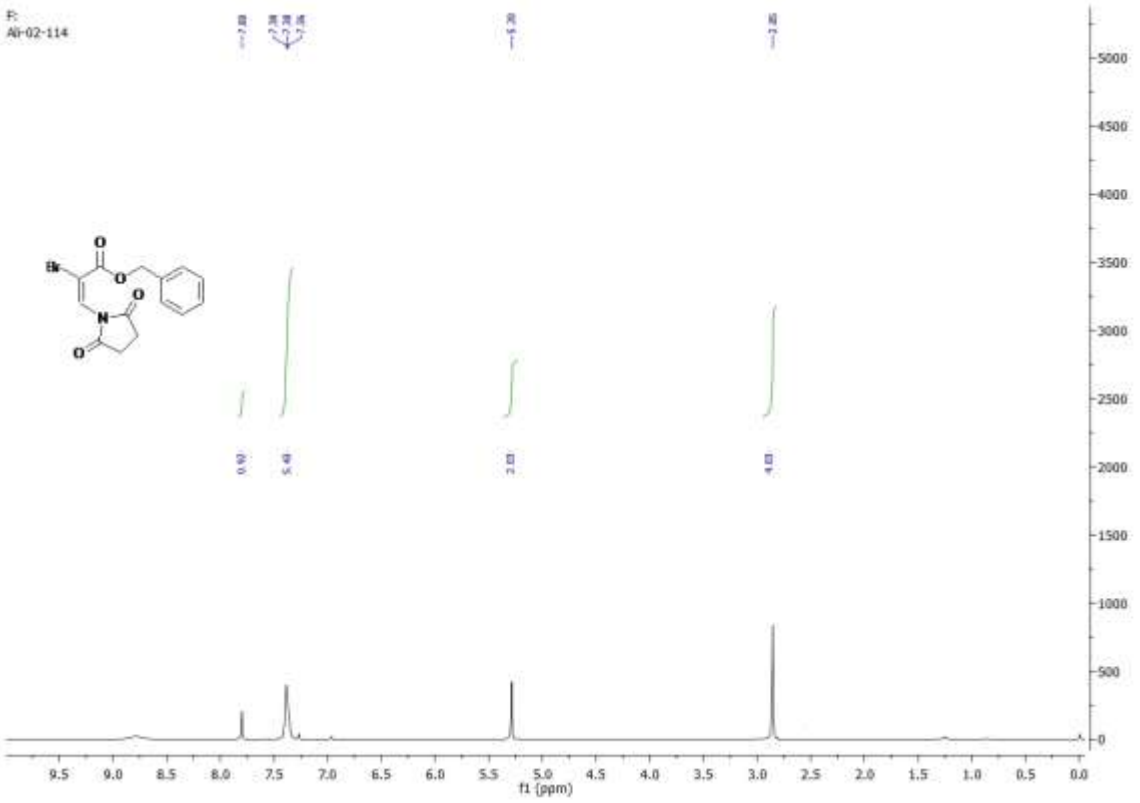


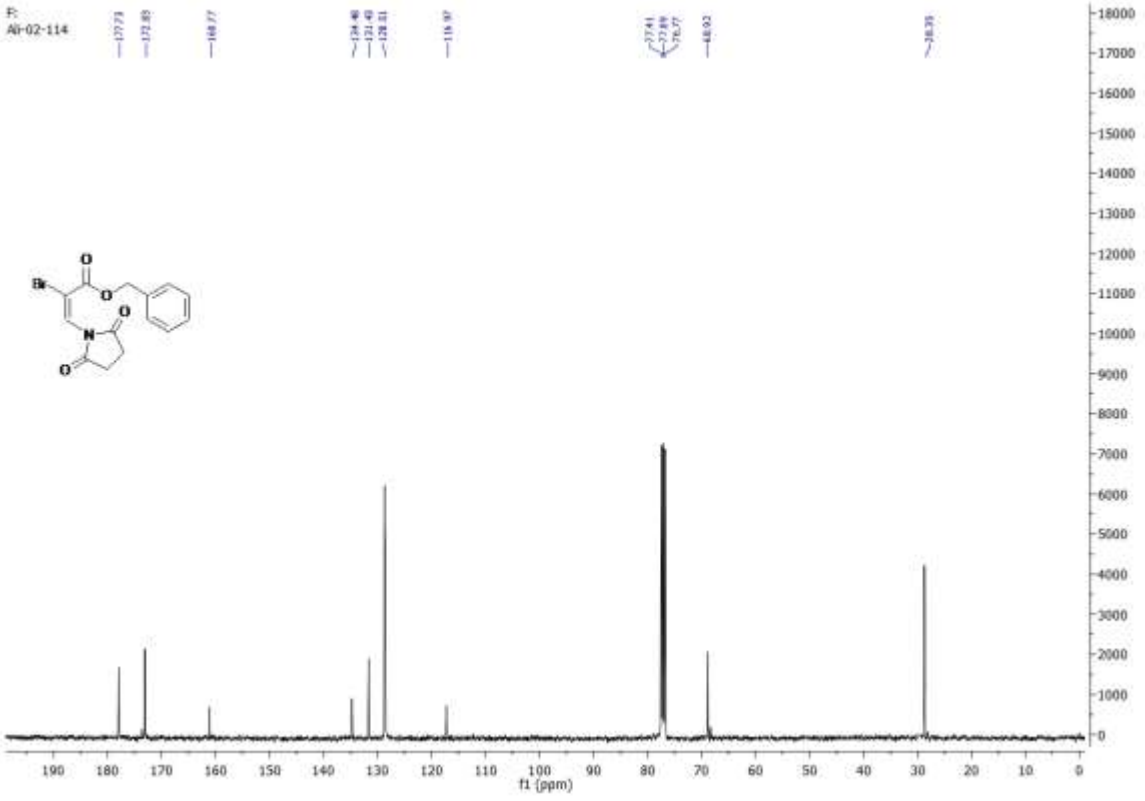


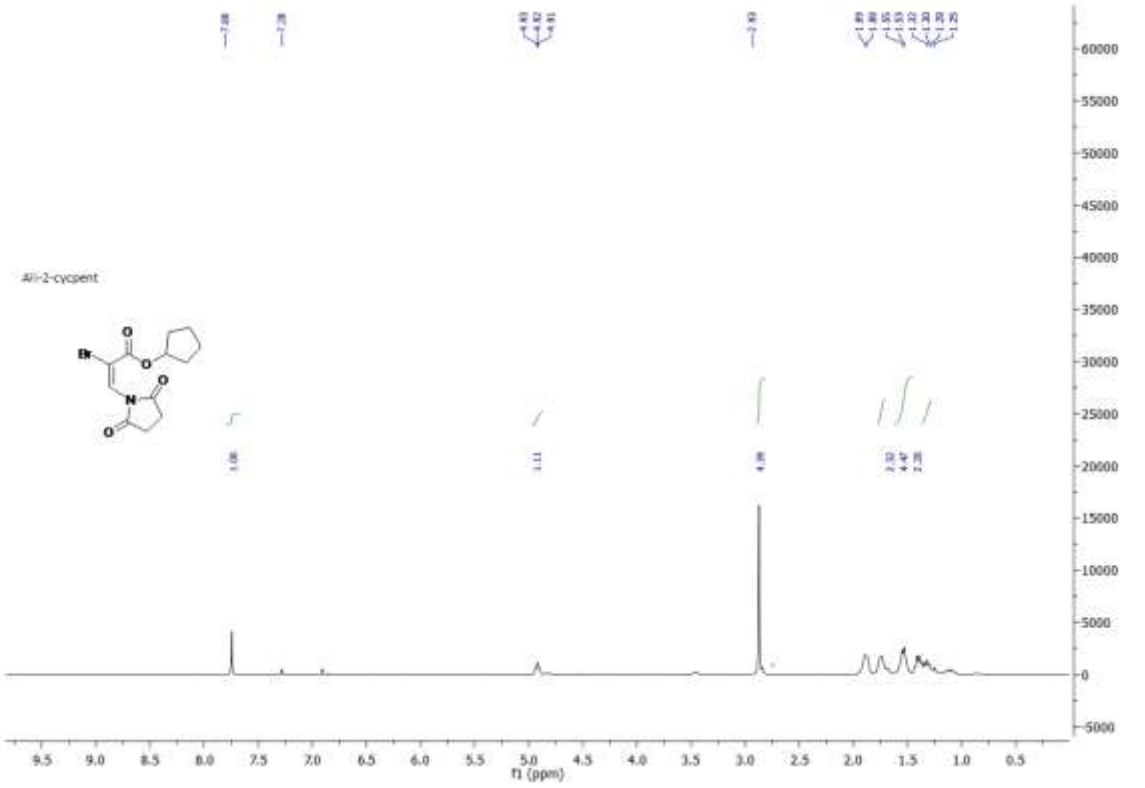


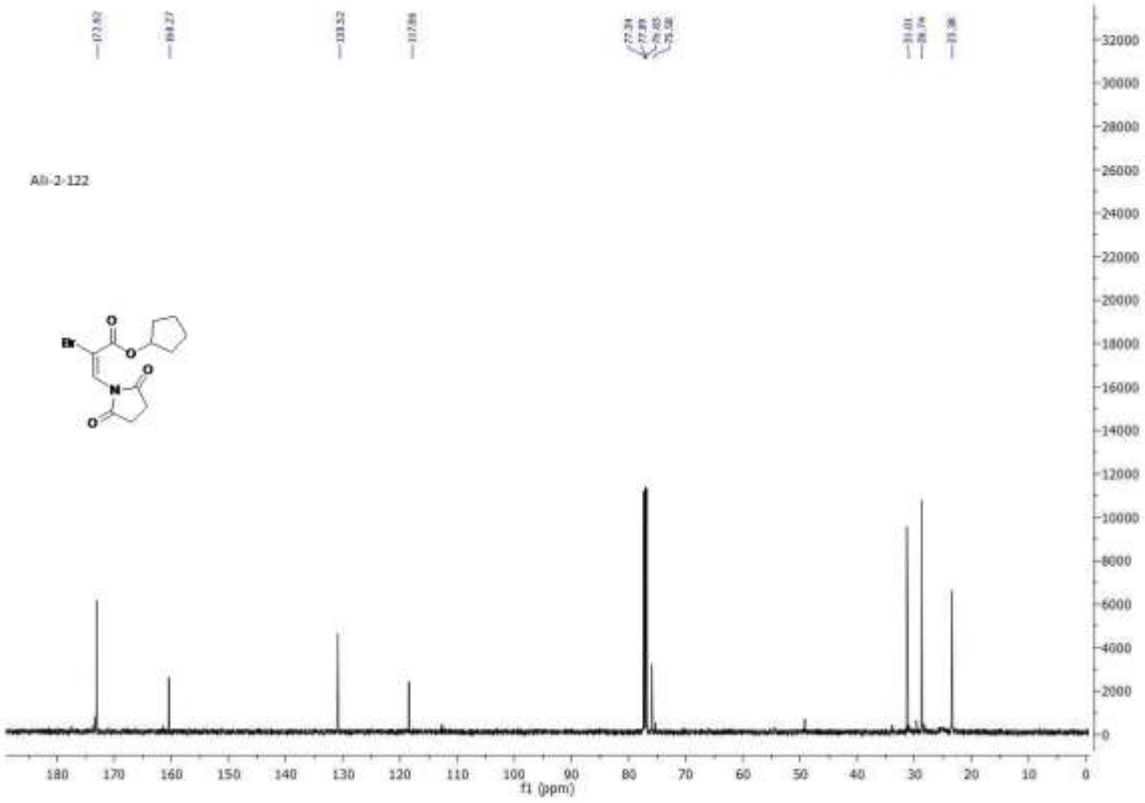


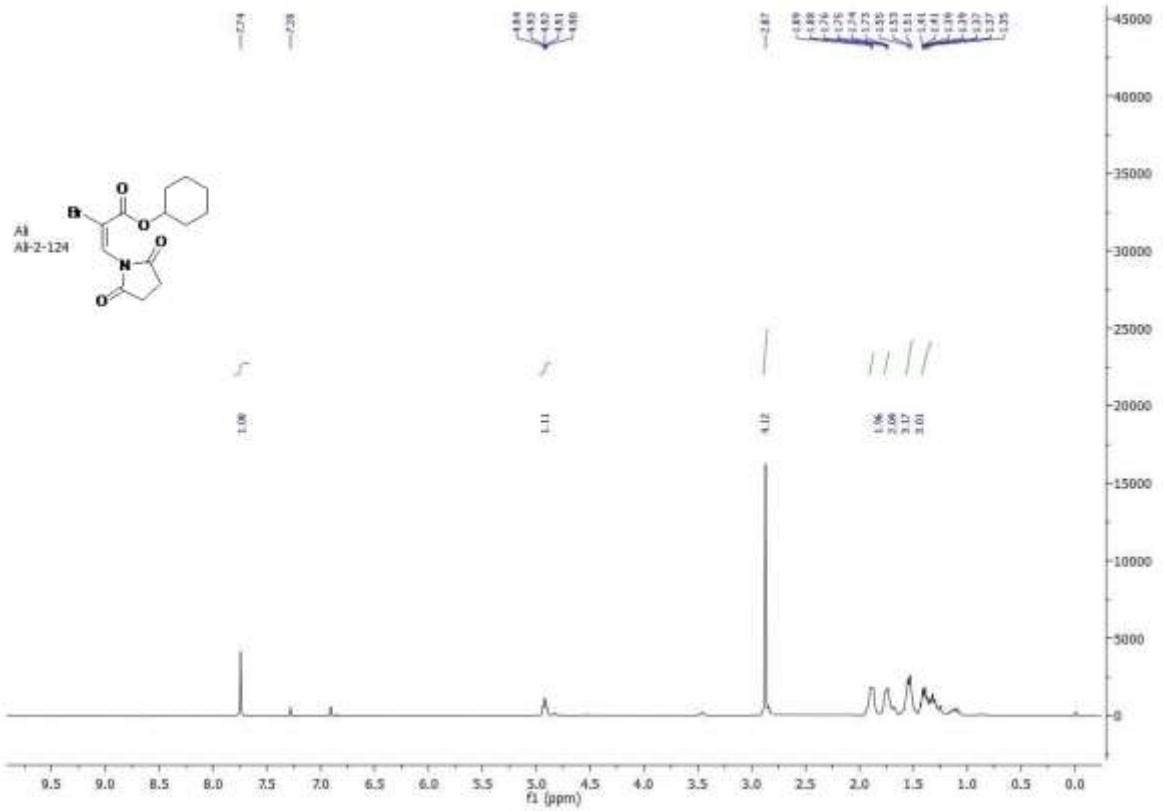


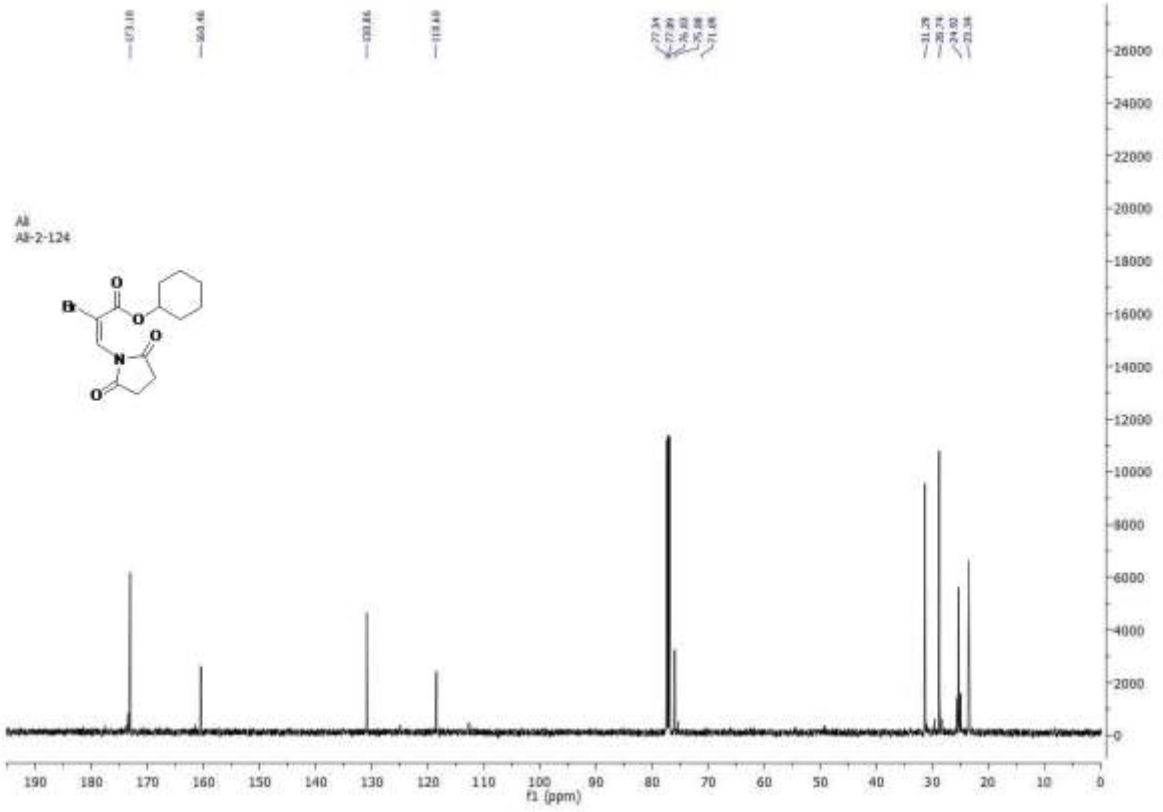


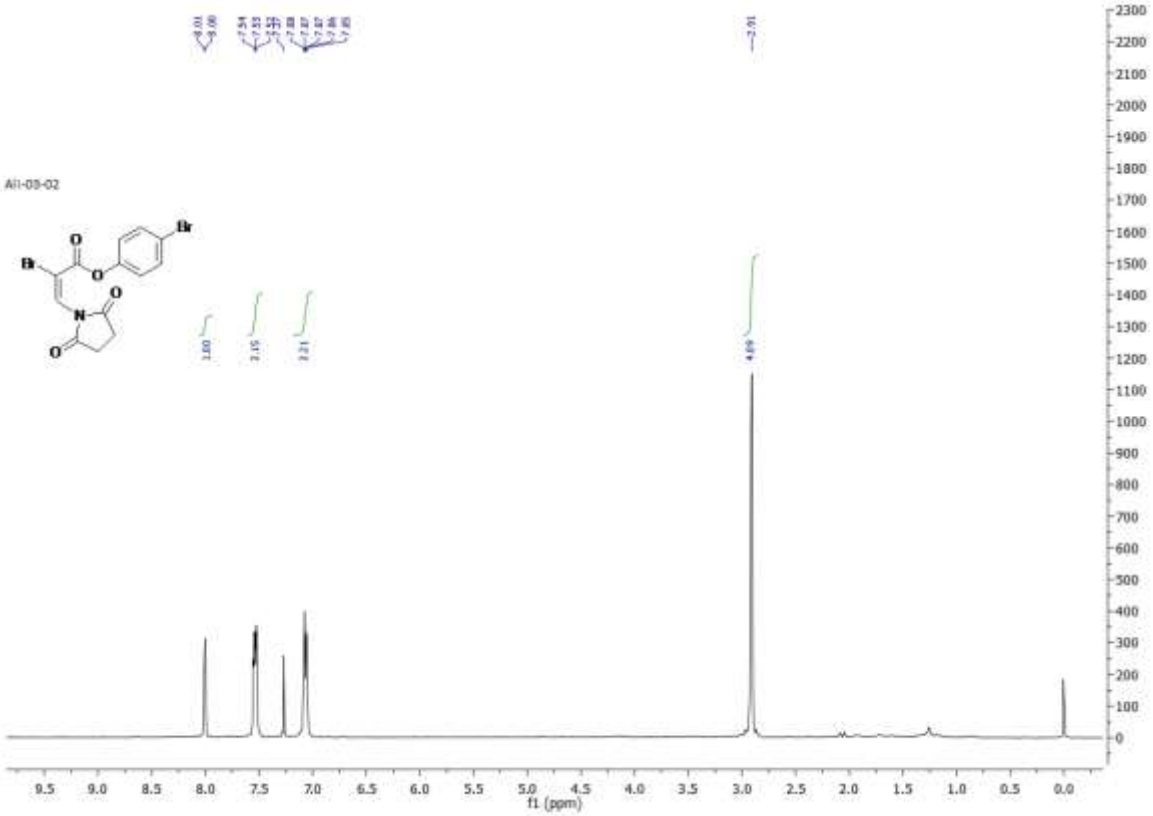


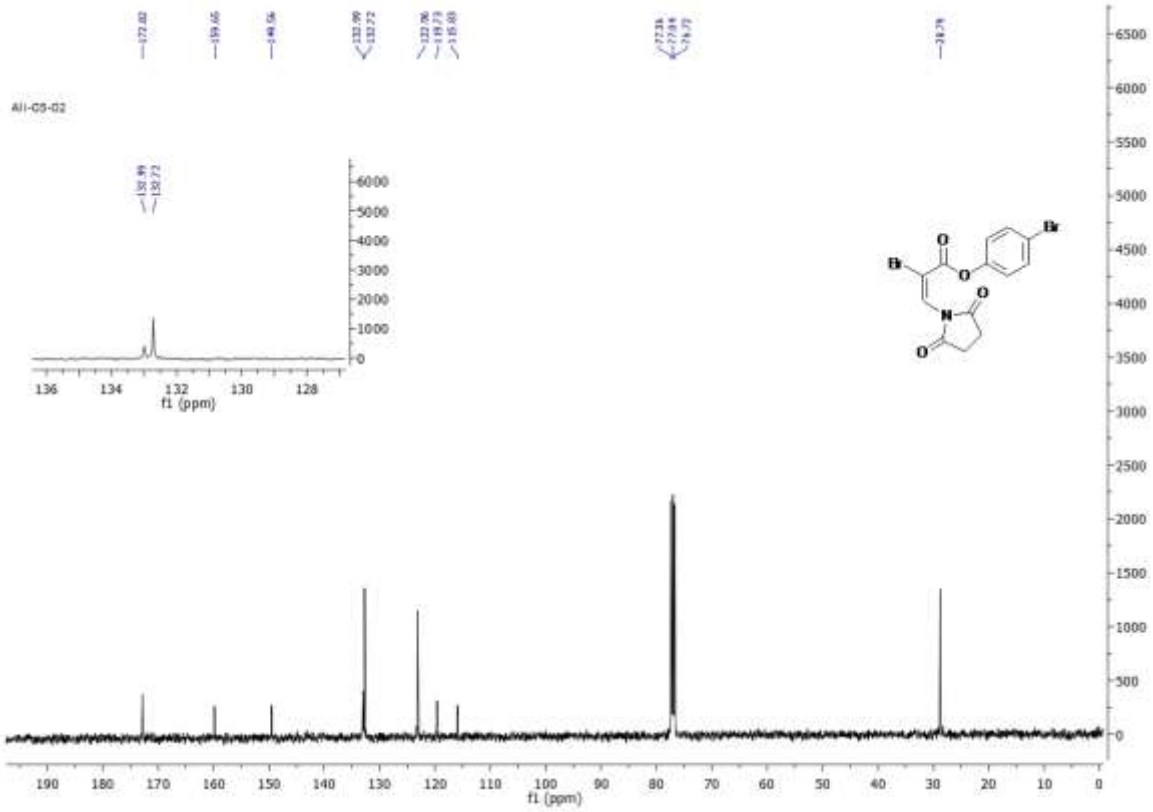


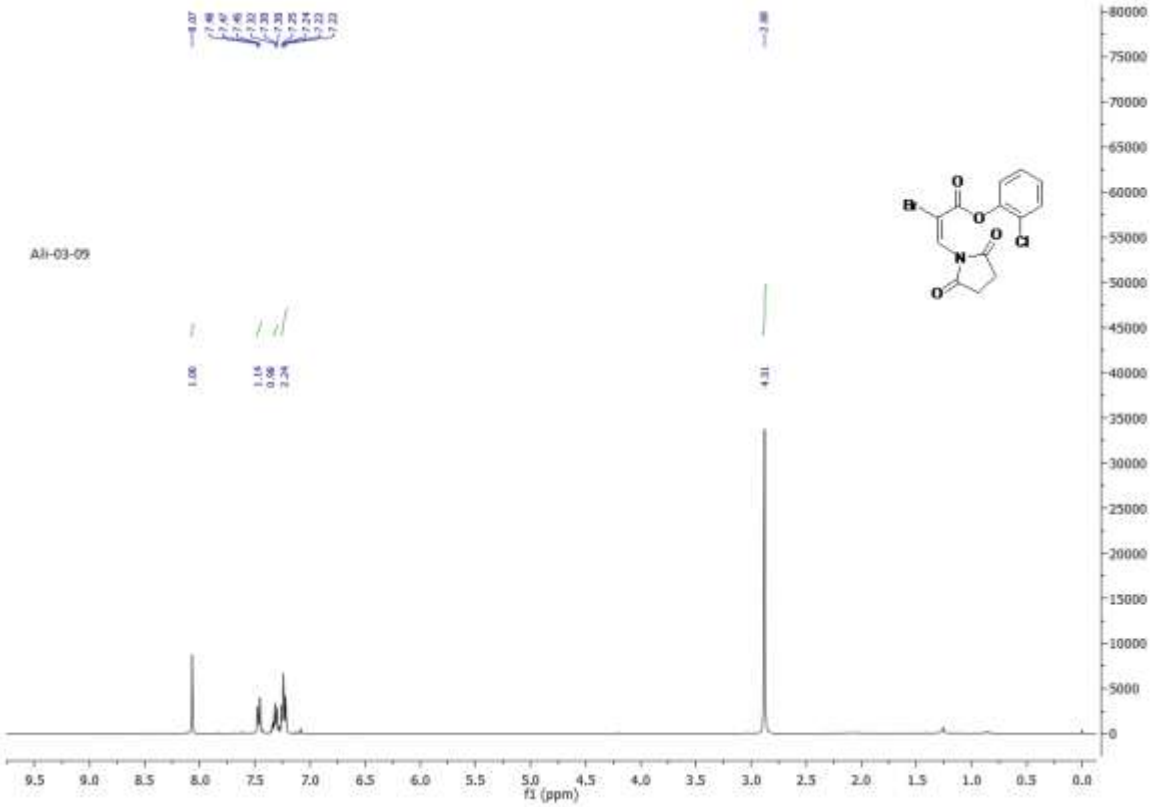


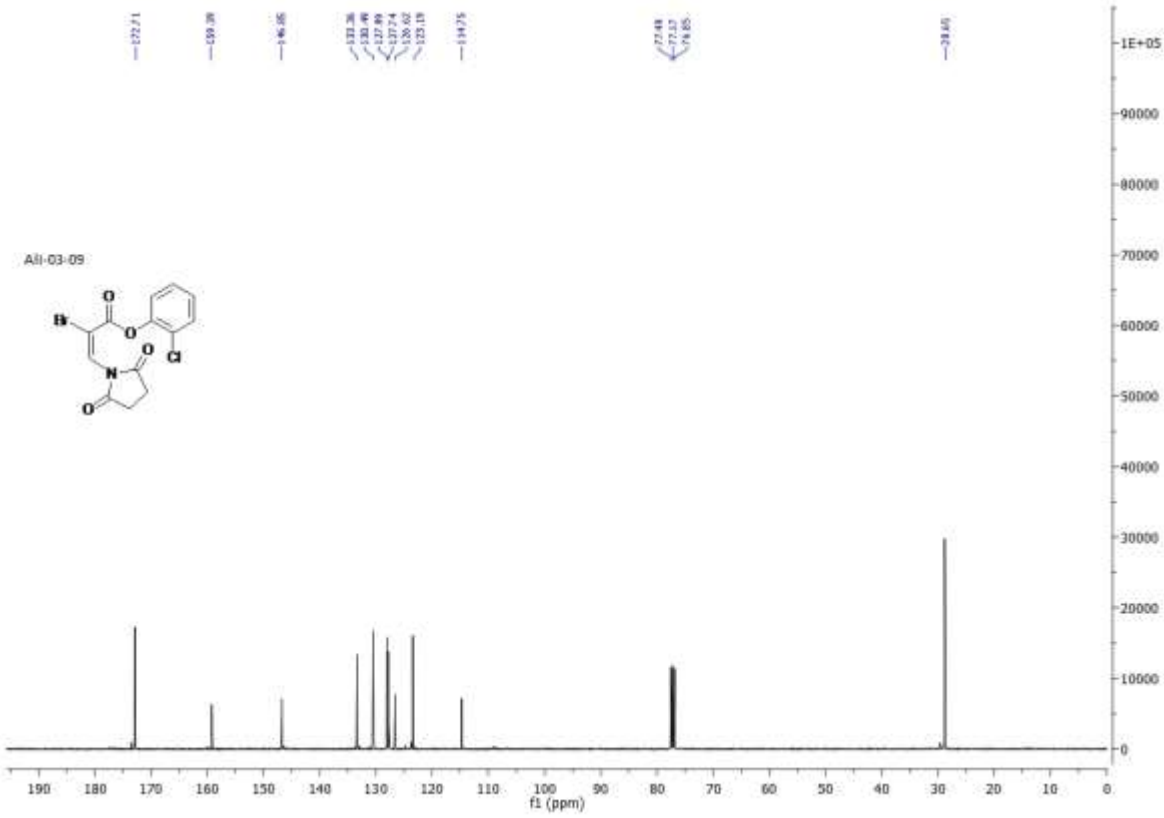

Ali
Ali-2-124
f1 (ppm)

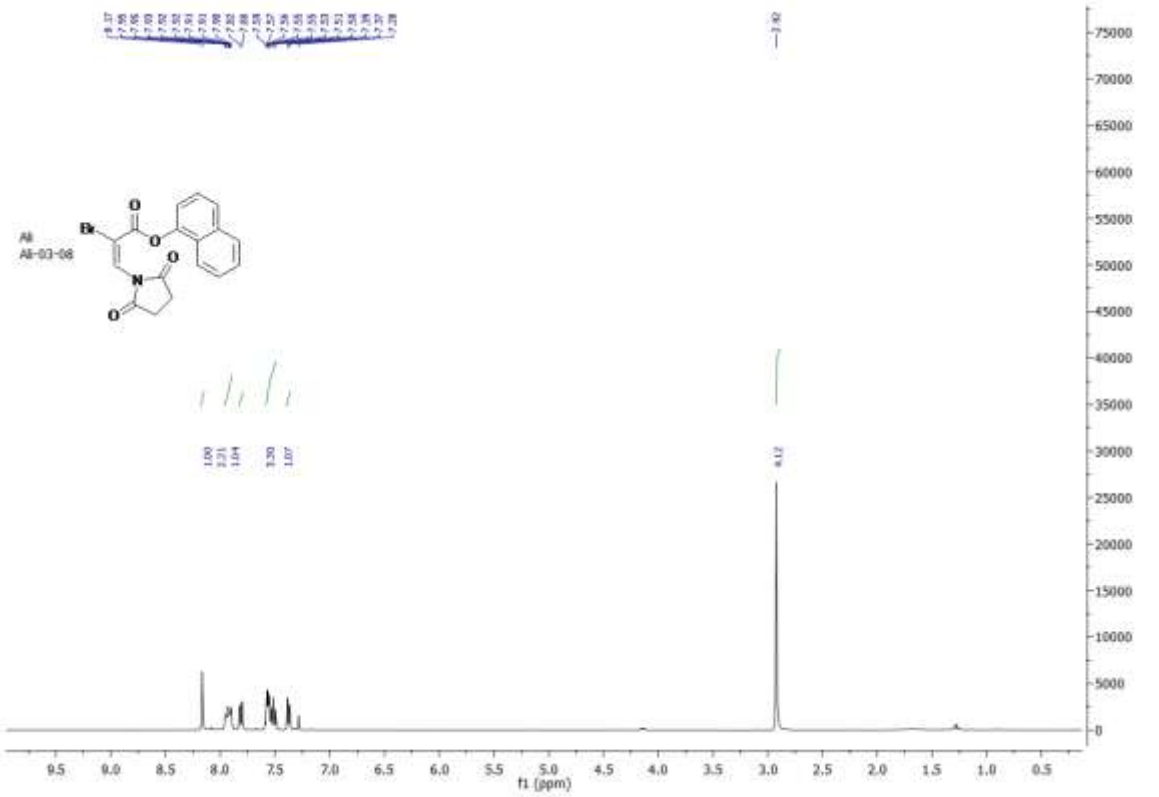

Ali
Ali-2-124
f1 (ppm)

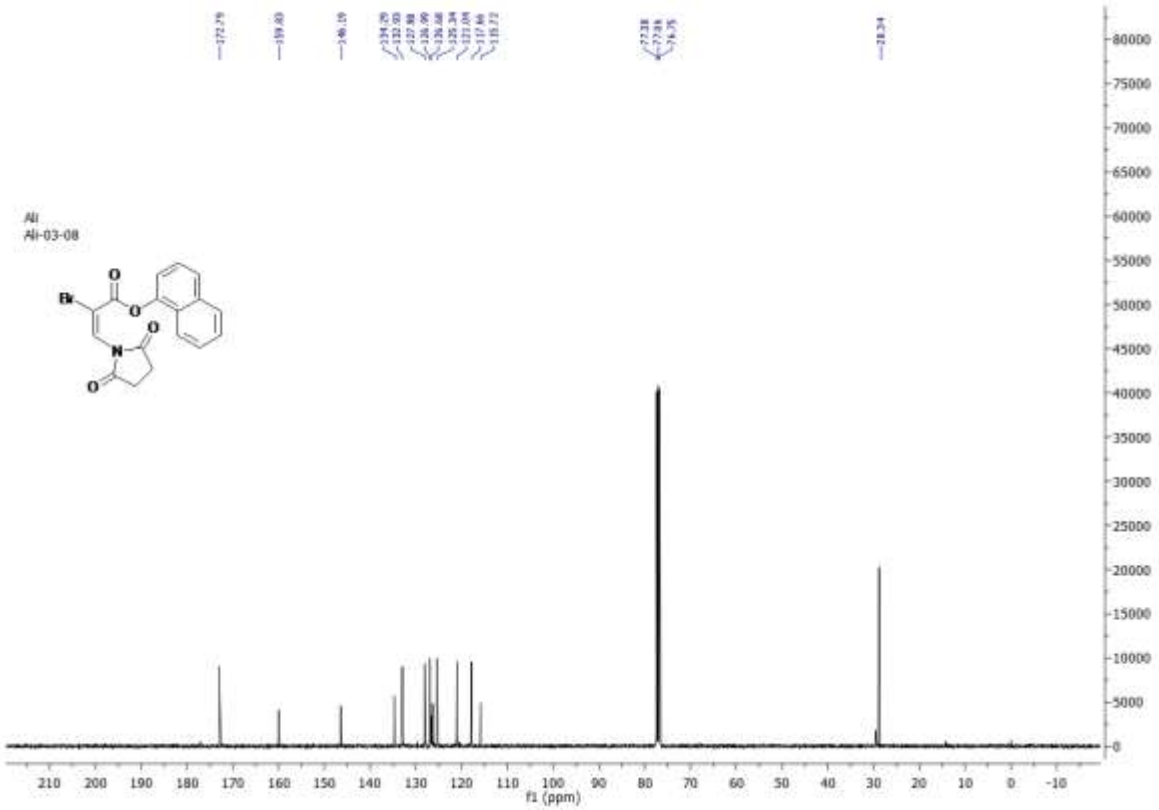


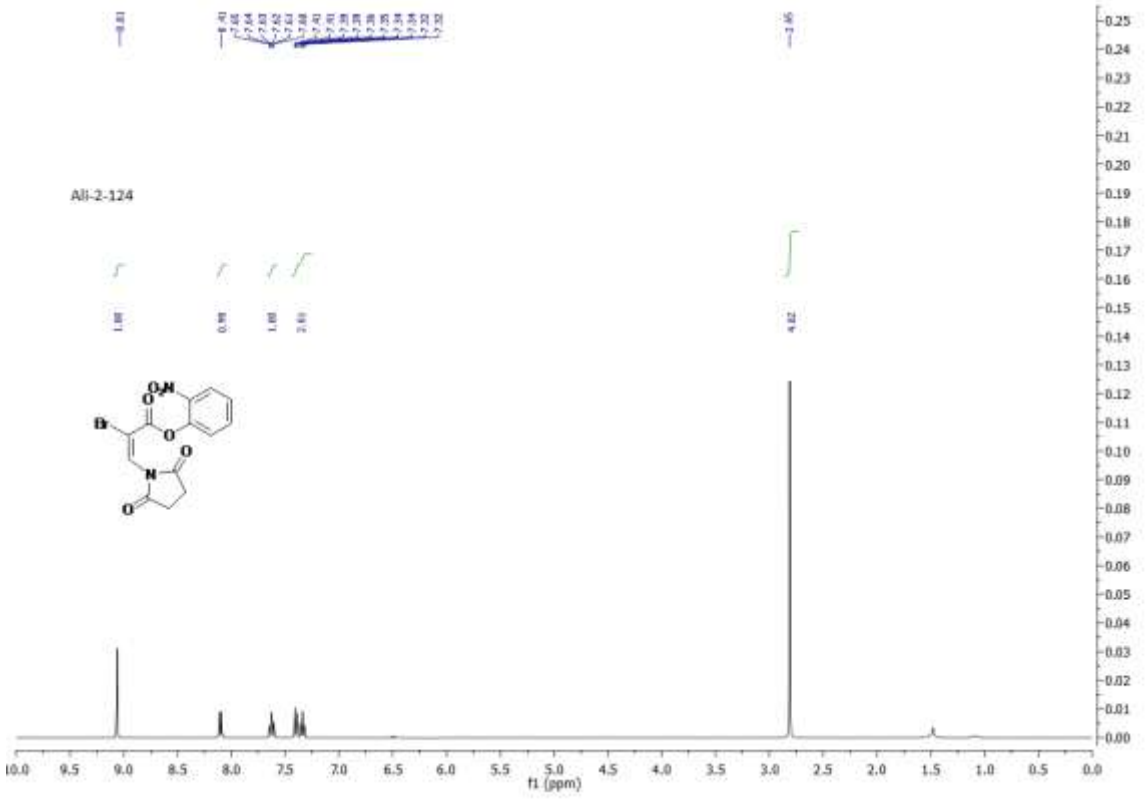


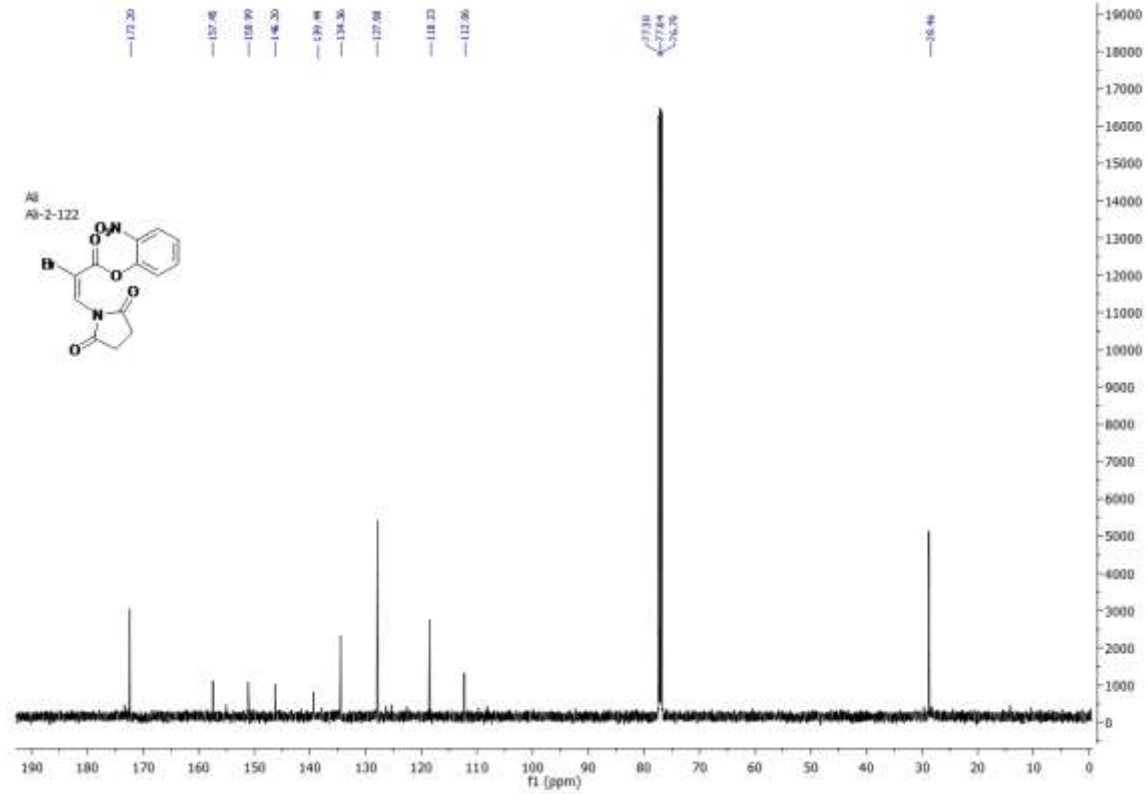

All-03-09
f1 (ppm)

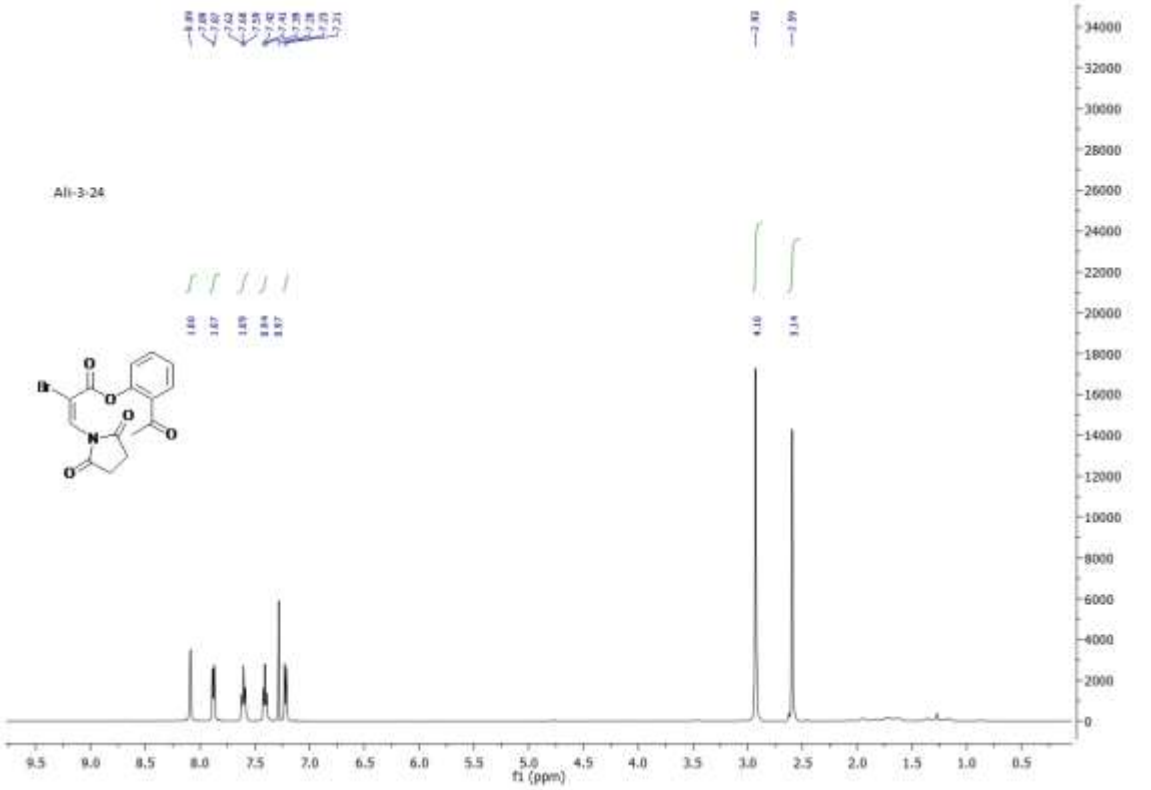

All-03-09
f1 (ppm)

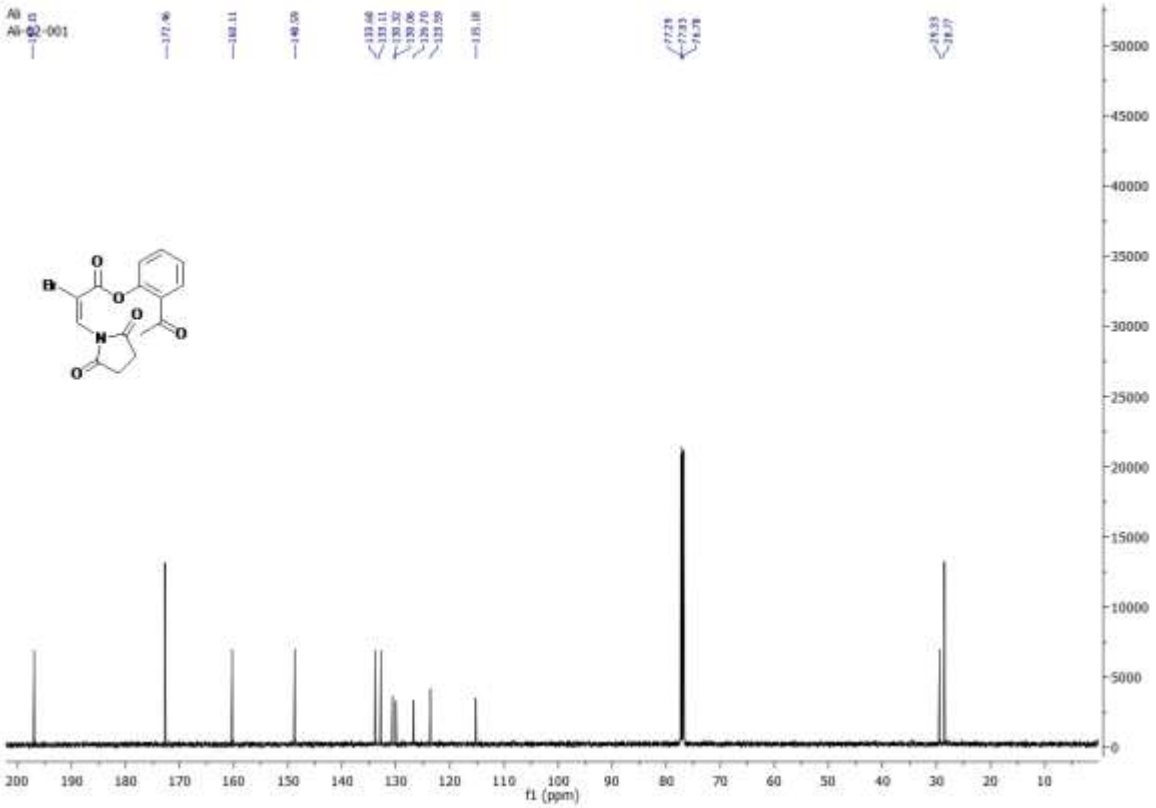

Ali
Ali-03-08
f1 (ppm)

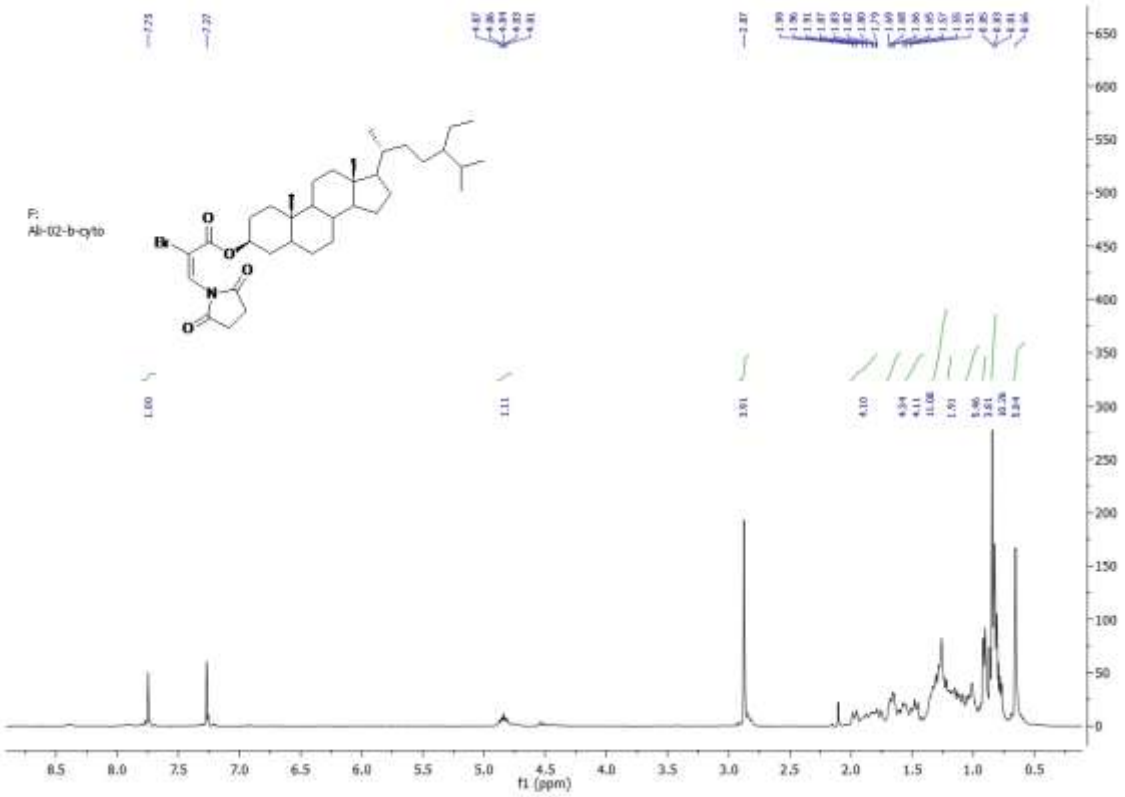

Ali
Ali-03-08
f1 (ppm)

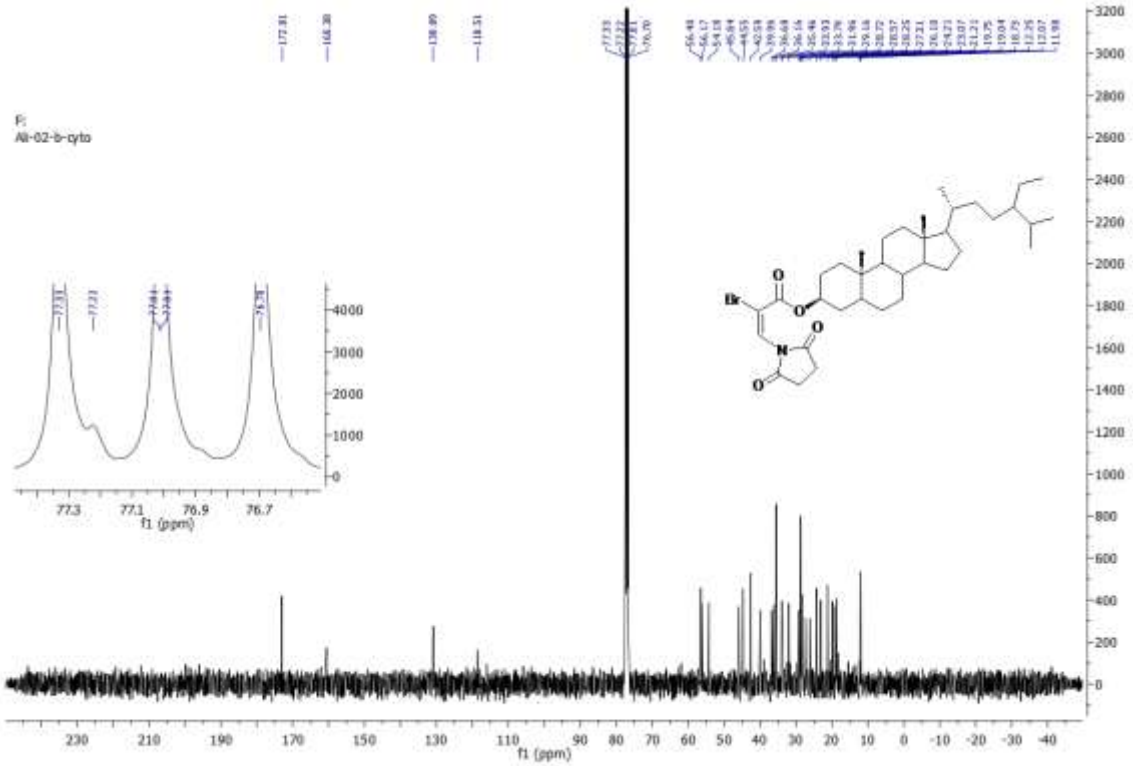

Ali-2-124
f1 (ppm)

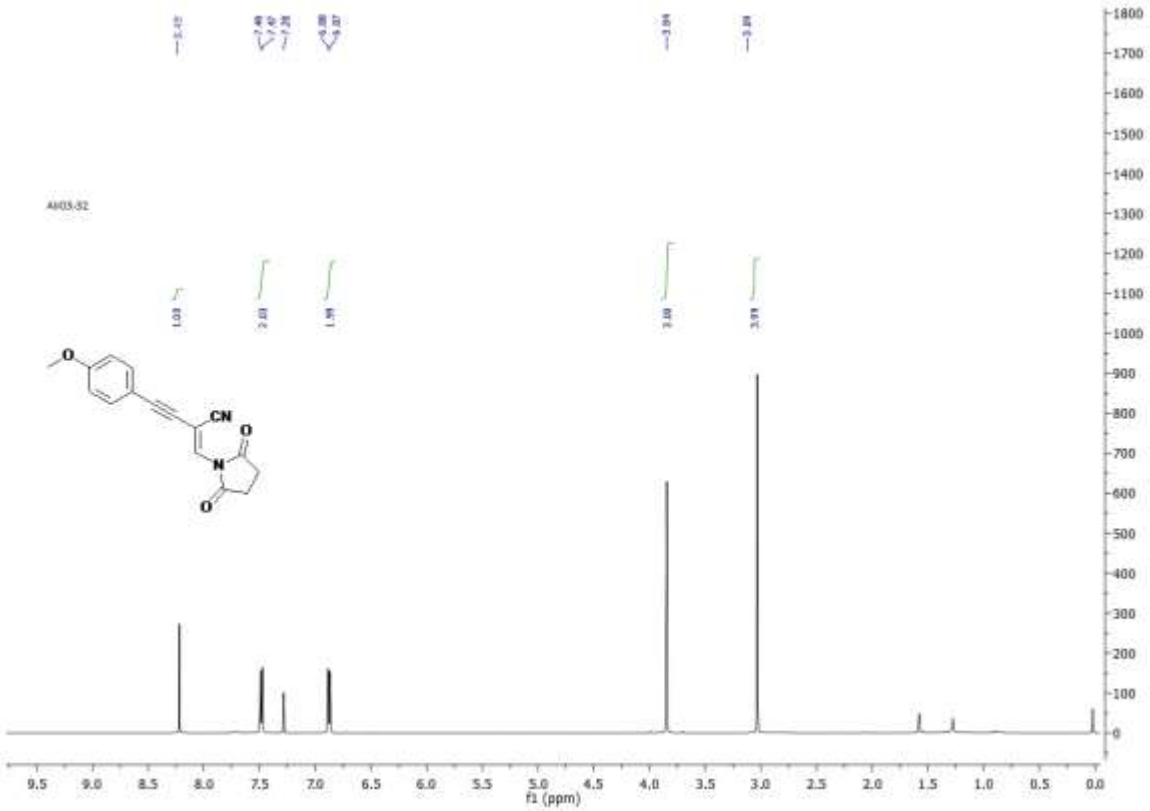

Ali
Ali-2-122
f1 (ppm)

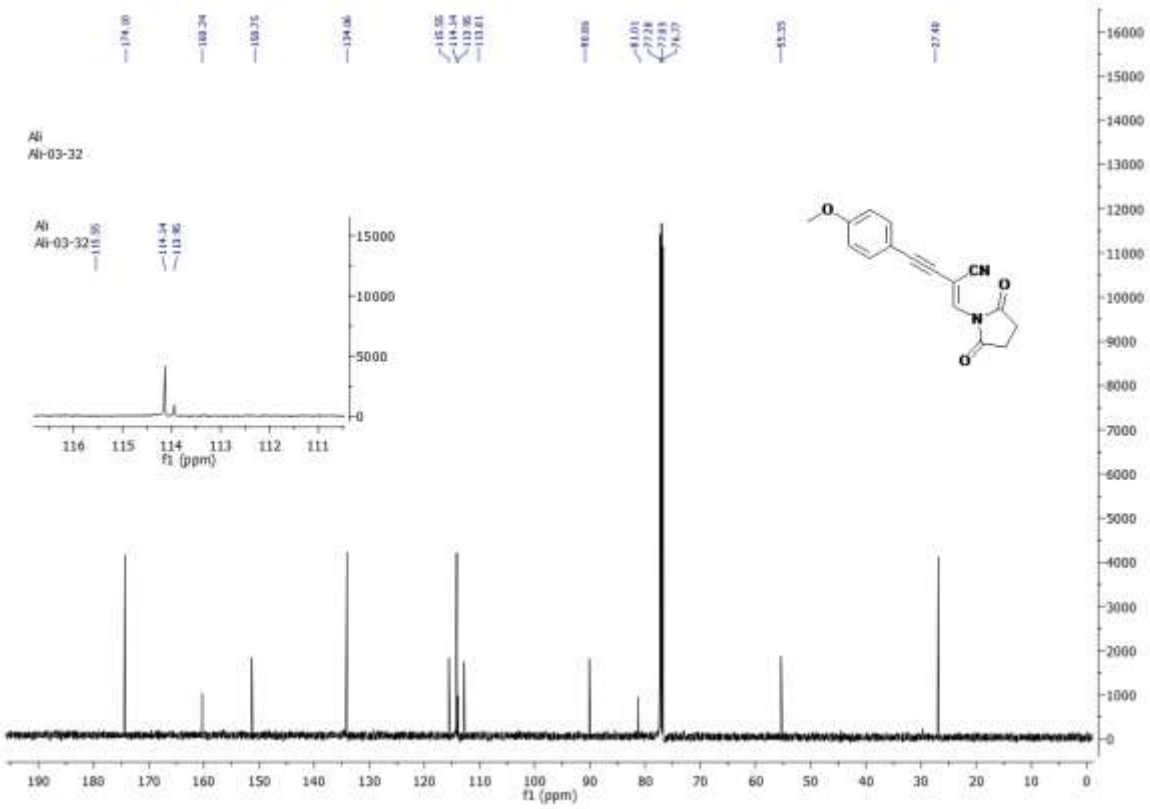


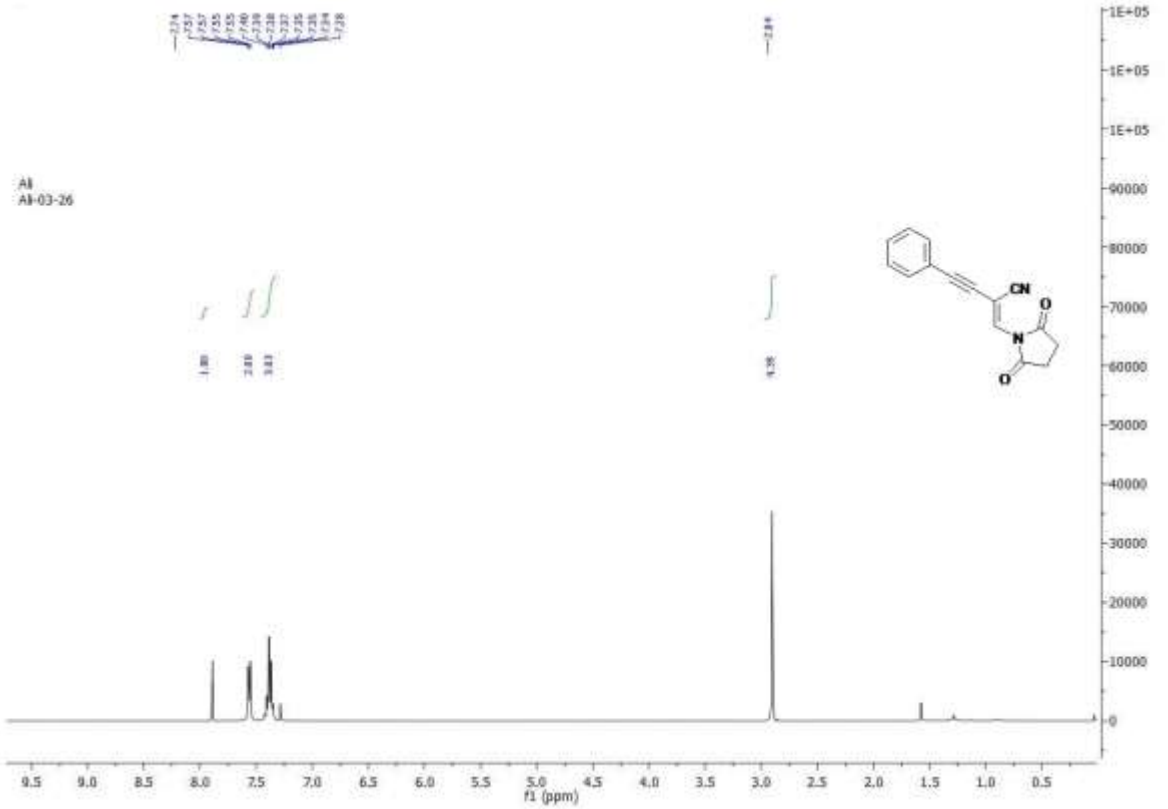


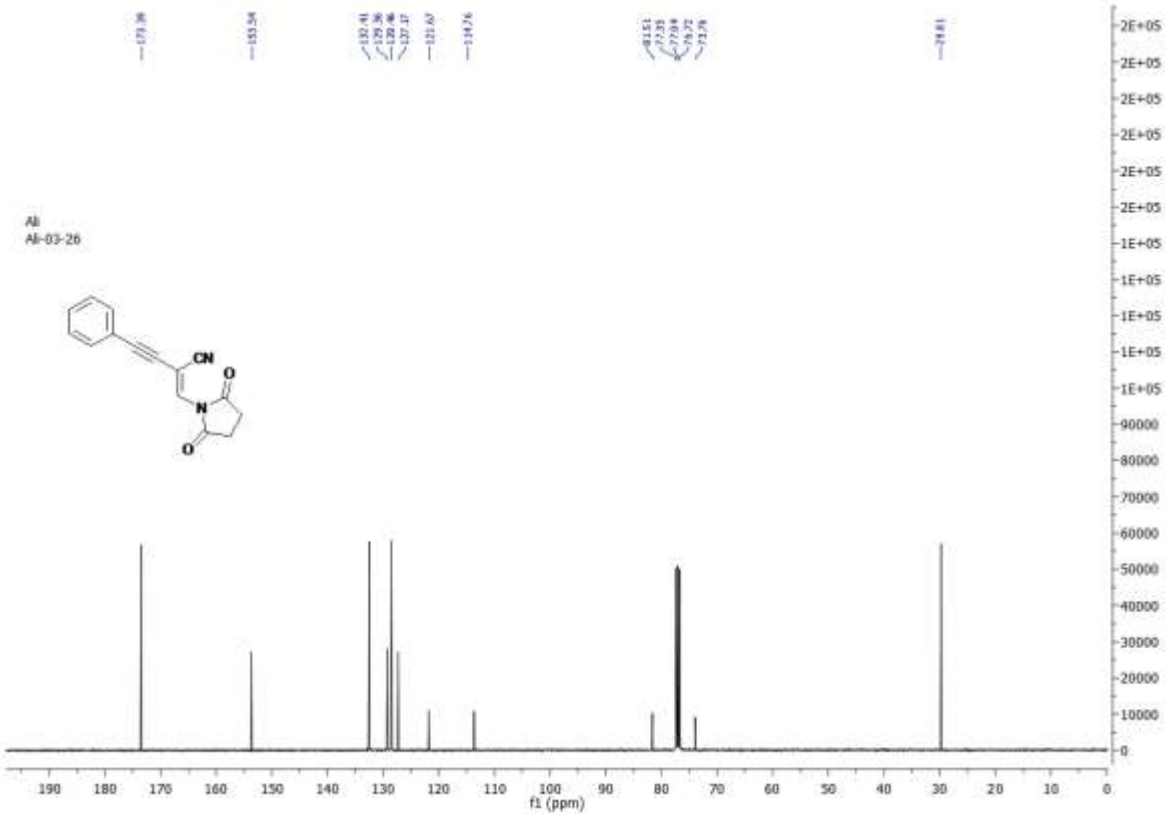


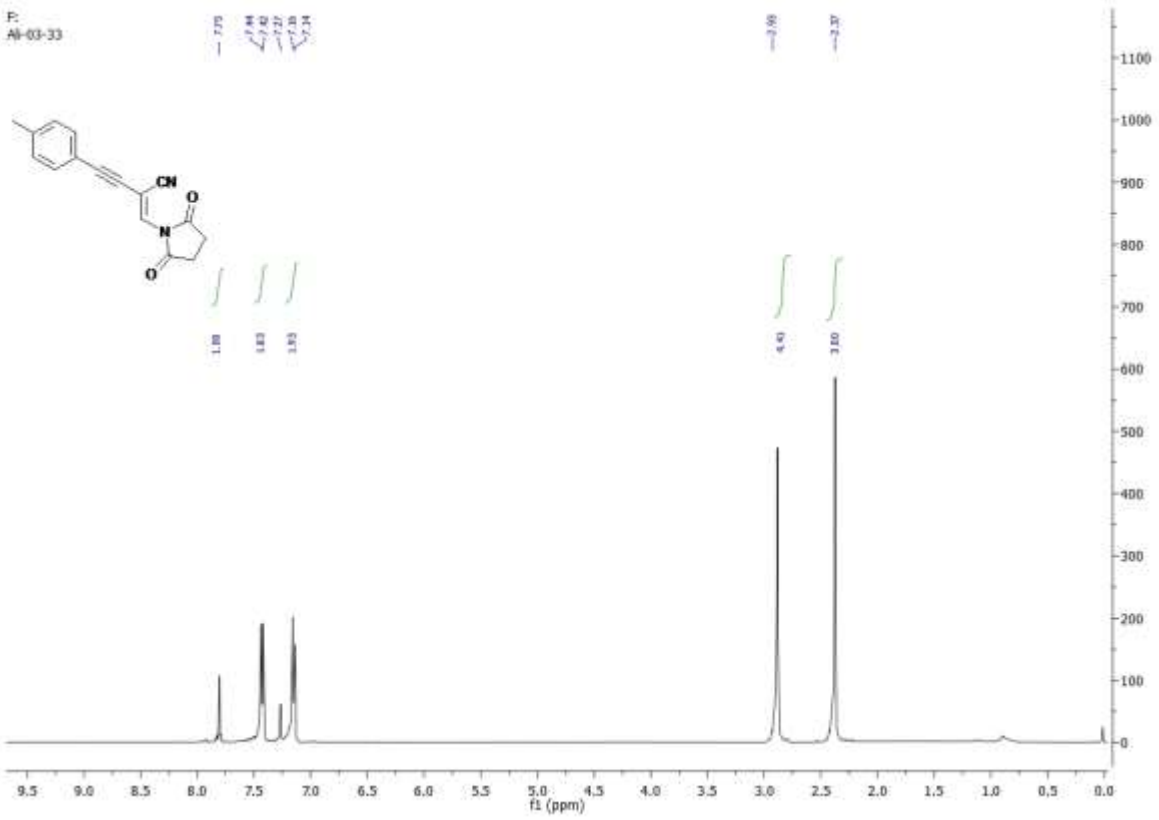


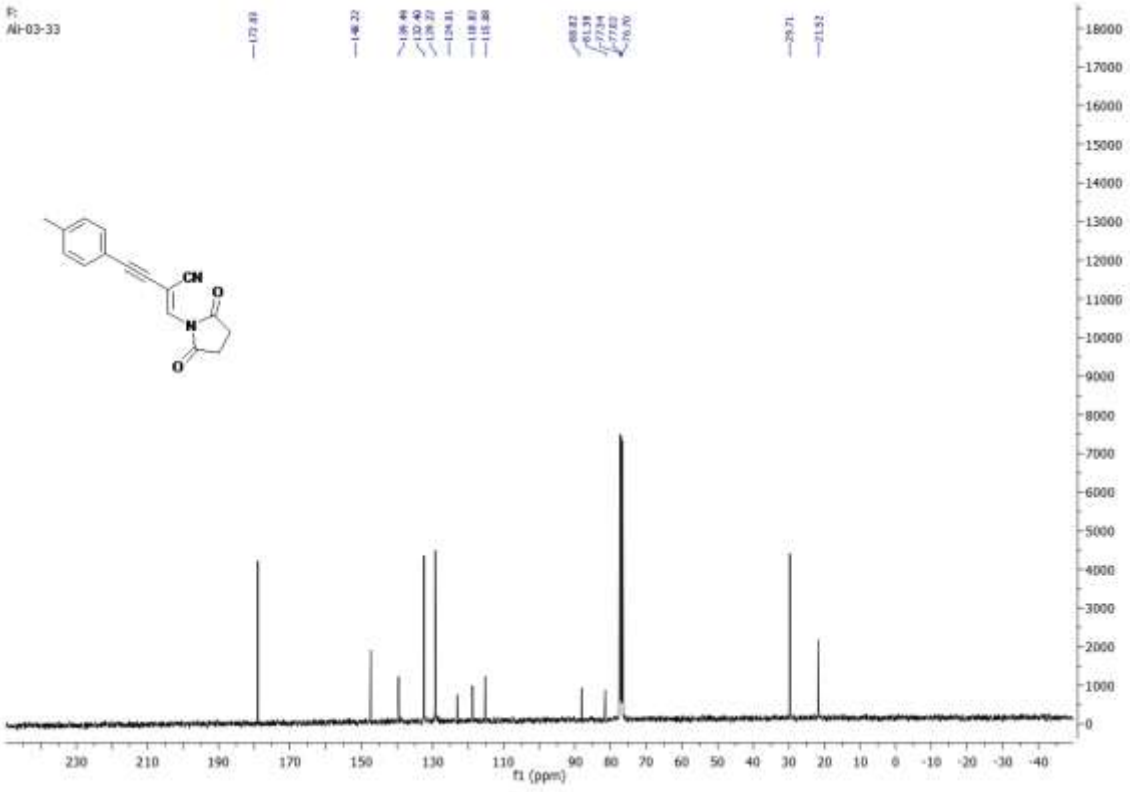

Ali-03-32
f1 (ppm)

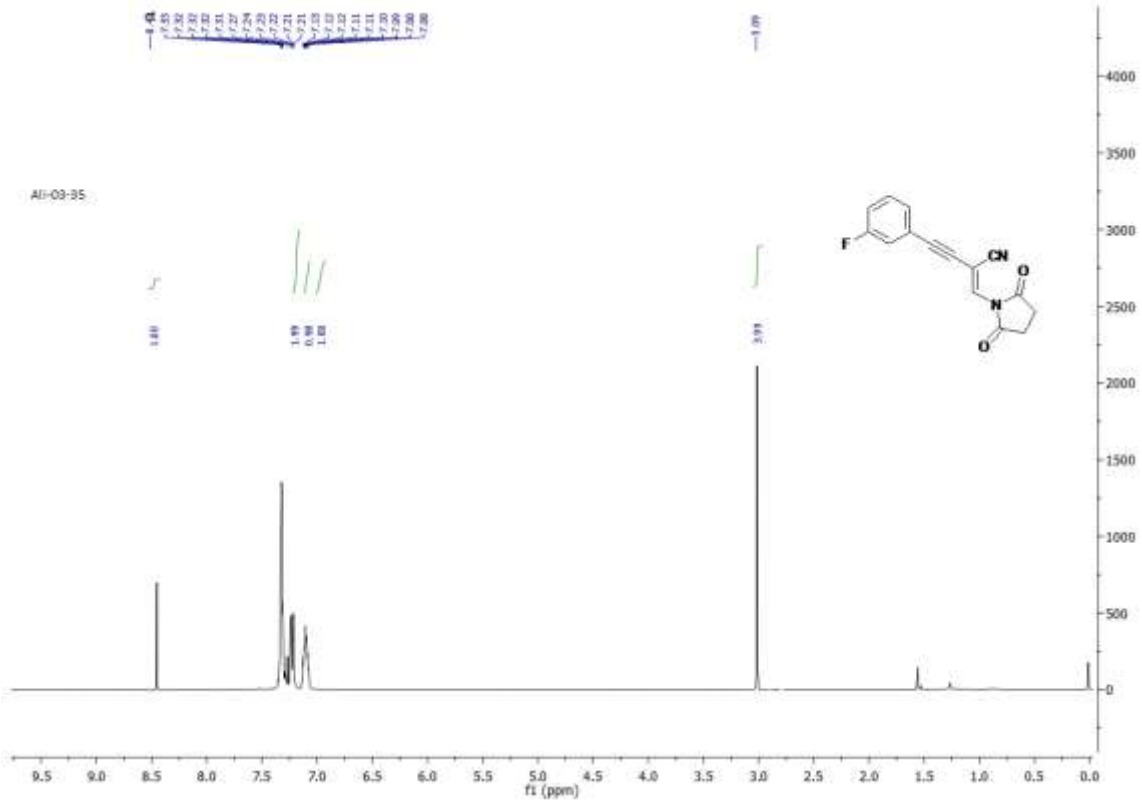

Ali
Ali-03-32
f1 (ppm)

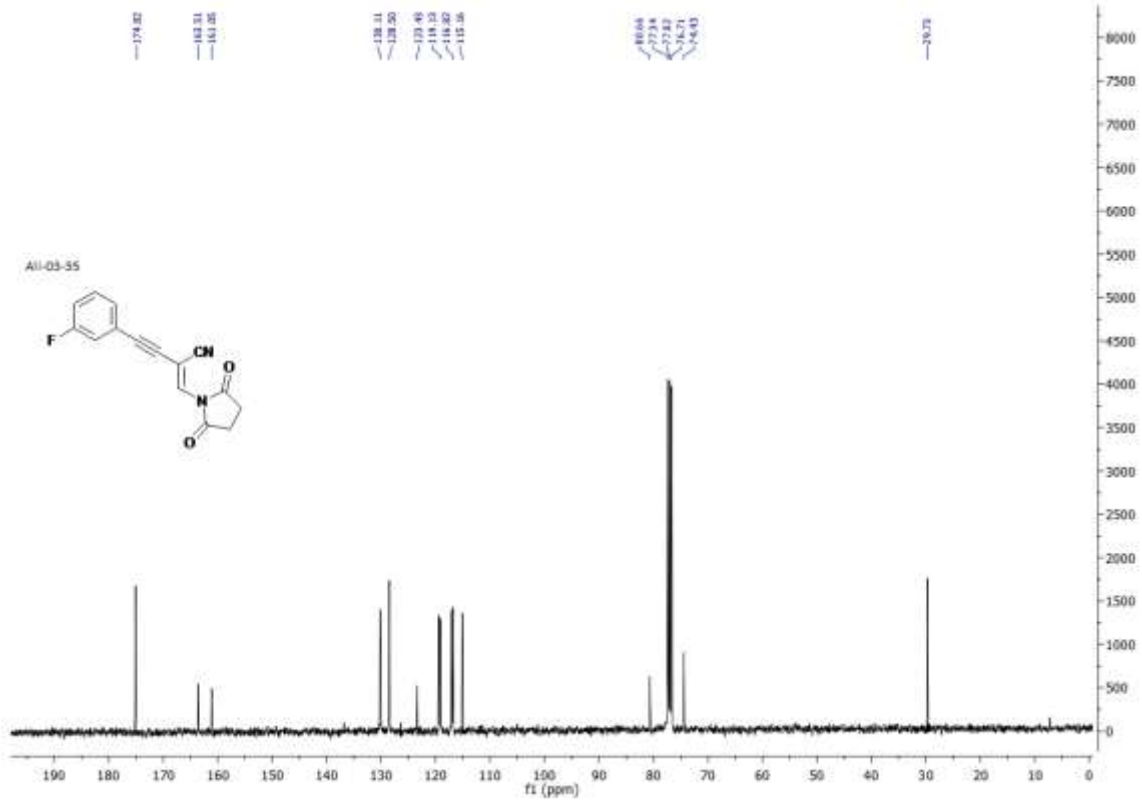


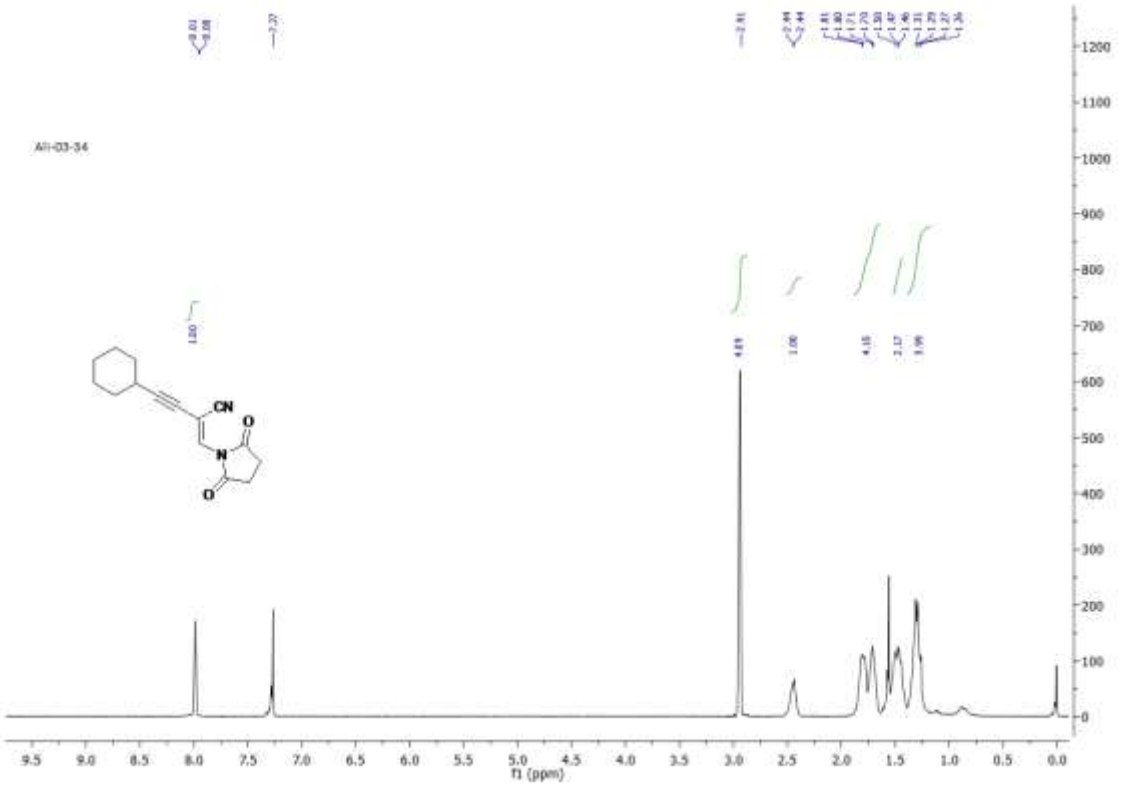


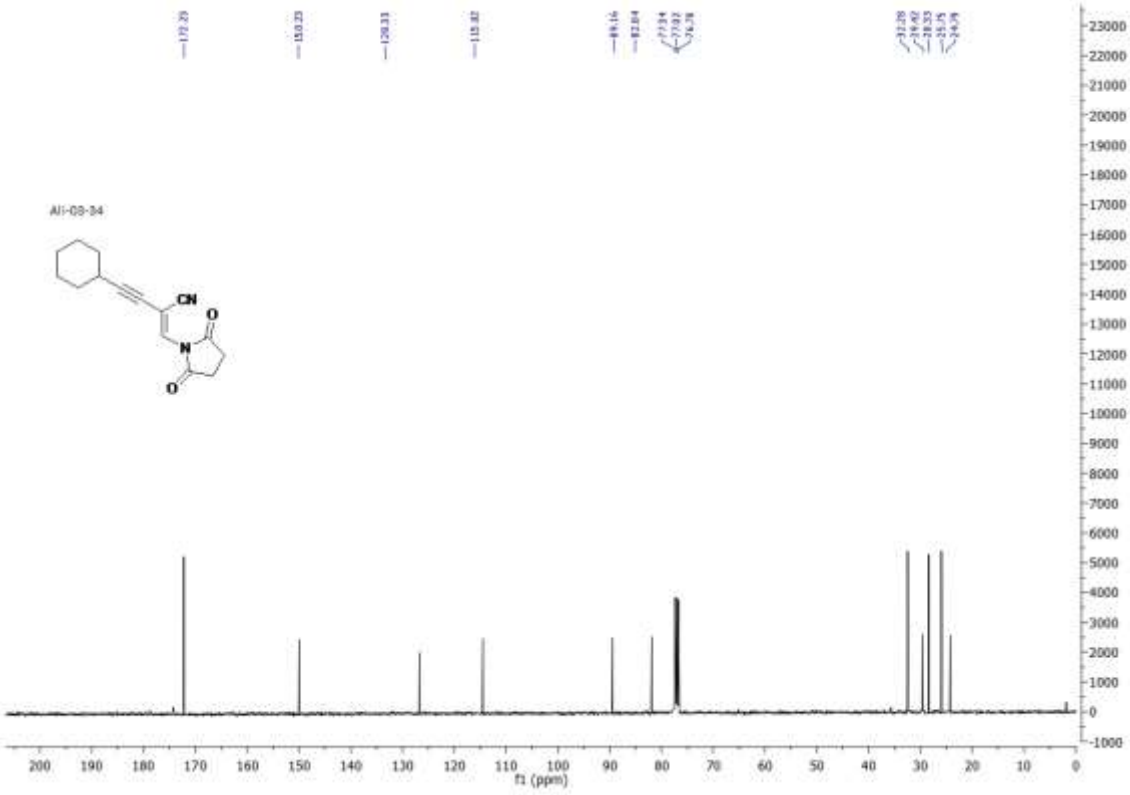


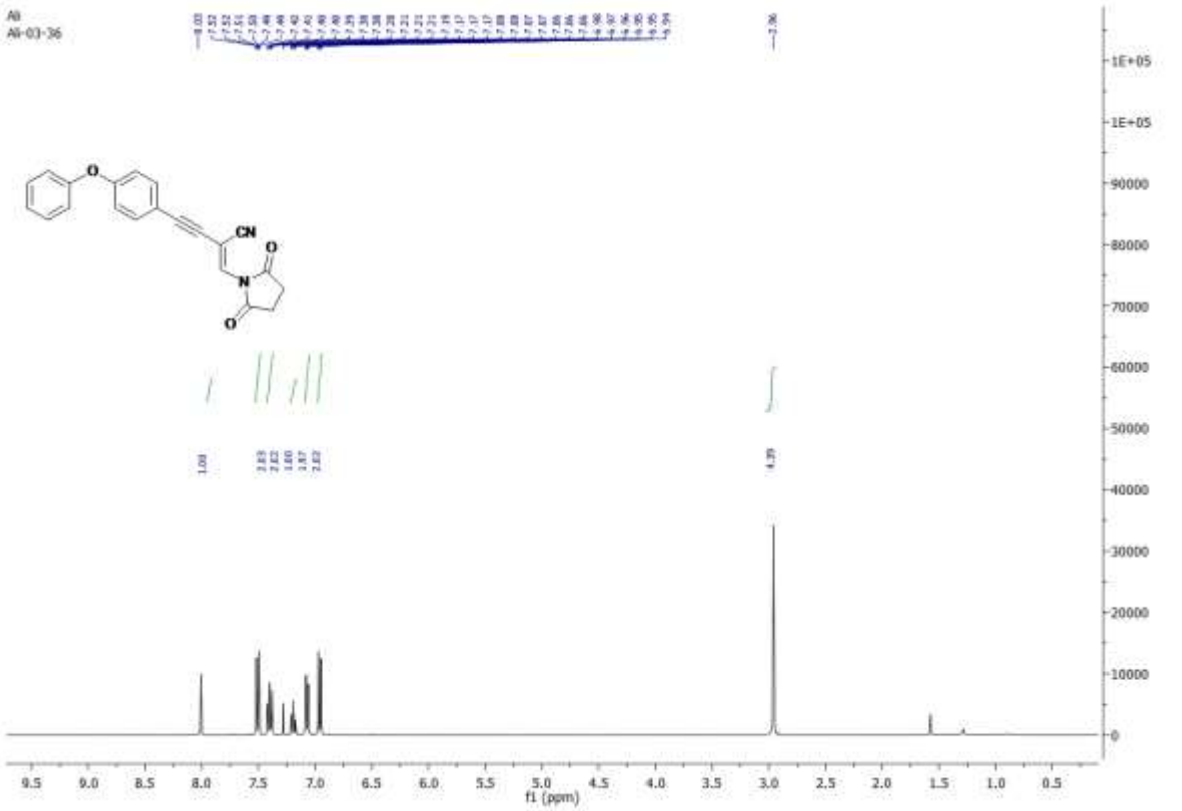


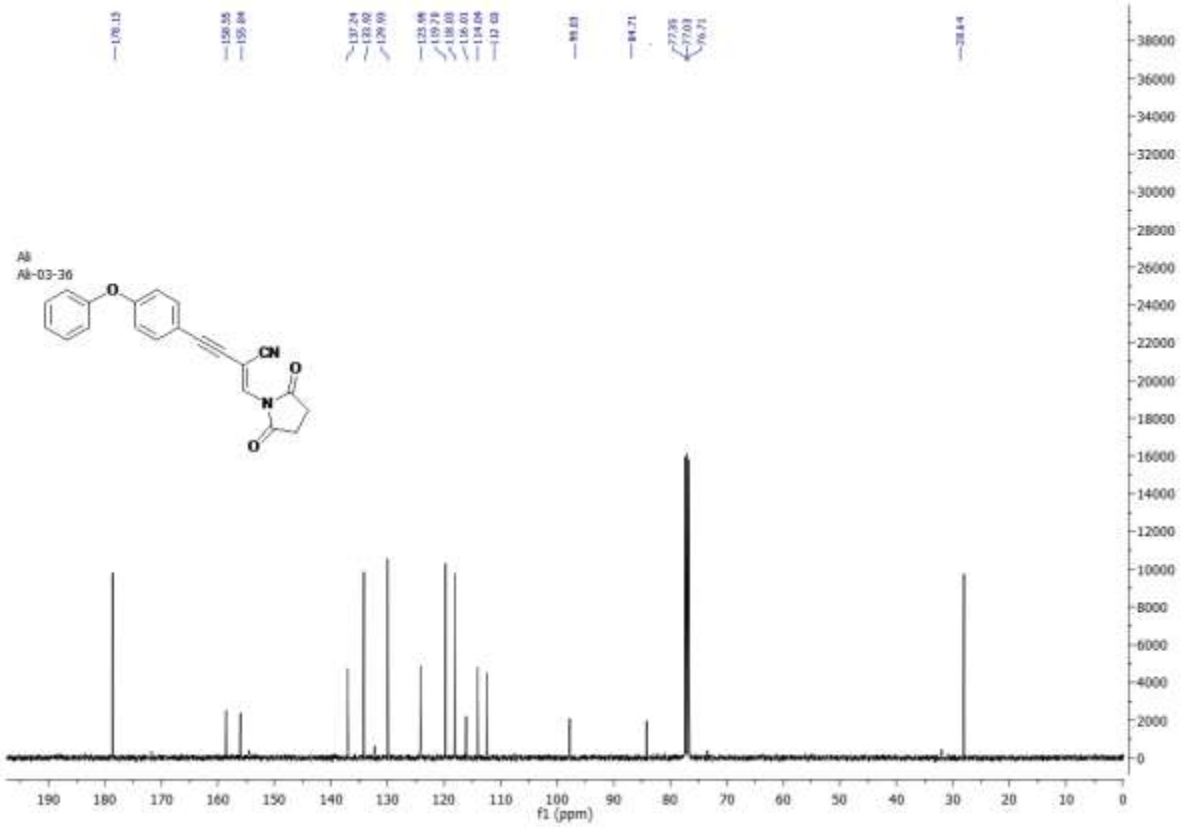

All-03-35
F
CN
O
N
O
f1 (ppm)

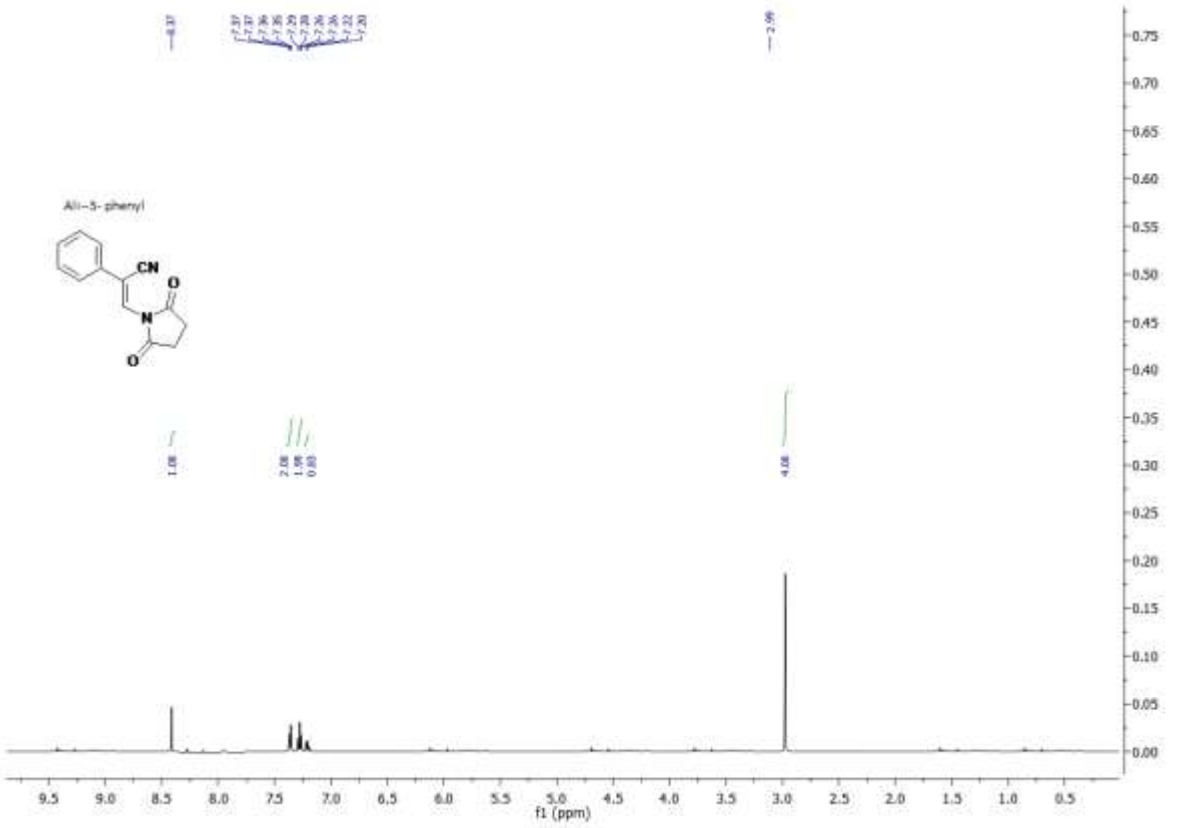

All-03-35
F
CN
O
N
O
f1 (ppm)

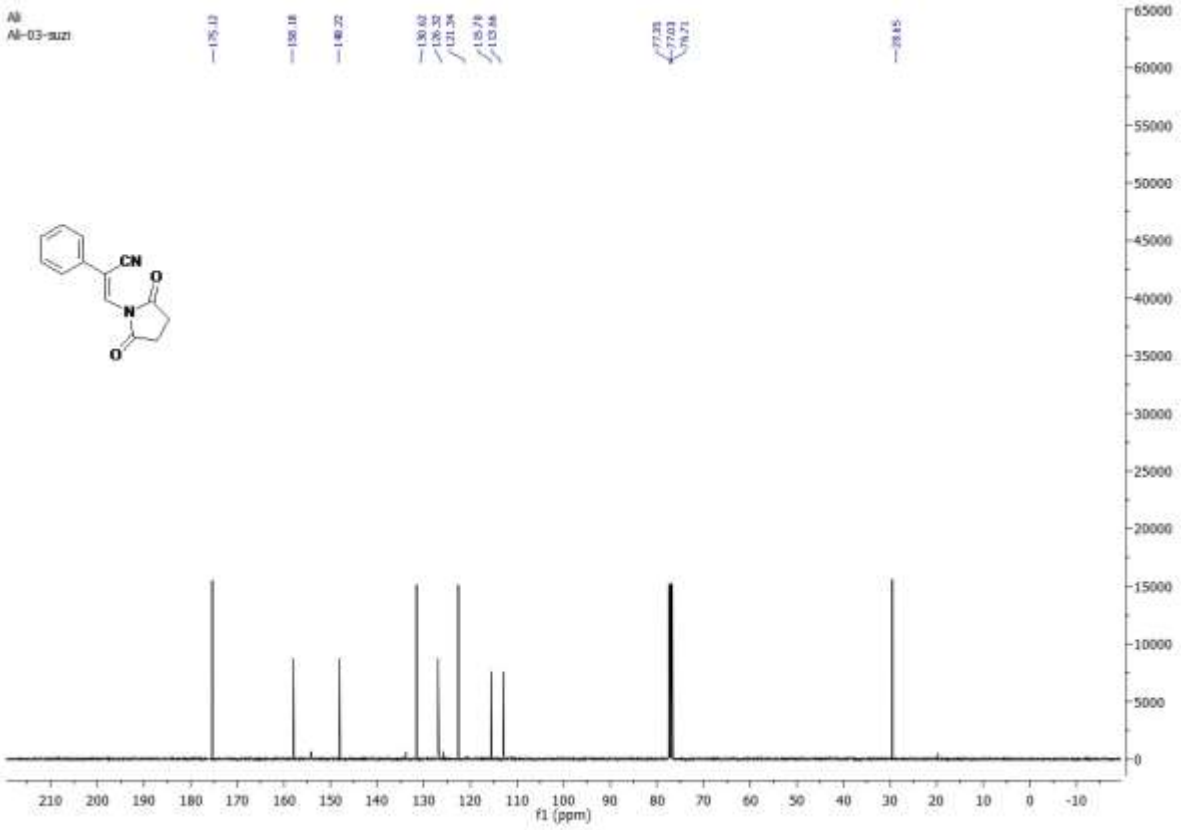

Ali-03-34
CN
O
N
O
f1 (ppm)

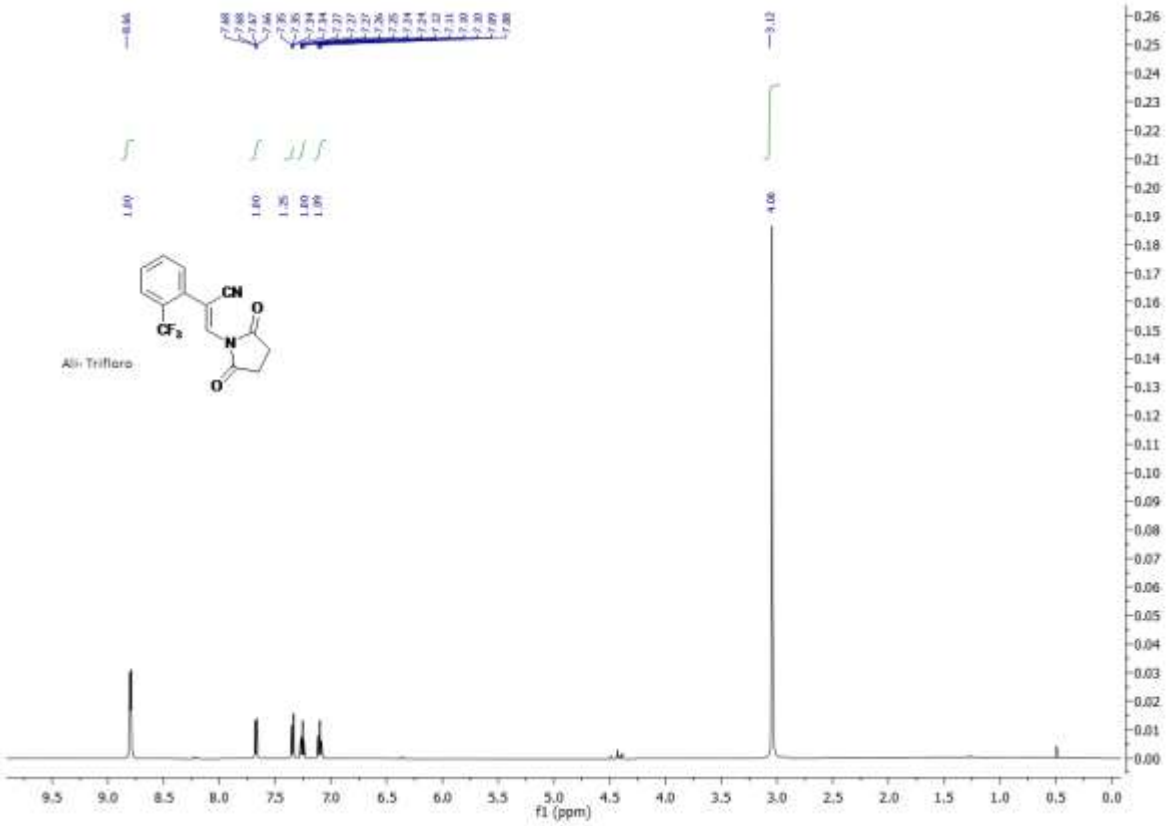

Ali-03-34
CN
O
N
O
f1 (ppm)

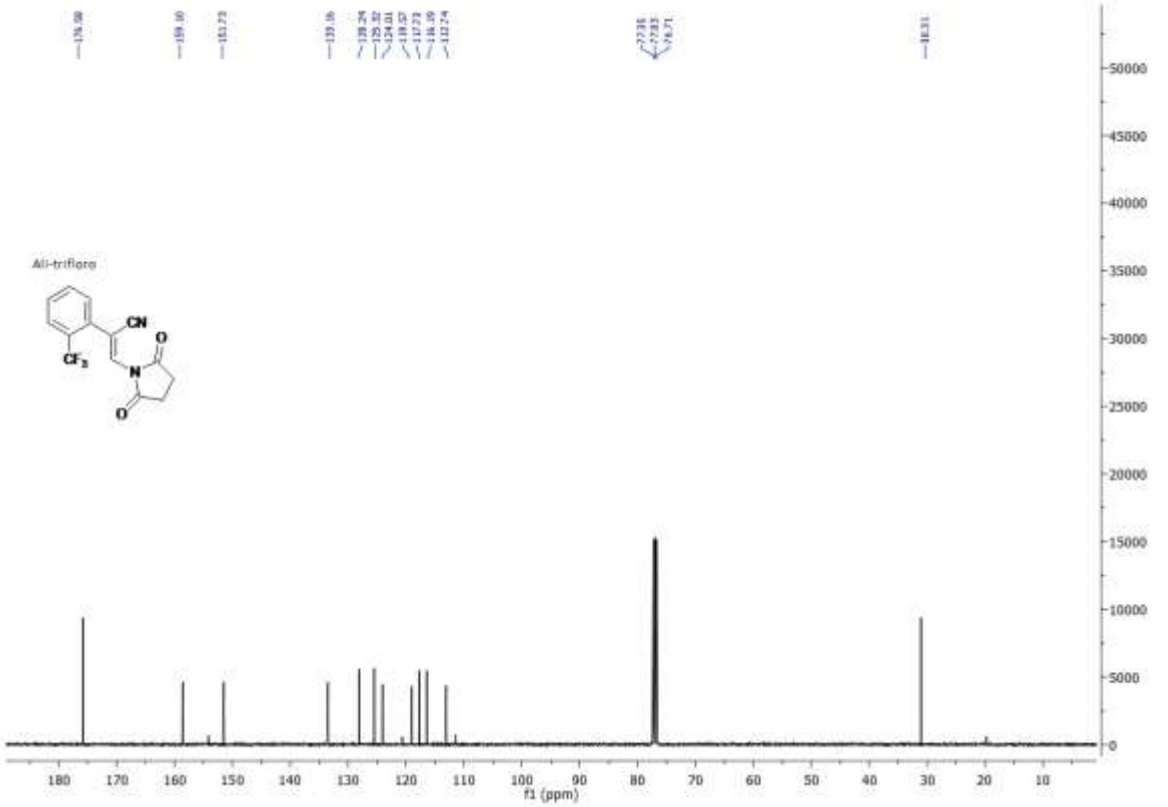

Ali
Ali-03-36
f1 (ppm)

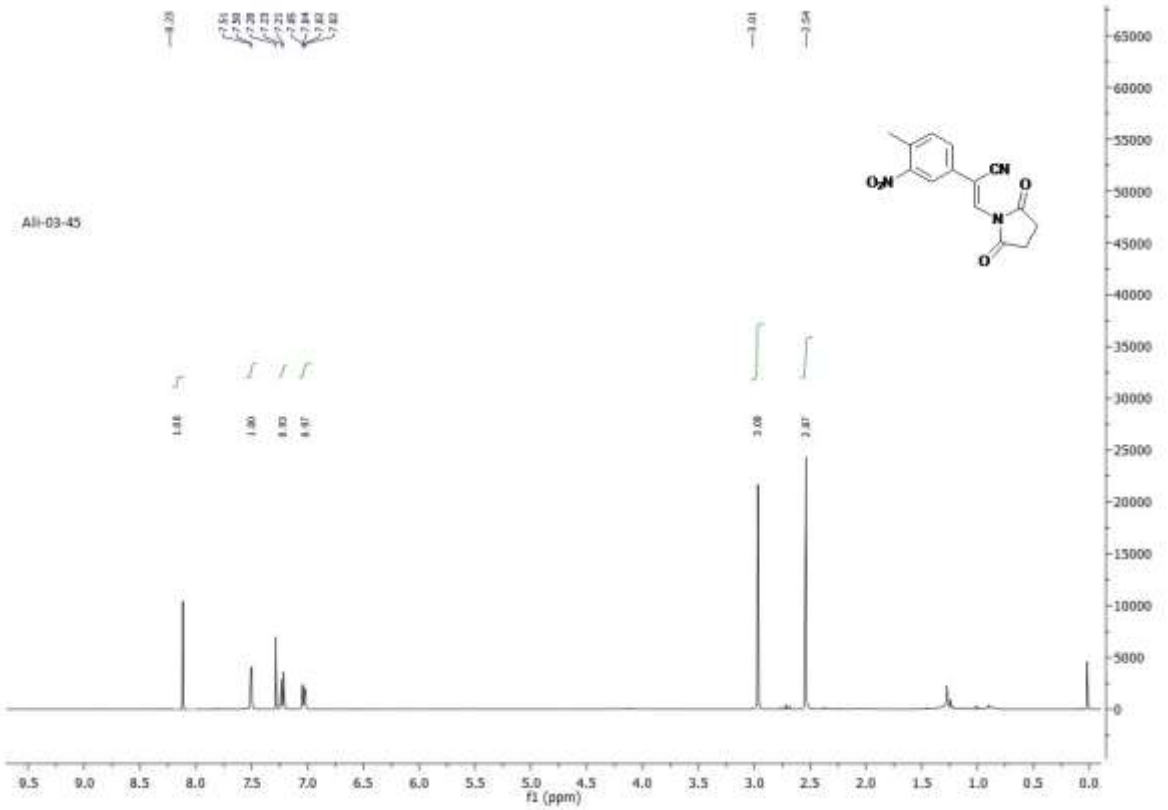

Ali
Ali-03-36
f1 (ppm)

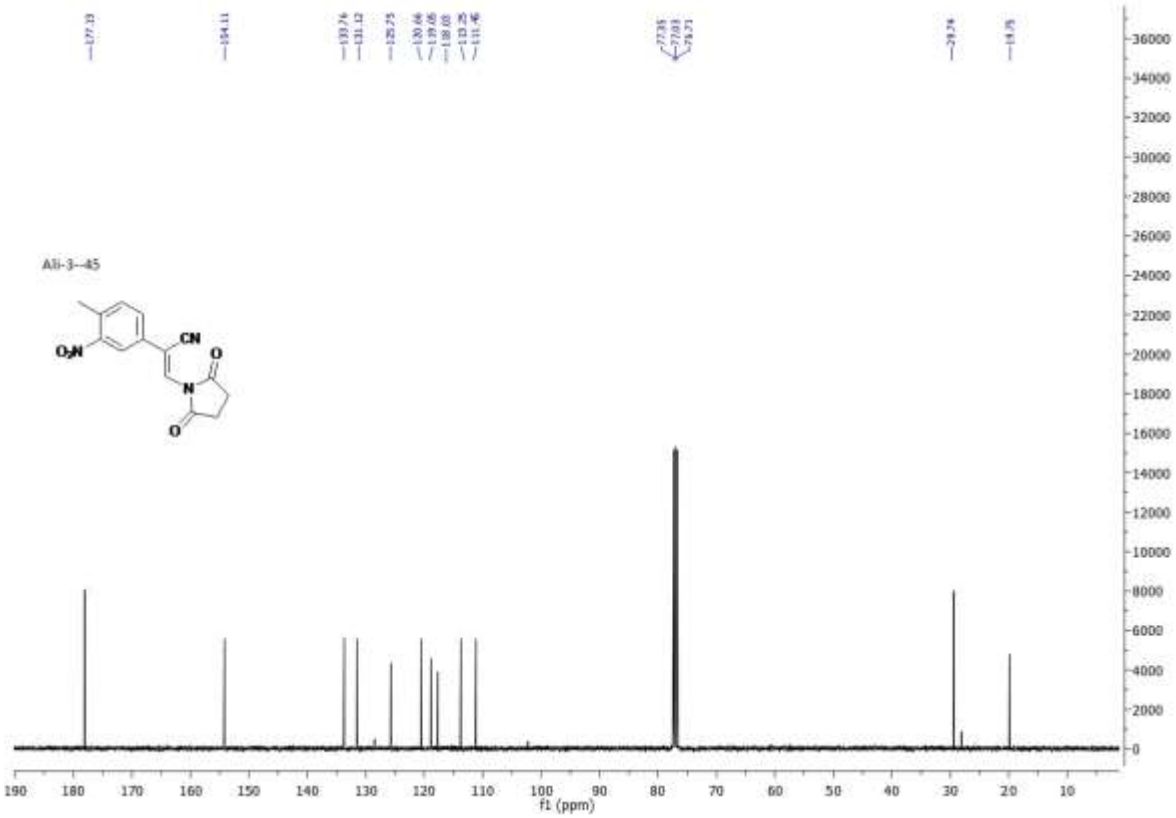

Ali-5-phenyl
CN
O
N
O
f1 (ppm)

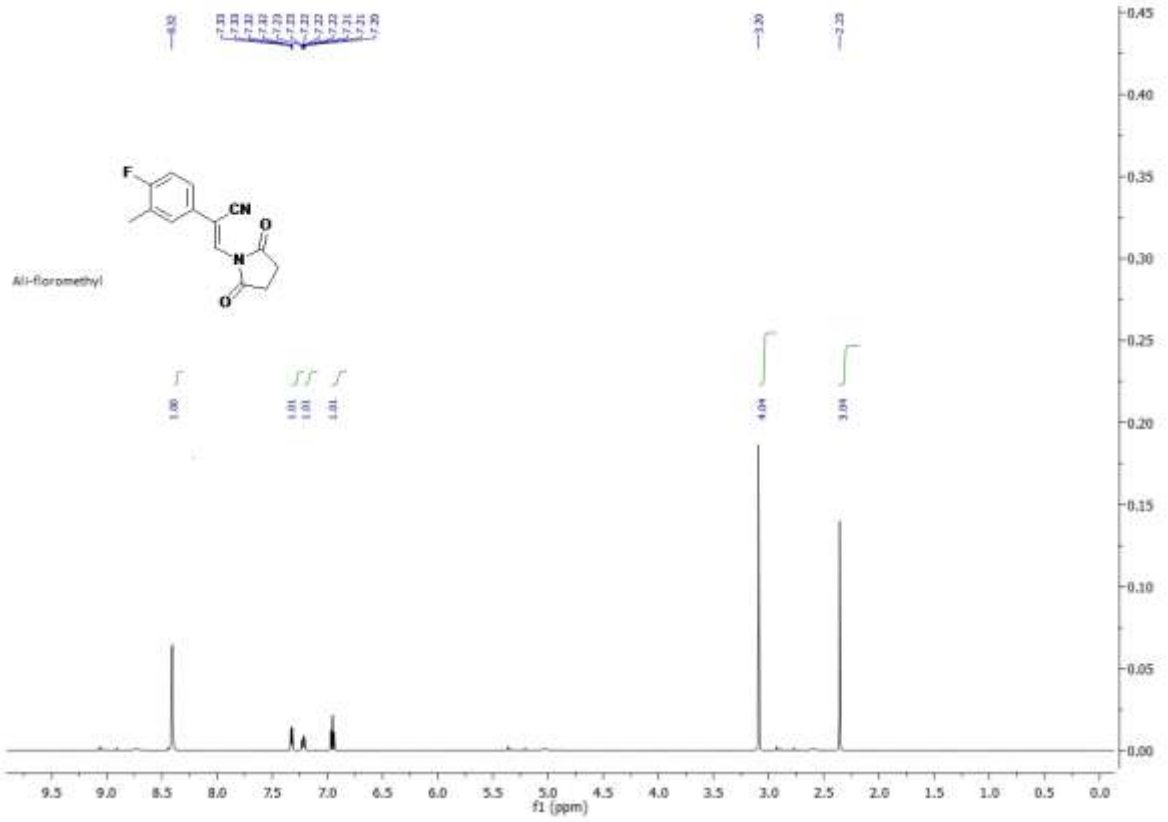

Ali
Ali-03-suzi
CN
O
N
O
f1 (ppm)

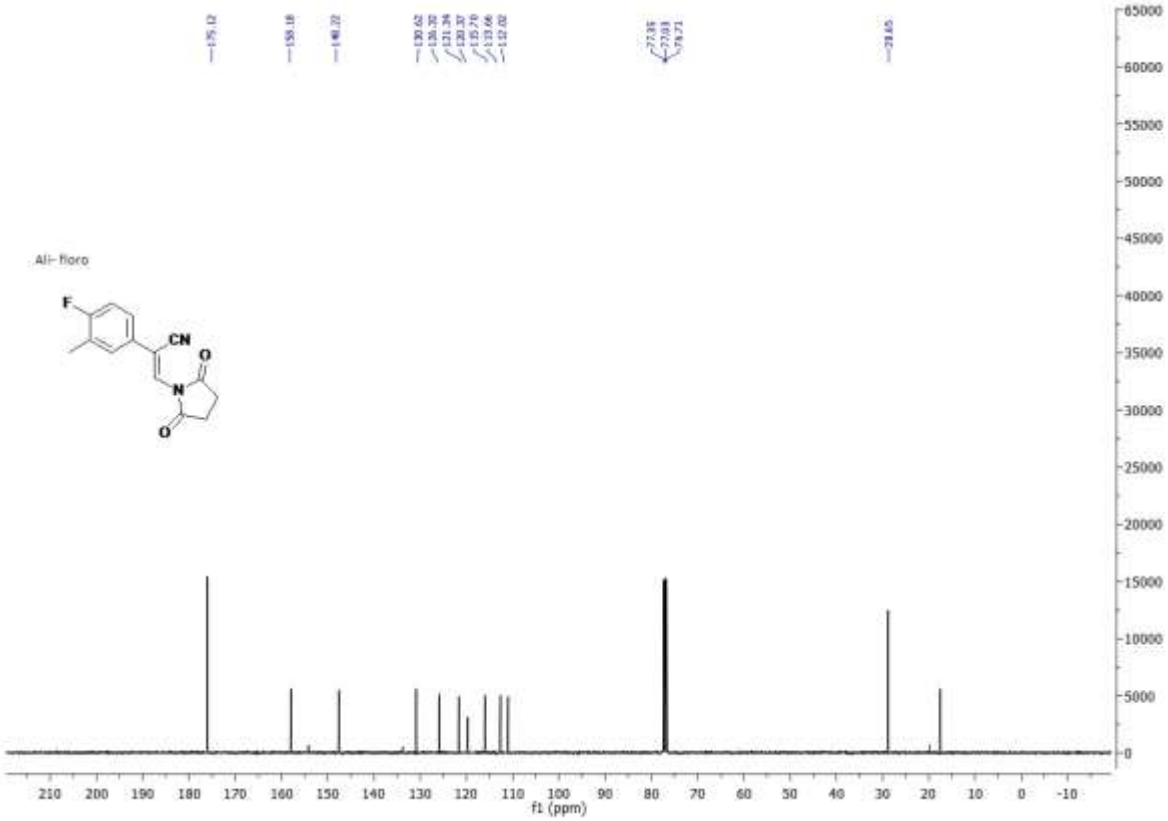









Ali-fluoromethyl
F
CN
O
N
O
f1 (ppm)

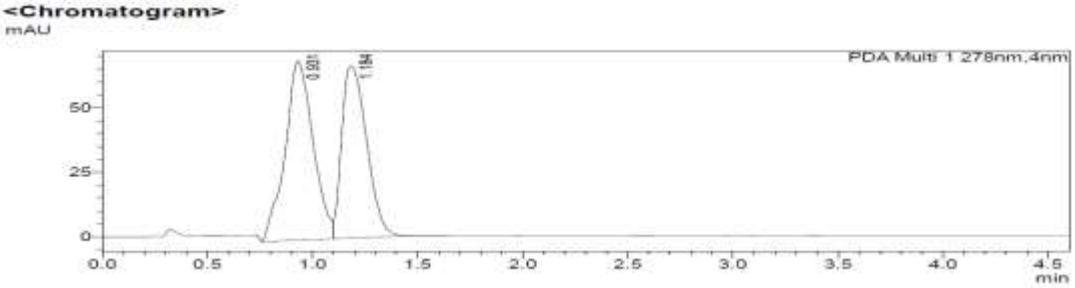

Ali- floro
F
CN
O
N
O
f1 (ppm)

SHIMADZU LabSolutions

Analysis Report

Data Filename : Ali 2 58 004.lcd
Method Filename : 80 20 MeOH water.lcm
Batch Filename : 26042013.lcb
Vial # : 1-31
Injection Volume : 5 uL

<Chromatogram>



Peak Table

PDA Ch1 278nm

Peak#	Ret. Time	Area	Height	Conc.	Name	Area%	Height%
1	0.931	645037	69476	0.000	RT 0.931	54.091	50.995
2	1.184	547459	66764	0.000	RT 1.184	45.909	49.005
Total		1192496	136239			100.000	100.000