Electronic Supplementary Material (ESI) for Chemical Communications

Zinc-Mediated Addition of Diethyl Bromomalonate to Alkynes for the Cascade Reaction towards Polysubstituted Pyranones and Tetracarbonyl Derivatives

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Supporting Information

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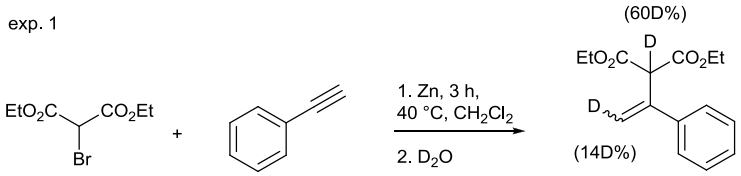
Deuterium labelling experiments

D_2O quenching experiment of the intermediate organo-zinc species:

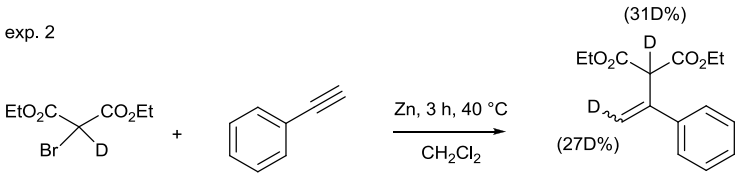
exp. 1



Reaction conditions: Diethyl bromomalonate (1 mmol), phenylacetylene (1.5 mmol) and zinc powder (1.5 mmol) in 1 mL CH_2Cl_2. Quenched after 3 h with 0.75 mL D_2O and filtration over short pad of silica, nmr analysis of the raw product.

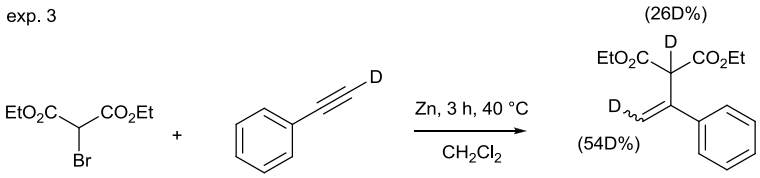
Realized deuterium labelling experiments:

exp. 2



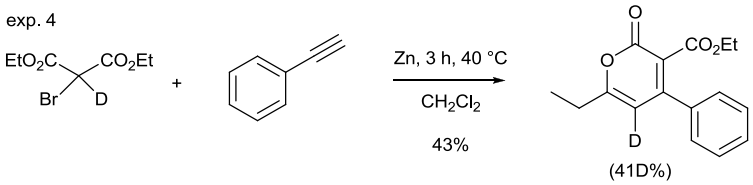
Reaction conditions: *d*-Diethyl bromomalonate (1 mmol), phenylacetylene (1.5 mmol) and zinc powder (1.5 mmol) in 1 mL CH_2Cl_2, 3 h at 40 °C, filtration over short pad of silica, nmr analysis of the raw product.

exp. 3



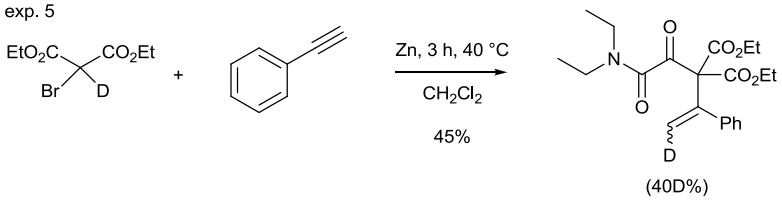
Reaction conditions: Diethyl bromomalonate (1 mmol), *d*-phenylacetylene (1.5 mmol) and zinc powder (1.5 mmol) in 1 mL CH_2Cl_2, 3 h at 40 °C, filtration over short pad of silica, nmr analysis of the raw product.

exp. 4



Reaction conditions: *d*-Diethyl bromomalonate (1 mmol), phenylacetylene (1.5 mmol) and zinc powder (1.5 mmol) in 1 mL CH_2Cl_2, 3 h at 40 °C, filtration over short pad of silica, flashchromatography on silica, nmr analysis.

exp. 5



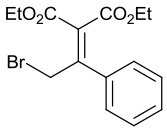
Reaction conditions: *d*-Diethyl bromomalonate (1 mmol), phenylacetylene (1.5 mmol) and zinc powder (1.5 mmol) in 1 mL CH_2Cl_2, 3 h at 40 °C, filtration over short pad of silica, flashchromatography on silica, nmr analysis.

Important: The malonate deuterium atome exchanges during column chromatography on silica gel with protons leading to an overall loss of deuterium labeling.

General procedure for the zinc-mediated synthesis of vinyl malonates

Diethyl bromomalonate (1.0 eq.) and alkyne (1.5 eq.) were dissolved in 1 mL anhydrous dichloromethane under an argon atmosphere in a flame dried Schlenk tube fitted with a teflon screwcap. Zinc powder (150 mol%) was added and the mixture was stirred for 3 h at 40 °C until complete conversion of diethyl bromomalonate was monitored by GC/MS. The reaction mixture was filtered over a short pad of silica gel (diethyl ether). The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel. The ratio of regioisomers after double bond migration was determined by integration of suitable ^{1}H NMR signals.

Diethyl 2-(2-bromo-1-phenylethylidene)malonate (4)



The product was prepared using phenylacetylene (77 mg, 0.75 mmol, 1.5 eq.). After quenching with bromine (26 μL, 0.50 mmol, 1.0 eq.), extraction from sodium thiosulphate solution (dichloromethane) and purification by column chromatography (pentane:ethyl acetate = 5:1) **4** was obtained as yellow oil (110 mg, 0.32 mmol, 65%). (Work-up differs from general procedure).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41 – 7.35 (m, 3H), 7.35 – 7.29 (m, 2H), 4.67 (s, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 3.97 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.1 Hz, 3H) ppm.

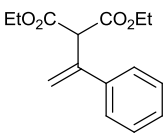
^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.3, 163.3, 152.3, 137.8, 129.1, 128.3, 127.5, 61.7, 61.3, 30.4, 14.0, 13.5 ppm.

IR (film, cm^{-1}): 2983, 1778, 1725, 1445, 1369, 1318, 1228, 1096, 1041, 767, 699.

MS (EI): m/z = 342 ([M^+], <1), 295 (8), 261 (48), 215 (97), 187 (100), 159 (21), 131 (31), 115 (81), 91 (18).

HRMS (ESI): calculated for $C_{15}H_{17}BrO_4Na$: 363.0208; found: 363.0202.

Diethyl 2-(1-phenylvinyl)malonate (5a)



The product was prepared using phenylacetylene (153 mg, 1.50 mmol, 1.5 eq.) and was obtained after purification by column chromatography (pentane:ethyl acetate = 5:1) as colorless oil (254 mg, 0.97 mmol, 97%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43 – 7.39 (m, 2H), 7.36 – 7.28 (m, 3H), 5.64 (s, 1H), 5.42 (d, *J* = 0.8 Hz, 1H), 4.62 (d, *J* = 0.7 Hz, 1H), 4.21 (qd, *J* = 7.1, 0.9 Hz, 4H), 1.24 (t, *J* = 7.1 Hz, 6H) ppm.

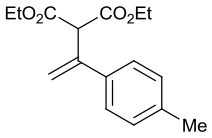
^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.9, 140.7, 140.2, 128.4, 127.9, 126.2, 117.6, 61.7, 57.2, 13.9 ppm.

IR (film, cm^{-1}): 3059, 1729, 1391, 1303, 1257, 1145, 1096, 1032, 913, 776, 736, 701, 577.

MS (EI): m/z = 262 ([M^+], 3), 216 (11), 189 (100), 171 (17), 161 (68), 115 (42), 91 (4).

HRMS (EI): calculated for $C_{15}H_{18}O_4$: 262.1205; found: 262.1208.

Diethyl 2-(1-*p*-tolylvinyl)malonate (5b)



The product was prepared using *p*-tolylacetylene (174 mg, 1.50 mmol, 1.5 eq.) and was obtained after purification by column chromatography (pentane:ethyl acetate = 20:1) as colorless oil (235 mg, 0.85 mmol, 85%). Ratio of regioisomers 95:5.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34 – 7.28 (m, 2H), 7.14 (dd, *J* = 7.4, 1.0 Hz, 2H), 5.61 (s, 1H), 5.36 (d, *J* = 0.7 Hz, 1H), 4.61 (d, *J* = 0.7 Hz, 1H), 4.21 (qd, *J* = 7.1, 0.8 Hz, 4H), 2.34 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 6H) ppm.

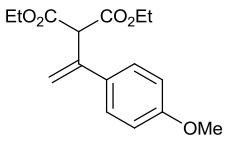
^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.9, 140.5, 137.8, 137.3, 129.1, 126.1, 116.8, 61.7, 57.2, 21.1, 13.9 ppm.

IR (film, cm^{-1}): 2983, 1728, 1618, 1513, 1369, 1304, 1226, 1145, 1096, 1033, 912, 823, 732.

MS (EI): m/z = 276 ([M^+], 7), 230 (18), 203 (100), 185 (21), 175 (91), 145 (22), 129 (53), 115 (48), 91 (20).

HRMS (ESI): calculated for $C_{16}H_{20}O_4Na$: 299.1259; found: 299.1254.

Diethyl 2-(1-(4-methoxyphenyl)vinyl)malonate (5c)



The product was prepared using 1-ethynyl-4-methoxybenzene (198 mg, 1.50 mmol, 1.5 eq.) and was obtained after purification by column chromatography (pentane:ethyl acetate = 10:1) as colorless oil (272 mg, 0.93 mmol, 93%). Ratio of regioisomers 75:25.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36 – 7.32 (m, 2H), 6.89 – 6.83 (m, 2H), 5.56 (s, 1H), 5.31 (d, *J* = 0.8 Hz, 1H), 4.59 (d, *J* = 0.7 Hz, 1H), 4.21 (qd, *J* = 7.1, 0.8 Hz, 4H), 3.80 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 6H) ppm.

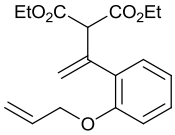
^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.0, 159.4, 140.12, 132.6, 127.4, 116.1, 113.8, 61.7, 57.3, 55.3, 14.0 ppm.

IR (film, cm^{-1}): 2981, 2838, 1728, 1607, 1512, 1463, 1445, 1367, 1246, 1178, 1145, 1029, 908, 835.

MS (EI): m/z = 292 ([M^+], 26), 246 (18), 219 (100), 201 (23), 191 (99), 145 (41), 133 (30), 103 (32), 77 (27).

HRMS (ESI): calculated for $C_{16}H_{20}O_5Na$: 315.1208; found: 315.1203.

Diethyl 2-(1-(2-(allyloxy)phenyl)vinyl)malonate (5d)



The product was prepared using 1-(allyloxy)-2-ethynylbenzene (118 mg, 0.75 mmol, 1.5 eq.) and was obtained after purification by column chromatography (pentane:diethyl ether = 5:1) as colorless oil (102 mg, 0.32 mmol, 64%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.27 – 7.26 (m, 1H), 7.25 – 7.24 (m, 1H), 6.92 (td, *J* = 7.5, 1.0 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.03 (ddt, *J* = 17.3, 10.5, 5.3 Hz, 1H), 5.52 (s, 1H), 5.45 (s, 1H), 5.40 (dq, *J* = 17.3, 1.6 Hz, 1H), 5.25 (dq, *J* = 10.5, 1.4 Hz, 1H), 4.69 (s, 1H), 4.53 (dt, *J* = 5.2, 1.5 Hz, 2H), 4.24 – 4.15 (m, 4H), 1.24 (t, *J* = 7.1 Hz, 6H) ppm.

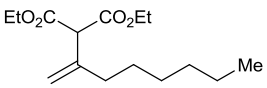
^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.1, 155.2, 140.1, 133.1, 130.7, 129.1, 120.9, 119.4, 117.4, 111.9, 69.1, 61.4, 56.8, 14.0 ppm.

IR (film, cm^{-1}): 2984, 1732, 1599, 1486, 1450, 1369, 1297, 1249, 1147, 1036, 923, 755.

MS (EI): m/z = 318 ([M^+], 1), 277 (36), 245 (15), 203 (100), 171 (15), 158 (23), 147 (20), 131 (46), 103 (10), 77 (10).

HRMS (EI): calculated for $C_{18}H_{22}O_5$: 318.1467; found: 318.1464.

Diethyl 2-(oct-1-en-2-yl)malonate (5e)



The product was prepared using 1-octyne (165 mg, 1.50 mmol, 1.5 eq.) and was obtained after purification by column chromatography (pentane:ethyl acetate = 50:1) as colorless oil (194 mg, 0.72 mmol, 72%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.09 (s, 1H), 5.06 (s, 1H), 4.20 (q, *J* = 7.1 Hz, 4H), 4.05 (s, 1H), 2.13 (t, *J* = 7.5 Hz, 2H), 1.51 – 1.39 (m, 2H), 1.29 – 1.24 (m, 12H), 0.87 (t, *J* = 6.7 Hz, 3H) ppm.

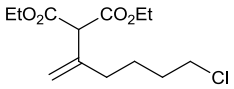
^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.0, 141.7, 114.9, 61.4, 58.4, 35.1, 31.7, 28.8, 27.4, 22.5, 14.0 ppm.

IR (film, cm^{-1}): 2957, 2929, 2858, 1732, 1646, 1464, 1446, 1390, 1303, 1237, 1142, 1036, 904, 864.

MS (EI): m/z = 270 ([M^+], 1), 225 (8), 197 (100), 169 (41), 139 (66), 123 (26), 111 (22), 81 (30), 67 (22), 55 (24).

HRMS (ESI): calculated for $C_{15}H_{26}O_4Na$: 293.1729; found 293.1723.

Diethyl 2-(6-chlorohex-1-en-2-yl)malonate (5f)



The product was prepared using 6-chloro-1-hexyne (175 mg, 1.50 mmol, 1.5 eq.) and was obtained after purification by column chromatography (pentane:diethyl ether = 10:1) as colorless oil (213 mg, 0.77 mmol, 77%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.12 (d, *J* = 1.9 Hz, 2H), 4.21 (q, *J* = 7.1 Hz, 4H), 4.06 (s, 1H), 3.55 (t, *J* = 6.5 Hz, 2H), 2.19 (t, *J* = 7.6 Hz, 2H), 1.80 (dt, *J* = 13.9, 6.8 Hz, 2H), 1.63 (dt, *J* = 14.6, 7.0 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 6H) ppm.

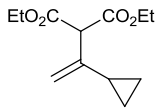
^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.9, 140.8, 115.7, 61.6, 58.4, 44.8, 33.9, 31.9, 24.6, 14.0 ppm.

IR (film, cm^{-1}): 2983, 2939, 1729, 1646, 1447, 1368, 1304, 1236, 1144, 1033, 910, 649.

MS (EI): m/z = 276 ([M^+], <1), 231 (7), 203 (100), 175 (71), 139 (41), 111 (22), 93 (19).

HRMS (ESI): calculated for $C_{13}H_{21}ClO_4Na$: 299.1026; found: 299.1021.

Diethyl 2-(1-cyclopropylvinyl)malonate (5g)



The product was prepared using cyclopropylacetylene (99 mg, 1.50 mmol, 1.5 eq.) and was obtained after purification by column chromatography (pentane:ethyl acetate = 20:1) as colorless oil (206 mg, 0.91 mmol, 91%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.95 (d, *J* = 1.4 Hz, 2H), 4.21 (q, *J* = 7.0 Hz, 4H), 4.12 (s, 1H), 1.58 – 1.47 (m, 1H), 1.27 (t, *J* = 7.1 Hz, 6H), 0.68 (dt, *J* = 6.1, 4.1 Hz, 2H), 0.48 (dt, *J* = 6.5, 4.2 Hz, 2H) ppm.

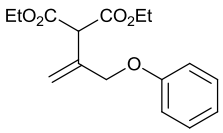
^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.0, 143.1, 112.6, 61.5, 58.6, 15.3, 14.0, 6.5 ppm.

IR (film, cm^{-1}): 2985, 1728, 1642, 1612, 1450, 1369, 1304, 1231, 1178, 1144, 1096, 1033.

MS (EI): m/z = 226 ([M^+], 4), 198 (10), 180 (13), 170 (24), 152 (61), 126 (88), 107 (60), 98 (24), 79 (100).

HRMS (ESI): calculated for $C_{12}H_{18}O_4Na$: 249.1103; found: 249.1098.

Diethyl 2-(3-phenoxyprop-1-en-2-yl)malonate (5h)



The product was prepared using (prop-2-ynyloxy)benzene (198 mg, 1.50 mmol, 1.5 eq.) and was obtained after purification by column chromatography (pentane:ethyl acetate = 20:1) as colorless oil (191 mg, 0.65 mmol, 65%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32 – 7.24 (m, 2H), 7.01 – 6.89 (m, 3H), 5.50 (t, *J* = 1.4 Hz, 1H), 5.34 (d, *J* = 0.6 Hz, 1H), 4.67 (s, 2H), 4.30 (s, 1H), 4.22 (qd, *J* = 7.1, 0.9 Hz, 4H), 1.27 (t, *J* = 7.1 Hz, 6H) ppm.

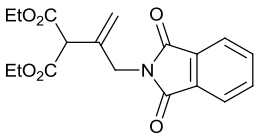
^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.6, 158.4, 136.9, 129.4, 121.1, 118.1, 114.8, 69.3, 61.8, 55.7, 14.0 ppm.

IR (film, cm^{-1}): 2983, 1730, 1598, 1588, 1495, 1368, 1302, 1236, 1172, 1147, 1032, 754, 692.

MS (EI): m/z = 292 ([M^+], 9), 246 (9), 219 (14), 199 (32), 171 (24), 143 (50), 125 (100), 97 (34), 81 (40), 53 (37).

HRMS (ESI): calculated for $C_{16}H_{20}O_5Na$: 315.1208; found: 315.1203.

Diethyl 2-(3-(1,3-dioxoisoindolin-2-yl)prop-1-en-2-yl)malonate (5i)



The product was prepared using *N*-propargylphthalimide (278 mg, 1.50 mmol, 1.5 eq.) and was obtained after purification by column chromatography (pentane:ethyl acetate = 5:1) as colorless oil (229 mg, 0.66 mmol, 66%).

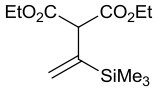
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.86 (dd, *J* = 5.3, 3.1 Hz, 2H), 7.73 (dd, *J* = 5.4, 3.1 Hz, 2H), 5.30 (d, *J* = 3.8 Hz, 2H), 4.44 (s, 2H), 4.22 – 4.15 (m, 5H), 1.23 (t, *J* = 7.1 Hz, 6H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.8, 167.3, 135.5, 134.0, 132.1, 123.4, 118.8, 61.8, 56.4, 41.6, 13.9 ppm.

IR (film, cm^{-1}): 2985, 2257, 1713, 1468, 1426, 1390, 1309, 1249, 1112, 1034, 908, 720.

HRMS (ESI): calculated for $C_{18}H_{19}NO_6Na$: 368.1110; found: 368.1105.

Diethyl 2-(1-(trimethylsilyl)vinyl)malonate (5j)



The product was prepared using ethynyltrimethylsilane (147 mg, 1.50 mmol, 1.5 eq.) and was obtained after purification by column chromatography (pentane:diethyl ether = 10:1) as colorless oil (225 mg, 0.87 mmol, 87%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.54 (d, *J* = 8.5 Hz, 1H), 4.68 (d, *J* = 8.5 Hz, 1H), 4.24 (s, 1H) 4.22 (qd, *J* = 7.1, 1.3 Hz, 4H), 1.28 (t, *J* = 7.1 Hz, 6H), 0.22 (s, 9H) ppm.

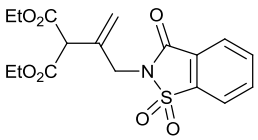
^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.9, 137.2, 132.5, 61.9, 55.6, 14.0, -2.1 ppm.

IR (film, cm^{-1}): 2981, 1735, 1449, 1368, 1248, 1183, 1147, 1096, 1028, 883, 838, 756.

MS (EI): m/z = 258 ([M^+], 100), 229 (4), 183 (11), 148 (13), 139 (47), 111 (16), 73 (47).

HRMS (ESI): calculated for $C_{12}H_{22}O_4SiNa$: 281.1185; found: 281.1180.

Diethyl (1-((1,1-dioxido-3-oxo-1,2-benzisothiazol-2(3*H*)-yl)methyl)vinyl)malonate (5k)



The product was prepared using *N*-propargylsaccharine (332 mg, 1.50 mmol, 1.5 eq.) and was obtained after purification by column chromatography (pentane:ethyl acetate = 3:1) as colorless oil (196 mg, 0.51 mmol, 51%).

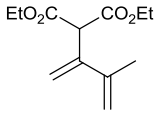
^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 7.1 Hz, 1H), 7.93 (d, *J* = 7.2 Hz, 1H), 7.88 (td, *J* = 7.5, 1.2 Hz, 1H), 7.84 (td, *J* = 7.5, 1.2 Hz, 1H), 5.51 (s, 1H), 5.41 (s, 1H), 4.56 (s, 2H), 4.29 (s, 1H), 4.24 (qd, *J* = 7.1, 0.7 Hz, 4H), 1.28 (t, *J* = 7.1 Hz, 6H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 167.2, 158.9, 137.9, 134.9, 134.3, 134.3, 127.2, 125.3, 121.0, 120.0, 61.9, 56.3, 42.3, 13.9 ppm.

IR (film, cm^{-1}): 2984, 1730, 1461, 1437, 1336, 1298, 1253, 1181, 1058, 1033, 753, 675, 586.

HRMS (ESI): calculated for $C_{17}H_{19}NO_7SNa$: 404.0780; found: 404.0774.

Diethyl 2-(3-methylbuta-1,3-dien-2-yl)malonate (5l)



The product was prepared using 2-methyl-1-buten-3-yne (99 mg, 1.50 mmol, 1.5 eq.) and was obtained after purification by column chromatography (pentane:diethyl ether = 10:1) as colorless oil (170 mg, 0.75 mmol, 75%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.47 (s, 1H), 5.23 (s, 1H), 5.02 (s, 1H), 4.99 (s, 1H), 4.50 (s, 1H), 4.21 (q, *J* = 7.1 Hz, 4H), 1.96 (s, 3H), 1.26 (t, *J* = 6.9 Hz, 6H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.2, 141.9, 140.1, 116.5, 113.1, 61.6, 55.37, 21.1, 14.0 ppm.

IR (film, cm^{-1}): 2983, 1731, 1602, 1447, 1369, 1305, 1240, 1210, 1137, 1034, 898, 863.

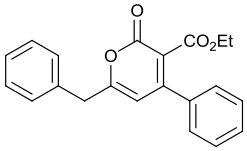
MS (EI): m/z = 226 ([M^+], 5), 181 (3), 152 (100), 135 (28), 125 (88), 107 (7), 79 (26).

HRMS (ESI): calculated for $C_{12}H_{18}O_4H$: 227.1283; found: 227.1278.

General procedure for the zinc-mediated synthesis of 2*H*-Pyran-2-ones

Diethyl bromomalonate (239 mg, 1.00 mmol, 1.0 eq.) and phenylacetylene (153 mg, 1.50 mmol, 1.5 eq.) were dissolved in 1 mL anhydrous dichloromethane under an argon atmosphere in a flame dried Schlenk tube fitted with a teflon screwcap. Zinc powder (150 mol%) was added and the mixture was stirred for 3 h at 40 °C until complete conversion of diethyl bromomalonate was monitored by GC/MS. The screwcap was changed to a septum and the reaction mixture was cooled to -40 °C. Acid chloride (3.0 eq.) was added dropwise via a syringe. The mixture was stirred overnight and allowed to warm to room temperature. After dilution with ethyl acetate the reaction mixture was washed with sodium bicarbonate solution (3x 20 mL) and brine and was dried over anhydrous magnesium sulphate. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel.

Ethyl 6-benzyl-2-oxo-4-phenyl-2*H*-pyran-3-carboxylate (8a)



The product was prepared using phenylacetyl chloride (0.40 mL, 3.00 mmol, 3.0 eq.) and was obtained after purification by column chromatography (pentane:ethyl acetate = 5:1) as yellow oil (254 mg, 0.76 mmol, 76%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.44 – 7.38 (m, 3H), 7.35 (dd, *J* = 7.6, 6.9 Hz, 4H), 7.31 – 7.27 (m, 3H), 6.03 (s, 1H), 4.13 (d, *J* = 7.1 Hz, 2H), 3.86 (s, 2H), 1.03 (t, *J* = 7.1 Hz, 3H) ppm.

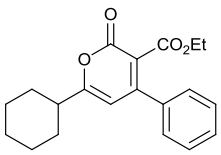
^{13}C NMR (126 MHz, $CDCl_3$): δ = 165.0, 164.8, 159.7, 154.9, 136.1, 134.5, 130.1, 129.2, 129.0, 128.8, 127.5, 127.2, 116.5, 105.8, 61.7, 40.2, 13.6 ppm.

IR (film, cm^{-1}): 2983, 1734, 1635, 1546,1449, 1247, 1098, 1029, 856, 762, 700.

MS (EI): m/z = 334 ([M^+], 23), 306 (13), 289 (31), 243 (100), 215 (86), 171 (25), 115 (11).

HRMS (ESI): calculated for $C_{21}H_{18}O_4Na$: 357.1103; found: 357.1097.

Ethyl 6-cyclohexyl-2-oxo-4-phenyl-2*H*-pyran-3-carboxylate (8b)



The product was prepared using cyclohexanecarbonyl chloride (0.40 mL, 3.00 mmol, 3.0 eq.) and was obtained after purification by column chromatography (pentane:ethyl acetate = 5:1) and recrystallization from ethanol as yellow crystals (225 mg, 0.69 mmol, 69%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50 – 7.35 (m, 5H), 6.09 (d, *J* = 0.4 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.46 (tt, *J* = 11.6, 3.3 Hz, 1H), 2.05 – 1.94 (m, 2H), 1.89 – 1.79 (m, 2H), 1.77 – 1.69 (m, 1H), 1.53 – 1.18 (m, 5H), 1.03 (t, *J* = 7.1 Hz, 3H) ppm.

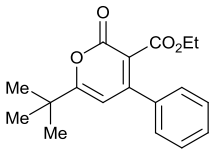
^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.5, 165.0, 160.1, 155.3, 136.5, 130.0, 128.8, 127.2, 116.2, 103.2, 61.6, 42.5, 30.4, 25.7, 25.6, 13.7 ppm

IR (film, cm^{-1}): 2930, 2856, 1737, 1704, 1632, 1546, 1448, 1292, 1251, 1100, 767, 697.

MS (EI): m/z = 326 ([M^+], 32), 298 (100), 281 (29), 243 (59), 226 (25), 215 (76), 171 (22).

HRMS (ESI): calculated for $C_{20}H_{22}O_4Na$: 349.1416; found 349.1410.

Ethyl 6-*tert*-butyl-2-oxo-4-phenyl-2*H*-pyran-3-carboxylate (8c)



The product was prepared using trimethylacetyl chloride (0.37 mL, 3.00 mmol, 3.0 eq.) and was obtained after purification by column chromatography (pentane:ethyl acetate = 8:1) and recrystallization from ethanol as orange crystals (198 mg, 0.66 mmol, 66%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47 – 7.38 (m, 5H), 6.15 (s, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 1.31 (s, 9H), 1.03 (t, *J* = 7.1 Hz, 3H) ppm.

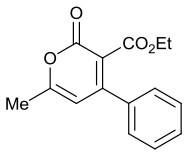
^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.3, 165.0, 164.9, 155.1, 136.6, 130.0, 128.8, 127.2, 116.2, 101.9, 61.6, 36.5, 27.8, 13.7 ppm.

IR (film, cm^{-1}): 2971, 1738, 1710, 1629, 1548, 1371, 1336, 1247, 1136, 1031, 763, 699.

MS (EI): m/z = 300 ([M^+], 27), 272 (34), 257 (48), 243 (86), 215 (100), 171 (24), 115 (13).

HRMS (ESI): calculated for $C_{18}H_{20}O_4Na$: 323.1259; found 323.1255.

Ethyl 6-methyl-2-oxo-4-phenyl-2*H*-pyran-3-carboxylate (8d)



The product was prepared using acetyl chloride (0.26 mL, 3.00 mmol, 3.0 eq.) and was obtained after purification by column chromatography (pentane:diethyl ether = 2:1) as yellow oil (160 mg, 0.62 mmol, 62%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47 – 7.36 (m, 5H), 6.13 (d, *J* = 0.8 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.32 (s, 3H), 1.03 (t, *J* = 7.1 Hz, 3H) ppm.

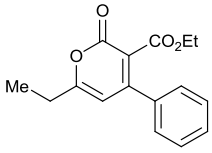
^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.8, 162.8, 160.0, 155.2, 136.1, 130.1, 128.8, 127.2, 116.1, 105.8, 61.6, 20.1, 13.6 ppm.

IR (film, cm^{-1}): 2983, 1707, 1637, 1546, 1444, 1373, 1340, 1249, 1201, 1098, 1033, 765, 698.

MS (EI): m/z = 258 ([M^+], 23), 230 (45), 213 (42), 202 (14), 185 (33), 158 (100), 128 (37), 115 (28), 77 (14).

HRMS (ESI): calculated for $C_{15}H_{14}O_4Na$: 281.0790; found: 281.0784.

Ethyl 6-ethyl-2-oxo-4-phenyl-2*H*-pyran-3-carboxylate (8e)



The product was prepared using propionyl chloride (0.26 mL, 3.00 mmol, 3.0 eq.) and was obtained after purification by column chromatography (pentane:diethyl ether = 2:1) and recrystallization from ethanol as yellow crystals (164 mg, 0.60 mmol, 60%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47 – 7.35 (m, 5H), 6.12 (s, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.59 (q, *J* = 7.5 Hz, 2H), 1.26 (t, *J* = 7.5 Hz, 3H), 1.02 (t, *J* = 7.1 Hz, 3H) ppm.

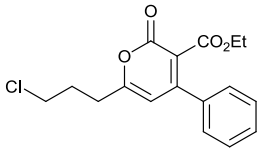
^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.64, 164.86, 160.01, 155.21, 136.26, 130.03, 128.75, 127.15, 116.18, 104.27, 61.63, 27.17, 13.63, 11.01 ppm.

IR (film, cm^{-1}): 2980, 1706, 1634, 1545, 1445, 1372, 1347, 1243, 1027, 857, 699.

MS (EI): m/z = 272 ([M^+], 36), 244 (69), 227 (61), 215 (56), 199 (21), 172 (100), 128 (33), 115 (46), 57 (27).

HRMS (ESI): calculated for $C_{16}H_{16}O_4Na$: 295.0946; found: 295.0941.

Ethyl 6-(3-chloropropyl)-2-oxo-4-phenyl-2*H*-pyran-3-carboxylate (8f)



The product was prepared using 4-chlorobutyryl chloride (0.34 mL, 3.00 mmol, 3.0 eq.) and was obtained after purification by column chromatography (pentane:ethyl acetate = 5:1) as yellow oil (176 mg, 0.55 mmol, 55%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48 – 7.36 (m, 5H), 6.20 (s, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.60 (t, *J* = 6.1 Hz, 2H), 2.75 (t, *J* = 7.4 Hz, 2H), 2.19 (tt, *J* = 13.0, 6.5 Hz, 2H), 1.04 (t, *J* = 7.1 Hz, 3H) ppm.

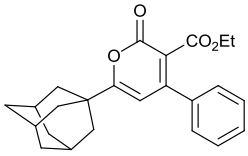
^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.7, 164.3, 159.8, 154.9, 135.9, 130.2, 128.8, 127.2, 116.6, 106.0, 61.7, 43.5, 31.1, 29.3, 13.6 ppm.

IR (film, cm^{-1}): 2935, 1720, 1633, 1551, 1453, 1373, 1245, 1174, 1132, 1031, 865.

MS (EI): m/z = 320 ([M^+], 39), 292 (100), 275 (43), 247 (30), 229 (51), 220 (69), 184 (29), 157 (33), 115 (41).

HRMS (ESI): calculated for $C_{17}H_{17}ClO_4Na$: 343.0713; found: 343.0708.

Ethyl 6-(1-adamantyl)-2-oxo-4-phenyl-2*H*-pyran-3-carboxylate (8g)



The product was prepared using 1-adamantanecarbonyl chloride (597 mg, 3.00 mmol, 3.0 eq.) and was obtained after purification by column chromatography (pentane:ethyl acetate = 10:1) as yellow crystals (196 mg, 0.52 mmol, 52%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41 – 7.30 (m, 5H), 6.00 (s, 1H), 4.06 (q, *J* = 7.1 Hz, 2H), 2.03 (s, 3H), 1.86 (d, *J* = 2.7 Hz, 6H), 1.78 – 1.60 (m, 6H), 0.96 (t, *J* = 7.1 Hz, 3H) ppm.

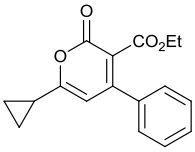
^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.2, 165.0, 160.1, 155.3, 136.7, 129.9, 128.7, 127.2, 116.1, 101.9, 61.6, 39.5, 38.2, 36.3, 27.9, 13.7 ppm.

IR (film, cm^{-1}): 2907, 2853, 1736, 1705, 1625, 1545, 1449, 1378, 1251, 1210, 1110, 1024.

MS (EI): m/z = 378 ([M^+], 19), 350 (100), 333 (16), 293 (8), 278 (24), 243 (29), 215 (32), 135 (11).

HRMS (ESI): calculated for $C_{24}H_{26}O_4Na$: 401.1729; found: 401.1723.

Ethyl 6-cyclopropyl-2-oxo-4-phenyl-2*H*-pyran-3-carboxylate (8h)



The product was prepared using cyclopropylcarbonyl chloride (0.27 mL, 3.00 mmol, 3.0 eq.) and was obtained after purification by column chromatography (pentane:ethyl acetate = 5:1) as yellow crystals (127 mg, 0.45 mmol, 45%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47 – 7.35 (m, 5H), 6.19 (s, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 1.83 (tt, *J* = 8.2, 5.0 Hz, 1H), 1.24 – 1.16 (m, 2H), 1.09 – 1.04 (m, 2H), 1.00 (t, *J* = 7.2 Hz, 3H) ppm.

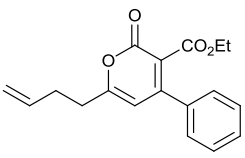
^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.6, 165.0, 159.7, 155.7, 136.5, 129.9, 128.7, 127.1, 103.9, 61.5, 14.7, 13.6, 12.6, 9.1.

IR (film, cm^{-1}): 2984, 1740, 1693, 1617, 1519, 1445, 1371, 1255, 1106, 1023, 896, 769, 699.

MS (EI): m/z = 284 ([M^+], 40), 256 (92), 239 (30), 211 (22), 184 (100), 155 (21), 115 (13).

HRMS (ESI): calculated for $C_{17}H_{16}O_4Na$: 307.0946; found: 307.0941.

Ethyl 6-(but-3-enyl)-2-oxo-4-phenyl-2*H*-pyran-3-carboxylate (8i)



The product was prepared using 4-penteneoyl chloride (0.33 mL, 3.00 mmol, 3.0 eq.) and was obtained after purification by column chromatography (pentane:ethyl acetate = 5:1) as yellow oil (124 mg, 0.42 mmol, 42%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47 – 7.37 (m, 5H), 6.13 (s, 1H), 5.80 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.15 – 5.02 (m, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.65 (t, *J* = 7.5 Hz, 2H), 2.52 – 2.41 (m, 2H), 1.04 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.5, 164.8, 160.0, 155.0, 136.2, 135.8, 130.1, 128.8, 127.2, 116.5, 112.3, 105.5, 61.7, 33.3, 31.7, 13.7 ppm.

IR (film, cm^{-1}): 2982, 1709, 1635, 1546, 1445, 1371, 1249, 1199, 1099, 1028, 917, 766, 735, 693.

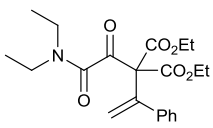
MS (EI): m/z = 298 ([M^+], 9), 270 (10), 253 (33), 229 (100), 215 (42), 171 (18), 155 (31), 115 (44), 55 (30).

HRMS (ESI): calculated for $C_{18}H_{18}O_4Na$: 321.1103; found: 321.1097.

General procedure for the zinc-mediated reaction sequence for the synthesis of tetracarbonyl derivatives

Diethyl bromomalonate (239 mg, 1.00 mmol, 1.0 eq.) and phenylacetylene (153 mg, 1.50 mmol, 1.5 eq.) were dissolved in 1 mL anhydrous dichloromethane under an argon atmosphere in a flame dried Schlenk tube fitted with a teflon screwcap. Zinc powder (150 mol%) was added and the mixture was stirred for 3 h at 40 °C until complete conversion of diethyl bromomalonate was monitored by GC/MS. The screwcap was changed to a septum and the reaction mixture was cooled to -40 °C. Oxalyl chloride (0.13 mL, 1.50 mmol, 1.5 eq.) was added dropwise via a syringe. The mixture was stirred overnight and allowed to warm to room temperature. Triethylamine (0.46 mL, 3.30 mmol, 3.3 eq) and amine (3.3 eq.) were added at 0 °C and the reaction was stirred 3-4 h, monitored by GC/MS or TLC. After dilution with ethyl acetate the reaction mixture was washed with 2M HCl (2x 20 mL) and brine and was dried over anhydrous magnesium sulphate. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel.

Diethyl 2-(2-(diethylamino)-2-oxoacetyl)-2-(1-phenylvinyl)malonate (10a)



The product was prepared using diethylamine (0.29 mL, 3.30 mmol, 3.3 eq.) and was obtained after purification by column chromatography (pentane:ethyl acetate = 3:1) as yellow oil (194 mg, 0.50 mmol, 50%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.34 – 7.30 (m, 2H), 7.28 – 7.23 (m, 3H), 5.60 (d, *J* = 3.8 Hz, 2H), 4.19 – 4.08 (m, 4H), 3.36 (q, *J* = 7.1 Hz, 2H), 3.32 (q, *J* = 7.1 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.12 (t, *J* = 7.1 Hz, 9H) ppm.

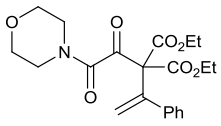
^{13}C NMR (126 MHz, $CDCl_3$): δ = 189.9, 165.8, 163.9, 142.1, 140.5, 128.2, 127.9, 127.6, 122.2, 73.9, 62.3, 42.2, 40.4, 14.0, 13.6, 12.1 ppm.

IR (film, cm^{-1}): 2982, 2937, 1729, 1645, 1443, 1368, 1244, 1208, 1092, 1061, 921, 808, 703.

MS (EI): m/z = 389 ([M^+], 3), 316 (11), 261 (100), 233 (11), 187 (29), 115 (14), 100 (35).

HRMS (ESI): calculated for $C_{21}H_{27}NO_6Na$: 412.1736; found: 412.1731.

Diethyl 2-(2-morpholino-2-oxoacetyl)-2-(1-phenylvinyl)malonate (10b)



The product was prepared using morpholine (0.29 mL, 3.30 mmol, 3.3 eq.) and was obtained after purification by column chromatography (pentane:diethyl ether = 1:2) as yellow oil (170 mg, 0.42 mmol, 42%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.32 – 7.29 (m, 2H), 7.29 – 7.26 (m, 3H), 5.61 (s, 1H), 5.59 (s, 1H), 4.25 – 4.11 (m, 4H), 3.70 (tt, *J* = 13.1, 4.6 Hz, 4H), 3.59 (t, *J* = 5.2 Hz, 2H), 3.52 (t, *J* = 5.1 Hz, 2H), 1.16 (t, *J* = 7.1 Hz, 6H) ppm.

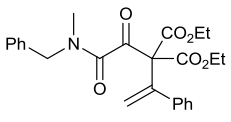
^{13}C NMR (126 MHz, $CDCl_3$): δ = 189.8, 175.5, 165.8, 163.4, 141.6, 140.3, 128.0, 128.0, 127.7, 122.4, 73.9, 66.4, 66.4, 62.5, 46.1, 42.4, 13.6 ppm.

IR (film, cm^{-1}): 2970, 2926, 2862, 1731, 1653, 1446, 1369, 1261, 1215, 1144, 1112, 1062, 1035.

MS (EI): m/z = 403 ([M^+], 1), 330 (6), 261 (100), 233 (10), 187 (37), 160 (9), 114 (35).

HRMS (ESI): calculated for $C_{21}H_{25}NO_7Na$: 426.1529; found: 426.1534.

Diethyl 2-(2-(benzyl(methyl)amino)-2-oxoacetyl)-2-(1-phenylvinyl)malonate (10c)



The product was prepared using *N*-benzylmethylamine (0.43 mL, 3.30 mmol, 3.3 eq.) and was obtained after purification by column chromatography (pentane:ethyl acetate = 4:1) as yellow oil (205 mg, 0.47 mmol, 47%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.26 – 7.12 (m, 10H), 5.53 (d, *J* = 3.6 Hz, 2H), 4.47 (s, 2H), 4.13 – 4.00 (m, 4H), 2.85 (s, 3H), 1.03 (t, *J* = 6.7 Hz, 6H) ppm.

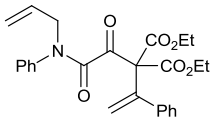
^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.9, 165.8, 164.7, 141.8, 140.4, 135.8, 128.6, 128.3, 128.2, 128.0, 127.9, 127.6, 122.3, 74.1, 62.4, 51.1, 34.6, 13.6 ppm.

IR (film, cm^{-1}): 2984, 1731, 1652, 1491, 1448, 1405, 1248, 1212, 1064, 893, 776, 702.

MS (EI): m/z = 437 ([M^+], 1), 364 (6), 261 (100), 233 (12), 187 (27), 115 (10), 91 (80).

HRMS (ESI): calculated for $C_{25}H_{27}NO_6Na$: 460.1736; found: 460.1731.

Diethyl 2-(2-(allyl(phenyl)amino)-2-oxoacetyl)-2-(1-phenylvinyl)malonate (10d)



The product was prepared using *N*-allylaniline (0.45 mL, 3.30 mmol, 3.3 eq.) and was obtained after purification by column chromatography (pentane:ethyl acetate = 5:1) as orange oil (136 mg, 0.29 mmol, 29%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38 – 7.32 (m, 5H), 7.20 – 7.09 (m, 3H), 6.95 (dd, *J* = 8.1, 1.5 Hz, 2H), 5.89 (ddt, *J* = 16.5, 10.3, 6.2 Hz, 1H), 5.50 (s, 1H), 5.37 (s, 1H), 5.19 (dd, *J* = 8.0, 1.3 Hz, 1H), 5.15 (t, *J* = 1.3 Hz, 1H), 4.37 (dt, *J* = 6.1, 1.2 Hz, 2H), 4.20 – 4.07 (m, 4H), 1.10 (t, *J* = 7.1 Hz, 6H) ppm.

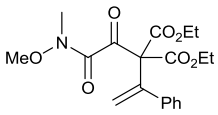
^{13}C NMR (75 MHz, $CDCl_3$): δ = 188.7, 165.7, 163.8, 141.6, 140.7, 140.1, 131.8, 128.9, 128.3, 128.0, 127.8, 127.7, 127.4, 121.5, 118.6, 73.9, 62.3, 52.8, 13.6 ppm.

IR (film, cm^{-1}): 2844, 1773, 1613, 1507, 1346, 1299, 1243, 1163, 1073, 1030, 953, 809.

MS (EI): m/z = 449 ([M^+], 1), 376 (3), 261 (100), 233 (8), 187 (22), 160 (28), 132 (12).

HRMS (ESI): calculated for $C_{26}H_{27}NO_6Na$: 472.1736; found: 472.1731.

Diethyl 2-(2-(methoxy(methyl)amino)-2-oxoacetyl)-2-(1-phenylvinyl)malonate (10e)



The product was prepared using *N*,*O*-dimethylhydroxylamine hydrochloride (323 mg, 3.30 mmol, 3.3 eq.) and was obtained after purification by column chromatography (pentane:ethyl acetate = 3:1) as yellow oil (80 mg, 0.21 mmol, 21%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34 – 7.21 (m, 5H), 5.72 (s, 1H), 5.50 (s, 1H), 4.31 – 4.07 (m, 4H), 3.65 (s, 3H), 3.22 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 6H) ppm.

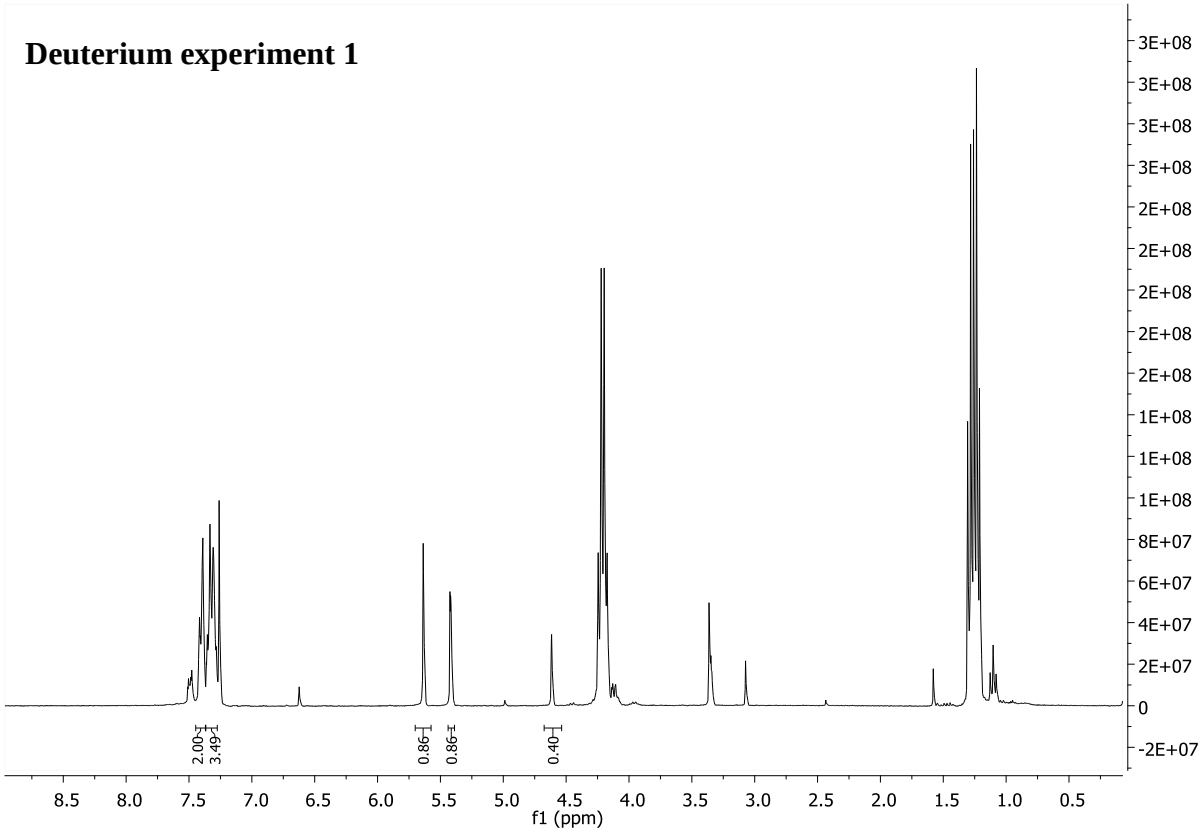
^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.0, 167.6, 165.7, 141.3, 139.7, 127.9, 127.7, 127.6, 121.7, 75.1, 62.6, 61.9, 32.8, 13.6 ppm.

IR (film, cm^{-1}): 2980, 1737, 1666, 1551, 1442, 1374, 1279, 1187, 1139, 1051, 1013, 864, 727.

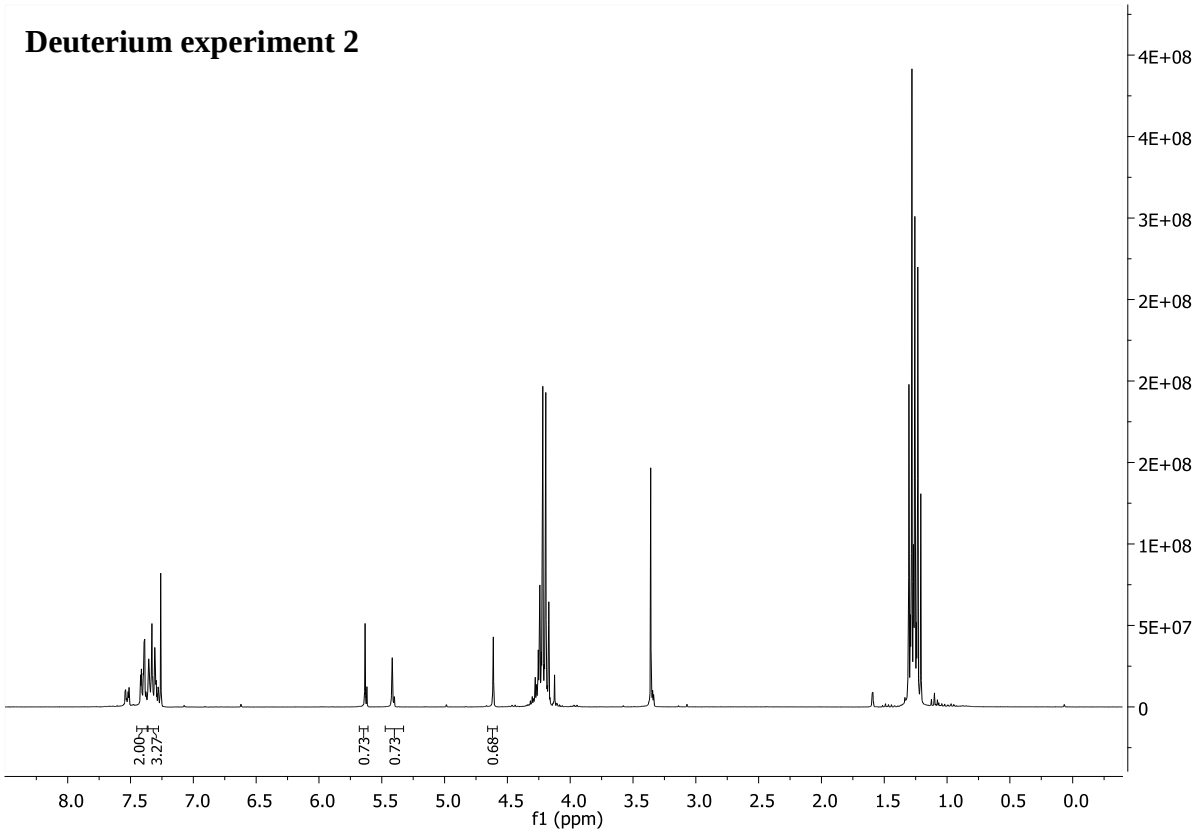
MS (EI): m/z = 377 ([M^+], 1), 261 (100), 243 (11), 216 (11), 187 (34), 171 (25), 131 (16), 115 (20).

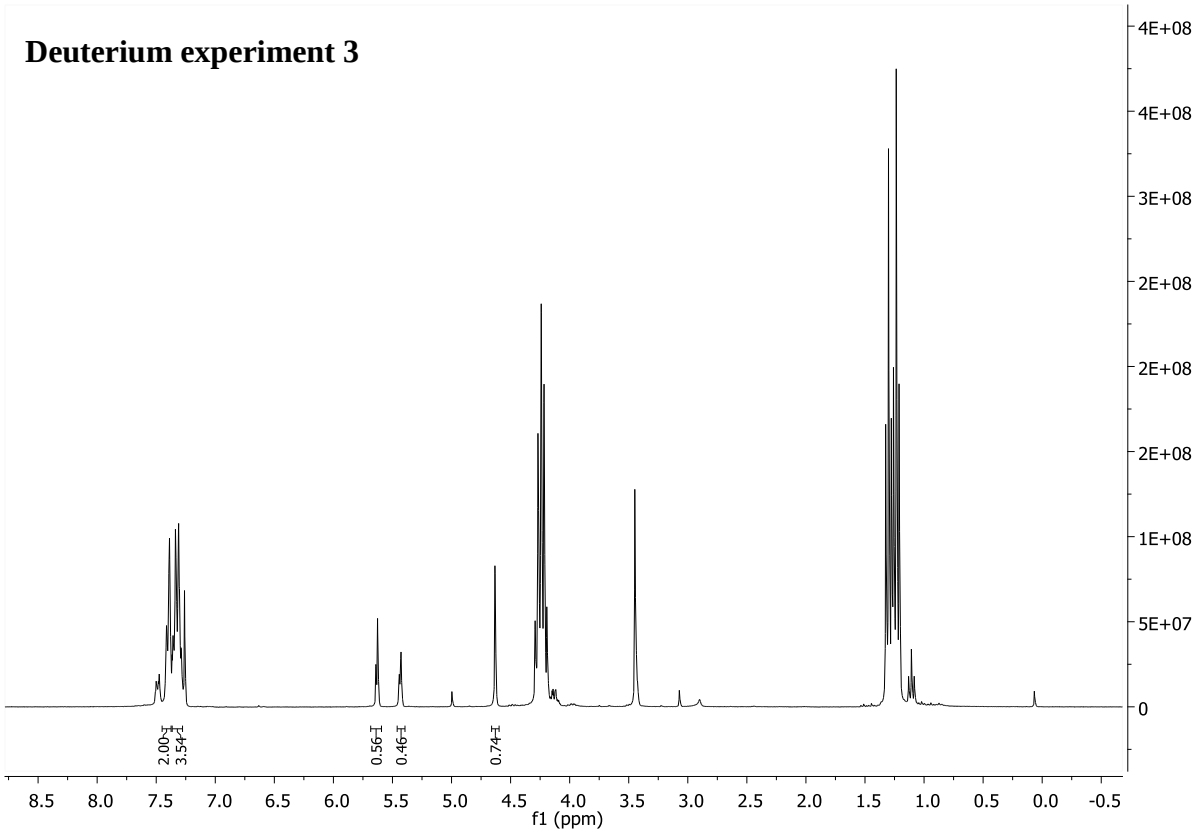
HRMS (ESI): calculated for $C_{19}H_{23}NO_7H$: 378.1553; found: 378.1547.

^{1}H and ^{13}C NMR Spectra

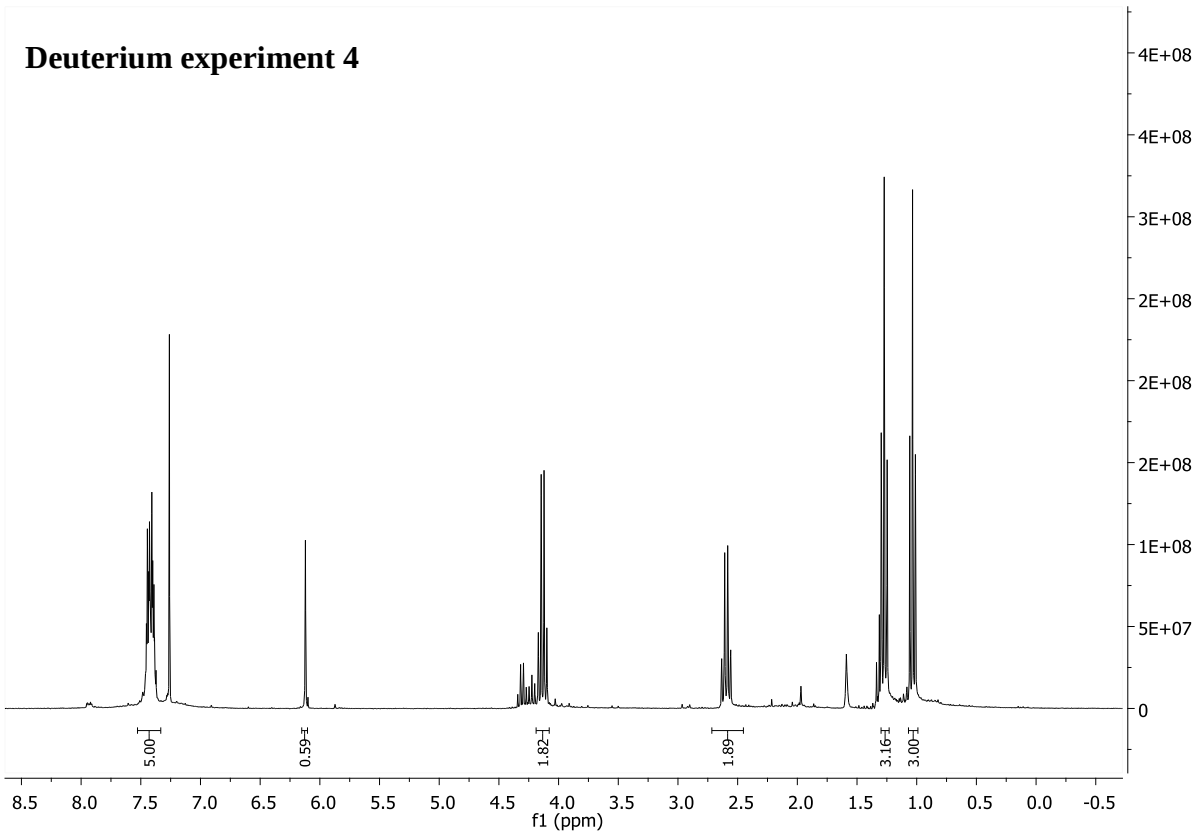


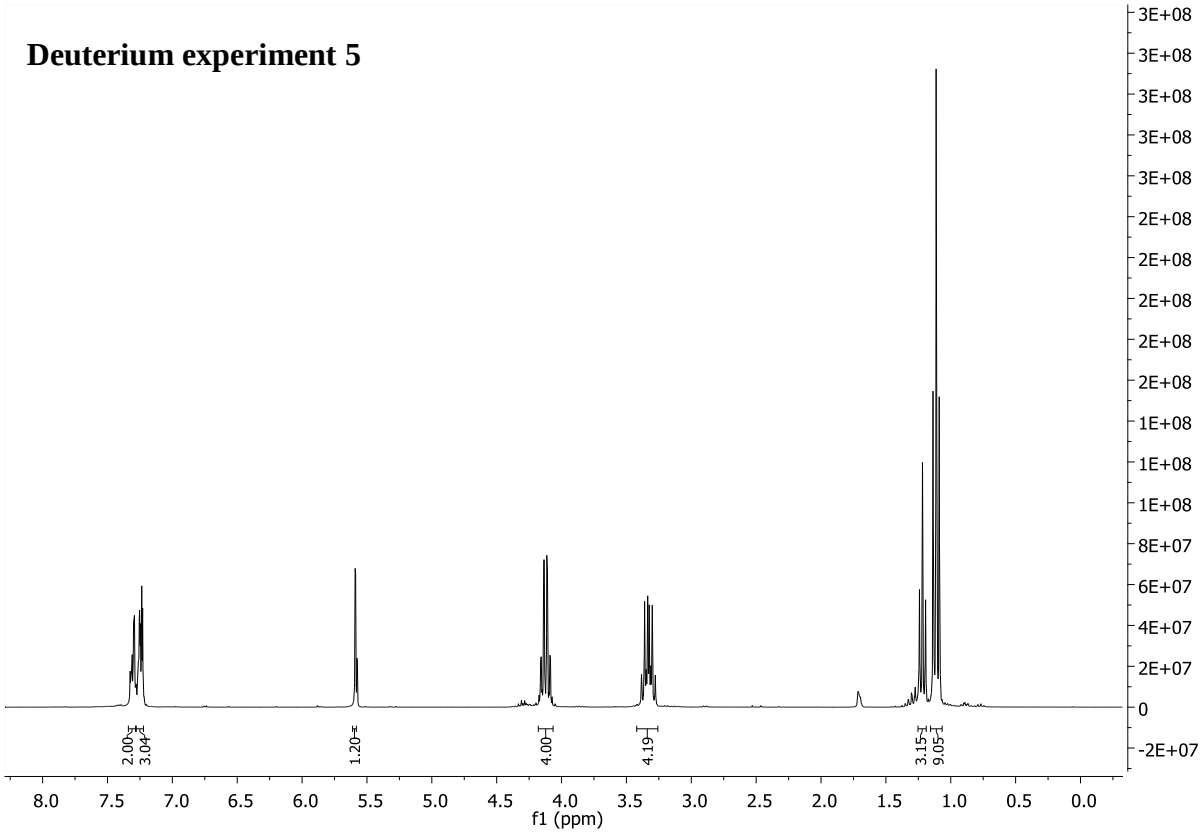
Raw NMR used, deuterium exchanged after purification by flashchromatography on silica gel

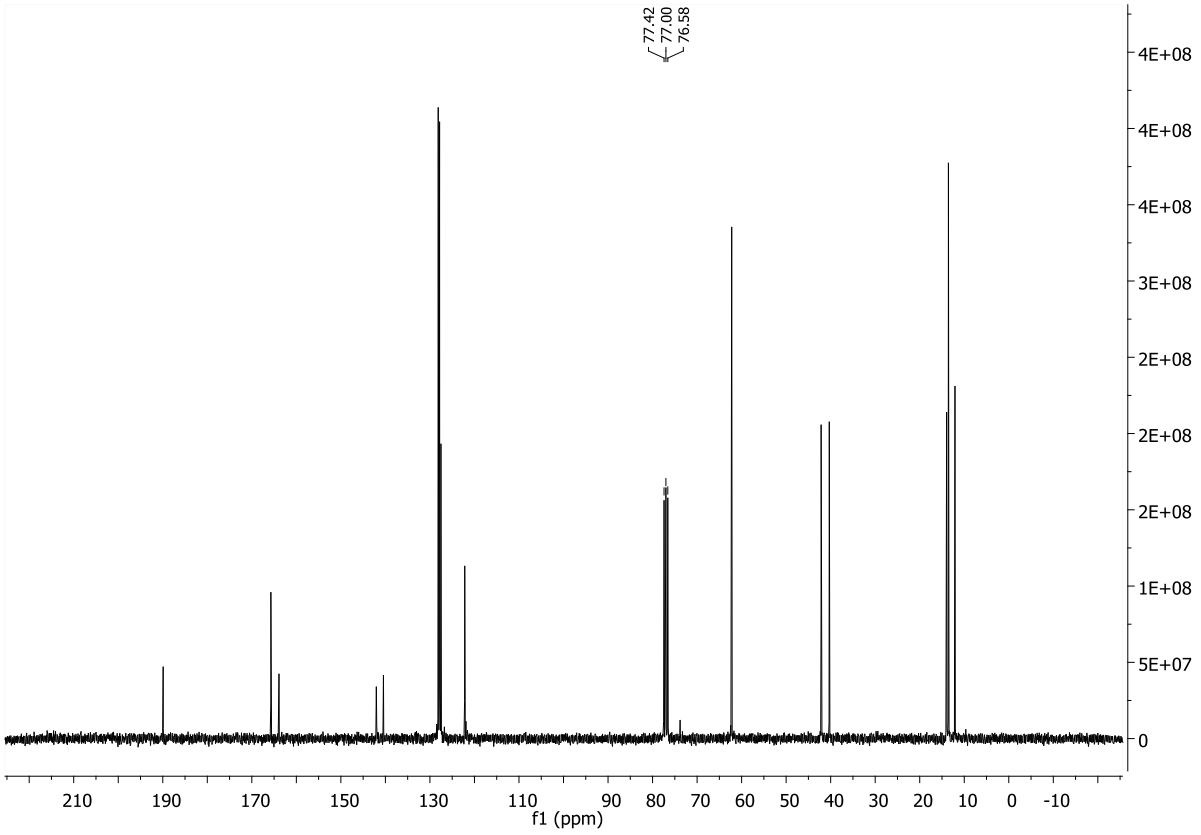




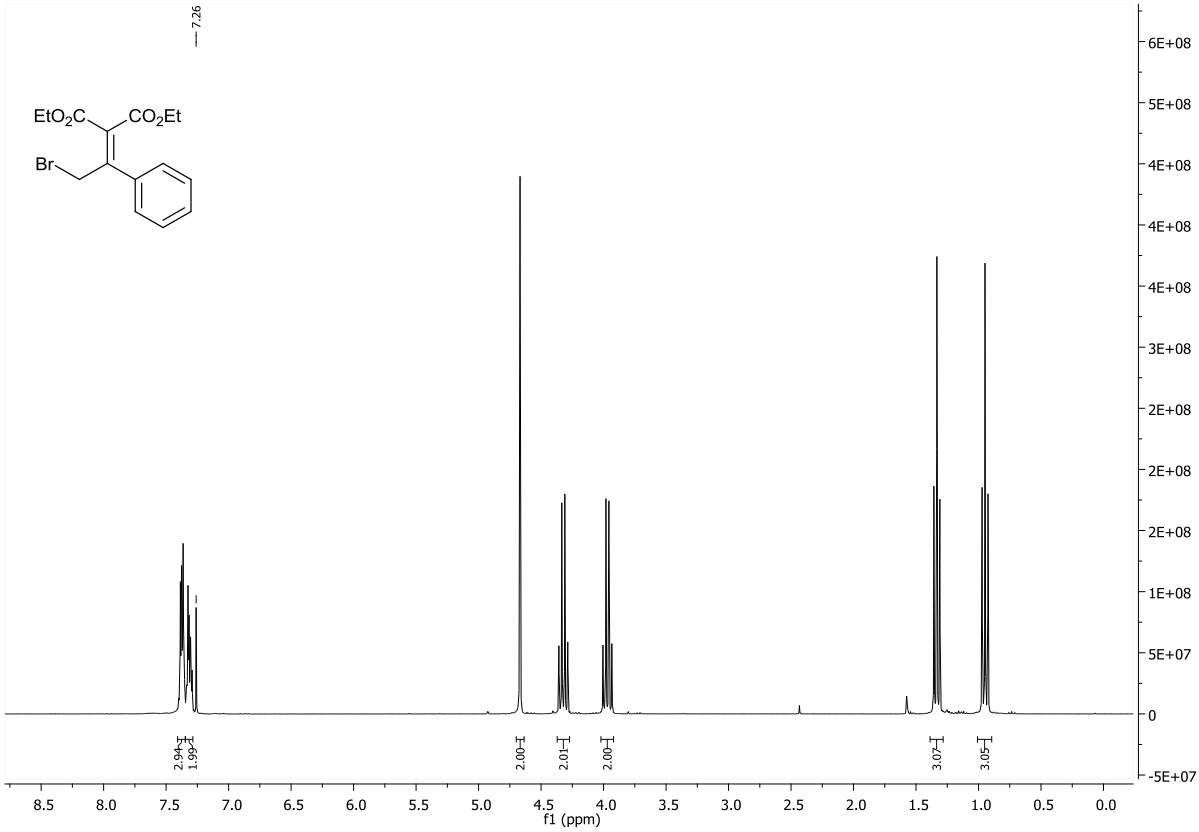
Raw NMR used, deuterium exchanged after purification by flashchromatography on silica gel

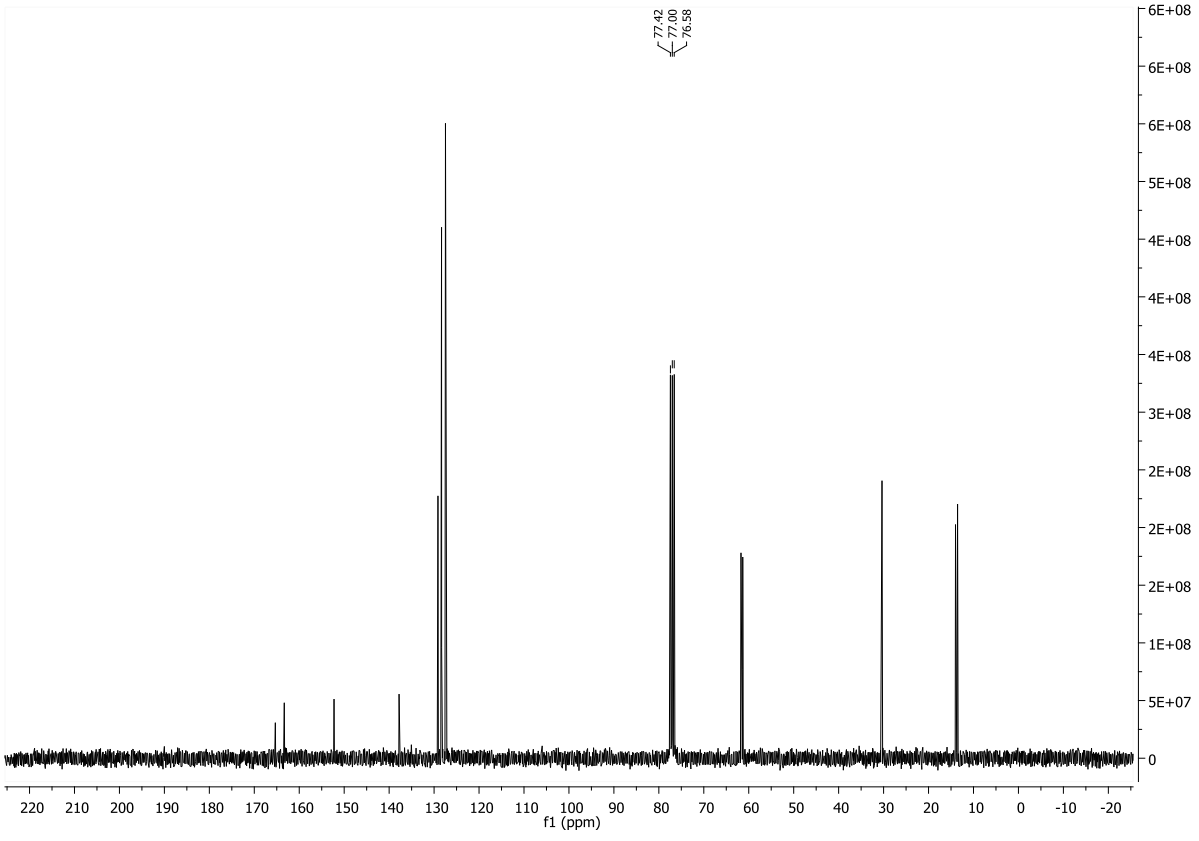




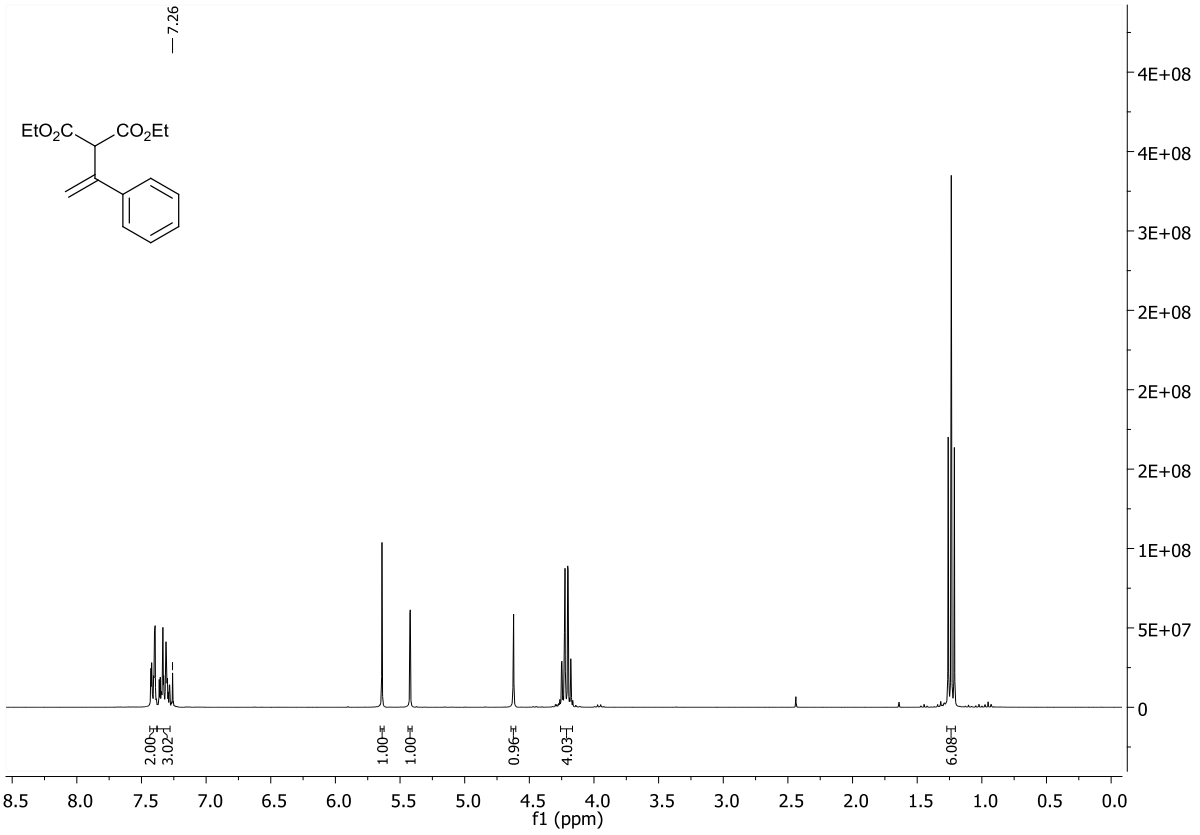


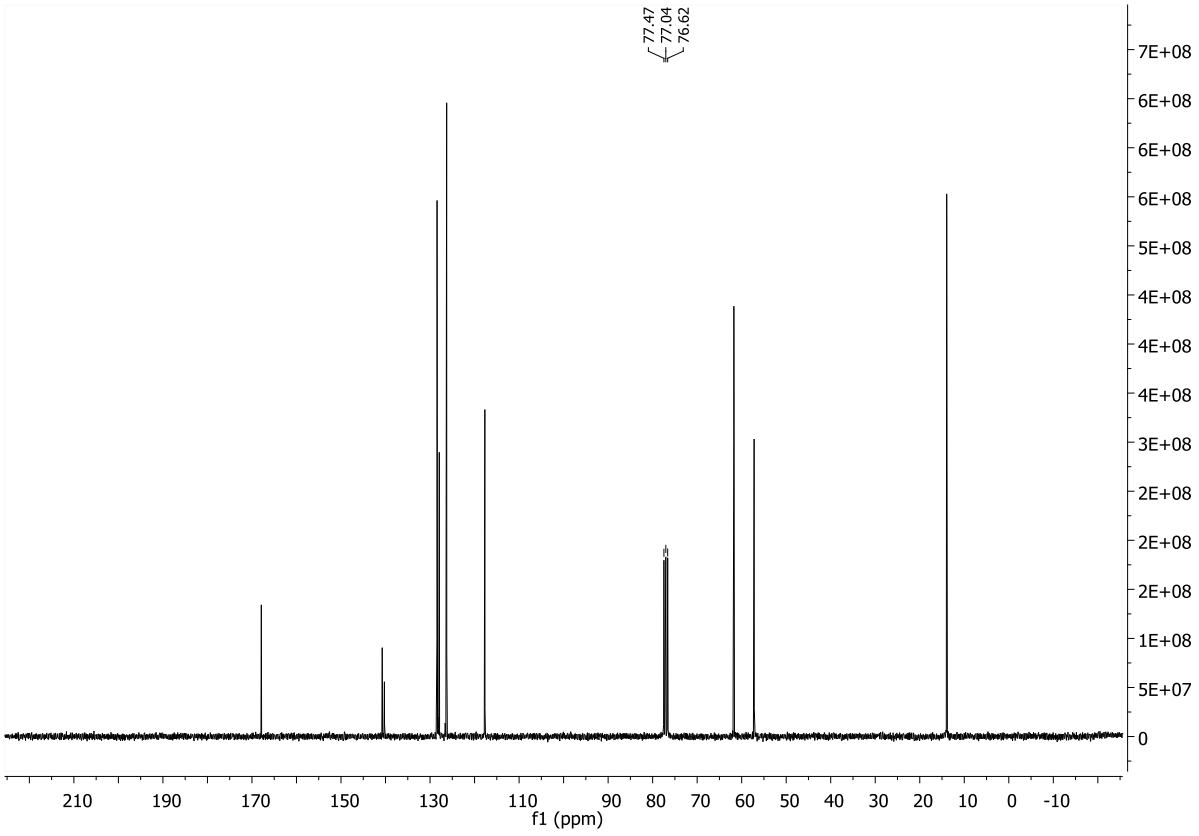
Diethyl 2-(2-bromo-1-phenylethylidene)malonate (4)



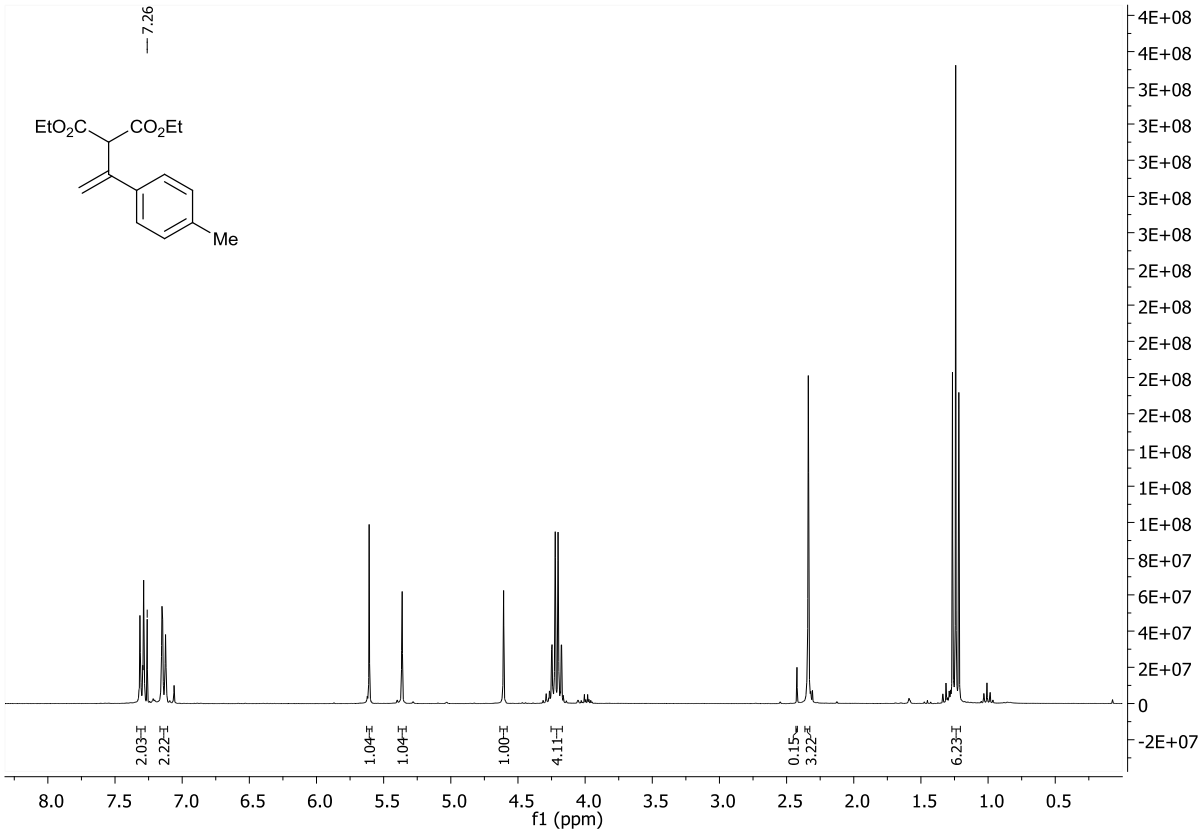


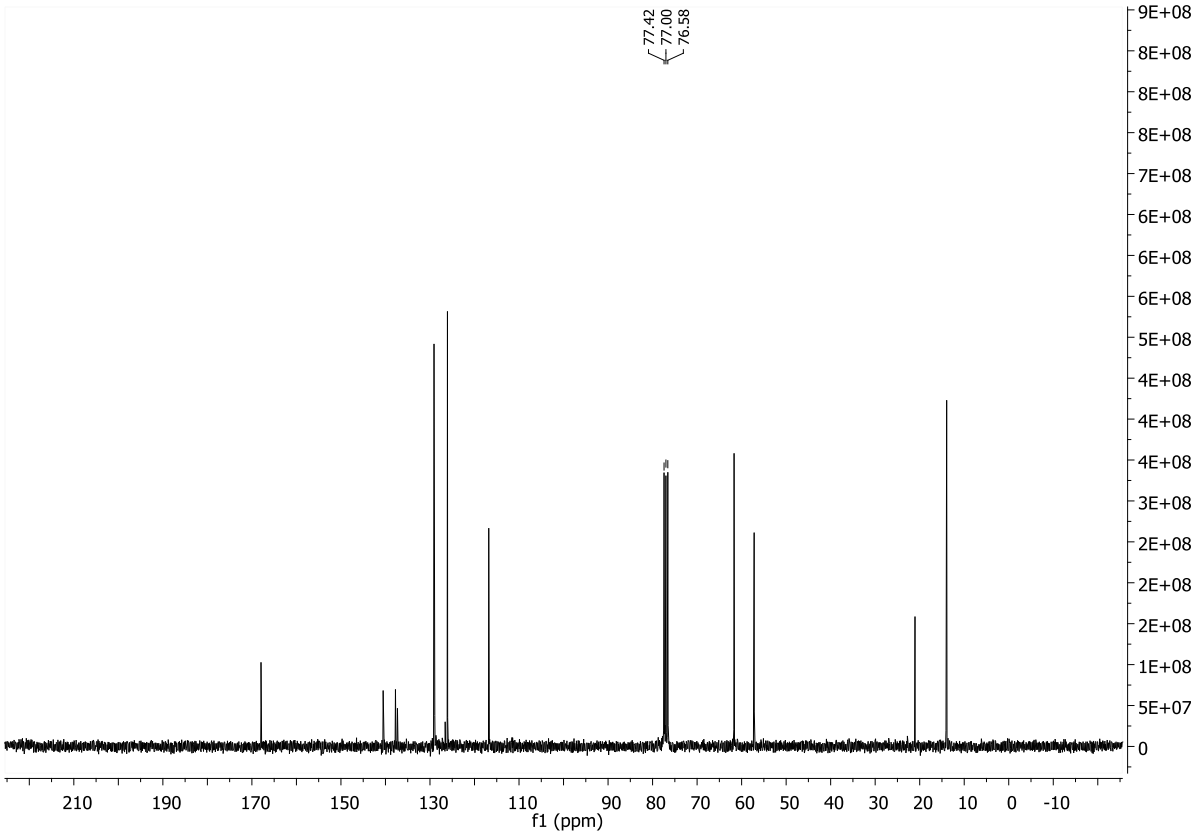
Diethyl 2-(1-phenylvinyl)malonate (5a)



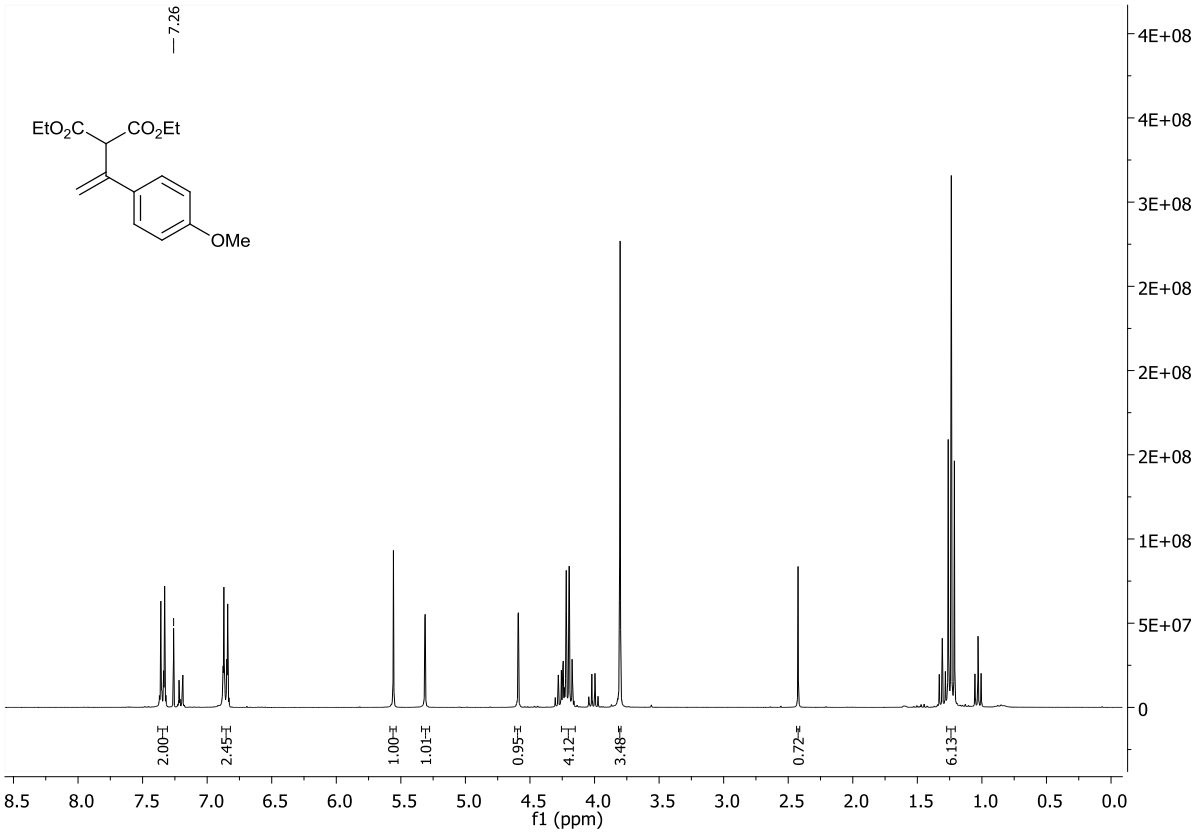


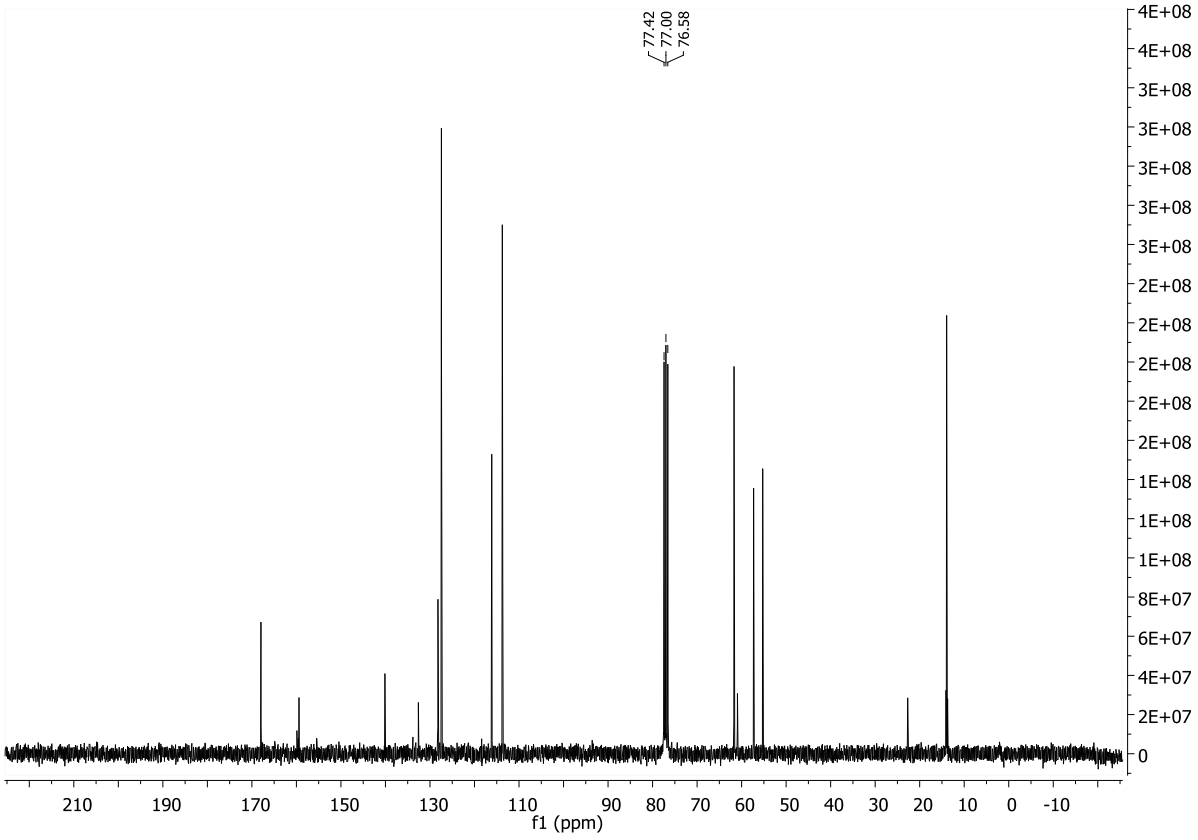
Diethyl 2-(1-*p*-tolylvinyl)malonate (5b)



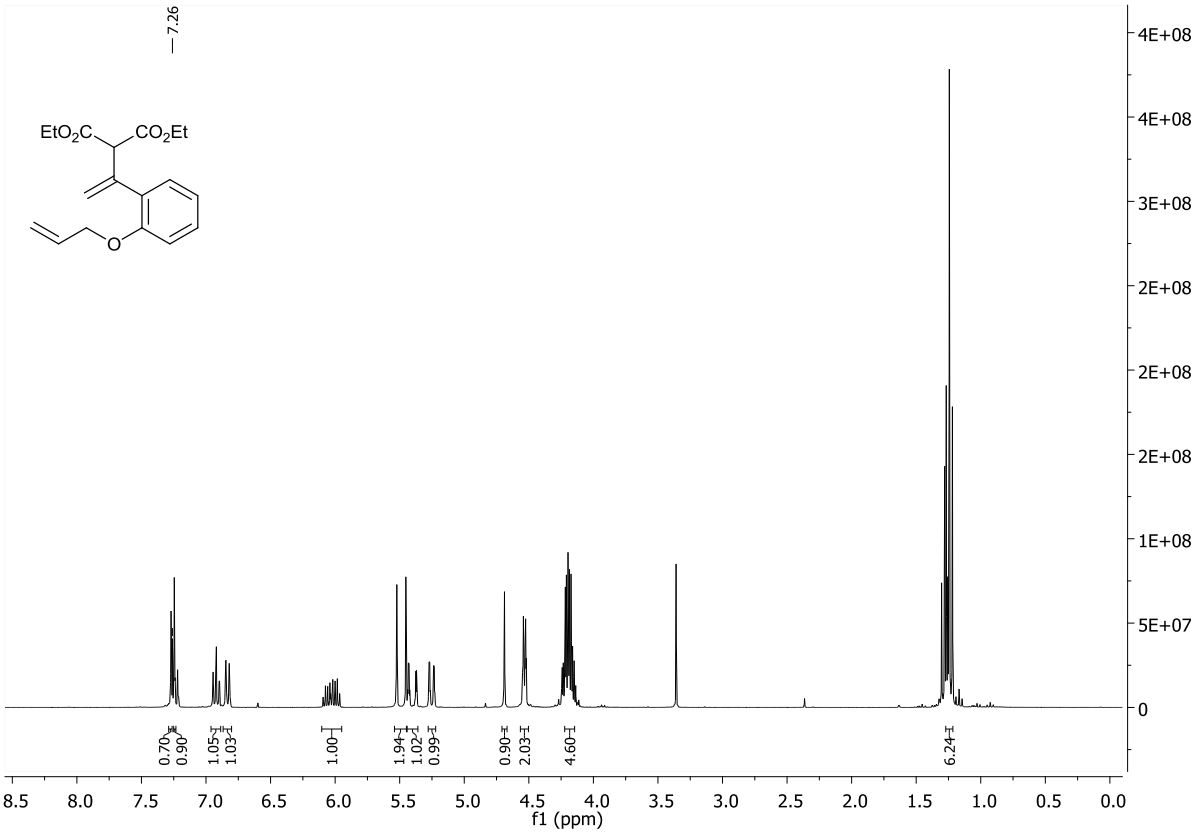


Diethyl 2-(1-(4-methoxyphenyl)vinyl)malonate (5c)

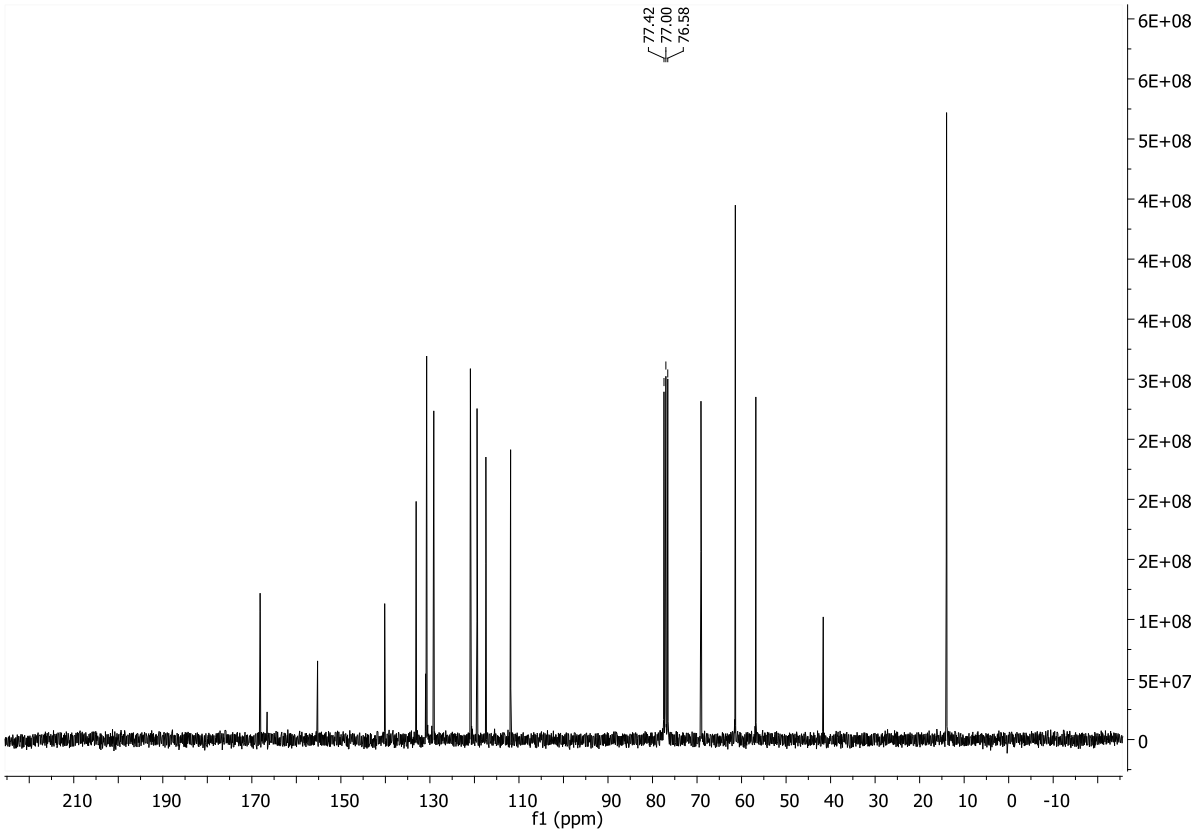




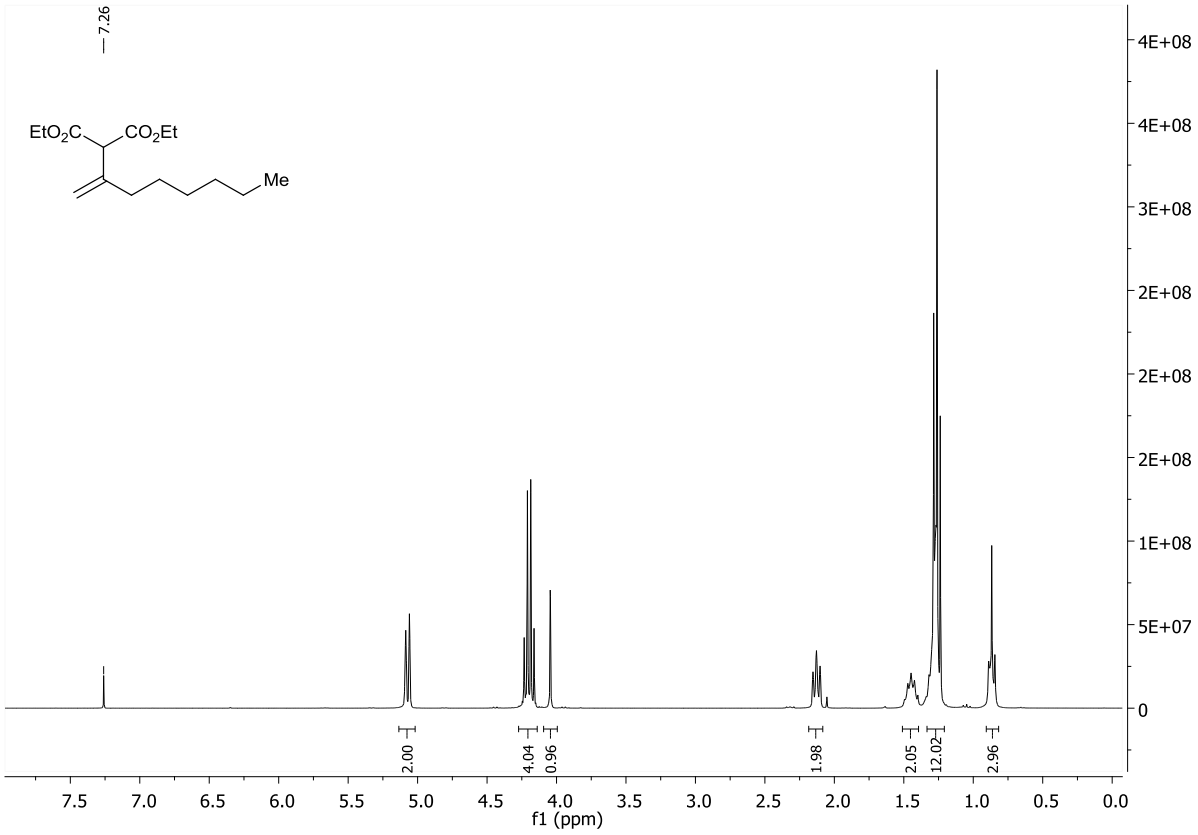
Diethyl 2-(1-(2-(allyloxy)phenyl)vinyl)malonate (5d)

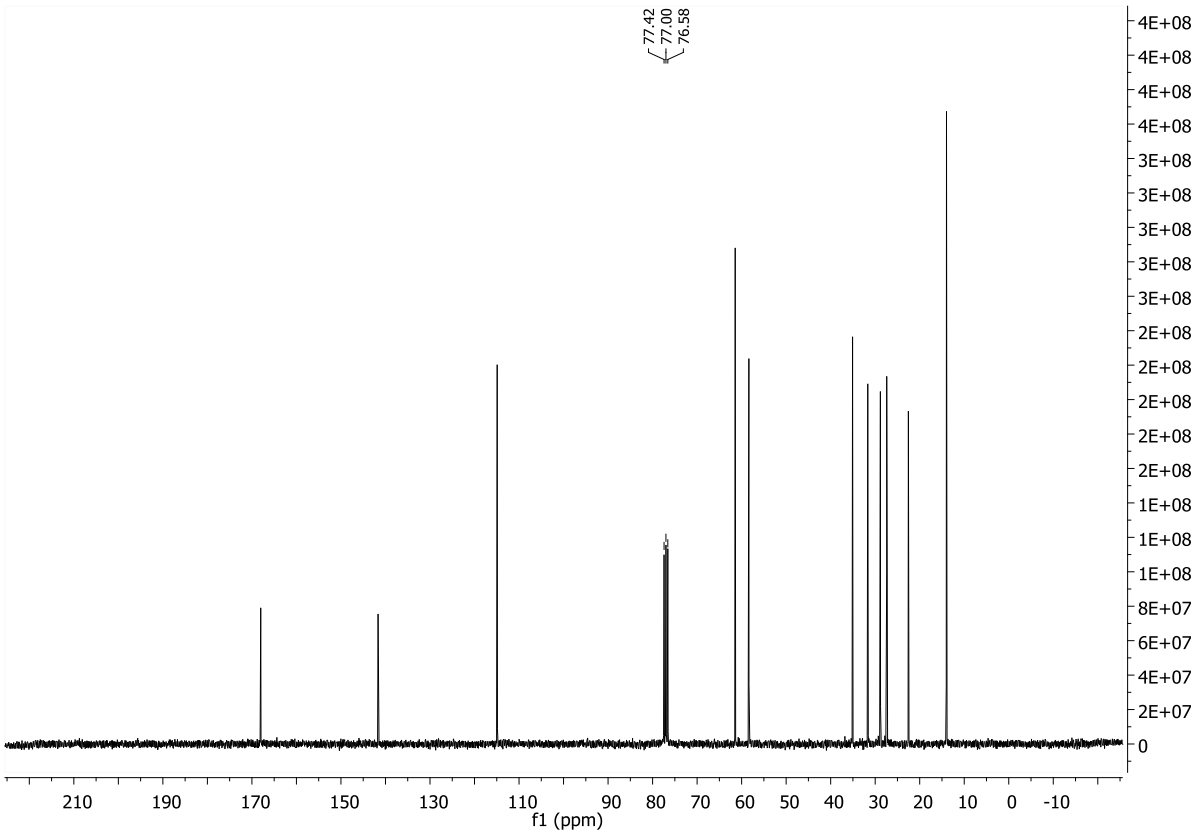


(The spectrum contains inseparable impurity of wurtz-coupling product)

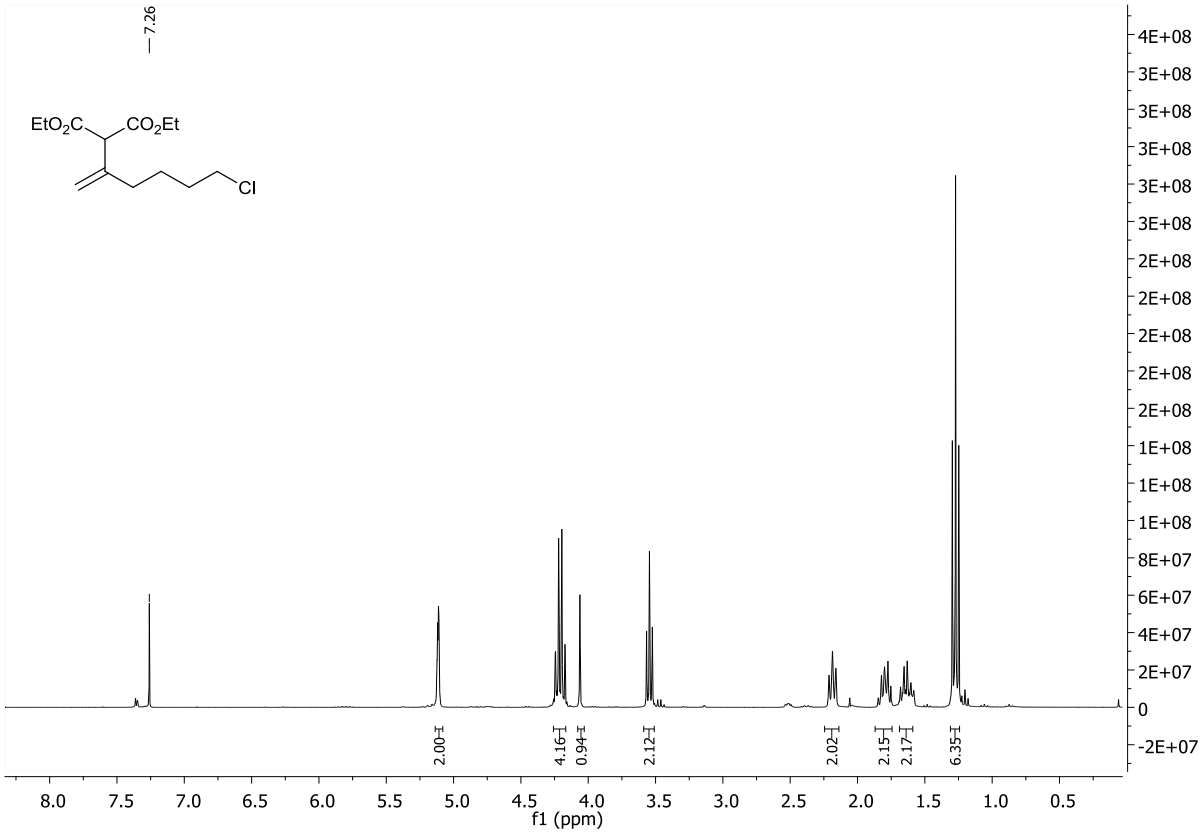


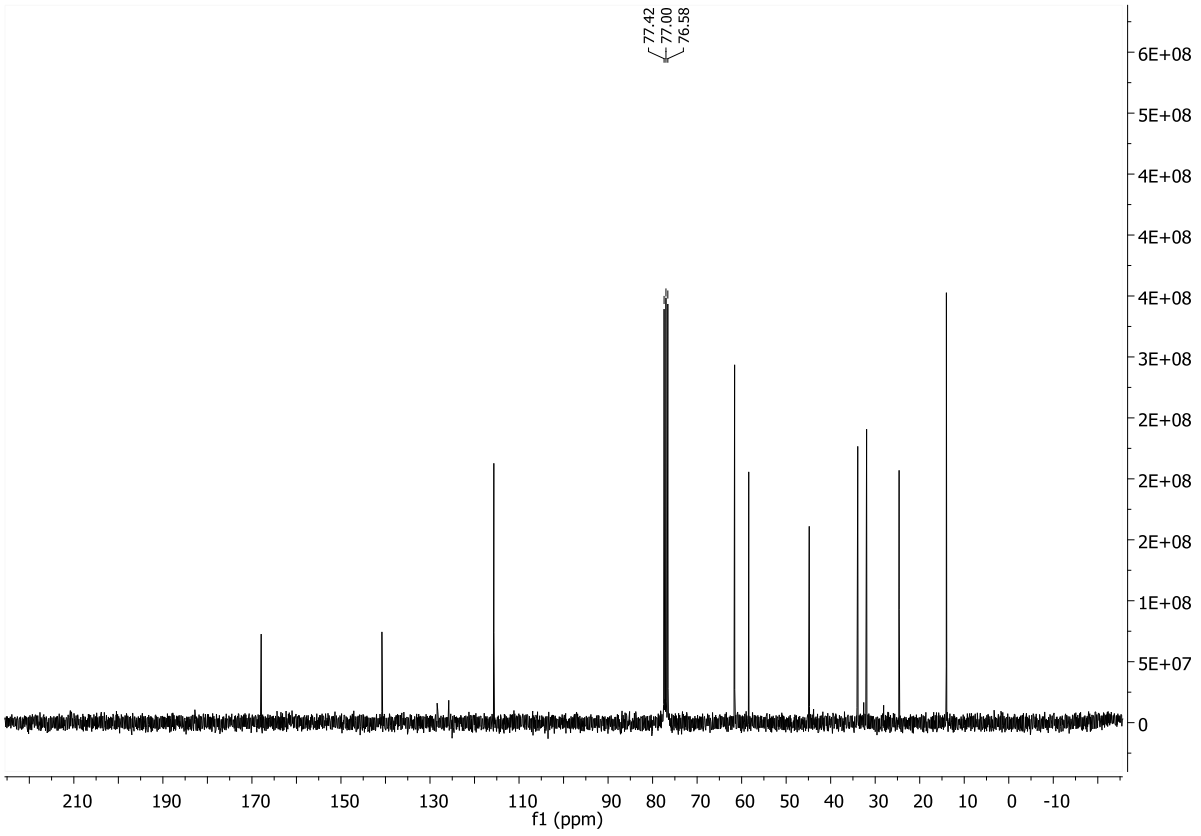
Diethyl 2-(oct-1-en-2-yl)malonate (5e)



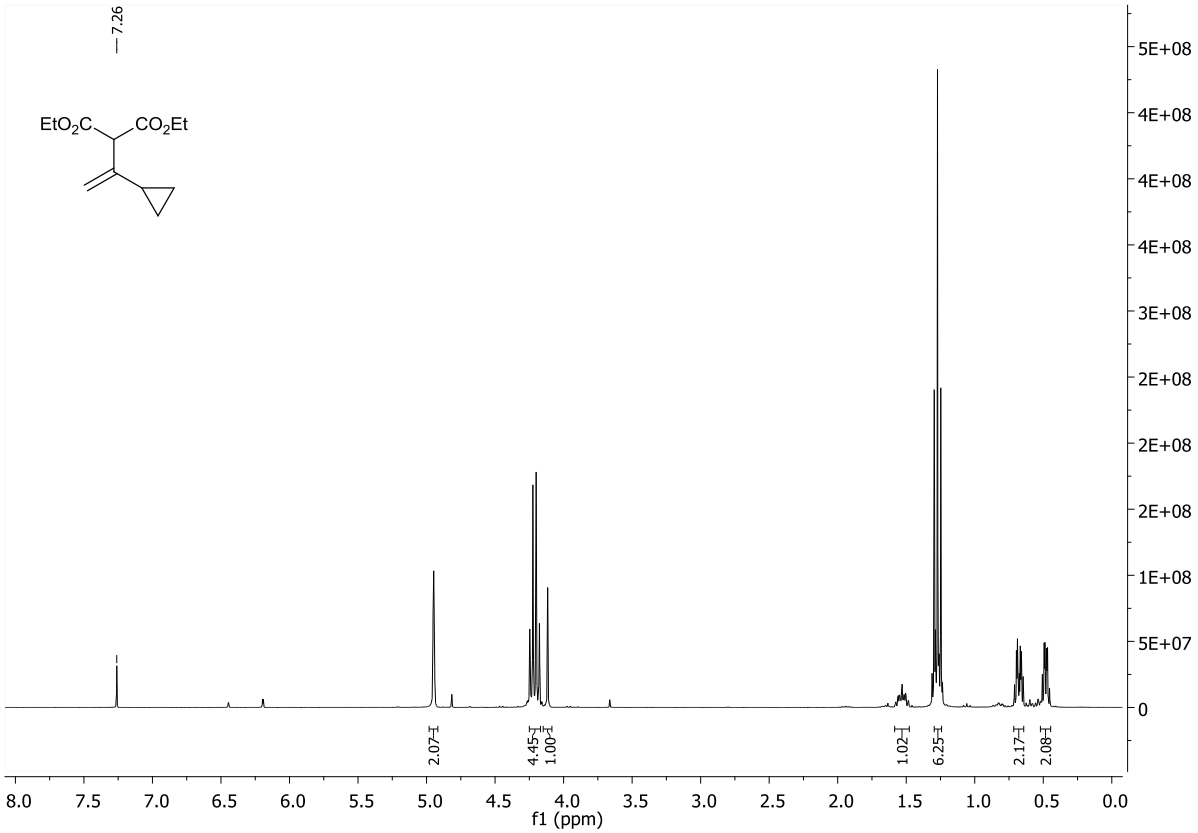


Diethyl 2-(6-chlorohex-1-en-2-yl)malonate (5f)

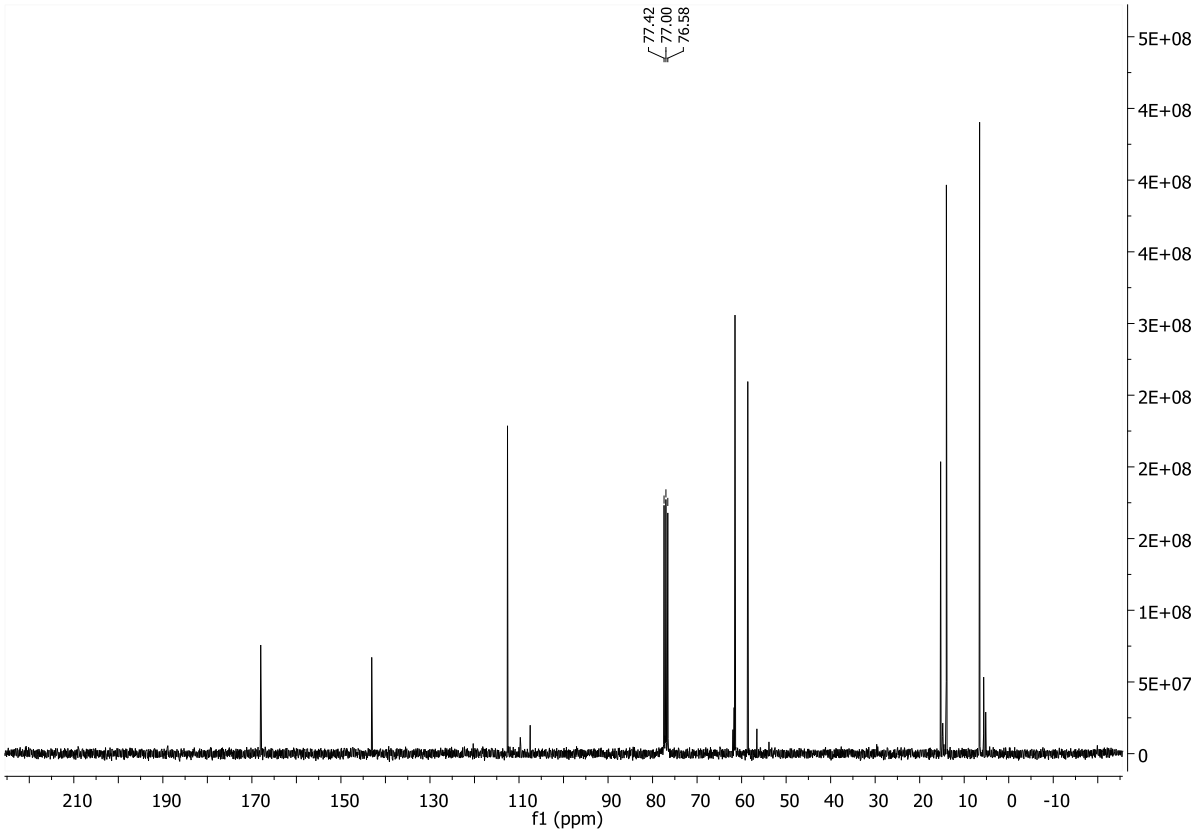




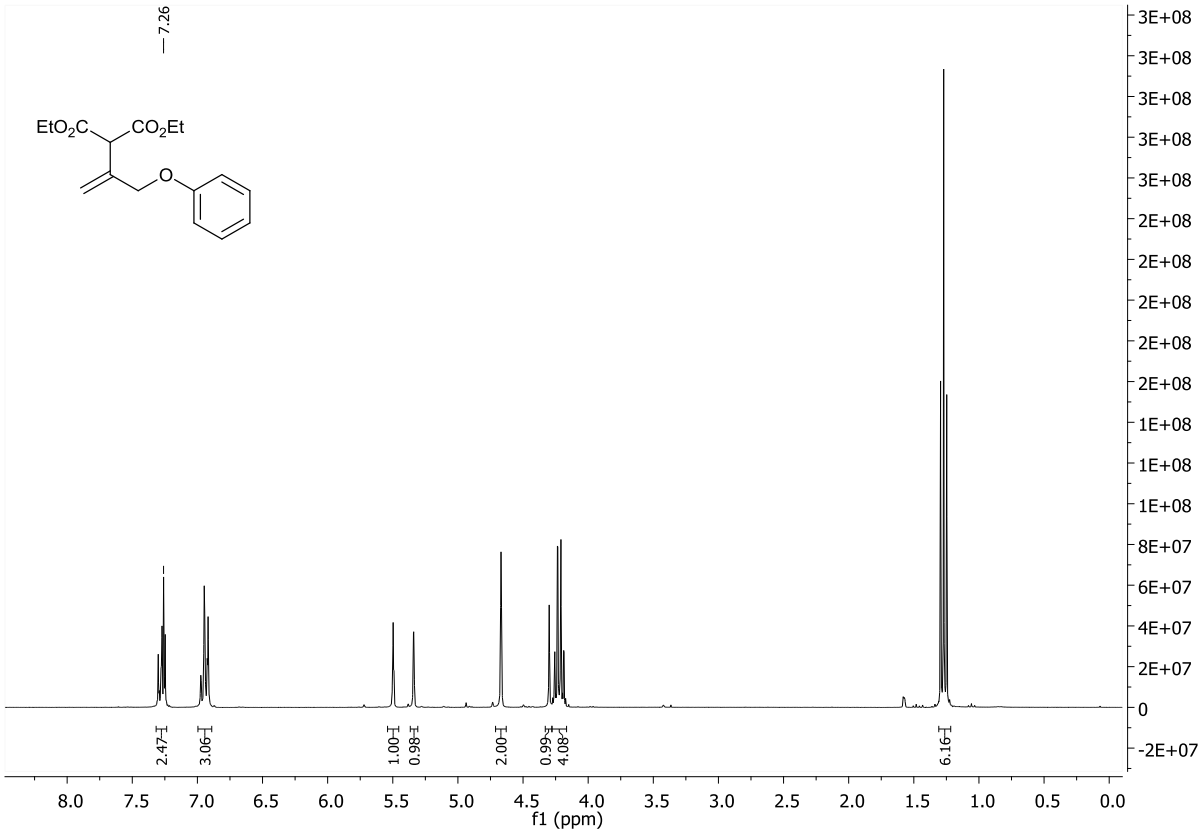
Diethyl 2-(1-cyclopropylvinyl)malonate (5g)

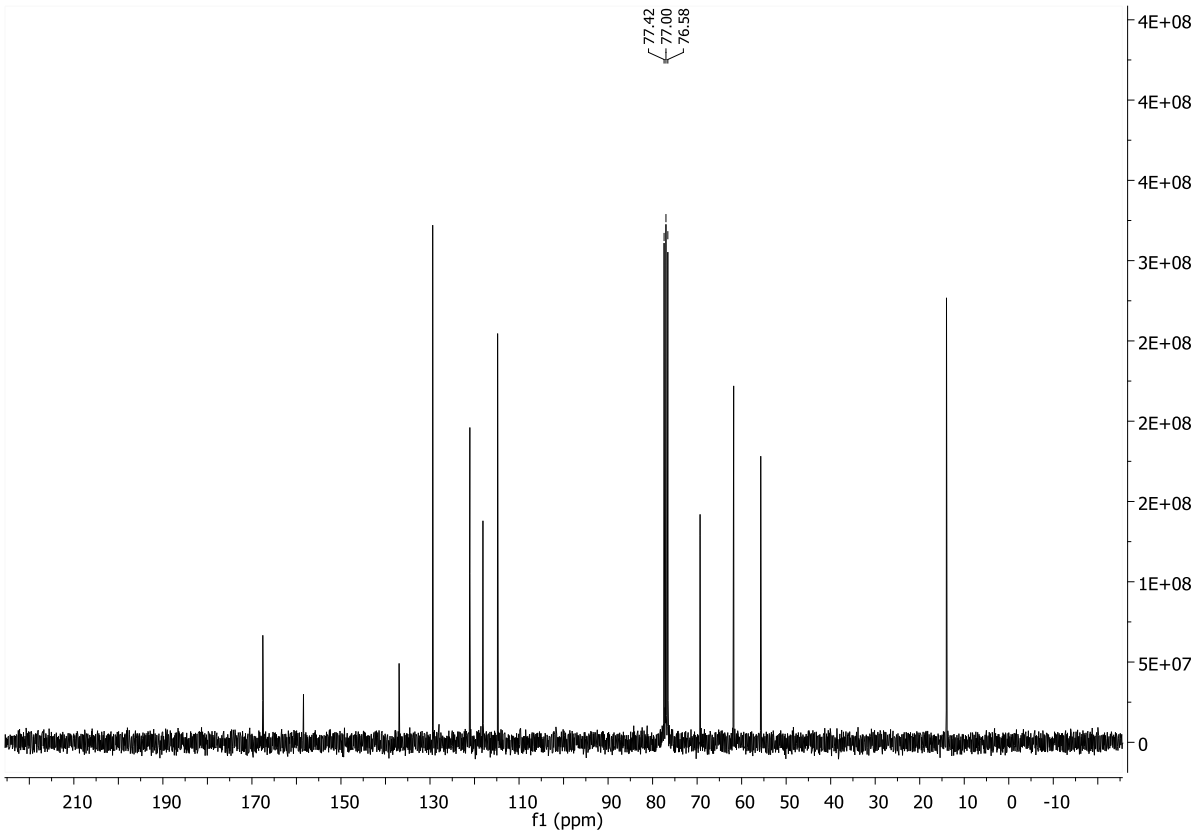


(The spectrum contains 4% ring opening product)

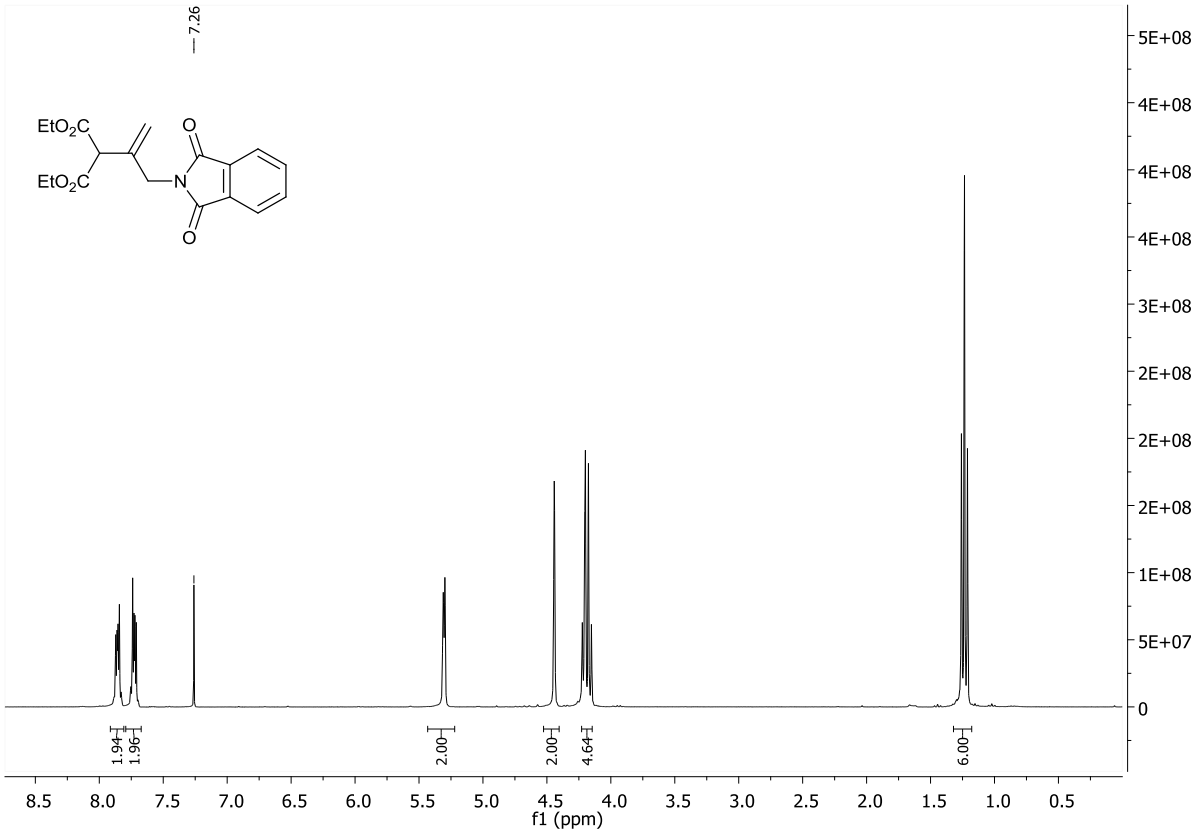


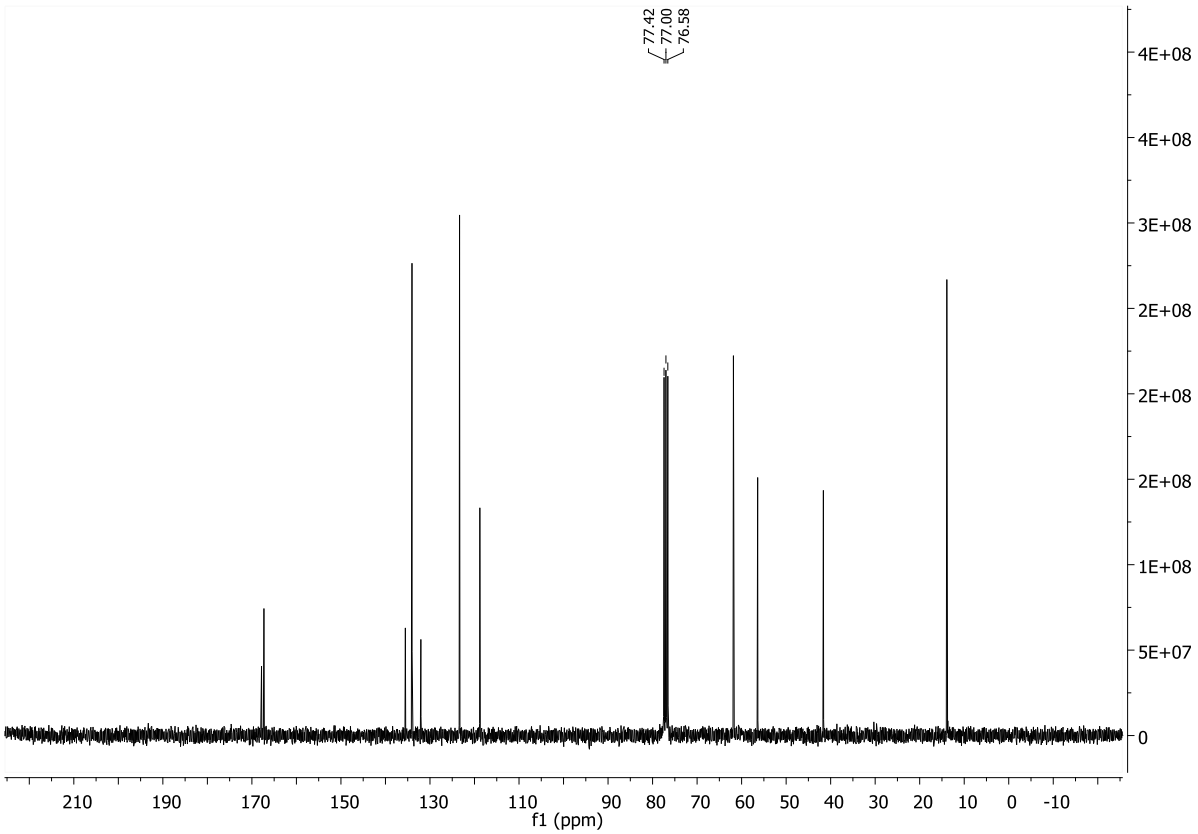
Diethyl 2-(3-phenoxyprop-1-en-2-yl)malonate (5h)



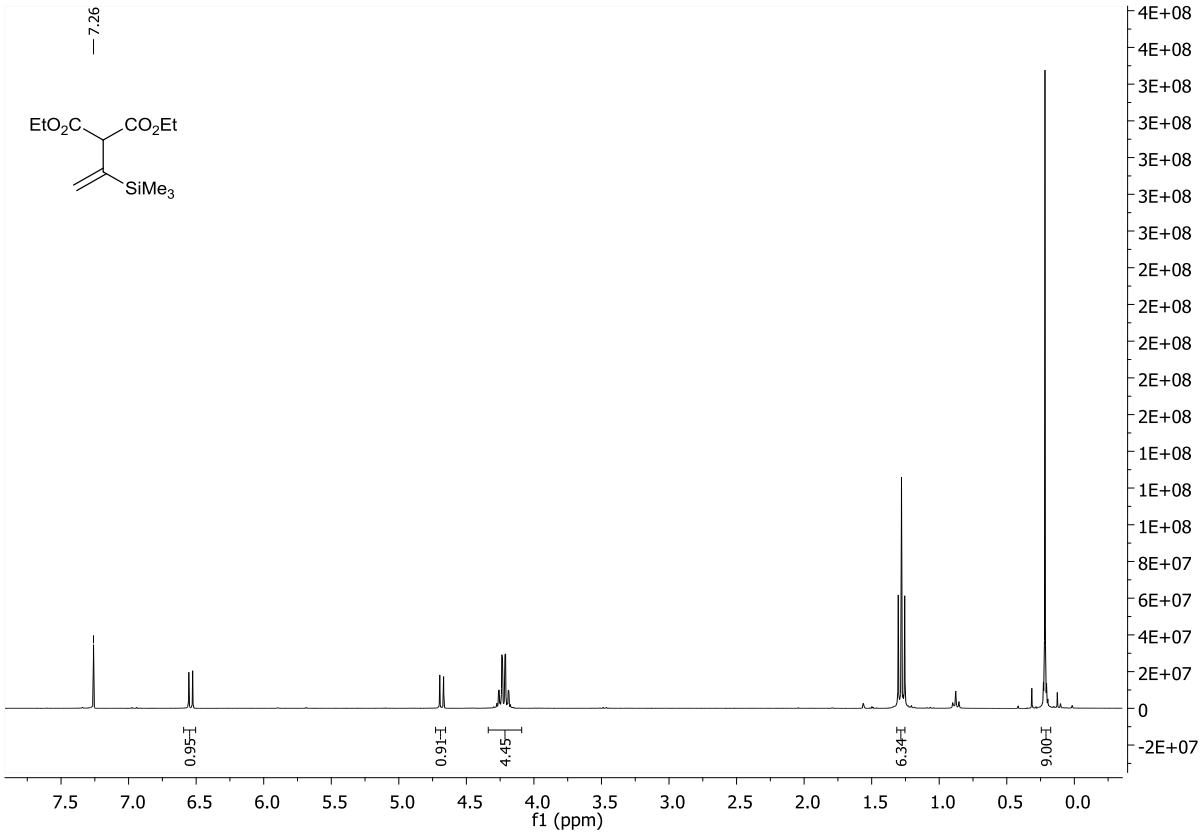


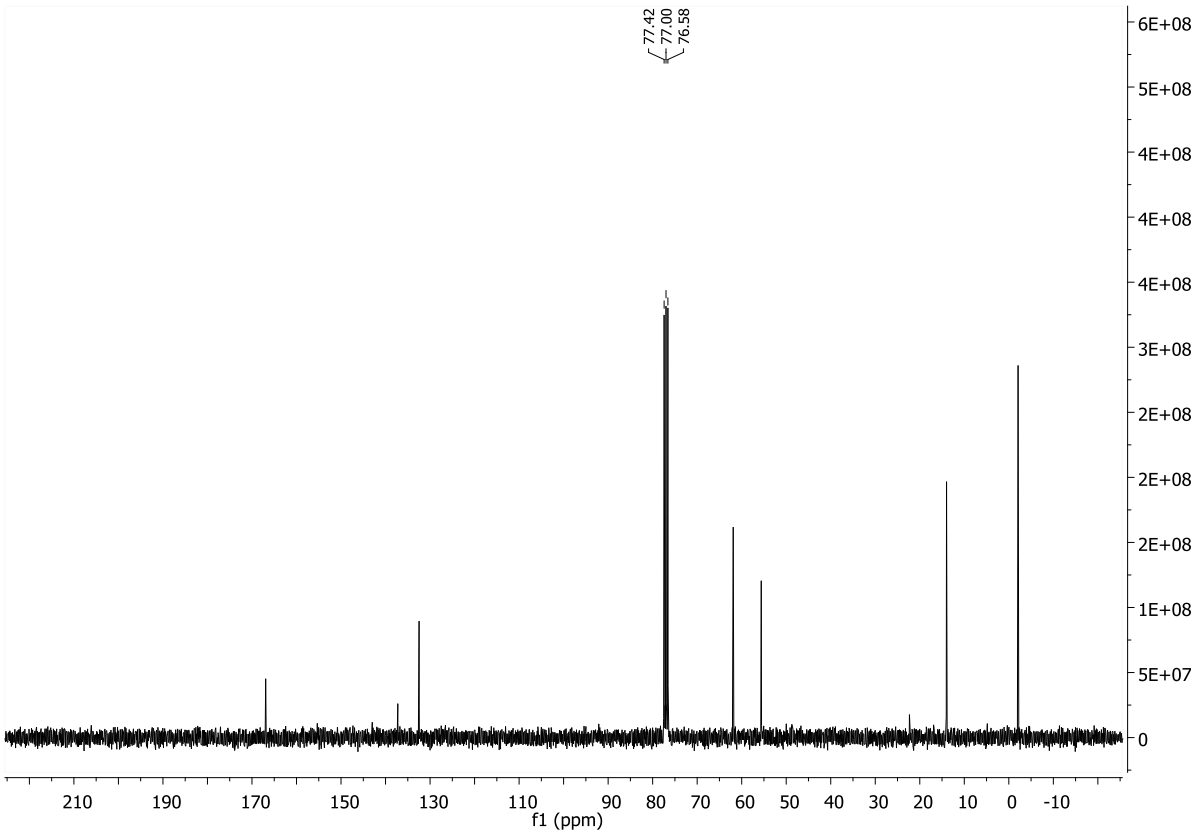
Diethyl 2-(3-(1,3-dioxoisoindolin-2-yl)prop-1-en-2-yl)malonate (5i)



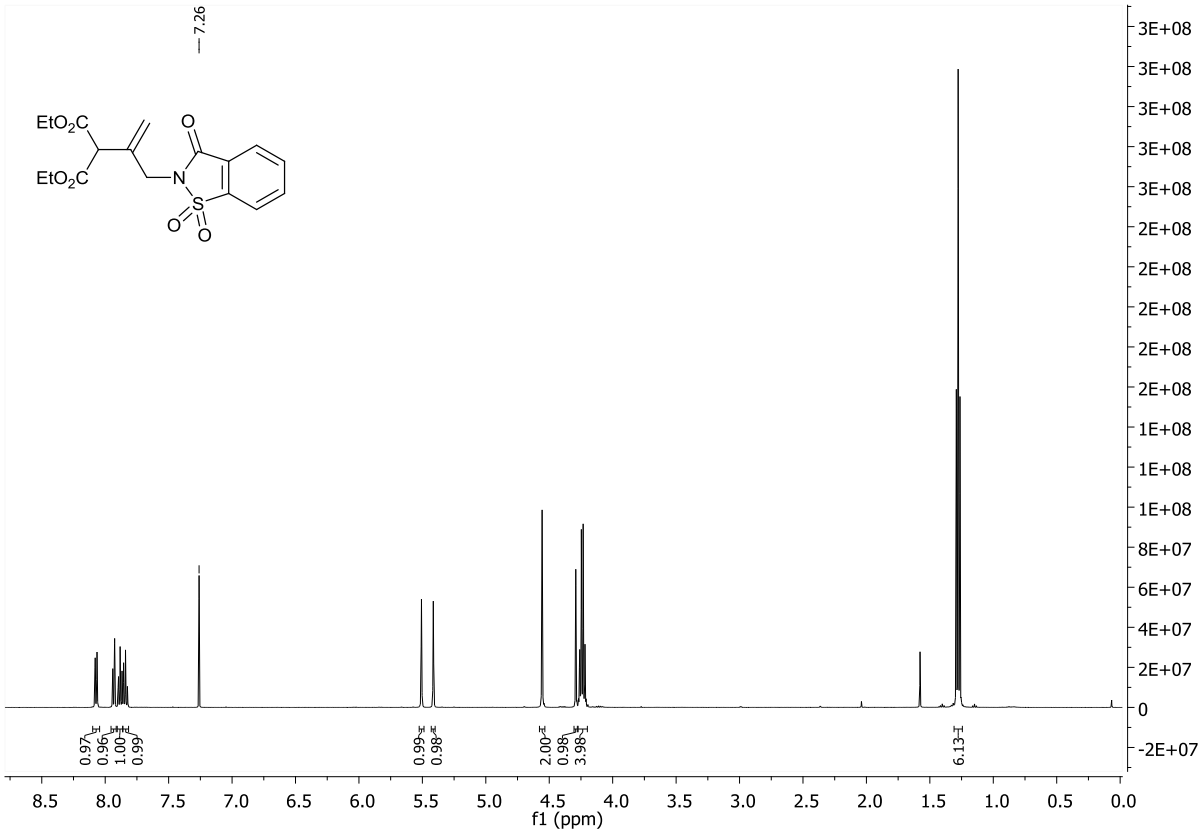


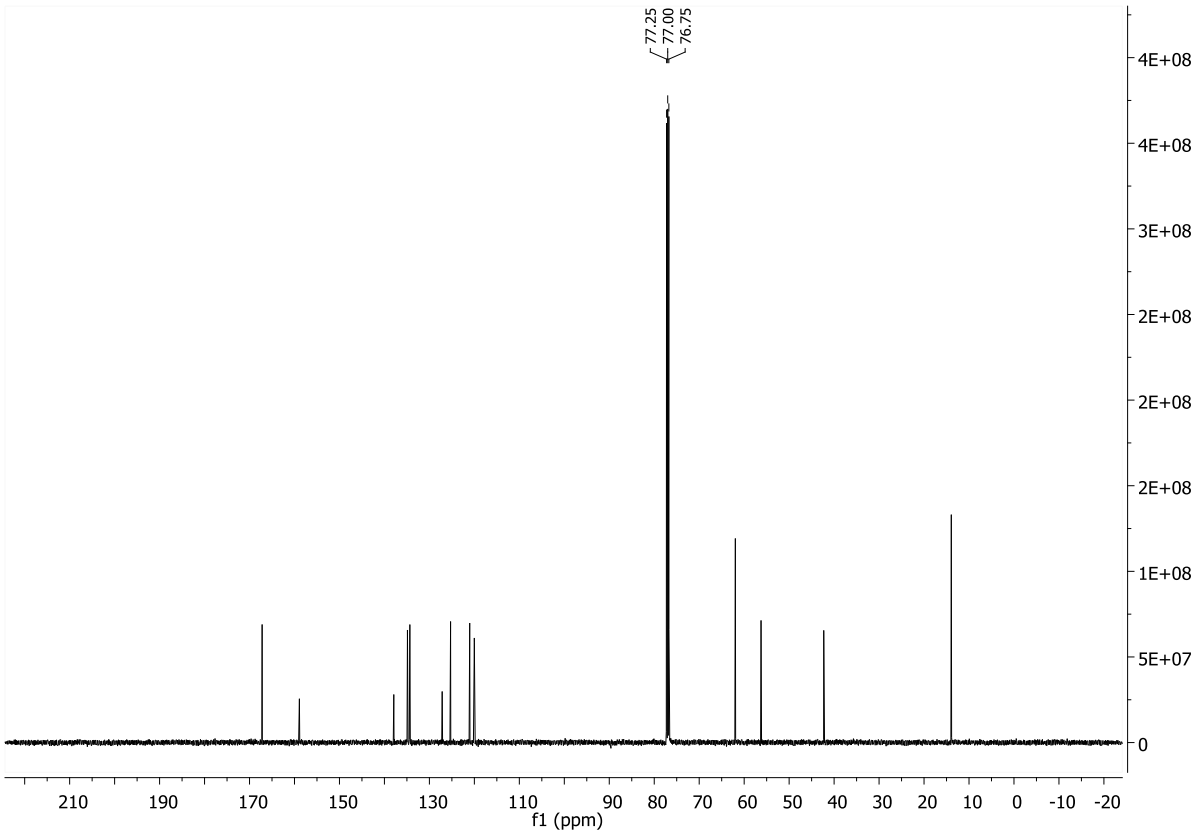
Diethyl 2-(1-(trimethylsilyl)vinyl)malonate (5j)



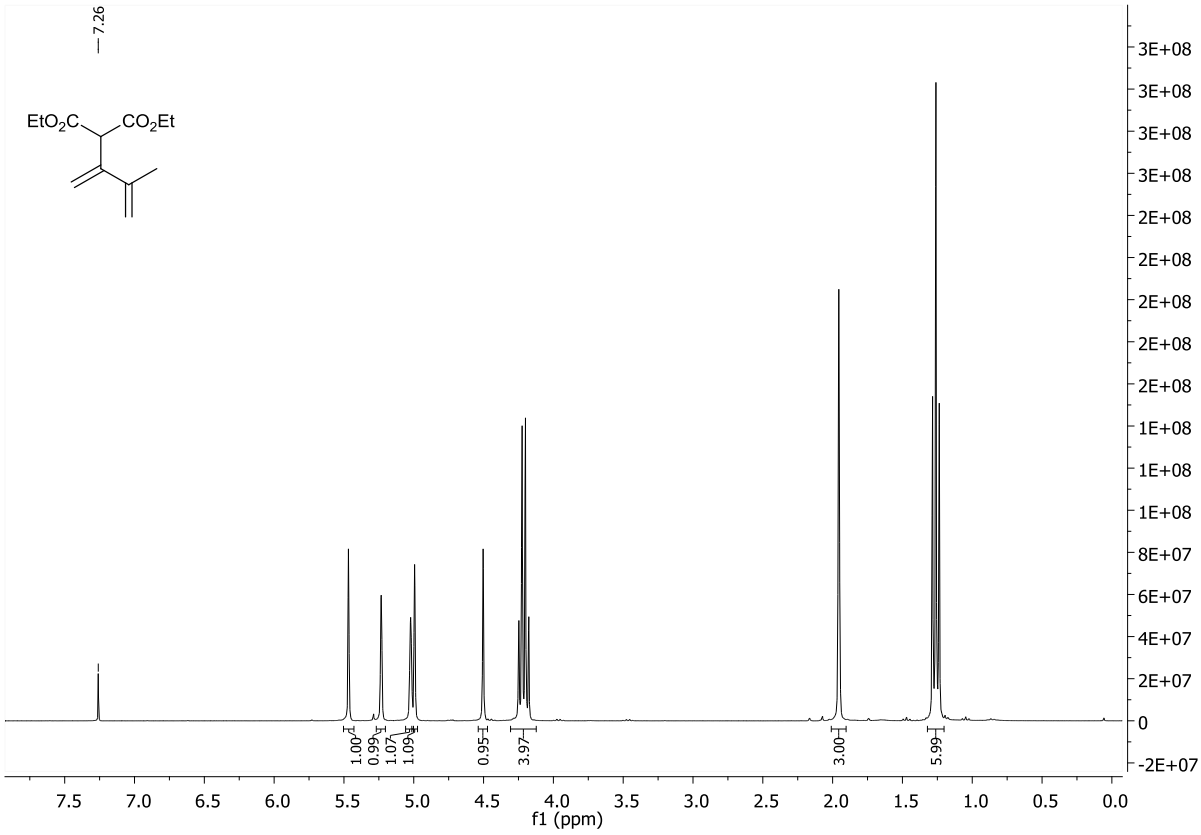


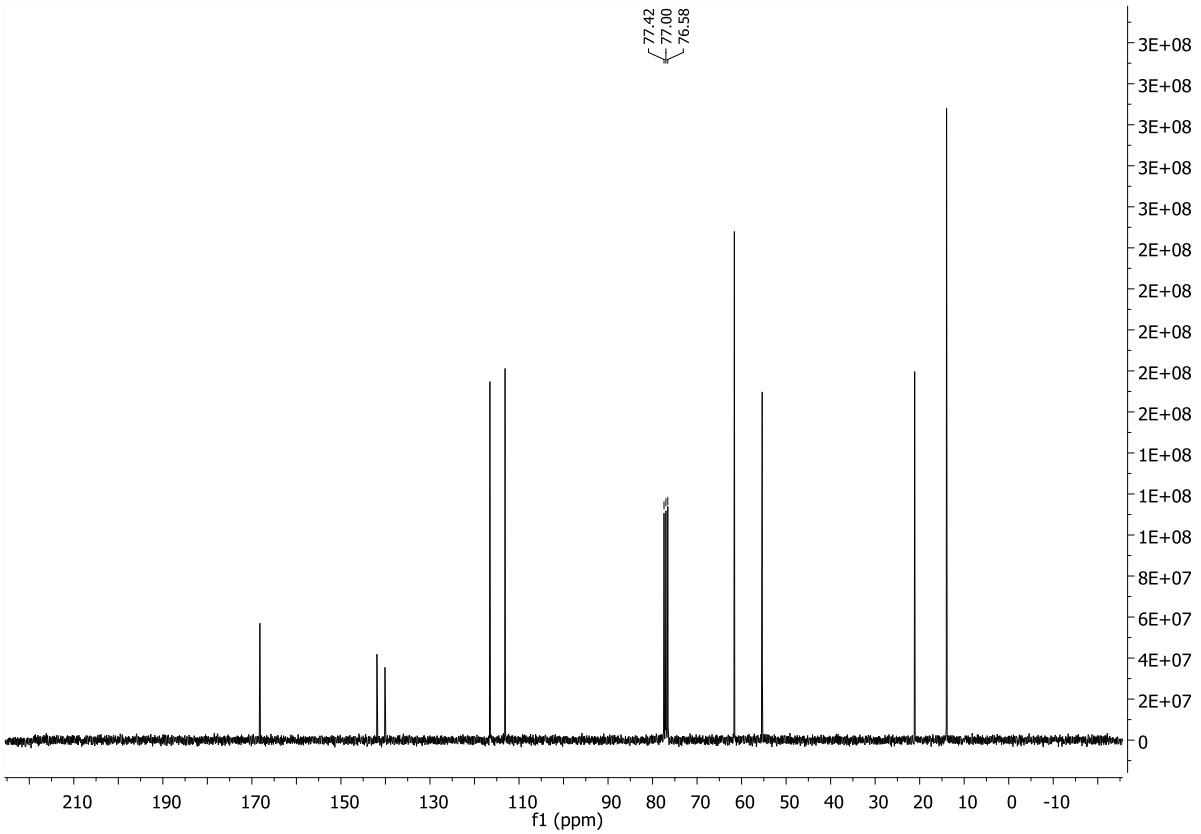
Diethyl (1-((1,1-dioxido-3-oxo-1,2-benzisothiazol-2(3*H*)-yl)methyl)vinyl)malonate (5k)



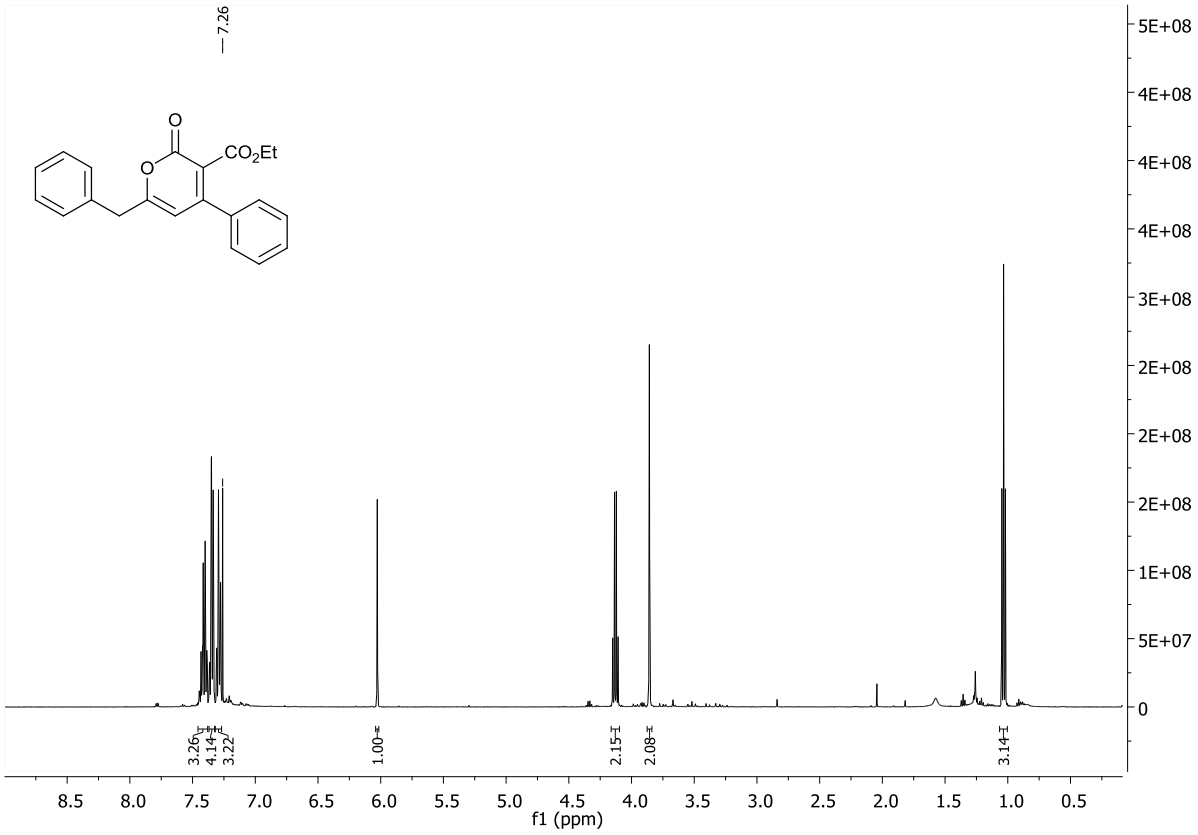


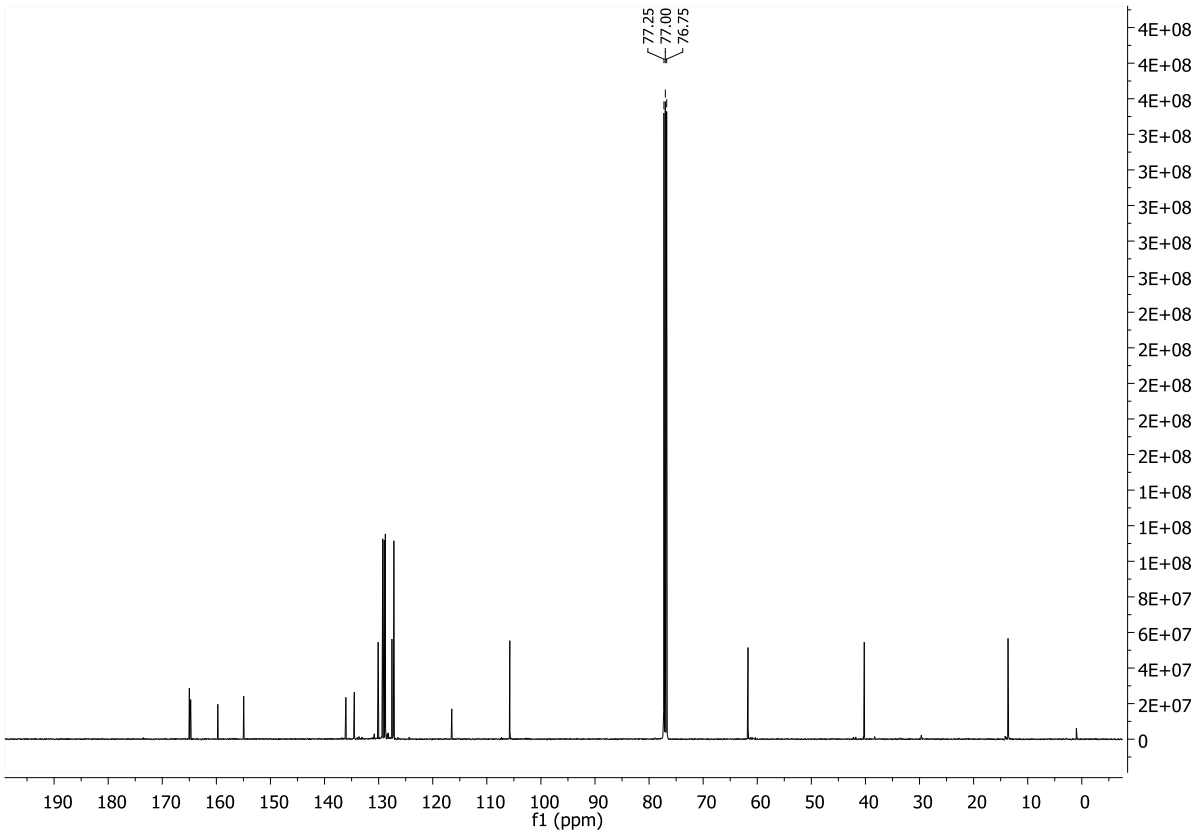
Diethyl 2-(3-methylbuta-1,3-dien-2-yl)malonate (5l)



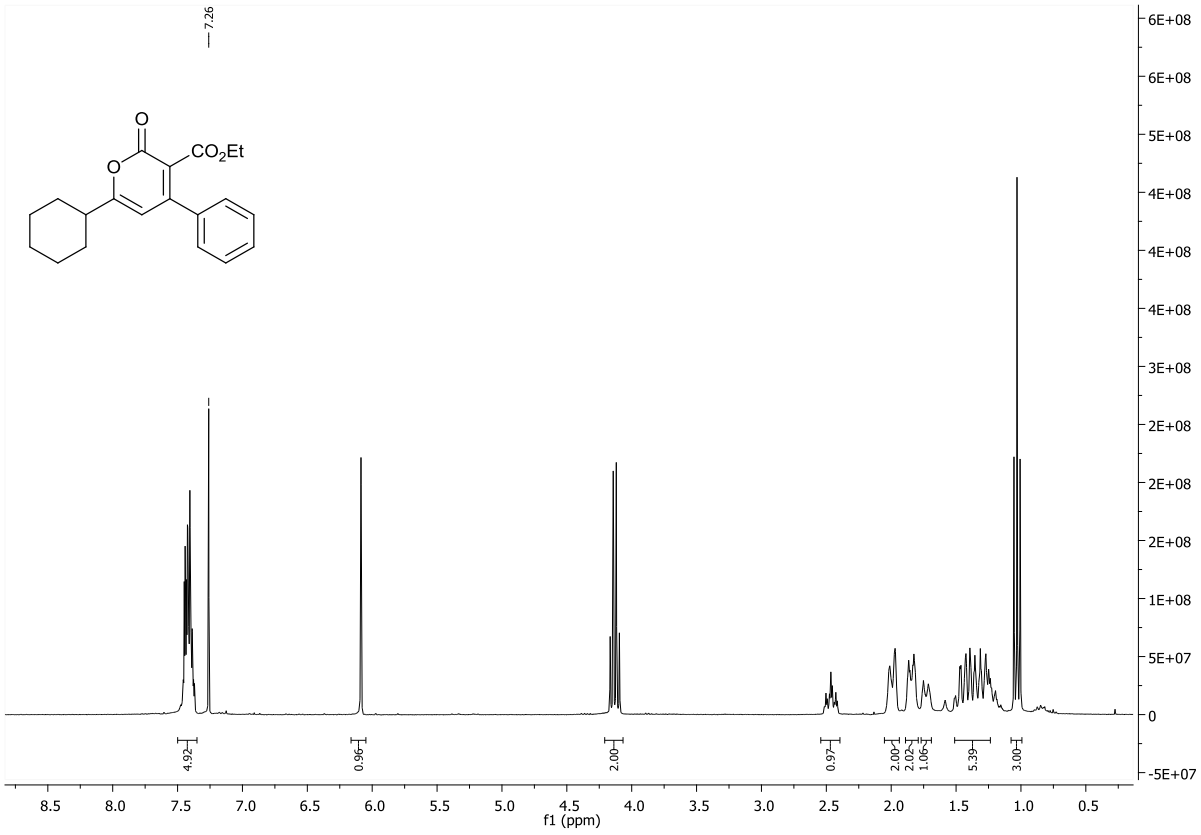


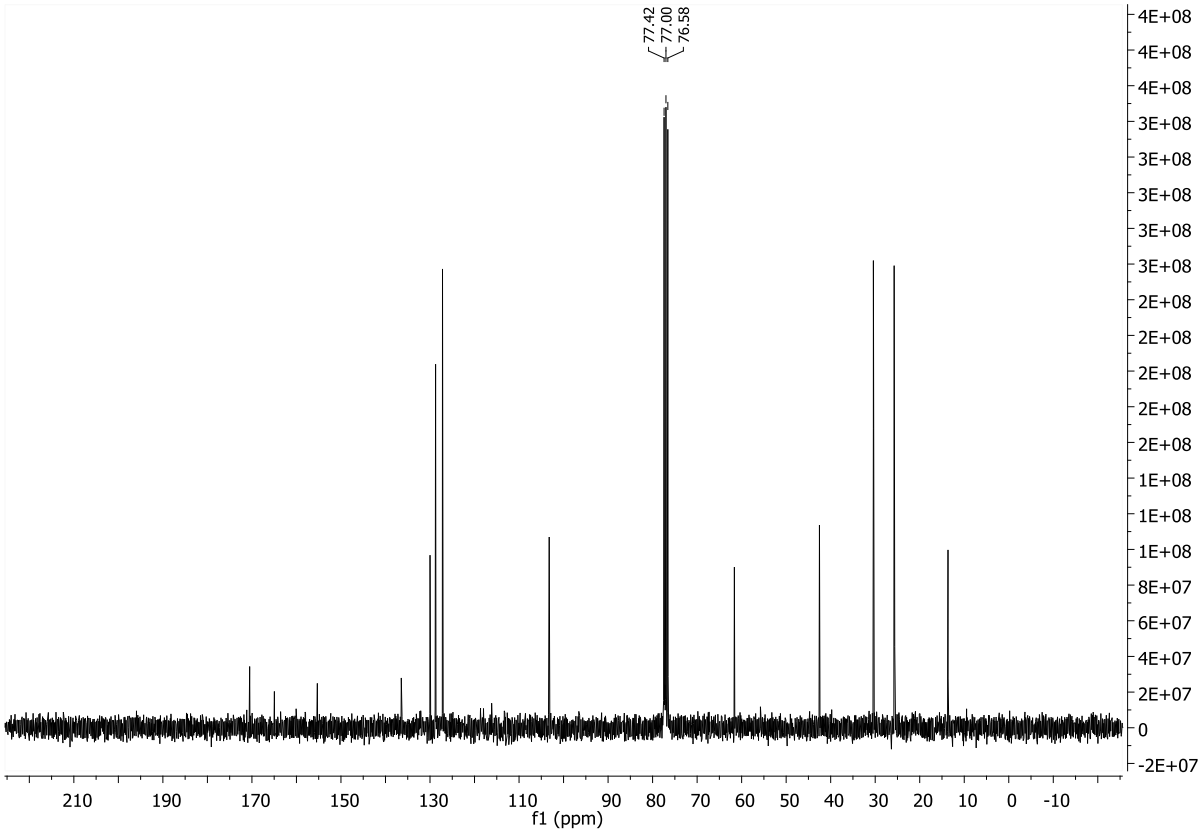
Ethyl 6-benzyl-2-oxo-4-phenyl-2*H*-pyran-3-carboxylate (8a)



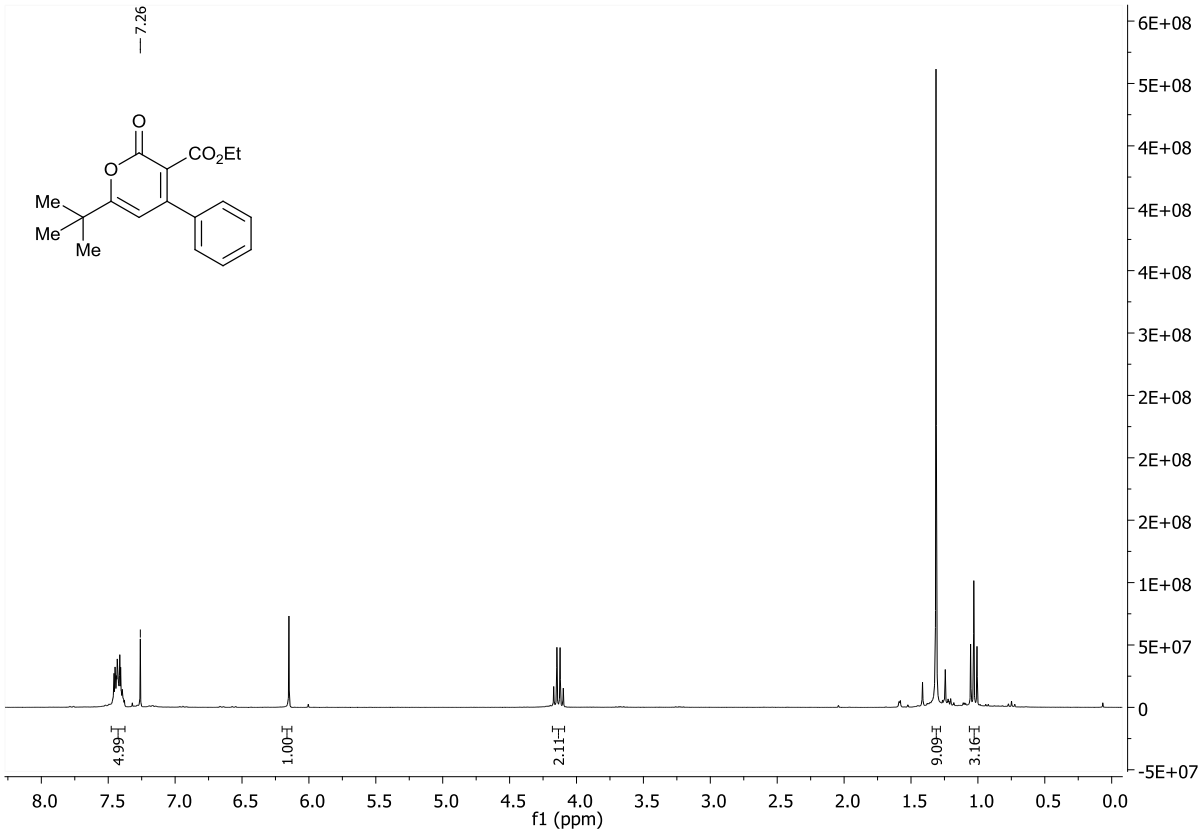


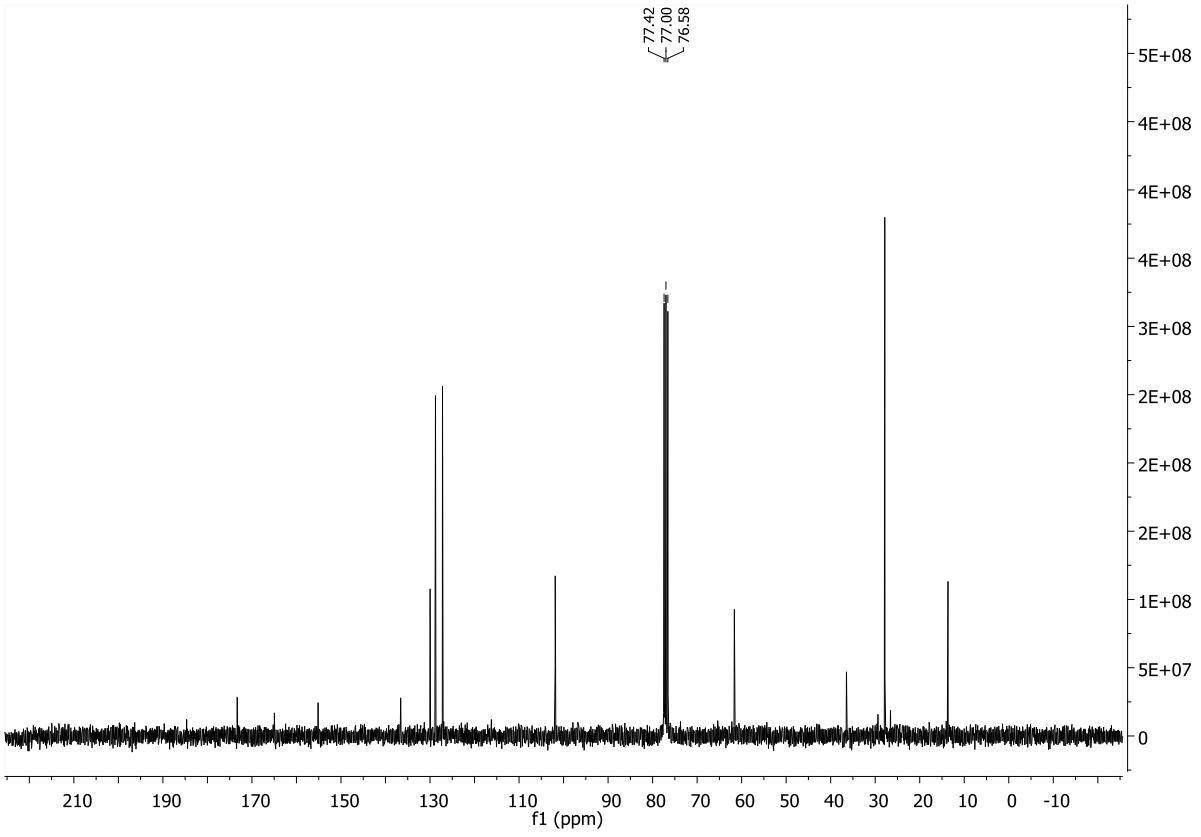
Ethyl 6-cyclohexyl-2-oxo-4-phenyl-2*H*-pyran-3-carboxylate (8b)



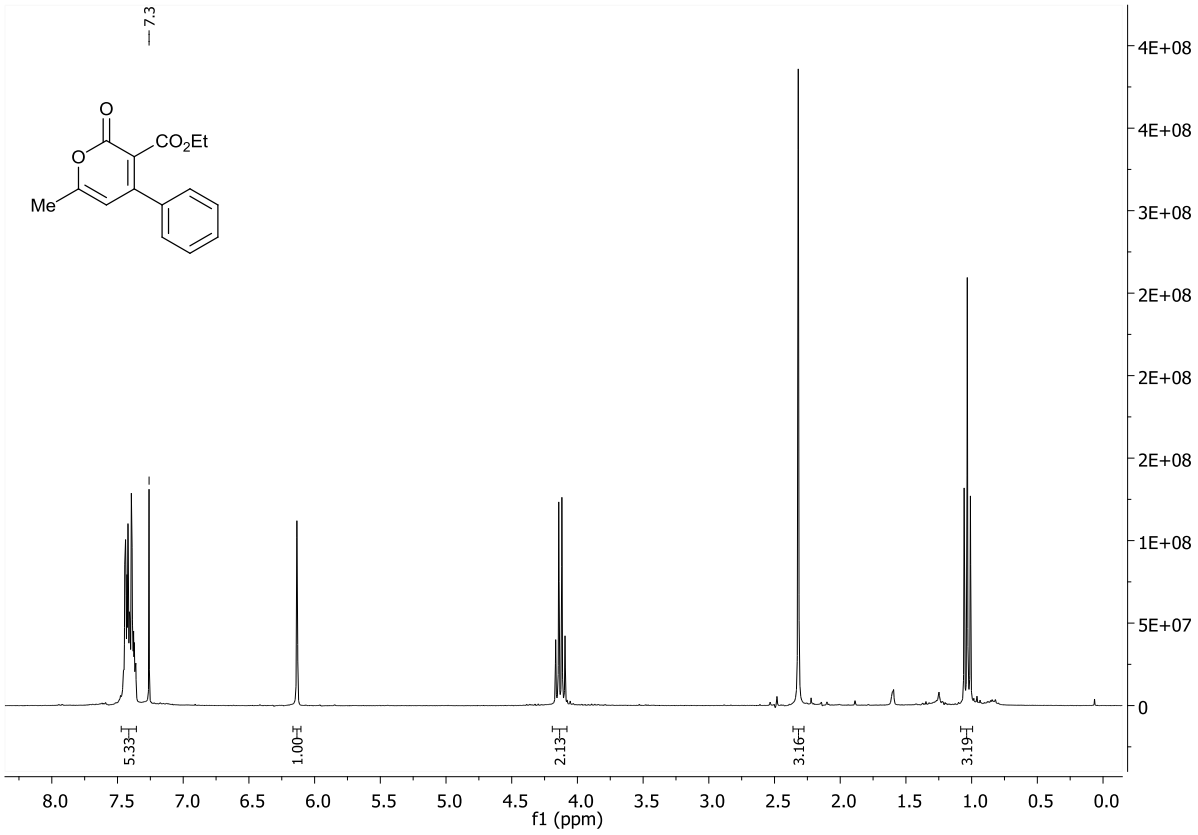


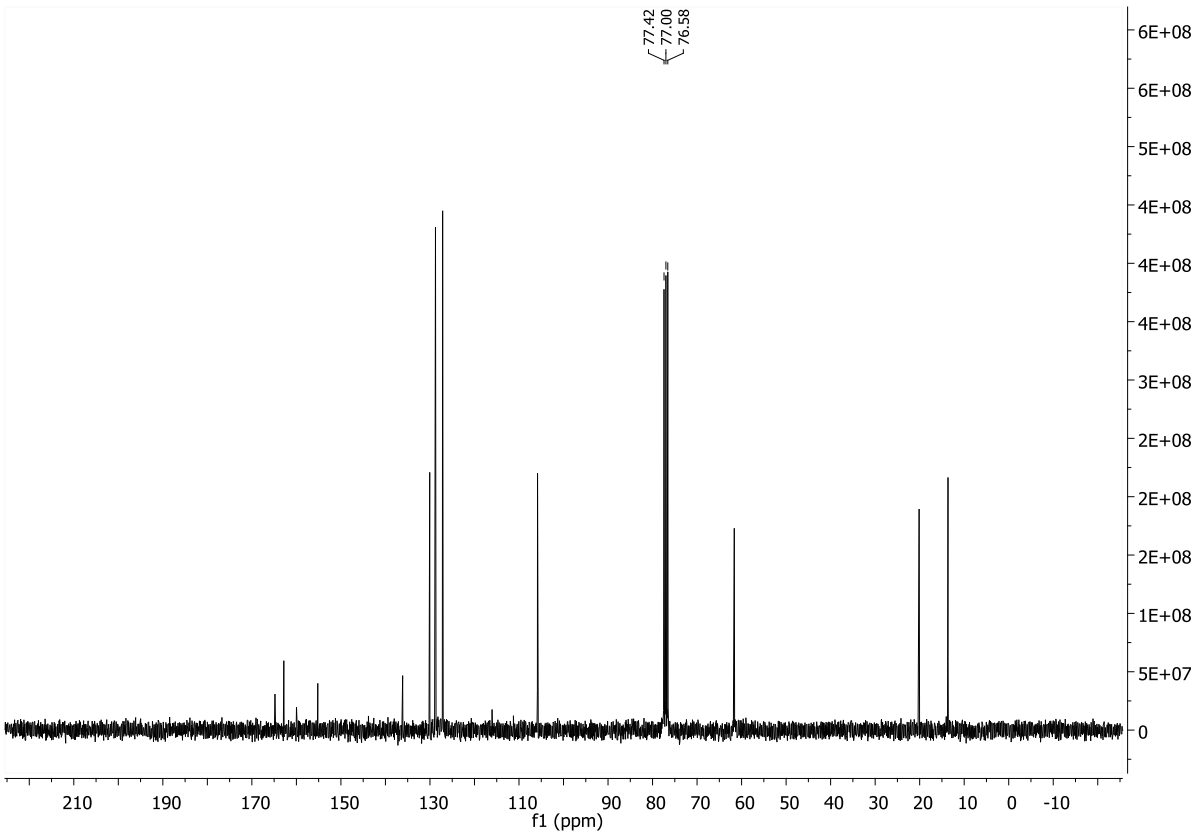
Ethyl 6-tert-butyl-2-oxo-4-phenyl-2*H*-pyran-3-carboxylate (8c)



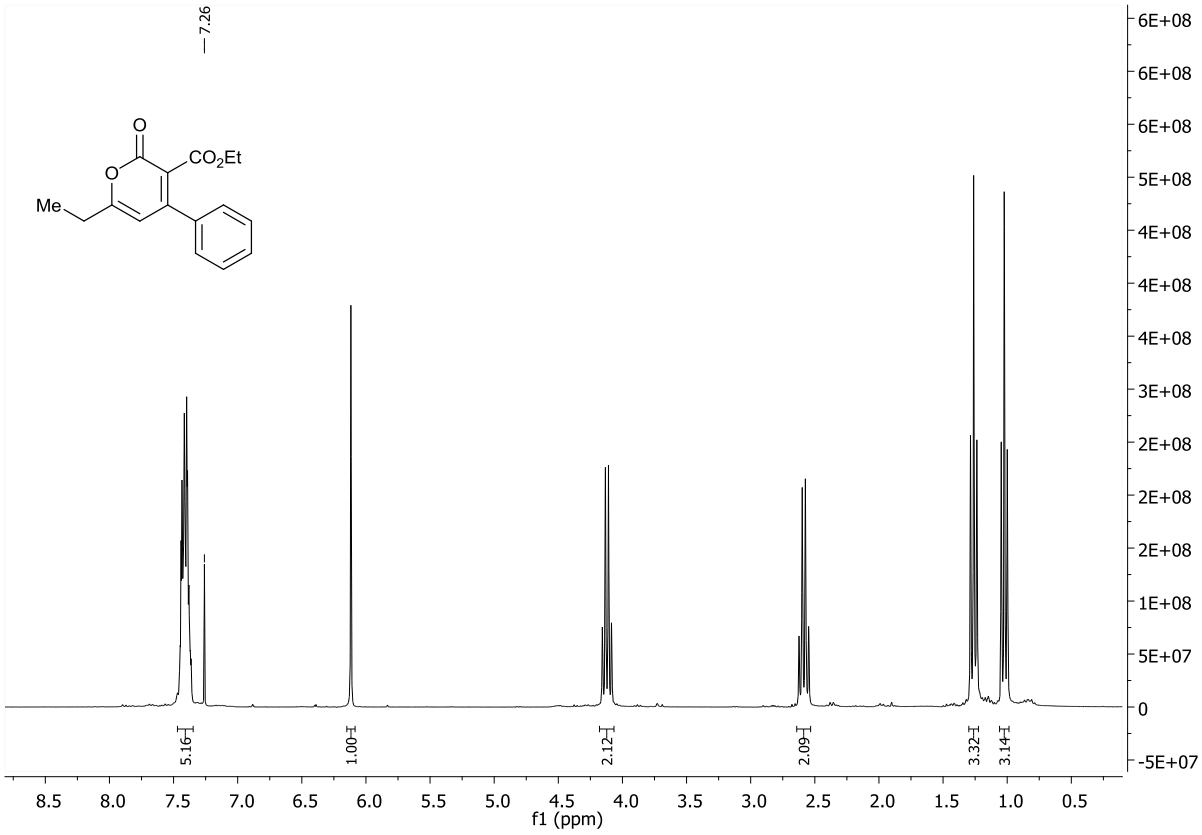


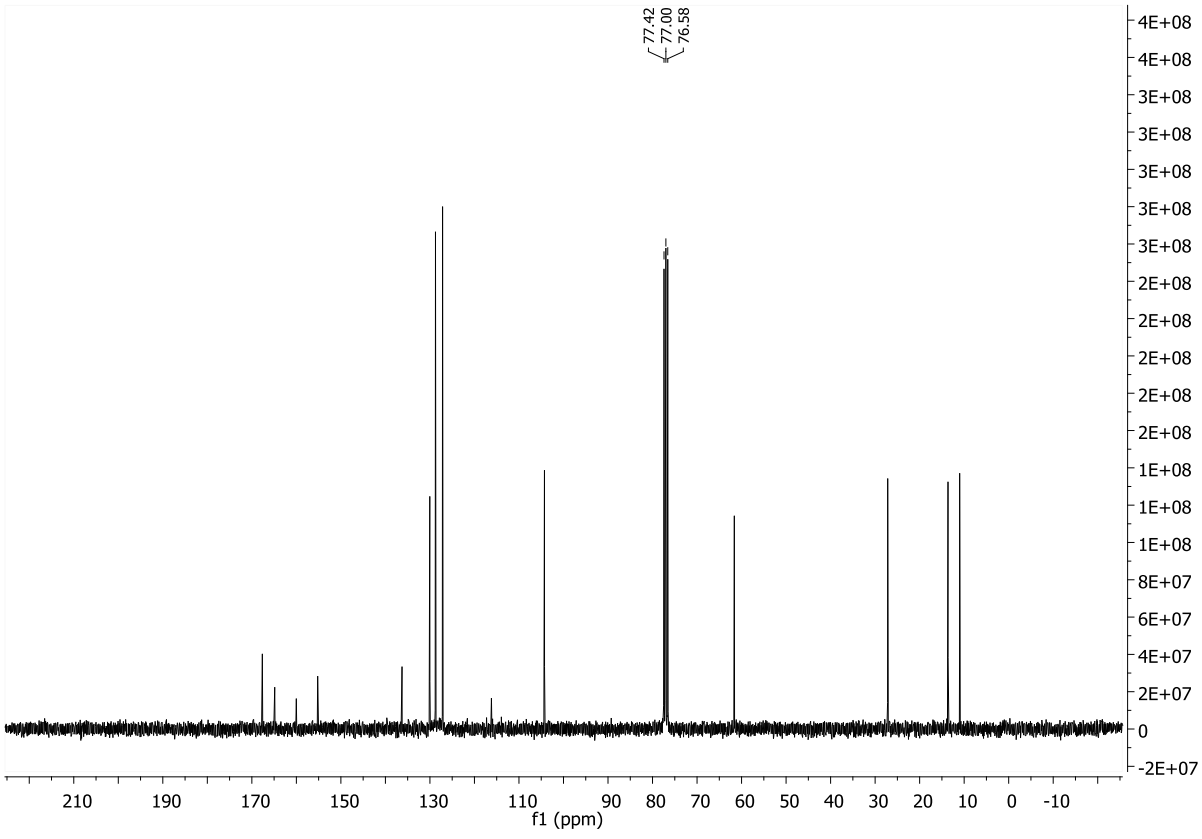
Ethyl 6-methyl-2-oxo-4-phenyl-2*H*-pyran-3-carboxylate (8d)



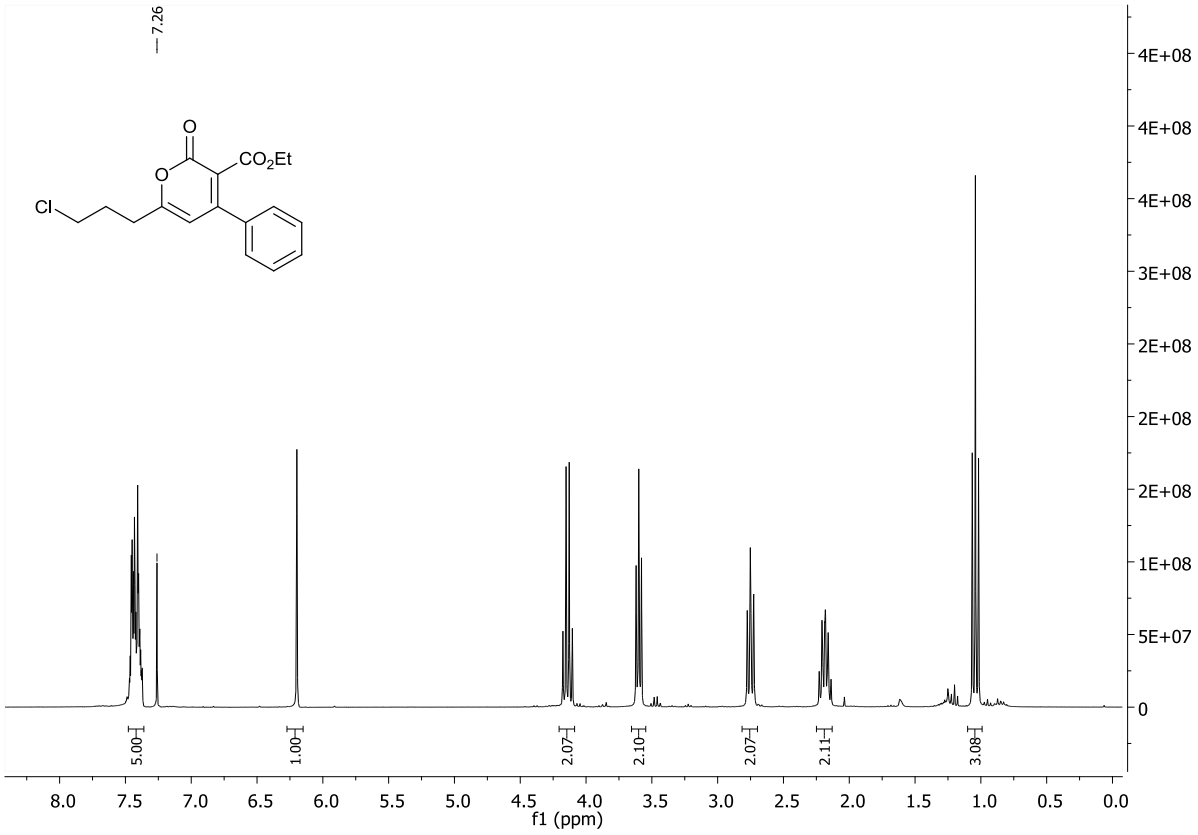


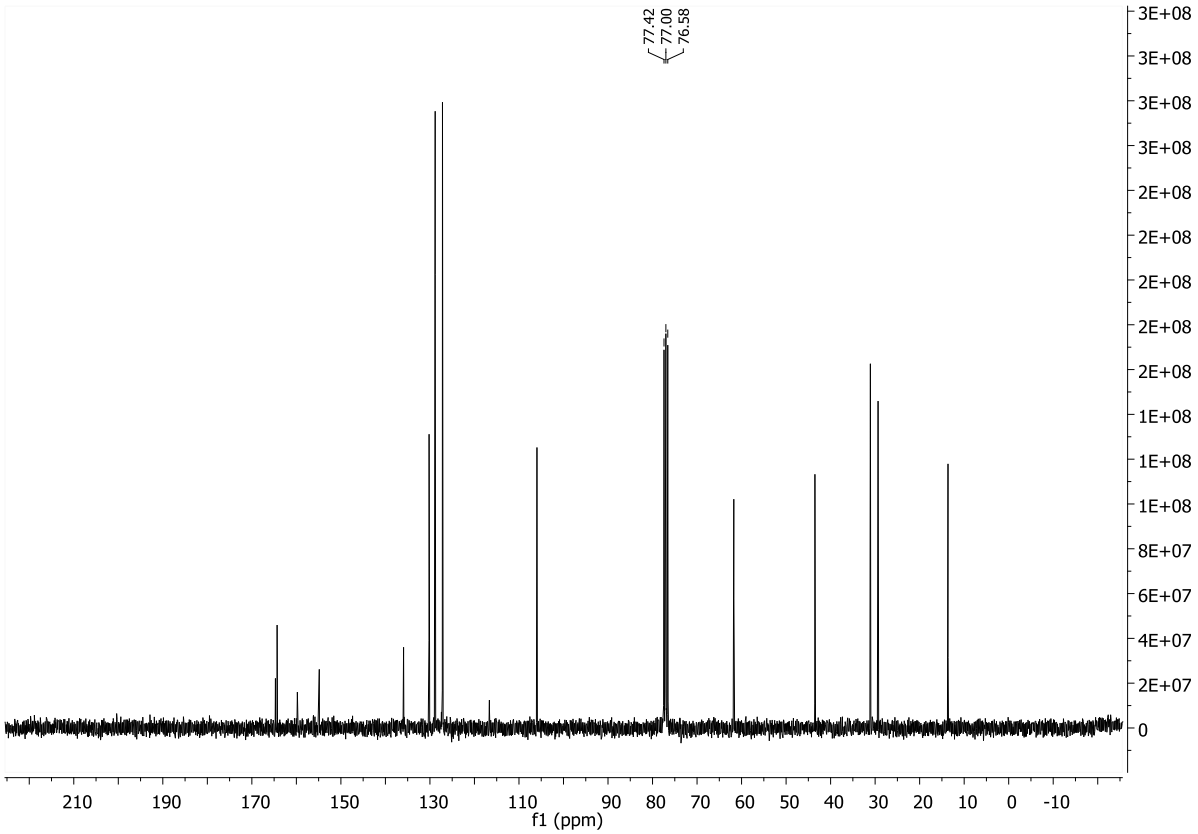
Ethyl 6-ethyl-2-oxo-4-phenyl-2*H*-pyran-3-carboxylate (8e)



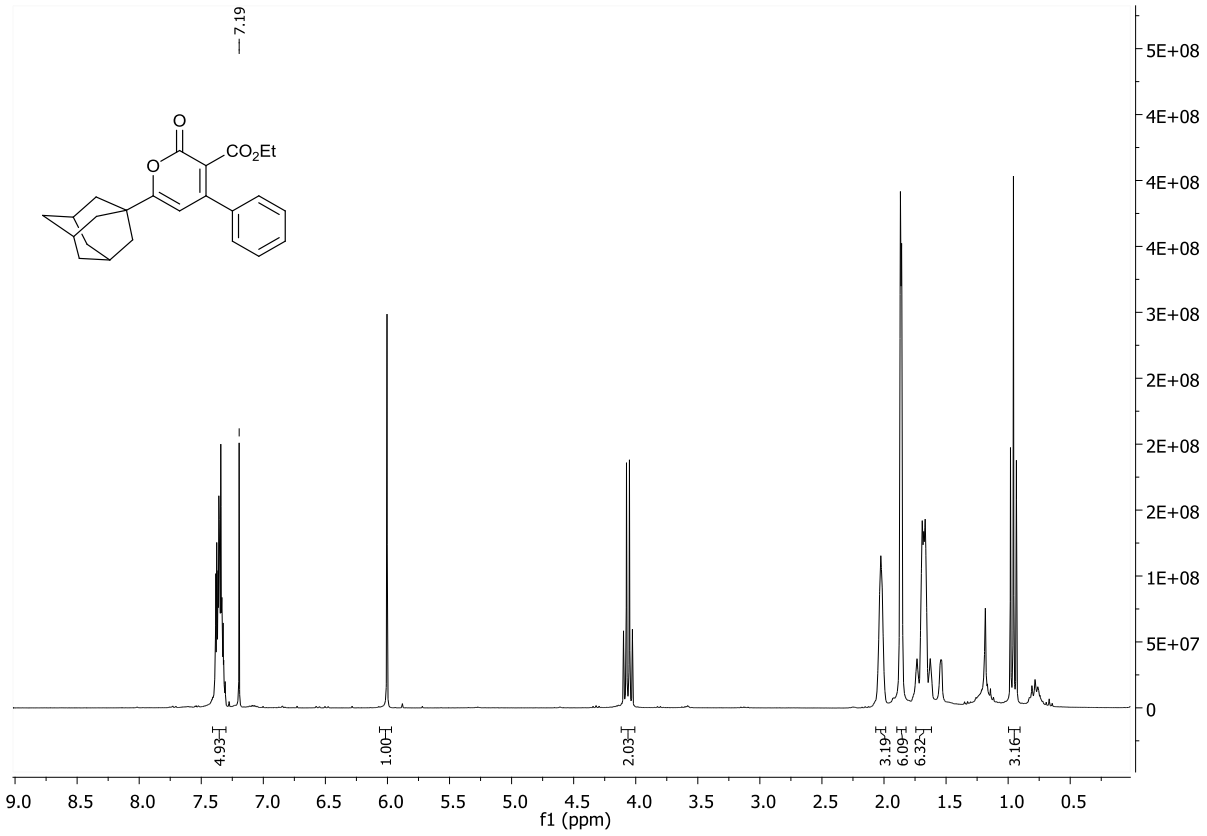


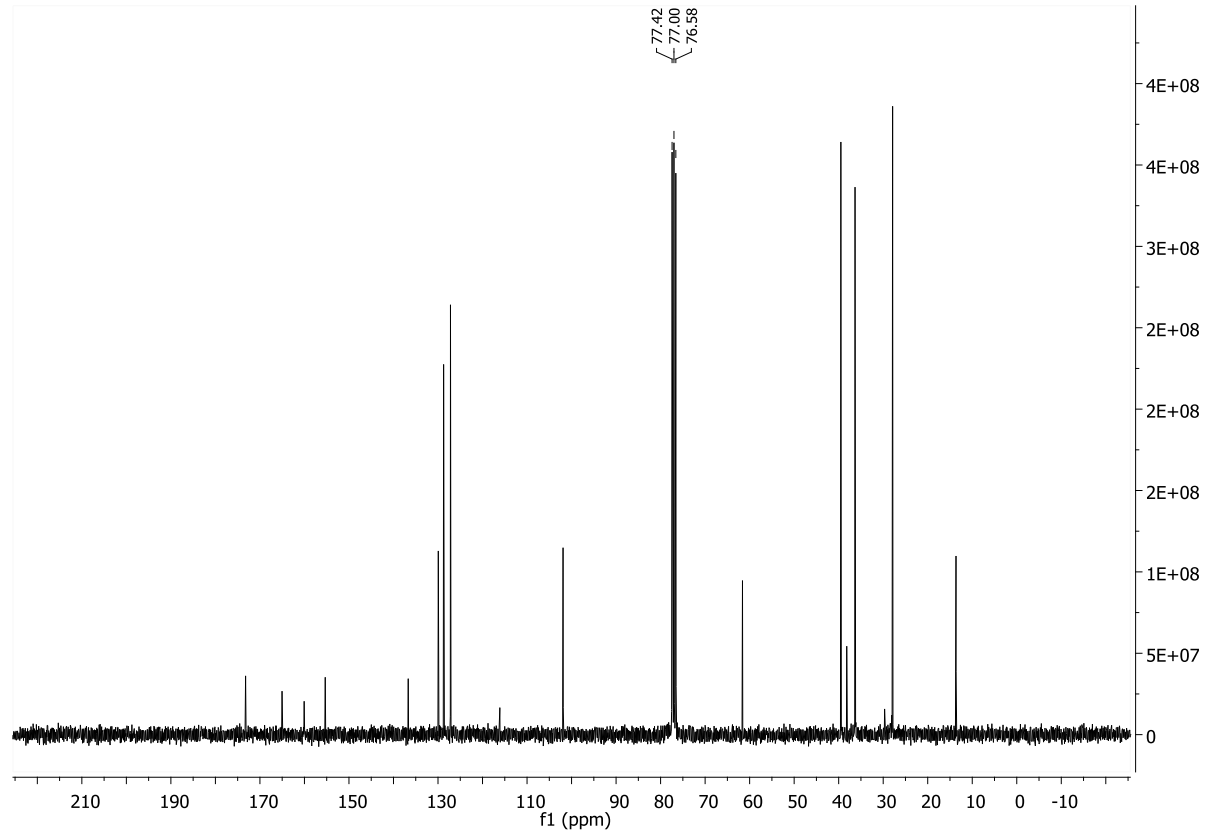
Ethyl 6-(3-chloropropyl)-2-oxo-4-phenyl-2*H*-pyran-3-carboxylate (8f)



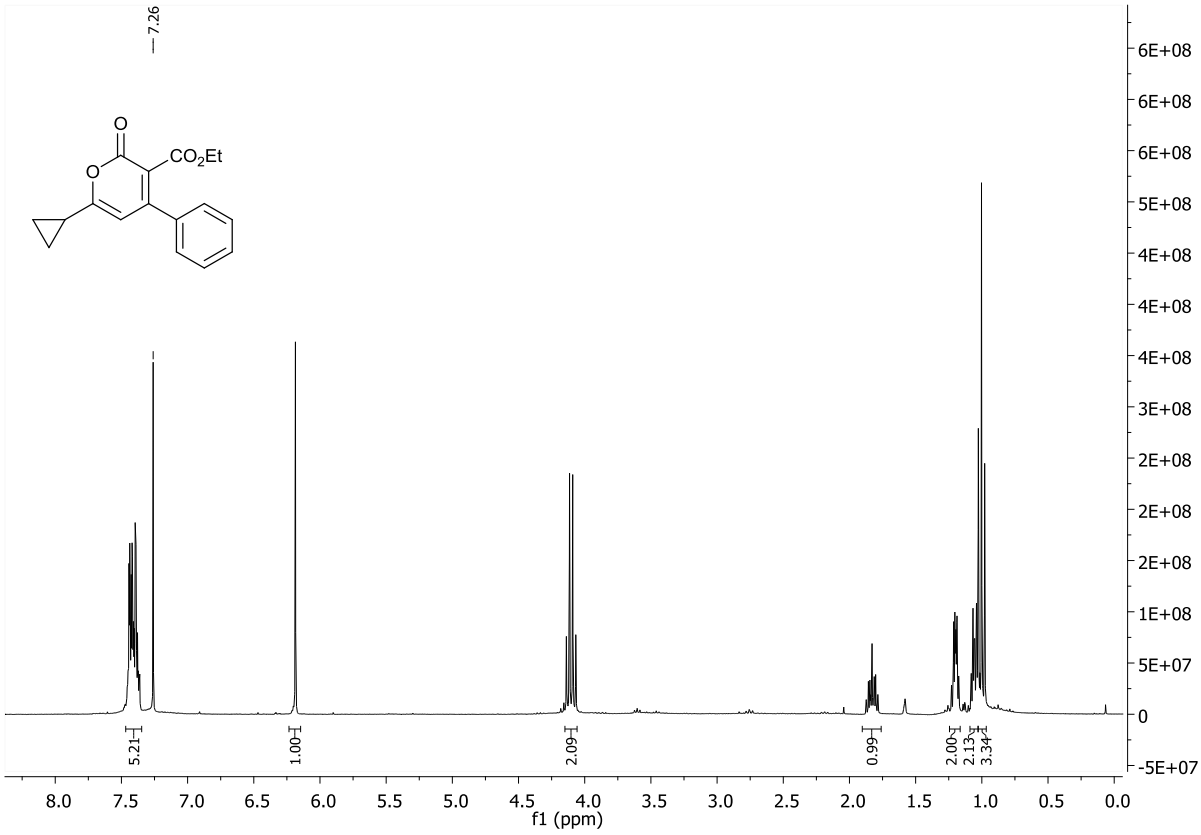


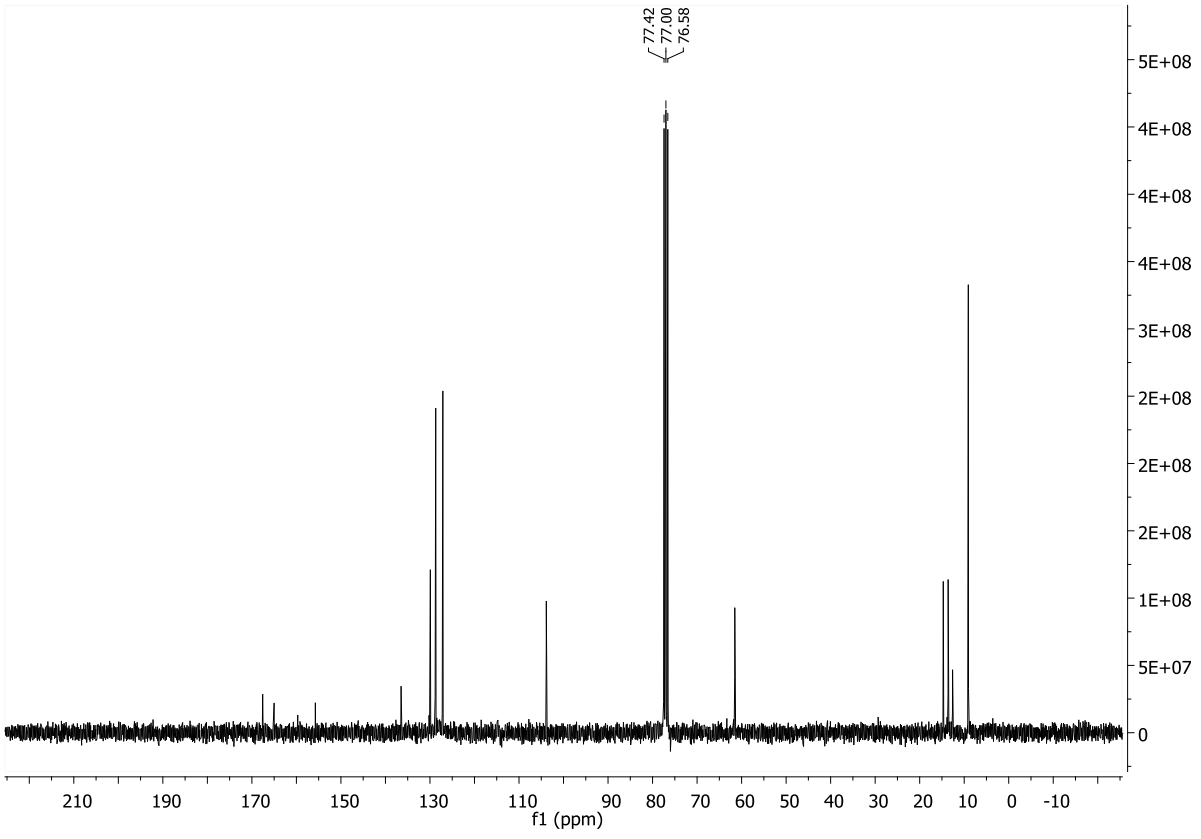
Ethyl 6-(1-adamantyl)-2-oxo-4-phenyl-2*H*-pyran-3-carboxylate (8g)



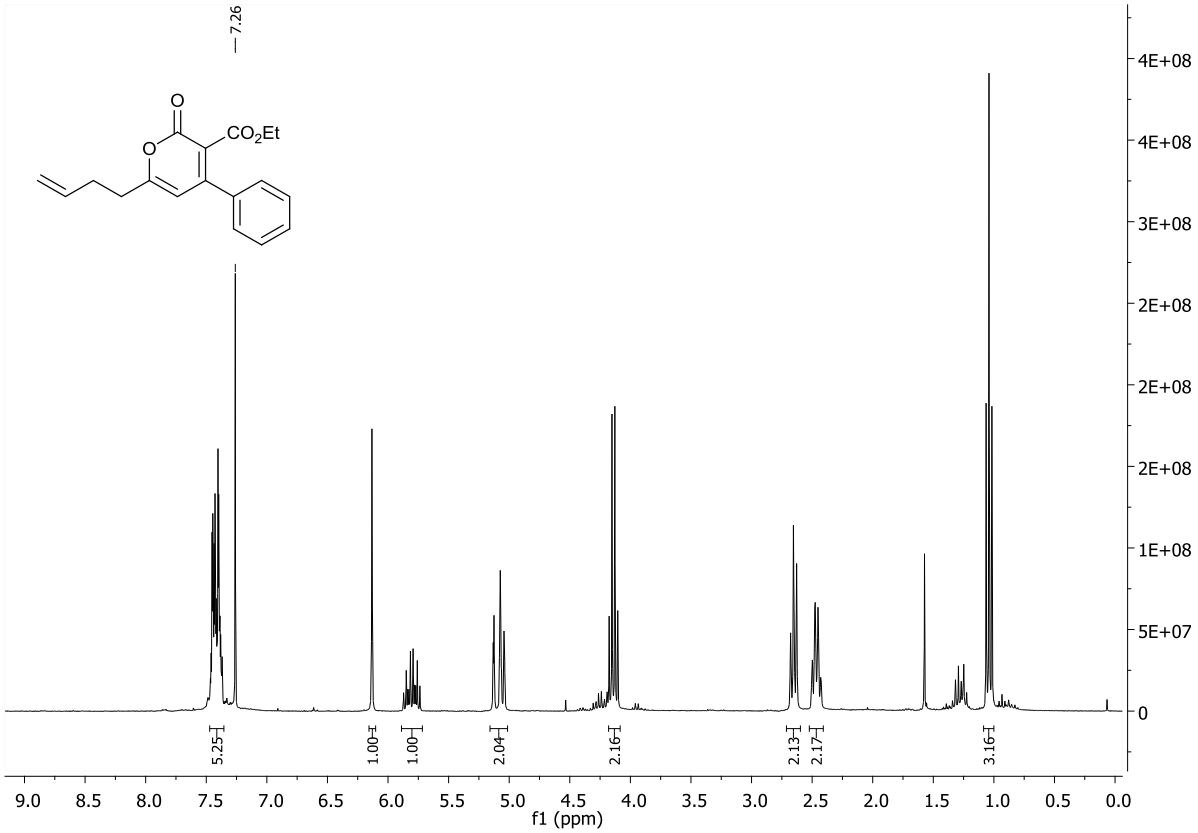


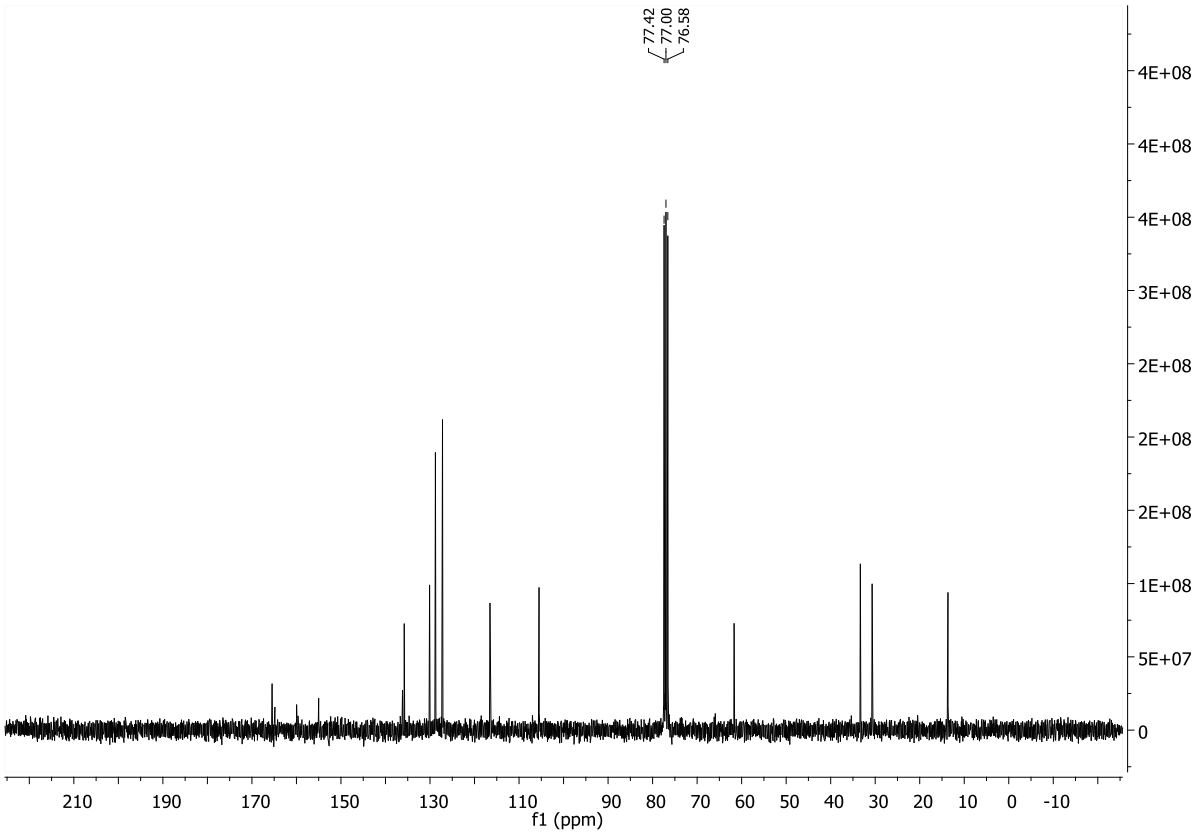
Ethyl 6-cyclopropyl-2-oxo-4-phenyl-2*H*-pyran-3-carboxylate (8h)



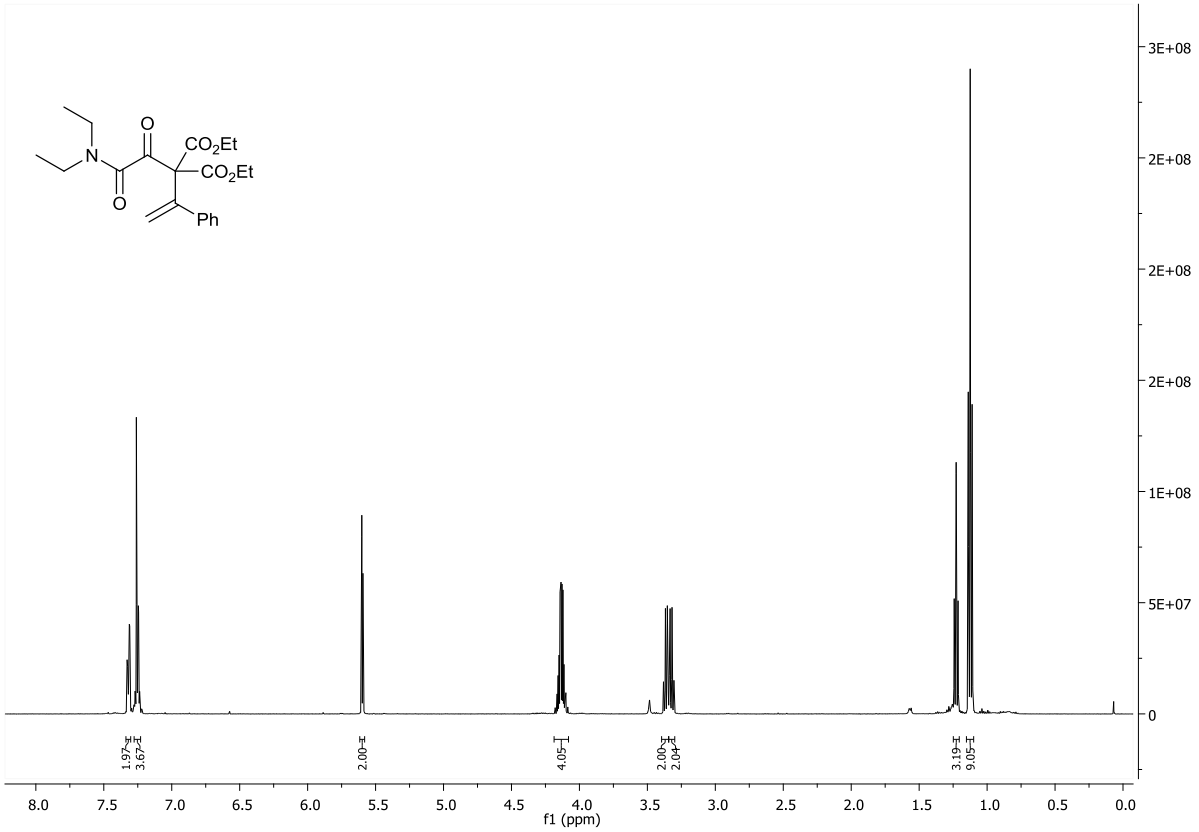


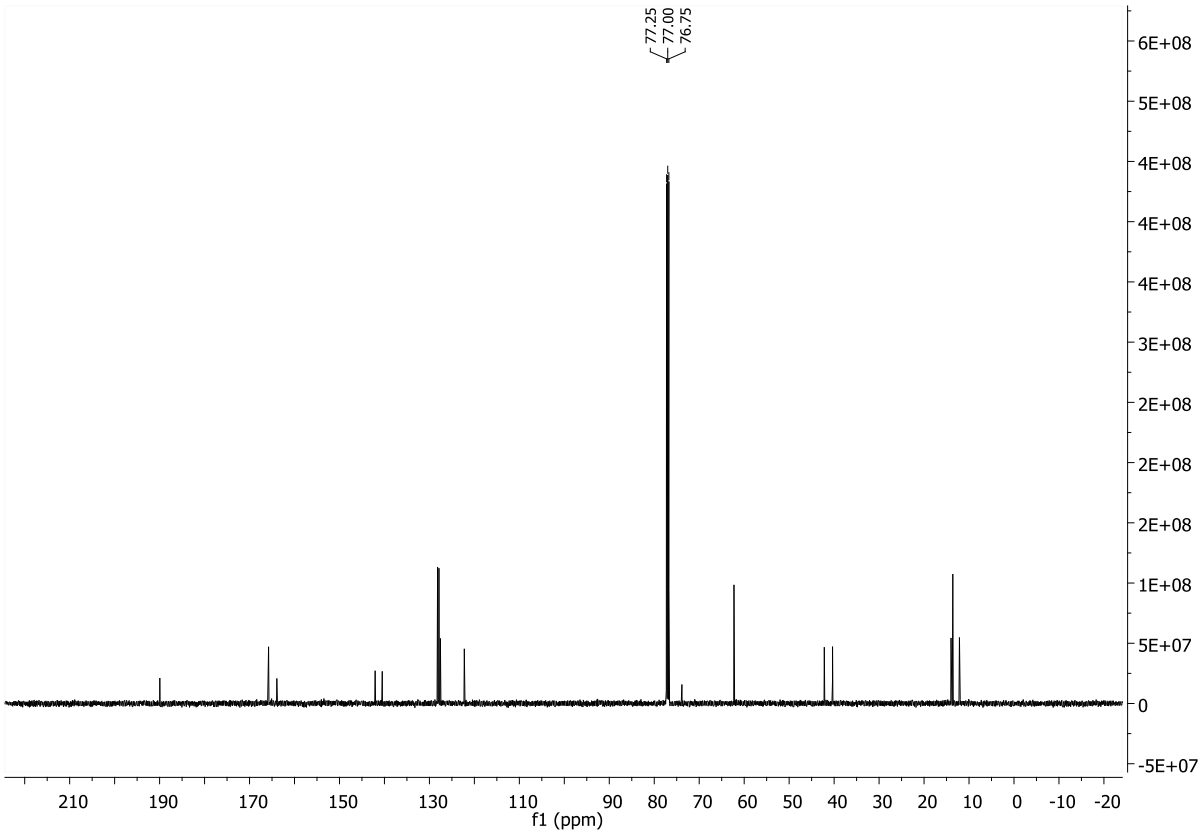
Ethyl 6-(but-3-enyl)-2-oxo-4-phenyl-2*H*-pyran-3-carboxylate (8i)



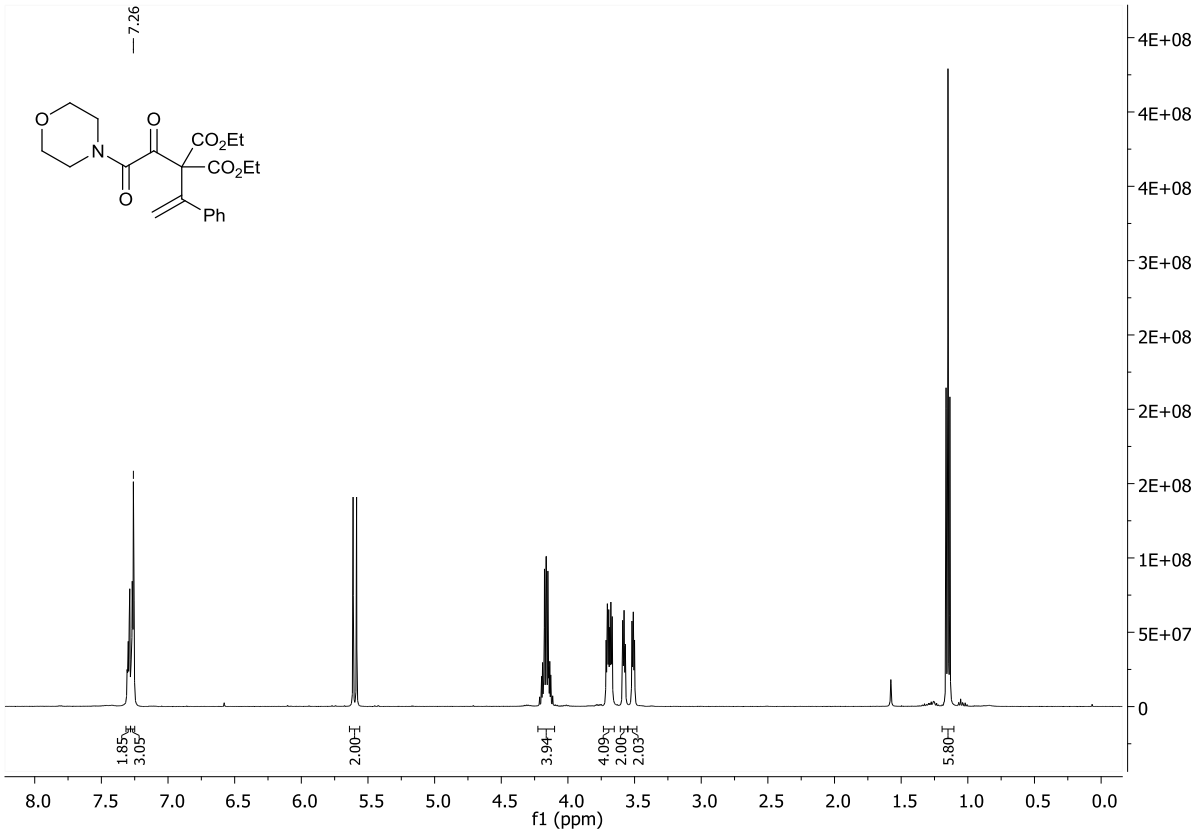


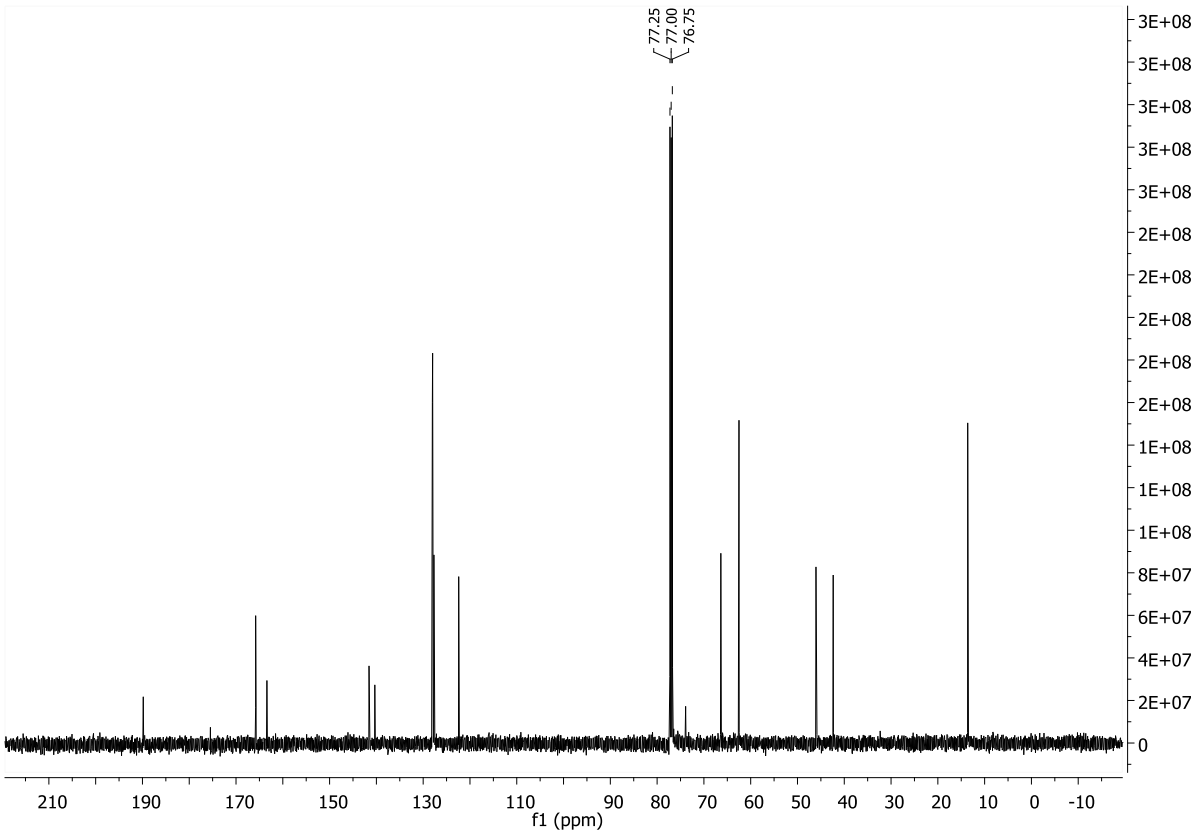
Diethyl 2-(2-(diethylamino)-2-oxoacetyl)-2-(1-phenylvinyl)malonate (10a)



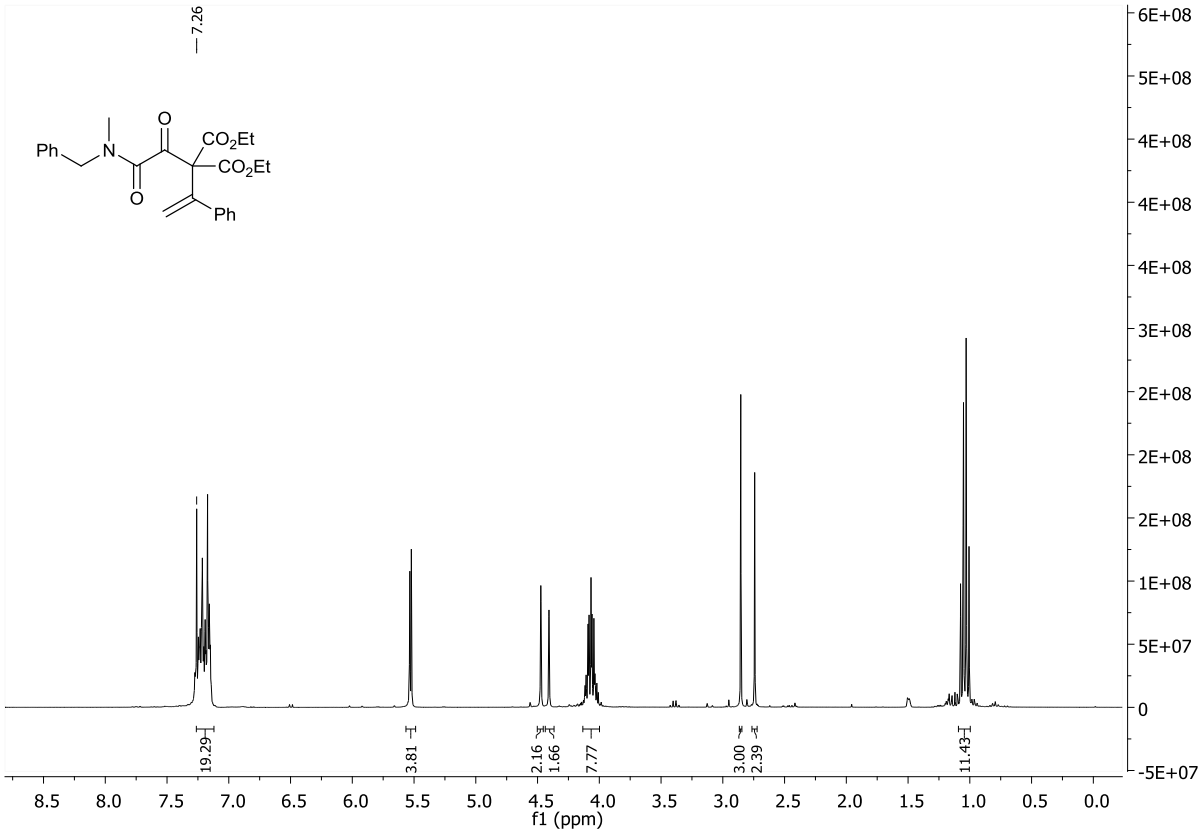


Diethyl 2-(2-morpholino-2-oxoacetyl)-2-(1-phenylvinyl)malonate (10b)

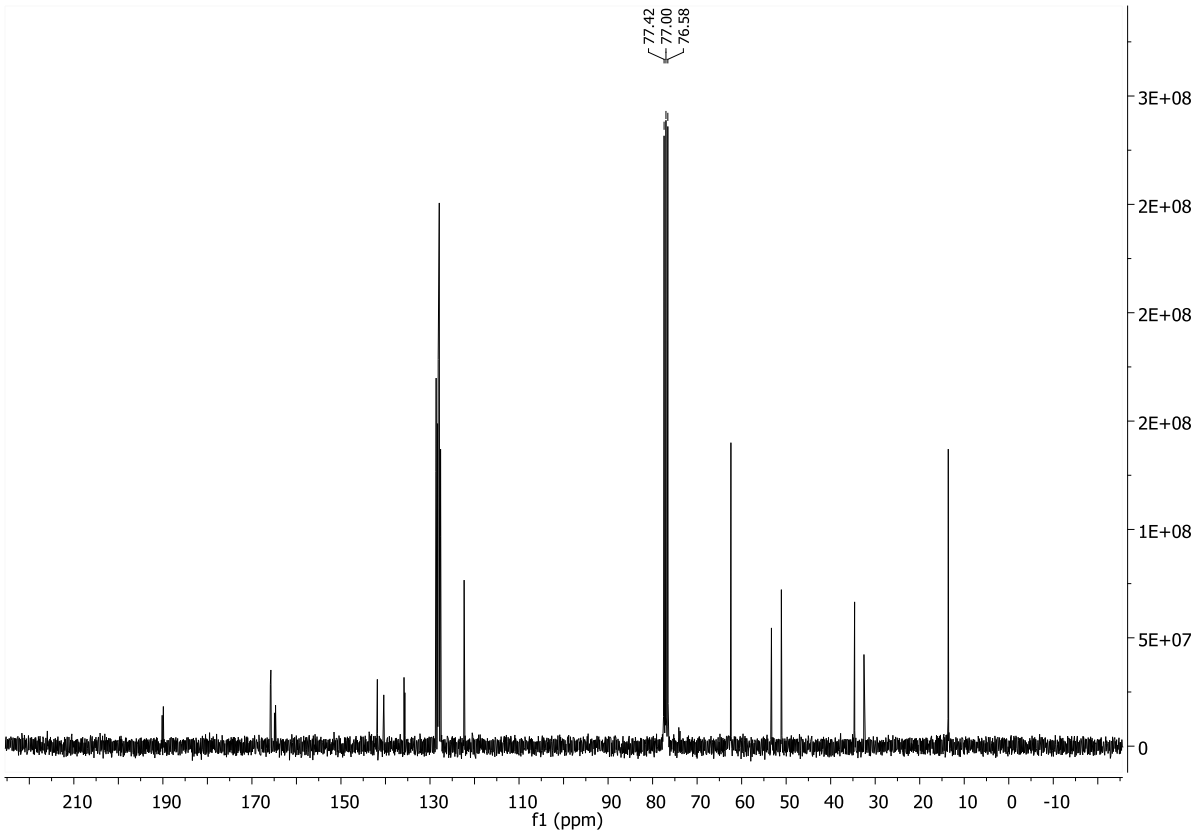




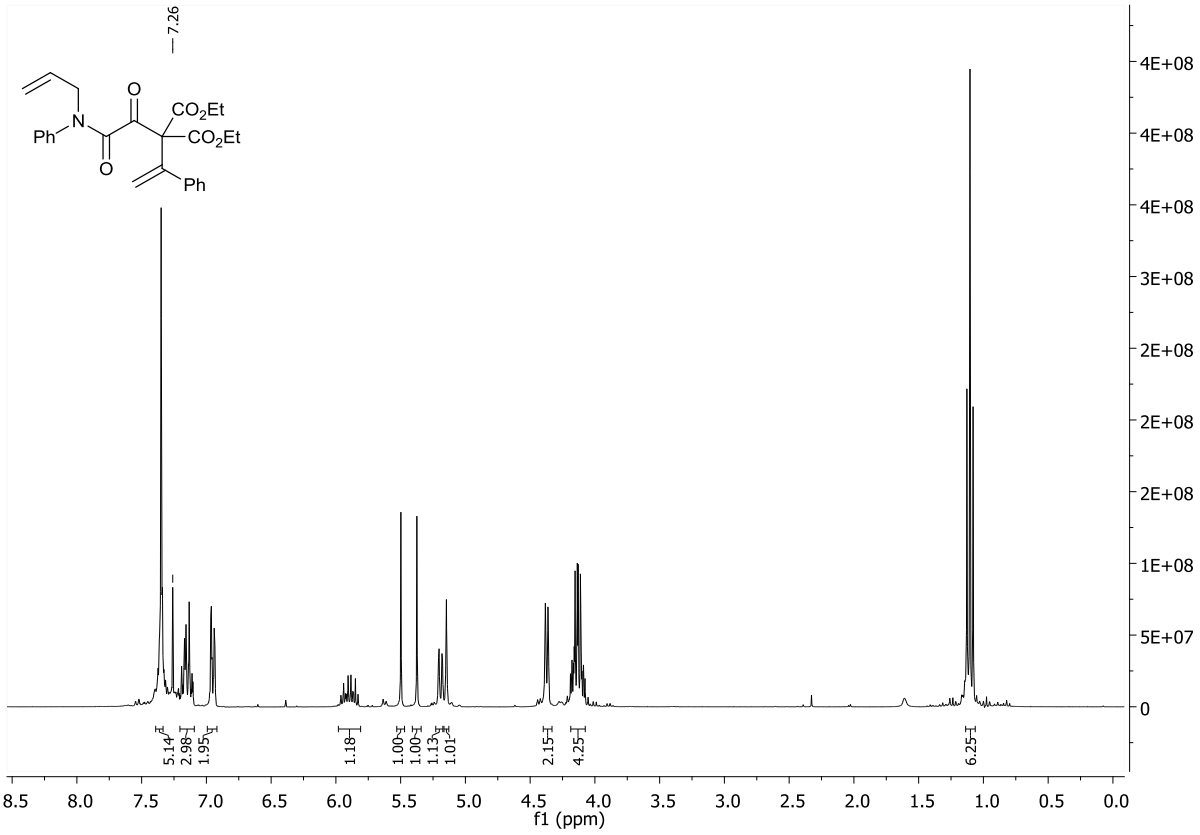
Diethyl 2-(2-(benzyl(methyl)amino)-2-oxoacetyl)-2-(1-phenylvinyl)malonate (10c)

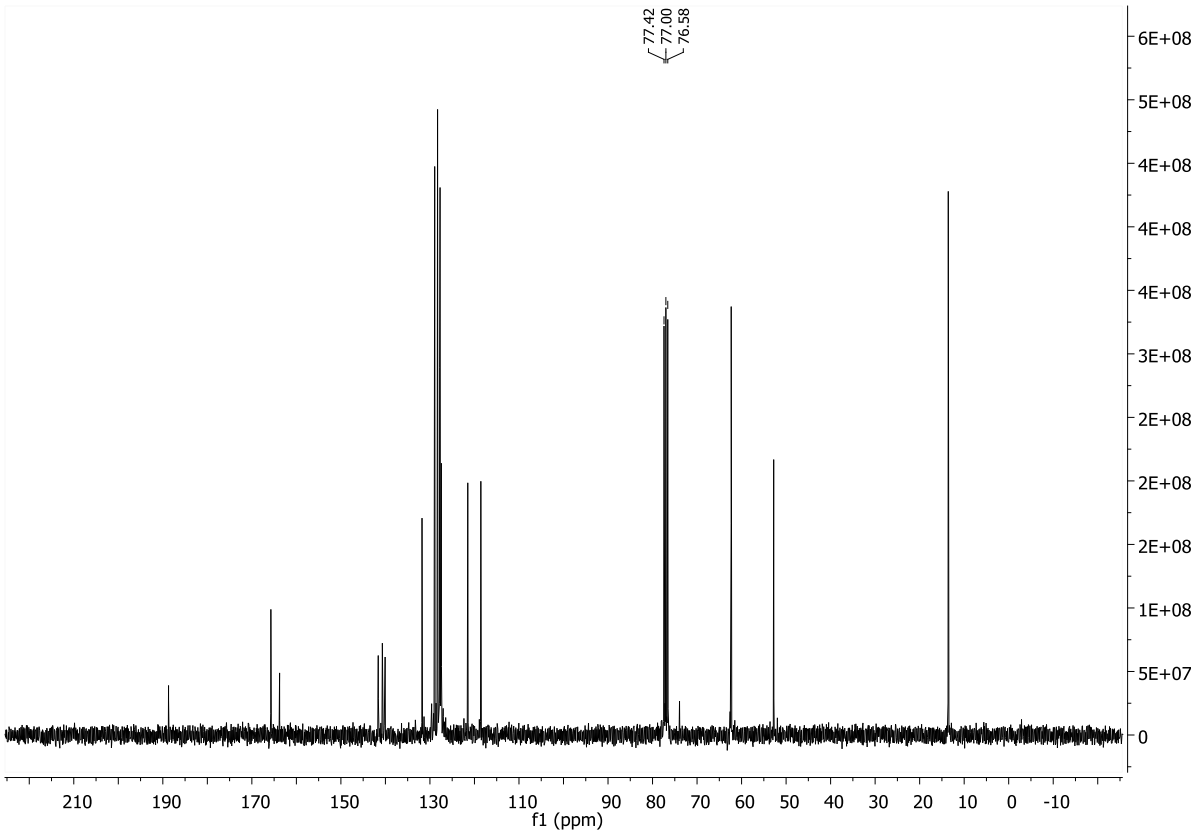


(The spectrum contains both isomers *E*/*Z* = 4:3)



Diethyl 2-(2-(allyl(phenyl)amino)-2-oxoacetyl)-2-(1-phenylvinyl)malonate (10d)





Diethyl 2-(2-(methoxy(methyl)amino)-2-oxoacetyl)-2-(1-phenylvinyl)malonate (10e)