Supporting Information

Visible-light-induced copper-catalyzed oxidative esterification of *α*-azidoketones with diazoacetates: access to *α*-acyloxyacetates

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Experimental section

Materials and methods

All the commercially available reagents and solvents were used for the reaction without further purification. The commercially available diazoacetates were used as starting material and α-azidoketones were synthesized using readily available phenacyl bromides and sodium azides. ^{1}H and ^{13}C NMR spectra were recorded with Bruker Advanced III HD 500 MHz and JEOL JNM-ECZ400R 400 MHz spectrometer using $CDCl_3$ as the solvent. Chemical shifts were reported in parts per million (ppm, δ), using tetramethyl silane (TMS) as an internal standard (0.00 ppm), and coupling constants (J) were reported in hertz (Hz). Carbon chemical shifts were referenced to the carbon signal of the solvent at 77.16 ppm ($CDCl_3$). The progress of reactions was monitored by thin layer chromatography (TLC) performed on silica gel 60 F 254 pre-coated aluminium sheets. TLC was visualized by a 254 nm UV lamp and iodine staining. The reaction mixture was purified by column chromatography (100-200 mesh silica gel) using ethyl acetate/hexane to increase polarity. PerkinElmer FT-IR spectrometer was used to record IR spectra and HRMS data were recorded by electrospray ionization with a quadrupole time-of-flight (Q-TOF) mass analyzer. The melting points were recorded by using the BUCHI melting Point M-560 instrument. The synthesized α-azidoketones were stored below room temperature and in the dark. All the synthesized compounds were characterized by their ^{1}H NMR, ^{13}C NMR, and FT-IR spectra obtained from the central instrumental facility of the institute. They were compared with literature reports in the case of known compounds.

Details of the light source and reaction setup:

Light source: The 7 W blue LEDs,

Manufacturer and model name:

- Brand name: Syska LED™; Model series: SSK-SMR-7W;
- Model name: Rainbow LED smart bulb

Power requirement: AC 230V, 50 Hz

Base: B22

Rated wattage: 7W

Color temperature: 6500K

Lumen: 480 lm

Material of the irradiation vessel: borosilicate glass

Distance from the light source to the irradiation vessel: 10 cm (approx)

Use of filters: none

Safety warning! Handling azides: organic azides are heat-sensitive and can easily decompose with little exposure to energy. *α*-Azidoketones easily decompose with the slightest input of energy. They should be handled with care while evaporating solvents using a rotary evaporator. The water bath temperature should be below 40 °C. All the synthesized *α*-azidoketones should be stored below room temperature and in the dark.

Synthetic Procedures

General experimental procedure for the synthesis of *α*-azidoketones:

All the *α*-azidoketones were synthesized using a known procedure reported in the literature, utilizing phenacyl bromides and sodium azides in acetone under ice bath conditions.[1]

General experimental procedure for the synthesis of *α*-acyloxyacetates *via* oxidative esterification of *α*-azidoketones with diazoacetates (3a-3u):

In a 25 mL round bottom flask, *α*-azidoketones **1a** (1 mmol), diazoacetates **2a** (1 mmol), and DBU (0.2 mmol) were dissolved in DCE (6 mL) and stirred for 2 hours. After 2 hours, $Cu(OAc)_2$ (0.1 mmol) was added to the reaction mixture and then stirred and irradiated with 7 W blue LEDs positioned approximately 10 cm away from the light source. The progress of the reaction was monitored using TLC until the completion of the reaction (12 hours). Next, the organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure to yield a crude product. Then, the crude product was purified by silica-gel (100-200 mesh) column chromatography using ethyl acetate/n-hexane in increasing polarity to yield compounds **3a-3u**.

Experimental procedure for gram-scale synthesis of 2-ethoxy-2-oxoethyl benzoate (3a):

In a 100 mL round bottom flask, 2-azido-1-phenylethan-1-one **1a** (0.967 g, 6 mmol), ethyl 2-diazoacetate **2a** (0.684 g, 5 mmol), and DBU (0.182 g, 1.2 mmol) were dissolved in DCE (36 mL) and stirred for 2 hours. After 2 hours, $Cu(OAc)_2$ (0.119 g, 0.6 mmol) was added to the reaction mixture and then stirred and irradiated with 7 W blue LEDs positioned approximately 10 cm away from the light source. The progress of the reaction was monitored using TLC until the completion of the reaction (24 hours). Next, the organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure to yield a crude product. Then, the crude product was purified by silica-gel (100-200 mesh) column chromatography using ethyl acetate/n-hexane in increasing polarity to yield compound **3a** (1.036 g, 83%).

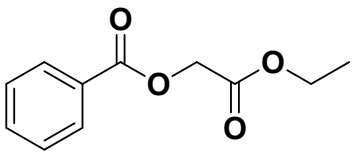
Photograph of the reaction set-up

(a) (b) (c)

Figure 1. Photograph of the reaction set up 0.5 mmol scale reaction (a & b); gram scale (6 mmol) reaction (c).

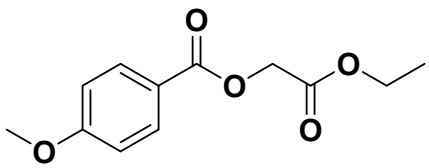
Characterization data of synthesized *α*-acyloxyacetates

2-Ethoxy-2-oxoethyl benzoate (3a)[2]



Prepared following the general procedure; Yield: 179 mg (86%), pale yellow oil, R_f = 0.65 (EtOAc/Hexane = 1:4); IR ($CHCl_3$, cm^{-1}) 2984, 1760, 1728, 1601, 1452, 1422, 1380, 1282, 1209, 1177, 1072, 1037, 804, 711; ^1H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, J = 6.9 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.8 Hz, 2H), 4.85 (s, 2H), 4.26 (q, J = 7.2 Hz, 2H), 1.30 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 168.0, 166.1, 133.6, 130.1, 129.3, 128.6, 61.6, 61.4, 14.3.

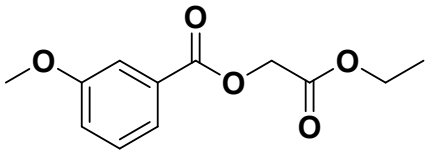
2-Ethoxy-2-oxoethyl 4-methoxybenzoate (3b)[2]



Prepared following the general procedure; Yield: 186 mg (78%), pale yellow oil, R_f = 0.47 (EtOAc/Hexane = 1:4); IR ($CHCl_3$, cm^{-1}) 3423, 2960, 2924, 2854, 1760, 1722, 1607, 1512, 1462, 1378, 1260, 1210, 1167, 1105, 1026, 770; ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.9

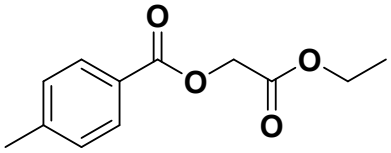
Hz, 2H), 6.92 (d, *J* = 9.0 Hz, 2H), 4.80 (s, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.85 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 168.7, 165.8, 163.9, 132.2, 121.7, 113.4, 61.6, 61.2, 55.6, 14.3.

2-Ethoxy-2-oxoethyl 3-methoxybenzoate (3c)[2]



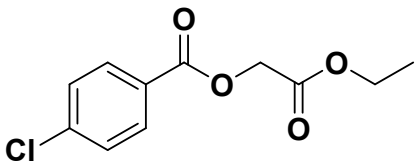
Prepared following the general procedure; Yield: 179 mg (75%) pale yellow oil, R_f = 0.47 (EtOAc/Hexane = 1:4); IR ($CHCl_3$, cm^{-1}) 3424, 2959, 2924, 2853, 1760, 1720, 1605, 1512, 1465, 1378, 1265, 1211, 1160, 1108, 1030, 775; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (dt, *J* = 7.7, 1.2 Hz, 1H), 7.61 (dd, *J* = 2.7, 1.5 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.14 (ddd, *J* = 8.3, 2.7, 1.0 Hz, 1H), 4.84 (s, 2H), 4.26 (q, *J* = 7.2 Hz, 2H), 3.86 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 168.0, 166.0, 159.7, 130.6, 129.7, 122.5, 120.3, 114.3, 61.7, 61.4, 55.6, 14.3.

2-Ethoxy-2-oxoethyl 4-methylbenzoate (3d)[2]



Prepared following the general procedure; Yield: 169 mg (76%), pale yellow oil, R_f = 0.67 (EtOAc/Hexane = 1:4); IR ($CHCl_3$, cm^{-1}) 2924, 2853, 1761, 1726, 1611, 1380, 1281, 1207, 1110, 1036, 753; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 4.82 (s, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 168.1, 166.2, 144.3, 130.1, 129.3, 126.6, 61.6, 61.2, 21.9, 14.3.

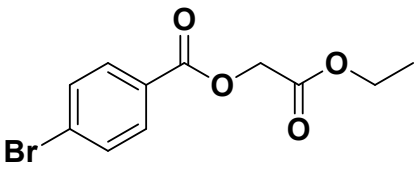
2-Ethoxy-2-oxoethyl 4-chlorobenzoate (3e)[2]



Prepared following the general procedure; Yield: 172 mg (71%), orange oil, R_f = 0.71 (EtOAc/Hexane = 1:4); mp: 40−41 °C. IR ($CHCl_3$, cm^{-1}) 2984, 1927, 1761, 1732, 1596, 1489,

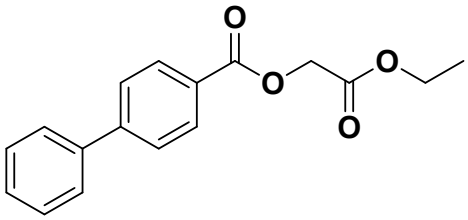
1422, 1402, 1381, 1360, 1288, 1278, 1211, 1173, 1036, 1016, 851, 824, 760, 684; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.7 Hz, 2H), 7.44 (d, *J* = 8.7 Hz, 2H), 4.84 (s, 2H), 4.26 (q, *J* = 7.2 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.8, 165.3, 140.1, 131.5, 129.0, 127.8, 61.7, 61.4, 14.3.

2-Ethoxy-2-oxoethyl 4-bromobenzoate (3f)[2]



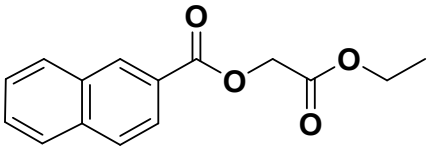
Prepared following the general procedure; Yield: 224 mg (72%), yellow oil, R_f = 0.65 (EtOAc/Hexane = 1:4); IR ($CHCl_3$, cm^{-1}) 2927, 2862, 1760, 1730, 1590, 1484, 1421, 1398, 1275, 1240, 1210, 1119, 1105, 1069, 1035, 847, 756; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.6 Hz, 2H), 7.60 (d, *J* = 8.6 Hz, 2H), 4.83 (s, 2H), 4.26 (q, *J* = 7.2 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.8, 165.4, 132.0, 131.6, 128.8, 128.2, 61.7, 61.5, 14.3.

2-Ethoxy-2-oxoethyl [1,1'-biphenyl]-4-carboxylate (3g)[2]



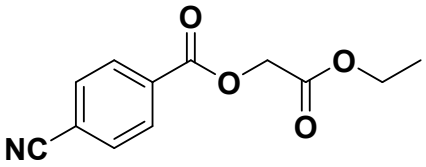
Prepared following the general procedure; Yield: 204 mg (72%), pale yellow solid, R_f = 0.6 (EtOAc/Hexane=1:4); mp: 83−84 °C. IR ($CHCl_3$, cm^{-1}) 2920, 1766, 1727, 1608, 1405, 1286, 1230, 1204, 1125, 1044, 1004, 858, 746; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 7.1 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 4.87 (s, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 168.0, 166.0, 146.3, 140.0, 130.6, 129.1, 128.4, 128.1, 127.4, 127.3, 61.6, 61.4, 14.3.

2-Ethoxy-2-oxoethyl 2-naphthoate (3h)[2]



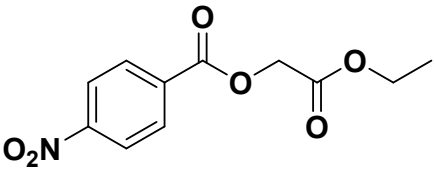
Prepared following the general procedure; Yield: 206 mg (80%), pale yellow oil, R_f = 0.60 (EtOAc/Hexane = 1:4); IR ($CHCl_3$, cm^{-1}) 2925, 1768, 1730, 1608, 1408, 1285, 1220, 1205, 1114, 1036, 1008, 857, 755; ^1H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 8.10 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.97 (d, *J* = 8.6 Hz, 1H), 7.92 – 7.86 (m, 2H), 7.65 – 7.51 (m, 2H), 4.91 (s, 2H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 168.1, 166.3, 135.9, 132.6, 131.8, 129.6, 128.6, 128.4, 127.9, 126.9, 126.6, 125.4, 61.7, 61.5, 14.3.

2-Ethoxy-2-oxoethyl 4-cyanobenzoate (3i)



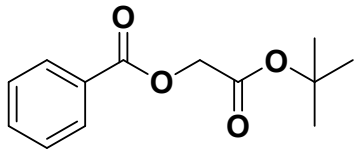
Prepared following the general procedure; Yield: 179.4 mg (77%), Pale yellow solid, R_f = 0.5 (EtOAc/Hexane = 1:4); mp: 87−88 °C. IR ($CHCl_3$, cm^{-1}) 3449, 2924, 2855, 2231, 1731, 1379, 1281, 1210, 1107, 1033, 860, 766; ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.7 Hz, 2H), 7.77 (d, *J* = 8.7 Hz, 2H), 4.88 (s, 2H), 4.27 (q, *J* = 7.2 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 205.8, 167.4, 164.5, 133.2, 132.4, 130.6, 118.0, 117.0, 61.9, 61.8, 14.3. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{12}H_{11}NO_4Na$ 256.0581; Found = 256.0585.

2-Ethoxy-2-oxoethyl 4-nitrobenzoate (3j)[2]



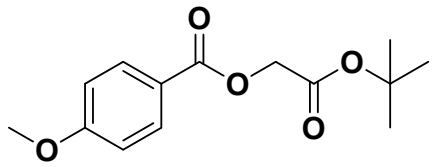
Prepared following the general procedure; Yield: 177 mg (70%), Pale yellow oil, R_f = 0.45 (EtOAc/Hexane = 1:4); IR ($CHCl_3$, cm^{-1}) 3424, 2925, 1758, 1732, 1526, 1380, 1346, 1280, 1207, 1103, 1033, 855, 772, 715; ^1H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 9.1 Hz, 2H), 8.27 (d, *J* = 9.1 Hz, 2H), 4.89 (s, 2H), 4.28 (q, *J* = 7.2 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 167.4, 164.3, 151.0, 134.7, 131.2, 123.8, 61.92, 61.85, 14.3.

2-(*tert*-Butoxy)-2-oxoethyl benzoate (3k)[3]



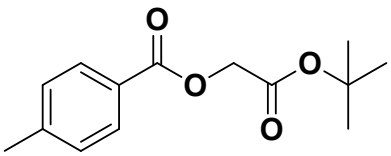
Prepared following the general procedure; Yield: 165 mg (71%), yellow oil, R_f = 0.75 (EtOAc/Hexane = 1:4); IR ($CHCl_3$, cm^{-1}) 3449, 2924, 2855, 2231, 1731, 1379, 1281, 1210, 1107, 1033, 860, 766; ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.06 (m, 2H), 7.62 – 7.54 (m, 1H), 7.49 – 7.41 (m, 2H), 4.74 (s, 2H), 1.49 (s, 9H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 165.9, 165.0, 132.3, 128.9, 128.3, 127.4, 81.5, 60.6, 27.0.

2-(*tert*-Butoxy)-2-oxoethyl 4-methoxybenzoate (3l)



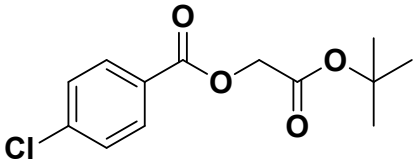
Prepared following the general procedure; Yield: 199 mg (75%), pale yellow oil, R_f = 0.57 (EtOAc/Hexane = 1:4); IR ($CHCl_3$, cm^{-1}) 2937, 2937, 2842, 1753, 1722, 1607, 1581, 1512, 1458, 1422, 1369, 1317, 1260, 1230, 1160, 1116, 1031, 948, 848, 770, 695, 617; ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 9.0 Hz, 2H), 6.92 (d, J = 8.9 Hz, 2H), 4.71 (s, 2H), 3.86 (s, 3H), 1.48 (s, 9H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 167.3, 165.8, 163.8, 132.1, 121.9, 113.8, 82.5, 61.6, 55.6, 28.2. HRMS (ESI) *m/z*: $[M + K]^+$ Calcd for $C_{14}H_{18}O_5K$ 305.0786; Found = 305.0787.

2-(*tert*-Butoxy)-2-oxoethyl 4-methylbenzoate (3m)



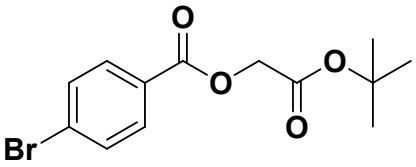
Prepared following the general procedure; Yield: 199 mg (78%), pale yellow oil, R_f = 0.77 (EtOAc/Hexane = 1:4); IR ($CHCl_3$, cm^{-1}) 2979, 1755, 1727, 1613, 1422, 1369, 1282, 1229, 1160, 1110, 1027, 844, 753; ^1H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 7.9 Hz, 2H), 4.72 (s, 2H), 2.41 (s, 3H), 1.49 (s, 9H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 167.2, 166.2, 144.2, 130.1, 129.3, 126.8, 82.6, 61.6, 28.2, 21.9. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{19}O_4$ 251.1278; Found = 251.1279.

2-(*tert*-Butoxy)-2-oxoethyl 4-chlorobenzoate (3n)[4]



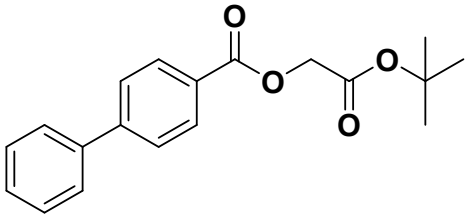
Prepared following the general procedure; Yield: 189 mg (70%), yellow oil, R_f = 0.82 (EtOAc/Hexane = 1:4); IR ($CHCl_3$, cm^{-1}) 2979, 1755, 1731, 1596, 1489, 1422, 1396, 1268, 1229, 1159, 1118, 1092, 1017, 849, 761; ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.7 Hz, 2H), 7.43 (d, *J* = 8.7 Hz, 2H), 4.73 (s, 2H), 1.49 (s, 9H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 166.9, 165.3, 140.0, 131.4, 129.0, 128.0, 82.8, 61.9, 28.2.

2-(*tert*-Butoxy)-2-oxoethyl 4-bromobenzoate (3o)



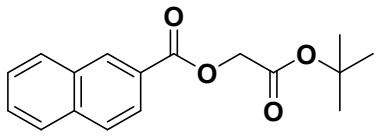
Prepared following the general procedure; Yield: 219 mg (70%), yellow oil, R_f = 0.77 (EtOAc/Hexane = 1:4); IR ($CHCl_3$, cm^{-1}) 2979, 1754, 1732, 1591, 1484, 1421, 1369, 1267, 1229, 1160, 1117, 1104, 1069, 1009, 847, 757; ^1H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.7 Hz, 2H), 7.60 (d, *J* = 8.8 Hz, 2H), 4.74 (s, 2H), 1.49 (s, 9H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 166.8, 165.4, 131.9, 131.5, 128.7, 128.4, 82.8, 61.9, 28.2. HRMS (ESI) *m/z*: $[M + K]^+$ Calcd for $C_{13}H_{15}O_4BrK$ 352.9786; Found = 352.9790.

2-(*tert*-Butoxy)-2-oxoethyl [1,1'-biphenyl]-4-carboxylate (3p)



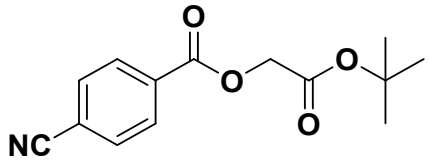
Prepared following the general procedure; Yield: 228 mg (73%), pale pink solid, R_f = 0.77 (EtOAc/Hexane=1:4); mp: 99−101°C. IR ($CHCl_3$,cm^{-1}) 3058, 2985, 1743, 1718, 1608, 1485, 1450, 1416, 1370, 1286, 1235, 1162, 1115, 1007, 916, 856, 751, 696; ^1H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 6.8 Hz, 2H), 7.68 (d, *J* = 6.7 Hz, 2H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 6.7 Hz, 2H), 7.40 (t, *J* = 6.7 Hz, 1H), 4.77 (s, 2H), 1.50 (s, 9H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 167.1, 166.0, 146.2, 140.1, 130.6, 129.1, 128.34, 128.26, 127.5, 127.3, 82.7, 61.8, 28.2. HRMS (ESI) *m/z*: $[M + K]^+$ Calcd for $C_{19}H_{20}O_4K$ 351.0994; Found = 351.0996.

2-(*tert*-Butoxy)-2-oxoethyl 2-naphthoate (3q)



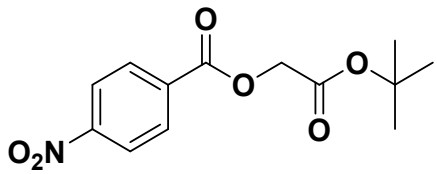
Prepared following the general procedure; Yield: 208.7 mg, (73%), pale yellow solid, R_f = 0.5 (EtOAc/Hexane = 1:20); mp: 110−111 °C. IR ($CHCl_3$, cm^{-1}) 3068, 2987, 1740, 1728, 1608, 1489, 1455, 1416, 1378, 1289, 1227, 1168, 1110, 1020, 930, 856, 755; ^1H NMR (500 MHz, $CDCl_3$) δ 8.69 (s, 1H), 8.11 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.93 – 7.86 (m, 2H), 7.64 – 7.57 (m, 1H), 7.59 – 7.52 (m, 1H), 4.81 (s, 2H), 1.51 (s, 9H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 167.1, 166.3, 135.9, 132.6, 131.7, 129.6, 128.6, 128.4, 127.9, 126.83, 126.75, 125.5, 82.7, 61.9, 28.2. HRMS (ESI) *m/z*: $[M + K]^+$ Calcd for $C_{17}H_{18}O_4K$ 325.0837; Found = 325.0839.

2-(*tert*-Butoxy)-2-oxoethyl 4-cyanobenzoate (3r)



Prepared following the general procedure; Yield: 182 mg (70%), white solid, R_f = 0.6 (EtOAc/Hexane = 1:4); mp: 73−74 °C. IR ($CHCl_3$, cm^{-1}) 2981, 2230, 1739, 1367, 1287, 1230, 1158, 1121, 1022, 856, 765; ^1H NMR (500 MHz, Chloroform-*d*) δ 8.19 (d, *J* = 8.7 Hz, 2H), 7.76 (d, *J* = 8.7 Hz, 2H), 4.77 (s, 2H), 1.49 (s, 9H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 166.5, 164.5, 133.3, 132.4, 130.5, 118.1, 116.9, 83.1, 62.2, 28.2. HRMS (ESI) *m/z*: $[M + K]^+$ Calcd for $C_{14}H_{15}NO_4K$ 300.0633; Found = 300.0625.

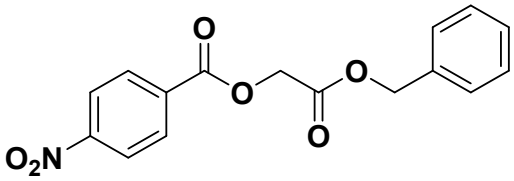
2-(*tert*-Butoxy)-2-oxoethyl 4-nitrobenzoate (3s)



Prepared following the general procedure; Yield: 200 mg (71%), pale yellow solid, R_f = 0.7 (EtOAc/Hexane = 1:4); mp: 87−88 °C. IR ($CHCl_3$, cm^{-1}) 3448, 2980, 1735, 1608, 1530, 1423, 1369, 1349, 1231, 1159, 1119, 1017, 857, 784, 741, 717; ^1H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 9.1 Hz, 2H), 8.27 (d, *J* = 9.2 Hz, 2H), 4.79 (s, 2H), 1.50 (s, 9H). $^{13}C\{^1H\}$ NMR (126

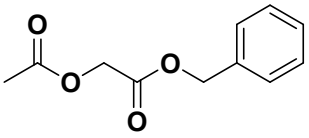
MHz, $CDCl_3$) δ 166.4, 164.3, 150.9, 134.9, 131.2, 123.8, 83.2, 62.2, 28.2. HRMS (ESI) *m/z*: $[M + K]^+$ Calcd for $C_{13}H_{15}NO_6K$ 320.0531; Found = 320.0533.

2-(Benzyloxy)-2-oxoethyl 4-nitrobenzoate (3t)



Prepared following the general procedure; Yield: 220 mg (70%), white solid, R_f = 0.55 (EtOAc/Hexane = 1:4); mp: 87−90 °C. IR ($CHCl_3$, cm^{-1}) 3034, 2958, 1953, 1720, 1607, 1527, 1497, 1420, 1347, 1270, 1151, 1101; ^1H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 9.1 Hz, 2H), 8.27 (d, *J* = 9.1 Hz, 2H), 7.43 – 7.31 (m, 5H), 5.24 (s, 2H), 4.94 (s, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 167.3, 164.3, 151.0, 135.0, 134.6, 131.2, 130.0, 128.8, 128.6, 123.8, 67.6, 61.8. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{16}H_{13}NO_6Na$ 338.0636; Found = 338.0638.

Benzyl 2-acetoxyacetate (3u)[6]

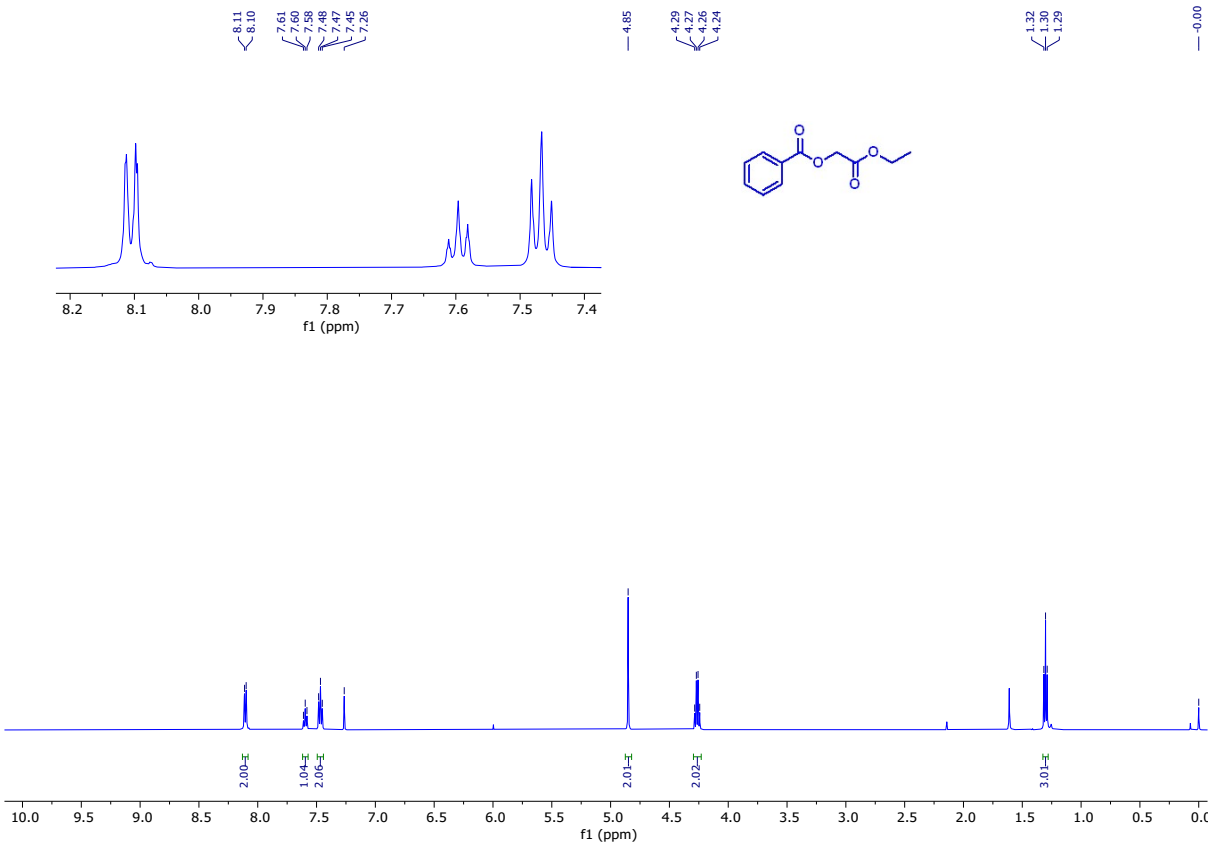


Prepared following the general procedure; Yield: 31.2 mg (15%), pale yellow oil, R_f = 0.68 (EtOAc/Hexane = 1:4); IR ($CHCl_3$, cm^{-1}) 2957, 1748, 1498, 1393, 1372, 1189, 1080, 1001, 842, 736; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.29 (m, 5H), 5.20 (s, 2H), 4.65 (s, 2H), 2.16 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 170.4, 167.8, 135.2, 128.8, 128.7, 128.5, 67.2, 60.8, 20.6. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{13}O_4$ 209.0809; Found = 209.0810.

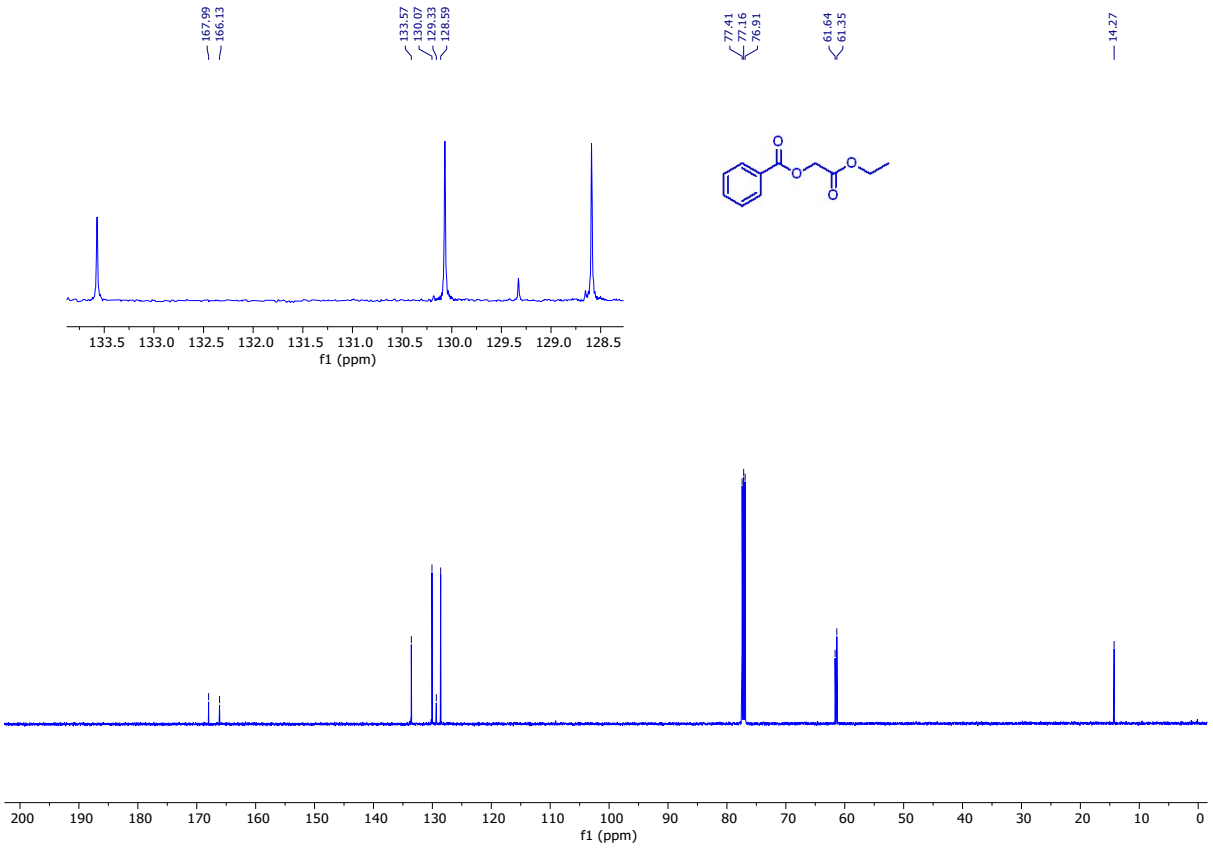
Supplementary References

1. R. A. Maurya, P. R. Adiyala, D. Chandraskhar, C. N. Reddy, J. S. Kapure and A. Kamal, *ACS Comb. Sci.*, 2014, **16**, 466-477.
2. L. Ju, C. Ma, M. Tang, Y. Wang, X. Yu and H. Ma, *Chin. J. Org. Chem.,* 2018, **38**, 3056–3062.
3. Y. Wang, H. Cui, L. Zhang and C.-Y. Su, *ChemCatChem.,* 2018, **10**, 3901 – 3906.
4. A. Bhowmick, P. K. Warghude, P. D. Dharpure and R. G. Bhat, *Org. Chem. Front.*, 2021, **8**, 4777–4784.
5. M. S. H. Salem, C. Dubois, Y. Takamura, A. Kitajima, T. Kawai, S. Takizawa, and M. Kirihara, *Green Chem.,* 2024, **26**, 375–383.
6. R. Nolla-Saltiel, U. A. Carrillo-Arcos, and S. Porcel, *Synthesis.*, 2014, **46**, 165–169.

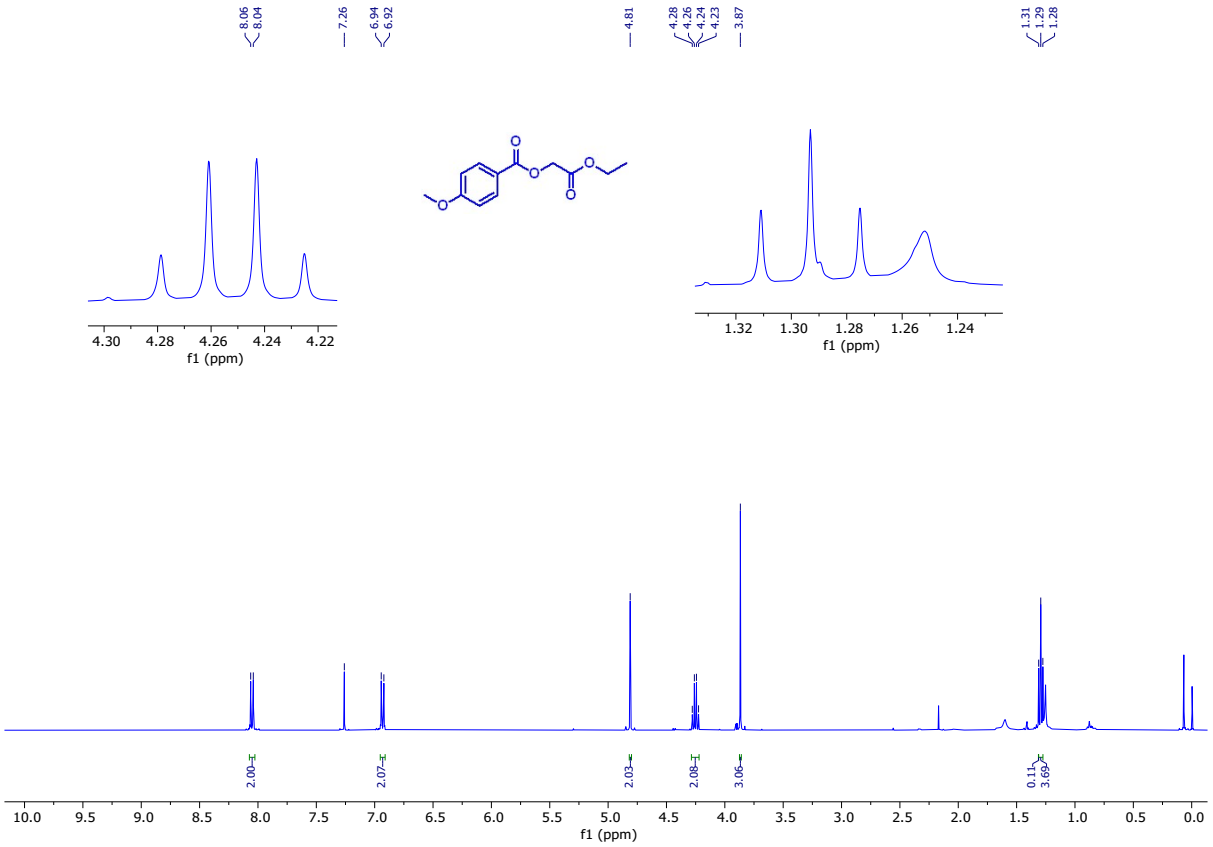
^{1}H NMR spectrum of 3a (500 MHz, $CDCl_3$)



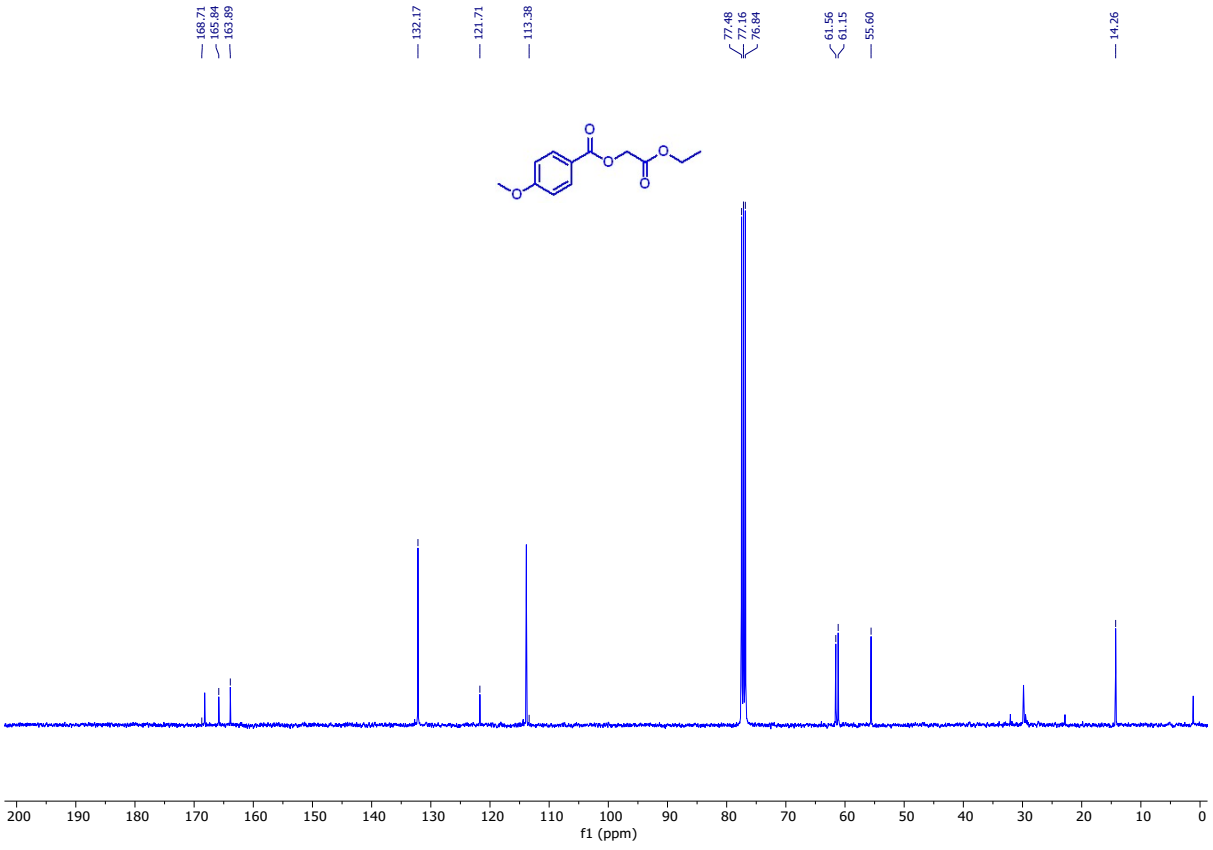
^{13}C{^{1}H} NMR spectrum of 3a (126 MHz, $CDCl_3$)



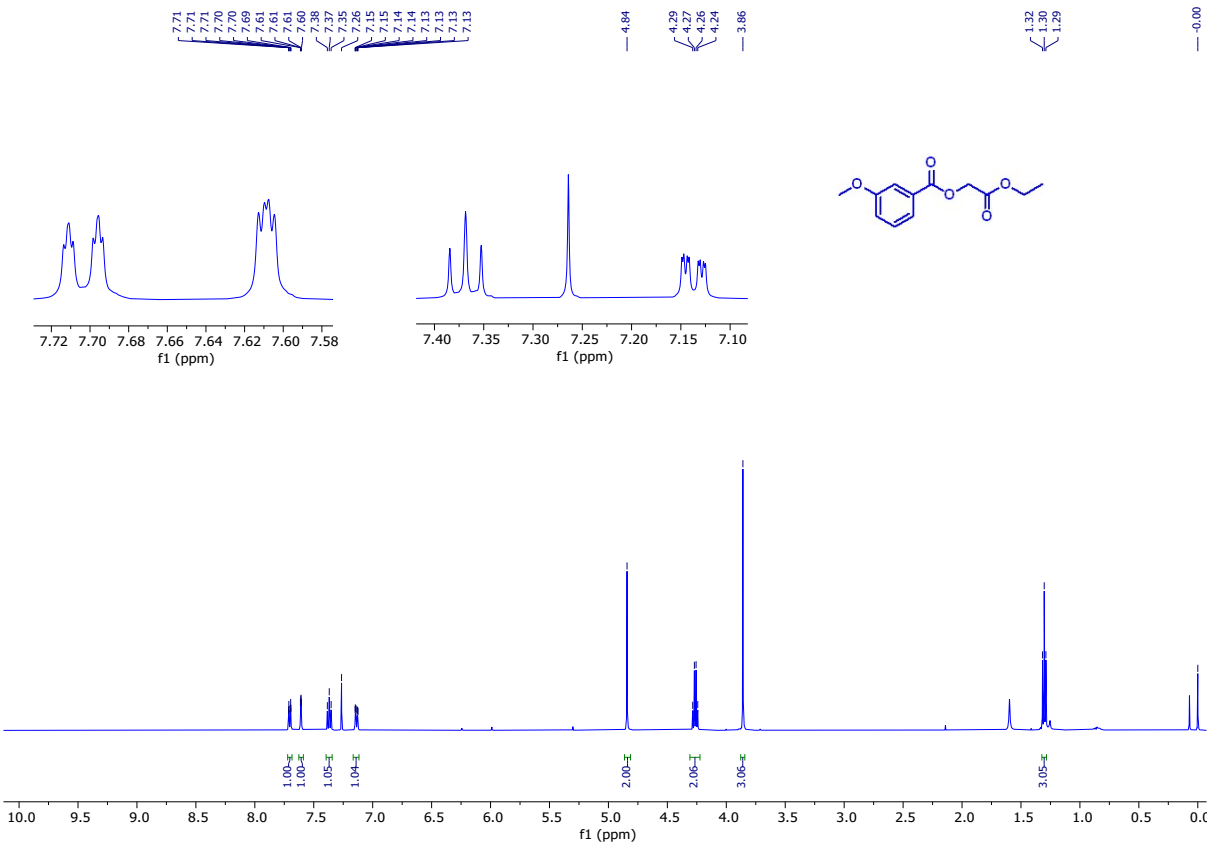
^{1}H NMR spectrum of 3b (400 MHz, $CDCl_3$)



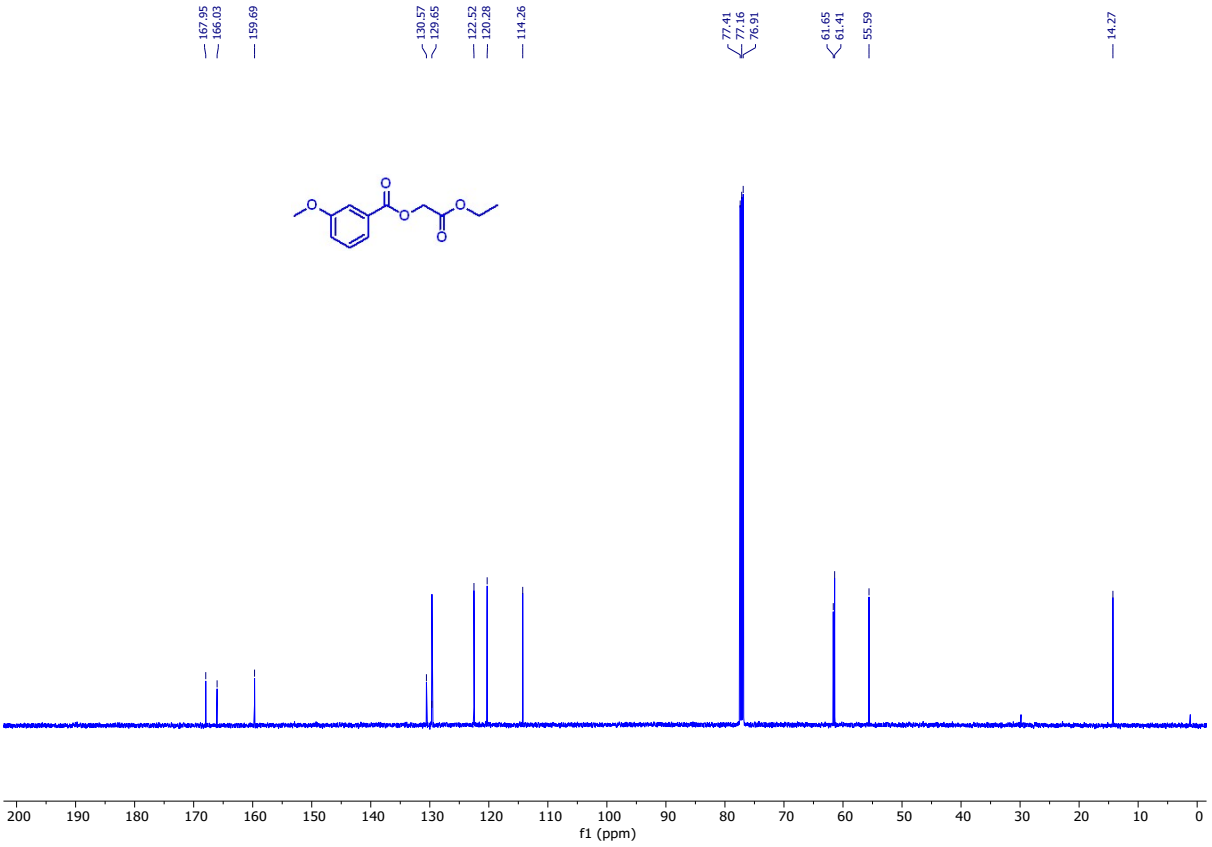
^{13}C{^{1}H} NMR spectrum of 3b (126 MHz, $CDCl_3$)



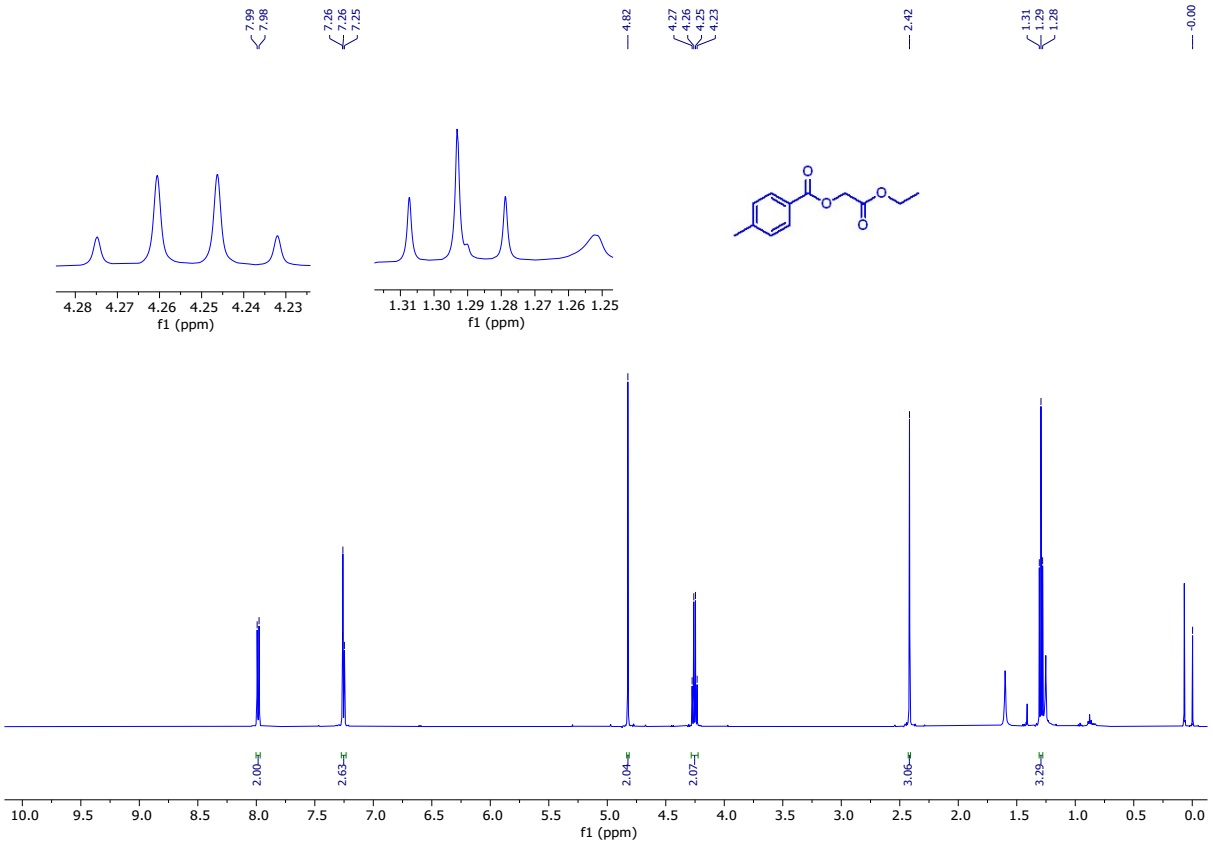
^{1}H NMR spectrum of 3c (400 MHz, $CDCl_3$)



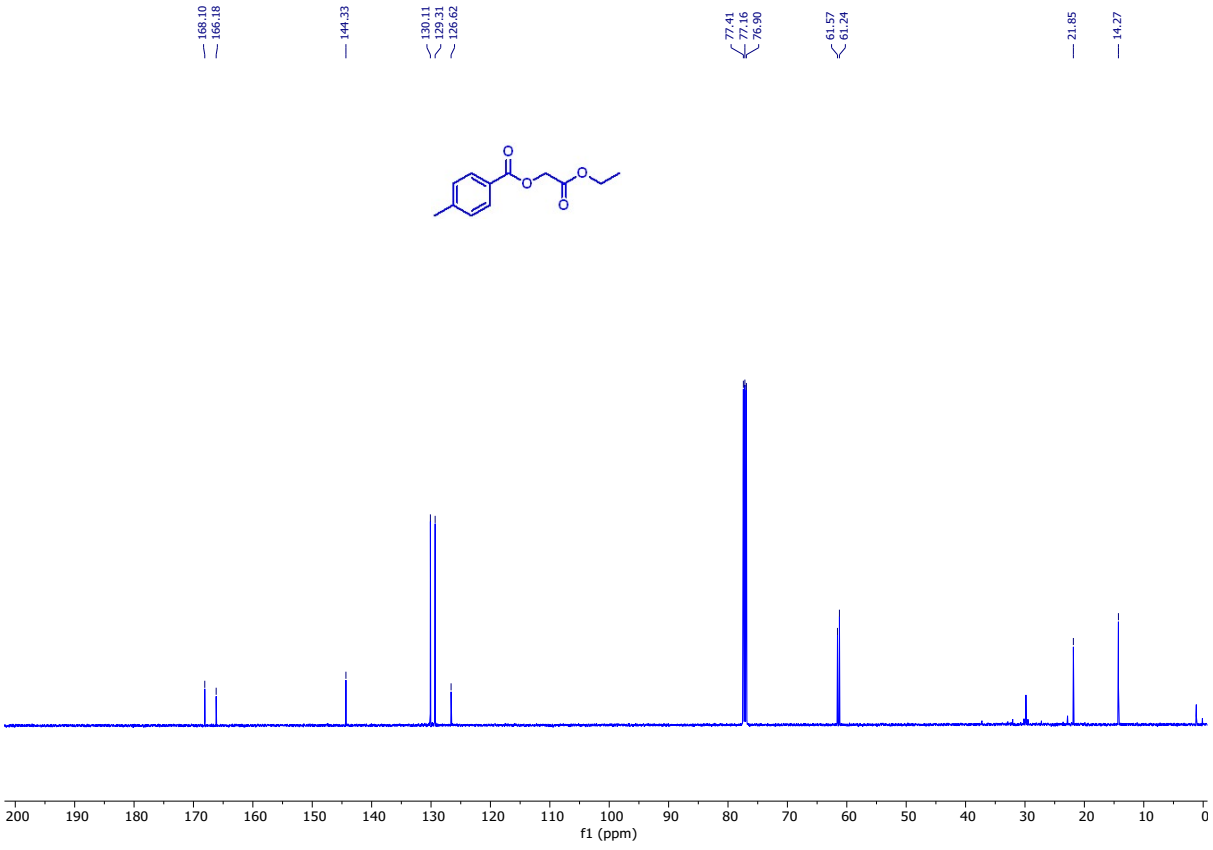
^{13}C{^{1}H} NMR spectrum of 3c (126 MHz, $CDCl_3$)



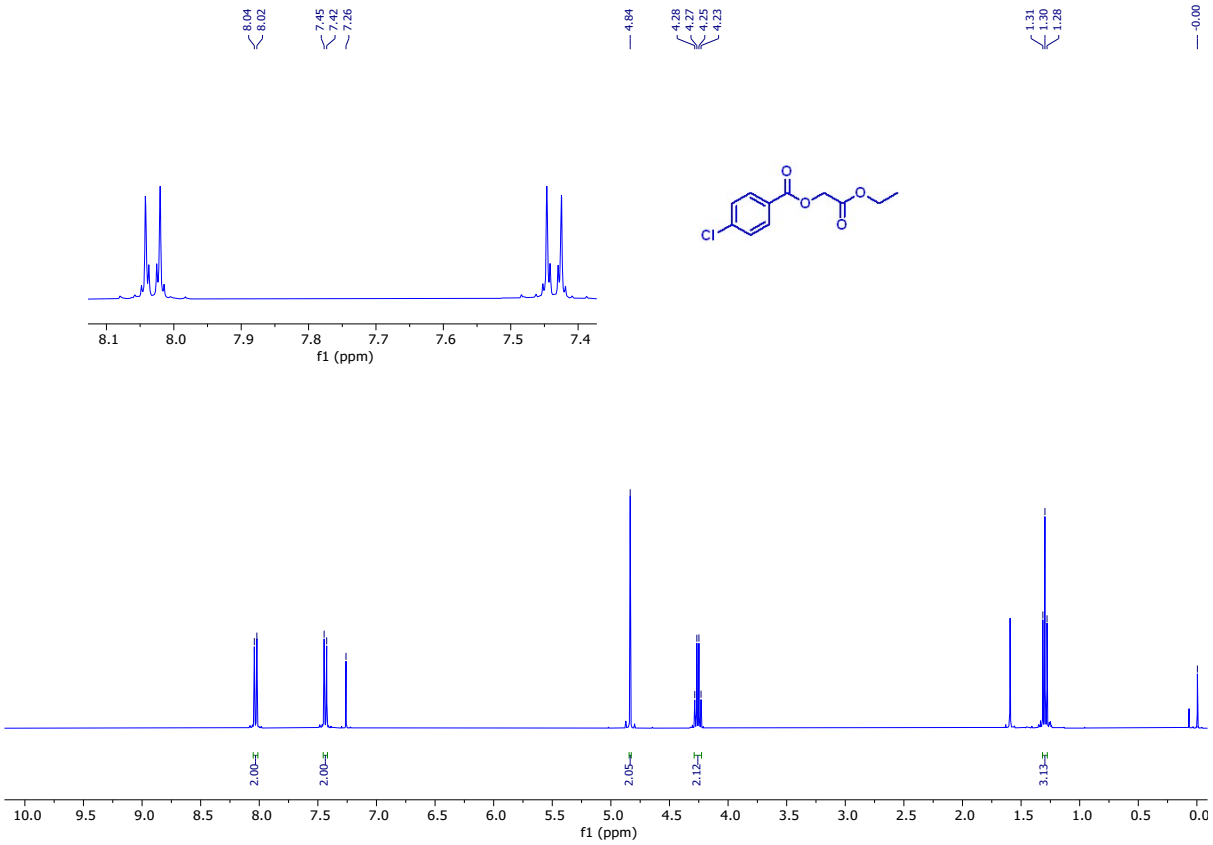
^{1}H NMR spectrum of 3d (500 MHz, $CDCl_3$)



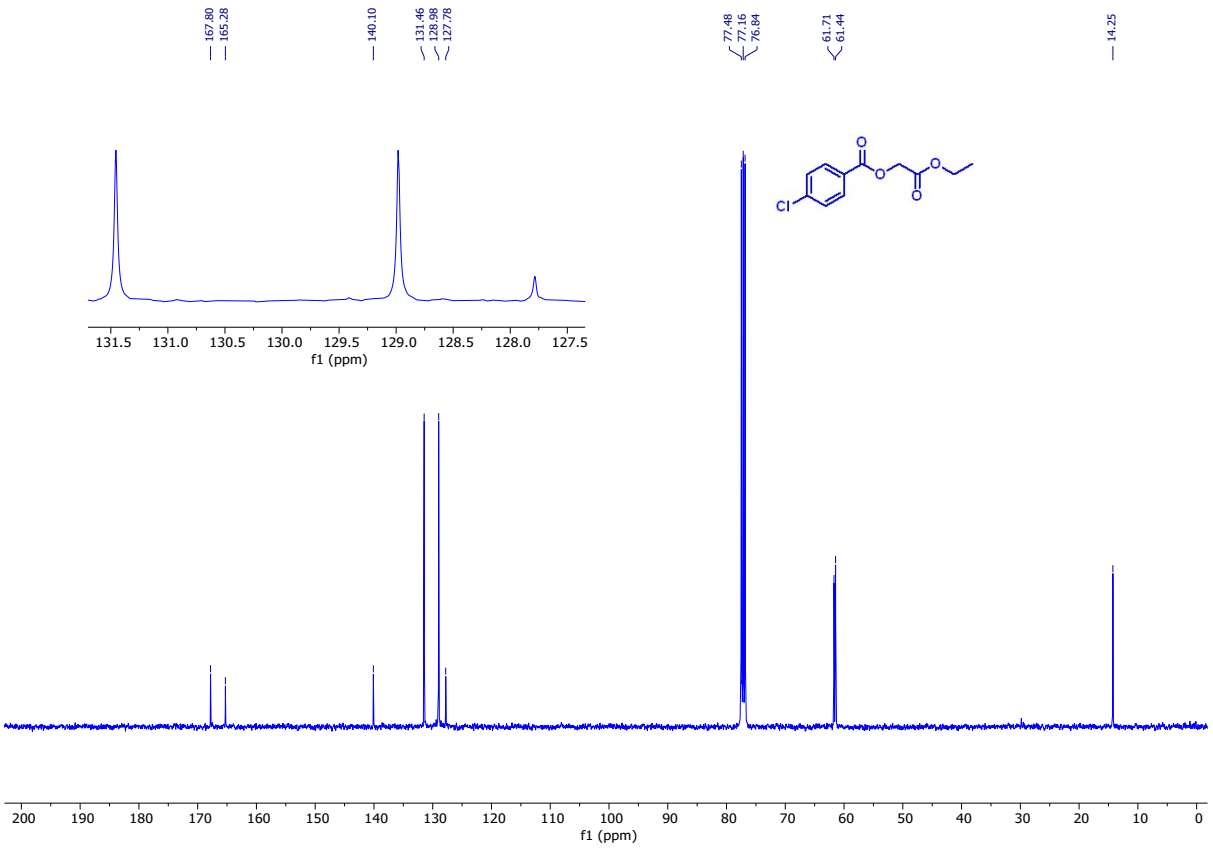
^{13}C{^{1}H} NMR spectrum of 3d (126 MHz, $CDCl_3$)



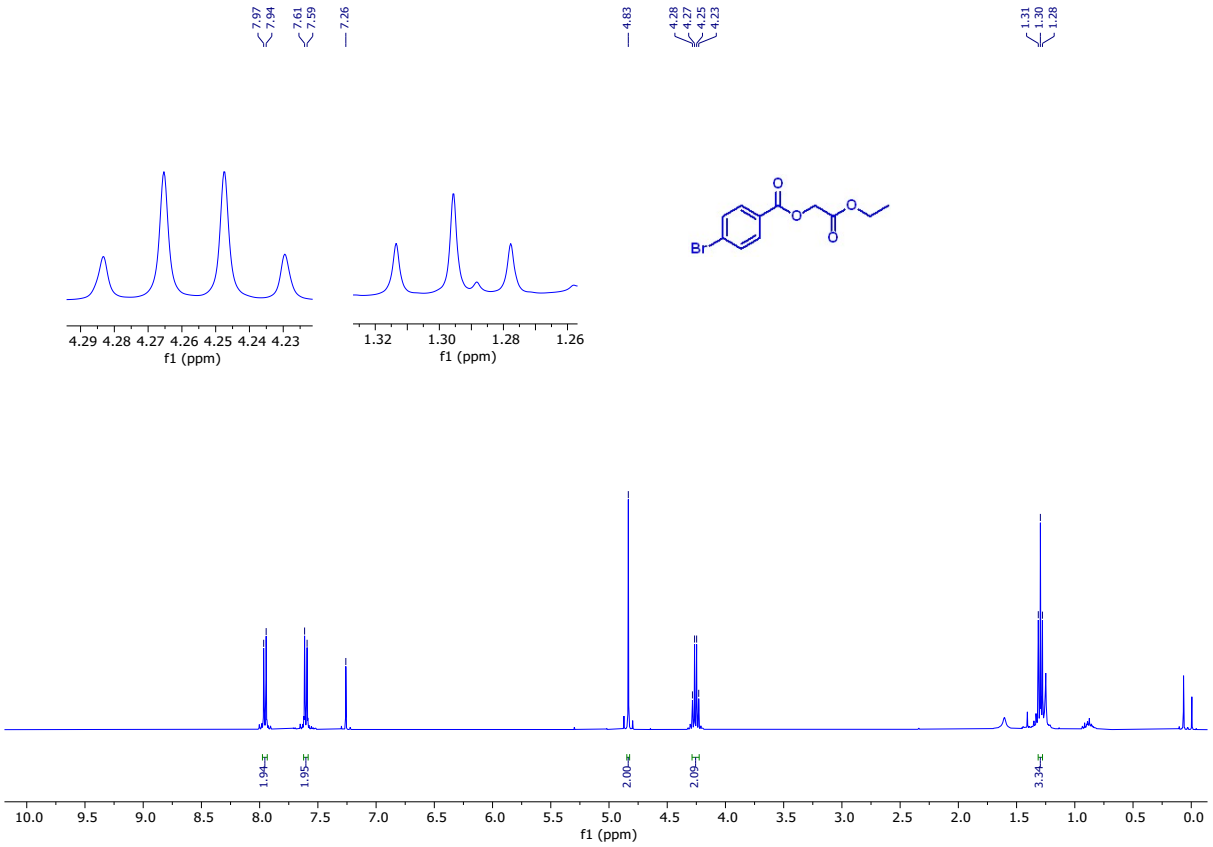
^{1}H NMR spectrum of 3e (400 MHz, $CDCl_3$)



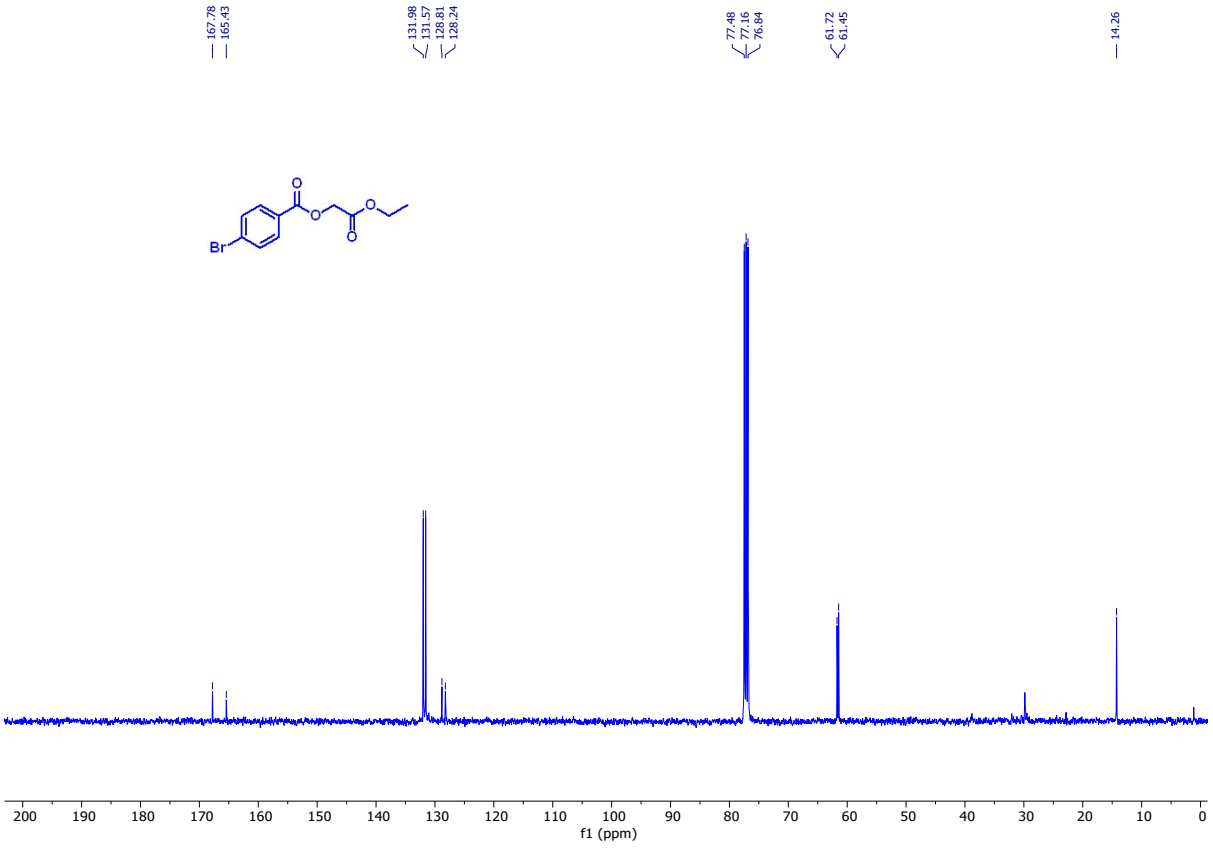
$^{13}C\{^{1}H\}$ NMR spectrum of 3e (101 MHz, $CDCl_3$)



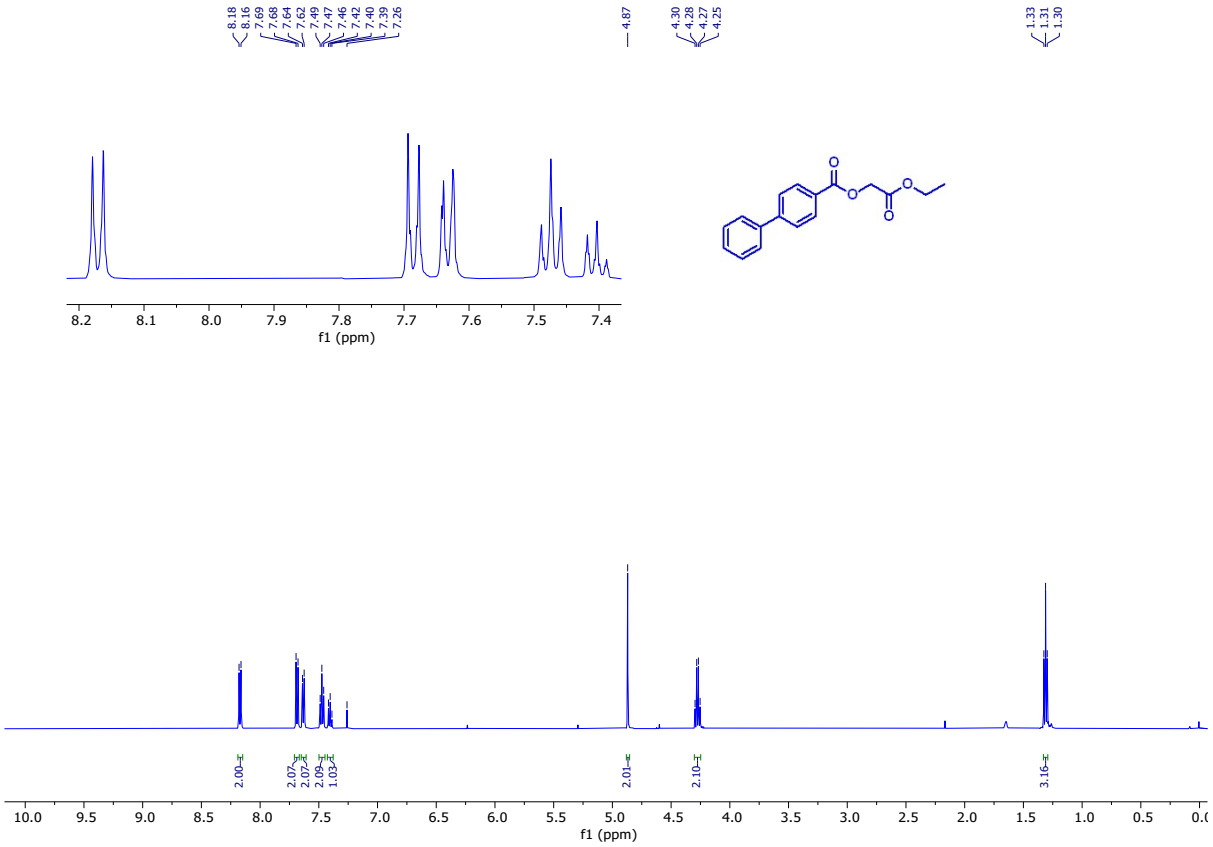
^{1}H NMR spectrum of 3f (400 MHz, $CDCl_3$)



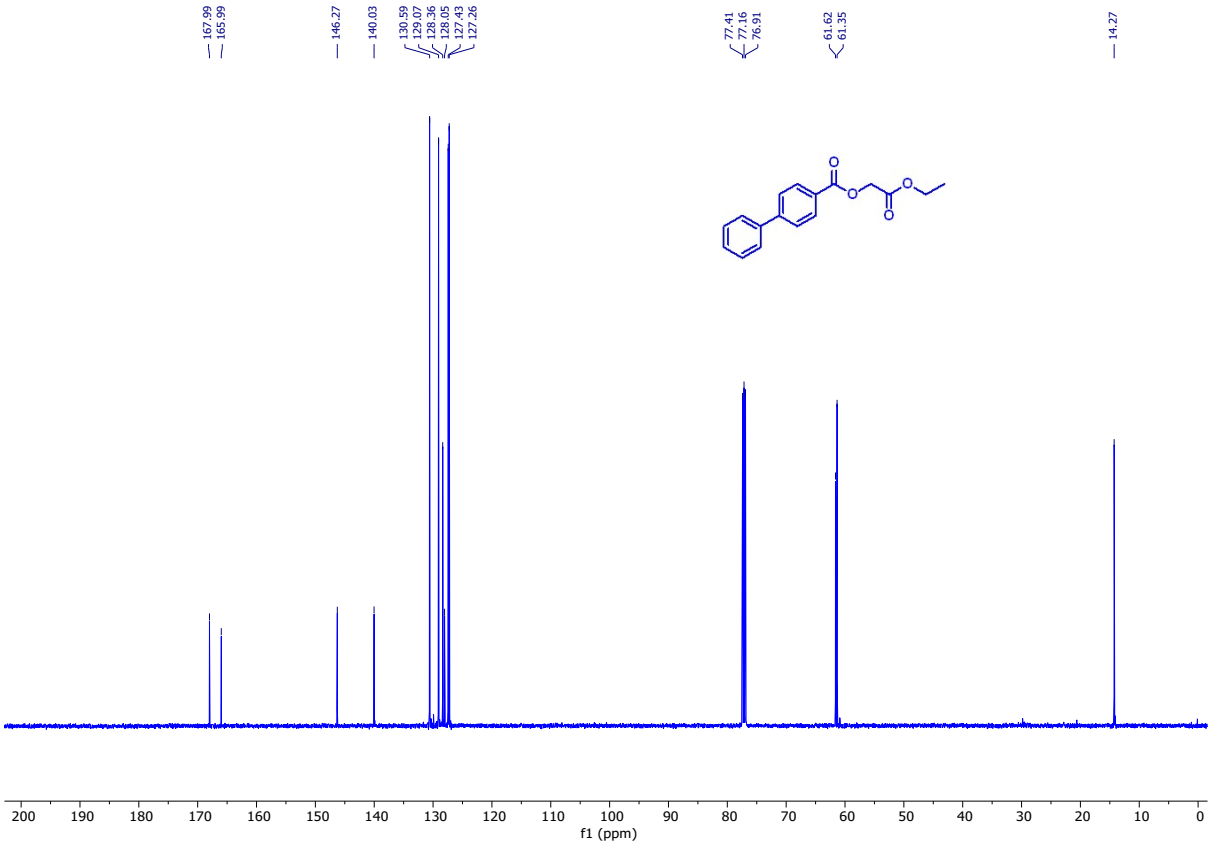
^{13}C{^{1}H} NMR spectrum of 3f (101 MHz, $CDCl_3$)



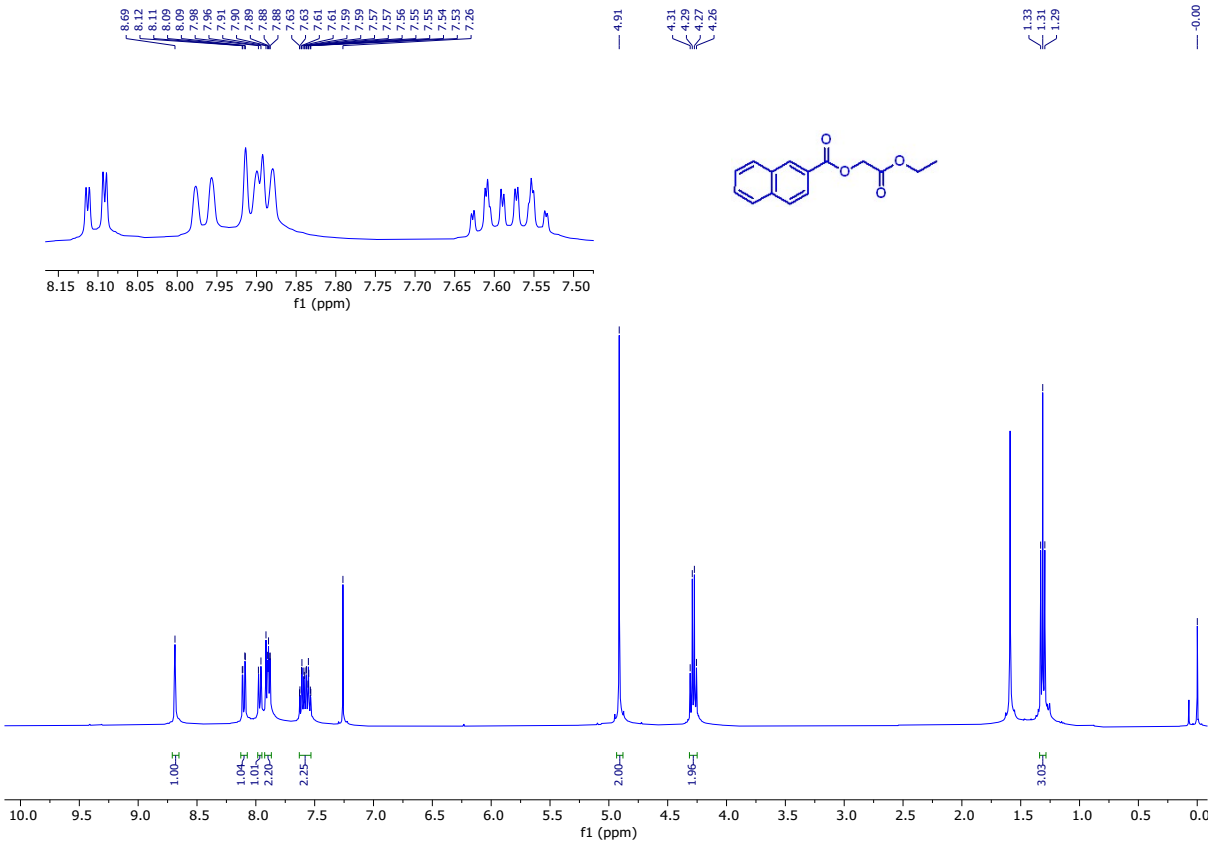
^{1}H NMR spectrum of 3g (500 MHz, $CDCl_3$)



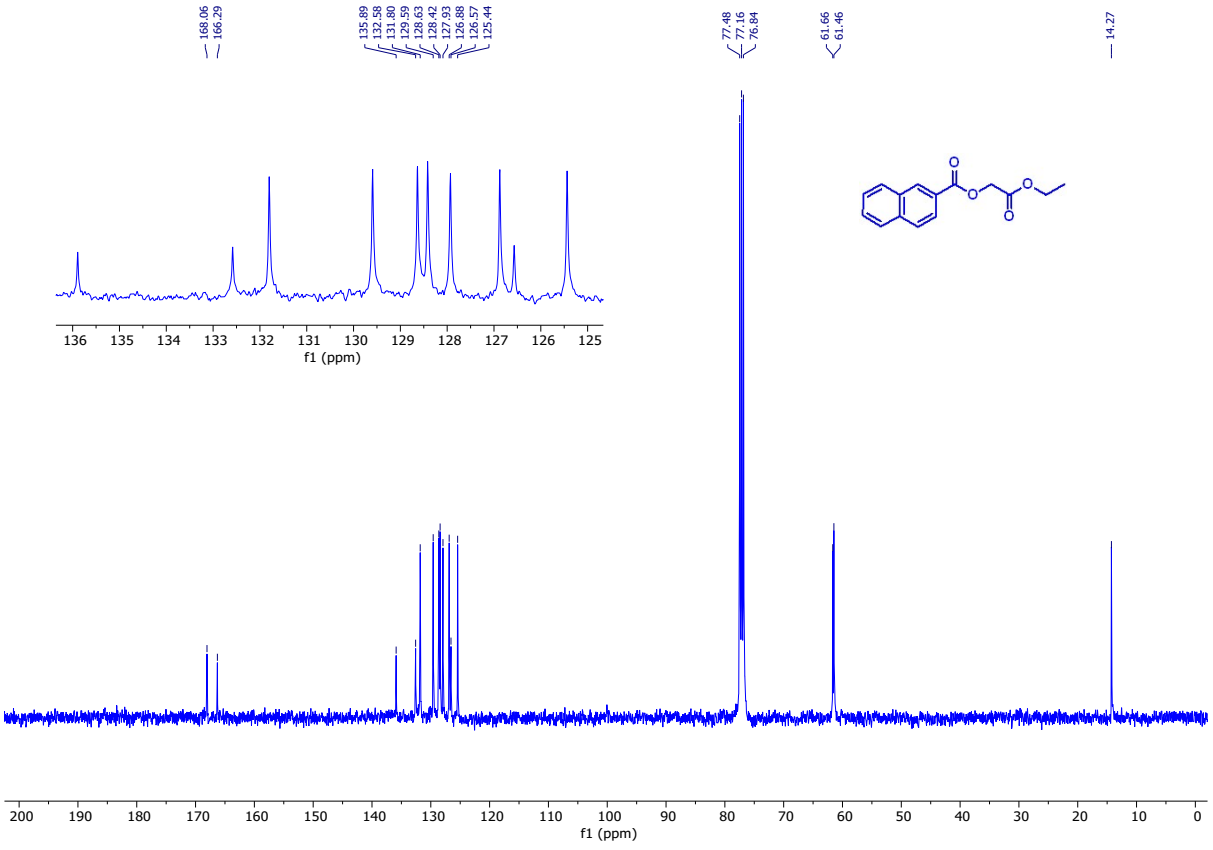
^{13}C{^{1}H} spectrum of 3g (126 MHz, $CDCl_3$)



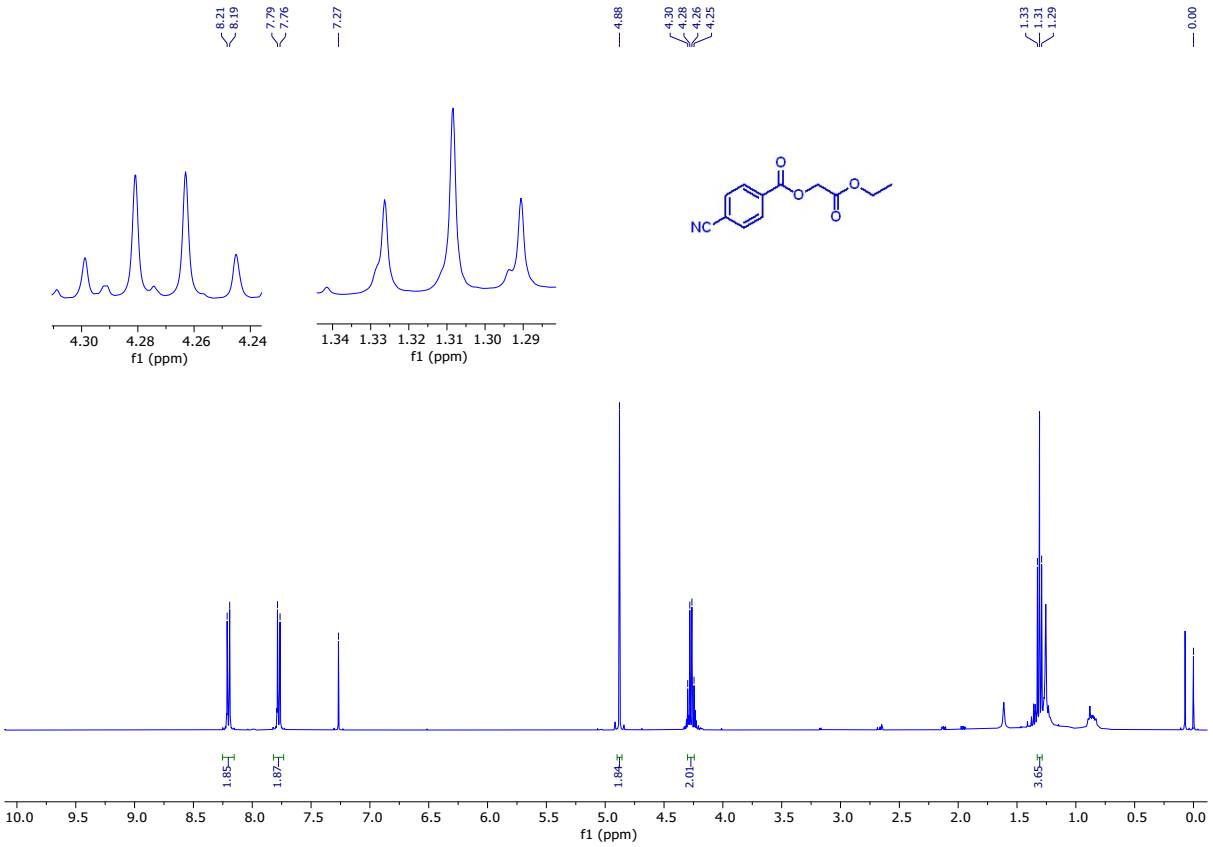
^{1}H NMR spectrum of 3h (400 MHz, $CDCl_3$)



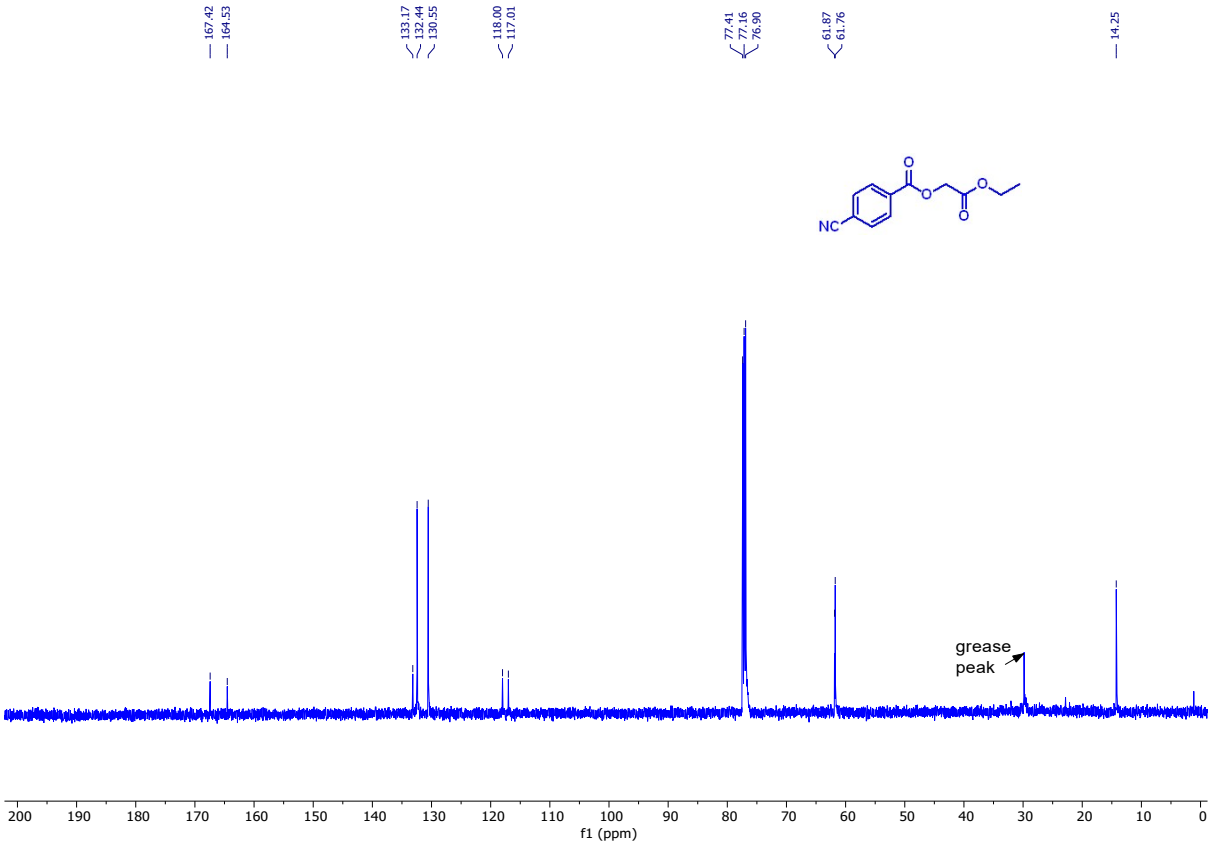
^{13}C{^{1}H} NMR spectrum of 3h (101 MHz, $CDCl_3$)



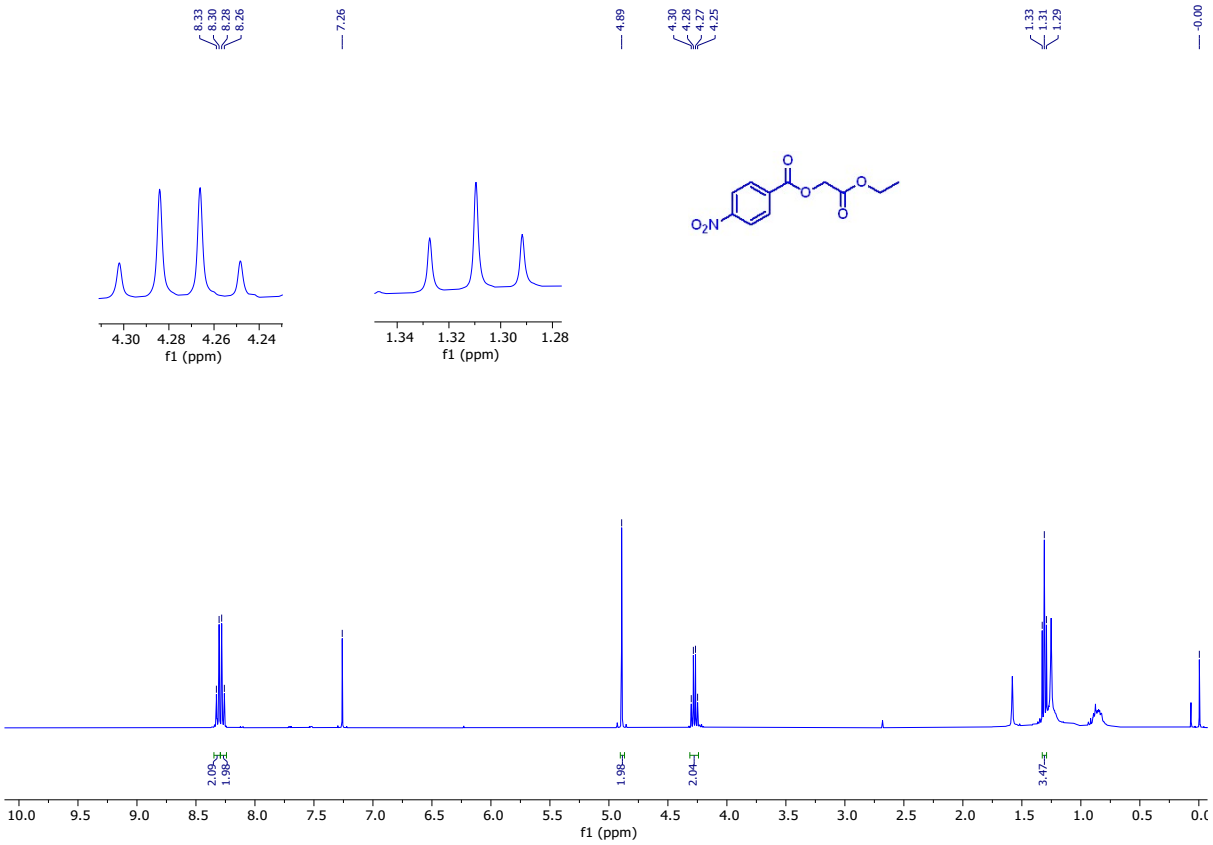
^{1}H NMR spectrum of 3i (400 MHz, $CDCl_3$)



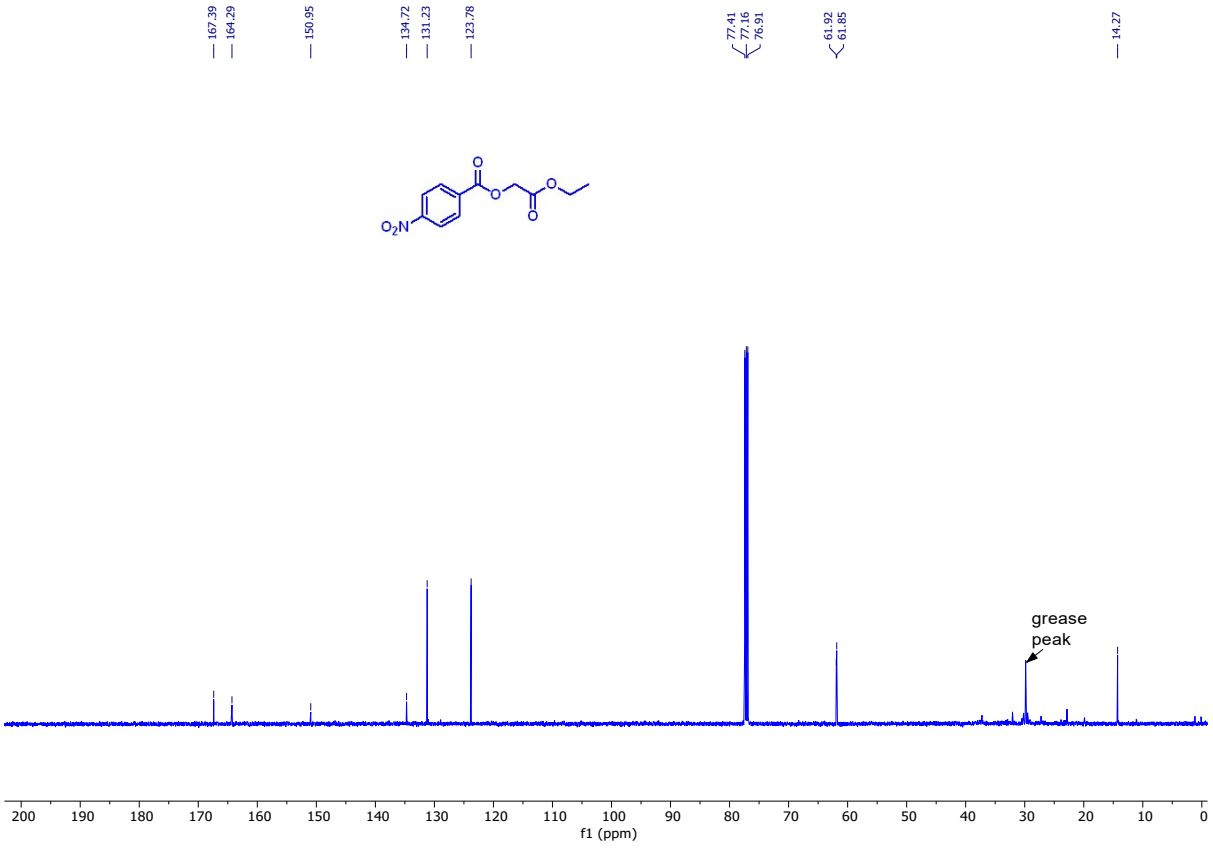
^{13}C{^{1}H} NMR spectrum of 3i (126 MHz, $CDCl_3$)



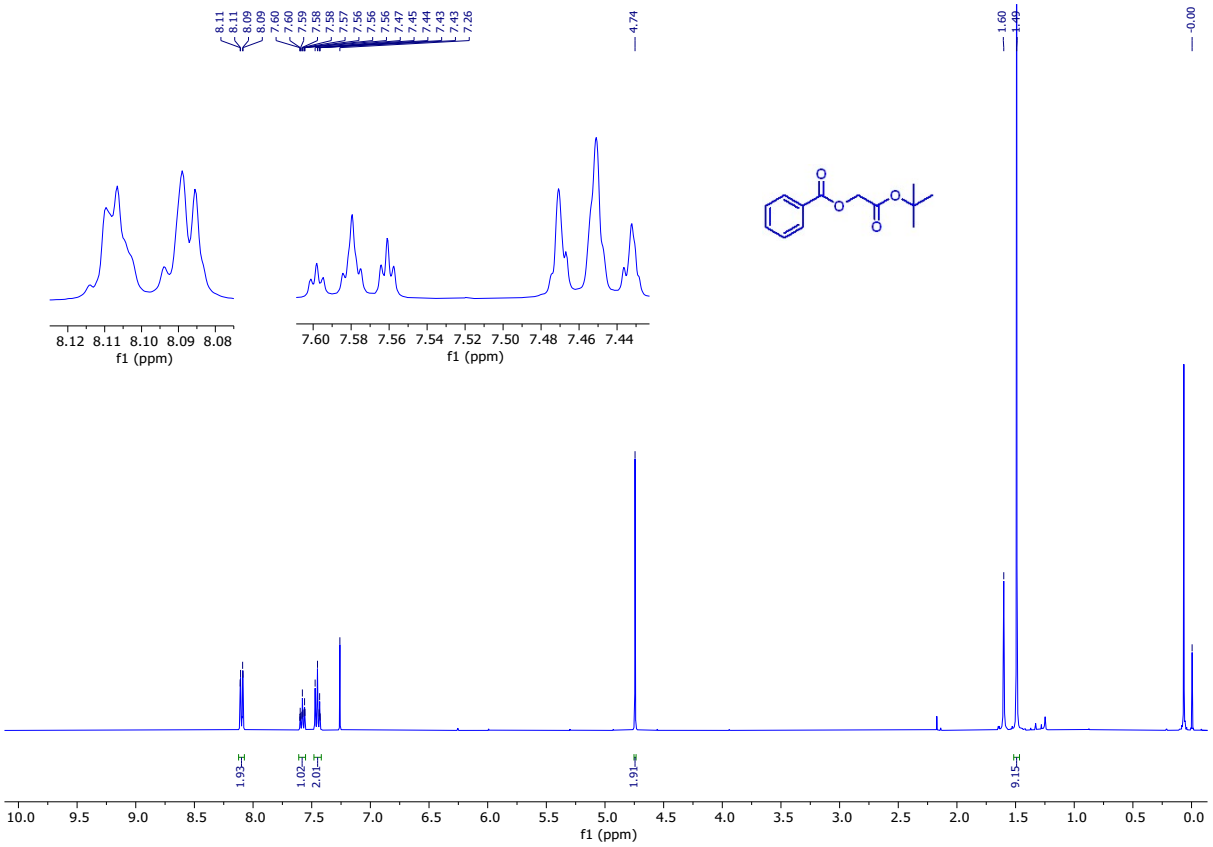
^{1}H NMR spectrum of 3j (400 MHz, $CDCl_3$)



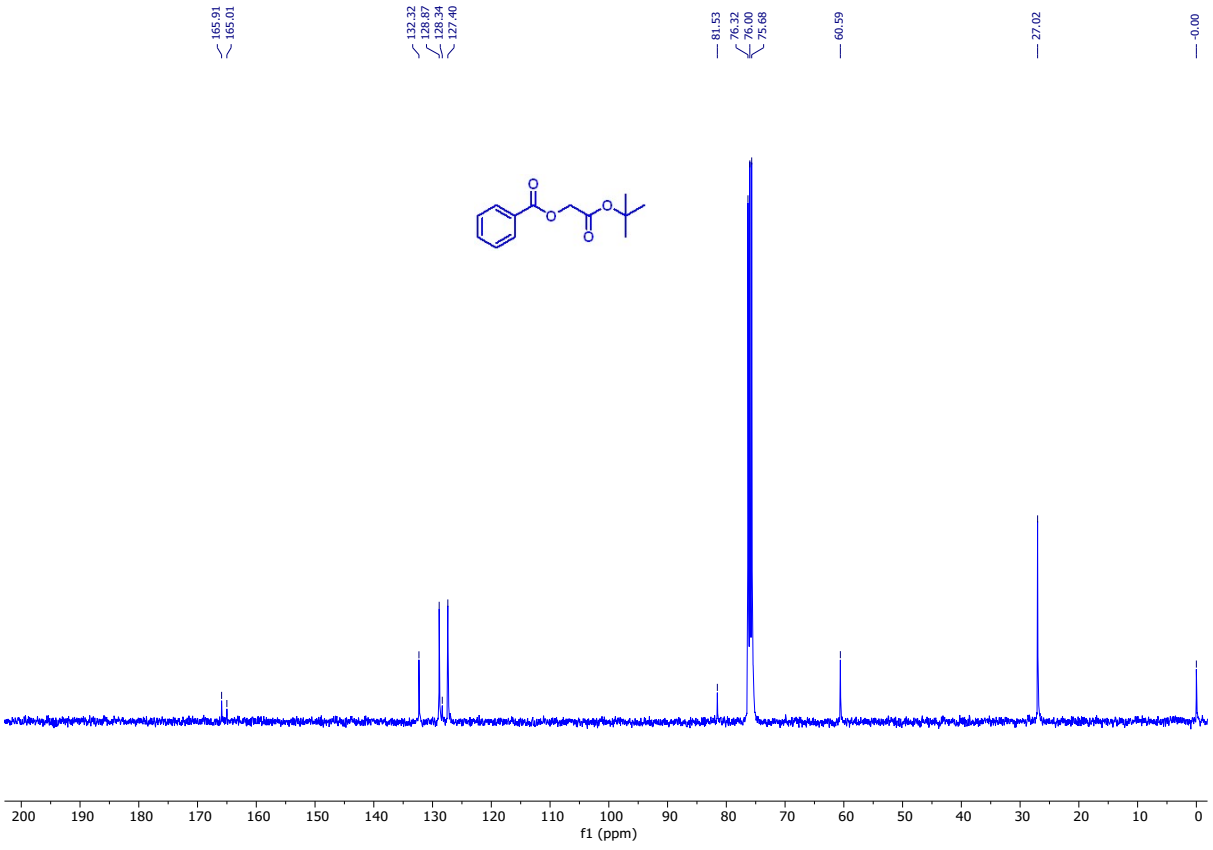
^{13}C{^{1}H} NMR spectrum of 3j (126 MHz, $CDCl_3$)



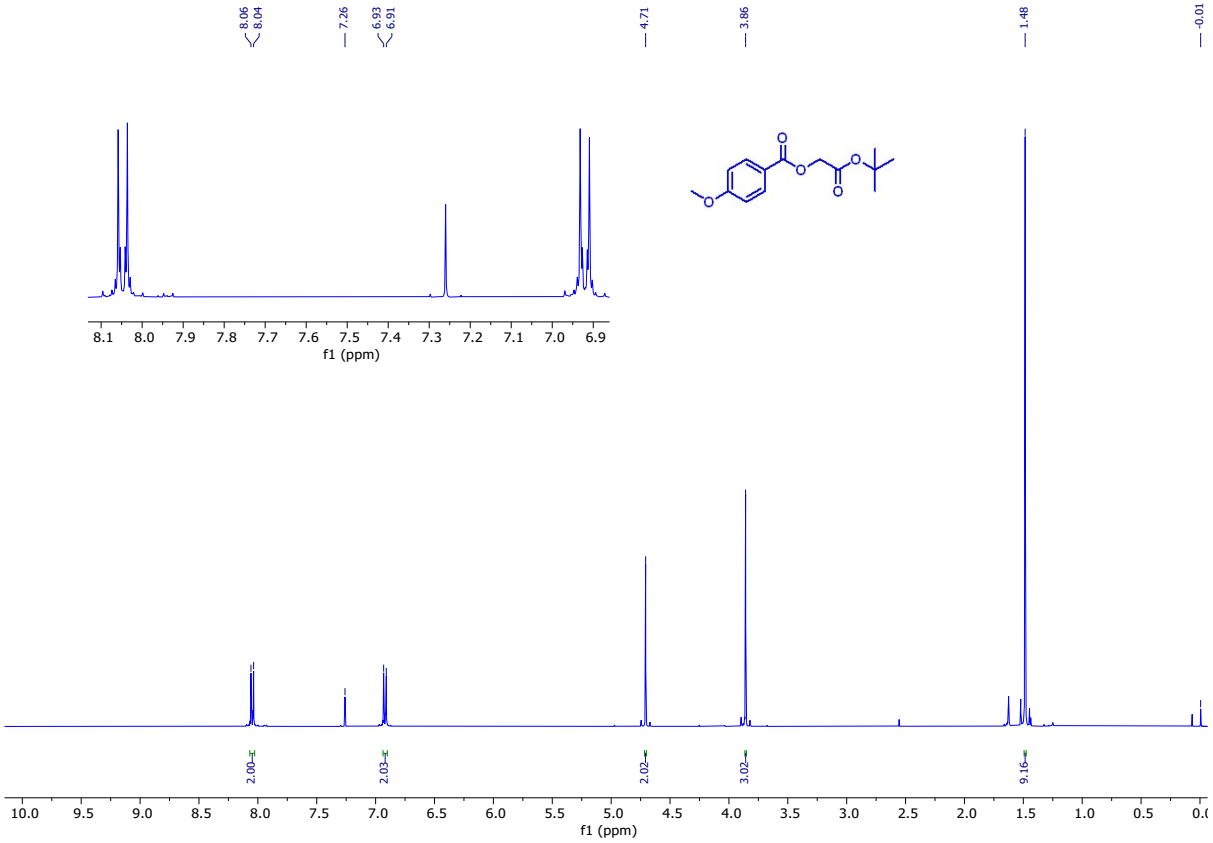
^{1}H NMR spectrum of 3k (400 MHz, $CDCl_3$)



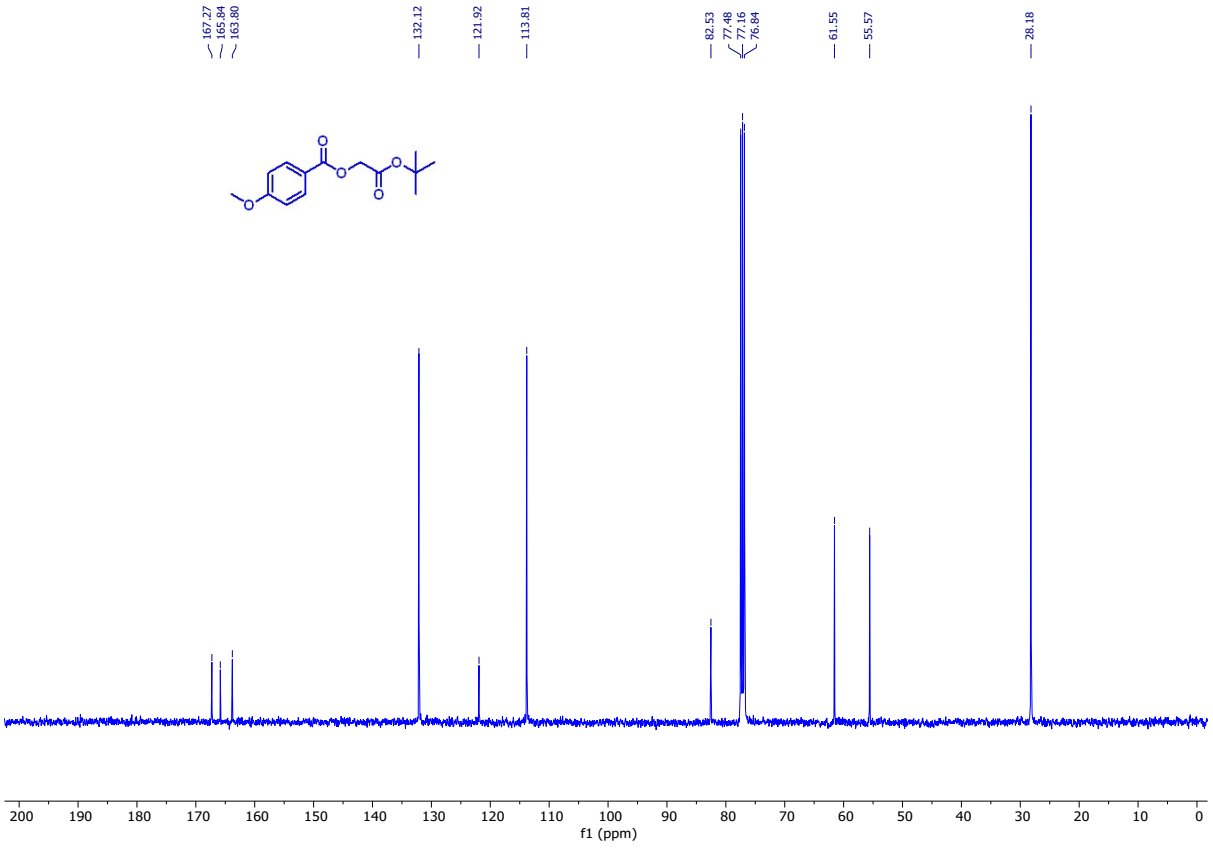
$^{13}C\{^{1}H\}$ NMR spectrum of 3k (101 MHz, $CDCl_3$)



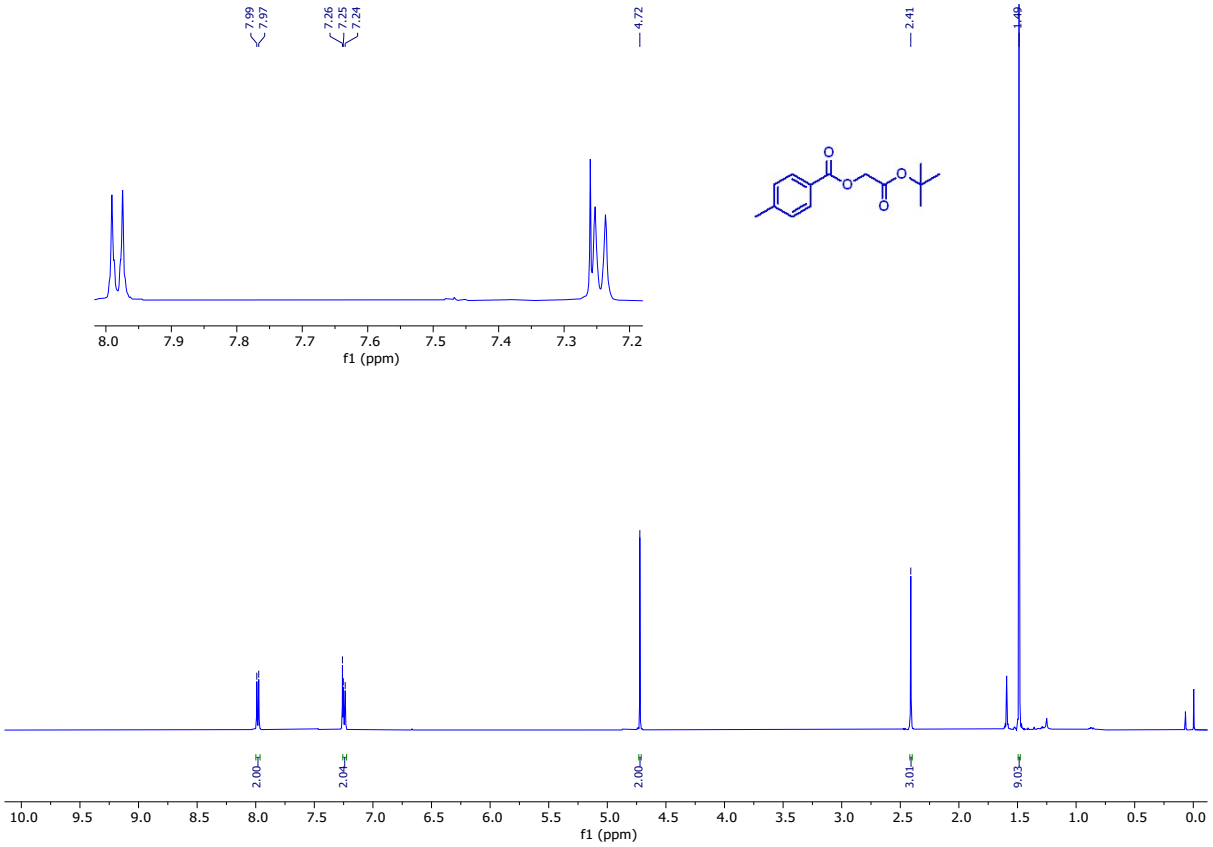
^{1}H NMR spectrum of 3l (400 MHz, $CDCl_3$)



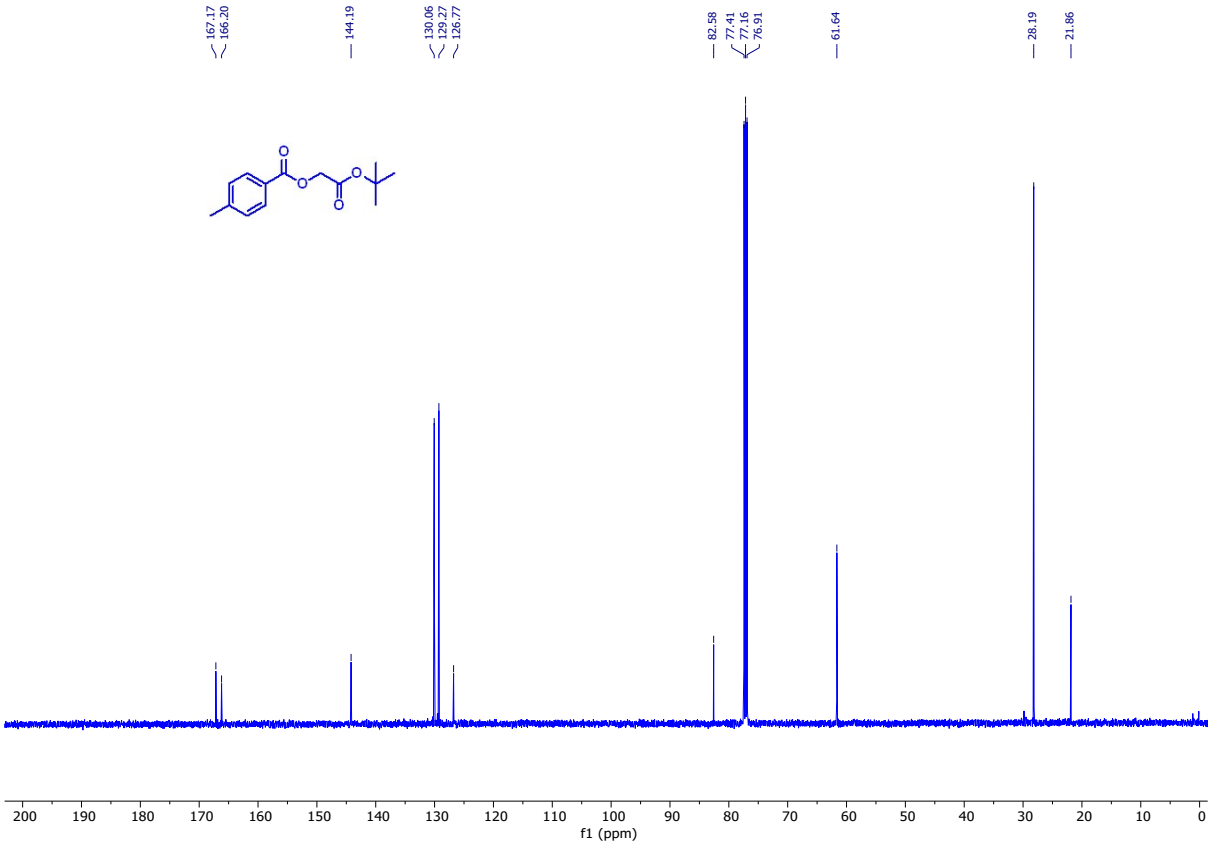
$^{13}C\{^{1}H\}$ NMR spectrum of 3l (101 MHz, $CDCl_3$)



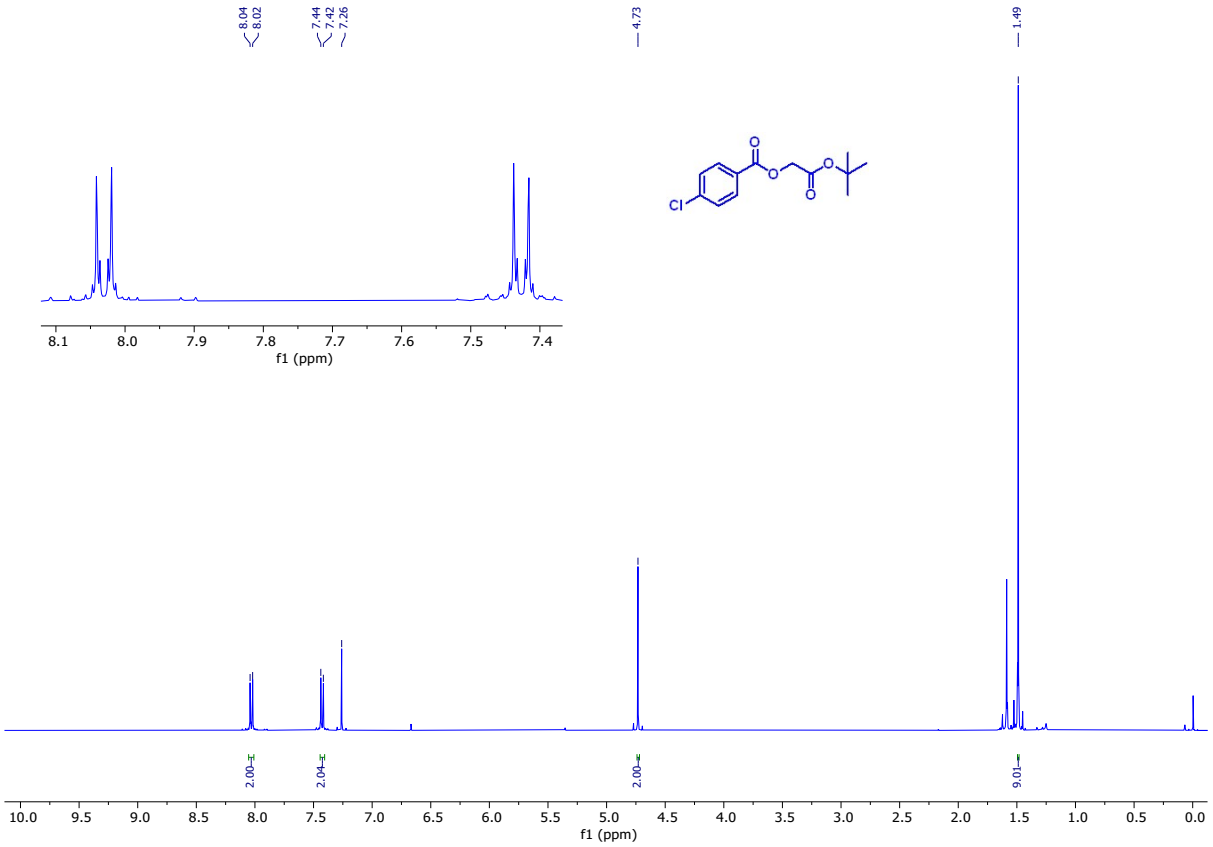
^{1}H NMR spectrum of 3m (500 MHz, $CDCl_3$)



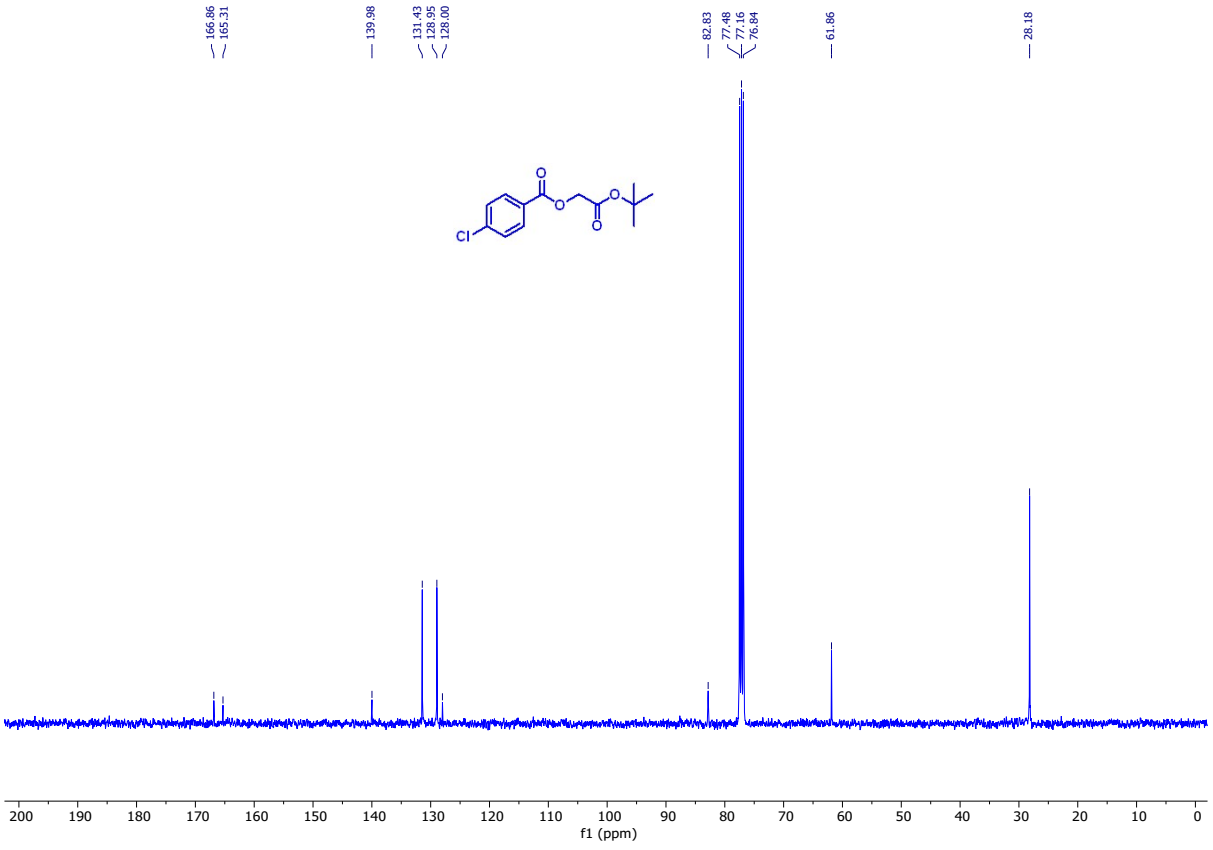
^{13}C{^{1}H} NMR spectrum of 3m (126 MHz, $CDCl_3$)



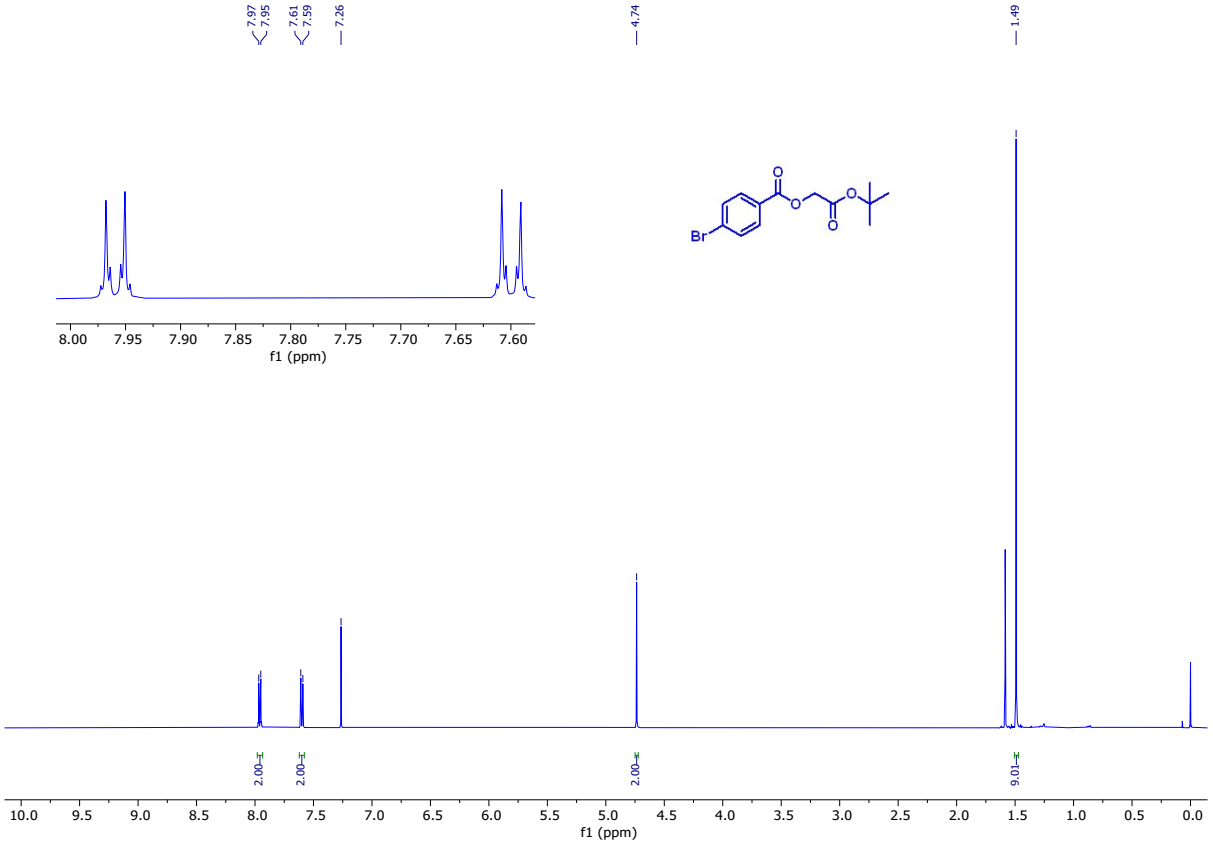
^{1}H NMR spectrum of 3n (500 MHz, $CDCl_3$)



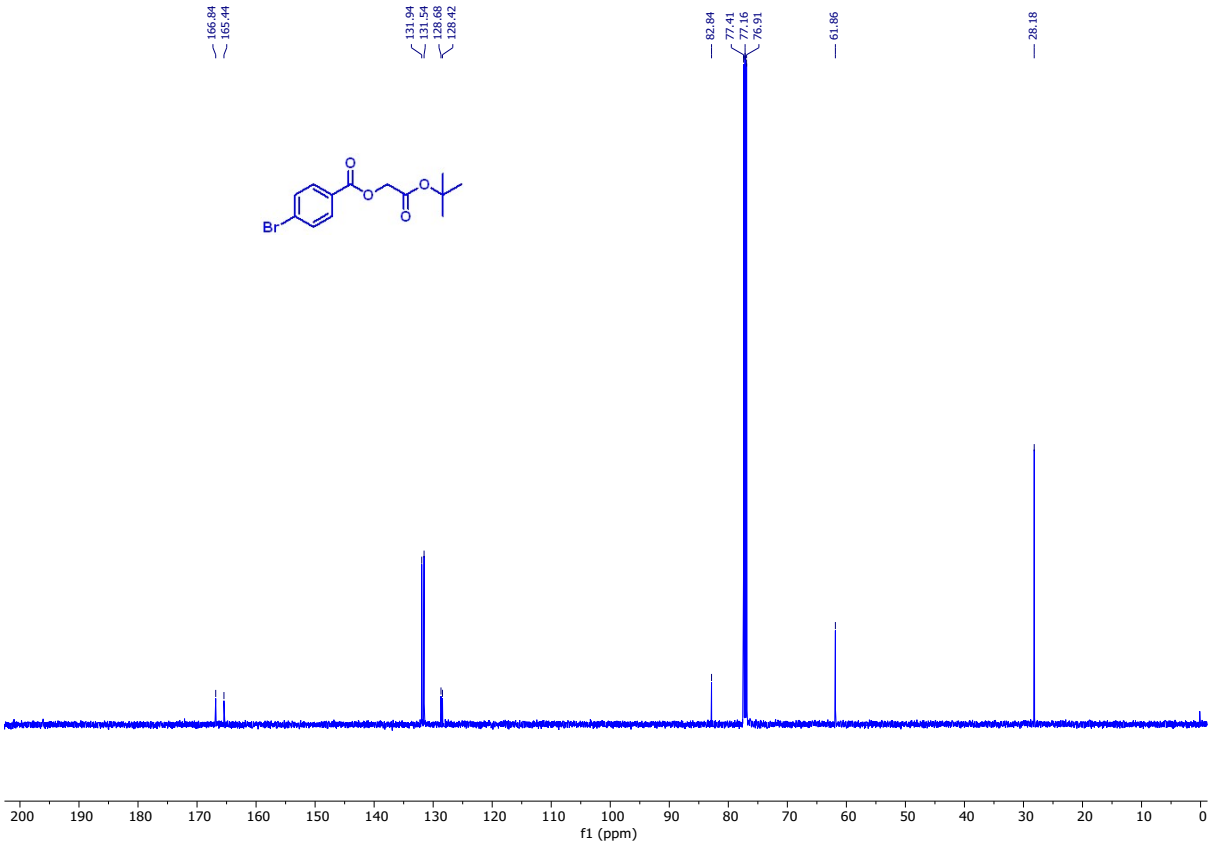
$^{13}C\{^{1}H\}$ NMR spectrum of 3n (126 MHz, $CDCl_3$)



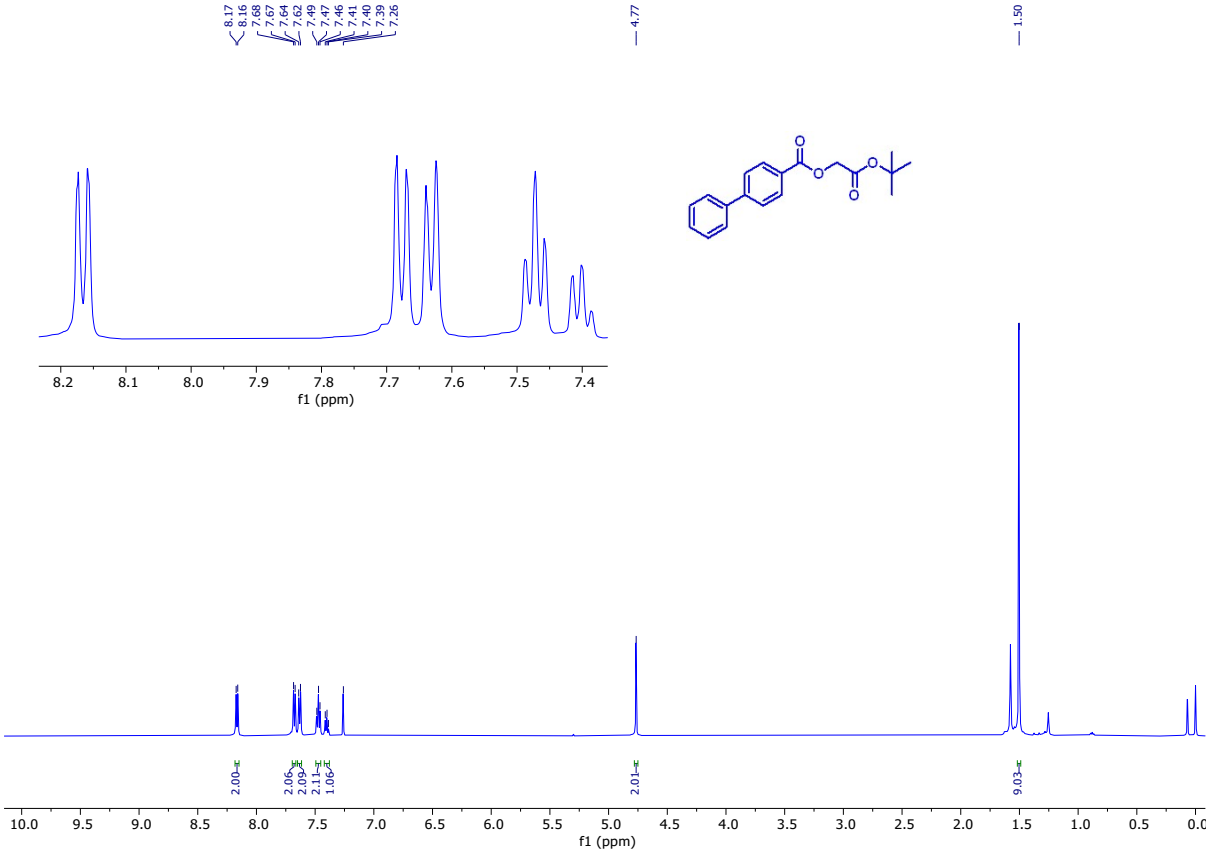
^{1}H NMR spectrum of 3o (500 MHz, $CDCl_3$)



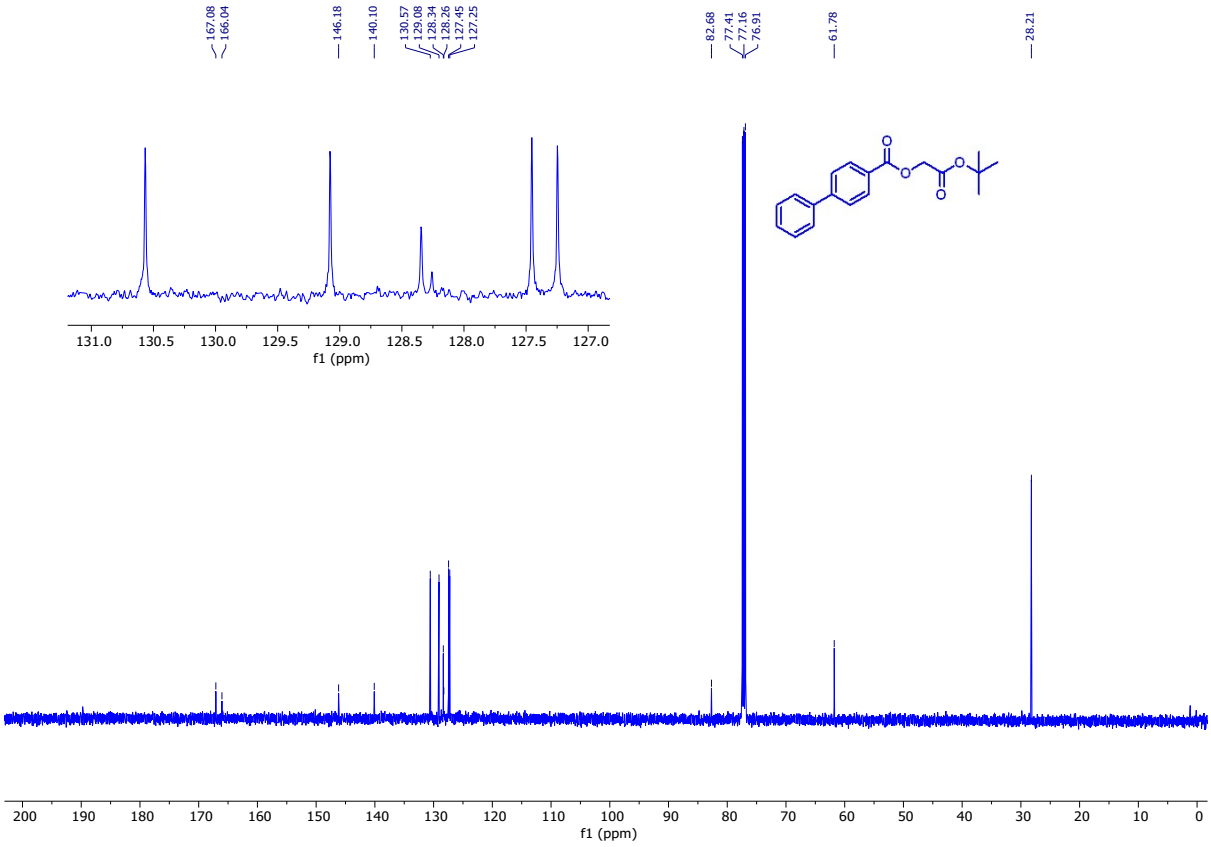
$^{13}C\{^{1}H\}$ NMR spectrum of 3o (126 MHz, $CDCl_3$)



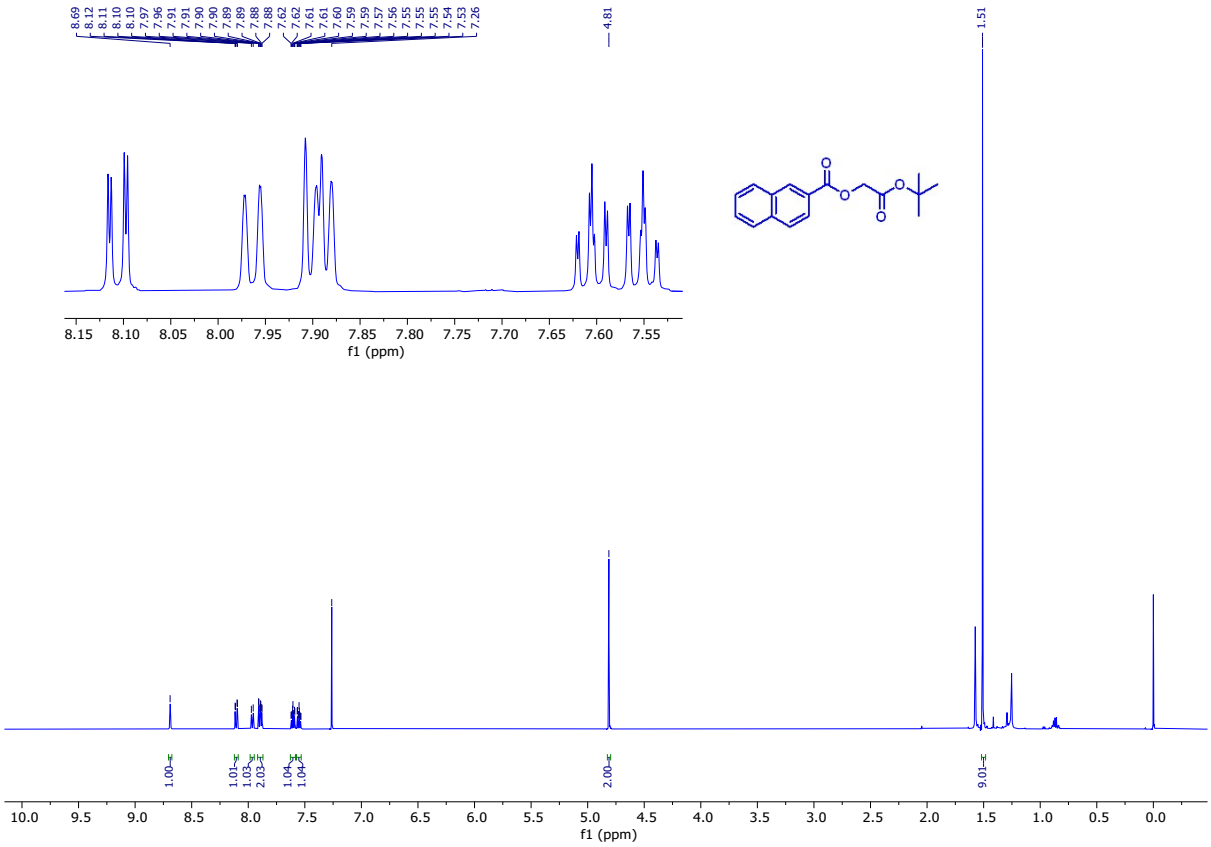
^{1}H NMR spectrum of 3p (500 MHz, $CDCl_3$)



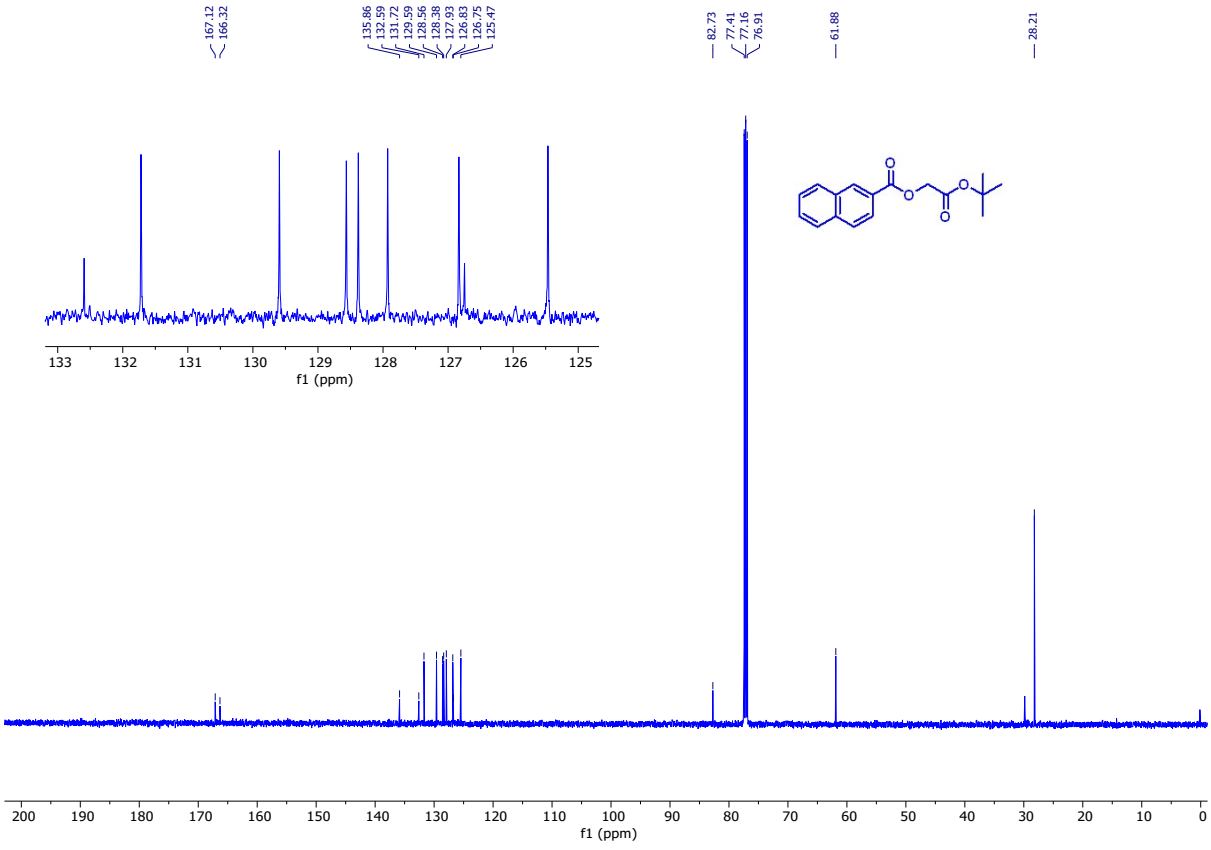
^{13}C{^{1}H} NMR spectrum of 3p (126 MHz, $CDCl_3$)



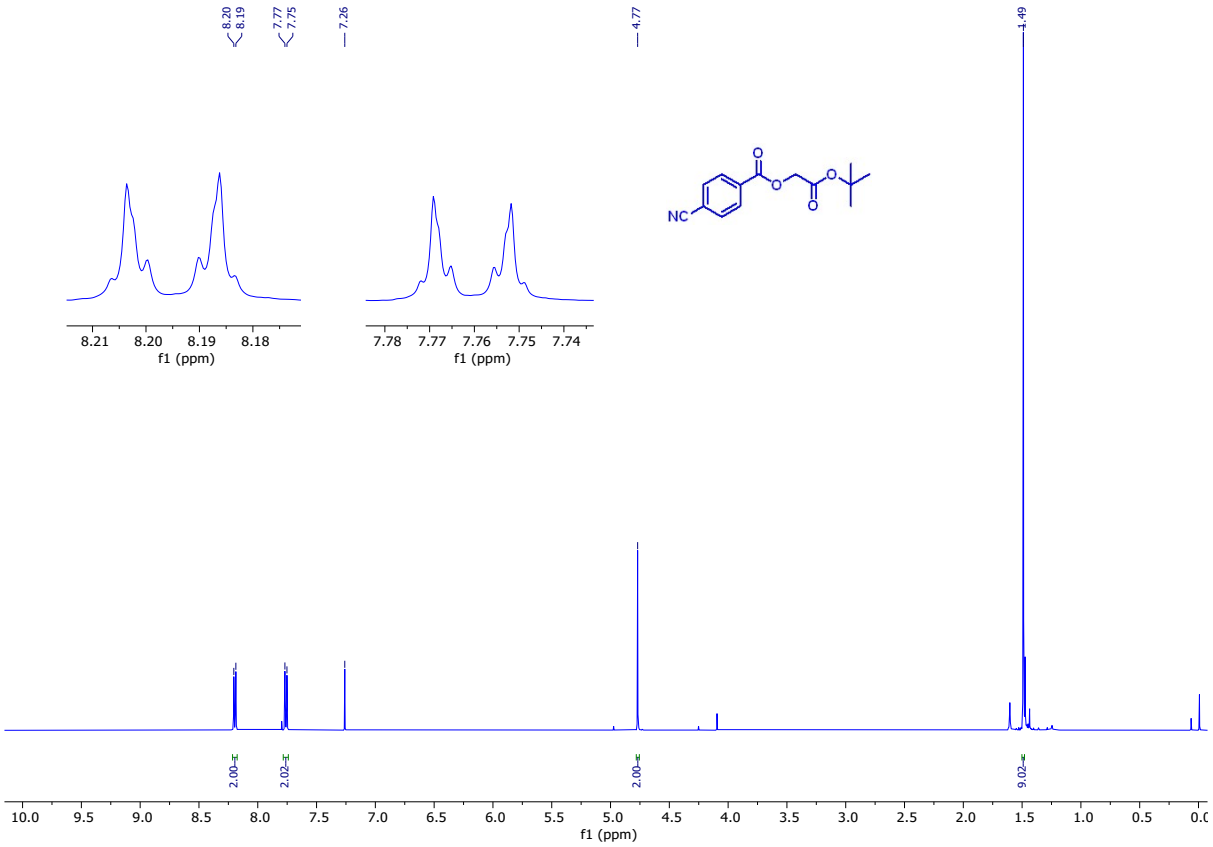
^{1}H NMR spectrum of 3q (500 MHz, $CDCl_3$)



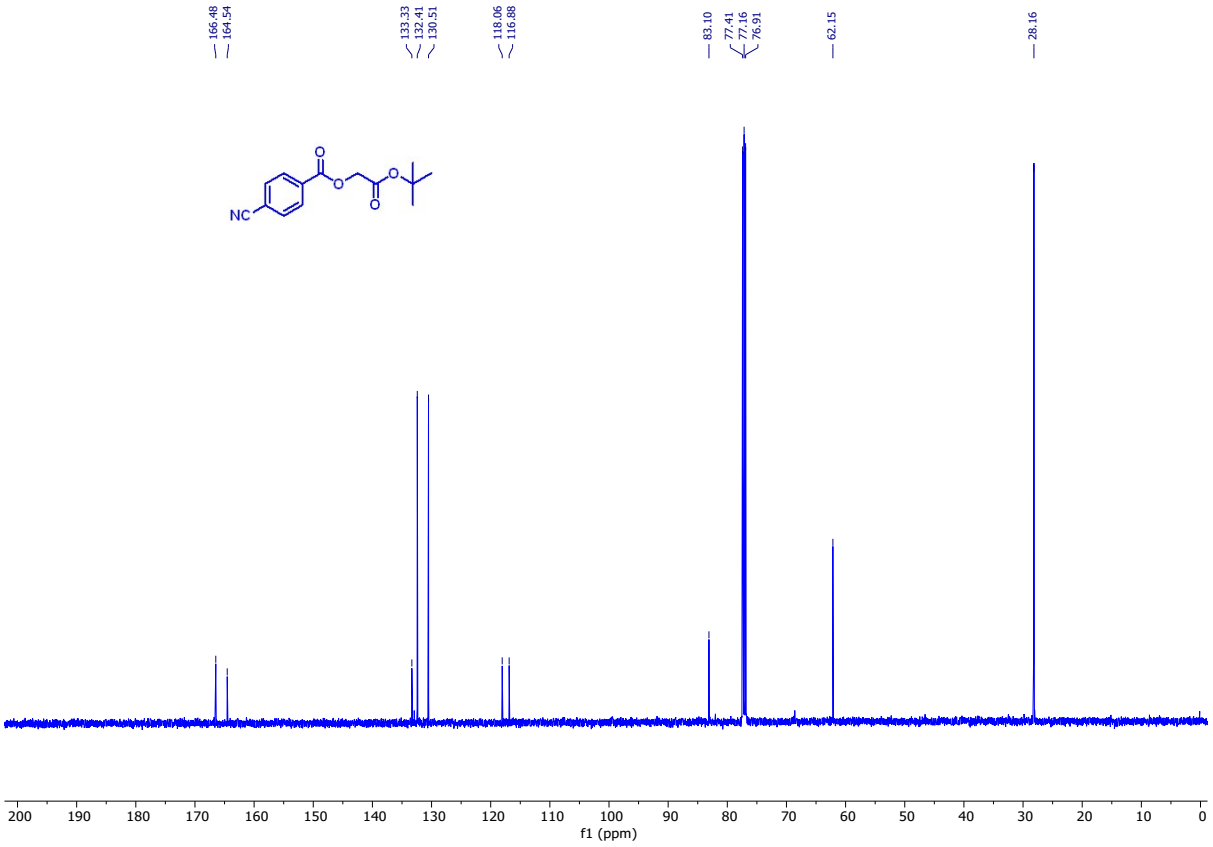
^{13}C{^{1}H} NMR spectrum of 3q (126 MHz, $CDCl_3$)



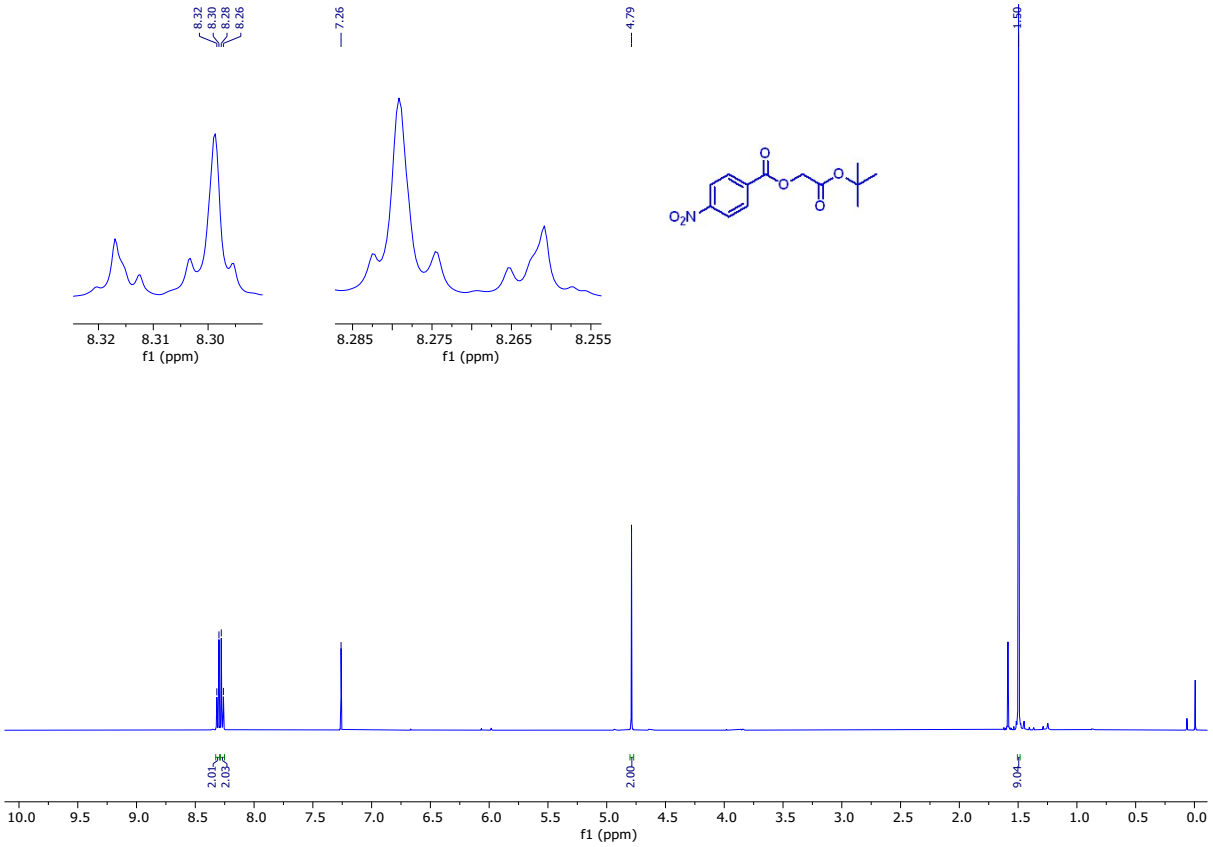
^{1}H NMR spectrum of 3r (500 MHz, $CDCl_3$)



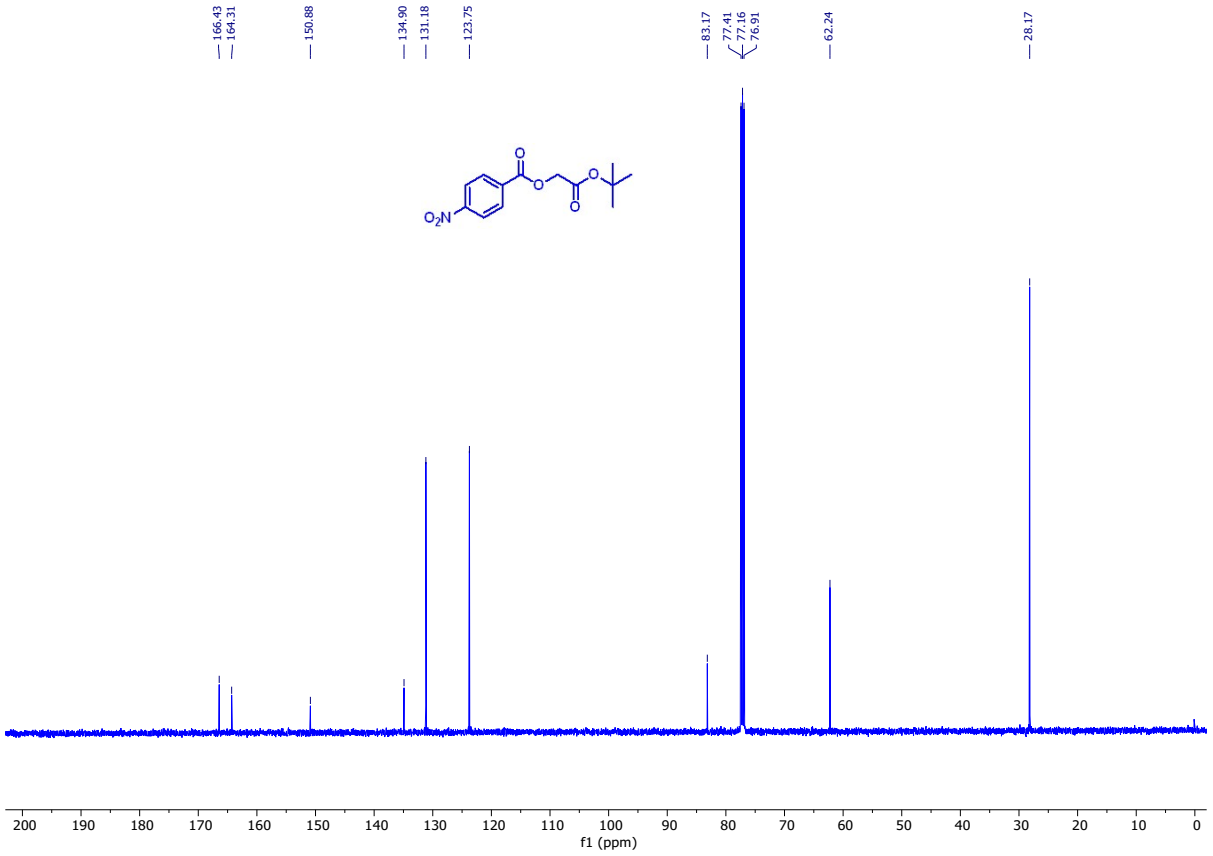
^{13}C{^{1}H} NMR spectrum of 3r (126 MHz, $CDCl_3$)



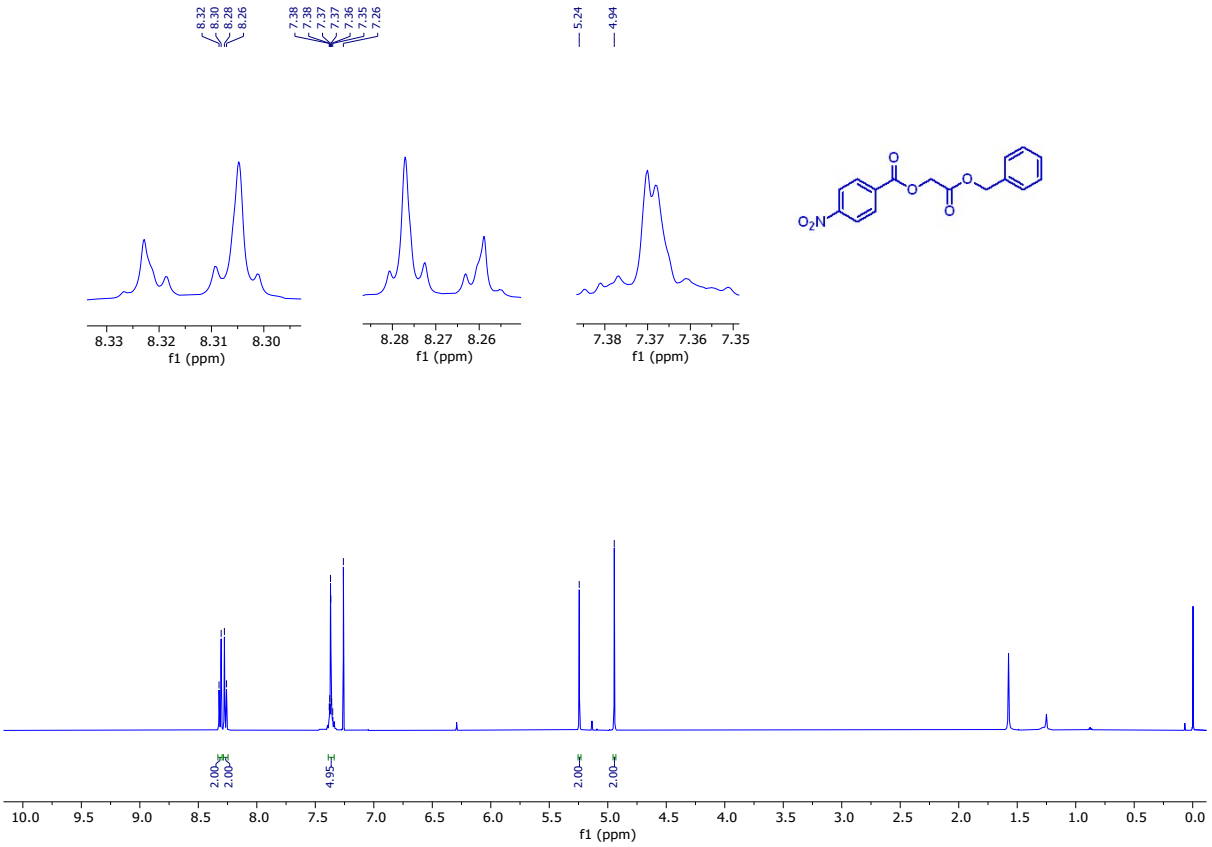
^{1}H NMR spectrum of 3s (500 MHz, $CDCl_3$)



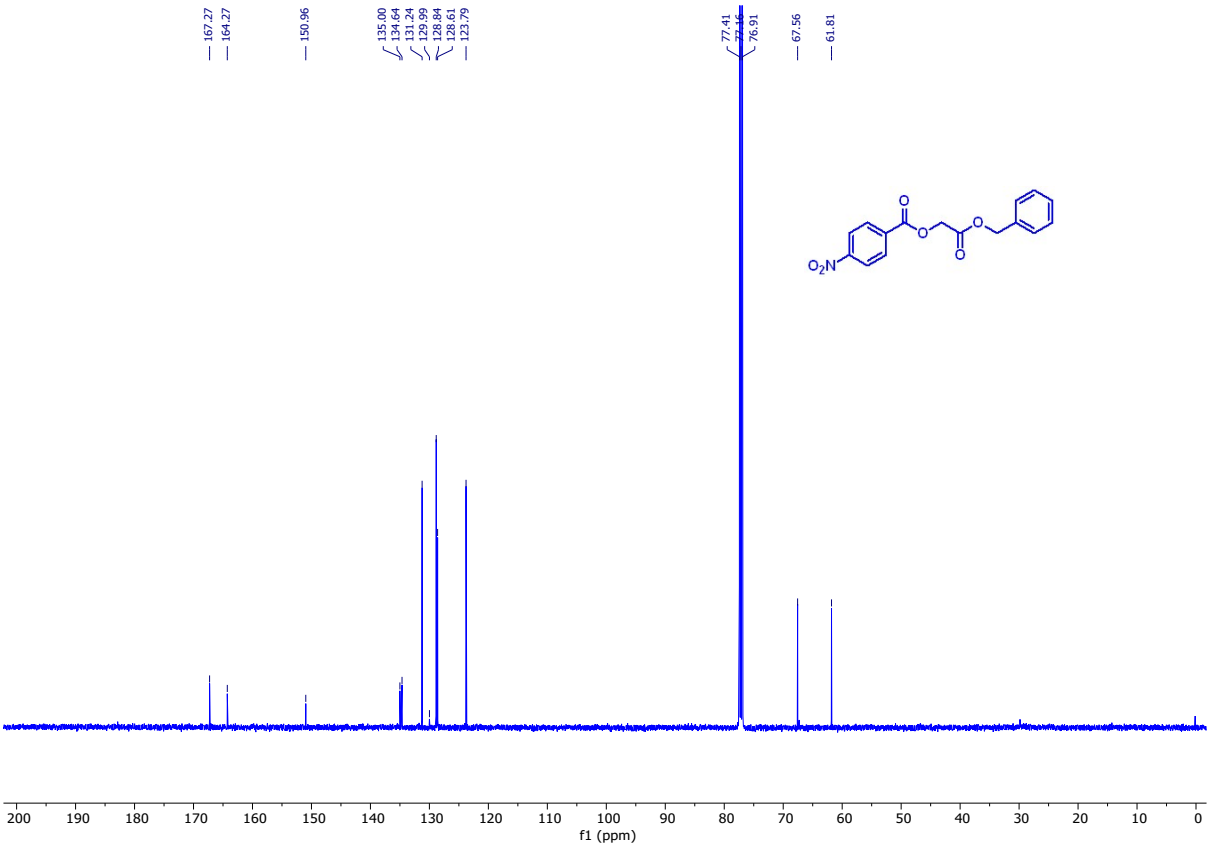
^{13}C{^{1}H} NMR spectrum of 3s (126 MHz, $CDCl_3$)



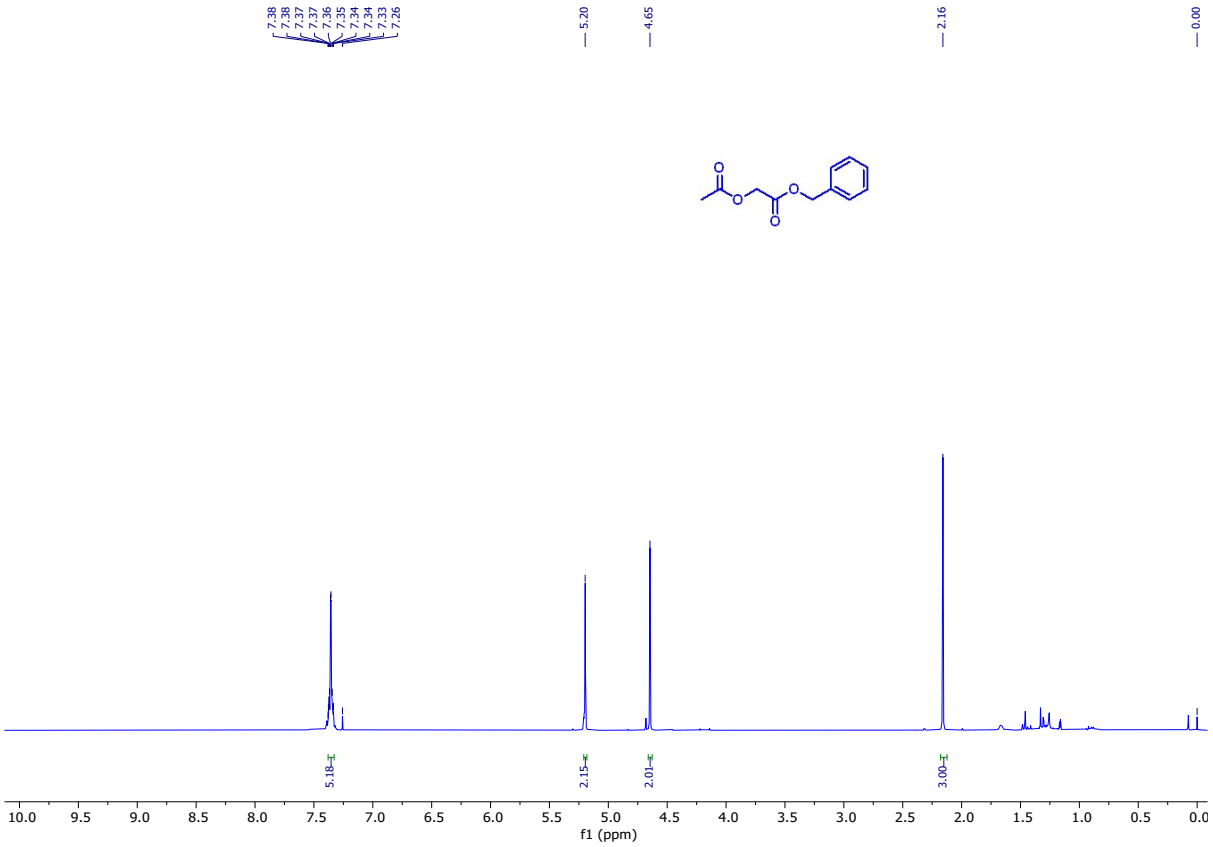
^{1}H NMR spectrum of 3t (500 MHz, $CDCl_3$)



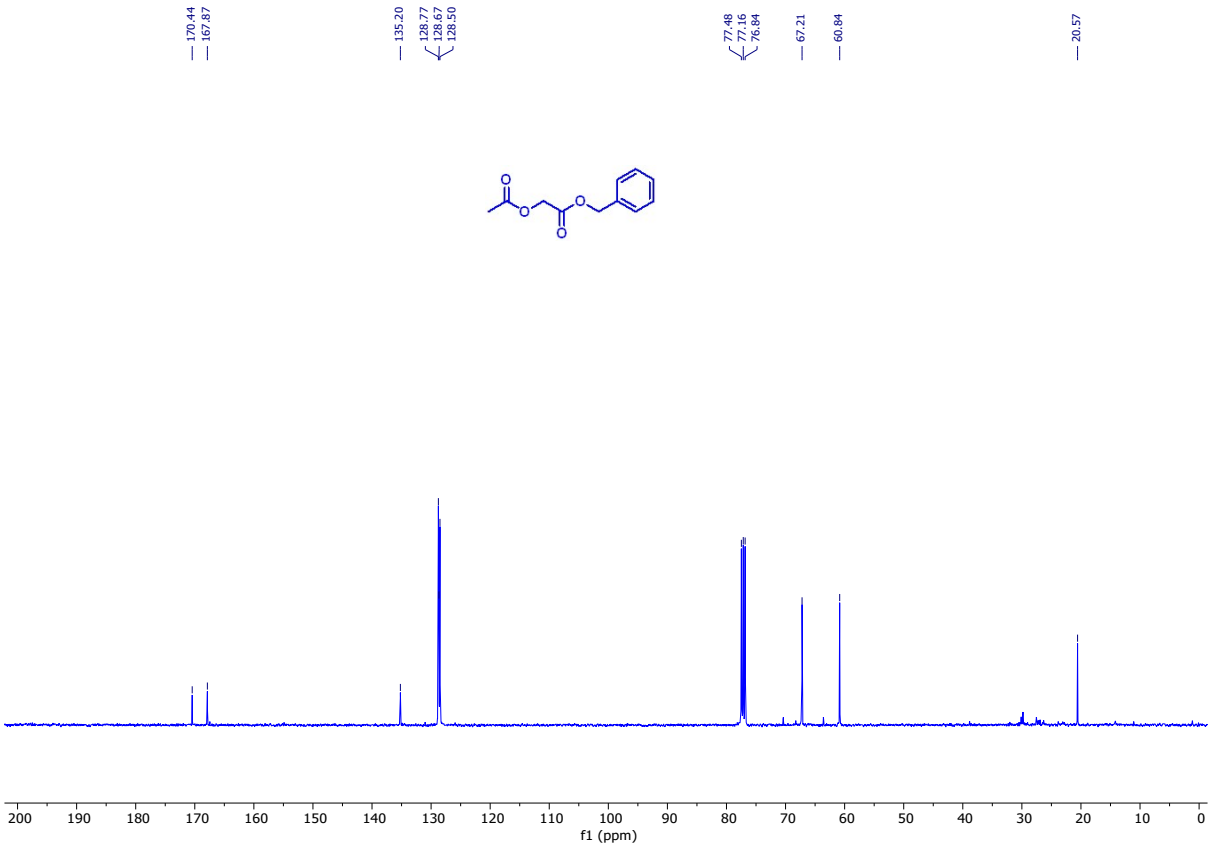
$^{13}C\{^{1}H\}$ NMR spectrum of 3t (126 MHz, $CDCl_3$)



^{1}H NMR spectrum of 3u (400 MHz, $CDCl_3$)

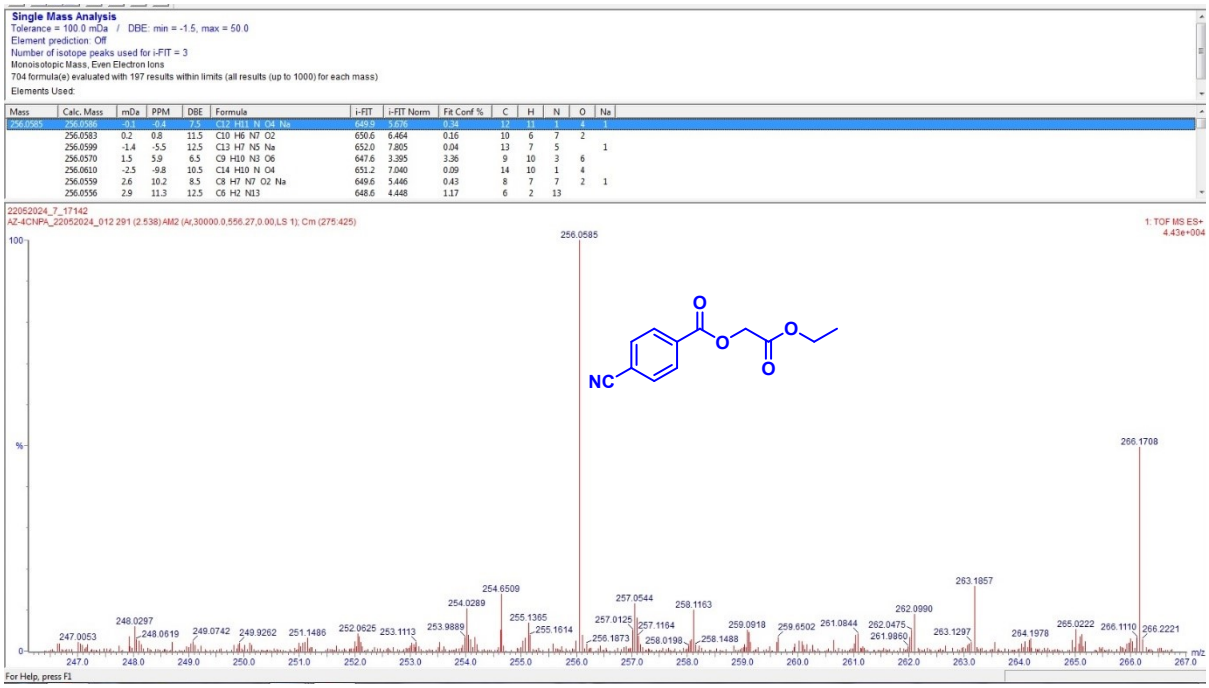


^{13}C{^{1}H} NMR spectrum of 3u (101 MHz, $CDCl_3$)

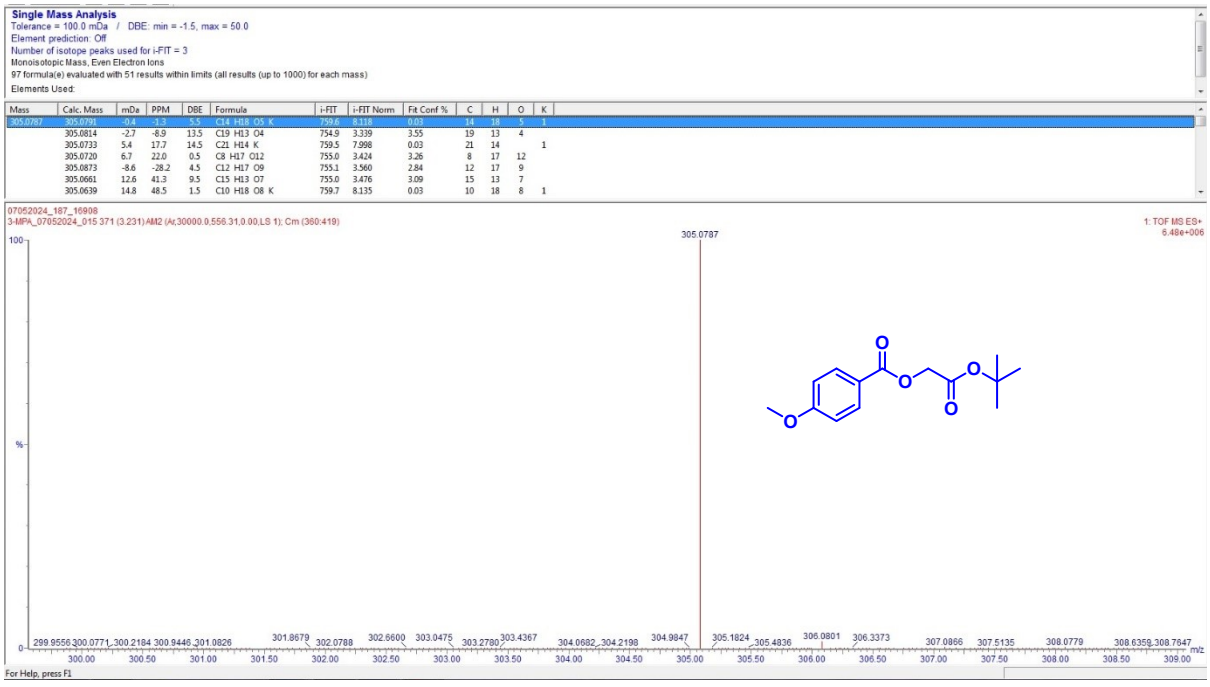


HRMS data

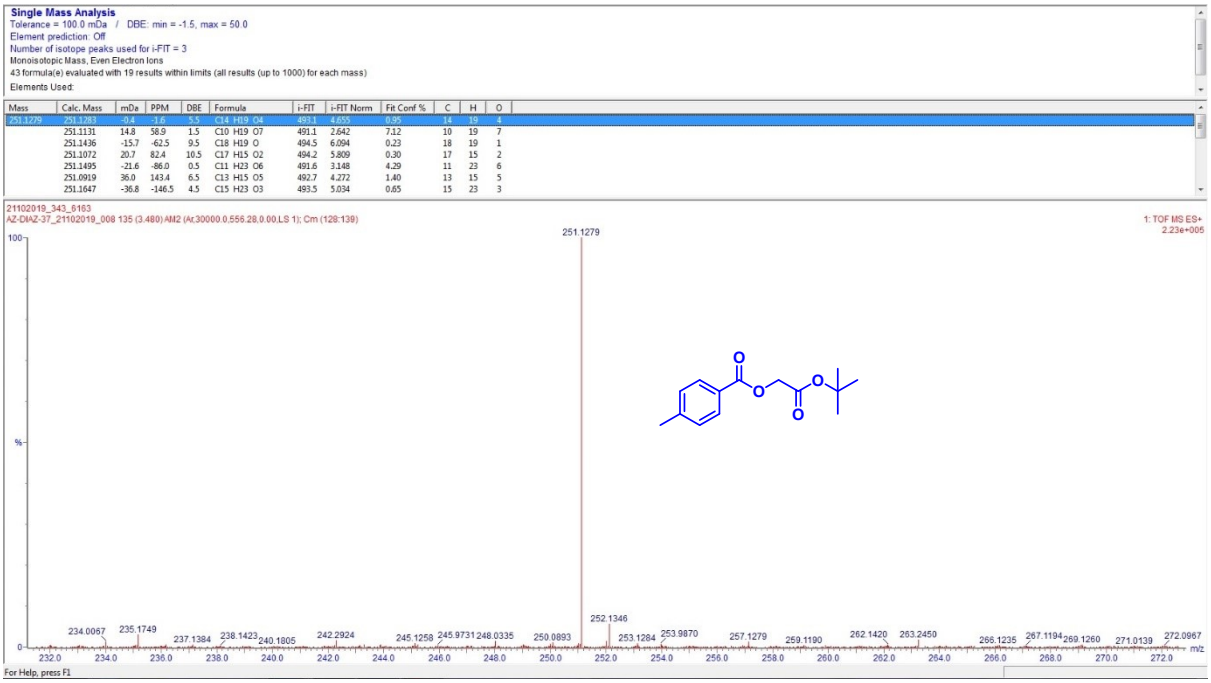
2-Ethoxy-2-oxoethyl 4-cyanobenzoate (3i)



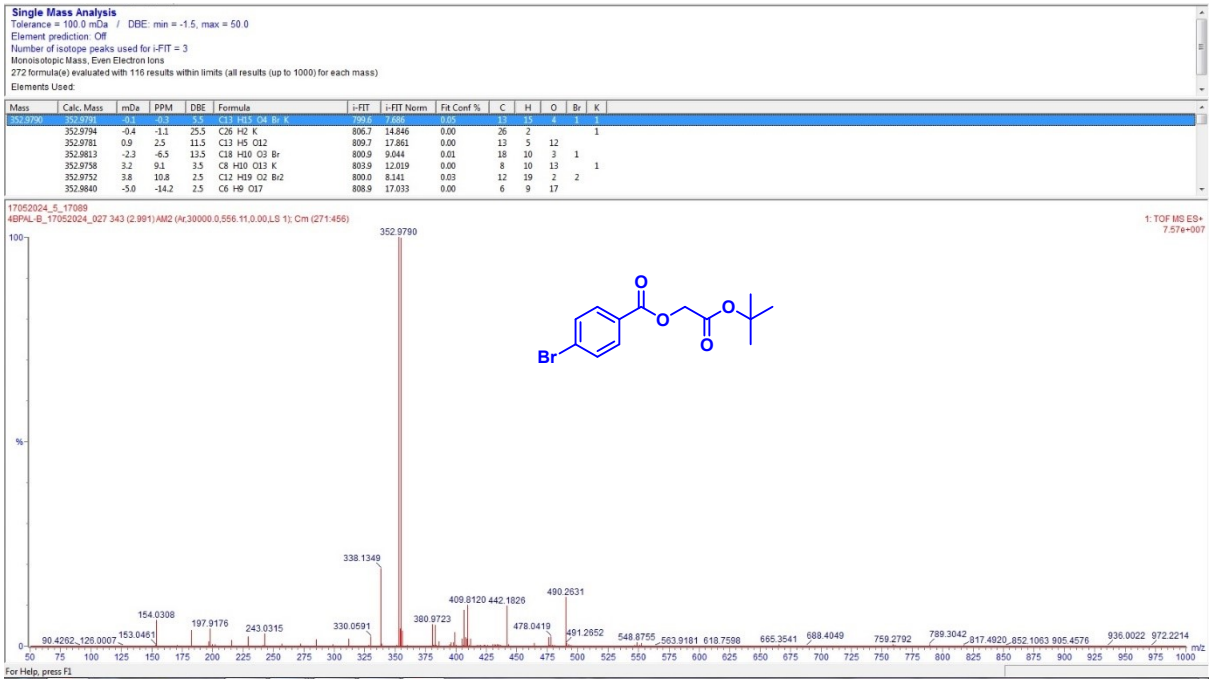
2-(*Tert*-Butoxy)-2-oxoethyl 4-methoxybenzoate (3l)



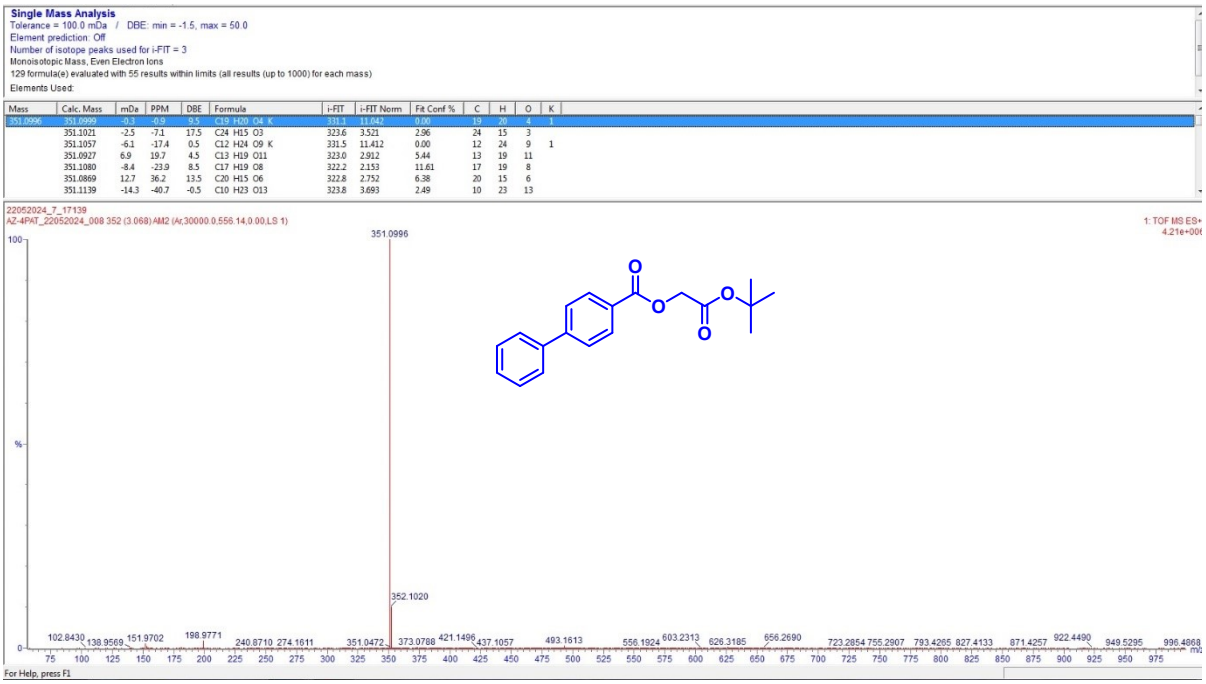
2-(*Tert*-butoxy)-2-oxoethyl 4-methylbenzoate (3m)



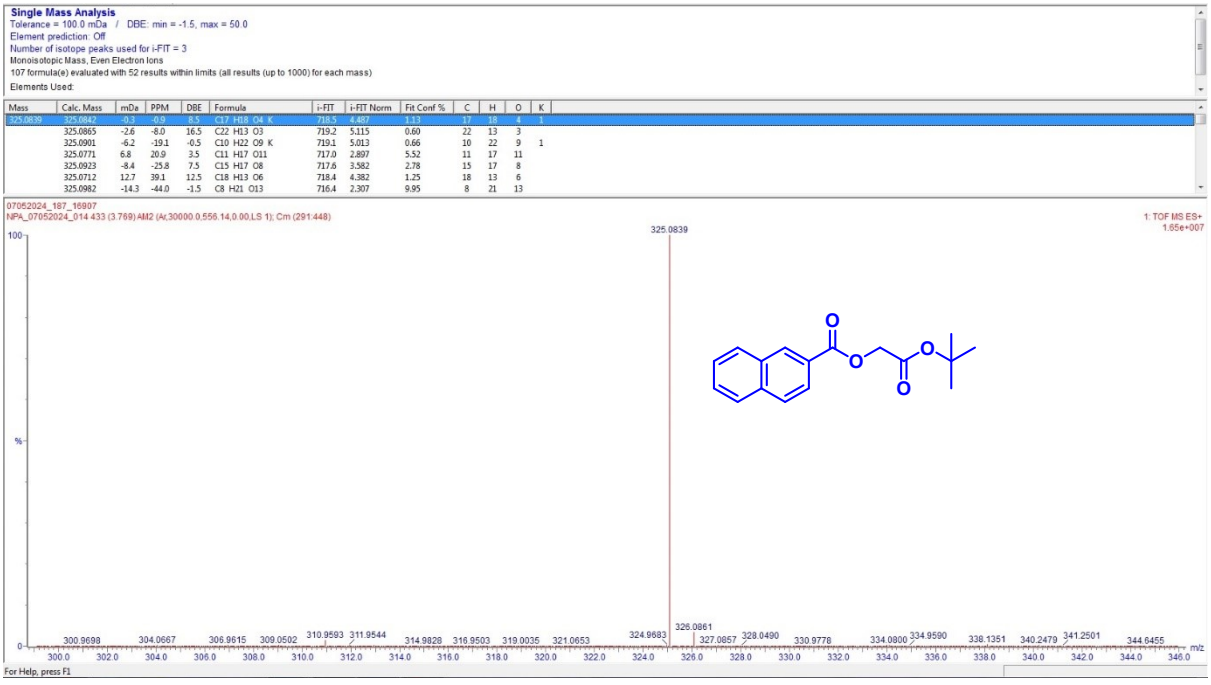
2-(*Tert*-butoxy)-2-oxoethyl 4-bromobenzoate (3o)



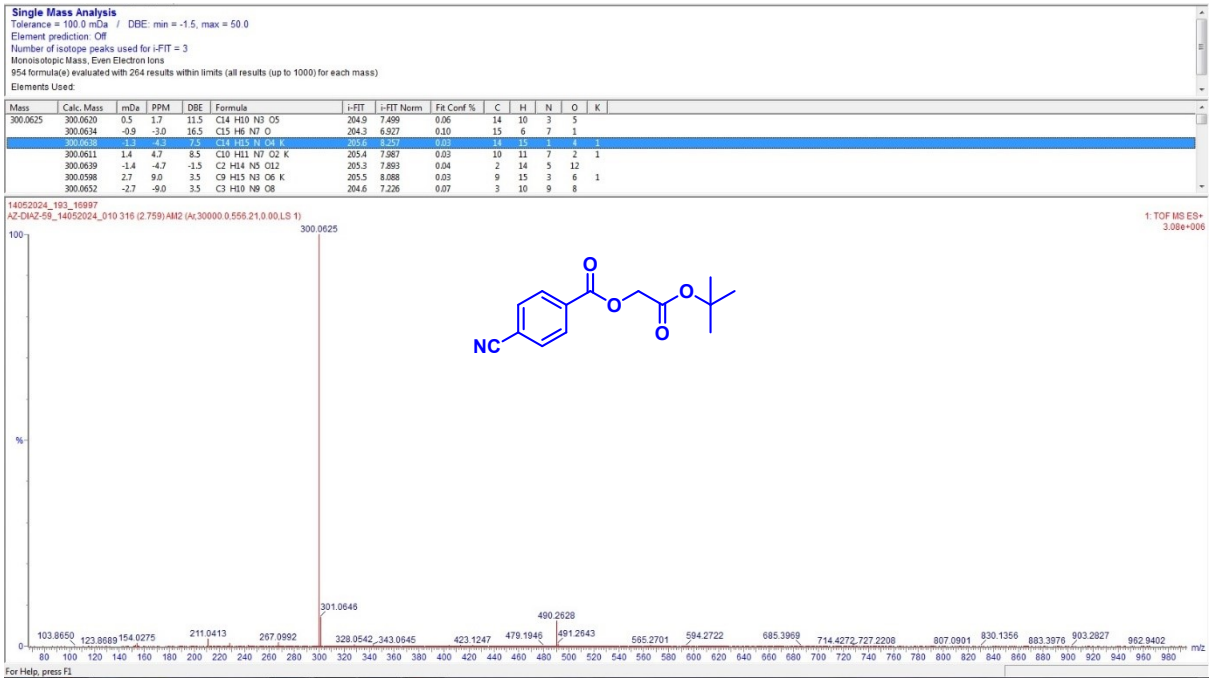
2-(*Tert*-butoxy)-2-oxoethyl [1,1'-biphenyl]-4-carboxylate (3p)



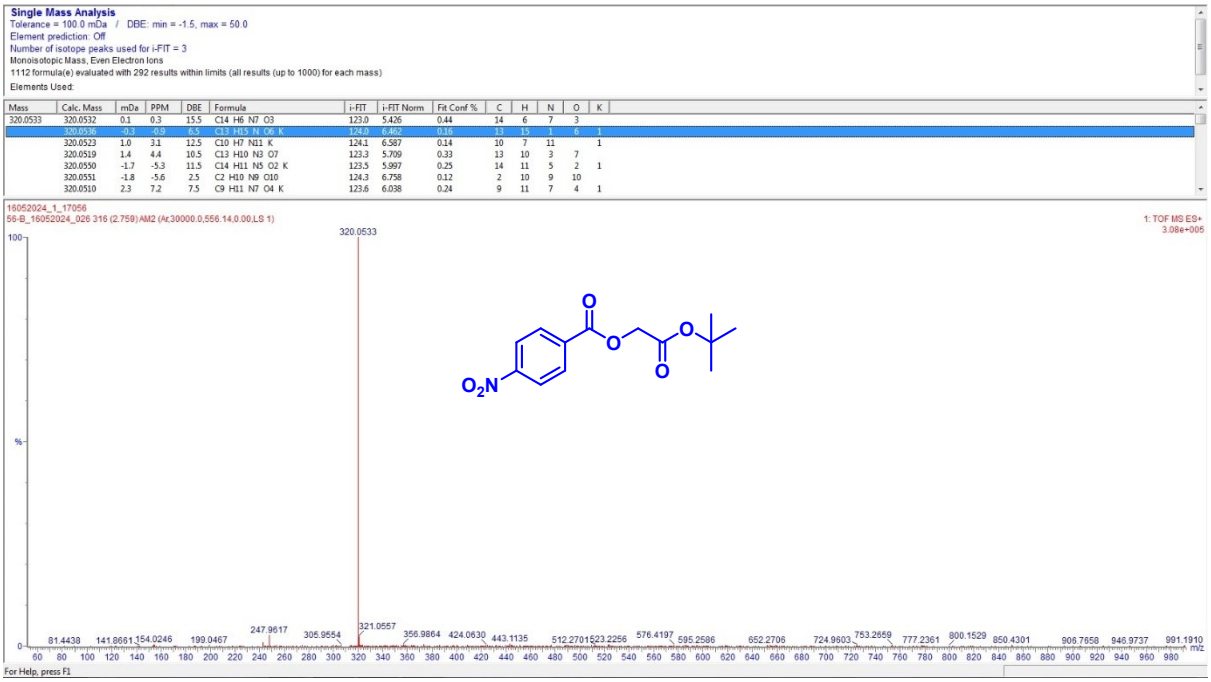
2-(*Tert*-butoxy)-2-oxoethyl 2-naphthoate (3q)



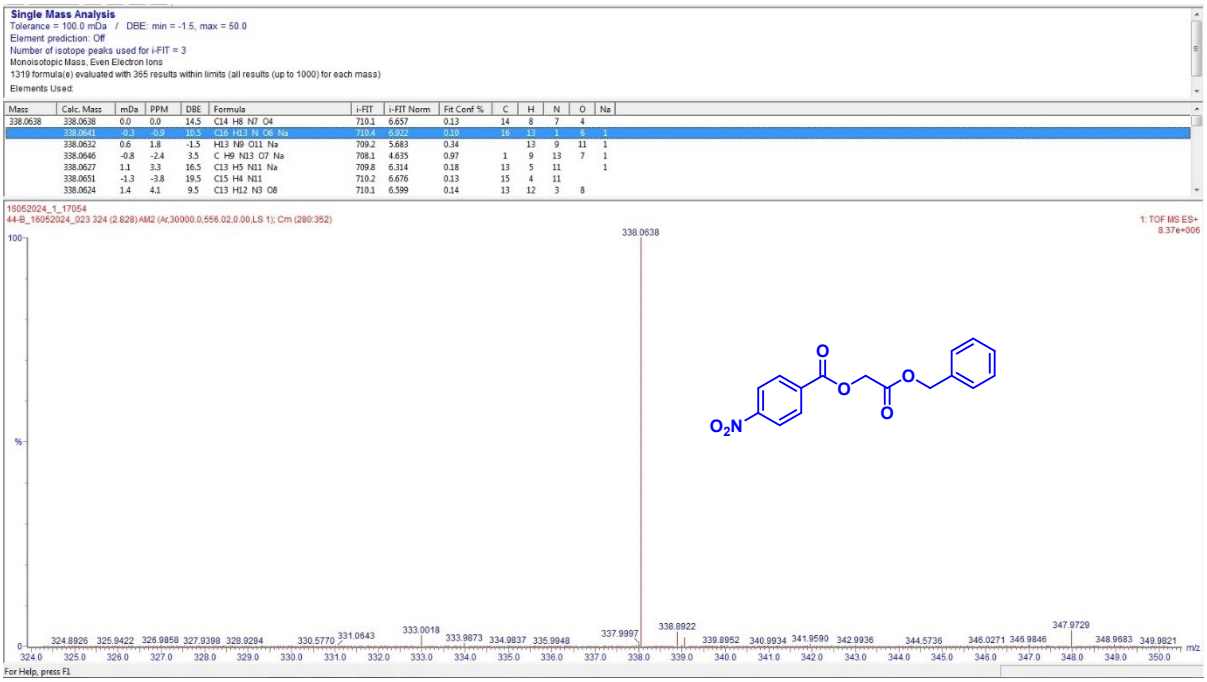
2-(*Tert*-butoxy)-2-oxoethyl 4-cyanobenzoate (3r)



2-(Tert-butoxy)-2-oxoethyl 4-nitrobenzoate (3s)



2-(Benzyloxy)-2-oxoethyl 4-nitrobenzoate (3t)



Benzyl 2-acetoxyacetate (3u)