Electronic Supplementary Material (ESI) for Organic .

SUPPORTING INFORMATION

FOR

$Bi(OTf)_3$-Catalyzed Three-Component Synthesis of α-Amino Acid Derivatives

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Contents

1 General

Solvents Solvents for reactions and column chromatography were obtained from different commercial suppliers in > 97 % purity and used as received.

Reagents *N*-(2,4-Dimethylbenzyl)-3-methyl-2-(1,3-dioxoisoindolin-2-yl)butanamide[1], 2-thiophenesulfonamide[2], isopropyl glyoxalate[3], benzyl glyoxalate[4], ethyl-4-methoxybenzoate[5], 2-methylpivalanilide[6], 3- ethylpivalanilide[6], *N*-tosylindole[7] and *N*-tosylpyrrole[8] were synthesized according to literature. Ethyl glyoxalate was obtained from different providers as 50 wt% solution in toluene (technical form). In order to avoid side reactions toluene was removed *in vacuo* (1 mbar, 3h). The resulting oil was redissolved in $MeNO_2$. The obtained solution was used directly for all reactions. Glyoxylic acid was obtained from Alfa Aeasar as 50 wt% solution in water and used as received.

Anhydrous $Bi(OTf)_3$ was obtained from different providers and used directly. No special precautions were taken to avoid exposure of $Bi(OTf)_3$ to moisture. Therefore we cannot rule out the formation of $Bi(OTf)_3 \times H_2O$ during storage. Indeed depending on the provider and storage time (or even the time for weighting out a defined amount for elemental analysis) $Bi(OTf)_3$ contained up to six molecules of water. However no changes in catalytic activity and yield even upon prolonged storage (>1 year) were observed. Therefore the amount of $Bi(OTf)_3$ used is always calculated on anhydrous $Bi(OTf)_3$. The actual catalyst loading for particular reactions might be slightly lower, depending on the batch quality and storage time.

All other starting materials were purchased from commercial sources and used without further purification.

Chromatography Column chromatography was performed with Silica 0.04-0.063 mm/ 230-400 mesh. Thin layer chromatography was done using aluminum plates coated with SiO_2. The spots were visualized by ultraviolet light, iodine or CAM.

NMR spectroscopy ^1H and ^{13}C NMR spectra were recorded at 300 or 400 MHz and 75 or 101 MHz, respectively. Chemical shifts are reported as δ - values relative to the residual $CDCl_3$-peak (δ = 7.26 ppm for ^1H and δ = 77.16 ppm for ^{13}C). Coupling constants (*J*) are given in Hz and multiplicities of the signals are abbreviated as follows: s = singlet; bs = broad singlet; d = doublet; bd = broad doublet; t = triplet; q = quartett; sp = septet; m = multiplet; dd = doublet of doublets and dt = doublet of triplets.

Mass Spectrometry Mass spectra (MS (ESI)) were measured on a *VG Plattform II* - spectrometer using ESI (electrospray ionization) techniques at the Department of Chemistry, high resolution mass spectra (HRMS(MALDI)) were measured on a *MALDI LTQ Orbitrap XL*- spectrometer (from *Thermo Fisher Scientific*).

Elemental analysis was determined with *vario MICRO cube* (from *Elementar*) by the Department of Chemistry.

Melting points are reported uncorrected and measured on *Büchi Melting Point B-540*.

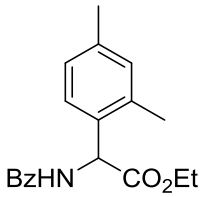
Reactions All yields refer to isolated yields of compounds estimated to be > 95% pure as determined by ^1H-NMR or elementary analysis.

TP: Typical Procedure for the Synthesis α-Amino Acid Derivatives

A 10 mL screw-cap vial was charged with $Bi(OTf)_3$ (1–5 mol%), amide (1.0 equiv.), and nitromethane (2 mL/mmol amide). Ethyl glyoxalate (1.2 equiv.) in nitromethane (2 mL/mmol amide) and the aromatic compound (3.0 – 4.0 equiv.) were added under vigorous stirring. The mixture was heated to 60 – 100 °C and stirred at this temperature for 16 h. After cooling to room temperature, the reaction mixture was diluted with EtOAc and filtered through a short plug of Celite. The plug was rinsed with additional EtOAc. The combined filtrates were concentrated under reduced pressure. Purification of the crude residue by column chromatography (hexane/EtOAc) afforded the analytically pure product.

2 Experimental Procedures

Ethyl-2-(benzamido)-2-(2,4-dimethylphenyl)acetate (4a)



Ethyl-2-(benzamido)-2-(2,4-dimethylphenyl)acetate (**4a**) was synthesized according to TP from benzamide (122 mg, 1.0 mmol), ethyl glyoxalate (122 mg, 1.2 mmol), *m*-xylene (0.37 mL, 3.0 mmol, 3 equiv.) and $Bi(OTf)_3$ (13 mg, 0.02 mmol, 2 mol%) in nitromethane (4 mL) at 80 °C for 16 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as colorless solid (276 mg, 89%).

m.p.: 91-93 °C.

EA (%): calc.: C 73.29 H 6.80 N4.50
found: C 73.26 H 6.53 N4.48.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.82 – 7.79 (m, 2H), 7.51–7.39 (m, 3H), 7.18 (d, J = 7.8 Hz, 1H), 7.06 – 6.99 (m, 3H), 5.93 (d, J = 7.1 Hz, 1H), 4.30 – 4.13 (m, 2H), 2.52 (s, 3H), 2.31 (s, 3H), 1.23 (t, J = 7.1 Hz, 3H).

^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 171.77, 166.67, 138.40, 136.97, 133.89, 132.49, 131.95, 131.91, 128.71, 127.35, 127.27, 126.44, 62.01, 53.53, 21.19, 19.58, 14.17.

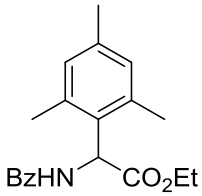
MS (ESI): m/z: calc. for $C_{19}H_{21}NO_3$ 311.15, found 312.02$[M+H]^+$.

IR (cm^{-1}): 3306 (m), 3043 (w), 2985 (m), 1746 (s), 1637 (s), 1578 (w), 1526 (s), 1487 (m), 1449 (w), 1371 (w), 1349 (w), 1322 (w), 1213 (m), 1188 (m), 1152 (w), 1097 (w), 1021 (w), 956 (w), 927 (w), 877 (w), 808 (w), 773 (w), 720 (w), 692 (w), 595 (w), 501 (w).

R_f (hexane/EtOAc 8:2): 0.3.

Analytical data are consistent with literature.[9]

Ethyl-2-(benzamido)-2-mesitylacetate (4b)



Ethyl-2-(benzamido)-2-mesitylacetate (**4b**) was synthesized according to TP from benzamide (121 mg, 1.0 mmol), ethyl glyoxalate (61 mg, 1.2 mmol), mesitylene (0.42 mL, 3 mmol, 3 equiv.) and $Bi(OTf)_3$ (7 mg, 0.01 mmol,

1 mol%) in nitromethane (4 mL) at 80 °C for 16 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as colorless solid (308 mg, 95%).

m.p.: 86-88 °C.

EA (%): calc.: C 73.82 H 7.12 N4.30
found: C 73.84 H 6.80 N4.05

IR (cm^{-1}): 3397 **(**m**),** 2963 (w), 1724 (s), 1658 (s), 1517 (s), 1483 (s), 1369 (w), 1306 (m), 1194 (w), 1088 (m), 1018 (w), 853 (w), 808 (w), 710 (w), 611 (w), 557 (w).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.82 – 7.79 (m, 2H), 7.50 – 7.40 (m, 3H), 7.18 (bd, *J* = 6.2 Hz, 1H), 6.86 (s, 2H), 6.19 (d, *J* = 6.6 Hz, 1H), 4.32 – 4.13 (m, 2H), 2.48 (s, 6H), 2.25 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H).

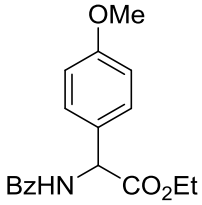
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 171.92, 166.58, 137.81, 137.11, 134.04, 131.83, 130.99, 130.15, 128.73, 127.22, 62.17, 52.81, 21.00, 20.49, 14.22.

MS (ESI): m/z: calc. for $C_{20}H_{23}NO_3$ 325.17, found $[M+H]^+$ 326.00.

R_f (hexane/EtOAc 7:3): 0.6.

Analytical data are consistent with literature.[9]

Ethyl-2-(benzamido)-2-(4-methoxyphenyl)acetate (4c)



Ethyl-2-(benzamido)-2-(4-methoxyphenyl)acetate (**4c**) was synthesized according to TP from benzamide (121 mg, 1.0 mmol), ethyl glyoxalate (122 mg, 1.2 mmol), anisole (0.32 mL, 3.0 mmol, 3 equiv.) and $Bi(OTf)_3$ (7 mg, 0.01 mmol, 1 mol%) in nitromethane (2 mL) at 80 °C for 16 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as colorless solid (236 mg, 75%, ratio of regioisomers 3:1).

m.p.: 82-84 °C.

EA (%): calc.: C 68.99 H 6.11 N 4.47
found: C 68.72 H 6.19 N 4.32.

IR (cm^{-1}): 3309 (m), 2983 (w), 1743 (s), 1637 (s), 1516 (s), 1530 (s), 1486 (w), 1297 (w), 1244 (m), 1212 (m), 1179 (m), 1098 (w), 1027 (w), 830 (w) 713 (w), 587 (w).

^{1}H-NMR (300 MHz, $CDCl_3$) (peaks listed only for major regioisomer): δ = 7.84 – 7.78 (m, 3H), 7.50 – 7.34 (m, 6H), 7.14 (bd, *J* = 6.7 Hz, 1H), 6.90 – 6.87 (m, 2H), 5.70 (d, *J* = 7.0 Hz, 1H), 4.30 – 4.15f (m, 2H), 3.79 (s, 3H), 1.26–1.17 (m, 4H).

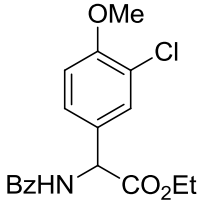
^{13}C-NMR (75 MHz, $CDCl_3$) (peaks listed only for major regioisomer): δ = 171.41, 166.62, 159.86, 133.91, 131.94, 129.02, 128.73, 128.69, 127.27, 114.51, 62.10, 56.44, 55.45, 14.19.

MS (ESI): m/z: calc. for $C_{18}H_{19}NO_4$ 313.13, found 314.00 $[M+H]^+$.

R_f (hexane/EtOAc 7:3): 0.5.

Analytical data are consistent with literature.[9]

Ethyl-2-(benzamido)-2-(3-chloro-4-methoxyphenyl)acetate (4d)



Ethyl-2-(benzamido)-2-(3-chloro-4-methoxyphenyl)acetate (**4d**) was synthesized according to TP from benzamide (121 mg, 1.0 mmol), ethyl glyoxalate (122 mg, 1.2 mmol), 2-chloroanisole (0.38 mL, 3.0 mmol, 3 equiv.) and $Bi(OTf)_3$ (13 mg, 0.02 mmol, 2 mol%) in nitromethane (4 mL) at 80 °C for 16 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as colorless solid (266 mg, 77%).

m.p.: 90-92 °C.

EA (%): calc.: C 62.16 H 5.22 N 4.03
found: C 61.40 H 5.25 N 3.95.

IR (cm^{-1}): 3319 (s), 2977 (w), 2842 (w), 1732 (s), 1537 (s), 1530 (s), 1346 (m), 1297 (s), 1191 (s), 1094 (m), 1053 (m), 1022 (s), 919 (w), 874 (w) 796 (w), 759 (w), 709 (s) 623 (m), 491 (w).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.85 – 7.79 (m, 2H), 7.55 – 7.41 (m, 4H), 7.33 (d, *J* = 8.5 Hz, 1H), 7.20 (d, *J* = 6.5 Hz, 1H), 6.91 (d, *J* = 8.5 Hz, 1H), 5.67 (d, *J* = 6.8 Hz, 1H), 4.33 – 4.14 (m, 2H), 3.89 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H).

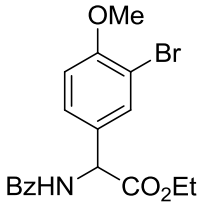
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 170.93, 166.58, 155.26, 133.66, 132.08, 130.09, 129.07, 128.77, 127.28, 127.09, 123.07, 112.37, 62.39, 56.35, 56.02, 14.17.

MS (ESI): m/z: calc. for $C_{18}H_{18}NClO_4$ 347.09, found 348.00$[M+H]^+$.

R_f (hexane/EtOAc 7:3): 0.5.

Analytical data are consistent with literature.[9]

Ethyl-2-(benzamido)-2-(3-bromo-4-methoxyphenyl)acetate (4e)



Ethyl-2-(benzamido)-2-(3-bromo-4-methoxyphenyl)acetate (**4e**) was synthesized according to TP from benzamide (121 mg, 1.0 mmol), ethyl glyoxalate (122 mg, 1.2 mmol), 2-bromoanisole (037 mL, 3.0 mmol, 3 equiv.) and $Bi(OTf)_3$ (13 mg, 0.02 mmol, 2 mol%) in nitromethane (4 mL) at 80 °C for 16 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as colorless solid (344 mg, 88%).

m.p.: 108-110 °C.

EA (%): calc.: C 55.12 H 4.63 N 3.57
found: C 54.94 H 4.37 N 3.32.

IR (cm^{-1}): 3389 (w), 2992 (w), 1738 (m), 1654 (m), 1601 (w), 1580 (w), 1518 (s), 1498 (s), 1484 (s), 1442 (w), 1411 (w), 1391 (w), 1367 (w), 1342 (w), 1286 (m), 1261 (s), 1240 (m), 1213 (s), 1178 (s), 1152 (m), 1096 (w), 1055 (m), 1012 (s), 926 (w), 868 (w), 849 (w), 827 (w), 815 (w), 800 (w), 764 (w), 714 (m), 687 (w), 665 (m), 617 (m9, 558 (m), 538 (m), 500 (m), 468 (w).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.88 – 7.78 (m, 2H), 7.61 (d, *J* = 2.2 Hz, 1H), 7.55 – 7.35 (m, 4H), 7.18 (d, *J* = 6.6 Hz, 1H), 6.88 (d, *J* = 8.5 Hz, 1H), 5.67 (d, *J* = 6.8 Hz, 1H), 4.34 – 4.14 (m, 2H), 3.88 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H).

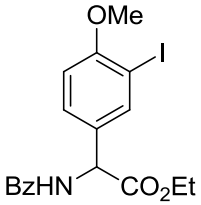
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 170.95, 166.58, 156.16, 133.67, 132.11, 132.09, 130.55, 128.79, 127.89, 127.29, 112.25, 112.20, 62.40, 56.46, 55.93, 14.18.

MS (ESI): m/z: calc. for $C_{18}H_{18}BrNO_4$ 391.04, found 392.60 $[M+H]^+$.

R_f (hexane/ EtOAc 7:3): 0.4.

Analytical data are consistent with literature.[9]

Ethyl-2-(benzamido)-2-(3-iodo-4-methoxyphenyl)acetate (4f)



Ethyl-2-(benzamido)-2-(3-iodo-4-methoxyphenyl)acetate (**4f**) was synthesized according to TP from benzamide (121 mg, 1.0 mmol), ethyl glyoxalate (122 mg, 1.2 mmol), 2-iodoanisole (0.40 mL, 3.0 mmol, 3 equiv.) and $Bi(OTf)_3$ (13 mg, 0.02 mmol, 2 mol%) in nitromethane (4 mL) at 80 °C for 16 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as colorless solid (355 mg, 81%).

m.p.: 123-125 °C.

EA (%):	calc.:	C 49.22	H 4.13	N 3.19
	found:	C 48.93	H 3.99	N 2.96.

IR (cm^{-1}): 3390 (m), 2989 (w), 1738 (s), 1655 (s), 1598 (w), 1579 (w), 1515 (m), 1483 (s), 1440 (m), 1407 (w), 1367 (m), 1343 (w), 1286 (m), 1258 (s), 1214 (m), 1181 (m), 1152 (m), 1096 (w), 1048 (m), 1011 (m), 926 (w), 869 (w), 844 (w), 828 (m), 814 (m), 798 (m), 765 (w), 714 (s), 687 (m), 658 (m), 611 (w), 555 (w), 535 (w), 496 (m), 469 (w).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.83–7.79 (m, 3H), 7.52 – 7.46 (m, 1H), 7.43 – 7.38 (m, 3H), 7.27 – 7.75 (m, 1H), 6.77 (d, *J* = 8.5 Hz, 1H), 5.65 (d, *J* = 6.9 Hz, 1H), 4.29 – 4.11 (m, 2H), 3.83 (s, 3H), 1.26–1.21 (m, 3H).

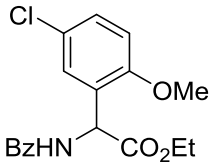
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 170.98, 166.58, 158.40, 138.17, 133.70, 132.07, 131.10, 128.95, 128.79, 127.30, 111.10, 86.52, 62.38, 56.59, 55.74, 14.19.

MS (ESI): m/z: calc. for $C_{18}H_{18}INO_4$ 439.03, found 440.12 $[M+H]^+$.

R_f (hexane/ EtOAc 7:3): 0.4.

Analytical data are consistent with literature.[9]

Ethyl-2-(benzamido)-2-(5-chloro-2-methoxyphenyl)acetate (4g)



Ethyl-2-(benzamido)-2-(5-chloro-2-methoxyphenyl)acetate (**4g**) was synthesized according to TP from benzamide (121 mg, 1.0 mmol), ethyl glyoxalate (122 mg, 1.2 mmol), 4-chloroanisole (0.49 mL, mmol, 4 equiv.) and $Bi(OTf)_3$ (32 mg, 0.05 mmol, 5 mol%) in nitromethane (4 mL) at 100 °C for 16 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as colorless solid (310 mg, 89%).

m.p.: 134-136 °C.

EA (%): calc.: C 62.16 H 5.22 N 4.03
found: C 61.56 H 5.28 N 3.86.

IR (cm^{-1}): 3267 (s), 3057 (w), 2962 (w), 2931 (w), 2835 (w), 1748 (s), 1641 (s), 1579 (w), 1528 (s), 1489 (s), 1364 (w), 1321 (m), 1249 (s), 1206 (m) 1132 (w), 1094 (m), 1026 (s) 976 (w), 901 (w), 869 (w), 809 (m), 718 (m), 687 (m), 641 (m), 601 (w).

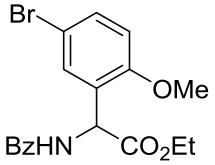
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.83 – 7.78 (m, 2H), 7.53 – 7.41 (m, 4H), 7.28 (d, *J* = 2.7 Hz, 1H), 7.25 (d, *J* = 2.6 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 1H), 5.88 (d, *J* = 8.0 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.85 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 170.71, 166.70, 155.86, 134.08, 131.88, 130.72, 129.54, 128.71, 127.52, 127.30, 126.05, 112.44, 62.03, 56.10, 53.48, 14.23.

MS (ESI): m/z: calc. for $C_{18}H_{18}ClNO_4$ 347.09, found 348.00 $[M+H]^+$.

R_f (hexane/EtOAc 7:3): 0.6.

Ethyl-2-(benzamido)-2-(5-bromo-2-methoxyphenyl)acetate (4h)



Ethyl-2-(benzamido)-2-(5-bromo-2-methoxyphenyl)acetate (**4h**) was synthesized according to TP from benzamide (122 mg, 1.0 mmol), ethyl glyoxalate (122 mg, 1.2 mmol), 4-bromoanisole (0.38 mL, 3.0 mmol, 3 equiv.) and $Bi(OTf)_3$ (33 mg, 0.05 mmol, 5 mol%) in nitromethane (4 mL) at 100 °C for 16 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as colorless solid (161 mg, 41%).

m.p.: 123-125 °C.

EA (%): calc.: C 55.12 H 4.63 N 3.57
found: C 54.86 H 4.50 N 3.42.

IR (cm^{-1}): 1738 (m), 1638 (s), 1576 (m), 1520 (m), 1486 (s), 1365 (s), 1337 (m), 1315 (s), 1247 (s), 1188 (s), 1176 (s), 1131 (m), 1087 (s), 1026 (s), 900 (m), 868 (m), 801 (s), 759 (w), 718 (m), 688 (s), 669 (s), 653 (s), 618 (s), 590 (s), 539 (m), 500 (w).

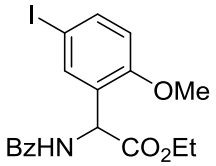
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.81 – 7.78 (m, 1H), 7.56 (d, *J* = 2.5 Hz, 1H), 7.53 – 7.39 (m, 4H), 7.28 – 7.26 (m, H), 6.78 (d, *J* = 8.7 Hz, 1H), 5.88 (d, *J* = 8.0 Hz, 1H), 4.21 (qd, *J* = 7.1, 0.8 Hz, 2H), 3.85 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 170.71, 166.69, 156.38, 134.09, 133.52, 132.54, 131.89, 128.72, 127.98, 127.31, 113.30, 112.95, 62.04, 56.05, 53.40, 14.24.

MS (ESI): m/z: calc. for $C_{18}H_{18}BrNO_4$ 391.04, found 392.70 $[M+H]^+$.

R_f (hexane/ EtOAc 4:1): 0.2.

Ethyl-2-(benzamido)-2-(5-iodo-2-methoxyphenyl)acetate (4i)



Ethyl-2-(benzamido)-2-(5-iodo-2-methoxyphenyl)acetate (**4i**) was synthesized according to TP from benzamide (121 mg, 1.0 mmol), ethyl glyoxalate (122 mg, 1.2 mmol), 4-iodoanisole (702 mg, 3.0 mmol, 3 equiv.) and $Bi(OTf)_3$ (33 mg, 0.05 mmol, 5 mol%) in nitromethane (4 mL) at 100 °C for 16 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as colorless solid (261 mg, 59%).

m.p.: 108-110 °C.

EA (%): calc.: C 49.22 H 4.13 N 3.19
found: C 49.14 H 4.01 N 2.90.

IR (cm^{-1}): 3267 (w), 2960 (w), 2834 (w), 1738 (s), 1637 (s), 1601 (m), 1577 (m), 1522 (s), 1486 (s), 1455 (w), 1391 (w), 1366 (w), 1336 (s), 1318 (m), 1293 (m), 1247 (s), 1187 (m), 1175 (m), 1133 (m), 1091 (m), 1025 (m), 899 (w), 867 (w), 848 (w), 810 (w), 799 (m) 758 (w), 715 (m), 688 (m9, 665 (m9, 652 (w), 609 (m9, 584 (m), 535 (w), 497 (w).

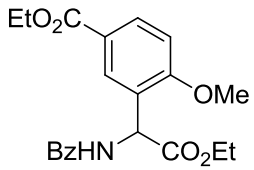
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.82 (dd, *J* = 5.9, 1.9 Hz, 3H), 7.54 – 7.39 (m, 4H), 7.16 (d, *J* = 6.7 Hz, 1H), 6.80 (d, *J* = 8.5 Hz, 1H), 5.65 (d, *J* = 6.8 Hz, 1H), 4.32 – 4.16 (m, 2H), 3.87 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 170.98, 166.58, 158.41, 138.17, 133.70, 132.07, 131.10, 128.95, 128.79, 127.30, 111.10, 86.52, 62.38, 56.59, 55.74, 14.19.

MS (ESI): m/z: calc. for $C_{18}H_{18}INO_4$ 439.03, found 440.60 $[M+H]^+$.

R_f (hexane/ EtOAc 4:1): 0.3.

Ethyl-3-(1-benzamido-2-ethoxy-2-oxoethyl)-4-methoxybenzoate (4j)



Ethyl-3-(1-benzamido-2-ethoxy-2-oxoethyl)-4-methoxybenzoate (**4j**) was prepared according to TP from benzamide (61 mg, 0.5 mmol), ethyl glyoxalate (61 mg, 0.6 mmol), ethyl-4-methoxybenzoate (360 mg, 2.0 mmol, 4 equiv.) and $Bi(OTf)_3$ (16 mg, 0.025 mmol, 5 mol%) in $MeNO_2$ at 100 °C for 3d. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as a yellow oil (77 mg, 40 %).

IR (cm^{-1}): 3342 (w), 2981 (w), 2843 (w), 1741 (m), 1711 (s), 1650 (s), 1608 (m), 1580 (m), 1506 (m), 1484 (m), 1465 (m), 1445 (m), 1391 (w), 1368 (m), 1322 (m), 1297 (m), 1265 (s), 1238 (s), 1204 (s), 1188 (s), 1130 (s), 1103 (m), 1023 (s), 913 (m), 862 (m), 831 (m), 801 (m), 771 (m), 713 (s), 692 (m), 647 (m), 630 (m), 589 (m), 541 (m), 473 (m).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 2.1 Hz, 1H), 8.04 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.82 – 7.79 (m, 2H), 7.53 – 7.43 (m, 3H), 7.27 (bs, 1H), 6.93 (d, *J* = 8.7 Hz, 1H), 6.00 (d, *J* = 8.0 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.92 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H).

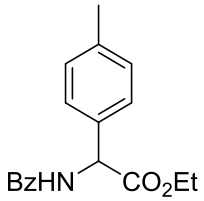
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 170.86, 166.73, 166.11, 160.76, 134.16, 132.20, 132.13, 131.84, 128.69, 127.31, 125.93, 123.56, 110.71, 61.98, 61.01, 56.06, 53.61, 14.53, 14.23.

MS (ESI): m/z: calc. for $C_{21}H_{23}NO_6$ 385.15 found 408.06 $[M+Na]^+$.

HRMS (MALDI): m/z: calc. for $C_{21}H_{23}NO_6$ 386.15981 $[M+H]^+$, found 386.16001.

R_f (hexane/EtOAc 7:3): 0.3.

Ethyl-2-(benzamido)-2-*p*-tolylacetate (4k)



Ethyl-2-(benzamido)-2-*p*-tolylacetate (**4k**) was prepared according to TP from benzamide (61 mg, 0.5 mmol), ethyl glyoxalate (61 mg, 0.6 mmol), toluene (0.22 mL, 2.1 mmol) and $Bi(OTf)_3$ (7 mg, 0.005 mmol, 2 mol%) in DCE at 100 °C for 16 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as a colourless solid (74 mg, 50%, ratio of regioisomers 3:1).

m.p.: 99-101 °C.

IR (cm^{-1}): 3290 (w), 1743 (s), 1636 (s), 1603 (m), 1581 (m), 1527 (s), 1488 (s), 1447 (m), 1372 (m), 1348 (m), 1330 (m), 1300 (w), 1275 (w), 1252 (m), 1206 (s), 1178 (s), 1153 (s), 1096 (m), 1075 (w), 1021 (s), 928 (w), 815 (m), 803 (w), 791 (w), 759 (m), 723 (s), 711 (s), 691 (s), 634 (m), 615 (m), 587 (s), 573 (m), 512 (m), 487 (m), 459 (w).

^{1}H-NMR (300 MHz, $CDCl_3$) (peaks listed only for major regioisomer): δ = 7.83 – 7.80 (m, 2H), 7.54 – 7.40 (m, 3H), 7.35 – 7.32 (m, *J* = 8.1 Hz, 2H), 7.24 – 7.16 (m, *J* = 15.2, 5.8 Hz, 2H), 7.11 (bd, *J* = 6.9 Hz, 1H), 5.73 (d, *J* = 7.0 Hz, 1H), 4.33–4.11 (m, 2H), 2.34 (s, 3H), 1.29–1.19 (m, 3H).

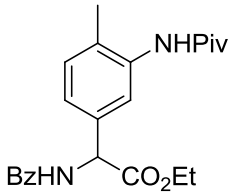
^{13}C-NMR (75 MHz, $CDCl_3$) (peaks are not assigned to regioisomers): δ = 171.33, 166.61, 138.51, 137.19, 135.48, 133.94, 131.93, 131.17, 129.81, 128.73, 128.60, 127.34, 127.28, 126.67, 126.45, 62.12, 56.75, 53.71, 21.30, 19.68, 14.18.

MS (ESI): m/z: calc. for $C_{18}H_{19}NO_3$ 297.1 found 298.5 $[M+H]^+$.

HRMS (MALDI): m/z: calc. for $C_{18}H_{19}NO_3$ 298.14377 $[M+H]^+$, found 298.14387.

R_f (hexane/EtOAc 4:1): 0.4.

Ethyl-2-benzamido-2-(4-methyl-3-pivalamidophenyl)acetate (4l)



Ethyl-2-benzamido-2-(4-methyl-3-pivalamidophenyl)acetate (**4l**) was prepared according to TP from benzamide (61 mg, 0.5 mmol), ethyl glyoxalate (61 mg, 0.6 mmol), 2-methylpivalanilide (287 mg, 1.5 mmol, 3 equiv.) and $Bi(OTf)_3$ (16 mg, 0.025 mmol, 5 mol%) in $MeNO_2$ at 100 °C for 24 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as a yellow solid (89 mg, 45%).

m.p.: 123-125 °C

IR (cm^{-1}): 2959 (w), 2923 (m), 2853 (w), 1744 (s), 1661 (s), 1643 (s), 1615 (w), 1602 (w), 1580 (w), 1519 (s), 1489 (s), 1446 (m), 1417 (w), 1399 (w), 1367 (m), 1340 (s), 1299 (s), 1265 (s), 1218 (m), 1194 (s), 1170 (s), 1092 (m), 1023 (m), 947 (w), 923 (w), 880 (w), 800 (w), 777 (m), 749 (w), 714 (s), 691 (s), 620 (s), 608 (s), 584 (s), 540 (m).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.91 (d, J = 9.0 Hz, 1H), 7.82 – 7.79 (m, 2H), 7.51 – 7.41 (m, 3H), 7.28 (s, 2H), 7.23 (bs, 1H), 7.12 (bd, J = 6.8 Hz, 1H), 5.68 (d, J = 6.9 Hz, 1H), 4.30 – 4.13 (m, 2H), 2.26 (s, 3H), 1.33 (s, 9H), 1.24 (t, J = 5.8 Hz, 3H).

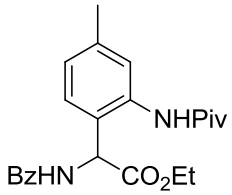
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 176.62, 171.17, 166.58, 136.33, 133.87, 133.12, 131.96, 129.73, 129.14, 128.74, 127.28, 125.76, 123.17, 62.22, 56.61, 39.95, 27.83, 17.83, 14.17.

MS (ESI): m/z: calc. for $C_{23}H_{28}N_2O_4$ 396.2, found 420.0 $[M+Na]^+$.

HRMS (MALDI): m/z: calc. for 435.16807 $C_{23}H_{28}N_2O_4$ $[M+K]^+$, found 435.16741.

R_f (hexane/ EtOAc 1:1): 0.5.

Ethyl-2-benzamido-2-(4-methyl-2-pivalamidophenyl)acetate (4m)



Ethyl-2-benzamido-2-(4-methyl-2-pivalamidophenyl)acetate (**4m**) was prepared according to TP from benzamide (61 mg, 0.5 mmol), ethyl glyoxalate (61 mg, 0.6 mmol), 3-methylpivalanilide (287 mg, 1.5 mmol, 3 equiv.) and $Bi(OTf)_3$ (16 mg, 0.025 mmol, 5 mol%) in $MeNO_2$ at 100 °C for 24 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as a yellow solid (133 mg, 67%, r.r. 21:1).

m.p.: 157-159 °C

IR (cm^{-1}): 3244 (w), 2962 (w), 1742 (s), 1666 (m), 1638 (s), 1600 (m), 1582 (w), 1524 (s), 1505 (s), 1481 (m), 1443 (m), 1399 (m), 1387 (m), 1369 (m), 1335 (s), 1252 (m), 1194 (s), 1158 (s), 1105 (m), 1076 (m), 1019 (m), 949 (w), 911 (m), 872 (m), 839 (w), 829 (w), 814 (w), 796 (w), 769 (m), 691 (s), 665 (m), 596 (m), 567 (w), 519 (w), 489 (w).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.80 – 7.78 (m, 2H), 7.52 – 7.48 (m, 1H), 7.44 – 7.37 (m, 4H), 7.31 (bs, 1H), 7.23 (d, J = 8.2 Hz, 1H), 7.08 (bd, J = 6.7 Hz, 1H), 5.90 (d, J = 6.9 Hz, 1H), 4.27 – 4.12 (m, 2H), 2.53 (s, 3H), 1.30 (s, 9H), 1.22 (t, J = 7.1 Hz, 3H).

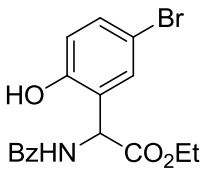
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 176.84, 171.55, 166.66, 138.19, 138.05, 133.76, 131.92, 131.21, 128.70, 127.23, 127.16, 122.30, 118.13, 62.08, 53.35, 39.73, 27.68, 19.71, 14.11.

MS (ESI): m/z: calc. for $C_{23}H_{28}N_2O_4$ 396.21, found 419.12 $[M+Na]^+$.

HRMS (MALDI): m/z: calc. for $C_{23}H_{28}N_2O_4$ 397.21218 $[M+H]^+$, found 397.21816.

R_f (hexane/ EtOAc 1:1) = 0.5.

Ethyl-2-(benzamido)-2-(5-bromo-2-hydroxyphenyl)acetate (4n)



Ethyl-2-(benzamido)-2-(5-bromo-2-hydroxyphenyl)acetate (**4n**) was prepared according to TP from benzamide (61 mg, 0.5 mmol), ethyl glyoxalate (61 mg, 0.6 mmol), 4-bromophenol (260 mg, 1.5 mmol) and $Bi(OTf)_3$ (3 mg, 0.005 mmol, 1 mol%) in DCE at 80°C for 16 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as a colourless solid (123 mg, 65%).

m.p.: 155–157 °C.

EA (%): calc.: C 53.99 H 4.26 N 3.70
found: C 53.84 H 4.46 N 3.55.

IR (cm^{-1}) = 3368 (w), 3098 (w), 1736 (s), 1622 (s), 1607 (m), 1591 (w), 1576 (w), 1530 (s), 1488 (m), 1430 (m), 1364 (m), 1344 (m), 1311 (m), 1300 (m), 1278 (s), 1237 (m), 1200 (s), 1184 (s), 1121 (w), 1091 (m), 1023 (s), 984 (w), 935 (w), 878 (m), 858 (w), 814 (s), 782 (w), 727 (s), 694 (m), 656 (m), 632 (w), 621 (s), 599 (s), 584 (m), 540 (m), 492 (m), 469 (w).

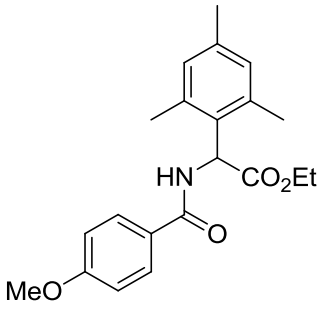
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 9.46 (bs, 1H), 7.83 – 7.80 (m, 2H), 7.61 (bd, *J* = 6.6 Hz, 1H), 7.57 – 7.53 (m, 1H), 7.47 – 7.44 (m, 2H), 7.33 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.13 (d, *J* = 2.4 Hz, 1H), 6.92 (d, *J* = 8.7 Hz, 1H), 5.83 (d, *J* = 6.9 Hz, 1H), 4.38–4.30 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 170.73, 168.46, 155.07, 133.45, 132.82, 132.13, 130.00, 128.95, 127.47, 126.26, 121.41, 112.70, 63.05, 51.91, 14.12.

MS (ESI): m/z: calc. for $C_{18}H_{18}BrNO_4$ 377.03, found 378.17 $[M+H]^+$.

R_f (hexane/EtOAc 4:1): 0.3.

Ethyl-2-mesityl-2-(4-methoxybenzamido)acetate (5a)



Ethyl-2-mesityl-2-(4-methoxybenzamido)acetate (**5a**) was prepared according to TP from 4-methoxybenzamide (76 mg, 0.5 mmol), ethyl glyoxalate (61 mg, 0.6 mmol), mesitylene (0.21 mL, 1.5 mmol, 3 equiv.) and $Bi(OTf)_3$ (7 mg, 0.01 mmol, 2 mol%) in nitromethane (2 mL) at 80 °C for 16 h. Purification by chromatography (cyclohexane/EtOAc 9:1 → 4:1) yielded the product as a colorless solid (145 mg, 81%).

m.p.: 108–109 °C.

EA (%): calc.: C 70.96 H 7.09 N 3.94
found: C 70.99 H 7.29 N 3.62.

IR (cm^{-1}): 3433 (w), 2980 (m), 1727 (s), 1652 (s), 1604 (m), 1523 (w), 1439 (m), 1213 (m), 1175 (s), 905 (w), 795 (w), 723 (m), 695 (w).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.84 – 7.65 (m, 2H), 7.07 (d, *J* = 6.4 Hz, 1H), 6.95 – 6.88 (m, 2H), 6.85 (s, 2H), 6.18 (d, *J* = 6.5 Hz, 1H), 4.33 – 4.08 (m, 2H), 3.84 (s, 3H), 2.47 (s, 6H), 2.25 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H).

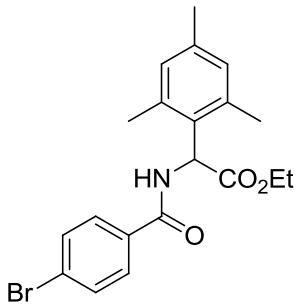
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 172.06, 166.12, 162.50, 137.74, 137.12, 131.18, 130.14, 129.05, 126.34, 113.93, 62.12, 55.54, 52.76, 21.01, 20.50, 14.23.

MS (ESI): m/z: calc. for $C_{21}H_{25}NO_4$ 355.2, found 356.2 $[M+H]^+$.

R_f (cyclohexane/EtOAc 4:1): 0.2.

Analytical data are consistent with literature.[9]

Ethyl-2-(4-bromobenzamido)-2-mesitylacetate (5b)



Ethyl-2-(4-bromobenzamido)-2-mesitylacetate (**5b**) was prepared according to TP from 4-bromobenzamide (100 mg, 0.5 mmol), ethyl glyoxalate (61 mg, 0.6 mmol), mesitylene (0.21 mL, 1.5 mmol, 3 equiv.) and $Bi(OTf)_3$ (7 mg, 0.01 mmol, 2 mol%) in nitromethane (2 mL) at 80 °C for 16 h. Purification by chromatography (cyclohexane/EtOAc 9:1 → 4:1) yielded the product as a colorless, highly viscous oil (161 mg, 80%).

EA (%): calc.: C 59.42 H 5.48 N 3.46
found: C 59.19 H 5.75 N 3.06.

IR (cm^{-1}): 3331 (w), 2980 (m), 1732 (s), 1651 (m), 1611 (w), 1590 (m), 1476 (s), 1211 (s), 1195 (s), 1068 (s), 1010 (s), 722 (w), 684 (w).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.73 – 7.62 (m, 2H), 7.62 – 7.48 (m, 2H), 7.14 (d, *J* = 6.2 Hz, 1H), 6.86 (s, 2H), 6.15 (d, *J* = 6.5 Hz, 1H), 4.33 – 4.11 (m, 2H), 2.46 (s, 6H), 2.25 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H).

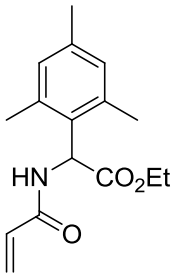
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 171.82, 165.63, 137.93, 137.09, 132.87, 131.99, 130.75, 130.19, 128.83, 126.58, 62.27, 52.88, 21.00, 20.47, 14.21.

MS (ESI): m/z: calc. for $C_{20}H_{22}BrNO_3$ 403.1, found 404.1 $[M+H]^+$.

R_f (cyclohexane/EtOAc 4:1): 0.5.

Analytical data are consistent with literature.[9]

Ethyl-2-acrylamido-2-mesitylacetate (5c)



Ethyl-2-acrylamido-2-mesitylacetate (**5c**) was prepared according to TP from acrylamide (71 mg, 1.0 mmol), ethyl glyoxalate (122 mg, 1.2 mmol), mesitylene (0.42 mL, 3.0 mmol, 3 equiv.) and $Bi(OTf)_3$ (7 mg, 0.01 mmol, 1 mol%) in nitromethane (4 mL) at 80 °C for 16 h. Purification by chromatography (cyclohexane/EtOAc 4:1 → 2:1) yielded the product as a colorless solid (226 mg, 82%).

m.p.: 118–119 °C.

EA (%): calc.: C 69.79 H 7.69 N 5.09
found: C 69.87 H 7.66 N 5.10.

IR (cm^{-1}): 3658 (w), 3303 (w), 2981 (s), 1748 (m), 1670 (w), 1653 (m), 1613 (m), 1520 (m), 1231 (m), 1071 (m), 1022 (m), 957 (s), 856 (m), 810 (m), 603 (m).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 6.84 (s, 2H), 6.55 (d, *J* = 6.1 Hz, 1H), 6.29 (dd, *J* = 17.0, 1.7 Hz, 1H), 6.21 – 6.04 (m, 2H), 5.66 (dd, *J* = 10.0, 1.7 Hz, 1H), 4.32 – 4.08 (m, 2H), 2.40 (s, 6H), 2.24 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H).

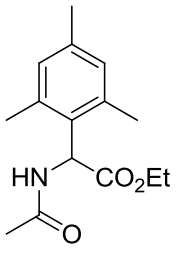
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 171.77, 164.74, 137.86, 137.06, 130.89, 130.34, 130.12, 127.38, 62.14, 52.40, 20.99, 20.40, 14.21.

MS (ESI): m/z: calc. for $C_{16}H_{21}NO_3$ 275.2, found 276.2 $[M+H]^+$.

R_f (cyclohexane/EtOAc 7:3): 0.3.

Analytical data are consistent with literature.[9]

Ethyl-2-acetamido-2-mesitylacetate (5d)



Ethyl-2-acetamido-2-mesitylacetate (**5d**) was prepared according to TP from acetamide (59 mg, 1.0 mmol), ethyl glyoxalate (122 mg, 1.2 mmol), mesitylene (0.42 mL, 3.0 mmol, 3 equiv.) and $Bi(OTf)_3$ (33 mg, 0.05 mmol, 5 mol%) in nitromethane (4 mL) at 80 °C for 16 h. Purification by chromatography (cyclohexane/EtOAc 4:1 → 1:1) yielded the product as a colorless, highly viscous oil (209 mg, 79%).

EA (%): calc.: C 68.42 H 8.04 N 5.32
found: C 68.16 H 8.32 N 5.09.

IR (cm^{-1}): 3302 (m), 2975 (w), 1748 (s), 1646 (m), 1484 (m), 1455 (m), 1211 (s), 1123 (m), 1022 (m), 855 (m), 811 (w), 796 (m), 683 (m).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 6.84 (s, 2H), 6.39 (d, *J* = 6.7 Hz, 1H), 6.02 (d, *J* = 7.2 Hz, 1H), 4.30 – 4.07 (m, 2H), 2.38 (s, 6H), 2.25 (s, 3H), 2.02 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H).

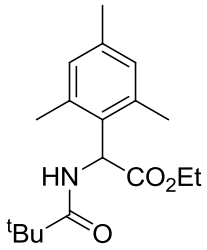
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 171.92, 169.40, 137.83, 137.01, 131.16, 130.07, 62.01, 52.25, 23.19, 20.98, 20.38, 14.21.

MS (ESI): m/z: calc. for $C_{15}H_{21}NO_3$ 263.2, found 264.2 $[M+H]^+$.

R_f (cyclohexane/EtOAc 1:1): 0.5.

Analytical data are consistent with literature.[9]

Ethyl-2-mesityl-2-pivalamidoacetate (5e)



Ethyl-2-mesityl-2-pivalamidoacetate (**5e**) was prepared according to TP from pivalamide (101 mg, 1.0 mmol), ethyl glyoxalate (122 mg, 1.2 mmol), mesitylene (0.42 mL, 3.0 mmol, 3 equiv.) and $Bi(OTf)_3$ (7 mg, 0.01 mmol, 1 mol%) in nitromethane (4 mL) at 80 °C for 16 h. Purification by chromatography (cyclohexane/EtOAc 9:1 → 4:1) yielded the product as a colorless, highly viscous oil (248 mg, 81%).

EA (%): calc.: C 70.79 H 8.91 N 4.59
found: C 70.01 H 9.09 N 4.59.

IR (cm^{-1}): 3449 (w), 2960 (m), 1730 (s), 1670 (s), 1492 (s), 1463 (m), 1216 (m), 1147 (m), 1016 (m), 907 (w), 838 (w), 721 (w), 626 (w).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 6.83 (s, 2H), 6.68 (d, *J* = 6.1 Hz, 1H), 5.96 (d, *J* = 6.7 Hz, 1H), 4.29 – 4.05 (m, 2H), 2.40 (s, 6H), 2.24 (s, 3H), 1.23 – 1.16 (m, 12H).

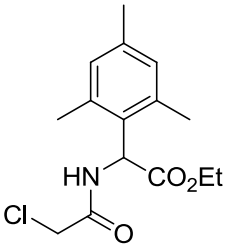
^{13}C- NMR (75 MHz, $CDCl_3$): δ = 177.74, 172.03, 137.60, 137.00, 131.14, 130.11, 61.96, 52.35, 38.90, 27.65, 20.99, 20.36, 14.19.

MS (ESI): m/z: calc. for $C_{18}H_{27}NO_3$ 305.2, found 306.2 $[M+H]^+$.

R_f (cyclohexane/EtOAc 4:1): 0.5.

Analytical data are consistent with literature.[9]

Ethyl-2-(2-chloroacetamido)-2-mesitylacetate (5f)



Ethyl 2-(2-chloroacetamido)-2-mesitylacetate (**5f**) was prepared according to TP from 2-chloroacetamide (47 mg, 0.5 mmol), ethyl glyoxalate (61 mg, 0.6 mmol), mesitylene (0.21 mL, 1.5 mmol, 3 equiv.) and $Bi(OTf)_3$ (7 mg, 0.01 mmol, 2 mol%) in nitromethane (2 mL) at 80 °C for 16 h. Purification by chromatography (cyclohexane/EtOAc 4:1 → 2:1) yielded the product as a colorless, highly viscous oil (121 mg, 81%).

IR (cm^{-1}): 3405 (w), 2980 (m), 1734 (s), 1662 (s), 1611 (w), 1517 (s), 1462 (m), 1212 (s), 1017 (s), 941 (w), 768 (m), 722 (w).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.59 (d, *J* = 6.2 Hz, 1H), 6.85 (s, 2H), 5.99 (d, *J* = 7.2 Hz, 1H), 4.29 – 3.99 (m, 4H), 2.40 (s, 6H), 2.25 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H).

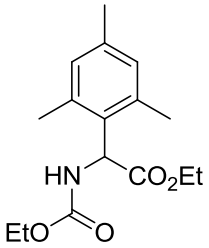
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 171.07, 165.26, 138.11, 137.07, 130.35, 130.20, 62.25, 52.47, 42.67, 21.01, 20.36, 14.20.

MS (ESI): m/z: calc. for $C_{15}H_{20}ClNO_3$ 297.1, found 298.2 $[M+H]^+$.

HRMS (MALDI): m/z: calc. for $C_{15}H_{21}ClNO_3$ 298.12045 $[M+H]^+$, found 298.12028.

R_f (cyclohexane/EtOAc 7:3): 0.6.

Ethyl-2-((ethoxycarbonyl)amino)-2-mesitylacetate (5g)



Ethyl-2-((ethoxycarbonyl)amino)-2-mesitylacetate (**5g**) was prepared according to TP from ethyl carbamate (45 mg, 0.5 mmol), ethyl glyoxalate (61 mg, 0.6 mmol), mesitylene (0.21 mL, 1.5 mmol, 3 equiv.) and $Bi(OTf)_3$ (7 mg, 0.01 mmol, 2 mol%) in nitromethane (2 mL) at 80 °C for 16 h. Purification by chromatography (cyclohexane/EtOAc 9:1 → 4:1) yielded the product as a colorless, highly viscous oil (126 mg, 86%).

EA (%): calc.: C 65.51 H 7.90 N 4.77
found: C 65.80 H 8.04 N 4.54.

IR (cm^{-1}): 3385 (w), 2980 (m), 1716 (s), 1611 (w), 1500 (m), 1212 (s), 1194 (s), 1054 (s), 852 (m), 776 (m), 735 (w), 631 (m).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 6.84 (s, 2H), 5.80 (d, *J* = 7.0 Hz, 1H), 5.66 (d, *J* = 5.5 Hz, 1H), 4.30 – 4.03 (m, 4H), 2.37 (s, 6H), 2.25 (s, 3H), 1.26–1.17 (m, 6H).

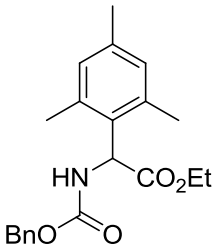
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 171.88, 156.03, 137.74, 136.91, 131.43, 130.06, 61.99, 61.30, 53.57, 20.99, 20.28, 14.67, 14.21.

MS (ESI): m/z: calc. for $C_{16}H_{23}NO_4$ 293.2, found 294.2 $[M+H]^+$.

R_f (cyclohexane/EtOAc 4:1): 0.3.

Analytical data are consistent with literature.[9]

Ethyl-2-(((benzyloxy)carbonyl)amino)-2-mesitylacetate (5h)



Ethyl-2-(((benzyloxy)carbonyl)amino)-2-mesitylacetate (**5h**) was prepared according to TP from benzyl carbamate (76 mg, 0.5 mmol), ethyl glyoxalate (61 mg, 0.6 mmol), mesitylene (0.21 mL, 1.5 mmol, 3 equiv.) and $Bi(OTf)_3$ (7 mg, 0.01 mmol, 2 mol%) in nitromethane (2 mL) at 80 °C for 16 h. Purification by chromatography (cyclohexane/EtOAc 9:1 → 4:1) yielded the product as a colorless solid (116 mg, 65%).

m.p.: 69–71 °C

EA (%): calc.: C 70.96 H 7.09 N 3.94
found: C 70.60 H 7.25 N 3.86.

IR (cm^{-1}): 3375 (w), 2980 (m), 1716 (s), 1611 (w), 1497 (s), 1454 (m), 1212 (s), 1195 (s), 1051 (s), 1027 (s), 774 (m), 697 (s).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.34 (s, 5H), 6.84 (s, 2H), 5.80 (d, *J* = 6.2 Hz, 2H), 5.08 (q, *J* = 12.1 Hz, 2H), 4.28–4.08 (m, 2H), 2.37 (s, 6H), 2.25 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H).

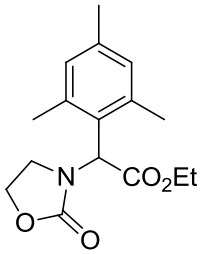
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 171.71, 155.75, 137.81, 136.93, 136.34, 131.26, 130.09, 128.65, 128.28, 67.19, 62.03, 53.70, 20.99, 20.30, 14.20.

MS (ESI): m/z: calc. for $C_{21}H_{25}NO_4$ 355.2, found 356.2 $[M+H]^+$.

R_f (cyclohexane/EtOAc 4:1): 0.4.

Analytical data are consistent with literature.[9]

Ethyl-2-mesityl-2-(2-oxooxazolidin-3-yl)acetate (5k)



Ethyl-2-mesityl-2-(2-oxooxazolidin-3-yl)acetate (**5k**) was prepared according to TP from oxazolidin-2-one (87 mg, 1.0 mmol), ethyl glyoxalate (122 mg, 1.2 mmol), mesitylene (0.42 mL, 3.0 mmol, 3 equiv.) and $Bi(OTf)_3$ (13 mg, 0.02 mmol, 2 mol%) in nitromethane (4 mL) at 80 °C for 16 h. Purification by chromatography (cyclohexane/EtOAc 4:1) yielded the product as a colorless solid (234 mg, 80%).

m.p.: 127–128 °C

EA (%): calc.: C 65.96 H 7.27 N 4.81
found: C 65.82 H 7.25 N 4.69.

IR (cm^{-1}): 2921 (w), 1732 (s), 1611 (w), 1486 (w), 1447 (m), 1239 (m), 1144 (w), 1023 (s), 884 (m), 738 (w), 699 (m), 676 (m).

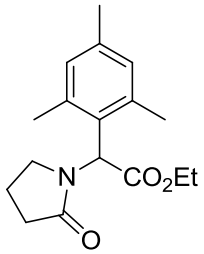
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 6.89 (s, 2H), 5.88 (s, 1H), 4.45 – 4.14 (m, 4H), 3.93 (dd, *J* = 17.2, 8.3 Hz, 1H), 3.13 (ddd, *J* = 9.0, 7.8, 4.9 Hz, 1H), 2.28 (d, *J* = 2.7 Hz, 9H), 1.26 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 171.43, 158.38, 138.57, 137.94, 130.30, 127.84, 62.51, 62.09, 55.55, 41.88, 20.98, 20.52, 14.25.

MS (ESI): m/z: calc. for $C_{16}H_{21}NO_4$ 291.2, found 292.2 $[M+H]^+$.

R_f (cyclohexane/EtOAc 7:3): 0.2.

Ethyl-2-mesityl-2-(2-oxopyrrolidin-1-yl)acetate (5l)



Ethyl-2-mesityl-2-(2-oxopyrrolidin-1-yl)acetate (**5l**) was prepared according to TP from pyrrolidin-2-one (85 mg, 1.0 mmol), ethyl glyoxalate (122 mg, 1.2 mmol), mesitylene (0.42 mL, 3.0 mmol, 3 equiv.) and $Bi(OTf)_3$ (13 mg, 0.02 mmol, 2 mol%) in nitromethane (4 mL) at 80 °C for 16 h. Purification by chromatography (cyclohexane/EtOAc 4:1) yielded the product as a colorless solid (182 mg, 63%).

m.p.: 141–142 °C

EA (%): calc.: C 70.56 H 8.01 N 4.84
found: C 70.47 H 7.97 N 4.66.

IR (cm^{-1}): 2988 (w), 2926 (w), 1743 (s), 1681 (s), 1610 (m), 1491 (m), 1460 (m), 1245 (m), 1187 (s), 1023 (m), 903 (w), 860 (m), 673 (m).

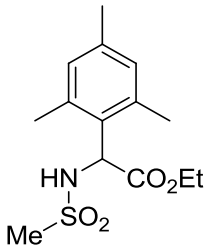
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 6.87 (s, 2H), 6.12 (s, 1H), 4.33 – 4.11 (m, 2H), 3.66 (dd, *J* = 16.6, 8.0 Hz, 1H), 2.93 (td, *J* = 8.9, 3.6 Hz, 1H), 2.56 – 2.35 (m, 2H), 2.26 (d, *J* = 4.5 Hz, 9H), 2.10 – 1.99 (m, 1H), 1.86–1.79 (m, 1H), 1.24 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 175.31, 171.65, 138.14, 130.10, 128.23, 61.84, 54.01, 44.21, 30.84, 20.96, 20.55, 18.33, 14.24.

MS (ESI): m/z: calc. for $C_{17}H_{23}NO_3$ 289.2, found 290.2 $[M+H]^+$.

R_f (cyclohexane/EtOAc 7:3): 0.2.

Ethyl-2-mesityl-2-(methylsulfonamido)acetate (7a)



Ethyl-2-mesityl-2-(methylsulfonamido)acetate (**7a**) was synthesized according to TP from methanesulfonamide (49 mg, 0.5 mmol), ethyl glyoxalate (61 mg, 0.6 mmol), mesitylene (0.21 mL, 1.5 mmol, 3 equiv.) and $Bi(OTf)_3$ (7 mg, 0.01 mmol, 2 mol%) in nitromethane (2 mL) at 80 °C for 20 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as colourless solid (81 mg, 54 %).

m.p.: 126-128 °C

IR (cm^{-1}): 3298 (w), 2966 (w), 2927 (w), 2111 (w), 1732 (s), 1609 (w), 1464 (w), 1413 (m), 1401 (m), 1366 (w), 1327 (s), 1311 (s), 1289 (s), 1254 (m), 1219 (s), 1199 (s), 1161 (s), 1145 (s), 1096 (s), 1021 (m), 987 (s), 970 (s), 909 (w), 872 (m), 855 (s), 827 (m), 784 (w), 762 (s), 721 (w), 636 (w), 602 (m), 555 (m), 528 (s), 513 (s), 475 (m).

^{1}H-NMR (300 MHz, $CDCl_3$) δ = 6.86 (s, 2H), 5.64 (d, *J* = 4.0 Hz, 1H), 5.41 (bd, *J* = 3.5 Hz, 1H), 4.29 – 4.13 (m, 2H), 2.61 (s, 3H), 2.35 (s, 6H), 2.26 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H).

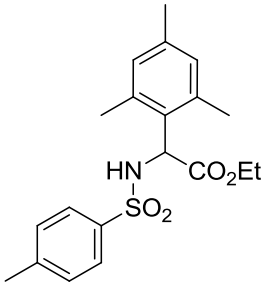
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 171.21, 138.51, 137.35, 130.28, 129.78, 62.68, 55.24, 42.03, 21.04, 20.10, 14.20.

MS (ESI): m/z: calc. for $C_{14}H_{21}NO_4S$ 299.12, found 322.03 $[M+Na]^+$.

HRMS (MALDI): m/z: calc. for $C_{14}H_{21}NO_4S$ 338.08229 $[M+K]^+$, found 338.08230.

R_f (hexane/ EtOAc 7:3): 0.5.

Ethyl-2-mesityl-2-(4-methylphenylsulfonamido)acetate (7b)



Ethyl-2-mesityl-2-(4-methylphenylsulfonamido)acetate (**7b**) was prepared according to TP from 4-methyl-benzenesulfonamide (87 mg, 0.5 mmol), ethyl glyoxalate (61 mg, 0.6 mmol), mesitylene (0.21 mL, 1.5 mmol) and $Bi(OTf)_3$ (7 mg, 0.01 mmol, 2 mol%) in nitromethane (2 mL) at 80 °C for 16 h. Purification by chromatography (hexane/EtOAc 9:1 → 4:1) yielded the product as a colourless solid (148 mg, 79%).

m.p.: 138-140 °C

IR (cm^{-1}): 3275 (w), 2923 (w), 1735 (s), 1611 (w), 1597 (w), 1451 (w), 1407 (w), 1367 (w), 1330 (m), 1289 (m), 1265 (m), 1228 (m), 1187 (w), 1163 (s), 1119 (w), 1095 (w), 1065 (m), 1023 (m), 972 (w), 938 (w), 911 (m), 870 (m), 838 (w), 825 (w), 809 (s), 778 (w), 721 (m), 705 (w), 670 (m), 586 (s), 552 (s), 530 (m), 486 (w).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 8.3 Hz, 2H), 7.07 (d, *J* = 8.1 Hz, 2H), 6.65 (s, 2H), 5.69 (d, *J* = 4.6 Hz, 1H), 5.51 (d, *J* = 4.7 Hz, 1H), 4.20 – 4.03 (m, 2H), 2.34 (s, 3H), 2.21 (s, 6H), 2.21 (s, 3H), 1.12 (t, *J* = 7.1 Hz, 3H).

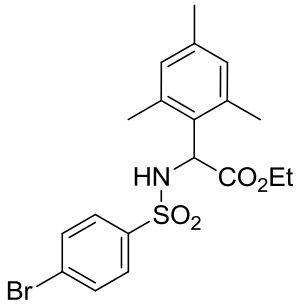
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 170.93, 143.13, 137.99, 137.18, 137.13, 129.84, 129.46, 129.17, 126.99, 62.55, 55.01, 21.59, 20.92, 20.12, 14.10.

MS (ESI): m/z: calc. for $C_{20}H_{25}NO_4S$ 375.15, found 398.06 $[M+Na]^+$.

HRMS (MALDI): m/z: calc. for $C_{20}H_{25}NO_4S$ 414.11359 $[M+K]^+$, found 414.11325.

R_f (cyclohexane/EtOAc 4:1): 0.3.

Ethyl-2-(4-bromophenylsulfonamido)-2-mesitylacetate (7c)



Ethyl-2-(4-bromophenylsulfonamido)-2-mesitylacetate (**7c**) was prepared according to TP from 4-bromo-benzenesulfonamide (120 mg, 0.5 mmol), ethyl glyoxalate (61 mg, 0.6 mmol), mesitylene (0.21 mL, 1.5 mmol) and $Bi(OTf)_3$ (7 mg, 0.01 mmol, 2 mol%) in nitromethane (2 mL) at 100 °C for 16 h. Purification by chromatography (hexane/EtOAc 4:1 → 7:3) yielded the product as a colourless solid (118 mg, 54%).

m.p.: 114-116 °C

IR (cm^{-1}): 3309 (w), 2965 (w), 1732 (s), 1610 (w), 1577 (w), 1473 (w), 1449 (w), 1391 (m), 1370 (m), 1323 (s), 1299 (m), 1278 (s), 1247 (m), 1223 (m), 1200 (m), 1159 (s), 1147 (s), 1090 (s), 1071 (s), 1033 (m), 1012 (m), 975 (w), 925 (m), 852 (m), 818 (s), 764 (w), 740 (s), 724 (m), 703 (w), 615 (s), 593 (m), 562 (s), 553 (s), 532 (m), 475 (m).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.37 – 7.30 (m, 4H), 6.63 (s, 2H), 5.84 (bd, *J* = 4.2 Hz, 1H), 5.57 (d, *J* = 4.3 Hz, 1H), 4.23 – 4.06 (m, 2H), 2.20 (s, 6H), 2.19 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H).

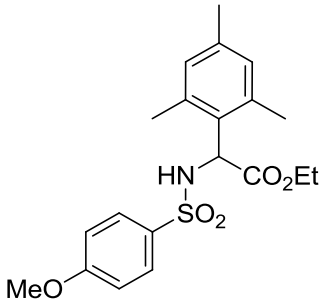
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 170.65, 139.23, 138.40, 137.17, 131.58, 129.83, 128.78, 128.32, 127.12, 62.68, 55.01, 20.88, 20.01, 14.09.

MS (ESI): m/z: calc. for $C_{19}H_{22}BrNO_4S$ 439.05, found 461.96 $[M+Na]^+$.

HRMS (MALDI): m/z: calc. for $C_{19}H_{22}BrNO_4S$ 478.00845 $[M+K]^+$, found 478.00689.

R_f (hexane/EtOAc 4:1): 0.6.

Ethyl-2-mesityl-2-(4-methoxyphenylsulfonamido)acetate (7d)



Ethyl-2-mesityl-2-(4-methoxyphenylsulfonamido)acetate (**7d**) was synthesized according to TP from 4-methoxybenzenesulfonamide (196 mg, 0.5 mmol), ethyl glyoxalate (61 mg, 0.6 mmol), mesitylene (0.21 mL, 1.5 mmol, 3 equiv.) and $Bi(OTf)_3$ (7 mg, 0.01 mmol, 2 mol%) in nitromethane (2 mL) at 80 °C for 18 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as colourless solid (126 mg, 64 %).

m.p.: 173-175 °C

IR (cm^{-1}): 3274 (w), 2923 (w), 1738 (m), 1594 (m), 1496 (m), 1437 (w), 1412 (m), 1329 (m), 1311 (w), 1288 (w), 1263 (s), 1228 (m), 1183 (m), 1157 (m), 1119 (w), 1096 (m), 1063 (m), 1024 (s), 939 (w), 913 (m), 870 (m), 828 (s), 801 (m), 779 (m), 722 (m), 674 (s), 628 (w), 585 (s), 559 (s).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.50 – 7.45 (m, 2H), 6.75 – 6.70 (m, 2H), 6.66 (s, 2H), 5.67 (bd, *J* = 4.5 Hz, 1H), 5.51 (d, *J* = 4.6 Hz, 1H), 4.20 – 4.04 (m, 2H), 3.80 (s, 3H), 2.21 (s, 6H), 2.19 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 3H).

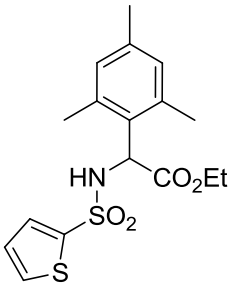
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 170.95, 162.74, 137.90, 137.17, 131.85, 129.87, 129.42, 129.09, 113.71, 62.55, 55.66, 55.00, 20.92, 20.13, 14.12.

MS (ESI): m/z: calc. for $C_{20}H_{25}NO_5S$ 391.15, found 414.08 $[M+Na]^+$.

HRMS (MALDI): m/z: calc. for $C_{20}H_{25}NO_5S$ 414.13456 $[M+Na]^+$ found 414.13382.

R_f (hexane/ EtOAc 4:1): 0.5.

Ethyl-2-mesityl-2-(thiophene-2-sulfonamido)acetate (7e)



Ethyl-2-mesityl-2-(thiophene-2-sulfonamido)acetate (**7e**) was prepared according to TP from 2-thiophene-sulfonamide (82 mg, 0.5 mmol), ethyl glyoxalate (61 mg, 0.6 mmol), mesitylene (0.21 mL, 1.5 mmol) and $Bi(OTf)_3$ (7 mg, 0.01 mmol, 2 mol%) in nitromethane (2 mL) at 80 °C for 16 h. Purification by chromatography (hexane/EtOAc 9:1 → 4:1) yielded the product as a colourless solid (123 mg, 67%).

m.p.: 158-160°C

IR (cm^{-1}): 3314 (w), 3115 (w), 2967 (w), 2083 (w), 1739 (s), 1612 (w), 1509 (w), 1480 (w), 1463 (w), 1407 (m), 1367 (w), 1329 (s), 1287 (s), 1225 (m), 1197 (m), 1157 (s), 1144 (s), 1091 (s), 1033 (m), 1014 (s), 976 (w), 925 (w), 852 (s), 828 (m), 782 (w), 739 (m), 729 (s), 666 (s), 641 (w), 608 (s), 589 (s), 570 (s), 546 (s), 528 (s), 468 (m).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.44 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.24 (dd, *J* = 3.8, 1.3 Hz, 1H), 6.88 – 6.85 (m, 1H), 6.72 (s, 2H), 5.87 (bd, *J* = 4.9 Hz, 1H), 5.59 (d, *J* = 5.0 Hz, 1H), 4.22 – 4.05 (m, 2H), 2.26 (s, 6H), 2.21 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H).

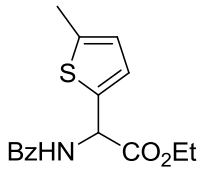
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 170.78, 141.13, 138.13, 137.21, 132.19, 131.93, 129.96, 129.35, 127.00, 62.67, 55.28, 20.96, 20.16, 14.11.

MS (ESI): m/z: calc. for $C_{17}H_{21}NO_4S_2$ 367.1, found 368.5 $[M+H]^+$.

HRMS (MALDI): m/z: calc. for $C_{17}H_{21}NO_4S_2$ 406.05436 $[M+K]^+$, found 406.05429.

R_f (hexane/EtOAc 4:1): 0.3.

Ethyl-2-(benzamido)-2-(5-methylthiophen-2-yl)acetate (9a)



A 10 mL screw-cap vial was charged with benzamide (61 mg, 0.5 mmol), ethyl glyoxalate (61 mg, 0.6 mmol), $Bi(OTf)_3$ (7 mg, 0.01 mmol, 2 mol%) and nitromethane (1 mL). The mixture was stirred at r.t. for 30 min. Then, a solution of 2-methylthiophene (0.15 mL, 1.5 mmol) in nitromethane (1 mL) was added over 2 h. The reaction was stirred at r.t. for 16 h. Purification by chromatography (cyclohexane/EtOAc 4:1) yielded the product **9a** as a colorless solid (97 mg, 64%, ratio of regioisomers 8:1).

m.p.: 66–68 °C.

IR (cm^{-1}): 3315 (w), 2981 (w), 2917 (w), 1737 (s), 1637 (s), 1603 (m), 1579 (m), 1523 (s), 1486 (s), 1446 (m), 1369 (m), 1327 (m), 1294 (m), 1229 (m), 1204 (s), 1172 (s), 1122 (m), 1083 (m), 1019 (s), 976 (m), 929 (w), 883 (w), 803 (m), 754 (m), 714 (s), 691 (s), 672 (s), 622 (m), 601 (s), 579 (s), 557 (s), 537 (s), 522 (s), 505 (m), 480 (m), 472 (m).

^{1}H-NMR (300 MHz, $CDCl_3$) (peaks listed only for major regioisomer): δ = 7.83–7.79 (m, 2H), 7.54–7.41 (m, 3H), 7.05 (bd, J = 5.5 Hz, 1H), 6.92–6.89 (m, 1H), 6.64–6.60 (m, 1H), 5.95 (d, J = 7.4 Hz, 1H), 4.36–4.18 (m, 2H), 2.44 (s, 3H), 1.32–1.22 (m, 3H).

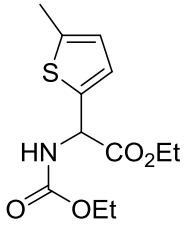
^{13}C-NMR (75 MHz, $CDCl_3$) (peaks are not assigned to regioisomers): δ = 171.21, 170.29, 166.66, 140.68, 136.33, 133.80, 133.68, 132.04, 131.94, 128.73, 127.32, 127.25, 126.37, 125.81, 125.26, 122.71, 62.39, 62.09, 52.63, 50.95, 15.43, 14.17, 13.25.

MS (ESI): m/z: calc. 303.10, found 304.30 $[M+H]^+$.

HRMS (MALDI): m/z: calc. for $C_{16}H_{17}NO_3S$ 326.08214 $[M+Na]^+$, found 326.08212.

R_f (cyclohexane/EtOAc 4:1): 0.3.

Ethyl-(ethoxycarbonyl)-(5-methylthiophen-2-yl)methylcarbamate (9b)



Ethyl-(ethoxycarbonyl)-(5-methylthiophen-2-yl)methylcarbamate (**9b**) was prepared according to TP from urethane (67 mg, 0.75 mmol), ethyl glyoxalate (51 mg, 0.5 mmol), 2-methylthiophene (0.15 mL, 1.5 mmol) and $Bi(OTf)_3$ (7 mg, 0.01 mmol, 2 mol%) in DCE at 60 °C for 16 h. Purification by chromatography (cyclohexane/EtOAc 9:1 → 4:1) yielded the product as a colourless oil (97 mg, 72%, ratio of regioisomers >25:1).

EA (%): calc.: C 53.12 H 6.32 N 5.16 S 11.82
found: C 53.05 H 6.27 N 5.51 S 12.91.

IR (cm^{-1}): 3333 (w), 2981 (w), 2936 (w), 1709 (s), 1506 (s), 1479 (m), 1446 (m), 1371 (m), 1318 (m), 1229 (s), 1200 (s), 1112 (m), 1095 (m), 1053 (s), 948 (w), 862 (w), 799 (m), 778 (m), 705 (w), 610 (m), 563 (m), 532 (m), 503 (m).

^{1}H-NMR (300 MHz, $CDCl_3$) (peaks listed only for major regioisomer): δ = 6.83 (bd, *J* = 3.4 Hz, 1H), 6.61 – 6.59 (m, 1H), 5.62 – 5.59 (m, 1H), 5.53 – 5.50 (m, 1H), 4.30 – 4.09 (m, 4H), 2.44 (s, 3H), 1.30 – 1.21 (m, 6H).

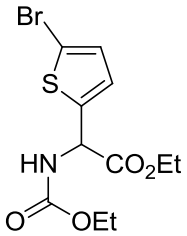
^{13}C-NMR (75 MHz, $CDCl_3$) (peaks listed only for major regioisomer): δ = 170.15, 155.59, 140.45, 136.51, 125.97, 125.08, 62.10, 61.38, 53.72, 15.30, 14.54, 14.05.

MS (ESI): m/z: calc. for $C_{12}H_{17}NO_4S$ 271.3, found 272.5 $[M+H]^+$.

R_f (hexane/EtOAc 4:1): 0.5.

Analytical data are consistent with literature.[9]

Ethyl-(ethoxycarbonyl)-(5-bromothiophen-2-yl)methylcarbamate (9c)



Ethyl-(ethoxycarbonyl)-(5-bromothiophen-2-yl)methylcarbamate (**9c**) was prepared according to TP from urethane (67 mg, 0.75 mmol), ethyl glyoxalate (51 mg, 0.5 mmol), 2-bromothiophene (0.16 mL, 1.5 mmol) and $Bi(OTf)_3$ (7 mg, 0.01 mmol, 2 mol%) in nitromethane (1 mL) at 60 °C for 16 h. Purification by chromatography (cyclohexane/EtOAc 9:1 → 4:1) yielded the product as a yellow solid (130 mg, 77%).

m.p.: 48-50 °C.

IR 3369 (w), 3161 (w), 2985 (w), 1733 (m), 1709 (s), 1596 (w), 1516 (m), 1468 (w), 1408 (w), 1365 (s), 1330 (m),1250 (m),1213 (s), 1191 (s), 1180 (s), 1155 (s), 1125 (s), 1090 (s), 1049 (s), 1023 (m), 899 (m), 873 (w), 829 (w), 814 (m), 780 (m), 740 (m), 703 (m), 672 (s), 613 (m), 585 (s), 542 (s), 513 (m), 487 (m), 457 (m).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.91 (d, J = 3.8 Hz, 1H), 6.81 (d, J = 3.7 Hz, 1H), 5.70 (bs, 1H), 5.53 (bd, J = 7.4 Hz, 1H), 4.28 – 4.21 (m, 2H), 4.14 (q, J = 7.1 Hz, 2H), 1.30 – 1.23 (m, 6H).

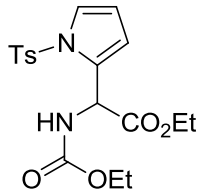
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 169.44, 155.62, 141.09, 129.92, 126.32, 112.62, 62.62, 61.72, 53.81, 14.63, 14.14.

MS (ESI): m/z: calc. for $C_{11}H_{14}BrNO_4S$ 334.98, found 336.08 $[M+H]^+$.

HRMS (MALDI): m/z: calc. for $C_{11}H_{14}BrNO_4$ 335.98997 $[M+H]^+$, found 335.99025 $[M+H]^+$.

R_f (cyclohexane/EtOAc 7:3): 0.6.

Ethyl-(ethoxycarbonyl)-(1-tosyl-1*H*-pyrrol-2-yl)methylcarbamate (9d)



Ethyl-(ethoxycarbonyl)-(1-tosyl-1*H*-pyrrol-2-yl)methylcarbamate (**9d**) was prepared according to TP from urethane (46 mg, 0.5 mmol), ethyl glyoxalate (61 mg, 0.6 mmol), *N*-tosylpyrrole (332 mg, 1.5 mmol) and $Bi(OTf)_3$ (7 mg, 0.01 mmol, 2 mol%) in DCE at 60 °C for 16 h. Purification by chromatography (hexane/EtOAc 9:1 → 4:1) yielded the product as a yellow solid (123 mg, 62%).

m.p: 130–132 °C.

IR (cm^{-1}): 3369 (w), 2984 (w),1733 (m), 1709 (s), 1596 (w), 1516 (m), 1468 (m), 1365 (s), 1329 (m), 1250 (m), 1213 (s), 1191 (s), 1180 (s), 1155 (s), 1125 (s), 1090 (s), 1049 (s), 899 (m), 813 (m), 780 (m), 740703 (m), 672 (s), 585 (s), 542 (s), 487 (m), 457 (m).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 8.4 Hz, 2H), 7.29 – 7.27 (m, 2H), 7.2 –7.24 (m, 1H), 6.30 (s, 1H), 6.23 (t, *J* = 3.4 Hz, 1H), 5.84 (d, *J* = 8.1 Hz, 1H), 5.43 (bd, *J* = 6.8 Hz, 1H), 4.19 – 4.07 (m, 4H), 2.40 (s, 3H), 1.24 – 1.16 (m, 6H).

^{13}C-NMR (101 MHz, CDCl3): δ = 169.85, 145.19, 136.35, 130.23, 130.04, 129.92, 127.12, 124.25, 116.07, 111.93, 62.13, 61.38, 51.26, 21.74, 14.65, 14.07.

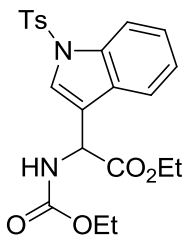
MS (ESI): m/z: calc. for $C_{18}H_{22}N_2O_6S$ 394.4 , found 395.9 $[M+H]^+$.

HRMS (MALDI): m/z: calc. for $C_{18}H_{22}N_2O_6S$ 417.10908 $[M+Na]^+$, found 417.10896.

R_f (hexane/EtOAc 4:1): 0.4.

Analytical data are consistent with literature.[9]

Ethyl-(ethoxycarbonyl)-(1-tosyl-1*H*-indol-3-yl)methylcarbamate (9e)



Ethyl-(ethoxycarbonyl)-(1-tosyl-1*H*-indol-3-yl)methylcarbamate (**9e**) was prepared according to TP from urethane (46 mg, 0.5 mmol), ethyl glyoxalate (61 mg, 0.6 mmol), 1-tosylindole (203 mg, 0.75 mmol) and $Bi(OTf)_3$

(7 mg, 0.01 mmol, 2 mol%) in DCE at 60 °C for 16 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as a yellow solid (171 mg, 78%).

m.p: 68–70 °C.

EA (%): calc.: C 59.45 H 5.44 N 6.30 S 7.21
found: C 59.38 H 5.24 N 5.95 S 6.93.

IR (cm^{-1}) = 3384 (w), 2981 (w), 1716 (m), 1596 (w), 1513 (w), 1447 (w), 1368 (m), 1305 (w), 1217 (w), 1188 (w), 1171 (s), 1134 (w), 1119 (m), 1093 (m), 1049 (m), 1019 (m), 975 (m), 859 (w), 812 (w), 746 (m), 704 (w), 63 (m), 569 (s), 536 (s).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.96 (bd, J = 8.3 Hz, 1H), 7.75 (d, J = 8.4 Hz, 2H), 7.64 (bd, J = 7.9 Hz, 1H), 7.59 (s, 1H), 7.33 (t, J = 7.5 Hz, 1H), 7.27–7.19 (m, 3H), 5.61 (bs, 1H), 4.26 – 4.09 (m, 4H), 2.34 (s, 3H), 1.26 – 1.16 (m, 6H).

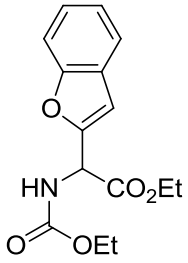
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 170.51, 155.83, 145.31, 135.32, 135.17, 130.07, 128.61, 127.03, 125.31, 124.86, 123.63, 120.17, 118.26, 113.81, 62.21, 61.53, 50.79, 21.67, 14.61, 14.11.

MS (ESI): m/z: calc. for $C_{22}H_{24}N_2O_6S$ 444.14 , found 445.24 $[M+H]^+$.

R_f (hexane/EtOAc 4:1): 0.3.

Analytical data are consistent with literature.[9]

Ethyl-(ethoxycarbonyl)-(benzofuran-2-yl)methylcarbamate (9f)



Ethyl-(ethoxycarbonyl)-(benzofuran-2-yl)methylcarbamate (**9f**) was prepared according to TP from urethane (46 mg, 0.5 mmol), ethyl glyoxalate (61 mg, 0.6 mmol) , benzofuran (0.16 mL, 1.5 mmol) and $Bi(OTf)_3$ (7 mg, 0.01 mmol, 2 mol%) in DCE at 60 °C for 16 h. Purification by chromatography (cyclohexane/EtOAc 9:1 → 4:1) yielded the product as a yellow solid (128 mg, 88%).

m.p: 58–60 °C.

EA (%): calc.: C 61.85 H 5.88 N 4.81
found: C 61.86 H 5.92 N 4.45.

IR (cm^{-1}): 3267 (w), 2986 (w), 1751 (m), 1743 (m), 1688 (m), 1641 (w), 1603 (w), 1585 (w), 1530 (s), 1490 (w), 1477 (w), 1453 (m), 1369 (m), 1319 (m), 1284 (w), 1255 (s), 1243 (s), 1202 (s), 1182 (s), 1157 (s), 1133 (w), 1093 (m), 1049 (s), 1018 (m), 954 (w), 937 (m), 881 (m), 861 (w), 850 (w), 815 (m), 793 (w), 778 (w), 752 (s), 717 (s), 690 (m), 675 (m), 624 (m), 570 (m), 524 (m).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.55 (d, J = 7.5 Hz, 1H), 7.45 (d, J = 7.9 Hz, 1H), 7.31 – 7.21 (m, 2H), 6.76 (s, 1H), 5.80 (bd, J = 6.4 Hz, 1H), 5.64 (bd, J = 8.1 Hz, 1H), 4.31 – 4.13 (m, 4H), 1.27 – 1.23 (m, 6H).

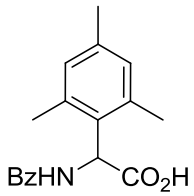
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 170.15, 155.59, 140.45, 136.51, 125.97, 125.08, 62.10, 61.38, 53.72, 15.30, 14.54, 14.05.

MS (ESI): m/z: calc. for $C_{15}H_{17}NO_5$ 291.10, found 292.32 $[M+H]^+$.

R_f (cyclohexane/EtOAc 4:1): 0.3.

Analytical data are consistent with literature.[9]

2-Benzamido-2-mesitylacetic acid (10a)



2-Benzamido-2-mesitylacetic acid (**10a**) was synthesized according to TP from benzamide (121 mg, 1.0 mmol), glyoxylic acid (50% w/w in H_2O, 0.13 mL, 1.2 mmol), mesitylene (0.42 mL, 3 mmol, 3 equiv.) and $Bi(OTf)_3$ (13 mg, 0.02 mmol, 2 mol%) in nitromethane (4 mL) at 80 °C for 21 h. After cooling to room temperature 1 M NaOH-solution (15 mL) was given to the reaction mixture. The aqueous phase was washed with EtOAc (2 x 10 mL), acidified with 2 N HCl to pH 4 and extracted with EtOAc (3 x 10 mL). The organic layer was dried with anhydrous $MgSO_2$, filtered and evaporated into dryness. Purification by chromatography (DCM/MeOH 20:1) yielded the product as colorless solid (211 mg, 71%).

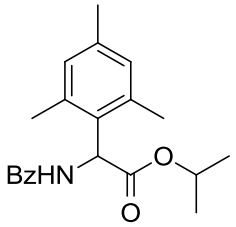
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 7.1 Hz, 2H), 7.51 – 7.39 (m, 3H), 7.09 (bd, *J* = 6.2 Hz, 1H), 6.87 (s, 2H), 6.25 (d, *J* = 6.5 Hz, 1H), 2.46 (s, 6H), 2.25 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 175.63, 167.09, 138.30, 137.16, 133.63, 132.07, 130.28, 128.81, 127.24, 52.58, 21.01, 20.50.

MS (ESI): m/z: calc. for $C_{18}H_{19}NO_3$ 297.1, found 298.4 $[M+H]^+$.

Analytical data are consistent with literature.[9]

Isopropyl-2-(benzamido)-2-mesitylacetate (10b)



Isopropyl-2-(benzamido)-2-mesitylacetate (**10b**) was prepared according to TP from benzamide (66 mg, 0.55 mmol), isopropyl glyoxalate (75 mg 0.65 mmol), mesitylene (0.21 mL, 3.0 mmol) and $Bi(OTf)_3$ (7 mg, 0.01 mmol, 2 mol%) in nitromethane (2 mL) at 80 °C for 16 h. Purification by chromatography (cyclohexane/EtOAc 4:1→ 1:1) yielded the product as colorless solid (94 mg, 50%).

m.p.: 104–106 °C.

EA (%): calc.: C 74.31 H 7.42 N 4.13
found: C 74.08 H 7.42 N 3.86.

IR (cm^{-1}): 3322 (w), 2975 (w), 2925 (w), 1748 (s), 1635 (s), 1603 (w), 1581 (w), 1532 (s), 1491 (m), 1463 (w), 1387 (w), 1373 (w), 1360 (w), 1343 (w), 1312 (w), 1212 (s), 1154 (m), 1108 (s), 1088 (s), 1027 (w), 973 (w), 960 (w), 936 (w), 903 (w), 853 (m), 828 (w), 802 (w), 787 (m), 712 (m), 690 (m), 625 (m), 613 (w), 593 (m), 552 (w), 538 (w), 512 (w), 494 (w), 458 (w).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.81 – 7.78 (m, 2H), 7.52 – 7.48 (m, 1H), 7.45 – 7.41 (m, 2H), 7.18 (bd, J = 6.2 Hz, 1H), 6.84 (s, 2H), 6.15 (bd, J = 6.6 Hz, 1H), 5.08 (hept, J = 6.3 Hz, 1H), 2.47 (s, 6H), 2.25 (s, 3H), 1.25 (d, J = 6.3 Hz, 3H), 1.12 (d, J = 6.2 Hz, 3H).

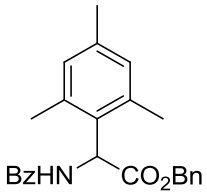
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 171.42, 166.56, 137.59, 134.15, 131.79, 131.15, 130.08, 128.73, 127.22, 69.91, 52.95, 21.80, 21.59, 21.00, 20.48.

MS (ESI): m/z: calc. for $C_{21}H_{25}NO_3$ 329.18, found 340.29 $[M+H]^+$.

R_f (cyclohexane/EtOAc 9:1): 0.2.

Analytical data are consistent with literature.[9]

Benzyl-2-(benzamido)-2-mesitylacetate (10c)



Benzyl-2-(benzamido)-2-mesitylacetate (**10c**) was prepared according to TP from benzamide (121 mg, 1.0 mmol), benzyl glyoxalate (213 mg, 1.3 mmol), mesitylene (0.42 mL, 3.0 mmol) and $Bi(OTf)_3$ (13 mg, 0.02 mmol, 2 mol%) in nitromethane (4 mL) at 80 °C for 24 h. Purification by chromatography (cyclohexane/EtOAc 4:1) yielded the product as colourless oil (266 mg, 69%).

EA (%): calc.: C 77.49 H 6.50 N 3.61
found: C 77.42 H 6.56 N 3.28.

IR (cm^{-1}): 3321 (w), 3063 (w), 3032 (w), 2956 (w), 2920 (w), 1732 (m), 1654 (s), 1602 (w), 1581 (w), 1511 (s), 1481 (s), 1455 (m), 1377 (m), 1344 (m), 1309 (m), 1258 (m), 1211 (m), 1188 (s), 1153 (s), 1087 (m), 1029 (m), 1001 (m), 969 (m), 908 (w), 852 (m), 800 (w), 766 (m), 734 (m), 709 (s), 695 (s), 608 (m), 591 (m), 543 (m), 481 (m), 459 (m).

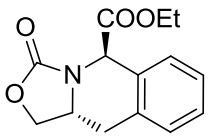
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.80 – 7.77 (m, 2H), 7.53 – 7.40 (m, 3H), 7.30 – 7.28 (m, 3H), 7.19 – 7.16 (m, 3H), 6.85 (s, 2H), 6.26 (d, *J* = 6.6 Hz, 1H), 5.20 (q, *J* = 12.5 Hz, 2H), 2.42 (s, 6H), 2.26 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 171.77, 166.60, 137.91, 137.15, 135.52, 133.98, 131.87, 130.79, 130.19, 128.75, 128.63, 128.39, 127.88, 127.22, 67.49, 52.85, 21.01, 20.48.

MS (ESI): m/z: calc. for $C_{25}H_{25}NO_3$ 387.47, found 388.12 $[M+H]^+$.

R_f (hexane/EtOAc 4:1): 0.4.

Ethyl-3,5,10,10a-tetrahydro-3-oxo-1*H*-oxazolo[3,4-b]isoquinoline-5-carboxylate (12)



Ethyl-3,5,10,10a-tetrahydro-3-oxo-1*H*-oxazolo[3,4-b]isoquinoline-5-carboxylate (**12**) was prepared according to TP from *(R)*-4-benzyloxazolidin-2-one (59 mg, 0.3 mmol), ethyl glyoxalate (61 mg, 0.6 mmol) and $Bi(OTf)_3$ (7 mg, 0.01 mmol, 2 mol%) in nitromethane (2 mL) at 80 °C for 24 h. Purification by chromatography (cyclohexane/EtOAc 4:1) yielded the product as a colorless solid (72 mg, 84 %).

m.p.: 58-59 °C.

EA (%): calc. C 64.36 H 5.79 N 5.36
found: C 63.95 H 5.82 N 5.20.

IR (cm^{-1}) = 2980 (w), 2936 (w), 2084 (w), 1760 (s), 1726 (s), 1477 (m), 1454 (m), 1408 (m), 1393 (m), 1365 (m), 1340 (m), 1322 (m), 1272 (s), 1237 (s), 1227 (s), 1205 (s), 1186 (s), 1167 (m), 1115 (m), 1099 (m), 1063 (s), 1017 (s), 983 (m), 938 (m), 917 (w), 892 (m), 876 (m), 824 (m), 810 (m), 759 (s), 745 (m), 715 (w), 697 (m), 671 (m), 620 (w), 585 (w), 534 (m), 509 (w), 495 (m).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.61 – 7.56 (m, 1H), 7.28 – 7.25 (m, 3H), 7.18 – 7.15 (m, 1H), 5.46 (s, 1H), 4.72 – 4.67 (m, 1H), 4.52 – 4.45 (m, 1H), 4.27 – 4.12 (m, 3H), 3.06 – 2.99 (m, 1H), 2.93 – 2.84 (m, 1H), 1.31 (t, *J* = 7.1 Hz, 3H).

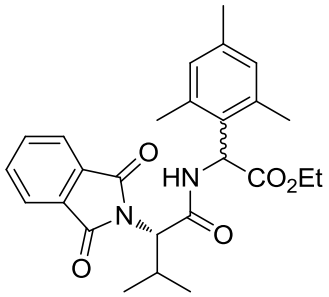
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 170.09, 157.14, 132.04, 129.88, 128.95, 128.31, 127.65, 127.31, 69.38, 62.16, 55.07, 49.62, 33.78, 14.25.

The structure was assigned by COSY.

MS (ESI): m/z: calc for $C_{14}H_{15}NO_4$ 261.10, found 262.22 $[M+H]^+$.

R_f (hexane/EtOAc 7:3) = 0.2

Ethyl-2-(3-methyl-(1,3-dioxoisoindolin-2-yl)butanamido)-2-mesitylacetate (14)



Ethyl-2-(3-methyl-(1,3-dioxoisoindolin-2-yl)butanamido)-2-mesitylacetate (**14**) was prepared according to TP from 3-methyl-2(1,3-dioxoisoindolin-2-yl)butanamide (246 mg, 1.0 mmol), ethyl glyoxalate (122 mg, 1.2 mmol), mesitylene (0.41 mL, 3.0 mmol) and $Bi(OTf)_3$ (13 mg, 0.02 mmol, 2 mol%) in nitromethane (4 mL) at 80 °C for 24 h. Purification by chromatography (hexane/EtOAc 4:1) yielded the product as a colorless solid (393 mg, 87%, ratio of diastereomers: 1.8:1).

m.p.: (Diastereomer a)**:** 63-65°C.

m.p.: (Diastereomer b)**:** 136-138°C.

IR (cm^{-1}): 3348 (w); 2966 (w); 2873 (w); 2050 (w); 1979 (w); 1776 (w); 1765 (w); 1730 (m); 1705 (s); 1676 (s); 1608 (w); 1525 (s); 1466 (m); 1383 (s); 1360 (m); 1331 (m); 1279 (m); 1240 (s); 1153 (m); 1099 (m); 1063 (s); 1026 (s); 982 (w); 947 (w); 908 (w); 885 (m); 868 (w); 854 (m); 827 (w); 806 (w); 766 (w); 725 (s); 708 (m); 688 (w); 613 (s); 604 (s).

^{1}H-NMR (300 MHz, $CDCl_3$, Diastereomer a): δ = 8.10 (bd, *J* = 7.2 Hz, 1H), 7.90 – 7.88 (m, 2H), 7.77 – 7.74 (m, 2H), 6.83 (s, 2H), 5.99 (d, *J* = 7.3 Hz, 1H), 4.44 (d, *J* = 11.5 Hz, 1H), 4.20 – 4.03 (m, 2H), 2.86 – 2.74 (m, 1H), 2.39 (s, 6H), 2.25 (s, 3H), 1.11 (t, *J* = 7.1 Hz, 3H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.83 (d, *J* = 6.6 Hz, 3H).

^{1}H-NMR (300 MHz, $CDCl_3$, Diastereomer b): δ = 7.95 (bd, *J* = 7.4 Hz, 1H), 7.85 – 7.82 (m, 2H), 7.74 – 7.71 (m, 2H), 6.79 (s, 2H), 6.04 (d, *J* = 7.5 Hz, 1H), 4.45 (d, *J* = 11.3 Hz, 1H), 4.24 – 4.09 (m, 2H), 3.03 – 2.90 (m, 1H), 2.36 (s, 6H), 2.21 (s, 3H), 1.20 – 1.14 (m, 6H), 0.86 (d, *J* = 6.6 Hz, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$, Diastereomer a): δ = 171.38, 168.61, 168.33, 137.69, 137.05, 134.54, 131.57, 130.90, 130.01, 123.88, 63.58, 61.85, 52.40, 27.89, 21.01, 20.29, 19.62, 14.11.

^{13}C-NMR (75 MHz, $CDCl_3$, Diastereomer b): δ = 171.43, 168.54, 168.50, 137.72, 137.08, 134.52, 131.51, 130.82, 129.99, 123.84, 63.29, 61.88, 52.10, 27.96, 20.97, 20.28, 19.91, 19.72, 14.18.

MS (ESI): m/z: calc. for $C_{26}H_{30}N_2O_5$ 450.21, found 451.42 $[M+H]^+$.

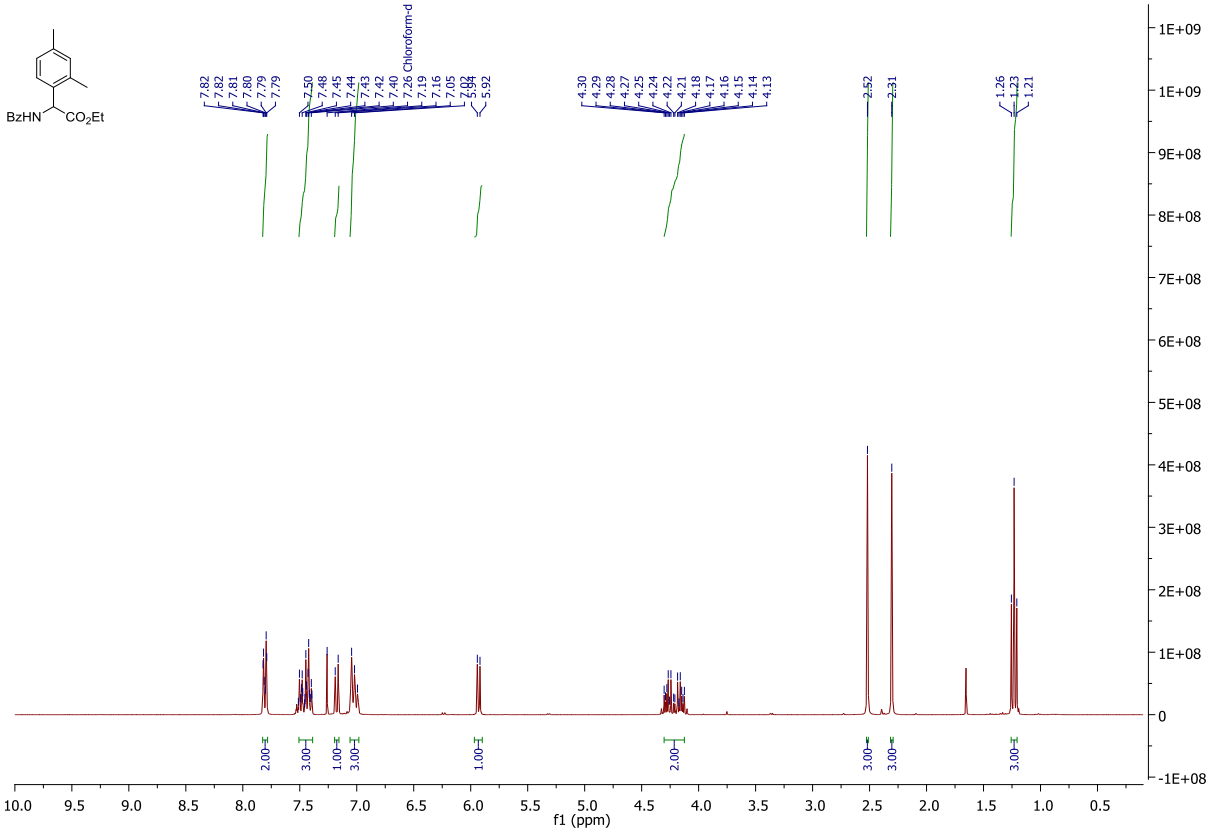
HRMS (MALDI): m/z: calc. for $C_{26}H_{30}N_2O_5$ 451.22275 $[M+H]^+$, found 451.22236.

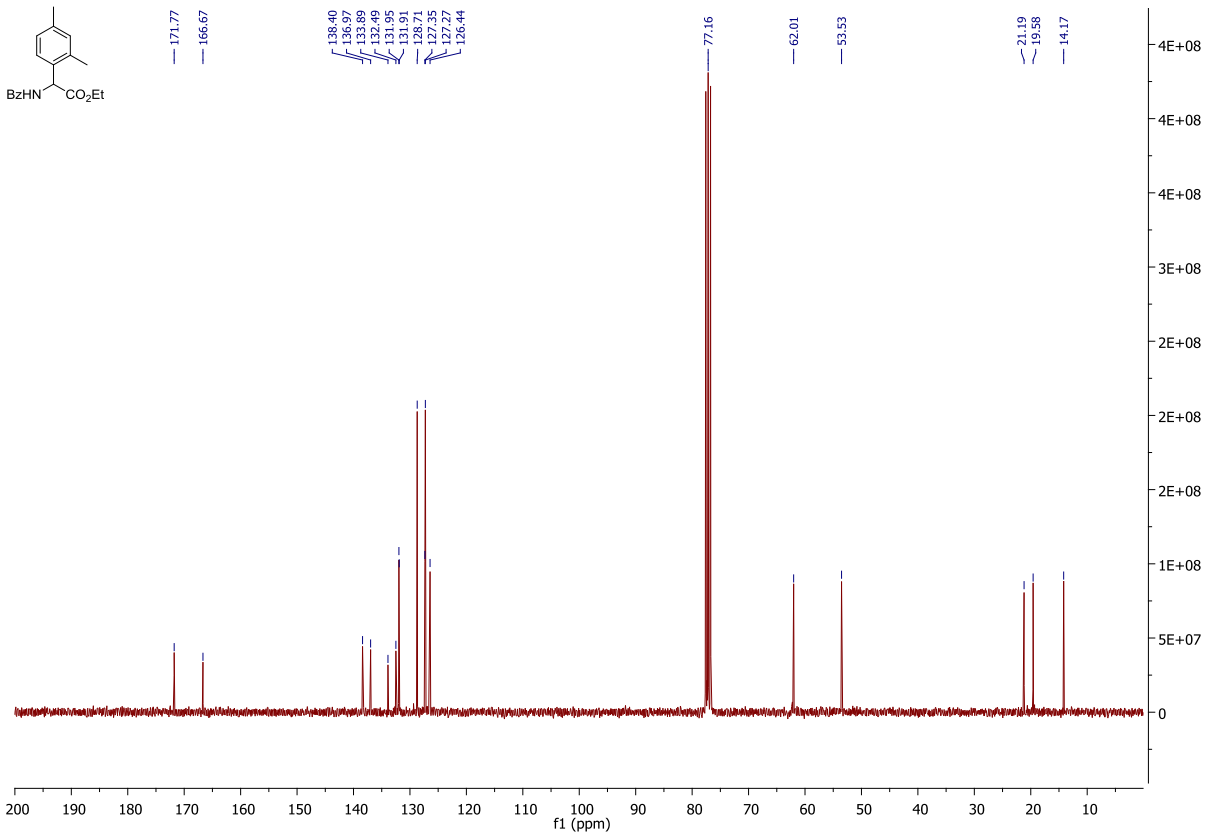
R_f (hexane/ EtOAc 4:1) (Diastereomer a): 0.2.

R_f (hexane/ EtOAc 4:1) (Diastereomer b): 0.3.

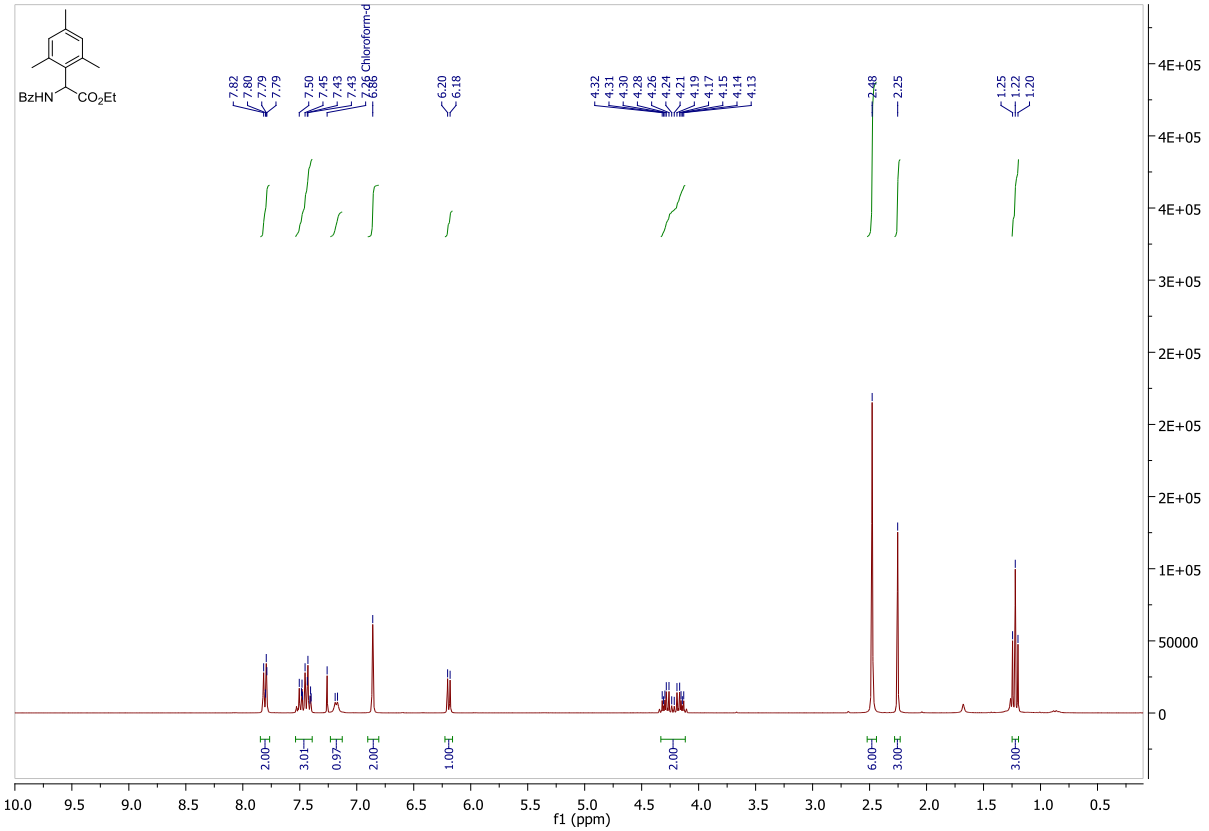
3 Spectra

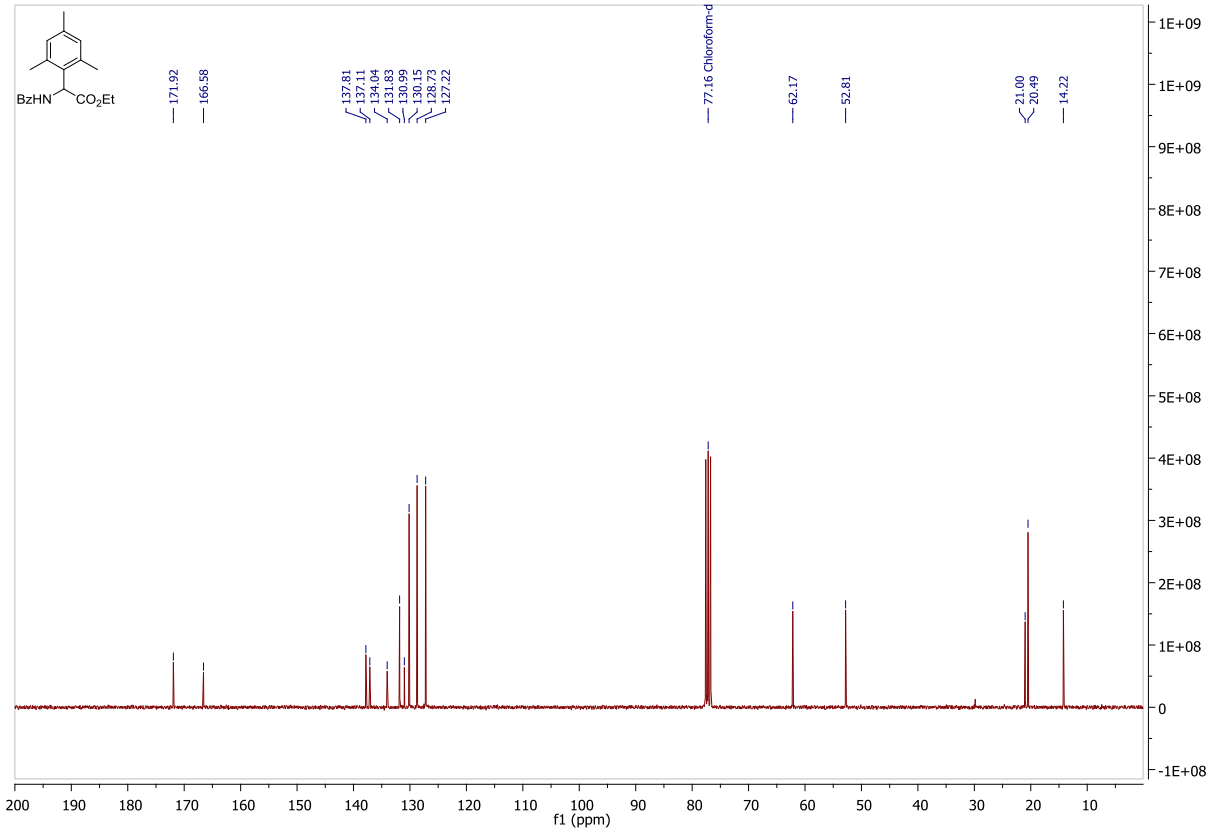
Ethyl-2-(benzamido)-2-(2,4-dimethylphenyl)acetate (4a)



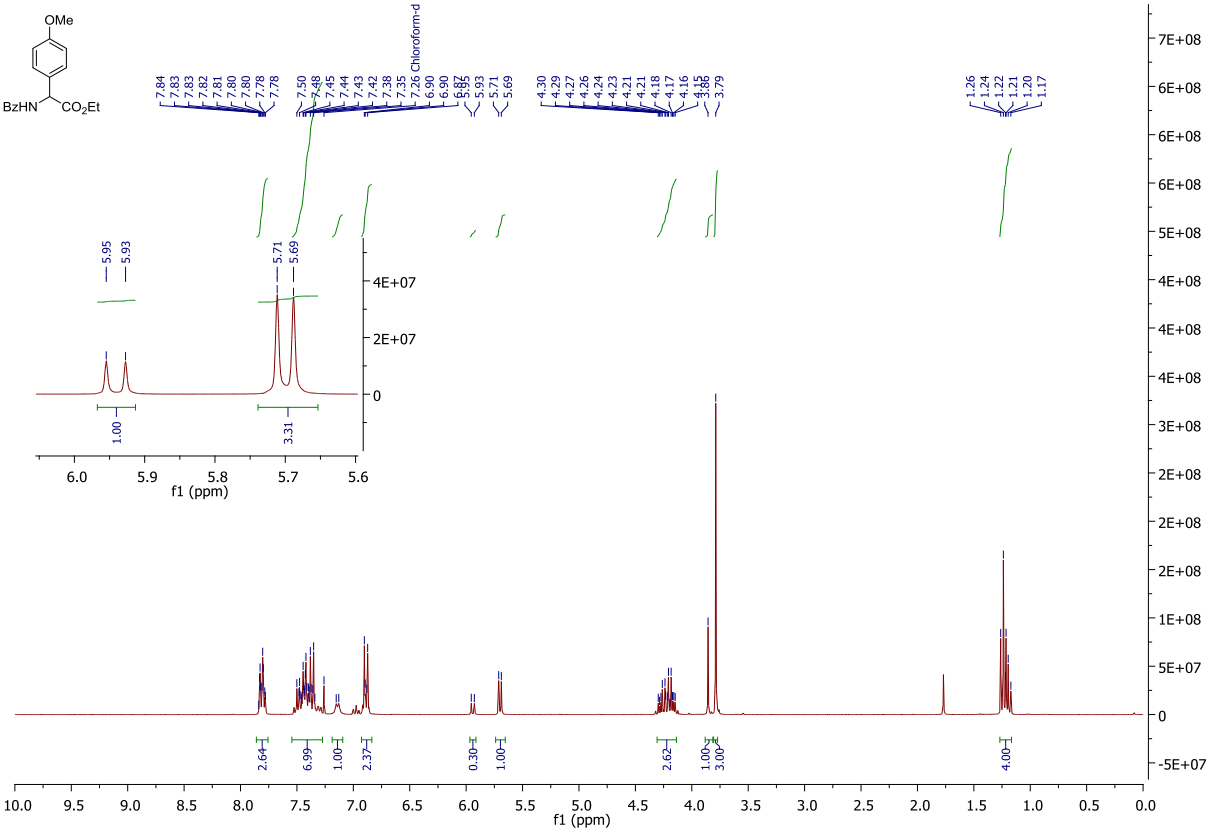


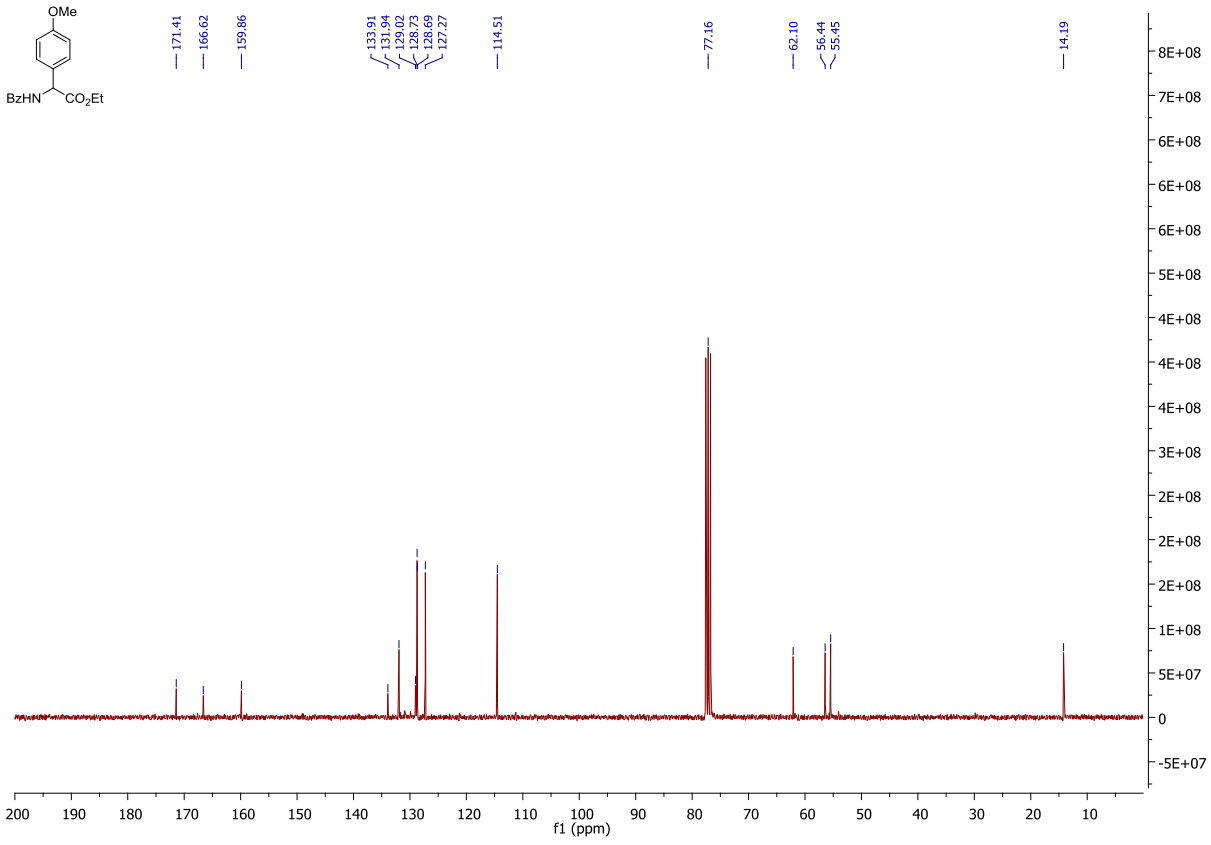
Ethyl-2-(benzamido)-2-mesitylacetate (4b)



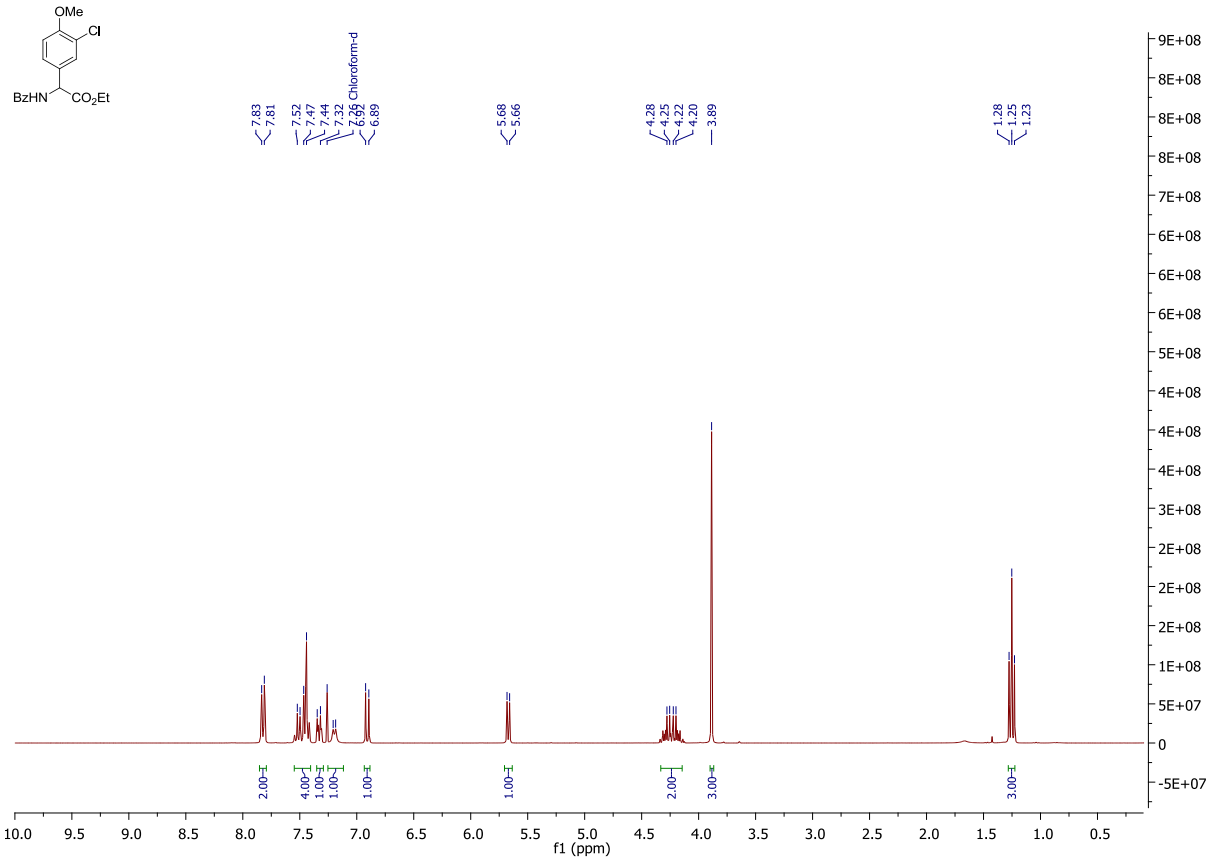


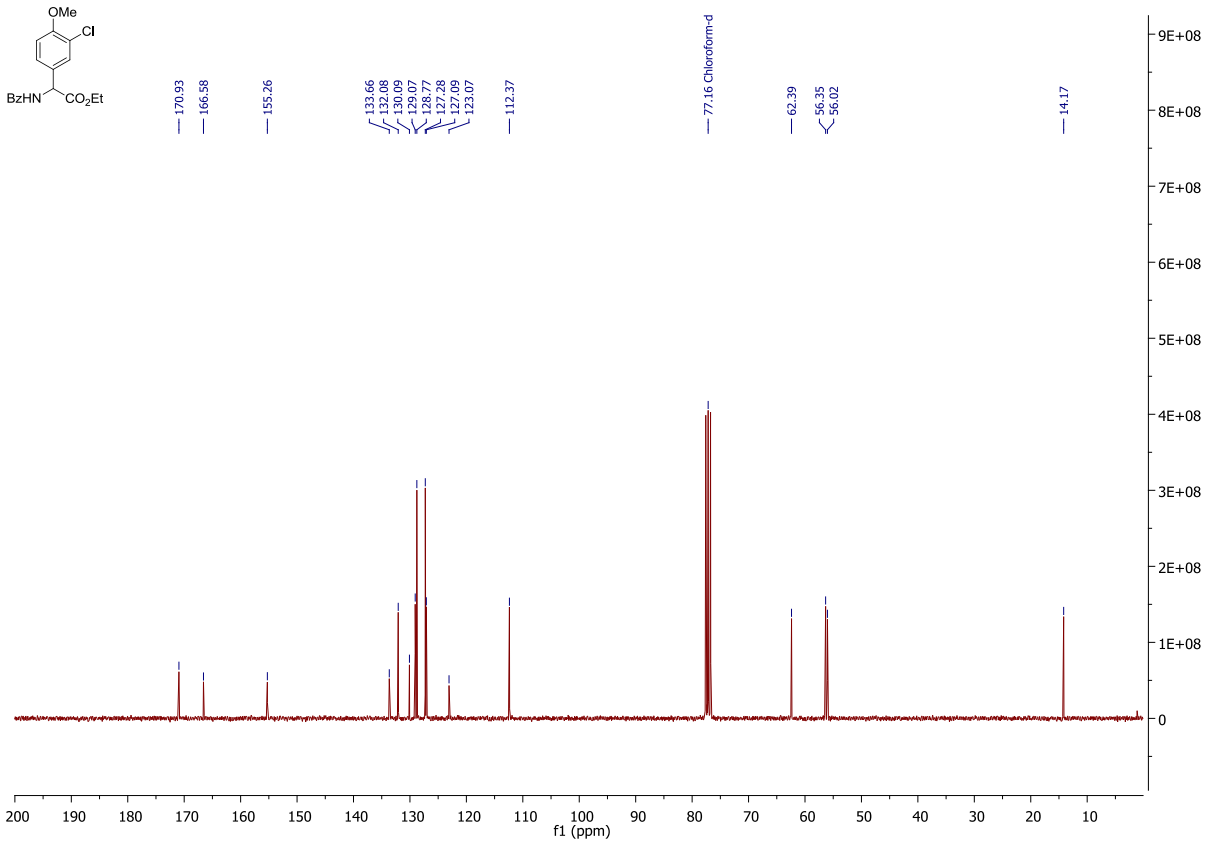
Ethyl-2-(benzamido)-2-(4-methoxyphenyl)acetate (4c)



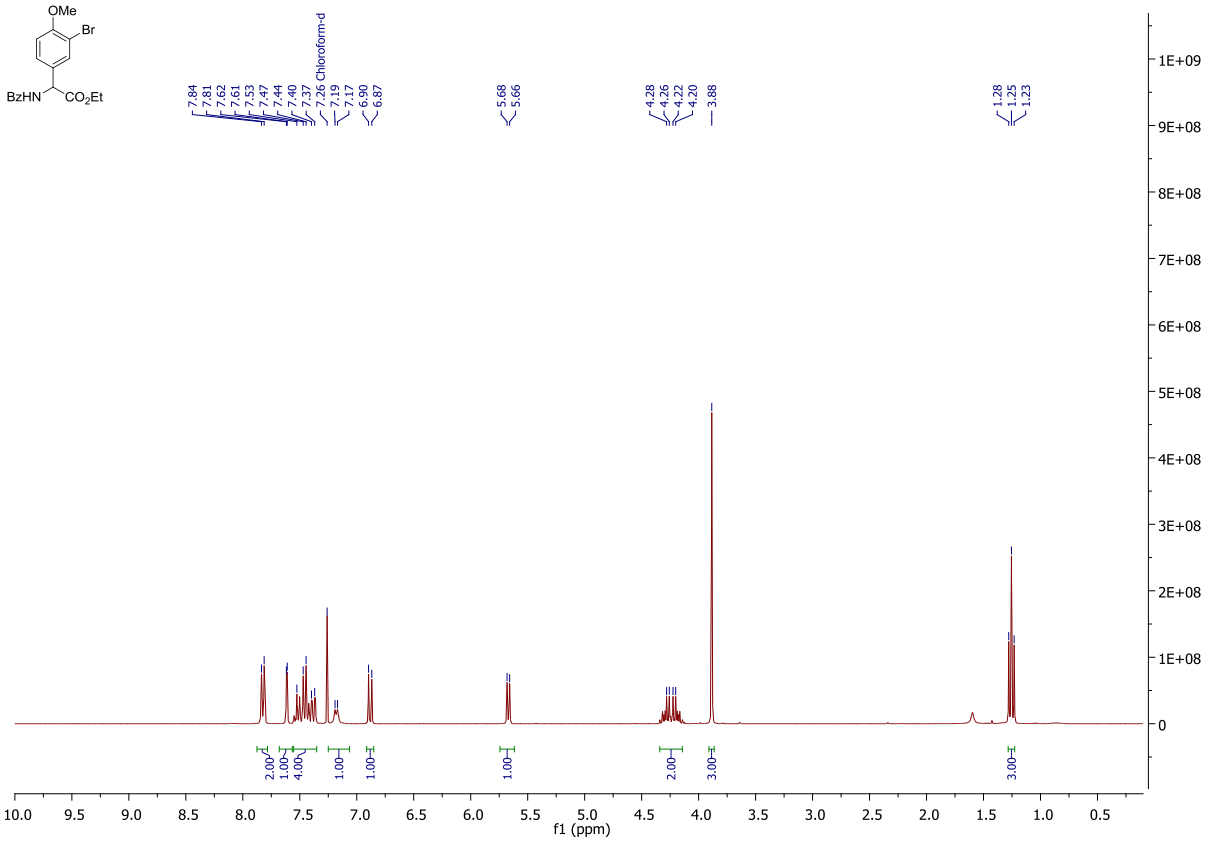


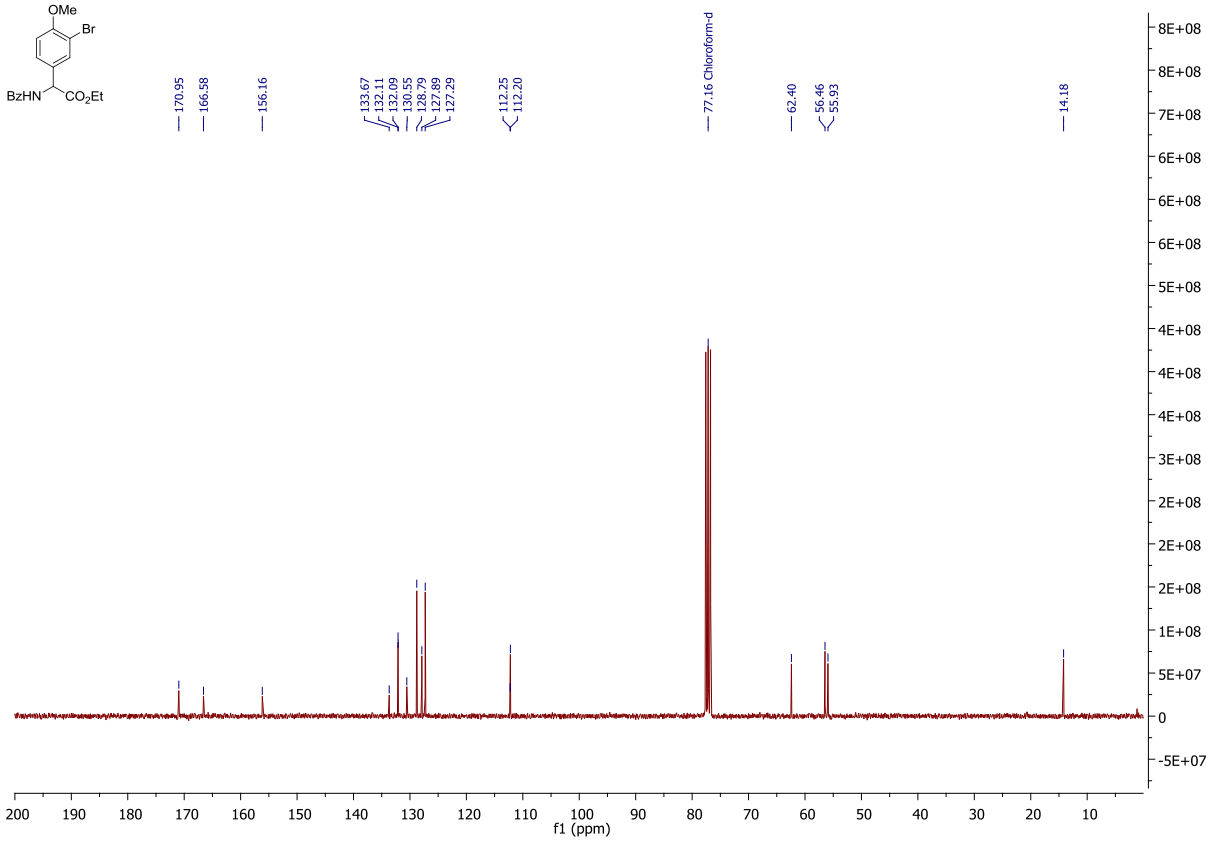
Ethyl-2-(benzamido)-2-(3-chloro-4-methoxyphenyl)acetate (4d)



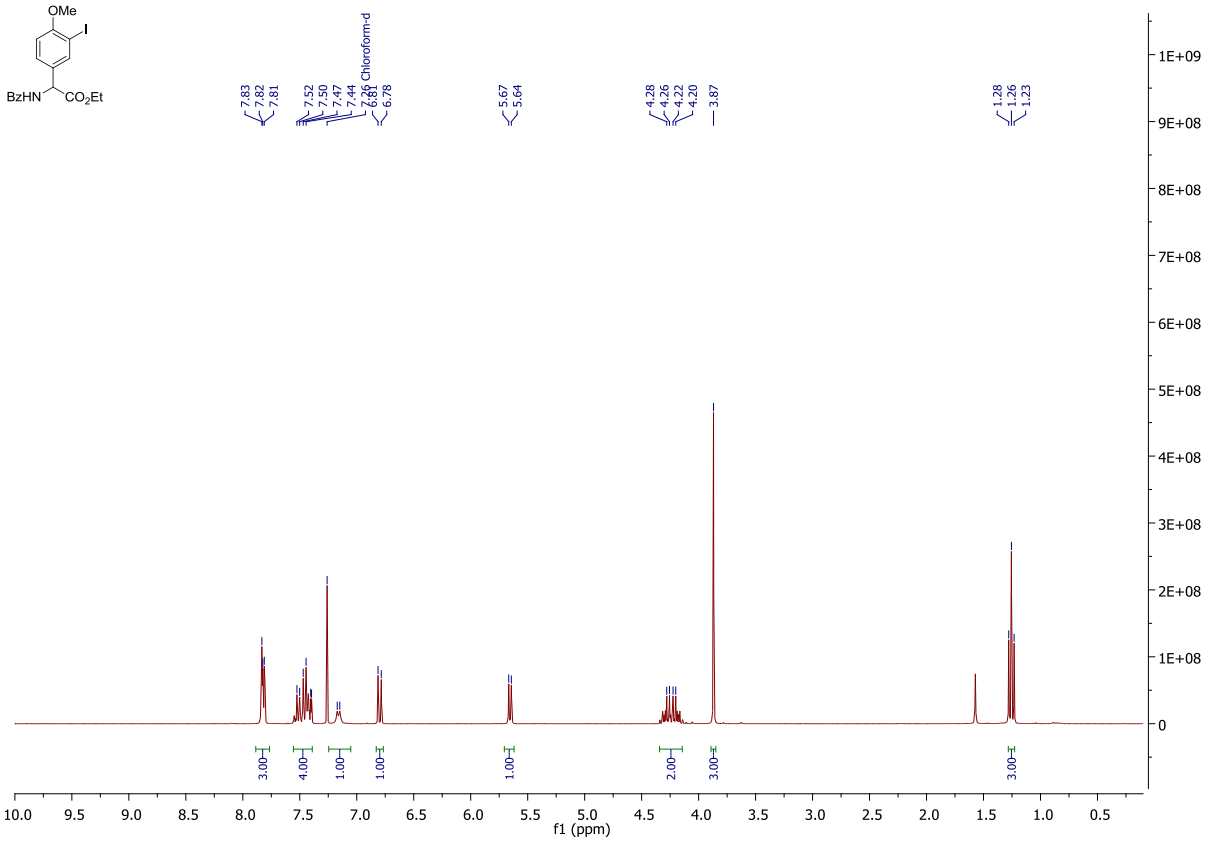


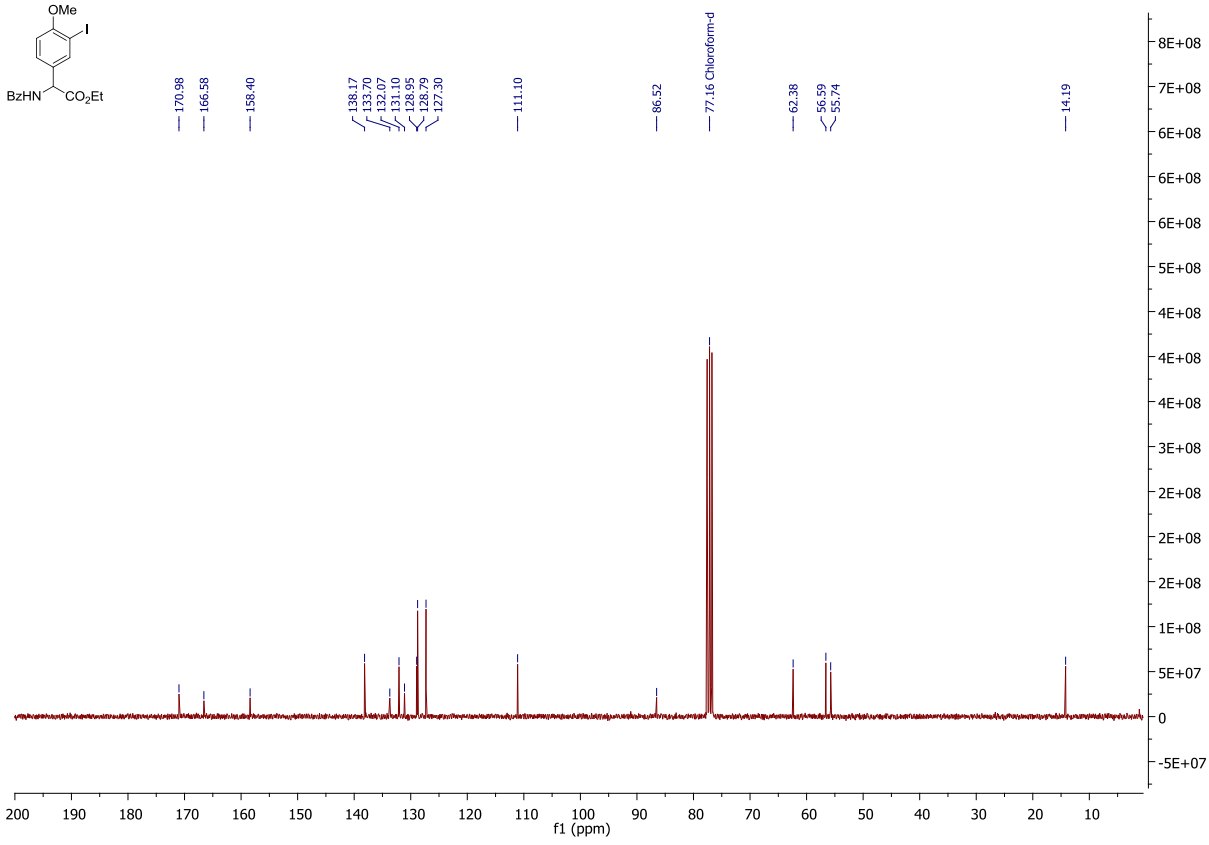
Ethyl-2-(benzamido)-2-(3-bromo-4-methoxyphenyl)acetate (4e)



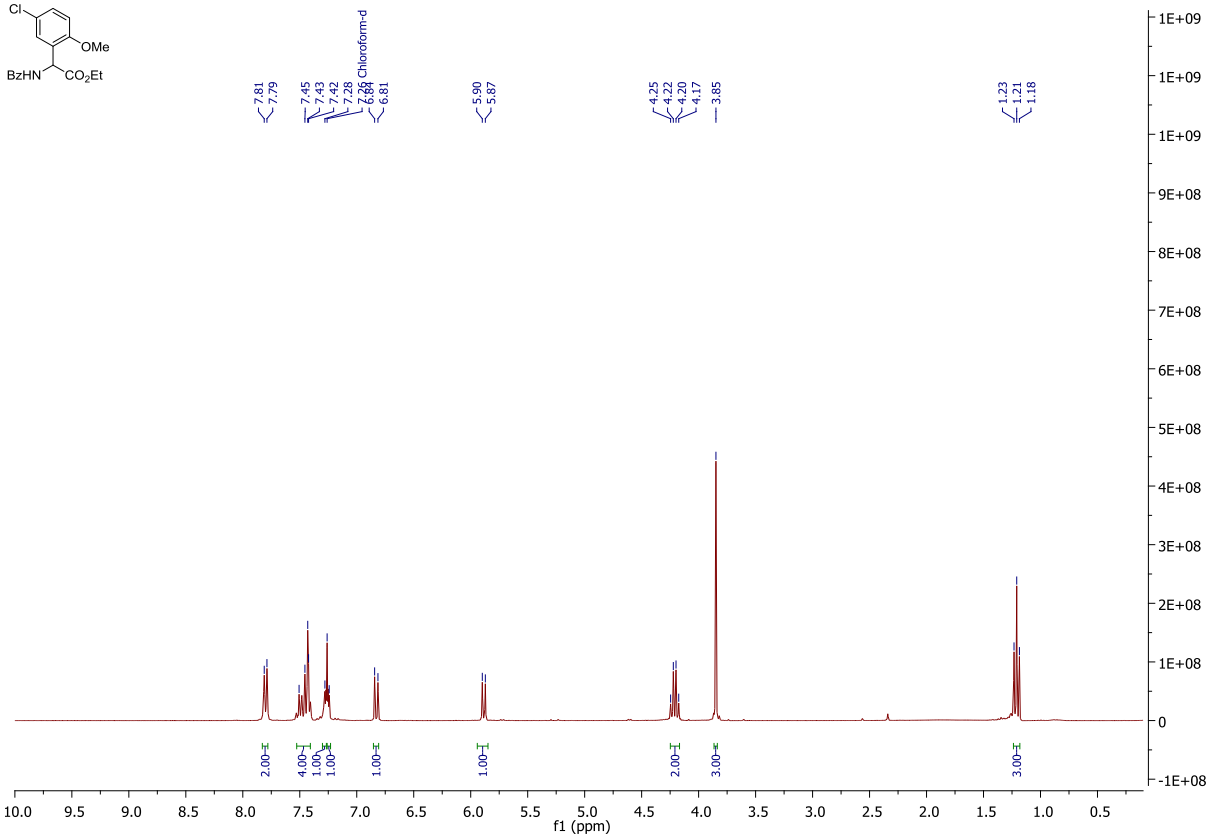


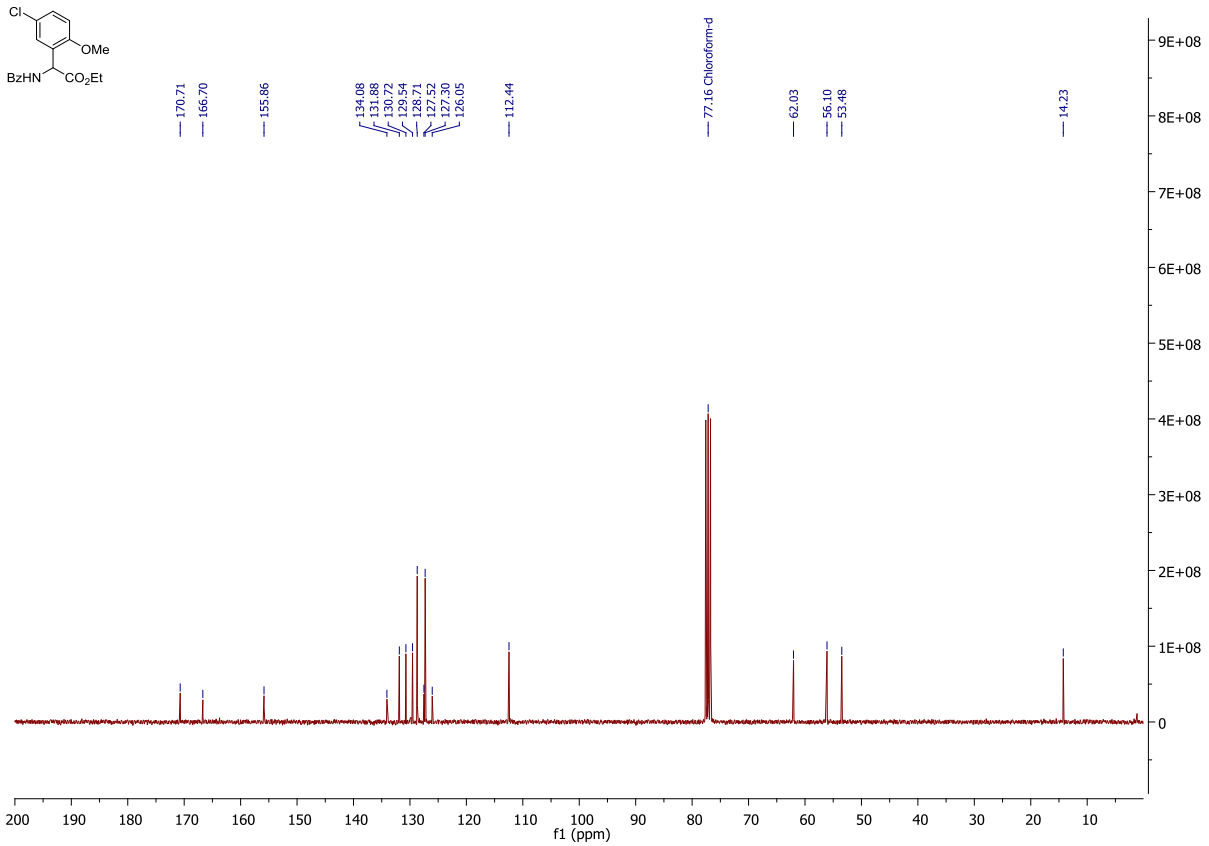
Ethyl-2-(benzamido)-2-(3-iodo-4-methoxyphenyl)acetate (4f)



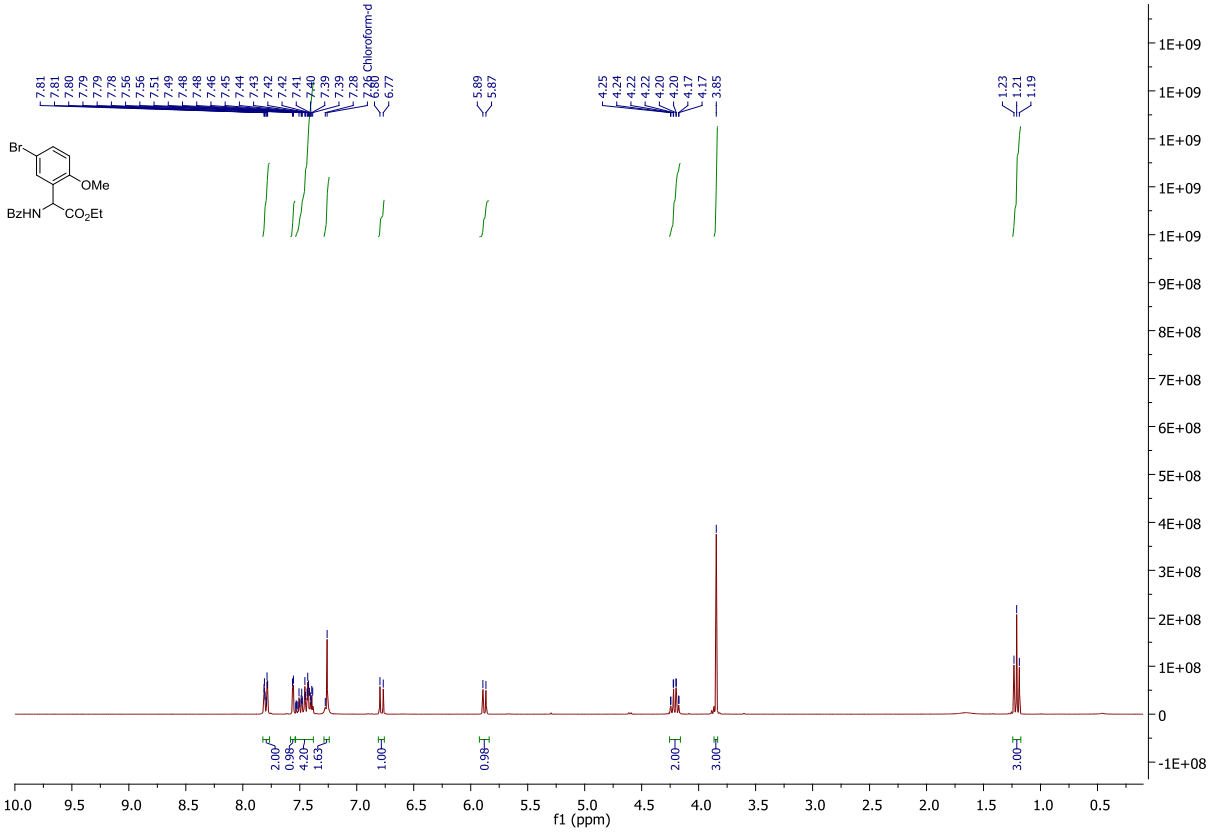


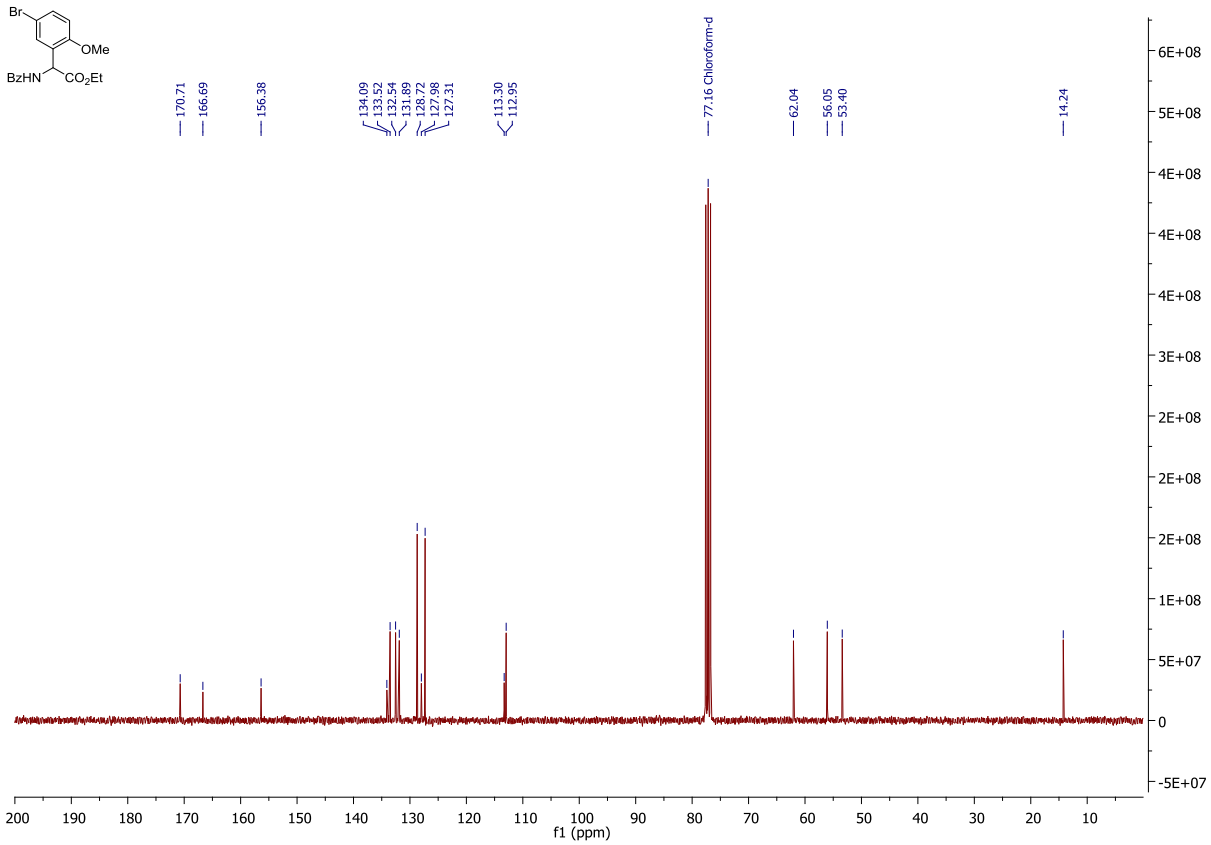
Ethyl-2-(benzamido)-2-(5-chloro-2-methoxyphenyl)acetate (4g)



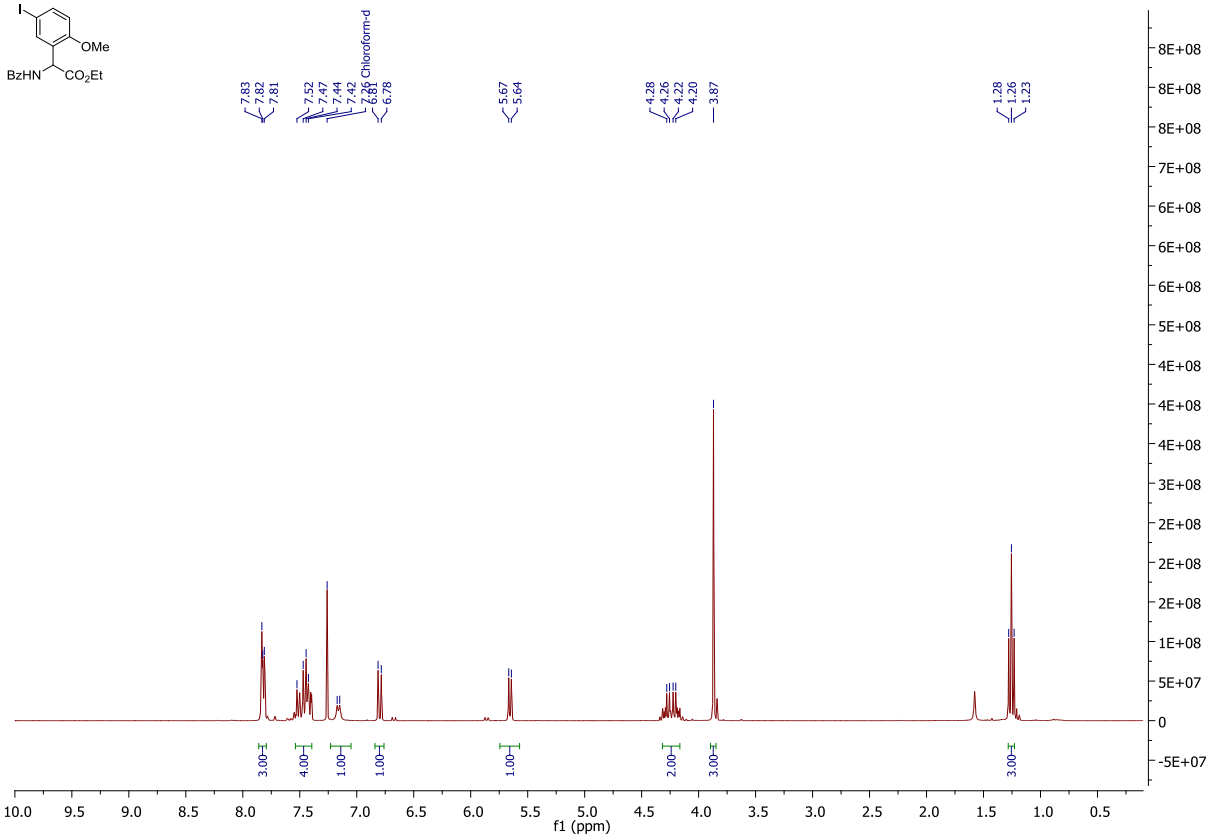


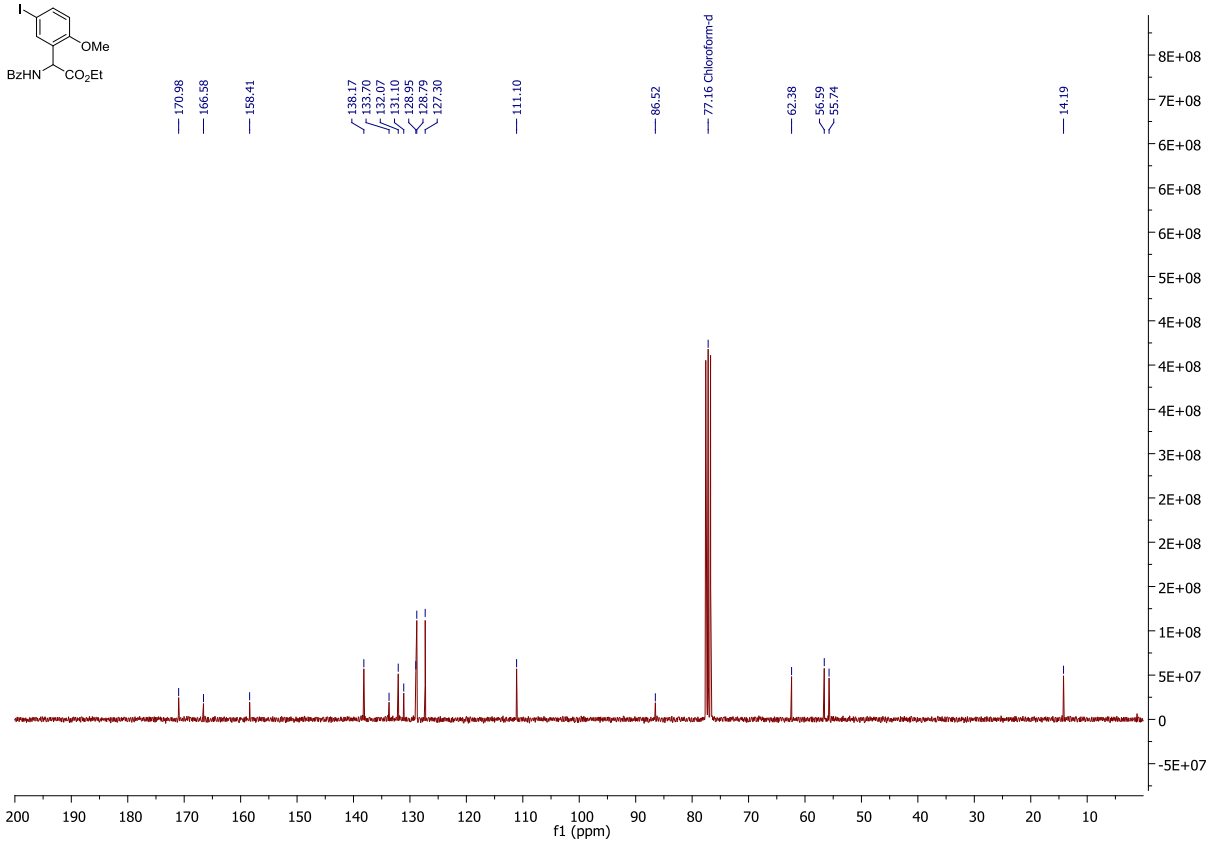
Ethyl-2-(benzamido)-2-(5-bromo-2-methoxyphenyl)acetate (4h)



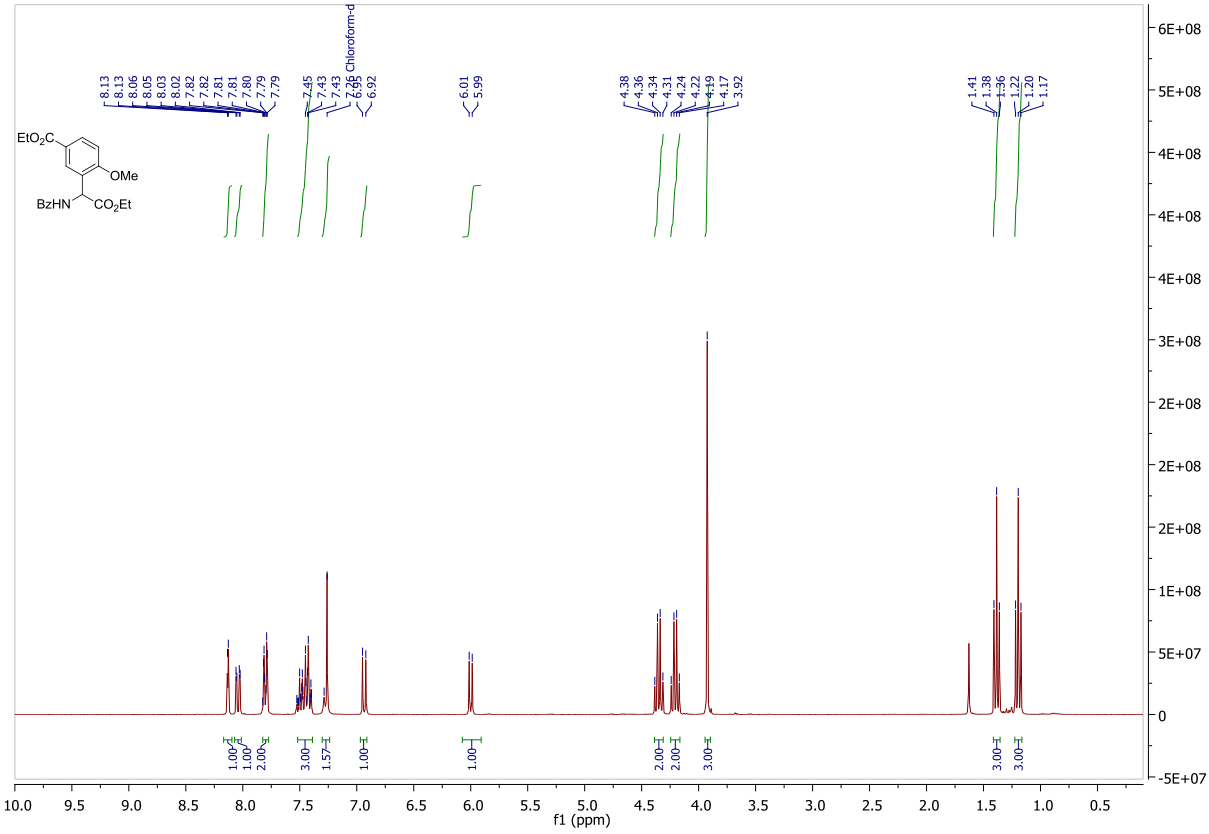


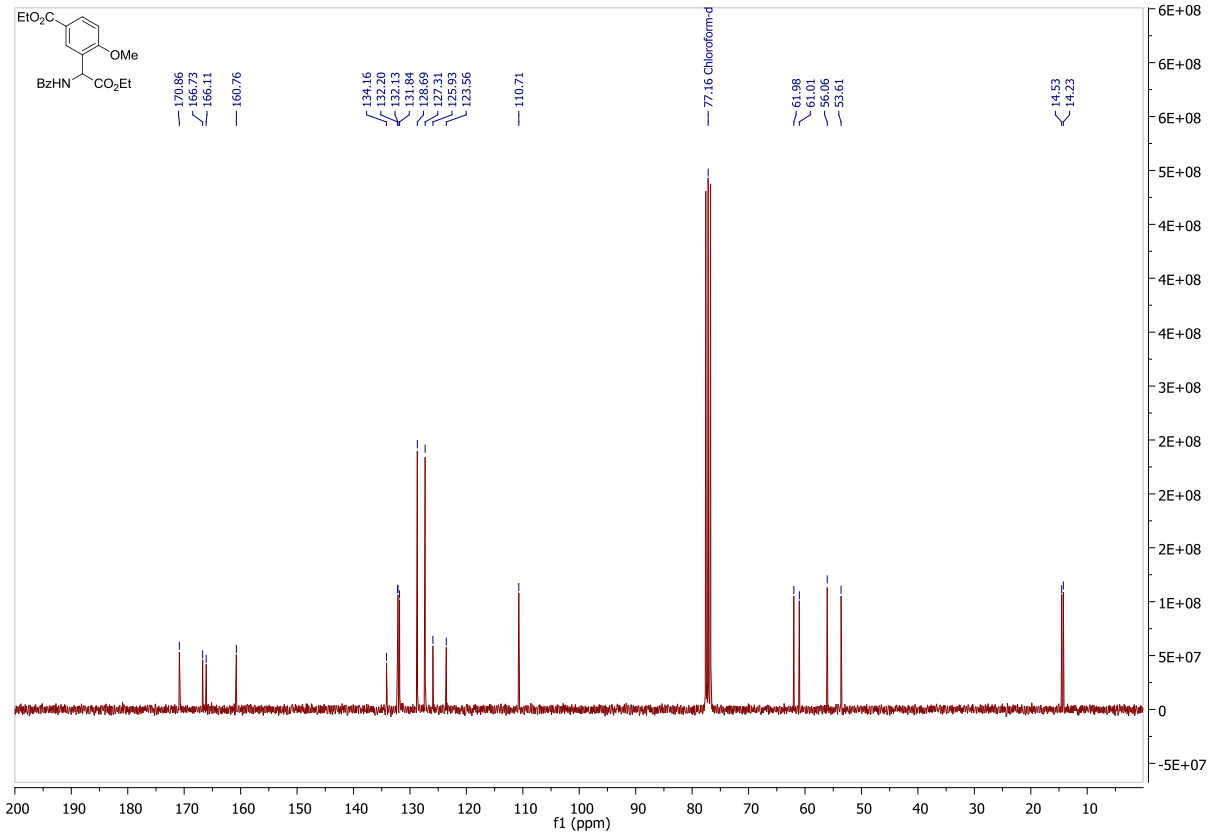
Ethyl-2-(benzamido)-2-(5-iodo-2-methoxyphenyl)acetate (4i)



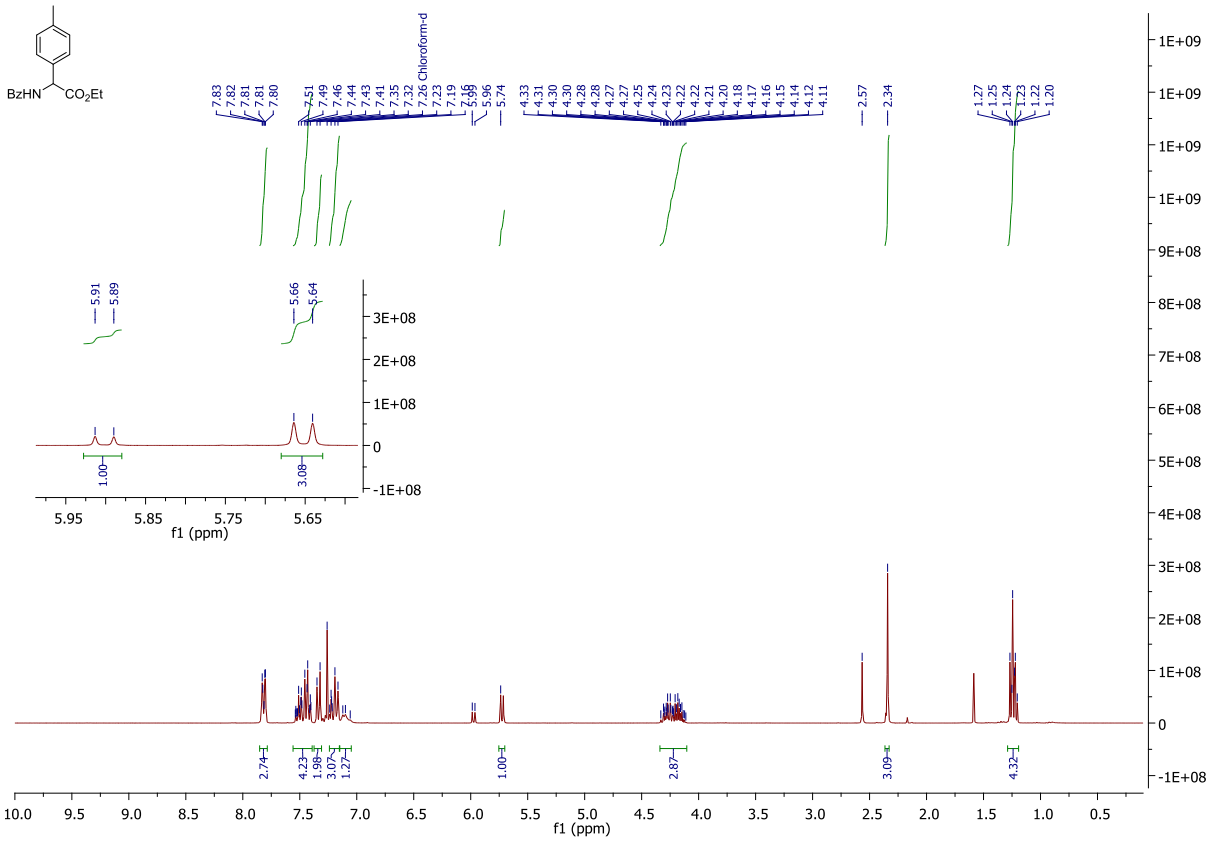


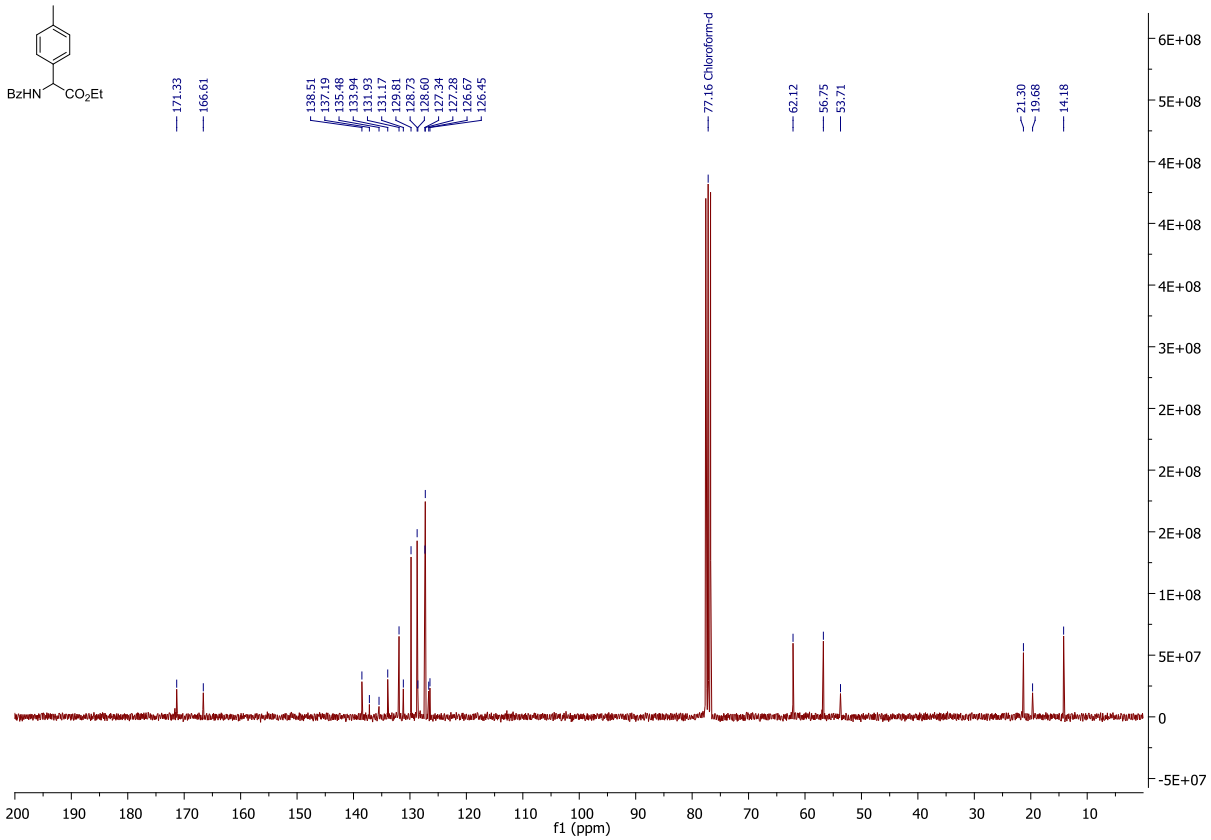
Ethyl-3-(1-benzamido-2-ethoxy-2-oxoethyl)-4-methoxybenzoate (4j)



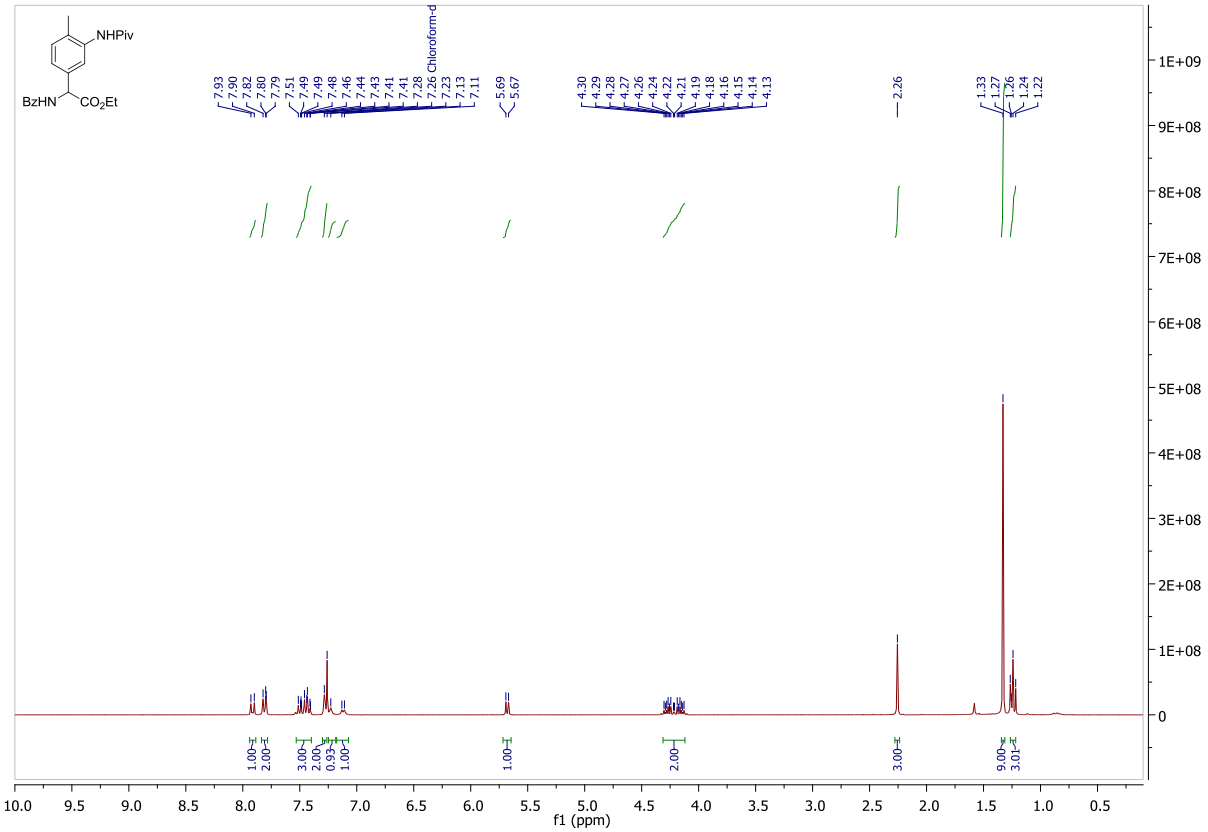


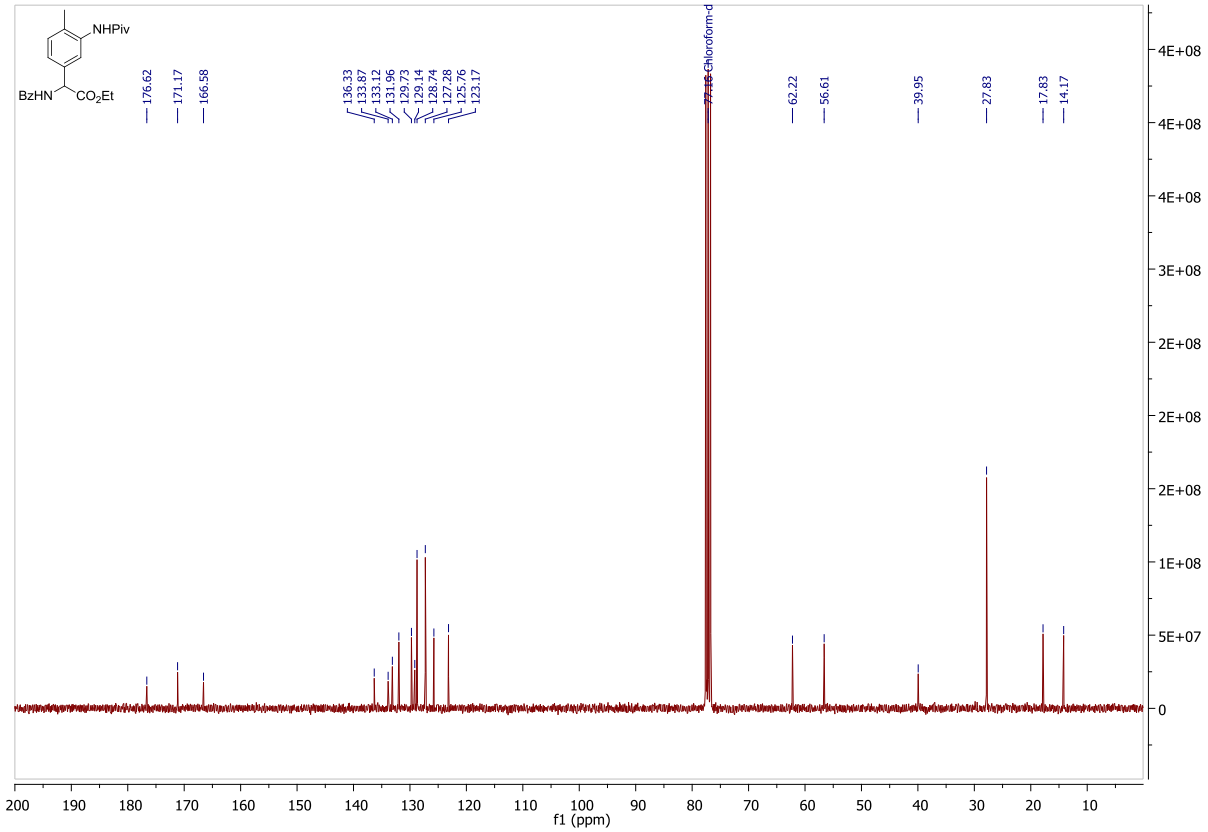
Ethyl-2-(benzamido)-2-*p*-tolylacetate (4k)



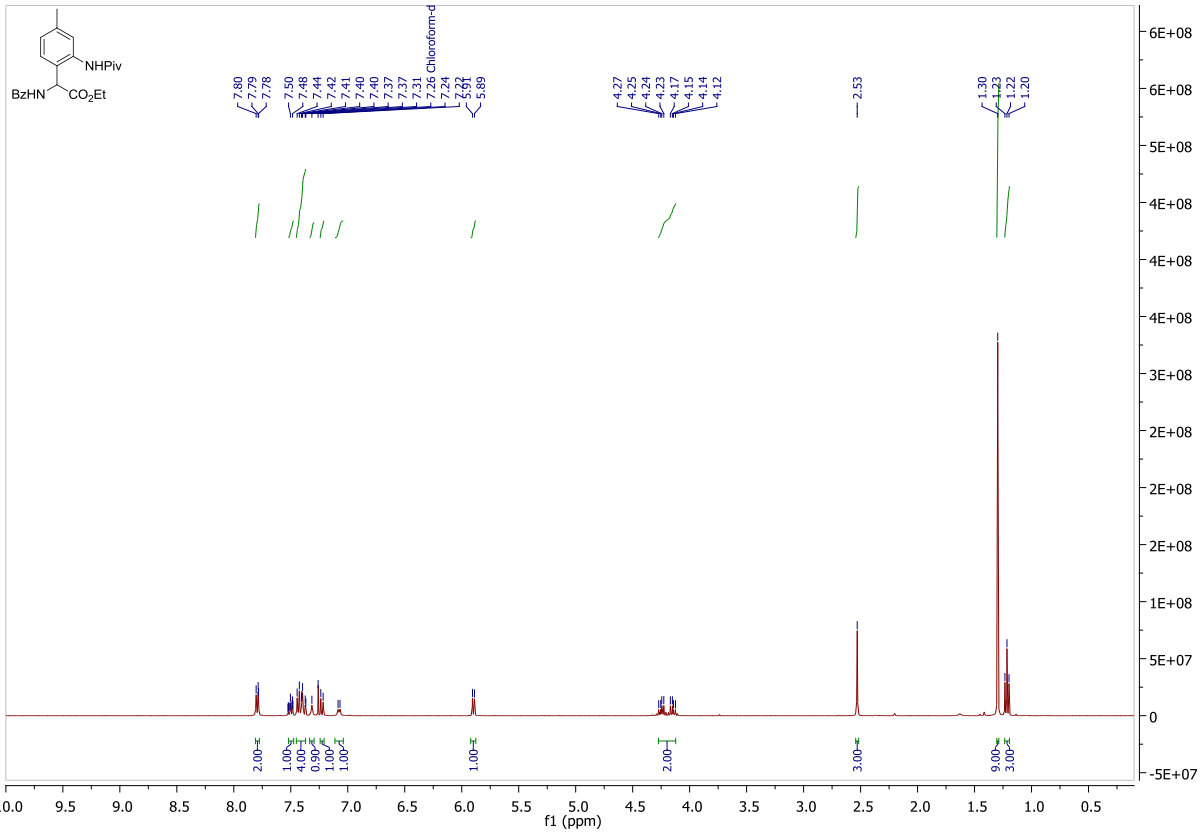


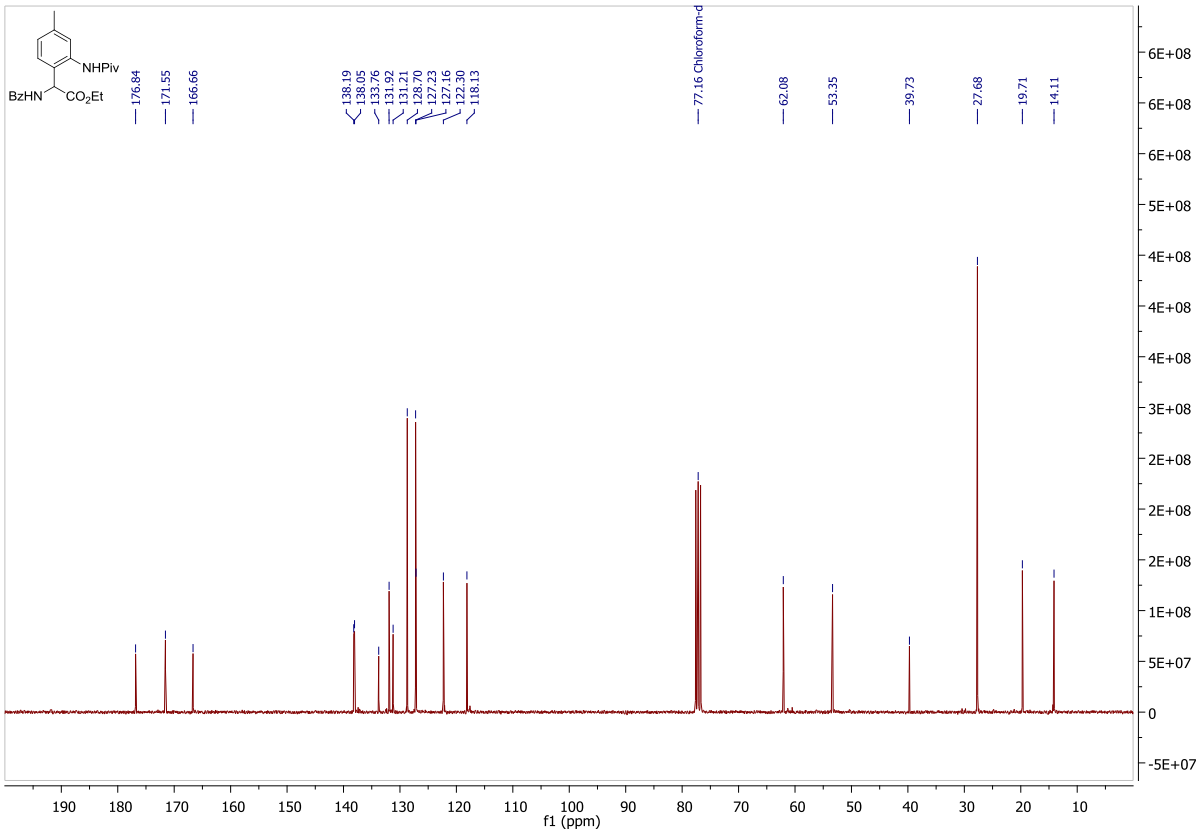
Ethyl-2-benzamido-2-(4-methyl-3-pivalamidophenyl)acetate (4l)



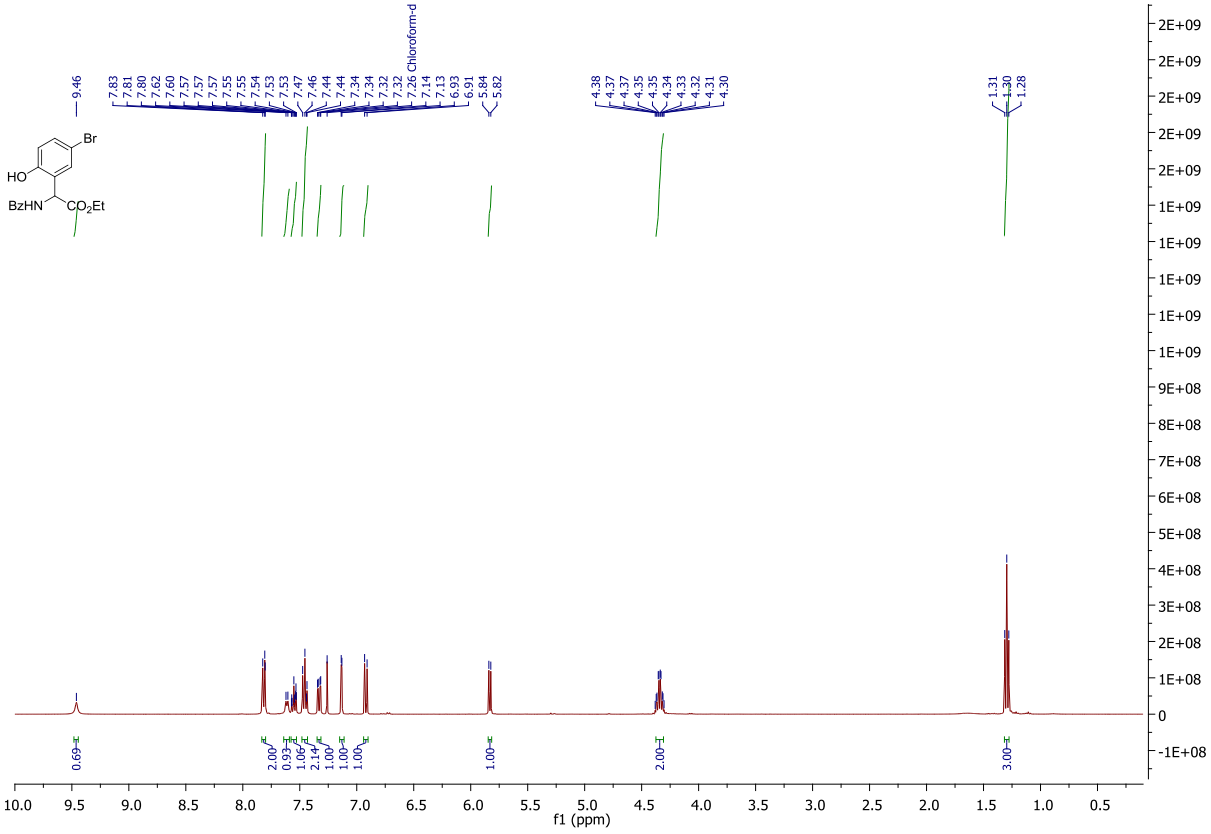


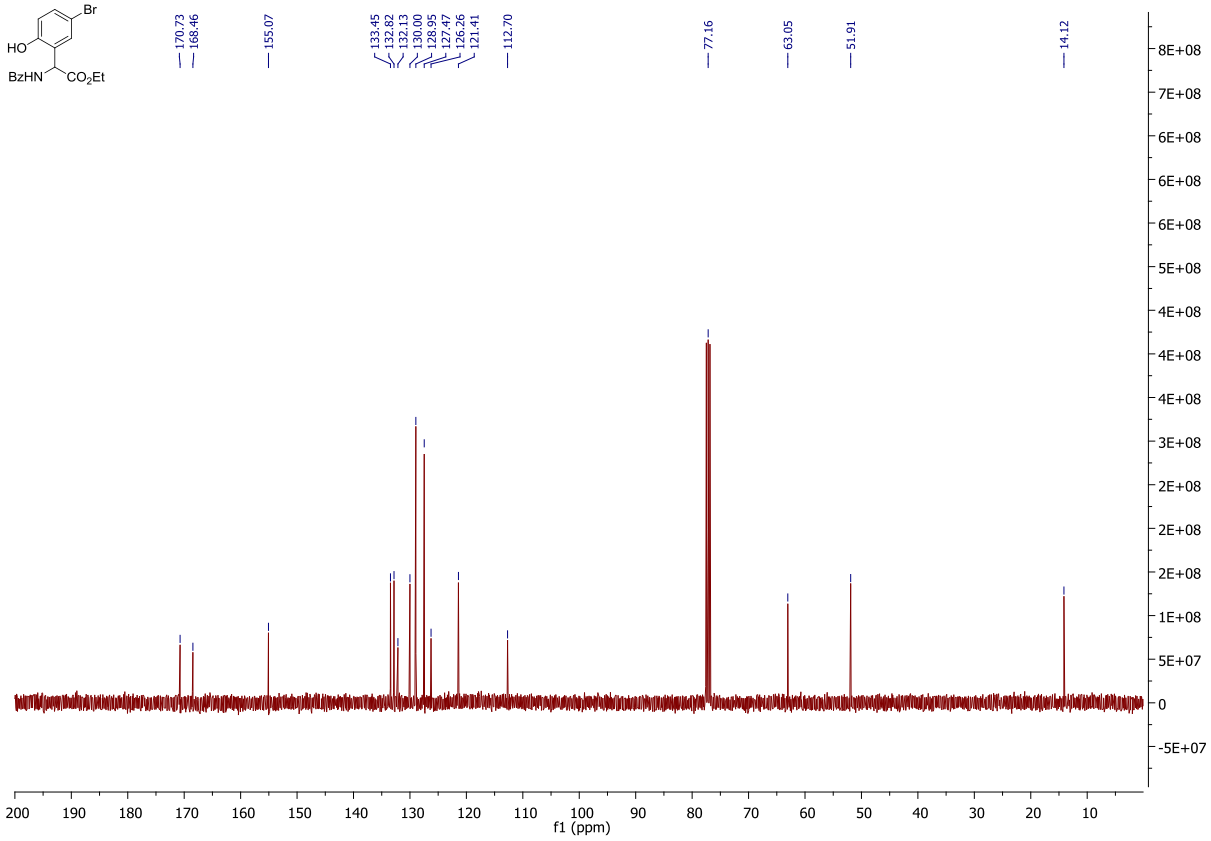
Ethyl-2-benzamido-2-(4-methyl-2-pivalamidophenyl)acetate (4m)



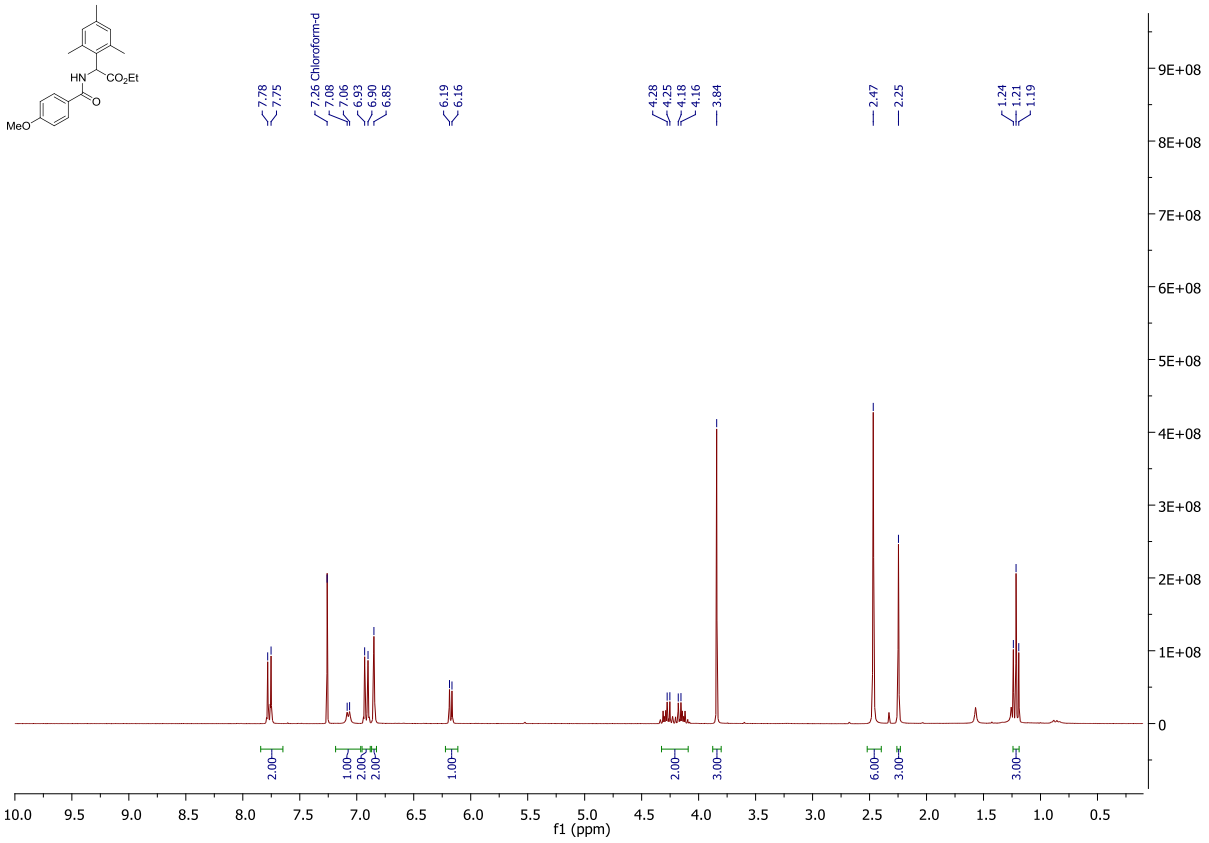


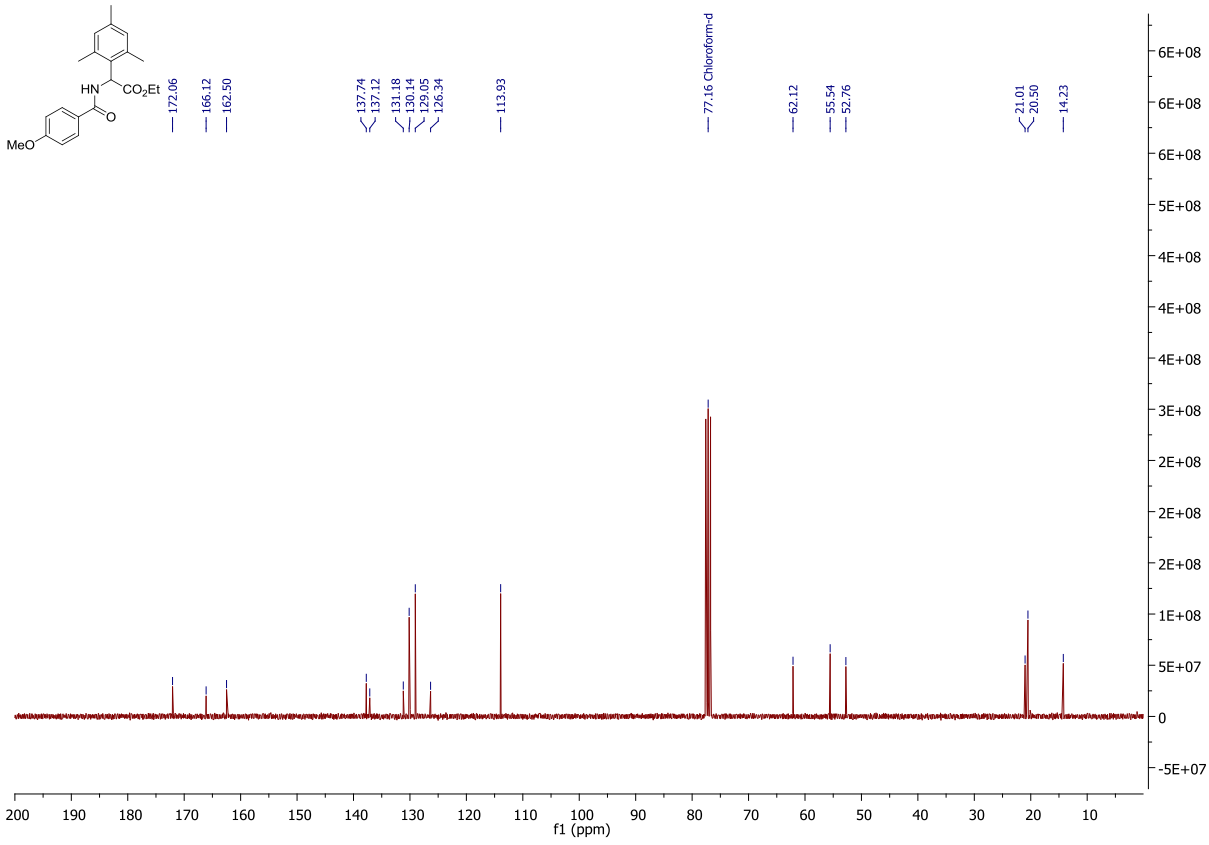
Ethyl-2-(benzamido)-2-(5-bromo-2-hydroxyphenyl)acetate (4n)



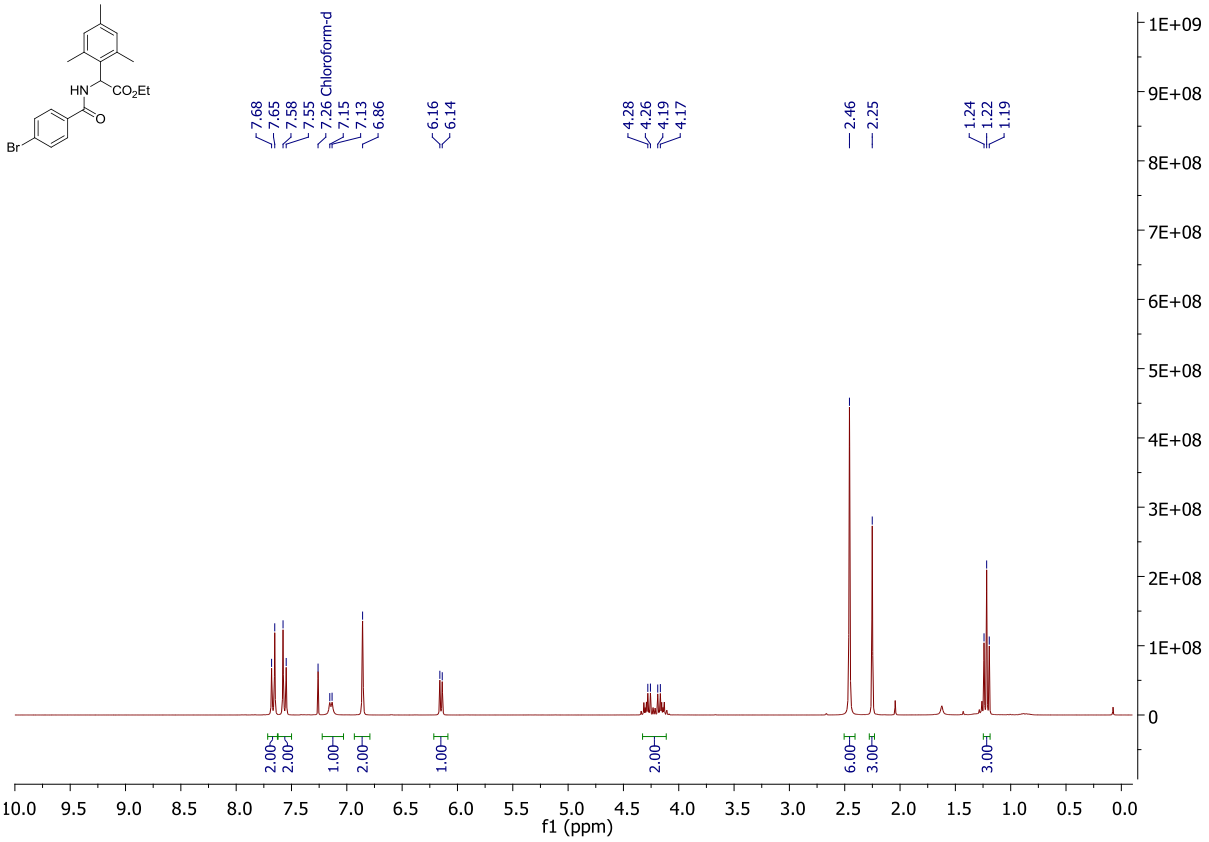


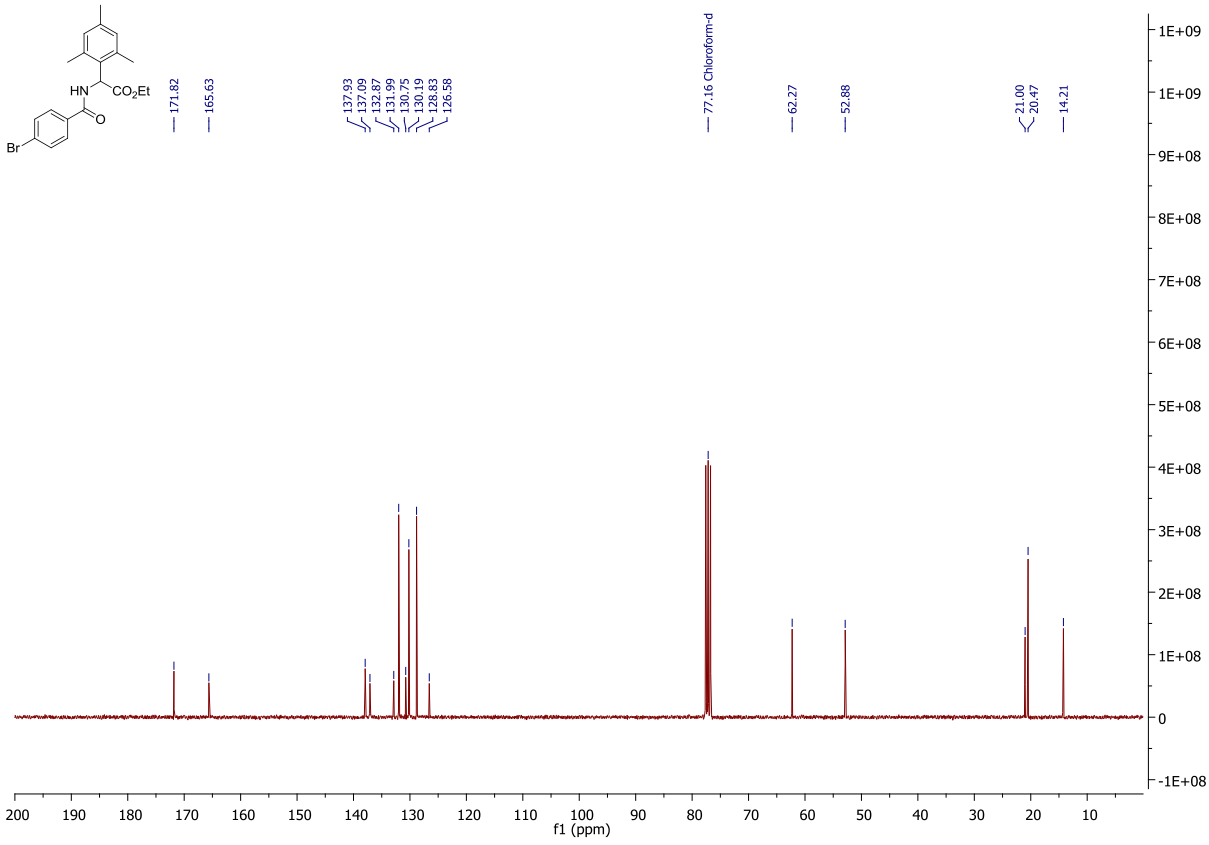
Ethyl-2-mesityl-2-(4-methoxybenzamido)acetate (5a)



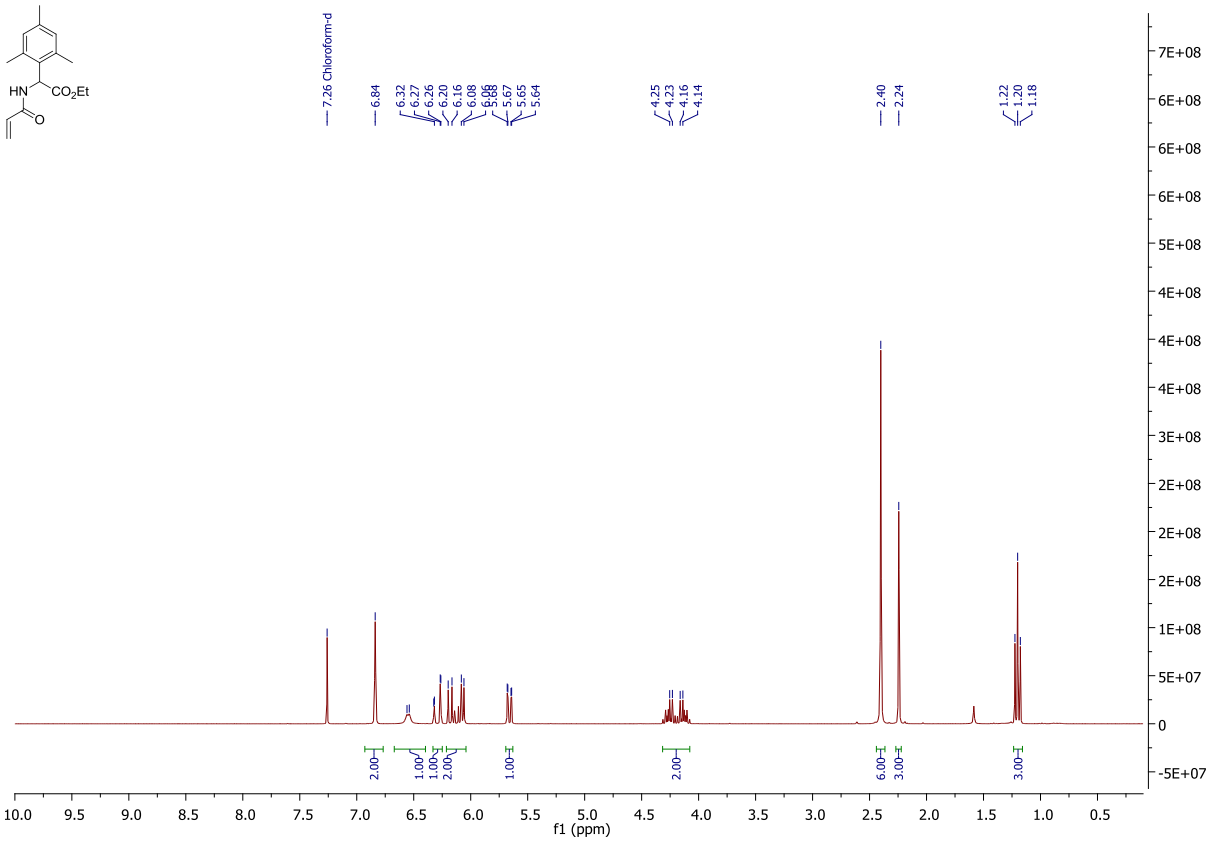


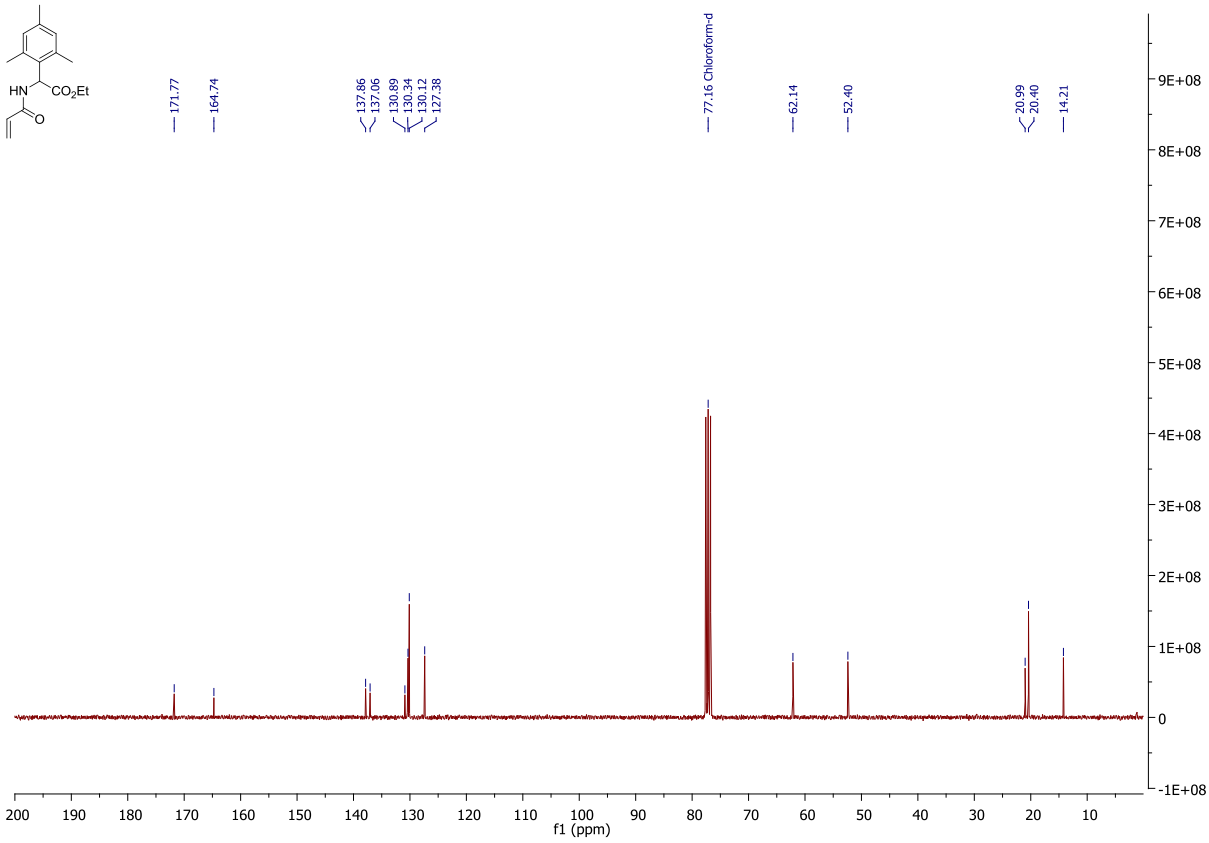
Ethyl-2-(4-bromobenzamido)-2-mesitylacetate (5b)



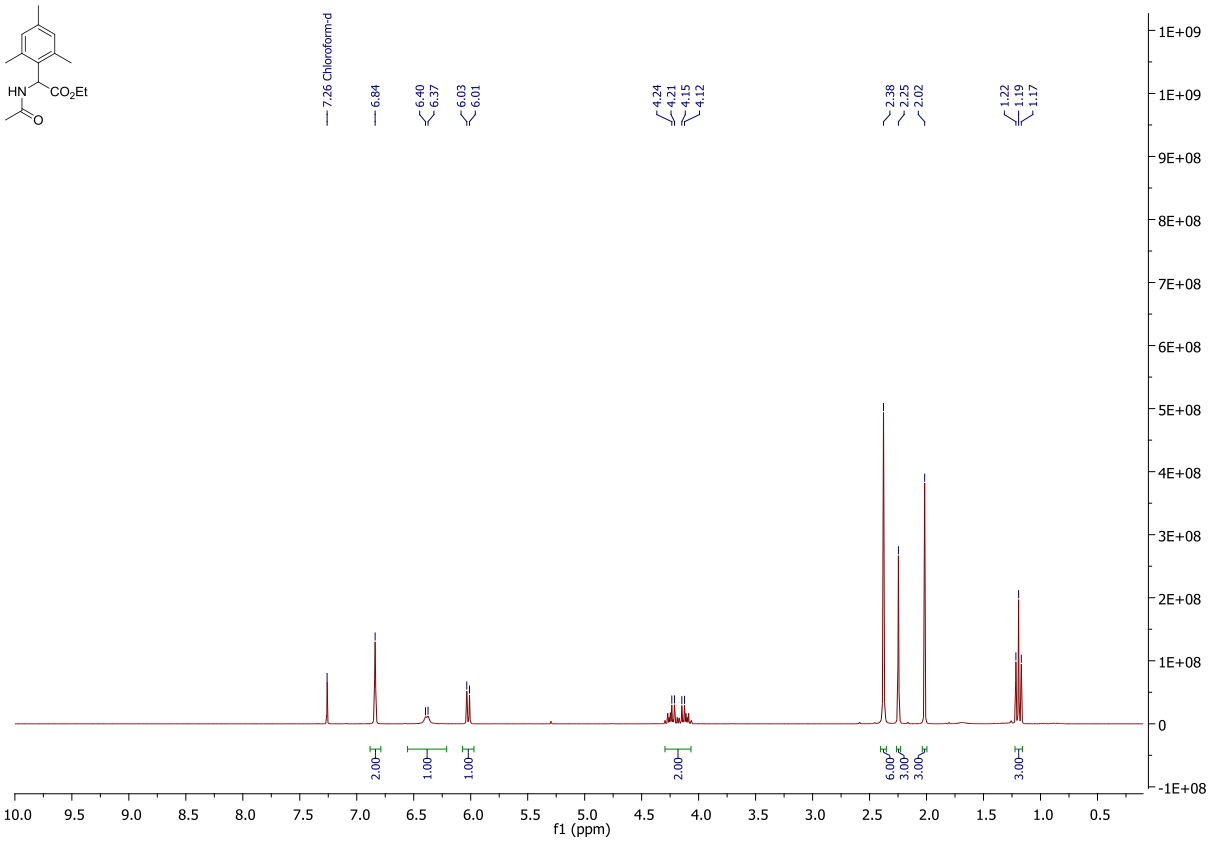


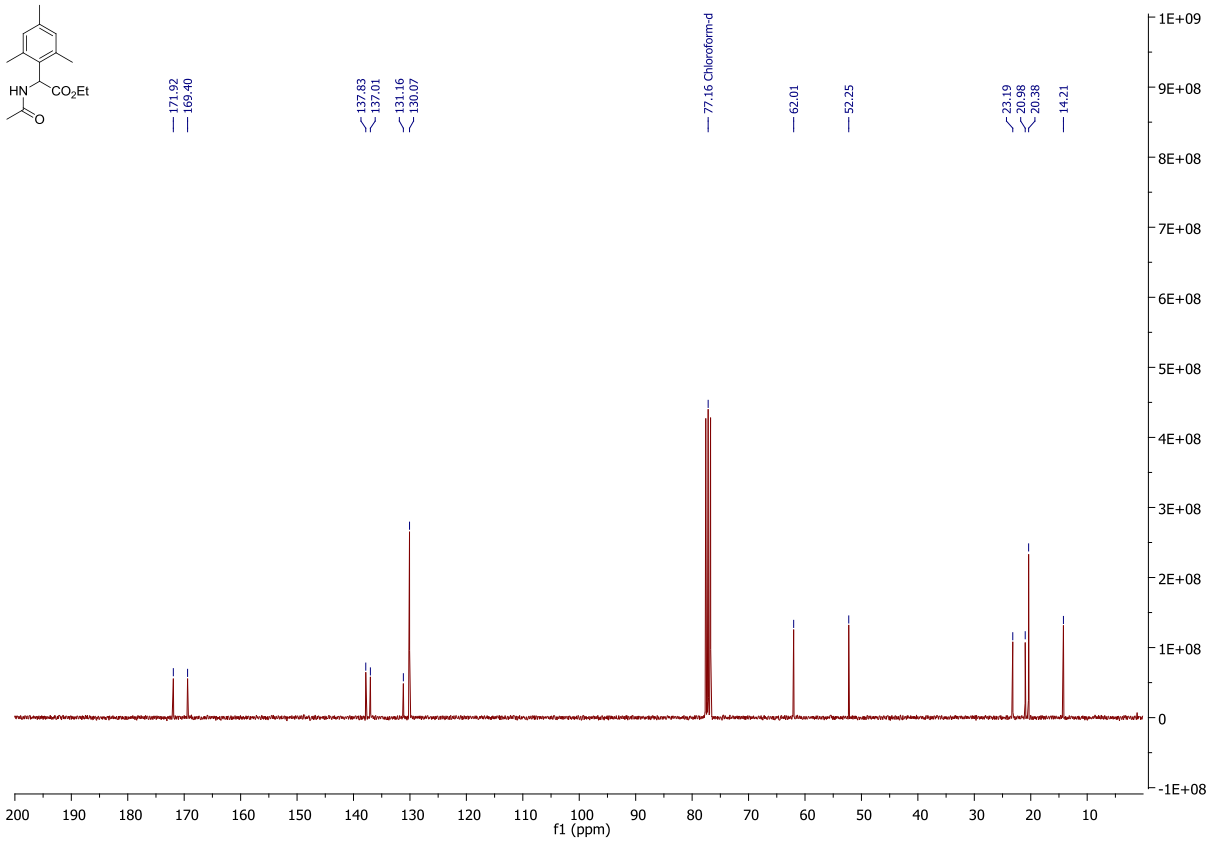
Ethyl-2-acrylamido-2-mesitylacetate (5c)



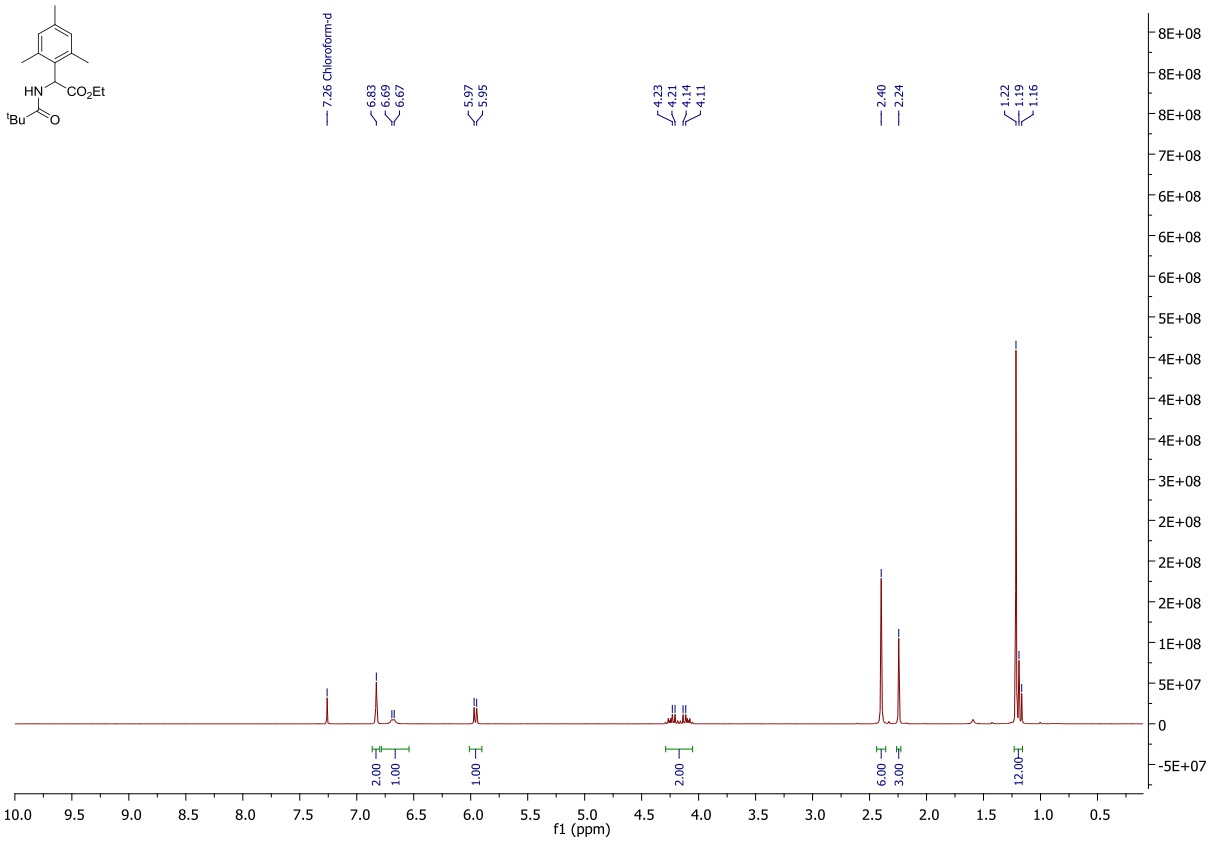


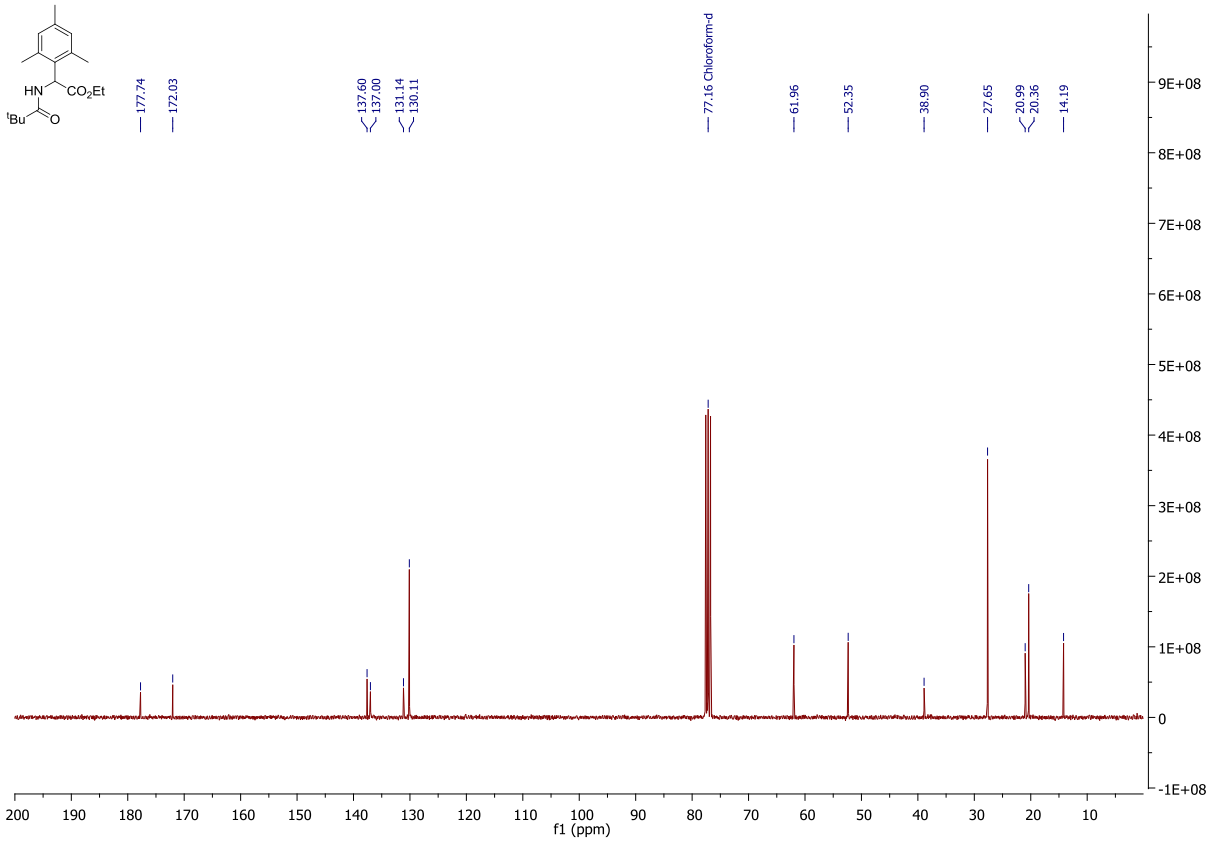
Ethyl-2-acetamido-2-mesitylacetate (5d)



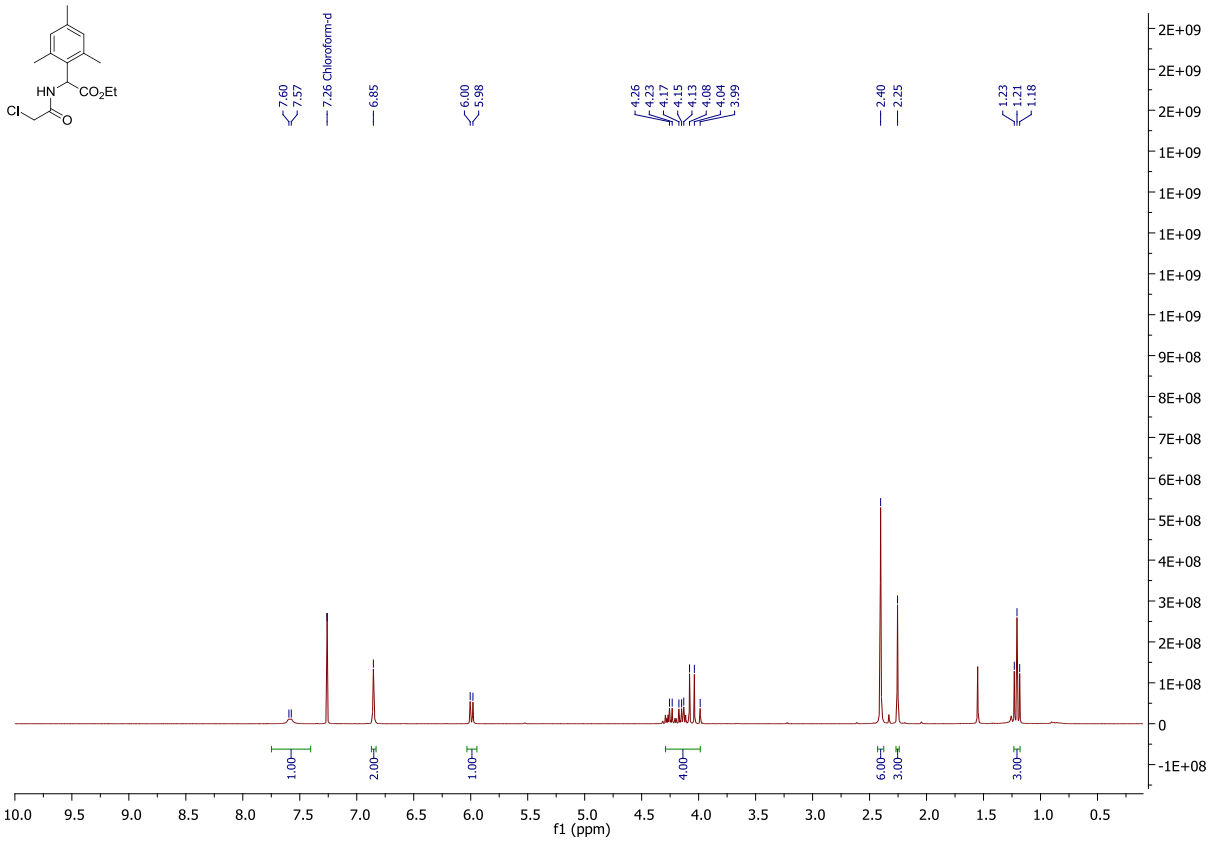


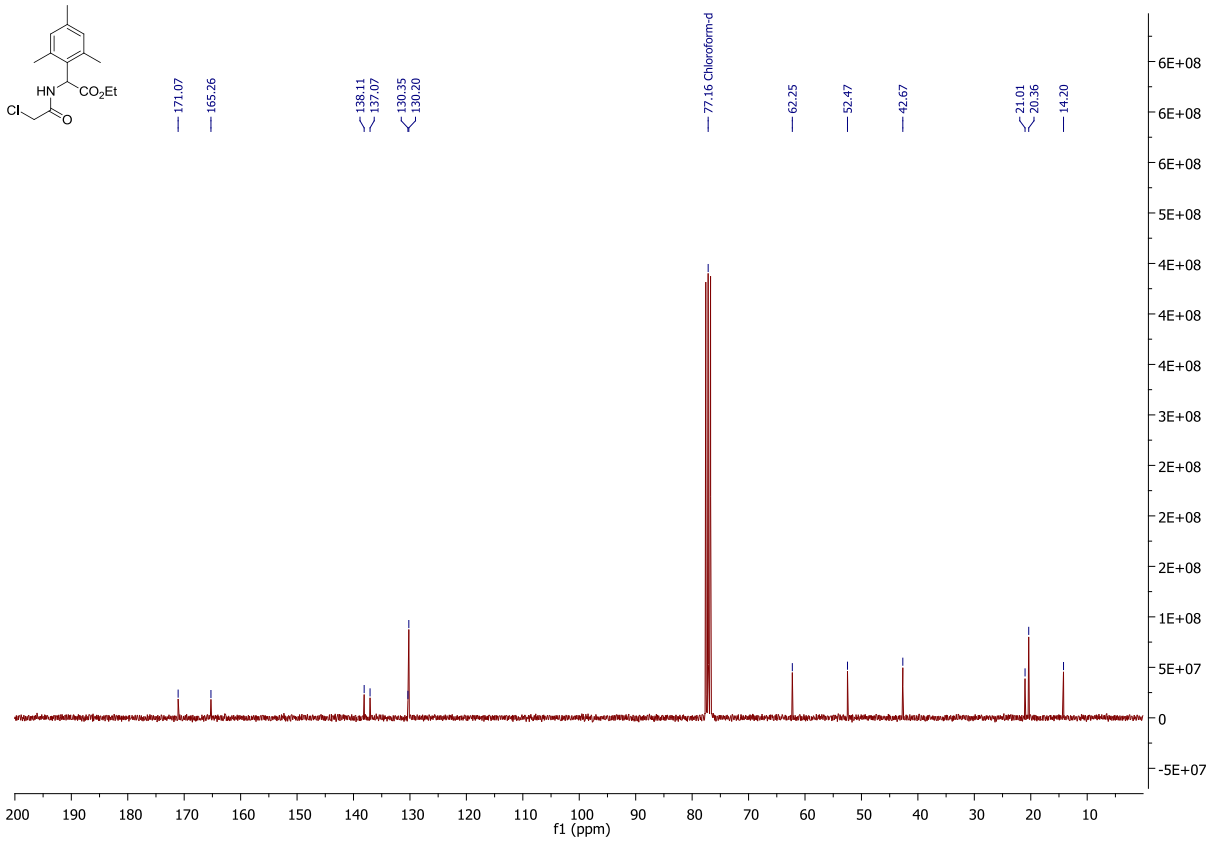
Ethyl-2-mesityl-2-pivalamidoacetate (5e)



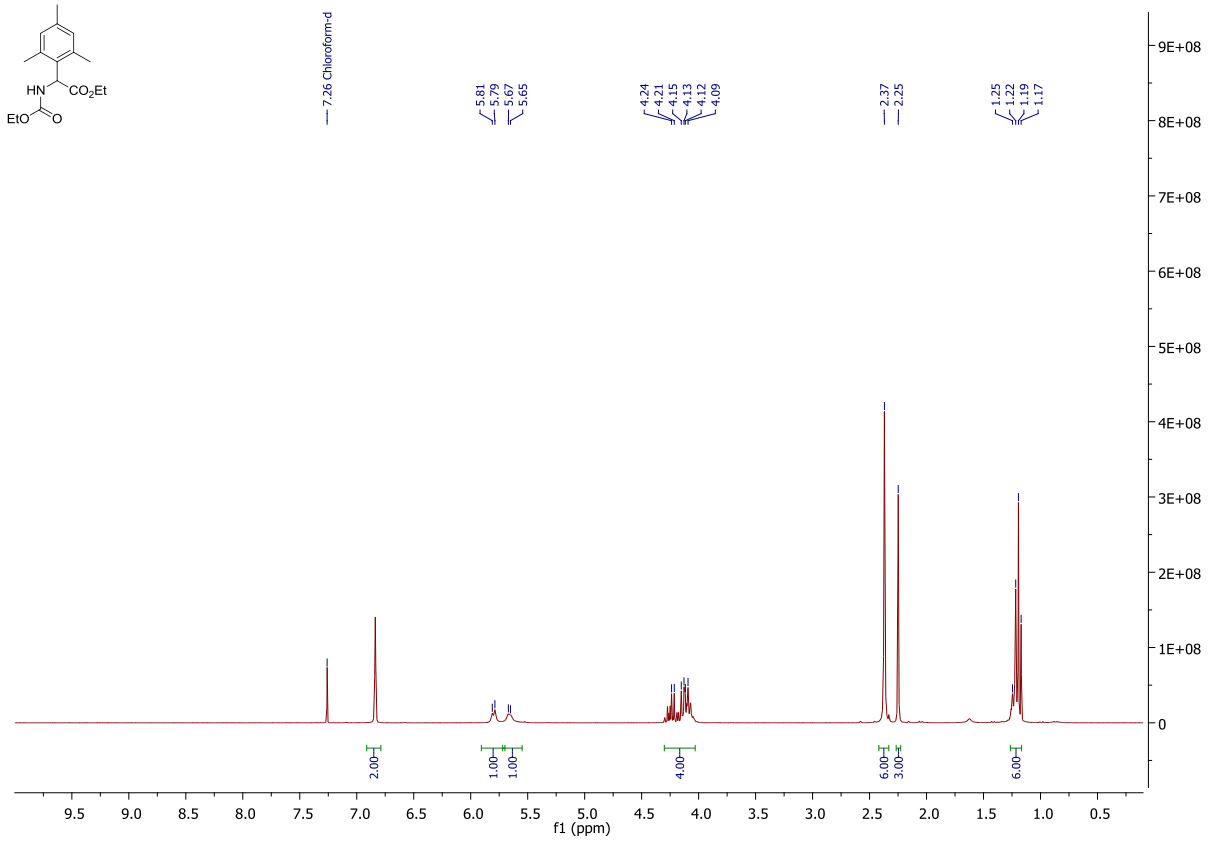


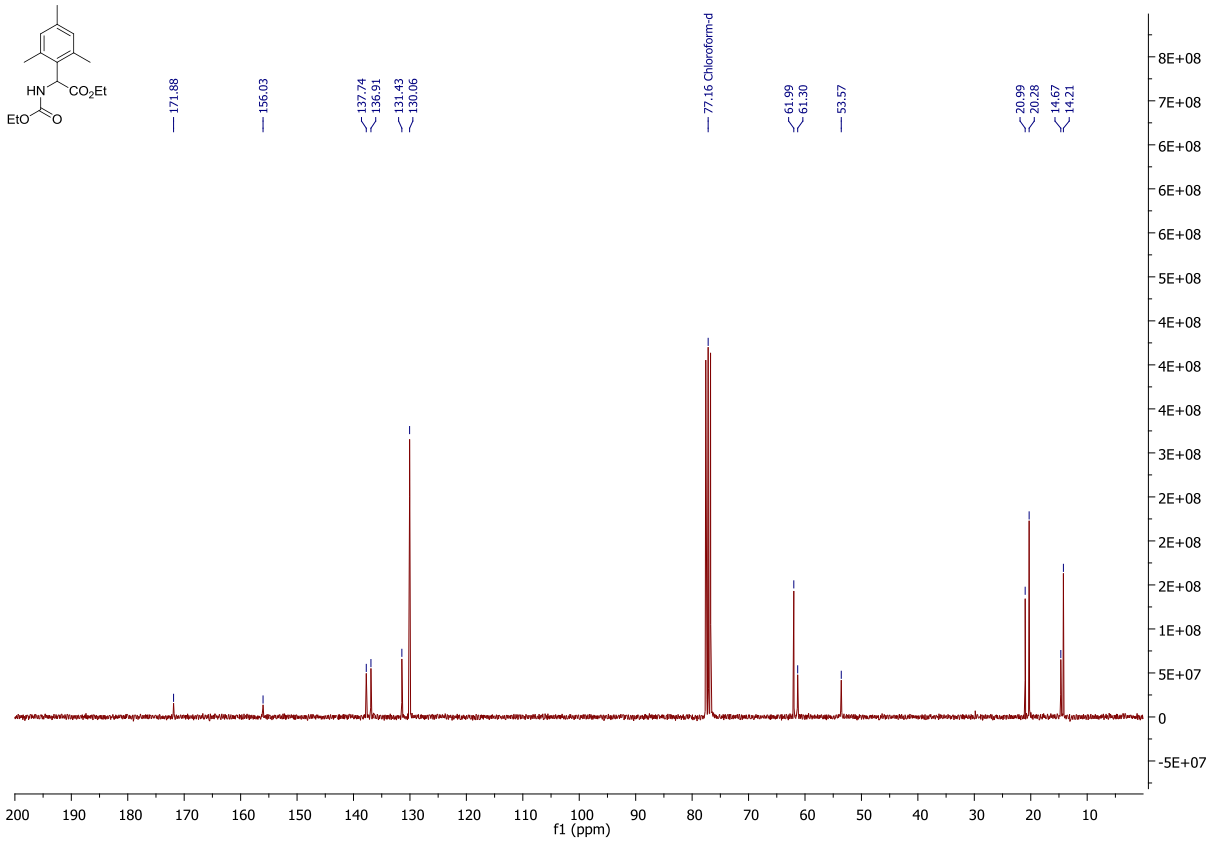
Ethyl-2-(2-chloroacetamido)-2-mesitylacetate (5f)



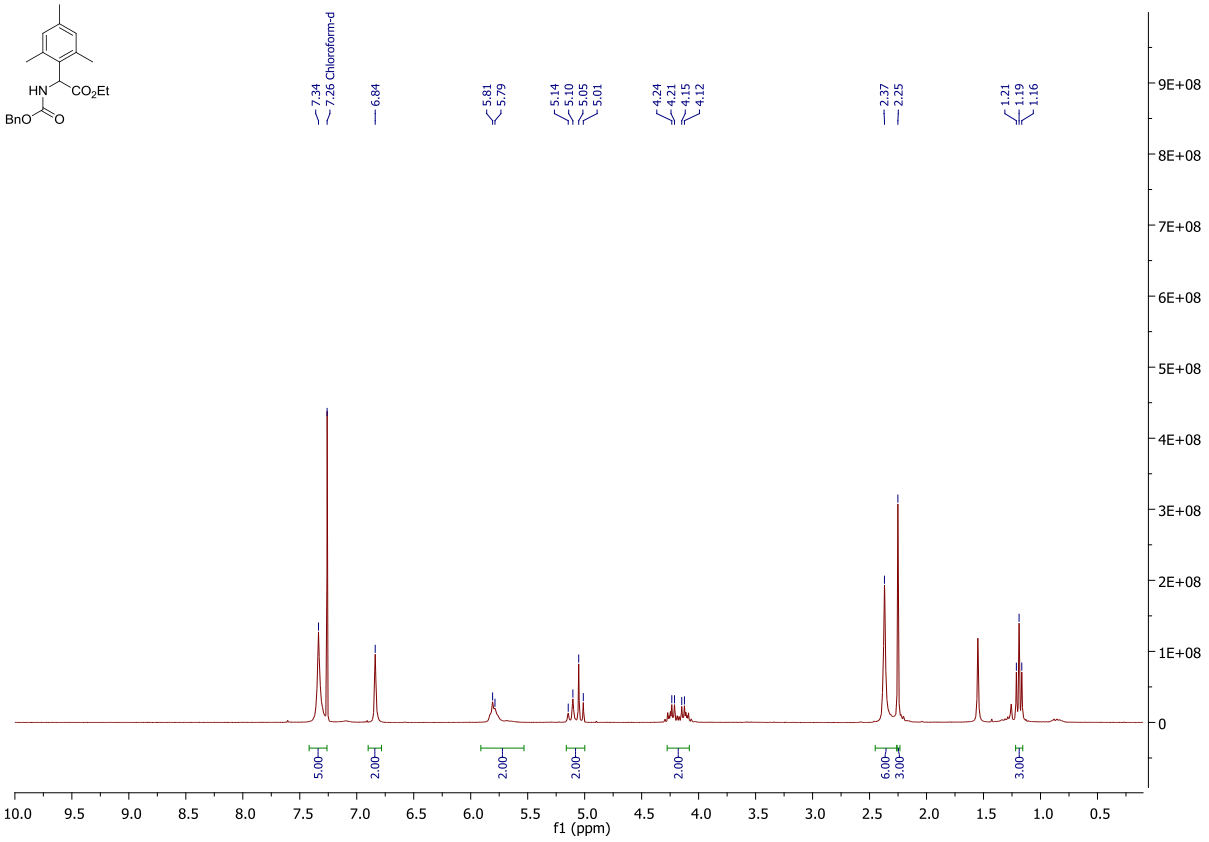


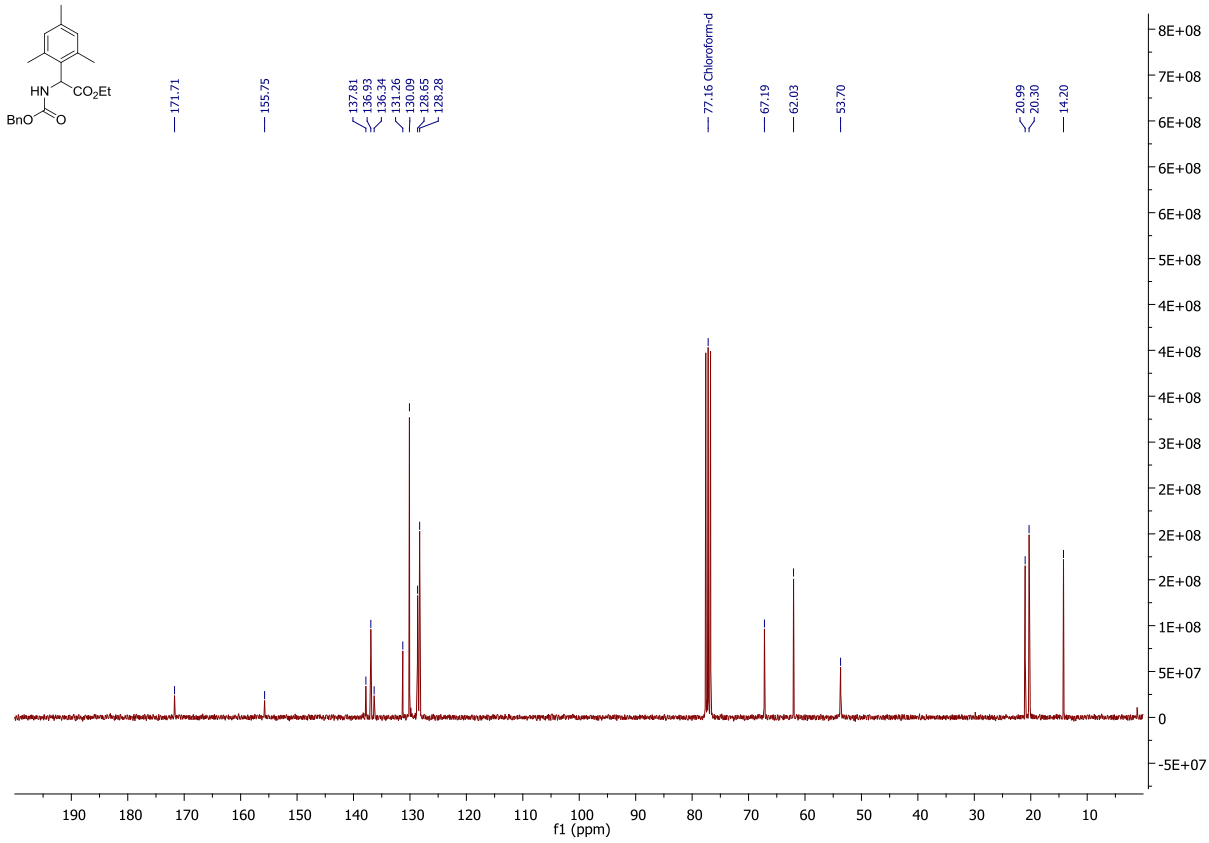
Ethyl-2-((ethoxycarbonyl)amino)-2-mesitylacetate (5g)



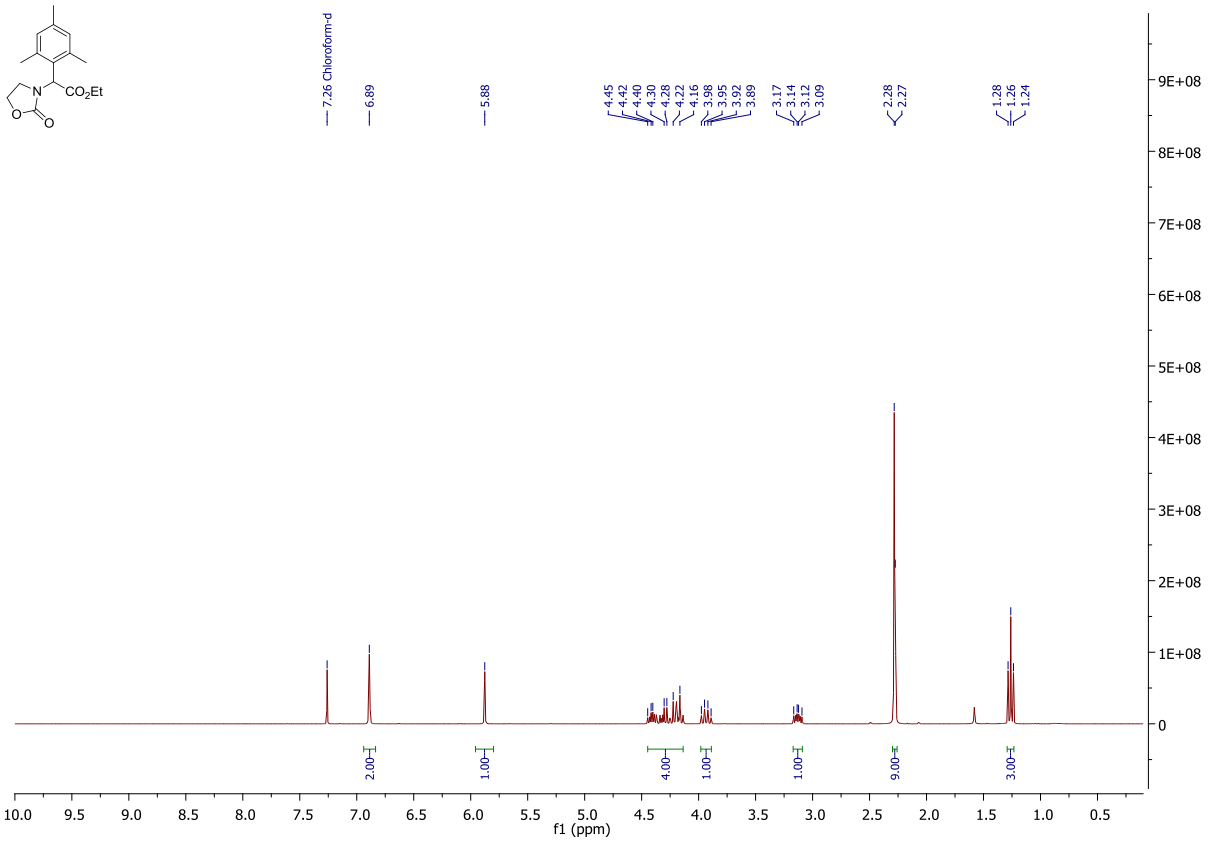


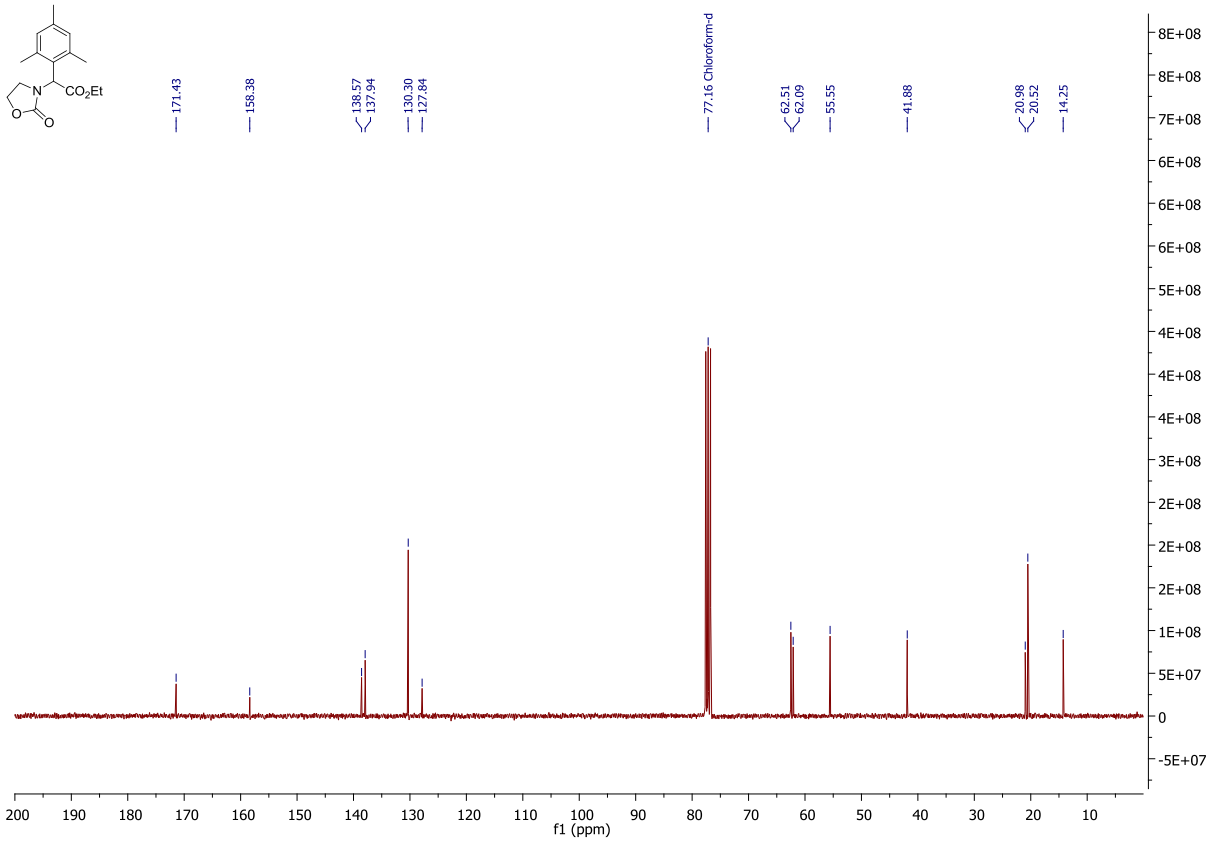
Ethyl-2-(((benzyloxy)carbonyl)amino)-2-mesitylacetate (5h)



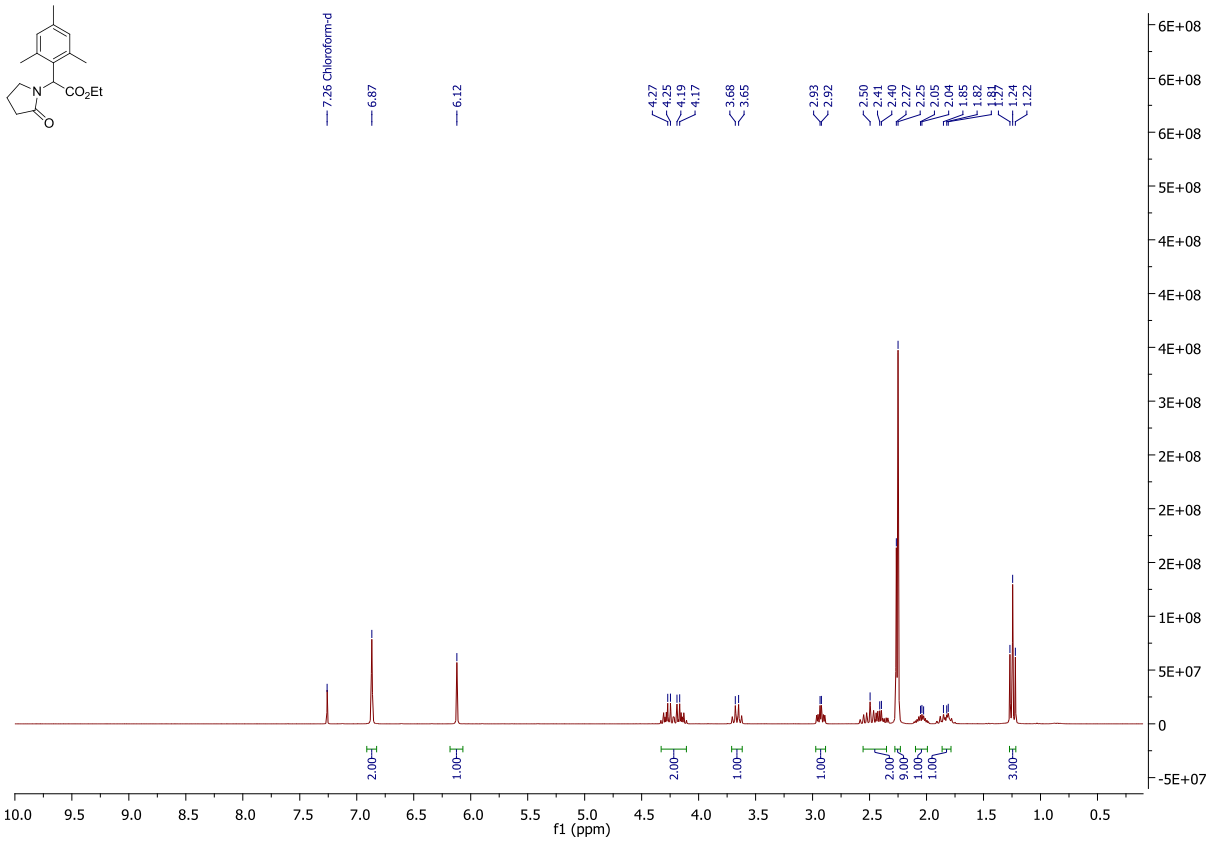


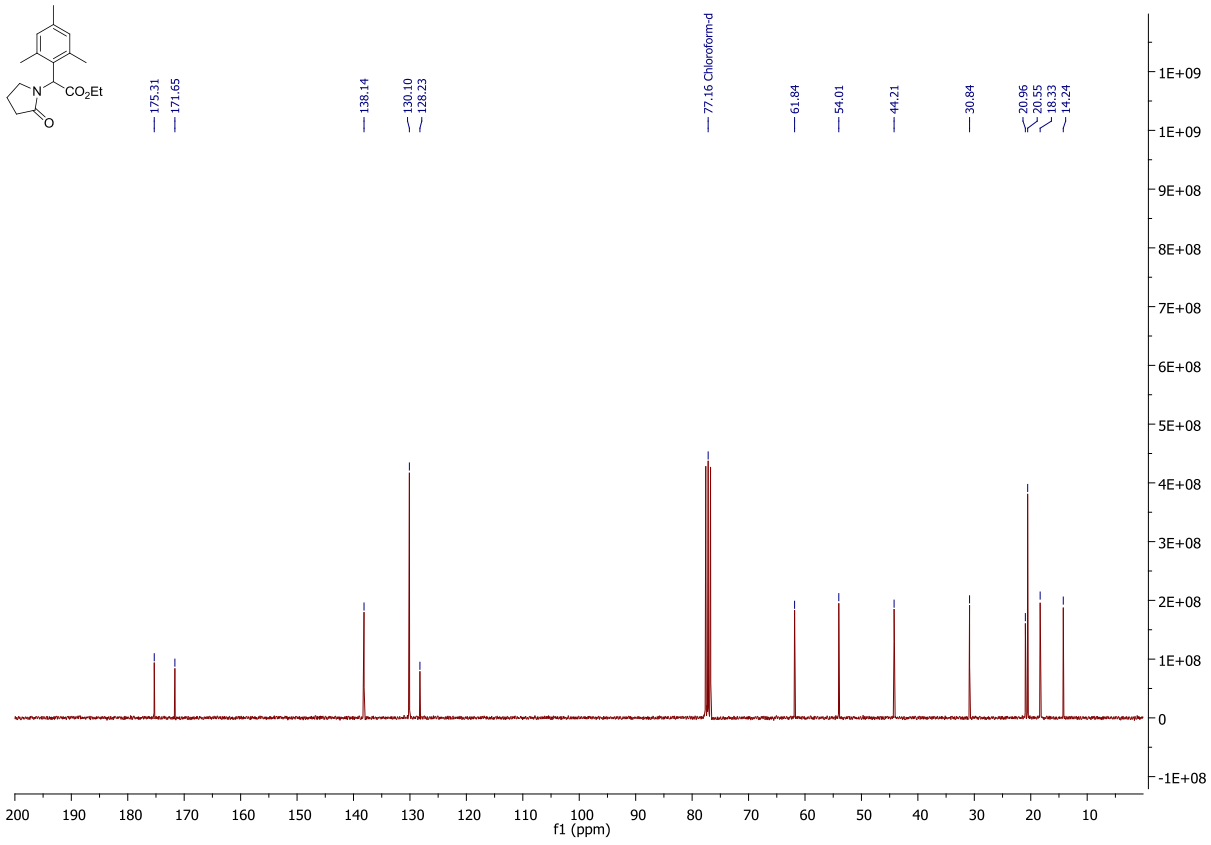
Ethyl-2-mesityl-2-(2-oxooxazolidin-3-yl)acetate (5k)





Ethyl-2-mesityl-2-(2-oxopyrrolidin-1-yl)acetate (5l)





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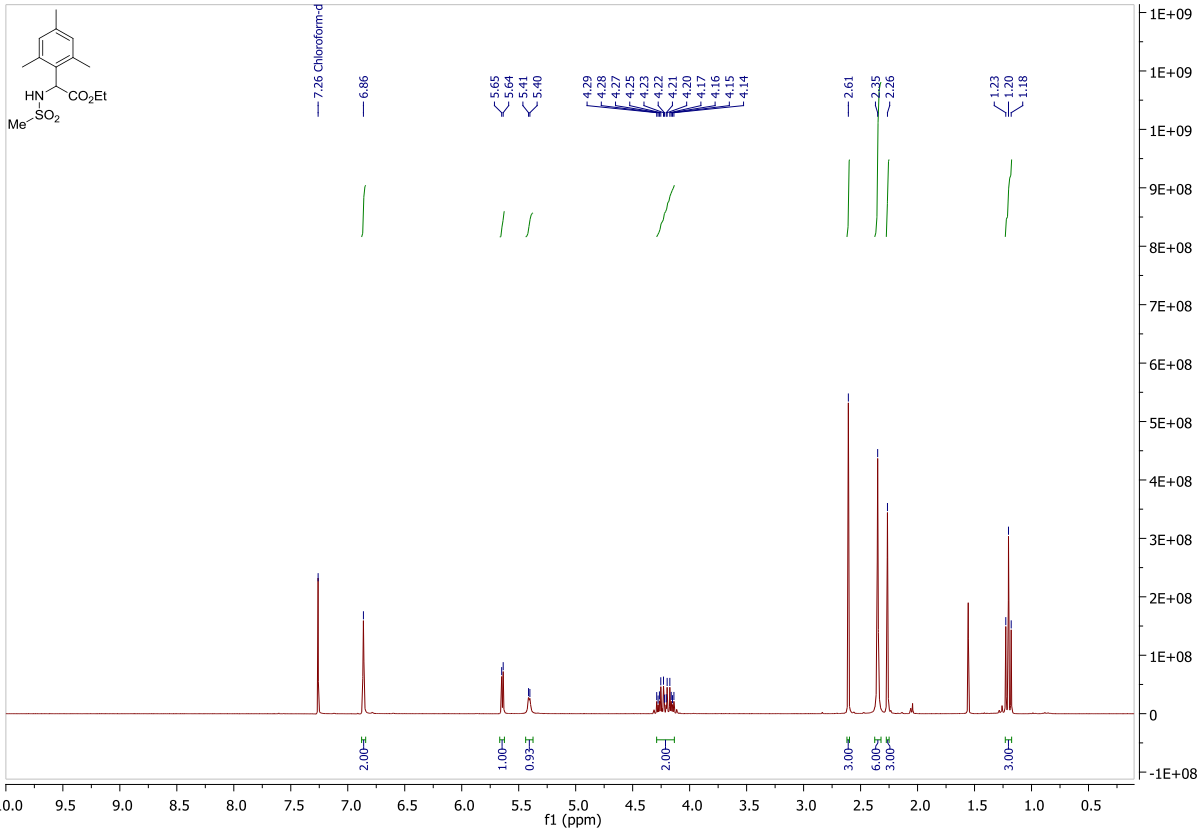

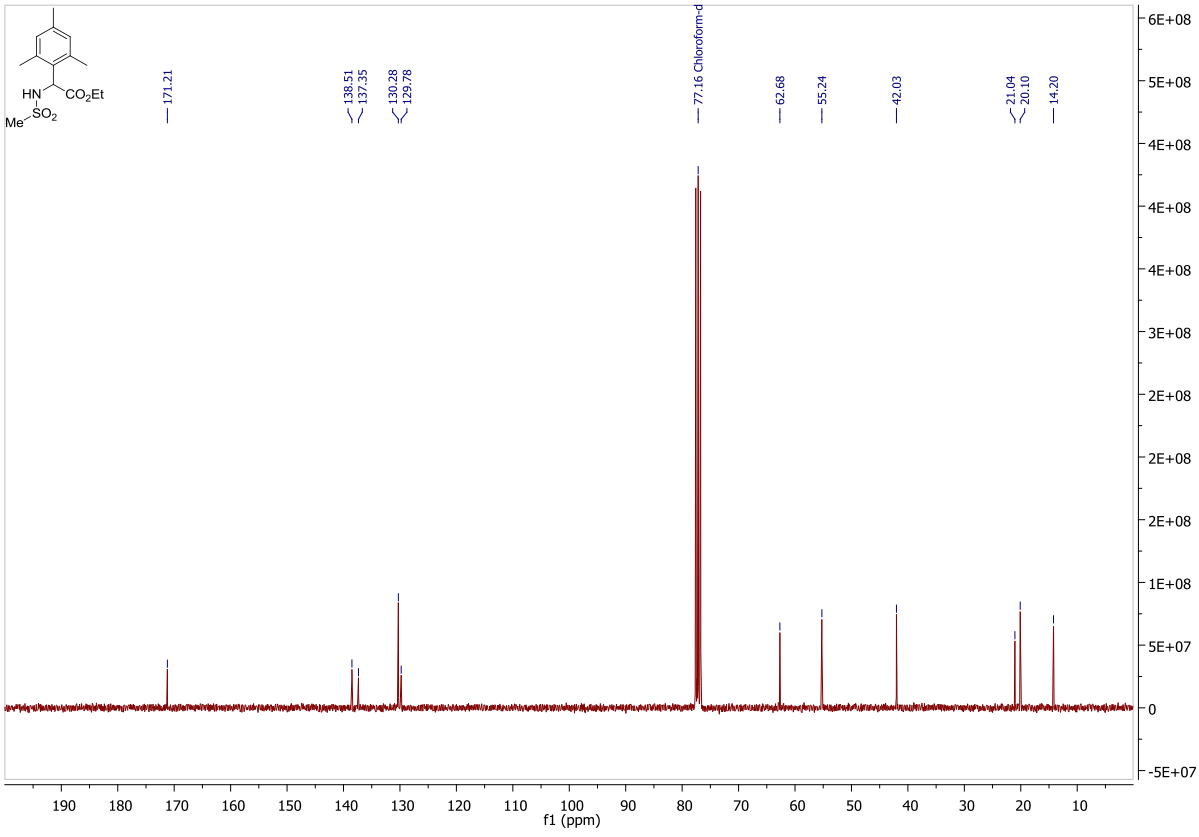

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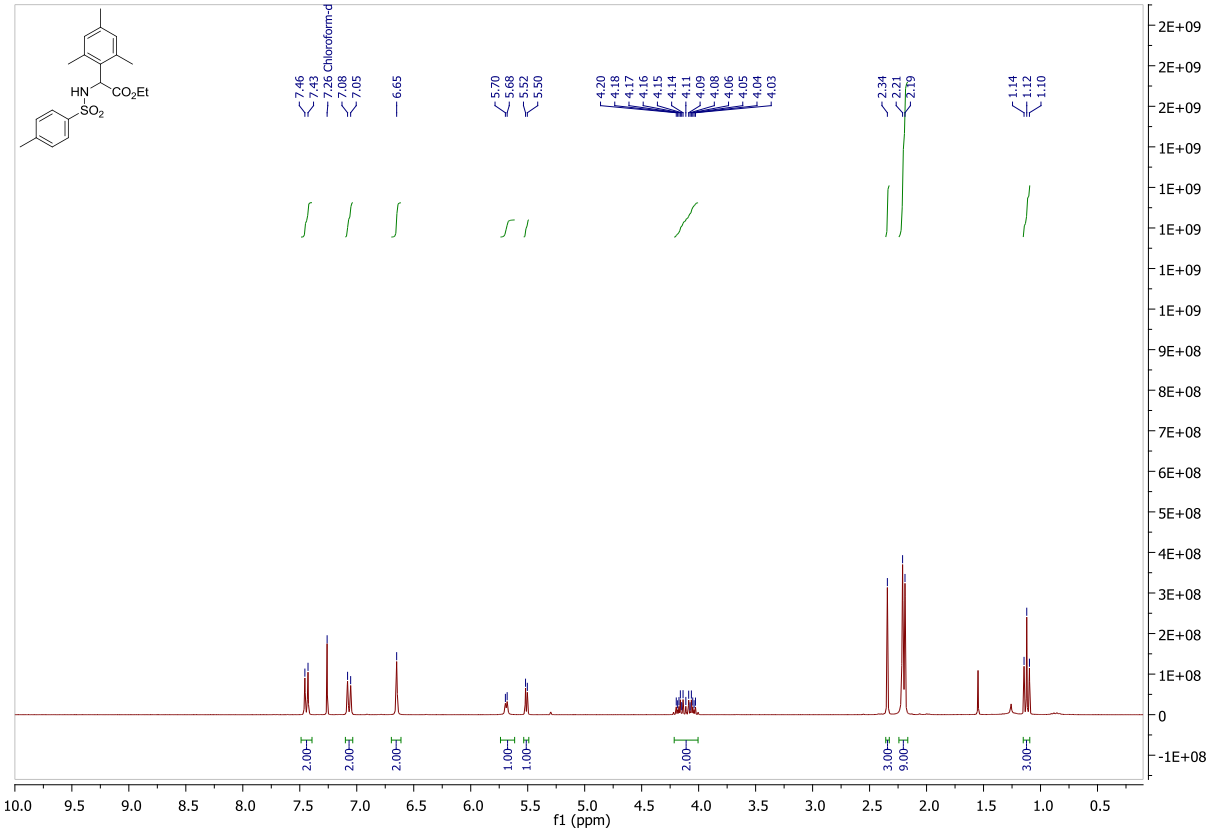
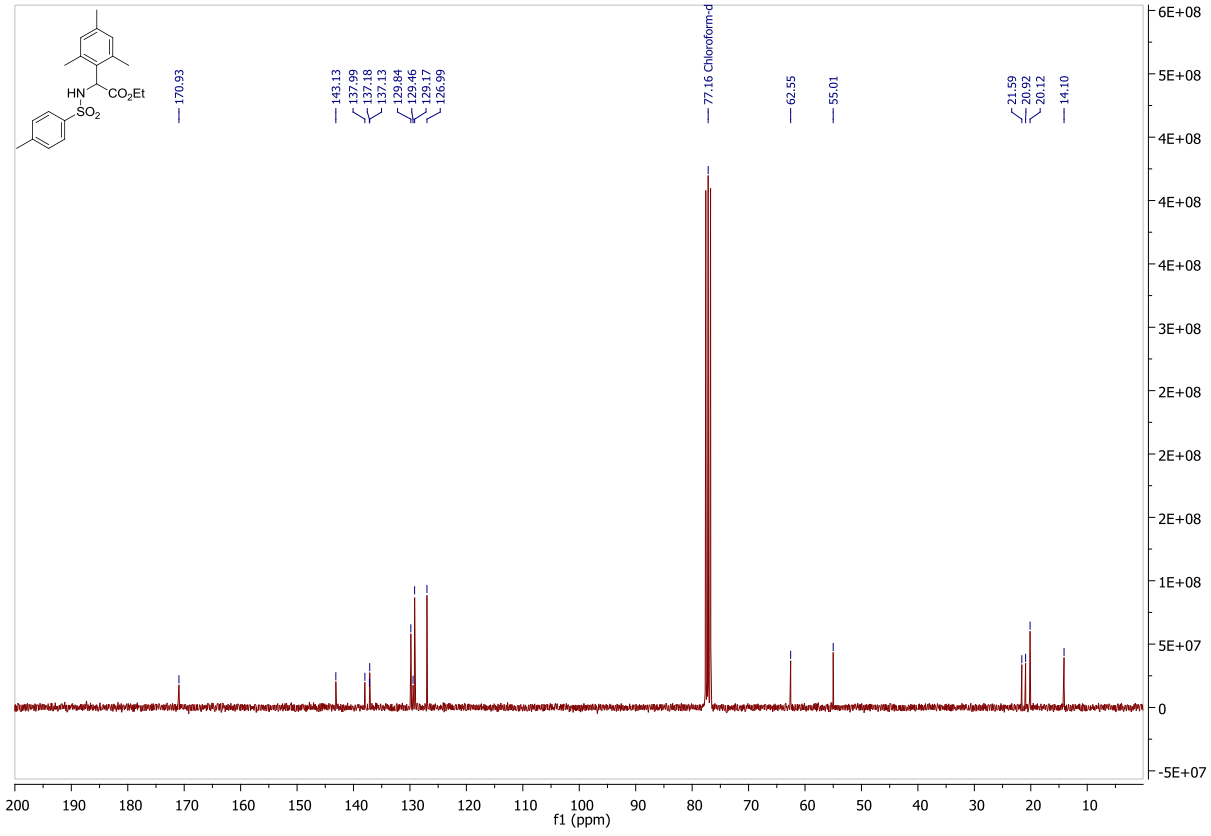
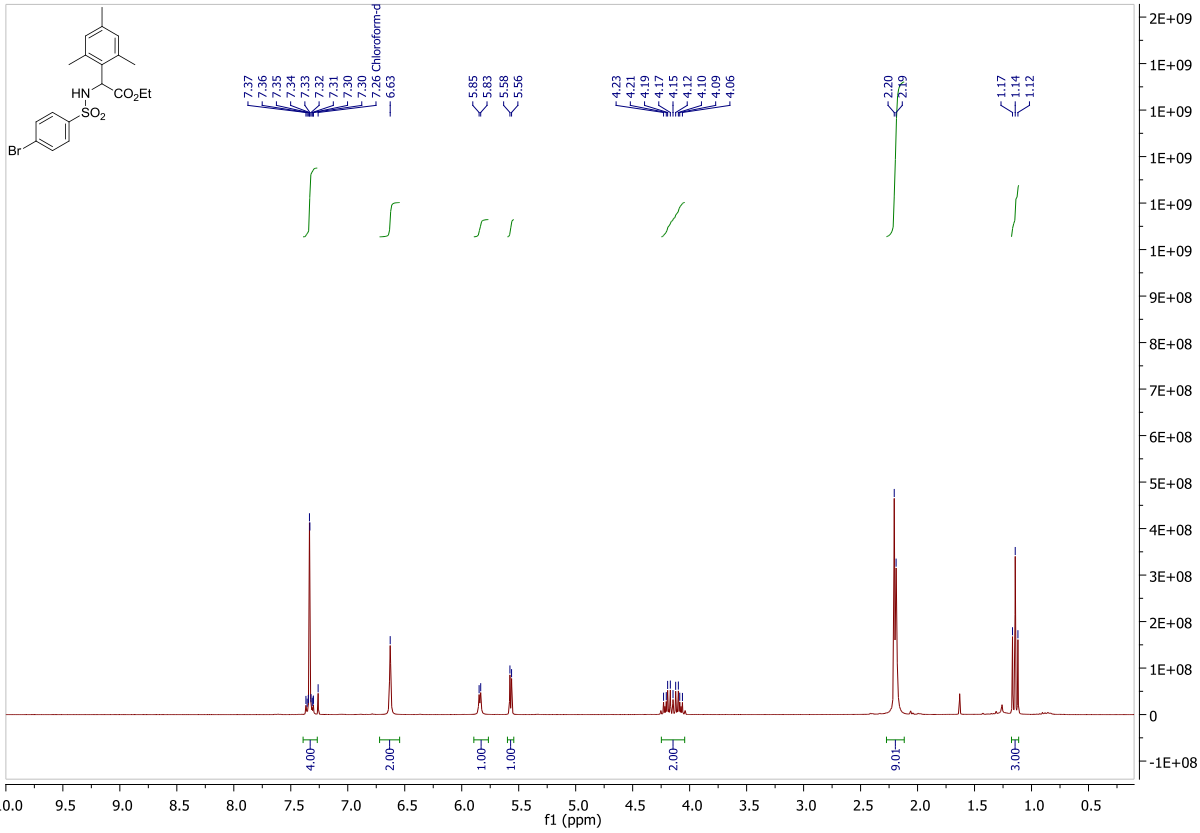
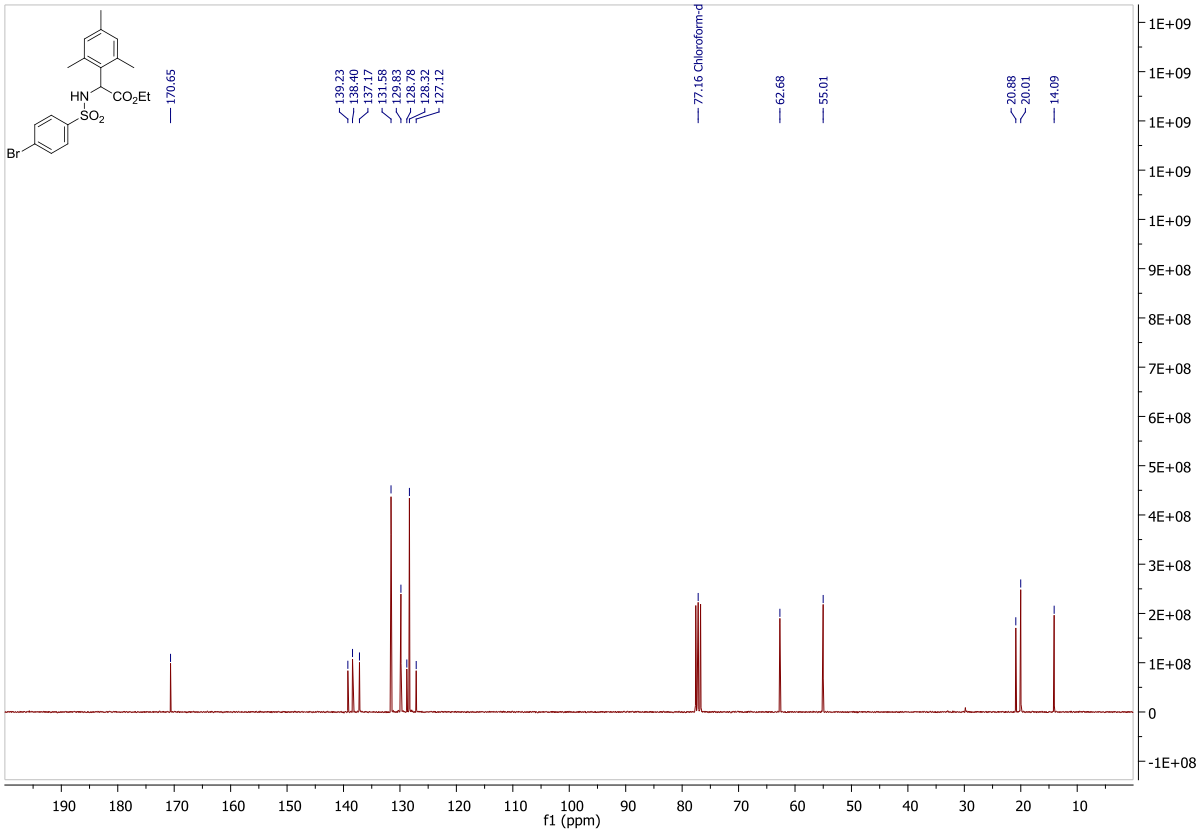




Ethyl-2-(4-bromophenylsulfonamido)-2-mesitylacetate (7c)





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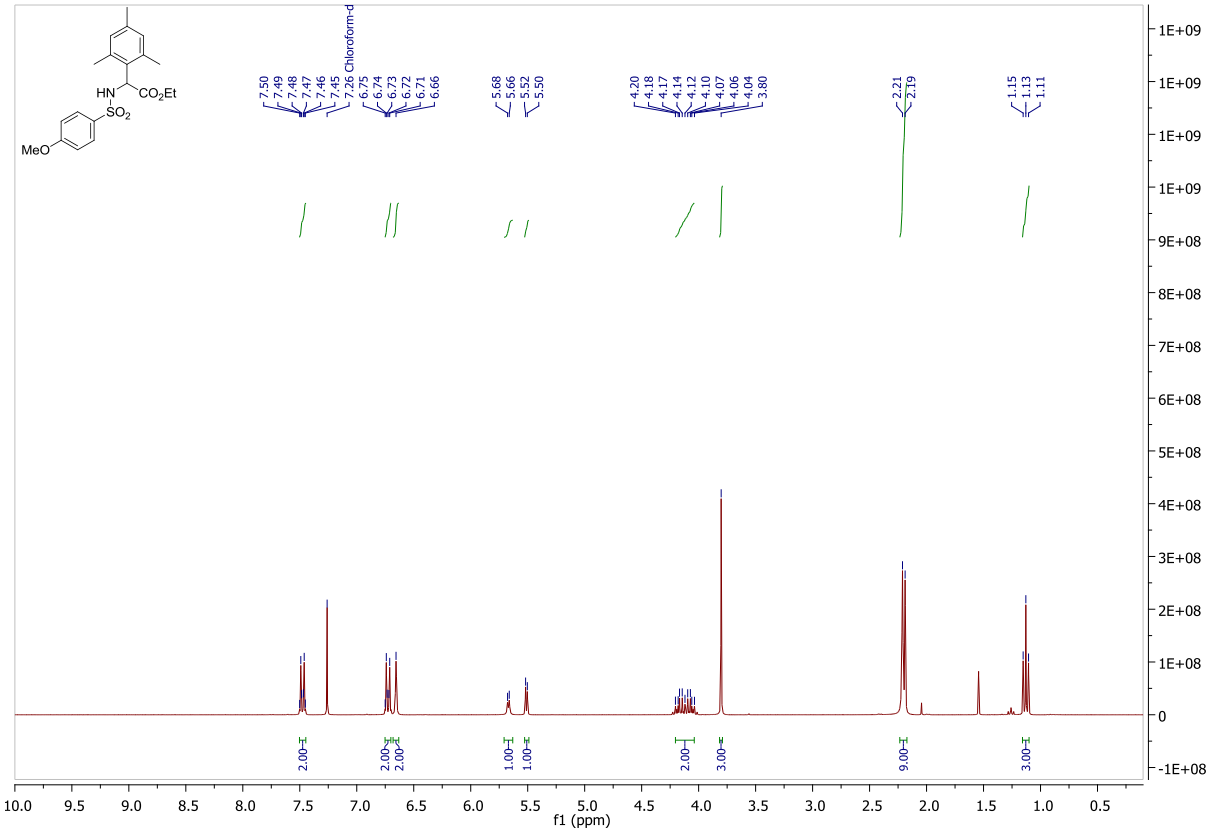
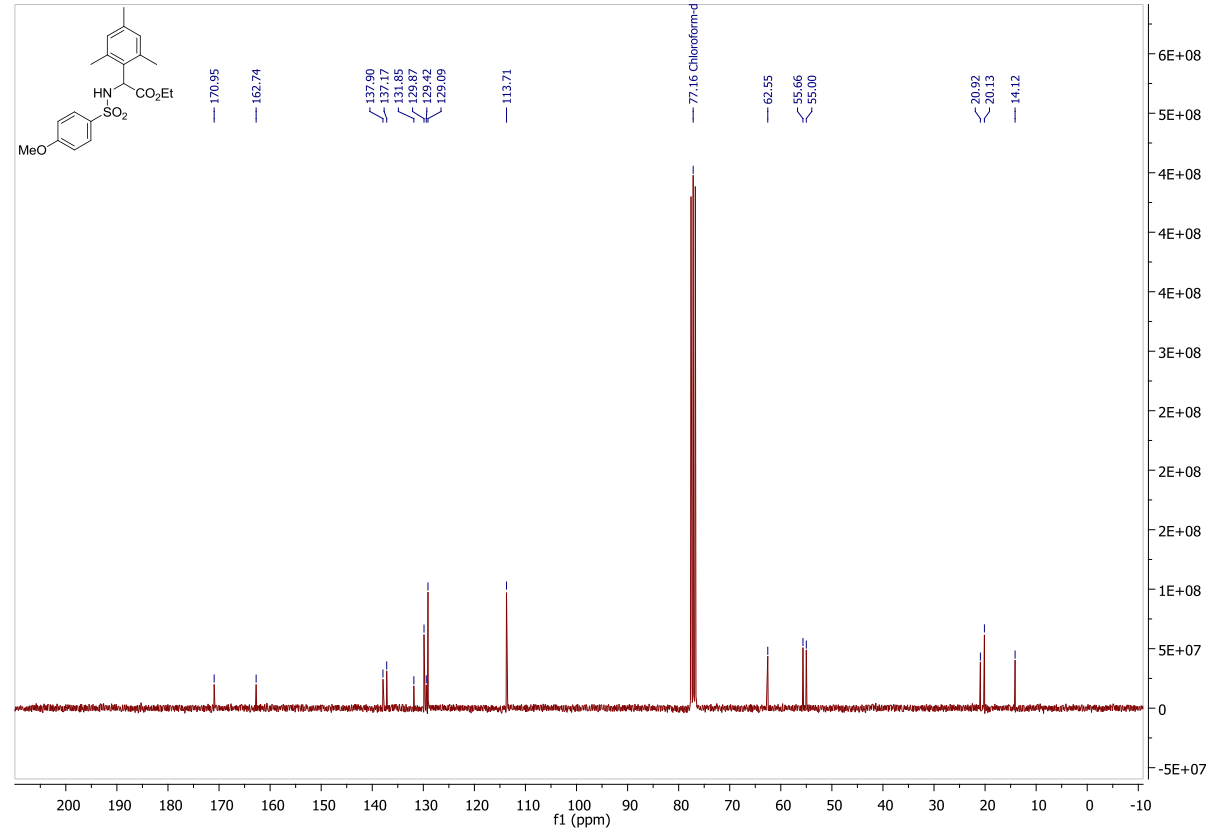
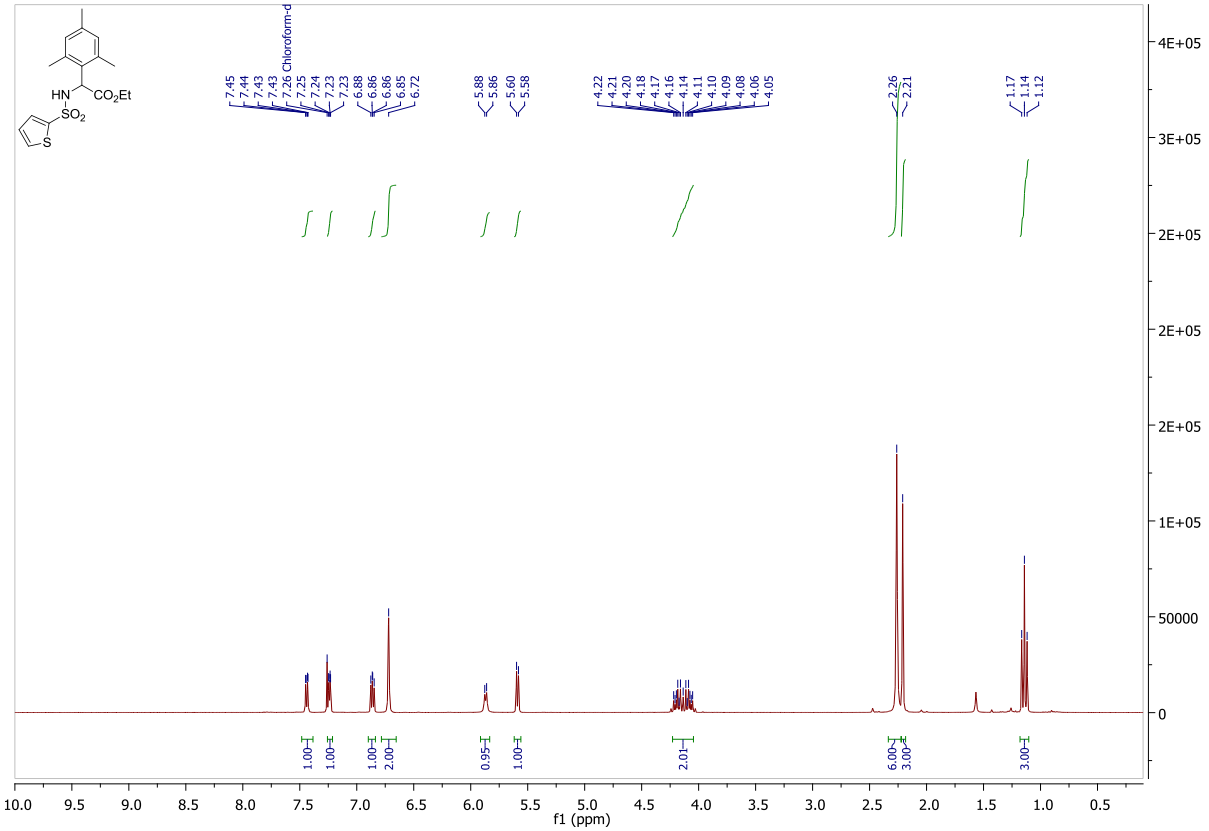
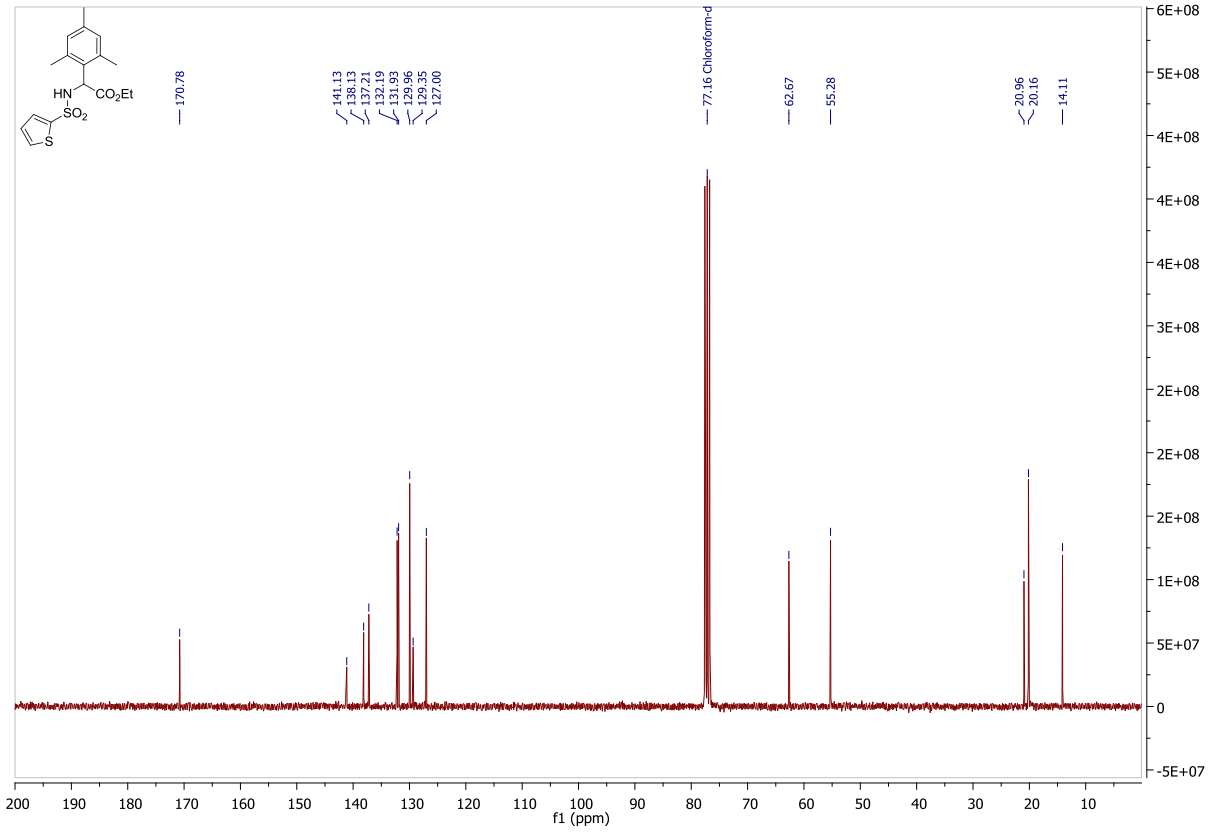


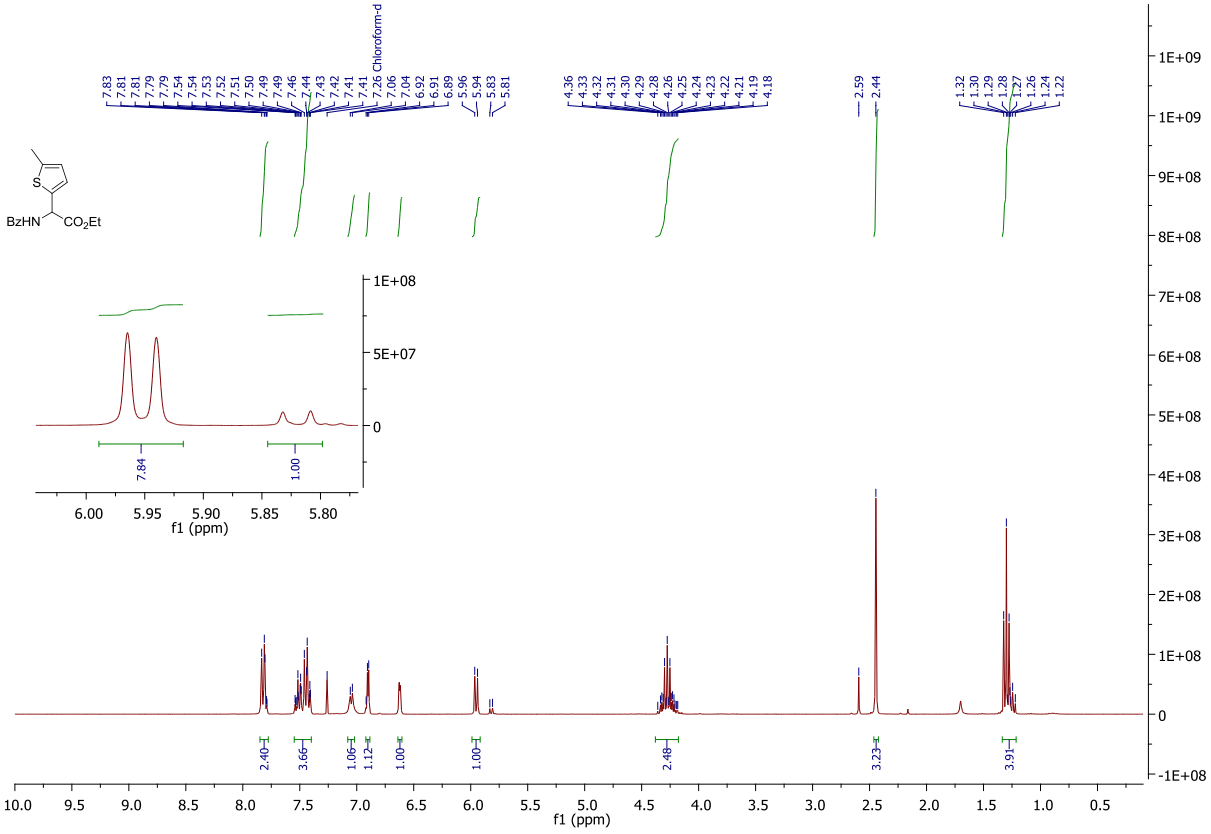


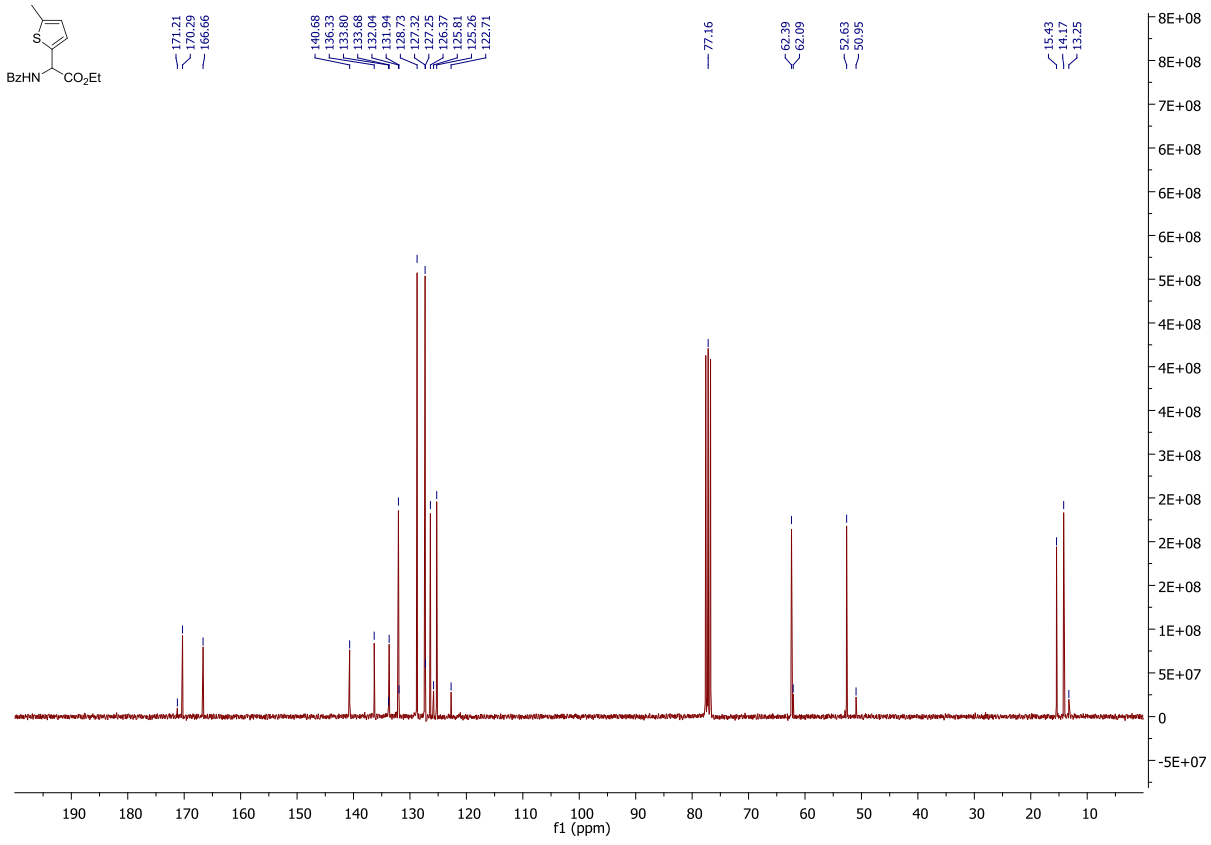
Ethyl-2-mesityl-2-(thiophene-2-sulfonamido)acetate (7e)



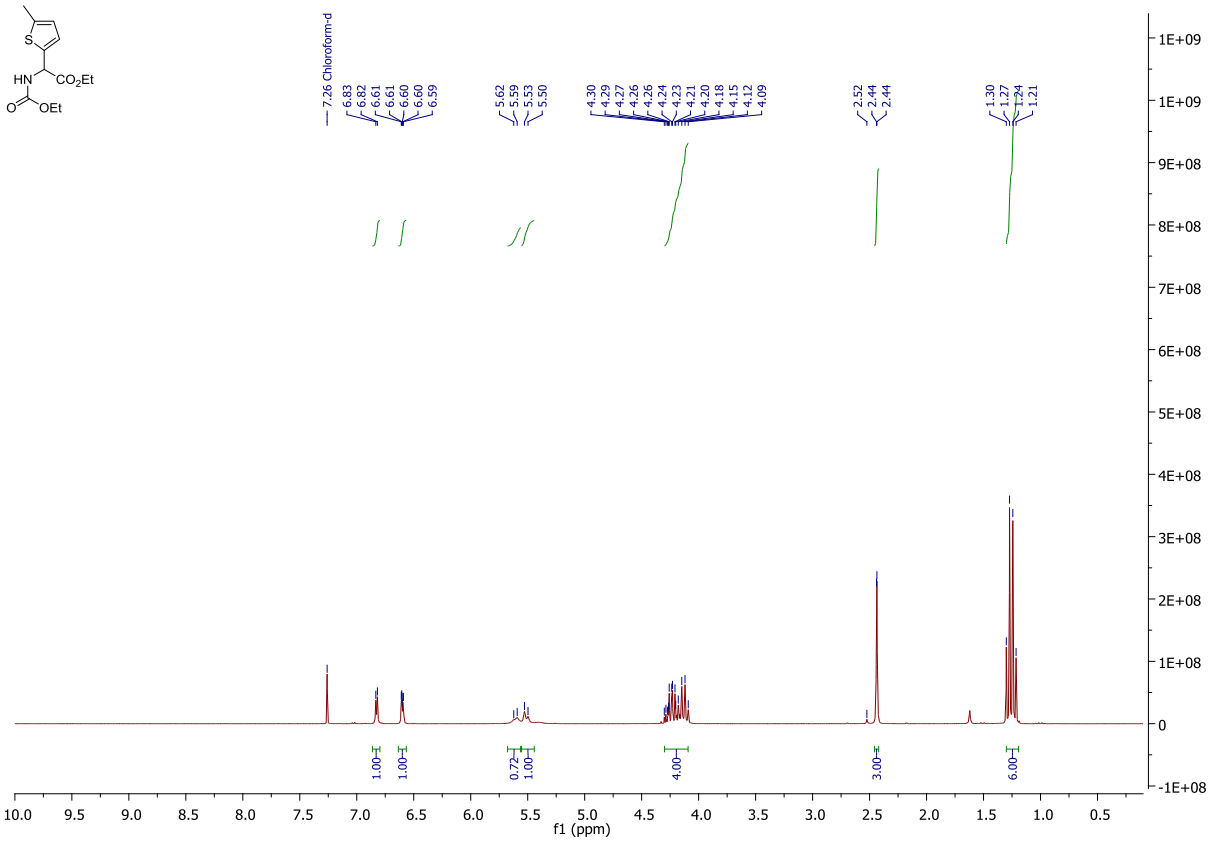


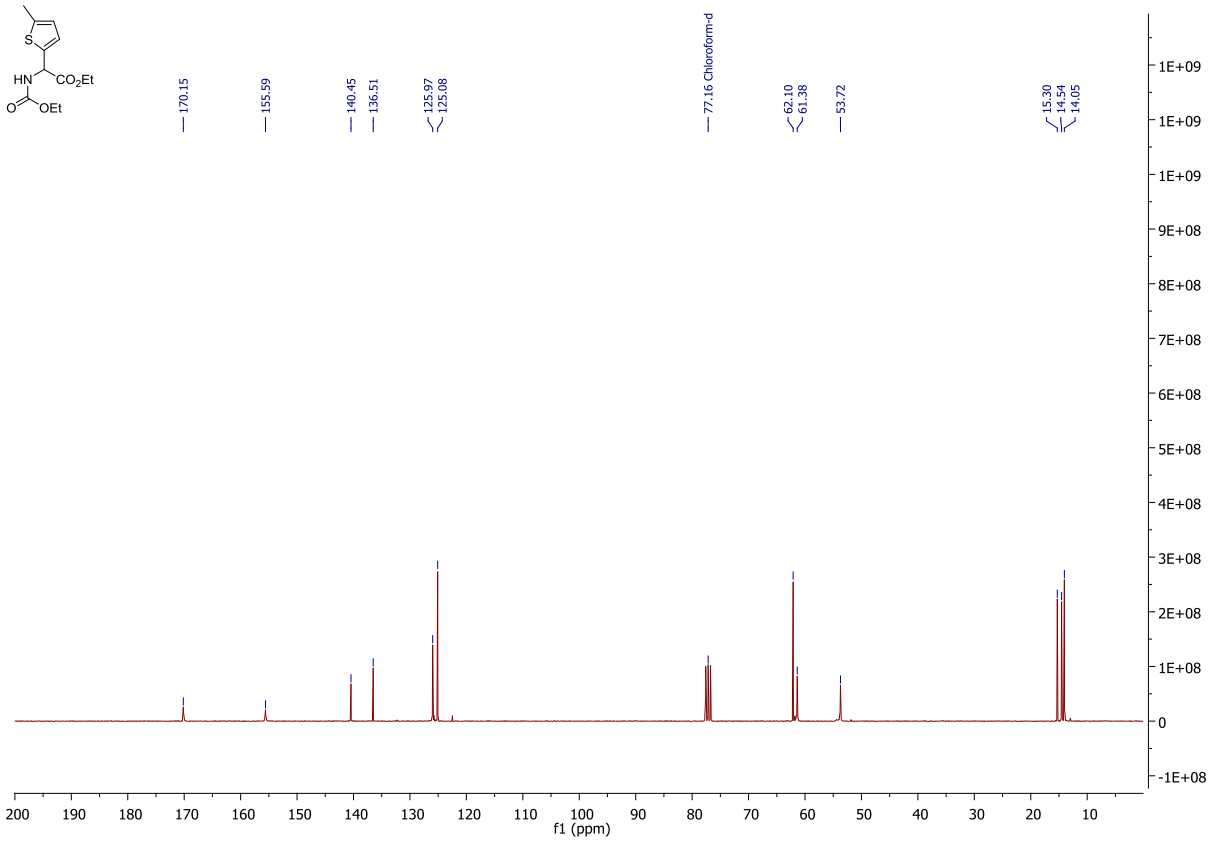
Ethyl-2-(benzamido)-2-(5-methylthiophen-2-yl)acetate (9a)





Ethyl-(ethoxycarbonyl)-(5-methylthiophen-2-yl)methylcarbamate (9b)





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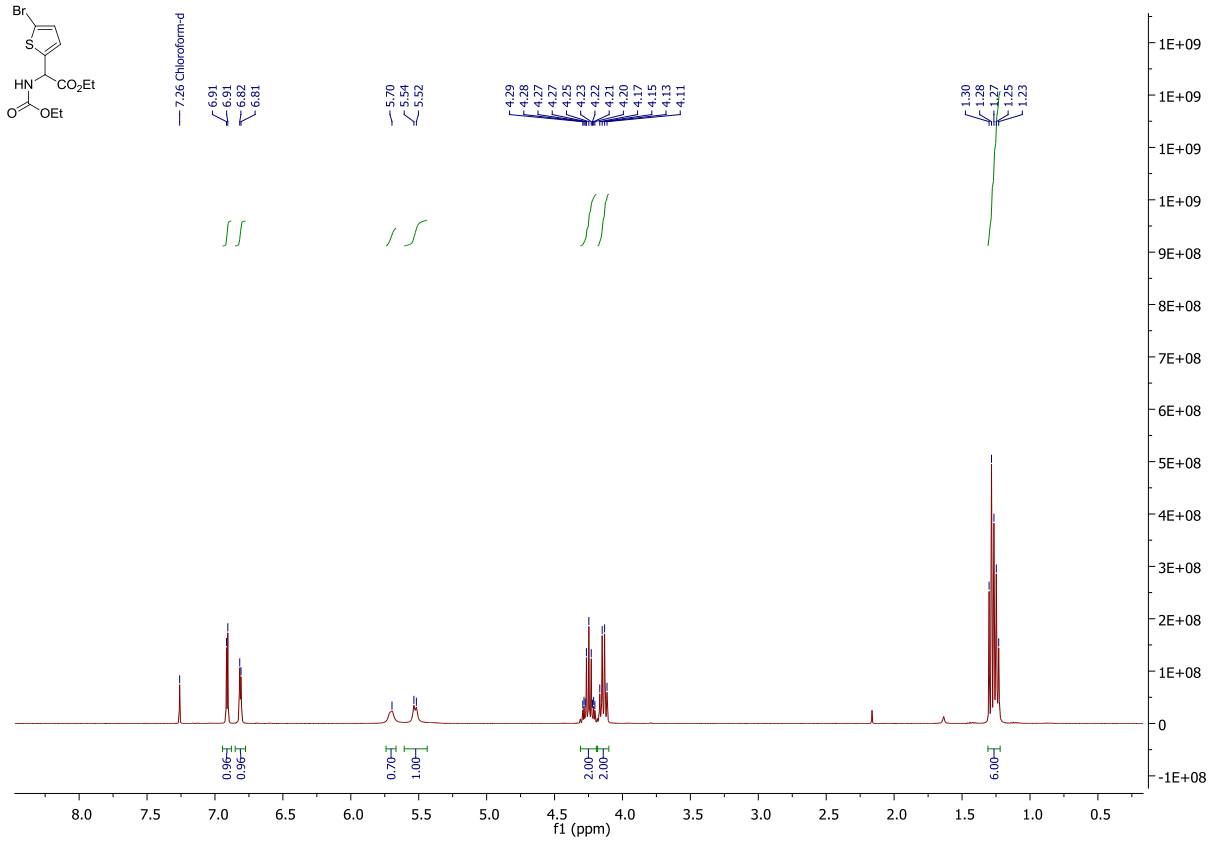
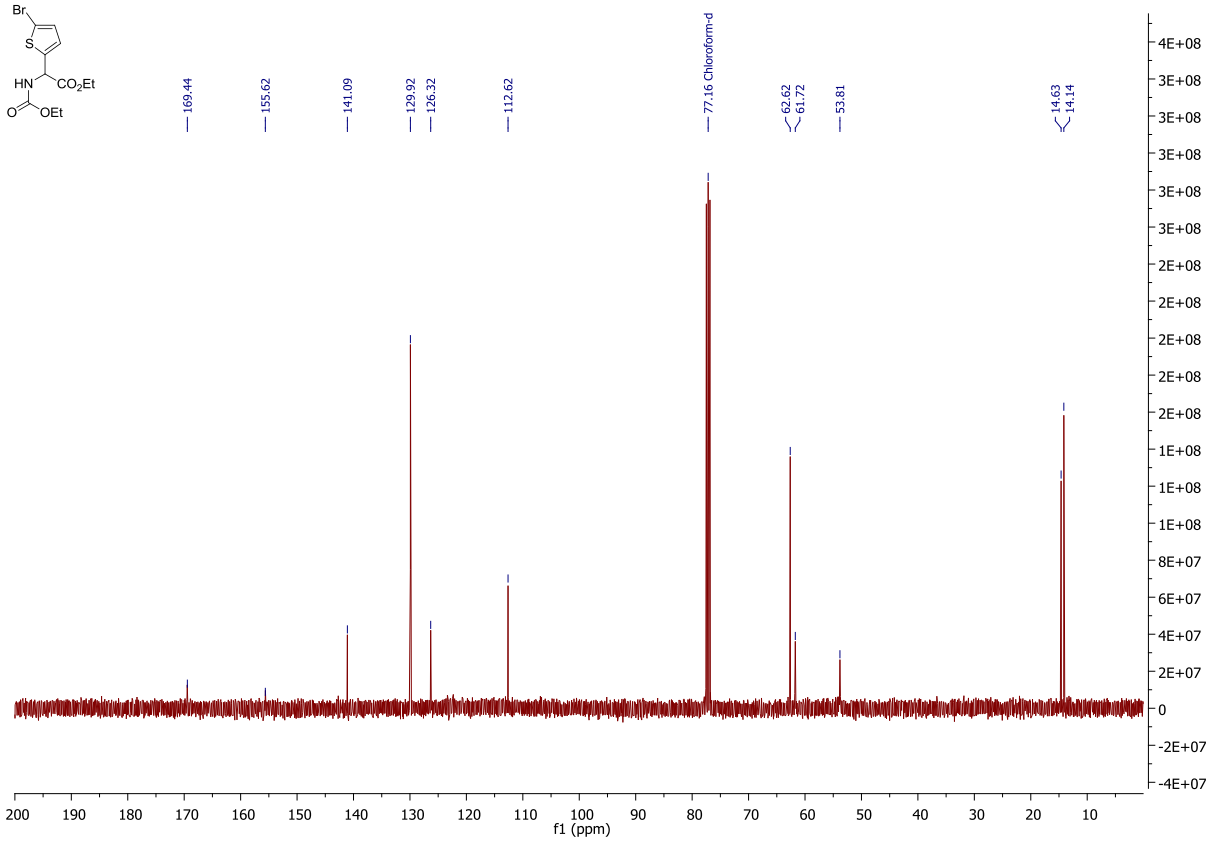
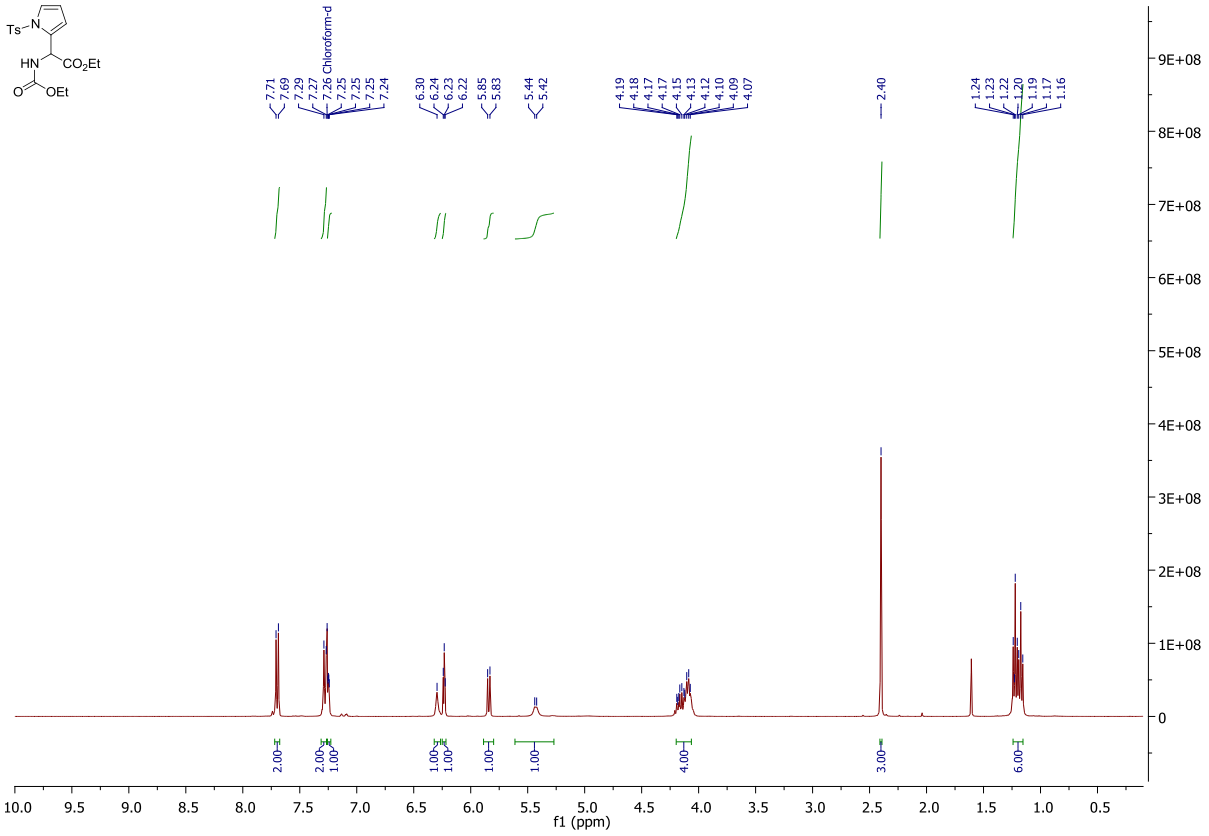
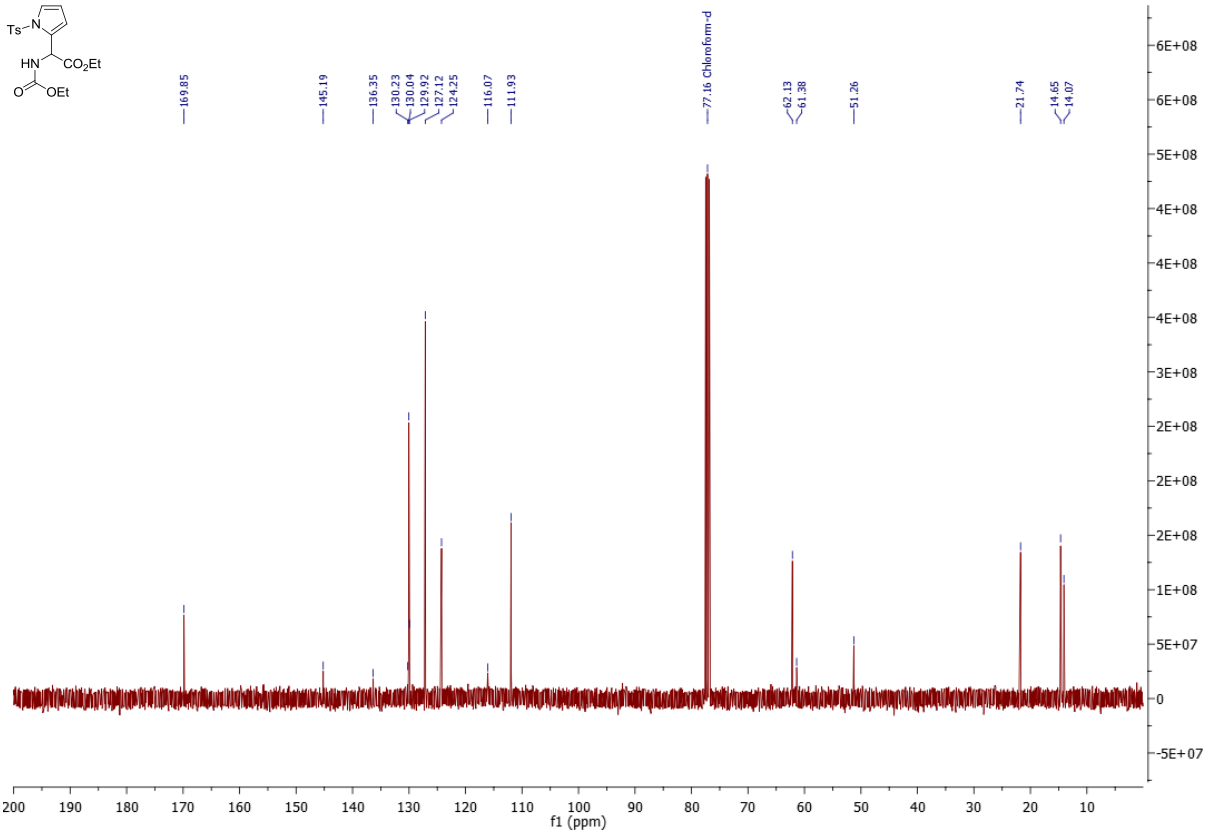


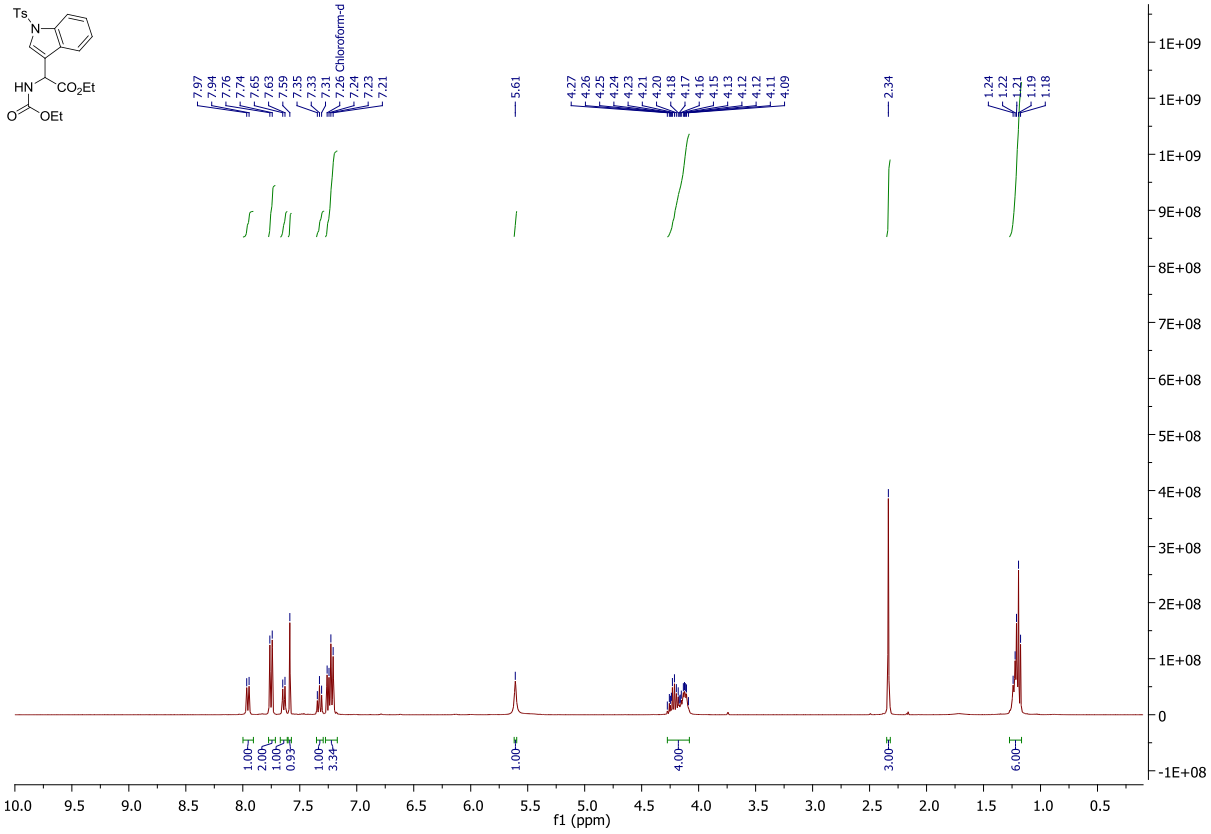


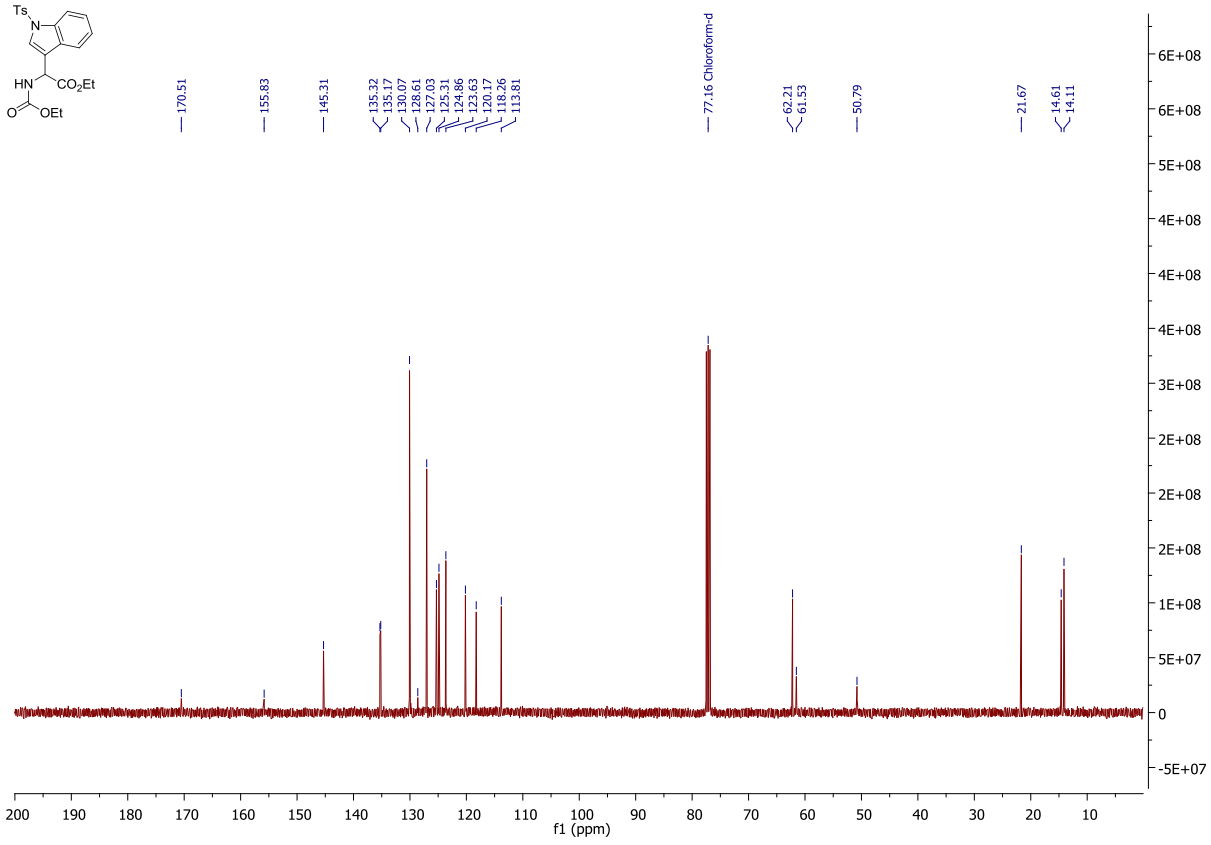
Ethyl-(ethoxycarbonyl)-(1-tosyl-1*H*-pyrrol-2-yl)methylcarbamate (9d)



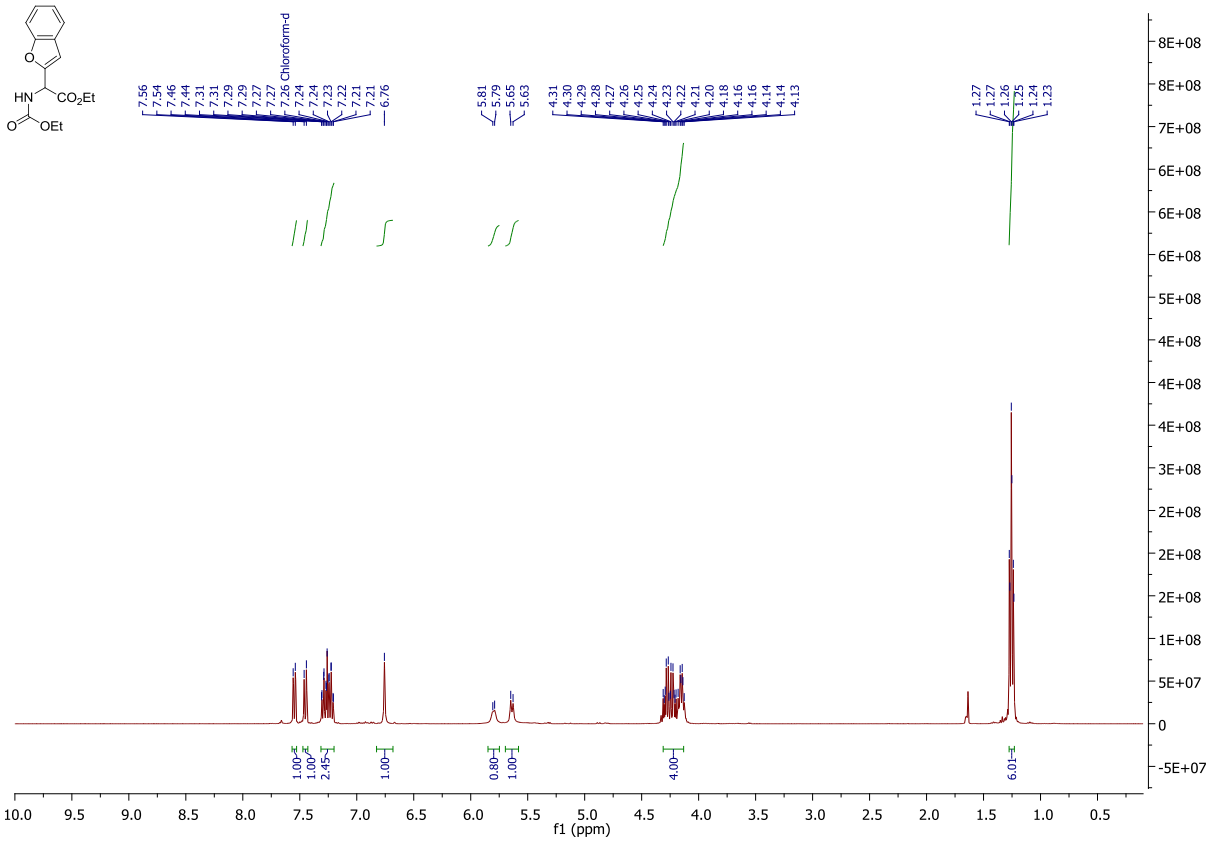


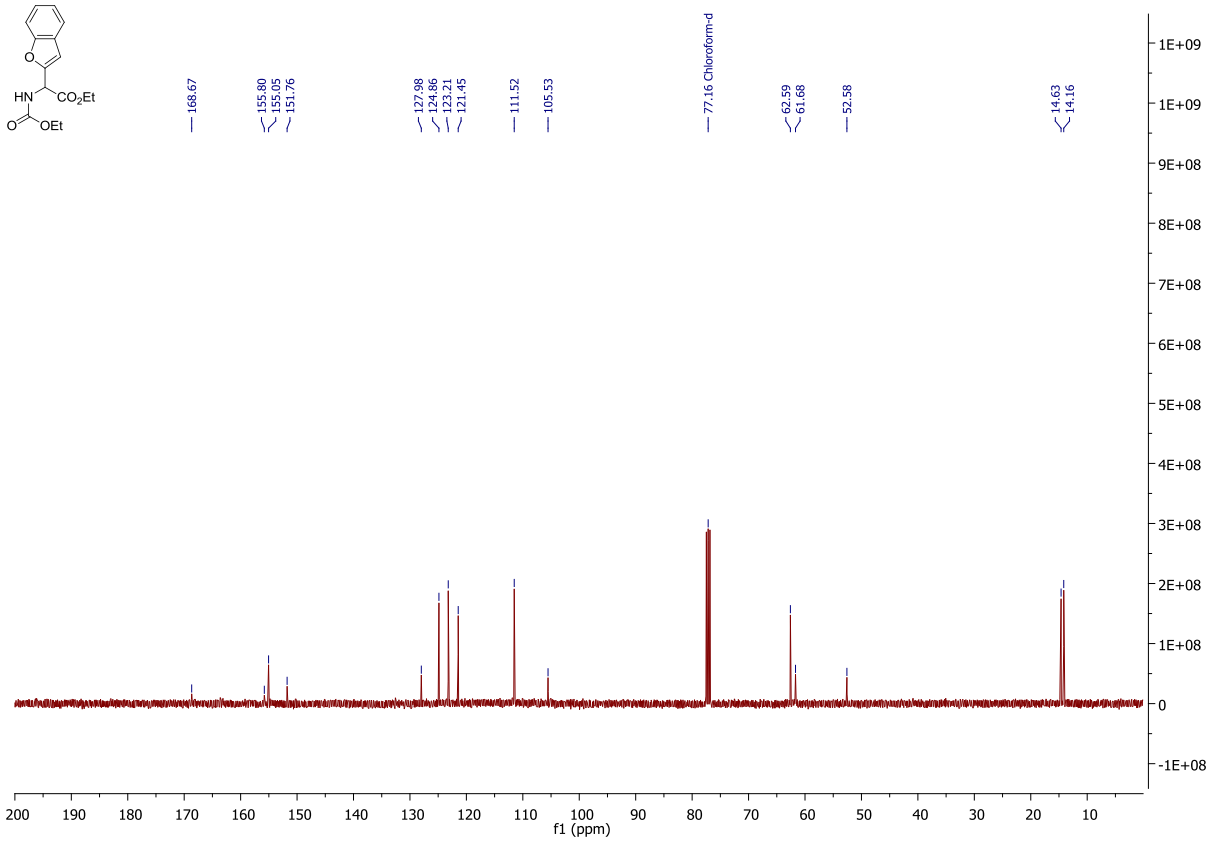
Ethyl-(ethoxycarbonyl)-(1-tosyl-1*H*-indol-3-yl)methylcarbamate (9e)



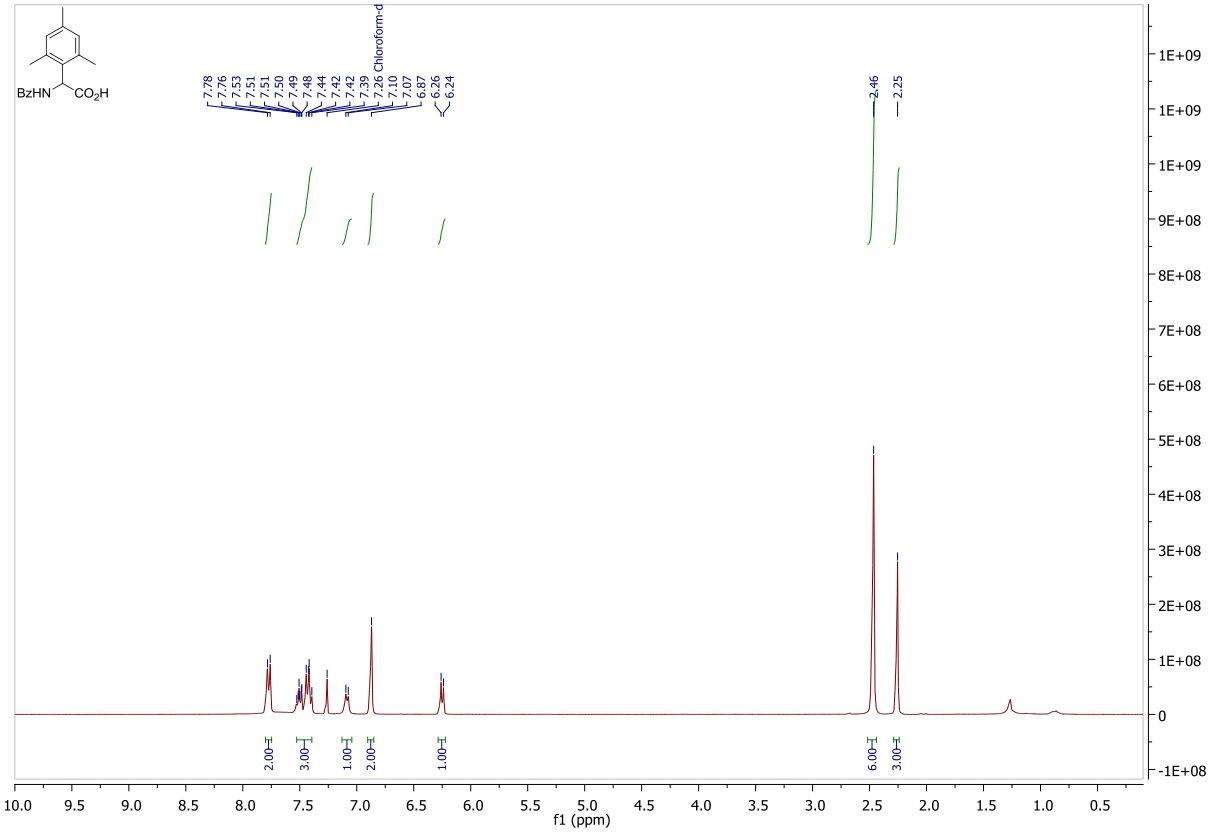


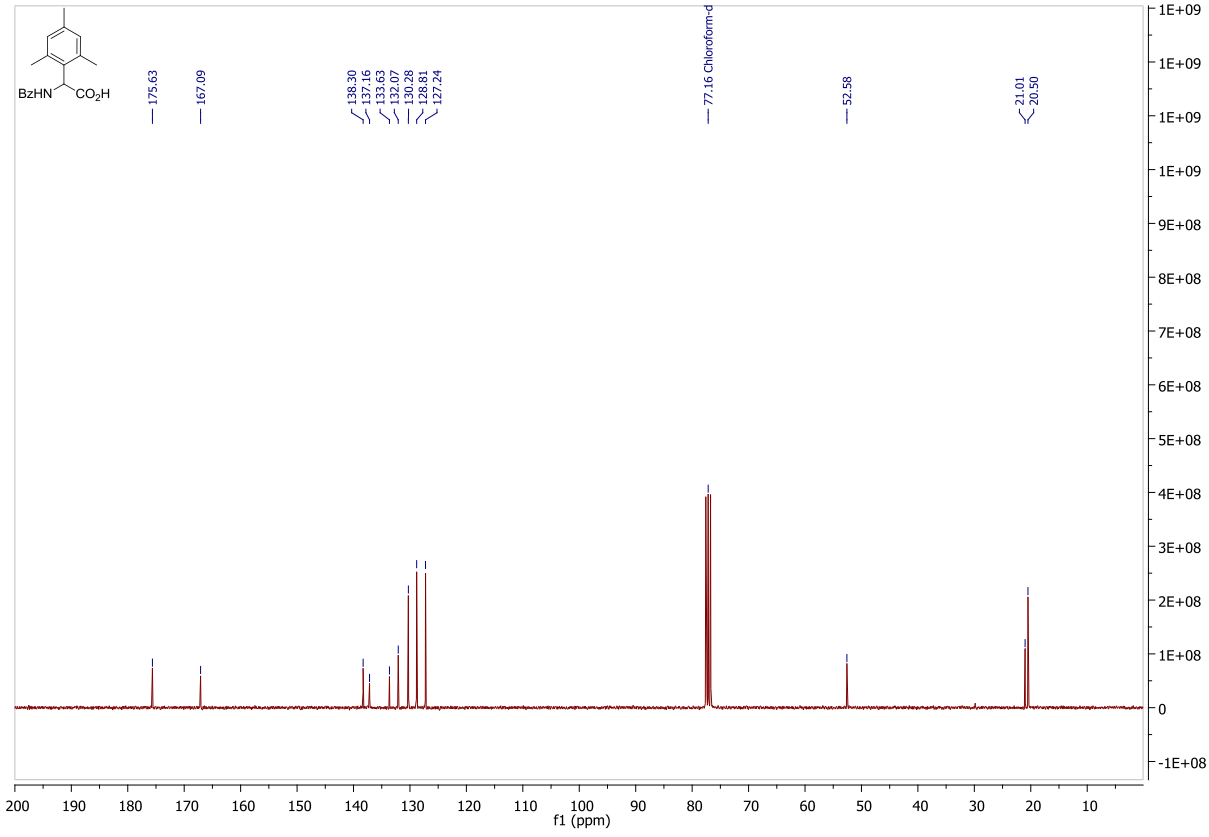
Ethyl-(ethoxycarbonyl)-(benzofuran-2-yl)methylcarbamate (9f)



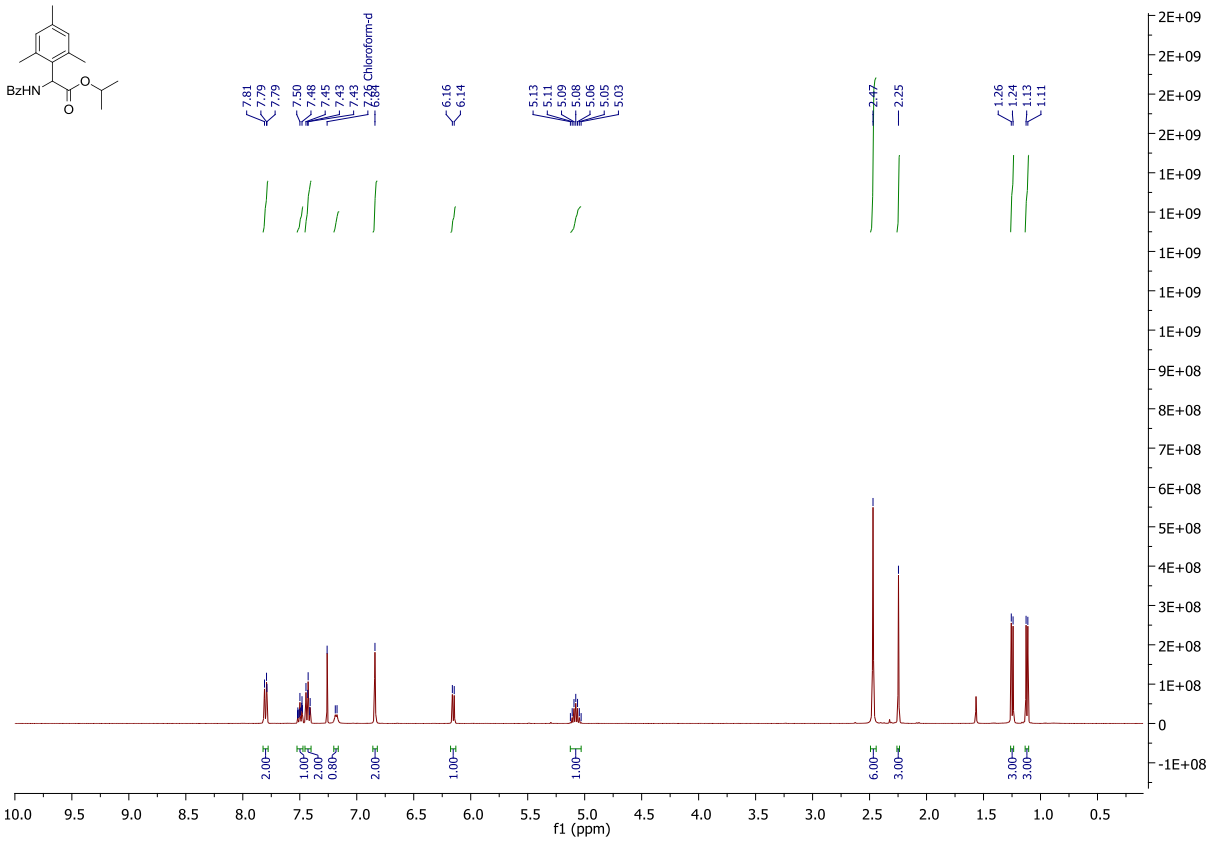


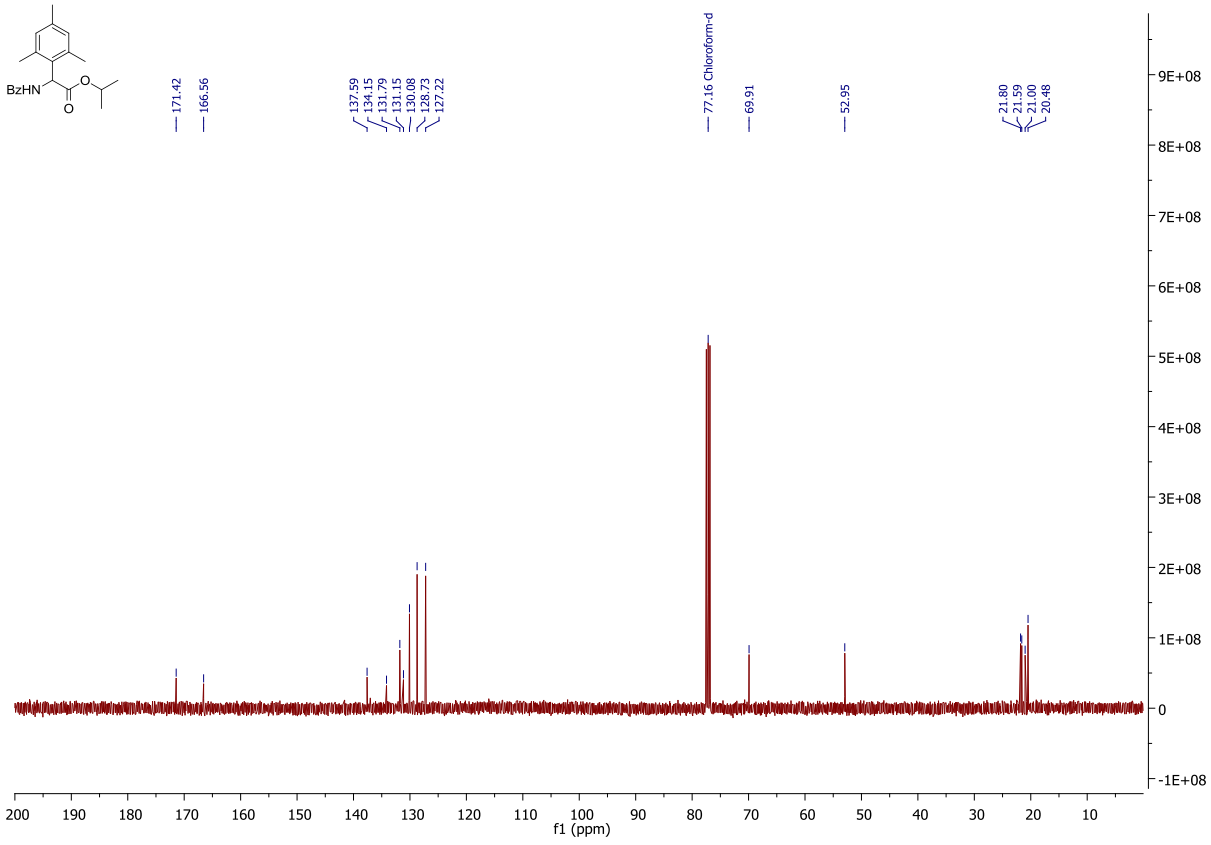
2-Benzamido-2-mesitylacetic acid (10a)



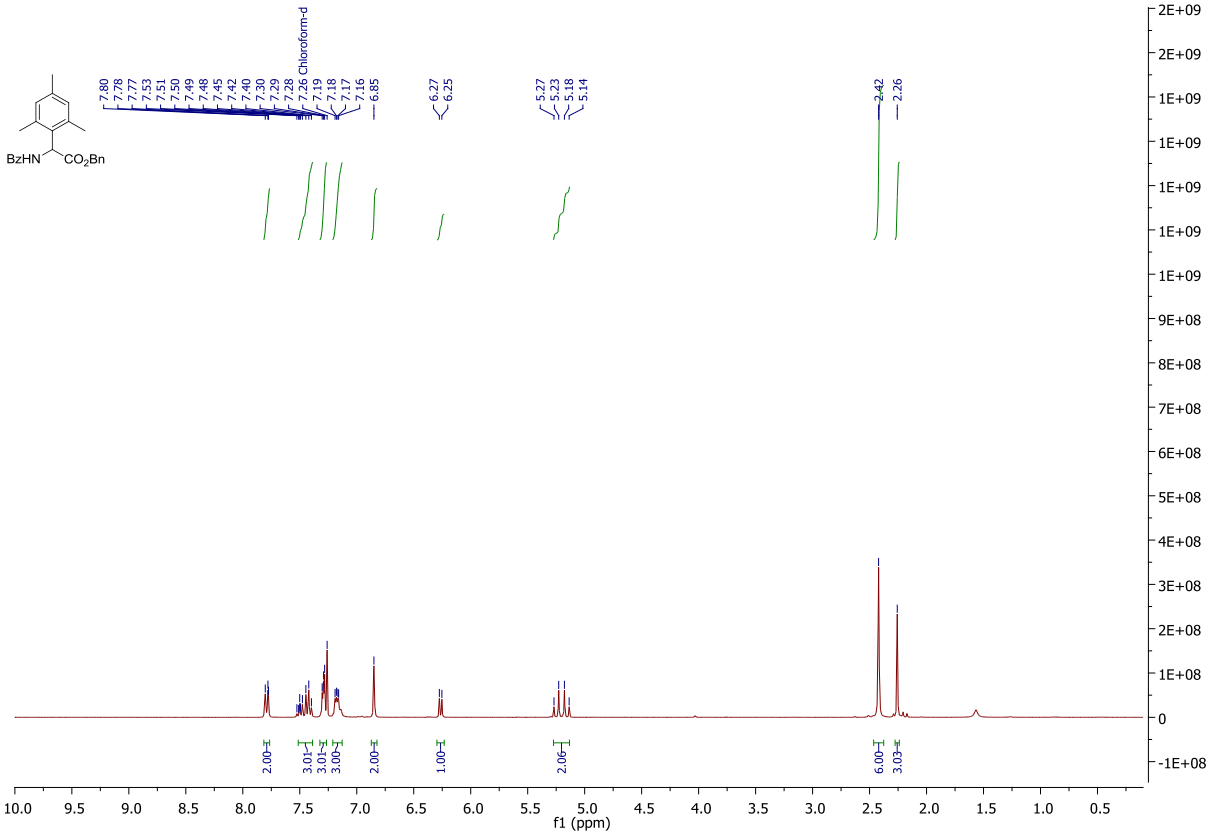


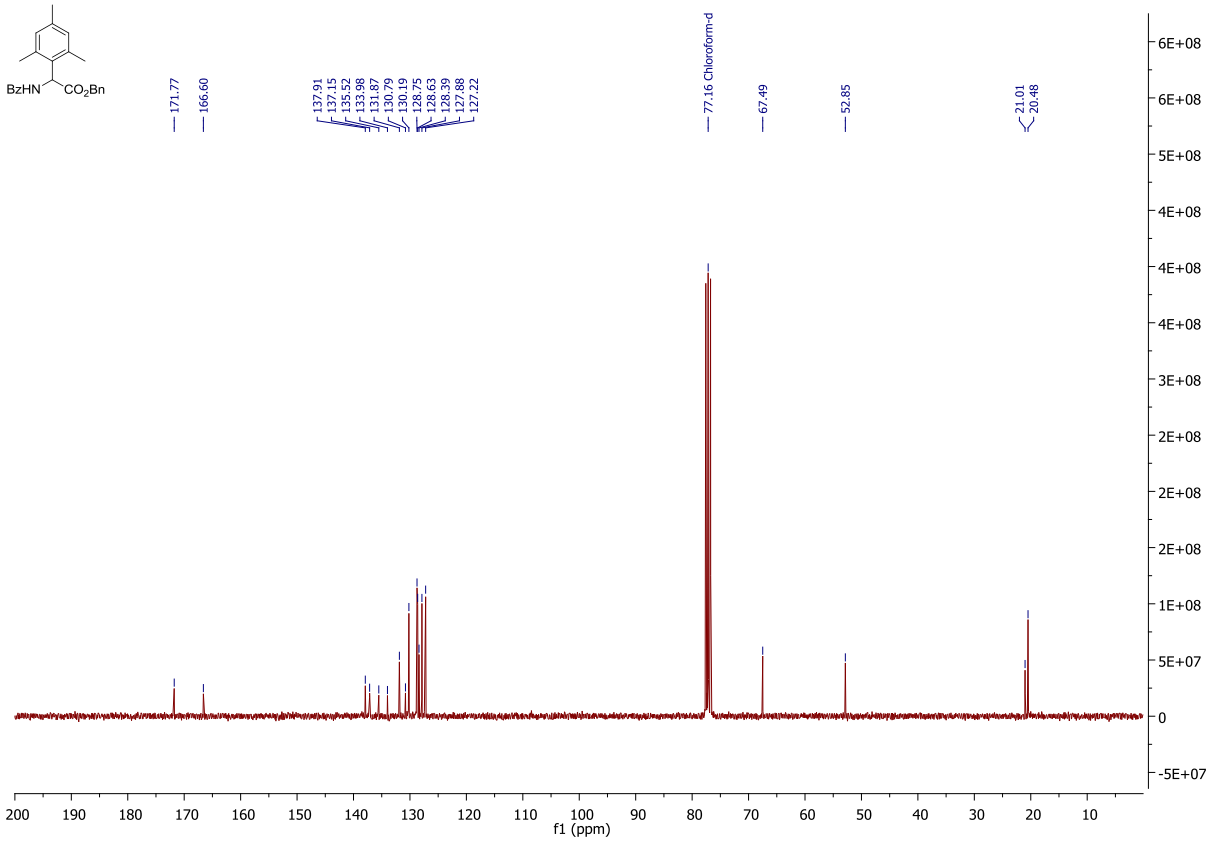
Isopropyl-2-(benzamido)-2-mesitylacetate (10b)



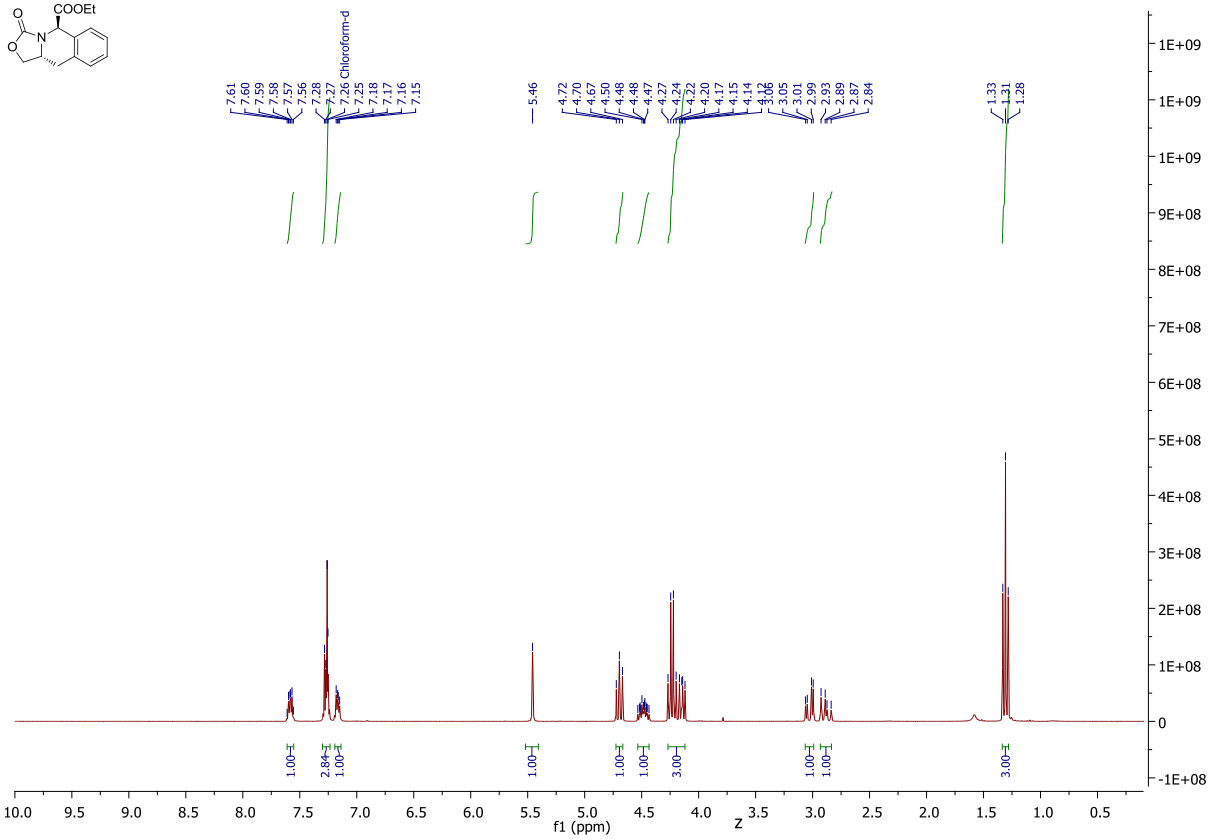


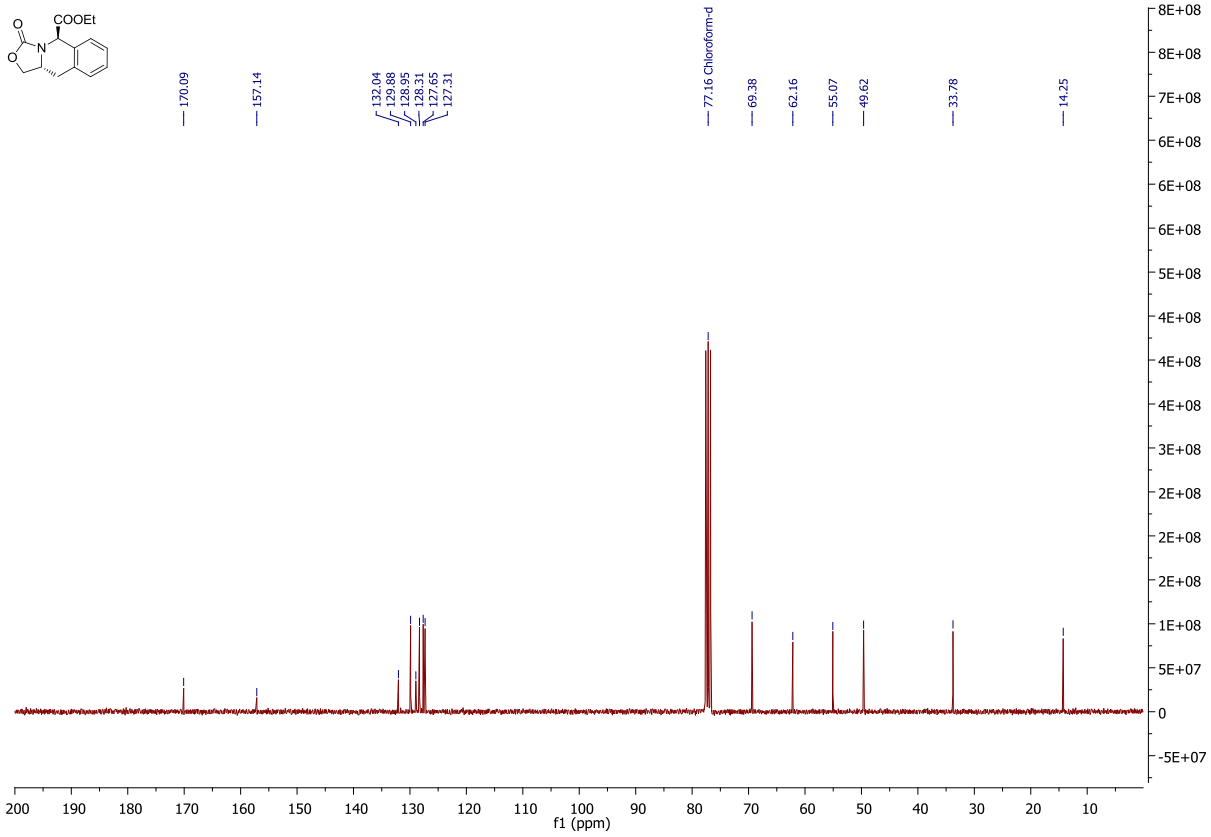
Benzyl-2-(benzamido)-2-mesitylacetate (10c)



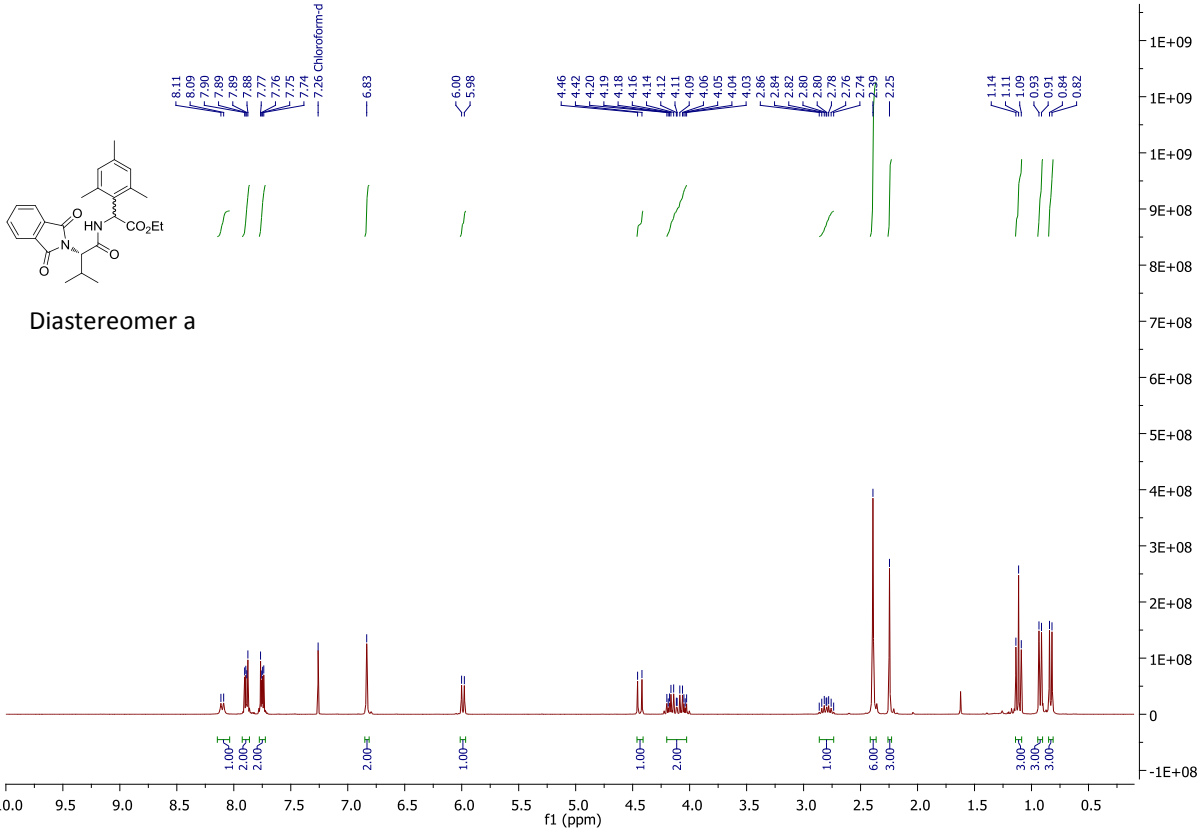


Ethyl-3,5,10,10a-tetrahydro-3-oxo-1*H*-oxazolo[3,4-b]isoquinoline-5-carboxylate (12)

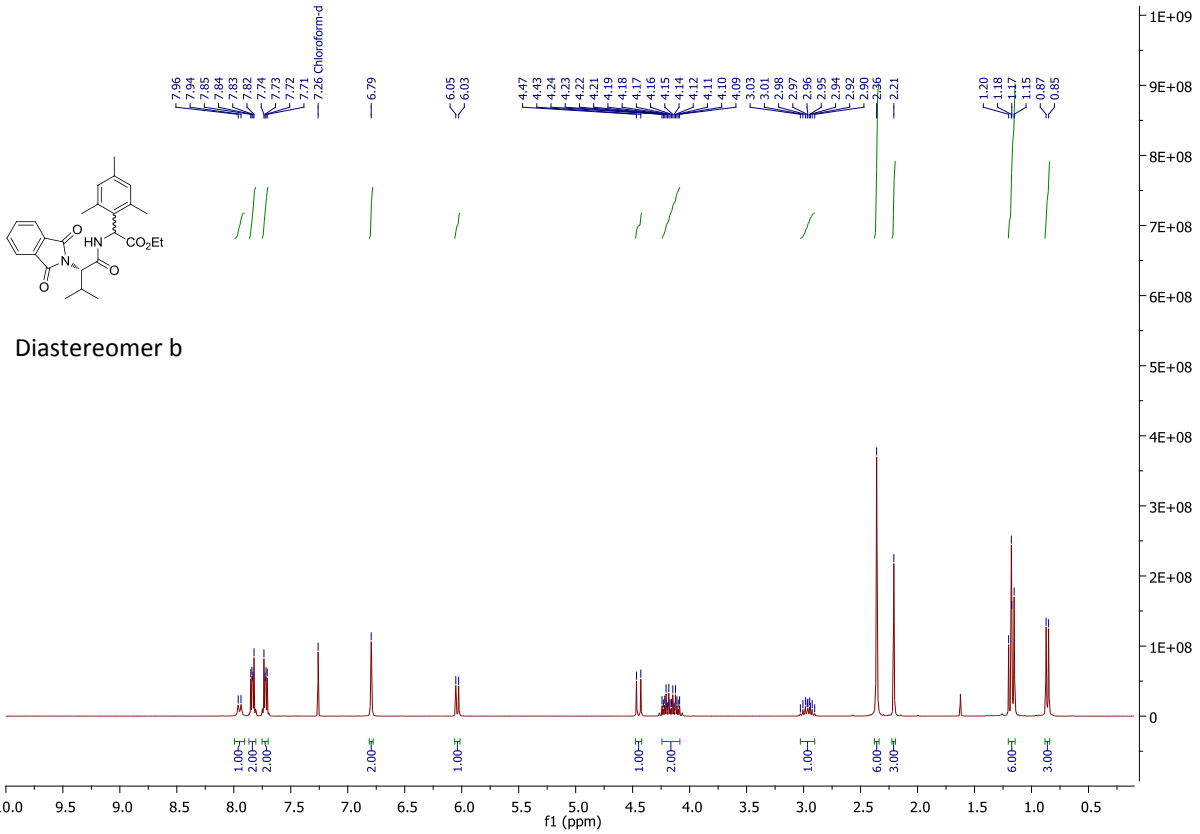




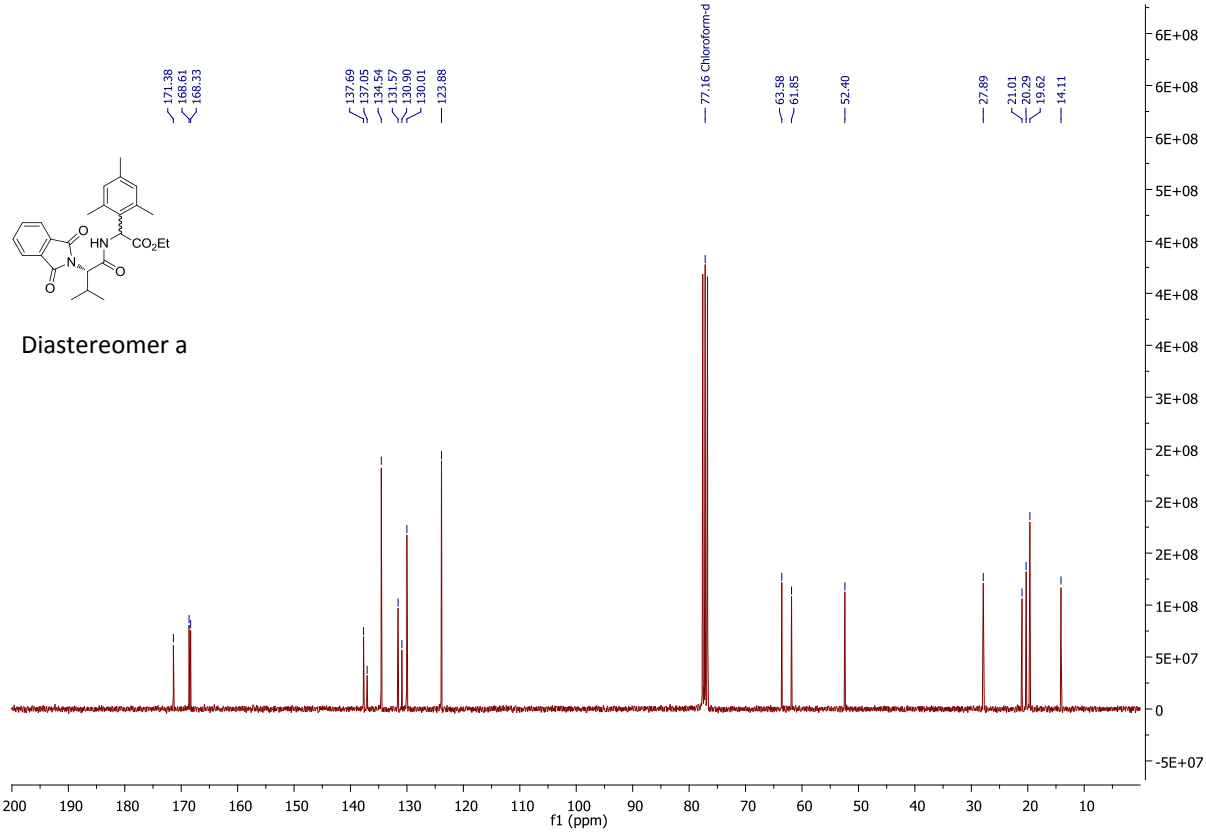
Ethyl-2-(3-methyl-(1,3-dioxoisoindolin-2-yl)butanamido)-2-mesitylacetate (14)



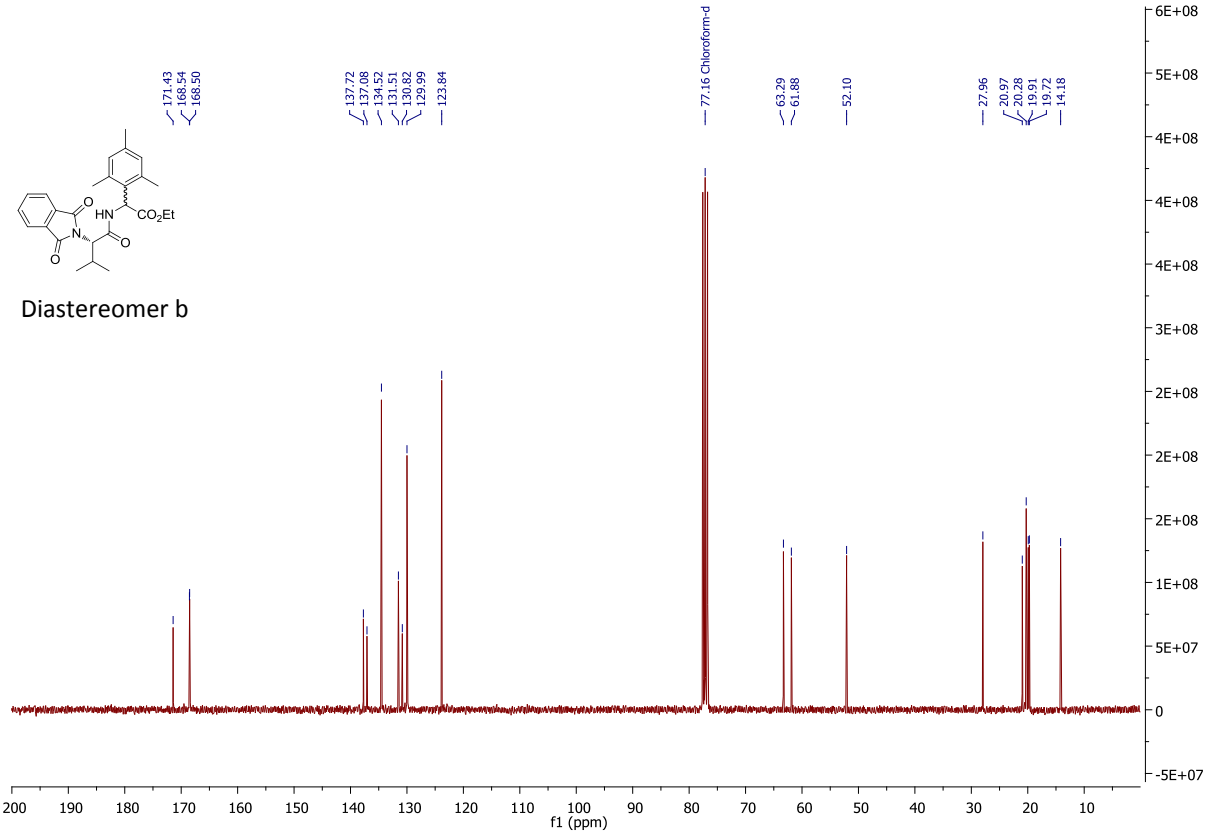
Diastereomer a



Diastereomer b



Diastereomer a



Diastereomer b

4 Literature

(1) (a) C. T.Hoang, F. Bouillère, S. Johannesen, A. Zulauf, C. Panel, A. Pouilhès, D. Gori, V. Alezra, C. Kouklovsky, *J. Org. Chem*., 2009, **74**, 4177. (b) A. Carocci, A. Catalano, F. Corbo, A. Duranti, R. Amoroso, C. Franchini, G. Lentini, V. Tortorella, *Tetrahedron: Asymmetry*, 2000, **11**, 3619.

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(5) Y. Li, H.-H. Chen, C.-F. Wang, X.-L. Xu, Y.-S. Feng, *Tetrahedron Lett.*, 2012, **53**, 5796.

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