# Highly Enantioselective Organocatalytic Michael Addition of Nitroalkanes to 4-Oxo-Enoates

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## Contents

## 1. General methods

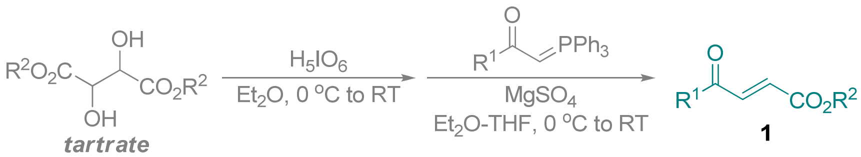
IR was recorded on a Perkin-Elmer PE-983 infrared spectrometer with absorption in $cm^{-1}$. Melting points were determined on X4 type melting point apparatus and were uncorrected. Proton and carbon nuclear magnetic resonance ($^{1}H$ & $^{13}C$ NMR) spectra were recorded on Varian-Mercury 400/600 (400/600 MHz) spectrometers. Chemical shifts ($\delta$) are reported in parts per million (ppm) relative to residual solvent signals ($CHCl_3$, 7.26 ppm for $^{1}H$ NMR, $CDCl_3$, 77.0 ppm for $^{13}C$ NMR). Data are reported as follows: chemical shift (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dd = doublet of triplets, m = multiplet, brs = broad signal), coupling constants (Hz). Mass spectra were measured on a Finnigan Trace MS spectrometer. Elementary analyses were taken on a Vario EL III elementary analysis instrument. Chromatographic purification of products was accomplished using nitrogen-forced-flow chromatography according to the method of Still.[1] The enantiomeric excess (ee) of the products was determined by chiral stationary phase HPLC. Optical rotations were measured with JASCO P-1020 polarimeter.

## 2. Materials

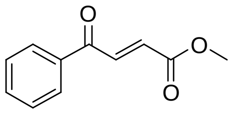
Commercial reagents were purified prior to use following the guidelines of Perrin and Armarego.[2] Flash chromatography was conducted using 60 silica (mesh 230-400). Catalysts **V-I** were prepared according to literature procedures.[3]

## 3. Experimental Procedures and Characterizations

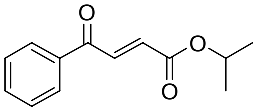
### Step A.



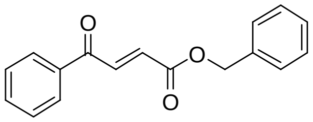
**Representative procedure for the preparation of 4-*oxo*-enoates.** Periodic acid dihydrate (10 mmol, 2.28 g) was added in portionwise to a stirred solution of dibenzyl tartrate (10 mmol, 3.30 g) in 20 mL of freshly distilled diethyl ether at RT. After stirred for 3 hours, the suspension was sunction-filtrated and the solid was washed with 25 mL of freshly distilled terahydrofuran. Magnesium sulfate (3.0 g) was added to the organic phase, and the mixture was then cooled by an ice bath. 30 minutes later, 2-(triphenylphosphoranylidene)acetophenone (15 mmol, 5.71 g) was added and the suspension was allowed to warm slowly to RT. After completed (monitored by TLC analysis), suction filtration and concentration, the residue was subjected to flash chromatography (petroleum ether/EtOAc = 15/1) to afford (*E*)-benzyl 4-phenyl-4-*oxo*-2-butenoate **1d** as a yellow solid in 72% yield (2 steps). *NOTE:* ***1a*** *was use as received.*



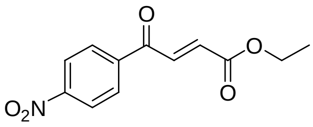
**(*E*)-Methyl 4-phenyl-4-*oxo*-2-butenoate (1b).** Yellow liquid, 46% yield. $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 8.00 (d, $J$ = 7.8 Hz, 2H), 7.93 (d, $J$ = 15.6 Hz, 1H), 7.62 (t, $J$ = 7.2 Hz, 1H), 7.51 (t, $J$ = 7.8 Hz, 2H), 6.90 (d, $J$ = 15.6 Hz, 1H), 3.85 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ (ppm) 189.3, 165.9, 136.5, 133.8, 132.0, 128.8, 128.8, 52.3; MS (EI) *m/z* 190 ($M^+$).



**(*E*)-Isopropyl 4-phenyl-4-*oxo*-2-butenoate (1c).** Yellow liquid, 67% yield. $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 8.00 (d, $J$ = 7.2 Hz, 2H), 7.89 (d, $J$ = 15.6 Hz, 1H), 7.63 (t, $J$ = 7.8 Hz, 1H), 7.52 (t, $J$ = 7.8 Hz, 2H), 6.86 (d, $J$ = 15.6 Hz, 1H), 5.19-5.13 (m, 1H), 1.33 (s, 3H), 1.32 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ (ppm) 189.4, 164.9, 136.5, 136.0, 133.6, 132.9, 128.7, 68.8, 21.6; MS (EI) *m/z* 219 ($M^+$+1).

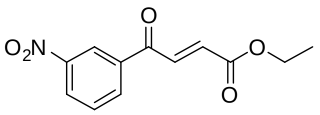


**(*E*)-Benzyl 4-phenyl-4-*oxo*-2-butenoate (1d).** Yellow solid, 72% yield. $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 7.99 (d, $J$ = 6.6 Hz, 2H), 7.93 (d, $J$ = 15.6 Hz, 1H), 7.62 (t, $J$ = 6.6 Hz, 1H), 7.51 (t, $J$ = 7.2 Hz, 2H), 7.44-7.35 (m, 5H), 6.93 (d, $J$ = 15.6 Hz, 1H), 5.28 (s, 2H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ (ppm) 189.3, 165.3, 136.7, 136.4, 135.2, 133.8, 132.1, 128.8, 128.7, 128.6, 128.4, 128.3, 67.0; MS (EI) *m/z* 266 ($M^+$).

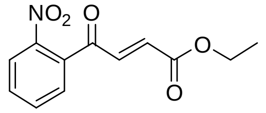


**(*E*)-Ethyl 4-(4-nitro-phenyl)-4-*oxo*-2-butenoate (1e).** Yellow solid, 65% yield. $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 8.37 (d, $J$ = 9.0 Hz, 2H), 8.16 (d, $J$ = 9.0 Hz, 2H), 7.87 (d, $J$ = 15.6 Hz, 1H), 6.94 (d, $J$ = 15.6 Hz, 1H), 4.33 (q, $J$ = 7.2 Hz, 2H), 1.37 (t, $J$ = 7.2 Hz, 3H); $^{13}$C

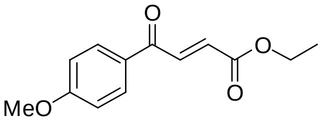
NMR (150 MHz, $CDCl_3$) $\delta$ (ppm) 188.1, 165.0, 150.5, 141.0, 135.1, 134.2, 130.0, 124.0, 61.6, 14.1; MS (EI) *m/z* 249 ($M^+$).



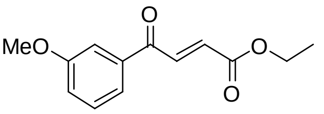
**(*E*)-Ethyl 4-(3-nitro-phenyl)-4-*oxo*-2-butenoate (1f).** Yellow solid, 73% yield. $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 8.82 (s, 1H), 8.49 (d, $J$ = 9.6 Hz, 1H), 8.33 (d, $J$ = 7.8 Hz, 1H), 7.90 (d, $J$ = 15.6 Hz, 1H), 7.75 (t, $J$ = 8.4 Hz, 1H), 6.97 (d, $J$ = 15.6 Hz, 1H), 4.34 (q, $J$ = 7.2 Hz, 2H), 1.37 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ (ppm) 187.3, 164.9, 148.4, 137.6, 134.7, 134.1, 134.0, 130.1, 127.8, 123.3, 61.6, 14.0; MS (EI) *m/z* 249 ($M^+$).



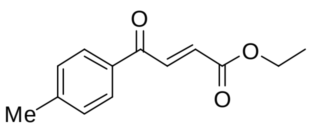
**(*E*)-Ethyl 4-(2-nitro-phenyl)-4-*oxo*-2-butenoate (1g).** Yellow solid, 64% yield. $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 8.22 (d, $J$ = 8.4 Hz, 1H), 7.80 (d, $J$ = 7.2 Hz, 1H), 7.70 (t, $J$ = 7.2 Hz, 1H), 7.47 (d, $J$ = 7.2 Hz, 1H), 7.31 (d, $J$ = 16.2 Hz, 1H), 6.37 (d, $J$ = 16.2 Hz, 1H), 4.25 (q, J = 7.2 Hz, 2H), 1.31 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ (ppm) 191.9, 164.8, 146.2, 139.3, 135.0, 134.5, 132.8, 132.3, 128.5, 124.5, 61.5, 14.0; MS (EI) *m/z* 249 ($M^+$).



**(*E*)-Ethyl 4-(4-methoxy-phenyl)-4-*oxo*-2-butenoate (1h).** Yellow solid, 80% yield. $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 8.01 (d, $J$ = 8.4 Hz, 2H), 7.92 (d, $J$ = 15.6 Hz, 1H), 6.98 (d, $J$ = 9.0 Hz, 2H), 6.87 (d, $J$ = 15.6 Hz, 1H), 4.30 (q, $J$ = 7.2 Hz, 2H), 3.90 (s, 3H), 1.37 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ (ppm) 187.4, 165.6, 164.0, 136.3, 132.6, 131.3, 129.5, 114.0, 61.1, 55.4, 14.0; MS (EI) *m/z* 234 ($M^+$).

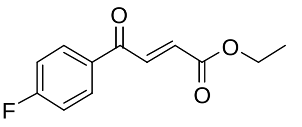


**(*E*)-Ethyl 4-(3-methoxy-phenyl)-4-*oxo*-2-butenoate (1i).** Yellow solid, 75% yield. $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 7.89 (d, $J$ = 15.6 Hz, 1H), 7.85 (d, $J$ = 7.8 Hz, 1H), 7.52 (s, 1H), 7.42 (t, $J$ = 7.8 Hz, 1H), 7.17 (d, $J$ = 8.4 Hz, 1H), 6.89 (d, $J$ = 15.6 Hz, 1H), 4.31 (q, $J$ = 7.2 Hz, 2H), 3.88 (s, 3H), 1.36 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ (ppm) 189.1, 165.4, 159.9, 137.8, 136.2, 132.4, 129.7, 121.4, 120.4, 112.6, 61.2, 55.3, 14.0; MS (EI) *m/z* 234 ($M^+$).

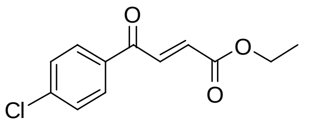


**(*E*)-Ethyl 4-(4-methyl-phenyl)-4-*oxo*-2-butenoate (1j).** Yellow liquid, 77% yield. $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 7.92-7.90 (m, 3H), 7.31 (d, $J$ = 7.8 Hz, 2H), 6.88 (d, $J$ = 15.6 Hz, 1H), 4.30 (q, $J$ = 7.2 Hz, 2H), 2.43 (s, 3H), 1.35 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ (ppm) 188.7, 165.5, 144.7, 136.3, 134.0, 132.0, 129.4, 128.8, 61.2, 21.6, 14.1; MS (EI) *m/z* 218 ($M^+$).

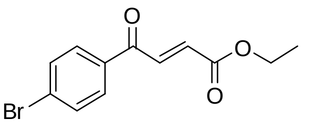
**(*E*)-Ethyl 4-(4-fluoro-phenyl)-4-*oxo*-2-butenoate (1k).** Yellow liquid, 73% yield. $^{1}$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 8.05 (dd, $J$ = 8.4 and 5.4 Hz, 2H), 7.88 (d, $J$ = 15.6 Hz, 1H), 7.19 (t, $J$ = 8.4 Hz, 2H), 6.89 (d, $J$ = 16.2 Hz, 1H), 4.31 (q, $J$ = 6.6 Hz, 2H), 1.36 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ (ppm) 187.6, 166.8, 165.3, 166.1, 135.8, 132.9, 132.8, 132.6, 131.5, 131.4, 116.0, 115.9, 61.3, 14.0; MS (EI) *m/z* 222 (M$^{+}$).



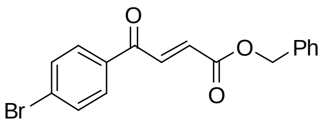
**(*E*)-Ethyl 4-(4-chloro-phenyl)-4-*oxo*-2-butenoate (1l).** Yellow liquid, 69% yield. $^{1}$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 7.95 (d, $J$ = 8.4 Hz, 2H), 7.87 (d, $J$ = 15.6 Hz, 1H), 7.50 (d, $J$ = 8.4 Hz, 2H), 6.90 (d, $J$ = 15.6 Hz, 1H), 4.31 (q, $J$ = 7.2 Hz, 2H), 1.36 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ (ppm) 188.2, 165.4, 140.4, 135.7, 134.9, 133.0, 129.2, 61.4, 14.1; MS (EI) *m/z* 237 (M$^{+}$-1), 239 (M$^{+}$+1).



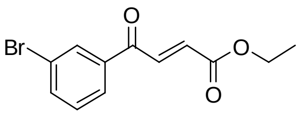
**(*E*)-Ethyl 4-(4-bromo-phenyl)-4-*oxo*-2-butenoate (1m).** Yellow liquid, 74% yield. $^{1}$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 7.87 (d, $J$ = 8.4 Hz, 2H), 7.85 (d, $J$ = 15.6 Hz, 1H), 7.60 (d, $J$ = 8.4 Hz, 2H), 6.90 (d, $J$ = 15.6 Hz, 1H), 4.31 (q, $J$ = 7.2 Hz, 2H), 1.35 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ (ppm) 188.4, 165.3, 135.6, 135.2, 133.0, 132.1, 130.0, 129.2, 61.4, 14.1; MS (EI) *m/z* 282 (M$^{+}$-1), 284 (M$^{+}$+1).



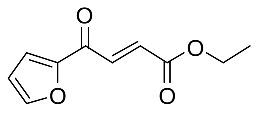
**(*E*)-Benzyl 4-(4- bromo-phenyl)-4-*oxo*-2-butenoate (1n).** Yellow solid, 85% yield. $^{1}$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 7.88 (d, $J$ = 15.6 Hz, 1H),7.85 (d, $J$ = 8.4 Hz, 2H), 7.65 (d, $J$ = 8.4 Hz, 2H), 6.94 (d, $J$ = 15.6 Hz, 1H), 5.28 (s, 2H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ (ppm) 188.3, 165.2, 136.1, 135.2, 132.6, 132.2, 130.2, 129.2, 128.2, 128.5, 128.4, 67.2; MS (EI) *m/z* 344 (M$^{+}$-1), 346 (M$^{+}$+1).



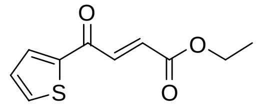
**(*E*)-Ethyl 4-(3-nitro-phenyl)-4-*oxo*-2-butenoate (1o).** Yellow solid, 72% yield. $^{1}$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 8.12 (s, 1H), 7.92 (d, $J$ = 7.8 Hz, 1H), 7.84 (d, $J$ = 15.6 Hz, 1H), 7.75 (d, $J$ = 8.4 Hz, 1H), 7.40 (t, $J$ = 7.8 Hz, 1H), 6.90 (d, $J$ = 15.6 Hz, 1H), 4.31 (q, $J$ = 7.2 Hz, 2H), 1.36 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ (ppm) 187.6, 164.9, 138.0, 136.3, 135.2, 132.9, 131.4, 130.1, 127.1, 122.9, 61.2, 13.9; MS (EI) *m/z* 282 (M$^{+}$-1), 284 (M$^{+}$+1).



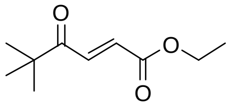
**(*E*)-Ethyl 4-(2-furanyl)-4-*oxo*-2-butenoate (1p).** Yellow solid, 74% yield. $^{1}$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 7.87 (d, $J$ = 4.8 Hz, 1H), 7.79 (d, $J$ = 15.6 Hz, 1H), 7.77 (d, $J$ = 4.8 Hz, 1H), 7.21 (t, $J$ = 4.8 Hz, 1H), 6.94 (d, $J$ = 15.6 Hz, 1H), 4.31 (q, $J$ = 7.2 Hz, 2H), 1.36 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR



(150 MHz, $CDCl_3$) $\delta$ (ppm) 181.0, 165.4, 144.2, 135.8, 135.6, 133.4, 132.0, 128.5, 61.3, 14.1; MS (EI) *m/z* 194 ($M^+$).

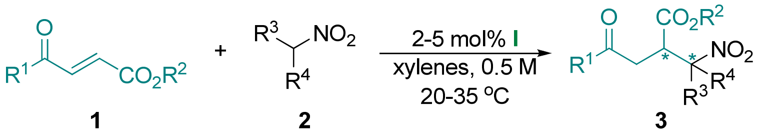


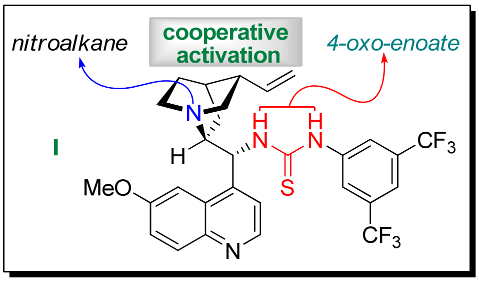
**(*E*)-Ethyl 4-(2-thienyl)-4-*oxo*-2-butenoate (1q).** Yellow solid, 76% yield. $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 7.87 (d, *J* = 4.2 Hz, 1H), 7.79 (d, *J* = 15.6 Hz, 1H), 7.77 (d, *J* = 4.8 Hz, 1H), 7.21 (t, *J* = 4.2 Hz, 1H), 6.94 (d, *J* = 15.6 Hz, 1H), 4.31 (q, *J* = 7.2 Hz, 2H), 1.36 (t, *J* = 7.2 Hz, 3H); $^{13}C$ NMR (150 MHz, $CDCl_3$) $\delta$ (ppm) 181.0, 165.4, 144.2, 135.8, 135.6, 133.4, 132.0, 128.5, 61.3, 14.1; MS (EI) *m/z* 210 ($M^+$).



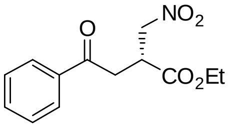
**(*E*)-Ethyl 4-(*tert*-butyl)-4-*oxo*-2-butenoate (1r).** Colorless liquid, 59% yield. $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 7.51 (d, *J* = 15.6 Hz, 1H), 6.77 (d, *J* = 15.6 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.20 (s, 9H); $^{13}C$ NMR (150 MHz, $CDCl_3$) $\delta$ (ppm) 203.0, 165.2, 135.0, 131.1, 60.8, 43.2, 25.4, 13.8; MS (EI) *m/z* 184 ($M^+$).

## Step B.

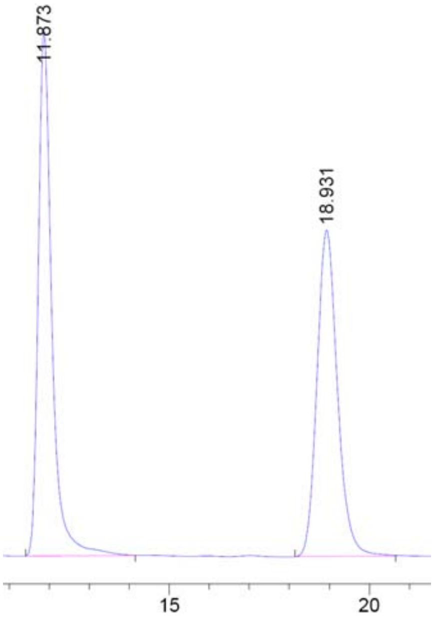




**General procedure for the asymmetric nitro-Michael reaction.** To a solution of nitroalkane **2**(1.0 mmol or 15 mmol) and 4-*oxo*-enoate **1** (0.25 or 5 mmol) in xylenes (0.5 mL or 10 mL) was added catalyst **I** at ambient temperature. After completed (monitored by TLC analysis), the mixture was purified by flash column chromatography on silica gel (PE/EA = 4/1 as eluant) to afford the desired product **3**.



**(*R*)-Ethyl 2-(nitromethyl)-4-*oxo*-4-phenylbutanoate (3a).** Prepared according to the general procedure from **1a** (0.25 mmol), **2a** (1.00 mmol), **I** (0.0125 mmol) and xylenes (0.5 mL) at 25 °C for 12 h to provide the title compound as a colorless oil (95% yield, 96% ee). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 7.96 (d, $J$ = 7.2 Hz, 2H), 7.60 (t, $J$ = 7.2 Hz, 1H), 7.49 (t, $J$ = 7.8 Hz, 2H), 4.87 (ABX, $J_{AB}$ = 14.4 Hz, $J_{AX}$ = 6.0 Hz, $J_{BX}$ = 5.4 Hz, 1H), 4.80 (ABX, $J_{AB}$ = 14.4 Hz, $J_{AX}$ = 6.0 Hz, $J_{BX}$ = 5.4 Hz, 1H), 4.24-4.21 (m, 2H), 3.78-3.74 (m, 1H), 3.61 (ABX, $J_{AB}$ = 18.6 Hz, $J_{AX}$ = 5.4 Hz, $J_{BX}$ = 6.6 Hz, 1H), 3.39 (ABX, $J_{AB}$ = 18.6 Hz, $J_{AX}$ = 5.4 Hz, $J_{BX}$ = 6.6 Hz, 1H), 1.26 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR(100



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  2  18.931 BB    0.5489 1628.56738   45.78645  48.3100
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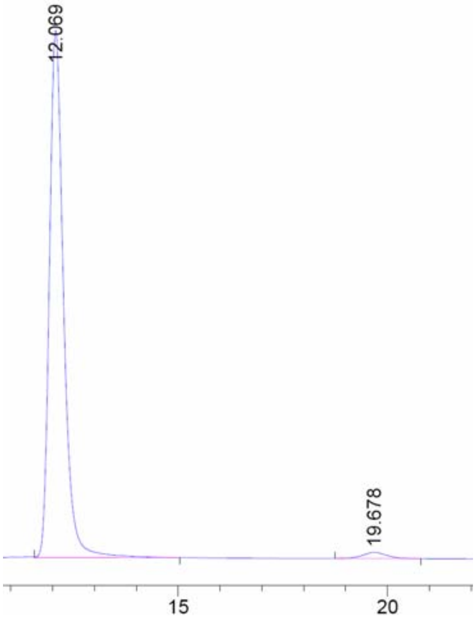

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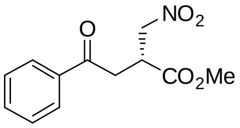
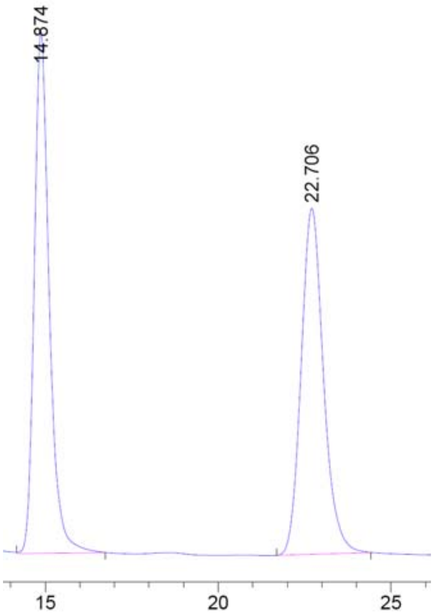
  1  12.069 VB    0.3619 5649.21240  240.05698  97.9998
  2  19.678 BB    0.6168  115.30109    2.78596   2.0002
```

MHz, $CDCl_3$) $\delta$ (ppm) 196.4, 170.8, 135.9, 133.8, 128.7, 128.0, 74.7, 61.8, 38.3, 36.9, 13.9; MS (EI) *m/z* 264 ($M^+$-1); *Anal. Calcd.* for $C_{13}H_{15}NO_5$: C, 58.86; H, 5.70; N, 5.28; Found: C, 58.95; H, 5.57; N, 5.18; $[\alpha]_D^{25}$ = -3.2 (c = 0.58, $CHCl_3$); the enantiomeric excess was determined by chiral HPLC (Chiralpak OD column: hexane/2-propanol = 80/20, 1 mL/min, 254 nm, $t_{major}$ = 12.07 min, $t_{minor}$ = 19.68 min.)



**(*R*)-Methyl 2-(nitromethyl)-4-*oxo*-4-phenylbutanoate (3b).** Prepared according to the general procedure from **1b** (0.25 mmol), **2a** (1.00 mmol), **I** (0.0125 mmol) and xylenes (0.5 mL) at 25 °C for 10 h to provide the title compound as a colorless oil (89% yield, 96% ee). $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 7.96 (d, $J$ = 7.2 Hz, 2H), 7.61 (t, $J$ = 7.2 Hz, 1H), 7.49 (t, $J$ = 7.8 Hz, 2H), 4.88 (ABX, $J_{AB}$ = 14.4 Hz, $J_{AX}$ = 6.0 Hz, $J_{BX}$ = 4.8 Hz, 1H), 4.80 (ABX, $J_{AB}$ = 14.4 Hz, $J_{AX}$ = 6.0 Hz, $J_{BX}$ = 4.8 Hz, 1H), 3.77 (s, 3H), 3.62 (ABX, $J_{AB}$ = 18.6 Hz, $J_{AX}$ = 5.4 Hz, $J_{BX}$ = 7.2 Hz, 1H), 3.41 (ABX, $J_{AB}$ = 18.6 Hz, $J_{AX}$ = 5.4 Hz, $J_{BX}$ = 7.2 Hz, 1H); $^{13}C$ NMR (150 MHz, $CDCl_3$) $\delta$ (ppm) 196.3, 171.3, 135.7, 133.8, 128.7, 128.0, 74.6, 38.1, 37.0, 13.9; *Anal. Calcd.* for $C_{12}H_{13}NO_5$: C, 57.37; H, 5.22; N, 5.58; Found: C, 57.43; H, 5.33; N, 5.47; the enantiomeric excess was determined by chiral HPLC (Chiralpak OD column: hexane/2-propanol = 80/20, 1 mL/min, 254 nm, $t_{major}$ = 14.45 min, $t_{minor}$ = 21.92 min.)



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   2  22.706 BB    0.6903 2391.65503   53.21703  49.7225
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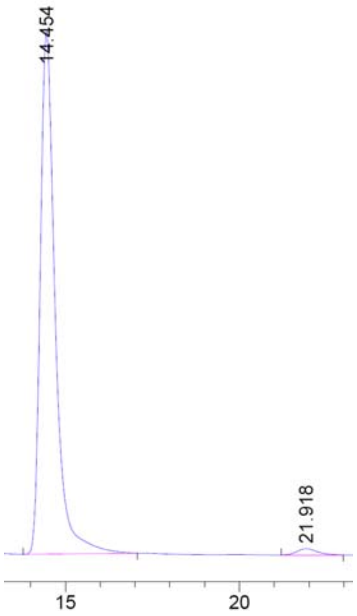

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Peak RetTime Type  Width     Area      Height     Area
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   1  14.454 PB    0.4492 1.00981e4  339.21661  98.3693
   2  21.918 BB    0.5906  167.39554    4.13217   1.6307
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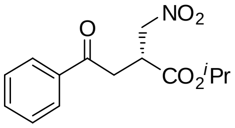
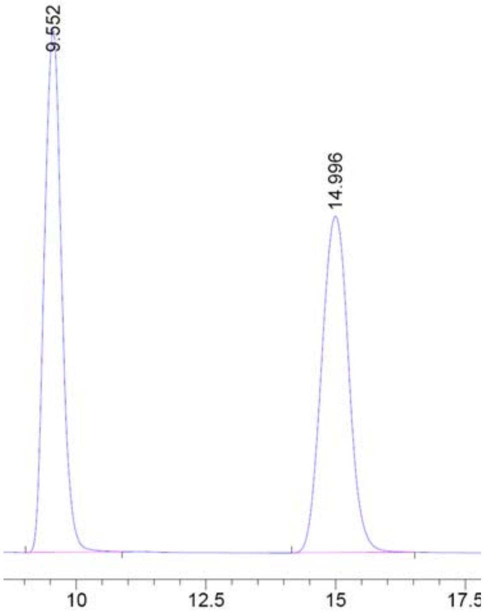


**(*R*)-Isopropyl 2-(nitromethyl)-4-*oxo*-4-phenylbutanoate (3c).** Prepared according to the general procedure from **1c** (0.25 mmol), **2a** (1.00 mmol), **I** (0.0125 mmol) and xylenes (0.5 mL) at 25 °C for 12 h to provide the title compound as a colorless oil (97% yield, 96% ee). $^1H$ NMR (600 MHz, $CDCl_3$)

$\delta$ (ppm) 7.96 (d, $J$ = 7.2 Hz, 2H), 7.61 (t, $J$ = 7.2 Hz, 1H), 7.49 (t, $J$ = 8.4 Hz, 2H), 5.10-5.06 (m, 1H), 4.85 (ABX, $J_{AB}$ = 14.4 Hz, $J_{AX}$ = 6.0 Hz, $J_{BX}$ = 5.4 Hz, 1H), 4.80 (ABX, $J_{AB}$ = 14.4 Hz, $J_{AX}$ = 6.0 Hz, $J_{BX}$ = 5.4 Hz, 1H), 3.74-3.70 (m, 1H), 3.60 (ABX, $J_{AB}$ = 18.0 Hz, $J_{AX}$ = 4.8 Hz, $J_{BX}$ = 7.2 Hz, 1H), 3.36 (ABX, $J_{AB}$ = 18.0 Hz, $J_{AX}$ = 4.8 Hz, $J_{BX}$ = 7.2 Hz, 1H), 1.23 (t, $J$ = 6.6 Hz, 6H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ (ppm) 196.5, 170.3, 135.9, 133.8, 128.7, 128.0, 74.8, 69.6, 38.5, 36.9, 21.5; *Anal. Calcd.* for $C_{14}H_{17}NO_5$: C, 60.21; H, 6.14; N, 5.02; Found: C, 60.27; H, 6.03; N, 4.95; the enantiomeric excess was determined by chiral HPLC (Chiralpak OD column: hexane/2-propanol = 80/20, 1 mL/min, 254 nm, $t_{major}$ = 9.57 min, $t_{minor}$ = 14.96 min.)



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   1   9.552 VB    0.3695 5249.95752  227.65446  49.6611
   2  14.996 BB    0.5773 5321.61230  146.78218  50.3389
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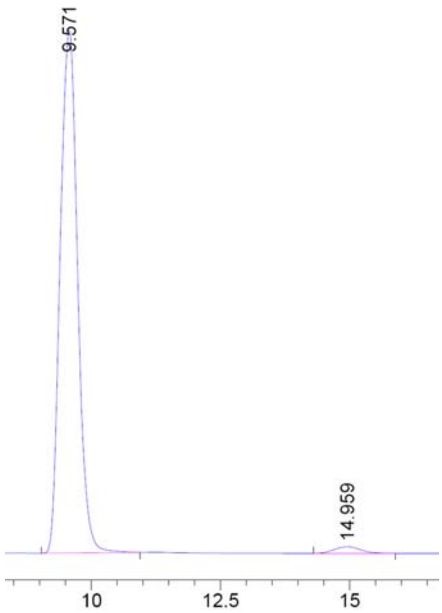

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Peak RetTime Type  Width      Area       Height      Area
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   1   9.571 PB    0.3762 7936.59082  339.45123  98.1072
   2  14.959 BB    0.5398  153.12097    4.38617   1.8928
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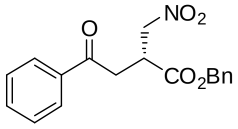
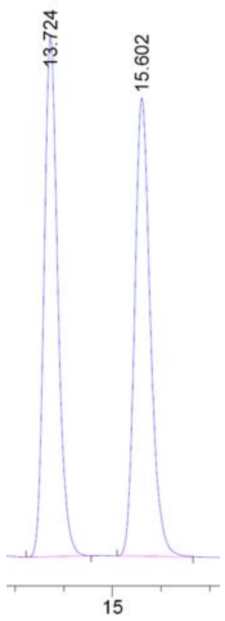


**(*R*)-Benzyl 2-(nitromethyl)-4-*oxo*-4-phenylbutanoate (3d).** Prepared according to the general procedure from **1d** (0.25 mmol), **2a** (1.00 mmol), **I** (0.0125 mmol) and xylenes (0.5 mL) at 25 °C for 12 h to provide the title compound as a colorless oil (98% yield, 96% ee). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 7.94 (d, $J$ = 7.2 Hz, 2H), 7.60 (t, $J$ = 7.2 Hz, 1H), 7.48 (t, $J$ = 6.6 Hz, 2H), 7.34 (br, 5H), 5.19 (s, 2H), 4.88 (ABX, $J_{AB}$ = 14.4 Hz, $J_{AX}$ = 5.4 Hz, $J_{BX}$ = 4.8 Hz, 1H), 4.81 (ABX, $J_{AB}$ = 14.4 Hz, $J_{AX}$ = 5.4 Hz, $J_{BX}$ = 4.8 Hz, 1H), 3.82 (br, 1H), 3.63 (ABX, $J_{AB}$ = 18.6 Hz, $J_{AX}$ = 4.8 Hz, $J_{BX}$ = 6.0 Hz, 1H), 3.40 (ABX, $J_{AB}$ = 18.6 Hz, $J_{AX}$ = 4.8 Hz, $J_{BX}$ = 6.0 Hz, 1H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ (ppm) 196.4, 170.7, 135.8, 135.0, 133.8, 128.7, 128.6, 128.5, 128.2, 128.0, 67.6, 38.3, 36.9; *Anal. Calcd.* for $C_{18}H_{17}NO_5$: C, 66.05; H, 5.23; N, 4.28; Found: C, 66.12; H, 5.19; N, 4.17; the enantiomeric excess was determined by chiral HPLC (Chiralpak AD column: hexane/2-propanol = 80/20, 1 mL/min, 254 nm, $t_{major}$ =13.70 min, $t_{minor}$ = 15.59 min.)



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   2  15.602 PB    0.3431 2597.21069  115.85150  50.1526
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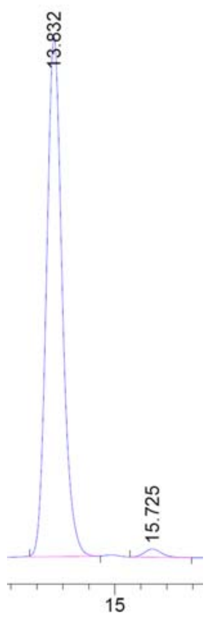

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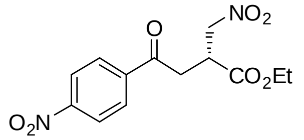
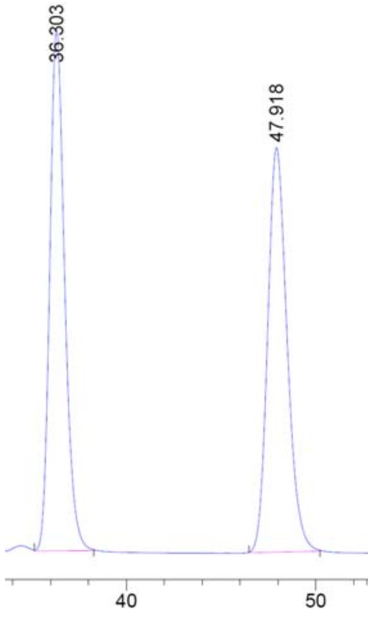
   1  13.702 VV    0.3091  984.35724   49.21328  98.1922
   2  15.590 MM    0.3948   18.12283 7.64977e-1   1.8078
```



**(*R*)-Ethyl 2-(nitromethyl)-4-(4-nitrophenyl)-4-oxobutanoate (3e).** Prepared according to the general procedure from **1e** (0.25 mmol), **2a** (1.00 mmol), **I** (0.0125 mmol) and xylenes (0.5 mL) at 25 °C for 8 h to provide the title compound as a colorless oil (94% yield, 97% ee). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ (ppm) 8.34 (d, $J$ = 8.4 Hz, 2H), 8.14 (d, $J$ = 8.4 Hz, 2H), 4.86 (dd, $J$ = 5.4 and 1.8 Hz, 2H), 4.26-4.21 (m, 2H), 3.81-3.76 (m, 1H), 3.69 (ABX, $J_{AB}$ = 18.6 Hz, $J_{AX}$ = $J_{BX}$ = 6.0 Hz, 1H),



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   1  36.303 VB    0.8361 4721.67383   86.52353  49.6823
   2  47.918 BB    1.0906 4782.06543   67.22177  50.3177
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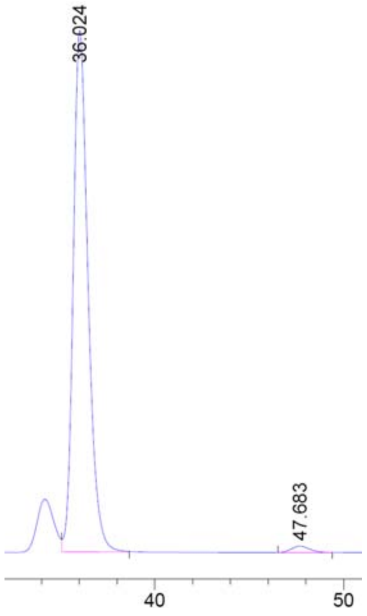

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Peak RetTime Type  Width     Area      Height     Area
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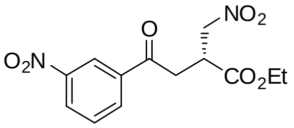
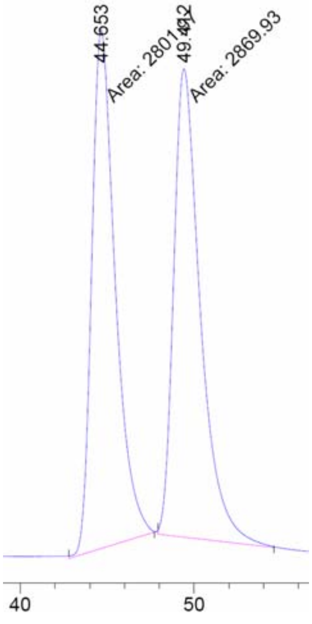
   1  36.024 VB    0.8296 1.76288e4  324.16568  98.4952
   2  47.683 BB    1.0359  269.32166    3.97075   1.5048
```

3.40 (ABX, $J_{AB}$ = 18.6 Hz, $J_{AX}$ = $J_{BX}$ = 6.0 Hz, 1H), 1.27 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ (ppm) 195.3, 170.3, 150.6, 140.2, 129.2, 124.0, 74.6, 62.1, 38.3, 37.4, 13.9; *Anal. Calcd.* for $C_{13}H_{14}N_2O_7$: C, 50.33; H, 4.55; N, 9.03; Found: C, 50.47; H, 4.36; N, 8.88; the enantiomeric excess was determined by chiral HPLC (Chiralpak AD column: hexane/2-propanol = 80/20, 1 mL/min, 254 nm, $t_{major}$ =36.02 min, $t_{minor}$ = 47.68 min.)



**(*R*)-Ethyl 2-(nitromethyl)-4-(3-nitrophenyl)-4-oxobutanoate (3f).** Prepared according to the general procedure from **1f** (0.25 mmol), **2a** (1.00 mmol), **I** (0.0125 mmol) and xylenes (0.5 mL) at 25 °C for 4 h to provide the title compound as a colorless oil (95% yield, 98% ee). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 8.78 (s, 1H), 8.46 (d, $J$ = 8.4 Hz, 1H), 8.31 (d, $J$ = 7.8 Hz, 1H), 4.90 (ABX, $J_{AB}$ = 14.4 Hz, $J_{AX}$ = 6.0 Hz, $J_{BX}$ = 5.4 Hz, 1H), 4.85 (ABX, $J_{AB}$ = 14.4 Hz, $J_{AX}$ = 6.0 Hz, $J_{BX}$ = 5.4 Hz, 1H), 4.26-4.20 (m, 2H), 3.83-3.79 (m, 1H), 3.71 (ABX, $J_{AB}$ = 18.0 Hz, $J_{AX}$ = 5.4 Hz, $J_{BX}$ = 6.0 Hz, 1H), 3.44 (ABX, $J_{AB}$ = 18.0 Hz, $J_{AX}$ = 5.4 Hz, $J_{BX}$ = 6.0 Hz, 1H), 1.27 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ (ppm) 194.6, 170.3, 148.4, 137.0, 133.6, 130.1, 127.9, 122.9, 74.6, 62.0, 38.2, 37.2, 13.9; *Anal. Calcd.* for $C_{13}H_{14}N_2O_7$: C, 50.33; H, 4.55; N, 9.03; Found: C, 50.29; H, 4.48; N, 8.54; $[\alpha]_D^{25}$ = -6.2 (c = 2.5, $CHCl_3$); the enantiomeric excess was determined by chiral HPLC (Chiralpak OD column: hexane/2-propanol = 80/20, 1 mL/min, 254 nm, $t_{major}$ = 44.54 min, $t_{minor}$ = 49.86 min.)



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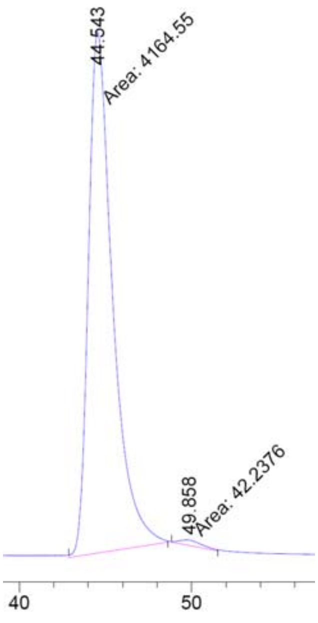

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   2  49.858 MM     1.5575   42.23763 4.51972e-1   1.0040
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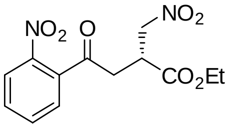
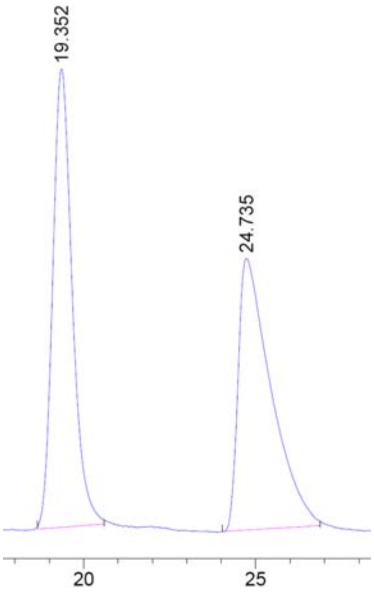


**(*R*)-Ethyl 2-(nitromethyl)-4-(2-nitrophenyl)-4-oxobutanoate (3g).** Prepared according to the general procedure from **1g** (0.25 mmol), **2a** (1.00 mmol), **I** (0.0125 mmol) and xylenes (0.5 mL) at 25 °C for 20 h to provide the title compound as a colorless oil (65% yield, 91% ee). $^1$H NMR (600 MHz, $CDCl_3$)

$\delta$ (ppm) 8.16 (d, $J$ = 7.8 Hz, 1H), 7.78 (t, $J$ = 7.8 Hz, 1H), 7.65 (t, $J$ = 8.4 Hz, 1H), 7.49 (d, $J$ = 7.8 Hz, 1H), 4.94-4.88 (m, 2H), 4.27-4.23 (m, 2H), 3.80-3.76 (m, 1H), 3.42 (ABX, $J_{AB}$ = 18.6 Hz, $J_{AX}$ = 4.8 Hz, $J_{BX}$ = 6.0 Hz, 1H), 3.29 (ABX, $J_{AB}$ = 18.6 Hz, $J_{AX}$ = 4.8 Hz, $J_{BX}$ = 6.0 Hz, 1H), 1.29 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ (ppm) 199.2, 170.5, 145.3, 136.8, 134.6, 130.9, 127.3, 124.6, 73.9, 62.0, 41.2, 38.0, 13.9; *Anal. Calcd.* for $C_{13}H_{14}N_2O_7$: C, 50.33; H, 4.55; N, 9.03; Found: C, 50.23; H, 4.66; N, 8.95; $[\alpha]_D^{25}$ = 13.8 (c = 2.1, CHCl$_3$); the enantiomeric excess was determined by chiral HPLC (Chiralpak OD column: hexane/2-propanol = 80/20, 1 mL/min, 254 nm, $t_{major}$ = 19.25 min, $t_{minor}$ = 25.06 min.)



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Peak RetTime Type  Width     Area      Height     Area
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   2  24.735 PB    0.8905  229.61728    3.46104 49.9059
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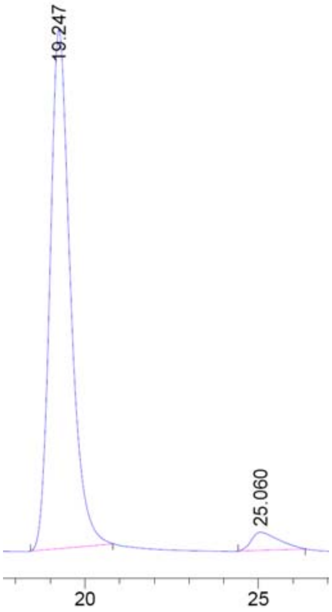

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Peak RetTime Type  Width     Area      Height     Area
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   2  25.060 BB    0.7204  107.22503    1.95363  4.4949
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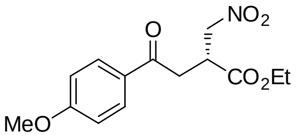
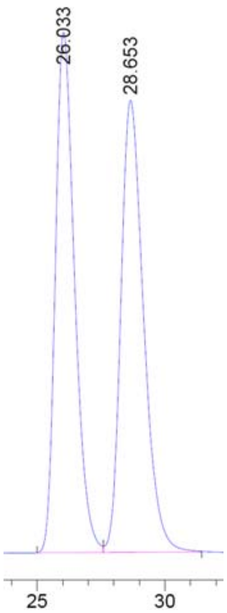
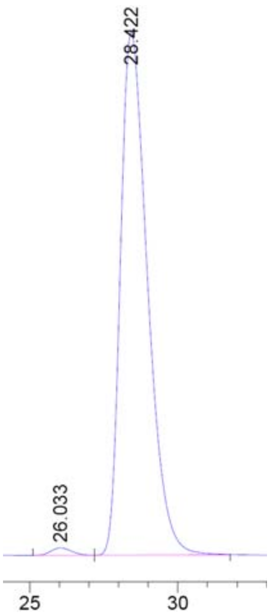


**(*R*)-Ethyl 4-(4-methoxyphenyl)-2-(nitromethyl)-4- oxobutanoate (3h).** Prepared according to the general procedure from **1h** (0.25 mmol), **2a** (1.00 mmol), **I** (0.0125 mmol) and xylenes (0.5 mL) at 25 °C for 14 h to provide the title compound as a colorless oil (84% yield, 98% ee). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ (ppm) 7.94 (d, $J$ = 8.4 Hz, 2H), 6.95 (d, $J$ = 8.4 Hz, 2H), 4.86 (ABX, $J_{AB}$ = 14.4 Hz, $J_{AX}$ = 6.6 Hz, $J_{BX}$ = 5.4 Hz, 1H), 4.76 (ABX, $J_{AB}$ = 14.4 Hz, $J_{AX}$ = 6.6 Hz, $J_{BX}$ = 5.4 Hz, 1H),4.23-4.20 (m, 2H), 3.88 (s, 3H), 3.76-3.72 (m, 1H), 3.55 (ABX, $J_{AB}$ = 18.0 Hz, $J_{AX}$ = 4.8 Hz, $J_{BX}$ = 7.2 Hz, 1H), 3.34 (ABX, $J_{AB}$ = 18.0 Hz, $J_{AX}$ = 4.8 Hz, $J_{BX}$ = 7.2 Hz, 1H), 1.26 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ (ppm) 194.8, 171.0, 163.9, 130.4, 128.9, 113.9, 74.8, 61.8, 55.5, 38.4, 36.5, 13.9; *Anal. Calcd.* for $C_{14}H_{17}NO_6$: C, 56.94; H, 5.80; N, 4.74; Found: C, 57.01; H, 5.76; N, 4.67; $[\alpha]_D^{25}$ = 4.4 (c = 1.3, CHCl$_3$); the enantiomeric excess was determined by chiral HPLC (Chiralpak AS column: hexane/2-propanol = 75/25, 1 mL/min, 254 nm, $t_{minor}$ = 26.03 min, $t_{major}$ = 28.42 min.)





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Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]  mAU    *s   [mAU    ]      %
----|-------|----|-------|----------|----------|--------|
   1  26.033 BV    0.8039 4663.16211   89.36094  49.2968
   2  28.653 VB    0.9511 4796.20361   77.60720  50.7032
```

```
Peak RetTime Type  Width     Area       Height      Area
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----|-------|----|-------|----------|----------|--------|
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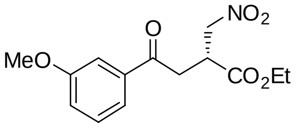
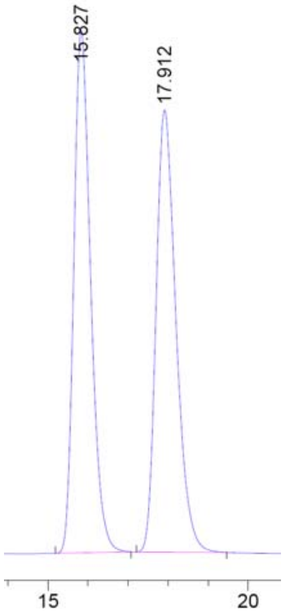
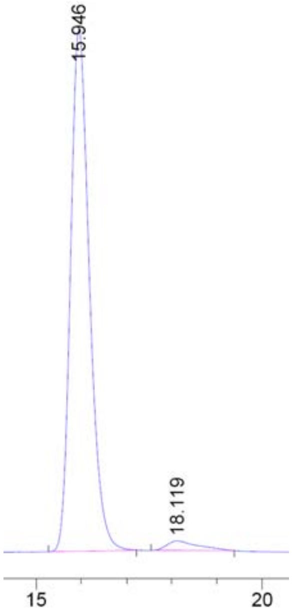
   2  28.422 VB    0.9737 1.27811e4   201.30963  98.9172
```



**(*R*)-Ethyl 4-(3-methoxyphenyl)-2-(nitromethyl)-4- oxobutanoate (3i).** Prepared according to the general procedure from **1i** (0.25 mmol), **2a** (1.00 mmol), **I** (0.0125 mmol) and xylenes (0.5 mL) at 25 °C for 14 h to provide the title compound as a colorless oil (91% yield, 94% ee). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 7.54 (d, $J$ = 7.8 Hz, 1H), 7.47 (s, 1H), 7.15 (d, $J$ = 7.8 Hz, 1H), 4.87 (ABX, $J_{AB}$ = 14.4 Hz, $J_{AX}$ = 6.0 Hz, $J_{BX}$ = 5.4 Hz, 1H), 4.79 (ABX, $J_{AB}$ = 14.4 Hz, $J_{AX}$ = 6.0 Hz, $J_{BX}$ = 5.4





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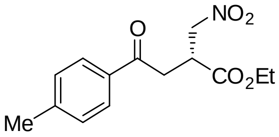
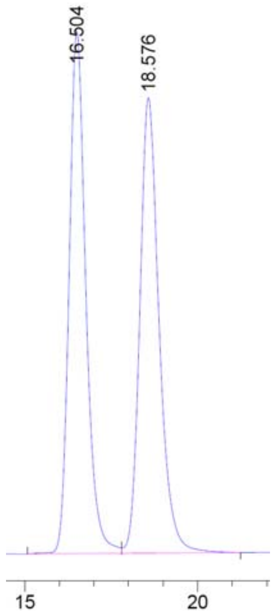
   1  15.827 BB    0.4481 2569.52319   88.07060  49.9596
   2  17.912 BB    0.5313 2573.68335   74.46767  50.0404
```

```
Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]  mAU    *s   [mAU    ]      %
----|-------|----|-------|----------|----------|--------|
   1  15.946 BB    0.4465 1541.16003   53.07421  97.0157
   2  18.119 BB    0.5988   47.40838 9.78347e-1   2.9843
```

Hz, 1H), 4.24-4.20 (m, 2H), 3.86 (s, 3H), 3.77-3.73 (m, 1H), 3.59 (ABX, $J_{AB}$ = 18.0 Hz, $J_{AX}$ = 4.8 Hz, $J_{BX}$ = 6.6 Hz, 1H), 3.38 (ABX, $J_{AB}$ = 18.0 Hz, $J_{AX}$ = 4.8 Hz, $J_{BX}$ = 6.6 Hz, 1H), 1.26 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ (ppm) 196.3, 170.8, 159.8, 137.1, 129.7, 120.6, 120.2, 112.2, 74.7, 61.8, 55.4, 38.3, 37.1, 13.9; *Anal. Calcd.* for $C_{14}H_{17}NO_6$: C, 56.94; H, 5.80; N, 4.74; Found: C, 57.02; H, 5.85; N, 4.47; $[\alpha]_D^{25}$ = 1.4 (c = 3.0, $CHCl_3$); the enantiomeric excess was determined by chiral HPLC (Chiralpak AS column: hexane/2-propanol = 75/25, 1 mL/min, 254 nm, $t_{major}$ = 15.95 min, $t_{minor}$ = 18.12 min.)



**(*R*)-Ethyl 2-(nitromethyl)-4-oxo-4-p-tolylbutanoate (3j).** Prepared according to the general procedure from **1j** (0.25 mmol), **2a** (1.00 mmol), **I** (0.0125 mmol) and xylenes (0.5 mL) at 25 °C for 7 h to provide the title compound as a colorless oil (93% yield, 96% ee). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 7.86 (d, $J$ = 7.8 Hz, 2H), 7.28 (d, $J$ = 7.8 Hz, 2H), 4.86 (ABX, $J_{AB}$ = 14.4 Hz, $J_{AX}$ = 6.0 Hz, $J_{BX}$ = 5.4 Hz, 1H), 4.79 (ABX, $J_{AB}$ = 14.4 Hz, $J_{AX}$ = 6.0 Hz, $J_{BX}$ = 5.4 Hz, 1H),4.24-4.19 (m, 2H), 3.76-3.73 (m, 1H), 3.58 (ABX, $J_{AB}$ = 18.0 Hz, $J_{AX}$ = 4.8 Hz, $J_{BX}$ = 7.2 Hz, 1H), 3.36 (ABX, $J_{AB}$ = 18.0 Hz, $J_{AX}$ = 4.8 Hz, $J_{BX}$ = 7.2 Hz, 1H), 2.42 (s, 3H), 1.26 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ (ppm) 196.0, 170.9, 144.7, 133.4, 129.4, 128.2, 74.7, 61.8, 38.4, 36.8, 21.7, 13.9; *Anal. Calcd.* for $C_{14}H_{17}NO_5$: C, 60.21; H, 6.14; N, 5.02; Found: C, 60.27; H, 6.09; N, 4.96; $[\alpha]_D^{25}$ = 6.3 (c = 1.6, $CHCl_3$); the enantiomeric excess was determined by chiral HPLC (Chiralpak OD column: hexane/2-propanol = 90/10, 1 mL/min, 254 nm, $t_{major}$ = 16.55 min, $t_{minor}$ = 18.73 min.)



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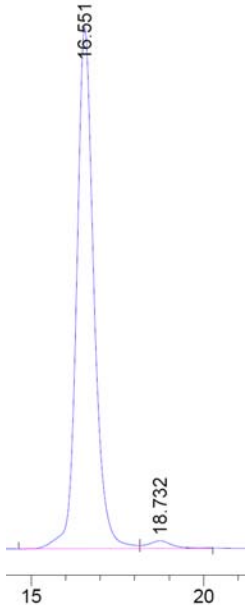
   2  18.576 VB    0.5860 8134.66699  209.93437  50.1676
```



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Peak RetTime Type  Width     Area      Height     Area
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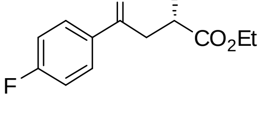
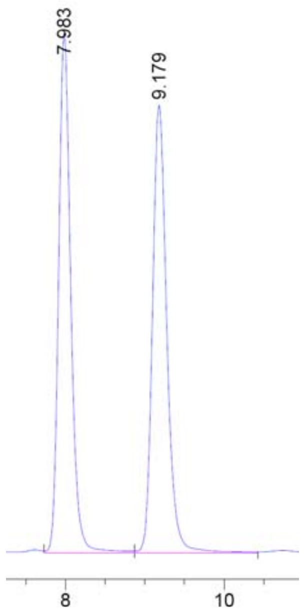
   1  16.551 VV    0.5234 9616.66797  275.69974  97.9705
   2  18.732 VB    0.7024  199.21292    4.08860   2.0295
```



**(*R*)-Ethyl 4-(4-fluorophenyl)-2-(nitromethyl)-4-oxobutanoate (3k).** Prepared according to the general procedure from **1k** (0.25 mmol), **2a** (1.00 mmol), **I** (0.0125 mmol) and xylenes (0.5 mL) at 25 °C for 8 h to provide the title compound as a colorless oil (93% yield, 96% ee). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 8.00 (d, $J$ = 8.4 and 5.4 Hz, 2H), 7.16 (t, $J$ = 9.0 Hz, 2H), 4.86 (ABX, $J_{AB}$ = 14.4 Hz, $J_{AX}$ = 6.0 Hz, $J_{BX}$ = 5.4 Hz, 1H), 4.81 (ABX, $J_{AB}$ = 14.4 Hz, $J_{AX}$ = 6.0 Hz, $J_{BX}$ = 5.4 Hz, 1H), 4.25-4.19 (m, 2H), 3.77-3.73 (m, 1H), 3.59 (ABX, $J_{AB}$ = 18.0 Hz, $J_{AX}$ = 5.4 Hz, $J_{BX}$ = 6.6 Hz, 1H), 3.35 (ABX, $J_{AB}$ = 18.0 Hz, $J_{AX}$ = 5.4 Hz, $J_{BX}$ = 6.6 Hz, 1H), 1.26 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ (ppm) 194.9, 170.7, 166.9, 165.2, 132.3, 132.3, 130.8, 130.7, 116.0, 115.8, 74.7, 61.9, 38.3, 36.8, 13.9; *Anal. Calcd.* for $C_{13}H_{14}FNO_5$: C, 55.12; H, 4.98; N, 4.94; Found: C, 55.03; H, 4.89; N, 4.78; $[\alpha]_D^{25}$ = -4.6 (c = 1.0, $CHCl_3$); the enantiomeric excess was determined by chiral HPLC (Chiralpak AD column: hexane/2-propanol = 70/30, 1 mL/min, 254 nm, $t_{major}$ = 7.81 min, $t_{minor}$ = 9.02 min.)



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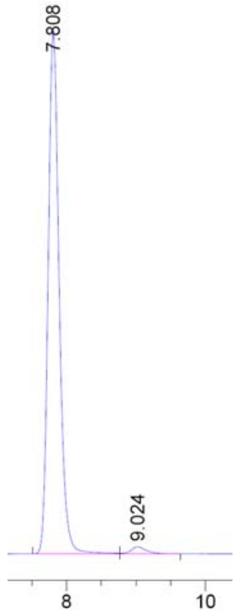

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Peak RetTime Type  Width     Area      Height     Area
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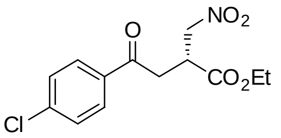
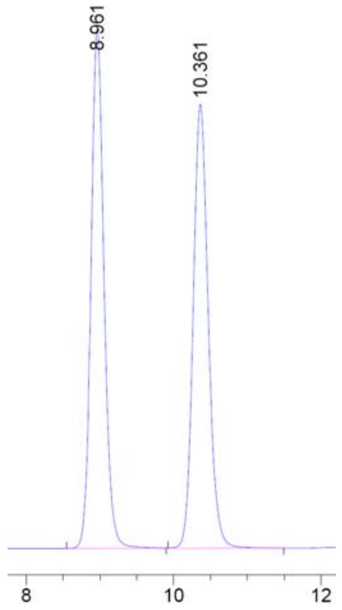
   2   9.024 VB     0.2309  128.51634    8.26793   1.8676
```



**(*R*)-Ethyl 4-(4-chlorophenyl)-2-(nitromethyl)-4-oxobutanoate (3l).** Prepared according to the general procedure from **1l** (0.25 mmol), **2a** (1.00 mmol), **I** (0.0125 mmol) and xylenes (0.5 mL) at 25 °C for 6 h to provide the title compound as a colorless oil (96% yield, 97% ee). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 7.91 (d, $J$ = 9.0 Hz, 2H), 7.47 (d, $J$ = 8.4 Hz, 2H), 4.86 (ABX, $J_{AB}$ = 14.4 Hz, $J_{AX}$ = $J_{BX}$ = 5.4 Hz, 1H), 4.81 (ABX, $J_{AB}$ = 14.4 Hz, $J_{AX}$ = $J_{BX}$ = 5.4 Hz, 1H), 4.25-4.20 (m, 2H), 3.76-3.72 (m, 1H), 3.59 (ABX, $J_{AB}$ = 18.0 Hz, $J_{AX}$ = 4.8 Hz, $J_{BX}$ = 6.6 Hz, 1H), 3.34 (ABX, $J_{AB}$ = 18.0 Hz, $J_{AX}$ = 4.8 Hz, $J_{BX}$ = 6.6 Hz, 1H), 1.26 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ (ppm) 195.3, 170.6, 140.2, 134.2, 129.4, 129.0, 74.7, 61.9, 38.3, 36.9, 13.9; *Anal. Calcd.* for $C_{13}H_{14}ClNO_5$: C, 52.10; H, 4.71; N, 4.67; Found: C, 52.15; H, 4.73; N, 4.55; $[\alpha]_D^{25}$ = 4.65 (c = 2.28, $CHCl_3$); the enantiomeric excess was determined by chiral HPLC (Chiralpak AD column: hexane/2-propanol = 70/30, 1 mL/min, 254 nm, $t_{major}$ = 8.96 min, $t_{minor}$ = 10.37 min.)



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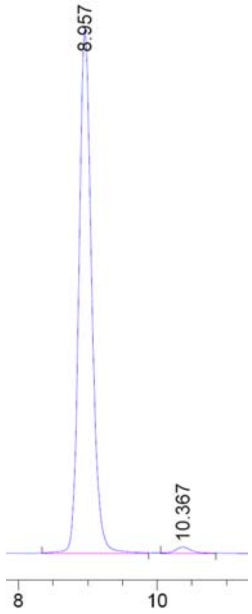
   2  10.361 BB    0.2178 4453.99756  314.12665  49.7445
```



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   2  10.367 BB    0.2513   70.51615    4.19752   1.5456
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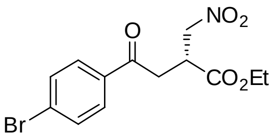
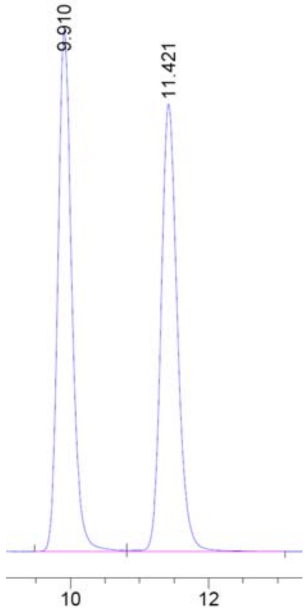


**(*R*)-Ethyl 4-(4-bromophenyl)-2-(nitromethyl)-4-oxobutanoate (3m).** Prepared according to the general procedure from **1m** (0.25 mmol), **2a** (1.00 mmol), **I** (0.0125 mmol) and xylenes (0.5 mL) at 25 °C for 8 h to provide the title compound as a colorless oil (91% yield, 97% ee). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 7.82 (d, $J$ = 8.4 Hz, 2H), 7.63 (d, $J$ = 8.4 Hz, 2H), 4.86 (ABX, $J_{AB}$ = 14.4 Hz, $J_{AX}$ = $J_{BX}$ = 5.4 Hz, 1H), 4.81 (ABX, $J_{AB}$ = 14.4 Hz, $J_{AX}$ = $J_{BX}$ = 5.4 Hz, 1H), 4.25-4.19 (m, 2H), 3.76-



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----|-------|----|-------|----------|----------|--------|
   1   9.910 BV    0.2172 5223.25586  369.75537  50.0028
   2  11.421 VB    0.2561 5222.66113  317.26877  49.9972
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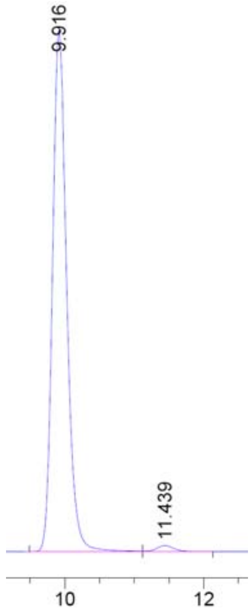

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Peak RetTime Type  Width      Area       Height      Area
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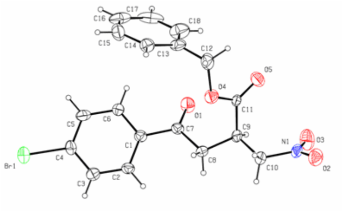
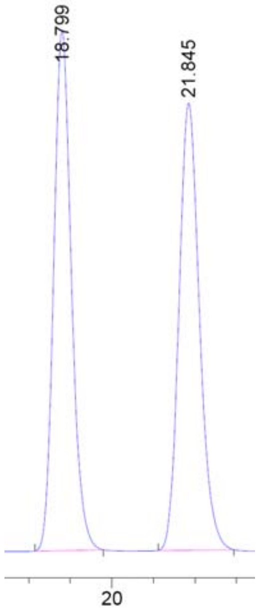
   1   9.916 BV    0.2175 1.01226e4   715.44275  98.5611
   2  11.439 VB    0.2674  147.78383    8.35865   1.4389
```

3.72 (m, 1H), 3.58 (ABX, $J_{AB}$ = 18.6 Hz, $J_{AX}$ = 5.4 Hz, $J_{BX}$ = 6.6 Hz, 1H), 3.33 (ABX, $J_{AB}$ = 18.6 Hz, $J_{AX}$ = 5.4 Hz, $J_{BX}$ = 6.6 Hz, 1H), 1.26 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ (ppm) 195.5, 170.1, 134.5, 132.0, 129.5, 129.0, 74.7, 61.9, 38.2, 36.8, 13.9; *Anal. Calcd.* for $C_{13}H_{14}BrNO_5$: C, 45.37; H, 4.10; N, 4.07; Found: C, 45.29; H, 4.17; N, 3.98; $[\alpha]_D^{25}$ = 5.0 (c = 1.0, CHCl$_3$); the enantiomeric excess was determined by chiral HPLC (Chiralpak AD column: hexane/2-propanol = 70/30, 1 mL/min, 254 nm, $t_{major}$ = 9.92 min, $t_{minor}$ = 11.44 min.)



**(*R*)-Benzyl 4-(4-bromophenyl)-2-(nitromethyl)-4- oxobutanoate (3n).** Prepared according to the general procedure from **1n** (0.50 mmol), **2a** (2.00 mmol), **I** (0.025 mmol) and xylenes (1.0 mL) at 25 °C for 10 h to provide the title compound as a white solid (85% yield, 97% ee). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ (ppm) 7.79 (d, $J$ = 8.4 Hz, 2H), 7.61 (d, $J$ = 8.4 Hz, 2H), 7.35-7.26 (m, 5H), 5.18 (s, 2H), 4.86 (ABX, $J_{AB}$ = 14.4 Hz, $J_{AX}$ = 4.8 Hz, $J_{BX}$ = 6.0 Hz, 1H), 4.82 (ABX, $J_{AB}$ = 14.4 Hz, $J_{AX}$ = 4.8 Hz, $J_{BX}$ = 6.0 Hz, 1H), 3.82-3.78 (m, 1H), 3.58 (ABX, $J_{AB}$ = 18.6 Hz, $J_{AX}$ = 5.4 Hz, $J_{BX}$ = 6.6 Hz, 1H), 3.34 (ABX, $J_{AB}$ = 18.6 Hz, $J_{AX}$ = 5.4 Hz, $J_{BX}$ = 6.6 Hz, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ (ppm) 195.4, 170.5, 134.9, 134.5, 132.0, 129.0, 128.6, 128.5, 128.2, 74.6, 67.6, 38.3, 36.8; *Anal. Calcd.* for $C_{18}H_{16}BrNO_5$: C, 53.22; H, 3.97; N, 3.45; Found: C, 53.26; H, 3.89; N, 3.37; $[\alpha]_D^{16}$ = -6.3 (c = 0.89, CH$_2$Cl$_2$); the enantiomeric excess was determined by chiral HPLC (Chiralpak AD column: hexane/2-propanol = 80/20, 1 mL/min, 254 nm, $t_{major}$ = 18.82 min, $t_{minor}$ = 21.92 min.)



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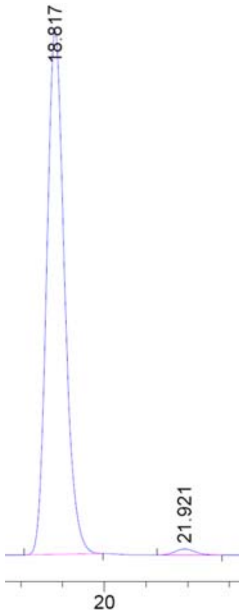
   2  21.845 BB    0.5271 1766.18652   51.64923 49.9321
```



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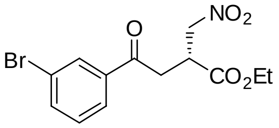
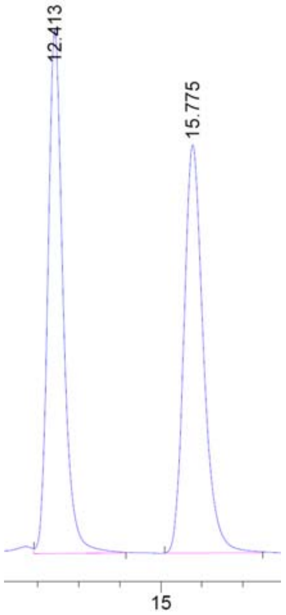
   2  21.921 BB    0.5253  341.79984  10.15180  1.2987
```



**(*R*)-Ethyl 4-(3-bromophenyl)-2-(nitromethyl)-4-oxobutanoate (3o).** Prepared according to the general procedure from **1n** (0.50 mmol), **2a** (2.00 mmol), **I** (0.025 mmol) and xylenes (1.0 mL) at 25 °C for 4 h to provide the title compound as a colorless oil (90% yield, 97% ee). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 8.09 (s, 1H), 7.89 (d, $J$ = 7.8 Hz, 1H), 7.73 (d, $J$ = 7.8 Hz, 1H), 7.38 (t, $J$ = 7.8 Hz, 1H), 4.86 (ABX, $J_{AB}$ = 14.4 Hz, $J_{AX}$ = $J_{BX}$ = 5.4 Hz, 1H), 4.81 (ABX, $J_{AB}$ = 14.4 Hz, $J_{AX}$ = $J_{BX}$ = 5.4 Hz, 1H), 4.25-4.20 (m, 2H), 3.77-3.73 (m, 1H), 3.59 (ABX, $J_{AB}$ = 18.0 Hz, $J_{AX}$ = 6.0 Hz, $J_{BX}$ = 6.6 Hz, 1H), 3.35 (ABX, $J_{AB}$ = 18.0 Hz, $J_{AX}$ = 6.0 Hz, $J_{BX}$ = 6.6 Hz, 1H), 1.26 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ (ppm) 195.2, 170.5, 137.5, 136.6, 131.1, 130.3, 126.6, 123.1, 74.6, 61.9, 38.2, 37.0, 13.9; *Anal. Calcd.* for $C_{13}H_{14}BrNO_5$: C, 45.37; H, 4.10; N, 4.07; Found: C, 45.33; H, 4.21; N, 4.00; $[\alpha]_D^{25}$ = -2.5 (c = 2.5, $CHCl_3$); the enantiomeric excess was determined by chiral HPLC (Chiralpak OD column: hexane/2-propanol = 80/20, 1 mL/min, 254 nm, $t_{major}$ = 12.40 min, $t_{minor}$ = 15.79 min.)



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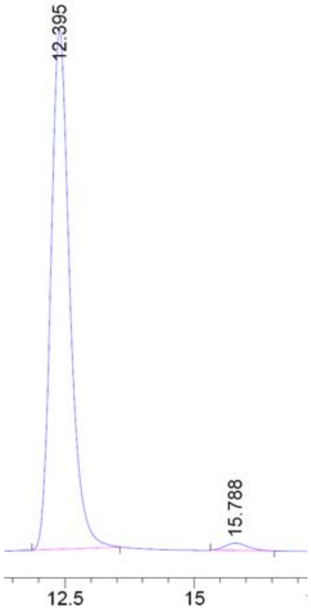
   1  12.413 VB    0.3907 1432.95679   55.65339  50.0132
   2  15.775 PB    0.5014 1432.20117   43.40817  49.9868
```



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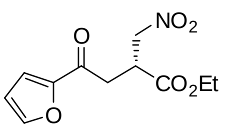
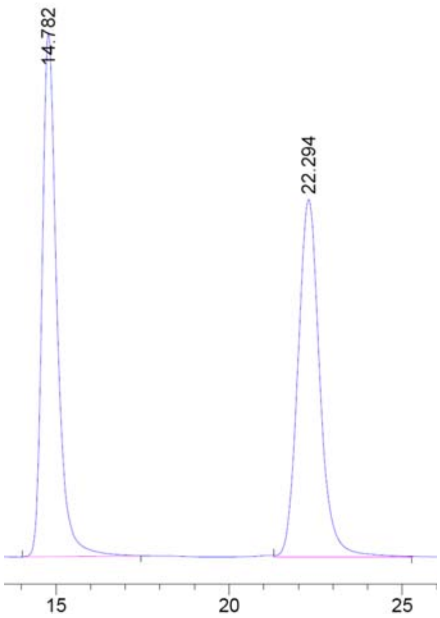
   1  12.395 BB    0.3860 1830.75842   72.23108  98.3133
   2  15.788 BB    0.3915   31.40881    1.03185   1.6867
```



**(*R*)-Ethyl 4-(furan-2-yl)-2-(nitromethyl)-4-oxobutanoate (3p).** Prepared according to the general procedure from **1n** (0.50 mmol), **2a** (2.00 mmol), **I** (0.025 mmol) and xylenes (1.0 mL) at 25 °C for 6 h to provide the title compound as a colorless oil (92% yield, 97% ee). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 7.76 (br, 1H), 7.69 (d, $J$ = 4.8 Hz, 1H), 7.15 (br, 1H), 4.85 (ABX, $J_{AB}$ = 14.4 Hz, $J_{AX}$ = 6.0 Hz, $J_{BX}$ = 5.4 Hz, 1H), 4.80 (ABX, $J_{AB}$ = 14.4 Hz, $J_{AX}$ = 6.0 Hz, $J_{BX}$ = 5.4 Hz, 1H), 4.24-4.18 (m, 2H), 3.74-3.71 (m, 1H), 3.55 (ABX, $J_{AB}$ = 18.0 Hz, $J_{AX}$ = 5.4 Hz, $J_{BX}$ = 6.6 Hz, 1H), 3.32 (ABX, $J_{AB}$ = 18.0 Hz, $J_{AX}$ = 5.4 Hz, $J_{BX}$ = 6.6 Hz, 1H), 1.24 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ (ppm) 189.2, 170.6, 142.8, 134.5, 132.6, 128.3, 74.6, 61.9, 38.3, 37.4, 13.9; *Anal. Calcd.* for $C_{11}H_{13}NO_6$: C, 51.77; H, 5.13; N, 5.49; Found: C, 51.90; H, 5.08; N, 5.37; $[\alpha]_D^{25}$ = -1.3 (c = 2.6, $CHCl_3$); the enantiomeric excess was determined by chiral HPLC (Chiralpak OD column: hexane/2-propanol = 80/20, 1 mL/min, 254 nm, $t_{major}$ = 14.72 min, $t_{minor}$ = 22.05 min.)



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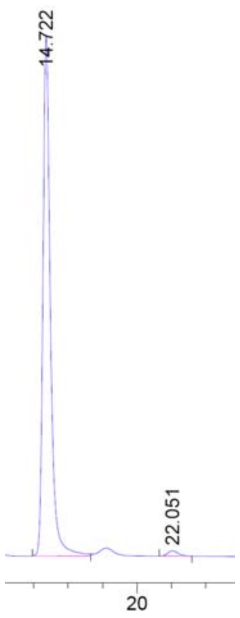
   1  14.782 BB    0.4474 1.65726e4   555.00879  49.9361
   2  22.294 VB    0.6745 1.66150e4   378.99146  50.0639
```



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   1  14.722 BB    0.4541 4751.51318  157.40144  98.6184
   2  22.051 PB    0.6492   66.56483    1.56916   1.3816
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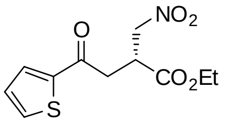
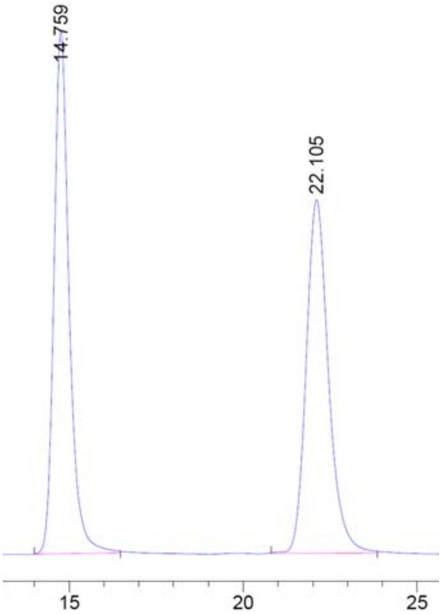


**(*R*)-Ethyl 2-(nitromethyl)-4-oxo-4-(thiophen-2-yl)butanoate (3q).** Prepared according to the general procedure from **1n** (0.50 mmol), **2a** (2.00 mmol), **I** (0.025 mmol) and xylenes (1.0 mL) at 25 °C for 4 h to provide the title compound as a colorless oil (86% yield, 98% ee). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 7.77 (d, $J$ = 3.6 Hz, 1H), 7.70 (d, $J$ = 4.8 Hz, 1H), 7.16 (t, $J$ = 3.6 Hz, 1H), 4.86 (ABX, $J_{AB}$ = 14.4 Hz, $J_{AX}$ = $J_{BX}$ = 5.4 Hz, 1H), 4.81 (ABX, $J_{AB}$ = 14.4 Hz, $J_{AX}$ = $J_{BX}$ = 5.4 Hz, 1H), 4.25-4.19



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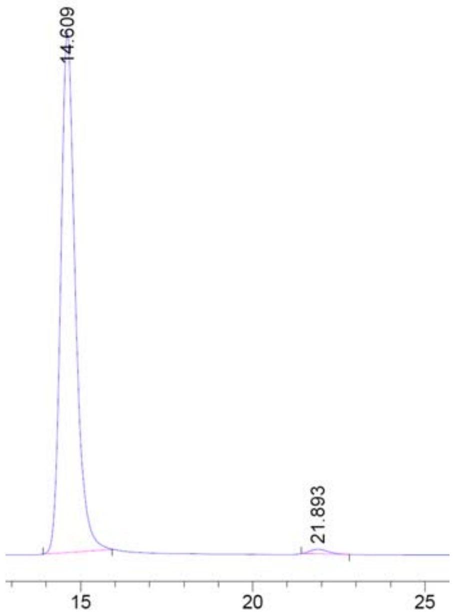
   1  14.759 BB    0.4550 3218.89355  106.34576  50.1783
   2  22.105 BB    0.6764 3196.01758   71.82056  49.8217
```



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Peak RetTime Type  Width      Area       Height      Area
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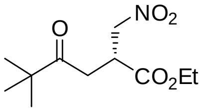
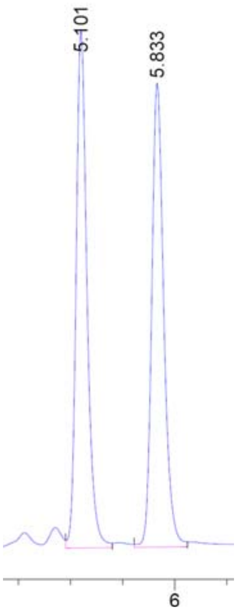
----|-------|----|-------|----------|----------|--------|
   1  14.609 BB    0.4486 1.36218e4   460.28171  98.8923
   2  21.893 BB    0.5728  152.57703    4.08356   1.1077
```

(m, 2H), 3.75-3.71 (m, 1H), 3.55 (ABX, $J_{AB}$ = 18.0 Hz, $J_{AX}$ = 5.4 Hz, $J_{BX}$ = 6.6 Hz, 1H), 3.33 (ABX, $J_{AB}$ = 18.0 Hz, $J_{AX}$ = 5.4 Hz, $J_{BX}$ = 6.6 Hz, 1H), 1.25 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ (ppm) 189.2, 170.6, 142.8, 134.5, 132.6, 128.3, 74.6, 61.9, 38.3, 37.3, 13.9; *Anal. Calcd.* for $C_{11}H_{13}NO_5S$: C, 48.70; H, 4.83; N, 5.16; Found: C, 48.80; H, 4.76; N, 5.03; $[\alpha]_D^{25}$ = -4.7 (c = 2.1, $CHCl_3$); the enantiomeric excess was determined by chiral HPLC (Chiralpak OD column: hexane/2-propanol = 80/20, 1 mL/min, 254 nm, $t_{major}$ = 14.61 min, $t_{minor}$ = 21.89 min.)



**(*R*)-Ethyl 5,5-dimethyl-2-(nitromethyl)-4-oxohexanoate (3r).** Prepared according to the general procedure from **3r** (0.25 mmol), **2a** (1.00 mmol), **I** (0.025 mmol) and xylenes (0.5 mL) at 25 °C for 4 h to provide the title compound as a colorless oil (47% yield, 80% ee). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 4.76 (ABX, $J_{AB}$ = 14.4 Hz, $J_{AX}$ = 6.0 Hz, $J_{BX}$ = 5.4 Hz, 1H), 4.67 4.76 (ABX, $J_{AB}$ = 14.4 Hz, $J_{AX}$ = 6.0 Hz, $J_{BX}$ = 5.4 Hz, 1H), 4.21-4.15 (m, 2H), 3.57-3.53 (m, 1H), 3.08 (ABX, $J_{AB}$ = 18.6 Hz, $J_{AX}$ = 5.4 Hz, $J_{BX}$ = 6.6 Hz, 1H), 2.91 (ABX, $J_{AB}$ = 18.6 Hz, $J_{AX}$ = 5.4 Hz, $J_{BX}$ = 6.6 Hz, 1H), 1.26 (t, $J$ = 7.2 Hz, 3H), 1.17 (s, 9H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ (ppm) 212.7, 170.8, 74.8, 61.7, 44.0, 38.2, 35.3, 26.3, 14.0; *Anal. Calcd.* $C_{11}H_{19}NO_5$: C, 53.87; H, 7.81; N, 5.71; Found: C, 53.81; H, 7.73; N, 5.63; the enantiomeric excess was determined by chiral HPLC (Chiralpak AD column: hexane/2-propanol = 80/20, 1 mL/min, 210 nm, $t_{major}$ = 14.61 min, $t_{minor}$ = 21.89 min.)



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   2   5.833 VV    0.1230 2493.39624  309.76343  49.8099
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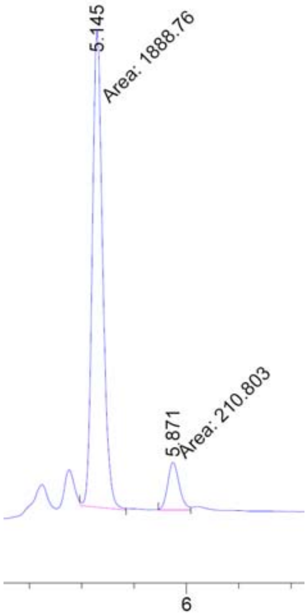

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   1   5.145 MM    0.1152 1888.75977  273.32944  89.9597
   2   5.871 MM    0.1283  210.80342   27.37632  10.0403
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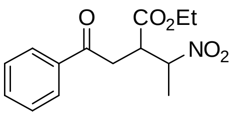
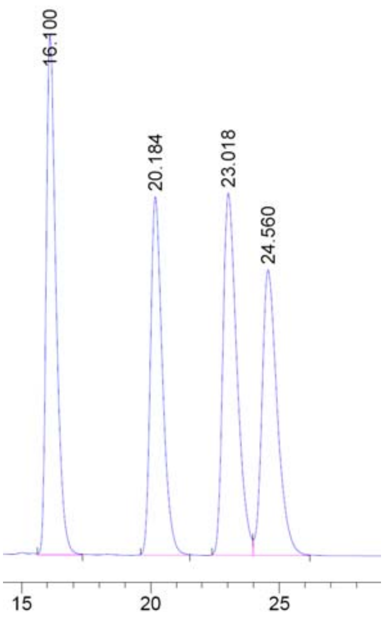


**Ethyl 2-(1-nitroethyl)-4-*oxo*-4-phenylbutanoate (3s).** Prepared according to the general procedure from **1a** (0.25 mmol), **2b** (1.00 mmol), **I** (0.0125 mmol) and xylenes (0.5 mL) at 25 °C for 4 h to provide the title compound as a colorless oil (89% yield, d.r. = 65 : 35, 97 and 96% ee). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 7.96 (d, $J$ = 7.8 Hz, 2H), 7.48 (t, $J$ = 8.4 Hz, 1H), 7.48 (t, $J$ = 9.6 Hz, 2H), 5.07-



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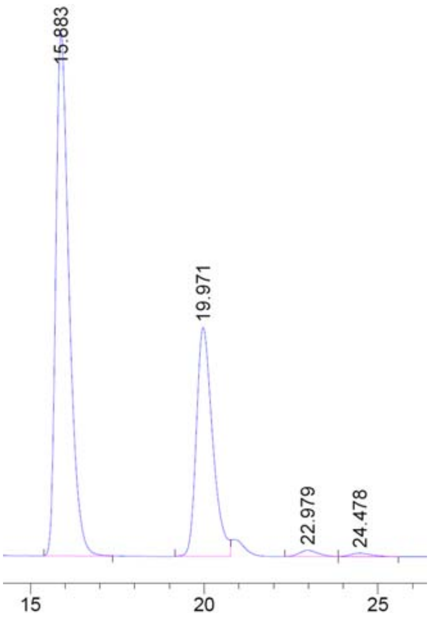
----|-------|----|-------|----------|----------|--------|
   1  16.100 VB    0.4057 2681.40063  101.04179  27.1492
   2  20.184 BB    0.4929 2245.94702   69.60684  22.7402
   3  23.018 BV    0.5833 2674.12915   70.34232  27.0756
   4  24.560 VB    0.6242 2275.05908   55.46027  23.0350
```



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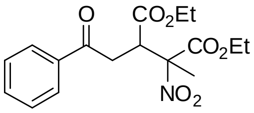
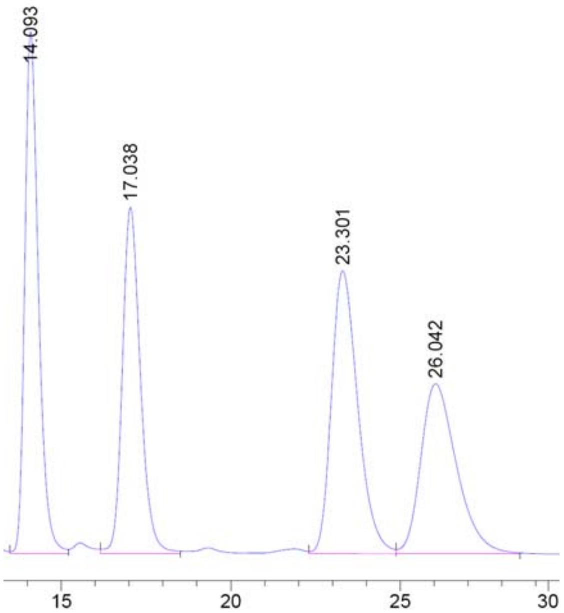
Peak RetTime Type  Width      Area       Height      Area
  #   [min]        [min]  mAU     *s   [mAU    ]       %
----|-------|----|-------|----------|----------|--------|
   1  15.883 BB    0.4043 2394.10742   89.78238  64.0028
   2  19.971 BV    0.4963 1279.00610   39.28443  34.1923
   3  22.979 BV    0.5895   41.61099    1.08659   1.1124
   4  24.478 VB    0.6091   25.90203 5.95825e-1   0.6925
```

5.02 (m, 1H), 4.24-4.17 (m, 2H), 3.82-3.79 (m, 1H), 3.67-3.56 (m, 2H), 3.29-3.05 (m, 1H), 1.63-1.62 (m, 3H), 1.27-1.23 (m, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ (ppm) 196.5, 170.6, 136.0, 135.9, 133.6, 128.7, 128.1, 128.0, 82.7, 82.3, 61.7, 44.3, 43.7, 36.0, 16.8, 13.9; *Anal. Calcd.* for $C_{14}H_{17}NO_5$: C, 60.21; H, 6.14; N, 5.02; Found: C, 60.27; H, 6.08; N, 4.96; $[\alpha]_D^{25}$ = 7.2 (c = 2.4, $CHCl_3$); the enantiomeric excess was determined by chiral HPLC (Chiralpak OJ column: hexane/2-propanol = 80/20, 1 mL/min, 254 nm, $t_{major}$ = 15.88 min, $t_{minor}$ = 22.98 min and $t_{major}$ = 19.97 min, $t_{minor}$ = 24.48 min.)



**Diethyl 2-methyl-2-nitro-3-(2-oxo-2-phenylethyl)succinate (3t).** Prepared according to the general procedure from **1a** (0.25 mmol), **2c** (1.00 mmol), **I** (0.0125 mmol) and xylenes (0.5 mL) at 25 °C for 4 h to provide the title compound as a colorless oil (99% yield, d.r. = 82 : 18, 68 and 92% ee). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 7.96 (d, $J$ = 7.2 Hz, 2H), 7.59 (t, $J$ = 7.2 Hz, 1H), 7.48 (t, $J$ = 7.2 Hz, 2H), 4.31-4.24 (m, 4H), 4.17-4.14 (m, 2H), 3.71-3.66 (m, 1H), 3.25 (d, $J$ = 17.4 Hz, 1H), 1.95 (s, 3H), 1.32-1.29 (m, 3H), 1.23-1.21 (m, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ (ppm) 196.3, 169.8, 165.9,135.9, 133.5, 128.6, 128.0, 127.9, 92.8, 63.3, 61.8, 45.7, 37.1, 20.2, 13.8, 13.6; *Anal. Calcd.* for $C_{17}H_{21}NO_7$: C, 58.11; H, 6.02; N, 3.99; Found: C, 58.15; H, 6.17; N, 3.89; the enantiomeric excess was determined by chiral HPLC (Chiralpak OJ column: hexane/2-propanol = 80/20, 1 mL/min, 254 nm, $t_{minor}$ = 14.69 min, $t_{major}$ = 24.65 min, and $t_{minor}$ = 17.95 min, $t_{major}$ = 28.00 min.)



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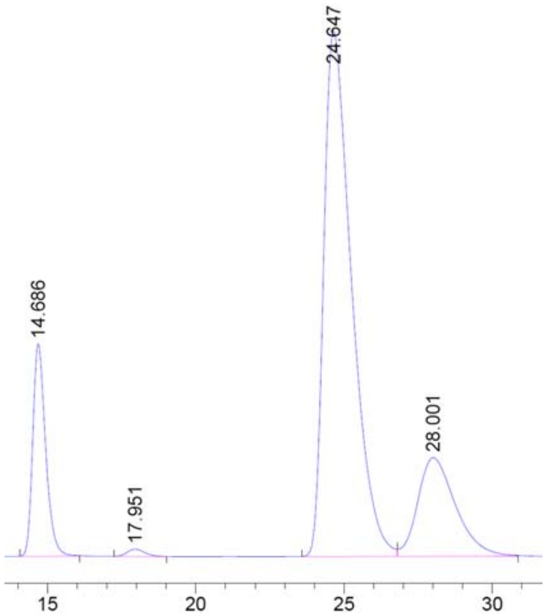
   1  14.093 VV    0.4296 1254.71460   44.67906  26.5211
   2  17.038 VB    0.5650 1095.34521   29.64609  23.1525
   3  23.301 VV    0.8363 1311.34033   24.19097  27.7180
   4  26.042 VB    1.1121 1069.60718   14.58085  22.6084
```



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Peak RetTime Type  Width     Area      Height     Area
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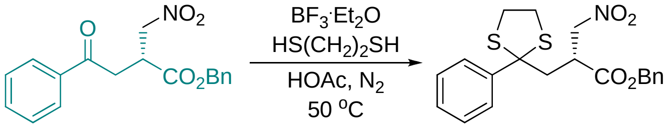
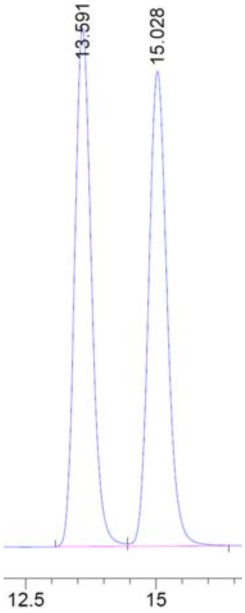
----|-------|----|-------|----------|----------|--------|
   1  14.686 BB    0.4647  953.74664   31.43013  12.9667
   2  17.951 BB    0.6286   44.86840    1.09033   0.6100
   3  24.647 BV    0.9874 5062.63428   77.68647  68.8293
   4  28.001 VB    1.3322 1294.09692   14.58433  17.5940
```

## 4. Synthesis of functionalized β$^2$-amino acid derivatives



**3d**: 96% ee **5**: 81%, 96% ee

**(*R*)-Benzyl 3-nitro-2-[(2-phenyl-1,3-dithiolan-2-yl)methyl] propanoate (5).** To an oven-dried three-necked flash equipped with a condenser was sequentially added (*R*)-benzyl 2-(nitromethyl)-4-*oxo*-4-phenylbutanoate (**3d**, 1.10 g), 1,2-ethanedithiol (1.5 mL), and HOAc (8.0 mL) was added $BF_3.Et_2O$ (1.5 mL) under nitrogen at room temperature. The mixture was then stirred at 50 °C under nitrogen for 48 h. Then HOAc was removed under high vacuum at 40 °C and the residue was purified by flash column chromatography to afford **5** (PE/EtOAc = 7/1, 1.10 g, 81%, 96% ee) as a pale yellow oil. $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 7.65 (d, $J$ = 7.2 Hz, 2H), 7.38-7.34 (m, 3H), 7.33-7.30 (m, 4H), 7.27-7.24 (m, 1H), 5.08 (q, $J$ = 12.0 Hz, 2H),4.56 (ABX, $J_{AB}$ = 14.4 Hz, $J_{AX}$ = 7.8 Hz, $J_{BX}$ = 4.2 Hz, 1H), 4.49 (ABX, $J_{AB}$ = 14.4 Hz, $J_{AX}$ = 7.8 Hz, $J_{BX}$ = 4.2 Hz, 1H), 3.39-3.33 (m, 3H), 3.28-3.25 (m, 2H), 2.99 (ABX, $J_{AB}$ = 15.0 Hz, $J_{AX}$ = $J_{BX}$ = 5.4 Hz, 1H), 2.39 (ABX, $J_{AB}$ = 15.0 Hz, $J_{AX}$ = $J_{BX}$ = 5.4 Hz, 1H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ (ppm) 171.41, 143.6, 135.0, 128.4, 128.3, 128.1, 127.6, 126.8, 75.6, 72.9, 67.3, 43.5, 41.9, 39.5, 39.2; MS (EI) *m/z* 403 ($M^+$); *Anal. Calcd.* for $C_{20}H_{21}NO_4S_2$: C, 59.53; H, 5.25; N, 3.47; Found: C, 59.61; H, 5.23; N, 3.40; the enantiomeric excess was determined by chiral HPLC (Chiralpak AD column: hexane/2-propanol = 80/20, 1 mL/min, 210 nm, $t_{minor}$ = 13.53 min, $t_{major}$ = 14.93 min.)



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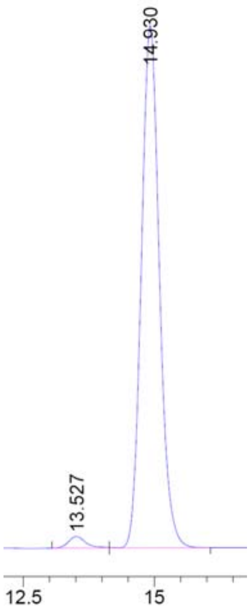
   1  13.591 BV    0.3479 1.44979e4  649.10455  49.8901
   2  15.028 VB    0.3794 1.45618e4  593.56940  50.1099
```



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RetTime Type  Width     Area      Height     Area
 [min]        [min]  mAU    *s   [mAU    ]     %
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 13.527 BV    0.3992  428.60034   16.34169   2.0882
 14.930 VB    0.3985 2.00963e4  767.92773  97.9118
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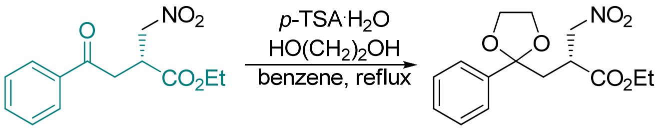
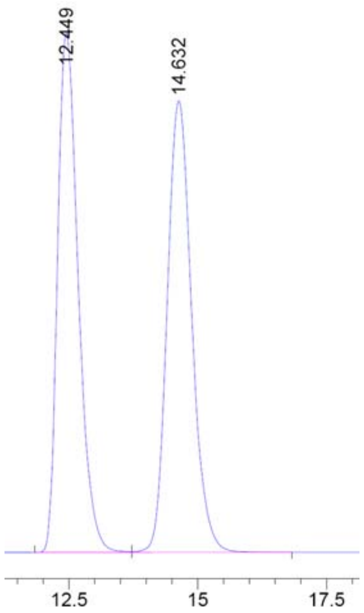


**3a**: 96% ee

**4**: 90%, 97% ee

**(*R*)-Ethyl 3-nitro-2-((2-phenyl-1,3-dioxolan-2-yl)methyl)propanoate (4).** To an oven-dried three-necked flash equipped with a water separator was sequentially charged with (*R*)-ethyl 2-(nitromethyl)-4-*oxo*-4-phenylbutanoate (**3a**, 0.56 g), benzene (25 mL) and $p$-TSA·$H_2O$ (80 mg). The mixture was then heated to reflux under nitrogen for 24 h. After cooling, the reaction system was diluted with ethyl acetate (50 mL), washed with sat. $NaHCO_3$ and dried over $MgSO_4$. Suction filtration and concentration afforded the residue, which was purified by flash column chromatography to obtain the desired product **4** (PE/EtOAc = 7/1, 0.56 g, 94%, 97% ee) as a colorless oil. $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 7.44 (br, 1H), 7.43 (br, 1H), 7.37-7.32 (m, 3H), 4.82 (ABX, $J_{AB}$ = 14.4 Hz, $J_{AX}$ = 9.0 Hz, $J_{BX}$ = 4.2 Hz, 1H), 4.74 (ABX, $J_{AB}$ = 14.4 Hz, $J_{AX}$ = 9.0 Hz, $J_{BX}$ = 4.2 Hz, 1H), 4.22-4.13 (m, 2H), 4.06-3.98 (m, 2H), 3.79-3.71 (m, 2H), 3.44-3.40 (m, 1H), 2.44 (ABX, $J_{AB}$ = 15.0 Hz, $J_{AX}$ = 4.8 Hz, $J_{BX}$ = 7.8 Hz, 1H), 2.16 (ABX, $J_{AB}$ = 15.0 Hz, $J_{AX}$ = 4.8 Hz, $J_{BX}$ = 7.8 Hz, 1H), 1.27 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ (ppm) 171.9, 141.3, 128.3, 125.4, 125.3, 75.1, 61.3, 38.8, 38.6, 13.9; MS (EI) *m/z* 413 ($M^+$); *Anal. Calcd.* for $C_{23}H_{27}NO_6$: C, 66.81; H, 6.58; N, 3.39; Found: C, 66.89; H, 6.38; N, 3.27; the enantiomeric excess was determined by chiral HPLC (Chiralpak OD column: hexane/2-propanol = 90/10, 1 mL/min, 210 nm, $t_{minor}$ = 12.48 min, $t_{major}$ = 14.63 min.)



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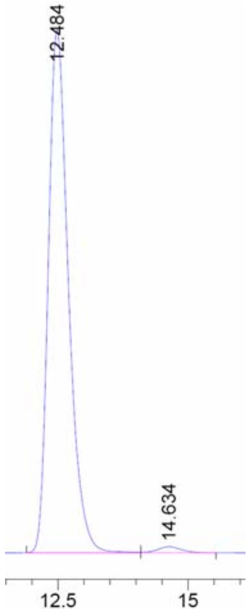
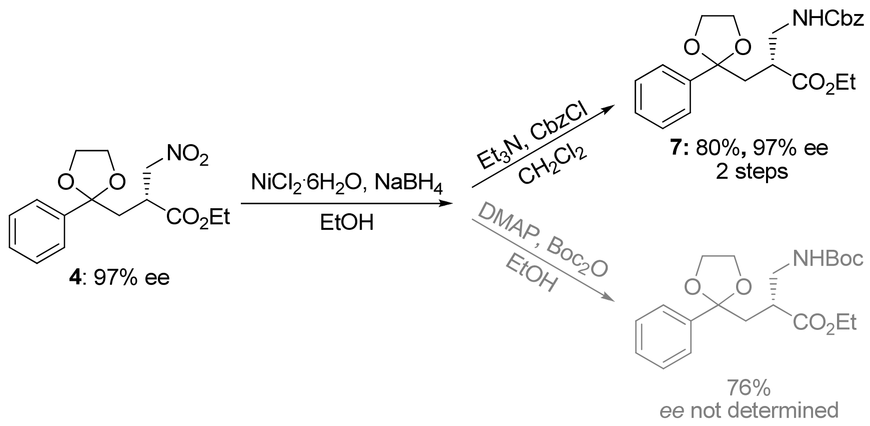
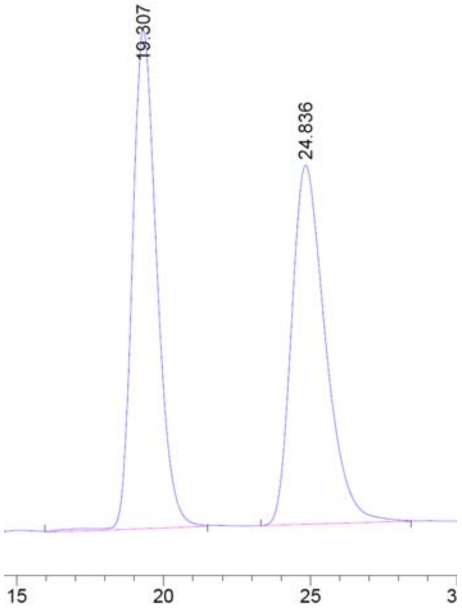
|---|---|---|---|---|---|---|
| 1 | 12.449 | VV | 0.4330 | 3.51122e4 | 1259.27332 | 49.2623 |
| 2 | 14.632 | VB | 0.5134 | 3.61638e4 | 1094.99072 | 50.7377 |



| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 12.484 | BV | 0.4121 | 1.27289e4 | 474.37021 | 98.6026 |
| 2 | 14.634 | VB | 0.4987 | 180.39078 | 5.46495 | 1.3974 |



**(*R*)-Ethyl 3-(benzyloxycarbonylamino)-2-((2-phenyl-1,3-dioxolan-2-yl)methyl) propanoate (7).** $NaBH_4$ (1.35 g) was added slowly in portionwise to a stirred solution of **4** (1.10 g) and $NiCl_2$•$6H_2O$ (0.98 g) in EtOH (20 mL) at 0 °C. The reaction was stirred at 0 °C for 0.5 h before quenched with saturated aqueous $NH_4Cl$ (50 mL). The mixture was diluted with $CH_2Cl_2$ (40 mL), extracted with $CH_2Cl_2$ (3 × 40 mL), dried over $MgSO_4$. Suction filtration over Celite and concetration *in vacuo* afforded the crude amine, which was dissolved in 20 mL of freshly distilled $CH_2Cl_2$. $Et_3N$ (0.7 mL) was added and the mixture was cooled by an ice-bath for 15 min. Then benzyl chloroformate (0.55 mL) was added dropwise via syringe over 15 min. 3 h later, the reaction was quenched with saturated aqueous $NH_4Cl$ and extracted with $CH_2Cl_2$. The combined organic phase was dried over $MgSO_4$. The residue obtained after filtration and concentration was subjected to flash chromatography to obtain the desired product **7** as a colorless oil (PE/EtOAc = 3/1, 1.07 g, 80%, 97% ee). $^1H$ NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 7.44 (d, $J$ = 7.2 Hz, 2H), 7.37-7.24 (m, 8H), 5.11-5.06 (m, 3H), 4.16-4.04 (m, 2H), 4.03-3.95 (m, 2H), 3.74 (br, 2H), 3.50-3.37 (m, 2H), 2.87 (br, 1H), 2.40 (ABX, $J_{AB}$ = 14.4 Hz, $J_{AX}$ = 7.8 Hz, $J_{BX}$ = 4.2 Hz, 1H), 2.03 (ABX, $J_{AB}$ = 14.4 Hz, $J_{AX}$ = 7.8 Hz, $J_{BX}$ = 4.2 Hz, 1H), 1.25 (t, $J$ = 7.2 Hz, 3H); $^{13}C$ NMR (150 MHz, $CDCl_3$) $\delta$ (ppm) 173.9,



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  2  24.836 PB    1.2541 1.46150e4  182.59918  49.7810
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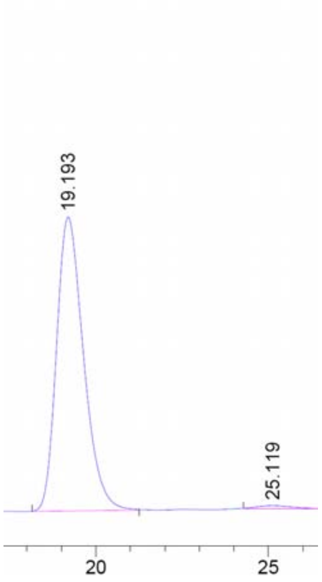

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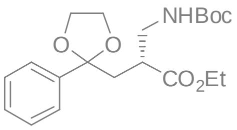
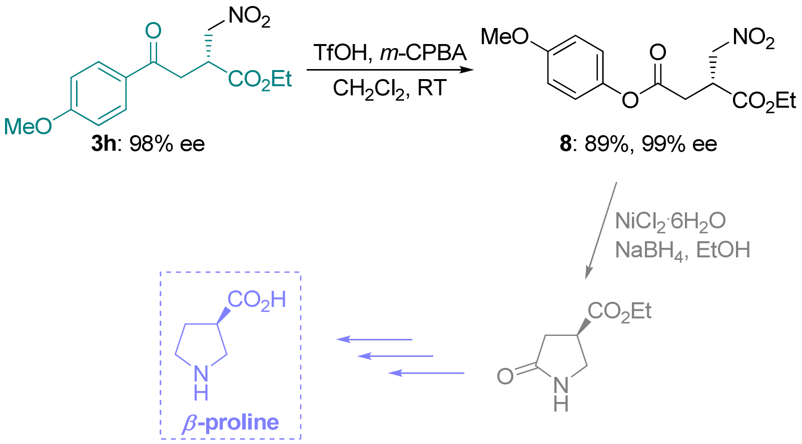
  1  19.193 BB    0.8390 1.37918e4  253.31885  98.6047
  2  25.119 BB    0.9870  195.16556    2.69664   1.3953
```

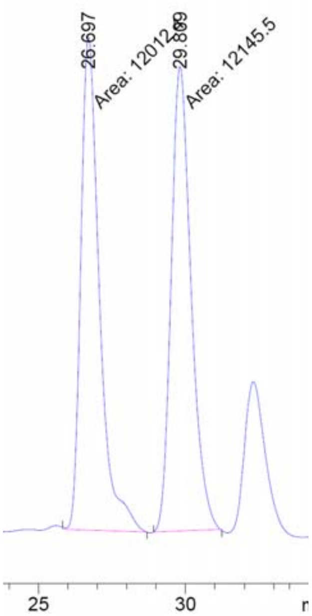
155.8, 141.8, 136.1, 127.8, 127.7, 127.5, 127.4, 127.3, 127.2, 124.9, 108.6, 65.7, 63.9, 63.8, 59.8, 59.7, 42.5, 40.6, 39.3, 13.5; MS (EI) *m/z* 413 ($M^+$); $[\alpha]_D^{20}$ = -5.1 (c = 5.0, $CH_2Cl_2$); *Anal. Calcd.* for $C_{23}H_{27}NO_6$: C, 66.81; H, 6.58; N, 3.39; Found: C, 66.89; H, 6.38; N, 3.27; the enantiomeric excess was determined by chiral HPLC (Chiralpak OD column: hexane/2-propanol = 90/10, 1 mL/min, 210 nm, $t_{major}$ = 19.19 min, $t_{minor}$ = 25.12 min.)



**(*R*)-Ethyl 3-(*tert*-butoxycarbonylamino)-2-((2-phenyl-1,3-dioxolan-2-yl)methyl)propanoate.** $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 7.45 (d, $J$ = 7.2 Hz, 2H), 7.34-7.28 (m, 3H), 4.82 (br, 1H), 4.17-4.09 (m, 2H), 4.05-3.96 (m, 2H), 3.74 (br, 2H), 3.39-3.29 (m, 2H), 2.83 (br, 1H), 2.40 (ABX, $J_{AB}$ = 15.0 Hz, $J_{AX}$ = 9.0 Hz, $J_{BX}$ = 4.2 Hz, 1H), 2.01 (ABX, $J_{AB}$ = 15.0 Hz, $J_{AX}$ = 9.0 Hz, $J_{BX}$ = 4.2 Hz, 1H),1.42 (s, 9H), 1.27 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ (ppm) 174.2, 155.3, 141.9, 127.7, 127.6, 125.1, 108.9, 78.5, 64.1, 64.0, 59.9, 42.3, 40.9, 39.5, 27.9, 13.8; MS (EI) *m/z* 379 ($M^+$); *Anal. Calcd.* for $C_{20}H_{29}NO_6$: C, 63.31; H, 7.70; N, 3.69; Found: C, 63.26; H, 7.75; N, 3.60;



**(*R*)-1-Ethyl 4-(4-methoxyphenyl) 2-(nitromethyl)succinate (8).**[4] To a three-necked flask containing **3h** (1 mmol, 295 mg) were sequentially added dichloromethane (5 mL), TfOH (20 mol%, 30 mg) and *m*-Chloro perbenzoic acid (430 mg, 2.0 equiv., ~80% purity) under nitrogen at RT. The mixture was stirred at RT for 21 h. Then the white solid was remoed by suction filtration and washed with dichloromethane. The organics were removed *in vacuo* and the residue was purified by column chromatography to provide the desired product as a colorless oil (89%, 99% ee). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 7.00 (d, $J$ = 9.0 Hz, 2H), 6.89 (d, $J$ = 9.0 Hz, 2H), 4.88 (ABX, $J_{AB}$ = 14.4 Hz, $J_{AX}$ = 6.0 Hz, $J_{BX}$ = 5.4 Hz, 1H), 4.80 (ABX, $J_{AB}$ = 14.4 Hz, $J_{AX}$ = 6.0 Hz, $J_{BX}$ = 5.4 Hz, 1H), 4.27-4.23 (m, 2H), 3.80 (s, 3H), 3.65-3.59 (m, 1H), 3.10 (ABX, $J_{AB}$ = 17.4 Hz, $J_{AX}$ = 6.0 Hz, $J_{BX}$ = 6.6 Hz, 1H), 2.97 3.10 (ABX, $J_{AB}$ = 17.4 Hz, $J_{AX}$ = 6.0 Hz, $J_{BX}$ = 6.6 Hz, 1H), 1.29 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ (ppm) 169.9, 169.5, 157.1, 143.5, 121.8, 114.1, 74.1, 61.7, 55.1, 38.7, 32.6, 13.6; MS (EI) *m/z* 311 ($M^+$); *Anal. Calcd.* for $C_{14}H_{17}NO_7$: C, 54.02; H, 5.50; N, 4.50; Found: C, 54.12; H, 5.39; N, 4.35; the enantiomeric excess was determined by chiral HPLC (Chiralpak AD column: hexane/2-propanol = 90/10, 1 mL/min, 210 nm, $t_{major}$ = 26.77 min, $t_{minor}$ = 29.89 min.)



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   2  29.809 MM    0.7870 1.21455e4   257.21219  50.2754
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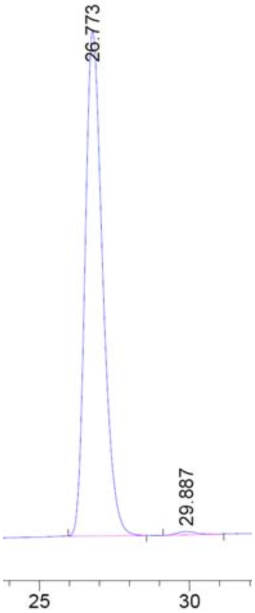

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   2  29.887 PB    0.6643   75.34167    1.66661   0.7348
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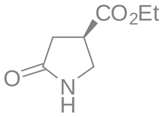

**(*R*)-ethyl 5-oxopyrrolidine-3-carboxylate.** $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ (ppm) 6.90 (br, 1H), 4.20 (q, $J$ = 7.2 Hz, 2H), 3.64-3.62 (m, 2H), 3.35-3.32 (m, 1H), 2.67 (ABX, $J_{AB}$ = 17.4 Hz, $J_{AX}$ = 7.8 Hz, $J_{BX}$ = 9.6 Hz, 1H), 2.58 (ABX, $J_{AB}$ = 17.4 Hz, $J_{AX}$ = 7.8 Hz, $J_{BX}$ = 9.6 Hz, 1H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ (ppm) 176.7, 172.6, 61.3, 44.4, 38.8, 33.1, 14.1; MS (EI) *m/z* 157 ($M^+$); *Anal. Calcd.* for $C_7H_{11}NO_3$: C, 53.49; H, 7.05; N, 8.91; Found: C, 53.57; H, 7.13; N, 8.83;

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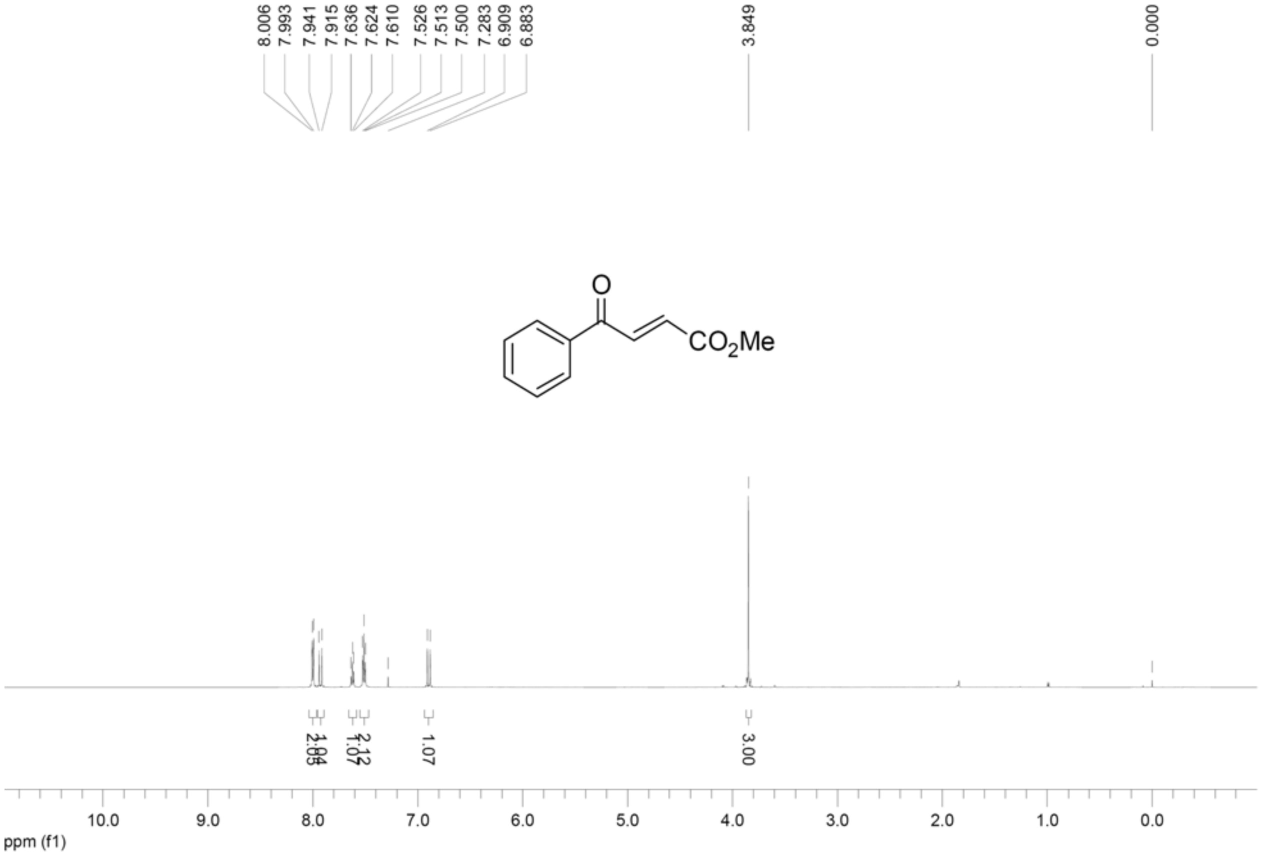
[1] Still, W. C.; Kahn, M.; Mitra, A. J. *J. Org. Chem.* **1978**, *43*, 2923.

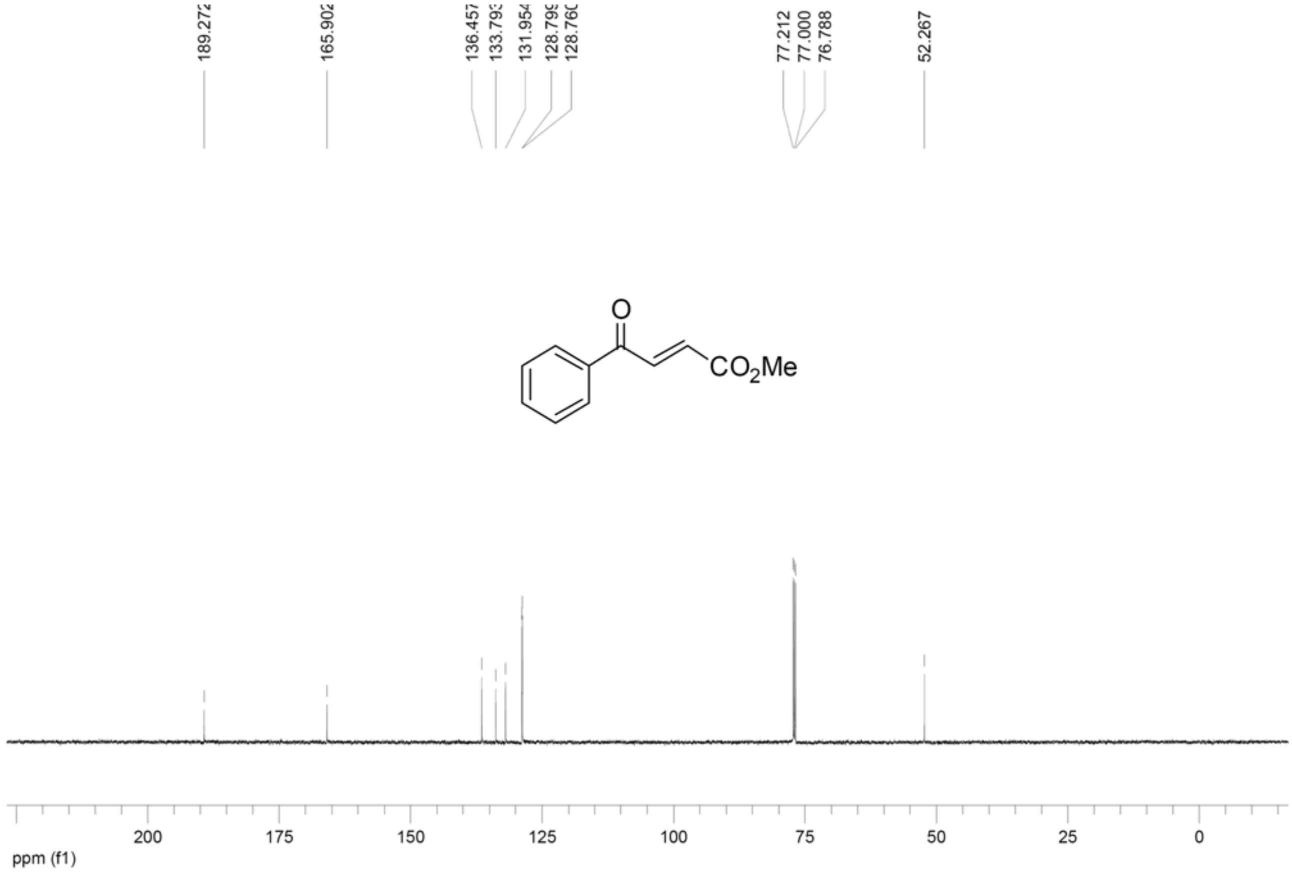
[2] Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals, 4th ed.*; Pergamon Press: Oxford, 1997.

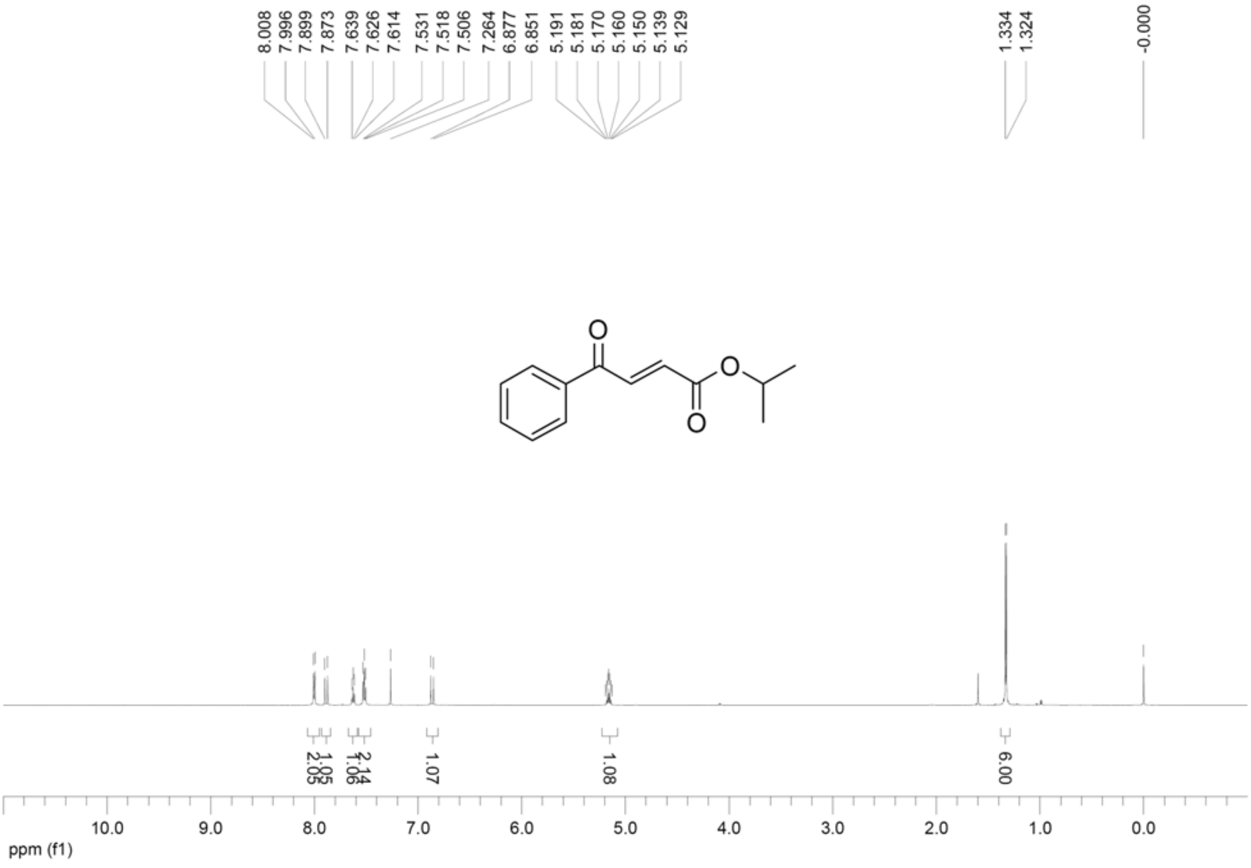
[3] a) Okino, T.; Hoashi, Y.; Takemoto, Y. *J. Am. Chem. Soc.* **2003**, *125*, 12672; b) Li, B.; Jiang, L.; Liu, M.; Chen, Y.; Ding, L.; Wu, Y. *Synlett* **2005**, 603; c) McCooey, S. H.; Connon, S. J. *Angew. Chem. Int. Ed.* **2005**, *44*, 6367; d) Ye, J.; Dixon, D. J.; Hynes, P. S. *Chem. Commun.* **2005**, 4481.

[4] Kotsuki, H.; Arimura, K.; Araki, T.; Shinohara, T. *Synlett* **1999**, 462.

## 5. NMR Spectra of 4-*oxo*-enoates 1b-t, γ-keto esters 3, 4, 5, 7 and 8



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6.851
5.191
5.181
5.170
5.160
5.150
5.139
5.129
1.334
1.324
-0.000
O
O
O
2.05
1.05
1.06
2.14
1.07
1.08
6.00
10.0
9.0
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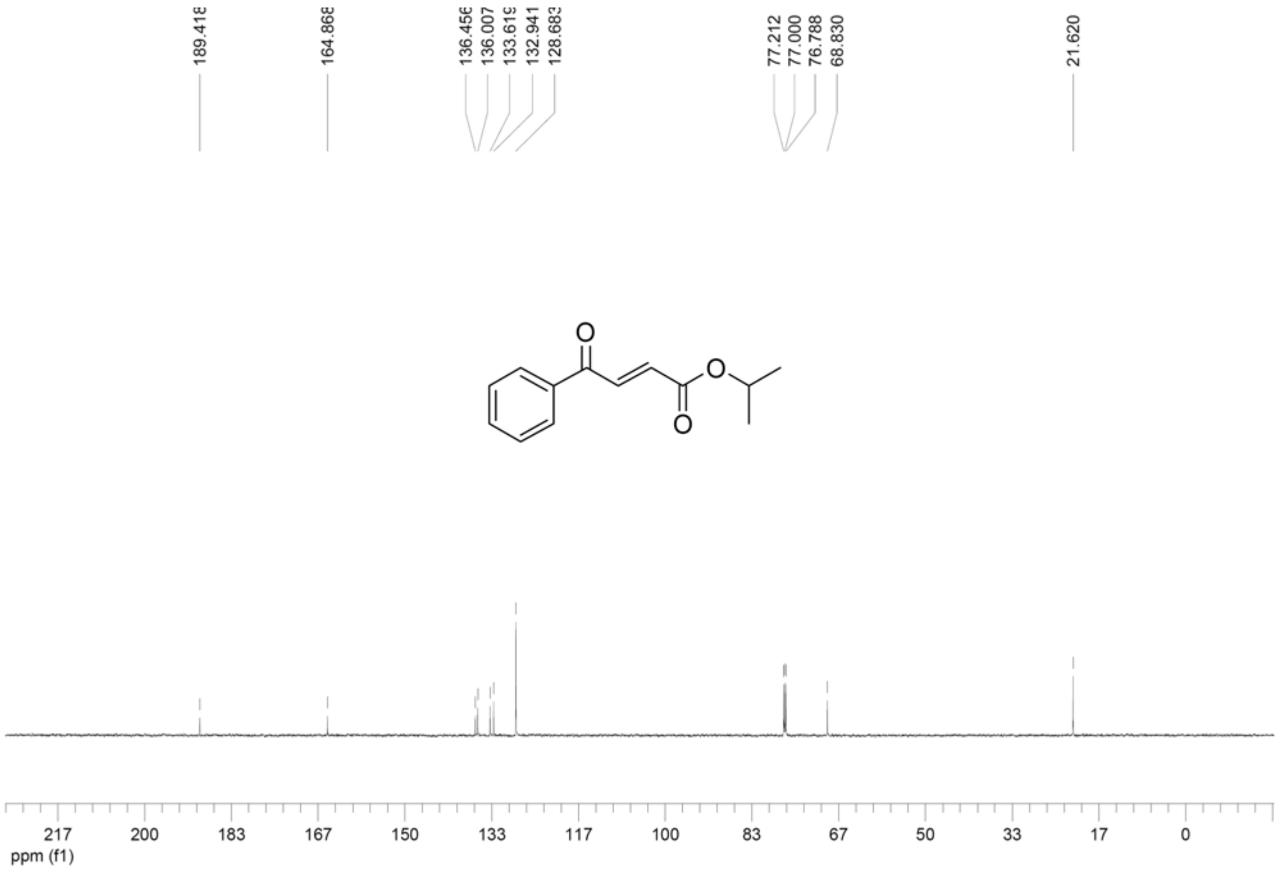
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)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136.007
133.619
132.941
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77.000
76.788
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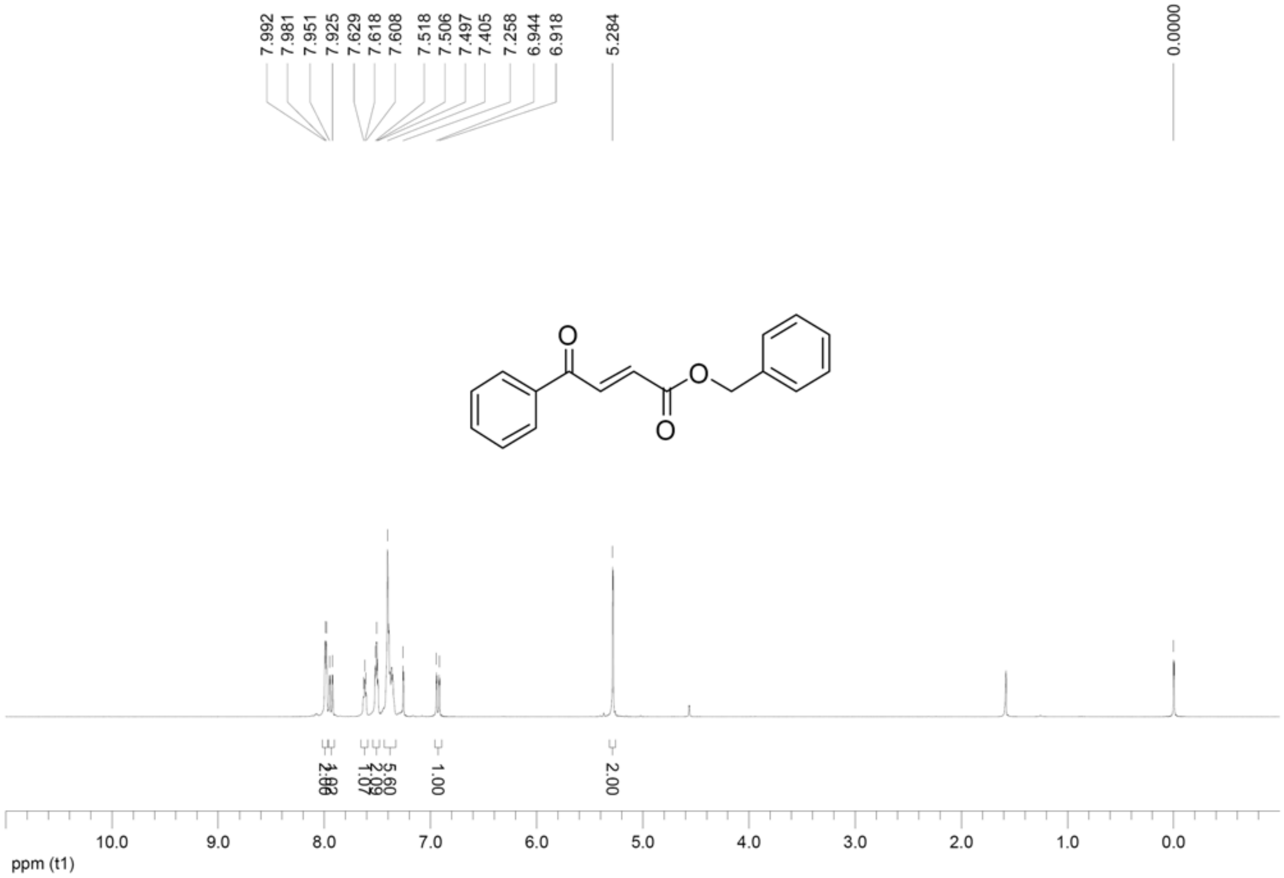
21.620
O
O
O
217
200
183
167
150
133
117
100
83
67
50
33
17
0
ppm (f1)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6.944
6.918
5.284
0.0000
O
O
O
2.06
1.02
1.07
2.09
5.60
1.00
2.00
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7.0
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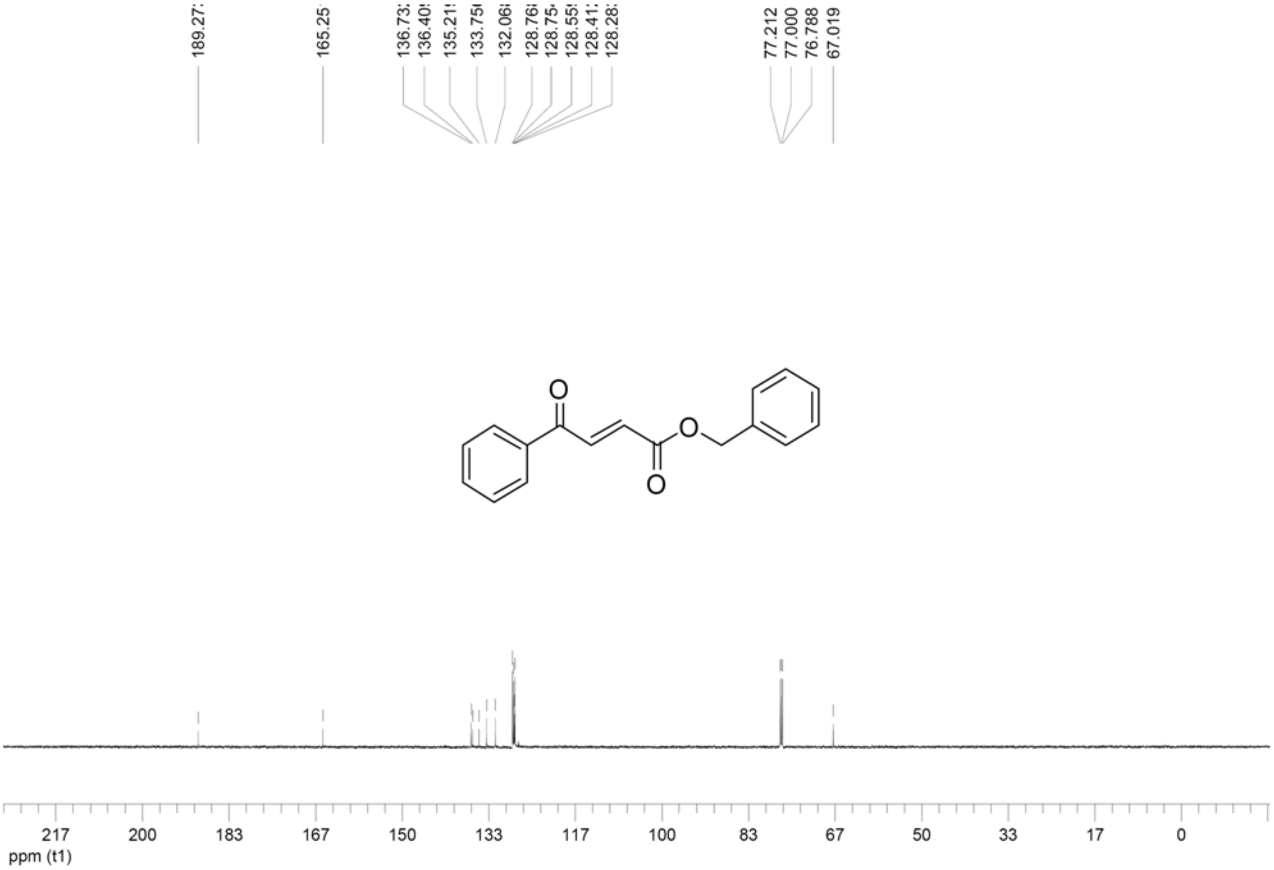
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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132.06
128.76
128.75
128.55
128.41
128.28
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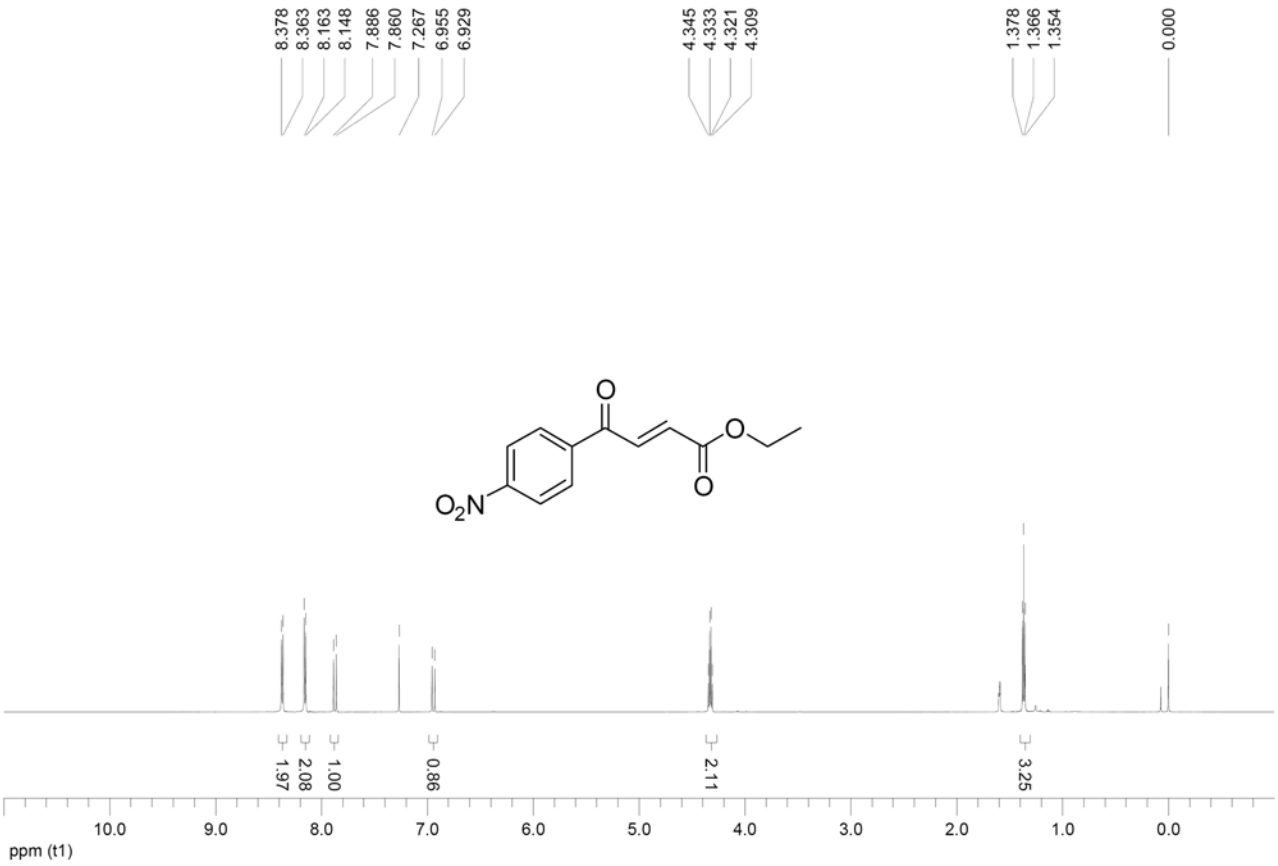
77.000
76.788
67.019
O
O
O
217
200
183
167
150
133
117
100
83
67
50
33
17
0
ppm (t1)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4.309
1.378
1.366
1.354
0.000
O
O
O
$O_2N$
1.97
2.08
1.00
0.86
2.11
3.25
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8.0
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2.0
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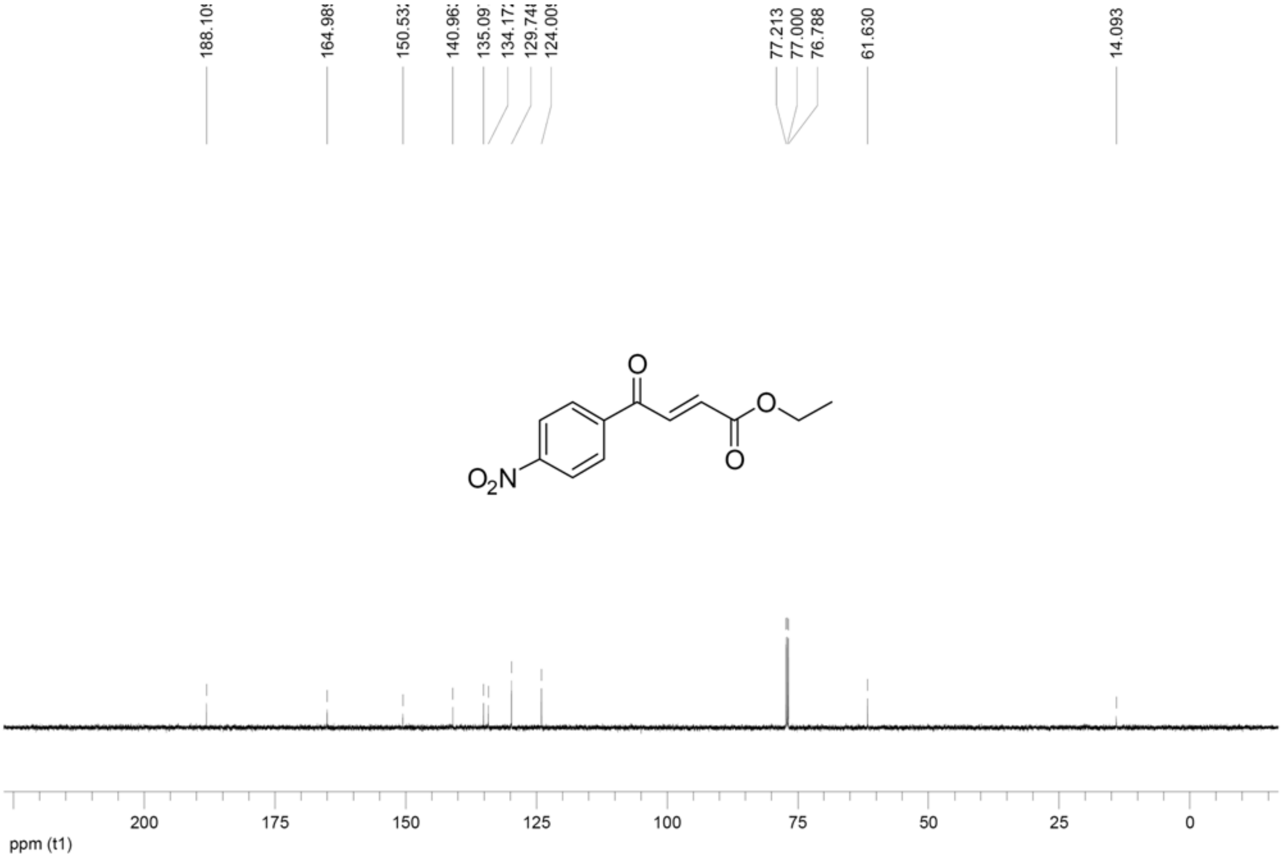
ppm (t1)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135.09
134.17
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124.00
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77.000
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14.093
O
O
O
$O_2N$
200
175
150
125
100
75
50
25
0
ppm (t1)


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8.482
8.340
8.327
7.918
7.892
7.767
7.753
7.740
7.269
6.983
6.957
4.354
4.342
4.330
4.318
1.385
1.373
1.361
0.0000
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$O_2N$
O
O
0.99
1.01
1.02
1.01
1.00
1.00
2.01
3.00
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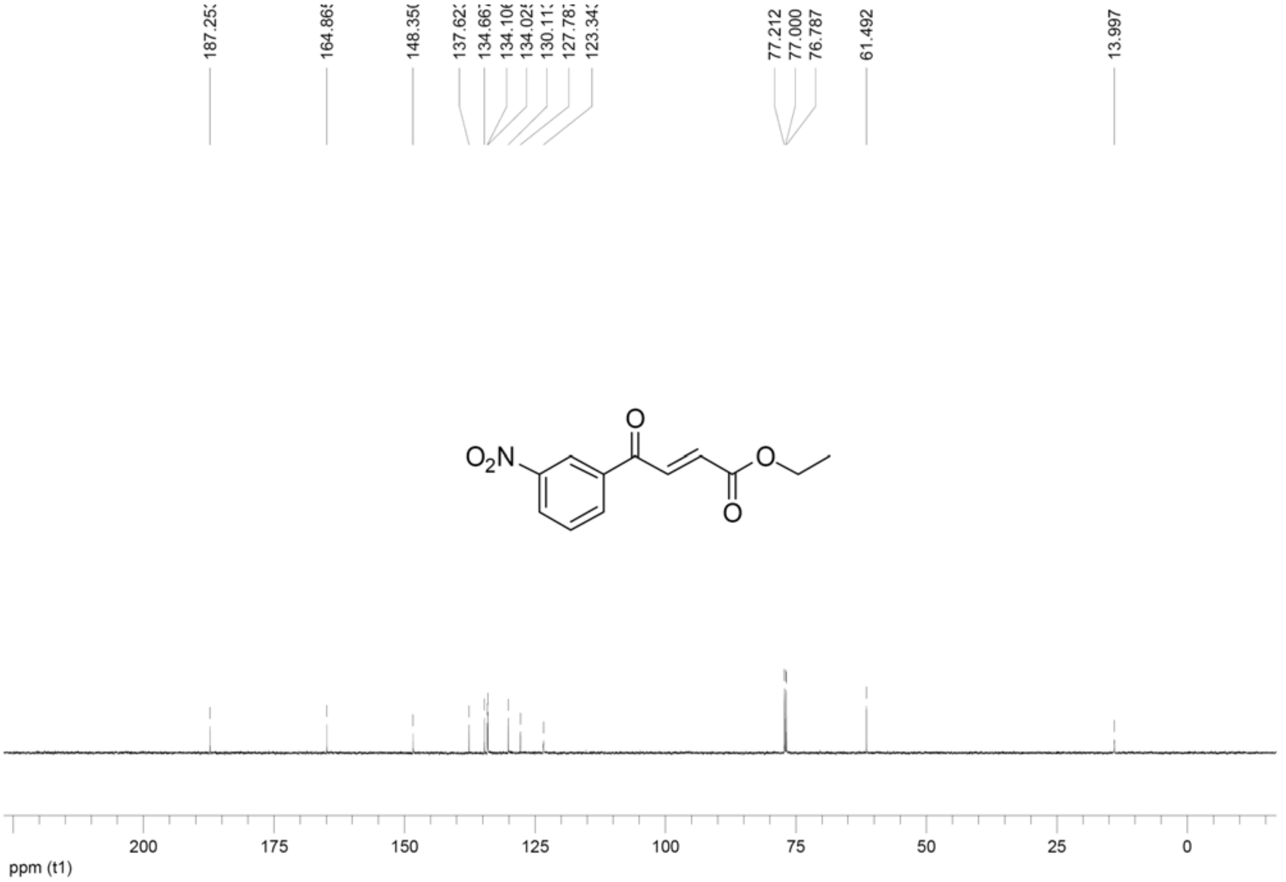
ppm (t1)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76.787
61.492
13.997
O
$O_2N$
O
O
200
175
150
125
100
75
50
25
0
ppm (t1)


8.225
8.211
7.807
7.795
7.782
7.711
7.699
7.687
7.473
7.461
7.321
7.294
7.268
6.382
6.355
4.272
4.260
4.248
4.236
1.322
1.310
1.298
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NO2
O
O
O
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1.07
1.05
0.96
0.95
0.96
1.94
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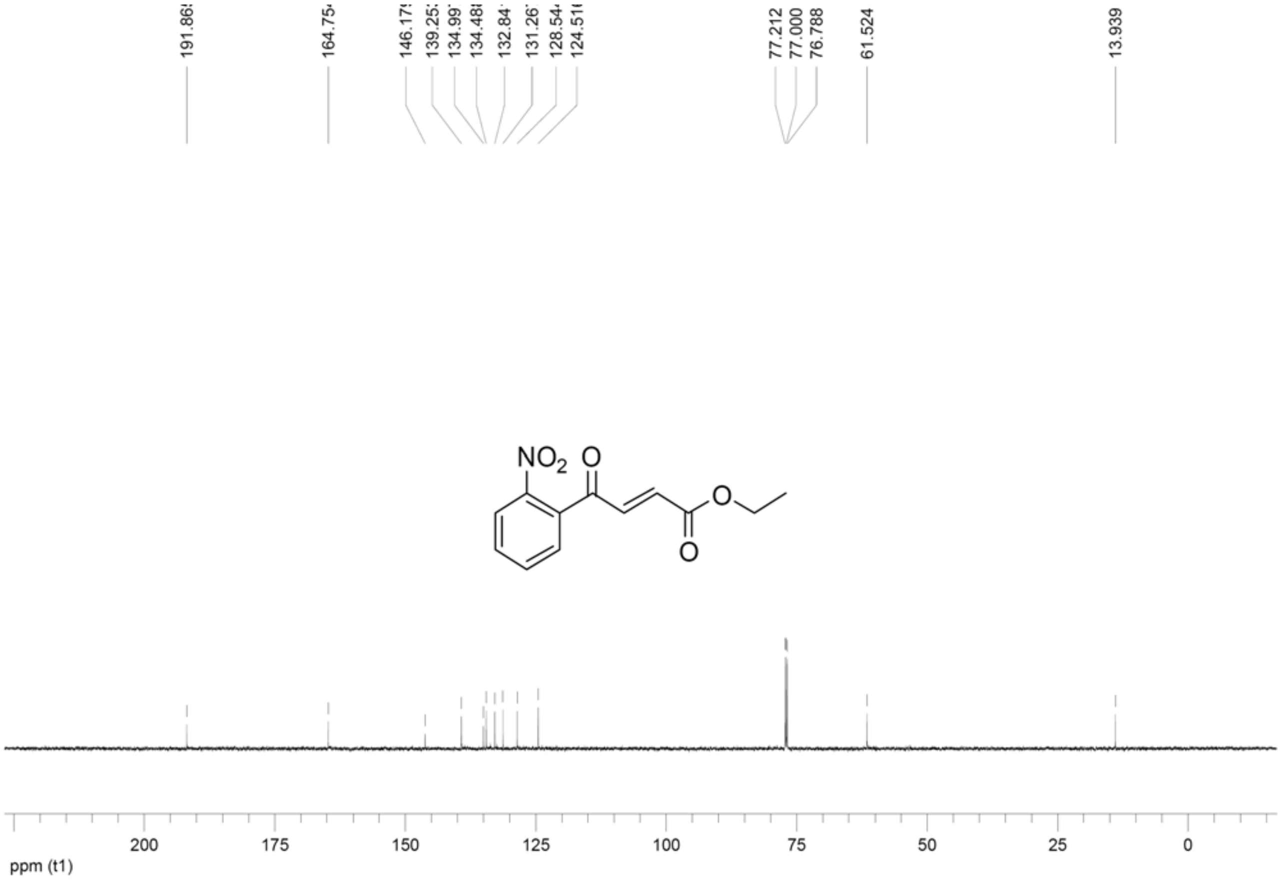
ppm (t1)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61.524
13.939
NO2
O
O
O
200
175
150
125
100
75
50
25
0
ppm (t1)


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8.005
7.935
7.909
7.270
6.992
6.977
6.886
6.860
4.319
4.307
4.295
4.283
3.897
1.364
1.352
1.340
0.000
MeO
O
O
O
1.91
1.00
1.98
0.95
2.01
3.20
3.00
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9.0
8.0
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6.0
5.0
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2.0
1.0
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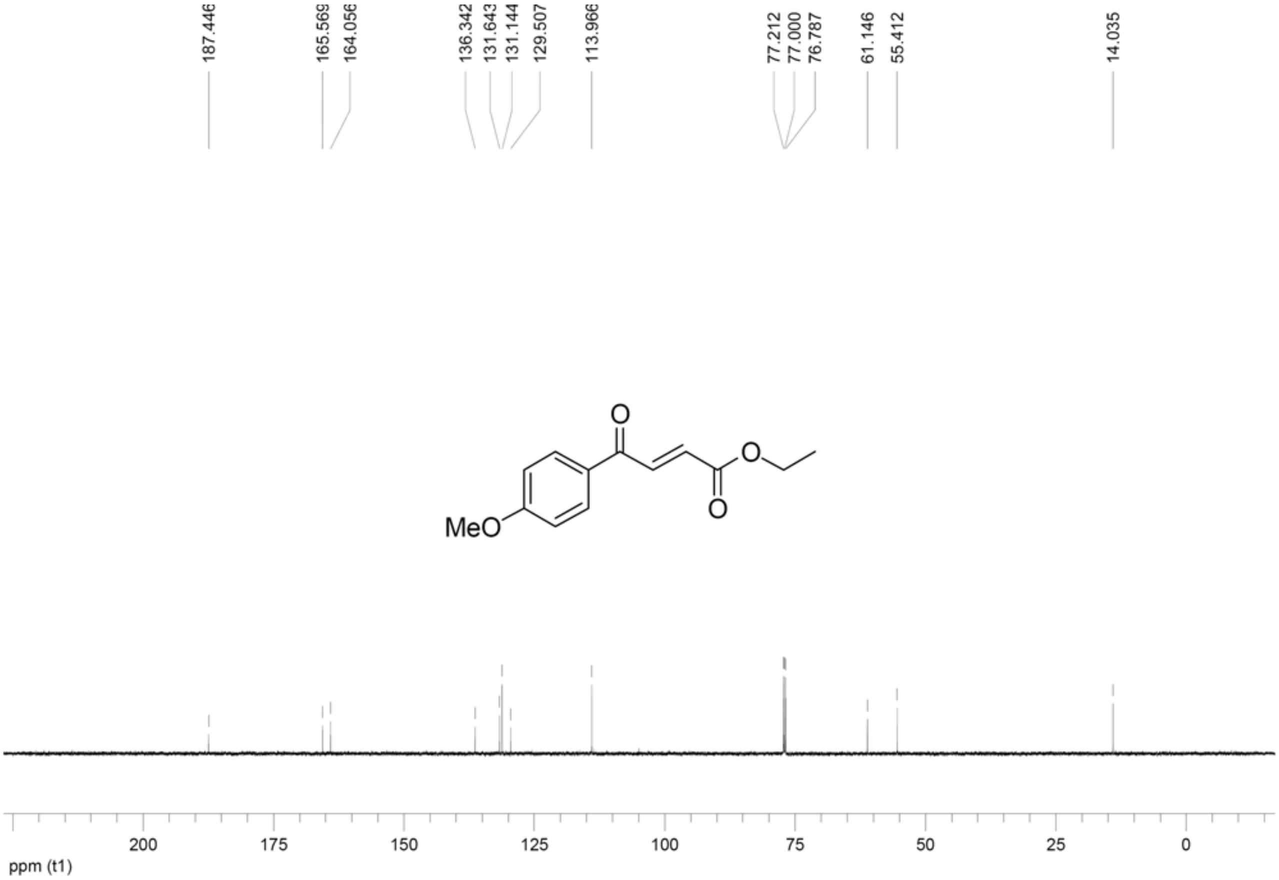
ppm (f1)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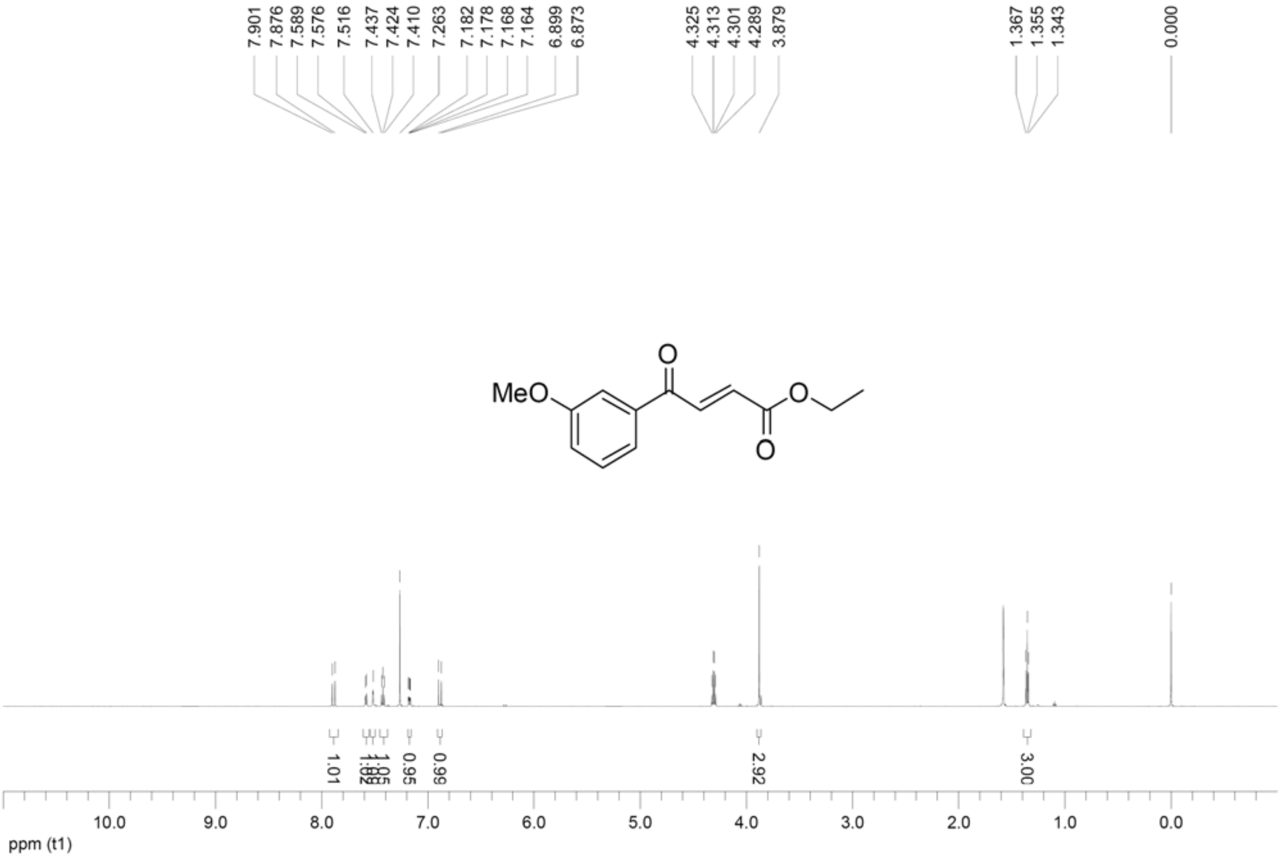
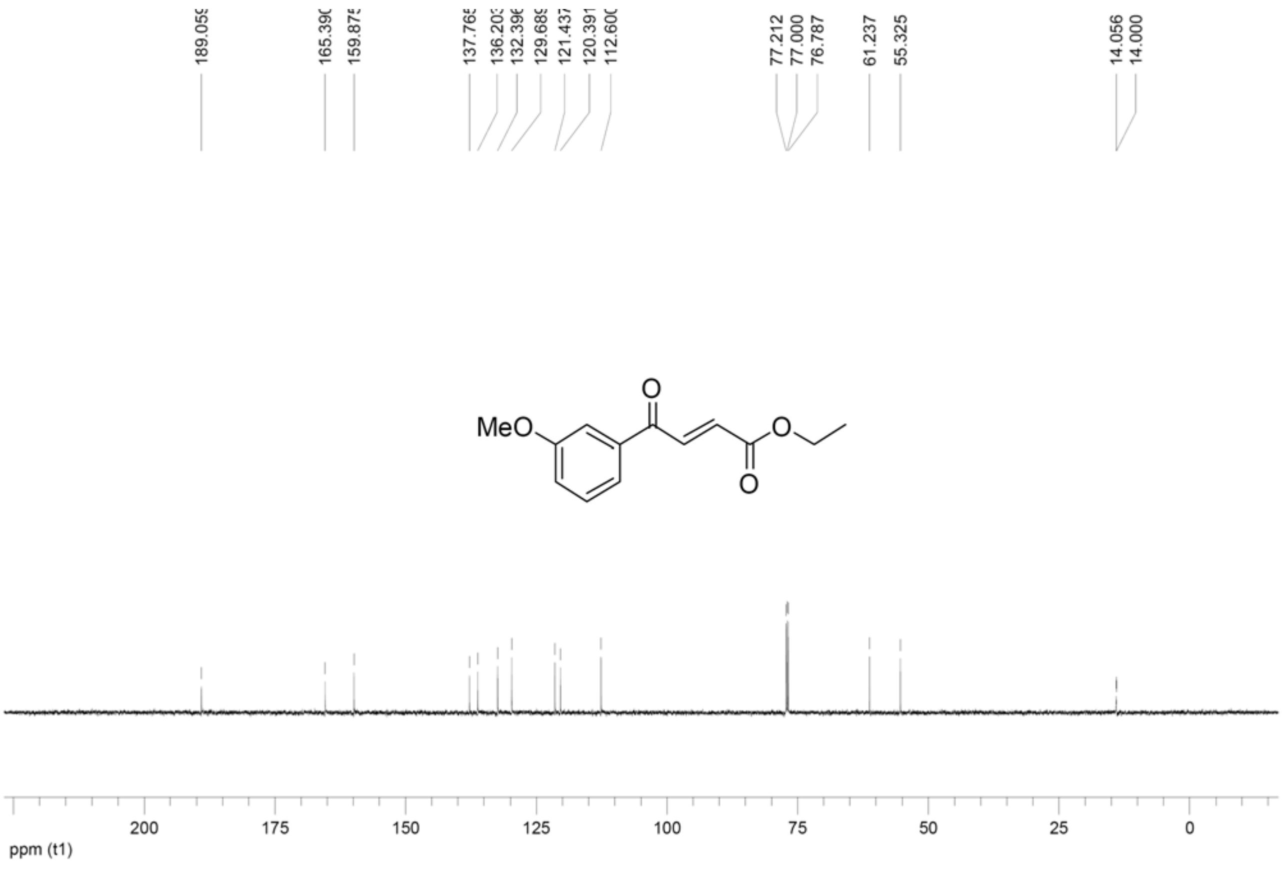
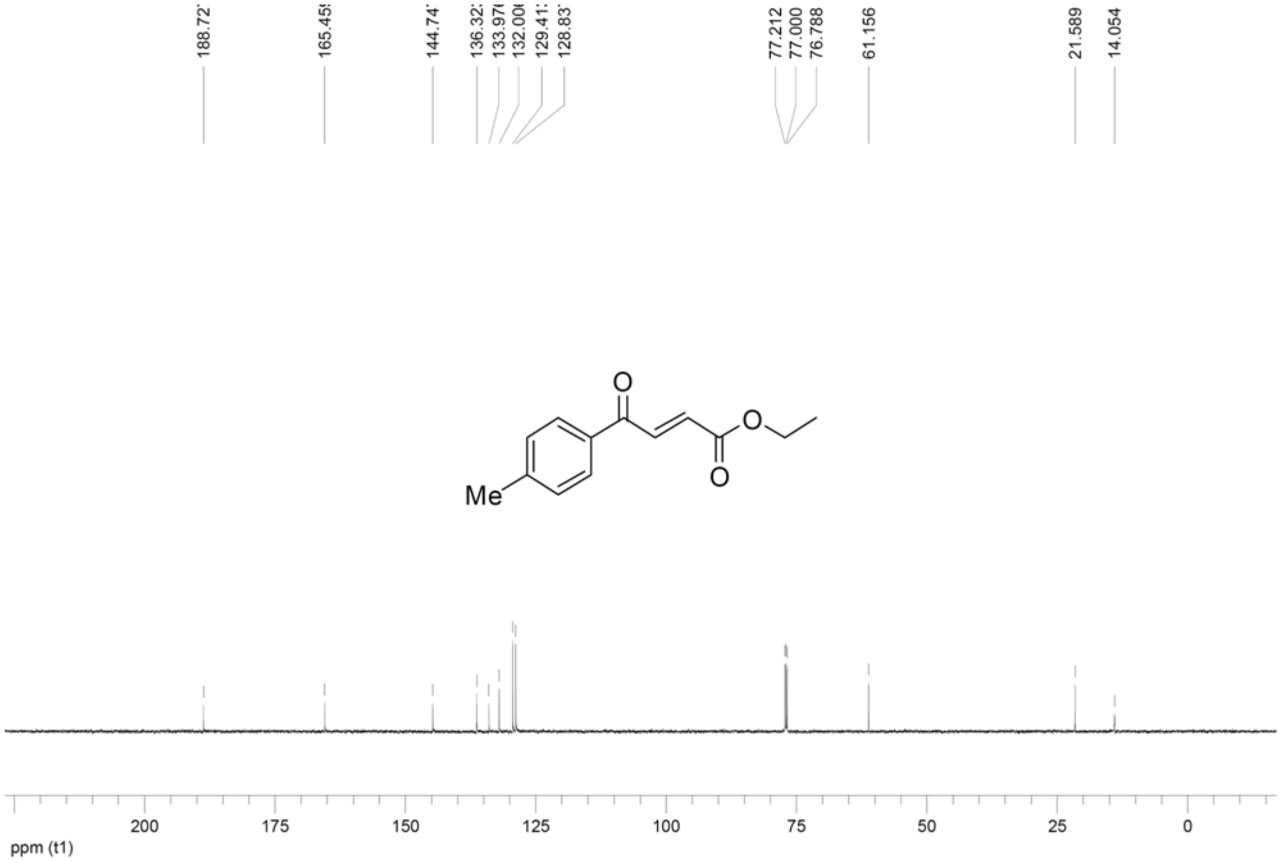
14.035
MeO
O
O
O
200
175
150
125
100
75
50
25
0
ppm (t1)

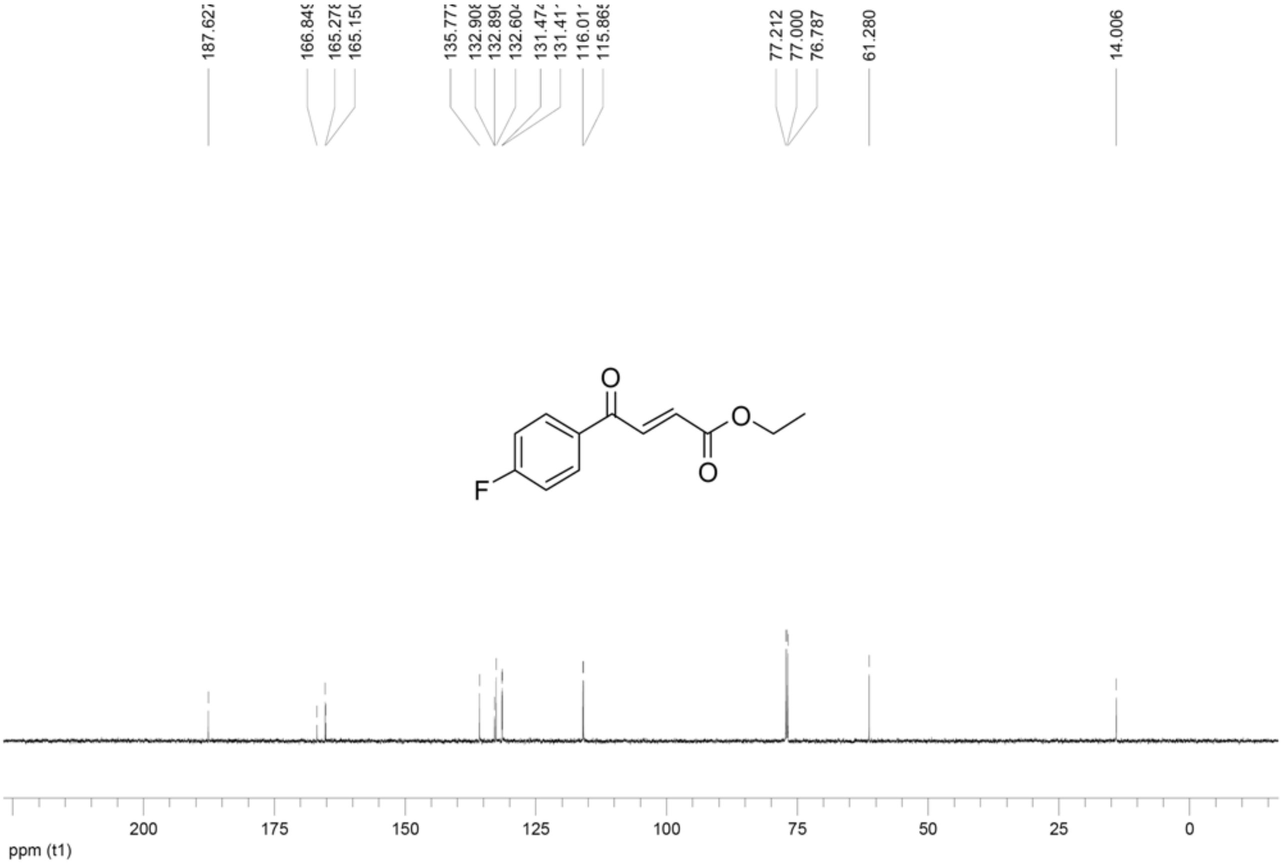

7.901
7.876
7.589
7.576
7.516
7.437
7.424
7.410
7.263
7.182
7.178
7.168
7.164
6.899
6.873
4.325
4.313
4.301
4.289
3.879
1.367
1.355
1.343
0.000
MeO
O
O
O
1.01
1.02
1.05
0.95
0.99
2.92
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

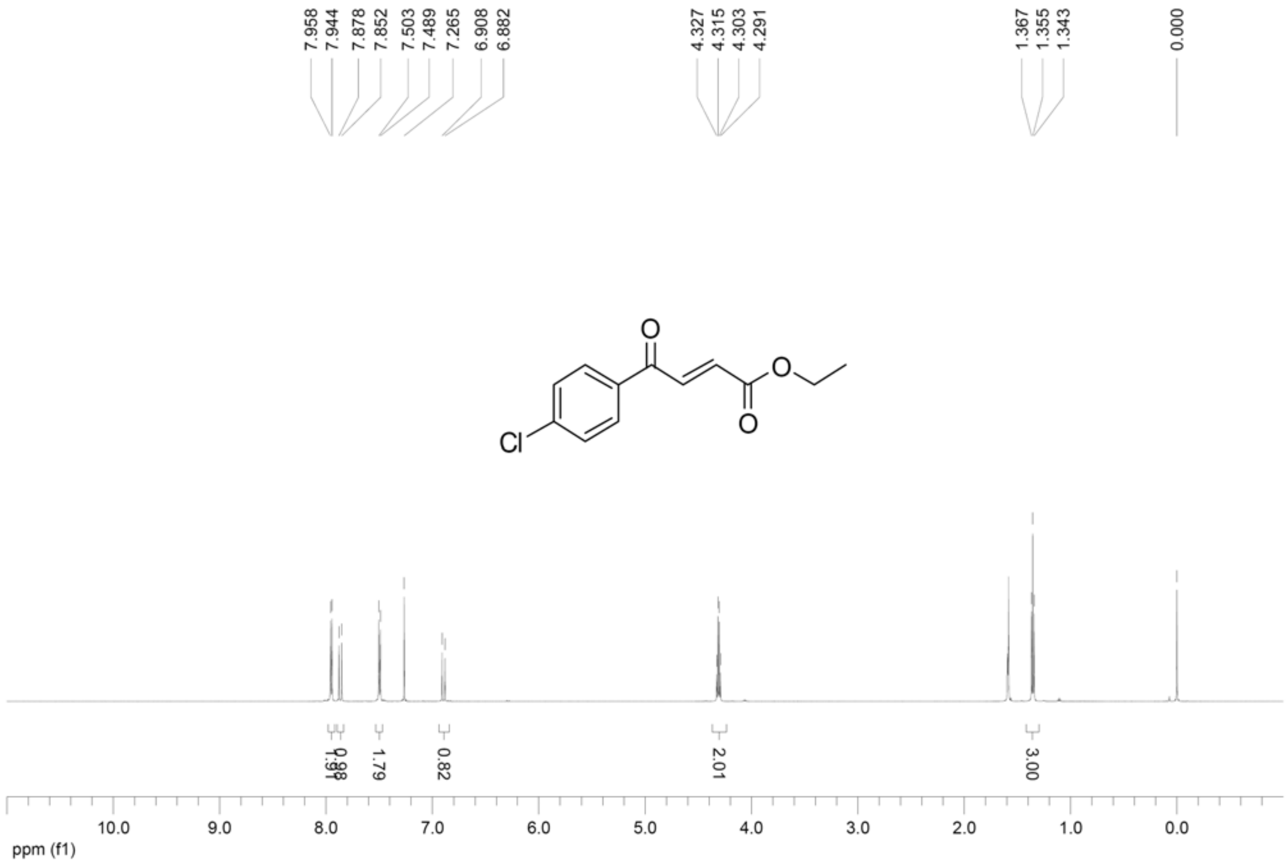

189.059
165.390
159.875
137.765
136.203
132.396
129.689
121.437
120.391
112.600
77.212
77.000
76.787
61.237
55.325
14.056
14.000
MeO
O
O
O
200
175
150
125
100
75
50
25
0
ppm (t1)


7.922
7.919
7.905
7.896
7.317
7.304
7.265
6.888
6.862
4.320
4.308
4.296
4.284
2.439
1.363
1.352
1.340
-0.000
O
O
O
Me
2.82
1.86
0.94
1.97
2.97
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


188.72
165.45
144.74
136.32
133.97
132.00
129.41
128.83
77.212
77.000
76.788
61.156
21.589
14.054
O
O
O
Me
200
175
150
125
100
75
50
25
0
ppm (t1)

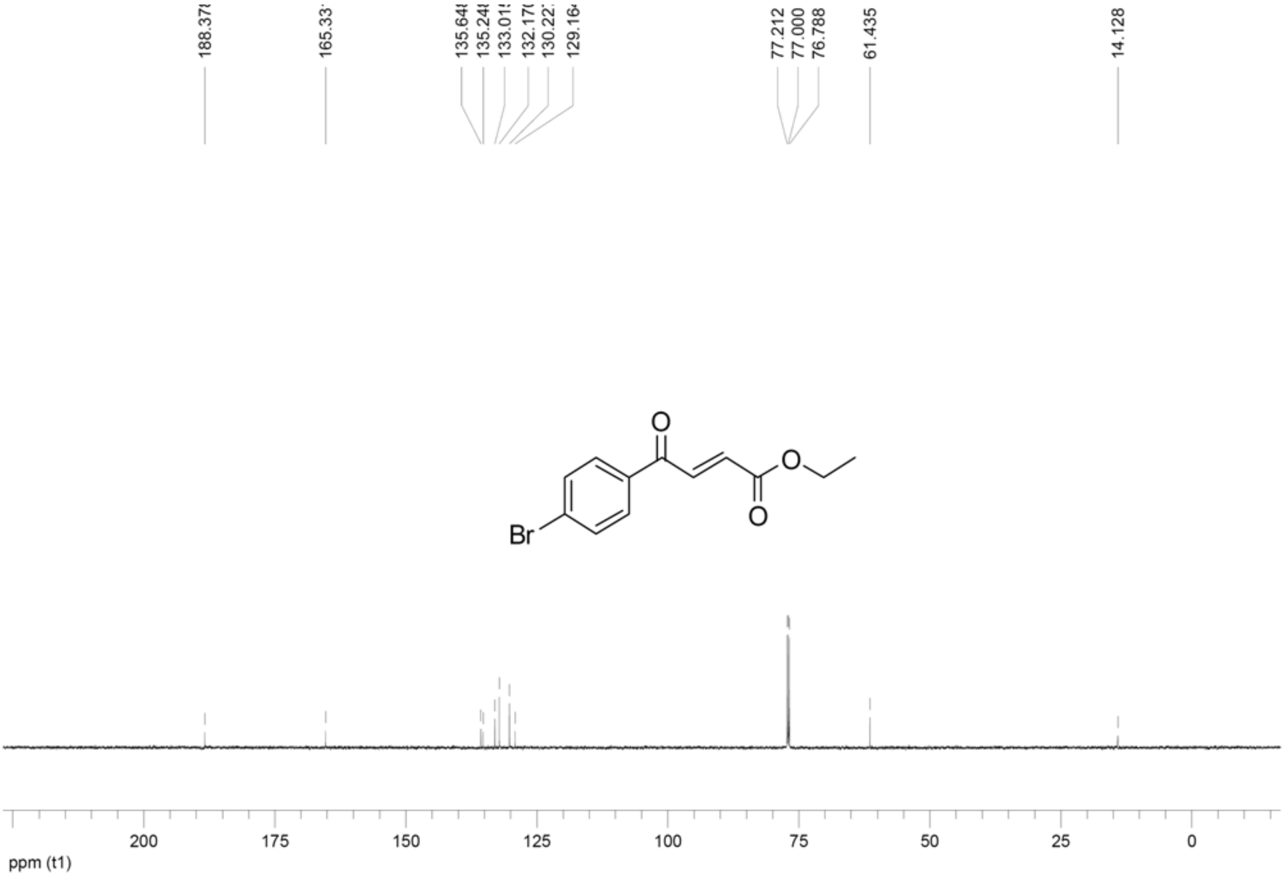

8.058
8.049
8.044
8.035
7.896
7.870
7.269
7.206
7.192
7.178
6.903
6.876
4.326
4.315
4.303
4.291
1.367
1.355
1.343
0.000
O
F
O
O
1.74
0.85
1.66
0.65
1.93
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

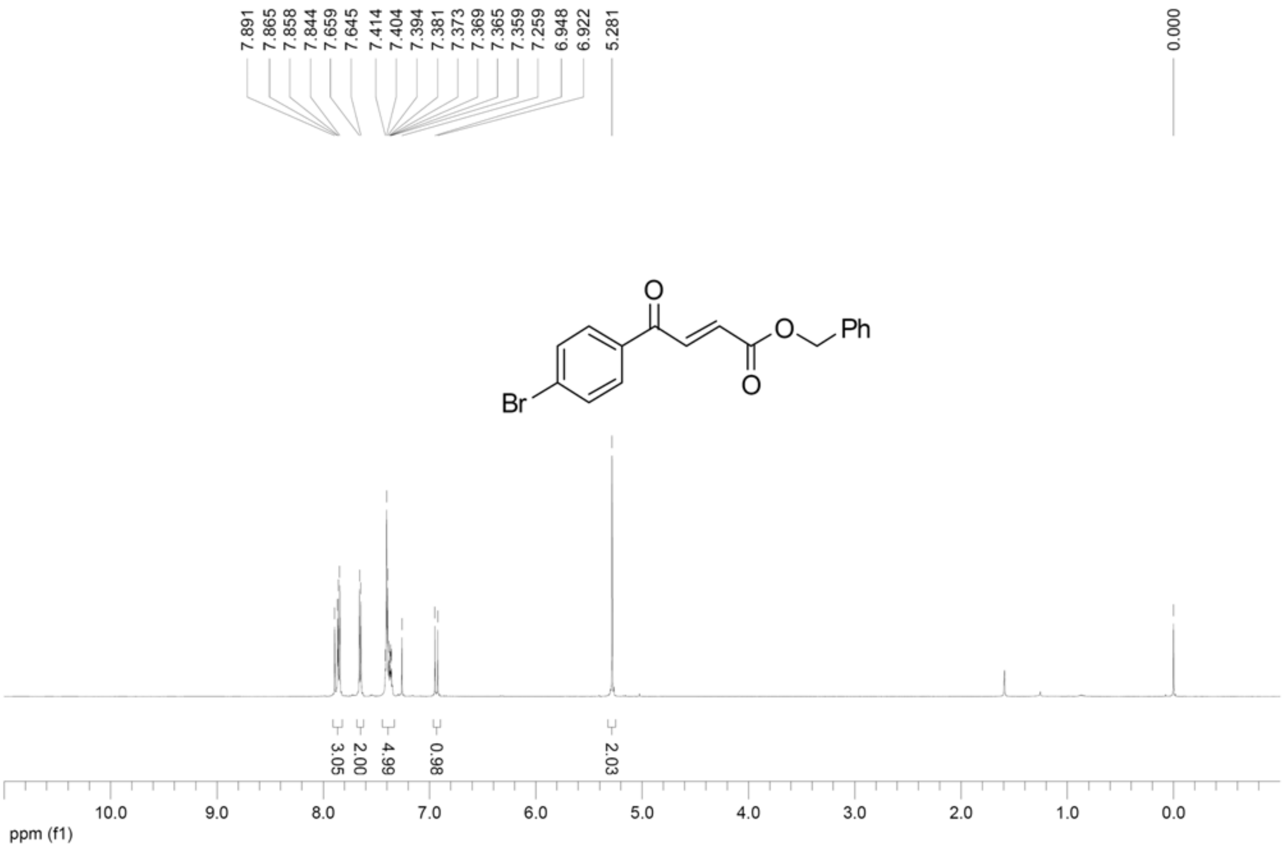

187.627
166.849
165.278
165.150
135.77
132.908
132.890
132.604
131.474
131.41
116.01
115.86
77.212
77.000
76.787
61.280
14.006
O
F
O
O
200
175
150
125
100
75
50
25
0
ppm (t1)

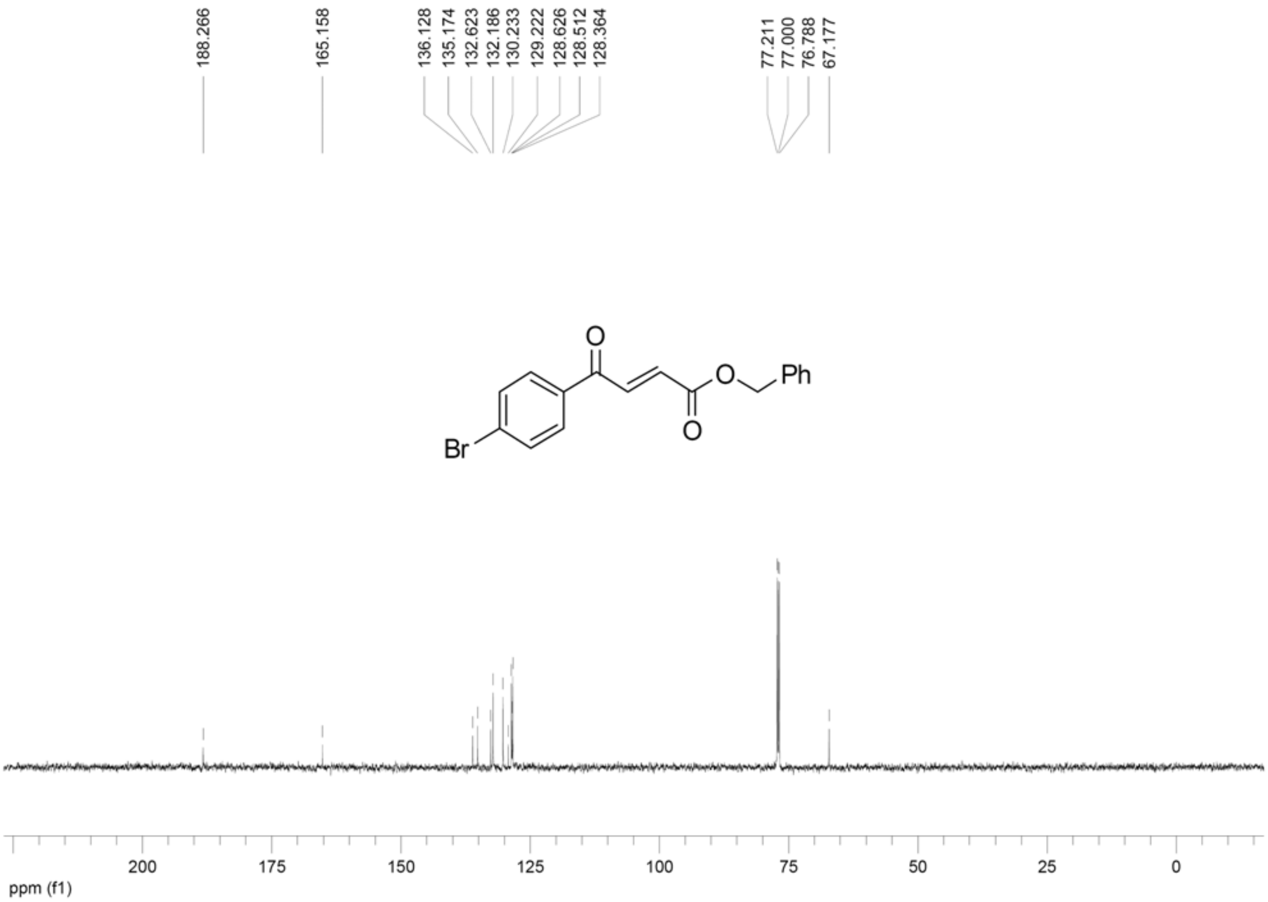

7.958
7.944
7.878
7.852
7.503
7.489
7.265
6.908
6.882
4.327
4.315
4.303
4.291
1.367
1.355
1.343
0.000
O
O
O
Cl
1.91
0.88
1.79
0.82
2.01
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

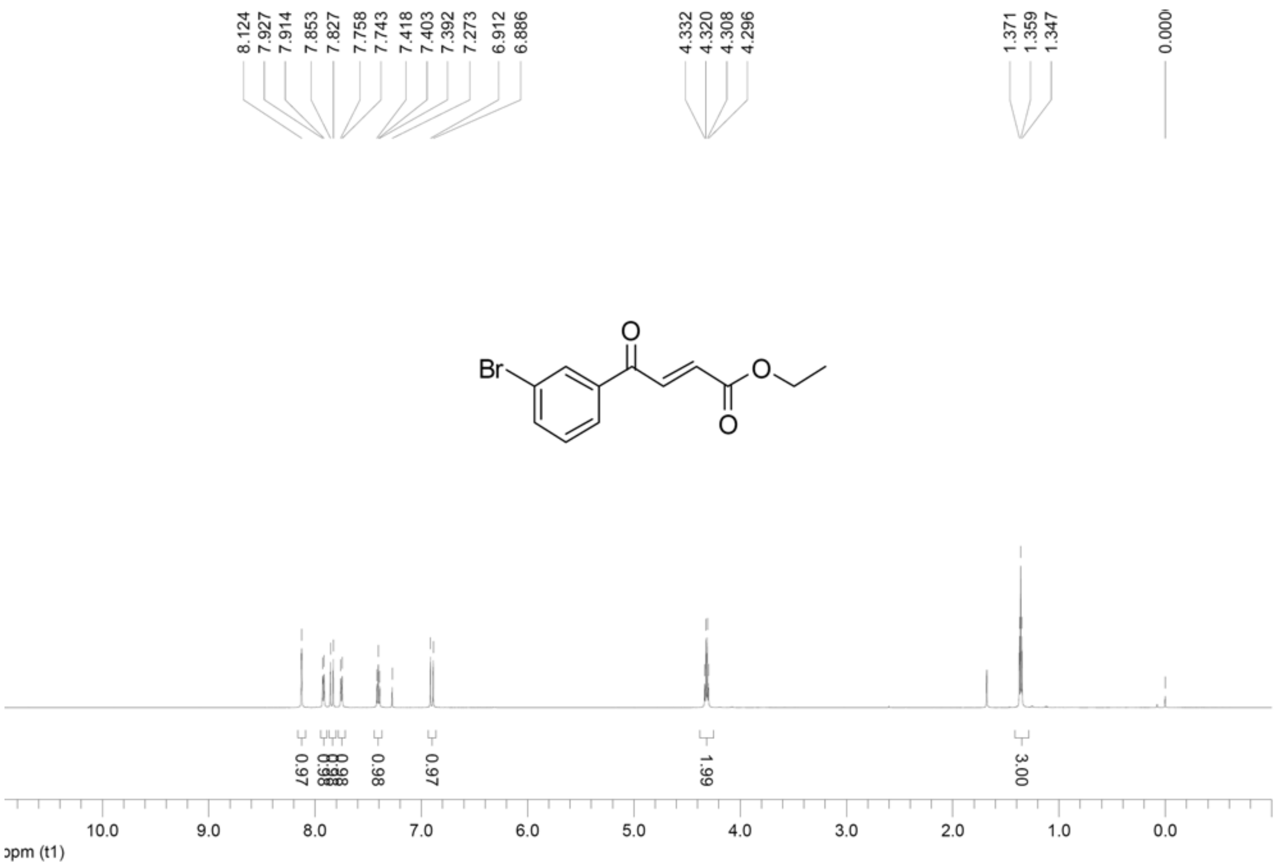

188.18
165.35
140.38
135.71
134.85
132.97
130.17
129.18
77.212
77.000
76.788
61.439
14.130
O
O
O
Cl
200
175
150
125
100
75
50
25
0
ppm (t1)

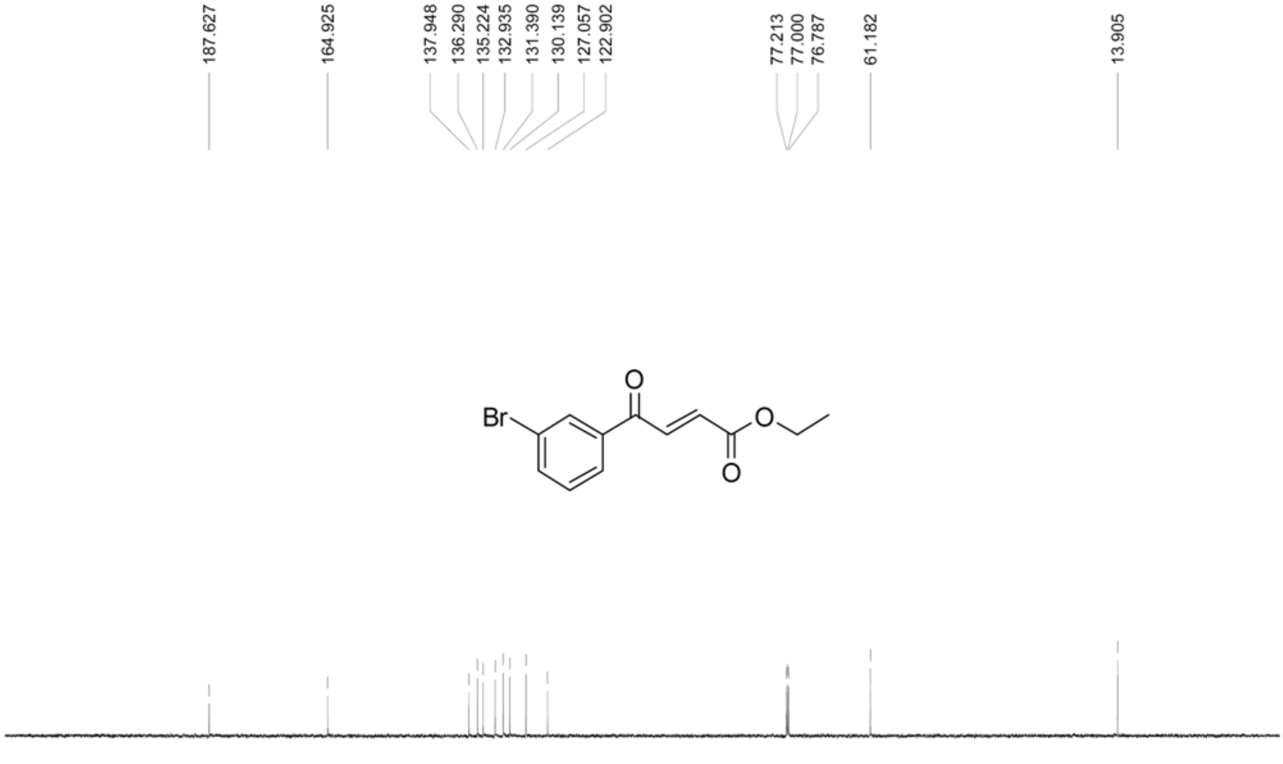

7.876
7.867
7.862
7.842
7.671
7.657
7.265
6.908
6.882
4.326
4.314
4.302
4.290
1.366
1.354
1.342
-0.000
O
O
O
Br
2.81
1.75
0.76
1.95
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

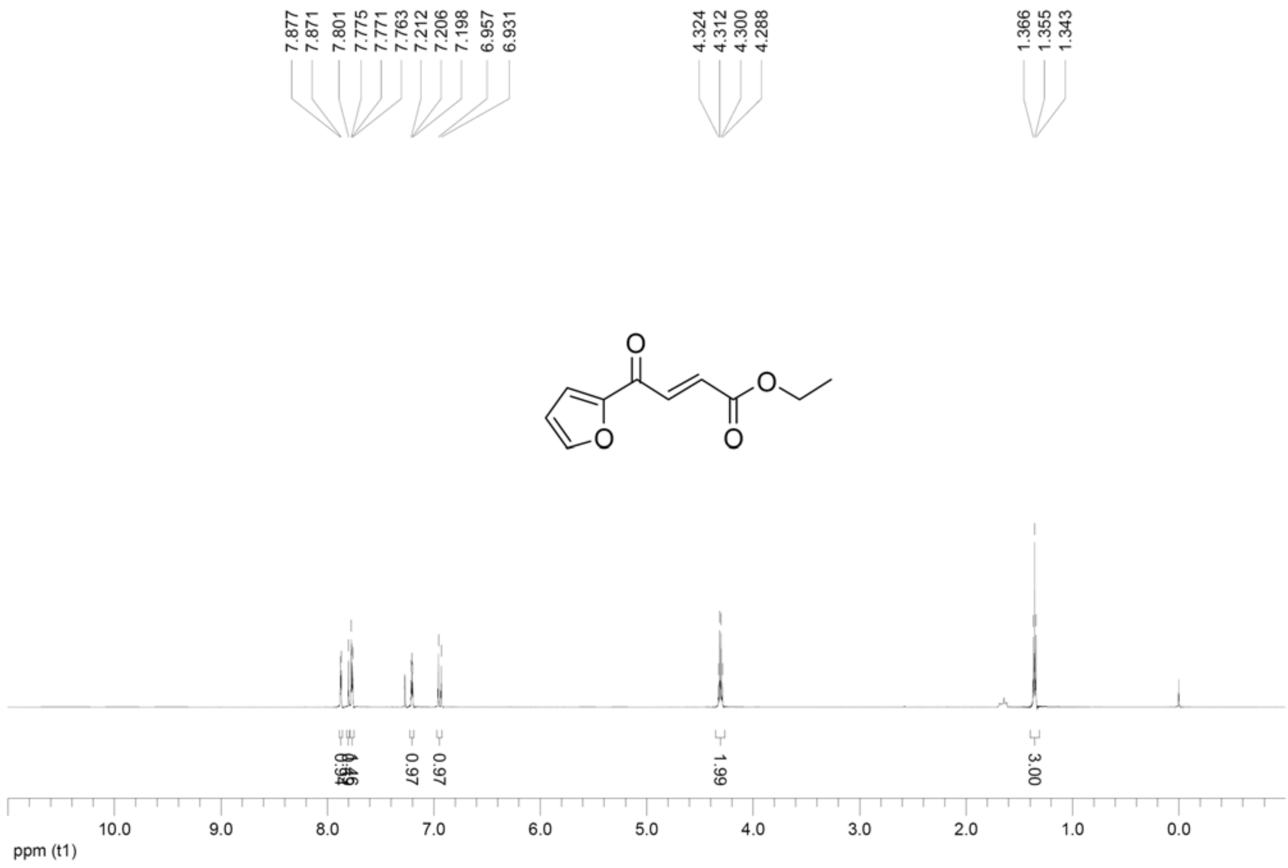

188.37
165.33
135.64
135.24
133.01
132.17
130.22
129.16
77.212
77.000
76.788
61.435
14.128
O
O
O
Br
200
175
150
125
100
75
50
25
0
ppm (t1)

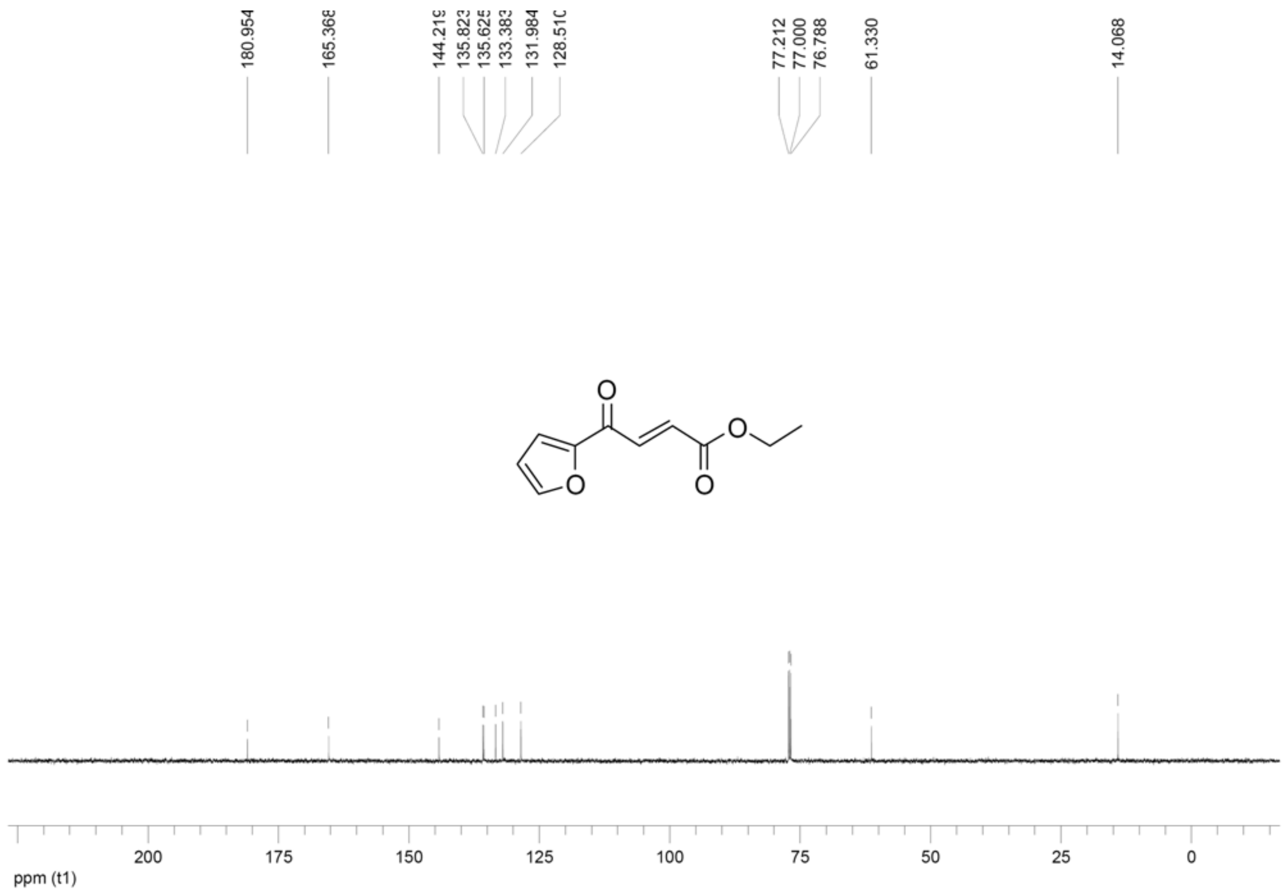

7.891
7.865
7.858
7.844
7.659
7.645
7.414
7.404
7.394
7.381
7.373
7.369
7.365
7.359
7.259
6.948
6.922
5.281
0.000
O
O
Ph
O
Br
3.05
2.00
4.99
0.98
2.03
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

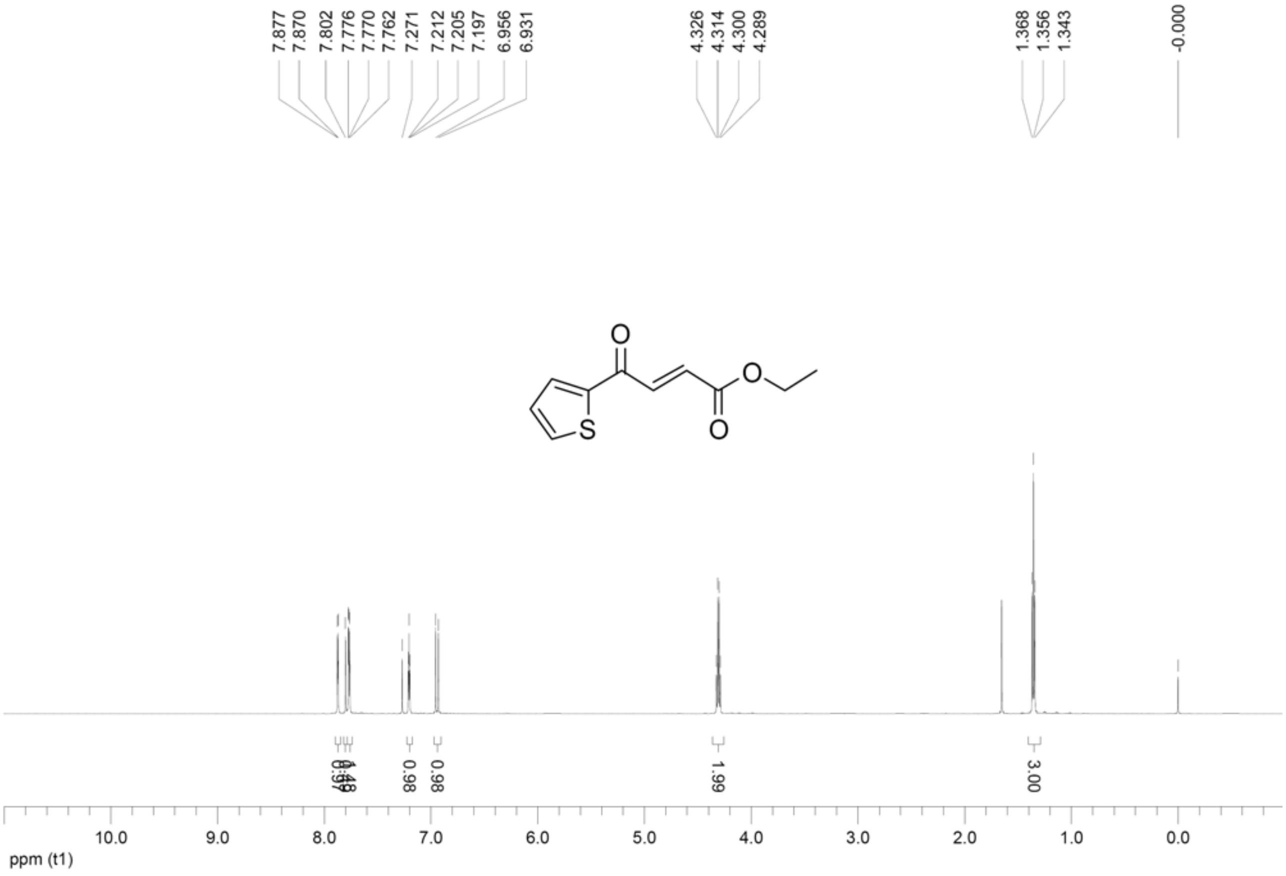

188.266
165.158
136.128
135.174
132.623
132.186
130.233
129.222
128.626
128.512
128.364
77.211
77.000
76.788
67.177
O
O
Ph
O
Br
200
175
150
125
100
75
50
25
0
ppm (f1)

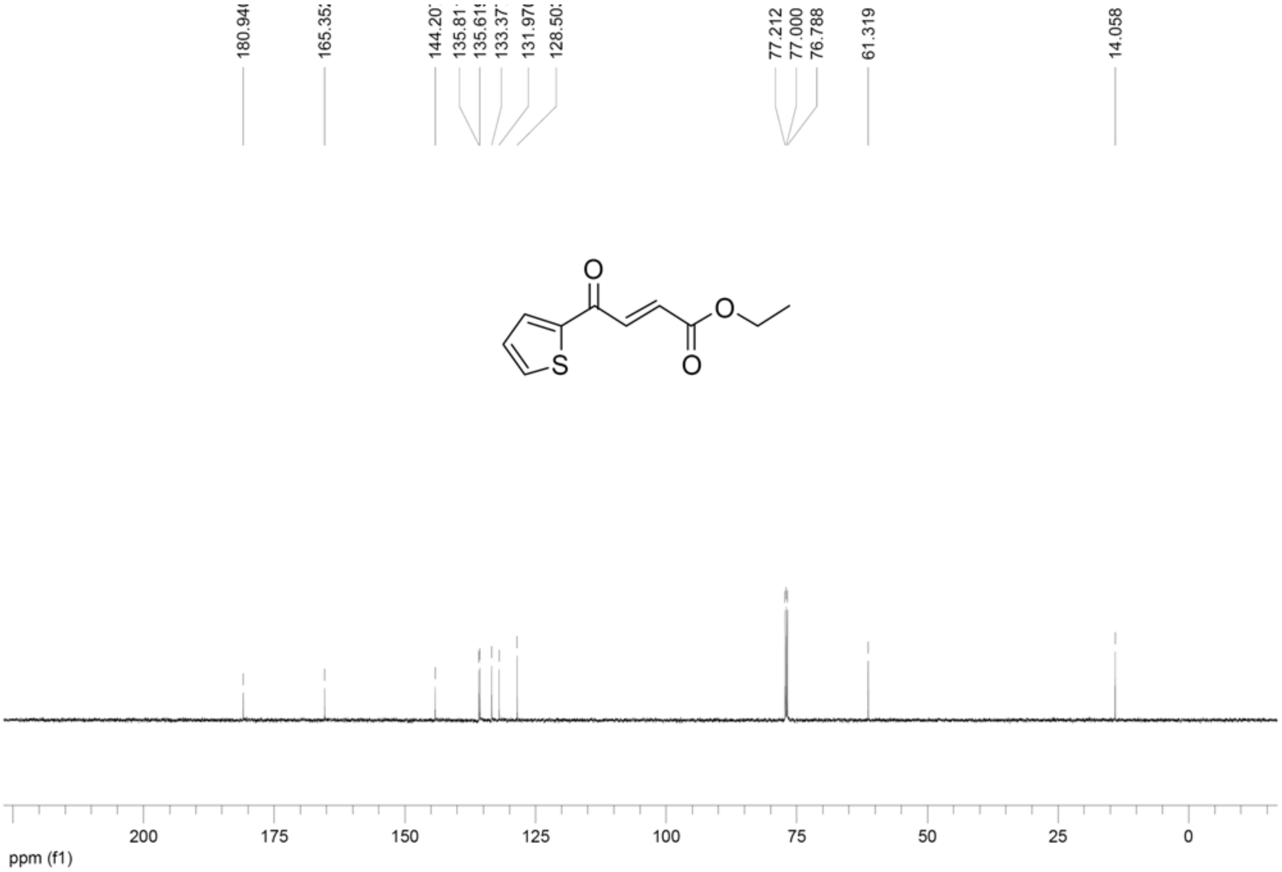

8.124
7.927
7.914
7.853
7.827
7.758
7.743
7.418
7.403
7.392
7.273
6.912
6.886
4.332
4.320
4.308
4.296
1.371
1.359
1.347
0.000
Br
O
O
O
0.97
0.98
0.97
1.99
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


187.627
164.925
137.948
136.290
135.224
132.935
131.390
130.139
127.057
122.902
77.213
77.000
76.787
61.182
13.905
Br
O
O
O
217
200
183
167
150
133
117
100
83
67
50
33
17
0
ppm (t1)

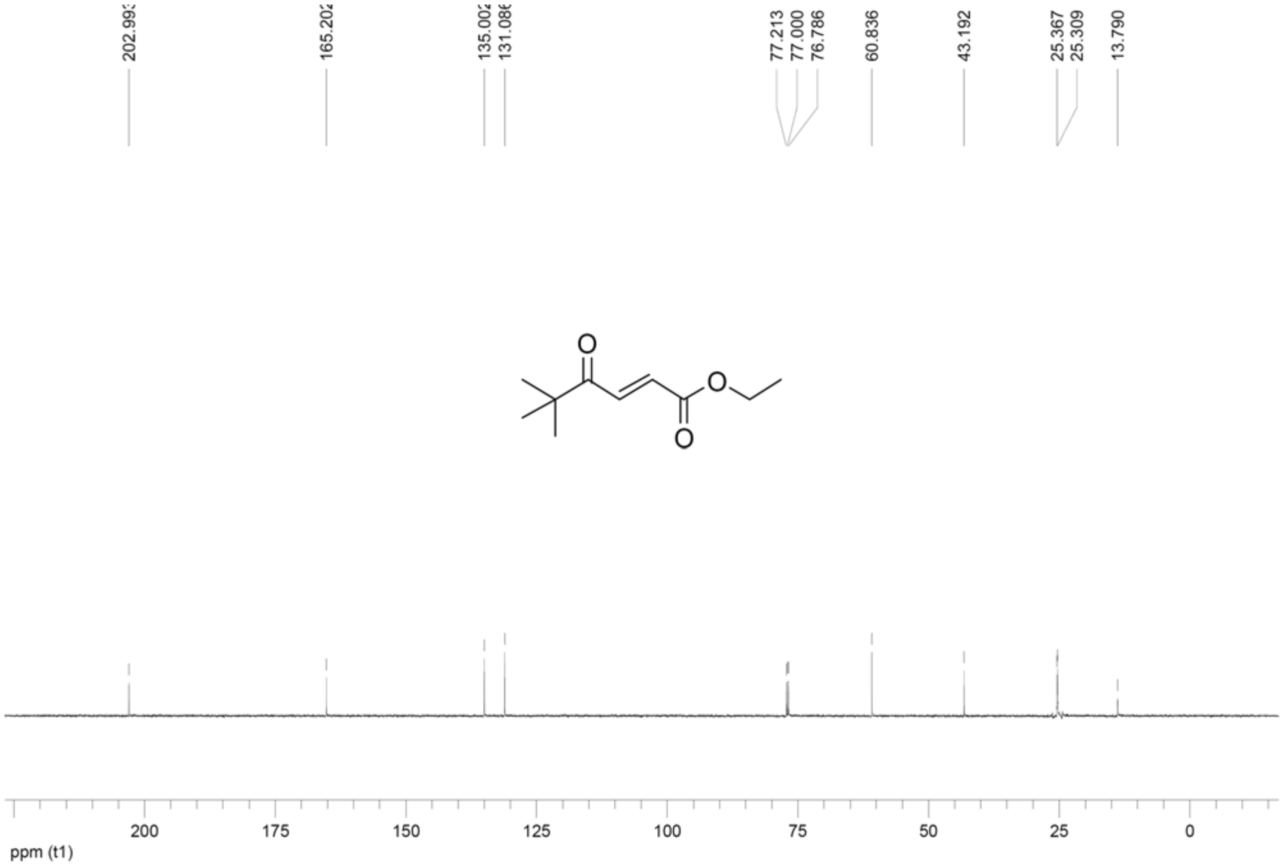

7.877
7.871
7.801
7.775
7.771
7.763
7.212
7.206
7.198
6.957
6.931
4.324
4.312
4.300
4.288
1.366
1.355
1.343
O
O
O
O
0.97
0.97
1.99
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

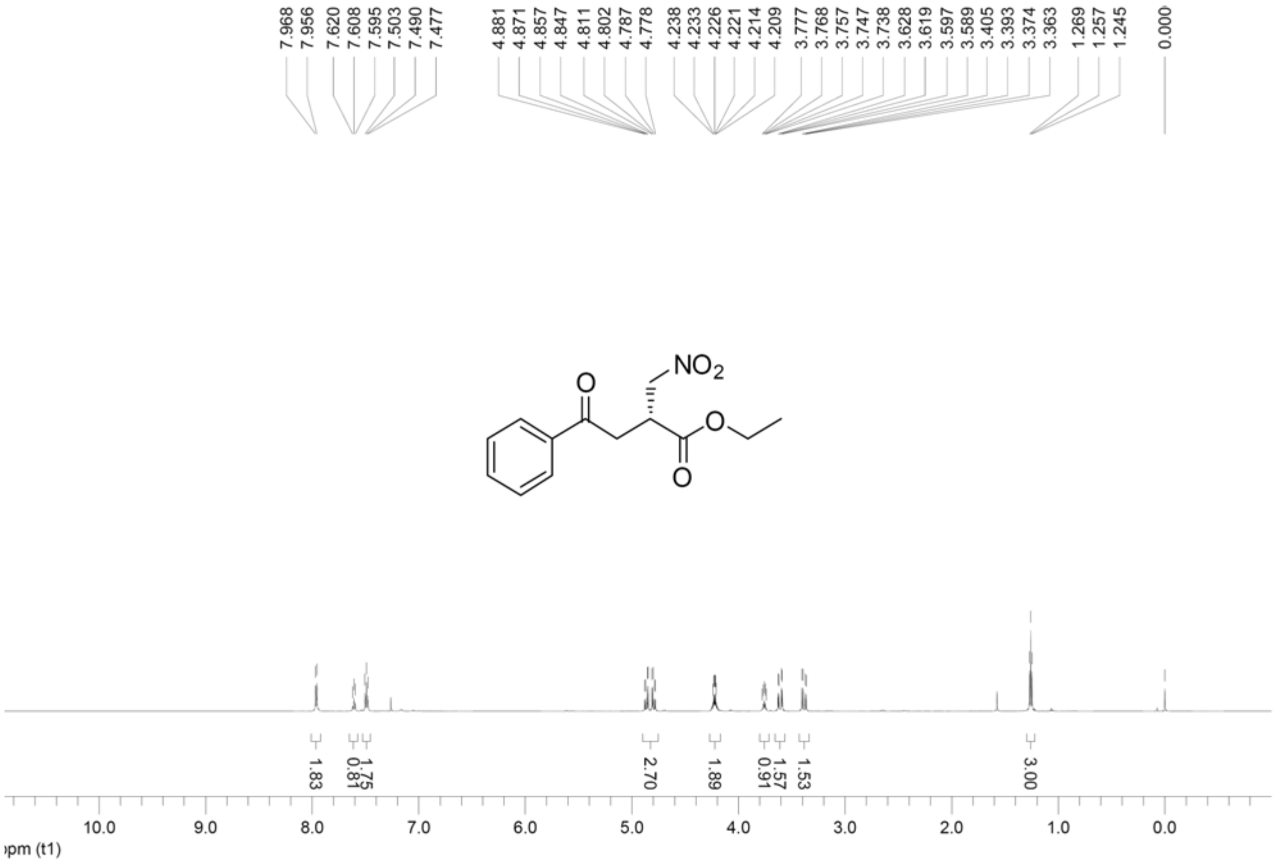

180.954
165.368
144.219
135.823
135.625
133.383
131.984
128.510
77.212
77.000
76.788
61.330
14.068
O
O
O
O
200
175
150
125
100
75
50
25
0
ppm (t1)


7.877
7.870
7.802
7.776
7.770
7.762
7.271
7.212
7.205
7.197
6.956
6.931
4.326
4.314
4.300
4.289
1.368
1.356
1.343
-0.000
O
O
O
S
0.98
0.98
1.99
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

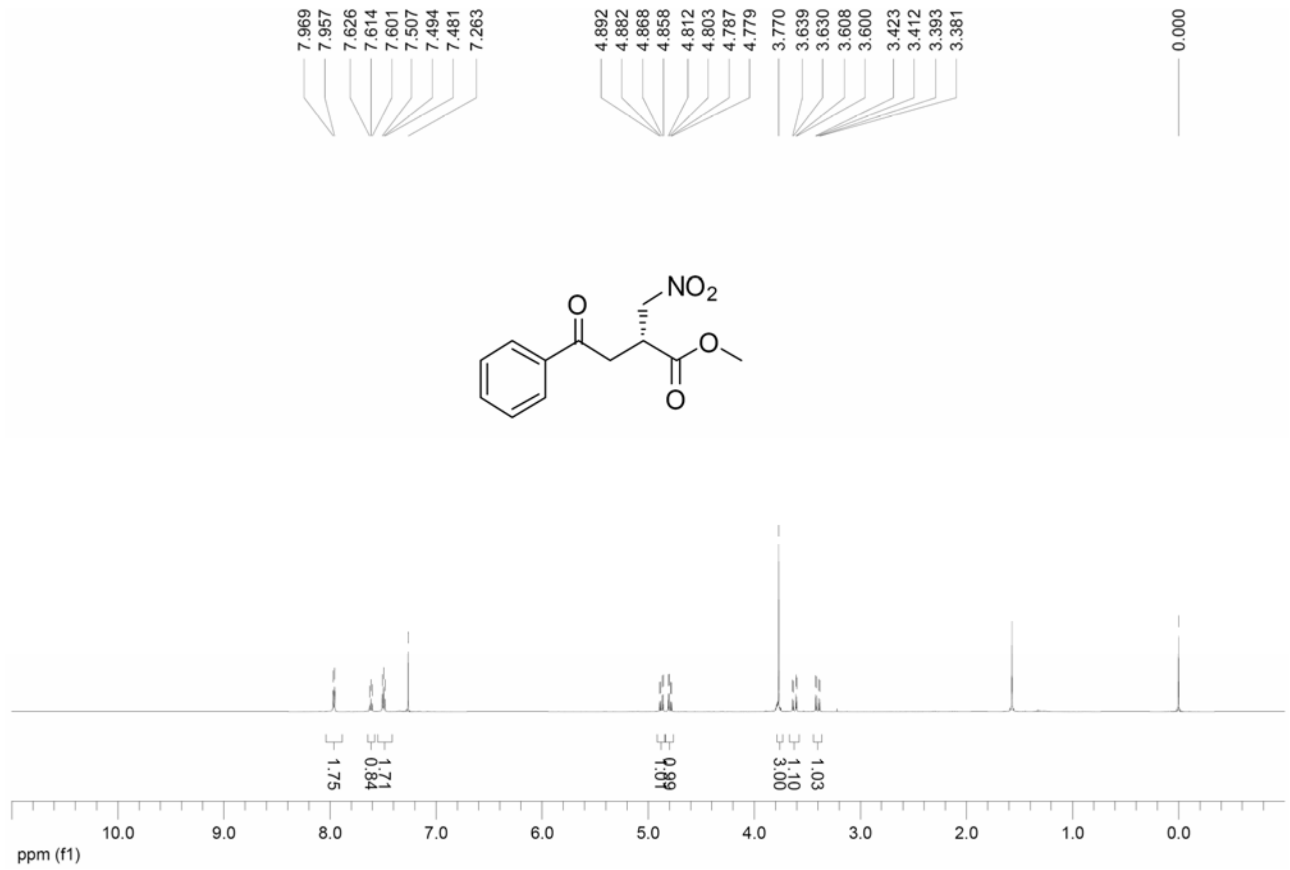

180.94
165.35
144.20
135.81
135.61
133.37
131.97
128.50
77.212
77.000
76.788
61.319
14.058
O
O
O
S
200
175
150
125
100
75
50
25
0
ppm (f1)


7.523
7.497
7.267
6.787
6.761
4.282
4.271
4.259
4.247
1.339
1.327
1.315
1.198
-0.000
O
O
O
0.92
0.93
1.95
2.96
9.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


202.99
165.202
135.002
131.08
77.213
77.000
76.786
60.836
43.192
25.367
25.309
13.790
O
O
O
200
175
150
125
100
75
50
25
0
ppm (t1)


7.968
7.956
7.620
7.608
7.595
7.503
7.490
7.477
4.881
4.871
4.857
4.847
4.811
4.802
4.787
4.778
4.238
4.233
4.226
4.221
4.214
4.209
3.777
3.768
3.757
3.747
3.738
3.628
3.619
3.597
3.589
3.405
3.393
3.374
3.363
1.269
1.257
1.245
0.000
O
NO2
O
O
1.83
0.81
1.75
2.70
1.89
0.91
1.57
1.53
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
pm (t1)


196.431
170.797
135.845
133.748
128.728
128.025
77.316
76.999
76.681
74.715
61.817
38.315
36.947
13.921
O
NO2
O
O
225
200
175
150
125
100
75
50
25
0
ppm (t1)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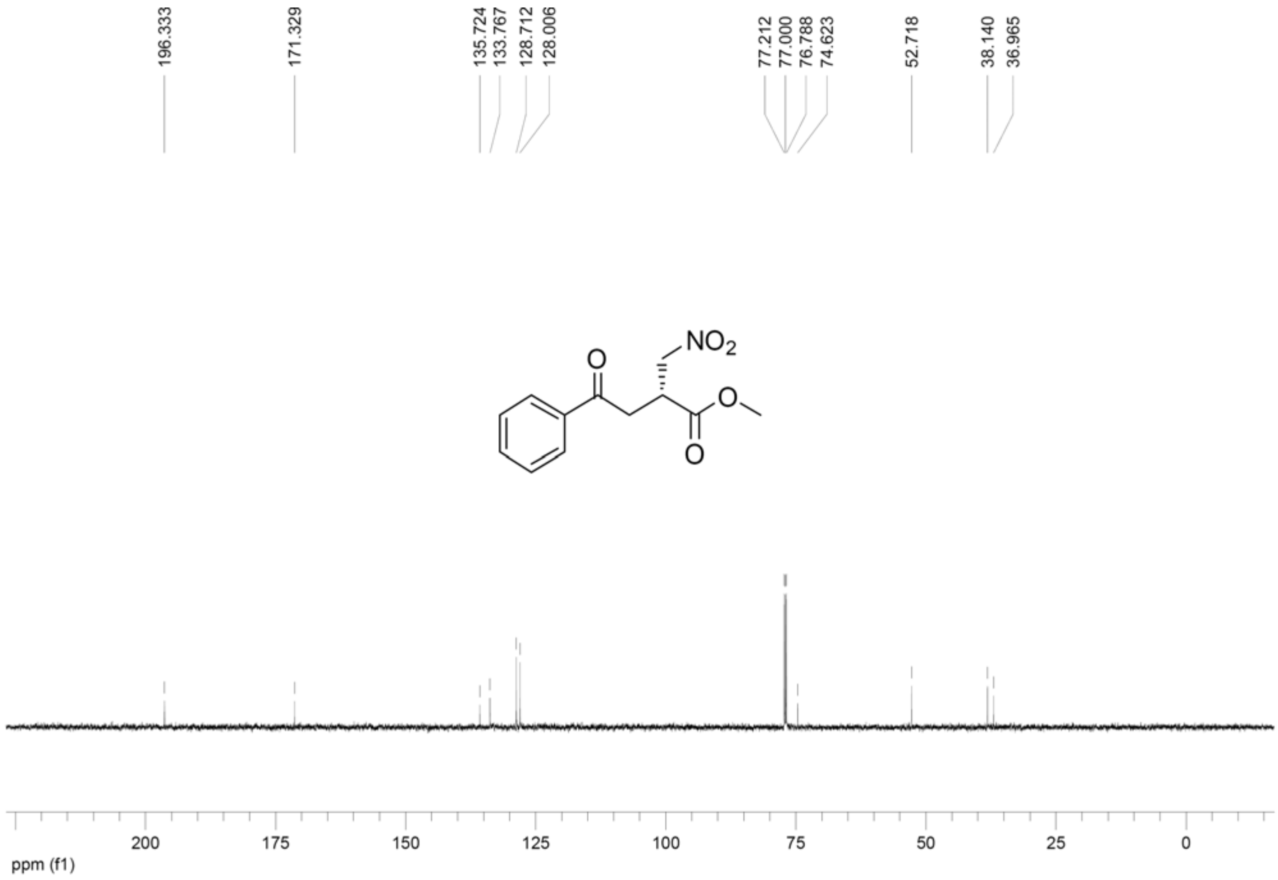
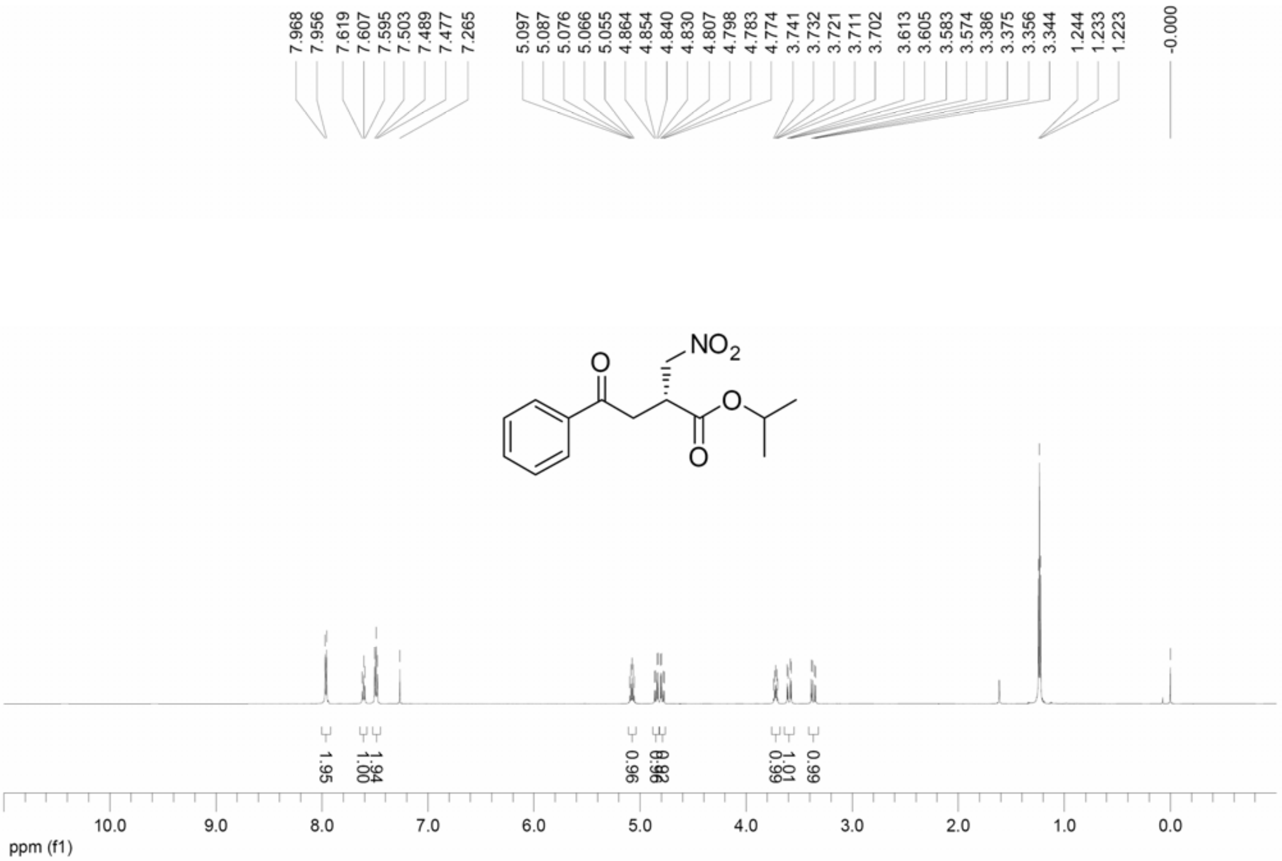
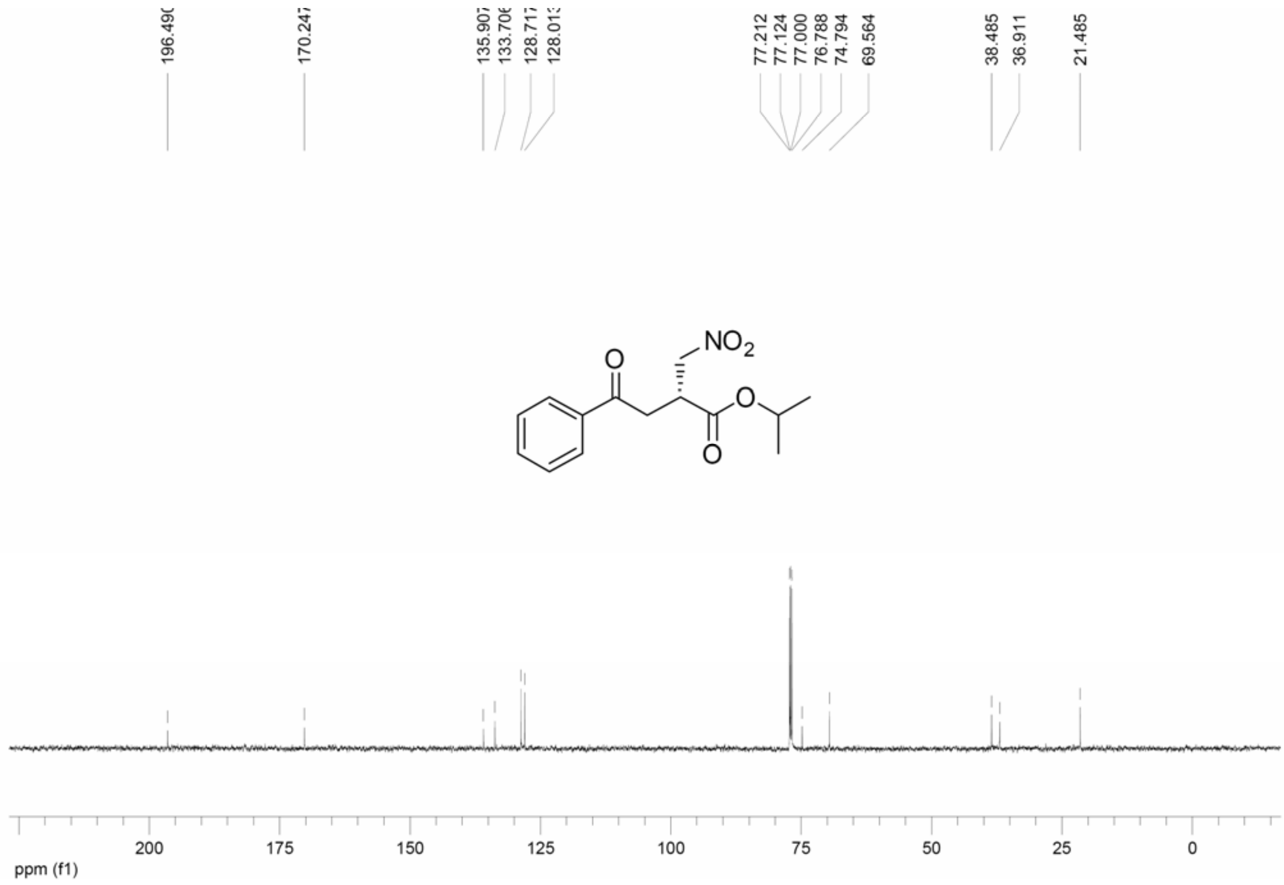
7.626
7.614
7.601
7.507
7.494
7.481
7.263
4.892
4.882
4.868
4.858
4.812
4.803
4.787
4.779
3.770
3.639
3.630
3.608
3.600
3.423
3.412
3.393
3.381
0.000
NO2
O
O
O
1.75
0.84
1.71
0.89
1.01
3.00
1.10
1.03
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


196.333
171.329
135.724
133.767
128.712
128.006
77.212
77.000
76.788
74.623
52.718
38.140
36.965
NO2
O
O
O
200
175
150
125
100
75
50
25
0
ppm (f1)


7.968
7.956
7.619
7.607
7.595
7.503
7.489
7.477
7.265
5.097
5.087
5.076
5.066
5.055
4.864
4.854
4.840
4.830
4.807
4.798
4.783
4.774
3.741
3.732
3.721
3.711
3.702
3.613
3.605
3.583
3.574
3.386
3.375
3.356
3.344
1.244
1.233
1.223
-0.000
NO2
O
O
O
1.95
1.00
1.94
0.96
0.96
0.92
0.99
1.01
0.99
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


196.49
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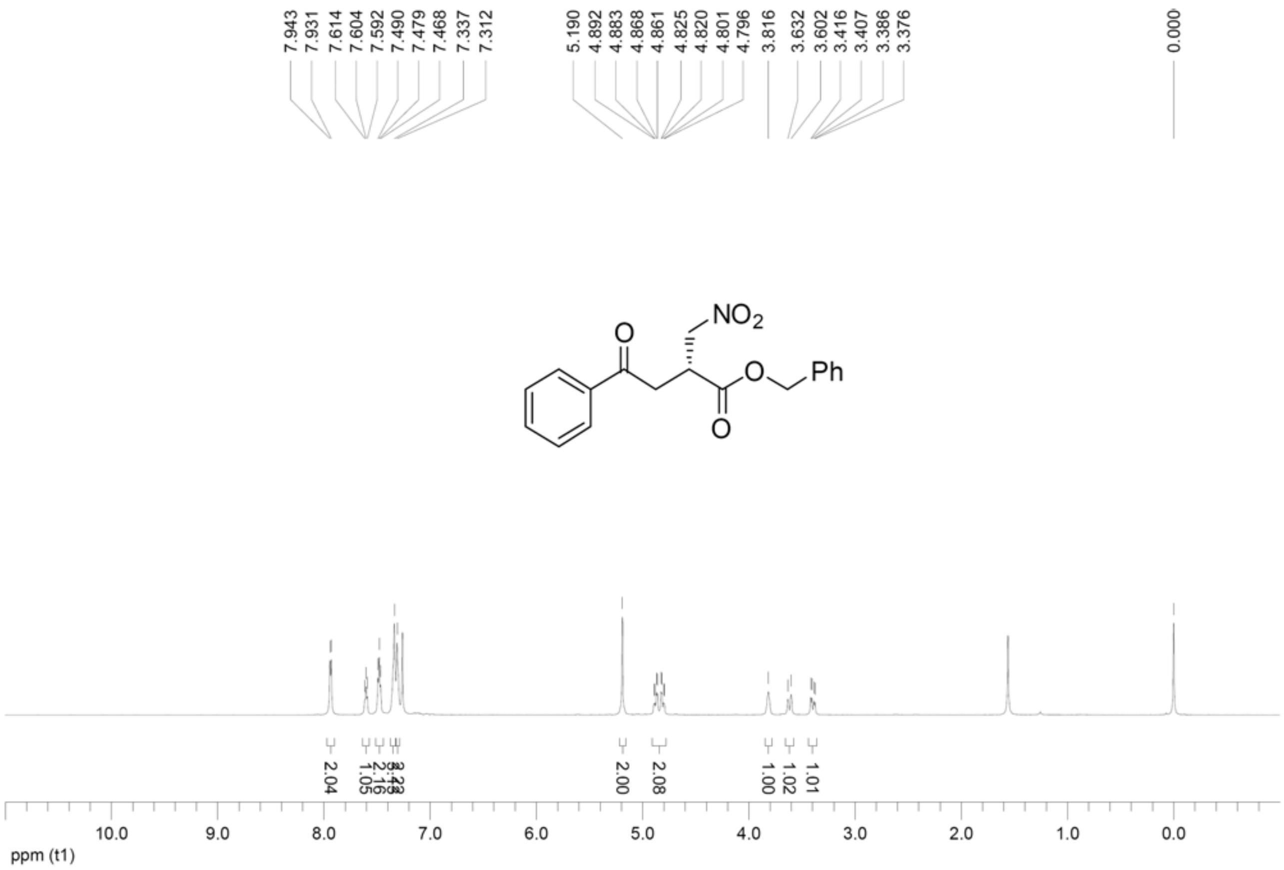
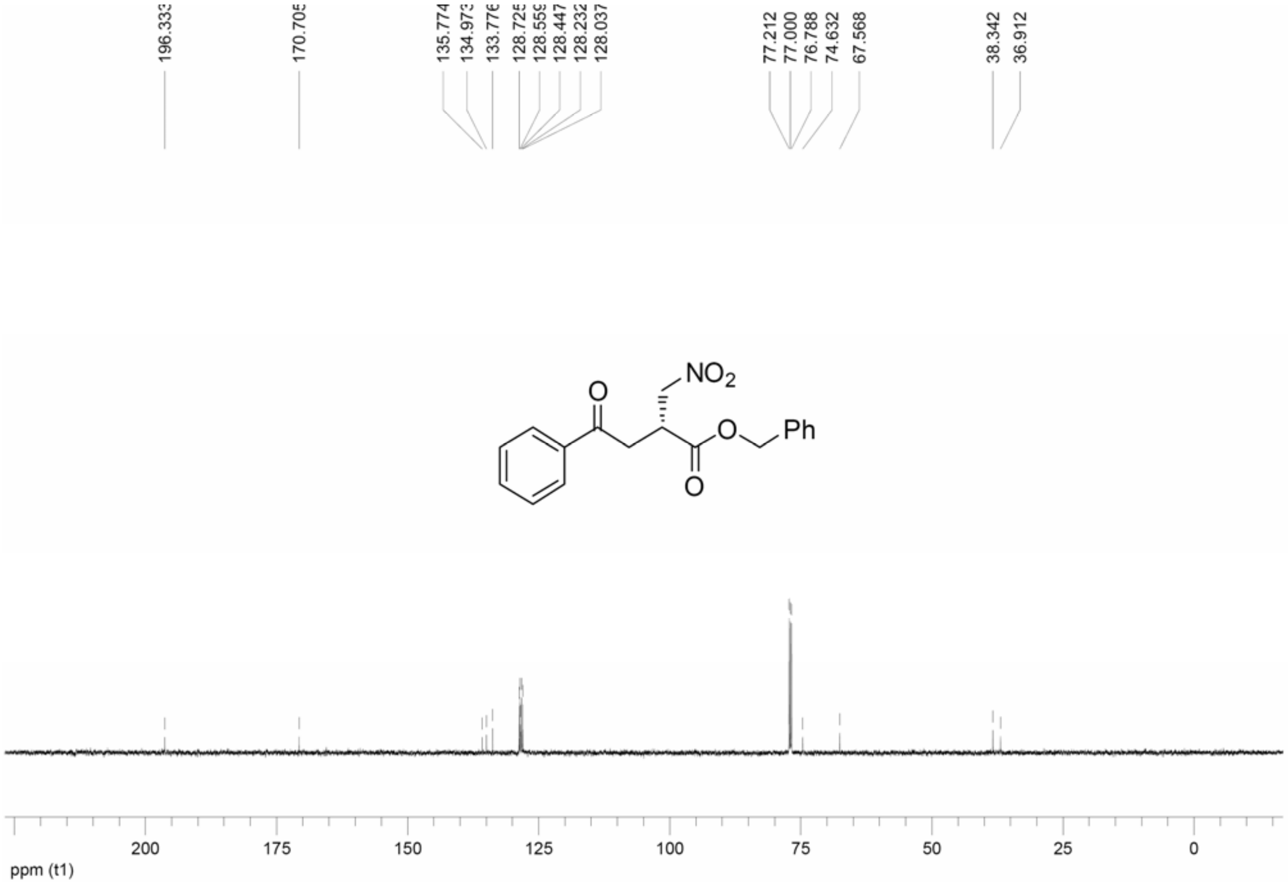
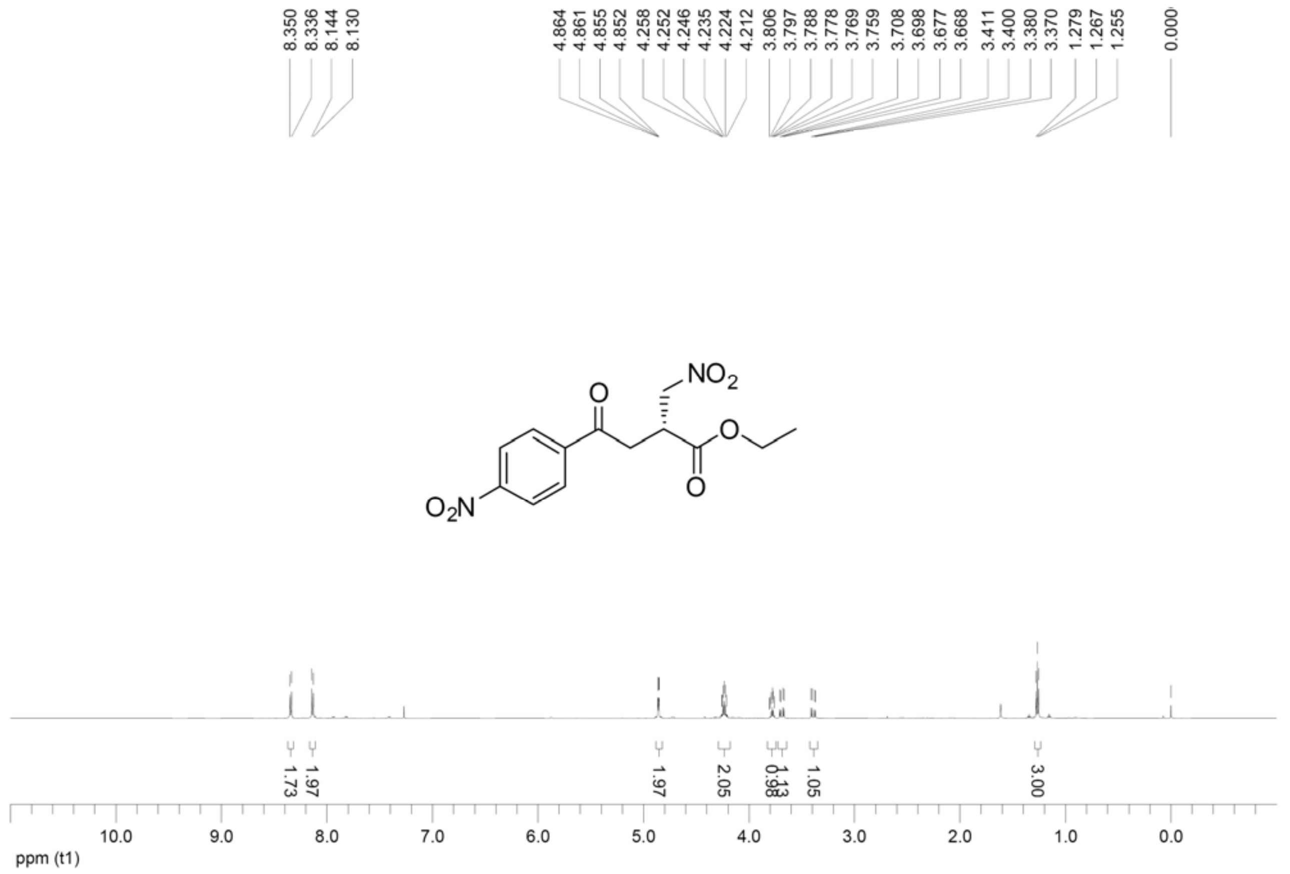
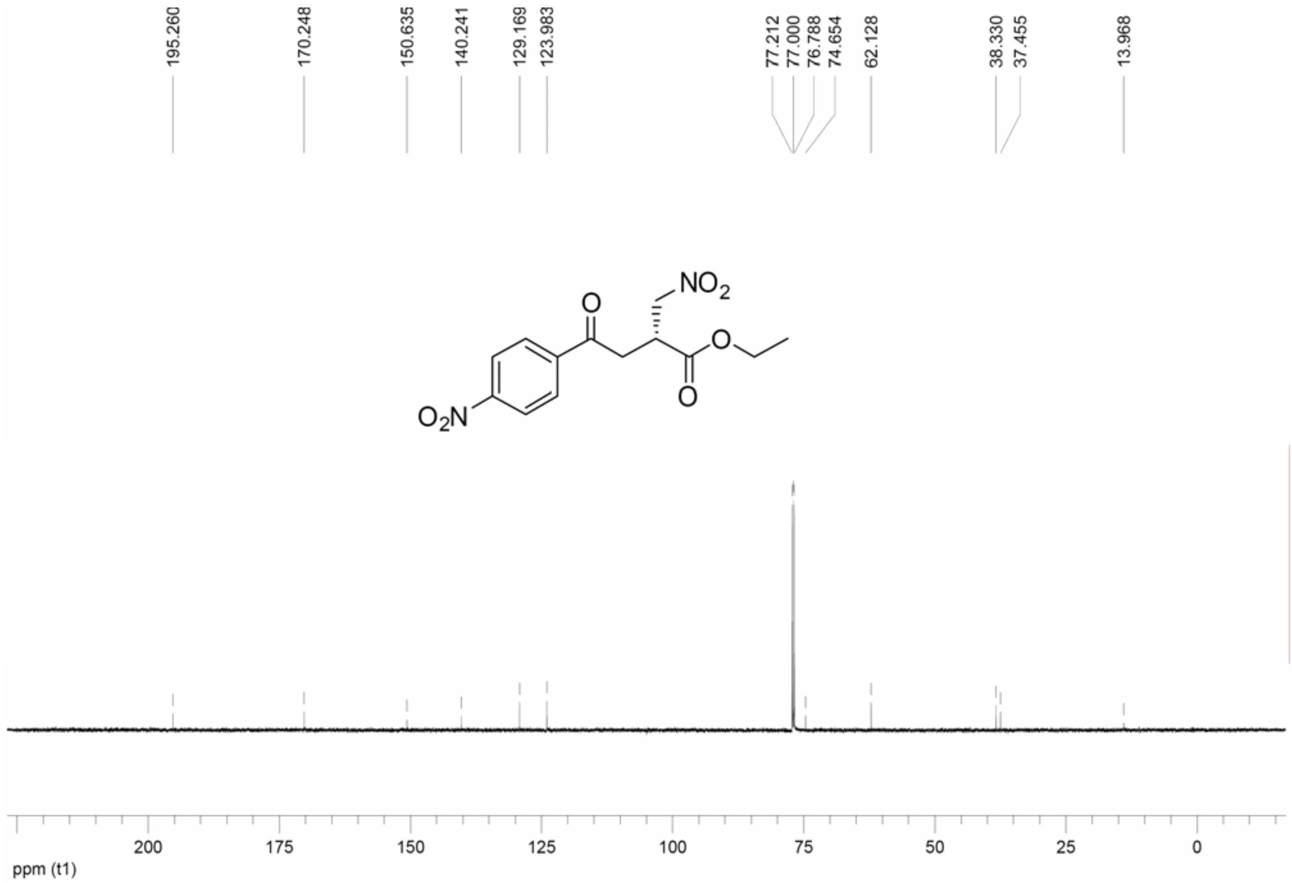
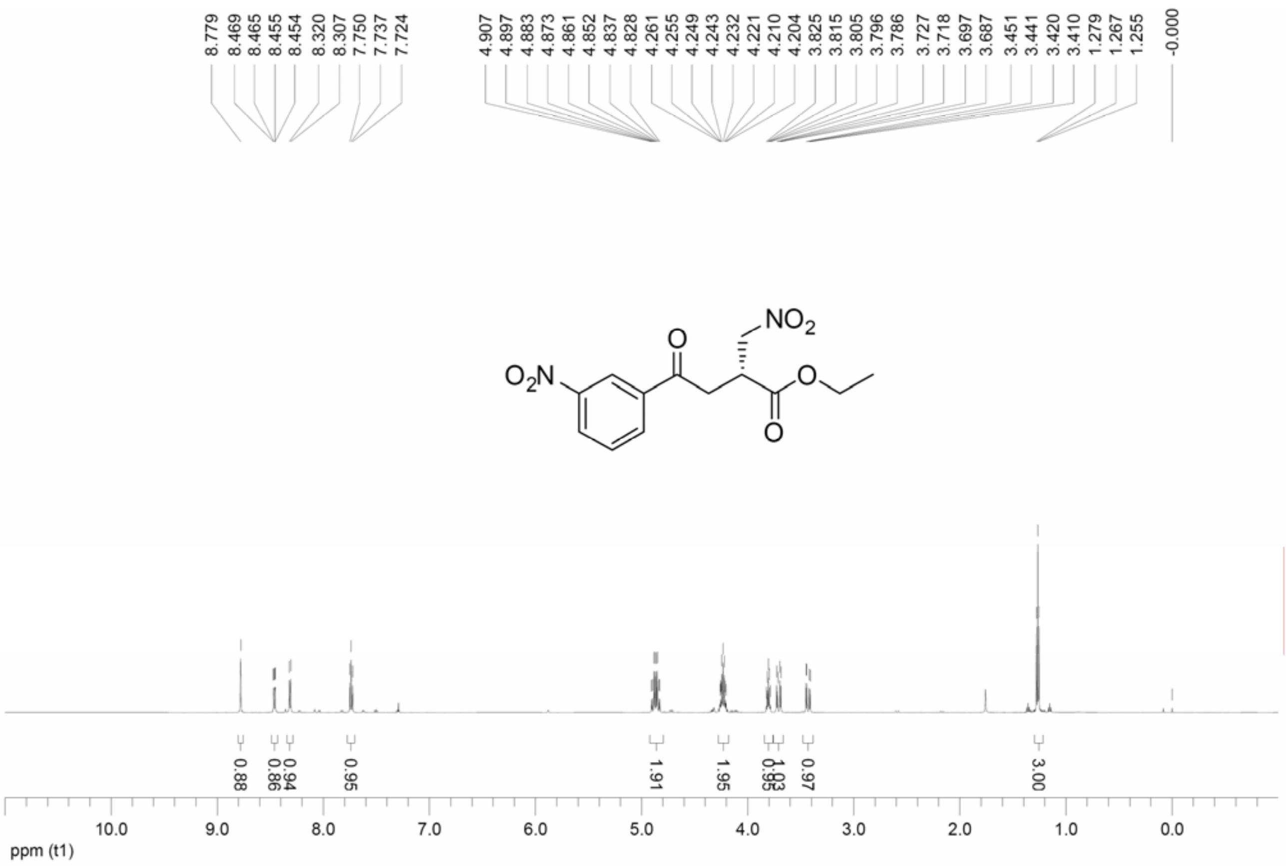
135.90
133.70
128.71
128.01
77.212
77.124
77.000
76.788
74.794
69.564
38.485
36.911
21.485
NO2
O
O
O
200
175
150
125
100
75
50
25
0
ppm (f1)


7.943
7.931
7.614
7.604
7.592
7.490
7.479
7.468
7.337
7.312
5.190
4.892
4.883
4.868
4.861
4.825
4.820
4.801
4.796
3.816
3.632
3.602
3.416
3.407
3.386
3.376
0.000
NO2
O
O
O
Ph
2.04
1.05
2.16
2.00
2.08
1.00
1.02
1.01
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


196.333
170.705
135.774
134.973
133.776
128.725
128.559
128.447
128.232
128.037
77.212
77.000
76.788
74.632
67.568
38.342
36.912
NO2
O
O
O
Ph
200
175
150
125
100
75
50
25
0
ppm (t1)


8.350
8.336
8.144
8.130
4.864
4.861
4.855
4.852
4.258
4.252
4.246
4.235
4.224
4.212
3.806
3.797
3.788
3.778
3.769
3.759
3.708
3.698
3.677
3.668
3.411
3.400
3.380
3.370
1.279
1.267
1.255
0.000
NO2
O
O
O
O2N
1.73
1.97
1.97
2.05
0.98
1.13
1.05
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


195.260
170.248
150.635
140.241
129.169
123.983
77.212
77.000
76.788
74.654
62.128
38.330
37.455
13.968
NO2
O
O
O
O2N
200
175
150
125
100
75
50
25
0
ppm (t1)


8.779
8.469
8.465
8.455
8.454
8.320
8.307
7.750
7.737
7.724
4.907
4.897
4.883
4.873
4.861
4.852
4.837
4.828
4.261
4.255
4.249
4.243
4.232
4.221
4.210
4.204
3.825
3.815
3.805
3.796
3.786
3.727
3.718
3.697
3.687
3.451
3.441
3.420
3.410
1.279
1.267
1.255
-0.000
NO2
O
O2N
O
O
0.88
0.86
0.94
0.95
1.91
1.95
0.95
1.03
0.97
3.00
10.0
9.0
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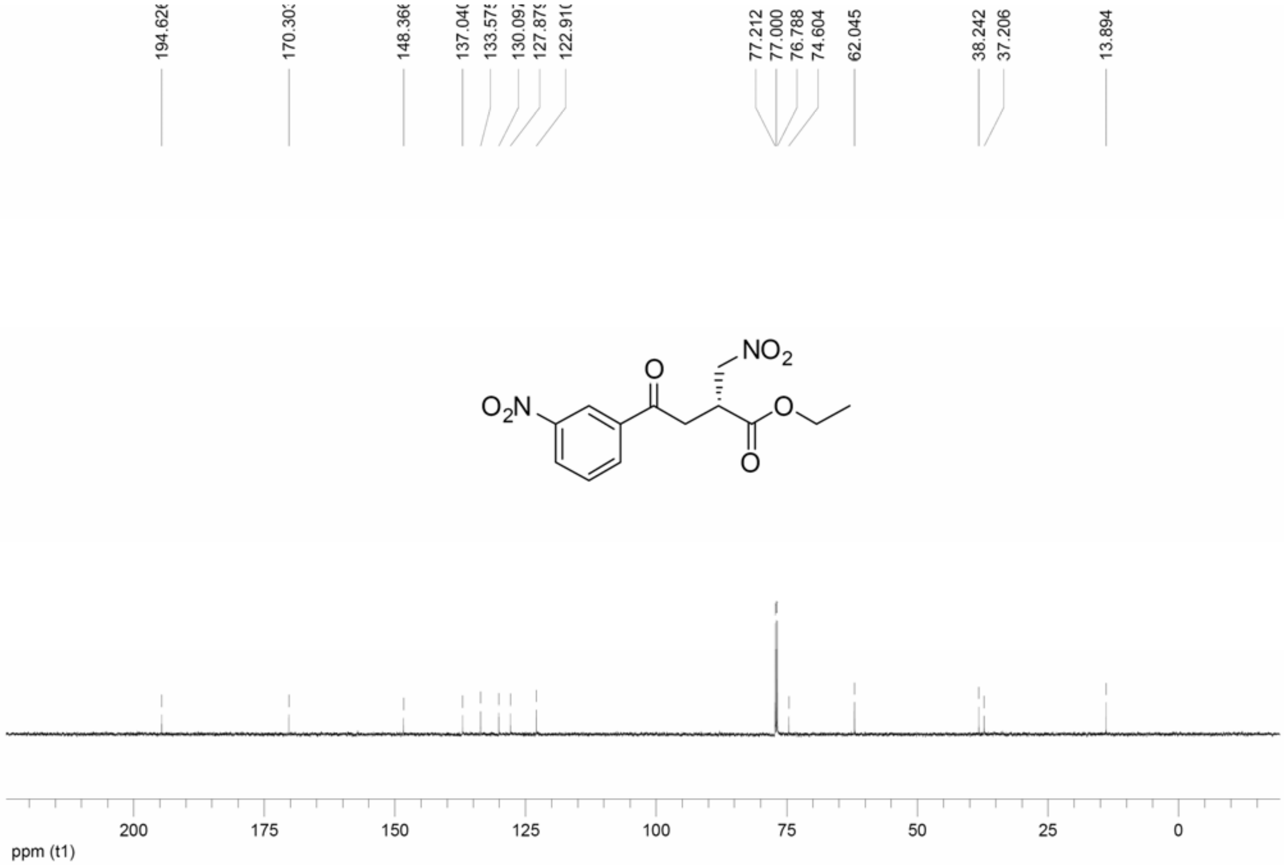
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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170.30
148.36
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133.57
130.09
127.87
122.91
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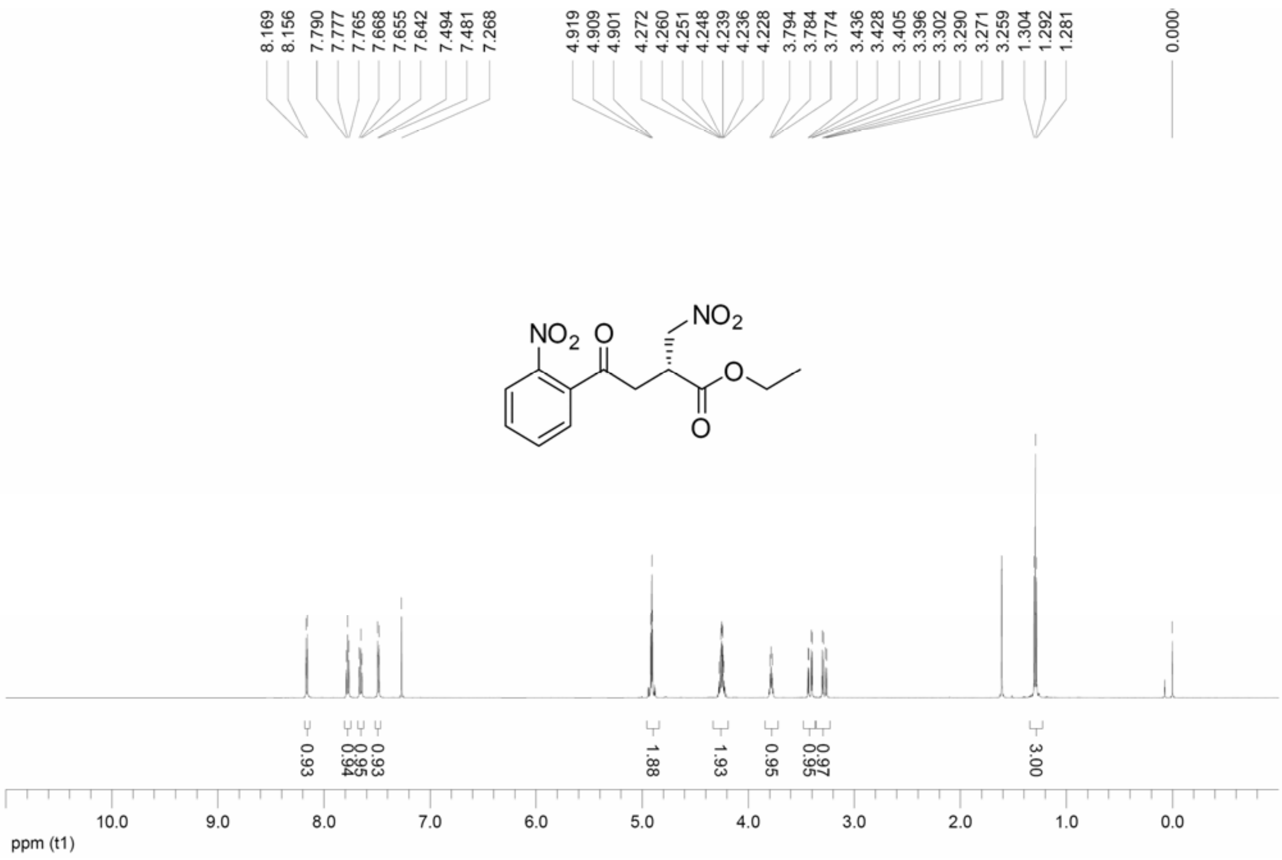
77.000
76.788
74.604
62.045
38.242
37.206
13.894
NO2
O
O2N
O
O
200
175
150
125
100
75
50
25
0
ppm (t1)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8.156
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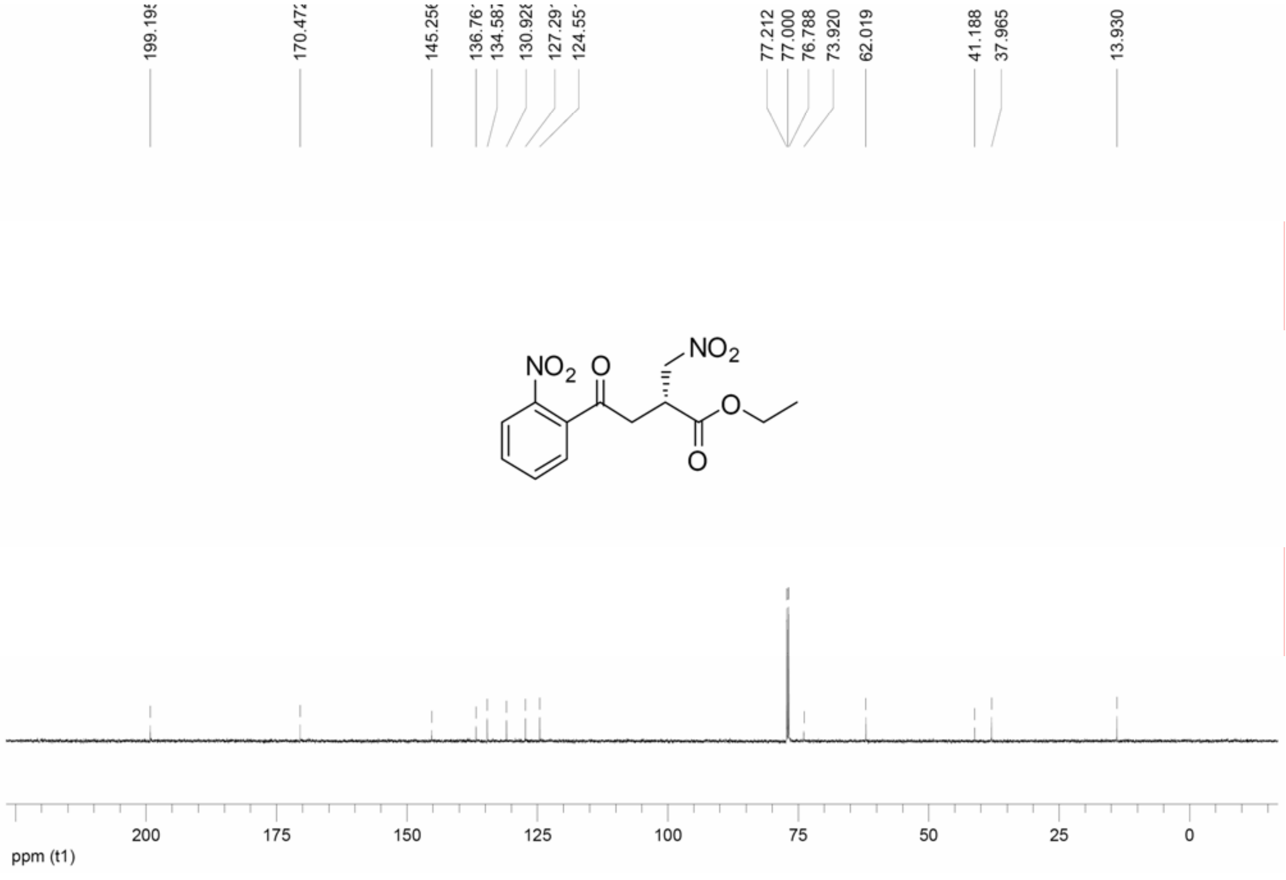
7.777
7.765
7.668
7.655
7.642
7.494
7.481
7.268
4.919
4.909
4.901
4.272
4.260
4.251
4.248
4.239
4.236
4.228
3.794
3.784
3.774
3.436
3.428
3.405
3.396
3.302
3.290
3.271
3.259
1.304
1.292
1.281
0.000
NO2
O
NO2
O
O
0.93
0.94
0.95
0.93
1.88
1.93
0.95
0.95
0.97
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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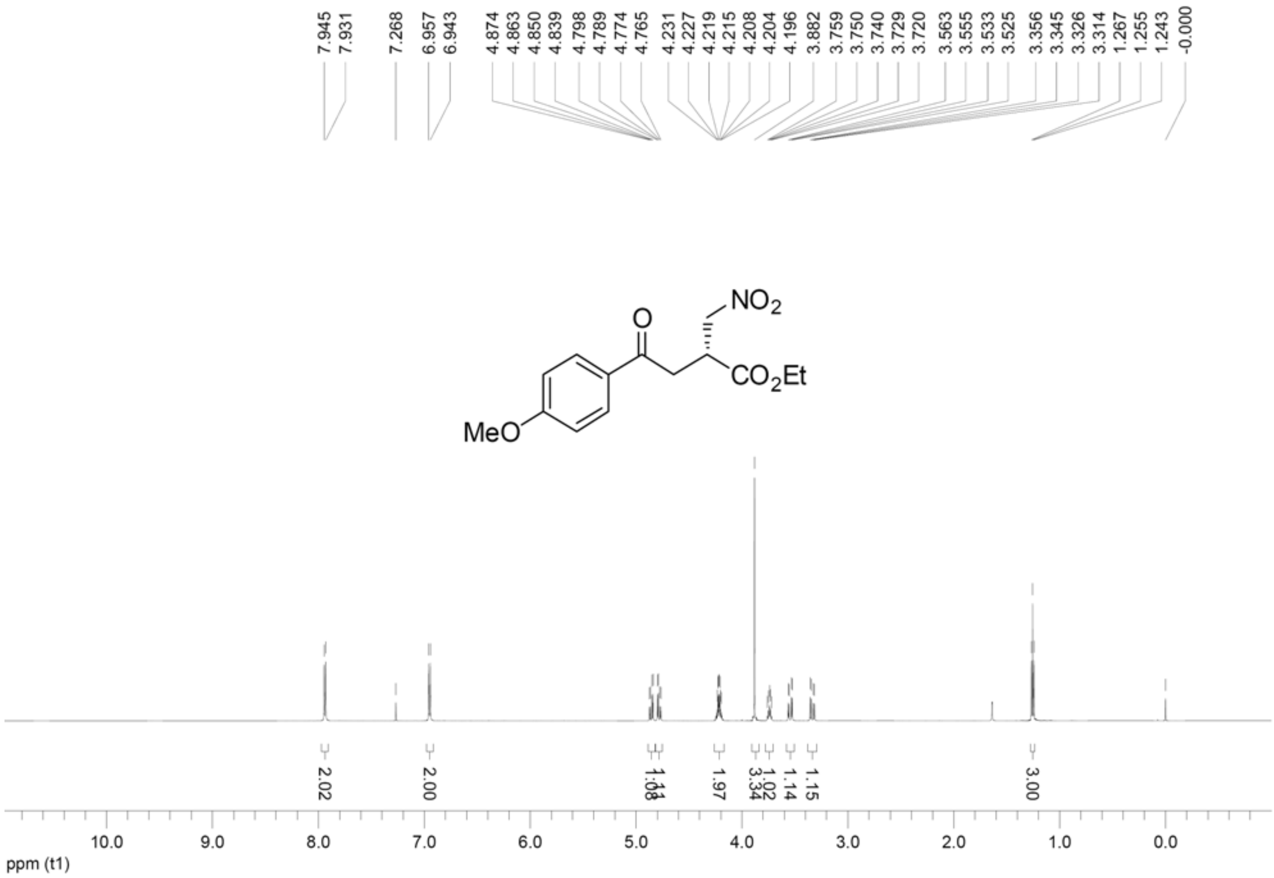
170.47
145.25
136.76
134.58
130.92
127.29
124.55
77.212
77.000
76.788
73.920
62.019
41.188
37.965
13.930
NO2
O
NO2
O
O
200
175
150
125
100
75
50
25
0
ppm (t1)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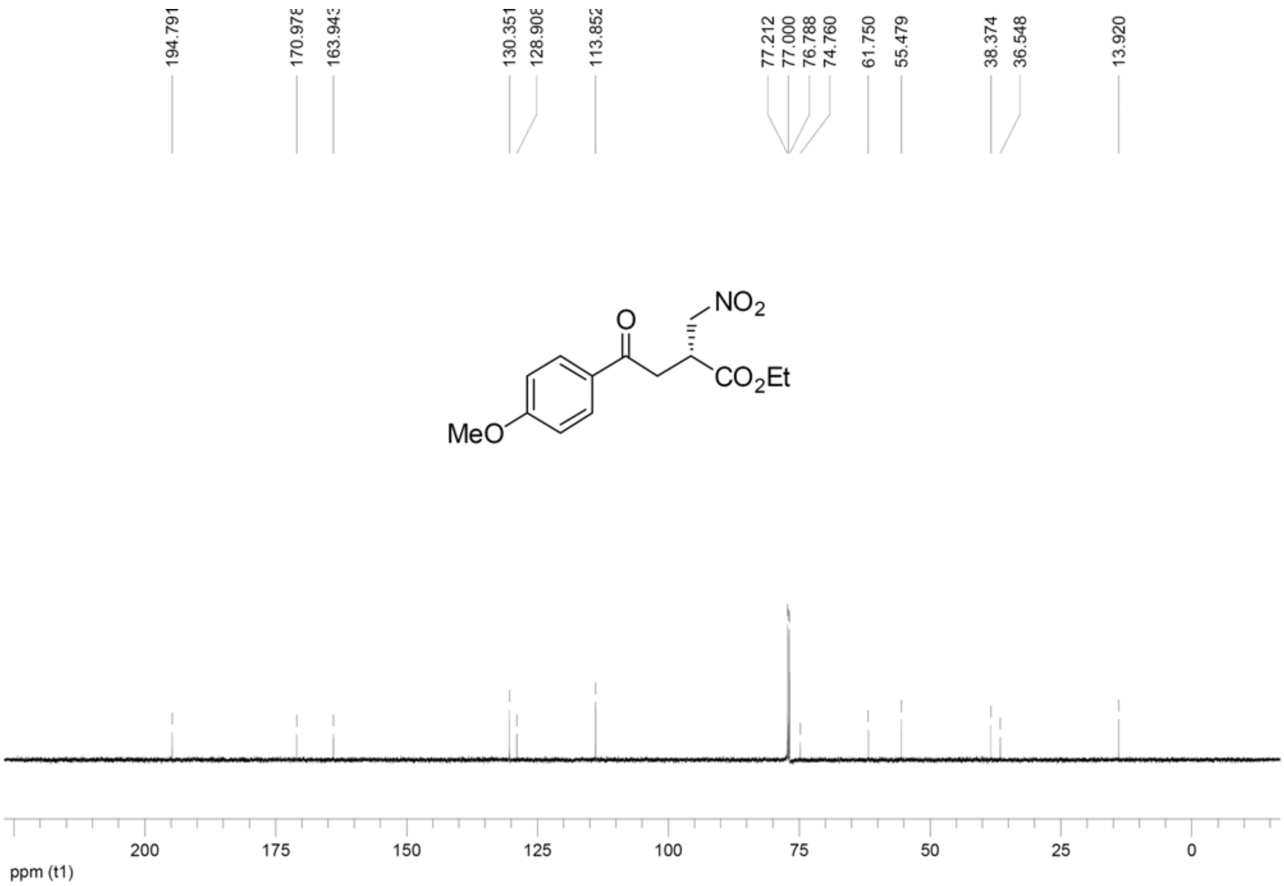
7.931
7.268
6.957
6.943
4.874
4.863
4.850
4.839
4.798
4.789
4.774
4.765
4.231
4.227
4.219
4.215
4.208
4.204
4.196
3.882
3.759
3.750
3.740
3.729
3.720
3.563
3.555
3.533
3.525
3.356
3.345
3.326
3.314
1.267
1.255
1.243
-0.000
NO2
O
CO2Et
MeO
2.02
2.00
1.11
1.08
1.97
3.34
1.02
1.14
1.15
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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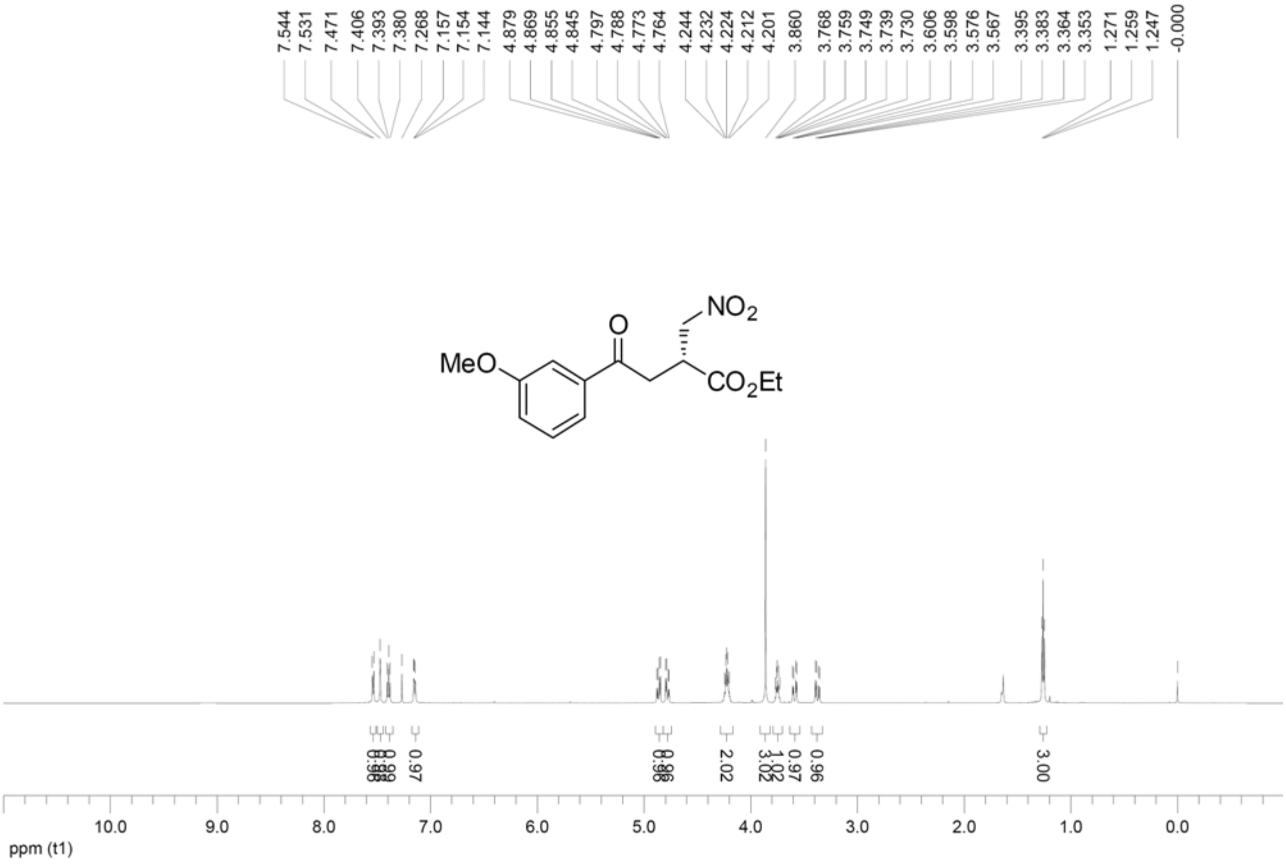
170.978
163.943
130.351
128.908
113.852
77.212
77.000
76.788
74.760
61.750
55.479
38.374
36.548
13.920
NO2
O
CO2Et
MeO
200
175
150
125
100
75
50
25
0
ppm (t1)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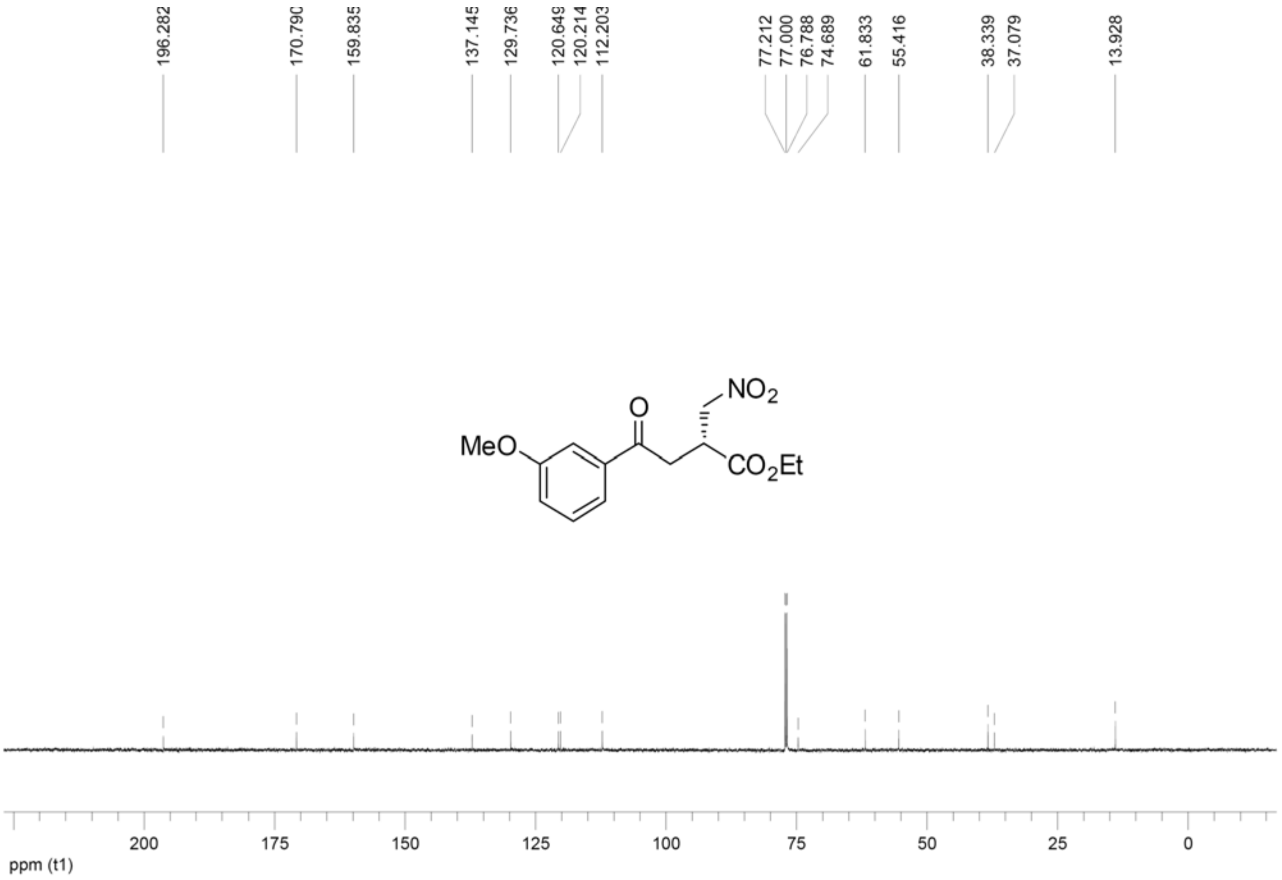
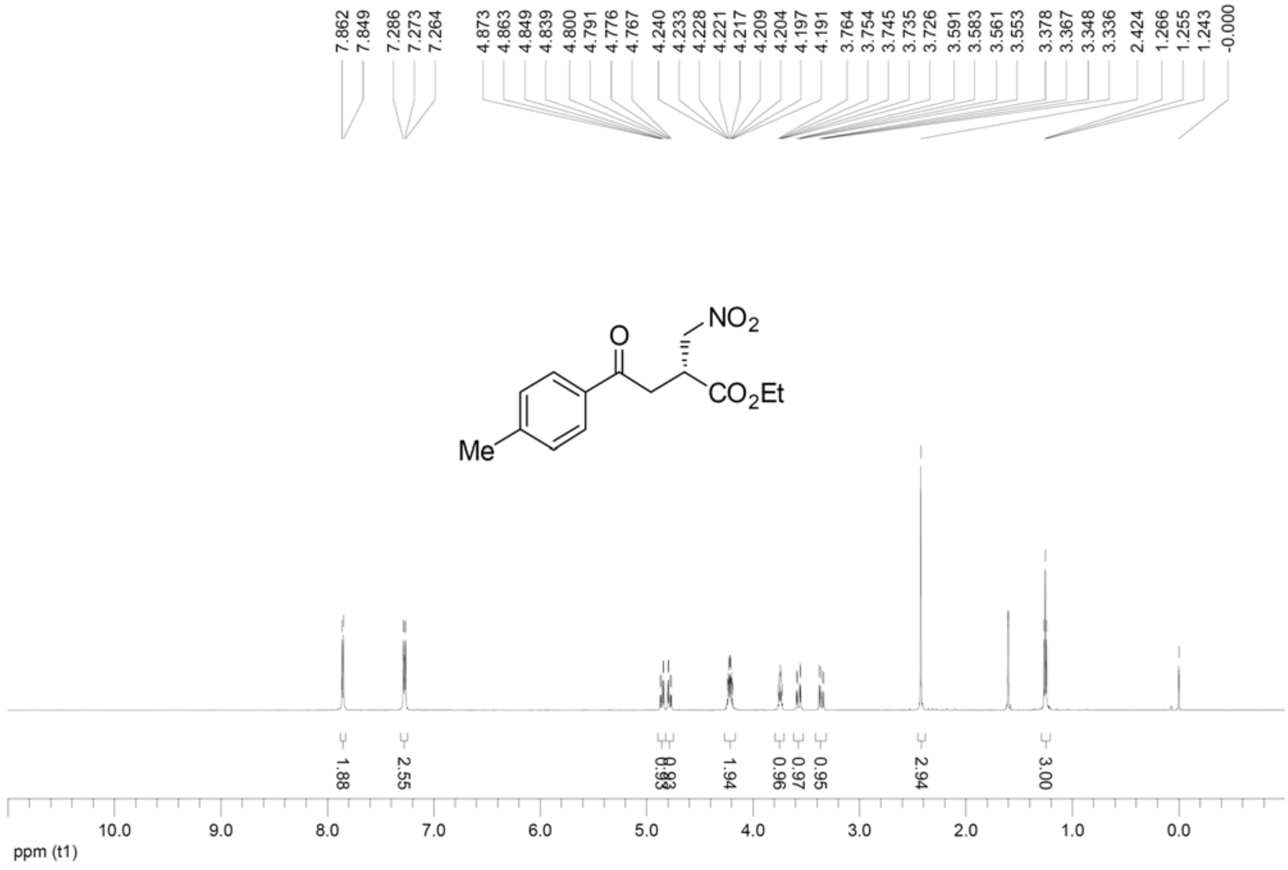
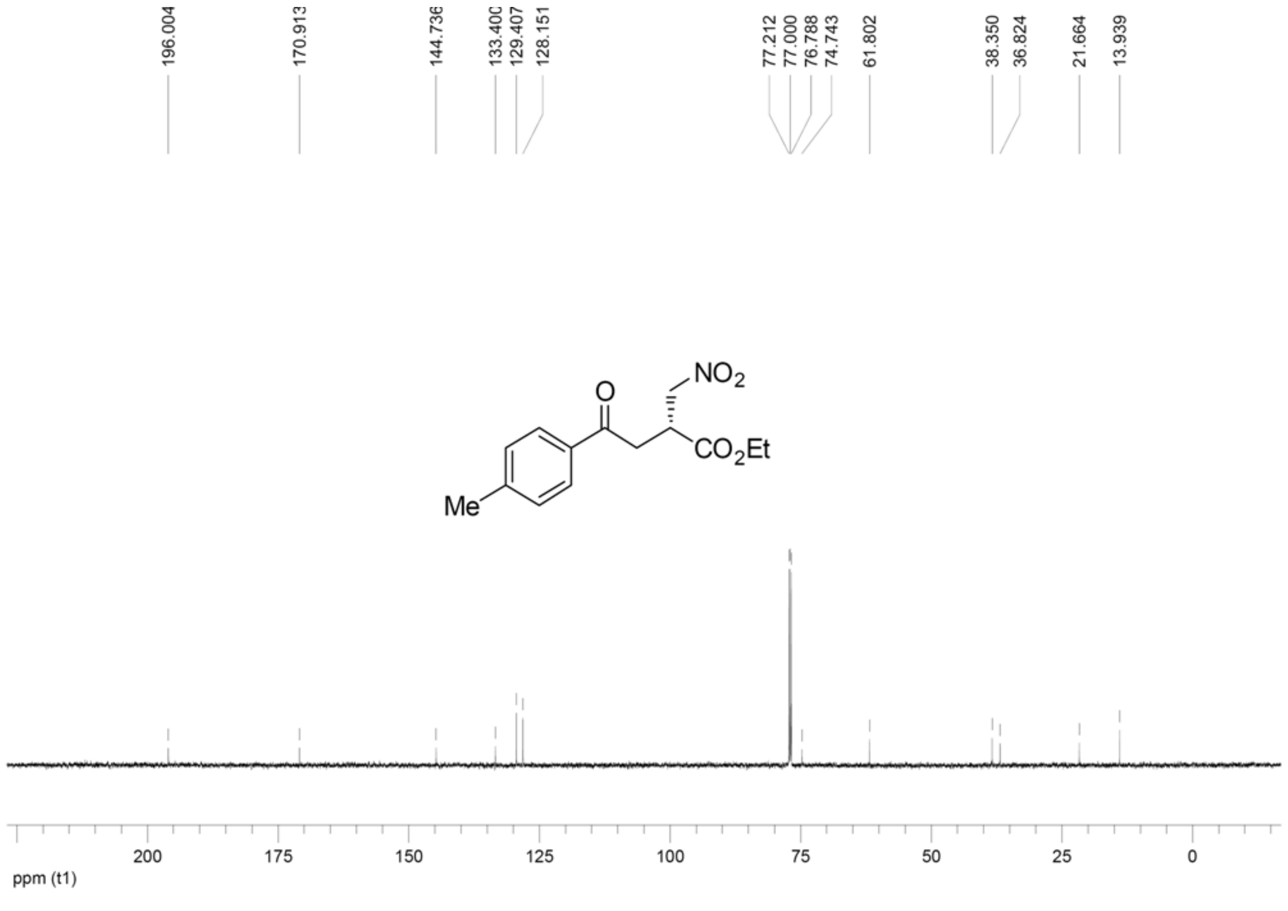
7.531
7.471
7.406
7.393
7.380
7.268
7.157
7.154
7.144
4.879
4.869
4.855
4.845
4.797
4.788
4.773
4.764
4.244
4.232
4.224
4.212
4.201
3.860
3.768
3.759
3.749
3.739
3.730
3.606
3.598
3.576
3.567
3.395
3.383
3.364
3.353
1.271
1.259
1.247
-0.000
MeO
O
NO2
CO2Et
0.97
2.02
3.02
0.97
0.96
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


196.282
170.790
159.835
137.145
129.736
120.649
120.214
112.203
77.212
77.000
76.788
74.689
61.833
55.416
38.339
37.079
13.928
MeO
O
NO2
CO2Et
200
175
150
125
100
75
50
25
0
ppm (t1)


7.862
7.849
7.286
7.273
7.264
4.873
4.863
4.849
4.839
4.800
4.791
4.776
4.767
4.240
4.233
4.228
4.221
4.217
4.209
4.204
4.197
4.191
3.764
3.754
3.745
3.735
3.726
3.591
3.583
3.561
3.553
3.378
3.367
3.348
3.336
2.424
1.266
1.255
1.243
-0.000
O
NO2
CO2Et
Me
1.88
2.55
0.93
0.93
1.94
0.96
0.97
0.95
2.94
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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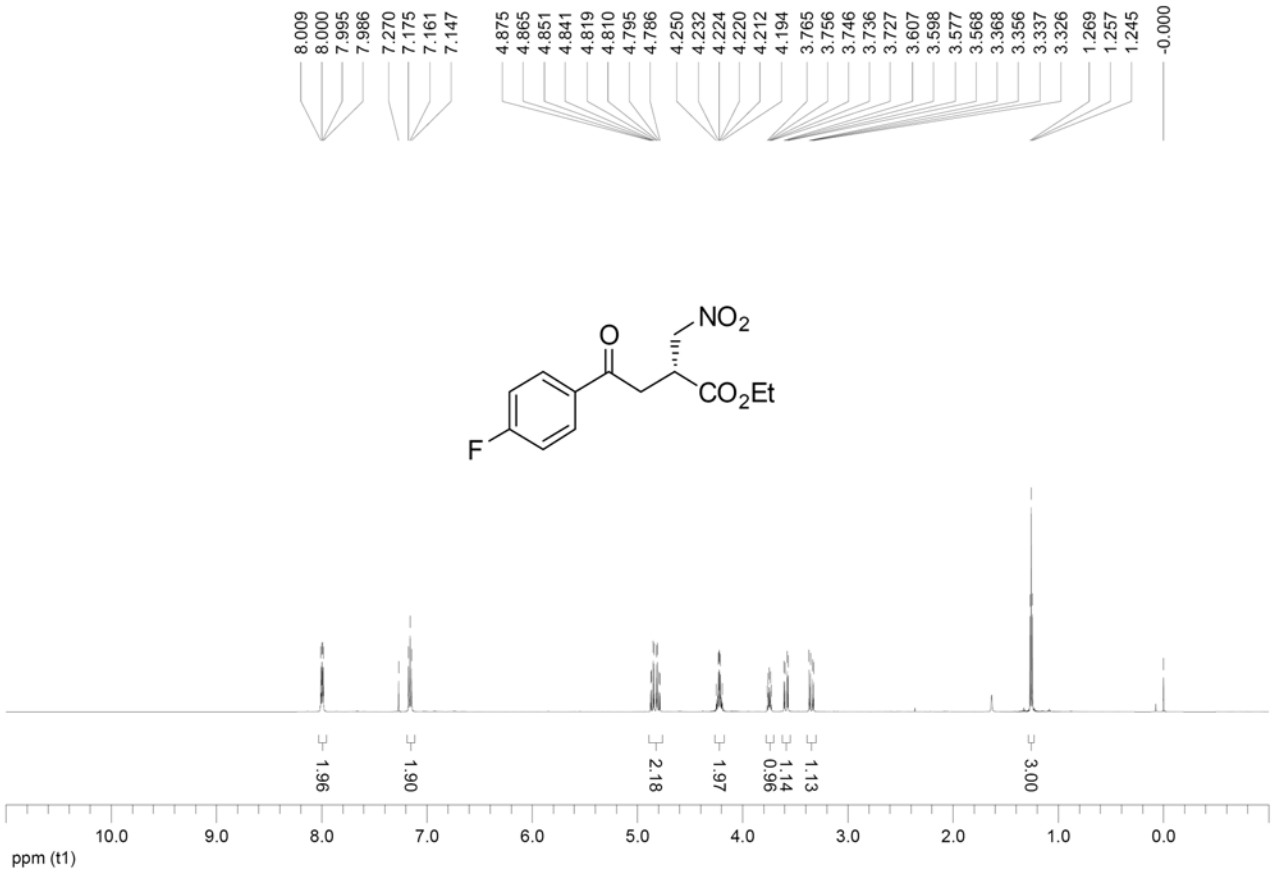
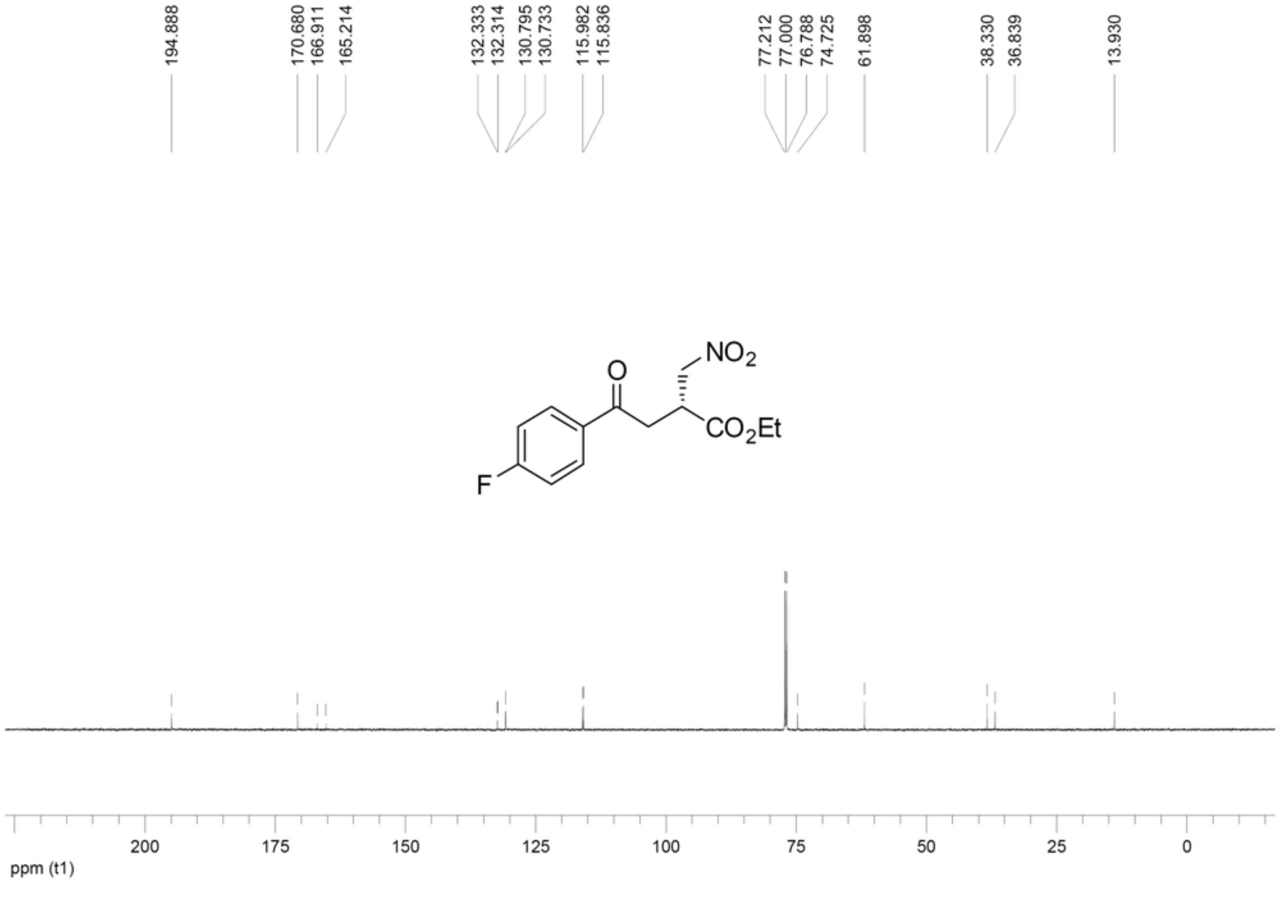
170.913
144.736
133.400
129.407
128.151
77.212
77.000
76.788
74.743
61.802
38.350
36.824
21.664
13.939
O
NO2
CO2Et
Me
200
175
150
125
100
75
50
25
0
ppm (t1)


8.009
8.000
7.995
7.986
7.270
7.175
7.161
7.147
4.875
4.865
4.851
4.841
4.819
4.810
4.795
4.786
4.250
4.232
4.224
4.220
4.212
4.194
3.765
3.756
3.746
3.736
3.727
3.607
3.598
3.577
3.568
3.368
3.356
3.337
3.326
1.269
1.257
1.245
-0.000
O
NO2
CO2Et
F
1.96
1.90
2.18
1.97
0.96
1.14
1.13
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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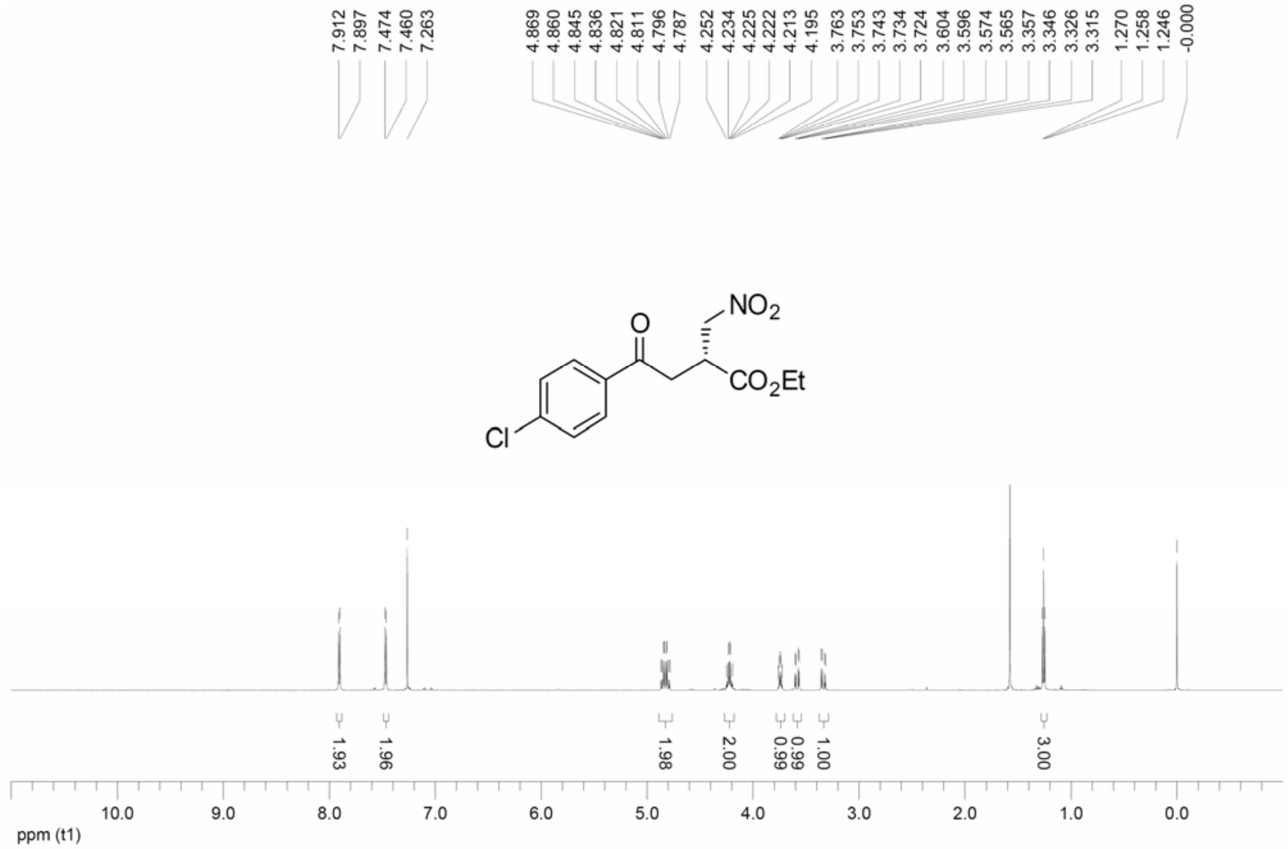
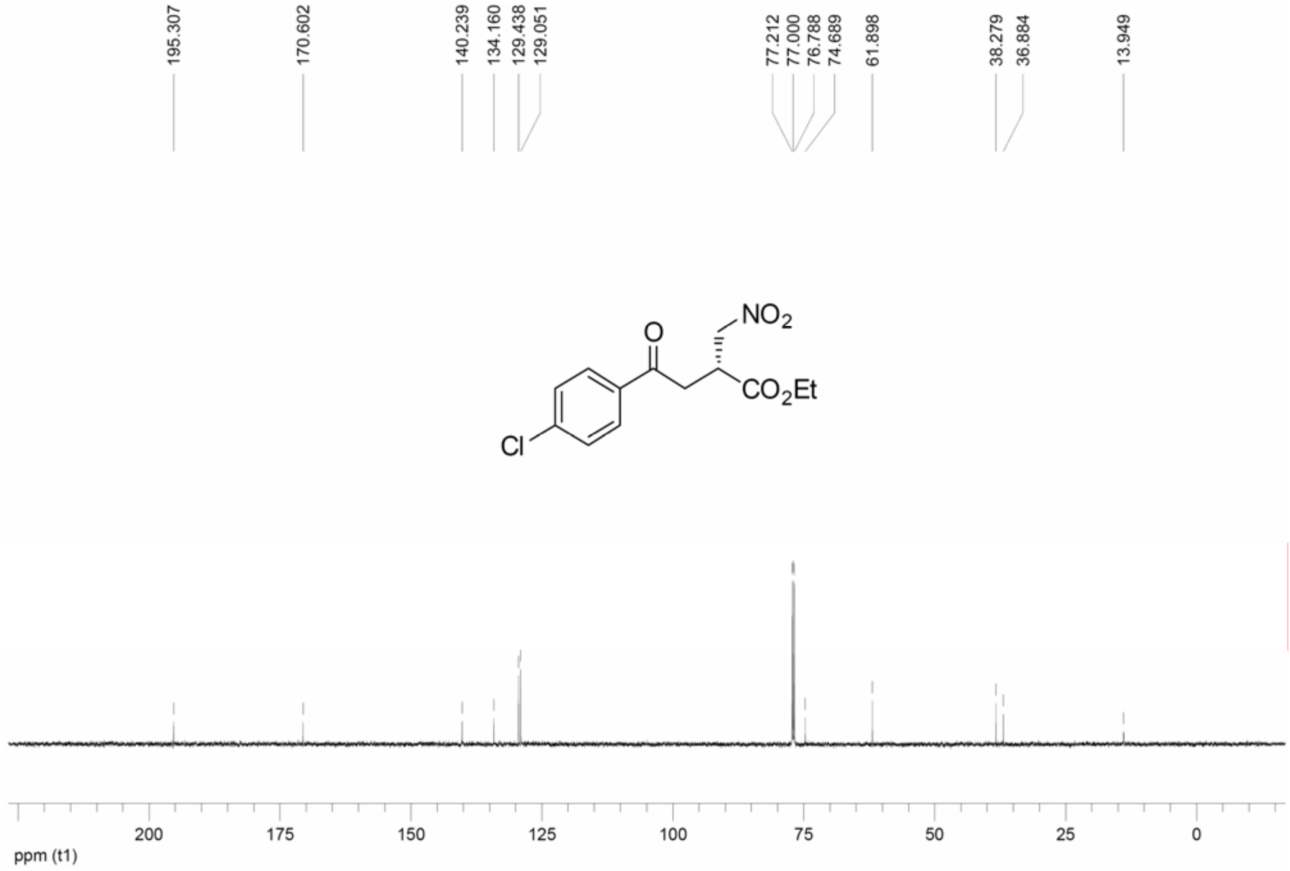
170.680
166.911
165.214
132.333
132.314
130.795
130.733
115.982
115.836
77.212
77.000
76.788
74.725
61.898
38.330
36.839
13.930
O
NO2
CO2Et
F
200
175
150
125
100
75
50
25
0
ppm (t1)


7.912
7.897
7.474
7.460
7.263
4.869
4.860
4.845
4.836
4.821
4.811
4.796
4.787
4.252
4.234
4.225
4.222
4.213
4.195
3.763
3.753
3.743
3.734
3.724
3.604
3.596
3.574
3.565
3.357
3.346
3.326
3.315
1.270
1.258
1.246
-0.000
NO2
O
CO2Et
Cl
1.93
1.96
1.98
2.00
0.99
0.99
1.00
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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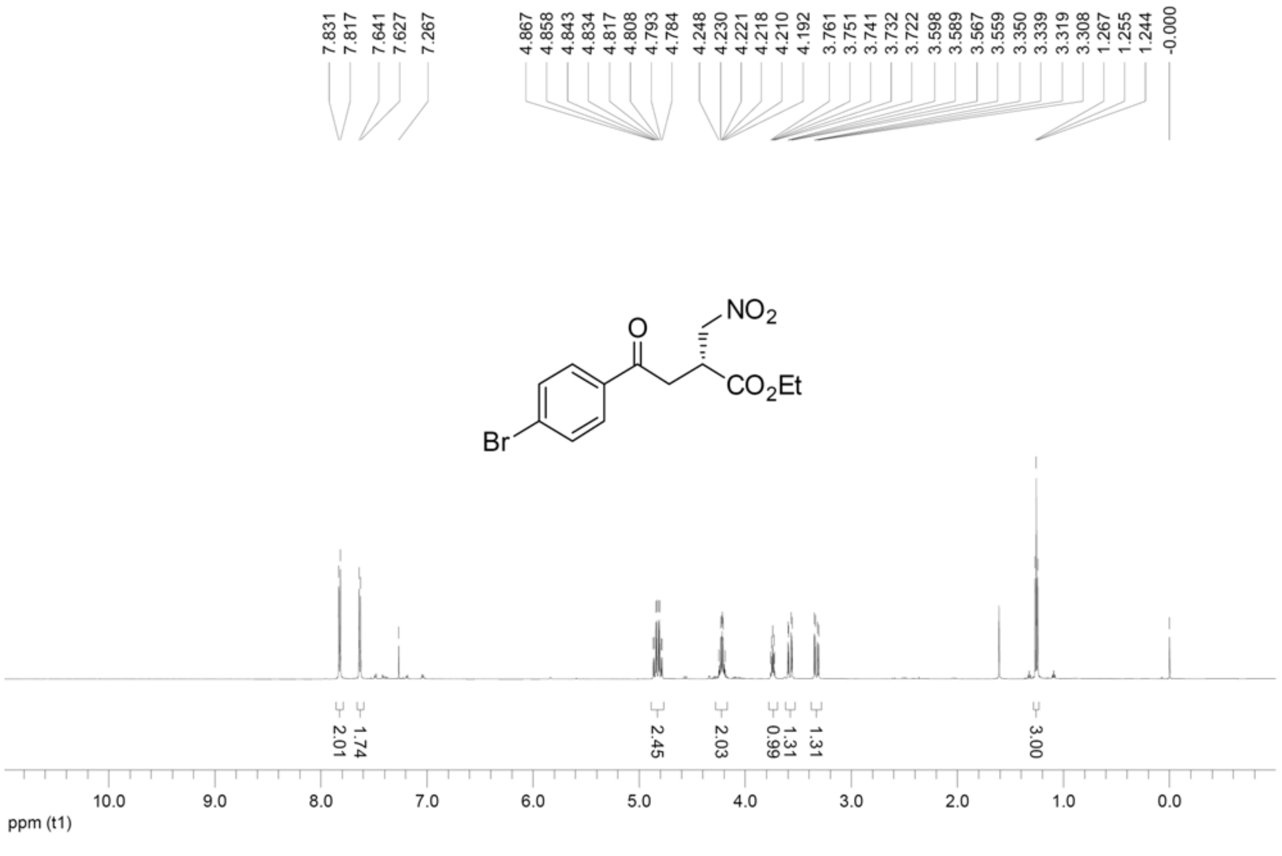
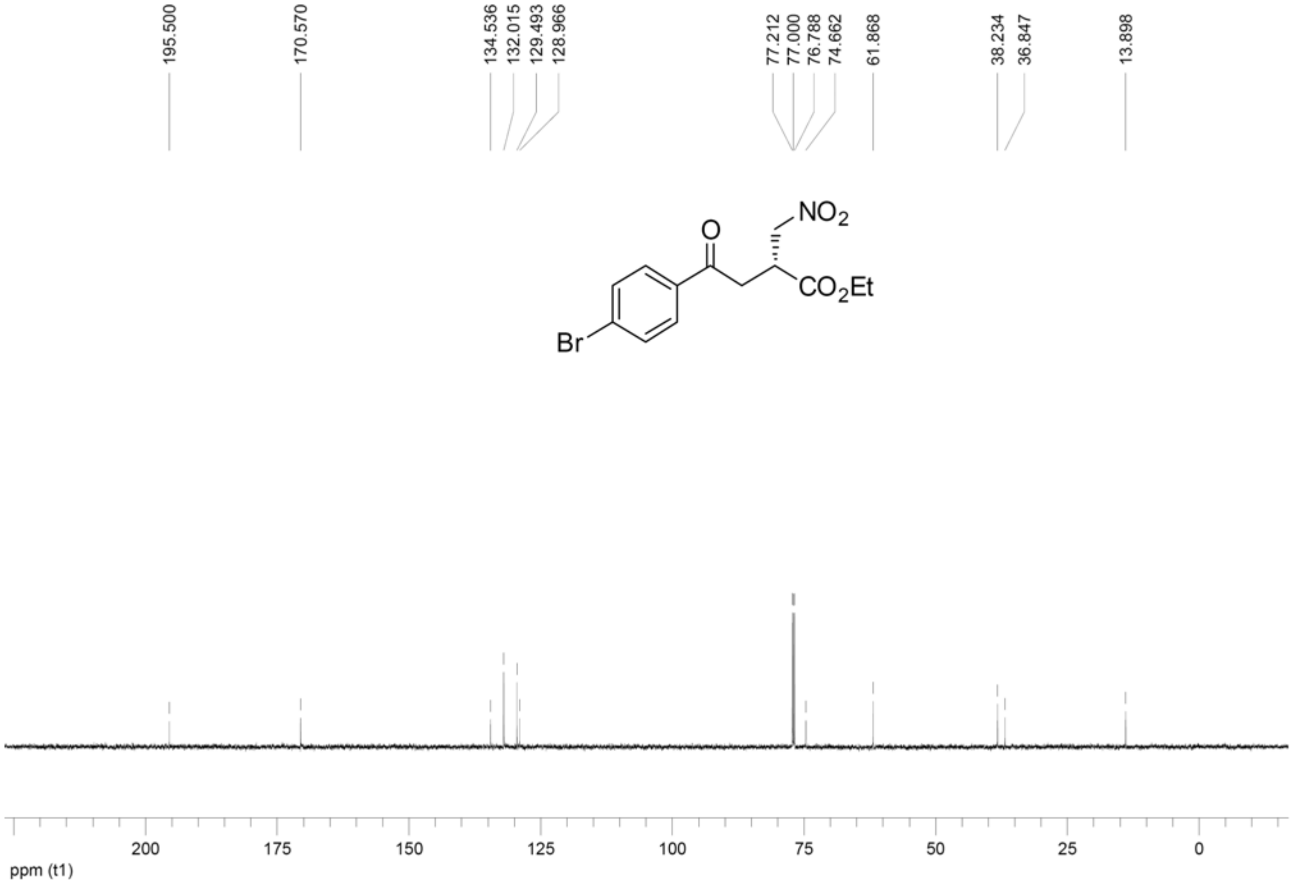
170.602
140.239
134.160
129.438
129.051
77.212
77.000
76.788
74.689
61.898
38.279
36.884
13.949
NO2
O
CO2Et
Cl
200
175
150
125
100
75
50
25
0
ppm (t1)


7.831
7.817
7.641
7.627
7.267
4.867
4.858
4.843
4.834
4.817
4.808
4.793
4.784
4.248
4.230
4.221
4.218
4.210
4.192
3.761
3.751
3.741
3.732
3.722
3.598
3.589
3.567
3.559
3.350
3.339
3.319
3.308
1.267
1.255
1.244
-0.000
NO2
O
CO2Et
Br
2.01
1.74
2.45
2.03
0.99
1.31
1.31
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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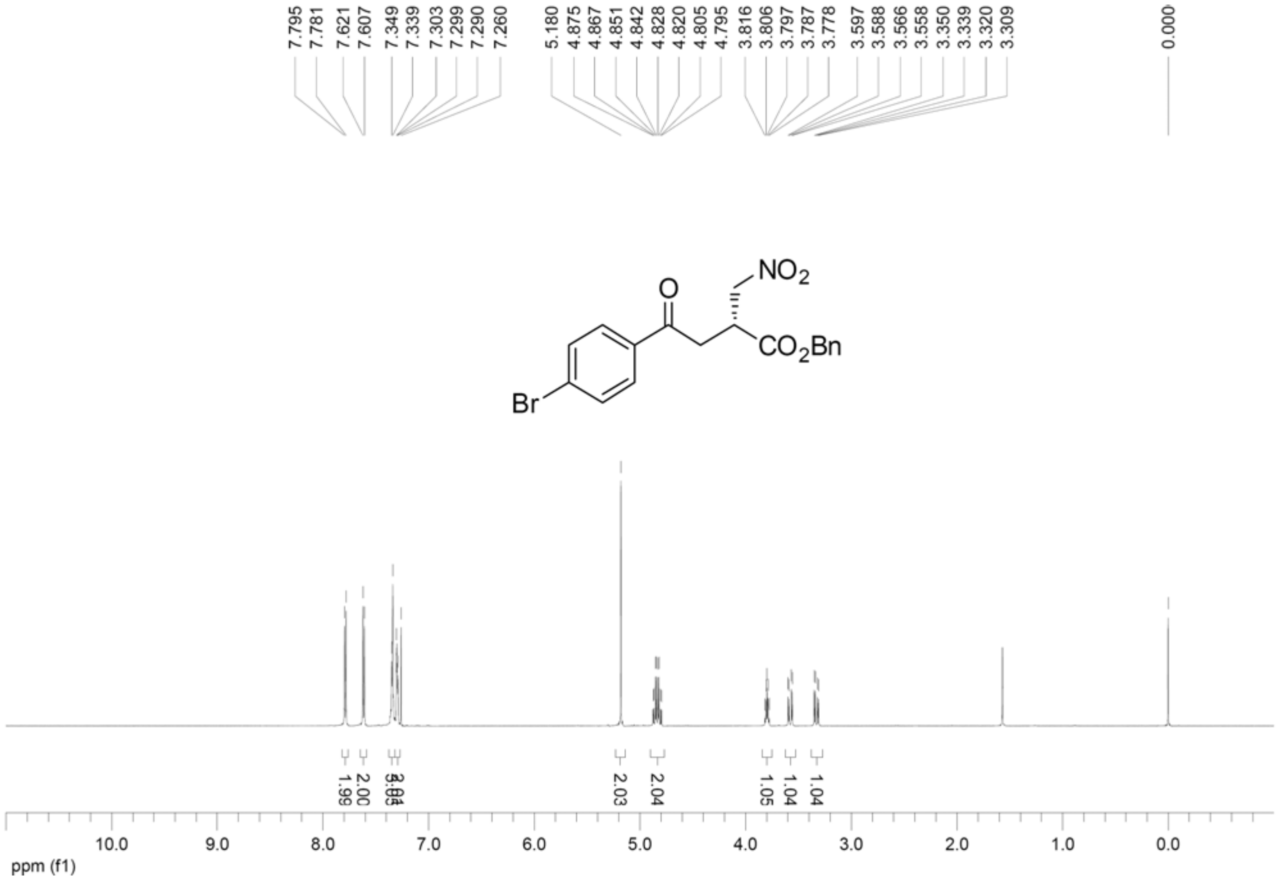
129.493
128.966
77.212
77.000
76.788
74.662
61.868
38.234
36.847
13.898
NO2
O
CO2Et
Br
200
175
150
125
100
75
50
25
0
ppm (t1)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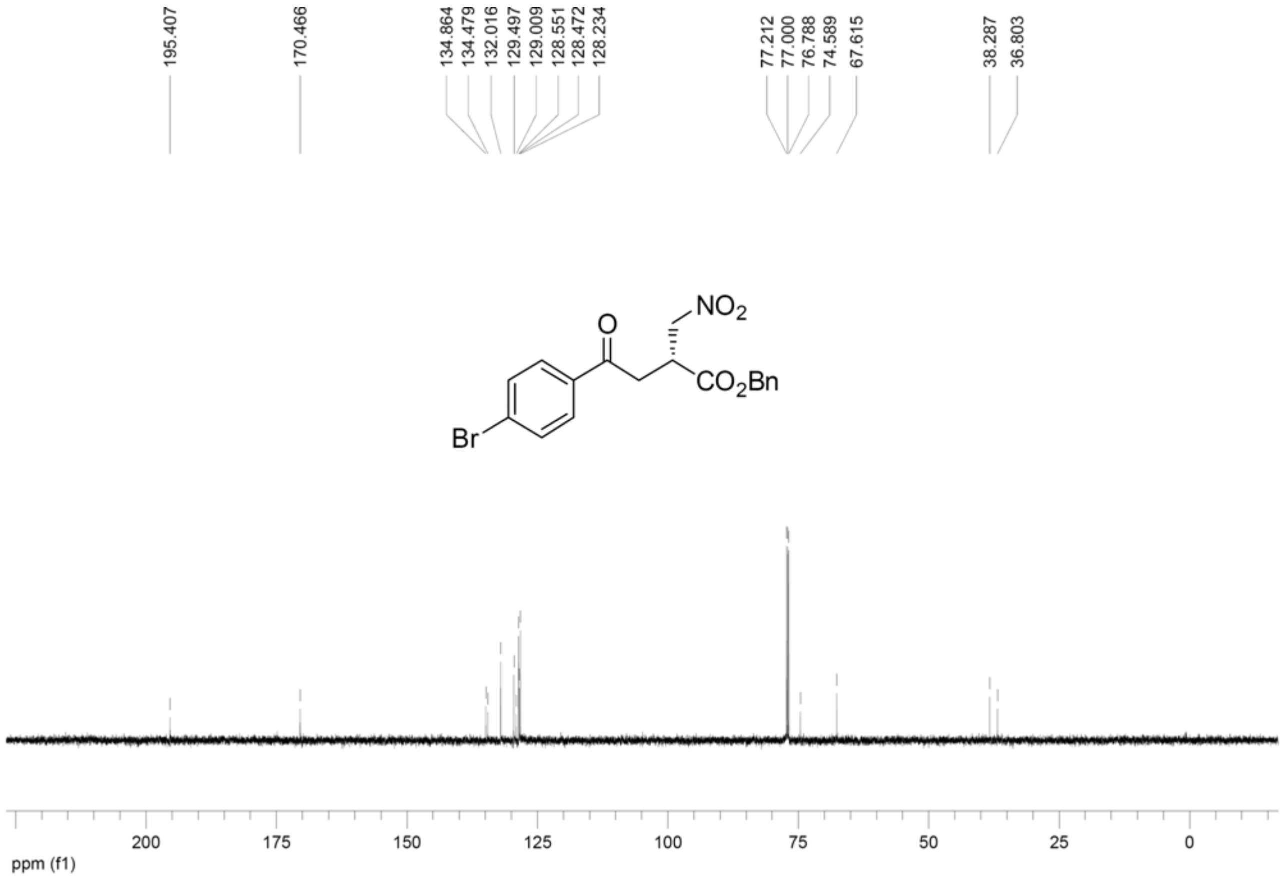
7.621
7.607
7.349
7.339
7.303
7.299
7.290
7.260
5.180
4.875
4.867
4.851
4.842
4.828
4.820
4.805
4.795
3.816
3.806
3.797
3.787
3.778
3.597
3.588
3.566
3.558
3.350
3.339
3.320
3.309
0.000
O
NO2
CO2Bn
Br
1.99
2.00
2.03
2.04
1.05
1.04
1.04
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)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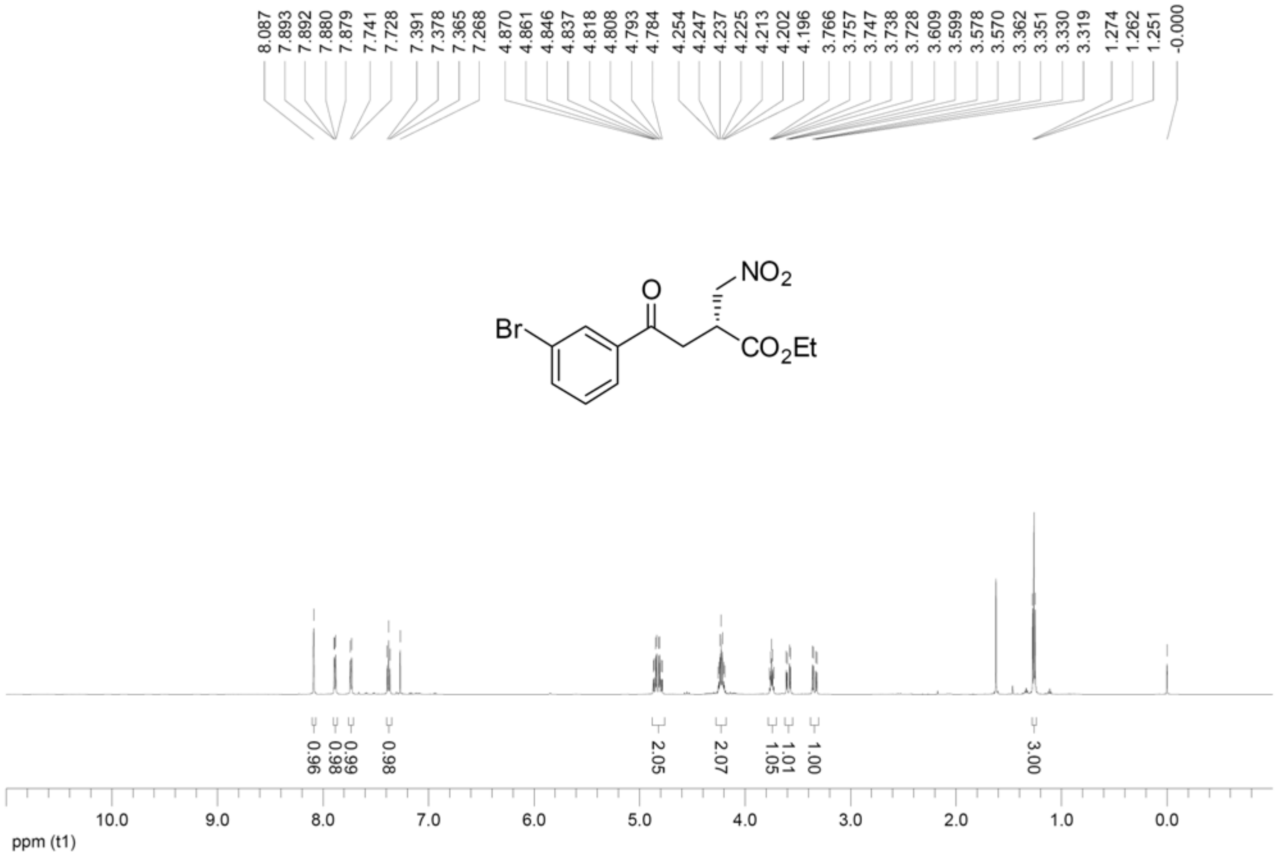
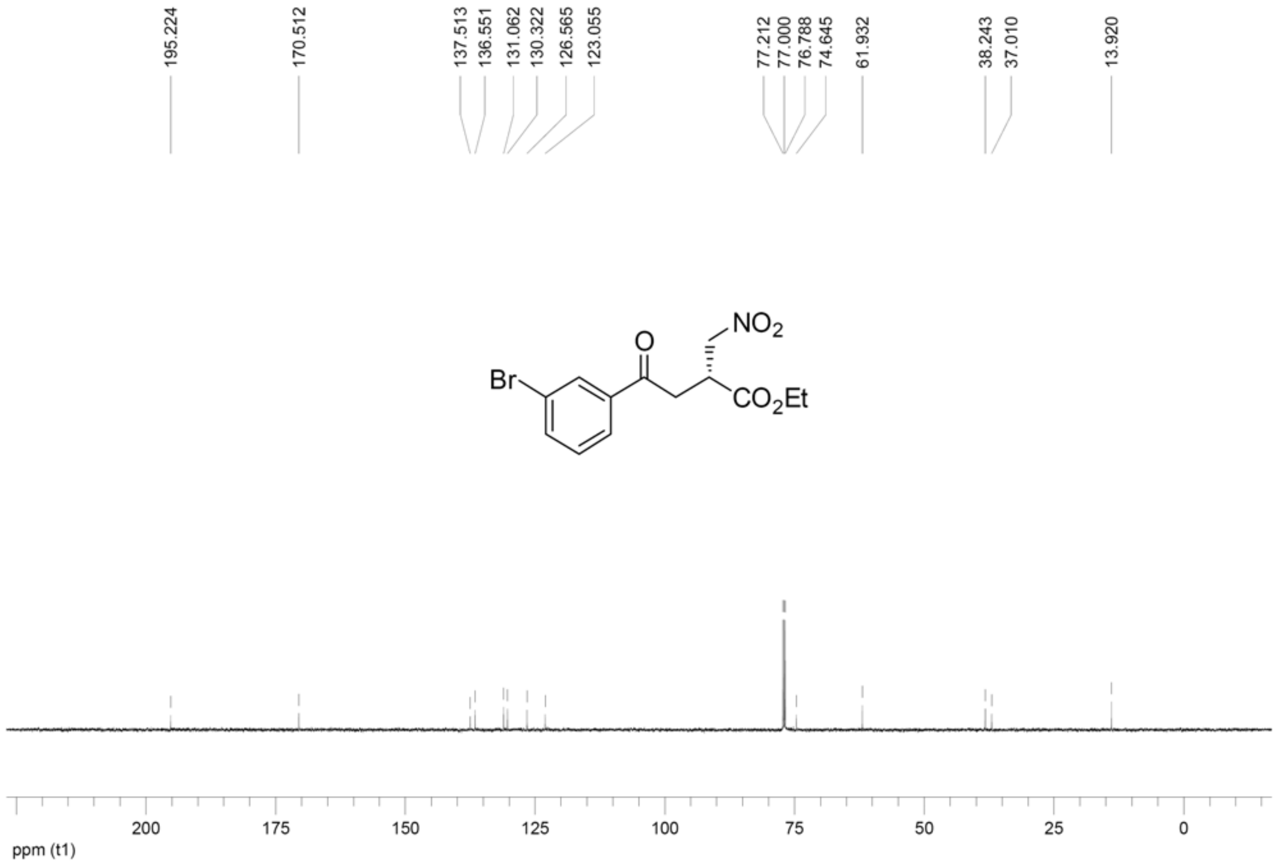
170.466
134.864
134.479
132.016
129.497
129.009
128.551
128.472
128.234
77.212
77.000
76.788
74.589
67.615
38.287
36.803
O
NO2
CO2Bn
Br
200
175
150
125
100
75
50
25
0
ppm (f1)


8.087
7.893
7.892
7.880
7.879
7.741
7.728
7.391
7.378
7.365
7.268
4.870
4.861
4.846
4.837
4.818
4.808
4.793
4.784
4.254
4.247
4.237
4.225
4.213
4.202
4.196
3.766
3.757
3.747
3.738
3.728
3.609
3.599
3.578
3.570
3.362
3.351
3.330
3.319
1.274
1.262
1.251
-0.000
NO2
O
Br
CO2Et
0.96
0.98
0.99
0.98
2.05
2.07
1.05
1.01
1.00
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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136.551
131.062
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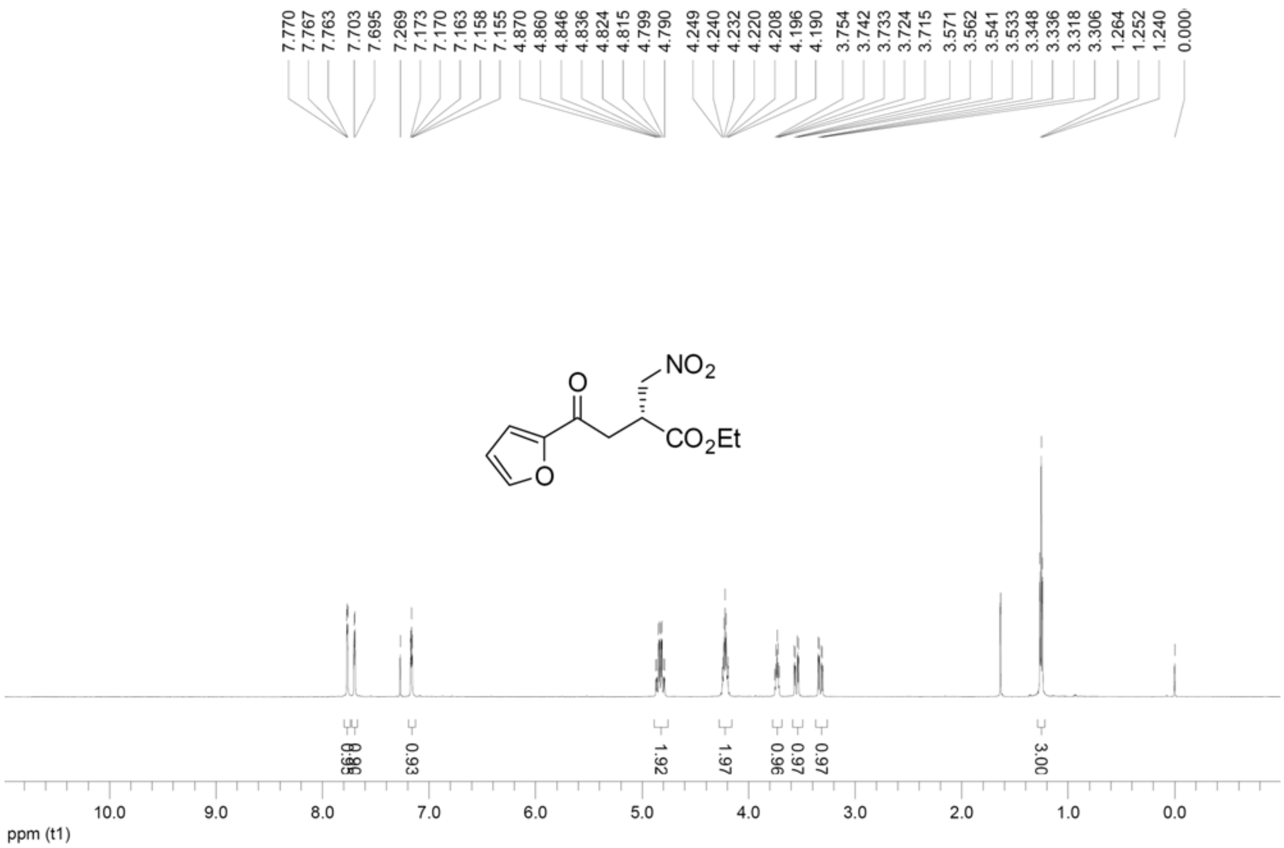
126.565
123.055
77.212
77.000
76.788
74.645
61.932
38.243
37.010
13.920
NO2
O
Br
CO2Et
200
175
150
125
100
75
50
25
0
ppm (t1)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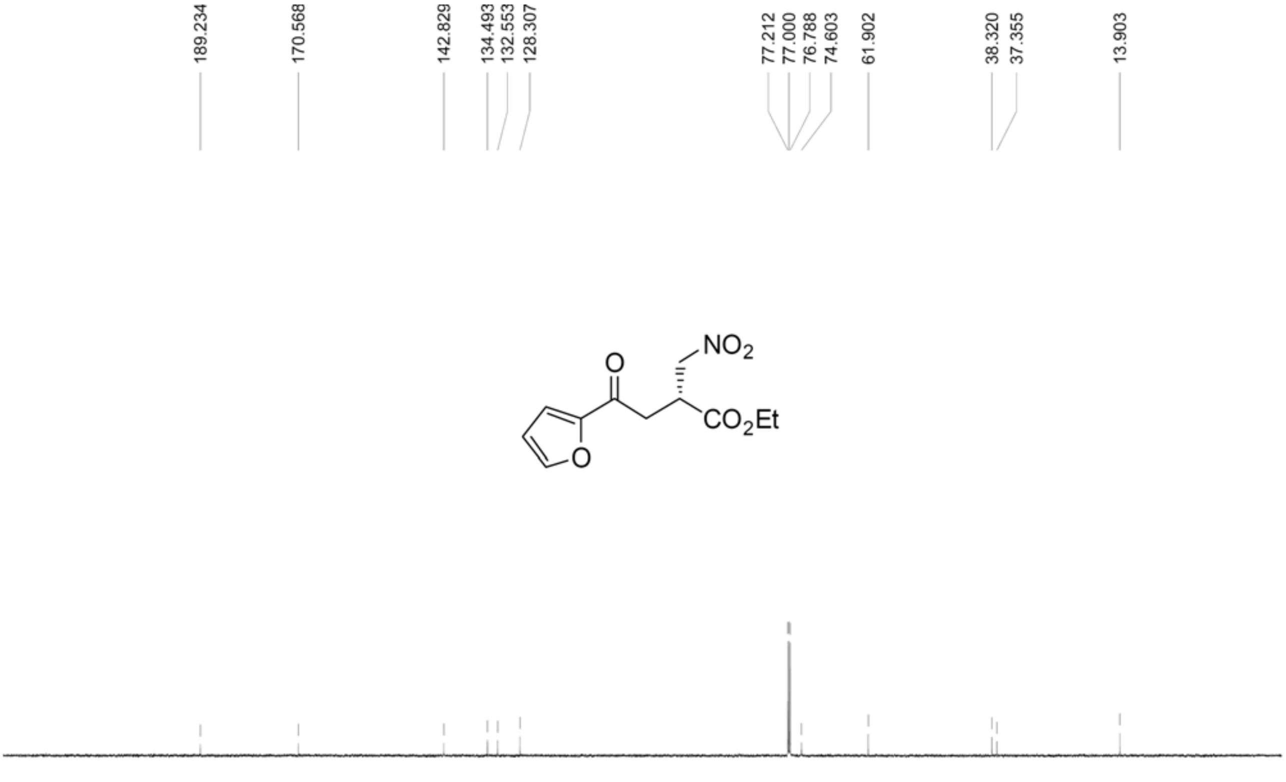
7.767
7.763
7.703
7.695
7.269
7.173
7.170
7.163
7.158
7.155
4.870
4.860
4.846
4.836
4.824
4.815
4.799
4.790
4.249
4.240
4.232
4.220
4.208
4.196
4.190
3.754
3.742
3.733
3.724
3.715
3.571
3.562
3.541
3.533
3.348
3.336
3.318
3.306
1.264
1.252
1.240
0.000
NO2
O
CO2Et
O
0.93
1.92
1.97
0.96
0.97
0.97
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


189.234
170.568
142.829
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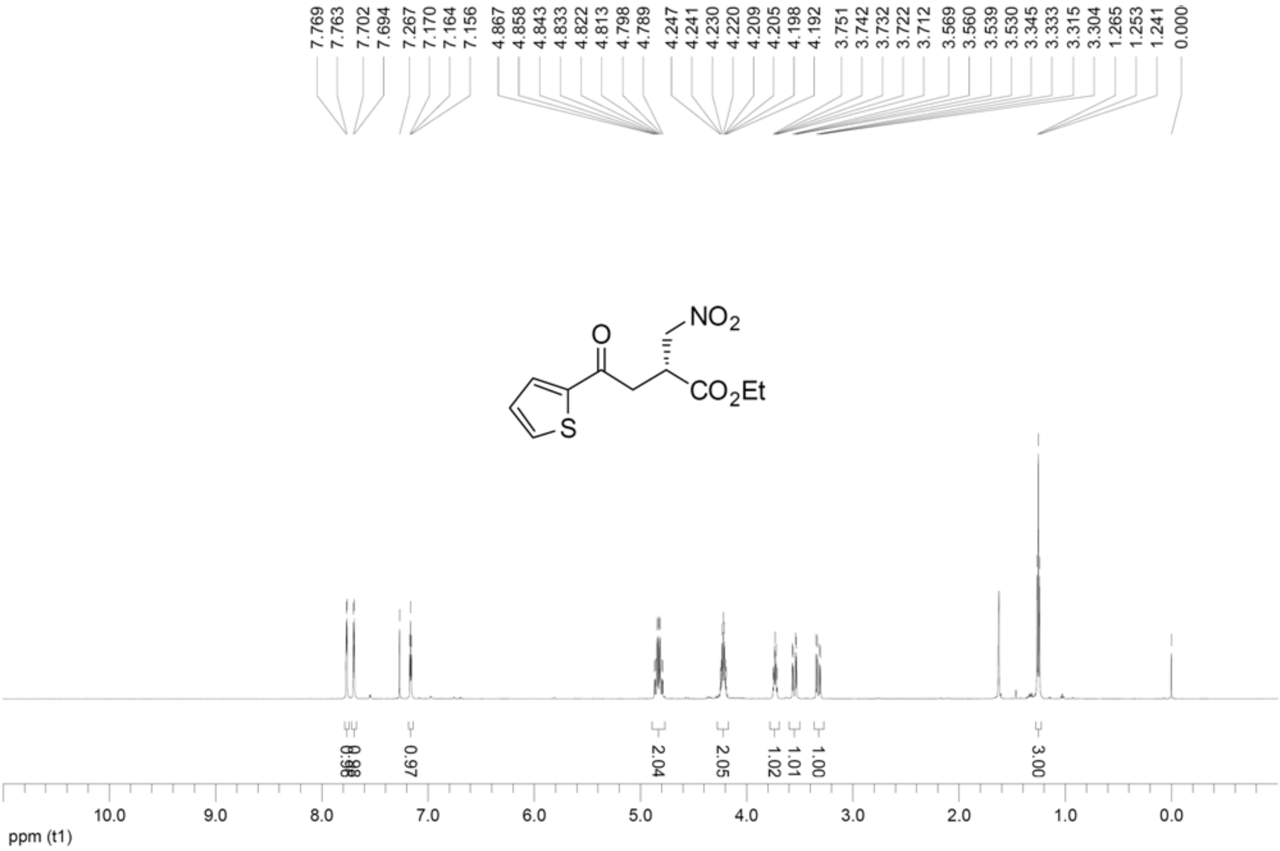
132.553
128.307
77.212
77.000
76.788
74.603
61.902
38.320
37.355
13.903
NO2
O
CO2Et
O
200
175
150
125
100
75
50
25
0
ppm (t1)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7.763
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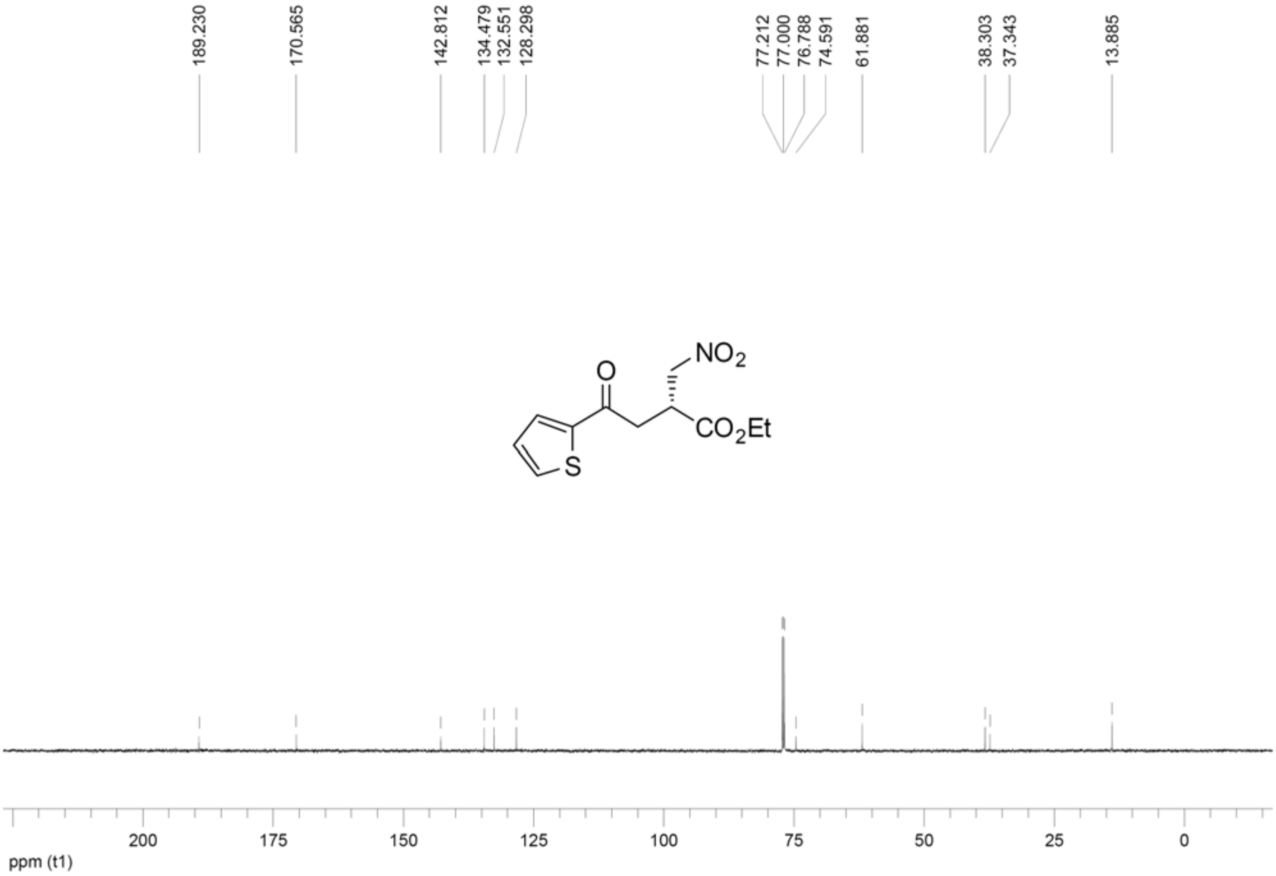
7.694
7.267
7.170
7.164
7.156
4.867
4.858
4.843
4.833
4.822
4.813
4.798
4.789
4.247
4.241
4.230
4.220
4.209
4.205
4.198
4.192
3.751
3.742
3.732
3.722
3.712
3.569
3.560
3.539
3.530
3.345
3.333
3.315
3.304
1.265
1.253
1.241
0.000
O
NO2
CO2Et
S
0.97
2.04
2.05
1.02
1.01
1.00
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


189.230
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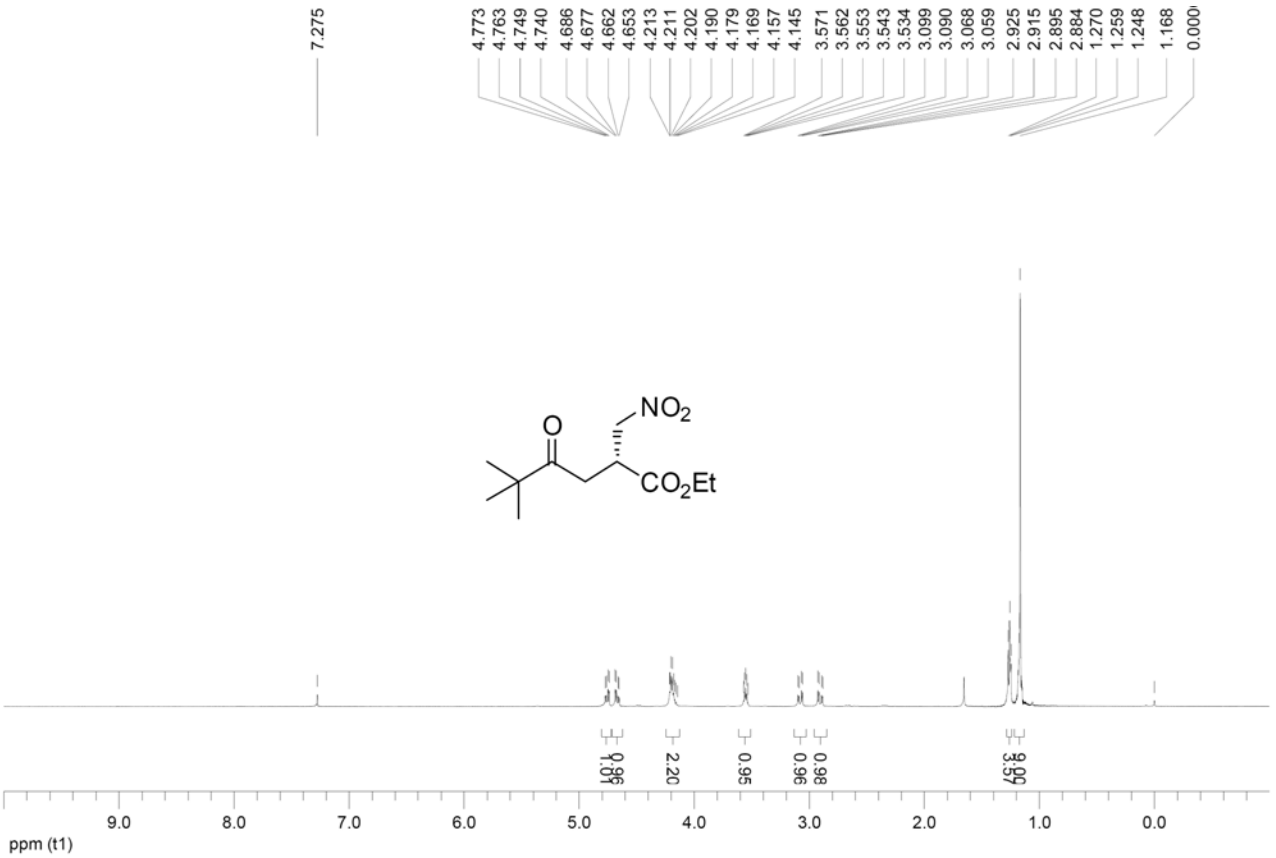
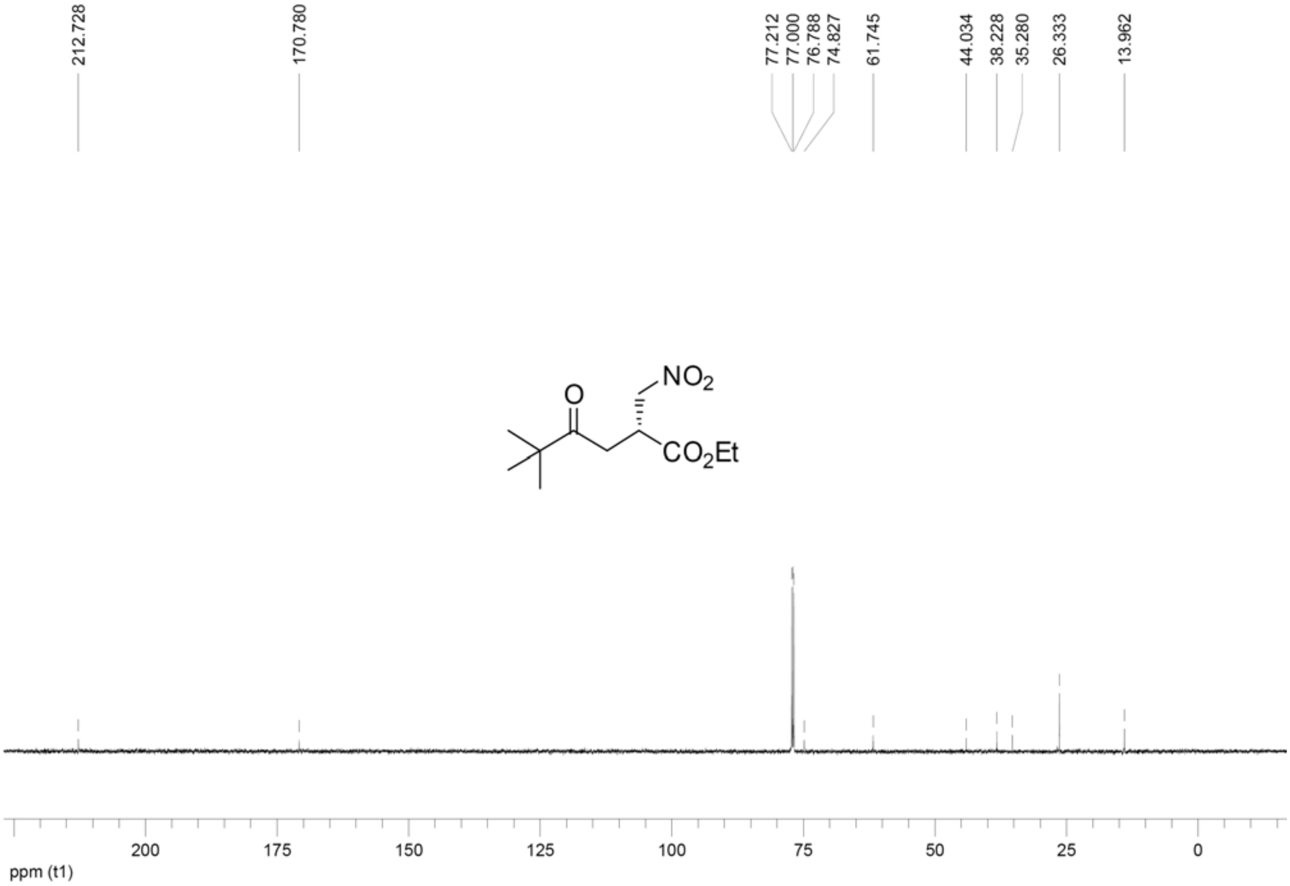
142.812
134.479
132.551
128.298
77.212
77.000
76.788
74.591
61.881
38.303
37.343
13.885
O
NO2
CO2Et
S
200
175
150
125
100
75
50
25
0
ppm (t1)


7.275
4.773
4.763
4.749
4.740
4.686
4.677
4.662
4.653
4.213
4.211
4.202
4.190
4.179
4.169
4.157
4.145
3.571
3.562
3.553
3.543
3.534
3.099
3.090
3.068
3.059
2.925
2.915
2.895
2.884
1.270
1.259
1.248
1.168
0.000
NO2
O
CO2Et
1.01
0.96
2.20
0.95
0.96
0.98
3.57
9.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


212.728
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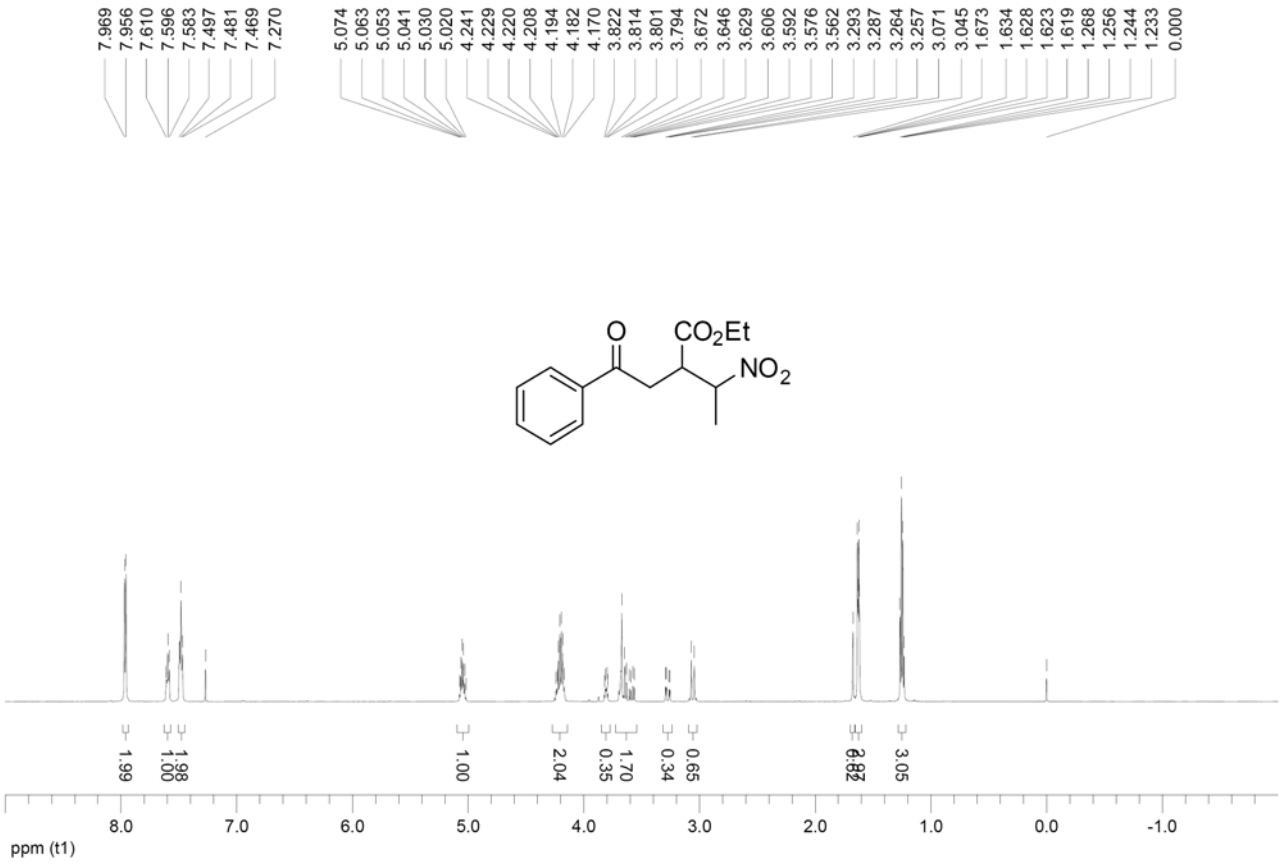
77.212
77.000
76.788
74.827
61.745
44.034
38.228
35.280
26.333
13.962
NO2
O
CO2Et
200
175
150
125
100
75
50
25
0
ppm (t1)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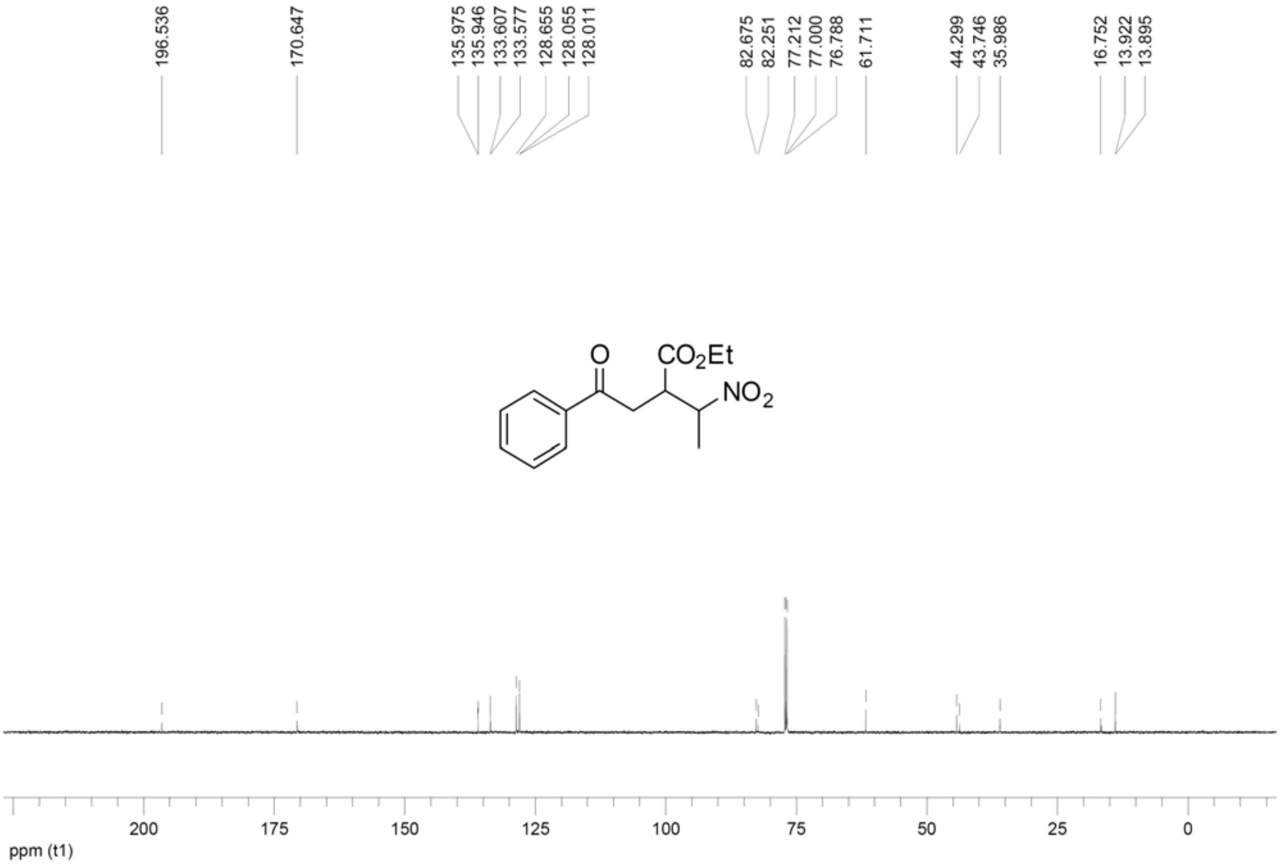
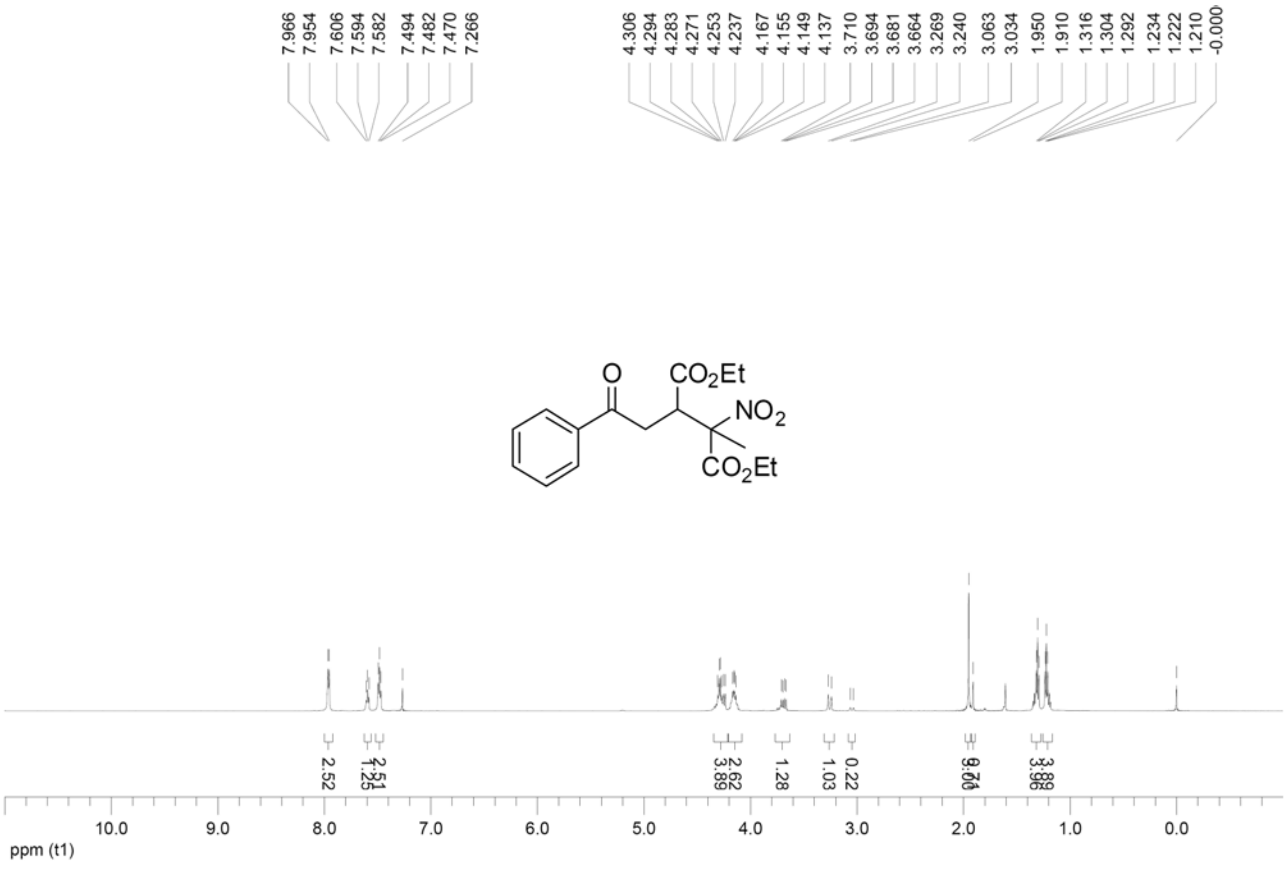
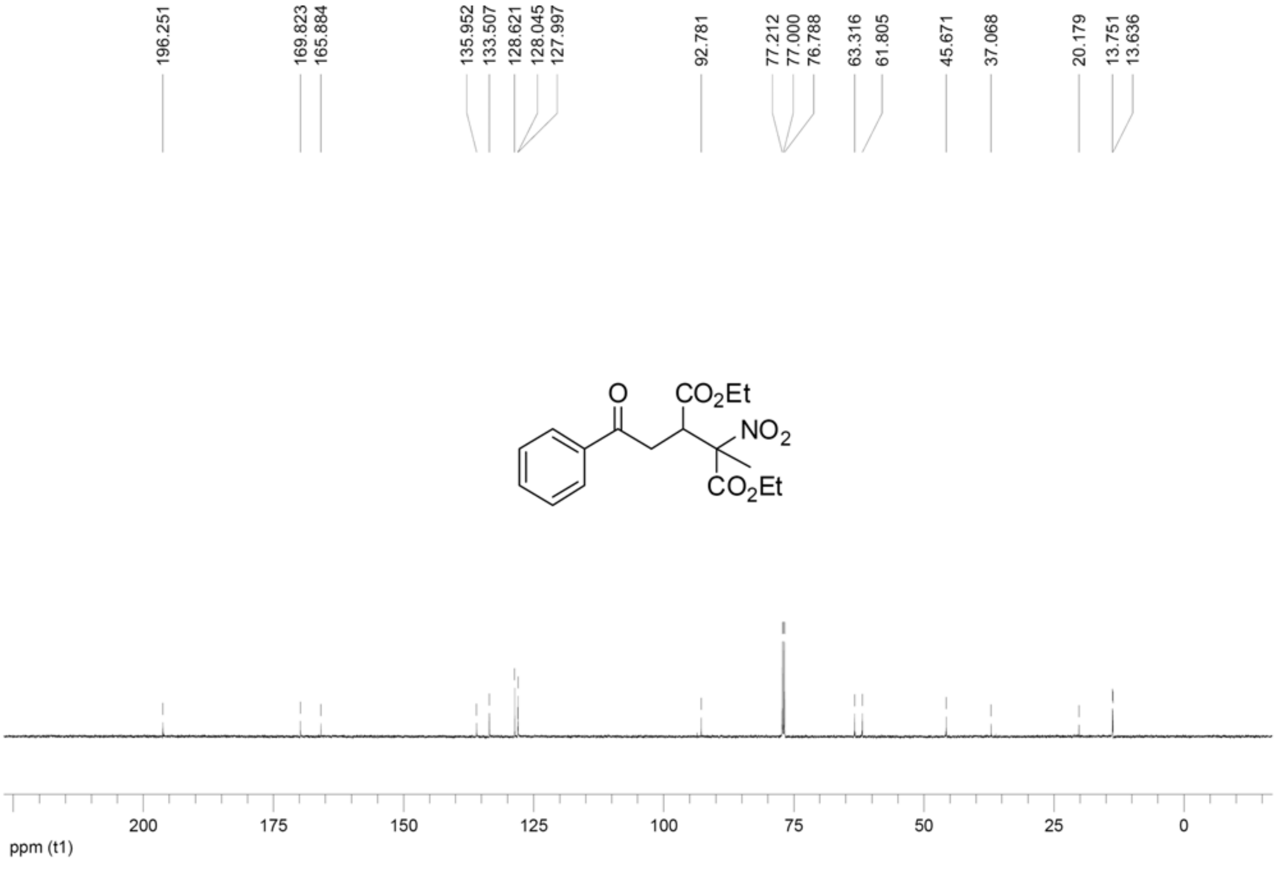
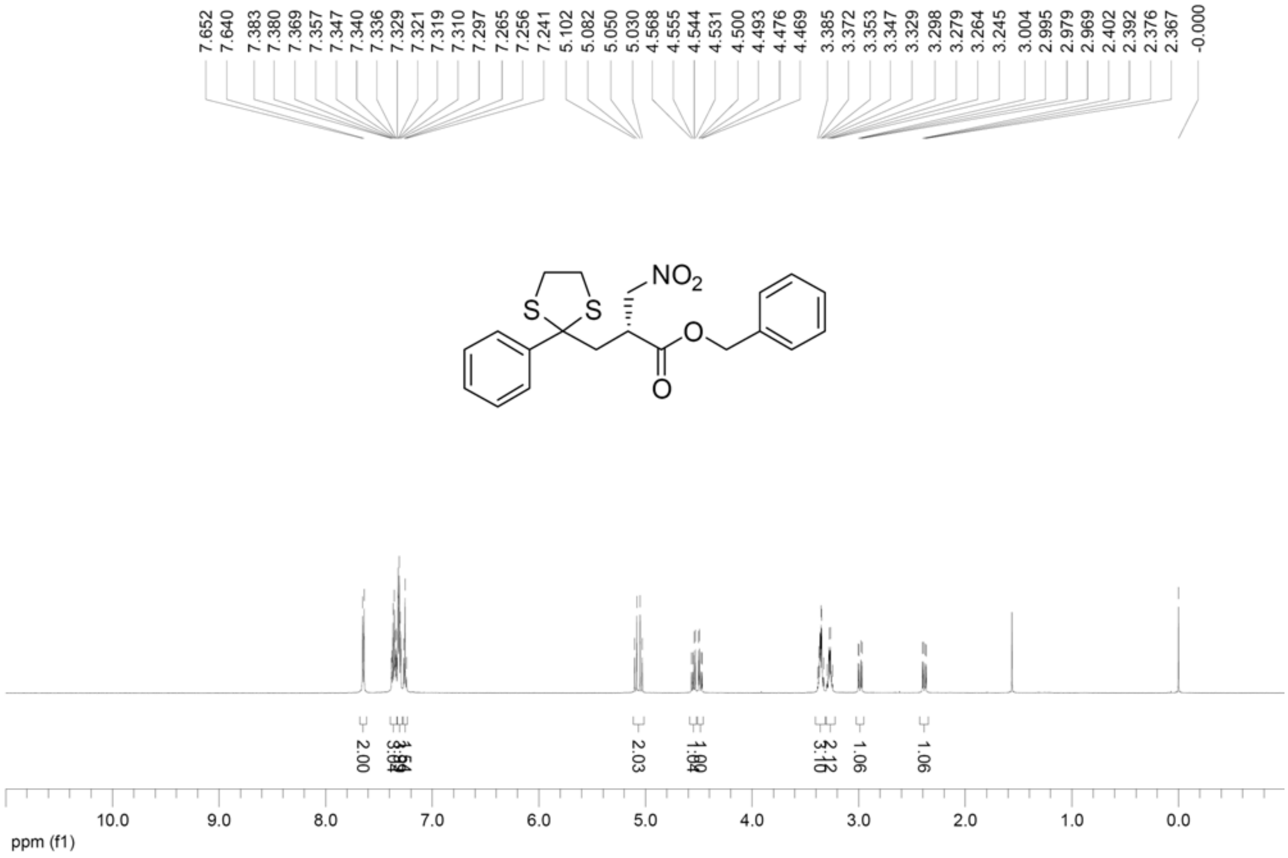
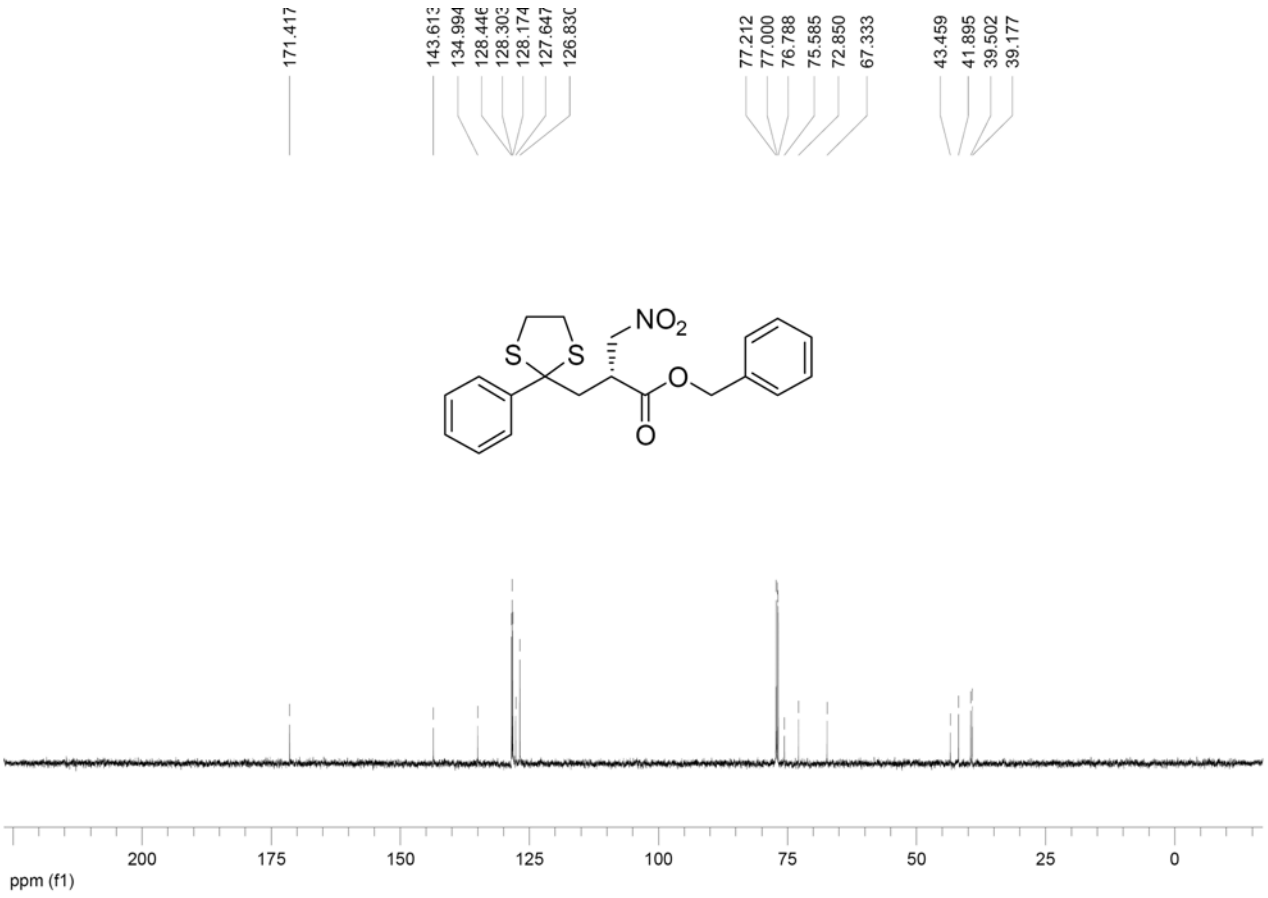
7.956
7.610
7.596
7.583
7.497
7.481
7.469
7.270
5.074
5.063
5.053
5.041
5.030
5.020
4.241
4.229
4.220
4.208
4.194
4.182
4.170
3.822
3.814
3.801
3.794
3.672
3.646
3.629
3.606
3.592
3.576
3.562
3.293
3.287
3.264
3.257
3.071
3.045
1.673
1.634
1.628
1.623
1.619
1.268
1.256
1.244
1.233
0.000
O
CO2Et
NO2
1.99
1.00
1.98
1.00
2.04
0.35
1.70
0.34
0.65
3.05
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
ppm (t1)

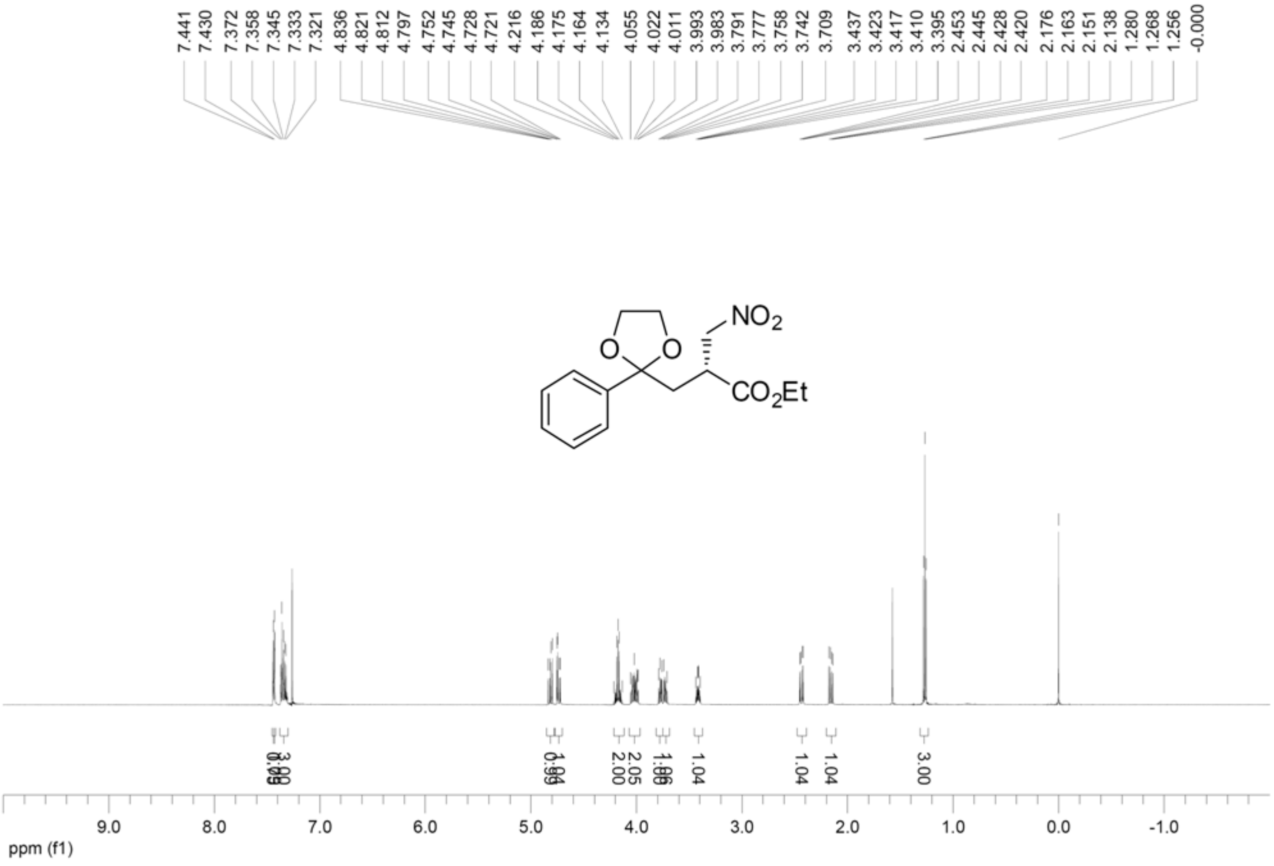

196.536
170.647
135.975
135.946
133.607
133.577
128.655
128.055
128.011
82.675
82.251
77.212
77.000
76.788
61.711
44.299
43.746
35.986
16.752
13.922
13.895
O
CO2Et
NO2
200
175
150
125
100
75
50
25
0
ppm (t1)

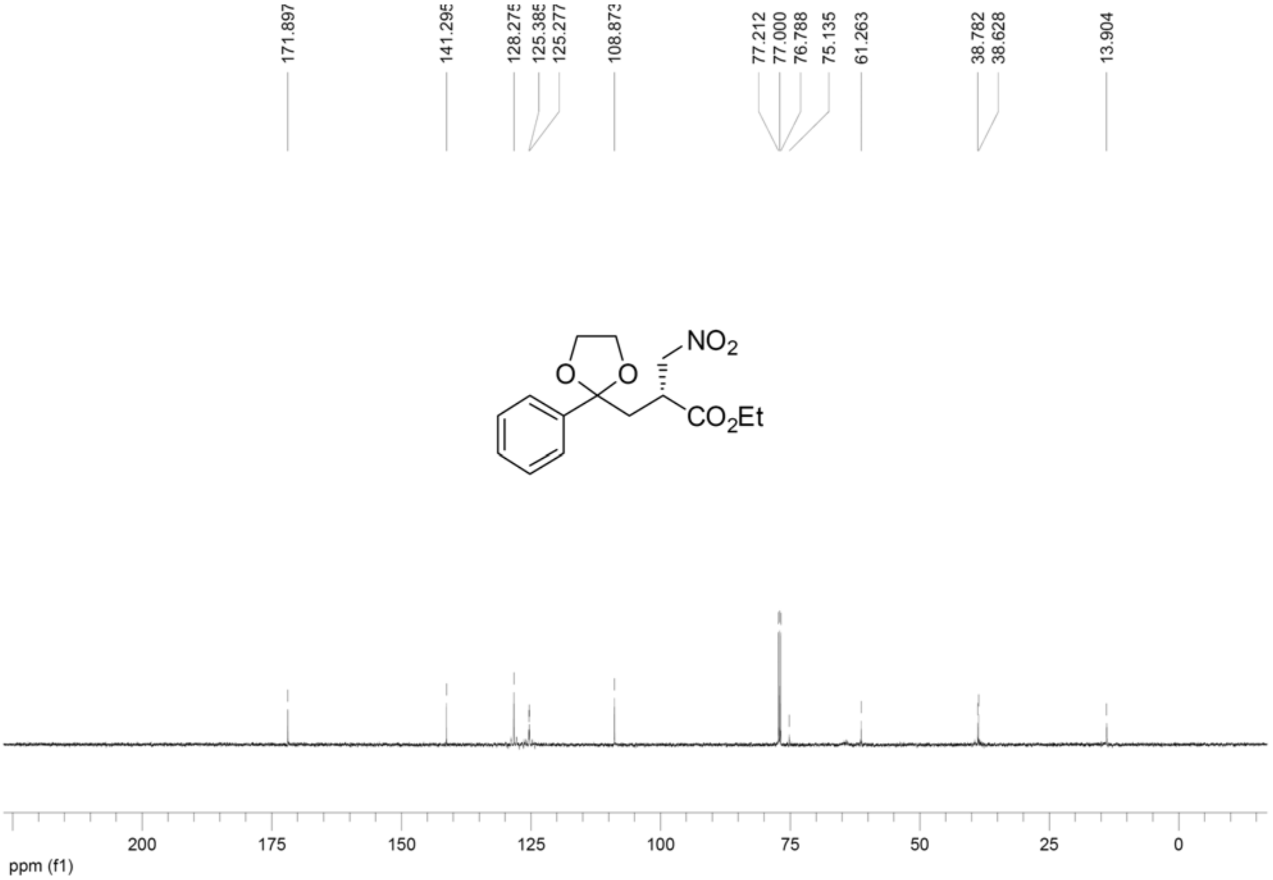

7.966
7.954
7.606
7.594
7.582
7.494
7.482
7.470
7.266
4.306
4.294
4.283
4.271
4.253
4.237
4.167
4.155
4.149
4.137
3.710
3.694
3.681
3.664
3.269
3.240
3.063
3.034
1.950
1.910
1.316
1.304
1.292
1.234
1.222
1.210
-0.000
O
CO2Et
NO2
CO2Et
2.52
1.25
2.51
3.89
2.62
1.28
1.03
0.22
3.96
3.89
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

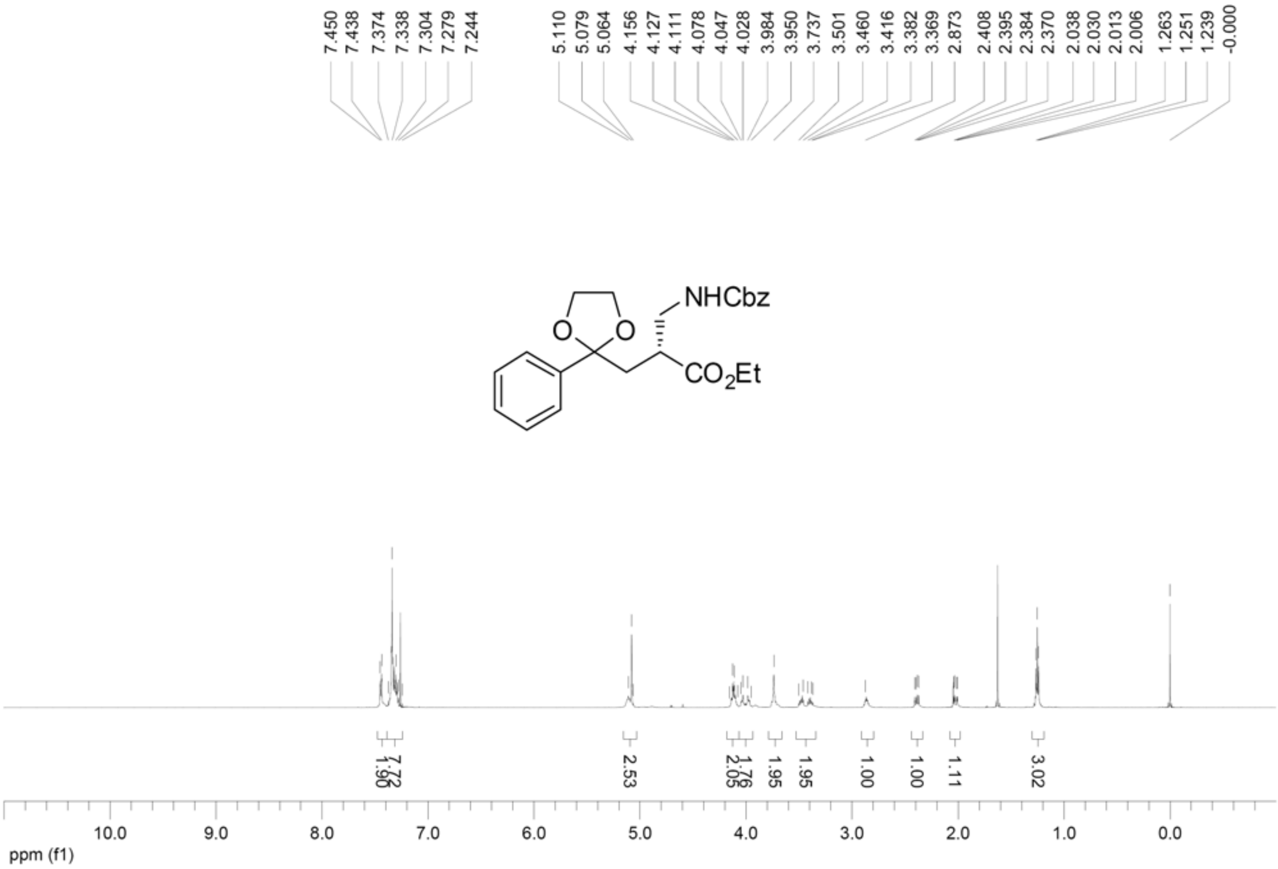

196.251
169.823
165.884
135.952
133.507
128.621
128.045
127.997
92.781
77.212
77.000
76.788
63.316
61.805
45.671
37.068
20.179
13.751
13.636
O
CO2Et
NO2
CO2Et
200
175
150
125
100
75
50
25
0
ppm (t1)

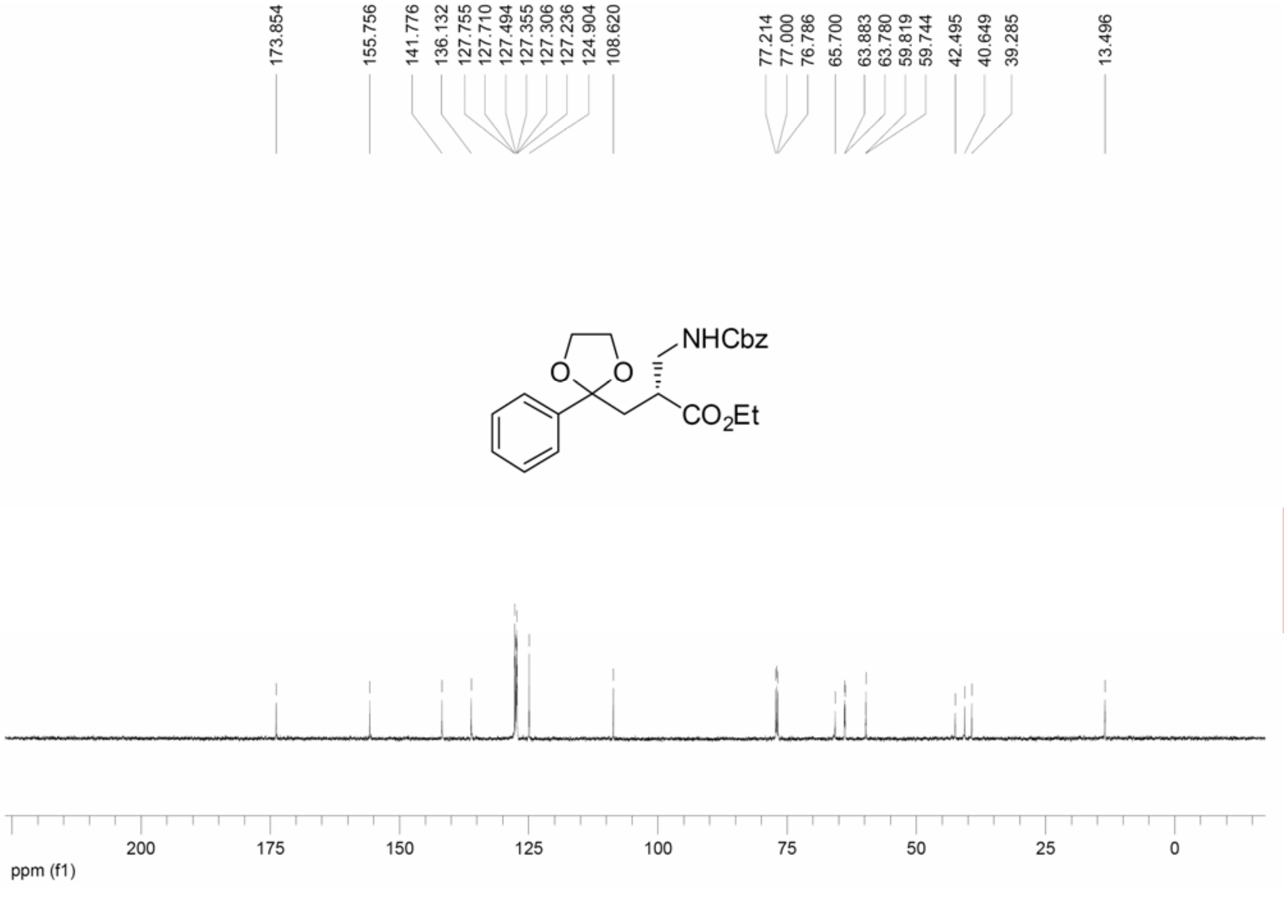

7.652
7.640
7.383
7.380
7.369
7.357
7.347
7.340
7.336
7.329
7.321
7.319
7.310
7.297
7.265
7.256
7.241
5.102
5.082
5.050
5.030
4.568
4.555
4.544
4.531
4.500
4.493
4.476
4.469
3.385
3.372
3.353
3.347
3.329
3.298
3.279
3.264
3.245
3.004
2.995
2.979
2.969
2.402
2.392
2.376
2.367
-0.000
NO2
S
S
O
O
2.00
2.03
3.10
2.12
1.06
1.06
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

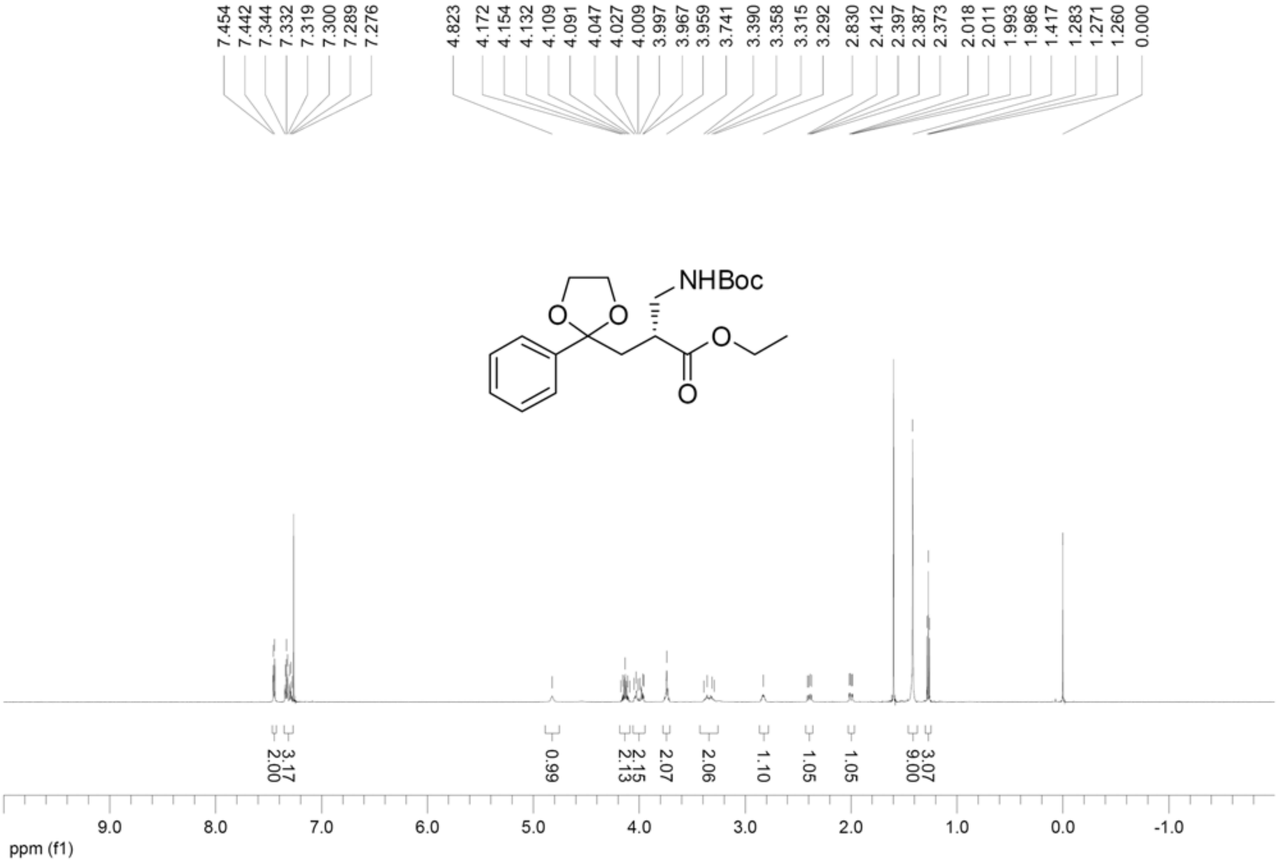

171.417
143.613
134.994
128.446
128.303
128.174
127.647
126.830
77.212
77.000
76.788
75.585
72.850
67.333
43.459
41.895
39.502
39.177
NO2
S
S
O
O
200
175
150
125
100
75
50
25
0
ppm (f1)

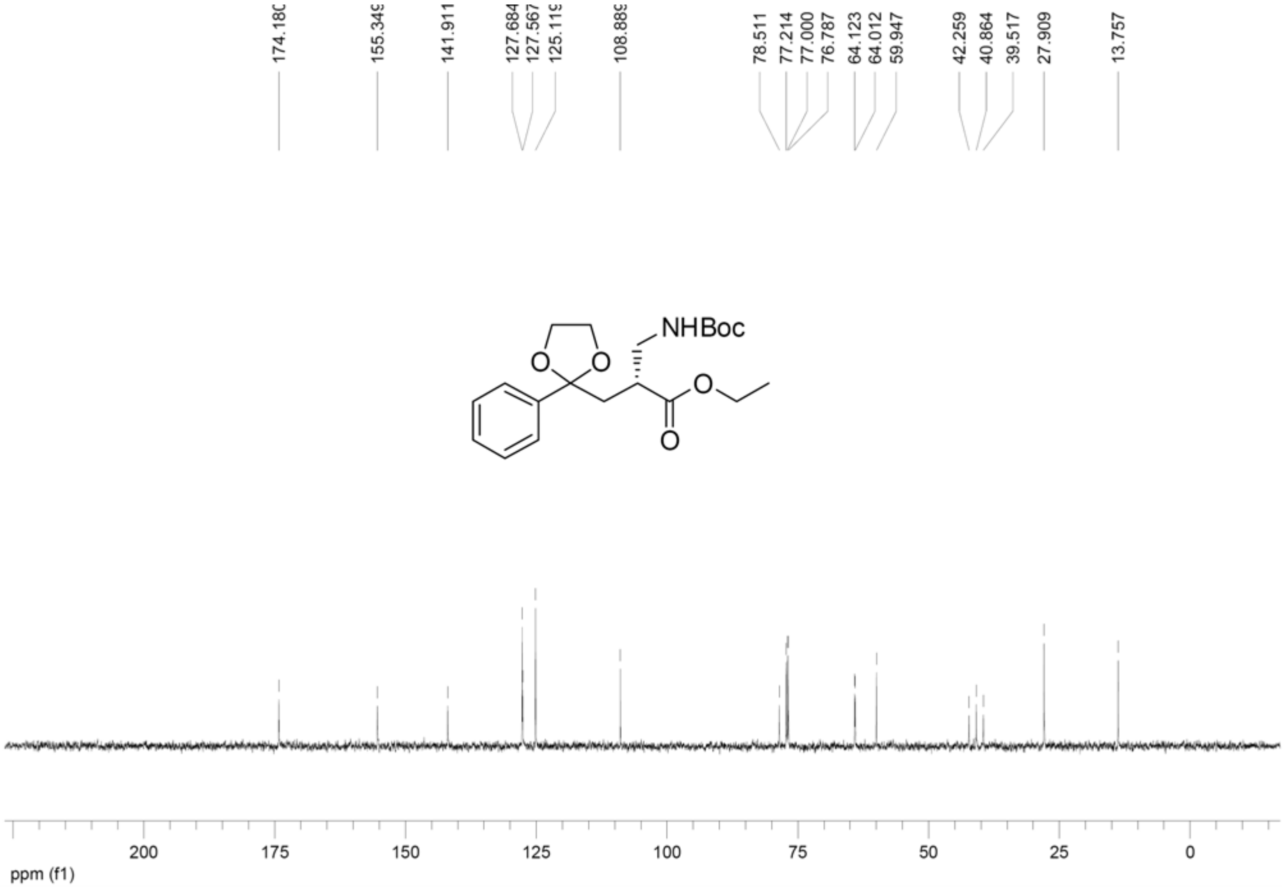

7.441
7.430
7.372
7.358
7.345
7.333
7.321
4.836
4.821
4.812
4.797
4.752
4.745
4.728
4.721
4.216
4.186
4.175
4.164
4.134
4.055
4.022
4.011
3.993
3.983
3.791
3.777
3.758
3.742
3.709
3.437
3.423
3.417
3.410
3.395
2.453
2.445
2.428
2.420
2.176
2.163
2.151
2.138
1.280
1.268
1.256
-0.000
NO2
O
O
CO2Et
3.00
2.00
2.05
1.04
1.04
1.04
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
ppm (f1)

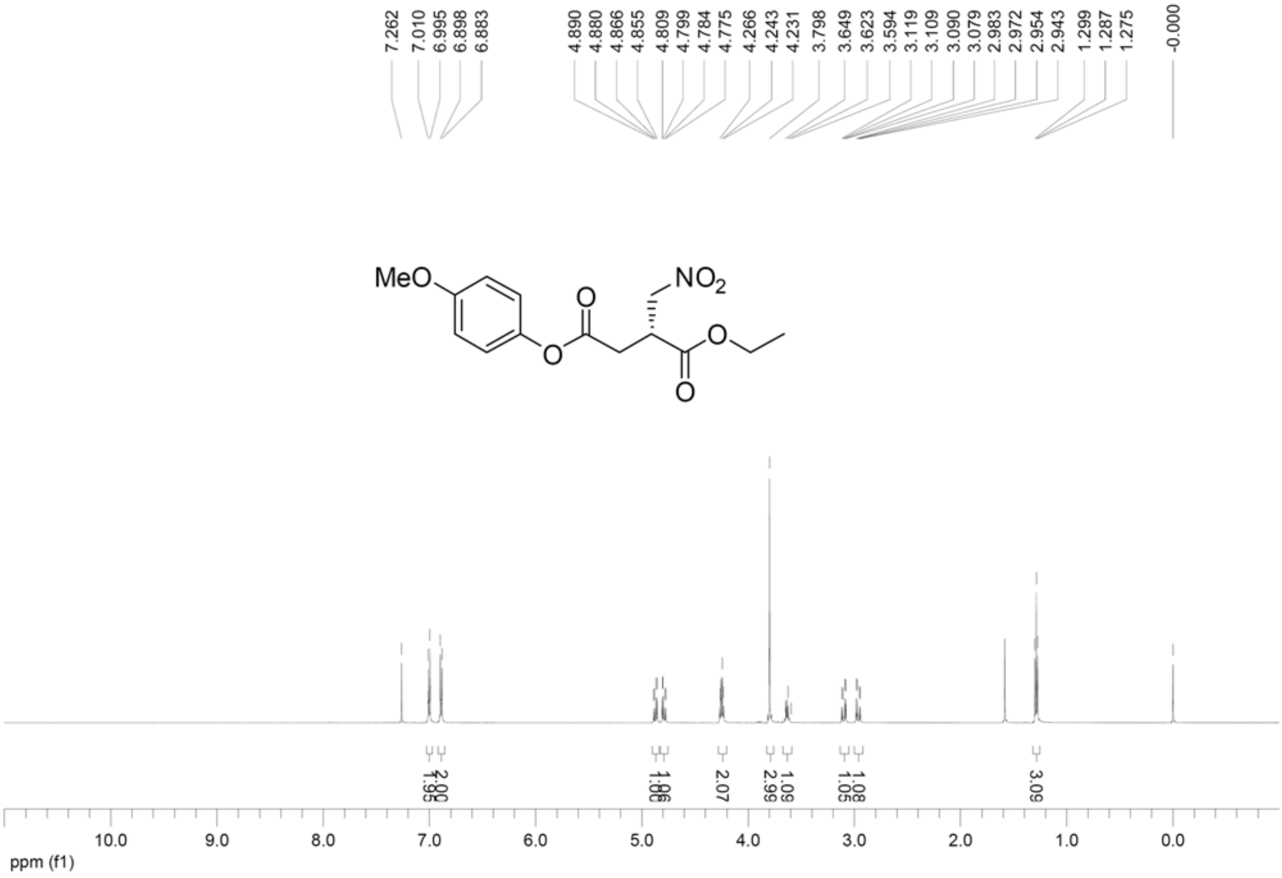

171.897
141.295
128.275
125.385
125.277
108.873
77.212
77.000
76.788
75.135
61.263
38.782
38.628
13.904
NO2
O
O
CO2Et
200
175
150
125
100
75
50
25
0
ppm (f1)

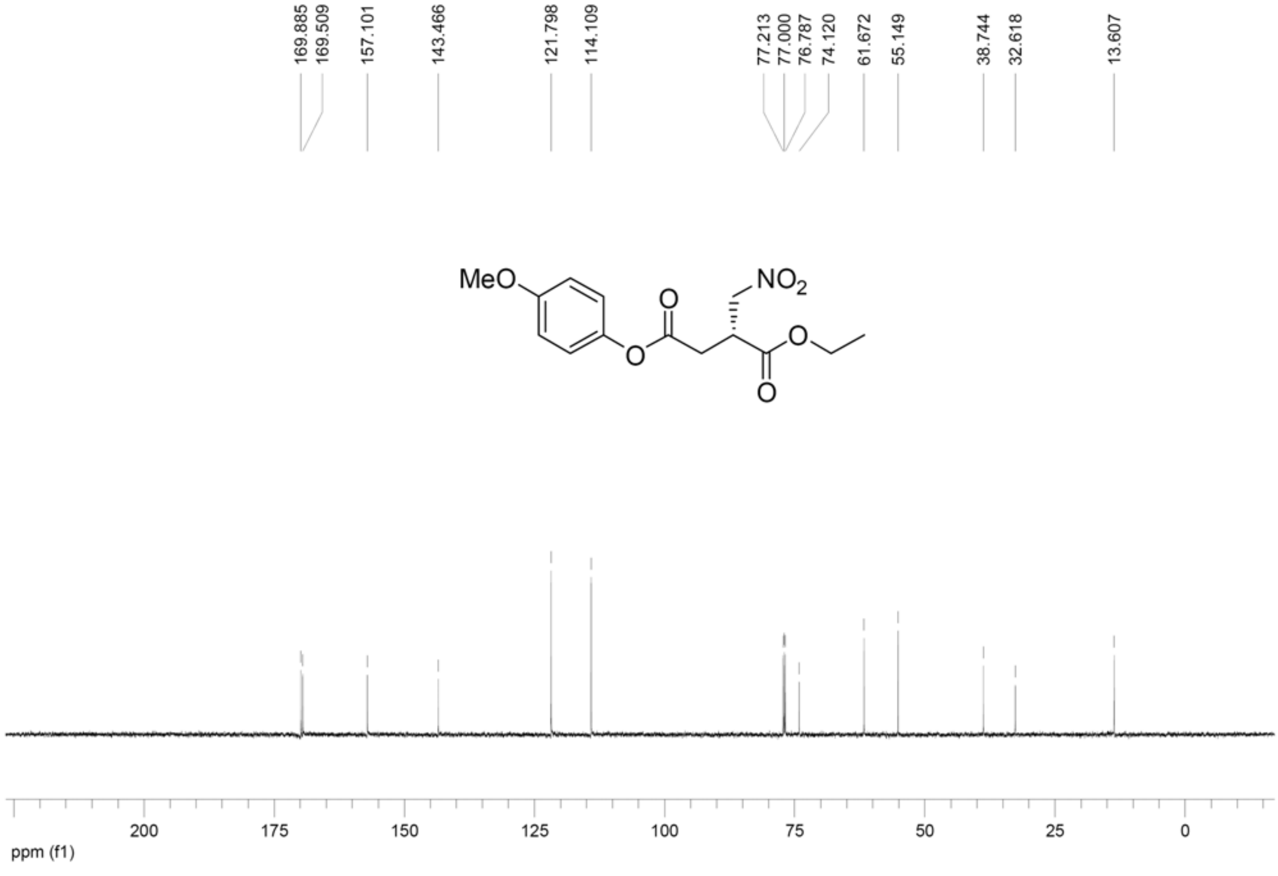

7.450
7.438
7.374
7.338
7.304
7.279
7.244
5.110
5.079
5.064
4.156
4.127
4.111
4.078
4.047
4.028
3.984
3.950
3.737
3.501
3.460
3.416
3.382
3.369
2.873
2.408
2.395
2.384
2.370
2.038
2.030
2.013
2.006
1.263
1.251
1.239
-0.000
NHCbz
O
O
CO2Et
1.90
7.72
2.53
2.05
1.76
1.95
1.95
1.00
1.00
1.11
3.02
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

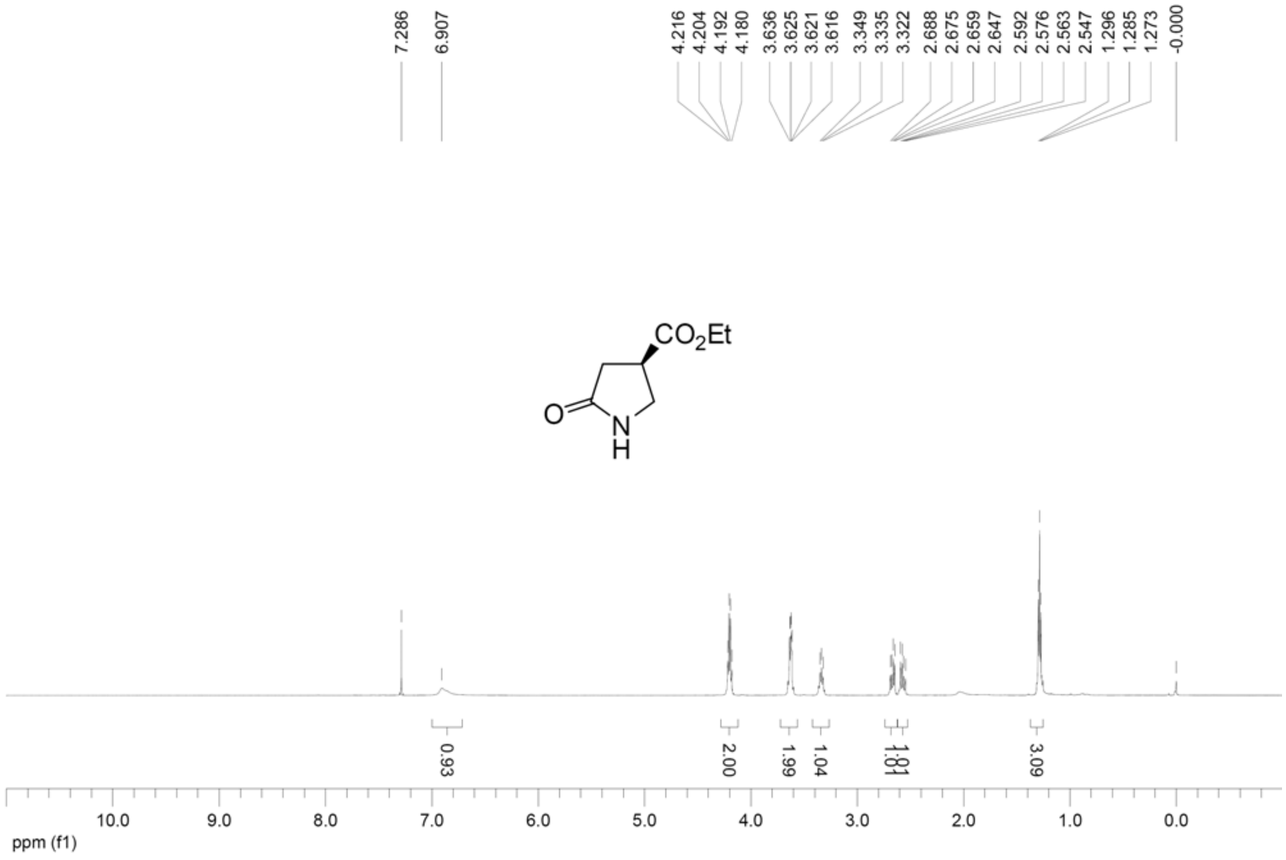

173.854
155.756
141.776
136.132
127.755
127.710
127.494
127.355
127.306
127.236
124.904
108.620
77.214
77.000
76.786
65.700
63.883
63.780
59.819
59.744
42.495
40.649
39.285
13.496
NHCbz
O
O
CO2Et
200
175
150
125
100
75
50
25
0
ppm (f1)

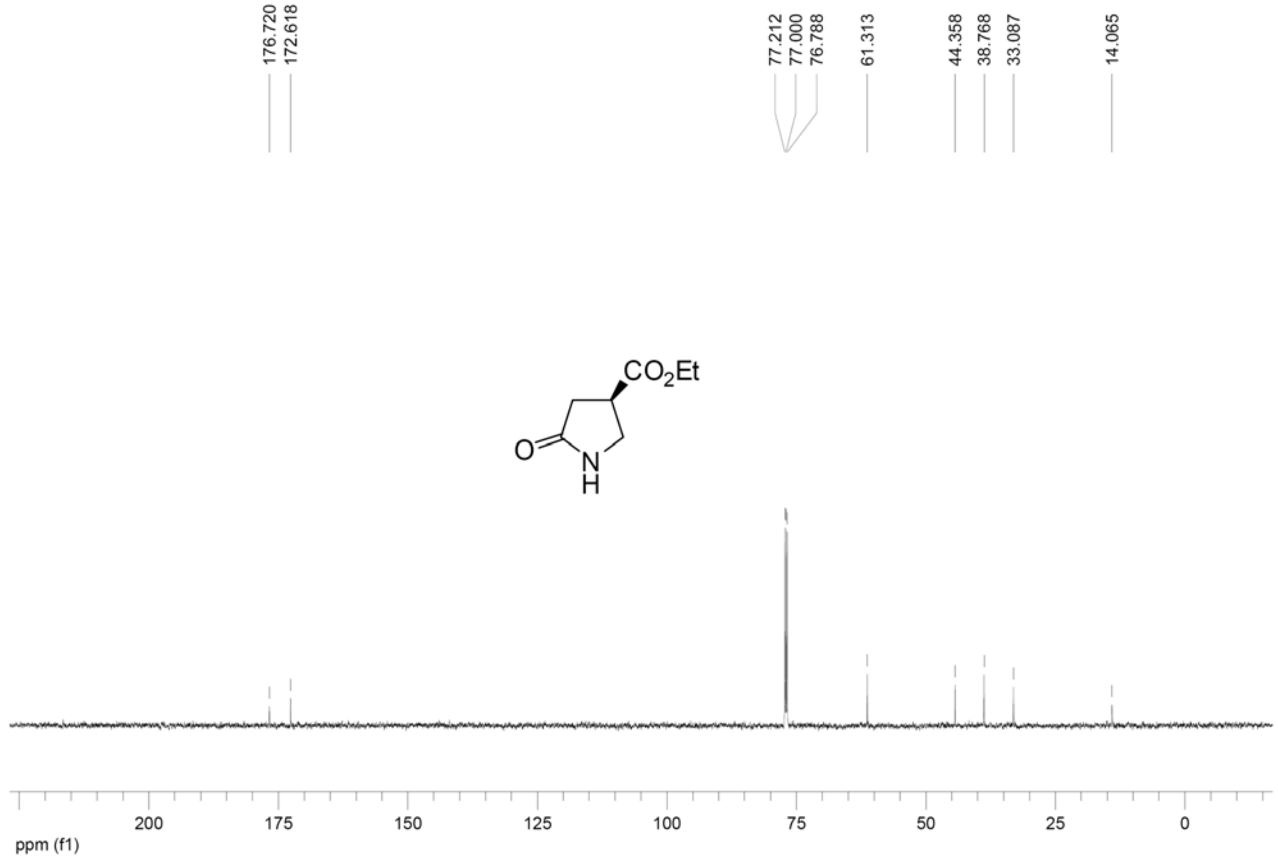

7.454
7.442
7.344
7.332
7.319
7.300
7.289
7.276
4.823
4.172
4.154
4.132
4.109
4.091
4.047
4.027
4.009
3.997
3.967
3.959
3.741
3.390
3.358
3.315
3.292
2.830
2.412
2.397
2.387
2.373
2.018
2.011
1.993
1.986
1.417
1.283
1.271
1.260
0.000
NHBoc
O
O
O
O
2.00
3.17
0.99
2.13
2.15
2.07
2.06
1.10
1.05
1.05
9.00
3.07
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
ppm (f1)


174.180
155.349
141.911
127.684
127.567
125.119
108.889
78.511
77.214
77.000
76.787
64.123
64.012
59.947
42.259
40.864
39.517
27.909
13.757
NHBoc
O
O
O
O
200
175
150
125
100
75
50
25
0
ppm (f1)


7.262
7.010
6.995
6.898
6.883
4.890
4.880
4.866
4.855
4.809
4.799
4.784
4.775
4.266
4.243
4.231
3.798
3.649
3.623
3.594
3.119
3.109
3.090
3.079
2.983
2.972
2.954
2.943
1.299
1.287
1.275
-0.000
MeO
O
O
NO2
O
O
1.95
2.00
1.00
1.06
2.07
2.99
1.09
1.05
1.08
3.09
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


169.885
169.509
157.101
143.466
121.798
114.109
77.213
77.000
76.787
74.120
61.672
55.149
38.744
32.618
13.607
MeO
O
O
NO2
O
O
200
175
150
125
100
75
50
25
0
ppm (f1)


7.286
6.907
4.216
4.204
4.192
4.180
3.636
3.625
3.621
3.616
3.349
3.335
3.322
2.688
2.675
2.659
2.647
2.592
2.576
2.563
2.547
1.296
1.285
1.273
-0.000
CO2Et
O
N
H
0.93
2.00
1.99
1.04
1.01
1.01
3.09
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


176.720
172.618
77.212
77.000
76.788
61.313
44.358
38.768
33.087
14.065
CO2Et
O
N
H
200
175
150
125
100
75
50
25
0
ppm (f1)