Supporting Information

Phosphine-Catalyzed Intramolecular γ-Umpolung Addition of α-Aminoalkylallenic Esters: Facile Synthesis of 3-Carbethoxy-2-alkyl-3-pyrrolines

Ian P. Andrews, Brian R. Blank, and Ohyun Kwon*

Department of Chemistry and Biochemistry, University of California, Los Angeles
607 Charles E. Young Drive East, Los Angeles, California, USA, 90095-1569

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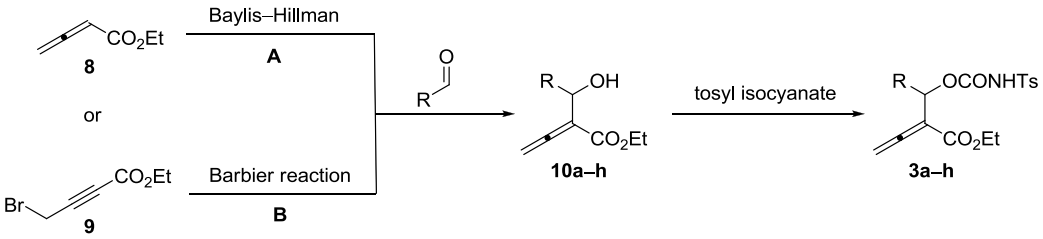
Materials and Methods

Unless otherwise stated, all reactions were performed in flame-dried glassware fitted with rubber septa, under an Ar atmosphere, and agitated with a Teflon-coated stirrer bar. All reaction solvents were distilled immediately prior to use [dichloromethane (CH_2Cl_2), acetonitrile (MeCN), benzene (PhH), and toluene (PhMe) from CaH_2; tetrahydrofuran (THF) from Na/benzophenone ketyl; methanol (MeOH) from magnesium methoxide] and transferred with an oven-dried needle and a disposable syringe using standard Schlenk techniques. Thin layer chromatography (TLC) was performed using SiliCycle silica gel 60 F-254–precoated glass-backed plates (thickness: 0.25 mm) and visualized under UV light and through permanganate staining. Flash column chromatography was performed through SiliCycle Silica-P silica gel (particle size: 40–63 μm). ^{1}H and ^{13}C NMR spectra were recorder using Bruker Avance-300, Avance-500, ARX-400, and ARX-500 MHz spectrometers (^{13}C operating frequencies of 75, 125, 100, and 125 MHz, respectively). Chemical shifts (δ) are reported with respect to the solvent (^{1}H: δ = 7.26 ppm for $CHCl_3$; ^{13}C :δ = 77 ppm for $CDCl_3$). ^{1}H NMR spectroscopic data are reported as follows: chemical shift (ppm), multiplicity, coupling constant (Hz), and number of protons. The following abbreviations are used to denote the multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; pent = pentet; sext = sextet; sept = septet; oct = octet; dd = doublet of doublets; dt = doublet of triplets; dq = doublet of quartets; d sept = doublet of septets; ddd = doublet of doublets of doublets; m = multiplet; br = broad; app = apparent. ^{13}C NMR spectroscopic data are reported with respect to chemical shift (ppm). MALDI mass spectra were recorded using an AB/PerSpective DE-STR instrument. Samples for MALDI mass spectrometric analysis were dissolved in 2,5-dihydroxybenzoic acid as the matrix.

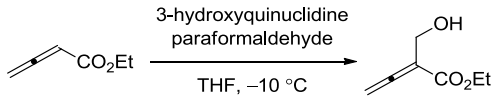
General strategy for the synthesis of allenylic carbamates



The allenylic carbamates **3a–h** were synthesized using the general strategy displayed above. The carbamates were synthesized by reacting the corresponding allenylic alcohols (**10a–h**) with tosyl isocyanate. The allenylic alcohols were synthesized by one of two methods: (i) a Baylis–Hillman reaction

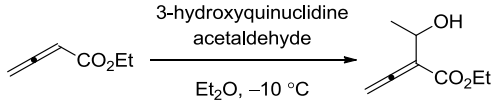
between ethyl 2,3-butadienoate (**8**) and the requisite aldehyde or (ii) a Barbier reaction between propargyl bromide (**9**) and the requisite aldehyde.[1]

Synthesis of allenylic alcohols (10a–h)



3-Ethoxycarbonyl-1,2-butadiene-4-ol (10a)

Paraformaldehyde (2.8 g, 89.2 mmol, 5 equiv) was dried under vacuum for 45 min in a flame-dried round-bottom flask heated at 55 °C in an oil bath. After cooling to room temperature, dry THF (10 mL) was added and the solution was cooled to –10 °C (ice water/salt bath). 3-Hydroxyquinuclidine (91 mg, 0.72 mmol, 0.2 equiv) was introduced as a solution in THF (5 mL). A solution of ethyl-2,3-butadienoate (400 mg, 3.57 mmol, 1 equiv) in dry THF (5 mL) was then added dropwise to the chilled reaction mixture. The reaction temperature was maintained at –10 °C for 1 h and then the flask was removed from the ice bath and warmed to room temperature with stirring for an additional 2.5 h. The reaction was quenched through the addition of saturated aqueous ammonium chloride. The layers were separated and the organic phase extracted with EtOAc. The combined organic extracts were washed sequentially with water and brine, dried (Na_2SO_4), and concentrated under reduced pressure. The crude material was purified through flash column chromatography (15% EtOAc/hexane). The product was isolated in 66% yield as a thick oil. Spectral data was in accordance with that reported in the literature.[2]



3-Ethoxycarbonyl-4-methyl-1,2-butadiene-4-ol (10b)

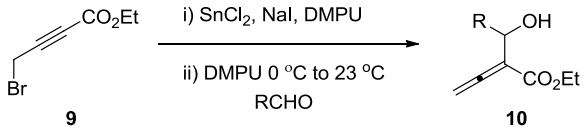
A flame-dried round-bottom flask equipped with a magnetic stirrer bar was charged with 3-hydroxyquinuclidine (114 mg, 0.9 mmol, 0.2 equiv) and placed under an Ar atmosphere. Diethyl ether (3 mL) was added and then the solution was cooled to –10 °C (ice water/salt bath). Ethyl-2,3-butadienoate (500 mg, 4.46 mmol, 1 equiv) and acetaldehyde (500 µL, 8.92 mmol, 2 equiv) were added sequentially.

[1] Y. Deng, X. Jin and S. Ma, *J. Org. Chem.*, 2007, **72**, 5901.

[2] C. Park and P. H. Lee, *Org. Lett.*, 2008, **10**, 3359.

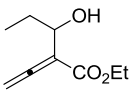
The reaction temperature was maintained at –15 °C for 1 h, at which point the reaction was complete (determined by TLC). The reaction was quenched through the addition of saturated aqueous ammonium chloride. The layers were separated and the aqueous phase extracted twice with diethyl ether. The combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated under reduced pressure. The crude material was purified through flash column chromatography (10% EtOAc/hexane). The product was isolated in 73% yield as a thick oil. IR (film) ν_{max} = 3433, 2982, 2935, 2907, 1966, 1708, 1266, 1059 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 5.19 (d, J = 2.2 Hz, 2H), 4.62–4.51 (m, 1H), 4.17 (d, J = 7.1 Hz, 1H), 4.12 (d, J = 7.1 Hz, 1H), 3.30 (d, J = 4.0 Hz, 1H), 1.25 (d, J = 6.4 Hz, 3H), 1.21 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.0, 167.1, 104.3, 80.8, 64.7, 61.1, 21.0, 14.1. LRMS MALDI-MS: calculated for $C_8H_{12}O_3$ $[M + Na]^+$, m/z 179.07; found: 179.04.

General procedure for the formation of α-hydroxyalkyl allenoic esters 10c–h[1]



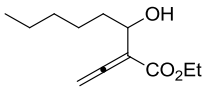
9 10

A flame-dried round-bottom flask equipped with a magnetic stirrer bar was placed under an Ar atmosphere and charged with propargyl bromide **9** (500 mg, 2.61 mmol, 1.25 equiv) and DMPU (4 mL). $SnCl_2$ (594 mg, 3.13 mmol, 1.5 equiv) and NaI (469 mg, 3.13 mmol, 1.5 equiv) were added sequentially as solids in single portions. The flask was covered with foil to protect the contents from light and then the mixture was stirred for 6 h. The flask was then cooled to 0 °C and a solution of the requisite aldehyde (2.1 mmol, 1 equiv) in DMPU (0.5 mL) was added over 15 min. The mixture was warmed to room temperature and stirred for 12 h; it was then cooled to 0 °C and diluted with diethyl ether. The reaction was quenched through the addition of saturated aqueous ammonium chloride. The aqueous phase was extracted four times with diethyl ether. The combined organic phases were combined, washed with brine, dried (Na_2SO_4), and filtered. The resulting solution was concentrated under reduced pressure and then the residue was purified through flash column chromatography (10–20% EtOAc/hexane).

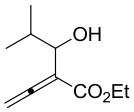


3-Ethoxycarbonyl-4-ethyl-1,2-butadiene-4-ol (10c). Isolated in 50% yield. IR (film) ν_{max} = 3435, 2978, 2937, 1964, 1708, 1262, 1067 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 5.22 (d, J = 1.8 Hz, 2H), 4.31

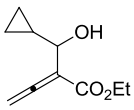
(br s, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.04 (br s, 1H), 1.65 (p, *J* = 7.2 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.93 (t, *J* = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.4, 167.1, 102.9, 80.5, 70.7, 61.2, 28.3, 14.2, 10.2. MALDI-MS: calculated for $C_9H_{14}O_3$ $[M + Na]^+$, *m*/*z* 193.1; found: 198.1.



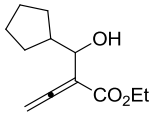
3-Ethoxycarbonyl-4-*n*-pentyl-1,2-butadiene-4-ol (10d). Isolated in 56% yield. IR (film) ν_{max} = 3445, 2933, 2860, 1965, 1712, 1259, 1069 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.21 (d, *J* = 1.9 Hz, 2H), 4.37 (t, *J* = 6.5 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.04 (br s, 1H), 1.65–1.57 (m, 2H), 1.49–1.39 (m, 1H), 1.33–1.20 (m, 8H), 0.85 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.4, 167.1, 103.2, 80.5, 69.2, 61.2, 35.3, 31.6, 25.4, 22.6, 14.1, 14.0. MALDI-MS: calculated for $C_{13}H_{22}O_3$ $[M + Na]^+$, *m*/*z* 235.3; found: 235.1.



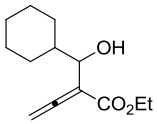
3-Ethoxycarbonyl-4-isopropyl-1,2-butadiene-4-ol (10e). Isolated in 57% yield. IR (film) ν_{max} = 3478, 2963, 2874, 1964, 1709, 1254, 1022 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.20 (d, *J* = 1.6 Hz, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 4.02 (t, *J* = 7.0 Hz, 1H), 2.93 (d, *J* = 7.4 Hz), 1.90 (app oct, *J* = 6.8 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.97 (d, *J* = 6.7 Hz, 3H), 0.87 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.9, 166.9, 102.1, 80.1, 75.3, 61.1, 33.0, 19.5, 17.9, 14.1. MALDI-MS: calculated for $C_{10}H_{16}O_3$ $[M + Na]^+$, *m*/*z* 207.10; found: 207.10.



3-Ethoxycarbonyl-4-cyclopropyl-1,2-butadiene-4-ol (10f). Isolated in 65% yield. IR (film) ν_{max} = 3465, 2986, 1963, 1710, 1256, 1208 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.25 (d, *J* = 1.9 Hz, 2H), 4.23 (q, *J* = 7.2 Hz, 2H), 3.73 (d, 7.9 Hz, 1H), 3.12 (d, *J* = 3.4 Hz, 1H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.18–1.10 (m, 1H), 0.63–0.56 (m, 1H), 0.52–0.40 (m, 2H), 0.27–0.21 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.7, 167.0, 102.9, 80.2, 73.7, 15.8, 14.0, 3.5, 2.6. MALDI-MS: calculated for $C_{10}H_{14}O_3$ $[M + Na]^+$, *m*/*z* 205.08; found: 205.08.

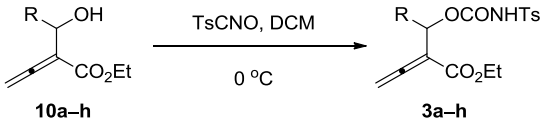


3-Ethoxycarbonyl-4-cyclopentyl-1,2-butadiene-4-ol (10g). Isolated in 62% yield. IR (film) ν_{max} = 3479, 2955, 2869, 1964, 1704, 1255, 1071, 1030 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.19 (s, 2H), 4.18 (q, J = 7.1 Hz, 2H), 3.19 (br s, 1H), 2.17 (sext, J = 8.1 Hz, 1H), 1.88–1.76 (m, 1H), 1.67–1.41 (m, 7H), 1.25 (t, J = 4.8 Hz, 3H), 1.18–1.10 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.9, 167.1, 102.6, 80.0, 74.1, 61.1, 44.2, 29.44, 29.11, 25.6, 25.5, 14.0. MALDI-MS: calculated for $C_{12}H_{18}O_3$ [M + Na]$^+$, m/z 233.12; found: 233.12.



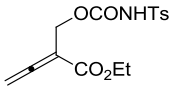
3-Ethoxycarbonyl-4-cyclohexyl-1,2-butadiene-4-ol (10h). Isolated in 80% yield. IR (film) ν_{max} = 3478, 2982, 2927, 2852, 1964, 1710, 1255, 1067 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.19 (d, J = 1.0 Hz, 2H), 4.19 (q, J = 7.1 Hz, 2H), 2.96 (br s, 1H), 1.97 (d, J = 12.8 Hz, 1H), 1.76–1.54 (m, 6H), 1.26 (t, J = 7.1 Hz, 3H), 1.22–1.09 (m, 3H), 1.02–0.93 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.8, 166.9, 101.5, 79.8, 74.7, 61.0, 42.5, 29.7, 28.4, 26.3, 25.9, 25.7, 14.0. MALDI-MS: calculated for $C_{13}H_{20}O_3$ [M + Na]$^+$, m/z 247.13; found: 247.12.

Synthesis of allenylic carbamates (3a–h)

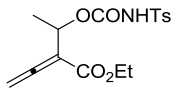


10a–h **3a–h**

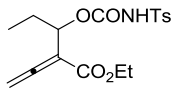
A flame-dried round-bottom flask equipped with a magnetic stirrer bar was charged with the requisite α-hydroxyalkylallenoate (**7**) (1.29 mmol, 1 equiv) and placed under an Ar atmosphere. Dry CH_2Cl_2 (10 mL) was added and the resulting solution cooled to 0 °C. Tosyl isocyanate (217 µL, 1.4 mmol, 1.1 equiv) was added in a single portion. The mixture was stirred without replacing the ice bath until all of the starting material had been consumed (TLC). The solution was concentrated under reduced pressure and then the crude residue was purified through flash chromatography (15% EtOAc/hexane).



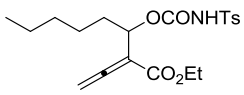
Ethyl-2-(tosylcarbamoyloxymethyl)-2,3-butadienoate (3a). Isolated in 82% yield as a white crystalline solid; m.p. 111–114 °C. This compound could also be recrystallized from EtOAc/hexanes. IR (film) ν_{max} = 3224, 2985, 1966, 1752, 1711, 1448, 1160 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.90 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 5.18 (t, J = 2.1 Hz, 2H), 4.76 (t, J = 2.1 Hz, 2H), 4.16 (q, J = 7.1 Hz, 2H), 2.42 (s, 1H), 1.22 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.6, 165.1, 150.2, 145.0, 135.5, 129.6, 128.5, 96.3, 81.0, 62.9, 61.5, 21.7, 14.1. MALDI-MS: calculated for $C_{15}H_{17}NO_6S$ [M + Na]$^+$: m/z 362.07; found: 362.06.



3-Ethoxycarbonyl)-(4-tosylcarbamoyloxy)-4-methyl-1,2-butadiene (3b). Isolated in 87% yield as a thick oil. IR (film) ν_{max} = 3232, 2988, 1967, 1750, 1717, 1450, 1357, 1286, 1224, 1162 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.2 Hz, 2H), 5.53–5.48 (m, 1H), 5.20 (dd, J = 14.7, 2.1 Hz, 1H), 5.15 (dd, J = 14.6, 2.1 Hz, 1H), 4.04 (q, J = 7.1 Hz, 2H), 2.35 (s, 3H), 1.28 (d, J = 6.5 Hz, 3H), 1.11 (t, J = 7.1 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.8, 164.7, 149.8, 144.7, 135.6, 129.3, 128.2, 101.8, 82.2, 69.4, 61.2, 60.4, 21.4, 18.9, 14.0, 13.8. MALDI-MS: calculated for $C_{16}H_{19}NO_6S$ [M + Na]$^+$: m/z 376.08; found: 376.04.

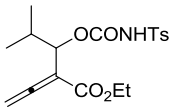


3-Ethoxycarbonyl-(4-tosylcarbamoyloxy)-4-ethyl-1,2-butadiene (3c). Isolated in 82% yield as a thick oil. IR (film) ν_{max} = 3231, 2981, 2938, 1970, 1750, 1717, 1447, 1162 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 5.38–5.35 (m, 1H), 5.20, (dd, J = 14.6, 1.9 Hz, 1H), 5.15 (dd, J = 14.6, 2.0 Hz, 1H), 4.11 (q, J = 7.1 Hz, 2H), 2.42 (s, 3H), 1.79–1.63 (m, 2H), 1.19 (t, J = 7.2 Hz, 3H), 0.82 (t, J = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.0, 164.7, 149.7, 144.8, 135.6, 129.4, 128.3, 100.6, 81.7, 74.2, 61.2, 26.3, 21.5, 13.9, 9.3. MALDI-MS: calculated for $C_{17}H_{21}NO_6S$ [M + Na]$^+$: m/z 390.41; found: 390.21.

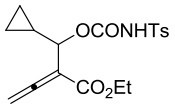


3-Ethoxycarbonyl-(4-tosylcarbamoyloxy)-4-*n*-pentyl-1,2-butadiene (3d). Isolated in 93% yield as a thick oil. IR (film) ν_{max} = 3236, 2950, 2921, 2862, 1748, 1713, 1450, 1164, 1082 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, J = 8.3 Hz, 2H) 7.29 (d, J = 8.2 Hz, 2H), 5.43–5.40 (m, 1H), 5.20 (dd, J = 14.5,

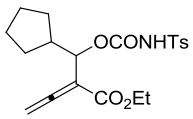
1.8 Hz, 1H), 5.14 (dd, *J* = 14.5, 1.9 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.40 (s, 3H), 1.71–1.58 (m, 2H), 1.22–1.15 (m, 9H), 0.83–0.79 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.9, 164.7, 149.8, 144.7, 135.6, 129.4, 128.2, 100.9, 81.8, 73.1, 61.1, 33.1, 31.1, 24.6, 22.2, 21.5, 13.9, 13.8. MALDI-MS: calculated for $C_{20}H_{27}NO_6S$ $[M + Na]^+$: *m*/*z* 432.49; found: 432.32.



3-Ethoxycarbonyl-(4-tosylcarbamoyloxy)-4-isopropyl-1,2-butadiene (3e). Isolated in 84% yield as a thick oil. IR (film) ν_{max} = 3230, 2970, 2926, 2874, 1970, 1750, 1714, 1447, 1258, 1162, 1091 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 5.23–5.21 (m, 1H), 5.15 (dd, *J* = 14.5, 1.6 Hz, 1H), 5.08 (dd, *J* = 14.5, 1.9 Hz, 1H), 4.13 (dq, *J* = 7.1, 1.0 Hz, 2H), 2.42 (s, 3H), 2.05 (app oct, *J* = 6.7 Hz, 1H), 1.21 (t, *J* = 7.2 Hz, 3H), 0.86 (d, *J* = 6.8 Hz, 3H), 0.81 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.2, 164.8, 149.8, 144.8, 135.6, 129.4, 128.2, 100.1, 81.4, 77.6, 61.2, 31.2, 21.5, 18.6, 17.1, 13.9. MALDI-MS: calculated for $C_{18}H_{23}NO_6S$ $[M + Na]^+$: *m*/*z* 404.11; found: 404.18.

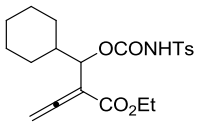


3-Ethoxycarbonyl-(4-tosylcarbamoyloxy)-4-cyclopropyl-1,2-butadiene (3f). Isolated in 78% yield as a thick oil. IR (film) ν_{max} = 3230, 2985, 1964, 1715, 1448, 1353, 1161 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 5.27 (dd, *J* = 14.6, 1.4 Hz, 1H), 5.23 (dd, *J* = 14.6, 1.3 Hz, 1H), 4.88 (d, *J* = 9.0 Hz, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 2.40 (s, 3H), 1.28–1.21 (m, 1H), 1.15 (t, *J* = 7.1 Hz, 3H), 0.52–0.40 (m, 3H), 0.32–0.28 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.7, 164.7, 150.0, 144.6, 135.7, 129.3, 128.2, 100.9, 81.6, 77.2, 61.2, 60.4, 21.5, 14.0, 13.9, 3.9, 2.9. MALDI-MS: calculated for $C_{18}H_{21}NO_6S$ $[M + Na]^+$: *m*/*z* 402.10; found: 402.11.



3-Ethoxycarbonyl-(4-tosylcarbamoyloxy)-4-cyclopentyl-1,2-butadiene (3g). Isolated in 83% yield as a thick oil. IR (film) ν_{max} = 3229, 2958, 2868, 1964, 1750, 1701, 1447, 1162. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 5.32 (d, *J* = 8.1 Hz, 1H), 5.19 (d, 14.6 Hz, 1H), 5.13 (d, *J* = 14.5, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 2.40 (s, 3H), 2.25 (app sext, *J* = 8.0 Hz, 1H), 1.61–1.34 (m, 6H), 1.26–1.20 (m, 2H), 1.74 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.7, 164.9, 150.0,

144.6, 135.7, 129.3, 128.2, 100.8, 81.5, 76.4, 61.1, 42.8, 28.6, 28.3, 25.2, 25.2, 21.5, 13.9. MALDI-MS: calculated for $C_{20}H_{25}NO_6S$ $[M + Na]^+$: *m*/*z* 430.13; found: 429.95.

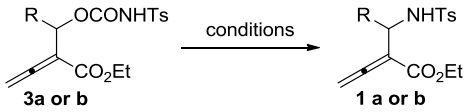


3-Ethoxycarbonyl-(4-tosylcarbamoyloxy)-4-cyclohexyl-1,2-butadiene (3h). Isolated in 74% yield as a thick oil. IR (film) ν_{max} = 3231, 2929, 2854, 1718, 1448, 1161, 1091 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.24–5.22 (m, 1H), 5.20 (dd, *J* = 14.6, 1.4 Hz, 1H), 5.14 (dd, *J* = 14.5, 1.6 Hz, 1H), 4.15 (q, *J* = 7.4 Hz, 2H), 2.44 (s, 3H), 1.73–1.59 (m, 4H), 1.54 (d, *J* = 12.7 Hz, 2H), 1.23 (t, *J* = 7.2 Hz, 3H), 1.20–0.84 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.3, 164.9, 150.0, 144.7, 135.7, 129.4, 128.2, 99.8, 81.4, 77.1, 61.1, 40.6, 28.8, 27.5, 25.9, 25.4, 21.5, 13.9. MALDI-MS: calculated for $C_{21}H_{27}NO_6S$ $[M + Na]^+$: *m*/*z* 444.15; found: 444.16.

Optimization of the decarboxylative rearrangement of allenylic carbamates

Our investigation began by slowly adding a MeCN solution of the allenoate **3a** (R = H) to 1 equivalent of DABCO in MeCN over a period of 12 h. Much to our delight, we obtained the desired α-aminomethyl allenic ester **1a** in 37% isolated yield (Table S1, entry 1). The reaction was facilitated by a number of different solvents, with CH_2Cl_2 and benzene (entries 2 and 3, respectively) resulting in the highest yield of 42%. Performing the reaction in THF yielded none of the desired product (entry 5). We also tested the allenylic carbamate **3c** (R = ethyl) as a substrate for the rearrangement. After slow addition of a benzene solution of the ethyl-substituted allenoate to 1 equivalent of DABCO, we isolated the desired product in 54% yield (entry 8). Decreasing the catalyst loading had a negative effect on the reaction, lowering the yield to 35% (entry 9); simply adding the catalyst quickly to a solution of the starting material decreased the yield further, to 18% (entry 10). We speculate that slow addition of the allenoate to a stoichiometric amount of the catalyst ensured that a very low concentration of unreacted allenoate was present in the reaction mixture, resulting in undesired reaction pathways. 3-Quinuclidinol also effected the reaction, albeit with lowered efficiency (36% yield, entry 11); in contrast, DMAP, DBU, pyridine, and imidazole all failed to yield any of the desired product (entries 12–15). In an interesting observation, we isolated the allenoate **1a** in the highest yield (56%) when using dimethyl sulfide as the catalyst in MeCN (entry 7). Dimethyl sulfide failed to provide any of the desired rearrangement products when any substituent larger than a hydrogen atom was present. It is possible that with the decreased steric demands for this substrate, direct displacement may have operated, rather than our proposed S_N2' displacement.

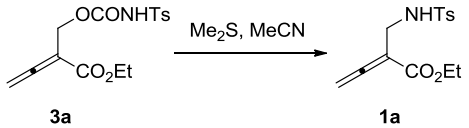
Table S1: Optimization of the decarboxylative rearrangement



entry	R (allenoate)	catalyst (equiv)	solvent	addition method[a]	product	yield (%)[b]
1	H (**3a**)	DABCO (1)	MeCN	A	**1a**	37
2	H (**3a**)	DABCO (1)	CH_2Cl_2	A	**1a**	42
3	H (**3a**)	DABCO (1)	PhH	A	**1a**	42
4	H (**3a**)	DABCO (1)	MeOH	A	**1a**	23
5	H (**3a**)	DABCO (1)	THF	A	**1a**	0
6	H (**3a**)	DABCO (1)	DMF	A	**1a**	35
7	H (**3a**)	dimethyl sulfide (1)	MeCN	A	**1a**	56
8	Et (**3b**)	DABCO (1)	PhH	A	**1b**	54
9	Et (**3b**)	DABCO (20 mol%)	PhH	A	**1b**	35
10	Et (**3b**)	DABCO (20 mol%)	PhH	B	**1b**	18
11	Et (**3b**)	3-quinuclidinol (1)	PhH	A	**1b**	36
12	Et (**3b**)	DMAP (1)	PhH	A	**1b**	0
13	Et (**3b**)	DBU	PhH	A	**1b**	0
14	Et (**3b**)	pyridine	PhH	A	**1b**	0
15	Et (**3b**)	imidazole	PhH	A	**1b**	0

[a]A: Slow addition of a solution of the allenoate to a solution of the catalyst; B: addition of the catalyst quickly to a solution of the allenoate.
[b]Isolated yield after SiO_2 column chromatography.

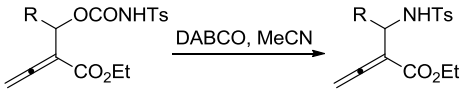
Synthesis of 3-ethoxycarbonyl-4-tosylamino-1,2-butadiene (1a)



A flame-dried round-bottom flask equipped with a magnetic stirrer bar was placed under an Ar atmosphere and then dry MeCN (2 mL) was added followed by dimethyl sulfide (10.9 µL, 0.147 mmol, 1

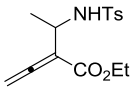
equiv). A solution of the allenylic carbamate **3a** (50 mg, 0.147 mmol, 1 equiv) in dry MeCN (2 mL) was added via syringe pump over the course of 6 h; the mixture was then stirred for an additional 12 h at room temperature. The solution was concentrated under reduced pressure and the residue purified through flash column chromatography (10–20% EtOAc/hexane). The product was isolated in 56% yield as a yellow solid. IR (film) ν_{max} = 3289, 2985, 1970, 1700, 1330, 1160 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, J = 8.1 Hz, 2H), 7.27 (d, J = 8.2 Hz, 2H), 5.22 (t, J = 6.4 Hz, 1H), 5.10 (t, J = 1.9 Hz, 2H), (4.11 (q, J = 7.1 Hz, 2H), 3.85–3.77 (m, 2H), 2.40 (s, 3H), 1.20 (t, J = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.0, 166.0, 143.3, 137.4, 129.5, 127.0, 96.5, 80.5, 77.2, 77.0, 76.7, 61.3, 42.2, 21.4, 14.0. MALDI-MS: calculated for $C_{14}H_{17}NO_4S$ [M + Na]$^+$: m/z 318.08; found: 318.04.

Synthesis of *β´*-alkyl-*α*-aminoalkylallenic esters (1b–h)

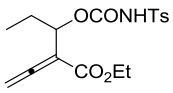


3 **1**

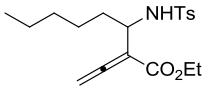
A flame-dried round-bottom flak equipped with a magnetic stirrer bar was charged with DABCO (63.5 mg, 0.566 mmol, 1 equiv), which was dissolved in dry benzene (8 mL) under an Ar atmosphere. The requisite allenylic carbamate **3** (0.566 mmol, 1 equiv) was dissolved in dry benzene (8 mL) and added via syringe pump over the course of 12 h. The solution was concentrated under reduced pressure and the crude residue purified through flash column chromatography (5–20% EtOAc/hexane).



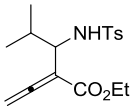
3-Ethoxycarbonyl-4-tosylamino-4-ethyl-1,2-butadiene (1b). Isolated in 65% yield as a thick oil. IR (film) ν_{max} = 3287, 2985, 2938, 1966, 1701, 1328, 1264, 1163 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, J = 8.3 Hz, 2H), 7.26 (d, J = 8.2 Hz, 2H), 5.29 (d, J = 9.8 Hz, 1H), 5.07 (d, J = 14.2 Hz, 1H), 5.03 (d, J = 14.3 Hz, 1H), 4.26–4.20 (m, 1H), 4.10 (dq, J = 7.1, 1.0 Hz, 2H), 2.41 (s, 3H), 1.35 (d, J = 6.9 Hz, 3H), 1.97 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.0, 165.3, 143.0, 137.9, 129.3, 127.1, 101.4, 80.6, 61.0, 49.6, 21.9, 21.3, 13.9. MALDI-MS: calculated for $C_{15}H_{19}NO_4S$ [M + Na]$^+$: m/z 332.09; found: 332.12.



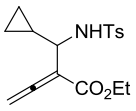
3-Ethoxycarbonyl-4-tosylamino-4-ethyl-1,2-butadiene (1c). Isolated in 54% yield as a thick oil. IR (film) ν_{max} = 3287, 2973, 2983, 1964, 1700, 1252, 1163 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, J = 8.3 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 5.39 (d, J = 10.3 Hz, 1H), 5.01 (dd, J = 14.3, 0.9 Hz, 1H), 4.94 (dd, J = 14.3, 0.7 Hz, 1H), 4.04 (q, J = 7.1 Hz, 2H), 4.00–3.91 (m, 1H), 2.39 (s, 3H), 1.72–1.62 (m, 2H), 1.16 (t, J = 7.1 Hz, 3H), 0.86 (t, J = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.7, 165.5, 143.1, 138.2, 129.4, 127.2, 99.7, 80.1, 61.1, 55.7, 28.7, 21.5, 14.1, 10.6. MALDI-MS: calculated for $C_{16}H_{21}NO_4S$ [M + Na]$^+$: m/z 346.11; found: 346.36.



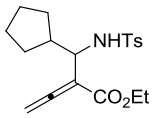
3-Ethoxycarbonyl-4-tosylamino-4-*n*-pentyl-1,2-butadiene (1d). Isolated in 27% yield as a thick oil. IR (film) ν_{max} = 3289, 2931, 2860, 1965, 1706, 1330, 1163 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, J = 8.3 Hz, 2H), 7.25 (d, J = 8.3 Hz, 2H), 5.30 (d, J = 10.1 Hz, 1H), 5.03 (dd, J = 14.3, 0.8 Hz, 1H), 4.97 (dd, 14.2, 0.7 Hz, 1H), 4.16–3.99 (m, 1H), 4.07 (q, J = 7.4 Hz, 2H), 2.41 (s, 3H), 1.69–1.60 (m, 2H), 1.31–1.17 (m, 9H), 0.84 (t, J = 6.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.5, 165.4, 142.9, 138.1, 129.2, 127.2, 99.9, 79.9, 60.9, 54.1, 35.3, 30.9, 25.4, 22.3, 21.3, 13.9, 13.8. MALDI-MS: calculated for $C_{19}H_{27}NO_4S$ [M + Na]$^+$: m/z 388.16; found: 387.99.



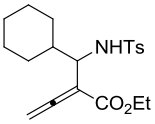
3-Ethoxycarbonyl-4-tosylamino-4-isopropyl-1,2-butadiene (1e). Isolated in 52% yield as a thick oil. IR (film) ν_{max} = 3282, 2967, 1976, 1695 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, J = 8.3 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 5.37 (d, J = 10.7 Hz, 1H), 4.96 (d, J = 14.3 Hz, 1H), 4.89 (d, J = 14.2 Hz, 1H), 3.75 (dd, J = 10.6, 7.9 Hz, 1H), 2.38 (s, 3H), 1.90 (app oct, J = 6.9 Hz, 1H), 1.16 (t, J = 7.1 Hz, 3H), 0.93 (d, J = 6.7 Hz, 3H), 0.83 (d, J = 6.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 213.0, 165.7, 143.1, 138.1, 129.3, 127.2, 99.3, 80.1, 61.1, 59.7, 32.6, 21.5, 19.7, 18.7, 14.1. MALDI-MS: calculated for $C_{17}H_{23}NO_4S$ [M + Na]$^+$: m/z 360.12; found: 360.15.



3-Ethoxycarbonyl-4-tosylamino-4-cyclopropyl-1,2-butadiene (1f). Isolated in 45% yield as a white solid. IR (film) ν_{max} = 3287, 3067, 2989, 1967, 1702, 1425, 1327, 1254, 1156 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, J = 8.2 Hz, 2H), 7.25 (d, J = 8.2 Hz, 2H), 5.50 (d, J = 9.4 Hz, 1H), 5.05 (d, J = 14.2 Hz, 1H), 4.99 (d, J = 14.2 Hz, 1H), 4.10 (q, J = 7.1 Hz, 2H), 3.41(t, J = 9.1 Hz, 1H), 2.41 (s, 3H), 1.25–1.18 (m, 4H), 0.54–0.44 (m, 2H), 0.34–0.29 (m, 1H), 0.27–0.23 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.7, 165.7, 143.0, 138.2, 129.2, 127.1, 99.1, 79.9, 61.1, 58.7, 21.4, 16.6, 14.0, 4.6, 3.9. MALDI-MS: calculated for $C_{17}H_{21}NO_4S$ [M + Na]$^+$: m/z 358.11; found: 358.07.



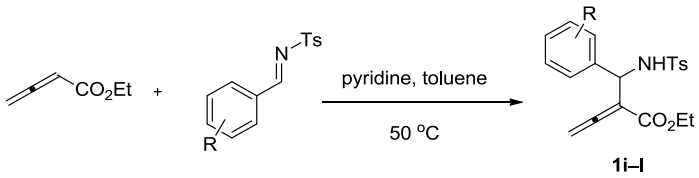
3-Ethoxycarbonyl-4-tosylamino-4-cyclopentyl-1,2-butadiene (1f). Isolated in 45% yield as a thick oil. IR (film) ν_{max} = 3293, 2954, 1700, 1162 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, J = 8.3 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 5.48 (d, J = 10.5 Hz, 1H), 4.98 (d, J = 14.0 Hz, 1H), 4.89 (d, J = 14.2 Hz, 1H), 4.04 (q, J = 7.1 Hz, 2H), 3.78 (t, J = 10.1 Hz, 1H), 2.40 (s, 3H), 2.20 (sext, J = 8.3 Hz, 1H), 1.84–1.77 (m, 1H), 1.62–1.46 (m, 5H), 1.40–1.32 (m, 1H), 1.17 (t, J = 7.1 Hz, 3H), 1.15–1.10 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.0, 165.6, 142.9, 138.1, 129.2, 127.1, 99.3, 79.4, 60.9, 58.8, 44.3, 29.9, 29.8, 25.1, 25.0, 21.4, 14.0. MALDI-MS: calculated for $C_{19}H_{25}NO_4S$ [M + Na]$^+$: m/z 386.14; found: 386.24.



3-Ethoxycarbonyl-4-tosylamino-4-cyclohexyl-1,2-butadiene (1g). Isolated in 51% yield as a thick oil. IR (film) ν_{max} = 3290, 2928, 2853, 1965, 1699, 1704, 1163 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, J = 8.3 Hz, 2H), 7.23 (d, J = 8.2 Hz, 2H), 5.37 (d, J = 10.7 Hz, 1H), 4.95 (d, J = 14.2 Hz, 1H), 4.87 (d, J = 14.2 Hz, 1H), 4.06 (q, J = 7.1 Hz, 2H), 3.78 (t, J = 8.6 Hz, 1H), 2.40 (s, 3H), 1.98 (d, J = 13.7 Hz, 1H), 1.64–1.55 (m, 5H), 1.17 (t, J = 7.2 Hz, 3H), 1.15–1.12 (m, 3H), 0.93–0.90 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.9, 165.6, 142.8, 138.1, 129.2, 127.1, 98.5, 79.5, 60.9, 59.1, 41.5, 29.9, 29.2, 26.0, 25.7, 25.6, 21.3, 13.9. MALDI-MS: calculated for $C_{20}H_{27}NO_4S$ [M + Na]$^+$: m/z 400.16; found: 400.16.

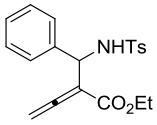
Synthesis of *β´*-aryl-*α*-aminoalkylallenic esters (1i–l)[3a]

[3] (a) B. J. Cowen, L. B. Saunders and S. Miller, *J. AM. Chem. Soc.*, 2009, **131**, 6105. (b) G.-L. Zhao and M. Shi, *J. Org. Chem.*, 2005, **70**, 9975.

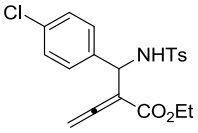


1i–l

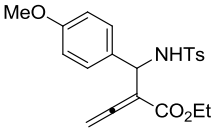
A flame-dried round-bottom flask equipped with a magnetic stirrer bar was charged with the requisite imine (1.78 mmol, 1 equiv), which was dissolved in dry toluene (8 mL) under an Ar atmosphere. Ethyl-2,3-butadienoate (300 mg, 2.68 mmol, 1.5 equiv) was added, followed by pyridine (28.7 µL, 0.356 mmol, 0.2 equiv). The mixture was heated at 50 °C for 12 h, at which point a second portion of pyridine was added (28.7 µL, 0.356 mmol, 0.2 equiv). The mixture was then stirred at 50 °C for an additional 12 h. The solution was concentrated under reduced pressure and the crude residue purified through flash column chromatography (20% EtOAc/hexane).



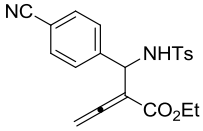
3-Ethoxycarbonyl-4-tosylamino-4-phenyl-1,2-butadiene (1i). Isolated in 56% yield as a yellow solid. All spectral data were in accordance with those in the literature.[3b]



3-Ethoxycarbonyl-4-tosylamino-4-*p*-chlorophenyl-1,2-butadiene (1j). Isolated in 54% yield as a yellow solid. All spectral data were in accordance with those in the literature.[3b]

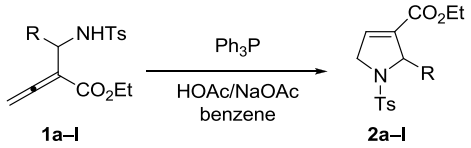


3-Ethoxycarbonyl-4-tosylamino-4-*p*-methoxyphenyl-1,2-butadiene (1k). Isolated in 33% yield as a yellow solid. All spectral data were in accordance with those in the literature.[3b]



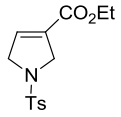
3-Ethoxycarbonyl-4-tosylamino-4-*p*-cyanophenyl-1,2-butadiene (1l). Isolated in 25% yield as a thick oil. IR (film) ν_{max} = 3274, 2985, 2220, 1700, 1339, 1163 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, J = 8.2 Hz, 2H), 7.52 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.2 Hz, 2H), 6.03 (d, J = 9.7 Hz, 1H), 5.32, (d, J = 9.7 Hz, 1H), 5.22 (d, J = 14.7 Hz, 1H), 5.12 (d, J = 14.8 Hz, 1H), 4.03 (q, J = 7.1 Hz, 2H), 2.41 (s, 3H), 1.13 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.9, 164.9, 144.5, 143.6, 132.1, 129.5, 127.3, 127.0, 118.4, 11.4, 99.8, 81.7, 61.5, 56.2, 21.4, 13.9. MALDI-MS: calculated for $C_{21}H_{20}N_2O_4S$ [M + Na]$^+$: m/z 419.10; found: 419.06.

Procedure for intramolecular γ-umpolung addition, formation of pyrrolines (2a–l)

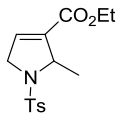


1a–l **2a–l**

A flame-dried round-bottom flask equipped with a magnetic stirrer bar was charged with the requisite allenoate **1** (0.123 mmol, 1 equiv), Ph_3P (6.46 mg, 0.025 mmol, 0.2 equiv), and NaOAc (5.04 mg, 0.062 mmol, 0.5 equiv), which were placed under an Ar atmosphere. Dry benzene (4.1 mL) was added to this mixture, followed by AcOH (3.52 µL, 0.62 mmol, 0.5 equiv). The mixture was stirred at room temperature and monitored (TLC) for consumption of the starting allenoate **1**. Upon completion of the reaction, the solution was concentrated under reduced pressure and the crude residue purified through flash column chromatography (10–20% EtOAc/hexane).

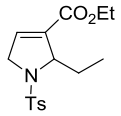


3-Carbethoxy-3-pyrroline (2a). Isolated in 62% yield. Following the same procedure as outlined above, but without the addition of NaOAc and AcOH, the product was isolated in 87% yield. All spectral data were in accordance with those reported in the literature.[4]

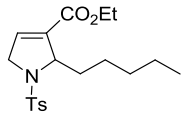


[4] J. M. Kim, K. Y. Lee, S. Lee and J. N. Kim, *Tetrahedron Lett.*, 2004, **45**, 2805.

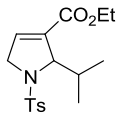
3-Carbethoxy-2-methyl-3-pyrroline (2b). Isolated in 99% yield as a thick oil. IR (film) ν_{max} = 2985, 2926, 2862, 1717, 1347, 1267, 1164 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 7.9 Hz, 2H), 6.53 (s, 1H), 4.78–4.67 (m, 1H), 4.41–4.26 (m, 1H), 4.26–4.12 (m, 3H), 2.41 (s, 3H), 1.53 (t, J = 6.3 Hz, 3H), 1.26 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.1, 143.5, 136.5, 135.1, 134.6, 129.7, 127.3, 62.0, 60.7, 54.4, 22.1, 21.4, 14.0. MALDI-MS: calculated for $C_{15}H_{19}NO_4S$ [M + Na]$^+$: m/z 332.09; found: 332.16.



3-Carbethoxy-2-ethyl-3-pyrroline (2c). Isolated in 97% yield as a thick oil. IR (film) ν_{max} = 2972, 1718, 1347, 1249, 1164, 1083, 1040 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.2 Hz, 2H), 6.59–6.57 (m, 1H), 4.81–4.79 (m, 1H), 4.24–4.22 (m, 2H), 4.19–4.13 (m, 2H), 2.41 (s, 3H), 2.08–2.00 (m, 1H), 1.94–1.87 (m, 1H), 1.25 (t, J = 7.1, 3H), 0.83 (t, J = 7.4, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.1, 143, 136.2, 134.6, 134.3, 129.7, 127.2, 66.6, 60.7, 55.3, 26.6, 21.4, 14.0, 7.4. MALDI-MS: calculated for $C_{16}H_{21}NO_4S$ [M + Na]$^+$: m/z 346.11; found: 346.13.

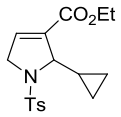


3-Carbethoxy-2-*n*-propyl-3-pyrroline (2d). Isolated in 69% yield as a thick oil. IR (film) ν_{max} = 2929, 2860, 1717, 1349, 1262, 1164, 1091 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 6.54 (br d, J = 1.6 Hz, 1H), 4.80 (app s, 1H), 4.27–4.21 (m, 2H), 4.20–4.11 (m, 2H), 2.41 (s, 3H), 1.98–1.90 (m, 1H), 1.88–1.80 (m, 1H), 1.38–1.11 (m, 6H), 1.25 (t, J = 11.3 Hz, 3H), 0.85 (t, J = 6.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.1, 143.5, 135.9, 134.9, 134.7, 129.7, 127.2, 66.0, 60.7, 55.1, 33.6, 31.6, 23.0, 22.4, 21.4, 14.0, 13.9. MALDI-MS: calculated for $C_{19}H_{27}NO_4S$ [M + Na]$^+$: m/z 388.18; found: 388.15.

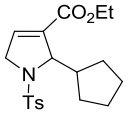


3-Carbethoxy-2-isopropyl-3-pyrroline (2e). Isolated in 97% yield as a thick oil. IR (film) ν_{max} = 3084, 2966, 2933, 2874, 1717, 1463, 1348, 1164 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, J = 8.3 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 6.49 (pent, J = 1.3 Hz, 1H), 4.75 (dt, J = 3.1, 1.0 Hz, 1H), 4.22 (dd, J = 18.3, 2.5

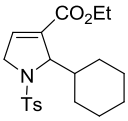
Hz, 1H), 4.14 (dq, *J* = 7.1, 1.4 Hz, 2H), 4.09 (ddd, *J* = 18.4, 4.4, 1.7 Hz, 1H) 2.39 (s, 3H), 2.2 (d sept, *J* = 6.9, 2.9 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.08 (d, *J* = 6.9 Hz, 3H), 0.85 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5, 143.5, 136.5, 135.3, 134.4, 129.6, 127.4, 71.3, 60.6, 55.9, 32.9, 21.4, 19.3, 16.7, 13.9. MALDI-MS: calculated for $C_{17}H_{23}NO_4S$ $[M + Na]^+$: *m*/*z* 360.12; found: 360.12.



3-Carbethoxy-2-cyclopropyl-3-pyrroline (2f). Isolated in 95% yield as a thick oil. IR (film) ν_{max} = 3078, 2979, 2916, 2852, 1717, 1346, 1261, 1163 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.3, 2H), 6.51 (s, 1H), 4.54 (t, *J* = 5.2 Hz), 4.28–4.12 (m, 4H), 2.40 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.12–1.01 (m, 1H), 0.81–0.71 (m, 1H), 0.60–0.37 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4, 143.5, 136.5, 135.5, 135.0, 129.6, 127.3, 28.3, 60.7, 54.9, 21.4, 16.0, 14.009, 3.4, 2.4. GC-MS: calculated for $C_{17}H_{21}NO_4S$ $[M]^+$: *m*/*z* 335.12; found: 335.1.

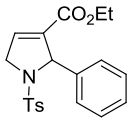


3-Carbethoxy-2-cyclopentyl-3-pyrroline (2g). Isolated in 85% yield as a thick oil. IR (film) ν_{max} = 2955, 2870, 1717, 1345, 1257, 1163, 1091. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 7.6 Hz, 2H), 6.43 (app. s, 1H), 4.92, (t, *J* = 4.1 Hz, 1H), 4.21 (dd, *J* = 18.4, 2.6 Hz, 1H), 4.18–4.09 (m, 3H), 2.39 (s, 3H), 2.31–2.24 (m, 1H), 1.74–1.66 (m, 3H), 1.63–1.45 (m, 4H), 1.33–1.26 (m, 1H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5, 143.5, 136.4, 135.9, 134.4, 129.6, 127.4, 68.5, 60.6, 55.7, 45.0, 28.5, 27.4, 25.0, 24.4, 21.4, 14.0. MALDI-MS: calculated for $C_{19}H_{25}NO_4S$ $[M + Na]^+$: *m*/*z* 386.14; found: 386.17.

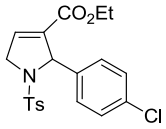


3-Carbethoxy-2-cyclohexyl-3-pyrroline (2h). Isolated in 69% yield (93% based on recovered starting material) as a thick oil. IR (film) ν_{max} = 2985, 2928, 2854, 1717, 1345, 1164 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.45 (s, 1H), 4.70 (app s, 1H), 4.20 (dd, *J* = 18.4, 2.7 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 4.06 (dd, *J* = 2.0, 2.74 Hz, 1H), 2.37 (s, 3H), 1.81–1.68 (m, 4H), 1.65–1.56 (m, 2H), 1.40 (dq, *J* = 12.5, 3.0 Hz, 1H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.18–1.02 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5, 143.5, 136.4, 135.1, 134.4, 129.5, 127.4, 71.0, 60.6, 55.8, 42.8, 30.0,

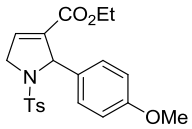
27.1, 26.3, 26.3, 26.11, 21.4, 14.0. MALDI-MS: calculated for $C_{20}H_{27}NO_4S$ [M + Na]$^+$: *m*/*z* 400.16; found: 400.16.



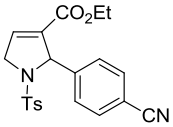
3-Carbethoxy-2-phenyl-3-pyrroline (2i). Isolated in 93% yield. All spectral data were in accordance with those reported in the literature.[4]



3-Carbethoxy-2-*p*-chlorophenyl-3-pyrroline (2j). Isolated in 88% yield (procedure was performed as described above, but without the addition of AcOH and NaOAc). All spectral data were in accordance with those reported in the literature.[5]

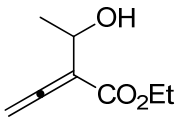


3-Carbethoxy-2-*p*-methoxyphenyl-3-pyrroline (2k). Isolated in 99% yield. All spectral data were in accordance with those reported in the literature.[5]

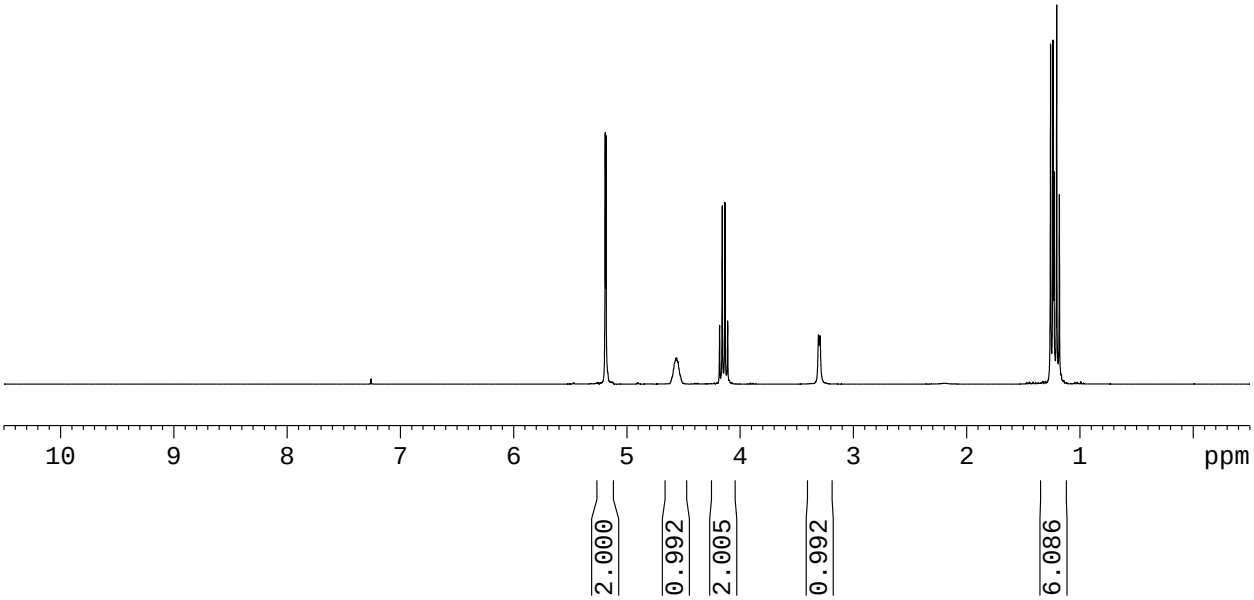


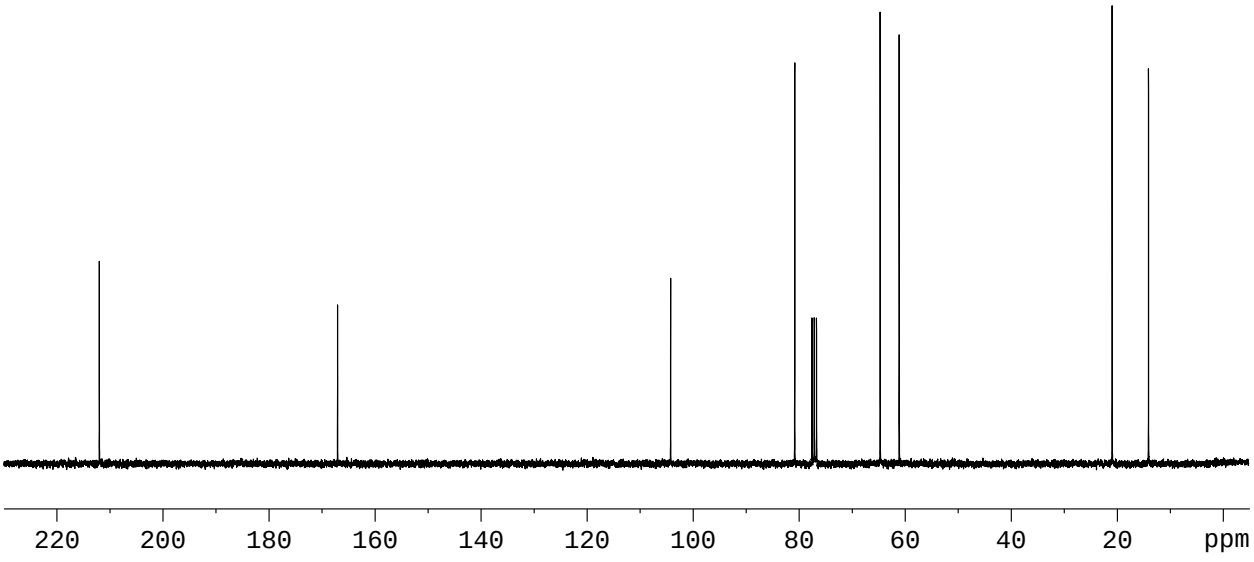
3-Carbethoxy-2-*p*-cyanophenyl-3-pyrroline (2l). Isolated in 85% yield. IR (film) ν_{max} = 3068, 2983, 2229, 1722, 1347, 1163, 1093 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 6.79 (*J* = 8.2 Hz, 2H), 6.79 (app d, *J* = 1.8 Hz, 1H), 5.68 (app s, 1H), 4.49–4.40 (m, 2H), 4.06–3.95 (m, 2H), 2.38 (s, 3H), 1.09 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.2, 145.1, 143.9, 136.4, 134.9, 134.8, 132.0, 129.7, 128.5, 127.0, 118.5, 111.6, 28.4, 61.0, 55.2, 21.4, 13.8. MALDI-MS: calculated for $C_{21}H_{20}N_2O_4S$ [M + Na]$^+$: *m*/*z* 419.10; found: 419.08.

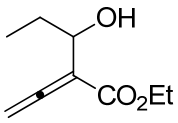
[5] A. Scherer and J. A. Gladysz, *Tetrahedron Lett.*, 2006, **47**, 6335.



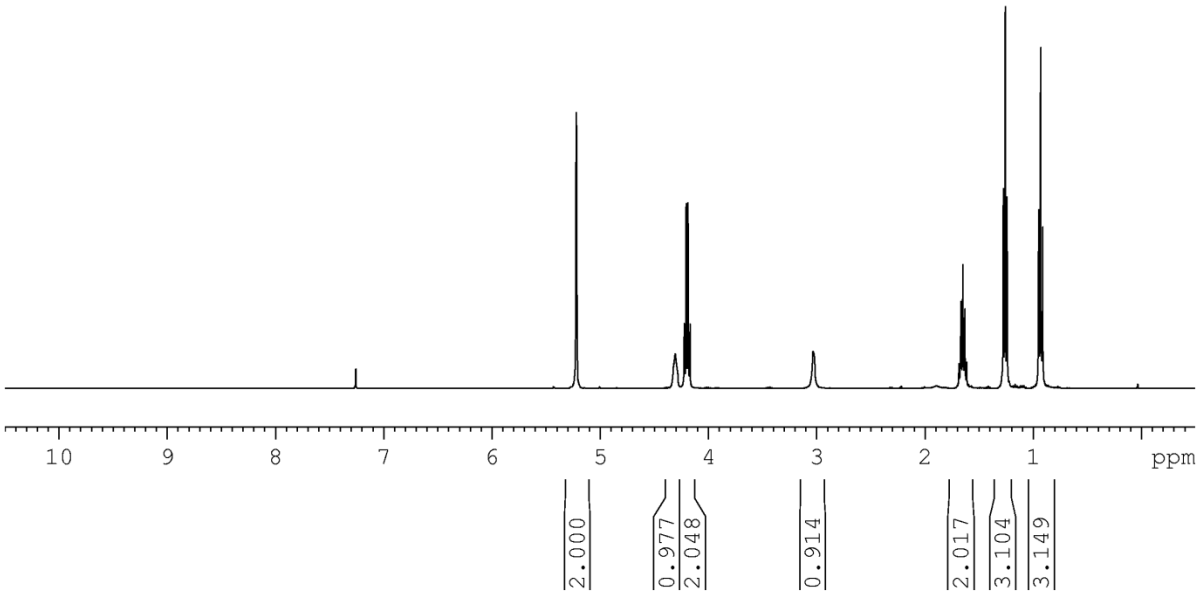
10b

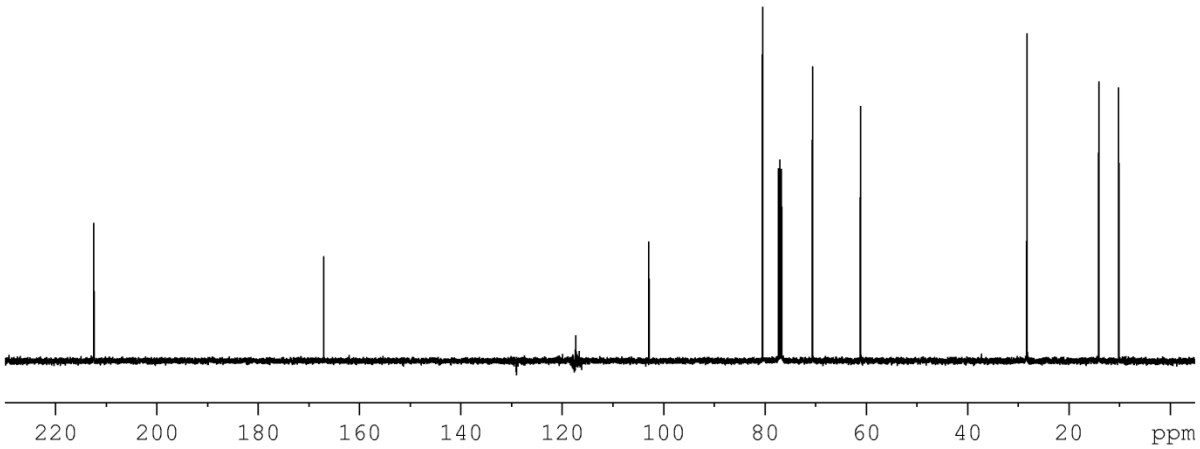


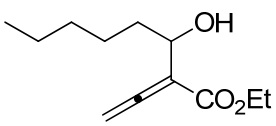




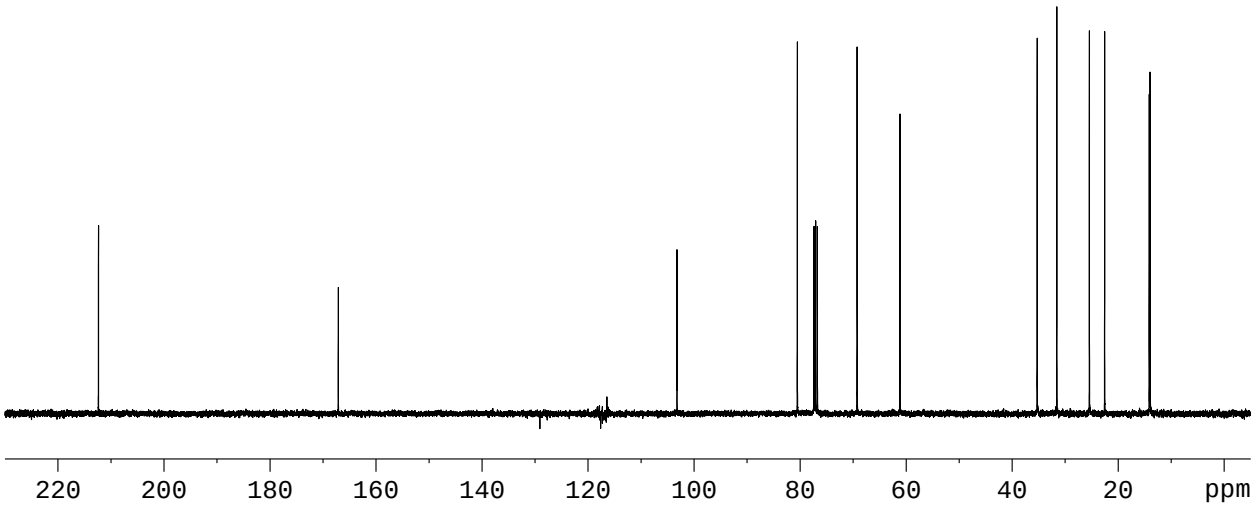
10c

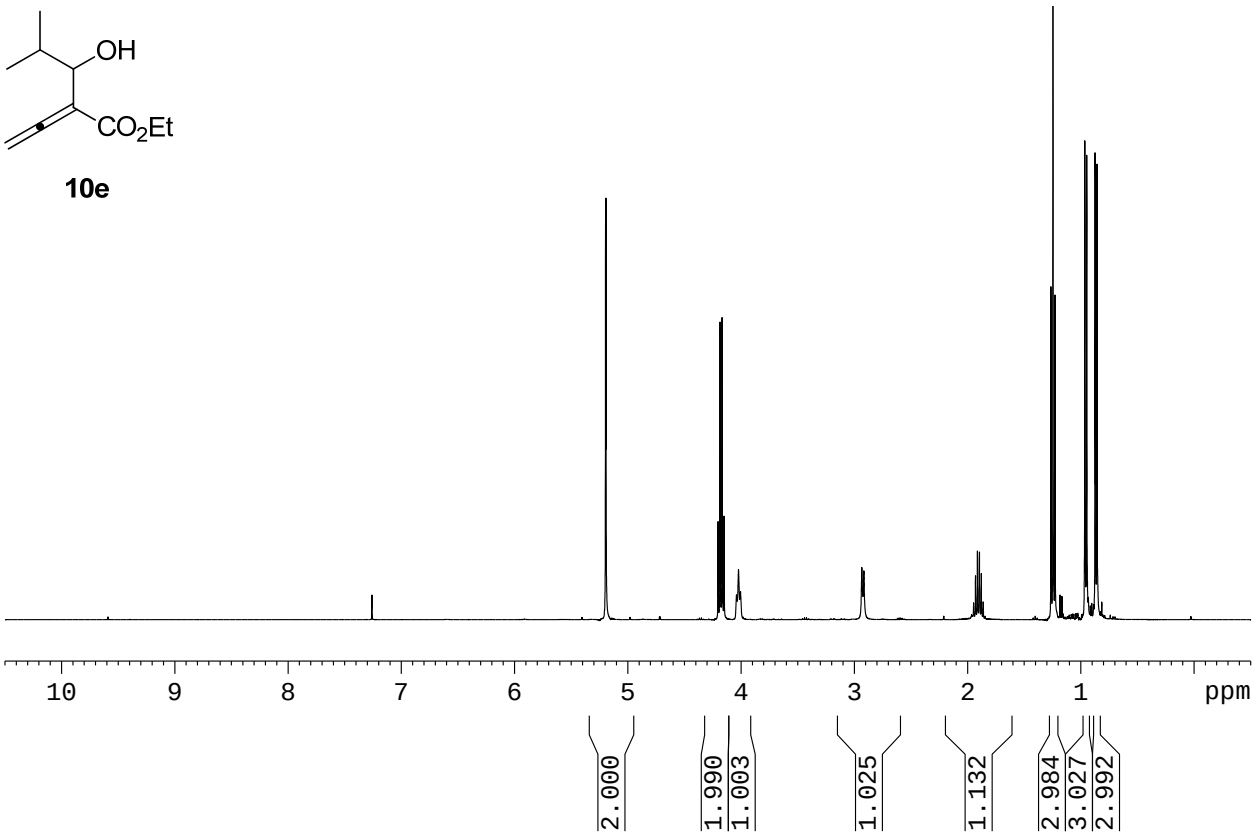


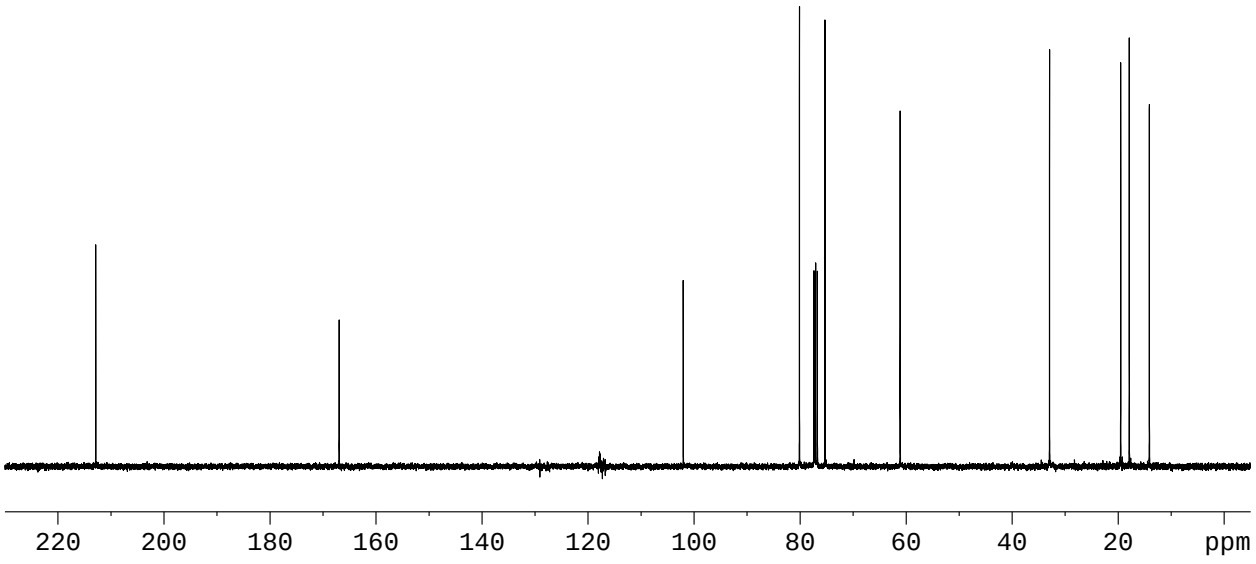


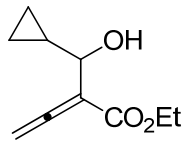


10d

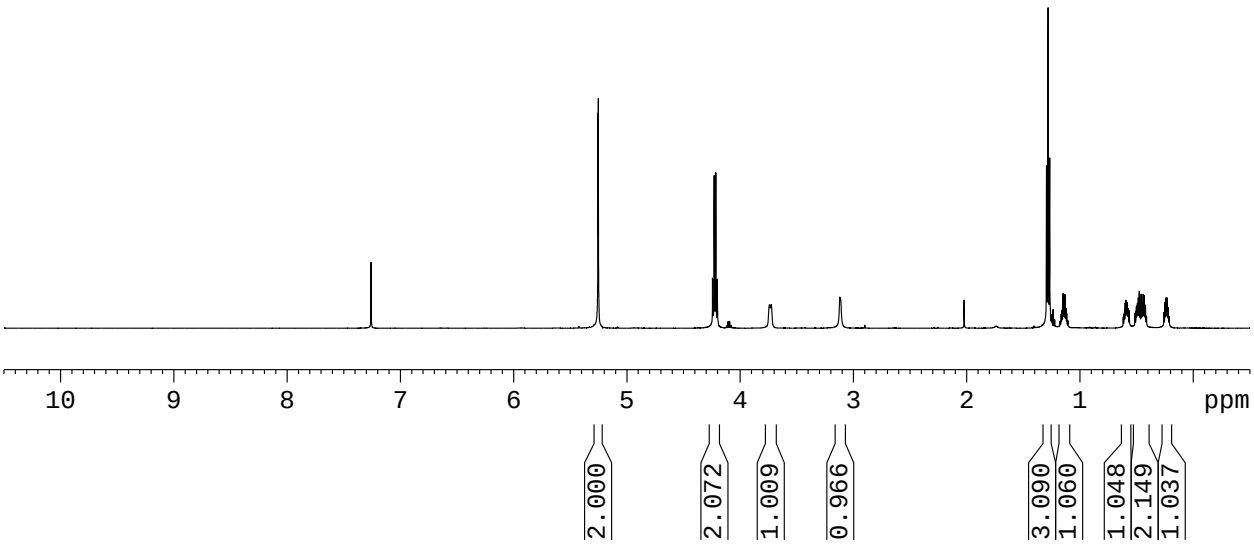


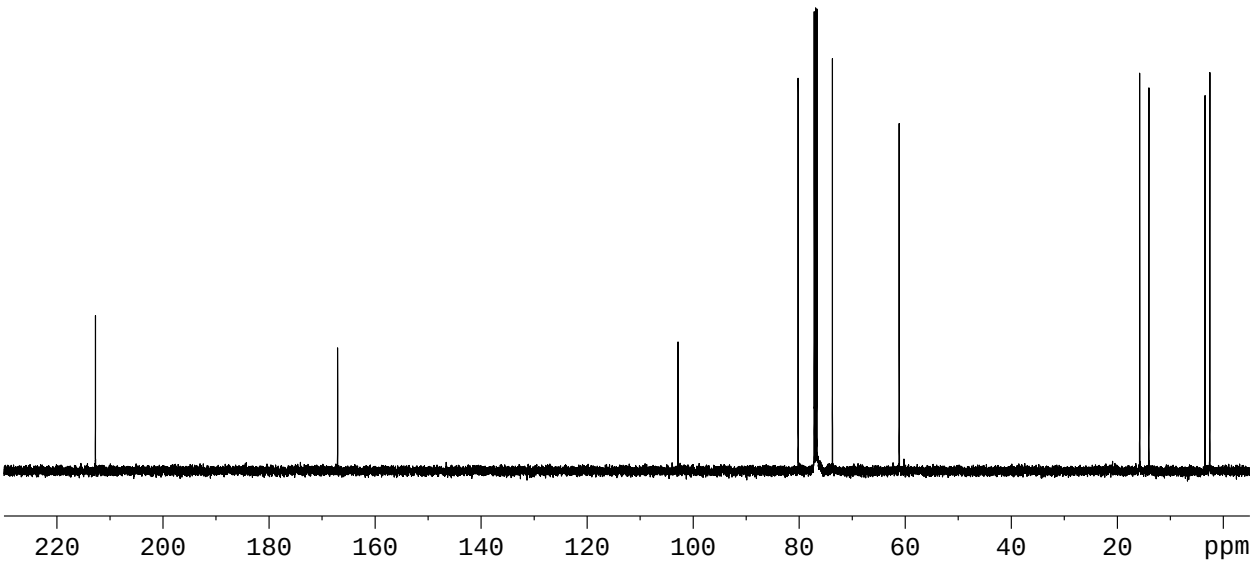


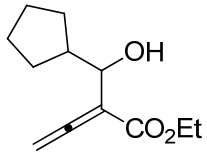




10f







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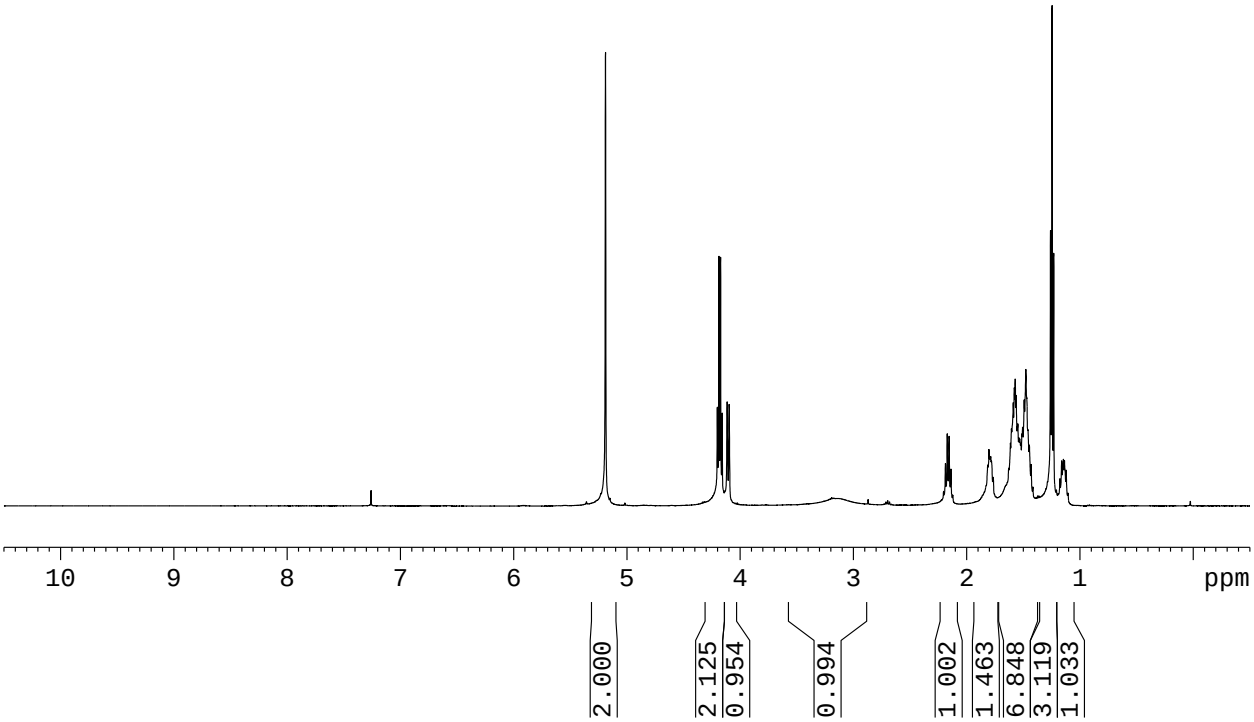

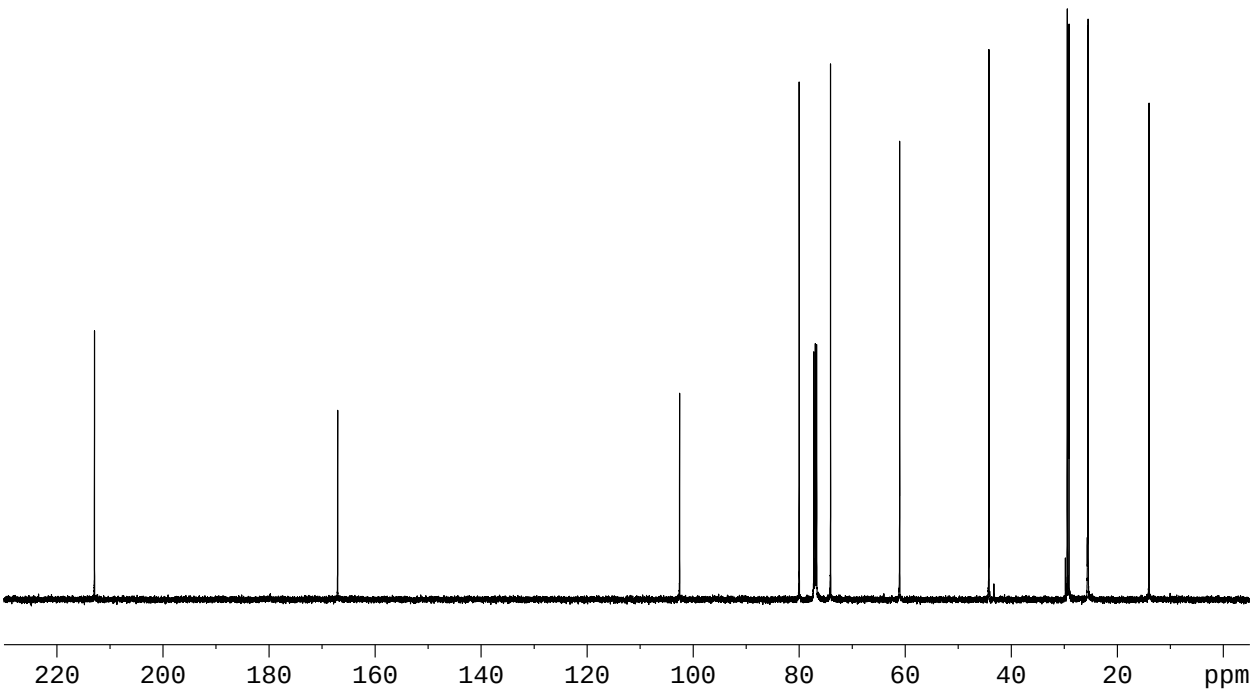

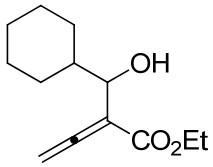

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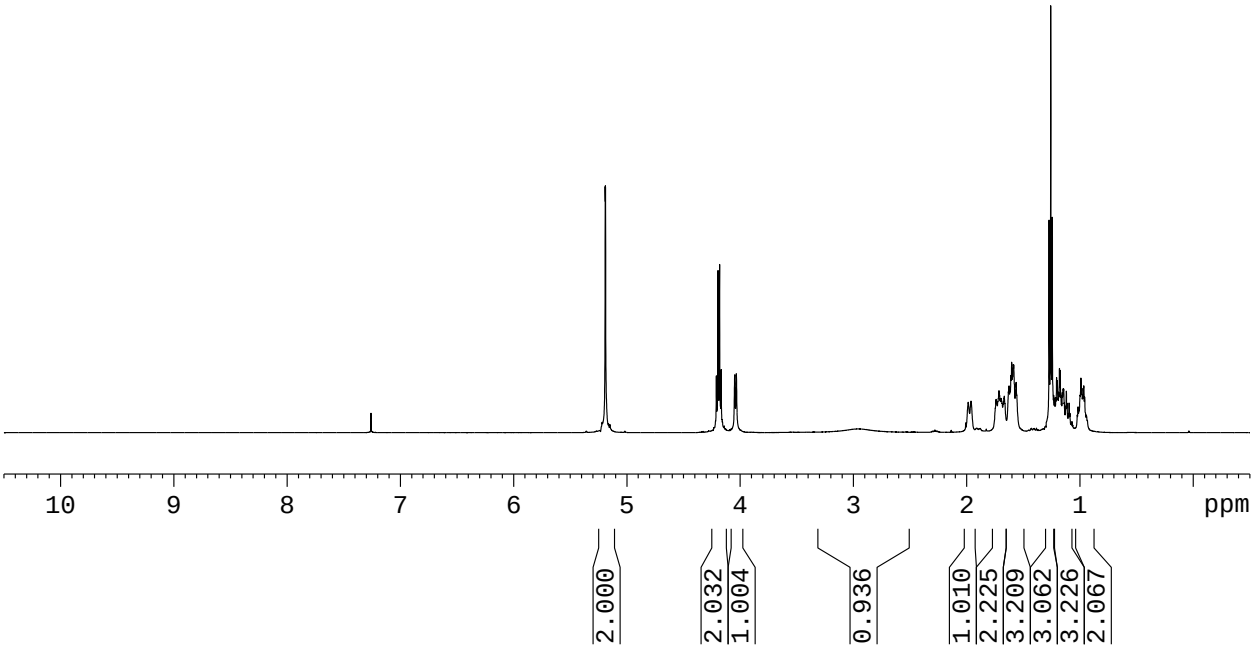

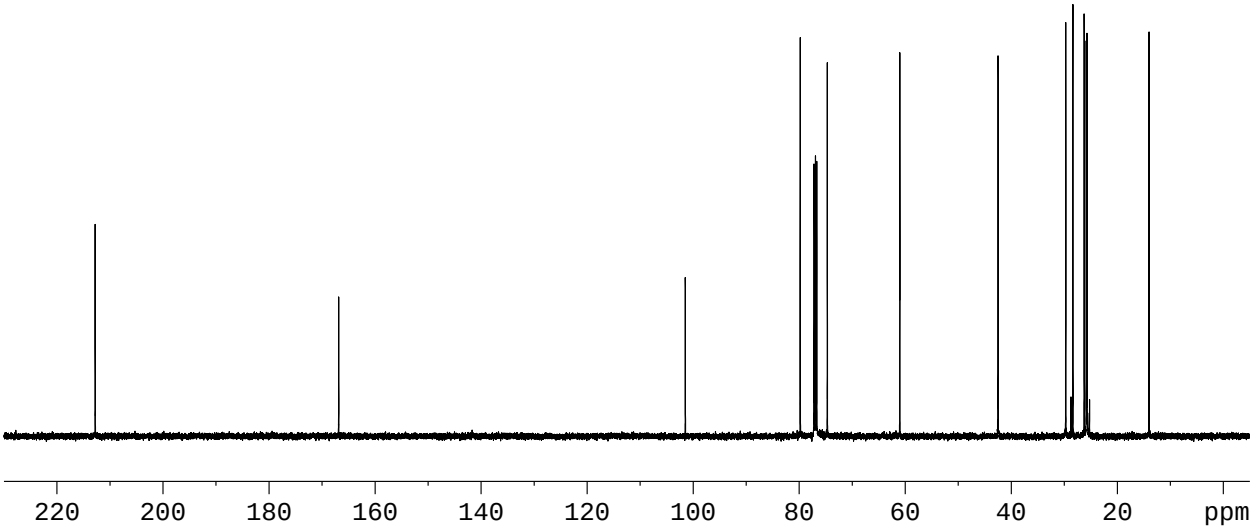

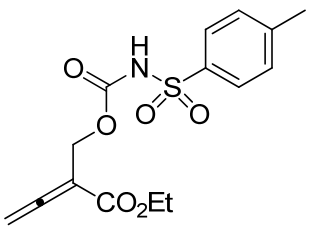

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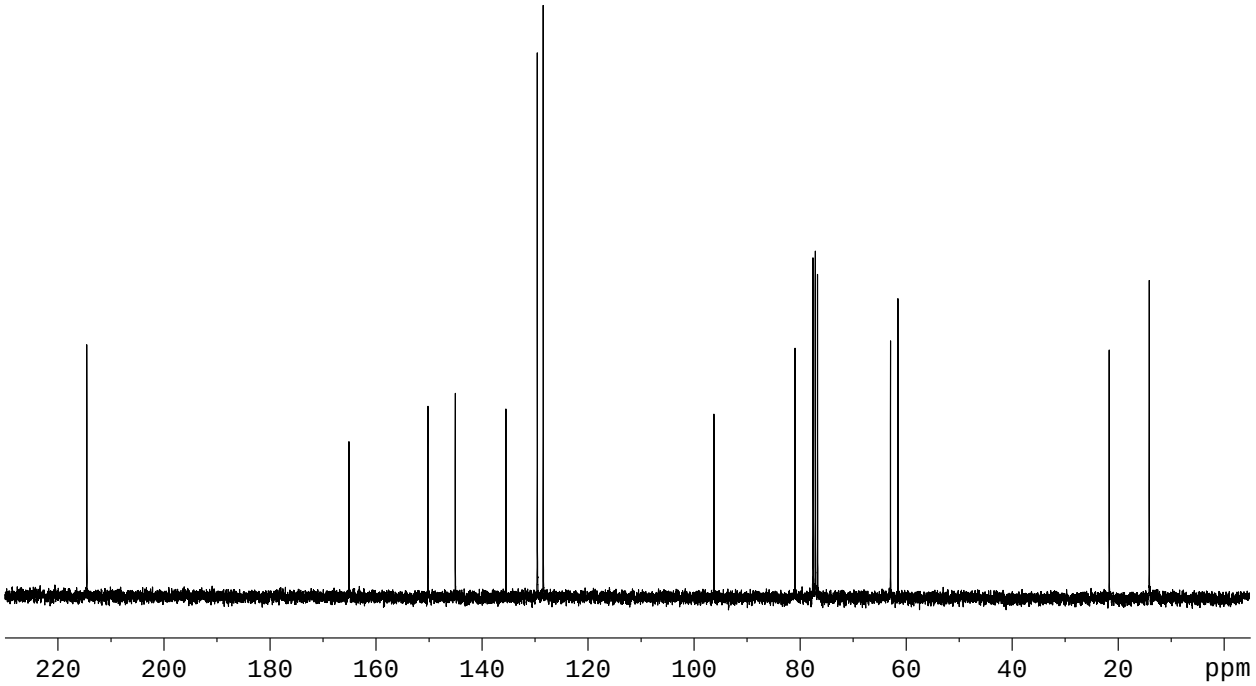

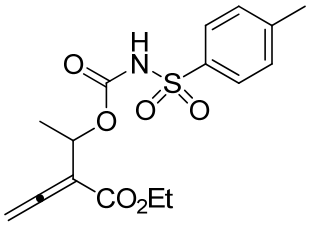

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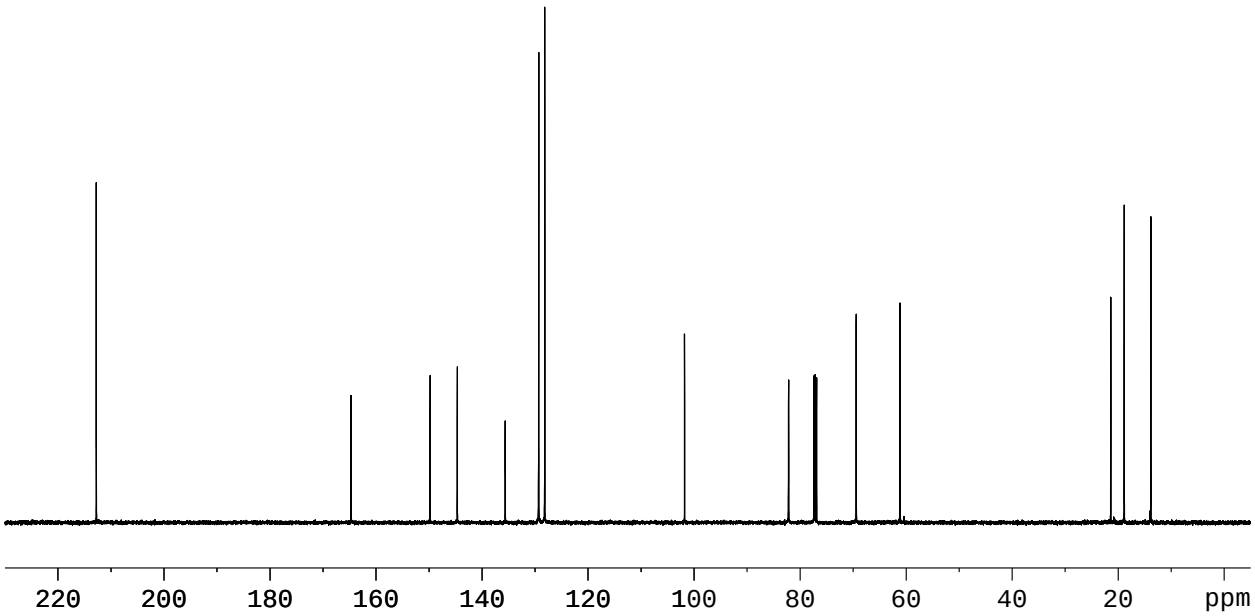

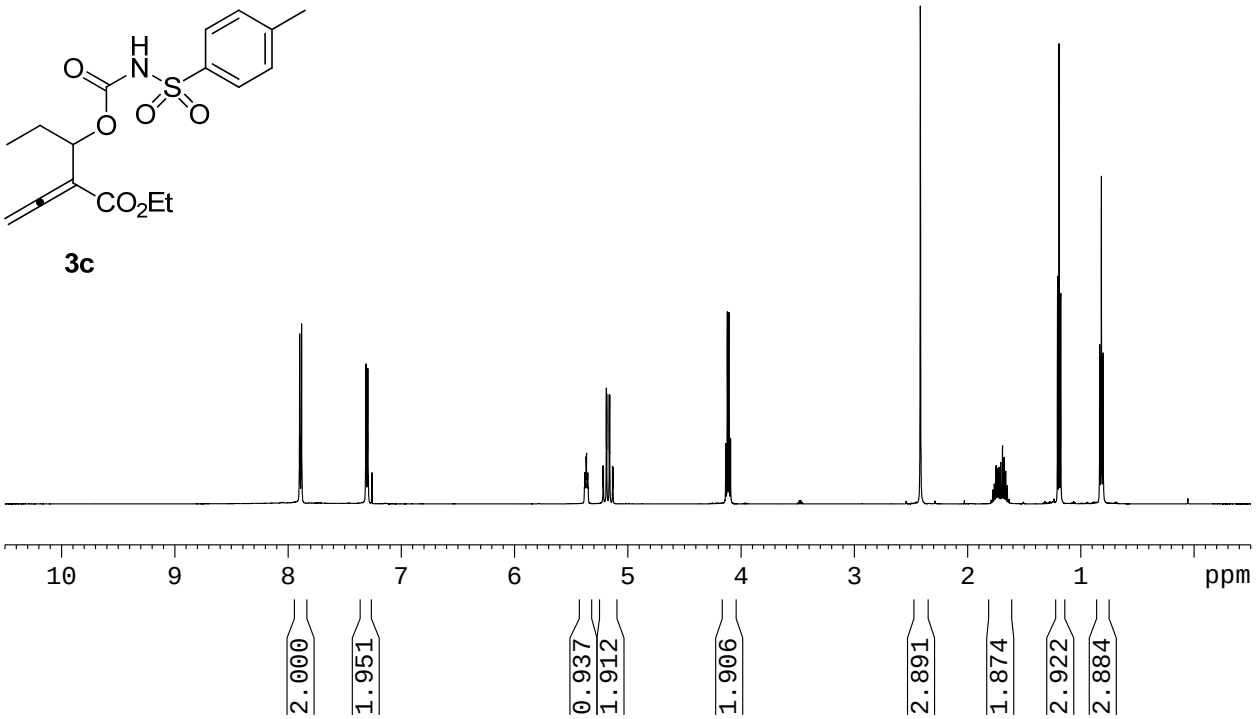

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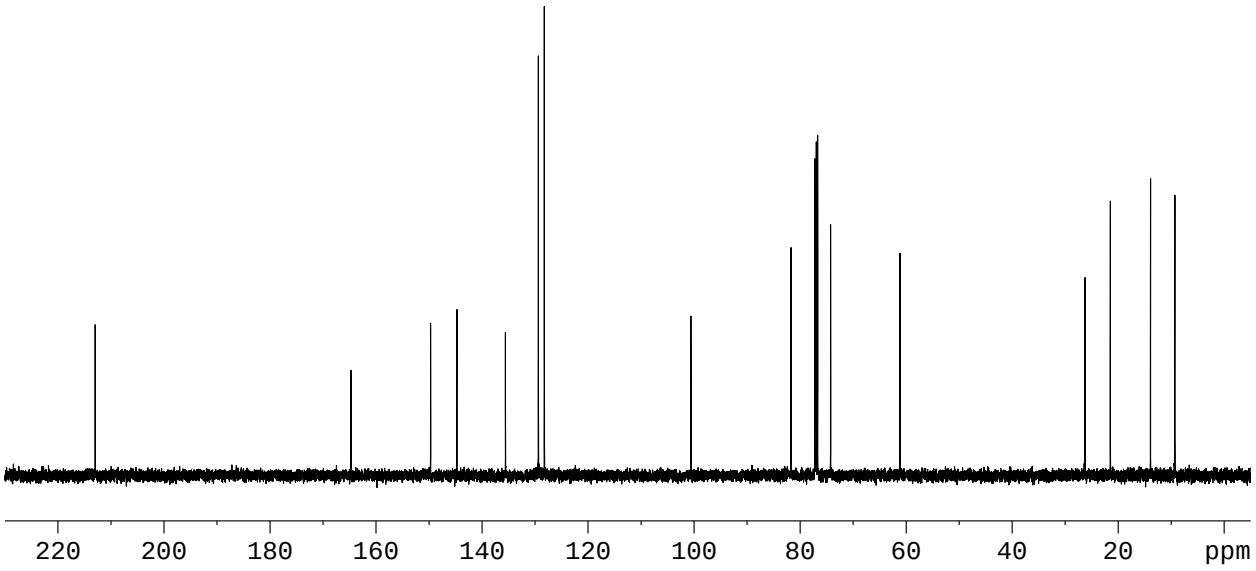

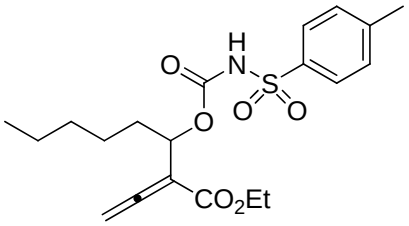

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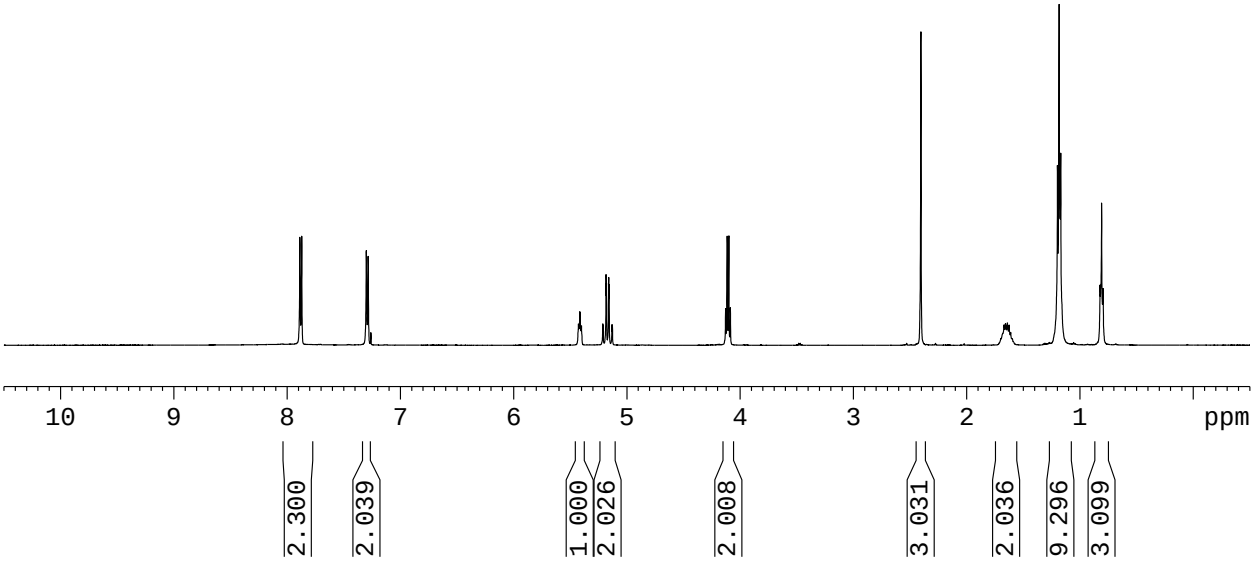

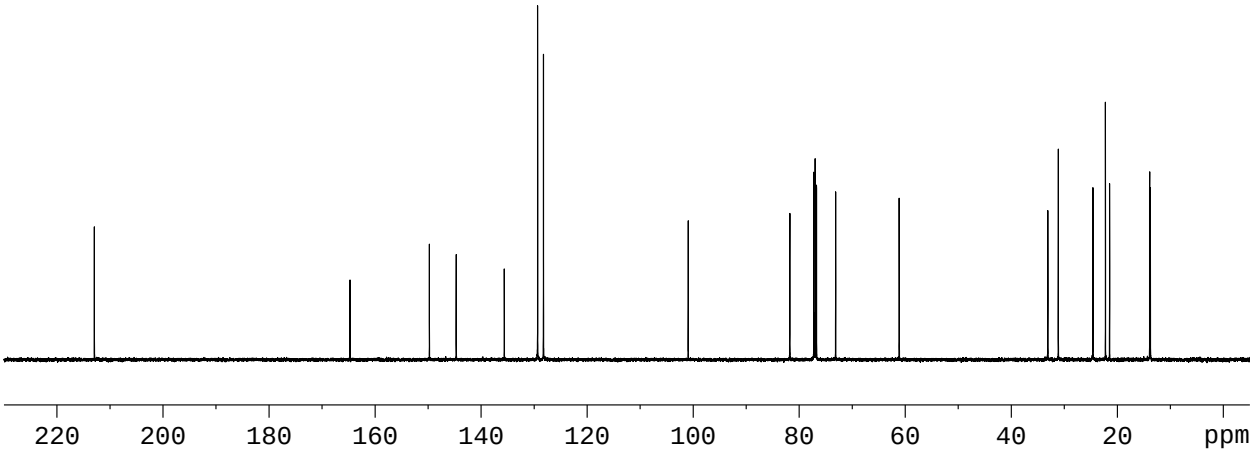

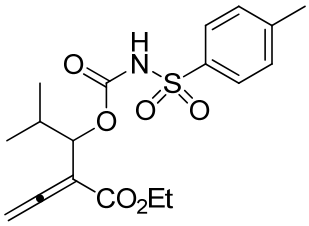

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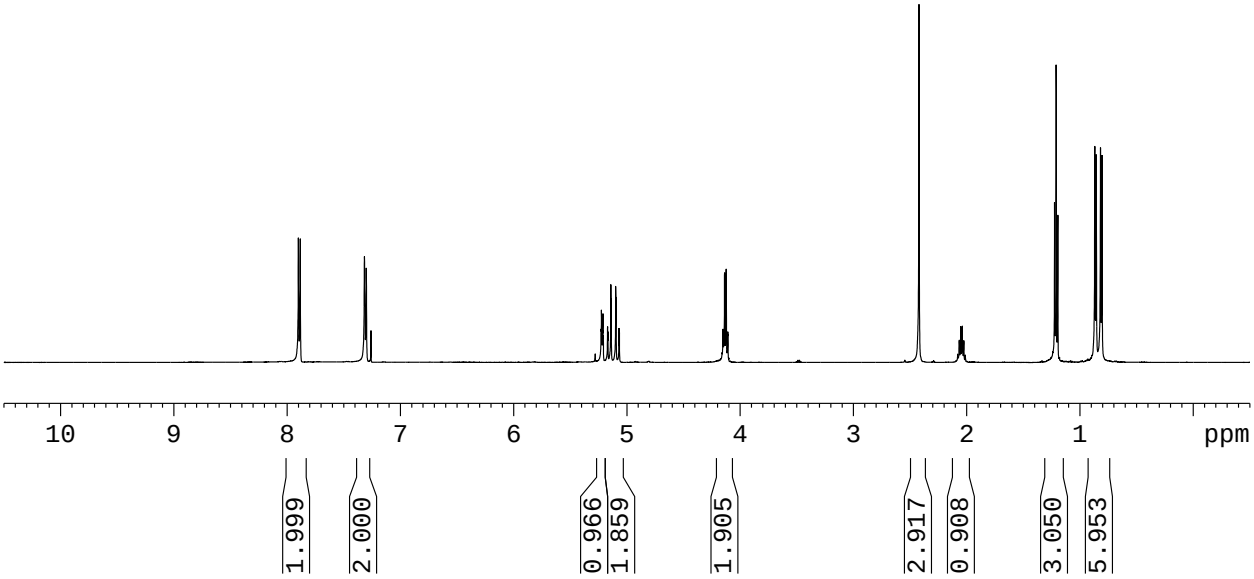

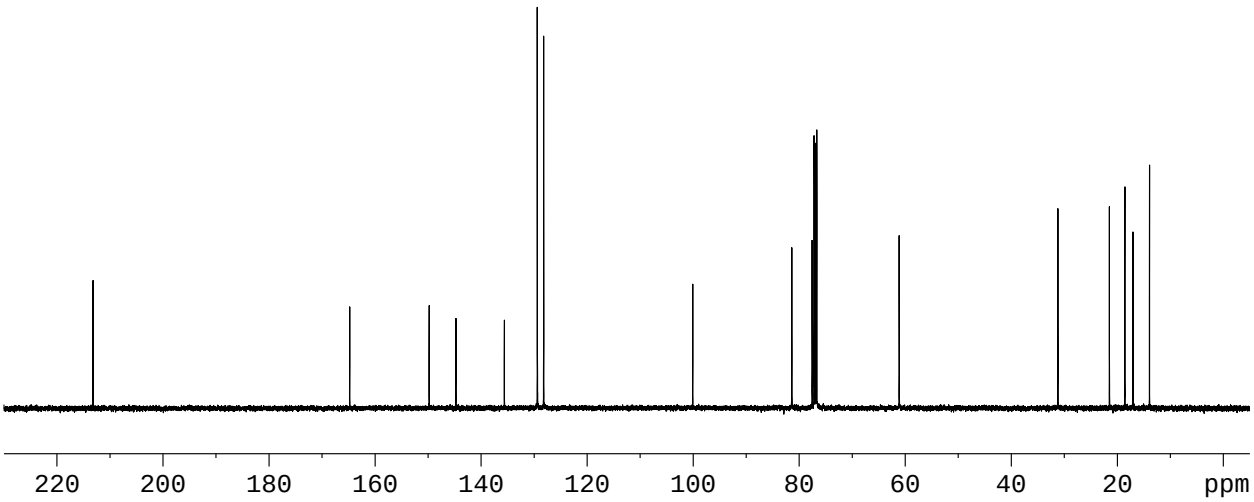

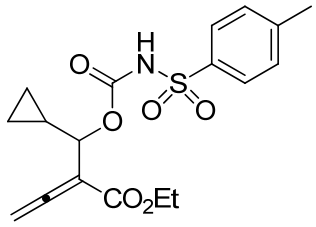

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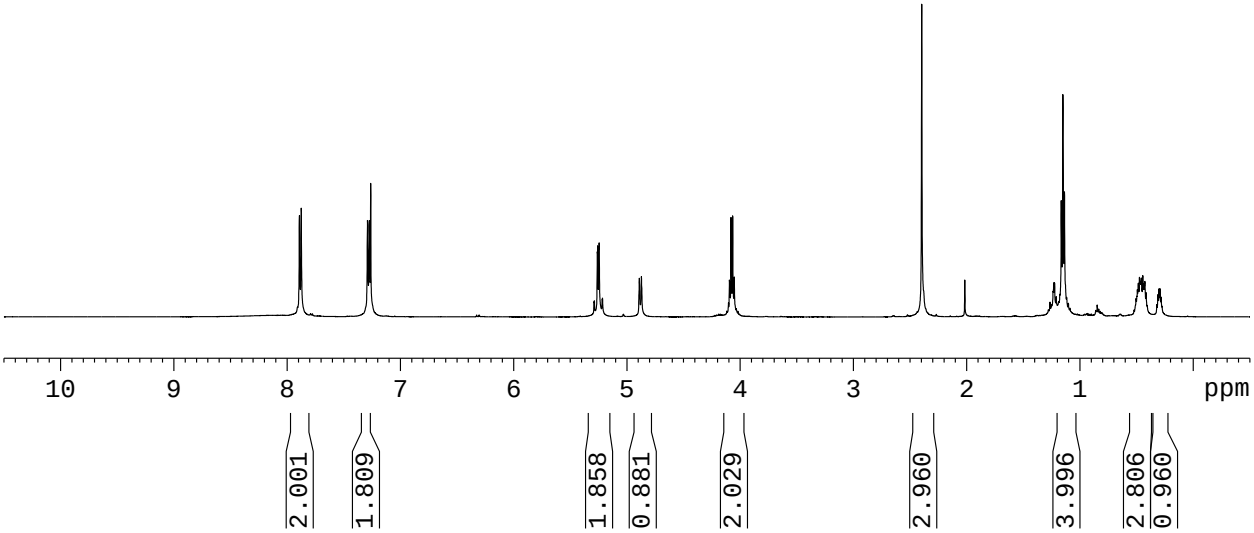

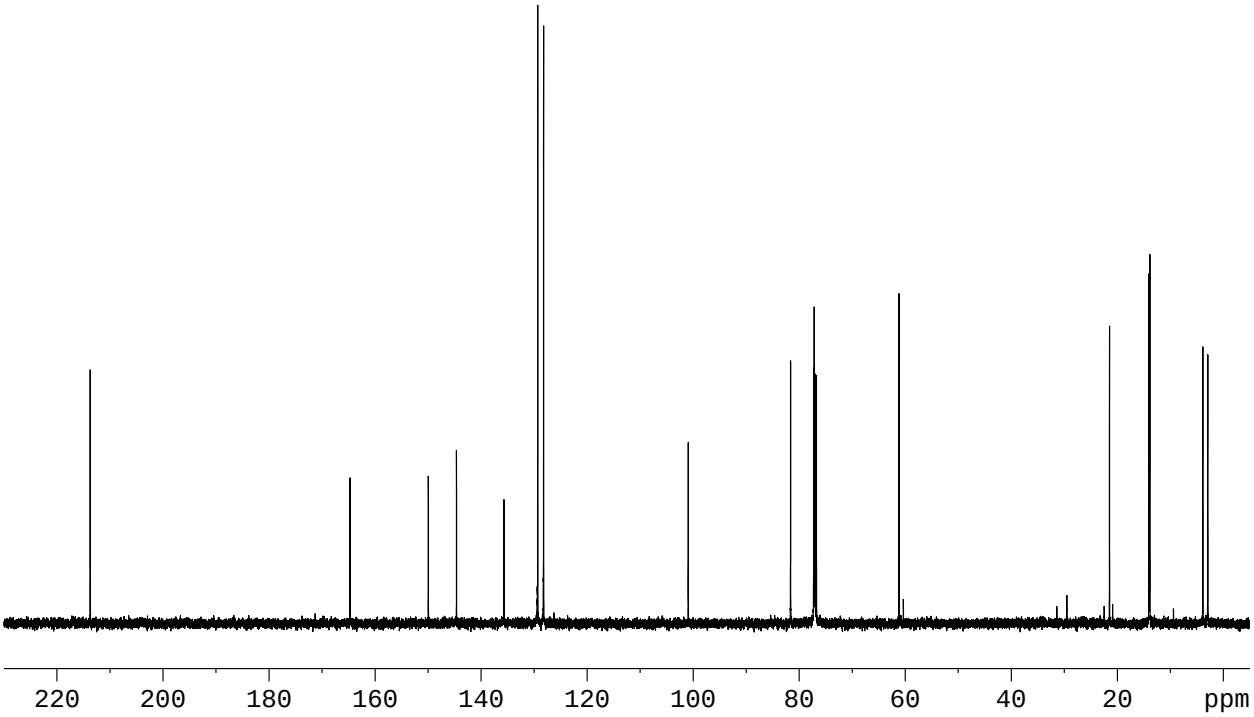

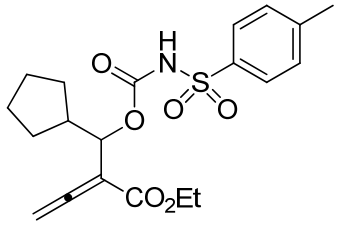

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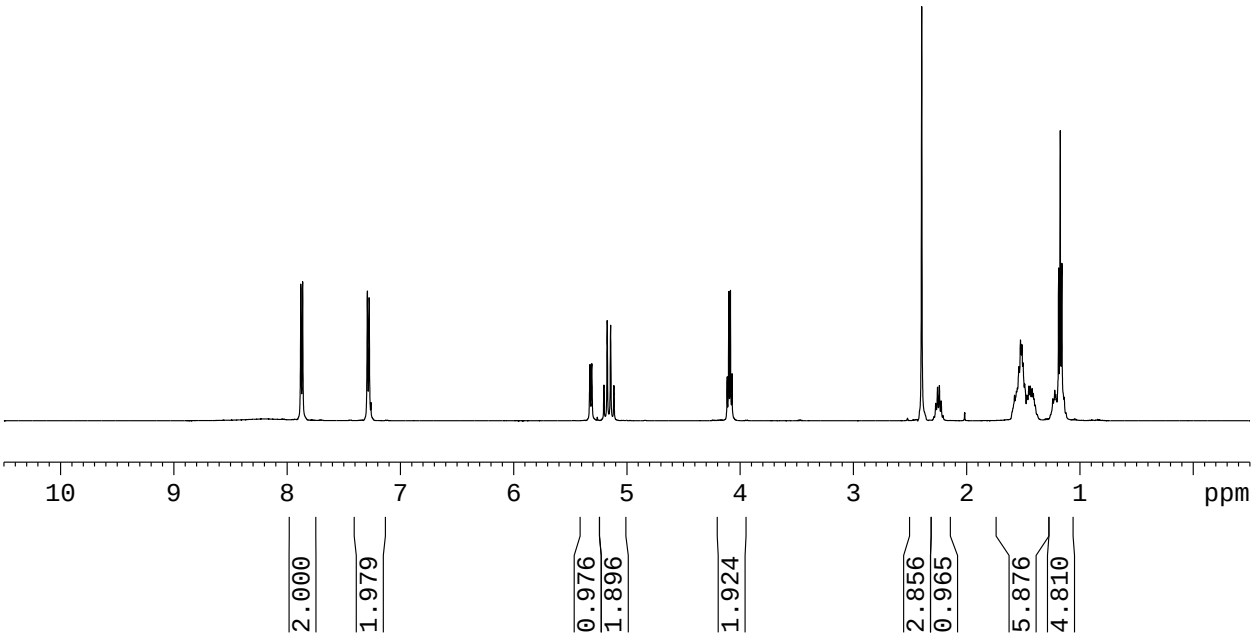

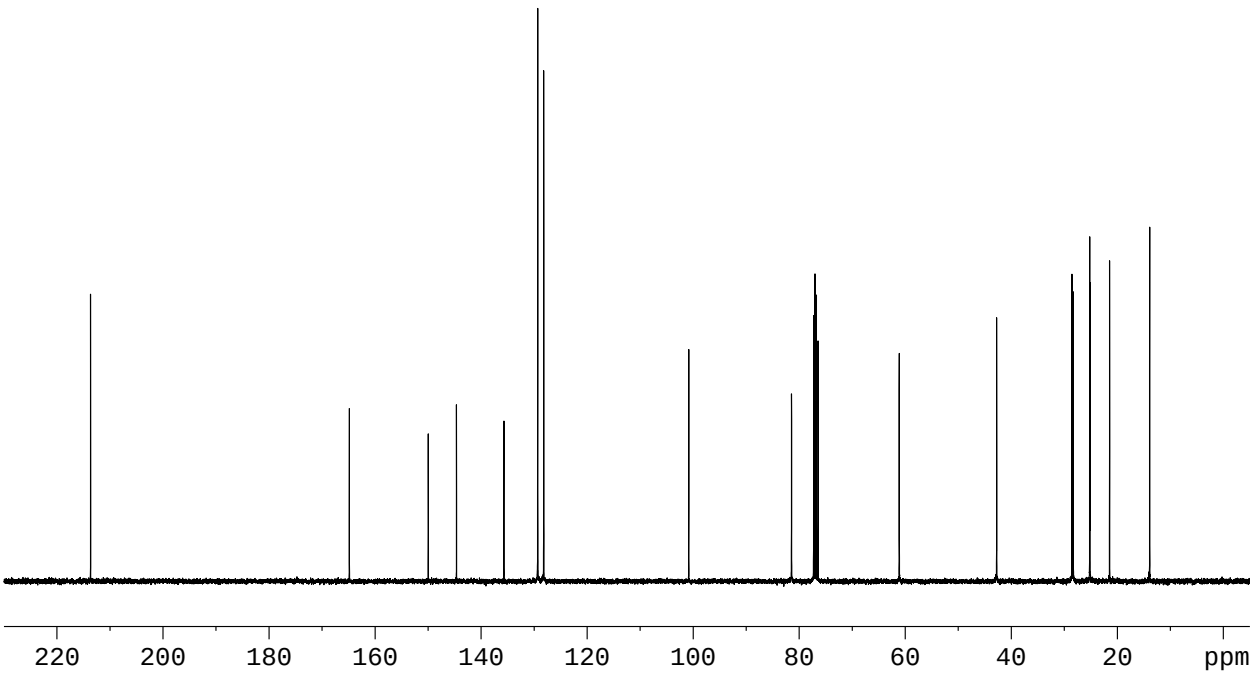

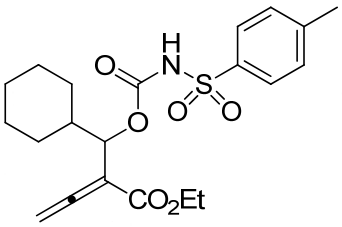
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3h

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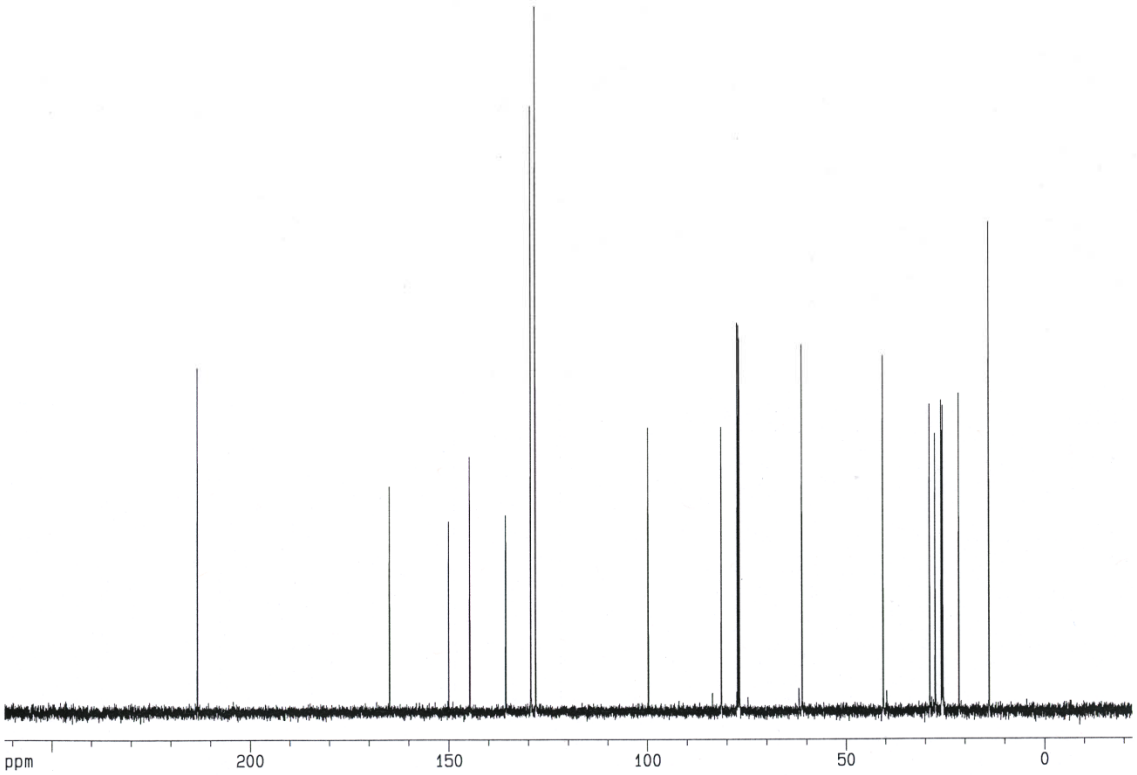
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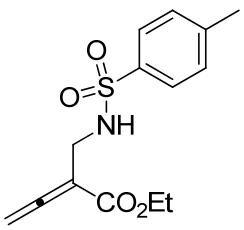

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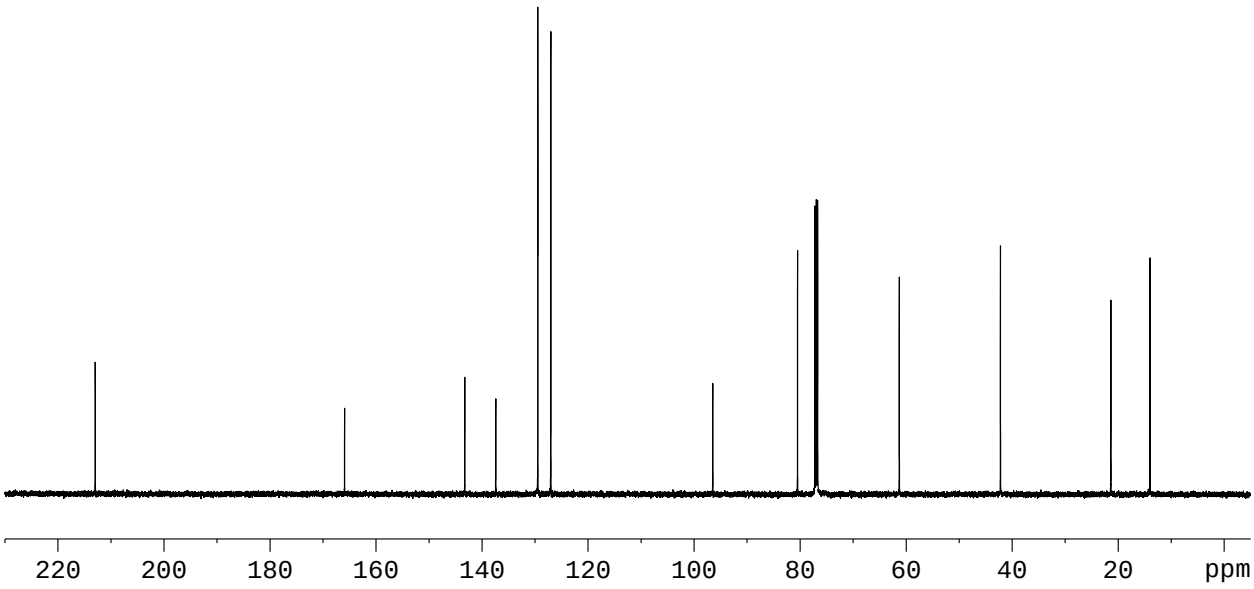

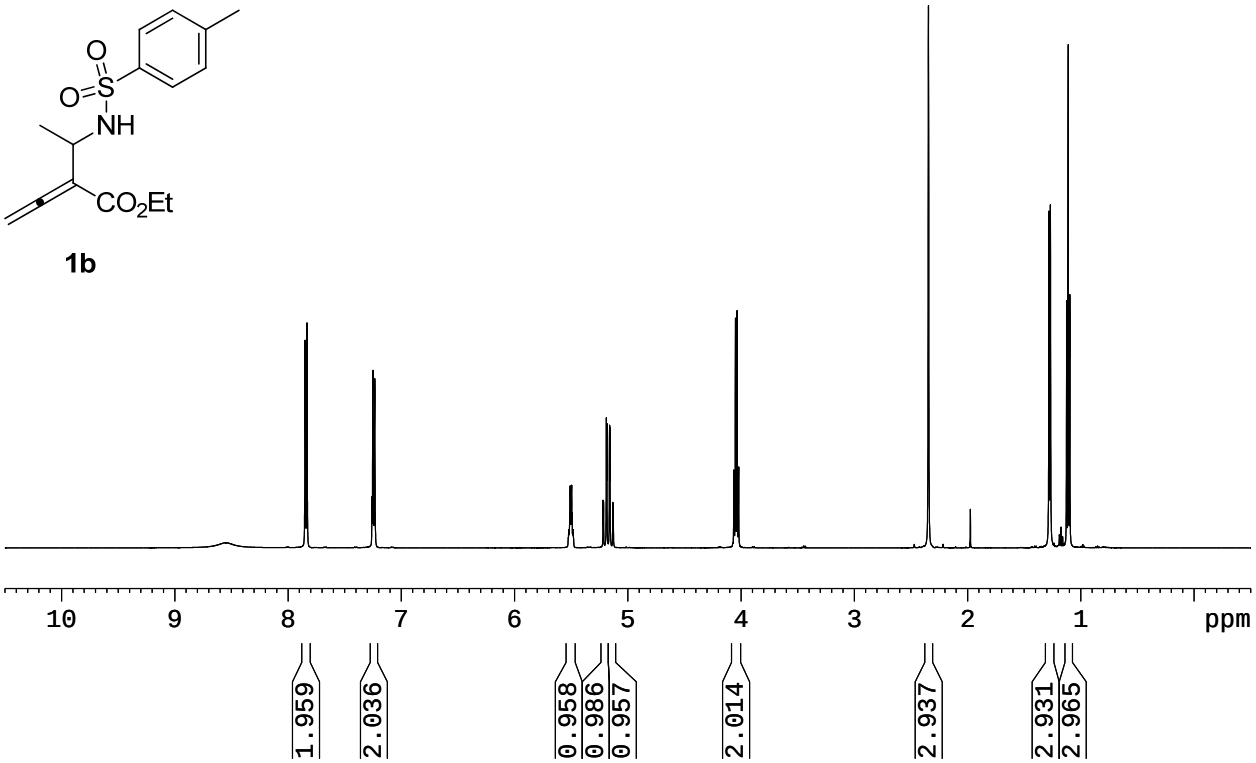

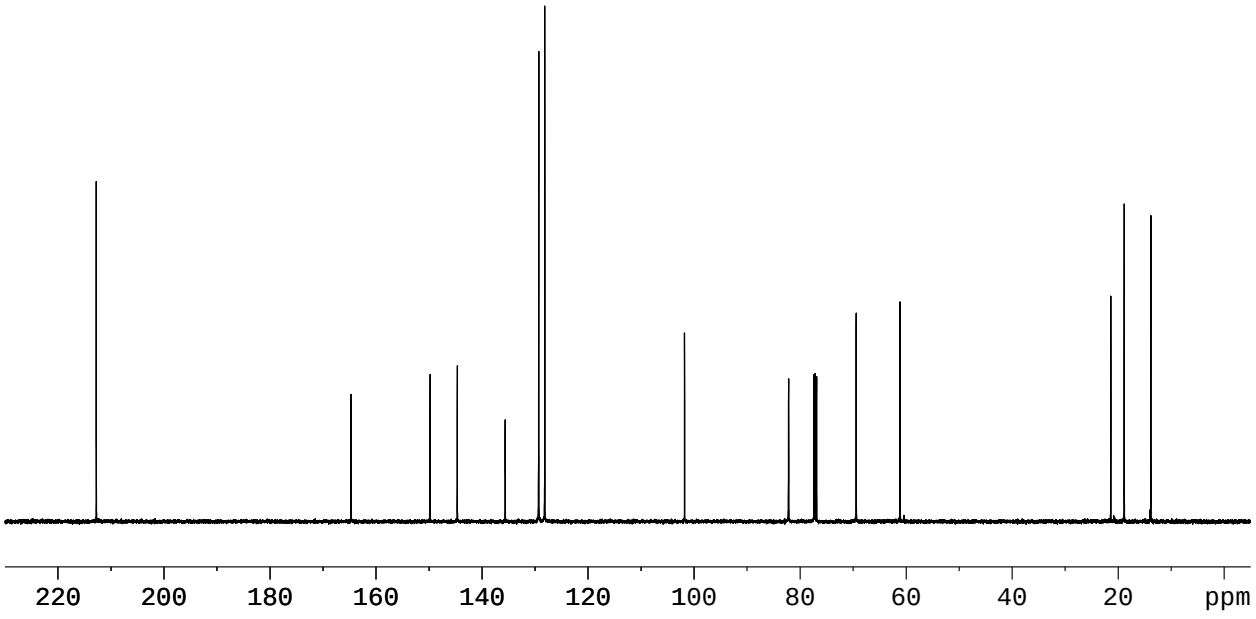

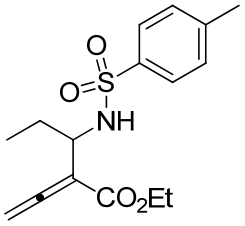
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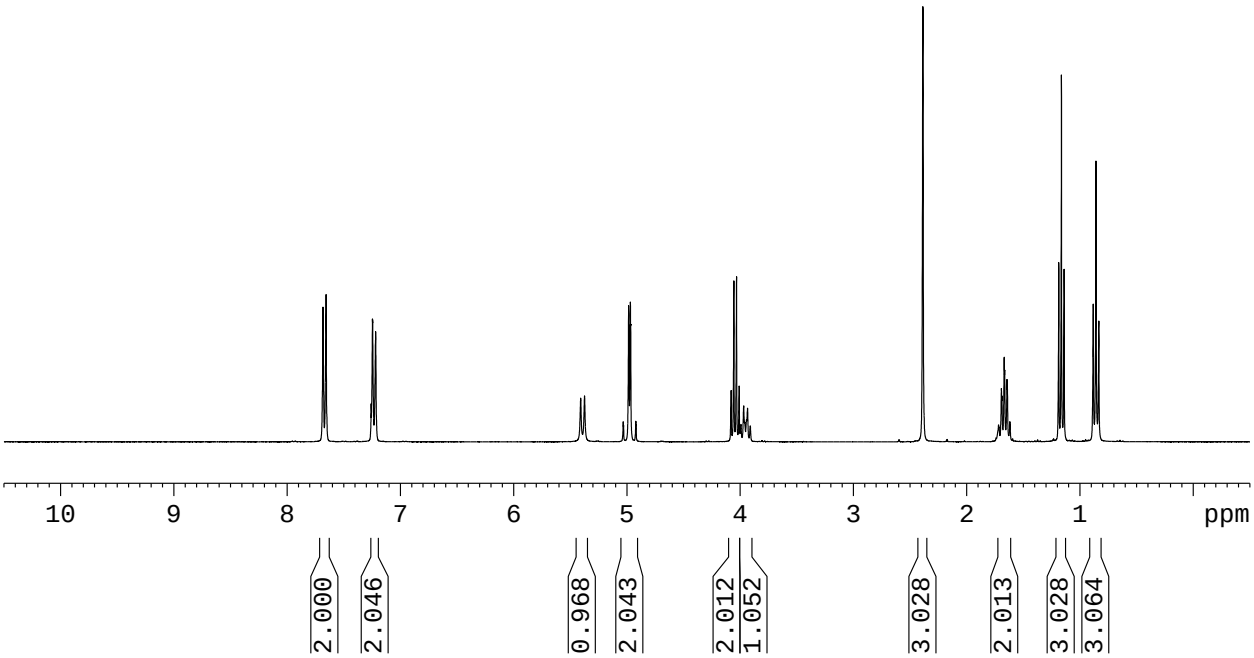
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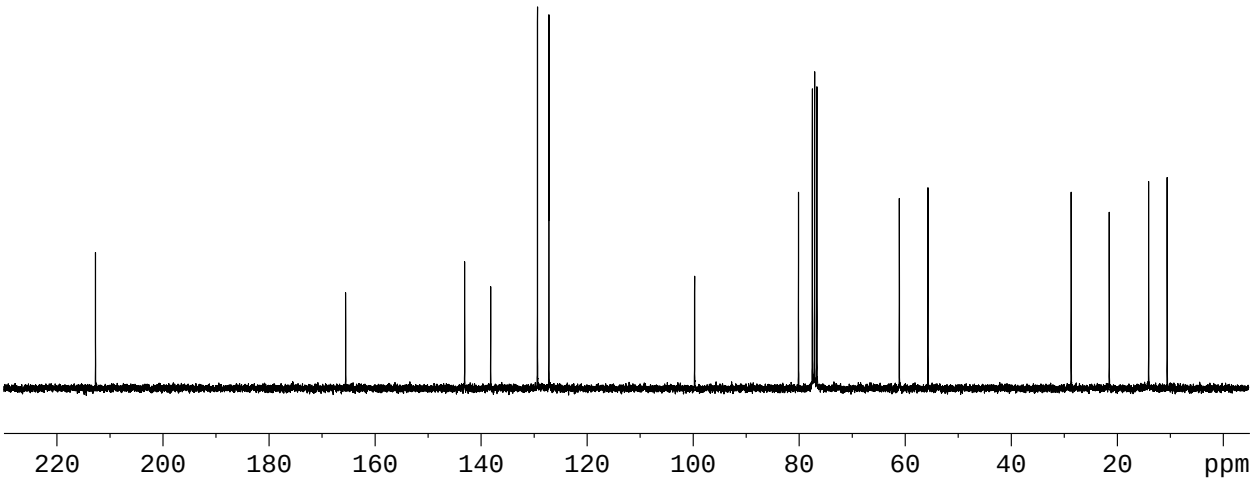
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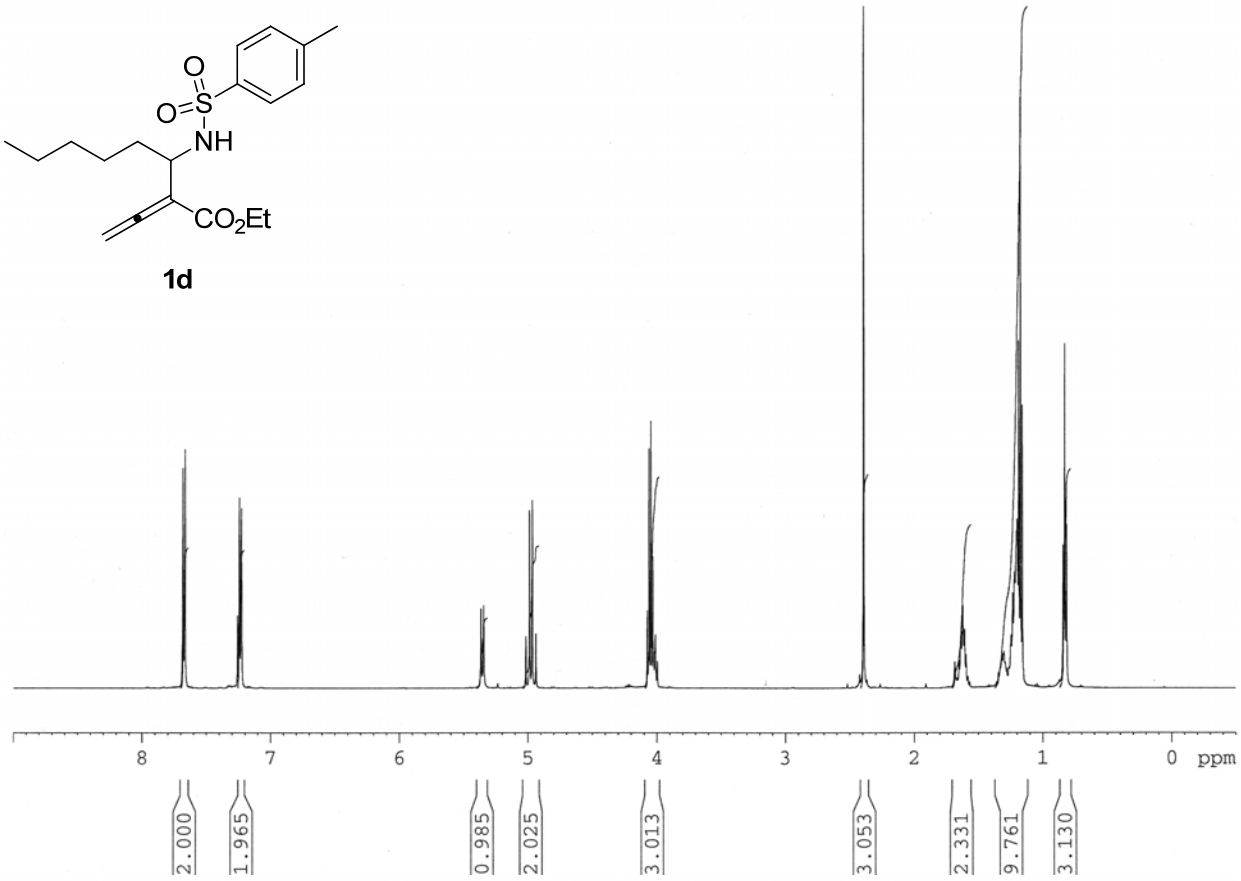

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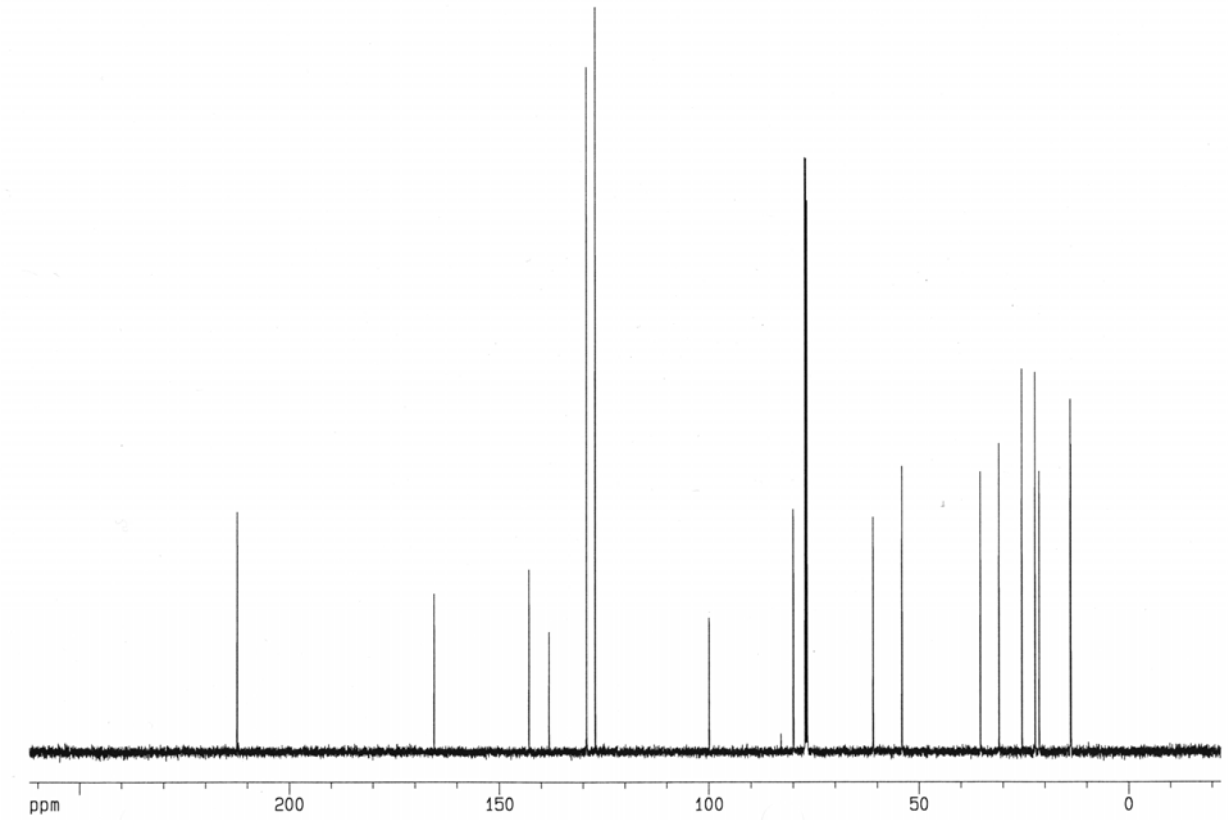

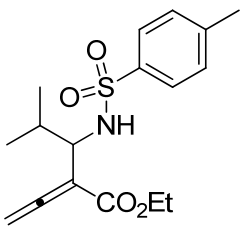

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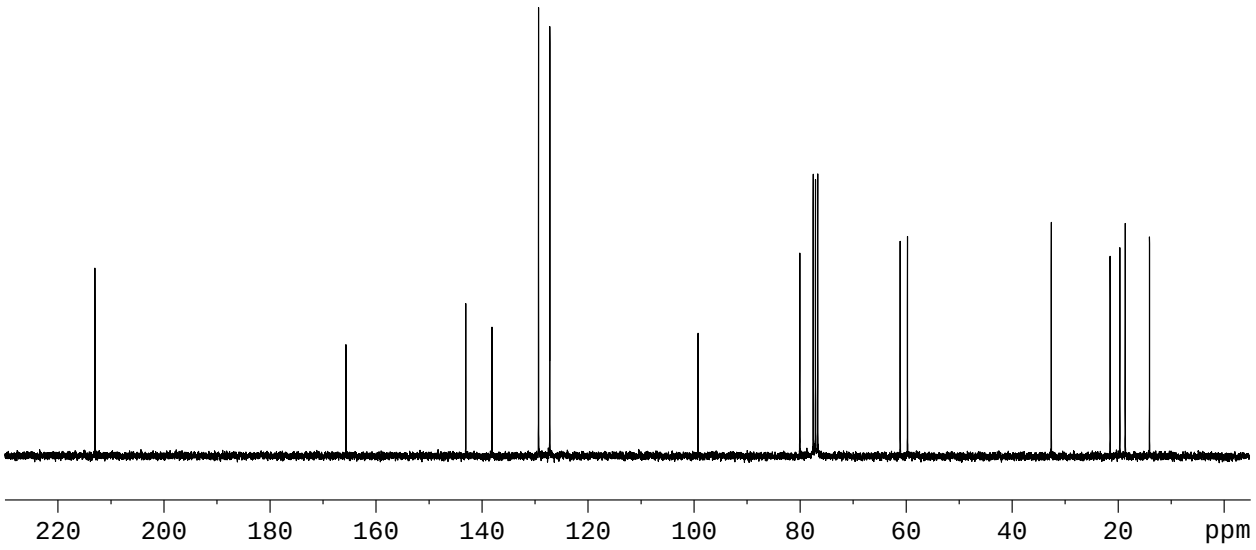

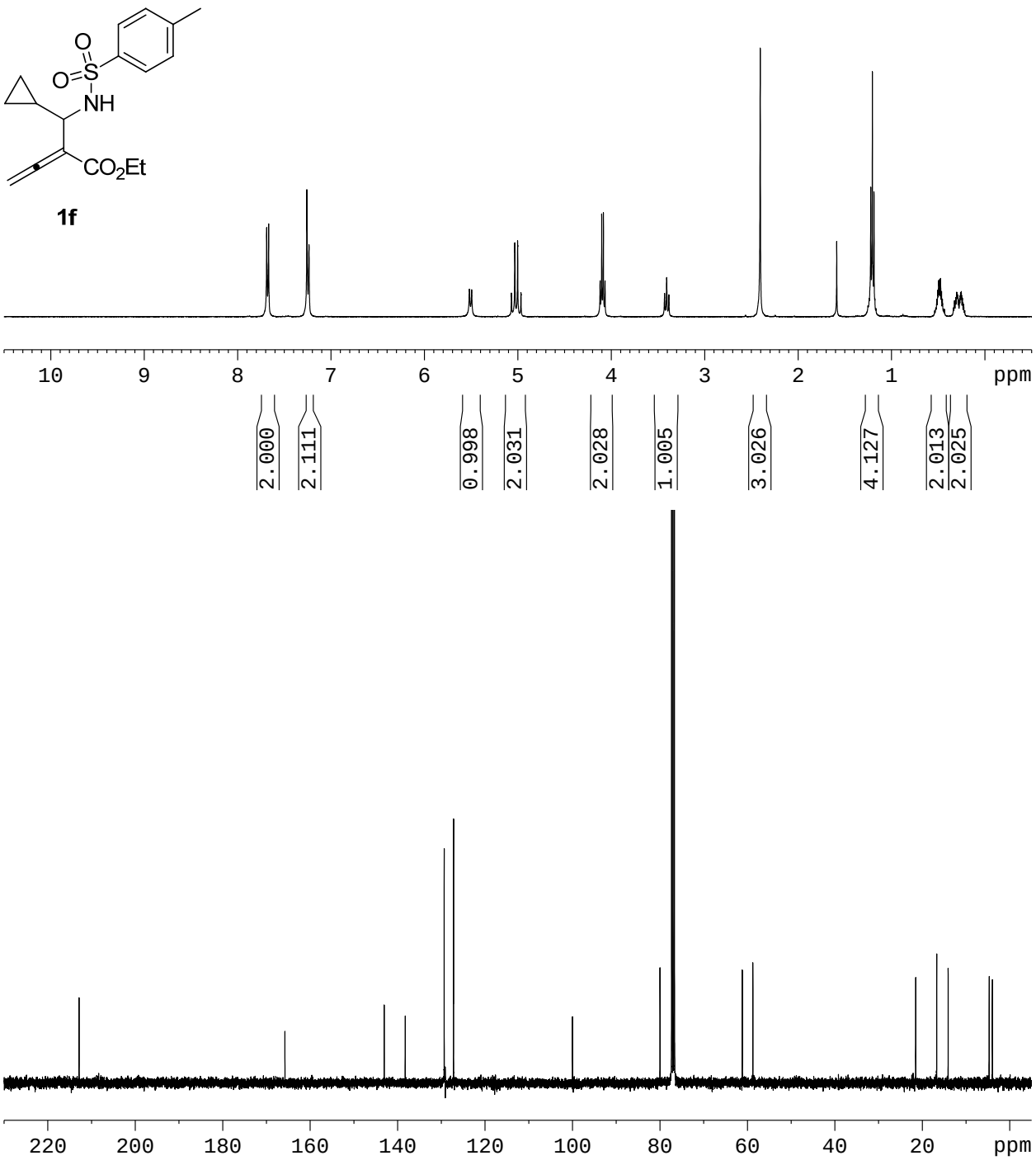

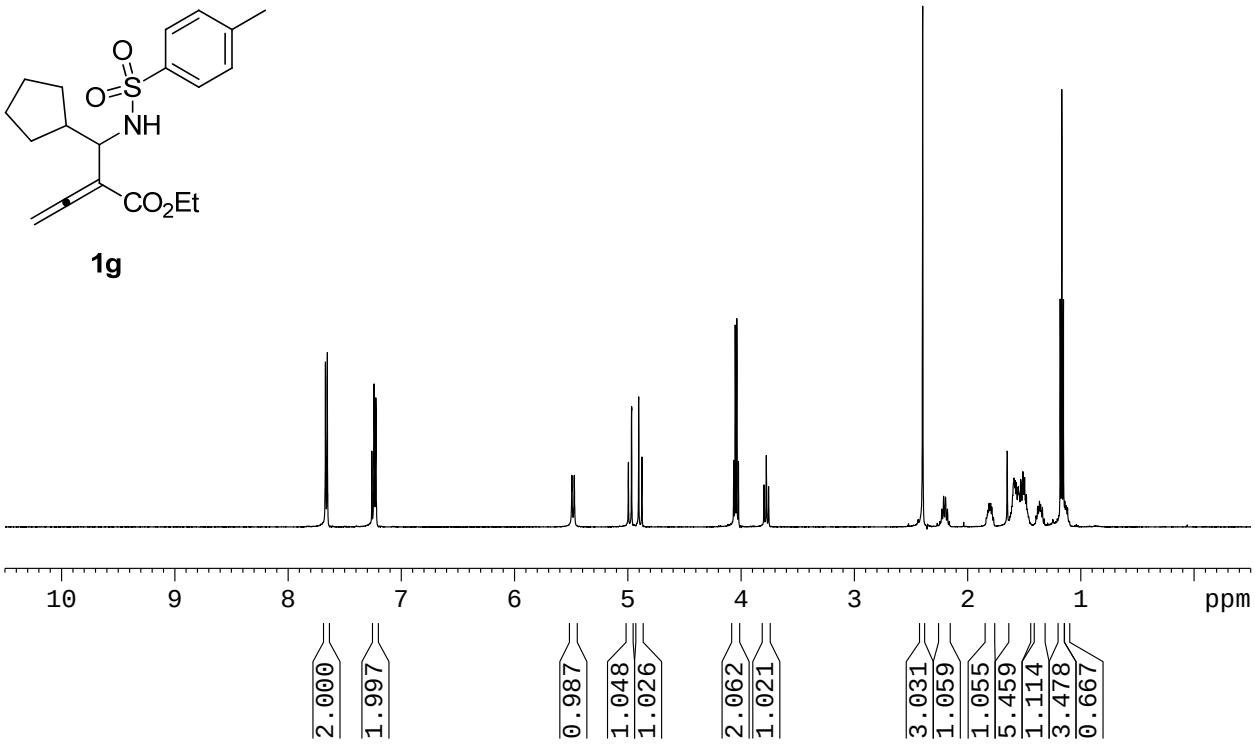

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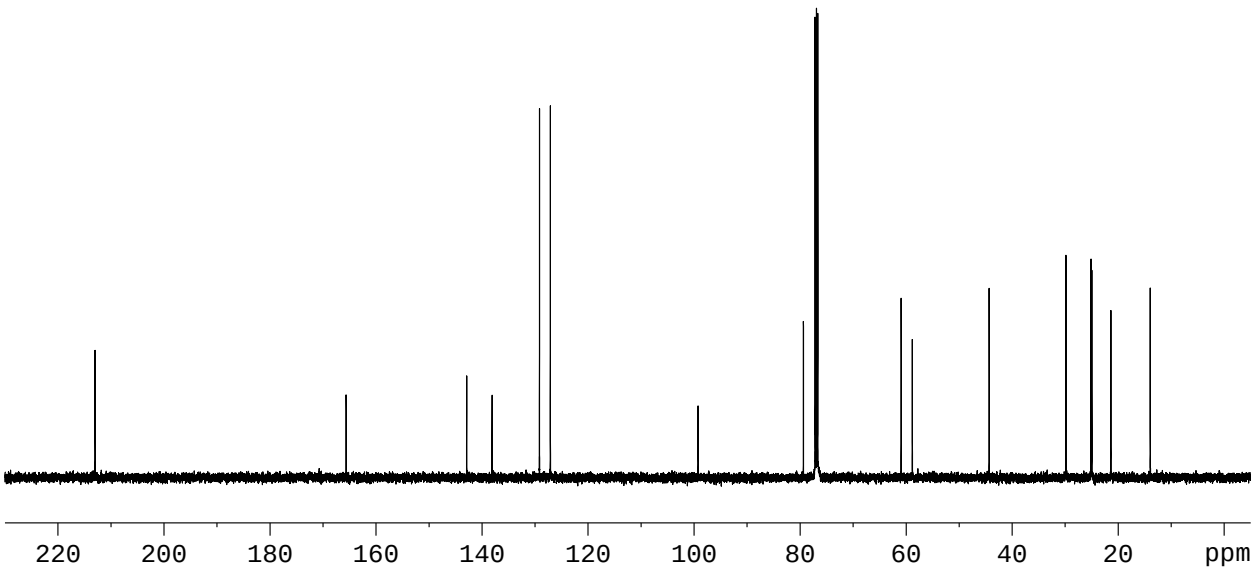

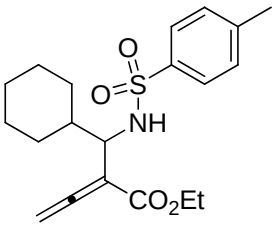

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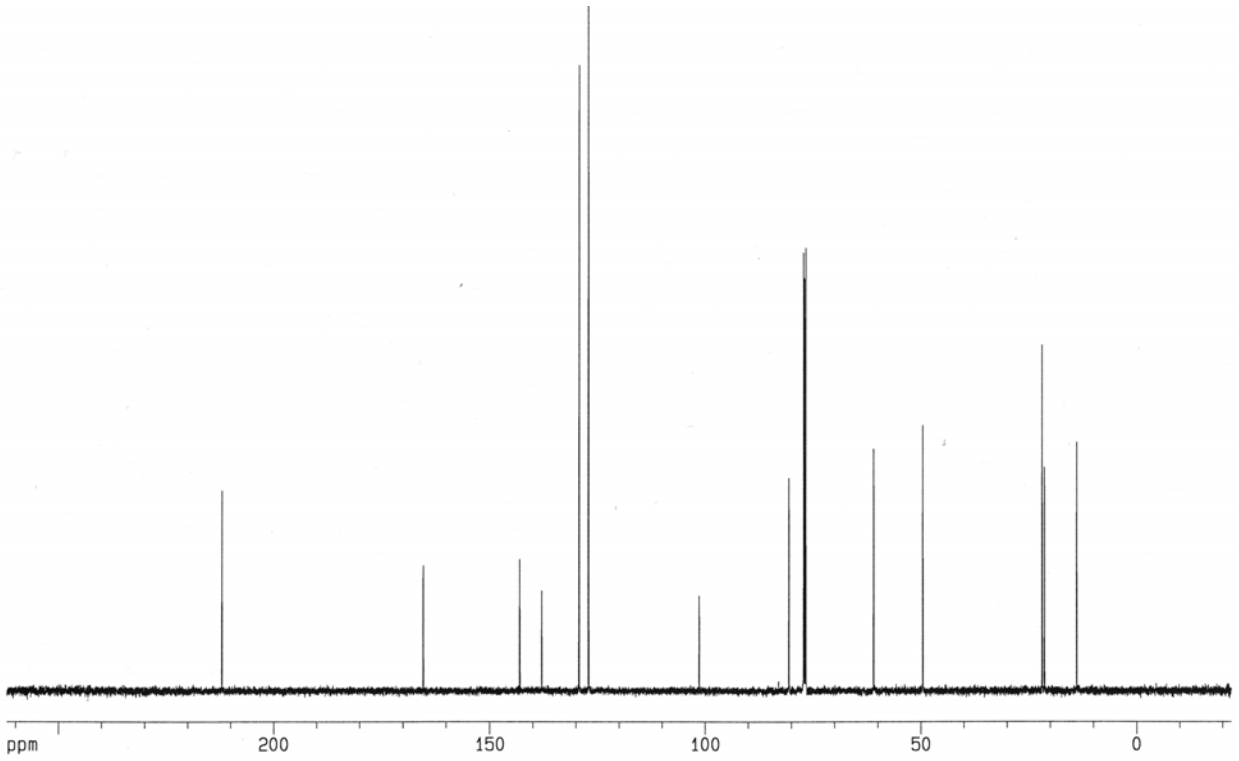

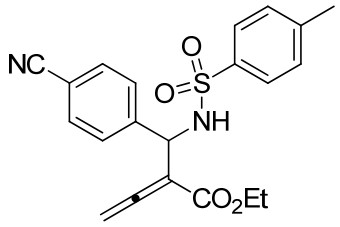

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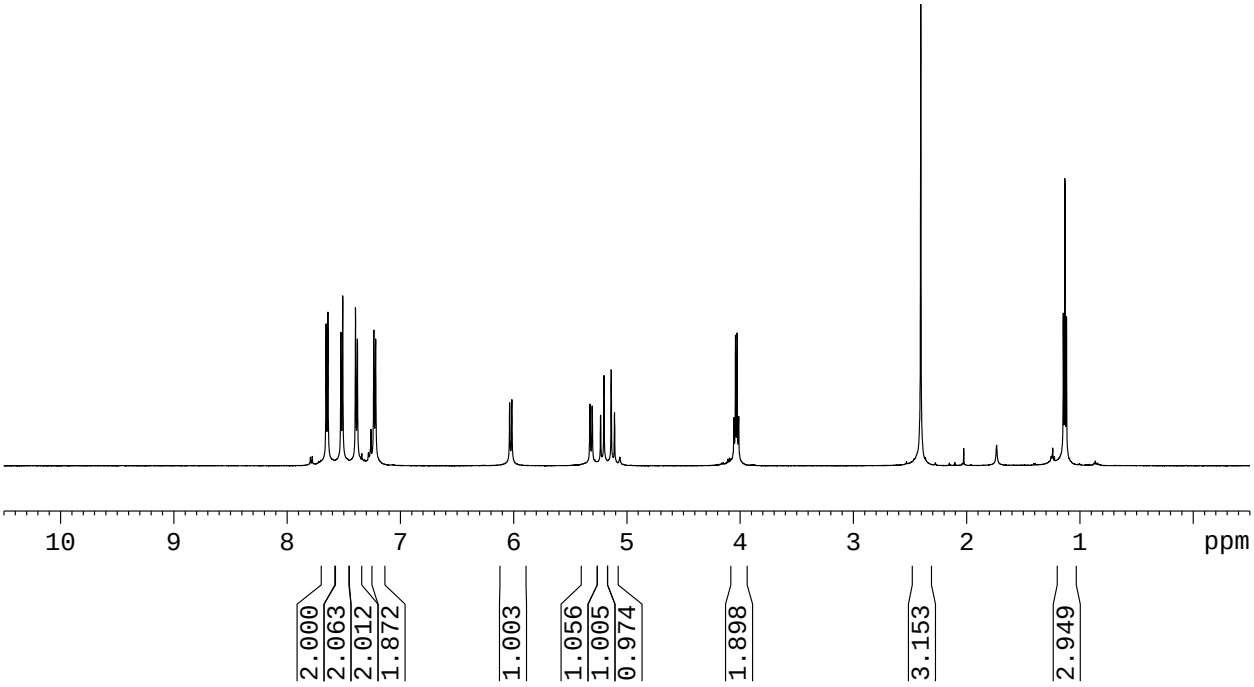

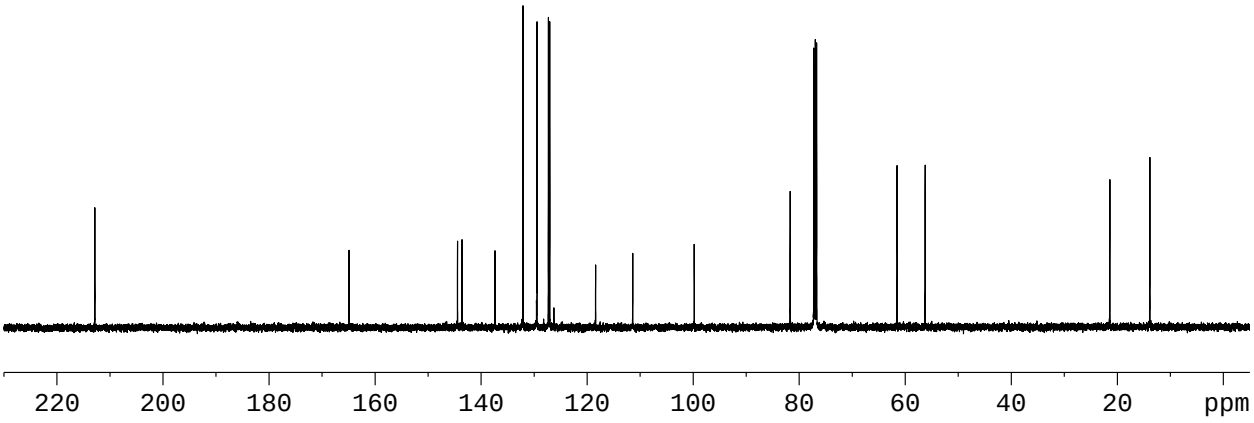

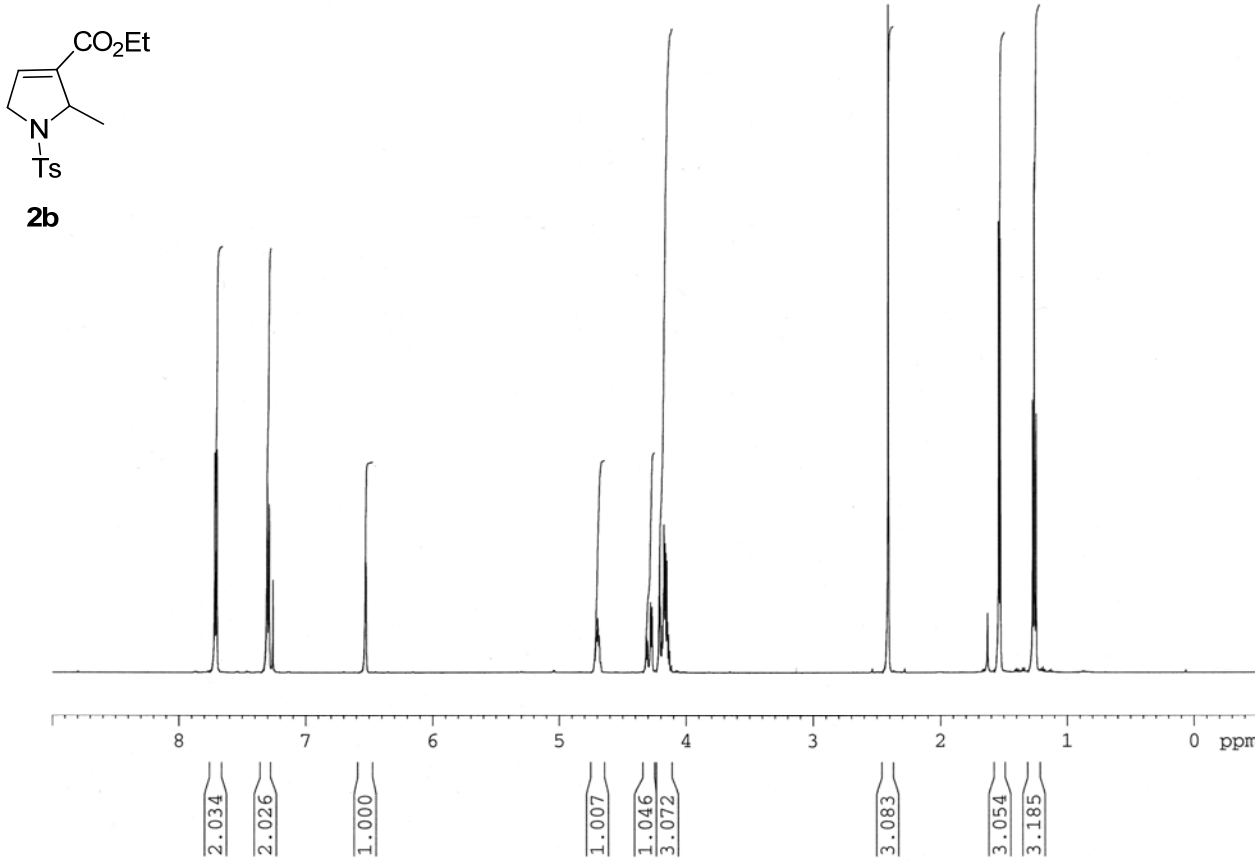

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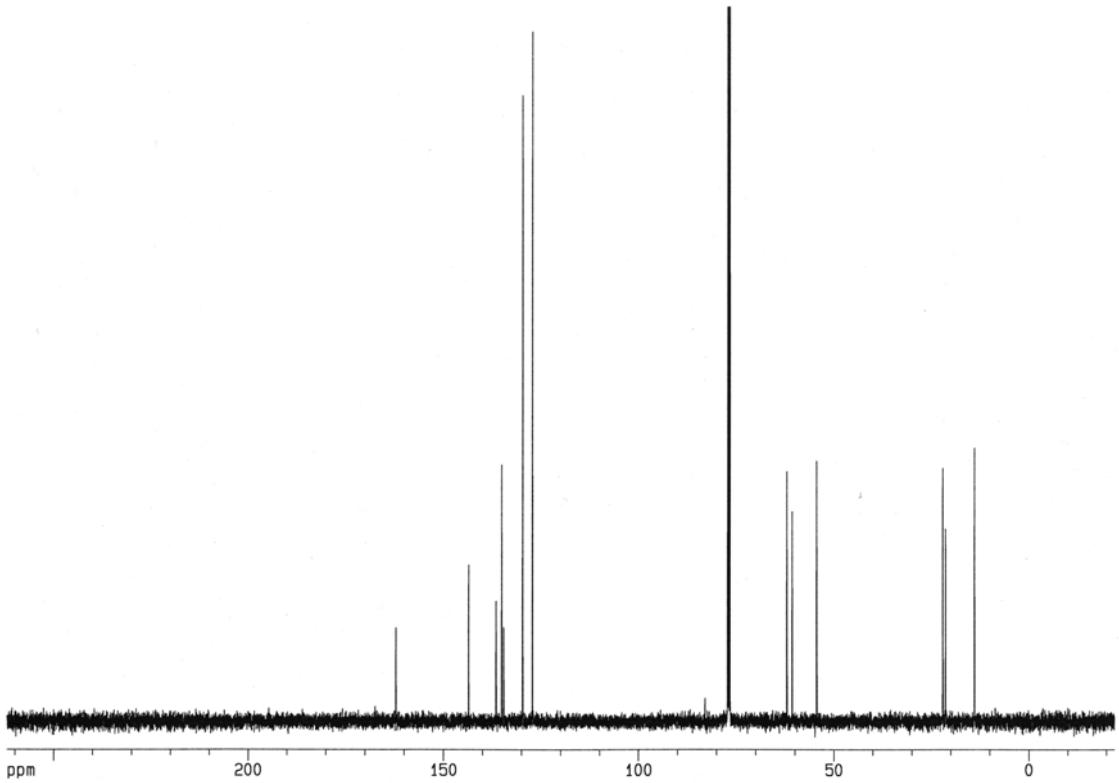

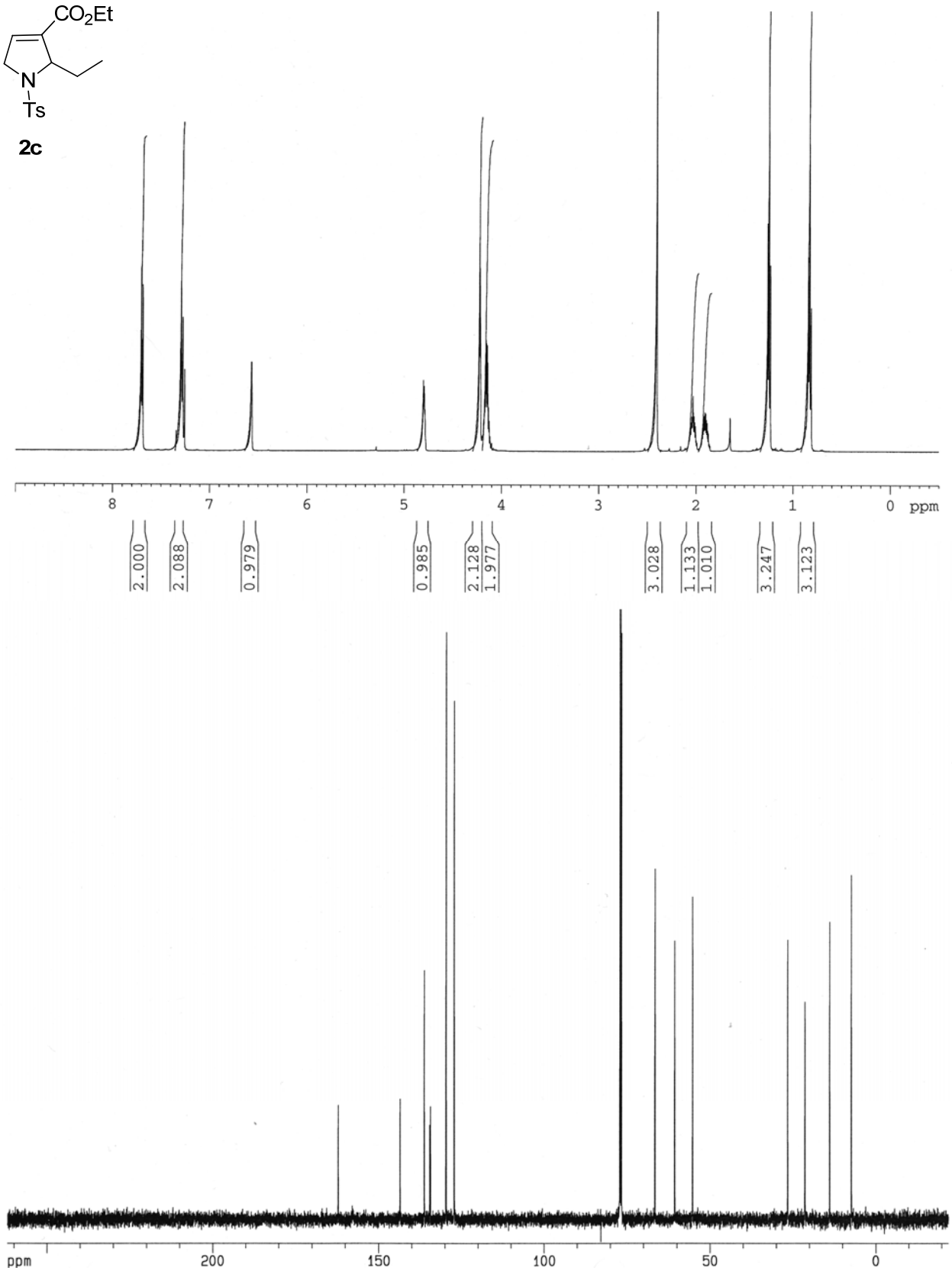

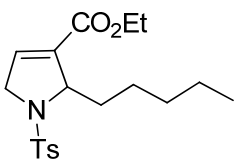

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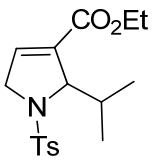

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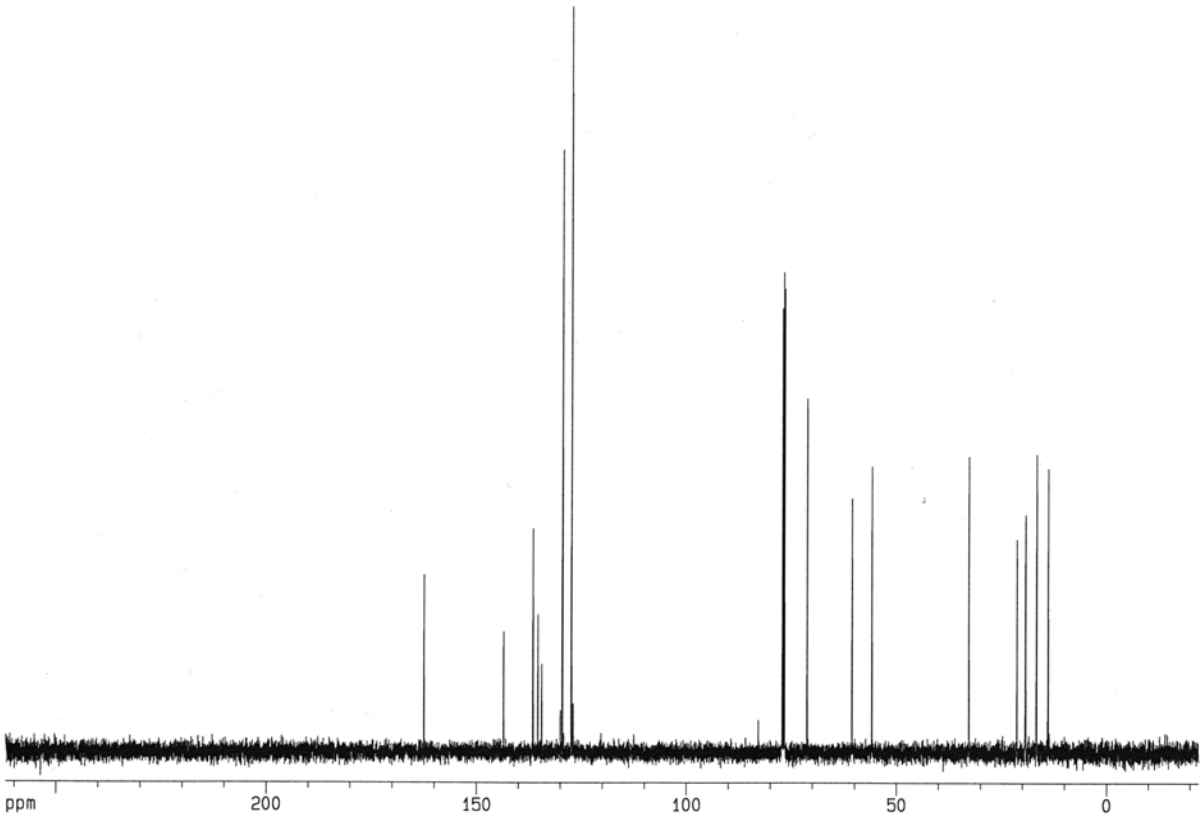

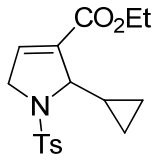
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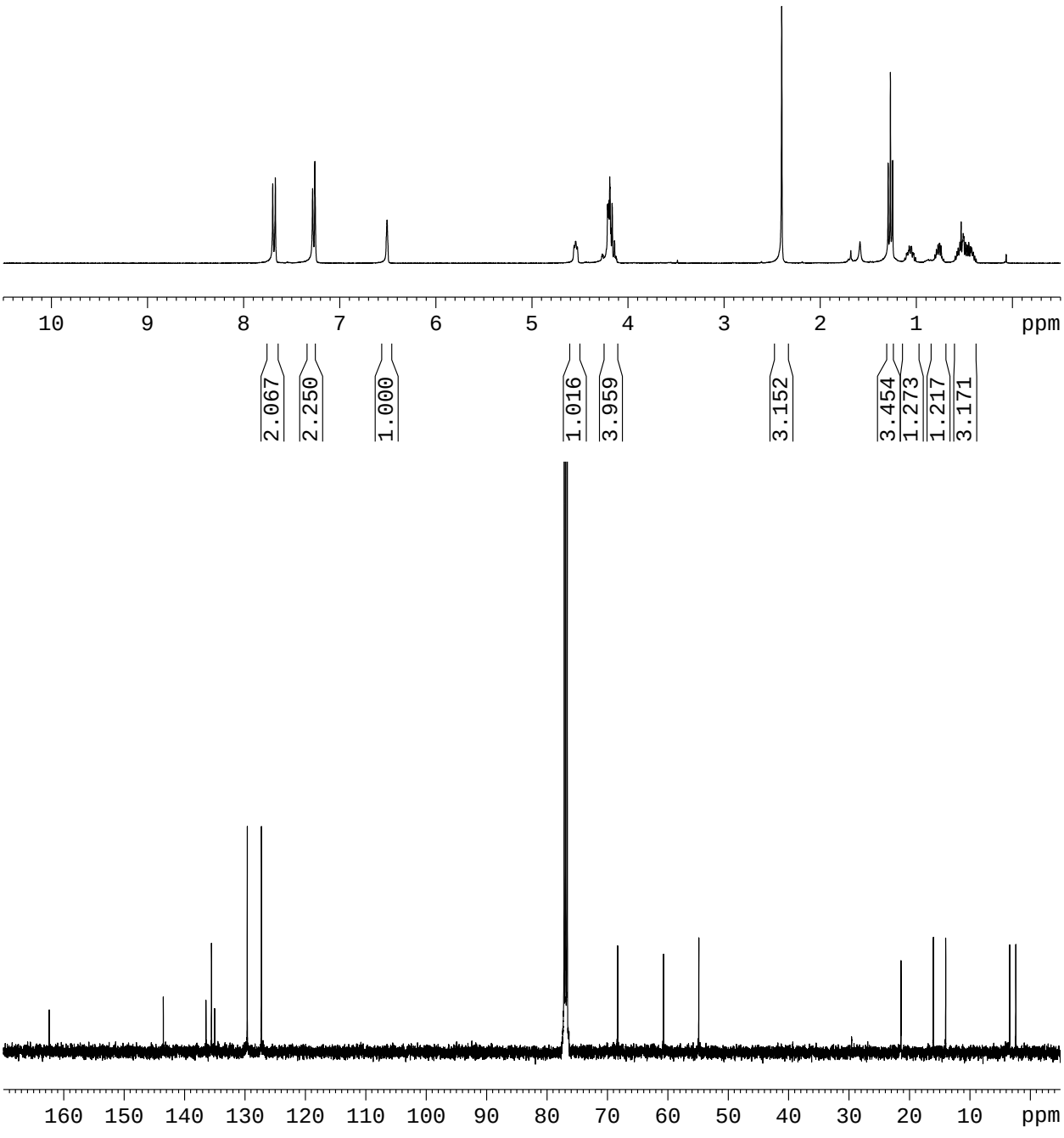
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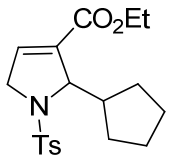

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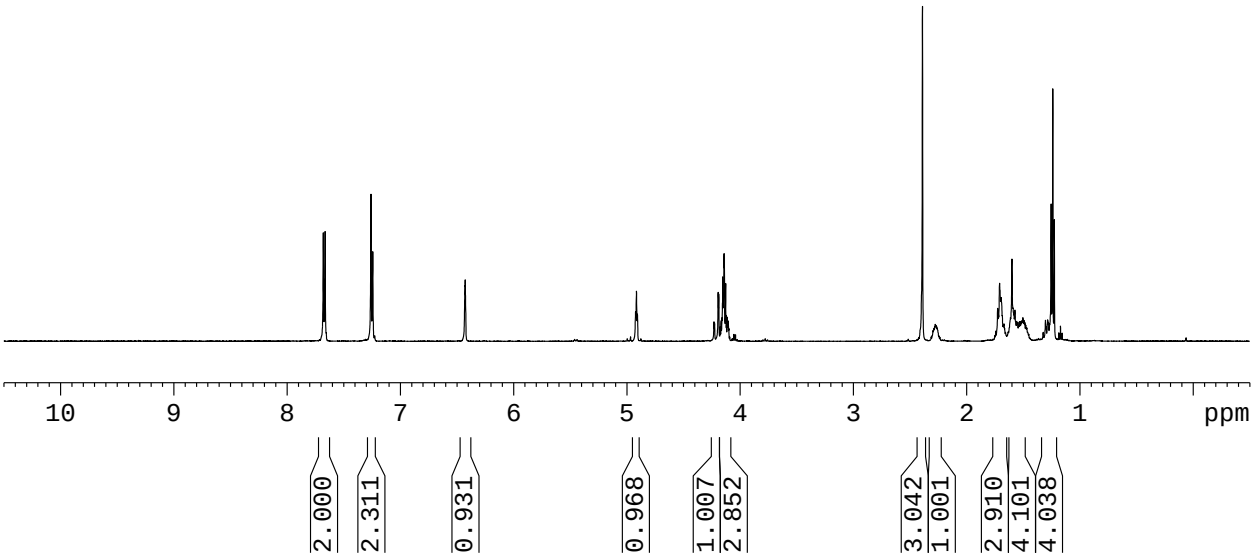

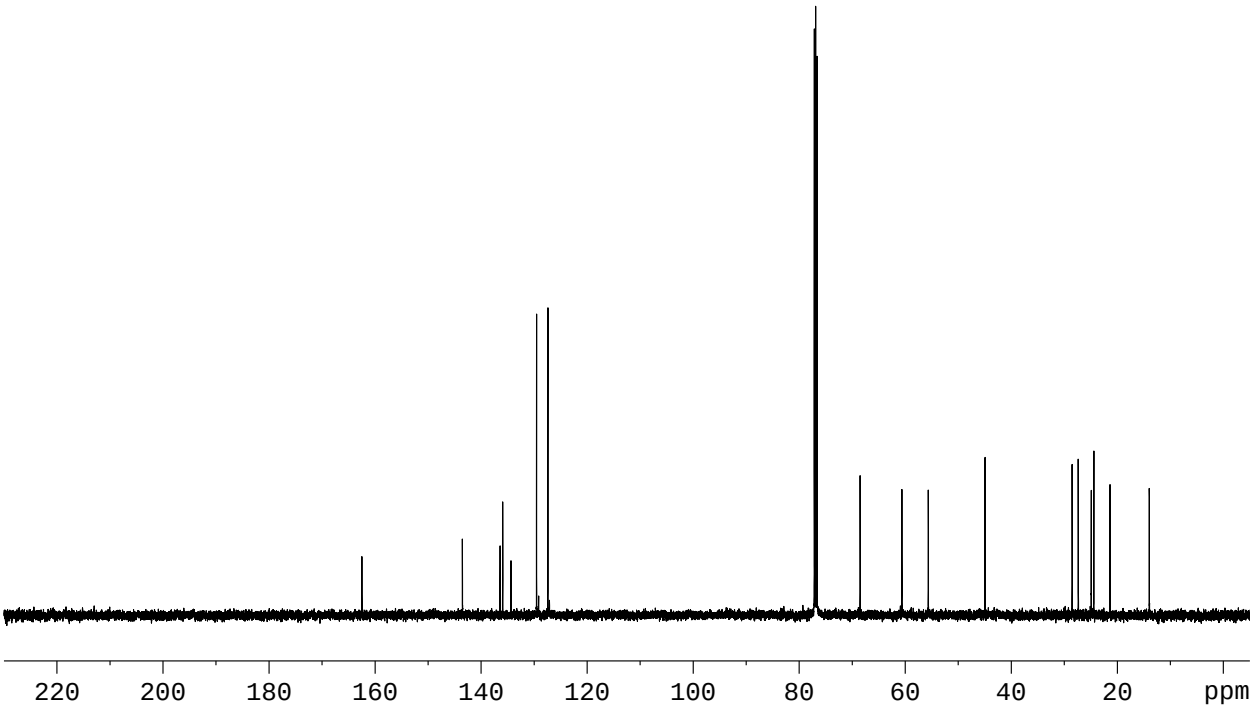

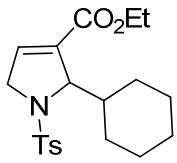

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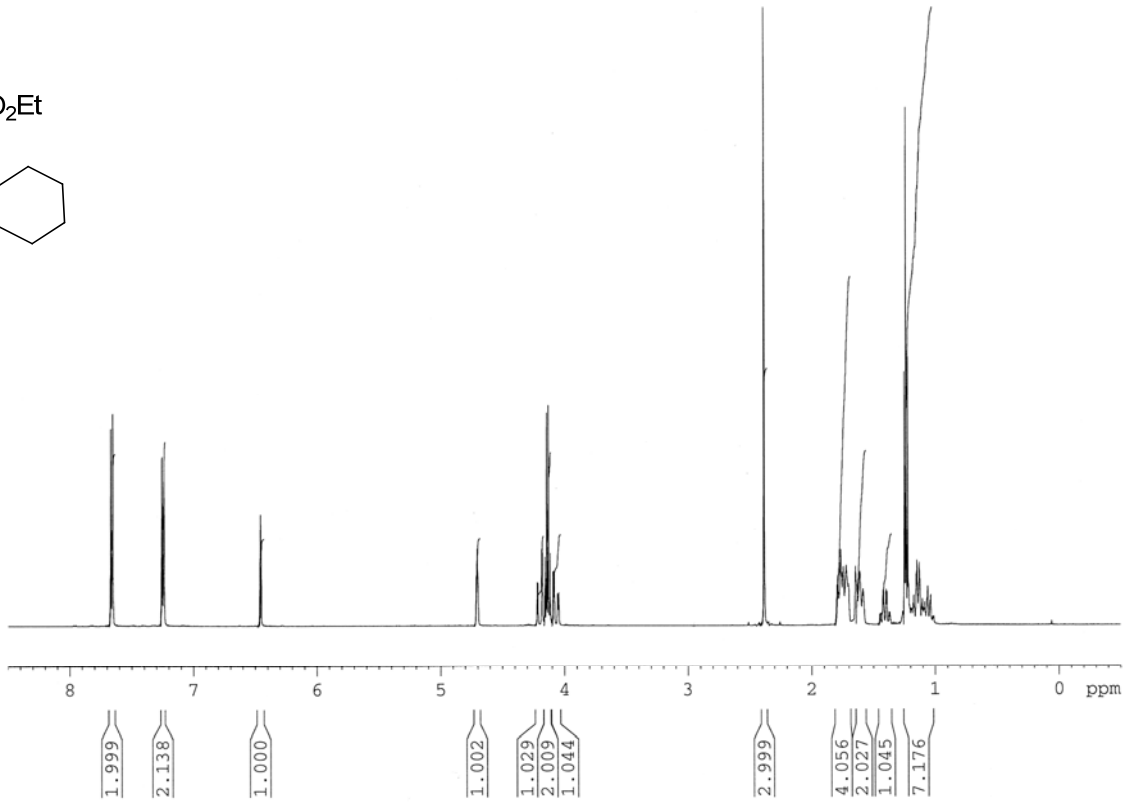

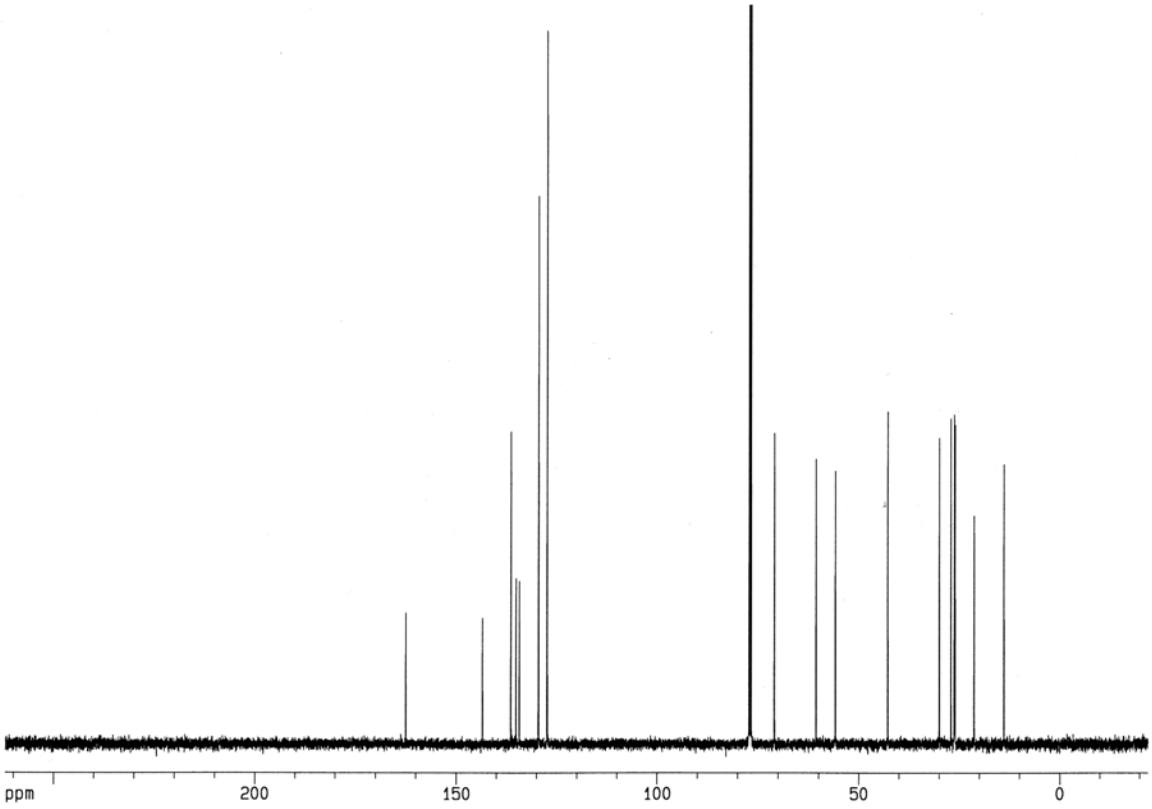

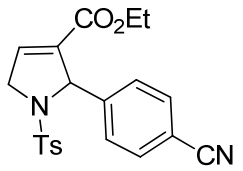

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