Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Z-Selective Phosphine Promoted 1,4-Reduction of Ynoates and Propynoic amides in the presence of water

Fabian Seifert[a], Denis Drikermann[a], Johannes Steinmetzer[b], You Zi[a], Stephan Kupfer[b] and Ivan Vilotijevic[a]*

[a] Friedrich Schiller University Jena, Institute of Organic Chemistry and Macromolecular Chemistry, Humboldtstraße 10, 07743 Jena, Germany

[b] Friedrich Schiller University Jena, Institute for Physical Chemistry and Abbe Center of Photonics, Helmholtzweg 4, 07743 Jena, Germany

E-mail: ivan.vilotijevic@uni-jena.de

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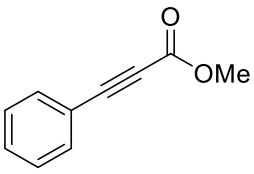
General remarks

Commercially available chemicals were used without purification. Technical grade solvents were distilled prior to use. Petrol ether refers to mixture of hydrocarbons with a boiling range 35 - 70 °C. Anhydrous 1,4-dioxane and anhydrous 1,4-dioxane-d_8 were distilled over sodium/benzophenone under nitrogen and stored in *Schlenk*-flasks. Anhydrous 1,4-dioxane-d_8 was stored over activated molecular sieve 4Å. Anhydrous PBu_3 was distilled over CaH_2 and stored in a *Schlenk*-flask. ^{1}H ^{13}C and ^{31}P NMR-spectra were recorded on a 250 MHz, a Fourier 300 MHz and a Bruker 400 MHz device. The shift was recorded in ppm and the solvent signal was used for reference (^{1}H NMR, $CDCl_3$: $\delta = 7.26$, ^{13}C NMR, $CDCl_3$: $\delta = 77.00$). High resolution mass spectra were measured by the MS platform with a Thermo Q-Exactive GC Orbitrap. Mass spectra were measured with a LC-MS system assembled from a ESI-Quadrupol-MS (Finnigan Mat LCQ) and Shimadzu HPLC-system.

Synthesis of 2-ynoates

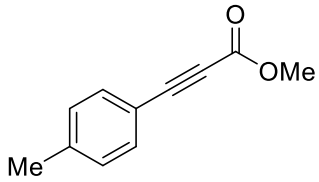
Methyl 3-phenylpropiolate (P-3)



A solution of *n*-BuLi in hexane (21.5 mL, 2.50 M, 53.9 mmol, 1.10 eq.) was added dropwise over a period of 5 min to a solution of phenylacetylene (5.38 mL, 49.0 mmol, 1.00 eq.) in 250 mL THF at -98 °C and the solution was stirred under nitrogen. The solution was allowed to warm up to rt and cooled to -98 °C again. Methyl chloroformate (4.16 mL, 53.9 mmol, 1.10 eq.) was added dropwise over 5 min. The solution was stirred at rt for 1.5 h. To the mixture, sat. NH_4Cl-solution (50 mL), H_2O (50 mL) and ethyl acetate (100 mL) were added. The layers were separated and the aqueous layer was extracted with ethyl acetate (100 mL). The combined organic layer was washed with brine (50 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude product was distilled under high vacuum (10^{-1} mbar, 90 – 110 °C).[1] The product was obtained as a colourless oil (6.79 g, 87% yield). Analytical data matches the literature.[1]

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.61 – 7.58 (m, 2H), 7.49 – 7.35 (m, 3H), 3.85 (s, 3H).

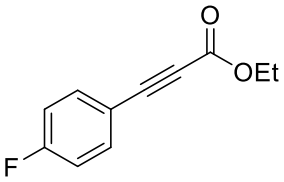
Methyl 3-(*p*-tolyl)propiolate (P-5)



A solution of *n*-BuLi (2.50 M in hexane) (4.52 mL, 11.3 mmol, 1.00 eq.) was added to a solution of *N*,*N*-diisopropylamine (1.59 mL, 11.3 mmol, 1.00 eq.) in THF (25 mL) at 0 °C and stirred under nitrogen. The mixture was cooled to –98 °C and methyl propiolate (1.00 mL, 11.3 mmol, 1.00 eq.) was added dropwise, followed by a solution of $ZnBr_2$ (2.55 g, 11.3 mmol, 1.00 eq.) in THF (20 mL), which was also added dropwise. 4-Iodotoluene (2.09 g, 9.61 mmol, 0.85 eq.) and $Pd(PPh_3)_4$ (0.26 g, 0.23 mmol, 0.02 eq.) were added simultaneously. The mixture was stirred at rt for 8 h. The mixture was diluted with ethyl acetate (200 mL) and washed with sat. NH_4Cl-solution (2 x 50 mL) and brine (50 mL). The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified via flash chromatography (10 % v/v% ethyl acetate/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the compound isolated as off-white solid (1.16 g, 69% yield). Analytical data matches the literature.[1]

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.49 (d, J = 9.0 Hz, 2H), 7.19 (d, J = 9.0 Hz, 2H), 3.84 (s, 3H), 2.39 (s, 3H).

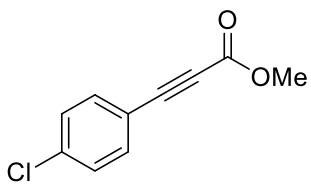
Ethyl 3-(4-fluorophenyl)propiolate (P-6)



A solution of *n*-BuLi (2.50 M in hexane) (6.78 mL, 17.0 mmol, 1.00 eq.) was added to a solution of *N*,*N*-diisopropylamine (2.38 mL, 17.0 mmol, 1.00 eq.) in THF (25 mL) at 0 °C and stirred under nitrogen. The mixture was cooled to –98 °C and ethyl propiolate (1.72 mL, 22.6 mmol, 1.00 eq.) was added dropwise, followed by a solution of $ZnBr_2$ (3.82 g, 17.0 mmol, 1.00 eq.) in THF (20 mL), which was also added dropwise. 4-Fluoroiodobenzene (1.68 mL, 14.4 mmol 0.85 eq.) and $Pd(PPh_3)_4$ (0.39 g, 0.34 mmol, 0.02 eq.) were added simultaneously. The mixture was stirred at rt for 5 h. The mixture was diluted with ethyl acetate (200 mL) and washed with sat. NH_4Cl-solution (2 x 50 mL) and brine (50 mL). The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified via flash chromatography (10 % v/v% ethyl acetate/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the compound was isolated as colourless solid (1.75 g, yield 63%). Analytical data matches the literature.[1]

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.63 – 7.56 (m, 2H), 7.12 – 7.04 (m, 2H), 4.31 (q, J = 6.0 Hz, 2H), 1.36 (t, J = 6.0 Hz, 3H).

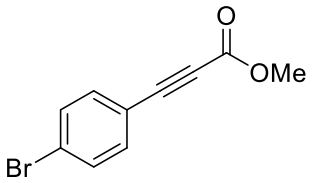
Methyl 3-(4-chlorophenyl)propiolate (P-8)



A solution of *n*-BuLi (2.50 M in hexane), (9.04 mL, 22.6 mmol, 1.00 eq.) was added to a solution of *N*,*N*-diisopropylamine (3.18 mL, 22.6 mmol, 1.00 eq.) in THF (25 mL) at 0 °C and stirred under nitrogen. The mixture was cooled to –98 °C and methyl propiolate (2.00 mL, 22.60 mmol, 1.00 eq.) was added dropwise, followed by a solution of $ZnBr_2$ (5.09 g, 22.6 mmol, 1.00 eq.) in THF (20 mL), which was also added dropwise. 4-Chloroiodobenzene (4.58 g, 19.2 mmol 0.85 eq.) and $Pd(PPh_3)_4$ (0.52 g, 0.45 mmol, 0.02 eq.) were added simultaneously. The mixture was stirred at rt for 6 h.

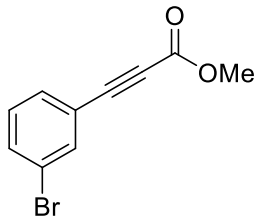
The mixture was diluted with ethyl acetate (200 mL) and washed with sat. NH_4Cl-solution (2 x 50 mL) and brine (50 mL). The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified via flash chromatography (10 % v/v% ethyl acetate/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the compound was isolated as orange solid (2.17 g, 58% yield). Analytical data matches the literature.[1]
^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.54 – 7.50 (m, 2H), 7.39 – 7.35 (m, 2H), 3.85 (s, 3H).

Methyl 3-(4-bromophenyl)propiolate (P-9)



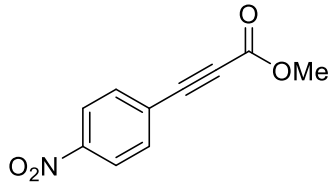
A solution of *n*-BuLi (2.50 M in hexane), (2.38 mL, 5.96 mmol, 1.00 eq) was added to a solution of *N*,*N*-diisopropylamine (0.84 mL, 5.96 mmol 1.00 eq.) in THF (25 mL) at 0 °C and stirred under nitrogen. The mixture was cooled to –98 °C and methyl propiolate (0.53 mL, 5.96 mmol, 1.00 eq.) was added dropwise, followed by a solution of $ZnBr_2$ (1.34 g, 5.96 mmol, 1.00 eq.) in THF (20 mL), which was also added dropwise. 4-Bromoiodobenzene (1.43 g, 5.07 mmol, 0.85 eq.) and $Pd(PPh_3)_4$ (0.14 g, 0.12 mmol, 0.02 eq.) were added simultaneously. The mixture was stirred at rt for 8 h. The mixture was diluted with ethyl acetate (200 mL) and washed with sat. NH_4Cl-solution (2 x 50 mL) and brine (50 mL). The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified via flash chromatography (10 % v/v% ethyl acetate/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the compound was isolated as orange solid (0.61 g, 51% yield). Analytical data matches the literature.[1]
^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.55 – 7.51 (m, 2H), 7.47 – 7.43 (m, 2H), 3.85 (s, 3H).

Methyl 3-(3-bromophenyl)propiolate (P-10)



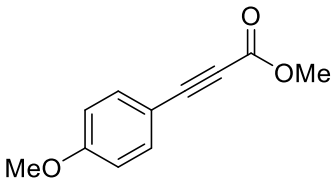
A solution of *n*-BuLi (2.50 M in hexane), (8.88 mL, 22.2 mmol, 1.00 eq) was added to a solution of *N*,*N*-diisopropylamine (3.12 mL, 22.2 mmol, 1.00 eq.) in THF (25 mL) at 0 °C and stirred under nitrogen. The mixture was cooled to –98 °C and methyl propiolate (1.97 mL, 22.20 mmol, 1.00 eq.) was added dropwise, followed by a solution of $ZnBr_2$ (5.00 g, 22.2 mmol, 1.00 eq.) in THF (20 mL), which was also added dropwise. 3-Bromoiodobenzene (5.34 g, 18.9 mmol, 0.85 eq.) and $Pd(PPh_3)_4$ (0.51 g, 0.44 mmol, 0.02 eq.) were added simultaneously. The mixture was stirred at rt for 15 h. The mixture was diluted with ethyl acetate (200 mL) and washed with sat. NH_4Cl-solution (2 x 50 mL) and brine (50 mL). The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified via flash chromatography (10 % v/v% ethyl acetate/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the compound was isolated as colourless solid (2.80 g, 62% yield). Analytical data matches the literature.[1]
^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.74 – 7.73 (m, 1H), 7.61 – 7.58 (m, 1H), 7.54 – 7.50 (m, 1H), 7.29 – 7.24 (m, 1H), 3.85 (s, 3H).

Methyl 3-(4-nitrophenyl)propiolate (P-11)



A solution of *n*-BuLi (2.50 M in hexane), (4.52 mL, 11.3 mmol, 1.00 eq) was added to a solution of *N*,*N*-diisopropylamine (1.59 mL, 11.3 mmol, 1.00 eq.) in THF (25 mL) at 0 °C and stirred under nitrogen. The mixture was cooled to –98 °C and methyl propiolate (1.00 mL, 11.3 mmol, 1.00 eq.) was added dropwise, followed by a solution of $ZnBr_2$ (2.54 g, 11.3 mmol, 1.00 eq.) in THF (20 mL), which was also added dropwise. 4-Nitroiodobenzene (2.39 g, 9.60 mmol, 0.85 eq.) and $Pd(PPh_3)_4$ (0.26 g, 0.23 mmol, 0.02 eq.) were added simultaneously. The mixture was stirred at rt for 15 h. The mixture was diluted with ethyl acetate (200 mL) and washed with sat. NH_4Cl-solution (2 x 50 mL) and brine (50 mL). The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified via flash chromatography (10 % v/v% ethyl acetate/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the compound was isolated as orange solid (1.20 g, 61% yield). Analytical data matches the literature.[1]
^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 8.26 (d, J = 9.0 Hz, 2H), 7.75 (d, J = 9.0 Hz, 2H), 3.88 (s, 3H).

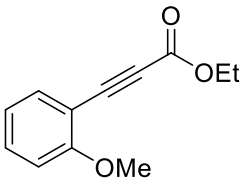
Methyl 3-(4-methoxyphenyl)propiolate (P-12)



A solution of *n*-BuLi (2.50 M in hexane), (10.3 mL, 25.7 mmol, 1.00 eq) was added to a solution of *N*,*N*-diisopropylamine (3.60 mL, 25.7 mmol, 1.00 eq.) in THF (25 mL) at 0 °C and stirred under nitrogen. The mixture was cooled to –98 °C and methyl propiolate (1.97 mL, 22.2 mmol, 1.00 eq.) was added dropwise, followed by a solution of $ZnBr_2$ (5.00 g, 22.2 mmol, 1.00 eq.) in THF (20 mL), which was also added dropwise. 4-Iodoanisole (5.00 g, 21.4 mmol, 0.83 eq.) and $Pd(PPh_3)_4$ (1.19 g, 1.03 mmol, 0.04 eq.) were added simultaneously. The mixture was stirred at rt for 15 h. The mixture was diluted with ethyl acetate (200 mL) and washed with sat. NH_4Cl-solution (2 x 50 mL) and brine (50 mL). The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified via flash chromatography (10 % v/v% ethyl acetate/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the compound was isolated as yellowish solid (2.00 g, 49% yield). Analytical data matches the literature.[1]

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.54 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 3.84 (s, 3H), 3.83 (s, 3H).

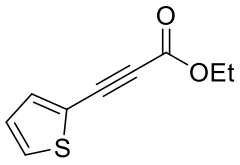
Ethyl 3-(2-methoxyphenyl)propiolate (P-13)



A solution of *n*-BuLi (2.50 M in hexane), (6.03 mL, 15.1 mmol, 1.00 eq) was added to a solution of *N*,*N*-diisopropylamine (2.12 mL, 15.1 mmol, 1.00 eq.) in THF (25 mL) at 0 °C and stirred under nitrogen. The mixture was cooled to –98 °C and ethyl propiolate (1.53 mL, 15.1 mmol, 1.00 eq.) was added dropwise, followed by a solution of $ZnBr_2$ (3.40 g, 15.1 mmol, 1.00 eq.) in THF (20 mL), which was also added dropwise. 1-Iodo-2-methoxybenzene (3.00 g, 12.8 mmol, 0.85 eq.) and $Pd(PPh_3)_4$ (0.30 g, 0.26 mmol, 0.02 eq.) were added simultaneously. The mixture was stirred at rt for 4 h. The mixture was diluted with ethyl acetate (200 mL) and washed with sat. NH_4Cl-solution (2 x 50 mL) and brine (50 mL). The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified via flash chromatography (10 % v/v% ethyl acetate/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the compound was isolated as orange solid (0.63 g, 24% yield). Analytical data matches the literature.[1]

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.53 (dd, *J* = 7.6 Hz, *J* = 1.7 Hz, 1H), 7.44 – 7.38 (m, 1H), 6.97 6.89 (m, 2H), 4.30 (q, *J* = 7.2 Hz, 1H), 3.90 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H).

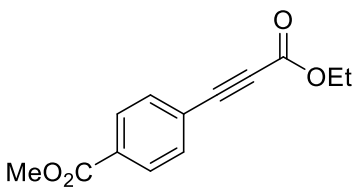
Ethyl 3-(thiophen-2-yl)propiolate (P-14)



A solution of *n*-BuLi (2.50 M in hexane), (6.32 mL, 15.8 mmol, 1.00 eq) was added to a solution of *N*,*N*-diisopropylamine (2.22 mL, 15.8 mmol, 1.00 eq.) in THF (25 mL) at 0 °C and stirred under nitrogen. The mixture was cooled to –75 °C and ethyl propiolate (1.60 mL, 15.8 mmol, 1.00 eq.) was added dropwise, followed by a solution of $ZnBr_2$ (3.55 g, 15.8 mmol, 1.00 eq.) in THF (20 mL), which was also added dropwise. 2-Iodothiophene (2.81 g, 13.4 mmol, 0.85 eq.) and $Pd(PPh_3)_4$ (0.37 g, 0.32 mmol, 0.02 eq.) were added simultaneously. The mixture was stirred at rt for 3 h. The mixture was diluted with ethyl acetate (200 mL) and washed with sat. NH_4Cl-solution (2 x 50 mL) and brine (50 mL). The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified via flash chromatography (10 % v/v% ethyl acetate/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the compound was isolated as yellowish oil (2.24 g, 93% yield). Analytical data matches the literature.[1]

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.49 – 7.45 (m, 2H), 7.05 (dd, *J* = 5.1 Hz, *J* = 3.7 Hz, 1H), 4.30 (d, *J* = 7.2 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H).

Methyl 4-(3-ethoxy-3-oxoprop-1-yn-1-yl)benzoate (P-15)

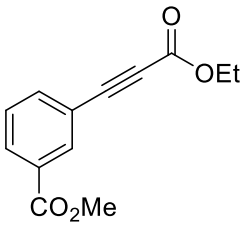


A solution of *n*-BuLi (2.50 M in hexane), (6.47 mL, 16.2 mmol, 1.00 eq) was added to a solution of *N*,*N*-diisopropylamine (2.27 mL, 16.2 mmol, 1.00 eq.) in THF (25 mL) at 0 °C and stirred under nitrogen. The mixture was cooled to –75 °C and ethyl propiolate (1.64 mL, 16.2 mmol, 1.00 eq.) was added dropwise, followed by a solution of $ZnBr_2$ (3.65 g, 16.2 mmol, 1.00 eq.) in THF (20 mL), which was also added dropwise. Methyl 4-iodobenzoate (4.10 g, 13.8 mmol, 0.85 eq.) and $Pd(PPh_3)_4$ (0.32 g, 0.28 mmol, 0.02 eq.) were added simultaneously.

The mixture was stirred at rt for 22 h. The mixture was diluted with ethyl acetate (200 mL) and washed with sat. NH_4Cl-solution (2 x 50 mL) and brine (50 mL). The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified via flash chromatography (10 - 40% v/v% ethyl acetate/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the compound was isolated as colourless solid (1.13 g, 35% yield). Analytical data matches the literature.[1]

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 8.06 – 8.03 (m, 2H), 7.67 – 7.64 (m, 2H), 4.32 (q, J = 7.1 Hz, 2H), 3.94 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H).

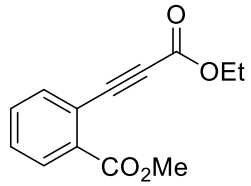
Methyl 3-(3-ethoxy-3-oxoprop-1-yn-1-yl)benzoate (P-16)



A solution of *n*-BuLi (2.50 M in hexane), (6.47 mL, 16.2 mmol, 1.00 eq) was added to a solution of *N*,*N*-diisopropylamine (2.27 mL, 16.2 mmol, 1.00 eq.) in THF (25 mL) at 0 °C and stirred under nitrogen. The mixture was cooled to –75 °C and ethyl propiolate (1.64 mL, 16.2 mmol, 1.00 eq.) was added dropwise, followed by a solution of $ZnBr_2$ (3.65 g, 16.2 mmol, 1.00 eq.) in THF (20 mL), which was also added dropwise. Methyl 2-iodobenzoate (4.10 g, 13.8 mmol, 0.85 eq.) and $Pd(PPh_3)_4$ (0.32 g, 0.28 mmol, 0.02 eq.) were added simultaneously. The mixture was stirred at rt for 22 h. The mixture was diluted with ethyl acetate (200 mL) and washed with sat. NH_4Cl-solution (2 x 50 mL) and brine (50 mL). The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified via flash chromatography (30 % v/v% ethyl acetate/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the compound was isolated as yellowish oil (0.38 g, 12% yield). Analytical data matches the literature.[1]

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 8.27 (s, 1H), 8.12 (d, J = 8.1 Hz, 1H), 7.76 (d, J = 7.7 Hz, 1H), 7.48 (t, J = 7.9 Hz, 1H), 4.32 (q, J = 7.1 Hz, 2H), 3.94 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H).

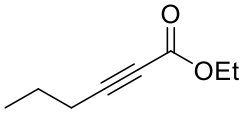
Methyl 2-(3-ethoxy-3-oxoprop-1-yn-1-yl)benzoate (P-17)



A solution of *n*-BuLi (2.50 M in hexane), (6.47 mL, 16.2 mmol, 1.00 eq) was added to a solution of *N*,*N*-diisopropylamine (2.27 mL, 16.2 mmol, 1.00 eq.) in THF (25 mL) at 0 °C and stirred under nitrogen. The mixture was cooled to –75 °C and ethyl propiolate (1.64 mL, 16.2 mmol, 1.00 eq.) was added dropwise, followed by a solution of $ZnBr_2$ (3.65 g, 16.2 mmol, 1.00 eq.) in THF (20 mL), which was also added dropwise. Methyl 2-iodobenzoate (4.10 g, 13.8 mmol, 0.85 eq.) and $Pd(PPh_3)_4$ (0.64 g, 0.55 mmol, 0.04 eq.) were added simultaneously. The mixture was stirred at rt for 22 h. The mixture was diluted with ethyl acetate (200 mL) and washed with sat. NH_4Cl-solution (2 x 50 mL) and brine (50 mL). The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified via flash chromatography (30 % v/v% ethyl acetate/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the compound was isolated as yellowish oil (0.84 g, 26% yield). Analytical data matches the literature.[1]

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 8.05 – 8.02 (m, 1H), 7.72 – 7.69 (m, 1H), 7.57 – 7.48 (m, 2H), 4.32 (q, J = 7.1 Hz, 2H), 3.97 (s, 3H), 1.37 (t, J = 7.2 Hz, 3H).

Ethyl hex-2-ynoate (P-18)

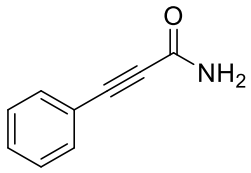


A solution of *n*-BuLi in hexane (22.3 mL, 2.50 M, 55.8 mmol, 1.10 eq.) was added dropwise over a period of 5 min to a solution of 1-pentyne (5.00 mL, 50.7 mmol, 1.00 eq.) in 100 mL THF at -78 °C and the solution was stirred under nitrogen. The solution was allowed to warm up to rt and cooled to -98 °C again. Ethyl chloroformate (5.33 mL, 55.8 mmol, 1.10 eq.) was added dropwise over 5 min. The solution was stirred at rt for 1.5 h. To the mixture, sat. NH_4Cl-solution (50 mL), H_2O (50 mL) and ethyl acetate (100 mL) were added. The layers were separated and the aqueous layer was extracted with ethyl acetate (100 mL). The combined organic layer was washed with brine (50 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude product was distilled under high vacuum (10^{-1} mbar, 58 °C). The product was obtained as a colourless oil (6.50 g, 80% yield). Analytical data matches the literature.[1]

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 4.21 (q, J = 7.1 Hz, 2H), 2.31 (t, J = 7.1 Hz, 3H), 1.67 – 1.55 (m, 2H), 1.30 (t, J = 7.1 Hz, 3H), 1.01 (t, J = 7.4 Hz, 3H).

Synthesis of propynoic amides

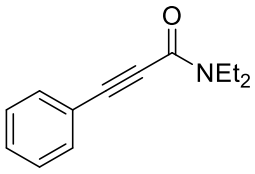
3-Phenylpropiolamide (P-20)



2-ynoate **P-3** (200 mg, 1.11 mmol, 1.00 equiv.) was mixed with aqueous solution of aqueous NH_3 (25 %) (1.88 mL, 6.24 mmol, 8.00 equiv.) and stirred vigorously for 16 h. Volatile compounds were removed under reduced pressure and the residue was purified by flash column chromatography (5 – 50 % v/v% ethyl acetate/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and obtained as a yellow solid (380 mg, 84% yield).[2] Analytical data matches the literature.[3]

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.58 – 7.54 (m, 2H), 7.48 – 7.535 (m, 3H), 5.81 (s, br, 2H).

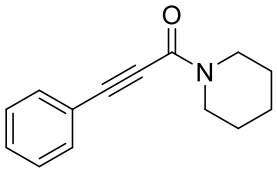
***N*,*N*-Diethyl-3-phenylpropiolamide (P-21)**



3-Phenylpropiolic acid (500 mg, 3.42 mmol, 1.00 equiv.) and triethylamine (3.79 mL, 6.84 mmol, 2.00 equiv.) were dissolved in CH_2Cl_2 (125 mL) and the solution was stirred under nitrogen at 0 °C. Oxalyl chloride (0.34 mL, 4.44 mmol, 1.30 equiv.) was added dropwise and diethylamine (0.39 mL, 3.76 mmol, 1.10 equiv.) was added subsequently. The solution was stirred at rt for 4.5 h. The solution was extracted with saturated aqueous NH_4Cl-solution (2 × 10 mL) and brine (10 mL). The solution was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (30 % v/v% ethyl acetate/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the product was obtained as a yellow oil (419 mg, 61% yield).[4] Analytical data matches the literature.[5]

^{1}H NMR (250 MHz, $CDCl_3$) δ ppm 7.57 - 7.54 (m, 2H), 7.46 - 7.34 (m, 3H), 3.68 (q, J = 7.1 Hz, 2H), 3.50 (q, J = 7.2 Hz, 2H), 1.30 (t, J = 7.1 Hz, 3H), 1.20 (t, J = 7.1 Hz, 3H).

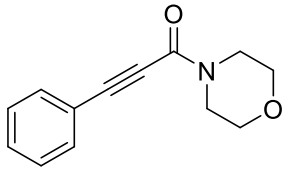
3-Phenyl-1-(piperidin-1-yl)prop-2-yn-1-one (P-22)



3-Phenylpropiolic acid (500 mg, 3.42 mmol, 1.00 equiv.) and triethylamine (3.79 mL, 6.84 mmol, 2.00 equiv.) were dissolved in CH_2Cl_2 (125 mL) and the solution was stirred under nitrogen at 0 °C. Oxalyl chloride (0.34 mL, 4.44 mmol, 1.30 equiv.) was added dropwise and piperidine (0.37 mL, 3.76 mmol, 1.10 equiv.) was added subsequently. The solution was stirred at rt for 4.5 h. The solution was extracted with saturated aqueous NH_4Cl-solution (2 × 10 mL) and brine (10 mL). The solution was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (30 % v/v% ethyl acetate/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the product was obtained as a yellow solid (494 mg, 68% yield). Analytical data matches the literature.[6]

^{1}H NMR (250 MHz, $CDCl_3$) δ ppm 7.57 - 7.54 (m, 2H), 7.44 - 7.33 (m, 3H), 3.79 (t, J = 4.9 Hz, 2H), 3.64 (t, J = 4.9 Hz, 2H), 1.68 - 1.58 (m, 6H).

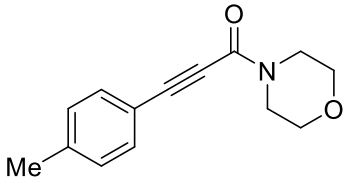
1-Morpholino-3-phenylprop-2-yn-1-one (P-23)



3-Phenylpropiolic acid (500 mg, 3.42 mmol, 1.00 equiv.) and triethylamine (3.79 mL, 6.84 mmol, 2.00 equiv.) were dissolved in CH_2Cl_2 (125 mL) and the solution was stirred under nitrogen at 0 °C. Oxalyl chloride (0.34 mL, 4.44 mmol, 1.30 equiv.) was added dropwise and the solution was stirred for 30 min. Morpholine (0.32 mL, 3.76 mmol, 1.10 equiv.) was added and the solution was stirred at rt for 4 h. The solution was extracted with saturated aqueous NH_4Cl-solution (2 × 10 mL) and brine (10 mL). The solution was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (30 % v/v% ethyl acetate/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the product was obtained as an orange solid (530 mg, 72% yield). Analytical data matches the literature.[7]

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.56 - 7.53 (m, 2H), 7.43 - 7.34 (m, 3H), 3.86 - 3.83 (m, 2H), 3.77 3.74 (m, 2H), 3.70 (s, 4H).

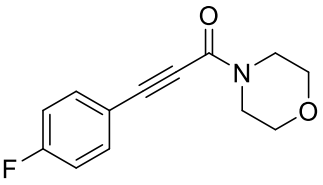
1-Morpholino-3-(*p*-tolyl)prop-2-yn-1-one (P-24)



2-ynoate **P-5** (200 mg, 1.15 mmol, 1.00 eq.) was dissolved in MeOH (10 mL) and added 1 M NaOH (5 mL). The mixture was and stirred at rt for 3 h. The solution was acidified with 1M HCl (10 mL) and extracted with CH_2Cl_2 (4 × 25 mL). The combined organic extracts were washed with brine (10 mL), dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was used without further purification. The residue was suspended in CH_2Cl_2 (50 mL) and triethylamine (1.27 mL, 2.30 mmol, 2.00 eq.) was added. The solution was cooled down to 0 °C and oxalyl chloride (128 µL, 1.49 mmol, 1.30 eq.) was added dropwise. Morpholine (109 µL, 1.26 mmol, 1.10 eq.) was added and the solution was stirred at rt for 4 h. The solution was extracted with saturated aqueous NH_4Cl-solution (2 × 10 mL) and brine (10 mL). The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (20 - 40 % v/v% ethyl acetate/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the product was isolated as yellow solid, **mp** = 100.1 °C, (211 mg, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.45 (d, J = 8.2 Hz, 2H), 7.18 (d, J = 7.8 Hz, 2H), 3.86 - 3.83 (m, 2H), 3.77 - 3.74 (m, 2H), 3.71 (s, 4H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 153.4 (s), 140.7 (s), 132.3 (s), 129.3 (s), 117.1 (s), 91.9 (s), 80.3 (s), 66.9 (s), 66.5 (s), 47.3 (s), 41.9 (s), 21.6 (s). **IR** ($\tilde{\nu}$ in cm^{-1}): 2207 (s), 1620 (s). **HR-MS** Calc. mass for $C_{14}H_{15}NO_2$: [M + H] = 229.1103, found: 229.1099.

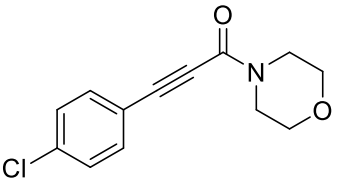
3-(4-Fluorophenyl)-1-morpholinoprop-2-yn-1-one (P-25)



2-ynoate **P-6** (200 mg, 1.04 mmol, 1.00 eq.) was dissolved in EtOH (10 mL) and added 1 M NaOH (5 mL). The mixture was and stirred at rt for 20 min and for 15 min at 100 °C. The solution was acidified with 1M HCl (10 mL) and extracted with CH_2Cl_2 (4 × 25 mL). The combined organic extracts were washed with brine (10 mL), dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was used without further purification. The residue was suspended in CH_2Cl_2 (50 mL) and triethylamine (1.15 mL, 2.08 mmol, 2.00 eq.) was added. The solution was cooled down to 0 °C and oxalyl chloride (116 µL, 1.35 mmol, 1.30 eq.) was added dropwise. Morpholine (99.0 µL, 1.14 mmol, 1.10 eq.) was added and the solution was stirred at rt for 4 h. The solution was extracted with saturated aqueous NH_4Cl-solution (2 × 10 mL) and brine (10 mL). The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (20 - 30 % v/v% ethyl acetate/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the product was isolated as yellow solid, **mp** = 105.1 °C, (199 mg, 82% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.56 - 7.51 (m, 2H), 7.09 - 7.09 (m, 2H), 3.83 - 3.80 (m, 2H), 3.76 - 3.73 (m, 2H), 3.69 (s, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 164.8 (s), 162.3 (s), 153.0 (s), 134.5 (s), 134.5 (s), 116.1 (s), 115.9 (s), 90.1 (s), 80.6 (s), 66.8 (s), 66.4 (s), 47.3 (s), 41.9 (s). **IR** ($\tilde{\nu}$ in cm^{-1}): 2187 (s), 1616 (s). **HR-MS** Calc. mass for $C_{13}H_{12}NO_2F$: [M + H] = 233.0852, found: 233.0847.

3-(4-Chlorophenyl)-1-morpholinoprop-2-yn-1-one (P-26)

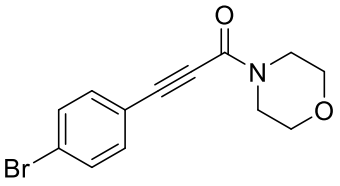


2-ynoate **P-8** (200 mg, 1.03 mmol, 1.00 eq.) was dissolved in MeOH (10 mL) and added 1 M NaOH (5 mL). The mixture was and stirred at rt for 20 min and for 15 min at 100 °C. The solution was acidified with 1M HCl (10 mL) and extracted with CH_2Cl_2 (4 × 25 mL). The combined organic extracts were washed with brine (10 mL), dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was used without further purification. The residue was suspended in CH_2Cl_2 (50 mL) and triethylamine (1.15 mL, 2.08 mmol, 2.00 eq.) was added. The solution was cooled down to 0 °C and oxalyl chloride (116 µL, 1.35 mmol, 1.30 eq.) was added dropwise. Morpholine (99.0 µL, 1.14 mmol, 1.10 eq.) was added and the solution was stirred at rt for 4 h. The solution was extracted with saturated aqueous NH_4Cl-solution (2 × 10 mL) and brine (10 mL). The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure.

The residue was purified by flash column chromatography (20 - 30 % v/v% ethyl acetate/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the product was isolated as yellow solid (159 mg, 62% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.49 - 7.46 (m, 2H), 7.37 - 7.34 (m, 2H), 3.84 - 3.81 (m, 2H), 3.77 - 3.74 (m, 2H), 3.70 (s, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 152.9 (s), 136.5 (s), 133.5 (s), 129.0 (s), 118.7 (s), 89.9 (s), 81.6 (s), 66.9 (s), 66.5 (s), 47.3 (s), 42.0 (s). **IR** ($\tilde{\nu}$ in cm^{-1}): 2207 (s), 1616 (s). **HR-MS** Calc. mass for $C_{13}H_{12}NO_2Cl$: [M + H] = 249.0557, found: 249.0554.

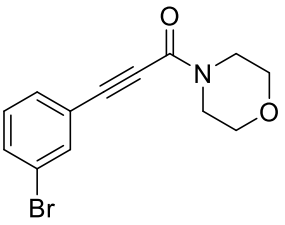
3-(4-Bromophenyl)-1-morpholinoprop-2-yn-1-one (P-27)



2-ynoate **P-9** (200 mg, 0.84 mmol, 1.00 eq.) was dissolved in MeOH (10 mL) and added 1 M NaOH (5 mL). The mixture was and stirred at rt for 20 min and for 20 min at 100 °C. The solution was acidified with 1M HCl (10 mL) and extracted with CH_2Cl_2 (4 × 25 mL). The combined organic extracts were washed with brine (10 mL), dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was used without further purification. The residue was suspended in CH_2Cl_2 (50 mL) and triethylamine (0.93mL, 1.67 mmol, 2.00 eq.) was added. The solution was cooled down to 0 °C and oxalyl chloride (93.0 µL, 1.09 mmol, 1.30 eq.) was added dropwise. Morpholine (92.0 µL, 1.07 mmol, 1.10 eq.) was added and the solution was stirred at rt for 4 h. The solution was extracted with saturated aqueous NH_4Cl-solution (2 × 10 mL) and brine (10 mL). The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (40% v/v% ethyl acetate/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the product was isolated as yellow solid, **mp** 127.9 °C, (66.0 mg, 26% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.53 - 7.50 (m, 2H), 7.42 - 7.39 (m, 2H), 3.83 - 3.81 (m, 2H), 3.76 - 3.74 (m, 2H), 3.70 (s, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 152.9 (s), 133.7 (s), 131.9 (s), 124.8 (s), 119.2 (s), 89.9 (s), 81.7 (s), 66.8 (s), 66.4 (s), 47.3 (s), 42.0 (s). **IR** ($\tilde{\nu}$ in cm^{-1}): 2207 (s), 1616 (s). **HR-MS** Calc. mass for $C_{13}H_{12}NO_2Br$: [M + H] = 293.0051, found: 293.0044.

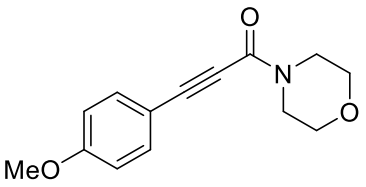
3-(3-Bromophenyl)-1-morpholinoprop-2-yn-1-one (P-28)



2-ynoate **P-10** (200 mg, 0.84 mmol, 1.00 eq.) was dissolved in MeOH (10 mL) and added 1 M NaOH (5 mL). The mixture was and stirred at rt for 20 min and for 20 min at 100 °C. The solution was acidified with 1M HCl (10 mL) and extracted with CH_2Cl_2 (4 × 25 mL). The combined organic extracts were washed with brine (10 mL), dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was used without further purification. The residue was suspended in CH_2Cl_2 (50 mL) and triethylamine (0.93mL, 1.67 mmol, 2.00 eq.) was added. The solution was cooled down to 0 °C and oxalyl chloride (93.0 µL, 1.09 mmol, 1.30 eq.) was added dropwise. Morpholine (92.0 µL, 1.07 mmol, 1.10 eq.) was added and the solution was stirred at rt for 4 h. The solution was extracted with saturated aqueous NH_4Cl-solution (2 × 10 mL) and brine (10 mL). The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (20% v/v% ethyl acetate/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the product was isolated as yellow solid, **mp** = 106.7 °C, (135 mg, 55% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.69 (t, J = 1.8 Hz, 1H), 7.58 - 7.56 (m, 1H), 7.49 (dt, J = 7.8, J = 1.2 Hz, 1H), 7.26 (t, J = 7.9 Hz, 1H), 3.84 - 3.82 (m, 2H), 3.78 - 3.75 (m, 2H), 3.71 (s, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 152.8 (s), 134.9 (s), 133.4 (s), 130.9 (s), 130.0 (s), 122.3 (s), 122.3 (s), 89.2 (s), 81.7 (s), 66.9 (s), 66.5 (s), 47.3 (s), 42.0 (s). **IR** ($\tilde{\nu}$ in cm^{-1}): 2207 (s), 1616 (s). **HR-MS** Calc. mass for $C_{13}H_{12}NO_2Br$: [M + H] = 293.0051, found: 293.0048.

3-(4-Methoxyphenyl)-1-morpholinoprop-2-yn-1-one (P-29)

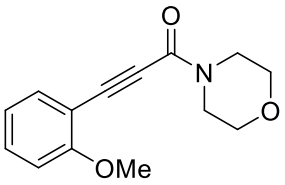


2-ynoate **P-12** (200 mg, 1.05 mmol, 1.00 eq.) was dissolved in MeOH (10 mL) and added 1 M NaOH (5 mL). The mixture was and stirred at rt for 20 min and for 20 min at 100 °C. The solution was acidified with 1M HCl (10 mL) and extracted with CH_2Cl_2 (4 × 25 mL). The combined organic extracts were washed with brine (10 mL), dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was used without further purification. The residue was suspended in CH_2Cl_2 (50 mL) and triethylamine (1.16 mL, 2.10 mmol, 2.00 eq.) was added. The solution was cooled down to 0 °C and oxalyl chloride (117 µL, 1.37 mmol, 1.30 eq.) was added dropwise. Morpholine (100 µL, 1.16 mmol, 1.10 eq.) was added and the solution was stirred at rt for 4 h. The solution was extracted with saturated aqueous NH_4Cl-solution (2 × 10 mL) and brine (10 mL). The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (40% v/v% ethyl acetate/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the product was isolated as yellow solid, **mp** = 97.5 °C, (197 mg, 76% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.51 - 7.49 (m, 2H), 6.90 - 6.87 (m, 2H), 3.85 - 3.83 (m, 5H), 3.76 - 3.74 (m, 2H), 3.70 (s, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 161.1 (s), 153.5 (s), 134.2 (s),

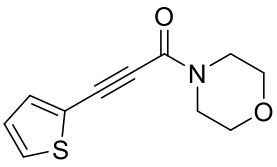
114.2 (s), 112.1 (s), 91.7 (s), 80.1 (s), 66.9 (s), 66.5 (s), 55.4 (s), 47.3 (s), 41.9 (s). **IR** ($\tilde{\nu}$ in cm^{-1}): 2210 (s), 1597 (s). **HR-MS** Calc. mass for $C_{14}H_{15}NO_3$: [M + H] = 245.1052, found: 245.1044.

3-(2-Methoxyphenyl)-1-morpholinoprop-2-yn-1-one (P-30)



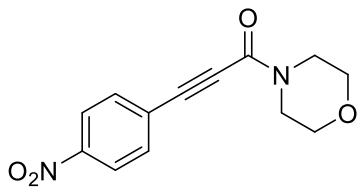
2-ynoate **P-13** (200 mg, 0.98 mmol, 1.00 eq.) was dissolved in EtOH (10 mL) and added 1 M NaOH (5 mL). The mixture was and stirred at rt for 20 min and for 20 min at 100 °C. The solution was acidified with 1M HCl (10 mL) and extracted with CH_2Cl_2 (4 × 25 mL). The combined organic extracts were washed with brine (10 mL), dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was used without further purification. The residue was suspended in CH_2Cl_2 (50 mL) and triethylamine (1.09 mL, 1.96 mmol, 2.00 eq.) was added. The solution was cooled down to 0 °C and oxalyl chloride (109 µL, 1.27 mmol, 1.30 eq.) was added dropwise. Morpholine (93.0 µL, 1.08 mmol, 1.10 eq.) was added and the solution was stirred at rt for 4 h. The solution was extracted with saturated aqueous NH_4Cl-solution (2 × 10 mL) and brine (10 mL). The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (40% v/v% ethyl acetate/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the product was isolated as yellow solid, **mp** = 101.1 °C, (179 mg, 75% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.51 (dd, J = 7.6, 1.8 Hz, 1H), 7.41 - 7.37 (m, 1H), 7.96 - 7.89 (m, 2H), 3.94 - 3.91 (m, 2H), 3.88 (s, 3H), 3.77 - 3.74 (m, 2H), 3.70 (s, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 161.1 (s), 153.4 (s), 134.3 (s), 131.8 (s), 120.6 (s), 110.7 (s), 109.6 (s), 87.8 (s), 84.9 (s), 67.0 (s), 66.5 (s), 55.8 (s), 47.3 (s), 41.9 (s). **IR** ($\tilde{\nu}$ in cm^{-1}): 2218 (s), 1624 (s). **HR-MS** Calc. mass for $C_{14}H_{15}NO_3$: [M + H] = 245.1052, found: 245.1045.

1-Morpholino-3-(thiophen-2-yl)prop-2-yn-1-one (P-31)



2-ynoate **P-14** (200 mg, 1.11 mmol, 1.00 eq.) was dissolved in MeOH (10 mL) and added 1 M NaOH (5 mL). The mixture was and stirred at rt for 20 min and for 20 min at 100 °C. The solution was acidified with 1M HCl (10 mL) and extracted with CH_2Cl_2 (4 × 25 mL). The combined organic extracts were washed with brine (10 mL), dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was used without further purification. The residue was suspended in CH_2Cl_2 (50 mL) and triethylamine (1.23 mL, 2.22 mmol, 2.00 eq.) was added. The solution was cooled down to 0 °C and oxalyl chloride (124 µL, 1.44 mmol, 1.30 eq.) was added dropwise. Morpholine (105 µL, 1.22 mmol, 1.10 eq.) was added and the solution was stirred at rt for 4 h. The solution was extracted with saturated aqueous NH_4Cl-solution (2 × 10 mL) and brine (10 mL). The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (20 - 30% v/v% ethyl acetate/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the product was isolated as yellow solid, **mp** = 52.4 °C, (192 mg, 78% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.44 - 7.42 (m, 2H), 7.05 (dd, J = 4.9, J = 3.9 Hz, 1H), 3.83 - 3.79 (m, 2H), 3.77 - 3.74 (m, 2H), 3.70 (s, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 153.0 (s), 135.3 (s), 130.2 (s), 127.4 (s), 119.9 (s), 84.9 (s), 84.7 (s), 66.8 (s), 66.4 (s), 47.2 (s), 41.9 (s). **IR** ($\tilde{\nu}$ in cm^{-1}): 2207 (s), 1605 (s). **HR-MS** Calc. mass for $C_{11}H_{11}NO_2S$: [M + H] = 221.0510, found: 221.0506.

1-Morpholino-3-(4-nitrophenyl)-prop-2-yn-1-one (P-32)

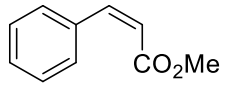


2-ynoate **P-11** (200 mg, 0.97 mmol, 1.00 eq.) was dissolved in MeOH (10 mL) and added 1 M NaOH (5 mL). The mixture was and stirred at rt for 20 min and for 20 min at 100 °C. The solution was acidified with 1M HCl (10 mL) and extracted with CH_2Cl_2 (4 × 25 mL). The combined organic extracts were washed with brine (10 mL), dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was used without further purification. The residue was suspended in CH_2Cl_2 (50 mL) and triethylamine (1.08 mL, 1.95 mmol, 2.00 eq.) was added. The solution was cooled down to 0 °C and oxalyl chloride (109 µL, 1.27 mmol, 1.30 eq.) was added dropwise. Morpholine (79.0 µL, 0.92 mmol, 1.10 eq.) was added and the solution was stirred at rt for 4 h. The solution was extracted with saturated aqueous NH_4Cl-solution (2 × 10 mL) and brine (10 mL). The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (40% v/v% ethyl acetate/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the product was isolated as yellow solid, **mp** = 192.2 °C, (61.0 mg, 25% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.27 - 8.24 (m, 2H), 7.73 - 7.70 (m, 2H), 3.85 - 3.82 (m, 2H), 3.79 - 3.77 (m, 2H), 3.73 (s, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 152.3 (s), 148.3 (s), 133.1 (s), 126.9 (s), 123.7 (s), 88.3 (s), 84.6 (s), 66.8 (s), 66.4 (s), 47.3 (s), 42.1 (s). **IR** ($\tilde{\nu}$ in cm^{-1}): 2214 (w), 1620 (s). **HR-MS** Calc. mass for $C_{13}H_{12}N_2O_4$: [M + H] = 260.0797, found: 260.0790.

Synthesis of 2-enoates

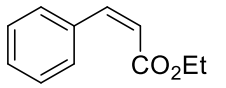
Methyl (*Z*)-3-phenylacrylate (*Z*-3)



2-ynoate **P-3** (100 mg, 0.62 mmol, 1.00 eq.) was dissolved in 1,4-dioxane (5 mL) and H_2O (11.3 µL, 0.62 mmol, 1.00 eq.) was added, followed by PBu_3 (156 µL, 0.62 mmol, 1.00 eq.). The solution was stirred at 70 °C for 30 min. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (10 % v/v% ethyl acetate/petrol ether with 2% TEA, silica gel: 60M, pore size 0.04 – 0.063 mm) and the product was isolated as colourless oil (94.0 mg, 93% yield, *E*/*Z* = 1 : 25). Analytical data matches the literature.[8]

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.62 - 7.59 (m, 2H), 7.45 - 7.35 (m, 3H), 6.97 (d, *J* = 12.7 Hz, 1H), 5.97 (d, *J* = 12.7 Hz, 1H), 3.73 (s, 3H).

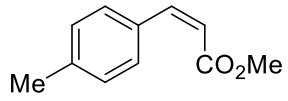
Ethyl (*Z*)-3-phenylacrylate (*Z*-4)



2-ynoate **P-4** (109 mg, 0.62 mmol, 1.00 eq.) was dissolved in 1,4-dioxane (5 mL) and H_2O (11.3 µL, 0.62 mmol, 1.00 eq.) was added, followed by PBu_3 (156 µL, 0.62 mmol, 1.00 eq.). The solution was stirred at 70 °C for 15 min. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (10 % v/v% ethyl acetate/petrol ether with 2% TEA, silica gel: 60M, pore size 0.04 – 0.063 mm) and the product was isolated as colourless oil (101 mg, 92% yield, *E*/*Z* = 1 : 11). Analytical data matches the literature.[9]

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.62 - 7.59 (m, 2H), 7.40 - 7.33 (m, 3H), 6.96 (d, *J* = 12.7 Hz, 1H) 5.97 (d, *J* = 12.7 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H).

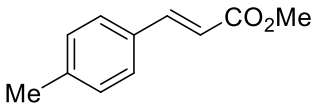
Methyl (*Z*)-3-(*p*-tolyl)acrylate (*Z*-5)



2-ynoate **P-5** (100 mg, 0.57 mmol, 1.00 eq.) was dissolved in 1,4-dioxane (5 mL) and H_2O (10.3 µL, 0.57 mmol, 1.00 eq.) was added, followed by PBu_3 (143 µL, 0.57 mmol, 1.00 eq.). The solution was stirred at 70 °C for 2 h. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (2.5% v/v% diethyl ether/toluene, silica gel: 60M, pore size 0.04 – 0.063 mm) and the product was isolated as colourless oil (76.0 mg, 75% yield, *E*/*Z* = 1 : 38). Analytical data matches the literature.[10]

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.55 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 6.93 (d, *J* = 12.6 Hz, 1H), 5.92 (d, *J* = 12.9 Hz, 1H), 3.73 (s, 3H), 2.38 (s, 3H).

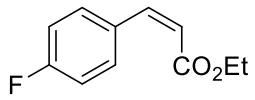
Methyl (*E*)-3-(p-tolyl)acrylate (*E*-5)



The compound was isolated as a colourless solid (2.00 mg, yield 2%. Total yield 77 % (*E* + *Z* isomers). Analytical data matches the literature.[11]

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.68 (d, *J* = 15.9 1H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 6.41 (d, *J* = 16.1 Hz, 1H), 3.81 (s, 3H), 2.38 (s, 3H).

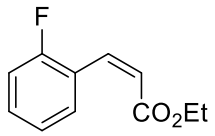
Methyl (*Z*)-3-(4-fluorophenyl)acrylate (*Z*-6)



2-ynoate **P-6** (120 mg, 0.62 mmol, 1.00 eq.) was dissolved in 1,4-dioxane (5 mL) and H_2O (11.2 µL, 0.62 mmol, 1.00 eq.) was added, followed by PBu_3 (156 µL, 0.62 mmol, 1.00 eq.). The solution was stirred at 70 °C for 30 min. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (5% v/v% diethyl ether/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the product was isolated as colourless solid (115 mg, 95% yield, *E*/*Z* = 1 : 33). Analytical data matches the literature.[12]

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.67 - 7.63 (m, 2H), 7.07 - 7.01 (m, 2H), 6.89 (d, *J* = 12.6 Hz, 1H), 5.94 (d, *J* = 12.9 Hz, 1H), 4.19 (q, *J* = 7.0 Hz, 2H), 1.27 (t, *J* = 7.0 Hz, 3H).

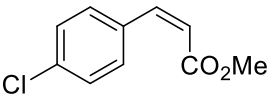
Methyl (*Z*)-3-(2-fluorophenyl)acrylate (*Z*-7)



2-ynoate **P-7** (100 mg, 0.52 mmol, 1.00 eq.) was dissolved in 1,4-dioxane (5 mL) and H_2O (9.40 µL, 0.52 mmol, 1.00 eq.) was added, followed by PBu_3 (130 µL, 0.52 mmol, 1.00 eq.). The solution was stirred at 70 °C for 30 min. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (5% v/v% diethyl ether/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the product was isolated as colourless solid (80.0 mg, 79% yield, *E*/*Z* = 1 : 3.8).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.62 - 7.58 (m, 1H), 7.37 - 7.29 (m, 1H), 7.19 - 7.02 (m, 3H), 6.08 (d, J = 12.6 Hz, 1H), 4.17 (q, J = 7.2 Hz, 2H), 1.23 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 166.8 (s), 165.8 (s), 135.5 (s), 135.4 (s), 130.9 (s), 130.8 (s), 130.6 (s), 130.6 (s), 123.5 (s), 123.5 (s), 122.3 (s), 122.3 (s), 115.3 (s), 115.1 (s), 60.4 (s), 14.0 (s). **IR** ($\tilde{\nu}$ in cm^{-1}): 1713 (s). **HR-MS** Calc. mass for $C_{11}H_{11}O_2F$: [M + H] = 194.0743, found: 194.0740.

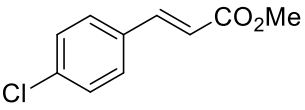
Methyl (*Z*)-3-(4-chlorophenyl)acrylate (*Z*-8)



2-ynoate **P-8** (100 mg, 0.51 mmol, 1.00 eq.) was dissolved in 1,4-dioxane (5 mL) and H_2O (9.30 µL, 0.51 mmol, 1.00 eq.) was added, followed by PBu_3 (128 µL, 0.51 mmol, 1.00 eq.). The solution was stirred at 70 °C for 17 min. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (5% v/v% diethyl ether/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the product was isolated as colourless solid (79.0 mg, 78% yield, *E*/*Z* = 1 : 5.4). Analytical data matches the literature.[10]

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.56 (d, J = 8.5 Hz, 2H), 7.33 (d, J = 8.5 Hz, 2H), 6.90 (d, J = 12.9 Hz, 1H), 5.98 (d, J = 12.6 Hz, 1H), 3.72 (s, 3H).

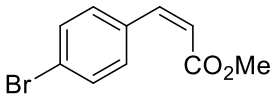
Methyl (*E*)-3-(4-chlorophenyl)acrylate (*E*-8)



The compound was isolated as a colourless solid (10.0 mg, yield 10%). Total yield 88% (*E* + *Z* isomers). Analytical data matches the literature.[13]

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.65 (d, J = 16.1 Hz, 1H), 7.47 (d, J = 8.6 Hz, 2H), 7.37 (d, J = 8.6 Hz, 2H), 6.42 (d, J = 15.9 Hz, 1H), 3.82 (s, 3H).

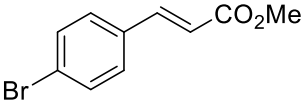
Methyl (*Z*)-3-(4-bromophenyl)acrylate (*Z*-9)



2-ynoate **P-9** (100 mg, 0.42 mmol, 1.00 eq.) was dissolved in 1,4-dioxane (5 mL) and H_2O (7.50 µL, 0.42 mmol, 1.00 eq.) was added, followed by PBu_3 (104 µL, 0.42 mmol, 1.00 eq.). The solution was stirred at 70 °C for 14 min. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (2.5% v/v% diethyl ether/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the product was isolated as colourless solid (54.0 mg, 54% yield, *E*/*Z* = 1 : 6.3).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.49 (s, 4H), 6.89 (d, J = 12.6 Hz, 1H), 5.99 (d, J = 12.9 Hz, 1H), 3.72 (s). **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 166.3 (s), 142.3 (s), 133.6 (s), 131.4 (s), 131.2 (s), 123.4 (s), 119.9 (s), 51.5 (s). **IR** ($\tilde{\nu}$ in cm^{-1}): 1713 (s). **HR-MS** Calc. mass for $C_{10}H_9O_2Br$: [M + H] = 239.9786, found: 239.9780.

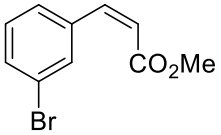
Methyl (*E*)-3-(4-bromophenyl)acrylate (*E*-9)



The compound was isolated as a colourless solid (32.0 mg, yield 32%). Total yield 67% (*E* + *Z* isomers). Analytical data matches the literature.[13]

^{1}H NMR (250 MHz, $CDCl_3$) δ ppm 7.64 (d, J = 15.9 Hz, 1H), 7.53 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.2 Hz, 2H), 6.44 (d, J = 16.1 Hz, 1H), 3.82 (s, 3H).

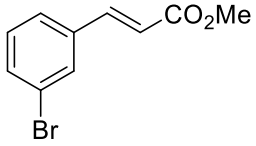
Methyl (*Z*)-3-(3-bromophenyl)acrylate (*Z*-10)



2-ynoate **P-10** (100 mg, 0.42 mmol, 1.00 eq.) was dissolved in 1,4-dioxane (5 mL) and H_2O (7.50 µL, 0.42 mmol, 1.00 eq.) was added, followed by PBu_3 (104 µL, 0.42 mmol, 1.00 eq.). The solution was stirred at 70 °C for 30 min. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (2.5% v/v% diethyl ether/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the product was isolated as colourless solid (35.0 mg, 35% yield, *E*/*Z* = 1 : 6).

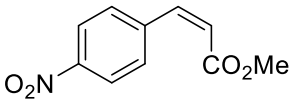
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.75 (s, 1H), 7.50 (dd, J = 15.4, J = 7.5 Hz, 2H), 7.28 - 7.23 (m, 1H), 6.90 (d, J = 12.6 Hz, 1H), 6.02 (d, J = 12.6 Hz, 1H), 3.74 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 166.1 (s), 141.6 (s), 136.7 (s), 132.4 (s), 131.9 (s), 129.5 (s), 128.2 (s), 122.0 (s), 120.7 (s), 51.5 (s). **IR** ($\tilde{\nu}$ in cm^{-1}): 1721 (s). **HR-MS** Calc. mass for $C_{10}H_9O_2Br$: [M + H] = 239.9786, found: 239.9781.

Methyl (*E*)-3-(3-bromophenyl)acrylate (*E*-10)



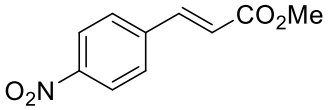
The compound was isolated as a colourless solid (51.0 mg, yield 51%). Total yield 80% (*E* + *Z* isomers). Analytical data matches the literature.[14]
^{1}H NMR (250 MHz, $CDCl_3$) δ ppm 7.68 (s, 1H), 7.62 (d, *J* = 16.1 Hz 1H), 7.52 (d, *J* = 7.9 Hz 1H), 7.45 (d, *J* = 7.7 Hz 1H), 7.30 - 7.24 (m, 1H), 6.44 (d, *J* = 16.1 Hz 1H), 3.82 (s, 3H).

Methyl (*Z*)-3-(4-nitrophenyl)acrylate (*Z*-11)



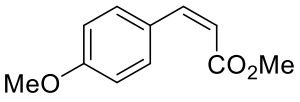
2-ynoate **P-11** (100 mg, 0.49 mmol, 1.00 eq.) was dissolved in 1,4-dioxane (5 mL) and H_2O (8.80 µL, 0.49 mmol, 1.00 eq.) was added, followed by PBu_3 (122 µL, 0.49 mmol, 1.00 eq.). The solution was stirred at 70 °C for 3 min. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (5% v/v% diethyl ether/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the product was isolated as colourless solid (35.0 mg, 35% yield, *E*/*Z* = 1 : 1.1).
^{1}H NMR (250 MHz, $CDCl_3$) δ ppm 8.22 (d, *J* = 8.6 Hz, 2H), 7.69 (d, *J* = 8.8 Hz, 2H), 7.04 (d, *J* = 12.3 Hz, 1H), 6.15 (d, *J* = 12.4 Hz, 1H), 3.73 (s, 3H). **^{13}C NMR** (63 MHz, $CDCl_3$) δ ppm 165.7 (s), 147.5 (s), 141.3 (s), 140.9 (s), 130.2 (s), 123.1 (s), 122.7 (s), 51.6 (s). **IR** ($\tilde{\nu}$ in cm^{-1}): 1717 (s). **HR-MS** Calc. mass for $C_{10}H_9NO_4$: [M + H] = 207.0532, found: 207.0525.

Methyl (*E*)-3-(4-nitrophenyl)acrylate (*E*-11)



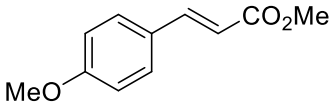
The compound was isolated as a colourless solid (32.0 mg, yield 32%). Total yield 67% (*E* + *Z* isomers). Analytical data matches the literature.[15]
^{1}H NMR (250 MHz, $CDCl_3$) δ ppm 8.26 (d, *J* = 8.8 Hz, 2H), 7.76 - 7.66 (m, 3H), 6.57 (d, *J* = 16.1 Hz, 1H), 3.85 (s, 3H).

Methyl (*Z*)-3-(4-methoxyphenyl)acrylate (*Z*-12)



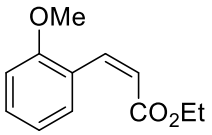
2-ynoate **P-12** (100 mg, 0.52 mmol, 1.00 eq.) was dissolved in 1,4-dioxane (5 mL) and H_2O (8.80 µL, 0.49 mmol, 0.94 eq.) was added, followed by PBu_3 (122 µL, 0.49 mmol, 0.94 eq.). The solution was stirred at 70 °C for 3 h. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (2.5% v/v% diethyl ether/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the product was isolated as colourless oil (74.0 mg, 73% yield, *E*/*Z* = 1 : 25). Analytical data matches the literature.[16]
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.70 (d, *J* = 8.8 Hz, 2H), 6.91 - 6.85 (m, 3H), 5.84 (d, *J* = 12.6 Hz, 1H), 3.84 (s, 3H), 3.74 (s, 3H).

Methyl (*E*)-3-(4-methoxyphenyl)acrylate (*E*-12)



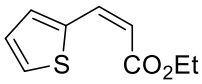
The compound was isolated as a colourless solid (3.00 mg, yield 3%). Total yield 76 % (*E* + *Z* isomers). Analytical data matches the literature.[11]
^{1}H NMR (250 MHz, $CDCl_3$) δ ppm 7.66 (d, *J* = 16.1 Hz, 1H) 7.49 (d, *J* = 8.6 Hz, 2H), 6.92 (d, *J* = 8.6 Hz, 2H), 6. 32 (d, *J* = 16.1 Hz, 1H), 3.85 (s, 3H), 3.80 (s, 3H).

Ethyl (*Z*)-3-(2-methoxyphenyl)acrylate (*Z*-13)



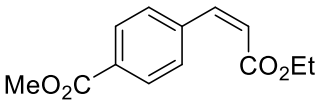
2-ynoate **P-13** (100 mg, 0.49 mmol, 1.00 eq.) was dissolved in 1,4-dioxane (5 mL) and H_2O (8.80 µL, 0.49 mmol, 1.00 eq.) was added, followed by PBu_3 (122 µL, 0.49 mmol, 1.00 eq.). The solution was stirred at 70 °C for 3 h. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (2.5% v/v% diethyl ether/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the product was isolated as colourless oil (66.0 mg, 65% yield, *E*/*Z* = 1 : 25).
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.56 (dd, *J* = 7.6, *J* = 1.5 Hz, 1H), 7.34 - 7.30 (m, 1H), 7.18 (d, *J* = 12.6 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 8.5 Hz, 1H), 5.98 (d, *J* = 12.3 Hz, 1H), 4.15 (q, *J* = 7.0 Hz, 1H), 3.85 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 166.3 (s), 157.0 (s), 139.0 (s), 130.7 (s), 130.3 (s), 124.1 (s), 120.0 (s), 119.8 (s), 110.2 (s), 60.0 (s), 55.4 (s), 14.0 (s). **IR** ($\tilde{\nu}$ in cm^{-1}): 1717 (s). **HR-MS** Calc. mass for $C_{12}H_{14}O_3$: [M + H] = 206.0943, found: 206.0936.

Ethyl (*Z*)-3-(thiophen-2-yl)acrylate (*Z*-14)



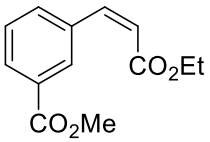
2-ynoate **P-14** (100 mg, 0.55 mmol, 1.00 eq.) was dissolved in 1,4-dioxane (5 mL) and H_2O (10.0 µL, 0.55 mmol, 1.00 eq.) was added, followed by PBu_3 (139 µL, 0.55 mmol, 1.00 eq.). The solution was stirred at 70 °C for 18 min. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (2.5% v/v% diethyl ether/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the product was isolated as colourless oil (80.0 mg, 79% yield, *E*/*Z* = 1 : 3.3).
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.52 (d, *J* = 5.3 Hz, 1H), 7.45 (d, *J* = 3.2 Hz, 1H), 7.11 - 7.04 (m, 2H), 5.75 (d, *J* = 12.6 Hz, 1H), 4.26 (q, *J* = 7.0 Hz, 2H), 1.33 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 166.4 (s), 137.5 (s), 135.6 (s), 131.9 (s), 130.8 (s), 128.3 (s), 117.0 (s), 60.2 (s), 14.3 (s). **IR** ($\tilde{\nu}$ in cm^{-1}): 1705 (s). **HR-MS** Calc. mass for $C_9H_{10}O_2S$: [M + H] = 182.0402, found: 182.0396.

Methyl (*Z*)-4-(3-ethoxy-3-oxoprop-1-en-1-yl)benzoate (*Z*-15)



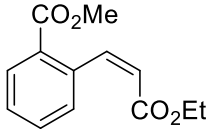
2-ynoate **P-15** (100 mg, 0.43 mmol, 1.00 eq.) was dissolved in 1,4-dioxane (5 mL) and H_2O (7.80 µL, 0.43 mmol, 1.00 eq.) was added, followed by PBu_3 (108 µL, 0.43 mmol, 1.00 eq.). The solution was stirred at 70 °C for 5 min. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (5% v/v% diethyl ether/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the product was isolated as colourless oil (89.0 mg, 88% yield, *E*/*Z* = 1 : 1).
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.05 - 8.00 (m, 2H), 7.59 - 7.57 (m, 2H), 6.51 (d, *J* = 12.6 Hz, 1H), 6.04 (d, *J* = 12.6 Hz, 1H), 4.16 (q, *J* = 7.0 Hz, 2H), 3.91 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 166.6 (s), 166.4 (s), 166.3 (s), 165.7 (s), 143.1 (s), 141.5 (s), 139.4 (s), 138.6 (s), 131.2 (s), 130.0 (s), 129.3 (s), 129.1 (s), 127.8 (s), 121.8 (s), 120.6 (s), 60.6 (s), 60.4 (s), 52.2 (s), 52.1 (s), 14.2 (s), 14.0 (s). **IR** ($\tilde{\nu}$ in cm^{-1}): 1713 (s). **HR-MS** Calc. mass for $C_{13}H_{14}O_4$: [M + H] = 234.0892, found: 234.0889.

Methyl (*Z*)-3-(3-ethoxy-3-oxoprop-1-en-1-yl)benzoate (*Z*-16)



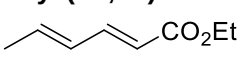
2-ynoate **P-16** (100 mg, 0.43 mmol, 1.00 eq.) was dissolved in 1,4-dioxane (5 mL) and H_2O (7.80 µL, 0.43 mmol, 1.00 eq.) was added, followed by PBu_3 (108 µL, 0.43 mmol, 1.00 eq.). The solution was stirred at 70 °C for 30 min. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (10% v/v% diethyl ether/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the product was isolated as colourless oil (87.0 mg, 86% yield, *E*/*Z* = 1 : 12.5).
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm δ = 8.17 (s, 1H), 8.00 (d, *J* = 7.6 Hz, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 1H), 6.99 (d, *J* = 12.3 Hz, 1H), 6.02 (d, *J* = 12.6 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.92 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 166.7 (s), 165.8 (s), 141.8 (s), 135.1 (s), 133.8 (s), 130.7 (s), 129.9 (s), 129.8 (s), 128.0 (s), 121.1 (s), 60.4 (s), 52.1 (s), 14.0 (s). **IR** ($\tilde{\nu}$ in cm^{-1}): 1713 (s). **HR-MS** Calc. mass for $C_{13}H_{14}O_4$: [M + H] = 234.0892, found: 234.0891.

Methyl (*Z*)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)benzoate (*Z*-17)



2-ynoate **P-17** (100 mg, 0.43 mmol, 1.00 eq.) was dissolved in 1,4-dioxane (5 mL) and H_2O (7.80 µL, 0.43 mmol, 1.00 eq.) was added, followed by PBu_3 (108 µL, 0.43 mmol, 1.00 eq.). The solution was stirred at 70 °C for 11 min. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (10% v/v% diethyl ether/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the product was isolated as colourless oil (69.0 mg, 68% yield, *E*/*Z* = 1.4 : 1).
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.03 (d, *J* = 7.9 Hz, 1H), 7.61 - 7.23 (m, 4H), 6.02 (d, *J* = 12.0 Hz, 1H), 4.03 (q, *J* = 7.0 Hz, 2H), 3.88 (s, 3H), 1.09 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 167.1 (s), 166.9 (s), 166.5 (s), 165.9 (s), 145.0 (s), 143.6 (s), 138.3 (s), 136.3 (s), 132.3 (s), 131.7 (s), 130.7 (s), 130.2 (s), 130.1 (s), 129.8 (s), 129.3 (s), 128.0 (s), 127.9 (s), 121.1 (s), 119.6 (s), 60.5 (s), 60.0 (s), 52.3 (s), 52.0 (s), 14.3 (s), 13.9 (s). **IR** ($\tilde{\nu}$ in cm^{-1}): 1713 (s). **HR-MS** Calc. mass for $C_{10}H_9O_2$: $[M\text{-}CO_2C_2H_5]^+$ = 161.0603, found: 161.0596.

Ethyl (2*E*,4*E*)-hexa-2,4-dienoate (*Z*-18)

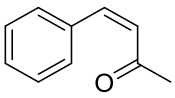


2-ynoate **P-18** (100 mg, 0.71 mmol, 1.00 eq.) was dissolved in 1,4-dioxane (5 mL) and H_2O (12.8 µL, 0.71 mmol, 1.00 eq.) was added, followed by PBu_3 (178 µL, 0.71 mmol, 1.00 eq.). The solution was stirred at 70 °C for 2 h.

The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (2.5% v/v% diethyl ether/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the product was isolated as colourless oil (26.0 mg, 26% yield). Analytical data matches the literature.[17]

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm δ = 7.30 - 7.23 (m, 1H), 6.24 - 6.10 (m, 2H), 5.78 (d, *J* = 15.5 Hz, 1H), 4.21 (q, *J* = 7.0 Hz, 2H), 1.87 (d, *J* = 5.9 Hz, 3H), 1.31 (t, *J* = 7.2 Hz, 1H).

(*Z*)-4-Phenylbut-3-en-2-one (*Z*-19)

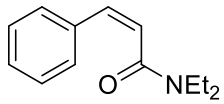


A solution of 4-phenylbut-3-yn-2-one (0.50 g, 3.47 mmol, 1.00 eq.), PPh_3 (0.91 g, 3.47 mmol, 1.00 eq.) and dest. H_2O (1.80 mL, 100 mmol, 29.0 eq.) in THF (20 mL) was heated to reflux for 7 h. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (10 % ethyl acetate, 2% triethylamine in petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm). The product was obtained as a colourless oil (299 mg, 59% yield). Analytical data matches the literature.[18]

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm δ = 7.51 – 7.35 (m, 5H), 6.92 (d, *J* = 12.67 Hz, 1H), 6.19 (d, *J* = 12.67 Hz, 1H), 2.17 (s, 3H).

Synthesis of α,β-unsaturated amides

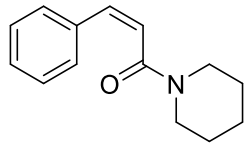
(*Z*)-*N*,*N*-Diethyl-3-phenylacrylamide (*Z*-21)



Propynoic amide **P-21** (63.0 mg, 0.31 mmol, 1.00 eq.) was dissolved in 1,4-dioxane (5 mL) and H_2O (5.60 µL, 0.31 mmol, 1.00 eq.) was added, followed by PBu_3 (78.0 µL, 0.31 mmol, 1.00 eq.). The solution was stirred at 70 °C for 4.5 h. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (40% v/v% ethyl acetate/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the product was isolated as colourless oil (35.0 mg, 55% yield, *E*/*Z* = 1 : 20).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.42 - 7.38 (m, 2H), 7.32 - 7.25 (m, 3H), 6.59 (d, *J* = 12.7 Hz, 1H), 6.06 (d, *J* = 12.7 Hz, 1H), 3.46 (q, *J* = 7.2 Hz, 2H), 3.25 (q, *J* = 7.1 Hz, 2H), 1.16 (t, *J* = 7.1 Hz, 2H), 0.95 (t, *J* = 7.1 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 168.2 (s), 135.5 (s), 132.7 (s), 128.4 (s), 128.4 (s), 123.8 (s), 42.6 (s), 38.9 (s), 13.9 (s), 12.4 (s). **IR** ($\tilde{\nu}$ in cm^{-1}): 1612 (s). **HR-MS** Calc. mass for $C_{13}H_{17}NO$: [M + H] = 203.1310, found: 203.1305.

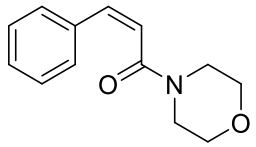
(*Z*)-3-Phenyl-1-(piperidin-1-yl)prop-2-en-1-one (*Z*-22)



Propynoic amide **P-22** (67.0 mg, 0.31 mmol, 1.00 eq.) was dissolved in 1,4-dioxane (5 mL) and H_2O (5.60 µL, 0.31 mmol, 1.00 eq.) was added, followed by PBu_3 (78.0 µL, 0.31 mmol, 1.00 eq.). The solution was stirred at 70 °C for 4.5 h. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (30% v/v% ethyl acetate/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the product was isolated as colourless oil (40.0 mg, 60% yield, *E*/*Z* = 1 : 16).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.41 - 7.29 (m, 5H), 6.65 (d, *J* = 12.6 Hz, 1H), 6.05 (d, *J* = 12.4 Hz, 1H), 3.62 (s, br, 2H), 3.31 (t, *J* = 5.5 Hz, 2H), 1.54 (t, *J* = 2.9 Hz, 4H), 1.18 (s, br, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ ppm 167.6 (s), 135.5 (s), 133.9 (s), 128.7 (s), 128.6 (s), 128.3 (s), 122.7 (s), 66.3 (s), 46.6 (s), 41.5 (s). **IR** ($\tilde{\nu}$ in cm^{-1}): 1609 (s). **HR-MS** Calc. mass for $C_{14}H_{17}NO$: [M + H] = 215.1310, found: 215.1300.

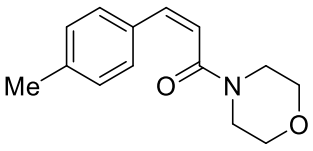
(*Z*)-1-Morpholino-3-phenylprop-2-en-1-one (*Z*-23)



Propynoic amide **P-23** (67.0 mg, 0.31 mmol, 1.00 eq.) was dissolved in 1,4-dioxane (5 mL) and H_2O (5.60 µL, 0.31 mmol, 1.00 eq.) was added, followed by PBu_3 (78.0 µL, 0.31 mmol, 1.00 eq.). The solution was stirred at 70 °C for 4.5 h. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (30% v/v% ethyl acetate/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the product was isolated as colourless oil (53.0 mg, 78% yield, *E*/*Z* = 1 : 20).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.38 - 7.30 (m, 5H), 6.73 (d, *J* = 12.8 Hz, 1H), 6.02 (d, *J* = 12.3 Hz, 1H), 3.68 - 3.59 (m, 4H), 3.32 - 3-18 (m, 4H).). **^{13}C NMR** (75 MHz, $CDCl_3$) δ ppm 167.5 (s), 135.4 (s), 133.9 (s), 128.7 (s), 128.6 (s), 128.3 (s), 122.7 (s), 66.24 (d, *J* = 3.6 Hz, 46.6 (s), 41.5 (s). **IR** ($\tilde{\nu}$ in cm^{-1}): 1611 (s), 1433 (vs). **HR-MS** Calc. mass for $C_{13}H_{15}NO_2$: [M + H] = 217.1103, found: 217.1097.

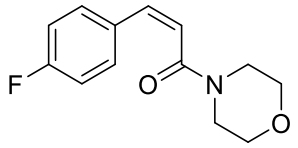
(*Z*)-1-Morpholino-3-(*p*-tolyl)prop-2-en-1-one (*Z*-24)



Propynoic amide **P-24** (50.0 mg, 0.22 mmol, 1.00 eq.) was dissolved in 1,4-dioxane (5 mL) and H_2O (4.00 µL, 0.22 mmol, 1.00 eq.) was added, followed by PBu_3 (54.0 µL, 0.22 mmol, 1.00 eq.). The solution was stirred at 70 °C for 3 h. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (40% v/v% ethyl acetate/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the product was isolated as colourless oil (17.0 mg, 34% yield, *E*/*Z* = 1 : 20).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.24 (d, *J* = 8.2 Hz, 2H), 6.67 (d, *J* = 7.9 Hz, 2H), 6.67 (d, *J* = 12.3 Hz, 2H), 5.95 (d, *J* = 12.6 Hz, 2H), 3.66 - 3.60 (m, 4H), 3.31 - 3.22 (m, 4H), 2.34 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 167.7 (s), 138.7 (s), 133.9 (s), 132.6 (s), 129.3 (s), 128.2 (s), 121.7 (s), 66.3 (s), 46.5 (s), 41.5 (s), 21.3 (s). **IR** ($\tilde{\nu}$ in cm^{-1}): 1612 (s). **HR-MS** Calc. mass for $C_{14}H_{17}NO_2$: [M + H] = 231.1259, found: 231.1257.

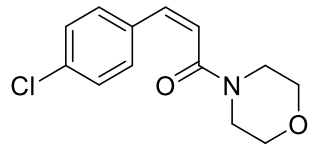
(*Z*)-3-(4-Fluorophenyl)-1-morpholinoprop-2-en-1-one (*Z*-25)



Propynoic amide **P-25** (50.0 mg, 0.21 mmol, 1.00 eq.) was dissolved in 1,4-dioxane (5 mL) and H_2O (3.90 µL, 0.21 mmol, 1.00 eq.) was added, followed by PBu_3 (52.0 µL, 0.21 mmol, 1.00 eq.). The solution was stirred at 70 °C for 5 h 20 min. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (40% v/v% ethyl acetate/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the product was isolated as colourless oil (12.0 mg, 24% yield, *E*/*Z* = 1 : 12).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.28 - 7.33 (m, 2H), 7.06 - 7.00 (m, 2H), 6.66 (d, *J* = 12.3 Hz, 1H), 6.00 (d, *J* = 12.6 Hz, 1H), 3.67 - 3.60 (m, 4H), 3.34 - 3.27 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 167.3 (s), 132.8 (s), 131.6 (s), 131.5 (s), 130.2 (s), 122.5 (s), 115.8 (s), 115.5 (s), 66.4 (d, *J* = 5.0 Hz), 46.6 (s), 41.5 (s). **IR** ($\tilde{\nu}$ in cm^{-1}): 1620 (s). **HR-MS** Calc. mass for $C_{13}H_{14}NO_2F$: [M + H] = 235.1009, found: 235.1003.

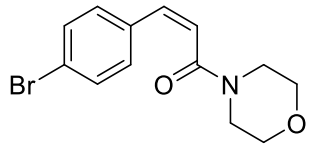
(*Z*)-3-(4-Chlorophenyl)-1-morpholinoprop-2-en-1-one (*Z*-26)



Propynoic amide **P-26** (50.0 mg, 0.20 mmol, 1.00 eq.) was dissolved in 1,4-dioxane (5 mL) and H_2O (3.60 µL, 0.20 mmol, 1.00 eq.) was added, followed by PBu_3 (50.0 µL, 0.20 mmol, 1.00 eq.). The solution was stirred at 70 °C for 4 h. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (20 - 50% v/v% ethyl acetate/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the product was isolated as colourless oil (35.0 mg, 69% yield, *E*/*Z* = 1 : 17.5).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.31 (s, 4H), 6.65 (d, *J* = 12.5 Hz, 1H), 6.04 (d, *J* = 12.6 Hz, 1H), 3.68 - 3.60 (m, 4H), 3.31 (s, br, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ ppm 167.1 (s), 134.5 (s), 133.8 (s), 132.7 (s), 129.6 (s), 128.8 (s), 123.2 (s), 66.4 (s), 66.3 (s), 46.5 (s), 41.5 (s). **IR** ($\tilde{\nu}$ in cm^{-1}): 1616 (s). **HR-MS** Calc. mass for $C_{13}H_{14}NO_2Cl$: [M + H] = 251.0713, found: 251.0708.

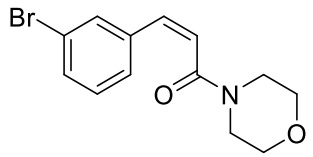
(*Z*)-3-(4-Bromophenyl)-1-morpholinoprop-2-en-1-one (*Z*-27)



Propynoic amide **P-27** (50.0 mg, 0.17 mmol, 1.00 eq.) was dissolved in 1,4-dioxane (5 mL) and H_2O (3.10 µL, 0.17 mmol, 1.00 eq.) was added, followed by PBu_3 (42.0 µL, 0.17 mmol, 1.00 eq.). The solution was stirred at 70 °C for 5 h 20 min. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (20 - 50% v/v% ethyl acetate/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the product was isolated as colourless oil (24.0 mg, 48% yield, *E*/*Z* = 1 : 24).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.50 - 7.46 (m, 2H), 7.26 - 7.24 (m, 2H), 6.64 (d, *J* = 12.6 Hz, 1H), 6.06 (d, *J* = 12.6 Hz, 1H), 3.68 - 3.62 (m, 4H), 3.33 (s, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 167.1 (s), 134.2 (s), 132.7 (s), 131.8 (s), 129.8 (s), 123.3 (s), 122.8 (s), 66.4 (s), 66.3 (s), 46.5 (s), 41.5 (s). **IR** ($\tilde{\nu}$ in cm^{-1}): 1616 (s). **HR-MS** Calc. mass for $C_{13}H_{14}NO_2Br$: [M + H] = 295.0208, found: 295.0201.

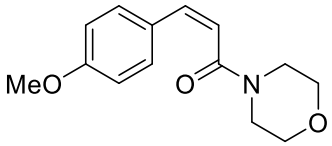
(*Z*)-3-(3-Bromophenyl)-1-morpholinoprop-2-en-1-one (*Z*-28)



Propynoic amide **P-28** (50.0 mg, 0.17 mmol, 1.00 eq.) was dissolved in 1,4-dioxane (5 mL) and H_2O (3.10 µL, 0.17 mmol, 1.00 eq.) was added, followed by PBu_3 (42.0 µL, 0.17 mmol, 1.00 eq.). The solution was stirred at 70 °C for 5 h 20 min. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (20 - 50% v/v% ethyl acetate/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the product was isolated as colourless oil (19.0 mg, 38% yield, *E*/*Z* = 1 : 4.8).

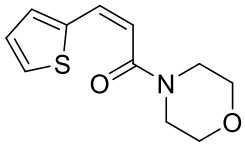
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.52 (s, 1H), 7.44 (d, *J* = 7.9 Hz, 1H), 7.31 - 7.27 (m, 1H), 7.24 - 7.20 (m, 1H), 6.63 (d, *J* = 12.6 Hz, 1H), 6.07 (d, *J* = 12.6 Hz, 1H), 3.67 - 3.64 (m, 4H), 3.32 - 3.24 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 166.9 (s), 137.4 (s), 132.2 (s), 131.6 (s), 131.2 (s), 130.2 (s), 126.9 (s), 124.1 (s), 122.7 (s), 66.4 (s), 66.3 (s), 46.6 (s), 41.5 (s). **IR** ($\tilde{\nu}$ in cm^{-1}): 1612 (s). **HR-MS** Calc. mass for $C_{13}H_{14}NO_2Br$: [M + H] = 295.0208, found: 295.0201.

(*Z*)-3-(4-Methoxyphenyl)-1-morpholinoprop-2-en-1-one (*Z*-29)



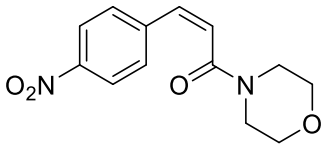
Propynoic amide **P-29** (50.0 mg, 0.20 mmol, 1.00 eq.) was dissolved in 1,4-dioxane (5 mL) and H_2O (3.70 µL, 0.20 mmol, 1.00 eq.) was added, followed by PBu_3 (51.0 µL, 0.20 mmol, 1.00 eq.). The solution was stirred at 70 °C for 6 h. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (40% v/v% ethyl acetate/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the product was isolated as colourless oil (15.0 mg, 30% yield, *E*/*Z* = 1 : 10).
^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.33 - 7.28 (m, 2H), 6.88 - 6.83 (m, 2H), 6.64 (d, *J* = 12.4 Hz, 1H), 5.90 (d, *J* = 12.4 Hz, 1H), 3.81 (s, 3H), 3.69 - 3.60 (m, 4H), 3.36 - 3.26 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ ppm 167.9 (s), 159.8 (s), 133.5 (s), 129.8 (s), 128.0 (s), 120.5 (s), 113.9 (s), 66.4 (s), 55.2 (s), 46.5 (s), 41.5 (s). **IR** ($\tilde{\nu}$ in cm^{-1}): 1605 (s). **HR-MS** Calc. mass for $C_{14}H_{17}NO_3$: [M + H] = 247.1208, found: 247.1201.

(*Z*)-1-Morpholino-3-(thiophen-2-yl)prop-2-en-1-one (*Z*-31)



Propynoic amide **P-31** (50.0 mg, 0.23 mmol, 1.00 eq.) was dissolved in 1,4-dioxane (5 mL) and H_2O (4.10 µL, 0.23 mmol, 1.00 eq.) was added, followed by PBu_3 (56.0 µL, 0.23 mmol, 1.00 eq.). The solution was stirred at 70 °C for 5 h 20 min. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (30% v/v% ethyl acetate/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the product was isolated as colourless oil (45.0 mg, 90% yield, *E*/*Z* = 1 : 48).
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.34 (d, *J* = 5.0 Hz, 1H), 7.15 (d, *J* = 3.5 Hz, 1H), 7.00 (dd, *J* = 5.1 Hz, *J* = 3.7 Hz, 1H), 6.82 (d, *J* = 12.6 Hz, 1H), 5.92 (d, *J* = 12.3 Hz, 1H), 3.72 (s, 4H), 3.55 - 3.51 (m, 4H).). **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 166.7 (s), 137.9 (s), 130.4 (s), 128.3 (s), 128.0 (s), 127.0 (s), 118.7 (s), 66.6 (s), 66.5 (s), 46.5 (s), 41.7 (s). **IR** ($\tilde{\nu}$ in cm^{-1}): 1608 (s). **HR-MS** Calc. mass for $C_{11}H_{13}NO_2S$: [M + H] = 223.0667, found: 223.0662.

(*Z*)-1-Morpholino-3-(4-nitrophenyl)prop-2-en-1-one (*Z*-32)



Propynoic amide **P-32** (50.0 mg, 0.19 mmol, 1.00 eq.) was dissolved in 1,4-dioxane (5 mL) and H_2O (3.50 µL, 0.19 mmol, 1.00 eq.) was added, followed by PBu_3 (48.0 µL, 0.19 mmol, 1.00 eq.). The solution was stirred at 70 °C for 40 min. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (50 - 70% v/v% ethyl acetate/petrol ether, silica gel: 60M, pore size 0.04 – 0.063 mm) and the product was isolated as colourless solid, mp = 100.8 °C, (22.0 mg, 44% yield, *E*/*Z* = 1 : 1.8).
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.22 - 8.19 (m, 2H), 7.58 - 7.55 (m, 2H), 6.77 (d, *J* = 12.6 Hz, 1H), 6.27 (d, *J* = 12.6 Hz, 1H), 3.70 - 3.64 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm 166.2 (s), 147.4 (s), 141.6 (s), 131.9 (s), 129.1 (s), 126.4 (s), 123.8 (s), 66.5 (s), 46.5 (s), 41.6 (s). **IR** ($\tilde{\nu}$ in cm^{-1}): 1643 (s). **HR-MS** Calc. mass for $C_{13}H_{14}N_2O_2$: [M + H] = 262.0954, found: 262.0947.

Computational details

Possible reaction mechanisms for the highly *Z*-selective reduction of **P-3** (Table 1 and Scheme 5) have been investigated by means of density functional theory (DFT) and coupled-cluster calculations. Relevant transition states (TSs) and intrinsic reaction coordinates (IRCs) – connecting the respective stationary points (SPs) along the 3*N*-6 dimensional mass-weighted coordinate space – could be obtained for path A (Scheme 5), allowing a comprehensive analysis of the associated barrier heights. Similarly, barrier heights and associated SPs could be calculated for key steps of path B, allowing a comparison of both paths.

All quantum chemical calculations have been performed using ORCA 4.2.0.[19]
Optimizations of stationary points (SPs, minima and first-order TSs) were carried out at the DFT level of theory. The nature of the obtained SPs was verified by subsequent vibrational analysis. Initial guesses for the TS optimizations were generated with pysisyphus.[20]
DFT calculations were conducted using the ωB97X-D3 exchange-correlation functional and the double-ζ basis set def2-SVP.[21] The utilized long-range corrected hybrid functional, i.e. ωB97X-D3, includes a dispersion correction, for an improved description of noncovalent interactions.[22] It was found to be accurate for a wide range of applications, e.g., thermochemistry and kinetics.[21d, 23] Hilton et al. successfully employed the predecessor functional ωB97X-D to unravel the mechanism of a C-C coupling reaction involving phosphorous species,[24] similar to the present reaction under investigation involving tributylphosphine. Solvent effects (1,4-dioxane, ε = 2.21, n = 1.33) were taken into account by the SMD model at the DFT level of theory.[25] Neutral charge and singlet multiplicity were assumed throughout.
Subsequently, improved single point energies (for the previously fully optimized SPs) were obtained from the domain based local pair natural orbital (DLPNO) coupled-cluster method with single and double excitations as well as perturbative triple excitations (CCSD(T)) and the quadruple- ζ basis set def2-QZVPP.[26] The corresponding auxiliary basis def2-QZVPP/C was used for density fitting[27] in the coupled-cluster calculations. Tight convergence criteria were enforced in the preceding Hartree-Fock calculations (keyword *tightscf*). Several benchmark studies showed that DLPNO-CCSD(T) is able to attain results within chemical accuracy, that is errors below 1 kcal/mol.[28]
Final solution-phase Gibbs free energies G_{sol} have been obtained as sum of coupled-cluster single point energies, as well as thermochemical and solvent corrections calculated at the DFT level of theory.[29]

$$G_{\mathrm{sol}} = E_{\mathrm{DLPNO-CCSD(T)}} + \Delta G_{\mathrm{DFT}} + \Delta G_{\mathrm{solv,DFT}} \quad (1)$$

$$\Delta G_{\mathrm{solv,DFT}} = E_{\mathrm{SMD,DFT}} - E_{\mathrm{gas,DFT}} \quad (2)$$

Barrier heights between educts (products) and the associated TS have been calculated as difference between G_{sol} of the TS ($G_{\mathrm{sol,TS}}$) and the sum of G_{sol} of the respective educts (products).

$$\Delta G_{\mathrm{sol}} = G_{\mathrm{sol,TS}} - \sum G_{\mathrm{sol},speciesi} \quad (3)$$

This way the correct number of terms is taken into account when calculating ΔG_{sol}, e.g., for the translational entropy.[29]

Molecular images were created using UCSF Chimera.[30] Carbon, hydrogen, oxygen and phosphorous atoms are shown in grey, white, red and orange, respectively.

Mechanistic investigation of path A

In the following, the distinct stages of the highly *Z*-selective reduction of methyl 3-phenylpropiolate **P-3** (Table 1) as proposed in path A of Scheme 5 are discussed.

Nucleophilic addition of PBu_3

The first step of all paths, *i.e.* paths A-C in Scheme 5, involves a nucleophilic addition of the phosphine to the alkyne, which may either yield intermediate **i** with *Z* (***Z*-i**) or *E* (***E*-i**) configuration. Formation of ***E*-i** is slightly favored over ***Z*-i**, with a barrier height of 93.4 kJ mol^{-1} compared to 106.5 kJ mol^{-1} for ***Z*-i**. Both reactions are endergonic, as translational entropy is lost in additions,[29] while ***E*-i** is 6.4 kJ mol^{-1} more stable, compared to ***Z*-i**.

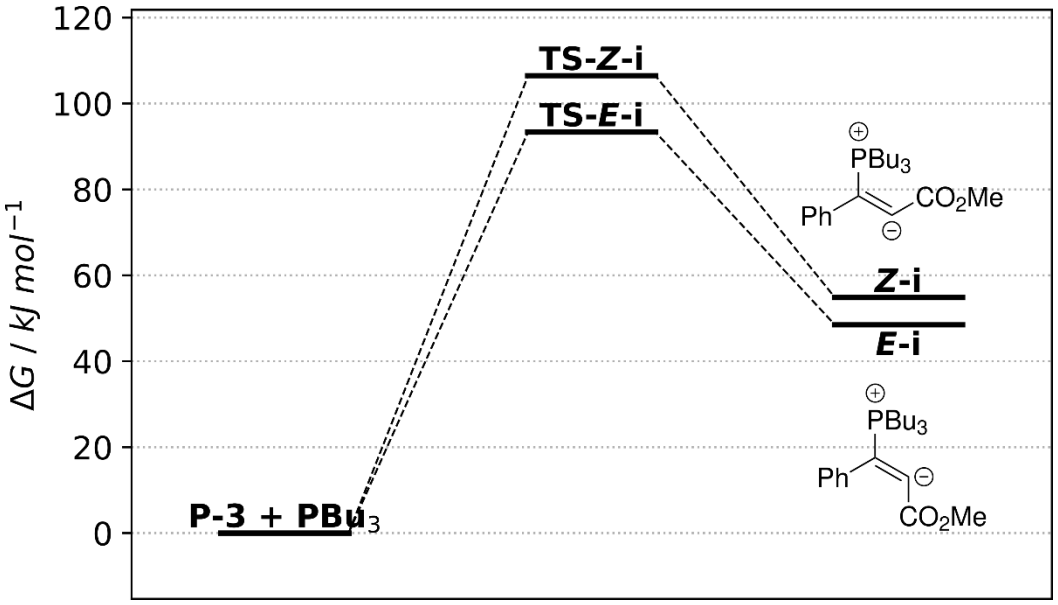


*Figure S1: Energy scheme for the nucleophilic addition of PBu_3 to **P-3**.*

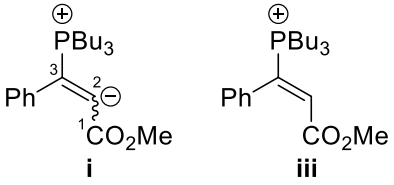


*Figure S2: Addition product **i** with enumerated carbons and postulated protonated intermediate **iii** with prochiral C2 and C3 alkene carbons.*

Water addition to C2

Products ***E*-i** and ***Z*-i** or their enolates can deprotonate sufficiently acidic protic additives, such as water, producing postulated intermediate **iii**, which can subsequently add hydroxide at C2. As the alkene carbons C2 and C3 of **iii** are prochiral, different enantiomers result from water addition to C2.

The calculations indicate that protonation of **i** at C2 by water is immediately followed by addition of the remaining hydroxide ion to the same carbon atom, yielding a phosphonium ylide **vii**. Energy profiles for the water addition reactions starting from ***E*-i** and ***Z*-i** are illustrated in Figure S3 and Figure S4. In each case, water attack from above and below the plane containing the phosphorous atom and the

alkene carbons was considered, resulting in different absolute configuration on C2 after addition of H^+ and OH^- in ***S*-vii** and ***R*-vii**.

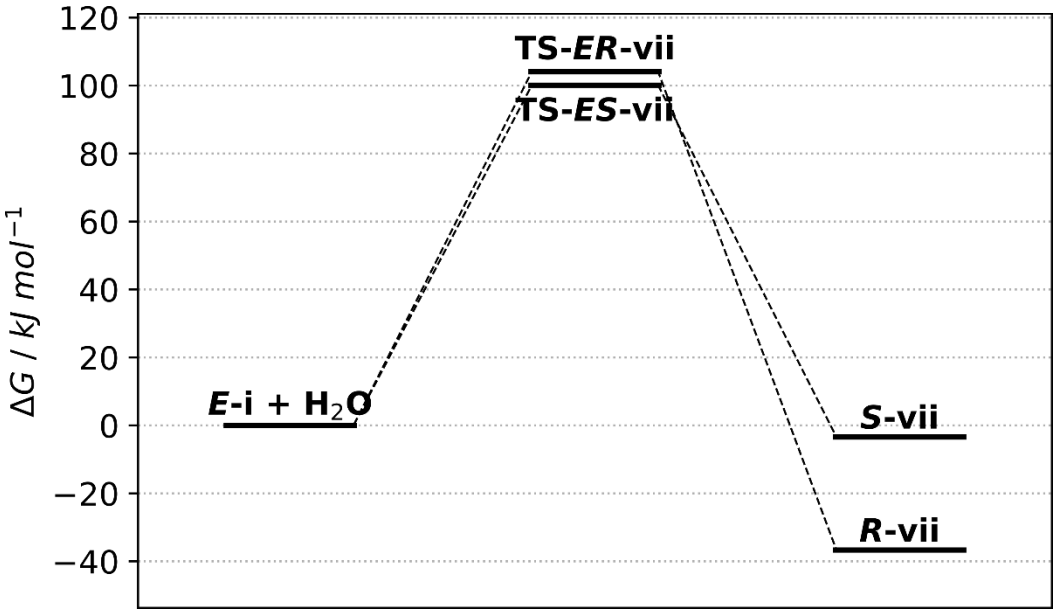


*Figure S3: Energy scheme for the water addition to **E-i**, yielding **S-vii** and **R-vii**.*

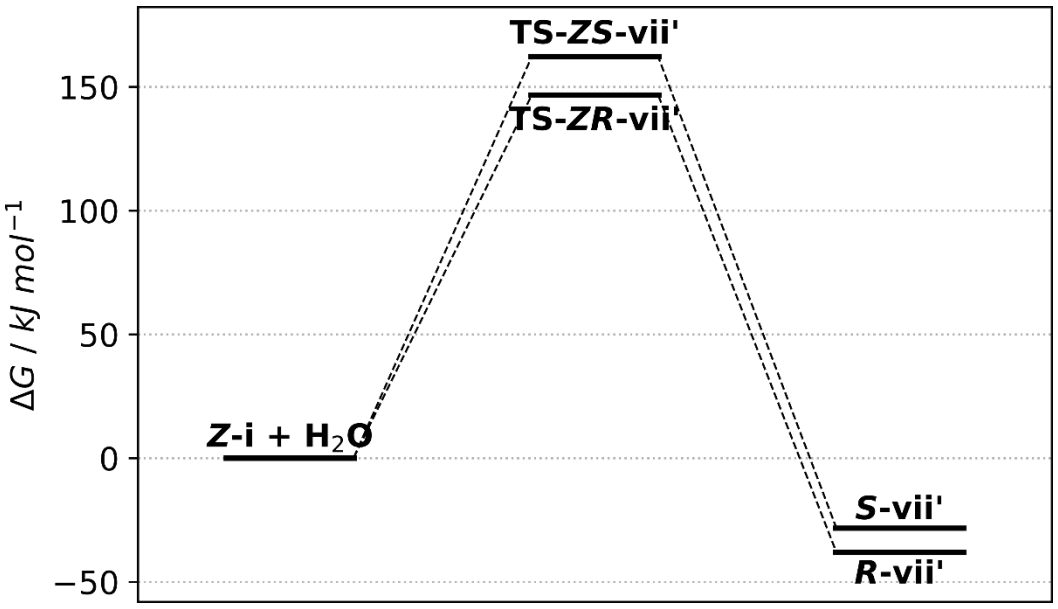


*Figure S4: Energy scheme for the water addition to **Z-i**, yielding **S-vii'** and **R-vii'.***

The calculated barriers for water addition to ***E*-i** are 100.1 kJ mol^{-1} for the reaction yielding phosphonium ylide ***S*-vii** and 104.5 kJ mol^{-1} for the reaction yielding ***R*-vii**. Formation of ***S*-vii** is only slightly exergonic (ΔG = -3.4 kJ mol^{-1}), whereas formation of ***R*-vii** is much more exergonic (ΔG = -36.7 kJ mol^{-1}) compared to the educts.

In comparison to ***E*-i**, much higher barriers must be overcome for the water addition to ***Z*-i**: Formation of ***S*-vii** has an activation energy of 163.6 kJ mol^{-1}, while forming ***R*-vii** requires a slightly lower activation energy of 146.8 kJ mol^{-1}. Again, the reaction is exergonic in both cases.

***R*-vii'** and ***R*-vii** obtained from ***Z*-i** and ***E*-i** represent the same compound, but in different conformations, mainly differing in the distortion around the central C2-C3 bond. An overlay of both conformers is shown in Figure S5.

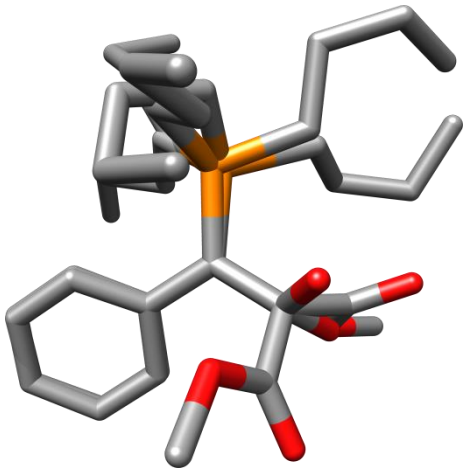
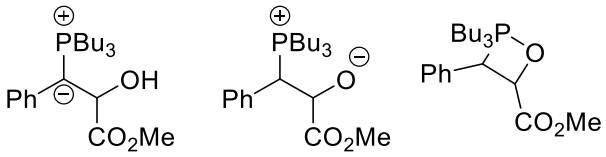


*Figure S5: Overlay of conformers **R-vii** and **R-vii'**, resulting from water addition to **E-i** and **Z-i**. Hydrogens are omitted for clarity.*



vii **viii** **ix**

*Figure S6: Water addition product, phosphonium ylide **vii**. Hydrogen transfer product, betaine **vii** and oxaphosphetane **ix**. Stereochemical assignments are omitted.*

Proton transfer onto C3 and ring formation

Proton transfer from the C2-hydroxide onto C3 in phosphonium ylide **vii** yields the intermediate betaine **viii**, which subsequently undergoes a ring closure, forming oxaphosphetane **ix**. Preliminary calculations revealed very high barriers for a purely intra-molecular proton transfer; considering an additional water molecule assisting in the proton transfer yields much lower activation energies.

Figure S7 and Figure S8 highlight the energies profiles for the water mediated proton transfer reaction, starting from the ***S*-vii'**, ***R*-vii'**, ***S*-vii** and ***R*-vii** conformers obtained from the water additions.

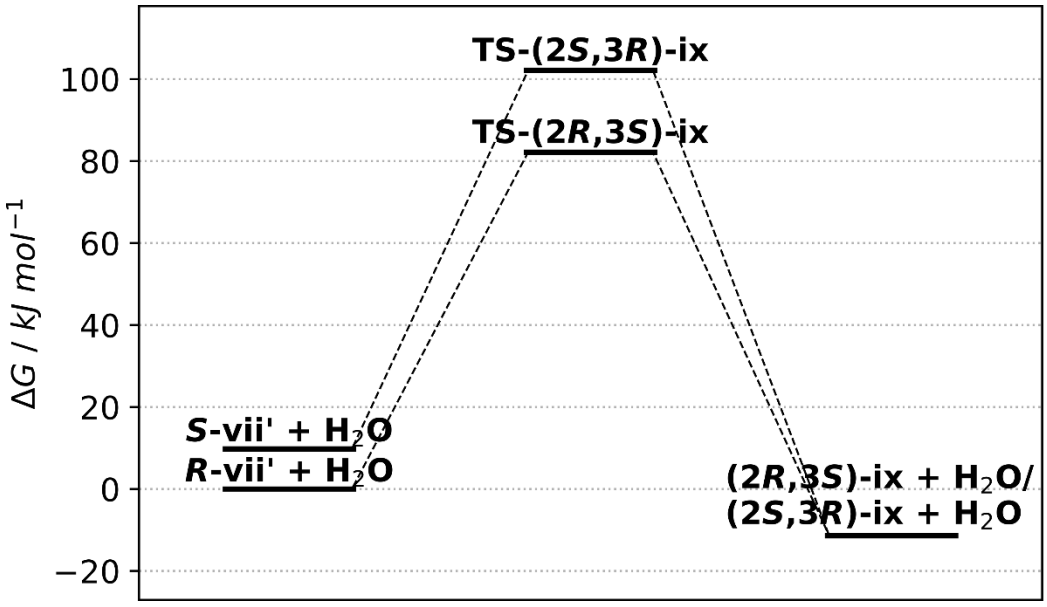


*Figure S7: Water assisted proton transfer from C2-hydroxide onto C3 starting from **S-vii'** and **R-vii'**, yielding oxaphosphetane enantiomers **(2S,3R)-ix** and **(2R,3S)-ix**. Both oxaphosphetanes ultimately fragment into **Z-3** and the phosphine oxide Bu_3PO.*

Similar barrier heights of 82.2 kJ mol^{-1} and 92.4 kJ mol^{-1} are obtained for the water assisted proton transfer starting from ***S*-vii'** and ***R*-vii'**. IRC integration confirms that **TS-(*S*2,*3*R)-ix** directly relaxes into the ring-closed oxaphosphetane **(2*S*,*3*R)-ix**, whereas the ring closure is not fully performed for **TS-(2*R*,*3S*)-ix**, yet it can be assumed that it is only hindered by a negligible barrier. In both cases, the reaction is slightly exergonic and the obtained oxaphosphetanes can ultimately fragment, yielding ***Z*-3** and the phosphine oxide Bu_3PO.

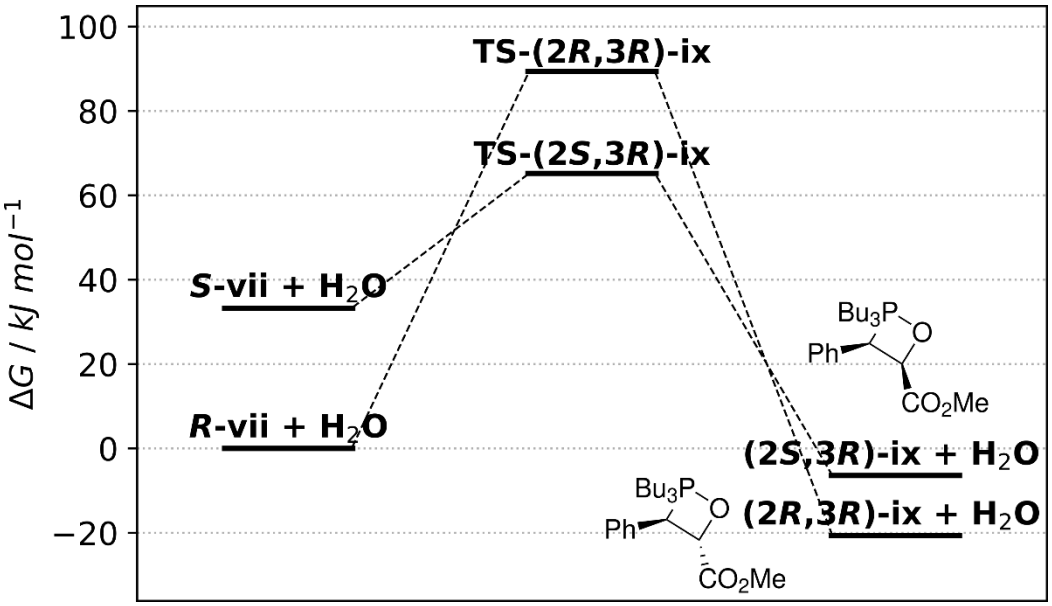


*Figure S8: Water assisted proton transfer from C2-hydroxide onto C3 starting from **S-vii'** and **R-vii'**, yielding oxaphosphetanes **(2S,3R)-ix** and **(2R,3R)-ix**. Whereas **(2S,3R)-ix** fragments into **Z-3** and phosphine oxide Bu_3PO, **(2R,3R)-ix** ultimately yields the corresponding E-alkene **E-3** and Bu_3PO.*

Starting from ***R*-vii** the water assisted proton transfer requires an activation energy of 89.4 kJ mol^{-1}, similar to ***S*-vii'** and ***R*-vii**'. The resulting oxaphosphetane **(2*R*,3*R*)-ix** ultimately fragments into the *E*-alkene ***E*-3** and Bu_3PO. In contrast to ***R*-vii**, a much lower action energy of only 31.9 kJ mol^{-1} is required for the proton transfer when starting from ***S*-vii**. The small barrier is a result of two factors: A stabilized TS and energetically destabilized educts. The educt destabilization may be partially explained by a missing hydrogen bond interaction in the ***S*-vii** + H_2O system, compared to ***R*-vii** + H_2O, see Figure S9. Absence of the hydrogen bond should also facilitate the proton abstraction from the C2-hydroxide, leading to a stabilized TS. The oxaphosphetane **(2*S*,3*R*)-ix** resulting from the proton transfer in ***S*-vii**' can fragment into ***Z*-3** and Bu_3PO.

Overall, the obtained quantum chemical results for the water assisted proton transfer are in line with the experimental findings – yielding primarily formation of ***Z*-3**.

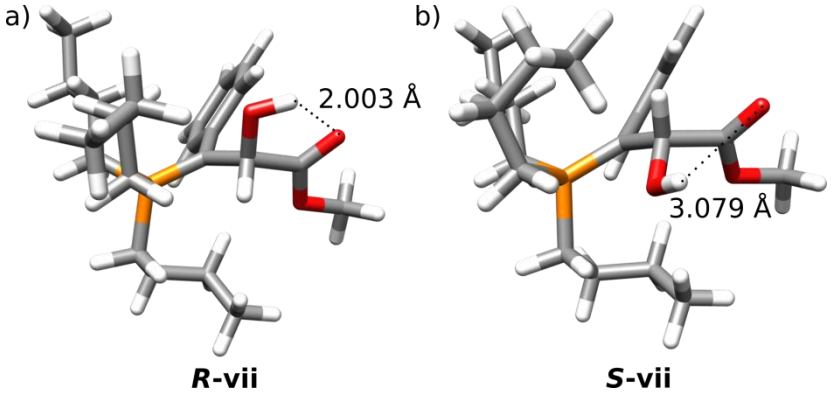


*Figure S9: Presence of a hydrogen bond interaction in a) **R-vii** and b) absence of it in **S-vii**, leading to a destabilization of **S-vii** compared to **R-vii**.*

Elimination of phosphine oxide

Oxaphosphetane **ix** readily fragments into phosphine oxide Bu_3PO and the respective alkene, requiring only a small activation energy (Figure S10). Fragmentation of **(2*S*,3*R*)-ix**, yielding ***Z*-3**, requires merely 23.7 kJ mol^{-1} and is strongly exothermic (-193.1 kJ mol^{-1}). Fragmentation of **(2*R*,3*R*)-ix**, yielding ***E*-3**, requires 28.0 kJ mol^{-1} and is also strongly exothermic (-226.1 kJ mol^{-1}). The *E*-alkene ***E*-3** is predicted to be 26 kJ mol^{-1} more stable compared to ***Z*-3**, explaining the subsequent isomerization of ***Z*-3** to ***E*-3**.

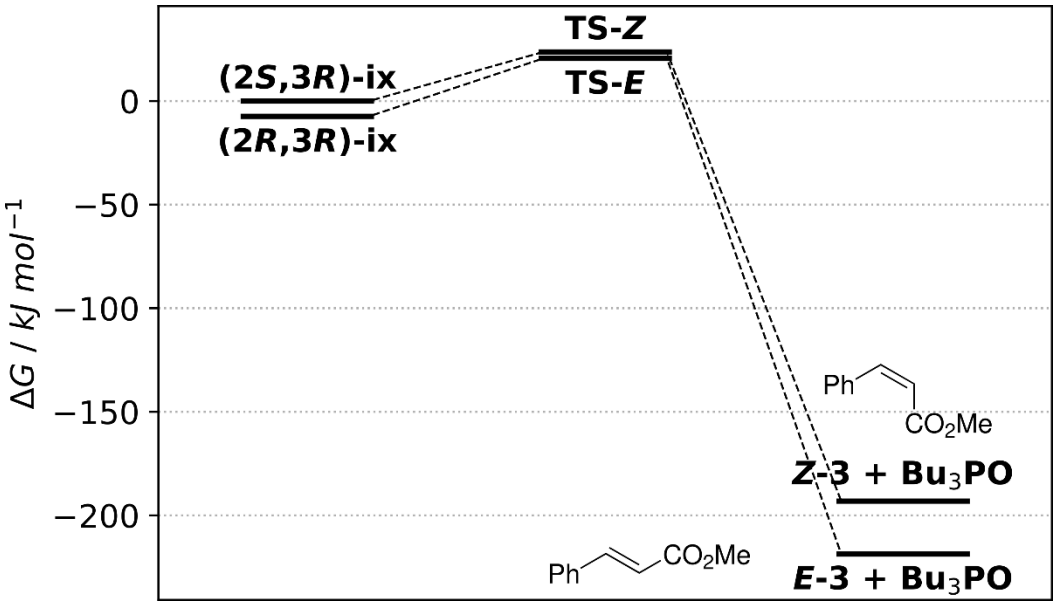


*Figure S10: Energy scheme for the fragmentation reactions of oxaphosphetanes **(2S,3R)-ix** and **(2R,3R)-ix** to phosphine oxide Bu_3PO and the alkenes **Z-3** and **E-3.***

Energies for full pathways yielding ***Z*-3** and ***E*-3** are illustrated in Figure S11 and Figure S12.

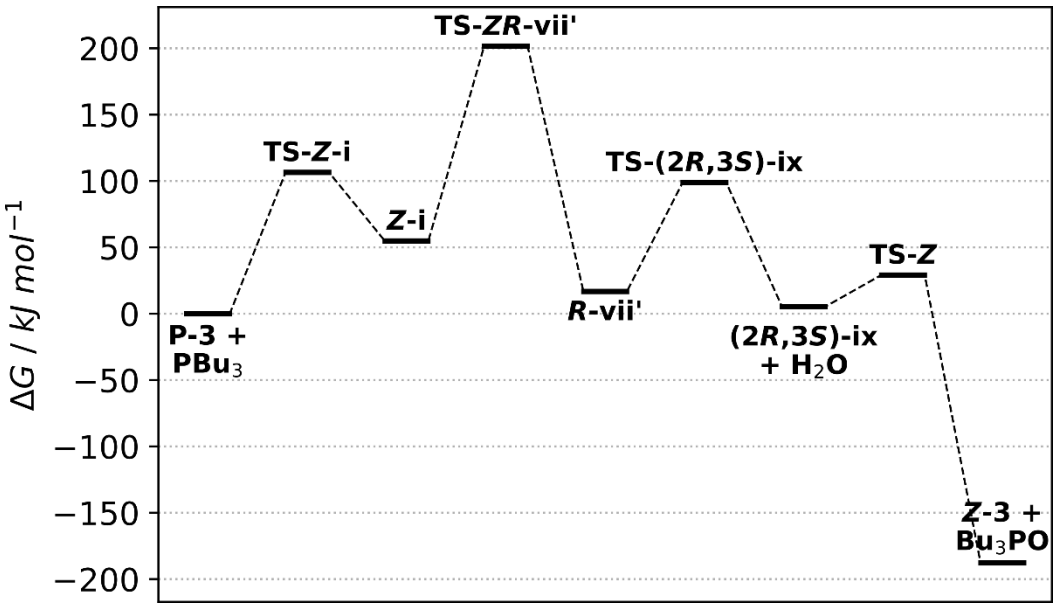


*Figure S11: Energy scheme for a pathway yielding **Z-3**.*

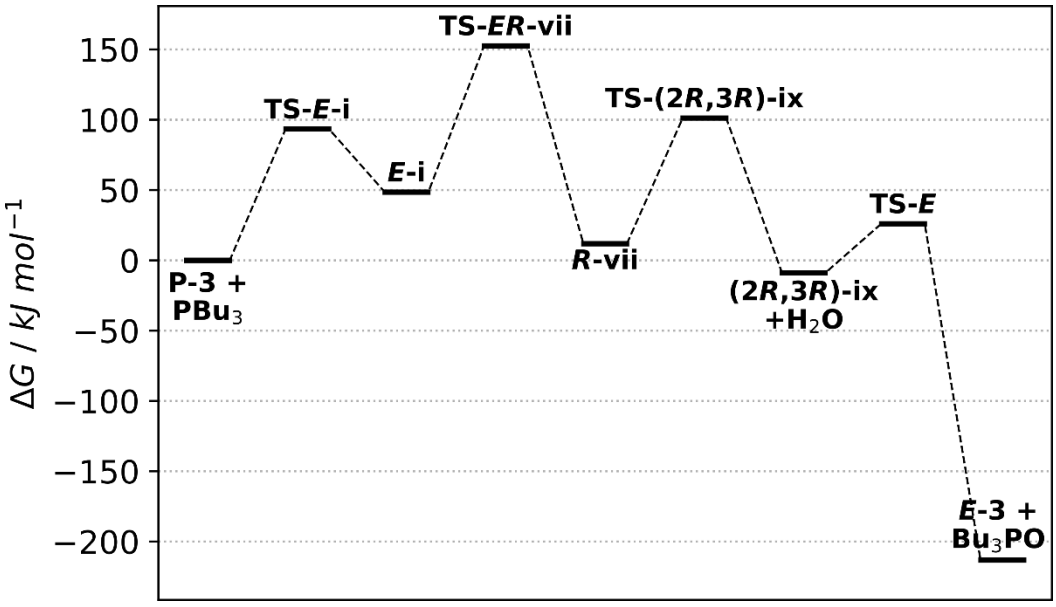


*Figure S12: Energy scheme for a pathway yielding **E-3**.*

Conclusion

In summary, path A, as proposed in Scheme 5 in the manuscript, was investigated using quantum chemical simulation, i.e., at the DLNPO coupled-cluster//DFT level of theory. Prominent (stationary) points on the reactants PES were identified, allowing a detailed assessment of the underlying reaction mechanism based on the reactant's thermodynamic properties, such as driving forces and associated barrier heights.

Starting from PBu_3 and **P-3**, zwitterions ***E*-i** and ***Z*-i** are formed, requiring an activation energy of about 100 kJ mol^{-1}, with the formation of ***E*-i** being slightly favored. The reaction proceeds with addition of a proton (provided via an adjacent water molecule) to the C2, immediately followed by addition of the remaining hydroxide anion to the same carbon. Water addition to ***Z*-i** requires much higher activation energies (163.6 and 146.8 kJ mol^{-1}) compared to ***E*-i** (100.1 and 104.5 kJ mol^{-1}). Subsequently, water assisted proton transfer onto C3 is predicted, which requires activation energies between 82.4 and 92.4 kJ mol^{-1} for ***S*-vii**, ***S*-vii'** and ***R*-vii'**. In particular, the proton transfer reaction for ***R*-vii** features a low barrier of 31.9 kJ mol^{-1}, ultimately facilitating the efficient formation of ***Z*-3**. Finally, the oxaphosphetanes fragment readily in the respective alkene and Bu_3PO.

Overall, water addition to the zwitterion appears to be the rate-limiting step in path A. The presented calculations are in line with the experimental finding, that the reduction of **P-3** using tributylphosphine is highly *Z*-selective, as three of four investigated pathways yield ***Z*-3**.

Mechanistic investigation of path B

Water addition to C2 was found to be the rate-limiting step in path A, with activation energies ranging between 100.1 kJ mol^{-1} for ***E*-i** and up to 163.6 kJ mol^{-1} for ***Z*-i**. Another possible route to the main product ***Z*-3** is given by path B.

There, following protonation of C2, addition of the remaining OH^- anion to phosphorous is considered. The OH^- anion is subsequently deprotonated by a base, leading to a fragmentation of the P-C3 bond

and formation of Bu_3PO, as well as a vinyl anion (**vi**). The key intermediates of path B are shown in Figure S13

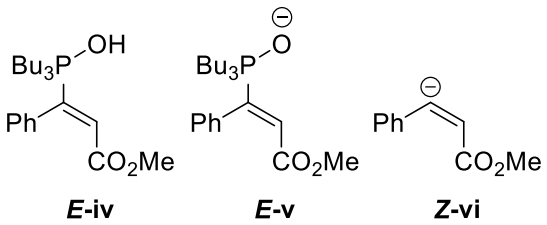


Figure S13: Key intermediates of path B.

Water addition to C2 and P

Protonation of C2 and subsequent addition of OH^- to the phosphorous was investigated for ***E*-i**, as this substrate affords the main product ***Z*-3**. An energy scheme for the reaction is shown in Figure S14. The corresponding TS is displayed in

Figure S15. In contrast to the high activation energies for the water addition to C2 (> 100 kJ mol^{-1}), protonation of C2 and OH^- addition to P has a much lower activation energy of only 61.7 kJ mol^{-1}. The C2-P bond length increases from 1.784 Å at ***E*-i**, to 1.848 Å at **TS-*E*-iv** up to 1.895 Å at the addition product ***E*-iv**, facilitating subsequent fragmentation of the C2-P bond.

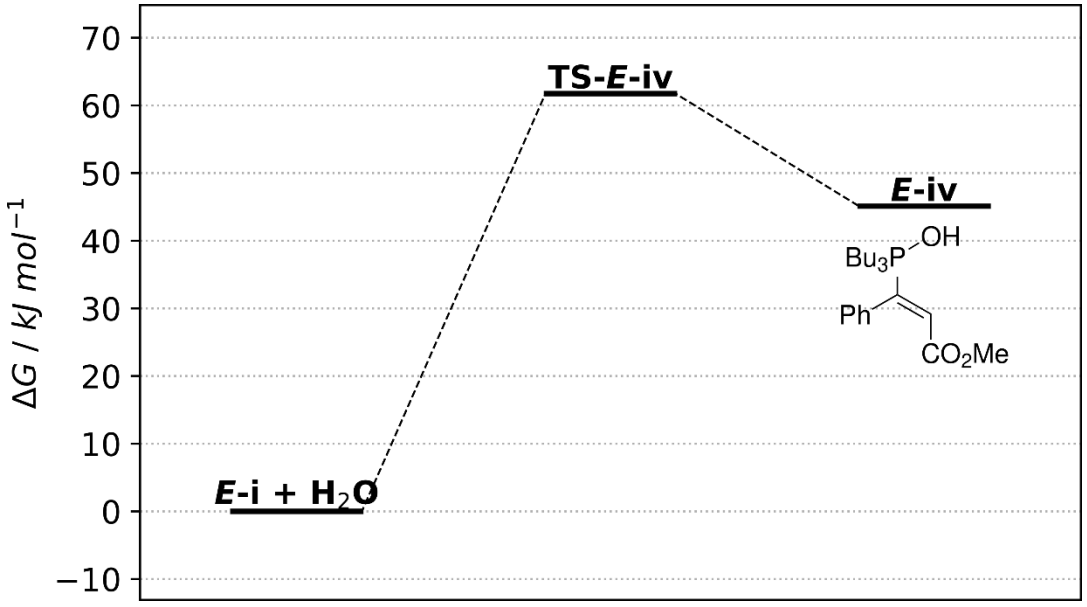
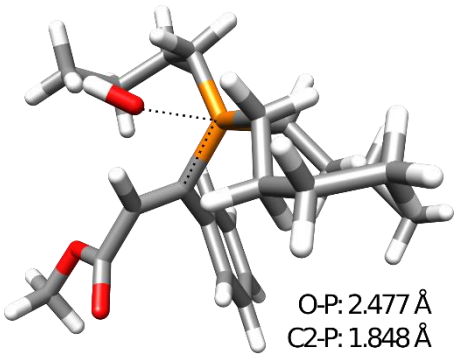


*Figure S14: Energy scheme for protonation of C2 in **E-I** and subsequent addition of OH^- to the phosphorous.*



TS-*E*-iv

*Figure S15: Optimized geometry of **TS-E-iv** and selected bond lengths.*

Deprotonation and Fragmentation of iv

The C2-P distance is further increased from 1.895 Å to 2.234 Å in the deprotonation product of ***E*-iv**, ***E*-v**. Whereas the Mayer bond-order obtained at the DFT level of theory is 1.05 in the zwitterion ***E*-I**, typical for a regular single bond, it is only 0.51 in ***E*-v**, indicating only loosely coupled Bu_3PO and vinyl anion fragments.[31] Because of the low C2-P bond order, the final fragmentation is expected to be barrierless or to exhibit only a very small energetic barrier.

Protonation of the vinyl anion ***Z*-vi**, affording the main product ***Z*-3**, should not be the rate-limiting step in path B and was not further investigated here.

Conclusion

The low activation energy of only 61.7 kJ mol^{-1} for the protonation of C2 and OH^- addition to P in ***E*-i** make it the preferred pathway for water addition to ***E*-I**, compared to water addition exclusively to C2. The stretched C2-P bond in ***E*-iv** facilitates the subsequent fragmentation of ***E*-iv** into Bu_3PO and the vinyl anion ***Z*-vi**, which readily happens upon deprotonation of ***E*-iv**.

Optimized geometries in XYZ format

Obtained at the DFT ωB97X-D3/def2-SVP level of theory using ORCA 4.2.0.

P-3

20

H	-0.19596844870889	2.62283410735723	2.34062069962454
C	-0.45381404785945	1.57827134460154	2.15289959249009
C	-1.78136592479097	1.19199187154303	1.99955806279923
H	-2.57478426476510	1.94020352227147	2.06662293181474
C	-2.09858157537164	-0.14510937314321	1.76129936156050
C	-1.08502055577826	-1.09962335907098	1.67755803396586
H	-1.33286674180051	-2.14712987222242	1.49045023470979
C	0.24503201557938	-0.72158797029932	1.83014364257013
H	1.04516937895697	-1.46219398526469	1.76573858660281
C	0.57070490704426	0.62265556699871	2.06842364397311
C	1.94224222395850	1.02089576030776	2.22274903765110
C	3.09859287285207	1.35697230219573	2.35217873891591
C	4.46650524792383	1.82660853448039	2.50908246808543
O	5.33603839032716	0.81575687547696	2.44304618519087
O	4.77613962993760	2.97581225784585	2.67814782792939
C	6.70415668940144	1.16995022731695	2.58763841437013
H	7.27095083688772	0.23644096050386	2.50278927860264
H	6.88414786832027	1.63758983348353	3.56645519128527
H	7.01082269342730	1.87521564285529	1.80174333185945
H	-3.14232119554168	-0.44539424723767	1.64057473599901

PBu_3

40

P	1.07023692101671	0.40773531474547	0.67302069304779
C	1.83627091994012	-0.85182462241019	1.81118525340853
H	2.13089500653946	-0.27731349852953	2.70637105388311
C	1.06487163144689	-2.10988233595566	2.21010020421408
C	1.90353239656456	-3.13509052434790	2.98038030685890
C	2.41597327278973	-2.64465144524327	4.33177441602562
H	1.58474085797732	-2.31146504580079	4.97464224568749
H	2.95109579794971	-3.44285120694192	4.86835578737364
H	3.11299593311926	-1.79877944633952	4.22666077754184
H	1.29525006450934	-4.04296906002687	3.13226391524159
H	2.75773898804009	-3.44794158858291	2.35339858051701

H	0.19149490800917	-1.82961766264322	2.82471885565066
H	0.65810816937740	-2.59793513059549	1.30825353895255
H	2.79180682787479	-1.13437730098282	1.33303164820214
C	-0.53543753857171	0.81575749258367	1.53414152086421
H	-0.26012332987288	0.93584345434762	2.59676395738062
C	-1.74991682194986	-0.10533355605750	1.38913952141577
C	-2.94597397464704	0.31471101865903	2.24915347533449
C	-2.72002390126578	0.17003263905535	3.75173122464384
H	-3.62417200689616	0.43484034676849	4.32044707552165
H	-1.90798852715536	0.82055244688653	4.11220787040047
H	-2.45428258380905	-0.86698423198848	4.01511027469995
H	-3.21523826727445	1.35956842909861	2.01284806659803
H	-3.81893398993435	-0.29292787728729	1.95689670016133
H	-1.47941698643297	-1.14499748856856	1.63821046938196
H	-2.06388370427475	-0.12278425629640	0.33245699983944
H	-0.81417285714079	1.82873560882110	1.19586404960958
C	0.50883082601748	-0.64041966186917	-0.75475811311341
H	-0.13733538157441	-1.47260554953405	-0.42810806769020
H	-0.12206810244056	0.01079029820623	-1.38553442799841
C	1.67530316379560	-1.17719474392922	-1.58371172163232
H	2.30703715123126	-1.83246770634178	-0.95660398149172
H	2.32537116847841	-0.33733773918078	-1.88756473114578
C	1.23364130872020	-1.95782507438991	-2.82085918173186
H	0.58063675647193	-2.79210926164915	-2.50878076144738
H	0.60558032663662	-1.30667708993161	-3.45438458576797
C	2.40105940043772	-2.49840634346036	-3.63897483443222
H	3.02629689939137	-3.17996998928802	-3.03969366054968
H	3.05105221138306	-1.68237112755015	-3.99308966484005
H	2.05484706552194	-3.05525648344957	-4.52276475061529

TS-*Z*-i

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C	-3.44934554130610	2.07398058559886	-2.65705223804630
C	-2.31160024416208	1.44872712879112	-2.15321176110390
C	-1.03209408264300	3.45182902313534	-2.55083322014005
C	-2.17101948210444	4.07794670876279	-3.04853640173218
C	-3.38466820783056	3.39297988429306	-3.10252340582518
H	-4.39258377374664	1.52393538385265	-2.70500150391355
H	-2.36885022321405	0.41116552946899	-1.81436335478485
H	-0.07640256362329	3.97865743507236	-2.50749985009420
H	-2.11059917221512	5.11241920062702	-3.39618071642484
H	-4.27847069114110	3.88563190951760	-3.49326684609431
C	1.39544009126650	1.52126552032600	-1.77253212808915
C	2.71127223027550	1.03090538567917	-1.53644630840961
O	3.45241707656319	1.87576196451848	-0.78538286056948
O	3.15156597245993	-0.02815667624674	-1.94238822683099
C	4.77731879937678	1.45286440733061	-0.52254797537928
H	5.34507180494476	1.32166035416671	-1.45560866071899
H	5.23508347473531	2.24012241849165	0.08837238309713
H	4.79141849374010	0.49710783800240	0.02376535722310
C	-1.08921777092994	2.12699576966152	-2.09266074718166
C	0.15101448842770	1.50858664698514	-1.61143122920747
P	-0.46646634245896	0.00330082137135	0.06747026154566
C	1.13829104260092	-0.08048043655514	0.95377608355343
H	1.83780279720079	-0.54560109354504	0.23870992541995
H	1.47328657605726	0.96472572718144	1.05127563628242
C	-1.78393564914798	0.21397904979642	1.34922968248847
H	-2.63241324934508	0.69487722954272	0.83225288938321
H	-1.39008205774588	0.98306411259715	2.03509965631869
C	-0.68209000373651	-1.69374862549874	-0.62173920688940
H	-0.36675446769059	-2.43538390346545	0.13345042195373
H	-1.76079325435062	-1.86120554048976	-0.78551584917355
C	0.08681063872753	-1.89143605144122	-1.93146041485701
H	-0.34889082428228	-1.23630883295428	-2.70605436211476
H	1.13130389185554	-1.54854758540993	-1.82922076649457
C	0.07601789167752	-3.33895112104375	-2.41630931275147
H	0.54933213278638	-3.98005772917355	-1.65118135501594
H	-0.96734682541117	-3.69321501595038	-2.50192947557512
C	0.79375490146647	-3.51726120504381	-3.74984391893049

H	0.80651960635577	-4.57159463677796	-4.06497094442915
H	0.30234874329755	-2.93679615033726	-4.54668508926179
H	1.83633829918390	-3.16880027822652	-3.68667684268686
C	-2.27662533444443	-1.01813390728590	2.11362460765968
H	-1.43083863862947	-1.52714209516286	2.60426316260880
H	-2.69170653176032	-1.74504110676150	1.39641179704513
C	-3.34591696003908	-0.69950096759430	3.16333376376695
H	-3.74604078128882	-1.65155467154030	3.55016578324635
H	-4.19616215046406	-0.19261503525784	2.67353155698854
C	-2.84730902809225	0.14493600088356	4.33226298368926
H	-3.63771349907072	0.29169788150856	5.08362106365991
H	-1.99597731580785	-0.34007279492600	4.83748945320822
H	-2.51660679836771	1.14466445498830	4.01058452129414
C	1.21516021979623	-0.80555699349534	2.29609148541472
H	0.55913773910205	-0.30683771297960	3.03160975199102
H	0.83301383840771	-1.83507707229646	2.19060732341063
C	2.63965872102245	-0.86724069136724	2.85724961146871
H	2.62203475076102	-1.45647879175201	3.78950701450184
H	3.27754168063666	-1.43306850446083	2.15527253187263
C	3.26616040812165	0.49692674922590	3.13179708039049
H	4.25579269866133	0.39145962274912	3.60091606900823
H	3.40286243292001	1.08052033589252	2.20847948312262
H	2.63792002262164	1.09562014702122	3.81179363111246

TS-*E*-i

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C	-0.99414469641169	3.98704310422428	1.34208392724174
C	-0.69718303369840	2.64942053334666	1.09451280287668
C	1.62522168649783	3.21923194880701	0.79417418600389
C	1.32643841028176	4.55664548416756	1.03431661306505
C	0.01576584269838	4.94671293116752	1.30905056209414
H	-2.02311344101631	4.28016131721566	1.56478320726031
H	-1.48997095355075	1.89912523936064	1.12015553024967
H	2.64884095547009	2.90401345305948	0.57963571426981
H	2.12530686942269	5.30197293963220	1.00414900244579
H	-0.21759974708621	5.99740523020654	1.49819077281169
C	1.97235999243598	0.07019937253236	0.64131502396215
C	2.68371864389992	-1.15603113683486	0.52998535468324
O	3.44623928993590	-1.18979612927367	-0.59057970709924
O	2.64236871586659	-2.08178982492487	1.31468928310314

C	4.24736602285768	-2.34712519462985	-0.75245672336909
H	3.62885708937241	-3.25444703012641	-0.82388041289428
H	4.81196285632658	-2.20327043824612	-1.68101381754665
H	4.94063929925486	-2.46735673299470	0.09347293860355
C	0.61275445387295	2.24775920772918	0.81914527704236
C	0.99591848669591	0.85360597493835	0.57112754065890
P	-0.68819761703059	-0.26220982674343	-0.49011271855113
C	0.11061379495292	-0.65204759607289	-2.10550726735757
H	1.18235084677308	-0.78922529979163	-1.88457741208204
H	-0.26956191431624	-1.63071259983183	-2.44312505056429
C	-0.63591395019953	-1.89008037142852	0.37070907400786
H	0.32982233898974	-2.35707929197870	0.11731587410741
H	-1.41663330461860	-2.52832405983222	-0.07783547302906
C	-2.46780804869938	-0.02778466773742	-0.96539652467516
H	-2.53327149887564	0.96741640942126	-1.43851845675085
H	-2.72840123970980	-0.76577214218384	-1.74572957331714
C	-3.45743126971786	-0.11659848944241	0.19595596956422
H	-3.46177145924133	-1.14255783165382	0.60276475525975
H	-3.12659951684416	0.53094853927074	1.02847676562644
C	-4.88180875470581	0.27199190054521	-0.19912581941381
H	-4.88033955132570	1.30867226346201	-0.57911860955107
H	-5.20778151987656	-0.35762419130081	-1.04585300035735
C	-5.87528848175089	0.14617267499917	0.95057351647421
H	-5.59077587347077	0.79200729042859	1.79667122180774
H	-6.89090538065219	0.43333079515414	0.64070156151892
H	-5.92139262117271	-0.88778325455555	1.32782415902030
C	-0.75793886488899	-1.81680402530962	1.89519070866962
H	-1.74740338662665	-1.41822811823452	2.18196270443023
H	-0.01110647459431	-1.09919813215162	2.26847302206338
C	-0.52347986622809	-3.16274004457861	2.58198694892118
H	-0.51983718402974	-2.99663083061379	3.67223837396127
H	0.49385728223080	-3.50471495105633	2.32666931935623
C	-1.55218659523267	-4.23750353039088	2.24189881763710
H	-1.37619769416790	-5.15591688323521	2.82205716594757
H	-2.57673448553739	-3.89579371435127	2.46647760352541
H	-1.52212080719580	-4.51993849447476	1.17715636734564
C	-0.09478051467869	0.39375348699300	-3.20724302025674
H	0.43020458516585	0.04012025181455	-4.11142480275193
H	-1.16209599818232	0.42522046560628	-3.48339856136796
C	0.38483921083515	1.80879200659701	-2.87562163376677

H	0.04259519102024	2.48570959891400	-3.67627642565564
H	-0.11175979766528	2.16671444393298	-1.95560743461842
C	1.89627559210422	1.94203230670434	-2.71831893057209
H	2.17361640452979	2.98353595923852	-2.50115779247408
H	2.28562869614952	1.32160159684667	-1.89716071874389
H	2.41997198535823	1.64076710766426	-3.63985077885026

***Z*-i**

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C	-3.58487724356829	1.71474357008862	-2.57489688652760
C	-2.44987504907429	1.14217979744998	-1.99870970598169
C	-1.22727266580430	3.17772093094209	-2.36449611085371
C	-2.35541219474322	3.74991455281983	-2.94078171965997
C	-3.54376105761821	3.02353297717214	-3.04525485951985
H	-4.50175124201650	1.12605157842296	-2.66451865078296
H	-2.50526770732860	0.10159221614330	-1.66375014735165
H	-0.28766186609568	3.73003739226980	-2.28599657646409
H	-2.31015394994872	4.77724125882361	-3.31203804960877
H	-4.43036707671528	3.47585618570353	-3.49661880887528
C	1.22016624034295	1.62811684170677	-1.70387380820088
C	2.51079962921854	1.13947477023694	-1.38945196315560
O	3.21627362641527	1.97487539675785	-0.56906837794068
O	3.02594411271463	0.11896602751791	-1.83762588521797
C	4.56745718098218	1.62310378191357	-0.36257028037383
H	5.13130007605074	1.61701313017941	-1.30756703157862
H	4.98416809295410	2.38082197901862	0.31340291885061
H	4.66630113762101	0.62395087278490	0.09200792321850
C	-1.25411126382854	1.86297048496365	-1.87684809653708
C	-0.00509423752931	1.28818737694467	-1.28395263118448
P	-0.22178485077366	0.02705023372846	-0.00149991641487
C	1.32330034270823	-0.15131298543436	0.93689757732879
H	2.04742351681987	-0.61607451060622	0.24811304858637
H	1.68628661600289	0.87357917501007	1.10794136910417
C	-1.53571447359427	0.48700288674780	1.18765270558488
H	-2.23673436653419	1.13974580621165	0.64416776498243
H	-1.03061165139890	1.13385845142925	1.92394384142570
C	-0.56868114070763	-1.62238472055574	-0.71690426594176
H	-0.25412228973979	-2.37128525558777	0.03003189850655
H	-1.65615809809478	-1.74753344253874	-0.84074932062971
C	0.16260782310033	-1.82731714192805	-2.04822306586675

H	-0.30610731569039	-1.18110243304037	-2.80988418232573
H	1.20566727235897	-1.46958330890307	-1.98128799666037
C	0.13820374824978	-3.28156769702798	-2.51134492080738
H	0.63853552484797	-3.91167267981876	-1.75415821472016
H	-0.90639813250707	-3.63902722374319	-2.55962631714044
C	0.81364733657440	-3.47429314981566	-3.86465186258558
H	0.81188210299891	-4.53161632252069	-4.16922745555279
H	0.30056716986220	-2.89885302256289	-4.65101847191634
H	1.85914205667366	-3.13080256292059	-3.83617212623523
C	-2.29478217337069	-0.65728480875263	1.86454799256023
H	-1.59078143728693	-1.38711168723591	2.29938316057175
H	-2.86832206412571	-1.20606809746117	1.09990104566385
C	-3.25464099158683	-0.17813748139661	2.95678459117325
H	-3.87592384174913	-1.03401478420231	3.26783809944147
H	-3.95330721461028	0.56124502318806	2.52739854110125
C	-2.56433463809859	0.41227291307767	4.18301681047797
H	-3.29662009065950	0.69009229262545	4.95499102693757
H	-1.86630425246119	-0.31206502400268	4.63403232840471
H	-1.99102498499105	1.32116577096698	3.94179402435849
C	1.23417220487023	-0.94308341415739	2.24232555460661
H	0.55282510405577	-0.43832255652723	2.94967000743205
H	0.80219677939197	-1.94084545331460	2.05426920816150
C	2.60138026411898	-1.11921193714127	2.91042133199480
H	2.47085075808642	-1.75924386719660	3.79877116031086
H	3.26548856601131	-1.67821253308696	2.22836980170733
C	3.26986455603390	0.18921191578035	3.32197625841259
H	4.20718232427162	-0.00084114243070	3.86520536096480
H	3.52004526386462	0.81683879159452	2.45279985074229
H	2.61643899989221	0.78148625070077	3.98350268887132

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C	-0.58097610011477	3.77370945413334	0.74127576466925
C	-0.31266378431393	2.62208139502936	0.00396316581646
C	0.72931773040494	1.62080146774430	1.93136764720415
C	0.46754127405175	2.77514951023111	2.66655153975808
C	-0.19907642001147	3.85049640334343	2.07967226940414
H	-1.08364379885055	4.61918392558114	0.26388612590909
H	-0.59736176554889	2.58547547240937	-1.05182751985342
H	1.25628649297597	0.77952914757474	2.38875198348306

H	0.78292698100236	2.83117877427848	3.71174260687167
H	-0.41338712893683	4.75043762228353	2.66169491499999
C	1.68950627565707	-0.49203167406268	-0.29656878370577
C	2.95087085889503	-0.13923598265475	0.30859075264013
O	3.76877131504067	0.52653710167080	-0.54067305103273
O	3.30344362489710	-0.45910691047810	1.42890994006794
C	5.05513579757860	0.83452495664748	-0.04440815292292
H	5.60766662768250	-0.07686735971181	0.23073087280862
H	5.57930777079976	1.35942349298279	-0.85288162260221
H	4.99726078634457	1.47978621968879	0.84548511861129
C	0.33074211855259	1.52209740217388	0.58929420195050
C	0.57573740112083	0.25179742235556	-0.15790204894131
P	-0.75587898077194	-0.69983132880426	-0.86863915034824
C	-0.45877309639904	-1.11551648711529	-2.61493046488349
H	0.51708783190855	-1.62586746012638	-2.60540174261340
H	-1.22061173349450	-1.86810246073307	-2.88057009351027
C	-0.90712962485937	-2.30554172449494	-0.00803934642099
H	-0.22857216571841	-2.99930488849868	-0.52900448795474
H	-1.93671889944683	-2.66241737258606	-0.18165801066478
C	-2.39954350690351	0.09717039422286	-0.78484657703540
H	-2.30652650944642	1.06510358488980	-1.30282674173270
H	-3.09690941860405	-0.51299792537201	-1.38449159304150
C	-2.93932521204466	0.31390151621120	0.63163333035005
H	-3.16943564197717	-0.66094828808815	1.09599006295062
H	-2.16201537711079	0.78092026230047	1.25954376827068
C	-4.18466277135759	1.19752288429499	0.65561840767754
H	-3.94195131834338	2.16448591566182	0.18096717200400
H	-4.97425824985734	0.73996383814480	0.03333531728787
C	-4.70553437417315	1.44043051180538	2.06726470058417
H	-3.93868643883238	1.92900933024678	2.68941230237949
H	-5.59505773249359	2.08773536800568	2.06325493965917
H	-4.98305725391219	0.49551848477430	2.56115606311405
C	-0.54988873576032	-2.26231620666750	1.48102139668043
H	-1.07821319129160	-1.43268794272975	1.98179644759695
H	0.52226647853488	-2.02753812118764	1.56206379882553
C	-0.85649740461863	-3.57027137308138	2.21229588455021
H	-0.40163758775809	-3.51528475681500	3.21448724564160
H	-0.34626175064110	-4.40352799096214	1.69781226441963
C	-2.34427725260745	-3.88064553982241	2.35422401664856
H	-2.50744478618890	-4.80784996216254	2.92356415463372

H	-2.86979252912189	-3.06913347884361	2.88407668453941
H	-2.83748786506692	-4.01282116939142	1.37763248815305
C	-0.47362493426362	0.04147378474684	-3.62200581201393
H	-0.48740835060499	-0.41101594827955	-4.62843153041902
H	-1.42488126129634	0.59623166229427	-3.54149349129676
C	0.70254256341177	1.02166327555910	-3.54443853932275
H	0.53983712664154	1.79172510218997	-4.31759258318351
H	0.69373455244705	1.55330220480094	-2.57937876414564
C	2.07329970229295	0.38072609920683	-3.73387134534870
H	2.85566386067200	1.15061209807902	-3.80091842762648
H	2.33938965717696	-0.26029457093621	-2.87897235670691
H	2.11292012465331	-0.22236416195783	-4.65655011283348

Water

3

O	-3.70913786068245	0.32845306960149	0.01925779733957
H	-2.74864462619566	0.31953278180484	-0.03071939176759
H	-3.98139751312189	0.16633414859367	-0.88882840557198

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C	-0.195537	3.580218	1.193669
C	-0.044727	2.525664	0.295903
C	0.736717	1.108314	2.081864
C	0.594511	2.165548	2.979993
C	0.116659	3.400906	2.541931
H	-0.548703	4.551142	0.836541
H	-0.262032	2.680557	-0.764675
H	1.106599	0.136186	2.422214
H	0.851462	2.020064	4.032307
H	-0.004466	4.225946	3.248384
C	1.711228	-0.506800	-0.476060
C	3.021168	-0.015381	0.049140
O	3.178859	1.294731	-0.195030
O	3.852338	-0.690216	0.592899
C	4.348818	1.890662	0.337014
H	5.255055	1.417832	-0.068845
H	4.310391	2.948156	0.052384
H	4.366603	1.796626	1.433174
C	0.402543	1.270078	0.729370

C	0.534836	0.127220	-0.220541
P	-0.920616	-0.736962	-0.795609
C	-0.702666	-1.340757	-2.503016
H	0.217430	-1.947386	-2.490075
H	-1.524806	-2.060775	-2.648748
C	-1.219281	-2.227095	0.181570
H	-0.257252	-2.782787	0.008776
H	-2.071655	-2.758520	-0.273579
C	-2.376829	0.362737	-0.811112
H	-2.085263	1.274978	-1.356177
H	-3.134519	-0.142771	-1.434468
C	-2.966145	0.723232	0.556200
H	-3.421002	-0.172447	1.008690
H	-2.166479	1.040308	1.243542
C	-4.005670	1.838008	0.467013
H	-3.559940	2.702515	-0.056115
H	-4.851949	1.505137	-0.159847
C	-4.504914	2.281395	1.837383
H	-3.673619	2.671582	2.446218
H	-5.262823	3.074735	1.755704
H	-4.956728	1.443175	2.390996
C	-1.373849	-2.036461	1.701244
H	-2.442711	-1.998676	1.977097
H	-0.947838	-1.068459	2.008731
C	-0.655442	-3.140086	2.480989
H	-0.728863	-2.919752	3.559798
H	0.404093	-3.087929	2.177327
C	-1.190002	-4.538905	2.196621
H	-0.695278	-5.289718	2.831107
H	-2.276261	-4.612880	2.376835
H	-0.997374	-4.827204	1.151420
C	-0.716775	-0.302077	-3.631842
H	-0.781884	-0.858968	-4.582556
H	-1.651302	0.281556	-3.575979
C	0.476915	0.655347	-3.707658
H	0.250159	1.412121	-4.476794
H	0.584476	1.207137	-2.758873
C	1.799831	-0.023742	-4.044147
H	2.607570	0.715042	-4.151347
H	2.109919	-0.727744	-3.257929

H	1.731507	-0.585810	-4.989555
H	1.780979	-1.413102	-1.085281
O	1.493743	-2.717900	0.162196
H	2.354787	-3.079543	0.399613

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C	0.162080	3.638583	-0.053432
C	0.149690	2.322212	-0.511543
C	1.138837	1.599980	1.554937
C	1.171107	2.915846	2.006153
C	0.673311	3.944199	1.206230
H	-0.225289	4.434157	-0.695234
H	-0.229724	2.121380	-1.514002
H	1.488965	0.796800	2.208962
H	1.570420	3.135595	2.999297
H	0.681254	4.976699	1.563999
C	1.560804	-1.071086	0.143059
C	2.974454	-0.724848	0.464388
O	3.411834	0.321464	-0.237314
O	3.653771	-1.343728	1.242726
C	4.759569	0.700227	-0.027257
H	5.439965	-0.123869	-0.286357
H	4.940236	1.560360	-0.681071
H	4.928592	0.977741	1.023935
C	0.634056	1.272180	0.283336
C	0.565214	-0.166495	-0.082994
P	-0.815825	-0.871479	-0.975880
C	-0.483636	-0.958504	-2.763820
H	0.350657	-1.704992	-2.779857
H	-1.397556	-1.407238	-3.191684
C	-1.107618	-2.618626	-0.545111
H	-0.125096	-3.087229	-0.752346
H	-1.768306	-2.969209	-1.355679
C	-2.331539	0.113499	-0.712725
H	-2.202013	1.018428	-1.328434
H	-3.158183	-0.448890	-1.179329
C	-2.663149	0.516868	0.727758
H	-3.095343	-0.339139	1.271309
H	-1.738171	0.783265	1.264229

C	-3.622031	1.703774	0.789466
H	-3.171822	2.547018	0.237009
H	-4.557481	1.453716	0.258031
C	-3.931538	2.141122	2.216115
H	-3.012278	2.442438	2.742638
H	-4.622693	2.996365	2.234479
H	-4.394785	1.325898	2.795555
C	-1.740303	-2.959796	0.807786
H	-2.025415	-4.025233	0.770066
H	-2.691593	-2.411383	0.909229
C	-0.879288	-2.725046	2.052187
H	-1.533900	-2.782469	2.937598
H	-0.483301	-1.695869	2.042991
C	0.261057	-3.726328	2.215006
H	0.913563	-3.455125	3.057192
H	-0.128390	-4.739617	2.403294
H	0.900312	-3.784644	1.320772
C	-0.110628	0.323861	-3.515878
H	-0.310518	0.134264	-4.584597
H	-0.800612	1.146393	-3.250628
C	1.344738	0.789700	-3.377411
H	1.417664	1.791261	-3.837171
H	1.609082	0.918865	-2.316110
C	2.363286	-0.157989	-4.000298
H	3.368822	0.290559	-3.973305
H	2.386835	-1.095041	-3.417443
H	2.123480	-0.376973	-5.054534
H	1.382317	-2.134366	0.204890
O	1.746464	-2.366354	-1.779350
H	2.528590	-2.925150	-1.849827

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C	0.19490875224991	3.49942410642864	0.38684474304822
C	0.15536206555848	2.23060811778524	-0.18322628121924
C	1.22972541033808	1.32408753025745	1.75889526732471
C	1.29922846884151	2.59885721712654	2.31351167596160
C	0.76812344172606	3.69966002975011	1.64190242568305
H	-0.20439818704464	4.34951388642391	-0.17419979552095
H	-0.23771852197432	2.12590356721402	-1.19689534111656

H	1.62134350429756	0.48152430682505	2.33573504447781
H	1.76059532441320	2.72814648386120	3.29675897076572
H	0.81305635744399	4.69833730430596	2.08247968143726
C	1.75296598034929	-1.18771232653612	0.22931456085562
C	3.11162616096697	-0.47184995028842	0.28027571356095
O	3.29698648696617	0.37652839831977	-0.72542031024827
O	3.94755104358335	-0.70707735626594	1.11654166988727
C	4.51113831582644	1.10668248284119	-0.71861305319316
H	5.37862148599146	0.43116214024606	-0.74373379392786
H	4.49310010513498	1.74002909218805	-1.61293873114691
H	4.57395196323744	1.73187886564842	0.18422978187771
C	0.64298696961983	1.09026896094776	0.49286657331723
C	0.59451283671709	-0.26691111191702	-0.05355266291451
P	-0.71872154517221	-0.86771420653538	-0.97533959404360
C	-0.53219023062448	-1.00836306039452	-2.80860079635204
H	0.20172538170286	-1.81571084763092	-2.96262888443607
H	-1.49592726415437	-1.37720255688950	-3.19914725152844
C	-1.23317309429675	-2.59816502022292	-0.59439927074565
H	-0.33789289087136	-3.21154688000706	-0.77051305259351
H	-1.95139020022983	-2.86207593980548	-1.38799436007321
C	-2.22644226552675	0.16312287420860	-0.78841249005872
H	-2.07184431073993	1.05951883976441	-1.40709093235493
H	-3.03356564143785	-0.40287132748298	-1.28428731682796
C	-2.63191724905968	0.58108867354090	0.62972843037379
H	-3.14549807440625	-0.25184427876303	1.13669194427152
H	-1.73571721053751	0.79639615028650	1.23063388802730
C	-3.53707569090349	1.81151279948383	0.63352563227629
H	-3.00942129833093	2.63636460563511	0.12297353264012
H	-4.44423475291082	1.60872405081256	0.03621412125976
C	-3.92439205343103	2.25256368361075	2.03996172467587
H	-3.02890027283172	2.50208002060903	2.63099564008250
H	-4.57110268998275	3.14270647956631	2.02105883598535
H	-4.46686237213831	1.45688003593591	2.57589890940305
C	-1.85624774218811	-2.89187581443273	0.77433869811209
H	-2.26429569839817	-3.91731080601796	0.73478184439030
H	-2.72932422428189	-2.23873002939626	0.92745446393978
C	-0.92000358697255	-2.78242030485188	1.98000759961830
H	-1.52857817980113	-2.85323828401473	2.89681324430563
H	-0.46091751569988	-1.78009527900273	1.99674400487336
C	0.16167634278634	-3.85817475251818	2.01585922766613

H	0.81671393977946	-3.73817932732205	2.89177772384668
H	-0.27900436745121	-4.86720605455284	2.06519840744695
H	0.80210534255358	-3.82134769575523	1.12075420580262
C	-0.11054523892605	0.25422110649300	-3.56938569790282
H	-0.29145501958081	0.06399339699422	-4.64219741290853
H	-0.78443907335750	1.09067828717737	-3.31021495283742
C	1.34342574113564	0.70386286139275	-3.39064625367159
H	1.48925003699111	1.60477210864692	-4.01066130088942
H	1.52304157450950	1.00665762550022	-2.34828272918461
C	2.37537971301861	-0.35400423385401	-3.76792314164189
H	3.38871196712344	0.07485758544022	-3.77286079531378
H	2.38104121600902	-1.17556196508451	-3.03622534235554
H	2.18722520768663	-0.77325538570131	-4.77114852992358
H	1.69698309142892	-1.69781853145216	1.21368685359539
O	1.82190937121410	-2.19131852460811	-0.78494086871424
H	2.45885567327281	-2.85840811823879	-0.50664458429730

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C	-0.33854577658025	3.81453542844405	0.31423511786273
C	-0.25597274913369	2.49804691852151	-0.13435458161747
C	0.80869824045475	1.86179648695713	1.92040414043551
C	0.75643708184943	3.18309277252549	2.35200290436061
C	0.16855247616024	4.17213283294031	1.56143536018803
H	-0.78305877124076	4.57445729673318	-0.33526209075393
H	-0.60462083845161	2.26604886486803	-1.14379172647236
H	1.22037603976175	1.09417532089405	2.57884807873726
H	1.16054514548298	3.43955742968062	3.33547592820170
H	0.11447197330841	5.20636194923707	1.90969898076179
C	1.51984436868429	-0.78354616446633	0.66071073890286
C	2.85061674566810	-0.03354447660019	0.60272102148856
O	3.06865367949884	0.57879507788163	-0.55180961812849
O	3.63910888065149	-0.03882041078863	1.51811573219712
C	4.25838308646900	1.34882754442600	-0.64160525067217
H	5.14511874104036	0.72394368823217	-0.46383556959679
H	4.27812791064017	1.76240246407571	-1.65583813577364
H	4.24084707596021	2.16152969654393	0.09839454215978
C	0.29630448772019	1.47194754128160	0.66105445343224
C	0.35900671403351	0.06898851193073	0.23919232899947
P	-0.91650564796284	-0.69935385874181	-0.59905020775353

C	-0.80801054902914	-0.95198514728739	-2.42843558449118
H	-0.05123161108219	-1.73940905250106	-2.58458735239351
H	-1.77004079920655	-1.38971936809797	-2.74551734343351
C	-1.10299090264103	-2.43156001132853	-0.02826839456347
H	-0.12087710446813	-2.90112240751923	-0.21429652228087
H	-1.81527605215194	-2.93712349064492	-0.70105080788355
C	-2.52211630300757	0.15647212024048	-0.38926297971353
H	-2.48387691096618	1.05084162130035	-1.02968974487000
H	-3.28397125088176	-0.50341764225508	-0.83751284684942
C	-2.89445587778803	0.55704293297507	1.04228316054920
H	-3.31552485417231	-0.31165997455567	1.57408746740251
H	-1.98814942250215	0.84549685671311	1.59717939737004
C	-3.88689887860804	1.71737229014340	1.08180384844534
H	-3.43308362693541	2.58067044370758	0.56409062362345
H	-4.79445504906291	1.45377147391956	0.50914355572752
C	-4.26485612922278	2.12029983478216	2.50220622182427
H	-3.37173345237718	2.41456129824248	3.07580094132945
H	-4.96160831624456	2.97201306355976	2.50818499894274
H	-4.74854410250506	1.28937325347844	3.04075923522409
C	-1.48334504550173	-2.58576383724901	1.44888080874894
H	-2.57686337908095	-2.48101205662367	1.55794633256597
H	-1.01567268745708	-1.77104624106922	2.02181638123864
C	-1.02726496252417	-3.91457621007289	2.05160756173130
H	-1.30307879525304	-3.92231977474596	3.11927681505028
H	0.07600662589205	-3.93609721136053	2.02798859143760
C	-1.59980907256005	-5.15390783642809	1.37111750130750
H	-1.27524546857378	-6.07505288380932	1.87809645212954
H	-2.70241550812980	-5.14189086270092	1.37914728652177
H	-1.27820904934261	-5.23341503966735	0.32020232281804
C	-0.47867070054623	0.28078333152381	-3.27790400412251
H	-0.71549380685006	0.03783893837595	-4.32870552276969
H	-1.16238820032242	1.10696083498881	-3.01355810728387
C	0.96915920681720	0.77694620087817	-3.19804543062826
H	1.04327796206557	1.69278162715077	-3.80806614617679
H	1.21400816288256	1.06592674938598	-2.16489290226699
C	2.00259206631319	-0.23509586659128	-3.68146971536386
H	3.00794486923704	0.21071484640956	-3.70418050282330
H	2.06254074672532	-1.10971303880770	-3.01452795412769
H	1.77650866629744	-0.59923691480789	-4.69751078700012
H	1.65494185162418	-1.60512194798620	-0.07675662696547

O	1.41084749677097	-1.34544161287547	1.95613293319386
H	2.28307718184475	-1.24336646227086	2.36766003079726

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C	-2.30055367029943	1.11871394535239	-2.20445260972371
C	-1.31566327065599	3.16860209572930	-1.41642825281982
C	-2.46865039557097	3.85750520577980	-1.78317108946911
C	-3.54726863721487	3.18162336444352	-2.35351965011091
H	-4.28735970172171	1.26825977605378	-3.02981110117062
H	-2.22875629032434	0.04535387057112	-2.40952831756848
H	-0.47570743111322	3.70481617472713	-0.96748060993154
H	-2.52535469462887	4.93669398801411	-1.61744277169664
H	-4.45086738119127	3.72584074167983	-2.63914715375590
C	1.25559937114896	1.60064600313081	-1.43574918109382
C	2.49684317965436	0.79571646856764	-1.46206338847101
O	3.60266442867825	1.51445983630543	-1.30769157880685
O	2.53333998654540	-0.39952810149917	-1.69678892812764
C	4.82585854424478	0.81012406278515	-1.36874276036793
H	4.94857787151762	0.31015274920240	-2.34111136737412
H	5.61536176202099	1.55606674498519	-1.22327761488335
H	4.88136172692147	0.04635649685207	-0.57775096481365
C	-1.21395946779503	1.78314887071014	-1.61571925627142
C	0.02338380007416	1.04250079128535	-1.23788589950366
P	-0.16210860649037	-0.33460046277352	-0.09712111832999
C	1.30371141465789	-0.33990573008372	0.99432519341938
H	2.06412566928321	-0.97524862228333	0.52135039228314
H	1.66056455524794	0.70259545040675	0.90564090938039
C	-1.60263595594740	0.07099527414270	0.95680616309145
H	-2.37482765282157	0.49105936731404	0.29529339060315
H	-1.26339951251012	0.91029564453853	1.58614165481999
C	-0.52436006828482	-1.98694981226689	-0.78792488088184
H	-0.43984401604327	-2.70475830028435	0.04686099803087
H	-1.59367469918293	-1.95872647027200	-1.06180867470638
C	0.31059520673125	-2.42766066505575	-1.98749172382985
H	0.26367522786377	-1.64694713515755	-2.76505950335919
H	1.37310354442226	-2.48022232126325	-1.71019694510384
C	-0.16013060083296	-3.76638504620691	-2.55258460261328
H	-0.10283405534610	-4.53827753053523	-1.76402935417110

H	-1.22797390429957	-3.69590890282293	-2.82764534060887
C	0.65187454411465	-4.20988973023971	-3.76440596402273
H	0.29821823235038	-5.17560866511738	-4.15488399099149
H	0.58281443633104	-3.47231127230180	-4.57953749050845
H	1.71781577282556	-4.32022918391175	-3.51047673602223
C	-2.19619343679000	-1.06879756888418	1.79027213569053
H	-1.40664949103084	-1.61489937094810	2.33269784663850
H	-2.66315245588098	-1.80209375571852	1.11300503188197
C	-3.24617024250439	-0.58403471359546	2.79460123076493
H	-3.73857931122537	-1.46834282901586	3.23129272636616
H	-4.03702284229050	-0.03364311028541	2.25549759095115
C	-2.68648101096908	0.28340288128836	3.91832754631214
H	-3.47421929106045	0.56114618605280	4.63390896281313
H	-1.90115339111207	-0.24884099238717	4.47955225342488
H	-2.24933135163358	1.22152995499097	3.54207001173969
C	1.15014187484804	-0.69057444224681	2.47439223900600
H	0.27382028523043	-0.18738141990232	2.91363984616482
H	0.98944616441461	-1.77444176971300	2.60235100397047
C	2.39317830847099	-0.24798765382911	3.25723416438152
H	2.35065046796079	-0.69532504881683	4.26421077361988
H	3.29230262736225	-0.67126858254261	2.77588981947202
C	2.52971734943628	1.26967314692489	3.37856173901676
H	3.44167435480417	1.53734938183233	3.93267509219458
H	2.57400948353341	1.78471535518693	2.40382871275697
H	1.67453471250322	1.69260567250673	3.93187218519822
O	1.82841458567354	3.03499806831946	0.19156264955765
H	0.94643346749771	3.06991420757613	0.58415564715339
H	1.49355583066533	2.74504251318902	-1.13397266036383

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C	-3.729479	1.812180	-2.083366
C	-2.577843	1.256539	-1.526380
C	-1.257647	2.997378	-2.510171
C	-2.401242	3.544778	-3.076588
C	-3.650627	2.958977	-2.865434
H	-4.695060	1.330129	-1.909333
H	-2.693662	0.341163	-0.942188
H	-0.289572	3.476333	-2.670093
H	-2.317763	4.449138	-3.685337

H	-4.550655	3.393400	-3.306711
C	1.144367	1.517354	-1.797469
C	2.519925	1.466448	-1.275302
O	2.668277	2.313958	-0.231650
O	3.456280	0.848310	-1.726834
C	3.988858	2.447202	0.263500
H	4.672138	2.802900	-0.521321
H	3.938735	3.177890	1.079584
H	4.372511	1.484485	0.636829
C	-1.310353	1.831751	-1.722481
C	-0.046980	1.302157	-1.140952
P	-0.159339	0.067292	0.127113
C	1.438769	-0.223645	0.943975
H	2.166995	-0.498495	0.165183
H	1.748576	0.753631	1.340781
C	-1.316884	0.580053	1.453396
H	-1.900097	1.423256	1.052056
H	-0.675242	1.003352	2.243108
C	-0.651200	-1.543217	-0.589049
H	-0.838403	-2.268980	0.219327
H	-1.610004	-1.383465	-1.105030
C	0.402445	-2.028371	-1.591467
H	0.771695	-1.176511	-2.198328
H	1.270796	-2.442255	-1.047775
C	-0.131400	-3.072790	-2.569919
H	-0.424511	-3.996585	-2.037863
H	-1.051758	-2.678289	-3.034940
C	0.888454	-3.374170	-3.662959
H	0.497186	-4.093829	-4.398061
H	1.152354	-2.442429	-4.187240
H	1.814773	-3.796440	-3.240548
C	-2.249993	-0.496335	2.011214
H	-1.666435	-1.371364	2.346983
H	-2.904108	-0.862547	1.202858
C	-3.118339	-0.001441	3.170332
H	-3.846382	-0.792113	3.415583
H	-3.714921	0.864319	2.833596
C	-2.335028	0.367589	4.427063
H	-3.011204	0.647214	5.248166
H	-1.722146	-0.479172	4.777524

H	-1.660561	1.222236	4.261700
C	1.407363	-1.296259	2.035387
H	0.639660	-1.053105	2.791020
H	1.114783	-2.263212	1.595012
C	2.758542	-1.456923	2.738131
H	2.703991	-2.340144	3.395527
H	3.531180	-1.687674	1.984501
C	3.181964	-0.243344	3.560346
H	4.130014	-0.431130	4.085384
H	3.330934	0.650558	2.934640
H	2.424730	0.006135	4.321323
H	1.160859	1.601753	-2.960641
O	1.352783	0.279183	-3.538481
H	2.310899	0.162198	-3.471230

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C	-3.49402729717866	1.33622317928278	-2.75535987010159
C	-2.37588905649448	0.87206164245521	-2.06756439403941
C	-1.31583324205995	3.00197153440252	-2.35164896834885
C	-2.42567380433484	3.45546504377793	-3.05450139181600
C	-3.53398472127925	2.63273581320142	-3.26175901700260
H	-4.33999336502223	0.66048695648693	-2.91251860610768
H	-2.37668495422216	-0.16960519320531	-1.73567143088639
H	-0.49099435508187	3.69916547645954	-2.17914980769897
H	-2.42939973094798	4.48109406579186	-3.43482177388152
H	-4.40742129616662	2.99469364974262	-3.80878520032606
C	1.19819896219203	2.00042142075071	-1.14064230390964
C	2.48358045395533	1.18267405397250	-1.26853490237499
O	3.51964406932882	1.75010520828646	-0.64920785399856
O	2.58871649562913	0.16332407654844	-1.90427795155195
C	4.76578716760896	1.09122903287243	-0.79502424577390
H	5.06241951981705	1.04133545595844	-1.85273050471554
H	5.49240613270201	1.68040355033432	-0.22426774053485
H	4.71696294306072	0.06444328975077	-0.40245039266131
C	-1.24257699697062	1.68637178181756	-1.82923713541053
C	-0.07913901144032	1.21960460911088	-1.07918545270478
P	-0.26589206976094	-0.04598593084513	0.07420339445444
C	1.27162104842195	-0.17875269614903	1.05072910612725
H	1.99604194887329	-0.70433894576078	0.40842902771798

H	1.63079323385030	0.85579458821345	1.16648539549631
C	-1.63586145354975	0.32356104471186	1.24310238216753
H	-2.36511085945830	0.90769747544916	0.65831165221272
H	-1.19269027790823	1.03358789571856	1.96132015331878
C	-0.58541689458493	-1.74747687321348	-0.56229970214726
H	-0.27100320966099	-2.46042605465463	0.22001460328509
H	-1.67394695958950	-1.88036137965284	-0.67189269020199
C	0.11924046899612	-2.02461478642876	-1.88853306095615
H	-0.23328026862422	-1.29176489725913	-2.63414275410563
H	1.19881507351452	-1.82474249727863	-1.79670102177860
C	-0.11384834192851	-3.44484231832119	-2.39843132190621
H	0.25149107708802	-4.17024251687776	-1.64930838510591
H	-1.19977042676566	-3.62793740153354	-2.48941426060946
C	0.56373720810889	-3.70746593596111	-3.73895285927003
H	0.37688616501542	-4.73247797851824	-4.09311719639401
H	0.19617022938195	-3.01335975528331	-4.51092204425993
H	1.65415027622514	-3.56894320996221	-3.66647647766738
C	-2.33817752746371	-0.83616314683498	1.95192288747616
H	-1.60235957561209	-1.53059393169865	2.39266004770098
H	-2.89933422794206	-1.42257357685524	1.20666592434721
C	-3.30220392359694	-0.37519717655358	3.04906794578729
H	-3.90613545909568	-1.24076744449823	3.36795236651901
H	-4.01692964280054	0.35038522252504	2.62230246165423
C	-2.61572891414596	0.23188472185038	4.26952419494628
H	-3.34831897000390	0.51154822433260	5.04083219976831
H	-1.91113446450970	-0.48313735377811	4.72525055416727
H	-2.04854037948500	1.14203767798163	4.01836947077882
C	1.18038354218690	-0.86981034884536	2.41032477385061
H	0.47803021136503	-0.32540325348469	3.06503190639835
H	0.77286145056749	-1.88852237898841	2.29543308572914
C	2.54338358498213	-0.95935121890364	3.10427795682842
H	2.41835752185876	-1.52163348791492	4.04457204987433
H	3.22472860567951	-1.56362023008336	2.47930119741148
C	3.18383195667740	0.39333788333619	3.40342246466247
H	4.13228105272890	0.26908308771657	3.94672915233660
H	3.40427953587740	0.96269653228090	2.48711589824175
H	2.52331519501921	1.01708272707183	4.02768465191566
O	1.36524130277755	2.95029258858651	-0.09157221891803
H	0.46865724802018	3.18121343792373	0.17049128813207
H	1.18908397208600	2.53376825910660	-2.11346396238884

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C	-3.45173151919364	2.17267336043254	-2.21120405824580
C	-2.37925895184363	1.41701484451855	-1.74571387801141
C	-0.88373693317901	3.21657863614280	-2.26245541774987
C	-1.95291040235519	3.95647692742012	-2.75520564152871
C	-3.25265584484160	3.45014630166692	-2.72981583110599
H	-4.45666434658764	1.74104269978859	-2.18893981155779
H	-2.58272736800149	0.39729102700165	-1.40656080185105
H	0.10571730369206	3.67791903807990	-2.23516380997793
H	-1.76742280567365	4.96105209756110	-3.14704751240362
H	-4.09172915624129	4.03906131143104	-3.10758563921443
C	1.46032683885949	1.36746959683697	-1.82403375613702
C	2.43596883926865	2.11106779547222	-0.91166597800769
O	1.98316891887063	3.29302555081886	-0.51499683786377
O	3.52349971401069	1.67709945933444	-0.60044065958139
C	2.83438070478604	4.05139906029126	0.33022633512446
H	3.81649723708119	4.20646005386324	-0.13842441772090
H	2.33105048346942	5.01094000901476	0.49012362791265
H	2.98322814672688	3.53884357895500	1.29200779095799
C	-1.05150310908034	1.90938675625814	-1.74390535451502
C	0.08570573630281	1.14359399791312	-1.24102036065379
P	-0.14788184124389	-0.10527712481790	-0.08415285648571
C	1.42847944253898	-0.46698383028625	0.75920688740654
H	2.14482540074515	-0.72952833982386	-0.03247914129767
H	1.76533331568215	0.49806519675157	1.16753536241722
C	-1.30692263770011	0.44046238073102	1.23388727336196
H	-1.92904878396333	1.23321853256686	0.79094910069067
H	-0.65525716997277	0.94487478257154	1.96625272917671
C	-0.76132402676020	-1.73543662832530	-0.69319968261283
H	-0.98896284370426	-2.38941281107702	0.16479473963545
H	-1.72142706112023	-1.53330130467417	-1.19612134032060
C	0.20354965748265	-2.41491457347025	-1.66352339759426
H	0.54584382701445	-1.68317183338732	-2.41283713032799
H	1.11480599331516	-2.72370221295767	-1.12008471105753
C	-0.40841698815009	-3.63330656456732	-2.35146773319596
H	-0.76490582130923	-4.34922815143138	-1.58928861064946
H	-1.30649919456895	-3.31736800129385	-2.91099197580760
C	0.56386304846274	-4.32946836829875	-3.29773297411420

H	0.09702063801672	-5.19356783278087	-3.79376775487291
H	0.91438550663295	-3.64077571271605	-4.08248212764753
H	1.45342536143380	-4.69379549669829	-2.75930503555124
C	-2.19092527012062	-0.61127009114003	1.90508831914371
H	-1.58006086070616	-1.45632705009124	2.26841820935660
H	-2.88047300902755	-1.03430504274539	1.15603020497529
C	-3.00925762151832	-0.05494495554206	3.07352146031224
H	-3.72553862295241	-0.82920101571473	3.39487813056303
H	-3.62014566688894	0.79312764038646	2.71780512507376
C	-2.17217482965613	0.37964783346149	4.27349656495867
H	-2.81096348843148	0.70474720893219	5.10791625346667
H	-1.54371506286866	-0.44837897360940	4.64096879256403
H	-1.50519326382279	1.22153882981855	4.03070114729738
C	1.40399627557463	-1.53107415775354	1.85518044355861
H	0.79466523736567	-1.17934261081501	2.70675639108666
H	0.91785500284270	-2.44927044031952	1.48597750528681
C	2.81003403912883	-1.88722738414540	2.34876542052371
H	2.72021977624805	-2.65678597761533	3.13373011523647
H	3.36551535501994	-2.36215047912477	1.52113263547716
C	3.61030059010442	-0.70201958510733	2.88143190501563
H	4.57792645666398	-1.03141466325796	3.28798843467285
H	3.82196688370846	0.03686411747664	2.09247260187647
H	3.06908821988999	-0.18513630430739	3.69147834376714
H	1.32566574440465	2.03387881942908	-2.69901901102531
O	2.09675879651259	0.17108643144199	-2.22503156701951
H	3.03385966017106	0.27292765168436	-2.00299602948588

TS-(2*S*,3*R*)-ix

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C	-2.41689175	0.16171831	-3.22389336
C	-1.81943485	0.48692278	-2.01012882
C	-0.10580108	1.68845602	-3.16528828
C	-0.72295570	1.40209859	-4.38200744
C	-1.86125067	0.59884859	-4.42556770
H	-3.32965445	-0.44032767	-3.22942685
H	-2.29271992	0.14863226	-1.08802731
H	0.80114197	2.29309854	-3.18812869
H	-0.28218170	1.79613726	-5.30227540
H	-2.32337520	0.32069695	-5.37632816
C	1.35830892	2.30433249	-0.71445268

C 2.48747207 1.79187782 -1.61265773
O 3.08917359 2.76878104 -2.28949248
O 2.80012941 0.63236373 -1.74922005
C 4.09280999 2.34517116 -3.20289339
H 3.65778475 1.66954471 -3.95410390
H 4.48476187 3.24839293 -3.68490433
H 4.89708668 1.81281312 -2.67526000
C -0.60320815 1.19041659 -1.94811257
C 0.14241842 1.36965690 -0.65618811
P 0.44699295 -0.15187018 0.30917077
C 2.13489639 -0.38522209 1.00624760
H 2.84953351 0.08582751 0.32721375
H 2.15140967 0.20443903 1.93448445
C -0.61291099 -0.09344072 1.79799646
H -0.21471216 0.78266089 2.33684016
H -0.42349838 -0.99790413 2.39908990
C 0.01047690 -1.67975566 -0.59691109
H 0.29999310 -2.51950868 0.05366538
H -1.08894592 -1.70966068 -0.64628715
C 0.59324595 -1.81159837 -2.00272498
H 0.18816066 -0.99579033 -2.61433522
H 1.68366712 -1.64877567 -2.00498661
C 0.23179552 -3.13118289 -2.68076644
H 0.85178973 -3.95070472 -2.27909068
H -0.81267450 -3.39622905 -2.43673658
C 0.37106164 -3.02298753 -4.19496303
H 0.10700914 -3.96238640 -4.70396298
H -0.29943132 -2.23827248 -4.58073223
H 1.39482649 -2.73979653 -4.48735731
C -2.09639430 0.17954776 1.54033914
H -2.60893464 -0.71257611 1.13539340
H -2.15515494 0.97016629 0.78082448
C -2.83832520 0.72139792 2.76532422
H -3.78063458 1.17517747 2.41248923
H -2.24029737 1.56089388 3.15636408
C -3.15197559 -0.29847462 3.85599590
H -3.70366337 0.17241317 4.68426651
H -3.77753358 -1.11968802 3.46879241
H -2.24189827 -0.74940753 4.28544825
C 2.51637254 -1.85280002 1.22554499

H	1.66547612	-2.43071121	1.62688344
H	2.74856630	-2.29939651	0.24577064
C	3.70859623	-2.04755361	2.16911690
H	4.18453810	-3.01483488	1.94008430
H	4.47565663	-1.28223406	1.95777910
C	3.31934365	-2.02598218	3.64559178
H	4.18839562	-2.21800621	4.29271272
H	2.87917277	-1.06148062	3.94736001
H	2.57391191	-2.80510667	3.86637869
O	1.85483948	2.53760325	0.56788328
H	1.02285521	2.81005237	1.08159128
H	1.00074910	3.24552109	-1.18043071
H	-0.46219049	2.08250679	0.22941615
O	-0.55098446	2.81180891	1.36461614
H	-1.01832318	3.64685221	1.26563380

TS-(2*R*,3*S*)-ix

66

C	-2.79124091369377	1.40430968505858	-3.67250149912739
C	-1.61498268635109	0.94548899553773	-3.08258686405860
C	-1.63540913278717	2.81697431180793	-1.57086581625335
C	-2.81186773636462	3.27616521113916	-2.16001641256785
C	-3.39304647245470	2.57614346892189	-3.21537315699188
H	-3.23680728571395	0.84795498932713	-4.50110717313754
H	-1.12343981626810	0.04736355866236	-3.46778382724627
H	-1.16893945183231	3.38895591482648	-0.76556693891002
H	-3.27637938004161	4.19099927319738	-1.78182194520007
H	-4.30401957134394	2.95087959255853	-3.68973392328669
C	1.43854971795264	2.14169331960050	-1.26384332719269
C	1.43910117383214	2.87449215894121	0.08327922534404
O	2.42892709747469	2.50245196236079	0.90032524317587
O	0.60965192602051	3.68970217957003	0.41307820101151
C	2.50827122822539	3.15676356332363	2.15899823375993
H	1.90234551470615	2.61482112532248	2.90032412803216
H	3.56023458974588	3.13425185954554	2.46739848515631
H	2.14491679572233	4.19003943128065	2.08977367672626
C	-1.01377188036754	1.64223981577685	-2.02081142118942
C	0.27392940445441	1.12038848300271	-1.43318800158567
P	0.03249466347948	-0.00742068582104	-0.07276778846641
C	1.65359705146290	-0.70024731702171	0.35338311798826

H	2.01841663337567	-1.17756889097554	-0.57158315195993
H	2.29460142905343	0.18567191839831	0.47436013997110
C	-0.67470744451949	0.84607387707903	1.38459731930019
H	-1.29018518611025	1.65499827565388	0.95621404529836
H	0.18325331744438	1.34615006493978	1.85827773539954
C	-1.10880921522065	-1.33085787901338	-0.57185336072218
H	-1.51011779767106	-1.80802392407176	0.33702331910247
H	-1.95718094681078	-0.82531589350438	-1.06293882818206
C	-0.46797179593373	-2.35941126157715	-1.50554750427426
H	0.16760085224831	-1.85047609430180	-2.25383981431702
H	0.22692871625329	-2.98808910631762	-0.92078506886541
C	-1.50042382996489	-3.25137303740980	-2.18812292319733
H	-2.14699773914876	-3.73240429062480	-1.43151132151550
H	-2.16930397089055	-2.62018714050836	-2.80090603699552
C	-0.83622464178548	-4.31061910481638	-3.05982709132625
H	-1.57277839621592	-4.93017817673293	-3.59393717371852
H	-0.18155730244784	-3.83781250270030	-3.80900442441521
H	-0.20940246214057	-4.98239037960583	-2.45056100414300
C	-1.49049626684858	0.08273373938375	2.42958028015911
H	-0.86012486355930	-0.65594718223282	2.95328826406358
H	-2.29352360913089	-0.48963196950471	1.93855901692911
C	-2.11639437866332	1.03156239006529	3.45603223036517
H	-2.75388351812199	0.43941168376554	4.13383089031051
H	-2.79427600720341	1.72413589846795	2.92730854286090
C	-1.10778844934369	1.82851654573281	4.28076470529341
H	-1.62284046027775	2.46084461835863	5.01947278685105
H	-0.42115326228160	1.16085017795084	4.82821022325842
H	-0.49395111237599	2.49750905609378	3.65744107741769
C	1.71783113906191	-1.62246333161490	1.57507166736676
H	0.97666939952066	-1.32157592111330	2.33488152095853
H	1.44404307511924	-2.64644603353352	1.27024212093866
C	3.09660426929104	-1.60398780294918	2.24965749970280
H	3.16547989728338	-2.42735581145840	2.98010595004617
H	3.87697311411715	-1.80798906913155	1.49694463063456
C	3.37005047385441	-0.27664240048677	2.95620036143725
H	4.34499649314229	-0.27244942101826	3.46630810983735
H	3.36064832631691	0.56267847499655	2.24525941434663
H	2.59899405679871	-0.07283776815526	3.71852836973848
H	1.20400681352528	2.94831957819905	-1.98870721754996
O	2.67919383796927	1.56812961882860	-1.49881555378918

H	2.53801286298171	0.80150930327329	-2.12769641005980
H	0.84337805380994	0.32795554852605	-2.29762440339995
O	1.72477474041679	-0.43466554200103	-2.88751772396561
H	1.74852029922496	-0.37676174127230	-3.84797340517156

(2*R*,3*S*)-ix

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C	-0.75901629384274	0.45934605558983	-4.69522687273500
C	-0.92822810535726	0.79633474040668	-3.35252636670039
C	1.43315413433125	0.54186131421550	-2.98110493030281
C	1.60716274905603	0.21161016774370	-4.32230898908428
C	0.51124809691393	0.16521525149324	-5.18525257197515
H	-1.62581966797186	0.42755006171179	-5.36012327518180
H	-1.92936480632581	1.02677894892961	-2.97639196569079
H	2.30223896706746	0.55320551154644	-2.31892564641729
H	2.60800642090540	-0.02136581449989	-4.69473921159237
H	0.64867432772552	-0.09980575749276	-6.23648350671676
C	0.69420104996758	2.29542641207016	-0.26903677966788
C	2.03046439696441	2.65048503004287	-0.91009753383283
O	1.87215064690897	3.58225322270519	-1.85617331107149
O	3.09498849515347	2.15290826619781	-0.64470684875568
C	3.02580516386668	3.92570078629143	-2.60424741286171
H	3.38090438760407	3.06130212647527	-3.18573224828793
H	2.72618616968935	4.73272137929888	-3.28228105043930
H	3.83728966543958	4.26183247348201	-1.94324442834023
C	0.15892517794404	0.84039937701875	-2.47251975529252
C	-0.06830078007654	1.17827502958094	-1.02459941463122
P	0.29423324620262	-0.04771140328191	0.36876771764363
C	1.99583872586018	-0.70709984749661	0.51913979453899
H	2.30314595621254	-1.04186731128917	-0.48522958835224
H	2.62853179227180	0.14869153789678	0.78179796037035
C	-0.65425809583575	-0.12601810287829	1.94945662500769
H	-0.01741201709912	0.35913720720186	2.70322194288015
H	-0.79753347953608	-1.18074041264116	2.22667824506635
C	-0.56931160251912	-1.55836163931217	-0.42286641377381
H	-0.90095434227608	-2.22698914030056	0.38998063738096
H	-1.50123040223742	-1.16419746565593	-0.86686821372142
C	0.17394476991780	-2.40621024257332	-1.45936470533272
H	0.59251127280976	-1.77382564995983	-2.25791637336970
H	1.03770955667214	-2.89337893661549	-0.97630659997286

C	-0.69315759353275	-3.49312072943644	-2.10343707262900
H	-0.03699643849102	-4.16864213884449	-2.67817779919891
H	-1.14608772386711	-4.11623157821510	-1.31122976040429
C	-1.78364651749005	-2.96047444890052	-3.02813202559153
H	-2.34799819905825	-3.78145021098109	-3.49596566155821
H	-2.51030753401843	-2.33088965416411	-2.49074673158684
H	-1.35054008415083	-2.34563920649200	-3.83348702310213
C	-1.99300349894863	0.60892248867362	1.86720294879178
H	-2.62620823366776	0.15964610321320	1.07959569106166
H	-1.79120430515714	1.64853961091271	1.56261437965064
C	-2.77300064044672	0.62048147403553	3.18399302564485
H	-3.65731784532811	1.26744503871800	3.05768661848663
H	-2.15573602251713	1.10323868814373	3.96156132371472
C	-3.22328726914043	-0.75573125229921	3.66464995538145
H	-3.83435903061635	-0.67938786768713	4.57650784367100
H	-3.83089509651902	-1.26631700550795	2.89955279267463
H	-2.36989743416096	-1.41053489860670	3.90026573796990
C	2.13811673287982	-1.85559973968997	1.51959366438450
H	1.92092455625605	-1.48458807760130	2.53630933036075
H	1.38996243206095	-2.64026725454271	1.31446695096414
C	3.53248099773249	-2.48770336115657	1.50241096045018
H	3.54042832361565	-3.33631155357735	2.20710515189675
H	3.71566947349725	-2.92410024618346	0.50401686409250
C	4.66097946786171	-1.52325224879519	1.85448989540683
H	5.63114179819343	-2.04144570878180	1.88616771283479
H	4.74724723165306	-0.70599702550165	1.12225239716179
H	4.49647517830604	-1.06318421645564	2.84233022885798
O	0.81396323709907	1.68753121280829	0.95597653547969
H	0.10545989826042	3.23336683792805	-0.24254155289978
H	-1.14421443671210	1.37761579308560	-0.88809929075436

TS-(2*R*,3*R*)-ix

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C	-0.02597749571094	3.83371874518611	-0.02509972195901
C	-0.06663659783361	2.44674288329200	-0.16620331521931
C	0.89891713754756	2.19338134626030	2.01502217593839
C	0.95813671138678	3.57642467112607	2.15272591667531
C	0.49374055393256	4.40643449807500	1.13230950873379
H	-0.39785893666862	4.46867219853256	-0.83341720675578
H	-0.46676809062031	2.02977947284988	-1.09078982382116

H	1.24007179641814	1.54407989330372	2.82340554771296
H	1.35874270470108	4.00790724890091	3.07360682631790
H	0.53169150352841	5.49320775761931	1.24229008952884
C	1.71465674221737	-0.70247661042772	0.67304321255447
C	2.88366095204475	0.25561283658079	0.90065318922986
O	3.12756350678864	0.97493013659539	-0.20791366257028
O	3.50027490872125	0.38150569965740	1.92044322210146
C	4.06300264763210	2.03236092293889	-0.07525185182845
H	5.03480327587467	1.65525535545293	0.27293138828799
H	4.16175647956927	2.48428419096803	-1.06878486762502
H	3.69314721415132	2.77971020677810	0.64327012485647
C	0.39527031196949	1.59725562810253	0.84573140423552
C	0.36380352147924	0.08909225831741	0.81617508570174
P	-0.95147088501208	-0.73254555652771	-0.06437914880545
C	-0.77314372500599	-1.03199130075731	-1.87053139314941
H	-0.02726900394740	-1.84027128450926	-1.95399618815493
H	-1.73591853948861	-1.49439582798490	-2.14685993192345
C	-1.11389480040087	-2.45051896789171	0.53235953272828
H	-0.07444749371822	-2.81281901917091	0.61509112390560
H	-1.60521484272214	-2.99461761928499	-0.29176783059820
C	-2.53445137319692	0.12752400066404	0.20494535490505
H	-2.63719913434161	0.92071510867975	-0.55332739353601
H	-3.31275604080720	-0.62293321488324	-0.01955488749694
C	-2.71326418055482	0.69743511161227	1.61933723463670
H	-2.27967097398598	0.01878474573160	2.37219821785961
H	-2.12865879814112	1.62679936224021	1.70214337994133
C	-4.17694187285324	0.98184660892095	1.94653720788715
H	-4.60244613660685	1.65297844461878	1.17890185876971
H	-4.75428991799668	0.04217965192379	1.88130990671842
C	-4.35709293199950	1.59917711568900	3.32877616893533
H	-3.81618600247268	2.55491037041982	3.41050534000375
H	-5.41713112248663	1.79439903789725	3.54967487348461
H	-3.96669066819553	0.93191889249110	4.11284264461960
C	-1.83920296195742	-2.67729219858576	1.86162663569197
H	-2.87749829676051	-2.30319543928791	1.79559731962916
H	-1.31109978773894	-2.10034408943873	2.64140351335421
C	-1.86528590490847	-4.15410957856361	2.26100406005319
H	-2.27805220700717	-4.21928985498356	3.28097169228428
H	-0.82697292592923	-4.52005607889070	2.33847658527667
C	-2.67097752154847	-5.06223555412640	1.33545639915120

H	-2.70212034554871	-6.09473849570226	1.71492596996180
H	-3.71255573285294	-4.71245921489183	1.24165545481493
H	-2.24442174301748	-5.10817886777353	0.32033704051828
C	-0.44043500444747	0.10432067721318	-2.84040340762378
H	-0.71661781301868	-0.24168946610817	-3.85106157651800
H	-1.09984553891213	0.96754207957729	-2.64888267380166
C	1.02520891389991	0.54914839636756	-2.85834658019903
H	1.09726142625208	1.45098916481962	-3.48876942536526
H	1.35117943845657	0.86354403648842	-1.85509754186204
C	1.99355079165957	-0.50548156167785	-3.38391508468445
H	3.02234325754786	-0.11762753987125	-3.38744259717714
H	2.00303245202231	-1.41250770623591	-2.75808360145466
H	1.74326096849305	-0.81337869242712	-4.41204814720695
H	1.84681249011818	-1.05846922383884	-0.36771180739113
O	1.75865382302215	-1.79100693216559	1.51707664738549
H	1.27580076135716	-1.52437973935167	2.37443674572013
O	0.14465246614978	-0.86904911197621	3.23815754965536
H	0.38431373881045	-0.36248648254923	4.01973336092549
H	0.10315485266345	-0.21802350600807	1.98555020603545

(2*R*,3*R*)-ix

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C	-0.99661685592203	4.52213350440280	0.40896650436862
C	-0.41477808474177	3.28587425436434	0.13735247571253
C	-0.58835924816650	2.69369594939616	2.45956600142694
C	-1.17048934737864	3.92780678209723	2.73726736734796
C	-1.38819268594849	4.84157704463166	1.70879908195226
H	-1.14924797938566	5.24017569451260	-0.40101097645464
H	-0.11033485259899	3.04881789646333	-0.88638994224066
H	-0.42397118005086	1.97638442902924	3.26948619945402
H	-1.46076318830036	4.17458074046763	3.76154148203605
H	-1.86239117461844	5.80148869592369	1.92333405162015
C	1.69707060154282	0.80075154227065	0.19617052119301
C	2.80585451216140	0.40062254649243	1.16270982455961
O	3.99585457047232	0.85002417396509	0.76639476305276
O	2.65200575678080	-0.28166863323887	2.14557892081140
C	5.11039149862697	0.44736058558787	1.54761150519641
H	5.19013471943598	-0.64890044820773	1.57588684234508
H	5.99503937876632	0.88040614505988	1.06804825013915
H	5.01773253772324	0.81682716431466	2.57921985991495

C	-0.22103516098650	2.34308141927567	1.15503001821722
C	0.34161860903610	0.97986803447980	0.87701726626515
P	-0.47122933012276	-0.18077275177809	-0.37057862950552
C	-0.71475849057834	0.25835321335254	-2.15603126235695
H	-1.67774342563816	-0.19328175452077	-2.44256043086106
H	-0.91601917740514	1.34271609619456	-2.13662054531355
C	-0.50807305973230	-1.98330581615373	-0.02616784975434
H	0.26668420038976	-2.43451839744253	-0.66041374410333
H	-1.48918397047063	-2.36478252725329	-0.35120780403349
C	-2.27981447376198	0.23675274698912	0.02842433780411
H	-2.42591294410366	1.26637851776642	-0.34195670836860
H	-2.92490061691685	-0.39680979675914	-0.60375590898613
C	-2.75092449204801	0.17740252714650	1.48635962761465
H	-3.12713418264290	-0.83310542134599	1.72506336010935
H	-1.91004838040942	0.34440025179193	2.17903972702649
C	-3.83259486292703	1.21421830044107	1.79402157035123
H	-3.47233165308609	2.20199830907345	1.45593221188276
H	-4.73002499444114	0.99417211692095	1.18914178919689
C	-4.19728777848754	1.29736664958329	3.27058307522025
H	-3.32632128547861	1.61851929074166	3.86553585686978
H	-5.00270292671163	2.02654654681014	3.44685785644137
H	-4.53429277983971	0.32473667402683	3.66372804859297
C	-0.21583503561503	-2.34165550020224	1.43394555351367
H	-0.93797969647558	-1.84649186613101	2.10544668825341
H	0.77795455290795	-1.94519182774497	1.69511145959594
C	-0.24349110688775	-3.84803444572079	1.70273707340055
H	0.13851568271928	-4.02313828119781	2.72207721685692
H	0.46990254689891	-4.34897195456814	1.02490896131689
C	-1.62151552394071	-4.48867507664486	1.56637073353009
H	-1.58728118963448	-5.56405567194849	1.79796134292315
H	-2.34562789683417	-4.02424010798534	2.25573237491976
H	-2.02610354335947	-4.38925247664141	0.54656372776535
C	0.36668066065119	-0.02563979831571	-3.19690768131277
H	0.00339195242942	0.39341688727910	-4.15368572965280
H	1.27587472428733	0.52908504731741	-2.92686446659711
C	0.73957903371867	-1.49310539418959	-3.41078500718303
H	1.49677254666571	-1.53581637878117	-4.21167364398508
H	1.24783931406917	-1.86024505779796	-2.50548247934414
C	-0.42835094939460	-2.40198110959769	-3.78128346764447
H	-0.08445482739999	-3.42569163668676	-3.99288249662375

H	-1.17244163709835	-2.47507729030102	-2.97156430343970
H	-0.95398137150493	-2.03740375943217	-4.67944622654342
H	2.02676440855843	1.70932736564323	-0.34842816754263
O	1.40296180363651	-0.27316130304510	-0.63614834252139
H	0.35962574956720	0.39871333981945	1.81282328556945

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C	-3.61253102729825	1.66755581323191	-2.49891622728663
C	-2.74513571983932	2.07986593637893	-1.49844719927587
C	-0.88455600724236	1.21541573030250	-2.74540450894060
C	-1.76225328143072	0.82133633968813	-3.75495624753339
C	-3.13487523147205	1.03167891144887	-3.64946073320342
H	-4.68545527756144	1.85236083517408	-2.38369123606945
H	-3.14994274550551	2.59143105073353	-0.61837499412406
H	0.17642102856124	0.99870603009982	-2.88092086690801
H	-1.35228396680152	0.33179376983007	-4.64459720927837
H	-3.81691107481504	0.71287138179515	-4.44099999377289
C	0.91604766432347	2.37950377258992	-0.37793061787736
C	1.72037102694545	2.43201710654820	-1.66359377418444
O	1.65025181900216	3.65517626782806	-2.18523576863914
O	2.32734685435771	1.52673651924303	-2.17792062850054
C	2.25438108420267	3.83299554995710	-3.45613008291661
H	1.74484350534326	3.21854376764323	-4.21243948183639
H	2.14257111045735	4.89468052942310	-3.70187540944480
H	3.31773437768618	3.55450045642194	-3.43087948667209
C	-1.33883278330781	1.87465275727918	-1.57226292761500
C	-0.52214066409985	2.28983580530327	-0.45893969015163
P	0.67302944610061	0.01362603629113	0.90930488156500
C	1.89606672603734	-0.97985906701126	1.81548025105150
H	2.76798179715965	-1.09035240705407	1.15166655016589
H	2.22683684706275	-0.33907772697303	2.64912970463733
C	-0.59517533892535	0.47024327786825	2.14273934167692
H	-0.44097768680234	1.54417094263121	2.32713632426325
H	-0.33052088704967	-0.05355871187328	3.07680230032137
C	-0.01655517766431	-1.04557279130042	-0.37965958968053
H	-0.53025977325521	-1.87529213136438	0.13650476323523
H	-0.78925236432235	-0.47394242100306	-0.91673634933608
C	1.03843131938961	-1.55931727930488	-1.36220406586258
H	1.58663296944907	-0.69847055468454	-1.78025718371000

H	1.78902711569825	-2.17553783528321	-0.83423283267588
C	0.40959161412303	-2.38138697067216	-2.48536757260835
H	-0.12960028419862	-3.24232584556591	-2.05100310808600
H	-0.35614218938078	-1.76598533467790	-2.98684448666534
C	1.43126109439801	-2.87124579256109	-3.50431545222733
H	0.95312597436137	-3.46142794018452	-4.30050857874934
H	1.95040336121414	-2.02516336618839	-3.98083448075461
H	2.19892320640777	-3.50615935307656	-3.03249429026044
C	-2.04880970547786	0.19226352508853	1.75067941084110
H	-2.21754328700721	-0.89848769045828	1.71407468558807
H	-2.22879989560616	0.57550559500700	0.73532458554680
C	-3.05902179632844	0.82775125964828	2.70674371355121
H	-4.06987591656891	0.62076004730027	2.31883095138882
H	-2.94269747274861	1.92536408331775	2.66827333371149
C	-2.96220403876518	0.34834157006787	4.15231204305276
H	-3.76679751390947	0.77699757684365	4.76797955316938
H	-3.04564489430069	-0.74936401297723	4.21668304776602
H	-2.00826237873580	0.63746316885168	4.62183887324436
C	1.39510630652424	-2.33952816275561	2.30655192512485
H	0.44221457559402	-2.22149211928755	2.85490238009229
H	1.16530262235081	-2.97506547560782	1.43531665886476
C	2.39367795525327	-3.07438155414841	3.20558003069789
H	2.01064882322712	-4.09259516548112	3.38339172692600
H	3.34555509658309	-3.20129802716090	2.66123144050975
C	2.65137411980330	-2.39421376628084	4.54673867911285
H	3.32155980070383	-2.99971179978367	5.17461981657154
H	3.12406258161839	-1.40663183770569	4.42882951024129
H	1.71317546642081	-2.25004533907729	5.10706854790587
O	1.59927233569738	1.19331183339230	0.41075154152481
H	-1.05229232349427	2.87976947481798	0.29612971305299
H	1.23916307785777	3.22416875745716	0.24535678944582

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C	4.63388613404314	1.33150460045405	0.09314813950404
C	3.32094661424227	1.37951791806301	-0.36468308776835
C	2.61421579283177	2.20553858491286	1.77519952712792
C	3.92637503318106	2.14944259374688	2.22978380268349
C	4.95750604065673	1.70733841988450	1.39724983219997
H	5.42111091010454	0.99068400771502	-0.58659759007071

H	3.12031738956574	1.07537615656235	-1.39658612983412
H	1.82742123092479	2.56128560401011	2.44873633432728
H	4.15041579697364	2.45907877144142	3.25522037960979
H	5.98887561960169	1.66425399918677	1.75433572341645
C	0.43390543966687	1.47731910940647	-1.29260083689492
C	-0.67754059155411	2.38348700457460	-1.75832128955351
O	-0.22809441975774	3.31236217345245	-2.60267460424275
O	-1.82418880858428	2.32984201818417	-1.38268956715417
C	-1.16019746631291	4.30627695492493	-2.99565675748736
H	-1.51072600518887	4.87769713812629	-2.12354733252422
H	-0.62893951466497	4.96721013463461	-3.68975622319384
H	-2.03119955190989	3.85276110957220	-3.49032805800526
C	2.25386136413289	1.81884806591041	0.45864383337159
C	0.86548938264034	1.82461666540999	0.05912193907074
P	-0.36066264005703	-0.61521308598138	0.07819962548931
C	-1.68720858671148	0.08199490563857	1.10899661164013
H	-1.67034913032037	-0.49783394562079	2.04919810861066
H	-1.37800803429045	1.10318540107724	1.35682173286110
C	-1.02522706768178	-2.17976766555087	-0.59075936349461
H	-0.26234773804692	-2.56113736244994	-1.28919815706146
H	-1.88146351879236	-1.88918559903716	-1.21829691748654
C	1.03531127183260	-1.11899416180037	1.12574272886135
H	1.40020081869573	-0.23365546786580	1.66291826734810
H	0.61361155095060	-1.81393639093566	1.87411686670790
C	2.17614443536244	-1.77990051682646	0.35105269401954
H	1.85591730802800	-2.76476529523425	-0.03405736148283
H	2.42313839414489	-1.16502263911911	-0.52929732994591
C	3.42686168157624	-1.94122669073296	1.21201275134940
H	3.72284812745869	-0.94820792152669	1.58957876736848
H	3.18395180472572	-2.55400978023266	2.09866865019668
C	4.59135337652944	-2.56252256542151	0.45146137189879
H	5.48170167572190	-2.65723876135633	1.09056561528716
H	4.34124544554962	-3.56694908101736	0.07300714501549
H	4.86957653519031	-1.93918770419782	-0.41319171302311
C	-1.41238146312503	-3.25029560851512	0.42899730005172
H	-2.11177478763961	-2.83212895413079	1.17586527815912
H	-0.51800415468002	-3.56537968232230	0.99154499311155
C	-2.05029058216954	-4.48869619725538	-0.20830274507301
H	-2.15616714380351	-5.26348050160871	0.56895361072218
H	-1.35430633803907	-4.90635099048852	-0.95689171930681

C	-3.41047791589218	-4.23717092989389	-0.85267636909877
H	-3.83646638862196	-5.16903282789569	-1.25281746326946
H	-4.12873265486820	-3.83090666388852	-0.12188845114830
H	-3.34974350305868	-3.52437429807690	-1.68981416327873
C	-3.07722686697919	0.06146999820266	0.46830433664462
H	-3.00443842205268	0.49508577701252	-0.54063387678840
H	-3.42521179154600	-0.97933810168098	0.35996067416726
C	-4.11416041652865	0.84857906156253	1.27523773717760
H	-5.09688794570804	0.69552429620799	0.79908519644458
H	-4.20235610865949	0.41557959866426	2.28825571883120
C	-3.83221795008497	2.34602090114560	1.36992502386645
H	-4.66731485756282	2.87322571001718	1.85532813367021
H	-2.92823867152280	2.56087189052975	1.96138631525912
H	-3.67495793948312	2.78026595802475	0.37122362410640
H	1.23094025022573	1.47302249946183	-2.04781950366235
O	-0.10351665760944	0.07302601403200	-1.35236455405602
H	0.20089620895070	2.47561634891406	0.63760277472807

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C	-1.17779517941162	3.30770319368944	-1.11798156745949
H	-1.65116164489391	4.12839569660893	-0.56535882862532
C	0.14396173928731	3.49948255415542	-1.30209026500802
H	0.56557768491789	4.41856914028503	-0.88855524129943
C	1.16589422762805	2.66525492317217	-1.97322873722331
O	2.36637507322268	3.25439916159071	-1.85871970761715
C	3.45656105332776	2.56797396589621	-2.44948009252261
H	3.56786282034912	1.56288069905377	-2.01753247926820
H	4.34785432217446	3.17034495743239	-2.24089367552004
H	3.31340626898002	2.46395950831112	-3.53530896884741
O	1.02509448539518	1.61385845448210	-2.55177788489117
C	-2.15610880367250	2.26316541168845	-1.46818752461058
C	-3.47242861138093	2.47142978693989	-1.01663539392091
H	-3.70375306746154	3.37431755412142	-0.44377680231864
C	-4.48271341243374	1.55397996491074	-1.28192847935787
H	-5.49624597607642	1.73880020510329	-0.91786244914573
C	-4.19571318746861	0.40236403109815	-2.01308563557387
H	-4.98487272612568	-0.32356892339854	-2.22632017457524
C	-2.89737058497138	0.18192627049383	-2.47052799130282
H	-2.66682545048883	-0.71872626110659	-3.04503107233084
C	-1.88327114934640	1.09802881437019	-2.20508053915341
H	-0.87022788155088	0.92086089110187	-2.56383648942794

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C	-1.16373435565092	3.32066771404992	-1.18174713630809
H	-1.66611029582094	3.83005357268453	-2.01269973059384
C	0.17553773122433	3.34532999858833	-1.19462330050435
H	0.79481689716166	2.87401256272496	-0.42816923377706
C	0.88771434406839	4.03872833653594	-2.29310648327646
O	2.21630940832834	3.95392882703181	-2.13718546780428
C	2.99984098999981	4.58746449763316	-3.13444378336389
H	2.80579842488963	4.14809008537356	-4.12406003791319
H	4.04663155044251	4.43035237785539	-2.84996992070337
H	2.77598643814512	5.66324040731103	-3.18382165617309
O	0.36733674627816	4.61207564811893	-3.21797763455119
C	-2.03645096909988	2.68740825780160	-0.18148215626479

C	-3.42542738133133	2.74973662700867	-0.36087111076756
H	-3.82732461416113	3.26576306215416	-1.23738356050455
C	-4.29350335420204	2.16449611002776	0.55754964917609
H	-5.37326913042062	2.22401915011421	0.39985455442372
C	-3.78406781529929	1.50679971833046	1.67477155754895
H	-4.46241593296206	1.04829563904956	2.39866945537327
C	-2.40285115853416	1.43747246806961	1.86727066816295
H	-1.99721808204878	0.92476311414026	2.74289777277532
C	-1.53791244675403	2.02136006821707	0.94943714905381
H	-0.45968699425275	1.95994175717905	1.11509040599161

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P	0.99146188446890	0.17594659210178	0.66715357983351
C	1.81508830576719	-0.98498562171170	1.81528825511246
H	2.73586768838612	-1.29287089468859	1.28963061552837
H	2.15570120475046	-0.34013692427227	2.64252053572270
C	-0.54590539224391	0.73687079571719	1.48930357021674
H	-0.74627542628467	1.71926280364175	1.02930619781362
H	-0.25965504470069	0.95115957349829	2.53291426616394
C	0.47071372207151	-0.79698966840610	-0.78946785591290
H	-0.16563401592085	-1.64654685560832	-0.48908915597395
H	-0.16508817637915	-0.11748685122165	-1.38398116683576
C	1.66422087783321	-1.25688963413587	-1.62653014731349
H	2.33136835570053	-0.39284590330105	-1.78552396748352
H	2.25398874532222	-1.99860190164656	-1.05781857849941
C	1.25969808774718	-1.86185190404172	-2.96956761890397
H	0.56867598650561	-2.70657778321795	-2.79812849840373
H	0.68313855509188	-1.11272409310621	-3.54049886778810
C	2.44999786429814	-2.33183455191180	-3.79811052260505
H	2.12985393015634	-2.74073244291690	-4.76819860544810
H	3.14746612429760	-1.50285069099339	-3.99801796860334
H	3.01520234694347	-3.12009279500152	-3.27493362760791
C	-1.78809790822613	-0.15549479546050	1.41651465619784
H	-1.54225866833481	-1.18570142367149	1.72654190735882
H	-2.11639114352787	-0.22837341375735	0.36683184093154
C	-2.95829607276451	0.34795010352087	2.26644054214822
H	-3.85089630000236	-0.25065609309199	2.01973370475340
H	-3.20025524489965	1.38456469086108	1.97338702582935
C	-2.71306794554948	0.28193887091355	3.77108977133711

H	-3.60049354679731	0.60648213123753	4.33468160806040
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H	-1.87693535110277	0.92700731935105	4.08326058968105
C	1.04759818714282	-2.20295871818856	2.32839537800826
H	0.19136098351271	-1.87351496365595	2.94317948054151
H	0.61650230503916	-2.75771918795685	1.47748301594167
C	1.90627358283358	-3.16669822707488	3.15377087012569
H	1.30023118877179	-4.05638738516491	3.39436249023925
H	2.74055958088212	-3.53067153829736	2.52844520727049
C	2.45770721763643	-2.56927993022299	4.44482301875118
H	3.01880803575053	-3.31984203258346	5.02147901710516
H	3.14198426210523	-1.72896769117142	4.25022150883476
H	1.64564059021975	-2.19403540993861	5.08880162953875
O	1.89962670890232	1.31391564170785	0.30738760939163

TS-*E*-iv

63

C	-0.34645491	3.73113071	0.23942297
C	-0.03138357	2.47756828	-0.28051474
C	0.41534311	1.66843497	1.94272467
C	0.10412681	2.92285369	2.46320485
C	-0.28710258	3.95618826	1.61396107
H	-0.63459391	4.53985065	-0.43679860
H	-0.06428587	2.32211280	-1.36177051
H	0.71870796	0.85791640	2.61068453
H	0.16605303	3.09079767	3.54140619
H	-0.53807386	4.93866643	2.02108721
C	1.92329348	-0.45044944	0.25087879
C	3.00803784	0.29509422	0.93476761
O	3.54890147	1.22276642	0.13698562
O	3.38211355	0.07841572	2.05837048
C	4.60154959	1.98892930	0.70350010
H	5.43068903	1.34119898	1.02232169
H	4.93691077	2.67688590	-0.08045655
H	4.24245674	2.55345691	1.57633670
C	0.34102831	1.42399746	0.56356289
C	0.70116232	0.06153657	0.05367744
P	-0.58053554	-0.99140996	-0.76068293
C	-0.54391616	-1.16643922	-2.58506413
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C -1.09294600 -2.50868818 0.12441363
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H -2.19343166 -2.53547839 0.07914062
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H -2.87001035 -0.47463750 -1.21847249
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H -1.90119425 0.56415594 1.50979015
C -3.81245319 1.27421652 0.84086530
H -3.41947372 2.22853835 0.44813056
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C -4.38513941 1.49516336 2.23593050
H -3.60555859 1.84796268 2.92996196
H -5.18914925 2.24632455 2.22841200
H -4.80234512 0.56362709 2.65084793
C -0.57051254 -2.57859485 1.56025533
H -0.85517595 -1.67642530 2.13174767
H 0.52752201 -2.59013301 1.50421723
C -1.04988838 -3.82353160 2.30831244
H -0.51541840 -3.87073671 3.27136483
H -0.73638506 -4.71998109 1.74608726
C -2.55333245 -3.87245017 2.56627645
H -2.82815676 -4.75737343 3.16006991
H -2.89110281 -2.98177452 3.12206358
H -3.13398202 -3.91970913 1.63127824
C -0.20173634 0.07731404 -3.41360669
H -0.40143269 -0.19125925 -4.46548943
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C 1.23699865 0.59945432 -3.30934491
H 1.35166634 1.41299976 -4.04588767
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C 2.30726955 -0.46290767 -3.52792093
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H 2.19609715 -0.96019432 -4.50579312
H 2.04402449 -1.50915880 -0.13332667
O 1.22989903 -2.66452821 -1.00002117
H 1.89711814 -2.83301381 -1.67276981

E-iv

63

C	-0.01255800	3.91358300	-1.00773900
C	0.45952900	2.61058900	-0.88883600
C	-0.17757000	2.58175500	1.43343000
C	-0.65270700	3.88692600	1.31496700
C	-0.59145700	4.54779200	0.09013600
H	0.06796900	4.43385200	-1.96503900
H	0.92111400	2.12332500	-1.74673000
H	-0.24387600	2.06280200	2.39318300
H	-1.09100700	4.38394900	2.18421900
H	-0.99852900	5.55715200	-0.00877300
C	1.74184900	0.09111700	1.24660900
C	2.56140600	1.01774800	2.08669900
O	3.30629100	1.84238300	1.34366600
O	2.58908400	0.99568900	3.28947400
C	4.15969700	2.72020800	2.06520400
H	4.84610100	2.14717200	2.70611800
H	4.72292200	3.29060100	1.31722100
H	3.56973000	3.39733100	2.69892600
C	0.35467900	1.91499200	0.32205700
C	0.76362300	0.48116300	0.41787600
P	-0.21200700	-0.80129100	-0.57996900
C	-0.43912300	-0.37523600	-2.37411800
H	-0.91306100	-1.28272800	-2.78593900
H	-1.20861900	0.40451100	-2.43424600
C	-0.80791400	-2.50180900	-0.08855400
H	-0.43730500	-3.18391700	-0.86710500
H	-1.90768200	-2.49680900	-0.13212200
C	-1.90170200	0.00455700	-0.10542900
H	-1.89880900	1.06131900	-0.42166300
H	-2.66202600	-0.49425700	-0.73562300
C	-2.32749800	-0.06922600	1.36362100
H	-2.66949700	-1.08803100	1.61814500
H	-1.45975900	0.11693900	2.02273500
C	-3.42770100	0.93778500	1.70203000
H	-3.07773400	1.93767300	1.38981600
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C	-3.82079200	0.98489800	3.17598500
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C -0.91727600 -4.31681500 1.71647300
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C 1.38499600 -1.06770500 -4.11235100
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C 0.43831000 -1.62862900 -5.17111000
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H 2.06215300 -1.05248300 -1.03139600

E-v

62

C 0.03704358 4.35363284 -0.92013019
C 0.49285046 3.03821143 -0.93476317
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C -0.40051053 4.18301990 1.43796359
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P -0.14210566 -0.85499836 -0.62948195
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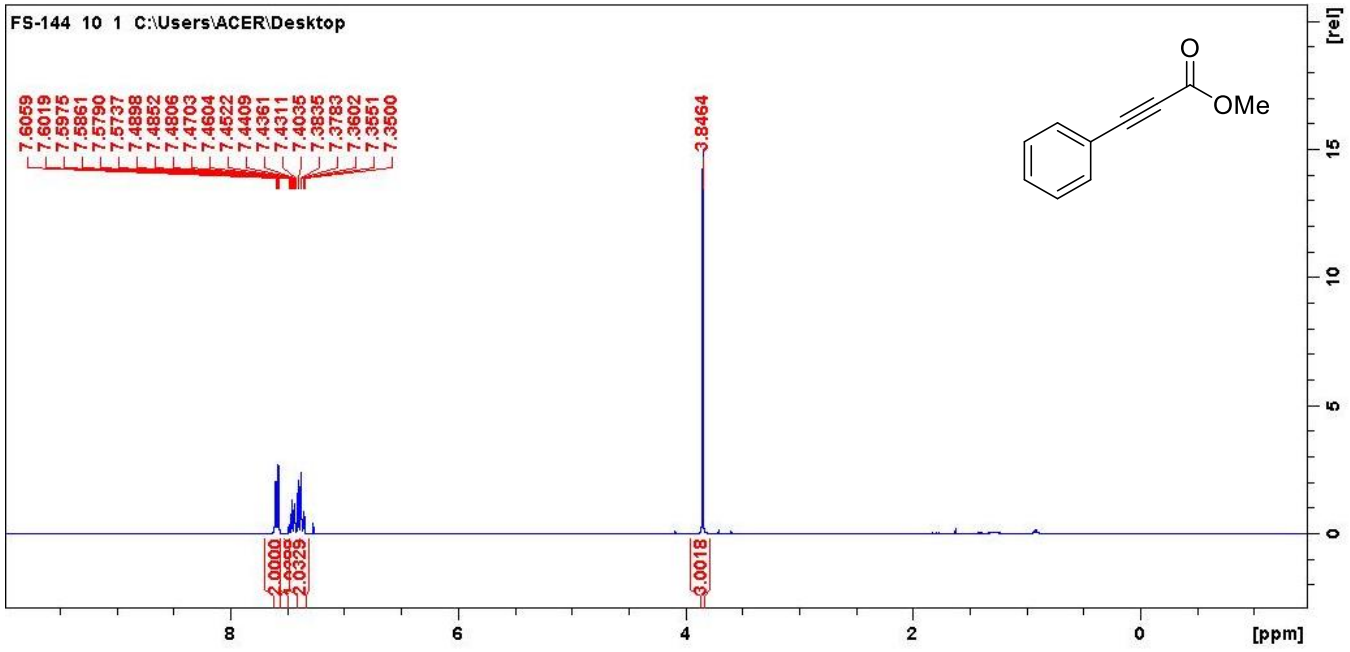
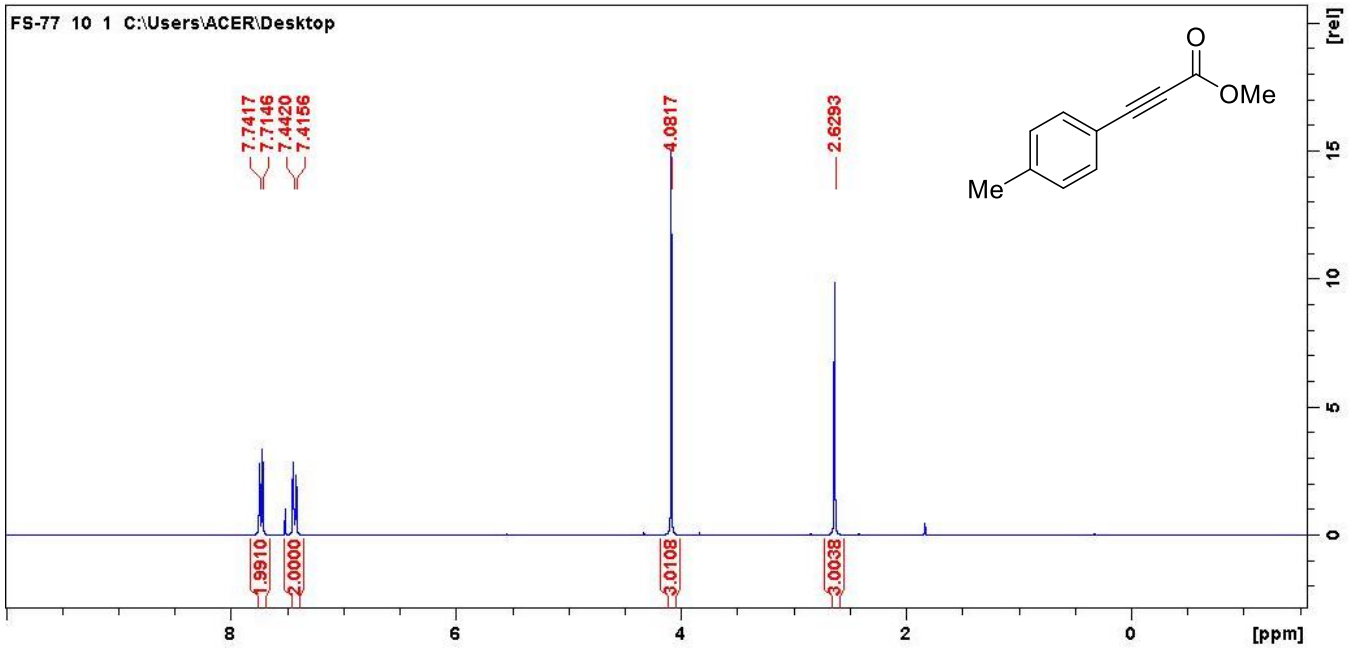
Copies of Spectra

NMR of 2-ynoates

Methyl 3-phenylpropiolate (P-3)



Methyl 3-(*p*-tolyl)propiolate (P-5)



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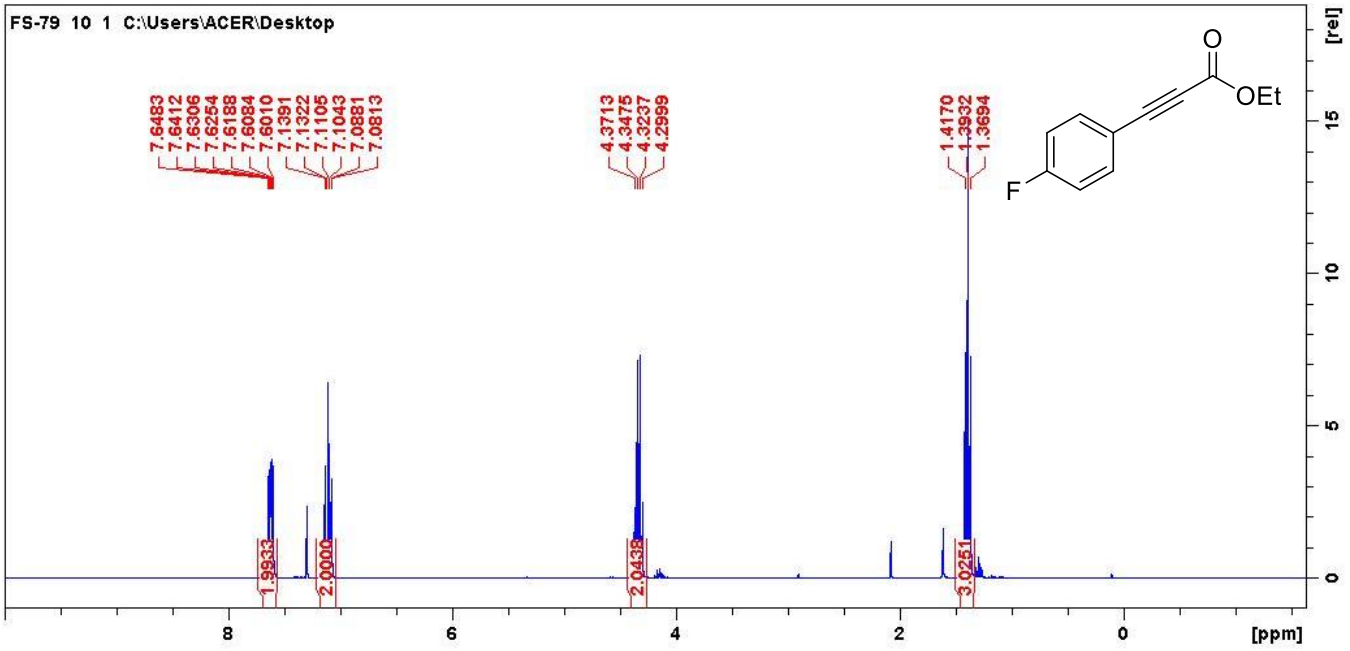

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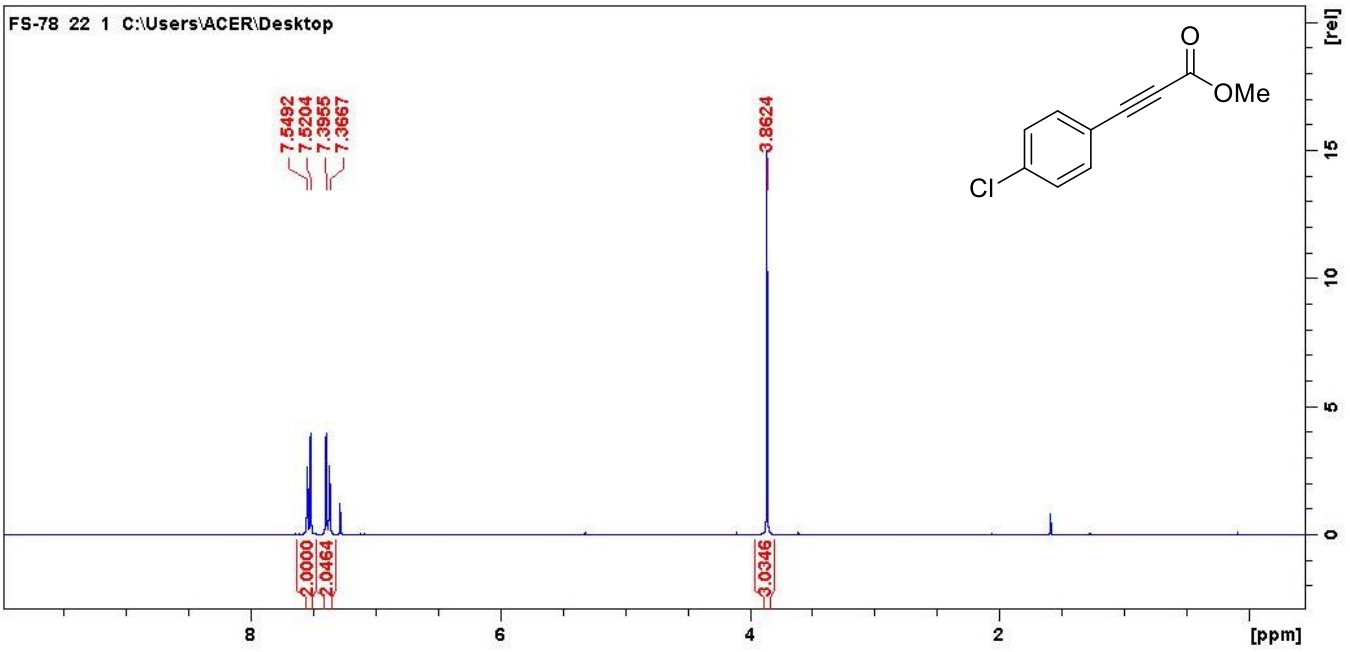

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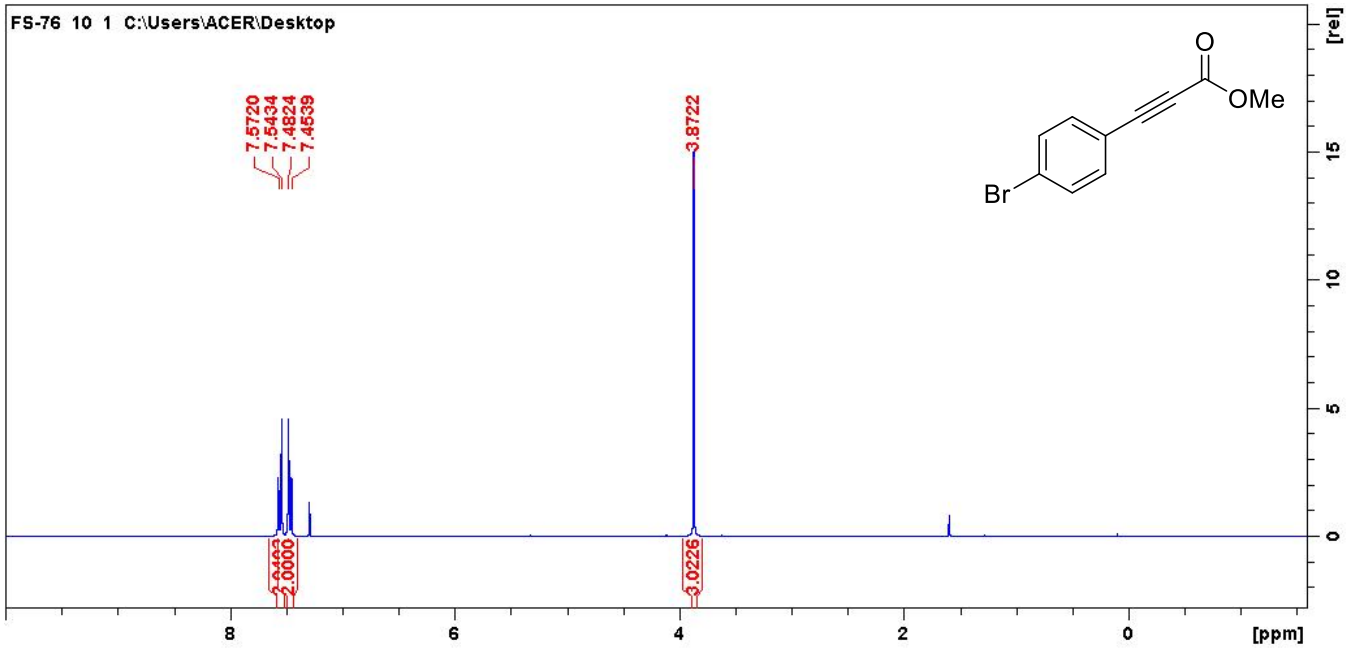

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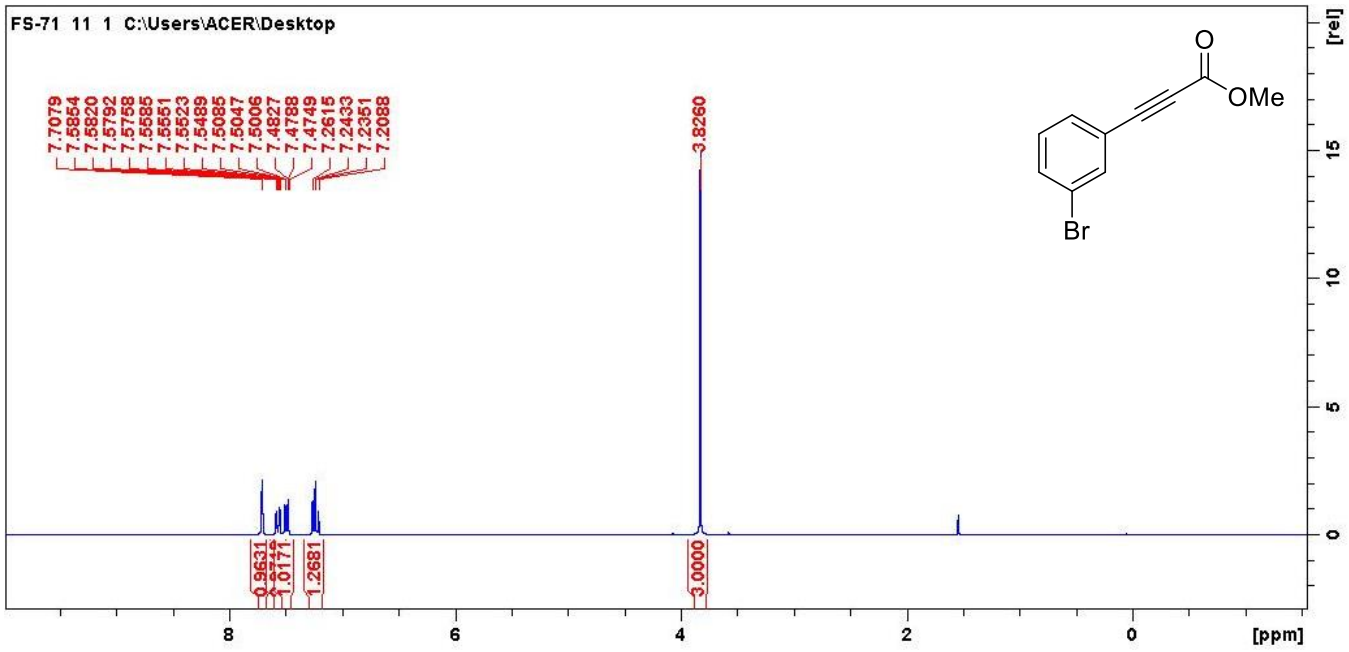

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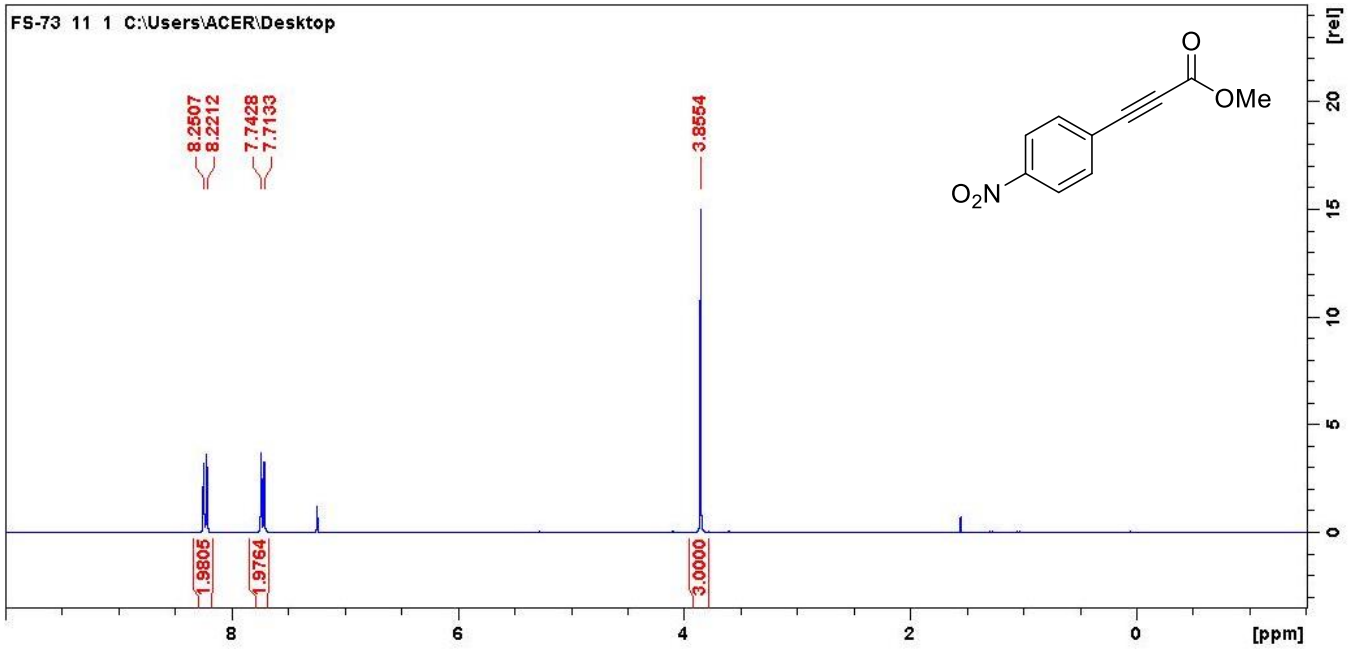

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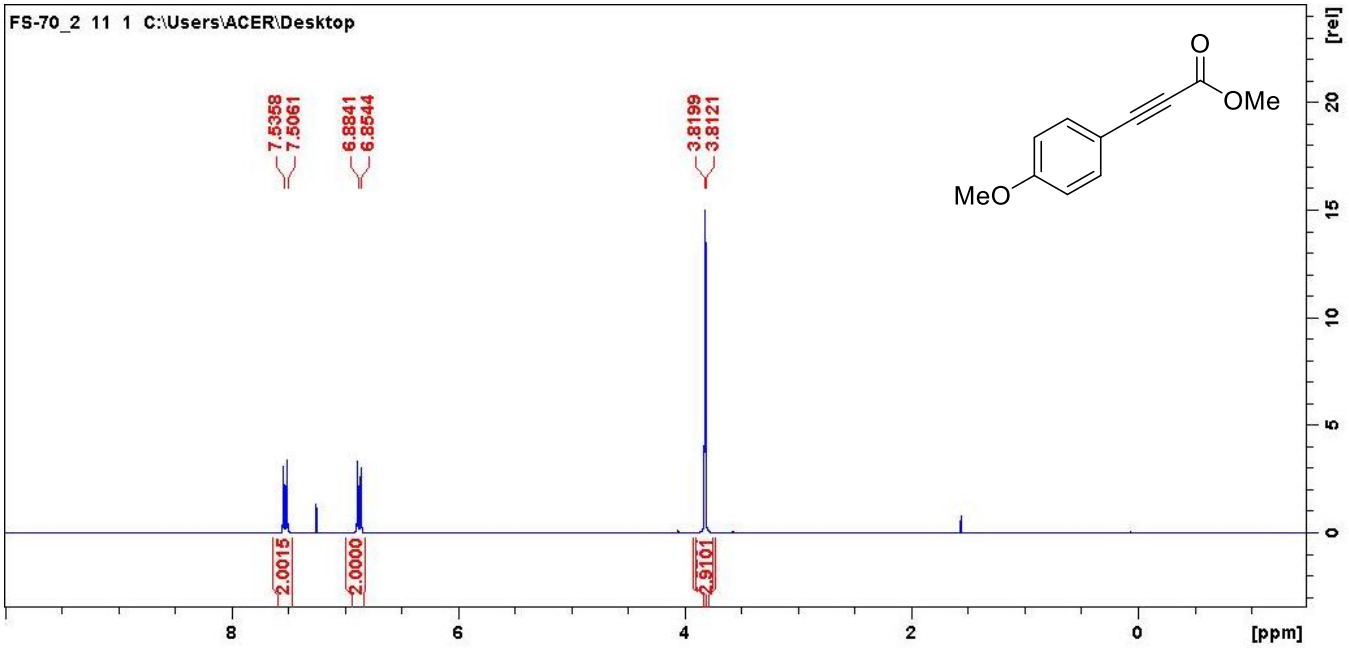

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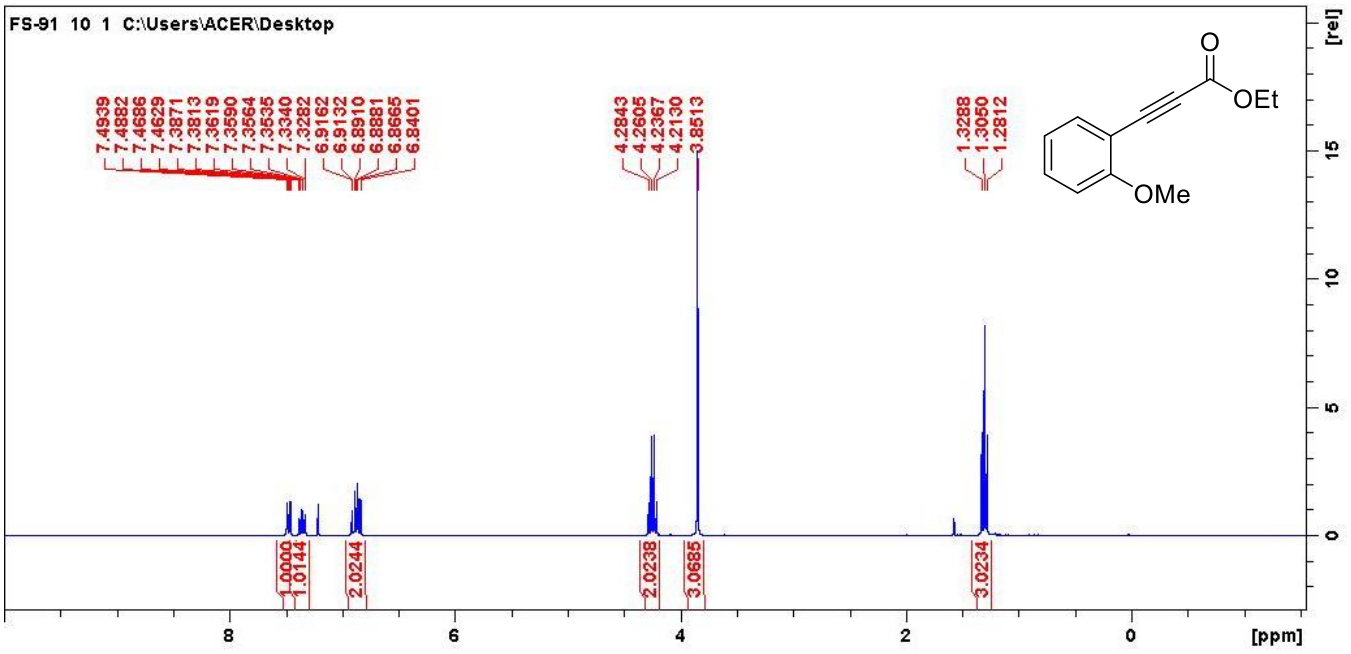

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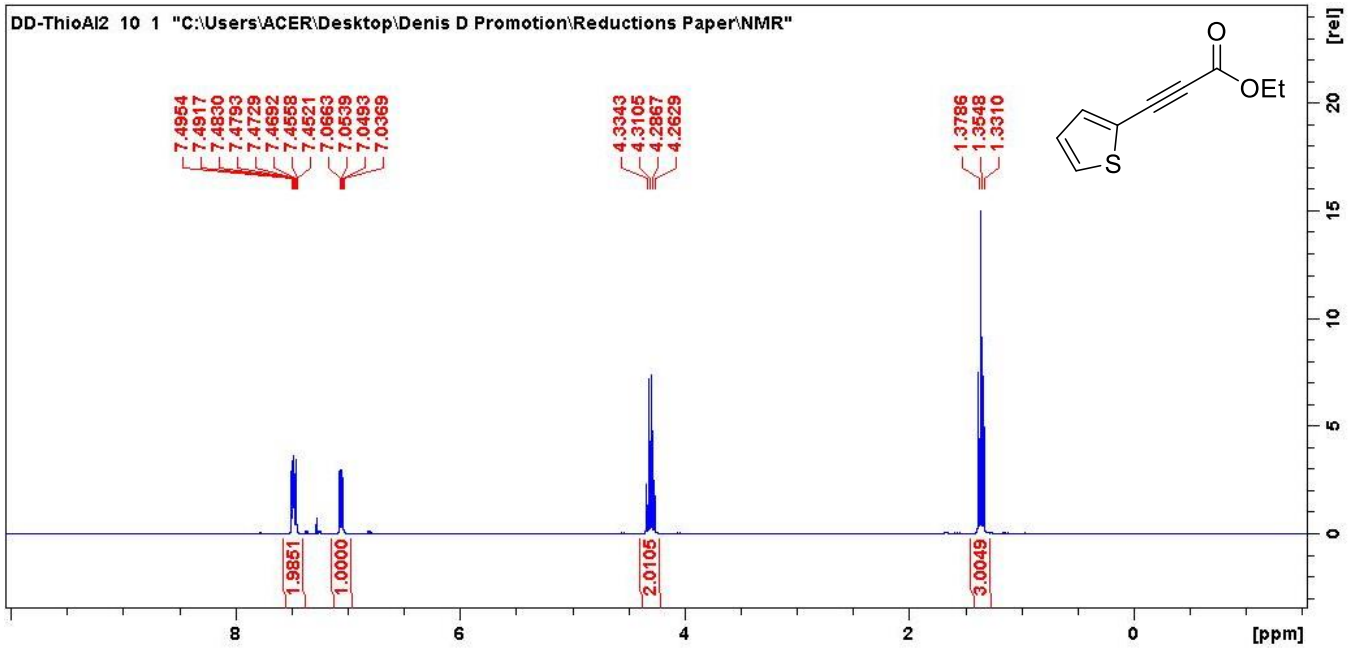
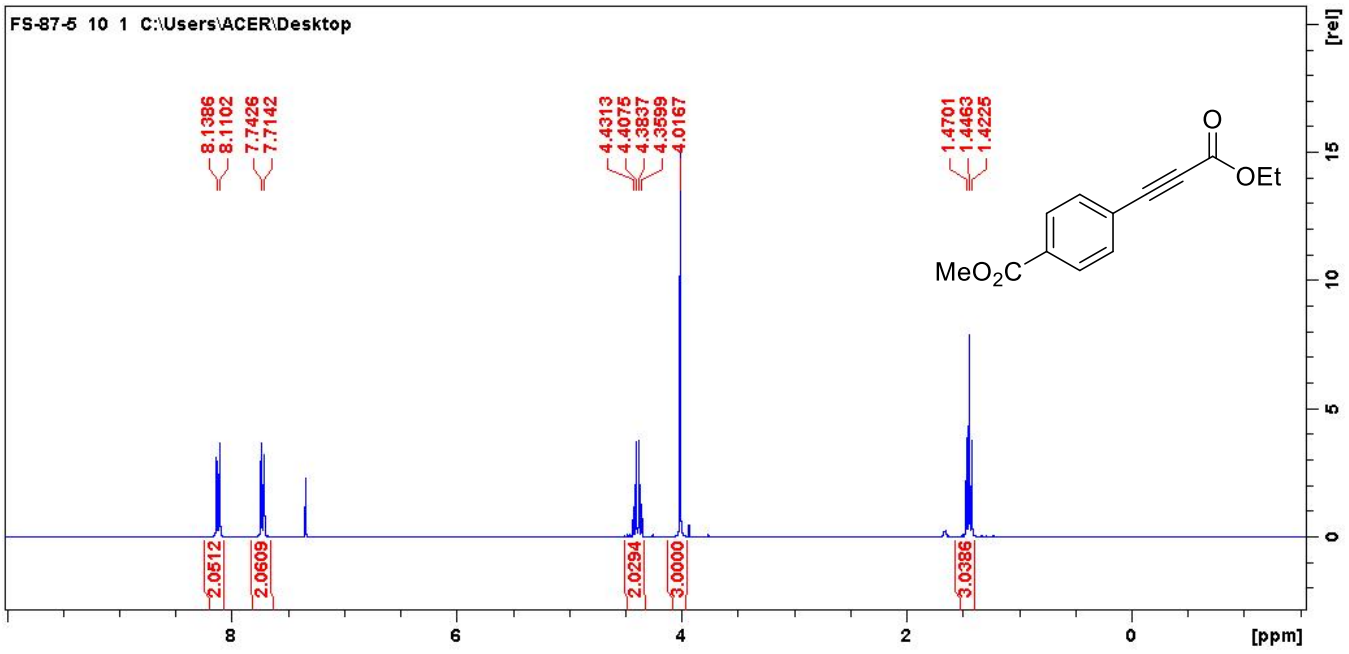
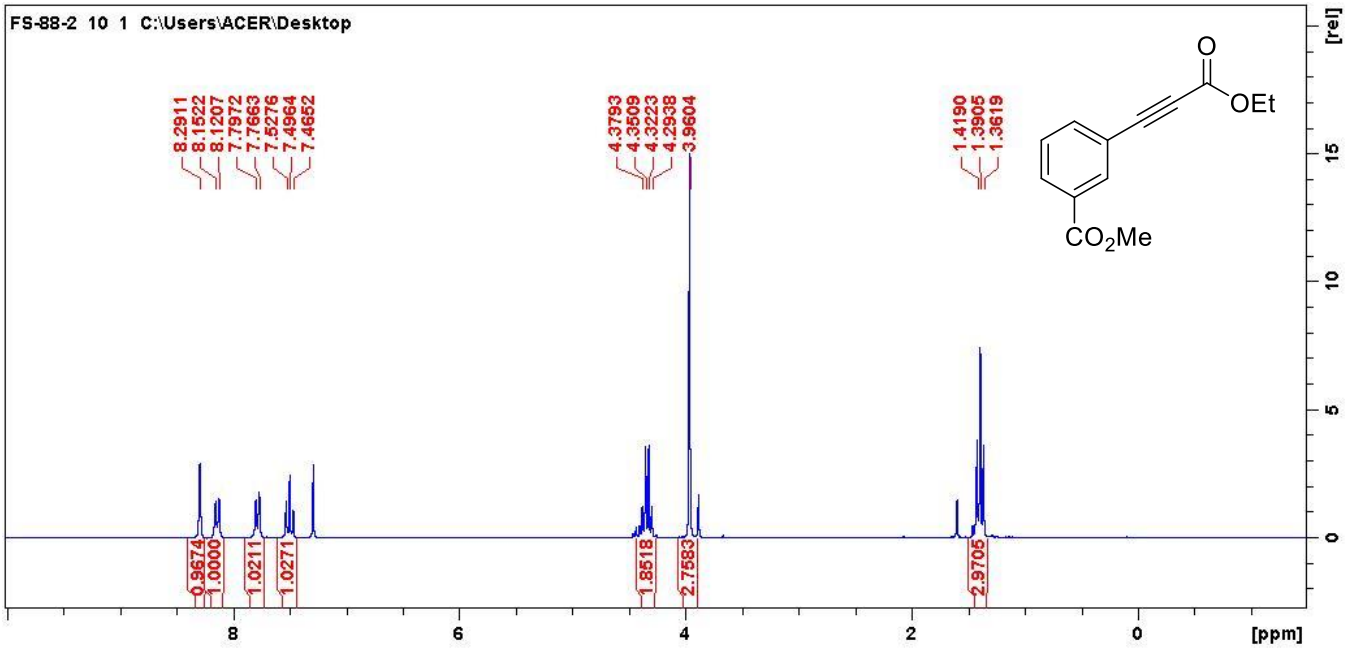


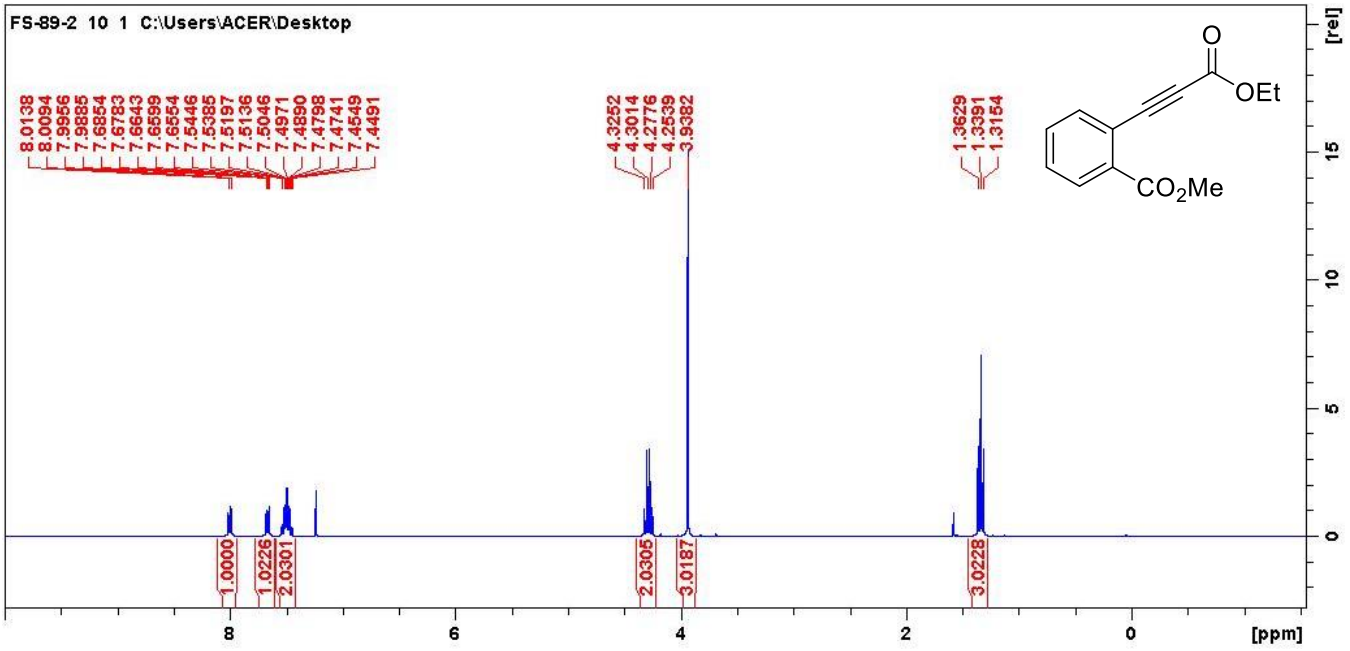
Methyl 4-(3-ethoxy-3-oxoprop-1-yn-1-yl)benzoate (P-15)



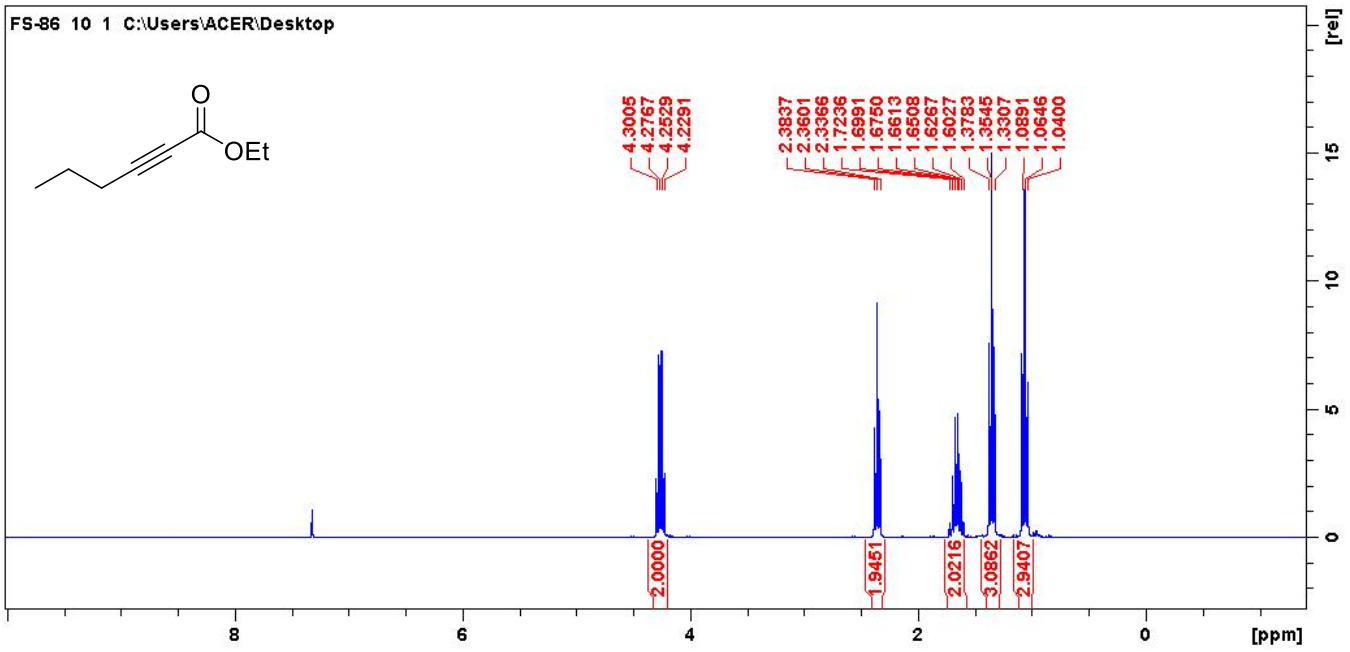
Methyl 3-(3-ethoxy-3-oxoprop-1-yn-1-yl)benzoate (P-16)



Methyl 2-(3-ethoxy-3-oxoprop-1-yn-1-yl)benzoate (P-17)

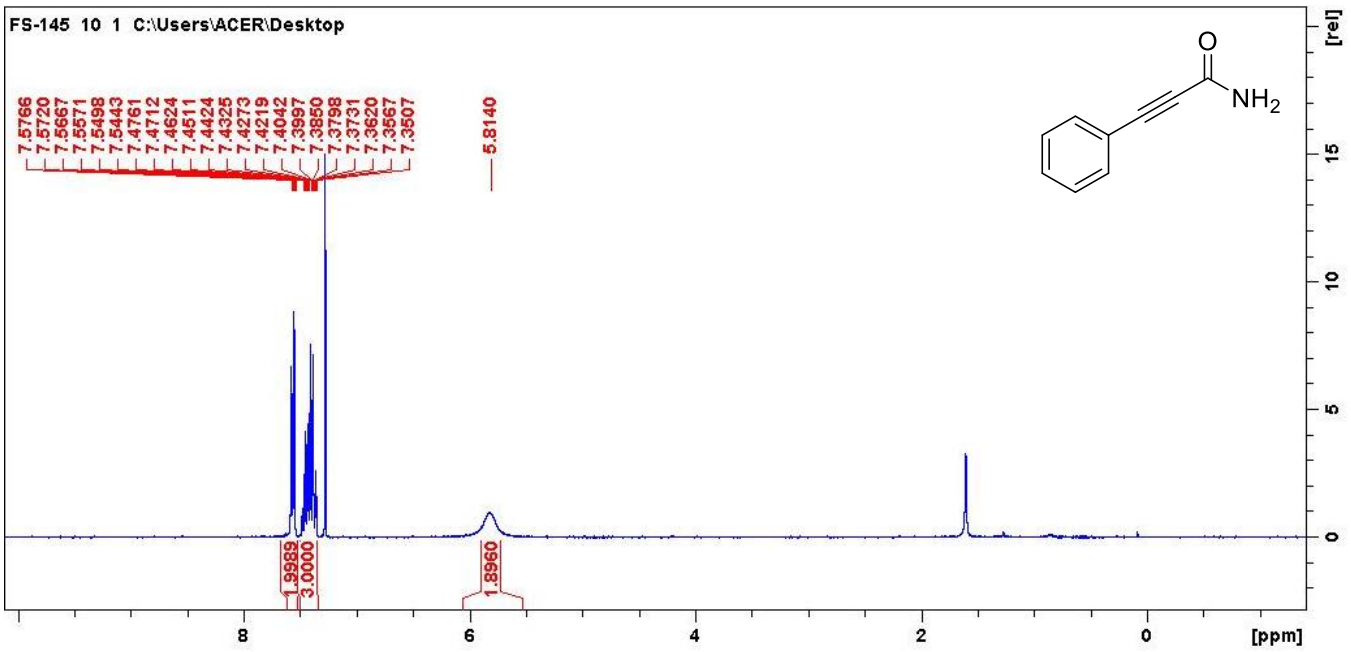


Ethyl hex-2-ynoate (P-18)

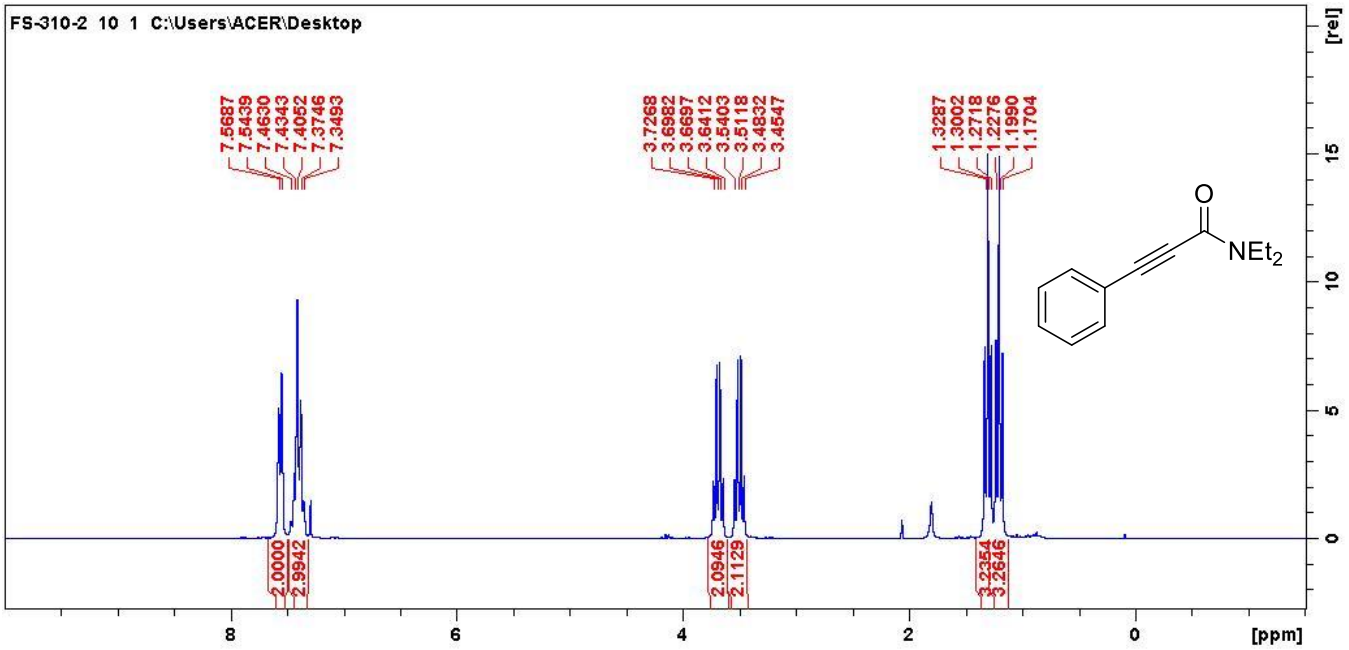


NMR of propynoic amides

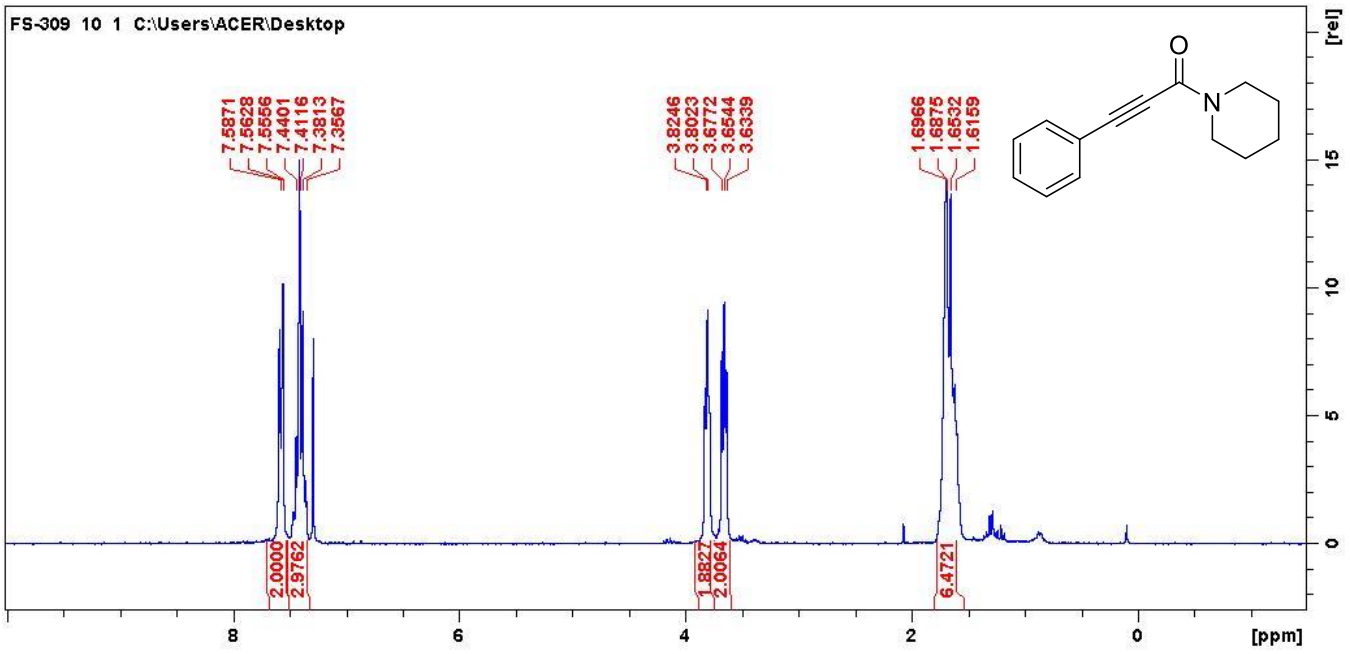
3-Phenylpropiolamide (P-20)



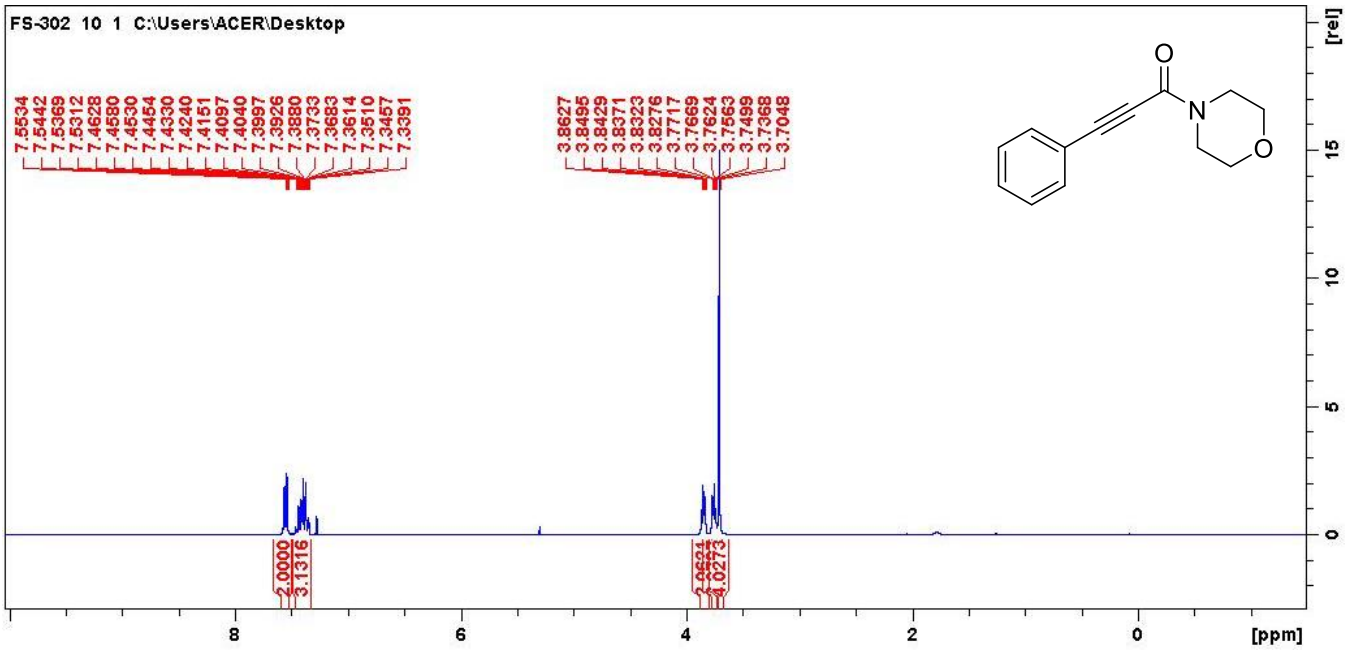
***N*,*N*-Diethyl-3-phenylpropiolamide (P-21)**



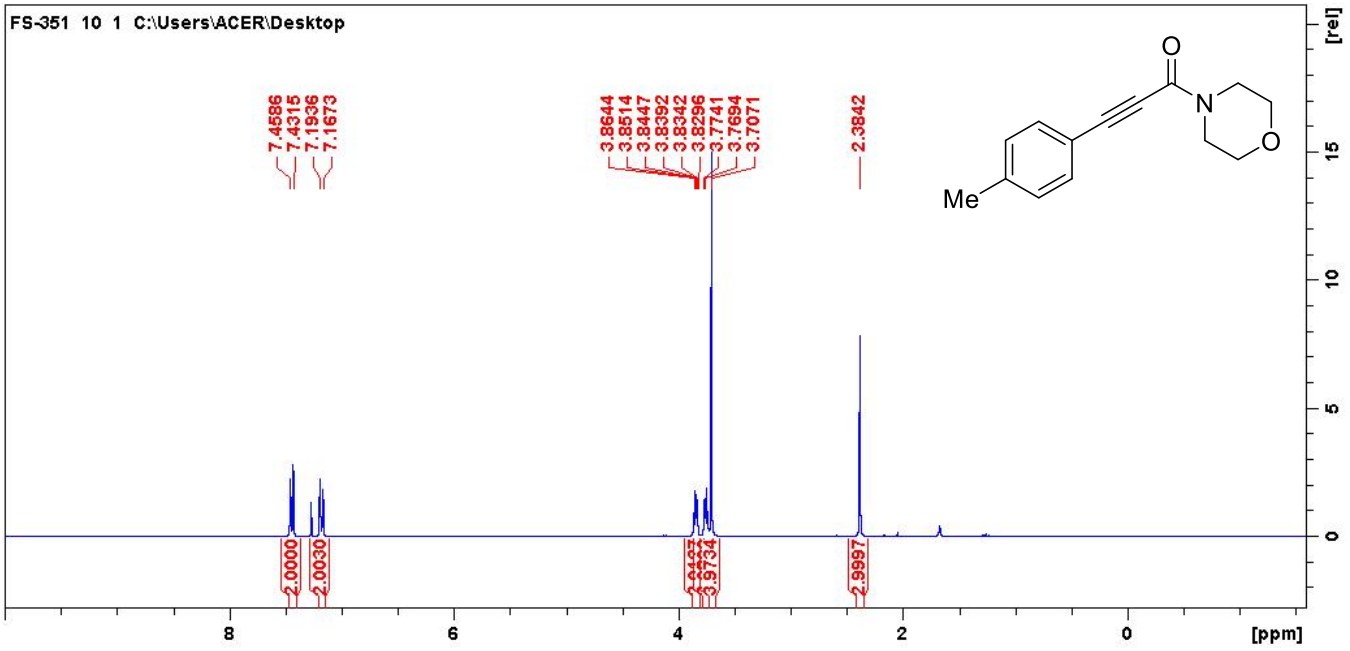
3-Phenyl-1-(piperidin-1-yl)prop-2-yn-1-one (P-22)

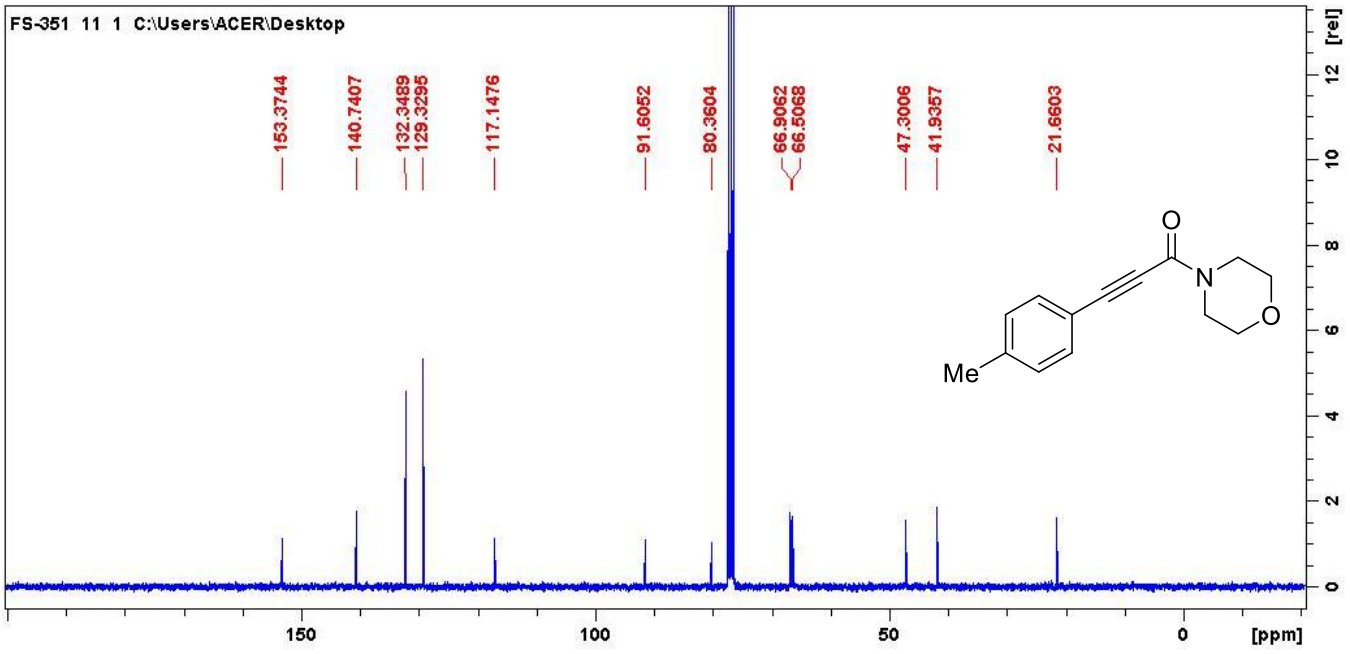


1-Morpholino-3-phenylprop-2-yn-1-one (P-23)

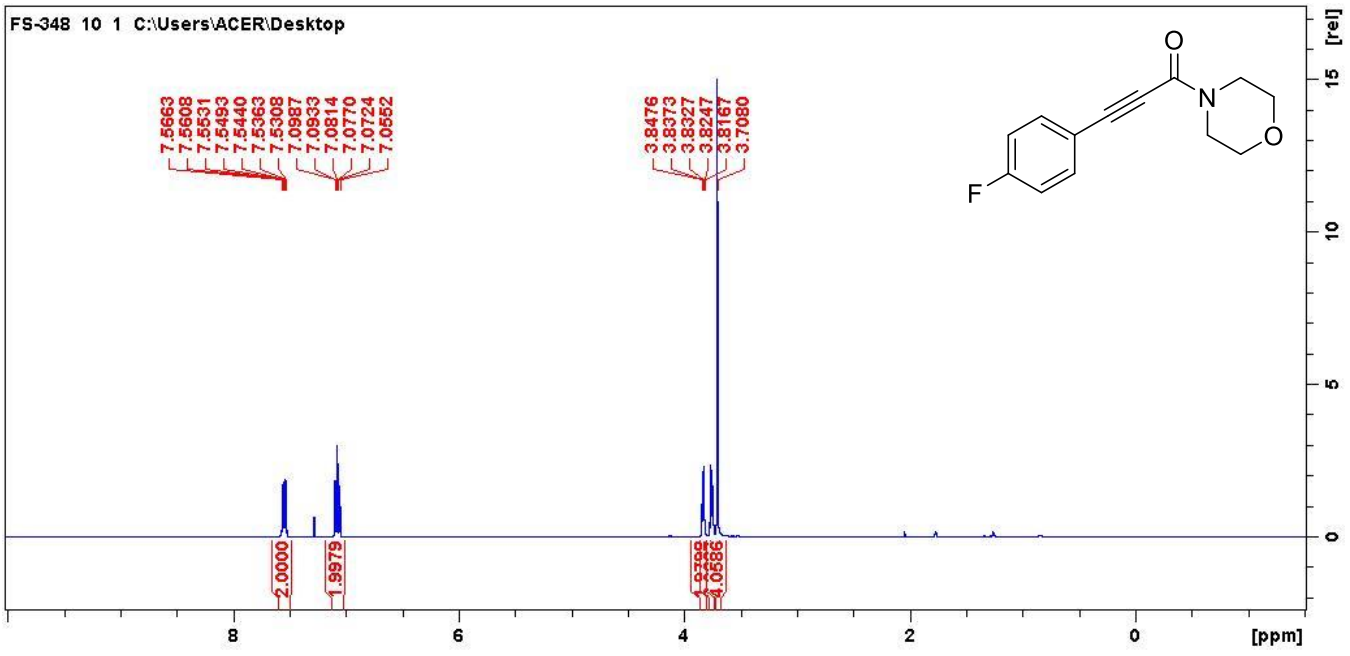


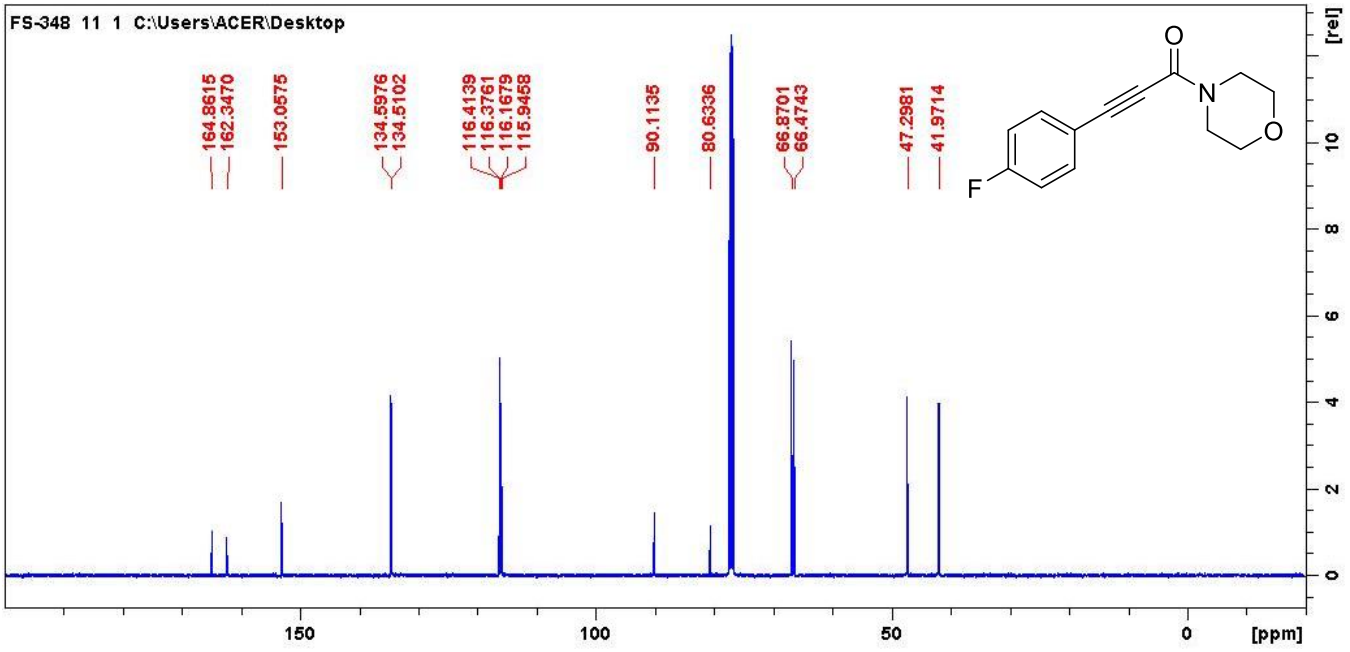
1-Morpholino-3-(*p*-tolyl)prop-2-yn-1-one (P-24)



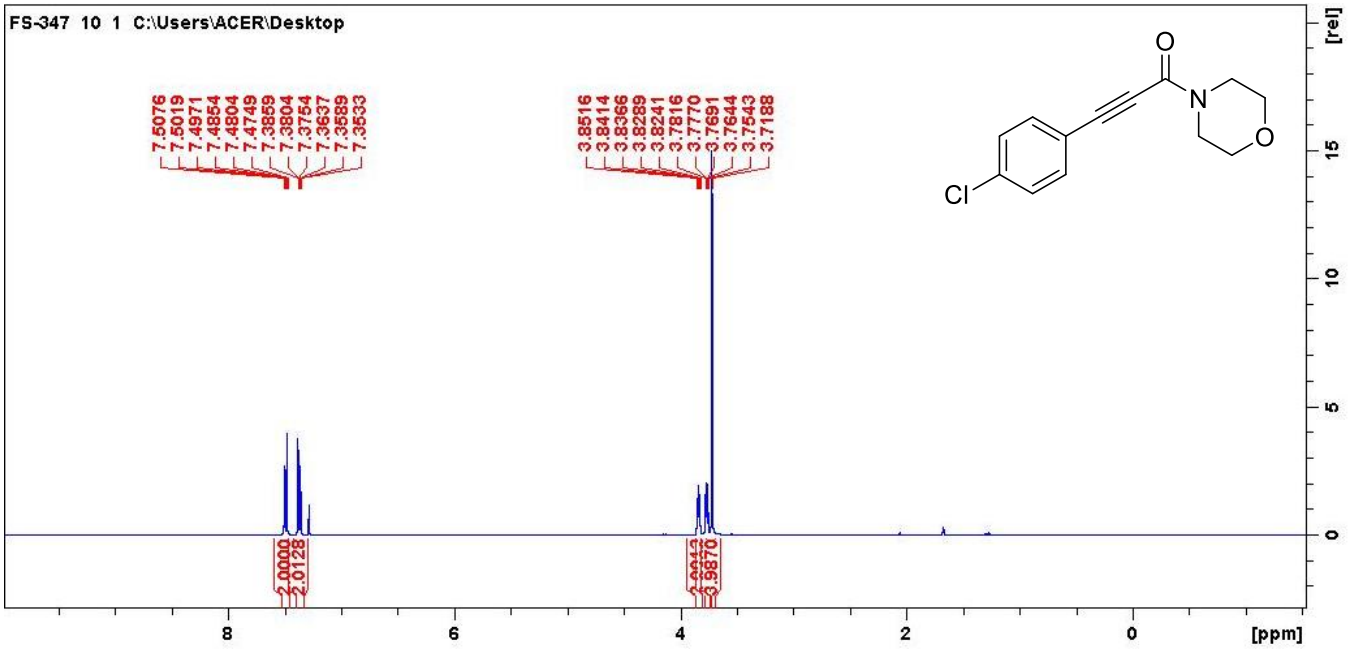


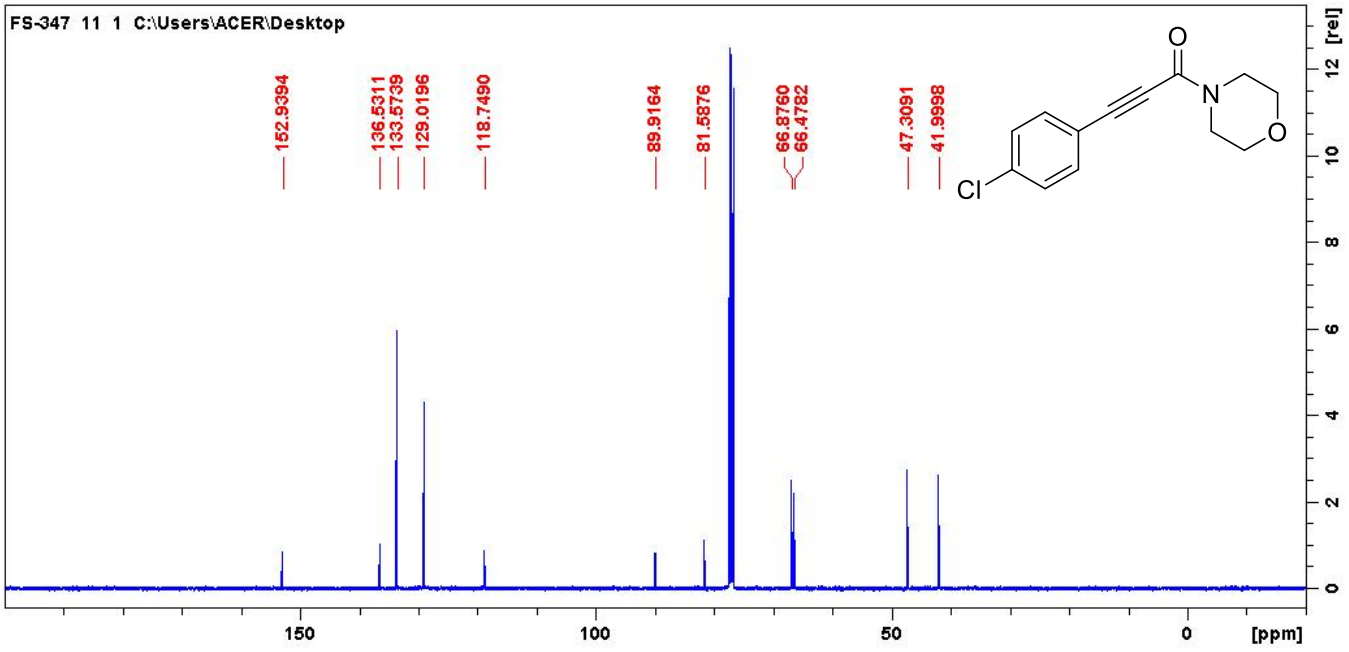
3-(4-Fluorophenyl)-1-morpholinoprop-2-yn-1-one (P-25)



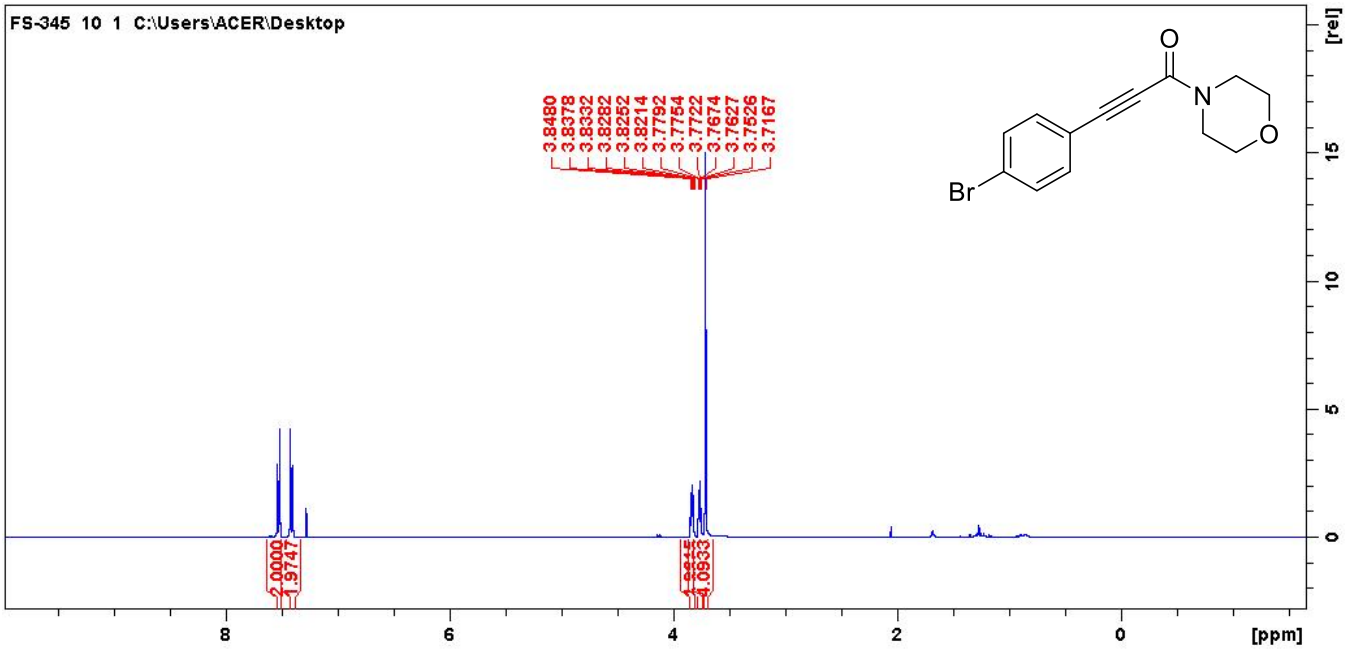


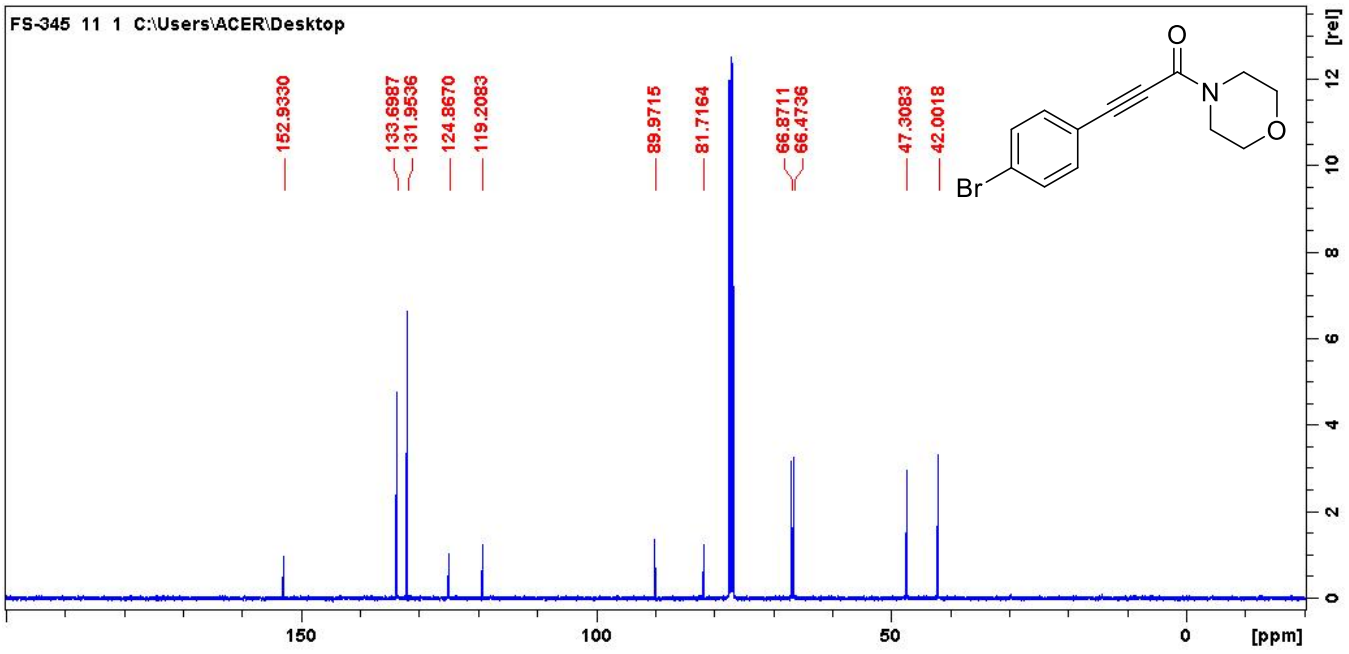
3-(4-Chlorophenyl)-1-morpholinoprop-2-yn-1-one (P-26)



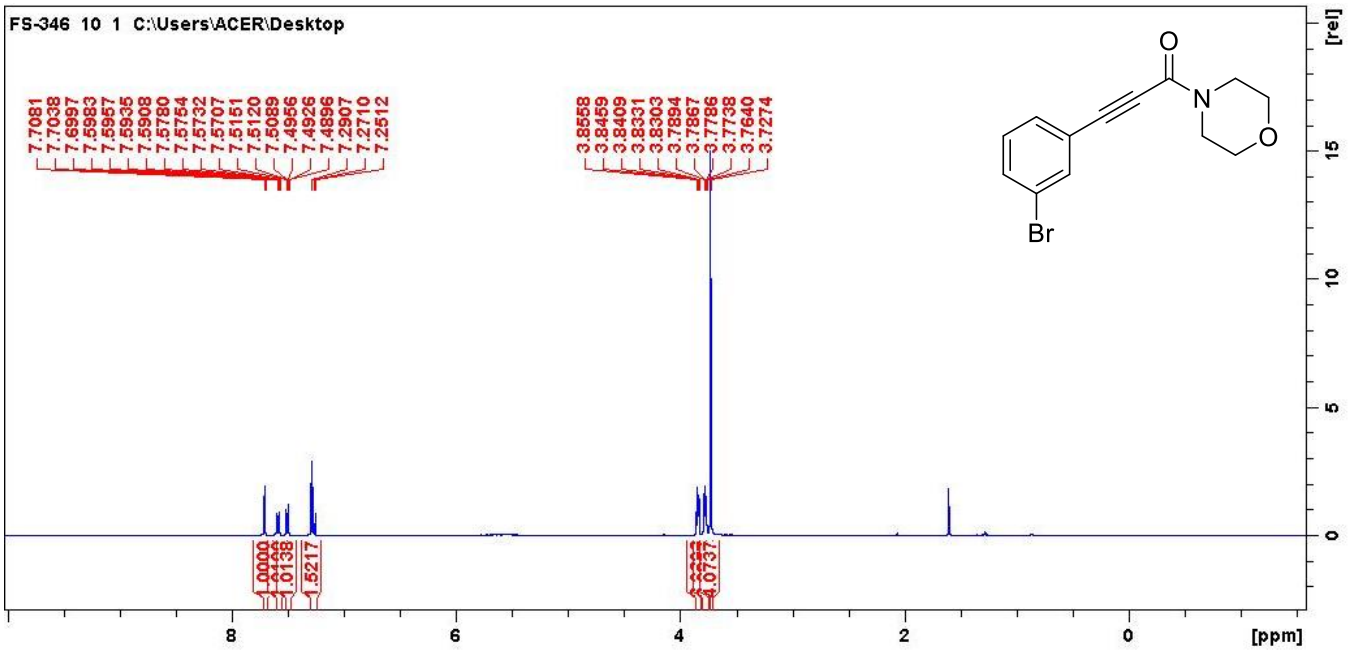


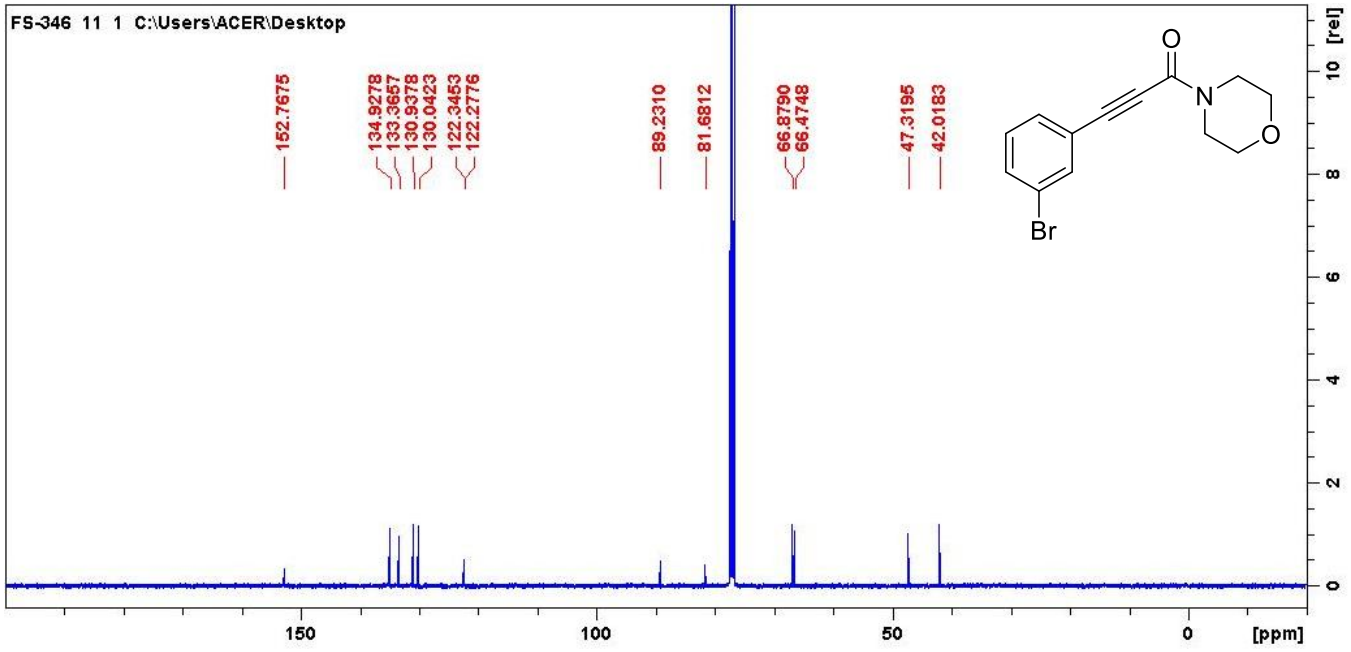
3-(4-Bromophenyl)-1-morpholinoprop-2-yn-1-one (P-27)



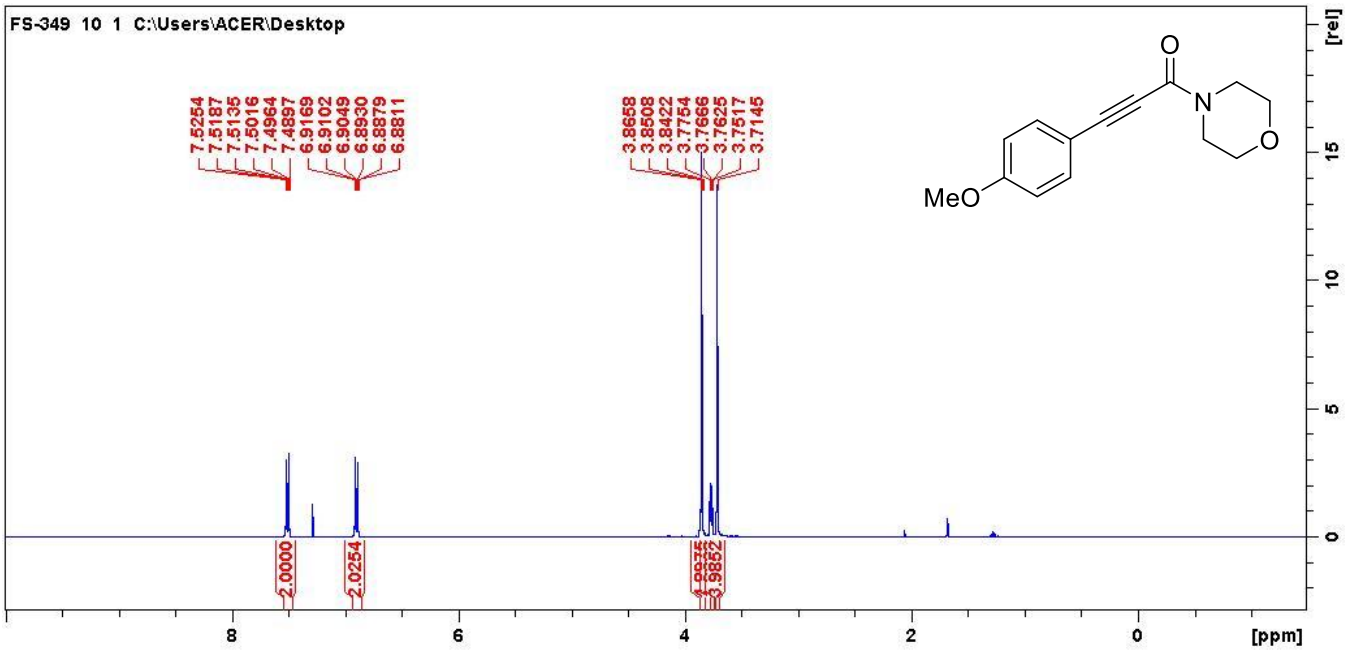


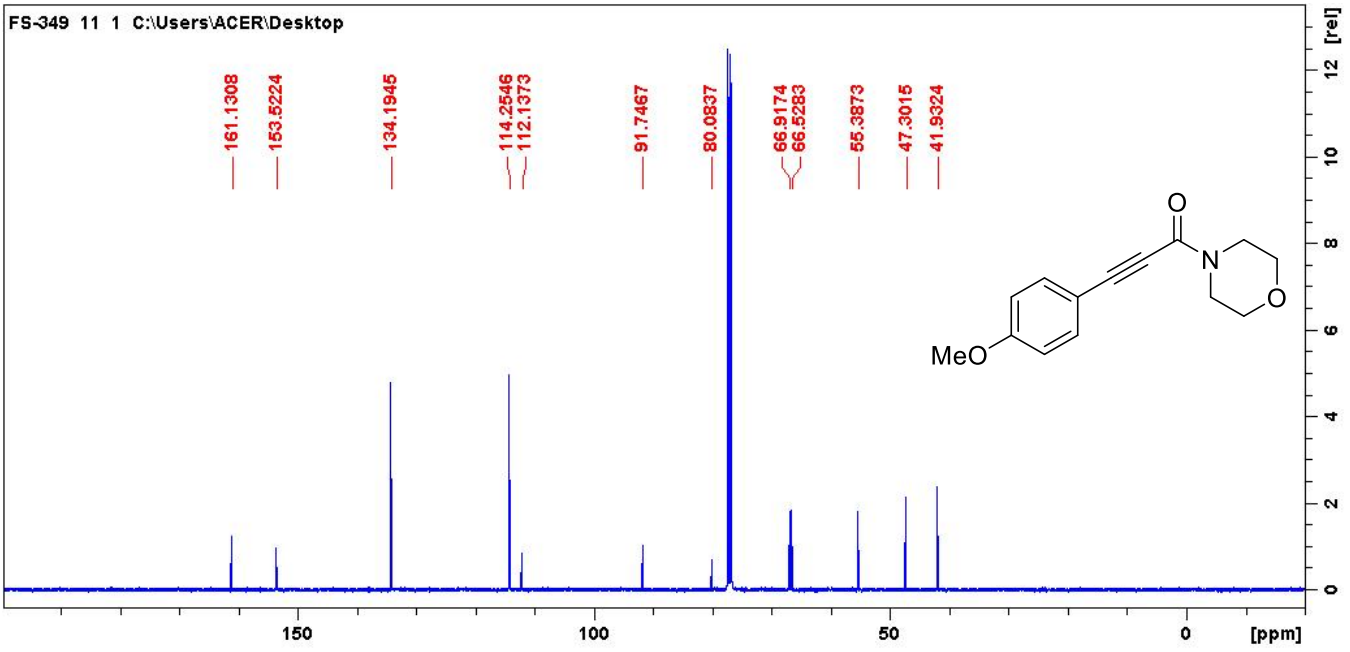
3-(3-Bromophenyl)-1-morpholinoprop-2-yn-1-one (P-28)



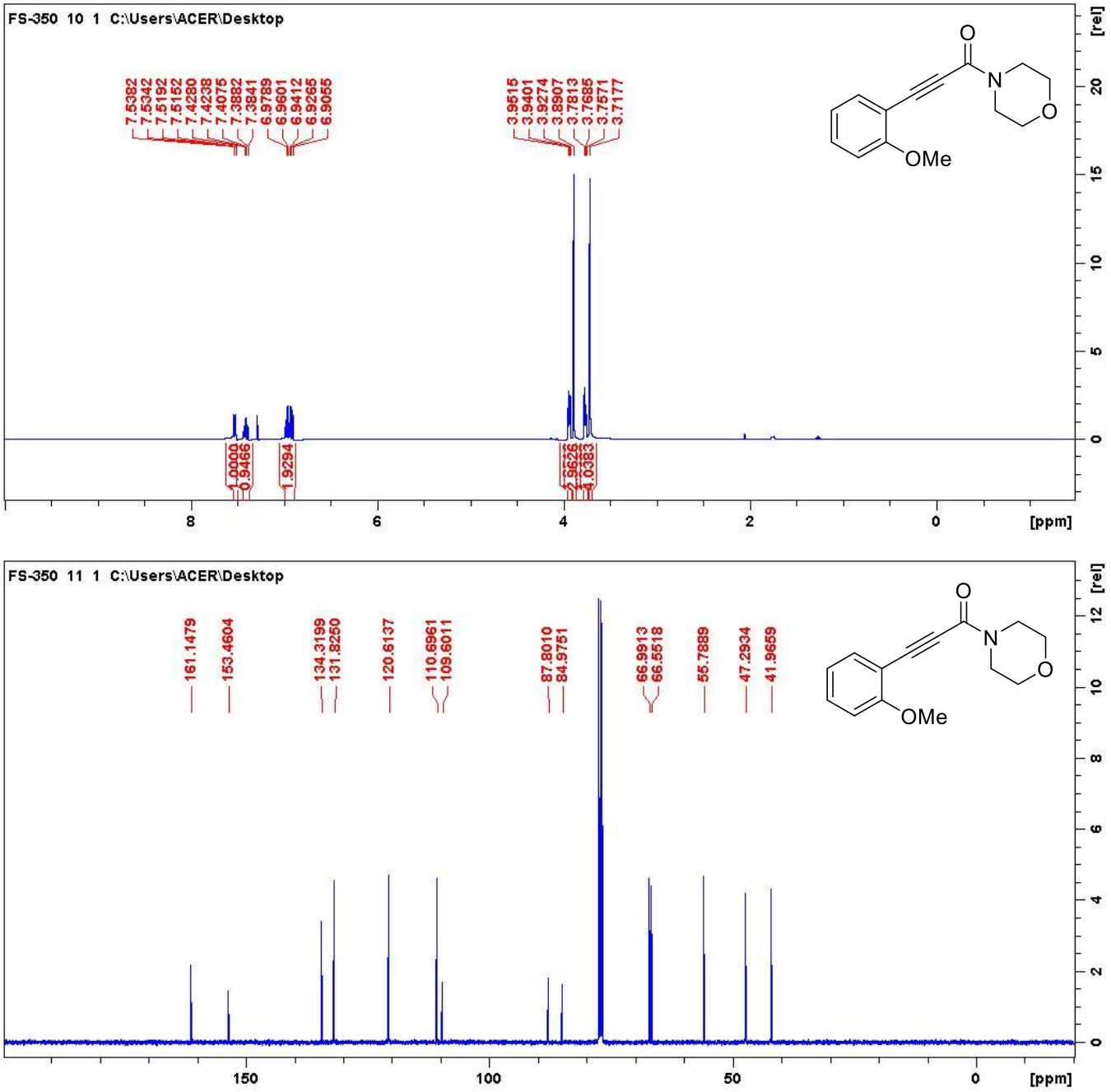


3-(4-Methoxyphenyl)-1-morpholinoprop-2-yn-1-one (P-29)

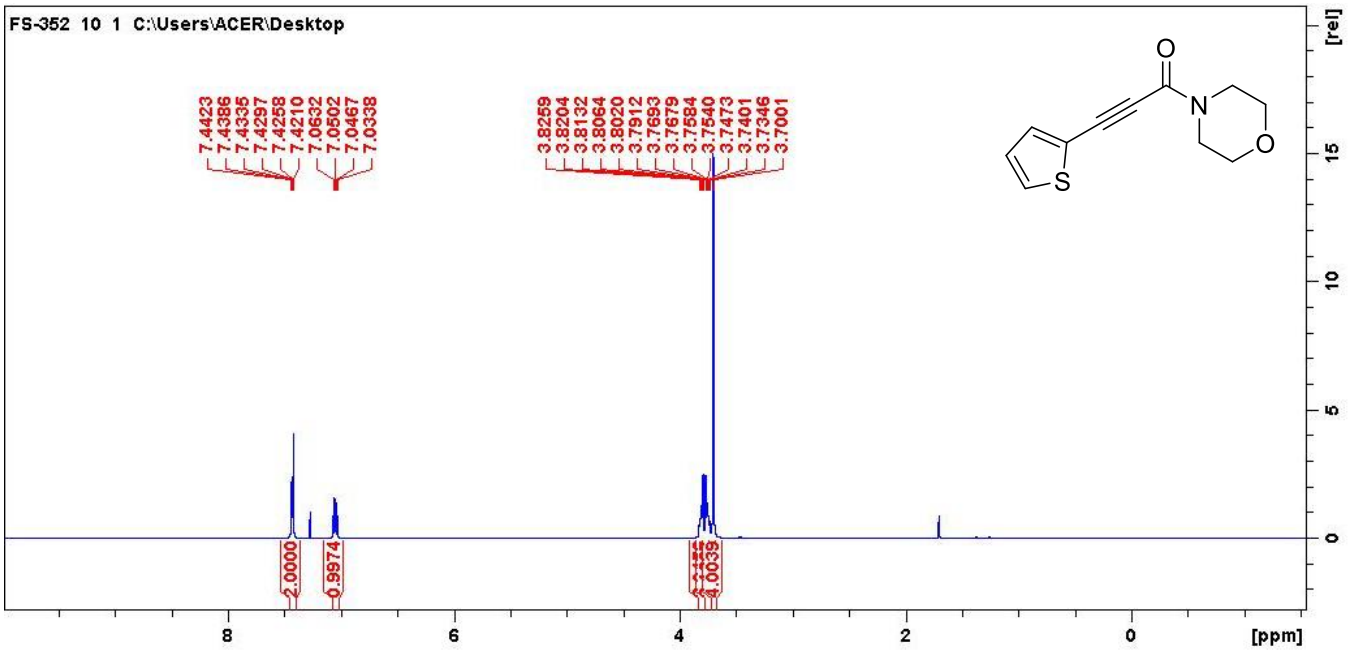


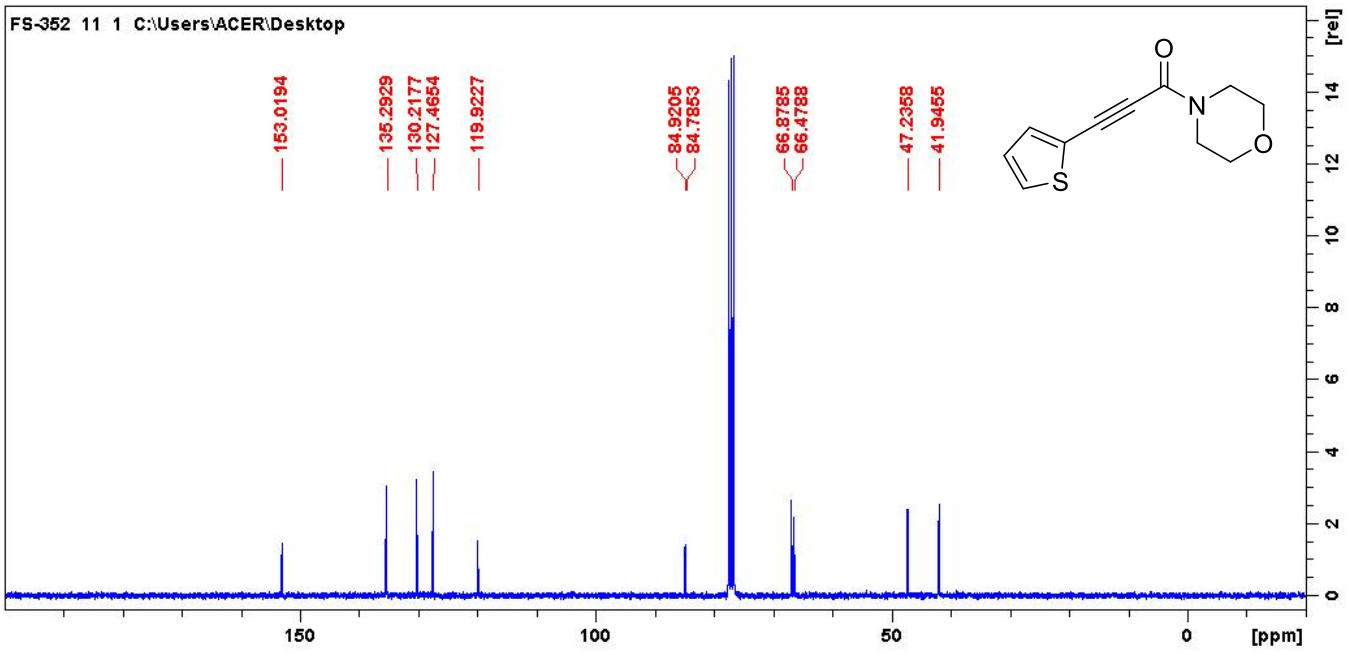


3-(2-Methoxyphenyl)-1-morpholinoprop-2-yn-1-one (P-30)

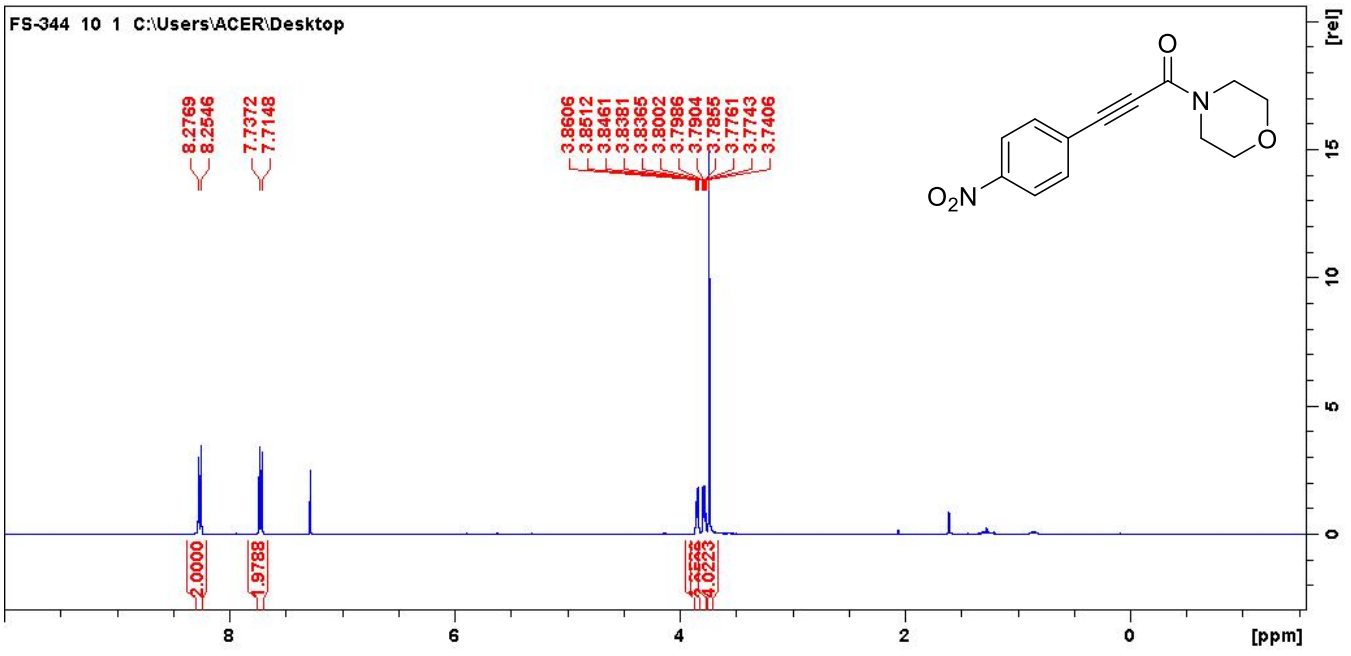


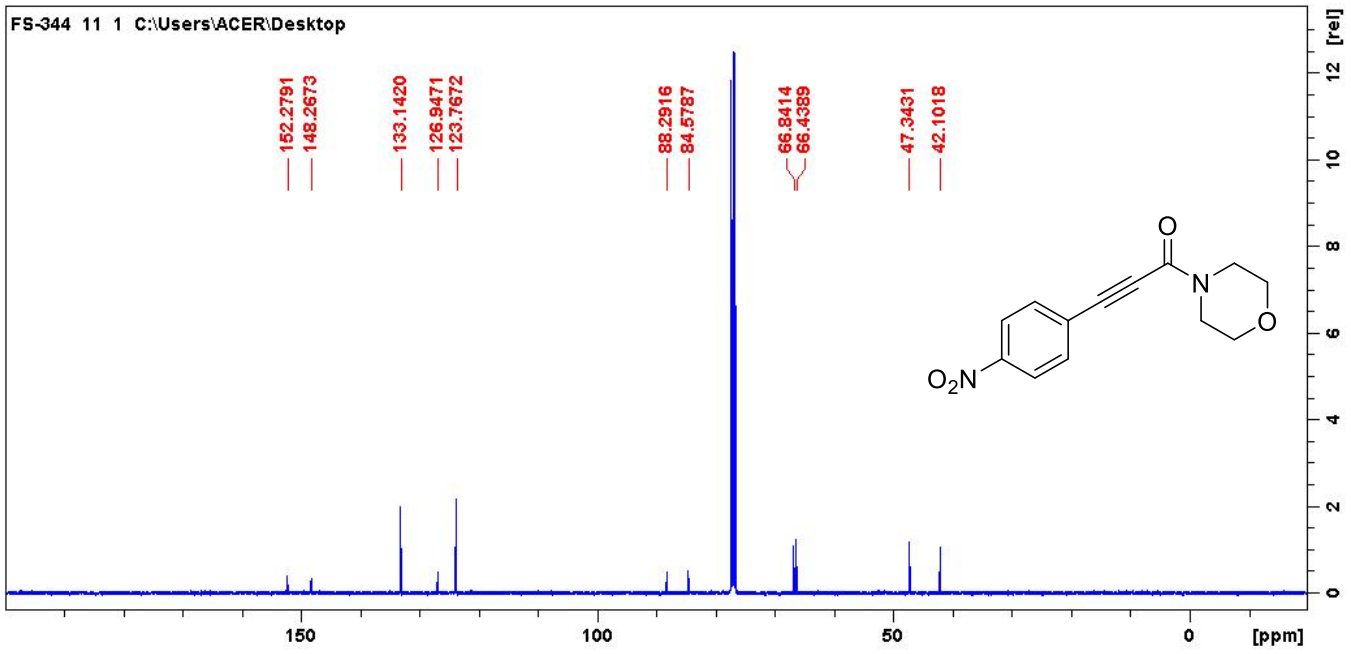
1-Morpholino-3-(thiophen-2-yl)prop-2-yn-1-one (P-31)





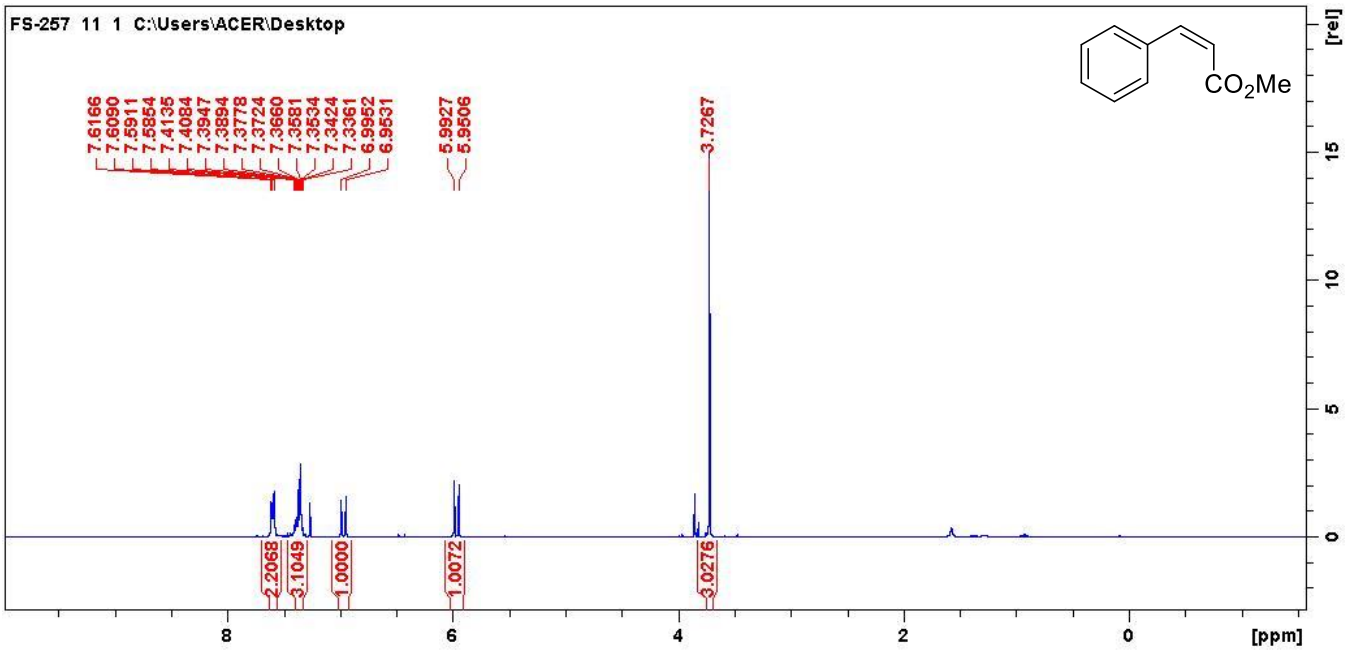
1-Morpholino-3-(4-nitrophenyl)-prop-2-yn-1-one (P-32)



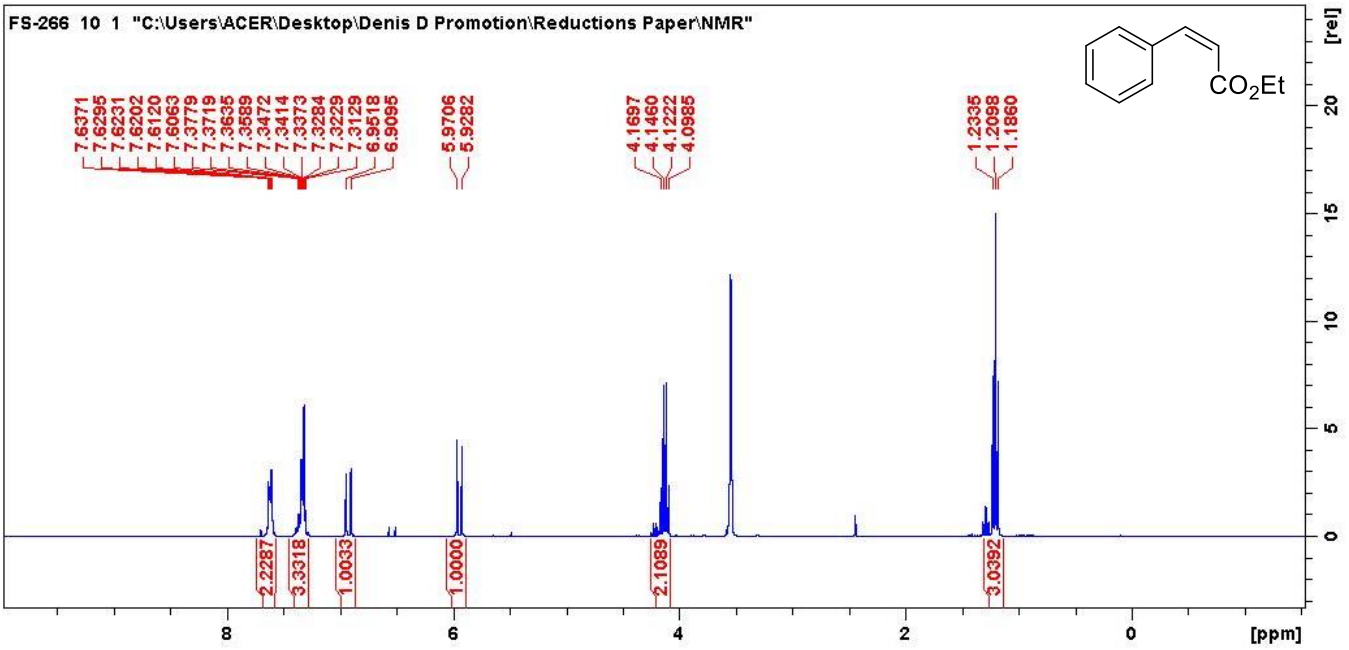


NMR of 2-enoates

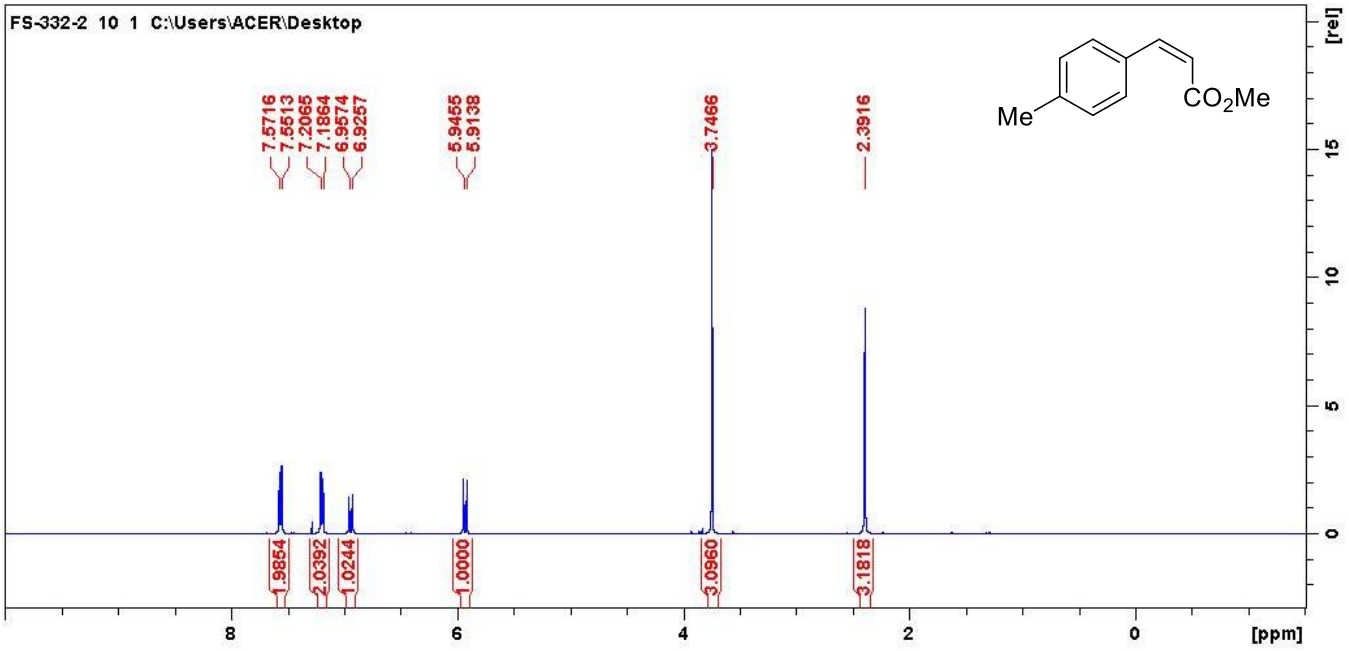
Methyl (*Z*)-3-phenylacrylate (*Z*-3)



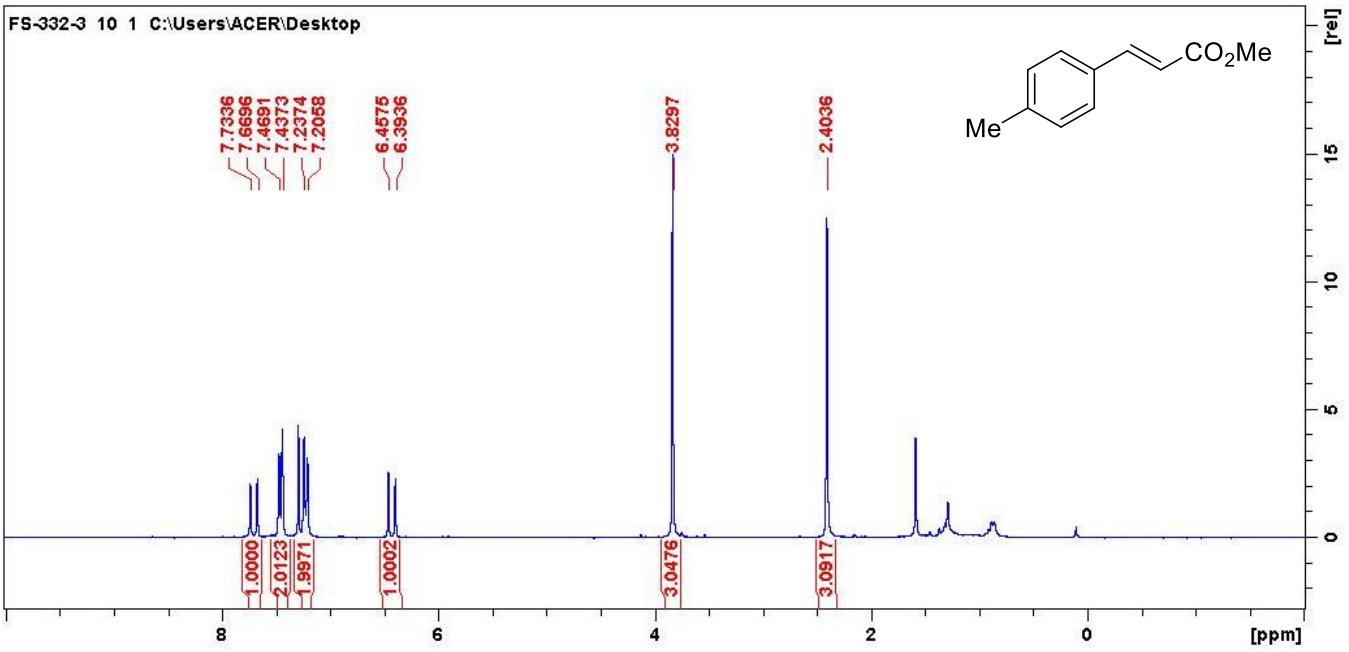
Ethyl (*Z*)-3-phenylacrylate (*Z*-4)



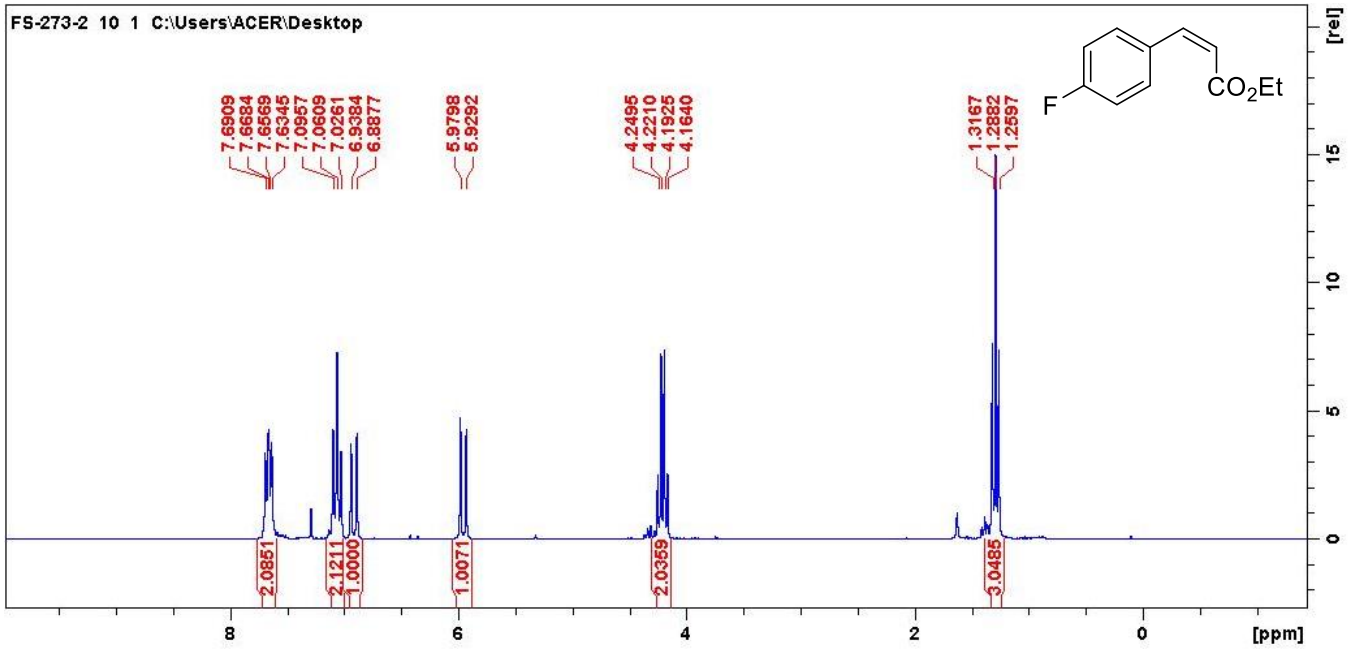
Methyl (*Z*)-3-(*p*-tolyl)acrylate (*Z*-5)



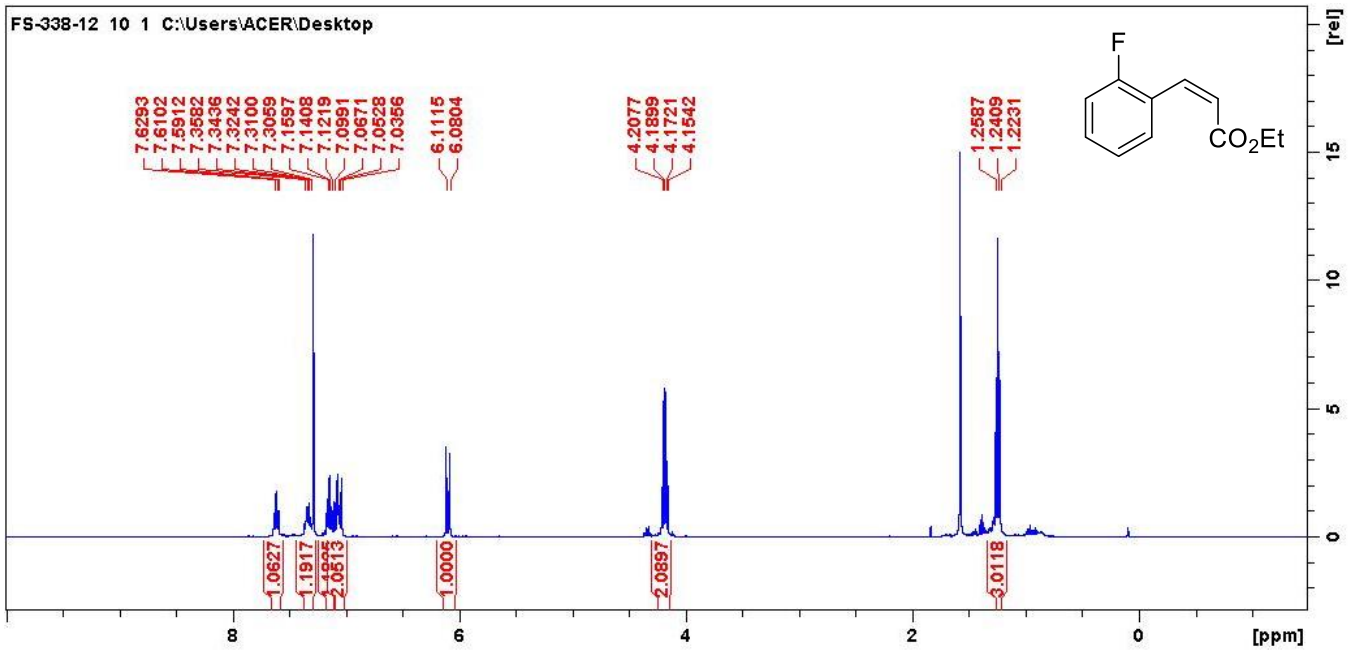
Methyl (*E*)-3-(p-tolyl)acrylate (*E*-5)

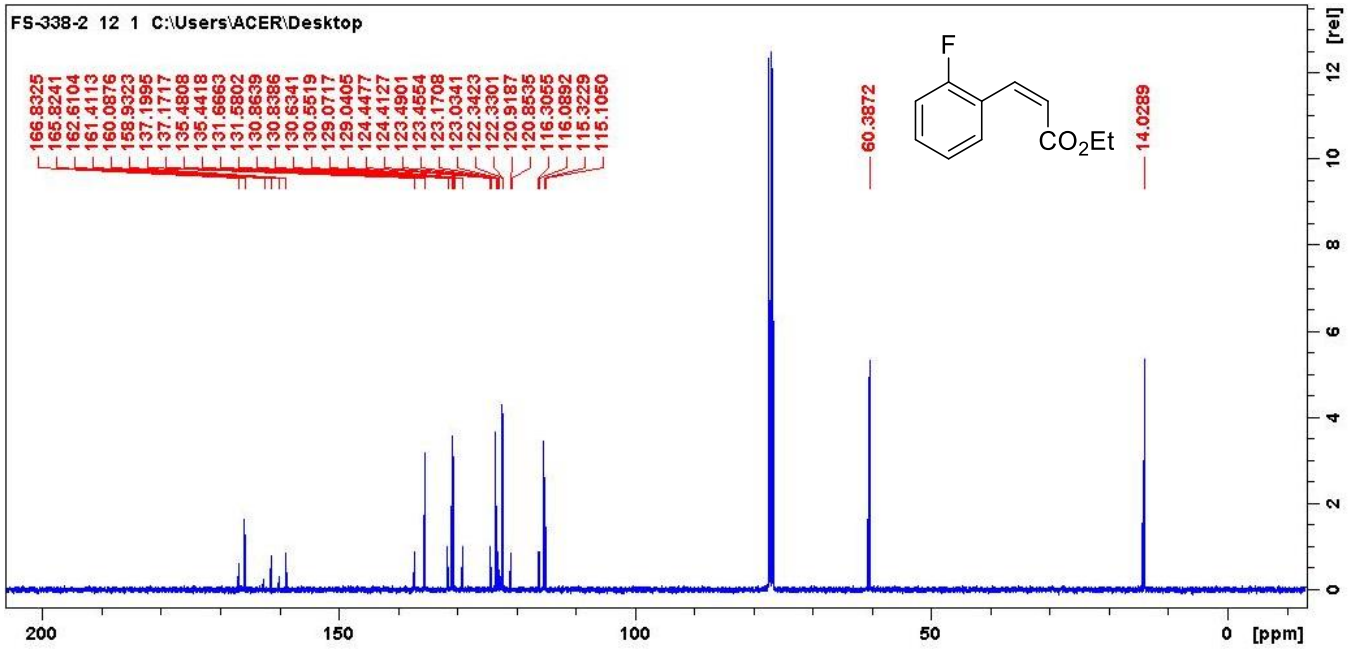


Methyl (*Z*)-3-(4-fluorophenyl)acrylate (*Z*-6)

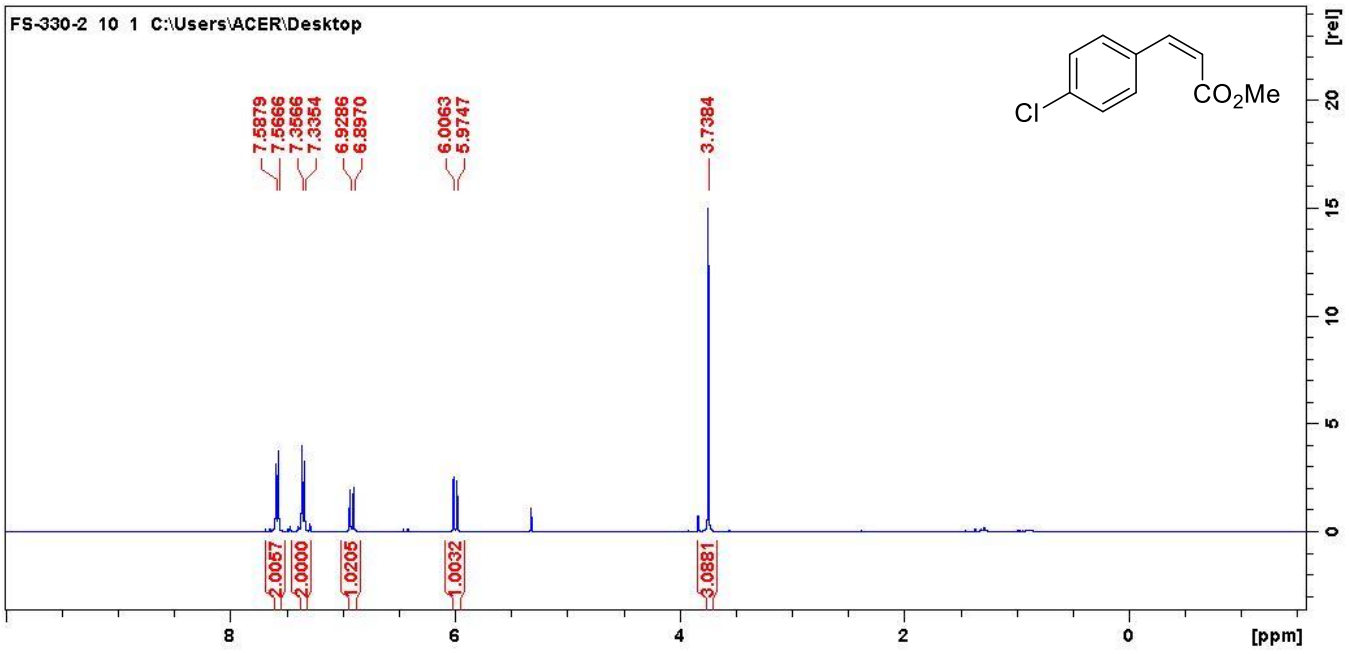


Methyl (*Z*)-3-(2-fluorophenyl)acrylate (*Z*-7)

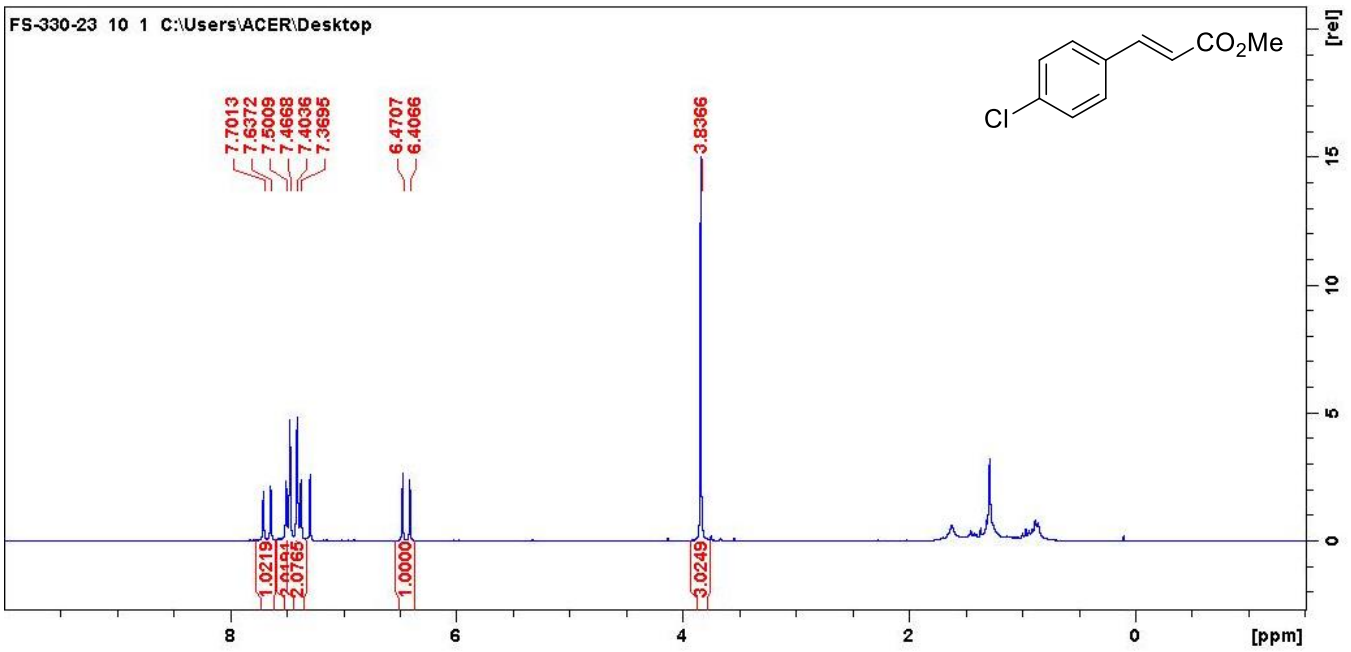




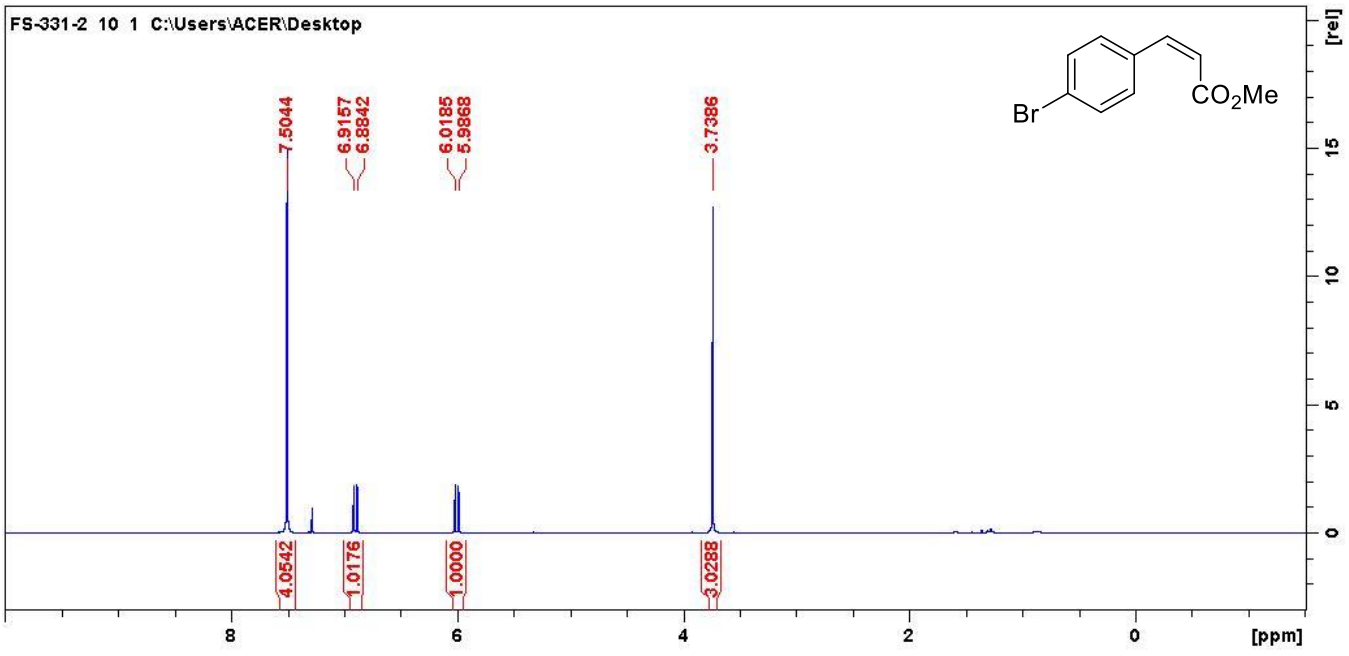
Methyl (*Z*)-3-(4-chlorophenyl)acrylate (*Z*-8)

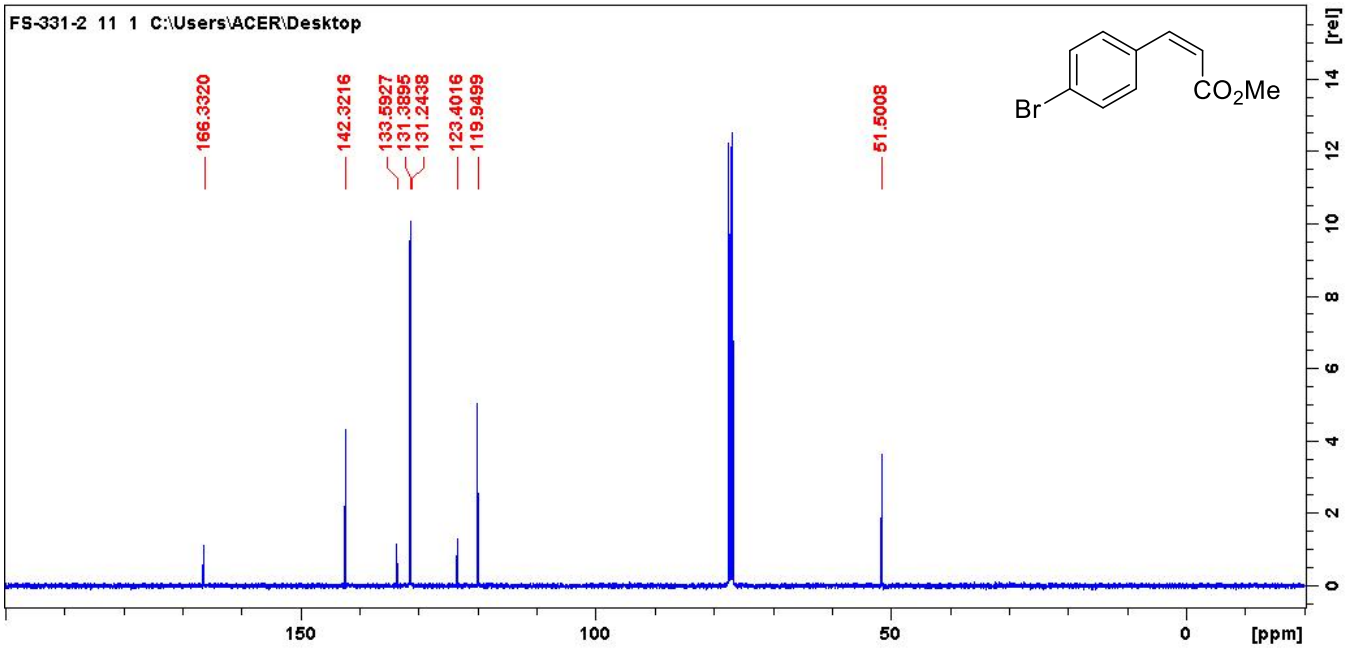


Methyl (*E*)-3-(4-chlorophenyl)acrylate (*E*-8)

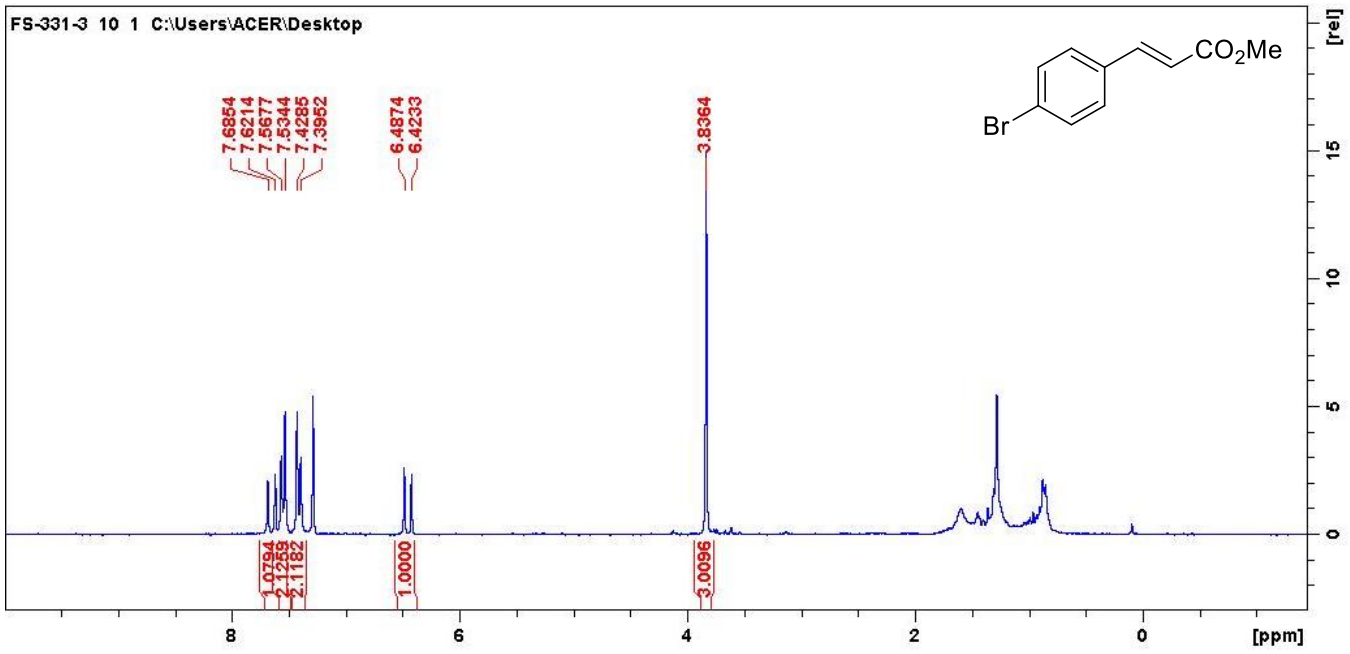


Methyl (*Z*)-3-(4-bromophenyl)acrylate (*Z*-9)

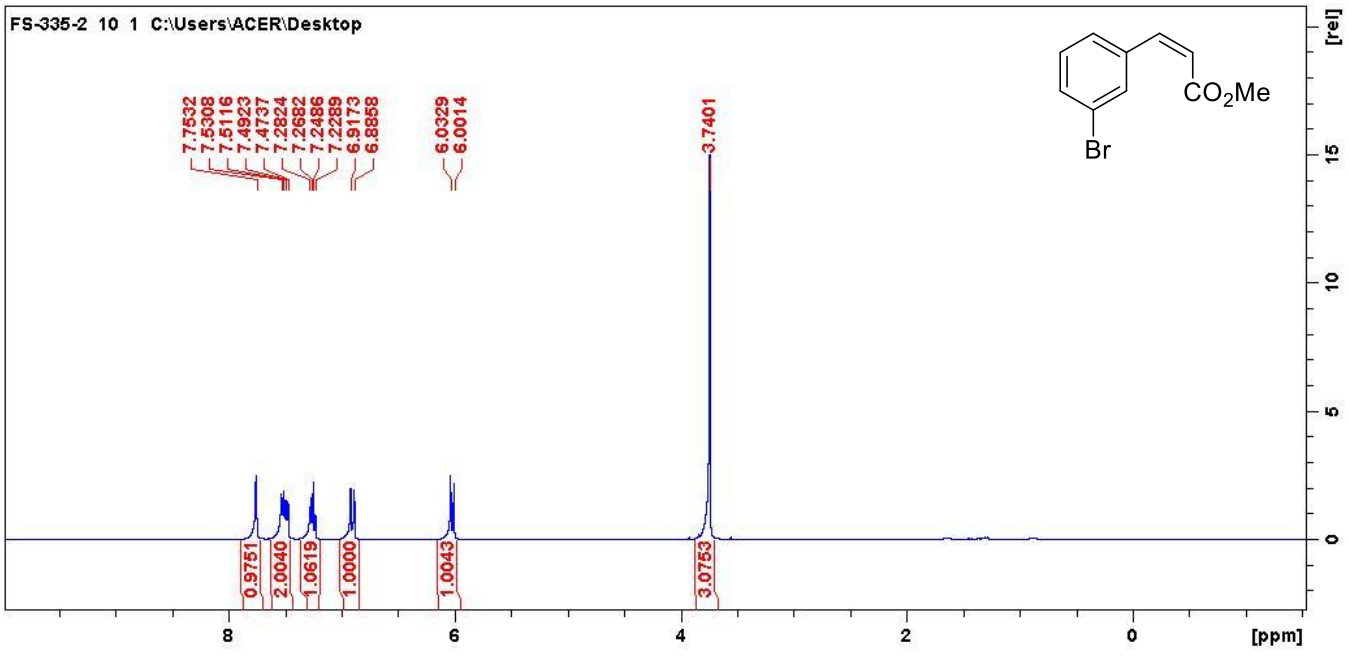


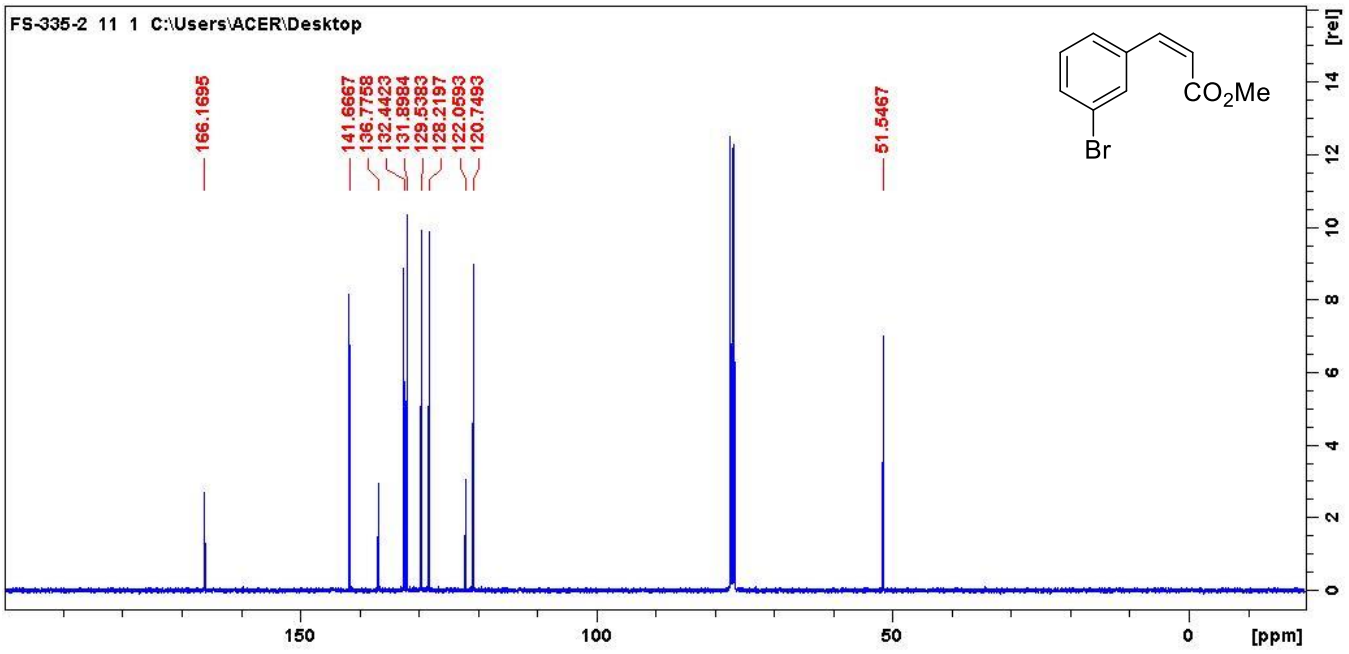


Methyl (*E*)-3-(4-bromophenyl)acrylate (*E*-9)

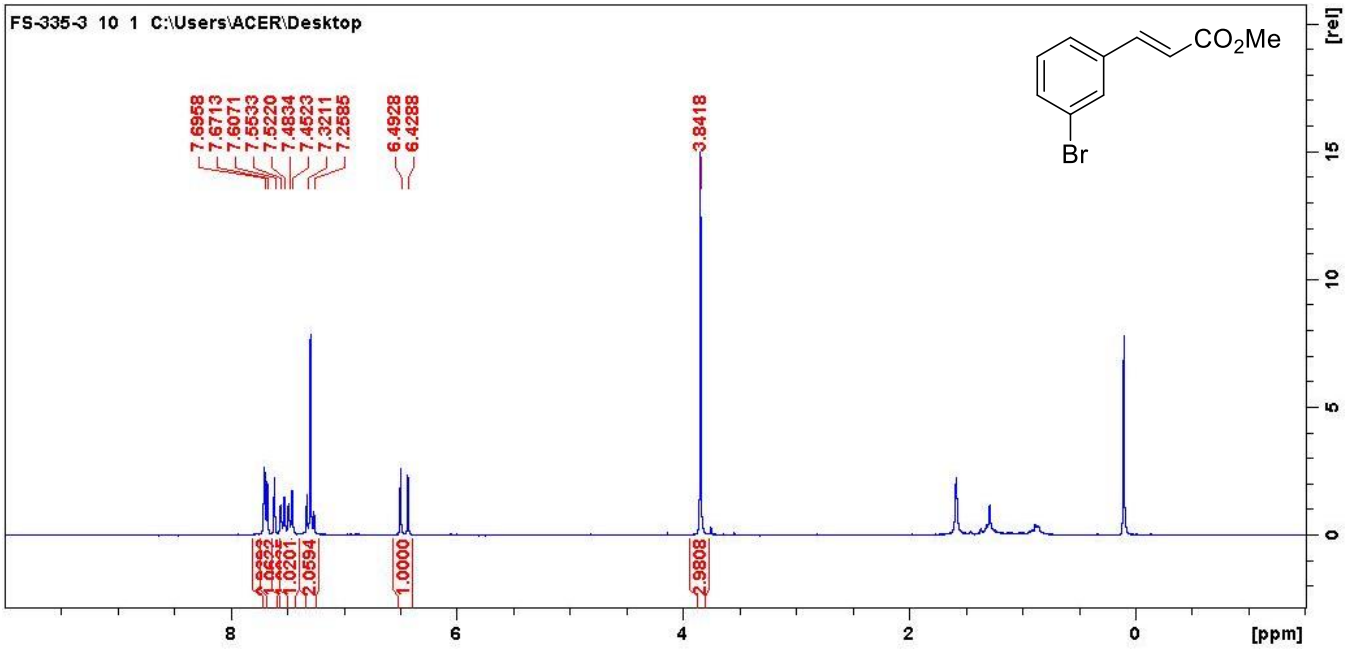


Methyl (*Z*)-3-(3-bromophenyl)acrylate (*Z*-10)

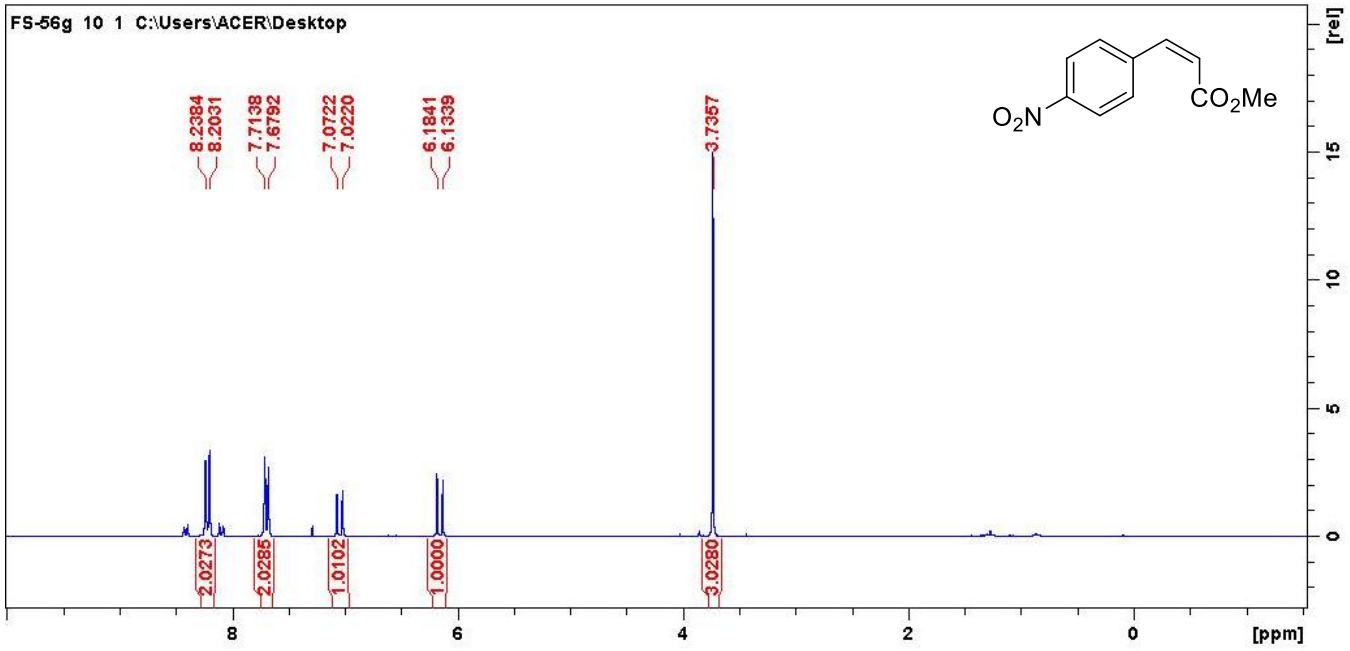


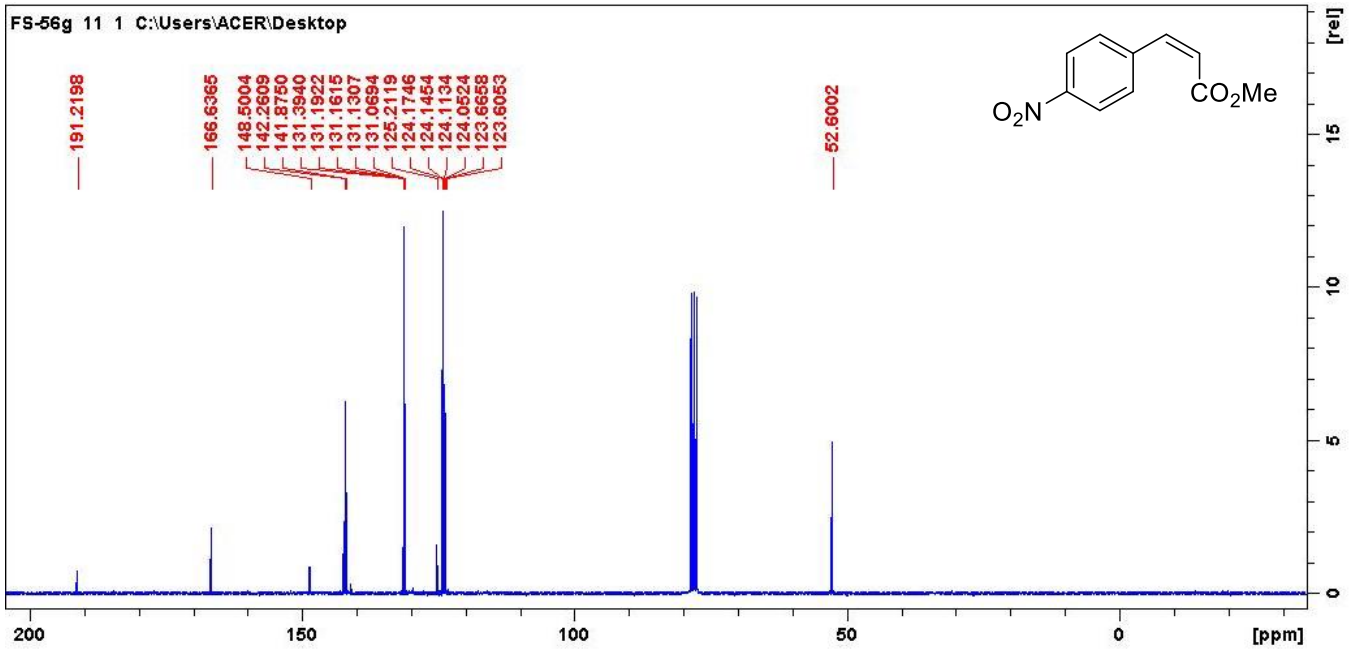


Methyl (*E*)-3-(3-bromophenyl)acrylate (*E*-10)

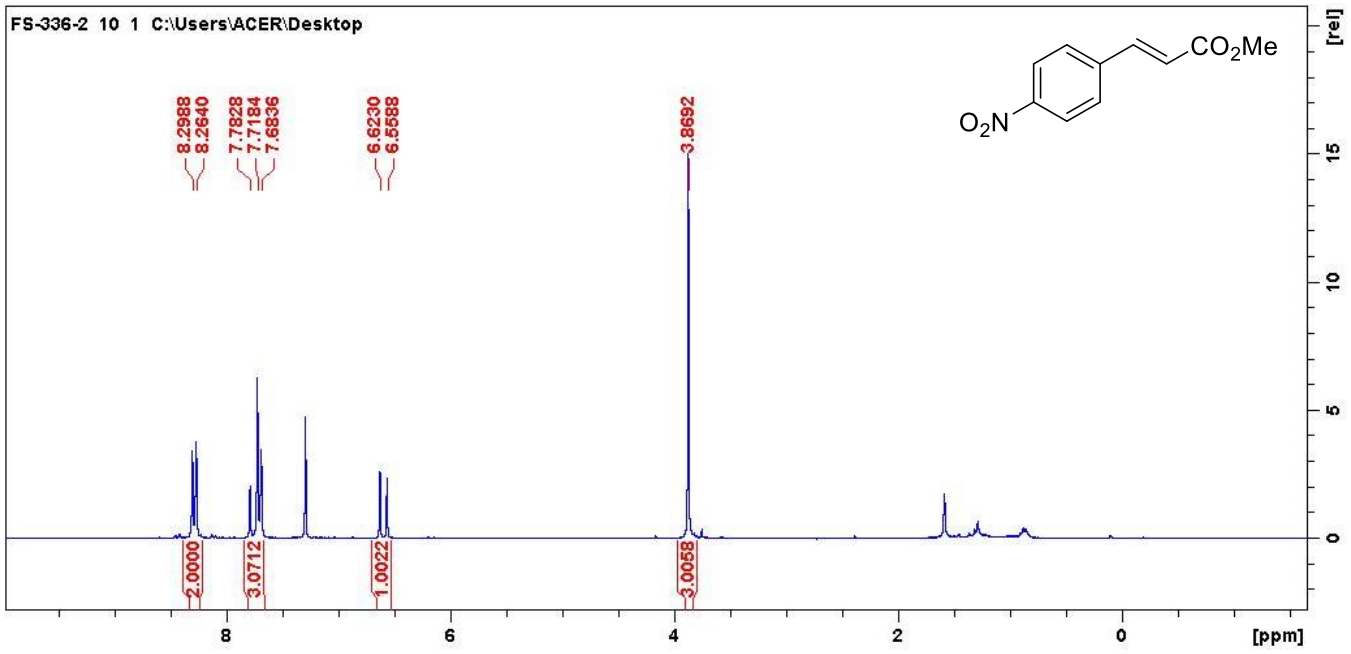


Methyl (*Z*)-3-(4-nitrophenyl)acrylate (*Z*-11)

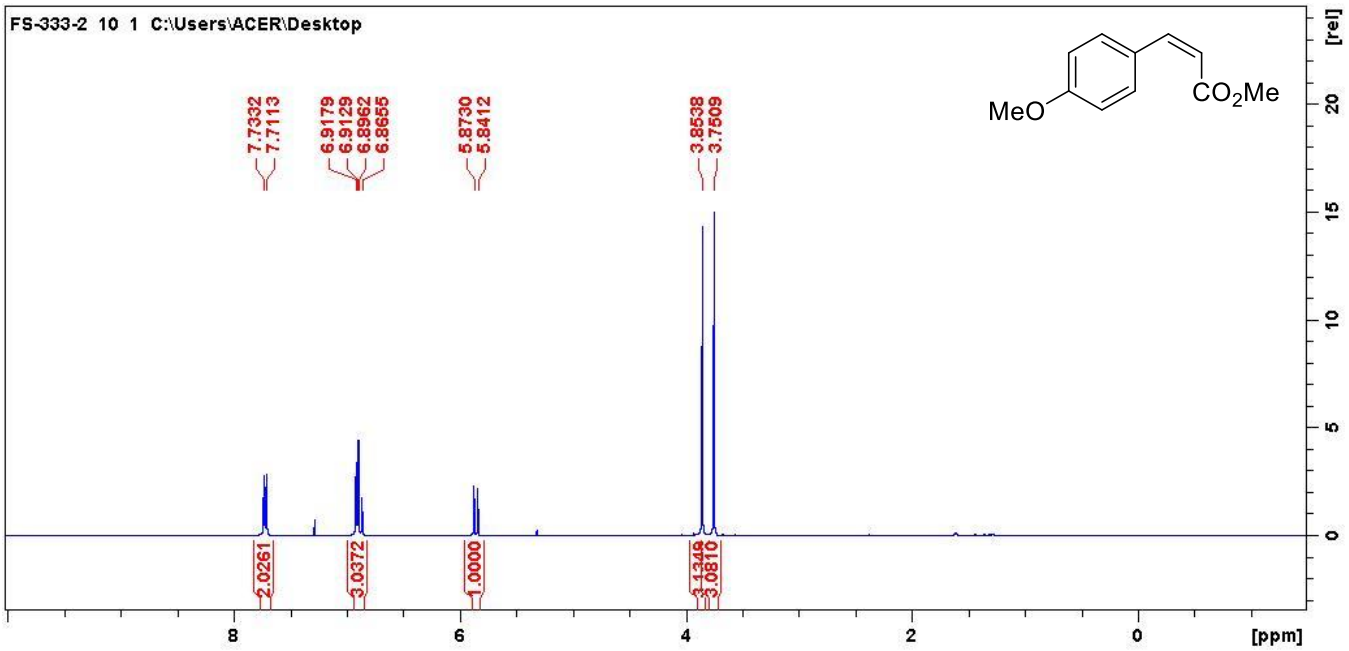




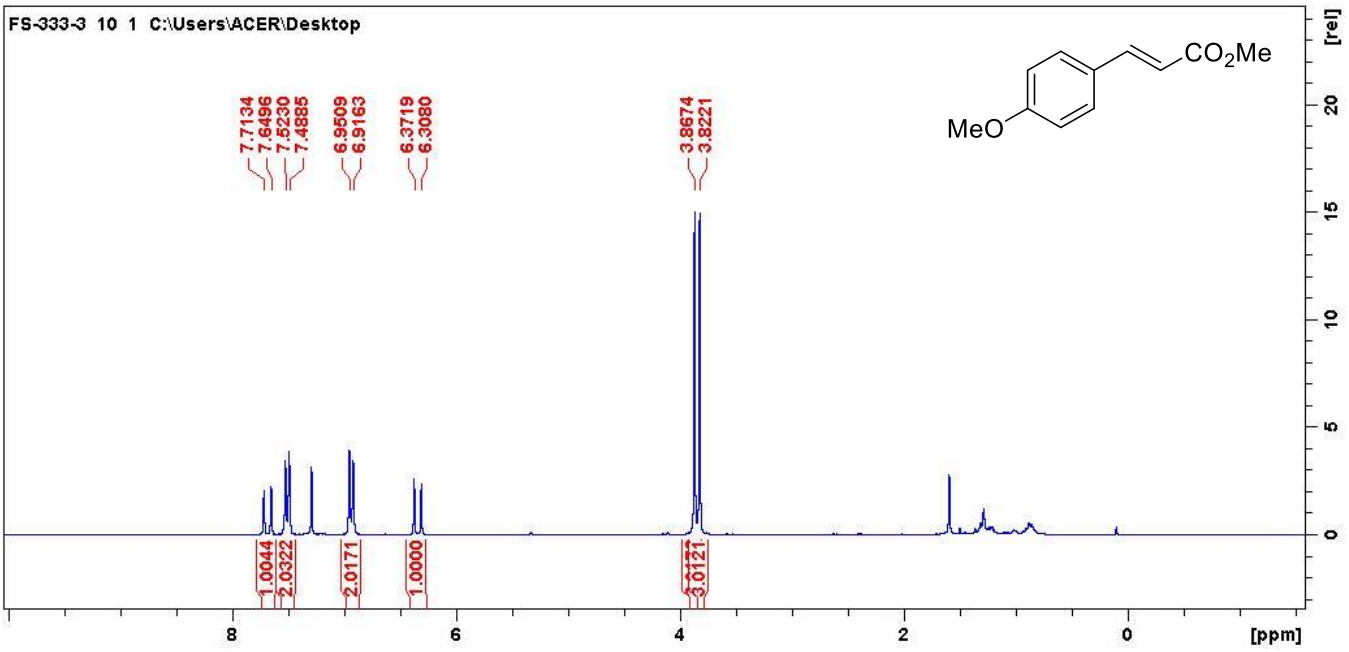
Methyl (*E*)-3-(4-nitrophenyl)acrylate (*E*-11)



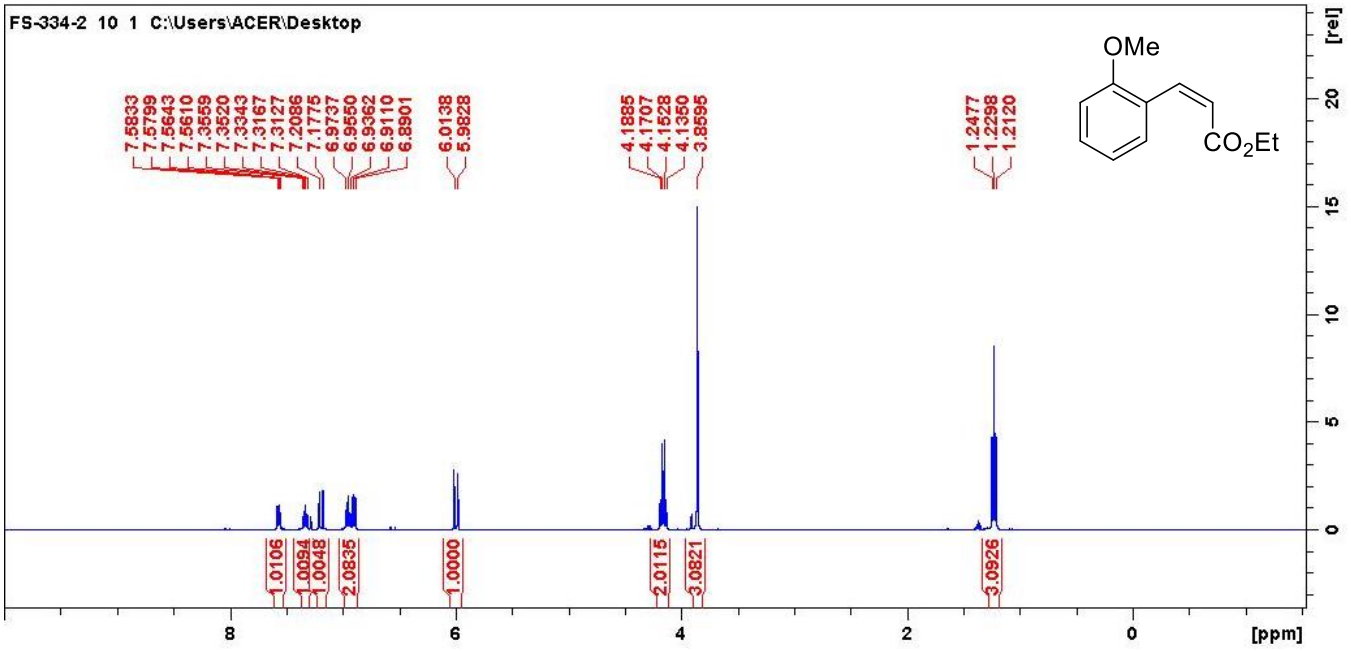
Methyl (*Z*)-3-(4-methoxyphenyl)acrylate (*Z*-12)

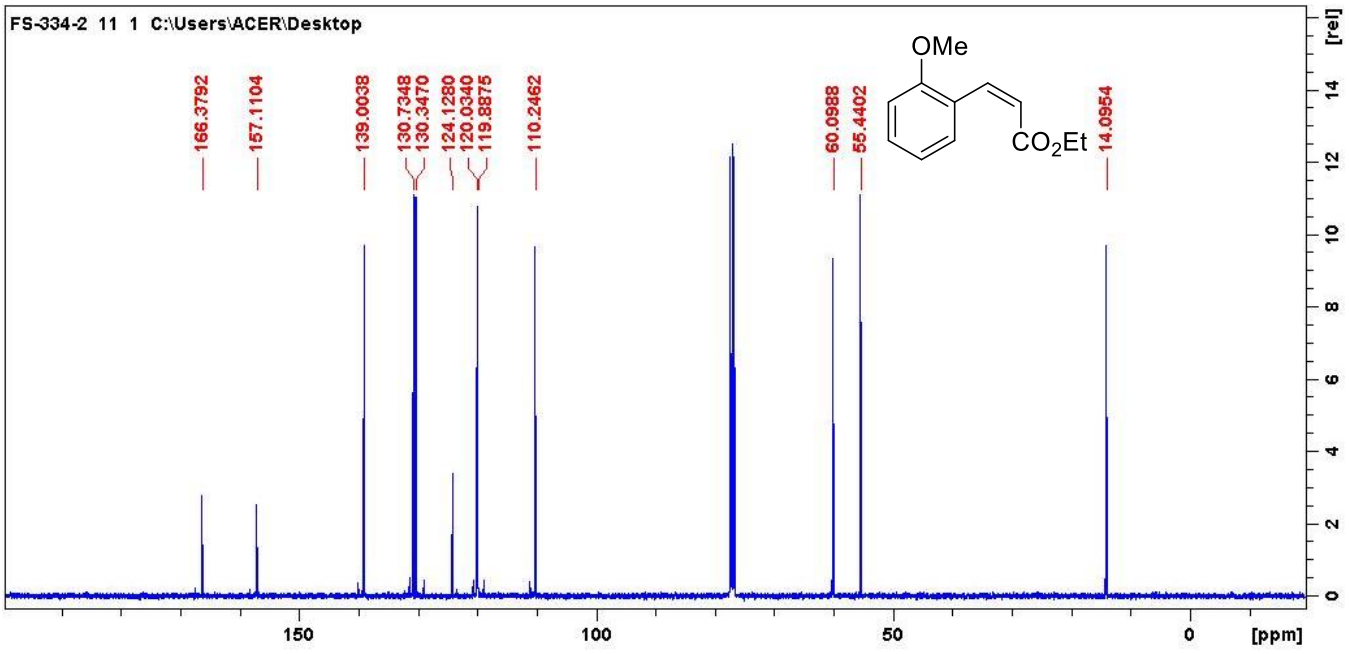


Methyl (*E*)-3-(4-methoxyphenyl)acrylate (*E*-12)

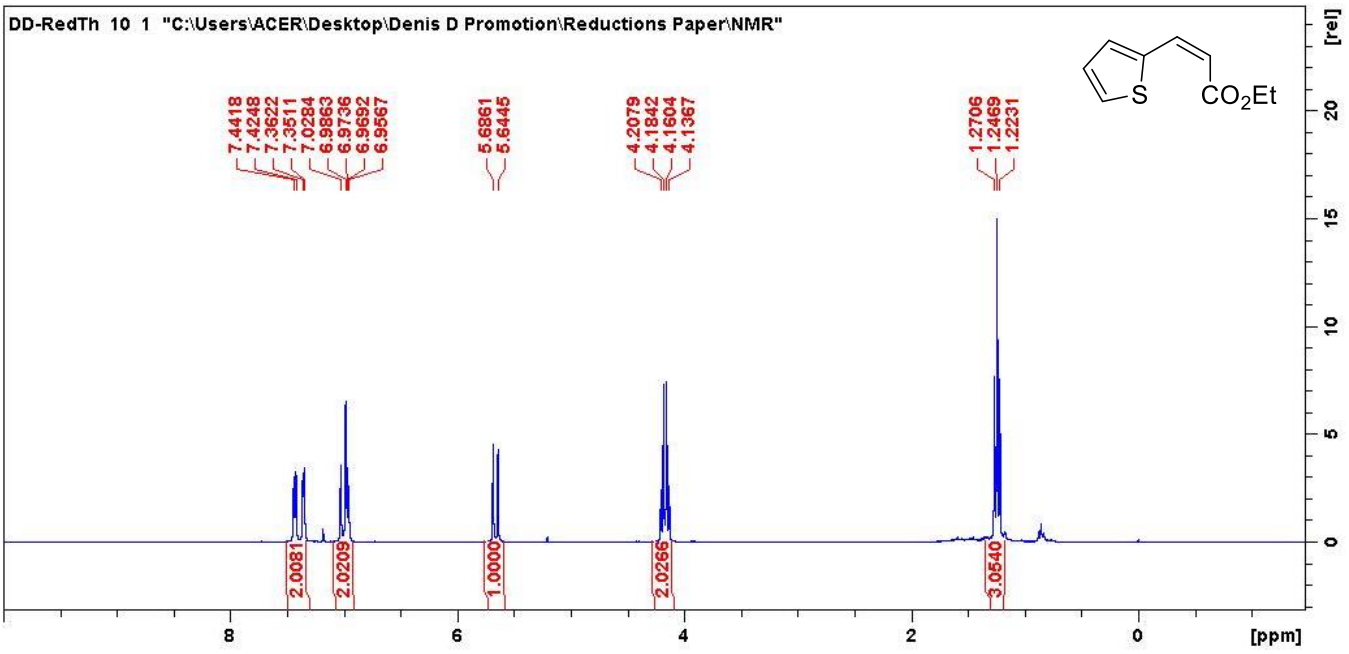


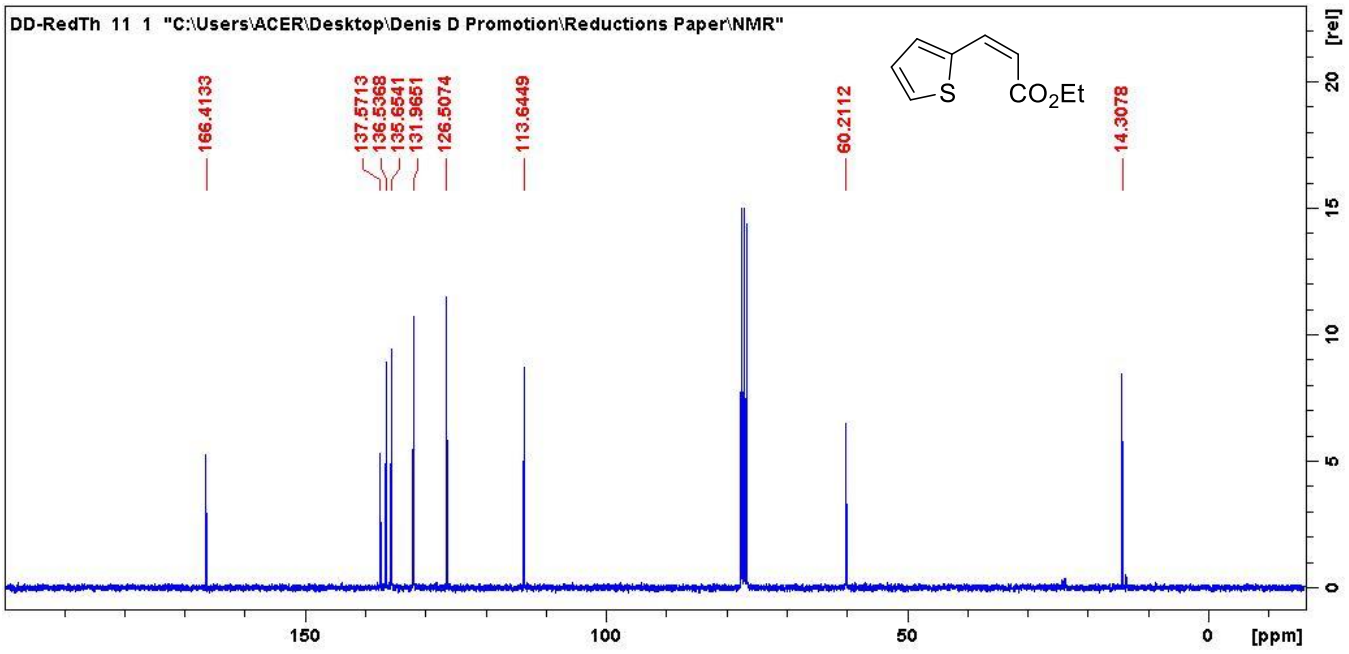
Ethyl (*Z*)-3-(2-methoxyphenyl)acrylate (*Z*-13)



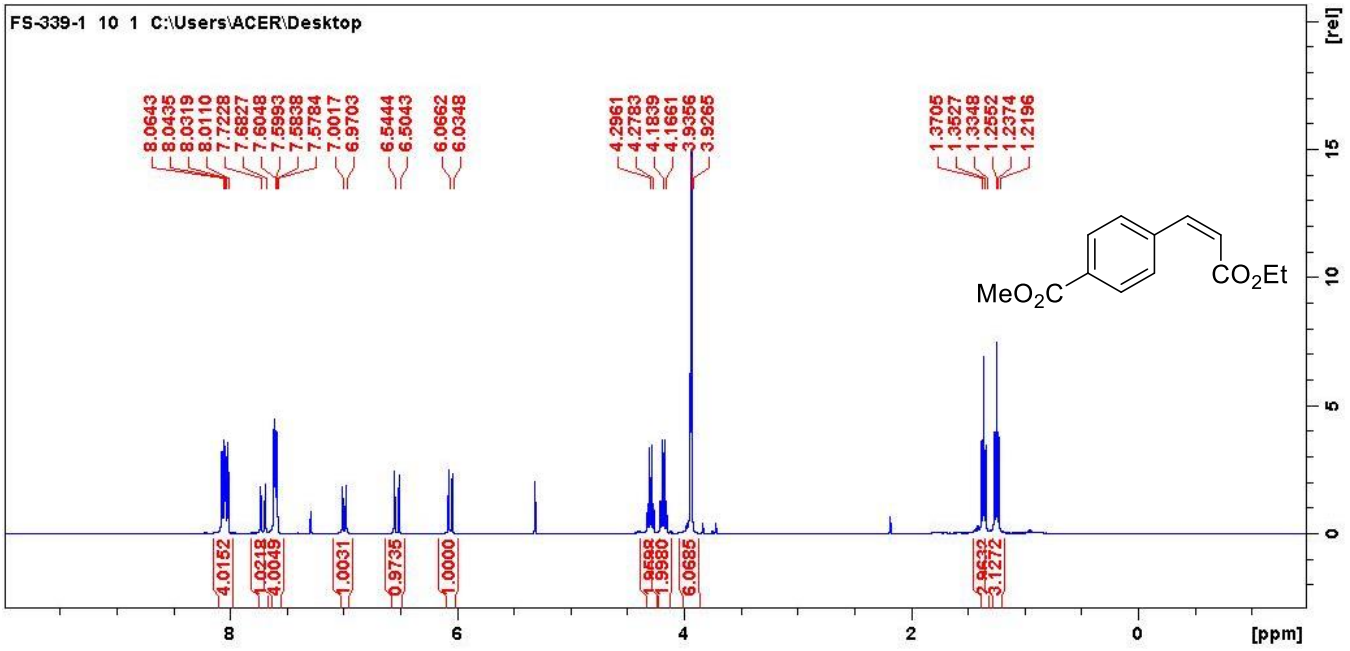


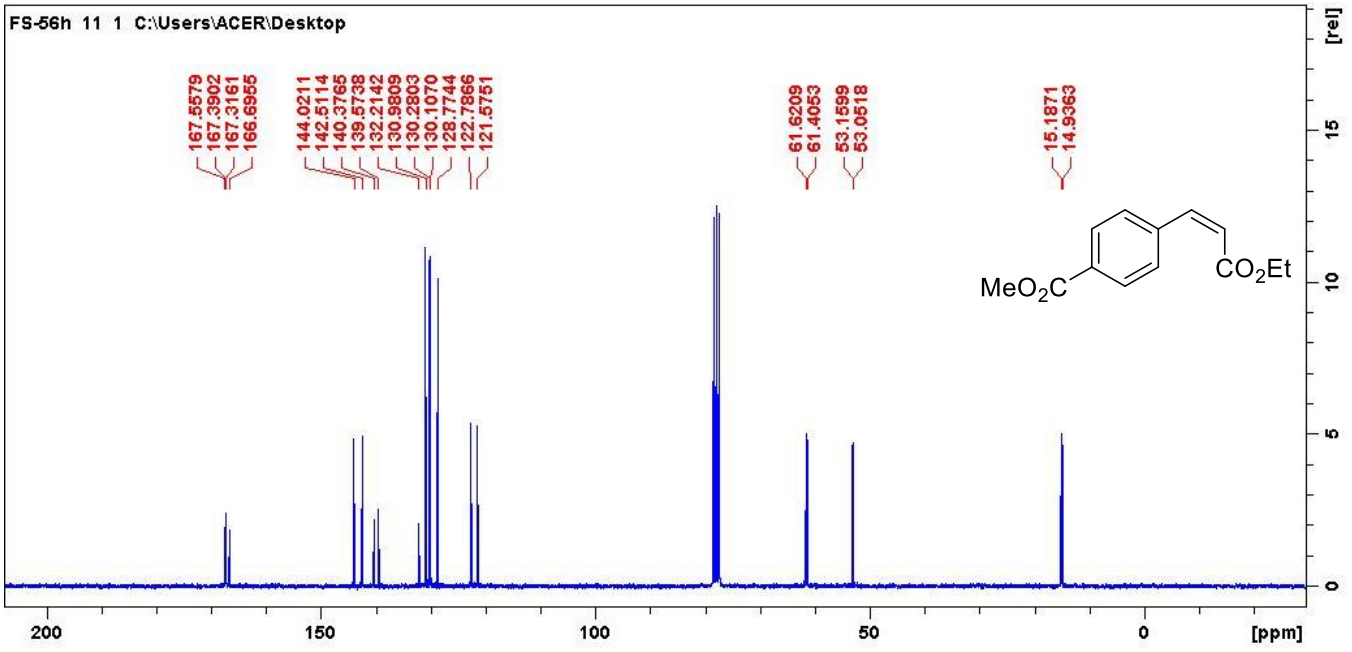
Ethyl (*Z*)-3-(thiophen-2-yl)acrylate (*Z*-14)



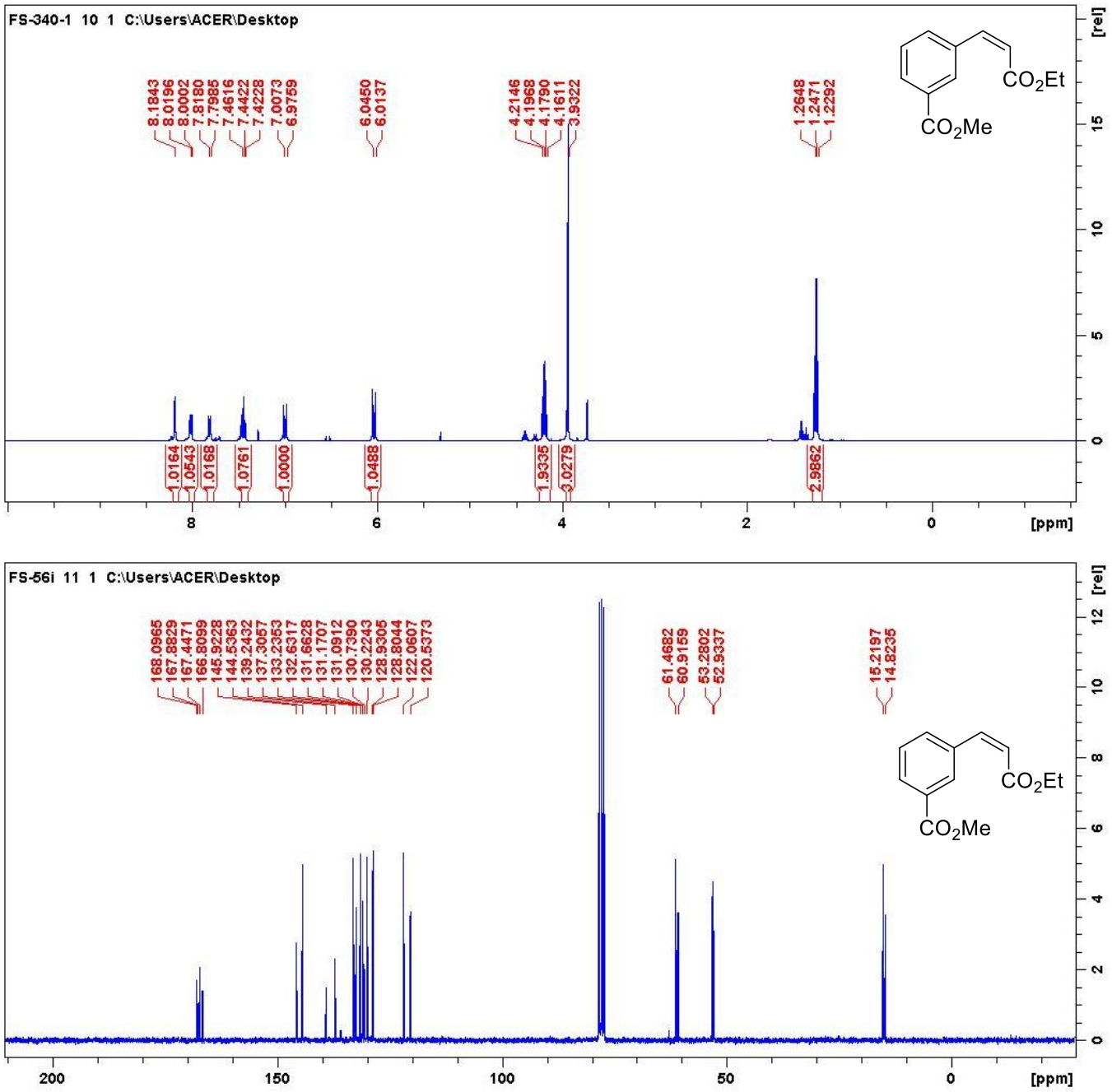


Methyl (*Z*)-4-(3-ethoxy-3-oxoprop-1-en-1-yl)benzoate (*Z*-15)

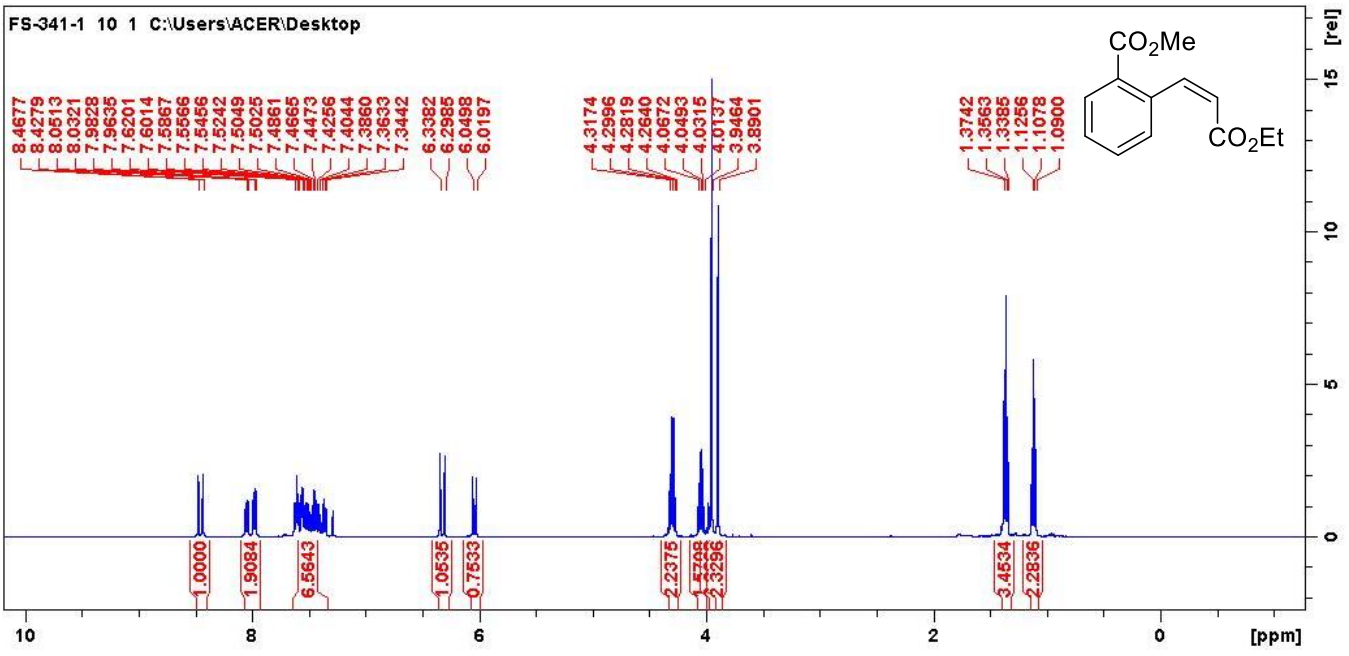


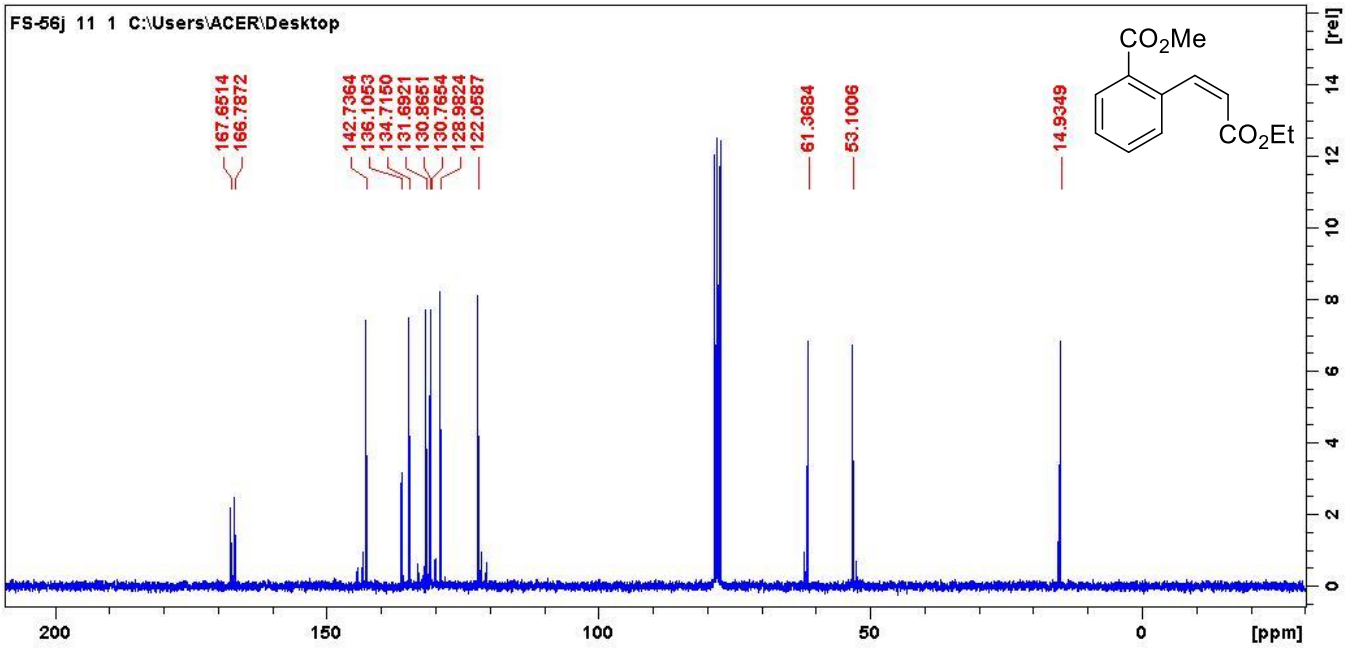


Methyl (*Z*)-3-(3-ethoxy-3-oxoprop-1-en-1-yl)benzoate (*Z*-16)

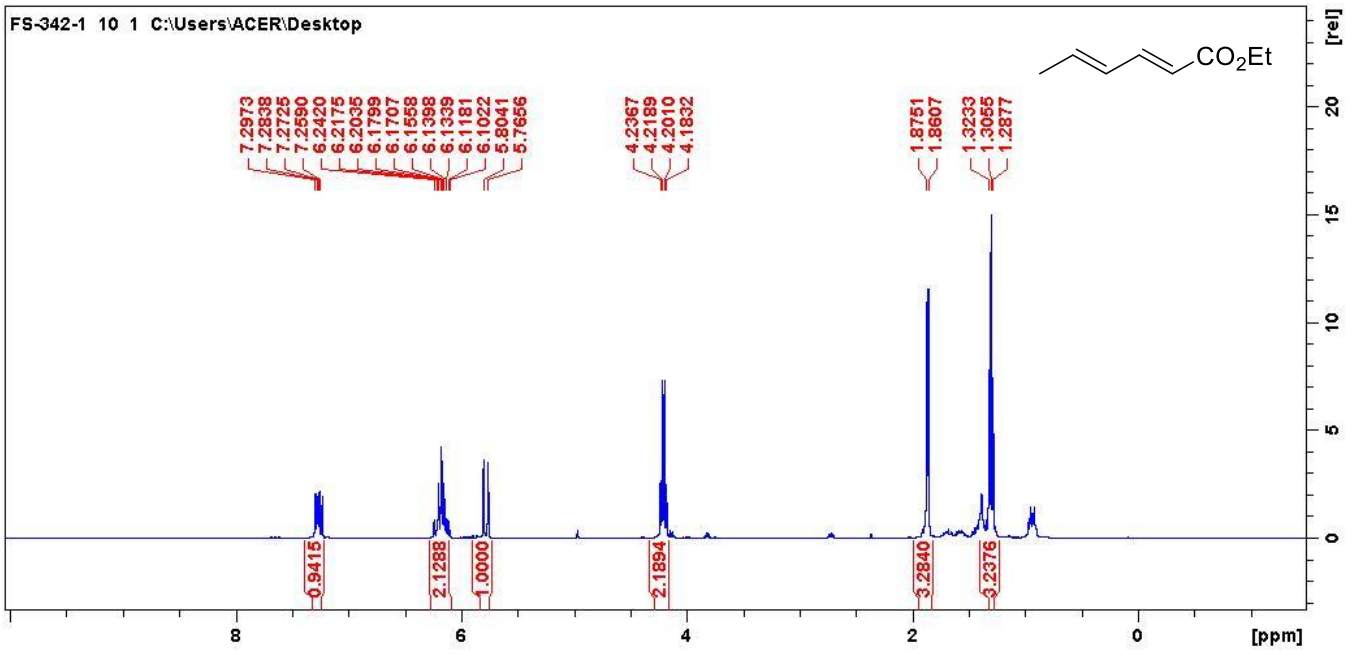


Methyl (*Z*)-2-(3-ethoxy-3-oxoprop-1-en-1-yl)benzoate (*Z*-17)

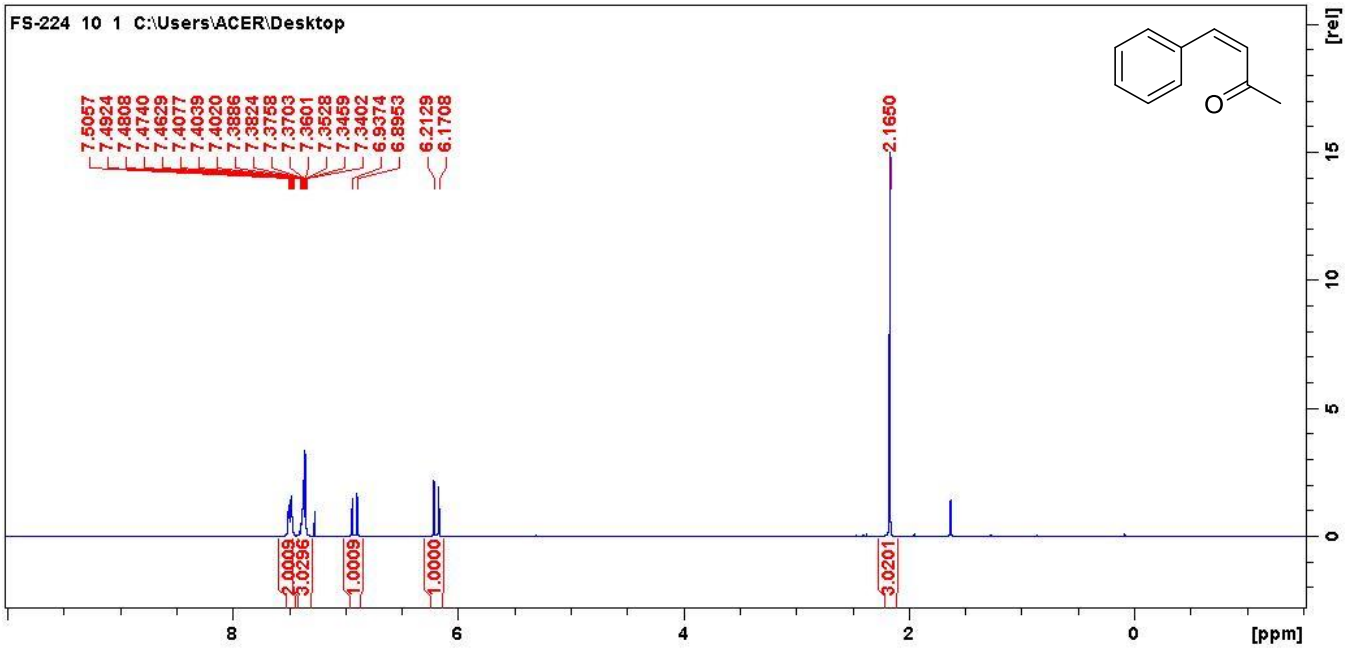




Ethyl (2*E*,4*E*)-hexa-2,4-dienoate (*Z*-18)

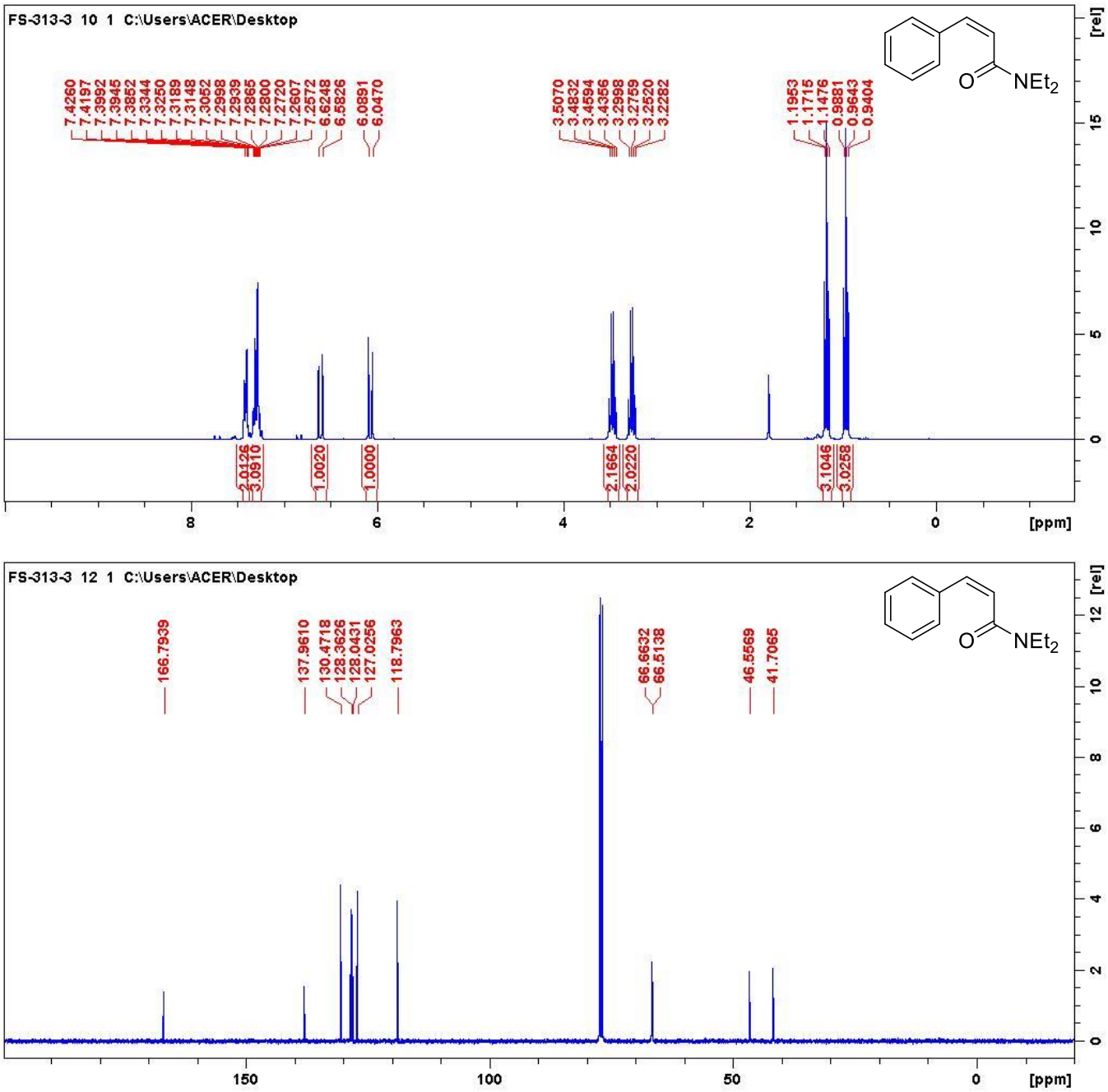


(*Z*)-4-Phenylbut-3-en-2-one (*Z*-19)

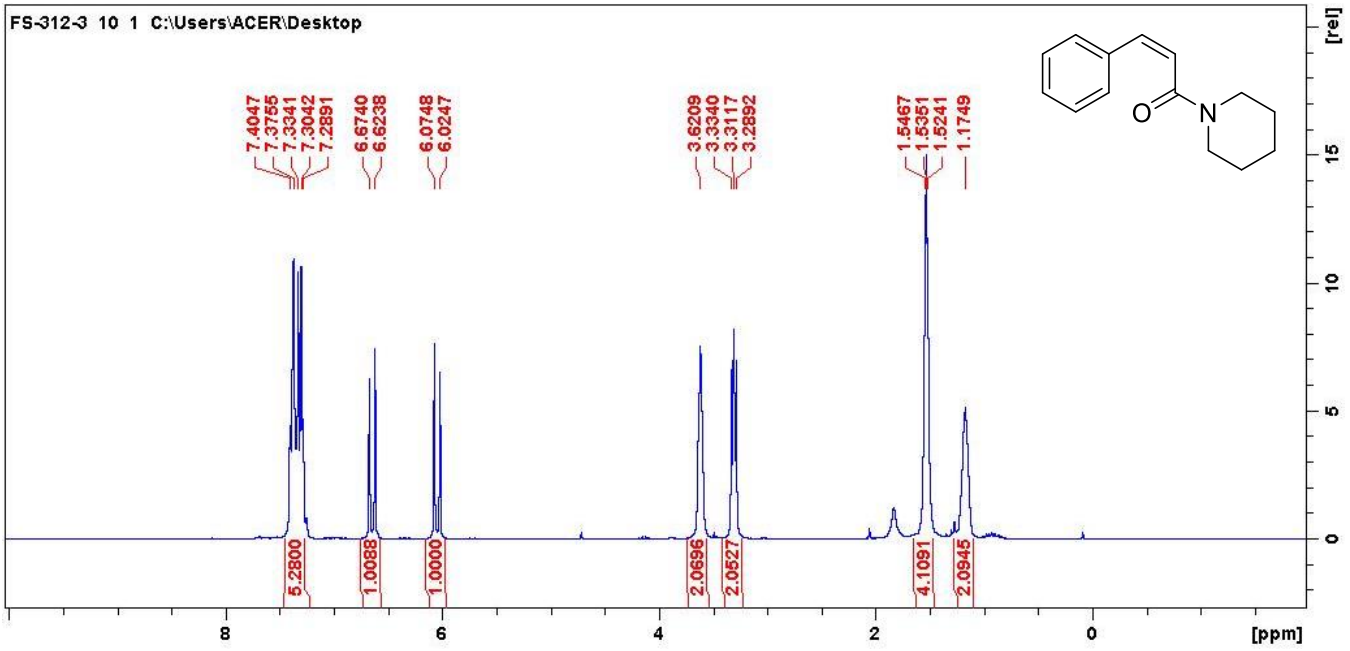


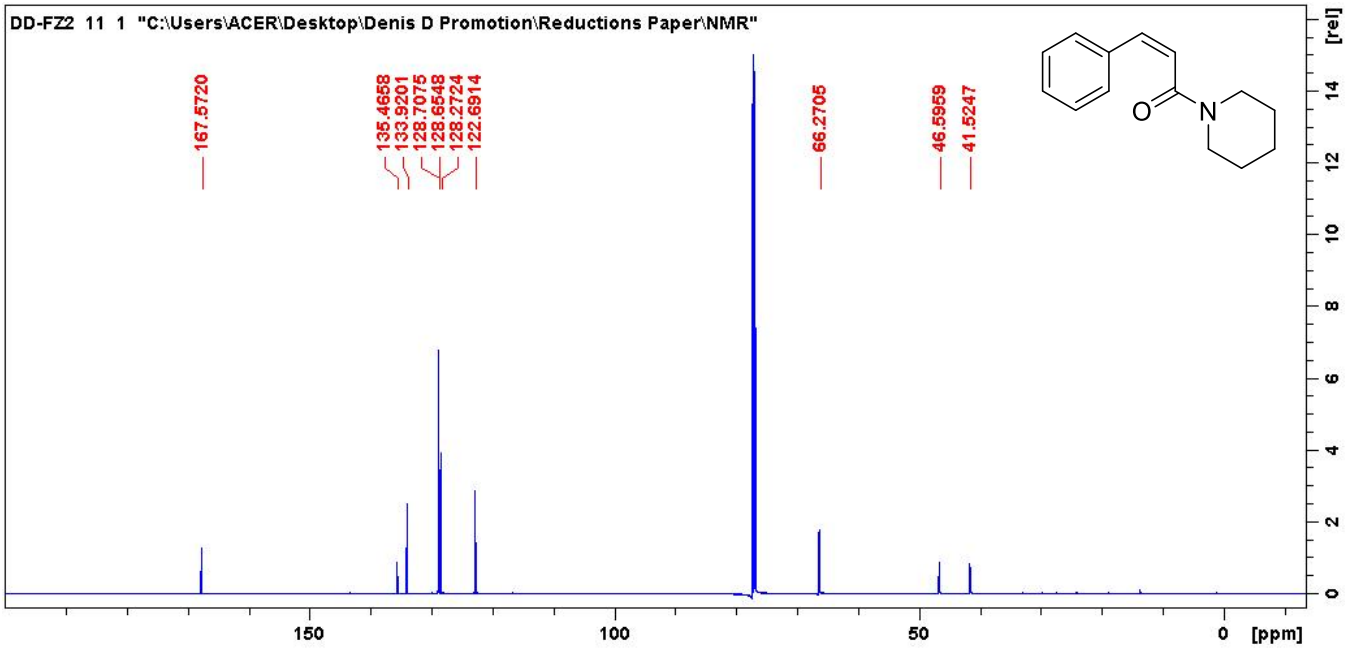
NMR of α,β-unsaturated amides

(*Z*)-*N*,*N*-Diethyl-3-phenylacrylamide (*Z*-21)

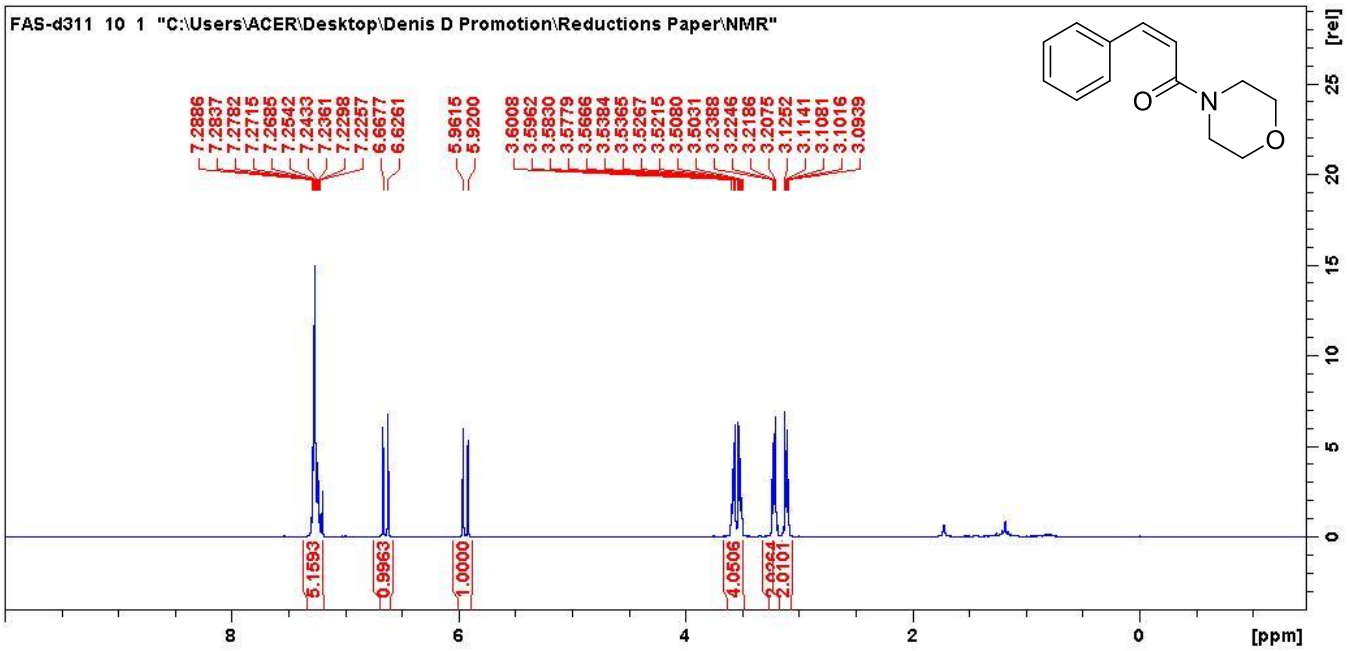


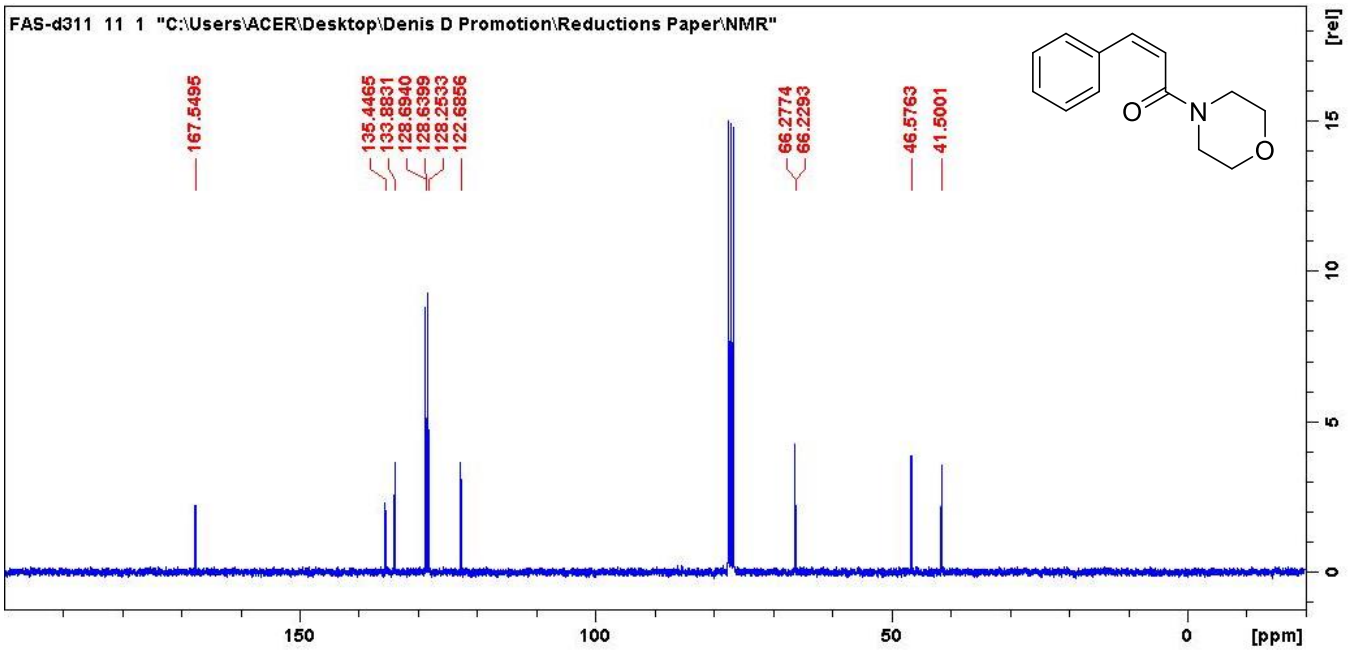
(*Z*)-3-Phenyl-1-(piperidin-1-yl)prop-2-en-1-one (*Z*-22)



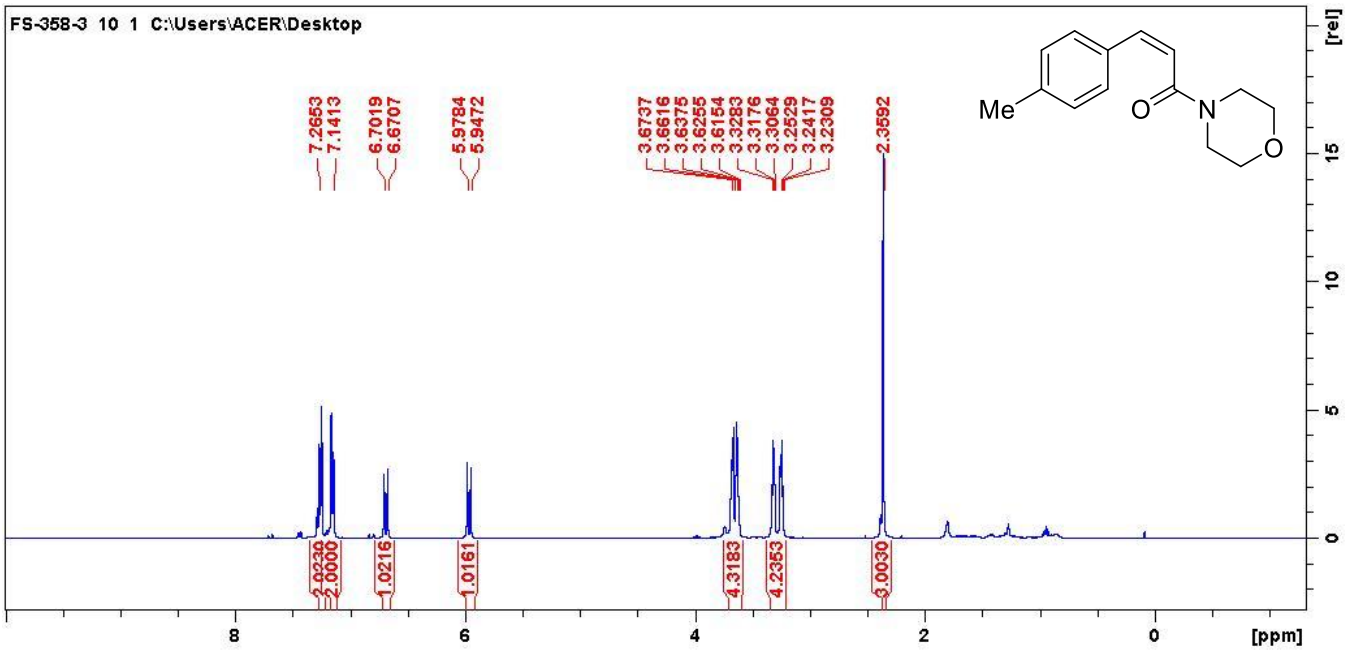


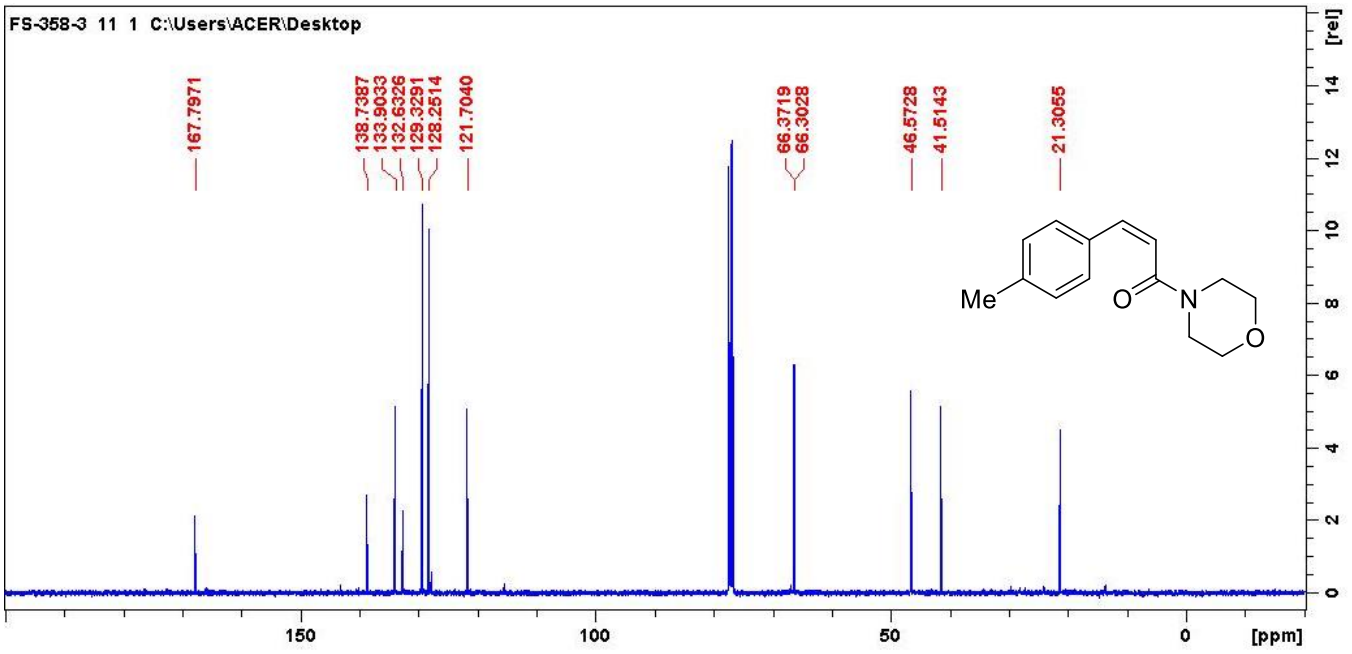
(*Z*)-1-Morpholino-3-phenylprop-2-en-1-one (*Z*-23)



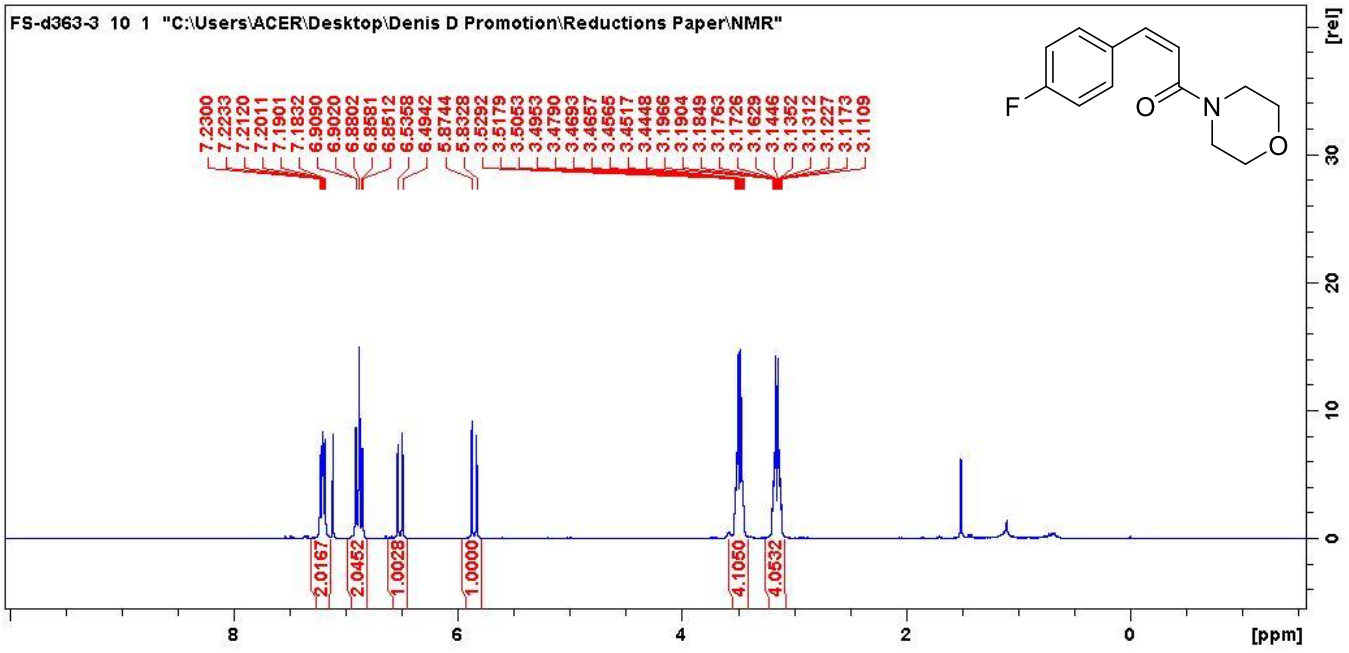


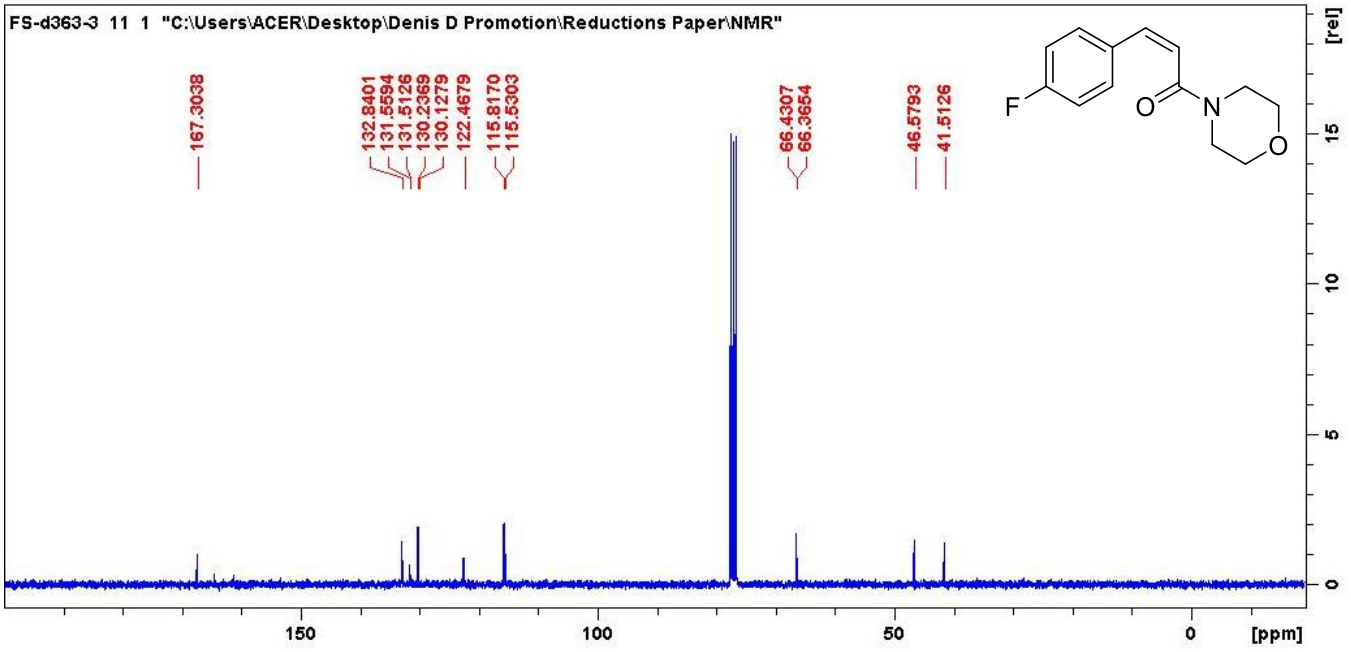
(*Z*)-1-Morpholino-3-(*p*-tolyl)prop-2-en-1-one (*Z*-24)



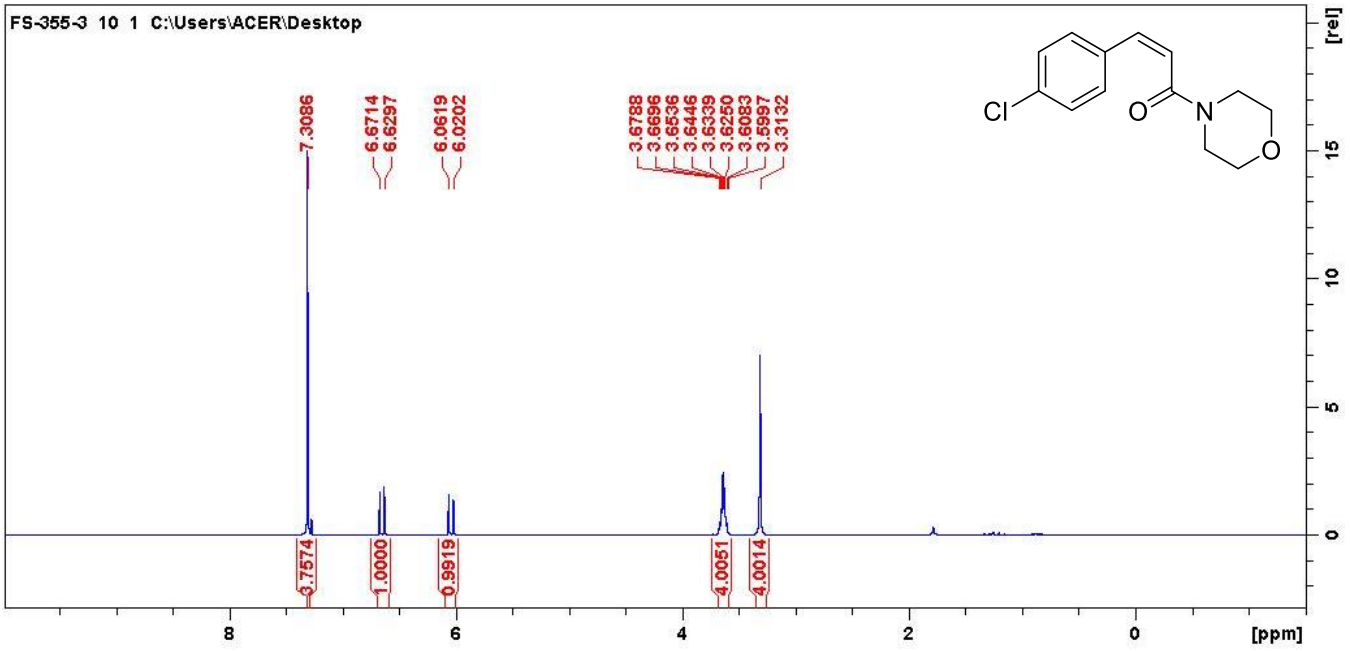


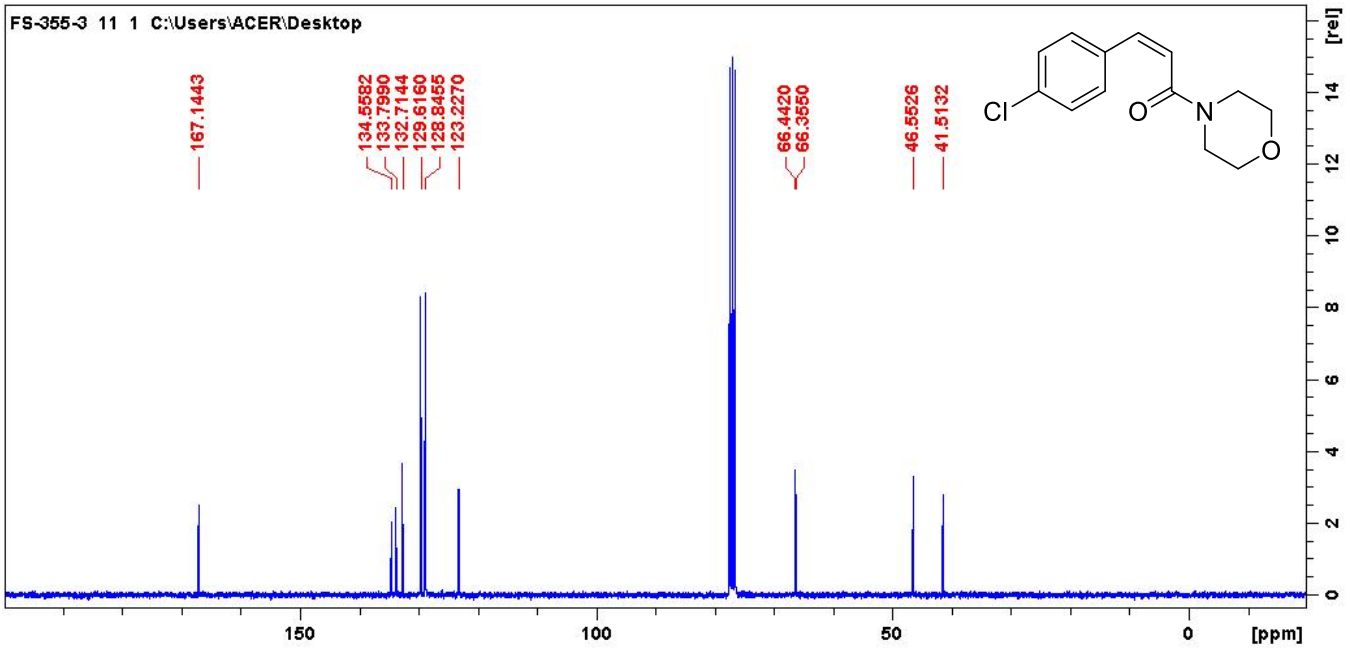
(*Z*)-3-(4-Fluorophenyl)-1-morpholinoprop-2-en-1-one (*Z*-25)



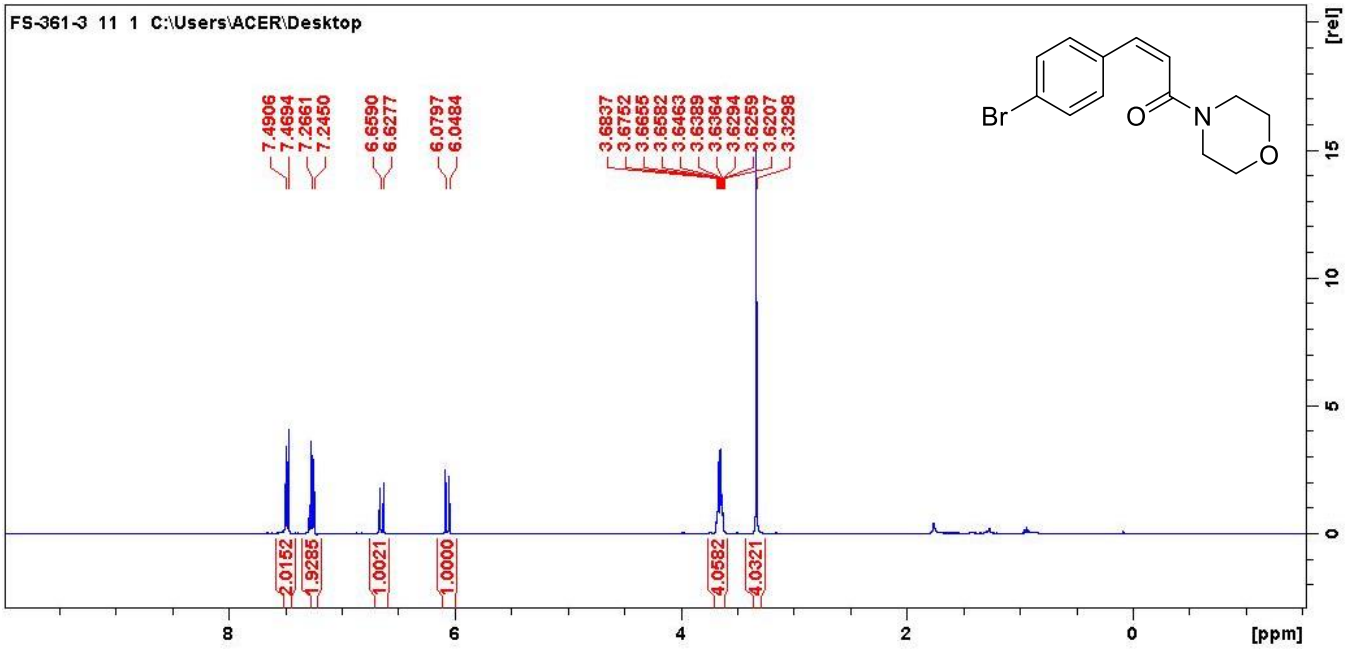


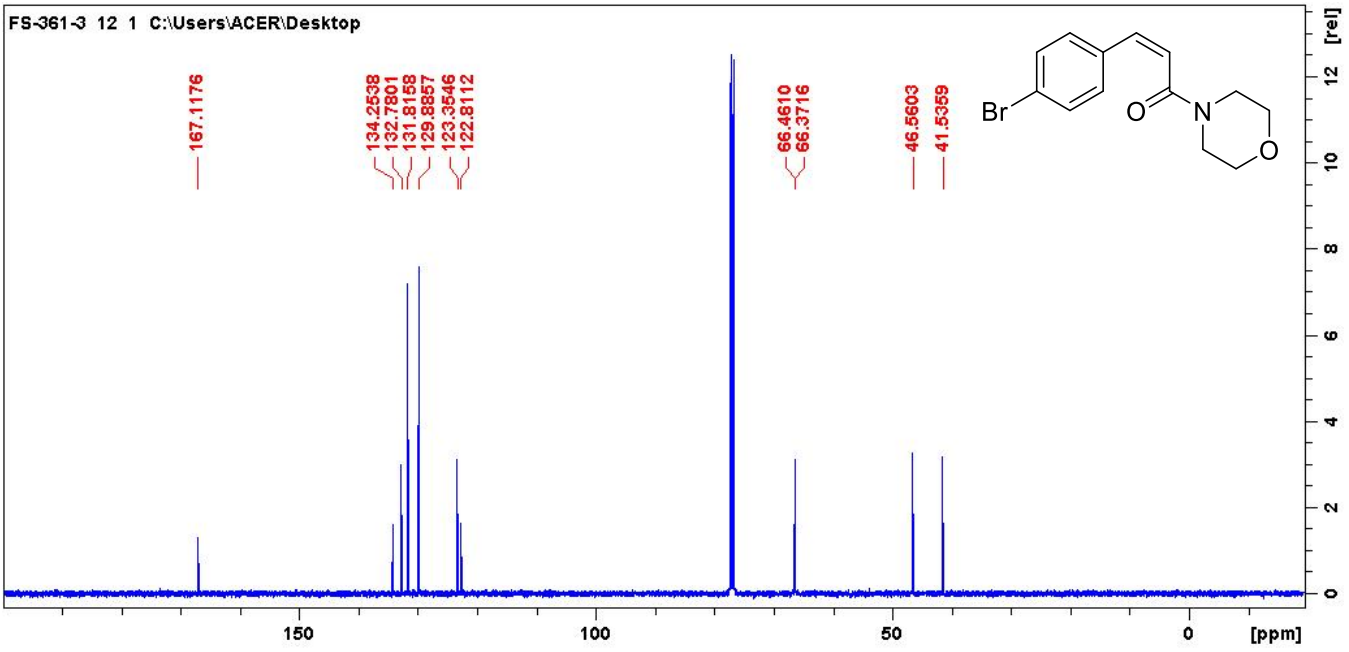
(*Z*)-3-(4-Chlorophenyl)-1-morpholinoprop-2-en-1-one (*Z*-26)



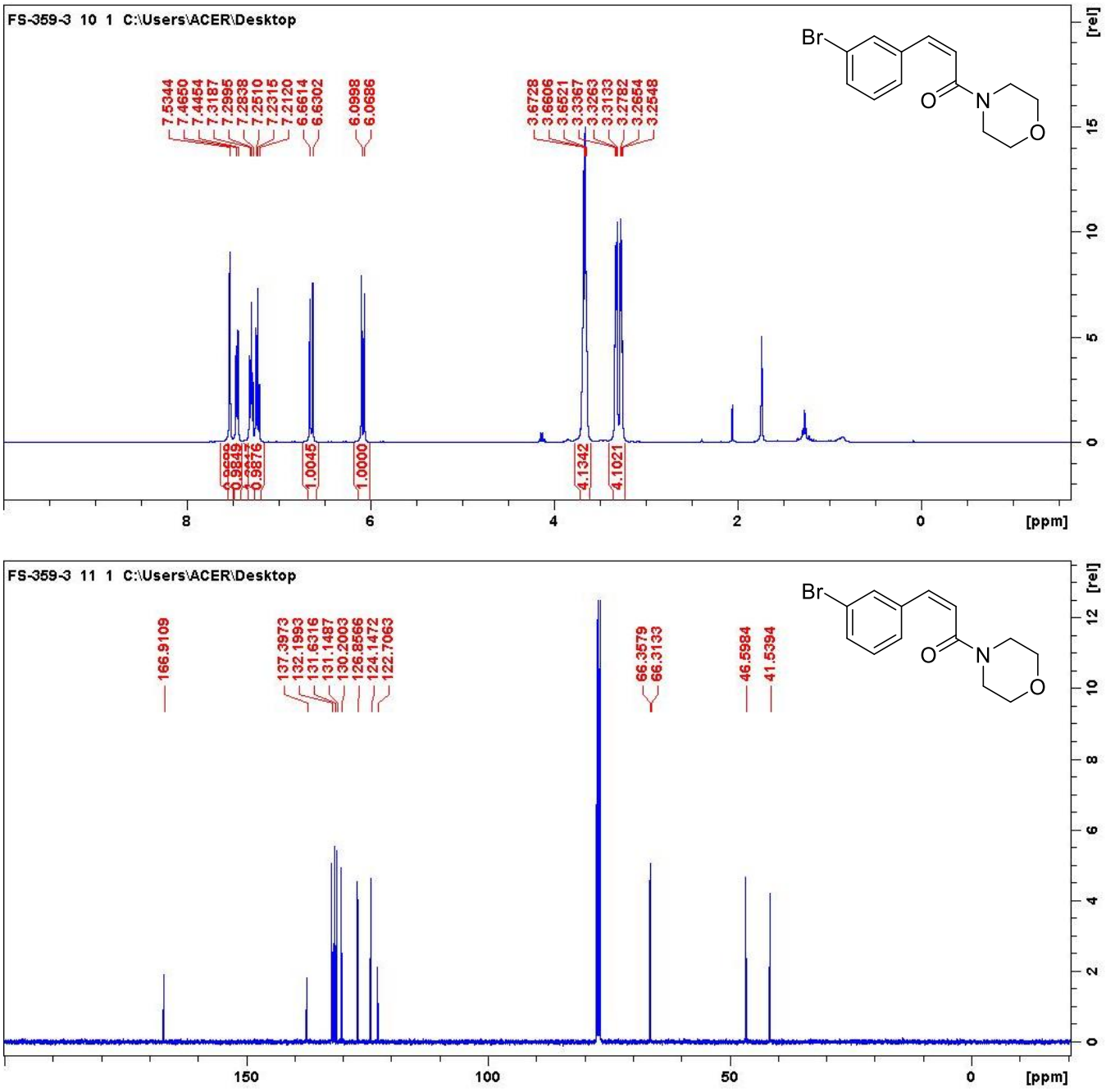


(*Z*)-3-(4-Bromophenyl)-1-morpholinoprop-2-en-1-one (*Z*-27)

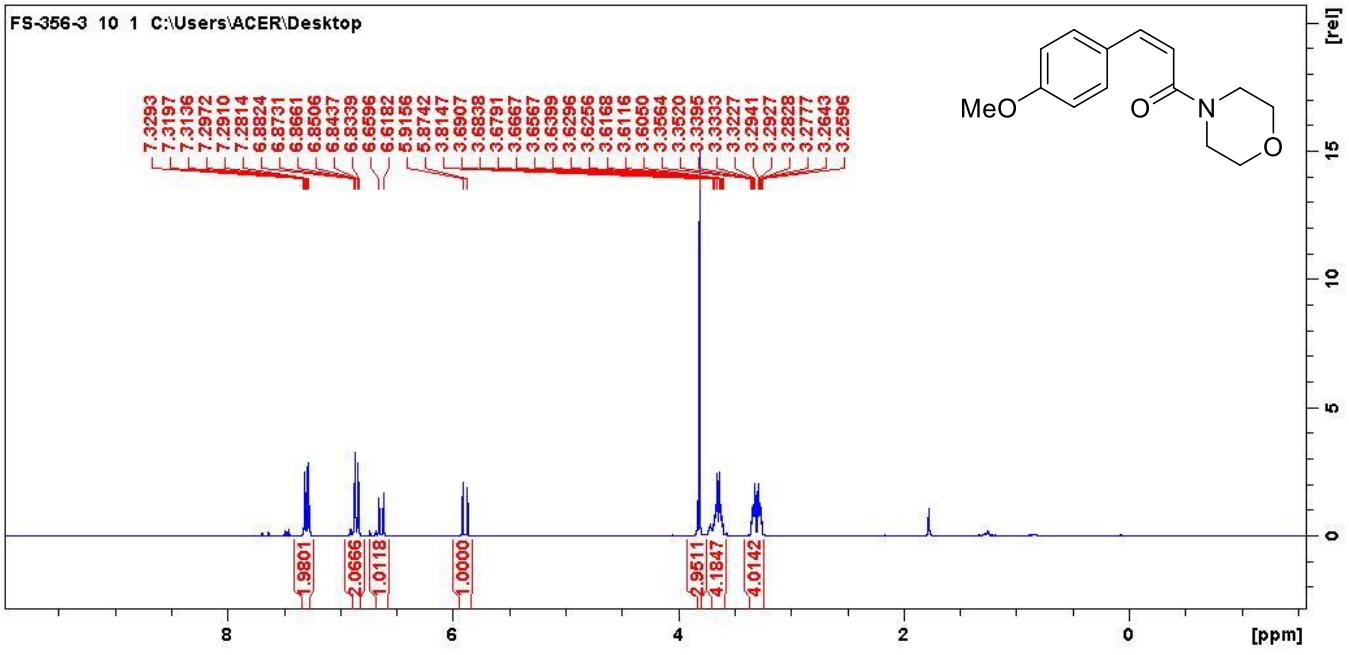


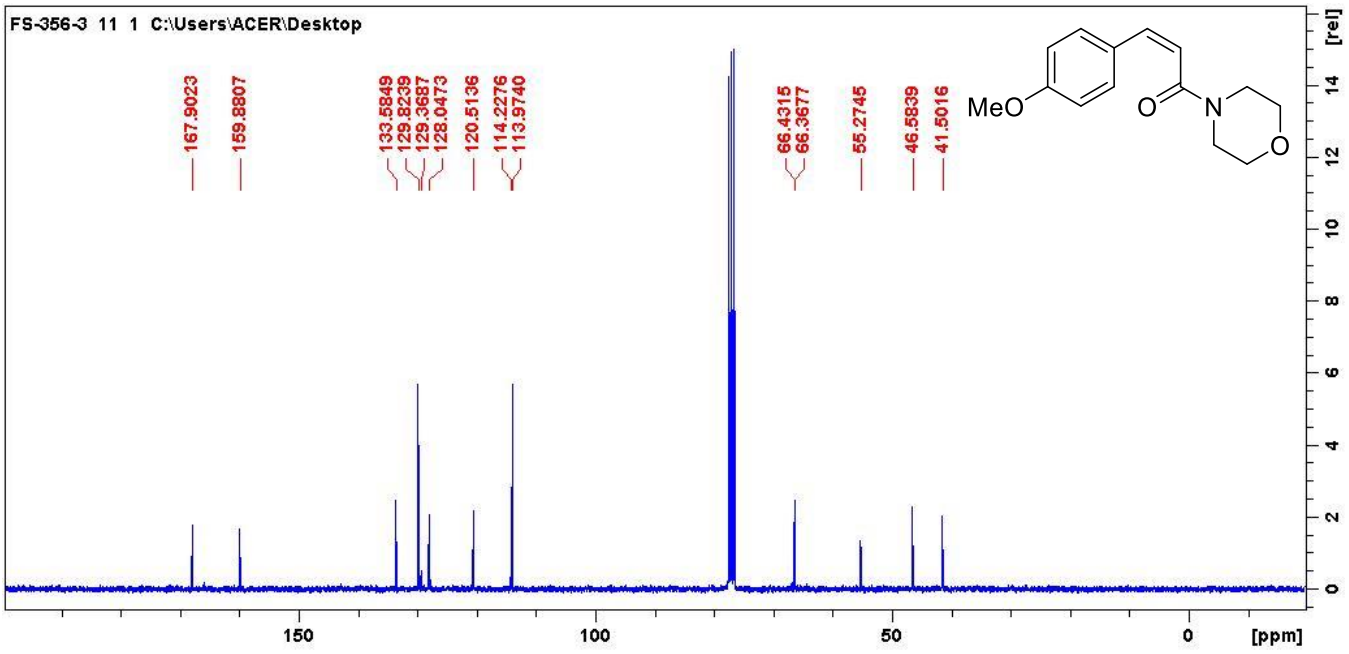


(*Z*)-3-(3-Bromophenyl)-1-morpholinoprop-2-en-1-one (*Z*-28)

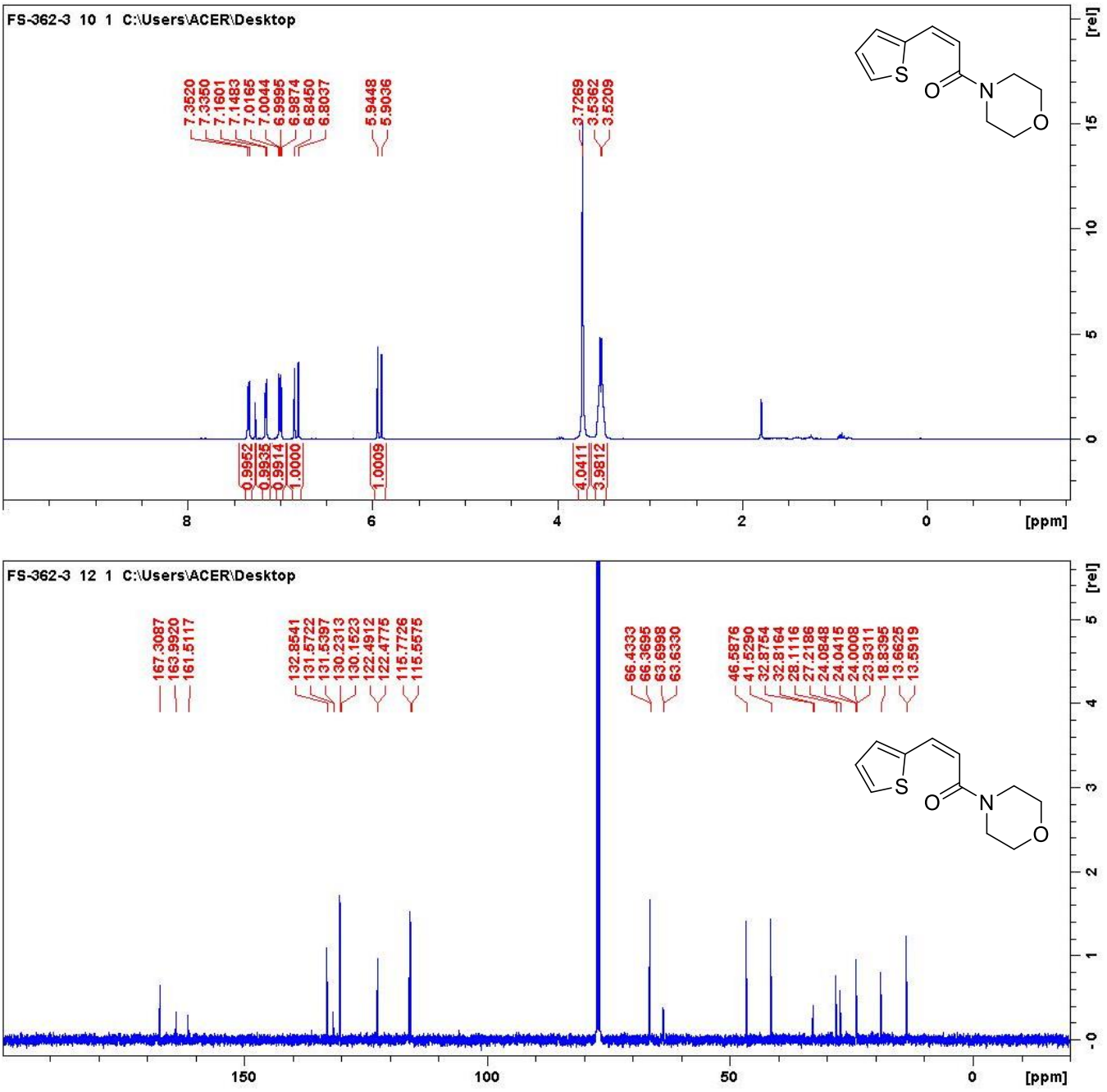


(*Z*)-3-(4-Methoxyphenyl)-1-morpholinoprop-2-en-1-one (*Z*-29)





(*Z*)-1-Morpholino-3-(thiophen-2-yl)prop-2-en-1-one (*Z*-31)



(*Z*)-1-Morpholino-3-(4-nitrophenyl)prop-2-en-1-one (*Z*-32)