Supporting Information

Click-Alkynylation of N- and P- Nucleophiles by Oxidative Cross-Coupling with Alkynylcopper Reagents: A General Synthesis of Ynamides and Alkynylphosphonates

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General Information

All solvents were reagent grade. Dimethylformamide, acetonitrile and N,N,N',N'-tetramethylethylenediamine were freshly distilled from calcium hydride. THF and toluene were freshly distilled from sodium/benzophenone under argon. All other reagents were used as supplied.

Reactions were magnetically stirred. Flash chromatography was performed with silica gel 60 (particle size 35-70 μ m) supplied by SDS. Yields refer to chromatographically and spectroscopically pure compounds.

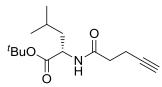
Proton NMR spectra were recorded using an internal deuterium lock at ambient temperature on a Bruker 300 MHz spectrometer. Internal references of $\delta_{\rm H}$ 7.26 was used for CDCl₃. Data are presented as follows: chemical shift (in ppm on the δ scale relative to $\delta_{\rm TMS} = 0$), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint. = quintuplet, hept. = heptuplet, m = multiplet, br. = broad, app. = apparent), coupling constant (*J*/Hz) and integration. Resonances that are either partially or fully obscured are denoted obscured (obs.). Carbon-13 NMR spectra were recorded at 75 MHz. Internal references of $\delta_{\rm C}$ 77.16 was used for CDCl₃. Phosphorus-31 NMR spectra were recorded at 121 MHz.

Optical rotations were recorded on a Perkin Elmer 341 polarimeter at 365 or 589 nm and reported as follows: $[\alpha]_{365}^{20}$ or $[\alpha]_{D}^{20}$, concentration (*c* in g/100 mL), and solvent. Melting points were recorded on a Buchi B-545. Infrared spectra were recorded on a Nicolet iS 10 (SMART iTR diamond ATR) spectrophotometer. High-resolution mass-spectra were obtained on a Waters Xevo Qtof spectrometer. Elemental analyses were obtained by combustion analysis (for C,H,N) and by inductively coupled plasma atomic emission spectroscopy (for Cu).

Experimental Procedures and Characterization Data for Unreported Starting materials

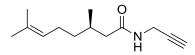


2-Azaspiro[4.4]non-7-en-1-one. A 100 mL round bottom flask was charged with 3,3diallylpyrrolidin-2-one (800 mg, 4.8 mmol). The flask was fitted with a condenser, evacuated under high vacuum and backfilled with argon. Dry and degassed toluene (50 mL) and benzylidene[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro-(tricyclohexylphosphine)ruthenium (Grubbs' second generation catalyst, 75 mg, 0.09 mmol) were successively added and the resulting purple reaction mixture was refluxed overnight. The reaction mixture was cooled to rt, concentrated and directly purified by flash chromatography over silica gel (EtOAc) to give the desired spirocyclic lactam (660 mg, 4.8 mmol, quant.) as a greyish solid. Mp: 133 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.08 (br. s, 1H), 5.64 (s, 2H), 3.31 (t, *J* = 6.7 Hz, 2H), 2.80 (d, *J* = 14.6 Hz, 2H), 2.29 (d, *J* = 14.5 Hz, 2H), 2.08 (t, *J* = 6.6 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 183.5, 128.6, 49.0, 43.3, 39.6, 38.0; IR (ATR) v_{max} 3180, 3057, 2907, 2166, 2016, 1677, 1436, 1369, 1294, 1223, 801, 671, 632 cm⁻¹; ESIMS (positive mode): 138.1; ESIHRMS *m*/*z* calcd for C₈H₁₂NO [M+H]⁺ 138.0919, found 138.0918.



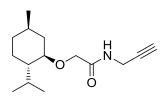
(*S*)-5-[(1-*tert*-Butoxy-4-methyl-1-oxopentan-2-yl)amino]-5-oxopent-1-yne. To a solution of (*S*)-leucine *tert*-butyl ester hydrochloride (2.4 g, 10.5 mmol) and pent-4-ynoic acid (981 mg, 10.0 mmol) in DMF (30 mL) was added 1-hydroxybenzotriazole (HOBt, 1.5 g, 11.1 mmol). 1-(3-Dimethylaminopropyl)-3-ethyl-carbodiimide hydrochloride (EDC, 1.9 g, 10.0 mmol) and *N*-methyl-morpholine (1.4 mL, 12.7 mmol) were next added at 0 °C and the solution was stirred for 16 hours while progressively warmed to rt. The yellow reaction mixture was quenched with

water and diluted with ethyl acetate. The aqueous layer was extracted with ethyl acetate and the combined organic layers were successively washed with a 1M HCl aqueous solution, 1M NaOH aqueous solution and brine, dried over MgSO₄, filtered and concentrated to give the desired leucine derivative (2.6 g, 9.8 mmol, 99%) as a pale yellow oil which can be used in the next step without further purification. [α]²⁰₃₆₅ +16 (*c* 1.5, CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ 6.52 (br. d, *J* = 8.3 Hz, 1H), 4.45 (dt, *J* = 8.7 and 5.4 Hz, 1H), 2.46-2.30 (m, 4H), 1.89 (t, *J* = 2.3 Hz, 1H), 1.66-1.39 (m, 3H), 1.36 (s, 9H), 0.83 (d, *J* = 6.3 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃): δ 172.6, 170.6, 82.9, 81.8, 69.2, 51.2, 41.8, 35.0, 27.9, 24.8, 22.7, 22.0, 14.7; IR (ATR) v_{max} 3306, 2955, 2128, 1740, 1645, 1547, 1369, 1247, 1140, 845, 746, 632 cm⁻¹; ESIMS (positive mode): 290.2, 234.1, 212.1, 166.1, 132.1; ESIHRMS *m*/*z* calcd for C₁₅H₂₅NO₃Na [M+Na]⁺ 290.1732, found 290.1742.



(*R*)-3-(3,7-Dimethyloct-6-enamido)prop-1-yne. To a solution of (*R*)-citronellic acid (1.0 g, 5.9 mmol) in THF (15 mL) were successively added *N*-methylmorpholine (770 µL, 7.0 mmol) and, after 5 minutes, isobutylchloroformate (775 µL, 7.0 mmol) at -78 °C. The resulting white slurry was stirred at -78 °C for 5 minutes and propargylamine (970 µL, 14.1 mmol) was slowly added. The reaction mixture was then warmed to rt over 1 hour and quenched by addition of a 1M HCl aqueous solution. The aqueous layer was extracted with ethyl acetate, combined organic layers were successively washed with 1M NaOH and brine, dried over MgSO₄, filtered and concentrated. The crude residue was purified by flash chromatography over silica gel (EtOAc/petroleum ether: 2/8) to give the desired amide (954 mg, 4.6 mmol, 78%) as a white solid. Mp: 57 °C; $[\alpha]_D^{20} 0 (c 0.5, CHCl_3)$; ¹H NMR (300 MHz, CDCl₃): δ 6.03 (br. s, 1H), 5.05 (t, *J* = 7.1 Hz, 1H), 4.02 (dd, *J* = 5.3 and 2.5 Hz, 2H), 2.25-2.16 (m, 2H), 2.02-1.91 (m, 4H), 1.65 (s, 3H), 1.57 (s, 3H), 1.38-1.28 (m, 1H), 1.23-1.13 (m, 1H), 0.91 (d, *J* = 6.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 172.5, 131.6, 124.4, 79.8, 71.5, 44.2, 37.0, 30.5, 29.1, 25.8, 25.5, 19.6, 17.7; IR (ATR) v_{max} 3290, 2967, 2904, 2182, 2020, 1637, 1535, 1448, 1373, 1262, 1223, 1065, 896,

682, 655, 608 cm⁻¹; ESIMS (positive mode): 209.2, 208.2, 153.1; ESIHRMS m/z calcd for C₁₃H₂₂NO [M+H]⁺ 208.1701, found 208.1703.



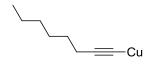
(1R,3R,4S)-Menthoxyacetic acid propargylamide. To a solution of (1R,3R,4S)-menthoxyacetic acid (2.1 g, 10.0 mmol) in THF (25 mL) were successively added N-methylmorpholine (1.3 mL, 12.0 mmol) and, after 5 minutes, isobutylchloroformate (1.6 mL, 12.0 mmol) at -78 °C. The resulting white slurry was stirred at -78 °C for 5 minutes and propargylamine (1.6 mL, 24.0 mmol) was slowly added. The reaction mixture was then warmed to rt over 1 hour and quenched by addition of a 1M HCl aqueous solution. The aqueous layer was extracted with ethyl acetate, combined organic layers were successively washed with 1M NaOH and brine, dried over MgSO₄, filtered and concentrated. The crude residue was purified by flash chromatography over silica gel (EtOAc/petroleum ether: 1/9) to give the desired amide (1.9 g, 7.6 mmol, 76%) as a colorless oil. $[\alpha]_{D}^{20}$ -83 (c 1.2, CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ 6.76 (br. s, 1H), 4.00 (A of AB syst., J = 2.9 Hz, 1H), 3.98 (B of AB syst., J = 2.9 Hz, 1H), 3.98 (A' of A'B' syst., J = 15.2 Hz, 1H), 3.78 (B' of A'B' syst., J = 15.2 Hz, 1H), 3.05 (td, J = 10.6 and 4.1 Hz, 1H), 2.17 (t, J = 2.5 Hz, 1H), 2.03 (hept d, J = 7.0 and 2.7 Hz, 1H), 1.98-1.93 (m, 1H), 1.59-1.52 (m, 2H), 1.32-1.15 (m, 2H), 0.96-0.71 (obs. m, 3H), 0.82 (d, J = 7.0 Hz, 6H), 0.68 (d, J = 7.0 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 170.0, 80.4, 79.3, 71.4, 67.6, 47.9, 40.0, 34.2, 31.3, 28.3, 25.9, 23.1, 22.1, 20.8, 16.1; IR (ATR) v_{max} 3432, 3314, 2955, 2915, 2872, 2135, 1665, 1511, 1448, 1239, 1105, 655 cm⁻¹; ESIMS (positive mode): 252.2, 114.1; ESIHRMS m/z calcd for C₁₅H₂₆NO₂ [M+H]⁺ 252.1964, found 252.1961.

Experimental Procedures and Characterization Data for Alkynylcopper Reagents

General procedure for the synthesis of alkynylcopper reagents:

• Method A using copper iodide in aqueous ammonia and ethanol. To a solution of copper iodide (3.8 g, 20.0 mmol) in a mixture of ammonium hydroxide (28% NH₃ solution, 50 mL) and ethanol (30 mL) was added the alkyne (10.0 mmol) dropwise. The deep blue reaction mixture was stirred overnight at room temperature under argon and the yellow precipitate was collected by filtration and successively washed with ammonium hydroxide (10% NH₃ solution, 3x50 mL), water (3x50 mL), ethanol (3x50 mL), and diethyl ether (3x50 mL). The bright yellow solid was then dried under high vacuum overnight to afford the desired polymeric alkynylcopper reagent which was used without further purification.

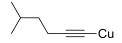
• Method B using copper iodide and potassium carbonate in DMF. To a suspension of copper iodide (762 mg, 4.0 mmol) in DMF (15 mL) was added a solution of the alkyne (4.0 mmol) in DMF (5 mL) *via* cannula and under argon. Finely powdered potassium carbonate (1.1 g, 8.0 mmol) was then added at rt and the resulting slurry was stirred under argon for 2 hours, slowly turning into a bright yellow and thick suspension of copper acetylide which was then collected by filtration and successively washed with ammonium hydroxide (10% NH₃ solution, 2x10 mL), water (2x10 mL), absolute ethanol (2x10 mL), and diethyl ether (2x10 mL). The bright yellow solid was then dried under high vacuum overnight to afford the desired polymeric alkynylcopper reagent.



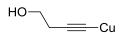
Oct-1-yn-1-ylcopper. This compound was obtained according to method A; Yield: 66%. Anal. Calcd for $C_8H_{13}Cu$: C, 55.63; H, 7.59; Cu, 36.79. Found: C, 55.31; H, 7.29; Cu, 36.69.



Pent-1-yn-1-ylcopper. This compound was obtained according to method A; Yield: 66%. Anal. Calcd for C₅H₇Cu: C, 45.96; H, 5.40; Cu, 47.94. Found: C, 45.36; H, 5.26; Cu, 48.64.



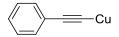
(5-Methylhex-1-yn-1-yl)copper. This compound was obtained according to method A; Yield: 64%. Anal. Calcd for $C_7H_{11}Cu$: C, 52.97; H, 6.99; Cu, 40.04. Found: C, 52.95; H, 6.73; Cu, 40.08.



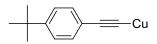
(4-Hydroxybut-1-yn-1-yl)copper. This compound was obtained according to method A; Yield: 28%. Anal. Calcd for C_4H_5CuO : C, 36.22; H, 3.80; Cu, 47.91. Found: C, 35.92; H, 3.62; Cu, 48.15.



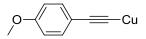
(3-Methylbut-3-en-1-yn-1-yl)copper. This compound was obtained according to method A; Yield: 12%. Anal. Calcd for C_5H_5Cu : C, 46.68; H, 3.92; Cu, 49.40. Found: C, 46.67; H, 3.86; Cu, 48.31.



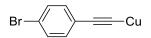
(**Phenylethynyl**)copper. This compound, which is also commercially available, was obtained according to method A; Yield: 59%. Anal. Calcd for C_8H_5Cu : C, 58.35; H, 3.06; Cu, 38.59. Found: C, 58.02; H, 3.08; Cu, 37.99.



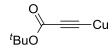
[(4-tert-Butylphenyl)ethynyl]copper. This compound was obtained according to method A; Yield: 43%. Anal. Calcd for $C_{12}H_{13}Cu$: C, 65.28; H, 5.94; Cu, 28.78. Found: C, 64.28; H, 5.84; Cu, 28.01.



[(**4-Methoxyphenyl**)ethynyl]copper. This compound was obtained according to method A; Yield: 38%. Anal. Calcd for C₉H₇CuO: C, 55.52; H, 3.62; Cu, 32.64. Found: C, 55.45; H, 3.57; Cu, 31.86.



[(**4-Bromophenyl**)ethynyl]copper. This compound was obtained according to method A; Yield: 57%. Anal. Calcd for C_8H_4BrCu : C, 39.45; H, 1.66; Cu, 26.09. Found: C, 40.34; H, 1.76; Cu, 25.19.

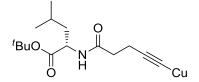


[(*tert*-Butoxycarbonyl)ethynyl]copper. This compound was obtained according to method A; Yield: 62%. Anal. Calcd for C₇H₉CuO₂: C, 44.56; H, 4.81; Cu, 33.68. Found: C, 44.79; H, 4.67; Cu, 33.21.

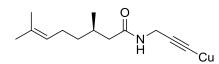
Click-Alkynylation of N- and P- Nucleophiles by Oxidative Cross-Coupling with Alkynylcopper Reagents



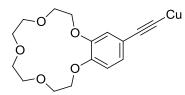
(**Ferrocenylethynyl**)copper. This compound was obtained according to method A; Yield: 97%. Anal. Calcd for C₁₂H₉CuFe: C, 52.87; H, 3.33; Cu, 23.31. Found: C, 53.02; H, 3.18; Cu, 22.97.



(*S*)-{5-[(1-*tert*-Butoxy-4-methyl-1-oxopentan-2-yl)amino]-5-oxopent-1-yn-1-yl}copper. This compound was obtained according to method B; Yield: 91%. Anal. Calcd for $C_{15}H_{24}CuNO_3$: C, 54.61; H, 7.33; Cu, 19.26; N, 4.25. Found: C, 54.82; H, 7.15; Cu, 18.94; N, 3.99.

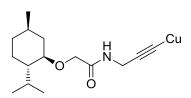


(*R*)-[3-(3,7-Dimethyloct-6-enamido)prop-1-yn-1-yl]copper. This compound was obtained according to method B; Yield: 94%. Anal. Calcd for $C_{13}H_{20}CuNO$: C, 57.86; H, 7.47; Cu, 23.55; N, 5.19. Found: C, 57.76; H, 7.25; Cu, 23.25; N, 5.37.

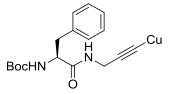


[(2,3,5,6,8,9,11,12-Octahydrobenzo[*b*][1,4,7,10,13]pentaoxacyclopentadecin-15-yl)ethynyl] copper. This compound has been previously reported.^{S1}

^{S1} Vasilevsky, S. F.; Krivenko, O. L.; Gorelik, V. R.; Alabugin, I. V. Tetrahedron 2008, 64, 8807.



(1*R*,3*R*,4*S*)-[(Menthoxyacetamido)prop-1-yn-1-yl]copper. This compound was obtained according to method B; Yield: 76%. Anal. Calcd for $C_{15}H_{24}CuNO_2$: C, 57.39; H, 7.71; Cu, 20.24; N, 4.46. Found: C, 57.33; H, 7.63; Cu, 20.01; N, 4.51.



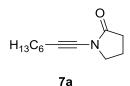
(*S*)-{3-[2-(*tert*-Butoxycarbonylamino)-3-phenylpropanamido]-prop-1-yn-1-yl}copper. This compound was obtained according to method B; Yield: 86%. Anal. Calcd for $C_{17}H_{21}CuN_2O_3$: C, 55.95; H, 5.80; Cu, 17.41; N, 7.68. Found: C, 56.08; H, 6.02; Cu, 16.99; N, 7.75.

Experimental Procedures and Characterization Data:

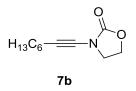
Ynamides from Alkynylcopper Reagents

General procedure for the synthesis of ynamides from alkynylcopper reagents.

A 5 mL round bottom flask was successively charged with the nitrogen nucleophile (8.0 mmol), the alkynylcopper reagent (2.0 mmol) and acetonitrile (4 mL). The resulting bright yellow slurry was then treated with N,N,N',N'-tetramethylethylenediamine (300 µL, 2.0 mmol) and the reaction mixture was vigorously stirred at room temperature and under an atmosphere of oxygen (balloon). After complete disappearance of the alkynylcopper reagent (complete dissolution to a deep blue homogeneous reaction mixture: typically 24-48h), the crude reaction mixture was concentrated under vacuum and the residue was finally purified by flash chromatography over silica gel to afford the desired ynamide.

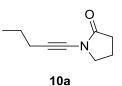


1-(Oct-1-yn-1-yl)pyrrolidin-2-one 7a. This compound has been previously reported.^{S2} Yield: 93% (92% on a 1.9 g scale).

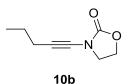


3-(Oct-1-yn-1-yl)oxazolidin-2-one 7b. This compound has been previously reported.^{S3} Yield: 86% (91% on a 2.0 g scale).

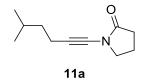
^{S2} Wei, L-L; Mulder, J. A.; Xiong, H.; Zificsak, C. A.; Douglas, C. J.; Hsung, R. P. *Tetrahedron* 2001, 57, 459.



1-(Pent-1-yn-1-yl)pyrrolidin-2-one 10a. Yield: 84% (82% on a 12.4 g scale). Pale yellow oil; ¹H NMR (300 MHz, CDCl₃): δ 3.60 (t, J = 7.5 Hz, 2H), 2.36 (t, J = 8.1 Hz, 2H), 2.25 (t, J = 7.2 Hz, 2H), 1.54-1.43 (m, 2H), 1.53-1.46 (m, 2H), 0.92 (t, J = 7.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 176.1, 72.4, 71.5, 50.1, 29.6, 22.3, 20.5, 18.6, 13.4; IR (ATR) v_{max} 2963, 2261, 1716, 1390, 1298, 1211, 1089, 639 cm⁻¹; ESIMS (positive mode): 152.1, 124.1; ESIHRMS *m/z* calcd for C₉H₁₄NO [M+H]⁺ 152.1076, found 152.1075.



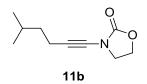
3-(Pent-1-yn-1-yl)oxazolidin-2-one 10b. Yield: 71%. Yellow oil; ¹H NMR (300 MHz, CDCl₃): δ 4.37 (t, J = 8.0 Hz, 2H), 3.83 (t, J = 7.0 Hz, 2H), 2.21 (t, J = 7.1 Hz, 2H), 1.48 (tq, J = 7.3 and 7.2 Hz, 2H), 0.92 (t, J = 7.3 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 156.7, 70.7, 70.2, 63.0, 47.0, 22.1, 20.2, 13.4; IR (ATR) ν_{max} 2963, 2257, 1756, 1409, 1215, 1117, 1034 cm⁻¹; ESIMS (positive mode): 154.1, 140.0, 129.0, 114.0, 110.1; ESIHRMS *m*/*z* calcd for C₈H₁₂NO₂ [M+H]⁺ 154.0868, found 154.0863.



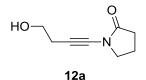
1-(5-Methylhex-1-yn-1-yl)pyrrolidin-2-one 11a. Yield: 70%. Yellow oil; ¹H NMR (300 MHz, CDCl₃): δ 3.57 (t, *J* = 7.0 Hz, 2H), 2.33 (t, *J* = 9.0 Hz, 2H), 2.25 (t, *J* = 8.0 Hz, 2H), 2.06-1.95

^{S3} Jouvin, K.; Couty, F.; Evano, G. Org. Lett. 2010, 12, 3272.

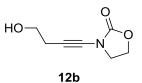
(m, 2H), 1.66-1.55 (m, 1H), 1.40-1.27 (m, 2H), 0.80 (d, J = 6.6 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃): δ 176.6, 73.1, 71.7, 50.6, 38.3, 30.0, 27.7, 22.6, 19.1, 17.0; IR (ATR) ν_{max} 2963, 2252, 1716, 1460, 1393, 1290, 1215, 1081 cm⁻¹; ESIMS (positive mode): 180.1, 149.0, 125.1, 124.1; ESIHRMS m/z calcd for C₁₁H₁₈NO [M+H]⁺ 180.1386, found 180.1388.



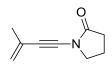
3-(5-Methylhex-1-yn-1-yl)oxazolidin-2-one 11b. Yield: 50%. Colorless oil; ¹H NMR (300 MHz, CDCl₃): δ 4.37 (t, *J* = 7.9 Hz, 2H), 3.81 (t, *J* = 8.2 Hz, 2H), 2.24 (t, *J* = 7.4 Hz, 2H), 1.66-1.55 (app. sept., *J* = 6.7 Hz, 1H), 1.40-1.32 (dt, *J* = 7.4 and 7.1 Hz, 2H), 0.82 (d, *J* = 7.5 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃): δ 156.7, 71.1, 70.0, 62.9, 47.0, 37.7, 27.1, 22.1, 16.3; IR (ATR) v_{max} 2957, 2923, 2864, 2272, 1760, 1480, 1412, 1203, 1105, 1030, 750 cm⁻¹; ESIMS (positive mode): 182.1, 129.0, 126.1; ESIHRMS *m*/*z* calcd for C₁₀H₁₆NO₂ [M+H]⁺ 182.1181, found 182.1176.



1-(4-Hydroxybut-1-yn-1-yl)pyrrolidin-2-one 12a. Yield: 68%. Yellow solid; Mp: 58 °C; ¹H NMR (300 MHz, CDCl₃): δ 3.66 (t, J = 6.4 Hz, 2H), 3.60 (t, J = 7.1 Hz, 2H), 3.53 (br. s, 1H), 2.52 (t, J = 6.9 Hz, 2H), 2.36 (t, J = 7.2 Hz, 2H), 2.05 (tt, J = 7.5 and 7.5 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 176.9, 72.7, 70.0, 61.1, 50.1, 29.8, 23.1, 18.8; IR (ATR) v_{max} 3428, 2963, 2896, 2257, 1700, 1397, 1219, 1046 cm⁻¹; ESIMS (positive mode): 154.1, 149.0; ESIHRMS *m*/*z* calcd for C₈H₁₂NO₂ [M+H]⁺ 154.0865, found 154.0868.

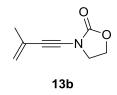


3-(4-Hydroxybut-1-yn-1-yl)oxazolidin-2-one 12b. Yield: 57%. Pale orange oil; ¹H NMR (300 MHz, CDCl₃): δ 4.31 (t, *J* = 6.6 Hz, 2H), 3.79 (t, *J* = 7.8 Hz, 2H), 3.69 (br. s, 1H), 3.57 (t, *J* = 6.6 Hz, 2H), 2.42 (t, *J* = 6.3 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 157.0, 71.0, 68.1, 63.2, 60.6, 46.7, 22.4; IR (ATR) v_{max} 3412, 2959, 2904, 2268, 1744, 1416, 1203, 1034 cm⁻¹; ESIMS (positive mode): 178.0, 173.0, 149.0; ESIHRMS *m*/*z* calcd for C₇H₁₀NO₃ [M+H]⁺ 178.0480, found 178.0485.



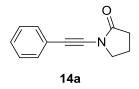
13a

1-(3-Methylbut-3-en-1-yn-1-yl)pyrrolidin-2-one 13a. Yield: 38%. Orange oil; ¹H NMR (300 MHz, CDCl₃): δ 5.21 (br. s, 1H), 5.13 (br. s, 1H), 3.64 (t, *J* = 10.5 Hz, 2H), 2.40 (t, *J* = 8.0 Hz, 2H), 2.10 (tt, *J* = 7.5 and 7.5 Hz, 2H), 1.87 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 176.2, 126.5, 120.8, 80.1, 74.3, 50.6, 30.1, 24.1, 19.2; IR (ATR) ν_{max} 2959, 2927, 2249, 1767, 1677, 1412, 1191, 1065, 730, 639 cm⁻¹; ESIMS (positive mode): 150.1; ESIHRMS *m/z* calcd for C₉H₁₂NO [M+H]⁺ 150.0920, found 150.0919.

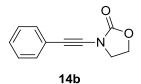


3-(3-Methylbut-3-en-1-yn-1-yl)oxazolidin-2-one 13b. Yield: 43%. Sticky colorless oil; ¹H NMR (300 MHz, CDCl₃): δ 5.20 (br. s, 1H), 5.14 (br. s, 1H), 4.40 (t, J = 9.0 Hz, 2H), 3.89 (t, J = 8.1 Hz, 2H), 1.85 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 156.2, 125.8, 121.2, 78.5, 72.5, 63.3,

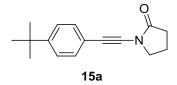
47.2, 23.6; IR (ATR) ν_{max} 2982, 2237, 1755, 1428, 1231, 1109, 1030 cm⁻¹; ESIMS (positive mode): 152.1, 151.1, 150.8, 148.5, 147.2; ESIHRMS *m*/*z* calcd for C₈H₁₀NO₂ [M+H]⁺ 152.0712, found 152.0702.



1-(Phenylethynyl)pyrrolidin-2-one 14a. This compound has been previously reported.^{S4} Yield: 76%.



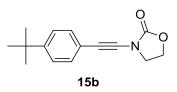
3-(Phenylethynyl)oxazolidin-2-one 14b. This compound has been previously reported^{S4} Yield: 58% (60% on a 2.2 g scale).



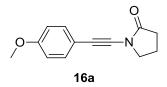
1-[(4-*tert***-Butylphenyl)ethynyl]pyrrolidin-2-one 15a.** Yield: 50%. Sticky colorless oil; ¹H NMR (300 MHz, CDCl₃): δ 7.39 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.7 Hz, 2H), 3.78 (t, J = 7.2 Hz, 2H), 2.49 (t, J = 8.1 Hz, 2H), 2.17 (tt, J = 7.7 Hz, 2H), 1.31 (s, 9H); ¹³C NMR (75 MHz, CDCl₃): δ 176.4, 151.8, 132.4, 125.9, 120.1, 80.4, 73.3, 50.9, 35.4, 31.8, 30.4, 18.9; IR (ATR)

^{S4} Jouvin, K.; Couty, F.; Evano, G. Org. Lett. 2010, 12, 3272.

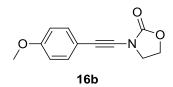
v_{max} 3677, 2947, 2896, 2241, 1712, 1401, 1231, 1069 cm⁻¹; ESIMS (positive mode): 242.2, 241.1, 226.1, 140.0; ESIHRMS m/z calcd for C₁₆H₂₀NO [M+H]⁺ 242.1548, found 242.1545.



3-[(4-tert-Butylphenyl)ethynyl]oxazolidin-2-one 15b. This compound has been previously reported.^{S5} Yield: 37%.



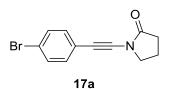
1-[(4-Methoxyphenyl)ethynyl]pyrrolidin-2-one 16a. This compound has been previously reported.^{S6} Yield: 96%.



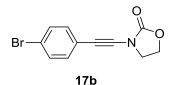
3-[(4-Methoxyphenyl)ethynyl]oxazolidin-2-one 16b. This compound has been previously reported.^{S7} Yield: 80%.

 ^{S5} Dooleweerdt, K.; Birkedal, H.; Skrydstrup, T.; Ruhland, T. J. Org. Chem. 2008, 73, 9447.
^{S6} Coste, A.; Karthikeyan, G.; Couty, F.; Evano, G. Angew. Chem. Int. Ed. 2009, 48, 4381.

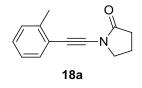
^{S7} Hamada, T.; Ye, X.; Stahl, S. S. J. Am. Chem. Soc. 2008, 130, 833.



1-[(4-Bromophenyl)ethynyl]pyrrolidin-2-one 17a. Yield: 61%. White solid; Mp: 88 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.38 (d, J = 10.2 Hz, 2H), 7,25 (d, J = 9.0 Hz, 2H), 3.72 (t, J = 7.2 Hz, 2H), 2.43 (t, J = 8.4 Hz, 2H), 2.18-2.07 (m, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 176.1, 133.2, 131.8, 122.3, 121.9, 81.8, 72.0, 50.3, 30.0, 19.2; IR (ATR) v_{max} 2986, 2900, 2237, 1720, 1400, 1207, 1144, 1073 cm⁻¹; ESIMS (positive mode): 266.0, 263.0, 187.0, 173.0, 149.0, 129.0, 111.0; ESIHRMS m/z calcd for C₁₂H₁₁BrNO [M+H]⁺ 264.0029, found 264.0024.

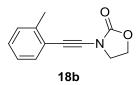


3-[(4-Bromophenyl)ethynyl]oxazolidin-2-one 17b. Yield: 58%. White solid; Mp: 154 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.39 (d, J = 8.4 Hz, 2H), 7,24 (d, J = 8.7 Hz, 2H), 4.45 (t, J = 7.8 Hz, 2H), 3.96 (t, J = 8.1 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 156.1, 133.2, 131.8, 122.7, 121.5, 80.3, 70.6, 63.4, 47.2; IR (ATR) v_{max} 2982, 2904, 2241, 1740, 1397, 1239, 1065 cm⁻¹; ESIMS (positive mode): 266.0, 265.0, 224.0, 187.0, 173.0, 149.0, 140.0; ESIHRMS *m*/*z* calcd for C₁₁H₉BrNO₂ [M+H]⁺ 265.9817, found 265.9821.

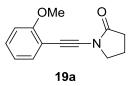


1-[(2-Tolyl)ethynyl]pyrrolidin-2-one 18a. Yield: 55%. White solid; Mp: 93 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.40 (d, J = 7.3 Hz, 1H), 7,19-7.17 (m, 2H), 7.15-7.08 (m, 1H), 3.78 (t, J = 7.1 Hz, 2H), 2.48 (t, J = 7.7 Hz, 2H), 2.44 (s, 3H), 2.17 (app. quint., J = 7.7 Hz, 2H); ¹³C NMR (75

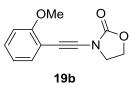
MHz, CDCl₃): δ 175.8, 139.8, 131.6, 129.4, 127.9, 125.5, 122.5, 84.4, 71.6, 50.3, 29.8, 20.9, 18.9; IR (ATR) v_{max} 2989, 2897, 2235, 1707, 1393, 1221, 1110, 1062, 761 cm⁻¹; ESIMS (positive mode): 222.1, 200.1, 201.1, 129.0; ESIHRMS m/z calcd for C₁₃H₁₄NO [M+H]⁺ 200.1075, found 200.1075.



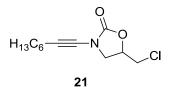
3-[(2-Tolyl)ethynyl]oxazolidin-2-one 18b. Yield: 59%. White solid; Mp: 104 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.39 (d, J = 7.4 Hz, 1H), 7,21-7.18 (m, 2H), 7,16-7.09 (m, 1H), 4.46 (t, J = 8.0 Hz, 2H), 3.98 (t, J = 8.0 Hz, 2H), 2.43 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 156.0, 139.9, 131.6, 129.5, 128.2, 125.6, 122.0, 82.9, 70.1, 63.1, 47.2, 20.8; IR (ATR) v_{max} 2993, 2909, 2247, 1746, 1473, 1446, 1404, 1209, 1194, 1110, 1025, 746 cm⁻¹; ESIMS (positive mode): 224.1, 202.1, 149.0, 129.0; ESIHRMS *m*/*z* calcd for C₁₂H₁₂NO₂ [M+H]⁺ 202.0868, found 202.0866.



1-[(2-Methoxyphenyl)ethynyl]pyrrolidin-2-one 19a. Yield: 62%. White solid; Mp: 95 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.41 (dd, J = 7.5 and 1.6 Hz, 1H), 7,25 (td, J = 7.9 and 1.7 Hz, 1H), 6.90-6.83 (m, 2H), 3.85 (s, 3H), 3.78 (t, J = 7.1 Hz, 2H), 2.45 (t, J = 7.7 Hz, 2H), 2.14 (app. quint., J = 7.7 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 175.8, 159.8, 133.7, 129.5, 120.4, 111.7, 110.5, 84.1, 68.7, 55.8, 50.2, 29.7, 18.9; IR (ATR) ν_{max} 2970, 2901, 2243, 1711, 1397, 1247, 1117, 1012, 754 cm⁻¹; ESIMS (positive mode): 238.1, 216.1, 213.1, 131.1; ESIHRMS *m/z* calcd for C₁₃H₁₄NO₂ [M+H]⁺ 216.1025, found 216.1026.



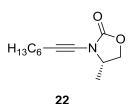
3-[(2-Methoxyphenyl)ethynyl]oxazolidin-2-one 19b. Yield: 75%. Yellow solid; Mp: 87 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.39 (dd, J = 7.5 and 1.7 Hz, 1H), 7,26 (td, J = 7.9 and 1.7 Hz, 1H), 6.87 (t, J = 7.5 Hz, 1H), 6.84 (d, J = 8.4 Hz, 1H), 4.42 (t, J = 7.6 Hz, 2H), 3.96 (t, J = 7.6 Hz, 2H), 3.83 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 159.9, 156.0, 133.7, 129.8, 120.4, 111.2, 110.6, 82.6, 67.3, 63.2, 55.7, 47.1; IR (ATR) v_{max} 2917, 2832, 2254, 1757, 1596, 1569, 1492, 1408, 1250, 1188, 1163, 1112, 1071, 1018, 746 cm⁻¹; ESIMS (positive mode): 435.2, 240.1, 218.1, 174.1, 146.1, 131.1; ESIHRMS *m*/*z* calcd for C₁₂H₁₂NO₃ [M+H]⁺ 218.0817, found 218.0816.



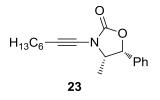
5-(Chloromethyl)-3-(oct-1-yn-1-yl)oxazolidin-2-one 21. Yield: 71%. Colorless oil; ¹H NMR (300 MHz, CDCl₃): δ 4.84-4.76 (m, 1H), 3.93 (A of ABX syst, J = 9.0 and 9.0 Hz, 1H), 3.73-3.65 (m, 3H), 2.24 (t, J = 7.0 Hz, 2H), 1.47 (app quint., J = 7.4 Hz, 2H), 1.37-1.20 (m, 6H), 0.84 (t, J = 6.6 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 155.5, 72.5, 71.4, 69.5, 49.6, 44.4, 31.3, 28.7, 28.5, 22.5, 18.3, 14.0; IR (ATR) v_{max} 2967, 2927, 2268, 1764, 1420, 1223, 1113, 1050, 742 cm⁻¹; ESIMS (positive mode): 301.1, 244.1, 183.0, 142.0, 111.0; ESIHRMS *m/z* calcd for C₁₂H₁₉ClNO₂ [M+H]⁺ 244.1104, found 244.1109.

Electronic Supplementary Material (ESI) for Chemical Science This journal is $\ensuremath{\mathbb{O}}$ The Royal Society of Chemistry 2012

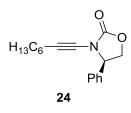
Click-Alkynylation of N- and P- Nucleophiles by Oxidative Cross-Coupling with Alkynylcopper Reagents



(S)-4-Methyl-3-(oct-1-yn-1-yl)oxazolidin-2-one 22. This compound has been previously reported.^{S8} Yield: 61%.

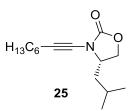


(4*S*,5*R*)-4-Methyl-3-(oct-1-yn-1-yl)-5-phenyloxazolidin-2-one 23. Yield: 72%. Sticky colorless oil; $[\alpha]_{D}^{20}$ -6 (*c* 1.0, CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ 7.39-7.34 (m, 3H), 7.27-7.23 (m, 2H), 5.68 (d, *J* = 8.1 Hz, 1H), 4.29 (dq, *J* = 8.1 and 6.6 Hz, 1H), 2.31 (t, *J* = 6.9 Hz, 2H), 1.57-1.47 (m, 2H), 1.41-1.26 (m, 6H), 0.90 (t, *J* = 6.6 Hz, 3H), 0.87 (t, *J* = 6.6 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 156.1, 134.2, 128.9, 128.7, 126.0, 79.5, 72.3, 69.1, 58.1, 31.3, 28.8, 28.6, 22.6, 18.5, 14.8, 14.0; IR (ATR) ν_{max} 2931, 2253, 1760, 1405, 1188, 1125 cm⁻¹; ESIMS (positive mode): 286.2, 242.2, 215.2, 172.1, 118.1; ESIHRMS *m*/*z* calcd for C₁₈H₂₄NO₂ [M+H]⁺ 286.1807, found 286.1809.

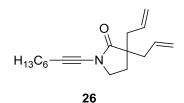


(*R*)-3-(Oct-1-yn-1-yl)-4-phenyloxazolidin-2-one 24. This compound has been previously reported.^{S9} Yield: 28%.

^{S8} Yao, B.; Liang, Z.; Niu, T.; Zhang, Y. J. Org. Chem. 2009, 74, 4630.



(*S*)-4-*iso*-Butyl-3-(oct-1-yn-1-yl)oxazolidin-2-one 25. Yield: 20%. Pale yellow oil; $[\alpha]_D^{20}$ +49 (*c* 0.8, CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ 4.51-4.43 (m, 1H), 4.01-3.95 (m, 2H), 2.31 (t, *J* = 6.9 Hz, 2H), 1.92-1.83 (m, 1H), 1.79-1.70 (m, 1H), 1.57-1.47 (m, 2H), 1.44-1.24 (m, 7H), 0.96 (d, *J* = 6.7 Hz, 3H), 0.94 (d, *J* = 6.5 Hz, 3H), 0.82 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 156.4, 72.5, 69.2, 69.1, 56.3, 41.9, 31.3, 28.7, 28.5, 24.5, 23.1, 22.6, 22.2, 18.5, 14.1; IR (ATR) ν_{max} 2963, 2923, 2864, 2264, 1771, 1468, 1409, 1196, 1109, 750 cm⁻¹; ESIMS (positive mode): 252.2, 196.1, 144.1; ESIHRMS *m*/*z* calcd for C₁₅H₂₆NO₂ [M+H]⁺ 252.1964, found 252.1965.



3,3-Diallyl-1-(oct-1-yn-1-yl)pyrrolidin-2-one 26. Yield: 82%. Colorless oil; ¹H NMR (300 MHz, CDCl₃): δ 5.63-5.50 (m, 2H), 4.97-4.92 (m, 4H), 3.31 (t, *J* = 7.1 Hz, 2H), 2.21 (dd, *J* = 13.8 and 6.6, 2H), 2.19 (t, *J* = 6.1 Hz, 2H), 2.03 (dd, *J* = 13.7 and 8.3 Hz, 2H), 1.82 (t, *J* = 7.3 Hz, 2H), 1.36 (app. quint., *J* = 7.1 Hz, 2H), 1.27-1.10 (m, 6H), 0.72 (t, *J* = 6.7 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 178.3, 132.9, 118.8, 71.8, 71.4, 47.0, 46.4, 41.1, 31.1, 28.6, 28.3, 27.2, 22.2, 18.3, 13.8; IR (ATR) v_{max} 2959, 2935, 2261, 1712, 1397, 1219, 1085, 912 cm⁻¹; ESIMS (positive mode): 547.4, 296.2, 274.2, 204.1; ESIHRMS *m/z* calcd for C₁₈H₂₈NO [M+H]⁺ 274.2171, found 274.2173.

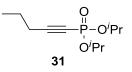
^{S9} Frederick, M. O.; Mulder, J. A.; Tracey, M. R.; Hsung, R. P.; Huang, J.; Kurtz, K. C. M.; Shen, L.; Douglas, C. J. *J. Am. Chem. Soc.* **2003**, *125*, 2368.

Experimental Procedures and Characterization Data: Alkynylphosphonates from Alkynylcopper Reagents

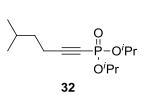
General procedure for the synthesis of alkynylphosphonates from alkynylcopper reagents.

A 5 mL round bottom flask was successively charged with dialkylphosphite (8.0 mmol), the alkynylcopper reagent (2.0 mmol) and DMF (4 mL). The resulting bright yellow slurry was then treated with *N*-methylimidazole (315 μ L, 4.0 mmol) and the reaction mixture was vigorously stirred at room temperature and under an atmosphere of oxygen (balloon). After complete disappearance of the alkynylcopper reagent (complete dissolution to a deep blue homogeneous reaction mixture: typically 12-24h), the reaction was diluted with an aqueous mixture of saturated ammonium chloride and 28% ammonium hydroxide (1:1 solution) and extracted with diethyl ether. Combined organic layers were washed with brine, dried over MgSO₄ and concentrated. The crude residue was finally purified by flash chromatography over silica gel to give the desired alkynylphosphonate.

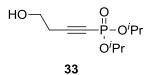
Diisopropyl (oct-1-yn-1-yl)phosphonate 30. Yield: 85% (91% on a 2.5 g scale). Colorless oil; ¹H NMR (300 MHz, CDCl₃): δ 4.51-4.34 (m, 2H), 2.01 (dt, J = 6.6 Hz and $J_{\text{H-P}} = 4.8$ Hz, 2H), 1.25 (tt, J = 7.8 and 7.2 Hz, 2H), 1.11-0.96 (m, 6H), 1.02 (d, J = 6.6 Hz, 12H), 0.56 (t, J = 6.3Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 102.5 (d, $J_{\text{C-P}} = 52.5$ Hz), 71.5 (d, $J_{\text{C-P}} = 300.0$ Hz), 71.0 (d, $J_{\text{C-P}} = 22.5$ Hz), 30.7, 28.1, 27.0, 23.4 (d, $J_{\text{C-P}} = 4.5$ Hz), 23.2 (d, $J_{\text{C-P}} = 4.9$ Hz), 22.1, 18.8, 13.5; ³¹P NMR (121 MHz, CDCl₃): δ -8.6; IR (ATR) v_{max} 2979, 2213, 1377, 1257, 983 cm⁻¹; ESIMS (positive mode): 275.2, 191.1, 110.0; ESIHRMS m/z calcd for C₁₄H₂₈O₃P [M+H]⁺ 275.1776, found 275.1778.



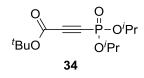
Diisopropyl (pent-1-yn-1-yl)phosphonate 31. Yield: 86% (92% on a 16.0 g scale). Colorless oil; ¹H NMR (300 MHz, CDCl₃): δ 4.67-4.60 (m, 2H), 2.24 (dt, J = 6.9 Hz and $J_{\text{H-P}} = 4.2$ Hz, 2H), 1.53 (tq, J = 7.5 and 7.2 Hz, 2H), 1.28 (d, J = 7.2 Hz, 12H), 0.93 (t, J = 6.6 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 102.1 (d, $J_{\text{C-P}} = 52.5$ Hz), 72.2 (d, $J_{\text{C-P}} = 300.0$ Hz), 72.0 (d, $J_{\text{C-P}} = 5.3$ Hz), 24.4 (d, $J_{\text{C-P}} = 4.5$ Hz), 23.7 (d, $J_{\text{C-P}} = 4.8$ Hz), 21.3, 21.2, 13.3; ³¹P NMR (121 MHz, CDCl₃): δ -8.7; IR (ATR) ν_{max} 2982, 2205, 1385, 1255, 981 cm⁻¹; ESIMS (positive mode): 233.1, 191.1, 149.0; ESIHRMS *m*/*z* calcd for C₁₁H₂₂O₃P [M+H]⁺ 233.1307, found 233.1305.



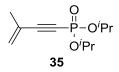
Diisopropyl (5-methylhex-1-yn-1-yl)phosphonate 32 Yield: 96%. Pale yellow oil; ¹H NMR (300 MHz, CDCl₃): δ 4.67-4.60 (m, 2H), 2.26 (dt, J = 6.3 Hz and $J_{\text{H-P}} = 4.5$ Hz, 2H), 1.61 (app. sept., J = 6.6 Hz, 1H), 1.39 (dt, J = 7.2 and 6.9 Hz, 2H), 1.28 (d, J = 6.3 Hz, 12H), 0.82 (d, J = 6.6 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃): δ 102.3 (d, $J_{\text{C-P}} = 52.5$ Hz), 72.0 (d, $J_{\text{C-P}} = 6.0$ Hz), 71.9 (d, $J_{\text{C-P}} = 300.0$ Hz), 36.4, 27.4, 24.0 (d, $J_{\text{C-P}} = 4.5$ Hz), 23.7 (d, $J_{\text{C-P}} = 4.8$ Hz), 22.2, 17.4; ³¹P NMR (121 MHz, CDCl₃): δ -8.7; IR (ATR) v_{max} 2982, 2197, 1381, 1257, 984 cm⁻¹; ESIMS (positive mode): 261.2, 219.1, 177.1; ESIHRMS m/z calcd for C₁₃H₂₆O₃P [M+H]⁺ 261.1620, found 261.1621.



Diisopropyl (4-hydroxybut-1-yn-1-yl)phosphonate 33. Yield: 35%. Pale yellow oil; ¹H NMR (300 MHz, CDCl₃): δ 4.68-4.61 (m, 2H), 3.72 (t, J = 6.6 Hz, 2H), 2.55 (td, J = 6.3 Hz and $J_{\text{H-P}} = 1.8$ Hz, 2H), 1.30 (d, J = 6.0 Hz, 12H); ¹³C NMR (75 MHz, CDCl₃): δ 100.0 (d, $J_{\text{C-P}} = 53.3$ Hz), 73.0 (d, $J_{\text{C-P}} = 300.0$ Hz), 72.6 (d, $J_{\text{C-P}} = 6.0$ Hz), 60.0, 24.0 (d, $J_{\text{C-P}} = 4.5$ Hz), 23.7 (d, $J_{\text{C-P}} = 4.9$ Hz), 23.7; ³¹P NMR (121 MHz, CDCl₃): δ -8.7; IR (ATR) ν_{max} 3405, 2986, 2197, 1381, 1241, 984 cm⁻¹; ESIMS (positive mode): 235.1, 151.0, 133.0, 121.0; ESIHRMS *m*/*z* calcd for C₁₀H₂₀O₃P [M+H]⁺ 235.1099, found 235.1100.

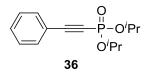


Diisopropyl (*tert*-butoxycarbonylethynyl)phosphonate 34. Yield: 48%. Orange-brown oil; ¹H NMR (300 MHz, CDCl₃): δ 4.67-4.60 (m, 2H), 1.38 (s, 9H), 1.26 (d, J = 6.3 Hz, 12H); ¹³C NMR (75 MHz, CDCl₃): δ 150.6, 87.4 (d, $J_{C-P} = 45.8$ Hz), 85.4, 74.0 (d, $J_{C-P} = 285.0$ Hz), 73.4 (d, $J_{C-P} = 5.3$ Hz), 28.0, 23.9 (d, $J_{C-P} = 4.5$ Hz), 23.6 (d, $J_{C-P} = 4.9$ Hz); ³¹P NMR (121 MHz, CDCl₃): δ -11.6; IR (ATR) ν_{max} 2975, 1708, 1369, 1255, 1151, 983 cm⁻¹; ESIMS (positive mode): 291.1, 257.1, 193.0, 151.0; ESIHRMS m/z calcd for C₁₃H₂₄O₅P [M+H]⁺ 291.1361, found 291.1359.

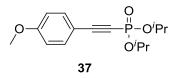


Diisopropyl (3-methylbut-3-en-1-yn-1-yl)phosphonate 35. Yield: 88%. Pale yellow oil; ¹H NMR (300 MHz, CDCl₃): δ 5.45 (br. s, 1H), 5.39 (br. s, 1H), 4.67-4.59 (m, 2H), 1.81 (s, 3H), 1.26 (d, J = 6.3 Hz, 12H); ¹³C NMR (75 MHz, CDCl₃): δ 127.5, 124.5, 99.3 (d, $J_{C-P} = 51.8$ Hz), 78.8 (d, $J_{C-P} = 300.0$ Hz), 72.2 (d, $J_{C-P} = 6.0$ Hz), 23.9 (d, $J_{C-P} = 4.5$ Hz), 23.7 (d, $J_{C-P} = 4.8$ Hz),

22.1; ³¹P NMR (121 MHz, CDCl₃): δ -8.6; IR (ATR) ν_{max} 2979, 2182, 1377, 1258, 983 cm⁻¹; ESIMS (positive mode): 231.1, 189.1, 147.0; ESIHRMS *m*/*z* calcd for C₁₁H₂₀O₃P [M+H]⁺ 231.1150, found 231.1145.

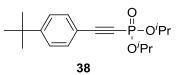


Diisopropyl (phenylethynyl)phosphonate 36. This compound has been previously reported.^{S10} Yield: 71% (97% on a 2.6 g scale).

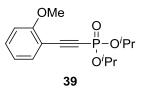


Diisopropyl [(4-methoxyphenyl)ethynyl]phosphonate 37. Yield: 58%. Pale yellow oil; ¹H NMR (300 MHz, CDCl₃): δ 7.45 (d, J = 9.0 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 4.80-4.72 (m, 2H), 3.79 (s, 3H), 1.37 (d, J = 6.0 Hz, 12H); ¹³C NMR (75 MHz, CDCl₃): δ 161.6, 134.5, 114.5, 111.9, 99.0 (d, $J_{C-P} = 52.5$ Hz), 79.2 (d, $J_{C-P} = 247.5$ Hz), 72.1 (d, $J_{C-P} = 5.3$ Hz), 55.4, 24.1 (d, $J_{C-P} = 4.5$ Hz), 23.9 (d, $J_{C-P} = 4.9$ Hz); ³¹P NMR (121 MHz, CDCl₃): δ -8.1; IR (ATR) ν_{max} 2975, 2186, 1507, 1251, 981 cm⁻¹; ESIMS (positive mode): 297.1, 255.1, 213.0; ESIHRMS *m*/*z* calcd for C₁₅H₂₂O₃P [M+H]⁺ 297.1256, found 297.1259.

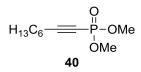
^{S10} Gao, Y.; Wang, G.; Chen, L.; Xu, P.; Zhao, Y.; Zhou, Y.; Han, L.-B. J. Am. Chem. Soc. 2009, 131, 7956.



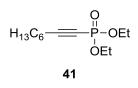
Diisopropyl [(4-*tert***-butylphenyl)ethynyl]phosphonate 38.** Yield: 56%. Pale yellow solid; Mp: 65 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.47 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.7 Hz, 2H), 4.84-4.73 (m, 2H), 1.38 (d, J = 6.0 Hz, 12H), 1.29 (s, 9H); ¹³C NMR (75 MHz, CDCl₃): δ 154.5, 132.6, 125.9, 117.0, 98.9 (d, J_{C-P} = 53.3 Hz), 79.6 (d, J_{C-P} = 292.5 Hz), 72.5 (d, J_{C-P} = 6.0 Hz), 35.3, 31.3, 24.2 (d, J_{C-P} = 4.5 Hz), 23.9 (d, J_{C-P} = 4.8 Hz); ³¹P NMR (121 MHz, CDCl₃): δ -8.1; IR (ATR) v_{max} 2967, 2178, 1255, 990 cm⁻¹; ESIMS (positive mode): 323.2, 281.1, 239.1, 149.0; ESIHRMS *m*/*z* calcd for C₁₈H₂₈O₃P [M+H]⁺ 323.1776, found 323.1774.



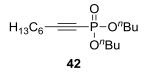
Diisopropyl [(2-methoxyphenyl)ethynyl]phosphonate 39. Yield: 93%. Yellow solid; Mp: 49 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.40-7.28 (m, 2H), 6.90-6.79 (m, 2H), 4.80-4.68 (m, 2H), 3.77 (s, 3H), 1.33 (d, *J* = 6.1 Hz, 6H), 1.32 (d, *J* = 5.9 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃): δ 161.4 (d, *J*_{C-P} = 1.7 Hz), 134.1, 132.1, 120.3, 110.7, 109.0 (d, *J*_{C-P} = 5.6 Hz), 95.4 (d, *J*_{C-P} = 53.0 Hz), 83.4 (d, *J*_{C-P} = 296.1 Hz), 72.1 (d, *J*_{C-P} = 5.6 Hz), 55.6, 23.8 (d, *J*_{C-P} = 4.5 Hz), 23.5 (d, *J*_{C-P} = 4.8 Hz); ³¹P NMR (121 MHz, CDCl₃): δ -8.2 (t, *J* = 9.0 Hz); IR (ATR) v_{max} 2978, 2181, 1596, 1485, 1259, 1245, 1160, 983, 888, 854, 747 cm⁻¹; ESIMS (positive mode): 319.1, 297.1, 213.0; ESIHRMS *m*/*z* calcd for C₁₅H₂₂O₄P [M+H]⁺ 297.1256, found 297.1257.



Dimethyl (oct-1-yn-1-yl)phosphonate 40. Yield: 65%. Colorless oil; ¹H NMR (300 MHz, CDCl₃): δ 3.46 (d, $J_{\text{H-P}} = 12.3$ Hz, 6H), 2.07 (dt, J = 6.3 Hz and $J_{\text{H-P}} = 4.8$ Hz, 2H), 1.28 (tt, J = 7.8 and 6.9 Hz, 2H), 1.14-0.97 (m, 6H), 0.59 (t, J = 6.6 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 103.8 (d, $J_{\text{C-P}} = 51.8$ Hz), 68.6 (d, $J_{\text{C-P}} = 300.0$ Hz), 52.7 (d, $J_{\text{C-P}} = 6.0$ Hz), 30.6, 28.0, 27.0, 22.1, 18.8, 13.6; ³¹P NMR (121 MHz, CDCl₃): δ -3.2; IR (ATR) v_{max} 2951, 2201, 1456, 1264, 1026 cm⁻¹; ESIMS (positive mode): 219.1, 173.0, 112.0; ESIHRMS *m*/*z* calcd for C₁₀H₂₀O₃P [M+H]⁺ 219.1150, found 219.1147.



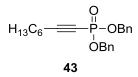
Diethyl (oct-1-yn-1-yl)phosphonate 41. This compound has been previously reported.^{S11} Yield: 83% (96% on a 2.4 g scale).



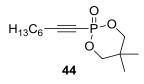
Dibutyl (oct-1-yn-1-yl)phosphonate 42. Yield: 87%. Colorless oil; ¹H NMR (300 MHz, CDCl₃): 3.99 (td, J = 6.6 Hz and $J_{H-P} = 6.6$ Hz, 4H), 2.26 (dt, J = 6.0 Hz and $J_{H-P} = 4.5$ Hz, 2H), 1.65-1.56 (m, 4H), 1.55-1.45 (m, 2H), 1.41-1.28 (m, 6H), 1.26-1.18 (m, 4H), 0.86 (t, J = 7.3 Hz, 3H), 0.83 (t, J = 7.2 Hz, 3H), 0.81 (t, J = 7.0 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 103.1 (d, $J_{C-P} = 52.5$ Hz), 70.3 (d, $J_{C-P} = 292.5$ Hz), 66.5 (d, $J_{C-P} = 5.3$ Hz), 32.1 (d, $J_{C-P} = 7.0$ Hz), 31.1, 28.3, 27.3, 22.4, 19.1, 18.7, 13.9, 13.5; ³¹P NMR (121 MHz, CDCl₃): δ -3.4; IR (ATR) ν_{max} 2959,

^{S11} Mavel, G.; Favelier R. J. Chim. Phys. 1967, 64, 627.

2201, 1247, 1020 cm⁻¹; ESIMS (positive mode): 303.2, 247.1, 191.1; ESIHRMS m/z calcd for C₁₆H₃₂O₃P [M+H]⁺ 303.2089, found 303.2090.



Dibenzyl (oct-1-yn-1-yl)phosphonate 43. Yield: 37%. Colorless oil; ¹H NMR (300 MHz, CDCl₃): 7.30-7.20 (m, 10H), 4.99 (d, $J_{\text{H-P}}$ = 8.7 Hz, 4H), 2.20 (dt, J = 6.3 Hz and $J_{\text{H-P}}$ = 4.5 Hz, 2H), 1.43 (tt, J = 7.5 and 6.6 Hz, 2H), 1.30-1.13 (m, 6H), 0.81 (t, J = 6.6 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 135.7, 128.5, 127.6, 127.0, 104.4 (d, $J_{\text{C-P}}$ = 53.3 Hz), 70.3 (d, $J_{\text{C-P}}$ = 292.5 Hz), 68.3 (d, $J_{\text{C-P}}$ = 5.3 Hz), 31.2, 28.5, 27.3, 22.4, 19.2, 14.0; ³¹P NMR (121 MHz, CDCl₃): δ -5.5; IR (ATR) v_{max} 2923, 2205, 1452, 1260, 990 cm⁻¹; ESIMS (positive mode): 371.18, 275.2, 191.1, 110.0; ESIHRMS *m*/*z* calcd for C₂₂H₂₈O₃P [M+H]⁺ 371.1776, found 371.1774.

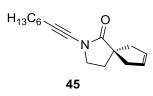


5,5-Dimethyl-2-(oct-1-yn-1-yl)-1,3,2-dioxaphosphinane 2-oxide 44. This compound has been previously reported.^{S12} Yield: 39%.

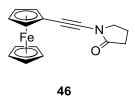
^{S12} Sajna, K. V.; Srinivas, V.; Kumara Swamy, K. C. Adv. Synth. Catal. 2010, 352, 3069.

Experimental Procedures and Characterization Data:

Complex Ynamides and Alkynylphosphonates

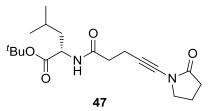


2-(Oct-1-yn-1-yl)-2-azaspiro[4.4]non-7-en-1-one 45. Yield: 80%. Colorless oil; ¹H NMR (300 MHz, CDCl₃): δ 5.63 (s, 2H), 3.58 (t, J = 6.7 Hz, 2H), 2.84 (d, J = 14.7 Hz, 2H), 2.32 (t, J = 7.0 Hz, 2H), 2.28 (d, J = 14.8 Hz, 2H), 2.05 (t, J = 6.8 Hz, 2H), 1.54 (app. quint., J = 7.9 Hz, 2H), 1.41-1.22 (m, 6H), 0.88 (t, J = 6.7 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 180.4, 128.3, 72.3, 72.0, 48.9, 47.5, 43.7, 36.0, 31.4, 29.0, 28.7, 22.6, 18.7, 14.2; IR (ATR) v_{max} 2923, 2260, 1724, 1393, 1298, 1207, 1038, 671 cm⁻¹; ESIMS (positive mode): 491.4, 268.2, 246.2, 176.1, 138.1; ESIHRMS *m/z* calcd for C₁₆H₂₄NO [M+H]⁺ 246.1858, found 246.1857.

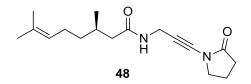


1-(Ferrocenylethynyl)pyrrolidin-2-one 46. Yield: 87%. Bright orange solid; Mp: 129 °C; ¹H NMR (300 MHz, CDCl₃): δ 4.39 (s, 2H), 4.18 (s, 5H), 4.15 (s, 2H), 3.67 (t, *J* = 7.1 Hz, 2H), 2.40 (t, *J* = 8.0 Hz, 2H), 2.08 (app. quint., *J* = 7.5 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 175.8, 76.4, 71.7, 71.0, 70.0, 68.7, 64.3, 50.1, 29.7, 18.7; IR (ATR) v_{max} 2979, 2892, 2241, 1712, 1385, 1219, 1061, 817 cm⁻¹; ESIMS (positive mode): 294.1, 293.1; ESIHRMS *m*/*z* calcd for C₁₆H₁₅NOFe [M]⁺ 293.0503, found 293.0506.

Click-Alkynylation of N- and P- Nucleophiles by Oxidative Cross-Coupling with Alkynylcopper Reagents

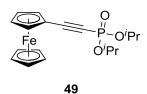


(*S*)-5-[(1-*tert*-Butoxy-4-methyl-1-oxopentan-2-yl)amino]-5-oxo-1-(2-oxopyrrolidin-1-yl)pent-1-yne 47. Yield: 90%. Brown oil; $[\alpha]_D^{20}$ -3 (*c* 0.9, CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ 6.14 (br. d, *J* = 8.1 Hz, 1H), 4.51 (dt, *J* = 11.9 and 6.3 Hz, 1H), 3.62 (t, *J* = 7.1 Hz, 2H), 2.65 (t, *J* = 7.0 Hz, 2H), 2.43 (t, *J* = 7.1 Hz, 2H), 2.39 (t, *J* = 8.2 Hz, 2H), 2.08 (app. quint., *J* = 7.5 Hz, 2H), 1.69-1.46 (m, 3H), 1.43 (s, 9H), 0.91 (d, *J* = 6.2 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃): δ 176.0, 172.2, 170.7, 81.4, 72.2, 70.9, 51.1, 49.7, 41.5, 35.5, 29.4, 27.8, 24.7, 22.6, 21.9, 18.5, 14.9; IR (ATR) ν_{max} 3294, 2967, 2908, 2363, 1724, 1665, 1535, 1373, 1255, 1144, 1065, 730 cm⁻¹; ESIMS (positive mode): 723.4, 374.2, 373.2, 351.2, 295.2, 182.1; ESIHRMS *m/z* calcd for C₁₉H₃₁N₂O₄ [M+H]⁺ 351.2284, found 351.2286.

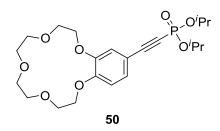


(*R*)-3-(3,7-Dimethyloct-6-enamido)-1-(2-oxopyrrolidin-1-yl)-prop-1-yne 48. Yield: 84%. White solid; Mp: 84 °C; $[\alpha]_{D}^{20}$ -1 (*c* 0.9, CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ 6.43 (br. t, *J* = 4.7 Hz, 1H), 4.95 (br. t, *J* = 5.9 Hz, 1H), 4.06 (d, *J* = 5.2 Hz, 2H), 3.54 (t, *J* = 7.1 Hz, 2H), 2.29 (t, *J* = 7.9 Hz, 2H), 2.09 (app. quint, *J* = 9.3 Hz, 1H), 2.00 (app. quint., *J* = 7.6 Hz, 2H), 1.93-1.81 (m, 4H), 1.54 (s, 3H), 1.46 (s, 3H), 1.28-1.19 (m, 1H), 1.12-1.02 (m, 1H), 0.80 (d, *J* = 6.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 176.3, 172.2, 131.1, 124.2, 73.8, 68.6, 49.7, 43.8, 36.7, 30.2, 29.4, 29.0, 25.5, 25.3, 19.3, 18.6, 17.5; IR (ATR) v_{max} 3278, 2967, 2900, 2261, 1728, 1649, 1535, 1401, 1223, 1069, 888, 730 cm⁻¹; ESIMS (positive mode): 313.2, 291.2, 140.1; ESIHRMS *m/z* calcd for C₁₇H₂₇N₂O₂ [M+H]⁺ 291.2073, found 291.2076.

Click-Alkynylation of N- and P- Nucleophiles by Oxidative Cross-Coupling with Alkynylcopper Reagents

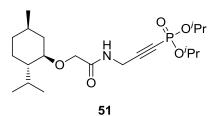


Diisopropyl (ferrocenylethynyl)phosphonate 49. Yield: 71%. Orange-brown solid; Mp: 47 °C; ¹H NMR (300 MHz, CDCl₃): 4.65-4.58 (m, 2H), 4.38 (app. t, J = 1.8 Hz, 2H), 4.14 (t, J = 1.9Hz, 2H), 4.07 (s, 5H), 1.25 (d, J = 6.3 Hz, 6H), 1.24 (d, J = 6.3 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃): δ 99.4 (d, $J_{C-P} = 54.5$ Hz), 76.0 (d, $J_{C-P} = 300.6$ Hz), 72.1 (d, $J_{C-P} = 1.6$ Hz), 71.6 (d, $J_{C-P} = 5.5$ Hz), 70.0, 69.8, 59.9 (d, $J_{C-P} = 5.7$ Hz), 23.6 (d, $J_{C-P} = 4.5$ Hz), 23.4 (d, $J_{C-P} = 4.8$ Hz); ³¹P NMR (121 MHz, CDCl₃): δ -8.0; IR (ATR) v_{max} 2982, 2896, 2158, 1385, 1255, 1058, 983, 927, 793 cm⁻¹; ESIMS (positive mode): 398.1, 397.1, 375.1, 374.1, 333.0, 291.0; ESIHRMS m/z calcd for C₁₈H₂₃O₃PFe [M]⁺ 374.0734, found 374.0732.

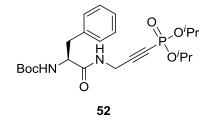


Diisopropyl [(2,3,5,6,8,9,11,12-octahydrobenzo[b][1,4,7,10,13]pentaoxacyclopentadecin-15yl)ethynyl]phosphonate 50. Yield: 34%. Colorless oil; ¹H NMR (300 MHz, CDCl₃): 7.08 (dd, J = 8.3 and 1.6 Hz, 1H), 6.94 (d, J = 1.7 Hz, 1H), 6.73 (d, J = 8.3 Hz, 1H), 4.78-4.67 (m, 2H), 4.09-4.03 (m, 4H), 3.85-3.82 (m, 4H), 3.68 (s, 8H), 1.33 (d, J = 6.2 Hz, 6H), 1.32 (d, J = 6.1 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃): δ 151.5, 148.7, 126.9, 117.3, 113.0, 111.9, 98.9 (d, $J_{C-P} = 53.3$ Hz), 78.5 (d, $J_{C-P} = 299.0$ Hz), 72.2 (d, $J_{C-P} = 5.5$ Hz), 71.1, 70.4, 70.3, 69.3, 69.2, 69.0, 68.7, 24.0 (d, $J_{C-P} = 4.5$ Hz), 23.7 (d, $J_{C-P} = 4.9$ Hz); ³¹P NMR (121 MHz, CDCl₃): δ -7.8; IR (ATR) v_{max} 2982, 2896, 2178, 1511, 1247, 1136, 987, 793, 726 cm⁻¹; ESIMS (positive mode): 480.2, 479.2, 457.2, 373.1; ESIHRMS *m*/*z* calcd for C₂₂H₃₄O₈P [M+H]⁺ 457.1991, found 457.1994.

Click-Alkynylation of N- and P- Nucleophiles by Oxidative Cross-Coupling with Alkynylcopper Reagents



(1*R*,3*R*,4*S*)-Diisopropyl (menthoxyacetamido)prop-1-yn-1-ylphosphonate **51.** Yield: 76%. Colorless oil; [α] $_{D}^{20}$ -37 (*c* 0.8, CHCl₃); ¹H NMR (300 MHz, CDCl₃): 6.79 (br. t, *J* = 5.4 Hz, 1H), 4.63-4.56 (m, 2H), 4.09 (A of AB syst., *J* = 4.2 Hz, 1H), 4.08 (B of AB syst., *J* = 4.2 Hz, 1H), 3.95 (A' of A'B' syst., *J* = 15.2 Hz, 1H), 3.74 (B' of A'B' syst., *J* = 15.2 Hz, 1H), 3.02 (td, *J* = 10.6 and 4.1 Hz, 1H), 1.99 (hept. d, *J* = 7.0 and 2.7 Hz, 1H), 1.94-1.88 (m, 1H), 1.55-1.48 (m, 2H), 1.31-1.10 (obs. m, 2H), 1.22 (d, *J* = 6.3 Hz, 12H), 0.91-0.69 (obs. m, 3H), 0.79 (d, *J* = 6.5 Hz, 6H), 0.65 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): *δ* 170.0, 95.1 (d, *J*_{C-P} = 50.6 Hz), 80.2, 74.4 (d, *J*_{C-P} = 4.3 Hz), 72.2 (d, *J*_{C-P} = 5.6 Hz), 67.4, 47.8, 39.8, 34.1, 31.2, 28.5 (d, *J*_{C-P} = 4.5 Hz), 25.8, 23.8 (d, *J*_{C-P} = 4.3 Hz), 23.6 (d, *J*_{C-P} = 4.5 Hz), 23.0, 22.0, 20.8, 16.0, ³¹P NMR (121 MHz, CDCl₃): *δ* -9.9 (quint, *J* = 6.3 Hz); IR (ATR) v_{max} 2971, 2919, 2209, 1677, 1519, 1381, 1255, 1105, 983, 774 cm⁻¹; ESIMS (positive mode): 853.5, 438.2, 416.3, 374.2, 236.1, 194.0; ESIHRMS *m*/*z* calcd for C₂₁H₃₉NO₅P [M+H]⁺ 416.2566, found 416.2561.



(*S*)-Diisopropyl {3-[2-(*tert*-Butoxycarbonylamino)-3-phenylpropanamido]-prop-1-yn-1-yl}phosphonate 52. Yield: 79%. Pale yellow oil; $[\alpha]_{D}^{20}$ -2 (*c* 0.9, CHCl₃); ¹H NMR (300 MHz, CDCl₃): 7.42 (br. t, *J* = 5.5 Hz, 1H), 7.26-7.10 (m, 5H), 5.31 (d, *J* = 8.1 Hz, 1H), 4.76-4.56 (m, 2H), 4.42-4.27 (br. m, 1H), 4.13-3.92 (br. m, 2H), 3.08 (A of ABX syst., *J* = 13.7 and 5.8 Hz, 1H), 2.89 (br. B of ABX syst., *J* = 13.2 and 6.4 Hz, 1H), 1.31-1.24 (m, 21H); ¹³C NMR (75 MHz, CDCl₃): δ 171.4, 155.3, 136.5, 129.3 128.4, 126.7, 95.9 (d, *J*_{C-P} = 50.9 Hz), 77.8 (d, *J*_{C-P} = 298.0 Hz), 74.1 (d, *J*_{C-P} = 5.7 Hz), 72.4, 55.3, 38.6, 29.1 (d, *J*_{C-P} = 4.4 Hz), 28.2, 23.8 (d, *J*_{C-P} =

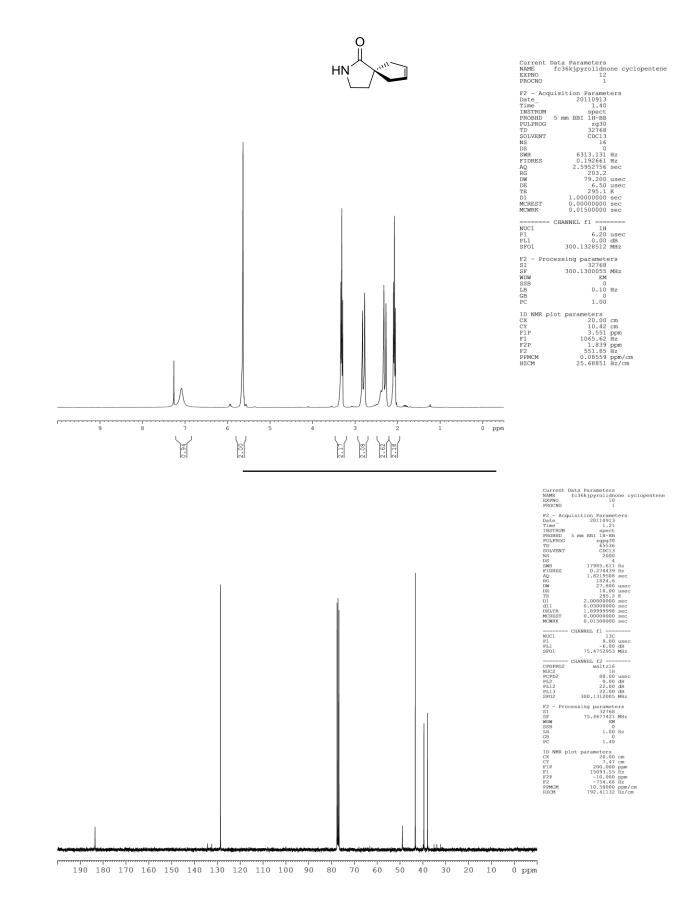
4.5 Hz), 23.6 (d, $J_{C-P} = 4.7$ Hz); ³¹P NMR (121 MHz, CDCl₃): δ -9.8; IR (ATR) ν_{max} 3278, 2986, 2217, 1681,1499, 1365, 1254, 1168, 990, 742 cm⁻¹; ESIMS (positive mode): 489.2, 467.2, 411.2, 367.2, 325.1; ESIHRMS *m*/*z* calcd for C₂₃H₃₆N₂O₆P [M+H]⁺ 467.2311, found 467.2310.

Click-Alkynylation of N- and P- Nucleophiles by Oxidative Cross-Coupling with Alkynylcopper Reagents

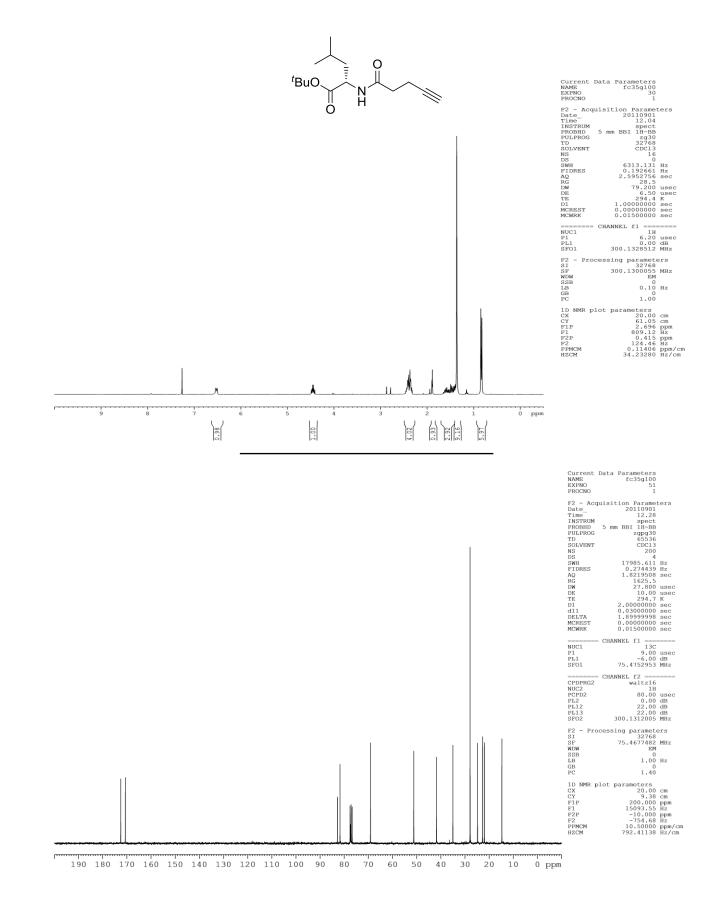
Supporting Information

¹H and ¹³C NMR spectra

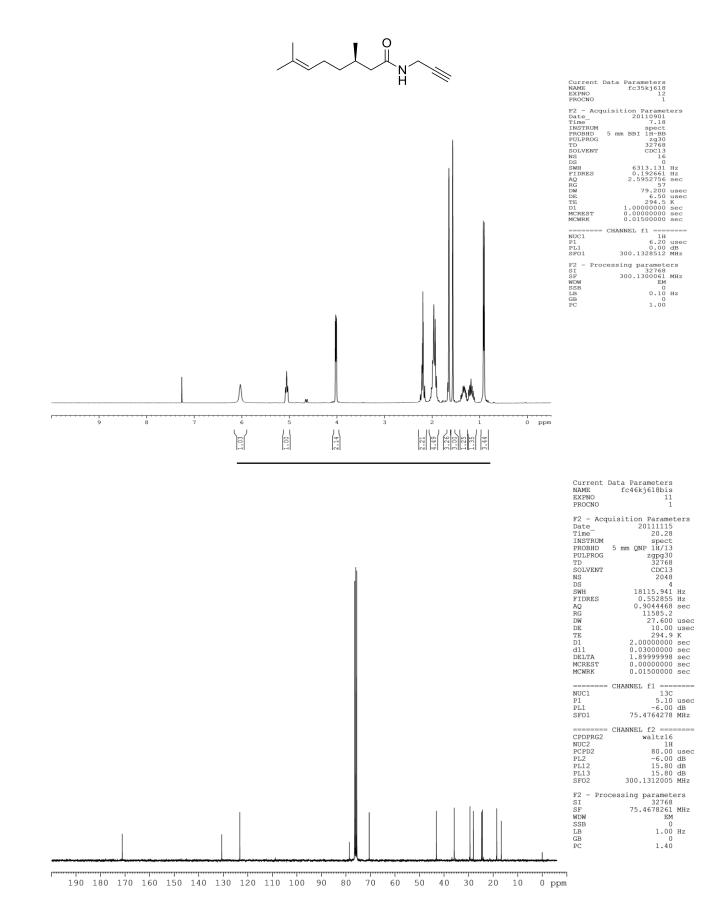
Click-Alkynylation of N- and P- Nucleophiles by Oxidative Cross-Coupling with Alkynylcopper Reagents



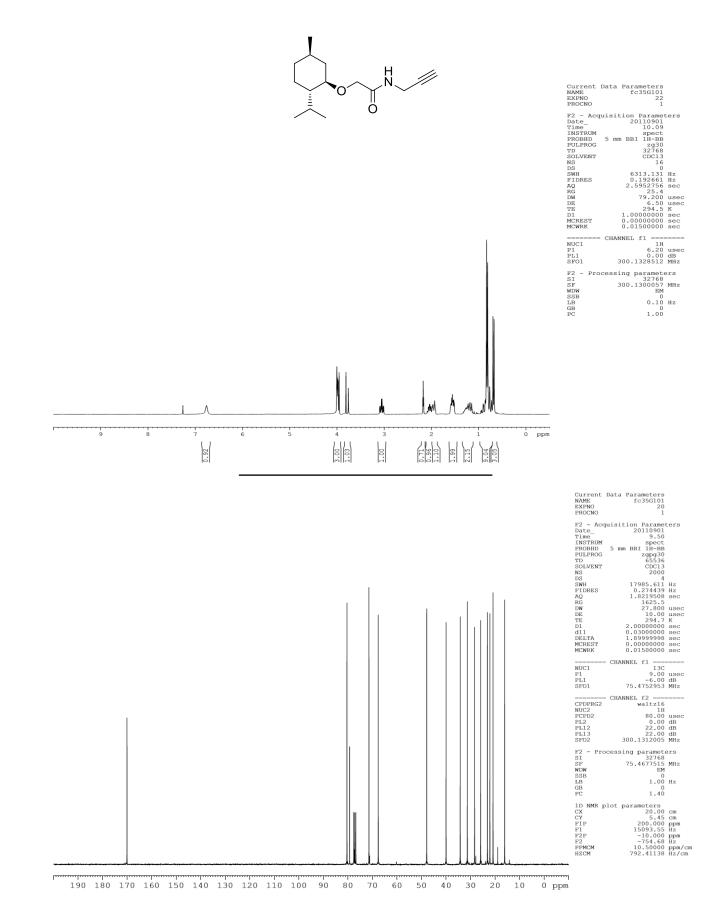
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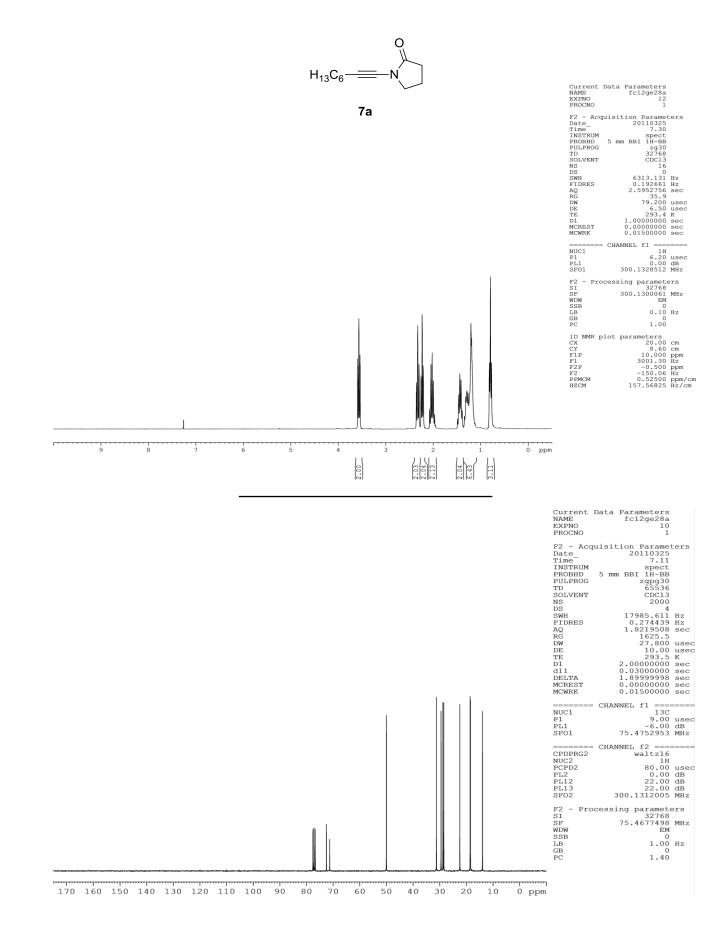


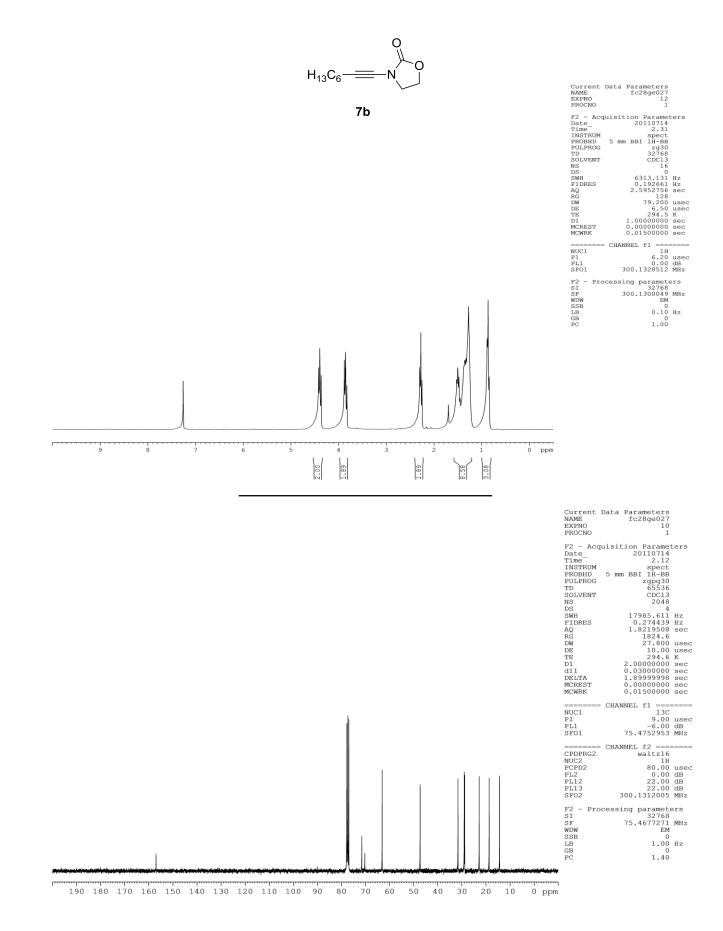
Click-Alkynylation of N- and P- Nucleophiles by Oxidative Cross-Coupling with Alkynylcopper Reagents

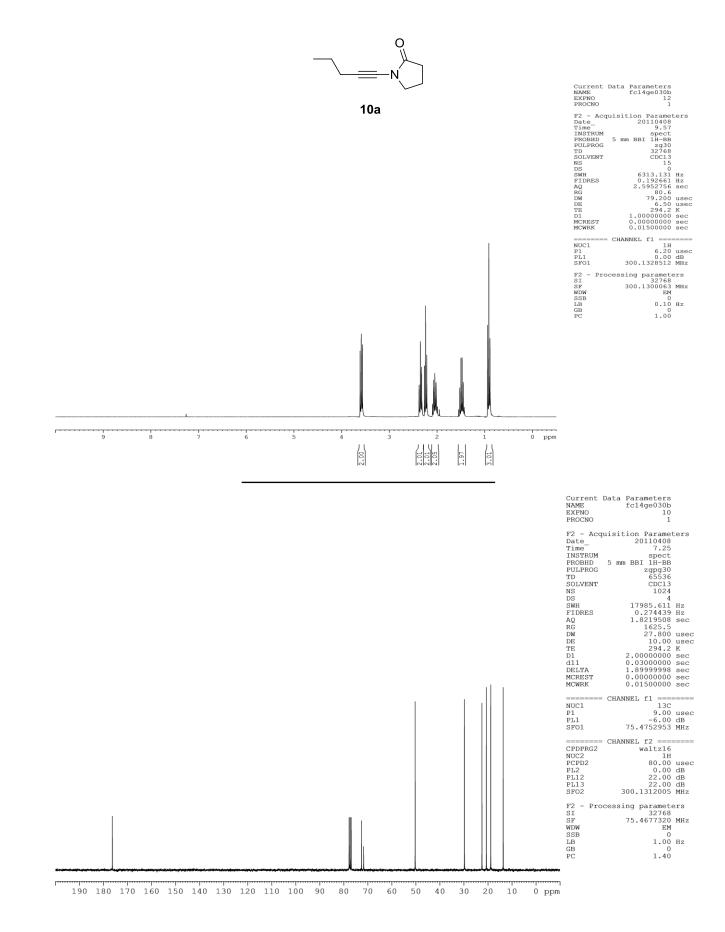


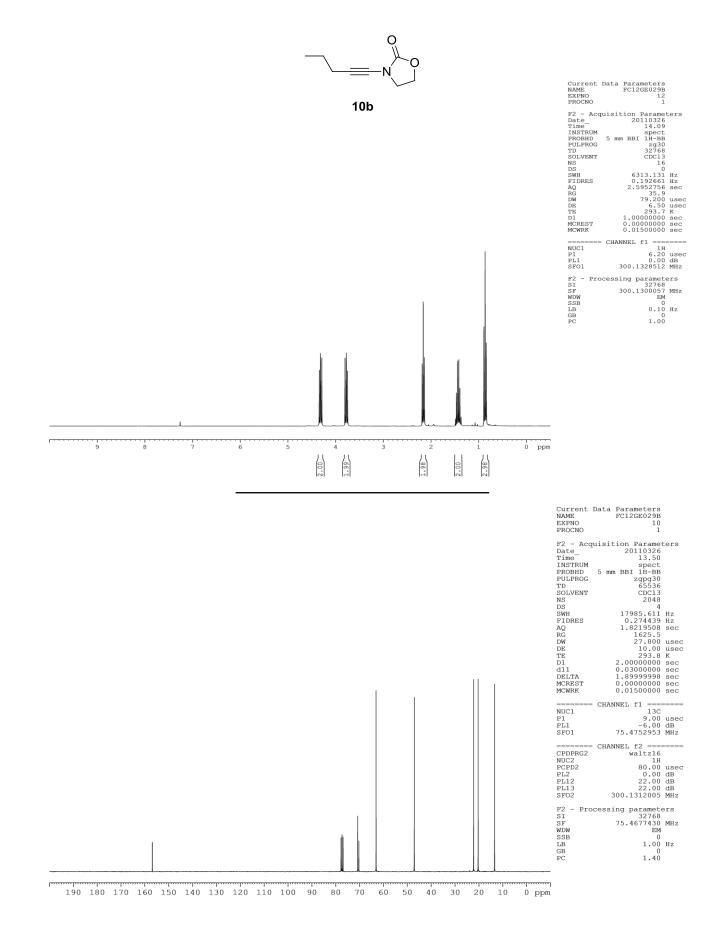
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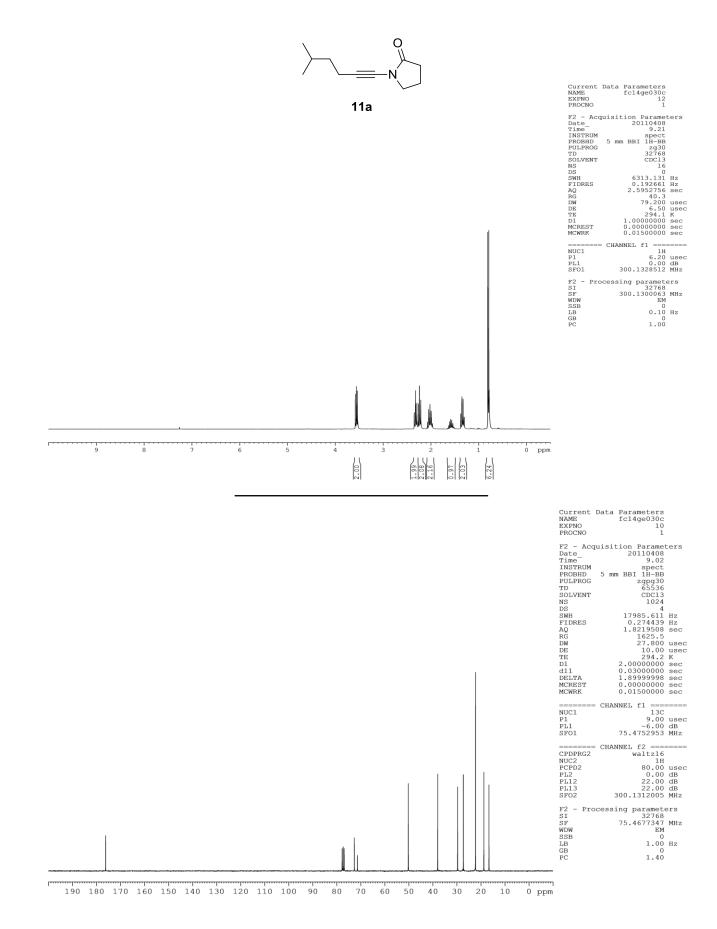


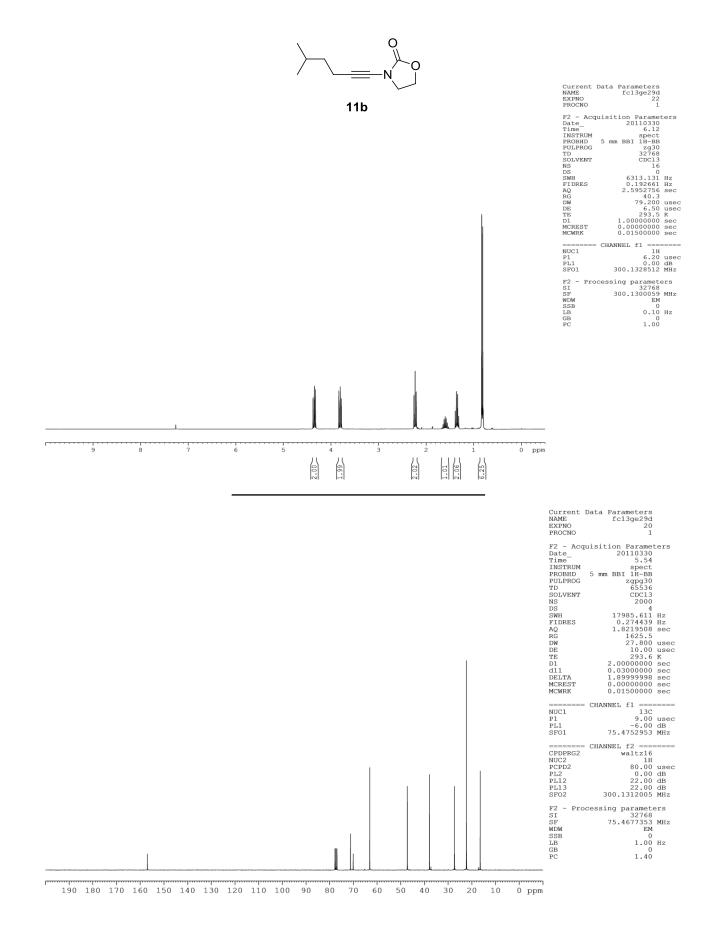


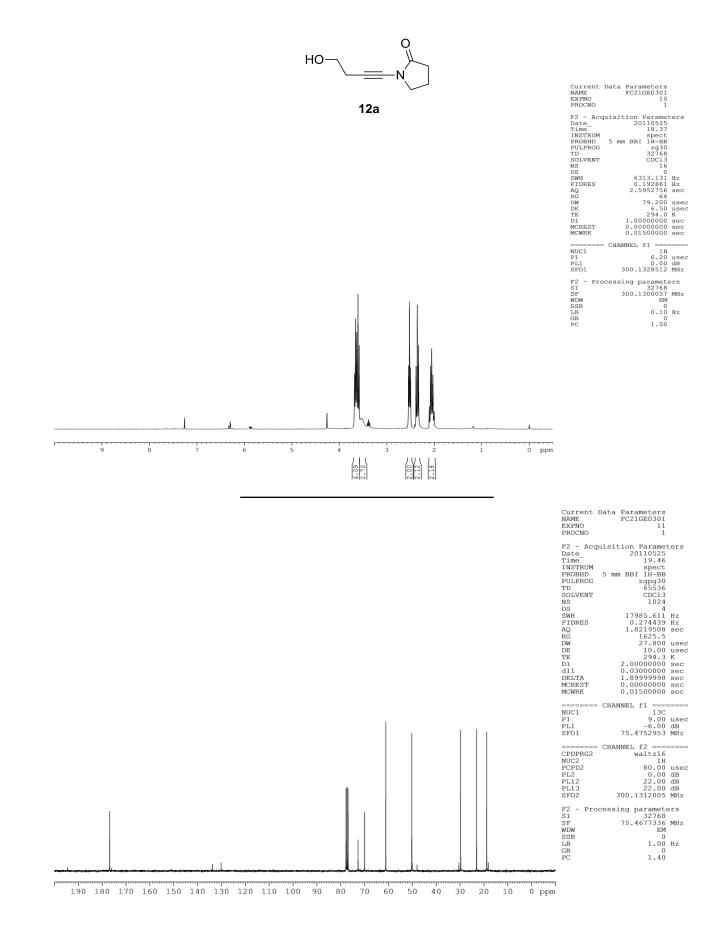


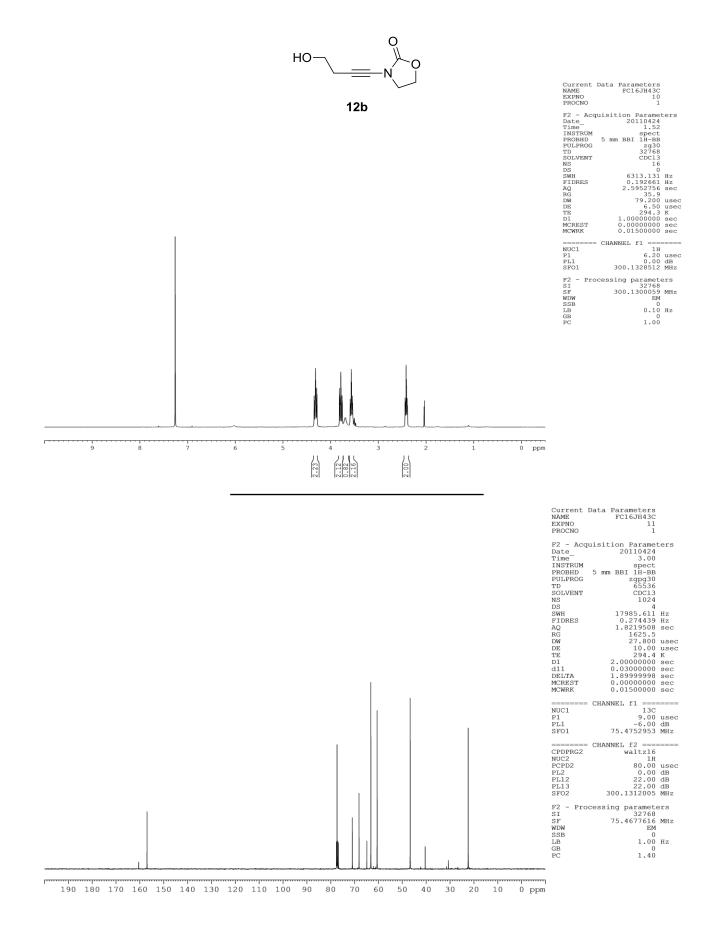


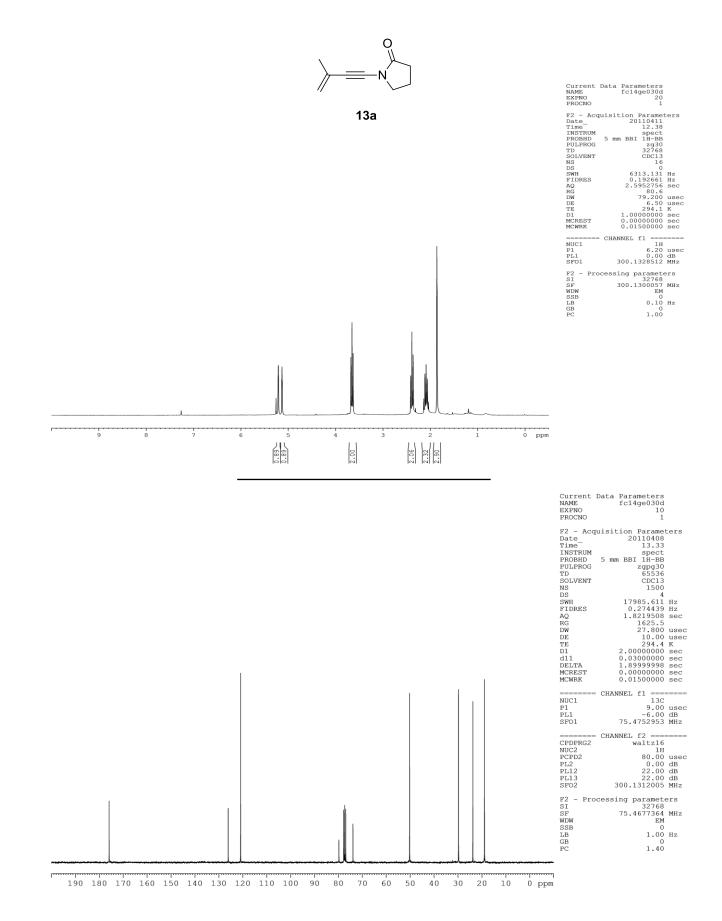


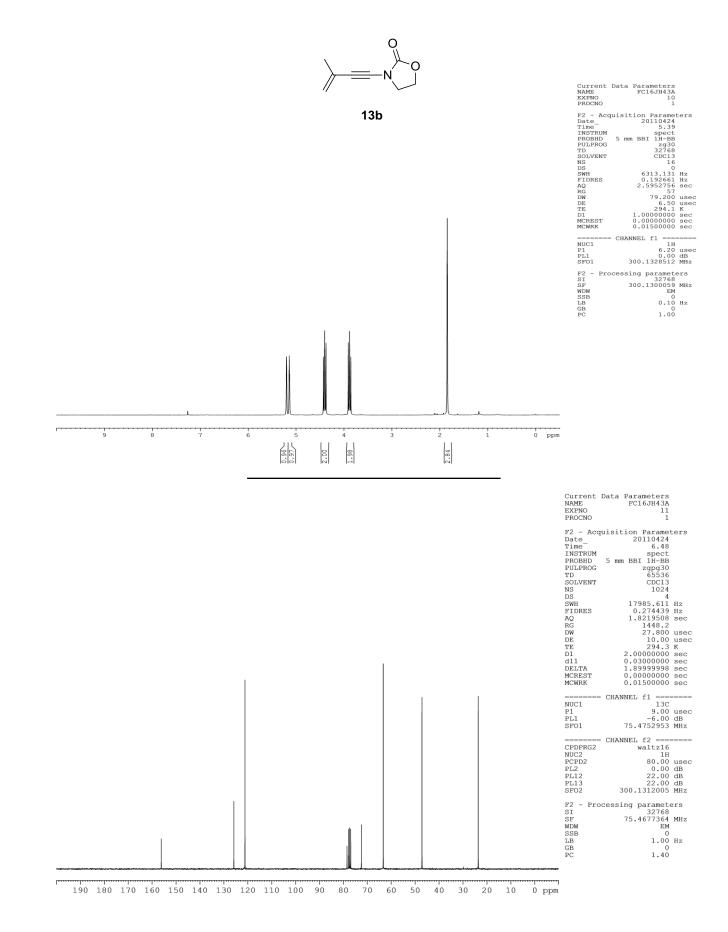


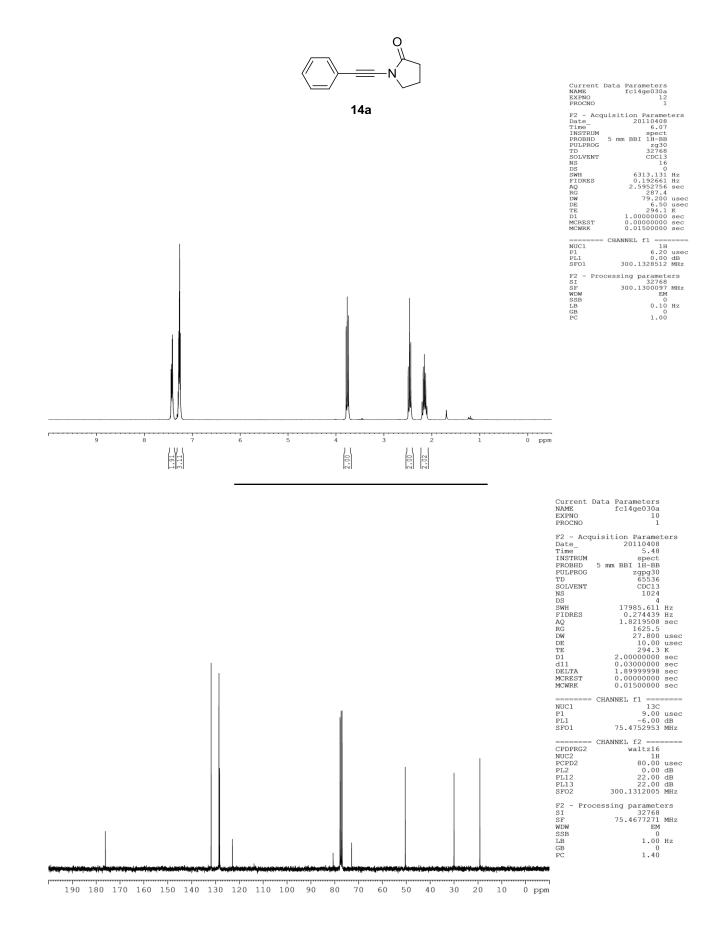


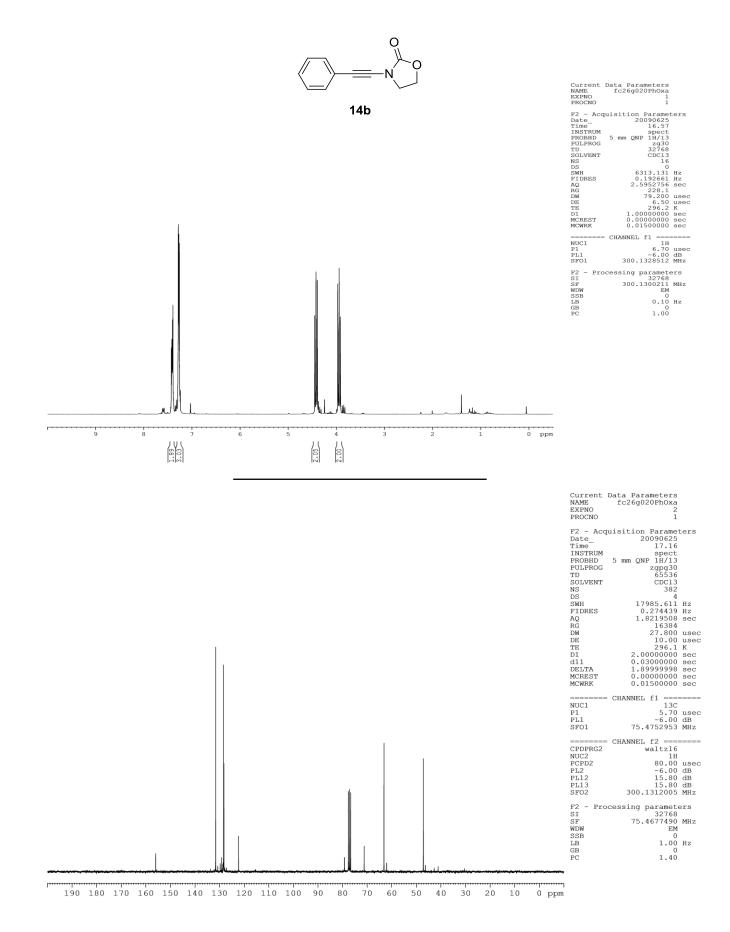


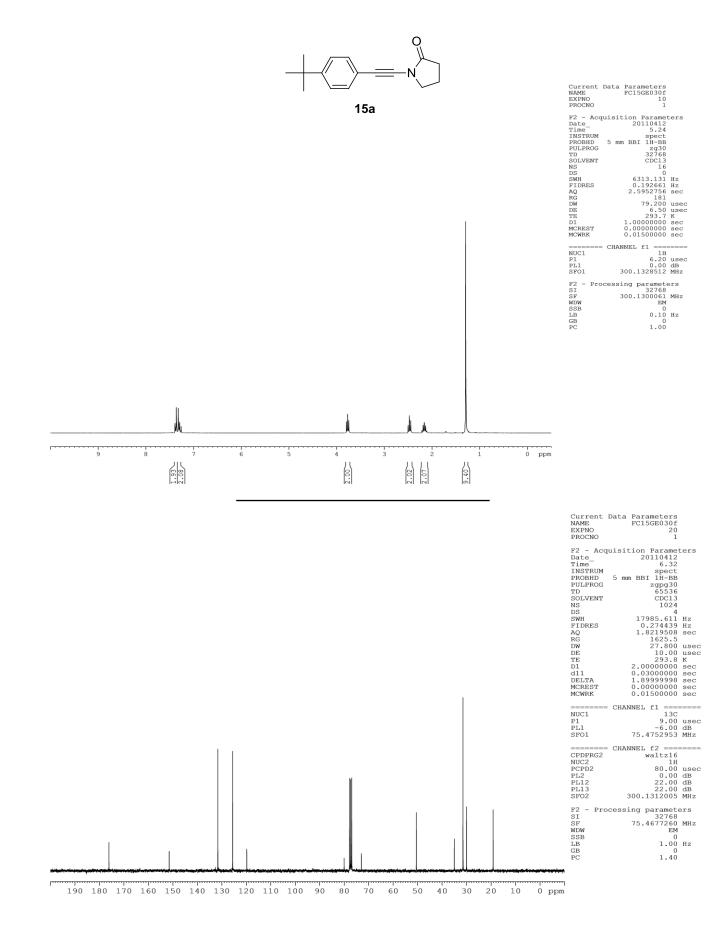


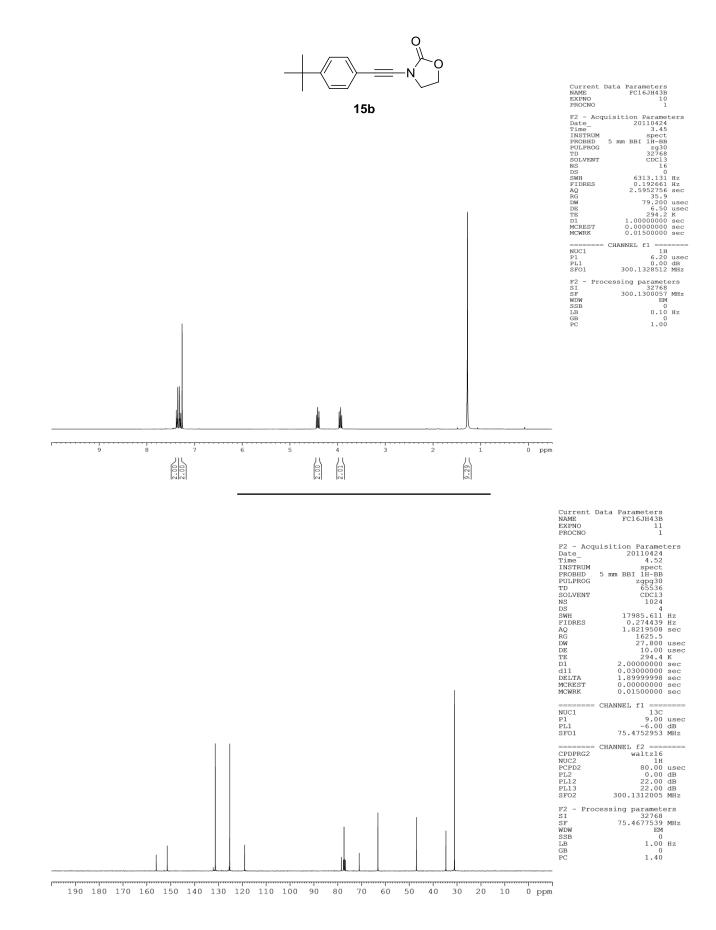


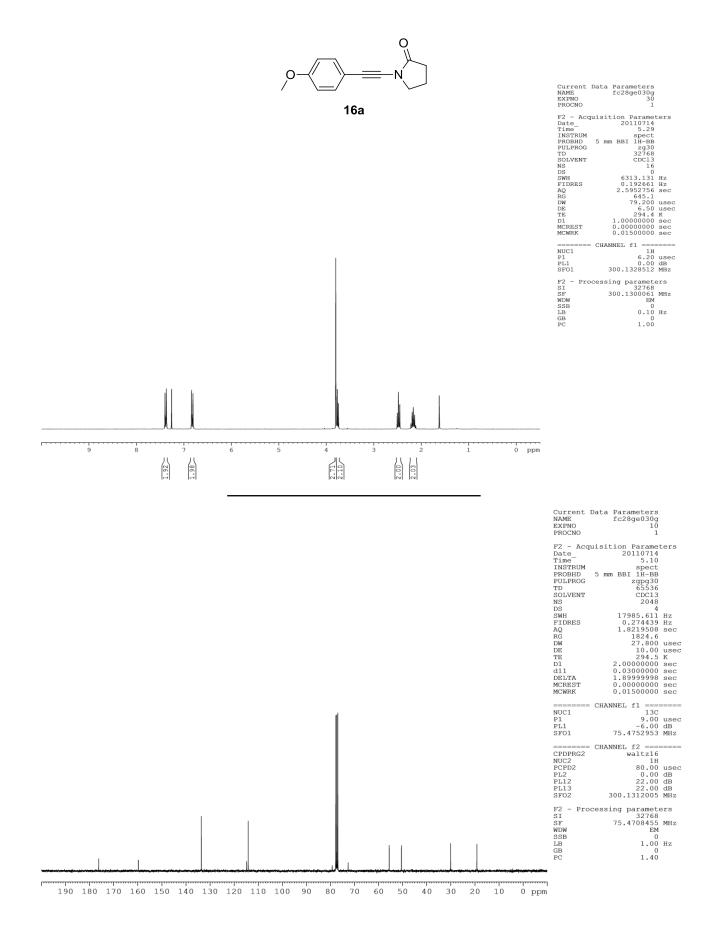


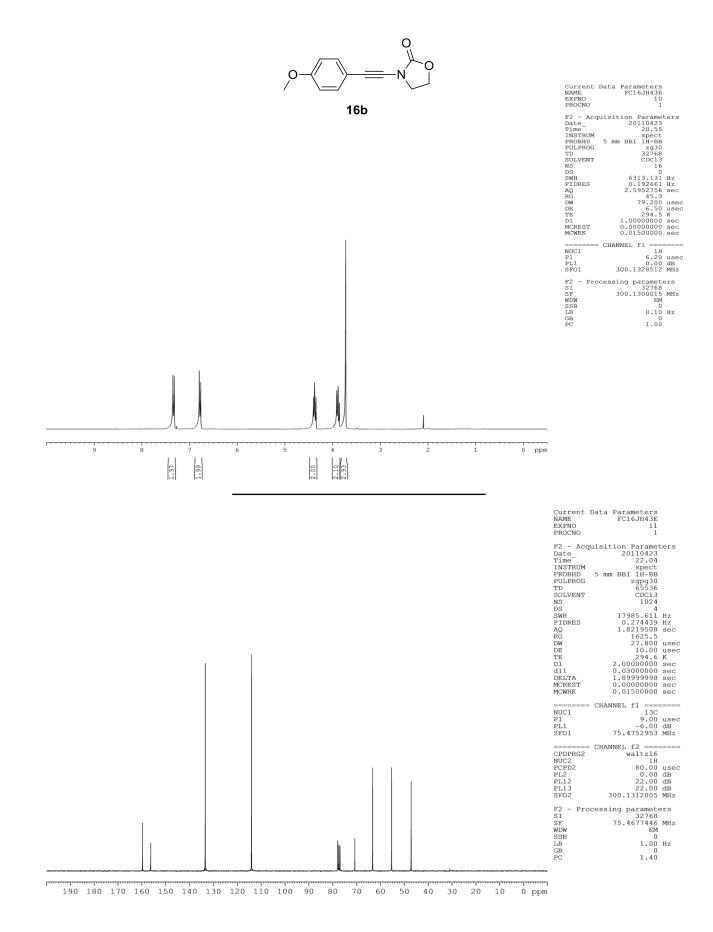


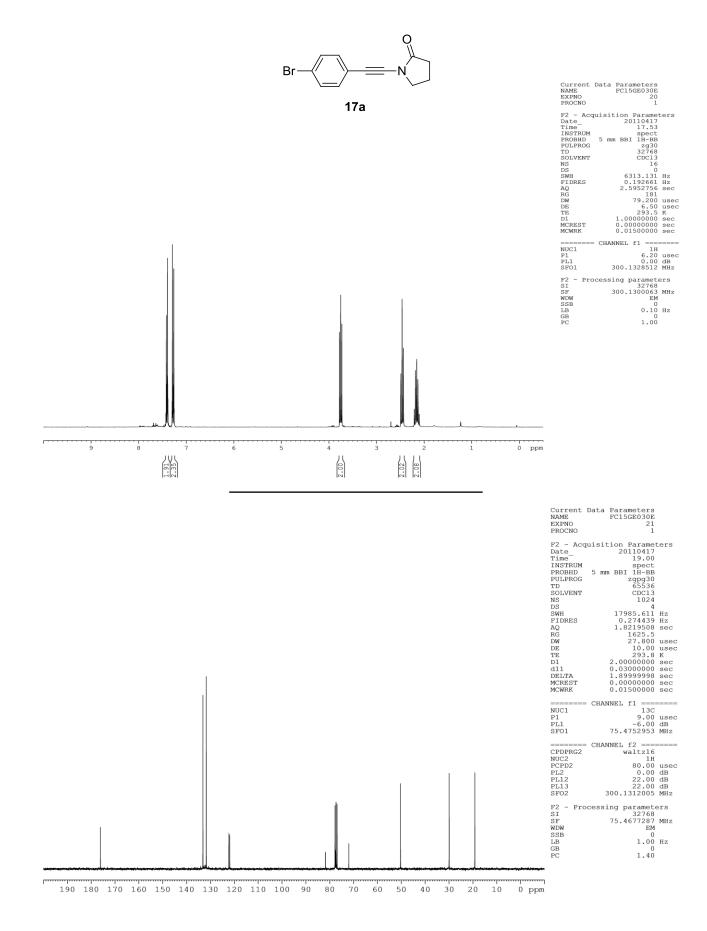


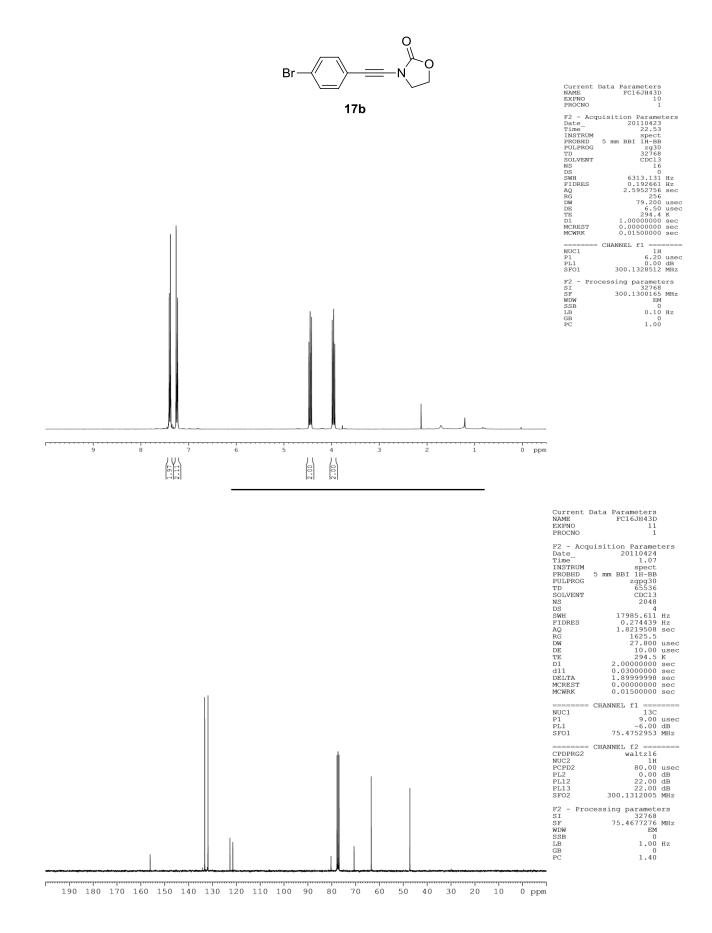


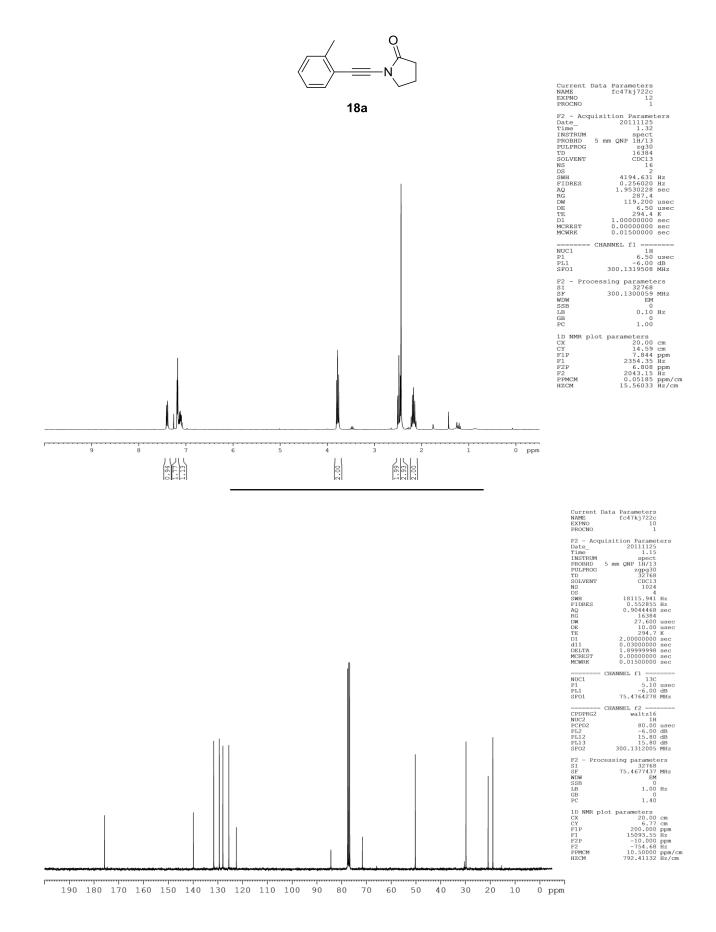


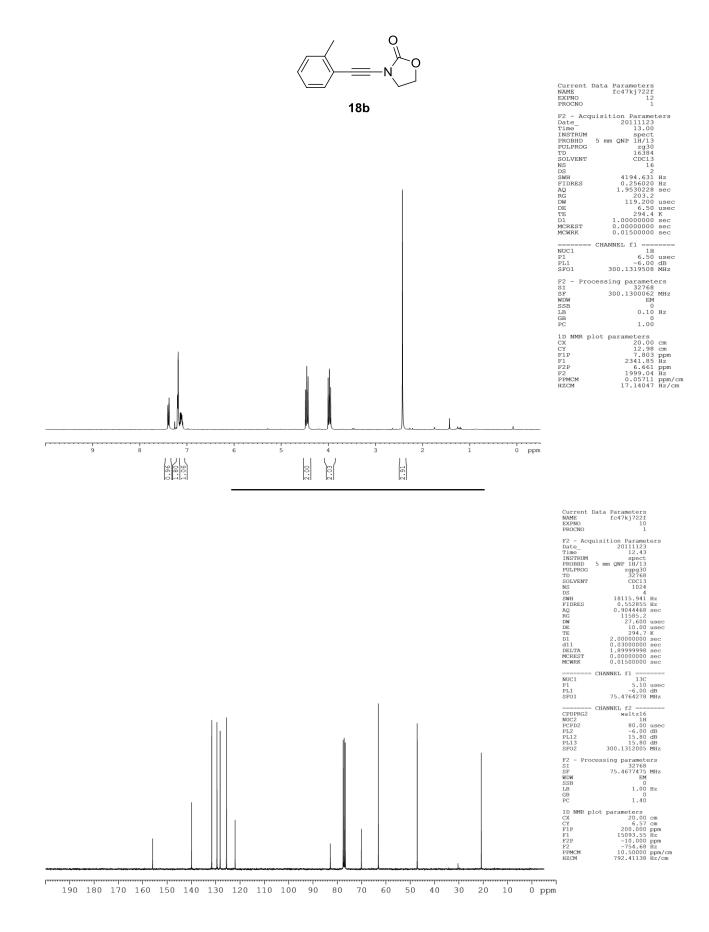


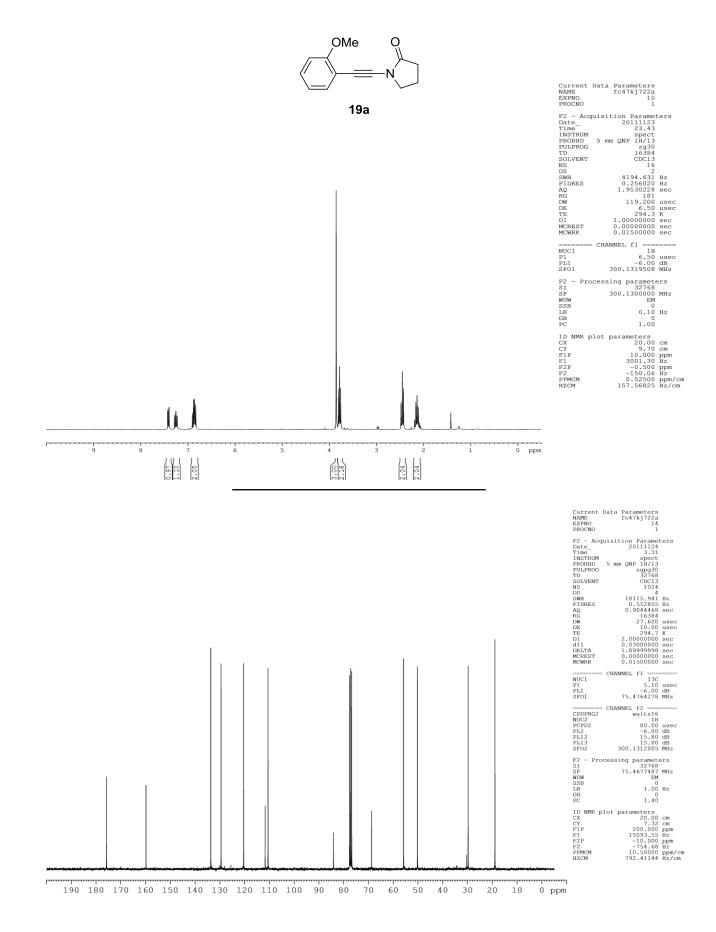


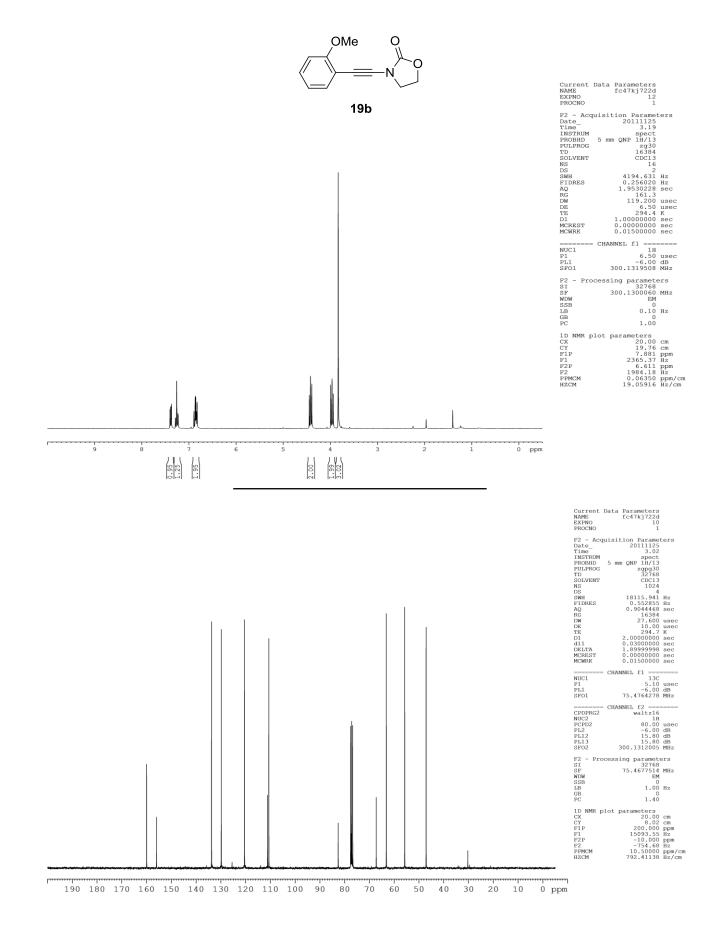


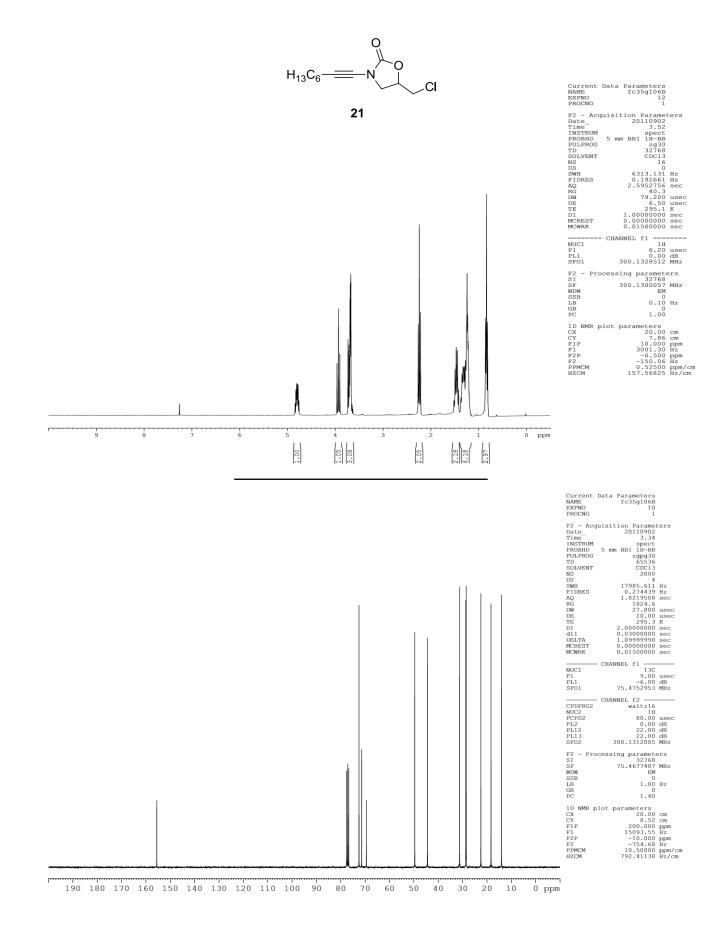


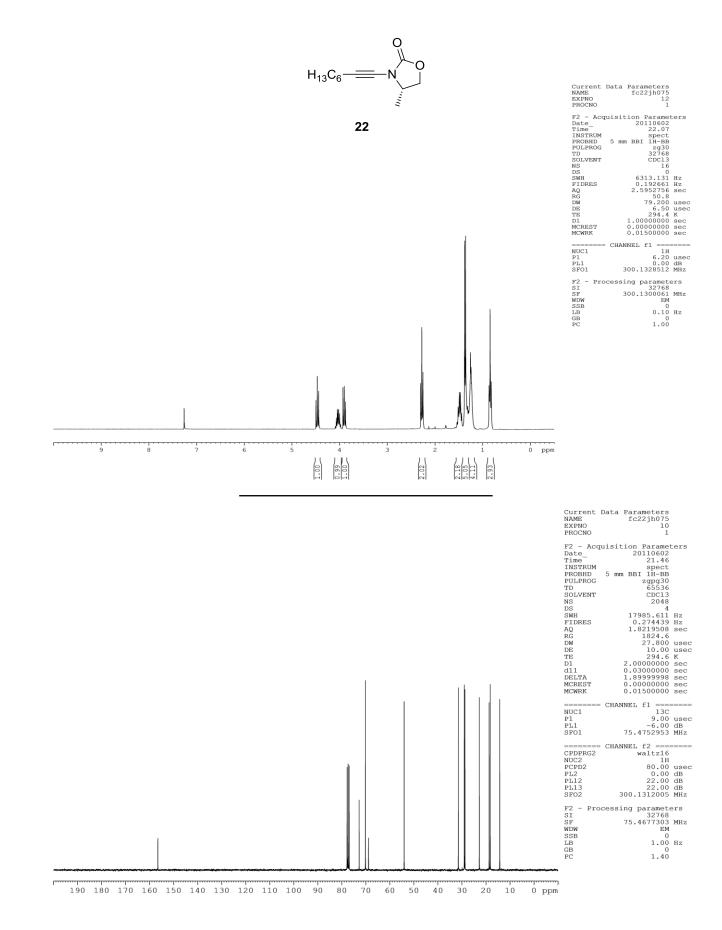


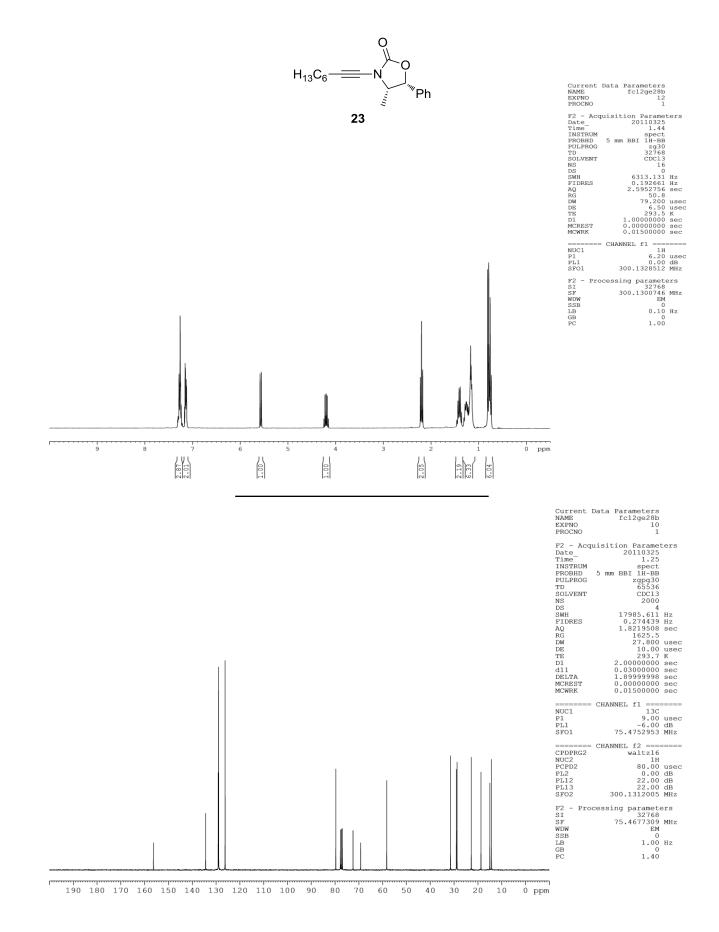


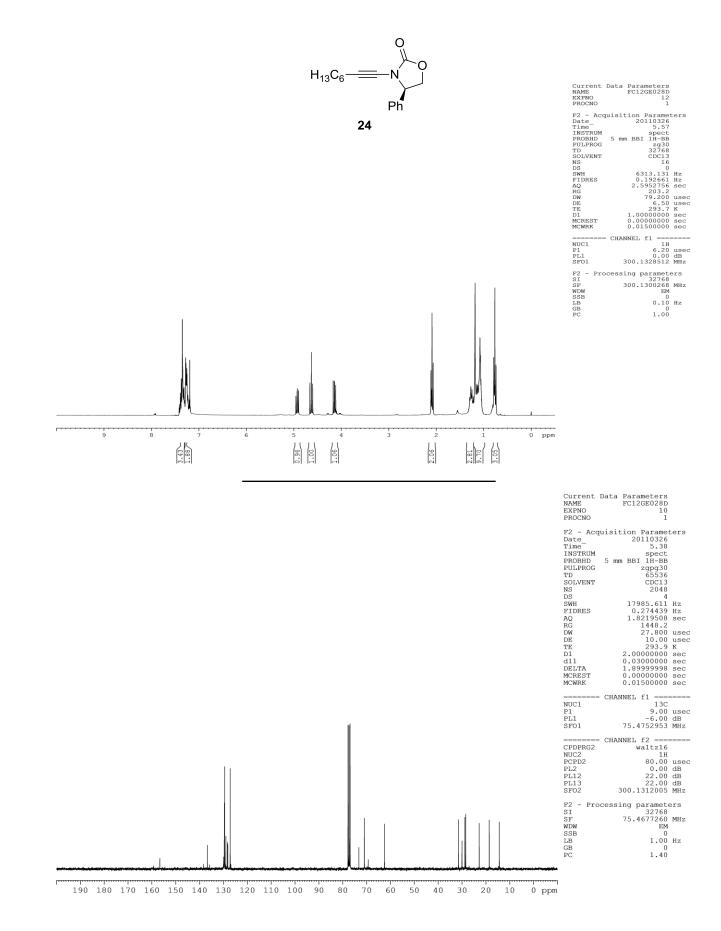


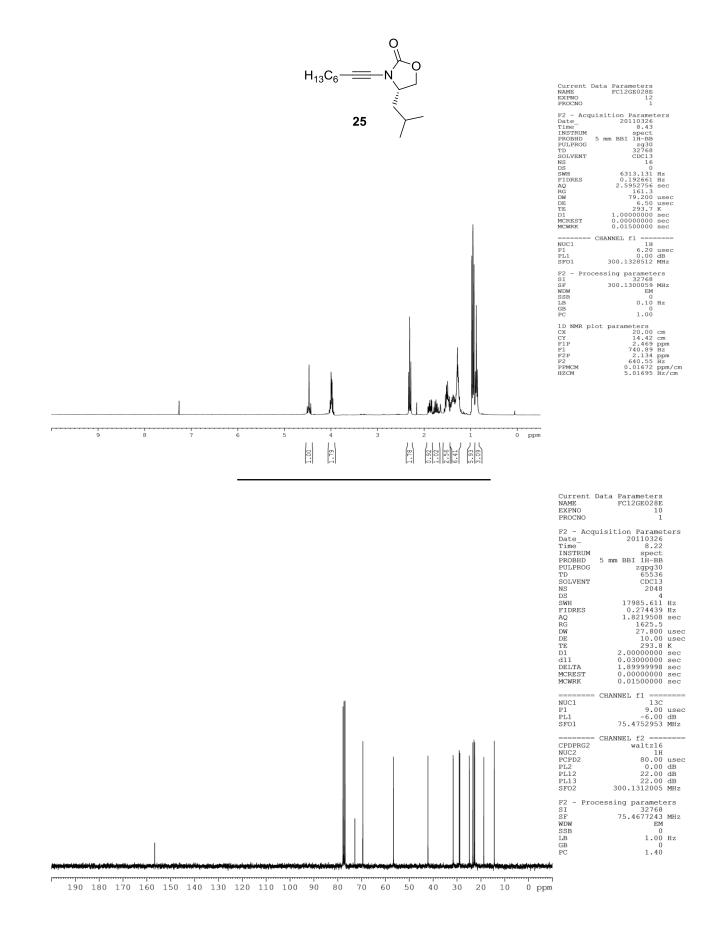


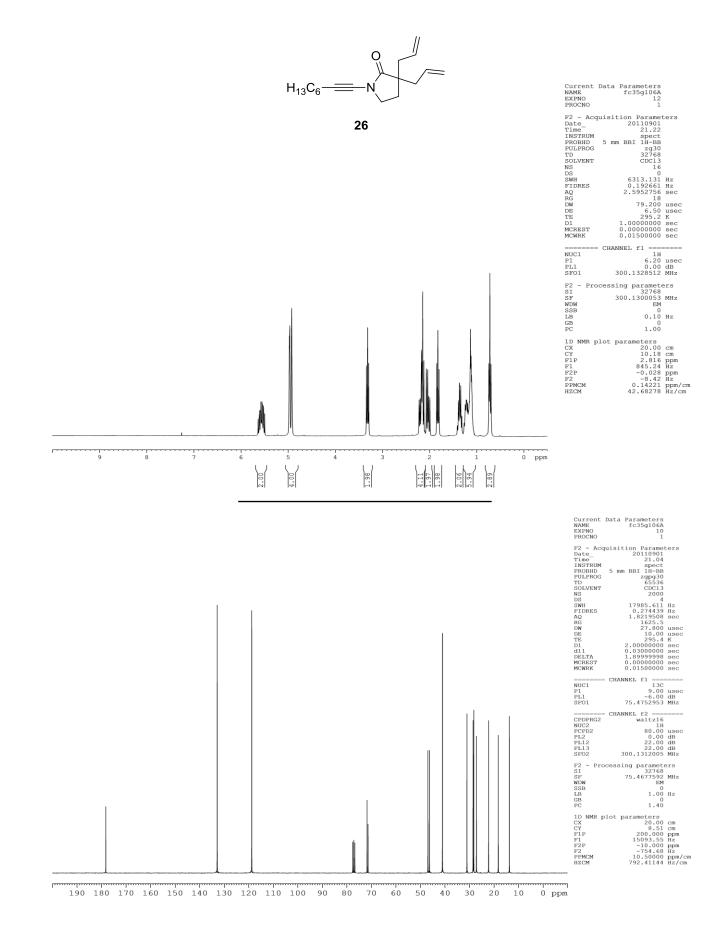


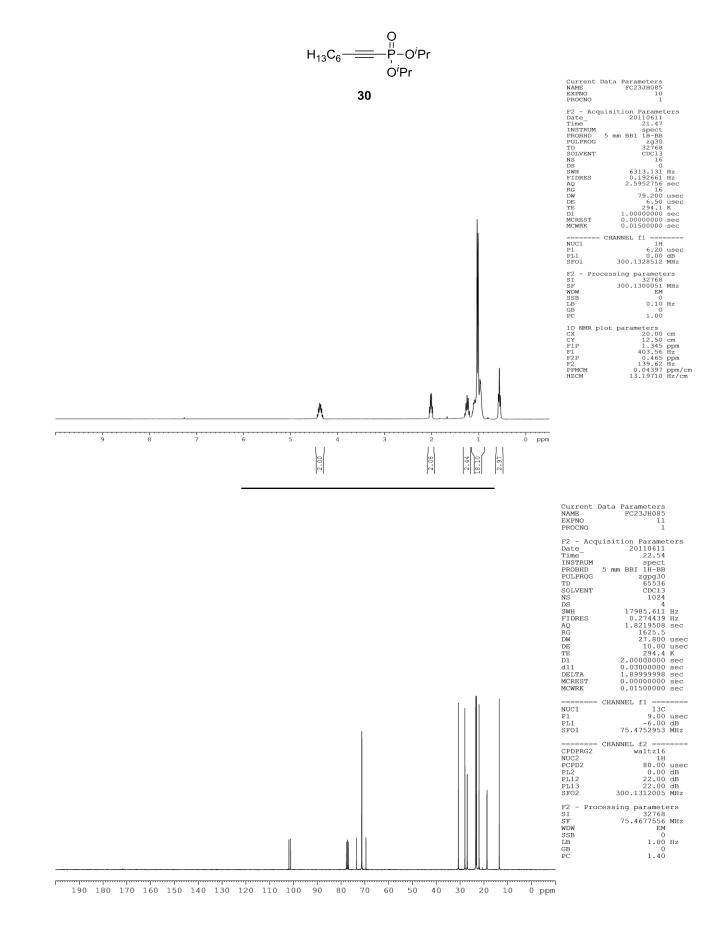


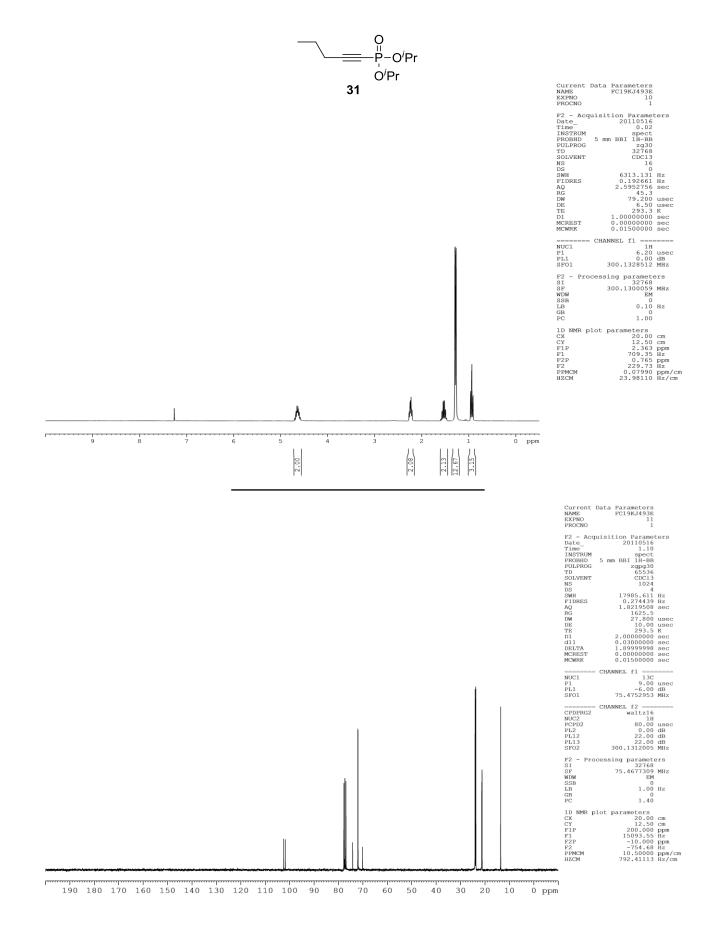


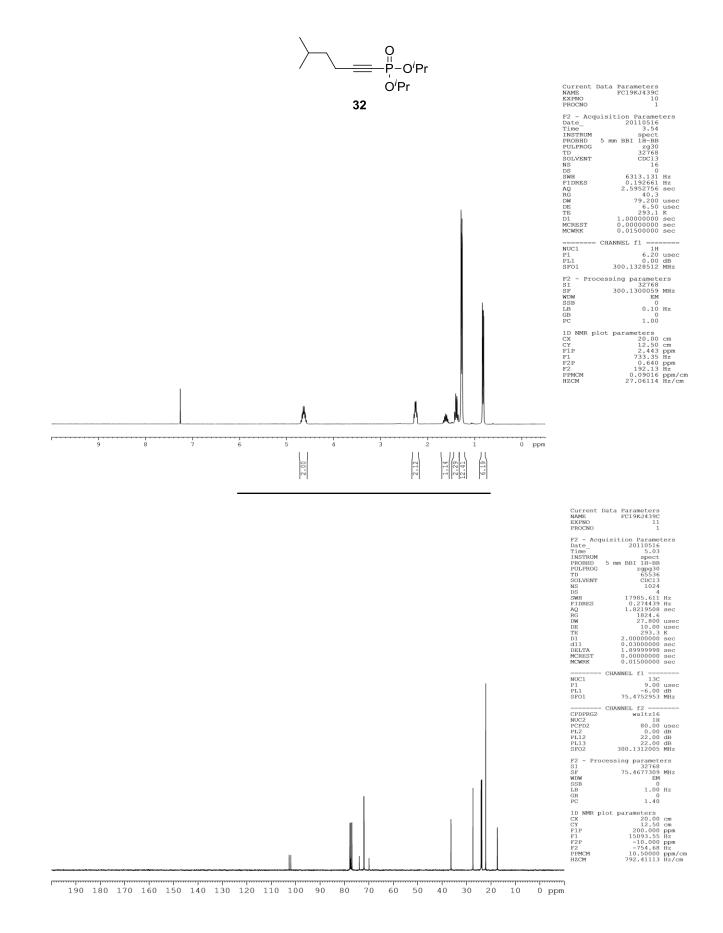


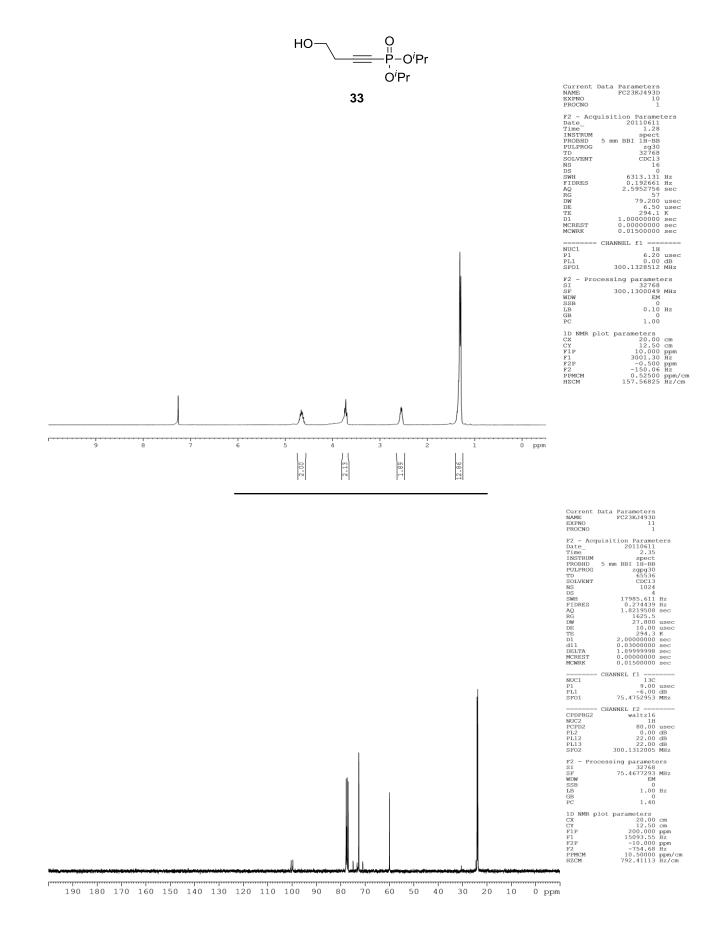


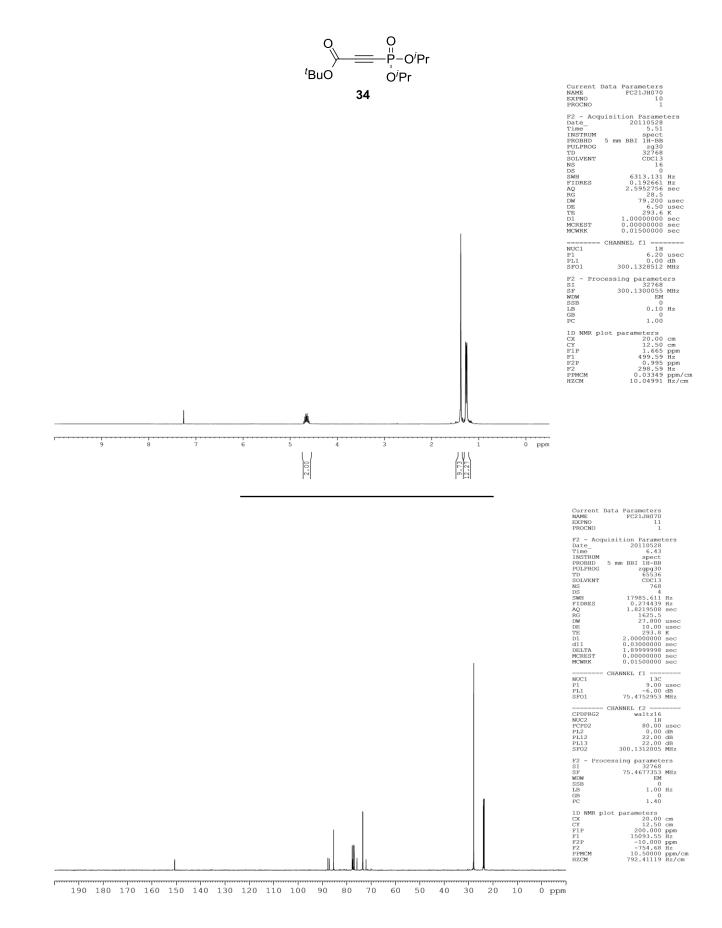












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