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Supporting Information

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Domino Copper-Catalyzed C-N coupling-Hydroamidation: A Highly efficient Synthesis of Nitrogen Heterocycles.

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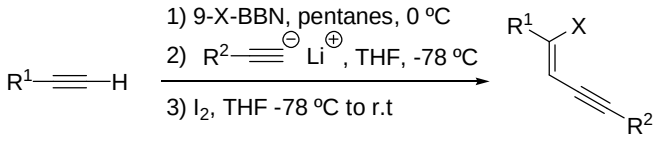
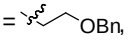
Experimental details

Reagents. All reactions were carried out under an argon atmosphere. CuI was obtained from Strem chemicals and used without further purification. *N,N´*-dimethylethylendiamine was obtained from Aldrich. Commercially available materials were used without further purification unless otherwise noted. Anhydrous potassium carbonate and cesium carbonate were purchased from Mallinckrodt Chemicals and stored in a desiccator.

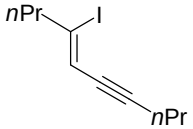
Analytical Methods. All new compounds were characterized by ^{1}H NMR, ^{13}C NMR, IR spectroscopy and elemental analysis. Known compounds were characterized by ^{1}H NMR and melting points (for solids) and compared to their literature values. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz. Infrared spectra were recorded on a Perkin-Elmer Model 2000 FT-IR using NaCl plates (thin film). Elemental analyses were preformed by Atlantic Microlabs Inc., Norcros, GA. All ^{1}H NMR experiments are reported in parts per million (ppm) downfield of TMS and were measured relative to the signals for chloroform (7.27 ppm). All ^{13}C NMR spectra were reported in ppm relative to residual chloroform (77 ppm) and were obtained with ^{1}H decoupling. Melting points were obtained on a Mel-Temp capillary melting point apparatus. Gas chromatographic analyses were preformed on Hewlett-Packard 6890 gas chromatography instrument with a FID detector using 25m x 0.20 mm capillary column with cross-linked methyl siloxane as a stationary phase. The yields in tables 1-2 refer to isolated yields (average of two runs) of compounds estimated to be = 95% pure as determined by ^{1}H NMR and GC analysis and/or combustion analysis.

<u>Synthesis of the starting haloenynes</u>.

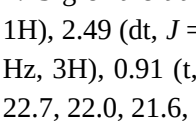


X = I, R^1 = R^2 = *n*Pr, 71%
X = Br, R^1 = R^2 = *n*Pr, 65%
X = I, R^1 =  , R^2 = *n*Pr, 66%
X = I, R^1 = Bn, R^2 =  , 57%
X = I, R^1 = *n*Bu, R^2 = CO_2Et, 18%

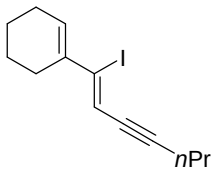
General Procedure A for the synthesis of iodoenynes using haloboration reaction.[1] **The preparation of (4*Z*)-4-iodo-4-decen-6-yne is representative**. A flask equipped with a magnetic stirring bar and a septum inlet was flushed with nitrogen. The flask was charged under nitrogen atmosphere with B-I-9-BBN (15.63 mL, 15.63 mmol, 1M hexanes) and 45 ml of dry pentane, and cooled to 0 ºC. Then, 1.29 ml of 1-pentyne (13.05 mmol) was added dropwise, and the solution was stirred for 2 h at 0 ºC. The reaction mixture was cooled to –78 ºC and l-lithio-1-pentyne (18.29 mmol)[2] was introduced gradually to give a pale yellow solution. After stirring for 20 min at that temperature, 5.80 g of iodine (22.44 mmol) in 10 ml of THF was added and the resulting dark orange suspension was stirred at –78 ºC for 30 min, and then at room temperature for 30 min. Finally, the mixture was oxidized with 34 ml of 3M NaOH and 34 ml of 30% hydrogen peroxide at 0 ºC for 1 h, and the product thus obtained was extracted with hexane (3 x 40 mL). The combined organic layers were washed with water brine (20 mL), dried over magnesium sulfate, and finally concentrated under vacuum and purified by column chromatography (silica gel, hexanes) to give 2.43 g of the title compound (71% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) d: 5.99 (s, 1H), 2.49 (dt, *J* = 7.6, 0.8 Hz, 2H), 2.34 (dt, *J* = 7.2, 2.0 Hz, 2H), 1.63-1.55 (m, 4H), 1.06 (t, *J* = 7.2 Hz, 3H), 0.91 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 118.5, 118.0, 94.5, 81.4, 46.6, 22.7, 22.0, 21.6, 13.6, 12.7. IR (neat, cm^{-1}): 2961, 2932, 2871, 1461, 1279, 1109, 821.



(4*Z*)-4-Bromo-4-decen-6-yne. The general procedure A was used with 1-pentyne (1.29 mL, 13.05 mmol), B-Br-9-BBN (15.63 mL, 15.63 mmol, 1M dichloromethane), pentanes (45 mL), 1-lithio-1-pentyne[2] (18.29 mmol) and I_2 (5.80 g, 22.44 mmol) in THF (10 mL). The product was purified by column chromatography on silica gel (hexanes) to give 1.82 g of the title compound (65%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) d: 5.91 (s, 1H), 2.46 (dt, *J* = 7.2, 0.7 Hz, 2H), 2.34 (dt, *J* = 7.2, 2.4 Hz, 2H), 1.65-1.56 (m, 4H), 1.04 (t, *J* = 7.2 Hz, 3H), 0.92 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 137.5, 110.8, 95.1, 77.9, 43.0, 22.0, 21.6, 21.4, 13.5, 12.9. IR (neat, cm^{-1}): 2962, 2933, 2872, 1653, 1558, 1457, 1380, 1338, 1118. Anal. Calcd for $C_{10}H_{15}Br$: C, 55.83; H, 7.03. Found: C, 55.88; H, 6.97.



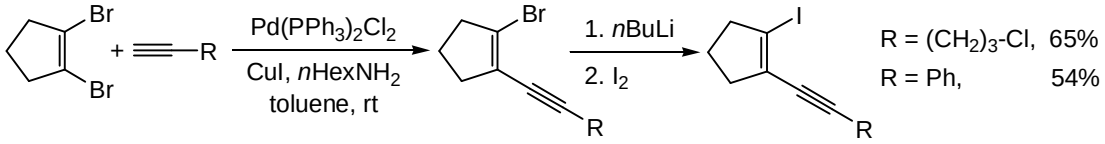
1-[(1*Z*)-1-Iodo-1-hepten-3-ynyl]-1-cyclohexene. The general procedure A was used with 1-ethynyl-1-cyclohexene (1.06 mL, 9.00 mmol), B-I-9-BBN (10.78 mL, 10.78 mmol, 1M hexanes), pentanes (35 mL), 1-lithio-1-pentyne[2] (12.62 mmol) and I_2 (4.00 g, 13.86 mmol) in THF (10 mL). The product was purified by column chromatography on silica gel (hexanes) to give 1.78 g of the title compound (66%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) d: 6.25 (t, *J* = 4.4 Hz, 1H), 6.14 (s, 1H), 2.39 (dt, *J* = 6.8, 2.0 Hz, 2H), 2.32-2.29 (m, 2H), 2.22-2.20 (m, 2H), 1.66-1.58 (m, 6H), 1.06 (t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 136.4, 136.3, 119.3, 115.3, 98.6, 83.0, 31.0, 28.2, 26.9, 26.4, 22.2, 22.0, 14.0. IR (neat, cm^{-1}): 2930, 2858, 2210, 1558, 1457, 1349, 1137. Anal. Calcd for $C_{13}H_{17}I$: C, 54.89; H, 6.45. Found: C, 55.07; H, 6.37.



[1] S. Hara, Y. Satoh, H. Ishiguro, A. Suzuki, *Tetrahedron Lett*. **1983**, *24*, 735.
[2] 1-Lithio-1-pentyne was prepared as follows. To 1.81 mL of 1-pentyne (18.29 mmol) in 10 mL THF was added at 0 ºC 8.05 mL *n*BuLi (20.10 mmol, 2.5M hexanes) and the mixture was stirred for 30 min at that temperature.

Ethyl (*Z*)-5-Iodo-4-nonen-2-ynoate. General procedure A was followed using 1-hexyne (1.40 mL, 12.50 mmol), B-Iodo-9-BBN (15.00 mL, 15.00 mmol, 1M in hexanes), pentanes (50 mL), ethyl 3-lithiopropiolate[3] (17.50 mmol) and I_2 (5.39 g, 21.25 mmol) in THF (20 mL). The crude material was purified by column chromatography on silica gel (hexanes/ethyl acetate 40:1) to give the title compound as a yellow oil (686 mg, 18%). ^{1}H NMR (400 MHz, $CDCl_3$) d: 6.23 (t, *J* = 1.3 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.61 (td, *J* = 7.6 Hz, 1.2 Hz, 2H), 1.55 (quint, *J* = 7.6 Hz, 2H), 1.33 (m, 5H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 153.9, 127.7, 115.3, 86.0, 83.3, 62.1, 45.5, 31.4, 21.3, 14.1, 13.7. IR (neat, cm^{-1}): 2959, 2209, 1708, 1257, 1106.

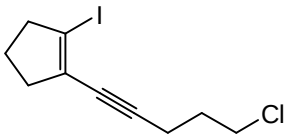
[(*Z*)-7-(Benzyloxy)-2-iodo-2-hepten-4-ynyl]benzene. General procedure A was followed using 3-phenyl-1-propyne (1.20 mL, 10.00 mmol), B-Iodo-9-BBN (12.00 mL, 12.00 mmol, 1M in hexanes), pentanes (40 mL), 1-lithio-4-benzyloxy-1-butyne (14.00 mmol) and I_2 (4.31 g, 17.00 mmol) in THF (15 mL). The crude material was purified by column chromatography on silica gel (hexanes/ethyl acetate 40:1) to give the title compound as a yellow oil (2.30 g, 57%). ^{1}H NMR (400 MHz, $CDCl_3$) d: 7.37-7.29 (m, 8H), 7.20 (d, *J* = 8.1 Hz, 2H), 6.03 (t, *J* = 1.4 Hz, 1H), 4.59 (s, 2H), 3.90 (s, 2H), 3.67 (t, *J* = 7.0 Hz, 2H), 2.69 (td, *J* = 6.9 Hz, 1.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 137.9, 137.7, 129.0, 128.5, 128.3, 127.6, 127.5, 126.9, 119.1, 116.4, 91.9, 82.0, 72.9, 68.1, 51.0, 21.0. IR (neat, cm^{-1}): 3028, 2861, 2220, 1603, 1495, 1453, 1102, 737. Anal. Calcd for $C_{20}H_{19}IO$: C, 59.71; H, 4.76. Found: C, 59.46; H, 4.76.



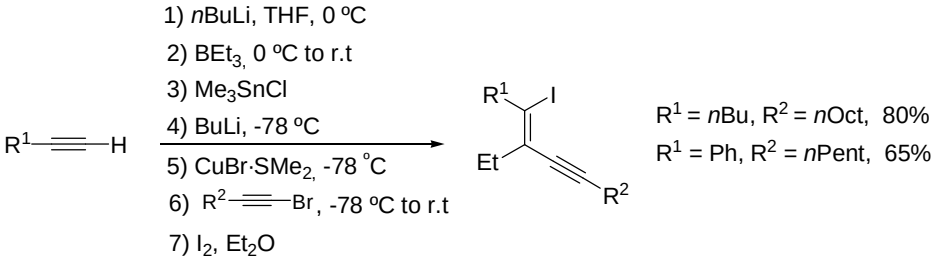
1-Bromo-2-(5-chloropent-1-ynyl)cyclopent-1-ene. 1,2-Dibromocyclopentene (1.10 mL, 9.22 mmol), 5-chloro-1-pentyne (0.39 mL, 3.69 mmol) and *n*hexylamine (2.40 mL, 18.44 mmol) were added to a solution of $Pd(PPh_3)_2Cl_2$ (78 mg, 3 mol%) and CuI (28 mg, 4 mol%) in toluene (15 mL) and the mixture was stirred overnight at room temperature. Saturated NH_4Cl solution (20 mL) was then added and the mixture extracted with ethyl acetate (3 × 15 mL). The combined organic layers were dried ($MgSO_4$) and filtered. Evaporation of the solvent gave the crude product which was purified by column chromatography on silica gel (hexanes/ethyl acetate 50:1) to give the title compound as a yellow oil (780 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) d: 3.73 (t, *J* = 6.4 Hz, 2H), 2.70 (m, 2H), 2.59 (t, *J* = 6.7 Hz, 2H), 2.45 (m, 2H), 2.07-1.95 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 126.2, 124.2, 94.3, 77.1, 43.5, 39.9, 35.8, 31.2, 22.3, 17.0. IR (neat, cm^{-1}): 2959, 2852, 1442, 1291, 1100, 837.

[3] Ethyl 3-lithiopropiolate was prepared as follows: ethyl propiolate (1.77 mL, 17.50 mmol) was added to a solution of LDA (17.50 mmol) in dry THF (40 mL) at -78 ºC and the mixture was stirred for 30 min at that temperature.

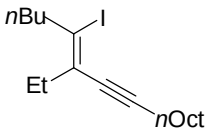
1-Iodo-2-(5-chloropent-1-ynyl)cyclopent-1-ene. *n*BuLi (2.5M in hexanes, 1.40 mL, 3.48 mmol) was added to a solution of 1-bromo-2-(5-chloropent-1-ynyl)cyclopent-1-ene (820 mg, 3.31 mmol) in dry THF (20 mL). After 30 min at that temperature, a solution of I_2 (925 mg, 3.64 mmol) in THF (5 mL) was added. The mixture was stirred for 1 h at -78 ºC and at room temperature for 1 h more. Saturated NH_4Cl solution (20 mL) was then added and the mixture extracted with ethyl acetate (3 × 15 mL). The combined organic layers were dried ($MgSO_4$) and evaporated. The crude product was purified by column chromatography on silica gel (hexanes) to give the title compound as a yellow oil (750 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) d: 3.74 (t, *J* = 6.4 Hz, 2H), 2.72 (m, 2H), 2.56 (t, *J* = 6.6 Hz, 2H), 2.42 (m, 2H), 2.05-1.92 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 132.0, 101.1, 94.0, 79.3, 44.0, 43.6, 36.4, 31.2, 23.8, 17.0. IR (neat, cm^{-1}): 2957, 2848, 1439, 1308, 1290, 829.



1-[2-(2-Iodocyclopent-1-enyl)ethynyl]benzene. *n*BuLi (2.5M in hexanes, 1.10 mL, 2.76 mmol) was added to a solution of 1-[2-(2-bromocyclopent-1-enyl)ethynyl]benzene)[4] (650 mg, 2.63 mmol) in dry THF (15 mL). After 30 min at that temperature, a solution of I_2 (734 mg, 2.89 mmol) in THF (5 mL) was added. The mixture was stirred for 1 h at -78 ºC and at room temperature for 1 h more. Saturated NH_4Cl solution (15 mL) was then added and the mixture extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried ($MgSO_4$) and evaporated. The crude product was purified by column chromatography on silica gel (hexanes) to give the title compound as a yellow oil (574 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) d: 7.52 (m, 2H), 7.34 (m, 3H), 2.81 (m, 2H), 2.58 (m, 2H), 2.04 (quint, *J* = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 131.7, 131.4, 128.2, 128.1, 122.8, 103.0, 94.7, 87.1, 44.3, 36.2, 23.8. IR (neat, cm^{-1}): 2953, 2847, 1487, 1441, 1315, 754, 689.



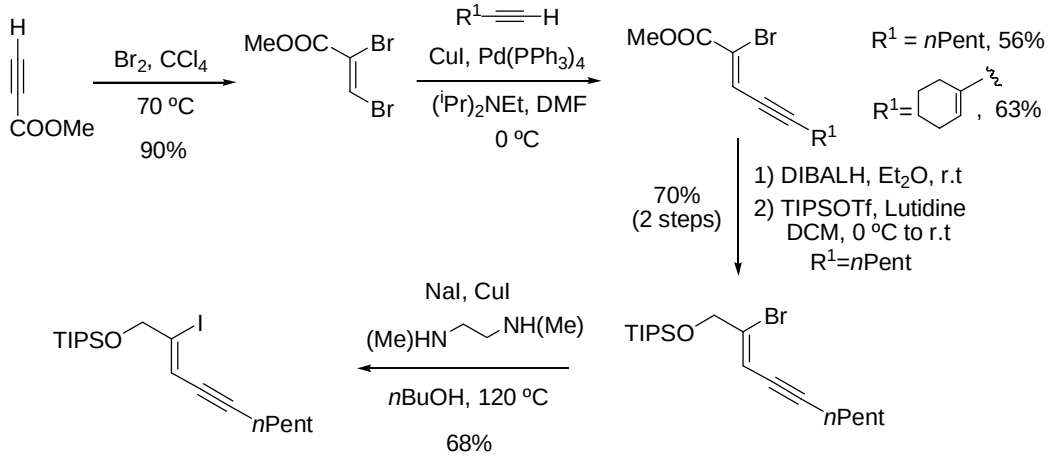
General Procedure B for the synthesis of iodoenynes having a tetrasubstituted central carbon-carbon double bond.[5] **The preparation of (5*Z*)-6-ethyl-5-iodo-5-hexadecen-7-yne is representative.** To a flask equipped with a low-temperature thermometer were successively added by syringes 15 mL of THF and 1.74 mL of 1-hexyne (15.00 mmol). *n*-Butyllithium (6.00 mL, 15.00 mmol, 2.5 M in hexanes) was then introduced dropwise at 0 ºC. After 15 min of stirring, triethylborane (15.00 mL, 15.00 mmol, 1.0 M in THF) was slowly introduced and the reaction mixture was then allowed to warm to rt and stirred for 1 h followed by the addition of 15 mL of a 1.0 M solution of trimethyltin chloride (15.00 mmol) in THF. After 1 h at rt, the reaction mixture



[4] C. Kosinski, A. Hirsch, F. W. Heinemann, F. Hampel, *Eur. J. Org. Chem.* **2001**, 3879.
[5] Z. Wang, K. K. Wang, *J. Org. Chem.* **1994**, *59*, 4738.

was cooled to –78 ºC and treated with 6 mL of a 2.5 M solution of *n*-butyllithium (15.00 mmol) in hexanes. After 15 min, the reaction mixture was transferred via cannula to a second flask containing 3.1 g of $CuBr{\cdot}SMe_2$ (15.00 mmol) in 30 mL of THF maintained at –78 ºC. After an additional 1 h at –78 ºC, 1-bromo-1-decyne (4.02 g, 18.60 mmol) was introduced dropwise and the reaction mixture was stirred for 1 h at –78 ºC before allowing to warm slowly to rt**.** The reaction mixture was treated with 15 mL of a 6 N NaOH solution and 15 mL of a 30% H_2O_2 solution. The organic layer was then separated, washed with water (30 mL), dried over $MgSO_4$, and concentrated to give the corresponding crude enynylstannane derivative. A solution of I_2 (3.90 g, 15.00 mmol) in 50 mL of Et_2O was added to the crude enynylstannane derivative in 30 mL of Et_2O. The resulting mixture was stirred for 1 h at rt followed by the addition of a saturated $Na_2S_2O_3$ solution (20 mL) to destroy the excess of I_2. An additional 40 mL of water and 50 mL of Et_2O were added and the organic layer was then separated, washed with brine (20 mL), dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography (silica gel, hexanes) to furnish 4.48 g of the title compound (80% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) d: 2.59 (t, *J* = 7.6 Hz, 2H), 2.38 (t, *J* = 6.8 Hz, 2H), 2.27 (q, *J* = 7.2 Hz, 2H), 1.61-1.50 (m, 6H), 1.42-1.36 (m, 10H), 1.12 (t, *J* = 7.6 Hz, 3H), 0.96-0.91 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 132.7, 110.9, 93.6, 85.2, 40.3, 31.9, 31.8, 29.2, 29.1, 28.9, 28.6, 26.7, 22.7, 21.7, 19.5, 14.1, 14.0, 13.6. IR (neat, cm^{-1}): 2957, 2928, 2856, 2111, 1593, 1462, 1377, 1114.

[(1*Z*)-2-Ethyl-1-iodo-1-nonen-3-ynyl]benzene. The general procedure B was used with phenyl acetylene (1.10 mL, 10.00 mmol), *n*-BuLi (10.00 mL, 10.00 mmol, 2.5M hexanes), BEt_3 (10.00 mL, 10.00 mmol, 1M THF), Me_3SnCl (10.00 mL, 10.00 mmol, 1M THF), *n*-BuLi (10.00 mL, 10.00 mmol, 2.5 M hexanes), $CuBr{\cdot}SMe_2$ (2.06 g, 10.00 mmol), 1-bromo-heptyne (2.16 g, 12.40 mmol) and I_2 (2.60 g, 10.00 mmol) in Et_2O (60 mL). The product was purified by column chromatography on silica gel (hexanes) to give 1.78 g of the title compound (65%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) d: 7.36-7.26 (m, 5H), 2.49 (t, *J* = 7.2 Hz, 2H), 2.18 (q, *J* = 7.6 Hz, 2H), 1.71-1.67 (m, 2H), 1.55-1.50 (m, 2H), 1..44-1.41 (m, 2H), 1.11 (t, *J* = 7.6 Hz, 3H), 0.98 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 143.0, 135.2, 128.4, 128.1, 128.0, 102.0, 96.4, 84.6, 31.1, 28.2, 27.9, 22.2, 19.6, 14.0, 13.7. IR (neat, cm^{-1}): 2958, 2931, 2858, 2214, 1600, 1486, 1459, 1441, 1375, 1215, 1071, 762, 695. Anal. Calcd for $C_{17}H_{21}I$: C, 57.96; H, 6.01. Found: C, 57.91; H, 6.11.



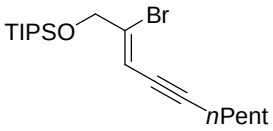
Methyl (2*Z*)-2,3-dibromo-2-propenoate. Methyl propiolate (3.20 mL, 35.70 mmol) and carbon tetrachloride (35 mL) were added in sequence to a round-bottomed flask. Then, bromine (1.95 mL, 37.72 mmol) was added dropwise while the solution of the methyl propiolate was being heated at 70 ºC. The red-brown solution was heated at 70 ºC for 30 min, allowed to cool to room temperature, and carbon tetrachloride and excess of bromine were removed by rotatory evaporation. The pale yellow concentrate was purified directly by column chromatography on silica gel (hexanes/ethyl acetate 20:1) to furnish 7.78 g of the title compound (90% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) d: 8.24 (s, 1H), 3.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 161.2, 126.8, 122.0, 53.7. IR (neat, cm^{-1}): 3011, 2940, 2180, 1707, 1574, 1429, 1284, 1254, 1218, 1052, 1035, 949, 773, 747, 615. Anal. Calcd for $C_4H_4Br_2O_2$: C, 19.70; H, 1.65. Found: C, 19.41; H, 1.57.

Methyl (2*Z*)-2-bromo-2-octenoate. An oven-dried flask was charged with methyl (2*Z*)-2,3-dibromo-2-propenoate prepared above (3.00 g, 12.40 mmol) and *N*,*N*-dimethylformamide (25 mL). Then, the solution was evacuated and flushed with argon (twice) at room temperature to deoxygenate the solution. The flask was cooled in an ice bath and 1-heptyne (2.70 mL, 20.54 mmol) and *N*,*N*-diisopropylethylamine (3.60 mL, 20.54 mmol) were added in sequence. The resulting pale yellow solution was deoxygenated as above. Then, CuI (0.57 g, 2.48 mmol) and tetrakis(triphenylphosphine)palladium (0.72 g, 0.62 mmol) were added, followed by a third deoxygenation cycle. The brown reaction mixture was maintained at 0 ºC until TLC analysis indicated consumption of the starting dibromide (4 hours). The reaction mixture was quenched by addition of water (100 mL), Et_2O (50 mL) and saturated aqueous ammonium chloride solution (40 mL). The resulting brown suspension was extracted with Et_2O (4 x 50 mL). The organic layers were combined and washed with brine (20 mL), then dried over magnesium sulfate and concentrated. The crude was purified by column chromatography on silica gel (hexanes/ethyl acetate 40:1) to give 1.79 g of the title compound (56% yield) as a brownish oil. ^{1}H NMR (400 MHz, $CDCl_3$) d: 7.28 (m, 1H), 3.83 (d, *J* = 1.2 Hz, 3H), 2.43 (dt, *J* = 6.8, 2.4 Hz, 2H), 1.61-1.57 (m, 2H), 1.45-1.31 (m, 4H), 0.89 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 162.6, 125.4, 121.8, 108.2, 77.8, 53.4, 30.8, 27.7, 22.0, 20.0, 13.8. IR (neat, cm^{-1}): 2955, 2860, 2215, 1732, 1591, 1435, 1264, 1166, 1046, 908, 747. Anal. Calcd for $C_{11}H_{15}BrO_2$: C, 50.98; H, 5.83. Found: C, 51.09; H, 5.95.

Methyl (2*Z*)-2-bromo-5-(1-cyclohexen-1-yl)-2-penten-4-ynoate. The procedure described above for the synthesis of methyl (2*Z*)-2-bromo-2-octenoate was used with methyl (2*Z*)-2,3-dibromo-2-propenoate (2.00 g, 8.27 mmol), 1-ethynyl-1-cyclohexene (1.61 mL, 13.70 mmol), CuI (0.32 g, 20 mol%), tetrakis(triphenylphosphine)palladium (0.48 g, 5 mol%), *N*,*N*-diisopropylethylamine (2.40 mL, 13.70 mmol) and *N*,*N*-dimethylformamide (16 mL). The product was purified by column chromatography on silica gel (hexanes/ethyl acetate, 40:1), to provide 1.40 g of the title compound (63% yield) as a white solid. M.p. 43-45 ºC. ^{1}H NMR (400 MHz, CDCl*3*) d: 7.40 (s, 1H), 6.34 (s, 1H), 3.83 (s, 3H), 2.20-2.14 (m, 4H), 1.66-1.59 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 162.6, 139.2, 124.8, 121.5, 120.4, 107.4, 84.2, 53.3, 28.5, 25.9, 21.9, 21.1. IR (neat, cm^{-1}): 3011, 2940, 2180, 1707, 1574, 1429, 1284, 1254,

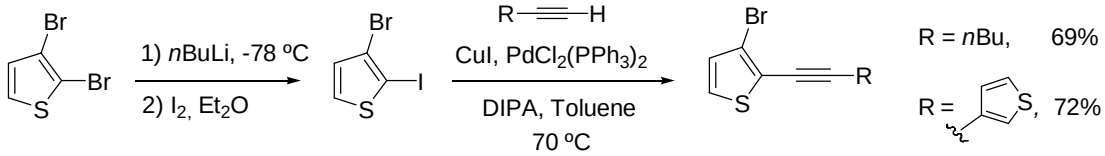
1218, 1052, 949, 919, 747, 615. Anal. Calcd for $C_{12}H_{13}BrO_2$: C, 53.55; H, 4.87. Found: C, 53.83; H, 4.87.

(2*Z*)-2-Bromo-2-decen-4-ynyl triisopropylsilyl ether. To a solution of methyl (2*Z*)-2-bromo-2-octenoate (1.73 g, 6.70 mmol) in Et_2O (40 mL) under nitrogen atmosphere was added at 0 ºC DIBALH (14.07 mL, 14.07 mmol, 1M in hexanes) dropwise. The mixture was then allowed to reach room temperature and stirred overnight. The reaction was then quenched by careful addition of HCl 2M (20 mL) and Et_2O (30 mL). The combined organic phases were then washed with brine (2 x 20 mL), dried over magnesium sulfate and concentrated. The residue was used directly in the next step without further purification.



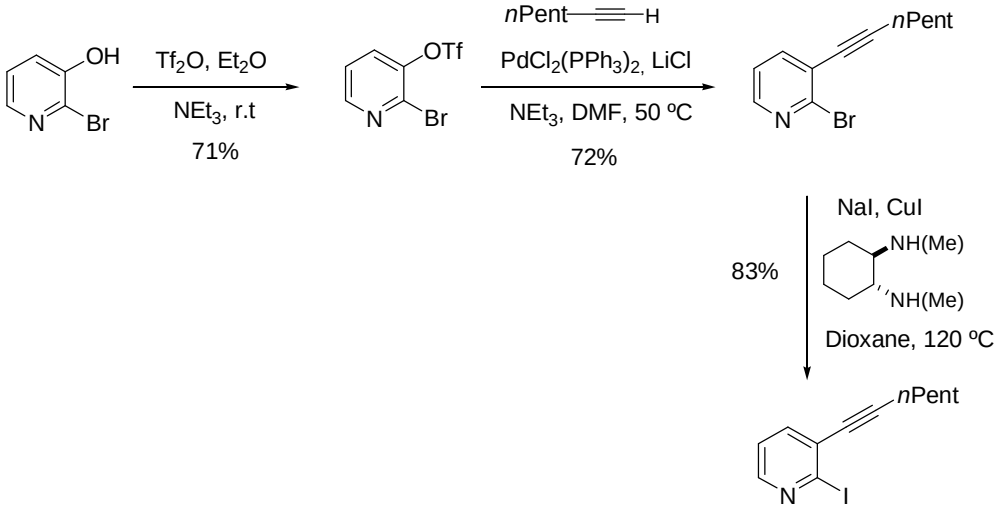
To a well stirred solution of the above crude alcohol in dichloromethane (15 mL) under nitrogen atmosphere was added lutidine (1.06 mL, 8.42 mmol) and stirred for 10 minutes at 0 ºC. Then triisopropyltrifluoromethanesulfonate (2.30 mL, 8.42 mmol) was added dropwise and the mixture was allowed to reach room temperature slowly. The reaction was quenched after 2 hours of further stirring by addition of saturated aqueous ammonium chloride solution (15 mL). The organic phase was washed twice with brine (10 mL), dried over magnesium sulfate and concentrated. The crude was purified by column chromatography on silica gel (hexanes) to afford 1.81 g of the title compound (70% yield, two steps) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) d: 6.40 (m, 1H), 4.42-4.38 (m, 2H), 2.39 (dt, *J* = 7.2, 2.0 Hz, 2H), 1.61-1.57 (m, 2H), 1.46-1.35 (m, 4H), 1.19-1.08 (m, 21H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 134.1, 108.9, 96.9, 77.1, 67.6, 31.0, 28.3, 22.2, 19.7, 17.9, 14.0, 11.9. IR (neat, cm^{-1}): 2943, 2226, 1617, 1464, 1368, 1248, 1122, 1066, 1018, 882, 834, 788. Anal. Calcd for $C_{19}H_{35}BrOSi$: C, 58.90; H, 9.10. Found: C, 58.55; H, 8.92.

(2*Z*)-2-Iodo-2-decen-4-ynyl triisopropylsilyl ether. A Schlenk tube was charged with CuI (8.51 mg, 5 mol%), NaI (0.19 g, 1.25 mmol), evacuated and backfilled with argon. *N*,*N*'-Dimethylethylenediamine (12 μL, 10 mol%), (2*Z*)-2-bromo-2-decen-4-ynyl triisopropylsilyl ether (0.32 g, 0.84 mmol), and *n*-butanol (1 mL) were added under argon. The Schlenk tube was sealed with a Teflon valve and the reaction mixture was stirred at 120 ºC for 55 h. The resulting tan suspension was allowed to reach room temperature, filtered through celite and concentrated. The residue was purified by column chromatography on silica gel (hexanes) to afford 0.25 g of the title compound (68% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) d: 6.51 (m, 1H), 4.42-4.38 (m, 2H), 2.37 (dt, *J* = 6.8, 1.6 Hz, 2H), 1.63-1.56 (m, 2H), 1.48-1.34 (m, 4H), 1.14-1.05 (m, 21H), 0.92 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 115.7, 114.9, 96.3, 80.5, 71.3, 31.0, 28.2, 22.2, 19.7, 17.9, 14.0, 11.9. IR (neat, cm^{-1}): 2949, 2867, 2220, 1617, 1457, 1371, 1249, 1129, 1050, 1023, 882.



3-Bromo-2-(1-hexynyl)thiophene. An oven-dried flask was charged with 3-bromo-2-iodothiophene [6] (1.50 g, 5.21 mmol), CuI (50 mg, 5 mol%) and *trans*-dichlorobis(triphenylphosphine)palladium (II) (38 mg, 1 mol%). The mixture was evacuated and flushed with argon (twice) at room temperature. Then, diisopropylamine (40 mL) and toluene (20 mL) were added via syringe and the solution was deoxygenated as above. 1-Hexyne (0.72 mL, 6.25 mmol) was added dropwise and the mixture was stirred at 70 ºC overnight. The brown mixture was quenched by addition of saturated aqueous ammonium chloride solution (40 mL) and Et_2O (40 mL). The organic layers were combined and washed with brine (10 mL), then dried over magnesium sulfate and concentrated. The crude was purified by column chromatography on silica gel (hexanes) to give 0.87 g of the title compound (69% yield) as a brownish oil. ^{1}H NMR (400 MHz, $CDCl_3$) d: 7.12 (d, *J* = 5.6 Hz, 2H), 6.93 (d, *J* = 5.6 Hz, 2H), 2.49 (t, *J* = 6.8 Hz, 2H), 1.65-1.59 (m, 2H), 1.57-1.50 (m, 2H), 0.98 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 129.7, 125.6, 121.6, 98.9, 72.2, 30.4, 21.9, 19.4, 13.6. IR (neat, cm^{-1}): 2957, 2932, 2871, 2227, 1508, 1464, 1428, 1348, 1150, 863, 707, 606. Anal. Calcd for $C_{10}H_{11}BrS$: C, 64.48; H, 7.58. Found: C, 64.50; H, 7.64.

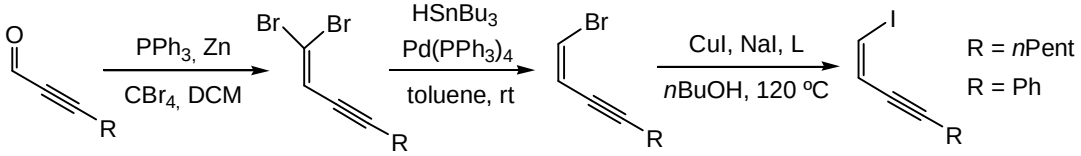
3-Bromo-2-(3-thienylethynyl)thiophene. The same procedure described above was followed using 3-bromo-2-iodothiophene[6] (1.59 g, 5.52 mmol), 3-ethynylthiophene (0.65 mL, 6.60 mmol), CuI (53 mg, 5 mol%), *trans*-dichlorobis(triphenylphosphine)palladium (II) (41 mg, 1 mol%), diisopropylamine (42 mL) and toluene (20 mL). The product was purified by column chromatography on silica gel (hexanes) to give the title compound as a colorless oil (1.07 g, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) d: 7.64 (d, *J* = 1.2 Hz, 1H), 7.33 (m, 1H), 7.27 (d, *J* = 5.0 Hz, 1H), 7.22 (dd, *J* = 5.4 Hz, 1.7 Hz, 1H), 7.02 (t, *J* = 5.4 Hz, 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 129.9, 129.5, 129.3, 127.0, 125.5, 121.1, 120.6, 115.8, 92.1, 80.5. IR (neat, cm^{-1}): 3106, 2211, 1433, 1346, 864, 780, 710. Anal. Calcd for $C_{10}H_5BrS_2$: C, 44.62; H, 1.87. Found: C, 44.91; H, 1.88.



[6] M. J. Marsella, Z-Q. Wang, R. J. Reid, K. Ion, *Org. Lett*. **2001**, *3*, 885.

2-Bromo-3-(1-heptynyl)pyridine. A mixture of 2-bromo-3-pyridinyl trifluoromethanesulfonate[7] (3.00 g, 9.84 mmol), 1-heptyne (1.72 mL, 13.14 mmol), $PdCl_2(PPh_3)_2$ (0.35 g, 7 mol%), LiCl (1.13 g, 26.70 mmol), Et_3N (2.71 mL, 19.44 mmol) and DMF (50 mL) was stirred at 55 ºC for 14 hours under nitrogen atmosphere. The mixture was diluted with H_2O (30 mL), and extracted with Et_2O (40 mL). The organic phases were washed with brine (10 mL), dried over magnesium sulfate and concentrated. The residue was then purified by column chromatography on silica gel (hexanes/ethyl acetate, 20:1) to give 1.78 g of the title compound (72% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) d: 8.22 (dd, *J* = 4.8, 2.0 Hz, 1H), 7.65 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.17 (dd, *J* = 7.6, 4.8 Hz, 1H), 2.46 (t, *J* = 6.8 Hz, 2H), 1.65-1.60 (m, 2H), 1.52-1.44 (m, 2H), 1.40-1.32 (m, 2H), 0.91 (t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 147.7, 144.3, 140.7, 124.1, 121.9, 98.6, 77.0, 30.9, 27.9, 22.1, 19.5, 13.9. IR (neat, cm^{-1}): 2930, 2859, 2231, 1653, 1547, 1446, 1387, 1118, 1079, 1052. Anal. Calcd for $C_{12}H_{14}BrN$: C, 57.16; H, 5.60. Found: C, 57.27; H, 5.65.

3-(1-Heptynyl)-2-iodopyridine. A Schlenk tube was charged with CuI (50.5 mg, 5 mol%), NaI (1.47 g, 9.74 mmol), evacuated and backfilled with argon. *trans-N,N'*-dimethylcyclohexyldiamine (77 µL, 10 mol%), 2-bromo-3-(1-heptynyl)pyridine (1.22 g, 4.87 mmol), and dioxane (5 mL) were added under argon. The Schlenk tube was sealed with a Teflon valve and the reaction mixture was stirred at 120 ºC for 12 hours. The resulting suspension was allowed to reach room temperature, filtered through celite and concentrated. The residue was purified by column chromatography on silica gel (hexanes/ethyl acetate 20:1) to afford 1.21 g of the title compound (83% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) d: 8.18 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.52 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.16 (dd, *J* = 8.0, 4.8 Hz, 1H), 2.45 (t, *J* = 7.2 Hz, 2H), 1.67-1.61 (m, 2H), 1.50-1.43 (m, 2H), 1.39-1.30 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 148.0, 138.9, 129.3, 124.1, 122.1, 98.4, 80.4, 31.0, 27.8, 22.1, 19.5, 14.0. IR (neat, cm^{-1}): 2930, 2858, 2228, 1565, 1542, 1441, 1379, 1113, 1071, 1044, 800, 727, 639.

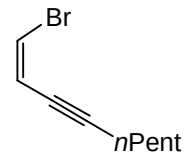


1,1-Dibromonon-1-en-3-yne. CBr_4 (11.93 g, 36.00 mmol) and zinc dust (2.36 g, 36.00 mmol) were placed in a flask and dichloromethane (100 mL) was added. Then, a solution of triphenylphosphine (9.45 g, 36.00 mmol) in dichloromethane (20 mL) was added dropwise at room temperature. After 30 minutes stirring, 2-octynal (2.57 mL, 18.00 mmol) was added dropwise and the mixture was stirred at room temperature overnight. The mixture was filtered directly through a short pad of silica gel, eluting with dichloromethane. The resulting crude was concentrated and the compound

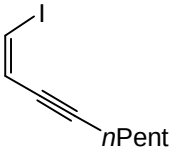
[7] A. Numata, Y. Kondo, T Sakamoto, *Synthesis* **1999**, 306.

was purified by column chromatography on silica gel (hexanes) to afford 4.80 g of the title compound (96% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) d: 6.54 (t, *J* = 2.2 Hz, 1H), 2.32 (td, *J* = 7.0 Hz, 2.2 Hz, 2H), 1.57 (quint, *J* = 7.1 Hz, 2H), 1.45-1.31 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 120.0, 100.1, 99.4, 77.7, 30.9, 27.9, 22.1, 19.7, 14.0. IR (neat, cm^{-1}): 2956, 2930, 2859, 2217, 1457, 859.

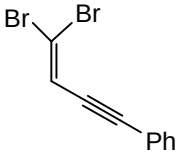
(*Z*)-1-Bromonon-1-en-3-yne. Tributyltin hydride (3.15 mL, 11.71 mmol) was added to a solution of 1,1-dibromonon-1-en-3-yne (3.00 g, 10.79 mmol) and $Pd(PPh_3)_4$ (624 mg, 5 mol%) in toluene (110 mL). The resulting mixture was stirred at room temperature for 1 h. Saturated NaCl solution (40 mL) was then added and the mixture extracted with EtOAc (3 × 30 mL). The combined organic layers were dried ($MgSO_4$) and evaporated. The residue was purified by column chromatography on silica gel (hexanes) to afford the title compound as a colorless oil (868 mg, 40%). ^{1}H NMR (400 MHz, $CDCl_3$) d: 6.48 (t, *J* = 7.4 Hz, 1H), 6.29 (dt, *J* = 7.4 Hz, 2.1 Hz, 1H), 2.38 (td, *J* = 7.0 Hz, 2.0 Hz, 2H), 1.58 (quint, *J* = 7.3 Hz, 2H), 1.45-1.31 (m, 4H), 0.91 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 116.0, 115.9, 99.1, 76.5, 30.9, 28.1, 22.1, 19.6, 13.9. IR (neat, cm^{-1}): 2957, 2926, 2855, 1726, 1463, 1260, 1074, 802.



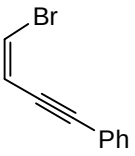
(*Z*)-1-Iodonon-1-en-3-yne. An oven-dried Schlenk tube was charged with CuI (32 mg, 5 mol%) and NaI (720 mg, 4.73 mmol), evacuated and backfilled with argon. *N*,*N*'-Dimethylethylenediamine (43 μL, 10 mol%), (Z)-1-bromonon-1-en-3-yne (630 mg, 3.15 mmol) and anhydrous *n*BuOH (3.5 mL) were then added. The mixture was stirred at 120 ºC for 48 h. The resulting suspension was poured into water (5 mL) and extracted with dichloromethane (3 × 10 mL). The combined organic phases were dried ($MgSO_4$), concentrated and the residue was purified by flash chromatography on silica gel (hexanes) to provide the desired product as a yellow oil (492 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) d: 6.64 (d, *J* = 8.1 Hz, 1H), 6.59 (dt, *J* = 8.1 Hz, 2.0 Hz, 1H), 2.37 (td, *J* = 7.0 Hz, 1.8 Hz, 2H), 1.61 (quint, *J* = 7.1 Hz, 2H), 1.49-1.33 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) d: 123.2, 98.8, 90.5, 80.1, 30.9, 28.0, 22.1, 19.7, 14.0. IR (neat, cm^{-1}): 3039, 2956, 2930, 2858, 2206, 1465, 1297, 705.



1-(4,4-Dibromobut-3-en-1-ynyl)benzene. CBr_4 (10.78 g, 32.76 mmol) and zinc dust (2.15 g, 32.76 mmol) were placed in a flask and dichloromethane (100 mL) was added. Then, a solution of triphenylphosphine (8.54 g, 32.76 mmol) in dichloromethane (20 mL) was added dropwise at room temperature. After 30 minutes stirring, 3-phenyl-2-propynal (2.00 mL, 16.38 mmol) was added dropwise and the mixture was stirred at room temperature overnight. The mixture was filtered directly through a short pad of silica gel, eluting with dichloromethane. The resulting crude was concentrated and the compound was purified by column chromatography on silica gel (hexanes/ethyl acetate 60:1) to afford 3.40 g of the title compound (73% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) d: 7.50 (m, 2H), 7.35 (m, 3H), 6.79 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 131.5, 128.9, 128.3, 122.3, 119.5, 101.8, 97.1, 86.2. IR (neat, cm^{-1}): 2201, 1488, 1441, 846, 754, 687.



1-[(*Z*)-4-Bromobut-3-en-1-ynyl]benzene.[8] Tributyltin hydride (1.90 mL, 7.17 mmol) was added to a solution of 1-(4,4-dibromobut-3-en-1-ynyl)benzene (1.85 g, 6.51 mmol) and $Pd(PPh_3)_4$ (377 mg, 5 mol%) in toluene (65 mL). The resulting mixture was stirred at room temperature for 1 h. Saturated NaCl solution (30 mL) was then added and the mixture extracted with EtOAc (3 × 30 mL). The combined organic layers were dried ($MgSO_4$) and evaporated. The residue was purified by column chromatography on silica gel (hexanes) to afford the title compound as a yellow oil (944 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) d: 7.54 (m, 2H), 7.35 (m, 3H), 6.65 (d, *J* = 7.6 Hz, 1H), 6.53 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 131.5, 128.7, 128.3, 122.5, 117.8, 115.6, 97.0, 85.2.



1-[(*Z*)-4-Iodobut-3-en-1-ynyl]benzene.[9] An oven-dried Schlenk tube was charged with CuI (17 mg, 5 mol%) and NaI (391 mg, 2.61 mmol), evacuated and backfilled with argon. *N*,*N*'-Dimethylethylenediamine (19 μL, 10 mol%), 1-[(Z)-4-bromobut-3-en-1-ynyl]benzene (360 mg, 1.74 mmol) and anhydrous *n*BuOH (2.0 mL) were then added. The mixture was stirred at 120 ºC for 72 h. The resulting suspension was poured into water (5 mL) and extracted with dichloromethane (3 × 10 mL). The combined organic phases were dried ($MgSO_4$), concentrated and the residue was purified by flash chromatography on silica gel (hexanes) to provide the desired product as a yellow oil (292 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) d: 7.58 (m, 2H), 7.39 (m, 3H), 6.87 (s, 1H).^{13}C NMR (100 MHz, $CDCl_3$) d: 131.5, 128.7, 128.3, 122.7, 122.6, 96.6, 92.8, 88.9.

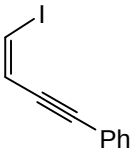


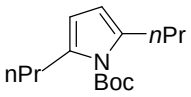
Table 1: General Procedure A for the synthesis of pyrroles through Cu-catalyzed domino amidation-hydroamidation of iodoenynes. An oven-dried Schlenk tube was charged with CuI (5 mol %), *tert*-butyl carbamate (1.2 equiv.) and Cs_2CO_3 (2 equiv.). The Schlenk tube was capped with a teflon screwcap and then evacuated and backfilled with argon (this sequence was carried out two times). Under a positive pressure of argon, *N*,*N*'-dimethylethylendiamine (20 mol%) and the iodoenyne (1 equiv.) were added via syringe, followed by the addition of THF (0.5 M). The tube was sealed and stirred at 80 ºC in a pre-heated oil bath for the indicated period of time. The reaction mixture was cooled to room temperature, diluted with ethyl acetate, filtered through a plug of celite, concentrated to dryness and purified by column chromatography on silica gel (2.5% NEt_3), eluting with hexanes/ethyl acetate mixtures.

Table 1: General Procedure B for the synthesis of pyrroles through Cu-catalyzed domino amidation-hydroamidation of bromoenynes. An oven-dried Schlenk tube was charged with CuI (5 mol %), *tert*-butyl carbamate (1.2 equiv.) and K_2CO_3 (2 equiv.). The Schlenk tube was capped with a teflon screwcap and then evacuated and backfilled with argon (this sequence was carried out two times). Under a positive pressure of argon, *N*,*N*'-dimethylethylendiamine (20 mol%) and the bromoenyne (1 equiv.) were added via syringe, followed by the addition of toluene (0.5 M). The tube was sealed and stirred at 110 ºC in a pre-heated oil bath for the indicated period of time. The

[8] J. Uenishi, R. Kawahama, O. Yonemitsu, J. Tsuji, *J. Org. Chem.* **1998**, *63*, 8965.
[9] H. Yoshida, E. Shirakawa, T. Kurahashi, Y. Nakao, T. Hiyama, *Organometallics* **2000**, *19*, 5671.

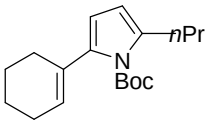
reaction mixture was cooled to room temperature, diluted with ethyl acetate, filtered through a plug of celite, concentrated to dryness and purified by column chromatography on silica gel (2.5% NEt_3), eluting with hexanes/ethyl acetate mixtures.

***tert*-Butyl 2,5-dipropyl-1*H*-pyrrole-1-carboxylate (Table 1, Entry 1).** The general procedure B was used with (4*Z*)-4-bromo-4-decen-6-yne (0.21 g, 1.00 mmol), CuI (9.60 mg, 5 mol %), *tert*-butyl carbamate (0.14 g, 1.20 mmol), *N*,*N*'-dimethylethylendiamine (22 μL, 20 mol %), K_2CO_3 (0.28 g, 2.00 mmol) and toluene (2 mL) for 14 hours. The product was purified by column chromatography on silica gel (2.5% NEt_3), eluting with hexanes/ethyl acetate 20:1 to provide 0.19 g of the title compound (74% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) d: 5.87 (s, 2H), 2.78 (t, *J* = 7.6 Hz, 4H), 1.64 (m, 13H), 1.01 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 150.5, 135.8, 109.0, 83.1, 31.7, 28.0, 22.4, 13.9. IR (neat, cm^{-1}): 2961, 1872, 1738, 1534, 1392, 1326, 1172, 1123, 1017, 852, 784. Anal. Calcd for $C_{15}H_{25}NO_2$: C, 71.67; H, 10.02. Found: C, 71.65; H, 10.05.

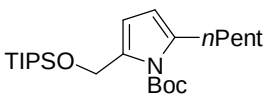


***tert*-Butyl 2,5-dipropyl-1*H*-pyrrole-1-carboxylate (Table 1, Entry 2).** The general procedure A was used with (4*Z*)-4-iodo-4-decen-6-yne (0.20 g, 0.75 mmol), CuI (7.20 mg, 5 mol %), tert-butyl carbamate (0.11 g, 0.90 mmol), *N*,*N*'-dimethylethylendiamine (16.50 μL, 20 mol %), Cs_2CO_3 (0.57 g, 1.50 mmol) and THF (1.5 mL) for 8 hours. The product was purified by column chromatography on silica gel (2.5% NEt_3), eluting with hexanes/ethyl acetate 20:1 to provide 0.14 g of the title compound (72% yield) as a colorless oil.

***tert*-Butyl 2-(1-cyclohexen-1-yl)-5-propyl-1*H*-pyrrole-1-carboxylate (Table 1, Entry 3).** The general procedure A was used with 1-[(1*Z*)-1-iodo-1-hepten-3-ynyl]-1-cyclohexene (0.15 g, 0.50 mmol), CuI (4.80 mg, 5 mol %), *tert*-butyl carbamate (71.00 mg, 0.60 mmol), *N*,*N*'-dimethylethylendiamine (11 μL, 20 mol %), Cs_2CO_3 (0.37 g, 1.00 mmol) and THF (1 mL) for 5 hours. The product was purified by column chromatography on silica gel (2.5% NEt_3), eluting with hexanes/ethyl acetate 20:1 to provide 0.12 g of the title compound (83% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) d: 5.92 (d, *J* = 3.2 Hz, 1H), 5.87 (d, *J* =3.2 Hz, 1H), 5.68 (br s, 1H), 2.73 (t, *J* = 7.2 Hz, 2H), 2.25-2.16 (m, 4H), 1.77-1.61 (m, 6H), 1.58 (s, 9H), 1.01 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 150.6, 137.5, 136.2, 131.9, 124.7, 109.6, 108.5, 83.1, 30.8, 29.2, 27.8, 25.4, 22.8, 22.3, 22.0, 14.0. IR (neat, cm^{-1}): 2931, 1740, 1457, 1368, 1308, 1174, 1135, 851, 785. Anal. Calcd for $C_{18}H_{27}NO_2$: C, 74.70; H, 9.40. Found: C, 74.65; H, 9.46.

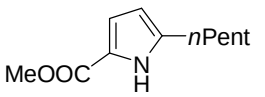


***tert*-Butyl 2-pentyl-5-{[(triisopropylsilyl)oxy]methyl}-1*H*-pyrrole-1-carboxylate (Table 1, Entry 4).** The general procedure A was used with (2*Z*)-2-iodo-2-decen-4-ynyl triisopropylsilyl ether (0.30 g, 0.69 mmol), CuI (6.62 mg, 5 mol %), *tert*-butyl carbamate (0.10 g, 0.83 mmol), *N*,*N*'-dimethylethylendiamine (15.20 μL, 20 mol %), Cs_2CO_3 (0.525 g, 1.38 mmol) and THF (1.4 mL) for 7 hours. The product was purified by column chromatography on silica gel (2.5% NEt_3), eluting with hexanes/ethyl acetate 40:1 to provide 0.25 g of the title compound (82% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) d: 6.20 (d, *J* = 3.2 Hz, 1H), 5.91 (d, *J* = 3.2 Hz, 1H), 4.93 (s, 2H),

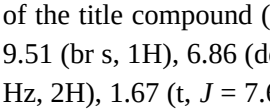


2.81 (t, *J* = 7.6 Hz, 2H), 1.61 (s, 11H), 1.39-1.33 (m, 4H), 1.19-1.07 (m, 21H), 0.92 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 150.1, 136.8, 135.3, 109.4, 109.3, 83.4, 61.1, 31.7, 29.5, 28.8, 28.0, 22.6, 18.1, 14.0, 12.0. IR (neat, cm^{-1}): 2941, 2866, 1743, 1537, 1463, 1393, 1369, 1328, 1255, 1172, 1123, 1013, 882, 852, 790. Anal. Calcd for $C_{24}H_{45}NO_3Si$: C, 68.03; H, 10.70. Found: C, 67.99; H, 10.77.

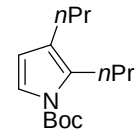
Methyl 5-pentyl-1*H*-pyrrole-2-carboxylate (Table 1, Entry 5). The general procedure B was used with methyl (2*Z*)-2-bromo-2-octenoate (0.19 g, 0.75 mmol), CuI (7.20 mg, 5 mol %), *tert*-butyl carbamate (0.11 g, 0.90 mmol), *N*,*N*'-dimethylethylendiamine (16.50 μL, 20 mol %), K_2CO_3 (0.21 g, 1.50 mmol) and toluene (1.50 mL) for 14 hours. The product was purified by column chromatography on silica gel (2.5% NEt_3), eluting with hexanes/ethyl acetate 10:1 to provide 0.12 g of the title compound (80% yield) as a white solid. M.p. 67-69 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) d: 9.51 (br s, 1H), 6.86 (dd, *J* = 3.6, 2.8 Hz, 1H), 5.99 (t, *J* = 2.8 Hz, 1H), 3.86 (s, 3H), 2.65 (t, *J* = 7.6 Hz, 2H), 1.67 (t, *J* = 7.6 Hz, 2H), 1.38-1.32 (m, 4H), 0.91 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 161.9, 139.3, 120.6, 116.0, 108.0, 51.2, 31.4, 29.0, 27.7, 22.4, 14.0. IR (neat, cm^{-1}): 3345, 2933, 1681, 1552, 1485, 1439, 1330, 1275, 1236, 1191, 1146, 1050, 1003. Anal. Calcd for $C_{11}H_{17}NO_2$: C, 67.66; H, 8.78. Found: C, 68.04; H, 8.78.



Methyl 5-(1-cyclohexen-1-yl)-1*H*-pyrrole-2-carboxylate (Table 1, Entry 6). The general procedure B was used with methyl (2*Z*)-2-bromo-5-(1-cyclohexen-1-yl)-2-penten-4-ynoate (0.20 g, 0.75 mmol), CuI (7.20 mg, 5 mol %), *tert*-butyl carbamate (0.11 g, 0.90 mmol), *N*,*N*'-dimethylethylendiamine (16.50 μL, 20 mol %), K_2CO_3 (0.21 g, 1.50 mmol) and toluene (1.50 mL) for 14 hours. The product was purified by column chromatography on silica gel (2.5% NEt_3), eluting with hexanes/ethyl acetate 10:1 to provide 0.12 g of the title compound (81% yield) as a white solid. M.p. 112-113 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) d: 9.10 (br s, 1H), 6.88 (dd, *J* = 3.6, 2.8 Hz, 1H), 6.22 (t, *J* = 3.2 Hz, 1H), 6.17 (br s, 1H), 3.86 (s, 3H), 2.35 (br s, 2H), 2.22 (br s, 2H), 1.77-1.66 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 161.6, 138.6, 128.0, 123.3, 121.4, 116.2, 106.4, 51.4, 25.8, 25.3, 22.4, 22.0. IR (neat, cm^{-1}): 3300, 2927, 2859, 1679, 1495, 1443, 1353, 1329, 1307, 1237, 1207, 1146, 1047, 1010, 932, 864, 787, 771. Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37. Found: C, 70.42; H, 7.51.



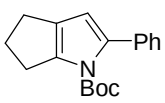
***tert*-Butyl 2,3-dipropyl-1*H*-pyrrole-1-carboxylate (Table 1, Entry 7).** The general procedure A was used with (*Z*)-4-iodo-5-propyl-7-(trimethylsilyl)-4-hepten-6-yne[10] (0.14 g, 0.42 mmol), CuI (4.02 mg, 5 mol %), *tert*-butyl carbamate (60.00 mg, 0.50 mmol), *N*,*N*'-dimethylethylendiamine (9.40 μL, 20 mol %), Cs_2CO_3 (0.48 g, 1.26 mmol) and THF (0.80 mL) for 8 hours. The product was purified by column chromatography on silica gel (2.5% NEt_3), eluting with hexanes/ethyl acetate 30:1 to provide 75 mg of the title compound (70% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) d: 7.17 (d, *J* = 3.6 Hz, 1H), 6.02 (d, *J* = 3.6 Hz, 1H), 2.78 (t, *J* = 7.6 Hz, 2H), 2.35 (t, *J* = 7.2 Hz, 2H), 1.61-1.49 (m, 13H), 0.96



[10] Y. Takayama, C. Delas, K. Muraoka, F. Sato, *Org. Lett.* **2003**, *5*, 365.

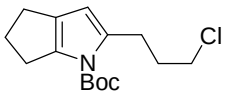
(m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 150.0, 131.0, 124.9, 119.7, 111.3, 82.8, 28.0, 27.9, 27.7, 23.8, 23.6, 14.1, 14.0. IR (neat, cm^{-1}): 2960, 2932, 2871, 1741, 1500, 1457, 1418, 1369, 1334, 1255, 1173, 1143, 1107, 1051, 966, 854. Anal. Calcd for $C_{15}H_{25}NO_2$: C, 71.67; H, 10.02. Found: C, 71.39; H, 10.06.

***tert*-Butyl 2-phenyl-5,6-dihydrocyclopenta[*b*]pyrrole-1(4*H*)-carboxylate (Table 1, Entry 8).**



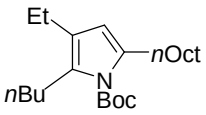
The general procedure A was used with [(2-iodo-1-cyclopenten-1-yl)ethynyl]benzene (0.22 g, 0.75 mmol), CuI (7.20 mg, 5 mol %), *tert*-butyl carbamate (0.11 g, 0.90 mmol), *N*,*N*'-dimethylethylendiamine (16.50 μL, 20 mol %), Cs_2CO_3 (0.56 g, 1.50 mmol) and THF (1.5 mL) for 6 hours. The product was purified by column chromatography on silica gel (2.5% NEt_3), eluting with hexanes/ethyl acetate 20:1 to provide 106 mg of the title compound (50% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) d: 7.49-7.43 (m, 2H), 7.37-7.30 (m, 3H), 6.85 (br s, 1H), 3.02 (t, *J* = 7.6 Hz, 2H), 2.55-2.50 (m, 2H), 1.97-1.93 (m, 2H), 1.51 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 151.9, 145.7, 131.2, 128.3, 127.9, 123.5, 98.3, 96.0, 84.2, 80.9, 32.6, 32.4, 28.2, 21.8. IR (neat, cm^{-1}): 2975, 2193, 1736, 1639, 1595, 1474, 1367, 1227, 1154, 1074, 969, 755, 690. Anal. Calcd for $C_{18}H_{21}NO_2$: C, 76.29; H, 7.47. Found: C, 76.17; H, 7.37.

***tert*-Butyl 2-(3-chloropropyl)-5,6-dihydrocyclopenta[*b*]pyrrole-1(4*H*)-carboxylate (Table 1, Entry 9).** The general procedure A was used with 1-(5-chloro-1-pentynyl)-2-iodo-1-cyclopentene



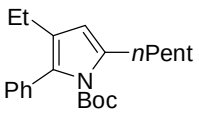
(0.15 g, 0.50 mmol), CuI (4.80 mg, 5 mol %), *tert*-butyl carbamate (71.00 mg, 0.60 mmol), *N*,*N*'-dimethylethylendiamine (11 μL, 20 mol %), Cs_2CO_3 (0.38 g, 1.0 mmol) and THF (1.0 mL) for 4 hours. The product was purified by column chromatography on silica gel (2.5% NEt_3), eluting with hexanes/ethyl acetate 20:1 to provide 0.11 g of the title compound (77% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) d: 6.69 (br s, 1H), 3.68 (t, *J* = 6.0 Hz, 2H), 2.93 (t, *J* = 6.8 Hz, 2H), 2.61 (t, *J* = 6.8 Hz, 2H), 2.36 (t, *J* = 7.0 Hz, 2H), 2.04-1.99 (m, 2H), 1.92-1.87 (m, 2H), 1.48 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 152.0, 144.6, 98.7, 94.6, 80.6, 76.2, 43.7, 32.6, 32.1, 31.5, 28.2, 21.7, 17.3. IR (neat, cm^{-1}): 2927, 1735, 1645, 1480, 1367, 1249, 1222, 1156, 991, 832.

***tert*-Butyl 2-butyl-3-ethyl-5-octyl-1*H*-pyrrole-1-carboxylate (Table 1, Entry 10).** The general

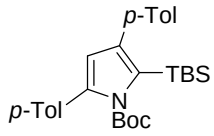


procedure A was used with (5*Z*)-6-ethyl-5-iodo-5-hexadecen-7-yne (0.19 g, 0.50 mmol), CuI (4.80 mg, 5 mol %), *tert*-butyl carbamate (73.00 mg, 0.60 mmol), *N*,*N*'-dimethylethylendiamine (11 μL, 20 mol %), Cs_2CO_3 (0.38 g, 1.0 mmol) and THF (1.0 mL) for 14 hours. The product was purified by column chromatography on silica gel (2.5% NEt_3), eluting with hexanes/ethyl acetate 40:1 to provide 0.15 g of the title compound (83% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) d: 5.82 (s, 1H), 2.77 (t, *J* = 7.6 Hz, 4H), 2.38 (q, *J* = 7.6 Hz, 2H), 1.62 (s, 9H), 1.60-1.58 (m, 2H), 1.47-1.31 (m, 14H), 1.15 (t, *J* = 7.6 Hz, 3H), 0.97-0.92 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 150.5, 135.0, 130.1, 124.2, 109.9, 82.8, 33.1, 31.9, 29.6, 29.5, 29.3, 29.1, 28.0, 25.9, 22.7, 19.0, 15.2, 14.1, 14.0. IR (neat, cm^{-1}): 2959, 2928, 2857, 1735, 1539, 1457, 1368, 1336, 1311, 1254, 1175, 1133, 1112, 1056, 853. Anal. Calcd for $C_{23}H_{41}NO_2$: C, 75.98; H, 11.37. Found: C, 75.97; H, 11.55.

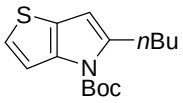
***tert*-Butyl 3-ethyl-5-pentyl-2-phenyl-1*H*-pyrrole-1-carboxylate (Table 1, Entry 11).** The general procedure A was used with [(1*Z*)-2-ethyl-1-iodo-1-nonen-3-ynyl]benzene (0.18 g, 0.50 mmol), CuI (4.80 mg, 5 mol %), *tert*-butyl carbamate (73.00 mg, 0.60 mmol), *N*,*N*'-dimethylethylendiamine (11 μL, 20 mol %), Cs_2CO_3 (0.38 g, 1.0 mmol) and THF (1.0 mL) for 10 hours. The product was purified by column chromatography on silica gel (2.5% NEt_3), eluting with hexanes/ethyl acetate 40:1 to provide 0.16 g of the title compound (91% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) d: 7.39-7.26 (m, 5H), 5.99 (s, 1H), 2.88 (t, *J* = 7.6 Hz, 2H), 2.34 (q, *J* = 7.2 Hz, 2H), 1.74-1.67 (m, 2H), 1.48-1.37 (m, 4H), 1.21 (s, 9H), 1.14 (t, *J* = 7.2 Hz, 3H), 0.97 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 150.2, 136.8, 135.1, 129.6, 129.3, 127.6, 126.5, 126.4, 109.6, 82.6, 31.8, 28.7, 28.6, 27.2, 22.6, 19.0, 15.3, 14.0. IR (neat, cm^{-1}): 2961, 2931, 2859, 1738, 1608, 1534, 1460, 1368, 1311, 1256, 1158, 1082, 854, 759, 700. Anal. Calcd for $C_{22}H_{31}NO_2$: C, 77.38; H, 9.15. Found: C, 77.22; H, 9.19.



***tert*-Butyl 2-[*tert*-butyl(dimethyl)silyl]-3,5-bis(4-methylphenyl)-1*H*-pyrrole-1-carboxylate (Table 1, Entry 12).** The general procedure A was used with *tert*-butyl[(1*Z*)-1-iodo-2,4-bis(4-methylphenyl)-1-buten-3-ynyl]dimethylsilane[11] (0.23 g, 0.50 mmol), CuI (4.80 mg, 5 mol %), *tert*-butyl carbamate (73.00 mg, 0.60 mmol), *N*,*N*'-dimethylethylendiamine (11 μL, 20 mol %), Cs_2CO_3 (0.38 g, 1.0 mmol) and THF (1.0 mL) for 14 hours. The product was purified by column chromatography on silica gel (2.5% NEt_3), eluting with hexanes/ethyl acetate 40:1 to provide 0.22 g of the title compound (94% yield) as a white solid. M.p. 111-113 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) d: 7.31-7.17 (m, 8H), 6.19 (s, 1H), 2.42 (s, 6H), 1.24 (s, 9H), 1.08 (s, 9H), -0.08 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 151.0, 139.7, 137.7, 136.6, 136.3, 135.7, 132.3, 130.0, 129.5, 128.5, 128.4, 128.1, 116.7, 83.3, 29.0, 27.2, 21.3, 18.3, -1.1. IR (neat, cm^{-1}): 2928, 1743, 1503, 1368, 1320, 1249, 1142, 991, 811, 693.



***tert*-Butyl 5-butyl-4*H*-thieno[3,2-*b*]pyrrole-4-carboxylate (Table 1, Entry 13).** The general procedure B was used with 3-bromo-2-(1-hexynyl)thiophene (0.26 g, 1.00 mmol), CuI (9.60 mg, 5 mol %), *tert*-butyl carbamate (0.15 mg, 1.20 mmol), *N*,*N*'-dimethylethylendiamine (22 μL, 20 mol %), K_2CO_3 (0.28 g, 2.00 mmol) and toluene (2.0 mL) for 15 hours. The product was purified by column chromatography on silica gel (2.5% NEt_3), eluting with hexanes/ethyl acetate 20:1 to provide 0.25 g of the title compound (85% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) d: 7.34 (d, *J* = 5.2 Hz, 1H), 7.09 (d, *J* = 5.2 Hz, 1H), 6.32 (s, 1H), 3.01 (t, *J* = 7.2 Hz, 2H), 1.70 (s, 9H), 1.68-1.64 (m, 2H), 1.51-1.43 (m, 2H), 1.0 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 149.3, 141.5, 138.6, 125.4, 122.4, 116.0, 104.3, 83.5, 31.1, 29.6, 28.1, 22.4, 14.0. IR (neat, cm^{-1}): 2957, 1740, 1496, 1393, 1369, 1322, 1251, 1151, 1118, 851, 707, 658. Anal. Calcd for $C_{15}H_{21}NO_2S$: C, 64.48; H, 7.58. Found: C, 64.50; H, 7.64.



[11] J. Barluenga, I. Llorente, L. J. Alvarez-Garcia, J. M. Gonzalez, P. J. Campos, M. R. Diaz, S. Garcia-Granda, *J. Am. Chem. Soc.* **1997**, *119*, 6933.

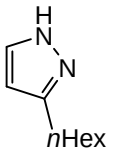
***tert*-Butyl 5-(3-thienyl)-4*H*-thieno[3,2-*b*]pyrrole-4-carboxylate (Table 1, Entry 14).** The general procedure B was used with 3-bromo-2-(3-thienylethynyl)thiophene (0.20 g, 0.75 mmol), CuI (7.20 mg, 5 mol %), *tert*-butyl carbamate (0.11 g, 0.9 mmol), *N*,*N*'-dimethylethylendiamine (16.50 μL, 20 mol %), K_2CO_3 (0.21 g, 1.50 mmol) and toluene (1.50 mL) for 15 hours. The product was purified by column chromatography on silica gel (2.5% NEt_3), eluting with hexanes/ethyl acetate 20:1 to provide 0.17 g of the title compound (73% yield) as a white solid. M.p. 114-116 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) d: 7.46 (d, *J* = 5.2 Hz, 1H), 7.37-7.33 (m, 2H), 7.25-7.19 (m, 2H), 6.57 (s, 1H), 1.54 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 149.0, 139.8, 134.4, 133.9, 129.3, 125.6, 124.3, 124.1, 123.2, 115.8, 107.8, 83.7, 27.8. IR (neat, cm^{-1}): 2978, 2930, 2360, 1731, 1487, 1455, 1369, 1345, 1320, 1252, 1142, 1130, 1007, 850, 832, 768. Anal. Calcd for $C_{15}H_{15}NO_2S_2$: C, 58.99; H, 4.95. Found: C, 58.60; H, 4.84.

***tert*-Butyl 2-pentyl-1*H*-pyrrolo[2,3-*b*]pyridine-1-carboxylate (Table 1, Entry 15).** The general procedure A was used with 3-(1-heptynyl)-2-iodopyridine (0.22 g, 0.75 mmol), CuI (7.20 mg, 5 mol %), *tert*-butyl carbamate (0.11 g, 0.90 mmol), *N*,*N*'-dimethylethylendiamine (16.50 μL, 20 mol %), Cs_2CO_3 (0.57 g, 1.50 mmol) and THF (1.5 mL) for 15 hours. The product was purified by column chromatography on silica gel (2.5% NEt_3), eluting with hexanes/ethyl acetate 20:1 to provide 0.16 g of the title compound (73% yield) as a white solid. M.p. 41-43 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) d: 8.41 (t, *J* = 4.8, 0.8 Hz, 1H), 7.73 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.11 (dd, *J* = 8.0, 4.8 Hz, 1H), 6.25 (s, 1H), 2.96 (t, *J* = 7.6 Hz, 2H), 1.68 (s, 9H), 1.65-1.62 (m, 2H), 1.39-1.35 (m, 4H), 0.92 (brs, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 149.6, 148.9, 142.2, 127.3, 121.8, 118.2, 118.1, 103.5, 84.0, 31.5, 30.1, 28.4, 28.0, 22.5, 13.9. IR (neat, cm^{-1}): 2930, 1736, 1559, 1406, 1369, 1313, 1256, 1157, 1115, 1090, 847, 808, 775. Anal. Calcd for $C_{17}H_{24}N_2O_2$: C, 70.80; H, 8.39. Found: C, 70.98; H, 8.26.

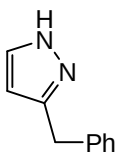
***tert*-butyl (1*Z*)-1-propyl-1-hepten-3-ynylcarbamate.** An oven-dried Schlenk tube was charged with CuI (9.60 mg, 5 mol %), *tert*-butyl carbamate (0.15 mg, 1.20 mmol) and Cs_2CO_3 (0.42 g, 1.10 mmol). The Schlenk tube was capped with a teflon screwcap and then evacuated and backfilled with argon (this sequence was carried out two times). Then *N*,*N*'-dimethylethylendiamine (11 μL, 10 mol %) and (4*Z*)-4-iodo-4-decen-6-yne (0.26 g, 1.0 mmol) were added via syringe, followed by the addition of THF (1 mL). The reaction mixture was allowed to stir at room temperature for 36 hours. The mixture was filtered through celite, concentrated to dryness and purified by column chromatography on silica gel (2.5% NEt_3), eluting with hexanes/ethyl 20:1 to afford 0.15 g of the title compound (59% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) d: 6.99 (br s, 1H), 4.50 (s, 1H), 2.54 (t, *J* = 7.6 Hz, 2H), 2.36 (t, *J* = 7.2 Hz, 2H), 1.61-1.56 (m, 4H), 1.46 (s, 9H), 0.99 (t, *J* = 7.2 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 151.6, 148.3, 96.2, 87.6, 80.1, 75.6, 34.2, 28.1, 22.2, 21.6, 21.2, 13.5, 13.4. IR (neat, cm^{-1}): 3390, 2964, 2933, 2873, 1739, 1629, 1483, 1392, 1367, 1339, 1244, 1156, 1079, 846. Anal. Calcd for $C_{15}H_{25}NO_2$: C, 71.67; H, 10.02. Found: C, 71.52; H, 10.10.

Table 2: General Procedure for the synthesis of pyrazoles through Cu-catalyzed domino amidation-hydroamidation of iodoenynes. An oven-dried Schlenk tube was charged with a magnetic stir bar, CuI (4.8 mg, 0.025 mmol, 5 mol%), di-*tert*-butyl hydrazodicarboxylate (139 mg, 0.60 mmol) and Cs_2CO_3 (244 mg, 0.75 mmol). The Schlenk tube was capped with a teflon screwcap and then evacuated and backfilled with argon (this sequence was repeated an additional time). Under a positive pressure of argon, *N*,*N*'-dimethylethylendiamine (11 μL, 0.10 mmol, 20 mol%), the iodoenyne (0.50 mmol) and dry THF (1.0 mL) were added via syringe. The tube was sealed and stirred at 80 ºC in a pre-heated oil bath for the indicated period of time. The reaction mixture was cooled to room temperature, diluted with ethyl acetate, filtered through a plug of celite eluting with additional ethyl acetate and concentrated to dryness. The resulting residue was dissolved in dry CH_2Cl_2 (2.0 mL) and trifluoroacetic acid (TFA, 385 μL, 5.00 mmol) was then added. After 2 h at room temperature, saturated $NaHCO_3$ solution (2 mL) was added. The organic layer was separated, dried ($MgSO_4$) and evaporated. The resulting residue was purified by column chromatography on silica gel eluting with hexanes/ethyl acetate mixtures.

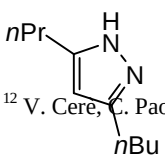
3-Hexyl-1*H*-pyrazole (Table 2, Entry 1). The general procedure was applied using CuI (4.8 mg, 0.025 mmol, 5 mol%), di-*tert*-butyl hydrazodicarboxylate (139 mg, 0.60 mmol), Cs_2CO_3 (244 mg, 0.75 mmol), *N*,*N*'-dimethylethylendiamine (11 μL, 0.10 mmol, 20 mol%) and (*Z*)-1-iodonon-1-en-3-yne (124 mg, 0.50 mmol) with THF (1.0 mL) as solvent for 9 h at 80 ºC, followed by treatment with TFA (385 μL, 5.00 mmol) in CH_2Cl_2 (2.0 mL) for 2 h at room temperature. The product was purified by column chromatography on silica gel (hexanes/ethyl acetate 2:1) to give the title compound as a yellow oil (70 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) d: 11.66 (br s, 1H), 7.53 (br s, 1H), 6.11 (br s, 1H), 2.71 (t, *J* = 7.7 Hz, 2H), 1.68 (quint, *J* = 7.4 Hz, 2H), 1.39-1.28 (m, 6H), 0.90 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 147.7, 135.0, 103.1, 31.6, 29.4, 29.0, 26.6, 22.5, 14.0. IR (neat, cm^{-1}): 3190, 2928, 2858, 1467, 936, 759. Anal. Calcd for $C_9H_{16}N_2$: C, 71.01; H, 10.59. Found: C, 70.45; H, 10.62.



3-Benzyl-1*H*-pyrazole (Table 2, Entry 2).[12] The general procedure was applied using CuI (4.8 mg, 0.025 mmol, 5 mol%), di-*tert*-butyl hydrazodicarboxylate (139 mg, 0.60 mmol), Cs_2CO_3 (244 mg, 0.75 mmol), *N*,*N*'-dimethylethylendiamine (11 μL, 0.10 mmol, 20 mol%) and 1-[(*Z*)-4-iodobut-3-en-1-ynyl]benzene (127 mg, 0.50 mmol) with THF (1.0 mL) as solvent for 9 h at 80 ºC, followed by treatment with TFA (385 μL, 5.00 mmol) in CH_2Cl_2 (2.0 mL) for 2 h at room temperature. The product was purified by column chromatography on silica gel (hexanes/ethyl acetate 1:1) to give the title compound as a white solid (73 mg, 92%). M.p. = 54-56 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) d: 7.45 (br s, 1H), 7.32 (m, 2H), 7.26 (m, 3H), 6.10 (br s, 1H), 4.05 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 147.7, 139.1, 133.4, 128.6, 128.5, 126.3, 104.3, 33.4. IR (neat, cm^{-1}): 3183, 2921, 1494, 1452, 1050, 717. Anal. Calcd for $C_{10}H_{10}N_2$: C, 75.92; H, 6.37. Found: C, 75.80; H, 6.42.



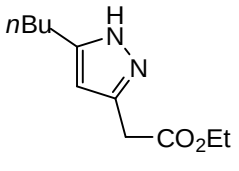
3-Butyl-5-propyl-1*H*-pyrazole (Table 2, Entry 3). The general procedure was applied using CuI (4.8 mg, 0.025 mmol, 5 mol%), di-*tert*-butyl hydrazodicarboxylate (139 mg, 0.60



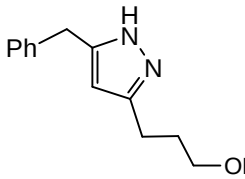
[12] V. Cere, C. Paolucci, S. Pollicino, E. Sandri, A. Fava, *J. Org. Chem.* **1998**, *53*, 5685.

mmol), Cs_2CO_3 (244 mg, 0.75 mmol), *N*,*N*'-dimethylethylendiamine (11 μL, 0.10 mmol, 20 mol%) and (*Z*)-4-iodo-4-decen-6-yne (131 mg, 0.50 mmol) with THF (1.0 mL) as solvent for 9 h at 80 ºC, followed by treatment with TFA (385 μL, 5.00 mmol) in CH_2Cl_2 (2.0 mL) for 2 h at room temperature. The product was purified by column chromatography on silica gel (hexanes/ethyl acetate 2:1) to give the title compound as a yellow oil (68 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) d: 11.13 (br s, 1H), 5.88 (br s, 1H), 2.62 (t, *J* = 8.3 Hz, 2H), 2.60 (t, *J* = 8.3 Hz, 2H), 1.72-1.59 (m, 4H), 1.43-1.34 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 149.1, 101.8, 31.6, 29.1, 26.8, 22.7, 22.4, 13.9, 13.8. IR (neat, cm^{-1}): 3192, 3103, 2958, 2873, 1580, 1465, 810.

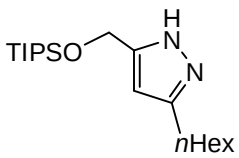
Ethyl 2-(5-butyl-1*H*-pyrazol-3-yl)acetate (Table 2, Entry 4). The general procedure was applied using CuI (4.8 mg, 0.025 mmol, 5 mol%), di-*tert*-butyl hydrazodicarboxylate (139 mg, 0.60 mmol), Cs_2CO_3 (244 mg, 0.75 mmol), *N*,*N*'-dimethylethylendiamine (11 μL, 0.10 mmol, 20 mol%) and ethyl (*Z*)-5-iodo-4-nonen-2-ynoate (153 mg, 0.50 mmol) with THF (1.0 mL) as solvent for 16 h at 80 ºC, followed by treatment with TFA (385 μL, 5.00 mmol) in CH_2Cl_2 (2.0 mL) for 2 h at room temperature. The product was purified by column chromatography on silica gel (hexanes/ethyl acetate 2:1) to give the title compound as a yellow oil (85 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) d: 9.22 (br s, 1H), 6.00 (s, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.66 (s, 2H), 2.60 (t, *J* = 7.6 Hz, 2H), 1.59 (quint, *J* = 7.6 Hz, 2H), 1.36-1.31 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.89 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 170.7, 147.2, 142.9, 103.2, 60.9, 33.7, 31.2, 25.9, 22.2, 14.0, 13.7. IR (neat, cm^{-1}): 3199, 2958, 2932, 2873, 1739, 1466, 1255, 1176, 1031. Anal. Calcd for $C_{11}H_{18}N_2O_2$: C, 62.83; H, 8.63. Found: C, 62.40; H, 8.66.



5-Benzyl-3-[3-(benzyloxy)propyl]-1*H*-pyrazole (Table 2, Entry 5). The general procedure was applied using CuI (4.8 mg, 0.025 mmol, 5 mol%), di-*tert*-butyl hydrazodicarboxylate (139 mg, 0.60 mmol), Cs_2CO_3 (244 mg, 0.75 mmol), *N*,*N*'-dimethylethylendiamine (11 μL, 0.10 mmol, 20 mol%) and [(*Z*)-7-benzyloxy-2-iodo-2-hepten-4-ynyl]benzene (201 mg, 0.50 mmol) with THF (1.0 mL) as solvent for 9 h at 80 ºC, followed by treatment with TFA (385 μL, 5.00 mmol) in CH_2Cl_2 (2.0 mL) for 2 h at room temperature. The product was purified by column chromatography on silica gel (hexanes/ethyl acetate 2:1) to give the title compound as a yellow oil (108 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) d: 7.42-7.26 (m, 10H), 5.89 (br s, 1H), 4.55 (s, 2H), 4.02 (s, 2H), 3.54 (t, *J* = 6.2 Hz, 2H), 2.76 (t, *J* = 7.4 Hz, 2H), 1.98 (quint, *J* = 6.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 148.7, 147.4, 139.3, 138.2, 128.6, 128.3, 128.2, 127.5, 127.4, 126.1, 102.9, 72.7, 69.2, 33.6, 29.1, 23.3. IR (neat, cm^{-1}): 3192, 3027, 2857, 1578, 1494, 1453, 1102, 733, 696.



3-Hexyl-5-(triisopropylsilyloxymethyl)-1*H*-pyrazole (Table 2, Entry 6). The general procedure was applied using CuI (3.3 mg, 0.017 mmol, 5 mol%), di-*tert*-butyl hydrazodicarboxylate (98 mg, 0.42 mmol), Cs_2CO_3 (171 mg, 0.53 mmol), *N*,*N*'-dimethylethylendiamine (7.5 μL, 0.07 mmol, 20 mol%) and (*Z*)-2-bromo-2-decen-4-ynyl triisopropylsilyl ether (152 mg, 0.35 mmol) with THF



(0.7 mL) as solvent for 11 h at 80 ºC, followed by treatment with TFA (270 μL, 3.50 mmol) in CH_2Cl_2 (1.5 mL) for 2 h at room temperature. The product was purified by column chromatography on silica gel (hexanes/ethyl acetate 5:1) to give the title compound as a yellow oil (90 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) d: 6.01 (s, 1H), 4.83 (s, 2H), 2.63 (t, *J* = 7.6 Hz, 2H), 1.64 (quint, *J* = 6.9 Hz, 2H), 1.37-1.28 (m, 6H), 1.21-1.07 (m, 21H), 0.89 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 101.0, 59.1, 31.6, 29.3, 28.9, 27.0, 22.6, 17.9, 14.0, 11.9. IR (neat, cm^{-1}): 3195, 2941, 2866, 1464, 1100, 882, 807, 682. Anal. Calcd for $C_{19}H_{38}N_2OSi$: C, 67.40; H, 11.31. Found: C, 67.14; H, 11.34.

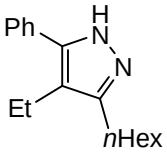
3-(4-Chlorobutyl)-1,4,5,6-tetrahydrocyclopenta[c]pyrazole (Table 2, Entry 7). The general procedure was applied using CuI (4.8 mg, 0.025 mmol, 5 mol%), di-*tert*-butyl hydrazodicarboxylate (139 mg, 0.60 mmol), Cs_2CO_3 (244 mg, 0.75 mmol), *N*,*N*'-dimethylethylendiamine (11 μL, 0.10 mmol, 20 mol%) and 1-iodo-2-(5-chloropent-1-ynyl)cyclopent-1ene (147 mg, 0.50 mmol) with THF (1.0 mL) as solvent for 13 h at 80 ºC, followed by treatment with TFA (385 μL, 5.00 mmol) in CH_2Cl_2 (2.0 mL) for 2 h at room temperature. The product was purified by column chromatography on silica gel (hexanes/ethyl acetate 2:1) to give the title compound as a pale yellow solid (94 mg, 95%). M. p. = 42-44 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) d: 3.56 (t, *J* = 6.1 Hz, 2H), 2.70 (t, *J* = 7.0 Hz, 2H), 2.64 (t, *J* = 7.0 Hz, 2H), 2.59 (t, *J* = 6.8 Hz, 2H), 2.44 (quint, *J* = 7.9 Hz, 2H), 1.81 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 160.0, 137.9, 122.4, 44.7, 31.9, 30.4, 25.8, 25.1, 24.3, 22.7. IR (neat, cm^{-1}): 3153, 3082, 2927, 2854, 1602, 1445, 1057. Anal. Calcd for $C_{10}H_{15}ClN_2$: C, 60.45; H, 7.61. Found: C, 60.08; H, 7.61.

3-Benzyl-1,4,5,6-tetrahydrocyclopenta[c]pyrazole (Table 2, Entry 8). The general procedure was applied using CuI (4.8 mg, 0.025 mmol, 5 mol%), di-*tert*-butyl hydrazodicarboxylate (139 mg, 0.60 mmol), Cs_2CO_3 (244 mg, 0.75 mmol), *N*,*N*'-dimethylethylendiamine (11 μL, 0.10 mmol, 20 mol%) and 1[2-(2-iodocyclopent-1-enyl]benzene (147 mg, 0.50 mmol) with THF (1.0 mL) as solvent for 6 h at 80 ºC, followed by treatment with TFA (385 μL, 5.00 mmol) in CH_2Cl_2 (2.0 mL) for 2 h at room temperature. The product was purified by column chromatography on silica gel (hexanes/ethyl acetate 1:1) to give the title compound as a white solid (87 mg, 88%). M. p. = 76-78 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) d: 11.19 (br s, 1H), 7.19-7.09 (m, 5H), 3.83 (s, 2H), 2.55 (br s, 2H), 2.23 (br s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 159.6, 138.3, 137.2, 128.6, 128.4, 126.3, 123.0, 32.2, 30.3, 24.2, 22.4. IR (neat, cm^{-1}): 3153, 3083, 2918, 2853, 1600, 1494, 1452, 1055, 745, 700.

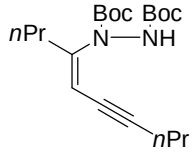
5-Butyl-4-ethyl-3-nonyl-1*H*-pyrazole (Table 2, Entry 9). The general procedure was applied using CuI (4.8 mg, 0.025 mmol, 5 mol%), di-*tert*-butyl hydrazodicarboxylate (139 mg, 0.60 mmol), Cs_2CO_3 (244 mg, 0.75 mmol), *trans*-1,2-cyclohexanediamine (12 μL, 0.10 mmol, 20 mol%) and (*Z*)-6-ethyl-5-iodo-5-hexadecen-7-yne (187 mg, 0.50 mmol) with THF (1.0 mL) as solvent for 14 h at 80 ºC, followed by treatment with TFA (385 μL, 5.00 mmol) in CH_2Cl_2 (2.0 mL) for 2 h at room temperature. The product was purified by column chromatography on silica gel (hexanes/ethyl acetate 4:1) to give the title compound as a white solid (88 mg, 63%). M. p. = 41-43

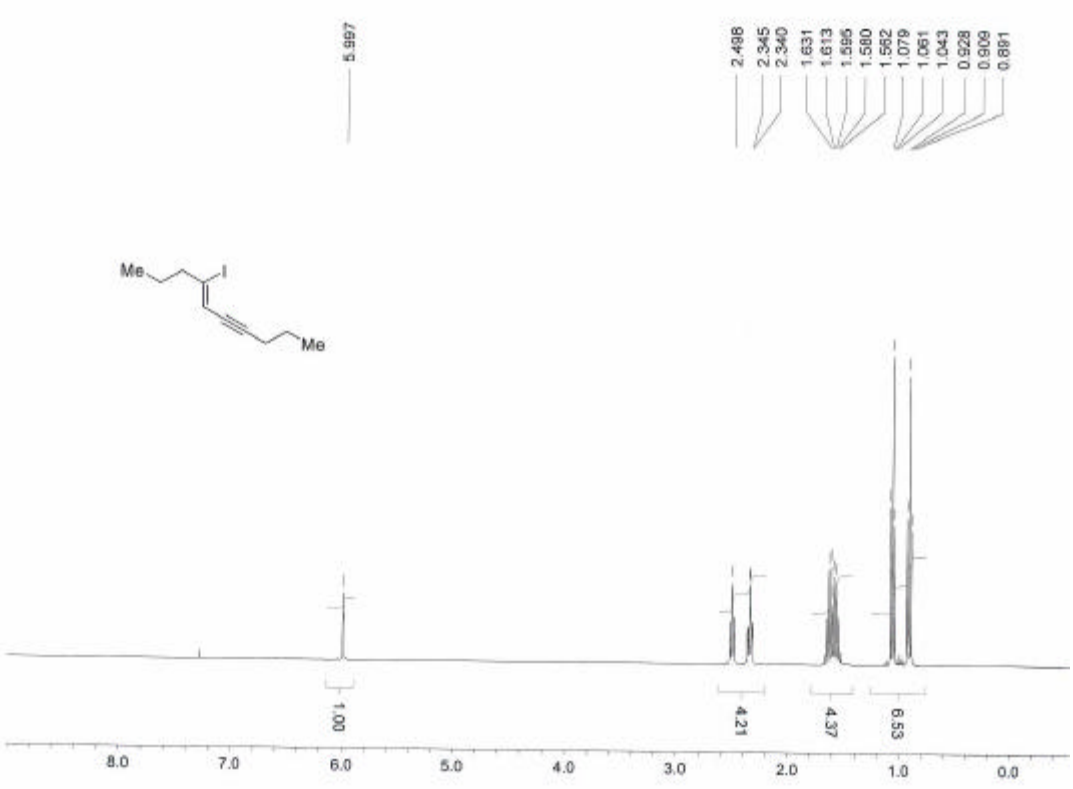
ºC. ^{1}H NMR (400 MHz, $CDCl_3$) d: 2.59-2.54 (m, 4H), 2.38 (q, *J* = 7.5 Hz, 2H), 1.66-1.60 (m, 4H), 1.42-1.27 (m, 15H), 1.09 (t, *J* = 7.5 Hz, 3H), 0.95 (t, *J* = 7.3 Hz, 3H), 0.89 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 146.1, 116.4, 31.9, 31.5, 29.6, 29.5, 29.4, 29.3, 25.7, 25.4, 22.6, 16.2, 15.8, 14.0, 13.9. IR (neat, cm^{-1}): 3193, 2959, 2926, 2856, 1465.

4-Ethyl-3-hexyl-5-phenyl-1*H*-pyrazole (Table 2, Entry 10). The general procedure was applied using CuI (4.8 mg, 0.025 mmol, 5 mol%), di-*tert*-butyl hydrazodicarboxylate (139 mg, 0.60 mmol), Cs_2CO_3 (244 mg, 0.75 mmol), *N*,*N*'-dimethylethylendiamine (11 μL, 0.10 mmol, 20 mol%) and [(*Z*)-2-ethyl-1-iodo-1-nonen-3-ynyl]benzene (176 mg, 0.50 mmol) with THF (1.0 mL) as solvent for 14 h at 80 ºC, followed by treatment with TFA (385 μL, 5.00 mmol) in CH_2Cl_2 (2.0 mL) for 2 h at room temperature. The product was purified by column chromatography on silica gel (hexanes/ethyl acetate 4:1) to give the title compound as a yellow oil (92 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) d: 7.57 (d, *J* = 7.3 Hz, 2H), 7.39 (t, *J* = 7.0 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 2.62-2.53 (m, 4H), 1.62-1.58 (m, 2H), 1.34-1.29 (m, 6H), 1.13 (t, *J* = 7.5 Hz, 3H), 0.90 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 146.0, 133.1, 128.4, 127.6, 127.4, 116.7, 31.6, 29.4, 29.2, 25.4, 22.6, 16.5, 15.7, 14.0. IR (neat, cm^{-1}): 3118, 3057, 2929, 1497, 1463, 697. Anal. Calcd for $C_{17}H_{24}N_2$: C, 79.64; H, 9.44. Found: C, 79.37; H, 9.51.



Di-*tert*-butyl [(*Z*)-1-propyl-1-hepten-3-ynyl]hydrazine-*N*,*N*'-dicarboxilate. An oven-dried Schlenk tube was charged with a magnetic stir bar, CuI (4.8 mg, 0.025 mmol, 5 mol%), di-*tert*-butyl hydrazodicarboxylate (139 mg, 0.60 mmol) and Cs_2CO_3 (163 mg, 0.50 mmol). The Schlenk tube was capped with a teflon screwcap and then evacuated and backfilled with argon (this sequence was repeated an additional time). Under a positive pressure of argon, *N*,*N*'-dimethylethylendiamine (11 μL, 0.10 mmol, 20 mol%), (*Z*)-4-iodo-4-decen-6-yne (131 mg, 0.50 mmol) and dry THF (1.0 mL) were added via syringe. The tube was sealed and stirred at 80 ºC in a pre-heated oil bath for 36 h (65% conversion). The reaction mixture was cooled to room temperature, diluted with ethyl acetate, filtered through a plug of celite eluting with additional ethyl acetate and concentrated to dryness. The crude material was purified by column chromatography on silica gel (hexanes/ethyl acetate 20:1) to afford the title compound as a colorless oil (88 mg, 48%). ^{1}H NMR (400 MHz, $CDCl_3$) d: 6.78-5.35 (br s, 1H), 5.23 (s, 1H), 2.28-2.24 (m, 4H), 1.56-1.50 (m, 4H), 1.44 (s, 18H), 0.95 (t, *J* = 7.3 Hz, 3H), 0.89 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) d: 154.7, 153.2, 151.3, 105.1, 95.5, 81.4, 80.9, 76.1, 35.8, 28.0, 27.9, 22.0, 21.5, 20.3, 13.5, 13.4. IR (neat, cm^{-1}): 3263, 2967, 2933, 2873, 1725, 1458, 1367, 1242, 1157.

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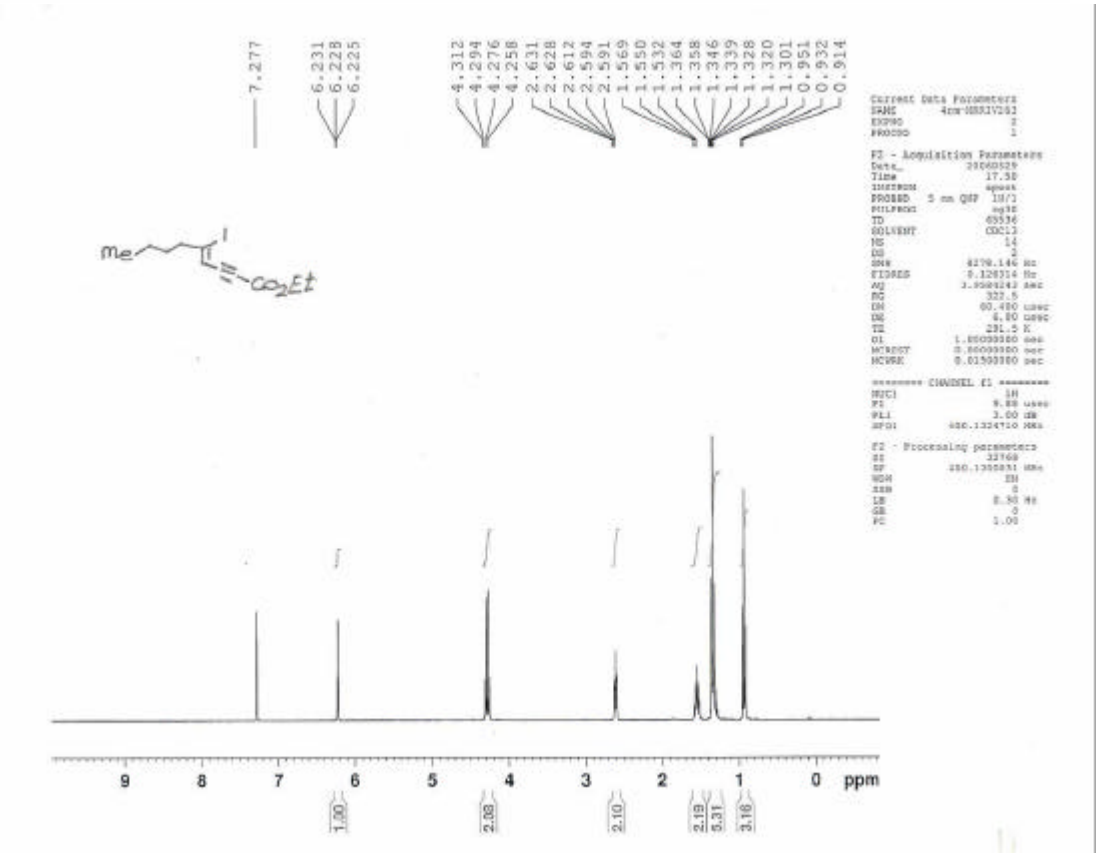
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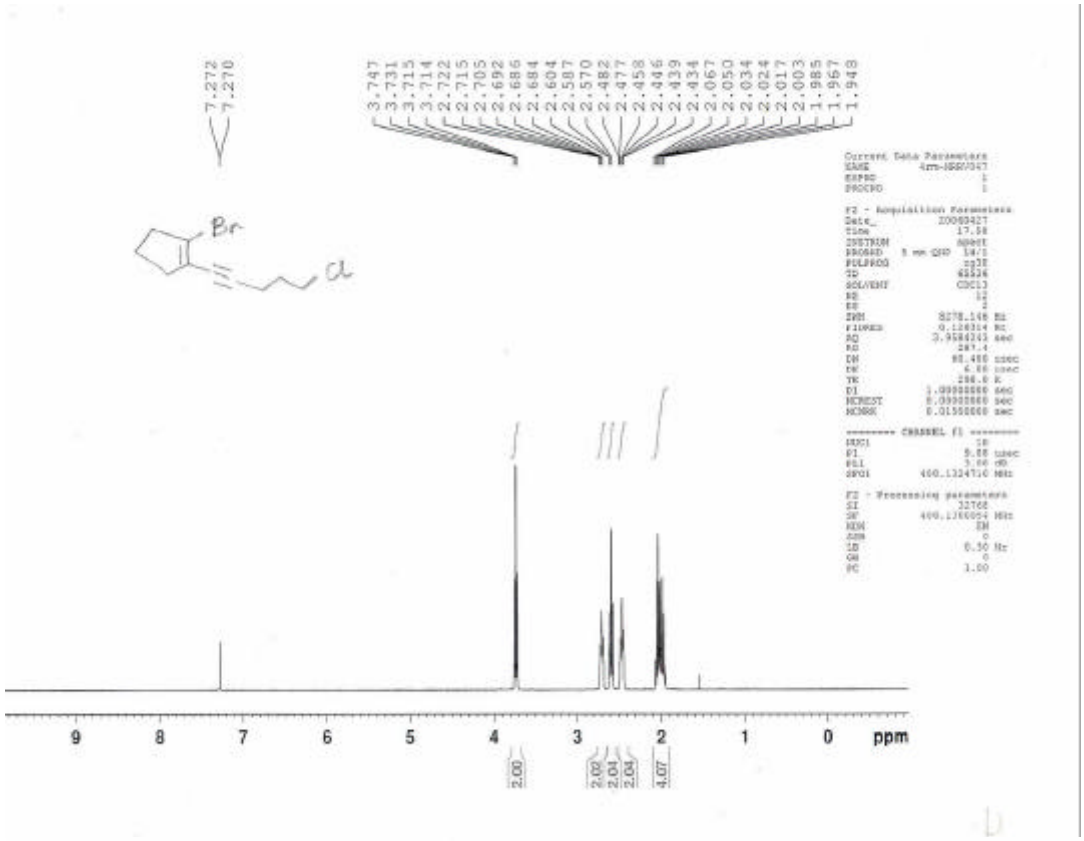
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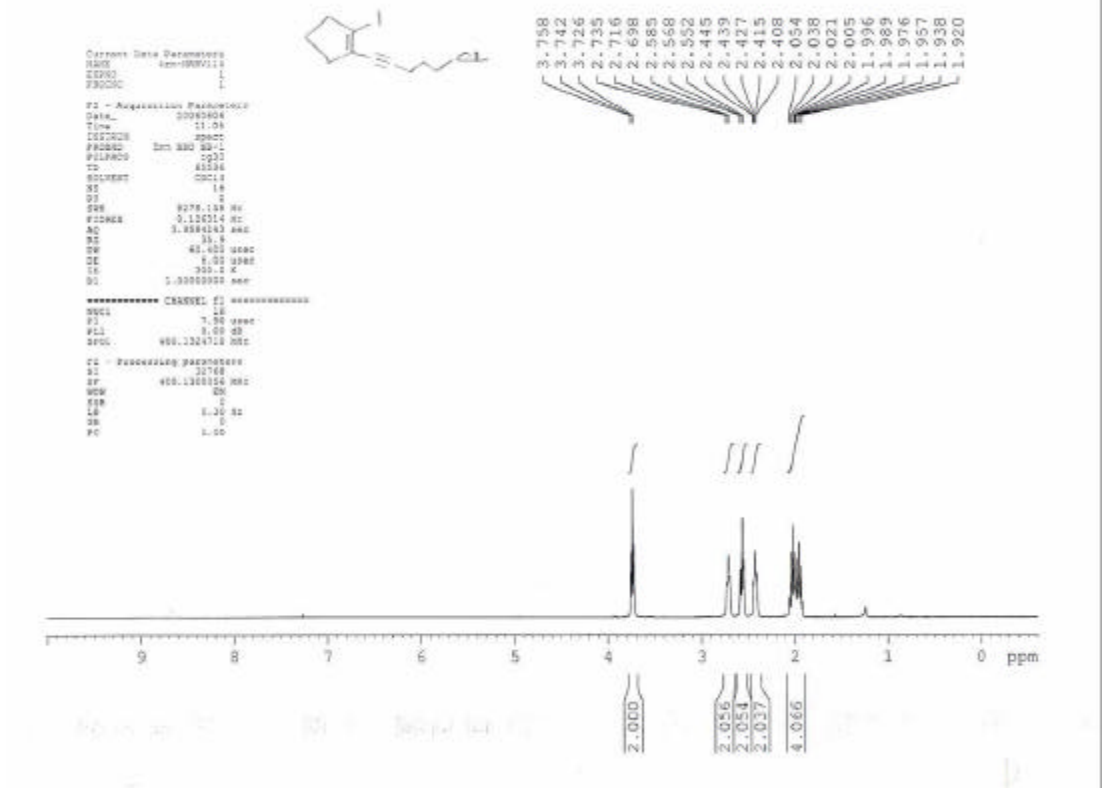
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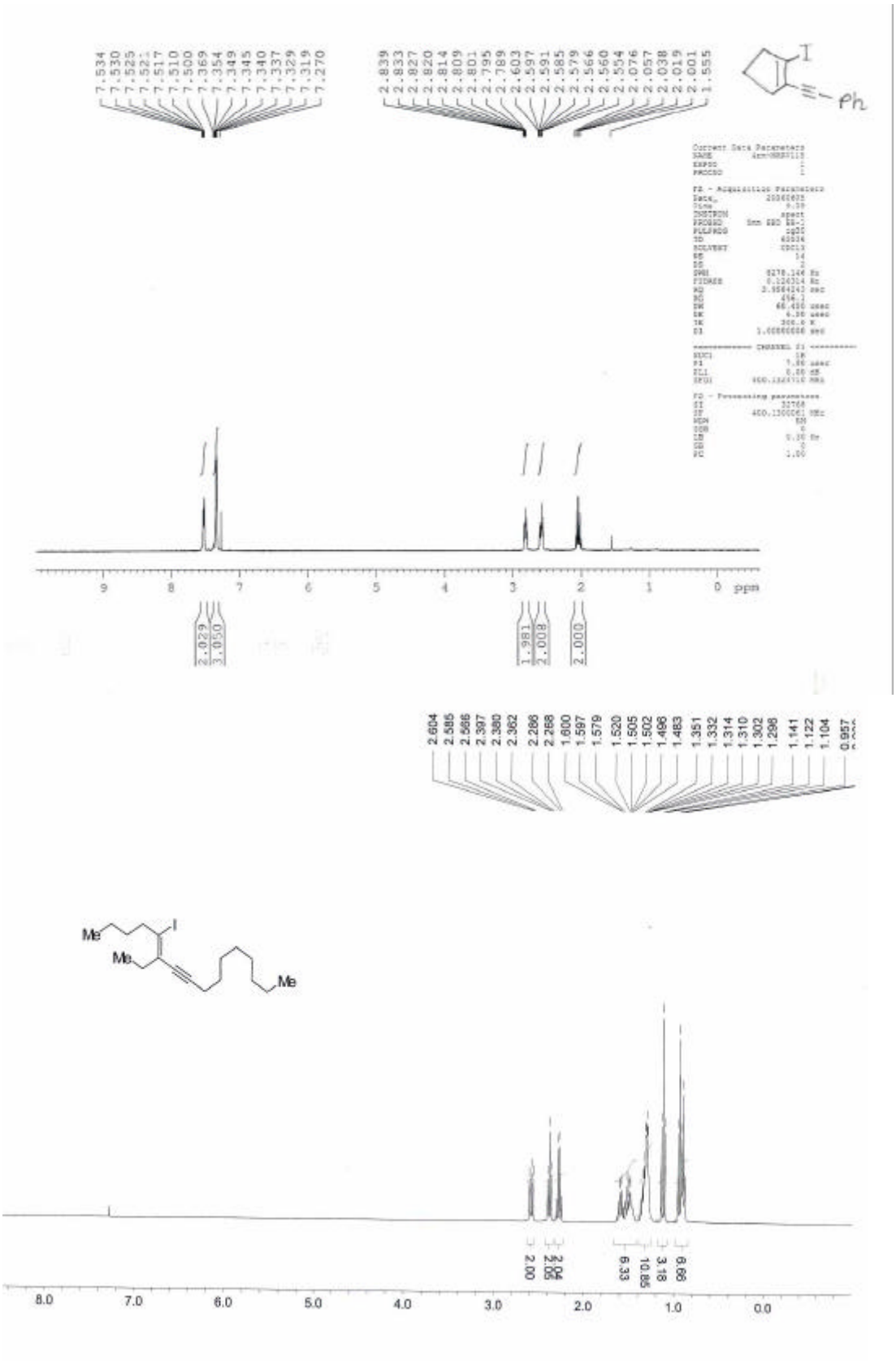
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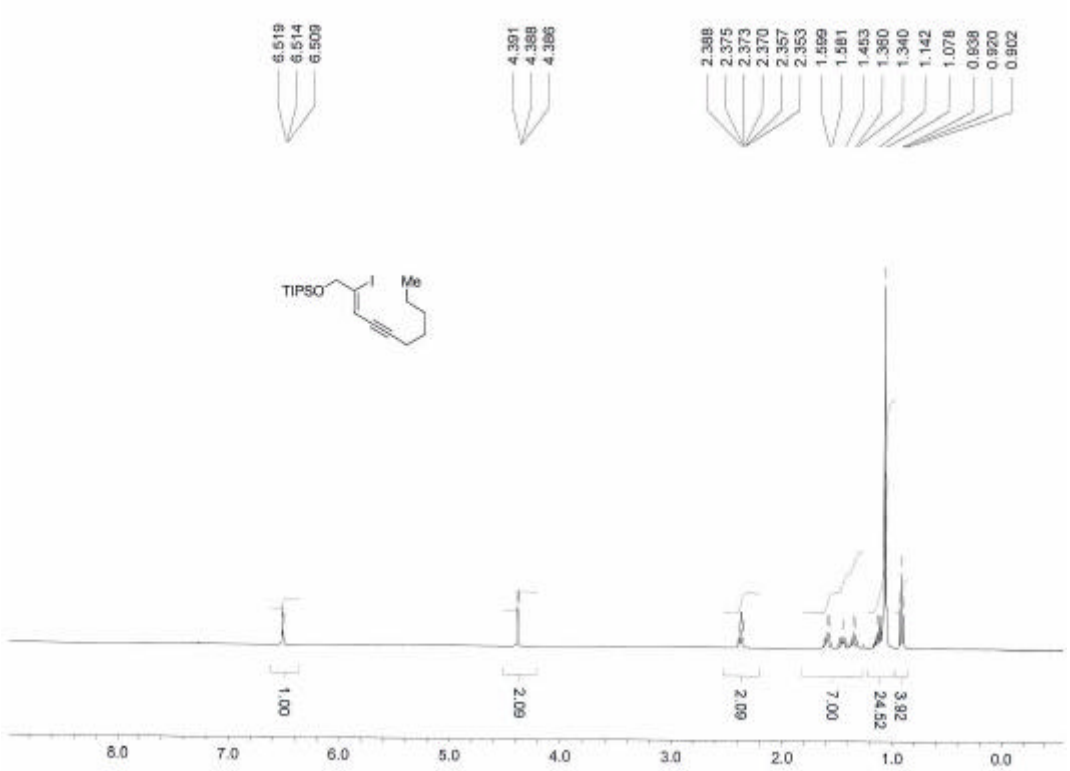
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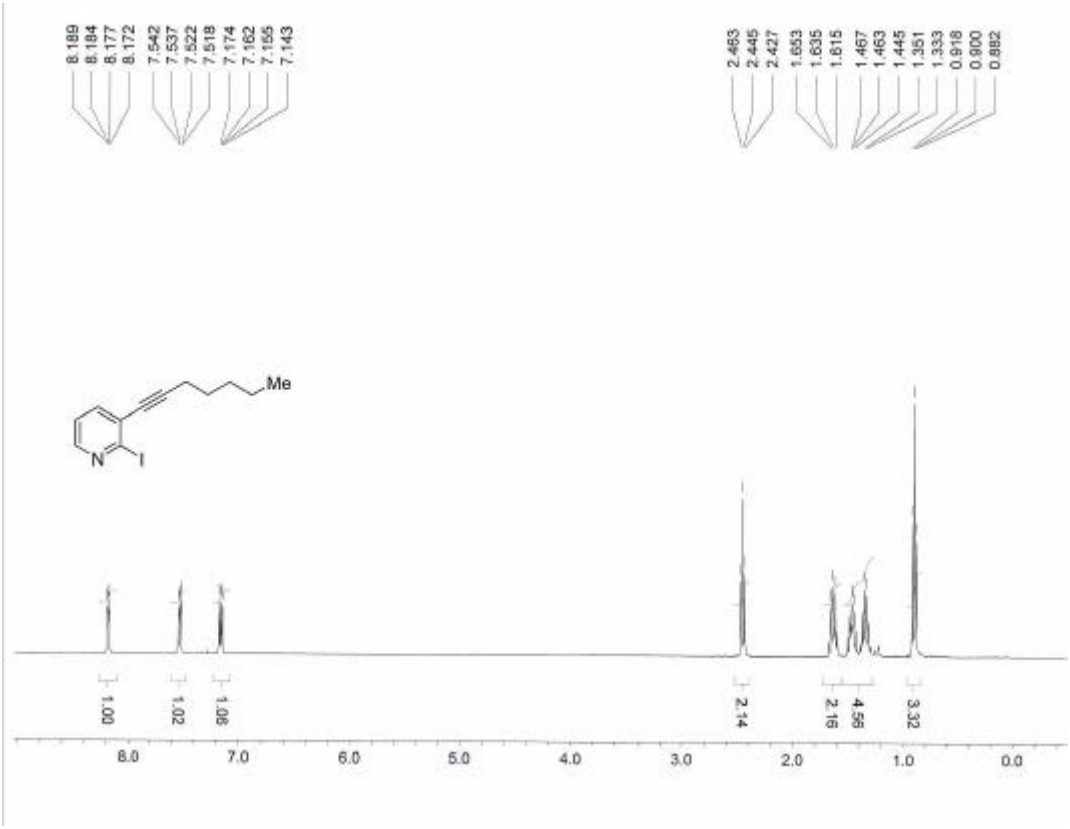
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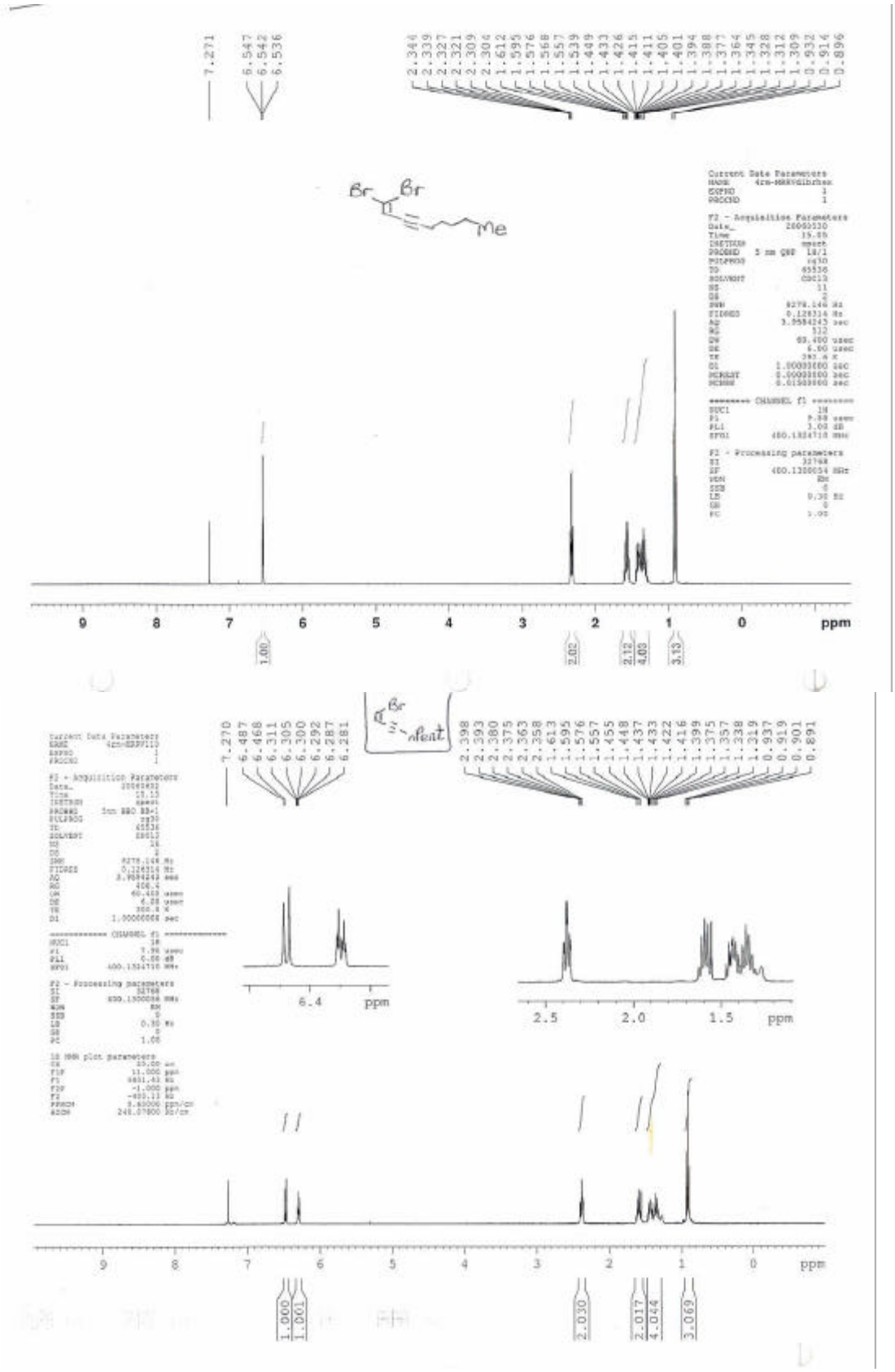
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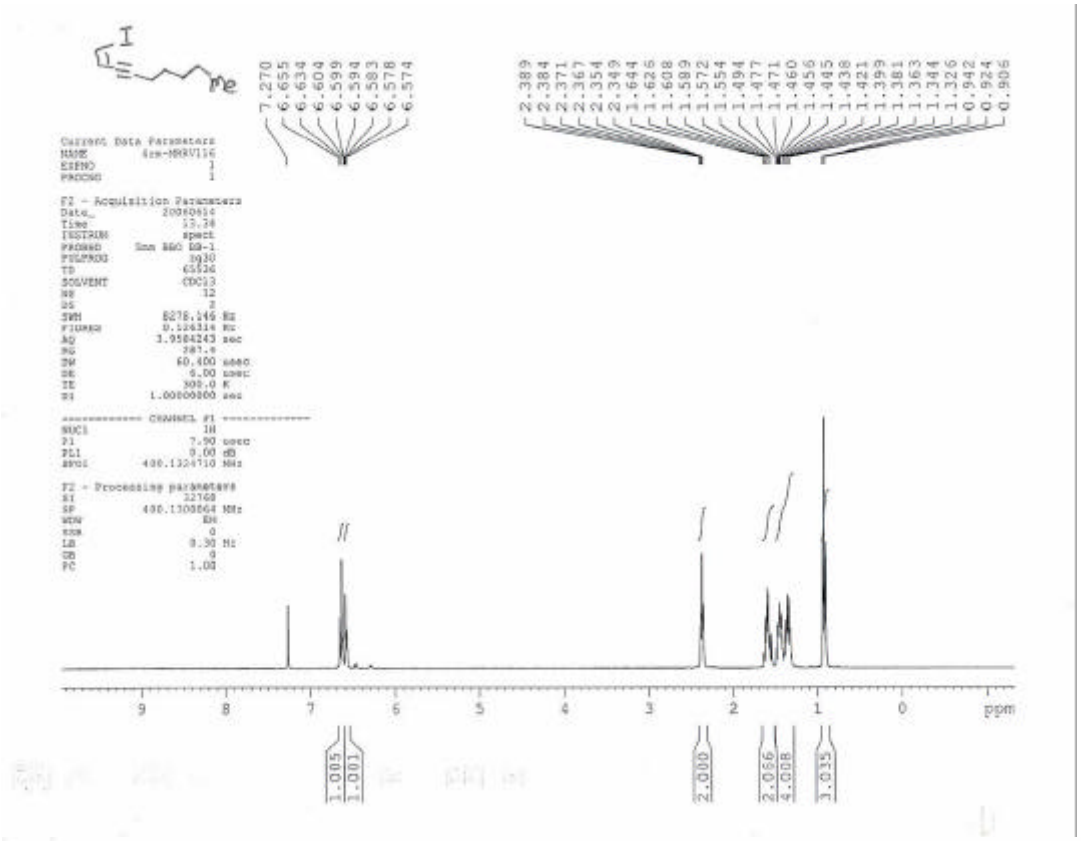
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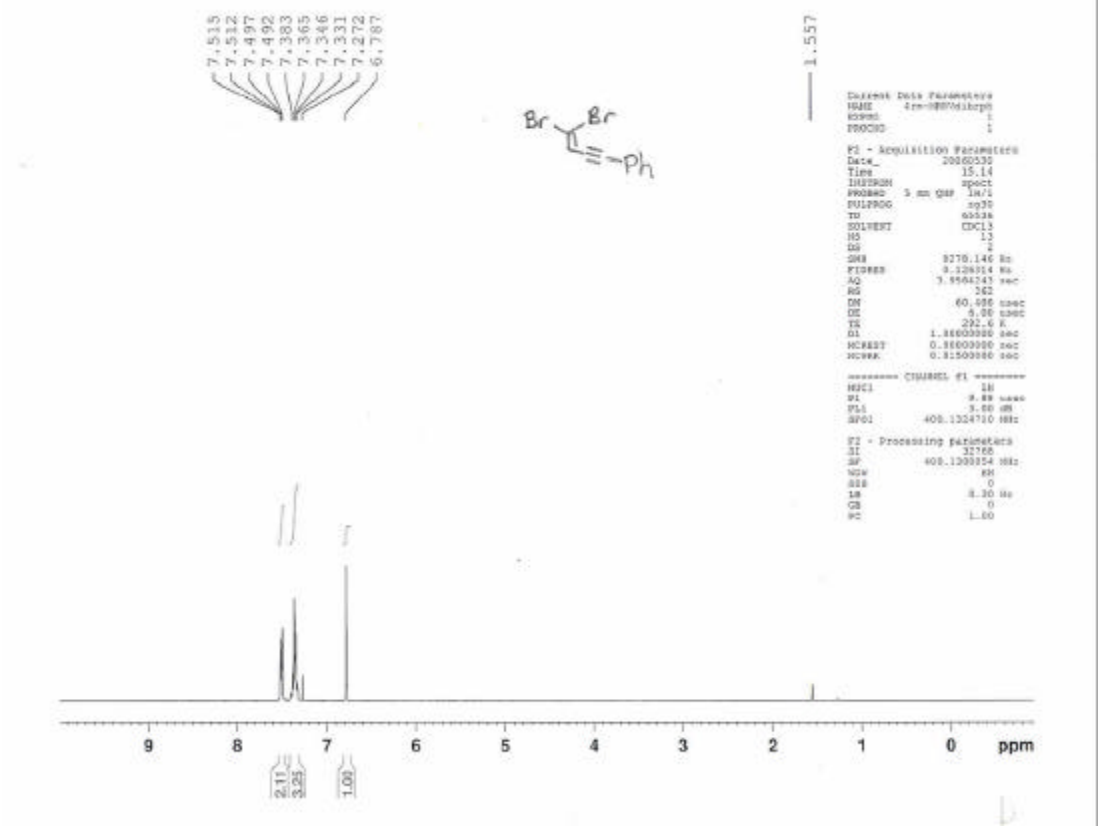
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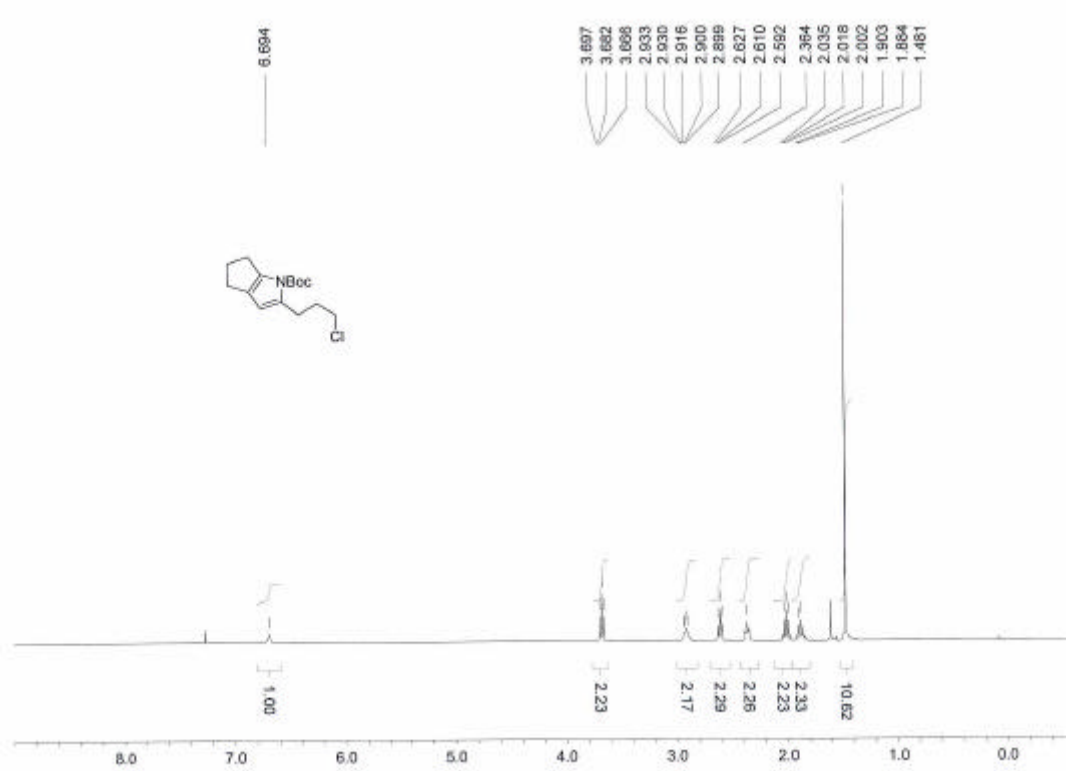
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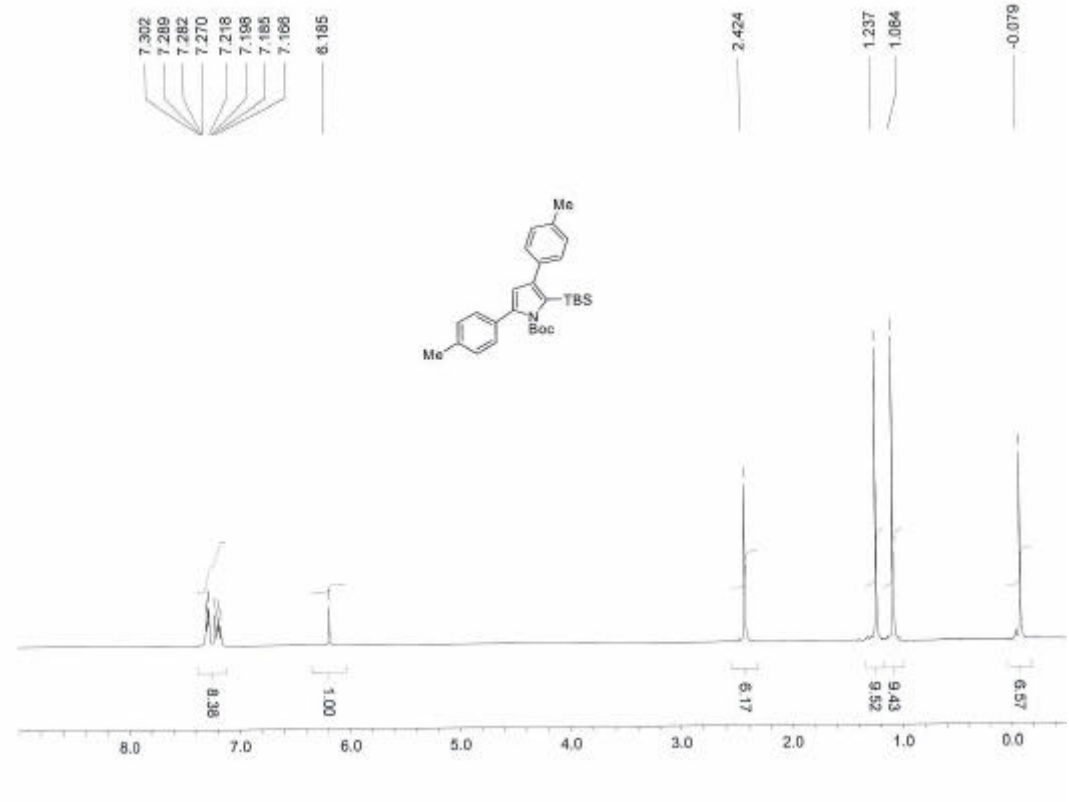
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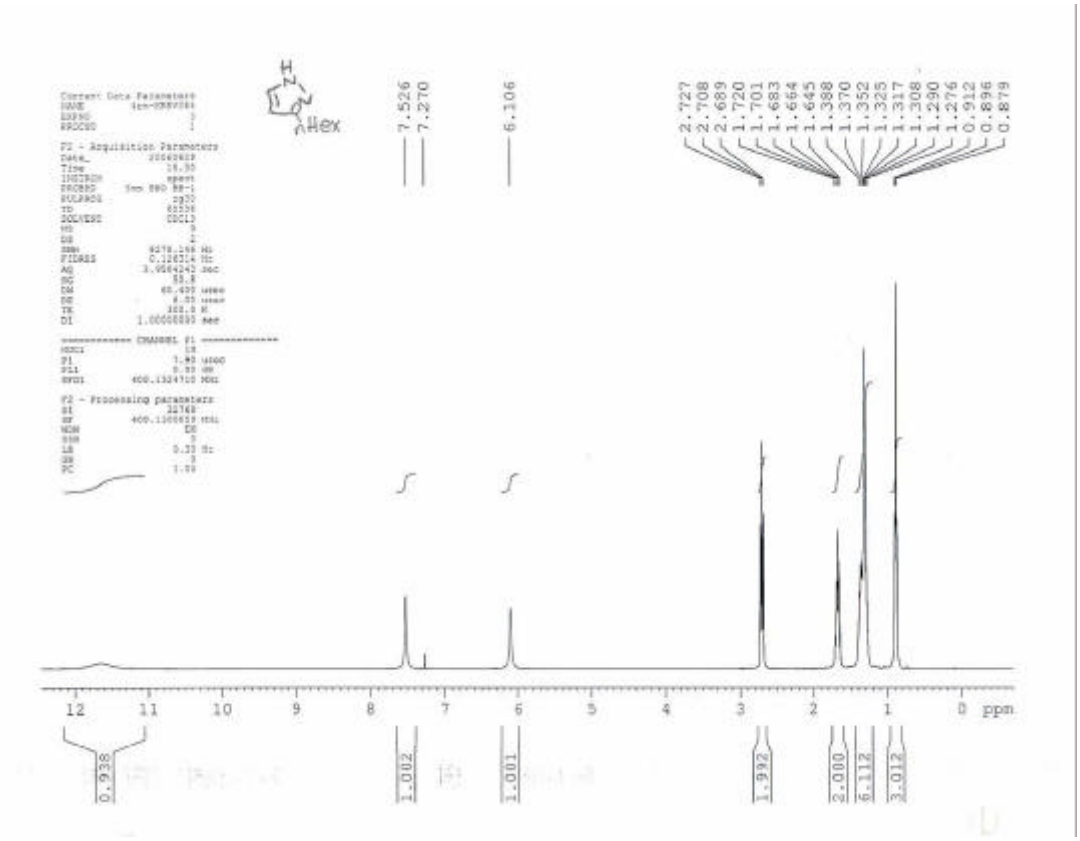
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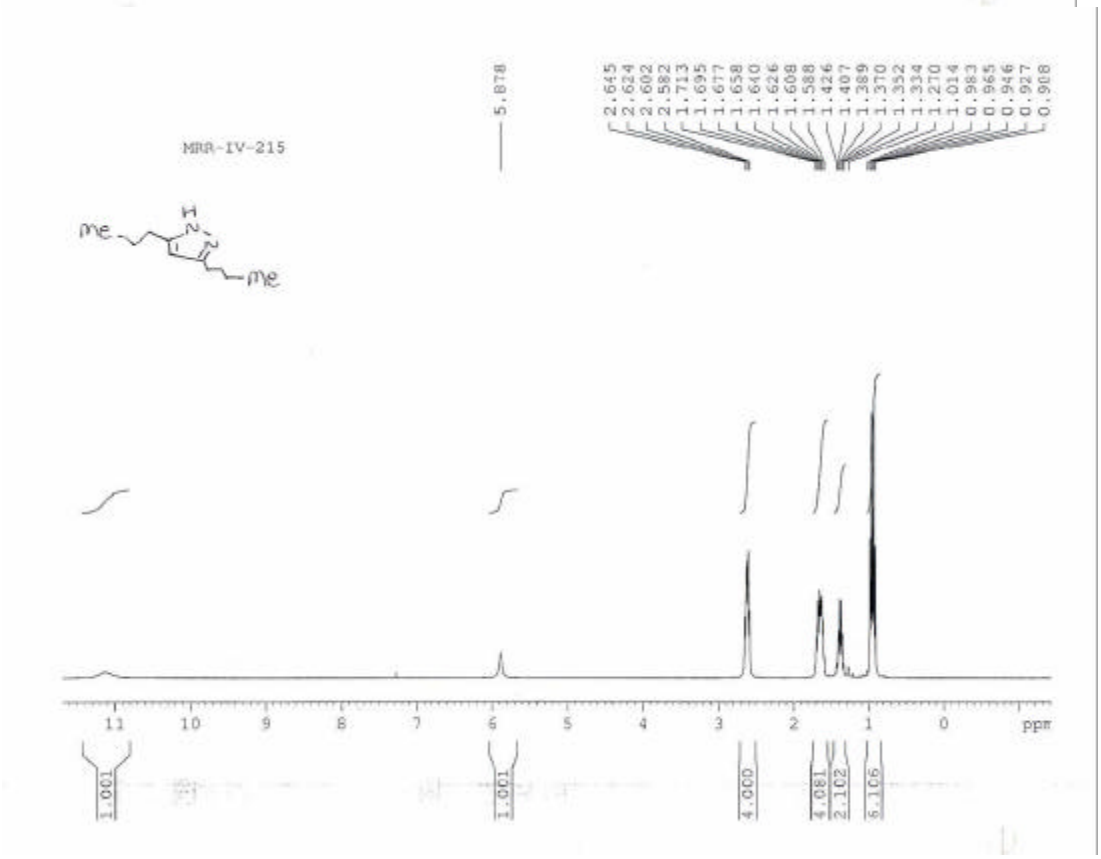
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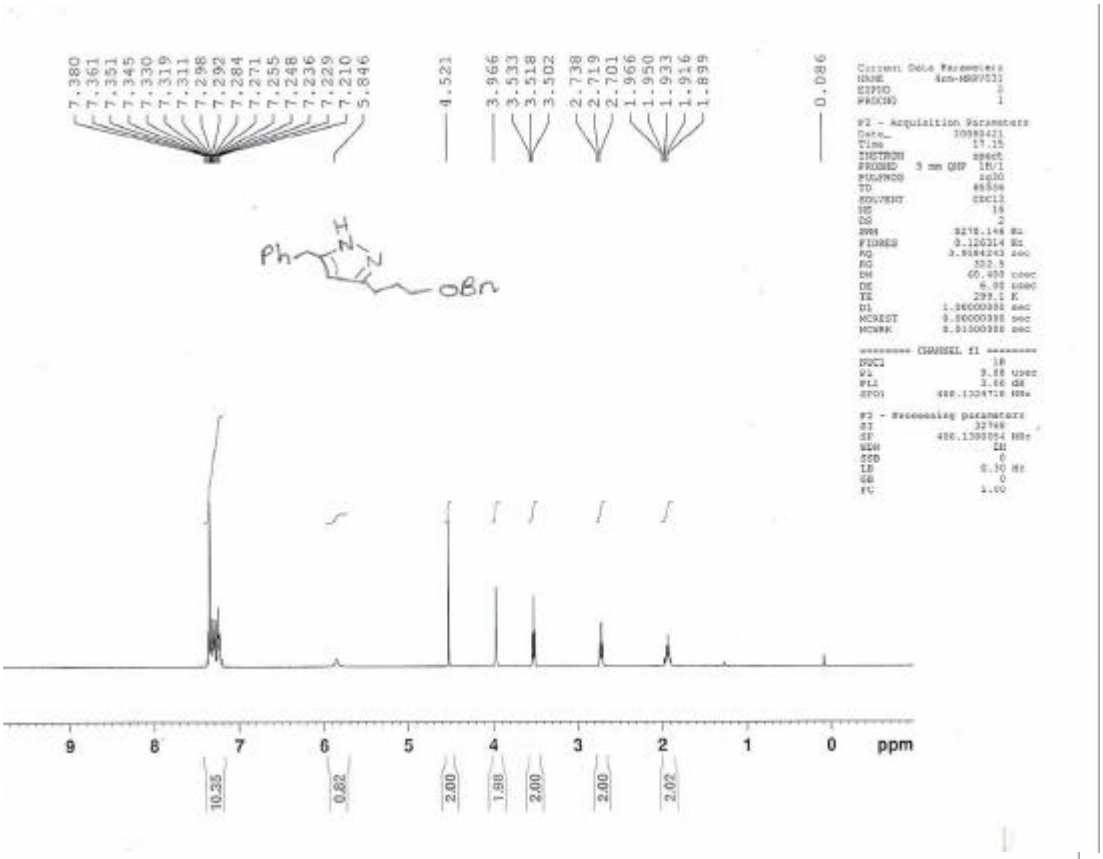
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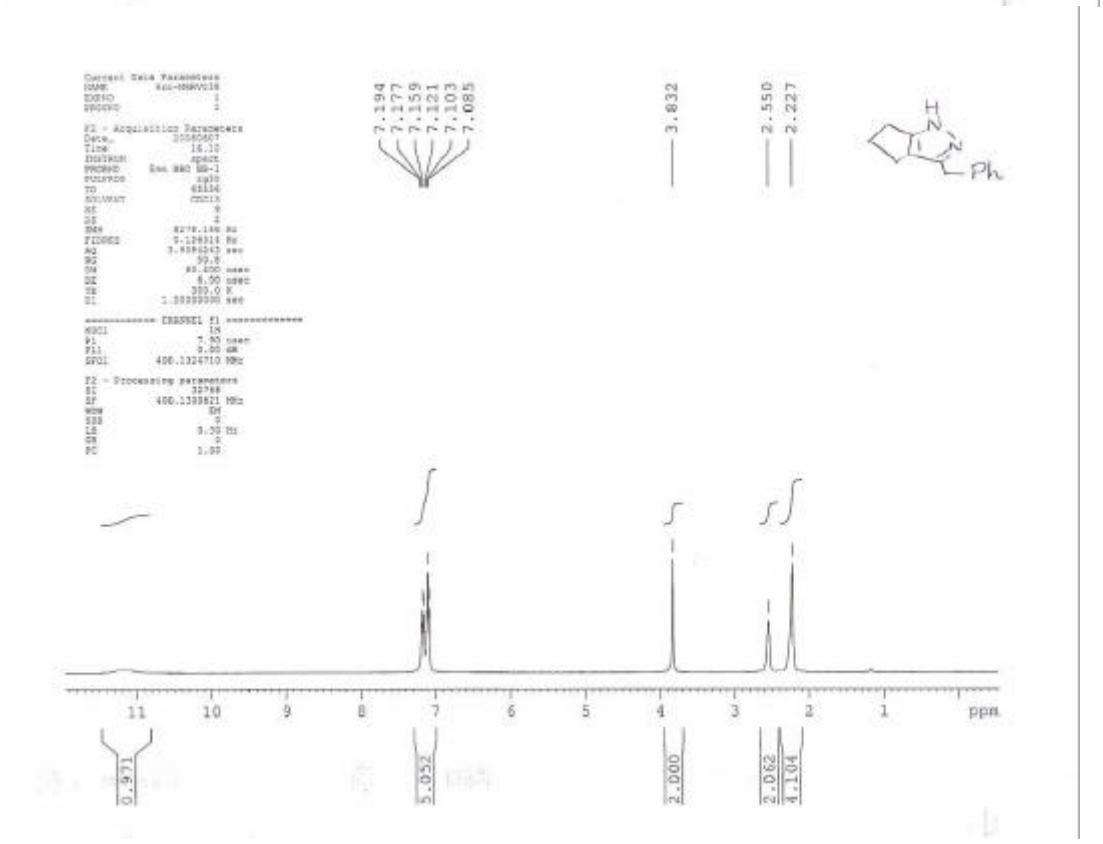
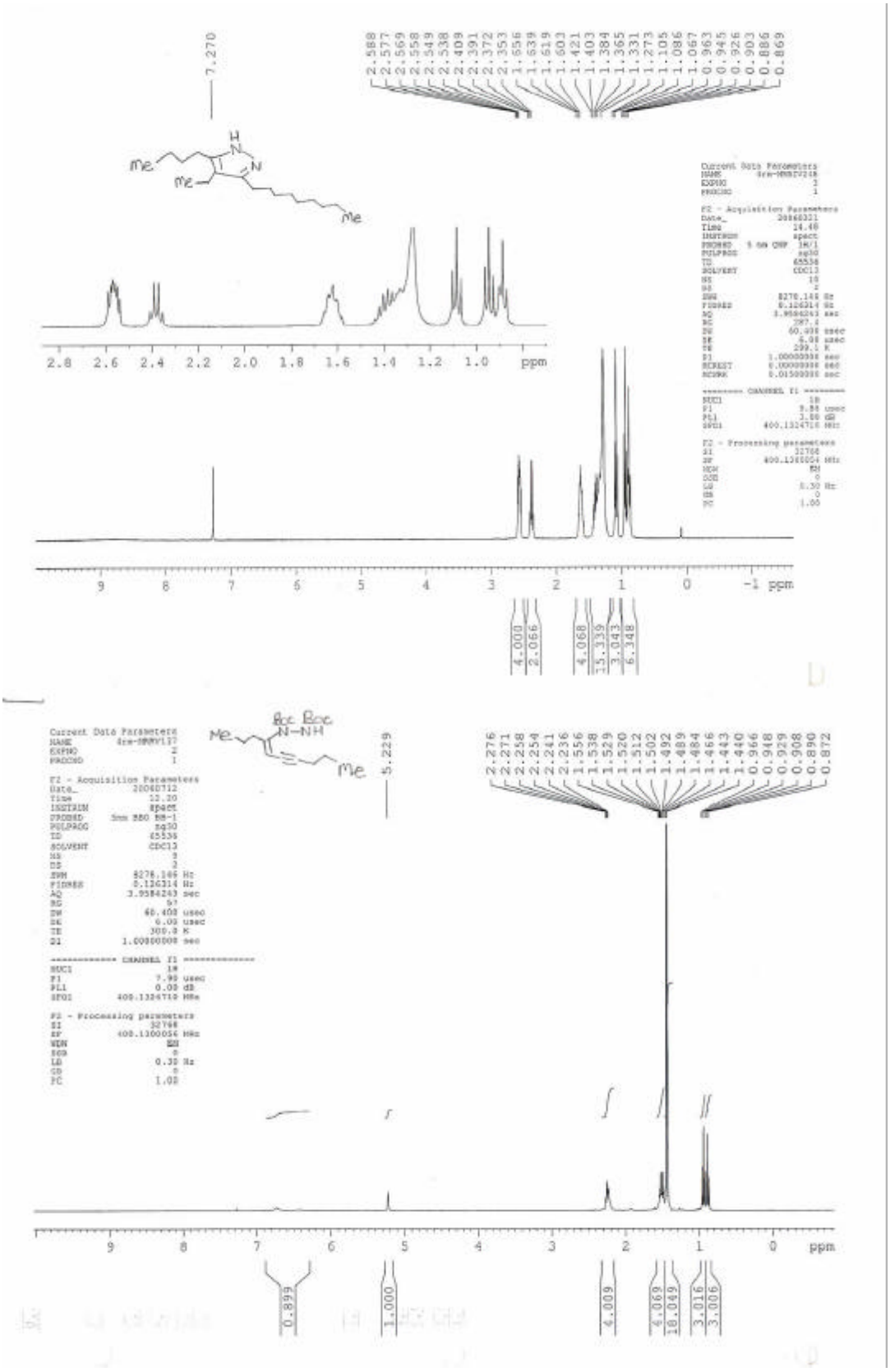

7.194
7.177
7.159
7.121
7.103
7.085
3.832
2.550
2.227
Ph
11
10
9
8
7
6
5
4
3
2
1
ppm
0.971
5.052
2.000
2.062
4.104


7.270
2.588
2.577
2.569
2.558
2.549
2.538
2.409
2.391
2.372
2.353
1.656
1.639
1.619
1.603
1.421
1.403
1.384
1.365
1.331
1.273
1.105
1.086
1.067
0.963
0.945
0.926
0.903
0.886
0.869
Me
Me
Me
2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 ppm
9 8 7 6 5 4 3 2 1 0 -1 ppm
4.000
2.066
4.068
15.339
3.043
6.348
Boc Boc
N–N-H
Me
Me
5.229
2.276
2.271
2.258
2.254
2.241
2.236
1.556
1.538
1.529
1.520
1.512
1.502
1.492
1.489
1.484
1.466
1.443
1.440
0.966
0.948
0.929
0.908
0.890
0.872
9 8 7 6 5 4 3 2 1 0 ppm
0.899
1.000
4.009
4.069
10.049
3.016
3.006