Copper-Catalyzed Vinylation of Hydrazides. A Regioselective Entry to Highly-Substituted Pyrroles.

*Marta Rodríguez Rivero and Stephen L. Buchwald**
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139

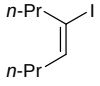
Supporting Information

Reagents: All reactions were carried out under an argon atmosphere. Anhydrous DMF and 1,10-phenanthroline were purchased from Aldrich and used without further purification. Copper (I) iodide was purchased from Strem chemicals. Anhydrous cesium carbonate was a gift from Chemetall (the batch used had a median particle size of 10-20 μm); the bulk of this reagent was stored in a nitrogen-atmosphere glovebox. Small portions (2-4 g) were removed from the glovebox in capped glass vials and stored in a dessicator for up to one month. Commercially available materials were used without further purification.

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. NMR spectra were recorded using a Bruker DRX 400 instrument. All ^{1}H NMR chemical shifts were reported in parts per million (ppm) relative to the residual protonated solvent peak (7.27 ppm for $CDCl_3$). Proton-decoupled ^{13}C NMR chemical shifts were reported relative to the solvent peak (77.0 ppm for $CDCl_3$). 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. Melting points were obtained on a Mel-Temp capillary melting point apparatus. Gas chromatographic analyses were performed 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 of compounds estimated to be ≥ 95% pure as determined by ^{1}H NMR and/or combustion analysis and are the average of two runs. The procedures described in this section are representative. Thus, the yields may differ slightly from those given in Tables 1 and 2. In cases where significant discoloration of the vinyl iodide was observed, passage through a short plug of basic alumina was employed.

Synthesis of vinyl iodides.

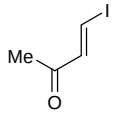
(*E*)-4-Iodo-4-octene.



DIBAL (1.0 M in hexanes, 100.0 mL, 100.0 mmol) was slowly added to a flask containing neat 4-octyne (14.7 mL, 100.0 mmol) at 0 ºC. The resulting solution was then heated at 50 ºC for 3 h. After

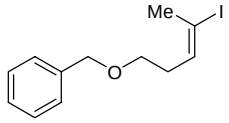
that time, the mixture was cooled to -78 ºC and a solution of I_2 (25.4 g, 100.0 mmol) in dry THF (160 mL) was slowly added. The solution was allowed to gradually warm up to room temperature. After stirring at room temperature for 1 h, the mixture was treated, slowly and at 0 ºC, with saturated aqueous $Na_2S_2O_3$ solution and then with 10% HCl. After extraction with EtOAc, the combined organic layers were dried ($MgSO_4$) and concentrated. The crude product was purified by silica gel column chromatography (hexanes) to afford the title compound (12.0 g, 50%) as a colorless oil. NMR spectral data were consistent with those reported.[1]

(*E*)-4-Iodo-3-buten-2-one.



A mixture of LiI (1.76 g, 13.15 mmol) and 3-butyn-2-one (0.85 mL, 10.96 mmol) in AcOH (11.00 mL) was stirred overnight at room temperature. After that time, water (10 mL) was added and the mixture was extracted with diethyl ether (15 mL x 3). The combined organic layers were dried ($MgSO_4$) and evaporated. The resulting residue was purified by silica gel column chromatography (hexanes:ethyl acetate 10:1) to afford the title compound as a white solid (1.28 g, 60%). After purification, this compound was used in the next step due to its instability. M.p. = 56-57 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77 (d, *J* = 15.1 Hz, 1H), 7.07 (d, *J* = 15.1 Hz, 1H), 2.18 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 194.9, 145.2, 99.6, 26.8. IR (neat, cm^{-1}): 3052, 1651, 1260, 1023, 959.

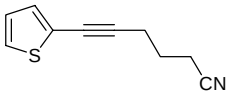
1-(((*E*)-4-Iodopent-3-enyloxy)methyl)benzene.



A solution of (*E*)-4-iodopent-3-en-1-ol[2] (1.00 g, 4.72 mmol) in anhydrous DMF (15 mL) was added to a suspension of NaH (60%, 226 mg, 5.66 mmol) in DMF (15 mL) at 0 °C. After 30 min at room temperature, benzyl bromide (0.84 mL, 7.07 mmol) was added and the mixture stirred at 80 °C for 8 h. After that time, water (20 mL) was added and the mixture was extracted with diethyl ether (20 mL x 3). The combined organic layers were dried ($MgSO_4$) and evaporated. The resulting residue was purified by silica gel column chromatography (hexanes:ethyl acetate 20:1) to afford the title compound as a pale yellow oil (1.28 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39-7.28 (m, 5H), 6.21 (m, 1H), 4.52 (s, 2H), 3.49 (t, *J* = 6.7 Hz, 2H), 2.39 (d, *J* = 0.8 Hz, 3H), 2.35 (q, *J* = 7.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 138.1, 137.3, 128.2, 127.6, 127.4, 95.2, 72.8, 68.5, 31.0, 27.5. IR (neat, cm^{-1}): 3029, 2855, 1453, 1361, 1099, 735, 697.

(1) Kropp, P. J.; Crawford, S. D. *J. Org. Chem.* **1994**, *59*, 3102.
(2) Commeiras, L.; Santelli, M.; Parrain, J.-L. *Org. Lett.* **2001**, *3*, 1713.

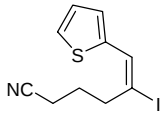
6-(Thiophen-2-yl)hex-5-ynenitrile.



An oven-dried flask was charged with CuI (118 mg, 0.62 mmol, 5 mol%) and *trans*-dichlorobis(triphenylphosphine)palladium (II) (173 mg, 0.25 mmol, 2 mol%). The mixture was evacuated and flushed with argon (twice) at room temperature. Then, anhydrous THF (50 mL), 2-iodothiphene (1.50 mL, 13.58 mmol), 5-hexynenitrile (1.30 mL, 12.35 mmol) and piperidine (9.20 mL, 92.63 mmol) were sequentially added via syringe. The mixture was stirred at 50 ºC overnight and then quenched by addition of saturated aqueous NH_4Cl solution (40 mL). After extraction with EtOAc (25 mL x 3), the combined organic layers were dried ($MgSO_4$) and concentrated. The crude product was purified by silica gel column chromatography (hexanes:ethyl acetate 10:1) to give the title compound (2.06 g, 95%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.22 (dd, *J* = 5.1, 0.8 Hz, 1H), 7.15 (d, *J* = 3.3 Hz, 1H), 6.96 (dd, *J* = 5.1, 3.6 Hz, 1H), 2.63 (t, *J* = 6.7 Hz, 2H), 2.56 (t, *J* = 7.2 Hz, 2H), 1.97 (quint, *J* = 7.0 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 131.2, 126.6, 126.2, 122.8, 118.8, 91.0, 75.0, 24.0, 18.3, 15.8. IR (neat, cm^{-1}): 3106, 2941, 2248, 1427, 1192, 847, 704. Anal. Calcd for $C_{10}H_9NS$: C, 68.53; H, 5.18. Found: C, 68.27; H, 5.08.

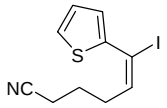
(*E*)-5-Iodo-6-(thiophen-2-yl)hex-5-enenitrile and (*E*)-6-iodo-6-(thiophen-2-yl)hex-5-enenitrile. Bu_3SnH (3.80 mL, 14.09 mmol) was added to a solution of 6-(thiophen-2-yl)hex-5-ynenitrile prepared above (1.90 g, 10.84 mmol) and $PdCl_2(PPh_3)_2$ (76 mg, 0.11 mmol, 1 mol%) in dry THF (50 mL) at room temperature. The mixture was stirred at that temperature for 1 h and then solvent was removed under vacuum. To a solution of the crude vinyl stannane in dry CH_2Cl_2 (70 mL) at 0 ºC was added I_2 (3.85 g, 15.18 mmol) in portions. After 1 h at room temperature, saturated aqueous $Na_2S_2O_3$ solution (40 mL) was added. The organic layer was separated, dried ($MgSO_4$) and concentrated. The resulting residue was purified by silica gel column chromatography (hexanes:ethyl acetate 15:1) to afford **(***E***)**-5-iodo-6-(thiophen-2-yl)hex-5-enenitrile (yellow solid, 0.46 g, 14%) and (*E*)-6-iodo-6-(thiophen-2-yl)hex-5-enenitrile (yellow oil, 2.27 g, 69%).

(*E*)-5-Iodo-6-(thiophen-2-yl)hex-5-enenitrile.



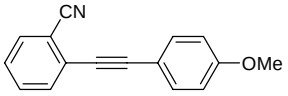
M.p. = 59-61 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36 (s, 1H), 7.28 (d, *J* = 4.8 Hz, 1H), 6.99-6.96 (m, 2H), 2.90 (t, *J* = 7.4 Hz, 2H), 2.38 (t, *J* = 7.2 Hz, 2H), 1.96 (quint, *J* = 7.3 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 138.4, 134.2, 128.0, 126.5, 125.6, 118.7, 101.1, 38.7, 24.6, 15.5. IR (neat, cm^{-1}): 3105, 2934, 2247, 1452, 1424, 1219, 702. Anal. Calcd for $C_{10}H_{10}INS$: C, 39.62; H, 3.32. Found: C, 39.62; H, 3.33.

(*E*)-6-Iodo-6-(thiophen-2-yl)hex-5-enenitrile.



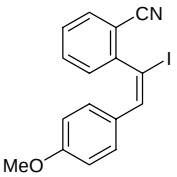
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.11 (dd, *J* = 3.6, 1.1 Hz, 1H), 6.97 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.42 (t, *J* = 7.5 Hz, 1H), 2.33 (q, *J* = 7.4 Hz, 2H), 2.27 (t, *J* = 7.2 Hz, 2H), 1.71 (quint, *J* = 7.3 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 142.4, 141.8, 129.0, 126.6, 126.4, 118.8, 87.0, 31.1, 24.4, 16.2. IR (neat, cm^{-1}): 3104, 2935, 2246, 1424, 1225, 705. Anal. Calcd for $C_{10}H_{10}INS$: C, 39.62; H, 3.32. Found: C, 39.90; H, 3.34.

2-(2-(4-Methoxyphenyl)ethynyl)benzonitrile.



An oven-dried flask was charged with CuI (59 mg, 0.31 mmol, 2 mol%), $PdCl_2(PPh_3)_2$ (216 mg, 0.31 mmol, 2 mol%) and 2-iodobenzonitrile (353 g, 15.42 mmol). The mixture was evacuated and flushed with argon (twice) at room temperature. Then, anhydrous THF (15 mL), triethylamine (15 mL) and 4-ethynylanisole (2.00 mL, 15.42 mmol) were sequentially added via syringe. The mixture was stirred at 60 ºC overnight, then diluted with CH_2Cl_2 (50 mL) and washed consecutively with 10% HCl (30 mL x 3) and brine (30 mL), dried ($MgSO_4$) and concentrated. The resulting residue was purified by silica gel column chromatography (hexanes:ethyl acetate 10:1) to give the title compound (3.17 g, 88%) as a white solid. M.p. = 87-88 ºC. NMR spectral data were in agreement with those reported in the literature.[3]

2-((*E*)-1-Iodo-2-(4-methoxyphenyl)vinyl)benzonitrile.

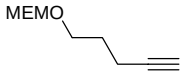


An oven-dried flak was charged with $PdCl_2(PPh_3)_2$ (120 mg, 0.17 mmol, 2 mol%) and 2-(2-(4-methoxyphenyl)ethynyl)benzonitrile prepared above (2.00 g, 8.57 mmol). Dry THF (15 mL) was added and the reaction mixture was stirred at room temperature for 10 min. Then, Bu_3SnH (3.22 mL, 12.00 mmol) was added via syringe over 90 min at room temperature. The resulting mixture was concentrated and used directly in the next step. To a solution of the crude vinyl stannane[5] in dry CH_2Cl_2 (15 mL) at 0 ºC was added a solution of I_2 (3.05 g, 12.00 mmol) in CH_2Cl_2 (60 mL). After 1 h at 0 ºC and 1 h more at room temperature, saturated aqueous $Na_2S_2O_3$ solution (40 mL) was added. The organic layer was separated, dried ($MgSO_4$) and concentrated. The resulting residue was

(3) Rubin, M.; Trofimov, A.; Gevorgyan, V. *J. Am. Chem. Soc.* **2005**, *127*, 10243.

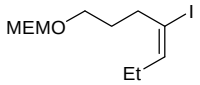
purified by silica gel column chromatography (hexanes:ethyl acetate 10:1) to afford the title compound (2.44 g, 79%) as a yellow solid. M.p. = 90-91 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.65-7.59 (m, 2H), 7.52 (s, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.40 (dt, *J* = 7.6, 1.1 Hz, 1H), 6.78 (m, 2H), 6.66 (m, 2H), 3.74 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 158.8, 146.0, 143.6, 133.0, 132.9, 129.4, 128.5, 128.3, 116.5, 113.3, 110.6, 86.9, 54.7. IR (neat, cm^{-1}): 2836, 2227, 1602, 1510, 1254, 1179, 762. Anal. Calcd for $C_{16}H_{12}INO$: C, 53.21; H, 3.35. Found: C, 53.48; H, 3.35.

5-((2-Methoxyethoxy)methoxy)pent-1-yne.



To a solution of 4-pentyn-1-ol (1.85 mL, 20.00 mmol) in dry CH_2Cl_2 (50 mL) were sequentially added diisopropylethylamine (6.97 mL, 40 mmol) and (2-methoxyethoxy)methyl chloride (6.85 mL, 60.00 mmol). The resulting solution was stirred at room temperature for 8 h. After that time, water (30 mL) was added. The organic layer was separated, dried ($MgSO_4$) and concentrated. The crude product was purified by silica gel column chromatography (hexanes:ethyl acetate 5:1) to afford the title compound (2.76 g, 80%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.72 (s, 2H), 3.71-3.69 (m, 2H), 3.66 (t, *J* = 6.2 Hz, 2H), 3.58-3.56 (m, 2H), 3.40 (s, 3H), 2.30 (dt, *J* = 7.1, 2.6 Hz, 2H), 1.95 (t, *J* = 2.6 Hz, 1H), 1.81 (quint, *J* = 6.7 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 95.2, 83.5, 71.6, 68.5, 66.5, 65.8, 58.8, 28.3, 15.0. IR (neat, cm^{-1}): 3292, 2927, 2879, 1117, 1094, 1043. Anal. Calcd for $C_9H_{16}O_3$: C, 62.77; H, 9.36. Found: C, 63.05; H, 9.55.

(*E*)-7-((2-Methoxyethoxy)methoxy)-4-iodohept-3-ene.[4]



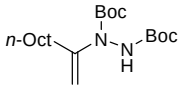
n-BuLi (2.5 M in hexanes, 5.34 mL, 13.35 mmol) was added to a solution of 5-((2-methoxyethoxy)methoxy)pent-1-yne prepared above (2.30 g, 13.35 mmol) in dry THF (13 mL) at 0 ºC. After 30 min at that temperature, triethylborane (1.0 M in THF, 13.35 mL, 13.35 mmol) was slowly added and the reaction mixture was then allowed to warm to room temperature and stirred for 1 h followed by the addition of trimethyltin chloride (1.0 M in THF, 13.35 mL, 13.35 mmol). After 1 h at room temperature, the reaction mixture was cooled to –78 ºC and treated with *n*-BuLi (2.5 M in hexanes, 5.34 mL, 13.35 mmol). Stirring was continued for 15 min at that temperature and then the mixture was transferred via cannula to a flask containing $CuBr{\cdot}SMe_2$ (2.74 g, 13.35 mmol) and THF (25 mL) at –78 ºC. After an additional 1 h at –78 ºC, MeOH (5 mL) was added and stirring was continued at –78 ºC for 3 h**.** The reaction mixture was then allowed to warm to 0 ºC and 6 N NaOH (13 mL) and 30% H_2O_2 solution (13 mL) were slowly added at that temperature. The mixture was extracted with EtOAc (20 mL x 3) and the combined organic layers were dried ($MgSO_4$) and evaporated. To a solution of the crude vinyl stannane in dry Et_2O (40 mL) was added

(4) Procedure described by Wang, K. W.; Chu, K.-H.; Lin, Y.; Chen, J.-H. *Tetrahedron* **1989**, *45*, 1105.

a solution of I_2 (3.39 g, 13.35 mmol) in Et_2O (30 mL). The resulting mixture was stirred for 1 h at room temperature followed by the addition of a saturated $Na_2S_2O_3$ solution (20 mL). The organic layer was separated, dried ($MgSO_4$) and concentrated to afford a 88:12 mixture of (*E*)-7-((2-methoxyethoxy)methoxy)-4-iodohept-3-ene and (*E*)-7-((2-methoxyethoxy)methoxy)-3-iodohept-3-ene (significant signal: 6.13 (t, *J* = 7.5 Hz, 1H)). The crude material was purified by silica gel column chromatography (hexanes:ethyl acetate 10:1) to give the title compound (2.63 g, 60%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.21 (t, *J* = 7.5 Hz, 1H), 4.71 (s, 2H), 3.71-3.69 (m, 2H), 3.58-3.54 (m, 4H), 3.41 (s, 3H), 2.48 (t, *J* = 7.1 Hz, 2H), 2.07 (quint, *J* = 7.5 Hz, 2H), 1.82-1.62 (m, 2H), 0.97 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 143.3, 101.6, 95.3, 71.6, 66.5, 65.9, 58.8, 34.9, 29.0, 24.0, 13.5. IR (neat, cm^{-1}): 2930, 2874, 1629, 1454, 1116, 1096, 1044. Anal. Calcd for $C_{11}H_{21}IO_3$: C, 40.26; H, 6.45. Found: C, 40.67; H, 6.62.

Table 1: General Procedure for the Cu-catalyzed coupling of vinyl iodides with *bis*-Boc-hydrazine. An oven-dried Schlenk tube was charged with CuI (5 mol%), 1,10-phenanthroline (10 mol%), di-*tert*-butyl hydrazodicarboxylate (1.2 equiv) and Cs_2CO_3 (1.2 equiv). 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, the vinyl iodide (1.0 equiv) and anhydrous DMF (2.0 mL/mmol of vinyl iodide) were added via syringe. The tube was sealed and stirred at 80 ºC in a pre-heated oil bath for 12-13 h. The reaction mixture was allowed to cool to room temperature and diluted with diethyl ether and water. The aqueous layer was extracted with ether and the combined ethereal layers were washed with brine, dried ($MgSO_4$) and evaporated. The resulting residue was purified by column chromatography on silica gel eluting with hexanes/ethyl acetate mixtures.

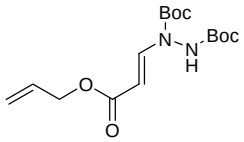
Di(*tert*-butyl) 1-(1-octylvinyl)-1,2-hydrazinedicarboxylate (Table 1, entry 1).



The general procedure was applied using CuI (29 mg, 0.15 mmol, 5 mol%), 1,10-phenanthroline (54 mg, 0.30 mmol, 10 mol%), di-*tert*-butyl hydrazodicarboxylate (836 mg, 3.60 mmol), Cs_2CO_3 (1.173 g, 3.60 mmol), and 2-iodo-1-decene[5] (798 mg, 3.00 mmol) with DMF (6.0 mL) as solvent for 13 h at 80 ºC. The product was purified by column chromatography on silica gel (hexanes/ethyl acetate 10:1) to give the title compound as a colorless oil (775 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.43-6.07 (m, 1H), 5.04 (m, 1H), 4.79 (s, 1H), 2.28 (t, *J* = 7.3 Hz, 2H), 1.54-1.22 (m, 30H), 0.88 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.0, 153.2, 147.2, 106.0, 81.1, 80.6, 33.2, 31.6, 29.1, 29.0, 28.8, 27.9, 27.8, 27.2, 22.3, 13.8. IR (neat, cm^{-1}): 3325, 2928, 2856, 1714, 1367, 1247, 1160. Anal. Calcd for $C_{20}H_{38}N_2O_4$: C, 64.83; H, 10.34. Found: C, 64.86; H, 10.36.

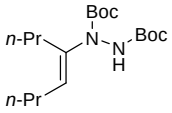
(5) Reddy, C. K.; Periasamy, M. *Tetrahedron Lett.* **1990**, *31*, 1919.

Di(*tert*-butyl) 1-[(*E*)-3-(allyloxy)-3-oxo-1-propenyl]-1,2-hydrazinedicarboxylate (Table 1, entry 2).



The general procedure was applied using CuI (4.8 mg, 0.025 mmol, 5 mol%), 1,10-phenanthroline (9.0 mg, 0.05 mmol, 10 mol%), di-*tert*-butyl hydrazodicarboxylate (232 mg, 1.00 mmol), Cs_2CO_3 (195 mg, 0.60 mmol), and (*E*)-allyl-3-iodo acrylate[6] (119 mg, 0.50 mmol) with DMF (1.0 mL) as solvent for 12 h at 80 ºC to afford a 96:4 mixture of mono:double-vinylation products. Purification by column chromatography on silica gel (hexanes/ethyl acetate 10:1) gave di(*tert*-butyl) 1,2-bis[(*E*)-3-(allyloxy)-3-oxo-1-propenyl]-1,2-hydrazinedicarboxylate (colorless oil, 5 mg, 2%) and di(*tert*-butyl) 1-[(*E*)-3-(allyloxy)-3-oxo-1-propenyl]-1,2-hydrazinedicarboxylate (white solid, 120 mg, 70%). **Di(*tert*-butyl) 1,2-bis[(*E*)-3-(allyloxy)-3-oxo-1-propenyl]-1,2-hydrazinedicarboxylate:** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.22-7.98 (m, 2H), 5.95-5.88 (m, 2H), 5.30 (dd, *J* = 18.4, 1.2 Hz, 1H), 5.23-5.21 (m, 2H), 5.15-5.06 (m, 2H), 4.60 (d, *J* = 4.4 Hz, 4H), 1.47-1.44 (m, 18H). **Di(*tert*-butyl) 1-[(*E*)-3-(allyloxy)-3-oxo-1-propenyl]-1,2-hydrazinedicarboxylate:** M.p. = 78-80 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.32-8.05 (m, 1H), 6.43-6.06 (m, 1H), 6.00-5.91 (m, 1H), 5.52 (d, *J* = 13.4 Hz, 1H), 5.34 (dd, *J* = 17.2, 1.5 Hz, 1H), 5.23 (dd, *J* = 10.4, 1.1 Hz, 1H), 4.64 (d, *J* = 5.6 Hz, 2H), 1.61-1.49 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.9, 153.7, 150.8, 141.8, 132.4, 117.6, 98.2, 83.8, 81.8, 64.5, 27.9, 27.7. IR (neat, cm^{-1}): 3296, 2981, 2935, 1746, 1640, 1370, 1246, 1149. Anal. Calcd for $C_{16}H_{26}N_2O_6$: C, 56.13; H, 7.54. Found: C, 56.27; H, 7.77.

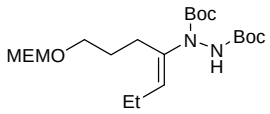
Di(*tert*-butyl) 1-[(*E*)-1-propyl-1-pentenyl]-1,2-hydrazinedicarboxylate (1, Table 1, entry 3).



The general procedure was applied using CuI (57 mg, 0.30 mmol, 5 mol%), 1,10-phenanthroline (108 mg, 0.60 mmol, 10 mol%), di-*tert*-butyl hydrazodicarboxylate (1.67 g, 7.20 mmol), Cs_2CO_3 (2.35 g, 7.20 mmol), and (*E*)-4-iodo-4-octene (1.43 g, 6.00 mmol) with DMF (12.0 mL) as solvent for 13 h at 80 ºC. The product was purified by column chromatography on silica gel (hexanes/ethyl acetate 10:1) to give the title compound as a white solid (1.76 g, 86%). M.p. = 62-64 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.40-6.04 (m, 1H), 5.61-5.46 (m, 1H), 2.16 (t, *J* = 7.4 Hz, 2H), 2.04 (q, *J* = 7.4 Hz, 2H), 1.48-1.36 (m, 22H), 0.92 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.1, 154.2, 138.4, 127.7, 80.6, 30.1, 29.2, 27.9, 22.3, 20.6, 13.7, 13.5. IR (neat, cm^{-1}): 3274, 2963, 2932, 1716, 1367, 1161. Anal. Calcd for $C_{18}H_{34}N_2O_4$: C, 63.13; H, 10.01. Found: C, 63.33; H, 10.10.

(6) Han, C.; Shen, R.; Su, S.; Porco, J. A. *Org. Lett.* **2004**, *6*, 27.

Di(*tert*-butyl) 1-((*E*)-1-{3-[(2-methoxyethoxy)methoxy]propyl}-1-butenyl)-1,2-hydrazinedicarboxylate (Table 1, entry 4).

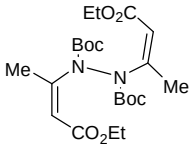


The general procedure was applied using CuI (29 mg, 0.15 mmol, 5 mol%), 1,10-phenanthroline (54 mg, 0.30 mmol, 10 mol%), di-*tert*-butyl hydrazodicarboxylate (836 mg, 3.60 mmol), Cs_2CO_3 (1.173 g, 3.60 mmol), and (*E*)-7-((2-methoxyethoxy)methoxy)-4-iodohept-3-ene (984 mg, 3.00 mmol) with DMF (6.0 mL) as solvent for 12 h at 80 ºC. The product was purified by column chromatography on silica gel (hexanes/ethyl acetate 3:1) to give the title compound as a colorless oil (1.12 g, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.53-6.15 (m, 1H), 5.60-5.47 (m, 1H), 4.72 (s, 2H), 3.71-3.69 (m, 2H), 3.58-3.55 (m, 4H), 3.41 (s, 3H), 2.28 (t, *J* = 7.3 Hz, 2H), 2.08 (quint, *J* = 7.6 Hz, 2H), 1.72 (quint, *J* = 7.6 Hz, 2H), 1.53-1.42 (m, 18H), 0.99 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.1, 154.0, 137.2, 129.4, 95.1, 80.6, 71.4, 67.0, 66.3, 58.6, 27.8, 27.3, 24.5, 20.3, 13.6. IR (neat, cm^{-1}): 3295, 2975, 2932, 1716, 1367, 1159. Anal. Calcd for $C_{21}H_{40}N_2O_7$: C, 58.31; H, 9.32. Found: C, 58.52; H, 9.41.

Di(*tert*-butyl) 1-[(*Z*)-3-ethoxy-1-methyl-3-oxo-1-propenyl]-1,2-hydrazinedicarboxylate (Table 1, entry 5).

The general procedure was applied using CuI (4.8 mg, 0.025 mmol, 5 mol%), 1,10-phenanthroline (9.0 mg, 0.05 mmol, 10 mol%), di-*tert*-butyl hydrazodicarboxylate (232 mg, 1.00 mmol), Cs_2CO_3 (195 mg, 0.60 mmol), and (*Z*)-β-iodo-β-methyl ethyl acrylate[7] (120 mg, 0.50 mmol) with DMF (1.0 mL) as solvent for 12 h at 80 ºC to afford a 91:9 mixture of mono:double-vinylation products. Purification by column chromatography on silica gel (hexanes/ethyl acetate 6:1) gave di(*tert*-butyl) 1,2-bis[(*Z*)-3-ethoxy-1-methyl-3-oxo-1-propenyl]-1,2-hydrazinedicarboxylate (colorless oil, 16 mg, 7%) and di(*tert*-butyl) 1-[(*Z*)-3-ethoxy-1-methyl-3-oxo-1-propenyl]-1,2-hydrazinedicarboxylate (white solid, 112 mg, 65%).

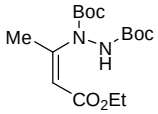
Di(*tert*-butyl) 1,2-bis[(*Z*)-3-ethoxy-1-methyl-3-oxo-1-propenyl]-1,2-hydrazinedicarboxylate.



^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.76 (s, 2H), 4.15 (q, *J* = 7.1 Hz, 4H), 2.48 (s, 6H), 1.50 (s, 18H), 1.28 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.1, 153.5, 151.0, 105.4, 83.8, 59.8, 27.9, 16.4, 14.2. IR (neat, cm^{-1}): 2980, 1742, 1714, 1628, 1302, 1144. Anal. Calcd for $C_{22}H_{36}N_2O_8$: C, 57.88; H, 7.95. Found: C, 58.20; H, 7.99.

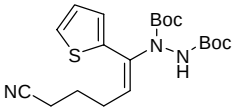
(7) Beruben, D.; Marek, I.; Normant, J. F.; Platzer, N. *J. Org. Chem.* **1995**, *60*, 2488.

Di(*tert*-butyl) 1-[(*Z*)-3-ethoxy-1-methyl-3-oxo-1-propenyl]-1,2-hydrazinedicarboxylate.



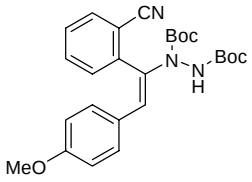
M.p. = 98-100 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.46-6.11 (m, 1H), 5.97 (s, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 2.48 (s, 3H), 1.50 (s, 18H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.2, 154.8, 154.6, 151.9, 105.7, 82.7, 81.2, 59.3, 27.8, 27.6, 16.6, 14.0. IR (neat, cm^{-1}): 3317, 2981, 1738, 1625, 1301, 1148. Anal. Calcd for $C_{16}H_{28}N_2O_6$: C, 55.80; H, 8.19. Found: C, 55.86; H, 8.21.

Di(*tert*-butyl) 1-[(*E*)-5-cyano-1-(2-thienyl)-1-pentenyl]-1,2-hydrazinedicarboxylate (Table 1, entry 6).



The general procedure was applied using CuI (19 mg, 0.10 mmol, 5 mol%), 1,10-phenanthroline (36 mg, 0.20 mmol, 10 mol%), di-*tert*-butyl hydrazodicarboxylate (557 mg, 2.40 mmol), Cs_2CO_3 (782 mg, 2.40 mmol), and (*E*)-6-iodo-6-(thiophen-2-yl)hex-5-enenitrile (606 mg, 2.00 mmol) with DMF (4.0 mL) as solvent for 12 h at 80 ºC. The product was purified by column chromatography on silica gel (hexanes/ethyl acetate 4:1) to give the title compound as a colorless oil (706 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.07 (m, 1H), 7.03 (dd, *J* = 5.0, 3.6 Hz, 1H), 6.58-6.18 (m, 1H), 5.97-5.80 (m, 1H), 2.49 (q, *J* = 7.3 Hz, 2H), 2.37 (t, *J* = 7.3 Hz, 2H), 1.84 (quint, *J* = 7.3 Hz, 2H), 1.48-1.43 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.9, 153.5, 137.9, 134.2, 127.2, 126.7, 125.6, 119.0, 81.6, 81.0, 27.9, 27.7, 26.9, 24.9, 16.1. IR (neat, cm^{-1}): 3318, 2978, 2932, 2247, 1719, 1367, 1247, 1155. Anal. Calcd for $C_{20}H_{29}N_3O_4S$: C, 58.94; H, 7.17. Found: C, 59.17; H, 7.29.

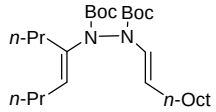
Di(*tert*-butyl) 1-[(*E*)-1-(2-cyanophenyl)-2-(4-methoxyphenyl)ethenyl]-1,2-hydrazinedicarboxylate (Table 1, entry 7).



The general procedure was applied using CuI (29 mg, 0.15 mmol, 5 mol%), 1,10-phenanthroline (54 mg, 0.30 mmol, 10 mol%), di-*tert*-butyl hydrazodicarboxylate (836 mg, 3.60 mmol), Cs_2CO_3 (1.173 g, 3.60 mmol), and 2-((*E*)-1-iodo-2-(4-methoxyphenyl)vinyl)benzonitrile (1.084 g, 3.00 mmol) with DMF (6.0 mL) as solvent for 13 h at 80 ºC. The product was purified by column chromatography on silica gel (hexanes/ethyl acetate 6:1) to give the title compound as a white solid (1.32 g, 95%). M.p. = 138-141 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72-7.60 (m, 2H), 7.50 (t, *J* =

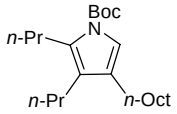
7.2 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.01-6.90 (m, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 6.67 (d, *J* = 8.7 Hz, 2H), 3.75 (s, 3H), 1.60-1.26 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.6, 155.2, 152.5, 141.1, 135.9, 132.7, 132.3, 131.4, 130.0, 128.0, 127.0, 126.1, 118.0, 113.4, 111.9, 82.0, 81.1, 80.7, 54.7, 27.9, 27.5. IR (neat, cm^{-1}): 3324, 2980, 2228, 1722, 1512, 1368, 1251, 1155.

Di(*tert*-butyl) 1-[(*E*)-1-decenyl]-2-[(*E*)-1-propyl-1-pentenyl]-1,2-hydrazinedicarboxylate (2).



An oven-dried Schlenk tube was charged with CuI (9.5 mg, 0.05 mmol, 10 mol%), 1,10-phenanthroline (18 mg, 0.10 mmol, 20 mol%), di(*tert*-butyl) 1-[(*E*)-1-propyl-1-pentenyl]-1,2-hydrazinedicarboxylate (**1**) (211 mg, 0.60 mmol) and Cs_2CO_3 (195 mg, 0.60 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, the (*E*)-1-iodo-1-decene (133 mg, 0.50 mmol) and anhydrous DMF (0.50 mL) were added via syringe. The tube was sealed and stirred at 80 ºC in a pre-heated oil bath for 30 h. 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 purified by column chromatography on silica gel (hexanes/ethyl acetate 10:1) to give the title compound as a colorless oil (194 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (conformers): 6.75-6.51 (m, 1H), 5.49-5.44 (m, 1H), 5.01-4.94 (m, 1H), 2.12-2.00 (m, 6H), 1.52-1.25 (m, 34H), 0.94-0.86 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (conformers): 152.8, 151.4, 136.8, 136.6, 125.6, 125.1, 110.3, 109.8, 81.6, 80.6, 31.8, 30.2, 30.1, 29.5, 29.4, 29.2, 28.9, 28.0, 22.6, 22.5, 22.0, 14.0, 13.7. IR (neat, cm^{-1}): 2960, 2927, 2855, 1720, 1367, 1308, 1162. Anal. Calcd for $C_{28}H_{52}N_2O_4$: C, 69.96; H, 10.90. Found: C, 70.08; H, 10.99.

***tert*-Butyl 4-octyl-2,3-dipropyl-1*H*-pyrrole-1-carboxylate (3).**

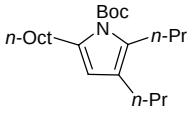


A solution of di(*tert*-butyl) 1-[(*E*)-1-decenyl]-2-[(*E*)-1-propyl-1-pentenyl]-1,2-hydrazinedicarboxylate (**2**, 144 mg, 0.30 mmol) in dry *m*-xylene (1.2 mL) was stirred in a Schlenk tube at 140 ºC for 30 h and then allowed to cool to room temperature. *p*-TsOH (114 mg, 0.60 mmol) was then added and the mixture stirred at room temperature for 1 h. After that time, saturated $NaHCO_3$ solution (2 mL) was added and the mixture was extracted with ethyl acetate. The organic layer was separated, dried ($MgSO_4$) and evaporated. The resulting residue was purified by silica gel (previously deactivated with Et_3N) column chromatography (hexanes) to give the title compound as a colorless oil (91 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.94 (s, 1H), 2.76 (t, *J* = 7.6 Hz, 2H),

2.37-2.29 (m, 4H), 1.60-1.31 (m, 25H), 1.00-0.96 (m, 6H), 0.92 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.5, 131.4, 125.8, 124.4, 116.4, 82.3, 31.9, 29.7, 29.5, 29.3, 28.1, 28.0, 26.5, 25.3, 24.2, 23.7, 22.7, 14.3, 14.1. IR (neat, cm^{-1}): 2959, 2929, 2856, 1738, 1369, 1164. Anal. Calcd for $C_{23}H_{41}NO_2$: C, 75.98; H, 11.37. Found: C, 76.39; H, 11.50.

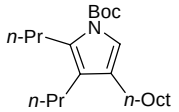
Table 2: Synthesis of pyrroles through sequential Cu-catalyzed vinylation of hydrazides/cyclization.[8]

***tert*-Butyl 5-octyl-2,3-dipropyl-1*H*-pyrrole-1-carboxylate (Table 2, entry 1).**



An oven-dried Schlenk tube was charged with CuI (9.5 mg, 0.05 mmol, 10 mol%), 1,10-phenanthroline (18 mg, 0.10 mmol, 20 mol%) and Cs_2CO_3 (195 mg, 0.60 mmol), evacuated and backfilled with argon (this sequence was repeated an additional time). Di(*tert*-butyl) 1-(1-octylvinyl)-1,2-hydrazinedicarboxylate (185 mg, 0.50 mmol), (*E*)-4-iodo-4-octene (119 mg, 0.50 mmol) and anhydrous DMF (0.50 mL) were then added. The resulting mixture was stirred at 80 ºC for 36 h and then filtered through a plug of celite eluting with ethyl acetate and concentrated to dryness. The resulting residue was dissolved in dry *m*-xylene (2.0 mL) and stirred in a Schlenk tube at 140 ºC for 36 h and then allowed to cool to room temperature. *p*-TsOH (199 mg, 1.00 mmol) was added and the mixture stirred at room temperature for 1 h. After that time, saturated $NaHCO_3$ solution (2 mL) was added and the mixture was extracted with ethyl acetate. The organic layer was separated, dried ($MgSO_4$) and evaporated. The resulting residue was purified by column chromatography on silica gel (previously deactivated with Et_3N) eluting with hexanes to give the title compound as a colorless oil (118 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.76 (s, 1H), 2.75-2.68 (m, 4H), 2.29 (t, J = 7.5 Hz, 2H), 1.59-1.28 (m, 25H), 0.96-0.87 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 150.5, 134.9, 130.4, 122.8, 110.5, 82.8, 31.9, 29.6, 29.5, 29.3, 29.1, 28.2, 28.1, 28.0, 27.9, 24.0, 23.9, 22.7, 14.2, 14.1, 14.0. IR (neat, cm^{-1}): 2958, 2928, 2856, 1735, 1320, 1133. Anal. Calcd for $C_{23}H_{41}NO_2$: C, 75.98; H, 11.37. Found: C, 75.89; H, 11.52.

***tert*-Butyl 4-octyl-2,3-dipropyl-1*H*-pyrrole-1-carboxylate (3, Table 2, entry 2).**

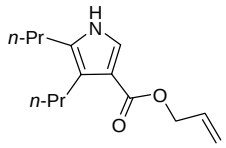


An oven-dried Schlenk tube was charged with di(*tert*-butyl) 1-[(*E*)-1-propyl-1-pentenyl]-1,2-hydrazinedicarboxylate (176 mg, 0.50 mmol), CuI (9.5 mg, 0.05 mmol, 10 mol%), 1,10-

(8) In some cases, during treatment with *p*-TsOH it is important to stop the reaction at the time indicated due to the instability of pyrroles in acidic media.

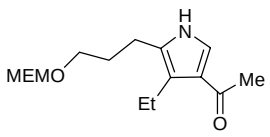
phenanthroline (18 mg, 0.10 mmol, 20 mol%) and Cs_2CO_3 (195 mg, 0.60 mmol), evacuated and backfilled with argon (this sequence was repeated an additional time). (*E*)-1-Iodo-1-decene (133 mg, 0.50 mmol) and anhydrous DMF (0.50 mL) were then added. The resulting mixture was stirred at 80 ºC for 30 h and then filtered through a plug of celite eluting with ethyl acetate and concentrated to dryness. The resulting residue was dissolved in dry *m*-xylene (2.0 mL) and stirred in a Schlenk tube at 140 ºC for 30 h and then allowed to cool to room temperature. *p*-TsOH (199 mg, 1.00 mmol) was added and the mixture stirred at room temperature for 1 h. After that time, saturated $NaHCO_3$ solution (2 mL) was added and the mixture was extracted with ethyl acetate. The organic layer was separated, dried ($MgSO_4$) and evaporated. The resulting residue was purified by column chromatography on silica gel (previously deactivated with Et_3N) eluting with hexanes to give the title compound as a colorless oil (126 mg, 69%).

Allyl 4,5-dipropyl-1*H*-pyrrole-3-carboxylate (Table 2, entry 3).



An oven-dried Schlenk tube was charged with di(*tert*-butyl) 1-[(*E*)-1-propyl-1-pentenyl]-1,2-hydrazinedicarboxylate (176 mg, 0.50 mmol), CuI (9.5 mg, 0.05 mmol, 10 mol%), 1,10-phenanthroline (18 mg, 0.10 mmol, 20 mol%) and Cs_2CO_3 (195 mg, 0.60 mmol), evacuated and backfilled with argon (this sequence was repeated an additional time). (*E*)-Allyl-3-iodo acrylate[6] (119 mg, 0.50 mmol) and anhydrous DMF (0.50 mL) were then added. The resulting mixture was stirred at 80 ºC for 22 h and then filtered through a plug of celite eluting with ethyl acetate and concentrated to dryness. The resulting residue was dissolved in dry *m*-xylene (2.0 mL), stirred in a Schlenk tube at 140 ºC for 40 h and concentrated. Purification by column chromatography on silica gel (previously deactivated with Et_3N) eluting with hexanes:ethyl acetate 6:1 afforded the title compound as a yellow oil (72 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03 (br s, 1H), 7.33 (d, *J* = 3.1 Hz, 1H), 6.06-5.97 (m, 1H), 5.38 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.23 (dd, *J* = 10.4, 1.4 Hz, 1H), 4.72 (dt, *J* = 5.5, 1.4 Hz, 2H), 2.65-2.61 (m, 2H), 2.52 (t, *J* = 7.5 Hz, 2H), 1.61-1.53 (m, 4H), 0.97-0.92 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.2, 133.0, 130.1, 122.7, 120.9, 117.2, 113.7, 63.9, 27.3, 26.7, 24.6, 23.2, 14.1, 13.8. IR (neat, cm^{-1}): 3327, 2958, 2931, 2871, 1681, 1155.

1-(4-Ethyl-5-{3-[(2-methoxyethoxy)methoxy]propyl}-1*H*-pyrrol-3-yl)ethanone (Table 2, entry 4).



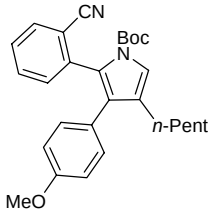
An oven-dried Schlenk tube was charged with (*E*)-4-iodo-3-buten-2-one (98 mg, 0.50 mmol), CuI (9.5 mg, 0.05 mmol, 10 mol%), 1,10-phenanthroline (18 mg, 0.10 mmol, 20 mol%) and Cs_2CO_3

(195 mg, 0.60 mmol), evacuated and backfilled with argon (this sequence was repeated an additional time). A solution of di(*tert*-butyl) 1-((*E*)-1-{3-[(2-methoxyethoxy)methoxy]propyl}-1-butenyl)-1,2-hydrazinedicarboxylate (216 mg, 0.50 mmol) in anhydrous DMF (0.50 mL) was then added. The resulting mixture was stirred at 80 ºC for 24 h and then filtered through a plug of celite eluting with ethyl acetate and concentrated to dryness. The resulting residue was dissolved in dry *m*-xylene (2.0 mL), stirred in a Schlenk tube at 140 ºC for 24 h and concentrated. Purification by column chromatography on silica gel (previously deactivated with Et_3N) eluting with hexanes:ethyl acetate 2:1 afforded the title compound as a yellow oil (71 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.08 (br s, 1H), 7.25 (d, *J* = 3.2 Hz, 1H), 4.76 (s, 2H), 3.77-3.75 (m, 2H), 3.63-3.59 (m, 4H), 3.43 (s, 3H), 2.73-2.66 (m, 4H), 2.38 (s, 3H), 1.83 (quint, *J* = 6.4 Hz, 2H), 1.11 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 193.9, 129.8, 123.9, 123.5, 122.4, 95.9, 71.8, 67.5, 67.1, 59.0, 30.1, 27.6, 21.5, 18.1, 15.9. IR (neat, cm^{-1}): 3291, 2928, 2876, 1703, 1632, 1114, 1040.

tert-Butyl 2-(2-cyanophenyl)-3-(4-methoxyphenyl)-4-pentyl-1*H*-pyrrole-1-carboxylate and 2-[3-(4-methoxyphenyl)-4-pentyl-1*H*-pyrrol-2-yl]benzonitrile (Table 2, entry 5).

An oven-dried Schlenk tube was charged with di(*tert*-butyl) 1-[(*E*)-1-(2-cyanophenyl)-2-(4-methoxyphenyl)ethenyl]-1,2-hydrazinedicarboxylate (233 mg, 0.50 mmol), CuI (9.5 mg, 0.05 mmol, 10 mol%), 1,10-phenanthroline (18 mg, 0.10 mmol, 20 mol%) and Cs_2CO_3 (195 mg, 0.60 mmol), evacuated and backfilled with argon (this sequence was repeated an additional time). (*E*)-1-Iodo-1-heptene[9] (112 mg, 0.50 mmol) and anhydrous DMF (0.50 mL) were then added. The resulting mixture was stirred at 80 ºC for 36 h and then filtered through a plug of celite eluting with ethyl acetate and concentrated to dryness. The resulting residue was dissolved in dry *m*-xylene (2.0 mL) and stirred in a Schlenk tube at 140 ºC for 32 h and then allowed to cool to room temperature. *p*-TsOH (199 mg, 1.00 mmol) was added and the mixture stirred at room temperature for 6 h. After that time, saturated $NaHCO_3$ solution (2 mL) was added and the mixture was extracted with ethyl acetate. The organic layer was separated, dried ($MgSO_4$) and evaporated. The resulting residue was purified by column chromatography on silica gel (previously deactivated with Et_3N) eluting with hexanes:ethyl acetate 20:1 to give *tert*-butyl 2-(2-cyanophenyl)-3-(4-methoxyphenyl)-4-pentyl-1*H*-pyrrole-1-carboxylate (colorless oil, 82 mg, 37%) and 2-[3-(4-methoxyphenyl)-4-pentyl-1*H*-pyrrol-2-yl]benzonitrile (colorless oil, 26 mg, 15%).

tert-Butyl 2-(2-cyanophenyl)-3-(4-methoxyphenyl)-4-pentyl-1*H*-pyrrole-1-carboxylate.

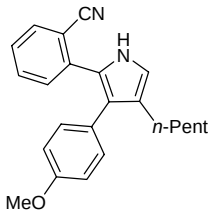


^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.42 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.31 (dt, *J* = 7.6, 1.1 Hz, 1H), 7.26 (s, 1H), 7.22 (d, *J* = 7.7 Hz, 1H), 6.97 (dd, *J* = 6.8, 2.0 Hz, 2H), 6.74

(9) Spino, C.; Gund, V. G.; Nadeau, C. *J. Comb. Chem.* **2005**, *7*, 345.

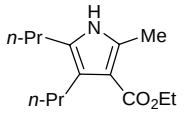
(dd, *J* = 6.9, 2.0 Hz, 2H), 3.76 (s, 3H), 2.37 (t, *J* = 7.6 Hz, 2H), 1.53-1.47 (m, 2H), 1.35 (s, 9H), 1.30-1.27 (m, 4H), 0.86 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.2, 148.9, 138.4, 132.1, 131.9, 131.7, 131.1, 130.1, 127.4, 126.4, 126.1, 125.8, 119.1, 118.2, 114.9, 113.3, 83.5, 55.0, 31.6, 29.1, 27.6, 25.4, 22.4, 14.0. IR (neat, cm^{-1}): 2926, 2850, 2226, 1738, 1368, 1247, 1156.

2-[3-(4-Methoxyphenyl)-4-pentyl-1*H*-pyrrol-2-yl]benzonitrile.



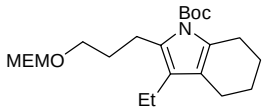
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.62 (br s, 1H), 7.63 (d, *J* = 7.7 Hz, 1H), 7.31 (dt, *J* = 7.7, 1.2 Hz, 1H), 7.21 (t, *J* = 6.7 Hz, 1H), 7.13-7.10 (m, 3H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 2.5 Hz, 1H), 3.83 (s, 3H), 2.45 (t, *J* = 7.6 Hz, 2H), 1.53 (m, 2H), 1.30 (m, 4H), 0.87 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.1, 136.8, 133.7, 132.3, 131.4, 130.6, 127.9, 126.2, 125.3, 124.6, 124.2, 119.5, 117.1, 113.8, 109.0, 55.1, 31.8, 30.0, 25.4, 22.5, 14.0. IR (neat, cm^{-1}): 3357, 2926, 2854, 2224, 1527, 1245.

Ethyl 2-methyl-4,5-dipropyl-1*H*-pyrrole-3-carboxylate (Table 2, entry 6).



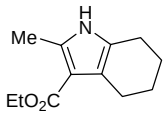
An oven-dried Schlenk tube was charged with di(*tert*-butyl) 1-[(*E*)-1-propyl-1-pentenyl]-1,2-hydrazinedicarboxylate (176 mg, 0.50 mmol), CuI (9.5 mg, 0.05 mmol, 10 mol%), 1,10-phenanthroline (18 mg, 0.10 mmol, 20 mol%) and Cs_2CO_3 (195 mg, 0.60 mmol), evacuated and backfilled with argon (this sequence was repeated an additional time). (*Z*)-β-Iodo-β-methyl ethyl acrylate[7] (120 mg, 0.50 mmol) and anhydrous DMF (0.50 mL) were then added. The resulting mixture was stirred at 80 ºC for 26 h and then filtered through a plug of celite eluting with ethyl acetate and concentrated to dryness. The resulting residue was dissolved in dry *m*-xylene (2.0 mL) and stirred in a Schlenk tube at 140 ºC for 30 h and then allowed to cool to room temperature. *p*-TsOH (199 mg, 1.00 mmol) was added and the mixture stirred at room temperature for 6 h. After that time, saturated $NaHCO_3$ solution (2 mL) was added and the mixture was extracted with ethyl acetate. The organic layer was separated, dried ($MgSO_4$) and evaporated. The resulting residue was purified by column chromatography on silica gel (previously deactivated with Et_3N) eluting with hexanes:ethyl acetate 10:1 to give the title compound as a white solid (66 mg, 56%). M.p. = 89-91 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (br s, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 2.58-2.54 (m, 2H), 2.49-2.45 (m, 5H), 1.60-1.49 (m, 4H), 1.34 (t, *J* = 7.1 Hz, 3H), 0.97-0.92 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.3, 133.9, 126.9, 121.0, 109.9, 58.9, 27.4, 27.2, 24.9, 23.4, 14.4, 14.2, 14.0, 13.8. IR (neat, cm^{-1}): 3321, 2958, 2930, 2870, 1665, 1102.

***tert*-Butyl 3-ethyl-2-{3-[(2-methoxyethoxy)methoxy]propyl}-4,5,6,7-tetrahydro-1*H*-indole-1-carboxylate (Table 2, entry 7).**



An oven-dried Schlenk tube was charged with CuI (7.6 mg, 0.04 mmol, 10 mol%), 1,10-phenanthroline (14.4 mg, 0.08 mmol, 20 mol%) and Cs_2CO_3 (156 mg, 0.48 mmol), evacuated and backfilled with argon (this sequence was repeated an additional time). Di(*tert*-butyl) 1-((*E*)-1-{3-[(2-methoxyethoxy)methoxy]propyl}-1-butenyl)-1,2-hydrazinedicarboxylate (173 mg, 0.40 mmol), 1-iodo-1-cyclohexene[10] (83 mg, 0.40 mmol) and anhydrous DMF (0.40 mL) were then added. The resulting mixture was stirred at 80 ºC for 30 h and then filtered through a plug of celite eluting with ethyl acetate and concentrated to dryness. The resulting residue was dissolved in dry *m*-xylene (1.6 mL), stirred in a Schlenk tube at 140 ºC for 30 h and concentrated. Purification by column chromatography on silica gel (previously deactivated with Et_3N) eluting with hexanes:ethyl acetate 10:1 afforded the title compound as a colorless oil (94 mg, 59%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.74 (s, 2H), 3.73-3.70 (m, 2H), 3.60-3.56 (m, 4H), 3.41 (s, 3H), 2.85 (t, *J* = 7.5 Hz, 2H), 2.76 (t, *J* = 5.7 Hz, 2H), 2.37 (t, *J* = 6.0 Hz, 2H), 2.32 (q, *J* = 7.5 Hz, 2H), 1.83-1.70 (m, 6H), 1.58 (s, 9H), 1.06 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 150.1, 128.7, 128.6, 124.5, 120.5, 95.4, 82.6, 71.8, 67.5, 66.6, 59.0, 30.7, 28.0, 25.7, 23.7, 22.7, 22.6, 21.7, 17.3, 15.4. IR (neat, cm^{-1}): 2930, 2874, 1729, 1367, 1308, 1131. Anal. Calcd for $C_{22}H_{37}NO_5$: C, 66.80; H, 9.43. Found: C, 66.78; H, 9.45.

Ethyl 2-methyl-4,5,6,7-tetrahydro-1*H*-indole-3-carboxylate (Table 2, entry 8).

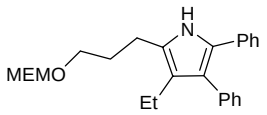


An oven-dried Schlenk tube was charged with di(*tert*-butyl) 1-[(*Z*)-3-ethoxy-1-methyl-3-oxo-1-propenyl]-1,2-hydrazinedicarboxylate (172 mg, 0.50 mmol), CuI (9.5 mg, 0.05 mmol, 10 mol%), 1,10-phenanthroline (18 mg, 0.10 mmol, 20 mol%) and Cs_2CO_3 (195 mg, 0.60 mmol), evacuated and backfilled with argon (this sequence was repeated an additional time). 1-Iodo-1-cyclohexene[10] (104 mg, 0.50 mmol) and anhydrous DMF (0.50 mL) were then added The resulting residue was dissolved in dry *m*-xylene (2.0 mL) and stirred in a Schlenk tube at 140 ºC for 30 h and then allowed to cool to room temperature. *p*-TsOH (199 mg, 1.00 mmol) was added and the mixture stirred at room temperature for 4 h. After that time, saturated $NaHCO_3$ solution (2 mL) was added and the mixture was extracted with ethyl acetate. The organic layer was separated, dried ($MgSO_4$) and evaporated. The resulting residue was purified by column chromatography on silica gel (previously deactivated with Et_3N) eluting with hexanes:ethyl acetate 10:1 to give the title

(10) Lee, K.; Wiemer, D. F. *Tetrahedron Lett.* **1993**, *34*, 2433.

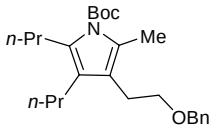
compound as a white solid (49 mg, 47%). M.p. = 132-134 ºC [lit.[11] = 127.5-129.5 ºC]. NMR data were in agreement with those described in the literature.[11]

3-Ethyl-2-{3-[(2-methoxyethoxy)methoxy]propyl}-4,5-diphenyl-1*H*-pyrrole (Table 2, entry 9).



An oven-dried Schlenk tube was charged with (*E*)-1-iodo-1,2-diphenylethene (122 mg, 0.40 mmol), CuI (7.6 mg, 0.04 mmol, 10 mol%), 1,10-phenanthroline (14.4 mg, 0.08 mmol, 20 mol%) and Cs_2CO_3 (156 mg, 0.48 mmol), evacuated and backfilled with argon (this sequence was repeated an additional time). Di(*tert*-butyl) 1-((*E*)-1-{3-[(2-methoxyethoxy)methoxy]propyl}-1-butenyl)-1,2-hydrazinedicarboxylate (173 mg, 0.40 mmol) and anhydrous DMF (0.40 mL) were then added. The resulting mixture was stirred at 80 ºC for 36 h and then filtered through a plug of celite eluting with ethyl acetate and concentrated to dryness. The resulting residue was dissolved in dry *m*-xylene (1.6 mL), stirred in a Schlenk tube at 140 ºC for 48 h and concentrated. Purification by column chromatography on silica gel (previously deactivated with Et_3N) eluting with hexanes:ethyl acetate 10:1 afforded the title compound as a colorless oil (122 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.55 (br s, 1H), 7.35-7.26 (m, 5H), 7.21-7.09 (m, 5H), 4.82 (s, 2H), 3.77-3.71 (m, 4H), 3.57-3.55 (m, 2H), 3.33 (s, 3H), 2.80 (t, *J* = 7.2 Hz, 2H), 2.42 (q, *J* = 7.5 Hz, 2H), 1.97 (quint, *J* = 6.3 Hz, 2H), 0.98 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 136.9, 133.4, 130.4, 128.3, 128.2, 128.1, 128.0, 126.2, 125.8, 125.4, 122.1, 122.0, 95.9, 71.7, 67.8, 67.2, 58.9, 30.0, 22.7, 17.4, 16.4. IR (neat, cm^{-1}): 3340, 3057, 2924, 1600, 1450, 1112, 1041. Anal. Calcd for $C_{25}H_{31}NO_3$: C, 76.30; H, 7.94. Found: C, 76.45; H, 8.22.

***tert*-Butyl 3-[2-(benzyloxy)ethyl]-2-methyl-4,5-dipropyl-1*H*-pyrrole-1-carboxylate (Table 2, entry 10).**

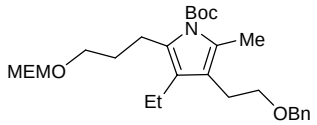


An oven-dried Schlenk tube was charged with di(*tert*-butyl) 1-[(*E*)-1-propyl-1-pentenyl]-1,2-hydrazinedicarboxylate (176 mg, 0.50 mmol), CuI (9.5 mg, 0.05 mmol, 10 mol%), 1,10-phenanthroline (18 mg, 0.10 mmol, 20 mol%) and Cs_2CO_3 (195 mg, 0.60 mmol), evacuated and backfilled with argon (this sequence was repeated an additional time). 1-(((*E*)-4-Iodopent-3-enyloxy)methyl)benzene (151 mg, 0.50 mmol) and anhydrous DMF (0.50 mL) were then added. The resulting mixture was stirred at 80 ºC for 24 h and then filtered through a plug of celite eluting with ethyl acetate and concentrated to dryness. The resulting residue was dissolved in dry *m*-xylene (2.0 mL) and stirred in a Schlenk tube at 140 ºC for 30 h and then allowed to cool to room

(11) Chiu, P.-K. ; Sammes, M. P. *Tetrahedron* **1990**, *46*, 3439.

temperature. *p*-TsOH (199 mg, 1.00 mmol) was added and the mixture stirred at room temperature for 1 h. After that time, saturated $NaHCO_3$ solution (2 mL) was added and the mixture was extracted with ethyl acetate. The organic layer was separated, dried ($MgSO_4$) and evaporated. The resulting residue was purified by column chromatography on silica gel (previously deactivated with Et_3N) eluting with hexanes:ethyl acetate 20:1 to give the title compound as a colorless oil (120 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36-7.29 (m, 5H), 4.54 (s, 2H), 3.46 (t, *J* = 7.6 Hz, 2H), 2.71-2.67 (m, 4H), 2.29-2.26 (m, 5H), 1.59 (s, 9H), 1.53-1.41 (m, 4H), 0.97-0.93 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.4, 138.4, 130.1, 128.3, 127.6, 127.5, 126.6, 123.0, 118.2, 82.7, 72.8, 70.5, 28.4, 28.0, 26.6, 25.0, 24.8, 24.1, 14.4, 14.1, 13.4. IR (neat, cm^{-1}): 2959, 2931, 2870, 1732, 1455, 1368, 1350, 1135. Anal. Calcd for $C_{25}H_{37}NO_3$: C, 75.15; H, 9.33. Found: C, 75.15; H, 9.35.

tert-Butyl 3-[2-(benzyloxy)ethyl]-4-ethyl-5-{3-[(2-methoxyethoxy)methoxy]propyl}-2-methyl-1*H*-pyrrole-1-carboxylate (Table 2, entry 11).



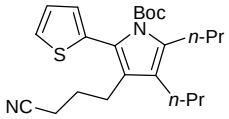
An oven-dried Schlenk tube was charged with CuI (7.6 mg, 0.04 mmol, 10 mol%), 1,10-phenanthroline (14.4 mg, 0.08 mmol, 20 mol%) and Cs_2CO_3 (156 mg, 0.48 mmol), evacuated and backfilled with argon (this sequence was repeated an additional time). Di(*tert*-butyl) 1-((*E*)-1-{3-[(2-methoxyethoxy)methoxy]propyl}-1-butenyl)-1,2-hydrazinedicarboxylate (173 mg, 0.40 mmol), 1-(((*E*)-4-iodopent-3-enyloxy)methyl)benzene (121 mg, 0.40 mmol) and anhydrous DMF (0.40 mL) were then added. The resulting mixture was stirred at 80 ºC for 30 h and then filtered through a plug of celite eluting with ethyl acetate and concentrated to dryness. The resulting residue was dissolved in dry *m*-xylene (1.6 mL), stirred in a Schlenk tube at 140 ºC for 32 h and concentrated. Purification by column chromatography on silica gel (previously deactivated with Et_3N) eluting with hexanes:ethyl acetate 10:1 afforded the title compound as a colorless oil (116 mg, 59%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35-7.28 (m, 5H), 4.73 (s, 2H), 4.54 (s, 2H), 3.72-3.70 (m, 2H), 3.58-3.56 (m, 4H), 3.47 (t, *J* = 7.7 Hz, 2H), 3.40 (s, 3H), 2.82 (t, *J* = 7.5 Hz, 2H), 2.69 (t, *J* = 8.1 Hz, 2H), 2.34 (q, *J* = 7.5 Hz, 2H), 2.31 (s, 3H), 1.79 (quint, *J* = 6.5 Hz, 2H), 1.59 (s, 9H), 1.04 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.3, 138.4, 128.9, 128.3, 127.5, 127.4, 126.9, 124.8, 118.1, 95.3, 82.9, 72.8, 71.7, 70.5, 67.4, 66.6, 59.0, 30.7, 28.0, 24.9, 22.9, 17.2, 16.1, 13.5. IR (neat, cm^{-1}): 2929, 2871, 1731, 1368, 1345, 1312, 1134. Anal. Calcd for $C_{28}H_{43}NO_6$: C, 68.68; H, 8.85. Found: C, 68.90; H, 9.06.

tert-Butyl 3-(3-cyanopropyl)-4,5-dipropyl-2-(2-thienyl)-1*H*-pyrrole-1-carboxylate and 4-[4,5-Dipropyl-2-(2-thienyl)-1*H*-pyrrol-3-yl]butanenitrile (Table 2, entry 12).

An oven-dried Schlenk tube was charged with CuI (9.5 mg, 0.05 mmol, 10 mol%), 1,10-phenanthroline (18 mg, 0.10 mmol, 20 mol%) and Cs_2CO_3 (195 mg, 0.60 mmol), evacuated and backfilled with argon (this sequence was repeated an additional time). A solution of di(*tert*-butyl) 1-

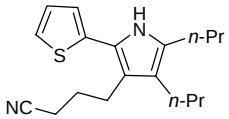
[(*E*)-5-cyano-1-(2-thienyl)-1-pentenyl]-1,2-hydrazinedicarboxylate (204 mg, 0.50 mmol) in anhydrous DMF (0.50 mL) and (*E*)-4-iodo-4-octene (119 mg, 0.50 mmol) were then added. The resulting mixture was stirred at 80 ºC for 36 h and then filtered through a plug of celite eluting with ethyl acetate and concentrated to dryness. The resulting residue was dissolved in dry *m*-xylene (2.0 mL) and stirred in a Schlenk tube at 140 ºC for 32 h and then allowed to cool to room temperature. *p*-TsOH (199 mg, 1.00 mmol) was added and the mixture stirred at room temperature for 1 h. After that time, saturated $NaHCO_3$ solution (2 mL) was added and the mixture was extracted with ethyl acetate. The organic layer was separated, dried ($MgSO_4$) and evaporated. The resulting residue was purified by column chromatography on silica gel (previously deactivated with Et_3N) eluting with hexanes:ethyl acetate 20:1 to give *tert*-butyl 3-(3-cyanopropyl)-4,5-dipropyl-2-(2-thienyl)-1*H*-pyrrole-1-carboxylate (colorless oil, 37 mg, 19%) and 4-[4,5-dipropyl-2-(2-thienyl)-1*H*-pyrrol-3-yl]butanenitrile (colorless oil, 57 mg, 38%).

***tert*-Butyl 3-(3-cyanopropyl)-4,5-dipropyl-2-(2-thienyl)-1*H*-pyrrole-1-carboxylate.**

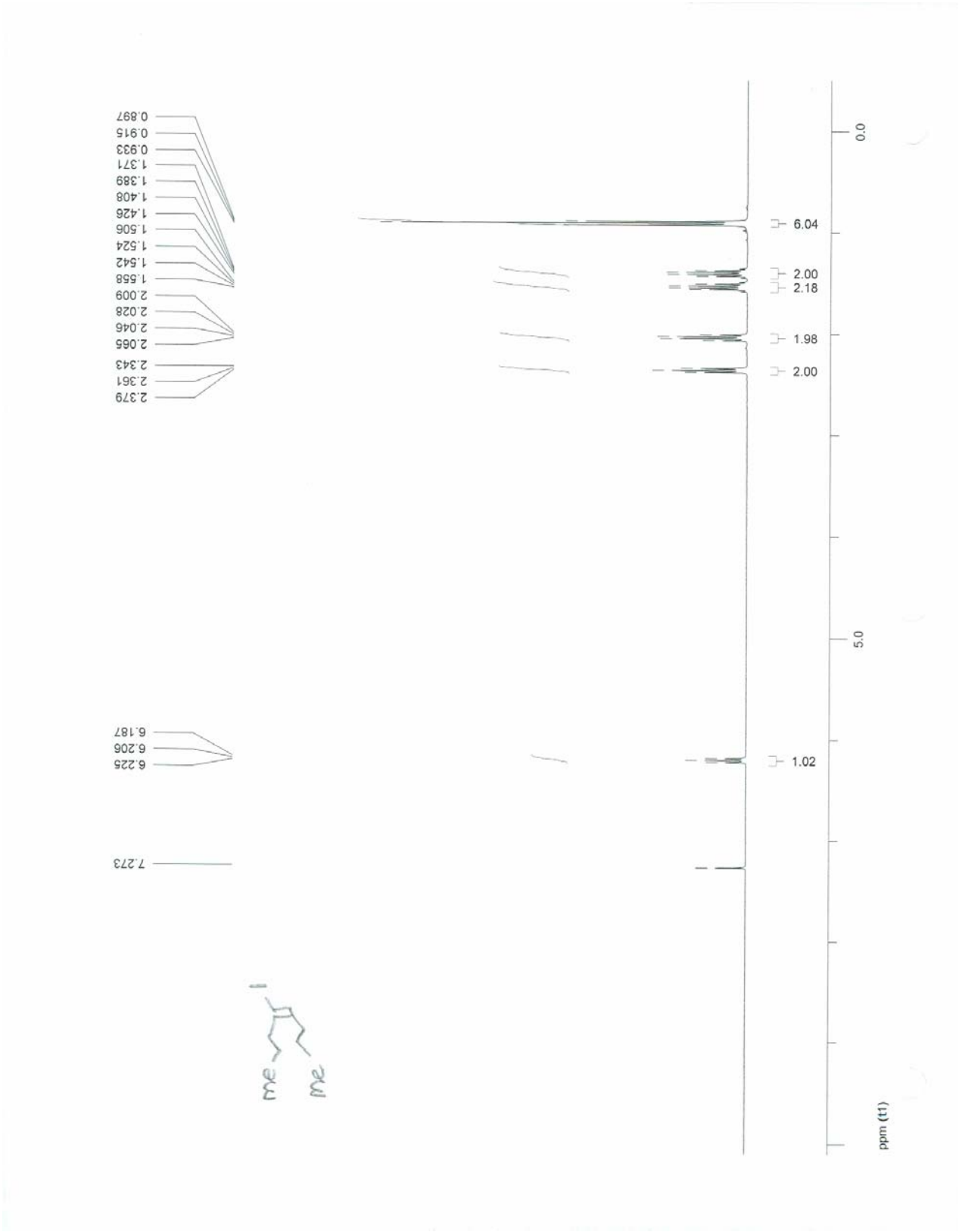


^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.05 (dd, *J* = 5.2, 3.6 Hz, 1H), 6.88 (dd, *J* = 3.2, 0.8 Hz, 1H), 2.75 (t, *J* = 7.6 Hz, 2H), 2.45 (t, *J* = 7.6 Hz, 2H), 2.36-2.32 (m, 2H), 2.21 (t, *J* = 7.6 Hz, 2H), 1.71 (quint, *J* = 7.6 Hz, 2H), 1.59-1.46 (m, 4H), 1.27 (s, 9H), 1.02-0.96 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.7, 135.3, 133.4, 127.9, 126.6, 125.9, 124.9, 122.3, 121.5, 119.6, 83.0, 27.9, 27.3, 26.6, 26.5, 24.8, 23.9, 23.7, 16.8, 14.4, 14.2. IR (neat, cm^{-1}): 2959, 2931, 2870, 2246, 1736, 1317, 1141. Anal. Calcd for $C_{23}H_{32}N_2O_2S$: C, 68.96; H, 8.05. Found: C, 69.28; H, 8.19.

4-[4,5-Dipropyl-2-(2-thienyl)-1*H*-pyrrol-3-yl]butanenitrile.



^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77 (br s, 1H), 7.19 (d, *J* = 5.0 Hz, 1H), 7.05 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.95 (d, *J* = 2.8 Hz, 1H), 2.76 (t, *J* = 7.7 Hz, 2H), 2.55 (t, *J* = 7.6 Hz, 2H), 2.39-2.33 (m, 4H), 1.88 (q, *J* = 7.4 Hz, 2H), 1.63 (m, 2H), 1.50 (m, 2H), 1.02-0.97 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.8, 129.4, 127.4, 122.7, 121.7, 120.6, 120.1, 119.9, 118.6, 28.0, 26.7, 26.5, 25.1, 24.0, 23.3, 16.9, 14.3, 14.1. IR (neat, cm^{-1}): 3366, 2956, 2929, 2868, 2246, 1535, 1454.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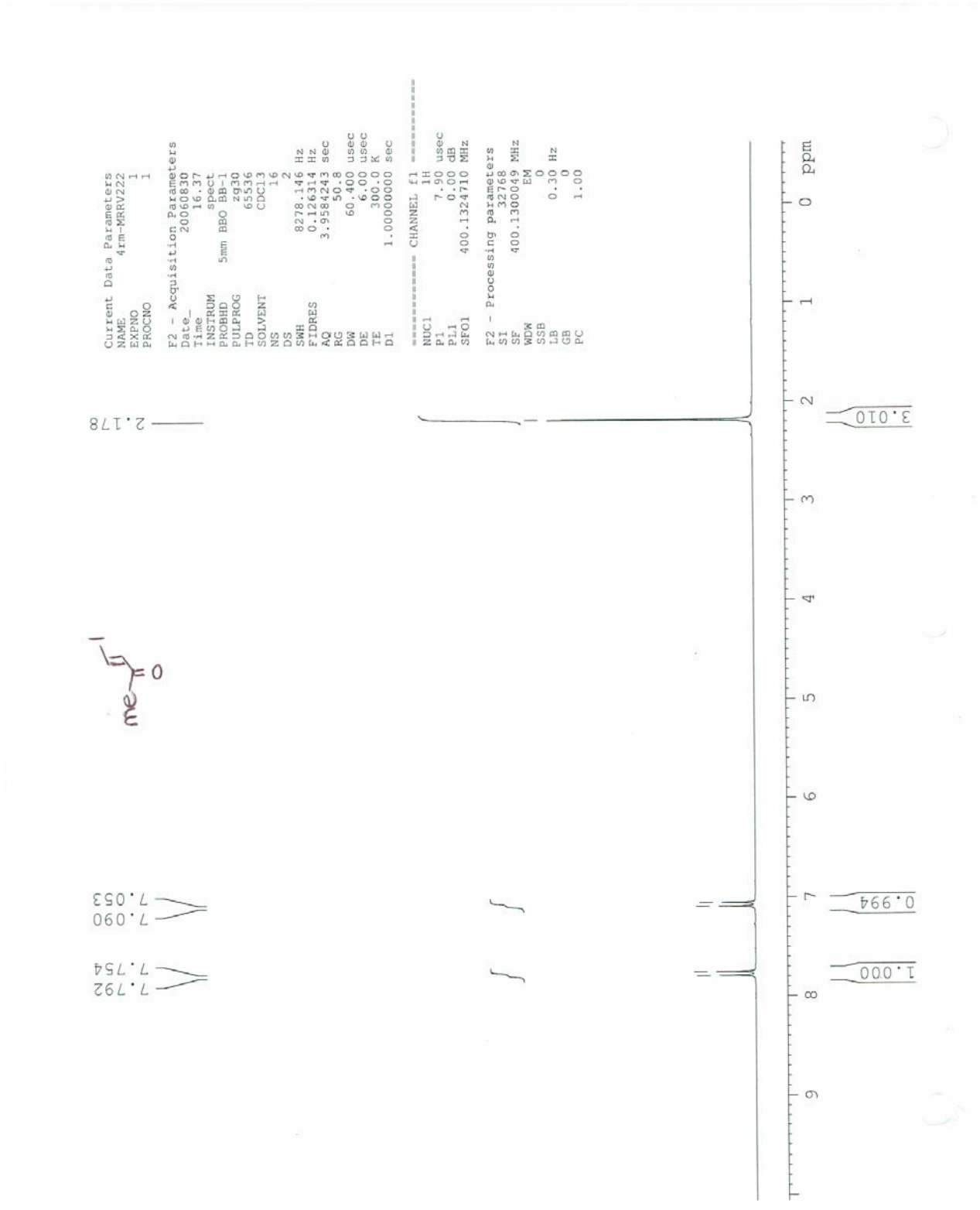
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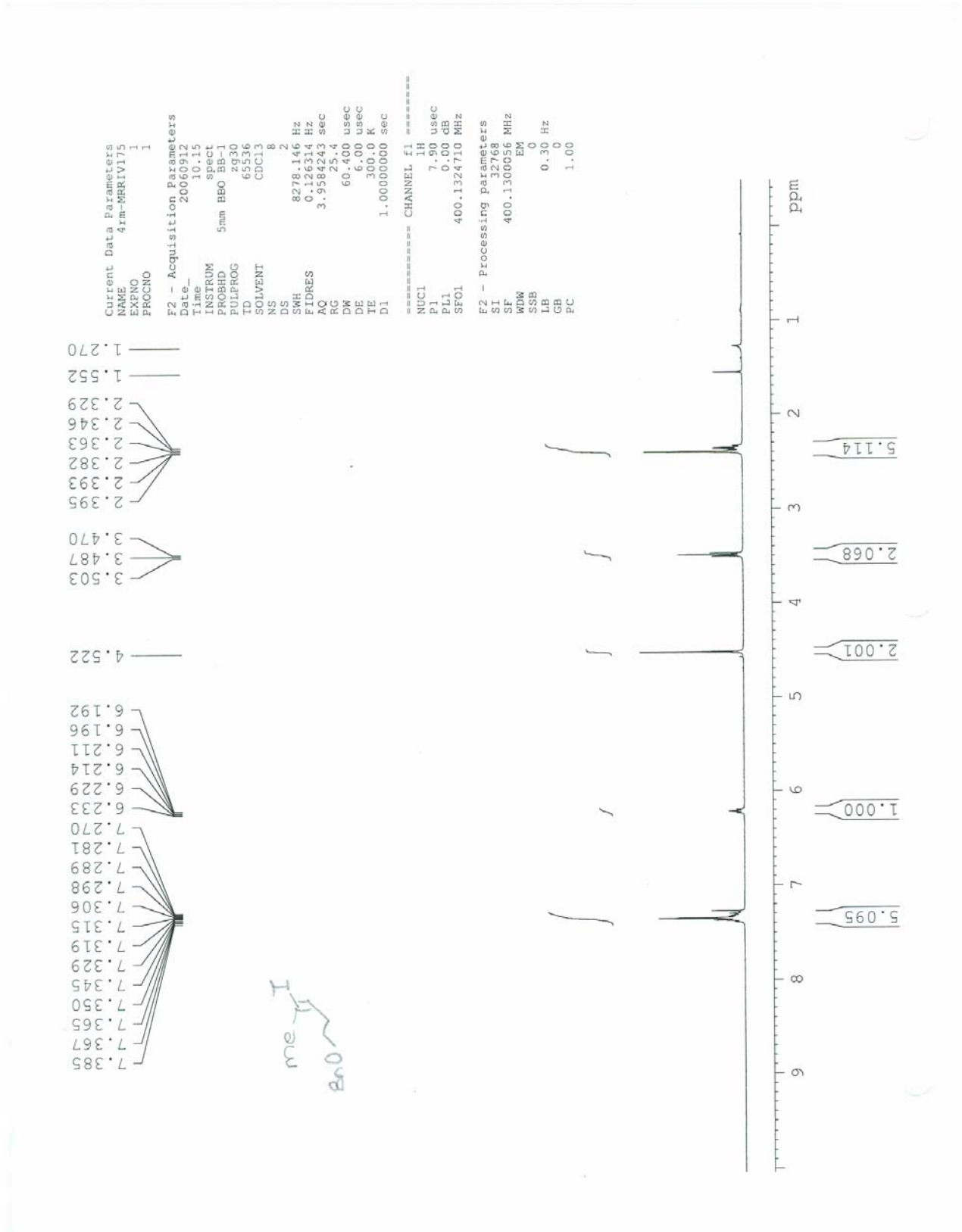
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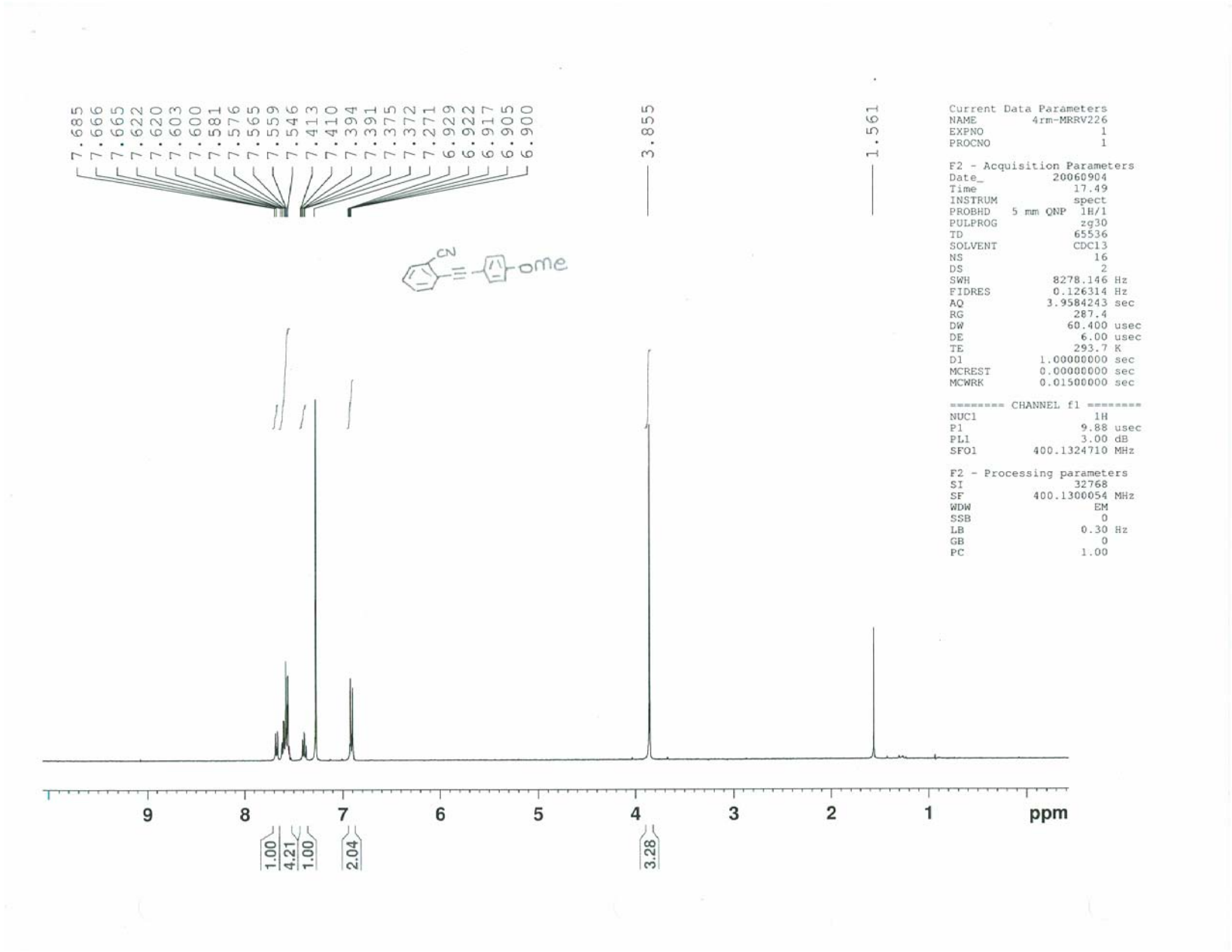
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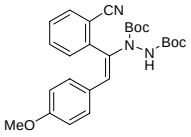
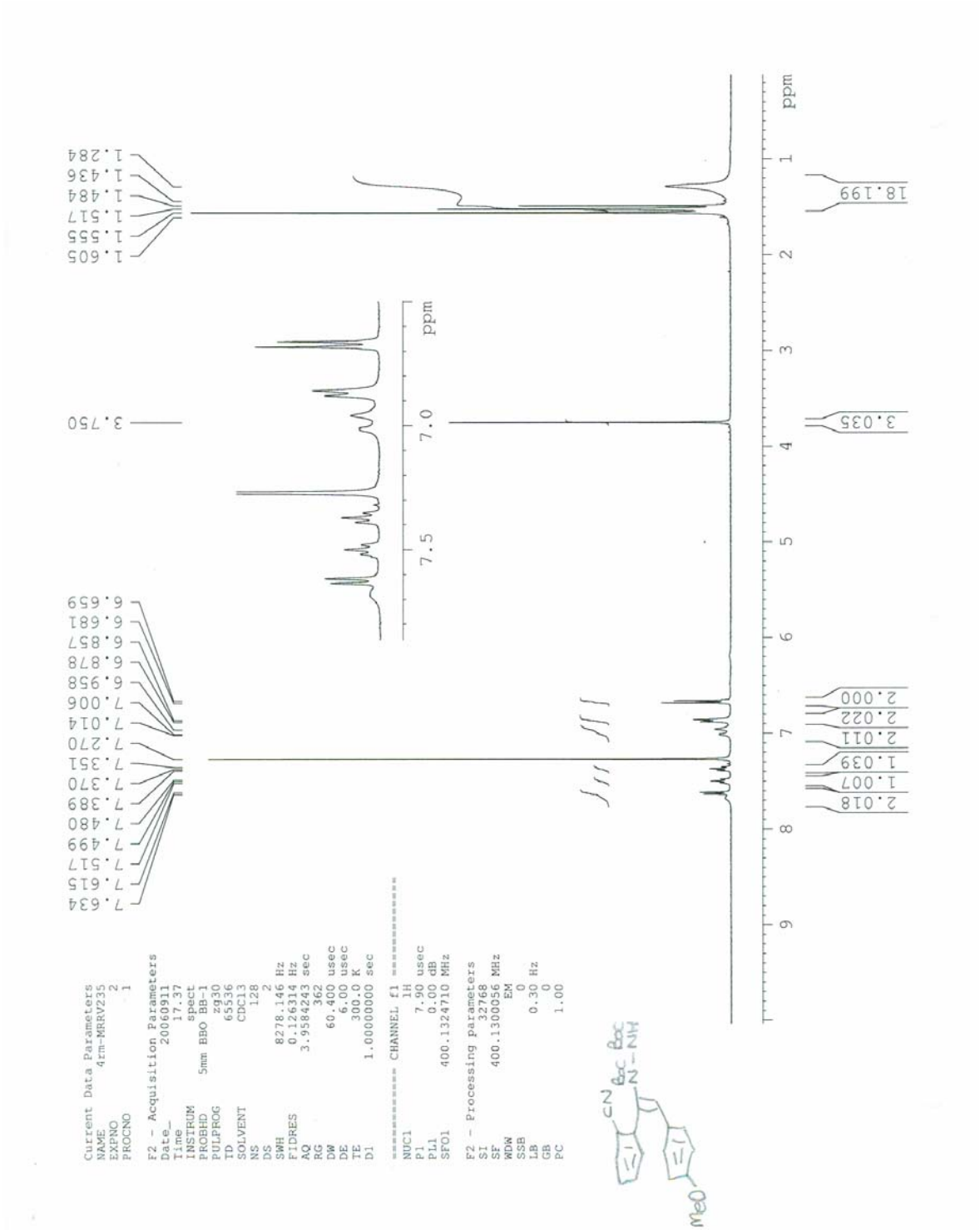
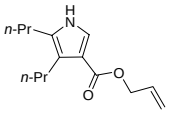
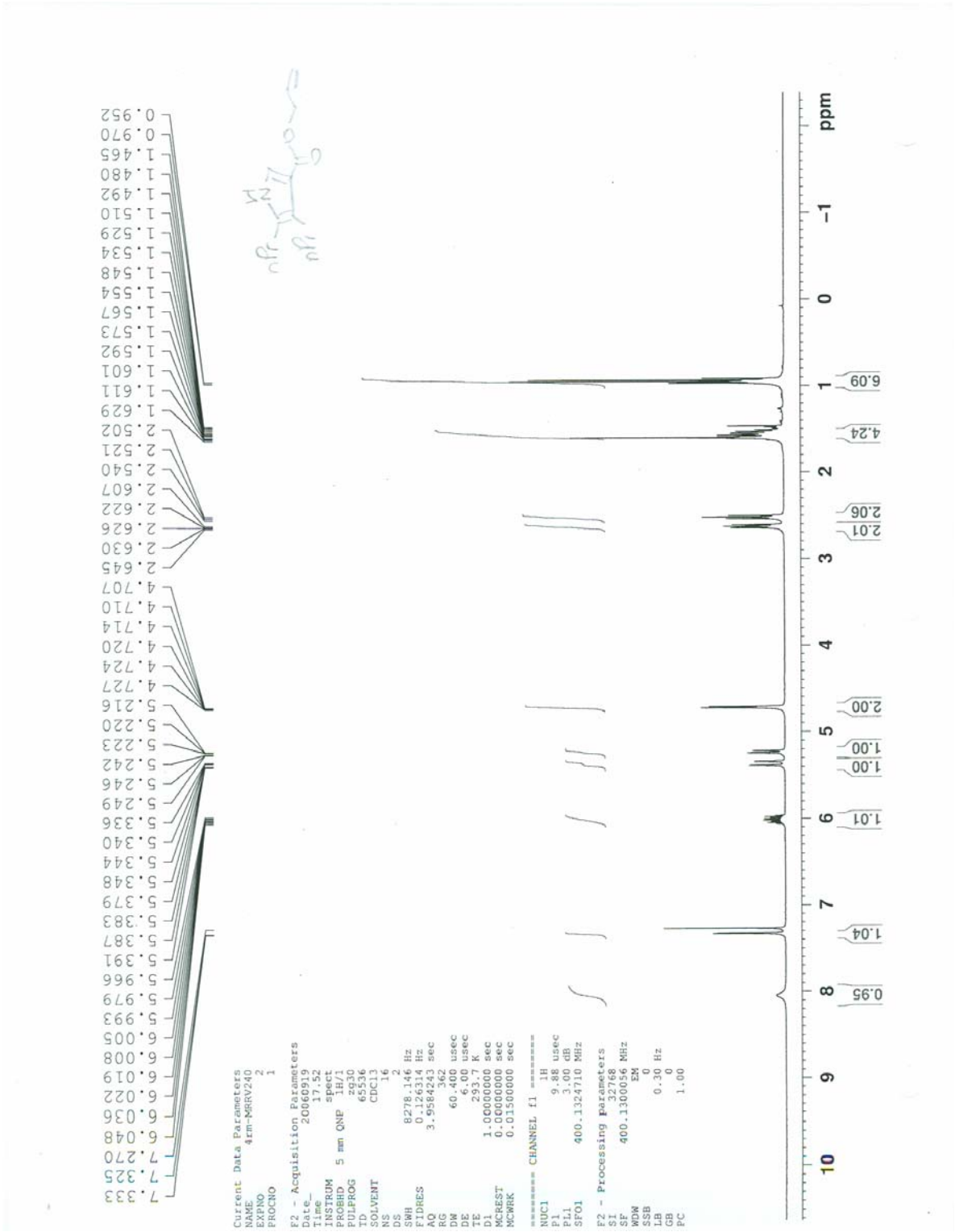
Di(*tert*-butyl) 1-[(*E*)-1-(2-cyanophenyl)-2-(4-methoxyphenyl)ethenyl]-1,2-hydrazinedicarboxylate (Table 1, entry 7)



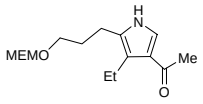


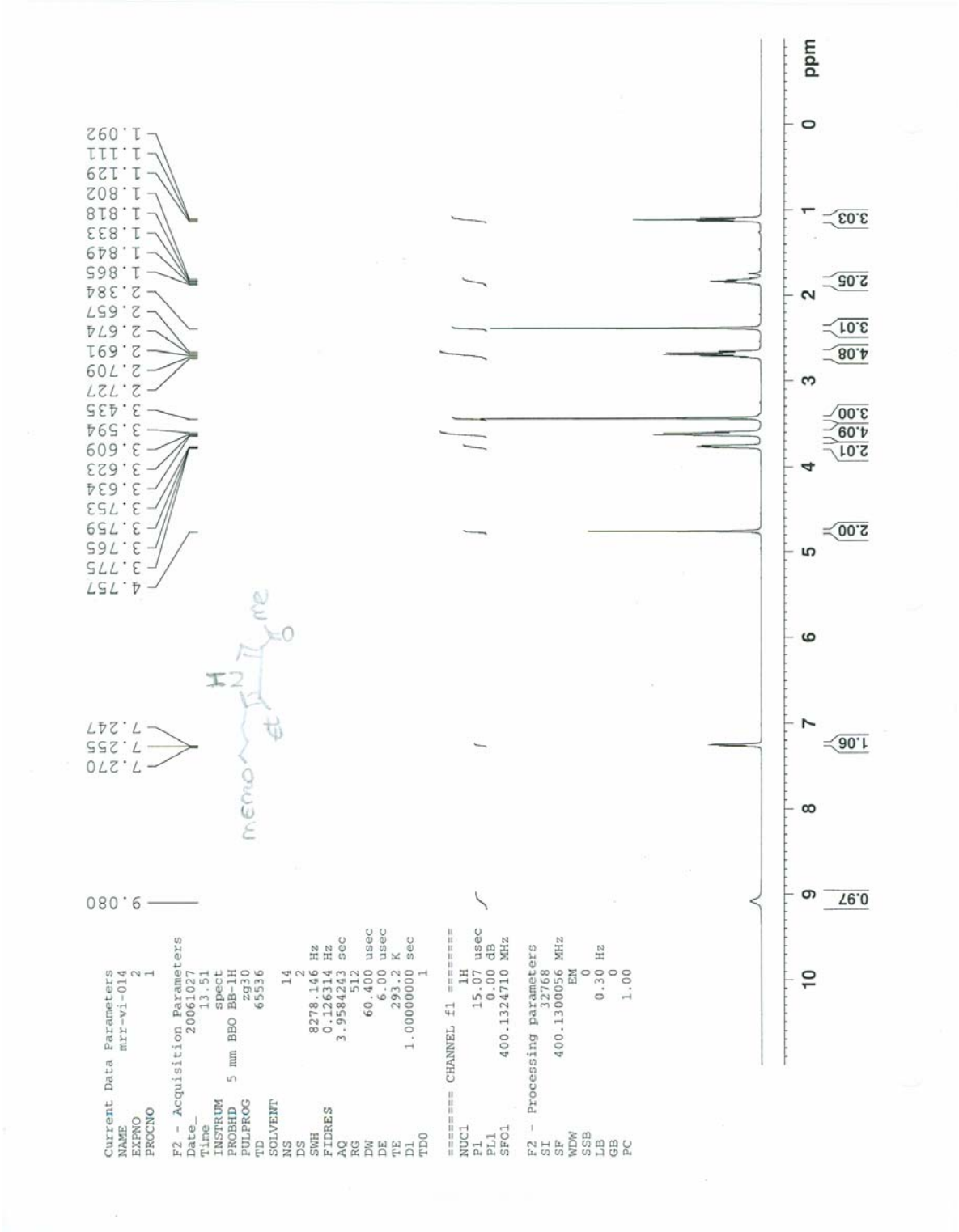
Allyl 4,5-dipropyl-1*H*-pyrrole-3-carboxylate (Table 2, entry 3).



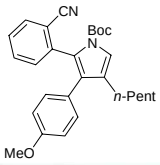


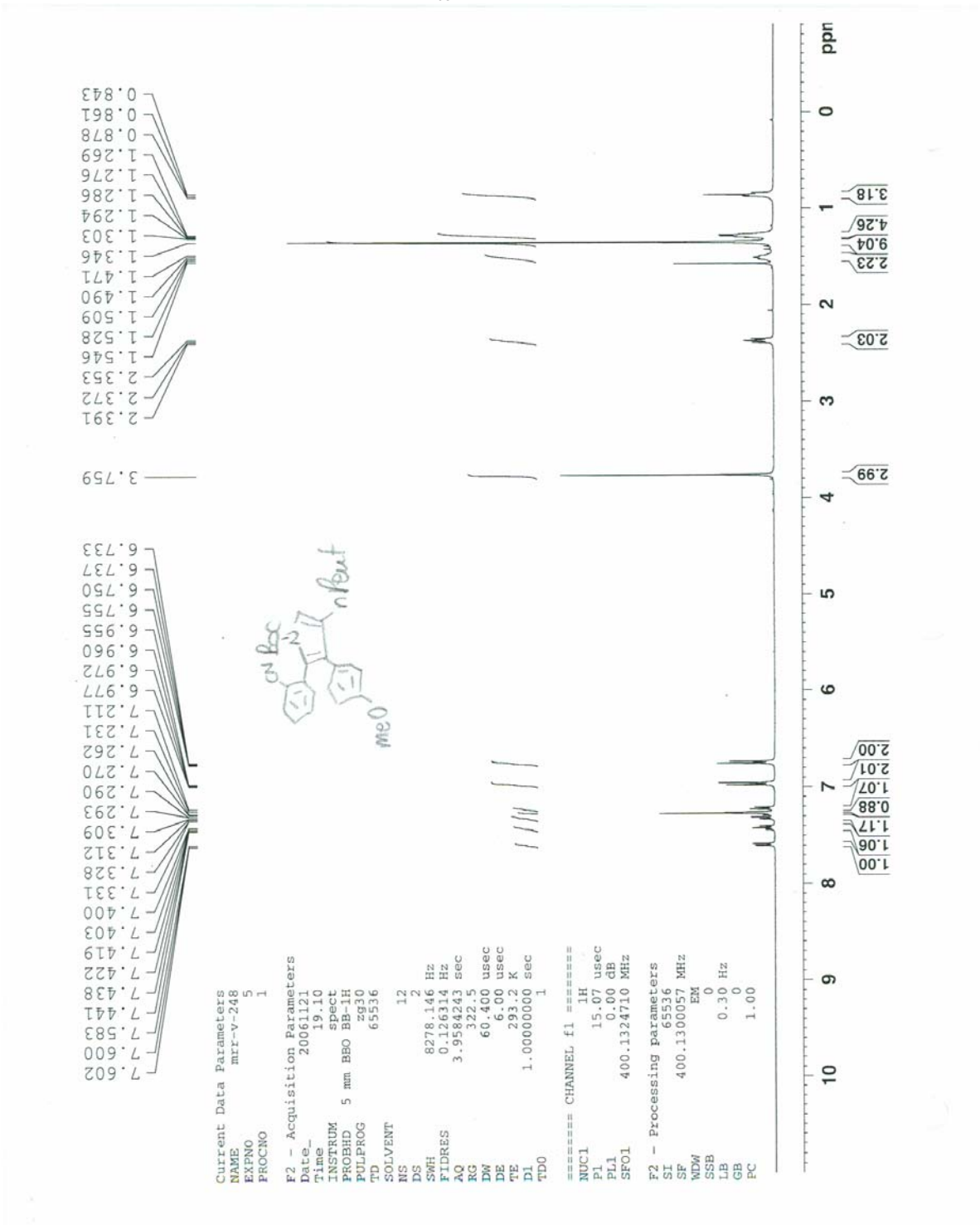
1-(4-Ethyl-5-{3-[(2-methoxyethoxy)methoxy]propyl}-1*H*-pyrrol-3-yl)ethanone (Table 2, entry 4).



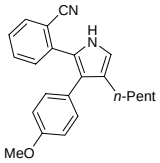


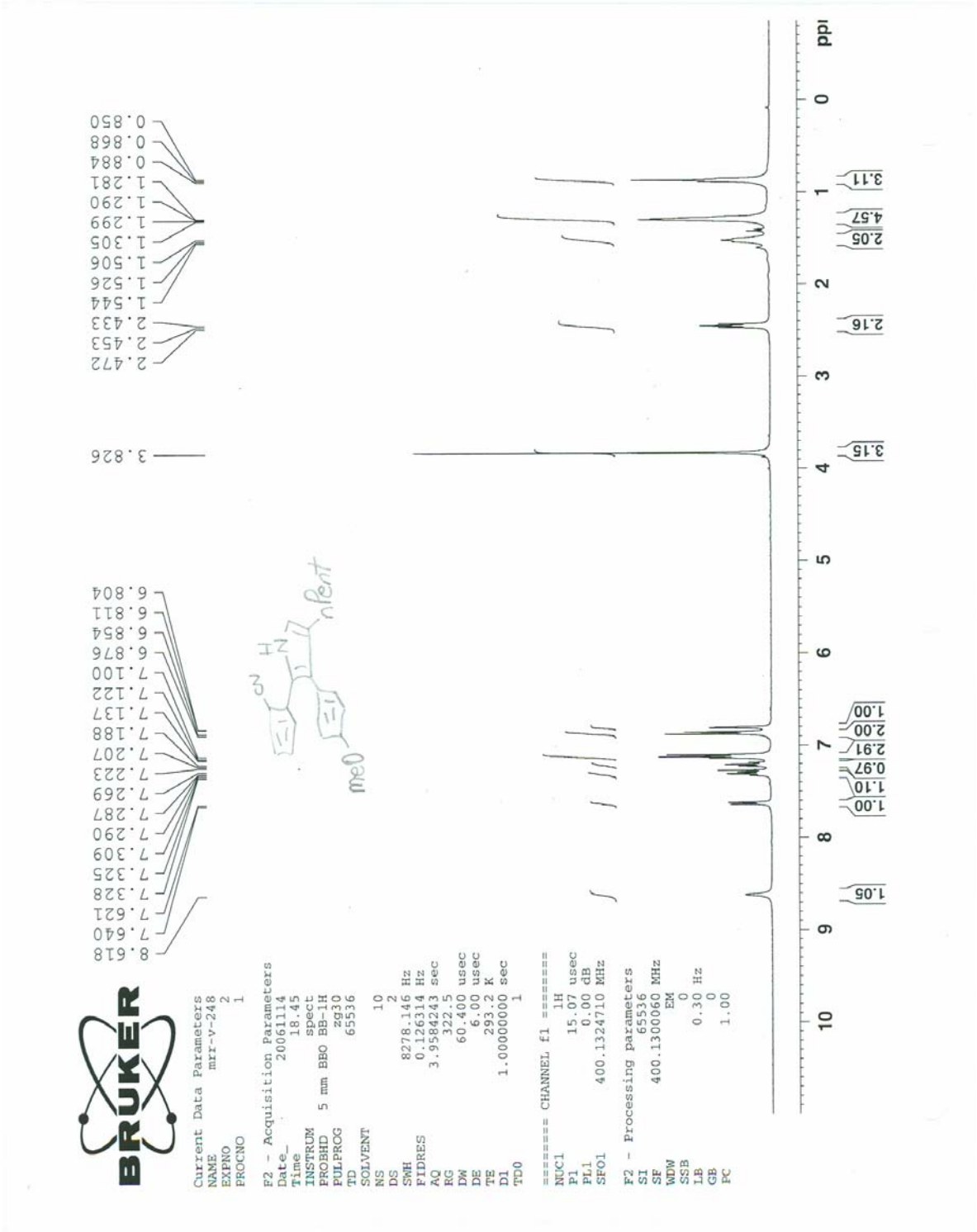
***tert*-Butyl 2-(2-cyanophenyl)-3-(4-methoxyphenyl)-4-pentyl-1*H*-pyrrole-1-carboxylate (Table 2, entry 5).**



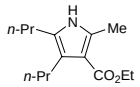


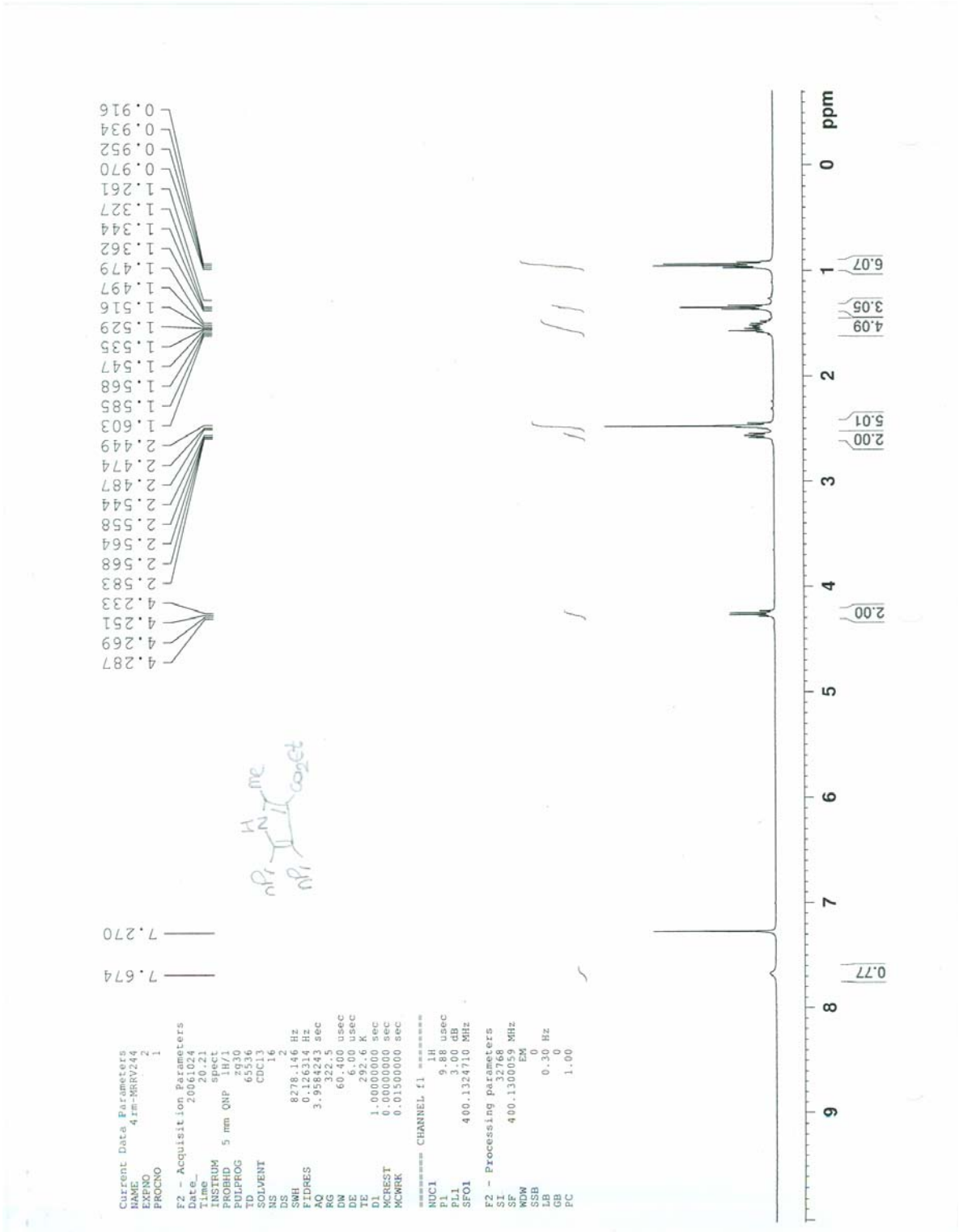
2-[3-(4-Methoxyphenyl)-4-pentyl-1*H*-pyrrol-2-yl]benzonitrile (Table 2, entry 5).



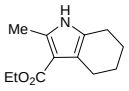


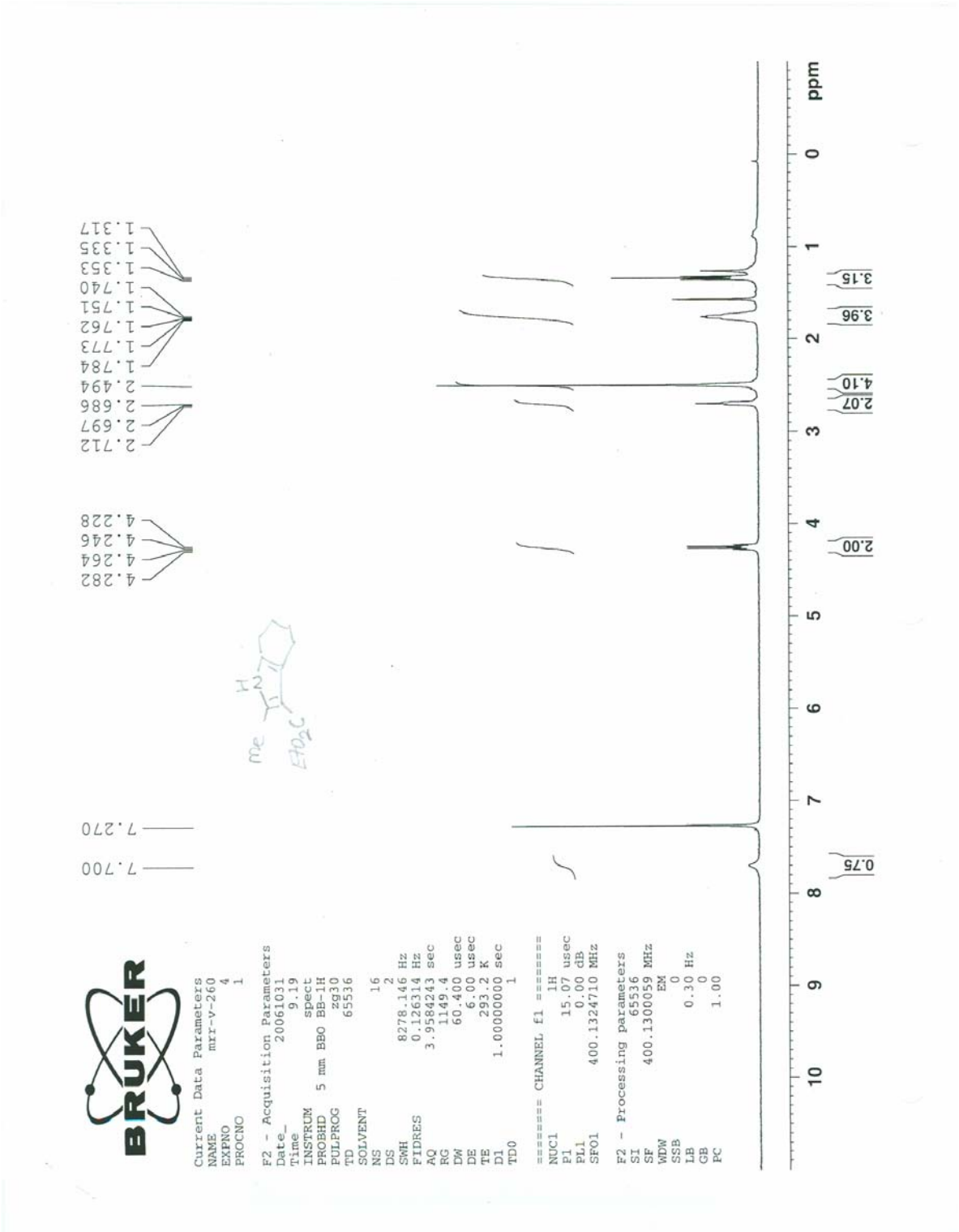
Ethyl 2-methyl-4,5-dipropyl-1*H*-pyrrole-3-carboxylate (Table 2, entry 6).



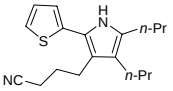


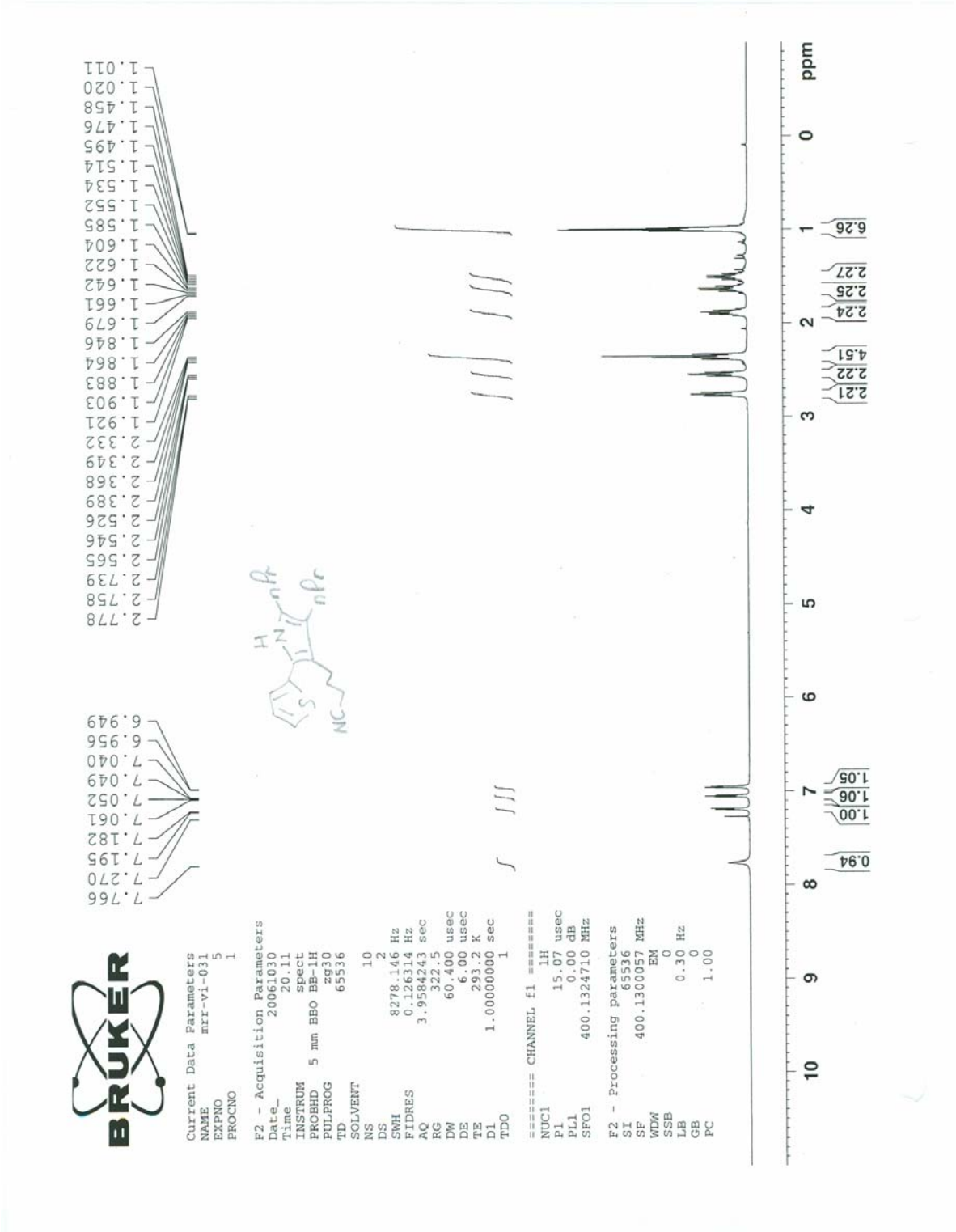
Ethyl 2-methyl-4,5,6,7-tetrahydro-1*H*-indole-3-carboxylate (Table 2, entry 8).

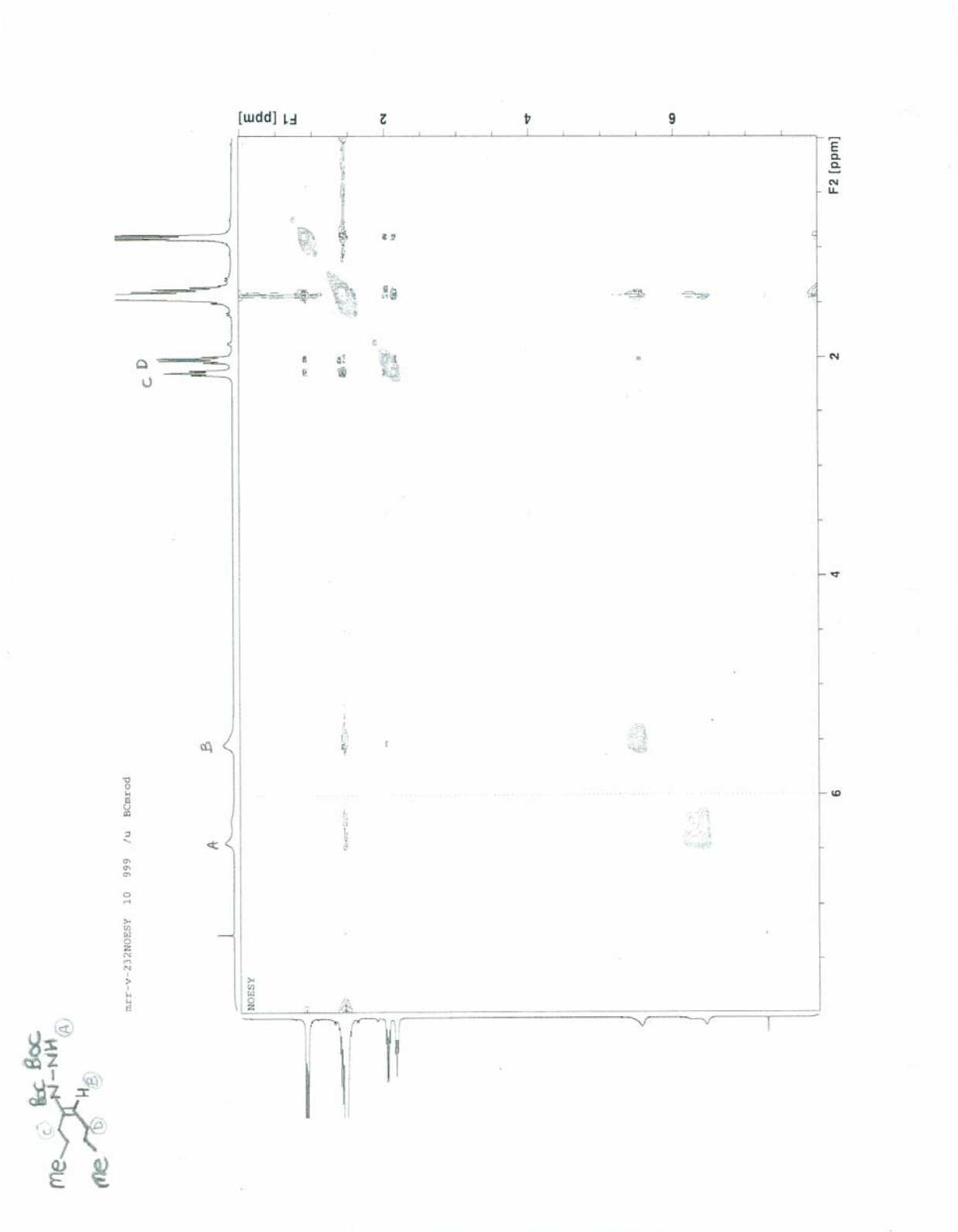




4-[4,5-Dipropyl-2-(2-thienyl)-1*H*-pyrrol-3-yl]butanenitrile (Table 2, entry 12).



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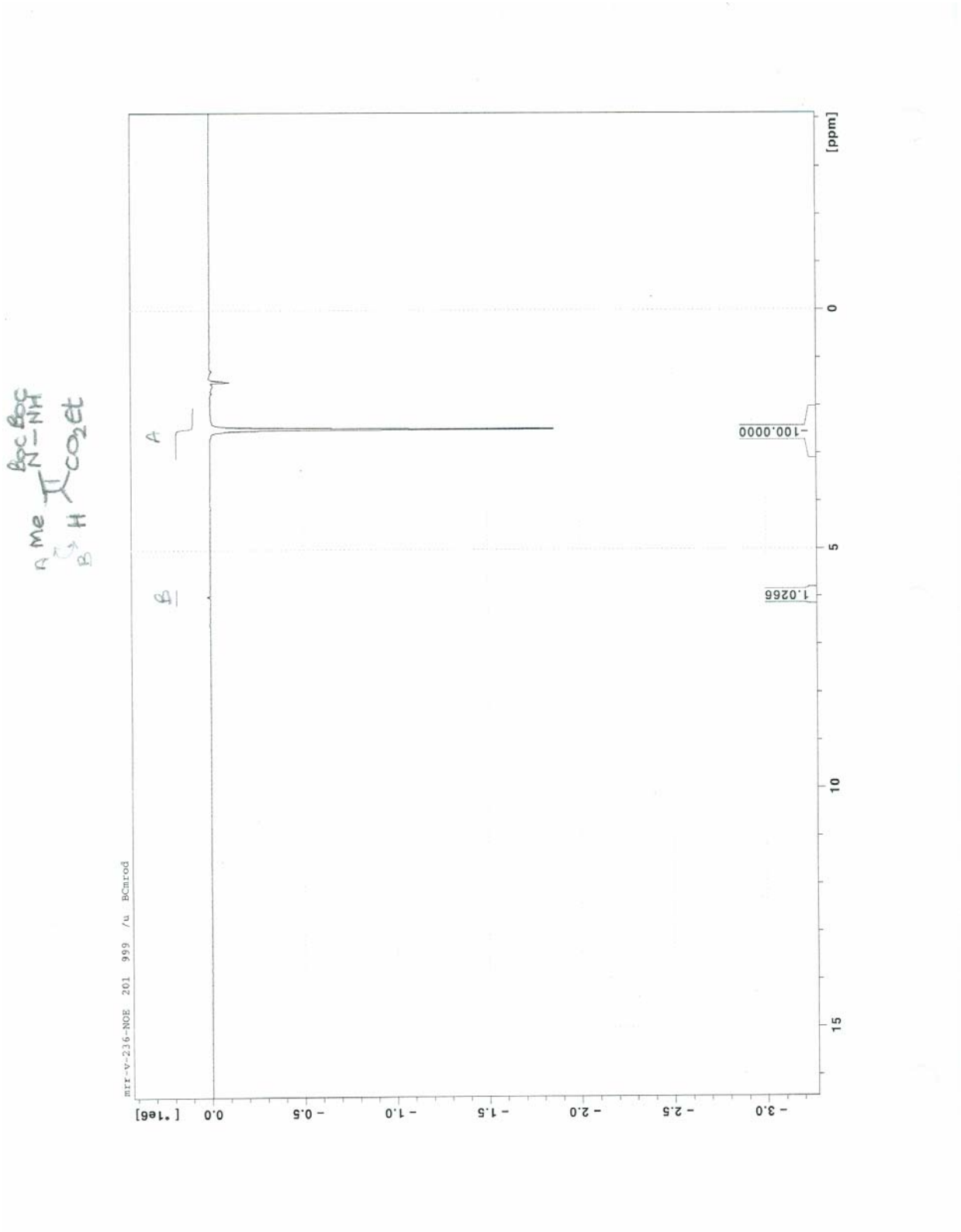
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