

Sonogashira Couplings of Aryl Bromides: Room Temperature, Water Only, No Copper

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Supporting Information

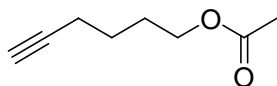
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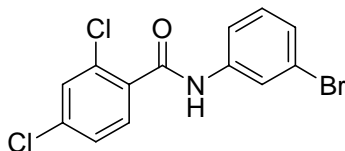
General Information. Reactions were performed in oven-dried glassware containing a Teflon coated stir bar and septum. Pd(dtbpf)Cl₂ (CAS# 95408-45-0) was generously supplied by Johnson Matthey, Neolyst™ CX31 (CAS# 884879-23-6) from Umicore AG & Co. KG., phosphine ligands **12-14** from Takasago, and PTS from Zymes, LLC. These and all other commercially available reagents were used without further purification, except for: Et₃N and CH₂Cl₂ which were distilled from CaH₂ prior to use. Water (HPLC grade) was purchased from Acros and degassed by sparging with argon prior to use. For TLC analyses Kieselgel 60 F₂₅₄ pre-coated silica gel plates (Merck, 0.25 mm thick) were used; and for silica gel chromatography Silia Flash® P60 (SiliCycle, 40-63 µm) was used. GC analyses were performed using Hewlett-Packard HP5890 (with a Restek RTX-1 capillary column) and/or Hewlett-Packard HP6890 (with an Agilent Technologies HP-1 capillary column) gas chromatographs. ¹H and ¹³C NMR spectra were obtained using a Varian UNITY INOVA 400 MHz NMR spectrometer. High-resolution mass spectral analyses were obtained using a VG70 double-focusing magnetic sector instrument (VG Analytical) for EI and a PE Sciex QStar Pulsar quadrupole/TOF instrument (API) for ESI. Melting points were measured using a Laboratory Devices, USA MEL-TEMP II melting point apparatus and are uncorrected.

Preparation of a degassed 3 wt % PTS aqueous solution. To a 50 mL round-bottom flask was added PTS (4.0 g), degassed on a high-vacuum manifold, and back-flushed with argon. Degassed water (36.0 mL) was added via syringe and the contents of the flask were swirled with periodic heating (via heat gun) until a clear, homogeneous solution was afforded (~5-10 min). This stock solution of 10 wt % PTS (0.3 mL) was diluted with *degassed* water (0.7 mL) to give the 3 wt % aqueous PTS solution (1.0 mL) that was used in each experiment.

Preparation of a non-degassed 3 wt % PTS aqueous solution. Same procedure as with the *degassed* PTS solution except the PTS was not degassed and *non-degassed* water was added. The *non-degassed* PTS solution was stored under argon.

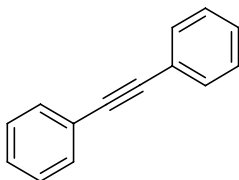


6-Acetoxy-1-hexyne. In a 5 mL round-bottom equipped with a stir bar under argon, Ac₂O (1.0 mL, 10.6 mmol) was added via syringe to a stirring solution of 5-hexyn-1-ol (1.0 mL, 9.07 mmol) and pyridine (860 µL, 10.6 mmol) in CH₂Cl₂ (5.0 mL) and the reaction was allowed to stir at rt. Reaction progress was monitored by GC. After 26 h the mixture was diluted with CH₂Cl₂, washed with water (2x), and the combined aqueous layers were back extracted with CH₂Cl₂ to afford a crude orange liquid after drying over anhydrous Na₂SO₄ and concentration by rotary evaporation. Kugelrohr distillation (0.1 mm Hg, 90-105 °C) of the crude material provided the titled product (1.01 g, 79%) as a clear colorless liquid; ¹H NMR (400 MHz, CDCl₃) matches previously reported spectra data.¹

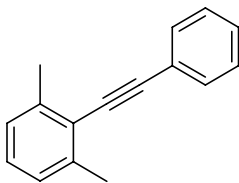


N-(3'-Bromophenyl)-2,4-dichlorobenzamide (15; Scheme 4). In a 25 mL round-bottom flask equipped with a stir bar under argon at 0 °C, 3,5-dichlorobenzoyl chloride (520 µL, 3.71 mmol) was

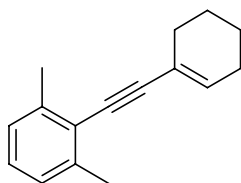
added via syringe to a stirring solution of 3-bromoaniline (400 μ L, 3.67 mmol) and Et₃N (1.0 mL, 7.18 mmol) in CH₂Cl₂ (7.0 mL) and the reaction was allowed to stir while gradually warming to rt. Reaction progress was monitored by TLC. After 35 min, the mixture was diluted with CH₂Cl₂ and washed with water (3x), the organic layer was dried over anhydrous Na₂SO₄ and concentrated by rotary evaporation. The crude material was purified by silica gel chromatography (eluent: gradient from hexanes to 8% ethyl acetate/hexanes) to afford the titled product (1.16 g, 92%) as a white solid; mp 125-127 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.94 (brs, 1H), 7.90 (s, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 2.0 Hz, 1H), 7.38 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.32 (dt, *J* = 8.4, 1.2 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 163.71, 138.71, 137.74, 133.18, 131.66 (2C), 130.65, 130.45, 128.26, 128.02, 123.27, 122.98, 118.80; HRESI-MS *m/z* Calcd. for C₁₃H₈BrCl₂NO ([M+Na]⁺) 365.9058, found 365.9042.



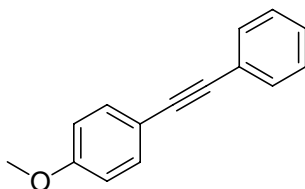
Standard Procedure A for Sonogashira Coupling: Diphenylacetylene (Scheme 2). To a 5 mL round-bottom flask equipped with a stir bar was added under argon Pd(CH₃CN)₂Cl₂ (1.3 mg, 0.005 mmol), X-Phos (5.8 mg, 0.012 mmol), and Cs₂CO₃ (543 mg, 1.66 mmol). Under a positive flow of argon were added via syringe first, *degassed* PTS solution (1.0 mL, 3 wt %), then bromobenzene (50.0 μ L, 0.48 mmol), and then phenylacetylene (60.0 μ L, 0.55 mmol). A milky, tan-colored mixture developed over 3 h while stirring at rt. Reaction progress was monitored by GC. After 4.5 h the mixture was diluted with brine and extracted with ethyl acetate (4x). The combined organic extracts was dried over anhydrous Na₂SO₄, filtered, and concentrated by rotary evaporation to give a crude brown oil. Purification by silica gel chromatography eluting with hexanes afforded the titled product (70 mg, 83%) as a light yellow solid; mp 58-60 °C; ¹H NMR (400 MHz, CDCl₃) matches previously reported spectra data.²



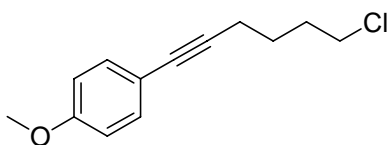
2,6-Dimethylphenylphenylacetylene (Table 1, entry 1a). Following standard procedure A, using Pd(CH₃CN)₂Cl₂ (1.5 mg, 0.006 mmol), X-Phos (6.4 mg, 0.013 mmol), Cs₂CO₃ (601 mg, 1.84 mmol), 2-bromo-*m*-xylene (70 μ L, 0.52 mmol), phenylacetylene (90 μ L, 0.82 mmol), and *degassed* PTS (1.0 mL, 3 wt %) for 20 h, the titled product (107 mg, 99%) was obtained as a colorless oil after silica gel chromatography (eluent: hexanes); ¹H NMR (400 MHz, CDCl₃) matches previously reported spectra data.³



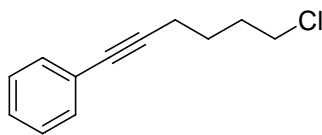
Standard Procedure B for Sonogashira Coupling: 2-(cyclohex-1-enylethynyl)-1,3-dimethylbenzene (Table 1, entry 1b). To a 5 mL round-bottom flask equipped with a stir bar was added under argon Pd(CH₃CN)₂Cl₂ (1.8 mg, 0.007 mmol) and X-Phos (6.9 mg, 0.014 mmol). Under a positive flow of argon were added via syringe, first *degassed* PTS solution (1.0 mL, 3 wt %), then Et₃N (150 μL, 1.08 mmol), then 2-bromo-*m*-xylene (70 μL, 0.52 mmol), and finally 1-ethynylcyclohexene (100 μL, 0.85 mmol). A milky brown mixture developed over 20 min while stirring at rt. Reaction progress was monitored by GC. After 23 h the mixture was diluted with brine and extracted with ethyl acetate (4x). The combined organic extracts was dried over anhydrous Na₂SO₄, filtered, and concentrated by rotary evaporation to give a crude brown oil that was purified by silica gel chromatography eluting with hexanes afforded the titled product (110 mg, quant) as a colorless oil; ¹H NMR (400 MHz, CDCl₃) matches previously reported spectra data.⁴



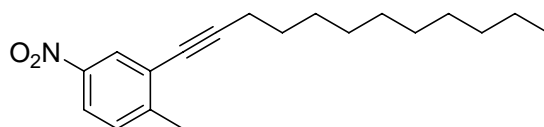
4-(Phenylethynyl)-anisole (Table 1, entry 2a). Following standard procedure A, using Pd(CH₃CN)₂Cl₂ (1.5 mg, 0.006 mmol), X-Phos (7.0 mg, 0.015 mmol), Cs₂CO₃ (548 mg, 1.68 mmol), 4-bromoanisole (60 μL, 0.48 mmol), phenylacetylene (70 μL, 0.64 mmol), and *degassed* PTS (1.0 mL, 3 wt %) for 20 h, the titled product (89 mg, 89%) was obtained as a yellow-tan solid after silica gel chromatography (eluent: hexanes); mp 57-59 °C; ¹H NMR (400 MHz, CDCl₃) matches previously reported spectra data.²



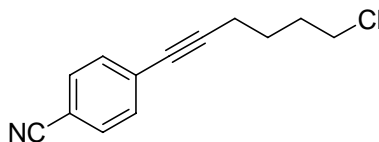
4-(6-Chlorohex-1-ynyl)-anisole (Table 1, entry 2b). Following standard procedure B, using Pd(CH₃CN)₂Cl₂ (1.3 mg, 0.005 mmol), X-Phos (6.0 mg, 0.012 mmol), Et₃N (140 μL, 1.00 mmol), 4-bromoanisole (60 μL, 0.48 mmol), 6-chloro-1-hexyne (90 μL, 0.74 mmol), and *degassed* PTS (1.0 mL, 3 wt %) for 25 h, the titled product (59 mg, 55%) was obtained as a yellow oil after silica gel chromatography (eluent: hexanes); ¹H NMR (400 MHz, CDCl₃) δ 7.34 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 3.62 (t, *J* = 6.6 Hz, 2H), 2.46 (t, *J* = 7.0 Hz, 2H), 2.01-1.94 (m, 2H), 1.80-1.72 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 159.29, 133.08, 116.09, 114.02, 87.84, 81.10, 55.46, 44.86, 31.83, 26.17, 18.92; HREI-MS *m/z* Calcd. for C₁₃H₁₅ClO (M⁺) 222.0811, found 222.0811.



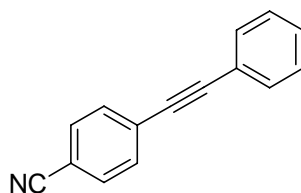
6-Chloro-1-phenylhex-1-yne (Table 1, entry 3). Following standard procedure B, using $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (1.3 mg, 0.005 mmol), X-Phos (6.2 mg, 0.013 mmol), Et_3N (140 μL , 1.00 mmol), bromobenzene (50 μL , 0.48 mmol), 6-chloro-1-hexyne (90 μL , 0.74 mmol), and *degassed* PTS (1.0 mL, 3 wt %) for 20 h, the titled product (75 mg, 82%) was obtained as a colorless oil after silica gel chromatography (eluent: hexanes); ^1H NMR (400 MHz, CDCl_3) matches previously reported spectra data.⁵



2-(Dodec-1-ynyl)-4-nitrotoluene (Table 1, entry 4). Following standard procedure B, using $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (1.6 mg, 0.006 mmol), X-Phos (6.4 mg, 0.013 mmol), Et_3N (150 μL , 1.08 mmol), 2-bromo-4-nitrotoluene (109 mg, 0.50 mmol), 1-dodecyne (140 μL , 0.65 mmol), and *degassed* PTS (1.0 mL, 3 wt %) for 18 h, the titled product (150 mg, 99%) was obtained as a yellow oil after silica gel chromatography (eluent: hexanes); ^1H NMR (400 MHz, CDCl_3) δ 8.20 (d, J = 2.4 Hz, 1H), 8.00 (dd, J = 8.4, 2.4 Hz, 1H), 7.32 (d, J = 8.8 Hz, 1H), 2.50 (s, 3H), 2.47 (t, J = 7.2 Hz, 2H), 1.67-1.60 (m, 2H), 1.49-1.44 (m, 2H), 1.32-1.28 (m, 12H), 0.88 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.75, 146.15, 130.19, 126.82, 125.62, 122.30, 97.60, 77.77, 32.11, 29.79, 29.74, 29.53, 29.34, 29.12, 28.80, 22.90, 21.26, 19.69, 14.33; HREI-MS m/z Calcd. for $\text{C}_{19}\text{H}_{27}\text{NO}_2$ (M^+) 301.2042, found 301.2051.

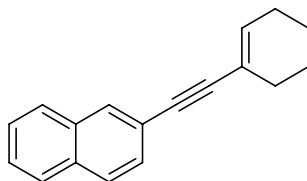


4-(6-Chlorohex-1-ynyl)benzonitrile (Table 1, entry 5a). Following standard procedure A, using $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (1.3 mg, 0.005 mmol), X-Phos (6.6 mg, 0.014 mmol), Cs_2CO_3 (574 mg, 1.76 mmol), 4-bromobenzonitrile (92 mg, 0.51 mmol), 6-chloro-1-hexyne (90 μL , 0.74 mmol), and *degassed* PTS (1.0 mL, 3 wt %) for 6 h, the titled product (102 mg, 93%) was obtained as a light yellow oil after silica gel chromatography (eluent: hexanes); ^1H NMR (400 MHz, CDCl_3) δ 7.58 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 3.61 (t, J = 6.6 Hz, 2H), 2.50 (t, J = 7.0 Hz, 2H), 1.99-1.92 (m, 2H), 1.82-1.75 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 132.29, 132.14, 128.97, 118.80, 111.16, 94.61, 80.17, 44.63, 31.77, 25.78, 19.03; HREI-MS m/z Calcd. for $\text{C}_{13}\text{H}_{12}\text{ClN}$ (M^+) 217.0658, found 217.0668.

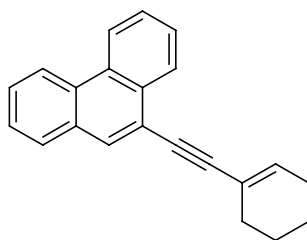


4-(Phenylethynyl)benzonitrile (Table 1, entry 5b). Following standard procedure A, using $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (1.5 mg, 0.006 mmol), X-Phos (6.6 mg, 0.014 mmol), Cs_2CO_3 (574 mg, 1.76 mmol), 4-

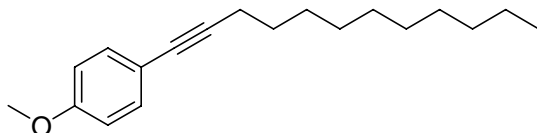
bromobenzonitrile (92 mg, 0.51 mmol), phenylacetylene (80 μ L, 0.73 mmol), and *degassed* PTS (1.0 mL, 3 wt %) for 4 h, the titled product (100 mg, 97%) was obtained as a light yellow solid after silica gel chromatography (eluent: gradient from hexanes to 1% diethyl ether/hexanes); mp 102-104 $^{\circ}$ C; 1 H NMR (400 MHz, CDCl_3) matches previously reported spectra data.³



2-(Cyclohex-1-enylethynyl)naphthalene (Table 1, entry 6). Following standard procedure B, using $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (1.3 mg, 0.005 mmol), X-Phos (6.9 mg, 0.014 mmol), Et_3N (150 μ L, 1.08 mmol), 2-bromonaphthalene (103 mg, 0.50 mmol), 1-ethynylcyclohexene (100 μ L, 0.85 mmol), and *degassed* PTS (1.0 mL, 3 wt %) for 21 h, the titled product (97 mg, 84%) was obtained as an off-white solid after silica gel chromatography (eluent: hexanes); mp 45-47 $^{\circ}$ C; 1 H NMR (400 MHz, CDCl_3) δ 7.95 (s, 1H), 7.82-7.76 (m, 3H), 7.50-7.45 (m, 3H), 6.28 (m, 1H), 2.30-2.26 (m, 2H), 2.21-2.16 (m, 2H), 1.75-1.62 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 135.65, 133.24, 132.74, 131.22, 128.73, 128.04, 127.92, 127.89, 126.62, 126.58, 121.27, 120.95, 91.86, 87.38, 29.46, 26.03, 22.56, 21.73; HREI-MS m/z Calcd. for $\text{C}_{18}\text{H}_{16}$ (M^+) 232.1252, found 232.1252.

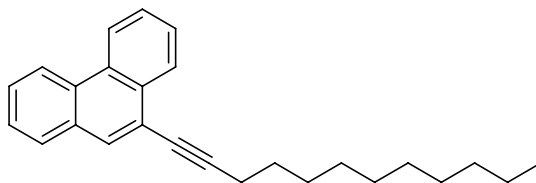


9-(Cyclohex-1-enylethynyl)phenanthrene (Table 1, entry 7). Following standard procedure B, using $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ (2.0 mg, 0.008 mmol), X-Phos (10.0 mg, 0.021 mmol), Et_3N (150 μ L, 1.08 mmol), 9-bromophenanthrene (129 mg, 0.50 mmol), 1-ethynylcyclohexene (100 μ L, 0.85 mmol), and *degassed* PTS (1.0 mL, 3 wt %) for 21 h, the titled product (133 mg, 98%) was obtained as a bright yellow solid after silica gel chromatography (eluent: hexanes); mp 105-107 $^{\circ}$ C; 1 H NMR (400 MHz, CDCl_3) δ 8.70-8.65 (m, 2H), 8.47-8.44 (m, 1H), 7.98 (s, 1H), 7.85 (d, J = 7.2 Hz, 1H), 7.72-7.58 (m, 4H), 6.39 (m, 1H), 2.39 (m, 2H), 2.23 (m, 2H), 1.80-1.68 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 135.79, 131.56, 131.41, 130.26, 128.64, 127.36, 127.20, 127.14, 127.07, 122.90, 122.77, 121.10, 120.31, 96.20, 85.25, 29.59, 26.07, 22.59, 21.76; HREI-MS m/z Calcd. for $\text{C}_{22}\text{H}_{18}$ (M^+) 282.1408, found 282.1417.

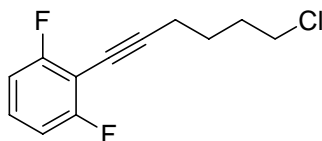


Standard Procedure C for Sonogashira Coupling: 4-(dodec-1-ynyl)-anisole (Table 2). To a 5 mL round-bottom flask equipped with a stir bar was added under argon $\text{Pd}(\text{OAc})_2$ (1.4 mg, 0.006 mmol) and **14** (4.1 mg, 0.012 mmol). Under a positive flow of argon were each added via syringe first *non-degassed* PTS solution (1.0 mL, 3 wt %), then Et_3N (200 μ L, 1.44 mmol), 4-bromoanisole (60 μ L, 0.48 mmol), and 1-dodecyne (160 μ L, 0.74 mmol). A milky, tan-colored mixture developed over 30 min

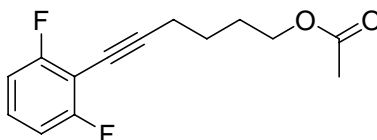
while stirring at rt. Reaction progress was monitored by GC. After 10 h the mixture was diluted with brine and extracted with ethyl acetate (4x). The combined organic extracts were dried over anhydrous Na_2SO_4 , filtered, and concentrated by rotary evaporation to give a crude brown oil that was purified by silica gel chromatography eluting with hexanes afforded the titled product (125 mg, 96%) as a light yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.34 (d, J = 8.8 Hz, 2H), 6.82 (d, J = 8.8 Hz, 2H), 3.81 (s, 3H), 2.39 (t, J = 7.0 Hz, 2H), 1.64-1.57 (m, 2H), 1.45 (m, 2H), 1.29 (brs, 12H), 0.90 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.14, 133.04, 116.45, 113.96, 89.03, 80.40, 55.43, 32.14, 29.81, 29.78, 29.56, 29.40, 29.16, 29.09, 22.91, 19.62, 14.35; HREI-MS m/z Calcd. for $\text{C}_{19}\text{H}_{28}\text{O}$ (M^+) 272.2140, found 272.2138.



9-(Dodec-1-ynyl)phenanthrene (Scheme 3). Following standard procedure C, using $\text{Pd}(\text{OAc})_2$ (1.7 mg, 0.008 mmol), **14** (7.2 mg, 0.020 mmol), Et_3N (200 μL , 1.44 mmol), 9-bromophenanthrene (128 mg, 0.50 mmol), 1-dodecyne (160 μL , 0.74 mmol), and *degassed* PTS (1.0 mL, 3 wt %) for 4 h, the titled product (140 mg, 82%) was obtained as a light yellow solid after silica gel chromatography (eluent: hexanes); mp 40-42 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.70-8.65 (m, 2H), 8.49-8.46 (m, 1H), 7.95 (s, 1H), 7.84 (dd, J = 8.0, 1.2 Hz, 1H), 7.72-7.57 (m, 4H), 2.61 (t, J = 7.2 Hz, 2H), 1.79-1.72 (m, 2H), 1.61-1.54 (m, 2H), 1.39-1.30 (m, 12H), 0.90 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 131.74, 131.59, 131.38, 130.28, 130.13, 128.51, 127.22 (2C), 127.07, 127.03, 122.89, 122.76, 120.66, 95.49, 78.91, 32.14, 29.81 (2C), 29.58, 29.43, 29.29, 29.13, 22.92, 19.98, 14.35; HREI-MS m/z Calcd. for $\text{C}_{26}\text{H}_{30}$ (M^+) 342.2348, found 342.2354.

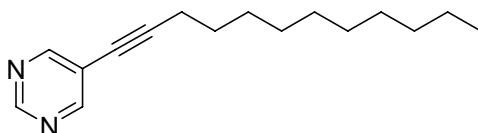


2-(6-Chlorohex-1-ynyl)-1,3-difluorobenzene (Scheme 3). Following standard procedure C, using $\text{Pd}(\text{OAc})_2$ (1.2 mg, 0.005 mmol), **14** (4.2 mg, 0.012 mmol), Et_3N (220 μL , 1.58 mmol), 1-bromo-2,6-difluorobenzene (60 μL , 0.53 mmol), 6-chloro-1-hexyne (110 μL , 0.91 mmol), and *degassed* PTS (1.0 mL, 3 wt %) for 4 h, the titled product (100 mg, 82%) was isolated as a colorless oil after silica gel chromatography (eluent: hexanes); ^1H NMR (400 MHz, CDCl_3) δ 7.25-7.18 (m, 1H), 6.92-6.86 (m, 2H), 3.63 (t, J = 6.6 Hz, 2H), 2.56 (t, J = 6.8 Hz), 2.04-1.96 (m, 2H), 1.85-1.78 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.73, 162.22, 129.11 (t, J = 9.9 Hz), 111.26 (dd, J = 19.0, 5.3 Hz), 100.14, 68.33, 44.76, 31.62, 25.73, 19.25; HREI-MS m/z Calcd. for $\text{C}_{12}\text{H}_{11}\text{ClF}_2$ (M^+) 228.0517, found 228.0517.

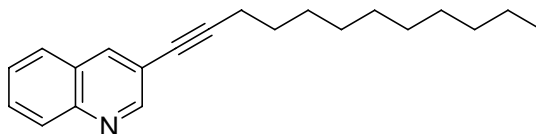


2-(6-Acetoxihex-1-ynyl)-1,3-difluorobenzene (Scheme 3). Following standard procedure C, using $\text{Pd}(\text{OAc})_2$ (1.2 mg, 0.005 mmol), **14** (4.2 mg, 0.012 mmol), Et_3N (220 μL , 1.58 mmol), 1-bromo-2,6-

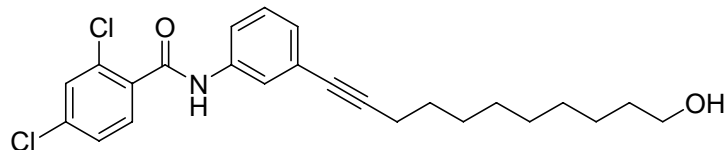
difluorobenzene (60 μ L, 0.53 mmol), 6-acetoxy-1-hexyne (130 μ L, 0.88 mmol), and *degassed* PTS (1.0 mL, 3 wt %) for 5 h, the titled product (132 mg, 98%) was obtained as a colorless oil after silica gel chromatography (eluent: gradient from hexanes to 3% ethyl acetate/hexanes); ^1H NMR (400 MHz, CDCl_3) δ 7.25-7.17 (m, 1H), 6.92-6.85 (m, 2H), 4.13 (t, J = 6.4 Hz, 2H), 2.55 (t, J = 6.8 Hz, 2H), 2.07 (s, 3H), 1.88-1.81 (m, 2H), 1.76-1.69 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.43, 164.73, 162.17, 129.05 (t, J = 9.9 Hz), 111.25 (dd, J = 18.6, 5.7 Hz), 100.35, 68.18, 64.19, 27.89, 25.14, 21.21, 19.65; HREI-MS m/z Calcd. for $\text{C}_{14}\text{H}_{14}\text{F}_2\text{O}_2$ (M^+) 252.0962, found 252.0961.



5-(Dodec-1-ynyl)pyrimidine (Scheme 3). Following standard procedure C, using $\text{Pd}(\text{OAc})_2$ (1.2 mg, 0.005 mmol), **14** (4.0 mg, 0.011 mmol), Et_3N (210 μ L, 1.51 mmol), 5-bromopyrimidine (81 mg, 0.51 mmol), 1-dodecyne (170 μ L, 0.79 mmol), and *non-degassed* PTS (1.0 mL, 3 wt %) for 6 h, the titled product (100 mg, 81%) was obtained as a golden oil after silica gel chromatography (eluent: gradient from hexanes to 2% ethyl acetate/hexanes); ^1H NMR (400 MHz, CDCl_3) δ 9.08 (s, 1H), 8.72 (s, 2H), 2.45 (t, J = 7.2 Hz, 2H), 1.66-1.59 (m, 2H), 1.46-1.41 (m, 2H), 1.38-1.27 (m, 12H), 0.88 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.94, 156.38, 120.78, 98.52, 74.16, 32.10, 29.78, 29.72, 29.52, 29.31, 29.12, 28.54, 22.90, 19.72, 14.34; HREI-MS m/z Calcd. for $\text{C}_{16}\text{H}_{24}\text{N}_2$ (M^+) 244.1939, found 244.1937.



3-(Dodec-1-ynyl)quinoline (Scheme 3). Following standard procedure C, using $\text{Pd}(\text{OAc})_2$ (1.2 mg, 0.005 mmol), **14** (4.2 mg, 0.012 mmol), Et_3N (220 μ L, 1.58 mmol), 3-bromoquinoline (70 μ L, 0.52 mmol), 1-dodecyne (180 μ L, 0.83 mmol), and *non-degassed* PTS (1.0 mL, 3 wt %) for 4 h, the titled product (148 mg, 98%) was isolated as an yellow oil after silica gel chromatography (eluent: gradient from hexanes to 1% ethyl acetate/hexanes); ^1H NMR (400 MHz, CDCl_3) δ 8.88 (d, J = 2.0 Hz, 1H), 8.16 (d, J = 1.6 Hz, 1H), 8.07 (d, J = 8.4 Hz, 1H), 7.75 (d, J = 8.4 Hz, 1H), 7.69 (td, J = 8.4, 1.6 Hz, 1H), 7.54 (td, J = 8.4, 1.2 Hz, 1H), 2.48 (t, J = 7.2 Hz, 2H), 1.69-1.62 (m, 2H), 1.50-1.44 (m, 2H), 1.40-1.19 (m, 12H), 0.88 (t, J = 6.6 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 152.72, 146.66, 138.12, 129.80, 129.47, 127.59, 127.53, 127.27, 118.43, 94.38, 78.09, 32.10, 29.79, 29.74, 29.53, 29.36, 29.17, 28.80, 22.89, 19.75, 14.32; HREI-MS m/z Calcd. for $\text{C}_{21}\text{H}_{27}\text{N}$ (M^+) 293.2144, found 293.2136.



2,4-Dichloro-N-(3'-(11-hydroxyundec-1-ynyl)phenyl)benzamide (16; Scheme 4). Following standard procedure C (monitored by TLC) using $\text{Pd}(\text{OAc})_2$ (3.6 mg, 0.016 mmol), **14** (11.3 mg, 0.032 mmol), Et_3N (210 μ L, 1.51 mmol), **15** (173 mg, 0.50 mmol), (160 μ L, 0.84 mmol), and *non-degassed* PTS (1.0 mL, 3 wt %) for 6 h, the titled product (169 mg, 78%) was obtained as a colorless oil that crystallizes to a white solid upon standing at rt after silica gel chromatography (eluent: gradient from

hexanes to 20% ethyl acetate/hexanes); mp 65-67 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.06 (brs, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.61 (brd, *J* = 9.2 Hz, 2H), 7.47-7.44 (m, 1H), 7.36 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 3.62 (t, *J* = 6.6 Hz, 2H), 2.41 (t, *J* = 7.0 Hz, 2H), 1.64-1.54 (m, 4H), 1.47-1.44 (m, 2H), 1.33 (brs, 8H); ¹³C NMR (100 MHz, CDCl₃) δ 163.75, 137.48, 133.62, 131.66, 131.60, 130.38, 129.24, 128.36, 127.95, 125.24, 123.21, 119.61, 91.38, 80.23, 63.26, 32.95, 29.57, 29.46, 29.14, 28.97, 28.75, 25.87, 19.56; HREI-MS *m/z* calcd. for C₂₄H₂₇Cl₂NO₂ (M⁺) 431.1419, found 431.1411.

¹ Sharma, S.; Oehlschlager, A. C. *J. Org. Chem.* **1989**, *54*, 5064–5073.

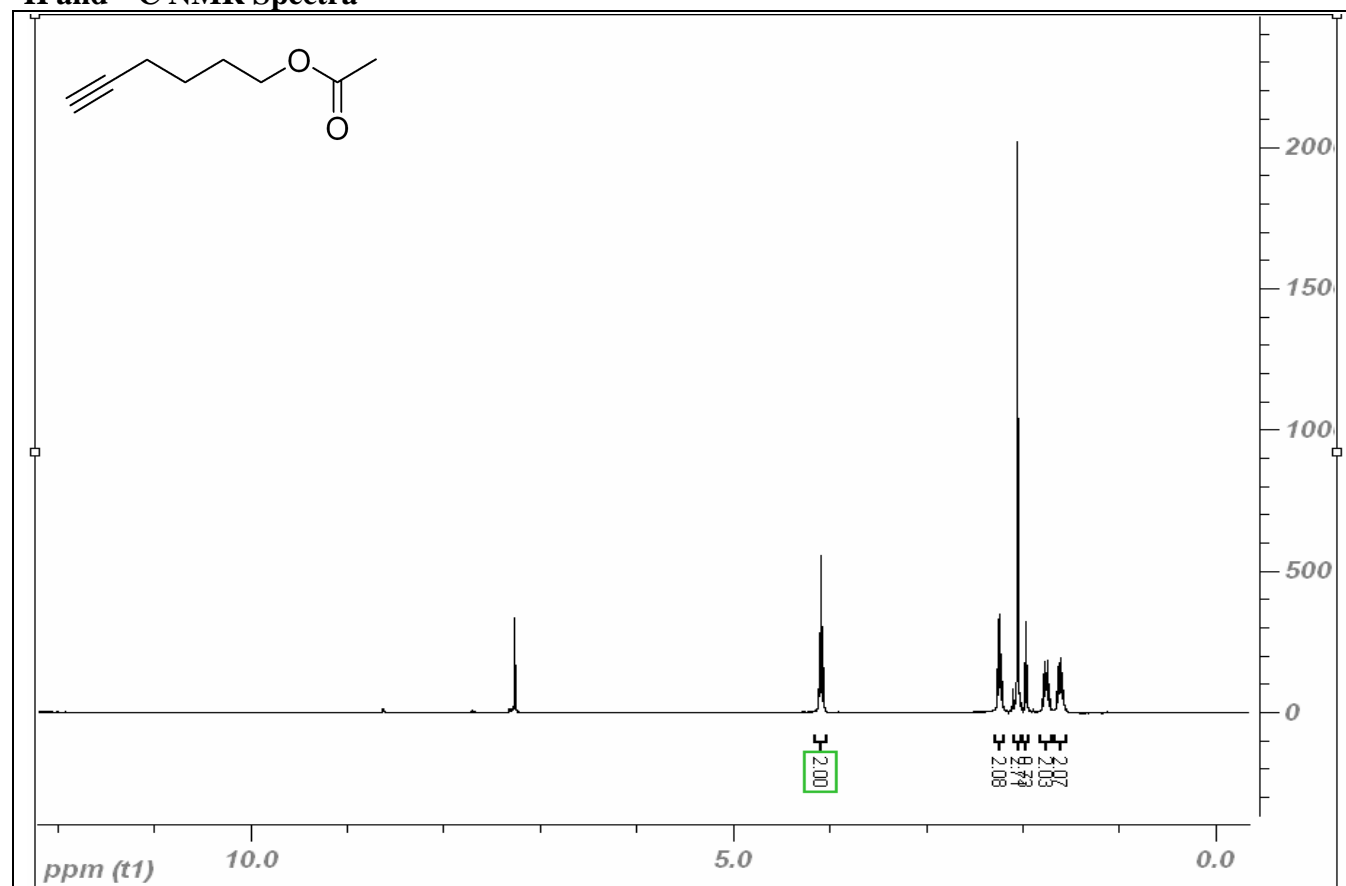
² Ma, Y.; Song, C.; Jian, W.; Wu, Q.; Wang, Y.; Liu, X.; Andrus, M. B. *Org. Lett.* **2003**, *5*, 3317–3319.

³ Hundertmark, T.; Littke, A. F.; Buchwald, S. L.; Fu, G. C. *Org. Lett.* **2000**, *2*, 1729–1731.

⁴ Gelman, D.; Buchwald, S. L. *Angew. Chem. Int. Ed.* **2003**, *42*, 5993–5996 and references cited therein.

⁵ Yus, M.; Ortiz, R.; Huerta, F. F. *Tetrahedron* **2003**, *59*, 8525–8542.

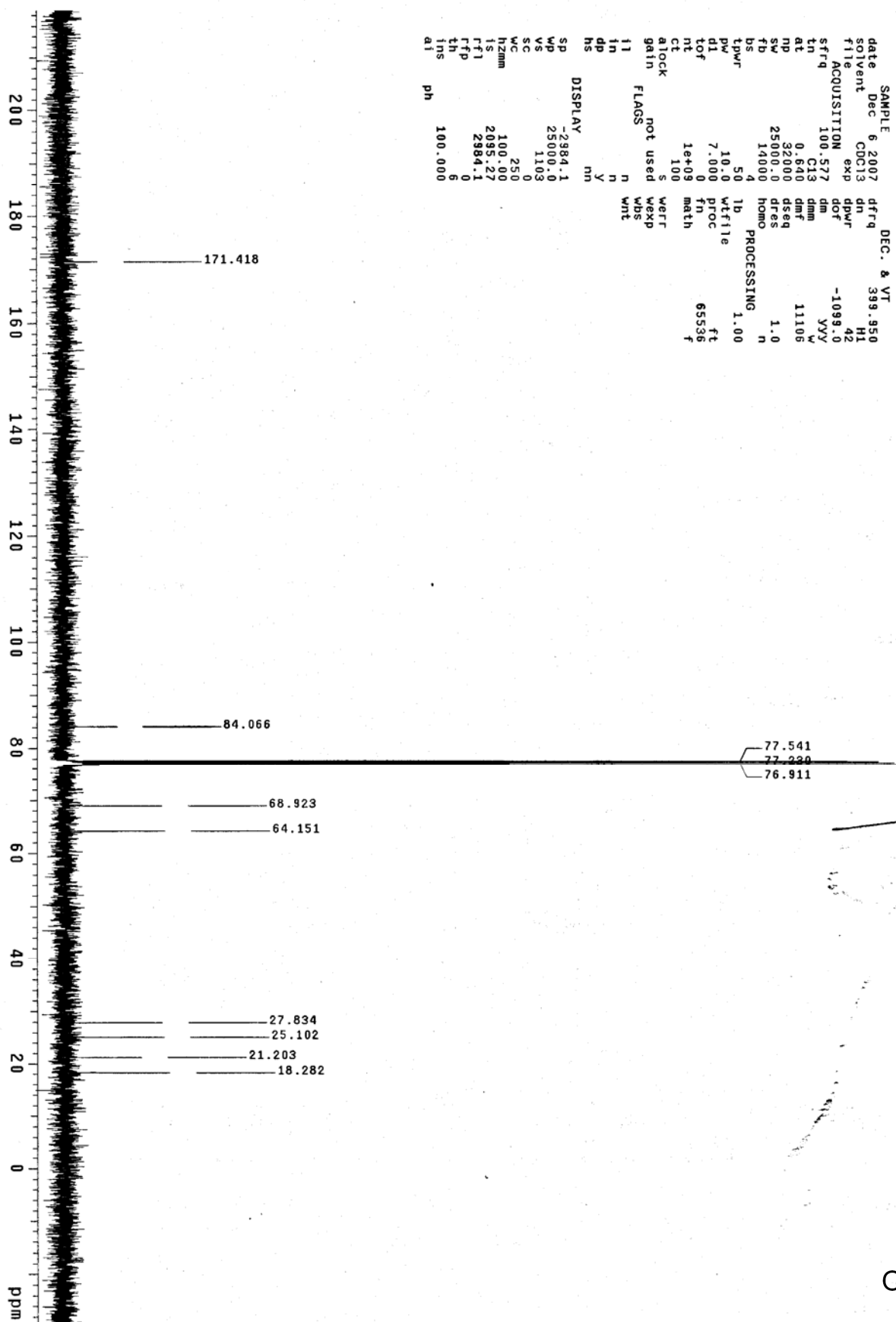
^1H and ^{13}C NMR Spectra

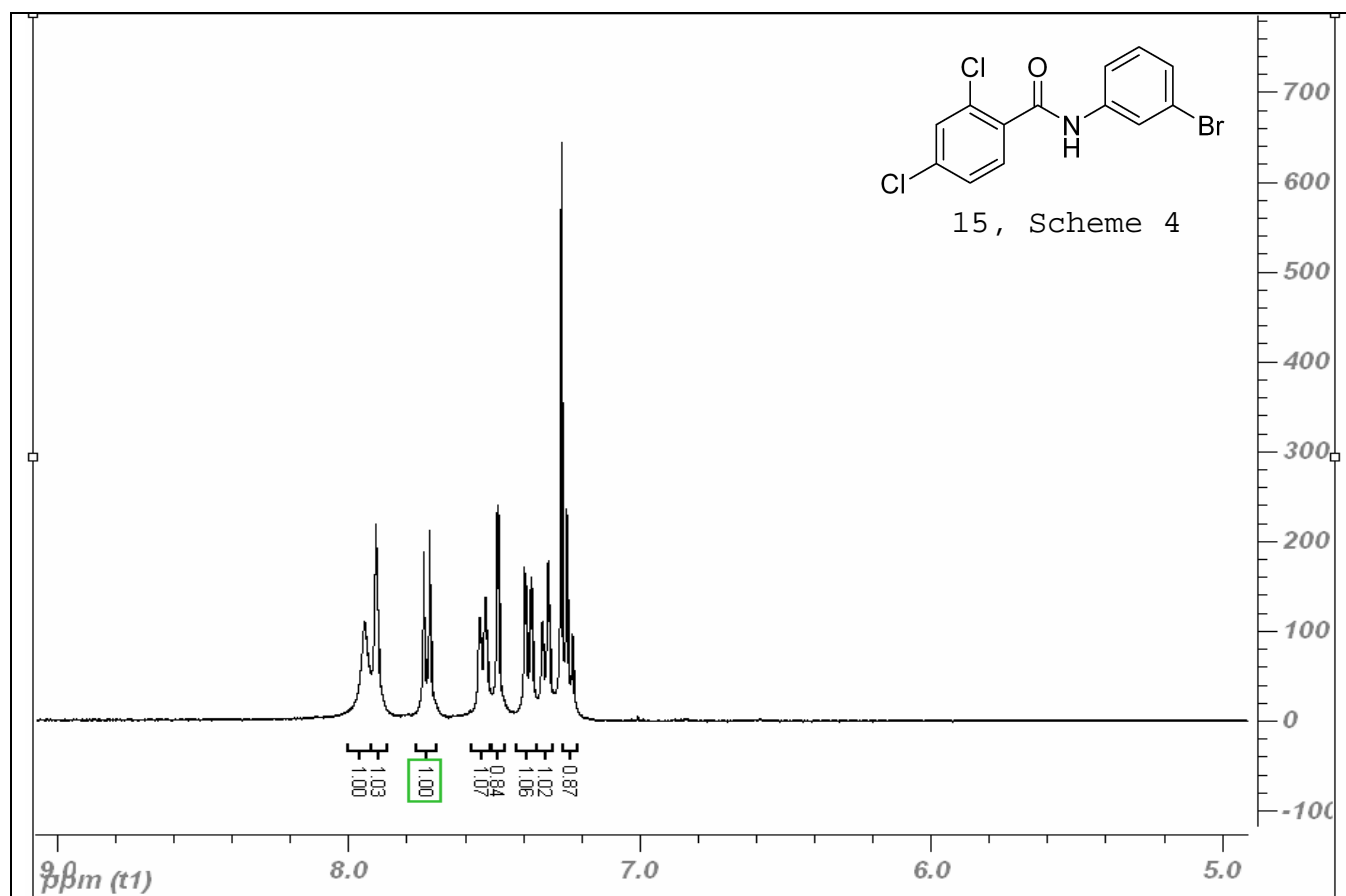


DWC-2-280-1, clear colorless liquid after Kugelrohr distillation

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 file ACQUISITION exp dpr 42
 sfreq 100.577 dm -109.0
 tn C13 dmm 3yy
 at 0.640 dmf 11106
 nd 32000 dseg
 sw 25000.0 dres 1.0
 fb 14000 homo n
 bs 4
 tpwr 50 lb
 pw 10.0 vfile 1.00
 dt 7.000 proc ft
 tof 0 tn 65536
 nt 1e+09 math f
 ct 100
 alock s
 gain not used
 flags WBS
 il n
 in y
 dp y
 hs nn
 DISPLAY
 sp -2984.1
 wp 25000.0
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 ins 100.000
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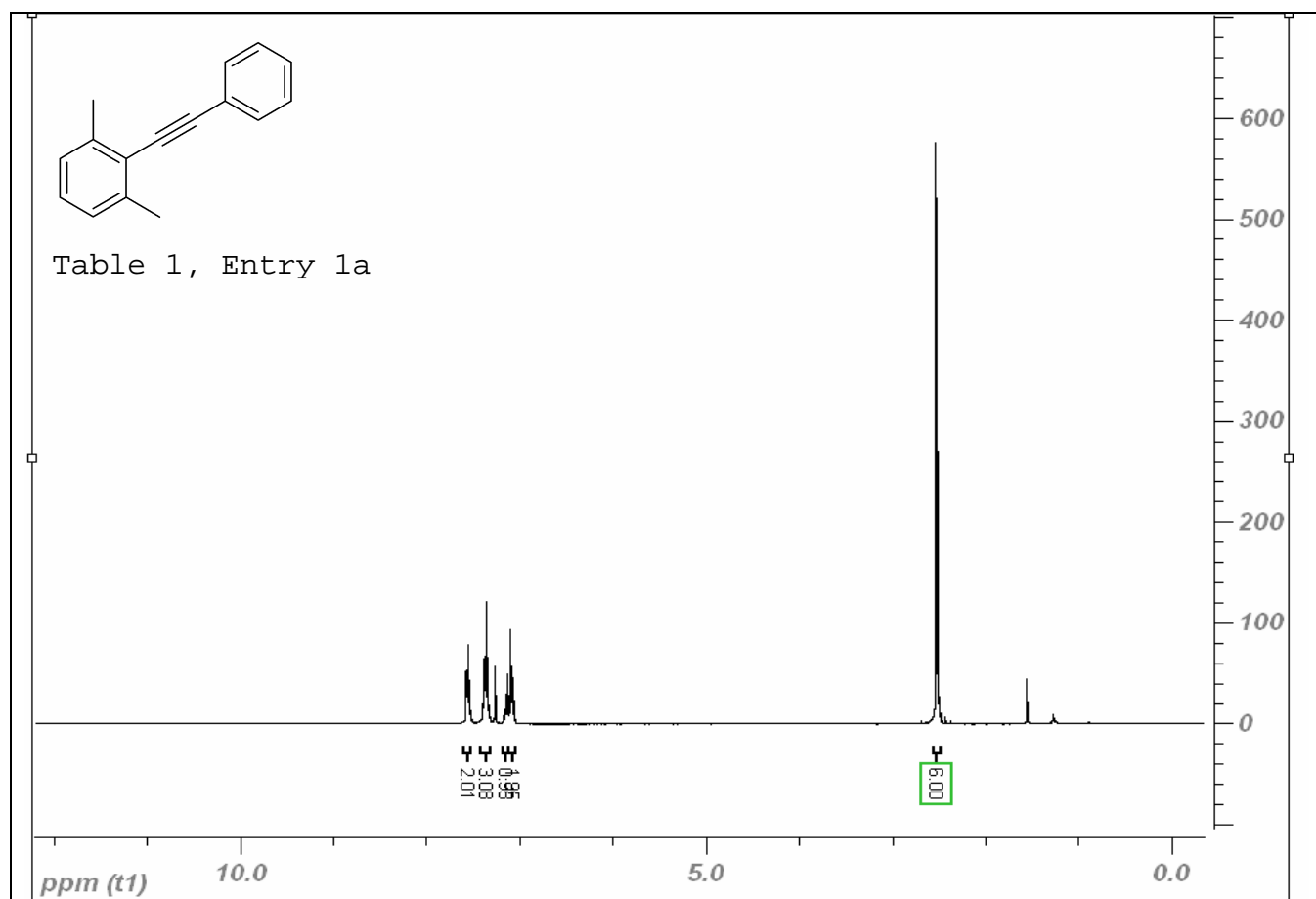
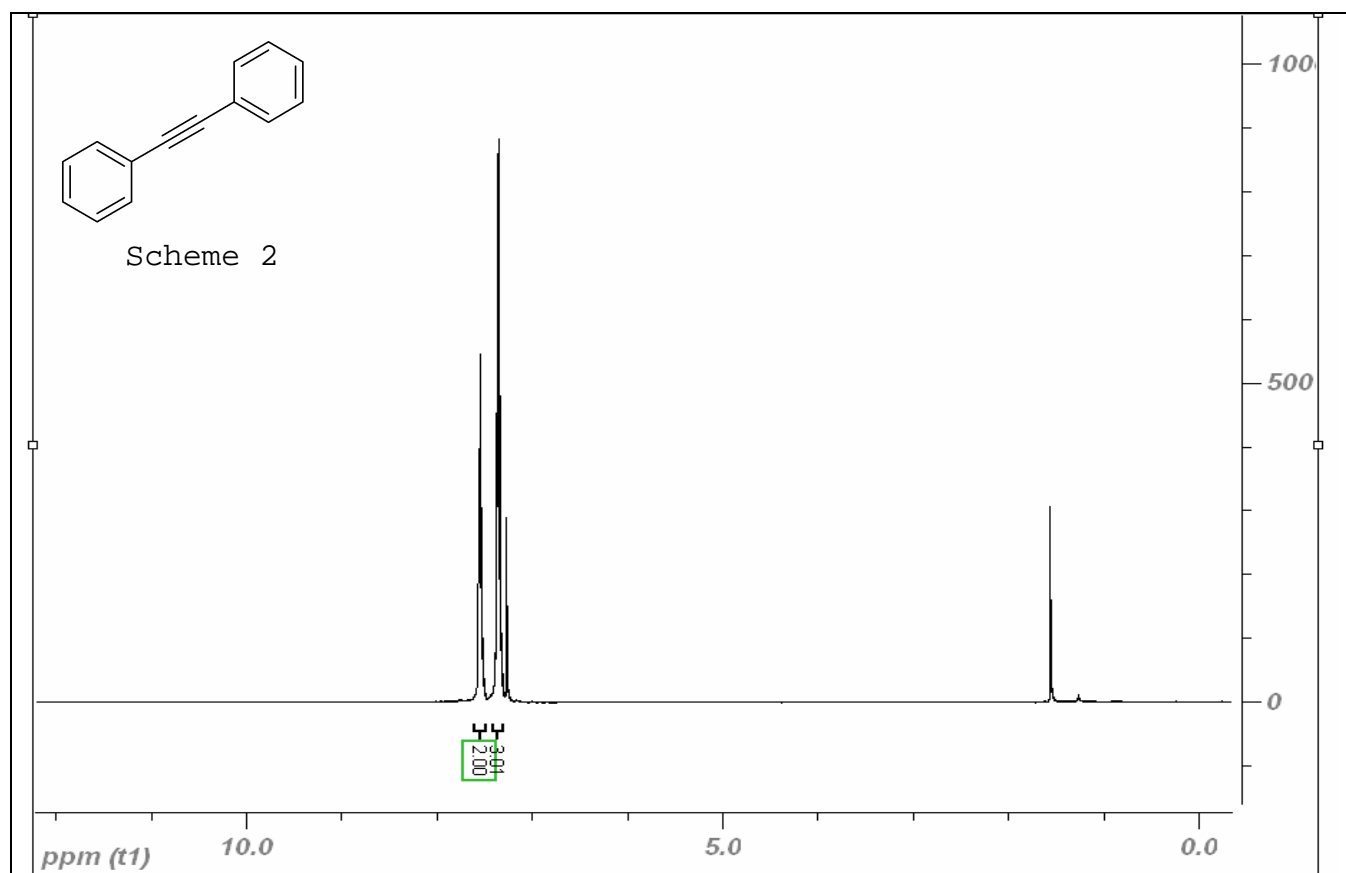


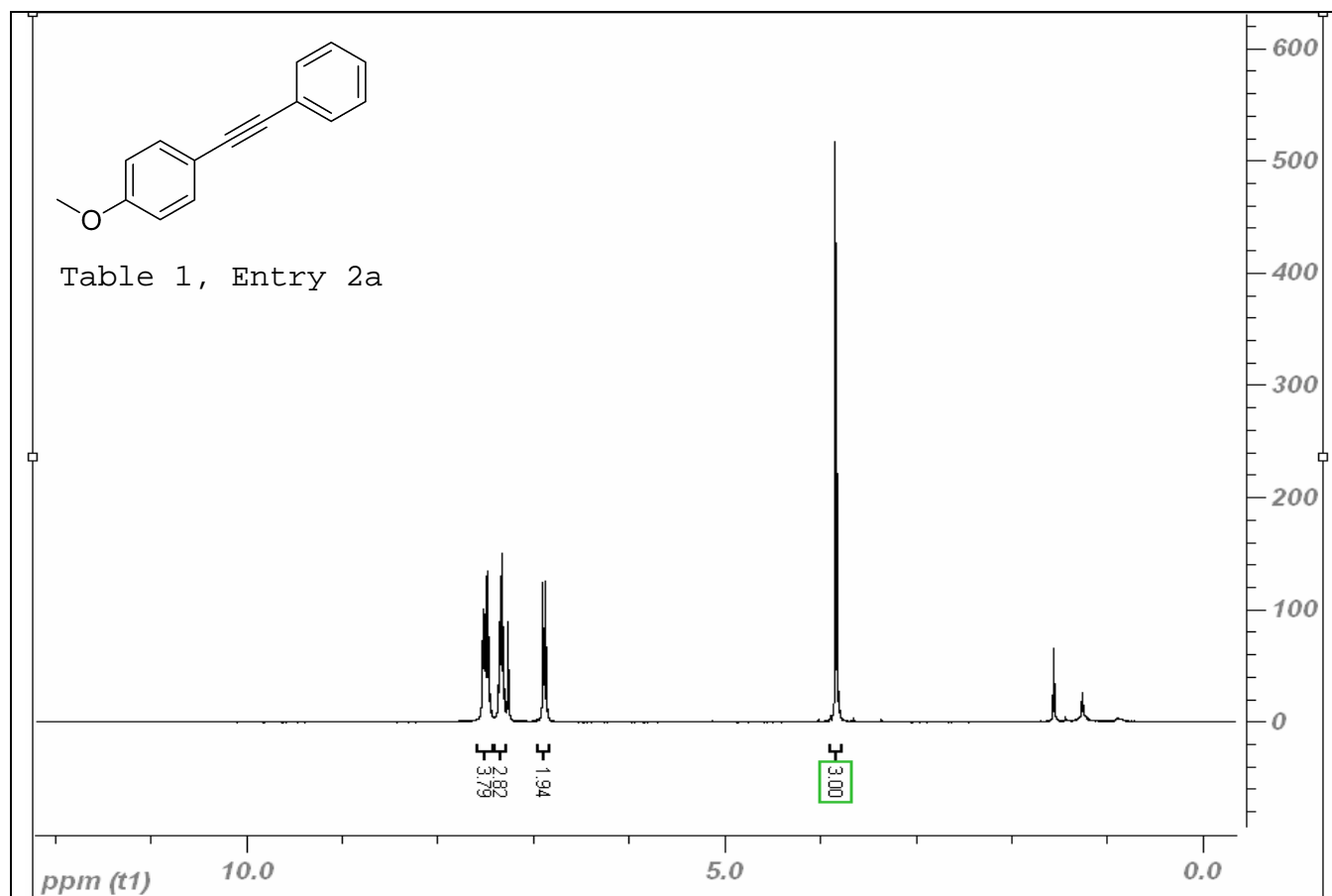
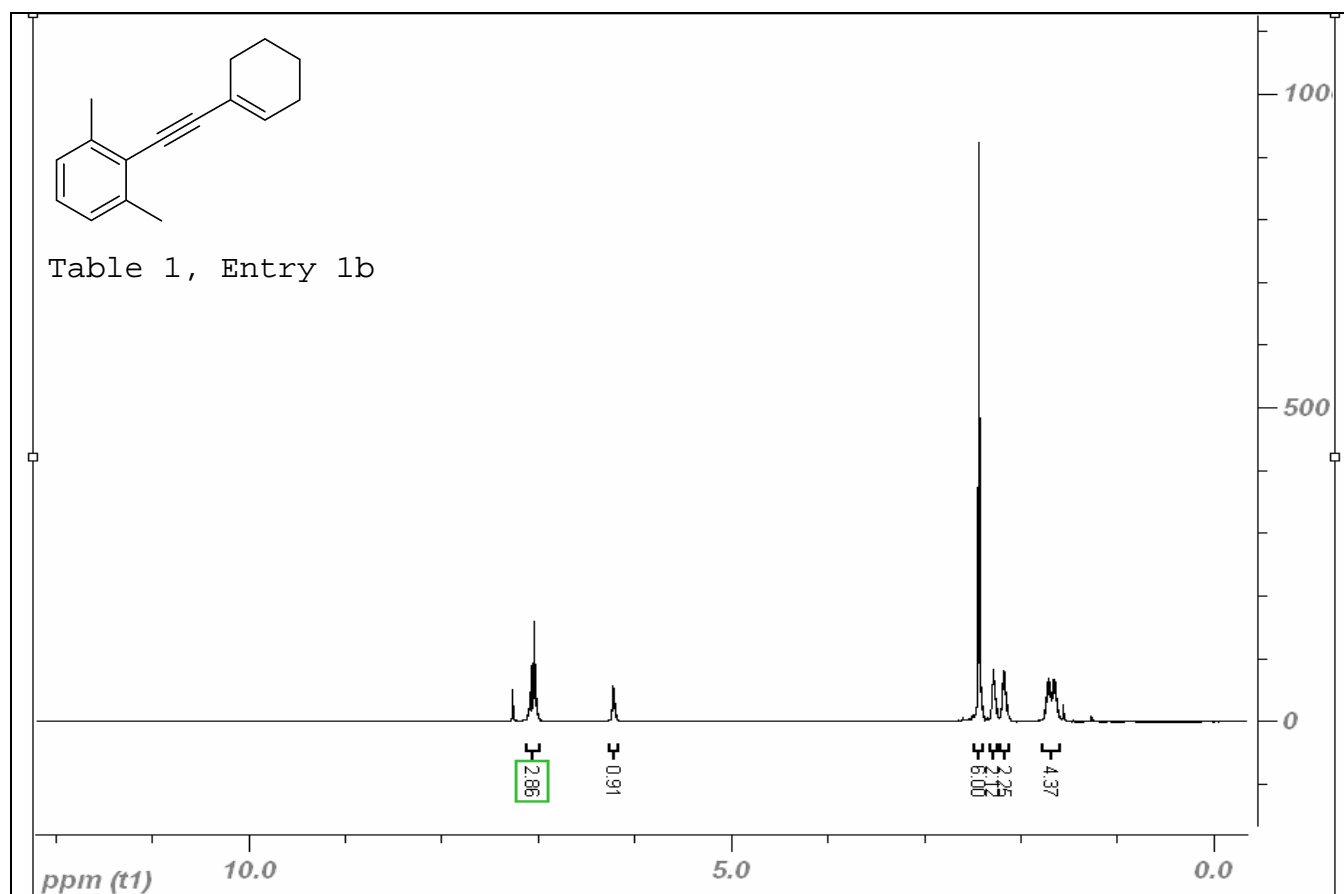


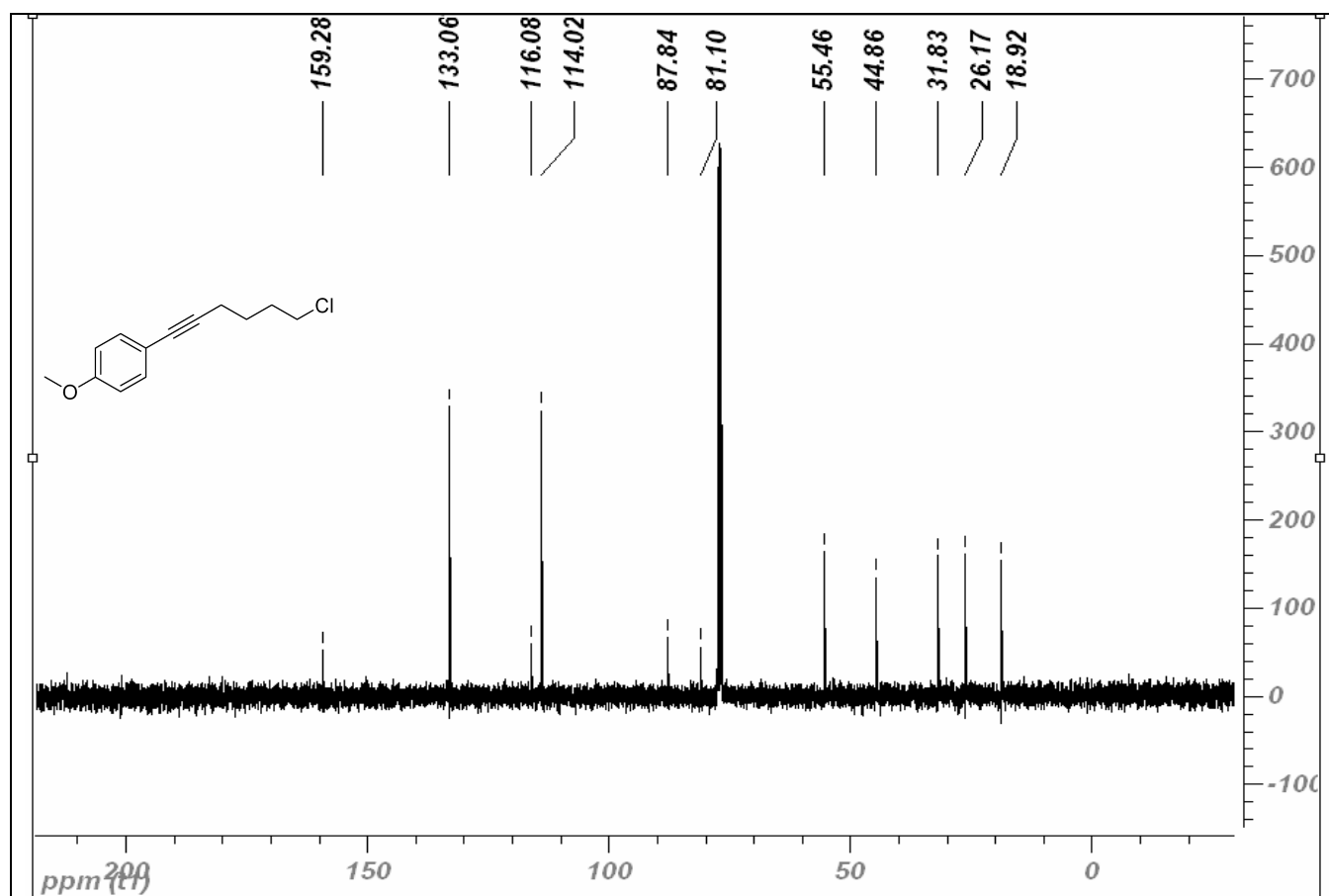
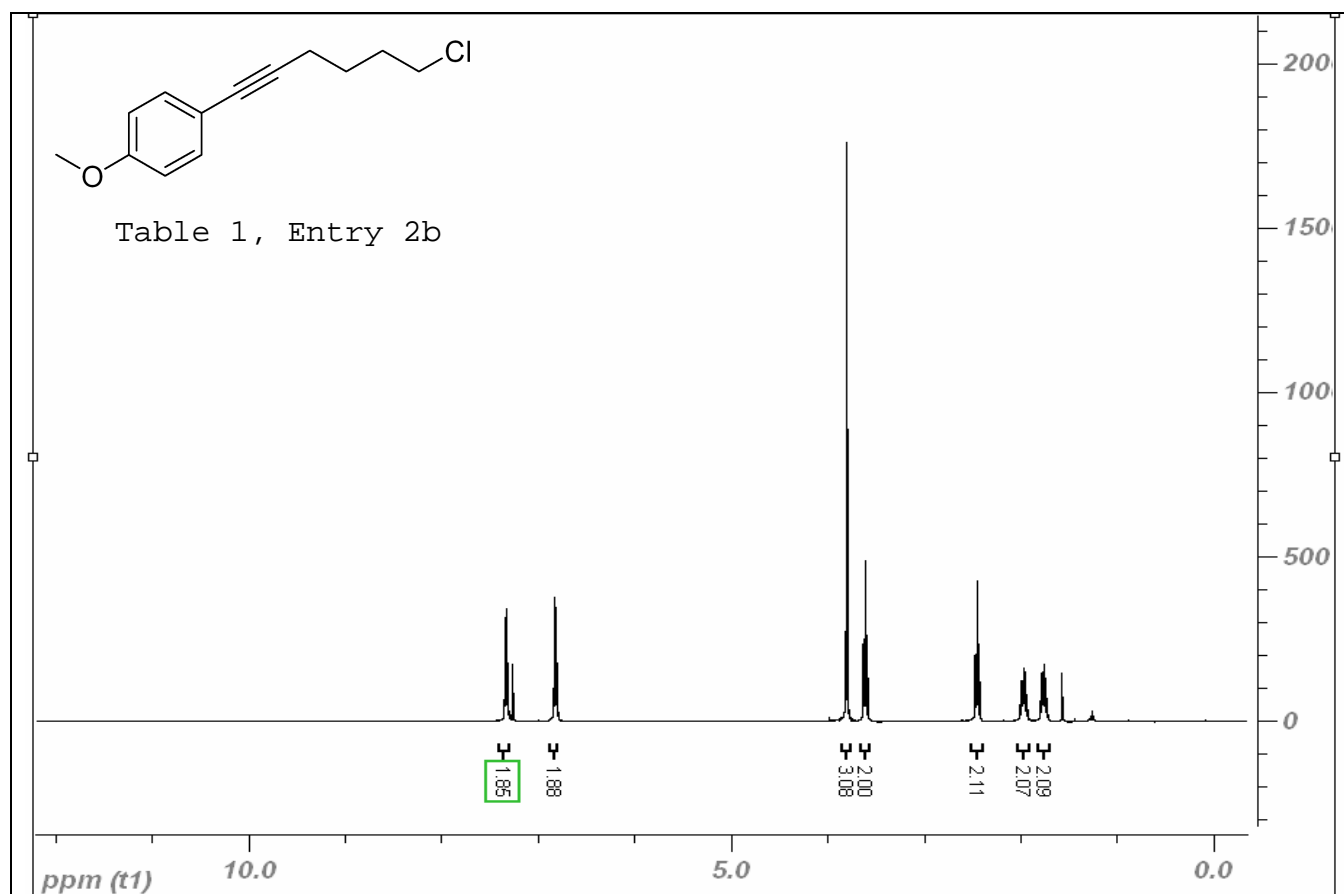
BLR-193-1, white solid after chromatogra
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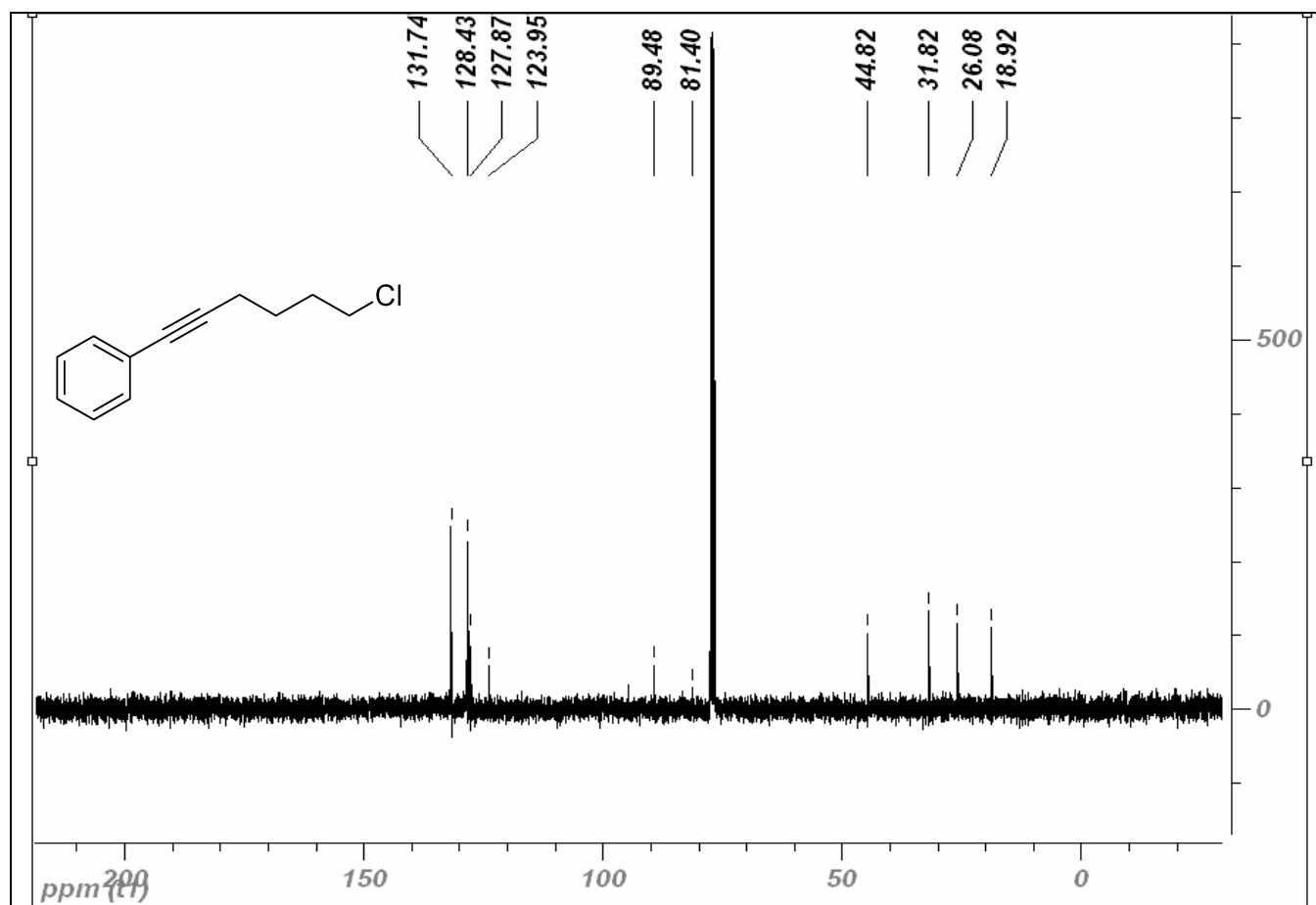
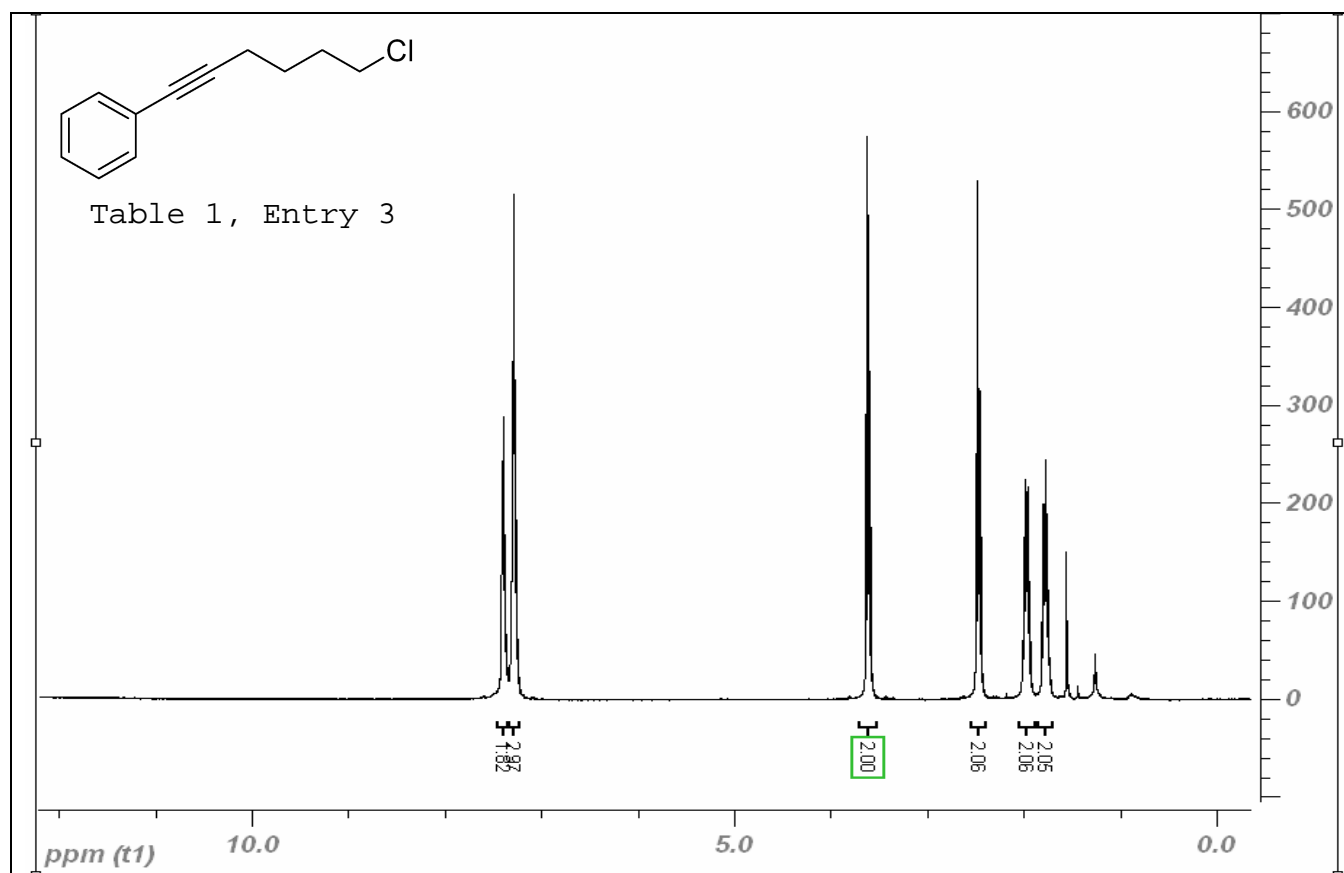
expt std13c

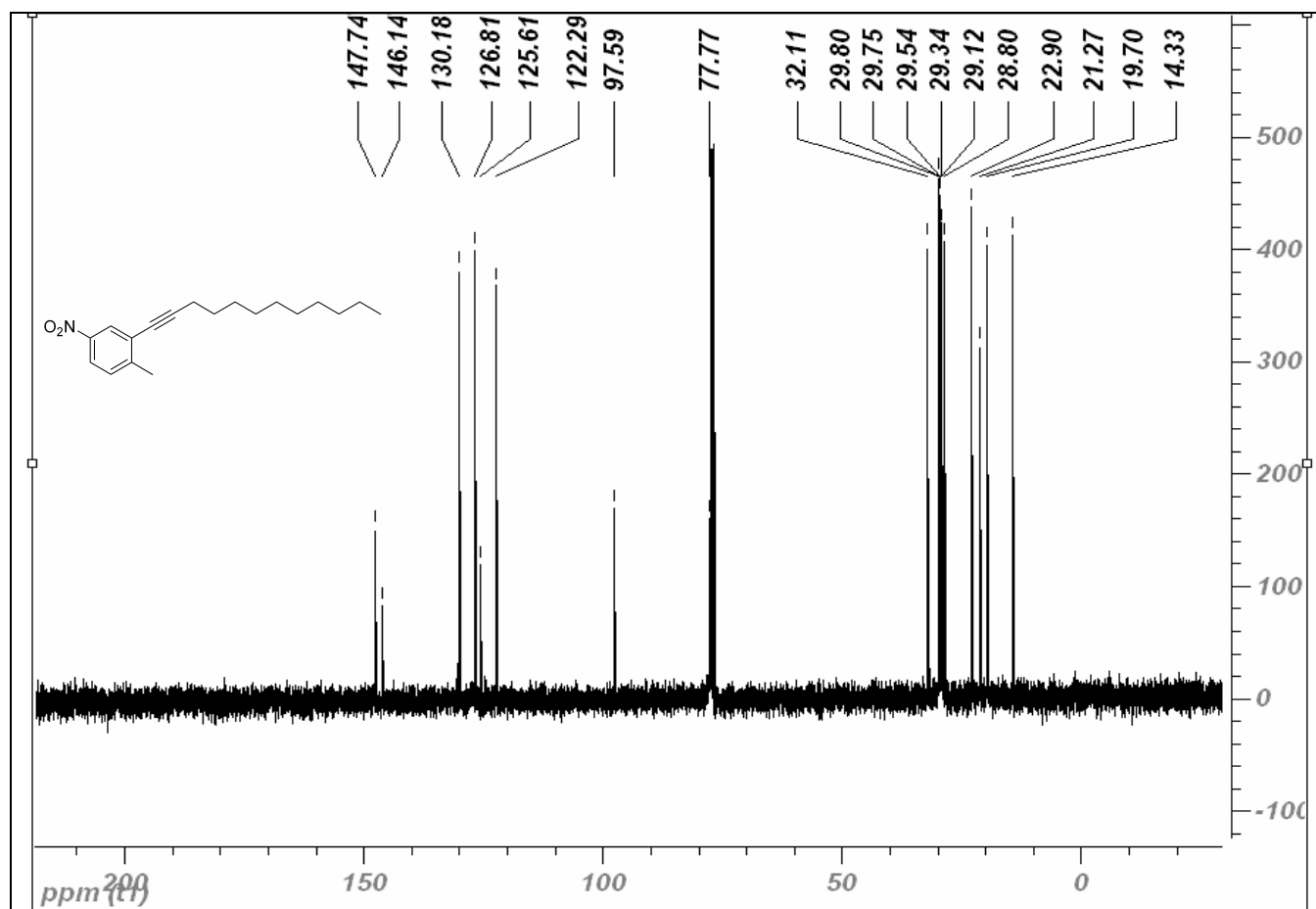
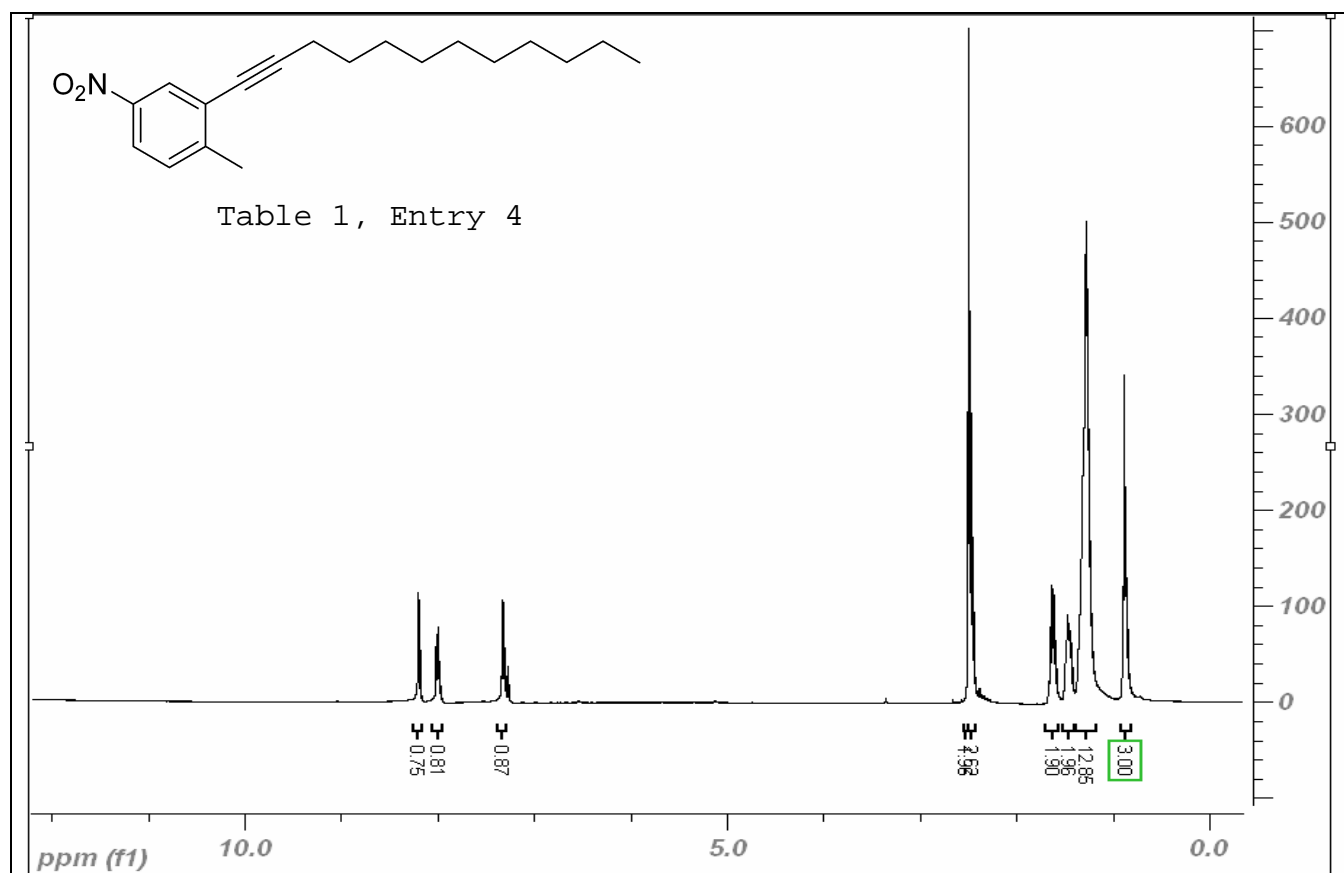
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L1solute/CHCl3/5% dfr 42
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ACQUISITION id dm 11106
sfrq 100.577 dseq
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np 32000
sw 25000.0 lb PROCESSING 1.00
fb 14000 wfttle
bs 4 proc
tpwr 50 fn
pw 10.0 math 65536
di 7.000
tof 0
nt 1e+09 werr
ct 108 wexp
a1ock s wbs
gain not used wnt
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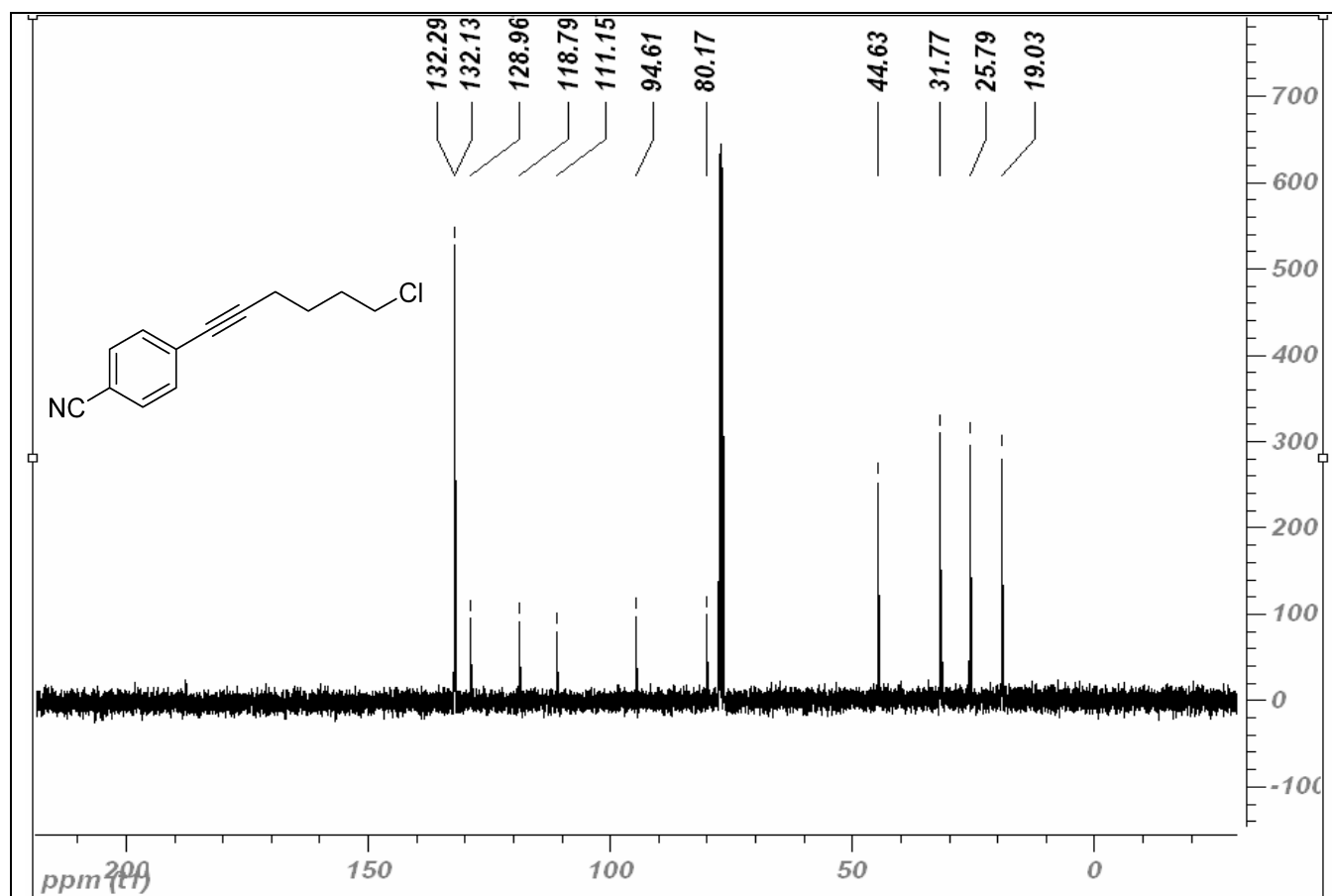
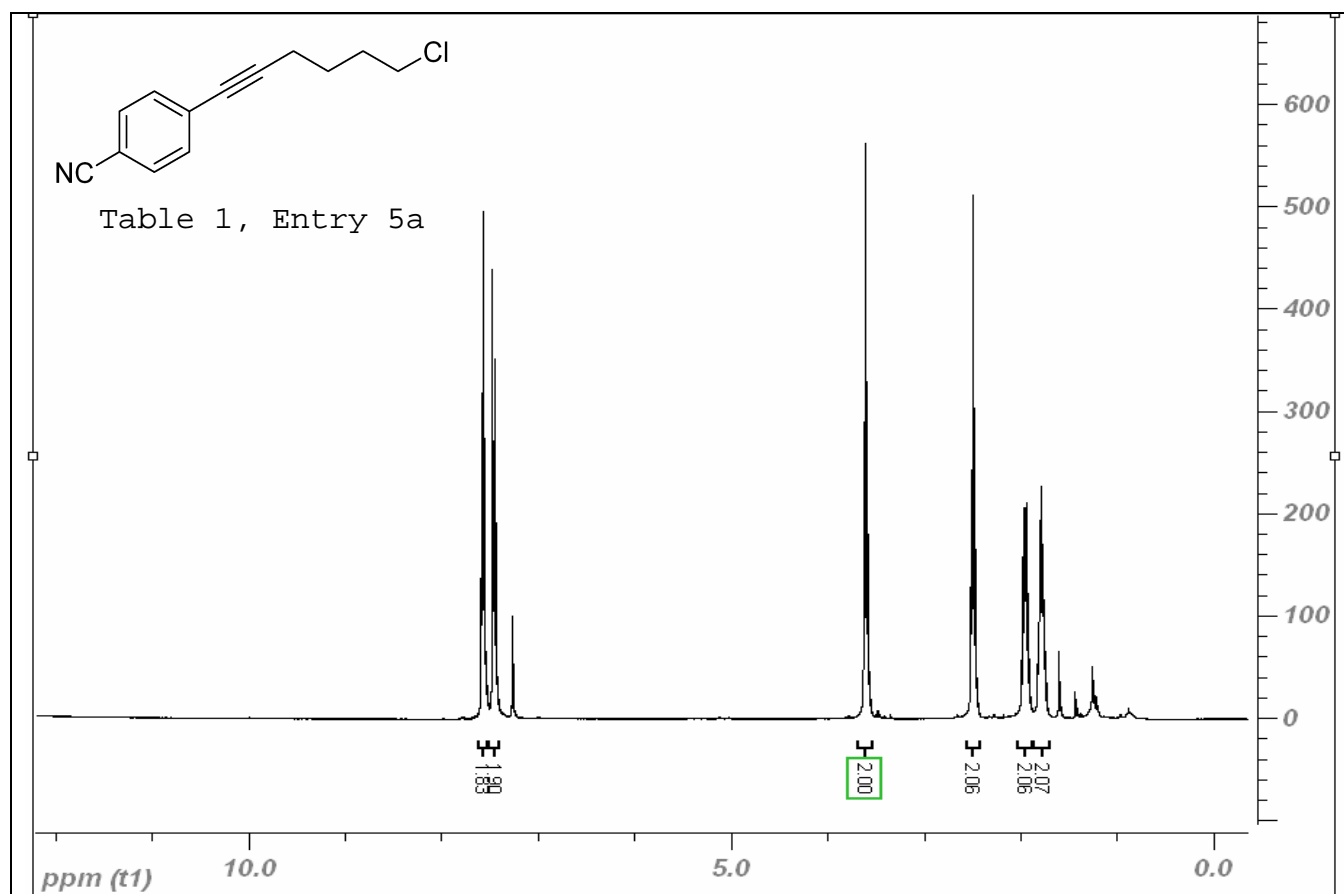


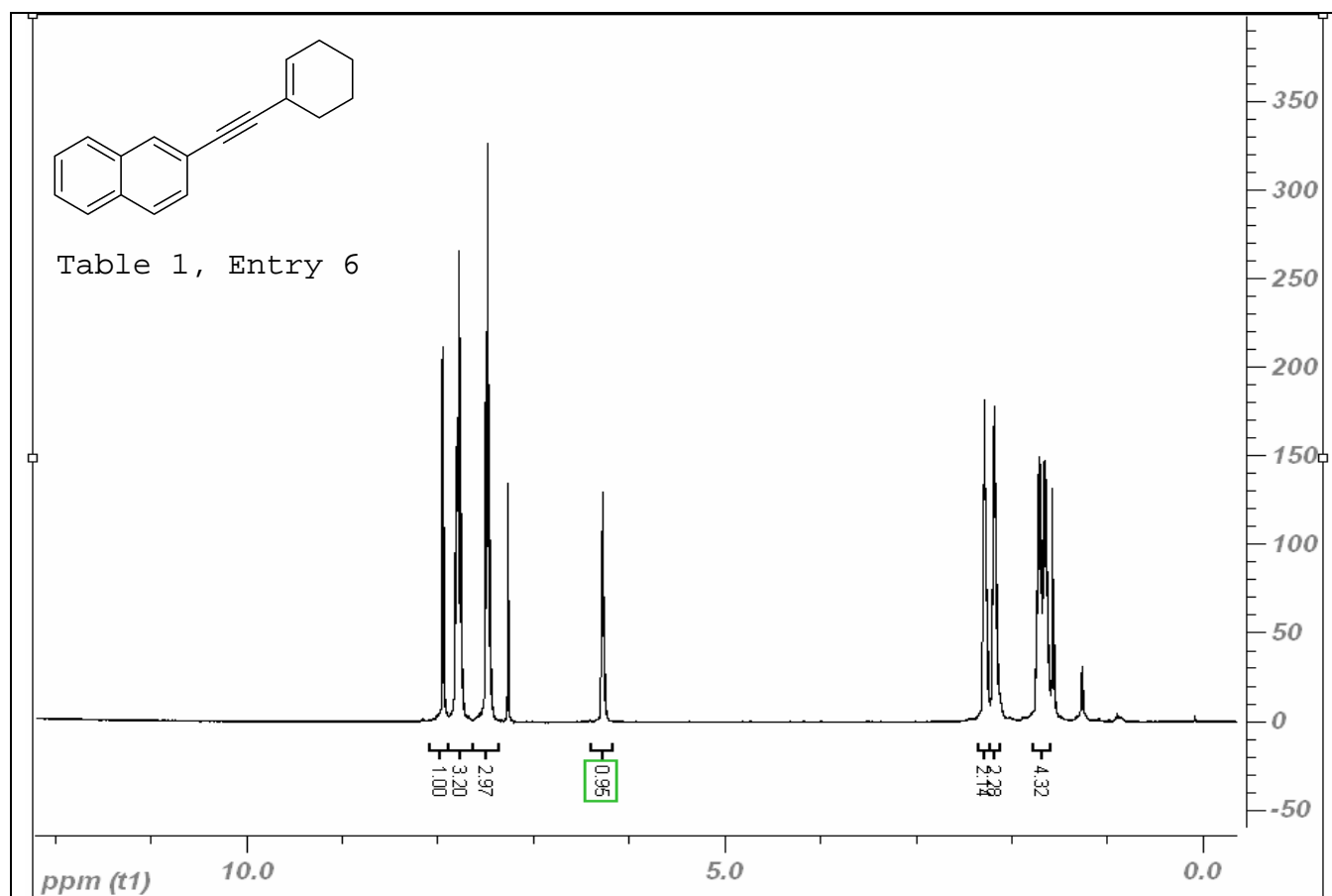
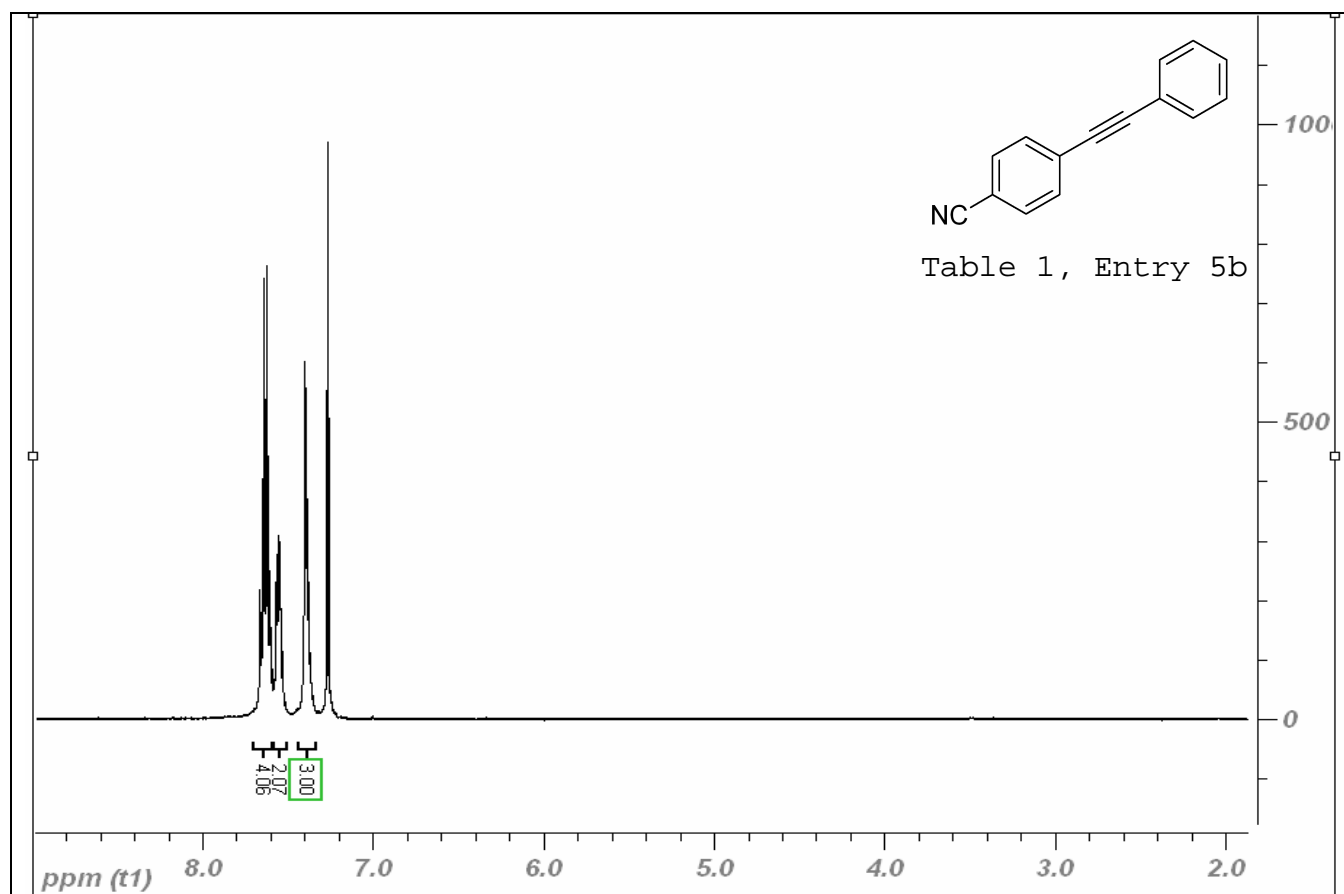


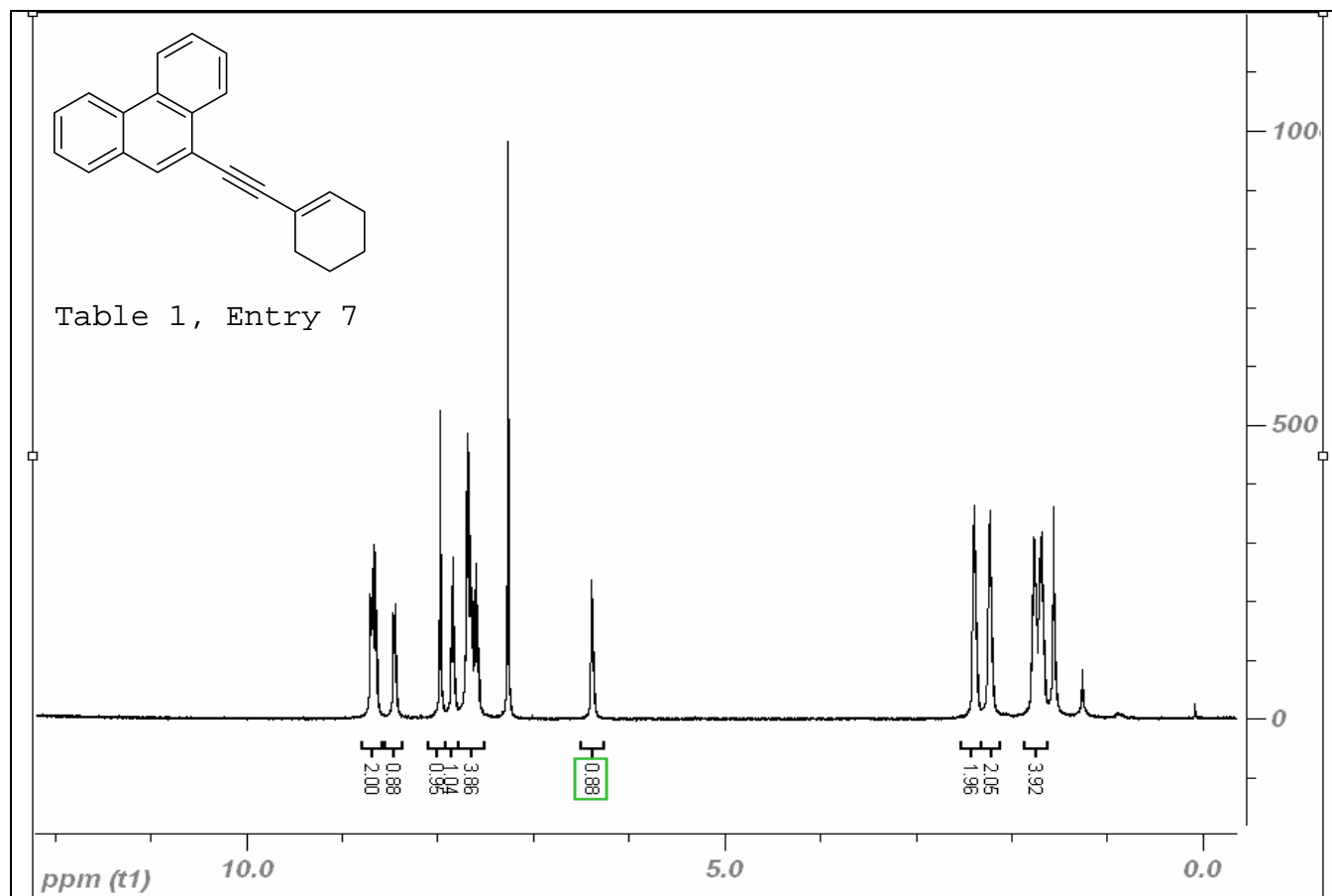
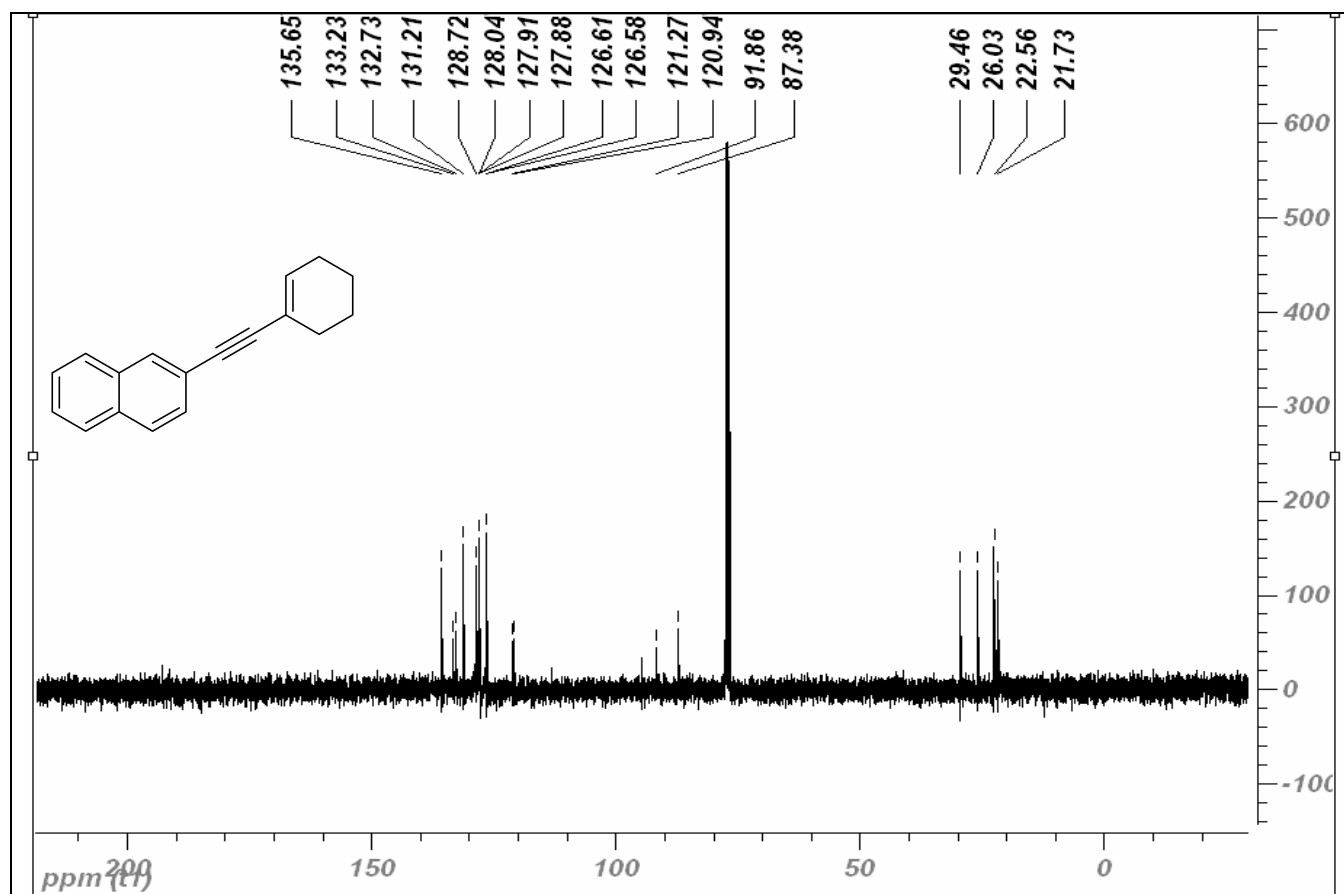


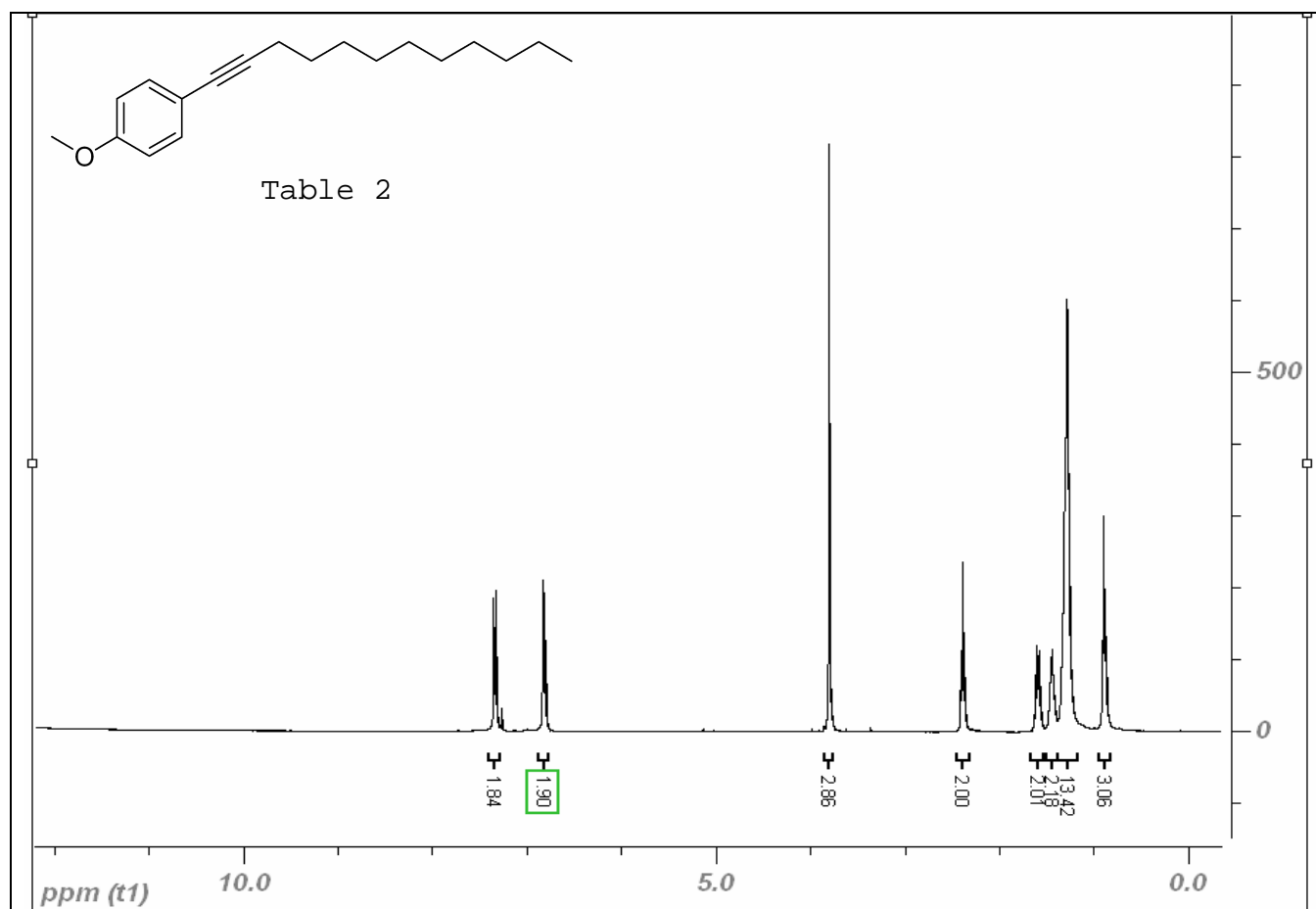
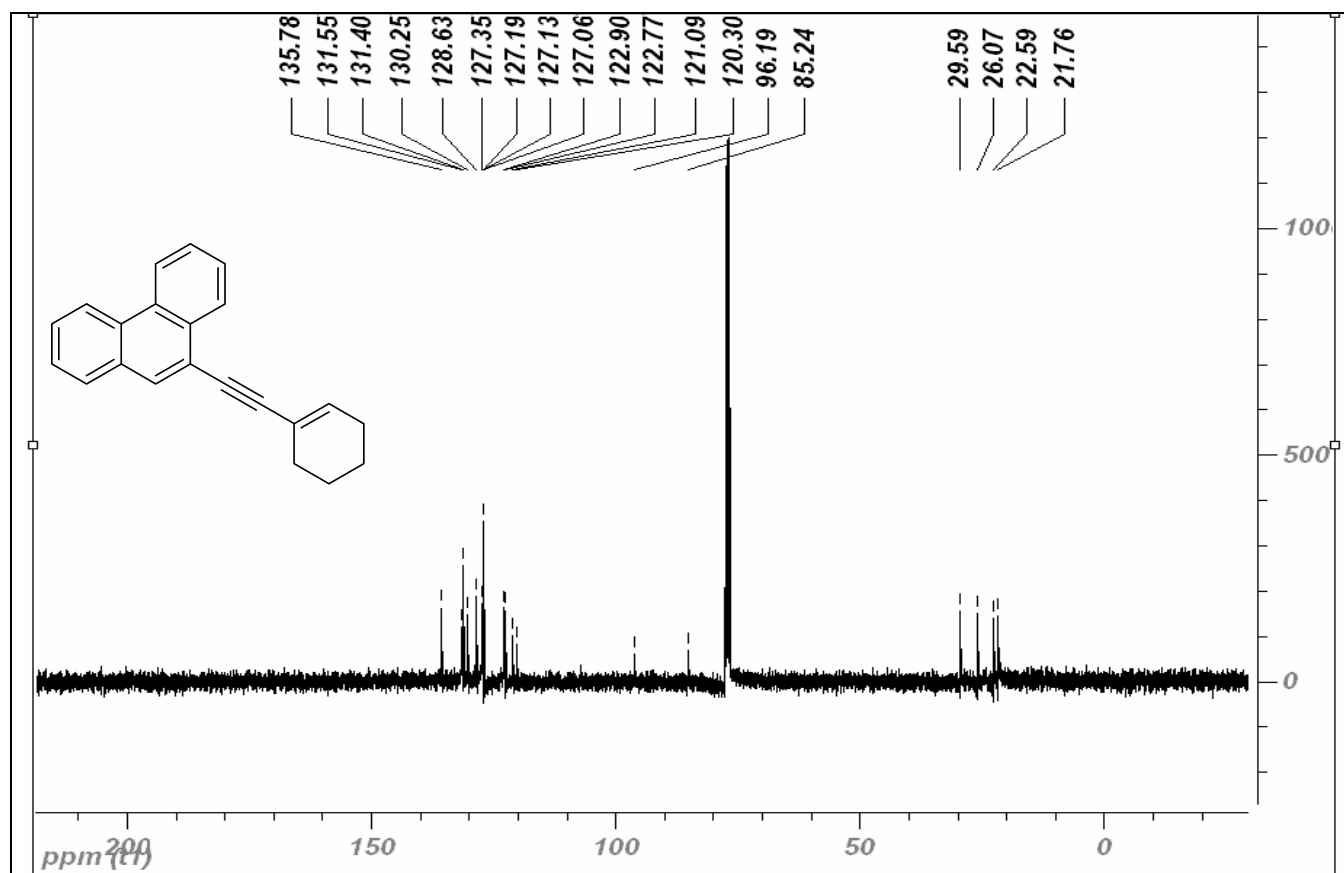


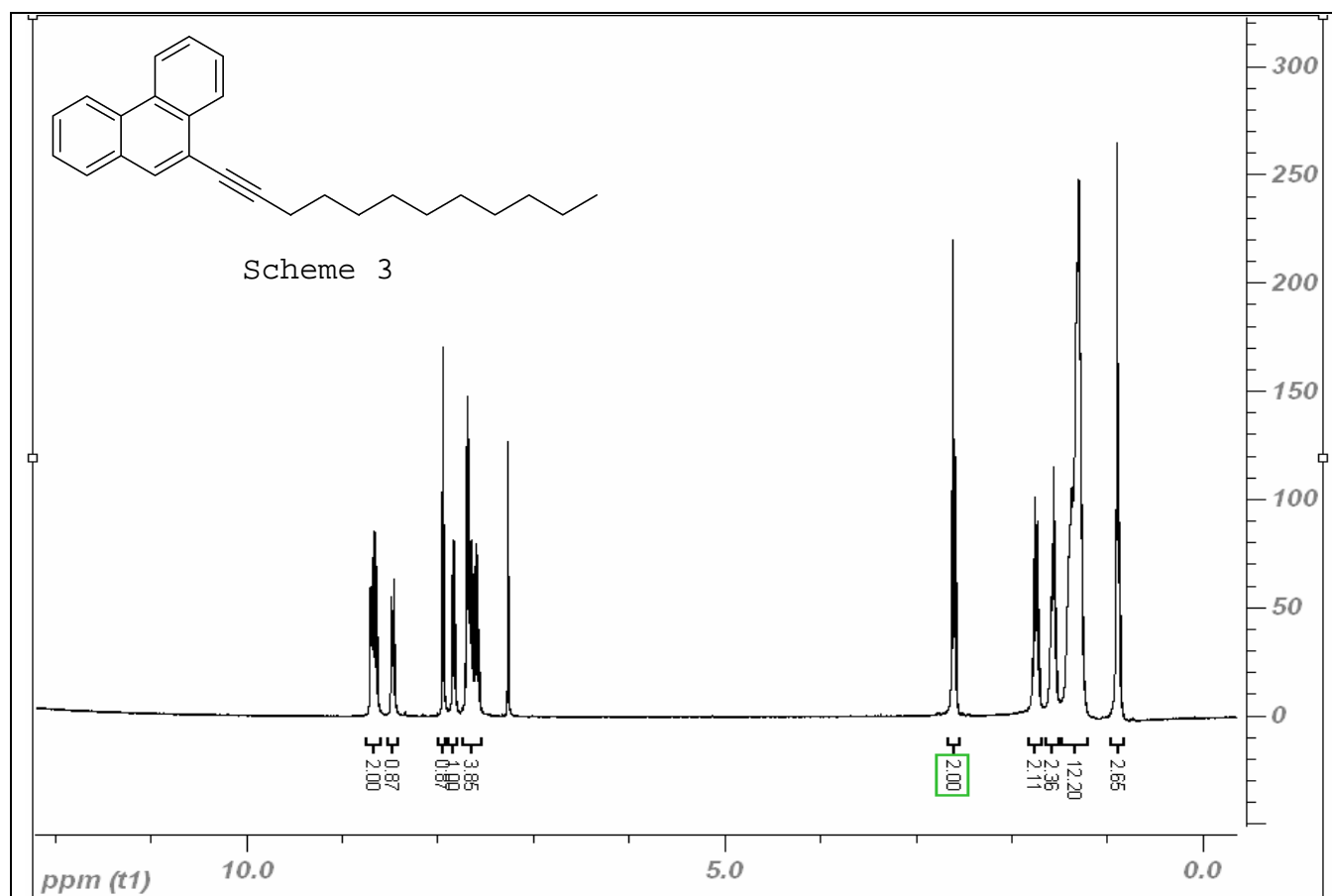
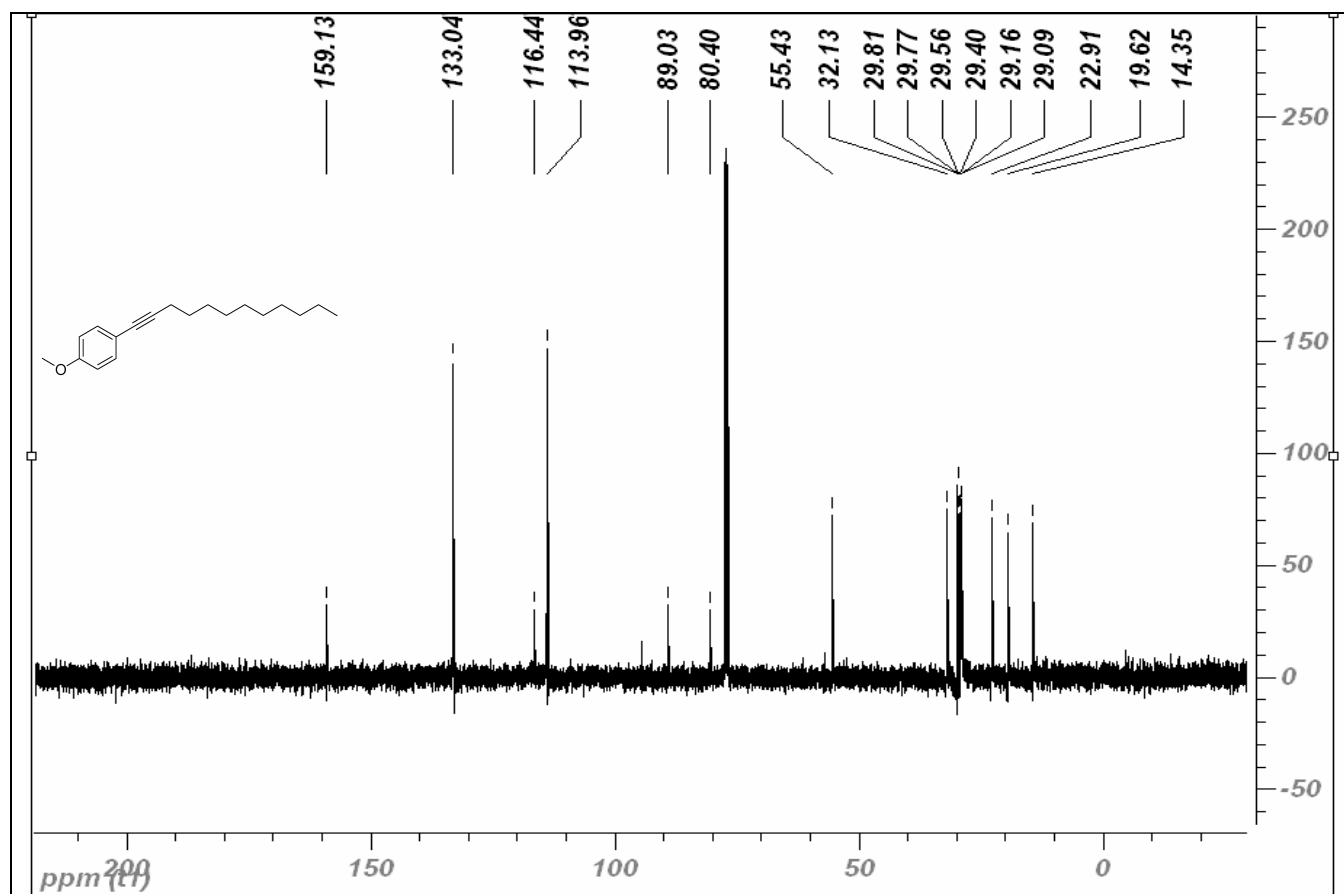












BLR-190-1, light yellow solid after chro
matography, 3-05-2008
exp8 std13c

SAMPLE DEC. & VT
date Mar 5 2008 dfrq 399.950
solvent CDC13 dn H1
file exp 42
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sw 25000.0 dres 1.0
fb 14000 homo
bs 4 PROCESSING 1.00
tpwr 50 lb write
pw 10.0 write
di 7.000 proc ft
tof tn 65536
nt 1e+03 math f
cl 108
atlock s wert
gain not used wds
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