Supplementary Material (ESI) for Chemical Communications


# Palladium-catalyzed three-component coupling of arynes with allylic acetates or halides and terminal alkynes promoted by cuprous iodide

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**Electronic Supplementary Information (ESI)**

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**Experimental section**

**General.** All reactions were conducted under nitrogen atmosphere on a dual-manifold Schlenk line unless otherwise mentioned and in oven-dried glass wares. All solvents were dried according to known methods and distilled prior to use.[1] Starting materials substituted benzyne precursor **1a-e**[2] were synthesized according to the literature procedures. Other reagents were commercially available and used as purchased.

**Optimization studies**. Various monodentate and bidentate phosphine palladium complexes were examined in the presence of CuI (3.0 mol %). The reaction conditions are: 2-trimethylsilylphenyl triflate (**1a**), allyl acetate (**2a**) and 1-heptyne (**3a**) in the presence of a Pd complex (3 mol%), and CsF (3.0 equiv.) at 50 1C for 5 h. The results show that monodentate phosphine palladium complex $PdCl_2(PPh_3)_2$ was active for the present reaction but gave **4a** in 60% yields. $Pd(PPh_3)_4$ gave **4a** in very high 95% yield. Bidentate phosphine complex $Pd(dba)_2$/dppe (3 mol %) was equally active affording **4a** in 93% yield. Other bidentate phosphine palladium complex $Pd(dba)_2$/dppm, dppp and dppb were less active affording **4a** in 45, 75 and 35% yields, respectively. The studies revealed that $Pd(PPh_3)_4$ and $Pd(dba)_2$/dppe are the most suitable catalysts for the present reaction.

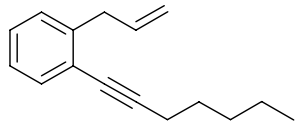
In the presence of $Pd(PPh_3)_4$ and CuI, various allylating reagents were tested. Allyl acetate, allyl chloride and allyl bromide were equally active for the present reaction affording **4a** in 95, 92 and 94% yields, respectively. Allyl carbonate and allyl alcohol failed to give the expected three component coupling products. The result for allyl carbonate is surprising, since this reagent is generally more reactive than allyl acetate. On the basis of these optimization studies, we chose $Pd(PPh_3)_4$ as the catalyst, CuI as promoter and $CH_3CN$ as solvent for this palladium-catalyzed three-component coupling reaction.

**General procedure for the coupling reaction of benzynes with allylic acetates or**

**halides and terminal alkynes.** A sealed tube containing $Pd(PPh_3)_4$ (0.030 mmol, 3.0 mol %), CuI (0.030 mmol, 3.0 mol %) and CsF (3.00 mmol) was evacuated and purged with nitrogen gas three times. Freshly distilled $CH_3CN$ (3.0 mL), benzyne precursor **1** (1.00 mmol), allyl acetate or hailde **2** (1.30 mmol) and terminal alkyne **3** (1.1 mmol) were sequentially added to the system and the reaction mixture was allowed to stir at 50 °C for 5 h. The mixture was filtered through a short Celite pad and washed with dichloromethane several times. The filtrate was concentrated and the residue was purified on a silica gel column using hexanes-ethyl acetate as eluent to afford the substituted 1-allyl-2-alkynylbenzene derivative **4**.

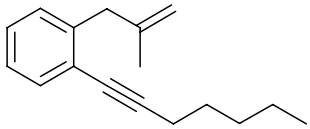
Spectral data and copies of $^1H$ and $^{13}C$ NMR spectra of all compounds are listed below.

**1-Allyl-2-(hept-1-ynyl)benzene** (**4a**).



Colorless oil; $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 7.2 Hz, 1 H), 7.18 - 7.12 (m, 3 H), 6.03 – 5.96 (m, 1 H), 5.12 - 5.05 (m, 2 H), 3.56 (d, *J* = 6.8 Hz, 2 H), 2.42 (t, *J* = 6.4 Hz, 2 H), 1.62 – 1.58 (m, 2 H), 1.52 – 1.40 (m, 2 H), 1.38 -1.27 (m, 2 H), 0.97 (t, *J* = 7.2 Hz, 3 H). $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 141.7, 136.8, 132.1, 128.6, 127.6, 125.9, 115.6, 94.4, 79.1, 38.7, 31.1, 28.5, 22.2, 19.5, 13.9; HRMS: calcd for $C_{16}H_{20}$ 212.1565, found 212.1560.

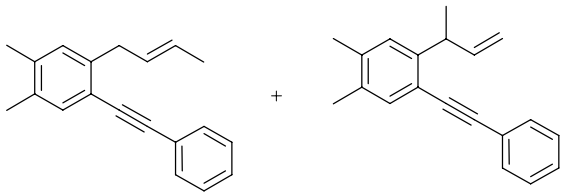
**1-(Hept-1-ynyl)-2-(2-methylallyl)benzene** (**4b**).



Colorless oil; $^1H$ NMR (500 MHz, $CDCl_3$): δ 7.37 (d, *J* = 7.0 Hz, 1 H), 7.19 - 7.12 (m, 3 H), 4.80 (s, 1 H), 4.65 (s, 1 H), 3.50 (s, 2 H), 2.41 (t, *J* = 7.5 Hz, 2 H), 1.70 (s, 3 H), 1.63 – 1.57 (m, 2 H), 1.46 – 1.32 (m, 4 H), 0.90 (t, *J* = 7.5 Hz, 3 H); $^{13}C$ NMR (125

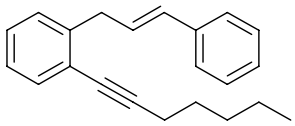
MHz, $CDCl_3$): δ 144.8, 141.4, 132.1, 128.9, 127.5, 125.9, 124.0, 111.7, 94.0, 79.3, 42.4, 31.1, 28.5, 22.3, 22.2, 19.5, 13.9; HRMS: calcd for $C_{17}H_{22}$ 226.1722, found 226.1725.

**1-((*E*)-But-2-enyl)-4,5-dimethyl-2-(2-phenylethynyl)benzene** (**4c**) **and 1-(But-3-en-2-yl)-4,5-dimethyl-2-(2-phenylethynyl)benzene** (**4d**).



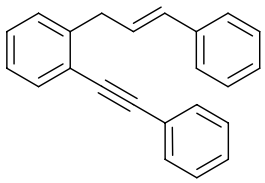
Colorless oil; $^1$H NMR (400MHz, $CDCl_3$): δ 7.54 (d, *J* = 6.2 Hz, 2 H), 7.38 - 7.24 (m, 4 H), 7.02 (s, 1 H), 6.16 – 6.07 (m, 1 H), 5.70 – 5.57 (m, 2 H), 5.20 (dd, *J* = 16.4, 6.4 Hz, 2 H), 4.10 – 4.05 (m, 1 H), 3.53 (d, *J* = 6.4 Hz, 2 H), 2.32 (s, 3 H), 2.29 (s, 3 H), 1.75 (d, *J* = 6.4 Hz, 3 H), 1.42 (d, *J* = 6.0 Hz, 3 H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 142.6, 140.4, 137.4, 134.1, 133.3, 133.1, 129.5, 128.3, 127.9, 127.7, 126.2, 123.8, 119.7, 113.1, 92.2, 88.5, 40.1, 37.3, 19.9, 19.8, 19.1, 17.9; HRMS: calcd for $C_{20}H_{20}$ 260.1565, found 260.1570.

**1-Cinnamyl-2-(hept-1-ynyl)benzene** (**4e**).



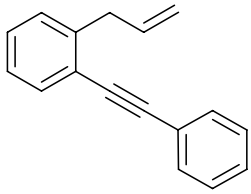
Colorless oil; $^1$H NMR (600 MHz, $CDCl_3$): δ 7.32 (d, *J* = 7.2 Hz, 1 H), 7.27 - 7.25 (m, 2 H), 7.20 – 7.18 (m, 2 H), 7.17 – 7.04 (m, 4 H), 6.38 (d, *J* = 15.8 Hz, 1 H), 6.32 – 6.27 (m, 1 H), 3.61 (d, *J* = 6.6 Hz, 2 H), 2.35 (t, *J* = 13.8 Hz, 2 H), 1.57 – 1.53 (m, 2 H), 1.43 – 1.34 (m, 2 H), 1.30 – 1.25 (m, 2 H), 0.83 (d, *J* = 7.2 Hz, 3 H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 141.8, 137.6, 132.2, 130.7, 128.7, 128.6, 128.4, 128.1, 127.7, 127.0, 126.1, 126.0, 123.6, 94.6, 79.1, 37.9, 31.1, 28.5, 22.2, 19.5, 13.9; HRMS: calcd for $C_{22}H_{24}$ 288.1878, found 288.1879.

**1-Cinnamyl-2-(phenylethynyl)benzene (4f).**



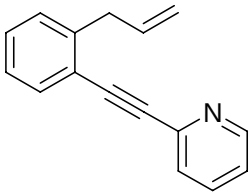
Colorless oil; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.41 - 7.22 (m, 14 H), 6.56 – 6.39 (m, 2 H), 3.80 (d, *J* = 6.6 Hz, 2 H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 139.3, 137.4, 136.6, 132.1, 131.0, 130.0, 129.7, 128.6, 128.5, 127.6, 127.1, 126.1, 126.7, 125.7, 92.9, 79.1, 36.6; HRMS: calcd for $C_{23}H_{18}$ 294.1409, found 294.1413.

**1-Allyl-2-(phenylethynyl)benzene** (**4g**).



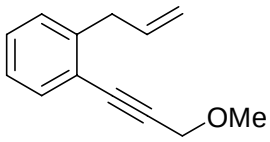
Colorless oil; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.60 – 7.56 (m, 3 H), 7.41 - 7.27 (m, 6 H), 6.19 – 6.02 (m, 1 H), 5.21 - 5.07 (m, 2 H), 3.70 (d, *J* = 6.8 Hz, 2 H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 141.9, 136.5, 132.2, 131.5, 128.8, 128.5, 128.4, 128.3, 126.1, 123.4, 122.7, 116.0, 93.3, 88.0, 38.8; HRMS: calcd for $C_{17}H_{14}$ 218.1096, found 218.1097.

**2-((2-Allylphenyl)ethynyl)pyridine** (**4h**).



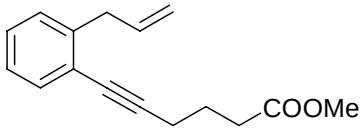

Colorless oil; $^{1}$H NMR (600 MHz, $CDCl_3$): δ 8.59 (d, *J* = 4.8 Hz, 1 H), 7.64 – 7.62 (m, 1 H), 7.62 (d, *J* = 7.2 Hz, 1 H), 7.57 (d, *J* = 7.2 Hz, 1 H), 7.48 (d, *J* = 7.8 Hz, 1 H), 7.28 – 7.17 (m, 3 H), 6.09 – 6.00 (m, 1 H), 5.12 - 5.06 (m, 2 H), 3.70 (d, *J* = 6.6 Hz, 2 H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 150.0, 143.5, 142.5, 136.3, 136.1, 132.7, 129.2, 128.8, 127.1, 126.1, 122.6, 121.6, 116.2, 92.4, 87.8, 38.7; HRMS: calcd for $C_{16}H_{13}N$ 219.1048, found 219.1049.

**1-Allyl-2-(3-methoxyprop-1-ynyl)benzene** (**4i**).



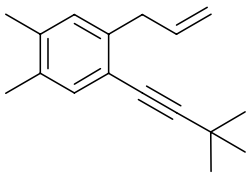

Colorless oil; $^{1}$H NMR (600 MHz, $CDCl_3$): δ 7. 43 (d, *J* = 6.2 Hz, 1 H)), 7.26 – 7.14 (m, 3 H), 5.99-5.95 (m, 1 H), 5.09 – 5.05 (m, 2 H), 4.35 (s, 2 H), 3.56 (d, *J* = 7.2 Hz, 2 H), 3.45 (s, 3 H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 142.0, 136.4, 132.4, 128.6, 128.2, 126.0, 122.1, 116.0, 88.8, 84.9, 60.4, 57.7, 38.6; HRMS: calcd for $C_{13}H_{14}O$ 186.1045, found 186.1047.

**Methyl 6-(2-allylphenyl)hex-5-ynoate** (**4j**).



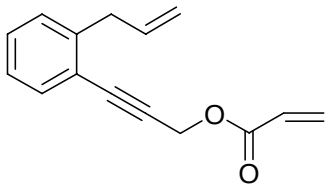

Colorless oil; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 4.8 Hz, 1 H), 7.26 – 7.14 (m, 3 H), 6.01-5.97 (m, 1 H), 5.07 – 5.00 (m, 2 H), 3.67 (s, 3 H), 3.51 (d, *J* = 6.4 Hz, 2 H), 2.51 (t, *J* = 7.2 Hz, 4 H), 1.96 – 1.89 (m, 2 H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 173.9, 141.7, 136.6, 131.5, 128.6, 127.8, 127.6, 125.9, 115.7, 92.7, 79.9, 51.4, 38.6, 32.8, 24.0, 19.0; HRMS: calcd for $C_{16}H_{18}O_2$ 242.1307, found 242.1310.

**1-Allyl-2-(3,3-dimethylbut-1-ynyl)-4,5-dimethylbenzene** (**4k**).



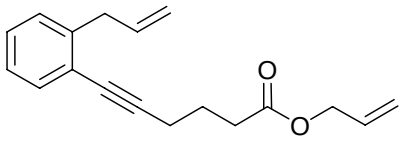
Colorless oil; $^{1}$H NMR (500 MHz, $CDCl_3$): δ 7.16 (s, 1 H), 6.93 (s, 1 H), 6.03-5.95 (m, 1 H), 5.12 – 5.03 (m, 2 H), 3.47 (d, *J* = 7.0 Hz, 2 H), 2.22 (s, 3 H), 2.18 (s, 3 H), 1.33 (s, 9 H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 139.0, 137.2, 136.3, 134.0, 132.3, 129.8, 120.5, 115.3, 101.4, 77.6, 38.4, 31.1, 28.1, 19.6, 18.9; HRMS: calcd for $C_{17}H_{22}$ 226.1722, found 226.1723.

**3-(2-Allylphenyl)prop-2-ynyl acrylate** (**4l**).



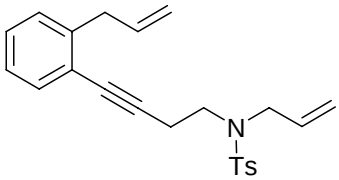
Colorless oil; $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 6.8 Hz, 1 H), 7.29 – 7.25 (m, 1 H), 7.20 – 7.16 (m, 2 H), 6.50 (d, *J* = 17.2 Hz, 1 H), 6.18 (dd, *J* = 17.2, 10.4 Hz, 1 H), 6.00 – 5.96 (m, 1 H), 5.94 (d, *J* = 7.2 Hz, 1 H), 5.15 – 4.99 (m, 2 H), 5.01 (s, 2 H), 3.57 (d, *J* = 6.4 Hz, 2 H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 165.4, 142.4, 136.3, 132.5, 131.8, 128.9, 128.2, 127.7, 125.9, 121.5, 116.0, 86.5, 85.1, 52.9, 38.6; HRMS: calcd for $C_{15}H_{14}O_2$ 226.0994, found 226.0995.

**Allyl 6-(2-allylphenyl)hex-5-ynoate** (**4m**).



Colorless oil; $^{1}$H NMR (600 MHz, $CDCl_3$): δ 7.36 (d, *J* = 6.6 Hz, 1 H), 7.26 – 7.12 (m, 3 H), 5.99 – 5.89 (m, 2 H), 5.32 – 5.21 (m, 2 H), 5.06 – 5.03 (m, 2 H), 4.58 (d, *J* = 6.6 Hz, 2 H ), 3.54 (d, *J* = 7.2 Hz, 2 H ), 2.55 – 2.47 (m, 4 H), 1.95 – 1.92 (m, 2 H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 172.8, 141.7, 136.7, 132.2, 131.5, 128.2, 127.9, 125.9, 123.2, 118.2, 115.8, 92.7, 79.9, 65.1, 38.7, 32.8, 23.9, 19.0; HRMS: calcd for $C_{18}H_{20}O_2$ 268.1463, found 268.1465.

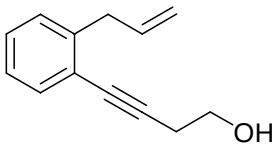
***N*-Allyl-*N*-(4-(2-allylphenyl)but-3-ynyl)-4-methylbenzenesulfonamide** (**4n**).



Colorless oil; $^{1}$H NMR (600MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.4 Hz, 2 H), 7.33 (d, *J* = 7.8 Hz, 1 H), 7.26 (d, *J* = 7.8 Hz, 2 H), 7.23 – 7.10 (m, 3 H), 5.99 - 5.91 (m, 1 H), 5.68 - 5.66 (m, 1 H), 5.21 - 5.15 (m, 2 H), 5.05 – 5.02 (m, 2 H), 3.87 (d, *J* = 6.6 Hz, 2 H), 3.48 (d, *J* = 6.6 Hz, 2 H), 3.36 (dd, *J* = 7.2, 5.2 Hz, 2 H), 2.69 (t, *J* = 7.2 Hz, 2 H),

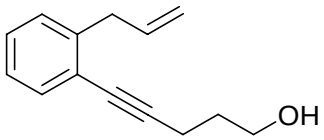
2.14 (s, 3 H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 143.3, 141.7, 136.9, 136.5, 133.0, 132.2, 129.7, 128.6, 128.1, 127.1, 125.9, 122.7, 119.2, 115.9, 90.3, 80.7, 51.2, 46.2, 38.6, 21.5, 20.3; HRMS: calcd for $C_{23}H_{25}NO_2S$ 379.1606, found 379.1609.

**4-(2-Allylphenyl)but-3-yn-1-ol** (**4o**).



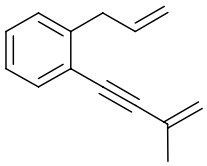

Colorless oil; $^1$H NMR (500 MHz, $CDCl_3$): δ 7.39 (d, *J* = 7.5 Hz, 1 H), 7.22 – 7.12 (m, 3 H), 6.01-5.93 (m, 1 H), 5.08 – 5.02 (m, 2 H), 3.80 (t, *J* = 6.0 Hz, 2 H), 3.53 (d, *J* = 6.5 Hz, 2 H), 2.70 (t, *J* = 7.0 Hz, 2 H), 1.97 (bs, 1 H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 141.7, 136.6, 132.2, 128.8, 128.2, 126.0, 122.8, 115.9, 90.2, 81.1, 61.2, 38.7, 23.9; HRMS: calcd for $C_{13}H_{14}O$ 186.1045, found 186.1050.

**5-(2-Allylphenyl)pent-4-yn-1-ol** (**4p**).




Colorless oil; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 7.5 Hz, 1 H), 7.23 – 7.11 (m, 3 H), 6.02-5.96 (m, 1 H), 5.10 – 5.08 (m, 2 H), 3.78 (t, *J* = 6.0 Hz, 2 H), 3.54 (d, *J* = 7.2 Hz, 2 H), 2.63 (bs, 1 H), 2.55 (t, *J* = 7.2 Hz, 2 H), 1.88 – 1.81 (m, 2 H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 141.6, 136.6, 132.1, 128.5, 127.7, 125.8, 122.6, 115.7, 93.2, 79.5, 61.4, 38.6, 31.4, 15.9; HRMS: calcd for $C_{14}H_{16}O$ 200.1201, found 200.1202.

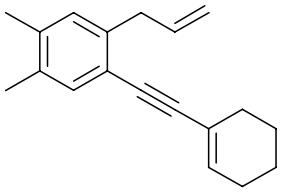
**1-Allyl-2-(3-methylbut-3-en-1-ynyl)benzene** (**4q**).



Colorless oil; $^1$H NMR (500 MHz, $CDCl_3$): δ 7.41 (d, *J* = 7.0 Hz, 1 H), 7.25 - 7.13 (m, 3 H), 6.00 - 5.94 (m, 1 H), 5.37 (s, 1 H), 5.28 (s, 1 H), 5.07 (t, *J* = 10.0 Hz, 2 H), 3.55

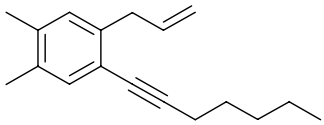
(d, *J* = 7.5 Hz, 2 H), 1.98 (s, 3 H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 141.3, 136.6, 132.1, 128.7, 128.4, 126.9, 126.0, 122.7, 121.6, 115.9, 94.5, 87.0, 38.8, 23.4; HRMS: calcd for $C_{14}H_{14}$ 182.1096, found 182.1099.

**1-Allyl-2-(cyclohexenylethynyl)-4,5-dimethylbenzene** (**4r**)**.**



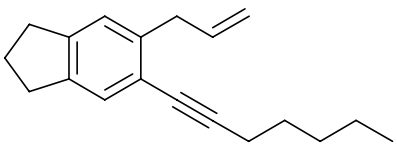
Colorless oil; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.18 (s, 1 H), 6.94 (s, 1 H), 6.19 (t, *J* = 2.4 Hz, 1 H), 5.97 – 5.94 (m, 1 H), 5.05 – 5.02 (m, 2 H), 3.52 (d, *J* = 7.2 Hz, 2 H), 2.14 – 2.10 (m, 4 H), 2.13 (s, 3 H), 2.11 (s, 3 H), 1.69 – 1.58 (m, 4 H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 139.0, 137.1, 136.7, 134.3, 134.2, 132.9, 128.0, 121.0, 120.3, 115.4, 94.2, 85.6, 38.4, 29.3, 25.7, 22.4, 21.5, 19.7, 19.0; HRMS: calcd for $C_{19}H_{22}$ 250.1722, found 250.1720.

**1-Allyl-2-(hept-1-ynyl)-4,5-dimethylbenzene** (**4s**).



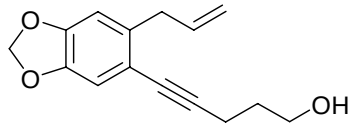
Colorless oil; $^1$H NMR (600 MHz, $CDCl_3$): δ 7.18 (s, 1 H), 6.95 (s, 1 H), 6.01 – 5.97 (m, 1 H), 5.10 – 5.04 (m, 2 H), 3.49 (d, *J* = 6.6 Hz, 2 H), 2.43 (t, *J* = 6.6 Hz, 2 H), 2.22 (s, 3 H), 2.19 (s, 3 H), 1.64 – 1.59 (m, 2 H), 1.48 – 1.35 (m, 4 H), 0.9 (t, *J* = 7.8 Hz, 3 H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 139.0, 137.2, 136.3, 134.1, 133.1, 129.9, 120.7, 115.3, 93.1, 79.2, 38.3, 36.1, 28.6, 22.2, 19.6, 19.5, 19.0, 14.0; HRMS: calcd for $C_{18}H_{24}$ 240.1878, found 240.1881.

**5-Allyl-6-(hept-1-ynyl)-2,3-dihydro-1H-indene** (**4t**).



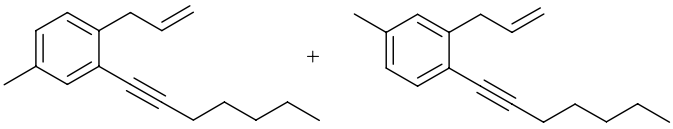
Colorless oil; $^1$H NMR (600 MHz, $CDCl_3$): δ 7.24 (s, 1 H), 7.03 (s, 1 H), 6.00 – 5.95 (m, 1 H), 5.08 – 5.01 (m, 2 H), 3.50 (d, *J* = 6.6, 2 H), 2.85 – 2.81 (m, 4 H), 2.42 (t, *J* = 6.6 Hz, 2 H), 2.03 – 2.01 (m, 2 H), 1.61 – 1.58 (m, 2 H), 1.44 – 1.34 (m, 4 H), 0.92 (t, *J* = 7.2 Hz, 3 H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 144.3, 141.9, 139.7, 137.4, 127.8, 124.5, 121.1, 115.3, 93.1, 79.6, 38.7, 32.8, 32.3, 31.1, 28.0, 25.4, 22.2, 19.5, 13.9; HRMS: calcd for $C_{19}H_{24}$ 252.1878, found 252.1880.

**5-(6-Allylbenzo[*d*][1,3]dioxol-5-yl)pent-4-yn-1-ol** (**4u**).




Colorless oil; $^1$H NMR (600 MHz, $CDCl_3$): δ 6.80 (s, 1 H), 6.64 (s, 1 H), 5.93 – 5.88 (m, 1 H), 5.90 (s, 2 H), 5.05 – 5.02 (m, 2 H), 3.79 (t, *J* = 6.0 Hz, 2 H), 3.43 (d, *J* = 7.2 Hz, 2 H), 2.53 (t, *J* = 7.2 Hz, 2 H), 1.86 – 1.81 (m, 2 H), 1.56 (bs, 1 H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 147.5, 145.6, 136.8, 136.5, 115.8, 111.6, 109.0, 101.1, 91.6, 79.6, 61.8, 38.5, 31.5, 16.1; HRMS: calcd for $C_{15}H_{16}O_3$ 244.1099, found 244.1098.

**1-Allyl-2-(hept-1-ynyl)-4-methylbenzene** (**4v**) **and 2-allyl-1-(hept-1-ynyl)-4-methylbenzene** (**4v'**).



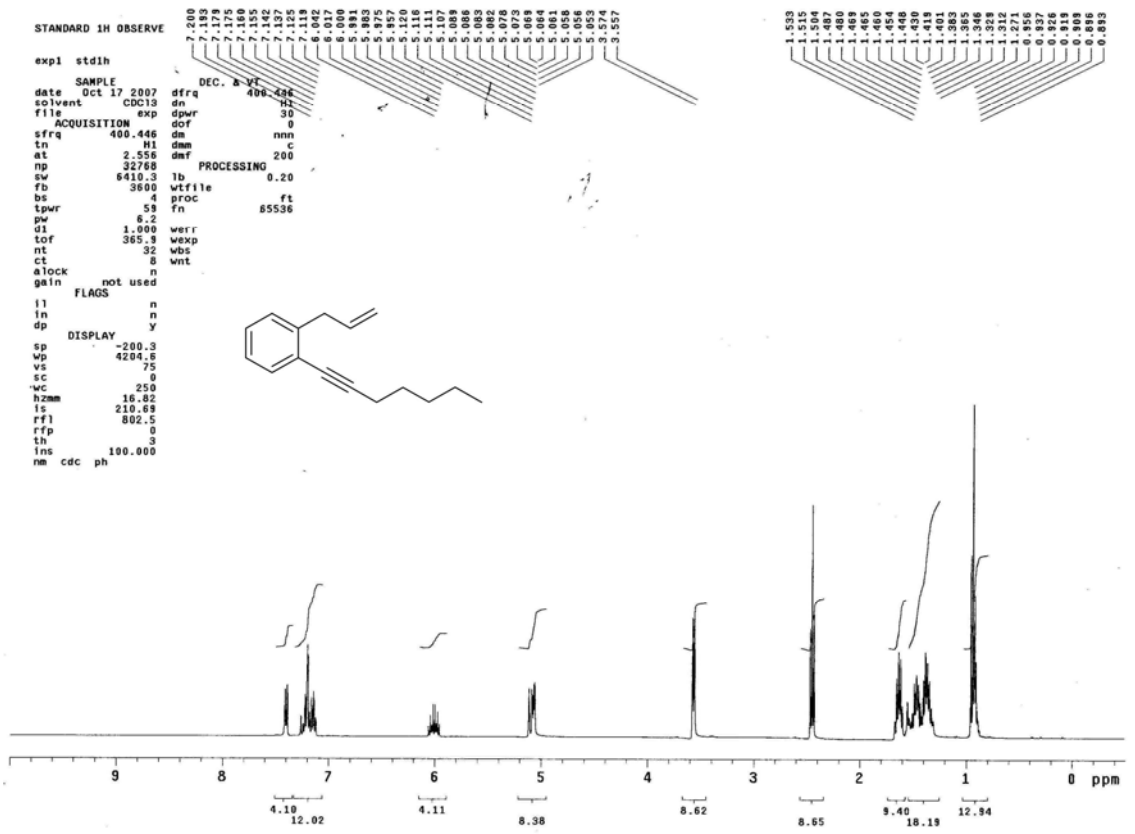

Colorless oil; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.29 – 7.21 (m, 2 H), 7.05 – 6.97 (m, 4 H), 6.07 – 5.95 (m, 2 H), 5.17 – 5.01 (m, 4 H), 3.52 (d, *J* = 6.4 Hz, 4 H), 2.40 (t, *J* = 6.0 Hz, 4 H), 2.23 (s, 3 H), 2.21 (s, 3 H), 1.64 – 1.62 (m, 4 H), 1.46 – 1.42 (m, 4 H), 1.39 – 1.31 (m, 4 H), 0.94 – 0.89 (m, 6 H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 141.5, 138.7, 137.5, 137.1, 136.9, 135.4, 132.6, 131.9, 129.3, 128.5, 128.4, 126.9, 126.7, 115.5, 115.4, 93.9, 93.5, 77.5, 77.3, 38.7, 38.3, 31.1, 30.9, 28.6, 28.0, 22.2, 22.1, 21.3, 20.7, 19.5, 19.1, 14.0, 13.9; HRMS: calcd for $C_{17}H_{22}$ 226.1722, found 226.1725.

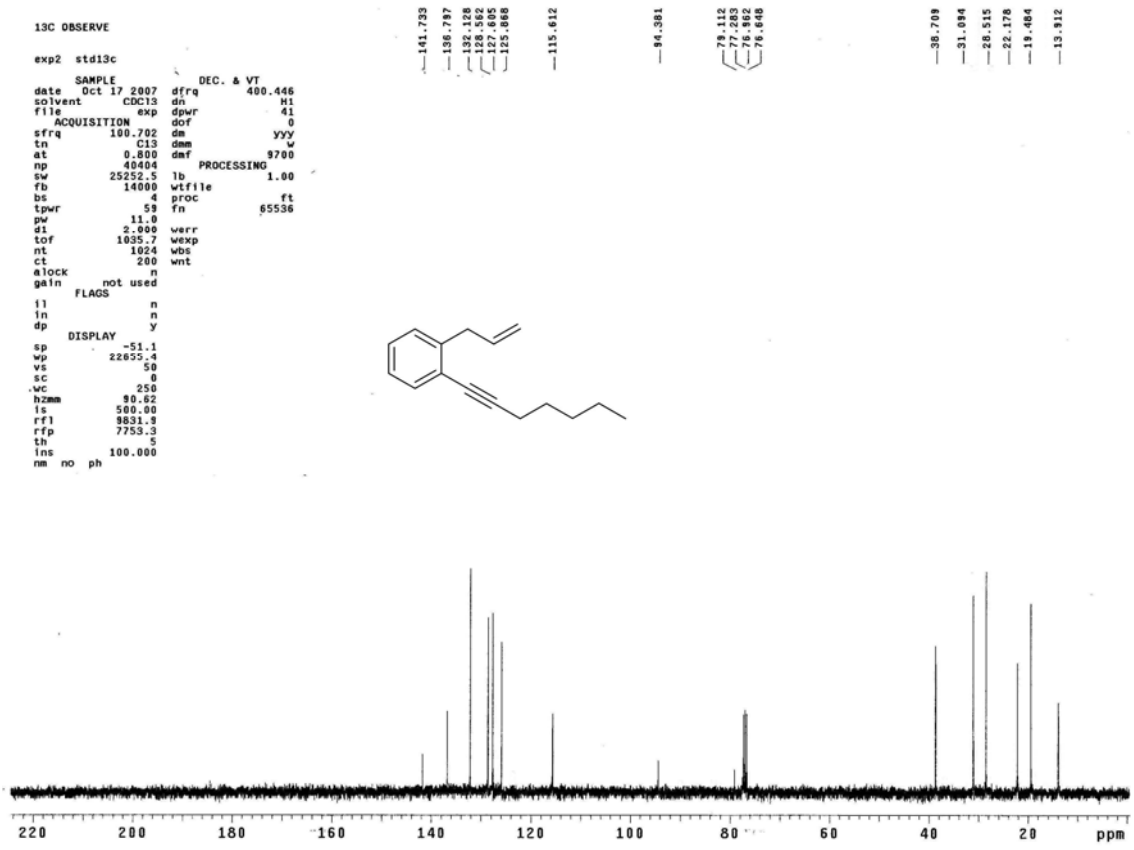
**References.**

1. D. D. Perrin and W. L. F. Armarego, *In Purification of Laboratory Chemicals*, 3rd edn, Pergamon Press: New York, 1988.

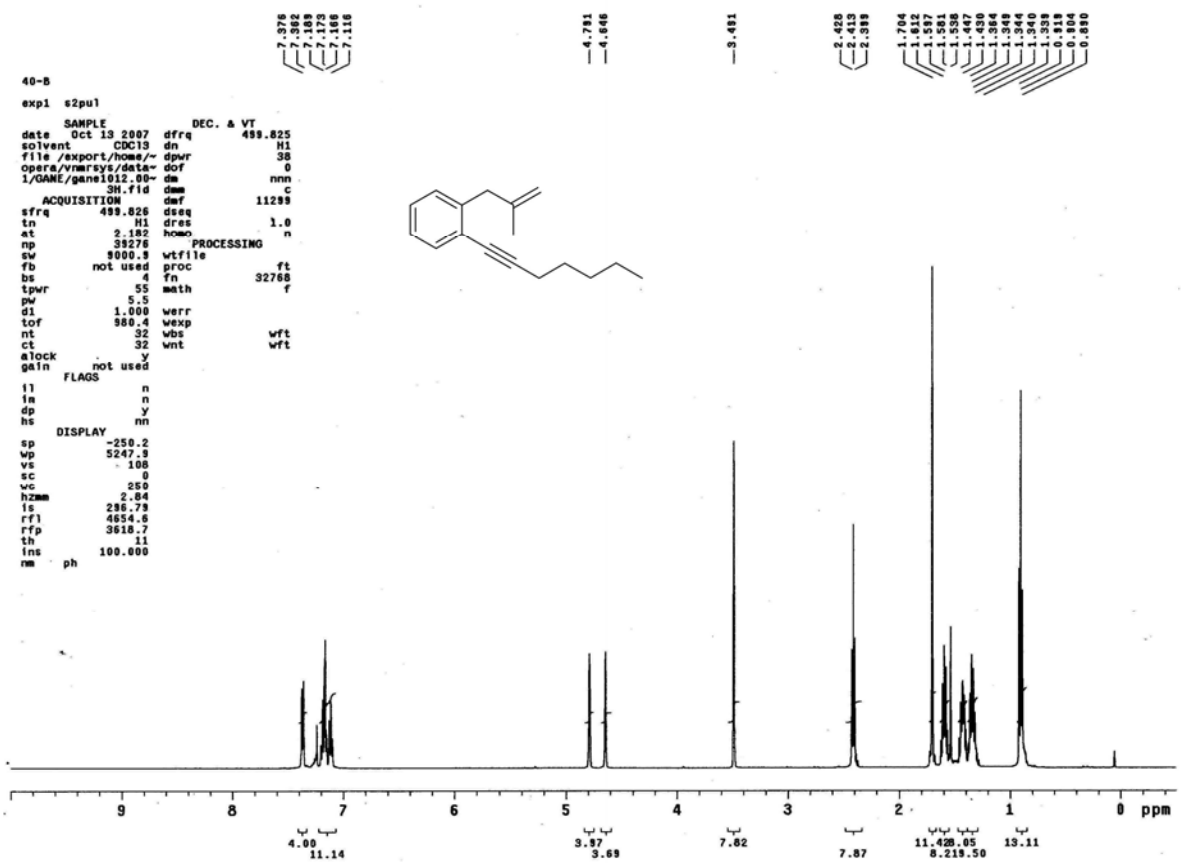
2. (a) Y. Himeshima, T. Sonoda and H. Kobayashi, *Chem. Lett*. 1983, 1211; (b) D. Pena, D. Perez, E. Guitian and L. Castedo, *J. Am. Chem.* Soc., 1999, **121**, 5827; (c) E. Yoshikawa, K. V. Radhakrishnan and Y. Yamamoto *J. Am. Chem. Soc*., 2000, **122**, 7280.

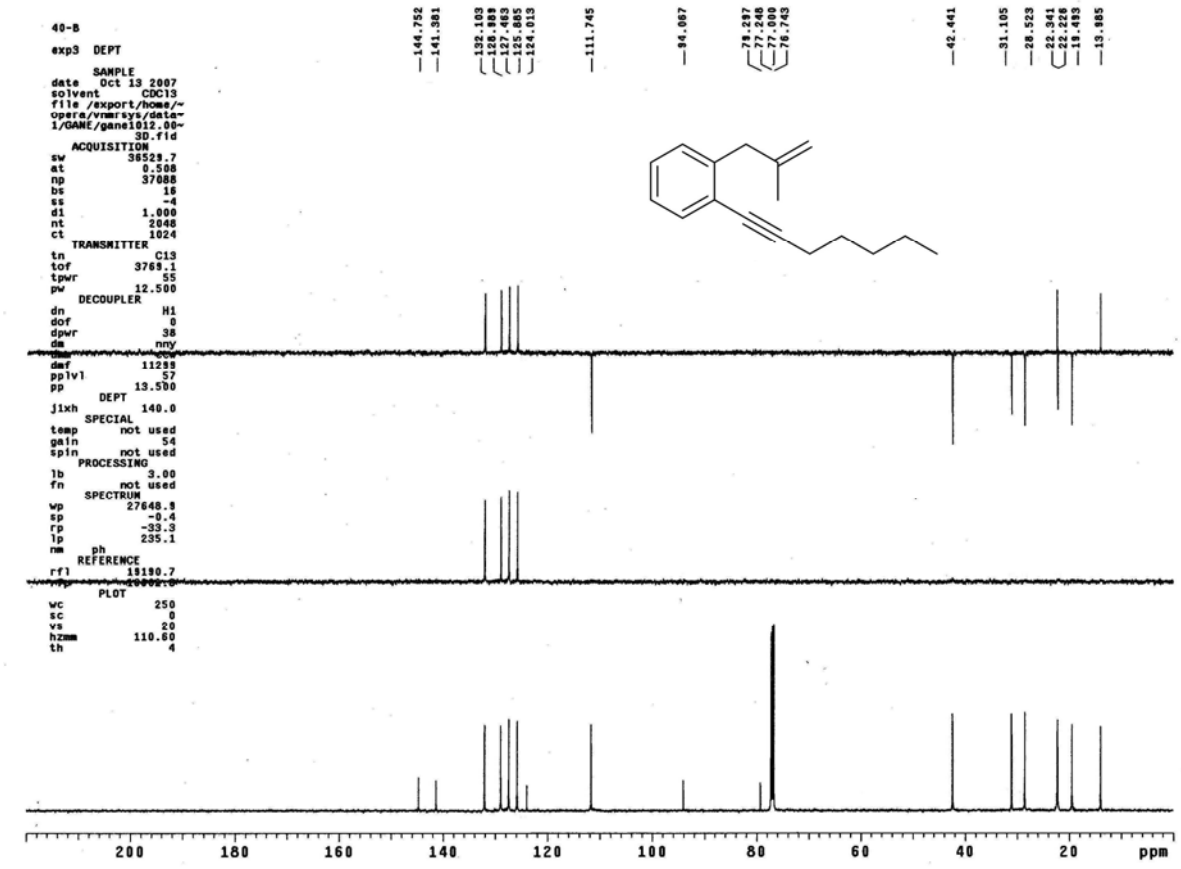
$^{1}$H and $^{13}$C NMR spectra of compound **4a**.



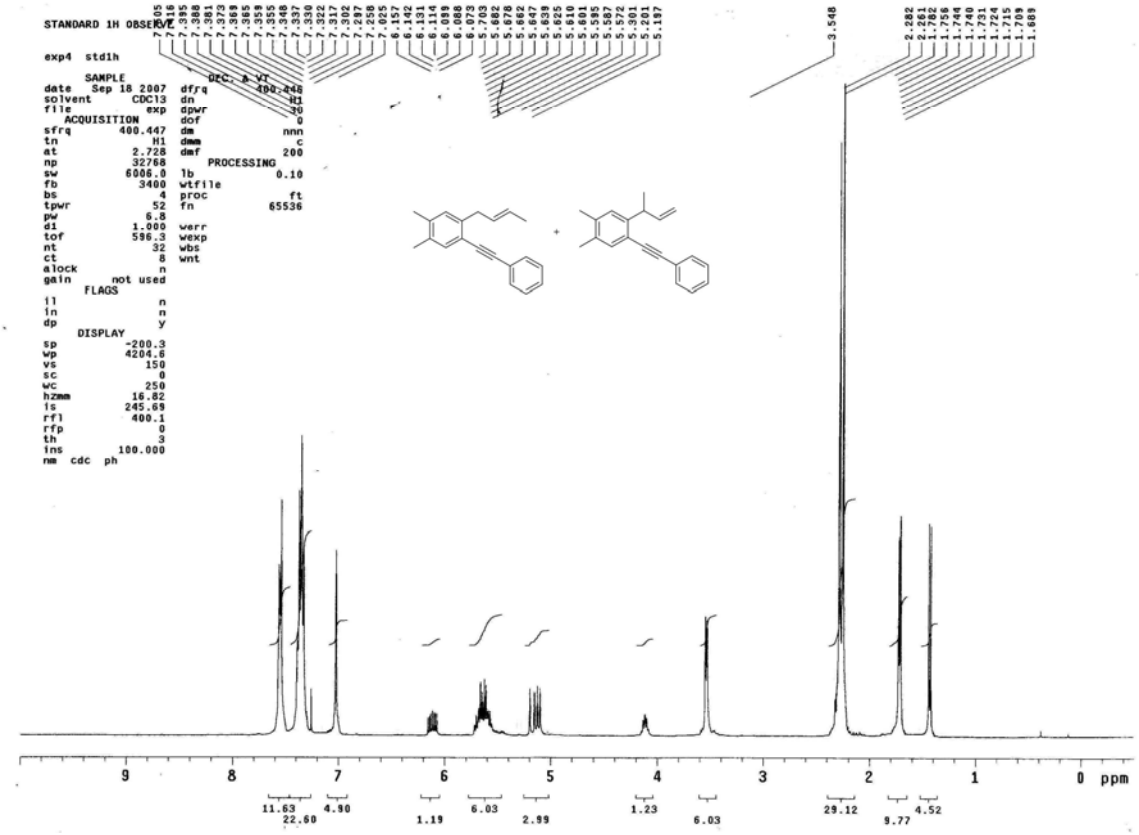



$^{1}H$ and $^{13}C$ NMR spectra of compound **4b**.

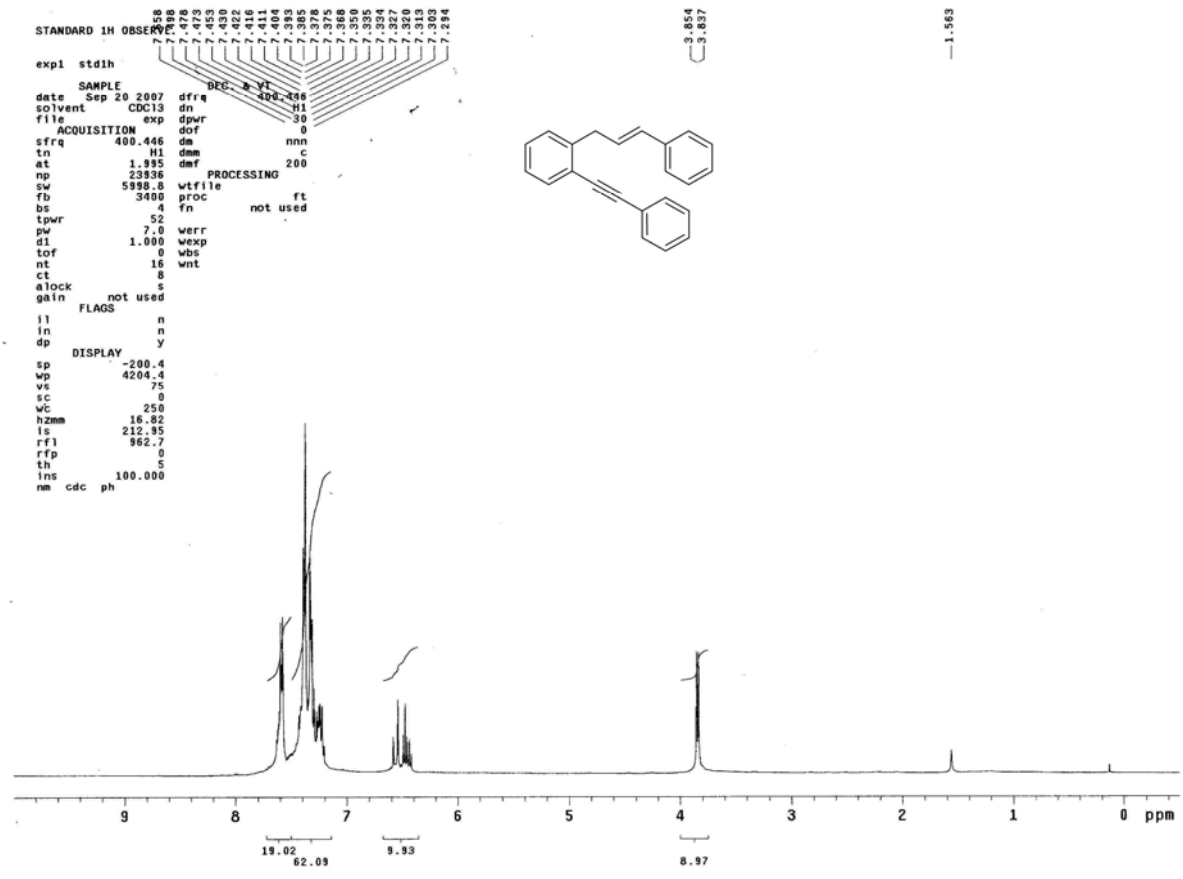


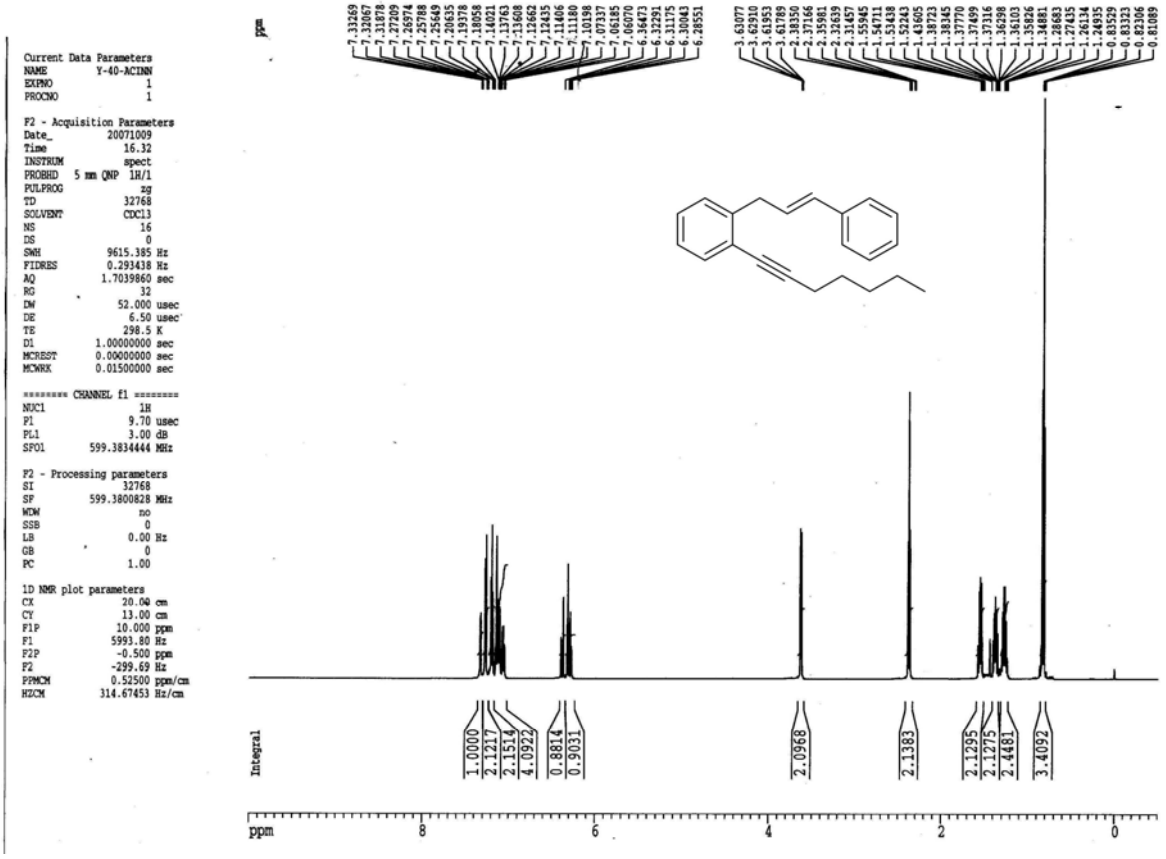
$^1$H NMR spectrum of compounds **4c** and **4d**.

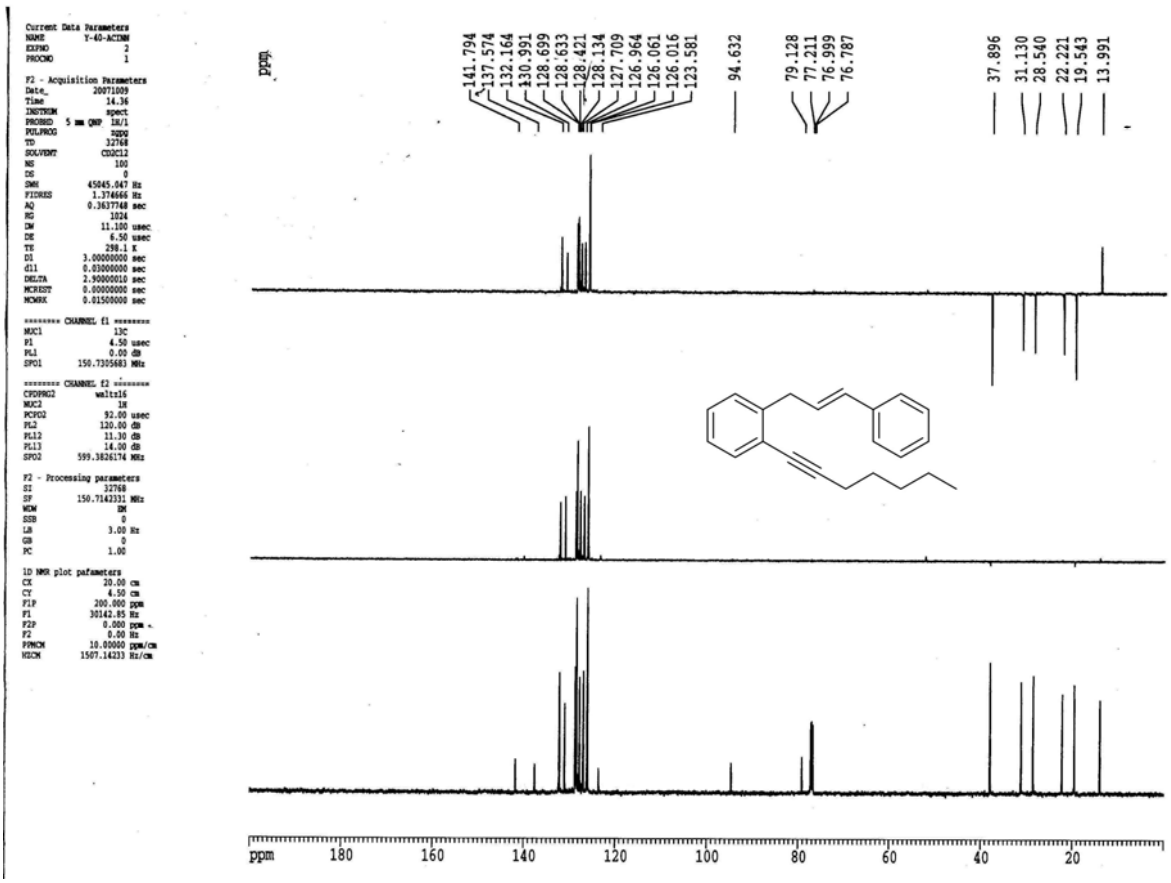



$^1$H NMR spectrum of compound **4f**.

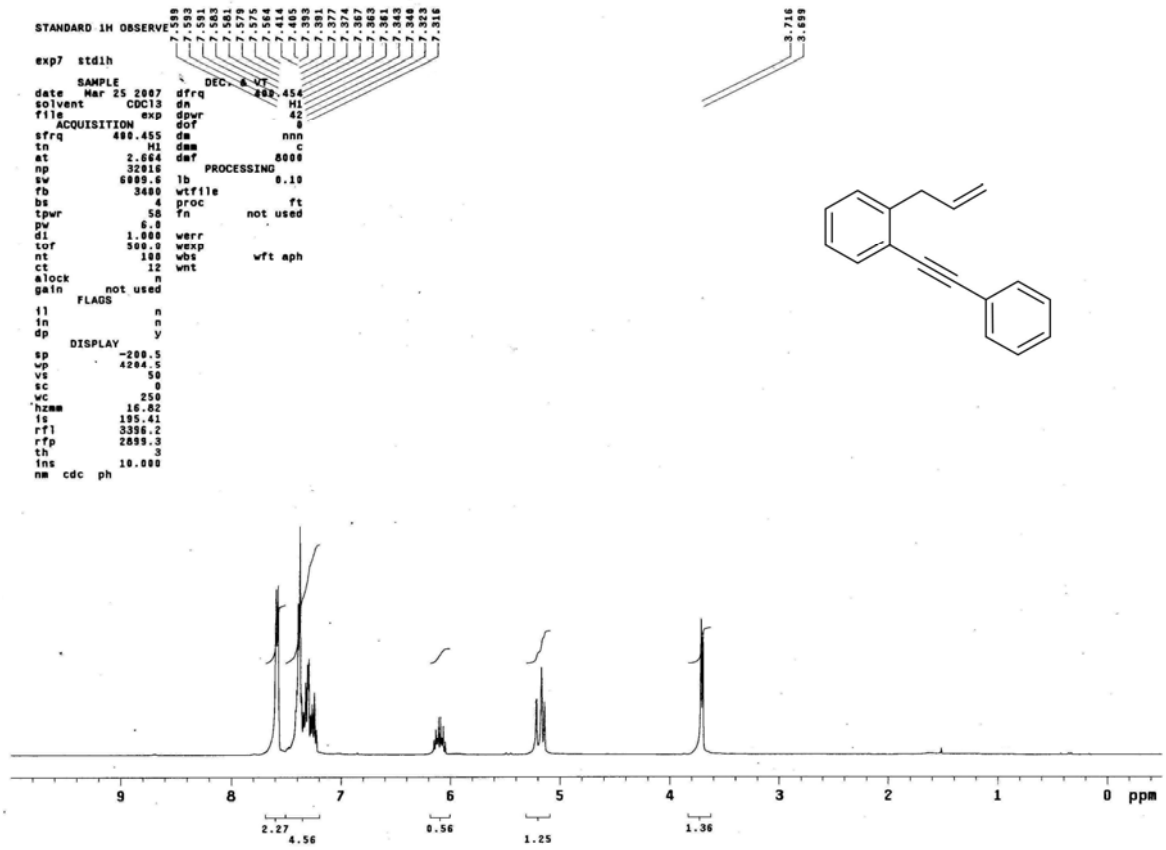


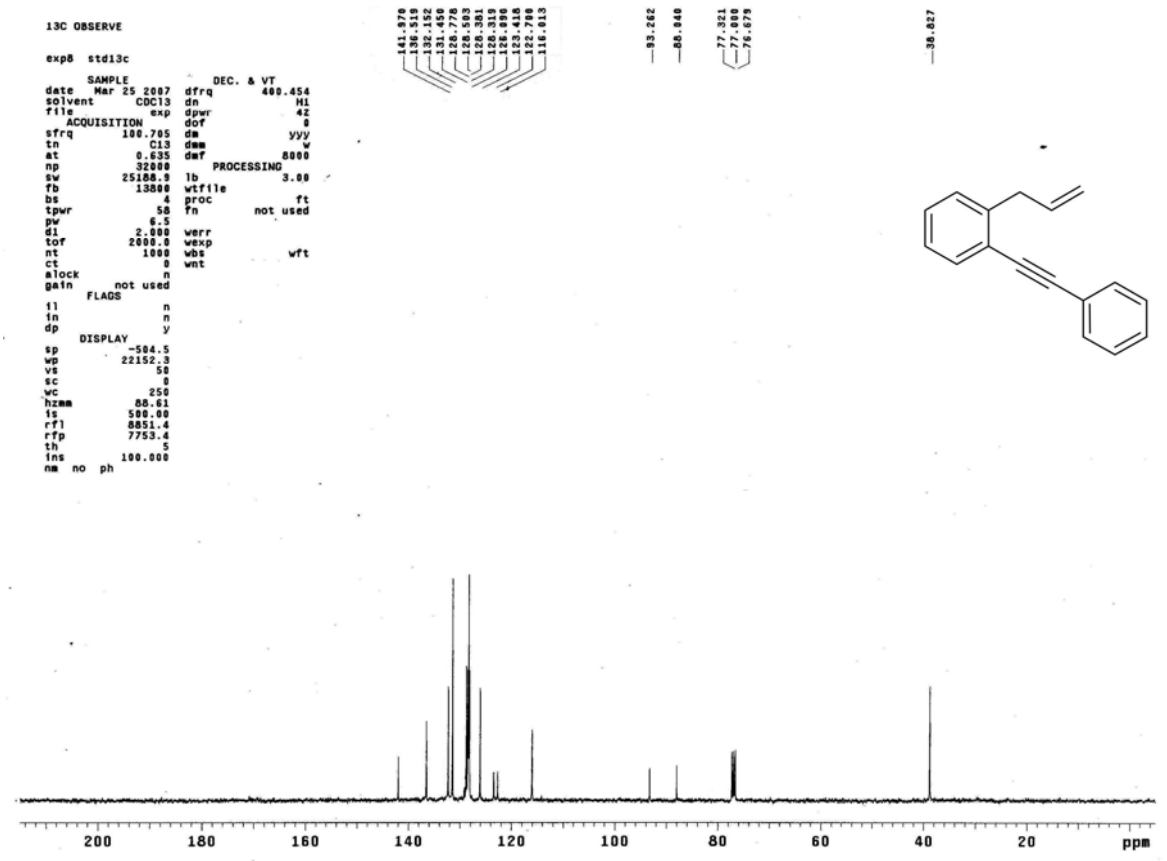
$^{1}$H and $^{13}$C NMR spectra of compound **4e**.



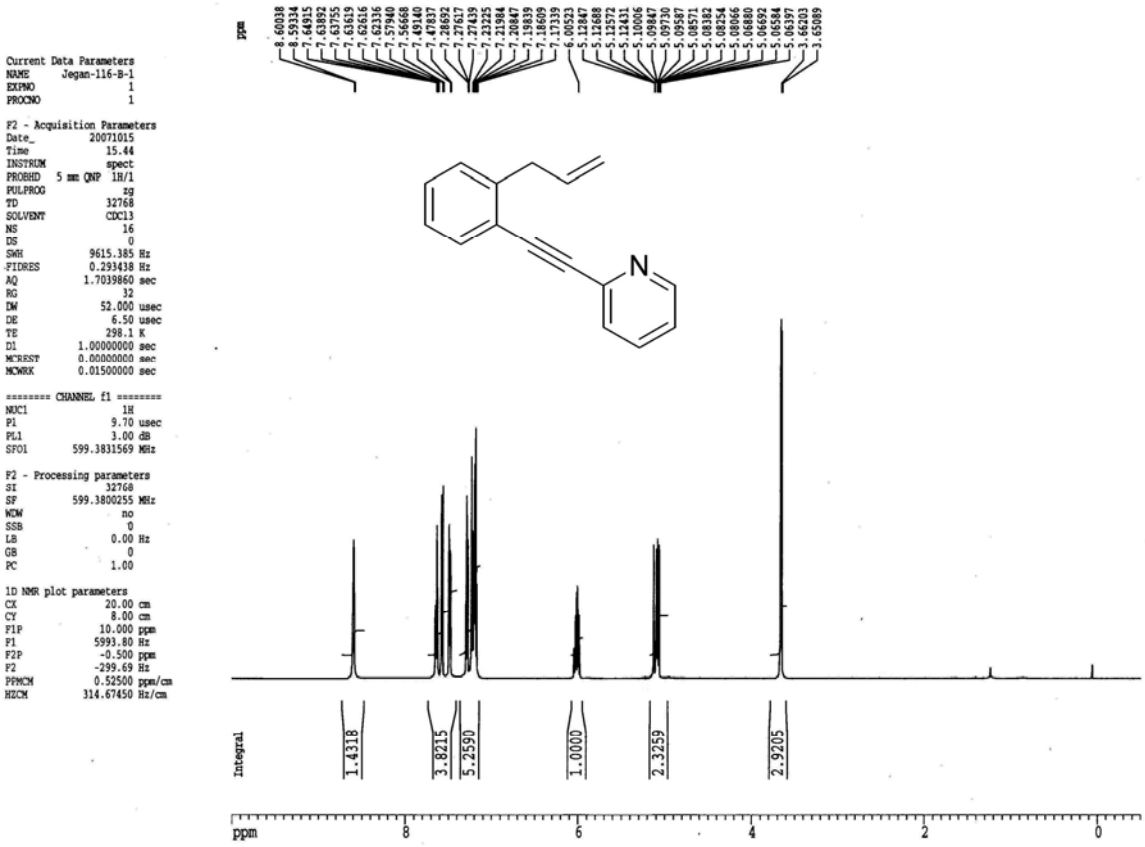



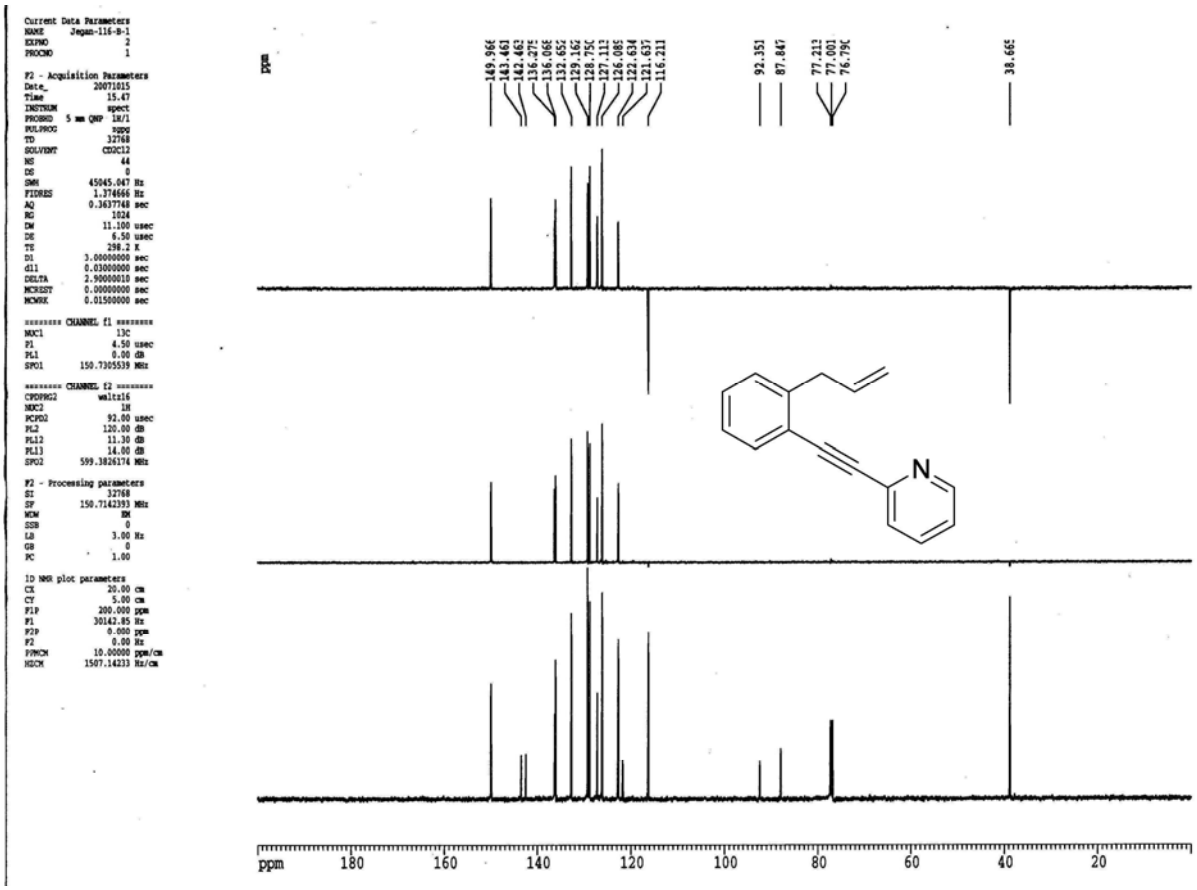
$^{1}H$ and $^{13}C$ NMR spectra of compound **4g**.



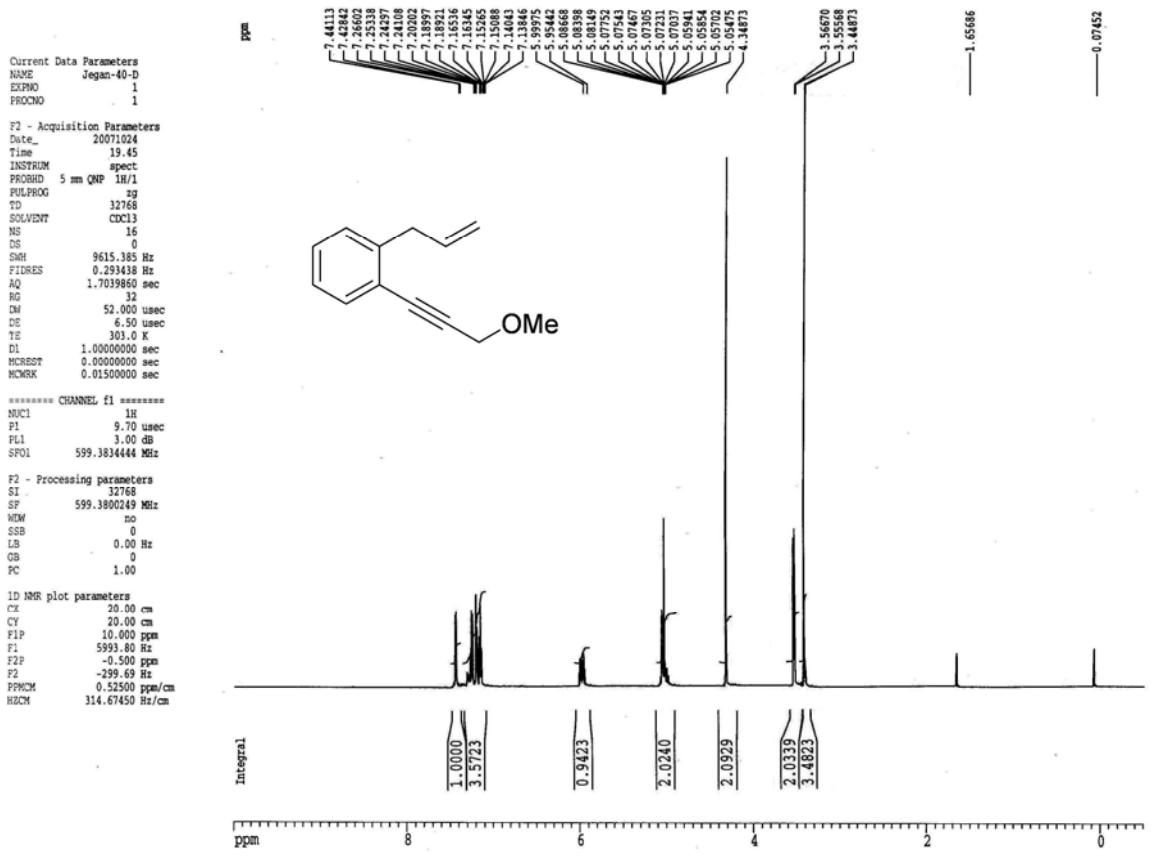



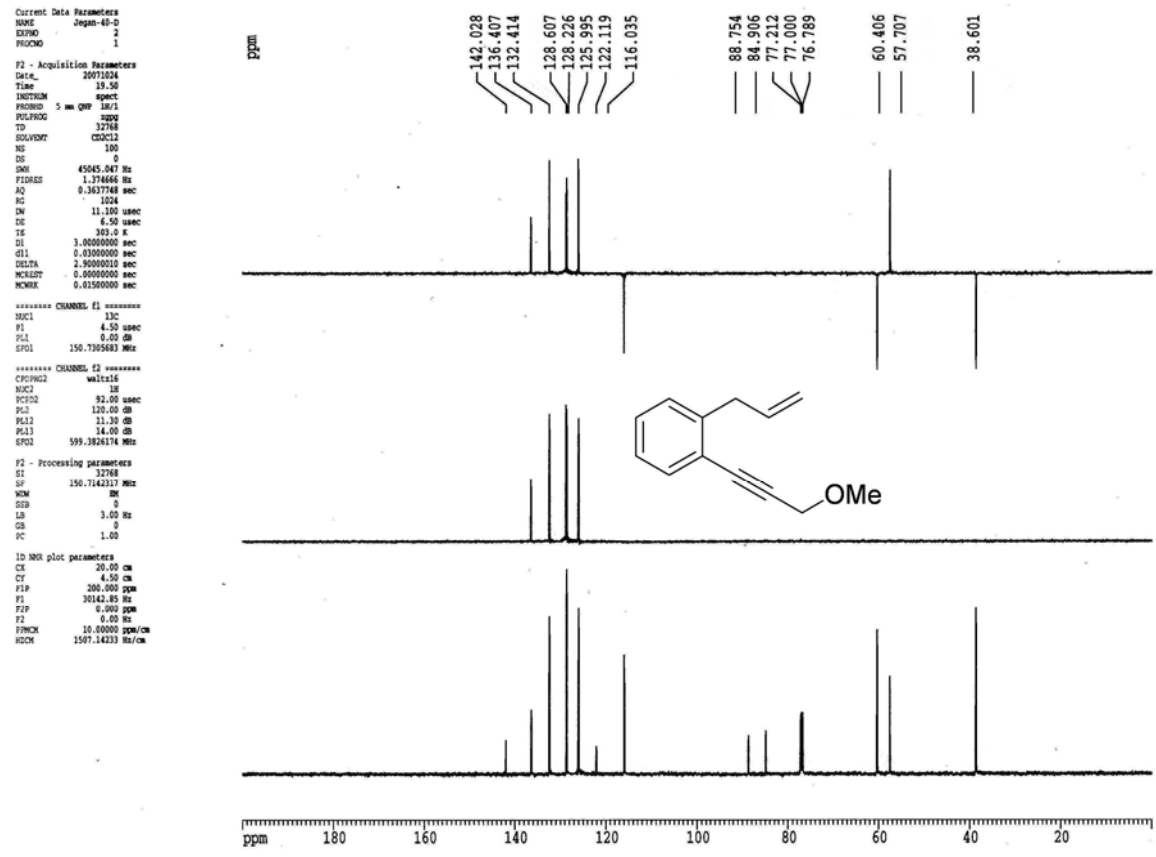
# $^{1}H$ and $^{13}C$ NMR spectra of compound **4h**.



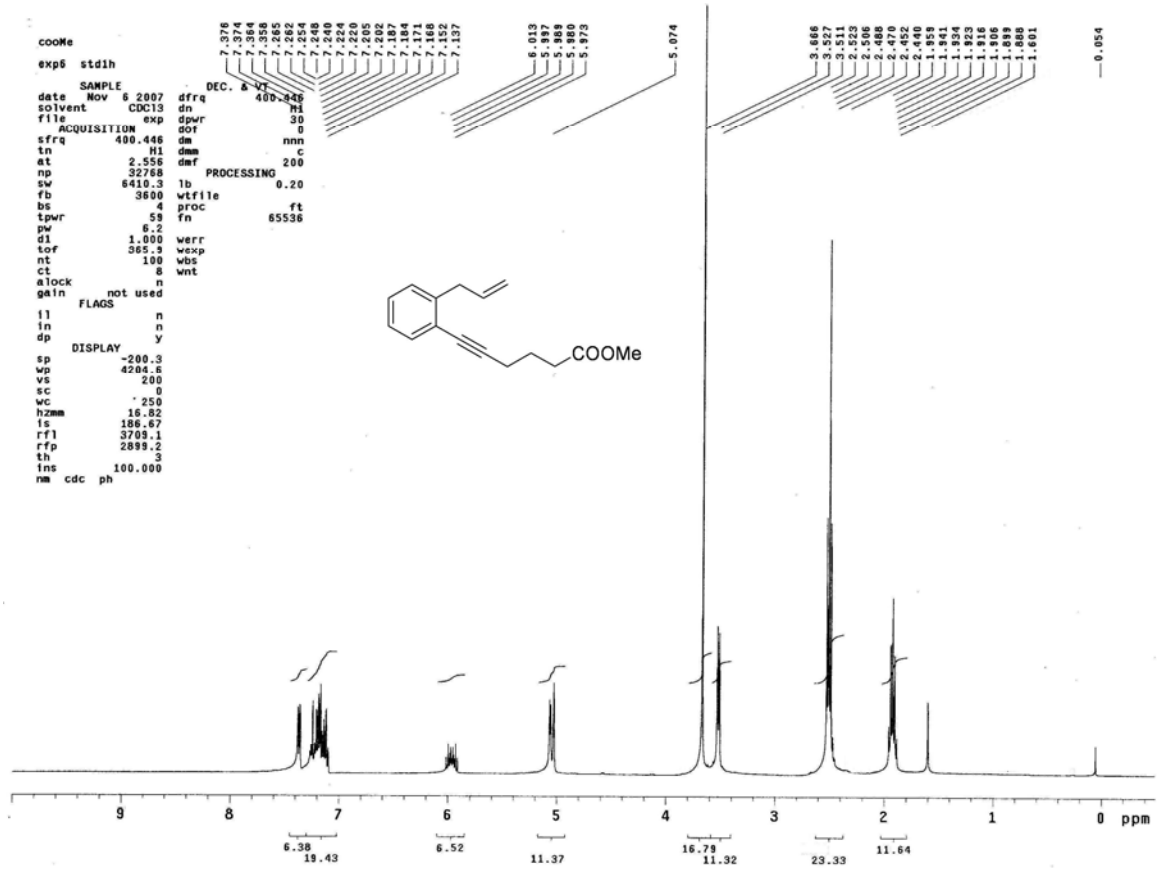



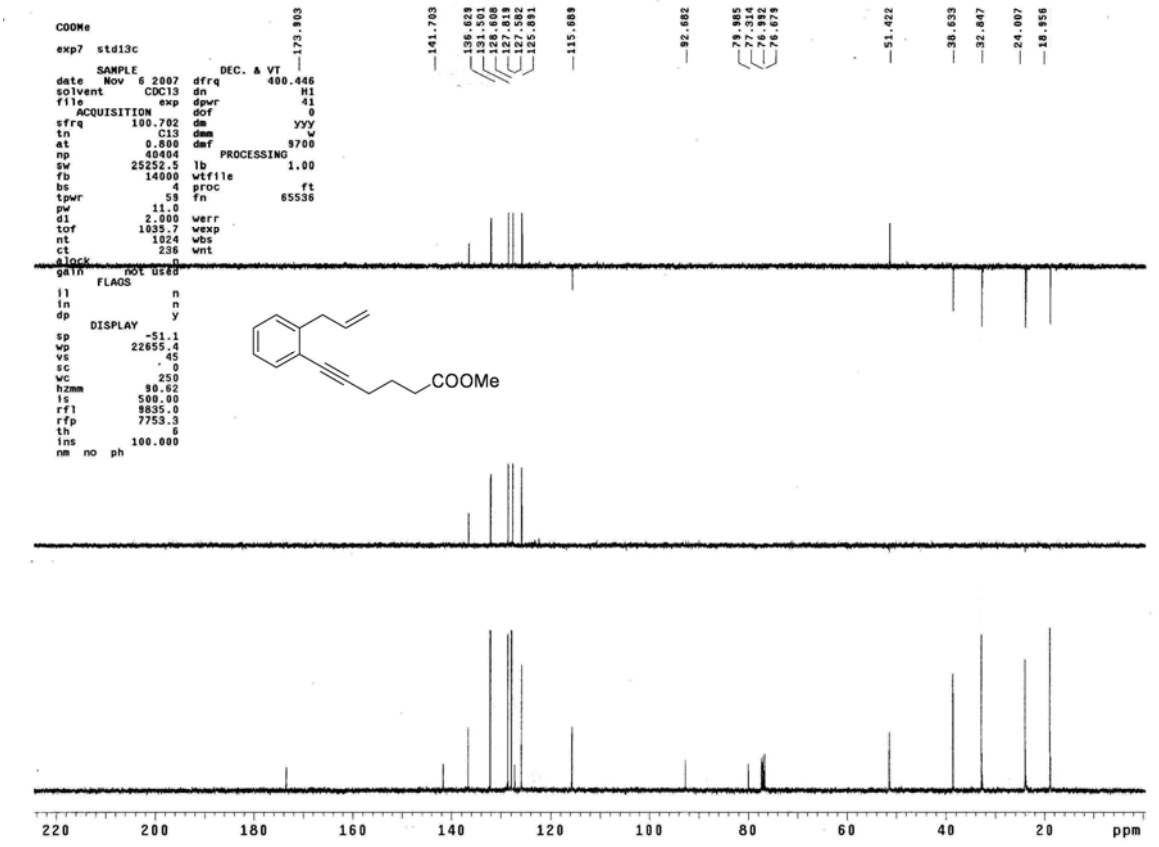
# $^{1}H$ and $^{13}C$ NMR spectra of compound **4i**.



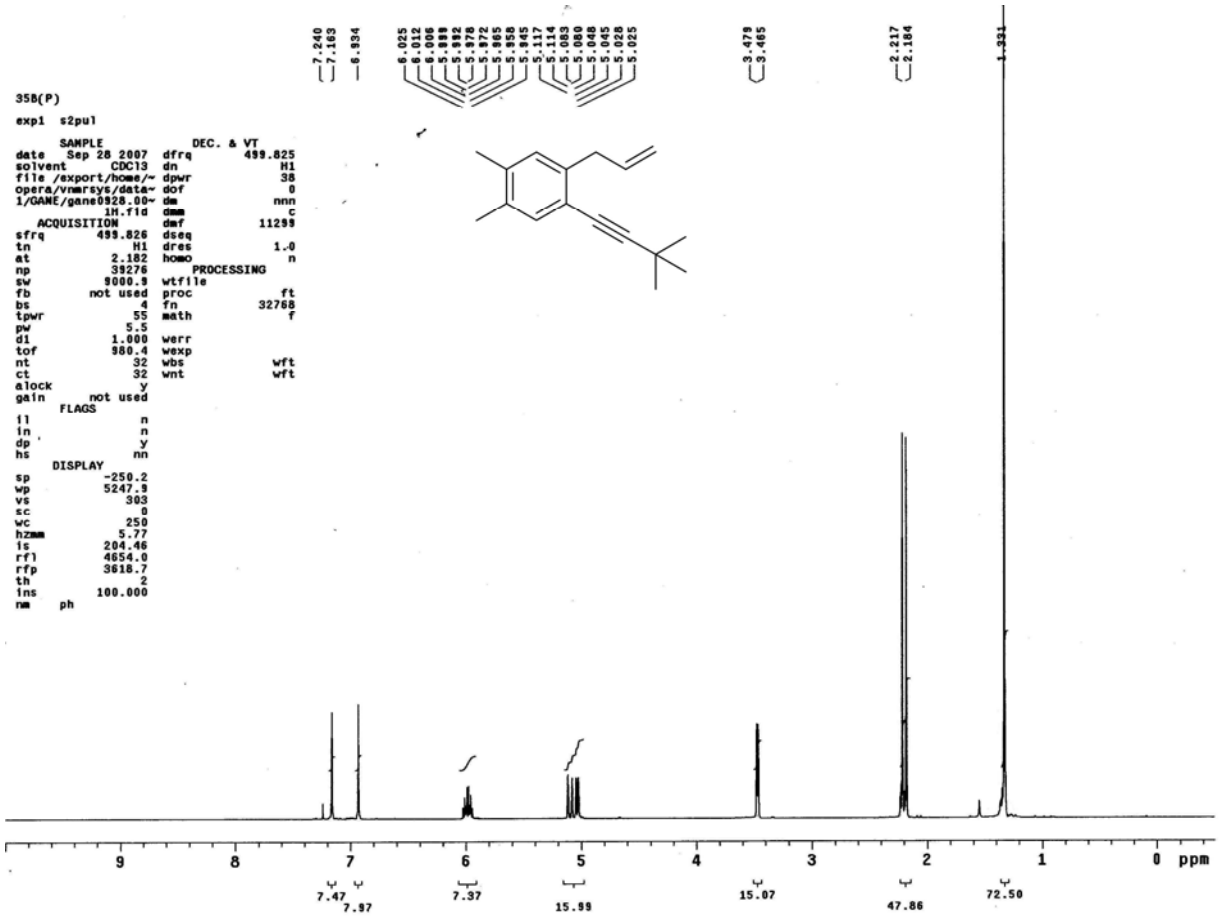



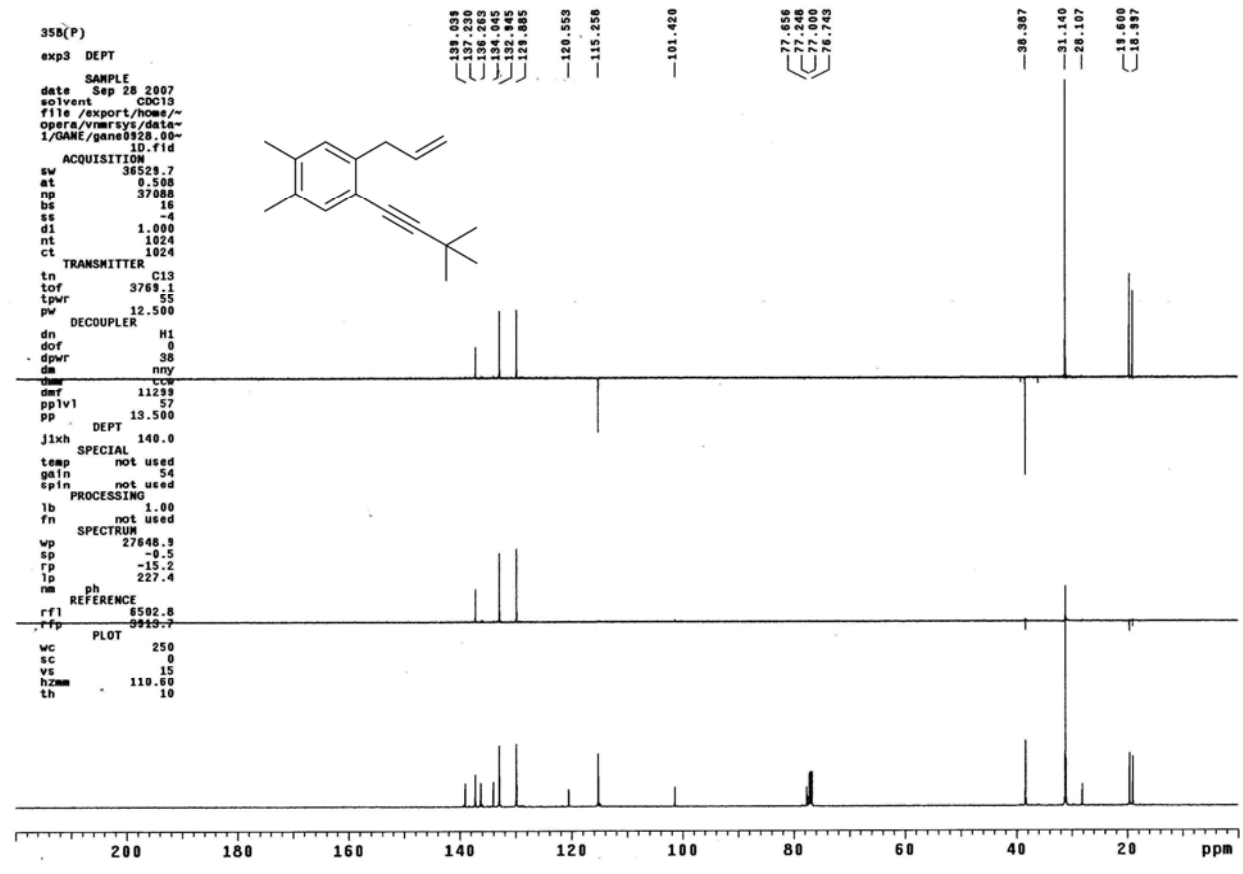
$^{1}$H and $^{13}$C NMR spectra of compound **4j**.



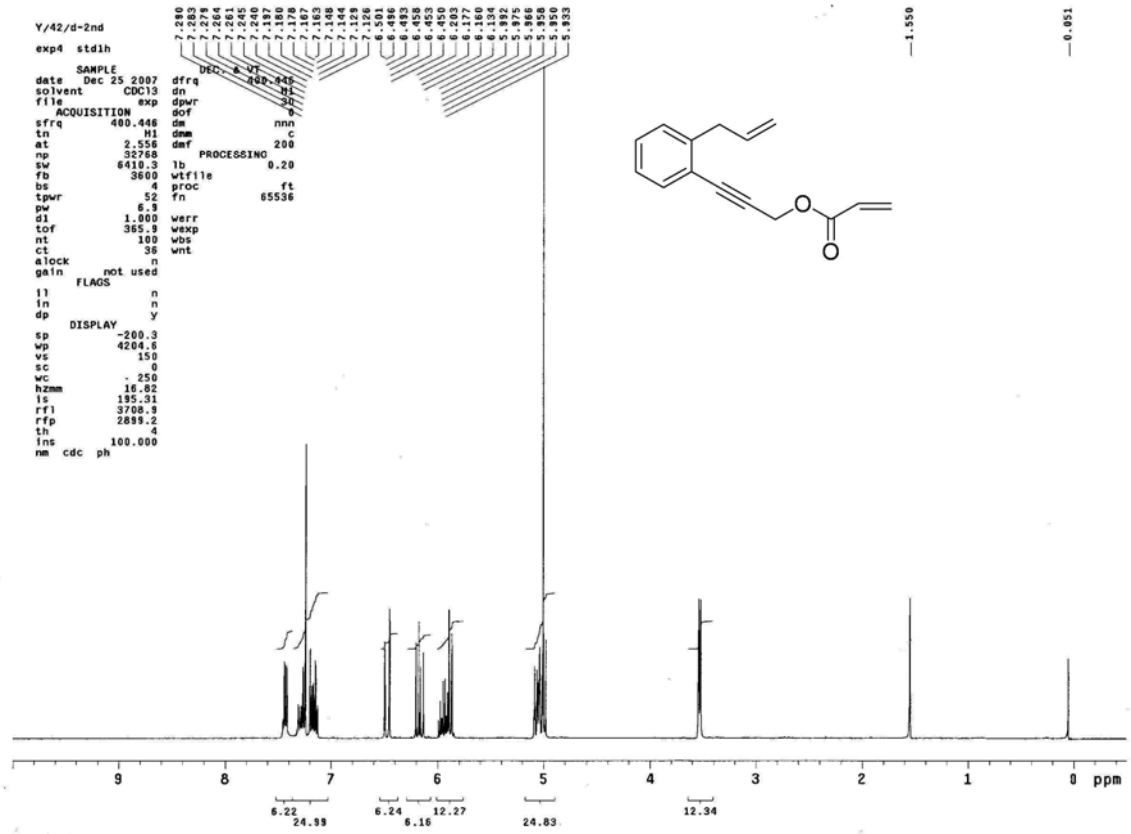



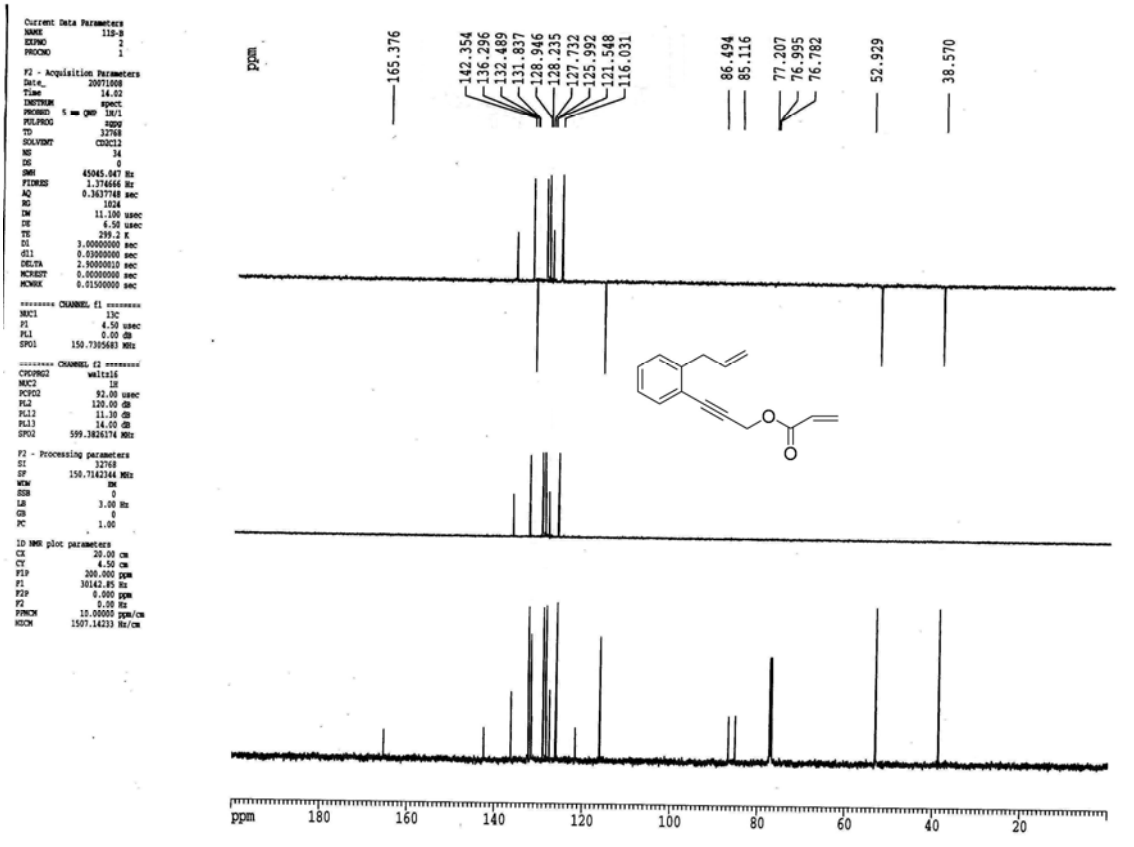
$^{1}$H and $^{13}$C NMR spectra of compound **4k**.



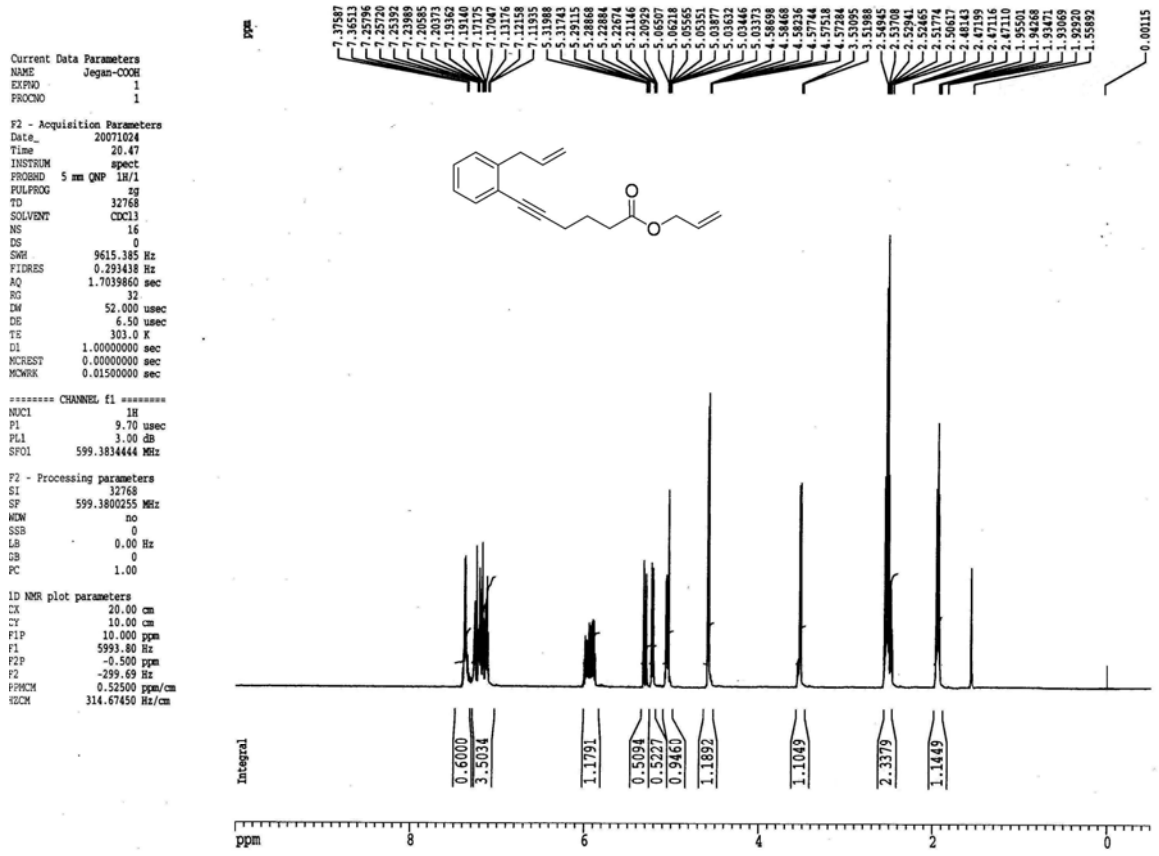



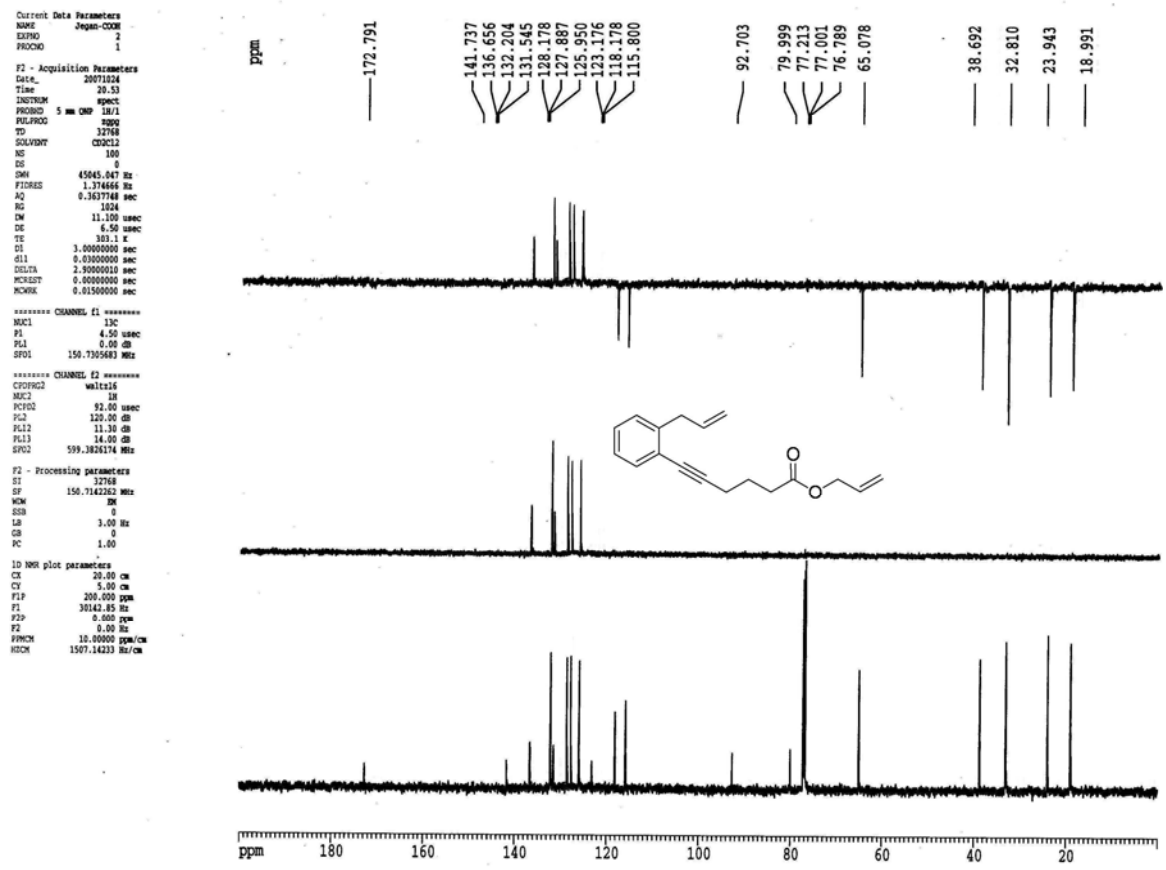
$^{1}$H and $^{13}$C NMR spectra of compound **4l**.



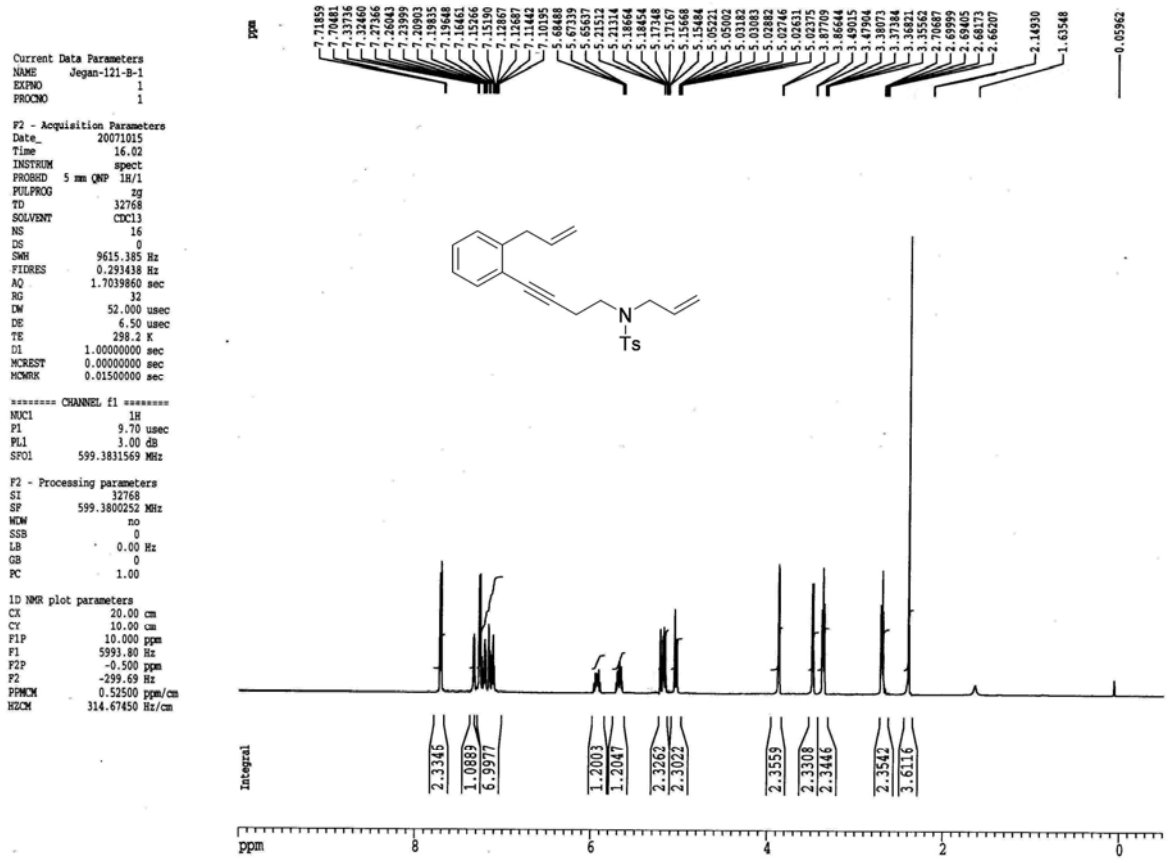



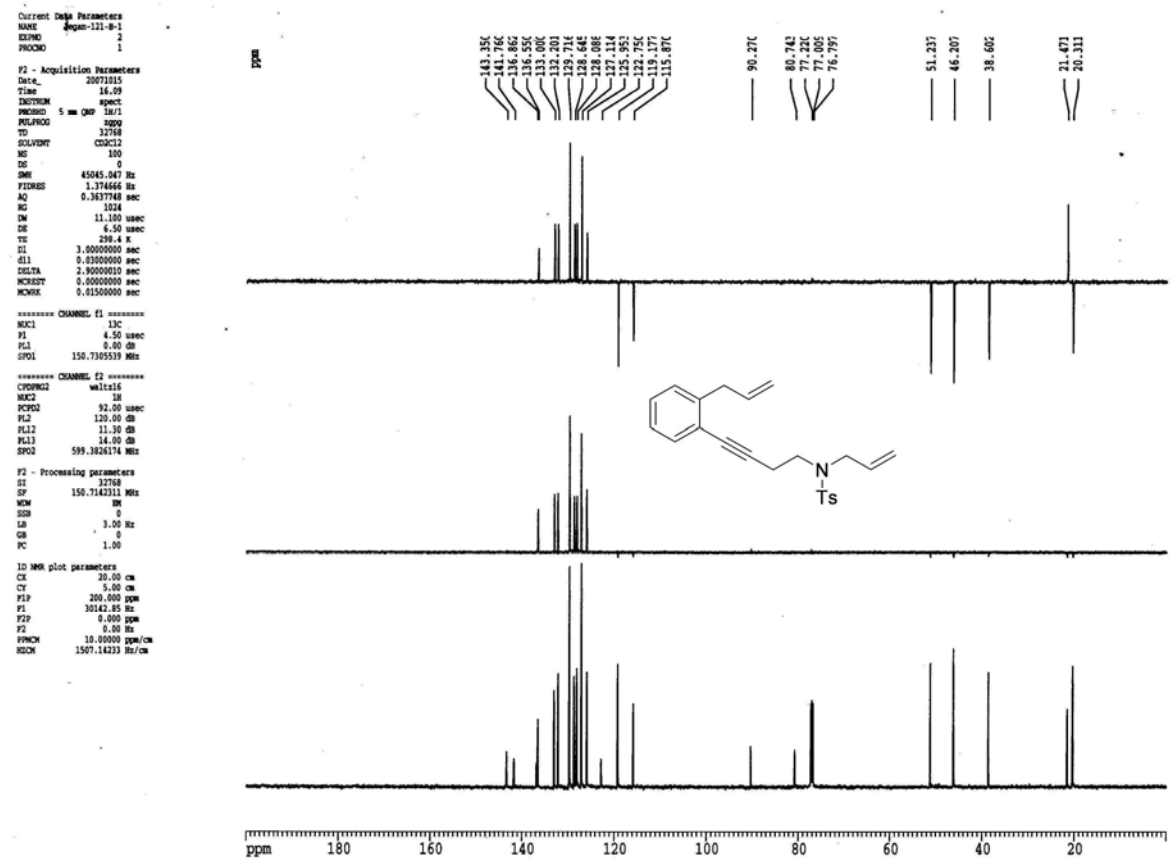
$^{1}H$ and $^{13}C$ NMR spectra of compound **4m**.



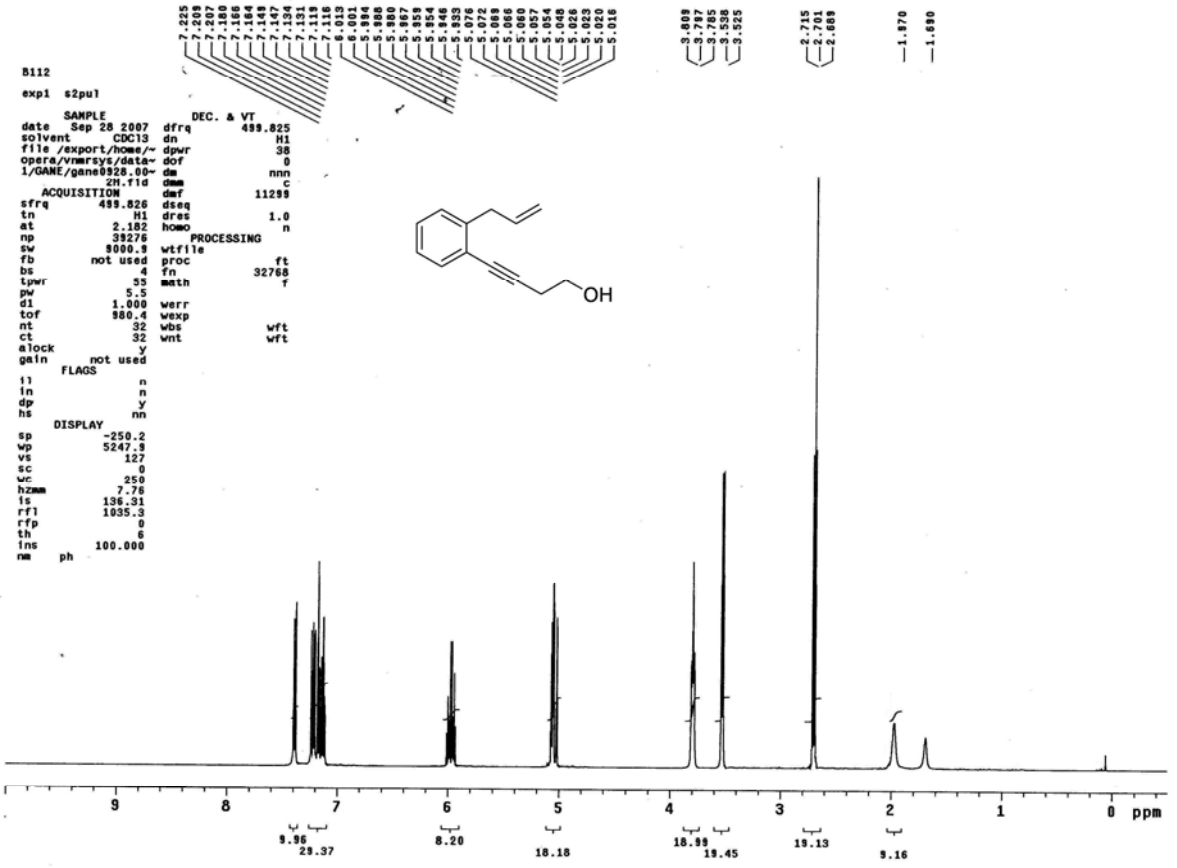



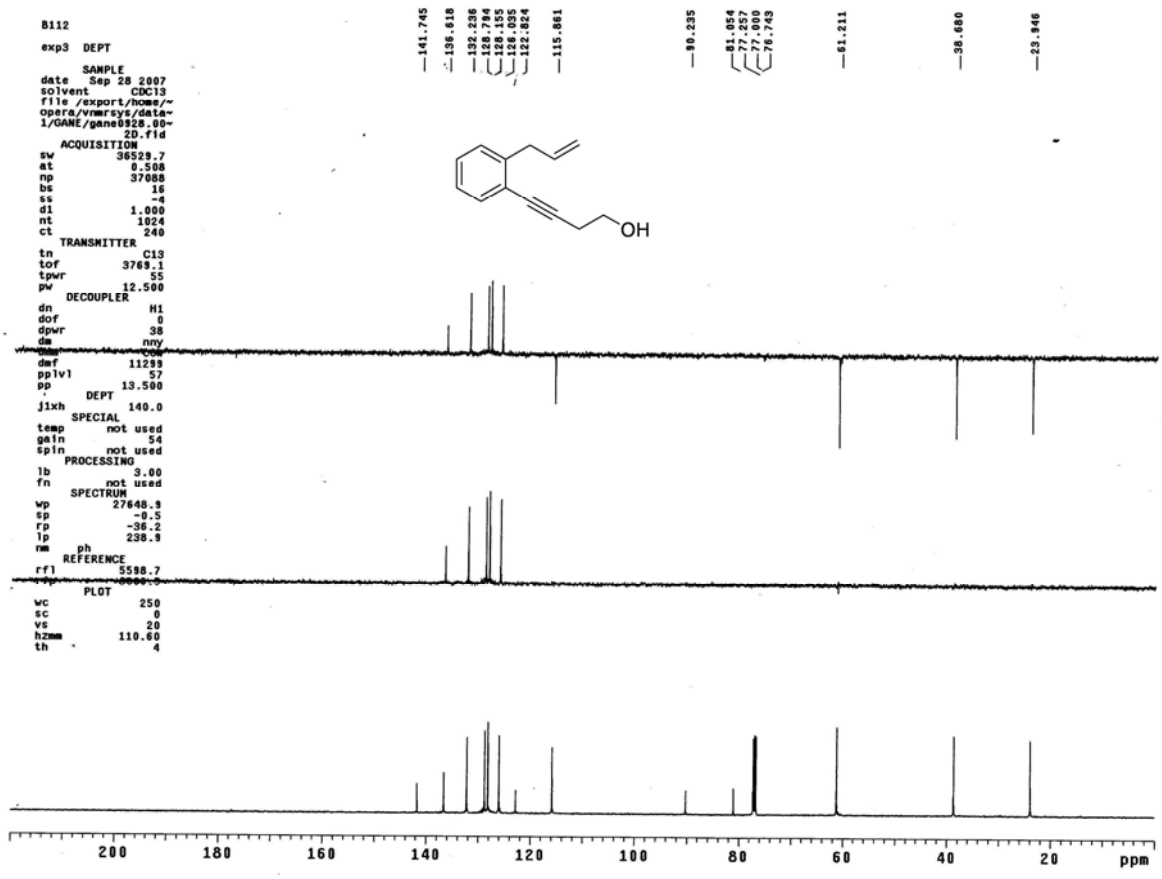
$^{1}$H and $^{13}$C NMR spectra of compound **4n**.



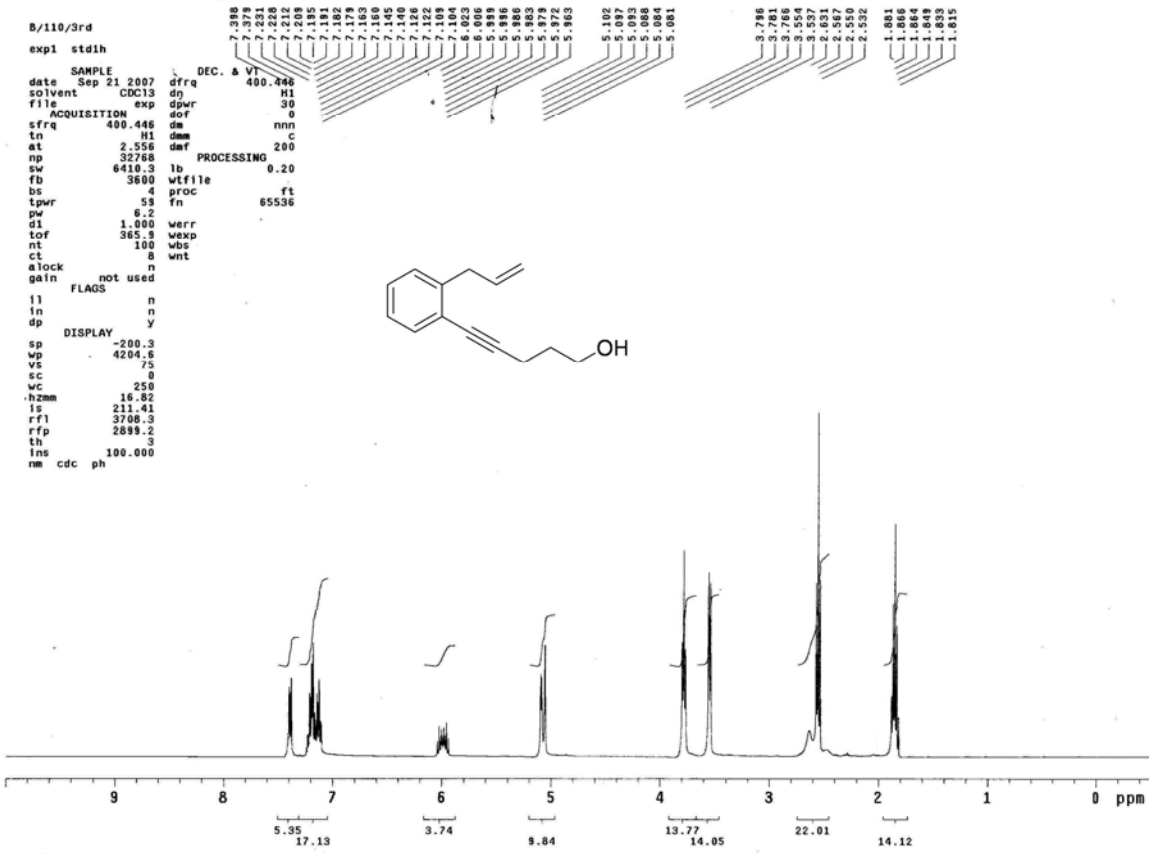



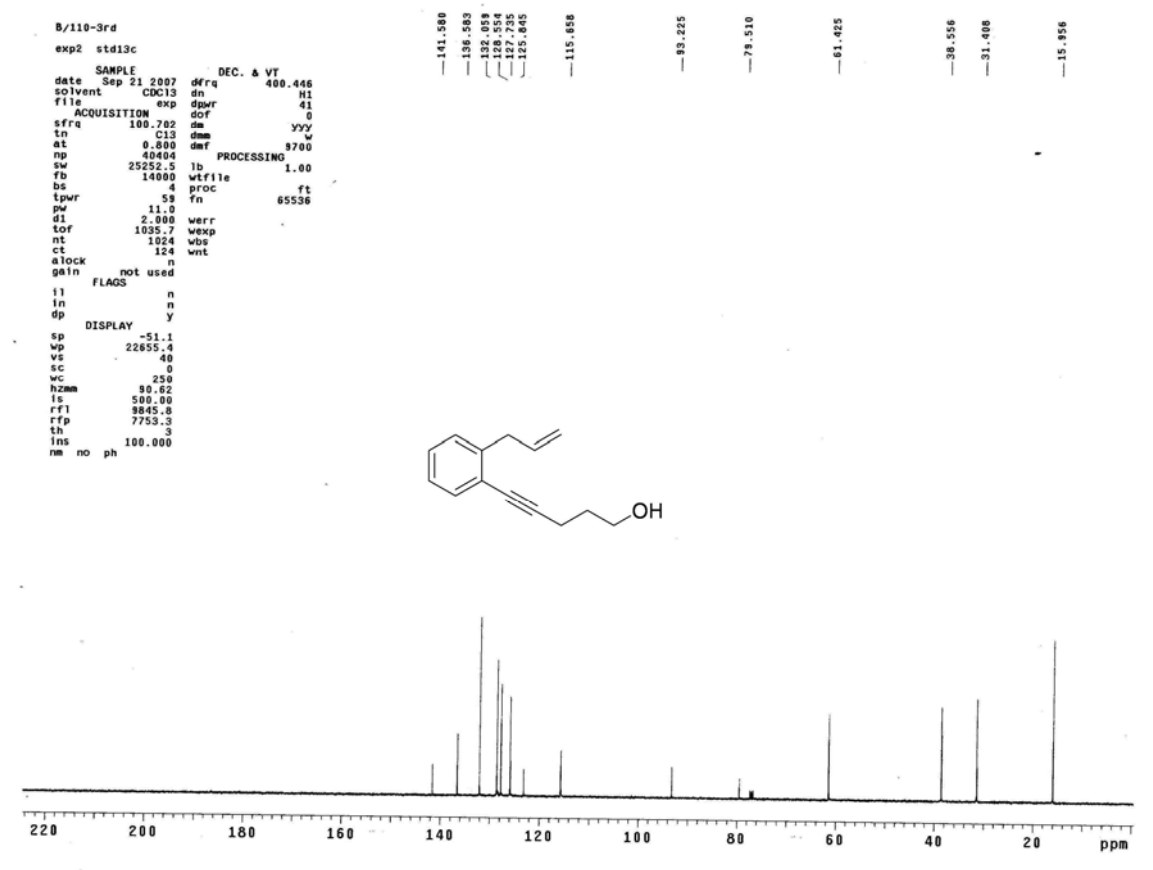
$^{1}H$ and $^{13}C$ NMR spectra of compound **4o**.



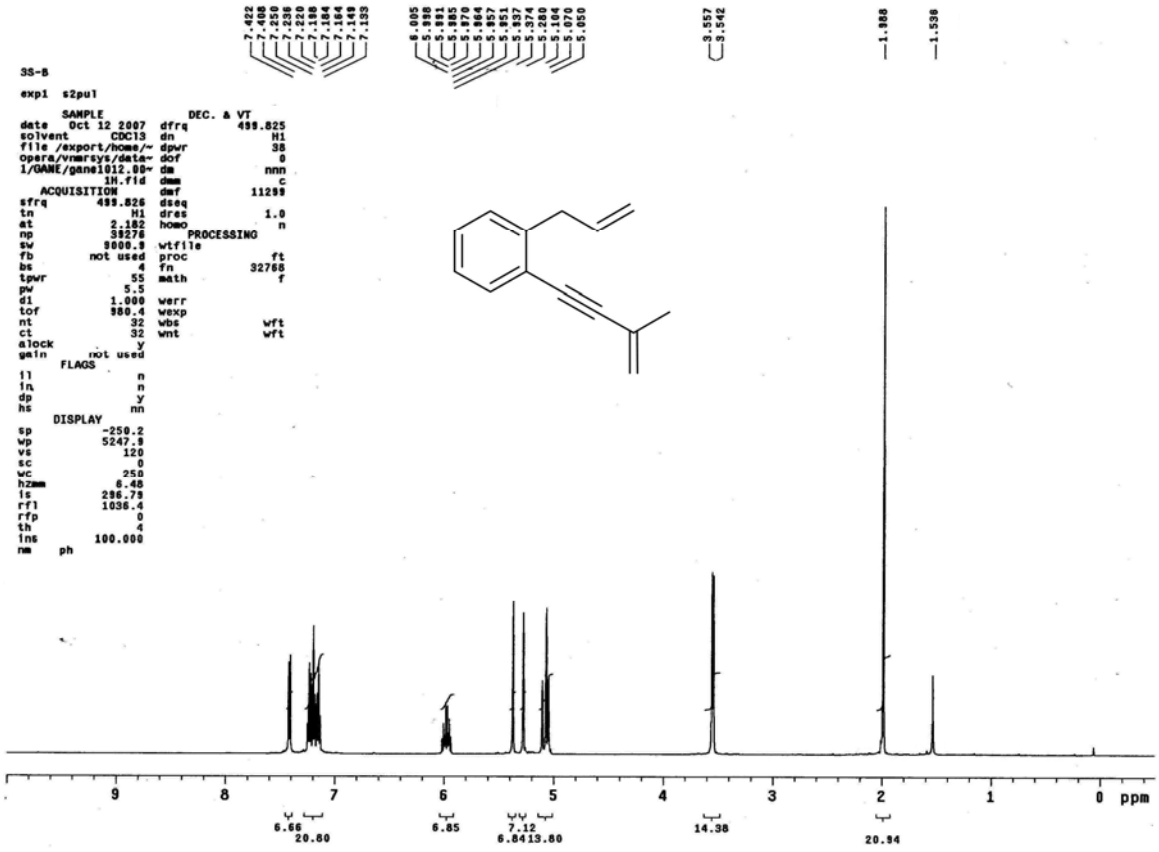



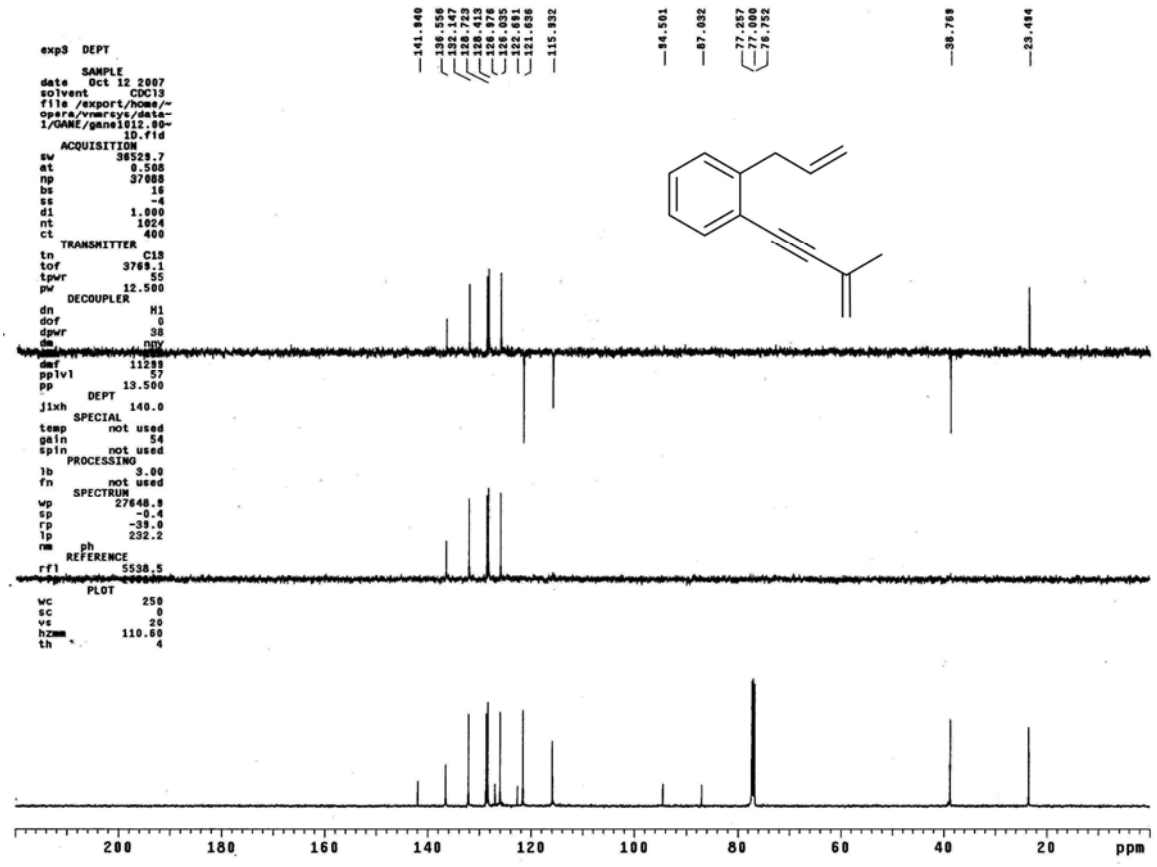
$^{1}$H and $^{13}$C NMR spectra of compound **4p**.



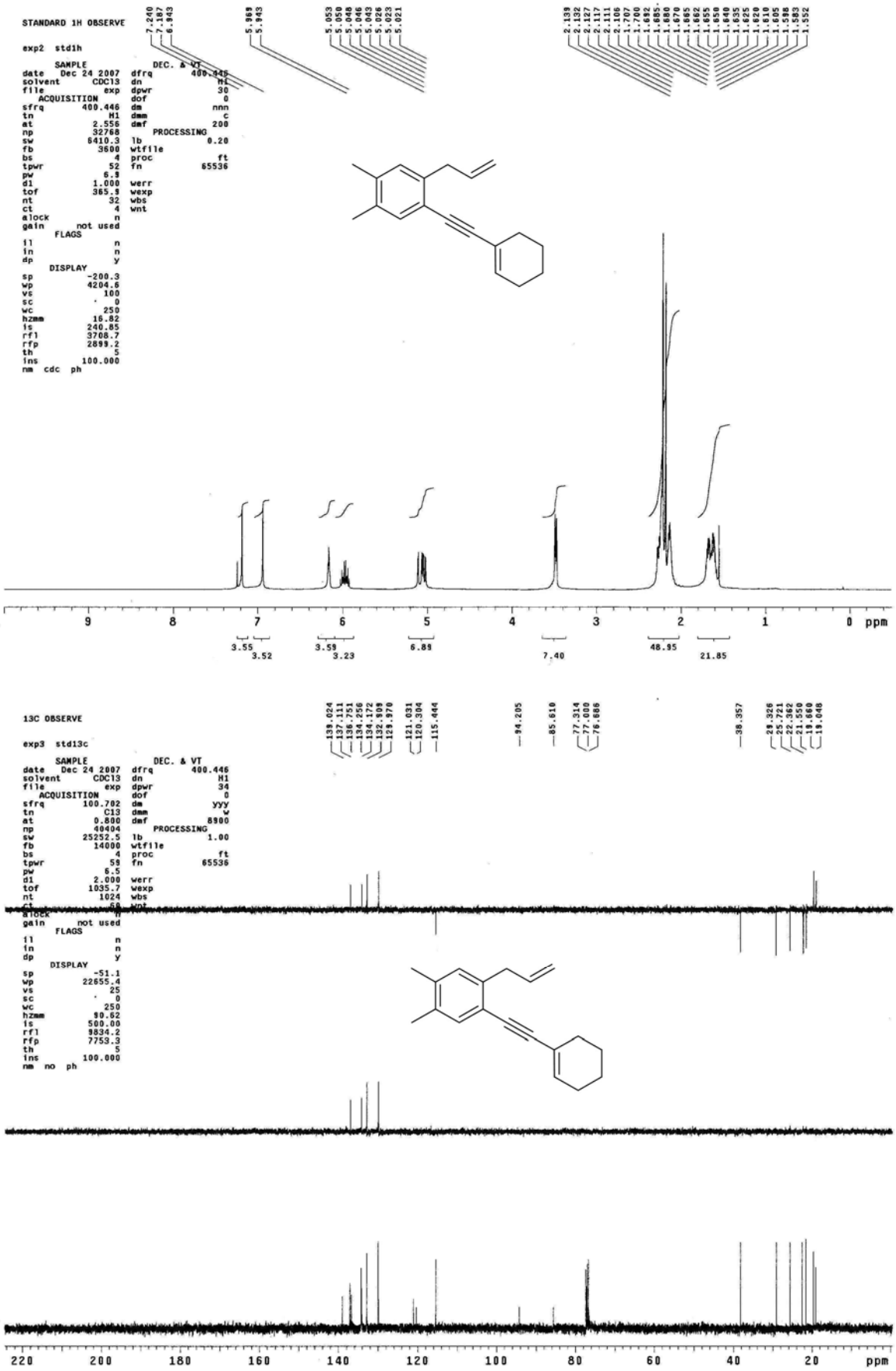



$^{1}$H and $^{13}$C NMR spectra of compound **4q**.

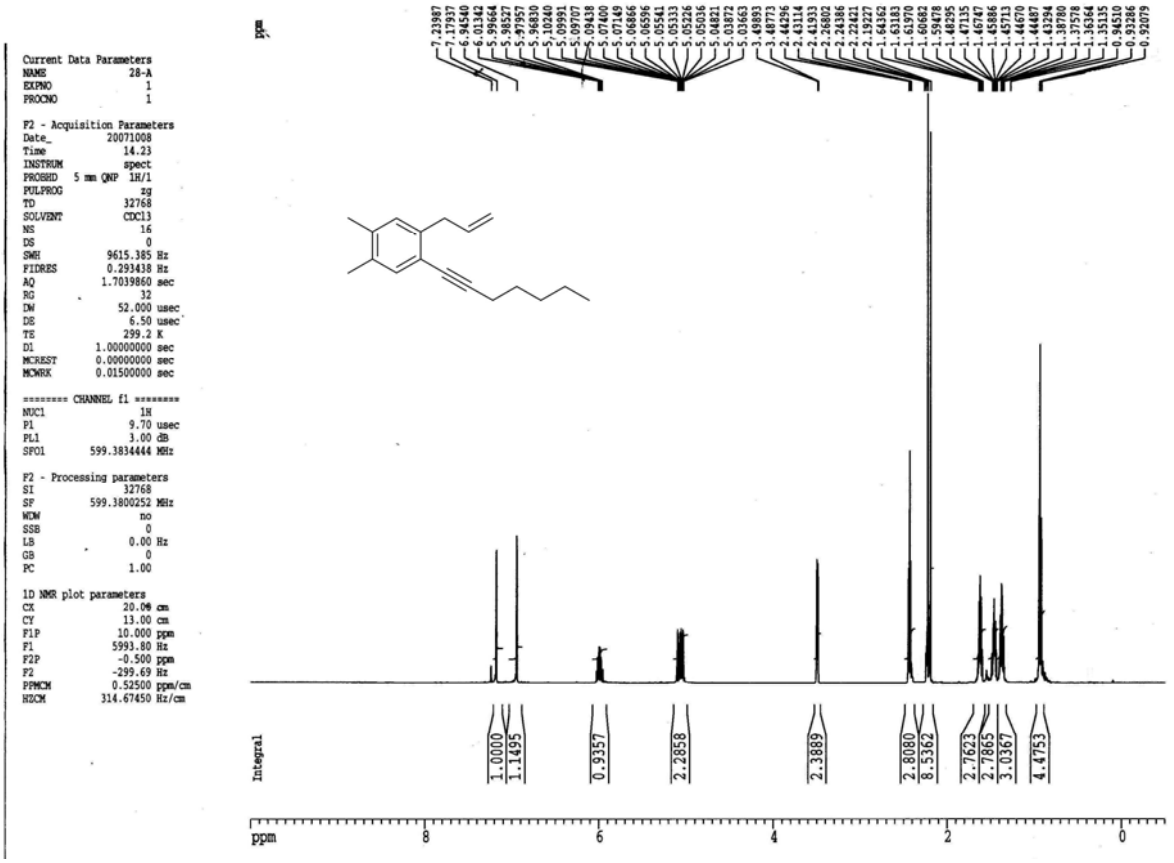


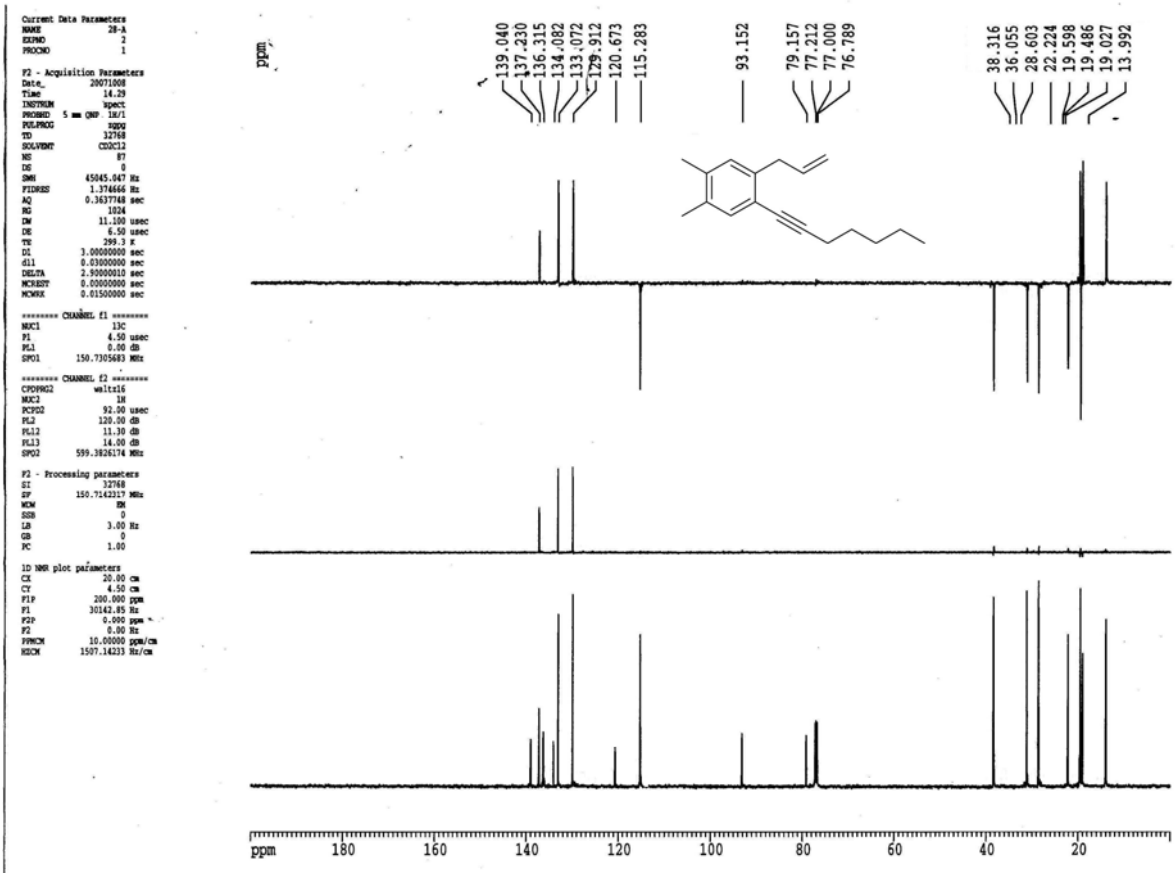



$^{1}$H and $^{13}$C NMR spectra of compound **4r**.

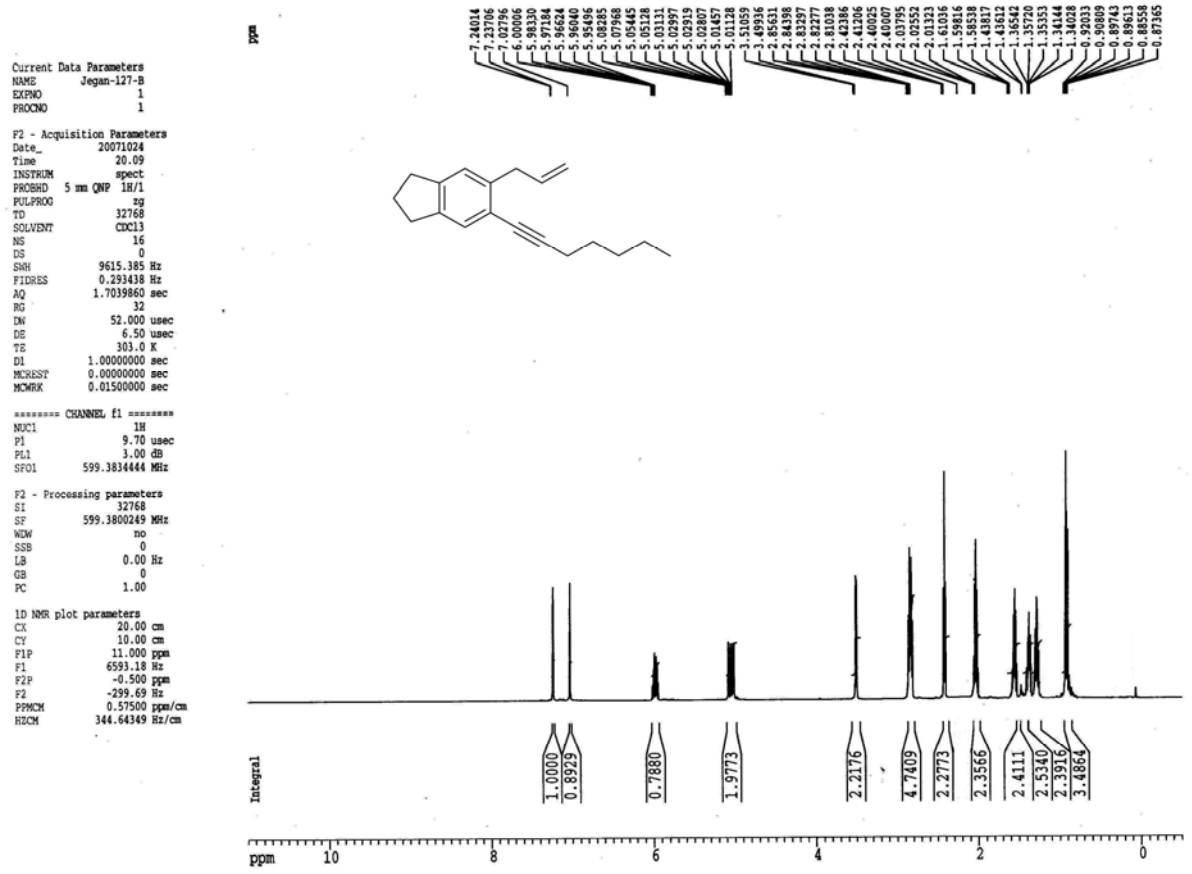


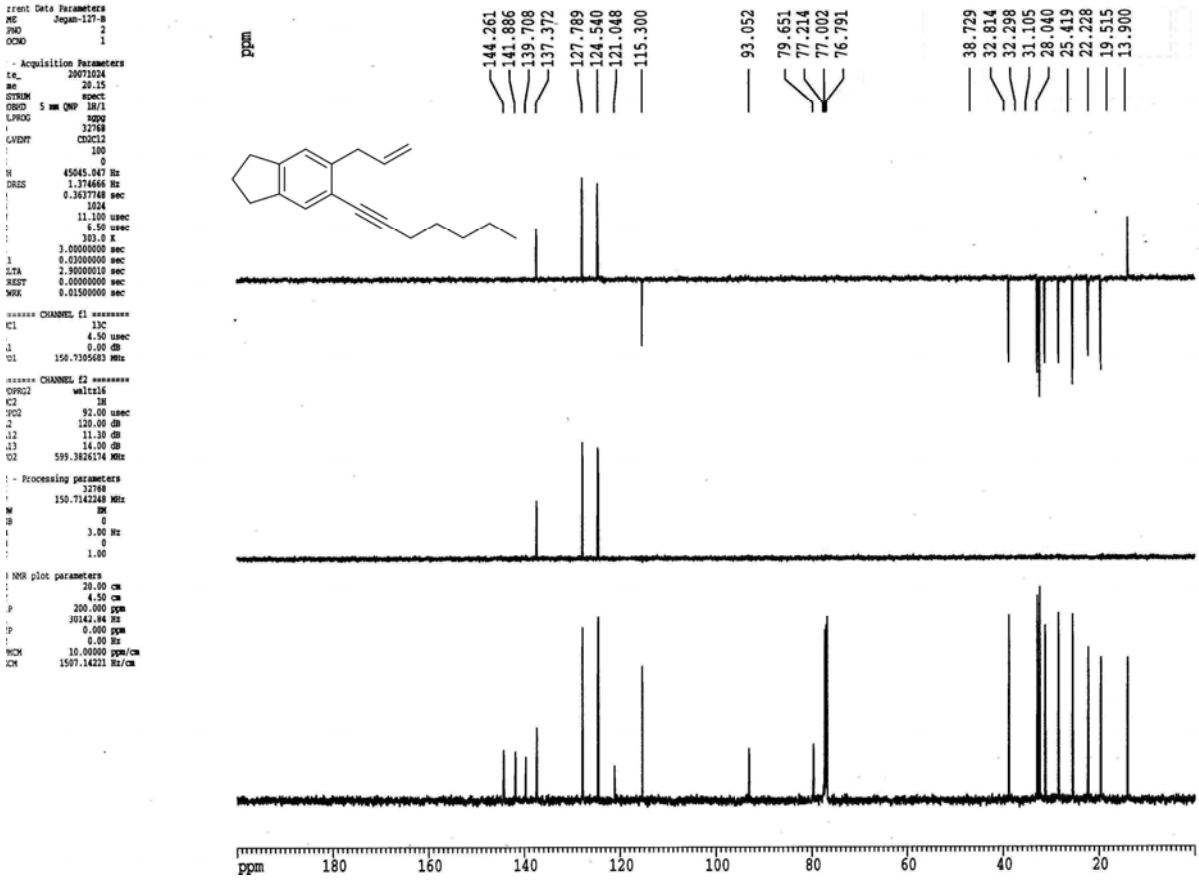
$^{1}$H and $^{13}$C NMR spectra of compound **4s**.



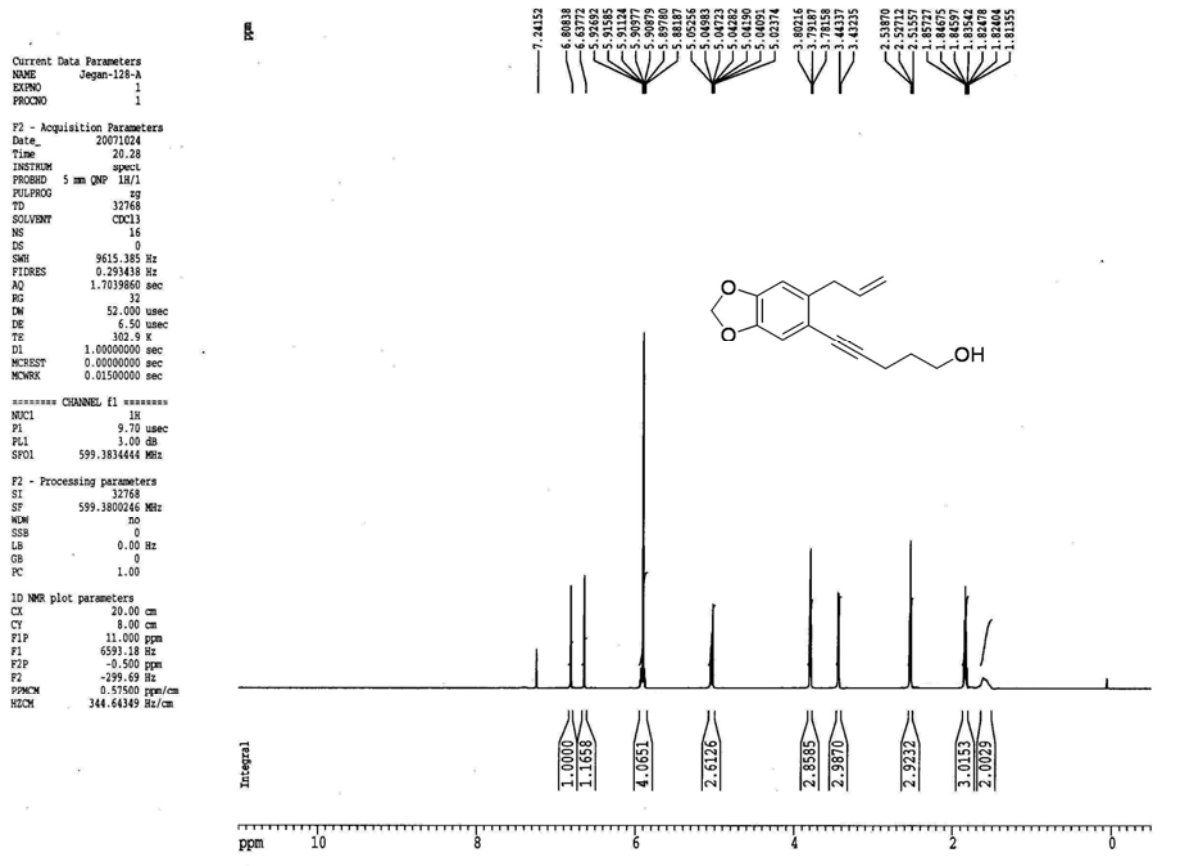



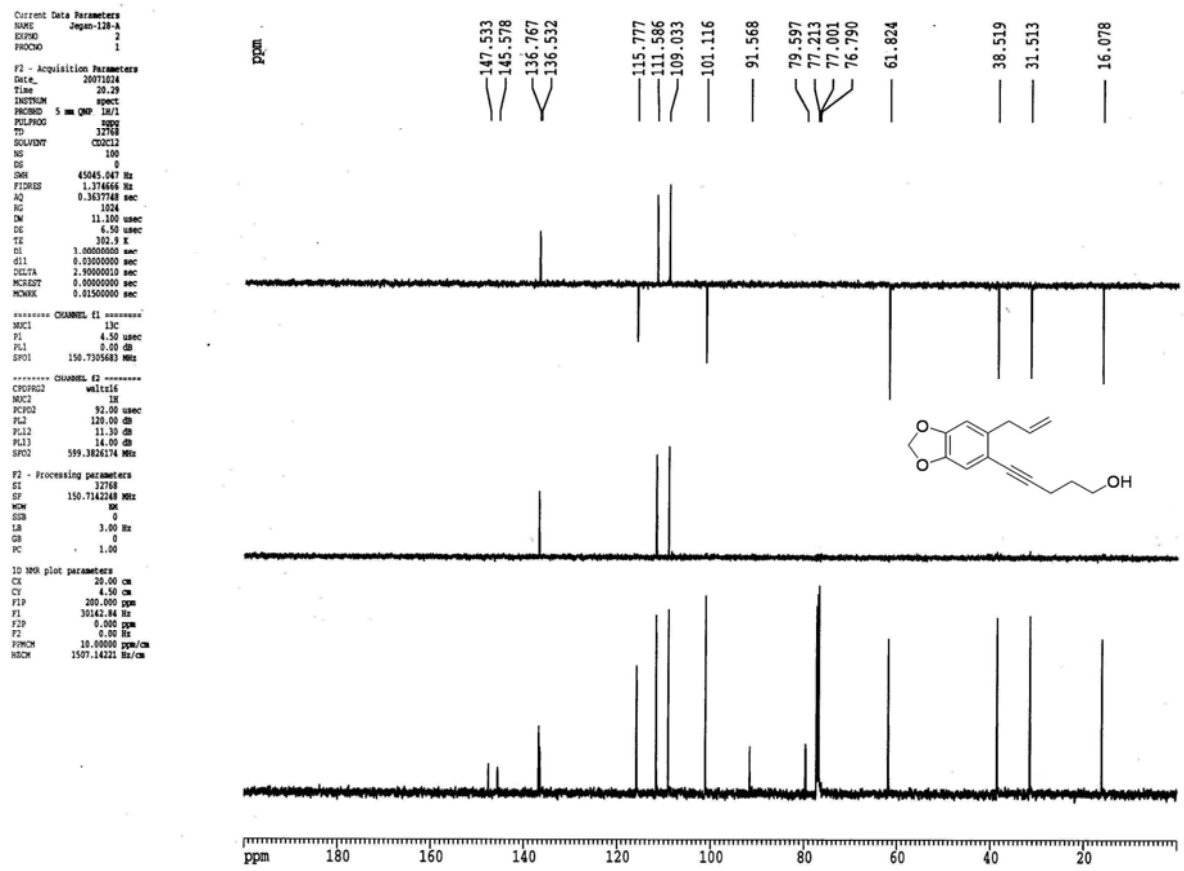
$^{1}$H and $^{13}$C NMR spectra of compound **4t**.



# $^{1}H$ and $^{13}C$ NMR spectra of compound **4u**.



$^{1}$H NMR spectrum of compounds **4v** and **4v'**.