Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information

Iron-Photocatalyzed Double Decarboxylative Coupling Reactions of Alkynoic Acids and Alkyl Carboxylic Acids: Access to Alkylated Alkynes

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Table of contents

General Information

All reagents were purchased and used without further purification. ^{1}H spectra were recorded in $CDCl_3$ or DMSO-d_6 on 500 MHz NMR and 400 MHz NMR spectrometers and data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. ^{13}C spectra were recorded in $CDCl_3$ or DMSO-d_6 on 126 MHz and 101 MHz NMR spectrometers and resonances (δ) are given in ppm. High resolution mass spectra were recorded on a time of flight (TOF) mass spectrometer. Aryl alkynoic acids were prepared according to the synthetic methods reported by our lab.[1]

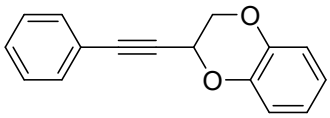
General procedure for the synthesis of product 3

Aryl alkynoic acid (1.0 mmol), alkyl carboxylic acid (5.0 mmol), $FeCl_2$ (13 mg, 0.1 mmol, 10 mol%), Tris(2-pyridylmethyl)amine (TPA) (58 mg, 0.2 mmol, 20 mol%), $PhI(OAc)_2$ (97 mg, 3.0 mmol) and MeCN (5.0 mL) were added to the reaction vial. The mixture was stirred at room temperature under blue light (40 W) for 12 h. The solution was cooled to room temperature. The reaction mixture diluted with ethyl acetate and washed with the saturated NaCl solution. The organic layer was dried over magnesium sulfate. Evaporation of the solvent under reduced pressure provided the crude product, which was purified by column chromatography on silica gel with hexane and ethyl acetate.

General procedure for the synthesis of product 4

Aryl alkynoic acid (1.0 mmol), alkyl carboxylic acid (5.0 mmol), $Fe(NO_3)_3{\cdot}9H_2O$ (40 mg, 0.1 mmol, 10 mol%), $PhI(OAc)_2$ (97 mg, 3.0 mmol) and MeCN (5.0 mL) were added to the reaction vial. The mixture was stirred at room temperature under blue light (40 W) for 12 h. The solution was cooled to room temperature. The reaction mixture diluted with ethyl acetate and washed with the saturated NaCl solution. The organic layer was dried over magnesium sulfate. Evaporation of the solvent under reduced pressure provided the crude product, which was purified by column chromatography on silica gel with hexane and ethyl acetate.

Characterization Data for the Products



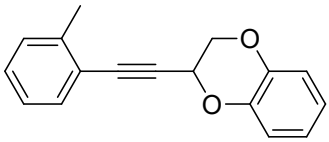
2-(Phenylethynyl)-2,3-dihydrobenzo[b][1,4]dioxine (3a):[2]

According to the general procedure, the reaction of 3-phenylpropiolic acid (146 mg, 1.0 mmol) and 1,4-benzodioxane-2-carboxylic acid (901 mg, 5.0 mmol) afforded the product **3a** (177 mg, 0.75 mmol, 75%) as a yellow oil after column chromatography eluting with *n*-hexane/EtOAc (400:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 2H), 7.37 – 7.30 (m, 3H), 6.98 – 6.94 (m, 1H), 6.91 (m, 1H), 6.90 – 6.86 (m, 2H), 5.12 (dd, *J* = 7.4, 2.5 Hz, 1H), 4.44 (dd, *J* = 11.3, 2.5 Hz, 1H), 4.21 (dd, *J* = 11.3, 7.4 Hz, 1H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.7, 142.4, 132.0, 129.1, 128.3, 121.9, 121.8, 121.6, 117.6, 117.2, 87.7, 82.5, 67.4, 64.6.

MS (EI) m/z = 236 (M^+)



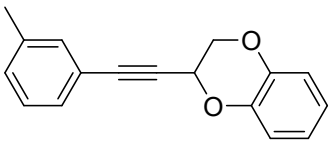
2-(*o*-Tolylethynyl)-2,3-dihydrobenzo[b][1,4]dioxine (3b):

According to the general procedure, the reaction of 3-(*o*-tolyl)propiolic acid (160 mg, 1.0 mmol) and 1,4-benzodioxane-2-carboxylic acid (901 mg, 5.0 mmol) afforded the product **3b** (148 mg, 0.59 mmol, 59%) as a yellow oil after column chromatography eluting with *n*-hexane/EtOAc (400:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 6.98 – 6.95 (m, 1H), 6.92 (m, 1H), 6.90 – 6.86 (m, 2H), 5.11 (dd, *J* = 7.4, 2.5 Hz, 1H), 4.44 (dd, *J* = 11.3, 2.5 Hz, 1H), 4.21 (dd, *J* = 11.3, 7.4 Hz, 1H), 2.33 (s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.9, 142.6, 138.2, 132.7, 130.1, 129.2, 128.4, 122.1, 122.0, 121.5, 117.8, 117.4, 88.1, 82.3, 67.6, 64.7, 21.3.

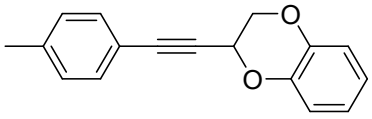
HRMS (FD-TOF) m/z: $[M]^+$ Calcd for $C_{17}H_{14}O_2$ 250.09883; Found: 250.09867.



2-(*m*-Tolylethynyl)-2,3-dihydrobenzo[b][1,4]dioxine (3c):

According to the general procedure, the reaction of 3-(*m*-tolyl)propiolic acid (160 mg, 1.0 mmol) and 1,4-benzodioxane-2-carboxylic acid (901 mg, 5.0 mmol) afforded the product **3c** (155 mg, 0.62 mmol, 62%) as a yellow oil after column chromatography eluting with *n*-hexane/EtOAc (400:1).

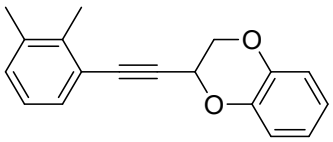
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.24 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.21 – 7.18 (m, 1H), 7.16 – 7.12 (m, 1H), 6.98 – 6.95 (m, 1H), 6.94 – 6.91 (m, 1H), 6.90 – 6.86 (m, 2H), 5.16 (dd, *J* = 6.9, 2.5 Hz, 1H), 4.45 (dd, *J* = 11.2, 2.5 Hz, 1H), 4.25 (dd, *J* = 11.2, 6.9 Hz, 1H), 2.39 (s, 3H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 143.0, 142.5, 140.9, 132.4, 129.6, 129.2, 125.7, 122.1, 122.0, 121.5, 117.9, 117.3, 86.7, 86.6, 67.7, 64.7, 20.7.
HRMS (FD-TOF) m/z: $[M]^+$ Calcd for $C_{17}H_{14}O_2$ 250.09883; Found: 250.09896.



2-(*p*-Tolylethynyl)-2,3-dihydrobenzo[b][1,4]dioxine (3d):[2]

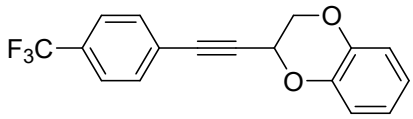
According to the general procedure, the reaction of 3-(*p*-tolyl)propiolic acid (160 mg, 1.0 mmol) and 1,4-benzodioxane-2-carboxylic acid (901 mg, 5.0 mmol) afforded the product **3d** (173 mg, 0.69 mmol, 69%) as a yellow oil after column chromatography eluting with *n*-hexane/EtOAc (400:1).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 6.98 – 6.95 (m, 1H), 6.94 – 6.91 (m, 1H), 6.90 – 6.86 (m, 2H), 5.11 (dd, *J* = 7.5, 2.5 Hz, 1H), 4.44 (dd, *J* = 11.3, 2.5 Hz, 1H), 4.21 (dd, *J* = 11.3, 7.5 Hz, 1H), 2.36 (s, 3H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 142.7, 142.4, 139.3, 131.9, 129.1, 121.9, 121.8, 118.5, 117.6, 117.2, 87.9, 81.8, 67.5, 64.6, 21.5.

MS (EI) m/z = 250 (M^+)



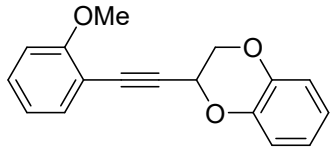
2-((2,3-Dimethylphenyl)ethynyl)-2,3-dihydrobenzo[b][1,4]dioxine (3e):

According to the general procedure, the reaction of 3-(2,3-dimethylphenyl)propiolic acid (174 mg, 1.0 mmol) and 1,4-benzodioxane-2-carboxylic acid (901 mg, 5.0 mmol) afforded the product **3e** (169 mg, 0.64 mmol, 64%) as a yellow oil after column chromatography eluting with *n*-hexane/EtOAc (400:1).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (s, 1H), 7.22 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.08 (d, *J* = 7.8 Hz, 1H), 6.98 – 6.94 (m, 1H), 6.94 – 6.90 (m, 1H), 6.90 – 6.86 (m, 2H), 5.10 (dd, *J* = 7.5, 2.5 Hz, 1H), 4.44 (dd, *J* = 11.3, 2.5 Hz, 1H), 4.20 (dd, *J* = 11.3, 7.5 Hz, 1H), 2.26 (s, 3H), 2.23 (s, 3H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 142.9, 142.6, 138.3, 136.8, 133.2, 129.8, 129.6, 122.0, 121.9, 118.9, 117.8, 117.3, 88.3, 81.7, 67.7, 64.8, 20.0, 19.7.
HRMS (FD-TOF) m/z: $[M]^+$ Calcd for $C_{18}H_{16}O_2$ 264.11448; Found: 264.11484.



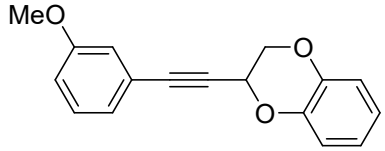
2-((4-(Trifluoromethyl)phenyl)ethynyl)-2,3-dihydrobenzo[b][1,4]dioxine (3f):

According to the general procedure, the reaction of 3-(4-(trifluoromethyl)phenyl)propiolic acid (214 mg, 1.0 mmol) and 1,4-benzodioxane-2-carboxylic acid (901 mg, 5.0 mmol) afforded the product **3f** (189 mg, 0.62 mmol, 62%) as a yellow solid after column chromatography eluting with *n*-hexane/EtOAc (500:1). M.P. = 86-90 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 4H), 6.99 – 6.95 (m, 1H), 6.95 – 6.87 (m, 3H), 5.15 (dd, J = 7.0, 2.5 Hz, 1H), 4.45 (dd, J = 11.3, 2.5 Hz, 1H), 4.24 (dd, J = 11.3, 7.0 Hz, 1H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 142.8, 142.3, 132.4, 131.0 (q, $J_{C,F}$ = 32.8 Hz), 125.5 (q, $J_{C,F}$ = 1.2 Hz), 125.4 (q, $J_{C,F}$ = 3.8 Hz), 123.9 (q, $J_{C,F}$ = 272.3 Hz), 122.3, 122.1, 117.8, 117.4, 86.3, 85.1, 67.3, 64.5.
HRMS (FD-TOF) m/z: $[M]^+$ Calcd for $C_{17}H_{11}O_2F_3$ 304.007057; Found: 304.07071.



2-((2-Methoxyphenyl)ethynyl)-2,3-dihydrobenzo[b][1,4]dioxine (3g):

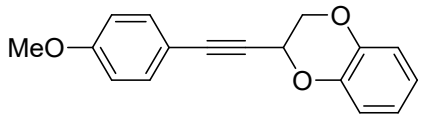
According to the general procedure, the reaction of 3-(2-methoxyphenyl)propiolic acid (176 mg, 1.0 mmol) and 1,4-benzodioxane-2-carboxylic acid (901 mg, 5.0 mmol) afforded the product **3g** (192 mg, 0.72 mmol, 72%) as a light yellow oil after column chromatography eluting with *n*-hexane/EtOAc (300:1).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (dd, J = 7.6, 1.7 Hz, 1H), 7.32 (m, 1H), 6.99 – 6.95 (m, 1H), 6.94 – 6.91 (m, 1H), 6.91 (m 1H), 6.90 – 6.86 (m, 3H), 5.16 (dd, J = 7.6, 2.5 Hz, 1H), 4.47 (dd, J = 11.3, 2.5 Hz, 1H), 4.23 (dd, J = 11.3, 7.6 Hz, 1H), 3.87 (s, 3H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 160.5, 142.9, 142.7, 134.2, 130.7, 122.0, 121.9, 120.5, 117.8, 117.3, 110.9, 110.8, 86.5, 84.4, 67.7, 64.9, 55.9.
HRMS (FD-TOF) m/z: $[M]^+$ Calcd for $C_{17}H_{14}O_3$ 266.09375; Found: 266.09374.



2-((3-Methoxyphenyl)ethynyl)-2,3-dihydrobenzo[b][1,4]dioxine (3h):

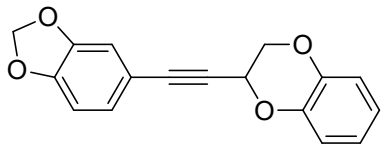
According to the general procedure, the reaction of 3-(3-methoxyphenyl)propiolic acid (176 mg, 1.0 mmol) and 1,4-benzodioxane-2-carboxylic acid (901 mg, 5.0 mmol) afforded the product **3h** (181 mg, 0.68 mmol, 68%) as a yellow oil after column chromatography eluting with *n*-hexane/EtOAc (300:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.21 (m, 1H), 7.09 – 7.06 (m, 1H), 7.00 (m, 1H), 6.99 – 6.95 (m, 1H), 6.92 (m, 1H), 6.91 – 6.90 (m, 1H), 6.88 (m, 2H), 5.12 (dd, *J* = 7.4, 2.5 Hz, 1H), 4.44 (dd, *J* = 11.3, 2.5 Hz, 1H), 4.22 (dd, *J* = 11.3, 7.4 Hz, 1H), 3.80 (s, 3H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 159.4, 142.9, 142.5, 129.6, 124.7, 122.7, 122.1, 122.0, 117.8, 117.4, 116.9, 115.9, 87.8, 82.4, 67.6, 64.7, 55.5.
HRMS (FD-TOF) m/z: $[M]^+$ Calcd for $C_{17}H_{14}O_3$ 266.09375; Found: 266.09382.



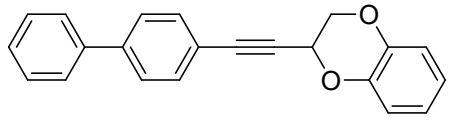
2-((4-Methoxyphenyl)ethynyl)-2,3-dihydrobenzo[b][1,4]dioxine (3i):

According to the general procedure, the reaction of 3-(4-methoxyphenyl)propiolic acid (176 mg, 1.0 mmol) and 1,4-benzodioxane-2-carboxylic acid (901 mg, 5.0 mmol) afforded the product **3i** (170 mg, 0.64 mmol, 64%) as a colorless oil after column chromatography eluting with *n*-hexane/EtOAc (300:1).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.40 (m, 2H), 6.96 (m. 1H), 6.91 (m, 1H), 6.90 – 6.86 (m, 2H), 6.86 – 6.83 (m, 2H), 5.10 (dd, *J* = 7.5, 2.5 Hz, 1H), 4.44 (dd, *J* = 11.3, 2.5 Hz, 1H), 4.20 (dd, *J* = 11.3, 7.6 Hz, 1H), 3.81 (s, 3H);
^{13}C NMR (126 MHz, $CDCl_3$) δ 160.2, 142.7, 142.5, 133.5, 121.9, 121.8, 117.6, 117.2, 113.9, 113.6, 87.8, 81.1, 67.5, 64.7, 55.3.
HRMS (FD-TOF) m/z: $[M]^+$ Calcd for $C_{17}H_{14}O_3$ 266.09375; Found: 266.09371.



2-(Benzo[d][1,3]dioxol-5-ylethynyl)-2,3-dihydrobenzo[b][1,4]dioxine (3j):

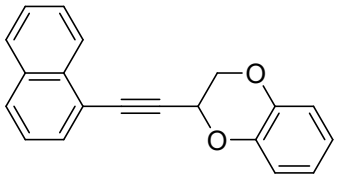
According to the general procedure, the reaction of 3-(benzo[d][1,3]dioxol-5-yl)propiolic acid (190 mg, 1.0 mmol) and 1,4-benzodioxane-2-carboxylic acid (901 mg, 5.0 mmol) afforded the product **3j** (151 mg, 0.54 mmol, 54%) as an orange oil after column chromatography eluting with *n*-hexane/EtOAc (300:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.98 – 6.94 (m, 1H), 6.94 – 6.90 (m, 2H), 6.88 (m, 2H), 6.75 (d, *J* = 8.0 Hz, 1H), 5.98 (s, 2H), 5.09 (dd, *J* = 7.4, 2.4 Hz, 1H), 4.43 (dd, *J* = 11.3, 2.5 Hz, 1H), 4.19 (dd, *J* = 11.3, 7.5 Hz, 1H);
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.7, 147.5, 142.9, 142.6, 127.1, 122.1, 122.0, 117.8, 117.4, 114.8, 112.0, 108.6, 101.6, 87.8, 81.0, 67.6, 64.7.
HRMS (FD-TOF) m/z: $[M]^+$ Calcd for $C_{17}H_{12}O_4$ 280.07301; Found: 280.07307.



2-([1,1'-Biphenyl]-4-ylethynyl)-2,3-dihydrobenzo[b][1,4]dioxine (3k):[2]

According to the general procedure, the reaction of 3-([1,1'-biphenyl]-4-yl)propiolic acid (222 mg, 1.0 mmol) and 1,4-benzodioxane-2-carboxylic acid (901 mg, 5.0 mmol) afforded the product **3k** (166 mg, 0.53 mmol, 53%) as a light yellow oil after column chromatography eluting with *n*-hexane/EtOAc (400:1).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 1.3 Hz, 1H), 7.59 – 7.53 (m, 5H), 7.47 – 7.43 (m, 2H), 7.39 – 7.35 (m, 1H), 7.00 – 6.96 (m, 1H), 6.95 – 6.91 (m, 1H), 6.91 – 6.87 (m, 2H), 5.15 (dd, *J* = 7.4, 2.5 Hz, 1H), 4.46 (dd, *J* = 11.3, 2.5 Hz, 1H), 4.24 (dd, *J* = 11.3, 7.4 Hz, 1H);

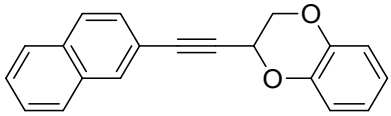
^{13}C NMR (126 MHz, $CDCl_3$) δ 142.9, 142.6, 142.0, 140.3, 132.6, 129.0, 127.9, 127.2, 127.1, 122.1, 122.0, 120.6, 117.8, 117.4, 87.8, 83.2, 67.6, 64.8.
MS (EI) m/z = 312 (M^+)



2-(naphthalen-1-ylethynyl)-2,3-dihydrobenzo[b][1,4]dioxine (3l):

According to the general procedure, the reaction of 3-(naphthalen-1-yl)propiolic acid (196 mg, 1.0 mmol) and 1,4-Benzodioxane-2-carboxylic Acid (901 mg, 5.0 mmol) afforded the product **3l** (212 mg, 0.74 mmol, 74%) as an orange solid after column chromatography eluting with *n*-hexane/EtOAc (400:1). M.P. = 106-110 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 – 8.19 (m, 1H), 7.85 (m, 2H), 7.71 (dd, *J* = 7.1, 1.1 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.43 (dd, *J* = 8.3, 7.2 Hz, 1H), 7.01 (m, 1H), 6.97 (m, 1H), 6.93 – 6.90 (m, 2H), 5.28 (dd, *J* = 6.7, 2.5 Hz, 1H), 4.54 (dd, *J* = 11.2, 2.5 Hz, 1H), 4.38 – 4.33 (dd, *J* = 11.2, 6.7 Hz 1H);

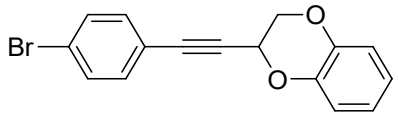
^{13}C NMR (126 MHz, $CDCl_3$) δ 143.0, 142.5, 133.4, 133.2, 131.2, 129.7, 128.4, 127.2, 126.7, 126.1, 125.2, 122.2, 122.0, 119.3, 117.9, 117.4, 87.6, 86.0, 67.7, 64.8.
HRMS (FD-TOF) m/z: $[M]^+$ Calcd for $C_{20}H_{14}O_2$ 286.09883; Found: 286.09878.



2-(Naphthalen-2-ylethynyl)-2,3-dihydrobenzo[b][1,4]dioxine (3m):

According to the general procedure, the reaction of 3-(naphthalen-2-yl)propiolic acid (196 mg, 1.0 mmol) and 1,4-benzodioxane-2-carboxylic acid (901 mg, 5.0 mmol) afforded the product **3m** (175 mg, 0.61 mmol, 61%) as a white solid after column chromatography eluting with *n*-hexane/EtOAc (400:1). M.P. = 79-82 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.84 – 7.76 (m, 3H), 7.52 – 7.47 (m, 3H), 6.98 (m, 1H), 6.93 (m, 1H), 6.91 – 6.87 (m, 2H), 5.17 (dd, *J* = 7.4, 2.5 Hz, 1H), 4.48 (dd, *J* = 11.3, 2.5 Hz, 1H), 4.26 (dd, *J* = 11.3, 7.4 Hz, 1H);

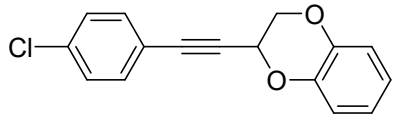
^{13}C NMR (126 MHz, $CDCl_3$) δ 142.9, 142.6, 133.4, 132.9, 132.5, 128.4, 128.2, 128.0, 127.9, 127.2, 126.8, 122.1, 122.0, 119.0, 117.8, 117.4, 88.2, 82.9, 67.6, 64.8.
HRMS (FD-TOF) m/z: $[M]^+$ Calcd for $C_{20}H_{14}O_2$ 286.09883; Found: 286.09886.



2-((4-Bromophenyl)ethynyl)-2,3-dihydrobenzo[b][1,4]dioxine (3n):

According to the general procedure, the reaction of 3-(4-bromophenyl)propiolic acid (225 mg, 1.0 mmol) and 1,4-benzodioxane-2-carboxylic acid (901 mg, 5.0 mmol) afforded the product **3n** (202 mg, 0.64 mmol, 64%) as a pale yellow solid after column chromatography eluting with *n*-hexane/EtOAc (400:1). M.P. = 73-78 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.44 (m, 2H), 7.35 – 7.31 (m, 2H), 6.97 – 6.94 (m, 1H), 6.93 – 6.91 (m, 1H), 6.89 (m, 2H), 5.11 (dd, *J* = 7.2, 2.5 Hz, 1H), 4.43 (dd, *J* = 11.3, 2.5 Hz, 1H), 4.21 (dd, *J* = 11.3, 7.2 Hz, 1H);

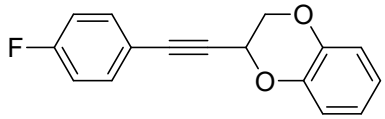
^{13}C NMR (126 MHz, $CDCl_3$) δ 142.7, 142.3, 133.4, 131.6, 123.5, 122.0, 121.9, 120.5, 117.6, 117.2, 86.6, 83.7, 67.3, 64.5.
HRMS (FD-TOF) m/z: $[M]^+$ Calcd for $C_{16}H_{11}O_2Br$ 313.99369; Found: 313.99374.



2-((4-Chlorophenyl)ethynyl)-2,3-dihydrobenzo[b][1,4]dioxine (3o):[2]

According to the general procedure, the reaction of 3-(4-chlorophenyl)propiolic acid (181 mg, 1.0 mmol) and 1,4-benzodioxane-2-carboxylic acid (901 mg, 5.0 mmol) afforded the product **3o** (179 mg, 0.66 mmol, 66%) as a pale yellow solid after column chromatography eluting with *n*-hexane/EtOAc (400:1).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 2H), 7.32 – 7.29 (m, 2H), 6.96 (m, 1H), 6.93 – 6.91 (m, 1H), 6.89 (m, 2H), 5.11 (dd, *J* = 7.2, 2.5 Hz, 1H), 4.43 (dd, *J* = 11.3, 2.5 Hz, 1H), 4.21 (dd, *J* = 11.3, 7.2 Hz, 1H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.7, 142.3, 135.2, 133.2, 128.7, 122.0, 121.9, 120.0, 117.6, 117.2, 86.5, 83.5, 67.3, 64.5.
MS (EI) m/z = 270 (M^+)



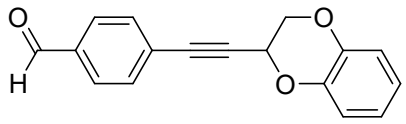
2-((4-Fluorophenyl)ethynyl)-2,3-dihydrobenzo[b][1,4]dioxine (3p):[2]

According to the general procedure, the reaction of 3-(4-fluorophenyl)propiolic acid (164 mg, 1.0 mmol) and 1,4-benzodioxane-2-carboxylic acid (901 mg, 5.0 mmol) afforded the product

3p (163 mg, 0.64 mmol, 64%) as a yellow solid after column chromatography eluting with *n*-hexane/EtOAc (400:1).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.44 (m, 2H), δ 7.04 – 6.99 (m, 2H), δ 6.96 (m, 1H), δ 6.93 – 6.90 (m, 1H), δ 6.90 – 6.86 (m, 2H), δ 5.11 (dd, J = 7.3, 2.4 Hz, 1H), δ 4.43 (dd, J = 11.3, 2.5 Hz, 1H), δ 4.21 (dd, J = 11.3, 7.3 Hz, 1H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.1 (d, $J_{C,F}$ = 252 Hz), 142.9, 142.5, 134.2, 134.1, 122.1, 122.0, 117.8, 117.4, 115.9 (d, $J_{C,F}$ = 21.4 Hz), 86.8, 82.5, 67.5, 64.6.

MS (EI) m/z = 254 (M^+)

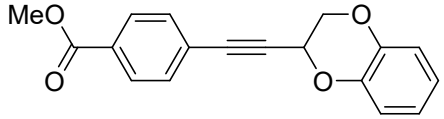


4-((2,3-Dihydrobenzo[b][1,4]dioxin-2-yl)ethynyl)benzaldehyde (3q):

According to the general procedure, the reaction of 3-(4- formylphenyl)propiolic acid (174 mg, 1.0 mmol) and 1,4-benzodioxane-2-carboxylic acid (901 mg, 5.0 mmol) afforded the product **3q** (153 mg, 0.58 mmol, 58%) as a yellow solid after column chromatography eluting with *n*-hexane/EtOAc (100:1). M.P. = 76-80 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.84 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.2 Hz, 2H), 6.99 – 6.94 (m, 1H), 6.94 – 6.91 (m, 1H), 6.91 – 6.87 (m, 2H), 5.16 (dd, J = 6.9, 2.5 Hz, 1H), 4.45 (dd, J = 11.3, 2.5 Hz, 1H), 4.25 (dd, J = 11.3, 6.9 Hz, 1H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 191.4, 142.8, 142.3, 136.2, 132.7, 129.6, 127.9, 122.3, 122.1, 117.8, 117.5, 86.7, 86.6, 67.3, 64.5.

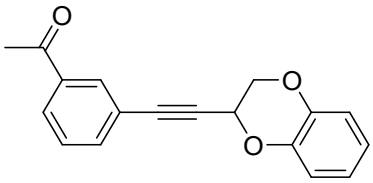
HRMS (FD-TOF) m/z: $[M]^+$ Calcd for $C_{17}H_{12}O_3$ 264.07810; Found: 264.07810.



Methyl 4-((2,3-dihydrobenzo[b][1,4]dioxin-2-yl)ethynyl)benzoate (3r):

According to the general procedure, the reaction of 3-(4-(methoxycarbonyl)phenyl)propiolic acid (204 mg, 1.0 mmol) and 1,4-benzodioxane-2-carboxylic acid (901 mg, 5.0 mmol) afforded the product **3r** (177 mg, 0.60 mmol, 60%) as a colorless oil after column chromatography eluting with *n*-hexane/EtOAc (200:1).
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.97 (m, 2H), 7.55 – 7.51 (m, 2H), 6.98 – 6.94 (m, 1H), 6.92 (m, 1H), 6.90 – 6.86 (m, 2H), 5.14 (dd, J = 7.1, 2.5 Hz, 1H), 4.44 (dd, J = 11.3, 2.5 Hz, 1H), 4.23 (dd, J = 11.3, 7.1 Hz, 1H), 3.92 (s, 3H);

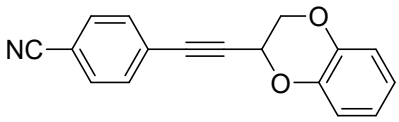
^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 142.8, 142.4, 132.1, 130.5, 129.6, 126.3, 122.2, 122.1, 117.8, 117.4, 86.9, 85.5, 67.4, 64.6, 52.5.
HRMS (FD-TOF) m/z: $[M]^+$ Calcd for $C_{18}H_{14}O_4$ 294.08866; Found: 294.08872.



1-(3-((2,3-Dihydrobenzo[b][1,4]dioxin-2-yl)ethynyl)phenyl)ethenone (3s):

According to the general procedure, the reaction of 3-(3-acetylphenyl)propiolic acid (188 mg, 1.0 mmol) and 1,4-benzodioxane-2-carboxylic acid (901 mg, 5.0 mmol) afforded the product **3s** (178 mg, 0.64 mmol, 64%) as a white oil after column chromatography eluting with *n*-hexane/EtOAc (100:1).
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (m, 1H), 7.94 (ddd, *J* = 7.8, 1.8, 1.2 Hz, 1H), 7.67 – 7.64 (m, 1H), 7.45 - 7.42 (m, 1H), 6.99 – 6.94 (m, 1H), 6.94 – 6.91 (m, 1H), 6.91 – 6.87 (m, 2H), 5.14 (dd, *J* = 7.1, 2.5 Hz, 1H), 4.45 (dd, *J* = 11.3, 2.5 Hz, 1H), 4.24 (dd, *J* = 11.3, 7.1 Hz, 1H), 2.60 (s, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 197.2, 142.8, 142.4, 137.3, 136.3, 132.1, 128.9, 128.8, 122.4, 122.2, 122.0, 117.8, 117.4, 86.7, 83.8, 67.4, 64.6, 26.8.
HRMS (FD-TOF) m/z: $[M]^+$ Calcd for $C_{18}H_{14}O_3$ 278.09375; Found: 278.09352.

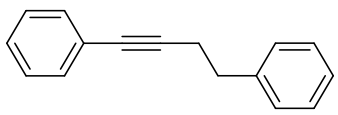


4-((2,3-Dihydrobenzo[b][1,4]dioxin-2-yl)ethynyl)benzonitrile (3t):

According to the general procedure, the reaction of 3-(4-cyanophenyl)propiolic acid (171 mg, 1.0 mmol) and 1,4-benzodioxane-2-carboxylic acid (901 mg, 5.0 mmol) afforded the product **3t** (154 mg, 0.59 mmol, 59%) as a white solid after column chromatography eluting with *n*-hexane/EtOAc (200:1). M.P. = 108-112 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 – 7.60 (m, 2H), 7.57 – 7.53 (m, 2H), 6.97 – 6.93 (m, 1H), 6.92 (m., 1H), 6.91 – 6.87 (m, 2H), 5.15 (dd, *J* = 6.7, 2.5 Hz, 1H), 4.43 (dd, *J* = 11.3, 2.5 Hz, 1H), 4.24 (dd, *J* = 11.3, 6.7 Hz, 1H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.8, 142.2, 132.7, 132.2, 126.6, 122.3, 122.1, 118.3, 117.8, 117.5, 112.7, 87.1, 85.8, 67.2, 64.4.

HRMS (FD-TOF) m/z: $[M]^+$ Calcd for $C_{17}H_{11}O_2N$ 261.07843; Found: 261.07868.

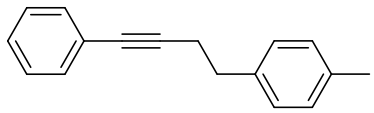


But-1-yne-1,4-diyldibenzene (4a):[7]

According to the general procedure, the reaction of 3-phenylpropiolic acid (146 mg, 1.0 mmol) and 3-phenylpropanoic acid (751 mg, 5.0 mmol) afforded the product **4a** (117 mg, 0.57 mmol, 57%) as a yellow liquid after column chromatography eluting with *n*-hexane.
^{1}H NMR (500 MHz, DMSO) δ 7.36 – 7.32 (m, 5H), 7.30 (m, 4H), 7.24 – 7.19 (m, 1H), 2.85 (t, J = 7.3 Hz, 2H), 2.70 (t, J = 7.3 Hz, 2H);

^{13}C NMR (126 MHz, DMSO) δ 140.4, 131.1, 128.5, 128.2, 127.9, 126.2, 123.1, 90.1, 81.1, 34.3, 20.9.

MS (EI) m/z = 206 (M^+)

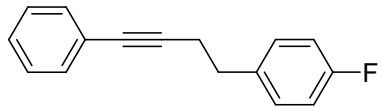


1-Methyl-4-(4-phenylbut-3-yn-1-yl)benzene (4b):[3]

According to the general procedure, the reaction of 3-phenylpropiolic acid (146 mg, 1.0 mmol) and 3-(*p*-tolyl)propanoic acid (821 mg, 5.0 mmol) afforded the product **4b** (130 mg, 0.59 mmol, 59%) as a colorless oil after column chromatography eluting with *n*-hexane.
^{1}H NMR (500 MHz, DMSO) δ 7.36 – 7.31 (m, 5H), 7.19 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 7.7 Hz, 2H), 2.80 (t, J = 7.3 Hz, 2H), 2.66 (t, J = 7.3 Hz, 2H), 2.27 (s, 3H);

^{13}C NMR (126 MHz, DMSO) δ 137.4, 135.1, 131.1, 128.8, 128.6, 128.4, 127.9, 123.2, 90.2, 81.0, 33.9, 21.0, 20.6.

MS (EI) m/z = 220 (M^+)

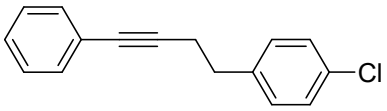


1- Fluoro -4-(4-phenylbut-3-yn-1-yl)benzene (4c):[3]

According to the general procedure, the reaction of 3-phenylpropiolic acid (146 mg, 1.0 mmol) and 3-(4-fluorophenyl)propanoic acid (841 mg, 5.0 mmol) afforded the product **4c** (150 mg, 0.67 mmol, 67%) as a yellow oil after column chromatography eluting with *n*-hexane.
^{1}H NMR (500 MHz, DMSO) δ 7.38 – 7.28 (m, 7H), 7.15 – 7.09 (m, 2H), 2.84 (t, J = 7.3 Hz, 2H), 2.69 (t, J = 7.3 Hz, 2H);

^{13}C NMR (126 MHz, DMSO) δ 160.9 (d, $J_{C,F}$ = 243 Hz), 136.6 (d, $J_{C,F}$ = 3.0 Hz), 131.1, 130.3 (d, $J_{C,F}$ = 7.56 Hz), 128.5, 127.9, 123.1, 114.8 (d, $J_{C,F}$ = 21.42 Hz), 89.9, 81.2, 33.4, 20.9.

MS (EI) m/z = 224 (M^+)

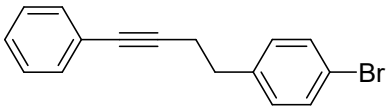


1- Chloro -4-(4-phenylbut-3-yn-1-yl)benzene (4d):[3]

According to the general procedure, the reaction of 3-phenylpropiolic acid (146 mg, 1.0 mmol) and 3-(4-chlorophenyl)propanoic acid (923 mg, 5.0 mmol) afforded the product **4d** (144 mg, 0.60 mmol, 60%) as a yellow oil after column chromatography eluting with *n*-hexane.
^{1}H NMR (500 MHz, DMSO) δ 7.39 – 7.28 (m, 9H), 2.84 (t, *J* = 7.2 Hz, 2H), 2.70 (t, *J* = 7.2 Hz, 2H);

^{13}C NMR (126 MHz, DMSO) δ 139.5, 131.1, 130.8, 130.5, 128.5, 128.1, 128.0, 123.1, 89.8, 81.3, 33.5, 20.6.

MS (EI) m/z = 240 (M^+)

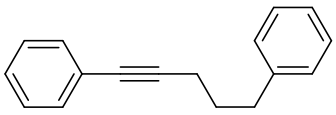


1-Bromo-4-(4-phenylbut-3-yn-1-yl)benzene (4e):[3]

According to the general procedure, the reaction of 3-phenylpropiolic acid (146 mg, 1.0 mmol) and 3-(4-bromophenyl)propanoic acid (1145 mg, 5.0 mmol) afforded the product **4e** (197 mg, 0.69 mmol, 69%) as a yellow oil after column chromatography eluting with *n*-hexane.
^{1}H NMR (500 MHz, DMSO) δ 7.49 (d, *J* = 8.2 Hz, 2H), 7.32 (m, 5H), 7.27 (d, *J* = 8.2 Hz, 2H), 2.82 (t, *J* = 7.2 Hz, 2H), 2.69 (t, *J* = 7.2 Hz, 2H);

^{13}C NMR (126 MHz, DMSO) δ 139.8, 131.1, 131.0, 130.8, 128.5, 127.9, 123.0, 119.3, 89.8, 81.3, 33.5, 20.6.

MS (EI) m/z = 284 (M^+)

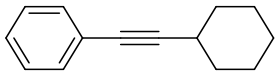


Pent-1-yne-1,5-diyldibenzene (4f):[4]

According to the general procedure, the reaction of 3-phenylpropiolic acid (146 mg, 1.0 mmol) and 4-phenylbutanoic acid (821 mg, 5.0 mmol) afforded the product **4f** (126 mg, 0.57 mmol, 57%) as a colorless oil after column chromatography eluting with *n*-hexane.
^{1}H NMR (500 MHz, DMSO) δ 7.40 (m, 2H), 7.37 – 7.32 (m, 3H), 7.29 (m, 2H), 7.23 (m, 2H), 7.19 (m, 1H), 2.76 – 2.68 (t, *J* = 7.6 Hz, 2H), 2.41 (t, *J* = 7.1 Hz, 2H), 1.88 – 1.80 (m, 2H);

^{13}C NMR (126 MHz, DMSO) δ 141.3, 131.2, 128.5, 128.4, 128.3, 127.9, 125.8, 123.2, 90.2, 81.0, 34.2, 29.9, 18.1.

MS (EI) m/z = 220 (M^+)

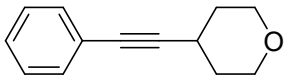


(Cyclohexylethynyl)benzene (4g):[2]

According to the general procedure, the reaction of 3-phenylpropiolic acid (146 mg, 1.0 mmol) and cyclohexanecarboxylic acid (641 mg, 5.0 mmol) afforded the product **4g** (112 mg, 0.61 mmol, 61%) as a colorless liquid after column chromatography eluting with *n*-hexane.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.38 (m, 2H), 7.30 – 7.26 (m, 2H), 7.26 – 7.24 (m, 1H), 2.63 – 2.53 (m, 1H), 1.88 (m, 2H), 1.79 – 1.72 (m, 2H), 1.55 (m, 3H), 1.35 (m, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 131.23, 127.80, 127.06, 123.75, 94.13, 80.13, 32.37, 29.31, 25.58, 24.58.

MS (EI) m/z = 184 (M^+)

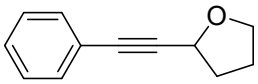


4-(Phenylethynyl)tetrahydro-2H-pyran (4h):[2]

According to the general procedure, the reaction of 3-phenylpropiolic acid (146 mg, 1.0 mmol) and tetrahydro-2H-pyran-4-carboxylic acid (651 mg, 5.0 mmol) afforded the product **4h** (125 mg, 0.67 mmol, 67%) as a yellow liquid after column chromatography eluting with *n*-hexane/EtOAc (400:1).
^{1}H NMR (500 MHz, DMSO) δ 7.42 – 7.37 (m, 2H), 7.37 – 7.31 (m, 3H), 3.80 (m, 2H), 3.44 (m, 2H), 2.91 – 2.84 (m, 1H), 1.87 – 1.79 (m, 2H), 1.64 – 1.55 (m, 2H);

^{13}C NMR (126 MHz, DMSO) δ 131.3, 128.5, 128.0, 122.9, 92.9, 81.0, 65.5, 32.0, 26.1.

MS (EI) m/z = 186 (M^+)



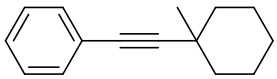
2-(Phenylethynyl)tetrahydrofuran (4i):[2]

According to the general procedure, the reaction of 3-phenylpropiolic acid (146 mg, 1.0 mmol) and tetrahydrofuran-2-carboxylic acid (581 mg, 5.0 mmol) afforded the product **4i** (108 mg,

0.63 mmol, 63%) as a yellow liquid after column chromatography eluting with *n*-hexane/EtOAc (400:1).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (m, 2H), 7.32 – 7.27 (m, 3H), 4.81 (m, 1H), 4.02 (m, 1H), 3.86 (m, 1H), 2.23 (m, 1H), 2.14 – 2.04 (m, 2H), 1.99 – 1.90 (m, 1H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 131.8, 128.4, 128.3, 122.9, 89.2, 84.6, 68.7, 68.1, 33.6, 25.6.

MS (EI) m/z = 172 (M^+)

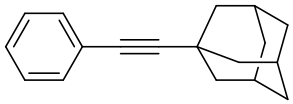


((1-Methylcyclohexyl)ethynyl)benzene (4j): [8]

According to the general procedure, the reaction of 3-phenylpropiolic acid (146 mg, 1.0 mmol) and 1-methylcyclohexanecarboxylic acid (711 mg, 5.0 mmol) afforded the product **4j** (121 mg, 0.61 mmol, 61%) as a colorless oil after column chromatography eluting with Pentane.
^{1}H NMR (500 MHz, DMSO) δ 7.36 (s, 2H), 7.33 (m, 3H), 1.73 (d, *J* = 12.6 Hz, 2H), 1.60 (m, 5H), 1.32 – 1.22 (m, 5H), 1.20 – 1.10 (m, 1H);

^{13}C NMR (126 MHz, DMSO) δ 131.2, 128.5, 127.8, 123.3, 96.5, 81.7, 38.9, 32.7, 29.9, 25.3, 23.0.

MS (EI) m/z = 198 (M^+)

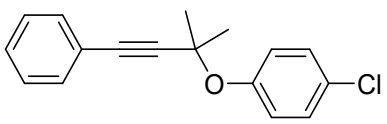


(3r,5r,7r)-1-(Phenylethynyl)adamantane (4k):[2]

According to the general procedure, the reaction of 3-phenylpropiolic acid (146 mg, 1.0 mmol) and (3r,5r,7r)-adamantane-1-carboxylic acid (901 mg, 5.0 mmol) afforded the product **4k** (149 mg, 0.63 mmol, 63%) as a colorless oil after column chromatography eluting with *n*-hexane.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.37 (m, 2H), 7.28 – 7.23 (m, 3H), 2.00 (m, 3H), 1.96 (m, 6H), 1.72 (m, 6H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 131.6, 128.1, 127.3, 124.1, 98.4, 79.3, 42.9, 36.4, 30.0, 28.0.

MS (EI) m/z = 236 (M^+)

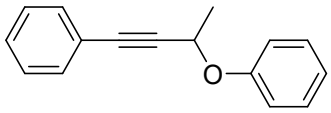


1-Chloro-4-((2-methyl-4-phenylbut-3-yn-2-yl)oxy)benzene (4l):

According to the general procedure, the reaction of 3-phenylpropiolic acid (146 mg, 1.0 mmol) and 2-(4-chlorophenoxy)-2-methylpropanoic acid (1073 mg, 5.0 mmol) afforded the product **4l** (168 mg, 0.62 mmol, 62%) as a yellow oil after column chromatography eluting with *n*-hexane/EtOAc (400:1).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 7.34 – 7.29 (m, 3H), 7.27 – 7.23 (m, 2H), 7.21 – 7.18 (m, 2H), 1.72 (s, 6H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.5, 131.6, 129.0, 128.6, 128.5, 128.2, 123.2, 122.6, 91.1, 86.3, 73.8, 29.8.

HRMS (FD-TOF) m/z: $[M]^+$ Calcd for $C_{17}H_{15}ClO$ 270.08059; Found: 270.08030.

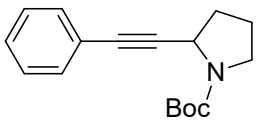


(3-Phenoxybut-1-yn-1-yl)benzene (4m):[6]

According to the general procedure, the reaction of 3-phenylpropiolic acid (146 mg, 1.0 mmol) and 2-phenoxypropanoic acid (831 mg, 5.0 mmol) afforded the product **4m** (151 mg, 0.68 mmol, 68%) as a colorless oil after column chromatography eluting with *n*-hexane/EtOAc (400:1).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 2H), 7.37 – 7.28 (m, 5H), 7.14 – 7.09 (m, 2H), 7.02 (m, 1H), 5.12 (q, J = 6.6 Hz, 1H), 1.78 (d, J = 6.6 Hz, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.7, 131.9, 129.5, 128.6, 128.3, 122.6, 121.4, 116.0, 88.5, 85.8, 64.4, 22.5.

MS (EI) m/z = 222 (M^+)



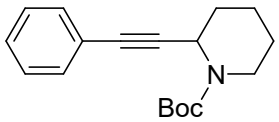
tert-Butyl 2-(phenylethynyl)pyrrolidine-1-carboxylate (4n):[5]

According to the general procedure, the reaction of 3-phenylpropiolic acid (146 mg, 1.0 mmol) and 1-(tert-butoxycarbonyl)pyrrolidine-2-carboxylic acid (1076 mg, 5.0 mmol) afforded the product **4n** (157 mg, 0.58 mmol, 58%) as a yellow oil after column chromatography eluting with *n*-hexane/EtOAc (70:1).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (s, 2H), 7.28 (s, 3H), 4.70 (m, 1H), 3.51 (s, 1H), 3.36 (s, 1H), 2.12 (m, 3H), 1.92 (s, 1H), 1.49 (s, 9H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.3, 131.7, 128.4, 128.1, 123.4, 90.1, 81.7, 79.8, 48.9, 45.8,

34.0, 28.7, 23.9.

MS (EI) m/z = 271 (M^+)

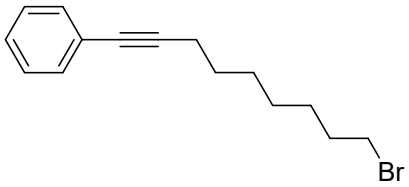


tert-Butyl 2-(phenylethynyl)piperidine-1-carboxylate (4o):[5]

According to the general procedure, the reaction of 3-phenylpropiolic acid (146 mg, 1.0 mmol) and 1-(tert-butoxycarbonyl)piperidine-2-carboxylic acid (1146 mg, 5.0 mmol) afforded the product **4o** (174 mg, 0.61 mmol, 61%) as a white solid after column chromatography eluting with *n*-hexane/EtOAc (70:1). M.P. = 95-98 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (s, 2H), 7.30 (m, 3H), 5.29 (s, 1H), 3.96 (d, *J* = 10.7 Hz, 1H), 3.11 (s, 1H), 1.85 (m, 2H), 1.76 – 1.60 (m, 3H), 1.58 – 1.31 (m, 10H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.8, 131.9, 128.4, 128.2, 123.3, 87.8, 84.2, 80.1, 45.0, 40.7, 30.9, 28.6, 25.5, 20.3.

MS (EI) m/z = 285 (M^+)



(9-Bromonon-1-yn-1-yl)benzene (4p):[9]

According to the general procedure, the reaction of 3-phenylpropiolic acid (146 mg, 1.0 mmol) and 8-bromooctanoic acid (1116 mg, 5.0 mmol) afforded the product **4p** (117.3 mg, 0.42 mmol, 61%) as an orange oil after column chromatography eluting with *n*-hexane;
^{1}H NMR (500 MHz, DMSO) δ 7.39 – 7.35 (m, 2H), 7.36 – 7.30 (m, 3H), 3.53 (m, 2H), 2.41 (t, J = 7.0 Hz, 2H), 1.84 – 1.77 (m, 2H), 1.57 – 1.50 (m, 2H), 1.41 (m, 4H), 1.33 (m, 2H);

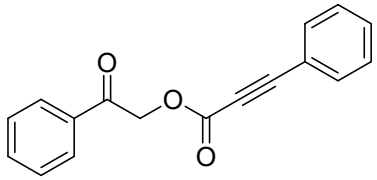
^{13}C NMR (126 MHz, DMSO) δ 131.2, 128.5, 127.8, 123.3, 90.6, 80.6, 35.1, 32.2, 28.1, 28.0, 27.6, 27.4, 18.5.

MS (EI) m/z = 278 (M^+)

Molecular Weight: 279.22

Formation of compound 7 and 8

3-Phenylpropiolic acid (146 mg, 1.0 mmol), 1,4-benzodioxane-2-carboxylic acid (901 mg, 5.0 mmol), $PhI(OAc)_2$ (97 mg, 3.0 mmol) and MeCN (5.0 mL) were added to the reaction vial. The mixture was stirred at room temperature for 12 h. The solution was cooled to room temperature. The reaction mixture diluted with ethyl acetate and washed with the saturated NaCl solution. The organic layer was dried over magnesium sulfate. Evaporation of the solvent under reduced pressure provided the crude product, which was purified by column chromatography on silica gel with hexane and ethyl acetate (20:1). Compound **7** (55.5 mg, 0.21 mmol) and compound **8** (125.8 mg (90% purity ->113.2 mg, 0.38 mmol)) were obtained.

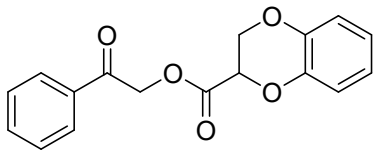


2-Oxo-2-phenylethyl 3-phenylpropiolate (7):[10]

M.P. = 87-89 °C;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 – 7.92 (m, 2H), 7.65 – 7.60 (m, 3H), 7.53 – 7.45 (m, 3H), 7.41 – 7.37 (m, 2H), 5.49 (s, 2H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 191.1, 153.4, 134.2, 134.1, 133.3, 131.0, 129.1, 128.7, 128.0, 119.5, 88.1, 80.1, 67.2.

MS (EI) m/z = 264 (M^+)



2-Oxo-2-phenylethyl 2,3-dihydrobenzo[b][1,4]dioxine-2-carboxylate (8):

M.P. = 89-92 °C;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.87 (m, 2H), 7.62 (m, 1H), 7.49 (m, 2H), 7.06 – 7.00 (m, 1H), 6.97 – 6.80 (m, 3H), 5.52 (dd, *J* = 16.2, 1.1 Hz, 1H), 5.44 – 5.38 (m, 1H), 5.03 (m, 1H), 4.56 – 4.46 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) 191.0, 167.6, 143.1, 142.3, 134.3, 134.2, 129.1, 127.9, 122.3, 122.1, 118.5, 117.5, 72.0, 66.9, 65.1.

HRMS (FD-TOF) m/z: $[M]^+$ Calcd for $C_{17}H_{14}O_5$ 298.08357; Found: 298.08339.

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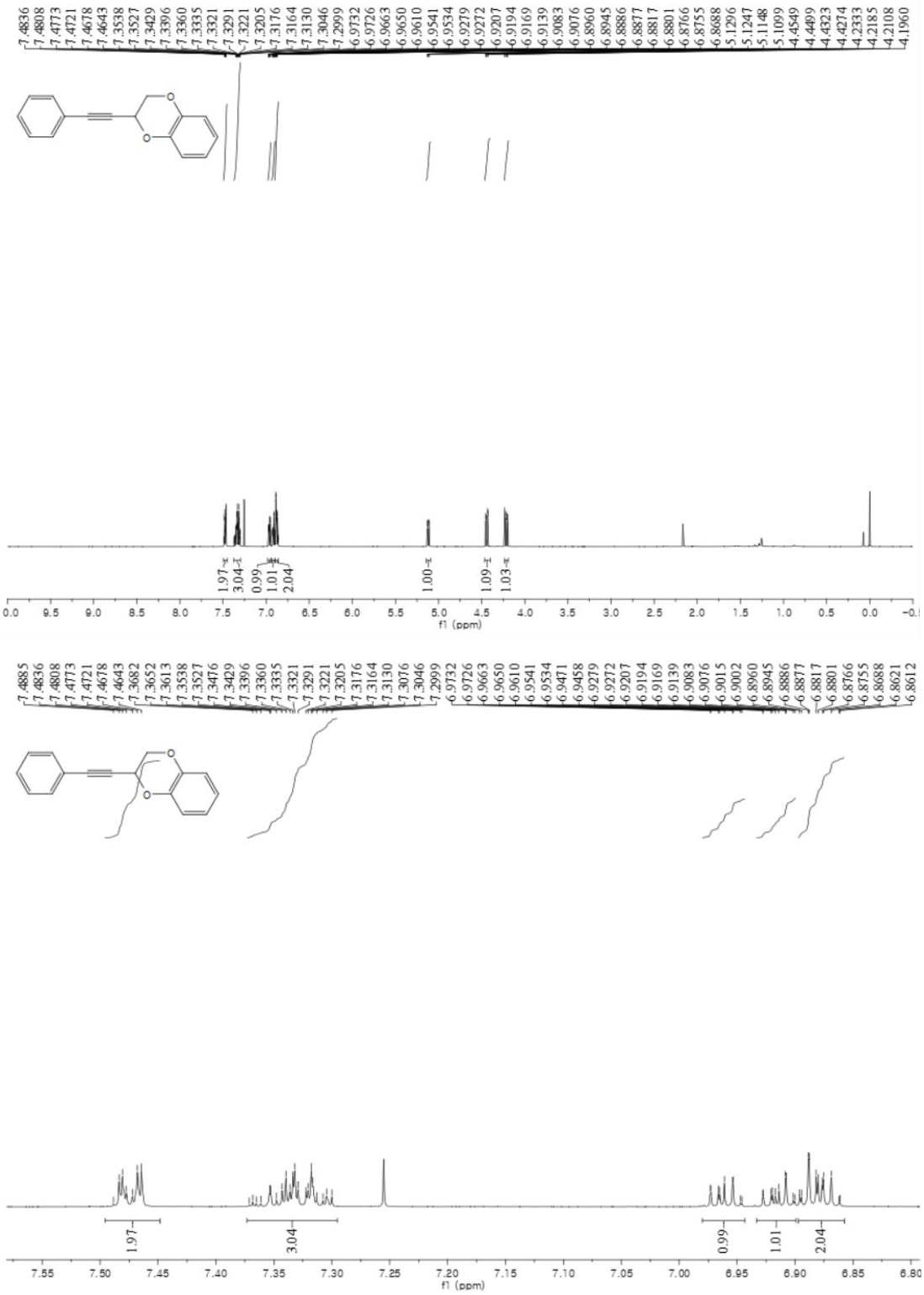
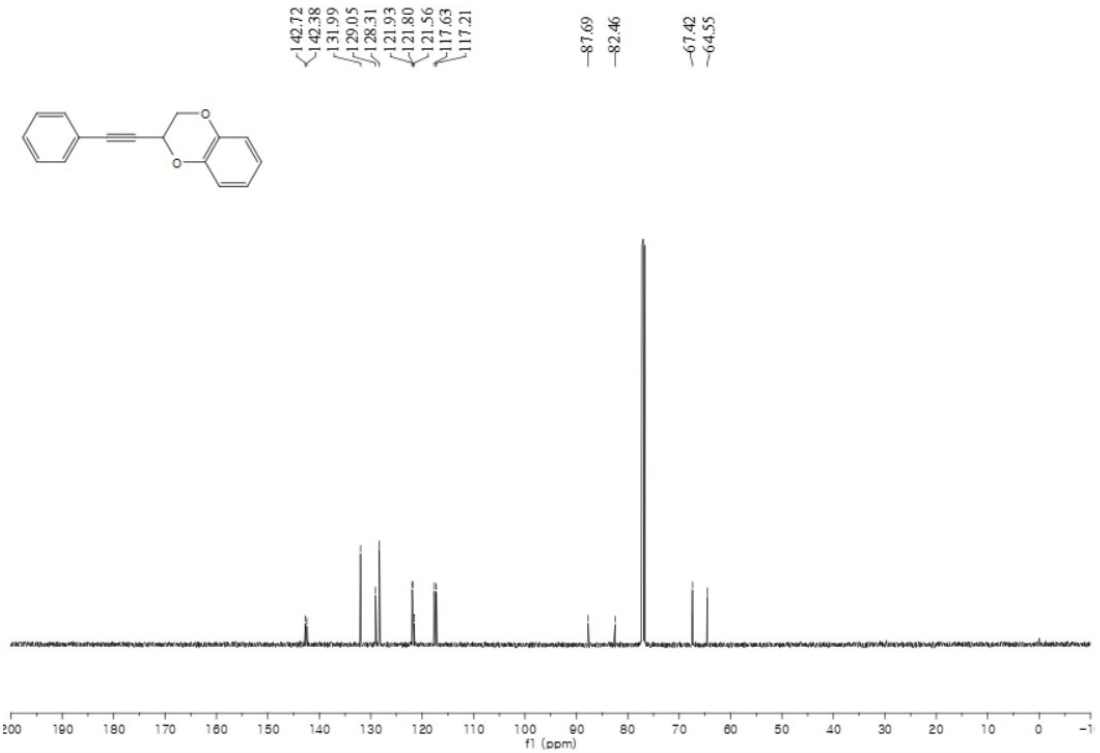
Copy of NMR Spectra

2-(Phenylethynyl)-2,3-dihydrobenzo[b][1,4]dioxine (3a)

^{1}H NMR

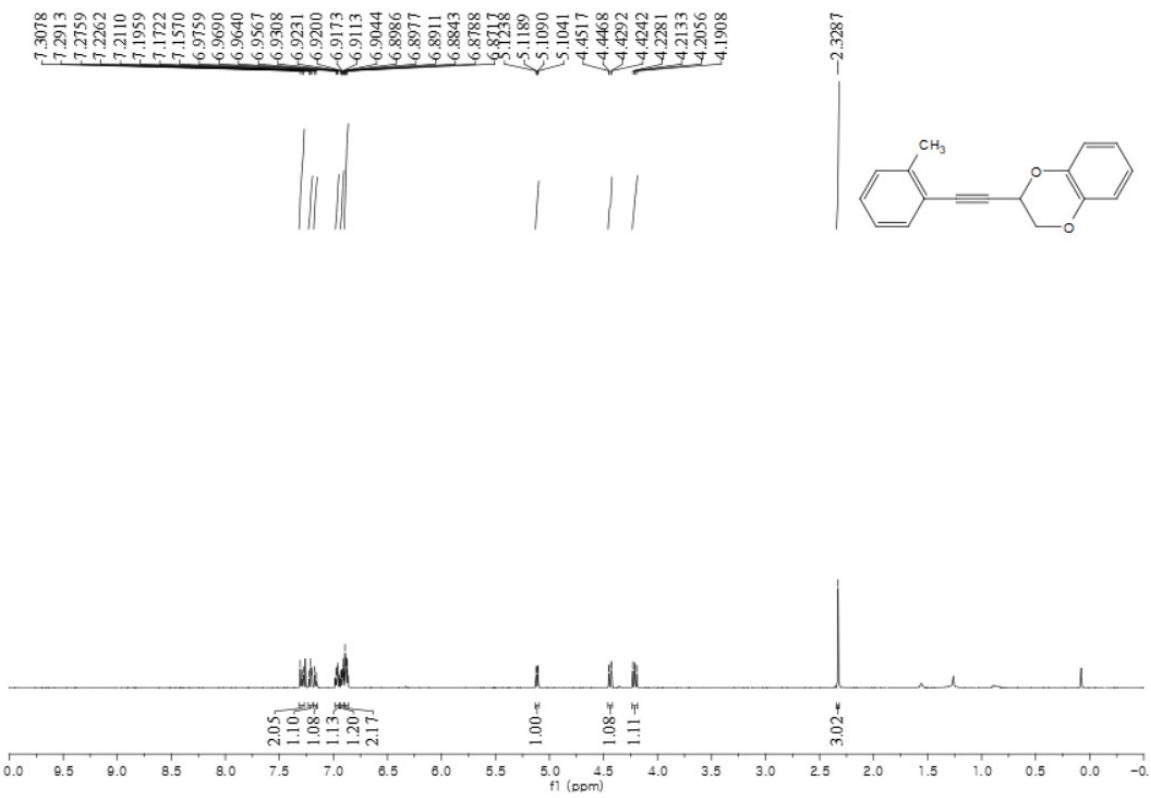


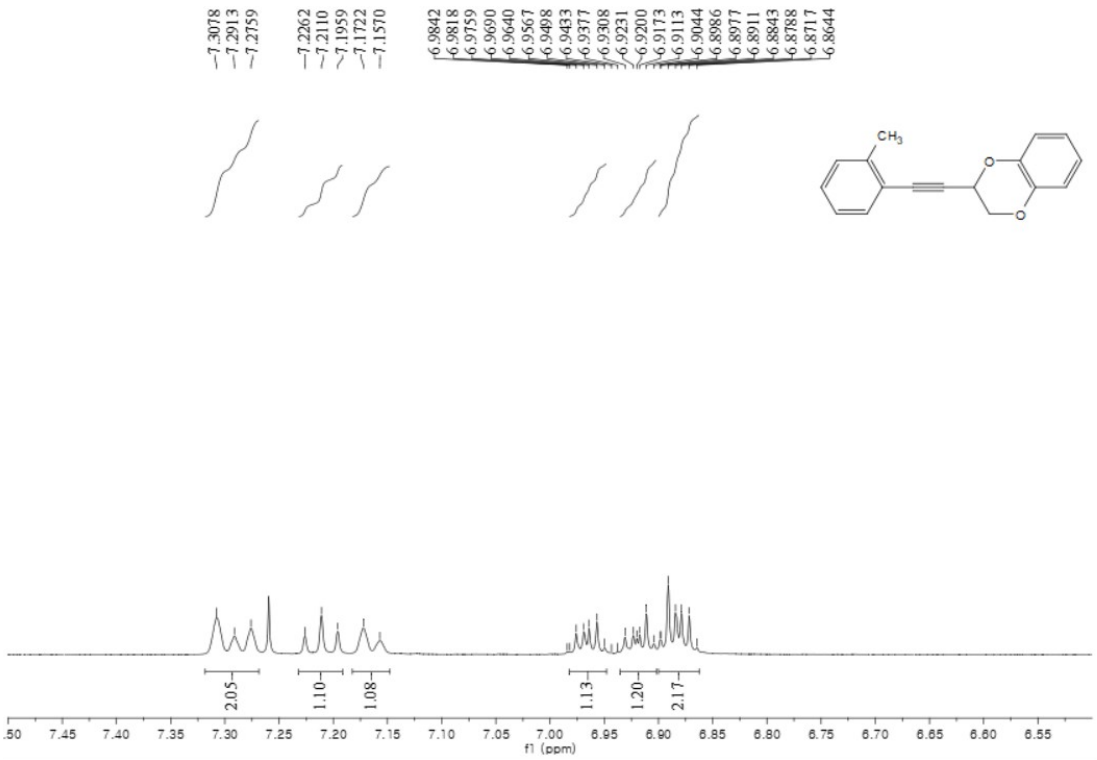
^{13}C NMR



2-(o-Tolylethynyl)-2,3-dihydrobenzo[b][1,4]dioxine (3b)

^{1}H NMR

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6.9567
6.9498
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6.9308
6.9231
6.9200
6.9173
6.9113
6.9044
6.8986
6.8977
6.8911
6.8843
6.8788
6.8717
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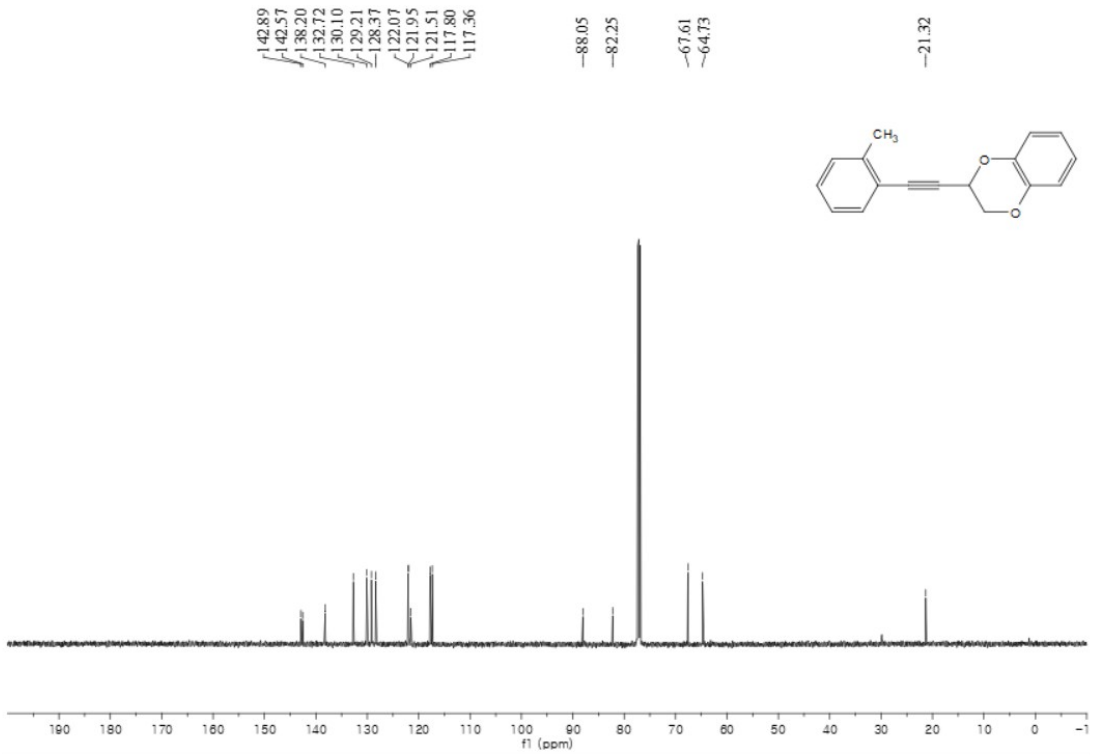
O
2.05
1.10
1.08
1.13
1.20
2.17
f1 (ppm)

^{13}C NMR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121.51
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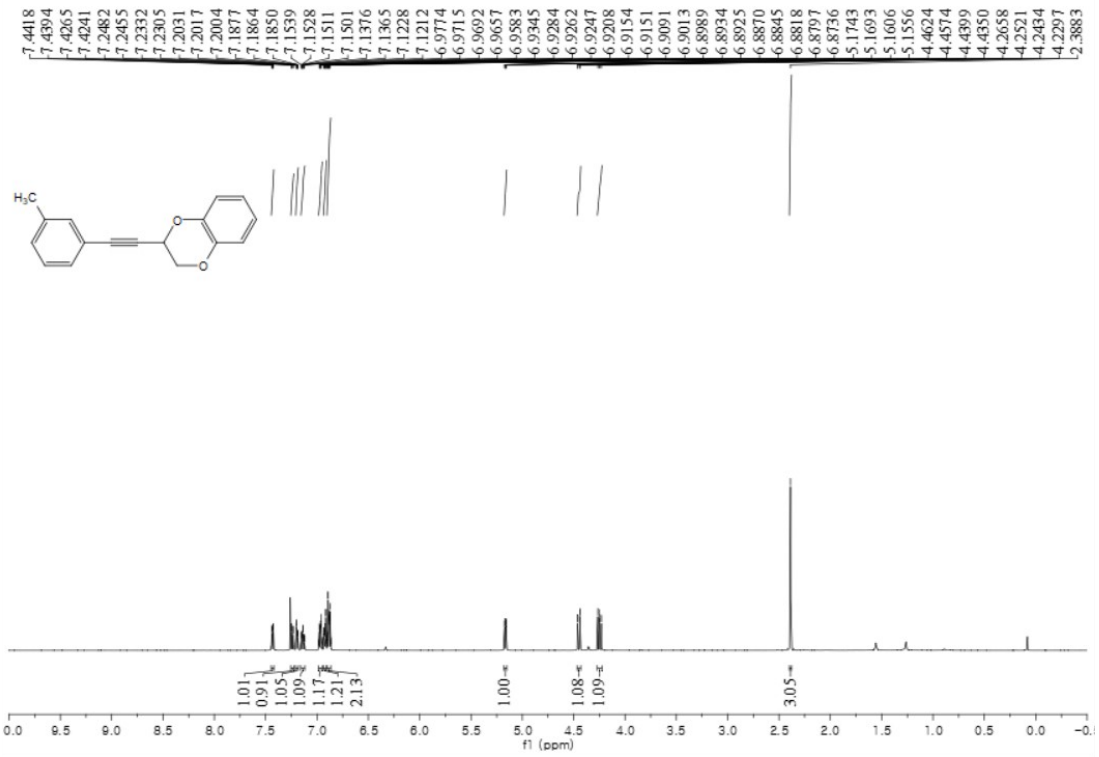
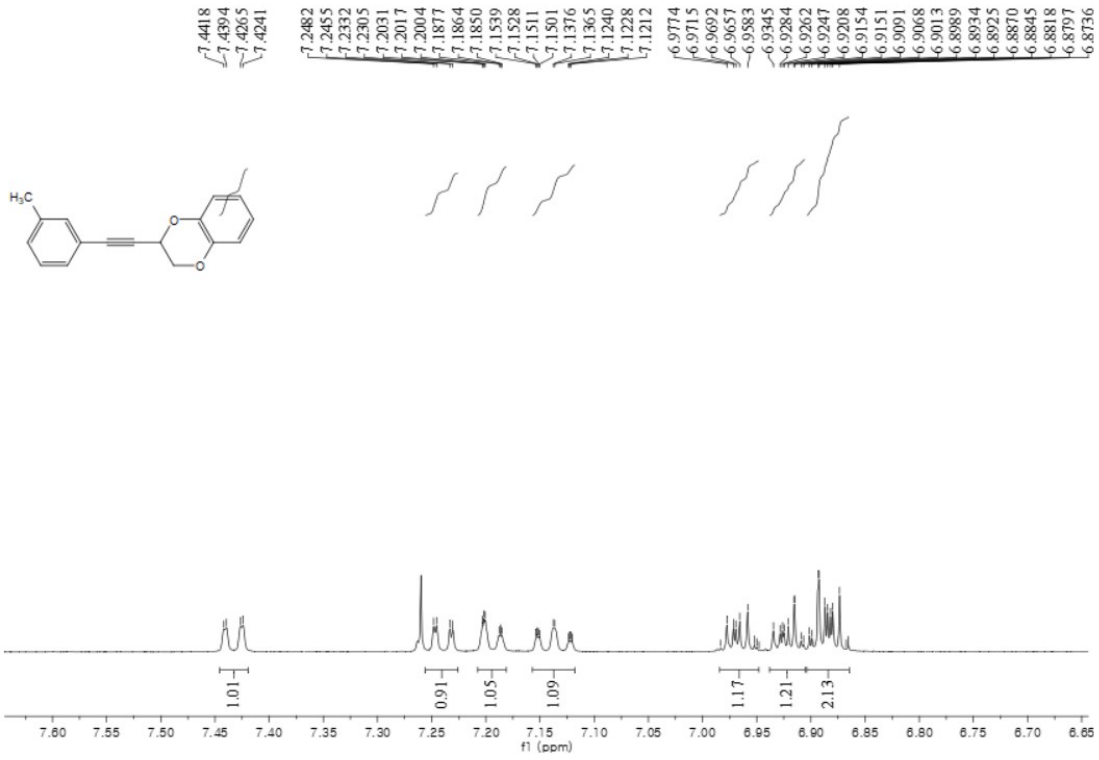
117.36
88.05
82.25
67.61
64.73
21.32
CH3
O
O
f1 (ppm)

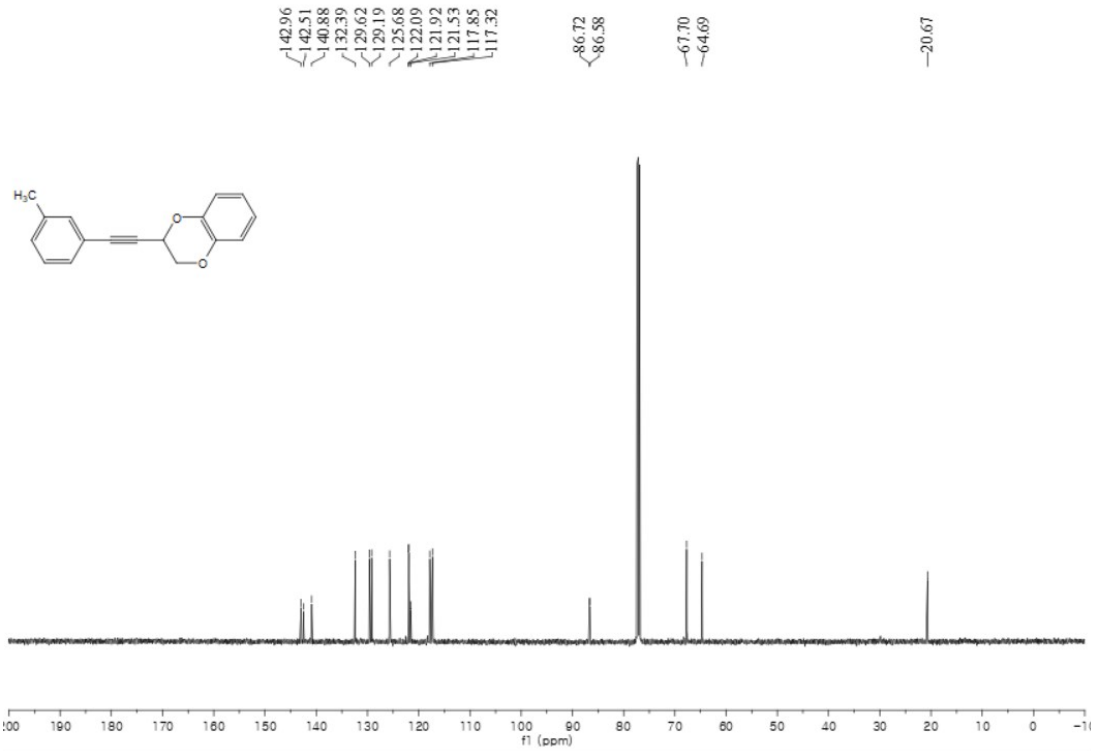
2-(m-Tolylethynyl)-2,3-dihydrobenzo[b][1,4]dioxine (3c)

^{1}H NMR



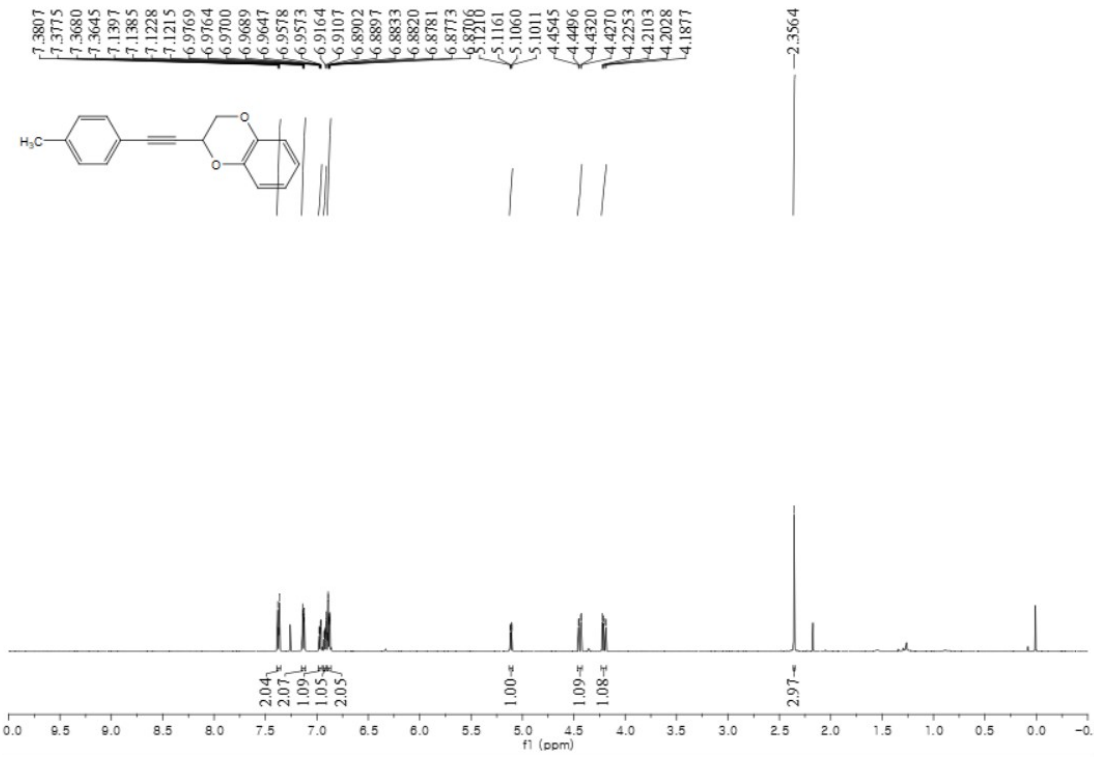


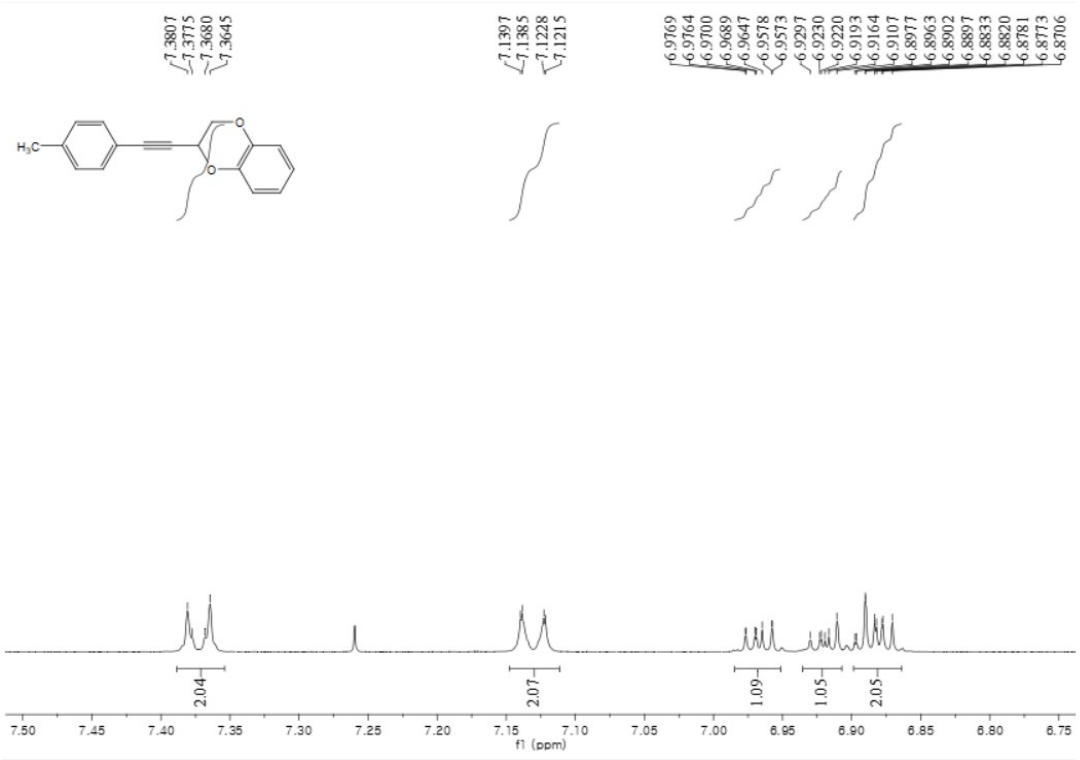
^{13}C NMR



2-(p-Tolylethynyl)-2,3-dihydrobenzo[b][1,4]dioxine (3d)

^{1}H NMR

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7.20
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6.80
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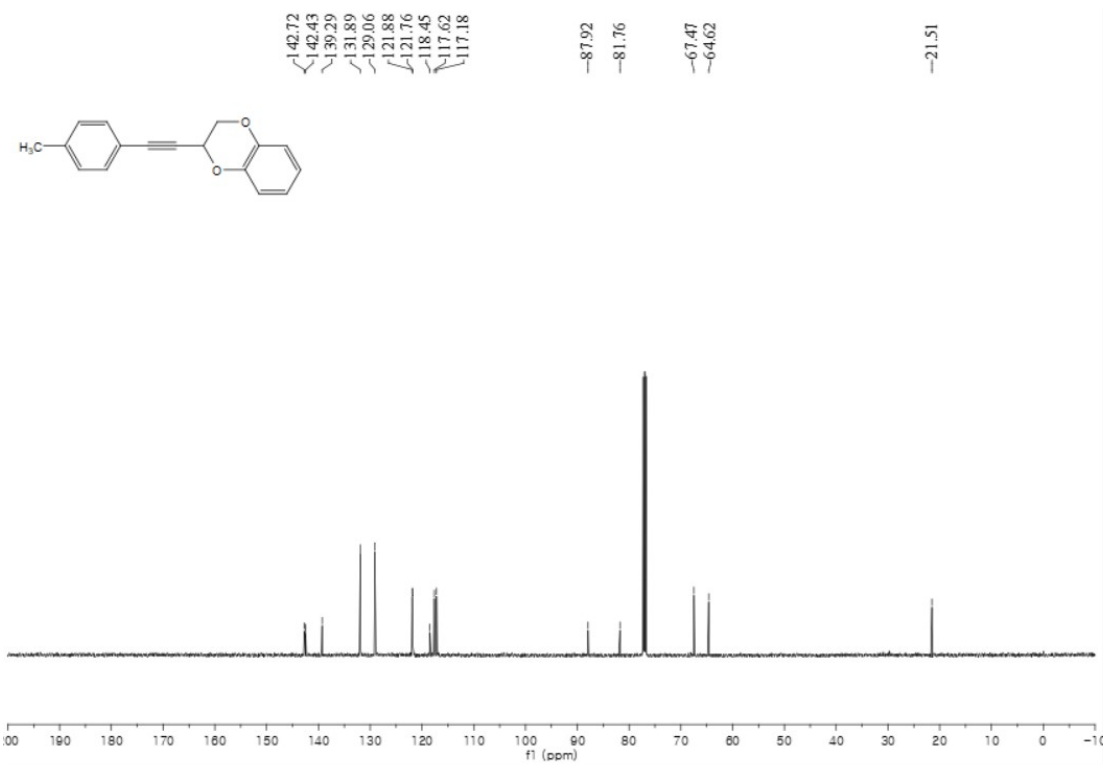
f1 (ppm)

^{13}C NMR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131.89
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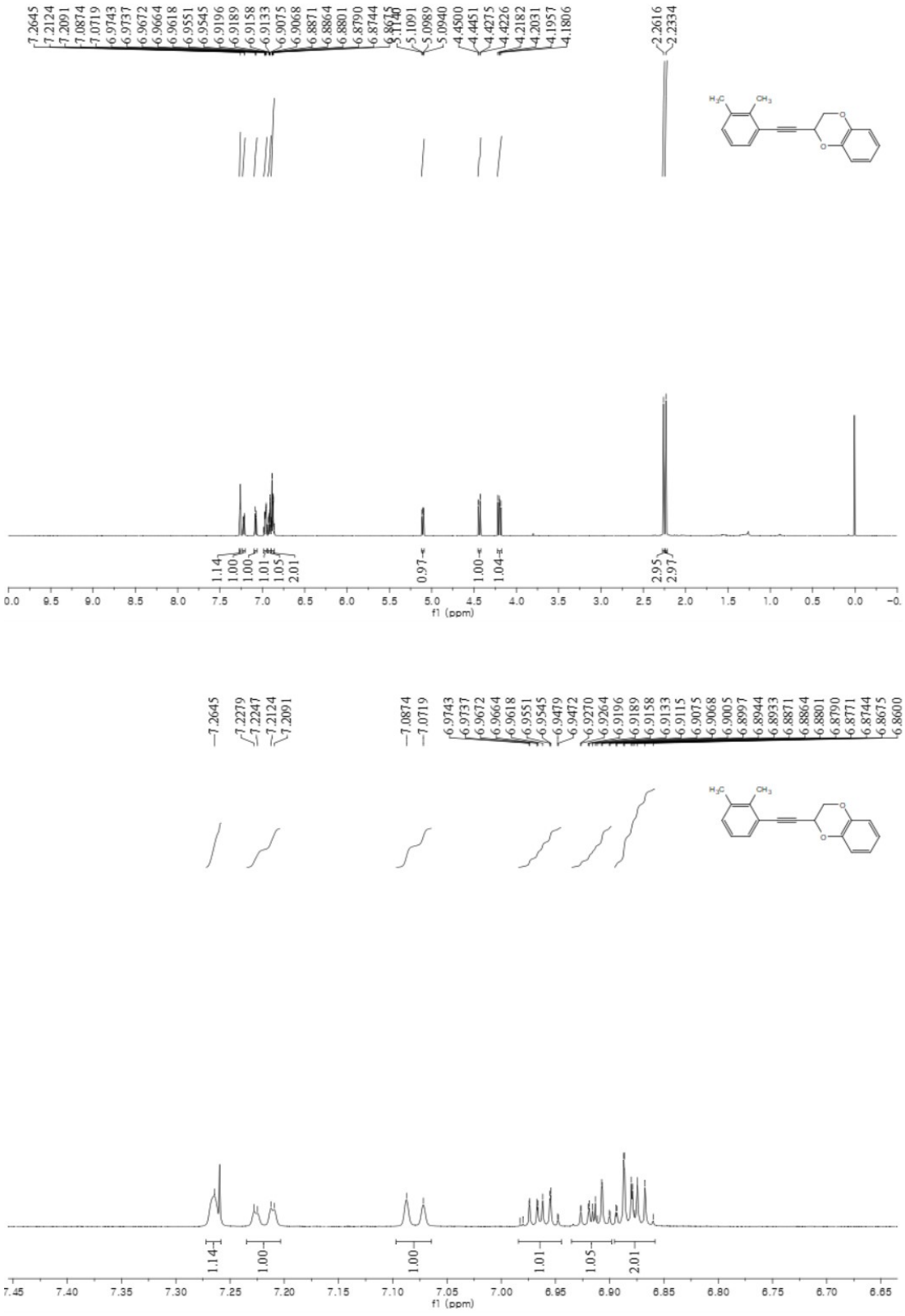
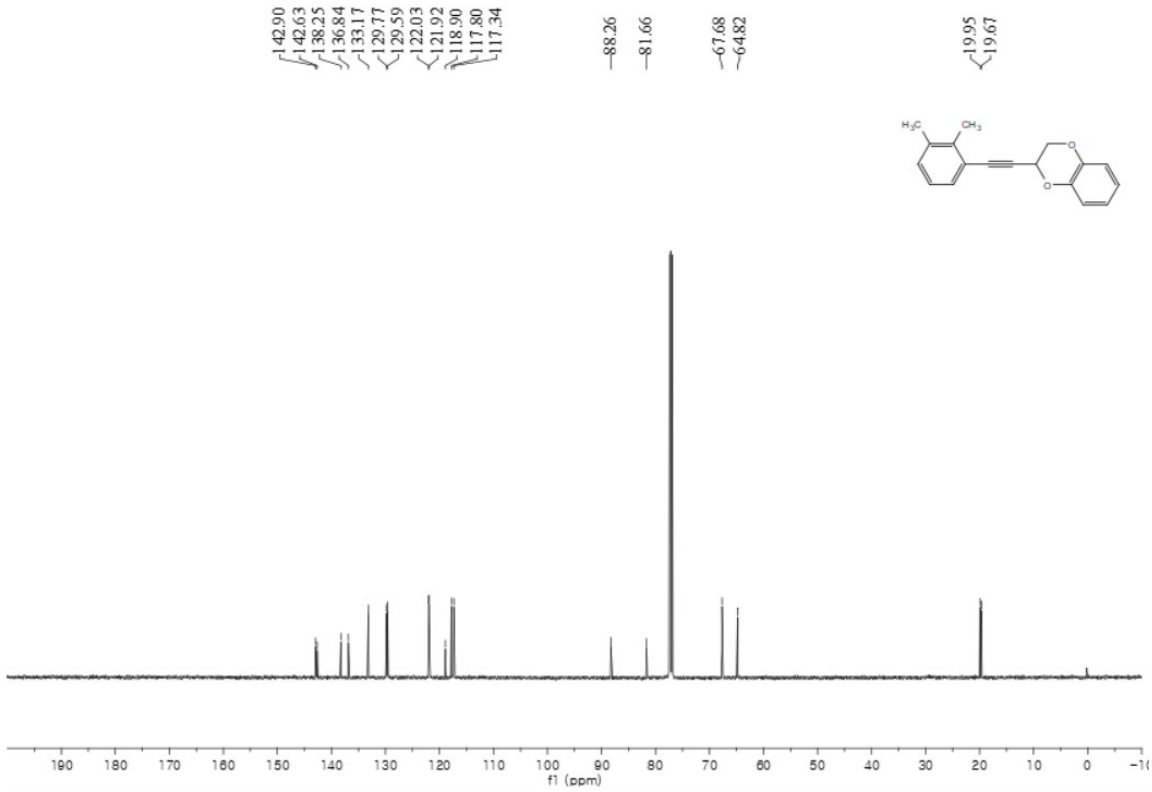
121.76
118.45
117.62
117.18
87.92
81.76
67.47
64.62
21.51
H3C
O
O
f1 (ppm)

2-((2,3-Dimethylphenyl)ethynyl)-2,3-dihydrobenzo[b][1,4]dioxine (3e)

^{1}H NMR

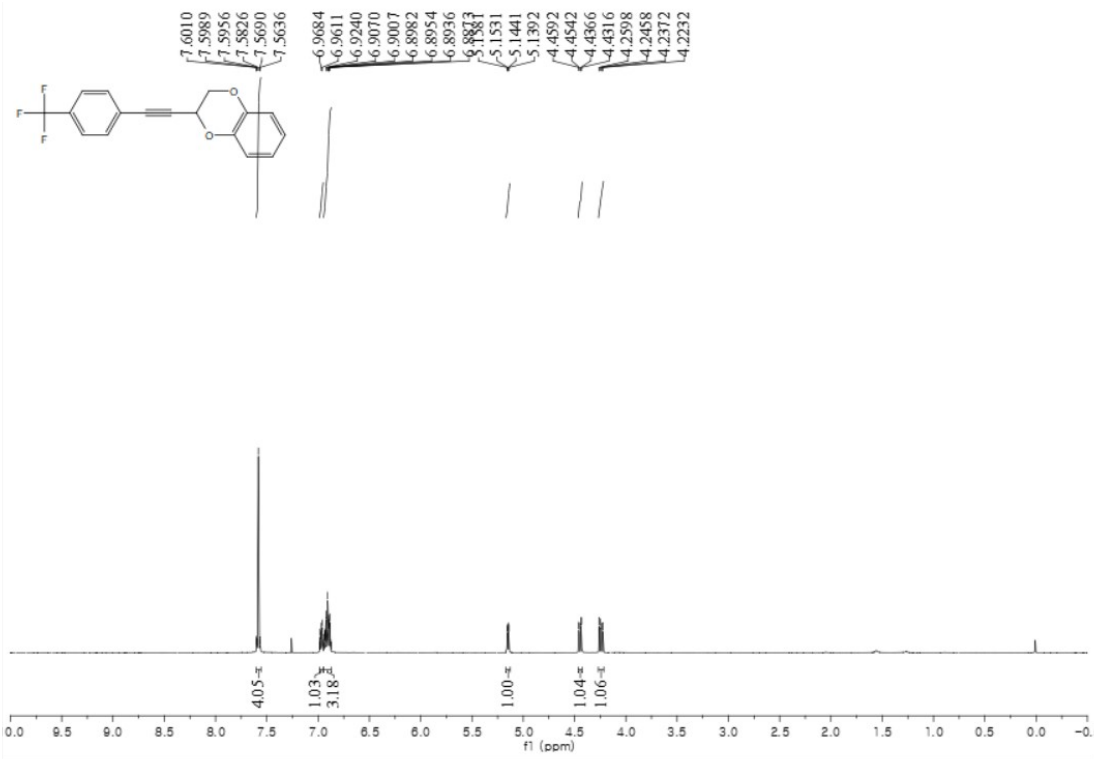


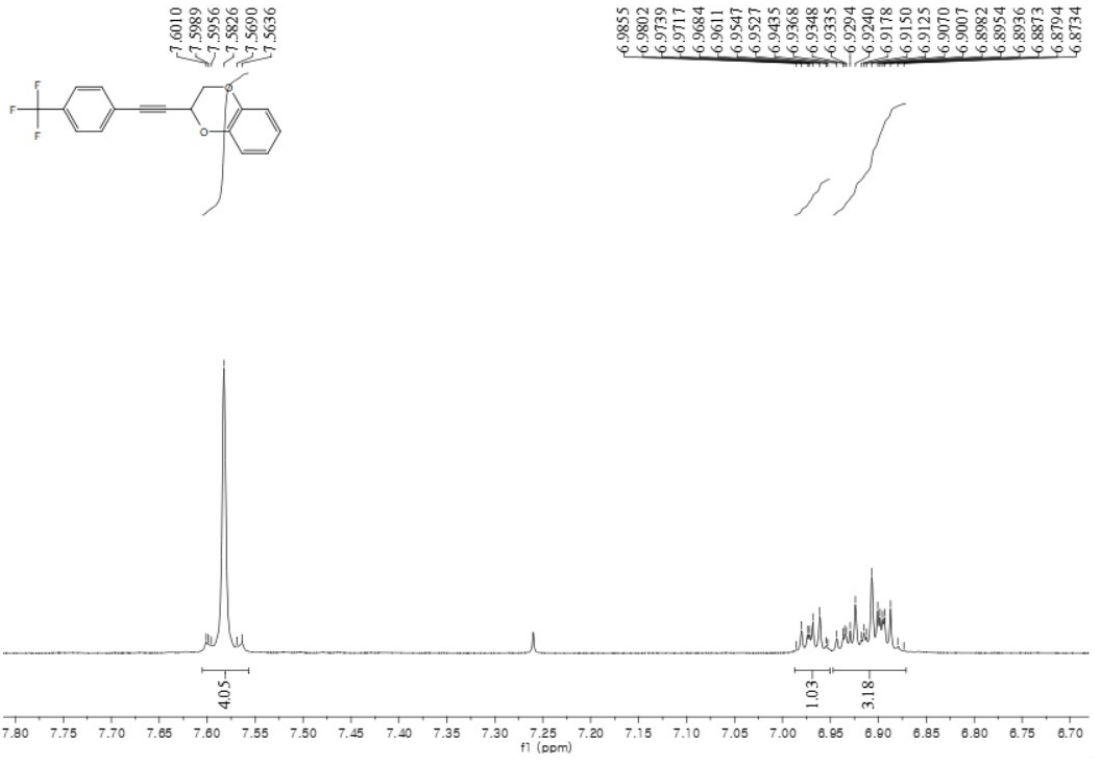
^{13}C NMR



2-((4-(Trifluoromethyl)phenyl)ethynyl)-2,3-dihydrobenzo[b][1,4]dioxine (3f)

^{1}H NMR

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6.9125
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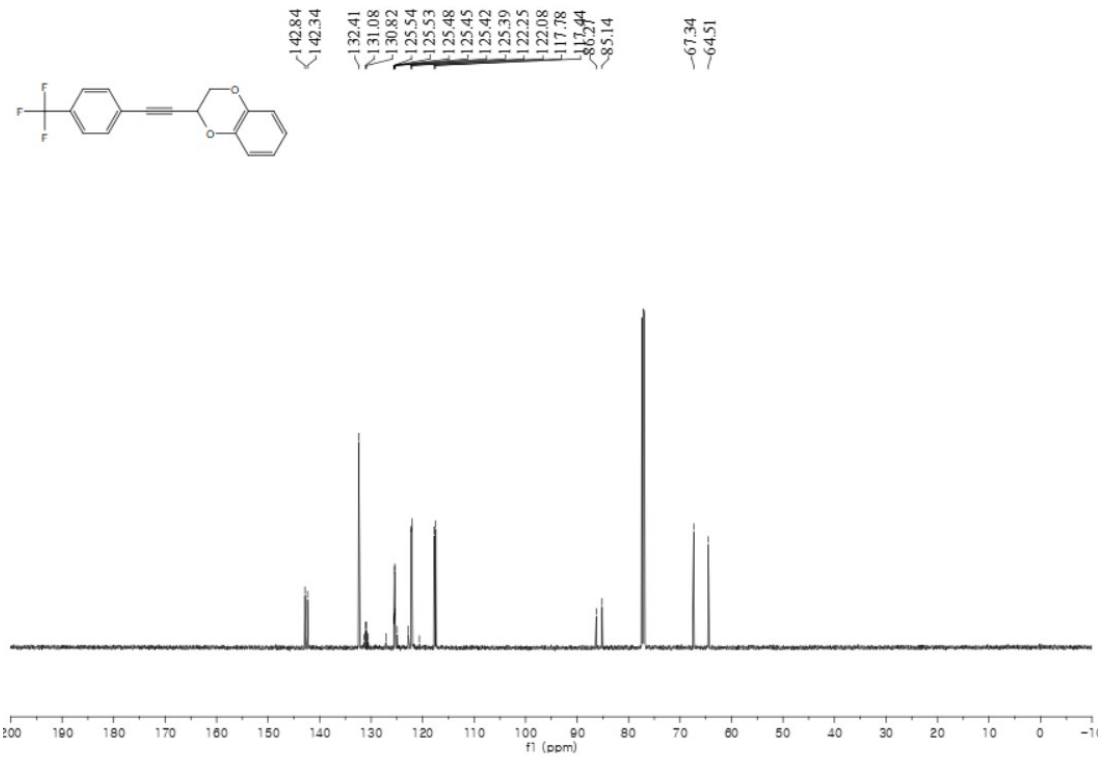
1.03
3.18
f1 (ppm)

^{13}C NMR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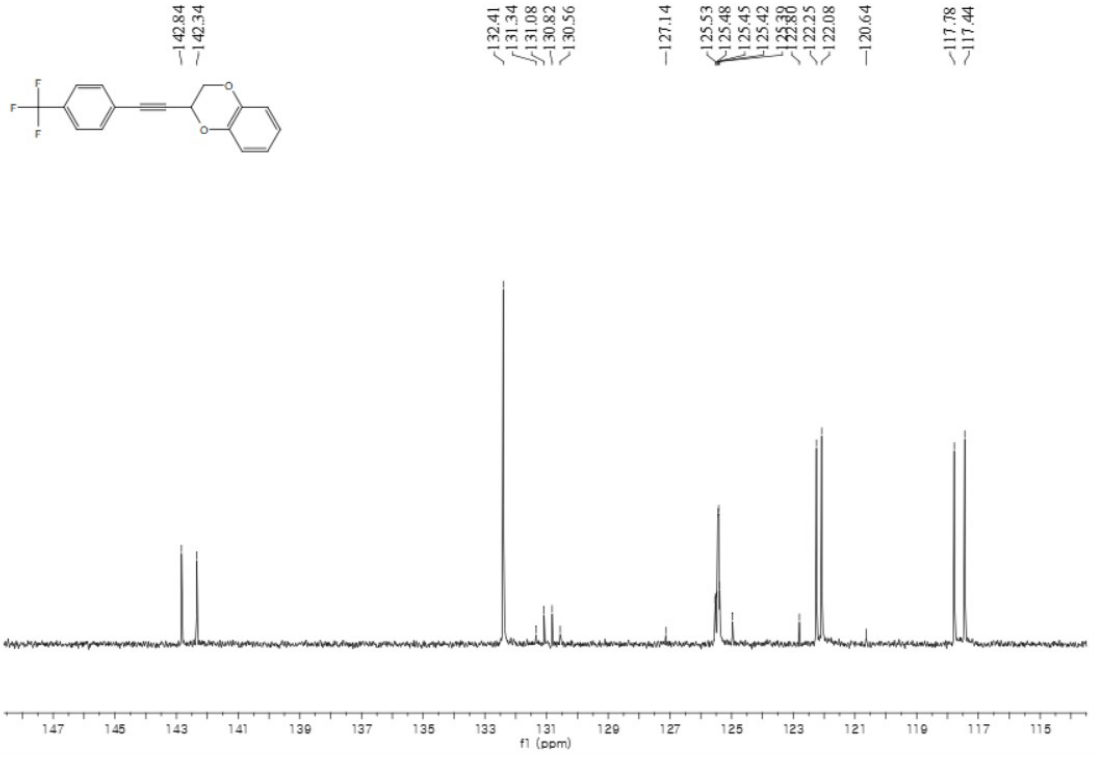
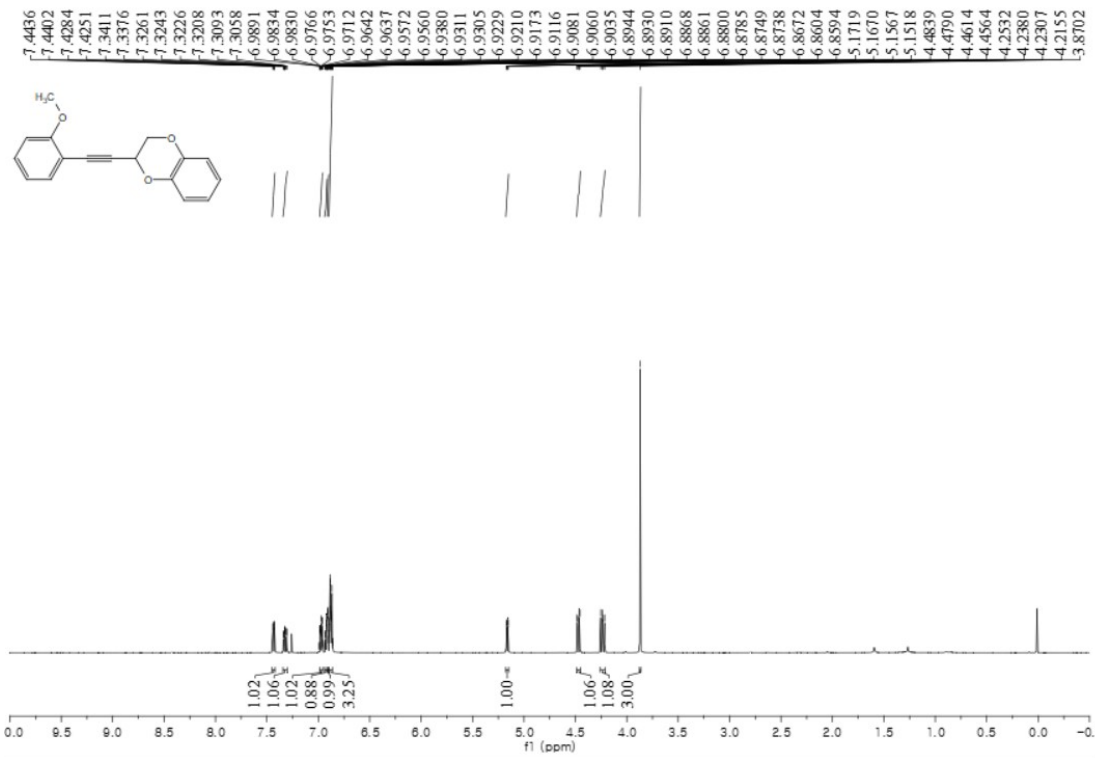
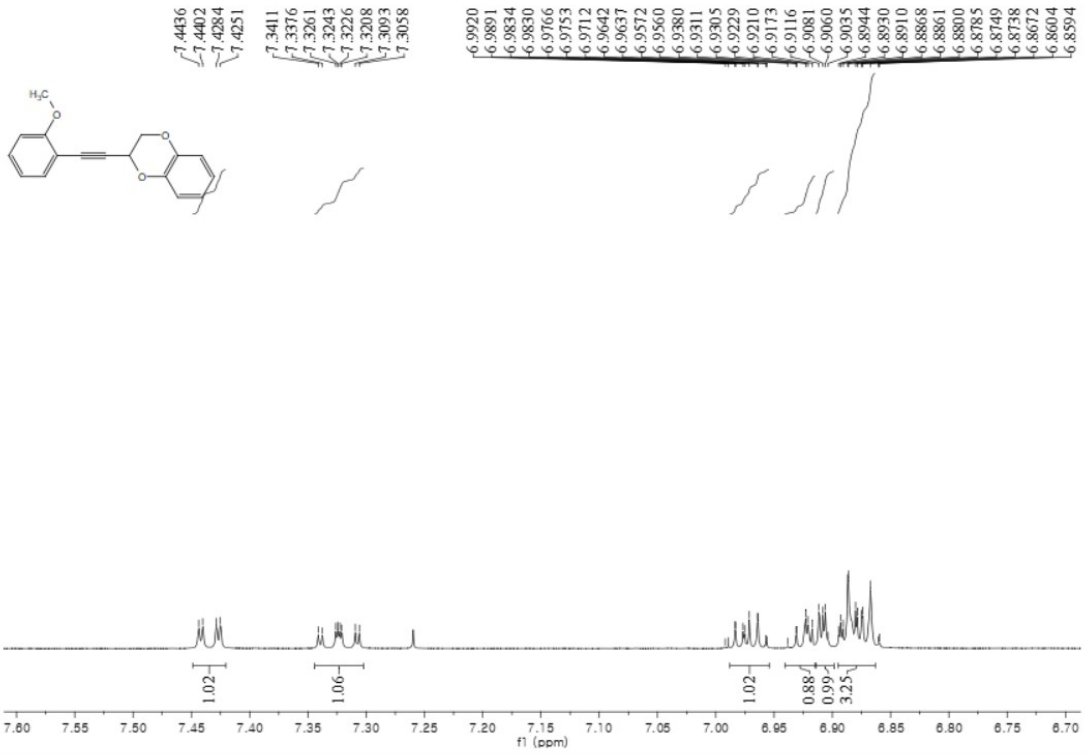
f1 (ppm)



2-((2-Methoxyphenyl)ethynyl)-2,3-dihydrobenzo[b][1,4]dioxine (3g)

^{1}H NMR

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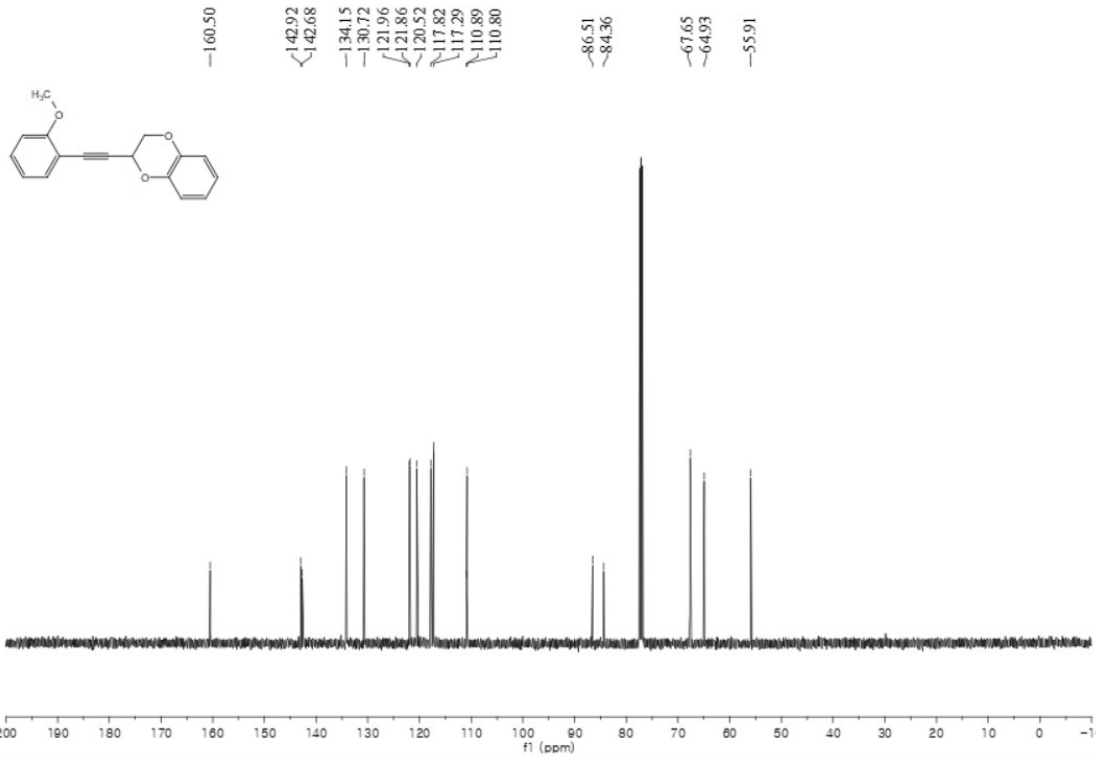
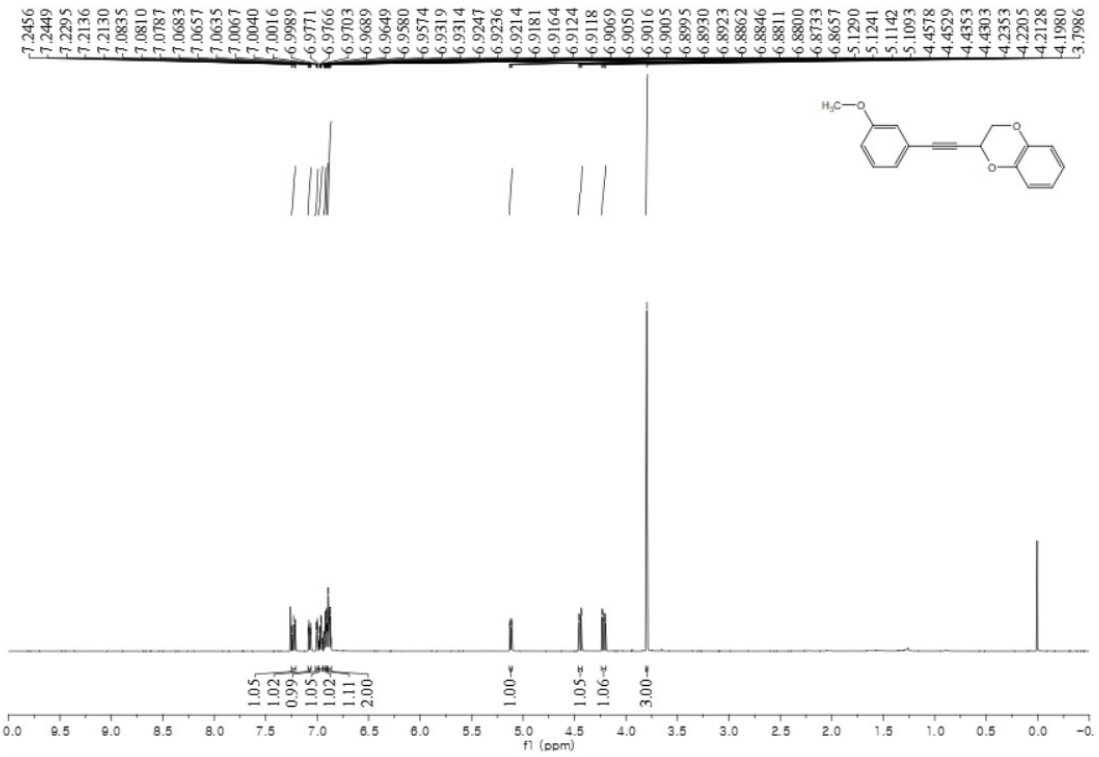
6.9834
6.9830
6.9766
6.9753
6.9712
6.9642
6.9637
6.9572
6.9560
6.9380
6.9311
6.9305
6.9229
6.9210
6.9173
6.9116
6.9081
6.9060
6.9035
6.8944
6.8930
6.8910
6.8868
6.8861
6.8800
6.8785
6.8749
6.8738
6.8672
6.8604
6.8594
1.02
1.06
1.02
0.88
0.99
3.25
f1 (ppm)

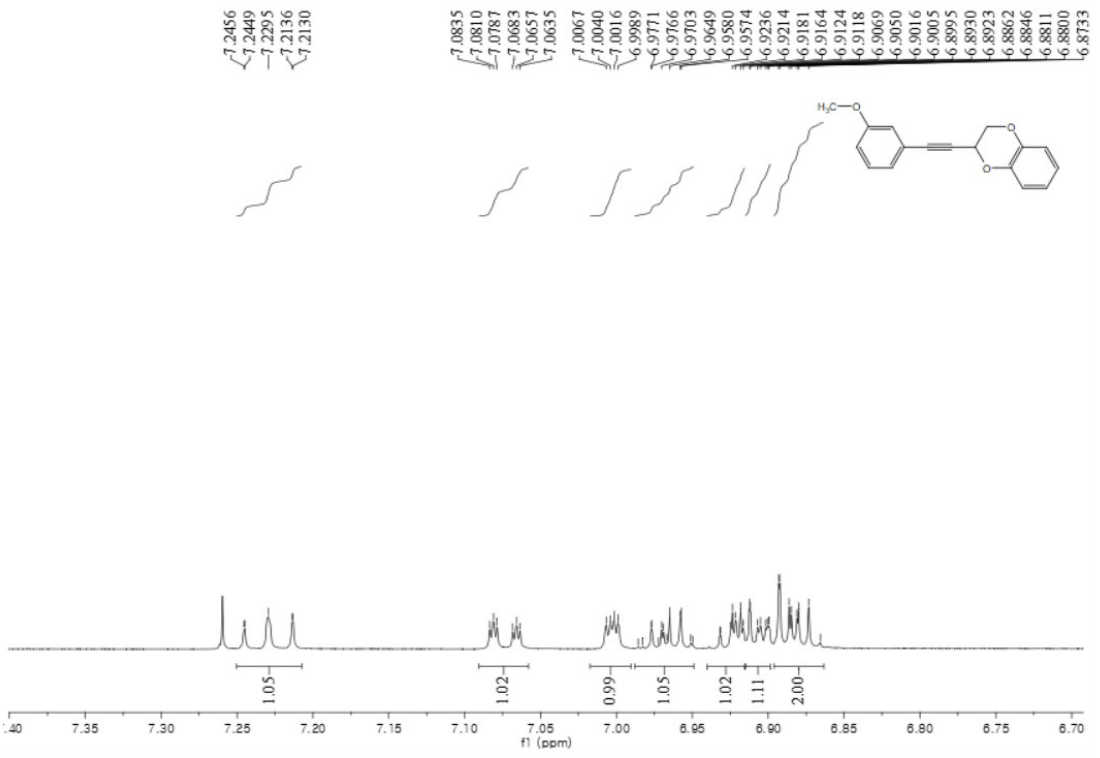
^{13}C NMR


160.50
142.92
142.68
134.15
130.72
121.96
121.86
120.52
117.82
117.29
110.89
110.80
86.51
84.36
67.65
64.93
55.91
f1 (ppm)

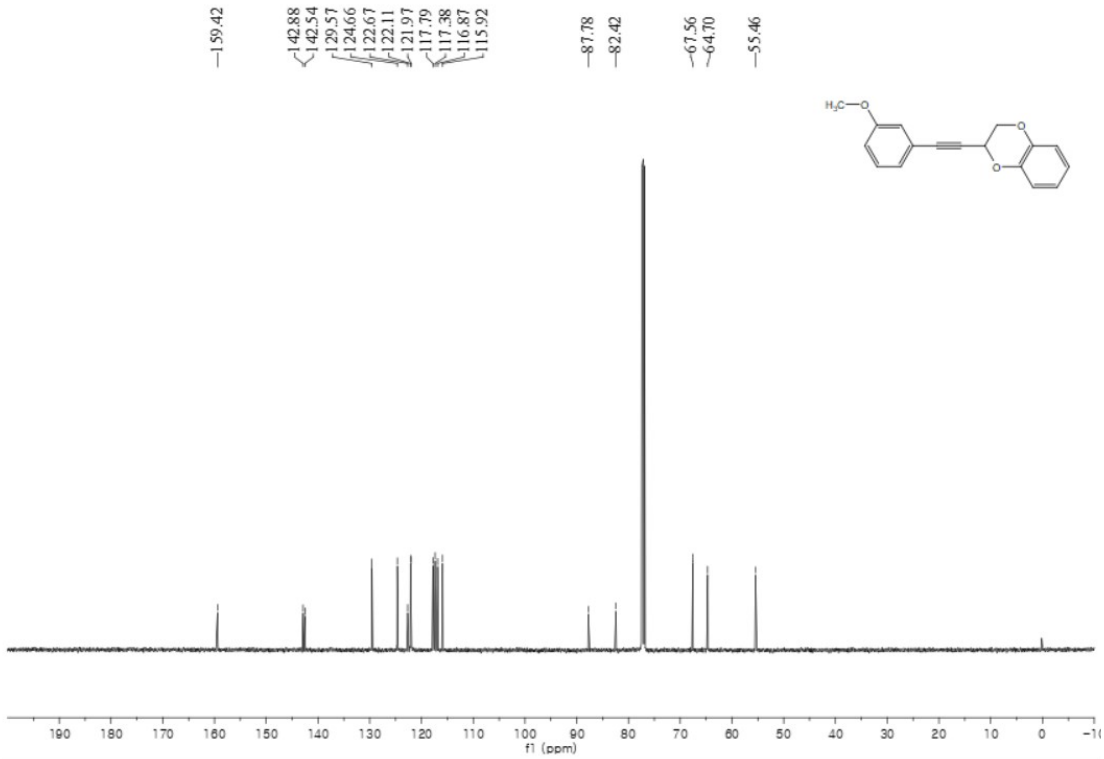
2-((3-Methoxyphenyl)ethynyl)-2,3-dihydrobenzo[b][1,4]dioxine (3h)

^{1}H NMR



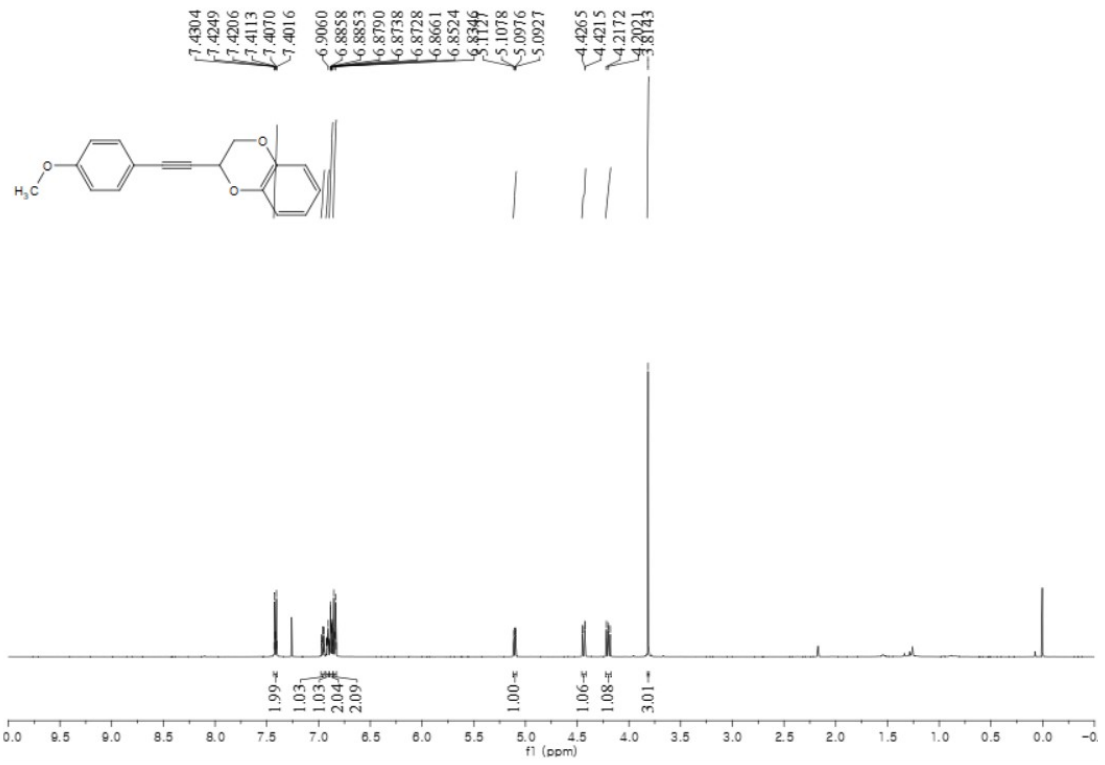


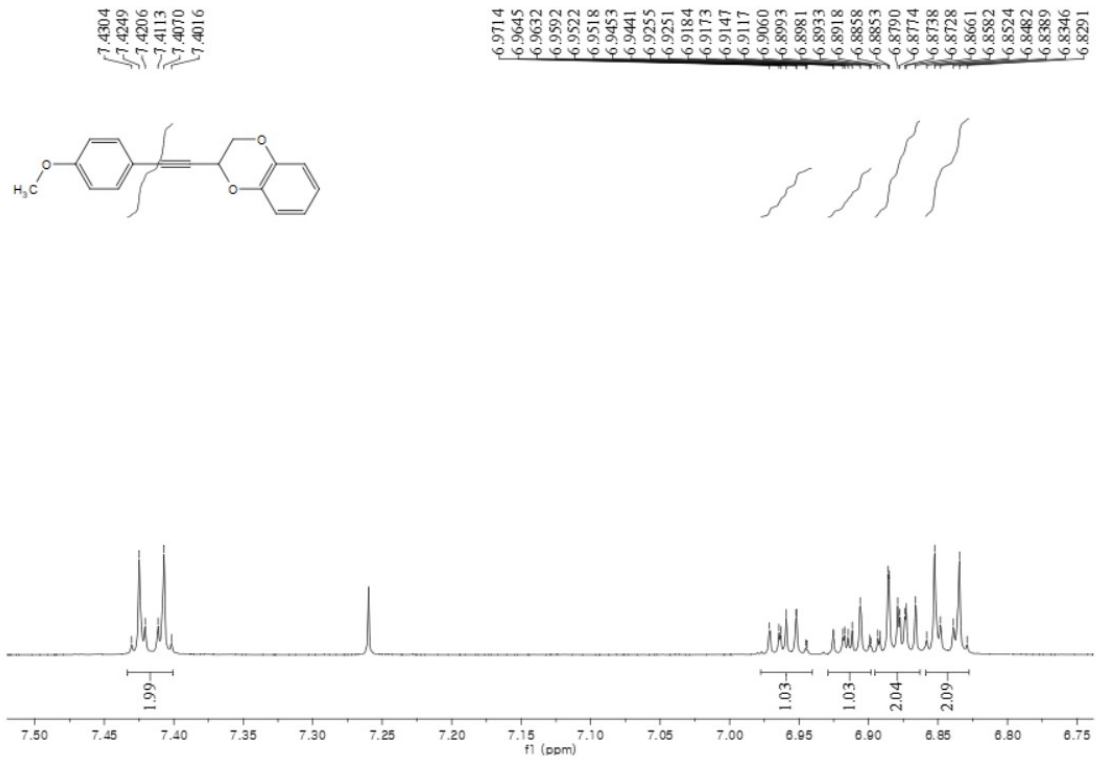
^{13}C NMR



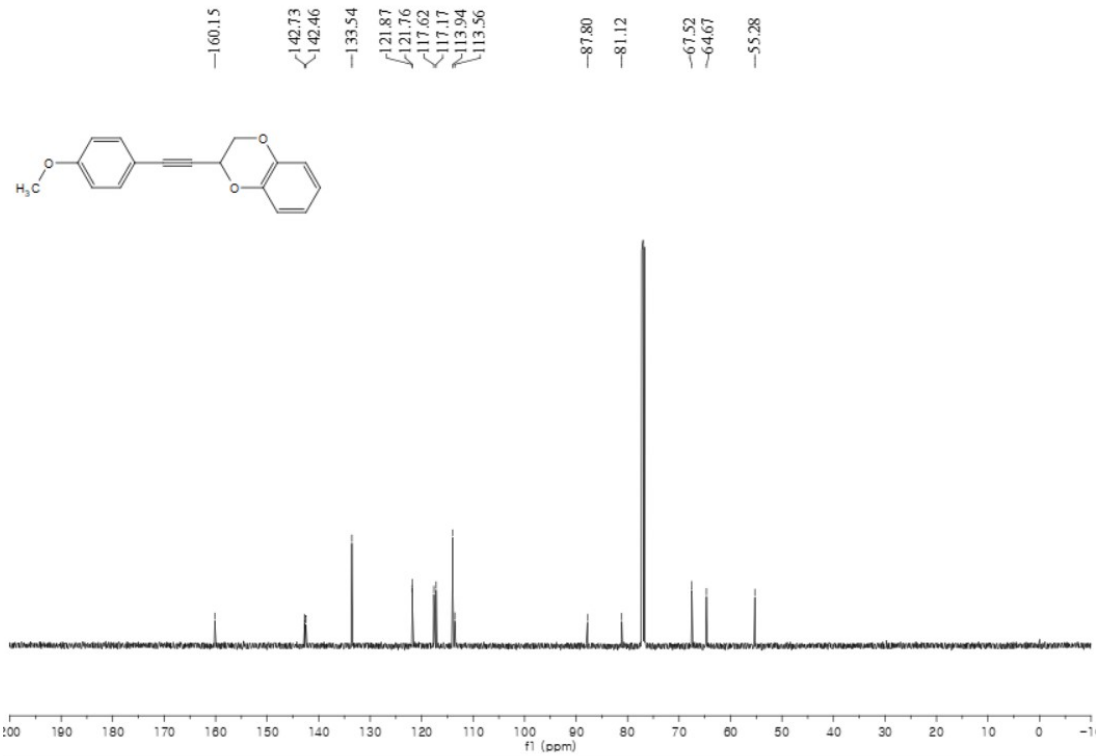
2-((4-Methoxyphenyl)ethynyl)-2,3-dihydrobenzo[b][1,4]dioxine (3i)

^{1}H NMR



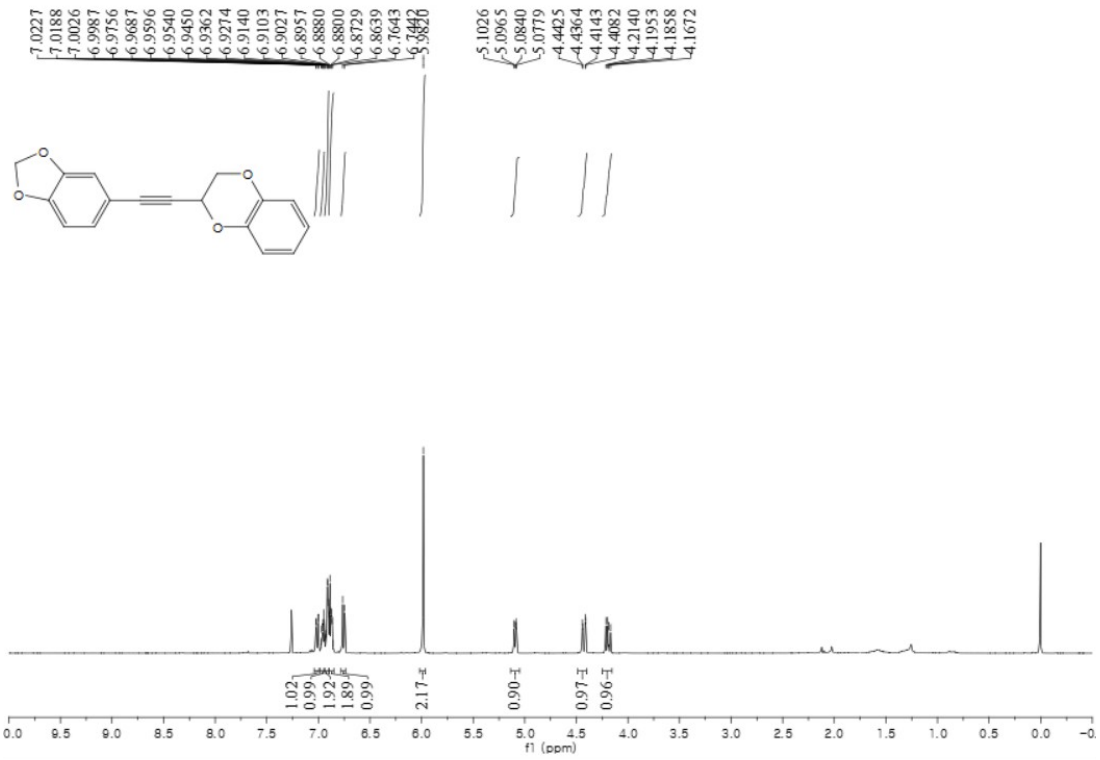

7.4304
7.4249
7.4206
7.4113
7.4070
7.4016
6.9714
6.9645
6.9632
6.9592
6.9522
6.9518
6.9453
6.9441
6.9255
6.9251
6.9184
6.9173
6.9147
6.9117
6.9060
6.8993
6.8981
6.8933
6.8918
6.8858
6.8853
6.8790
6.8774
6.8738
6.8728
6.8661
6.8582
6.8524
6.8482
6.8389
6.8346
6.8291
O
H3C
O
O
1.99
1.03
1.03
2.04
2.09
7.50
7.45
7.40
7.35
7.30
7.25
7.20
7.15
7.10
7.05
7.00
6.95
6.90
6.85
6.80
6.75
f1 (ppm)

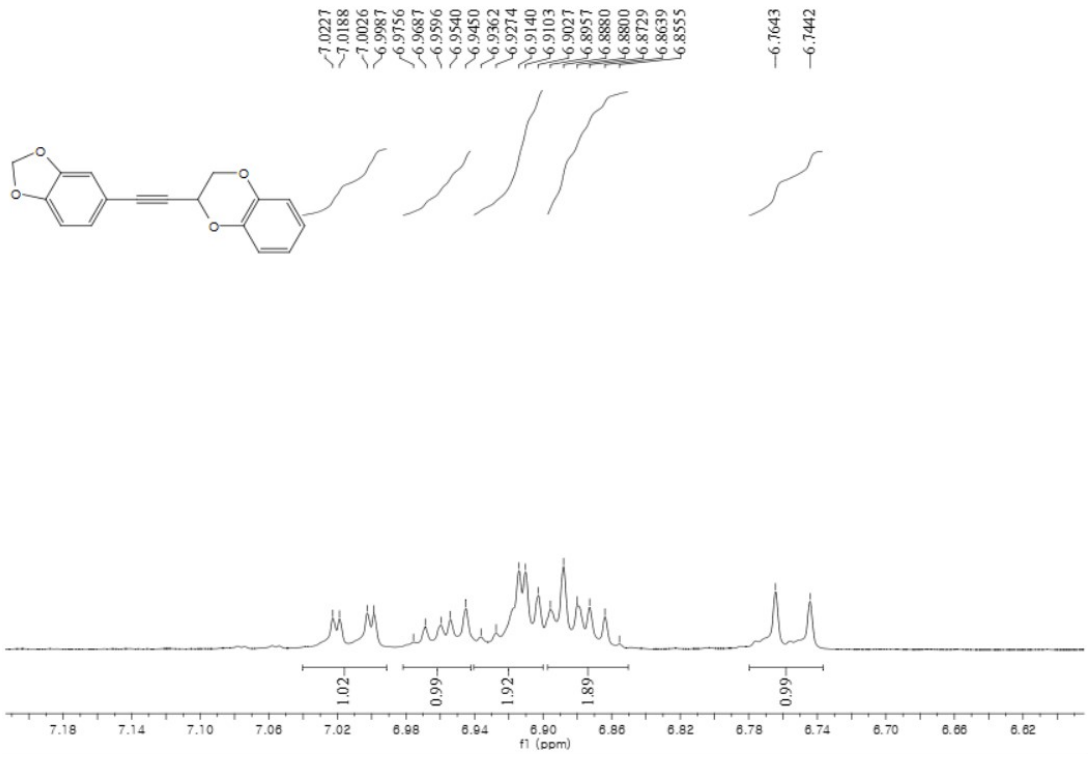
^{13}C NMR


160.15
142.73
142.46
133.54
121.87
121.76
117.62
117.17
113.94
113.56
87.80
81.12
67.52
64.67
55.28
O
H3C
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

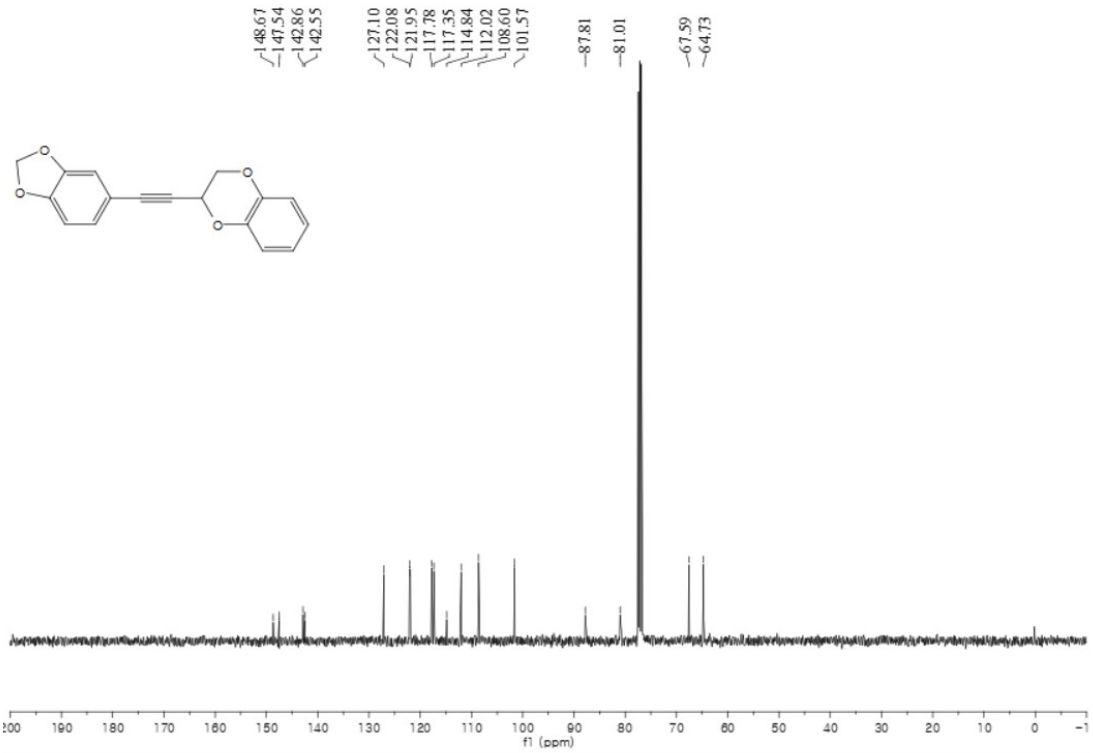
2-(Benzo[d][1,3]dioxol-5-ylethynyl)-2,3-dihydrobenzo[b][1,4]dioxine (3j)

^{1}H NMR



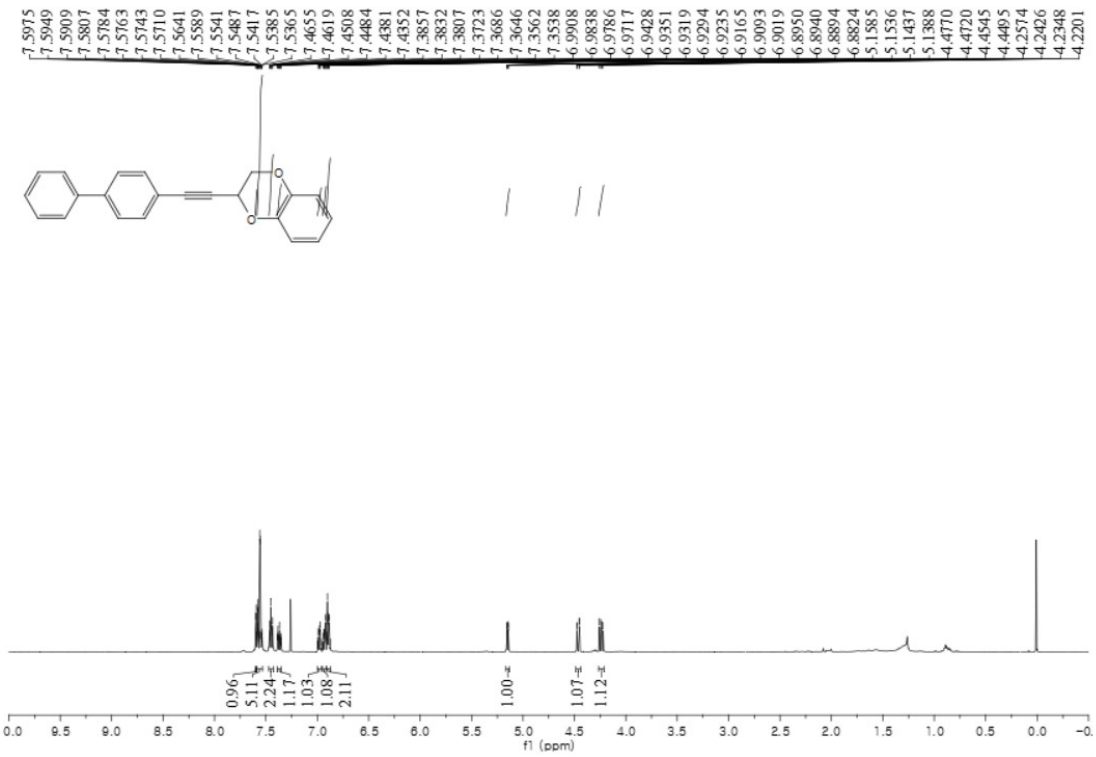


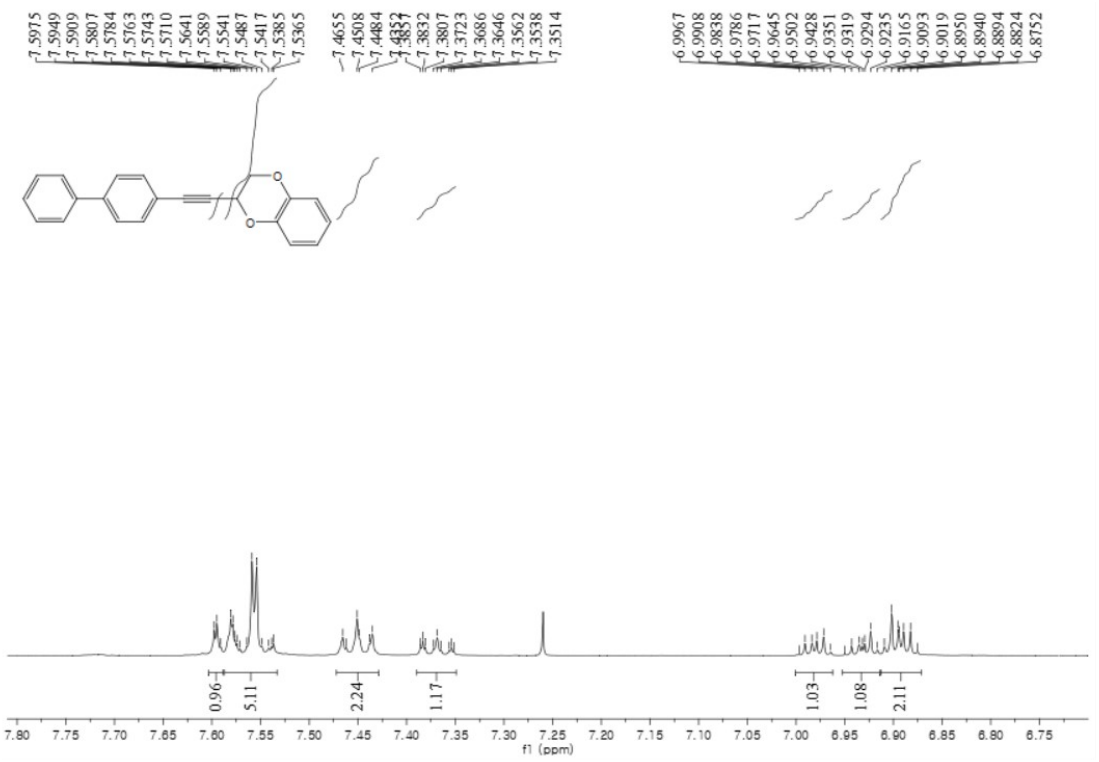
^{13}C NMR



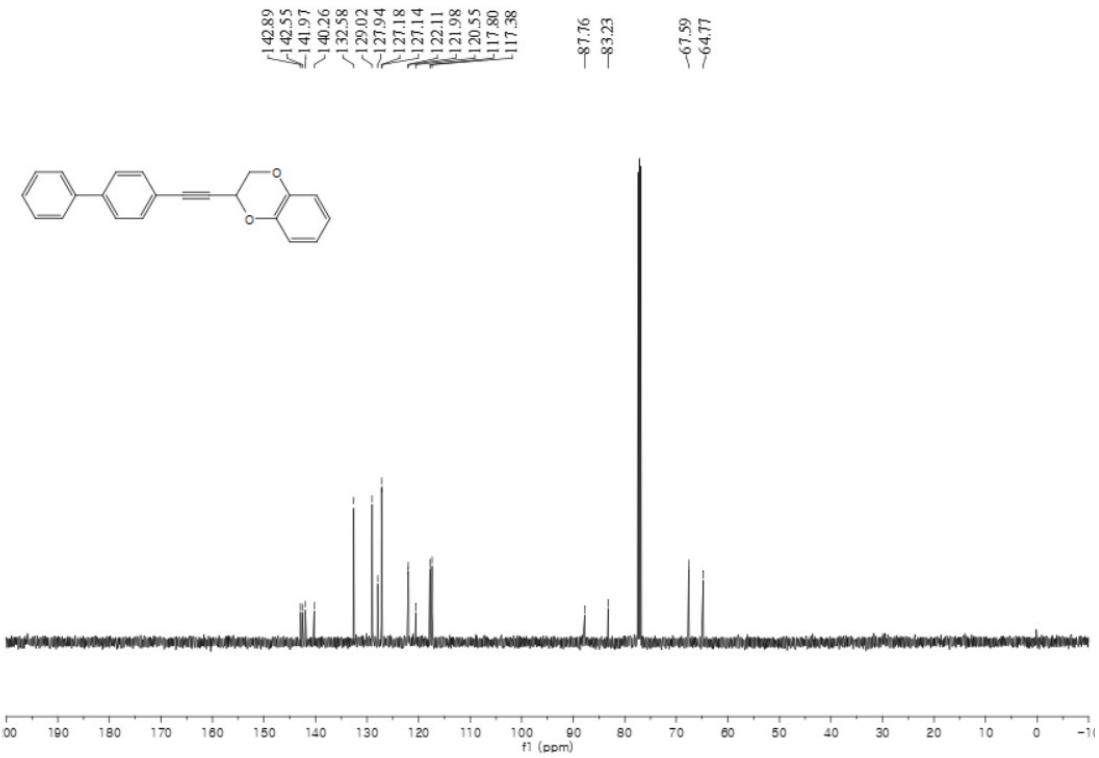
2-([1,1'-Biphenyl]-4-ylethynyl)-2,3-dihydrobenzo[b][1,4]dioxine (3k)

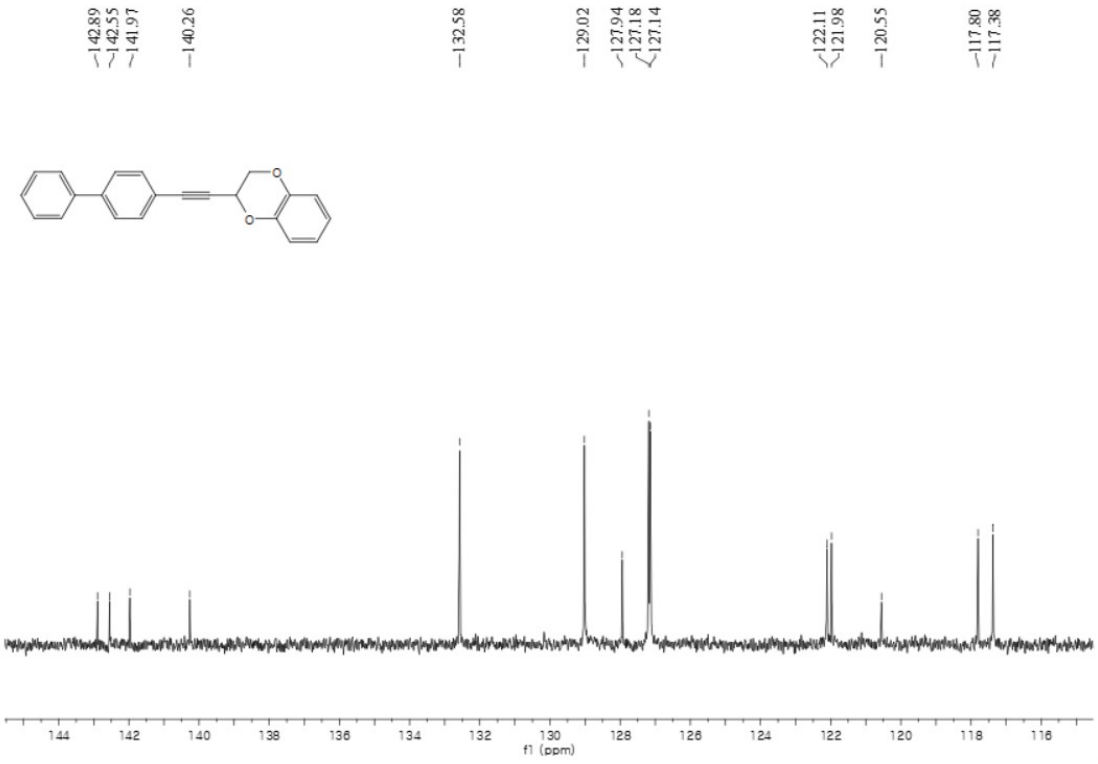
^{1}H NMR




7.5975
7.5949
7.5909
7.5807
7.5784
7.5763
7.5743
7.5710
7.5641
7.5589
7.5541
7.5487
7.5417
7.5385
7.5365
7.4655
7.4508
7.4484
7.3832
7.3807
7.3723
7.3686
7.3646
7.3562
7.3538
7.3514
6.9967
6.9908
6.9838
6.9786
6.9717
6.9645
6.9502
6.9428
6.9351
6.9319
6.9294
6.9235
6.9165
6.9093
6.9019
6.8950
6.8940
6.8894
6.8824
6.8752
0.96
5.11
2.24
1.17
1.03
1.08
2.11
f1 (ppm)

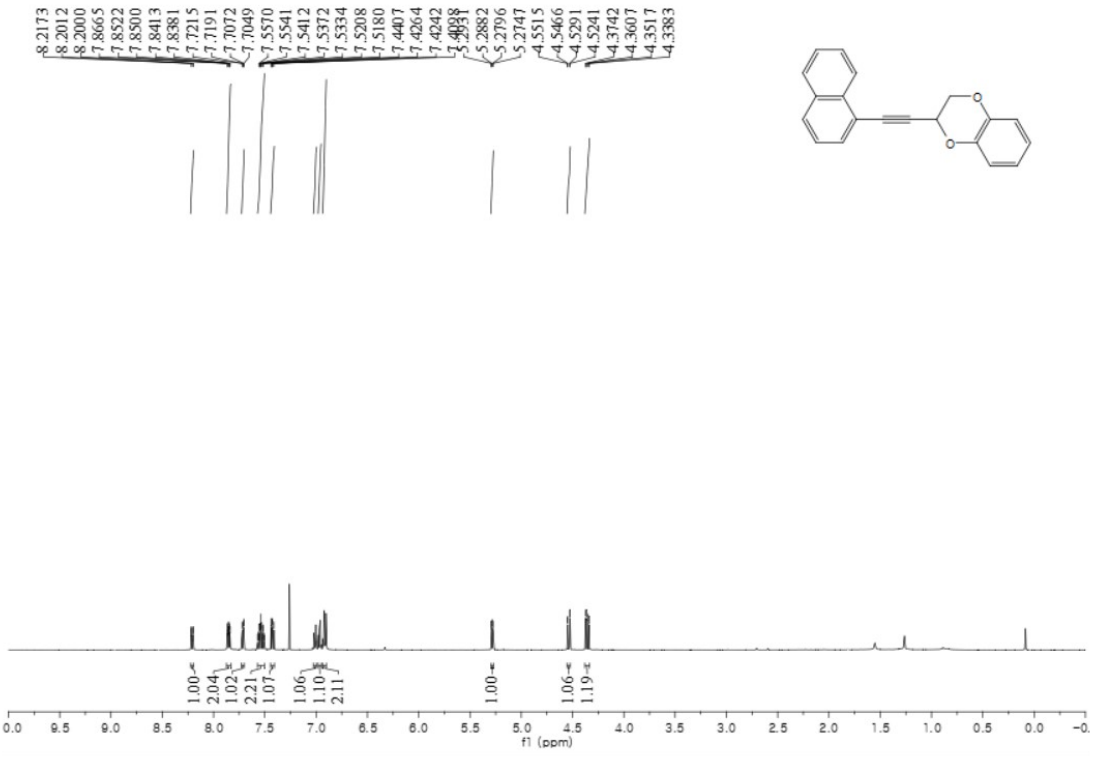
^{13}C NMR

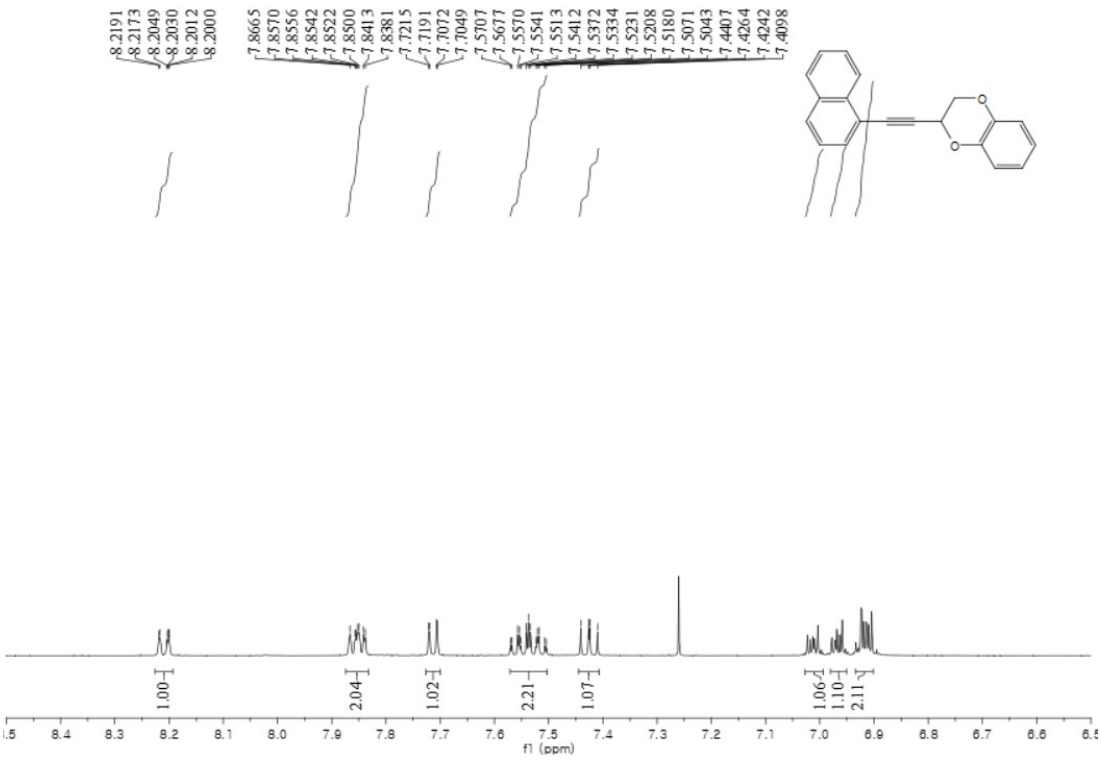

142.89
142.55
141.97
140.26
132.58
129.02
127.94
127.18
127.14
122.11
121.98
120.55
117.80
117.38
87.76
83.23
67.59
64.77
f1 (ppm)



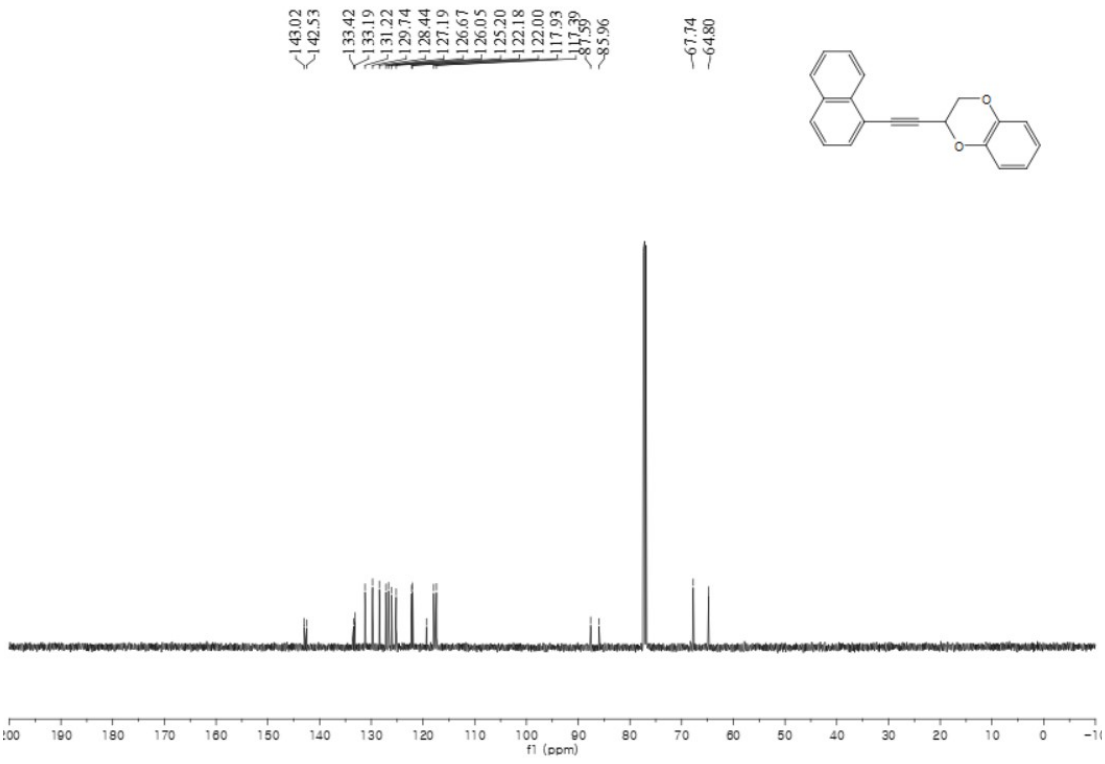
2-(Naphthalen-1-ylethynyl)-2,3-dihydrobenzo[b][1,4]dioxine (3l)

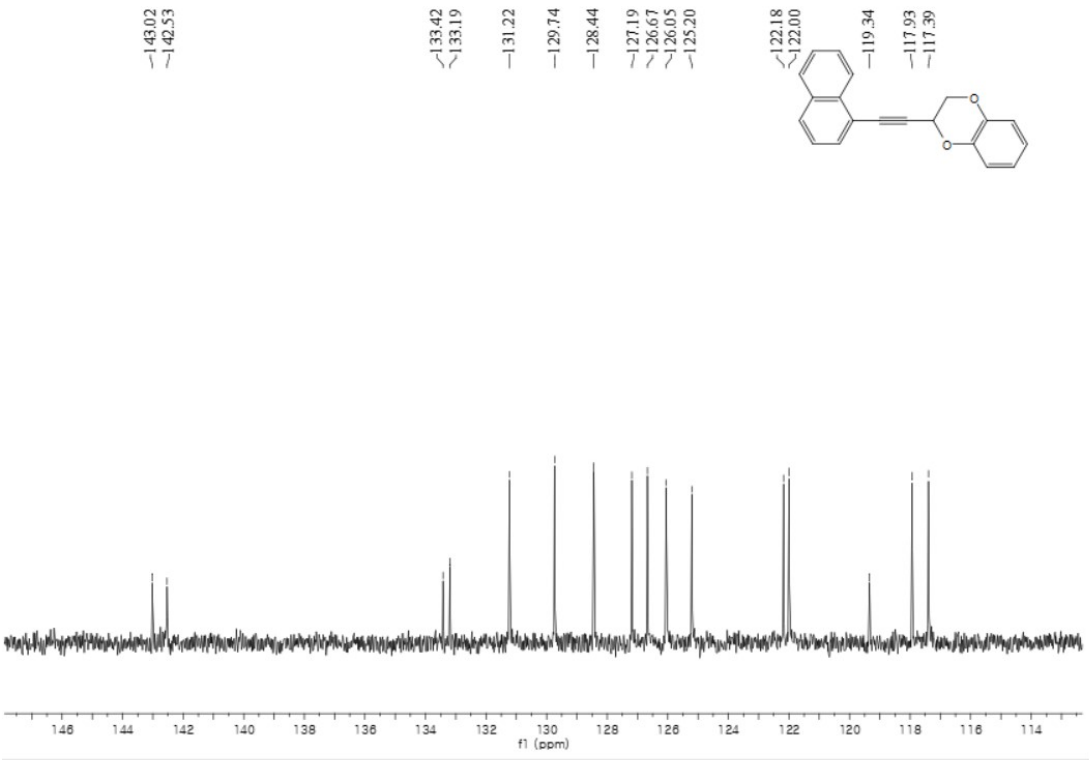
^{1}H NMR




8.2191
8.2173
8.2049
8.2030
8.2012
8.2000
7.8665
7.8570
7.8556
7.8542
7.8522
7.8500
7.8413
7.8381
7.7215
7.7191
7.7072
7.7049
7.5707
7.5677
7.5570
7.5541
7.5513
7.5412
7.5372
7.5334
7.5231
7.5208
7.5180
7.5071
7.5043
7.4407
7.4264
7.4242
7.4098
1.00
2.04
1.02
2.21
1.07
1.06
1.10
2.11
f1 (ppm)

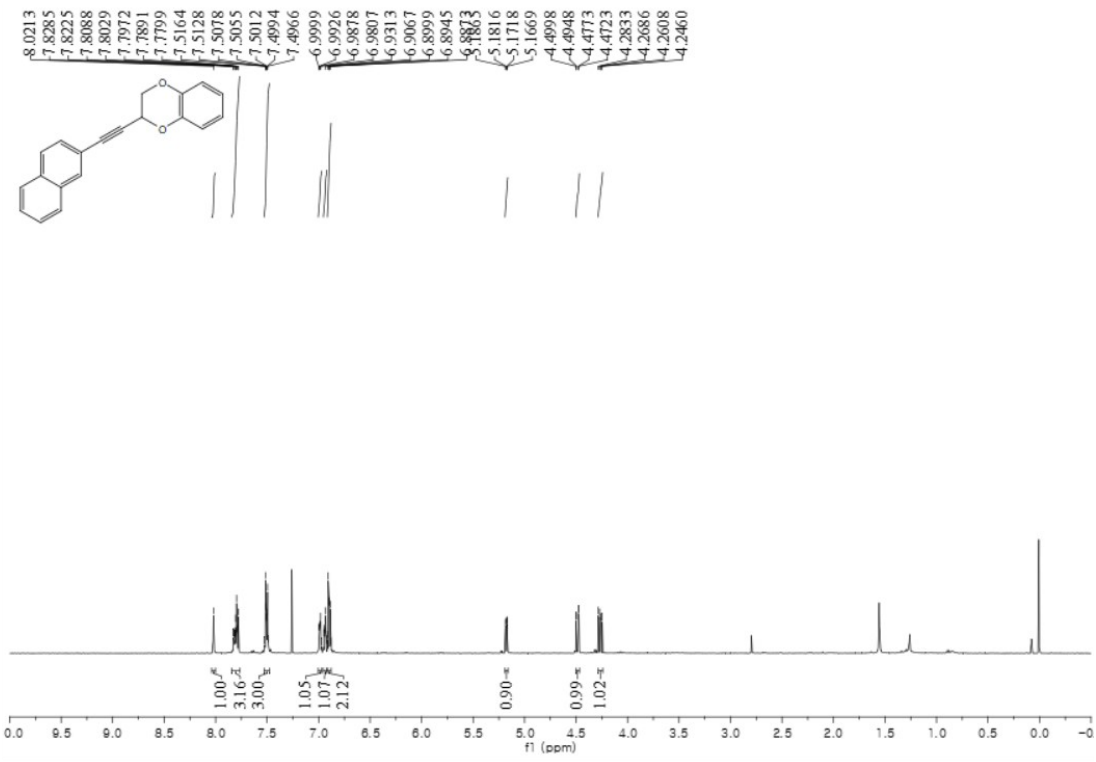
^{13}C NMR

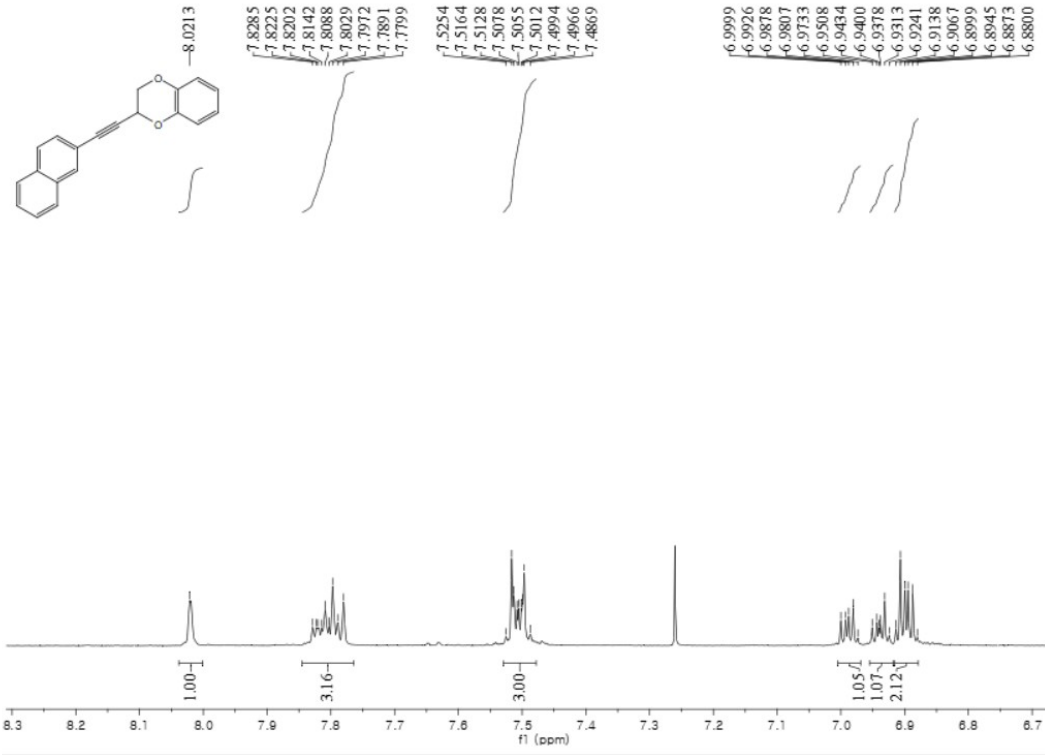

143.02
142.53
133.42
133.19
131.22
129.74
128.44
127.19
126.67
126.05
125.20
122.18
122.00
117.93
87.59
85.96
67.74
64.80
f1 (ppm)



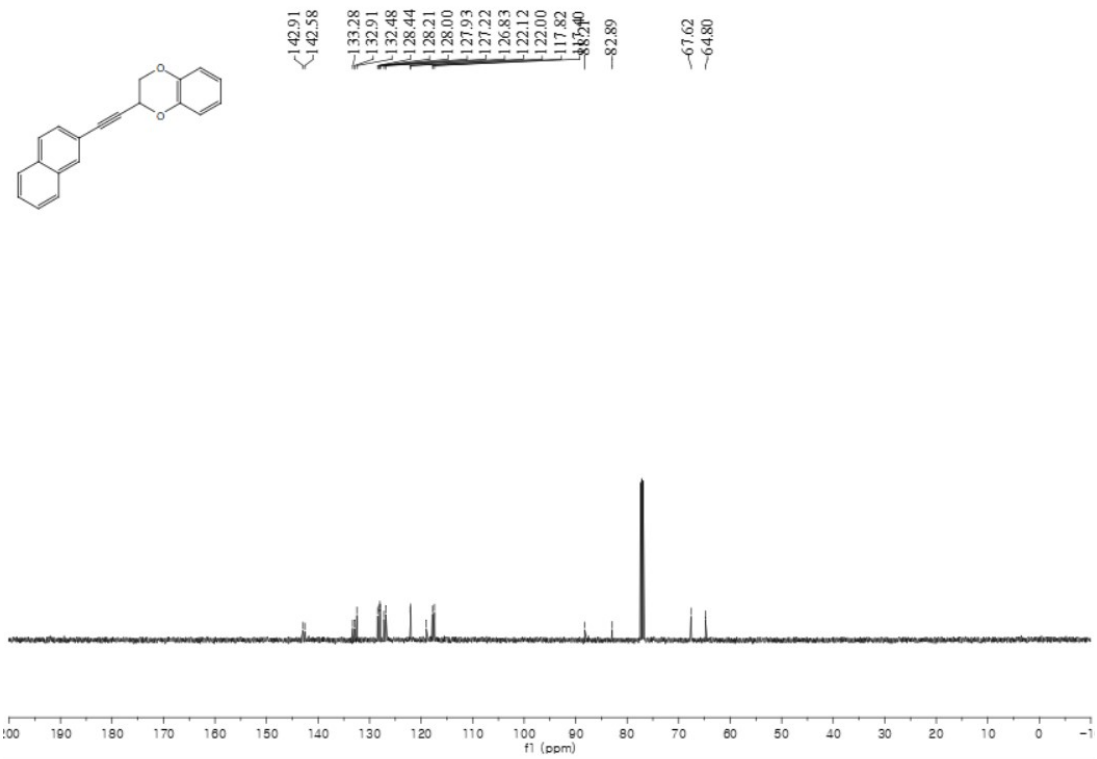
2-(Naphthalen-2-ylethynyl)-2,3-dihydrobenzo[b][1,4]dioxine (3m)

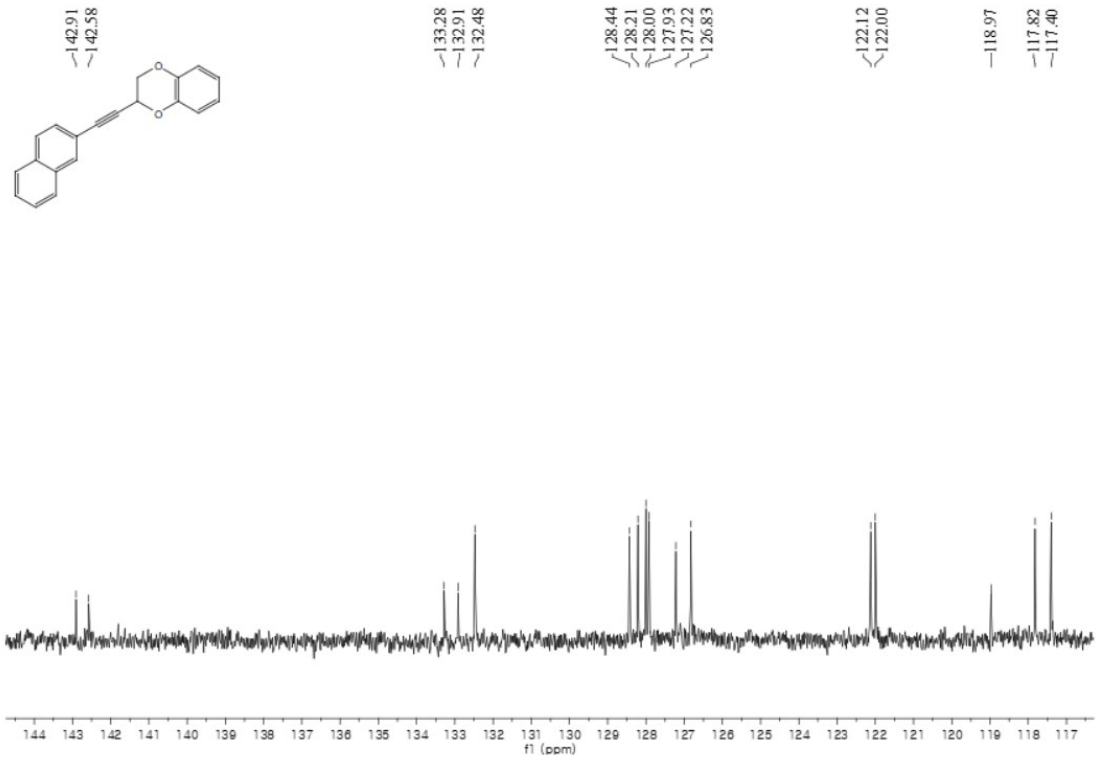
^{1}H NMR




8.0213
7.8285
7.8225
7.8202
7.8142
7.8088
7.8029
7.7972
7.7891
7.7799
7.5254
7.5164
7.5128
7.5078
7.5055
7.5012
7.4994
7.4966
7.4869
6.9999
6.9926
6.9878
6.9807
6.9733
6.9508
6.9434
6.9400
6.9378
6.9313
6.9241
6.9138
6.9067
6.8999
6.8945
6.8873
6.8800
1.00
3.16
3.00
1.05
1.07
2.12
f1 (ppm)

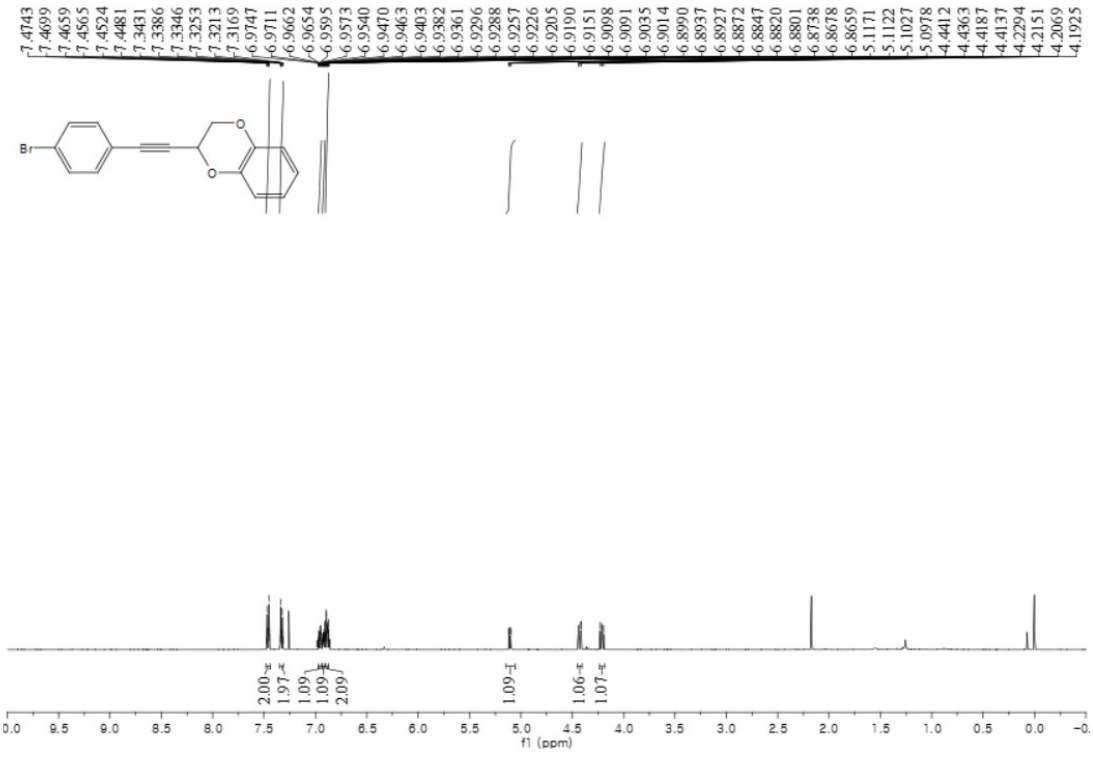
^{13}C NMR

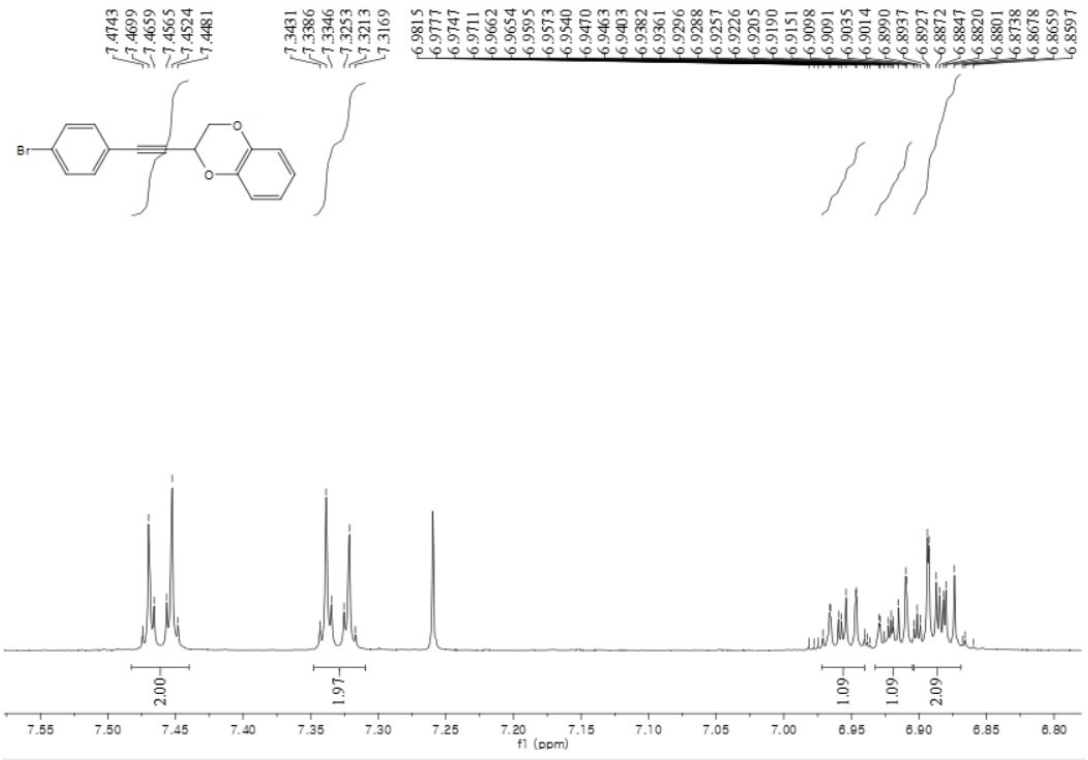

142.91
142.58
133.28
132.91
132.48
128.44
128.21
128.00
127.93
127.22
126.83
122.12
122.00
117.82
82.89
67.62
64.80
f1 (ppm)



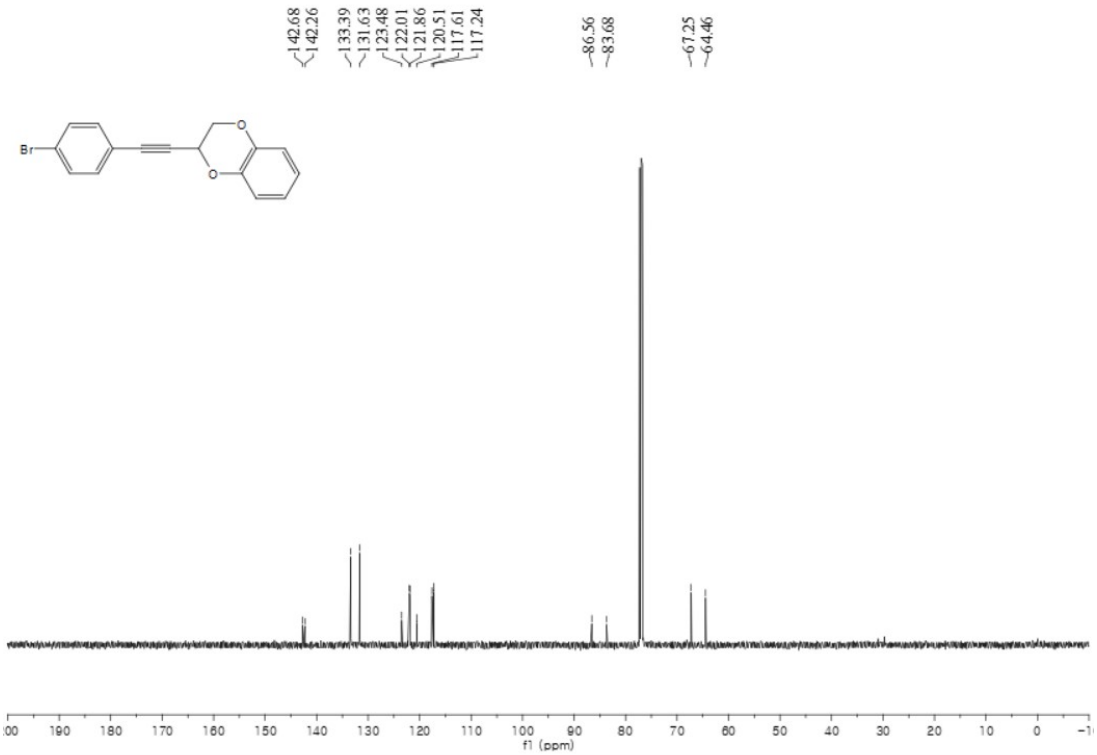
2-((4-Bromophenyl)ethynyl)-2,3-dihydrobenzo[b][1,4]dioxine (3n)

^{1}H NMR



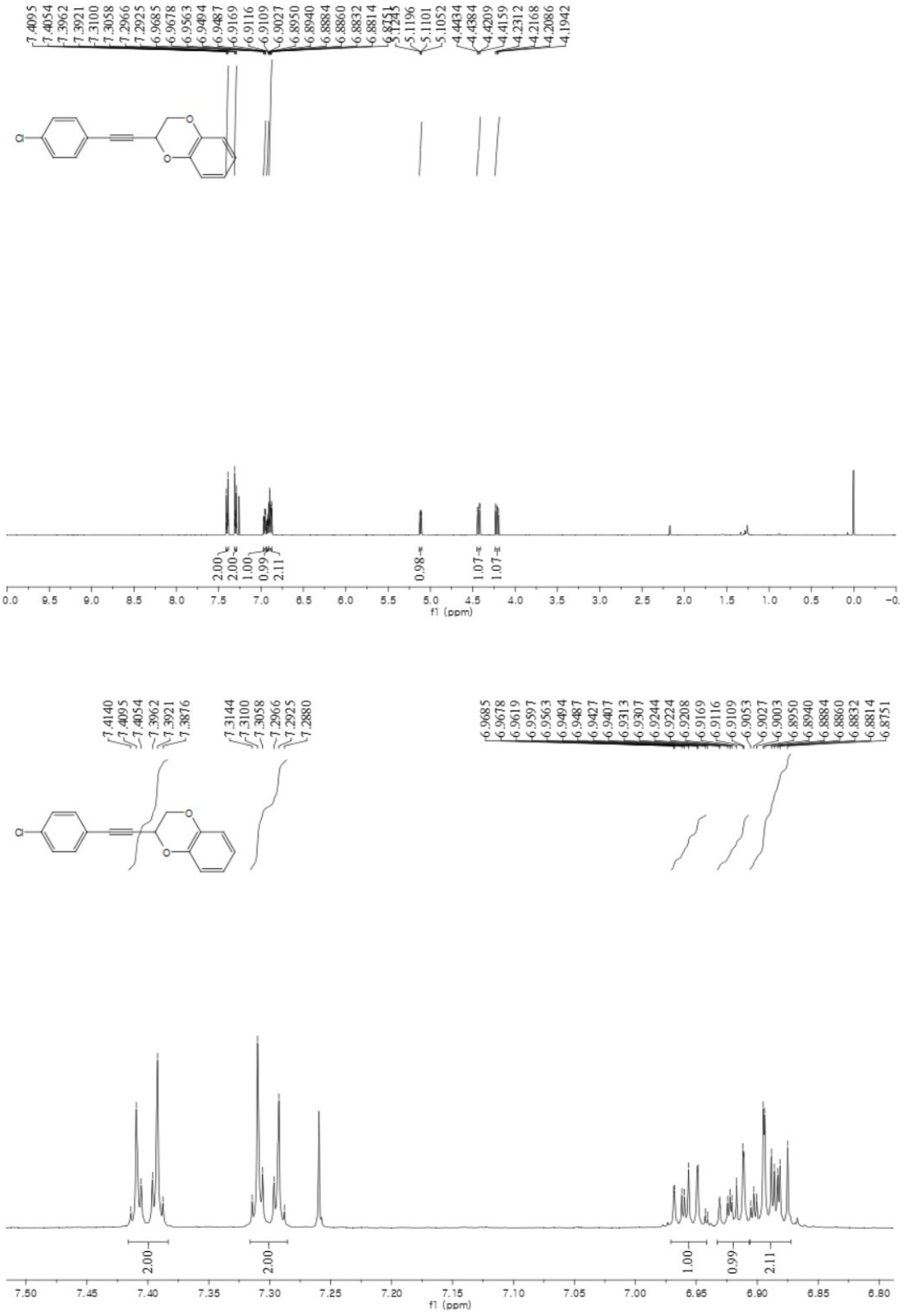

7.4743
7.4699
7.4659
7.4565
7.4524
7.4481
7.3431
7.3386
7.3346
7.3253
7.3213
7.3169
6.9815
6.9777
6.9747
6.9711
6.9662
6.9654
6.9595
6.9573
6.9540
6.9470
6.9463
6.9403
6.9382
6.9361
6.9296
6.9288
6.9257
6.9226
6.9205
6.9190
6.9151
6.9098
6.9091
6.9035
6.9014
6.8990
6.8937
6.8927
6.8872
6.8847
6.8820
6.8801
6.8738
6.8678
6.8659
6.8597
Br
O
O
2.00
1.97
1.09
1.09
2.09
7.55
7.50
7.45
7.40
7.35
7.30
7.25
7.20
7.15
7.10
7.05
7.00
6.95
6.90
6.85
6.80
f1 (ppm)

^{13}C NMR

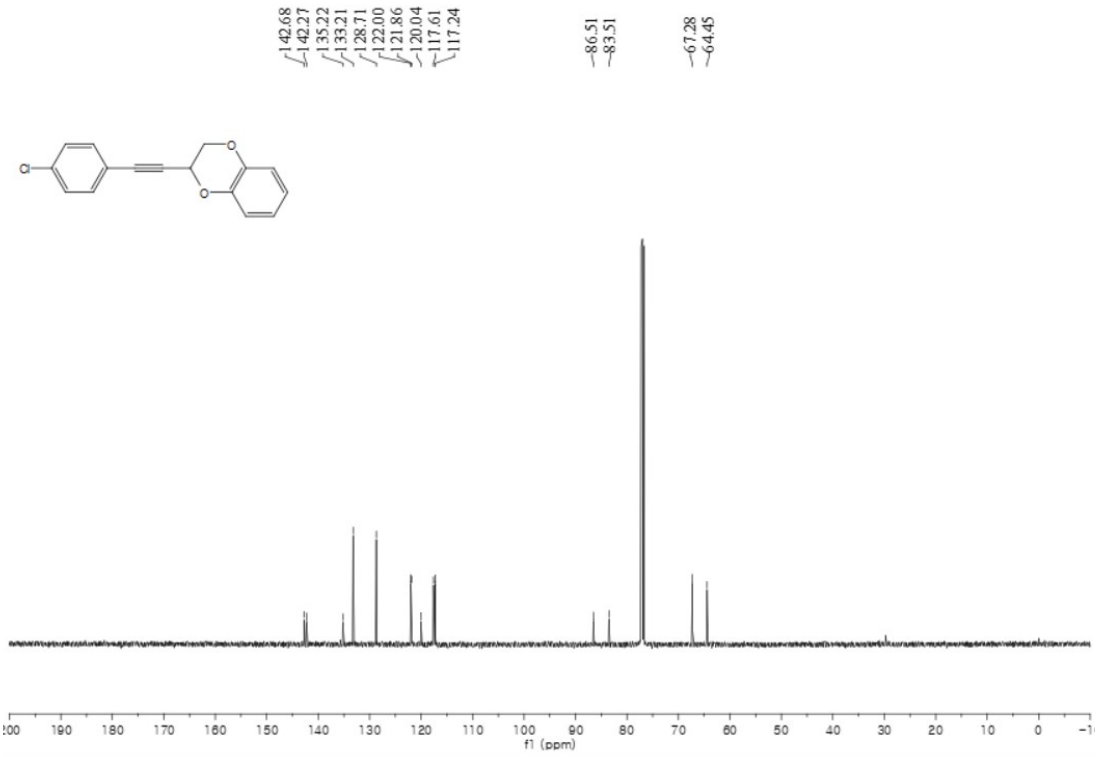

142.68
142.26
133.39
131.63
123.48
122.01
121.86
120.51
117.61
117.24
86.56
83.68
67.25
64.46
Br
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2-((4-Chlorophenyl)ethynyl)-2,3-dihydrobenzo[b][1,4]dioxine (3o)

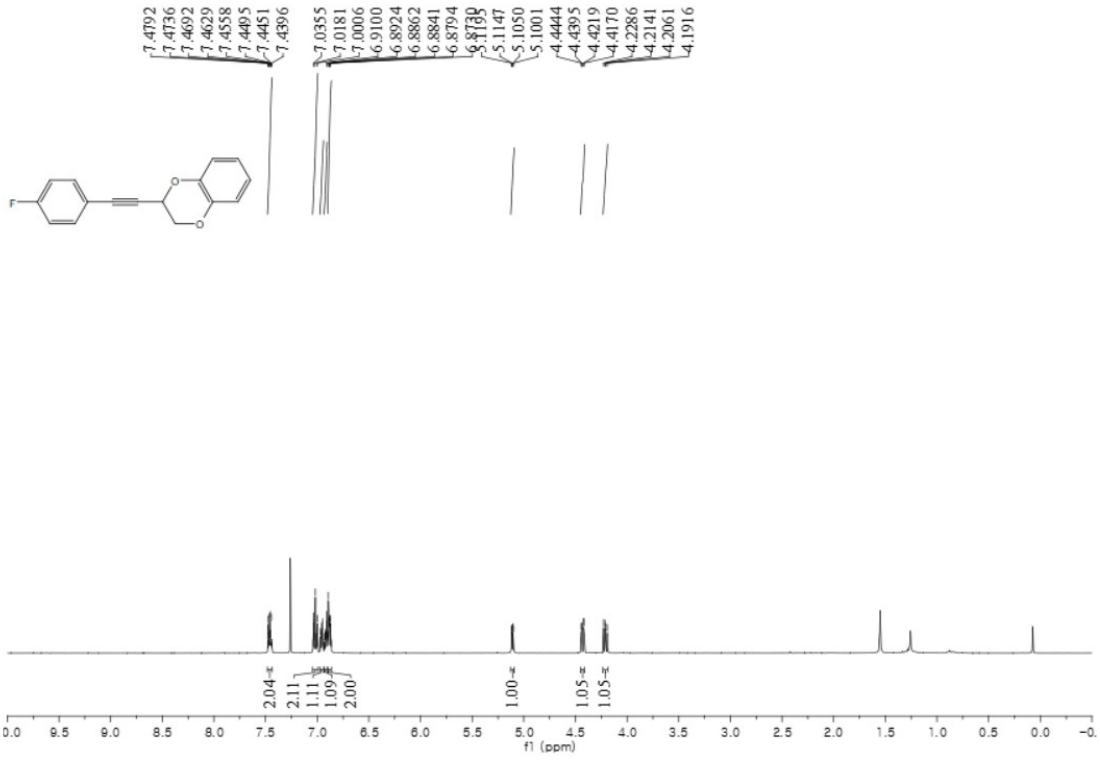
^{1}H NMR

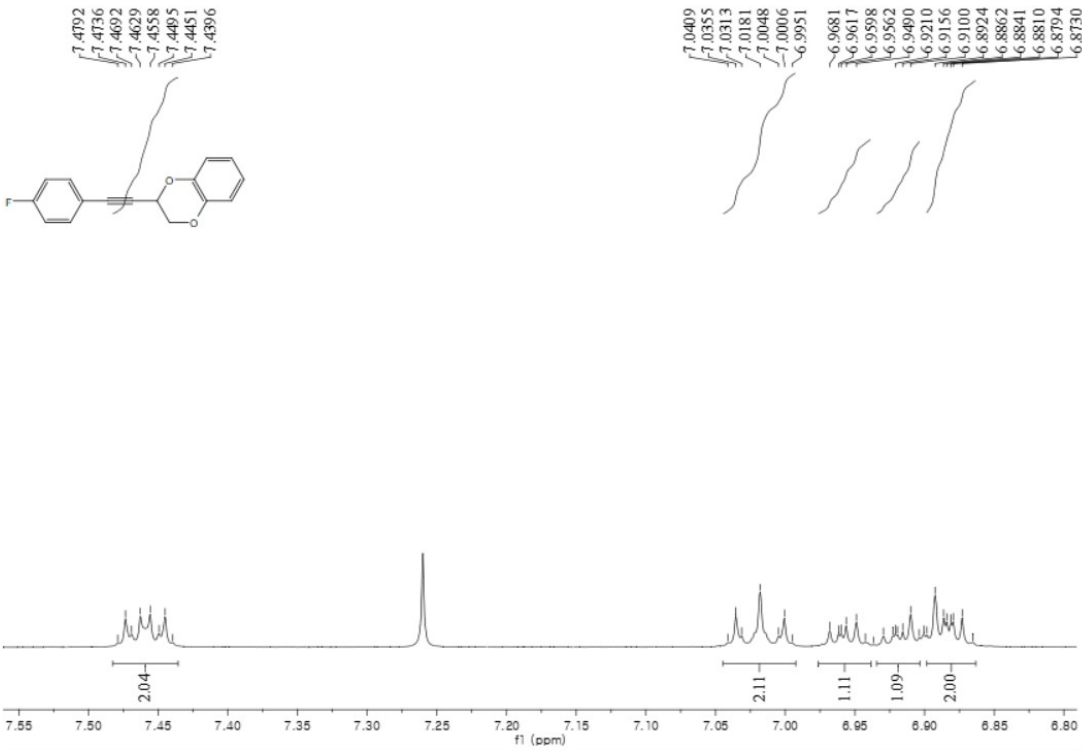


^{13}C NMR

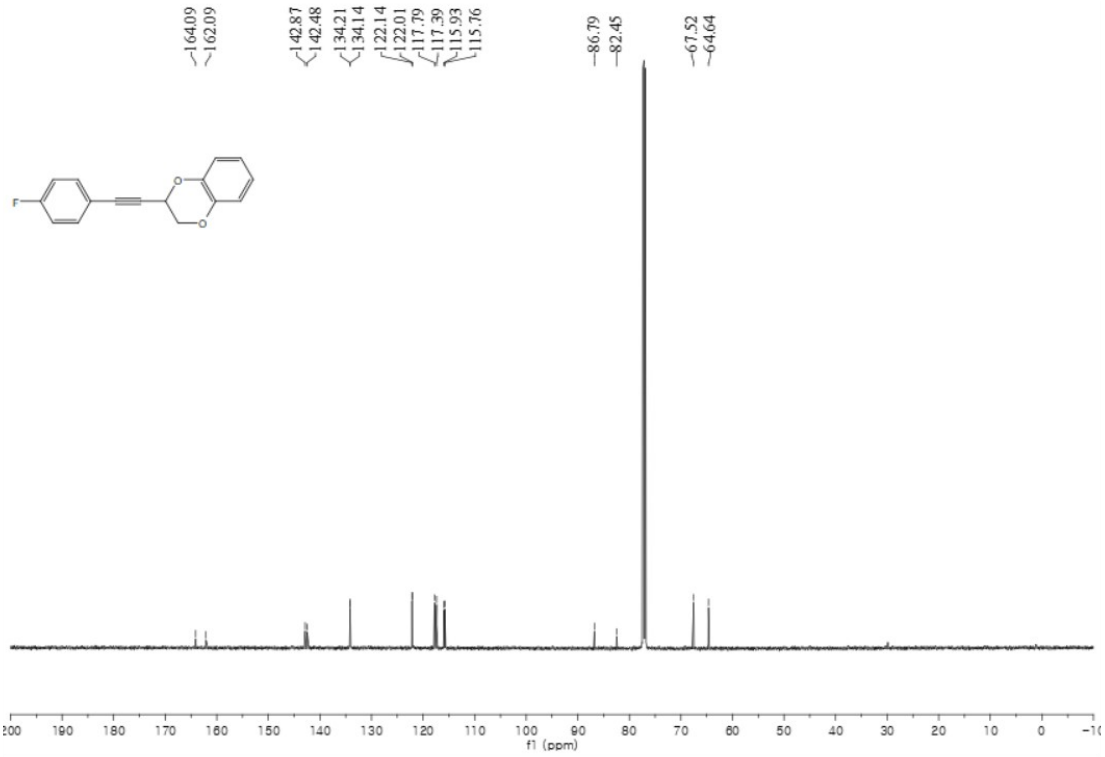


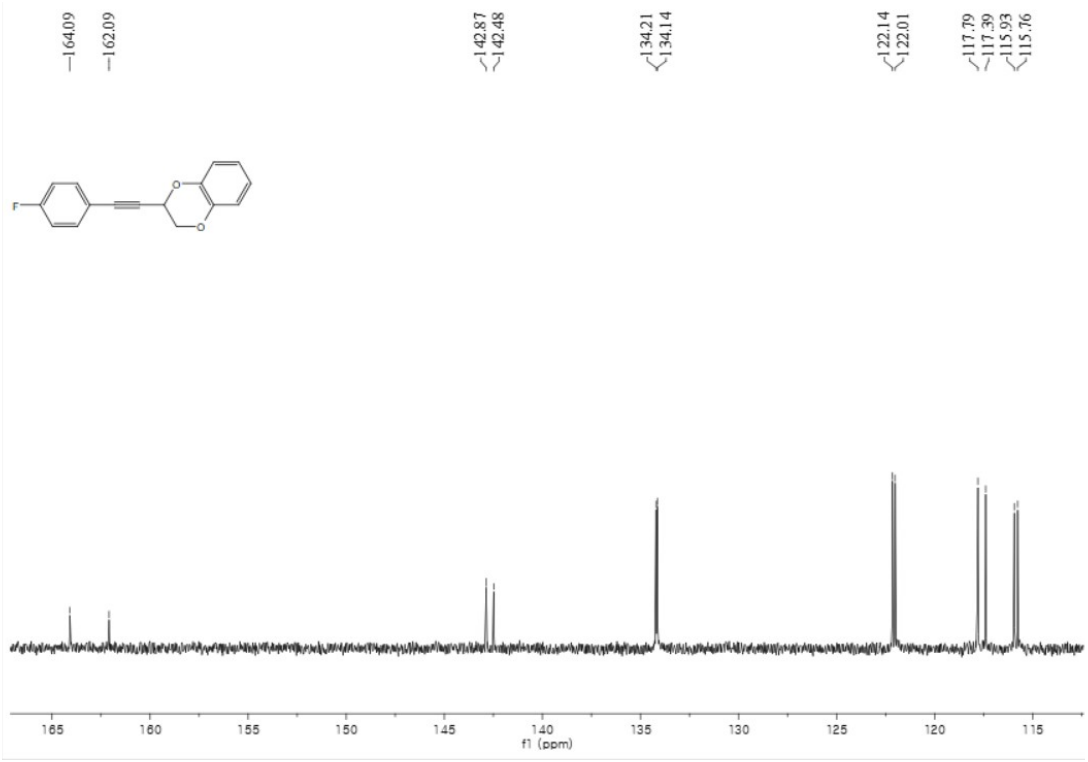
2-((4-Fluorophenyl)ethynyl)-2,3-dihydrobenzo[b][1,4]dioxine (3p)




7.4792
7.4736
7.4692
7.4629
7.4558
7.4495
7.4451
7.4396
7.0409
7.0355
7.0313
7.0181
7.0048
7.0006
6.9951
6.9681
6.9617
6.9598
6.9562
6.9490
6.9210
6.9156
6.9100
6.8924
6.8862
6.8841
6.8810
6.8794
6.8730
F
O
O
2.04
2.11
1.11
1.09
2.00
7.55
7.50
7.45
7.40
7.35
7.30
7.25
7.20
7.15
7.10
7.05
7.00
6.95
6.90
6.85
6.80
f1 (ppm)

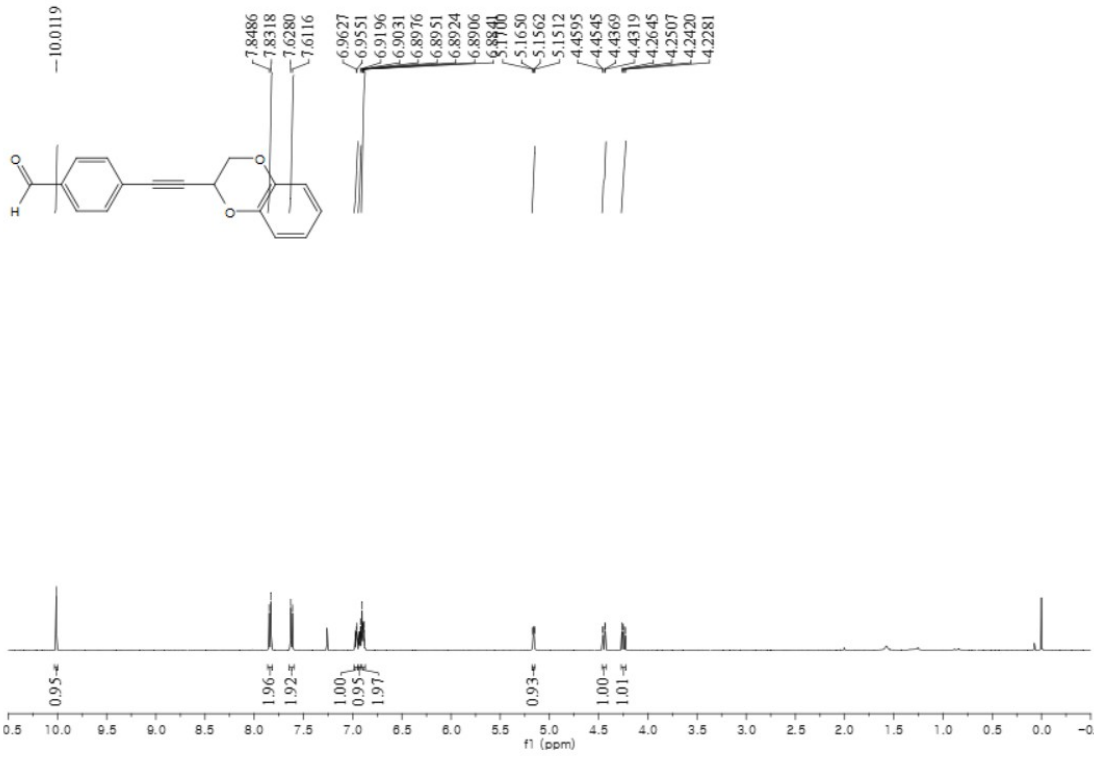
^{13}C NMR

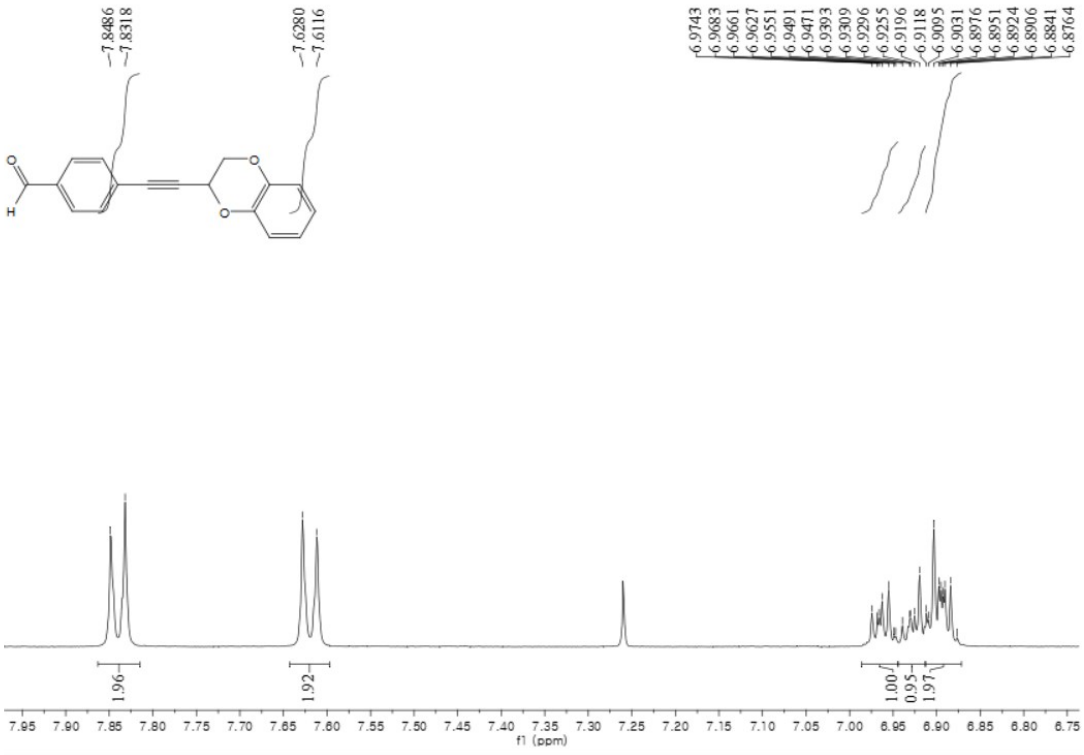

164.09
162.09
142.87
142.48
134.21
134.14
122.14
122.01
117.79
117.39
115.93
115.76
86.79
82.45
67.52
64.64
F
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



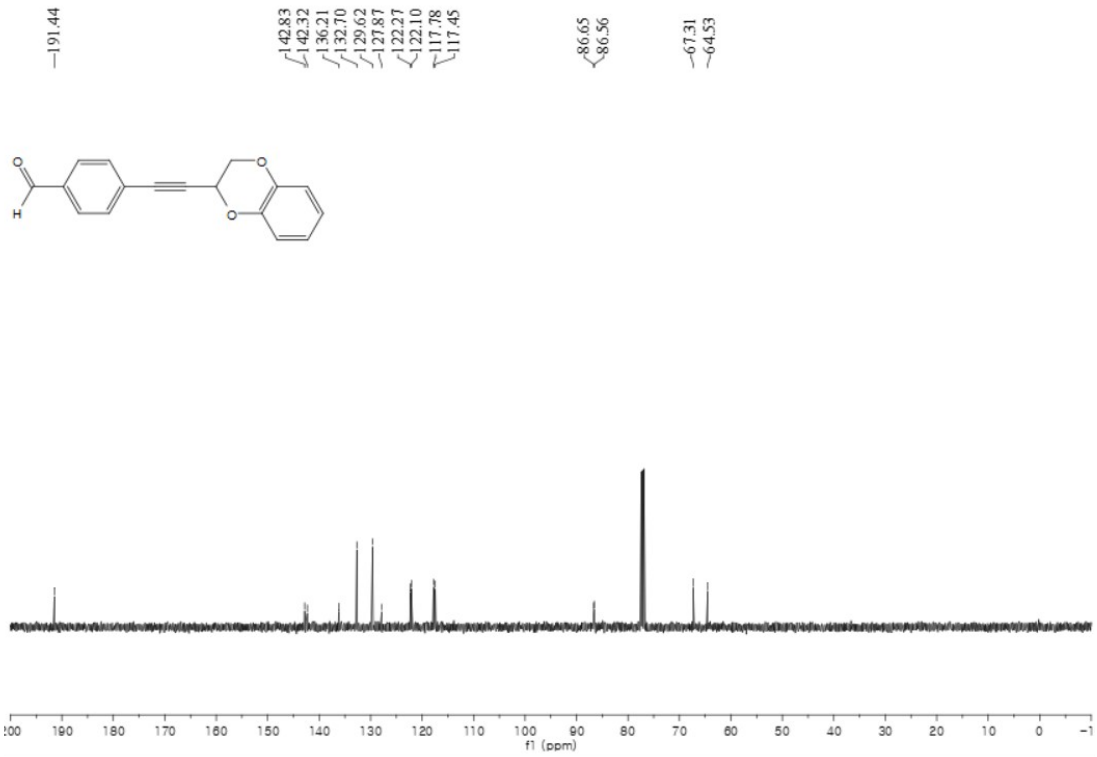
4-((2,3-Dihydrobenzo[b][1,4]dioxin-2-yl)ethynyl)benzaldehyde (3q)

^{1}H NMR



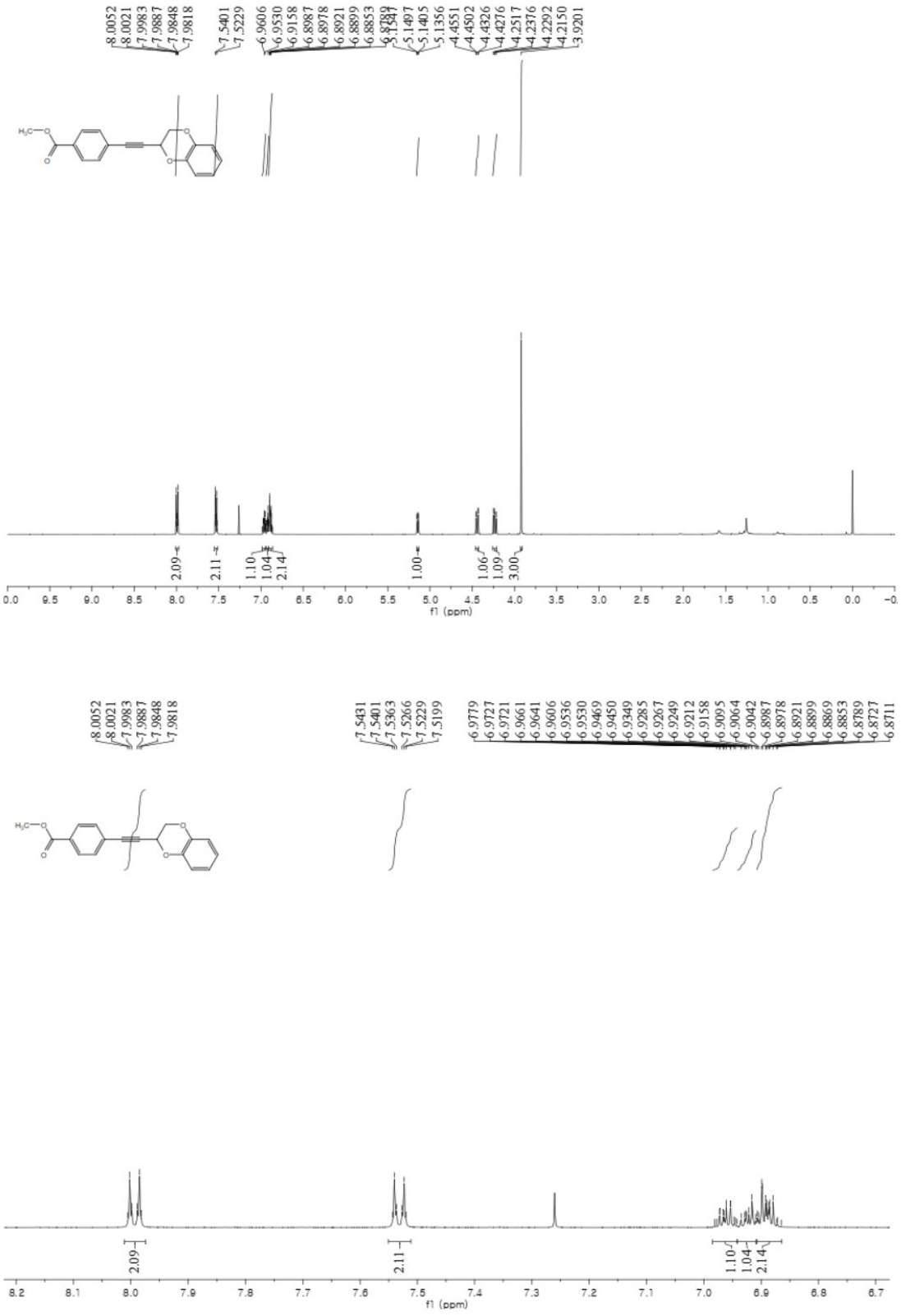

7.8486
7.8318
7.6280
7.6116
6.9743
6.9683
6.9661
6.9627
6.9551
6.9491
6.9471
6.9393
6.9309
6.9296
6.9255
6.9196
6.9118
6.9095
6.9031
6.8976
6.8951
6.8924
6.8906
6.8841
6.8764
1.96
1.92
1.00
0.95
1.97
f1 (ppm)

^{13}C NMR

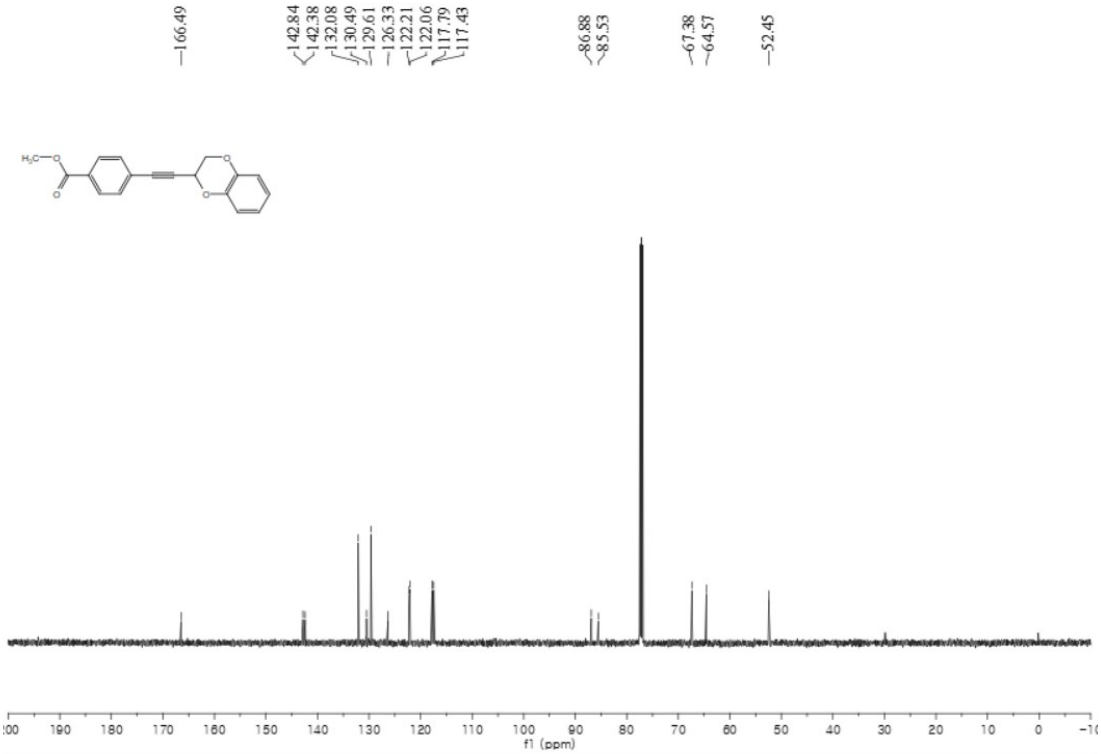

191.44
142.83
142.32
136.21
132.70
129.62
127.87
122.27
122.10
117.78
117.45
86.65
86.56
67.31
64.53
f1 (ppm)

Methyl 4-((2,3-dihydrobenzo[b][1,4]dioxin-2-yl)ethynyl)benzoate (3r)

^{1}H NMR

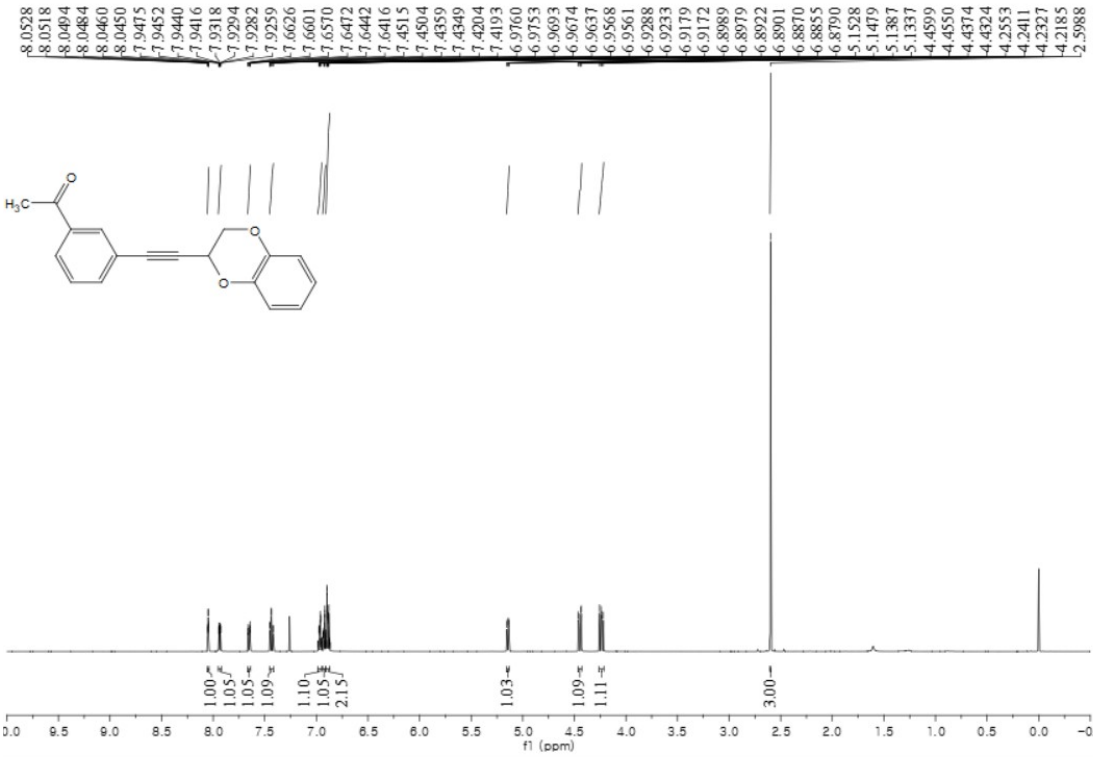


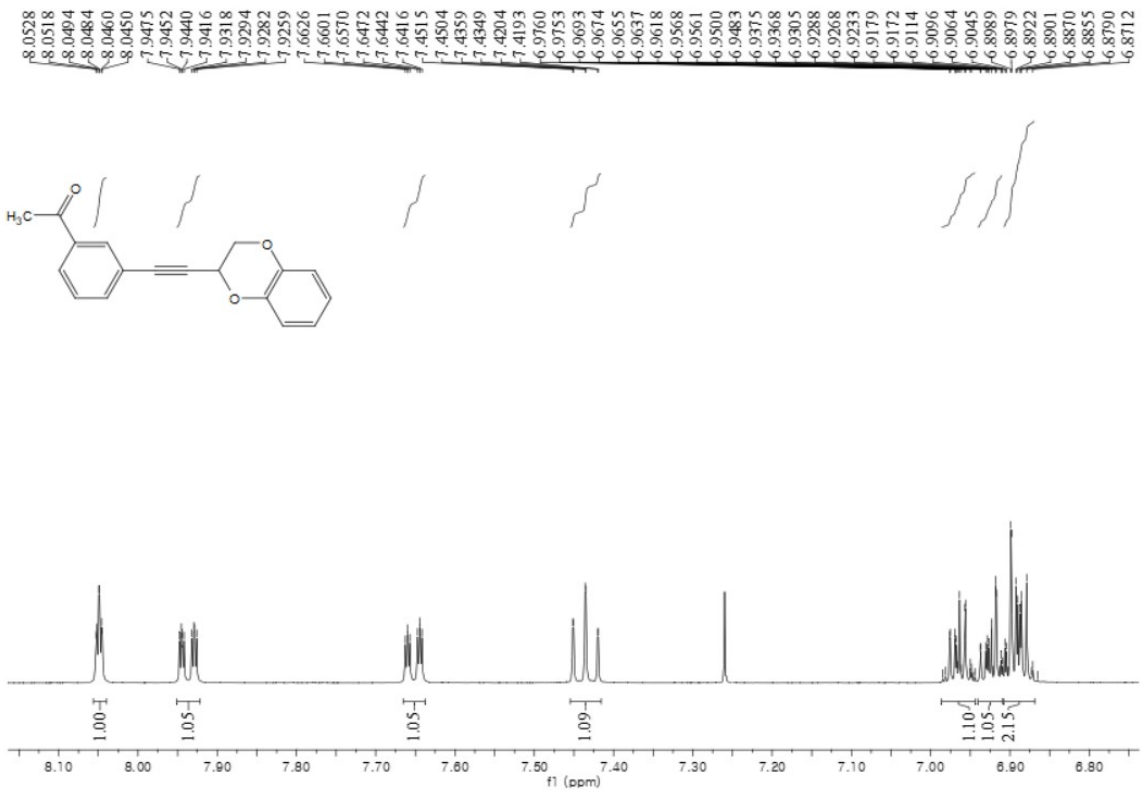
^{13}C NMR



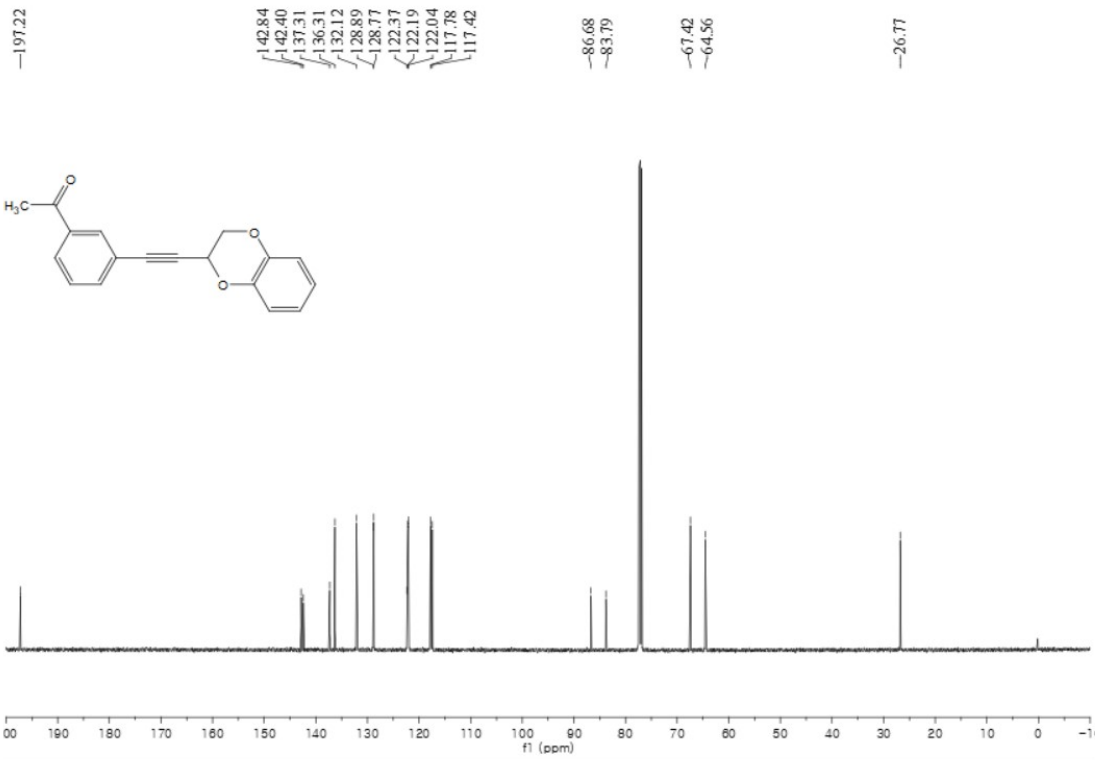
1-(3-((2,3-Dihydrobenzo[b][1,4]dioxin-2-yl)ethynyl)phenyl)ethenone (3s)

^{1}H NMR



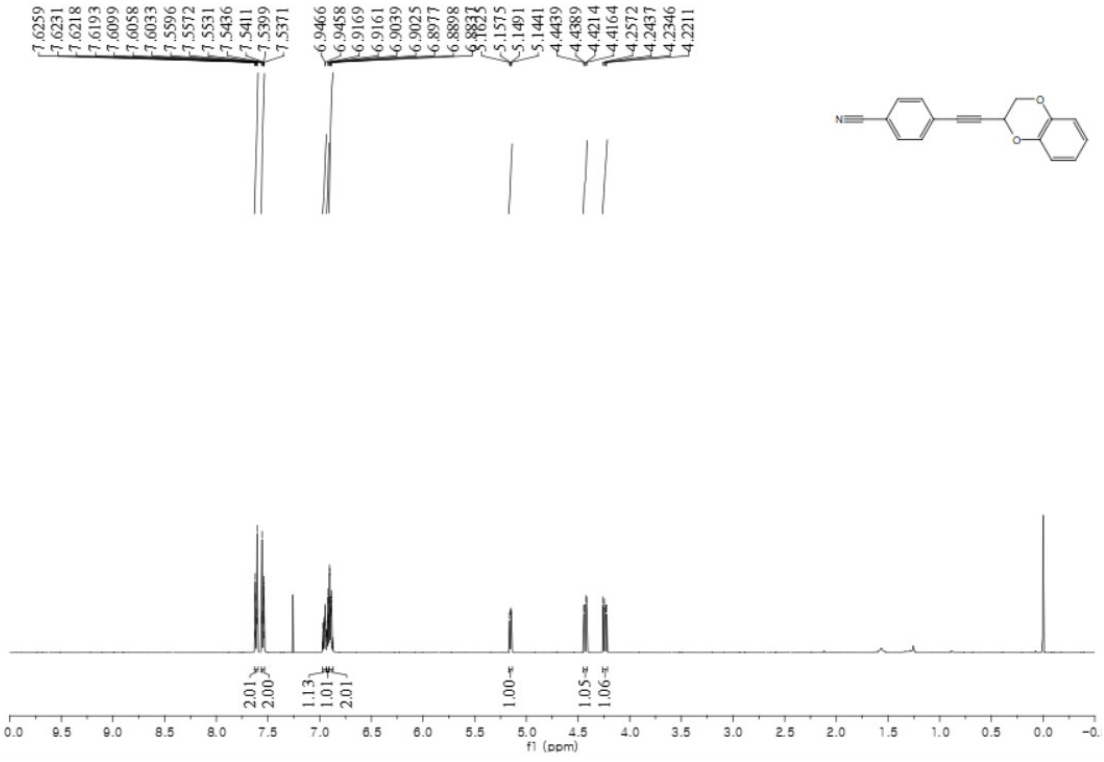

8.0528
8.0518
8.0494
8.0484
8.0460
8.0450
7.9475
7.9452
7.9440
7.9416
7.9318
7.9294
7.9282
7.9259
7.6626
7.6601
7.6570
7.6472
7.6442
7.6416
7.4515
7.4504
7.4359
7.4349
7.4204
7.4193
6.9760
6.9753
6.9693
6.9674
6.9655
6.9637
6.9618
6.9568
6.9561
6.9500
6.9483
6.9375
6.9368
6.9305
6.9288
6.9268
6.9233
6.9179
6.9172
6.9114
6.9096
6.9064
6.9045
6.8989
6.8979
6.8922
6.8901
6.8870
6.8855
6.8790
6.8712
H3C
O
O
O
1.00
1.05
1.05
1.09
1.10
1.05
2.15
8.10
8.00
7.90
7.80
7.70
7.60
7.50
7.40
7.30
7.20
7.10
7.00
6.90
6.80
f1 (ppm)

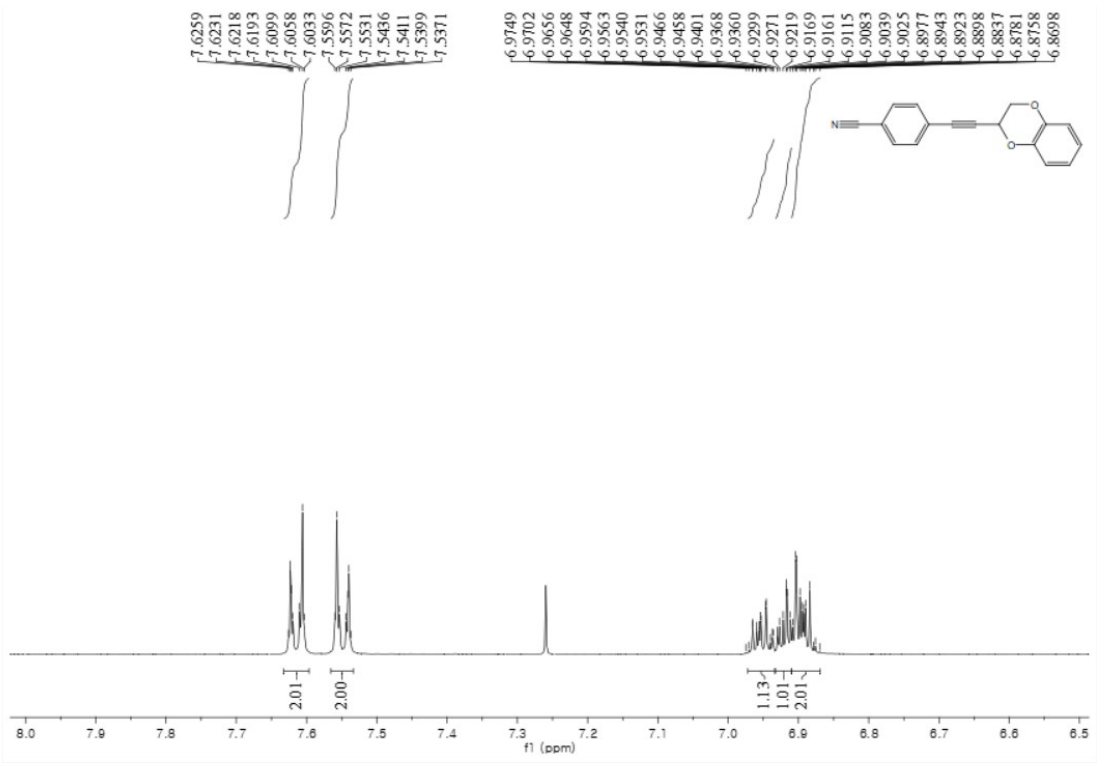
^{13}C NMR


197.22
142.84
142.40
137.31
136.31
132.12
128.89
128.77
122.37
122.19
122.04
117.78
117.42
86.68
83.79
67.42
64.56
26.77
H3C
O
O
O
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

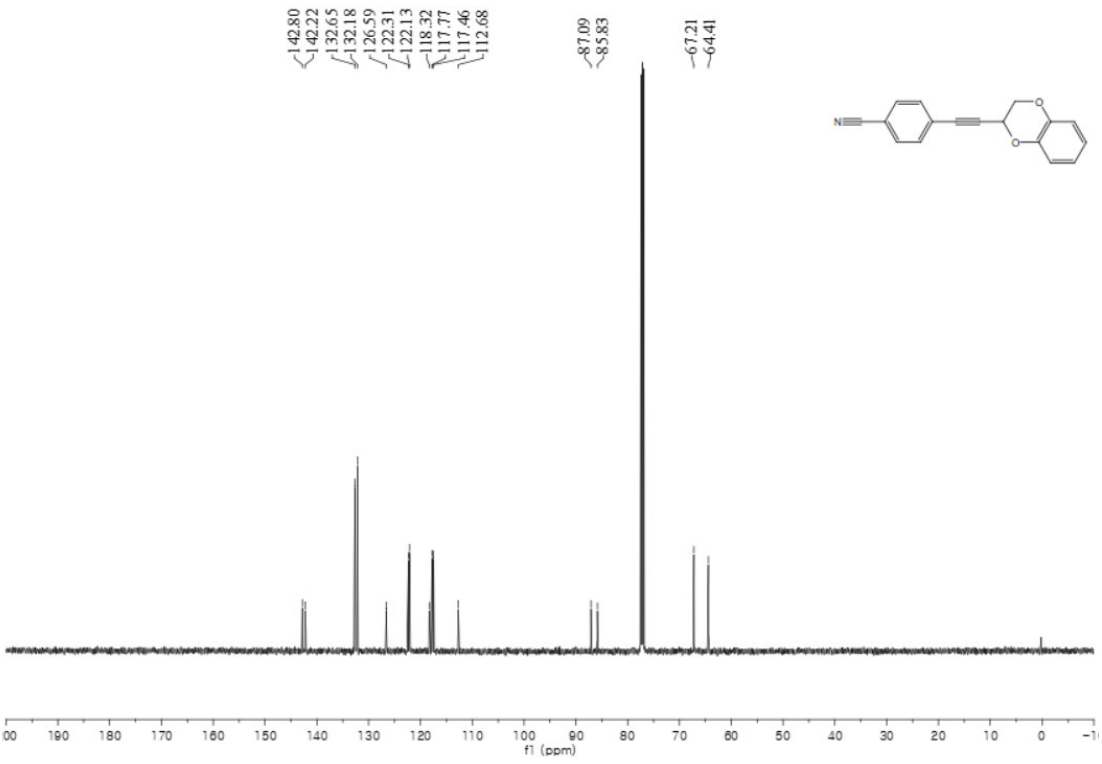
4-((2,3-Dihydrobenzo[b][1,4]dioxin-2-yl)ethynyl)benzonitrile (3t)

^{1}H NMR



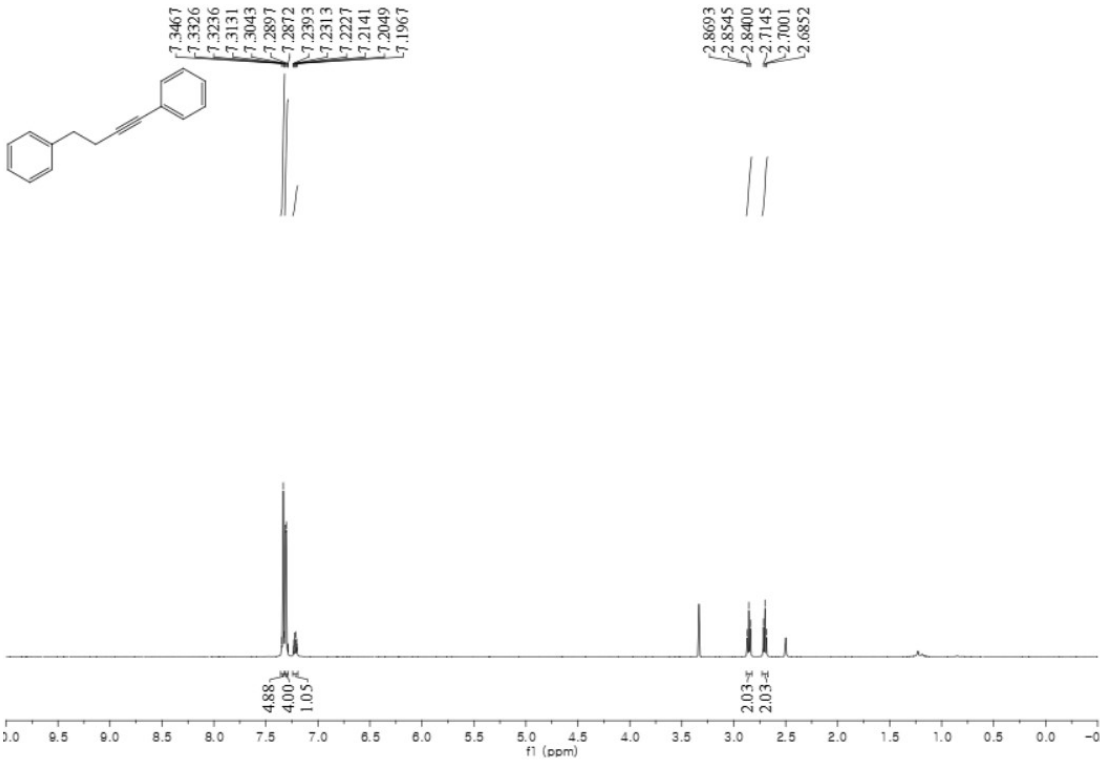


^{13}C NMR

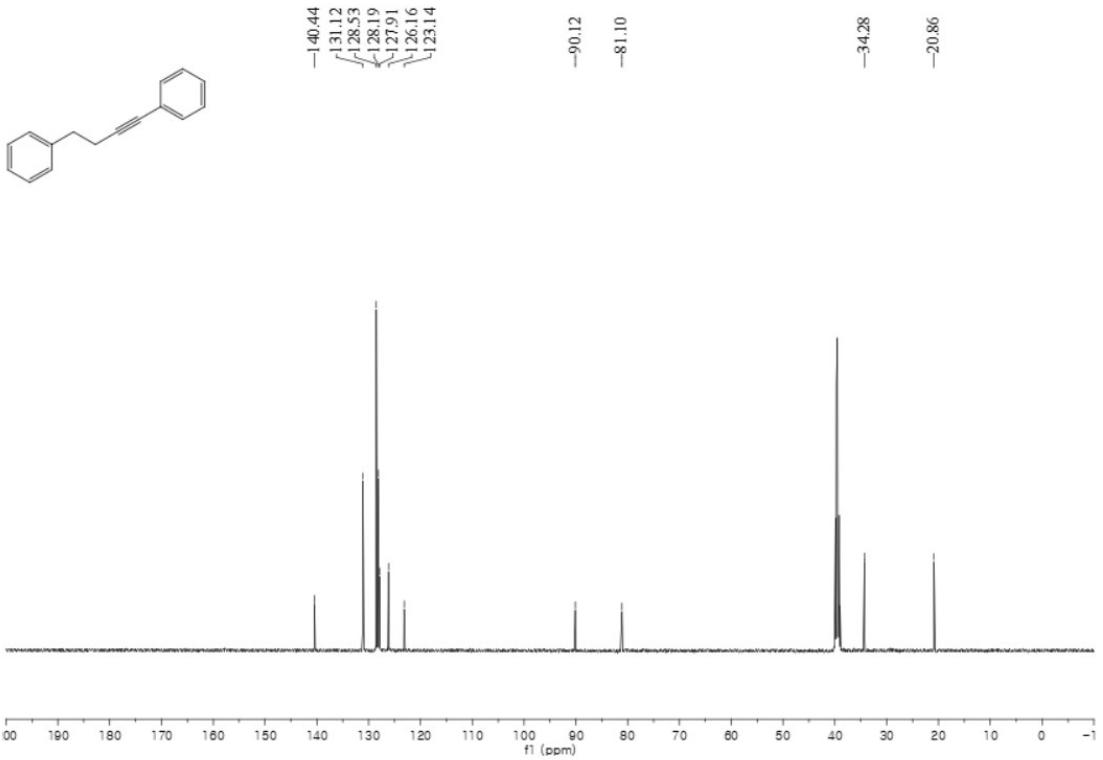

142.80
142.22
132.65
132.18
126.59
122.31
122.13
118.32
117.77
117.46
112.68
87.09
85.83
67.21
64.41
f1 (ppm)

But-1-yne-1,4-diyldibenzene (4a)

^{1}H NMR

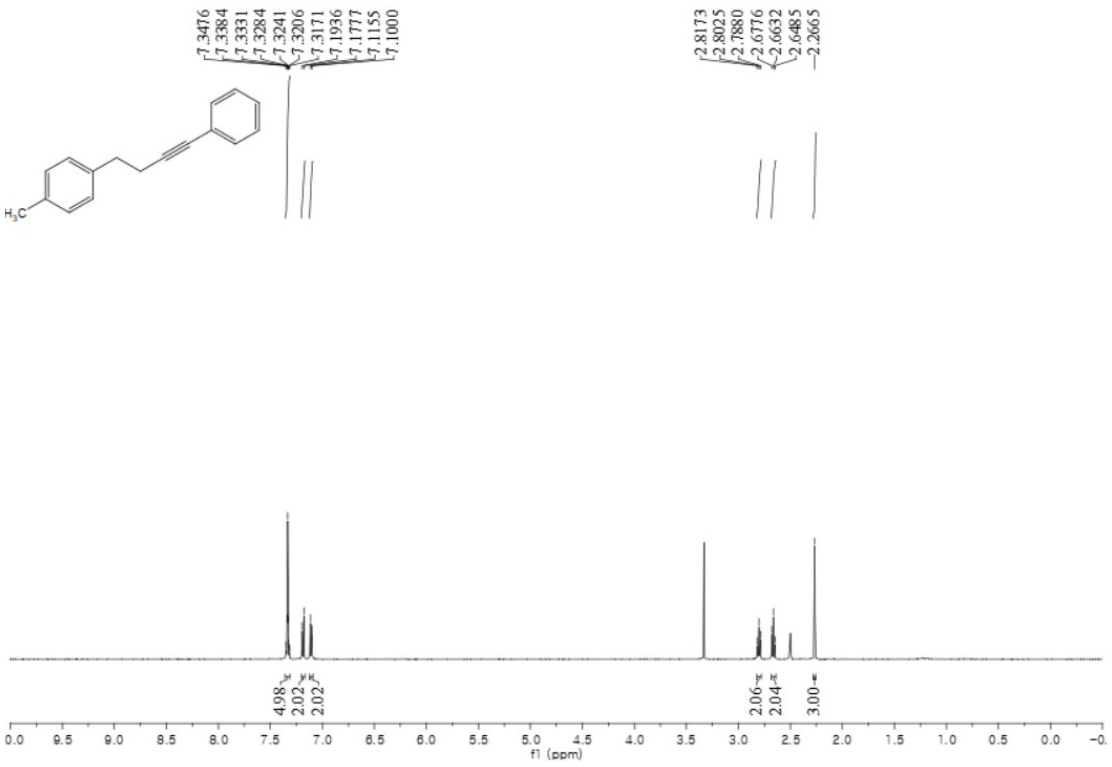


^{13}C NMR

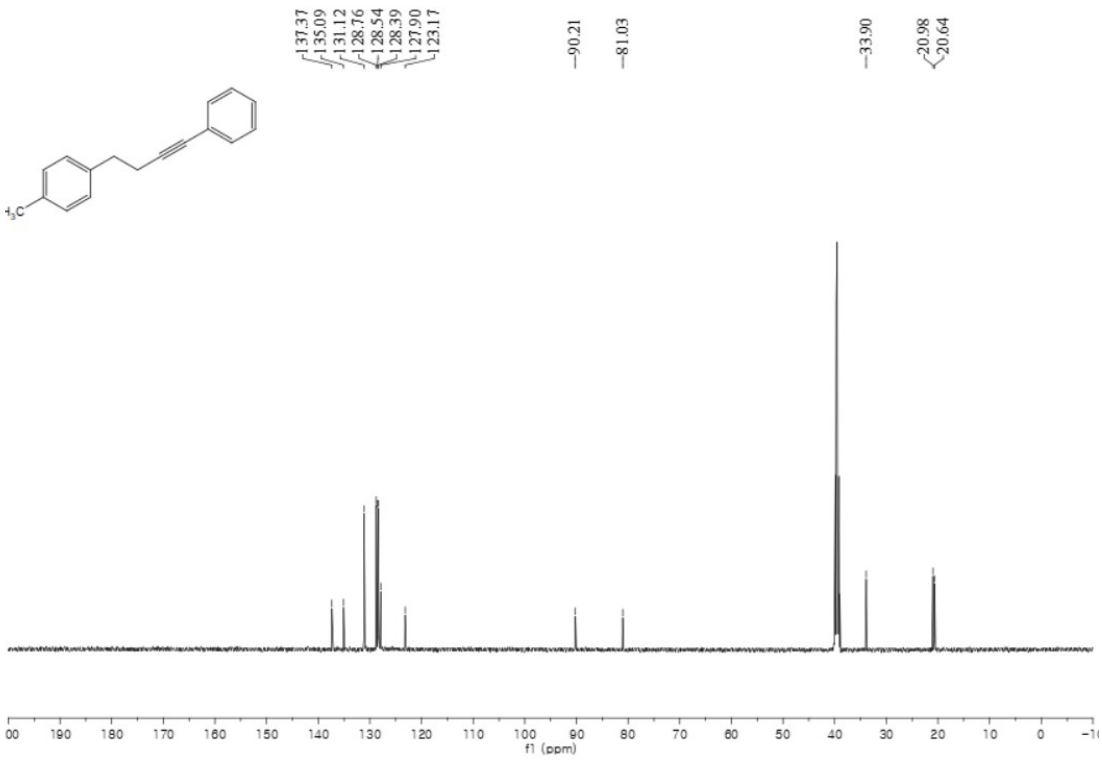


1-Methyl-4-(4-phenylbut-3-yn-1-yl)benzene (4b)

^{1}H NMR

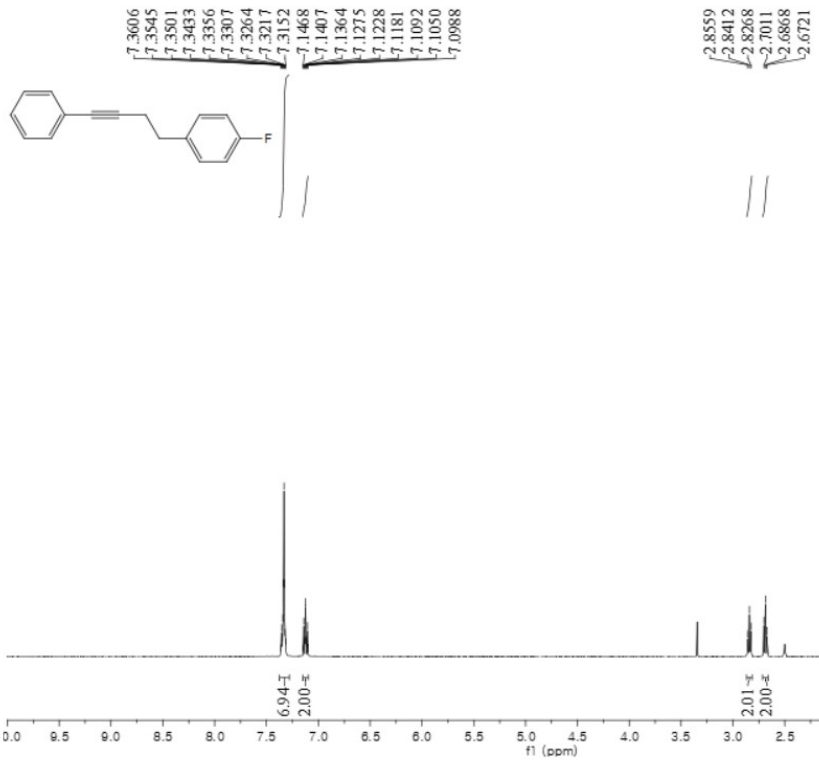


^{13}C NMR

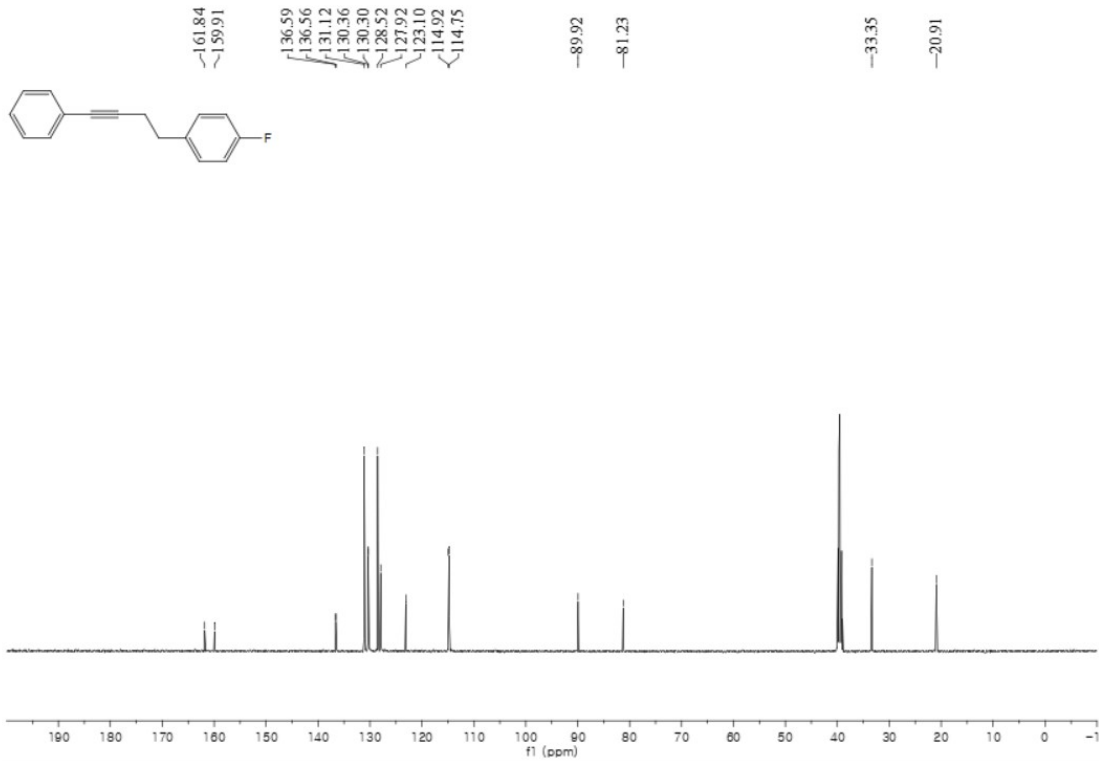


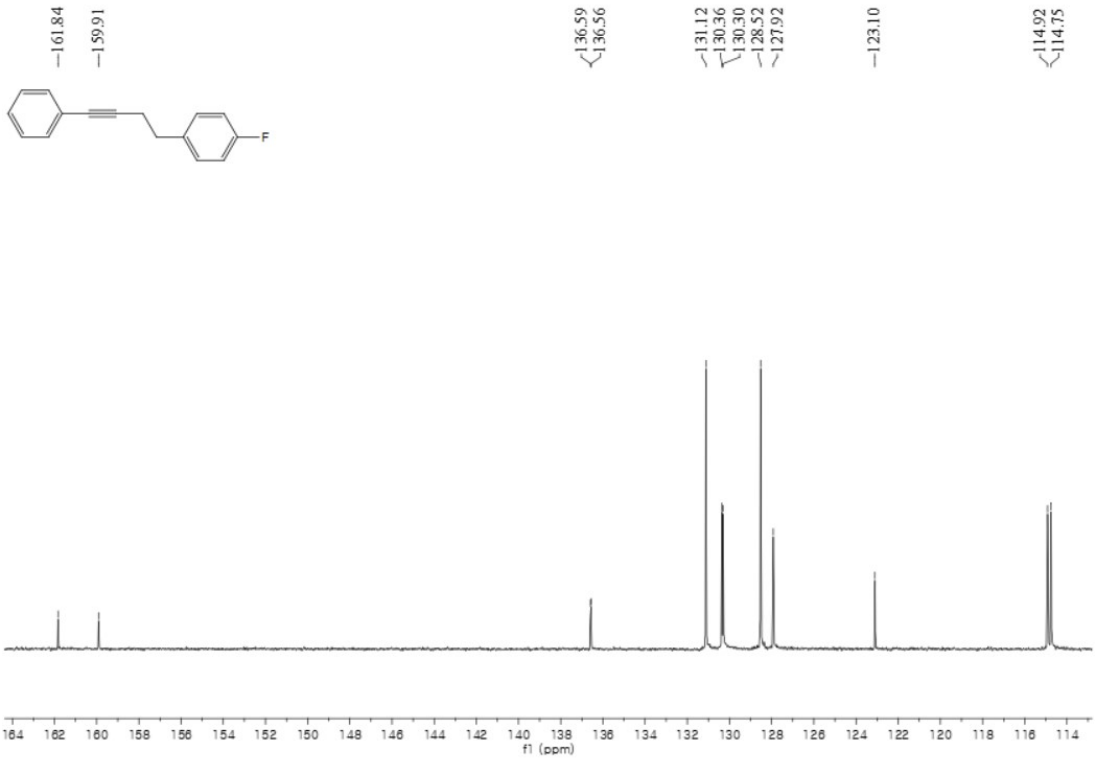
1- Fluoro -4-(4-phenylbut-3-yn-1-yl)benzene (4c)

^{1}H NMR



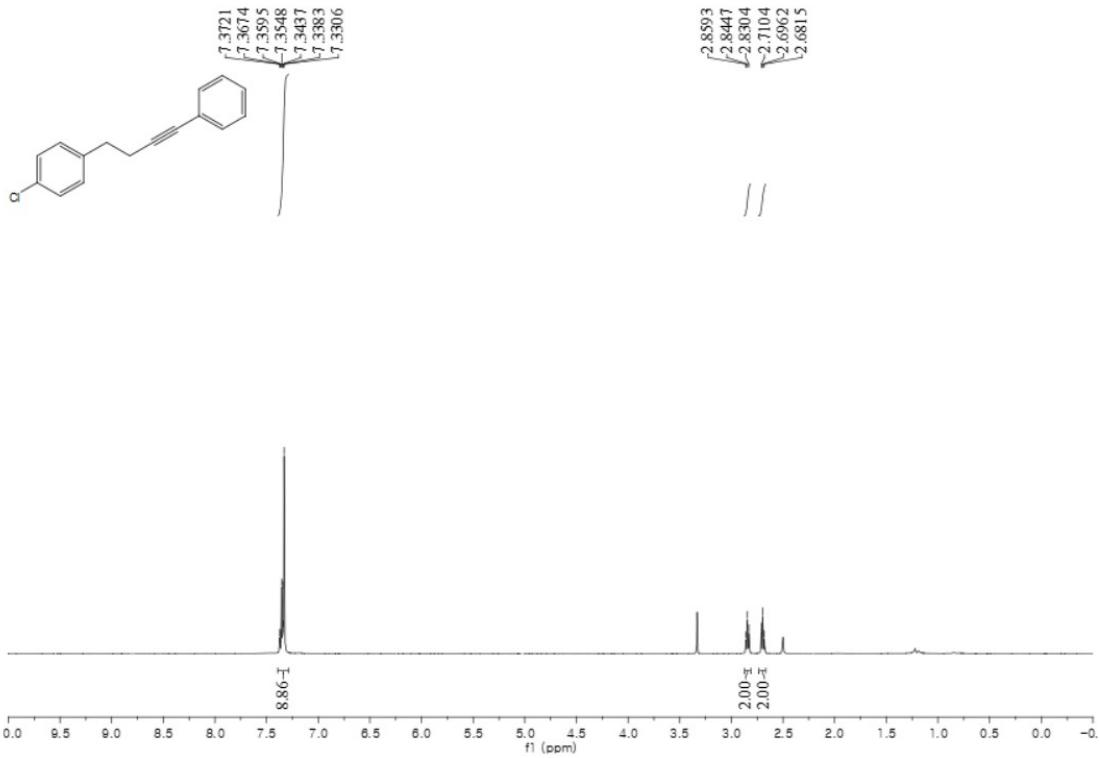
^{13}C NMR



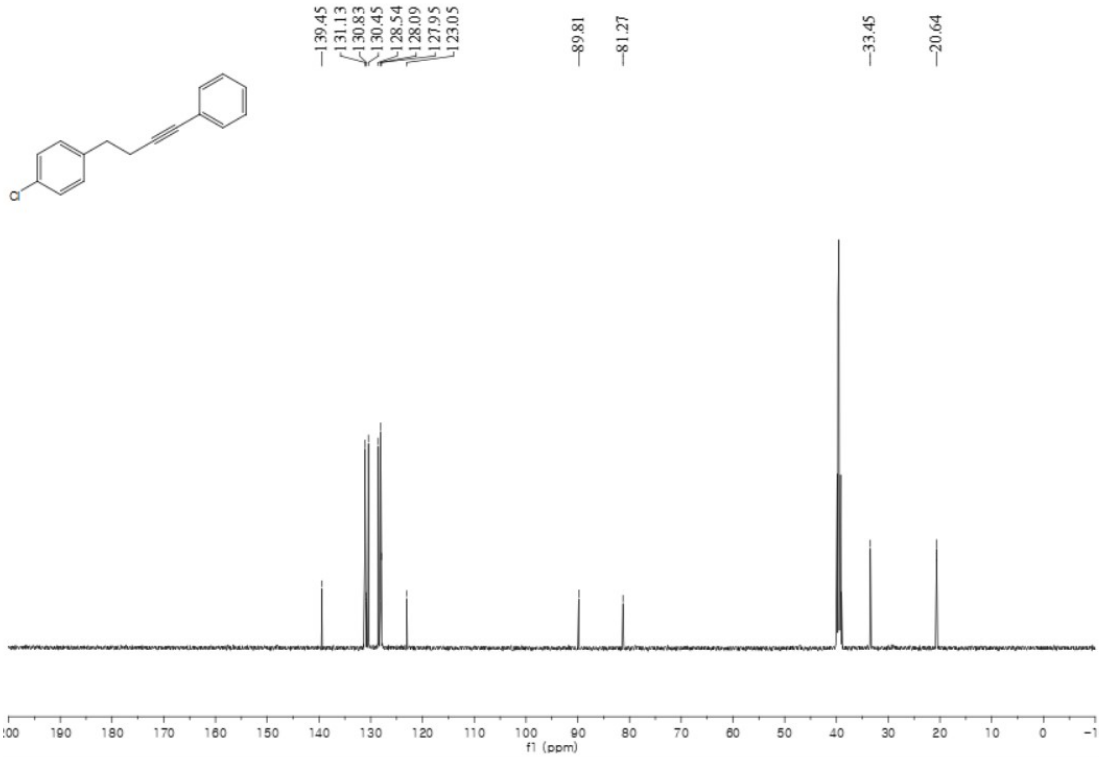


1- Chloro -4-(4-phenylbut-3-yn-1-yl)benzene (4d)

^{1}H NMR

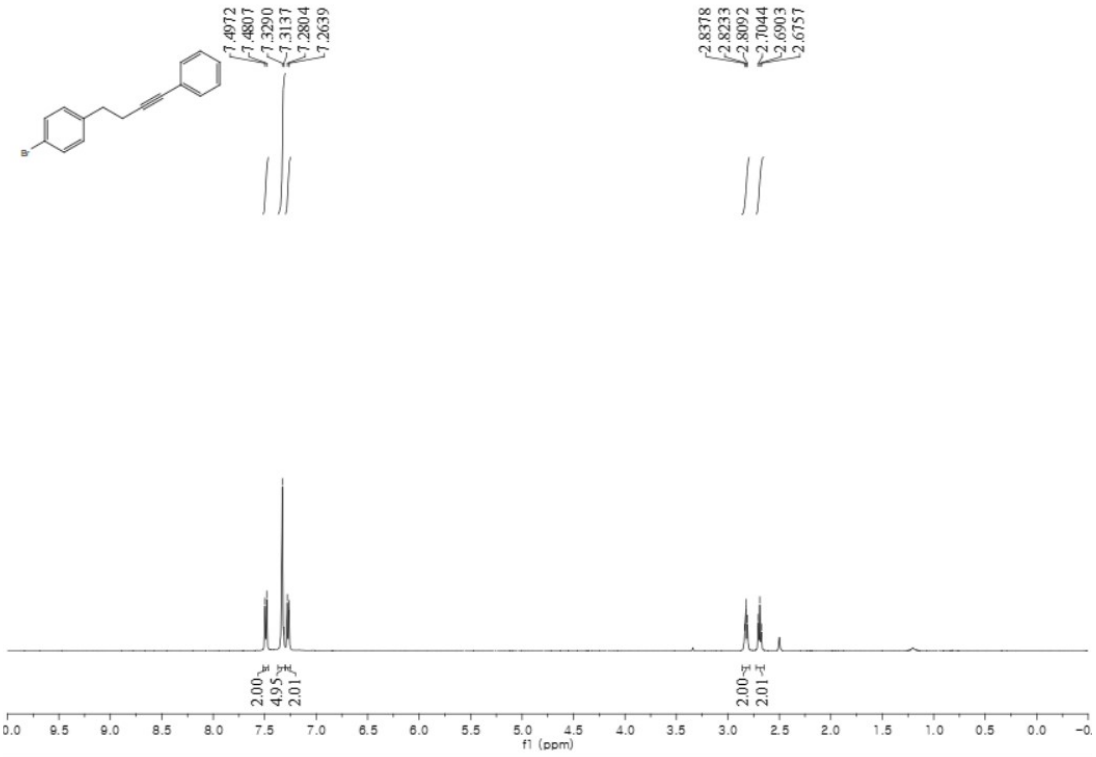


^{13}C NMR

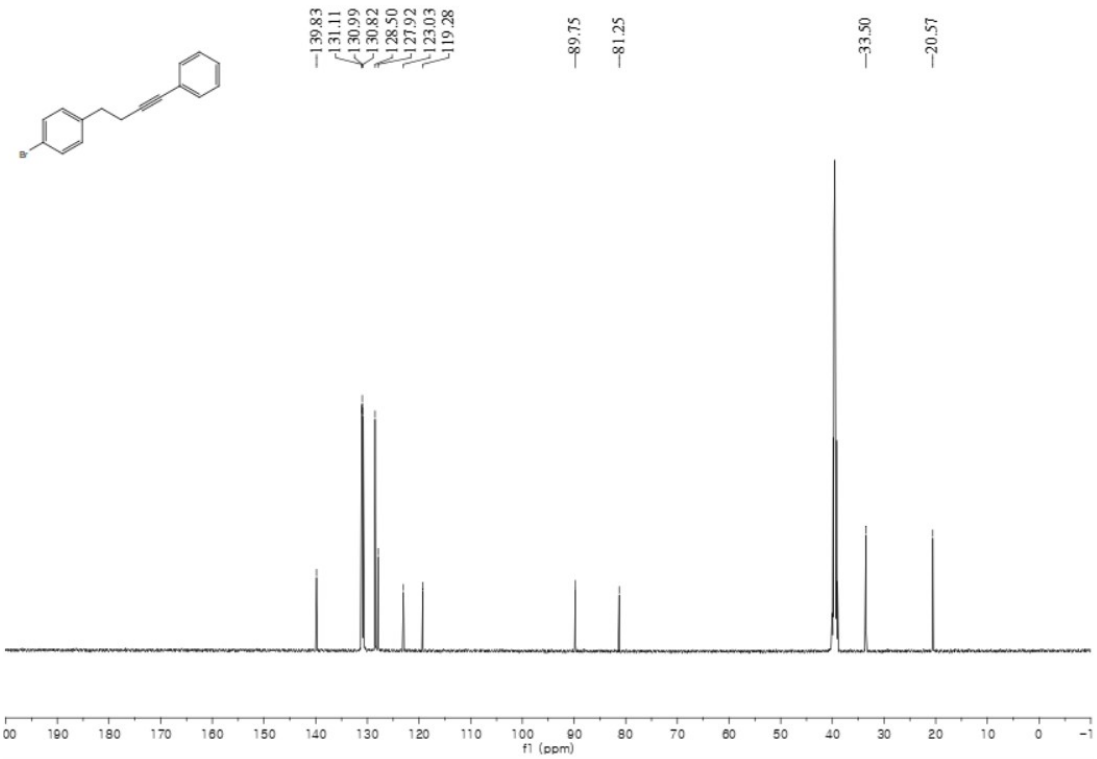


1- Bromo -4-(4-phenylbut-3-yn-1-yl)benzene (4e)

^{1}H NMR

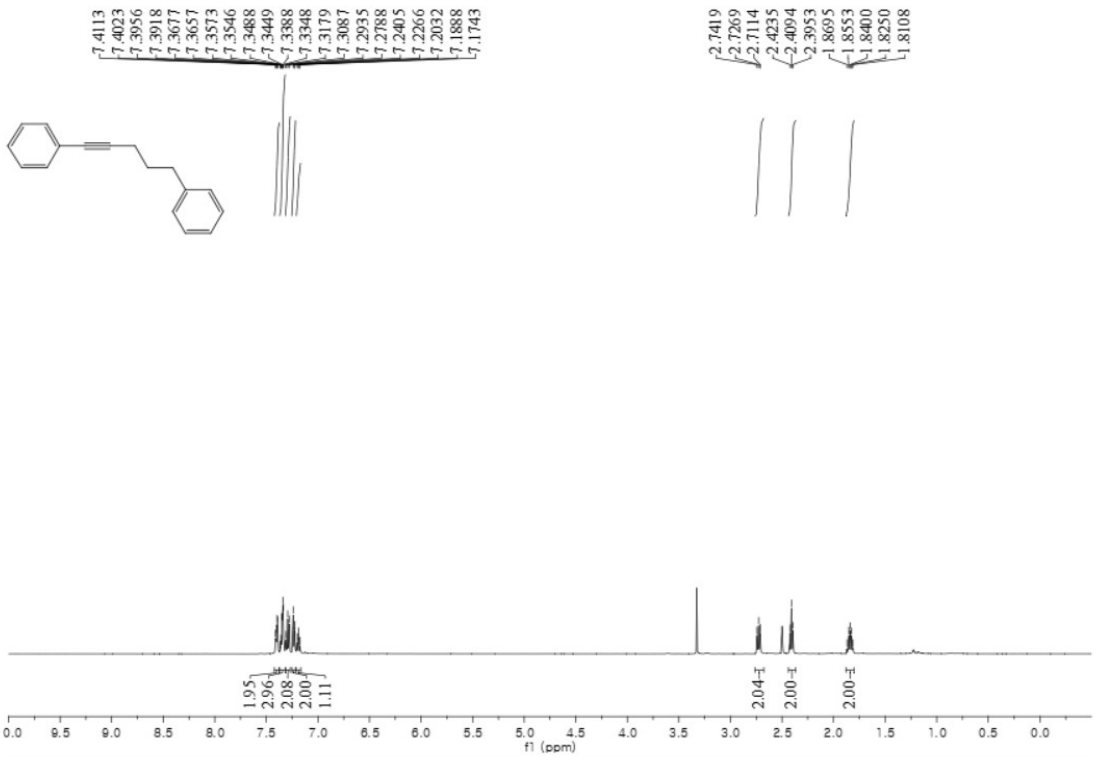


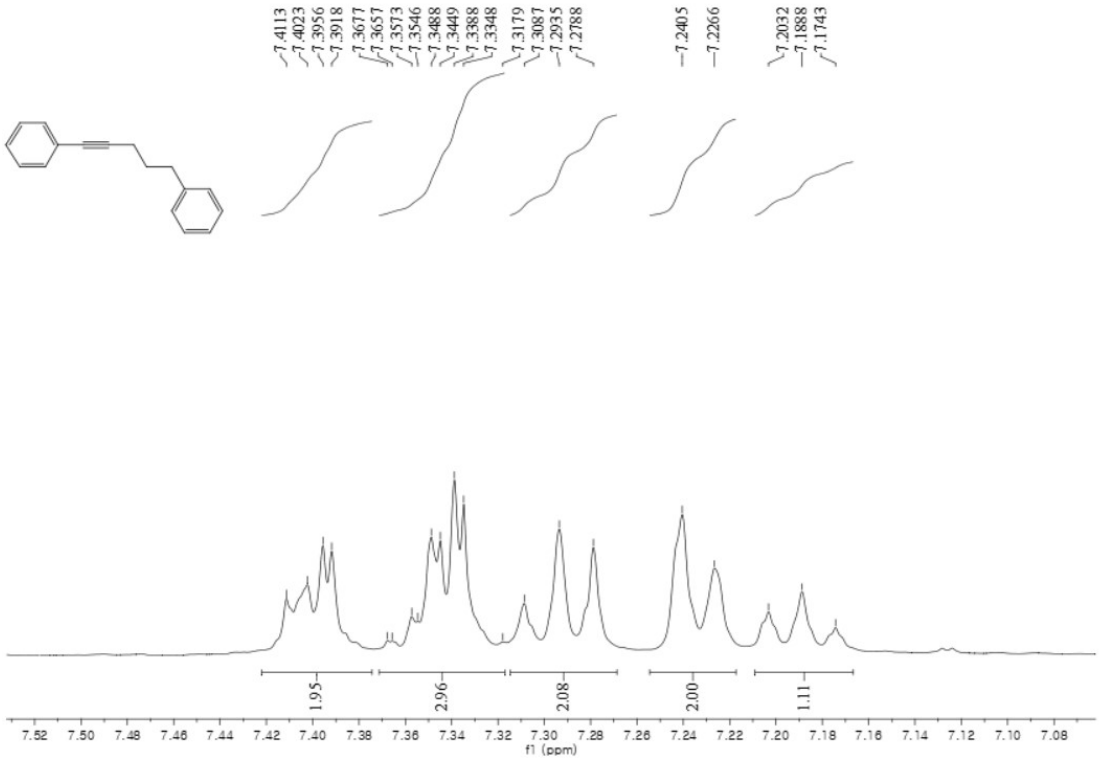
^{13}C NMR



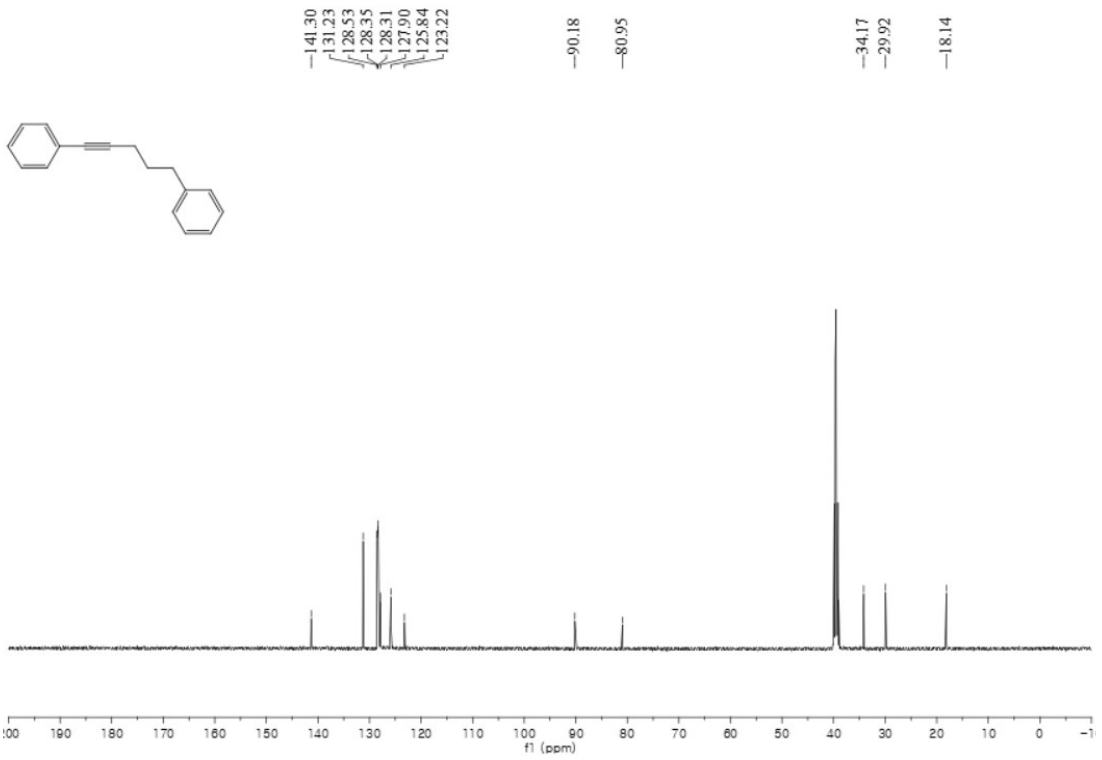
Pent-1-yne-1,5-diyldibenzene (4f)

^{1}H NMR



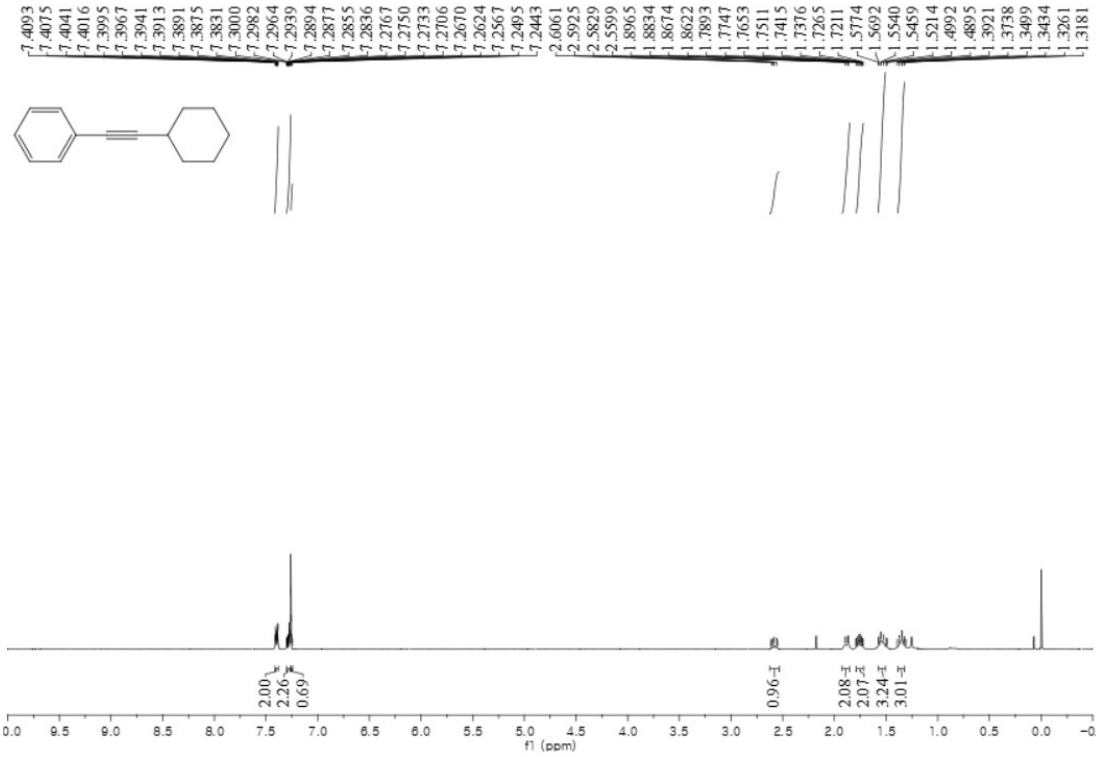

7.4113
7.4023
7.3956
7.3918
7.3677
7.3657
7.3573
7.3546
7.3488
7.3449
7.3388
7.3348
7.3179
7.3087
7.2935
7.2788
7.2405
7.2266
7.2032
7.1888
7.1743
1.95
2.96
2.08
2.00
1.11
f1 (ppm)

^{13}C NMR

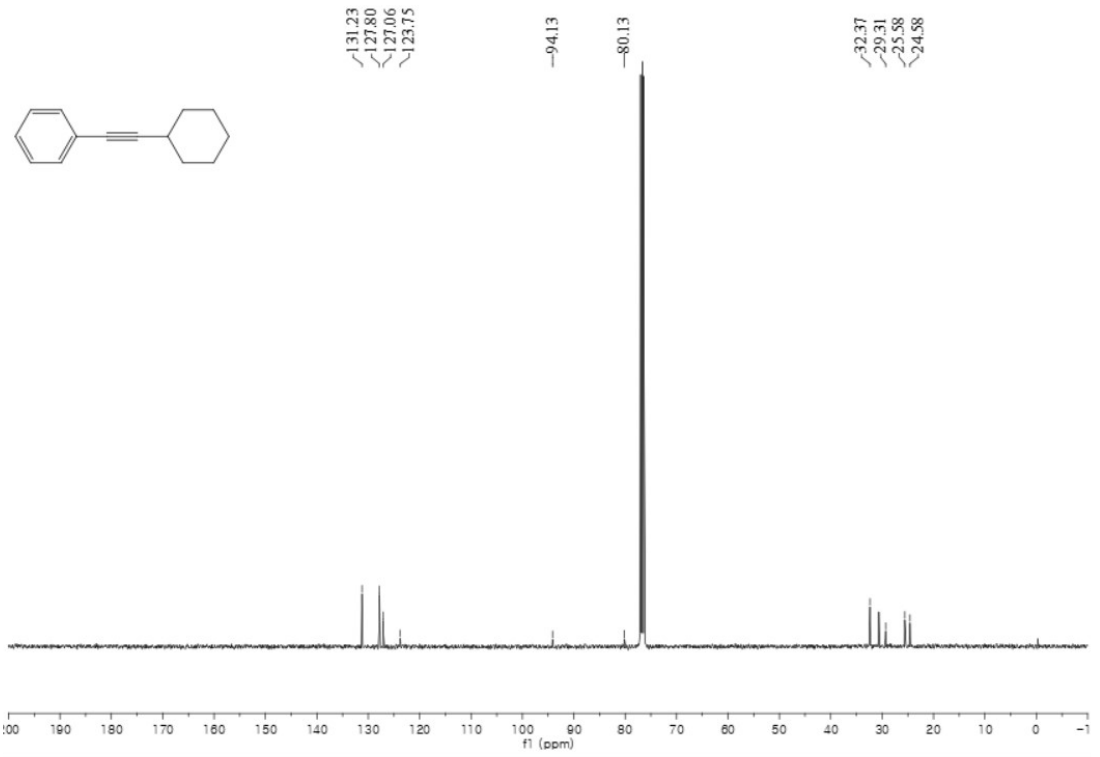

141.30
131.23
128.53
128.35
128.31
127.90
125.84
123.22
90.18
80.95
34.17
29.92
18.14
f1 (ppm)

(Cyclohexylethynyl)benzene (4g)

^{1}H NMR

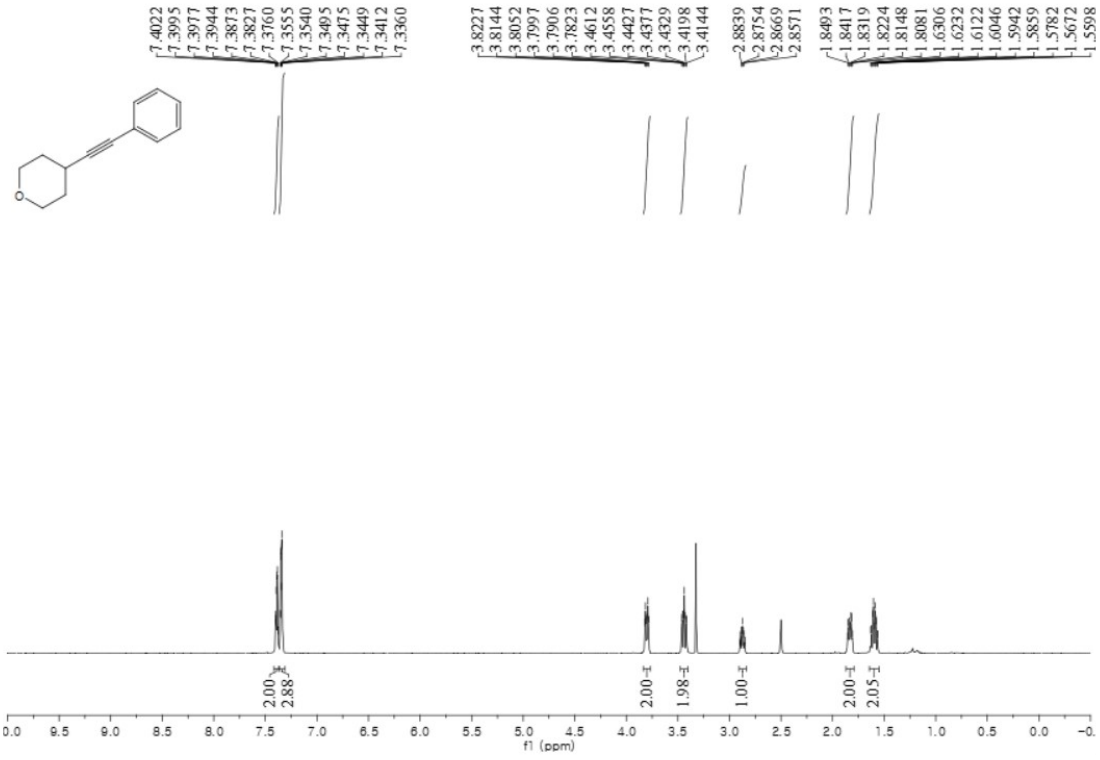


^{13}C NMR

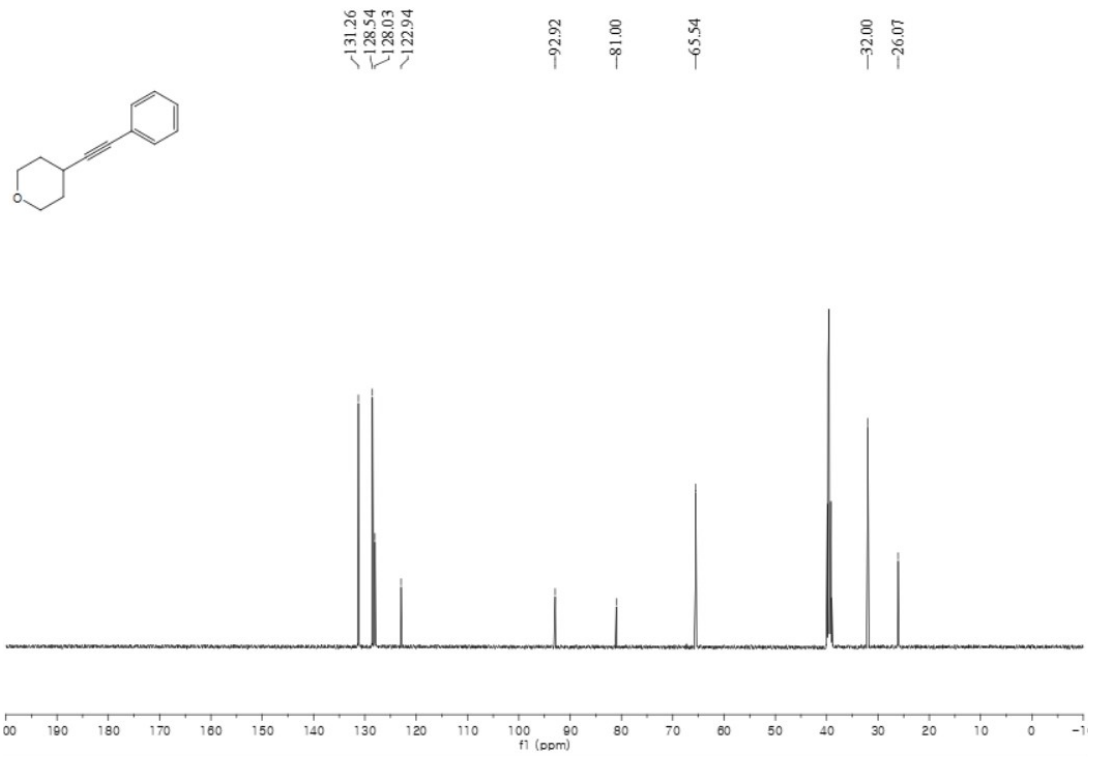


4-(Phenylethynyl)tetrahydro-2H-pyran (4h)

^{1}H NMR

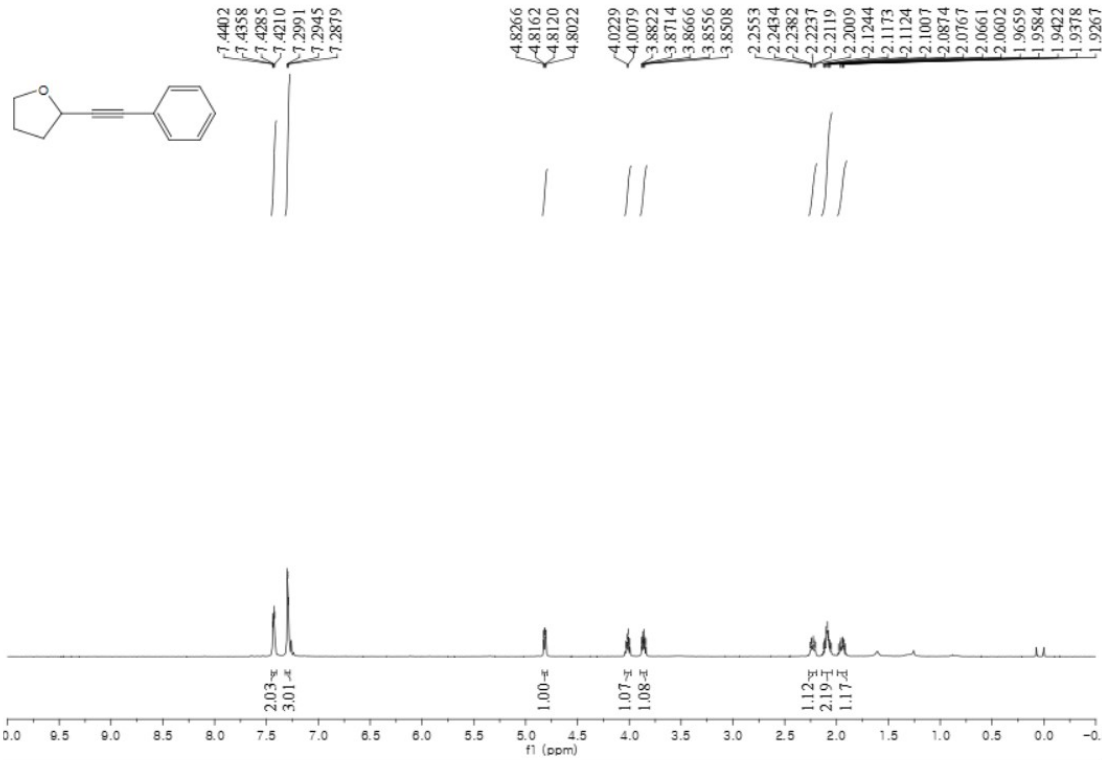


^{13}C NMR

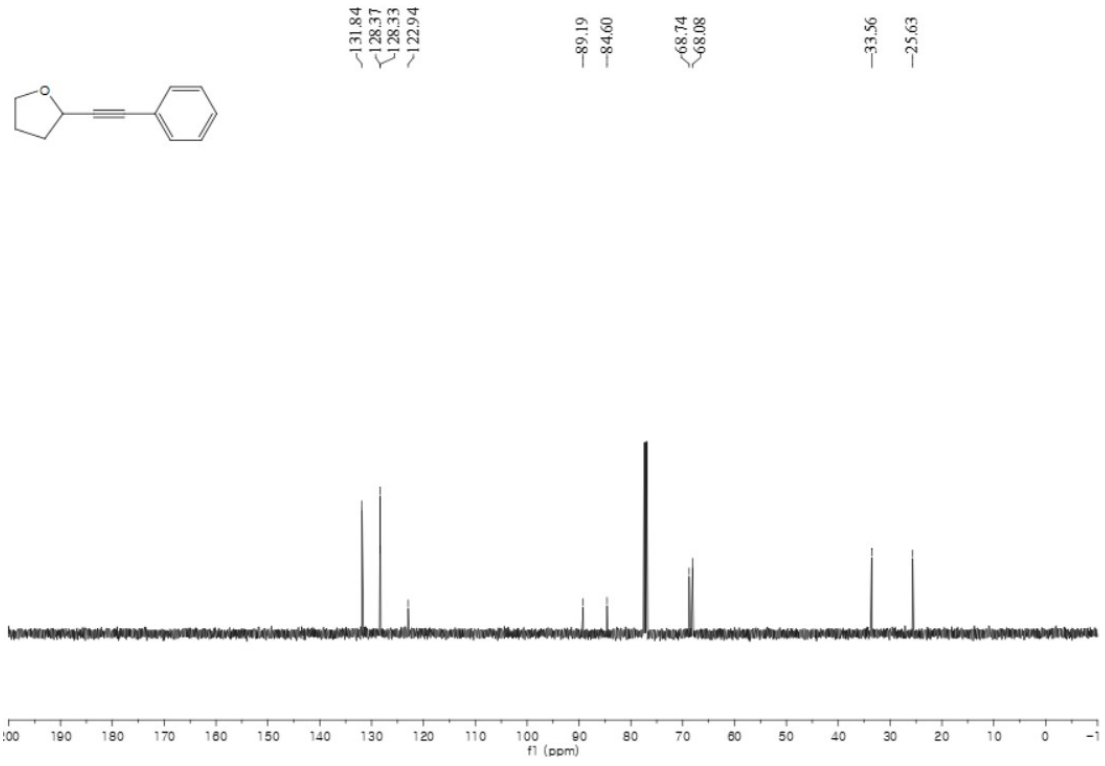


2-(Phenylethynyl)tetrahydrofuran (4i)

^{1}H NMR

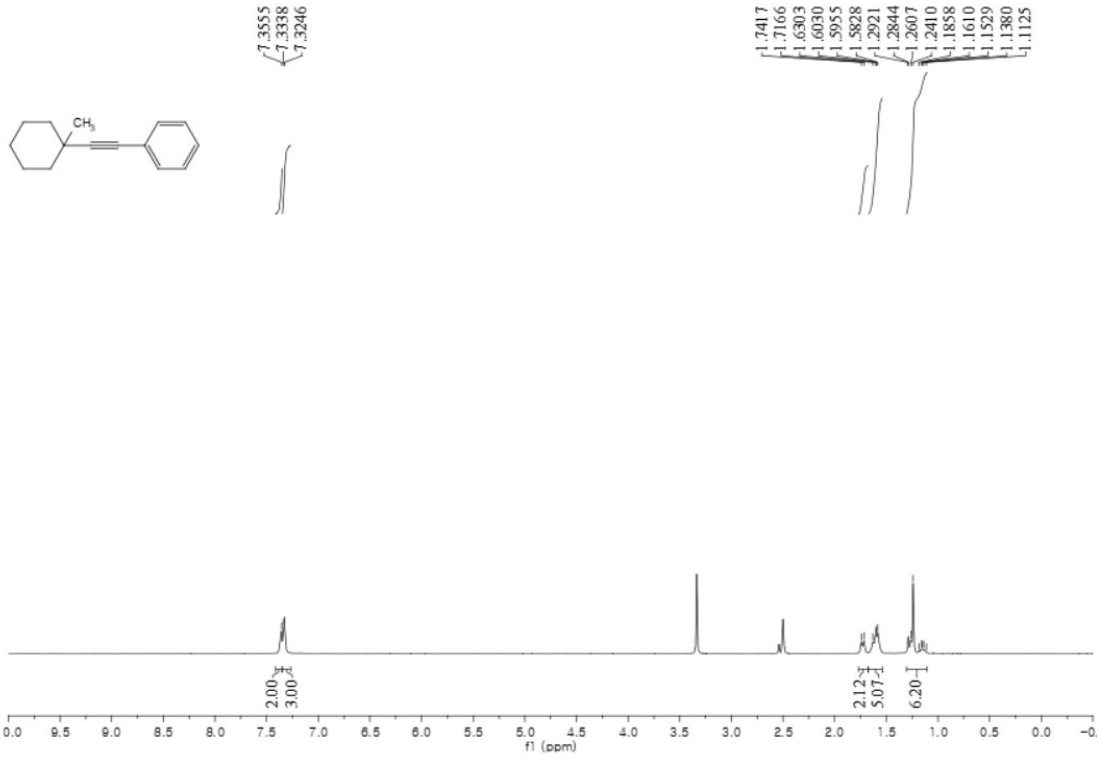


^{13}C NMR

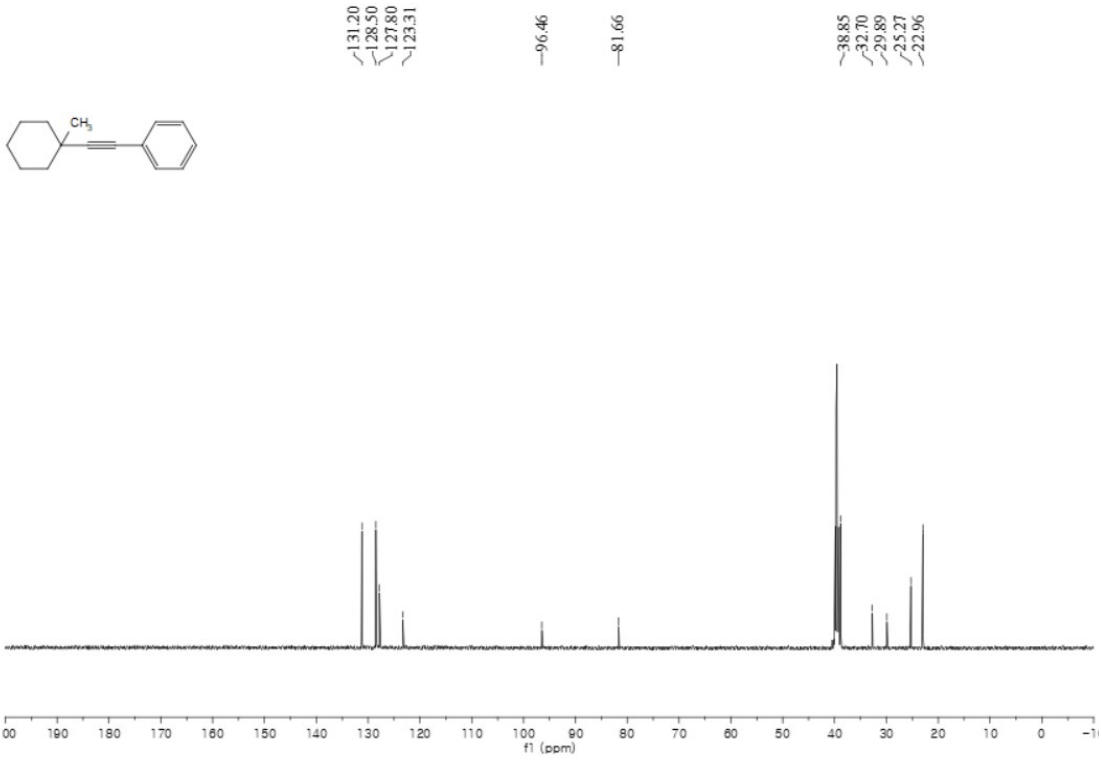


((1-Methylcyclohexyl)ethynyl)benzene (4j)

^{1}H NMR

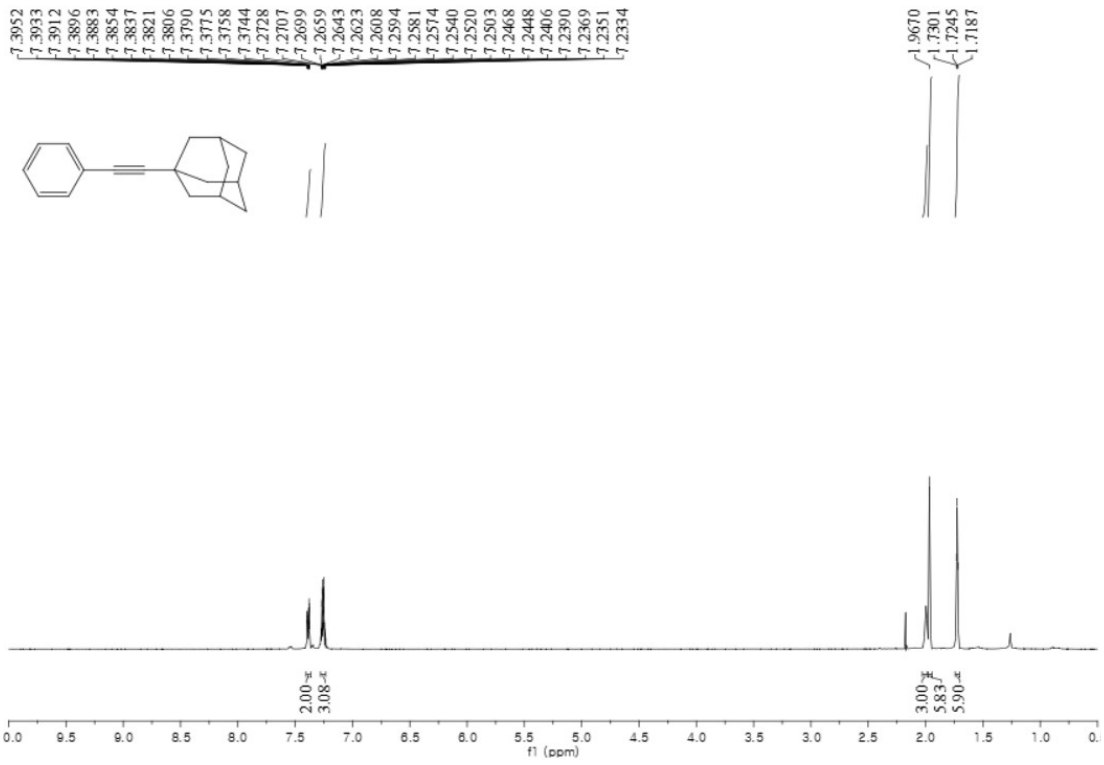


^{13}C NMR

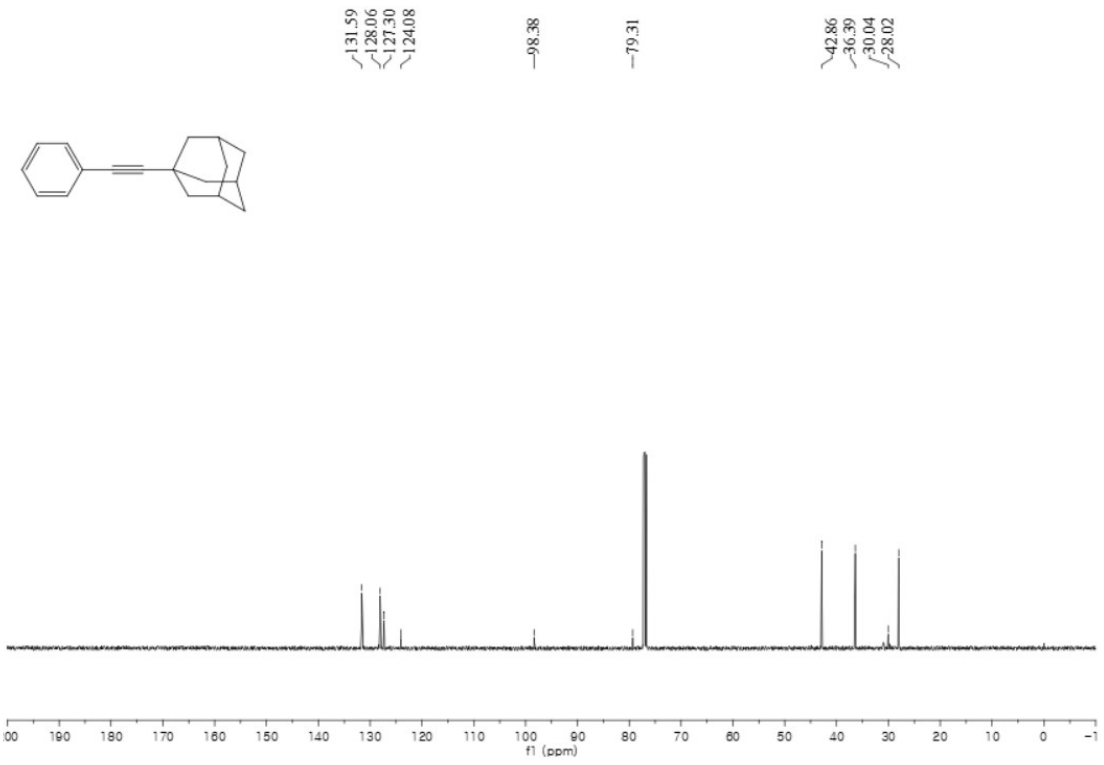


(3r,5r,7r)-1-(Phenylethynyl)adamantane (4k)

^{1}H NMR

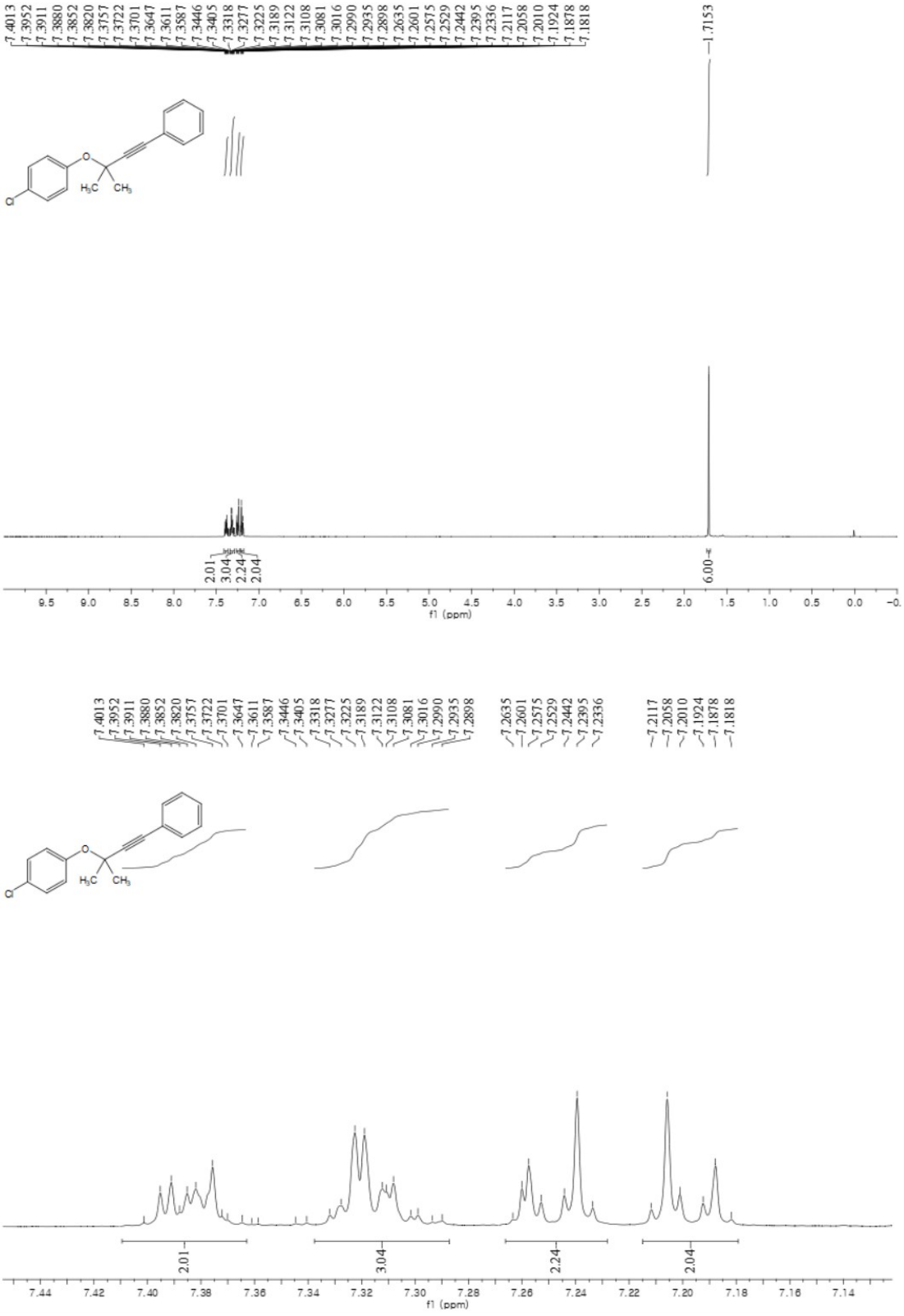


^{13}C NMR

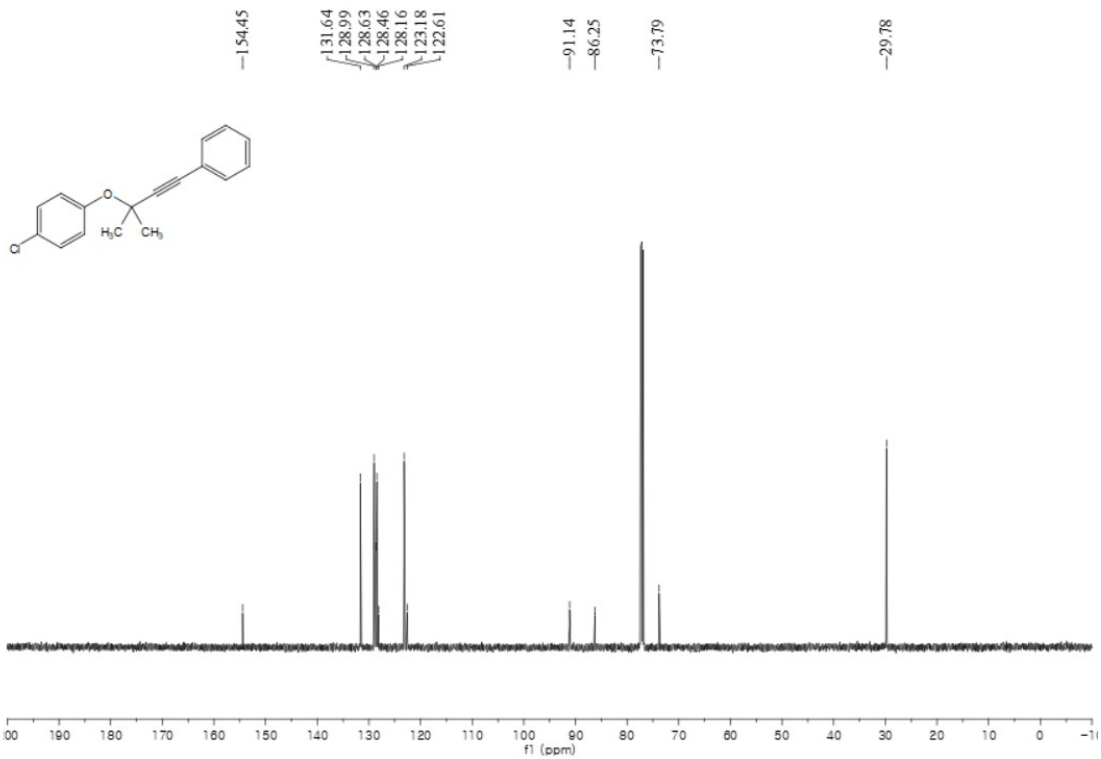


1-Chloro-4-((2-methyl-4-phenylbut-3-yn-2-yl)oxy)benzene (4l)

^{1}H NMR

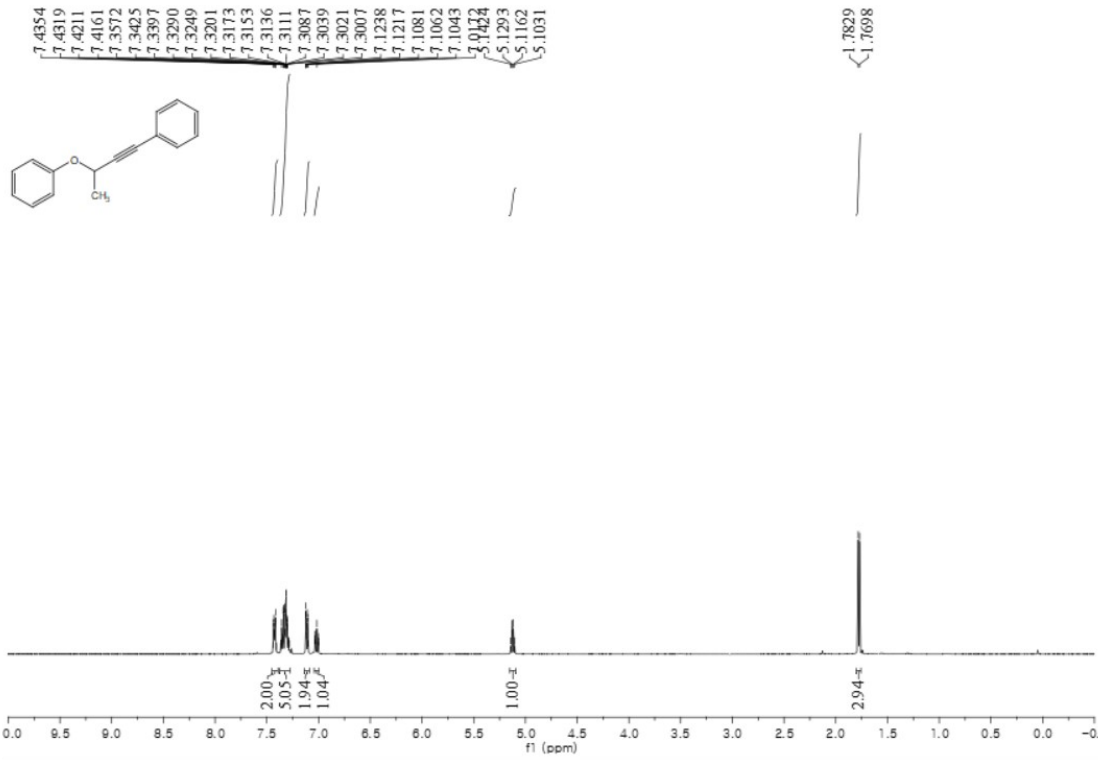


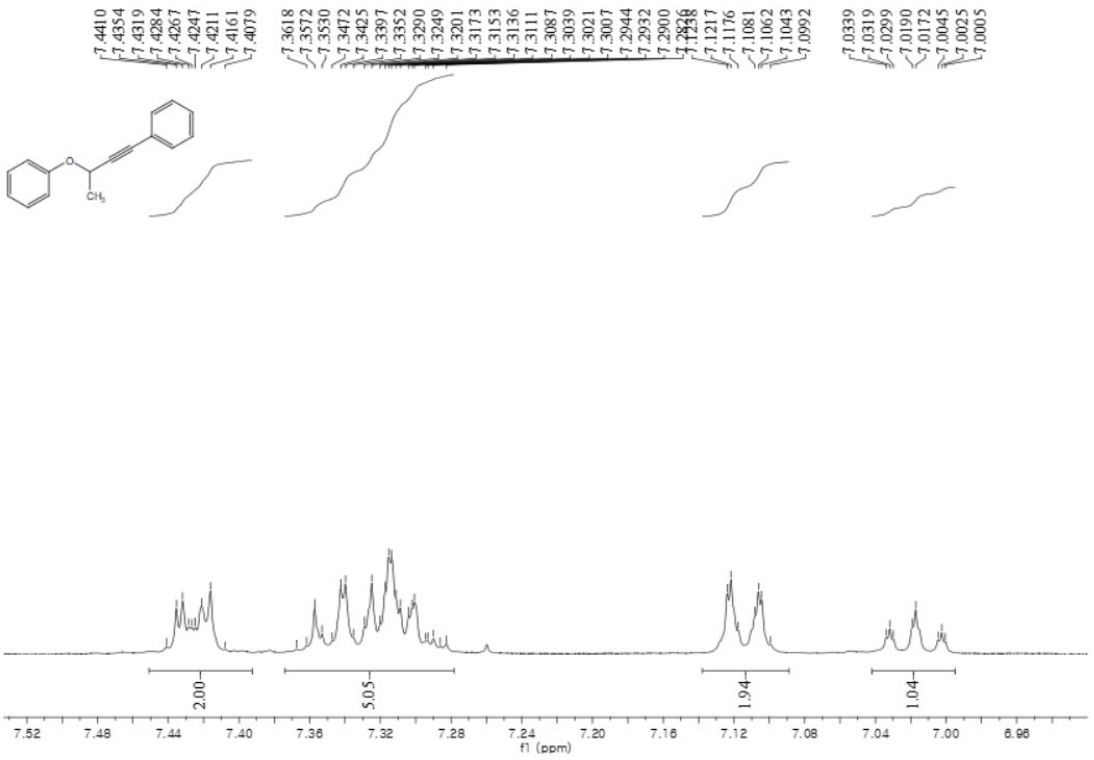
^{13}C NMR



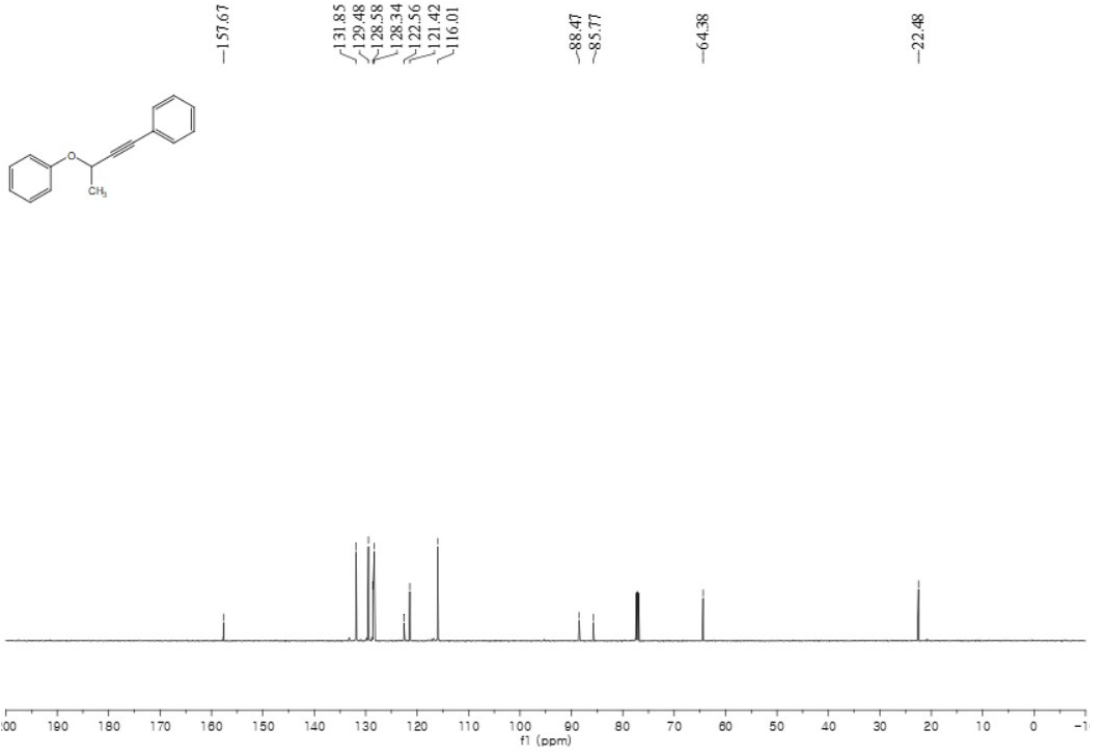
(3-Phenoxybut-1-yn-1-yl)benzene (4m)

^{1}H NMR



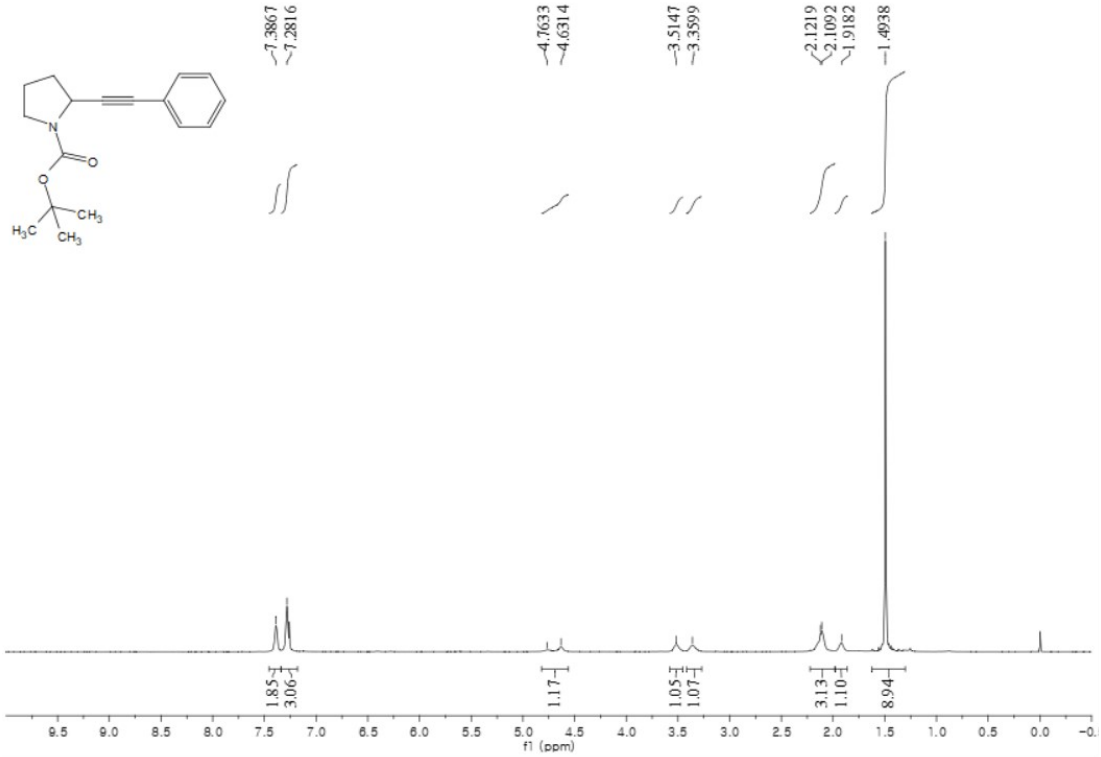

7.4410
7.4354
7.4319
7.4284
7.4267
7.4247
7.4211
7.4161
7.4079
7.3618
7.3572
7.3530
7.3472
7.3425
7.3397
7.3352
7.3290
7.3249
7.3201
7.3173
7.3153
7.3136
7.3111
7.3087
7.3039
7.3021
7.3007
7.2944
7.2932
7.2900
7.1217
7.1176
7.1081
7.1062
7.1043
7.0992
7.0339
7.0319
7.0299
7.0190
7.0172
7.0045
7.0025
7.0005
O
CH3
2.00
5.05
1.94
1.04
7.52
7.48
7.44
7.40
7.36
7.32
7.28
7.24
7.20
7.16
7.12
7.08
7.04
7.00
6.96
f1 (ppm)

^{13}C NMR

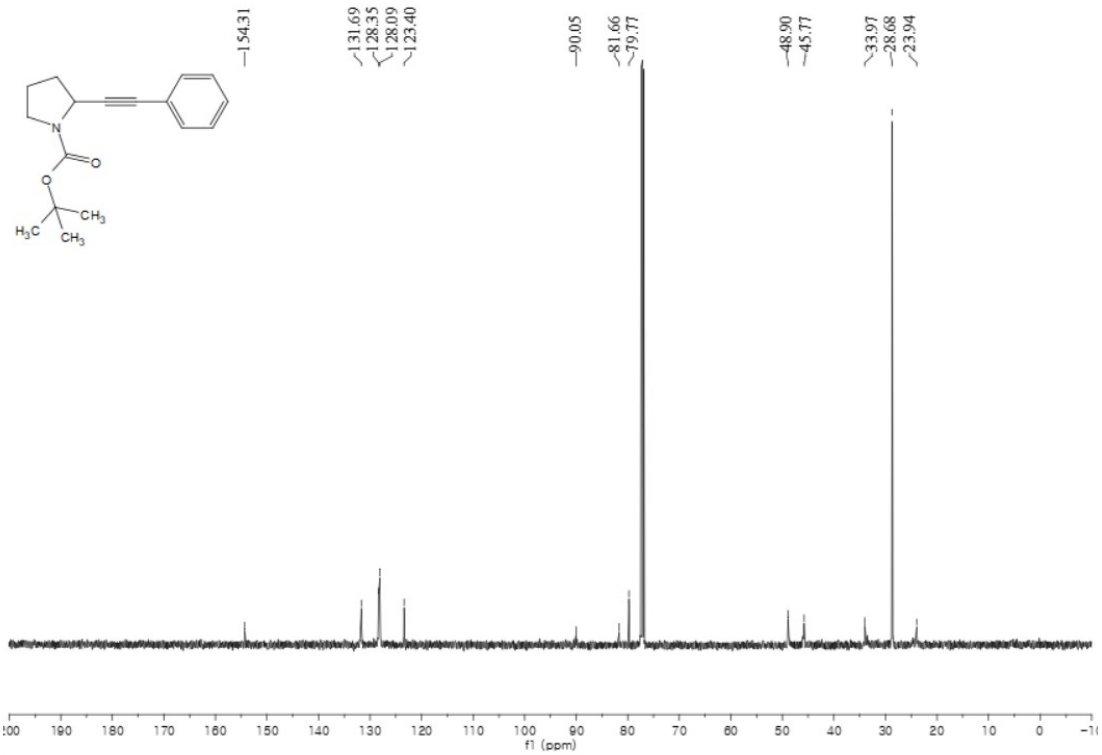

157.67
131.85
129.48
128.58
128.34
122.56
121.42
116.01
88.47
85.77
64.38
22.48
O
CH3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

tert-Butyl 2-(phenylethynyl)pyrrolidine-1-carboxylate (4n)

^{1}H NMR

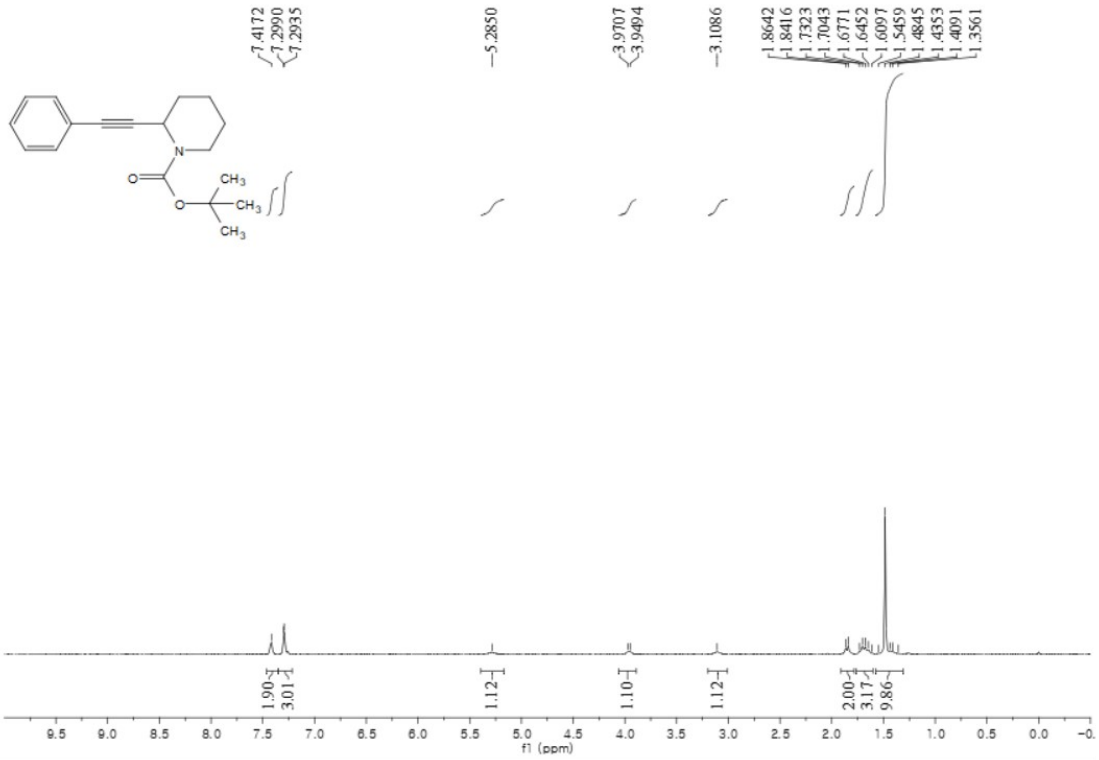


^{13}C NMR

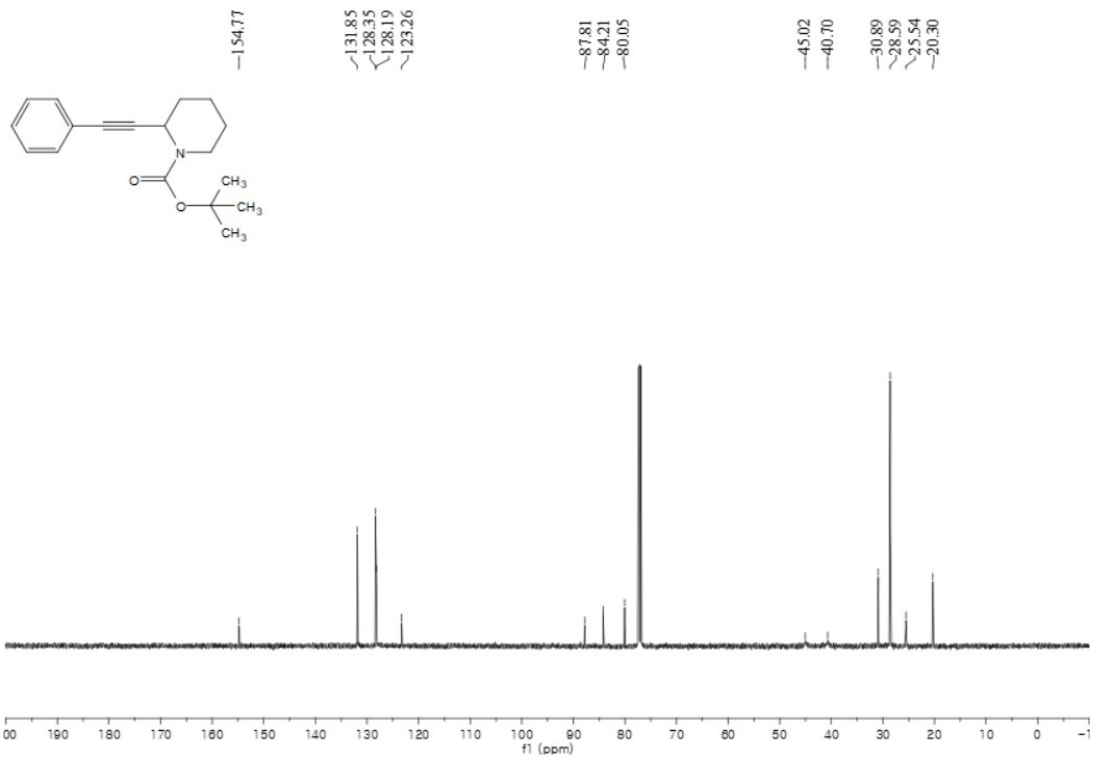


tert-Butyl 2-(phenylethynyl)piperidine-1-carboxylate (4o)

^{1}H NMR

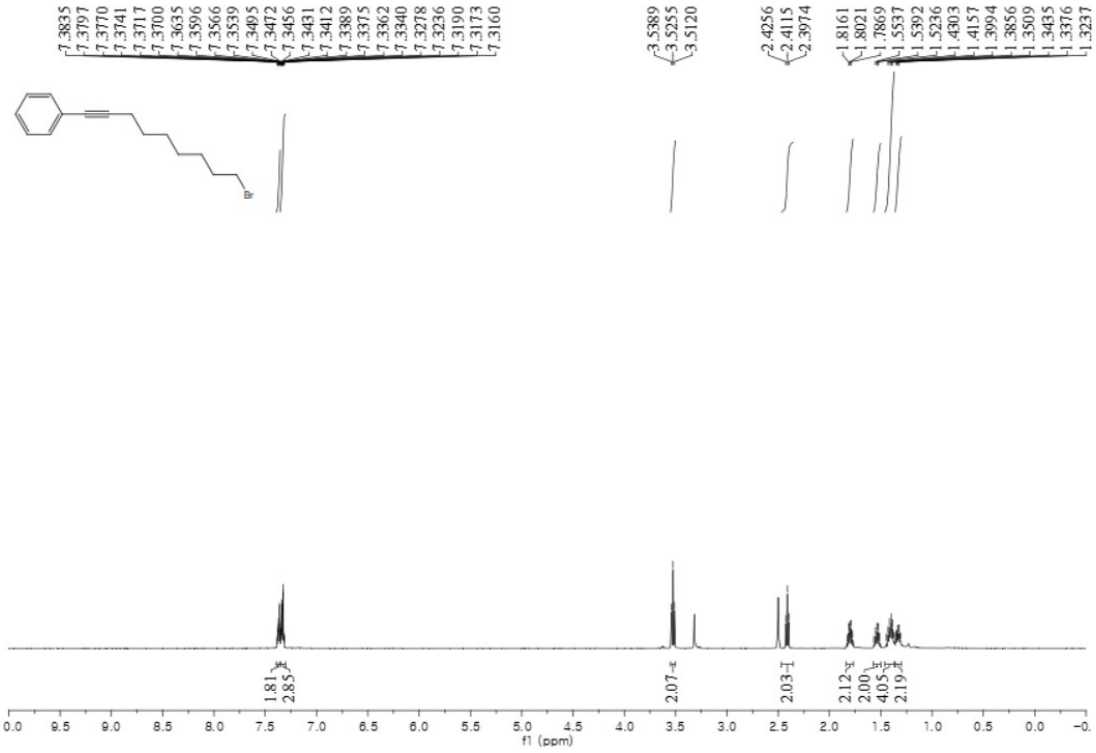


^{13}C NMR

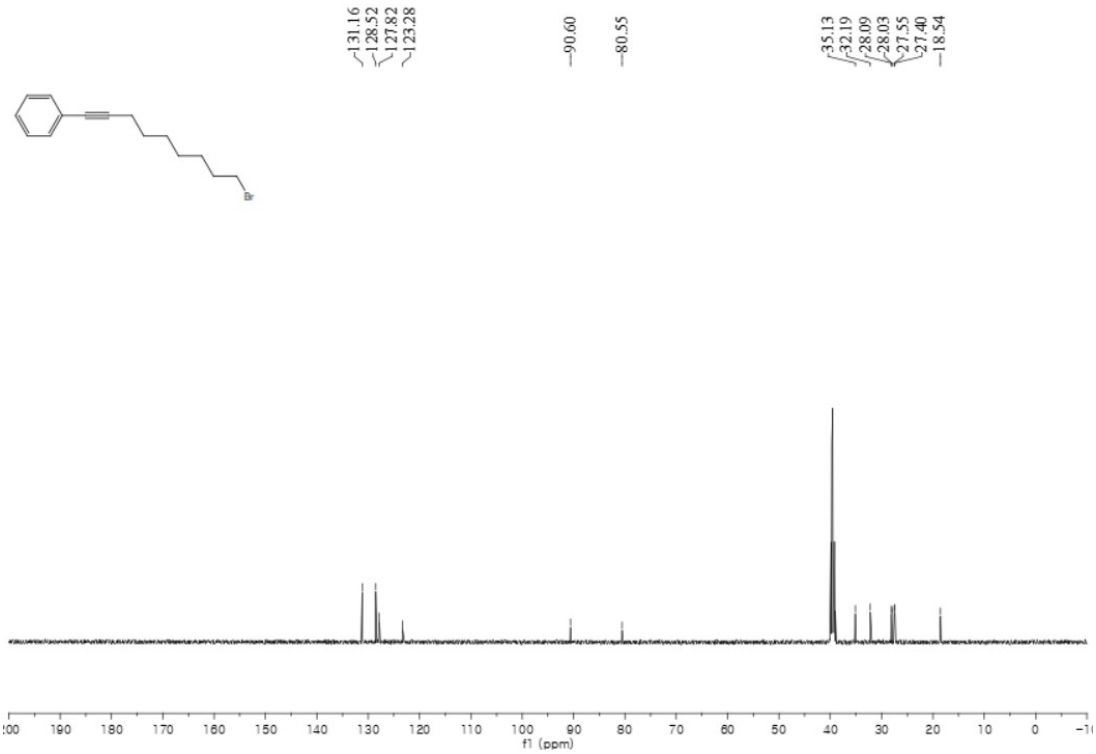


(9-Bromonon-1-yn-1-yl)benzene (4p)

^{1}H NMR

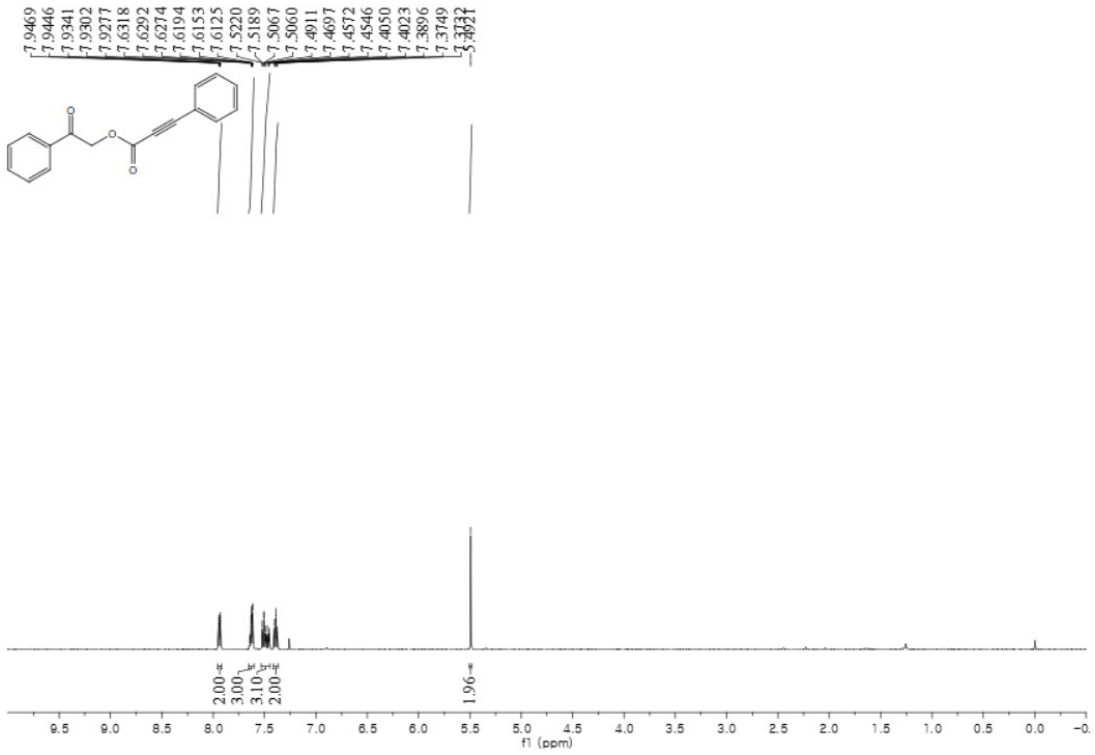


^{13}C NMR

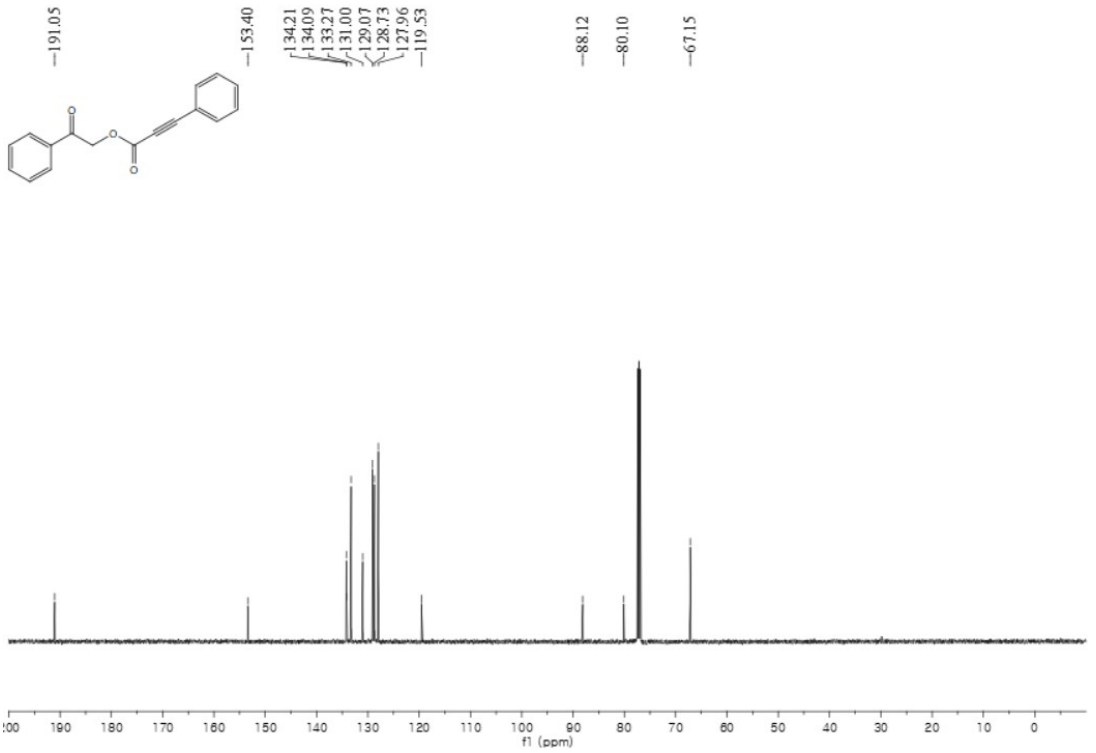


2-Oxo-2-phenylethyl 3-phenylpropiolate (7)

^{1}H NMR

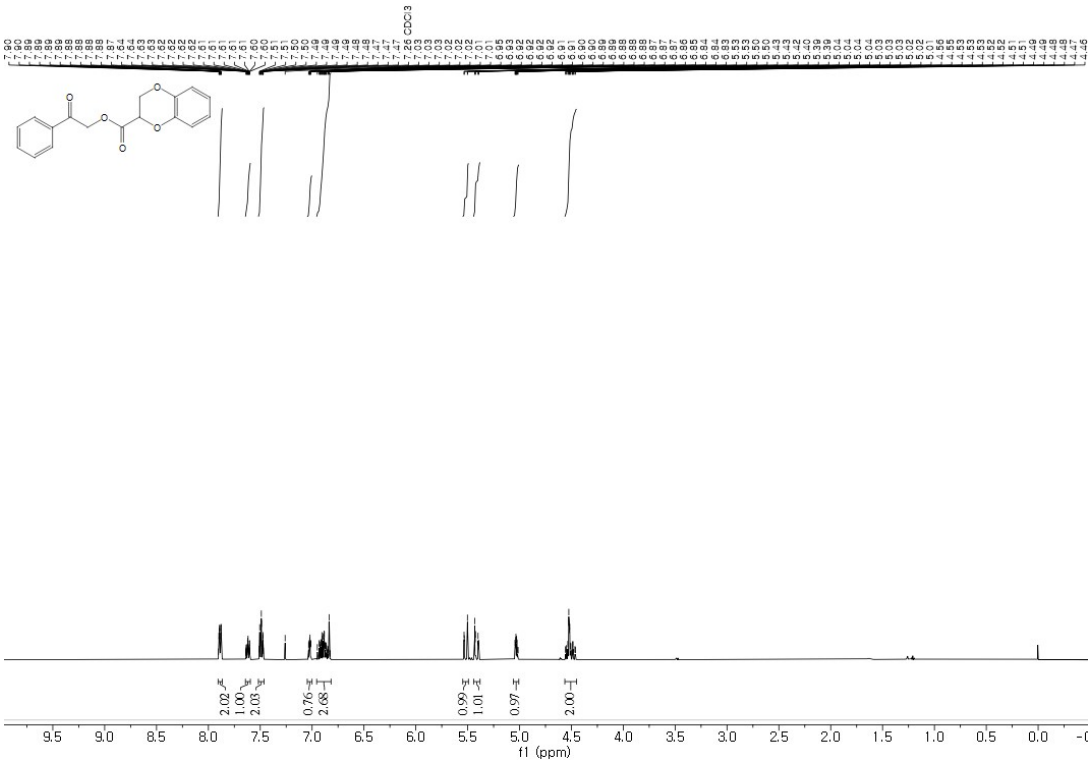


^{13}C NMR



2-Oxo-2-phenylethyl 2,3-dihydrobenzo[b][1,4]dioxine-2-carboxylate (**8**)

^{1}H NMR



^{13}C NMR