Supporting Information

Alkynylation/Dearomatizative Cyclization to Construct Spiro[5.5]undecanes

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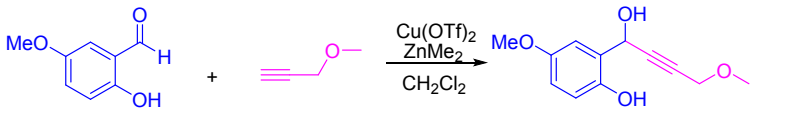
General Information

All reactions under standard conditions were monitored by thin-layer chromatography (TLC) on GF254 plates. The silica gel (200-300 meshes) was used for column chromatography, and the distillation range of petro ether was 60- 90°C. CH_2Cl_2 was dried by distillation over CaH_2. Benzene and THF was dried by distillation over Na/K alloy. CH_3NO_2 was distilled over anhydrous $CaCl_2$ and further dried over 4Å molecular sieve. Commercially available reagents and solvents were used without any purification. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution on Bruker AX-400 MHz instruments and spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard. High-resolution mass spectral analysis (HRMS) data were measured on the Bruker Apex II by means of the ESI technique.

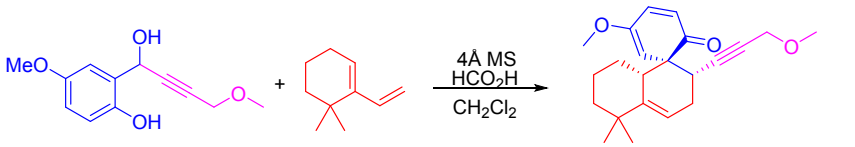
Experimental Procedures and Analytical Data

Preparation of 5a. $Cu(OTf)_2$ (21.2mg, 0.0588mmol) was added in dry CH_2Cl_2 (2.0ml) under Ar atmosphere. Then, $ZnMe_2$ in toluene (1.2M, 3.06ml) was added. After 10min, **2a** (245μL, 2.94mmol) was added. 2 h later, the solution was cooled to 0 °C and treated with compound **1a** (112mg, 0.735mmol) dissolved in CH_2Cl_2 (2.0ml). The resulting mixture was stirred at room temperature for 12h. After the reaction was completed (monitoring with TLC), it was quenched with saturated aqueous NH_4Cl solution. The mixture was extracted with EtOAc (3×20 mL). The organic layers were washed with brine, dried over Na_2SO_4, and concentrated under vacuum. The residue was purified by flash column chromatography to afford compound **5a** as a light yellow liquid (147mg, 90%yeild).

2-(1-hydroxy-4-methoxybut-2-yn-1-yl)-4-methoxyphenol **(5a).** ^1H NMR (400 MHz, $CDCl_3$) δ 7.03 (s, 1H), 6.91 (d, 1H, J = 2.8Hz), 6.75-6.82 (m, 2H), 5.67 (s, 1H), 4.18 (d, 2H, J = 1.2Hz), 3.75 (s, 3H), 3.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 148.7, 125.5, 117.6, 114.9, 113.3, 84.6, 83.4, 63.4, 59.9, 57.7, 55.8.



1a **2a** **5a 90% yield**



5a **3a** **4a 22% yield**

General procedure. $Cu(OTf)_2$ (21.2mg, 0.0588mmol) was added in dry CH_2Cl_2 (2.0ml) under Ar atmosphere. Then, $ZnMe_2$ in toluene (1.2M, 3.06ml) was added. After 10min, terminal alkyne (2.94mmol) was added. 2 h later, the solution was cooled to 0 °C and treated with substituted

salicylaldehyde (0.735mmol) dissolved in CH_2Cl_2 (2.0ml). The resulting mixture was stirred at room temperature for 12h. After salicylaldehyde was disappeared (monitoring with TLC), the solution was opened to atmosphere, 4 Å molecular sieve and functionalized 1, 3-butadiene (3.675mmol) was added. 5min later, dropped HCO_2H (1.10mmol). The mixture was stirred 12h at room temperature and filtered through short diatomite columns to afford crude product. Further purification by flash column chromatography afforded product.

3-methoxy-2'-(3-methoxyprop-1-yn-1-yl)-5',5'-dimethyl-3',5',6',7',8',8a'-hexahydro-2'H-spiro[cyclohexane-1,1'-naphthalene]-2,4-dien-6-one (**4a**).

The title compound was obtained in 46% yield as a light yellow solid. m.p. 102-104℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (dd, 1H, *J*=3.2Hz, *J*=10.0Hz), 6.09 (d, 1H, *J*=10.0Hz), 5.51-5.52 (m, 1H), 5.15 (d, 1H, *J*=3.2Hz), 3.94 (t, 2H, *J*=1.8Hz), 3.66 (s, 3H), 3.23 (s, 3H), 2.85-2.89 (m, 2H), 2.27-2.32 (m, 2H), 1.46-1.55 (m, 1H), 1.37-1.43 (m, 3H), 1.14-1.22 (m, 2H), 1.11 (s, 3H), 1.05 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.9, 152.4, 145.3, 141.4, 127.6, 114.3, 104.7, 86.2, 76.8, 59.7, 56.9, 55.6, 55.0, 44.2, 40.2, 37.1, 36.1, 29.9, 29.4, 28.8, 28.6, 21.1. IR[ν_{max} cm^{-1}] 3263, 3051, 2924, 2849, 2666, 2367, 2222, 1993, 1871, 1783, 1718, 1670, 1638, 1587, 1461, 1408, 1363, 1237, 1188, 1096, 1040, 1004, 906, 829, 773, 738, 691, 605, 539, 489, 455. MS-ESI: m/z = 358 $[M+NH_4]^+$. HRMS-ESI (m/z): $[M+Na]^+$ calcd 363.1931; found 363.1936.

2'-(3-methoxyprop-1-yn-1-yl)-3,5',5'-trimethyl-3',5',6',7',8',8a'-hexahydro-2'H-spiro[cyclohexane-1,1'-naphthalene]-2,4-dien-6-one (**4b**).

The title compound was obtained in 36% yield as a light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (dd, 1H, *J*=2.2Hz, *J*=9.8Hz), 6.05-6.08 (m, 2H), 5.51-5.53 (m, 1H), 3.94 (dd, 2H, *J*=2.0Hz, *J*=3.2Hz), 3.24 (s, 3H), 2.84-2.90 (m, 2H), 2.27-2.31 (m, 2H), 2.01 (d, 3H, *J*=1.2Hz), 1.36-1.52 (m, 5H), 1.16-1.24 (m, 1H), 1.11 (s, 3H), 1.05 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.5, 145.4, 145.2, 135.6, 131.5, 126.4, 114.4, 86.3, 77.2, 59.8, 56.9, 56.7, 44.2, 40.2, 36.6, 36.1, 29.9, 29.5, 28.8, 28.5, 21.5, 21.2. IR[ν_{max} cm^{-1}] 3274, 3050, 2925, 2866, 2821, 2372, 2230, 1990, 1871, 1719, 1670, 1640, 1570, 1450, 1408, 1381, 1357, 1258, 1231, 1188, 1137, 1097, 1042, 1004, 947, 906, 824, 767, 737, 703, 643, 600, 507, 490, 437. MS-ESI: m/z = 342 $[M+NH_4]^+$. HRMS-ESI (m/z): $[M+Na]^+$ calcd 347.1982; found 347.1987.

2'-(3-methoxyprop-1-yn-1-yl)-5',5'-dimethyl-3',5',6',7',8',8a'-hexahydro-2'H-spiro[cyclohexane-1,1'-naphthalene]-2,4-dien-6-one (**4c**).

The title compound was obtained in 20% yield as a light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99-7.03 (m, 1H), 6.41-6.48 (m, 2H), 6.10 (d, 1H, *J*=9.6Hz), 5.52-5.54 (m, 1H), 3.94 (t, 2H, *J*=1.6Hz), 3.25 (s, 3H), 2.89-2.96 (m, 2H), 2.27-2.34 (m, 2H), 1.37-1.49 (m, 4H), 1.15-1.25 (m, 2H), 1.10 (s, 3H), 1.05 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 206.4, 145.1, 141.8, 141.1, 126.8, 124.2, 114.5, 85.9, 76.9, 59.8, 57.8, 57.2, 44.1, 40.2, 36.6, 36.2, 30.0, 29.6, 28.8, 28.5, 21.2. IR[ν_{max} cm^{-1}] 3381, 3045, 2925, 2853, 2726, 2376, 2235, 1718, 1660, 1631, 1608, 1562, 1508, 1460, 1418, 1378, 1364, 1304, 1234, 1189, 1098, 1028, 1002, 951, 905, 822, 770, 736, 691, 640, 600, 525, 497. MS-ESI: m/z = 328 $[M+NH_4]^+$. HRMS-ESI (m/z): $[M+Na]^+$ calcd 333.1825; found 333.1830.

3-bromo-2'-(3-methoxyprop-1-yn-1-yl)-5',5'-dimethyl-3',5',6',7',8',8a'-hexahydro-2'H-spiro[cyclohexane-1,1'-naphthalene]-2,4-dien-6-one (**4d**).

The title compound was obtained in 28% yield as a light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (dd, 1H, *J*=2.4Hz, *J*=10.0Hz), 6.60 (d, 1H, *J*=2.4Hz), 6.04 (d, 1H, *J*=10.0Hz), 5.52-5.54 (m, 1H), 3.97 (s, 2H), 3.28 (s, 3H), 2.86-2.90 (m, 2H), 2.22-2.39 (m, 2H), 1.38-1.54 (m, 4H), 1.19-1.26 (m, 2H), 1.11 (s, 3H), 1.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.8, 144.8, 144.7, 140.7, 128.2, 116.0, 114.5, 85.3, 77.7, 60.7, 59.8, 57.2, 44.3, 40.1, 36.8, 36.2, 29.9, 29.5, 28.9, 28.7, 21.2. IR[ν_{max} cm^{-1}] 3314, 3052, 2925, 2852, 2368, 2234, 1719, 1665, 1617, 1563, 1509, 1463, 1415, 1380, 1363, 1329, 1272, 1223, 1189, 1152, 1098, 1028, 1003, 946, 905, 848, 822, 795, 736, 706, 647, 600, 559, 505. MS-ESI: m/z = 411 $[M+Na]^+$. HRMS-ESI (m/z): $[M+Na]^+$ calcd 411.0930; found 411.0934.

3-chloro-2'-(3-methoxyprop-1-yn-1-yl)-5',5'-dimethyl-3',5',6',7',8',8a'-hexahydro-2'H-spiro[cyclohexane-1,1'-naphthalene]-2,4-dien-6-one (**4e**).

The title compound was obtained in 22% yield as a light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (dd, 1H, *J*=2.8Hz, *J*=10.0Hz), 6.39 (d, 1H, *J*=2.8Hz), 6.11 (d, 1H, *J*=10.0Hz), 5.52-5.54 (m, 1H), 3.97 (t, 2H, *J*=1.4Hz), 3.27 (s, 3H), 2.87-2.92 (m, 2H), 2.26-2.34 (m, 2H), 1.38-1.50 (m, 4H), 1.14-1.26 (m, 2H), 1.11 (s, 3H), 1.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.1, 144.8, 143.1, 136.3, 128.2, 128.1, 114.5, 85.3, 77.7, 59.8, 59.2, 57.1, 44.5, 40.1, 36.9, 36.2, 29.9, 29.5, 28.9, 28.7, 21.1. IR[ν_{max} cm^{-1}] 3318, 3052, 2926, 2852, 2725, 2368, 2235, 1720, 1666, 1623, 1569, 1534, 1462, 1393, 1379, 1364, 1330, 1259, 1224, 1189, 1150, 1099, 1052, 1028, 1003, 948, 906, 855, 822, 737, 653, 619, 567, 506. MS-ESI: m/z = 362 $[M+NH_4]^+$. HRMS-ESI (m/z):

$[M+Na]^+$ calcd 367.1435; found 367.1440.

ethyl-2'-(3-methoxyprop-1-yn-1-yl)-5',5'-dimethyl-6-oxo-3',5',6',7',8',8a'-hexahydro-2'H-spiro[cyclohexane-1,1'-naphthalene]-2,4-diene-3-carboxylate (**4f**).

The title compound was obtained in 5% yield as a light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, 1H, *J*=2.4Hz, *J*=10.0Hz), 7.44 (d, 1H, *J*=2.0Hz), 6.19 (d, 1H, *J*=10.0Hz), 5.58-5.59 (m, 1H), 4.32 (q, 2H, *J*=7.2Hz), 3.92 (d, 2H, *J*=1.2Hz), 3.21 (s, 3H), 2.96-3.02 (m, 2H), 2.32-2.37 (m, 2H), 1.42-1.49 (m, 4H), 1.37 (t, 3H, *J*=7.2Hz), 1.19-1.23 (m, 2H), 1.13 (s, 3H), 1.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.8, 164.4, 150.2, 144.8, 138.7, 128.8, 127.0, 114.7, 85.2, 77.7, 61.4, 59.8, 57.8, 57.1, 44.4, 40.0, 37.0, 36.3, 29.9, 29.5, 29.3, 28.7, 21.3, 14.3. IR[ν_{max} cm^{-1}] 3317, 3053, 2926, 2853, 2726, 2593, 2375, 1720, 1666, 1638, 1611, 1579, 1545, 1461, 1412, 1366, 1276, 1254, 1225, 1191, 1098, 1063, 1025, 953, 906, 867, 825, 769, 735, 705, 645, 608, 550, 498. MS-ESI: m/z = 405 $[M+Na]^+$. HRMS-ESI (m/z): $[M+Na]^+$ calcd 405.2036; found 405.2041.

2'-(hept-1-yn-1-yl)-3,4-dimethoxy-5',5'-dimethyl-3',5',6',7',8',8a'-hexahydro-2'H-spiro[cyclohexane-1,1'-naphthalene]-2,4-dien-6-one **(4g)**.

The title compound was obtained in 53% yield as a white solid. m.p. 85-87℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.56 (s, 1H), 5.50-5.51 (m, 1H), 5.23 (s, 1H), 3.82 (s, 3H), 3.73 (s, 3H), 2.91-2.94 (m, 1H), 2.80-2.85 (m, 1H), 2.16-2.34 (m, 2H), 1.97-2.01 (m, 2H), 1.51-1.55 (m, 1H), 1.30-1.43 (m, 5H), 1.14-1.25 (m, 6H), 1.10 (s, 3H), 1.05 (s, 3H), 0.87 (t, 3H, *J*=6.8Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.7, 166.4, 148.4, 145.4, 114.5, 107.7, 102.6, 81.6, 79.5, 56.3, 55.9, 55.5, 43.3, 40.3, 36.8, 36.1, 30.8, 30.5, 29.5, 28.9, 28.8, 28.6, 22.1, 21.2, 18.6, 13.9. IR[ν_{max} cm^{-1}] 3255, 3162, 2928, 2860, 2726, 2664, 2377, 2236, 2099, 1871, 1635, 1586, 1454, 1404, 1349, 1319, 1251, 1232, 1189, 1174, 1139, 1071, 1044, 1002, 949, 916, 836, 798, 733, 684, 648, 538, 514, 495, 460. MS-ESI: m/z = 397 $[M+H]^+$. HRMS-ESI (m/z): $[M+Na]^+$ calcd 419.2557; found 419.2560. HPLC on Daicel Chiralpak AS-H, Hexanes / IPA = 90 / 10, 1.0 mL/min^{-1}, λ = 220 nm, t (minor 1) = 4.919 min, t (major 1) =5.714 min, t (minor 2) = 7.280 min, t (major 2) = 8.030 min.

2'-(hept-1-yn-1-yl)-3-methoxy-5',5'-dimethyl-3',5',6',7',8',8a'-hexahydro-2'H-spiro[cyclohexane-1,1'-naphthalene]-2,4-dien-6-one **(4h)**.

The title compound was obtained in 42% yield as a light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (dd, 1H, *J*=3.2Hz, *J*=10.0Hz), 6.06 (d, 1H, *J*=10.0Hz), 5.50-5.51 (m, 1H), 5.15 (d, 1H, *J*=2.8Hz), 3.66 (s, 3H), 2.87-2.90 (m, 1H), 2.75-2.79 (m, 1H), 2.21-2.27 (m, 2H), 1.97-2.01

(m, 2H), 1.46-1.54 (m, 1H), 1.31-1.40 (m, 5H), 1.12-1.26 (m, 6H), 1.10 (s, 3H), 1.05 (s, 3H), 0.88 (t, 3H, *J*=6.8Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.4, 152.4, 145.3, 141.3, 127.8, 114.6, 105.2, 81.6, 79.4, 56.1, 55.0, 44.2, 40.3, 37.3, 36.1, 30.8, 30.5, 29.5, 28.9, 28.8, 28.5, 22.2, 21.2, 18.5, 13.9. IR[ν_{max} cm^{-1}] 3276, 3166, 3049, 2927, 2861, 2666, 2379, 2223, 1947, 1718, 1670, 1640, 1588, 1460, 1407, 1381, 1364, 1327, 1236, 1219, 1182, 1125, 1043, 1016, 979, 896, 828, 797, 778, 730, 690, 624, 532, 488, 458. MS-ESI: m/z = 367 $[M+H]^+$. HRMS-ESI (m/z): $[M+H]^+$ calcd 367.2632; found 367.2637.

2'-(cyclopropylethynyl)-3-methoxy-5',5'-dimethyl-3',5',6',7',8',8a'-hexahydro-2'H-spiro[cyclohexane-1,1'-naphthalene]-2,4-dien-6-one **(4i)**.

The title compound was obtained in 32% yield as a light yellow solid. m.p. 86-88℃ ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (dd, 1H, *J*=3.2Hz, *J*=10.0Hz), 6.05 (d, 1H, *J*=10.0Hz), 5.48-5.50 (m, 1H), 5.12 (d, 1H, *J*=2.8Hz), 3.66 (s, 3H), 2.88-2.90 (m, 1H), 2.69-2.73 (m, 1H), 2.19-2.25 (m, 2H), 1.46-1.54 (m, 1H), 1.34-1.43 (m, 3H), 1.14-1.21 (m, 2H), 1.10 (s, 3H), 1.00-1.05 (m, 4H), 0.59-0.63 (m, 2H), 0.41-0.45 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.2, 152.4, 145.2, 141.3, 127.8, 114.5, 105.2, 84.7, 74.6, 56.2, 55.1, 44.0, 40.3, 37.4, 36.1, 30.4, 29.5, 28.9, 21.2, 8.2, 8.0, -0.6. IR[ν_{max} cm^{-1}] 3401, 3091, 3007, 2927, 2866, 2664, 2370, 2210, 1892, 1736, 1670, 1640, 1587, 1460, 1407, 1364, 1324, 1257, 1235, 1181, 1124, 1039, 978, 901, 828, 797, 748, 690, 622, 545, 490, 448. MS-ESI: m/z = 337 $[M+H]^+$. HRMS-ESI (m/z): $[M+H]^+$ calcd 337.2162; found 337.2169. HPLC on Daicel Chiralpak AS-H, Hexanes / IPA = 90 / 10, 1.0 mL/min^{-1}, λ = 220 nm, t (major 1) =4.358 min, t (major 2) =4.945 min, t (minor 1) = 5.980 min, t (minor 2) = 6.505 min.

3-methoxy-5',5'-dimethyl-2'-(phenylethynyl)-3',5',6',7',8',8a'-hexahydro-2'H-spiro[cyclohexane-1,1'-naphthalene]-2,4-dien-6-one **(4j)**.

The title compound was obtained in 25% yield as a light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 5H), 6.87 (dd, 1H, *J*=2.8Hz, *J*=10.4Hz), 6.12 (d, 1H, *J*=10.4Hz), 5.55-5.56 (m, 1H), 5.21 (d, 1H, *J*=2.8Hz), 3.68 (s, 3H), 2.96-3.02 (m, 2H), 2.34-2.40 (m, 2H), 1.40-1.46 (m, 4H), 1.16-1.29 (m, 2H), 1.13 (s, 3H), 1.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.1, 152.6, 145.5, 141.5, 131.6, 128.1, 127.9, 127.6, 123.6, 114.4, 105.0, 89.4, 81.7, 56.0, 55.2, 44.0, 40.4, 37.9, 36.2, 30.0, 29.5, 28.9, 28.8, 21.2. IR[ν_{max} cm^{-1}] 3368, 3053, 2926, 2854, 2725, 2376, 2200, 1952, 1720, 1669, 1639, 1588, 1489, 1460, 1407, 1379, 1236, 1167, 1123, 1035, 974, 913, 828, 798, 757, 692, 631, 536, 489. MS-ESI: m/z = 373 $[M+H]^+$. HRMS-ESI (m/z): $[M+H]^+$ calcd 373.2162; found

373.2168.

3-methoxy-5',5'-dimethyl-2'-((trimethylsilyl)ethynyl)-3',5',6',7',8',8a'-hexahydro-2'H-spiro[cyclohexane-1,1'-naphthalene]-2,4-dien-6-one **(4k)**.

The title compound was obtained in 23% yield as a light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (dd, 1H, *J*=2.8Hz, *J*=10.0Hz), 6.07 (d, 1H, *J*=10.0Hz), 5.49-5.51 (m, 1H), 5.13 (d, 1H, *J*=2.8Hz), 3.66 (s, 3H), 2.88-2.91 (m, 1H), 2.75-2.79 (m, 1H), 2.24-2.30 (m, 2H), 1.37-1.54 (m, 4H), 1.13-1.26 (m, 2H), 1.11 (s, 3H), 1.05 (s, 3H), 0.03 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.9, 152.6, 145.3, 141.5, 128.0, 114.2, 106.4, 104.9, 85.7, 56.0, 55.1, 43.9, 40.3, 38.2, 36.2, 30.0, 29.5, 28.9, 21.2, -0.02. IR[ν_{max} cm^{-1}] 3398, 3051, 2927, 2855, 2663, 2373, 2174, 1946, 1785, 1736, 1671, 1641, 1588, 1460, 1407, 1381, 1323, 1250, 1236, 1182, 1123, 1040, 1007, 961, 895, 843, 797, 760, 694, 672, 628, 536, 489. MS-ESI: m/z = 369 $[M+H]^+$. HRMS-ESI (m/z): $[M+Na]^+$ calcd 391.2064; found 391.2069.

4-methoxy-11-(3-methoxyprop-1-yn-1-yl)-8,9-dimethylspiro[5.5]undeca-2,4,8-trien-1-one **(4l-1)**.

The title compound was obtained in 43% yield as a light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (dd, 1H, *J*=2.8Hz, *J*=10.0Hz), 6.11 (d, 1H, *J*=10.0Hz), 5.25 (d, 1H, *J*=2.8Hz), 3.95 (t, 2H, *J*=1.8Hz), 3.63 (s, 3H), 3.24 (s, 3H), 3.00-3.06 (m, 1H), 2.53-2.57 (m, 1H), 2.24-2.27 (m, 2H), 1.76 (d, 1H, *J*=16Hz), 1.68 (s, 3H), 1.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.5, 151.8, 141.6, 127.6, 123.2, 123.0, 105.6, 86.6, 76.9, 59.8, 56.9, 55.0, 51.3, 42.3, 35.5, 35.3, 18.9, 18.5. IR[ν_{max} cm^{-1}] 3331, 3050, 2909, 2840, 2733, 2230, 1990, 1720, 1669, 1641, 1587, 1449, 1406, 1356, 1313, 1261, 1237, 1210, 1186, 1147, 1096, 1022, 948, 907, 872, 828, 769, 737, 673, 627, 581, 540, 484. MS-ESI: m/z = 304 $[M+NH_4]^+$. HRMS-ESI (m/z): $[M+Na]^+$ calcd 309.1461; found 309.1467.

6-methoxy-4-(3-methoxyprop-1-yn-1-yl)-2-methyl-2-(prop-1-en-2-yl)chromane **(4l-2)**.

The title compound was obtained in 37% yield as a light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, 1H, *J*=2.4Hz), 6.73-6.79 (m, 2H), 5.12 (s, 1H), 4.89 (t, 1H, *J*=1.4Hz), 4.14 (d, 2H, *J*=2.0Hz), 3.90-3.94 (m, 1H), 3.77 (s, 3H), 3.39 (s, 3H), 2.20 (dd, 1H, *J*=5.6Hz, *J*=13.6Hz), 2.05 (dd, 1H, *J*=11.2Hz, *J*=13.6Hz), 1.86 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 148.4, 146.8, 121.0, 118.0, 114.7, 113.2, 110.5, 87.5, 77.6, 77.5, 60.1, 57.5, 55.7, 37.5, 26.0, 22.9, 18.8. IR[ν_{max} cm^{-1}] 3438, 3092, 2932, 2835, 2375, 2058, 1690, 1646, 1617, 1588, 1490, 1431, 1375, 1281, 1226, 1087, 1039, 964, 906, 817, 736, 704, 561, 491. MS-ESI: m/z = 304 $[M+NH_4]^+$.

HRMS-ESI (m/z): $[M+Na]^+$ calcd 309.1461; found 309.1469.

4-methoxy-11-(3-methoxyprop-1-yn-1-yl)-8-methylspiro[5.5]undeca-2,4,8-trien-1-one **(4m-1)**.

The title compound was obtained in 30% yield as a light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (dd, 1H, *J*=3.2Hz, *J*=10.0Hz), 6.11 (d, 1H, *J*=10.4Hz), 5.40-5.41 (m, 1H), 5.28 (d, 1H, *J*=3.2Hz), 3.95 (t, 2H, *J*=1.6Hz), 3.63 (s, 3H), 3.24 (s, 3H), 3.06-3.10 (m, 1H), 2.51-2.56 (m, 1H), 2.16-2.32 (m, 2H), 1.90 (dd, 1H, *J*=5.6Hz, *J*=17.2Hz), 1.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.7, 151.8, 141.6, 131.5, 127.6, 118.4, 105.4, 86.5, 77.2, 59.8, 57.0, 55.0, 50.3, 36.5, 35.4, 33.9, 22.9. IR[ν_{max} cm^{-1}] 3332, 2926, 2851, 2731, 2372, 2230, 1980, 1721, 1668, 1642, 1587, 1449, 1407, 1358, 1332, 1258, 1235, 1208, 1186, 1137, 1098, 1026, 1003, 946, 912, 856, 829, 792, 768, 671, 560, 535, 489, 440. MS-ESI: m/z = 290 $[M+NH_4]^+$. HRMS-ESI (m/z): $[M+Na]^+$ calcd 295.1305; found 295.1311.

6-methoxy-4-(3-methoxyprop-1-yn-1-yl)-2-methyl-2-vinylchromane **(4m-2)**.

The title compound was obtained in 35% yield as a light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (s, 1H), 6.73-6.79 (m, 2H), 6.03 (dd, 1H, *J*=10.8Hz, *J*=17.6Hz), 5.33 (d, 1H, *J*=17.2Hz), 5.12 (d, 1H, *J*=11.2Hz), 4.13 (s, 2H), 3.91-3.95 (m, 1H), 3.77 (s, 3H), 3.38 (s, 3H), 2.15 (dd, 1H, *J*=6.0Hz, *J*=13.6Hz), 2.01 (dd, 1H, *J*=10.8Hz, *J*=13.6Hz), 1.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 146.6, 142.5, 120.9, 118.1, 114.7, 113.4, 113.1, 87.6, 77.5, 75.5, 60.1, 57.4, 55.7, 38.5, 25.9, 23.4. IR[ν_{max} cm^{-1}] 3417, 3088, 2930, 2836, 2596, 2378, 2237, 2060, 1854, 1736, 1689, 1618, 1489, 1431, 1375, 1284, 1221, 1096, 1038, 990, 929, 868, 818, 734, 705, 680, 555, 512. MS-ESI: m/z = 290 $[M+NH_4]^+$. HRMS-ESI (m/z): $[M+Na]^+$ calcd 295.1305; found 295.1308.

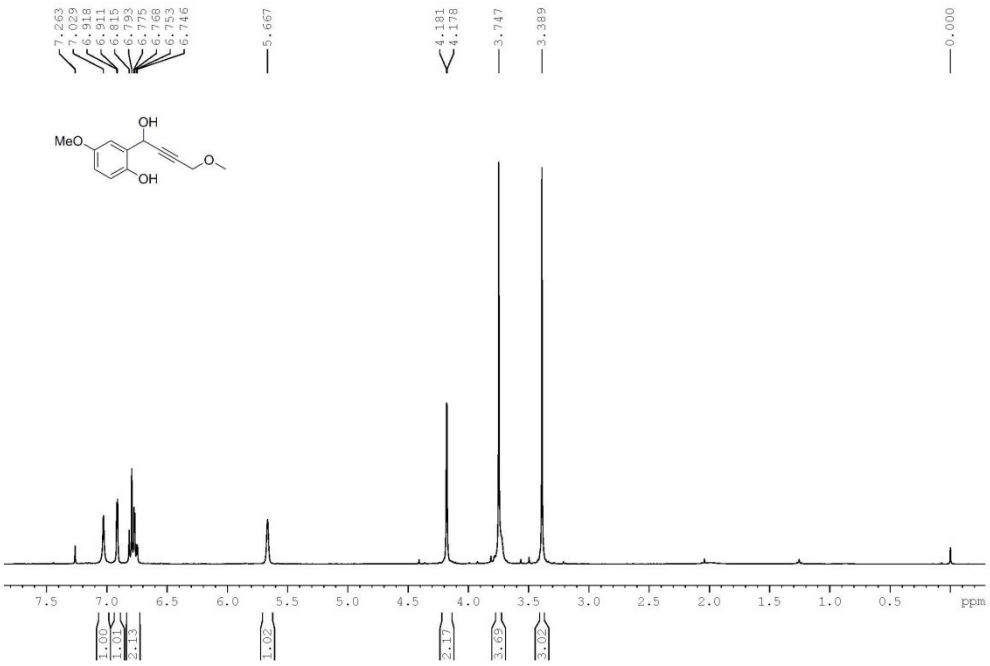
4-methoxy-8-methyl-11-(phenylethynyl)spiro[5.5]undeca-2,4,8-trien-1-one **(4n-1)**. The title compound was obtained in 23% yield as a light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23(s, 5H), 6.91 (dd, 1H, *J*=2.8Hz, *J*=10.0Hz), 6.16 (d, 1H, *J*=10.0Hz), 5.43-5.44 (m, 1H), 5.33 (d, 1H, *J*=2.8Hz), 3.65 (s, 3H), 3.20 (dd, 1H, *J*=6.0Hz, *J*=11.6Hz), 2.60-2.65 (m, 1H), 2.24-2.40 (m, 2H), 1.94 (dd, 1H, *J*=5.2Hz, *J*=17.2Hz), 1.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.9, 151.9, 141.6, 131.5, 131.4, 128.0, 127.8, 127.6, 123.4, 118.4, 105.4, 89.4, 81.7, 55.0, 50.5, 36.3, 36.0, 33.9, 23.0. IR[ν_{max} cm^{-1}] 3330, 3059, 2916, 2849, 2372, 2346, 2200, 1949, 1878, 1852, 1774, 1738, 1687, 1666, 1639, 1589, 1562, 1544, 1509, 1460, 1407, 1375, 1232, 1207, 1174, 1104, 1031, 854, 825, 789, 758, 724, 692, 535, 488.

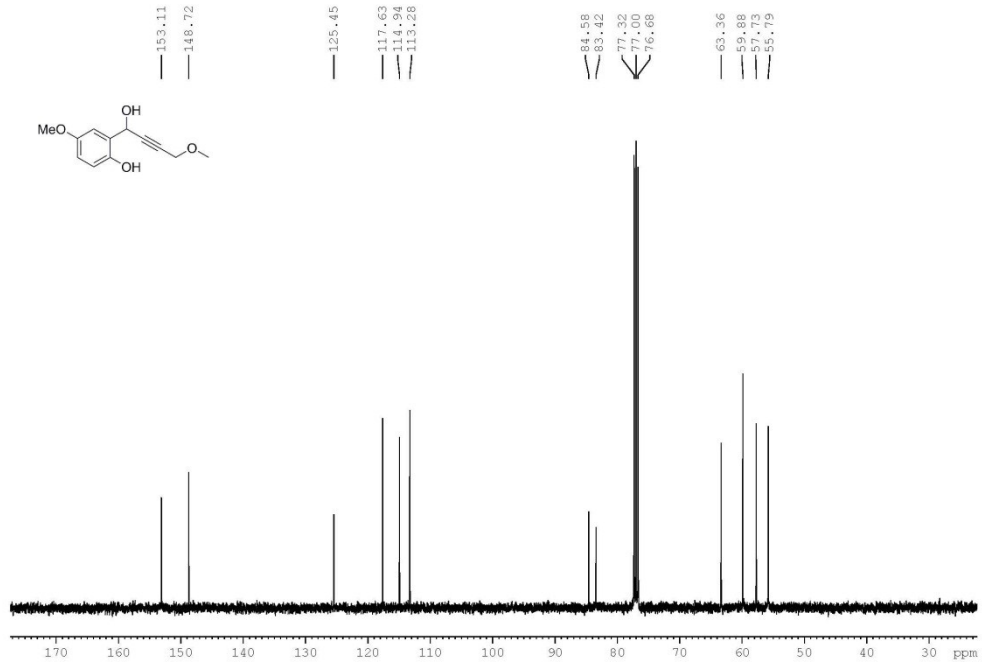
MS-ESI: m/z = 305 $[M+H]^+$. HRMS-ESI (m/z): $[M+H]^+$ calcd 305.1536; found 305.1532.

6-methoxy-2-methyl-4-(phenylethynyl)-2-vinylchromane **(4n-2)**.

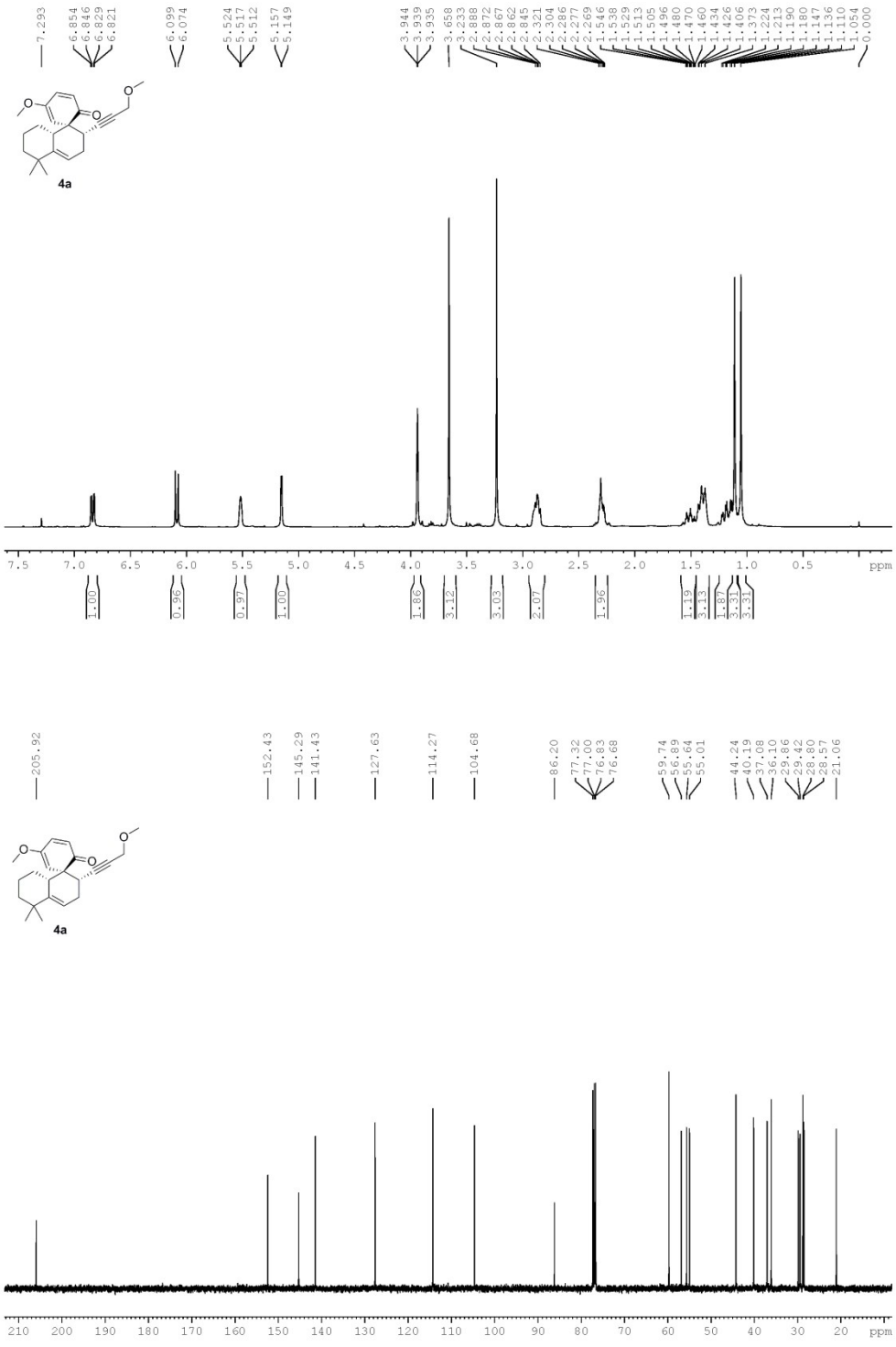
The title compound was obtained in 44% yield as a light yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.43 (m, 2H), 7.28-7.30 (m, 3H), 7.10 (d, 1H, *J*=2.4Hz), 6.75-6.84 (m, 2H), 6.06 (dd, 1H, *J*=10.8Hz, *J*=17.2Hz), 5.36 (dd, 1H, *J*=0.8Hz, *J*=17.2Hz), 5.15 (dd, 1H, *J*=0.8Hz, *J*=10.8Hz), 4.10 (dd, 1H, *J*=6.0Hz, *J*=10.4Hz), 3.77 (s, 3H), 2.22 (dd, 1H, *J*=6.0Hz, *J*=13.6Hz), 2.11 (dd, 1H, *J*=10.4Hz, *J*=13.6Hz), 1.38 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 146.6, 142.5, 131.6, 128.2, 127.9, 123.3, 121.1, 118.1, 114.7, 113.4, 113.2, 90.5, 82.0, 75.6, 55.7, 38.4, 26.4, 23.5. IR[ν_{max} cm^{-1}] 3059, 2929, 2855, 2375, 2226, 2066, 1954, 1878, 1689, 1598, 1492, 1427, 1373, 1266, 1219, 1146, 1093, 1039, 927, 911, 812, 757, 692, 531, 485. MS-ESI: m/z = 305 $[M+H]^+$. HRMS-ESI (m/z): $[M+H]^+$ calcd 305.1536; found 305.1529.

^{1}H and ^{13}C NMR Spectra of Compound **5a**

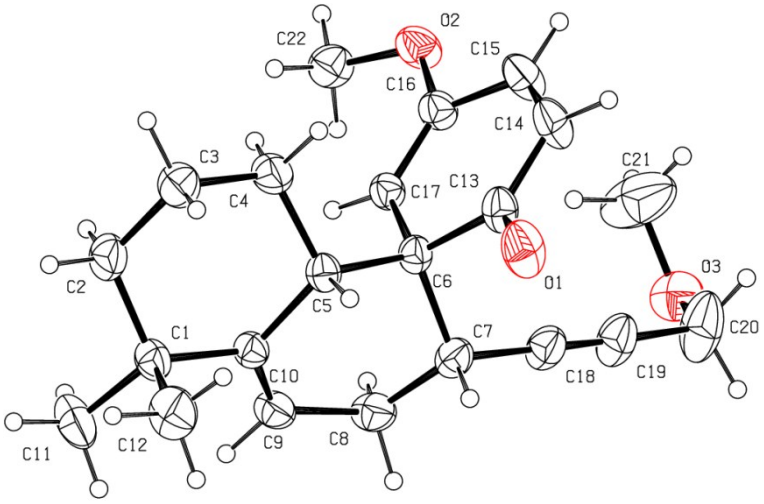




^{1}H and ^{13}C NMR Spectra of Compound **4a**



X-ray Analysis of Compound **4a**.

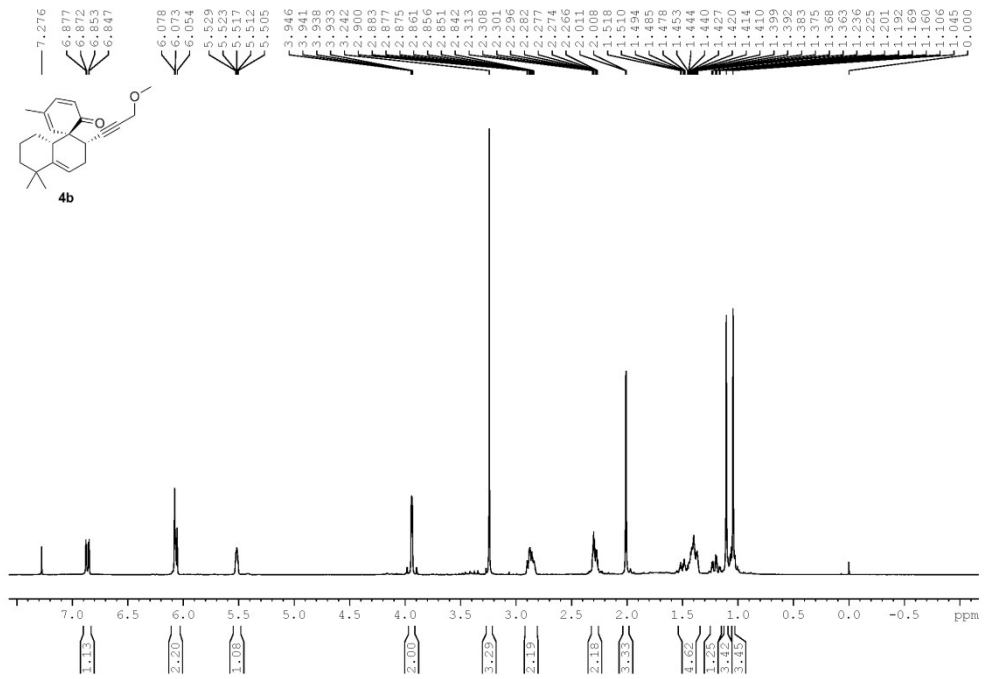


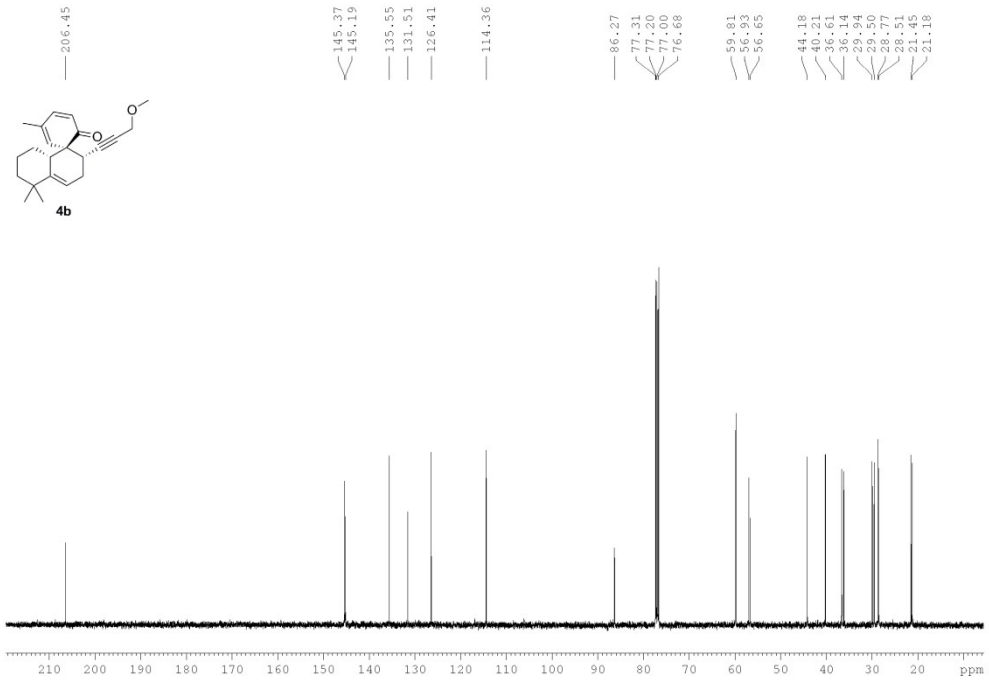
The crystallographic data of **4a** were summarized in the following table.

Bond precision:	C-C = 0.0032 A		Wavelength=0.71073
Cell:	a=7.9086(8)	b=9.3782(9)	c=13.0792(8)
	alpha=93.991(6)	beta=93.766(6)	gamma=94.466(8)
Temperature: 293 K			
	Calculated		Reported
Volume	962.30(15)		962.30(15)
Space group	P -1		P -1
Hall group	-P 1		-P 1
Moiety formula	C22 H28 O3		C22 H28 O3
Sum formula	C22 H28 O3		C22 H28 O3
Mr	340.44		340.44
Dx, g cm-3	1.175		1.175
Z	2		2
Mu (mm-1)	0.076		0.076
F000	368.0		368.0
F000'	368.17		
h, k, lmax	9, 11, 16		9, 11, 16
Nref	3801		3788
Tmin, Tmax	0.965, 0.977		0.724, 1.000
Tmin'	0.965		
Correction method= MULTI-SCAN			
Data completeness= 0.997		Theta(max)= 26.018	
R(reflections)= 0.0616(2450)		wR2(reflections)= 0.1789(3788)	
S = 1.032	Npar= 231		

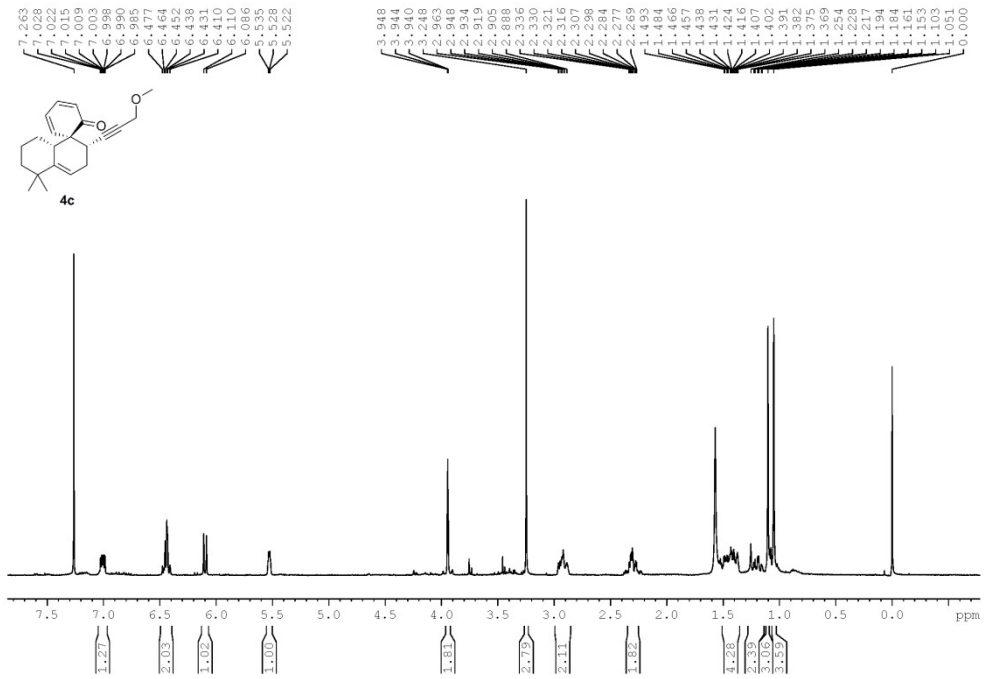
CIF file of **4a** can be obtained from the Cambridge Crystallographic Data Centre using deposition number CCDC 1447716. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax:+44(1223)336033; e-mail: deposit@ccdc.cam.ac.uk].

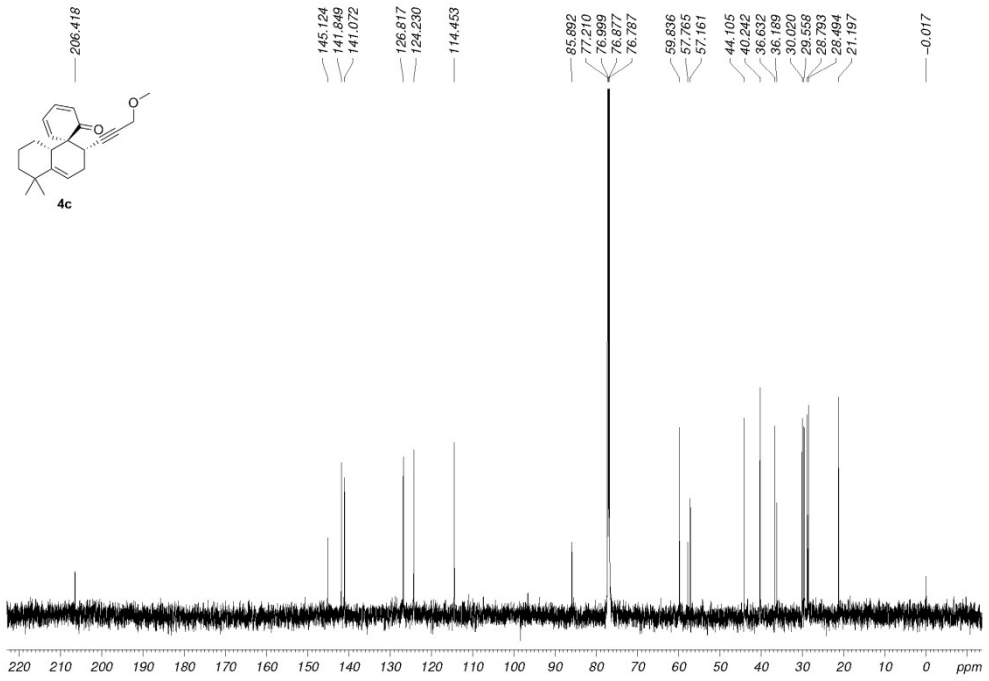
^{1}H and ^{13}C NMR Spectra of Compound **4b**



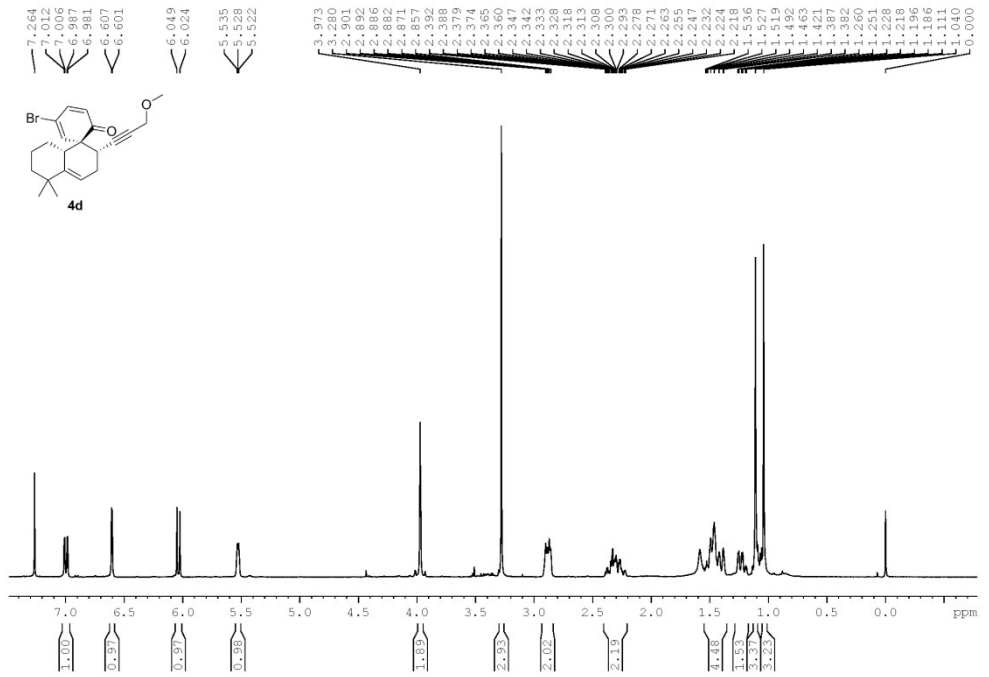


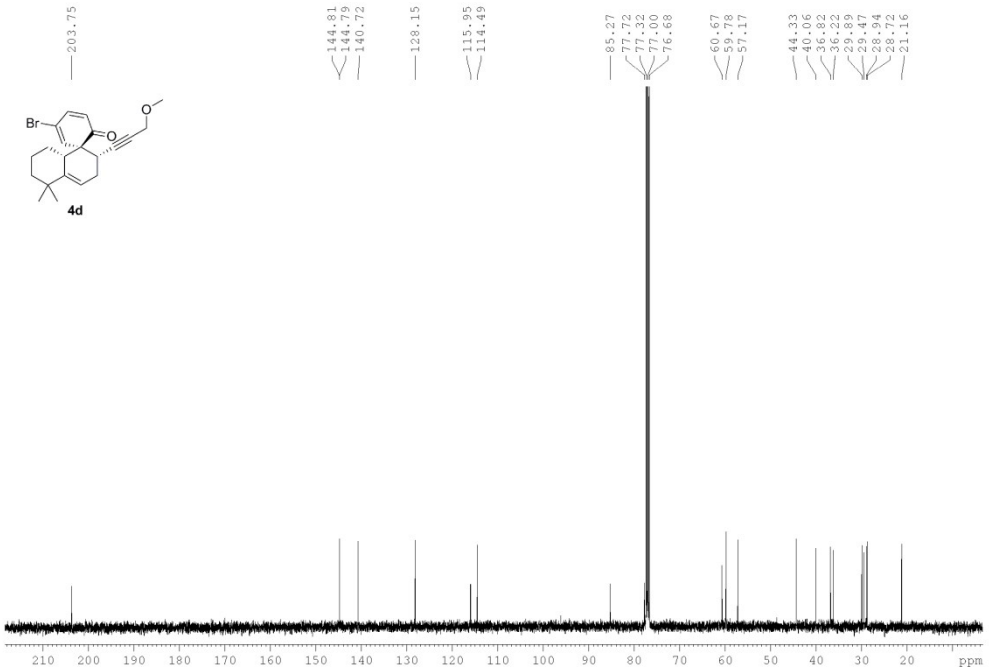
^{1}H and ^{13}C NMR Spectra of Compound **4c**



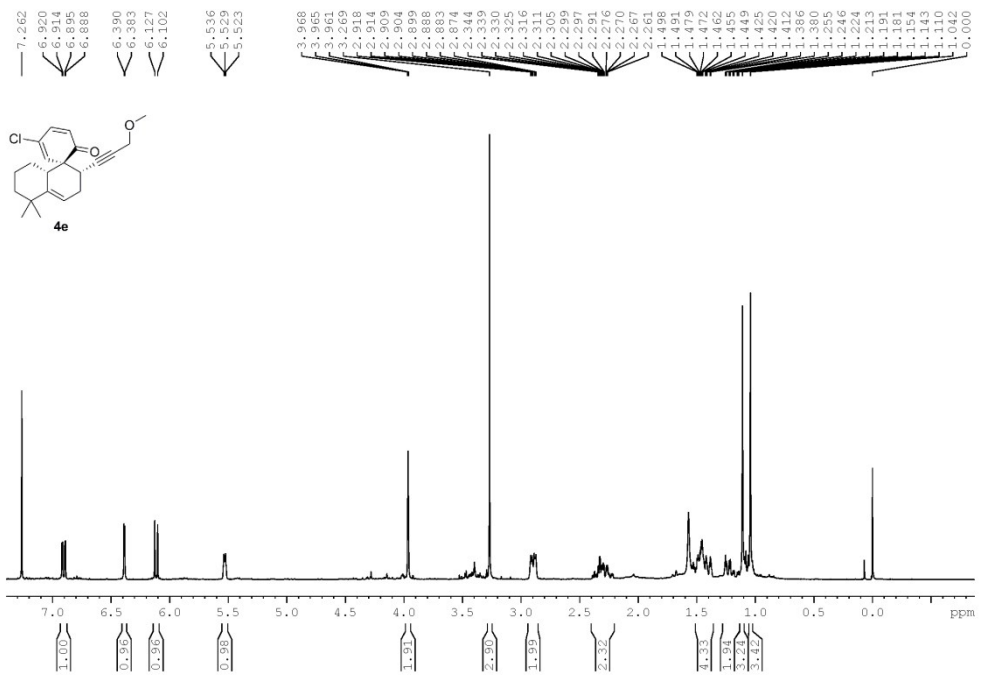


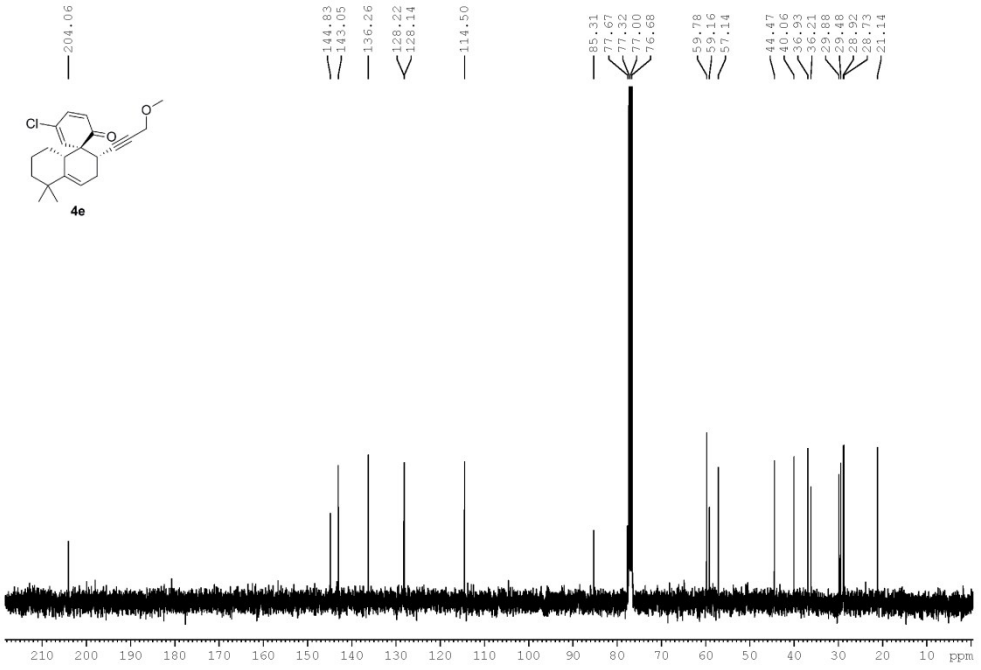
^{1}H and ^{13}C NMR Spectra of Compound **4d**



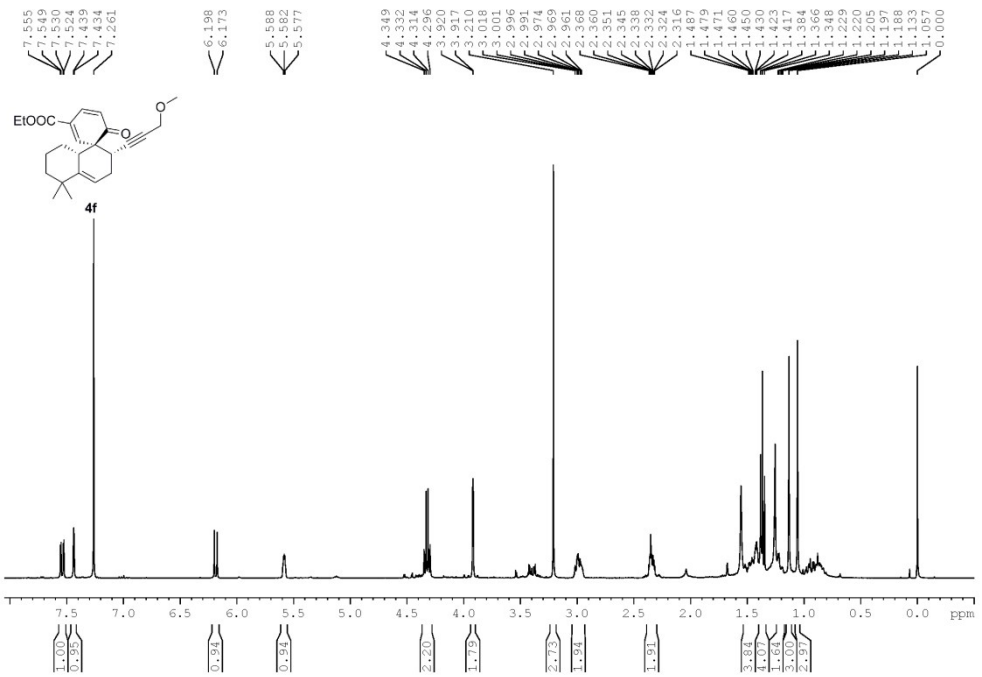


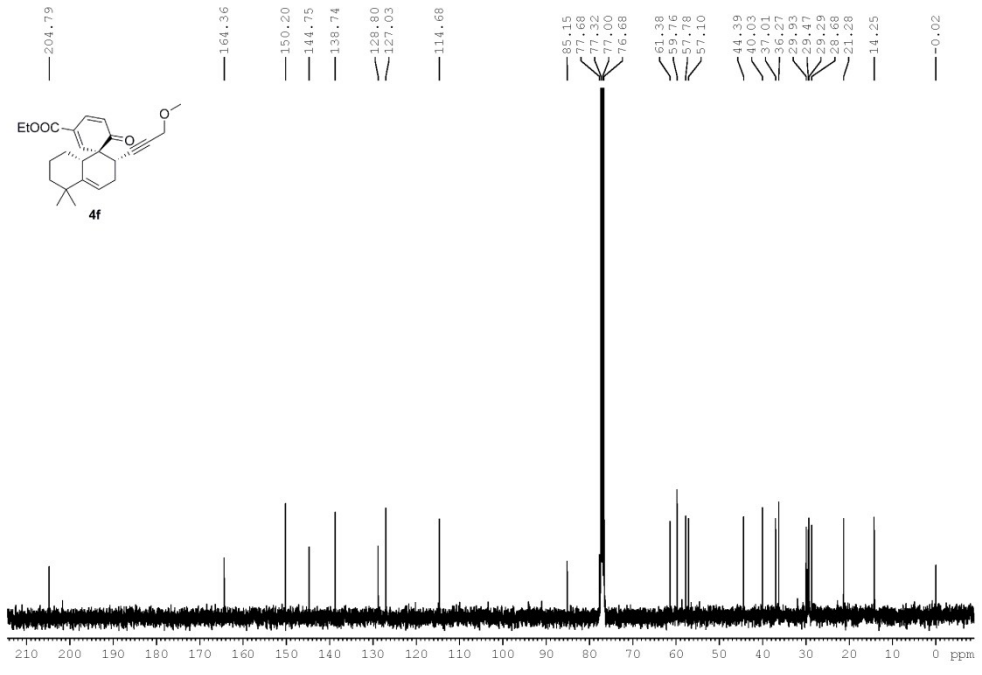
^{1}H and ^{13}C NMR Spectra of Compound **4e**



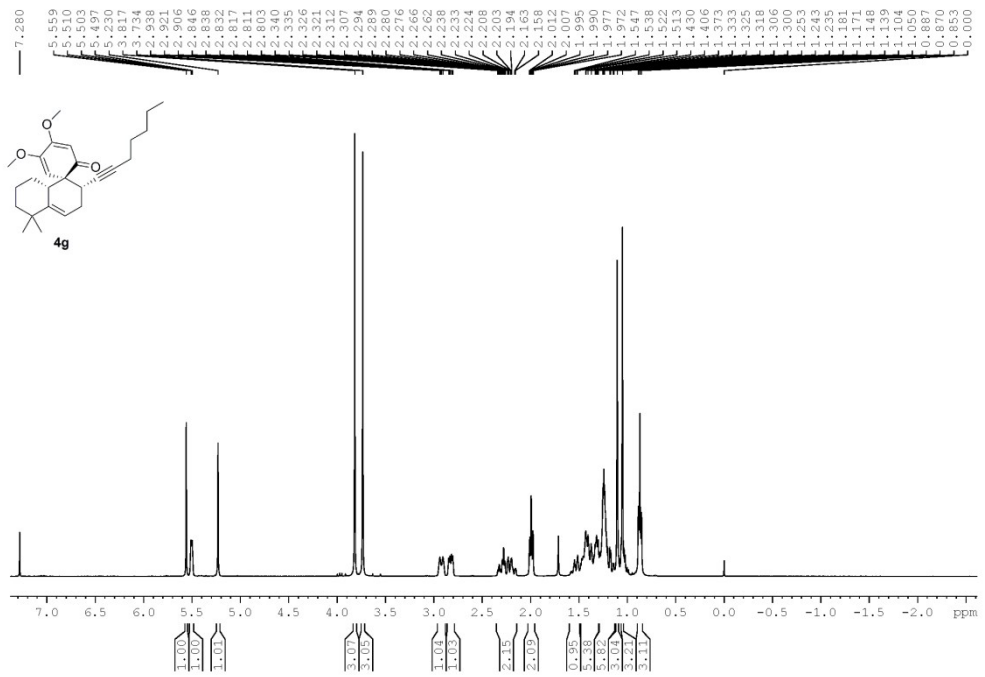


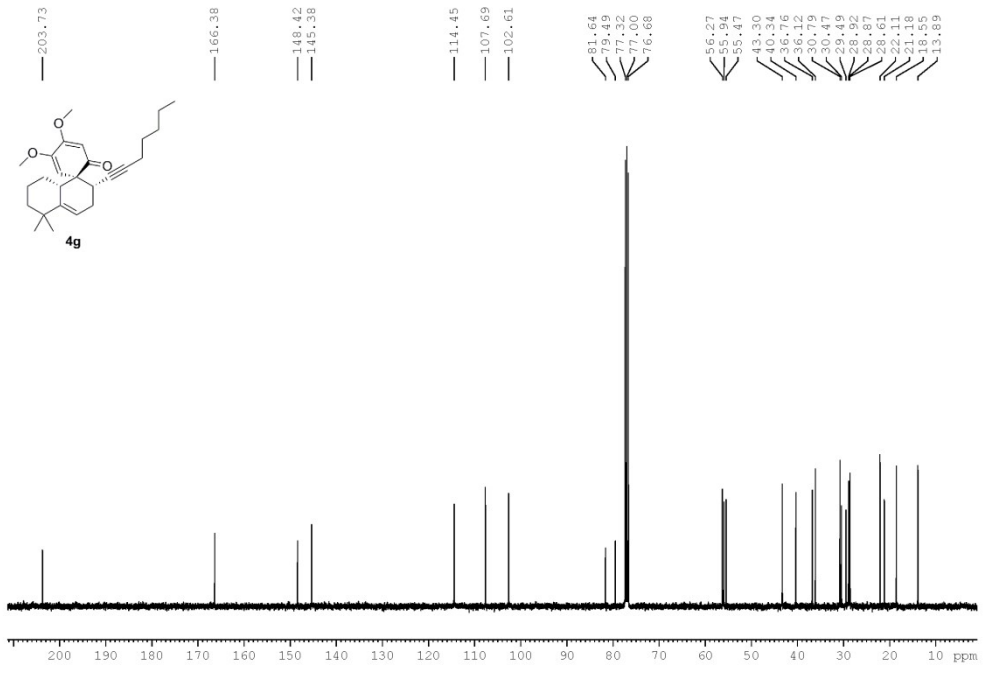
^{1}H and ^{13}C NMR Spectra of Compound **4f**



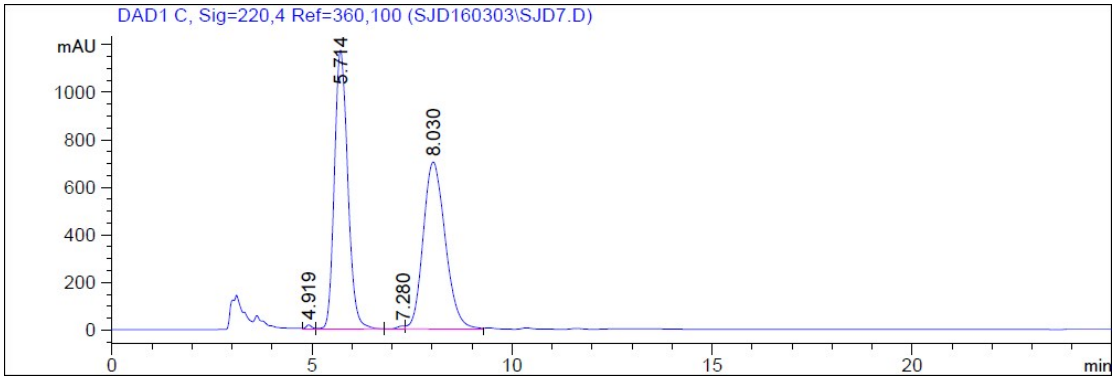


^{1}H and ^{13}C NMR Spectra of Compound **4g**





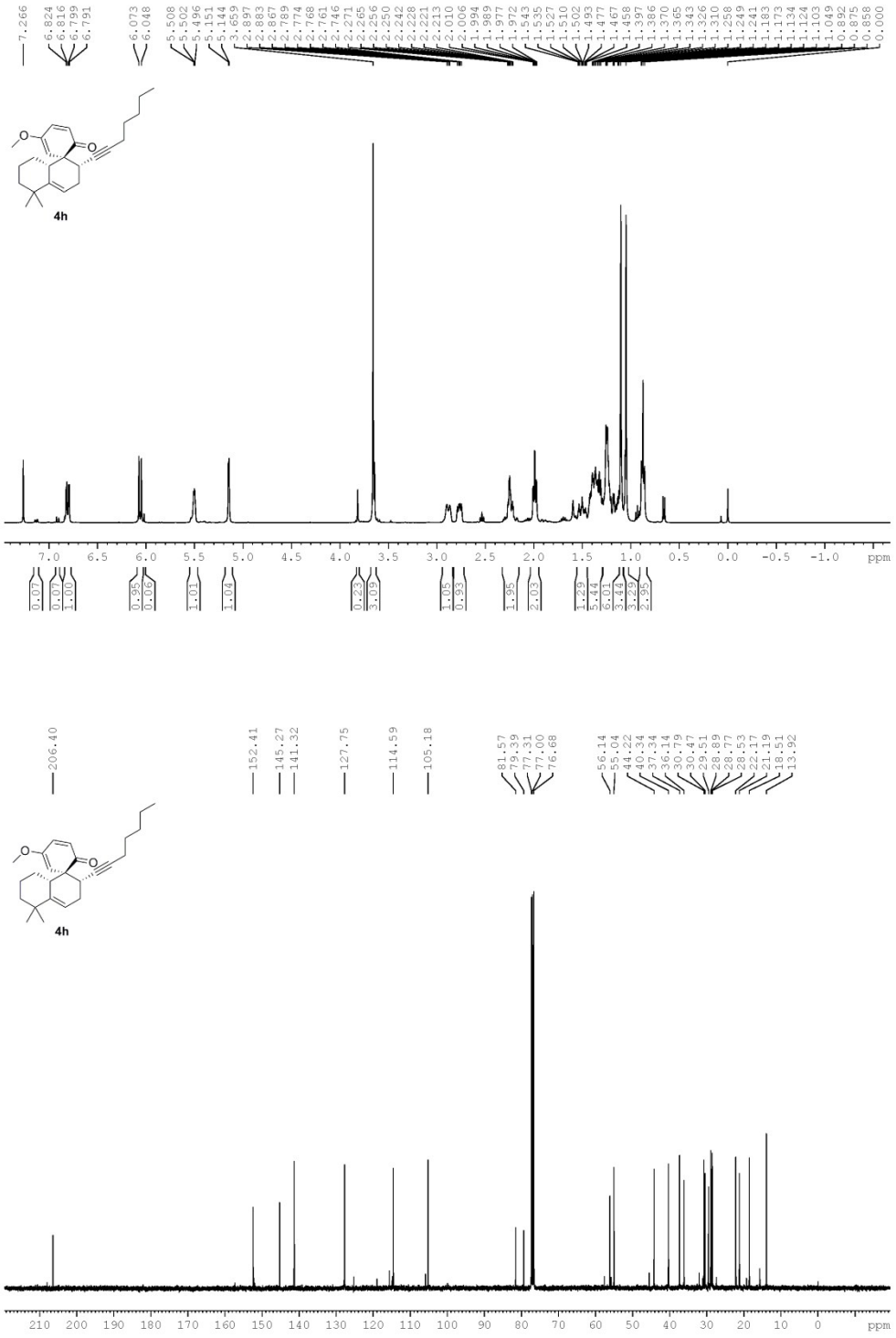
HPLC Spectra of Compound **4g**



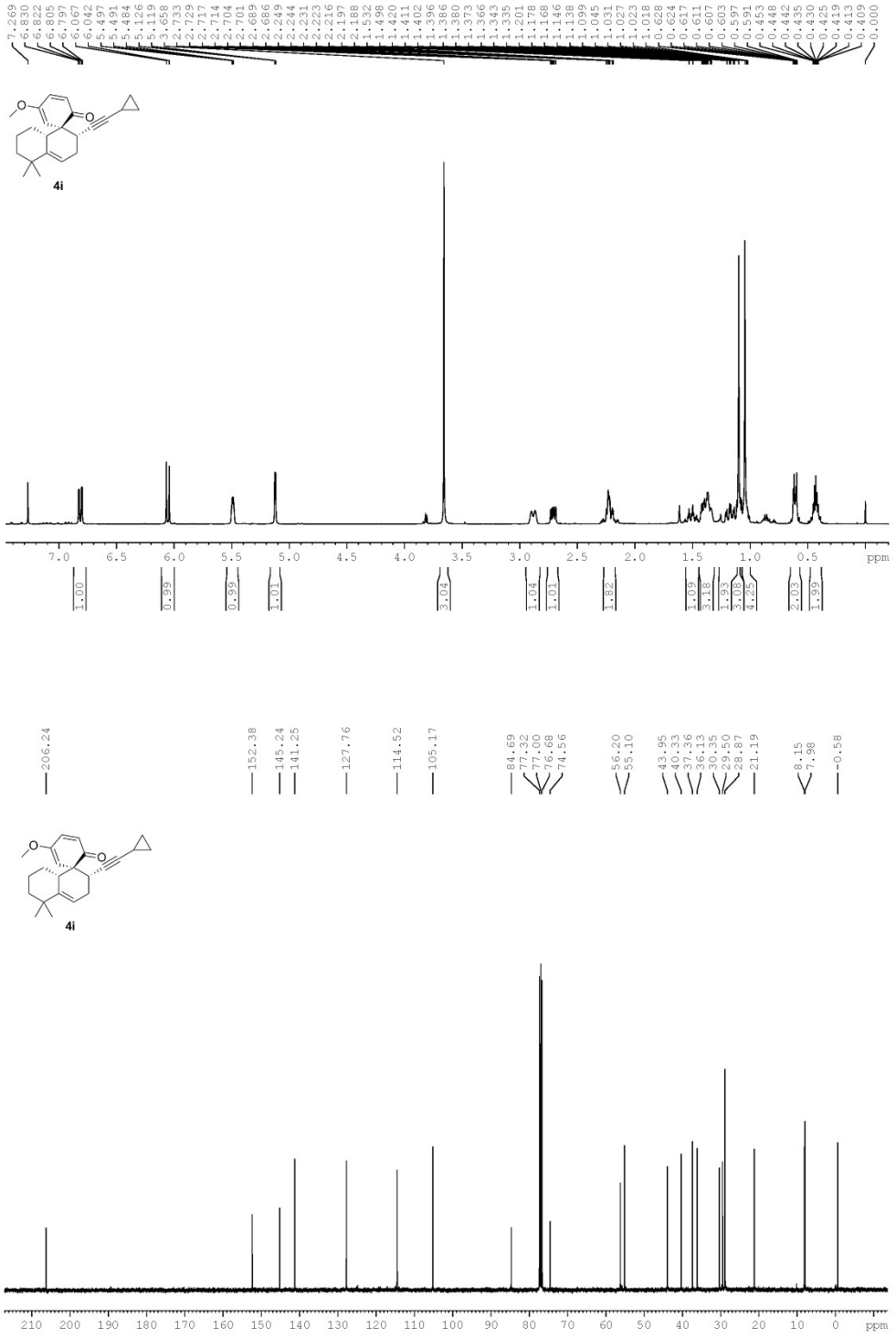
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰面积 %	名称
1	4.919	VV	0.1500	182.33575	0.3336	?
2	5.714	VB	0.3635	2.72960e4	49.9474	?
3	7.280	BV	0.1930	152.86998	0.2797	?
4	8.030	VV	0.5988	2.70183e4	49.4392	?

总量 : 5.46495e4

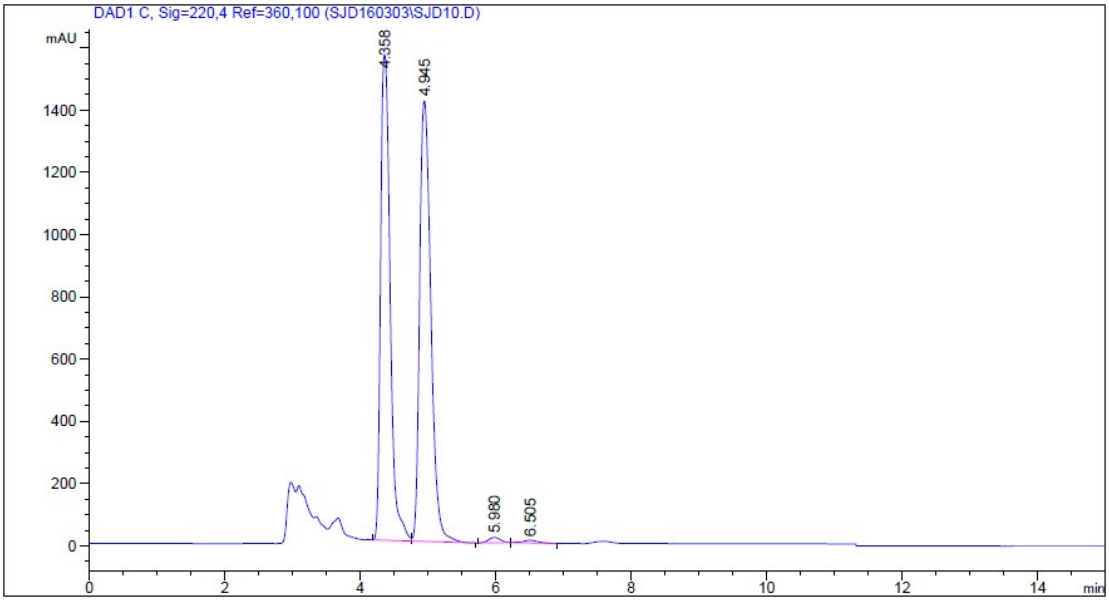
^{1}H and ^{13}C NMR Spectra of Compound **4h**



^{1}H and ^{13}C NMR Spectra of Compound **4i**



HPLC Spectra of Compound **4i**

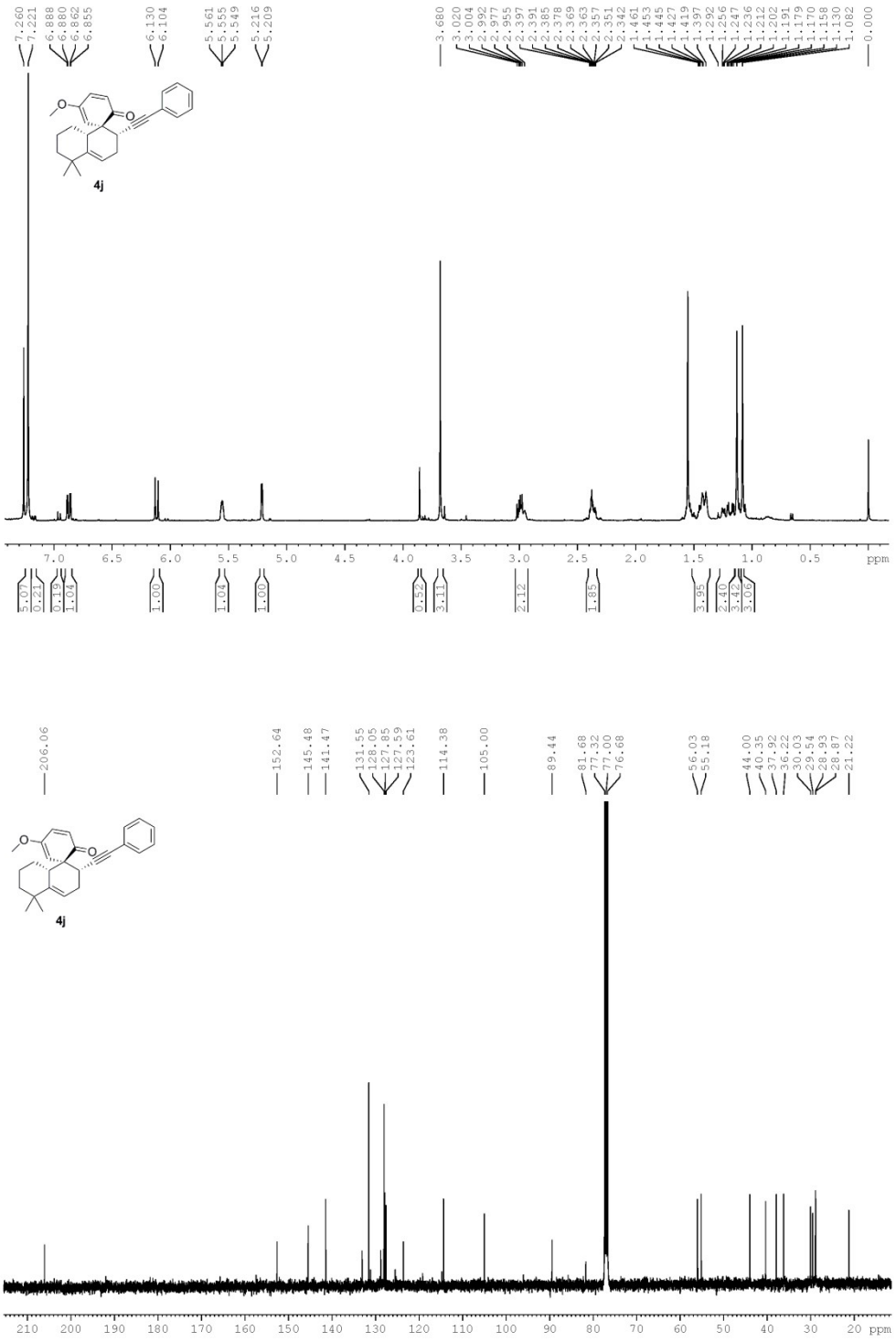


信号 1: DAD1 C, Sig=220,4 Ref=360,100

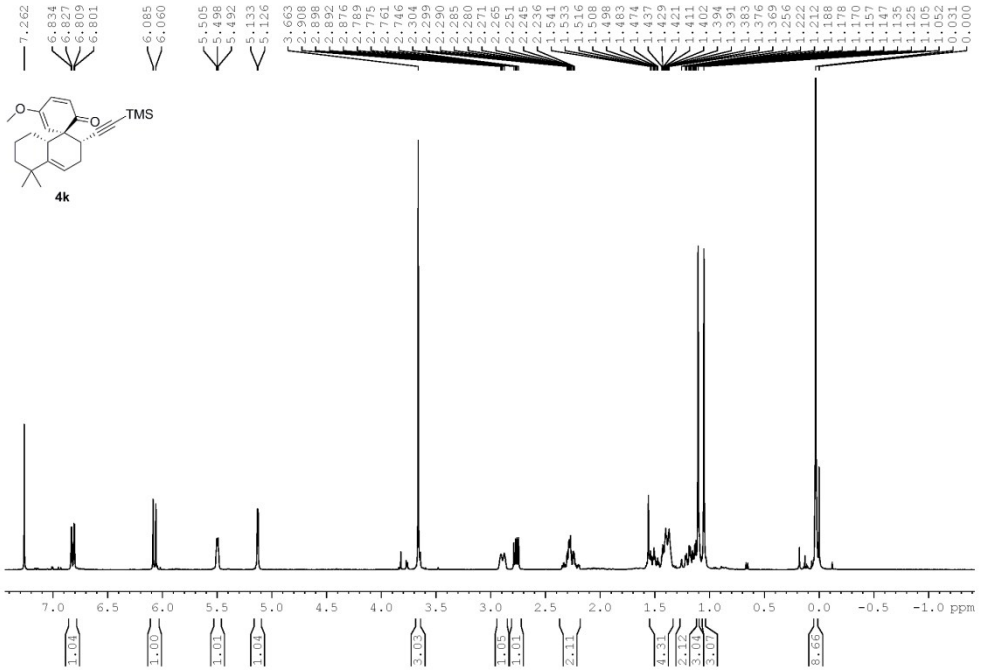
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰面积 %	名称
1	4.358	BV	0.1540	1.52575e4	47.9092	?
2	4.945	VB	0.1820	1.62590e4	51.0539	?
3	5.980	BB	0.1925	201.99136	0.6343	?
4	6.505	BB	0.2117	128.23123	0.4027	?

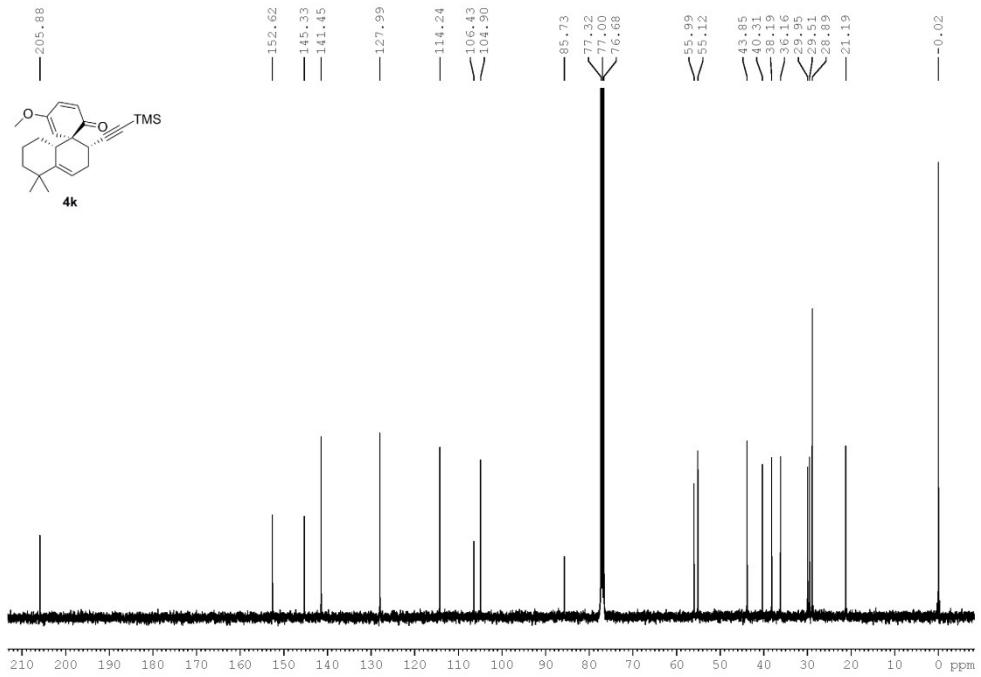
总量 : 3.18467e4

^{1}H and ^{13}C NMR Spectra of Compound **4j**

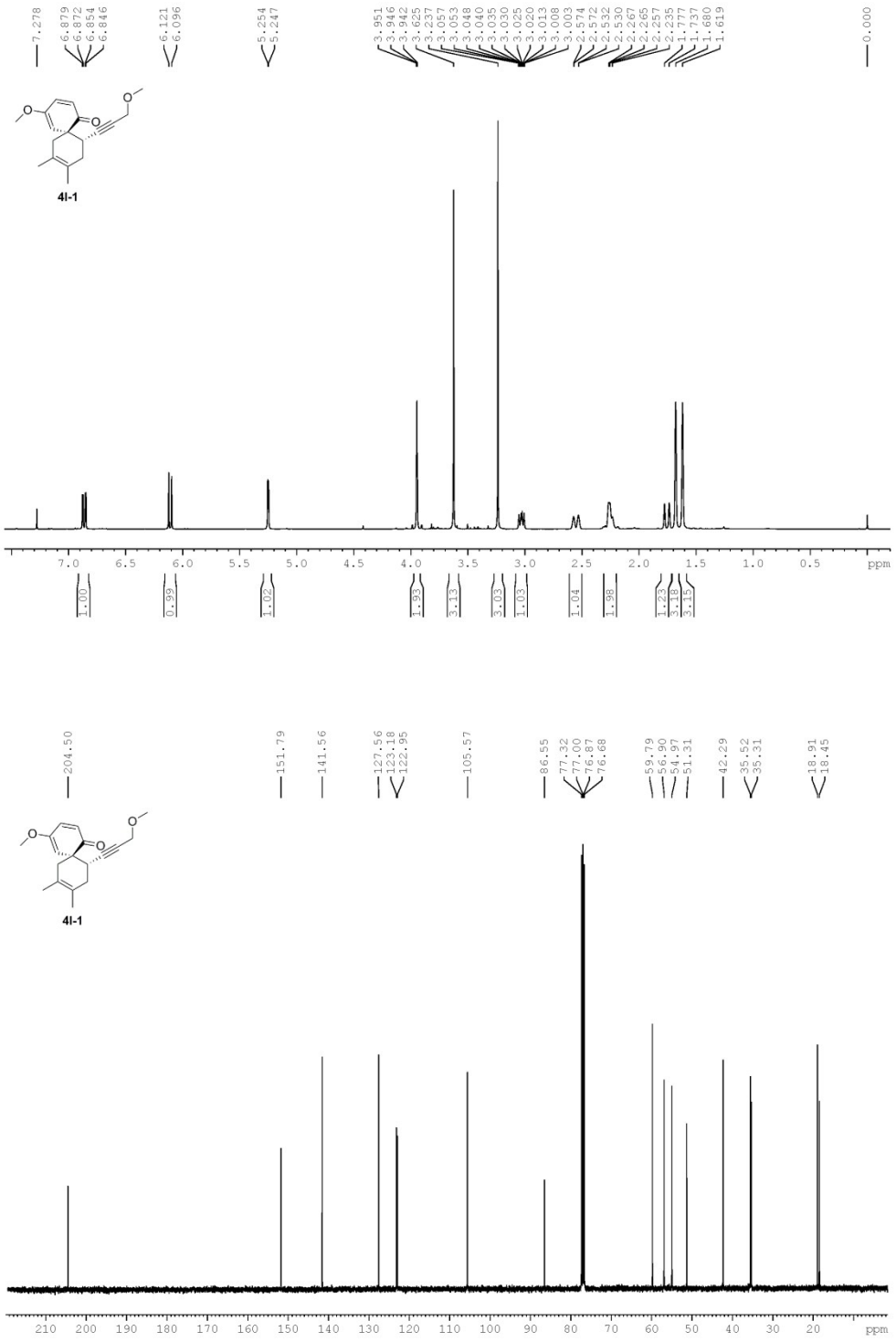


^{1}H and ^{13}C NMR Spectra of Compound **4k**

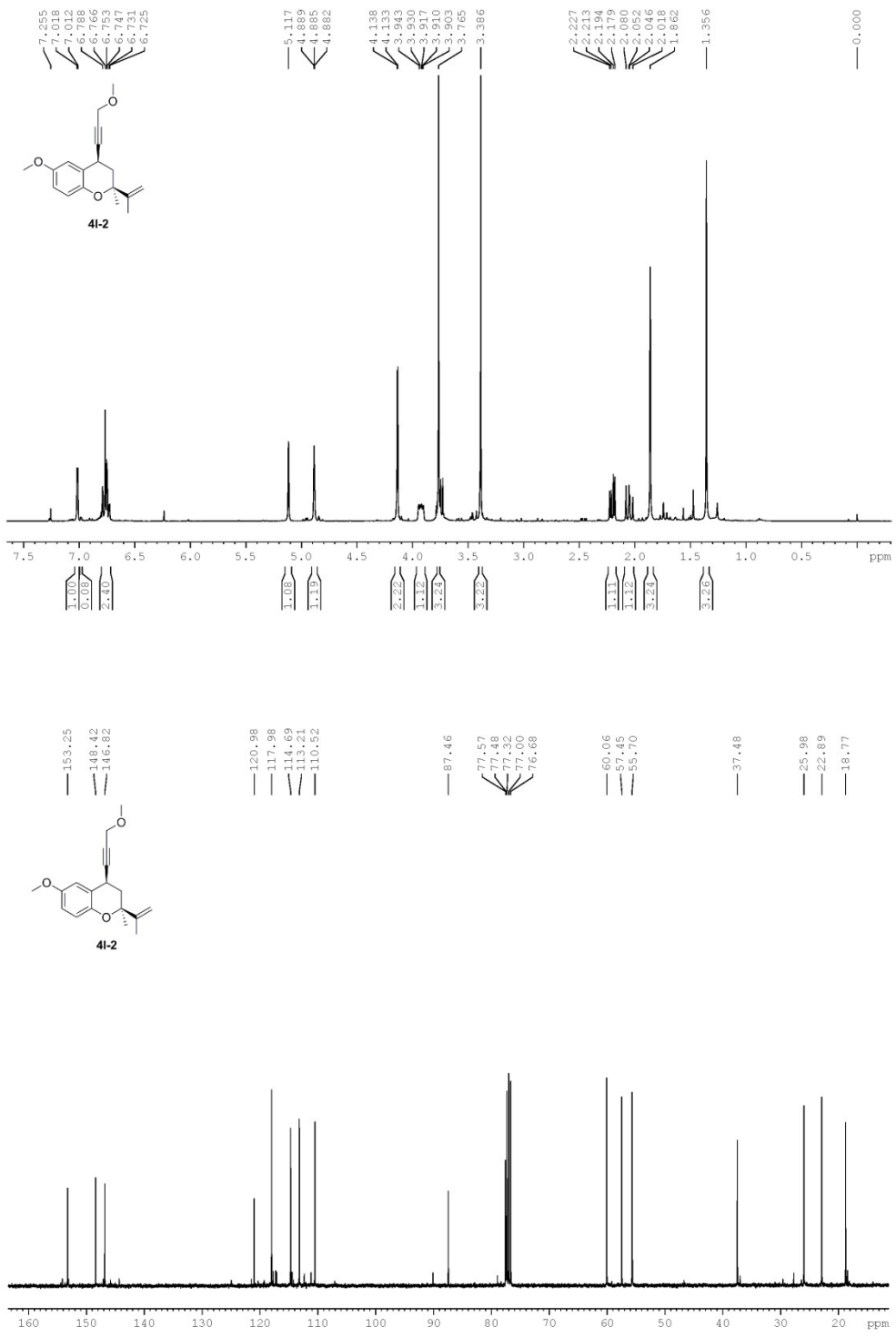




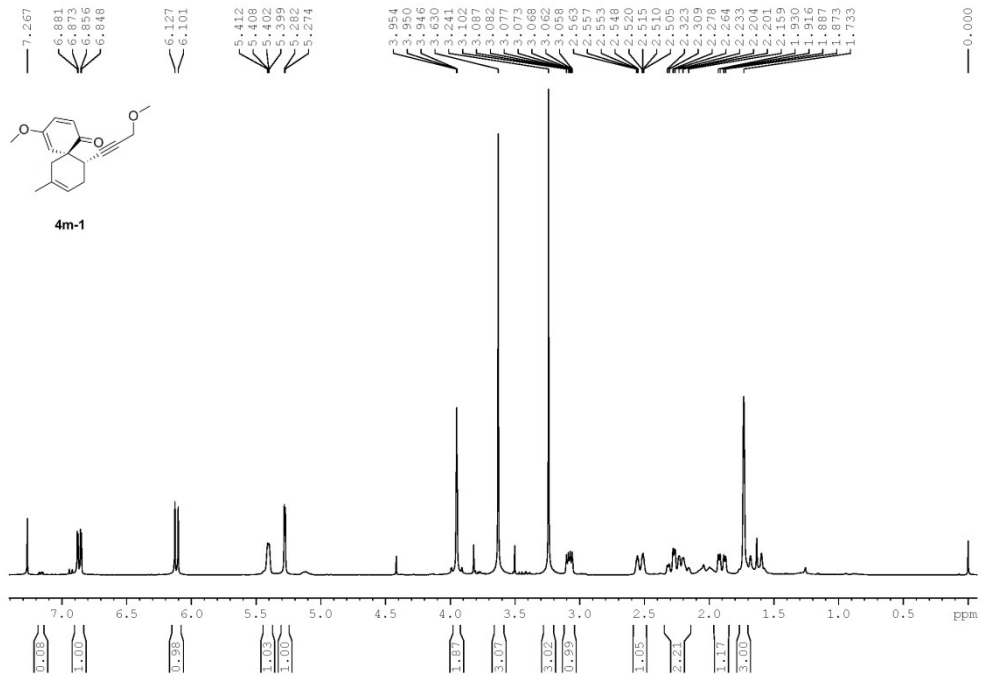
^{1}H and ^{13}C NMR Spectra of Compound **4l-1**

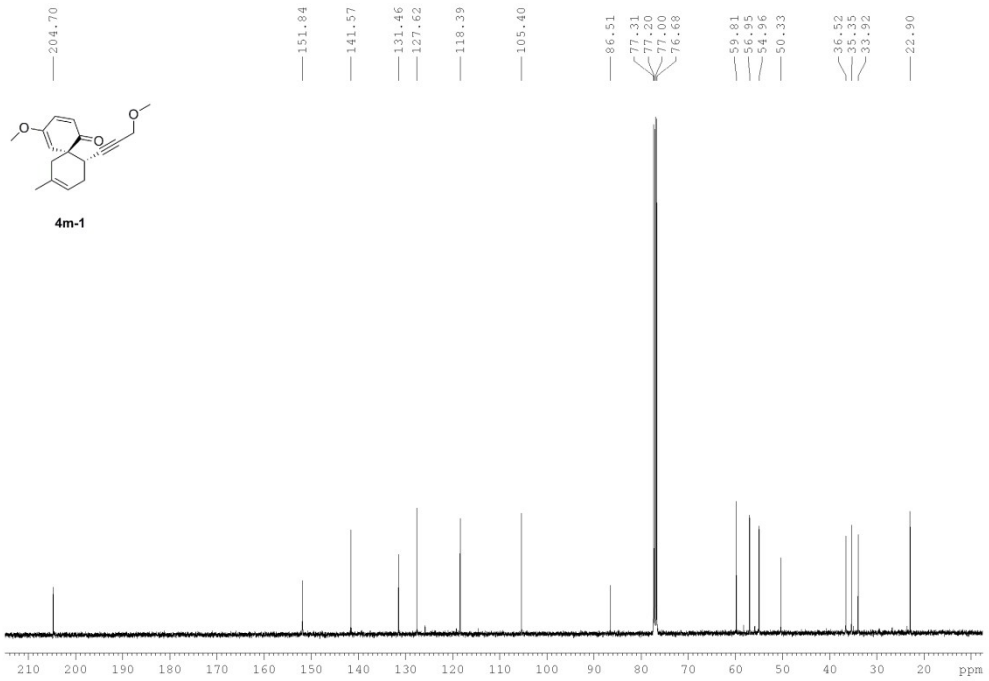


^{1}H and ^{13}C NMR Spectra of Compound **4l-2**

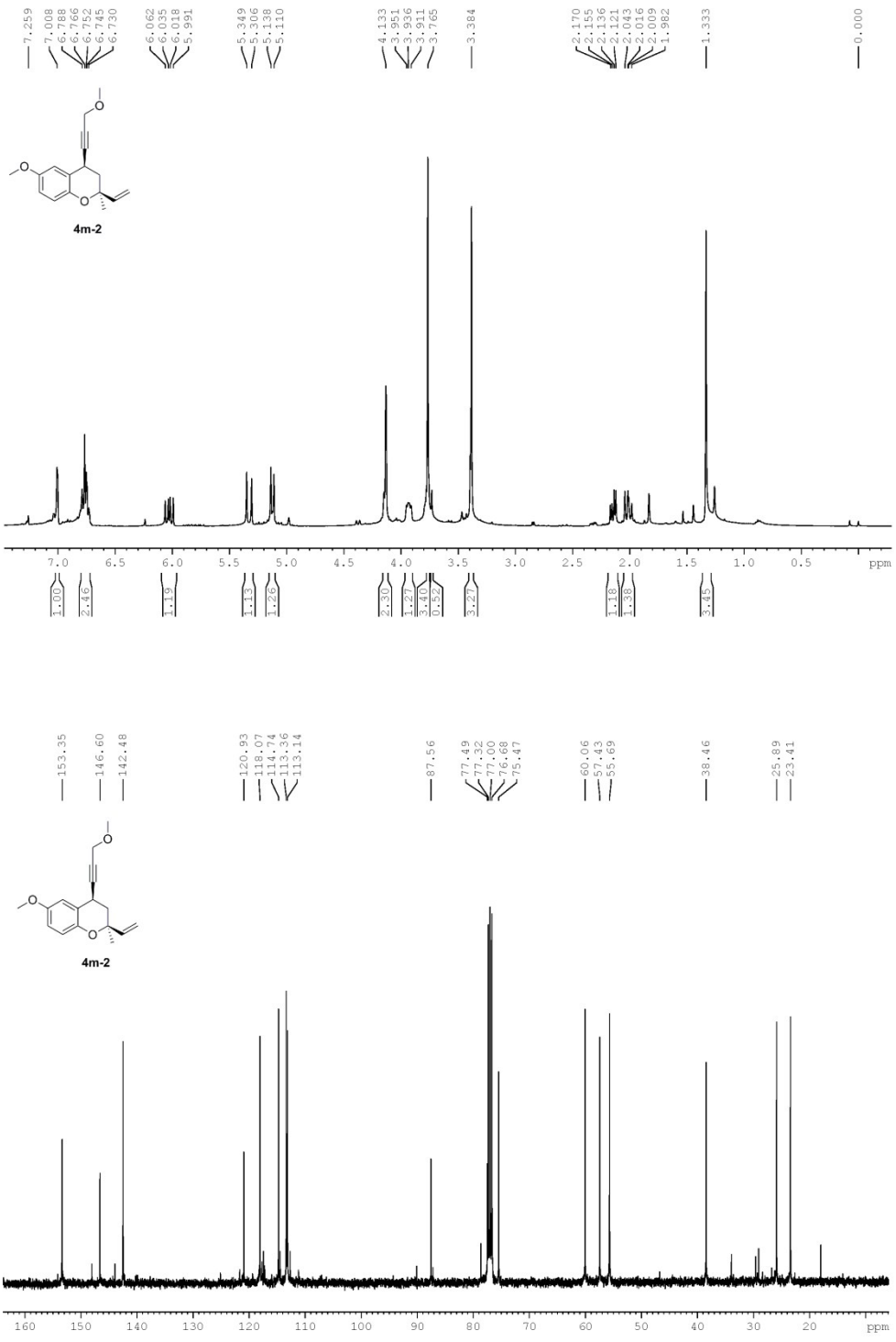


^{1}H and ^{13}C NMR Spectra of Compound **4m-1**

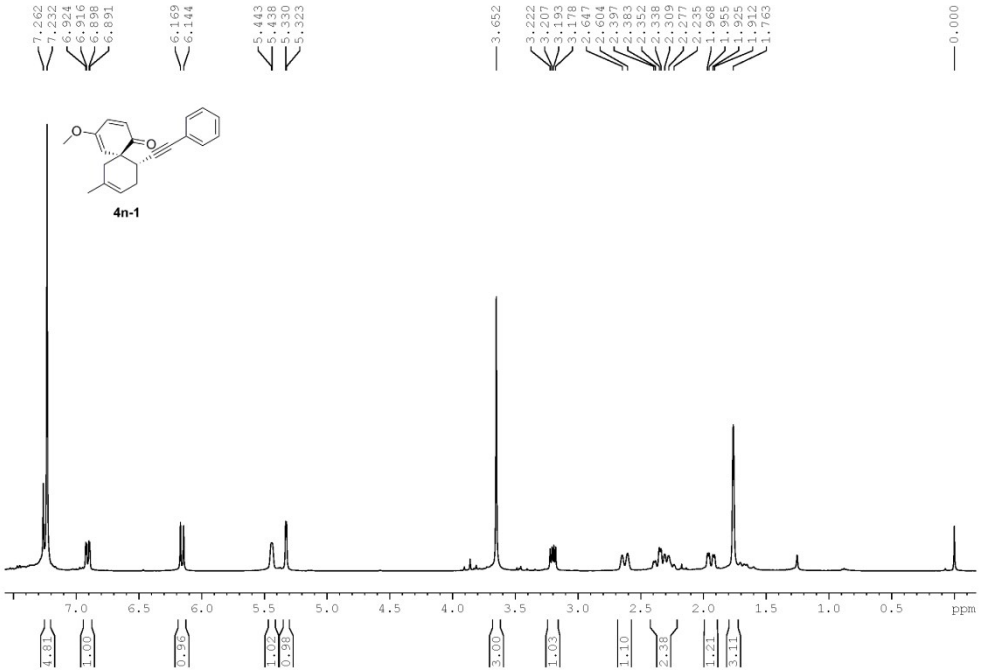


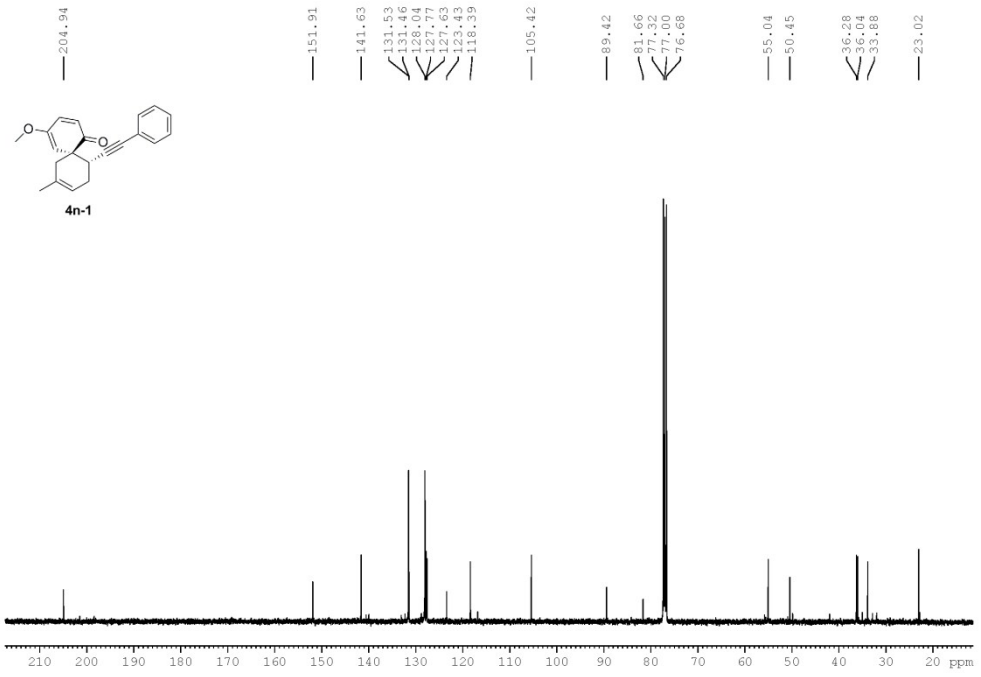


^{1}H and ^{13}C NMR Spectra of Compound **4m-2**

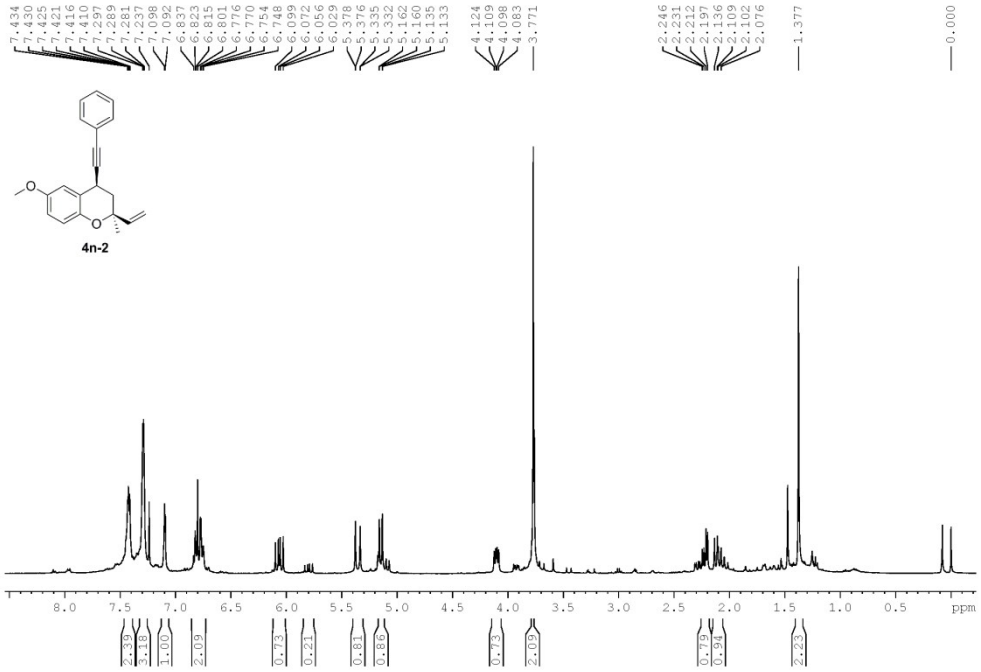


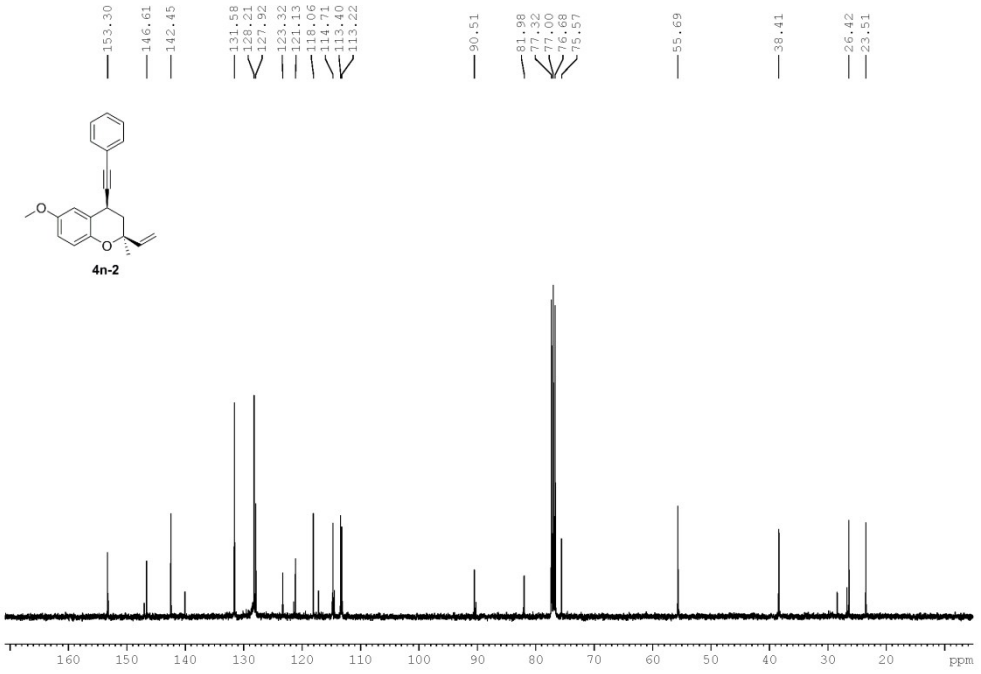
^{1}H and ^{13}C NMR Spectra of Compound **4n-1**





^{1}H and ^{13}C NMR Spectra of Compound **4n-2**


7.434
7.430
7.425
7.421
7.416
7.410
7.297
7.289
7.281
7.237
7.098
7.092
6.837
6.823
6.815
6.801
6.776
6.770
6.754
6.748
6.099
6.072
6.056
6.029
5.378
5.376
5.335
5.332
5.162
5.160
5.135
5.133
4.124
4.109
4.098
4.083
3.771
2.246
2.231
2.222
2.197
2.136
2.109
2.102
2.076
1.377
0.000
4n-2
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.39
2.38
1.00
2.09
0.73
0.21
0.81
0.86
0.73
2.09
0.79
0.84
2.23


153.30
146.61
142.45
131.58
128.21
127.92
123.32
121.13
118.06
114.71
113.40
113.22
90.51
81.98
77.32
77.00
76.68
75.57
55.69
38.41
26.42
23.51
4n-2
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm