Asymmetric Au(I)-Catalyzed Synthesis of Bicyclo[4.1.0]heptene Derivatives *via* a Cycloisomerization process of 1,6-enynes

Supporting Information

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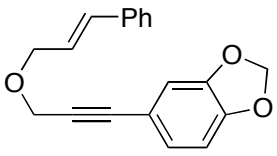
General information

All manipulations were carried out under argon atmosphere. ^{1}H NMR and ^{13}C NMR were recorded on a Bruker AV 300 instrument. All signals were expressed as ppm (δ) and internally referenced to residual protio solvent signals. Coupling constants (*J*) are reported in Hz and refer to apparent peak multiplicities. Mass spectrometry analyses (direct introduction by chemical ionization with ammoniac or electrospray) were performed at the Ecole Nationale Supérieure de Chimie de Paris. High resolution mass spectra were performed at the University Pierre and Marie Curie (Paris). The circular dichroism was performed are the University Pierre and Marie Curie on a Jasco J-815 CD spectrometer equipped with a Jasco CDF-426L Peltier thermostat (2 mm quartz cell). Enantiomeric excesses were determined by High pressure liquid chromatography analyses (HPLC) on Waters instruments (Waters 486 detector, 717 autosampler equipped with Daicel Chiralcel OD-H, OJ and Chiralpak AD and AS-H, λ = 215 nm). Optical rotation measurements were conducted on a Perkin-Elmer 241 polarimeter at 589 nm. Rotatory strengths (R) and static Optical Rotation (a) were computed using the Development Version of the Gaussian code[1] at DFT level using the hybrid PBE0 functional[2] and the 6-31+G(d) basis.
Enynes **1a**,[3] **1d**,[4] and **1k**[5] were prepared in analogy with published procedures. Other enynes were prepared from (3-prop-2-ynyloxy-propenyl)-benzene[6] and 5-(3-prop-2-ynyloxy-propenyl)-benzo[1,3]dioxole[7] *via* a Sonogashira cross-coupling.[8]
The chiral gold complex (*R*)-4-MeO-3,5-(*t*-Bu)$_2$-MeOBIPHEP-(AuCl)$_2$ was prepared according to literature procedure.[9]

Standard procedure for the Sonogashira cross-coupling

Under an inert atmosphere (Ar) CuI (10% eq.), [Pd(PPh$_3$)$_2$Cl$_2$] (5% eq.) were added to a solution of the aryl iodide (1.3 eq.), enyne (1 eq.) in diisopropylamine (1 mol/L). The mixture was stirred at RT (0.5 to 2 hours) until completion of the reaction. After hydrolysis with saturated aqueous NH_4Cl solution, the aqueous phase was extracted 3 times with AcOEt. The organic phase is washed with saturated aqueous NH_4Cl solution, dried over $MgSO_4$, filtered and then evaporated under reduced pressure. The crude mixture was purified by silica gel flash chromatography to give the desired product.

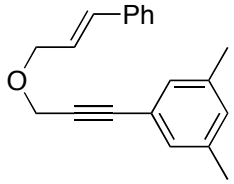
(*E*)-5-(3-(cinnamyloxy)prop-1-ynyl)benzo[*d*][1,3]dioxole **1b**



TLC (cyclohexane/ethyl acetate: 80/20) R_f = 0.54. ^{1}H-NMR (300 MHz, $CDCl_3$) : δ = 7.42-7.24 (m, 5H), 6.99 (dd, *J*=8.0Hz, *J*=1.6Hz, 1H), 6.90 (d, *J*=1.4Hz, 1H), 6.75 (d, *J*=8.1Hz, 1H), 6.67 (d, *J*=15.9Hz, 1H), 6.32 (dt, *J*=15.9Hz, *J*=6.1Hz, 1H), 5.97 (s, 2H), 4.40 (s, 2H), 4.29 (dd, *J*=6.2Hz, *J*=1.4Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) : δ = 148.0, 147.3, 136.6 (Cq), 133.2 (CH), 128.5 (2C), 127.7, 126.5 (2C), 126.5 (2C), 125.3 (CH), 115.8 (Cq), 111.8, 108.4 (CH), 101.3 (CH_2), 86.2 (C≡C), 83.4 (C≡C), 70.3 (CH_2), 57.9 (CH_2). HRMS (CI-NH_3) calculated for $C_{19}H_{16}O_3$: 292.1099; found: 338.2136.

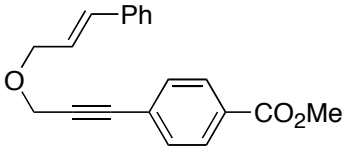
[1] Devevlopment Version Revision G01, M. J. Frisch et al. Gaussian Inc. Wallingford CT, 2007.
[2] Adamo, C.; Barone, V. *J. Chem. Phys.* **1999**, *10*, 6158.
[3] Takayuki, K.;Tomoko, M.; Mitsuhito, S.; Masashi, Y.; Teruhiko, I.; Seiki, S.; Hisayoshi, K. *J. Am. Chem. Soc.* **2007**, *129*, 4939.
[4] Blum, J.; Beer-Kraft. H.; Badrieh. Y. *J. Org. Chem.* **1995**, *60*, 5569. Bartlett, A. J.; Laird, T.; Ollis, W. D. *J. Chem. Soc., Perkin Trans. 1*.**1975**, 1315.
[5] Morito, T.; Fuji, K.; Kakiuchi, K., *J. Am. Chem. Soc.* **2002**, *124*, 3806.
[6] Méndez, M.; Munoz, M.P.; Nevado, C.; Cárdenas, D.J.; Echavarren, A. M. *J. Am. Chem. Soc.* **2001**, *123,* 10511.
[7] Charruault, L.; Michelet, V.; Genêt, J.-P. *Tetrahedron Lett.* **2002**, *43*, 4757.
[8] Nieto-Oberhuber, C.; Lopez, S.; Echavarren, A. M. *J. Am. Chem. Soc.* **2005**, *127*, 6178.
[9] Liu, C.; Widenhoefer, R. A. *Org. Lett.*, 2007, **9**, 1935.

(*E*)-1-(3-(cinnamyloxy)prop-1-ynyl)-3,5-dimethylbenzene **1c**



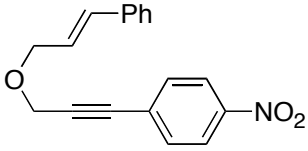
TLC (cyclohexane/ethyl acetate: 90/10) R_f = 0.59. ^{1}H-NMR (300 MHz, $CDCl_3$) : δ = 7.43-7.40 (m, 2H), 7.36-7.25 (m, 3H), 7.10 (t, *J*=0.6Hz, 2H), 6.97 (t, *J*=0.9Hz, 1H), 6.68 (d, *J*=15.9Hz, 1H), 6.34 (dt, *J*=15.9Hz, *J*=6.2Hz, 1H), 4.43 (s, 2H), 4.30 (dd, *J*=6.2Hz, *J*=3.0Hz, 2H), 2.29 (s, 6H).^{13}C-NMR (75 MHz, $CDCl_3$) : δ = 137.8 (2C), 136.6 (Cq), 133.2, 130.3, 129.5 (2C), 128.5 (2C), 127.7, 126.5 (2C), 125.4 (CH), 122.2 (Cq), 86.7 (C≡C), 84.3 (C≡C), 70.2 (CH_2), 57.9 (CH_2), 21.1 (2C) (CH_3). HRMS (CI-NH_3) calculated for $C_{20}H_{20}O$: 276.1514; found: 338.2136.

(*E*)-methyl 4-(3-(cinnamyloxy)prop-1-ynyl)benzoate **1e**



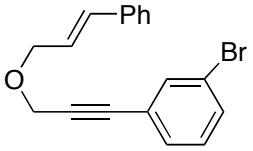
TLC (cyclohexane/ethyl acetate: 90/10) R_f = 0.27. ^{1}H-NMR (300 MHz, $CDCl_3$) : δ = 7.99 (d, *J*=6.7Hz, 2H), 7.49 (d, *J*=6.7Hz, 2H), 7.32 (m, 5H), 6.68 (d, *J*=15.9Hz, 1H), 6.34 (dt, *J*=15.9Hz, *J*=6.2Hz, 1H), 4.44 (s, 2H), 4.30 (dd, *J*=6.2Hz, *J*=1.4Hz, 2H), 3.92 (s, 3H).^{13}C-NMR (75 MHz, $CDCl_3$) : δ = 166.5 (C=O), 136.5 (Cq), 133.4, 131.7 (2C), 129.7 (2C) (CH), 129.4 (Cq), 128.5 (2C), 127.9 (CH), 127.3 (Cq), 126.5 (2C), 125.1 (CH), 88.2 (C≡C), 85.6 (C≡C), 70.5 (CH_2), 57.8 (CH_2), 52.2 (CH_3). HRMS (CI-NH_3) calculated for $C_{20}H_{18}O_3$: 306.1256; found: 338.2136.

(*E*)-1-(3-(cinnamyloxy)prop-1-ynyl)-4-nitrobenzene **1f**



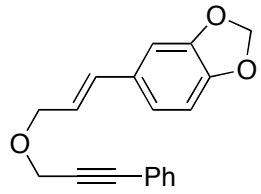
TLC (cyclohexane/ethyl acetate: 98/2) R_f = 0.09. ^{1}H-NMR (300 MHz, $CDCl_3$) : δ = 8.17 (d, *J*=8.8Hz, 2H), 7.58 (d, *J*=8.9Hz, 2H), 7.42-7.39 (m, 2H), 7.35-7.30 (m, 3H), 6.68 (d, *J*=15.9Hz, 1H), 6.30 (dt, *J*=15.9Hz, *J*=6.2Hz, 1H), 4.45 (s, 2H), 4.30 (dd, *J*=7.5Hz, *J*=1.3Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) : δ = 147.2, 136.4 (Cq), 133.6, 132.4 (2C) (CH), 129.4 (Cq), 128.6 (2C), 127.9, 126.5 (2C), 124.9, 123.5 (2C) (CH), 90.7 (C≡C), 84.5 (C≡C), 70.8 (CH_2), 57.7 (CH_2). HRMS (CI-NH_3) calculated for $C_{18}H_{15}O_3N$: 293.1052; found: 338.2136.

(*E*)-1-bromo-3-(3-(cinnamyloxy)prop-1-ynyl)benzene **1g**



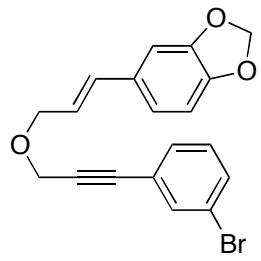
TLC (cyclohexane/ethyl acetate: 90/10) R_f = 0.51. ^{1}H-NMR (300 MHz, $CDCl_3$) : δ = 7.60 (t, *J*=1.7Hz, 1H), 7.46 (ddd, *J*=7.8Hz, *J*=1.8Hz, *J*=0.9Hz, 1H), 7.42-7.73 (m, 6H), 7.18 (t, *J*=8.1Hz, 1H), 6.67 (d, *J*=15.9Hz, 1H), 6.31 (dt, *J*=15.9Hz, *J*=6.2Hz, 1H), 4.42 (s, 2H), 4.30 (dd, *J*=6.2Hz, *J*=1.3Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) : δ = 136.5 (Cq), 134.5, 133.4, 131.6, 130.3, 129.7, 128.5 (2C), 127.8, 126.5 (2C), 125.1 (CH), 124.6, 122.0 (Cq), 86.6 (C≡C), 84.8 (C≡C), 70.5 (CH_2), 57.7 (CH_2). HRMS (CI-NH_3) calculated for $C_{18}H_{15}OBr$: 326.0306; found: 338.2136.

(*E*)-5-(3-(3-phenylprop-2-ynyloxy)prop-1-enyl)benzo[*d*][1,3]dioxole **1h**



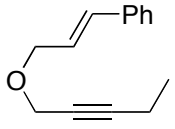
TLC (cyclohexane/ethyl acetate: 95/5) R_f = 0.23. ^{1}H-NMR (300 MHz, $CDCl_3$) : δ = 7.98 (dt, *J*=8.5Hz, *J*=1.6Hz, 2H), 7.50 (dt, *J*=8.5Hz, *J*=1.6Hz, 2H), 6.93 (d, *J*=1.8Hz, 1H), 6.83 (dd, *J*=7.8, *J*=1.5Hz, 1H), 6.75 (d, *J*=7.8Hz, 1H), 6.58 (d, *J*=8.0Hz, 1H), 6.15 (dt, *J*=15.8Hz, *J*=6.4Hz, 1H), 5.95 (t, *J*=1.1Hz, 2H), 4.42 (s, 2H), 4.27 (dd, *J*=6.3Hz, *J*=1.4Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) : δ = 148.0, 147.4 (Cq), 133.1, 131.8 (2C) (CH), 131.0 (Cq), 128.4, 128.2 (2C), 123.2 (CH), 122.6 (Cq), 121.3, 108.3, 105.8 (CH), 101.1 (CH_2), 86.3 (C≡C), 85.1 (C≡C), 70.3, 57.8 (CH_2). HRMS (CI-NH_3) calculated for $C_{19}H_{16}O_3$: 292.1099; found: 338.2136.

(E)-5-(3-(3-(3-bromophenyl)prop-2-ynyloxy)prop-1-enyl)benzo[*d*][1,3]dioxole **1i**



TLC (cyclohexane/ethyl acetate: 95/5) R_f = 0.23. ^{1}H-NMR (300 MHz, $CDCl_3$) : δ = 7.59 (t, *J*=1.7Hz, 1H), 7.45 (ddd, *J*=8.1Hz, *J*=2.1Hz, *J*=1.2Hz, 1H), 7.37 (dt, *J*=7.8Hz, 1.2Hz, 1H), 7.18 (t, *J*=8.1Hz, 1H), 6.94 (d, *J*=1.8, 1H), 6.83 (dd, *J*=7.8Hz, *J*=1.5Hz, 1H), 6.75 (d, *J*=7.8Hz, 1H), 6.57 (d, *J*=15.9Hz, 1H), 6.14 (dt, *J*=15.8Hz, *J*=6.3Hz, 1H), 5.95 (s, 2H), 4.40 (s, 2H), 4.26 (dd, *J*=6.3Hz, *J*=1.4Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) : δ = 148.0, 147.4 (Cq), 134.4, 133.2, 131.6 (CH), 131.0 (Cq), 130.2, 129.7 (CH), 124.6 (Cq), 123.3 (CH), 122.1 (Cq), 108.3, 105.8 (CH), 101.1 (CH_2), 86.6 (C≡C), 84.8 (C≡C), 70.5, 57.7 (CH_2). HRMS (CI-NH_3) calculated for $C_{19}H_{15}O_3Br$: 370.0205; found: 338.2136.

(*E*)-(3-(pent-2-ynyloxy)prop-1-enyl)benzene **1j**

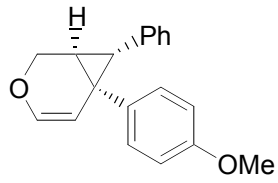


TLC (cyclohexane/ethyl acetate: 80/20) R_f = 0.69. ^{1}H-NMR (300 MHz, $CDCl_3$) : δ = 7.38 (m, 2H), 7.26 (m, 3H), 6.64 (d, *J*=15.9Hz, 1H) 6.29 (dt, *J*=15.9Hz, *J*=6.3Hz, 1H), 4.21 (dd, *J*=6.3Hz, *J*=1.2Hz, 2H), 4.18 (t, *J*=2.4Hz, 2H), 2.25 (qt, *J*=7.8Hz, *J*=2.4Hz, 2H), 1.16 (t, *J*=7.8Hz, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) : δ = 136.6 (Cq), 133.0, 128.5 (2C), 127.7, 126.5 (2C), 125.5 (CH), 88.5 (C≡C), 75.2 (C≡C), 70.1 (CH_2), 57.7 (CH_2), 13.8 (CH_2), 12.5 (CH_3). HRMS (CI-NH_3) calculated for $C_{14}H_{16}O$: 200.1201; found: 338.2136.

General Procedure for Au(I) -catalyzed cycloisomerization reactions of enynes.

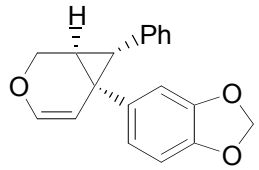
A mixture of *L*-$(AuCl)_2$ (L=*(R)*-4-MeO-3,5-(*t*-Bu)$_2$MeOBIPHEP) (3 mol %) and AgOTf (6 mol %) in distilled toluene (0.5 M) was stirred under argon atmosphere at room temperature for 30 minutes. Enyne (1 eq) was then added and the mixture stirred until completion of the reaction. The mixture was then filtered through a short pad of silica to eliminate the catalyst (EtOAc) and the solvents were concentrated under reduced pressure. The crude product was purified by silica gel flash chromatography (petroleum ether/ethyl acetate, 98/2 to 80/20 *v/v*) if necessary.

6-(4-methoxyphenyl)-7-phenyl-3-oxabicyclo[4.1.0]hept-4-ene **2a**



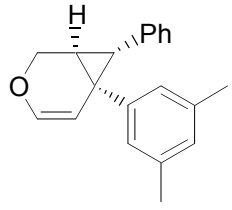
TLC (cyclohexane/ethyl acetate: 90/10) R_f = 0.55. ^{1}H-NMR (300 MHz, $CDCl_3$) : δ = 7.06 -6.97(m, 5H), 6.78-6.69 (m, 4H), 6.24 (d, *J*=5.9Hz, 1H), 5.30 (dd, *J*=5.9Hz, *J*=1.1Hz, 1H), 4.40 (dd, *J*=10.5Hz, *J*=1.1Hz, 1H), 4.07 (dd, *J*=10.5Hz, *J*=2.1Hz, 1H), 3.73 (s, 3H), 2.72 (d, *J*=5.9Hz, 1H), 2.38 (d, *J*=4.6Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) : δ = 158.0 (Cq), 140.3 (CH), 137.8, 131.9 (Cq), 130.7 (2C), 127.6 (2C), 125.5, 113.6 (2C), 111.9 (CH), 61.4 (CH_2), 55.1 (CH_3), 37.2 (CH), 30.2 (Cq), 30.1 (CH). HRMS (CI-NH_3) calculated for $C_{19}H_{18}O_2$: 278.1307; found: 338.2136. Product ratio was determined by HPLC using a Chiralcel AS-H (hexane/isopropanol: 90/10, 1.0 mL/min). The retention times for the two enantiomers were 5.7 and 6.3 min. $[\alpha]_D^{22}$ –12.7 ($CHCl_3$, c 1.00) at 93% *ee*.

5-(7-phenyl-3-oxabicyclo[4.1.0]hept-4-en-6-yl)benzo[*d*][1,3]dioxole **2b**



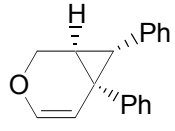
TLC (cyclohexane/ethyl acetate: 90/10) R_f = 0.51. ^{1}H-NMR (300 MHz, $CDCl_3$) : δ = 7.09-7.04 (m, 3H), 6.79 (dd, *J*=8.0Hz, *J*=1.5Hz, 2H), 6.61 (d, *J*=7.3Hz, 1H), 6.54(d, *J*=8.0Hz, 2H), 6.23 (d, *J*=5.2Hz, 1H), 5.86 (dd, *J*=5.2Hz, *J*=1.5Hz, 2H), 5.28 (d, *J*=5.6Hz, 1H), 4.37 (dd, *J*=10.5Hz, *J*=1.2Hz, 1H), 4.05 (dd, *J*=10.5Hz, *J*=1.8Hz, 1H), 2.71 (d, *J*=6.0Hz, 1H), 2.37 (d, *J*=5.3Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) : δ = 146.3, 144.9 (Cq), 139.4 (CH), 136.5, 132.7 (Cq), 126.7 (2C), 126.5 (2C), 124.6, 121.9, 110.7, 109.2, 106.9 (CH), 99.7, 60.3 (CH_2), 36.3 (CH), 29.7 (Cq), 29.2 (CH). HRMS (CI-NH_3) calculated for $C_{19}H_{16}O_3$: 292.1099; found: 338.2136. Product ratio was determinated by HPLC using a Chiralcel AD (hexane/isopropanol: 95/5, 1.0 mL/min). The retention times for the two enantiomers were 7.0 and 7.7 min. $[\alpha]_D^{22}$ –24.1 ($CHCl_3$, c 0.99) at 96% *ee*.

6-(3,5-dimethylphenyl)-7-phenyl-3-oxabicyclo[4.1.0]hept-4-ene **2c**

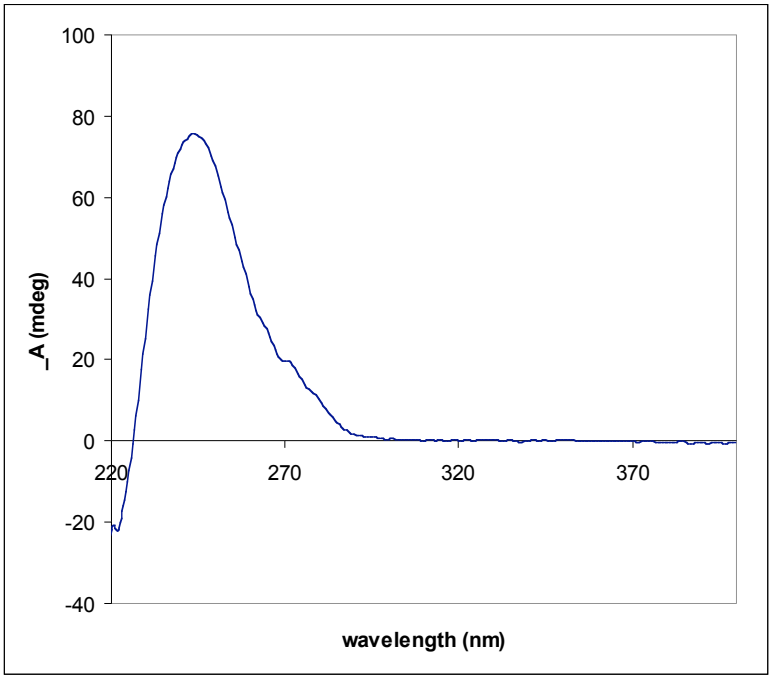


TLC (cyclohexane/ethyl acetate: 95/5) R_f = 0.58. ^{1}H-NMR (300 MHz, $CDCl_3$) : δ = 7.11-7.00 (m, 3H), 6.81-6.75(m, 3H), 6.70-6.69 (m, 1H), 6.26 (d, *J*=5.7Hz, 1H), 5.34 (dd, *J*=5.9Hz, *J*=0.9Hz, 1H), 4.40 (dd, *J*=10.7Hz, *J*=1.4Hz, 1H), 4.09 (dd, *J*=10.7Hz, *J*=2.1Hz, 1H), 2.73 (d, *J*=6.0Hz, 1H), 2.40 (dd, *J*=6.3Hz, *J*=1.2Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) : δ = 140.4 (CH), 139.5, 137.8 (Cq), 137.5, 128.0, 127.7 (2C), 127.6 (2C), 127.5 (2C), 125.5, 111.8 (CH) 61.4 (CH_2), 37.3 (CH), 30.7 (Cq), 30.0 (CH), 21.2 (2C), (CH_3). HRMS (CI-NH_3) calculated for $C_{20}H_{20}O$: 276.1514; found: 338.2136. Product ratio was determined by HPLC using a Chiralcel OD-H (hexane/isopropanol: 99.5/0.5, 1.0 mL/min). The retention times for the two enantiomers were 8.2 and 9.0 min. $[\alpha]_D^{22}$ +6.6 ($CHCl_3$, c 0.51) at 94% *ee*.

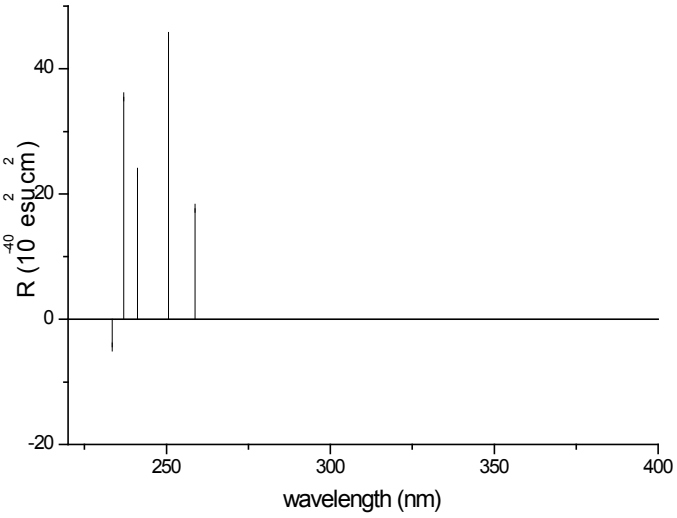
6,7-diphenyl-3-oxabicyclo[4.1.0]hept-4-ene **2d**



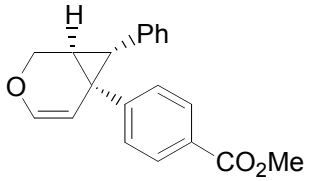
^{1}H, ^{13}C and mass spectroscopy data for compound **2d** were identical to literature values (Blum, J.; Beer-Kraft. H.; Badrieh. Y. *J. Org. Chem.* **1995**, *60*, 5569). Product ratio was determined by HPLC using a Chiralcel OD-H (hexane/isopropanol: 95/5, 1.0 mL/min). The retention times for the two enantiomers were 6.3 and 6.9 min. $[\alpha]_D^{22}$ +18.5 ($CHCl_3$, c 1.00) at 98% *ee*.



Sample concentration: 4 10-4 M in dichloromethane
Cell pathlength: 0.2 cm

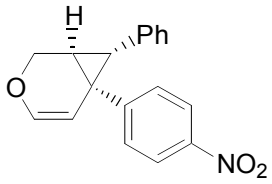


methyl 4-(7-phenyl-3-oxabicyclo[4.1.0]hept-4-en-6-yl)benzoate **2e**



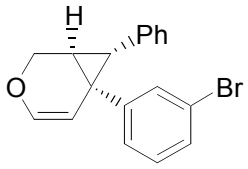
TLC (cyclohexane/ethyl acetate: 90/10) R_f = 0.34. ^{1}H-NMR (300 MHz, $CDCl_3$) : δ = 7.83 (dd, *J*=6.6Hz, *J*=1.9Hz, 2H), 7.16-7.13 (m, 2H), 7.05-7.01 (m, 3H), 6.75 (dd, *J*=6.6Hz, *J*=1.9Hz, 2H), 6.29 (d, *J*=6.0Hz, 1H), 5.33 (dd, *J*=6.0Hz, *J*=1.1Hz, 1H), 4.42 (dd, *J*=10.6Hz, *J*=1.2Hz 1H), 4.09 (dd, *J*=10.6Hz, ^{3}*J*=2.1Hz, 1H), 2.83 (d, *J*=6Hz, 1H), 2.51 (dd, *J*=5.3Hz, *J*=0.6Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) : δ = 166.9 (C=O), 145.1 (Cq), 141.1 (CH), 136.9 (Cq), 129.6 (2C), 129.5 (2C) (CH), 128.2 (Cq), 127.8 (2C), 127.6 (2C), 125.9, 110.4 (CH), 61.2 (CH_2), 51.9 (CH_3), 37.8 (CH), 30.7 (Cq), 29.4 (CH). HRMS (CI-NH_3) calculated for $C_{20}H_{18}O_3$: 306.1256; found: 338.2136. Product ratio was determined by HPLC using a Chiralcel OD-H (hexane/isopropanol: 90/10, 1.0 mL/min). The retention times for the two enantiomers were 7.7 and 9.3 min. $[\alpha]_D^{22}$ –13.8 ($CHCl_3$, c 0.68) at 94% *ee*.

6-(4-nitrophenyl)-7-phenyl-3-oxabicyclo[4.1.0]hept-4-ene **2f**



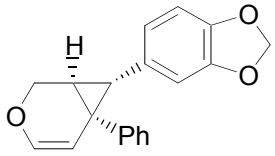
TLC (cyclohexane/ethyl acetate: 90/10) R_f = 0.28. ^{1}H-NMR (300 MHz, $CDCl_3$) : δ = 8.01 (d, *J*= 11.4Hz, 2H), 7.25-7.20 (m, 2H), 7.09-7.03 (m, 3H), 6-80-6.77 (m, 2H), 6.32 (d, *J*=6.0Hz, 1H), 5.30 (dd, *J*=6.1Hz, *J*=0.9Hz, 1H), 4.43 (dd, *J*=10.7Hz, *J*=1.2Hz, 1H), 4.10 (dd, *J*=10.7Hz, *J*=2.0Hz, 1H), 2.90 (d, *J*=6.1Hz, 1H), 2.56 (d, *J*=6.1Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) : δ = 147.6, 146.4 (Cq), 141.6 (CH), 136.3 (Cq), 130.3 (2C), 128.1 (2C), 127.6 (2C), 126.3, 123.4 (2C), 109.4 (CH), 61.1 (CH_2), 38.1 (CH), 30.5 (Cq), 29.4 (CH). HRMS (CI-NH_3) calculated for $C_{18}H_{15}O_3N$: 293.1052; found: 338.2136. Product ratio was determined by HPLC using a Chiralcel AD (hexane/isopropanol: 95/5, 1.0 mL/min). The retention times for the two enantiomers were 10.6 and 12.0 min. $[\alpha]_D^{22}$ –8.2 ($CHCl_3$, c 1.09) at 96% *ee*.

6-(3-bromophenyl)-7-phenyl-3-oxabicyclo[4.1.0]hept-4-ene **2g**



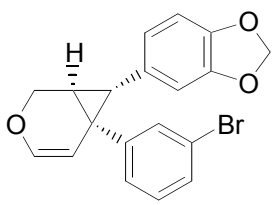
TLC (cyclohexane/ethyl acetate: 95/5) R_f = 0.66. ^{1}H-NMR (300 MHz, $CDCl_3$) : δ = 7.27-7.23 (m, 2H), 7.03 -7.03 (m, 3H), 6.99 (d, *J*=7.3Hz, 1H), 6.94(dt, *J*=7.8Hz, *J*=1.5Hz, 1H), 6.78 (dt, *J*=6.3Hz, *J*=2.1Hz, 2H), 6.27 (d, *J*=6.0Hz, 1H), 5.29 (dd, *J*=6.0Hz, *J*=1.1Hz, 1H), 4.40 (dd, *J*=10.6Hz, *J*=1.2Hz, 1H), 4.07 (dd, *J*=10.6Hz, *J*=2.1Hz, 1H), 2.78 (d, *J*=6.0Hz, 1H), 2.43 (dt, *J*=6.0Hz, *J*=0.7Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) : δ = 142.2 (Cq), 140.9 (CH), 136.9 (Cq), 132.7, 129.7, 129.5, 128.4, 127.8 (2C), 127.6 (2C), 125.9 (CH), 122.1 (Cq), 110.6 (CH) 61.2 (CH_2), 37.4 (CH), 30.4 (Cq), 29.6 (CH). HRMS (CI-NH_3) calculated for $C_{18}H_{15}OBr$: 326.0306; found: 338.2136. Product ratio was determined by HPLC using a Chiralcel OD-H (hexane/isopropanol: 90/10, 1.0 mL/min). The retention times for the two enantiomers were 5.9 and 6.8 min. $[\alpha]_D^{22}$ –24.8 ($CHCl_3$, c 1.00) at 95% *ee*.

5-(6-phenyl-3-oxabicyclo[4.1.0]hept-4-en-7-yl)benzo[*d*][1,3]dioxole **2h**



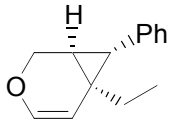
TLC (cyclohexane/ethyl acetate: 95/5) R_f = 0.33. ^{1}H-NMR (300 MHz, $CDCl_3$) : δ = 7.19-7.7.08 (m, 5H), 6.52 (d, *J* = 8.0 Hz, 1H), 6.32 (dd, *J*=8.0, *J*=1.8Hz, 1H), 6.25 (d, *J* = 5.2Hz, 2H), 5.81 (s, 2H), 5.35 (dd, *J*=6.0Hz, *J*=1.0Hz, 1H), 4.40 (dd, *J*=10.5Hz, 1.3Hz, 1H), 4.05 (dd, *J*=10.5Hz, *J*=1.9Hz, 1H), 2.70 (d, *J*=5.9Hz, 1H), 2.37 (d, *J*=6.6Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) : δ = 147.1, 145.5 (Cq), 140.5 (CH), 139.7, 131.5 (Cq), 129.5 (2C), 128.2 (2C), 126.4, 120.9, 111.4, 108.1, 107.6 (CH), 100.6, 61.3 (CH_2), 37.1 (CH), 30.5 (Cq), 29.6 (CH). HRMS (CI-NH_3) calculated for $C_{19}H_{16}O_3$: 292.1099; found: 338.2136. Product ratio was determined by HPLC using a Chiralcel AS-H (hexane/isopropanol: 90/10 1.0 mL/min). The retention times for the two enantiomers were 7.3 and 8.8 min. $[\alpha]_D^{22}$ +25.5 ($CHCl_3$, c=0.99) at 90% *ee*.

5-(6-(3-bromophenyl)-3-oxabicyclo[4.1.0]hept-4-en-7-yl)benzo[*d*][1,3]dioxole **2i**



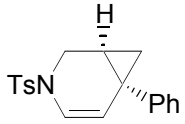
TLC (cyclohexane/ethyl acetate: 95/5) R_f = 0.28. ^{1}H-NMR (300 MHz, $CDCl_3$) : δ = 7.26-7.7.23 (m, 2H), 7.03 (t, *J*=7.6Hz, 1H), 6.96 (dt, *J*=7.5Hz, *J*=1.3Hz, 1H), 6.55 (d, *J* = 8.0 Hz, 1H), 6.32 (dd, *J*=8.0, *J*=1.7Hz, 1H), 6.25 (d, *J* = 5.2Hz, 2H), 5.83 (s, 2H), 5.28 (d, *J*=5.1Hz, 1H), 4.38 (dd, *J*=10.6Hz, 1.1Hz, 1H), 4.03 (dd, *J*=10.6Hz, *J*=1.9Hz, 1H), 2.71 (d, *J*=6.0Hz, 1H), 2.35 (d, *J*=5.6Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) : δ = 147.3, 145.7, 142.2 (Cq), 140.9, 132.6 (CH), 130.6 (Cq), 129.6, 128.2, (CH), 122.2 (Cq), 121.0, 110.6, 108.1, 107.7 (CH), 100.8, 61.1 (CH_2), 37.4 (CH), 30.0 (Cq), 29.5 (CH). HRMS (CI-NH_3) calculated for $C_{19}H_{15}O_3Br$: 370.0205; found: 338.2136. Product ratio was determined by HPLC using a Chiralcel AD (hexane/isopropanol: 90/10, 1.0 mL/min). The retention times for the two enantiomers were 7.5 and 8.2 min. $[\alpha]_D^{22}$ –11.0 ($CHCl_3$, c 1.01) at 96% *ee*.

6-ethyl-7-phenyl-3-oxabicyclo[4.1.0]hept-4-ene **2j**



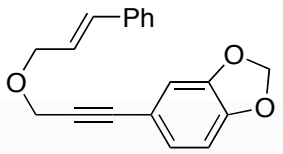
TLC (cyclohexane/ethyl acetate: 98/2) R_f = 0.63. ^{1}H-NMR (300 MHz, $CDCl_3$) : δ = 7.30-7.24 (m, 2H), 7.20-7.15 (m, 3H), 6.28 (d, *J* = 6.0 Hz, 1H), 5.20 (d, *J* = 6.0Hz, 1H), 4.25 (d, *J*=10.4Hz, 1H), 3.87 (dd, *J*=10.4Hz, 2.3Hz, 1H), 2.48 (d, *J*=5.9Hz, 1H), 1.78 (d, *J*=5.9Hz, 1H), 1.32-1.23 (m, 1H), 1.00 (dq, *J*=7.1Hz, *J*=15.4Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) : δ = 141.9 (CH), 138.1 (Cq), 128.7 (2C), 127.9 (2C), 125.9, 109.5 (CH), 61.9 (CH_2), 35.9, 27.5 (CH), 24.8 (Cq), 24.4 (CH_2), 11.2 (CH_3). HRMS (CI-NH_3) calculated for $C_{14}H_{16}O$: 200.1201; found: 338.2136. Product ratio was determined by HPLC using a Chiralcel OD-H (hexane/ispopropanol: 98/2, 1.0 mL/min). The retention times for the two enantiomers were 5.4 and 5.8 min. $[\alpha]_D^{22}$ +56.3 ($CHCl_3$, c 0.53) at 91% *ee*.

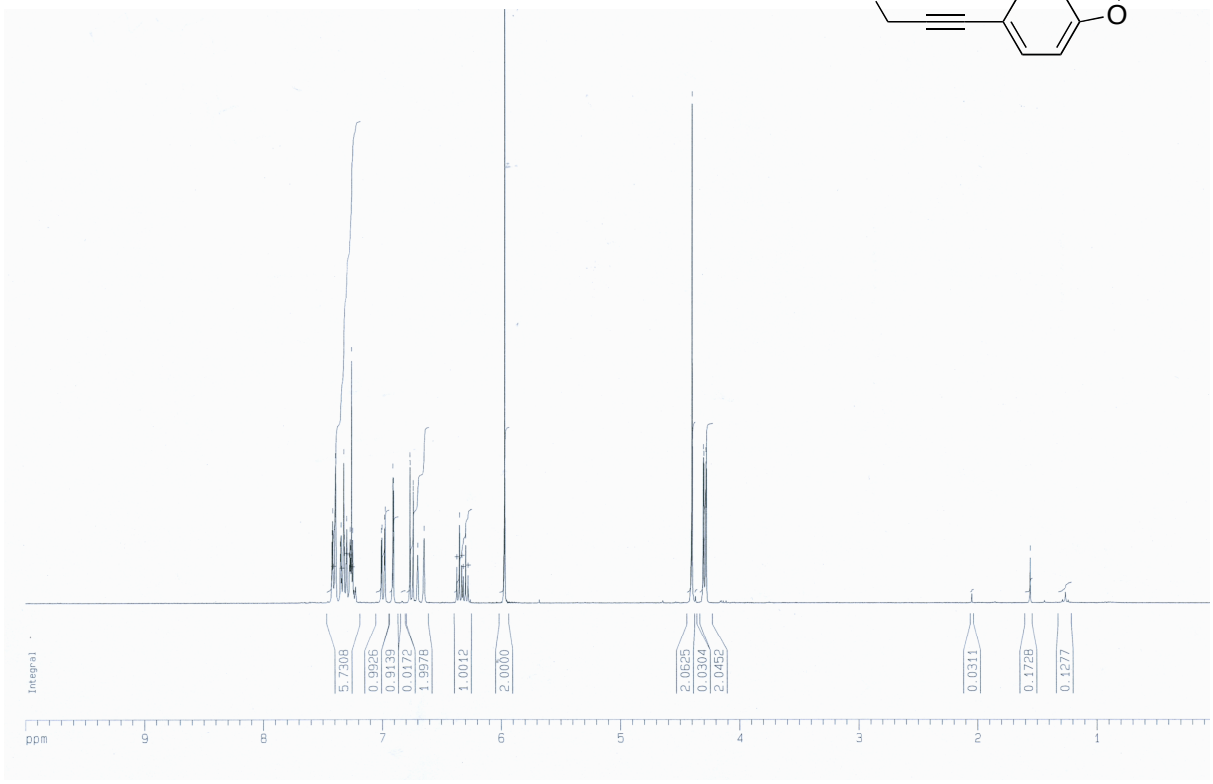
6-phenyl-3-tosyl-3-azabicyclo[4.1.0]heptane **2k**

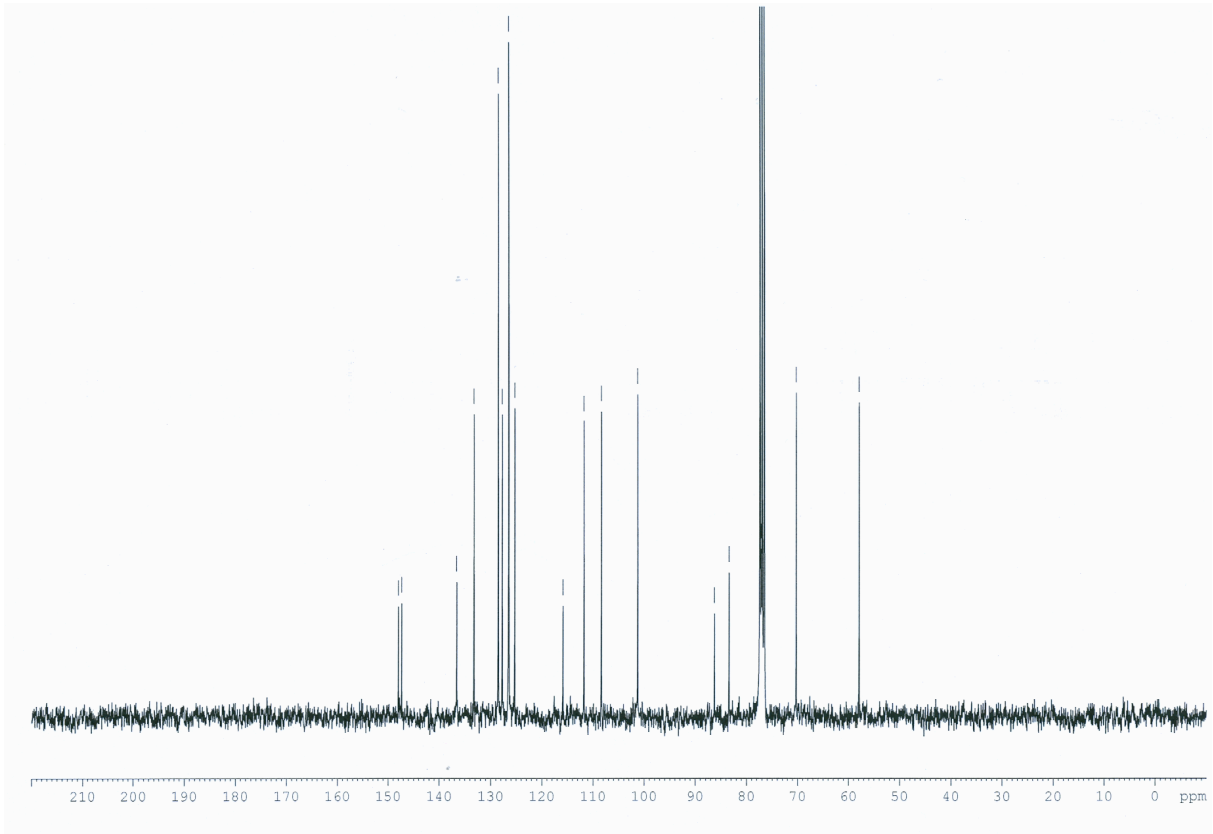


^{1}H, ^{13}C and mass spectroscopy data for compound **2k** were identical to literature values (Fürstner, A.; Szillat, H.; Stelzer, F. *J. Am. Chem. Soc.* **2000**, *122*, 6785). Product ratio was determined by HPLC using a Chiralcel OD-H (hexane/isopropanol: 99/1, 1.0 mL/min). The retention times for the two enantiomers were 23.5 and 28.4 min. $[\alpha]_D^{22}$ –68.0 ($CHCl_3$, c 0.59) at 98% *ee*.

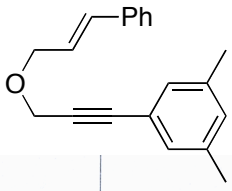
(*E*)-5-(3-(cinnamyloxy)prop-1-ynyl)benzo[*d*][1,3]dioxole **1b**

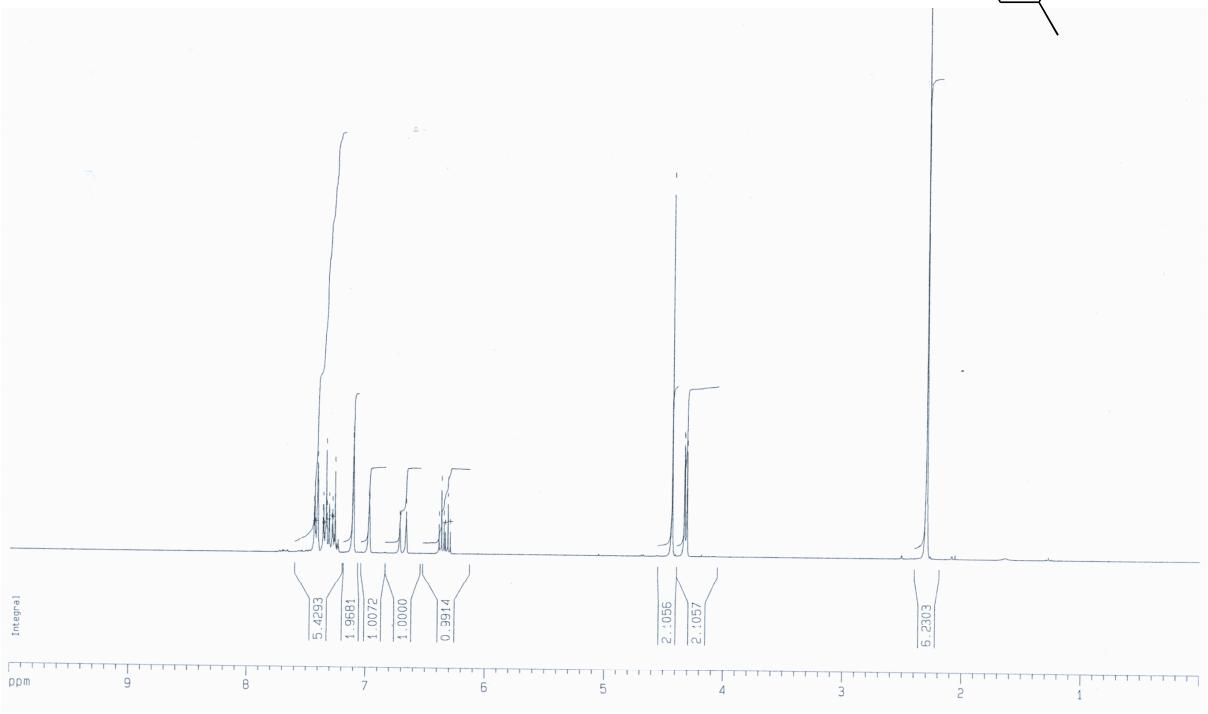


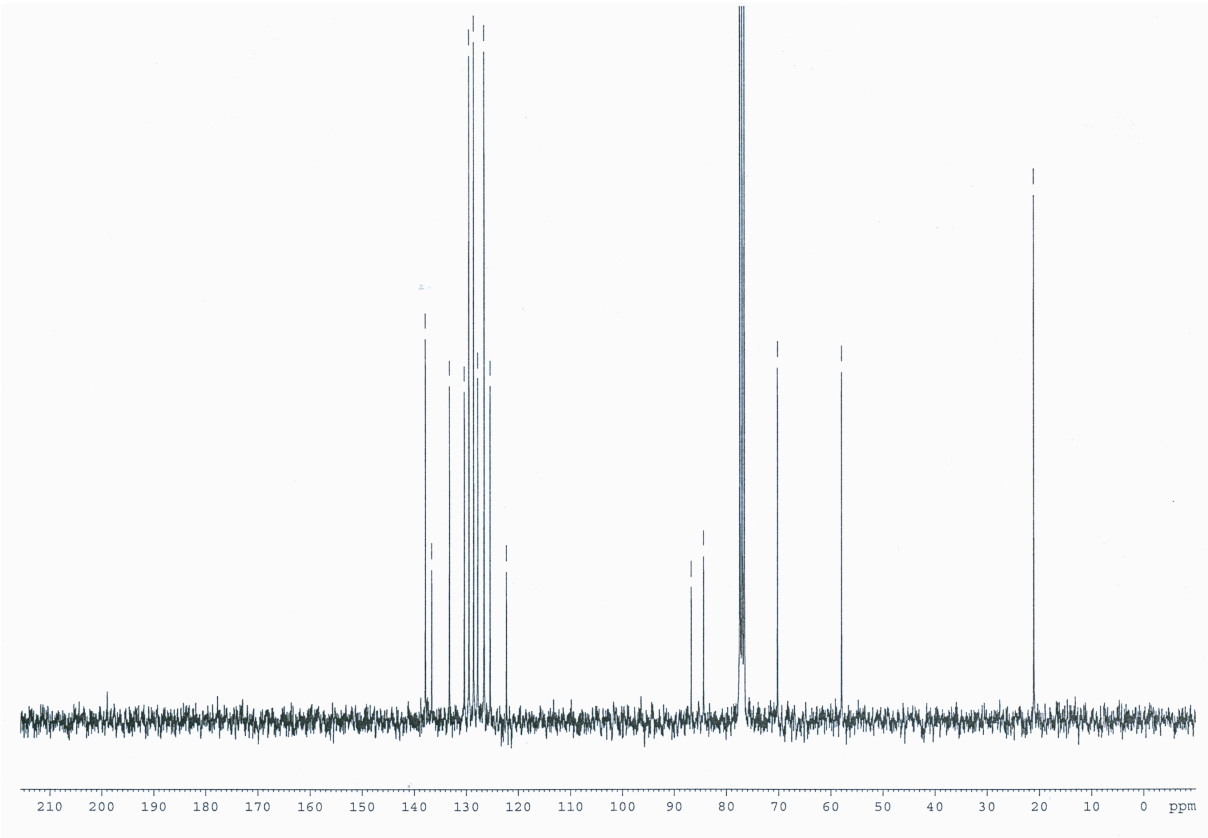




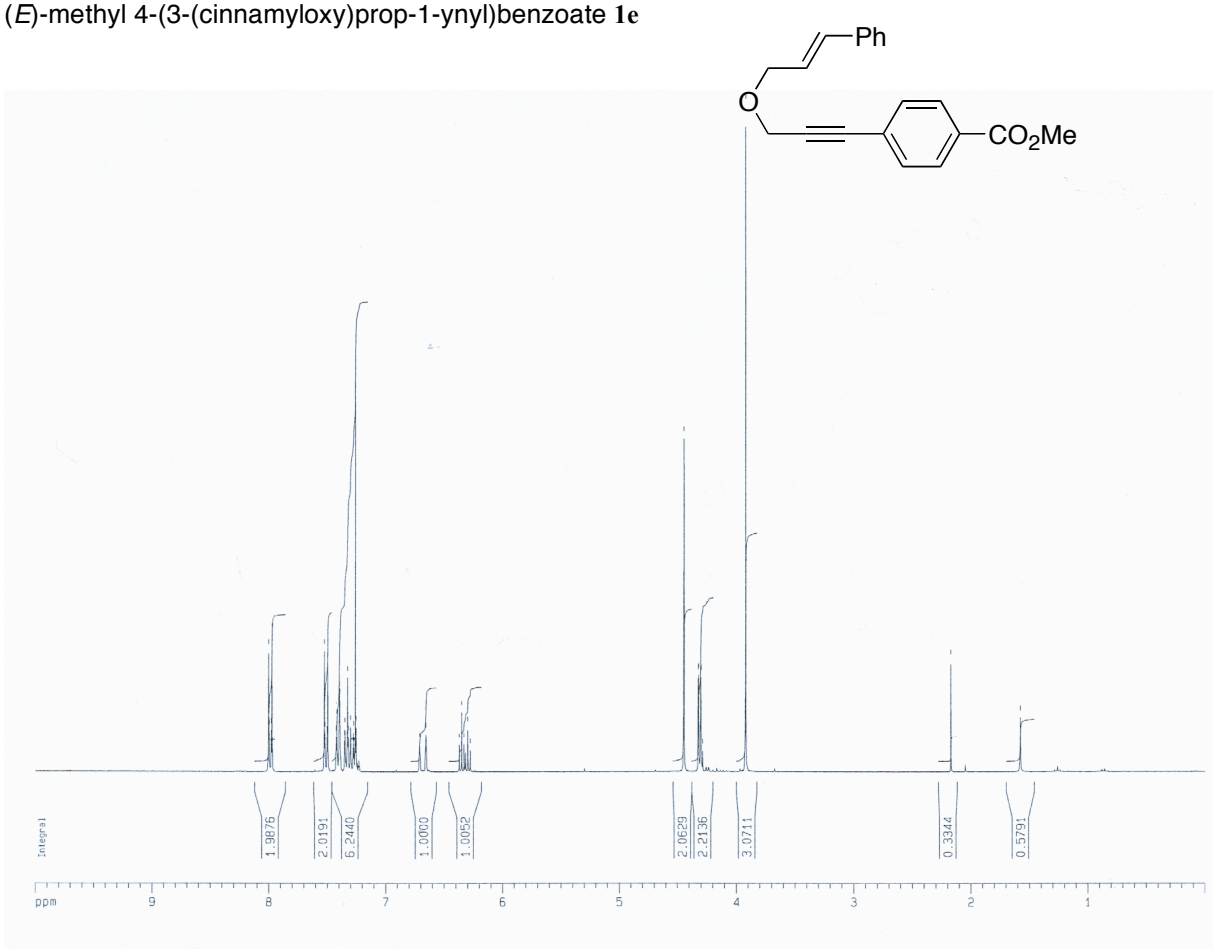
(*E*)-1-(3-(cinnamyloxy)prop-1-ynyl)-3,5-dimethylbenzene **1c**

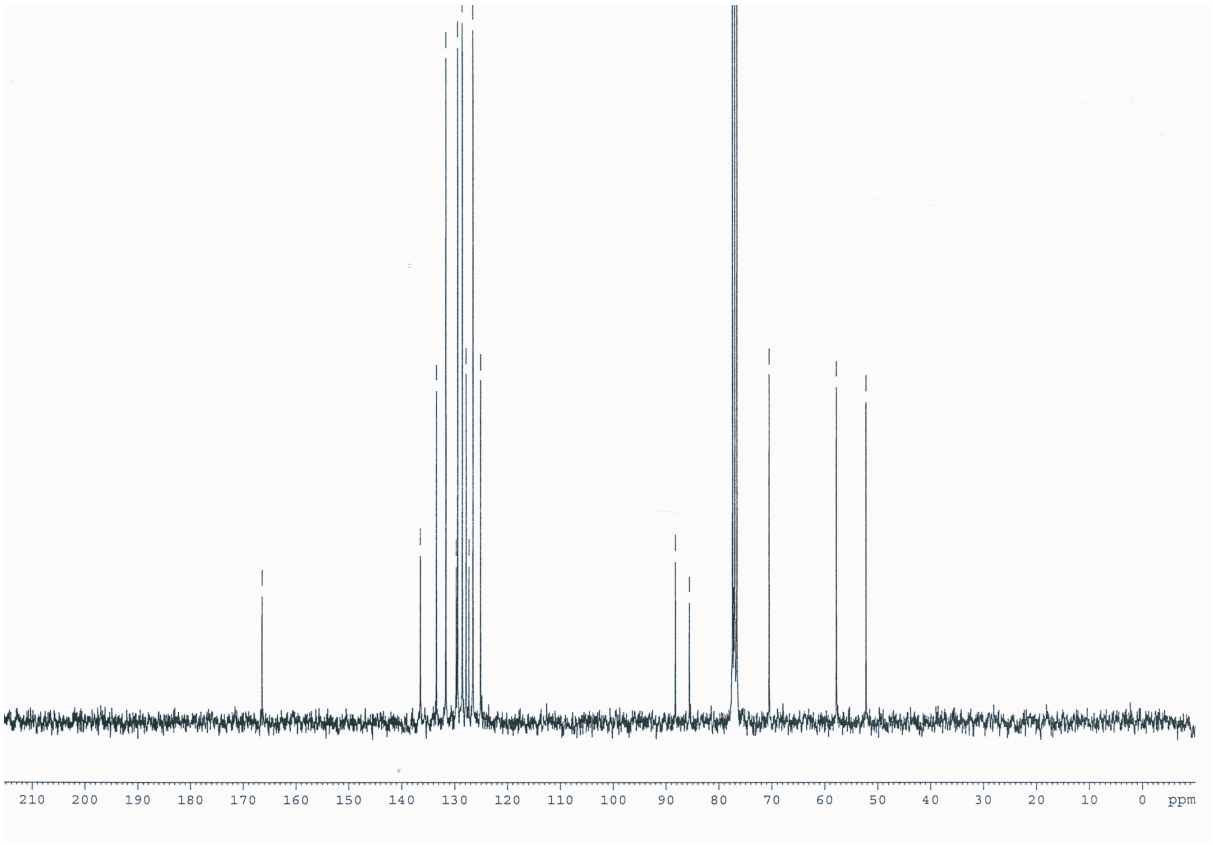




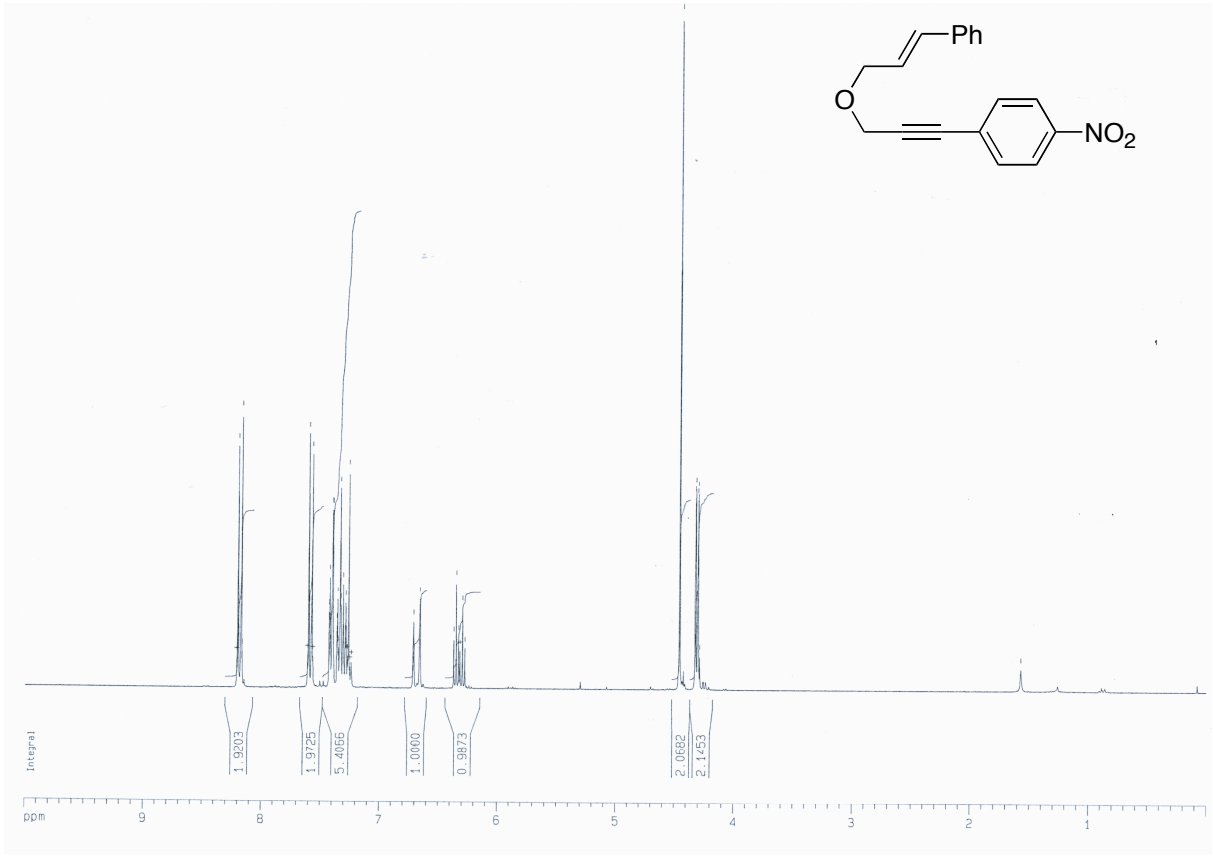


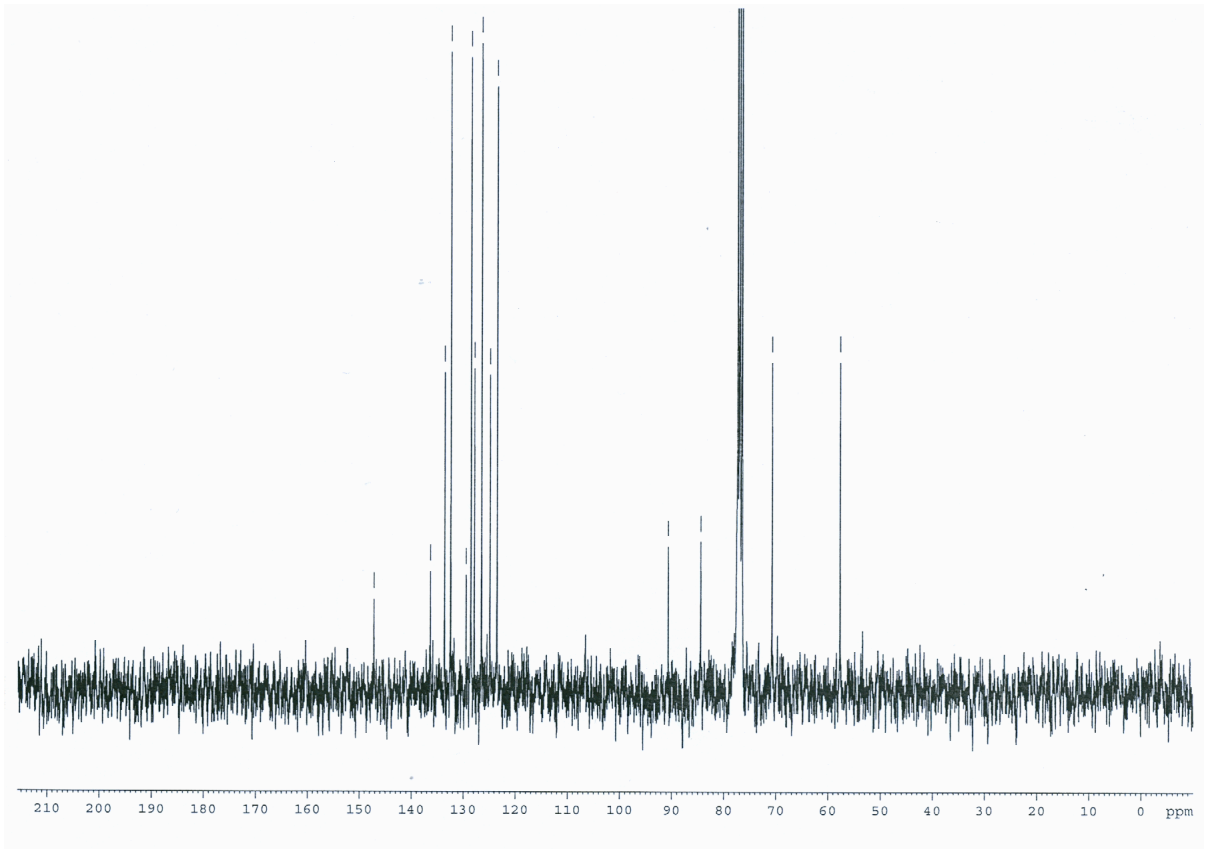
(*E*)-methyl 4-(3-(cinnamyloxy)prop-1-ynyl)benzoate **1e**



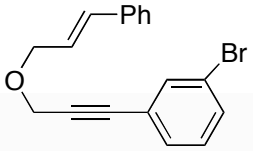


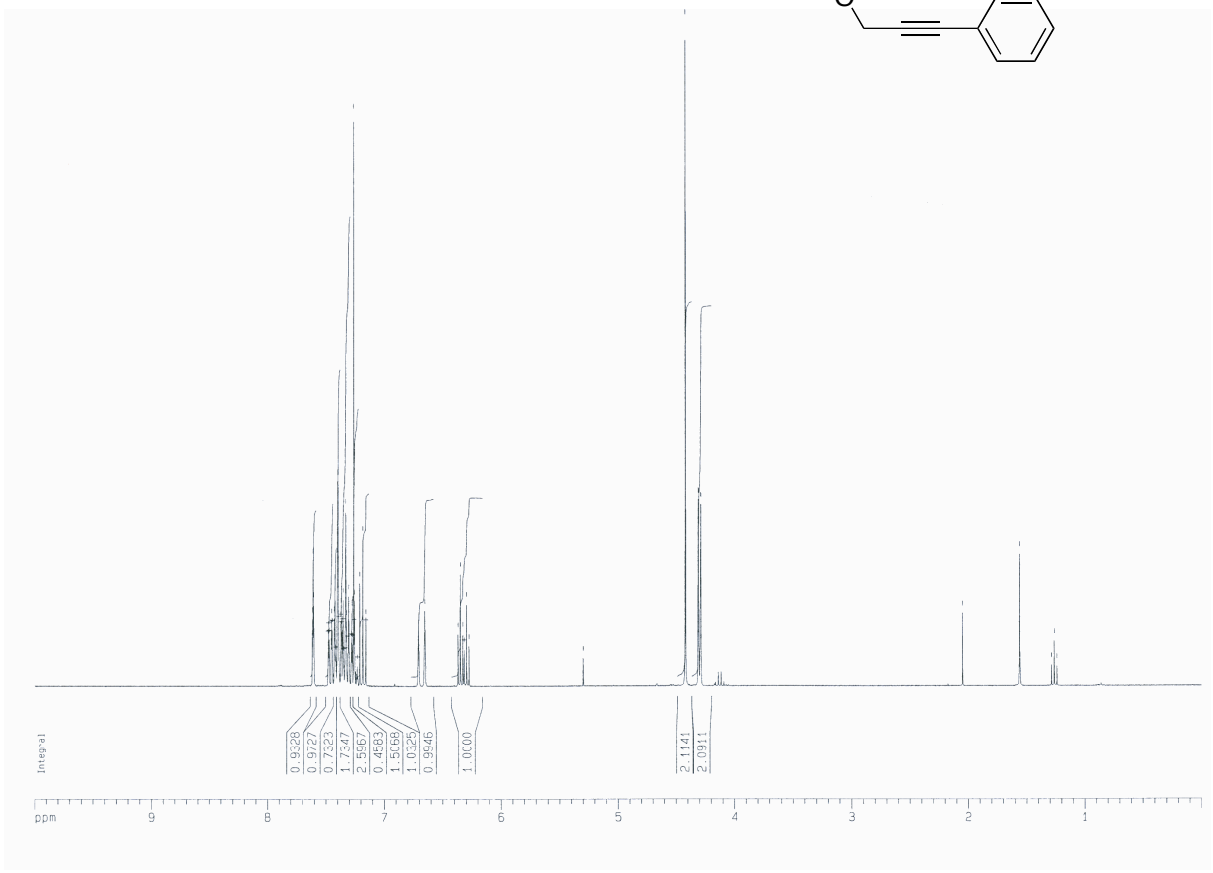
(*E*)-1-(3-(cinnamyloxy)prop-1-ynyl)-4-nitrobenzene **1f**

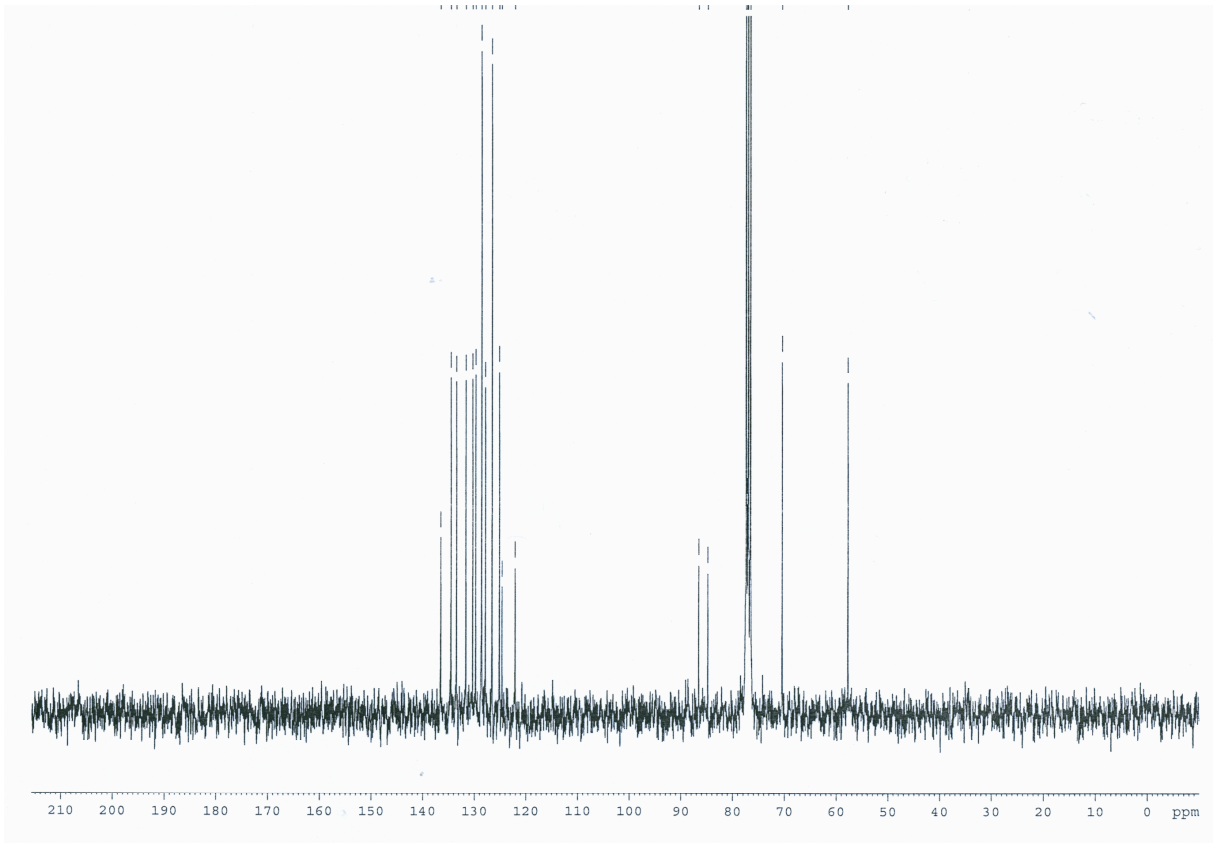




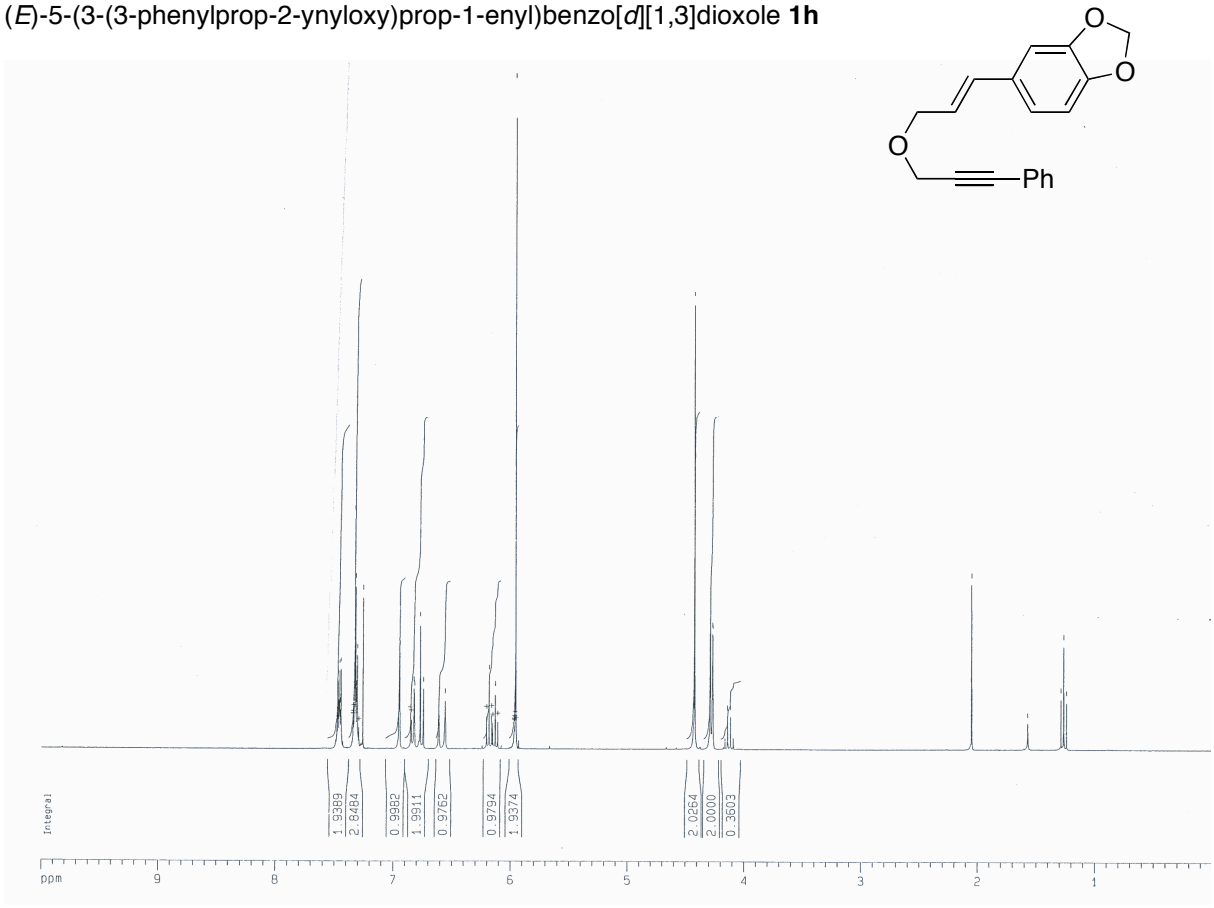
(*E*)-1-bromo-3-(3-(cinnamyloxy)prop-1-ynyl)benzene **1g**

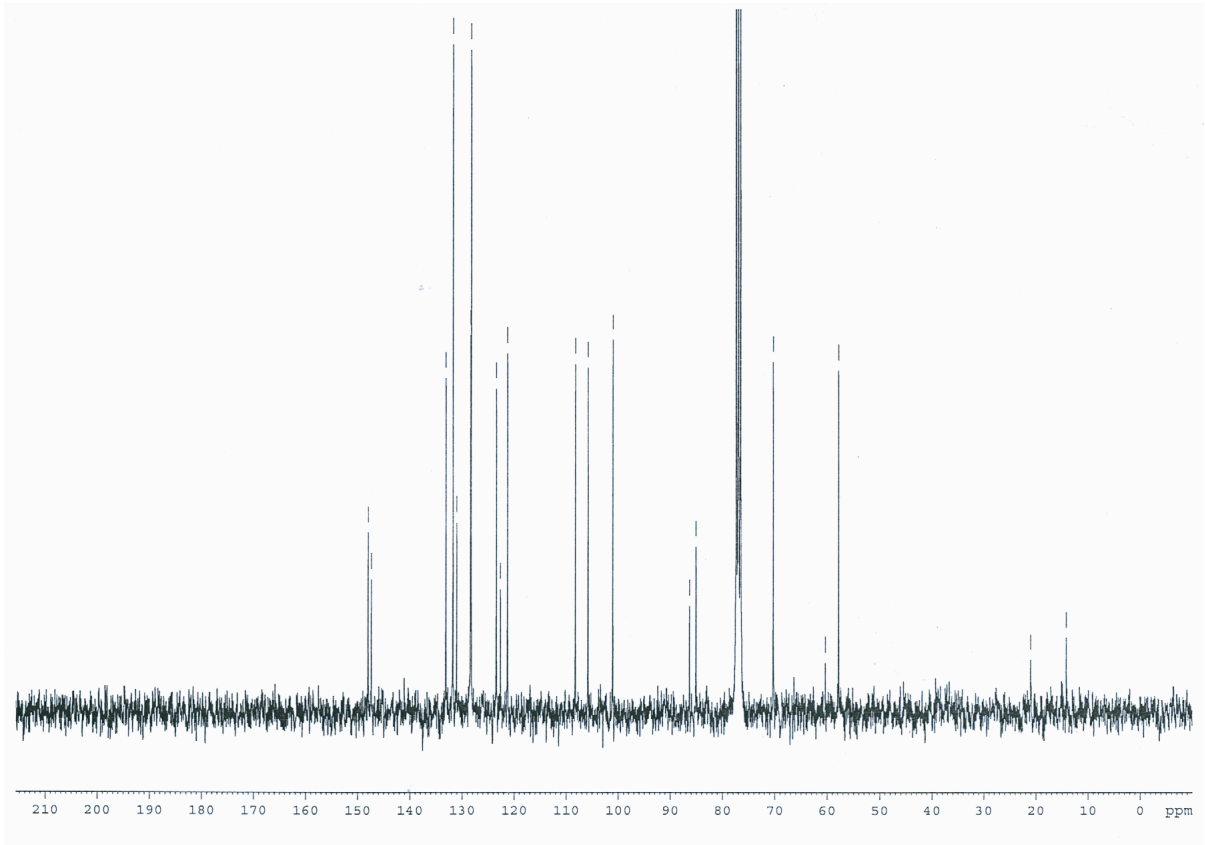




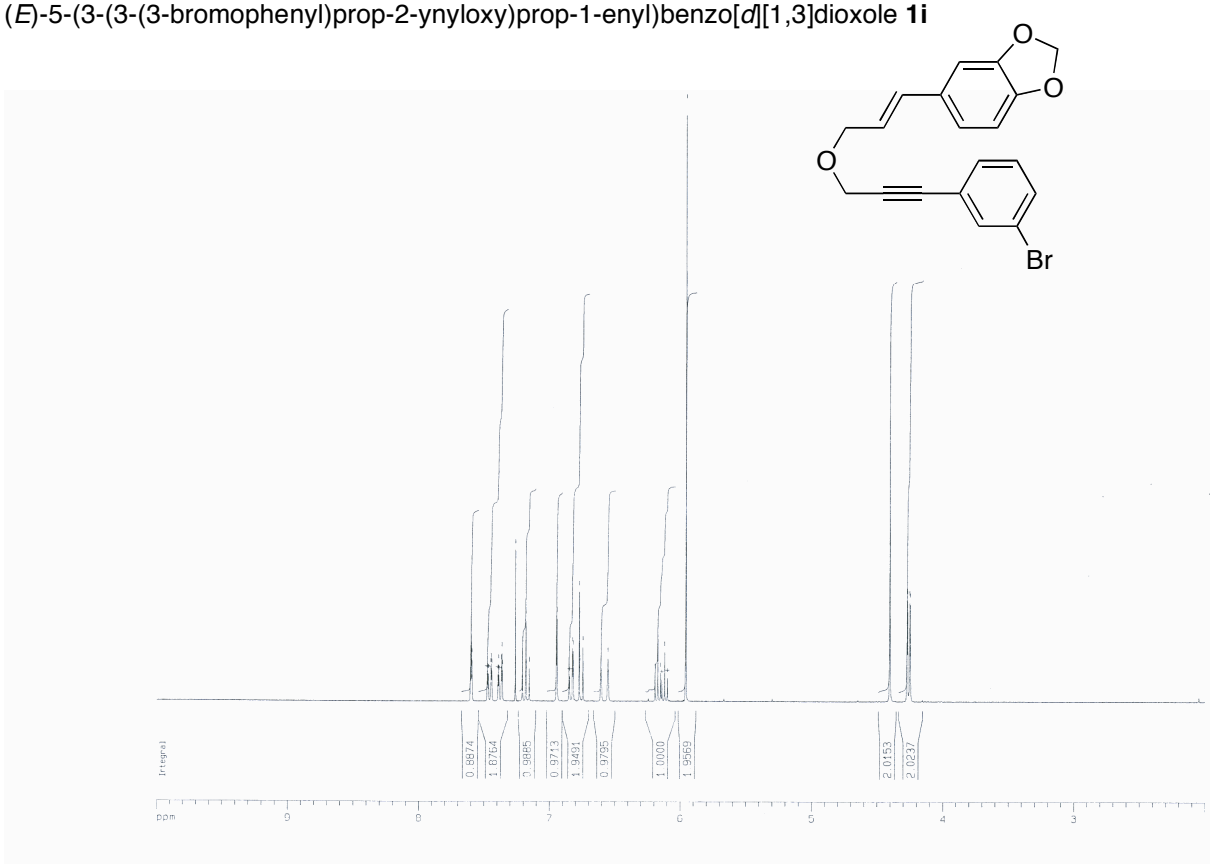


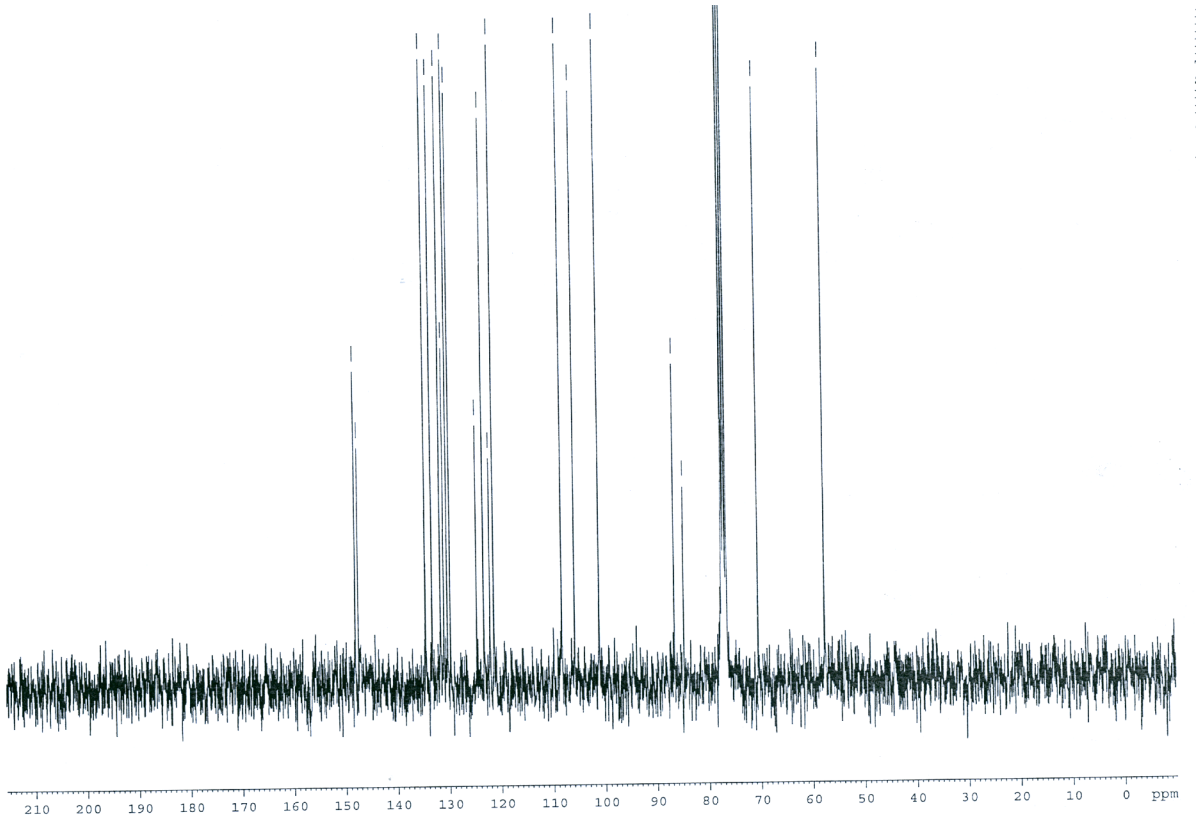
(*E*)-5-(3-(3-phenylprop-2-ynyloxy)prop-1-enyl)benzo[*d*][1,3]dioxole **1h**



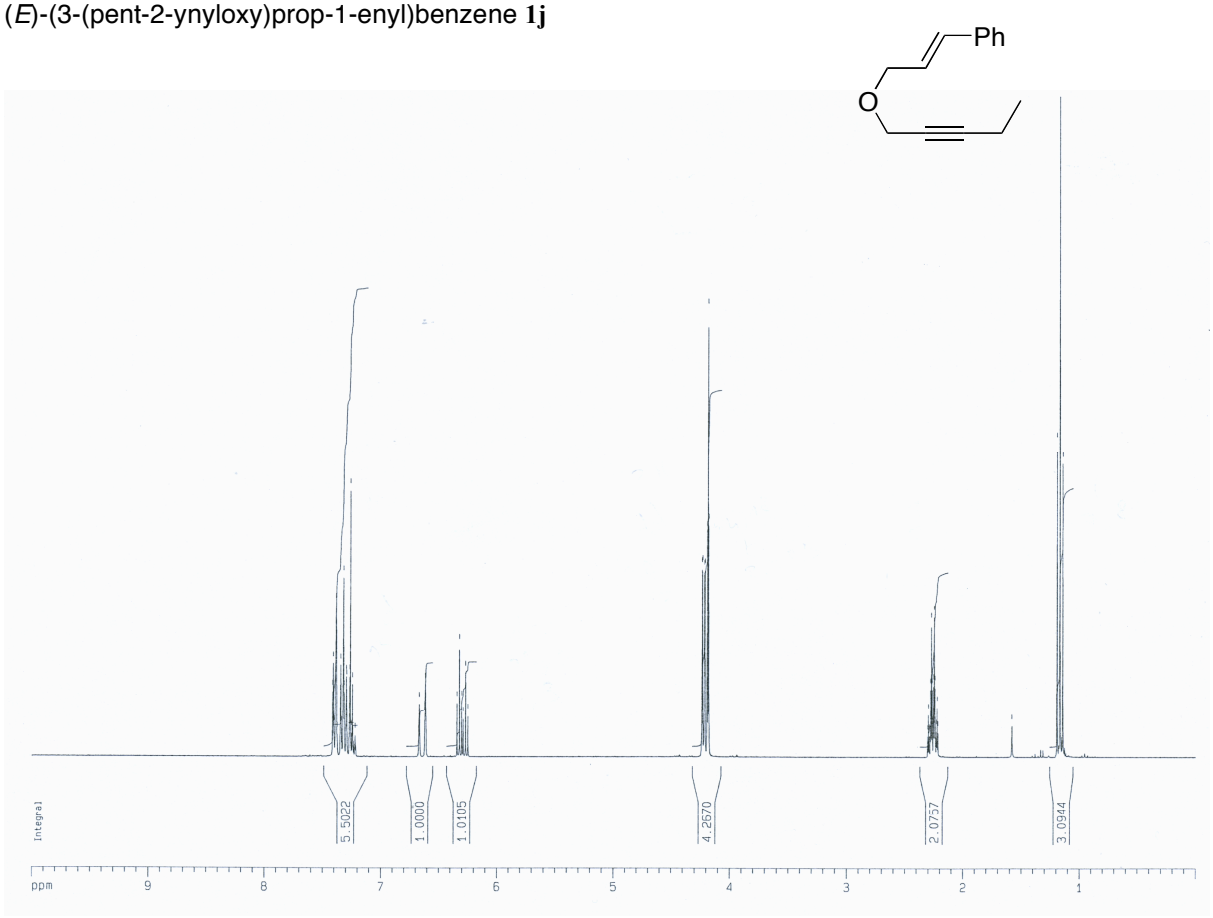


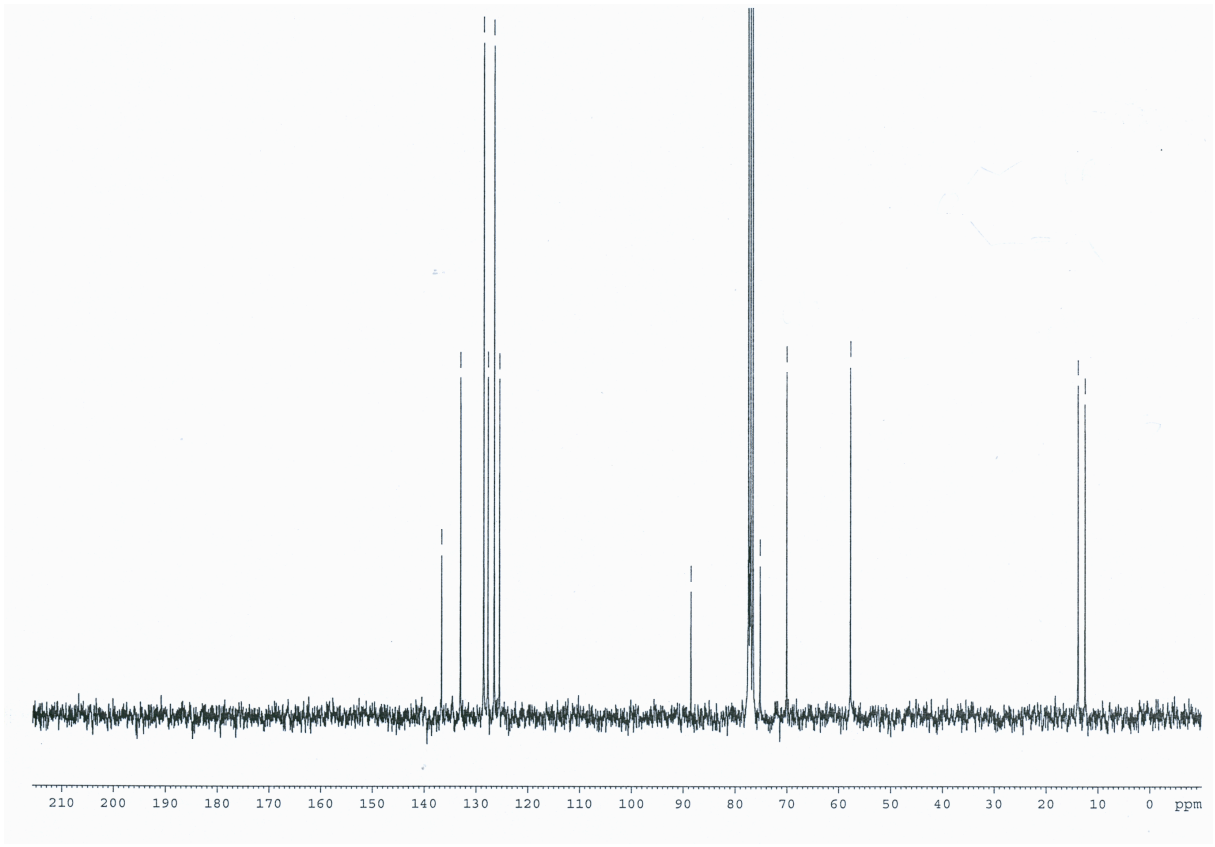
(*E*)-5-(3-(3-(3-bromophenyl)prop-2-ynyloxy)prop-1-enyl)benzo[*d*][1,3]dioxole **1i**



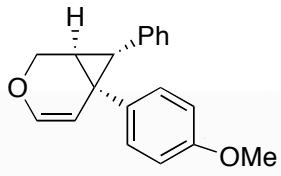


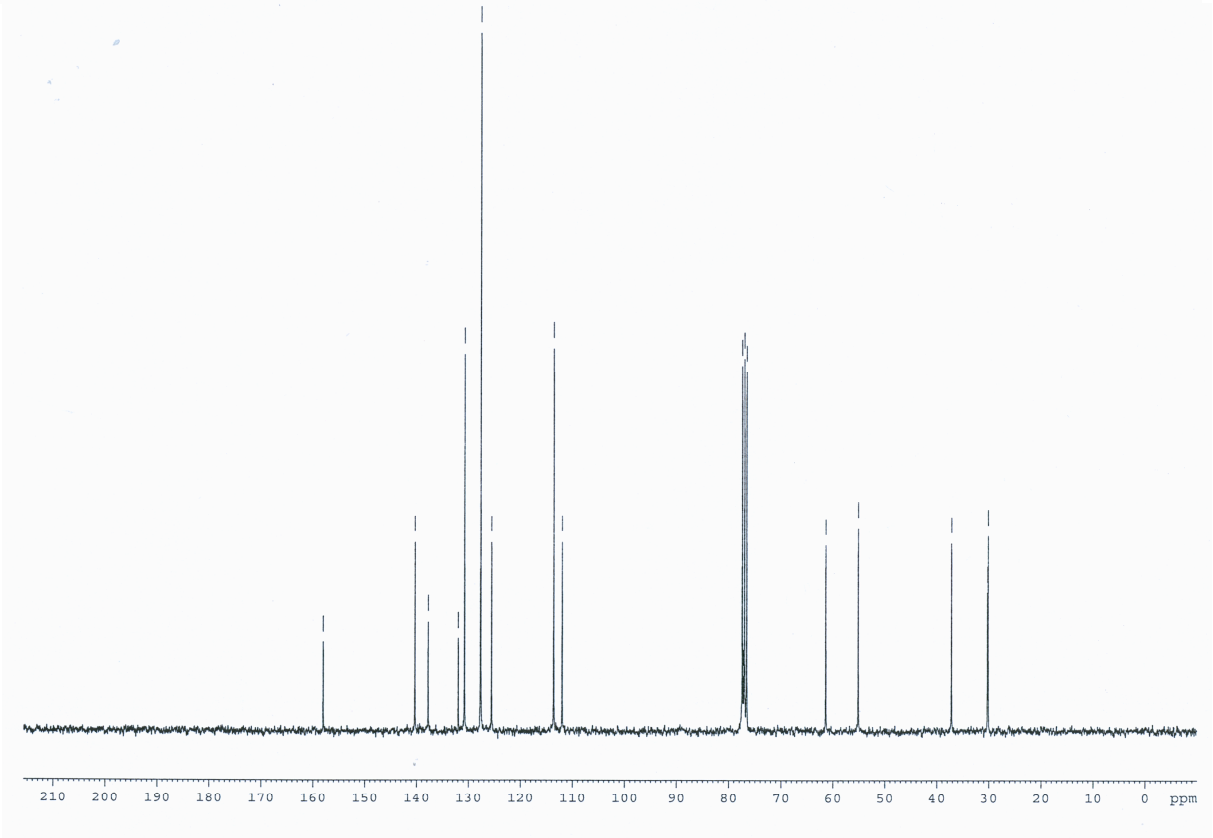
(*E*)-(3-(pent-2-ynyloxy)prop-1-enyl)benzene **1j**



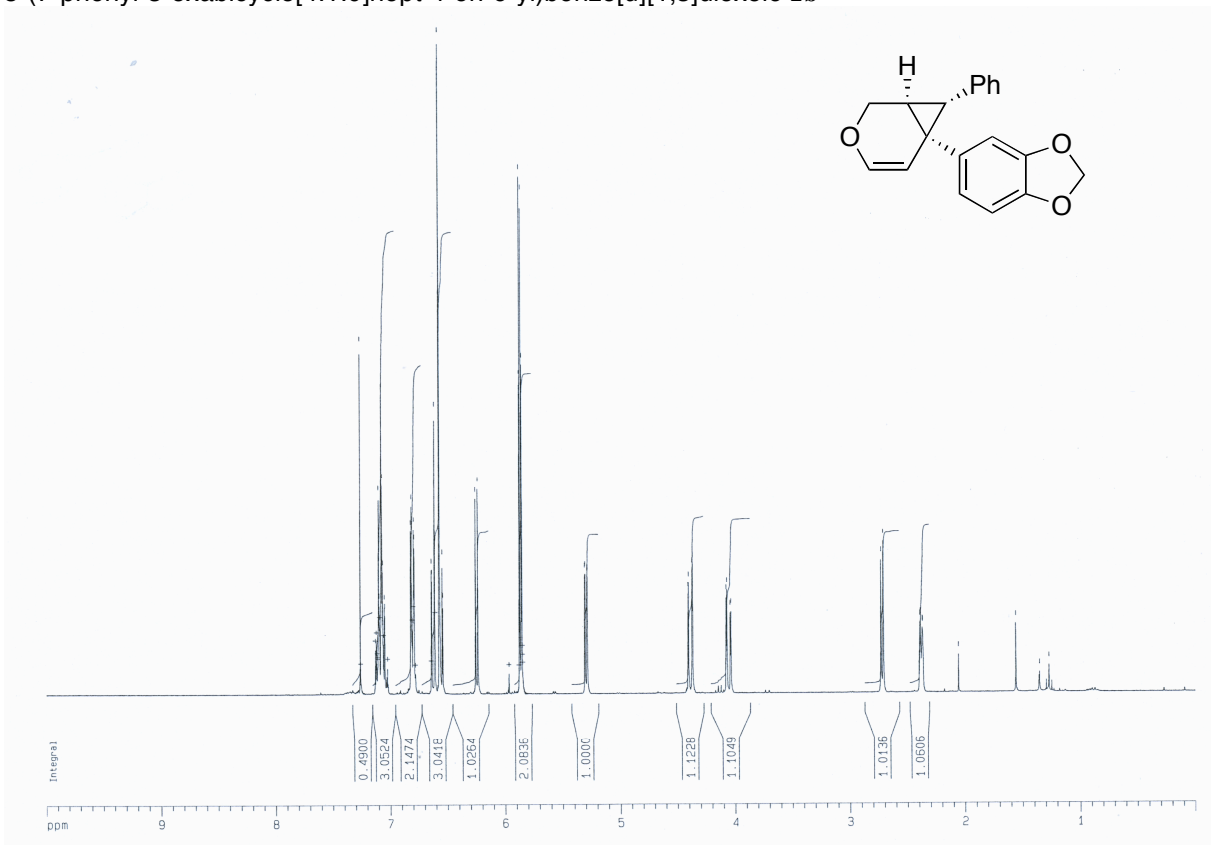


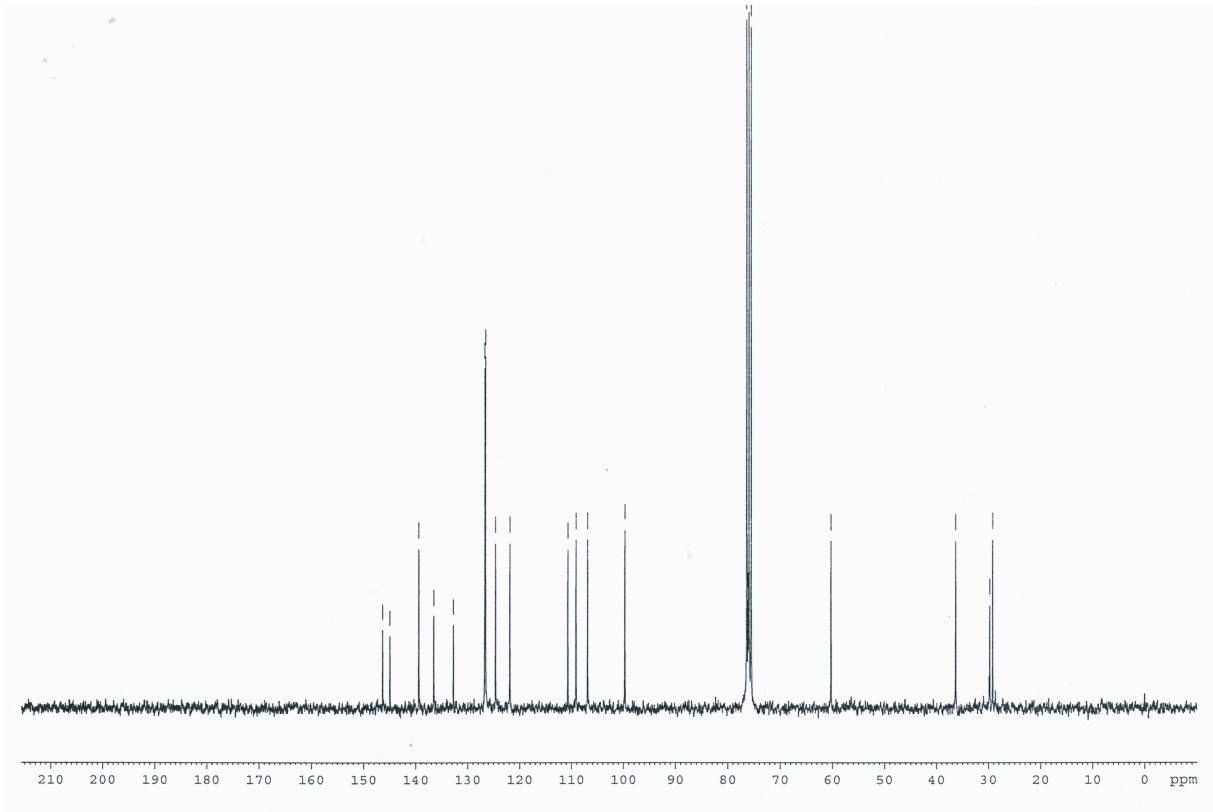
6-(4-methoxyphenyl)-7-phenyl-3-oxabicyclo[4.1.0]hept-4-ene **2a**



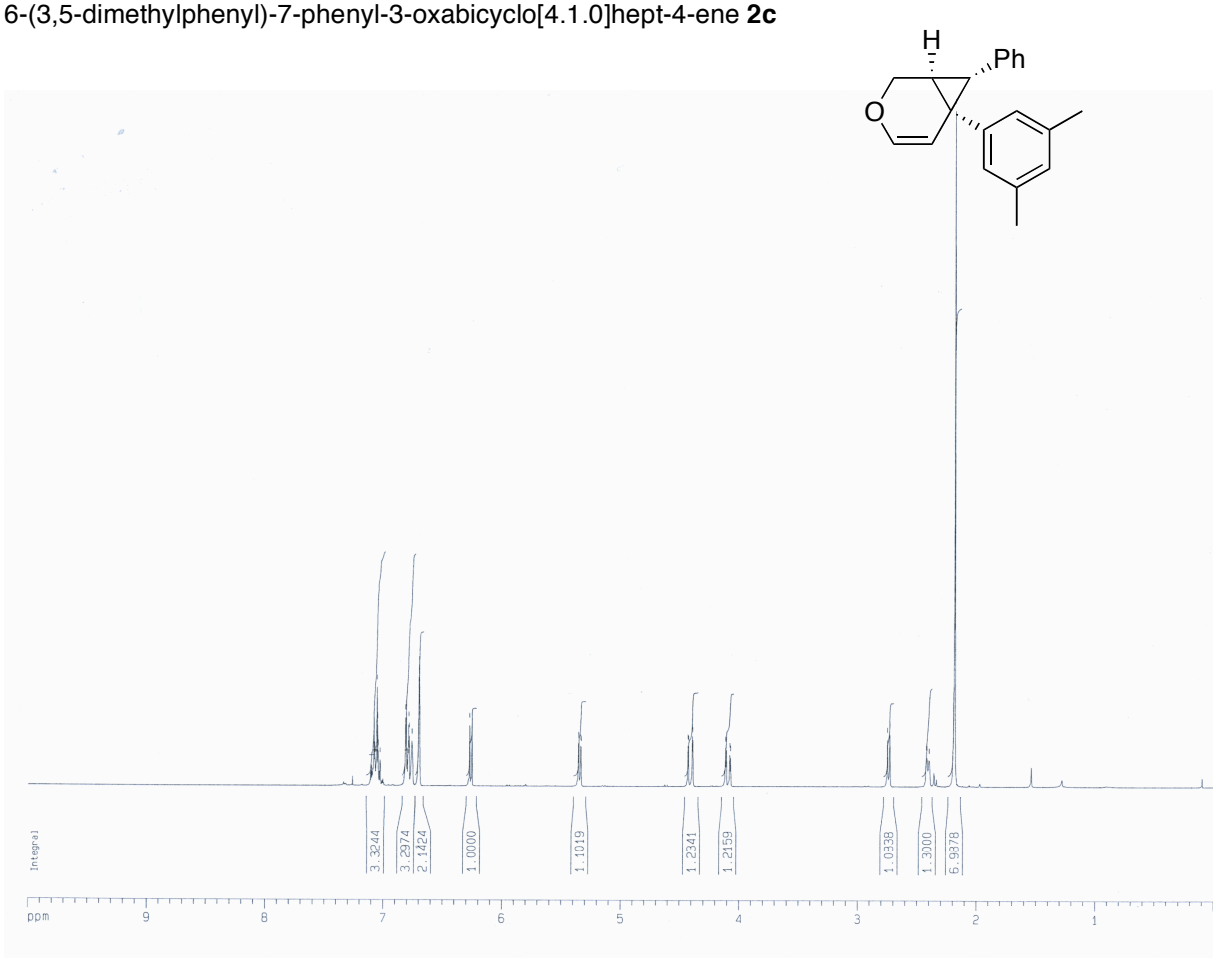


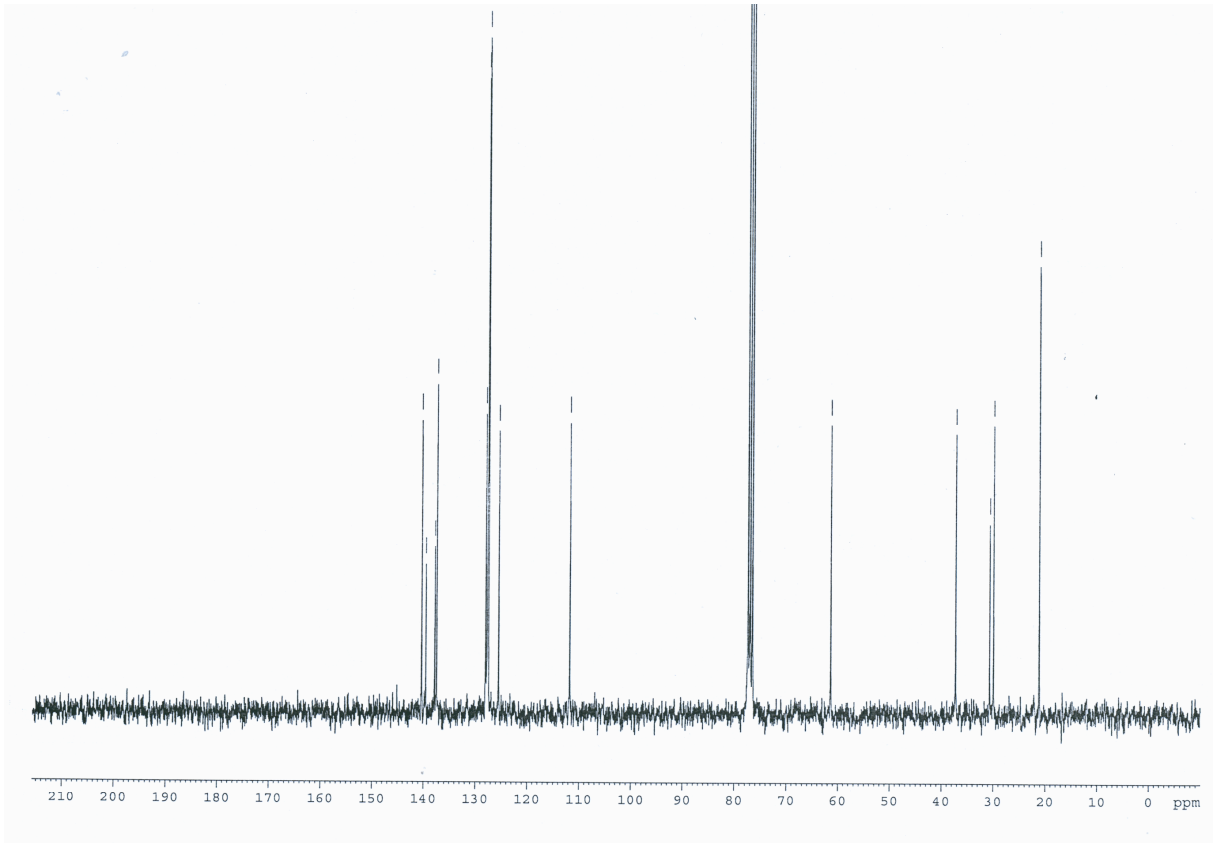
5-(7-phenyl-3-oxabicyclo[4.1.0]hept-4-en-6-yl)benzo[*d*][1,3]dioxole **2b**



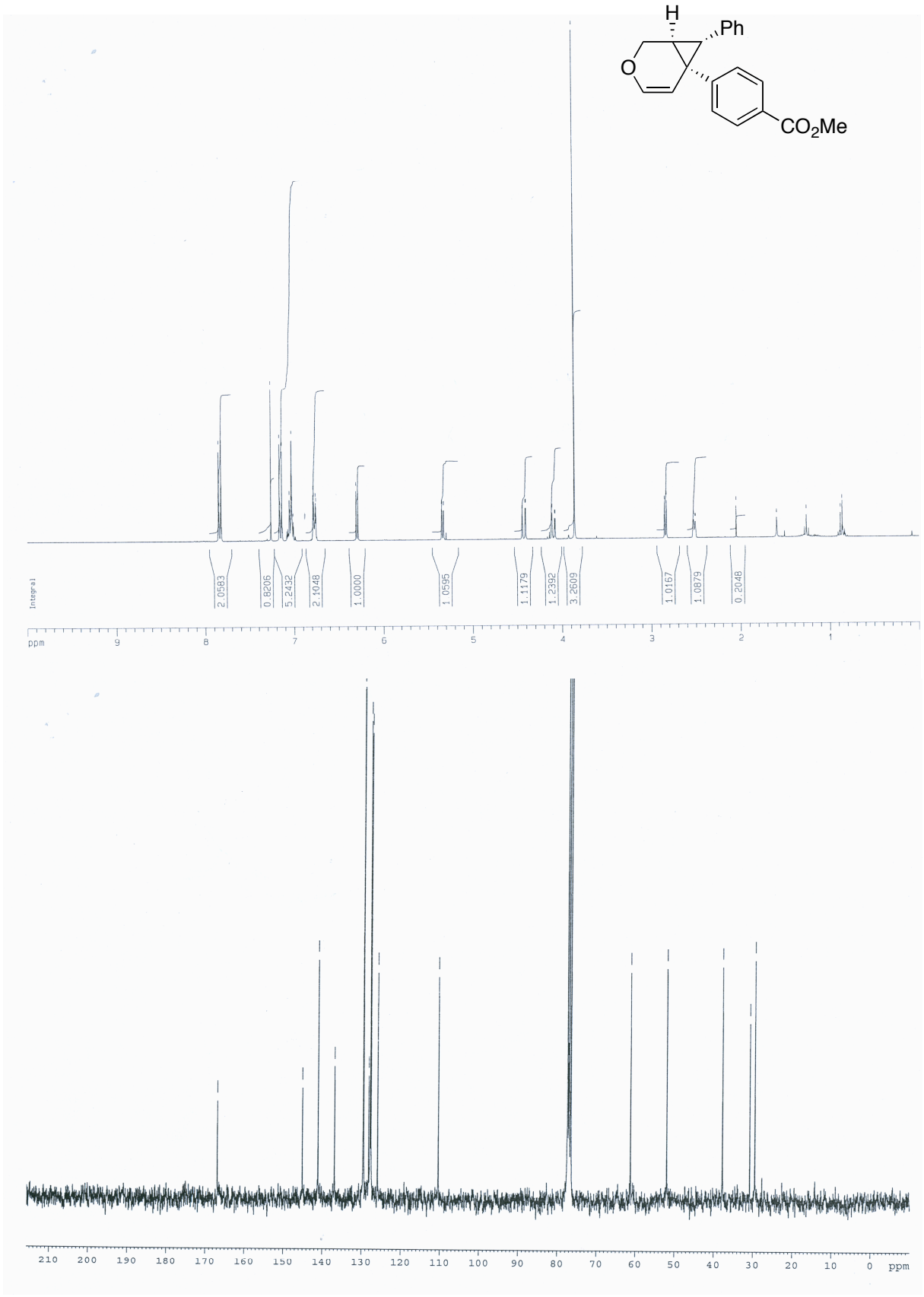


6-(3,5-dimethylphenyl)-7-phenyl-3-oxabicyclo[4.1.0]hept-4-ene **2c**

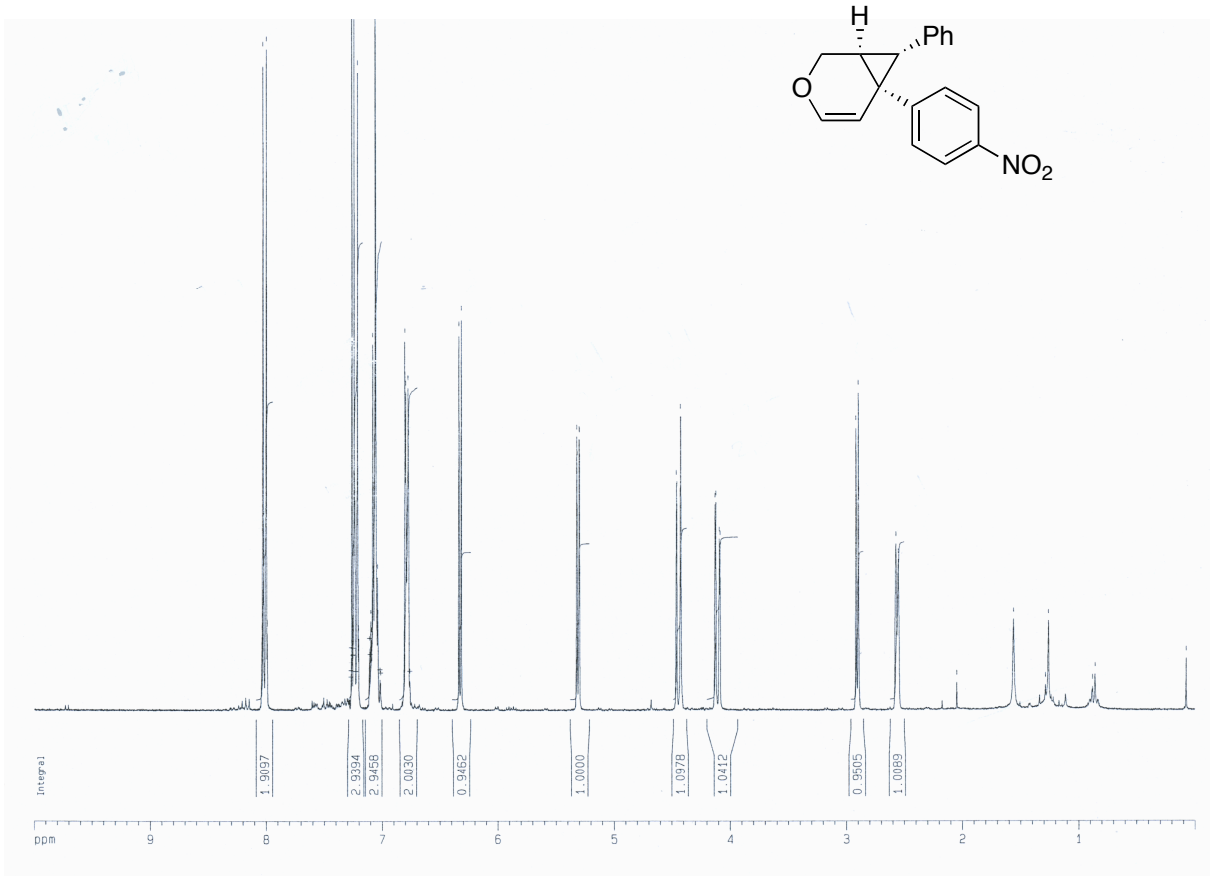


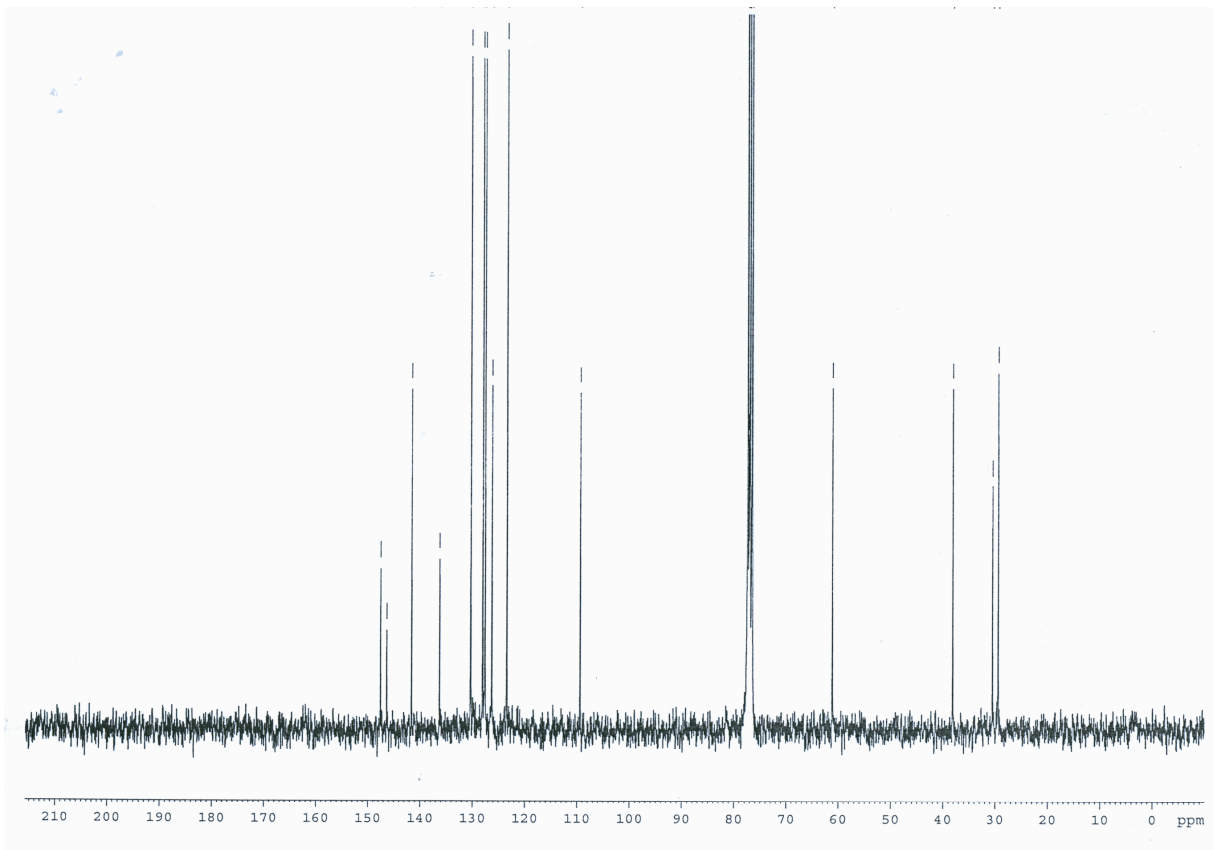


Methyl 4-(7-phenyl-3-oxabicyclo[4.1.0]hept-4-en-6-yl)benzoate **2e**

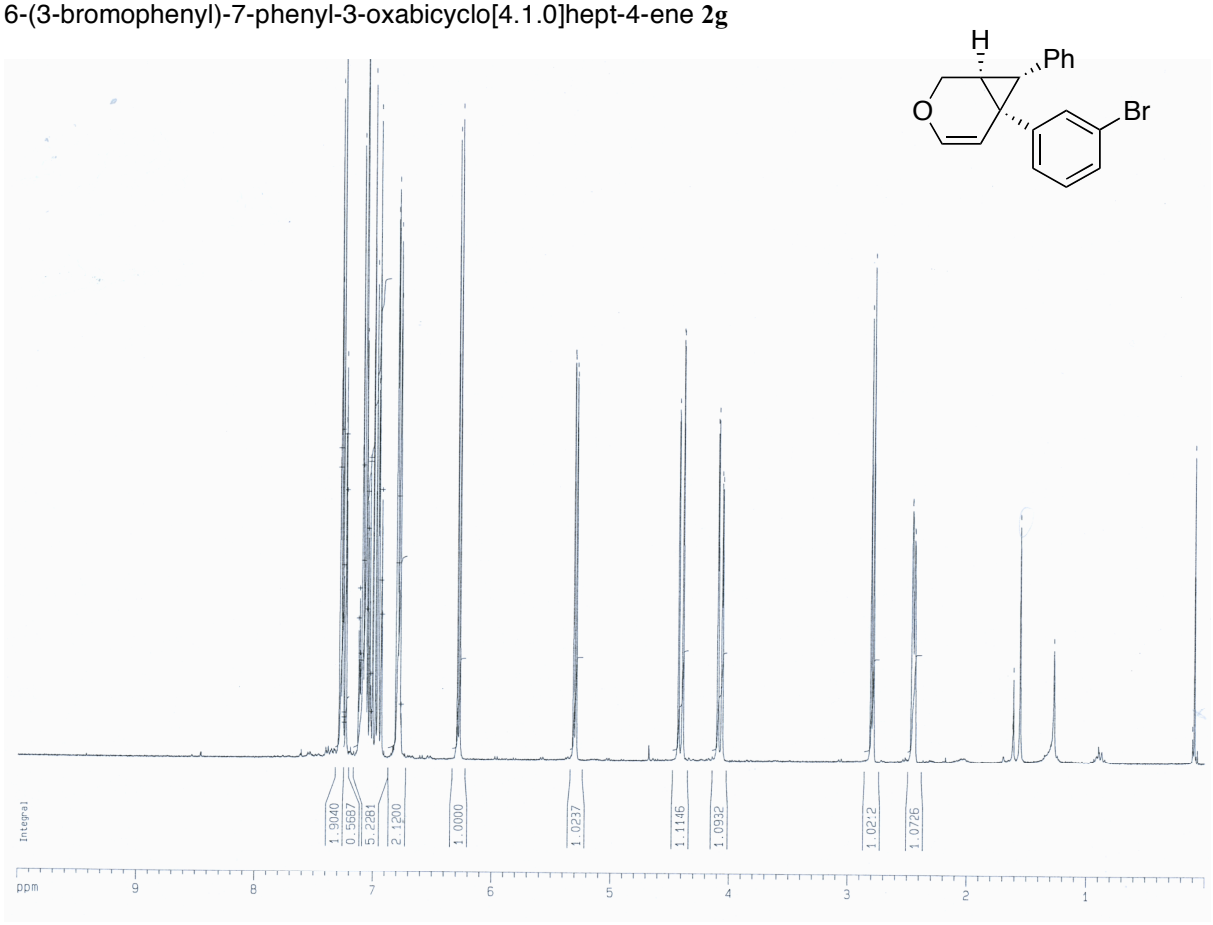


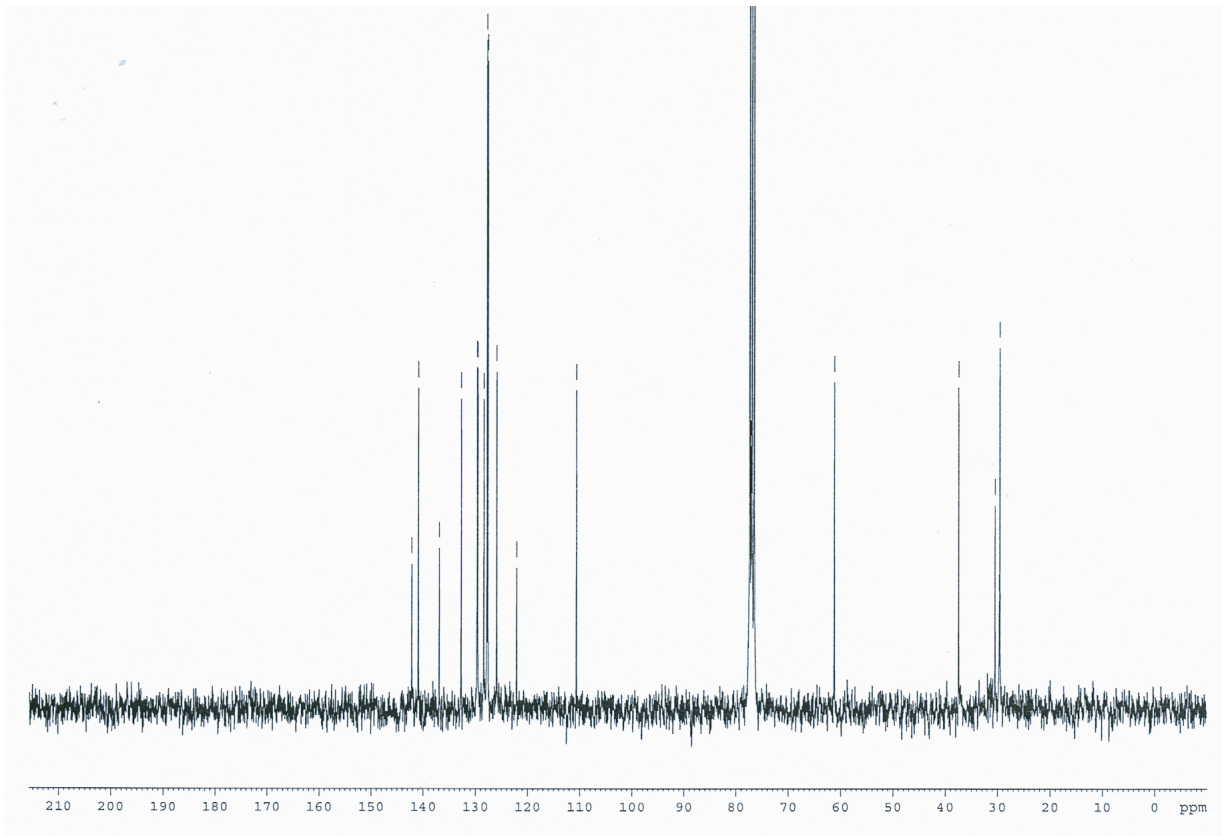
6-(4-nitrophenyl)-7-phenyl-3-oxabicyclo[4.1.0]hept-4-ene **2f**



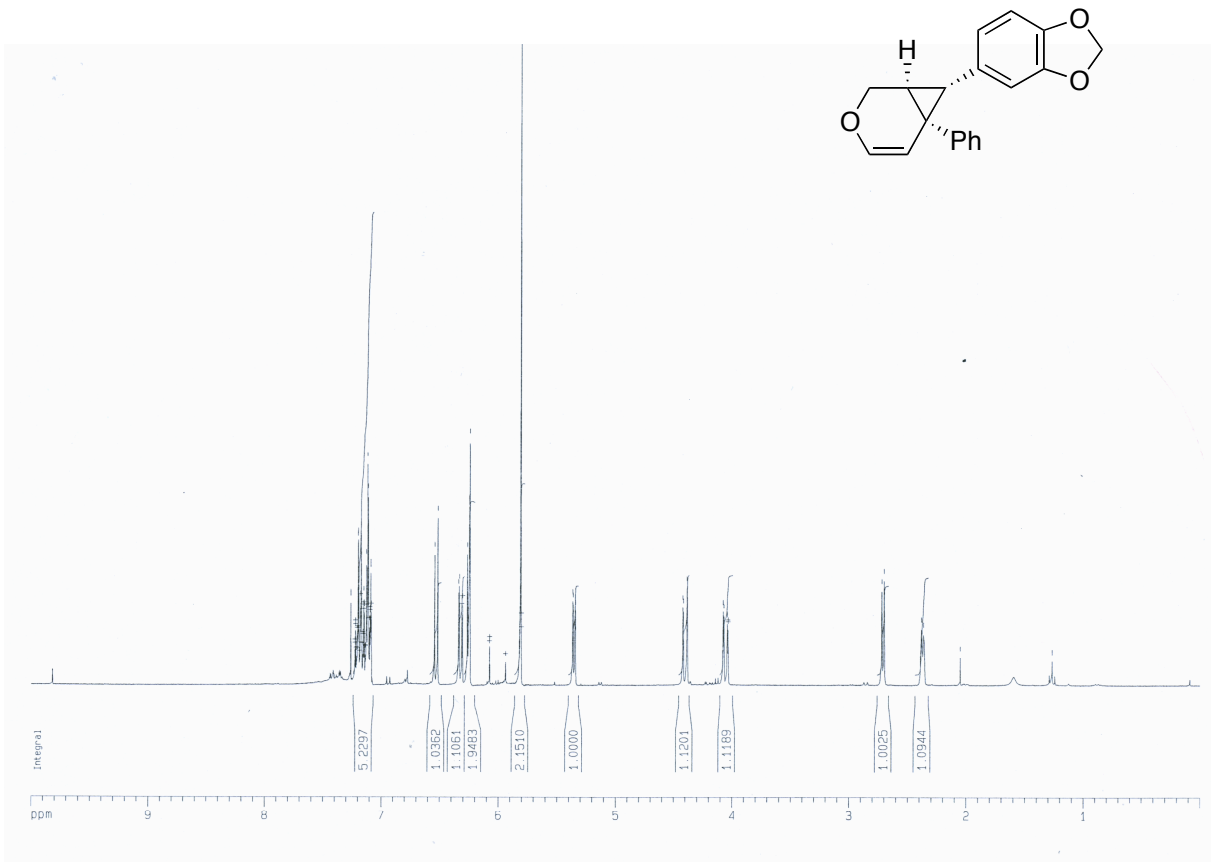


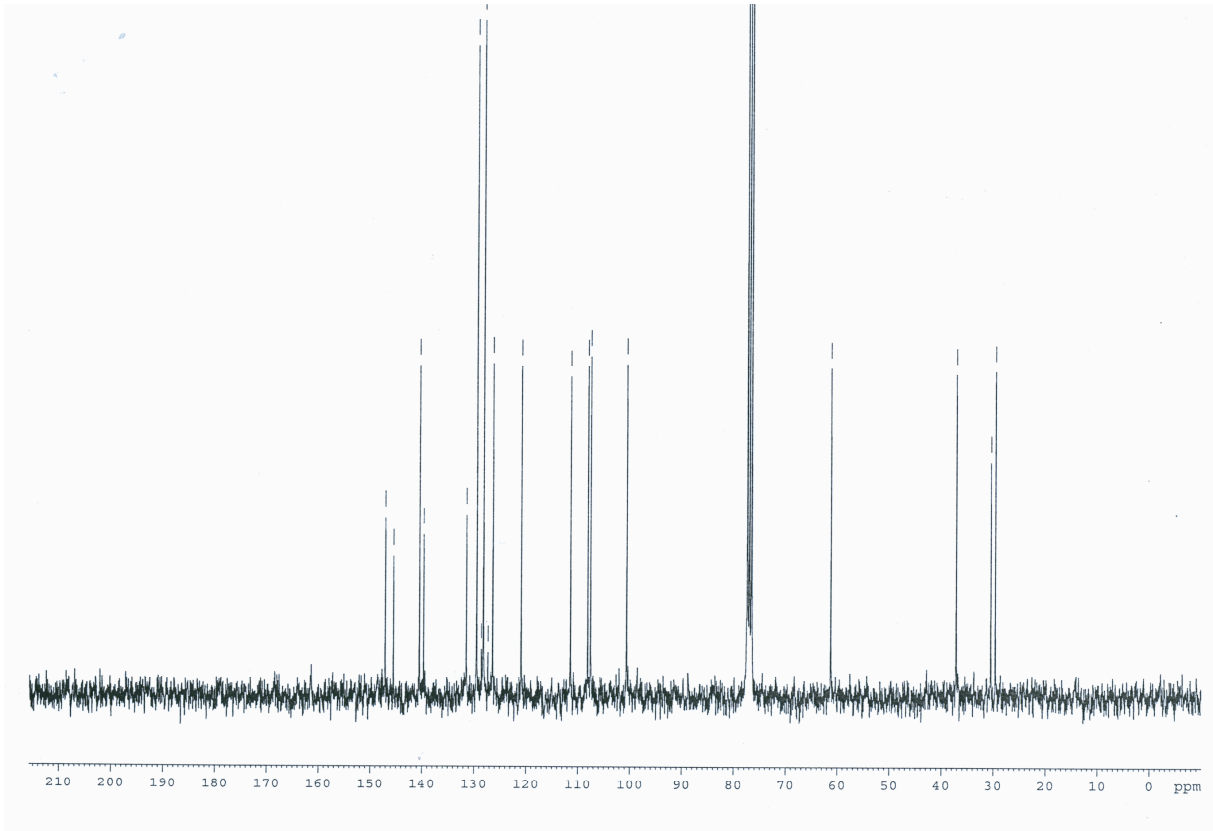
6-(3-bromophenyl)-7-phenyl-3-oxabicyclo[4.1.0]hept-4-ene **2g**



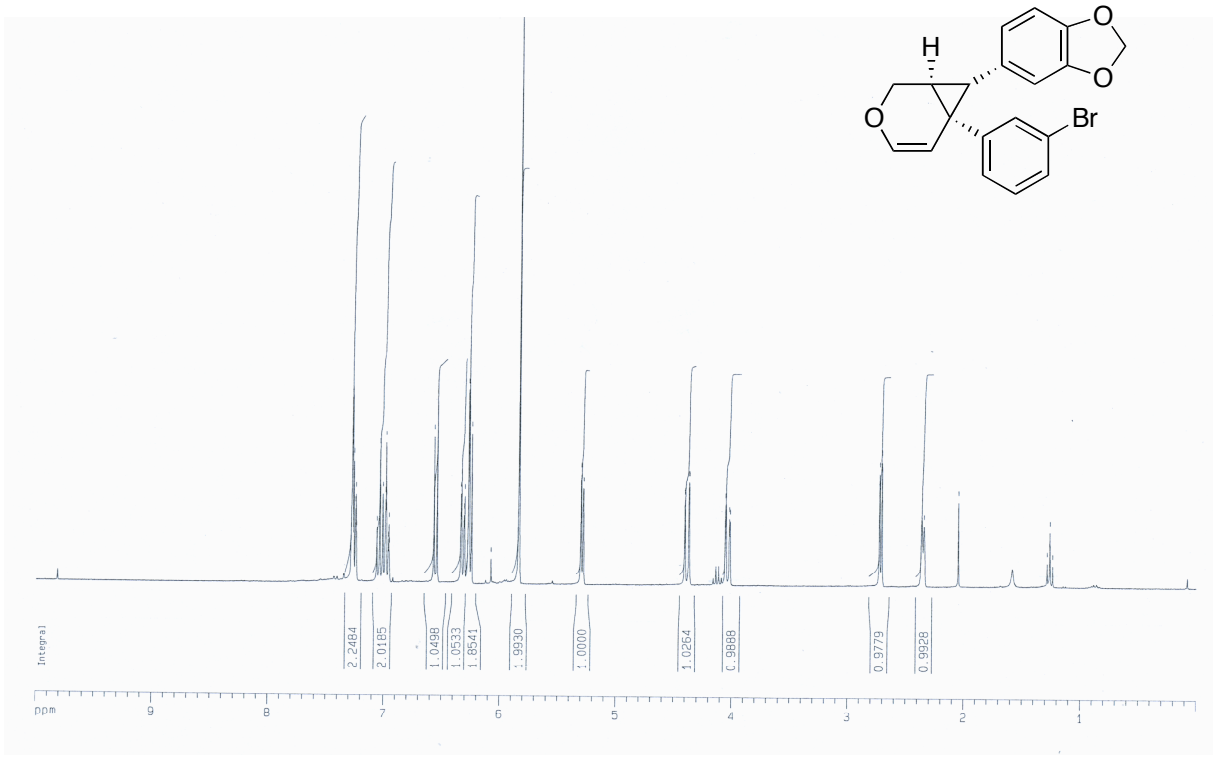


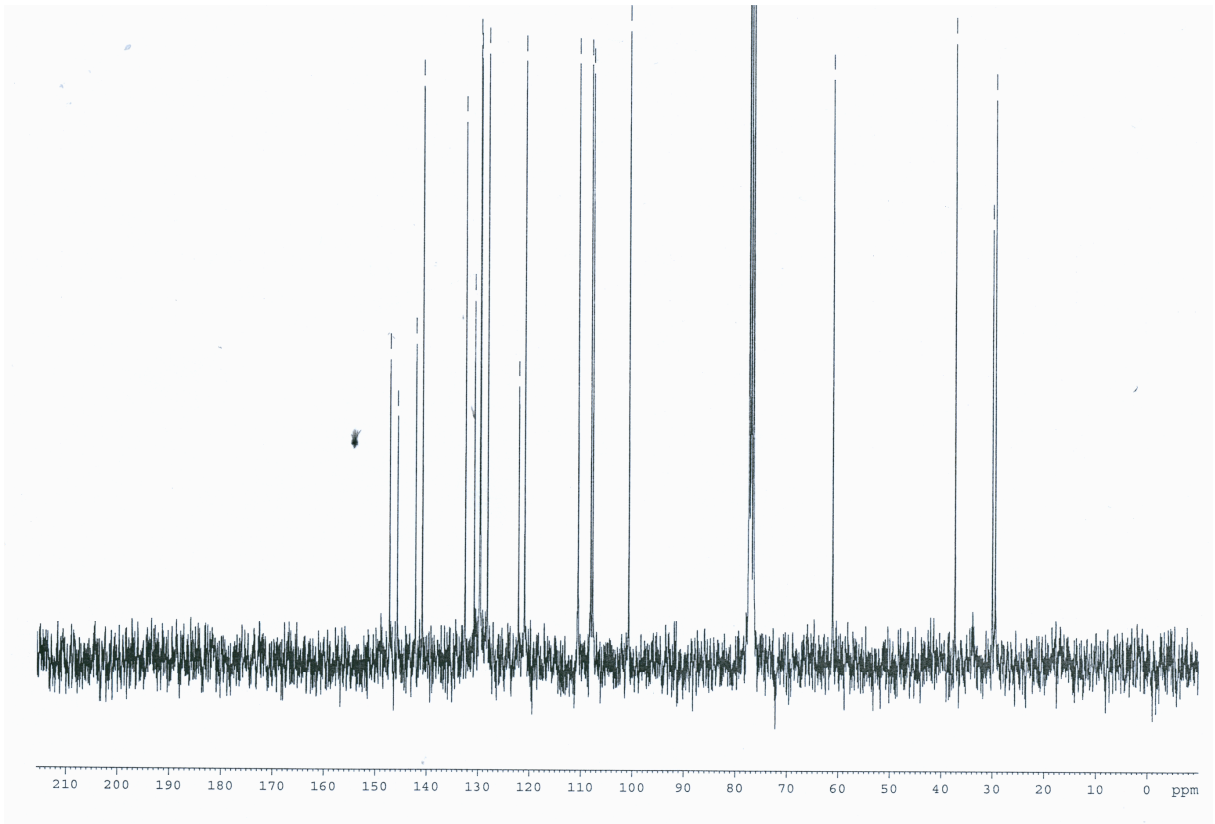
5-(6-phenyl-3-oxabicyclo[4.1.0]hept-4-en-7-yl)benzo[*d*][1,3]dioxole **2h**





5-(6-(3-bromophenyl)-3-oxabicyclo[4.1.0]hept-4-en-7-yl)benzo[*d*][1,3]dioxole **2i**





6-Ethyl-7-phenyl-3-oxabicyclo[4.1.0]hept-4-ene **2j**