Supporting Information

Rhodium-Catalyzed Olefin Isomerization/Enantioselective Intramolecular Alder-Ene Reaction Cascade

Ryuichi Okamoto,[†] Eri Okazaki,[†] Keiichi Noguchi,[‡] and Ken Tanaka*[,†]

[†] *Department of Applied Chemistry, Graduate School of Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan*

[‡] *Instrumentation Analysis Center, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan*

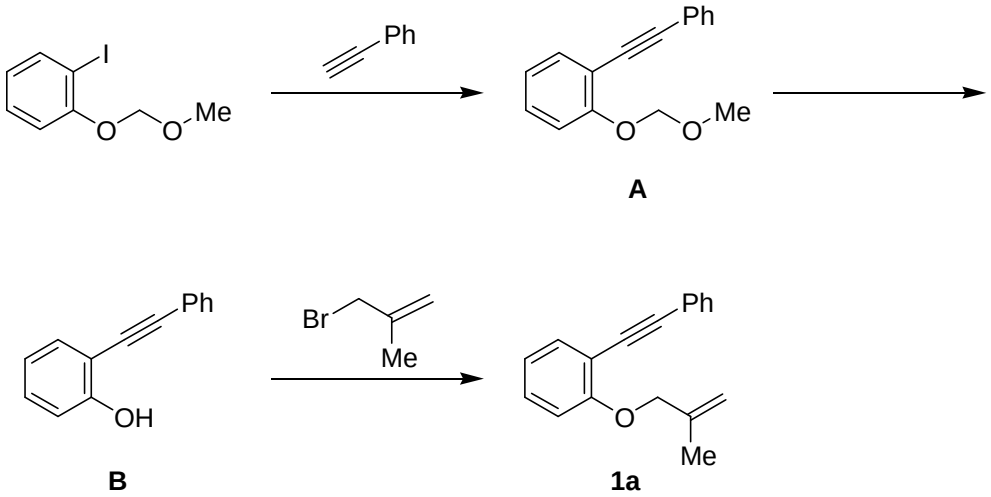
Table of Contents

I. General

Anhydrous CH_2Cl_2 (No. 27,099-7) and $(CH_2Cl)_2$ (No. 28,450-5) were obtained from Aldrich and used as received. Solvents for the synthesis of substrates were dried over Molecular Sieves 4A (Wako) prior to use. All other reagents were obtained from commercial sources and used as received. All reactions were carried out under an atmosphere of argon or nitrogen in oven-dried glassware with magnetic stirring.

II. Synthesis of 1,7-Enynes

1-(2-Methylallyloxy)-2-phenylethynylbenzene (1a)[1]



To a stirred suspension of 1-iodo-2-methoxymethoxybenzene[2] (2.64 g, 10.0 mmol), $PdCl_2(PPh_3)_2$ (0.0702 g, 0.100 mmol), and CuI (0.0381 g, 0.200 mmol) in Et_3N (40 ml) at room temperature was added phenylacetylene (1.12 g, 11.0 mmol). The resulting mixture was stirred at 50 °C for 5 h. The mixture was allowed to cool to room temperature, diluted with Et_2O, filtered, and concentrated. The residue was purified by a silica gel column chromatography (hexane/EtOAc = 20:1), which furnished 1-methoxymethoxy-2-phenylethynylbenzene (**A**)[2] (2.38 g, >99% yield) as a yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.59–7.49 (m, 2H), 7.50 (dd, J = 7.5, 1.5 Hz, 1H), 7.41–7.21 (m, 4H), 7.13 (dd, J = 8.4, 1.2 Hz, 1H), 7.00 (td, J = 7.5, 1.2 Hz, 1H), 5.29 (s, 2H), 3.55 (s, 3H).

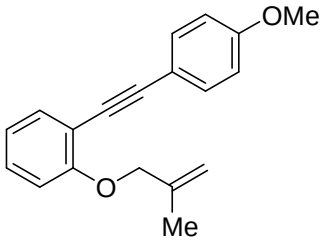
To a stirred solution of 1-methoxymethoxy-2-phenylethynylbenzene (**A**)[2] (1.43 g, 6.00 mmol) in THF/*i*-PrOH (1:1, 24 mL) at room temperature was added 6 N aqueous HCl (12 mL). The resulting solution was stirred at room temperature for 16 h. After the solution was concentrated, the residue was diluted with water and EtOAc. The organic extract was washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by a silica gel column chromatography (hexane/EtOAc = 20:1), which furnished 2-phenylethynylphenol (**B**)[2] (1.08 g, 5.56 mmol, 93% yield) as a pale yellow solid.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.60–7.49 (m, 2H), 7.48–7.30 (m, 4H), 7.32–7.21 (m, 1H), 7.03–6.94 (m, 1H), 6.91 (td, J = 7.5, 0.9 Hz, 1H), 5.82 (s, 1H).

A mixture of 2-phenylethynylphenol (**B**)[2] (0.777 g, 4.00 mmol), 3-bromo-2-methylpropene (0.648 g, 4.80 mmol), and K_2CO_3 (1.11 g, 8.00 mmol) in CH_3CN (10 mL) was stirred at room temperature for 15 h. The reaction was quenched by the addition of water and diluted with Et_2O. The organic extract was washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by a silica gel column chromatography (hexane/toluene = 5:1), which furnished **1a**[1] (0.897 g, 3.61 mmol, 91% yield) as a yellow oil.

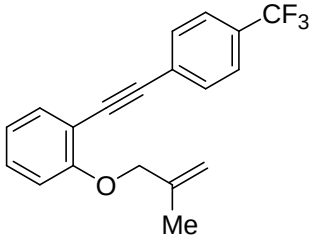
^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.61–7.43 (m, 3H), 7.43–7.18 (m, 4H), 6.94–6.84 (m, 1H), 6.94 (td, *J* = 7.5, 1.1 Hz, 1H), 5.28–5.17 (m, 1H), 5.07–4.95 (m, 1H), 4.52 (s, 2H), 1.94–1.84 (m, 3H).

1-(2-Methylallyloxy)-2-(4-methoxyphenylethynyl)benzene (1b)



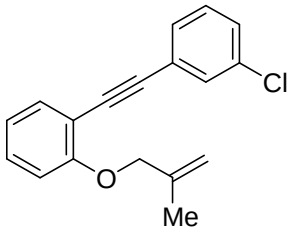
The title compound was prepared by following the procedure for the synthesis of **1a** using 4-methoxyphenylacetylene instead of phenylacetylene. Pale yellow solid; Mp 32.0–33.0 °C; IR (KBr) 2936, 2534, 2215, 1286, 1030 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.51–7.43 (m, 3H), 7.28–7.19 (m, 1H), 6.91 (td, *J* = 7.5, 0.9 Hz, 1H), 6.91–6.82 (m, 3H), 5.26–5.19 (m, 1H), 5.04–4.96 (m, 1H), 4.50 (s, 2H), 3.80 (s, 3H), 1.92–1.84 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.4, 159.0, 140.7, 133.1, 133.0, 129.2, 120.6, 115.9, 113.9, 113.5, 112.34, 112.30, 93.4, 84.4, 72.1, 55.3, 19.4; HRMS (ESI) calcd for $C_{19}H_{18}O_2Na$ $[M+Na]^+$ 301.1199, found 301.1211.

1-(2-Methylallyloxy)-2-(4-trifluoromethylphenylethynyl)benzene (1c)



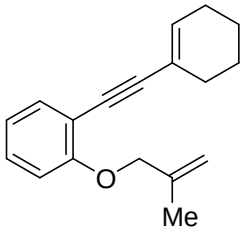
The title compound was prepared by following the procedure for the synthesis of **1a** using 4-trifluoromethylphenylacetylene instead of phenylacetylene. Yellow solid; Mp 39.5–40.5 °C; IR (KBr) 3076, 2915, 2220, 1920, 1331, 1134 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.66–7.54 (m, 4H), 7.50 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.35–7.25 (m, 1H), 7.00–6.90 (m, 1H), 6.90 (d, *J* = 8.2 Hz, 1H), 5.26–5.17 (m, 1H), 5.06–4.98 (m, 1H), 4.52 (s, 2H), 1.92–1.84 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.4, 140.5, 133.4, 131.7, 130.2, 129.8, 129.4, 127.6, 125.8, 125.3, 125.23, 125.18, 125.1, 122.2, 120.7, 112.4, 112.34, 112.28, 92.0, 88.4, 72.0, 19.3; HRMS (ESI) calcd for $C_{19}H_{15}F_3ONa$ $[M+Na]^+$ 339.0967, found 339.0973.

1-(3-Chlorophenylethynyl)-2-(2-methylallyloxy)benzene (1d)



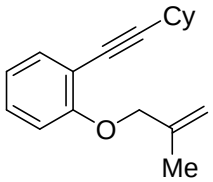
The title compound was prepared by following the procedure for the synthesis of **1a** using 3-chlorophenylacetylene instead of phenylacetylene. Yellow oil; IR (neat) 3075, 2914, 1493, 1242, 750 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.58–7.46 (m, 1H), 7.48 (dd, J = 7.5, 1.5 Hz, 1H), 7.44–7.35 (m, 1H), 7.34–7.18 (m, 3H), 6.93 (t, J = 7.5 Hz, 1H), 6.88 (d, J = 8.4 Hz, 1H), 5.21 (s, 1H), 5.02 (s, 1H), 4.51 (s, 2H), 1.88 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.3, 140.5, 134.1, 133.4, 131.3, 129.9, 129.6, 129.5, 128.2, 125.5, 120.7, 112.6, 112.4, 112.3, 92.0, 87.1, 72.0, 19.3; HRMS (ESI) calcd for $C_{18}H_{15}ClONa$ $[M+Na]^+$ 305.0704, found 305.0704.

1-(1-Cyclohexenylethynyl)-2-(2-methylallyloxy)benzene (1e)



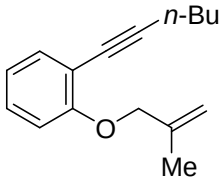
The title compound was prepared by following the procedure for the synthesis of **1a** using 1-cyclohexenylacetylene instead of phenylacetylene. Yellow oil; IR (neat) 2930, 1445, 1238, 902, 749 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.48 (dd, J = 7.5, 1.6 Hz, 1H), 7.26–7.15 (m, 1H), 6.93–6.79 (m, 2H), 6.20 (tt, J = 4.1, 2.1 Hz, 1H), 5.23–5.14 (m, 1H), 5.04–4.94 (m, 1H), 4.48 (s, 2H), 2.35–2.14 (m, 2H), 2.23–2.06 (m, 2H), 1.92–1.80 (m, 3H), 1.75–1.54 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 158.9, 140.6, 134.6, 133.1, 128.9, 121.0, 120.5, 113.6, 112.3, 112.2, 95.4, 83.0, 72.0, 29.2, 25.8, 22.4, 21.6, 19.3; HRMS (ESI) calcd for $C_{18}H_{20}Ona$ $[M+Na]^+$ 275.1406, found 275.1406.

Cyclohexylethynyl-2-(2-methylallyloxy)benzene (1f)



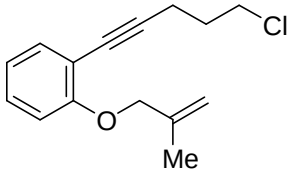
The title compound was prepared by following the procedure for the synthesis of **1a** using cyclohexylacetylene instead of phenylacetylene. Colorless oil; IR (neat) 2930, 2853, 1492, 1446, 1254, 749 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.42–7.32 (m, 1H), 7.27–7.12 (m, 1H), 6.93–6.77 (m, 2H), 5.26–5.13 (m, 1H), 5.06–4.91 (m, 1H), 4.46 (s, 2H), 2.79–2.50 (m, 1H), 2.04–1.61 (m, 4H), 1.86 (s, 3H), 1.70–1.42 (m, 3H), 1.49–1.21 (m, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 159.0, 140.7, 133.3, 128.6, 120.5, 113.8, 112.23, 112.17, 98.6, 76.5, 71.9, 32.7, 29.9, 26.0, 24.8, 19.3; HRMS (ESI) calcd for $C_{18}H_{22}Ona$ $[M+Na]^+$ 277.1563, found 277.1566.

1-(1-Hexynyl)-2-(2-methylallyloxy)benzene (1g)



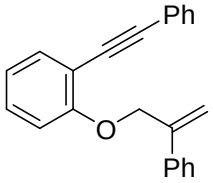
The title compound was prepared by following the procedure for the synthesis of **1a** using 1-hexyne instead of phenylacetylene. Pale yellow oil; IR (neat) 2932, 1491, 1445, 1260, 749 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.36 (dd, J = 7.5, 1.8 Hz, 1H), 7.24–7.14 (m, 1H), 6.86 (td, J = 7.4, 0.9 Hz, 1H), 6.86–6.79 (m, 1H), 5.21–5.13 (m, 1H), 5.03–4.94 (m, 1H), 4.47 (s, 2H), 2.46 (t, J = 7.0 Hz, 2H), 1.93–1.77 (m, 3H), 1.69–1.40 (m, 4H), 0.94 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.1, 140.7, 133.4, 128.6, 120.5, 113.8, 112.32, 112.27, 94.5, 76.6, 72.0, 30.9, 22.0, 19.4, 19.3, 13.6; HRMS (ESI) calcd for $C_{16}H_{20}Ona$ $[M+Na]^+$ 251.1406, found 251.1406.

1-(5-Chloro-1-pentynyl)-2-(2-methylallyloxy)benzene (1h)



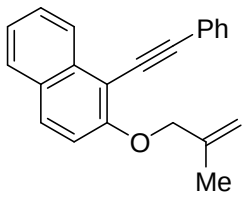
The title compound was prepared by following the procedure for the synthesis of **1a** using 5-chloro-1-pentyne instead of phenylacetylene. Pale yellow oil; IR (neat) 2914, 1490, 1259, 751 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.36 (dd, J = 7.5, 1.6 Hz, 1H), 7.29–7.15 (m, 1H), 6.94–6.77 (m, 2H), 5.22–5.08 (m, 1H), 5.05–4.93 (m, 1H), 4.47 (s, 2H), 3.74 (t, J = 6.6 Hz, 2H), 2.65 (t, J = 6.6 Hz, 2H), 2.06 (quint, J = 6.6 Hz, 2H), 1.93–1.75 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.2, 140.6, 133.3, 128.9, 120.5, 113.3, 112.5, 112.2, 92.1, 77.7, 72.0, 43.7, 31.6, 19.3, 17.1; HRMS (ESI) calcd for $C_{15}H_{17}ClONa$ $[M+Na]^+$ 271.0860, found 271.0859.

1-(2-Phenylallyloxy)-2-phenylethynylbenzene (1i)



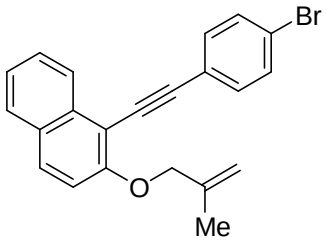
The title compound was prepared by following the procedure for the synthesis of **1a** using toluene-4-sulfonic acid 2-phenylallyl ester[3] instead of 3-bromo-2-methylpropene. Yellow oil; IR (neat) 3058, 2922, 1496, 1241, 1025, 753 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.59–7.45 (m, 3H), 7.48–7.38 (m, 2H), 7.40–7.24 (m, 7H), 7.03–6.89 (m, 2H), 5.73–5.54 (m, 2H), 4.99 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.0, 142.8, 138.5, 133.2, 131.5, 129.5, 128.4, 128.2, 128.0, 127.9, 126.2, 123.6, 120.9, 114.6, 113.3, 112.5, 93.6, 85.7, 70.1; HRMS (ESI) calcd for $C_{23}H_{18}Ona$ $[M+Na]^+$ 333.1250, found 333.1251.

2-(2-Methylallyloxy)-1-phenylethynylnaphthalene (1j)



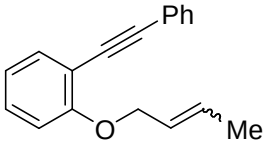
The title compound was prepared by following the procedure for the synthesis of **1a** using 1-iodo-2-methoxymethoxynaphthalene[4] instead of 1-iodo-2-methoxymethoxybenzene. Pale yellow solid; Mp 40.0–41.5 °C; IR (KBr) 3055, 2915, 2203, 1276, 1087, 751 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.36 (d, J = 8.4 Hz, 1H), 7.84–7.72 (m, 2H), 7.72–7.58 (m, 2H), 7.61–7.49 (m, 1H), 7.46–7.29 (m, 4H), 7.23 (d, J = 9.0 Hz, 1H), 5.26 (s, 1H), 5.03 (s, 1H), 4.68 (s, 2H), 1.92 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 158.2, 140.8, 134.5, 131.5, 129.9, 128.7, 128.3, 128.1, 128.0, 127.2, 125.3, 124.3, 124.0, 114.5, 112.7, 107.3, 98.9, 84.1, 73.1, 19.4; HRMS (ESI) calcd for $C_{22}H_{18}Ona$ $[M+Na]^+$ 321.1250, found 321.1251.

1-(4-Bromophenylethynyl)-2-(2-methylallyloxy)naphthalene (1k)



The title compound was prepared by following the procedure for the synthesis of **1a** using 1-iodo-2-methoxymethoxynaphthalene[4] and 4-bromophenylacetylene instead of 1-iodo-2-methoxymethoxybenzene and phenylacetylene, respectively. Pale yellow solid; Mp 80.0–82.0 °C; IR (KBr) 3062, 2852, 2204, 1277, 1089, 821 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.31 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 9.0 Hz, 1H), 7.78 (d, J = 7.8 Hz, 1H), 7.64–7.42 (m, 5H), 7.39 (t, J = 7.2 Hz, 1H), 7.22 (d, J = 9.0 Hz, 1H), 5.24 (s, 1H), 5.03 (s, 1H), 4.67 (s, 2H), 1.91 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 158.3, 140.7, 134.3, 132.9, 131.6, 130.2, 128.7, 128.1, 127.3, 125.2, 124.3, 122.9, 122.2, 114.4, 112.7, 106.8, 97.8, 85.3, 73.0, 19.4; HRMS (ESI) calcd for $C_{22}H_{17}BrONa$ $[M+Na]^+$ 399.0355, found 399.0355.

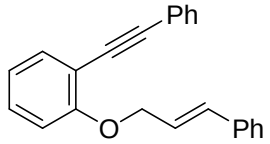
1-(2-Butenyloxy)-2-phenylethynylbenzene (1l, *E*/*Z* = 82:18)



The title compound was prepared by following the procedure for the synthesis of **1a** using an *E*/*Z* mixture of 1-bromo-2-butene instead of 3-bromo-2-methylpropene. The olefin geometries were determined by coupling constants between olefinic protons. Pale yellow oil; IR (neat) 3030, 2916, 1496, 1277, 752 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) *E*-isomer: δ 7.61–7.49 (m, 2H), 7.49 (dd, J = 7.5, 1.7 Hz, 1H), 7.42–7.18 (m, 4H), 6.93 (td, J = 7.5, 1.2 Hz, 2H), 6.90 (d, J = 8.4 Hz, 2H), 5.93 (dqt, J = 15.4, 6.3, 1.2 Hz, 1H), 5.85–5.67 (m, 1H), 4.66–4.49 (m, 2H), 1.76 (dq, J = 6.3, 1.4 Hz, 3H), methylene protons of *Z*-isomer: δ 4.78–4.66 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.2, 133.4, 131.6, 129.7, 129.5,

128.2, 128.0, 125.9, 125.7, 123.7, 120.6, 113.1, 112.6, 112.5, 93.4, 85.9, 69.4, 64.8, 17.8, 13.5; HRMS (ESI) calcd for $C_{18}H_{16}Ona$ $[M+Na]^+$ 271.1093, found 271.1092.

1-[(*E*)-3-Phenylallyloxy]-2-phenylethynylbenzene (1m)[5]

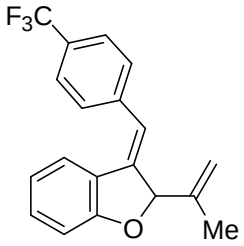


The title compound was prepared by following the procedure for the synthesis of **1a** using cinnamyl bromide instead of 3-bromo-2-methylpropene. Colorless solid; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.61–7.51 (m, 2H), 7.52 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.48–7.15 (m, 9H), 7.04–6.88 (m, 2H), 6.94–6.78 (m, 1H), 6.46 (dt, *J* = 15.9, 5.1 Hz, 1H), 4.82 (dd, *J* = 5.1, 1.8 Hz, 2H).

III. Rhodium-Catalyzed Olefin Isomerization/Enantioselective Intramolecular Alder-Ene Reaction Cascade of 1,7-Enynes

General Procedure (Table 2, entry 3). $[Rh(cod)_2]BF_4$ (6.1 mg, 0.015 mmol) and ®-BINAP (9.3 mg, 0.015 mmol) were dissolved in CH_2Cl_2 (2.0 mL) and the mixture was stirred at room temperature for 0.5 h. H_2 was introduced to the resulting solution in a Schlenk tube. After stirring at room temperature for 1 h, the resulting solution was concentrated to dryness. To a solution of the residue dissolved in $(CH_2Cl)_2$ (0.5 mL) was added a solution of **1c** (94.9 mg, 0.300 mmol) in $(CH_2Cl)_2$ (1.0 mL) at room temperature. After stirring at 70 °C for 48 h, The resulting solution was diluted with hexane, passed through a short column of a silica gel eluting with Et_2O, concentrated, and purified by a preparative TLC (hexane/toluene = 5:1), which furnished **3c** (72.4 mg, 0.229 mmol, 76% yield) as a yellow oil.

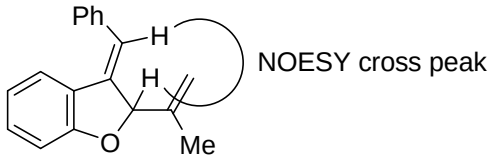
(–)-(*E*)-2-Isopropenyl-3-(4-trifluoromethylbenzylidene)-2,3-dihydrobenzofuran [(–)-3c, Table 2, entry 3]



The olefin geometry was determined with ^1H NMR by analogy to **3a**. Yellow oil; $[\alpha]^{25}_D$ −1.8° (*c* 3.62, $CHCl_3$, 98% ee); IR (neat) 3080, 2977, 1462, 1324, 1126, 749 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.63 (d, *J* = 8.1 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.26–7.13 (m, 1H), 7.25 (d, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 8.1 Hz, 1H), 6.71 (t, *J* = 7.5 Hz, 1H), 6.43–6.29 (m, 1H), 5.63 (d, *J* = 2.7 Hz, 1H), 5.20 (s, 1H), 5.19–5.05 (m, 1H), 1.73 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.2, 143.4, 140.7, 140.5, 131.4, 129.0, 128.7, 126.0, 125.5, 125.44, 125.39, 125.3, 123.8, 123.6, 122.4, 120.4, 118.3, 116.2, 110.7, 91.0, 15.8; HRMS (ESI) calcd for $C_{19}H_{16}F_3O$ $[M+H]^+$ 317.1148, found 317.1147; doubly connected CHIRALCEL OJ-H and CHIRALPAK AD-H, hexane/*i*-PrOH = 98:2, 0.5 mL/min, retention times: 34.8 min [major

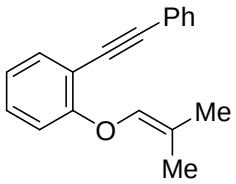
(–)-isomer] and 37.7 min [minor (+)-isomer].

(–)-(*E*)-3-Benzylidene-2-isopropenyl-2,3-dihydrobenzofuran [(–)-3a, Table 2, Entry 1; Table 1, entry 10]



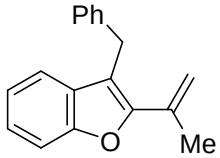
The title compound was isolated as a mixture of **2a** and **3a** (56.9 mg, 0.229 mmol, **2a**/**3a** = 10:90, **2a**: 8% yield, **3a**: 69% yield). Pure **2a** and **3a** were isolated by a gel permeation chromatography (GPC). The olefin geometry was determined by the NOESY experiment. Pale yellow oil; $[\alpha]^{25}_{D}$ −1.6° (*c* 1.82, $CHCl_3$, 98% ee); IR (neat) 3078, 2974, 1461, 1206, 990, 750 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.47–7.31 (m, 4H), 7.34–7.23 (m, 2H), 7.21–7.08 (m, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.67 (td, *J* = 7.5, 0.9 Hz, 1H), 6.39 (d, *J* = 2.7 Hz, 1H), 5.62 (d, *J* = 2.7 Hz, 1H), 5.24–5.13 (m, 1H), 5.10 (quint, *J* = 1.5 Hz, 1H), 1.78–1.68 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 163.9, 143.7, 138.5, 136.9, 130.7, 128.4, 128.3, 127.2, 124.4, 123.6, 120.2, 120.1, 115.9, 110.4, 90.9, 15.8; HRMS (ESI) calcd for $C_{18}H_{16}Ona$ $[M+Na]^+$ 271.1093, found 271.1087; CHIRALPAK AD-H, hexane/*i*-PrOH = 98:2, 0.5 mL/min, retention times: 8.6 min [minor (+)-isomer] and 11.4 min [major (–)-isomer].

1-(2-Methylpropenyloxy)- 2-phenylethynylbenzene (2a, Table 1, entry 10)



Pale yellow solid; Mp 33.5–34.5 °C; IR (KBr) 3060, 2916, 1236, 1125, 753 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.63–7.41 (m, 3H), 7.41–7.18 (m, 4H), 7.04–6.90 (m, 2H), 6.30 (sept, *J* = 1.5 Hz, 1H), 1.86–1.74 (m, 3H), 1.76–1.64 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 158.1, 135.0, 133.4, 131.6, 129.5, 128.2, 128.1, 123.6, 121.6, 118.1, 114.1, 113.1, 93.7, 85.5, 19.4, 15.3; HRMS (ESI) calcd for $C_{18}H_{16}Ona$ $[M+Na]^+$ 271.1093, found 271.1090.

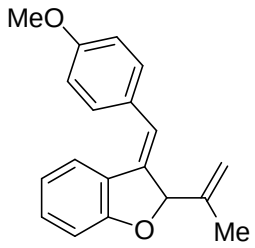
3-Benzyl-2-isopropenylbenzofuran (4a, Table 1, entry 10)



Pale yellow solid; Mp 47.5–48.5 °C; IR (KBr) 3026, 2921, 1452, 1109, 898 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.44 (dt, *J* = 8.1, 0.8 Hz, 1H), 7.31 (ddd, *J* = 7.7, 1.4, 0.8 Hz, 1H), 7.30–7.15 (m, 6H), 7.18–7.08 (m, 1H), 5.55–5.42 (m, 1H), 5.22 (quint, *J* = 1.5 Hz, 1H), 4.22 (s, 2H), 2.21 (dd, *J* = 1.5, 0.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 153.5, 153.2, 139.6, 134.4, 130.4, 128.5, 128.0, 126.1, 124.4, 122.4, 119.8, 115.9, 114.1, 110.9, 30.1, 21.0; HRMS (APCI) calcd for $C_{18}H_{17}O$ $[M+H]^+$ 249.1274,

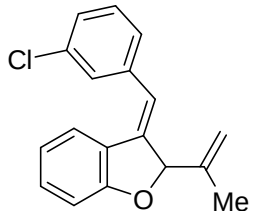
found 249.1263.

(+)-(*E*)-2-Isopropenyl-3-(4-methoxybenzylidene)-2,3-dihydrobenzofuran [(+)-3b, Table 2, entry 2]



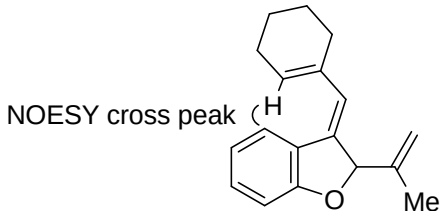
The title compound was isolated as a mixture of **3b** and **4b** (61.5 mg, 0.221 mmol, **3b**/**4b** = 93:7, **3b**: 69% yield, **4b**: 5% yield). Pure **3b** was isolated by a gel permeation chromatography (GPC). The olefin geometry was determined with ^{1}H NMR by analogy to **3a**. Pale yellow oil; $[\alpha]^{25}_D$ +12.6° (*c* 2.63, $CHCl_3$, 97% ee); IR (neat) 2952, 2835, 1508, 1458, 1249, 749 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.40–7.28 (m, 3H), 7.21–7.08 (m, 1H), 6.97–6.85 (m, 2H), 6.85 (d, *J* = 7.8 Hz, 1H), 6.68 (td, *J* = 7.5, 0.9 Hz, 1H), 6.33 (d, *J* = 2.7 Hz, 1H), 5.61 (d, *J* = 2.7 Hz, 1H), 5.23–5.10 (m, 1H), 5.08 (quint, *J* = 1.5 Hz, 1H), 3.84 (s, 2H), 1.78–1.66 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 163.8, 158.8, 143.8, 137.5, 130.4, 129.6, 129.2, 124.6, 123.5, 120.1, 119.9, 115.7, 113.8, 110.3, 90.9, 55.2, 15.8; HRMS (APCI) calcd for $C_{19}H_{19}O$ $[M+H]^+$ 279.1380, found 279.1381; CHIRALPAK AD-H, hexane/*i*-PrOH = 98:2, 1.0 mL/min, retention times: 5.6 min [minor (–)-isomer] and 6.4 min [major (+)-isomer].

(–)-(*E*)-3-(3-Chlorobenzylidene)-2-isopropenyl-2,3-dihydrobenzofuran [(–)-3d, Table 2, entry 4]



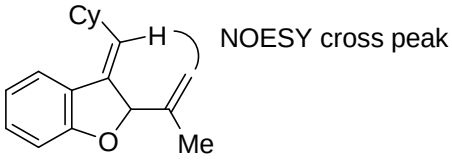
The olefin geometry was determined with ^{1}H NMR by analogy to **3a**. Yellow oil; $[\alpha]^{25}_D$ –6.4° (*c* 3.59, $CHCl_3$, 97% ee); IR (neat) 3078, 2975, 1460, 992, 911, 750 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.43–7.36 (m, 1H), 7.35–7.20 (m, 4H), 7.23–7.12 (m, 1H), 6.92–6.82 (m, 1H), 6.71 (td, *J* = 7.7, 1.2 Hz, 1H), 6.30 (d, *J* = 2.7 Hz, 1H), 5.60 (d, *J* = 2.7 Hz, 1H), 5.23–5.12 (m, 1H), 5.10 (quint, *J* = 1.5 Hz, 1H), 1.77–1.66 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.0, 143.5, 139.8, 138.7, 134.3, 131.1, 129.7, 128.4, 127.3, 126.5, 124.0, 123.6, 120.3, 118.4, 116.0, 110.6, 90.8, 15.8; HRMS (APCI) calcd for $C_{18}H_{16}ClO$ $[M+H]^+$ 283.0884, found 283.0885; CHIRALPAK AD-H, hexane/*i*-PrOH = 99:1, 0.5 mL/min, retention times: 10.5 min [minor (+)-isomer] and 12.7 min [major (–)-isomer].

(–)-(*E*)-3-Cyclohex-1-enylmethylene-2-isopropenyl-2,3-dihydrobenzofuran [(–)-3e, Table 2, entry 5]



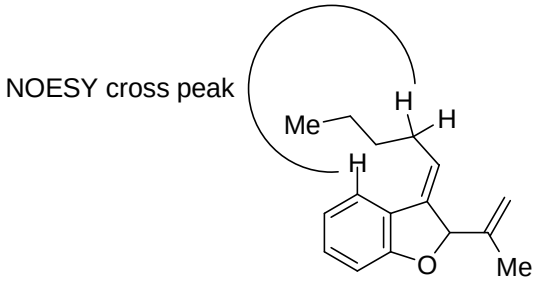
The olefin geometry was determined by the NOESY experiment. Yellow oil; $[\alpha]^{25}_{D}$ −14.7° (*c* 2.56, $CHCl_3$, 98% ee); IR (neat) 2932, 2833, 1458, 1210, 990, 749 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.75 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.21–7.06 (m, 1H), 6.83 (d, *J* = 8.1 Hz, 1H), 6.80 (td, *J* = 7.7, 1.2 Hz, 1H), 5.93 (m, 1H), 5.76–5.60 (m, 1H), 5.49 (d, *J* = 2.4 Hz, 1H), 5.14–5.05 (m, 1H), 5.02 (quint, *J* = 1.5 Hz, 1H), 2.25–2.08 (m, 1H), 2.15–1.99 (m, 2H), 1.81–1.56 (m, 7H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 163.5, 143.9, 135.5, 134.0, 129.9, 125.8, 125.1, 124.0, 123.5, 120.1, 115.4, 110.2, 90.6, 28.5, 25.2, 22.8, 22.1, 15.7; HRMS (APCI) calcd for $C_{18}H_{21}O$ $[M+H]^+$ 253.1587, found 253.1587; CHIRALPAK AD-H, hexane/*i*-PrOH = 99:1, 0.5 mL/min, retention times: 14.2 min [minor (+)-isomer] and 15.1 min [major (−)-isomer].

(–)-(*E*)-3-Cyclohexylmethylene-2-isopropenyl-2,3-dihydrobenzofuran [(–)-3f, Table 2, entry 6]



The olefin geometry was determined by the NOESY experiment. Colorless oil; $[\alpha]^{25}_{D}$ −43.0° (*c* 2.69, $CHCl_3$, 99% ee); IR (neat) 2925, 2849, 1460, 1209, 904, 744 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.45 (d, *J* = 7.5 Hz, 1H), 7.15 (td, *J* = 7.8, 1.2 Hz, 1H), 6.97–6.76 (m, 2H), 5.46 (d, *J* = 2.4 Hz, 1H), 5.24 (dd, *J* = 9.0, 2.4 Hz, 1H), 5.12–5.04 (m, 1H), 5.01 (quint, *J* = 1.5 Hz, 1H), 2.87–2.60 (m, 1H), 1.92–1.62 (m, 5H), 1.69–1.56 (m, 3H), 1.50–1.02 (m, 5H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 163.1, 143.9, 134.3, 129.5, 128.2, 125.6, 124.1, 120.5, 115.3, 110.1, 90.3, 37.0, 32.62, 32.59, 26.0, 25.9, 15.7; HRMS (APCI) calcd for $C_{18}H_{23}O$ $[M+H]^+$ 255.1743, found 255.1751; CHIRALPAK AD-H, hexane/*i*-PrOH = 98:2, 0.5 mL/min, retention times: 9.3 min [minor (+)-isomer] and 12.1 min [major (–)-isomer].

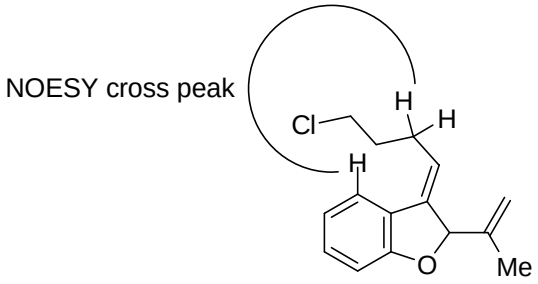
(–)-(*E*)-2-Isopropenyl-3-pentylidene-2,3-dihydrobenzofuran [(–)-3g, Table 2, entry 7]



The olefin geometry was determined by the NOESY experiment. Pale yellow oil; $[\alpha]^{25}_{D}$ −42.5° (*c* 2.26, $CHCl_3$, 88% ee); IR (neat) 2956, 1460, 1210, 986, 745 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.50 (d, *J* = 7.5 Hz, 1H), 7.16 (td, *J* = 7.8, 1.2 Hz, 1H), 6.96–6.78 (m, 2H), 5.47 (q, *J* = 2.4 Hz, 1H), 5.38 (td, *J* = 7.5, 2.4 Hz, 1H), 5.13–5.03 (m, 1H), 5.01 (quint, *J* = 1.5 Hz, 1H), 2.45 (qd, *J* = 7.5, 2.4 Hz, 2H),

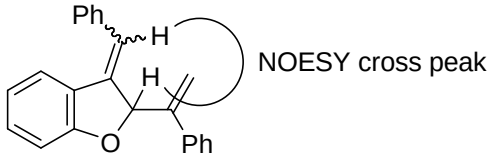
1.70–1.58 (m, 3H), 1.58–1.30 (m, 4H), 0.93 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 163.1, 144.0, 135.9, 129.4, 126.1, 124.2, 122.5, 120.5, 115.1, 110.1, 90.3, 31.6, 28.0, 22.5, 15.8, 14.0; HRMS (APCI) calcd for $C_{16}H_{21}O$ $[M+H]^+$ 229.1587, found 229.1587; CHIRALPAK AD-H, hexane/*i*-PrOH = 98:2, 0.5 mL/min, retention times: 7.4 min [minor (+)-isomer] and 9.1 min [major (–)-isomer].

(–)-(*E*)-3-(4-Chlorobutylidene)-2-isopropenyl-2,3-dihydrobenzofuran [(–)-3h, Table 2, entry 8]



The olefin geometry was determined by the NOESY experiment. Colorless oil; $[\alpha]^{25}_D$ –11.6° (*c* 1.23, $CHCl_3$, 86% ee); IR (neat) 2955, 1461, 1211, 748 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.54 (d, J = 7.5 Hz, 1H), 7.24–7.13 (m, 1H), 6.98–6.80 (m, 2H), 5.47 (q, J = 2.4 Hz, 1H), 5.34 (td, J = 7.5, 2.4 Hz, 1H), 5.13–5.04 (m, 1H), 5.02 (quint, J = 1.5 Hz, 1H), 3.61 (t, J = 6.5 Hz, 2H), 2.63 (qd, J = 7.5, 2.4 Hz, 2H), 2.07–1.91 (m, 2H), 1.68–1.59 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 163.2, 143.8, 137.5, 129.9, 125.6, 124.3, 120.6, 119.8, 115.3, 110.2, 90.3, 44.5, 32.2, 25.6, 15.8; HRMS (APCI) calcd for $C_{15}H_{18}ClO$ $[M+H]^+$ 249.1041, found 249.1039; CHIRALPAK AD-H, hexane/*i*-PrOH = 99:1, 0.5 mL/min, retention times: 16.2 min [minor (+)-isomer] and 20.4 min [major (–)-isomer].

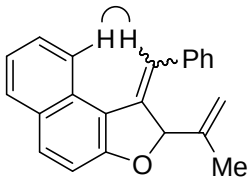
(–)-3-Benzylidene-2-(1-phenylvinyl)-2,3-dihydrobenzofuran [(–)-3i, Table 2, entry 9, *E*/*Z* = 94:6]



Isolated as a mixture of *E*/*Z* isomers. The olefin geometry was determined by the NOESY experiment. Yellow oil; $[\alpha]^{25}_D$ –107.2° [*c* 0.68, $CHCl_3$, 94% ee]; IR (neat) 3056, 1460, 1207, 750, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) *E*-isomer: δ 7.49–7.38 (m, 2H), 7.41–7.19 (m, 9H), 7.22–7.09 (m, 1H), 6.92–6.80 (m, 1H), 6.74–6.61 (m, 1H), 6.35 (d, J = 2.7 Hz, 1H), 6.07 (d, J = 2.7 Hz, 1H), 5.60 (d, J = 1.2 Hz, 1H), 5.55–5.47 (m, 1H), partial protons of *Z*-isomer: δ 7.05 (d, J = 2.7 Hz, 1H), 6.46 (d, J = 2.7 Hz, 1H), 5.45 (s, 1H), 5.39 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 163.3, 146.8, 138.7, 138.2, 136.8, 130.7, 128.4, 128.3, 128.2, 127.8, 127.4, 127.2, 126.6, 124.3, 123.9, 120.9, 120.4, 117.8, 110.7, 89.0; HRMS (ESI) calcd for $C_{23}H_{18}Ona$ $[M+Na]^+$ 333.1250, found 333.1255; CHIRALPAK AD-H, hexane/*i*-PrOH = 99:1, 0.5 mL/min, retention times: 24.6 min [minor (+)-*E*-isomer] and 33.0 min [major (–)-*E*-isomer].

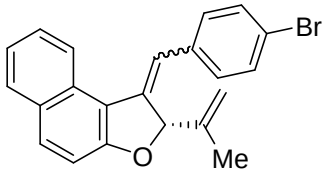
(–)-1-Benzylidene-2-isopropenyl-1,2-dihydronaphtho[2,1-b]furan [(–)-3j, Table 2, entry 10, *E*/*Z* = 9:91]

NOESY cross peak



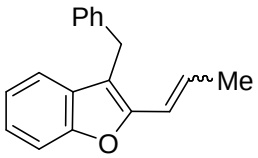
Isolated as a mixture of *E*/*Z* isomers. The olefin geometry was determined by the NOESY experiment. Yellow solid; Mp 92.0–105.0 °C; $[\alpha]^{25}_{D}$ –289.2° (*c* 1.96, $CHCl_3$, 98% ee); IR (KBr) 3051, 2918, 1457, 1234, 936, 765 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) *Z*-isomer: δ 8.43 (d, *J* = 8.7 Hz, 1H), 7.89–7.79 (m, 1H), 7.73 (d, *J* = 8.7 Hz, 1H), 7.65–7.54 (m, 1H), 7.52 (d, *J* = 2.4 Hz, 1H), 7.44–7.28 (m, 5H), 7.29–7.17 (m, 1H), 7.14 (d, *J* = 8.7 Hz, 1H), 5.97 (d, *J* = 2.4 Hz, 1H), 5.21–5.06 (m, 1H), 5.00 (quint, *J* = 1.5 Hz, 1H), 1.86–1.76 (m, 1H), partial protons of *E*-isomer: δ 7.05–6.92 (m, 1H), 6.89–6.75 (m, 1H), 6.54 (d, *J* = 2.4 Hz, 1H), 5.77 (d, *J* = 2.4 Hz, 1H), 5.28–5.21 (m, 1H), 1.79–1.73 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 160.7, 140.9, 139.9, 137.2, 132.1, 130.0, 129.6, 129.3, 129.2, 128.6, 128.3, 127.8, 127.7, 126.9, 126.8, 126.0, 123.3, 123.0, 122.3, 122.2, 118.0, 116.7, 112.7, 112.5, 88.5, 18.5, 16.4; HRMS (APCI) calcd for $C_{22}H_{19}O$ $[M+H]^+$ 299.1430, found 299.1440; CHIRALPAK AD-H, hexane/*i*-PrOH = 98:2, 0.5 mL/min, retention times: 24.2 min [major (–)-*Z*-isomer] and 35.1 min [minor (+)-*Z*-isomer].

(*S*)-(–)-1-(4-Bromobenzylidene)-2-isopropenyl-1,2-dihydronaphtho[2,1-b]furan [(*S*)-(–)-3k, Table 2, entry 11, *E*/*Z* = 7:93]



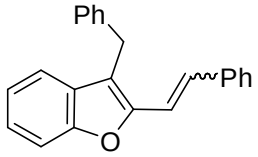
Isolated as a mixture of *E*/*Z* isomers. The olefin geometry was determined with ^1H NMR by analogy to **3j**. The absolute configuration of (–)-**3k** was unambiguously determined to be *S* by the anomalous dispersion method. Yellow solid; Mp 97.5–104.5 °C; $[\alpha]^{25}_{D}$ –230.2° (*c* 2.76, $CHCl_3$, 97% ee); IR (KBr) 3079, 2972, 2906, 1613, 1379, 737 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) *Z*-isomer: δ 8.39 (d, *J* = 8.7 Hz, 1H), 7.90–7.82 (m, 1H), 7.76 (d, *J* = 8.7 Hz, 1H), 7.66–7.55 (m, 1H), 7.54–7.32 (m, 3H), 7.44 (d, *J* = 2.7 Hz, 1H), 7.30–7.20 (m, 2H), 7.14 (d, *J* = 8.7 Hz, 1H), 5.92 (d, *J* = 2.7 Hz, 1H), 5.17–5.07 (m, 1H), 5.02 (quint, *J* = 1.5 Hz, 1H), 1.84–1.74 (m, 3H), partial protons of *E*-isomer: δ 7.04–6.94 (m, 2H), 6.85–6.76 (m, 1H), 6.44 (d, *J* = 2.7 Hz, 1H), 5.75 (d, *J* = 2.7 Hz, 1H), 5.28–5.21 (m, 1H), 5.15 (quint, *J* = 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 161.0, 140.8, 140.5, 136.1, 132.4, 131.4, 130.9, 130.1, 130.0, 129.7, 129.2, 127.9, 123.4, 122.1, 120.7, 120.6, 117.7, 117.0, 112.7, 88.5, 18.4; HRMS (APCI) calcd for $C_{22}H_{18}BrO$ $[M+H]^+$ 377.0536, found 377.0536; CHIRALPAK AD-H, hexane/*i*-PrOH = 98:2, 1.0 mL/min, retention times: 12.6 min [major (*S*)-(–)-*Z*-isomer] and 16.0 min [minor (*R*)-(+)-*Z*-isomer].

3-Benzyl-2-propenylbenzofuran (4l, Scheme 3, *E*/*Z* = 95:5)



Isolated as a mixture of *E*/*Z* isomers. The olefin geometries were determined by ^{1}H NMR coupling constants between olefinic protons. Pale yellow oil; IR (neat) 3030, 2911, 1454, 1262, 956, 744 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) *E*-isomer: δ 7.43–7.34 (m, 1H), 7.33–7.12 (m, 7H), 7.08 (td, *J* = 7.5, 0.9 Hz, 1H), 6.52 (dq, *J* = 15.6, 5.7 Hz, 1H), 6.49–6.37 (m, 1H), 4.03 (s, 2H), 1.94 (d, *J* = 5.7 Hz, 3H), partial protons of *Z*-isomer: δ 6.36 (dq, *J* = 11.7, 1.8 Hz, 1H), 5.84 (dq, *J* = 11.7, 7.2 Hz, 1H), 2.23 (dd, *J* = 7.2, 1.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.1, 151.2, 139.6, 129.8, 128.5, 128.3, 128.2, 126.2, 124.1, 122.3, 119.6, 117.9, 115.8, 113.5, 110.6, 30.4, 29.4, 18.8; HRMS (APCI) calcd for $C_{18}H_{17}ClO$ $[M+H]^+$ 249.1274, found 249.1288.

3-Benzyl-2-styrylbenzofuran (4m, Scheme 3, *E*/*Z* = 92:8)

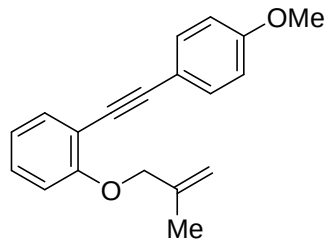


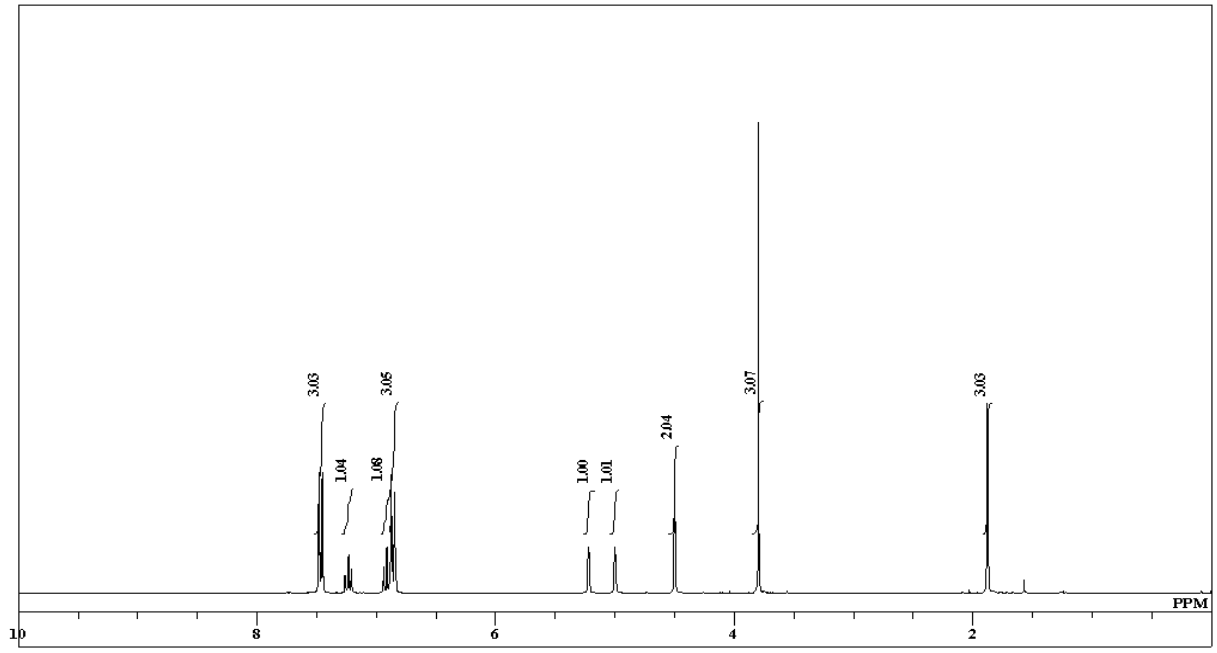
Isolated as a mixture of *E*/*Z* isomers. *E*-Isomer was already reported in the literature.[2] The olefin geometries were determined by ^{1}H NMR coupling constants between olefinic protons. Pale yellow solid; Mp 127.0–134.0 °C; IR (KBr) 3022, 2910, 1604, 1274 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) *E*-isomer: δ 7.56–7.47 (2H, m), 7.50–7.41 (1H, m), 7.43–7.16 (11H, m), 7.18–7.08 (1H, m), 7.07 (1H, d, *J* = 15.9 Hz), 4.16 (2H, s), partial protons of *Z*-isomer: δ 6.77–6.64 (1H, m), 6.53 (1H, d, *J* = 12.6 Hz), 4.03 (2H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.4, 151.3, 139.3, 136.8, 129.8, 129.7, 128.7, 128.6, 128.4, 128.0, 126.6, 126.4, 124.8, 122.5, 119.8, 116.6, 114.3, 110.8, 29.7; HRMS (ESI) calcd for $C_{23}H_{18}Ona$ $[M+Na]^+$ 333.1250, found 333.1251.

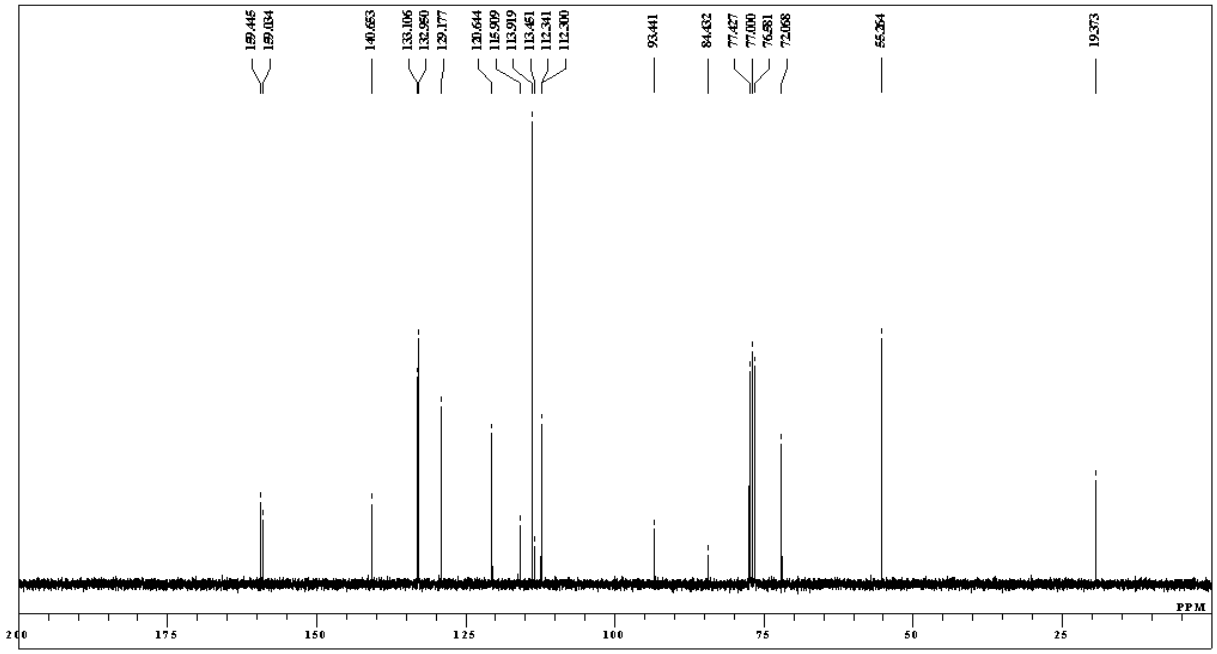
IV. References

(1) Cacchi, S.; Fabrizi, G.; Moro, L. *Synlett* **1998**, 741.
(2) Okitsu, T.; Nakazawa, D.; Taniguchi, R.; Wada, A. *Org. Lett.* **2008**, *10*, 4967.
(3) Quan, L. G.; Lee, H. G.; Cha, J. K. *Org. Lett.* **2007**, *9*, 4439.
(4) Cironi, P.; Albericio, F.; Alvarez, M. *Tetrahedron Lett*. **2004**, *45*, 7311.
(5) Kanazawa, C.; Goto, K.; Terada, M. *Chem. Commun.* **2009**, 5248.

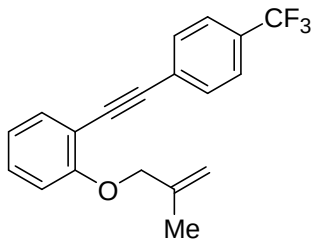
1-(2-Methylallyloxy)-2-(4-methoxyphenylethynyl)benzene (1b)

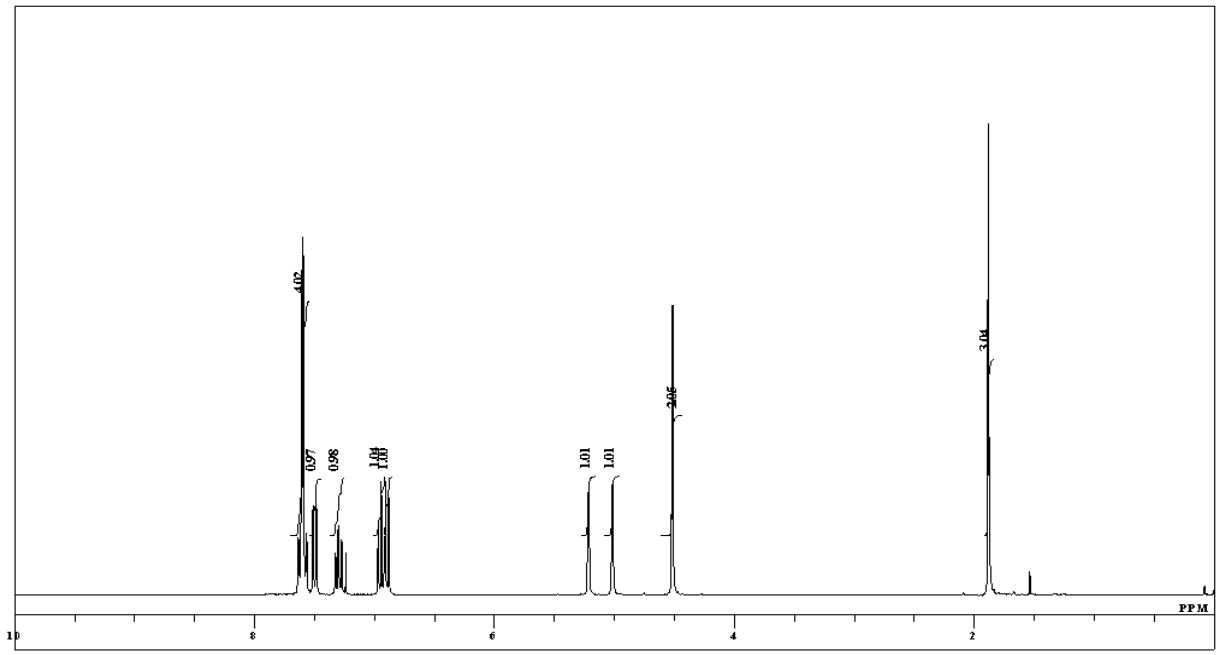


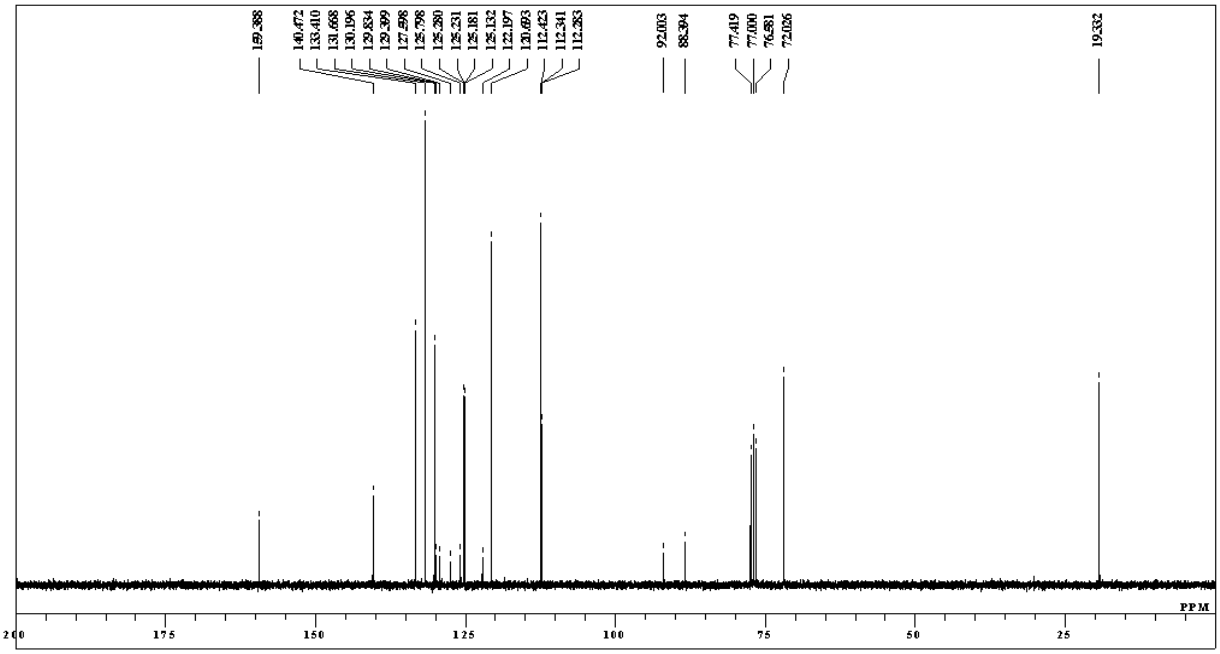




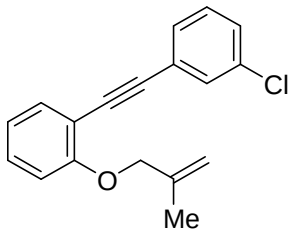
1-(2-Methylallyloxy)-2-(4-trifluoromethylphenylethynyl)benzene (1c)

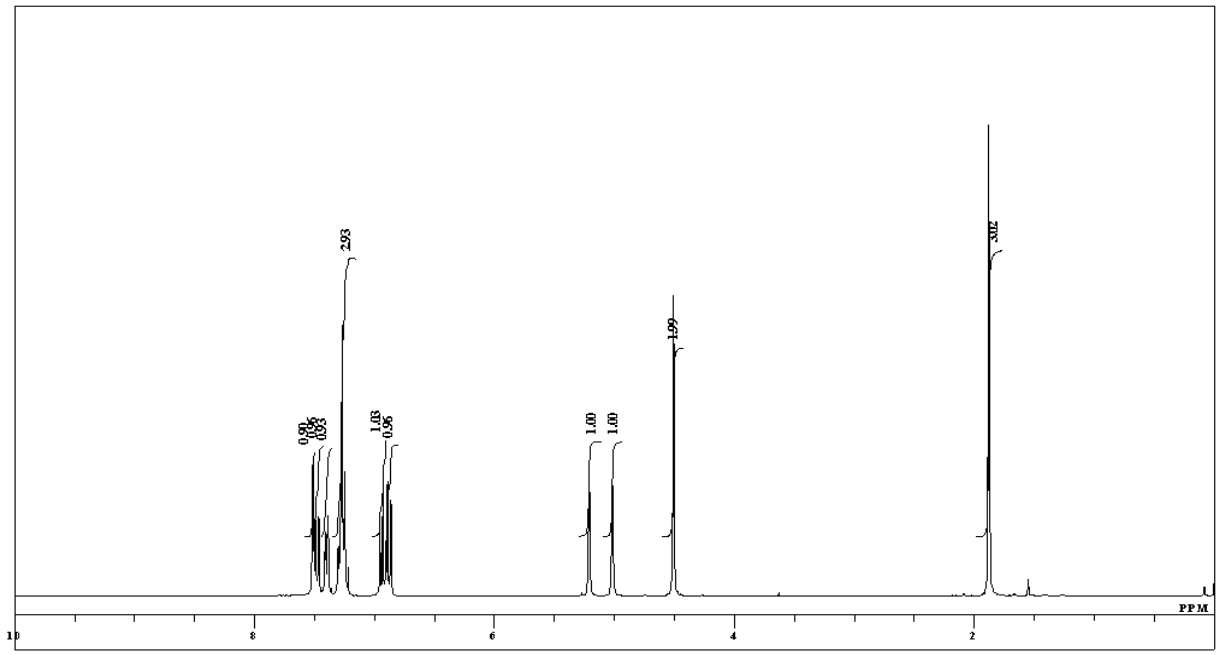


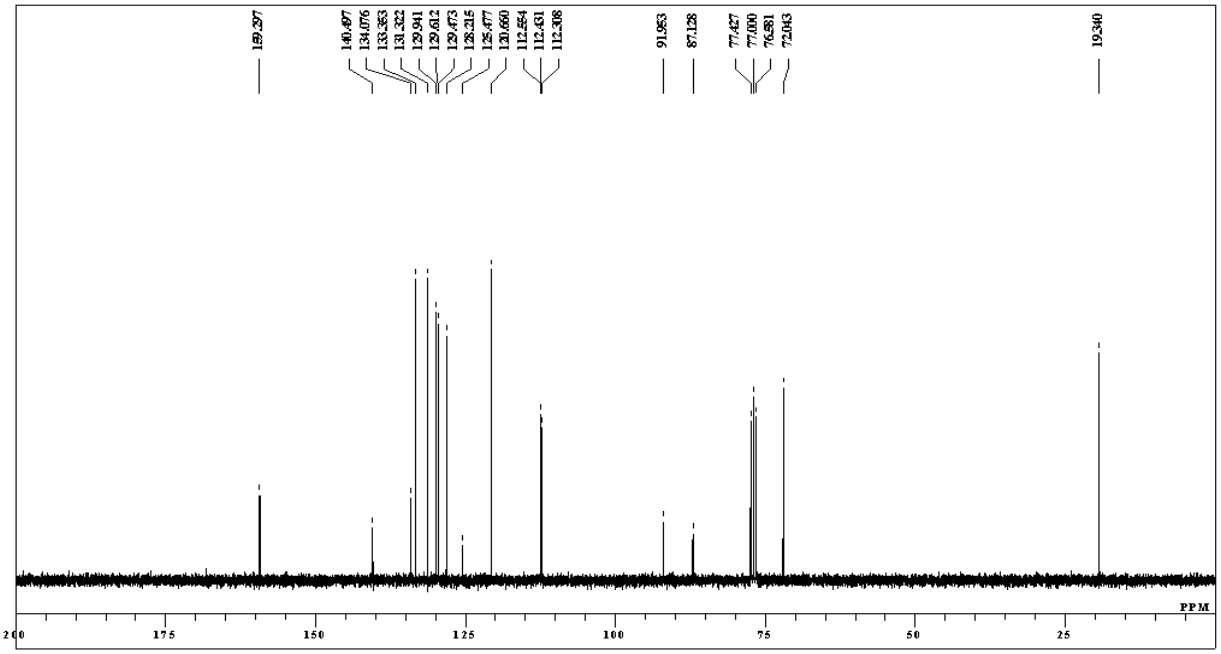




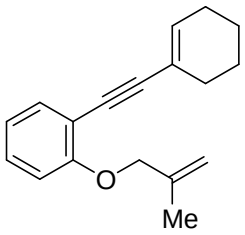
1-(3-Chlorophenylethynyl)-2-(2-methylallyloxy)benzene (1d)

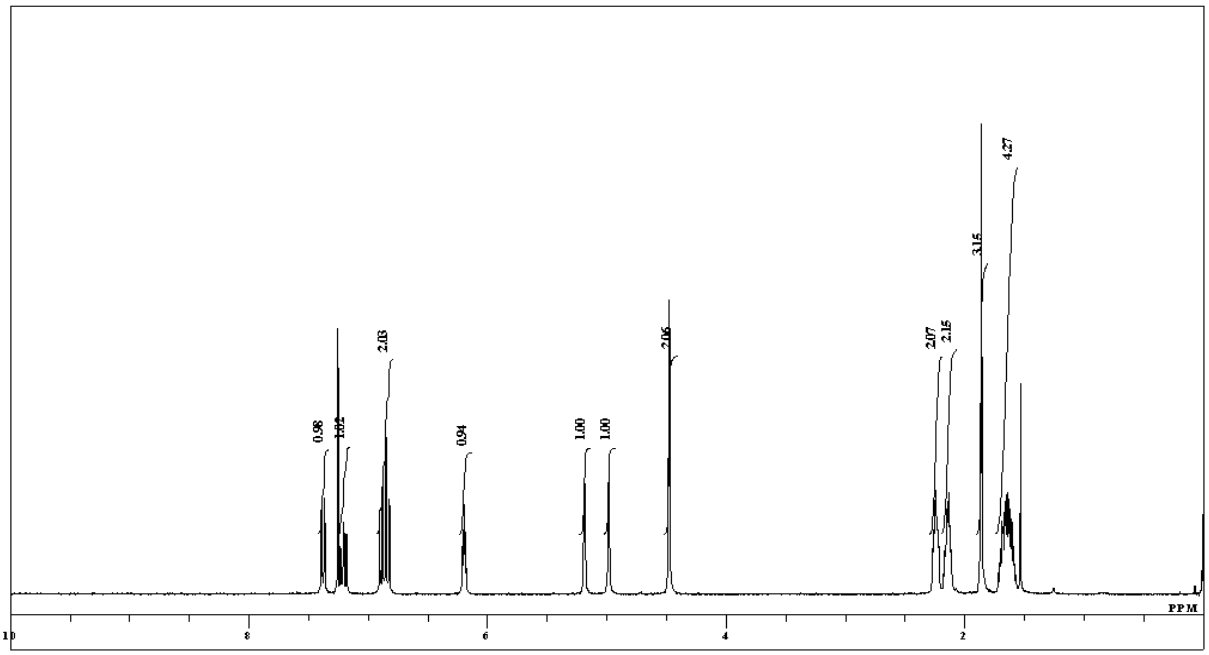


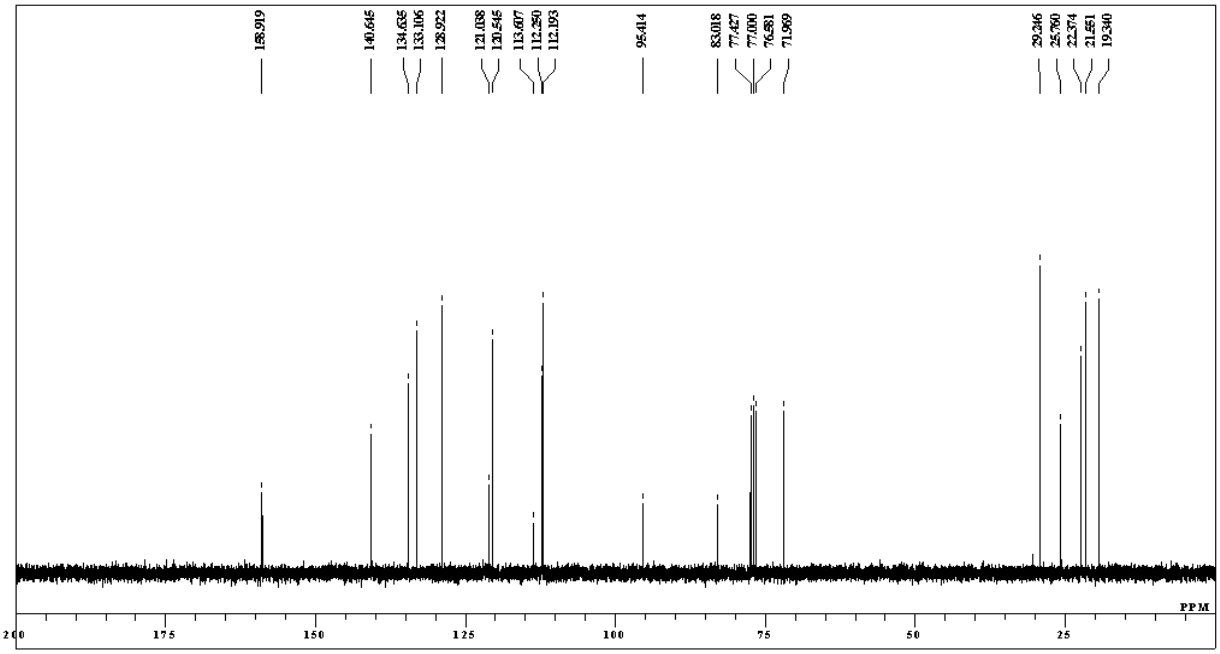




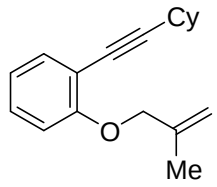
1-(1-Cyclohexenylethynyl)-2-(2-methylallyloxy)benzene (1e)

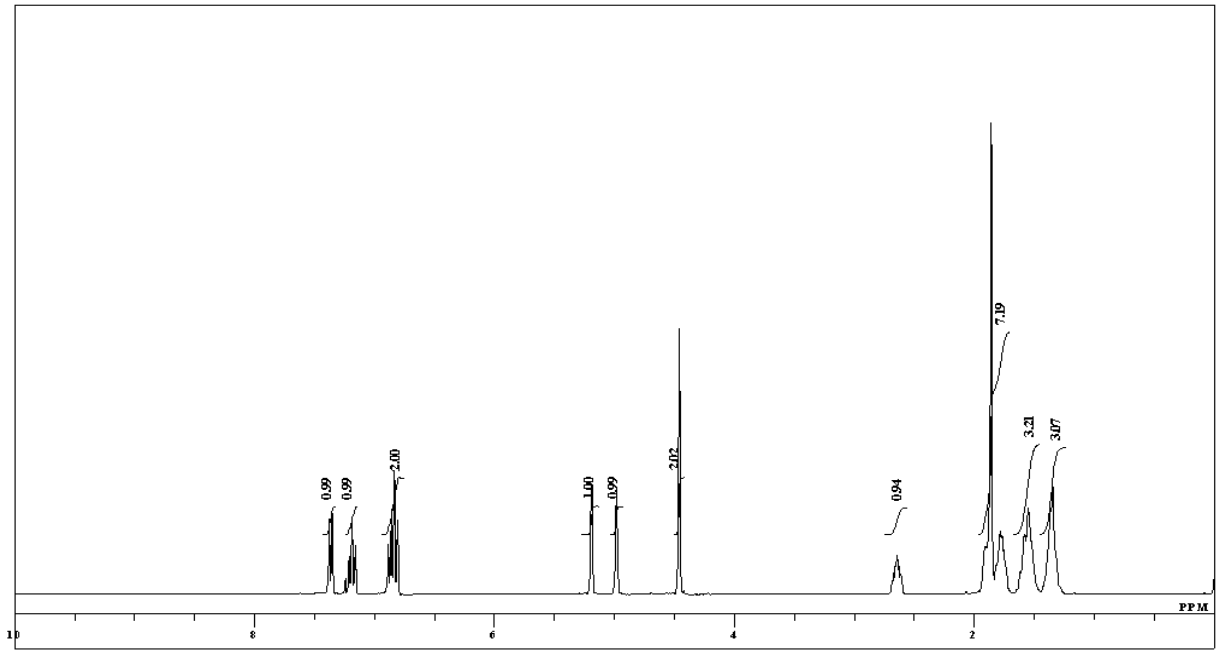


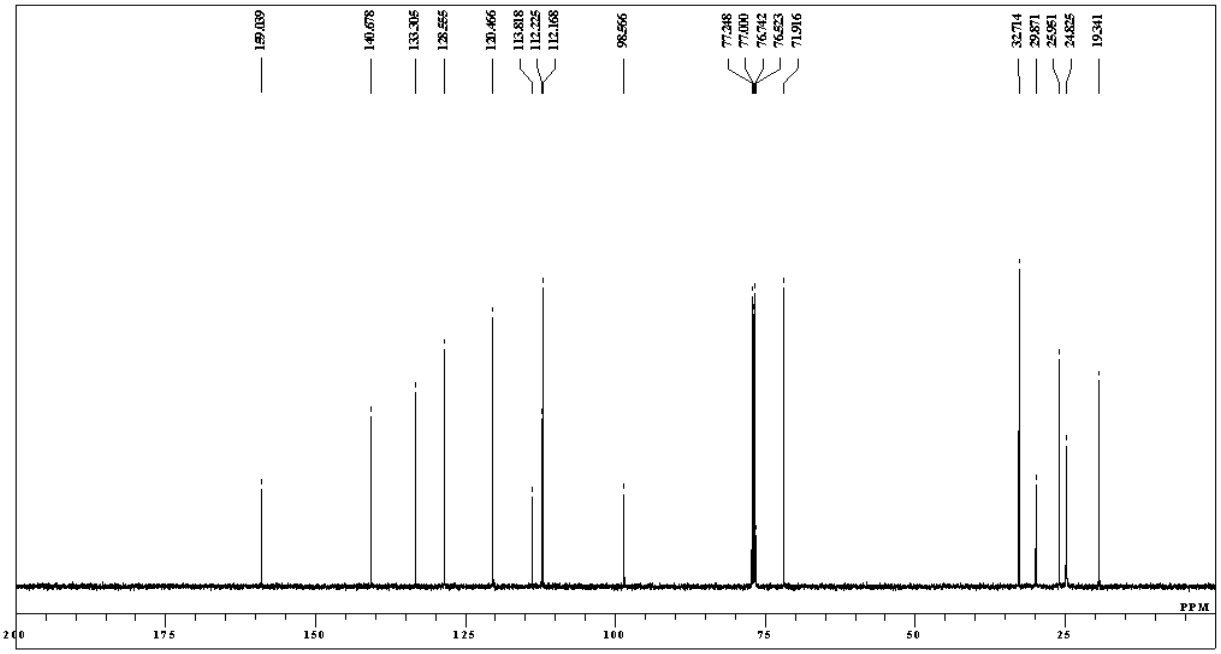




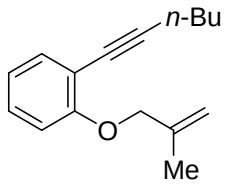
1-Cyclohexylethynyl-2-(2-methylallyloxy)benzene (1f)

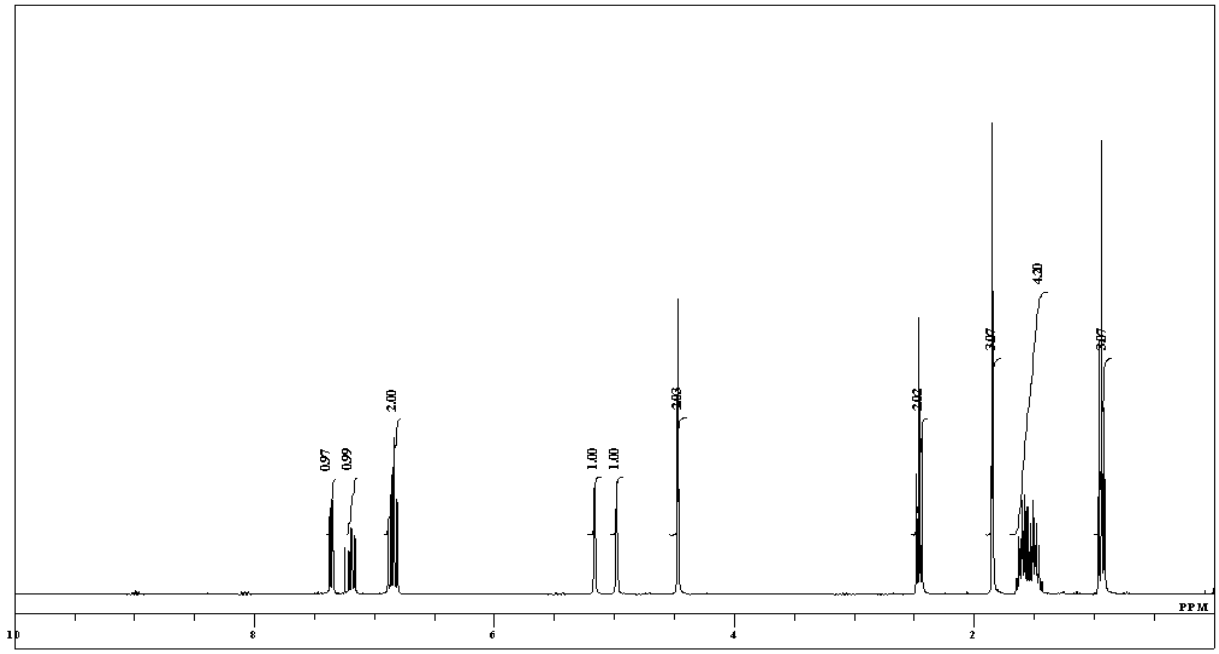


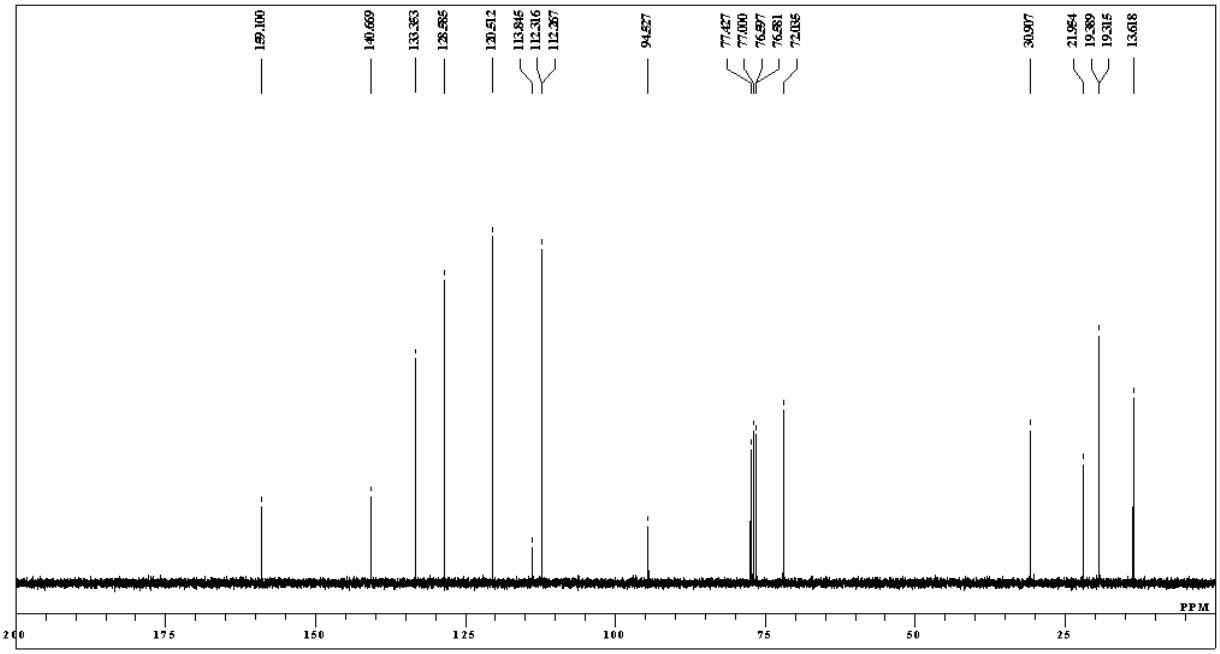




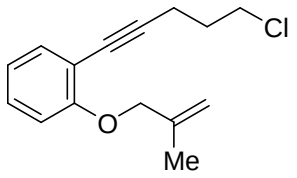
1-(1-Hexynyl)-2-(2-methylallyloxy)benzene (1g)

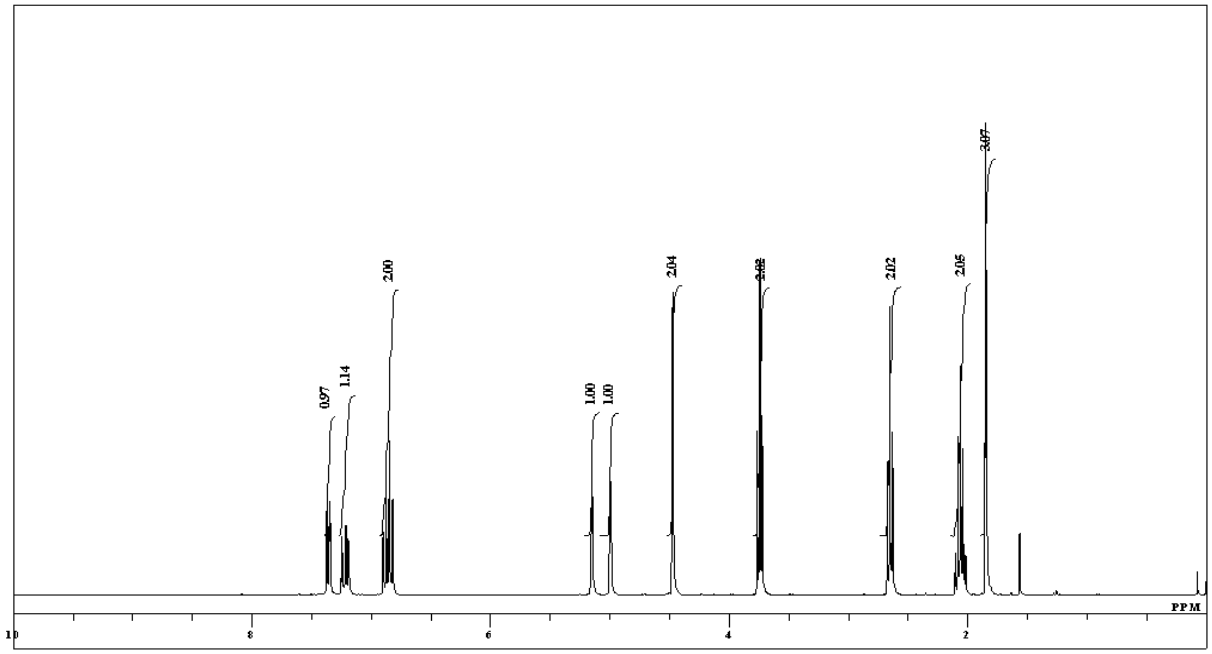


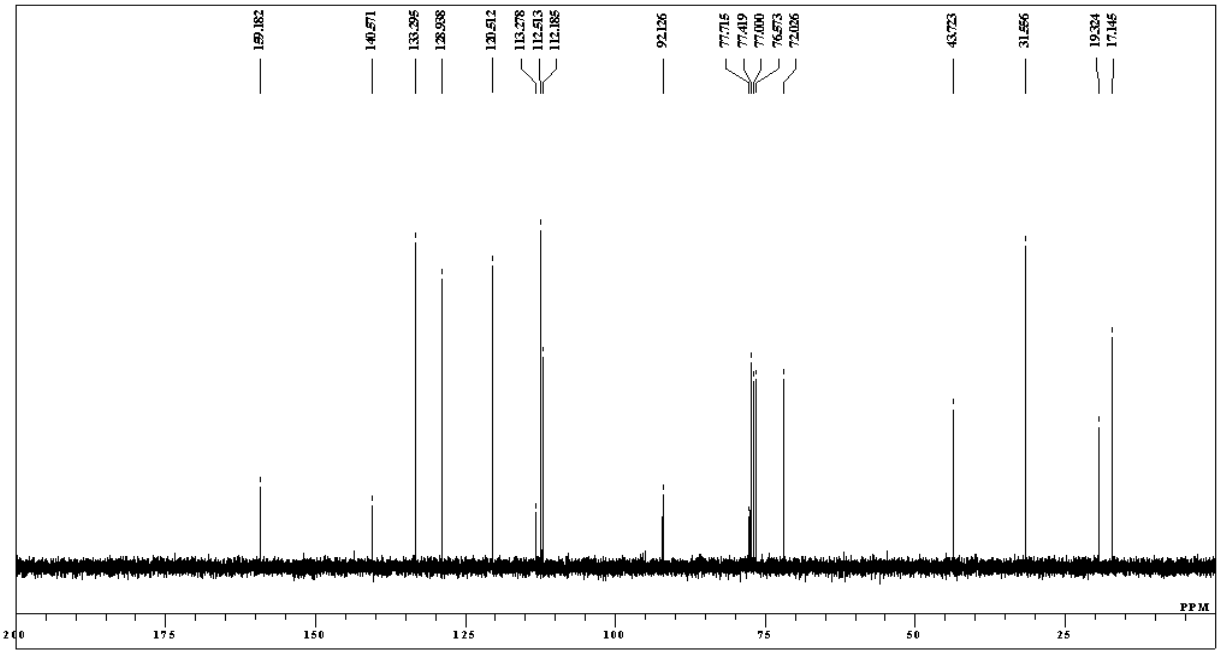




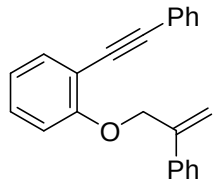
1-(5-Chloro-1-pentynyl)-2-(2-methylallyloxy)benzene (1h)

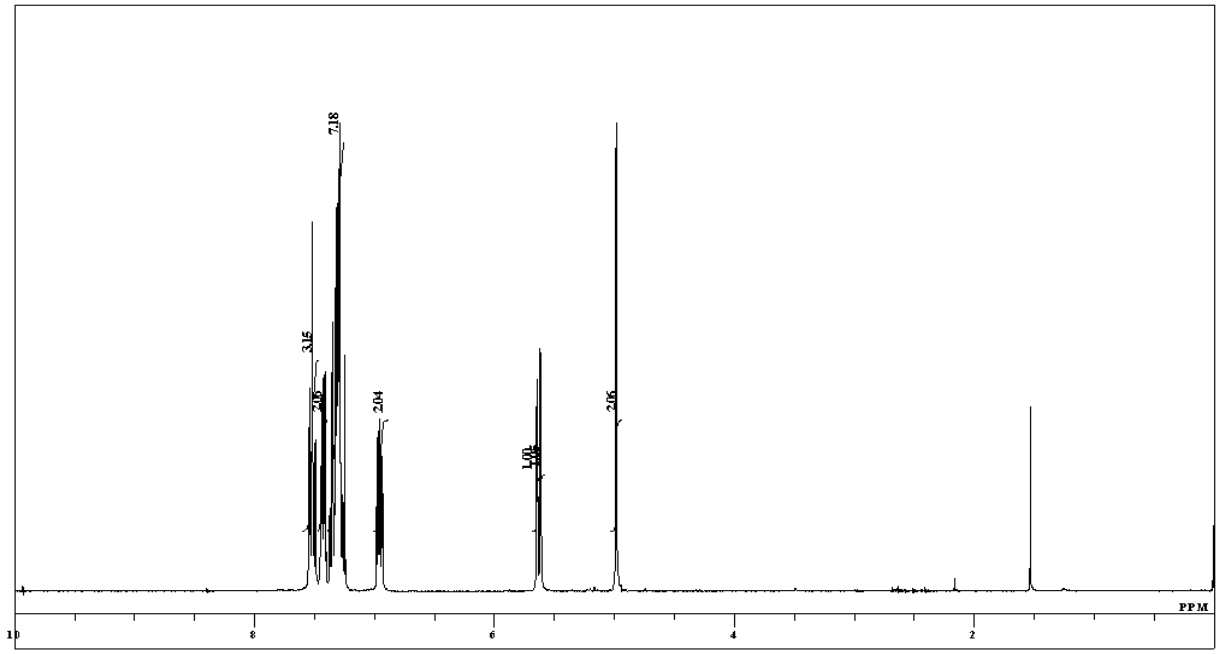


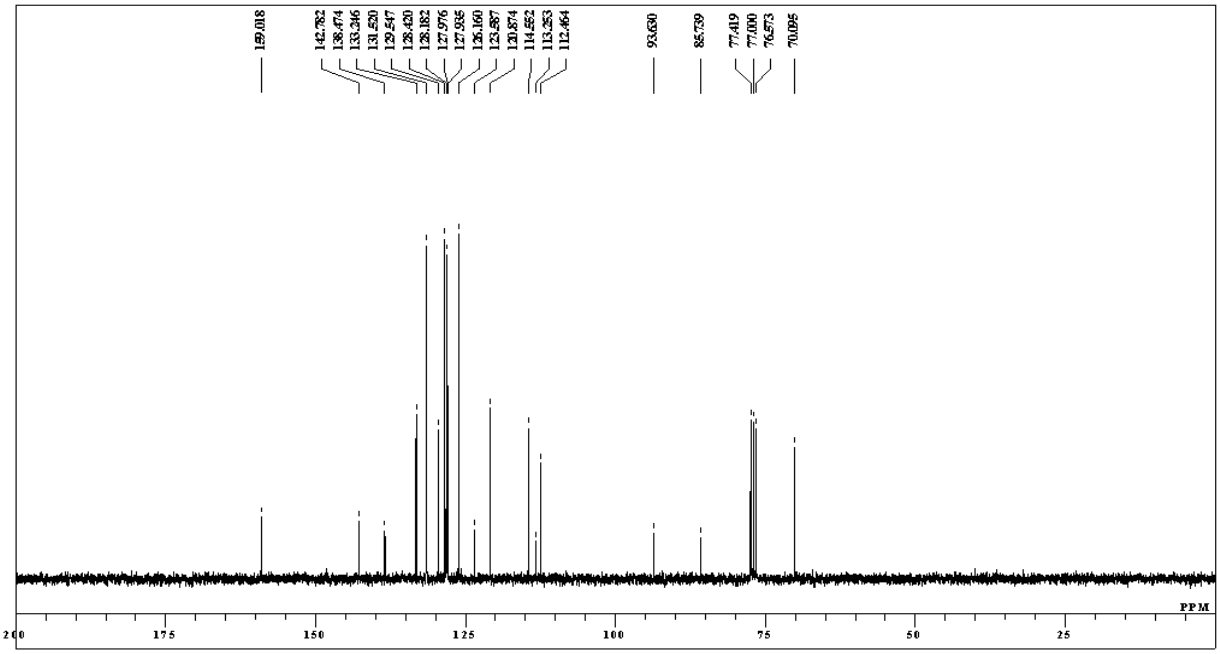




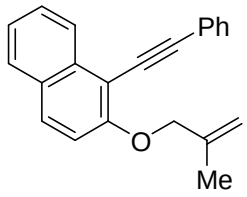
1-(2-Phenylallyloxy)-2-phenylethynylbenzene (1i)

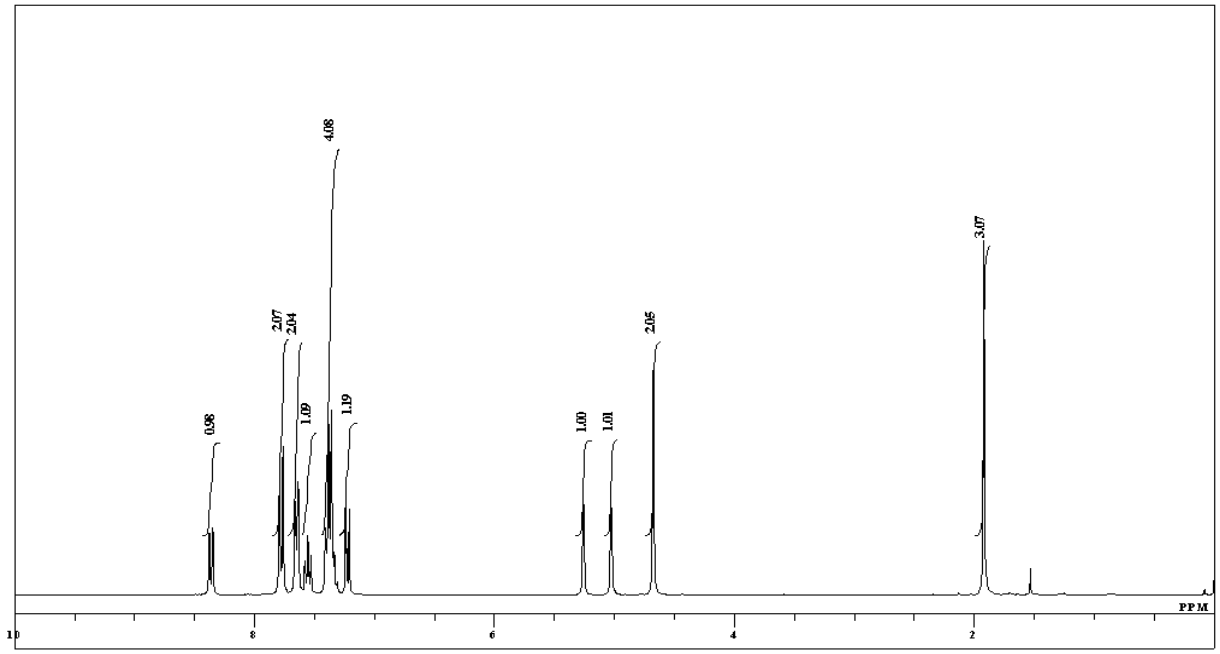


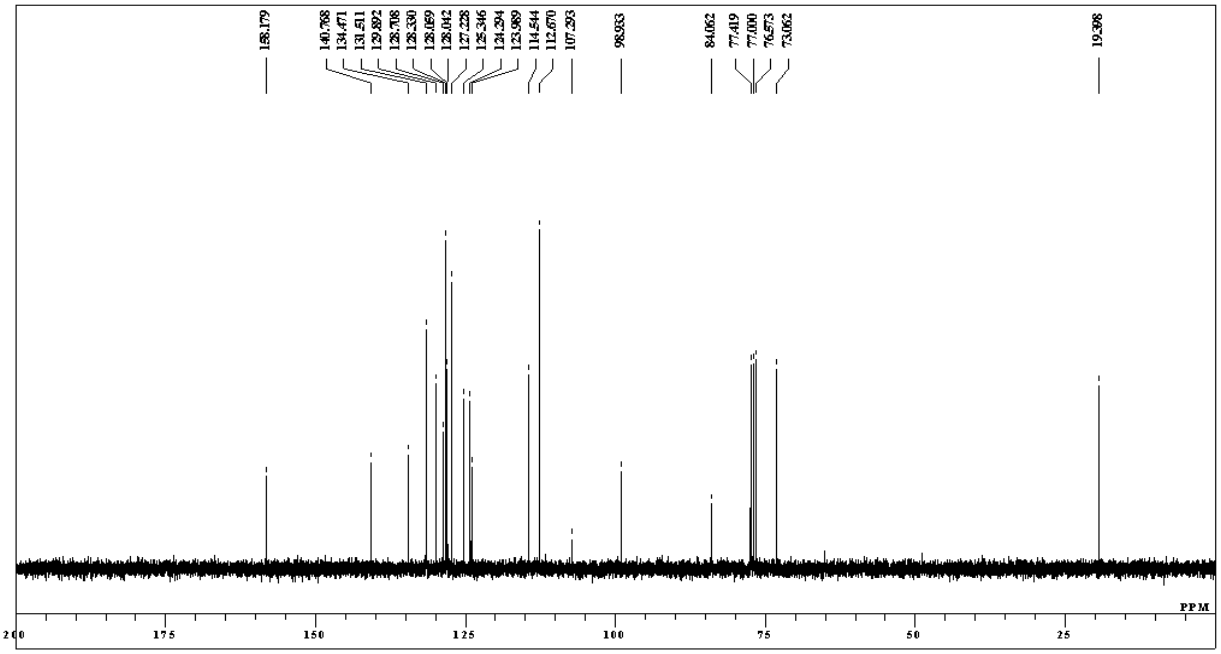




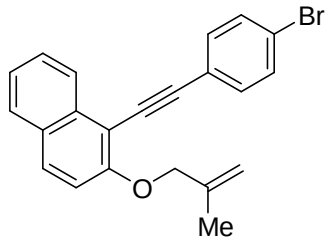
2-(2-Methylallyloxy)-1-phenylethynylnaphthalene (1j)

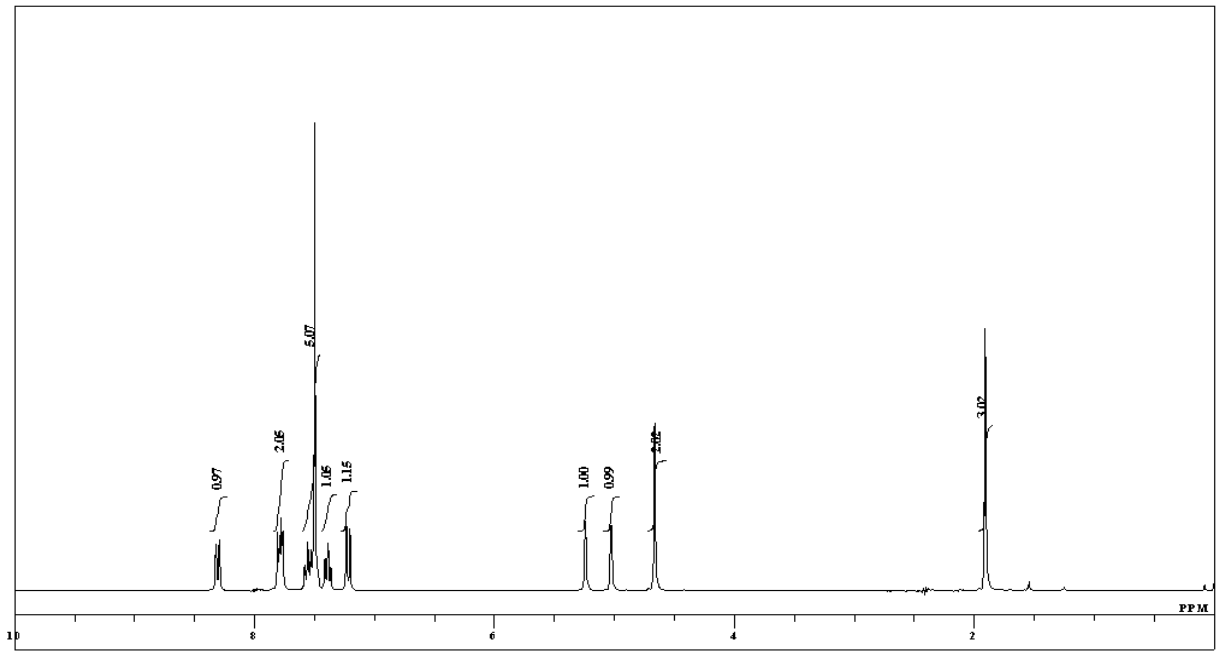


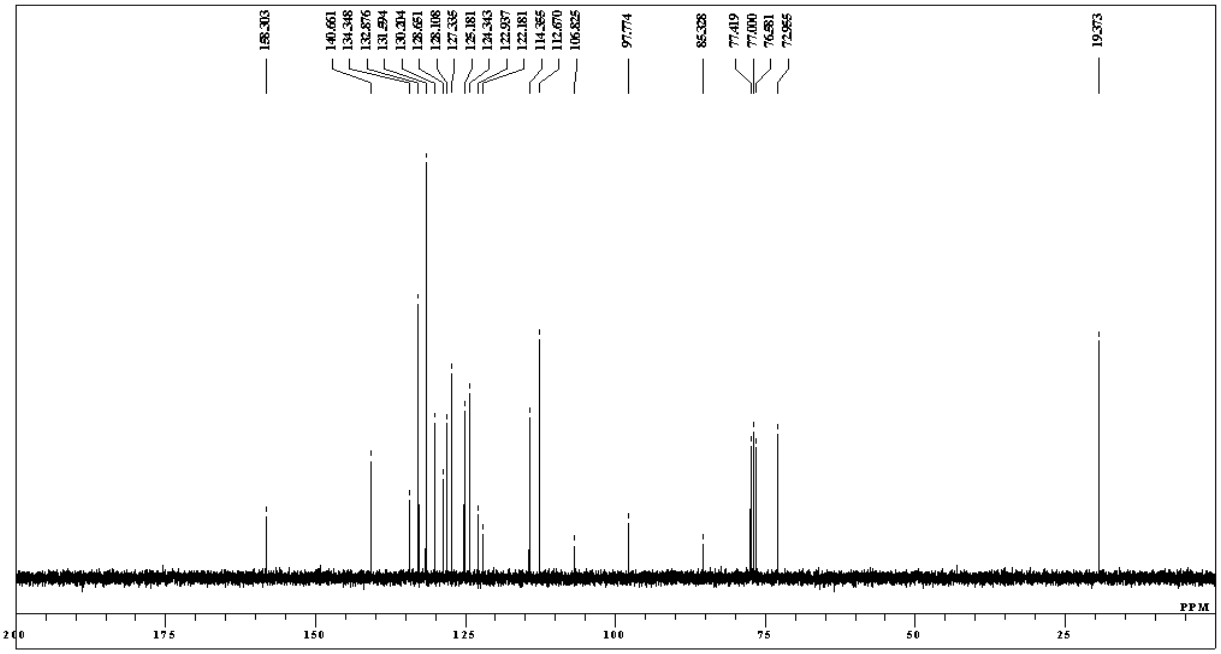




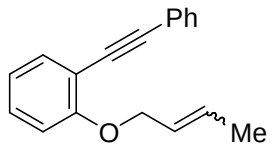
1-(4-Bromophenylethynyl)-2-(2-methylallyloxy)naphthalene (1k)

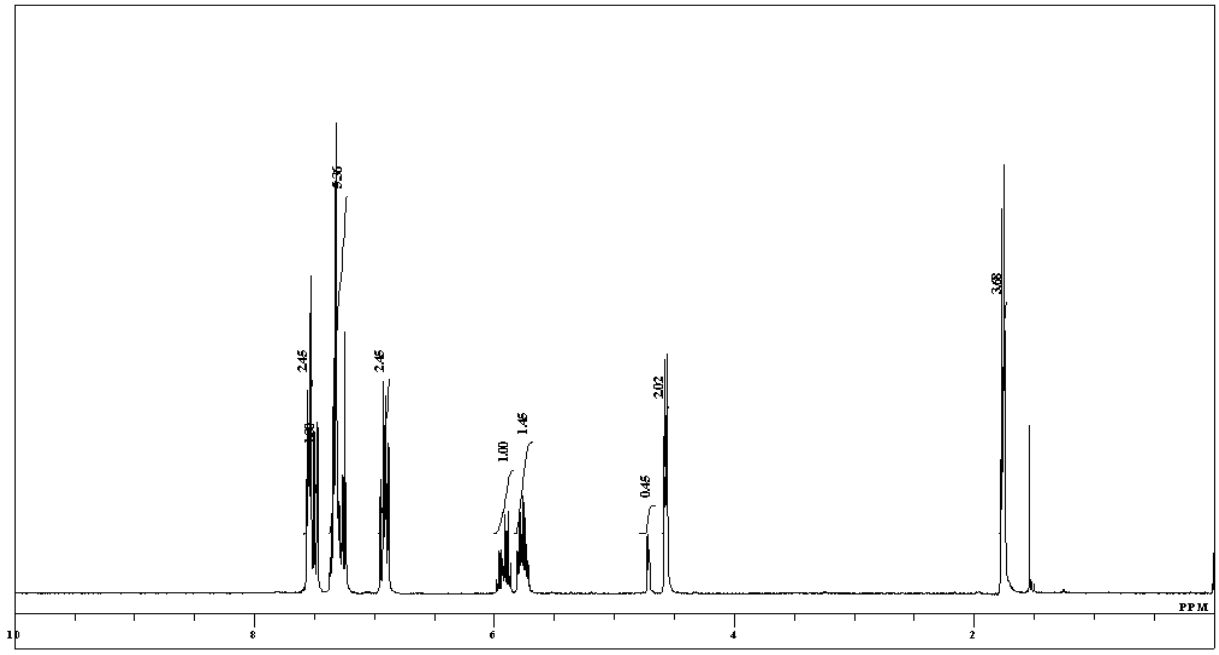


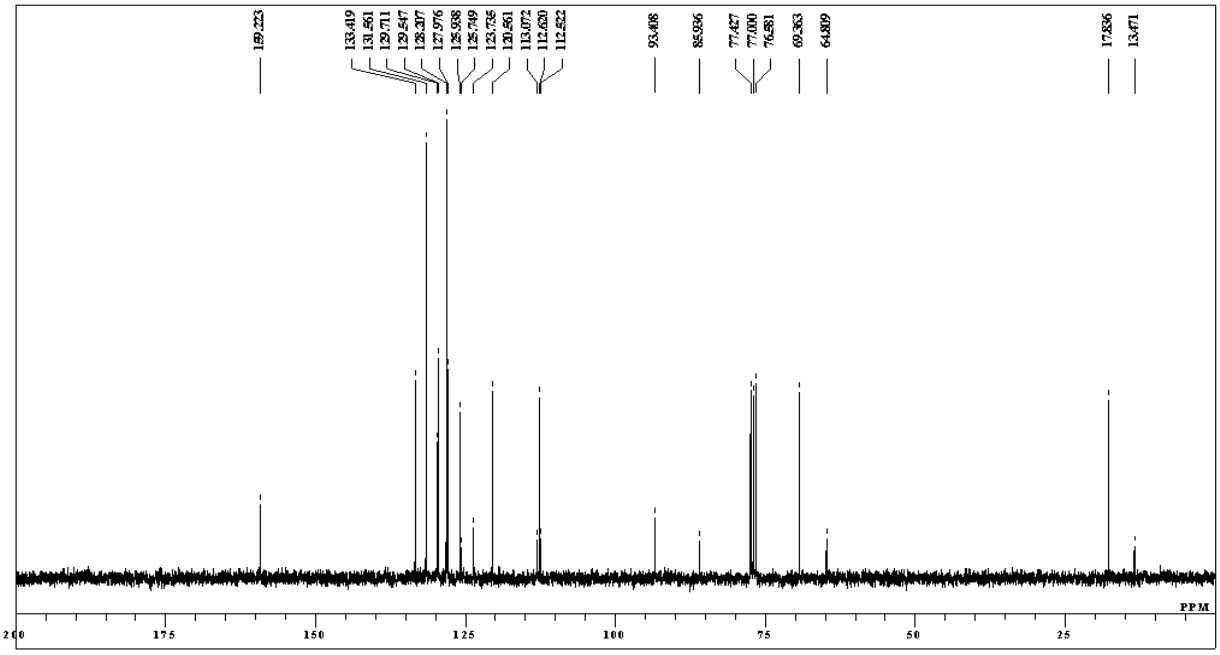




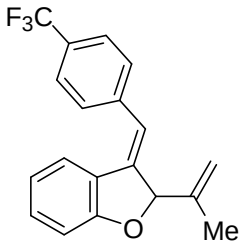
1-(2-Butenyloxy)-2-phenylethynylbenzene (1l, *E*/*Z* = 82:18)

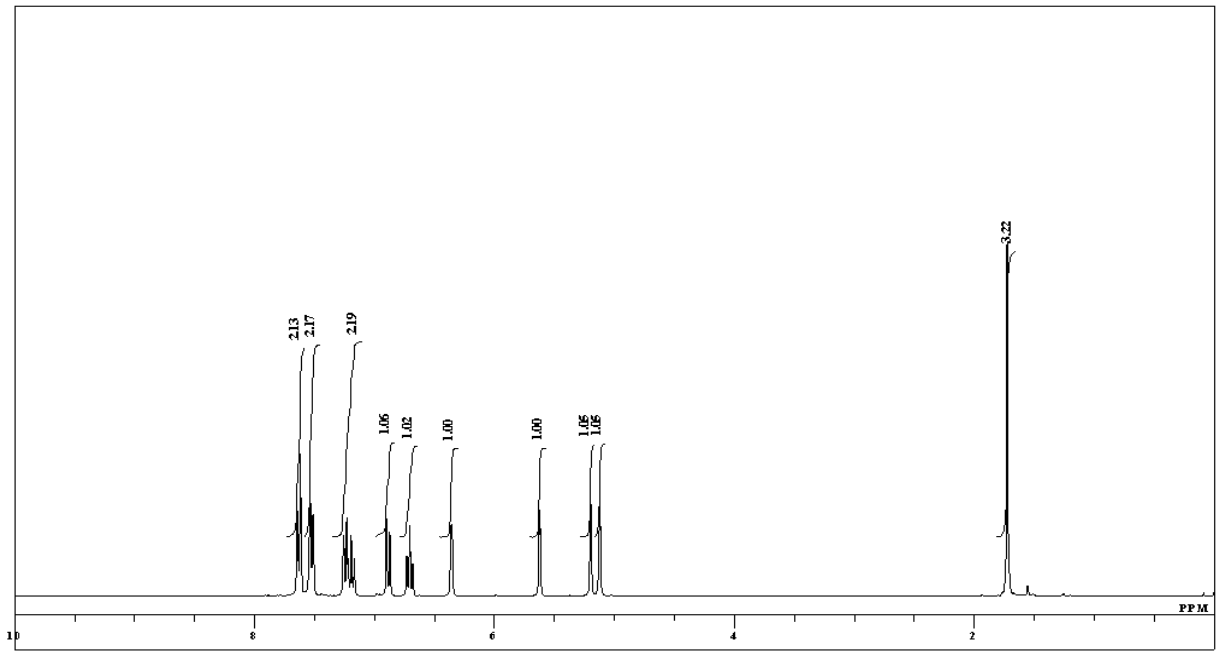


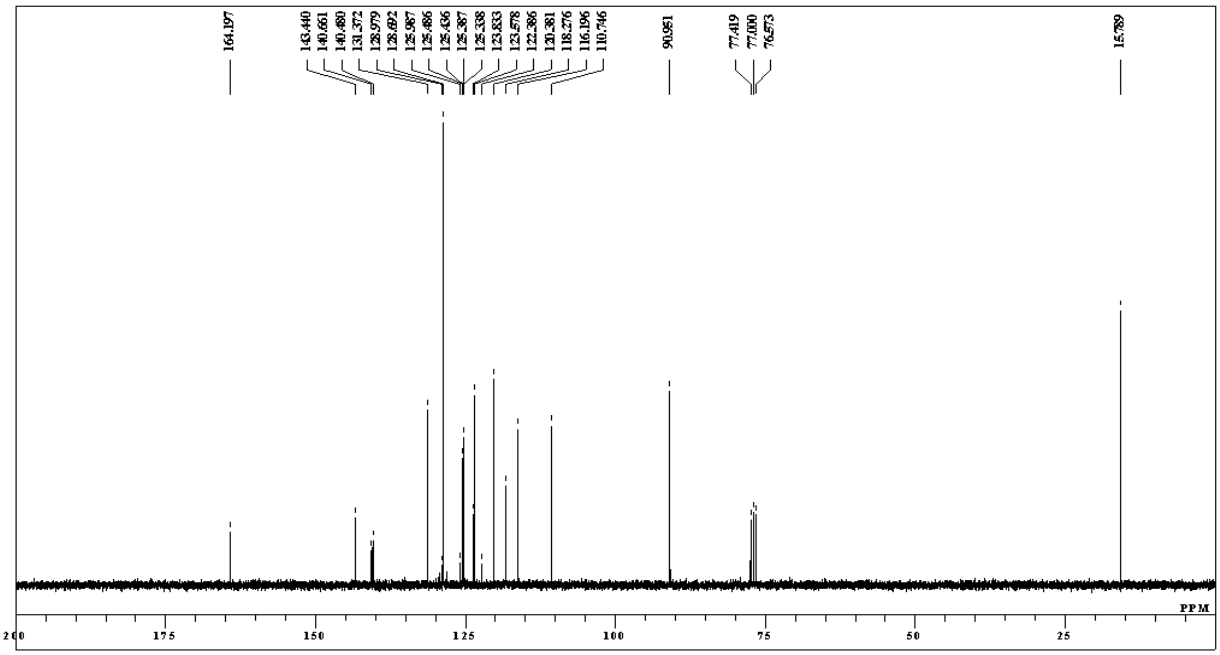




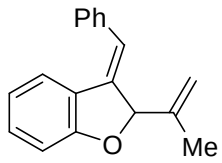
(–)-(*E*)-2-Isopropenyl-3-(4-trifluoromethylbenzylidene)-2,3-dihydrobenzofuran [(–)-3c]

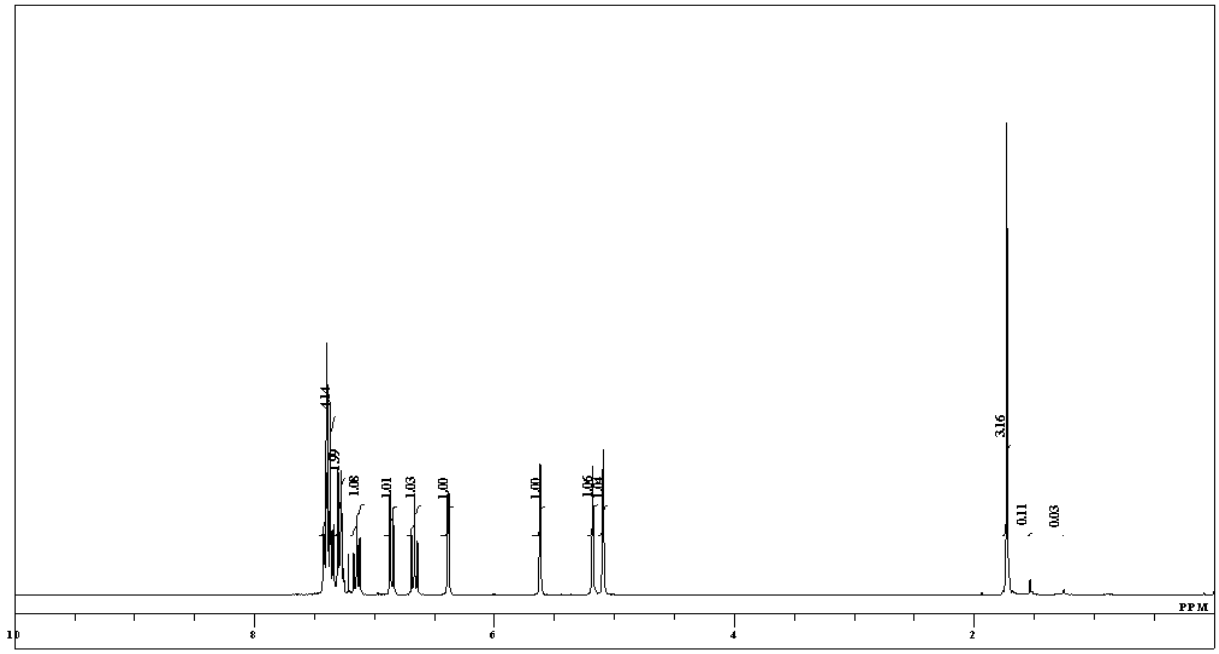


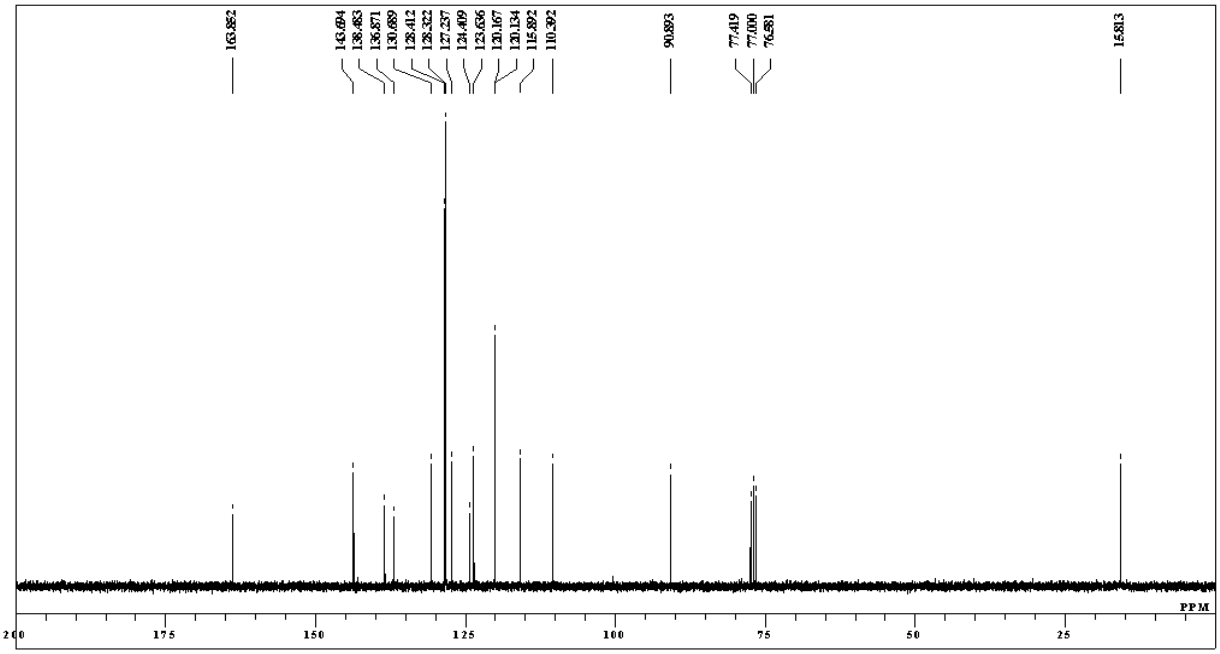




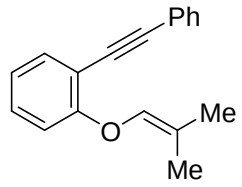
(–)-(*E*)-3-Benzylidene-2-isopropenyl-2,3-dihydrobenzofuran [(–)-3a]

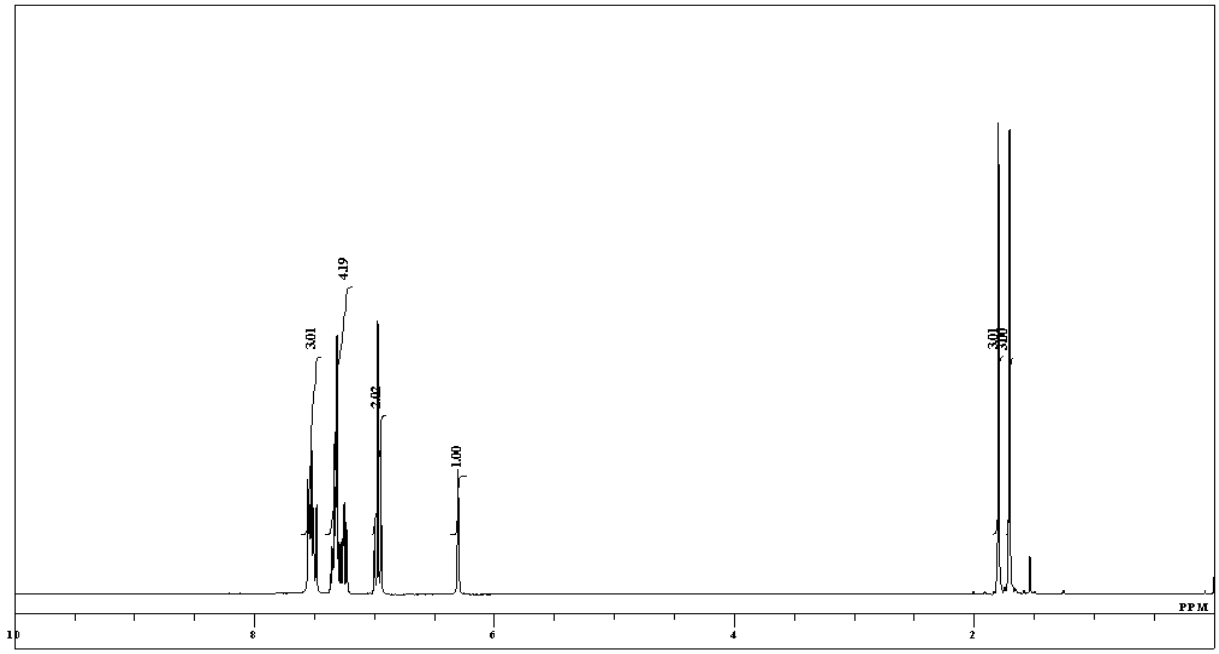


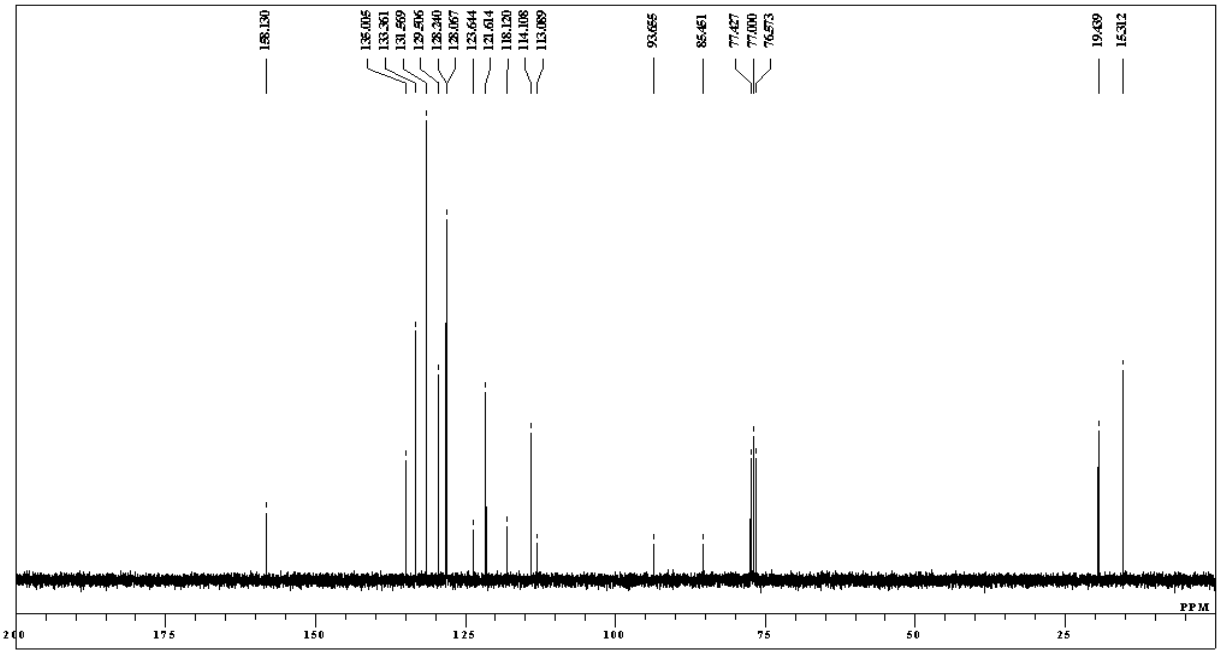




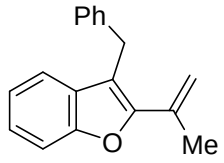
1-(2-Methylpropenyloxy)-2-phenylethynylbenzene (2a)

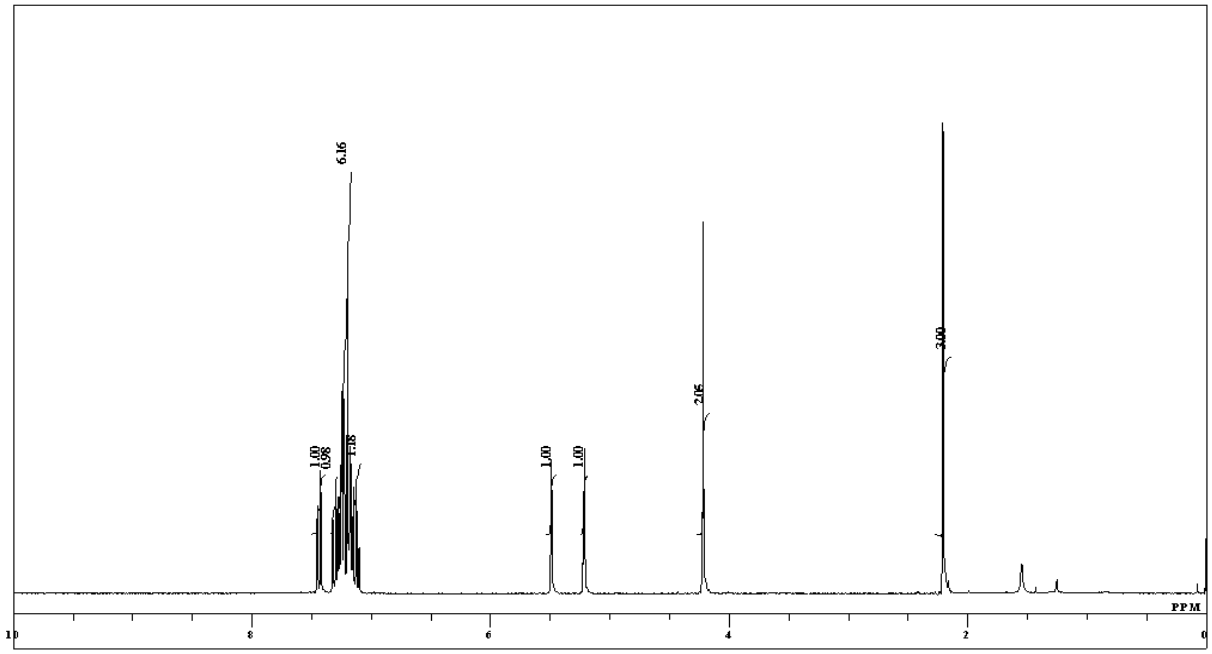


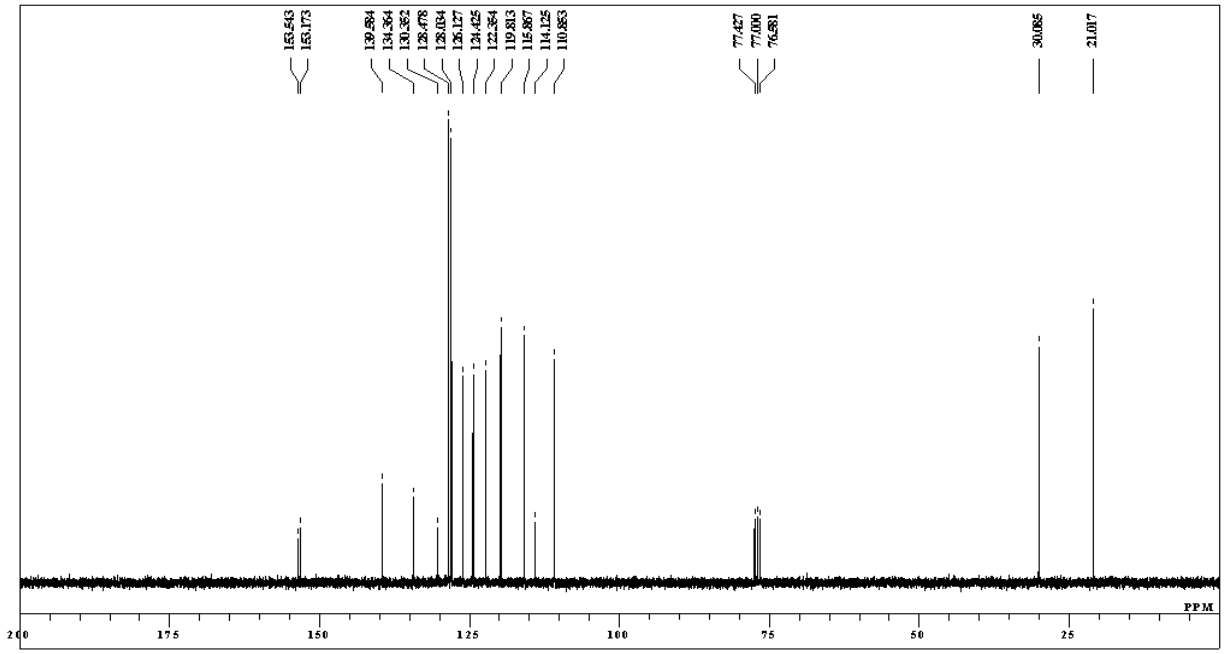




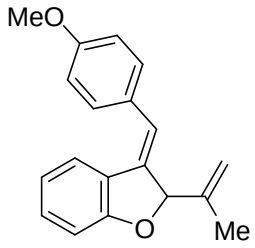
3-Benzyl-2-isopropenylbenzofuran (4a)

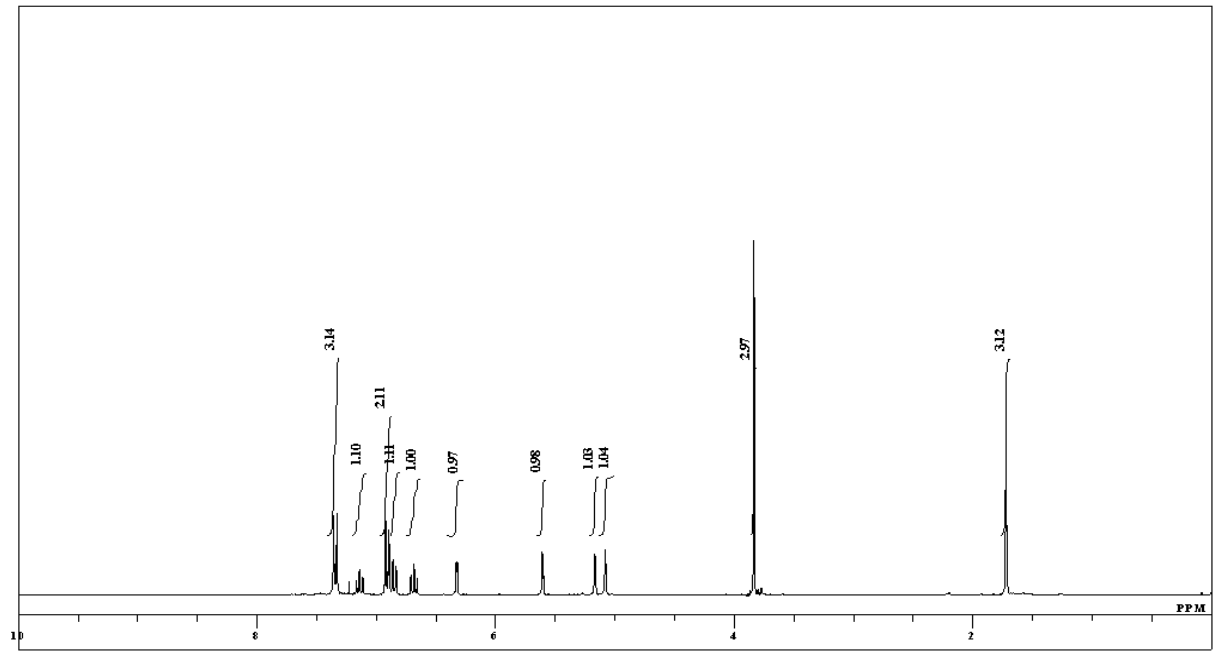


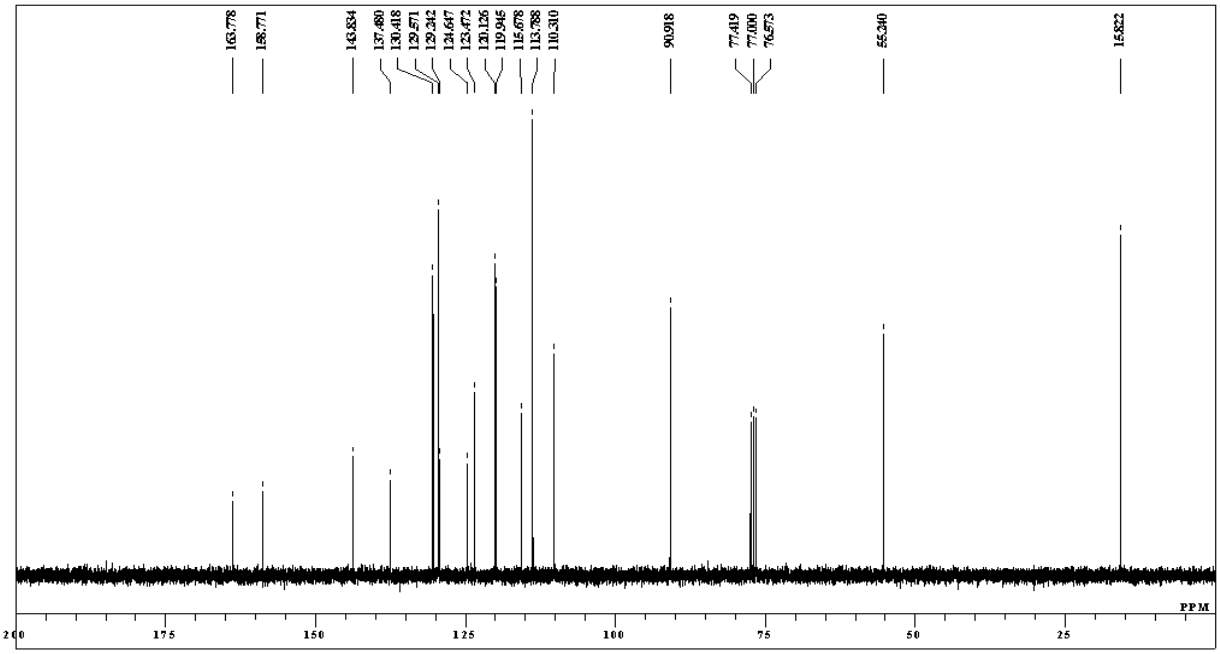




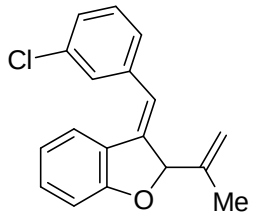
(+)-(*E*)-2-Isopropenyl-3-(4-methoxybenzylidene)-2,3-dihydrobenzofuran [(+)-3b]

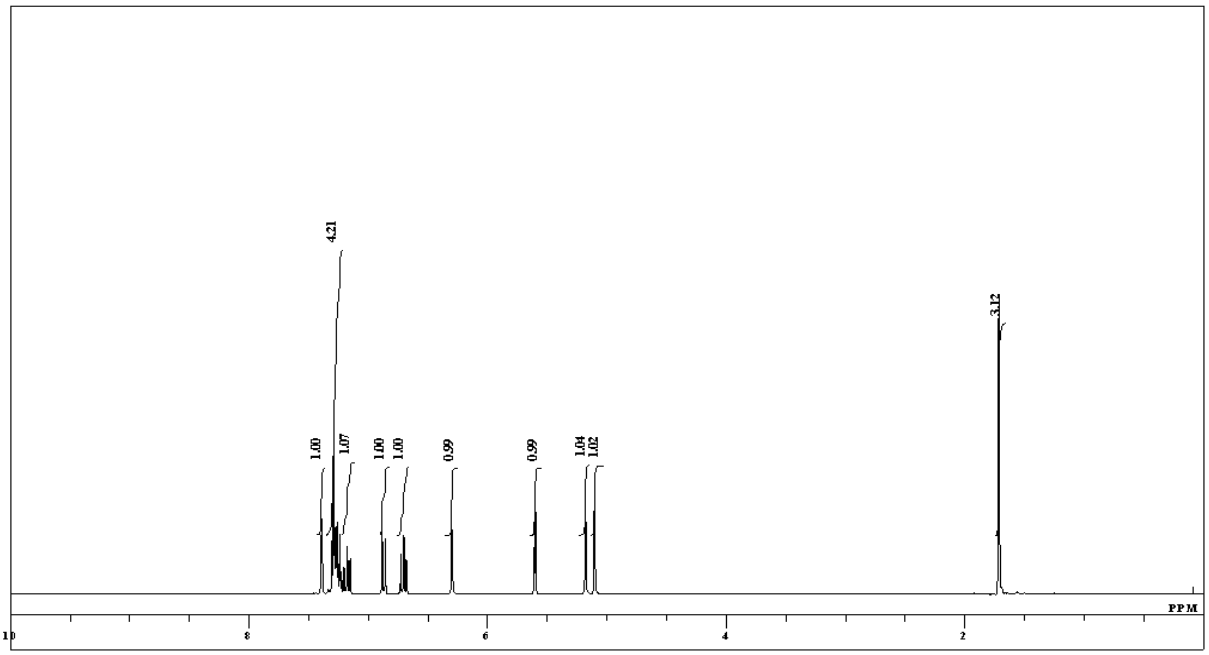


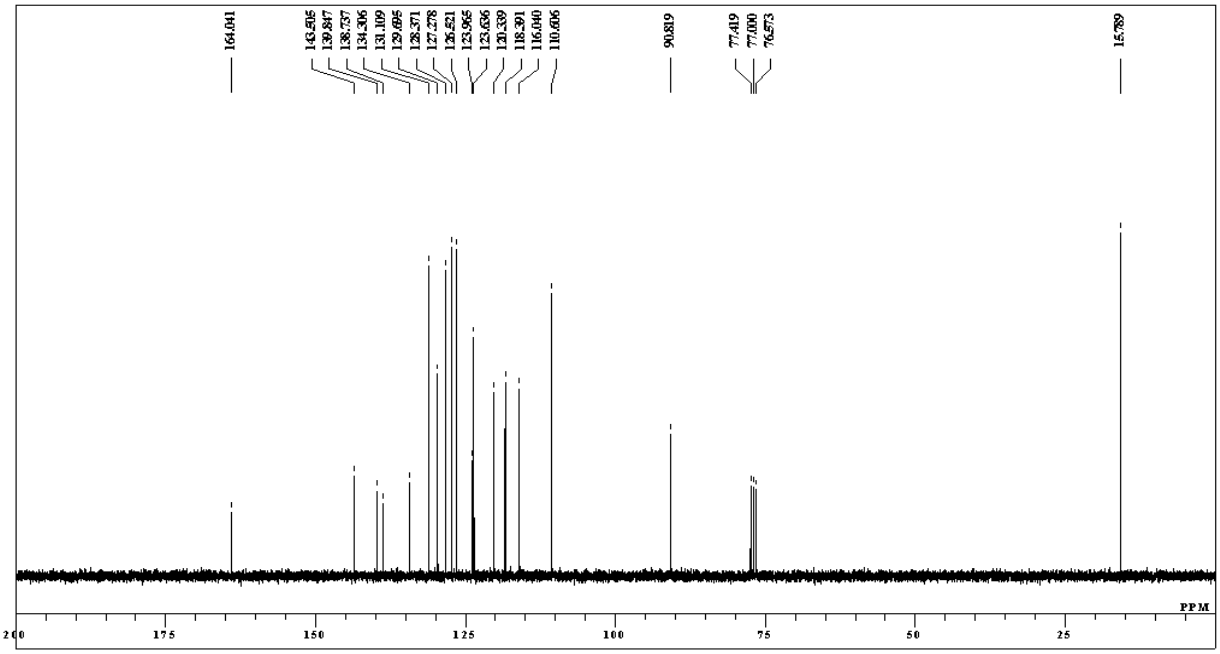




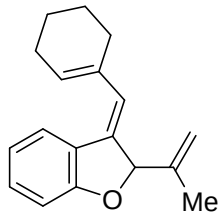
(–)-(*E*)-3-(3-Chlorobenzylidene)-2-isopropenyl-2,3-dihydrobenzofuran [(–)-3d]

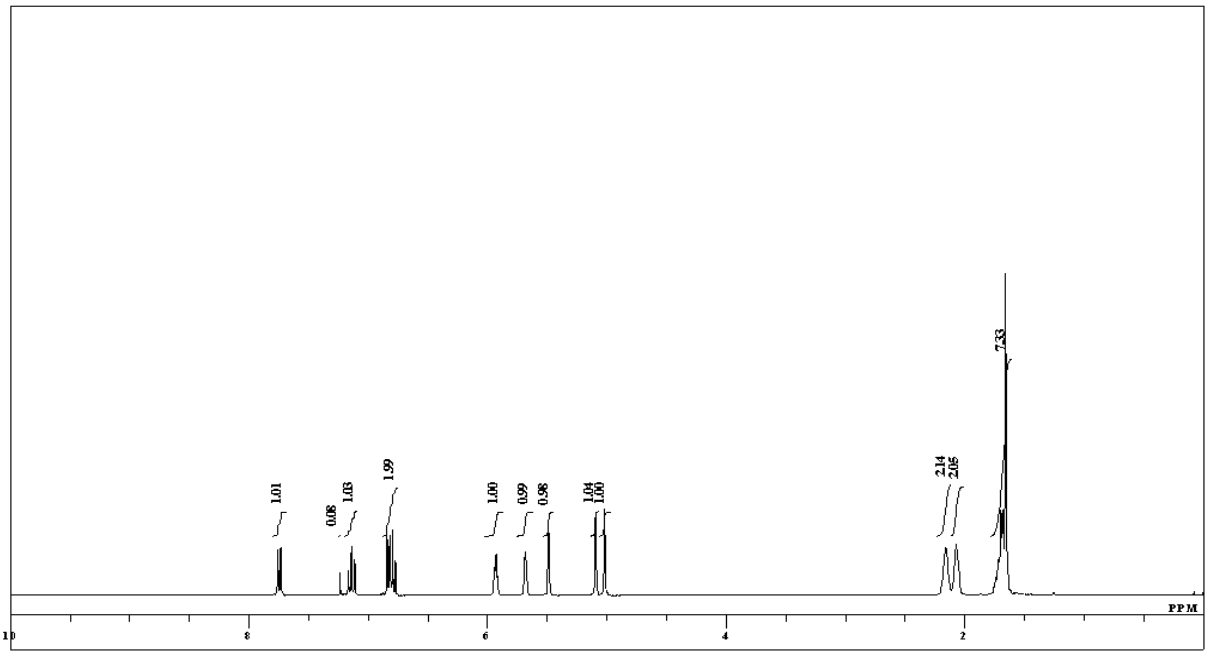


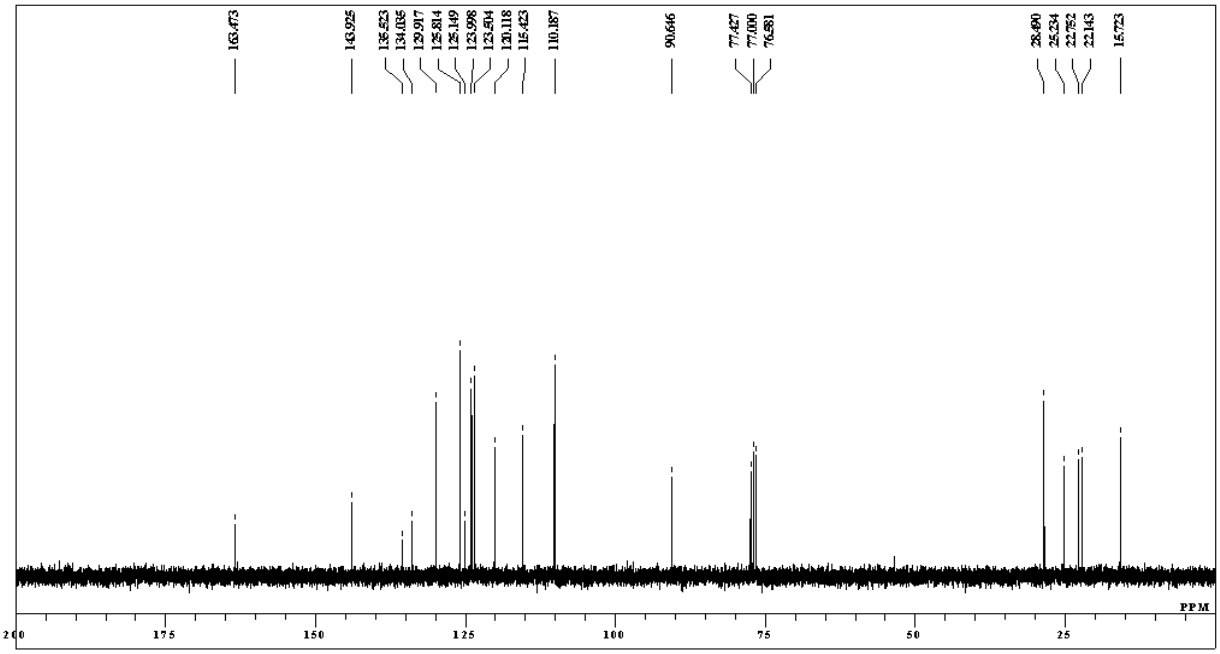




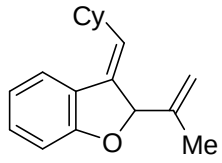
(–)-(*E*)-3-Cyclohex-1-enylmethylene-2-isopropenyl-2,3-dihydrobenzofuran [(–)-3e]

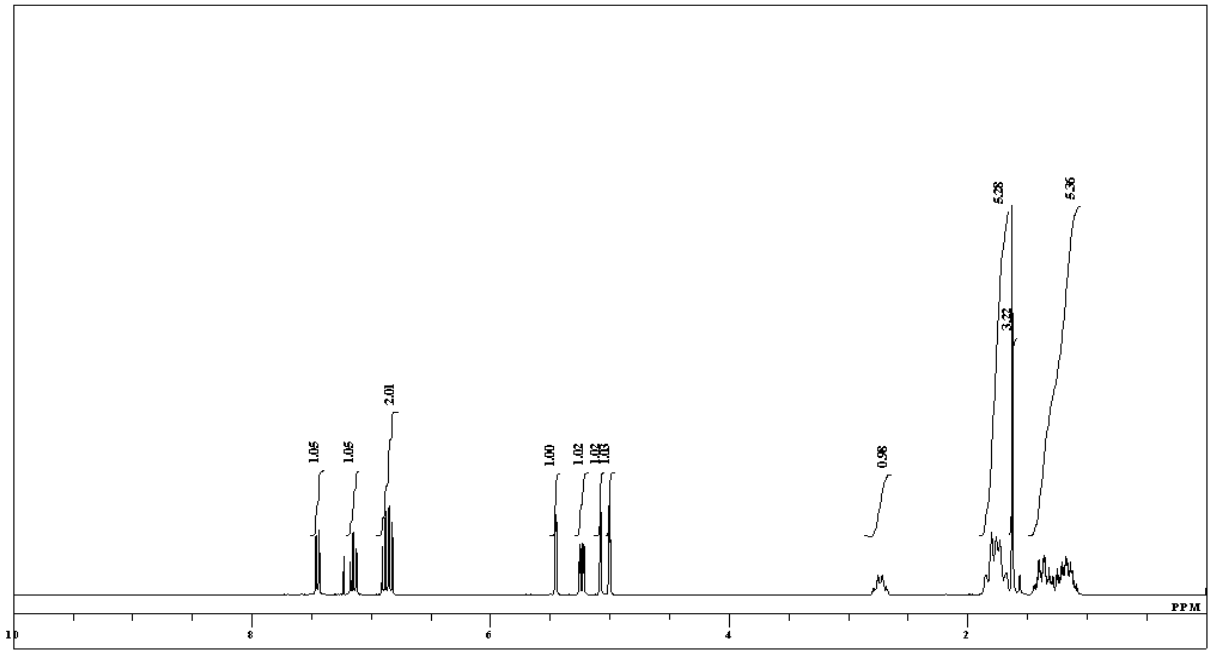


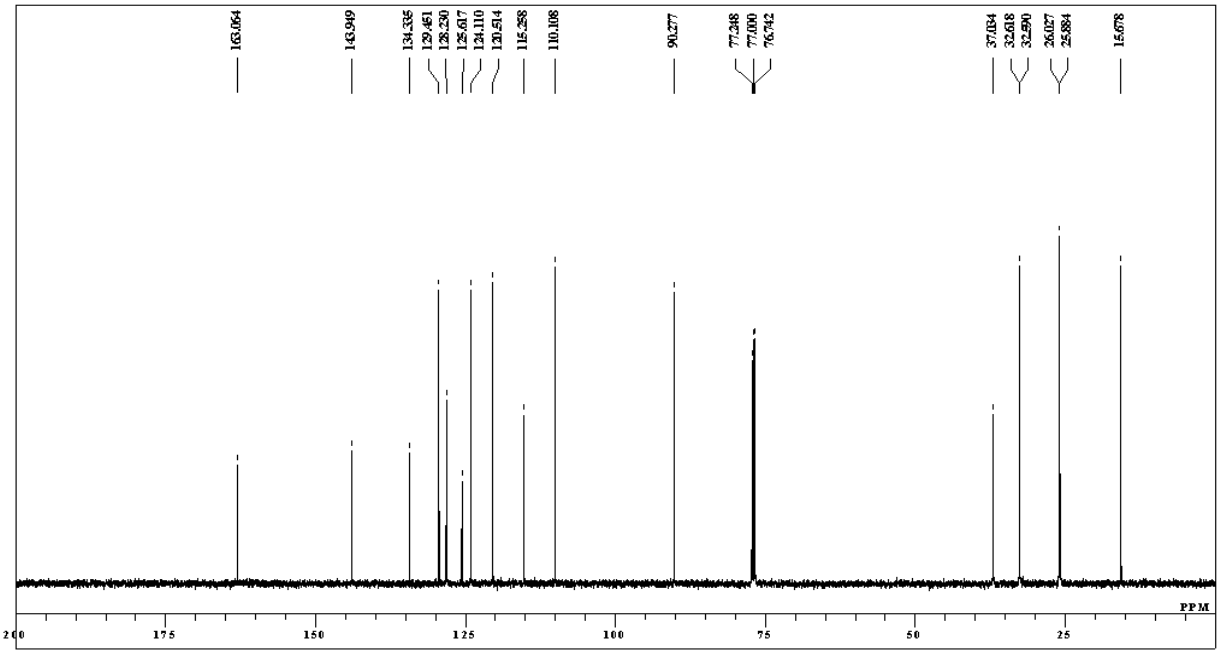




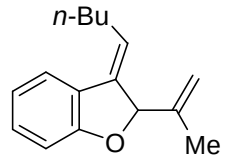
(–)-(*E*)-3-Cyclohexylmethylene-2-isopropenyl-2,3-dihydrobenzofuran [(–)-3f]

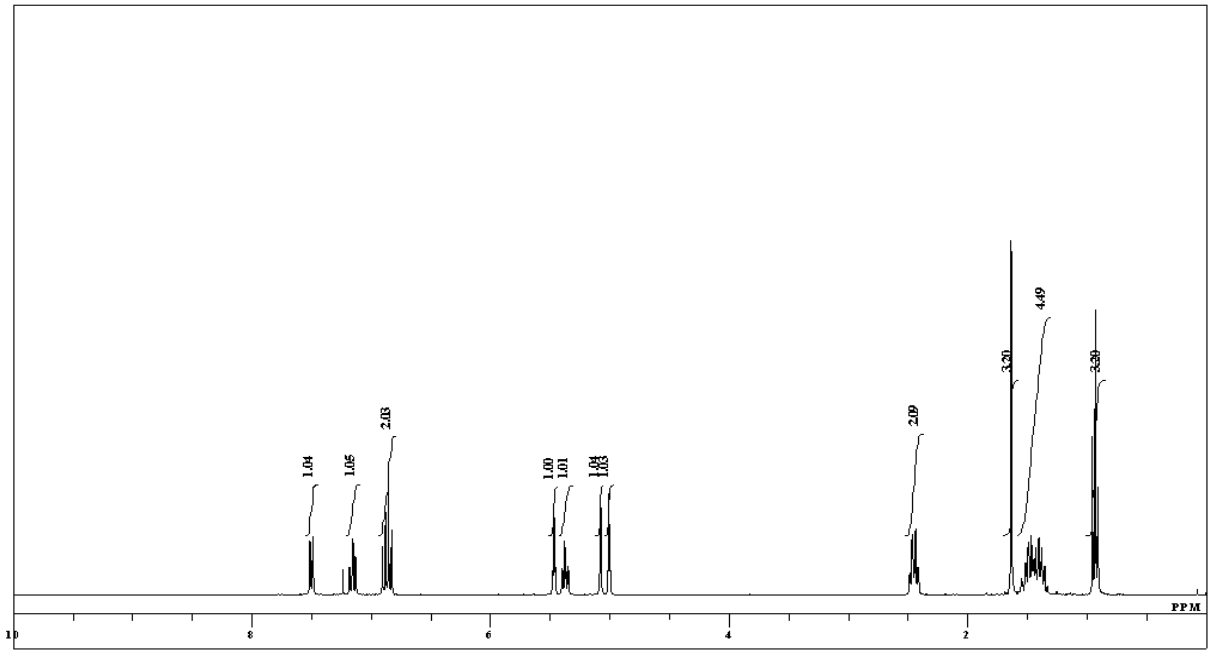


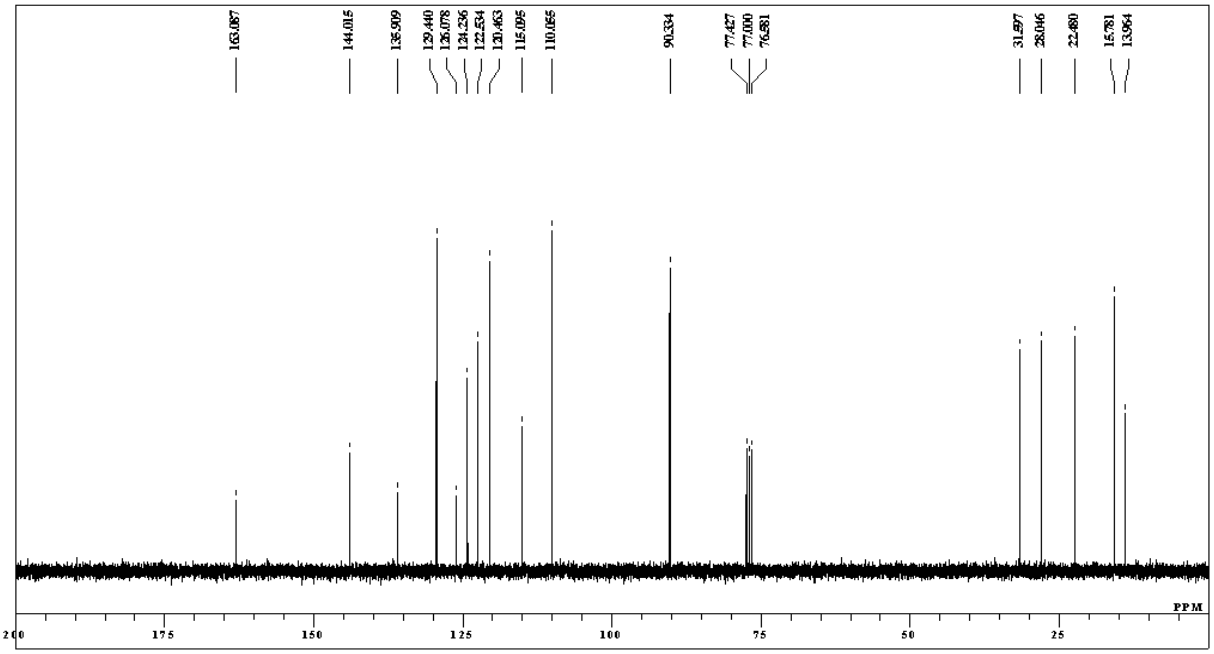




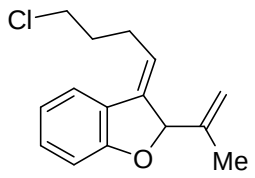
(–)-(*E*)-2-Isopropenyl-3-pentylidene-2,3-dihydrobenzofuran [(–)-3g]

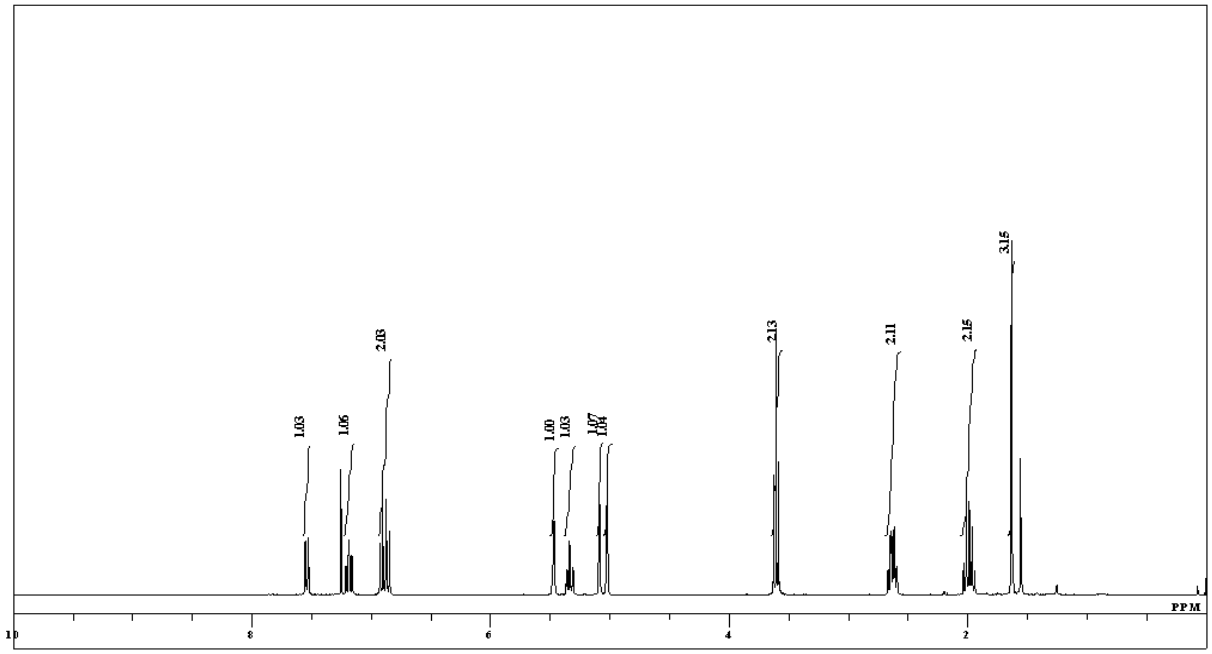


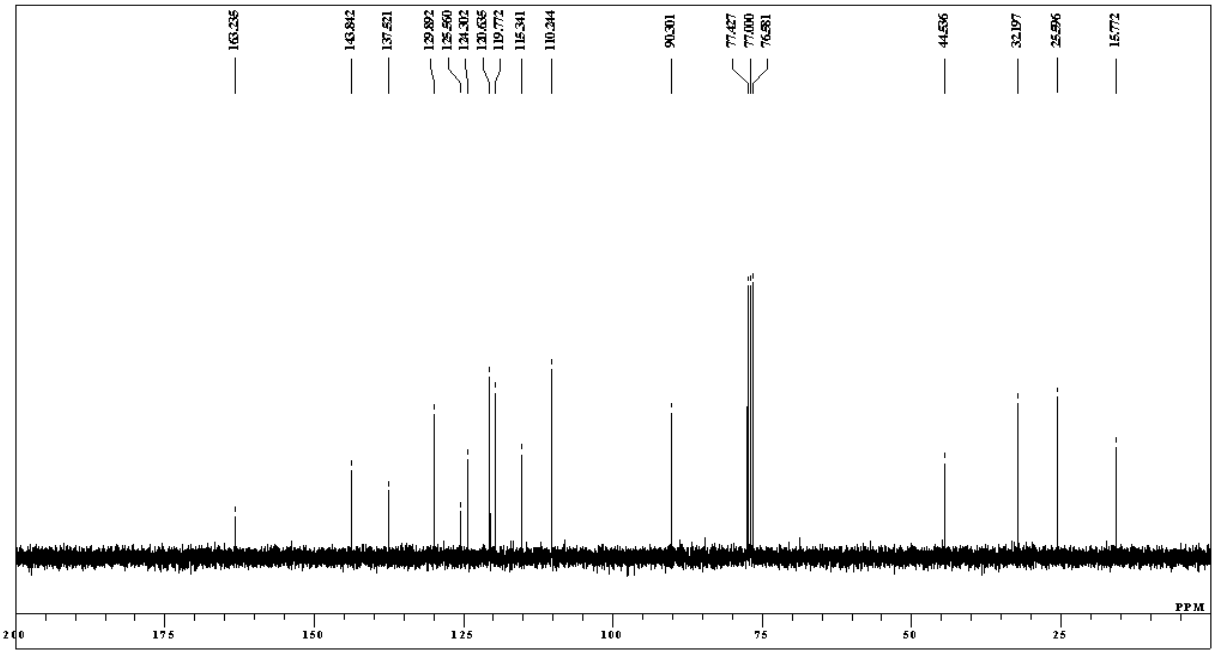




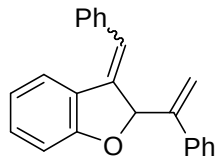
(–)-(*E*)-3-(4-Chlorobutylidene)-2-isopropenyl-2,3-dihydrobenzofuran [(–)-3h]

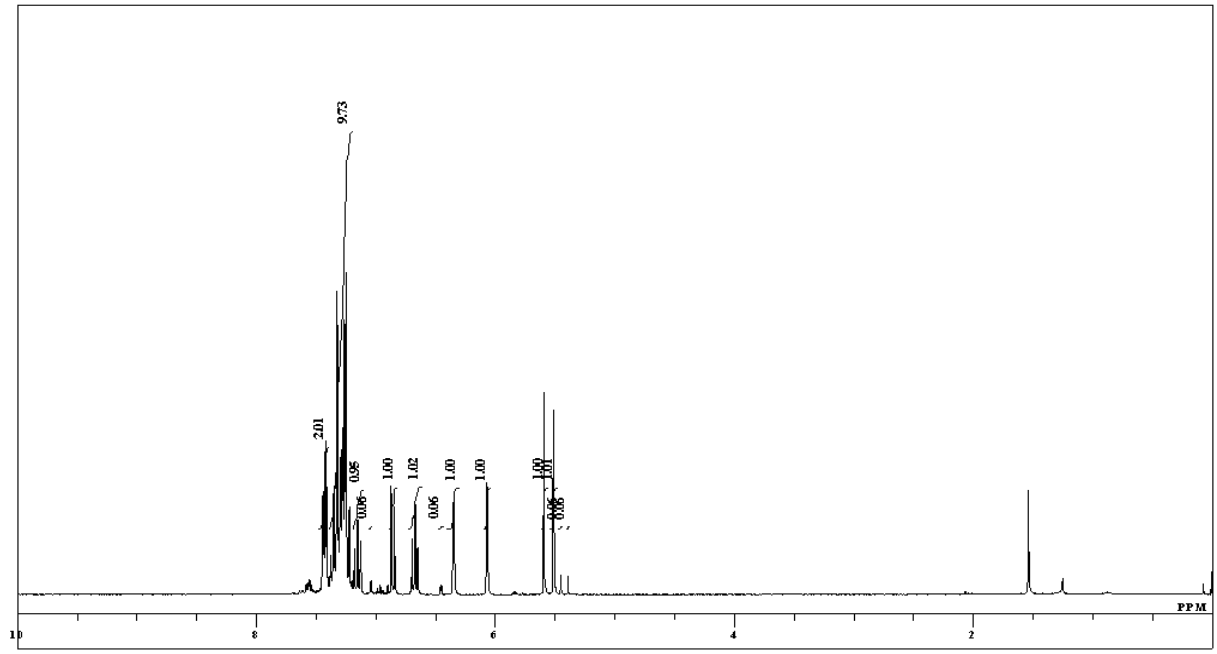


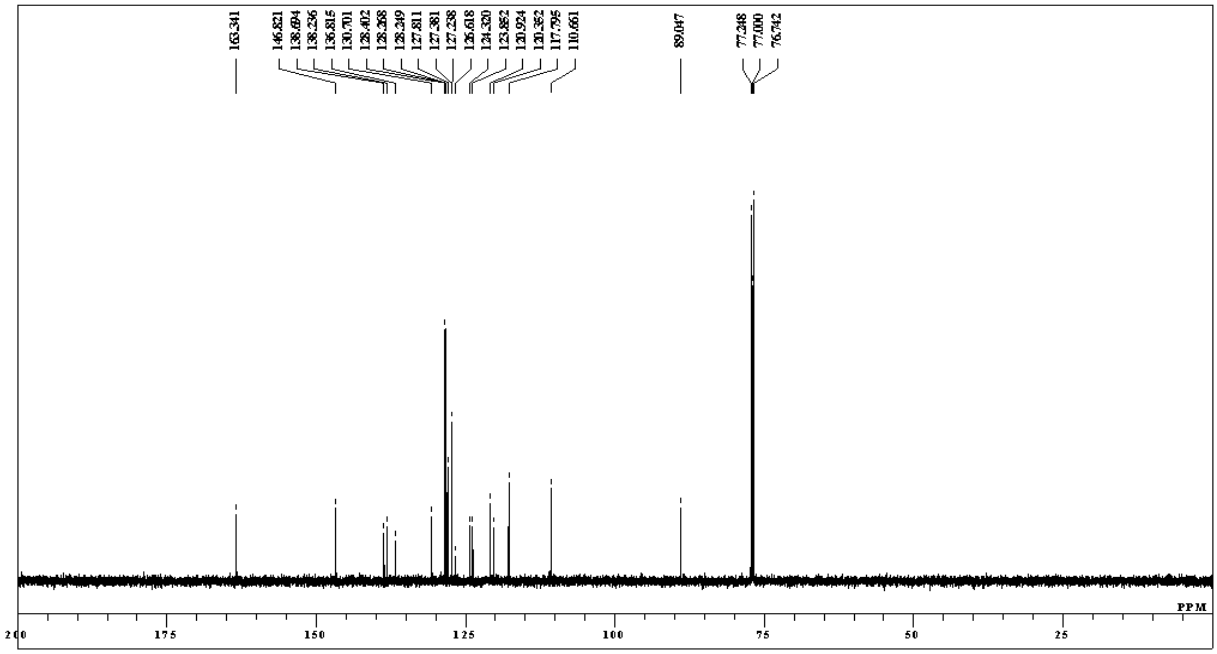




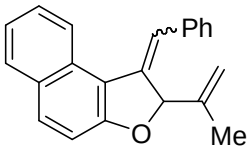
(–)-3-Benzylidene-2-(1-phenylvinyl)-2,3-dihydrobenzofuran [(–)-3i, *E*/*Z* = 94:6]

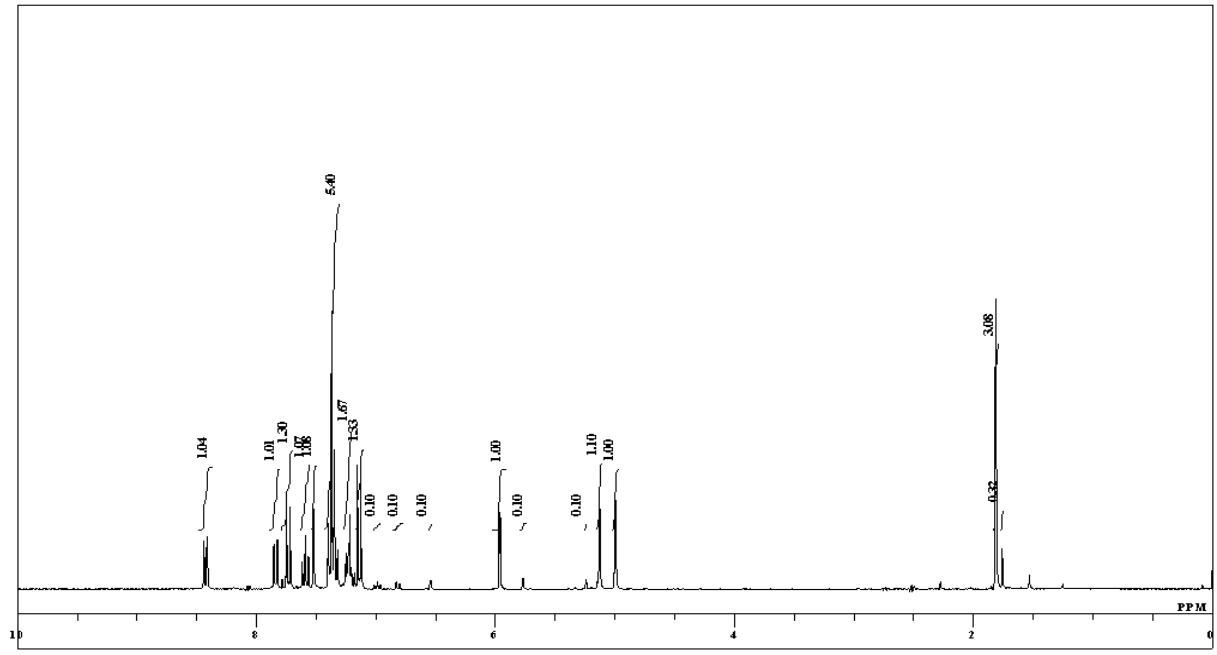


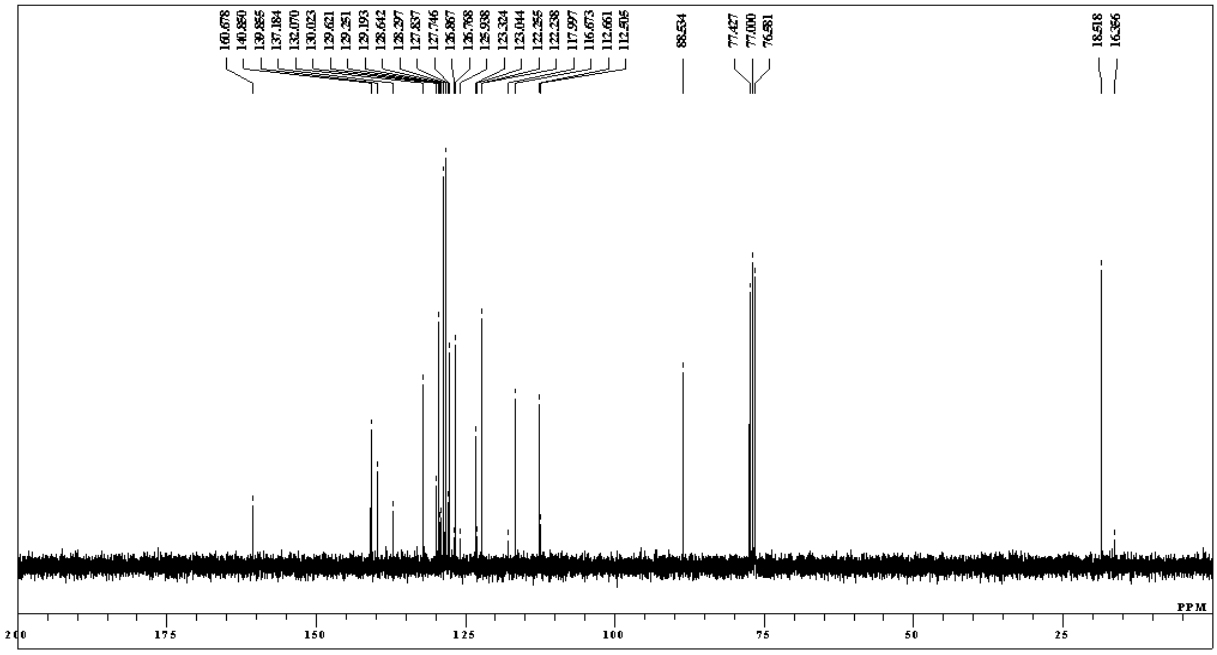




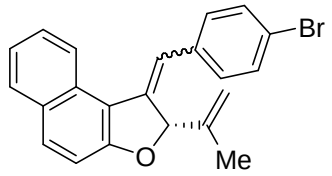
(–)-1-Benzylidene-2-isopropenyl-1,2-dihydronaphtho[2,1-b]furan [(–)-3j, *E*/*Z* = 9:91]

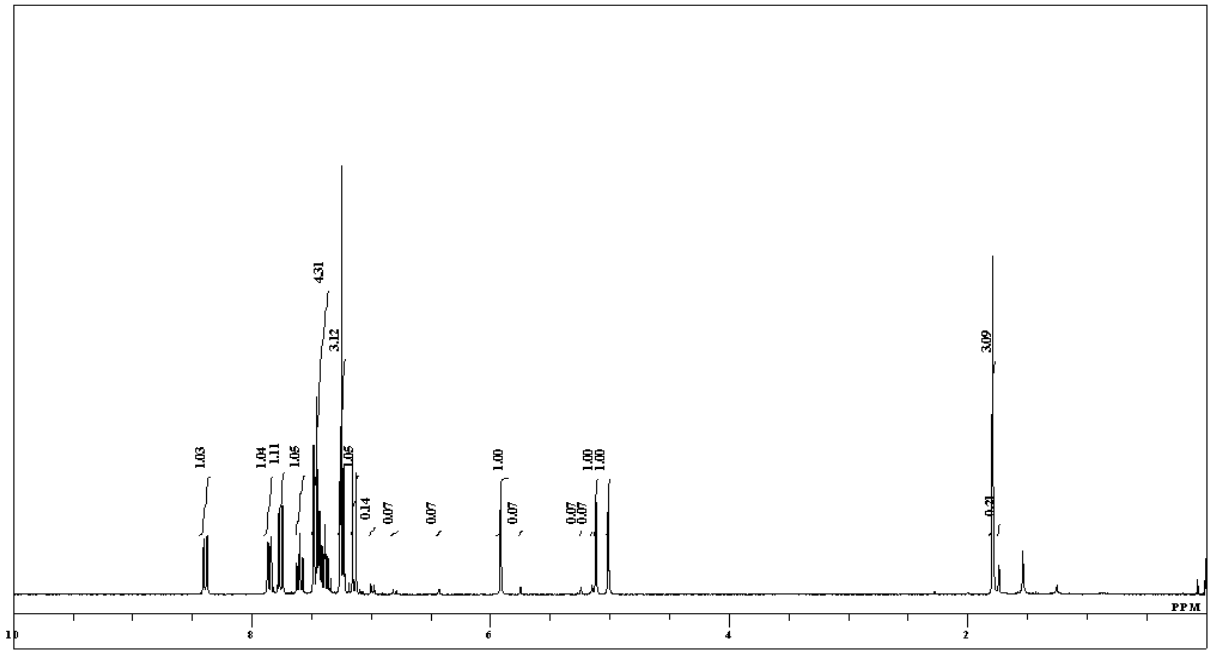


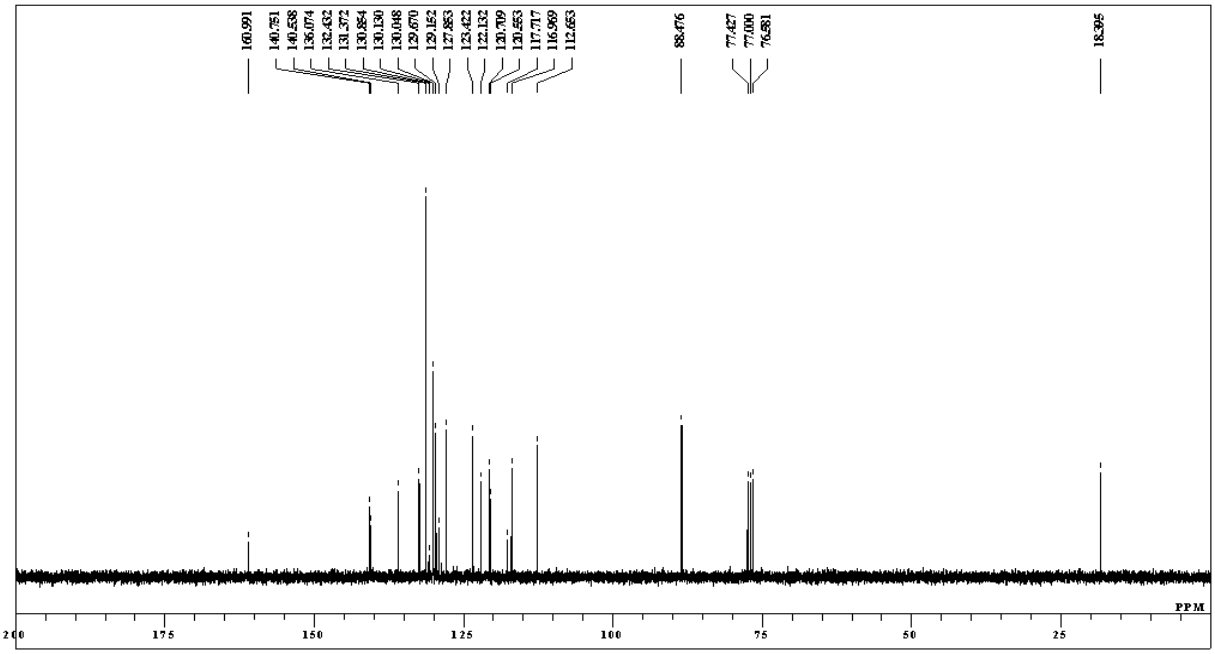




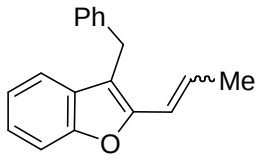
(*S*)-(–)-1-(4-Bromobenzylidene)-2-isopropenyl-1,2-dihydronaphtho[2,1-b]furan [(*S*)-(–)-3k, *E*/*Z* = 7:93]

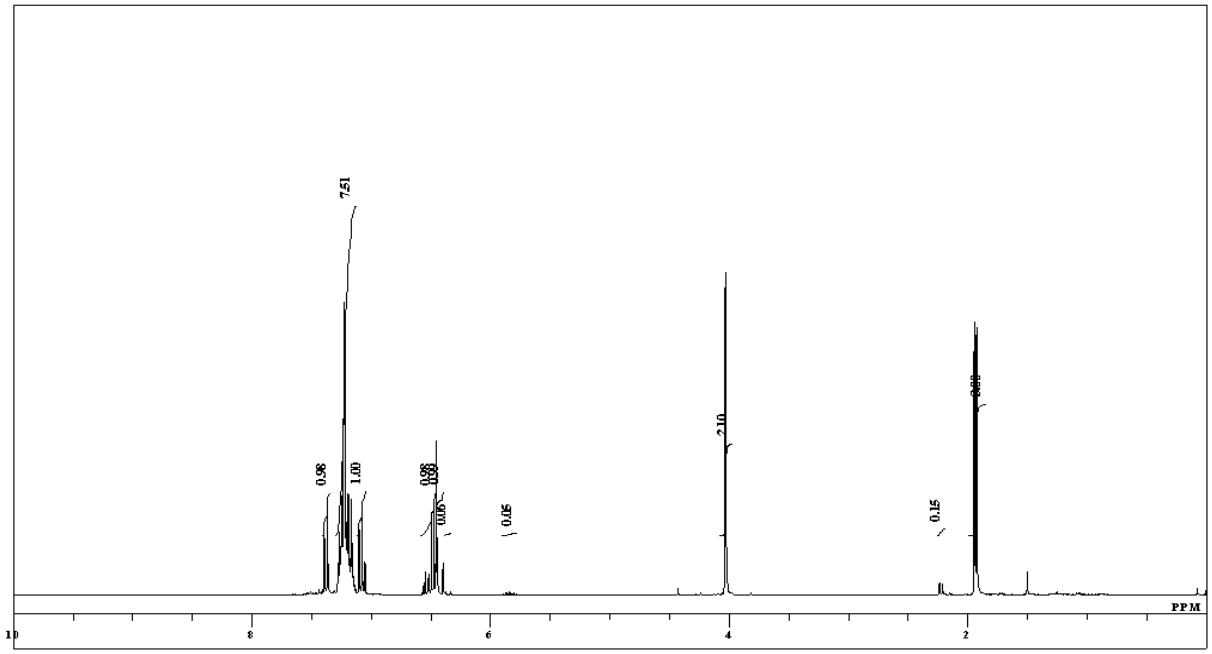


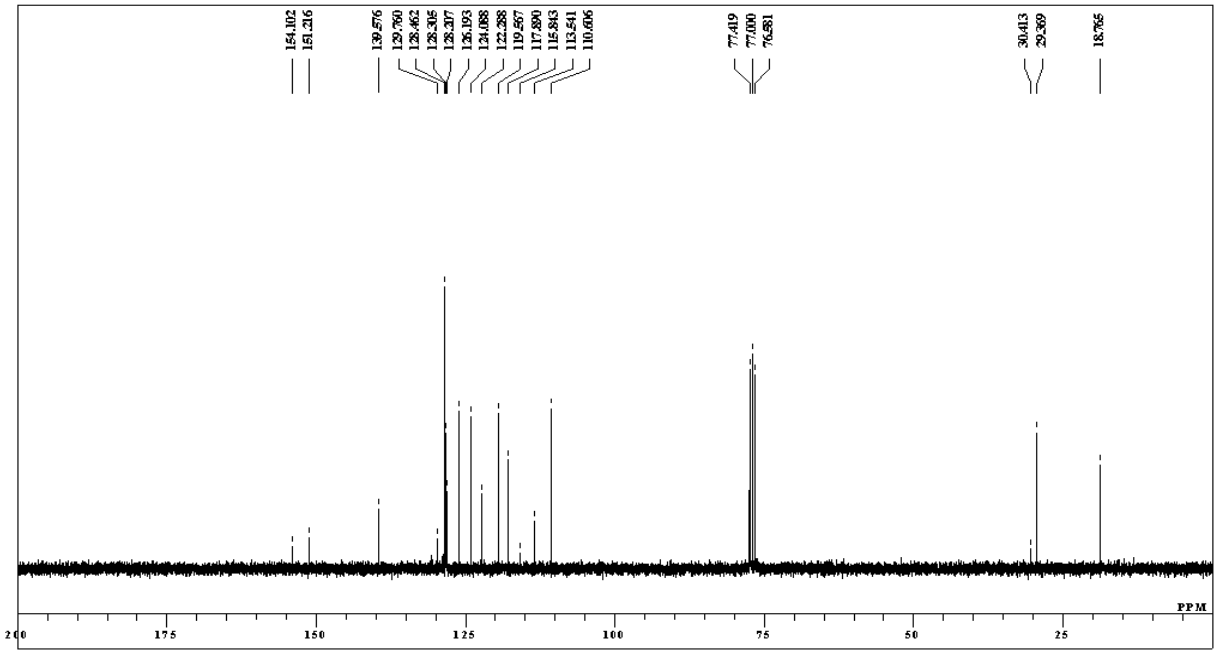




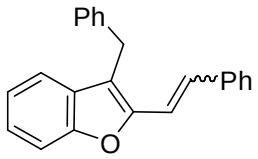
3-Benzyl-2-propenylbenzofuran (4l, *E*/*Z* = 95:5)

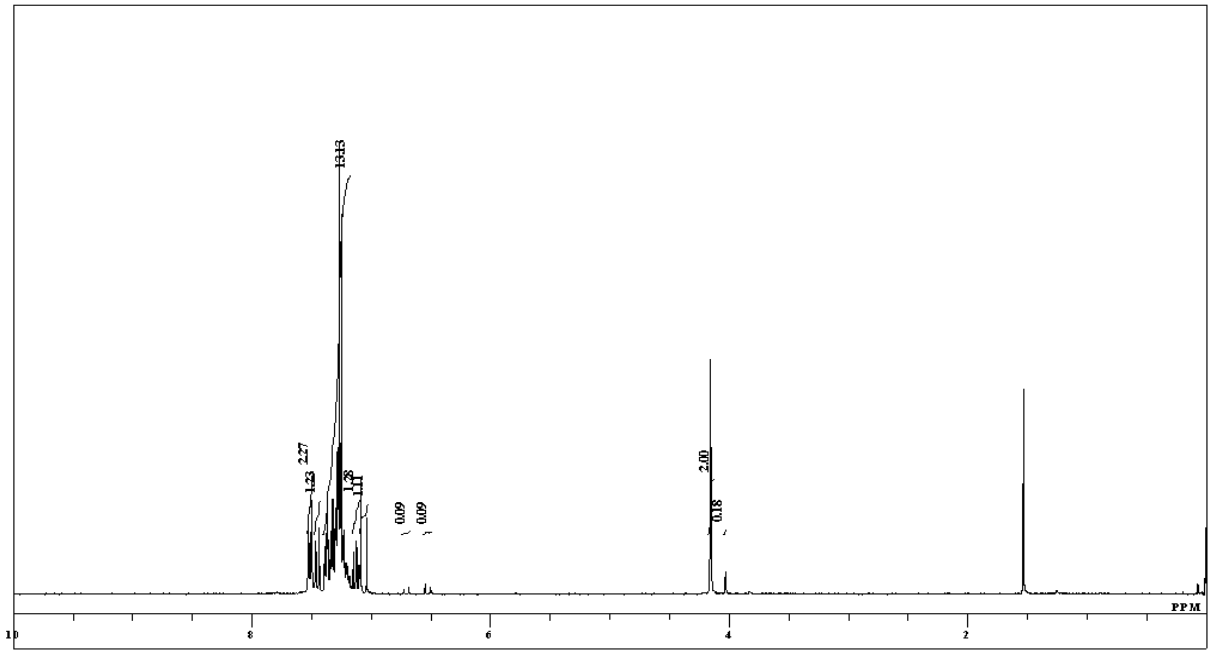


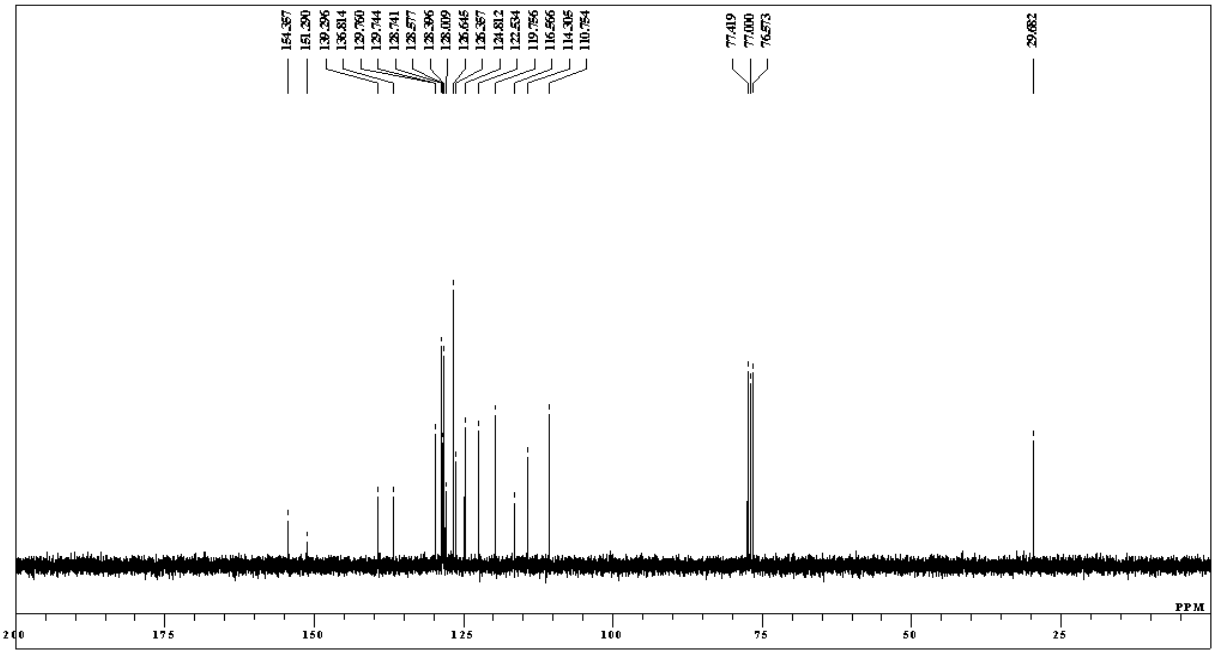




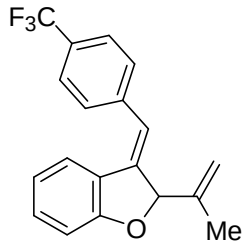
3-Benzyl-2-styrylbenzofuran (4m, *E*/*Z* = 92:8)

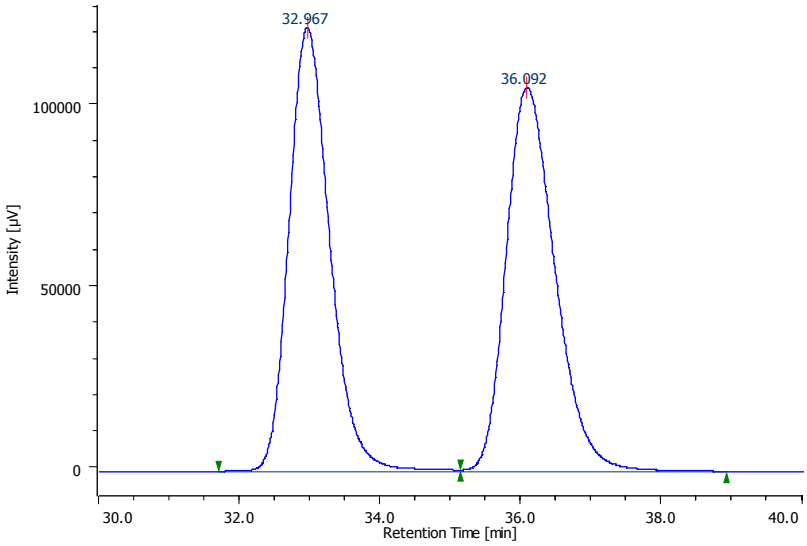




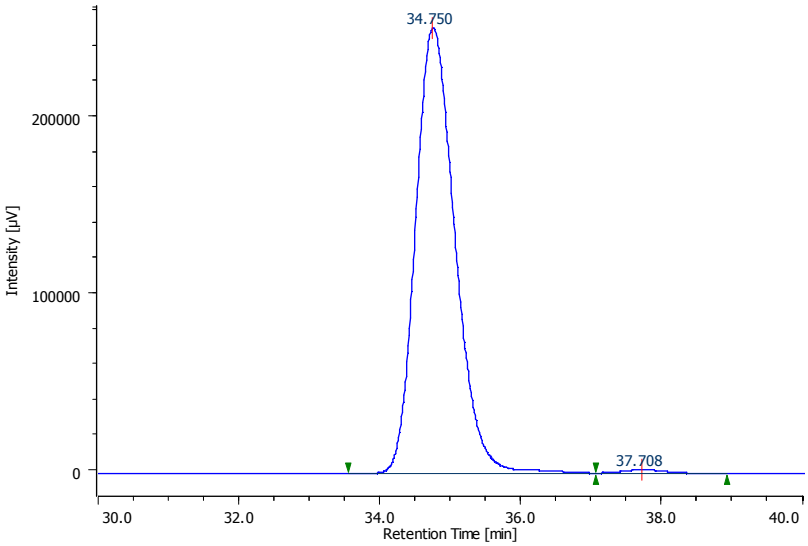


(–)-(*E*)-2-Isopropenyl-3-(4-trifluoromethylbenzylidene)-2,3-dihydrobenzofuran [(–)-3c]



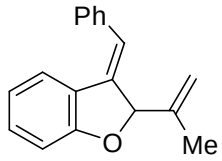


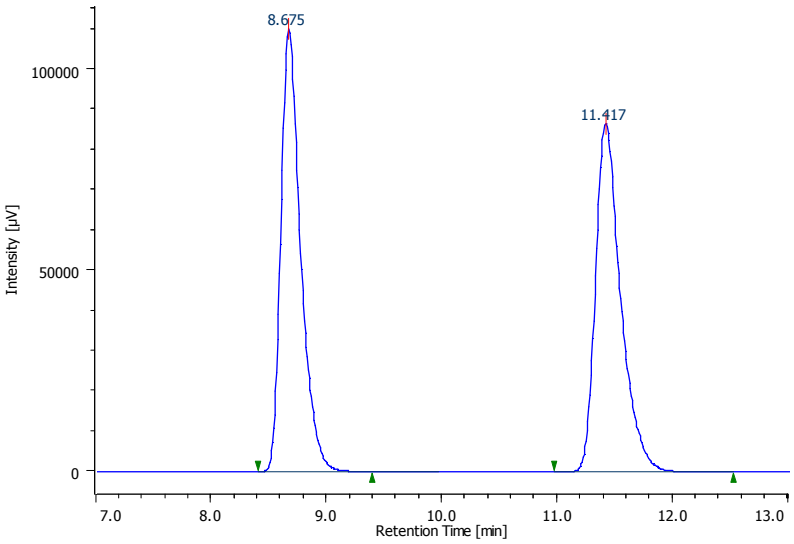
Peak No.	Retention Time (min)	Area (%)
1	32.967	49.153
2	36.092	50.847



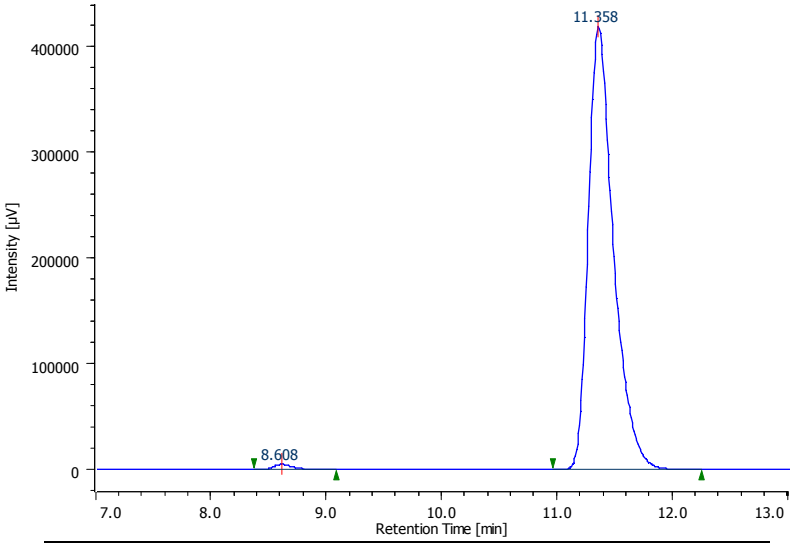
Peak No.	Retention Time (min)	Area (%)
1	34.750	99.106
2	37.708	0.894

(–)-(*E*)-3-Benzylidene-2-isopropenyl-2,3-dihydrobenzofuran [(–)-3a]



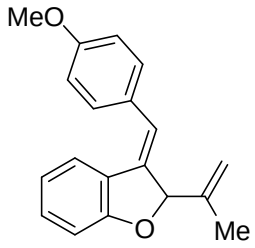


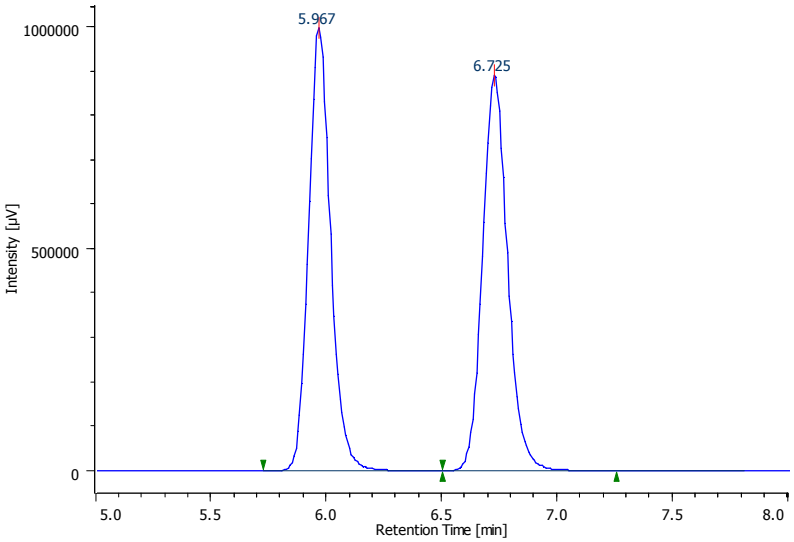
Peak No.	Retention Time (min)	Area (%)
1	8.675	49.871
2	11.417	50.129



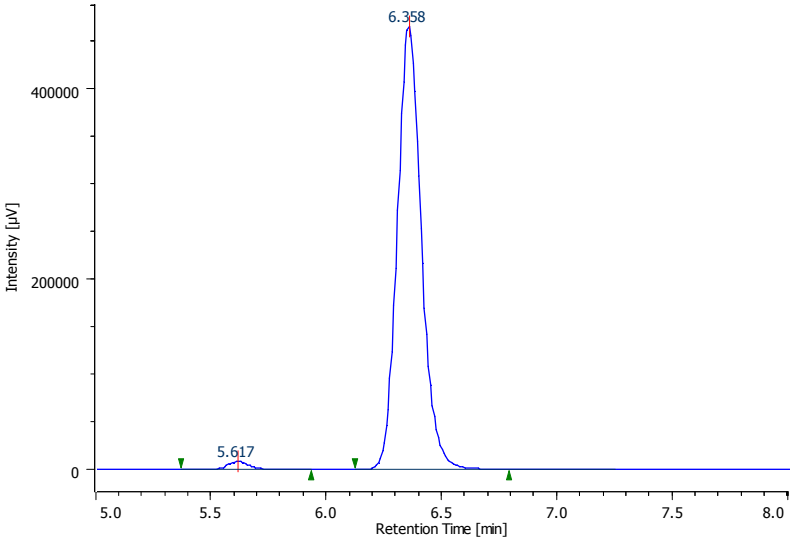
Peak No.	Retention Time (min)	Area (%)
1	8.608	0.869
2	11.358	99.131

(+)-(*E*)-2-Isopropenyl-3-(4-methoxybenzylidene)-2,3-dihydrobenzofuran [(+)-3b]



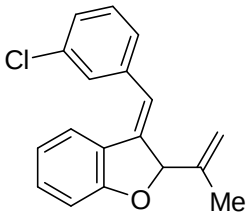


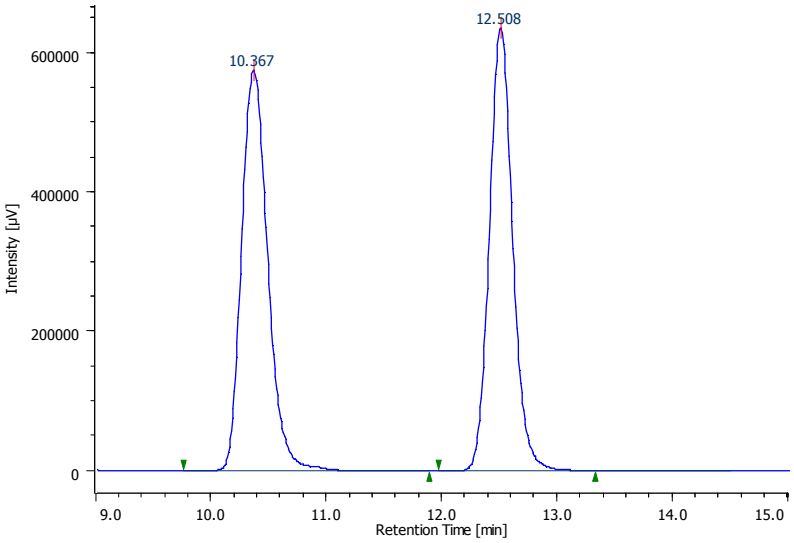
Peak No.	Retention Time (min)	Area (%)
1	5.967	49.890
2	6.725	50.110



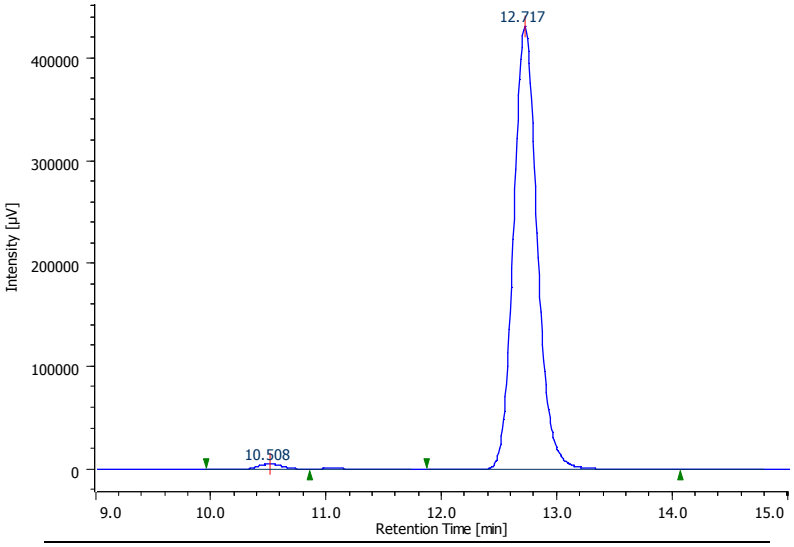
Peak No.	Retention Time (min)	Area (%)
1	5.617	1.617
2	6.358	98.383

(–)-(*E*)-3-(3-Chlorobenzylidene)-2-isopropenyl-2,3-dihydrobenzofuran [(–)-3d]



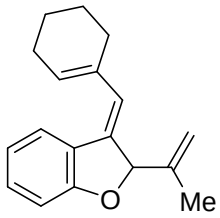


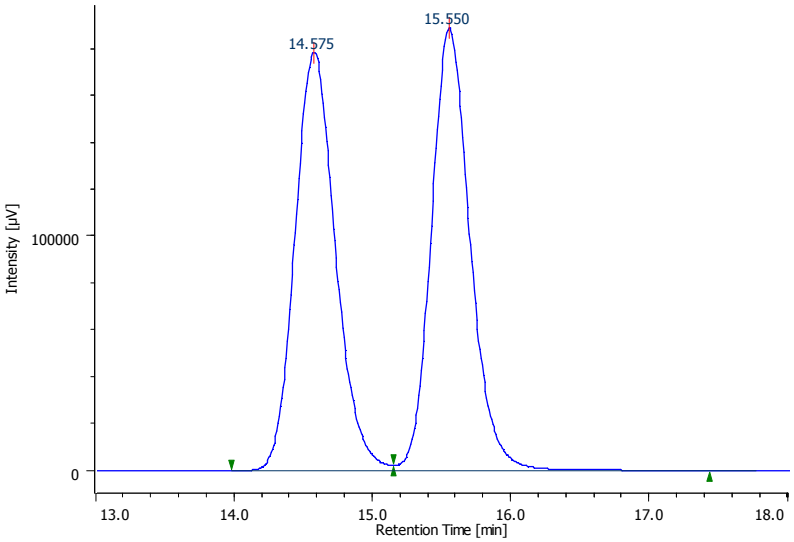
Peak No.	Retention Time (min)	Area (%)
1	10.367	50.352
2	12.508	49.648



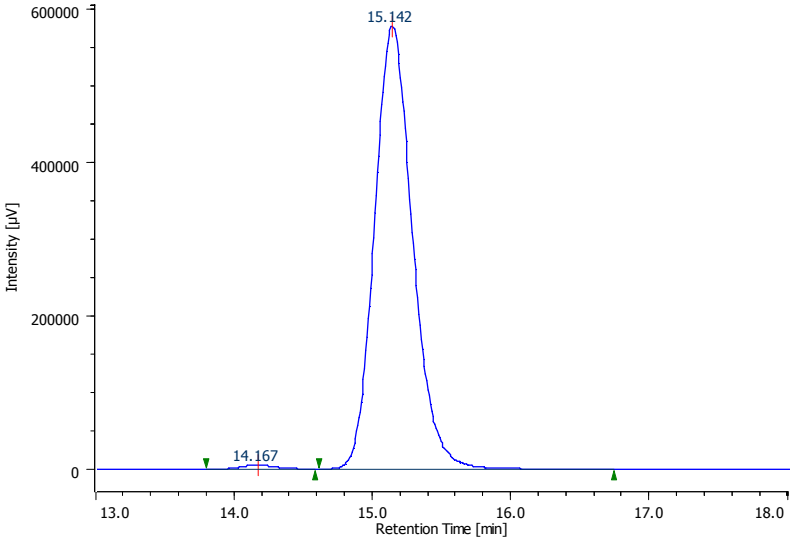
Peak No.	Retention Time (min)	Area (%)
1	10.508	1.311
2	12.717	98.689

(–)-(*E*)-3-Cyclohex-1-enylmethylene-2-isopropenyl-2,3-dihydrobenzofuran [(–)-3e]



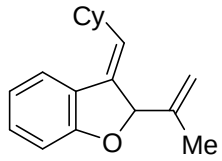


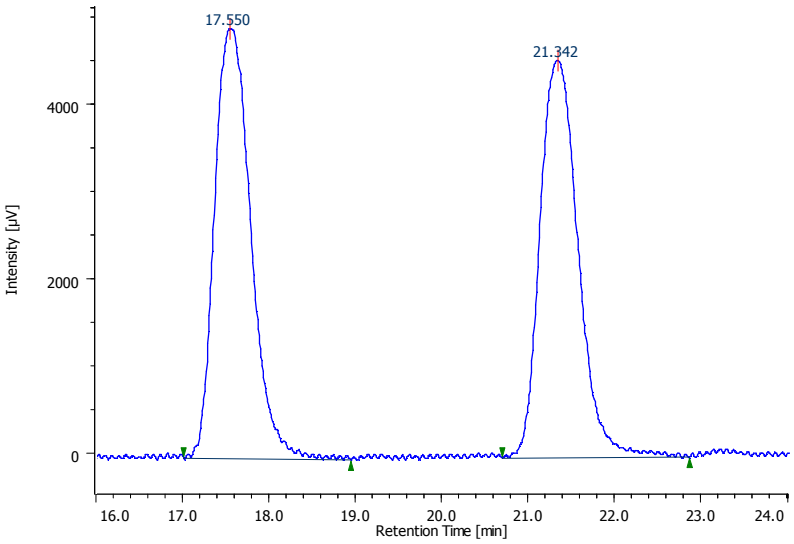
Peak No.	Retention Time (min)	Area (%)
1	14.575	49.674
2	15.550	50.326



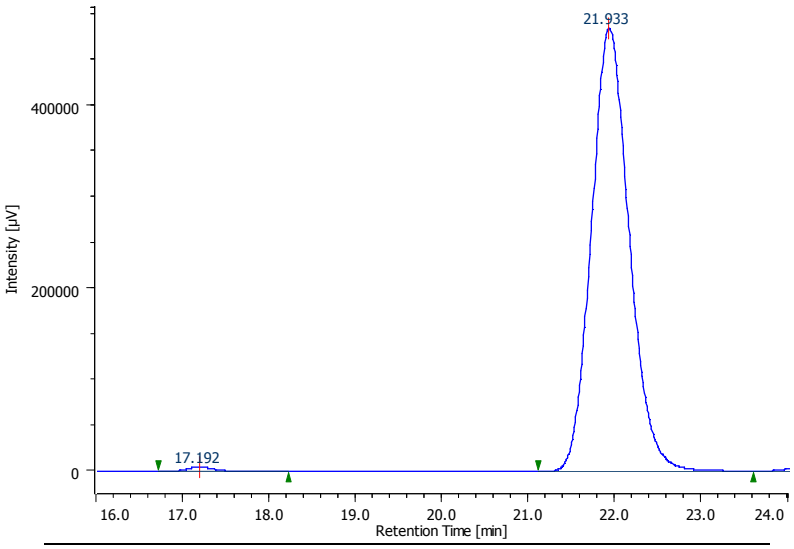
Peak No.	Retention Time (min)	Area (%)
1	14.167	0.826
2	15.142	99.174

(–)-(*E*)-3-Cyclohexylmethylene-2-isopropenyl-2,3-dihydrobenzofuran [(–)-3f]



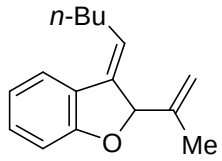


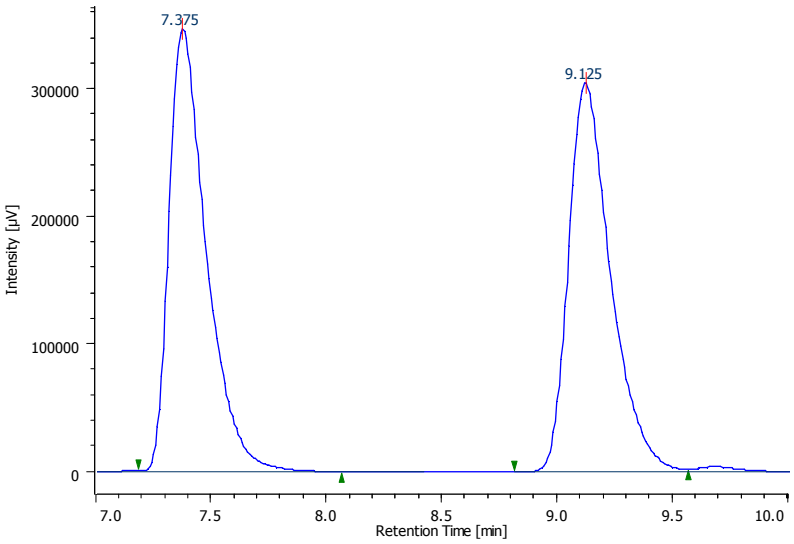
Peak No.	Retention Time (min)	Area (%)
1	17.550	50.610
2	21.342	49.390



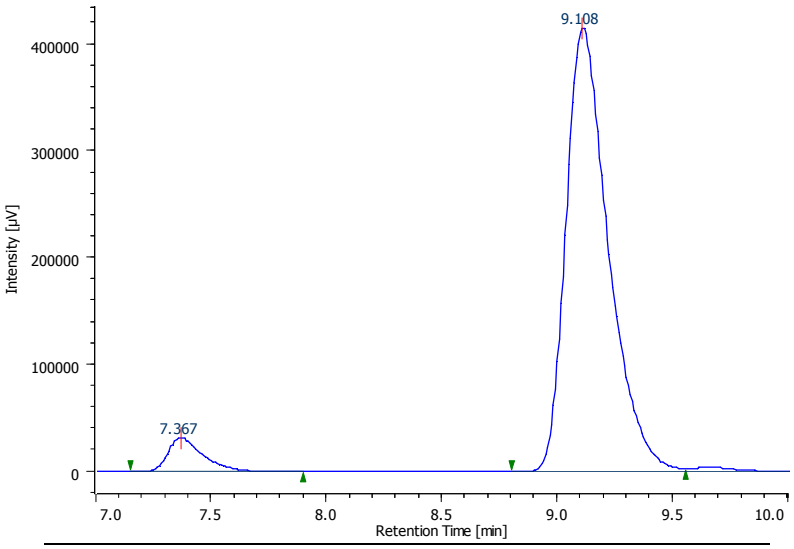
Peak No.	Retention Time (min)	Area (%)
1	17.192	0.732
2	21.933	99.268

(–)-(*E*)-2-Isopropenyl-3-pentylidene-2,3-dihydrobenzofuran [(–)-3g]



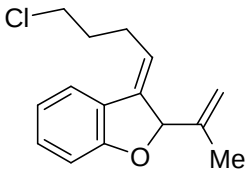


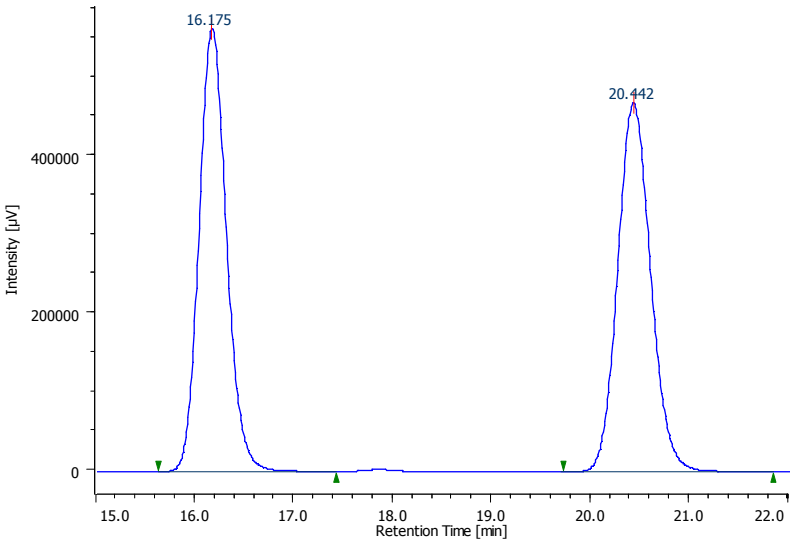
Peak No.	Retention Time (min)	Area (%)
1	7.375	50.271
2	9.125	49.729



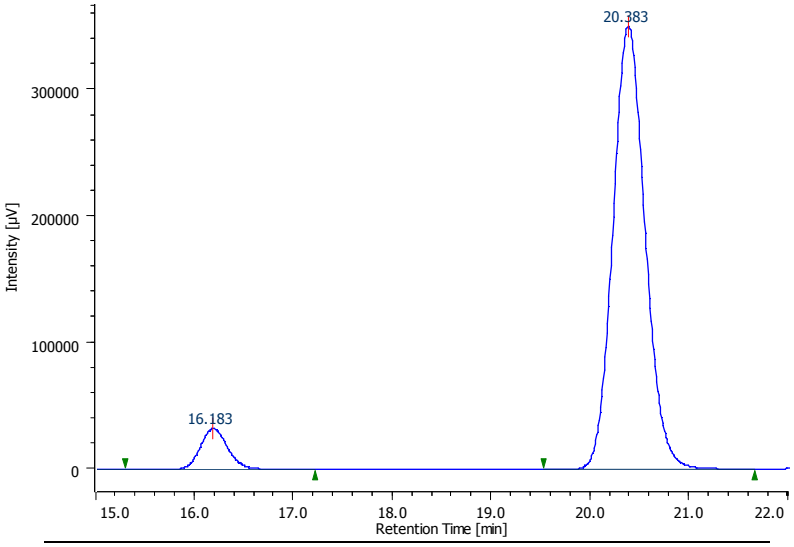
Peak No.	Retention Time (min)	Area (%)
1	7.367	5.850
2	9.108	94.150

(–)-(*E*)-3-(4-Chlorobutylidene)-2-isopropenyl-2,3-dihydrobenzofuran [(–)-3h]



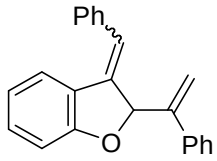


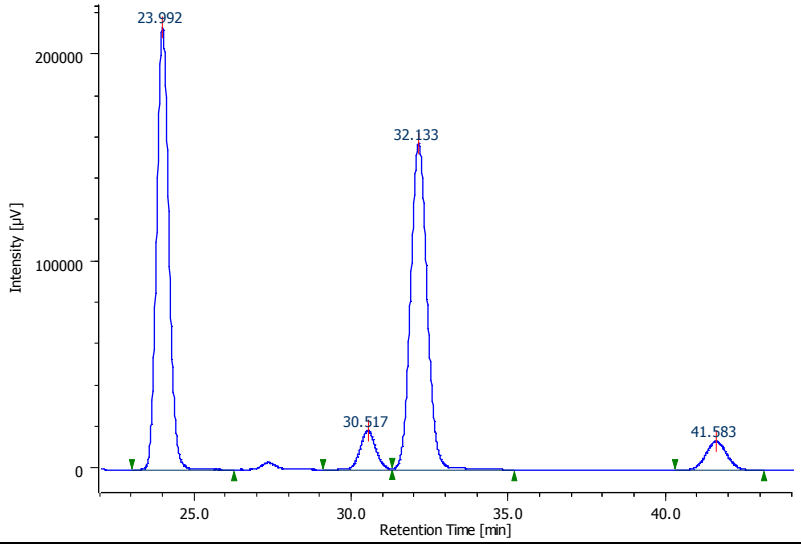
Peak No.	Retention Time (min)	Area (%)
1	16.175	49.878
2	20.442	50.122



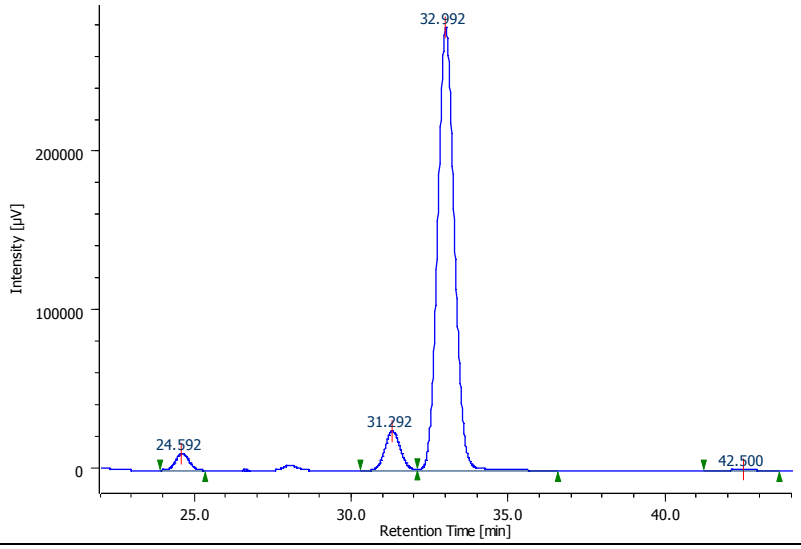
Peak No.	Retention Time (min)	Area (%)
1	16.183	7.233
2	20.383	92.767

(–)-3-Benzylidene-2-(1-phenylvinyl)-2,3-dihydrobenzofuran [(–)-3i, *E*/*Z* = 94:6]



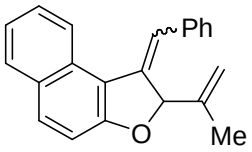


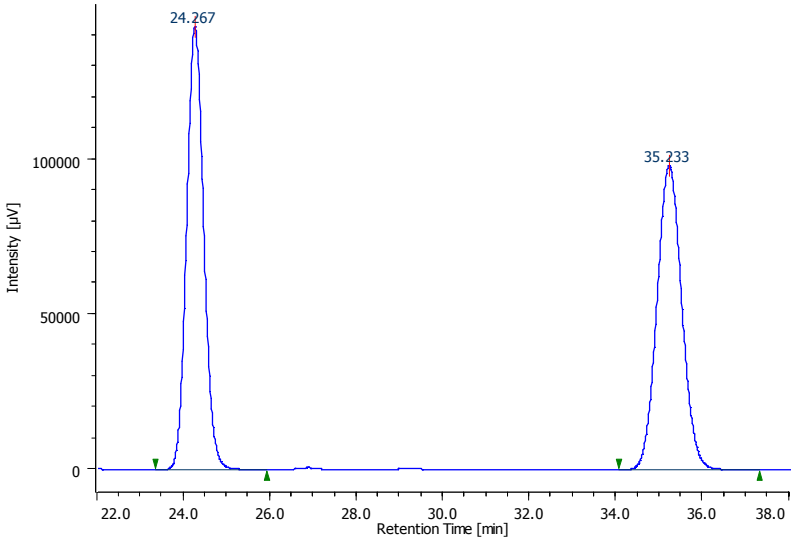
Peak No.	Retention Time (min)	Area (%)	
1	23.992	44.867	*E*-isomer
2	30.517	5.073	*Z*-isomer
3	32.133	45.048	*E*-isomer
4	41.583	5.012	*Z*-isomer



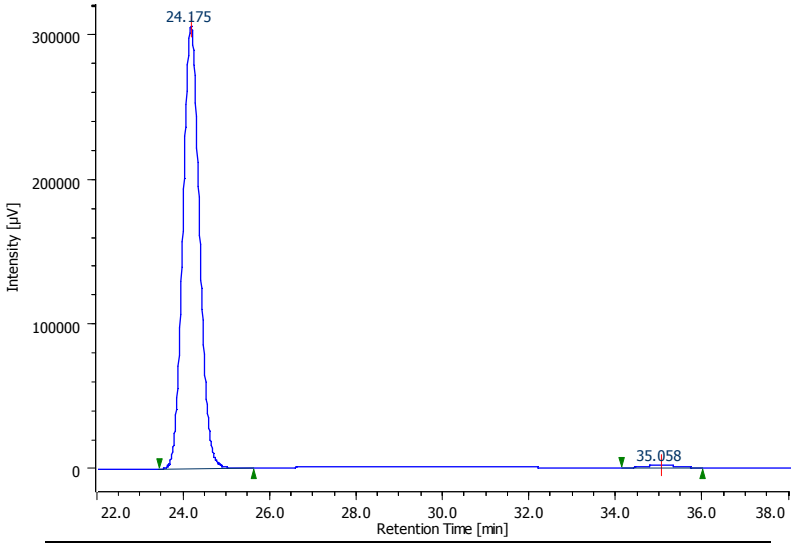
Peak No.	Retention Time (min)	Area (%)	
1	24.592	2.743	minor *E*-isomer
2	31.292	7.510	major *Z*-isomer
3	32.992	89.273	major *E*-isomer
4	42.500	0.474	minor *Z*-isomer

(–)-1-Benzylidene-2-isopropenyl-1,2-dihydronaphtho[2,1-b]furan [(–)-3j, *E*/*Z* = 9:91]



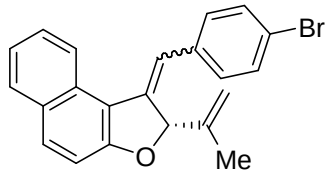


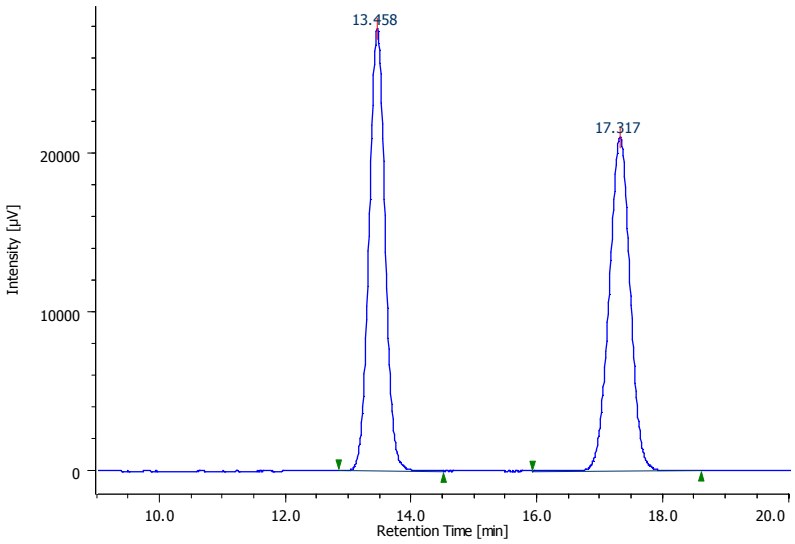
Peak No.	Retention Time (min)	Area (%)
1	24.267	50.081
2	35.233	49.919



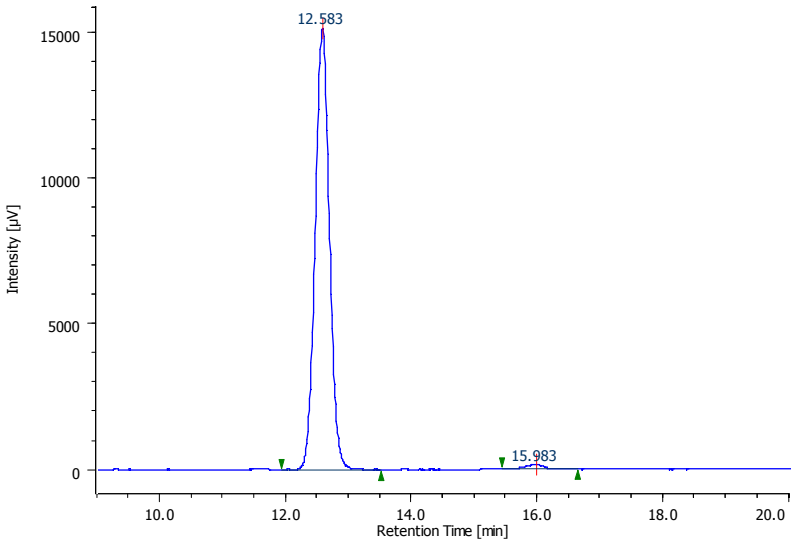
Peak No.	Retention Time (min)	Area (%)
1	24.175	99.147
2	35.058	0.853

(*S*)-(–)-1-(4-Bromobenzylidene)-2-isopropenyl-1,2-dihydronaphtho[2,1-b]furan [(*S*)-(–)-3k, *E*/*Z* = 7:93]





Peak No.	Retention Time (min)	Area (%)
1	13.458	50.205
2	17.317	49.795



Peak No.	Retention Time (min)	Area (%)
1	12.583	98.703
2	15.983	1.297