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Supplementary Information

An Efficient Approach to Generate Aryl Carbene: Gold-Catalyzed Sequential Activation of 1,6-Diynes

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Contents

1. Experimental procedures and spectroscopy

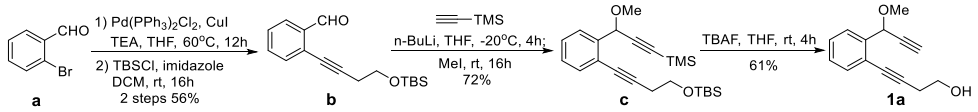
1.1 General information

All reactions were carried out under an inert atmosphere of dry N_2 in Schlenk tube, solvents were purified by standard method. ^1H, ^{13}C, ^{19}F NMR spectra were recorded on a Bruker AVANCE 400 (400 MHz for ^1H; 100 MHz for ^{13}C; 376 MHz for ^{19}F) ^1H NMR and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 and $CDCl_3$ at δ 77.16. Chemical shifts (δ) are reported in *ppm*, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d =doublet, t = triplet, q = quartet, m = multiplet, br = broad. Infrared (IR) spectra are recorded on a Nicolet 210 spectrophotometer.

All reagents were obtained from commercial sources, unless specified otherwise, or prepared as described in the literature. Spectral data of the known compounds were consistent with data reported in the literature. The related literatures were signed following the spectral date.

1.2 Preparation of substrates

1.2.1 General procedure for 1,6-diynes (using 1a for demonstration)

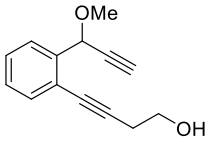


To the suspension of $Pd(PPh_3)_2Cl_2$ (0.05 eq), CuI (0.1 eq) in THF were added aldehyde **a** (1.0 eq), 3-Butyn-1-ol (1.1 eq), and TEA (5.0 eq) sequentially under nitrogen atmosphere. The resulting reaction mixture was stirred at 60°C for 12h. After cooled to room temperature, the solvent was evaporated under reduced pressure. The residue was dissolved in DCM, and TBSCl (1.2 eq), imidazole (3.0 eq) were added, the resulting solution was stirred at room temperature for 16h. The reaction mixture was quenched with water, and extracted with DCM. The combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure to afford brown viscous oil which was purified by silica gel chromatography to give the aldehyde **b**.

To the solution of trimethylsilyl acetylene (1.2 eq) in dry THF was add n-BuLi (1.2 equiv., 2.5 M in hexane) slowly at -20°C under nitrogen atmosphere. After stirred for 30 min, the THF solution of aldehyde **2** (1.0 eq) was added slowly, and the stirring maintained for 4 h before MeI (1.5 eq) was added. The resulting mixture was allowed to warm up to room temperature and stirred for another 16 h. The reaction mixture was quenched with saturated NH_4Cl (aq) and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, removed the solvent to give an oil which was purified by silica gel chromatography to give the corresponding diyne **c**.

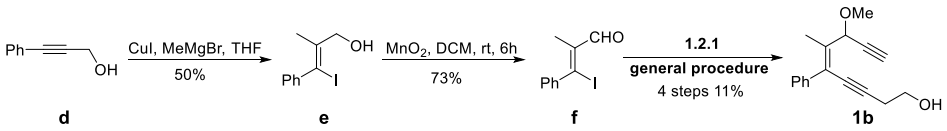
The product **c** (1.0 eq) was subject to TBAF (2.4 eq) in THF and stirred for 4 h at room temperature. The mixture was washed with water and brine, dried over Na_2SO_4. The solvent was removedunder reduced pressure to afford viscous oil which was purified by silica gel chromatography to furnish **1a** as colorless oil.

4-(2-(1-methoxyprop-2-yn-1-yl)phenyl)but-3-yn-1-ol (1a)



Colorless viscous oil, purified by chromatography (petroleum/ethyl acetate = 4/1), yield = 24% (4 steps). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.7 Hz, 1H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.27 (t, *J* = 7.4 Hz, 1H), 5.51 (s, 1H), 3.81 (t, *J* = 5.8 Hz, 2H), 3.44 (s, 3H), 2.73 (br, 1H), 2.70 (t, *J* = 6.1 Hz, 2H), 2.65 (d, *J* = 1.9 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.3, 132.3, 128.5, 128.3, 127.4, 122.7, 92.5, 81.0, 79.9, 75.7, 70.9, 61.2, 56.1, 24.1. **IR** (KBr) *ν*max 3288, 2939, 2885, 2823, 1483, 1447, 1328, 1187, 1078, 984, 953, 761, 651 cm^{-1}. **HR-MS** (ESI) calcd. for $[C_{14}H_{14}O_2+Na]^+$ 237.0886, found: 237.0884.

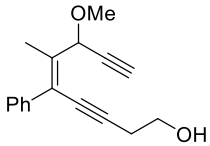
1.2.2 Preparation of 1,6-diyne 1b[1]



To the suspension of propargylic alcohol **d** (1.0 eq), CuI (0.1 eq) in dry THF was added MeMgBr (2.5 eq, 3 M in THF) slowly under nitrogen atmosphere at 0^{o}C. Upon complete addition, the mixture was allowed to warm up to room temperature and stirred for 16 h, then the resulting suspension was re-cooled to -78 ^{o}C and a THF solution of I_2 (1.1 eq) was added via syringe. After warming up to room temperature and stirring at room temperature for 1 h, the miture was kept in refrigerator at 0-5^{o}C overnight. The mixture was quenched with saturated NH_4Cl (aq), extracted with ethyl acetate, washed with saturated $Na_2S_2O_3$ (aq), brine and dried over Na_2SO_4. The solvent was removed under vaccum and the concentrate was purified by silica gel chromatography to give **e** as oil.

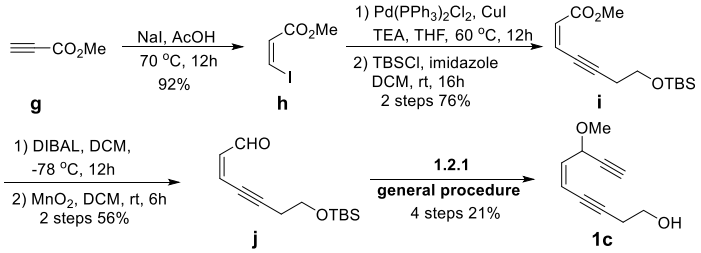
The product **e** (1.0 eq) was dissolved in DCM, and MnO_2 (15.0 eq) was added, stirred for 6 h. The mixture was filtrated, and the filtrate was concentrated under vaccum to give colorless oil **f** which was used for next step directly according the **1.2.1 general procedure** in further four steps to furnish **1b**.

(Z)-7-methoxy-6-methyl-5-phenylnona-5-en-3,8-diyn-1-ol (1b)



Colorless viscous oil, purified by chromatography (petroleum/ethyl acetate = 4/1), yield = 4% (6 steps). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 4H), 7.30 – 7.24 (m, 1H), 5.42 (d, *J* = 2.0 Hz, 1H), 3.71 (t, *J* = 6.4 Hz, 2H), 3.43 (s, 3H), 2.61 (t, *J* = 6.4 Hz, 2H), 2.53 (d, *J* = 1.9 Hz, 1H), 2.38 (s, 1H), 1.86 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.6, 138.5, 128.9, 128.2, 127.6, 123.2, 92.5, 81.1, 81.0, 74.3, 73.0, 61.1, 56.4, 24.0, 14.2. **IR** (KBr) *ν*max 3286, 2939, 2885, 2823, 1598, 1492, 1443,1377, 1325, 1187, 1080, 1021, 950, 767, 701, 660 cm^{-1}. **HR-MS** (ESI) calcd. for $[C_{17}H_{18}O_2+Na]^+$ 277.1199, found: 277.1202.

1.2.3 Preparation of 1,6-diyne 1c[2]

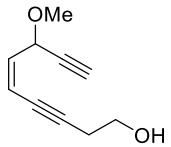


Methyl propiolate **g** (1.0 eq) was added to a solution of sodium iodide (1.5 eq) in acetic acid at room temperature and then stirred at 70°C for 12 h. The mixture was cooled to room temperature, diluted with water and diethyl ether, then the separated aqueous phase was extracted with diethyl ether. The combined organic extracts were neutralised with a 3M aqueous solution of potassium hydroxide, washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo to leave the vinyl iodide **h** as a yellow oil.

To the suspension of $Pd(PPh_3)_2Cl_2$ (0.05 eq), CuI (0.1 eq) in THF were added ester **h** (1.0 eq), 3-Butyn-1-ol (1.1 eq), and TEA (5.0 eq) sequentially under nitrogen atmosphere, then reaction was stirred at 60°C for 12h. After cooled to room temperature, the solvent was evaporated under reduced pressure. The residue was dissolved in DCM, and TBSCl (1.2 eq), imidazole (3.0 eq) were added, the resulting solution was stirred at room temperature for 16h. The reaction mixture was quenched with water, and extracted with DCM. The organic layers were combined, washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure to afford brown viscous oil which was purified by silica gel chromatography to give the ester **i**.

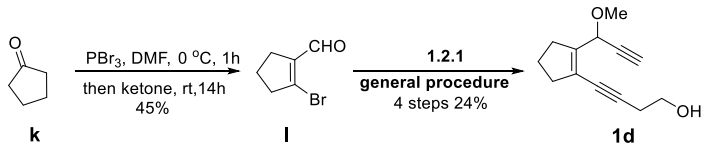
To the DCM solution of ester **i** was added the DIBAL under nitrogen atmosphere at -78 °C, then stirred for 12h before quenched with 2M aqueous HCl and stirred for another 30 min, extracted with DCM. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo to leave a light yellow oil, which was purified by silica gel chromatography to furnish **j**. The product **j** was evolved to the final product **1c** according the **1.2.1 general procedure** in further four steps.

(Z)-7-methoxynona-5-en-3,8-diyn-1-ol (1c)



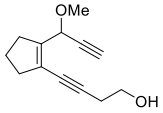
Colorless viscous oil, purified by chromatography (petroleum/ethyl acetate = 4/1), yield = 8% (9 steps). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.91 (dd, *J* = 10.4, 8.7 Hz, 1H), 5.71 (dt, *J* = 10.6, 1.7 Hz, 1H), 4.97 (dd, *J* = 8.5, 1.7 Hz, 1H), 3.76 (t, *J* = 6.3 Hz, 2H), 3.41 (s, 3H), 2.63 (td, *J* = 6.3, 2.1 Hz, 2H), 2.54 (d, *J* = 2.2 Hz, 1H), 2.26 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.9, 113.3, 94.2, 80.9, 77.5, 74.5, 68.2, 61.1, 56.1, 24.0. **IR** (KBr) *ν*max 3287, 2942, 2885, 2824, 1717, 1613, 1512, 1306, 1084, 1052, 946, 846, 648 cm^{-1}. **HR-MS** (ESI) calcd. for $[C_{10}H_{12}O_2+Na]^+$ 187.0730, found: 187.0729.

1.2.4 Preparation of 1,6-diyne 1d[3]



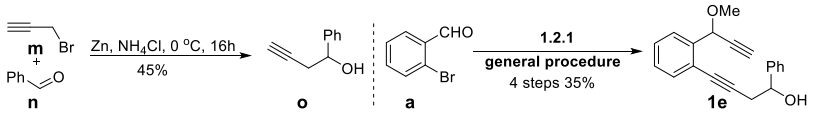
Phosphrous tribromide (2.4 eq) was added dropwise to a stirred solution of DMF (3.0 eq) in dry chloroform at 0°C. The resulting solution was stirred for 1h, before the ketone **k** (1.0 eq) in chloroform was added to the solution at 0°C. The reaction mixture was stirred at room temperature for 14 h. The solvent was removed on a rotary evaporator, then ice was added to the residue. Sodium bicarbonate was added to the mixture until the solution was neutralised. The solution was extracted with ethyl acetate. The extract was washed with water and saturated sodium chloride solution, dried with sodium sulfate, and the solvent was removed on a rotary evaporator. The residue was purified by silica gel chromatography to furnish **l** as a brown oil which was evolved to the final product **1d** according the **1.2.1 general procedure** in further four steps.

4-(2-(1-methoxyprop-2-yn-1-yl)cyclopent-1-en-1-yl)but-3-yn-1-ol (1d)



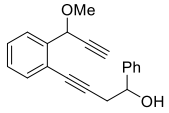
Colorless viscous oil, purified by chromatography (petroleum/ethyl acetate = 4/1), yield = 11% (5 steps). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.97 (s, 1H), 3.75 (t, *J* = 6.3 Hz, 2H), 3.37 (s, 3H), 2.64 (t, *J* = 6.3 Hz, 2H), 2.61 – 2.43 (m, 5H), 2.09 (br, 1H), 1.97 – 1.85 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.2, 123.6, 92.7, 80.7, 77.7, 74.1, 68.1, 61.2, 56.4, 37.2, 31.3, 24.1, 22.2. **IR** (KBr) *ν*max 3286, 2948, 2888, 2823, 1731, 1554, 1400, 1182, 1080, 961, 916, 737 cm^{-1}. **HR-MS** (ESI) calcd. for $[C_{13}H_{16}O_2+Na]^+$ 227.1043, found: 227.1044.

1.2.5 Preparation of 1,6-diyne 1e[4]



Aldehyde **n** (1.0 eq) and 3-Bromopropyne **m** (1.5 eq) was dissolved in THF, then saturated aqueous NH_4Cl (0.1 mmol SM/1 mL) and portions of activated zinc dust (2.0 eq) were added slowly at 0°C. The resulting suspension was stirred overnight at this temperature. The THF layer was separated from the aqueous layer, which was extracted with diethyl ether. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography to give **o**, which was evolved to the final product **1e** according the **1.2.1 general procedure** in further four steps.

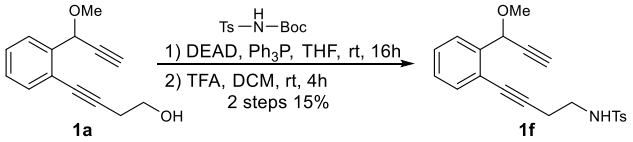
4-(2-(1-methoxyprop-2-yn-1-yl)phenyl)-1-phenylbut-3-yn-1-ol (1e)



Colorless viscous oil, purified by chromatography (petroleum/ethyl acetate = 8/1), yield = 16% (5 steps). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.3 Hz, 2H), 7.47 –

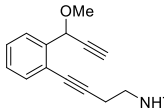
7.34 (m, 10H), 7.35 – 7.23 (m, 6H), 5.42 (s, 1H, isomer), 5.40 (s, 1H, isomer), 4.98 (t, *J* = 6.1 Hz, 2H), 3.37 (s, 3H, isomer), 3.35 (s, 3H, isomer), 3.00 (s, 2H), 2.91 (d, *J* = 6.3 Hz, 4H), 2.63 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.8, 139.5, 132.4, 128.6, 128.5, 128.4, 128.0, 127.9, 127.5, 127.3, 125.9, 125.8, 122.6, 122.5, 91.9, 91.8, 81.2, 81.1, 80.7, 80.6, 75.6, 75.5, 72.7, 72.6, 70.8, 70.7, 56.0, 55.9, 30.9, 30.8. **IR** (KBr) *ν*max 3289, 3063, 2927, 1661, 1483, 1450, 1323, 1251, 1190, 934, 758, 696, 652 cm^{-1}. **HR-MS** (ESI) calcd. for $[C_{20}H_{18}O_2+Na]^+$ 313.1199, found: 313.1207.

1.2.6 Preparation of 1,6-diyne 1f[5]



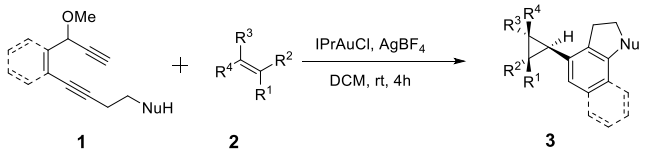
A solution of **1a** (1.0 eq), triphenylphosphine (1.5 eq) and tert-butyl tosylcarbamate (1.5 eq) in dry THF was stirred for 10 minutes, then diisopropyl azodicarboxylate (1.5 eq) was added at 0°C slowly, and stirred at rt for 16 h. The solvent was removed by a rotary evaporator and the residue was purified by silica gel chromatography to afford a colorless oil, which was subject to a DCM solution of TFA (5 eq) and stirred for 4h at room temperature. The reaction was quenched by saturated aqueous $NaHCO_3$ solution and was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash chromatography to afford the desired substrate **1f**.

N-(4-(2-(1-methoxyprop-2-yn-1-yl)phenyl)but-3-yn-1-yl)-4-methylbenzenesulfonamide (1f)



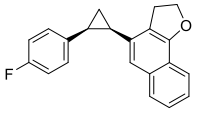
Colorless viscous oil, purified by chromatography (petroleum/ethyl acetate=12/1), yield = 15% (2 steps). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.8 Hz, 2H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.41 – 7.25 (m, 5H), 5.54 (s, 1H), 5.44 (s, 1H), 3.40 (s, 3H), 3.21 (ddt, *J* = 18.7, 12.6, 6.3 Hz, 2H), 2.67 (s, 1H), 2.60 (t, *J* = 6.2 Hz, 2H), 2.41 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.5, 139.2, 137.5, 132.5, 129.8, 128.6, 128.4, 127.7, 127.2, 122.4, 91.9, 80.9, 80.6, 76.1, 70.9, 55.4, 42.1, 21.6, 21.1. **IR** (KBr) *ν*max 3284, 2928, 2824, 1483, 1329, 1159, 1084, 814, 761, 661, 549 cm^{-1}. **HR-MS** (ESI) calcd. for $[C_{21}H_{21}NO_3S+Na]^+$, 390.1134, found: 390.1139.

2. General procedure for the cascade cyclization reaction



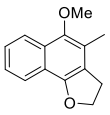
To a DCM (1 mL) solution of diyne **1** (1.0 eq, 0.19 mmol) and styrene (3.0 eq, 0.56 mmol) in Schlenk tube with a magnetic bar was added a mixture solution of IPrAuCl (0.05 eq, 0.01 mmol) and $AgBF_4$ (0.05 eq, 0.01 mmol) in DCM (1 mL) under nitrogen atmosphere. The mixture was stirred at room temperature for 4 h, filtered through a short silica gel pad, evaporated the solvent to leave a residue which was purified by silica gel chromatography with eluent of petroleum/ethyl acetate to give the corresponding product **3**.

4-(2-(4-fluorophenyl)cyclopropyl)-2,3-dihydronaphtho[1,2-b]furan (3a)



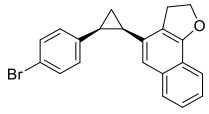
Light yellow solid, melting point: 116.0-118.9 °C, purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 74% (47 mg), *trans:cis* = 1:13.4. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 – 7.82 (m, 1H), 7.71 (dd, *J* = 5.5, 3.9 Hz, 1H), 7.41 – 7.34 (m, 2H), 7.06 (s, 1H), 6.89 – 6.81 (m, 2H), 6.76 – 6.67 (m, 2H), 4.69 (dt, *J* = 10.2, 8.1 Hz, 1H), 4.58 (dt, *J* = 10.1, 8.1 Hz, 1H), 3.31 (ddd, *J* = 15.0, 10.3, 7.5 Hz, 1H), 2.98 (ddd, *J* = 15.0, 10.3, 7.6 Hz, 1H), 2.51 (t, *J* = 7.5 Hz, 2H), 1.59 – 1.49 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.4, 159.9, 154.9, 134.4, 134.3, 134.0, 132.9, 129.1, 129.0, 127.6, 125.6, 124.7, 121.6, 121.3, 119.5, 114.7, 114.5, 71.8, 29.8, 23.8, 22.9, 11.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.7. **IR** (KBr) *ν*max 3056, 2970, 2898, 2857, 1569, 1449, 1401, 1338, 1283, 1227, 1040, 893, 871 cm^{-1}. **HR-MS** (ESI) calcd. for $[C_{21}H_{17}FO+Na]^+$ 327.1156, found: 327.1154.

5-methoxy-4-methyl-2,3-dihydronaphtho[1,2-b]furan (4a)



Colorless viscous oil, purified by chromatography (petroleum//ethyl acetate = 100/1), yield =12% (under the general procedure using PPh_3AuCl as the catalyst instead of IPrAuCl). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.9 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.49 – 7.33 (m, 2H), 4.77 (t, *J* = 8.9 Hz, 2H), 3.86 (s, 3H), 3.30 (t, *J* = 8.9 Hz, 2H), 2.37 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.1, 147.4, 127.8, 125.7, 124.8, 123.8, 122.3, 121.8, 120.6, 119.6, 71.7, 61.7, 30.3, 13.4. **IR** (KBr) *ν*max 3060, 2920, 2853, 1586, 1450, 1370, 1251, 1508, 1019, 974, 754, 642 cm^{-1}. **HR-MS** (MALDI) calcd. for $[C_{14}H_{14}O_2+H]^+$ 215.1067, found: 215.1066.

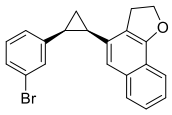
4-(2-(4-bromophenyl)cyclopropyl)-2,3-dihydronaphtho[1,2-b]furan (3b)



Light yellow solid, melting point: 114.2-118.3 °C, purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 70% (48mg), *trans:cis* = 1:15. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.77 (m, 1H), 7.68 (dd, *J* = 5.8, 3.5 Hz, 1H), 7.39 – 7.31 (m, 2H), 7.11 (s, 1H), 7.08 (d, *J* = 5.0 Hz, 2H), 6.72 (d, *J* = 8.4 Hz, 2H), 4.66 (dt, *J* = 10.2, 8.2 Hz, 1H), 4.60 – 4.48 (m, 1H), 3.27 (ddd, *J* = 15.0, 10.3, 7.4 Hz, 1H), 2.91 (ddd, *J* = 15.0, 10.3, 7.7 Hz, 1H), 2.53 (dd, *J* = 15.9, 8.3 Hz, 1H), 2.43 (td, *J* = 8.8, 6.4 Hz, 1H), 1.61 – 1.46 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.0, 138.0, 134.0, 132.6, 130.8, 129.3, 127.7, 125.7, 124.8, 121.6, 121.4, 119.6, 119.4, 71.9, 29.8, 24.4, 23.1, 11.6. **IR** (KBr) *ν*max 3061, 2895, 2830, 1642, 1594, 1516, 1489, 1448,

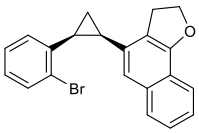
1400, 1337, 1280, 1112, 1075, 1008, 986, 951, 892, 845, 823 cm^{-1}. **HR-MS** (ESI) calcd. for $[C_{21}H_{17}BrO+Na]^+$ 387.0355, found: 387.0352.

4-(2-(3-bromophenyl)cyclopropyl)-2,3-dihydronaphtho[1,2-b]furan (3c)



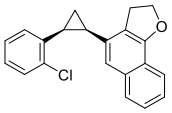
Light yellow solid, melting point: 96.8-100.0 °C, purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 71% (48 mg), *trans:cis* = 1:15.6. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.77 (m, 1H), 7.72 – 7.64 (m, 1H), 7.38 – 7.31 (m, 2H), 7.19 (s, 1H), 7.10 – 7.04 (m, 1H), 7.06 (s, 1H), 6.79 (t, *J* = 7.9 Hz, 1H), 6.64 (d, *J* = 7.8 Hz, 1H), 4.68 (dt, *J* = 10.2, 8.1 Hz, 1H), 4.61 – 4.51 (m, 1H), 3.30 (ddd, *J* = 15.0, 10.2, 7.5 Hz, 1H), 2.96 (ddd, *J* = 15.0, 10.2, 7.6 Hz, 1H), 2.55 (dd, *J* = 16.3, 8.0 Hz, 1H), 2.46 (dd, *J* = 15.7, 8.1 Hz, 1H), 1.58 – 1.53 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.9, 141.3, 134.0, 132.4, 131.3, 129.2, 128.7, 127.7, 125.7, 125.6, 124.8, 121.8, 121.5, 121.3, 119.5, 71.9, 29.9, 24.4, 23.3, 11.4. **IR** (KBr) *ν*max 3059, 3007, 2965, 2898, 2855, 1642, 1595, 1565, 1516, 1477, 1450, 1401, 1385, 1282, 1235, 1185, 1075, 1041, 1017, 989, 952, 927, 873, 845, 768, 683 cm^{-1}. **HR-MS** (ESI) calcd. for $[C_{21}H_{17}BrO+Na]^+$ 387.0355, found: 387.0353.

4-(2-(2-bromophenyl)cyclopropyl)-2,3-dihydronaphtho[1,2-b]furan (3d)



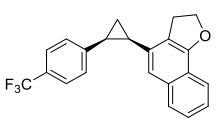
Yellow viscous oil, purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 65% (44 mg), *trans:cis* = 1:11.9. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 – 7.75 (m, 1H), 7.57 – 7.51 (m, 1H), 7.38 – 7.33 (m, 1H), 7.30 – 7.25 (m, 2H), 6.95 (dd, *J* = 11.3, 3.8 Hz, 1H), 6.88 – 6.81 (m, 2H), 6.73 (s, 1H), 4.71 (q, *J* = 8.7 Hz, 1H), 4.63 (q, *J* = 8.8 Hz, 1H), 3.36 (t, *J* = 8.9 Hz, 2H), 2.84 – 2.75 (m, 1H), 2.63 (dt, *J* = 15.4, 7.8 Hz, 1H), 1.68 (q, *J* = 6.2 Hz, 1H), 1.58 (td, *J* = 8.5, 5.7 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.7, 137.2, 133.7, 132.7, 132.3, 128.7, 127.6, 127.5, 126.6, 125.5, 124.5, 121.8, 121.2, 119.3, 117.7, 71.9, 29.9, 26.0, 23.5, 11.3. **IR** (KBr) *ν*max 3057, 2966, 2897, 2855, 1642, 1595, 1568, 1517, 1745, 1438, 1402, 1386, 1337, 1282, 1160, 1121, 1076, 1048, 1034, 1022, 988, 953, 927, 895, 839, 765 cm^{-1}. **HR-MS** (ESI) calcd. for $[C_{21}H_{17}BrO+Na]^+$ 387.0355, found: 387.0352.

4-(2-(2-chlorophenyl)cyclopropyl)-2,3-dihydronaphtho[1,2-b]furan (3e)



Light yellow oil, purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 60% (36 mg), *trans:cis* = 1:11.3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 5.8, 3.4 Hz, 1H), 7.56 (dd, *J* = 6.0, 3.3 Hz, 1H), 7.28 (dd, *J* = 6.1, 3.1 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 1H), 6.94 – 6.85 (m, 2H), 6.85 – 6.79 (m, 1H), 6.77 (s, 1H), 4.70 (dd, *J* = 17.6, 8.9 Hz, 1H), 4.62 (dd, *J* = 17.7, 8.8 Hz, 1H), 3.39 – 3.23 (m, 2H), 2.82 (dd, *J* = 15.7, 8.5 Hz, 1H), 2.61 (dd, *J* = 15.6, 8.5 Hz, 1H), 1.69 (q, *J* = 6.1 Hz, 1H), 1.59 – 1.51 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.7, 135.7, 133.7, 132.7, 129.0, 128.5, 127.6, 127.1, 126.0, 125.5, 124.5, 121.8, 121.2, 119.3, 117.8, 71.9, 29.7, 23.4, 23.0, 10.6. **IR** (KBr) *ν*max 3059, 3008, 2896, 1641, 1595, 1569, 1516, 1479, 1443, 1401, 1385, 1337, 1280, 1237, 1018, 987, 951, 927, 895, 867, 840 cm^{-1}. **HR-MS** (ESI) calcd. for $[C_{21}H_{17}ClO+Na]^+$ 343.0860, found: 343.0860.

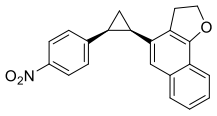
4-(2-(4-(trifluoromethyl)phenyl)cyclopropyl)-2,3-dihydronaphtho[1,2-b]furan (3f)



Light yellow solid, melting point: 111.5-114.2 °C, purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 49% (33 mg), *trans:cis* = 1:13.5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 6.0, 3.2 Hz, 1H), 7.70 (dd, *J* = 6.2, 3.1

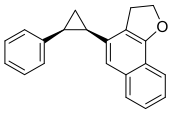
Hz, 1H), 7.39 – 7.33 (m, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.12 (s, 1H), 6.95 (d, *J* = 8.2 Hz, 2H), 4.66 (dt, *J* = 10.2, 8.1 Hz, 1H), 4.55 – 4.47 (m, 1H), 3.28 (ddd, *J* = 15.0, 10.3, 7.5 Hz, 1H), 2.86 (ddd, *J* = 15.0, 10.3, 7.6 Hz, 1H), 2.62 (dd, *J* = 16.0, 8.3 Hz, 1H), 2.53 (dt, *J* = 15.2, 7.6 Hz, 1H), 1.65 – 1.56 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.1, 143.5, 134.0, 132.3, 127.7, 125.8, 125.0, 124.7 (q, *J* = 3.9 Hz), 121.5, 121.4, 119.8, 119.7, 71.9, 29.8, 25.0, 23.4, 12.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.3. **IR** (KBr) *v*max 3060, 2970, 2900, 1642, 1617, 1570, 1450, 1401, 1282, 1237, 1163, 1116, 987, 892, 848, 749 cm^{-1}. **HR-MS** (ESI) calcd. for $[C_{22}H_{17}F_3O+Na]^+$ 377.1124, found: 377.1124.

4-(2-(4-nitrophenyl)cyclopropyl)-2,3-dihydronaphtho[1,2-b]furan (3g)



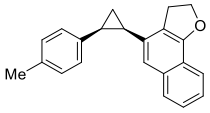
Light yellow solid, melting point: 181.9-185.1 °C, purified by chromatography (petroleum/ethyl acetate = 60/1), yield = 40% (25 mg), *trans:cis* = 1:16.4. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 14.3, 5.5 Hz, 3H), 7.72 (dd, *J* = 6.8, 2.3 Hz, 1H), 7.42 – 7.32 (m, 2H), 7.15 (s, 1H), 6.98 (d, *J* = 8.8 Hz, 2H), 4.67 (dt, *J* = 10.2, 8.2 Hz, 1H), 4.56 – 4.46 (m, 1H), 3.29 (ddd, *J* = 15.1, 10.3, 7.4 Hz, 1H), 2.83 (ddd, *J* = 15.0, 10.3, 7.7 Hz, 1H), 2.72 (dd, *J* = 16.2, 8.2 Hz, 1H), 2.59 (dt, *J* = 15.1, 7.5 Hz, 1H), 1.74 – 1.62 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.2, 147.6, 146.0, 134.0, 131.6, 127.9, 127.6, 126.0, 125.2, 123.0, 121.4, 121.3, 119.8, 119.7, 71.8, 29.8, 25.9, 23.6, 12.9. **IR** (KBr) *v*max 3109, 3007, 2897, 2831, 1641, 1512, 1400, 1340, 1281, 1075, 863, 748 cm^{-1}. **HR-MS** (ESI) calcd. for $[C_{21}H_{17}NO_3+Na]^+$ 354.1101, found: 354.1105.

4-(2-phenylcyclopropyl)-2,3-dihydronaphtho[1,2-b]furan (3h)



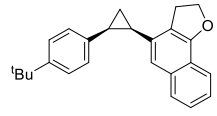
Colorless viscous oil, purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 72% (39mg), *trans:cis* = 1:12.5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 – 7.76 (m, 1H), 7.70 – 7.63 (m, 1H), 7.32 (p, *J* = 7.1 Hz, 2H), 7.07 (s, 1H), 7.02 – 6.92 (m, 3H), 6.86 (d, *J* = 7.4 Hz, 2H), 4.63 (dd, *J* = 18.2, 8.3 Hz, 1H), 4.49 (dd, *J* = 18.2, 8.1 Hz, 1H), 3.25 (ddd, *J* = 15.2, 10.2, 7.6 Hz, 1H), 2.92 (ddd, *J* = 15.1, 10.1, 7.8 Hz, 1H), 2.49 (t, *J* = 7.5 Hz, 2H), 1.56 – 1.49 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.8, 138.8, 134.0, 133.2, 127.7, 125.6, 125.5, 124.6, 121.8, 121.3, 119.7, 119.4, 71.8, 29.8, 24.2, 23.6, 11.4. **IR** (KBr) *v*max 3059, 3025, 2896, 1642, 1598, 1569, 1516, 1496, 1452, 1401, 1385, 1337, 1281, 1236, 1184, 1161, 1075, 1041, 986, 951, 926, 892, 869, 843, 766, 700 cm^{-1}. **HR-MS** (ESI) calcd. for $[C_{21}H_{18}O+Na]^+$ 309.1250, found: 309.1248.

4-(2-(4-methylphenyl)cyclopropyl)-2,3-dihydronaphtho[1,2-b]furan (3i)



Light yellow solid, melting point: 98.3-101.0 °C, purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 70% (39 mg), *trans:cis* = 1:12. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.79 (m, 1H), 7.73 – 7.66 (m, 1H), 7.40 – 7.30 (m, 2H), 7.10 (s, 1H), 6.80 (q, *J* = 8.3 Hz, 4H), 4.68 (dt, *J* = 10.2, 8.2 Hz, 1H), 4.60 – 4.50 (m, 1H), 3.30 (ddd, *J* = 15.1, 10.2, 7.4 Hz, 1H), 2.99 (ddd, *J* = 15.0, 10.3, 7.7 Hz, 1H), 2.49 (t, *J* = 7.5 Hz, 2H), 2.16 (s, 3H), 1.55 – 1.50 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.7, 135.6, 135.0, 134.0, 133.4, 128.5, 127.7, 127.5, 125.5, 124.6, 121.9, 121.2, 119.6, 119.4, 71.9, 29.9, 24.0, 23.3, 21.0, 11.1. **IR** (KBr) *v*max 3049, 3008, 2969, 2857, 1642, 1596, 1569, 1366, 1282, 1186, 1075, 1040, 987, 818, 772 cm^{-1}. **HR-MS** (ESI) calcd. for $[C_{22}H_{20}O+Na]^+$ 323.1406, found: 323.1408.

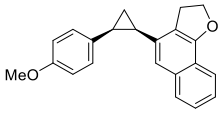
4-(2-(4-(tert-butyl)phenyl)cyclopropyl)-2,3-dihydronaphtho[1,2-b]furan (3j)



Light yellow solid, melting point: 103.5-105.0 °C, purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 87% (56 mg), *trans:cis* = 1:9.5. **^{1}H**

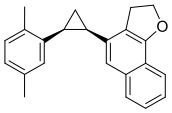
NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.82 (m, 1H), 7.71 (dd, *J* = 5.5, 3.9 Hz, 1H), 7.40 – 7.34 (m, 2H), 7.11 (s, 1H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 4.69 (dt, *J* = 10.2, 8.1 Hz, 1H), 4.53 (dt, *J* = 10.2, 8.2 Hz, 1H), 3.31 (ddd, *J* = 15.1, 10.2, 7.6 Hz, 1H), 2.98 (ddd, *J* = 15.0, 10.2, 7.5 Hz, 1H), 2.54 – 2.46 (m, 2H), 1.55 (ddd, *J* = 12.5, 8.8, 5.8 Hz, 2H), 1.21 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.8, 148.4, 135.8, 134.1, 133.5, 127.7, 127.4, 125.5, 124.7, 124.6, 122.0, 121.2, 119.8, 119. 5, 71.9, 34.3, 31.4, 29.9, 24.0, 23.2, 11. 8. **IR** (KBr) *v*max 3005, 2962, 2901, 2866, 1727, 1642, 1596, 1516, 1473, 1440, 1360, 1338, 1162, 1112, 1076, 987, 951, 893, 869, 844, 771, 658 cm^{-1}. **HR-MS** (ESI) calcd. for $[C_{25}H_{26}O+Na]^+$ 365.1876, found: 365.1876.

4-(2-(4-methoxyphenyl)cyclopropyl)-2,3-dihydronaphtho[1,2-b]furan 3k)



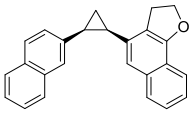
Light yellow solid, melting point: 118.3-123.1 °C, purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 96% (57 mg), *trans:cis* = 1:7.7. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.79 (m, 1H), 7.68 (dd, *J* = 5.5, 3.8 Hz, 1H), 7.38 – 7.31 (m, 2H), 7.05 (s, 1H), 6.84 – 6.78 (m, 2H), 6.59 – 6.54 (m, 2H), 4.68 (dt, *J* = 10.2, 8.2 Hz, 1H), 4.57 (dt, *J* = 10.1, 8.0 Hz, 1H), 3.64 (s, 3H), 3.31 (ddd, *J* = 15.0, 10.2, 7.4 Hz, 1H), 3.01 (ddd, *J* = 15.0, 10.3, 7.7 Hz, 1H), 2.47 (t, *J* = 7.4 Hz, 2H), 1.50 (t, *J* = 7.1 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.6, 154.7, 134.0, 133.4, 130.6, 128.7, 127.7, 125.5, 124.6, 121.8, 121.2, 119.4, 113.3, 71.8, 55.1, 29.9, 23.6, 23.0, 11.1. **IR** (KBr) *v*max 3060, 3002, 2889, 2833, 1596, 1514, 1385, 1249, 1179, 1179, 1107, 1075, 870, 844, 828 cm^{-1}. **HR-MS** (ESI) calcd. for $[C_{22}H_{20}O_2+Na]^+$ 339.1356, found: 339.1360.

4-(2-(2,5-dimethylphenyl)cyclopropyl)-2,3-dihydronaphtho[1,2-b]furan (3l)



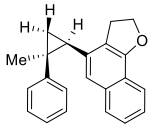
Colorless viscous oil, purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 78% (46 mg), *trans:cis* = 1:12. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.4 Hz, 1H), 7.44 – 7.37 (m, 1H), 7.24 (dt, *J* = 12.4, 7.6 Hz, 2H), 6.85 (s, 1H), 6.78 (dd, *J* = 17.5, 7.6 Hz, 2H), 6.45 (s, 1H), 4.75 – 4.64 (m, 2H), 3.44 – 3.33 (m, 1H), 3.31 – 3.21 (m, 1H), 2.55 – 2.41 (m, 2H), 2.15 (s, 3H), 2.14 (s, 3H), 1.60 – 1.51 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.5, 135.6, 135.0, 134.5, 133.9, 133.8, 129.5, 129.1, 127.6, 126.8, 125.4, 124.3, 121.1, 118.9, 116.7, 71.7, 29.9, 24.3, 21.7, 21.2, 19.3, 12.0. **IR** (KBr) *v*max 3047, 3014, 2969, 2919, 2857, 1642, 1596, 1570, 1516, 1501, 1450, 1385, 1338, 1288, 1235, 1159, 1077, 1041, 1017, 993, 952, 932, 871, 838, 810, 770, 694, 646 cm^{-1}. **HR-MS** (ESI) calcd. for $[C_{23}H_{22}O+Na]^+$ 337.1563, found: 337.1566.

4-(2-(naphthalen-2-yl)cyclopropyl)-2,3-dihydronaphtho[1,2-b]furan (3m)



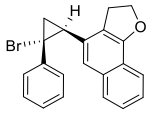
Light yellow solid, melting point: 86.5-89.8 °C, purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 74% (46 mg), *trans:cis* = 1:14.5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.3 Hz, 1H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.43 – 7.38 (m, 2H), 7.32 – 7.24 (m, 4H), 7.13 (s, 1H), 6.91 (d, *J* = 8.6 Hz, 1H), 4.59 (dd, *J* = 17.7, 8.8 Hz, 1H), 4.42 (dd, *J* = 17.6, 8.7 Hz, 1H), 3.33 – 3.20 (m, 1H), 3.00 – 2.89 (m, 1H), 2.68 – 2.51 (m, 2H), 1.68 (q, *J* = 5.9 Hz, 1H), 1.59 (dd, *J* = 14.1, 8.3 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.8, 136.6, 134.0, 133.2, 133.1, 131.9, 127.6, 127.5, 127.4, 127.2, 126.2, 126.1, 125.8, 125.5, 125.0, 124.6, 121.7, 121.3, 119.6, 119.5, 71.8, 29.8, 24.4, 23.9, 11.6. **IR** (KBr) *v*max 3054, 3007, 2968, 2856, 1632, 1597, 1568, 1513, 1473, 1449, 1401, 1386, 1357, 1338, 1283, 1236, 1186, 1162, 1127, 1076, 1040, 988, 958, 926, 900, 854, 817 cm^{-1}. **HR-MS** (ESI) calcd. for $[C_{25}H_{20}O+Na]^+$ 359.1406, found: 359.1410.

4-(2-methyl-2-phenylcyclopropyl)-2,3-dihydronaphtho[1,2-b]furan (3n)



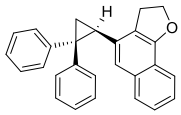
Colorless viscous oil, purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 73% (41 mg), *trans:cis* = 1:5.5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.3 Hz, 1H), 7.45 (d, *J* = 7.4 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.26 – 7.21 (m, 2H), 7.07 – 7.00 (m, 3H), 6.98 – 6.92 (m, 1H), 6.49 (s, 1H), 4.72 (t, *J* = 9.5 Hz, 2H), 3.44 – 3.25 (m, 2H), 2.26 – 2.20 (m, 1H), 1.77 (t, *J* = 5.6 Hz, 1H), 1.62 (s, 3H), 1.29 (dd, *J* = 8.5, 5.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.6, 142.1, 128.8, 127.9, 127.7, 126.6, 125.9, 125.4, 124.3, 121.1, 119.0, 117.0, 71.7, 30.4, 30.2, 30.1, 28.9, 19.2. **IR** (KBr) *v*max 3059, 3024, 2958, 2896, 1642, 1597, 1568, 1516, 1497, 1445, 1401, 1386, 1337, 1282, 1234, 1161, 1071, 1013, 984, 953, 924, 868, 840, 699 cm^{-1}. **HR-MS** (ESI) calcd. for $[C_{22}H_{20}O+Na]^+$ 323.1406, found: 323.1404.

4-(2-bromo-2-phenylcyclopropyl)-2,3-dihydronaphtho[1,2-b]furan (3o)



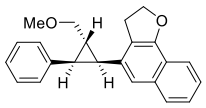
Brown oil, purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 42% (29 mg), *trans:cis* = 1:3.8. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.32 – 7.21 (m, 4H), 7.10 – 7.01 (m, 3H), 6.37 (s, 1H), 4.83 (t, *J* = 9.1 Hz, 2H), 3.64 – 3.47 (m, 2H), 3.07 (dd, *J* = 9.6, 7.7 Hz, 1H), 2.17 (t, *J* = 7.2 Hz, 1H), 2.03 (dd, *J* = 9.8, 7.1 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.1, 139.0, 133.9, 131.6, 129.8, 128.3, 128.1, 127.8, 125.8, 124.9, 121.3, 120.9, 119.5, 116.7, 71.9, 38.2, 33.1, 30.3, 21.2. **IR** (KBr) *v*max 3058, 2961, 2925, 2855, 1642, 1596, 1570, 1516, 1494, 1446, 1400, 1338, 1285, 1185, 1160, 1080, 1062, 1039, 991, 951, 924, 869, 840, 696, 633 cm^{-1}. **HR-MS** (MALDI) calcd. for $[C_{21}H_{17}OBr+H]^+$ 365.0536, found: 365.0534.

4-(2,2-diphenylcyclopropyl)-2,3-dihydronaphtho[1,2-b]furan (3p)



Light yellow solid, melting point: 143.2-148.5 ^oC, purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 81% (55 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.79 (m, 1H), 7.49 – 7.45 (m, 1H), 7.39 – 7.33 (m, 2H), 7.31 – 7.23 (m, 4H), 7.18 (dd, *J* = 10.4, 4.1 Hz, 1H), 7.05 – 6.91 (m, 5H), 6.57 (s, 1H), 4.72 (t, *J* = 8.9 Hz, 2H), 3.50 – 3.34 (m, 2H), 2.87 (dd, *J* = 8.8, 6.8 Hz, 1H), 2.24 – 2.14 (m, 1H), 1.78 (dd, *J* = 8.9, 5.3 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.8, 146.9, 140.5, 133.9, 133.5, 130.3, 128.6, 128.1, 128.0, 127.7, 126.3, 125.6, 124.6, 121.2, 121.0, 119.2, 117.7, 71.8, 39.6, 30.5, 30.4, 20.1. **IR** (KBr) *v*max 3057, 3025, 2963, 2901, 2857, 1660, 1642, 1597, 1569, 1515, 1494, 1446, 1401, 1386, 1337, 1279, 1262, 1234, 1186, 1160, 1137, 1076, 1042, 1021, 992, 954, 925, 868, 819, 700, 664 cm^{-1}. **HR-MS** (ESI) calcd. for $[C_{27}H_{22}O+Na]^+$ 385.1563, found: 385.1559.

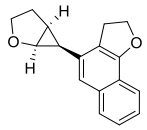
4-(2-(methoxymethyl)-3-phenylcyclopropyl)-2,3-dihydronaphtho[1,2-b]furan (3q)



Colorless viscous oil, purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 49% (31 mg), *dr* = 1:15.5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.2 Hz, 1H), 7.66 (d, *J* = 7.7 Hz, 1H), 7.33 (p, *J* = 6.4 Hz, 2H), 7.10 (s, 1H), 6.99 (d, *J* = 6.1 Hz, 3H), 6.86 (d, *J* = 6.7 Hz, 2H), 4.64 (dd, *J* = 17.6, 8.8 Hz, 1H), 4.49 (dd, *J* = 17.5, 8.8 Hz, 1H), 3.67 (dt, *J* = 16.8, 10.2 Hz, 2H), 3.46 (s, 3H), 3.32 – 3.21 (m, 1H), 2.96 – 2.85 (m, 1H), 2.43 (dt, *J* = 14.9, 9.2 Hz, 2H), 2.21 (p, *J* = 6.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.9, 138.0, 134.0, 132.2, 127.9, 127.7, 125.8, 125.6, 124.7, 121.6, 121.3, 119.8, 119.5, 75.7, 71.9, 58.7, 29.8, 29.4, 28.9, 24.7. **IR** (KBr) *v*max 3059, 2975, 2925, 2894, 1643, 1598, 1569, 1517, 1498, 1451, 1397, 1338,

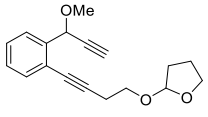
1281, 1238, 1194, 1159, 1134, 1102, 1066, 1030, 999, 949, 924, 872, 793, 696, 654 cm^{-1}. **HR-MS** (MALDI) calcd. for $[C_{23}H_{22}O_2+H]^+$ 331.1693, found: 331.1691.

4-(2-oxabicyclo[3.1.0]hexan-6-yl)-2,3-dihydronaphtho[1,2-b]furan (3r)



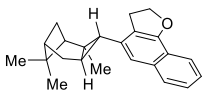
Colorless viscous oil, purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 16% (7.5 mg), *dr* = 1:6.4. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.38 – 7.31 (m, 2H), 6.77 (s, 1H), 4.80 (t, *J* = 8.9 Hz, 2H), 4.16 (td, *J* = 9.1, 2.9 Hz, 1H), 4.05 (d, *J* = 5.5 Hz, 1H), 3.72 (q, *J* = 8.6 Hz, 1H), 3.48 – 3.38 (m, 2H), 2.33 – 2.23 (m, 1H), 2.19 – 2.12 (m, 2H), 2.09 (dd, *J* = 10.0, 5.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.1, 135.1, 134.4, 127.5, 126.0, 124.6, 121.5, 120.0, 119.3, 114.6, 71.9, 68.1, 67.2, 29.8, 28.8, 25.4. **IR** (KBr) *ν*max 2961, 2894, 1640, 1595, 1567, 1516, 1450, 1404, 1384, 1338, 1276, 1262, 1112, 1090, 1065, 983, 922, 897 cm^{-1}. **HR-MS** (MALDI) calcd. for $[C_{17}H_{16}O_2+H]^+$ 253.1223, found: 253.1221.

2-((4-(2-(1-methoxyprop-2-yn-1-yl)phenyl)but-3-yn-1-yl)oxy)tetrahydrofuran (3r')



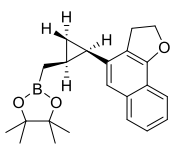
Colorless viscous oil, purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 32% (17 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.7 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.26 (dd, *J* = 8.2, 6.9 Hz, 1H), 5.50 (d, *J* = 1.9 Hz, 1H), 5.20 (s, 1H), 3.97 – 3.82 (m, 3H), 3.65 (dt, *J* = 9.6, 7.1 Hz, 1H), 3.47 (s, 3H), 2.73 (t, *J* = 7.0 Hz, 2H), 2.59 (d, *J* = 2.1 Hz, 1H), 2.07 – 1.98 (m, 1H), 1.97 – 1.91 (m, 2H), 1.89 – 1.79 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.8, 132.3, 128.4, 127.2, 123.1, 104.2, 92.4, 81.7, 78.8, 75.2, 70.8, 67.2, 65.6, 56.9, 32.6, 23.6, 21.3. **IR** (KBr) *ν*max 3285, 3067, 2986, 2945, 2882, 2821, 1597, 1569, 1483, 1447, 1399, 1327, 1261, 1185, 1120, 1082, 1038, 980, 922 cm^{-1}. **HR-MS** (ESI) calcd. for $[C_{18}H_{20}O_3+Na]^+$ 307.1305, found: 307.1312.

4-(2,7,7-trimethyltricyclo[4.1.1.02,4]octan-3-yl)-2,3-dihydronaphtho[1,2-b]furan (3s)



Light yellow solid, melting point: 81.3-84.0°C, purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 67% (40 mg), *dr* = 1:3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.5 Hz, 1H), 7.72 (d, *J* = 7.5 Hz, 1H), 7.38 – 7.31 (m, 2H), 7.07 (s, 1H), 4.76 (t, *J* = 9.0 Hz, 2H), 3.33 (td, *J* = 16.7, 8.8 Hz, 1H), 3.25 – 3.11 (m, 1H), 2.34 (d, *J* = 4.7 Hz, 1H), 2.30 – 2.14 (m, 2H), 2.01 (t, *J* = 5.4 Hz, 1H), 1.87 (d, *J* = 13.5 Hz, 1H), 1.77 (s, 1H), 1.50 – 1.43 (m, 1H), 1.32 (s, 3H), 1.30 – 1.28 (m, 1H), 1.08 (s, 3H), 0.79 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.8, 136.6, 134.3, 127.6, 125.6, 124.4, 121.6, 121.4, 119.3, 118.0, 71.9, 47.3, 41.6, 41.3, 31.6, 30.1, 27.8, 27.1, 26.8, 21.2, 20.1, 19.8. **IR** (KBr) *ν*max 3057, 2969, 2946, 2903, 2865, 1642, 1596, 1515, 1475, 1448, 1388, 1338, 1277, 1223, 1186, 1162, 1111, 1076, 1057, 993, 923, 847 cm^{-1}. **HR-MS** (MALDI) calcd. for $[C_{23}H_{26}O+H]^+$ 319.2056, found: 319.2054.

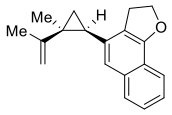
2-((2-(2,3-dihydronaphtho[1,2-b]furan-4-yl)cyclopropyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3t)



Colorless viscous oil, purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 65% (43 mg), *trans:cis* = 1:1.7. Major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7.83 (m, 1H), 7.73 – 7.65 (m, 1H), 7.37 – 7.30 (m, 2H), 7.00 (s, 1H), 4.82 – 4.72 (m, 2H), 3.48 – 3.36 (m, 2H), 2.10 – 2.02 (m, 1H), 1.39 – 1.29 (m, 1H), 1.18 (d, *J* = 5.8 Hz, 6H), 1.14 (s, 6H), 1.08 – 1.03 (m, 1H), 0.84 – 0.76 (m, 1H), 0.61 (dd, *J* = 16.4, 6.3 Hz, 1H), 0.44 (dd, *J* =

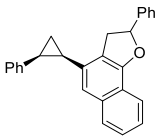
16.4, 8.2 Hz, 1H). Monir isomer, only clearly assignable signals are listed: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7.83 (m, 1H), 7.72 – 7.65 (m, 1H), 7.36 – 7.30 (m, 2H), 6.90 (s, 1H), 4.77 (ddd, *J* = 9.7, 8.2, 6.2 Hz, 2H), 3.48 – 3.36 (m, 2H), 1.69 – 1.62 (m, 1H), 1.25 (s, 12H), 0.97 (dd, *J* = 15.8, 7.1 Hz, 1H), 0.83 – 0.76 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.8, 138.9, 134.8, 134.5, 134.0, 127.6, 127.5, 125.6, 124.4, 124.3, 121.9, 121.3, 120.9, 119.4, 119.0, 118.4, 114.5, 83.3, 83.1, 71.9, 29.9, 29.8, 25.0, 24.9, 24.8, 22.6, 20.0, 18.1, 16.4, 14.0, 10.5. **IR** (KBr) *ν*max 3063, 2977, 2898, 1642, 1596, 1569, 1516, 1468, 1449, 1383, 1344, 1320, 1278, 1212, 1143, 1108, 1068, 997, 968, 920, 882 cm^{-1}. **HR-MS** (ESI) calcd. for $[C_{22}H_{27}BO_3+Na]^+$ 373.1945, found: 373.1949.

4-(2-methyl-2-(prop-1-en-2-yl)cyclopropyl)-2,3-dihydronaphtho[1,2-b]furan (3u)



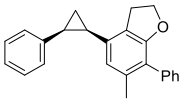
Colorless viscous oil, purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 32% (16 mg), *trans:cis* = 1:1.1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 – 7.74 (m, 2H), 7.67 – 7.57 (m, 2H), 7.33 – 7.22 (m, 4H), 6.99 (s, 1H), 6.75 (s, 1H), 4.87 – 4.61 (m, 8H), 3.39 – 3.17 (m, 2H), 2.15 (t, *J* = 7.4 Hz, 1H), 1.90 (t, *J* = 7.1 Hz, 1H), 1.76 (s, 3H), 1.52 (t, *J* = 5.3 Hz, 1H), 1.33 (s, 3H), 1.24 (d, *J* = 13.9 Hz, 3H), 1.19 – 1.13 (m, 1H), 1.05 (t, *J* = 5.3 Hz, 1H), 0.97 – 0.91 (m, 1H), 0.84 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.1, 154.6, 150.1, 145.6, 134.9, 134.4, 134.3, 134.1, 127.9, 127.7, 125.8, 125.6, 124.7, 124.4, 121.6, 121.5, 121.3, 121.2, 119.6, 119.3, 118.7, 116.4, 113.1, 109.6, 72.0, 71.8, 32.4, 30.4, 30.3, 29.2, 28.7, 27.9, 25.8, 20.8, 20.6, 18.2, 18.1, 17.2. **IR** (KBr) *ν*max 3062, 2922, 2859, 1639, 1593, 1514, 1445, 1393, 1338, 1276, 1230, 1176, 1073, 1018, 982, 881, 648 cm^{-1}. **HR-MS** (MALDI) calcd. for $[C_{19}H_{20}O+H]^+$ 265.1587, found: 265.1585.

2-phenyl-4-(2-phenylcyclopropyl)-2,3-dihydronaphtho[1,2-b]furan (3v)



Colorless viscous oil, purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 71% (50 mg), *trans:cis* = 1:7.5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 20.3, 7.8 Hz, 2H), 7.69 (t, *J* = 9.2 Hz, 2H), 7.32 (ddt, *J* = 22.4, 14.8, 7.3 Hz, 10H), 7.19 (dd, *J* = 16.2, 8.4 Hz, 4H), 7.11 (s, 1H), 7.01 – 6.97 (m, 2H), 6.96 – 6.91 (m, 3H), 6.91 – 6.85 (m, 4H), 6.75 (d, *J* = 7.5 Hz, 2H), 5.76 (dd, *J* = 9.7, 7.1 Hz, 1H), 5.65 (t, *J* = 8.8 Hz, 1H), 3.68 (dd, *J* = 15.6, 10.2 Hz, 1H), 3.38 (dd, *J* = 15.3, 9.9 Hz, 1H), 3.23 (dd, *J* = 15.3, 7.8 Hz, 1H), 2.94 (dd, *J* = 15.6, 6.7 Hz, 1H), 2.51 – 2.37 (m, 4H), 1.57 – 1.44 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.3, 142.7, 142.4, 138.8, 138.6, 134.2, 133.2, 128.8, 128.7, 128.6, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 126.2, 125.8, 125.7, 125.6, 125.5, 124.7, 124.6, 121.6, 121.5, 121.1, 120.1, 120.0, 119.4, 119.3, 84.7, 84.6, 38.7, 38.1, 24.3, 24.1, 23.6, 23.3, 11.4, 11.2. **IR** (KBr) *ν*max 2955, 2918, 1587, 1457, 1378, 1198, 1077, 1032, 967, 850, 693 cm^{-1}. **HR-MS** (ESI) calcd. for $[C_{27}H_{22}O+Na]^+$ 385.1563, found: 385.1564.

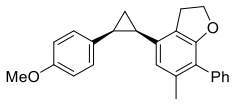
6-methyl-7-phenyl-4-(2-phenylcyclopropyl)-2,3-dihydrobenzofuran (3w)



Light yellow solid, melting point: 80.1-82.0 ^{o}C, purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 56% (36 mg), *trans:cis* = 1:14.5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 (t, *J* = 7.4 Hz, 2H), 7.28 (dt, *J* = 4.1, 1.7 Hz, 1H), 7.25 – 7.21 (m, 2H), 7.12 – 7.04 (m, 3H), 6.94 – 6.89 (m, 2H), 6.44 (s, 1H), 4.39 (ddd, *J* = 9.9, 8.6, 7.5 Hz, 1H), 4.24 (ddd, *J* = 9.9, 8.7, 7.4 Hz, 1H), 3.16 – 3.05 (m, 1H), 2.81 – 2.70 (m, 1H), 2.49 – 2.34 (m, 2H), 2.03 (s, 3H), 1.49 (dd, *J* = 11.5, 5.2 Hz, 1H), 1.39 (dd, *J* = 11.8, 6.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.3, 139.1, 136.8, 135.2, 133.3, 130.1, 128.2, 127.9, 127.7, 126.9, 125.6, 125.3, 122.8, 122.1, 71.4, 29.1, 23.5, 23.4, 20.1, 11.7. **IR** (KBr) *ν*max 3058, 3026, 2971, 2896, 1602, 1580, 1496,

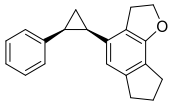
1482, 1446, 1404, 1306, 1275, 1259, 1209, 1184, 1078, 1034, 942, 851, 804, 764, 700 cm^{-1}. **HR-MS** (ESI) calcd. for $[C_{24}H_{22}O+Na]^+$ 349.1563, found: 349.1564.

4-(2-(4-methoxyphenyl)cyclopropyl)-6-methyl-7-phenyl-2,3-dihydrobenzofuran (3x)



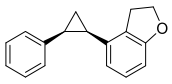
Light yellow oil, purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 76% (52 mg), *trans:cis* = 1:8.4. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (t, *J* = 7.5 Hz, 2H), 7.32 – 7.24 (m, 3H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.66 (d, *J* = 8.6 Hz, 2H), 6.40 (s, 1H), 4.45 – 4.36 (m, 1H), 4.34 – 4.24 (m, 1H), 3.72 (s, 3H), 3.17 – 3.05 (m, 1H), 2.88 – 2.75 (m, 1H), 2.44 – 2.36 (m, 1H), 2.31 (dd, *J* = 15.5, 8.7 Hz, 1H), 2.03 (s, 3H), 1.43 (td, *J* = 8.6, 5.3 Hz, 1H), 1.32 (dd, *J* = 11.9, 6.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.7, 157.3, 136.8, 135.1, 133.6, 131.0, 130.1, 129.0, 128.2, 126.9, 125.2, 122.6, 122.0, 113.3, 71.4, 55.3, 29.2, 22.9, 22.8, 20.1, 11.4. **IR** (KBr) *ν*max 3001, 2957, 2900, 2834, 1726, 1613, 1580, 1514, 1404, 1248, 1035, 987, 848, 767 cm^{-1}. **HR-MS** (ESI) calcd. for $[C_{25}H_{24}O_2+Na]^+$ 379.1669, found: 379.1674.

4-((1R,2S)-2-phenylcyclopropyl)-3,6,7,8-tetrahydro-2H-indeno[4,5-b]furan (3y)



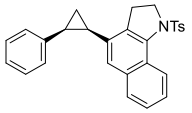
Colorless viscous oil, purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 28% (15 mg), *trans:cis* = 1:7.0. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.09 – 7.00 (m, 3H), 6.86 (d, *J* = 7.1 Hz, 2H), 6.45 (s, 1H), 4.45 (dd, *J* = 17.2, 8.6 Hz, 1H), 4.30 (dd, *J* = 17.1, 8.6 Hz, 1H), 3.12 – 3.01 (m, 1H), 2.80 – 2.70 (m, 5H), 2.44 – 2.31 (m, 2H), 2.04 – 1.98 (m, 2H), 1.44 (dd, *J* = 13.9, 8.3 Hz, 1H), 1.33 (dd, *J* = 11.7, 6.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.3, 145.4, 139.3, 132.6, 127.8, 127.7, 125.5, 125.4, 122.6, 116.8, 71.6, 33.0, 29.1, 28.8, 25.7, 23.7, 23.4, 11.8. **IR** (KBr) *ν*max 3026, 2954, 2889, 2843, 1588, 1495, 1444, 1419, 1306, 1276, 1261, 1222, 1184, 1080, 1023, 985, 764, 697 cm^{-1}. **HR-MS** (ESI) calcd. for $[C_{20}H_{20}O+Na]^+$ 299.1406, found: 299.1405.

4-(2-phenylcyclopropyl)-2,3-dihydrobenzofuran (3z)



Colorless viscous oil, purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 12% (5 mg), *trans:cis* = 1:6.2. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.10 – 7.00 (m, 3H), 6.91 (t, *J* = 7.8 Hz, 1H), 6.88 – 6.82 (m, 2H), 6.51 (dd, *J* = 18.4, 7.9 Hz, 2H), 4.45 (ddd, *J* = 10.0, 8.6, 7.4 Hz, 1H), 4.35 – 4.25 (m, 1H), 3.18 – 3.06 (m, 1H), 2.84 – 2.73 (m, 1H), 2.50 – 2.32 (m, 2H), 1.49 – 1.43 (m, 1H), 1.42 – 1.36 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.5, 138.9, 135.0, 127.9, 127.7, 127.5, 126.0, 125.7, 120. 8, 107.2, 71.1, 29.0, 23.5, 23.4, 11.5. **IR** (KBr) *ν*max 3019, 2923, 2855, 1703, 1595, 1550, 1491, 1451, 1231, 1023, 983, 948, 885, 775, 697 cm^{-1}. **HR-MS** (MALDI) calcd. for $[C_{17}H_{16}O+H]^+$ 237.1274, found: 237.1273.

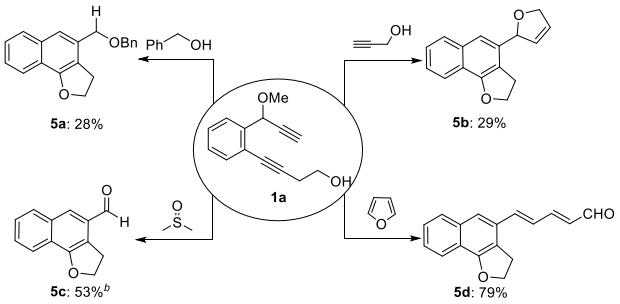
4-(2-phenylcyclopropyl)-1-tosyl-2,3-dihydro-1H-benzo[g]indole (3aa)



White solid, melting point: 159.7-161.8 ^oC, purified by chromatography (petroleum/ethyl acetate = 60/1), yield = 68% (57 mg), *trans:cis* = 1:8. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.5 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.46 (ddd, *J* = 8.4, 6.8, 1.3 Hz, 1H), 7.43 – 7.37 (m, 1H), 7.23 (d, *J* = 8.3 Hz, 3H), 7.05 (d, *J* = 8.0 Hz, 2H), 7.03 – 6.99 (m, 3H), 6.81 – 6.72 (m, 2H), 4.13 (dt, *J* = 12.7, 6.2 Hz, 1H), 3.79 (dt, *J* = 13.0, 8.5 Hz, 1H), 2.45 – 2.38 (m, 1H), 2.37 (s, 3H), 2.23 – 2.14 (m, 3H), 1.47 (td, *J* = 8.6, 5.4 Hz, 1H), 1.36 (dt, *J* = 10.5, 5.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.0, 138.4, 138.3, 136.1, 134.3, 133.9, 131.8, 129.4, 127.9, 127.8, 127.6, 127.0, 126.0, 125.9, 125.8, 125.6, 53.5, 28.5, 24.0, 23.3, 21.7, 11.8. **IR** (KBr) *ν*max 3057,

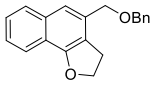
2957, 2905, 2856, 1596, 1495, 1456, 1399, 1350, 1291, 1184, 1165, 1088, 1020, 992, 956, 888, 848, 814, 776, 694, 663, 614, 576 cm^{-1}. **HR-MS** (ESI) calcd. for $[C_{28}H_{25}NO_2S+Na]^+$ 462.1498, found: 462.1503.

3. Further transformation of 1a



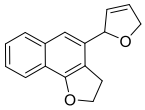
To a DCM (1 mL) solution of diyne **1a** (40 mg, 1.0 eq, 0.19 mmol) and furan/DMSO/propargyl alcohol/benzyl alcohol (3.0 eq, 0.56 mmol) in schlenk tube with a magnetic bar was added a mixture solution of IPrAuCl (0.05 eq, 0.01 mmol) and $AgBF_4$ (0.05 eq, 0.01 mmol) in DCM (1 mL) under nitrogen atmosphere. The mixture was stirred at room temperature for 4 h (60°C, 8 h for DMSO itself), filtered through a short silica gel pad, evaporated the solvent to leave a residue which was purified by silica gel chromatography with eluent of petroleum/ethyl acetate to give the corresponding product **5**.

4-((benzyloxy)methyl)-2,3-dihydronaphtho[1,2-b]furan (5a)



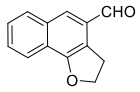
Colorless viscous oil, purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 28% (15 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 – 7.89 (m, 1H), 7.82 – 7.77 (m, 1H), 7.43 – 7.39 (m, 2H), 7.38 – 7.33 (m, 5H), 7.33 – 7.27 (m, 1H), 4.79 (t, *J* = 9.0 Hz, 2H), 4.67 (s, 2H), 4.57 (s, 2H), 3.37 (t, *J* = 9.0 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.0, 138.4, 134.1, 132.8, 128.6, 128.0, 127.9, 126.0, 125.4, 121.5, 120.4, 119.5, 119.4, 72.2, 71.2, 29.5. **IR** (KBr) *ν*max 3052, 2920, 2854, 1581, 1509, 1454, 1391, 1346, 1280, 1224, 1110, 1060, 914, 840, 741, 695, 652 cm^{-1}. **HR-MS** (MALDI) calcd. for $[C_{20}H_{18}O_2+H]^+$ 291.1380, found: 291.1379.

4-(2,5-dihydrofuran-2-yl)-2,3-dihydronaphtho[1,2-b]furan (5b)



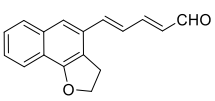
Light yellow oil, purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 29% (13 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 5.6, 3.9 Hz, 1H), 7.80 – 7.74 (m, 1H), 7.43 – 7.37 (m, 2H), 7.29 (s, 1H), 6.07 (ddd, *J* = 5.8, 3.9, 1.6 Hz, 1H), 5.95 (ddd, *J* = 6.3, 4.2, 2.2 Hz, 1H), 5.91 (ddd, *J* = 6.3, 4.0, 2.3 Hz, 1H), 4.94 – 4.81 (m, 2H), 4.82 – 4.74 (m, 2H), 3.38 (t, *J* = 9.0 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.3, 136.2, 134.1, 128.7, 128.1, 127.2, 126.0, 125.4, 121.5, 120.4, 118.5, 117.7, 87.5, 76.0, 72.2, 29.1. **IR** (KBr) *ν*max 3060, 2892, 2841, 1594, 1570, 1515, 1453, 1399, 1343, 1313, 1277, 1261, 1223, 1114, 1071, 986, 950, 924, 846 cm^{-1}. **HR-MS** (MALDI) calcd. for $[C_{16}H_{14}O_2+H]^+$ 239.1067, found: 239.1065.

2,3-dihydronaphtho[1,2-b]furan-4-carbaldehyde (5c)



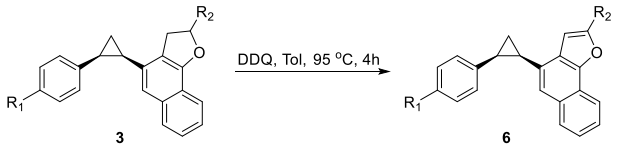
Brown solid, melting point: 138.8-141.5 ^{o}C, purified by chromatography (petroleum/ethyl acetate = 40/1), yield = 53% (20 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.14 (s, 1H), 7.98 (dd, *J* = 14.5, 8.3 Hz, 2H), 7.85 (s, 1H), 7.60 (ddd, *J* = 8.3, 6.9, 1.2 Hz, 1H), 7.56 – 7.49 (m, 1H), 4.85 (t, *J* = 9.1 Hz, 2H), 3.70 (t, *J* = 9.1 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.0, 157.2, 133.4, 131.7, 129.4, 128.7, 128.5, 127.0, 123.4, 122.0, 118.1, 73.1, 30.4. **IR** (KBr) *v*max 2920, 2847, 2739, 1688, 1584, 1532, 1512, 1455, 1394, 1334, 1275, 1224, 1162, 1072, 986, 922, 889, 851, 769, 732, 657 cm^{-1}. **HR-MS** (ESI) calcd. for $[C_{13}H_{10}O_2+Na]^+$ 221.0573, found: 221.0579.

(2E,4E)-5-(2,3-dihydronaphtho[1,2-b]furan-4-yl)penta-2,4-dienal (5d)



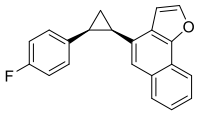
Yellow solid, melting point: 128.0-132.0 ^{o}C, purified by chromatography (petroleum/ethyl acetate = 60/1), yield = 79% (37 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.63 (d, *J* = 7.9 Hz, 1H), 7.94 – 7.88 (m, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.54 (s, 1H), 7.44 (dd, *J* = 9.6, 5.3 Hz, 2H), 7.28 (dd, *J* = 14.3, 9.3 Hz, 1H), 7.06 (dt, *J* = 15.6, 13.0 Hz, 2H), 6.29 (dd, *J* = 15.1, 7.9 Hz, 1H), 4.82 (t, *J* = 8.9 Hz, 2H), 3.48 (t, *J* = 8.9 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.6, 156.3, 152.3, 141.3, 134.0, 131.8, 130.7, 128.4, 127.8, 126.6, 126.5, 121.7, 121.1, 120.1, 118.4, 71.9, 30.5. **IR** (KBr) *v*max 3058, 2969, 2899, 2815, 1675, 1608, 1564, 1512, 1475, 1398, 1342, 1299, 1278, 1262, 1194, 1156, 1122, 1074, 1058, 985, 951, 868, 664 cm^{-1}. **HR-MS** (ESI) calcd. for $[C_{17}H_{14}O_2+Na]^+$ 273.0886, found: 273.0889.

4. Oxidation reaction of dihydronaphthofuran 3



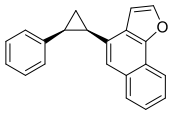
The solution of **3** (1.0 eq, 0.15 mmol) and DDQ (1.5 eq, 0.23 mmol) in toluene (1.5 mL) was stirred at 95^{o}C for 4h, then evaporated the solvent to give a residue which was purified by silica gel chromatography to give the corresponding naphthofuran **6** (50-80%).

4-(2-(4-fluorophenyl)cyclopropyl)naphtho[1,2-b]furan (6a)



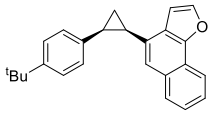
Colorless viscous oil, purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 72% (33 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.65 (d, *J* = 2.1 Hz, 1H), 7.47 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.39 (ddd, *J* = 8.2, 7.0, 1.3 Hz, 1H), 7.17 (s, 1H), 6.91 (d, *J* = 2.1 Hz, 1H), 6.87 – 6.82 (m, 2H), 6.65 – 6.57 (m, 2H), 2.77 – 2.69 (m, 1H), 2.65 – 2.54 (m, 1H), 1.62 – 1.54 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.2 (d, *J* = 243.4 Hz), 150.1, 143.9, 134.1 (d, *J* = 3.0 Hz), 131.4, 129.9, 129.6 (d, *J* = 7.9 Hz), 128.1, 125.8, 125.1, 124.8, 122.2, 120.5, 119.9, 114.5 (d, *J* = 21.2 Hz), 106.5, 23.4, 22.7, 10.8. **IR** (KBr) *v*max 3057, 3009, 2925, 2856, 1738, 1596, 1506, 1445, 1321, 1223, 1149, 1086, 1031, 959, 883, 818, 801, 743, 604, 522 cm^{-1}. **HR-MS** (MALDI) calcd. for $[C_{21}H_{15}OF+H]^+$ 303.1180, found: 303.1178.

4-(2-phenylcyclopropyl)naphtho[1,2-b]furan (6h)



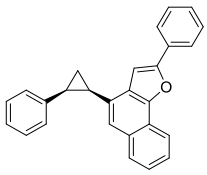
Colorless viscous oil, purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 72% (31 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.1 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.54 (s, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.12 (s, 1H), 6.89 – 6.76 (m, 6H), 2.66 (dd, *J* = 15.9, 8.3 Hz, 1H), 2.54 (dd, *J* = 15.5, 8.4 Hz, 1H), 1.59 – 1.53 (m, 1H), 1.52 – 1.45 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.1, 143.8, 138.5, 131.5, 130.2, 128.2, 128.1, 127.7, 126.0, 125.6, 125.0, 124.9, 122.3, 120.5, 119.9, 106.6, 24.1, 23.0, 10.8. **IR** (KBr) *ν*max 3057, 2963, 2925, 2857, 1705, 1596, 1538, 1500, 1452, 1408, 1321, 1270, 1169, 1133, 1081, 1031, 962, 884, 799, 744, 701, 606 cm^{-1}. **HR-MS** (MALDI) calcd. for $[C_{21}H_{16}O+H]^+$ 285.1274, found: 285.1273.

4-(2-(4-(tert-butyl)phenyl)cyclopropyl)naphtho[1,2-b]furan (6j)



Colorless viscous oil, purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 50% (26 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.2 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 2.1 Hz, 1H), 7.47 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.38 (ddd, *J* = 6.9, 4.9, 1.3 Hz, 1H), 7.17 (s, 1H), 6.99 – 6.97 (m, 1H), 6.97 – 6.94 (m, 2H), 6.86 – 6.82 (m, 2H), 2.78 – 2.67 (m, 1H), 2.60 (dd, *J* = 16.4, 7.6 Hz, 1H), 1.62 – 1.55 (m, 2H), 1.12 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.1, 148.5, 143.8, 135.5, 131.5, 130.5, 128.1, 128.0, 125.6, 125.0, 124.9, 124.6, 122.3, 120.4, 119.9, 106.7, 34.3, 31.4, 23.8, 22.8, 11.3. **IR** (KBr) *ν*max 3058, 2957, 2861, 1589, 1509, 1459, 1361, 1322, 1272, 1134, 1032, 958, 883, 838, 794, 745 cm^{-1}. **HR-MS** (ESI) calcd. for $[C_{25}H_{24}O+Na]^+$ 363.1719, found: 363.1720.

2-phenyl-4-(2-phenylcyclopropyl)naphtho[1,2-b]furan (6v)



Colorless viscous oil, purified by chromatography (petroleum/ethyl acetate = 100/1), yield = 80% (43 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.2 Hz, 1H), 7.92 – 7.87 (m, 2H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.49 – 7.42 (m, 3H), 7.39 – 7.29 (m, 2H), 7.18 (d, *J* = 4.2 Hz, 2H), 6.99 – 6.84 (m, 5H), 2.77 (dd, *J* = 15.4, 8.7 Hz, 1H), 2.71 – 2.61 (m, 1H), 1.69 – 1.57 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.0, 149.9, 138.4, 131.5, 131.0, 129.9, 128.9, 128.3, 128.2, 127.7, 126.8, 125.7, 125.6, 125.0, 124.7, 122.4, 120.3, 119.9, 101.6, 24.2, 22.9, 10.8. **IR** (KBr) *ν*max 3058, 2924, 2855, 1598, 1488, 1450, 1342, 1210, 1160, 1084, 1030, 967, 907, 844, 807, 690 cm^{-1}. **HR-MS** (ESI) calcd. for $[C_{27}H_{20}O+Na]^+$ 383.1406, found: 383.1405.

5. References

[1] Larock, R. C.; Doty, M. J.; Han, X. *J. Org. Chem.* **1999**, *64*, 8770.

[2] a) Akpınar, G. E.; Kuş, M.; Üçüncü, M.; Karakuş, E.; Artok, L. *Org. Lett.* **2011**, *13*, 748. b) Zhu, S.; Huang, X.; Zhao, T.-Q.; Ma, T.; Jiang, H. *Org. Biomol. Chem.* **2015**, *13*, 1225.

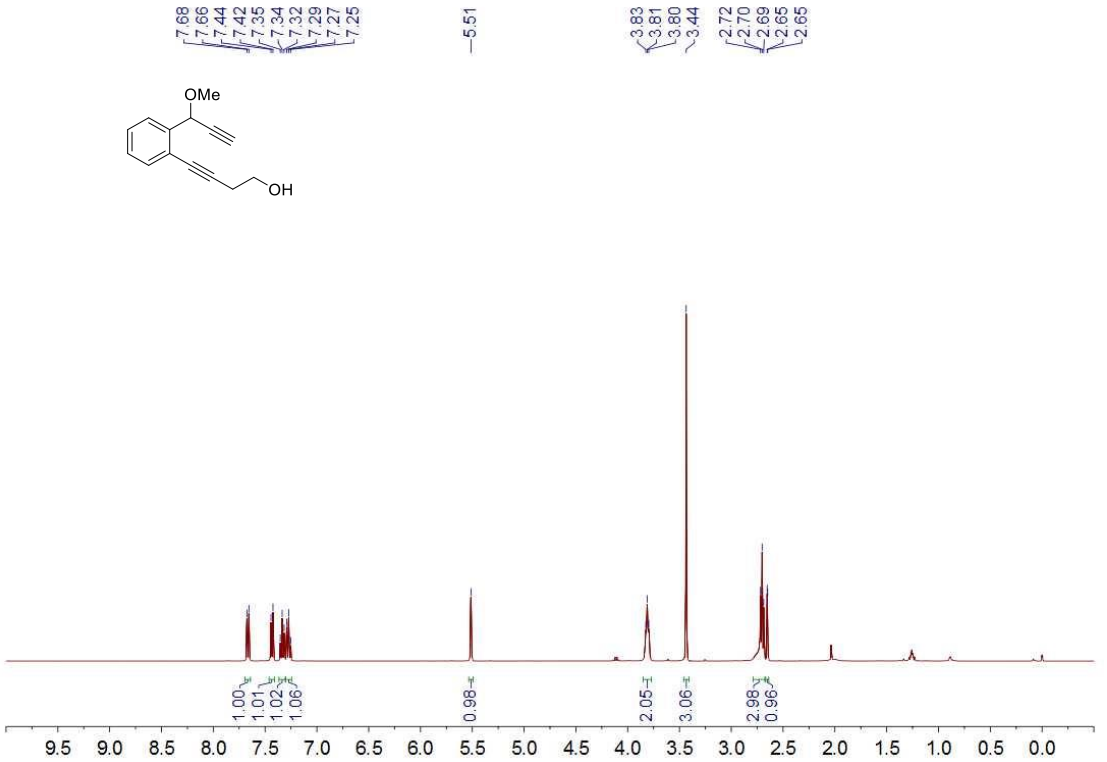
[3] a) Ray, D.; Ray, J. K. *Org. Lett.* **2007**, *9*, 191. b) Zhu, S.; Huang, X.; Zhao, T.-Q.; Ma, T.; Jiang, H. *Org. Biomol. Chem.* **2015**, *13*, 1225.

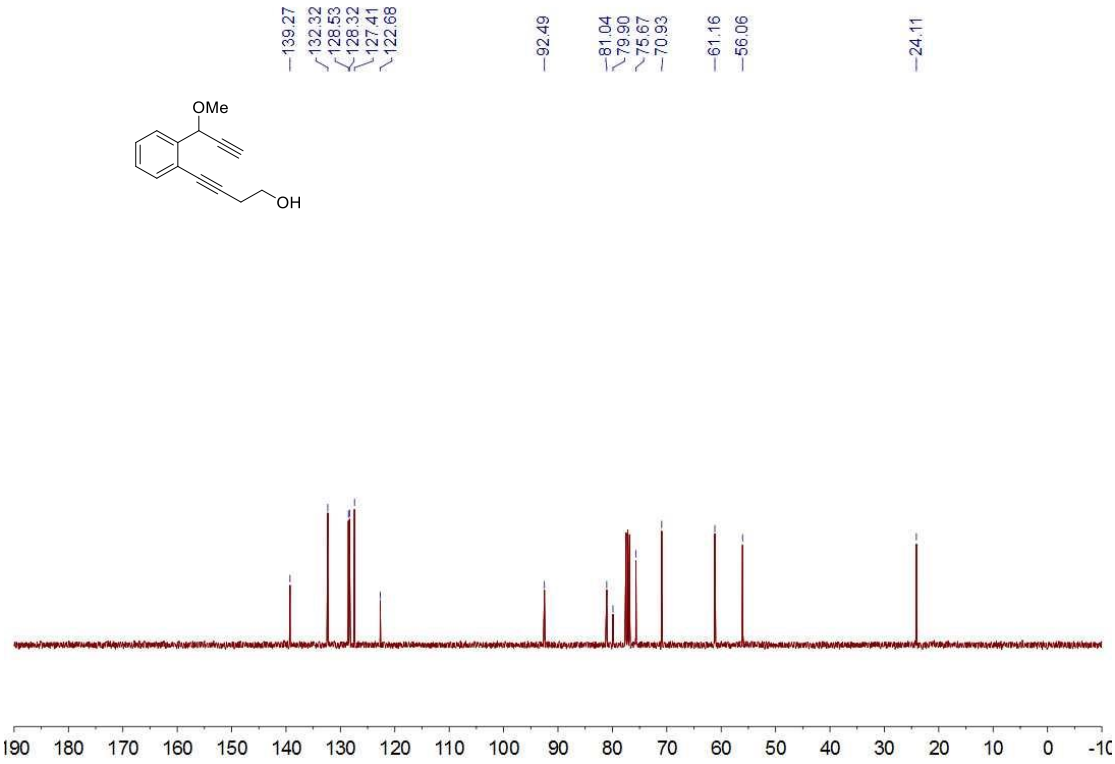
[4] Gao, P.; Shen, Y.-W.; Fang, R.; Hao, X.-H.; Qiu, Z.-H.; Yang, F.; Yan, X.-B.; Wang, Q.; Gong, X.-J.; Liu, X.-Y.; Liang, Y.-M. *Angew. Chem., Int. Ed*. **2014**, *53*, 7629.

[5] Kim, S.; Chung, Y. K. *Org*. *Lett.* **2014**, *16*, 4352.

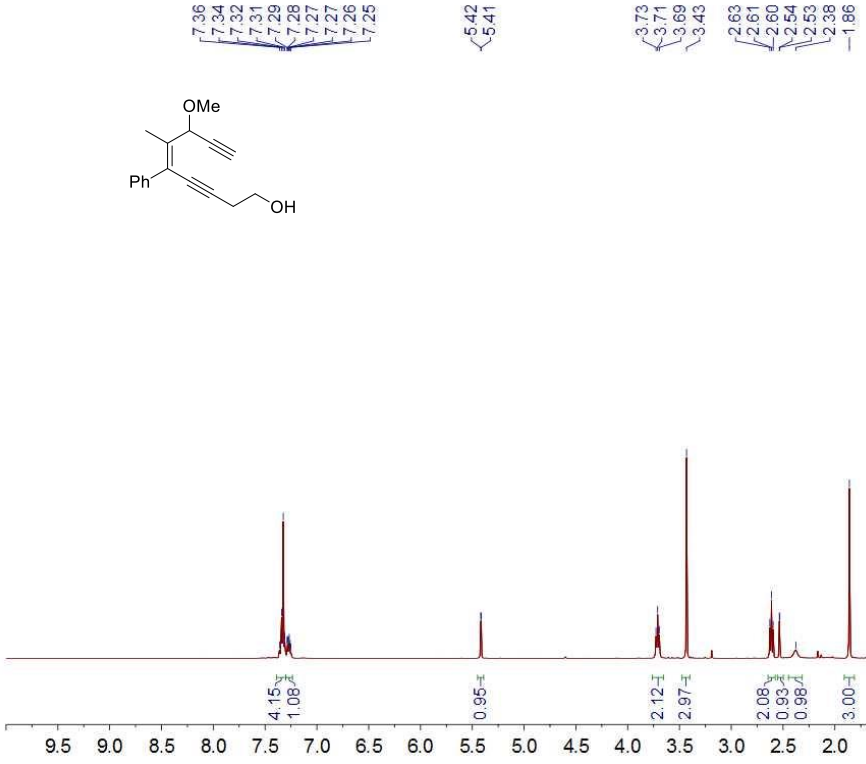
6. Copies of NMR Spectra

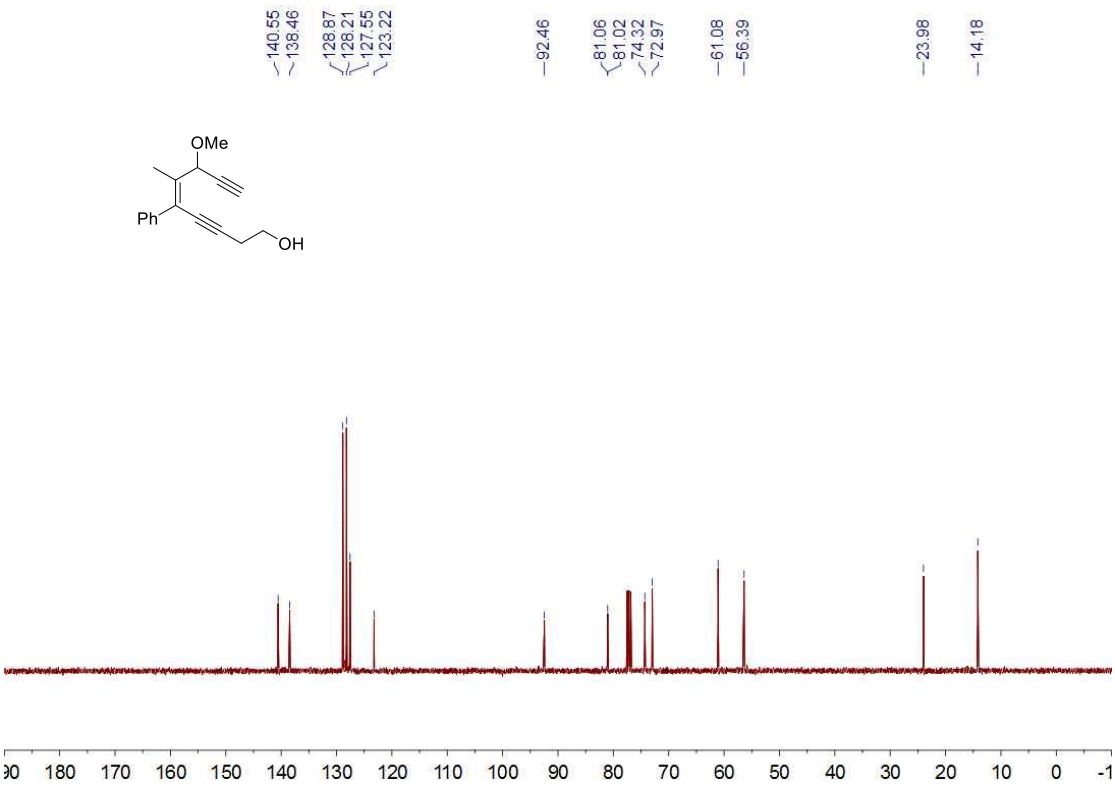
4-(2-(1-methoxyprop-2-yn-1-yl)phenyl)but-3-yn-1-ol (1a)



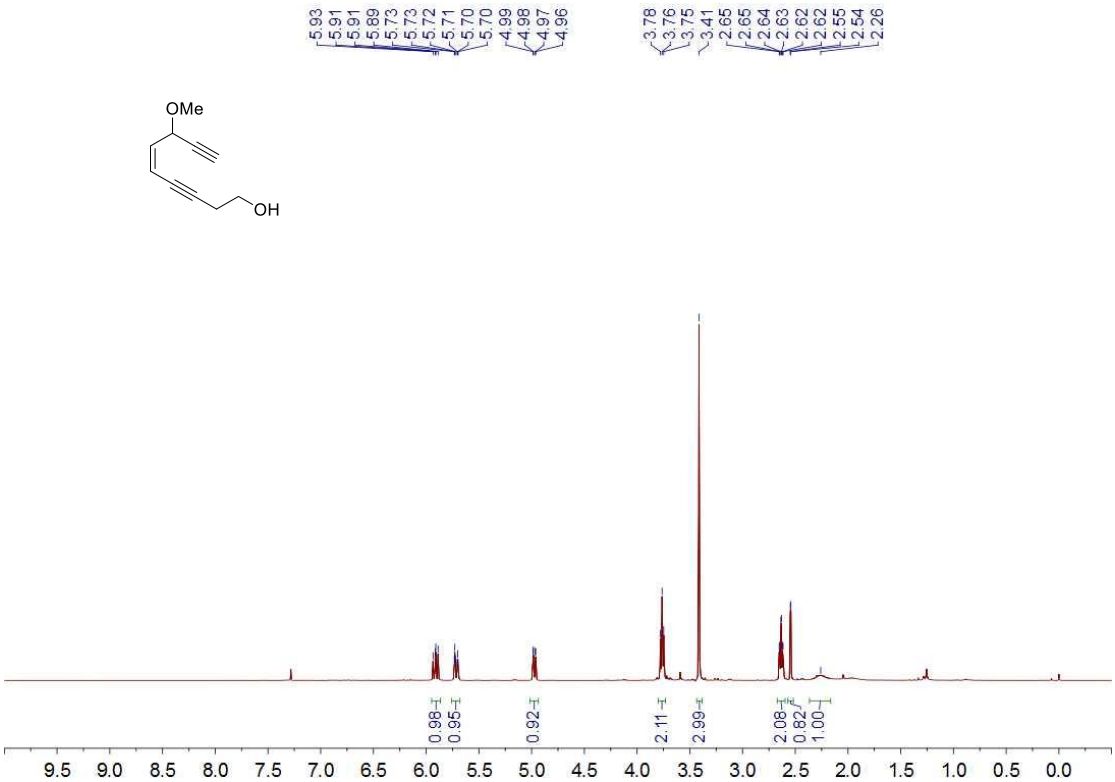


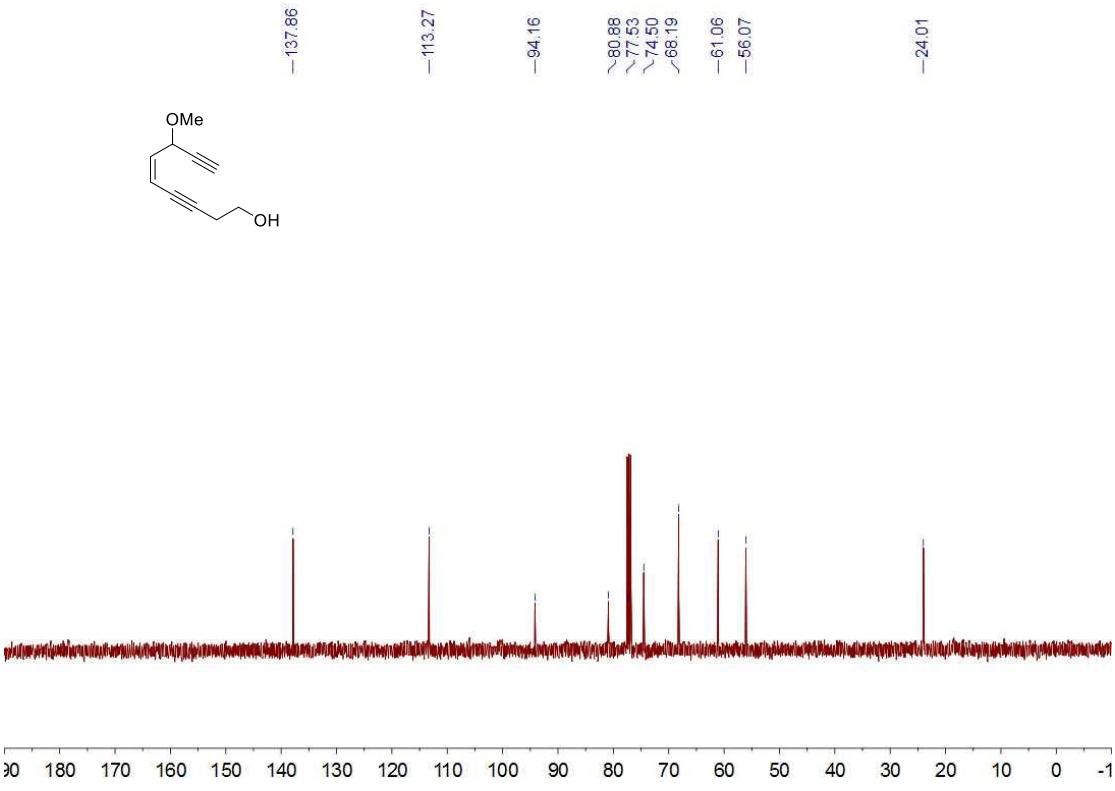
(Z)-7-methoxy-6-methyl-5-phenylnona-5-en-3,8-diyn-1-ol (1b)



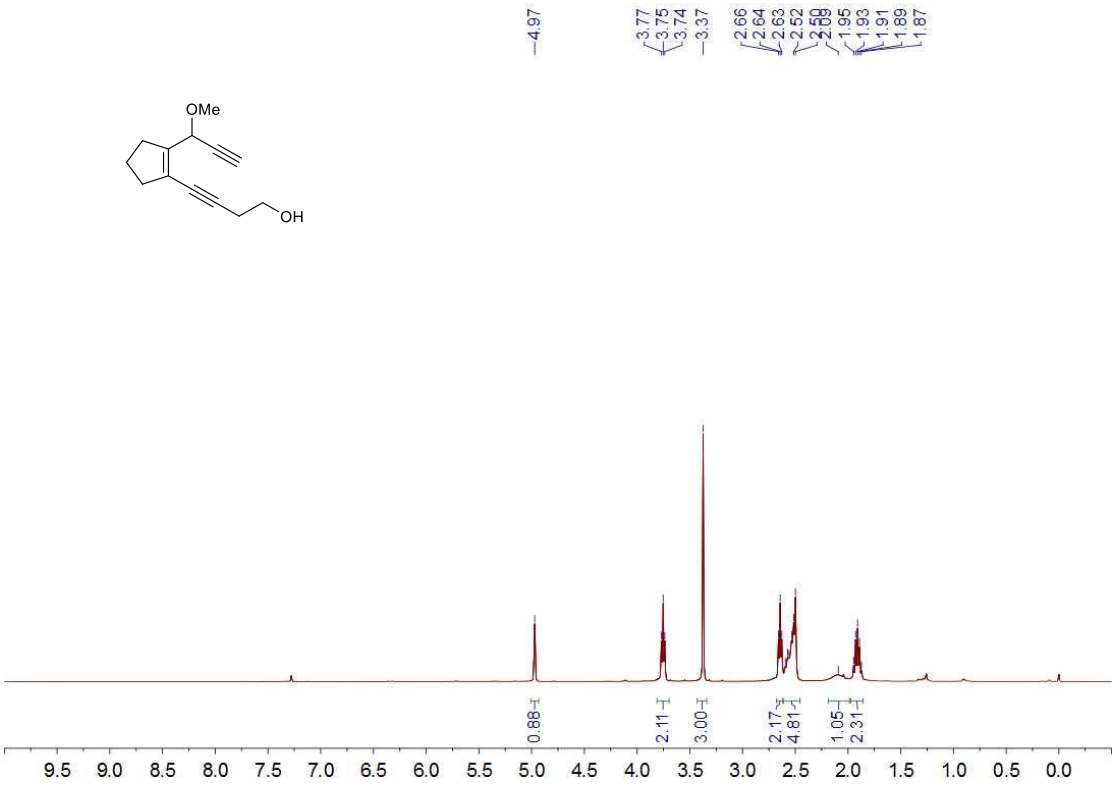


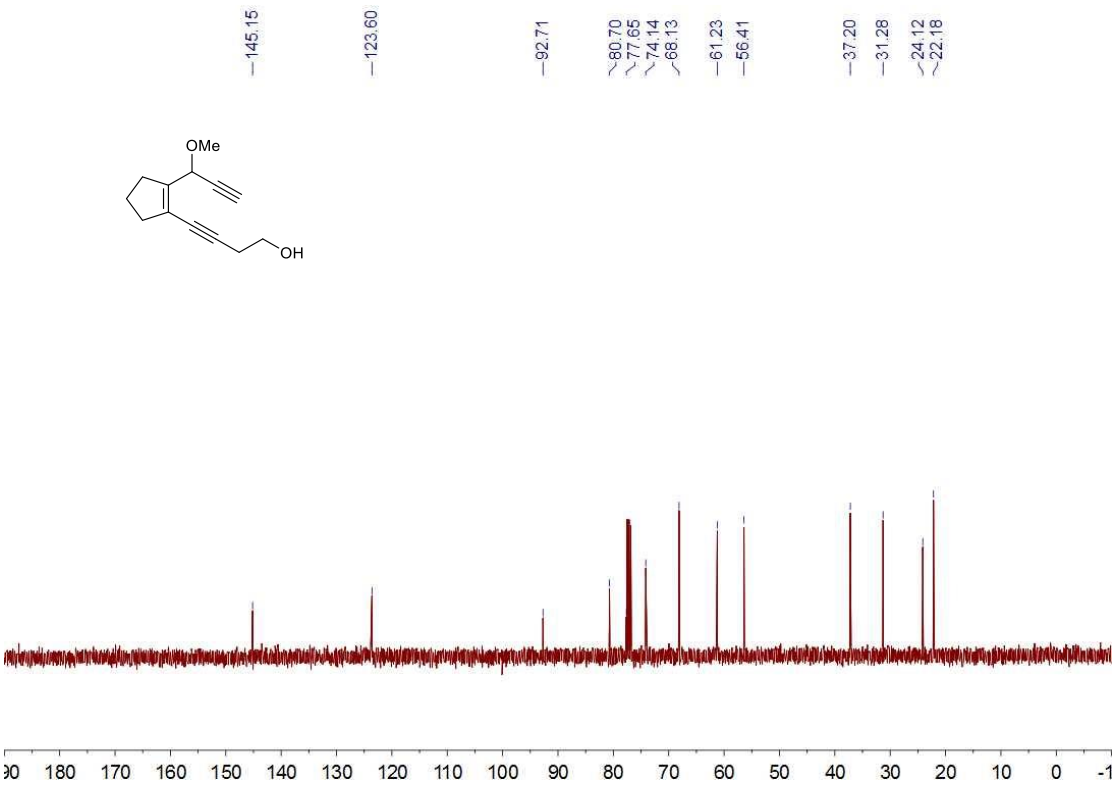
(Z)-7-methoxynona-5-en-3,8-diyn-1-ol (1c)



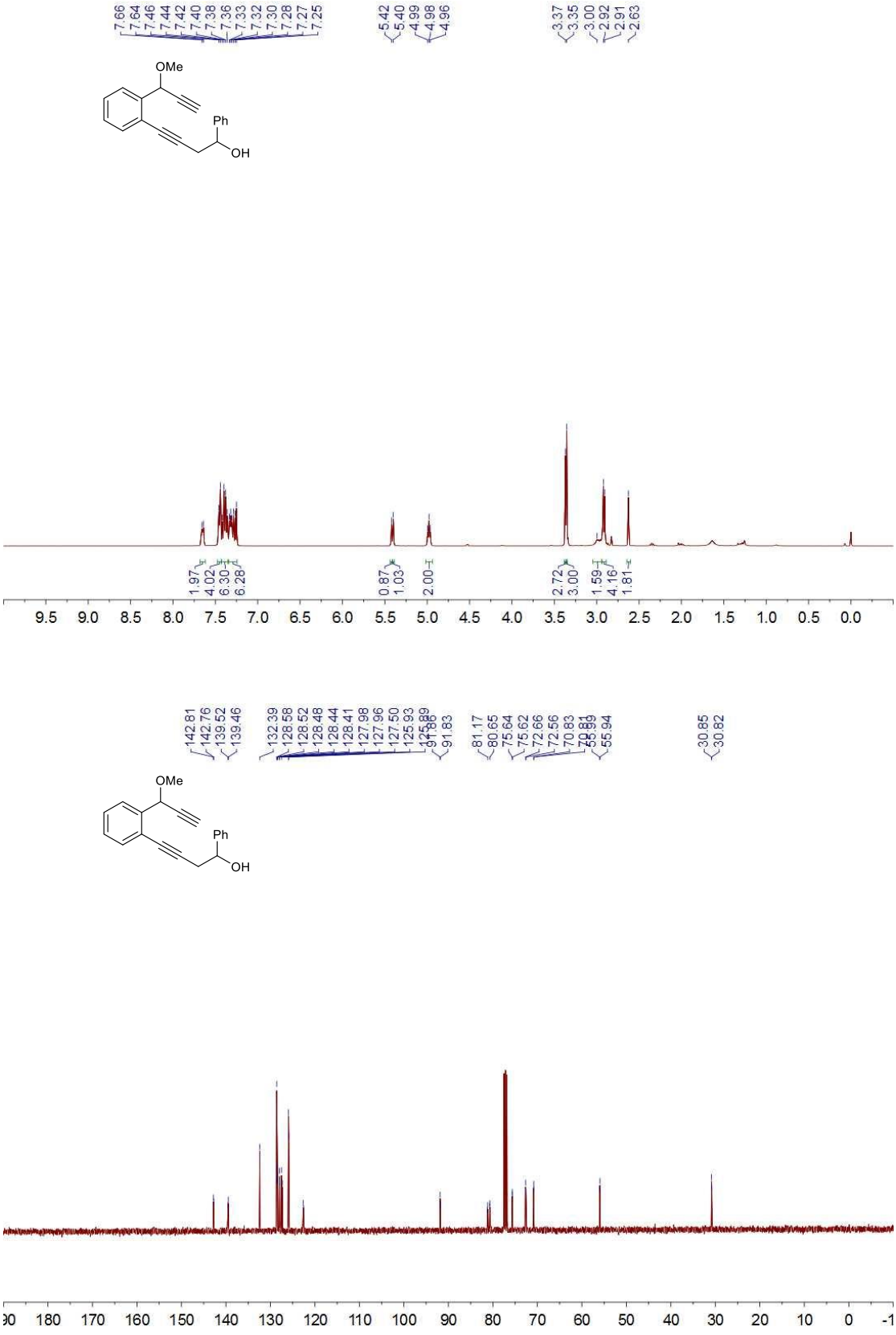


4-(2-(1-methoxyprop-2-yn-1-yl)cyclopent-1-en-1-yl)but-3-yn-1-ol (1d)

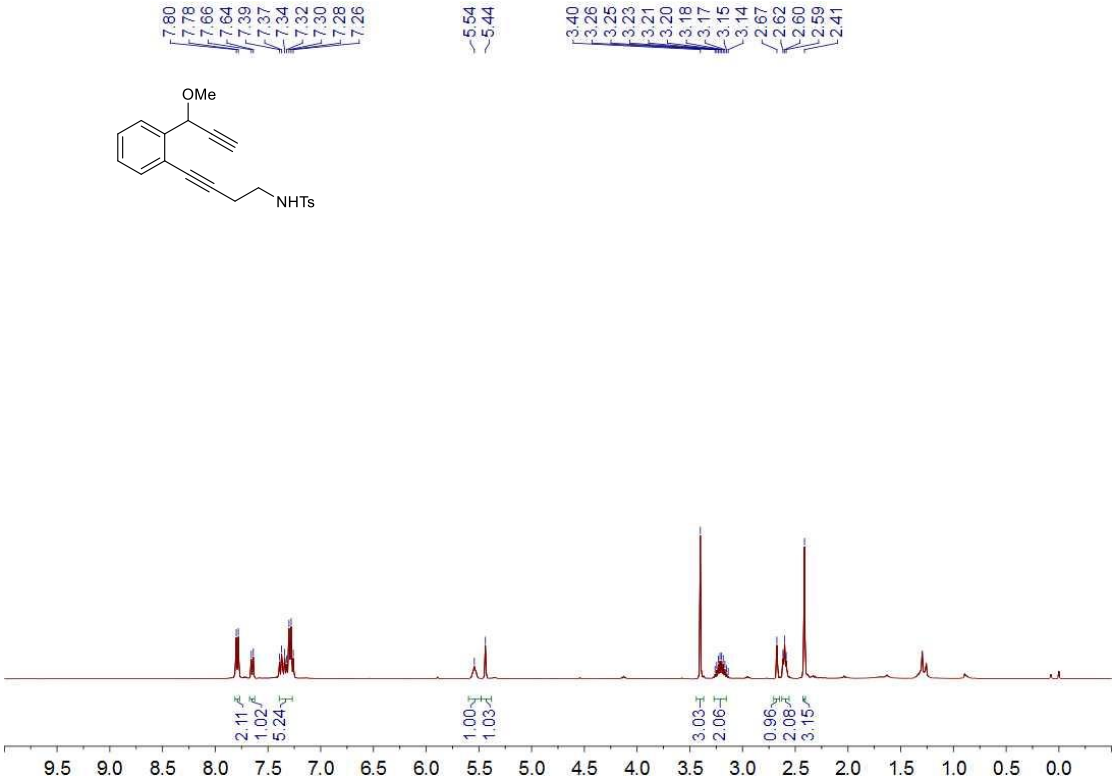


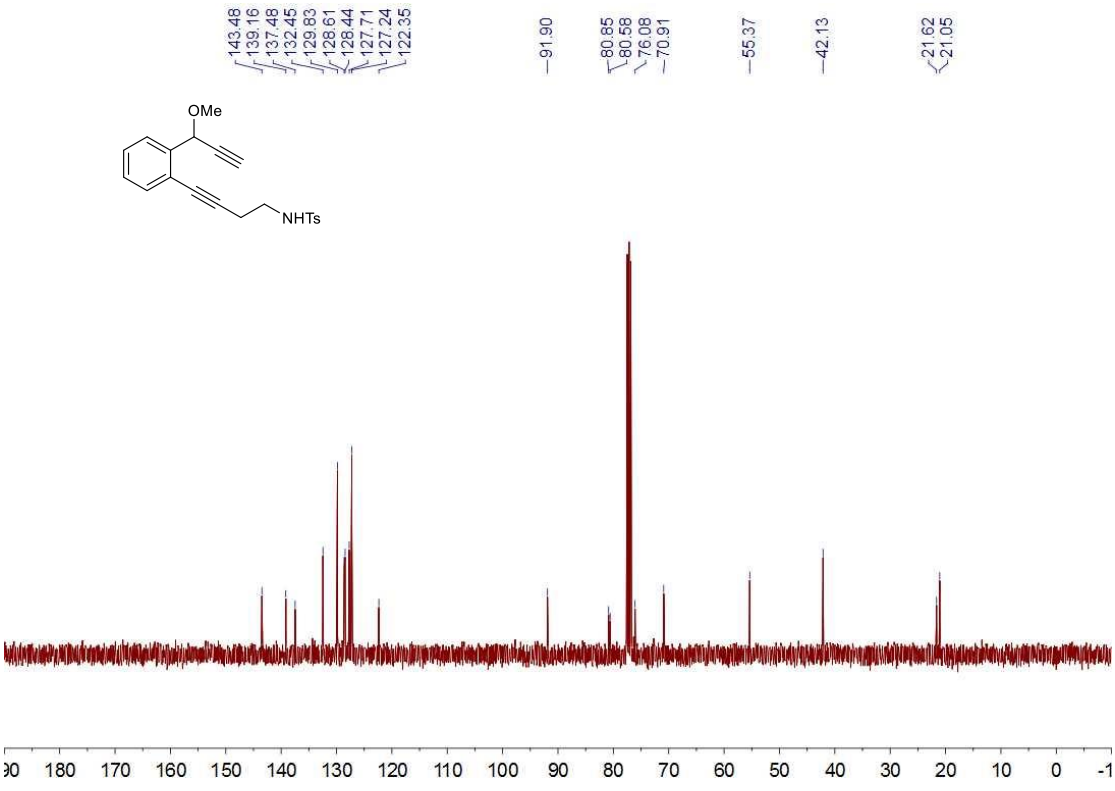


4-(2-(1-methoxyprop-2-yn-1-yl)phenyl)-1-phenylbut-3-yn-1-ol (1e)

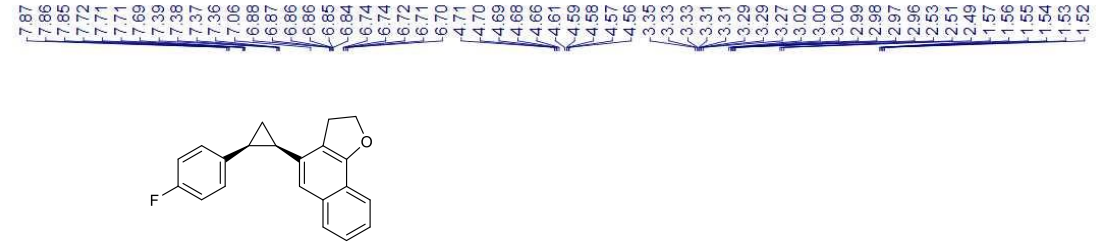


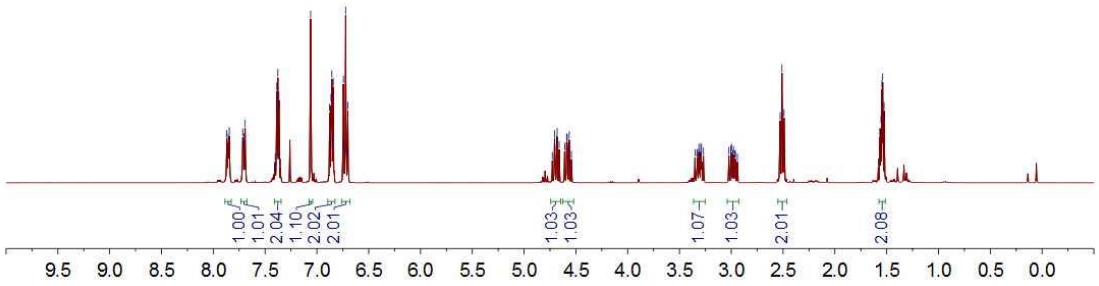
N-(4-(2-(1-methoxyprop-2-yn-1-yl)phenyl)but-3-yn-1-yl)-4-methylbenzenesulfonamide (1f)

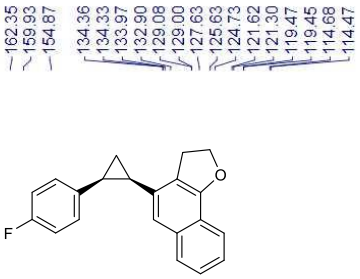


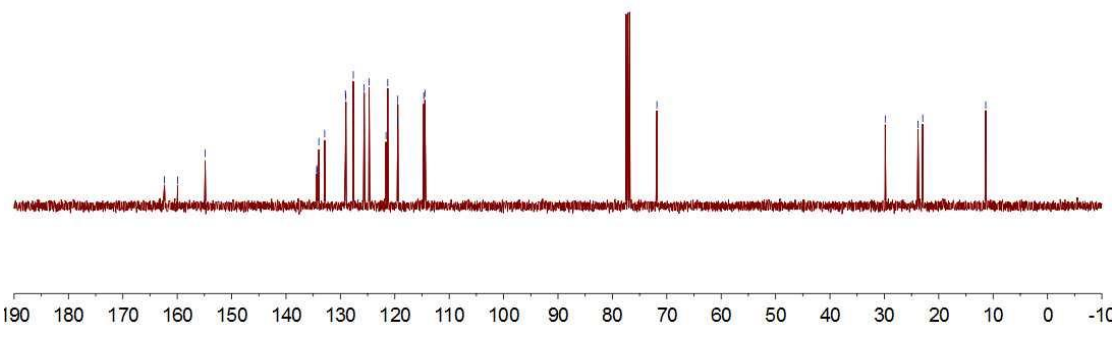


4-(2-(4-fluorophenyl)cyclopropyl)-2,3-dihydronaphtho[1,2-b]furan (3a)









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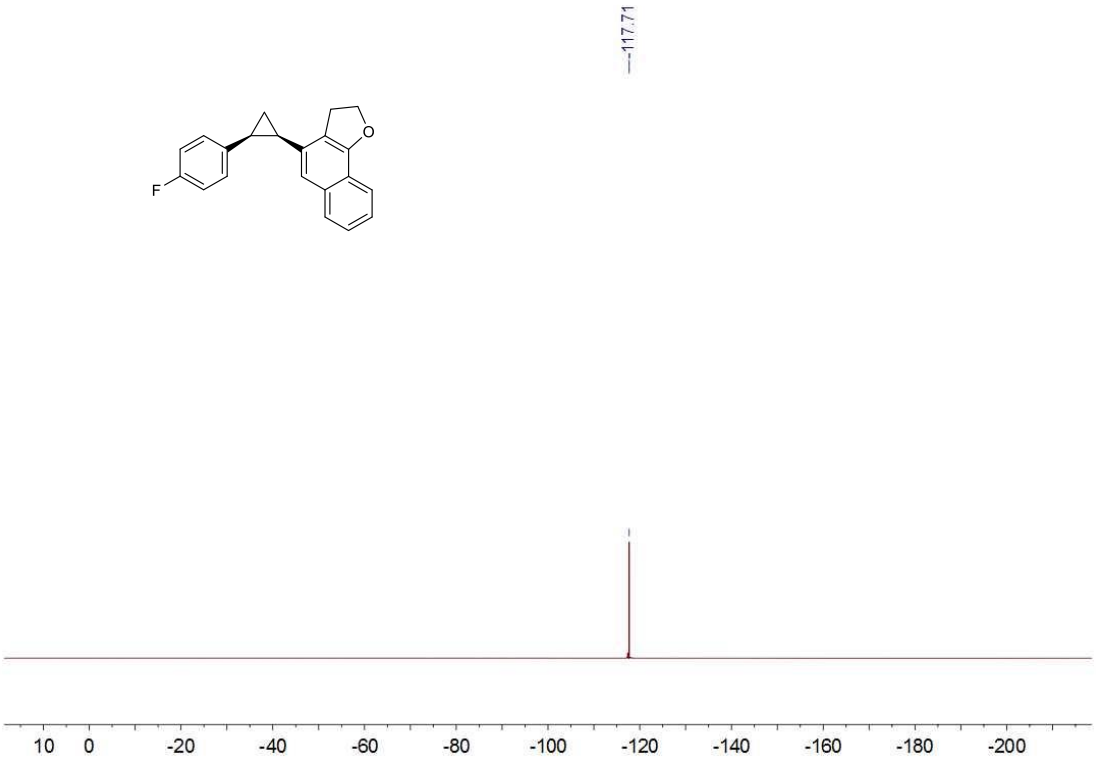
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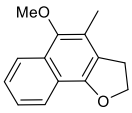
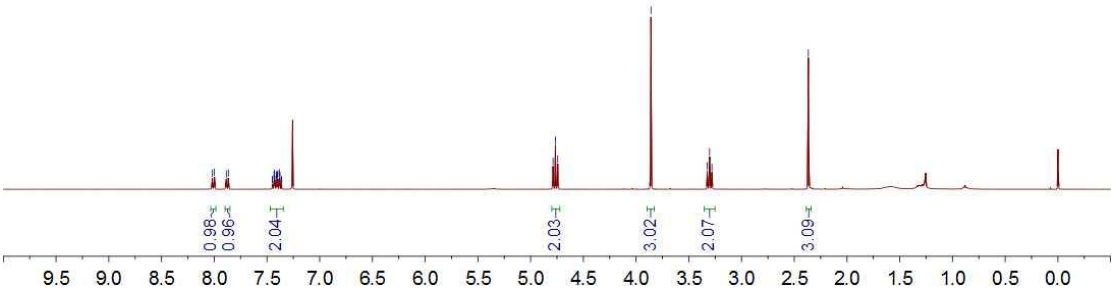
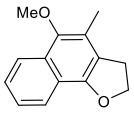
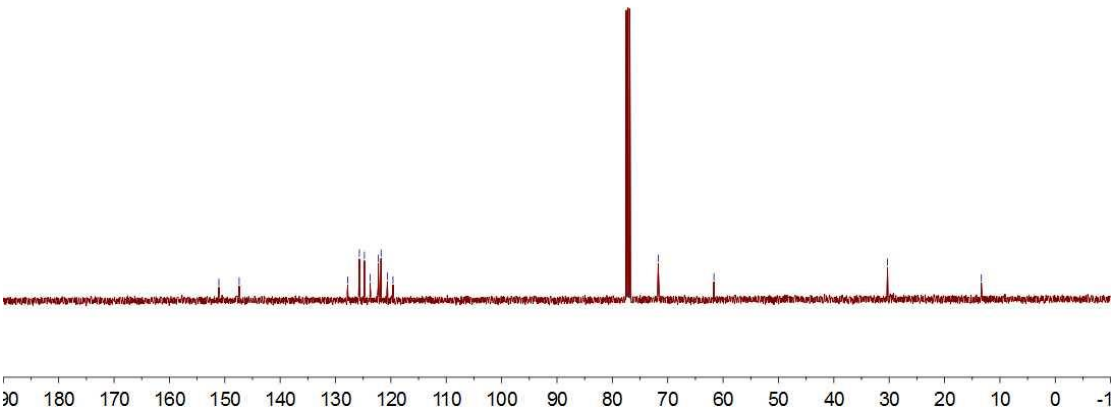
5-methoxy-4-methyl-2,3-dihydronaphtho[1,2-b]furan (4a)

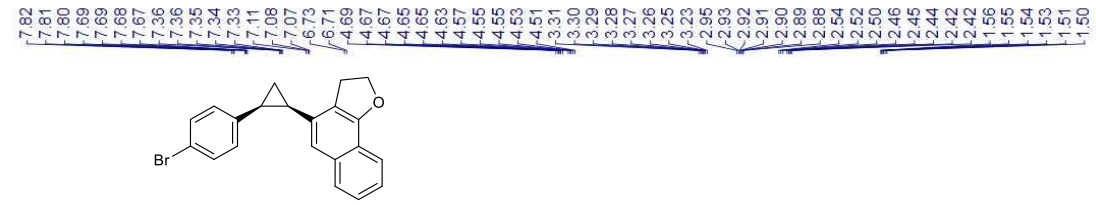


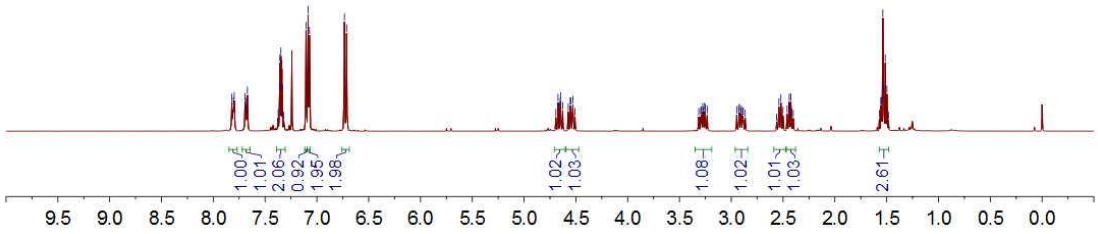


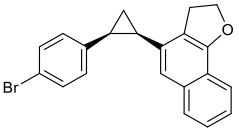


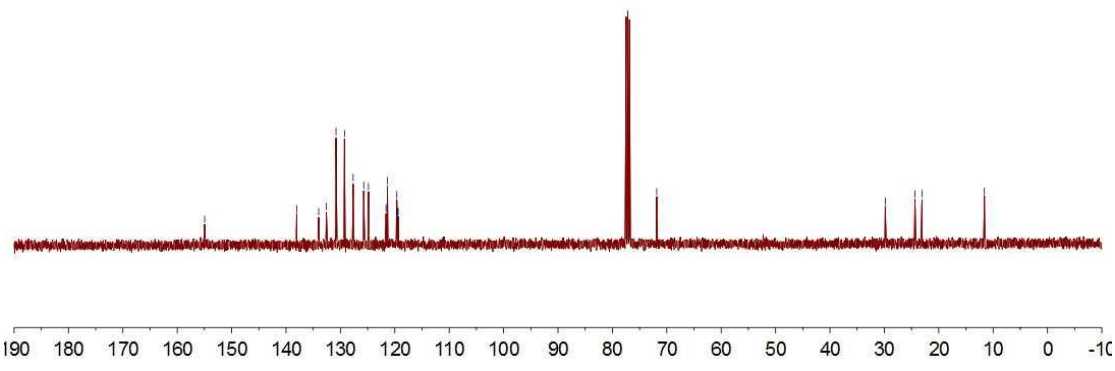


4-(2-(4-bromophenyl)cyclopropyl)-2,3-dihydronaphtho[1,2-b]furan (4b)

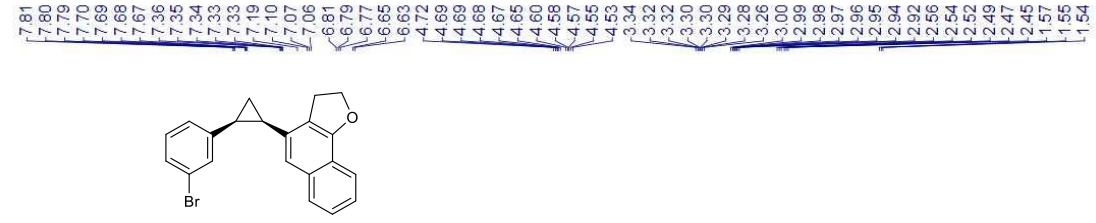


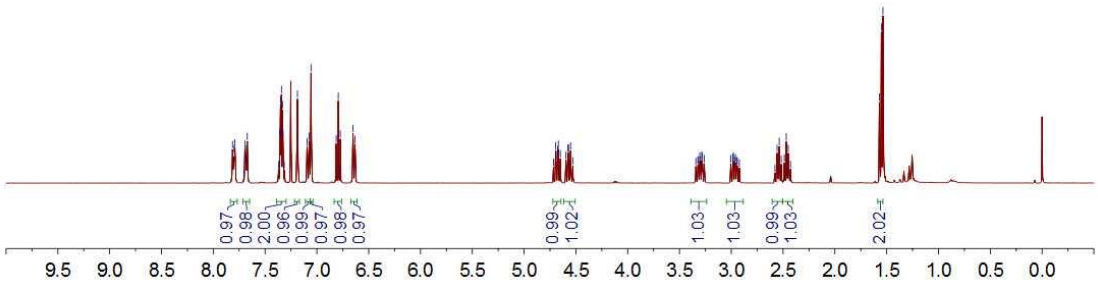


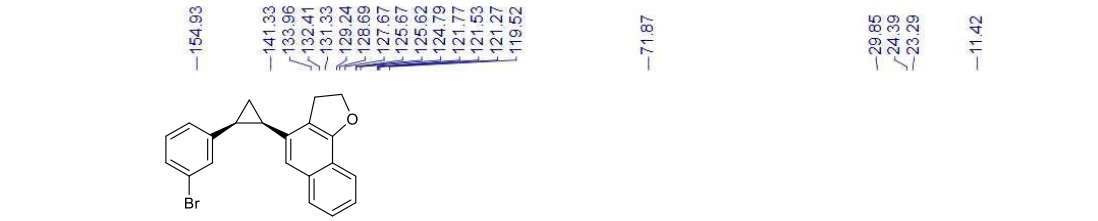


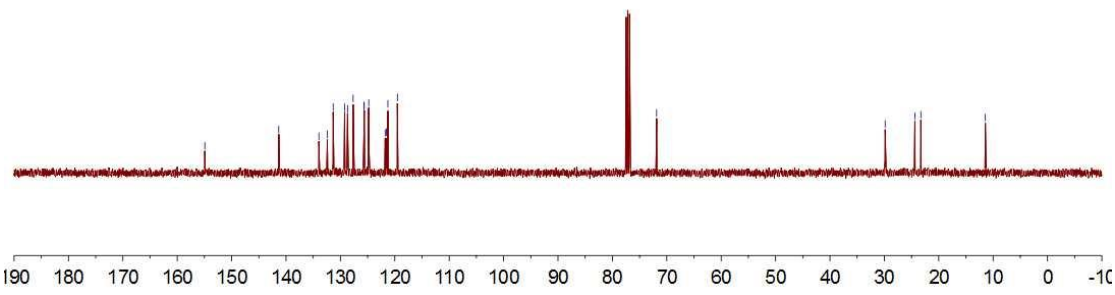


4-(2-(3-bromophenyl)cyclopropyl)-2,3-dihydronaphtho[1,2-b]furan (4c)

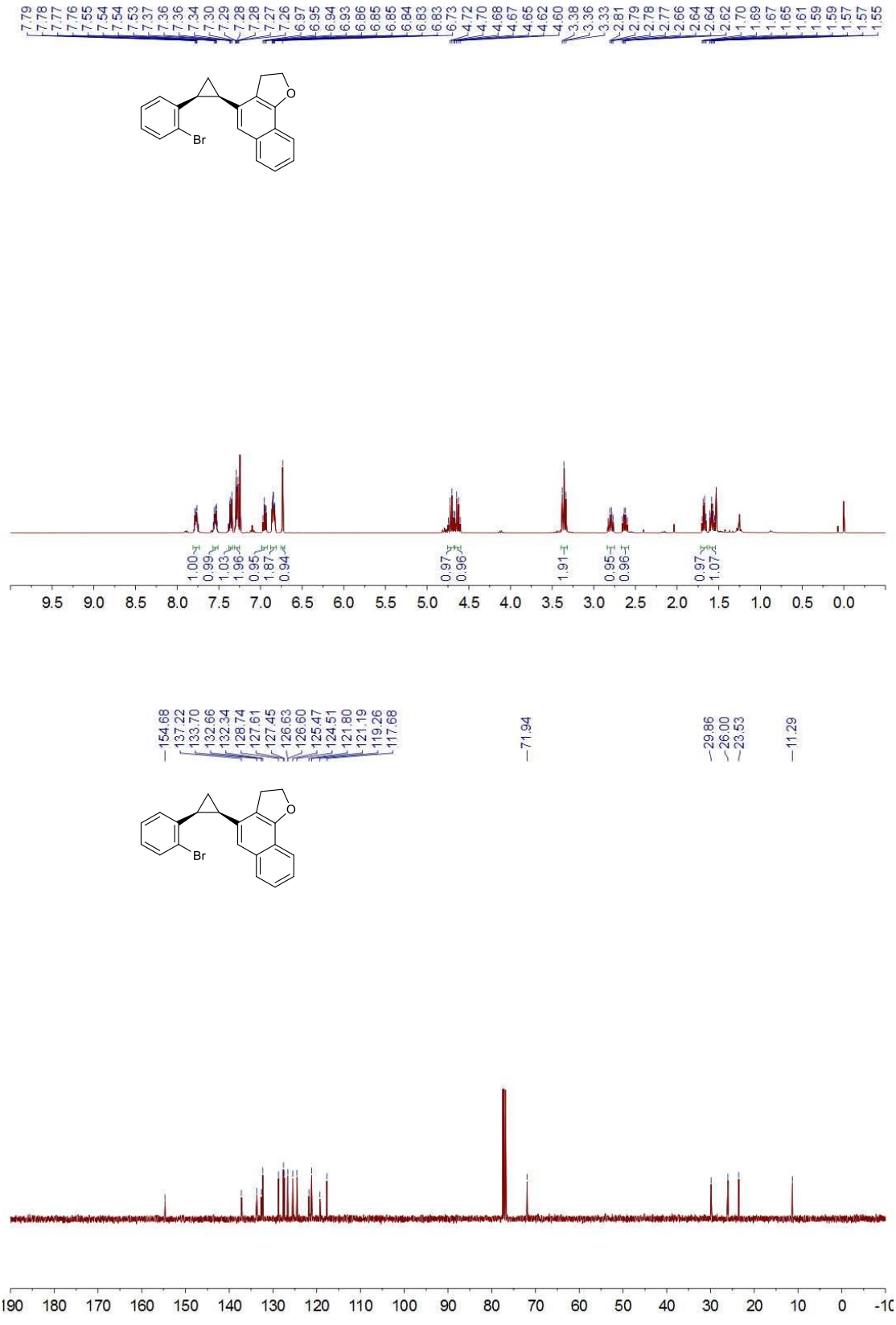








4-(2-(2-bromophenyl)cyclopropyl)-2,3-dihydronaphtho[1,2-b]furan (3d)



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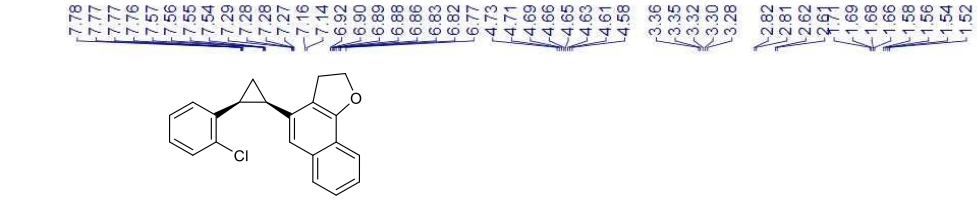
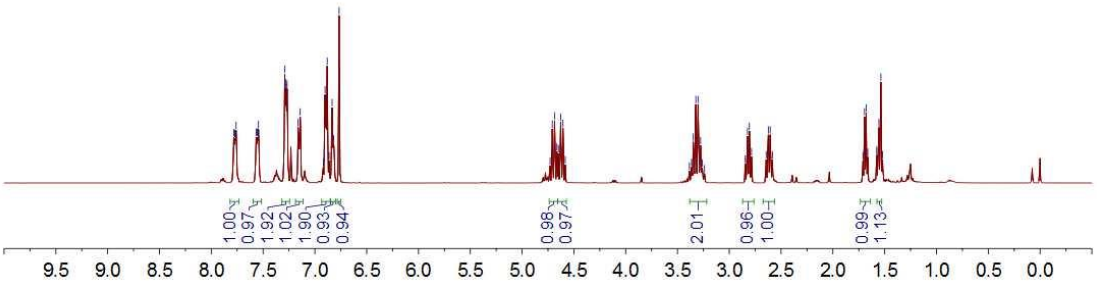
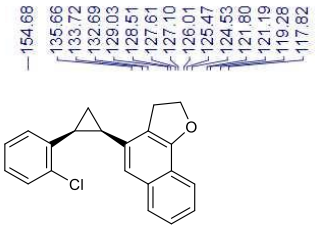
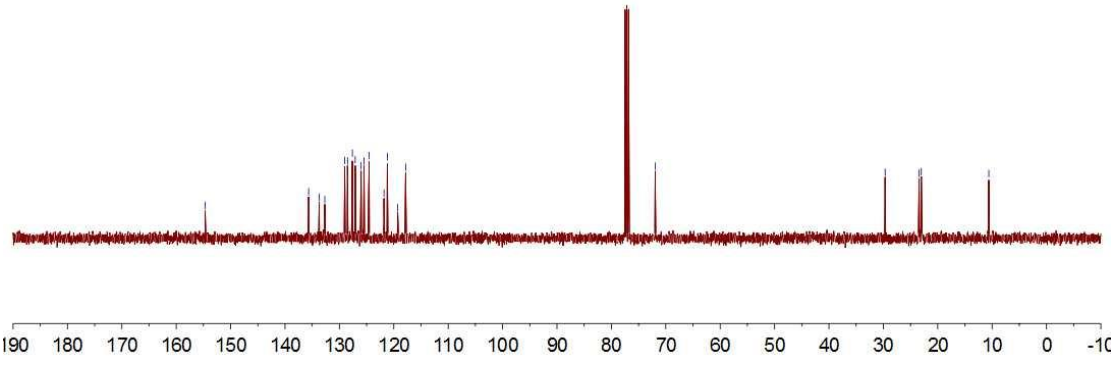
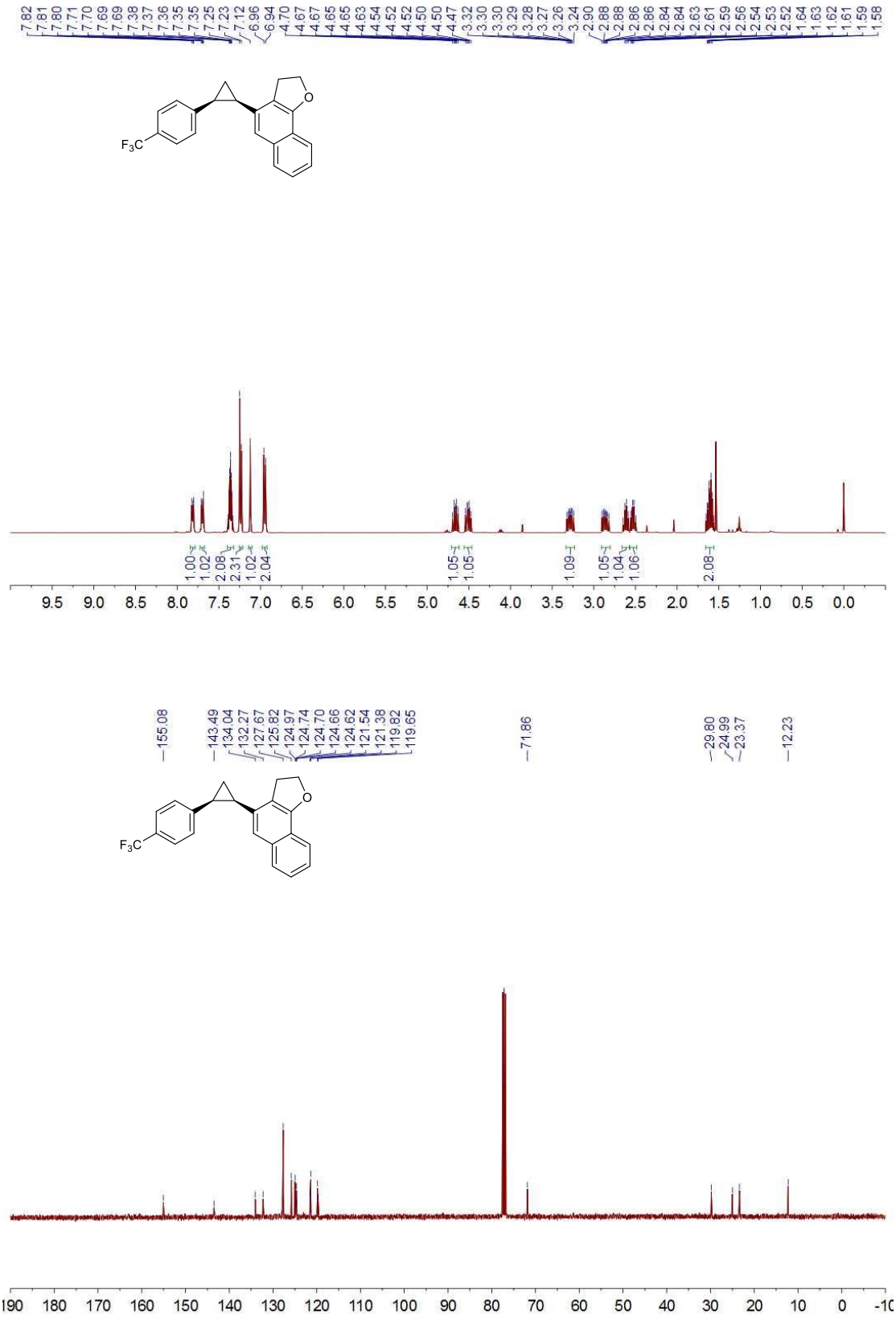


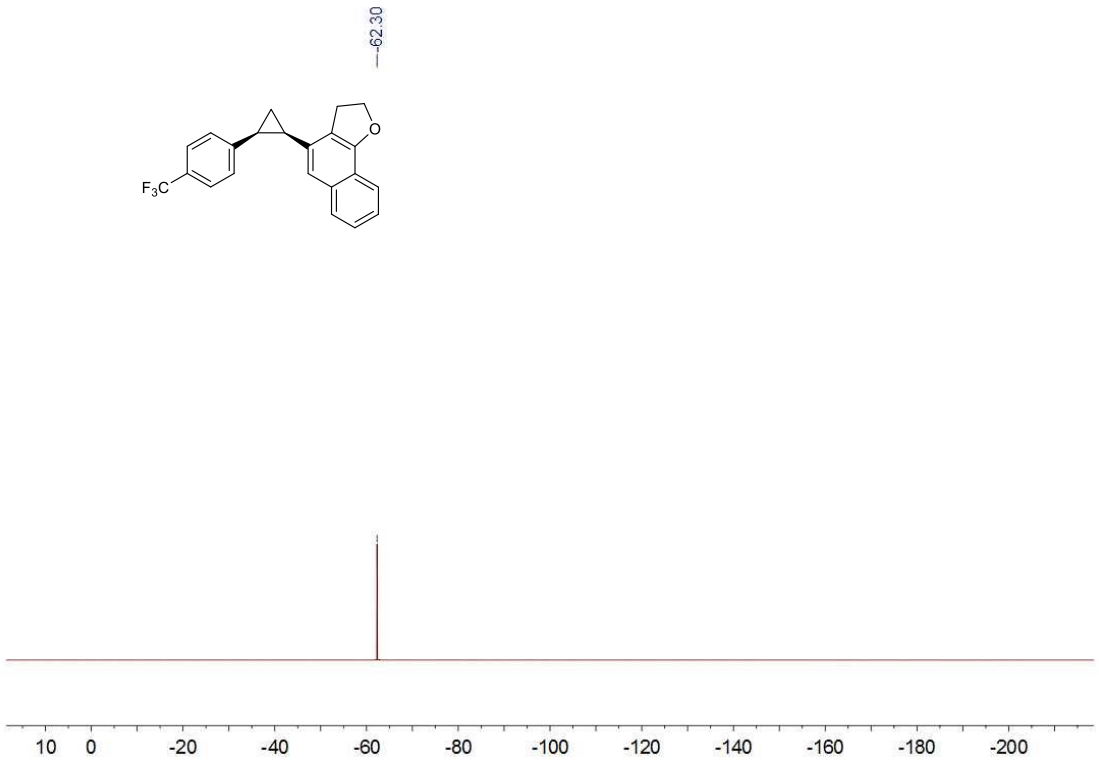






4-(2-(4-(trifluoromethyl)phenyl)cyclopropyl)-2,3-dihydronaphtho[1,2-b]furan (3f)

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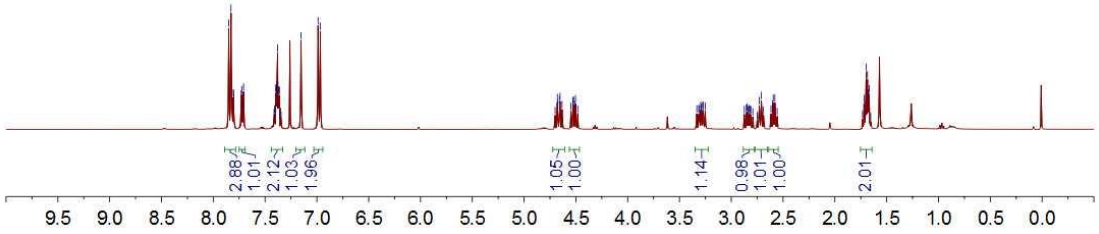
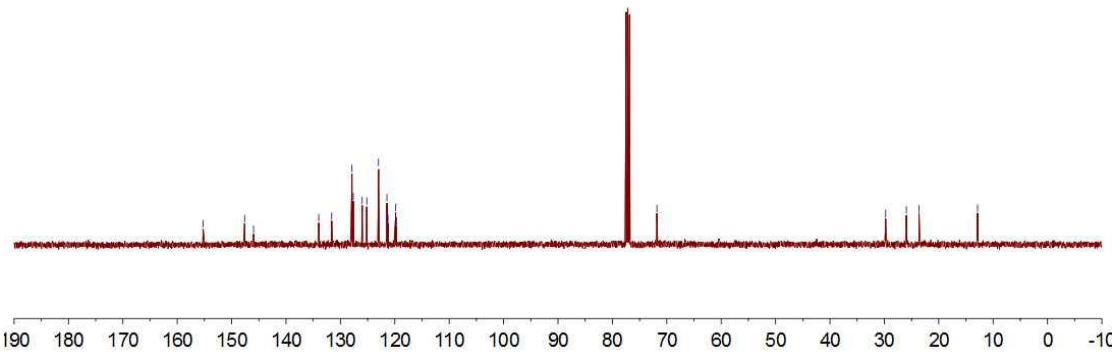
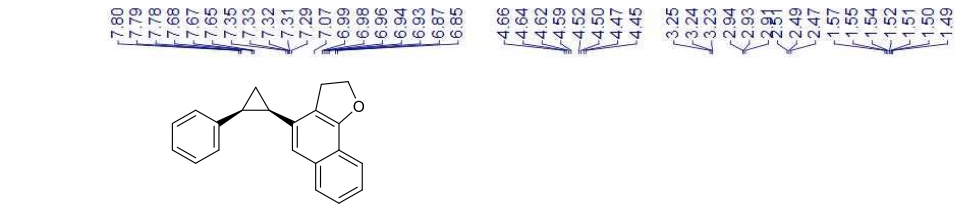
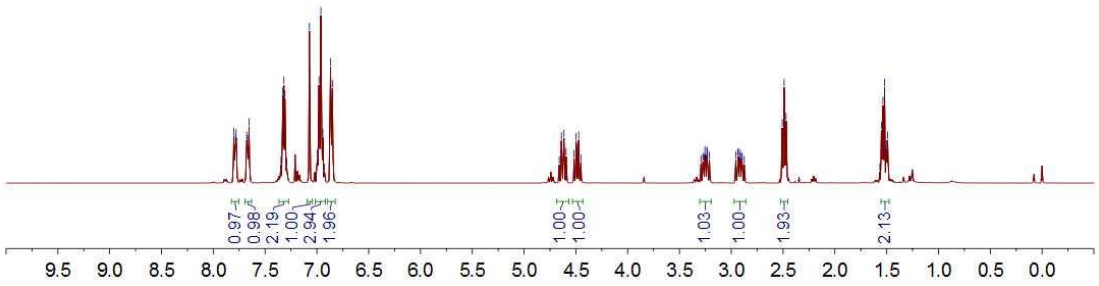
4-(2-(4-nitrophenyl)cyclopropyl)-2,3-dihydronaphtho[1,2-b]furan (3g)

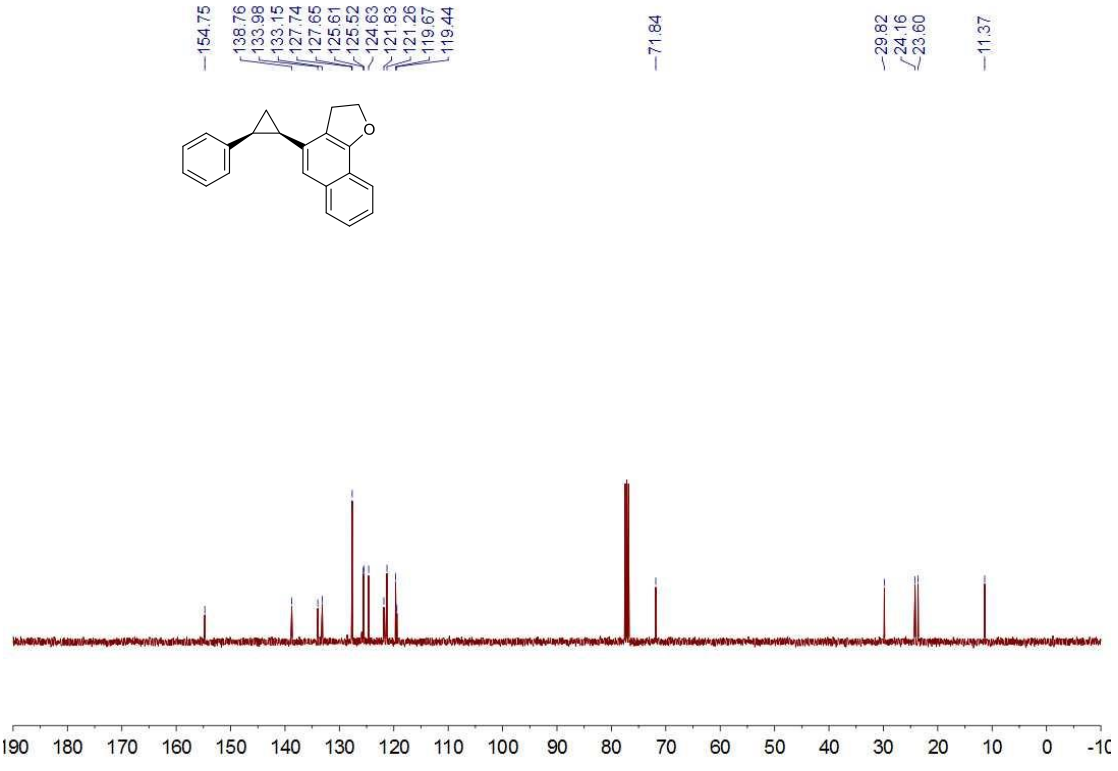




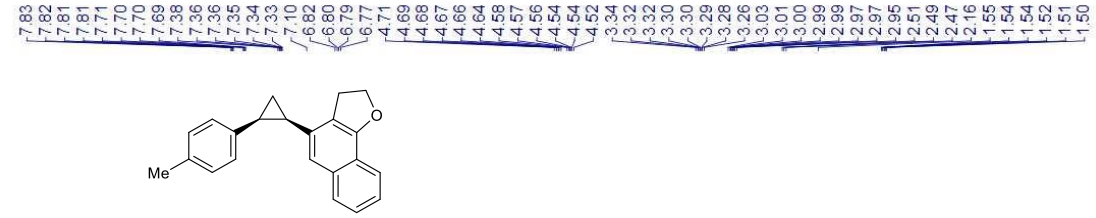
4-(2-phenylcyclopropyl)-2,3-dihydronaphtho[1,2-b]furan (3h)

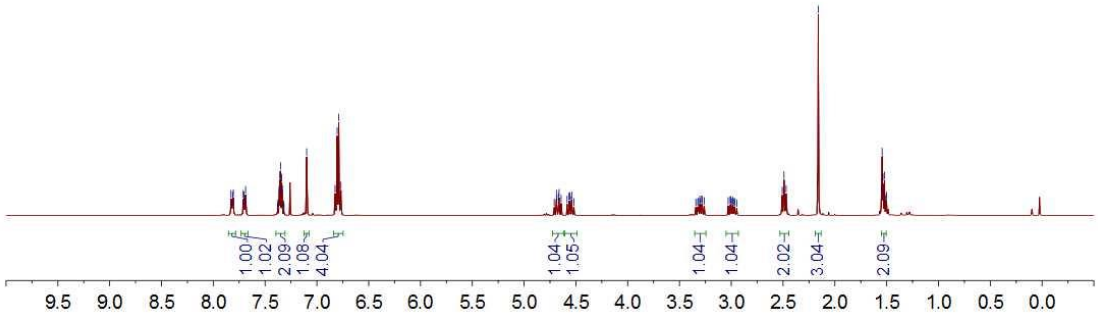


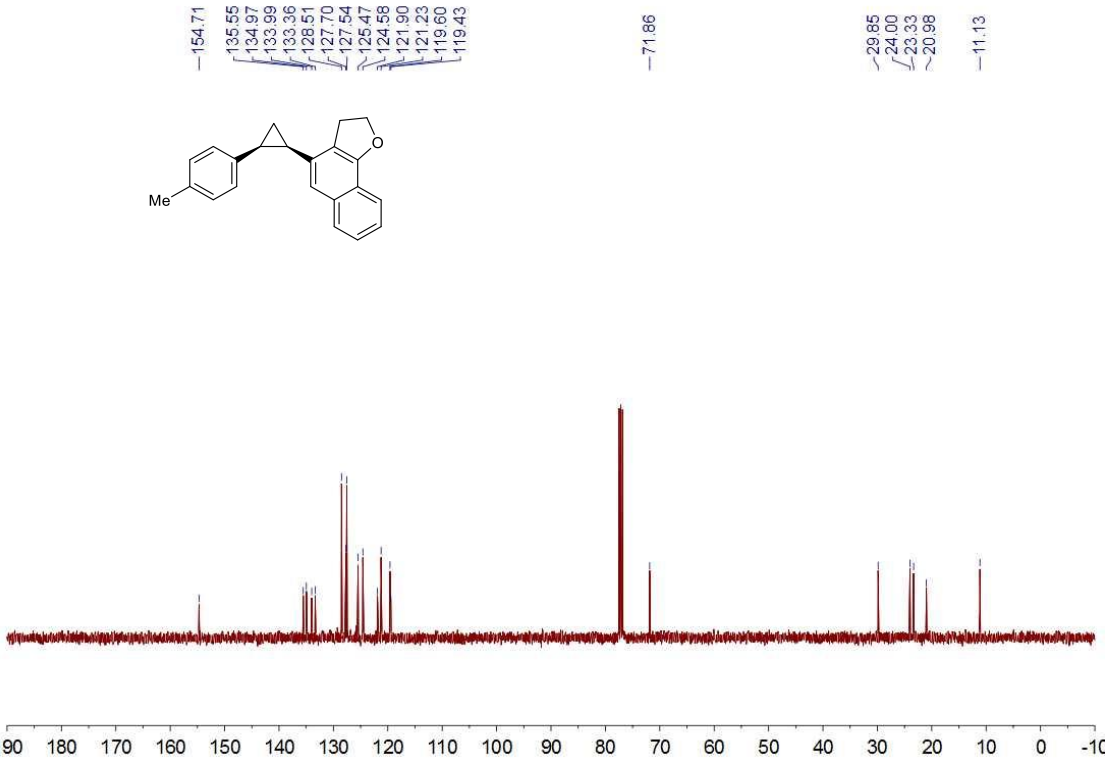




4-(2-(4-methylphenyl)cyclopropyl)-2,3-dihydronaphtho[1,2-b]furan (3i)







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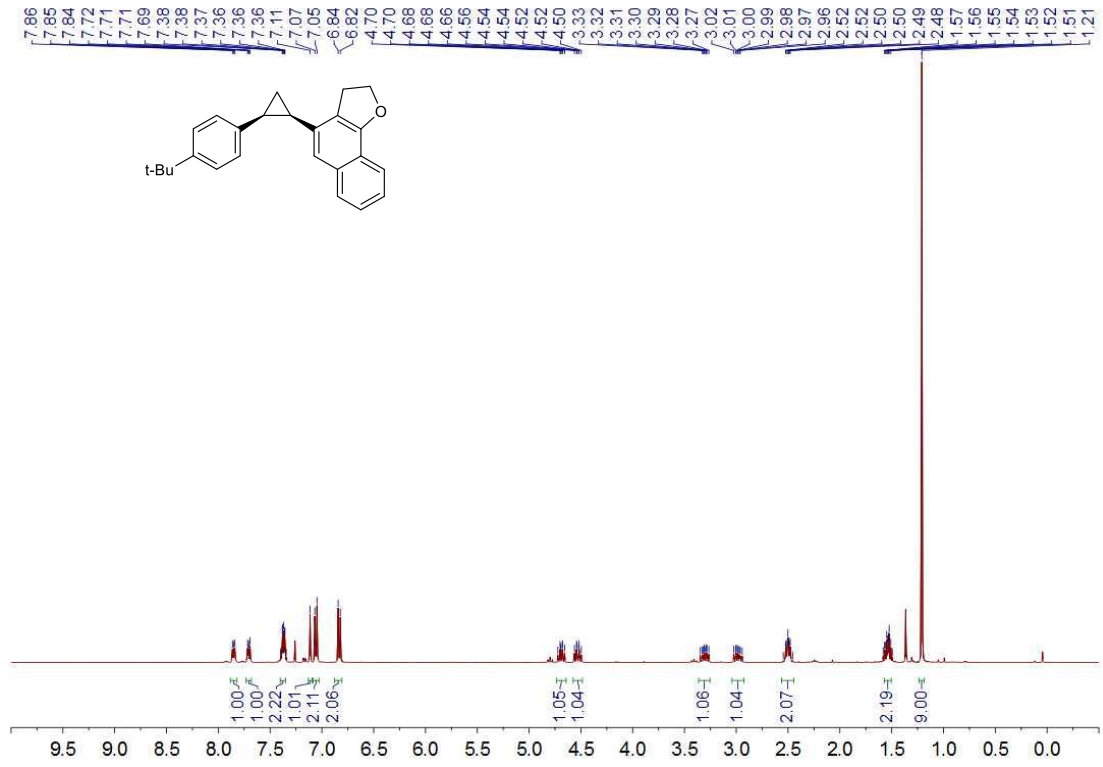
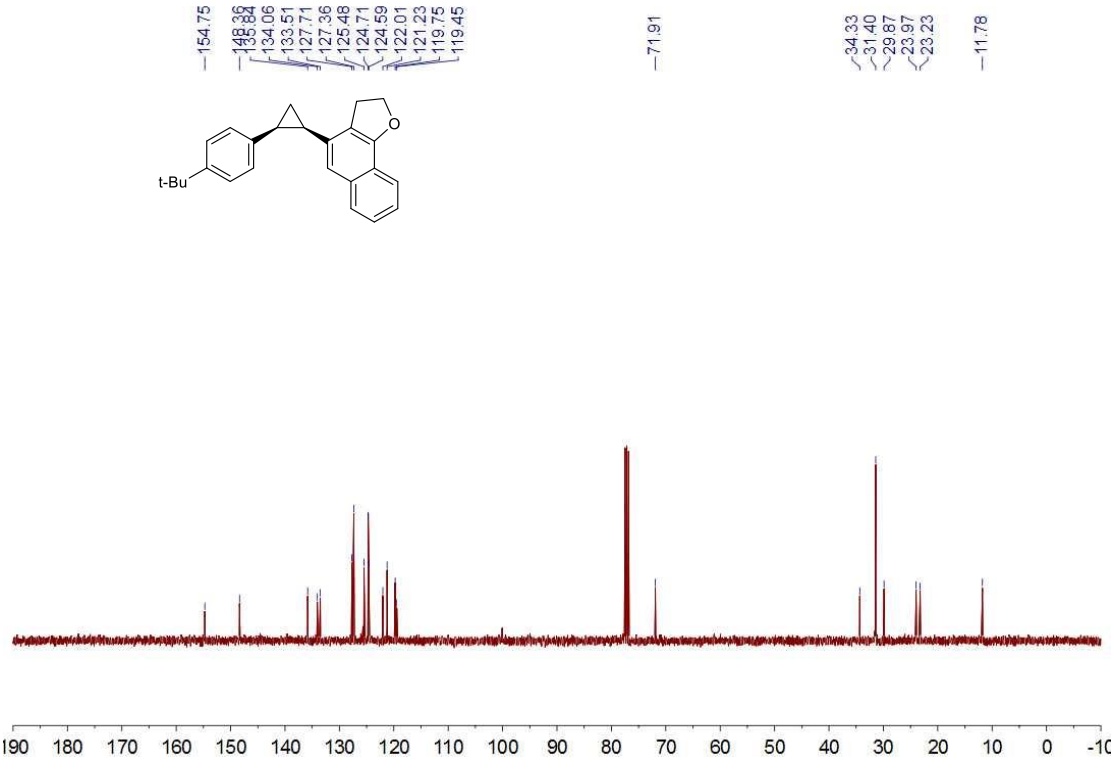
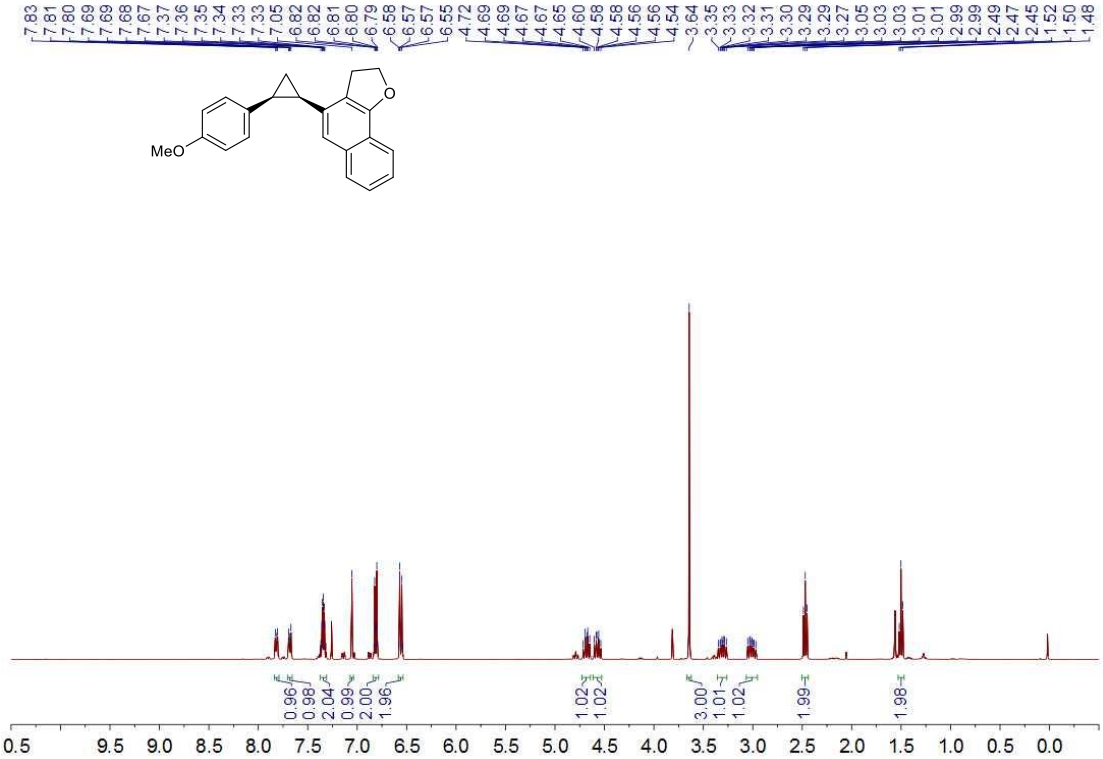
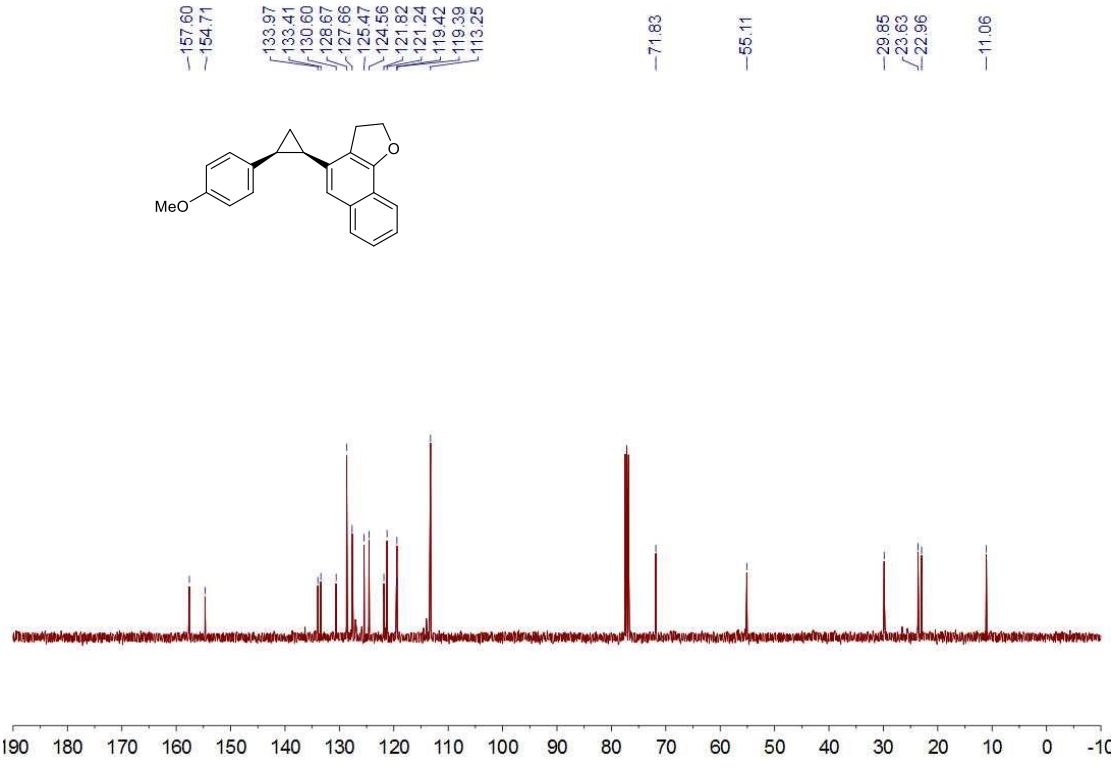




4-(2-(4-methoxyphenyl)cyclopropyl)-2,3-dihydronaphtho[1,2-b]furan (3k)





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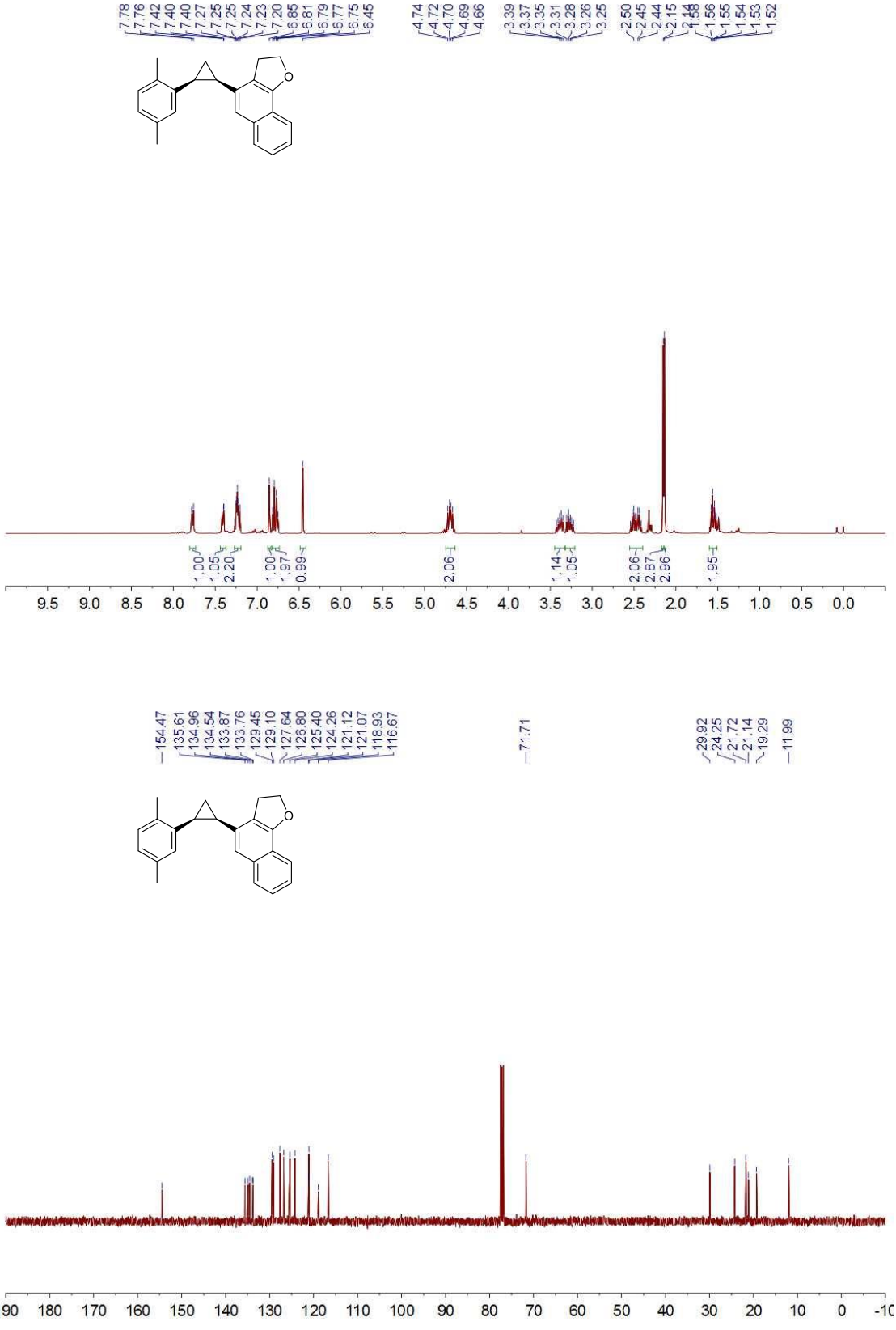
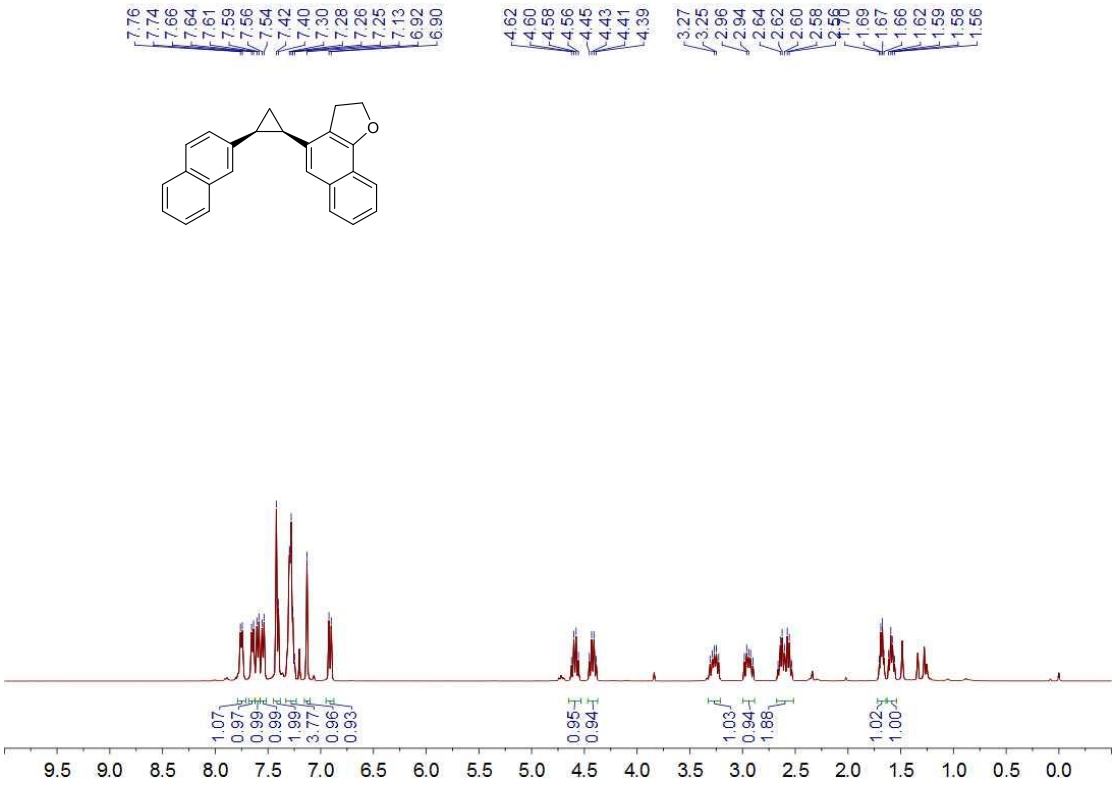
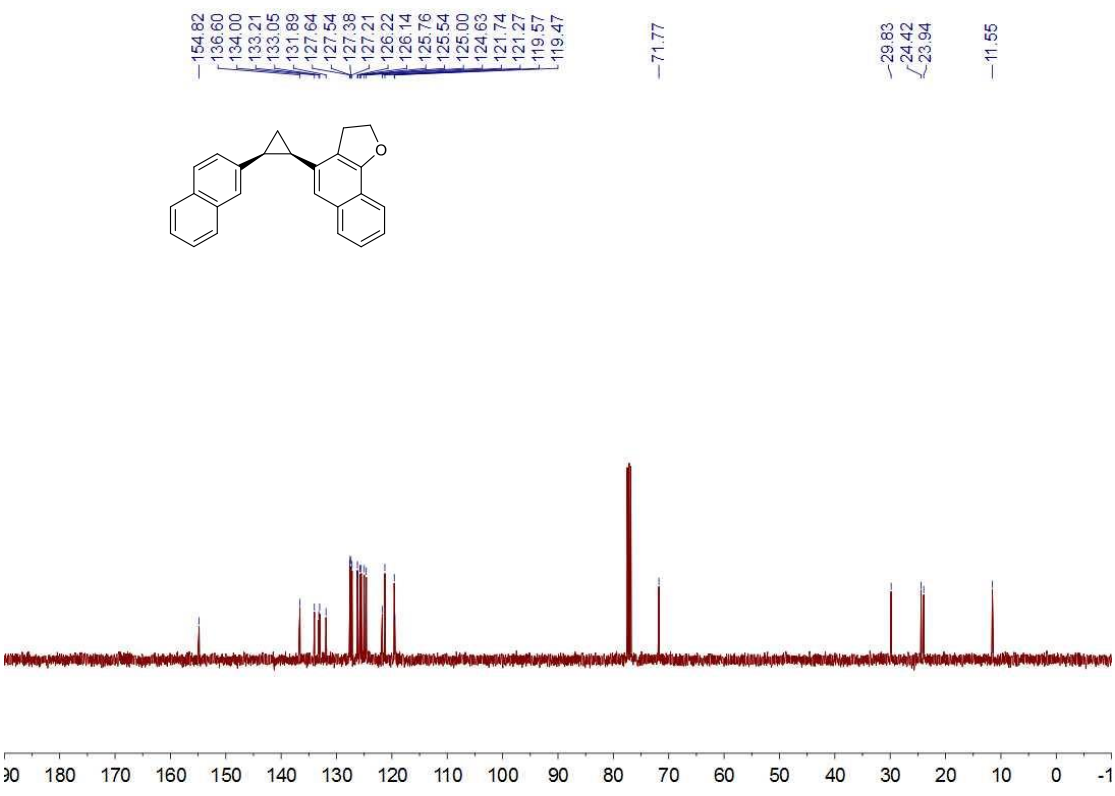
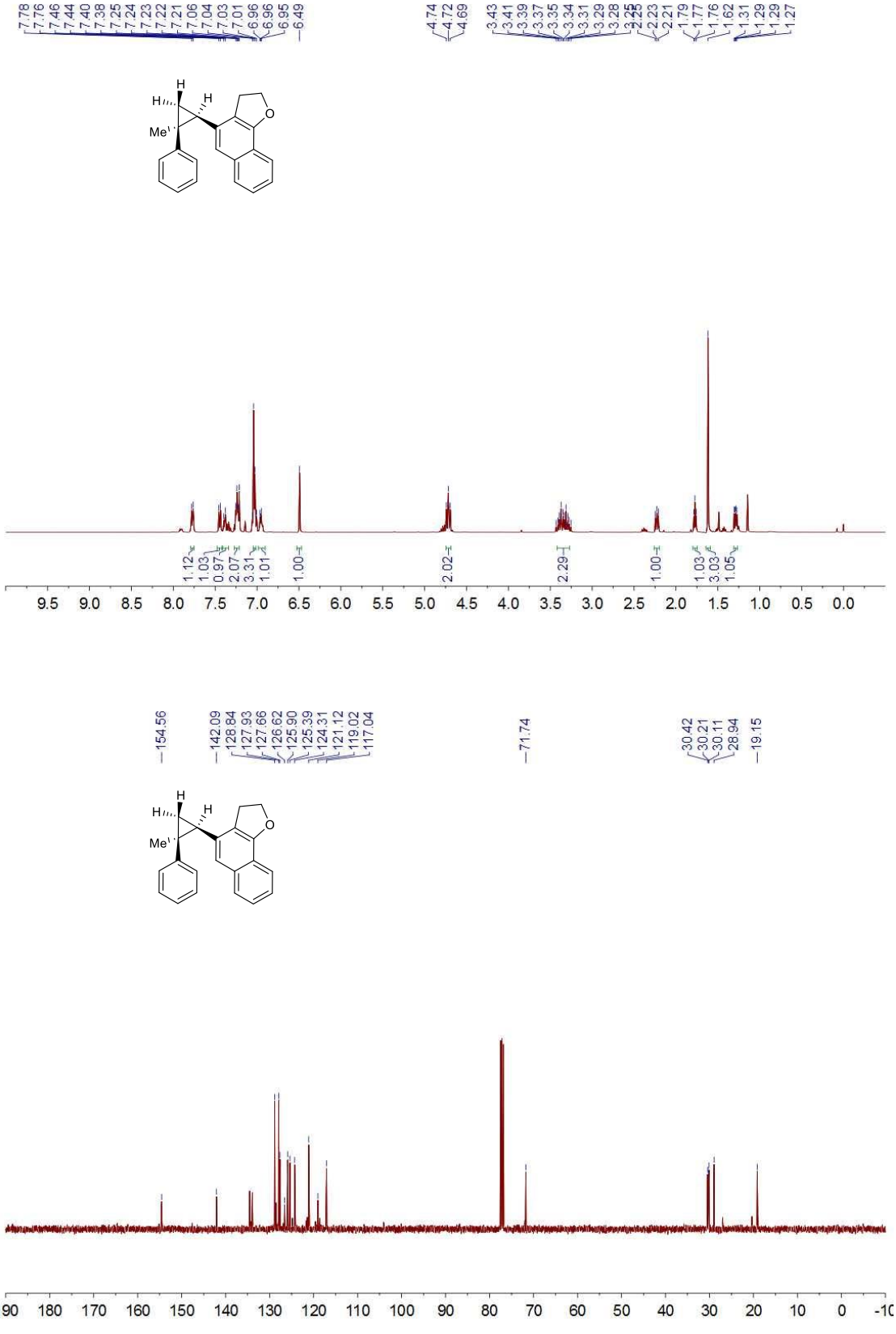


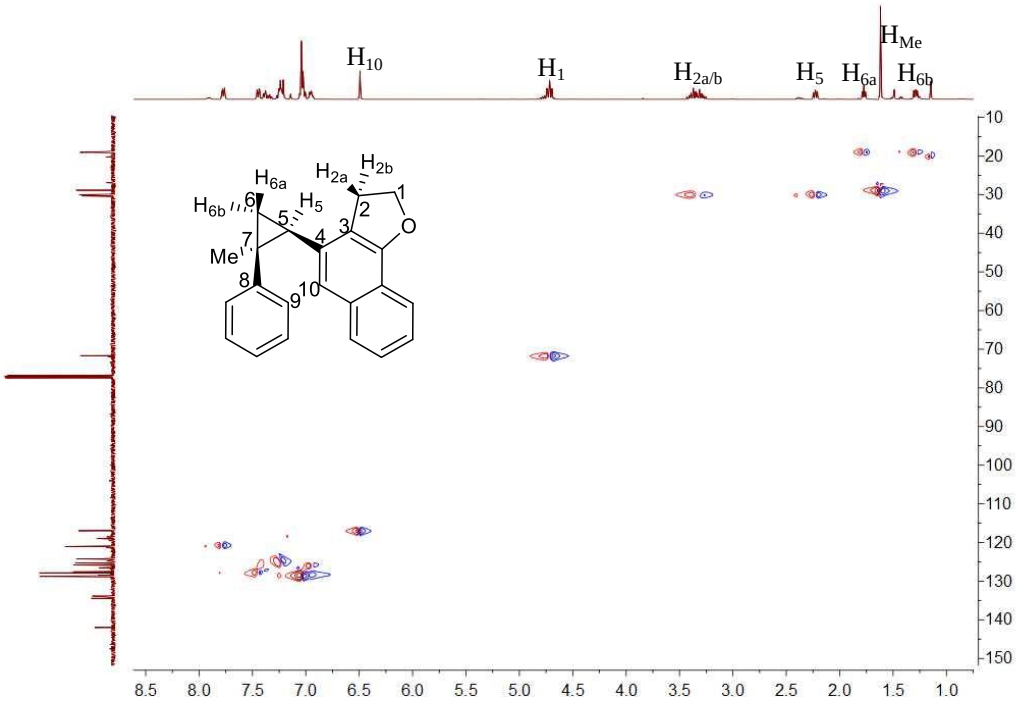
4-(2-(naphthalen-2-yl)cyclopropyl)-2,3-dihydronaphtho[1,2-b]furan (3m)

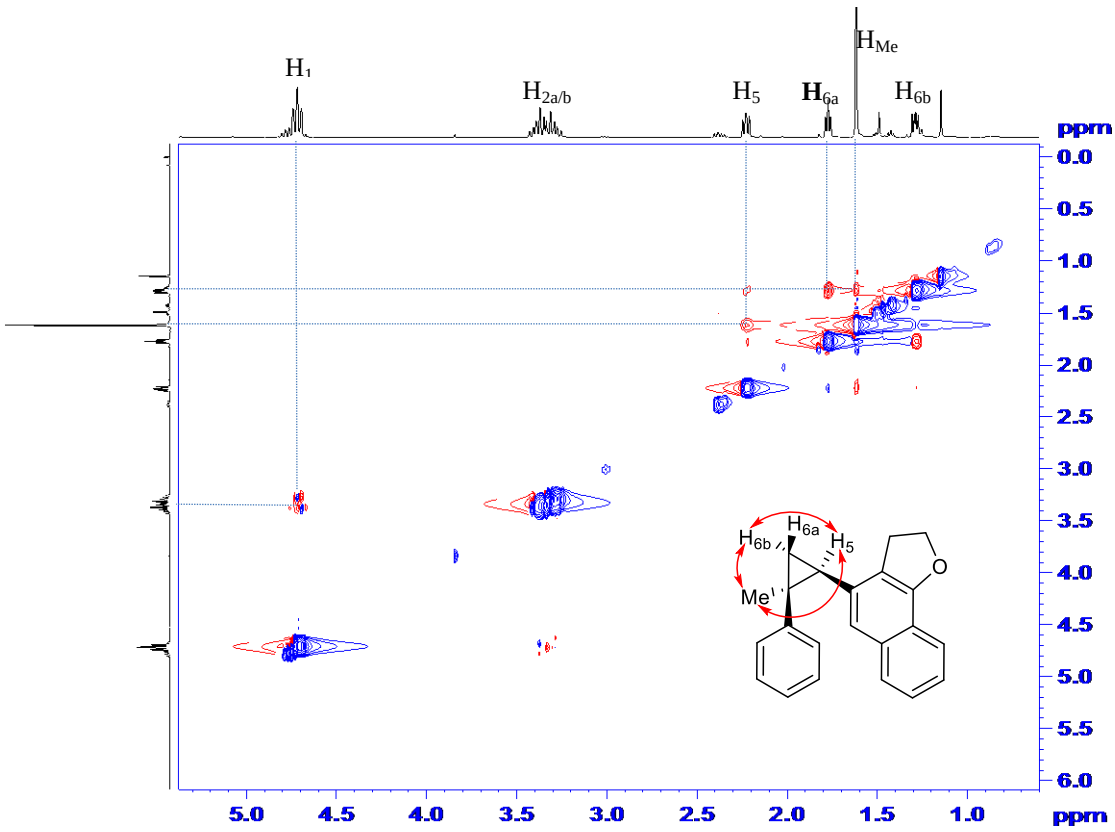


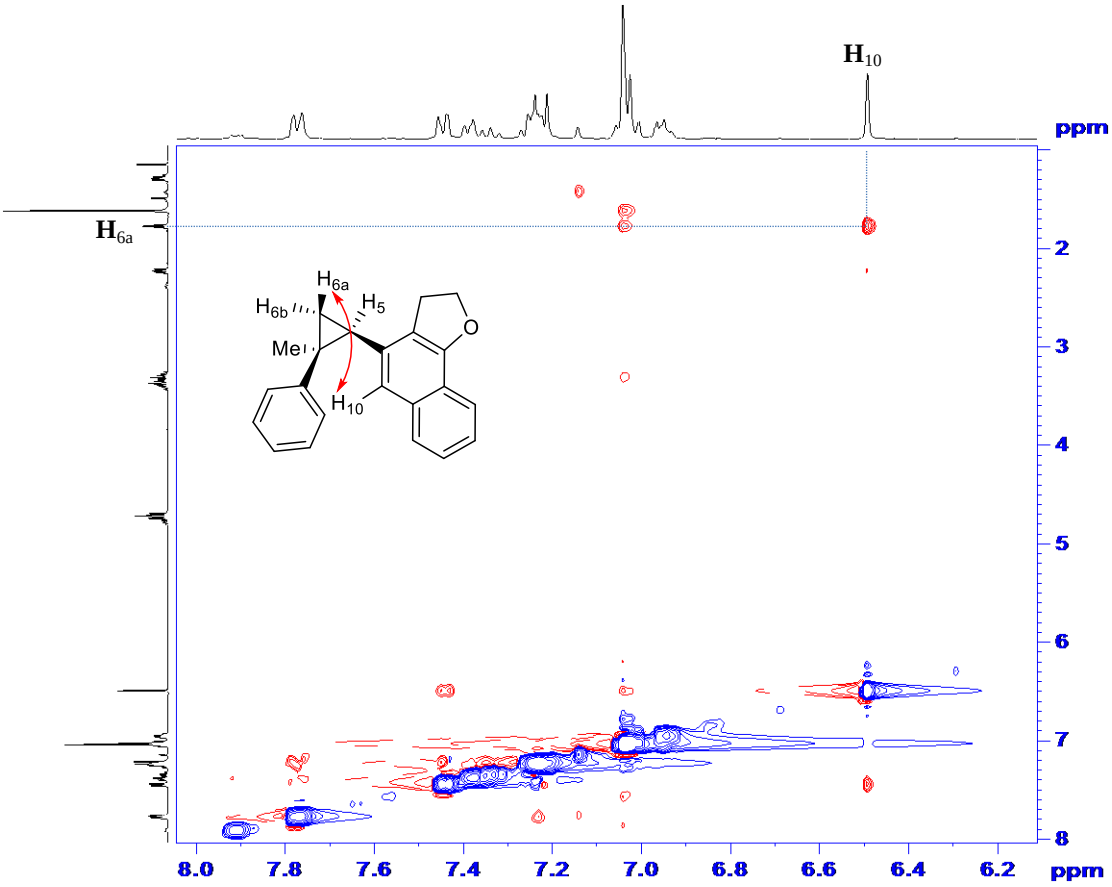


4-(2-methyl-2-phenylcyclopropyl)-2,3-dihydronaphtho[1,2-b]furan (3n)

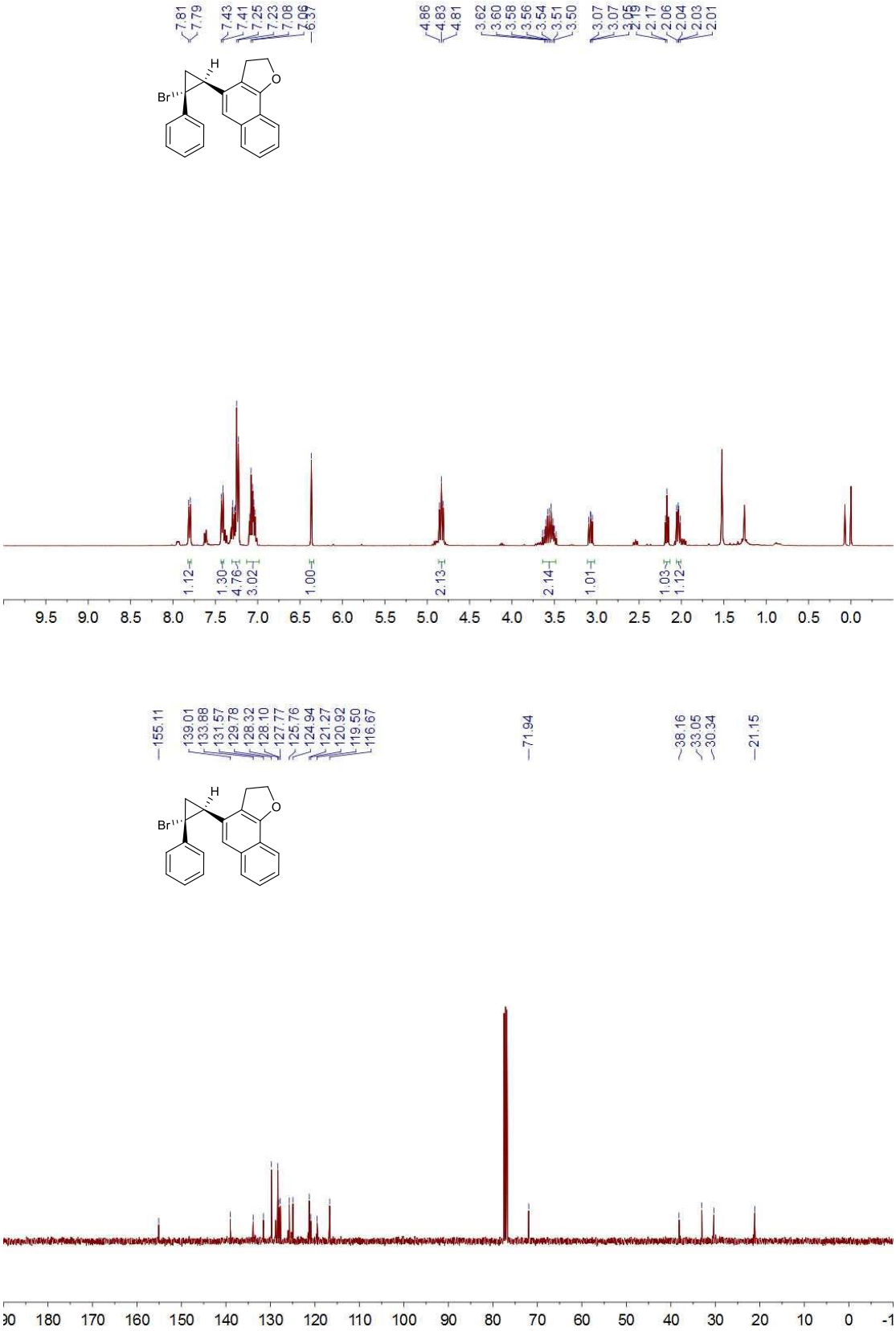



H10
H1
H2a/b
H5
H6a
H6b
HMe
H6a
H2a
H2b
H6b
H5
Me
O
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0

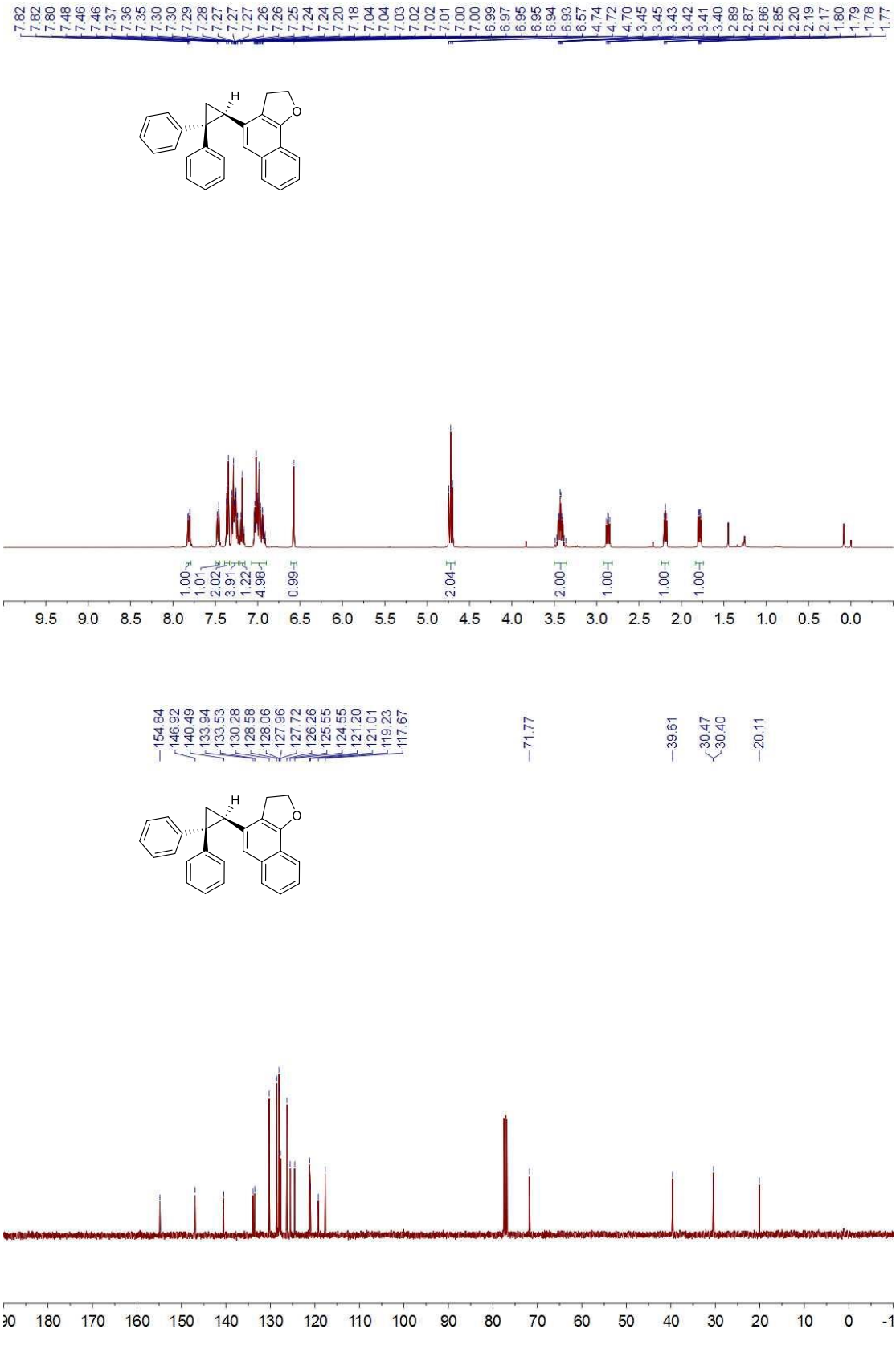

H1
H2a/b
H5
H6a
HMe
H6b
ppm
H6b
H6a
H5
Me
O
5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
ppm


H10
ppm
H6a
H6a
H6b
H5
Me
H10
O
2
3
4
5
6
7
8
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
ppm

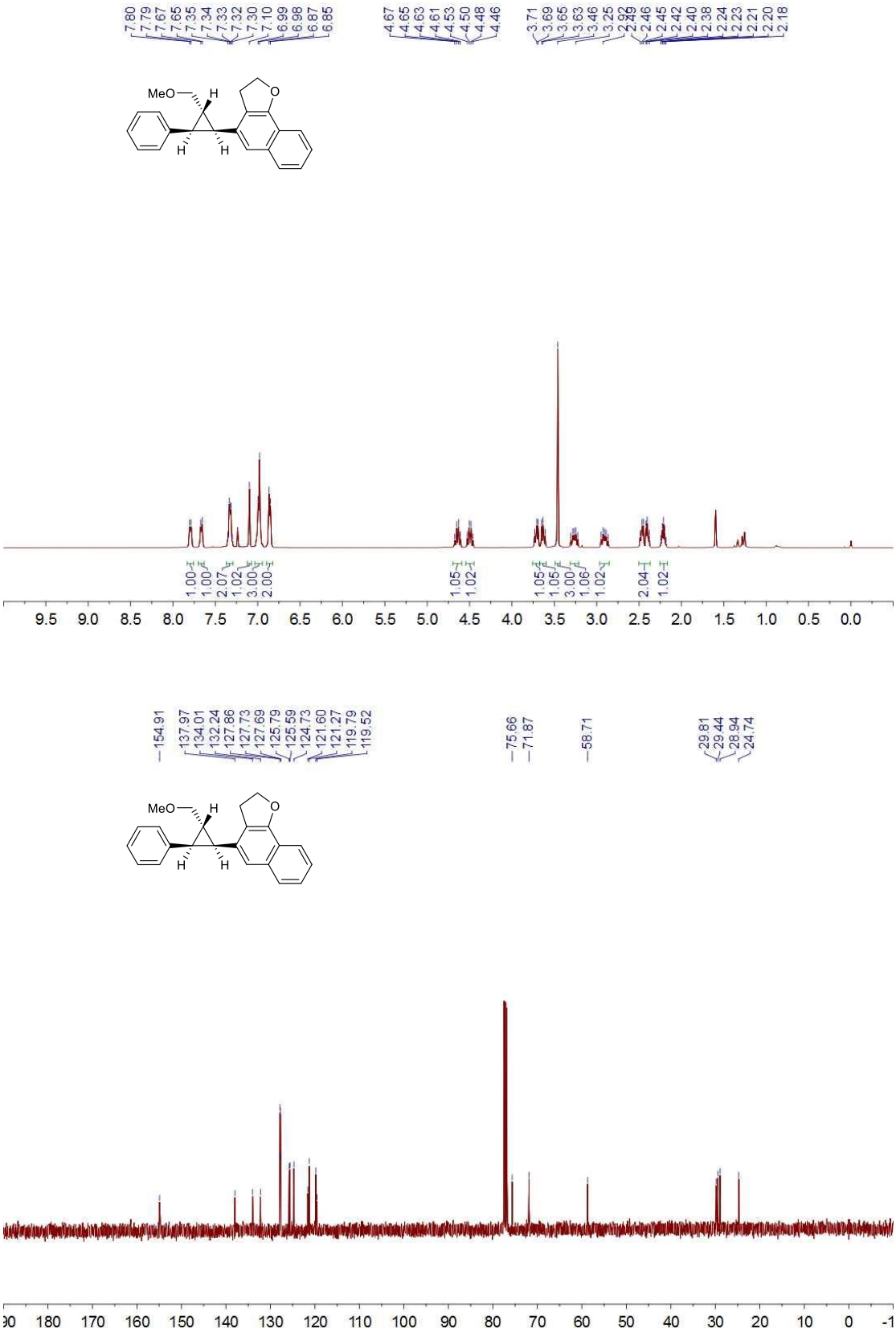
4-(2-bromo-2-phenylcyclopropyl)-2,3-dihydronaphtho[1,2-b]furan (3o)

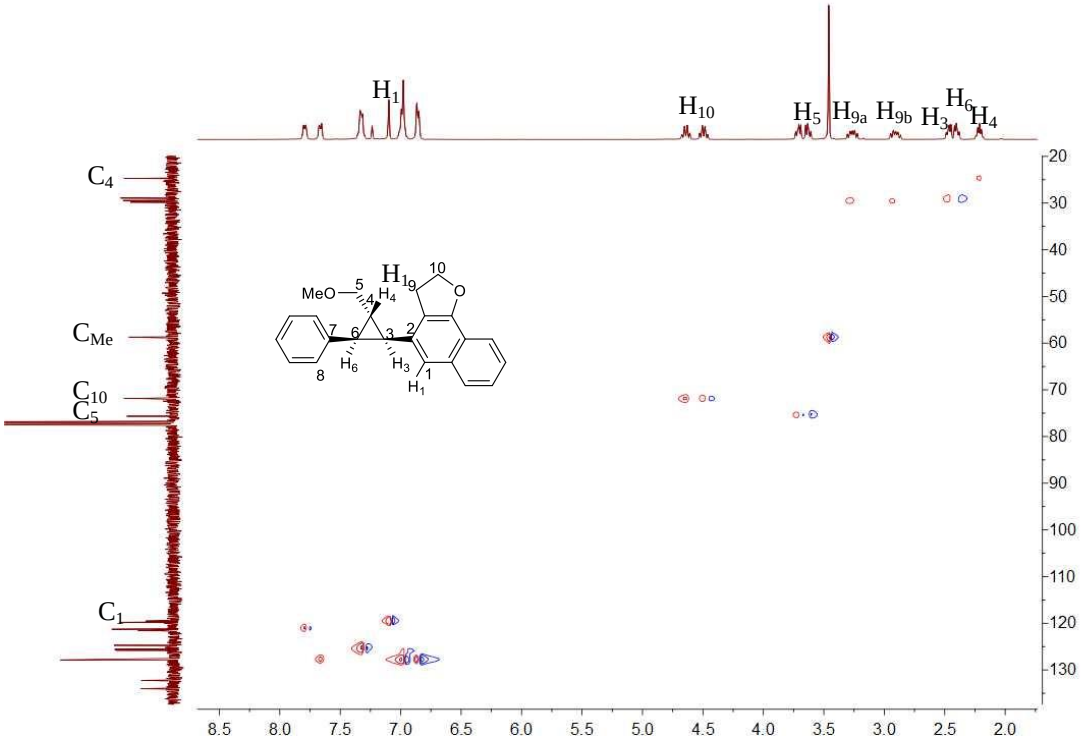


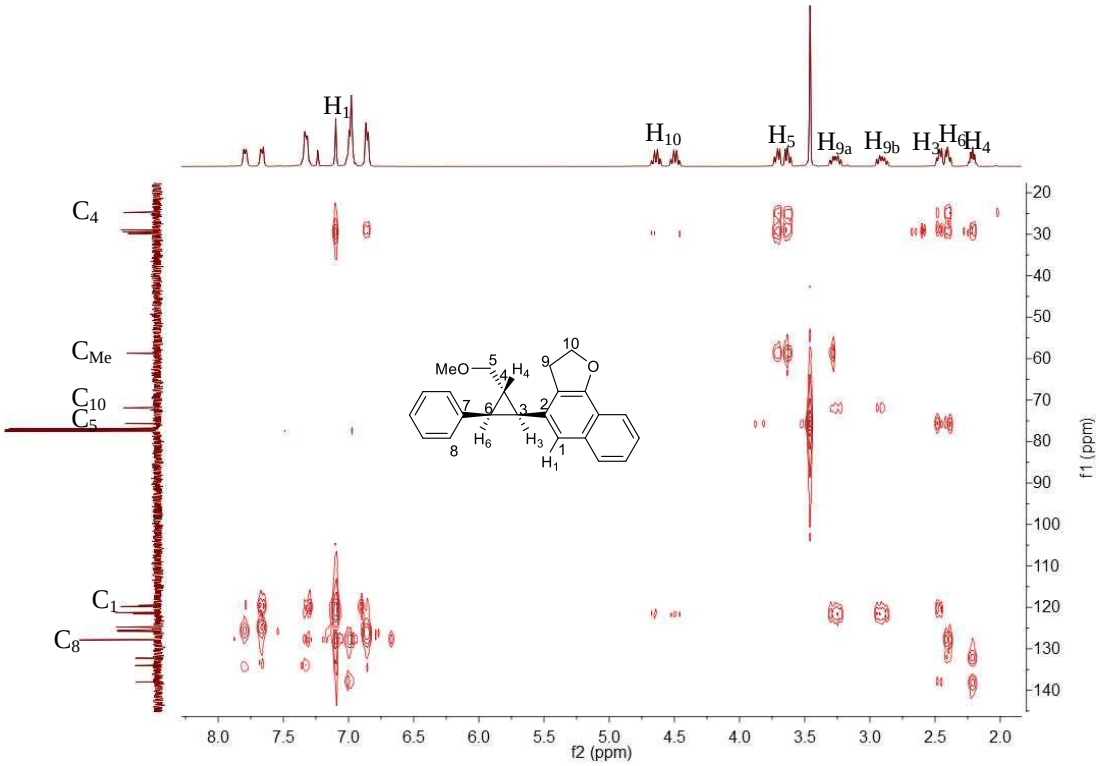
4-(2,2-diphenylcyclopropyl)-2,3-dihydronaphtho[1,2-b]furan (3p)

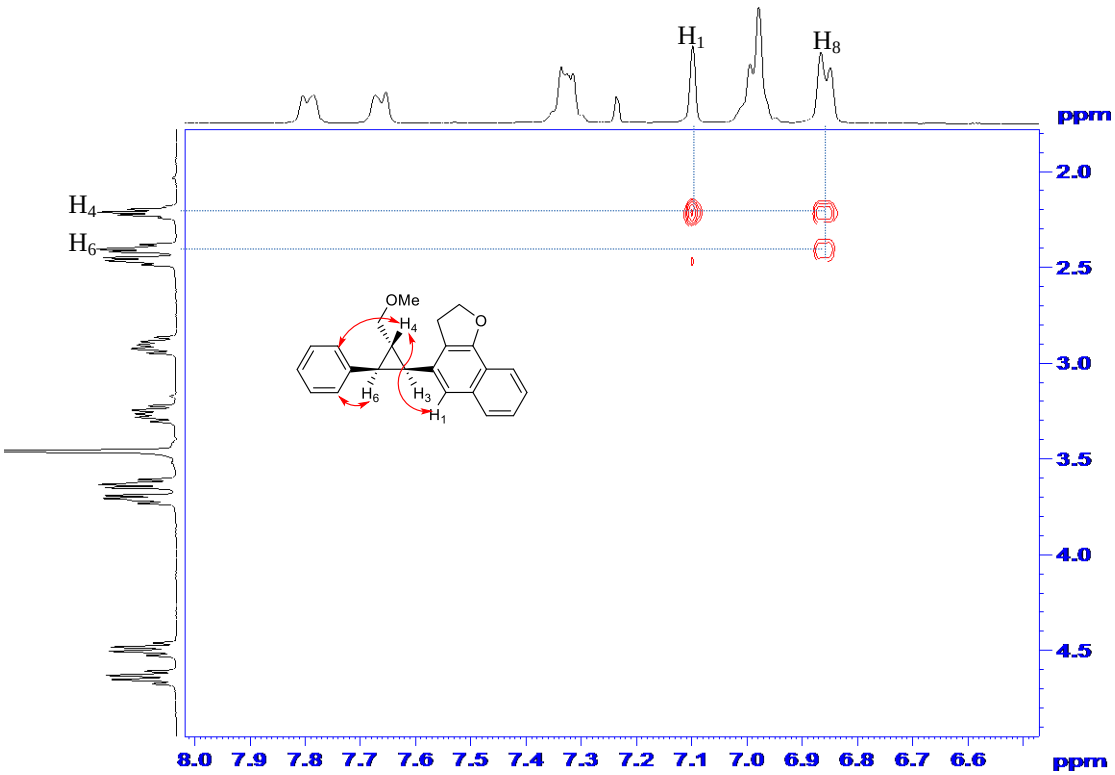


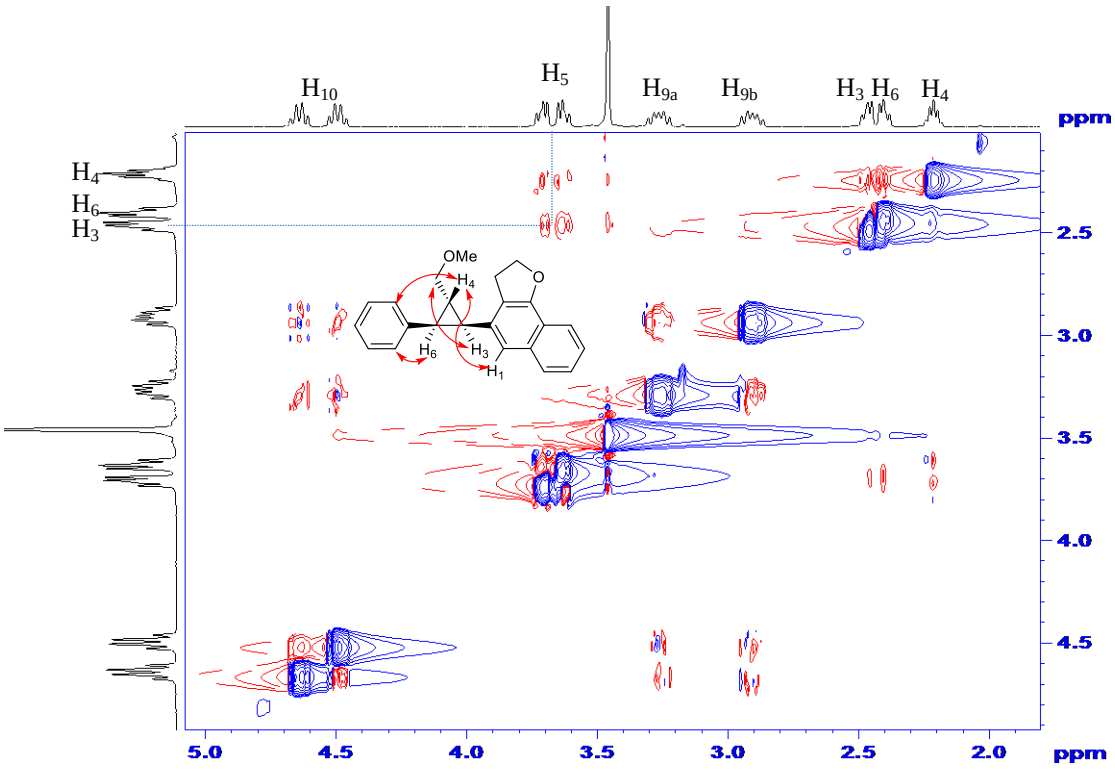
4-(2-(methoxymethyl)-3-phenylcyclopropyl)-2,3-dihydronaphtho[1,2-b]furan (3q)



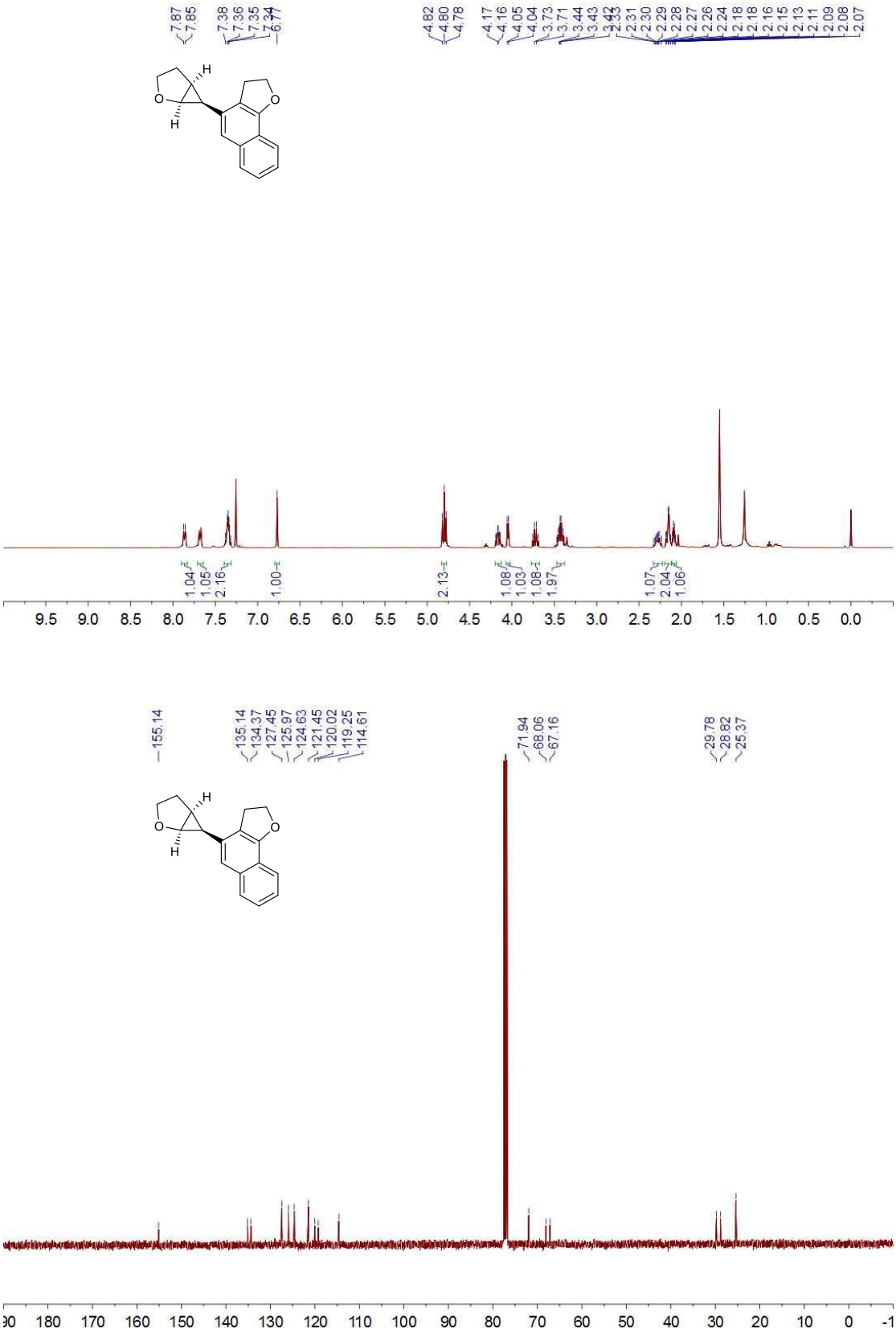

H1
H10
H5
H9a
H9b
H3
H6
H4
C4
CMe
C10
C5
C1
MeO
H9
10
O
5
4
H4
7
6
3
2
H6
H3
8
1
H1
20
30
40
50
60
70
80
90
100
110
120
130
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0


H1
H10
H5
H9a
H9b
H3
H6
H4
C4
CMe
C10
C5
C1
C8
MeO
10
9
O
5
4
H4
7
6
3
2
H6
H3
8
1
H1
20
30
40
50
60
70
80
90
100
110
120
130
140
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f2 (ppm)
f1 (ppm)

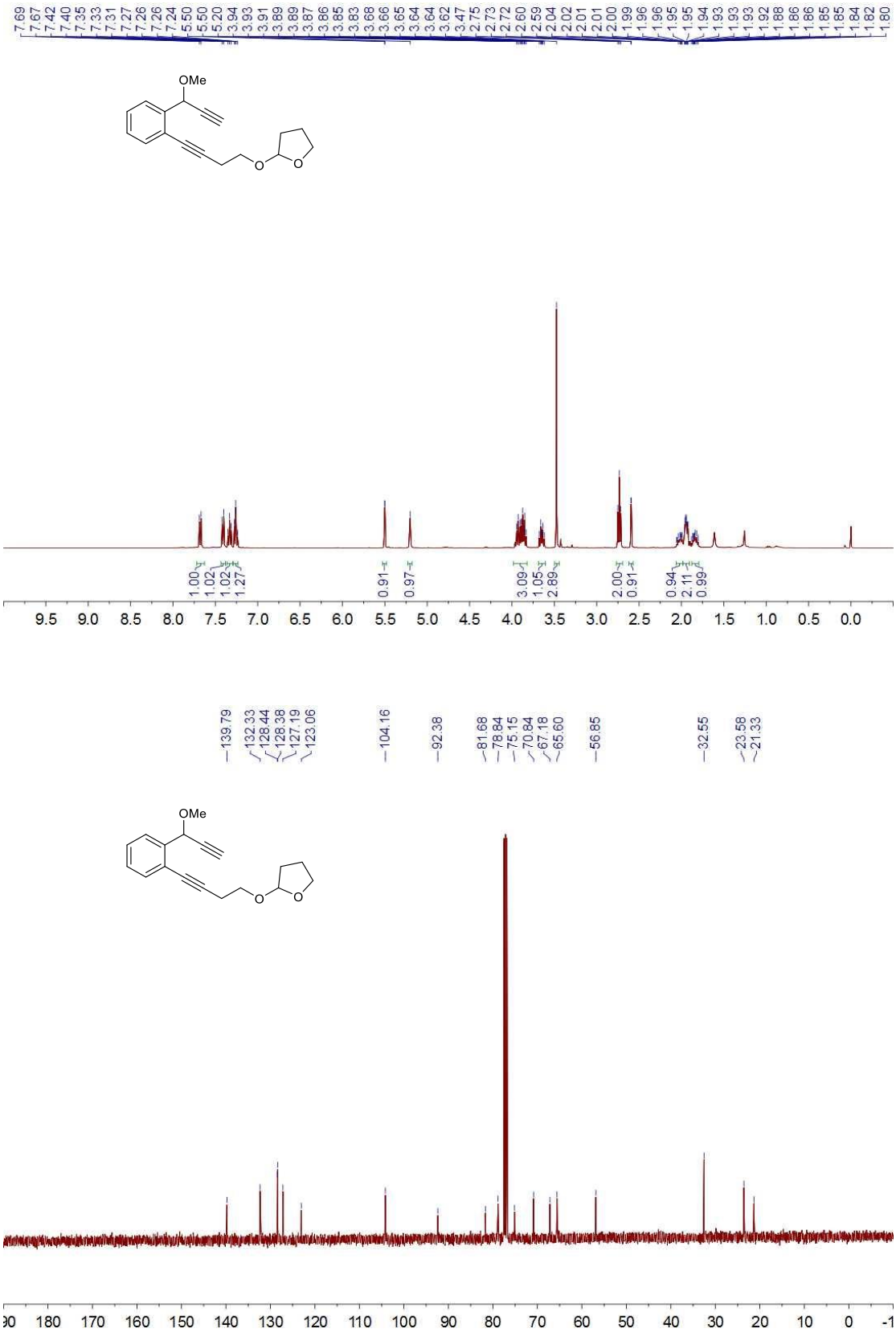

H1
H8
H4
H6
OMe
H4
O
H6
H3
H1
ppm
2.0
2.5
3.0
3.5
4.0
4.5
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6
ppm


H10
H5
H9a
H9b
H3 H6
H4
H4
H6
H3
OMe
H4
O
H6
H3
H1
ppm
2.5
3.0
3.5
4.0
4.5
5.0 4.5 4.0 3.5 3.0 2.5 2.0
ppm

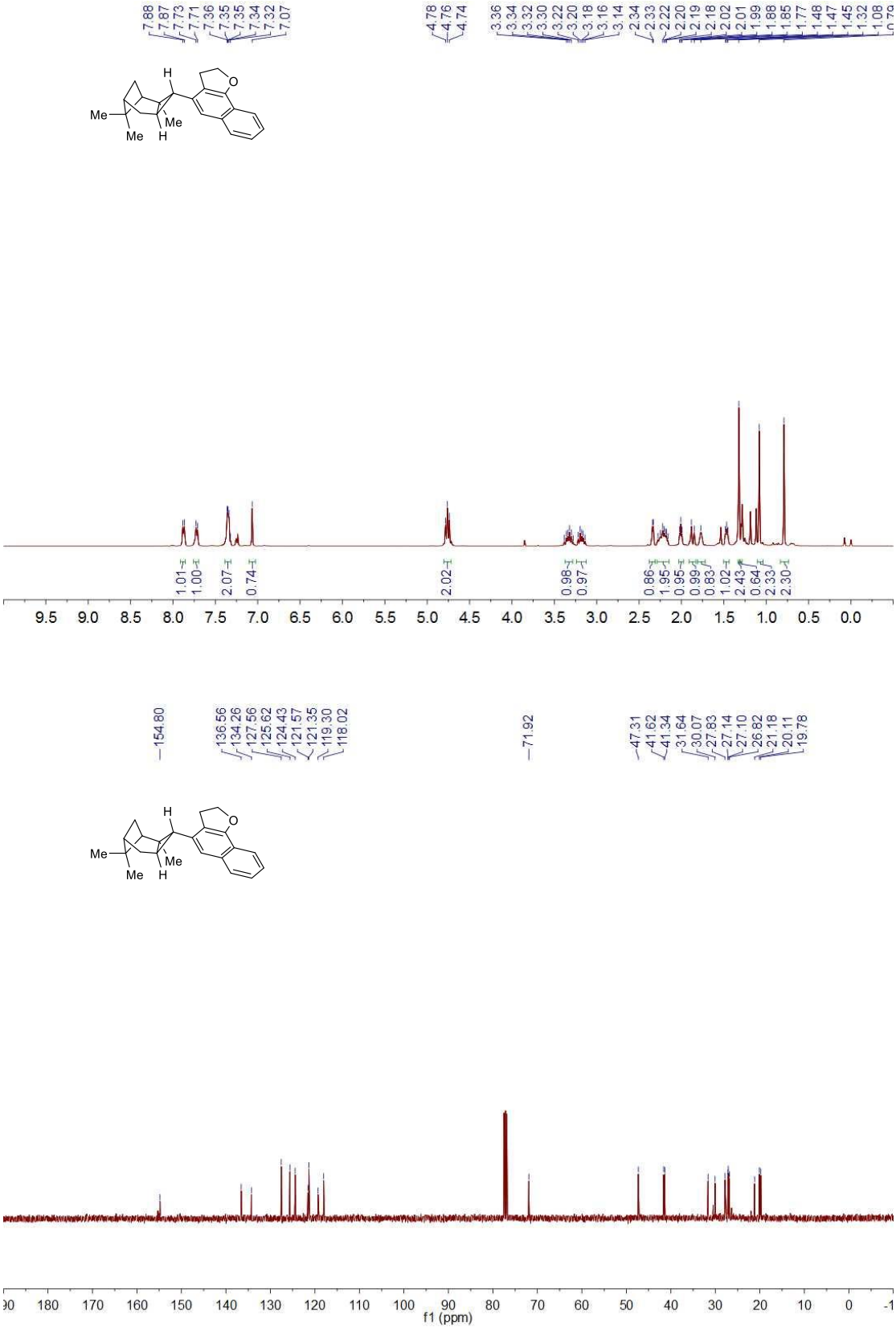
4-(2-oxabicyclo[3.1.0]hexan-6-yl)-2,3-dihydronaphtho[1,2-b]furan (3r)



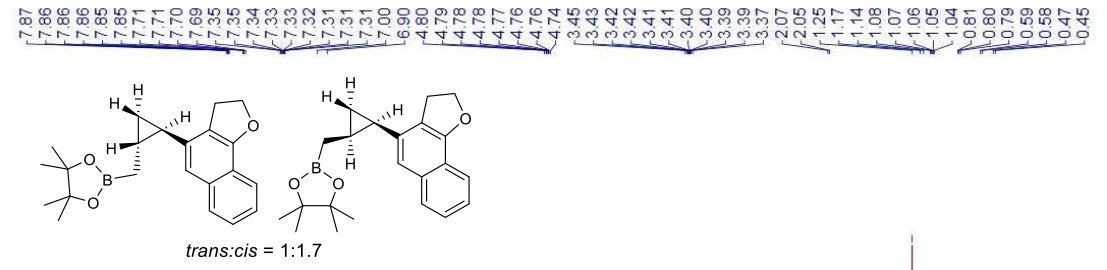
2-((4-(2-(1-methoxyprop-2-yn-1-yl)phenyl)but-3-yn-1-yl)oxy)tetrahydrofuran (3r')



4-(2,7,7-trimethyltricyclo[4.1.1.02,4]octan-3-yl)-2,3-dihydronaphtho[1,2-b]furan (3s)



2-((2-(2,3-dihydronaphtho[1,2-b]furan-4-yl)cyclopropyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3t)



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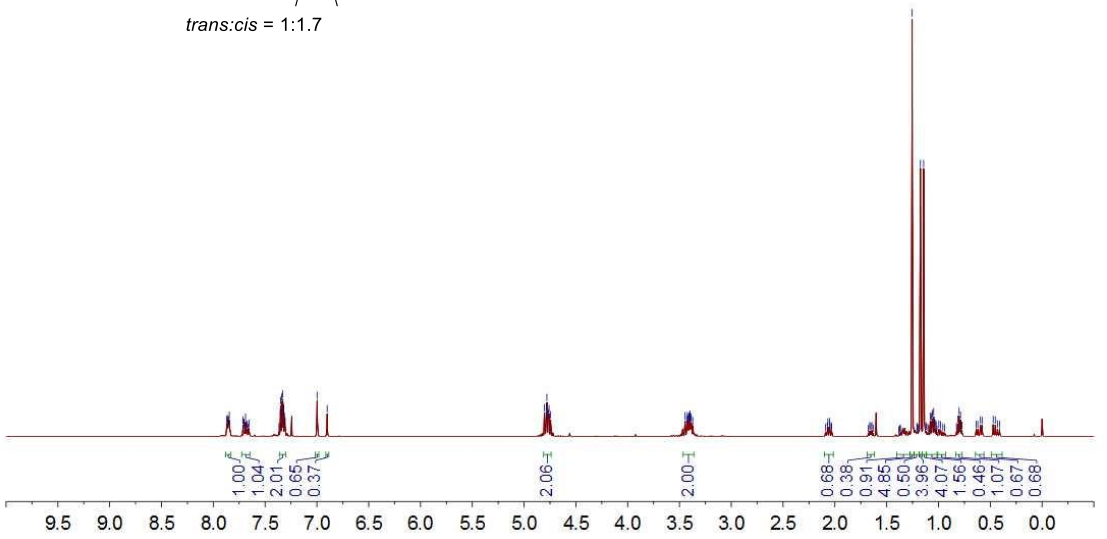
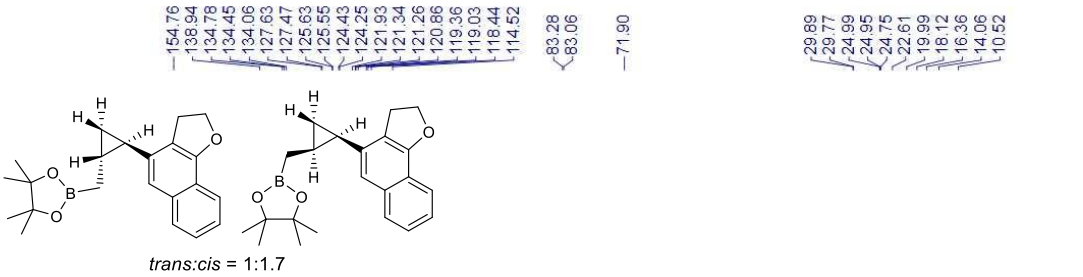
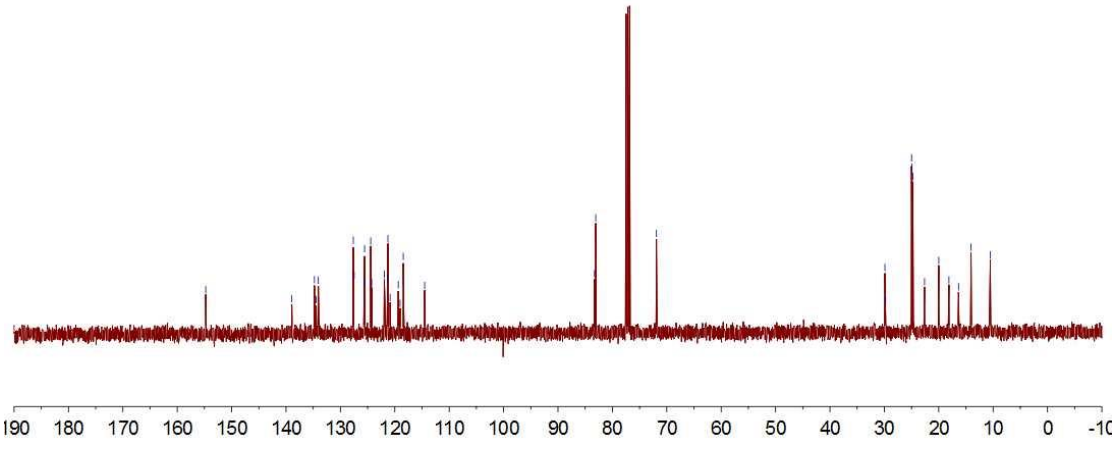
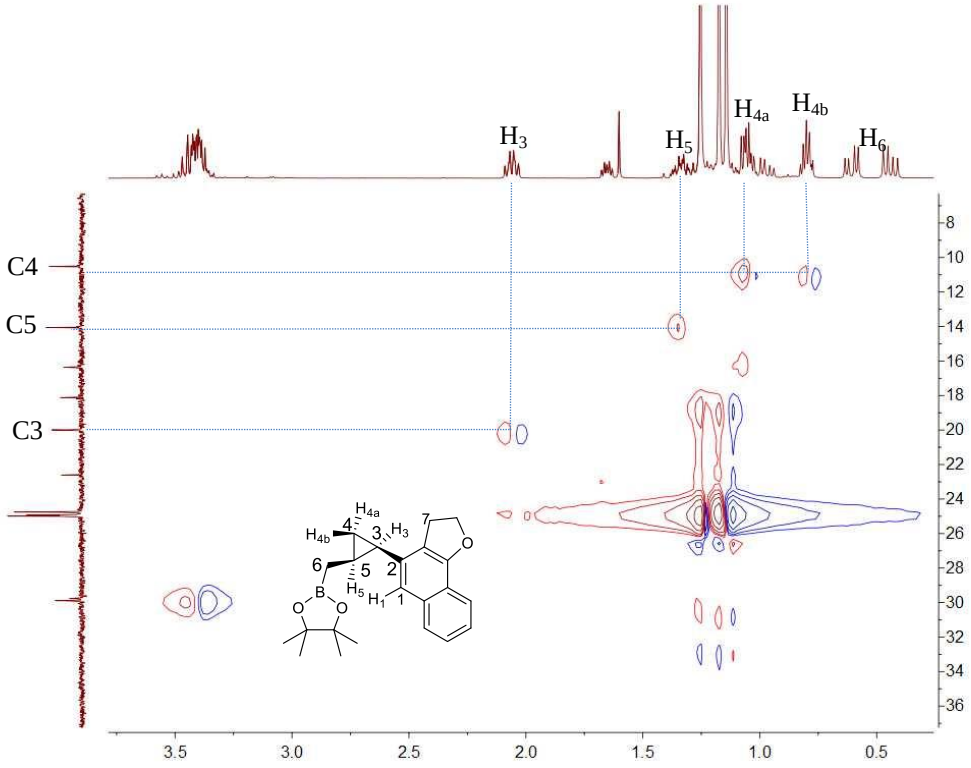
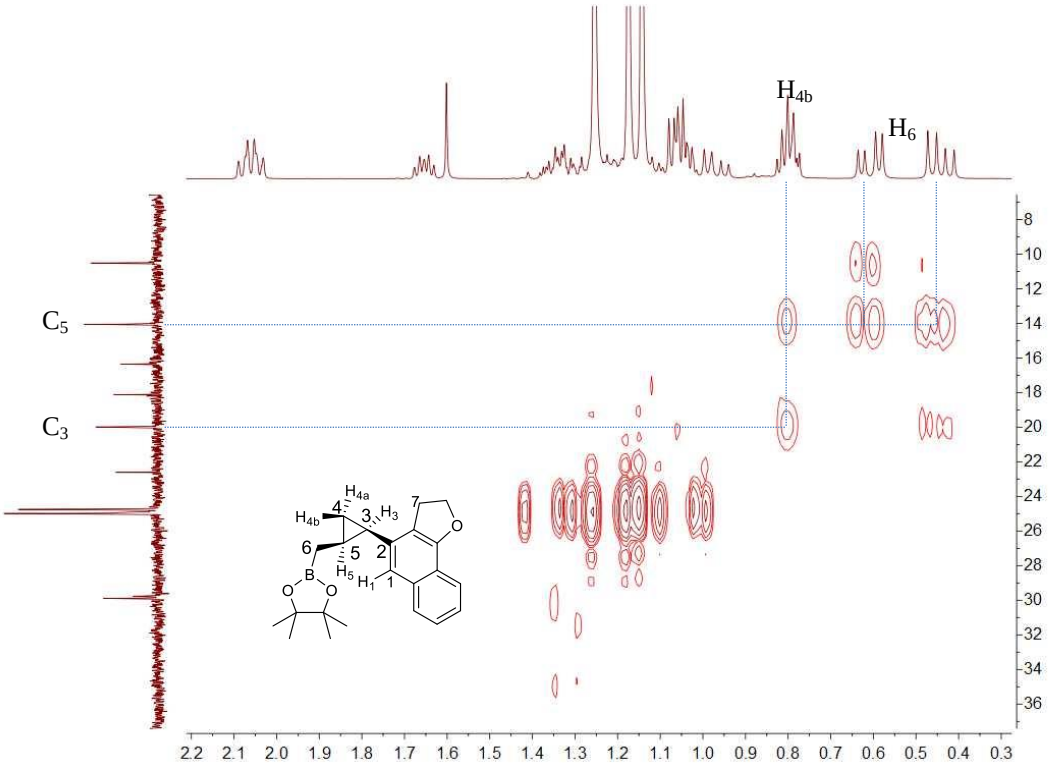


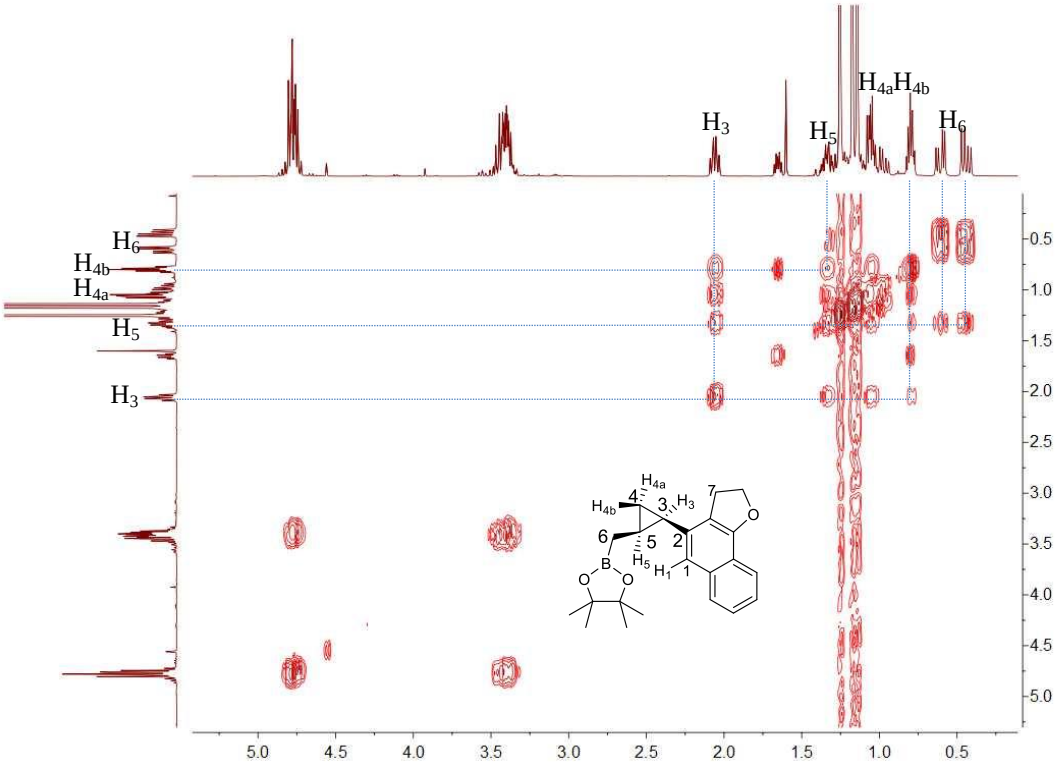


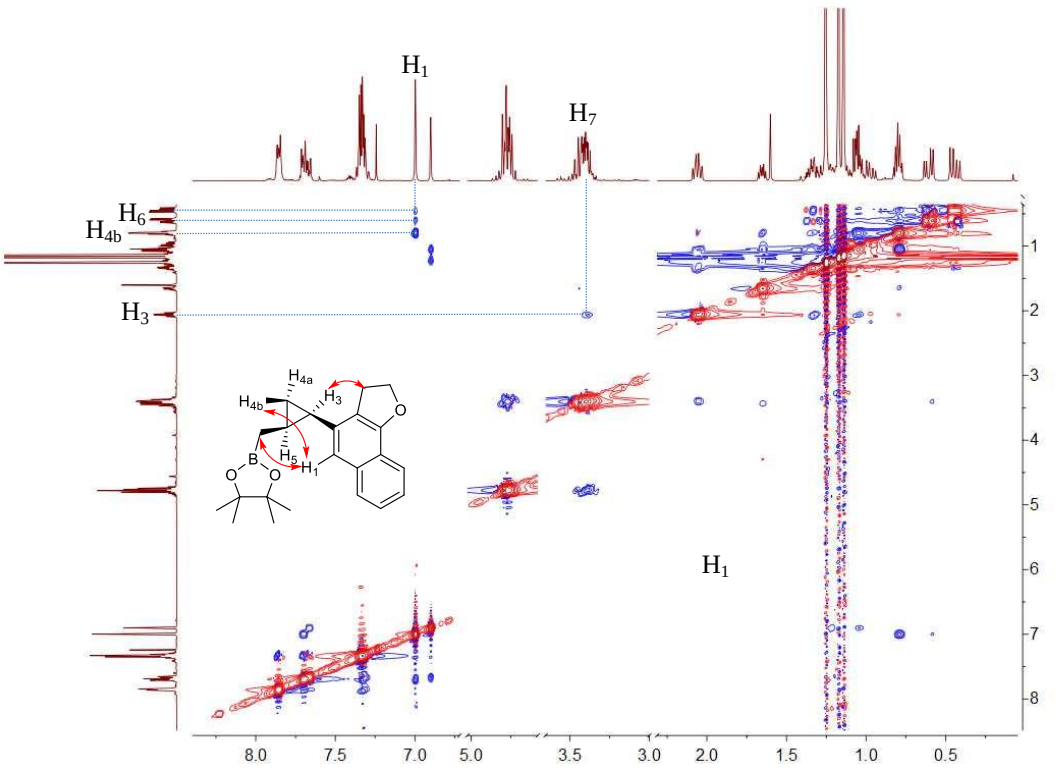
trans:cis = 1:1.7



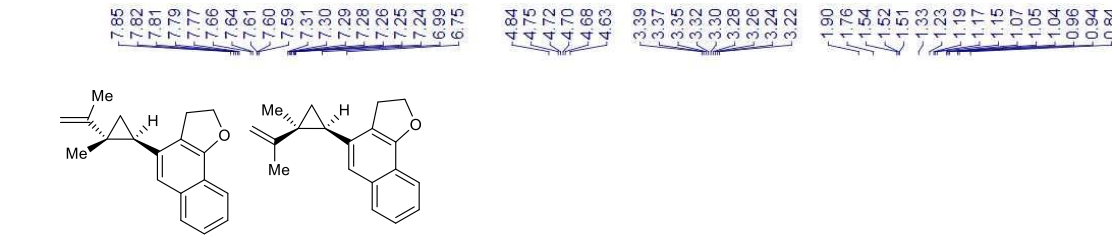

H3
H5
H4a
H4b
H6
C4
C5
C3
H4a
H4b
4
3
H3
7
O
6
5
2
H5
H1
1
B
O
O
8
10
12
14
16
18
20
22
24
26
28
30
32
34
36
3.5
3.0
2.5
2.0
1.5
1.0
0.5


H4b
H6
C5
C3
H4a
H4b
4
3
H3
7
O
6
5
2
H5
H1
1
B
O
O
8
10
12
14
16
18
20
22
24
26
28
30
32
34
36
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3


H3
H5
H4aH4b
H6
H6
H4b
H4a
H5
H3
4
3
7
6
5
2
1
O
B
O
O
H4a
H4b
H3
H5
H1
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


H1
H7
H6
H4b
H3
H4a
H4b
H3
H5
H1
O
B
O
O
H1
8.0
7.5
7.0
5.0
3.5
3.0
2.0
1.5
1.0
0.5

4-(2-methyl-2-(prop-1-en-2-yl)cyclopropyl)-2,3-dihydronaphtho[1,2-b]furan (3u)



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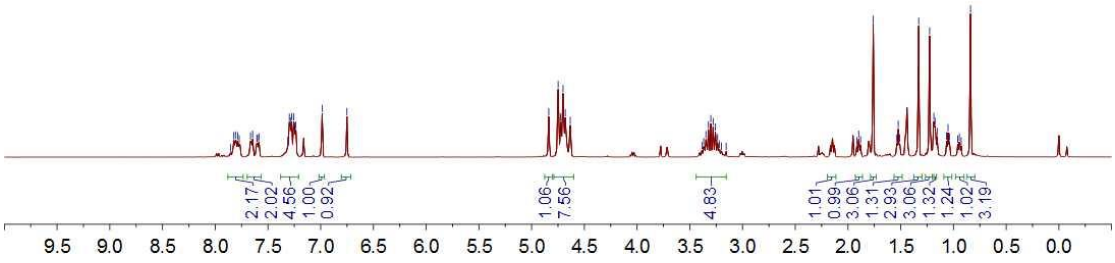
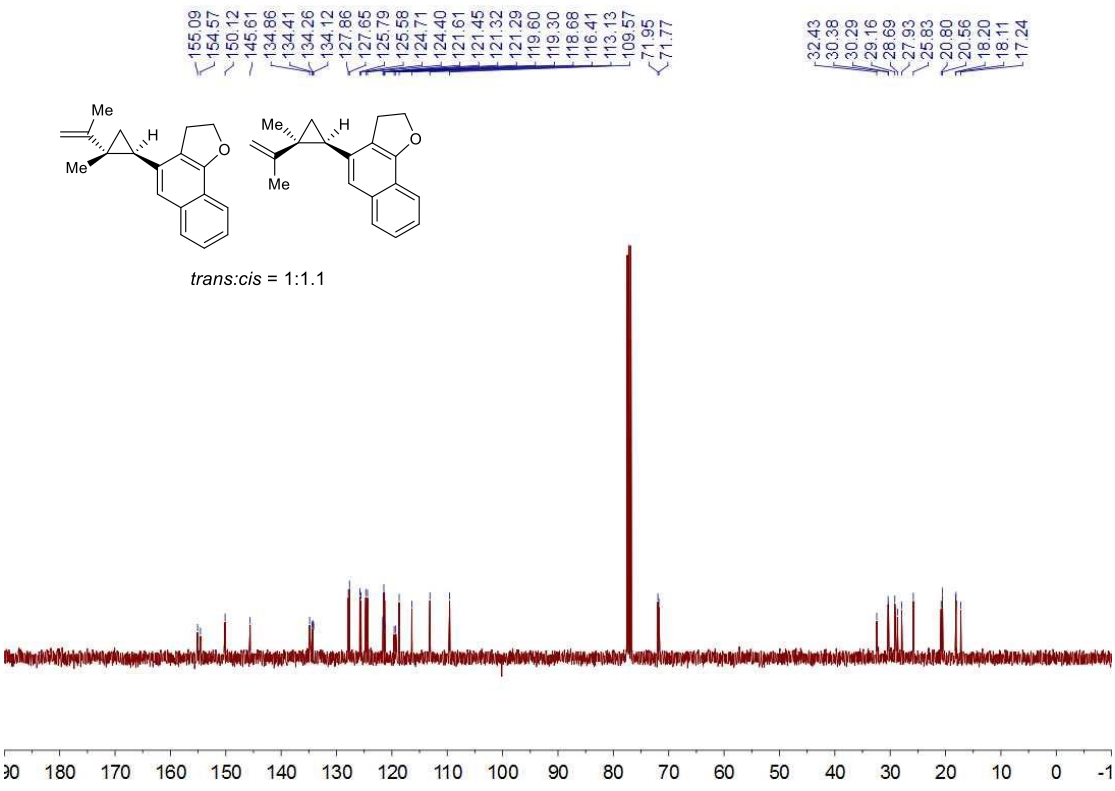
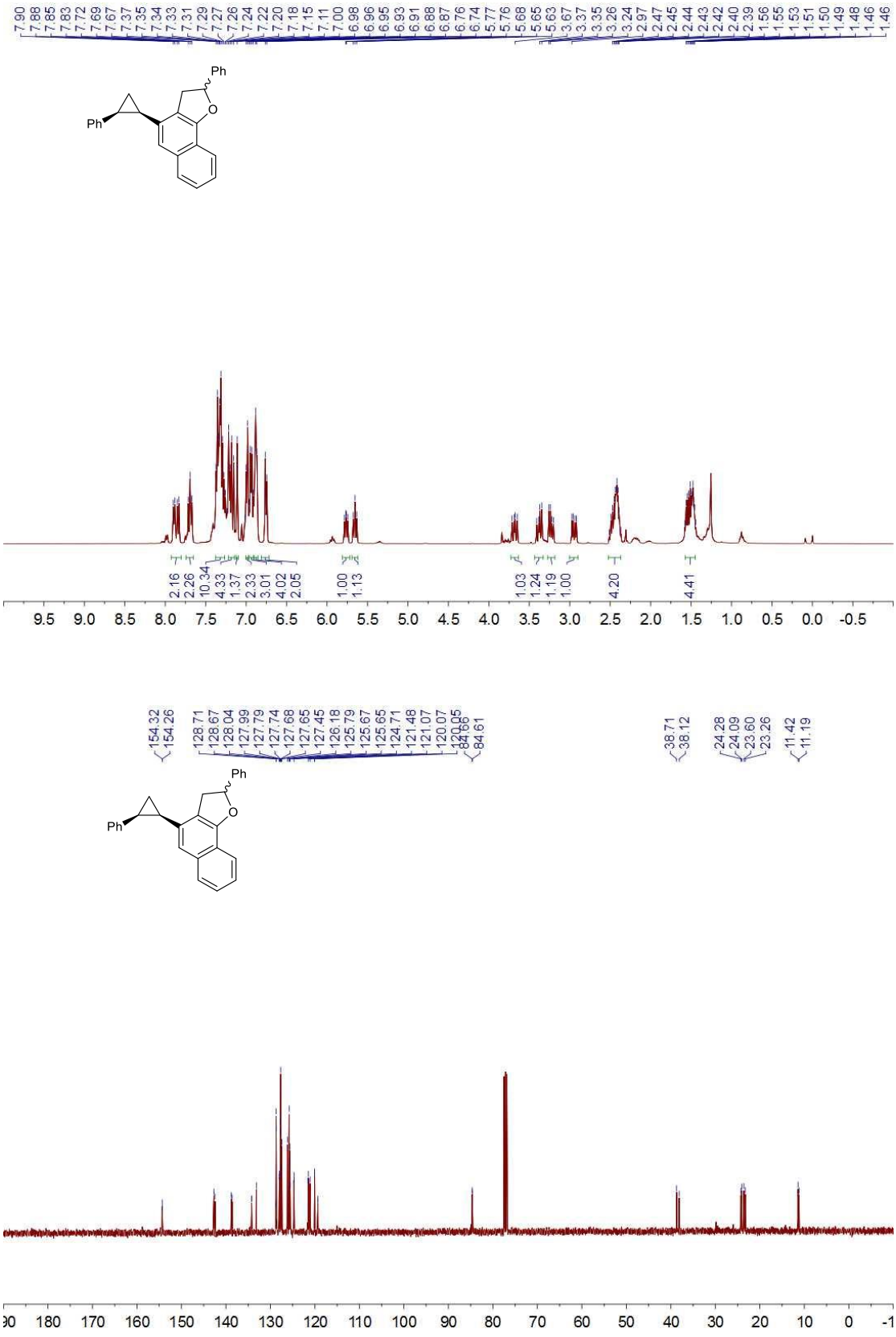


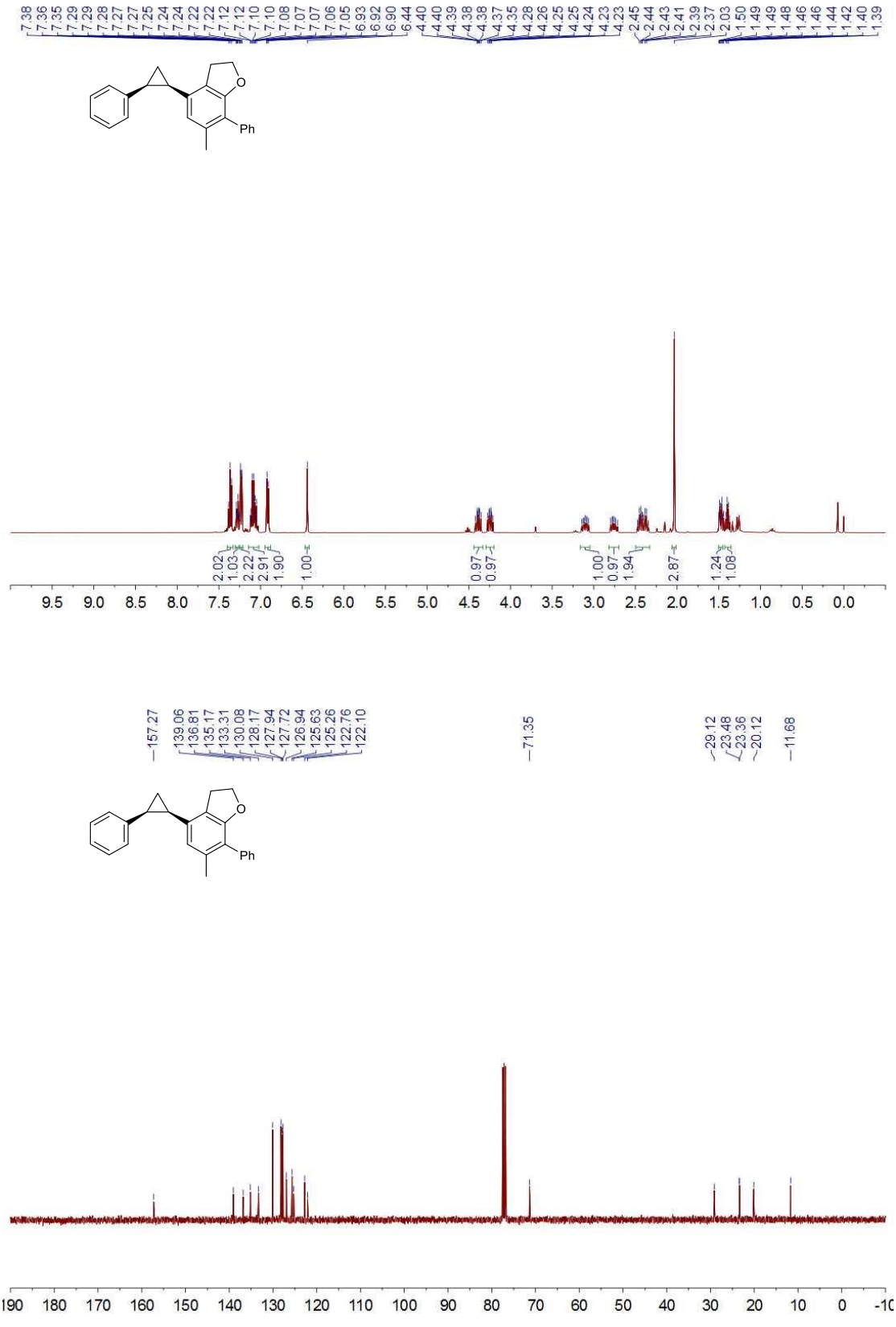


trans:cis = 1:1.1

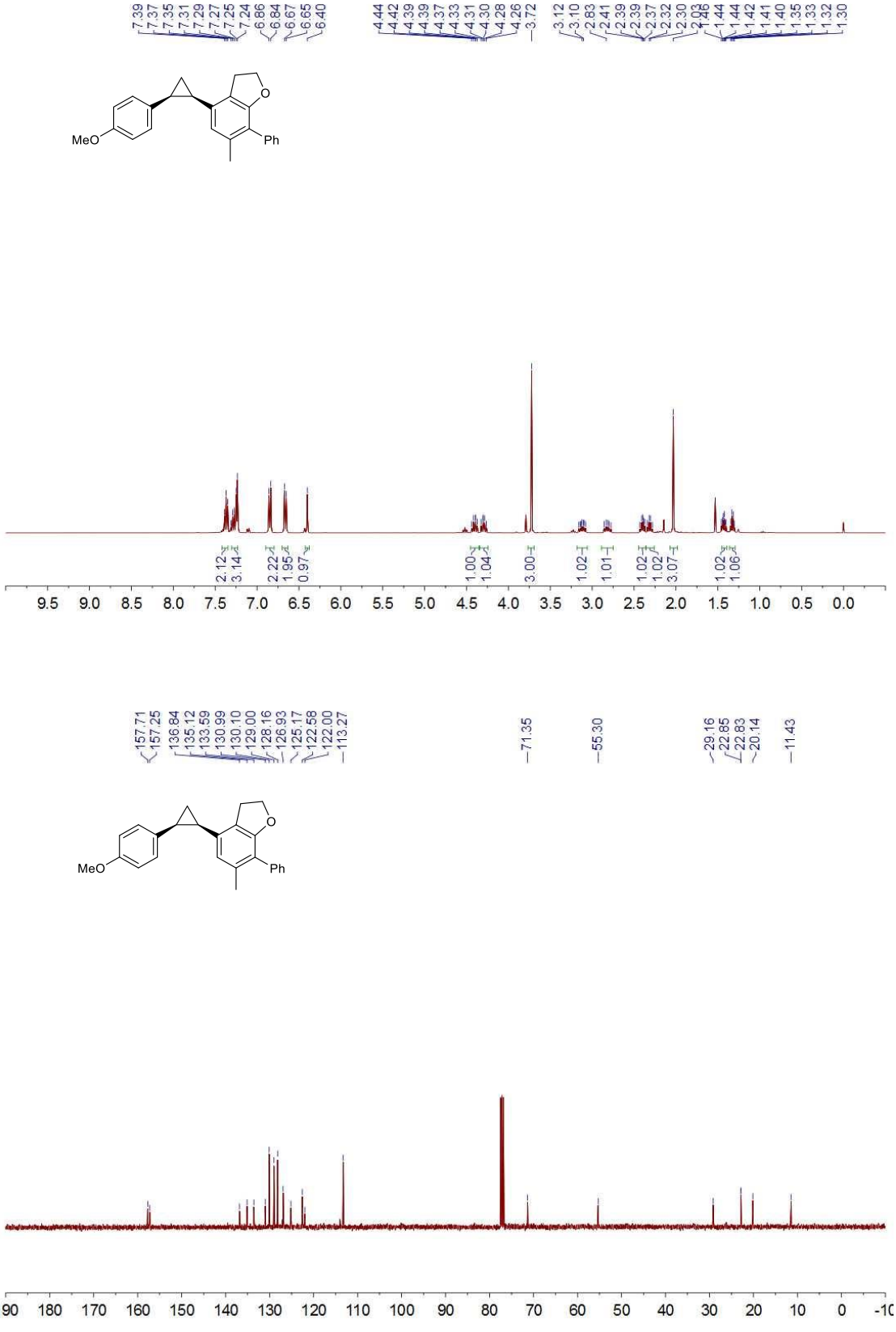
2-phenyl-4-(2-phenylcyclopropyl)-2,3-dihydronaphtho[1,2-b]furan (3v)



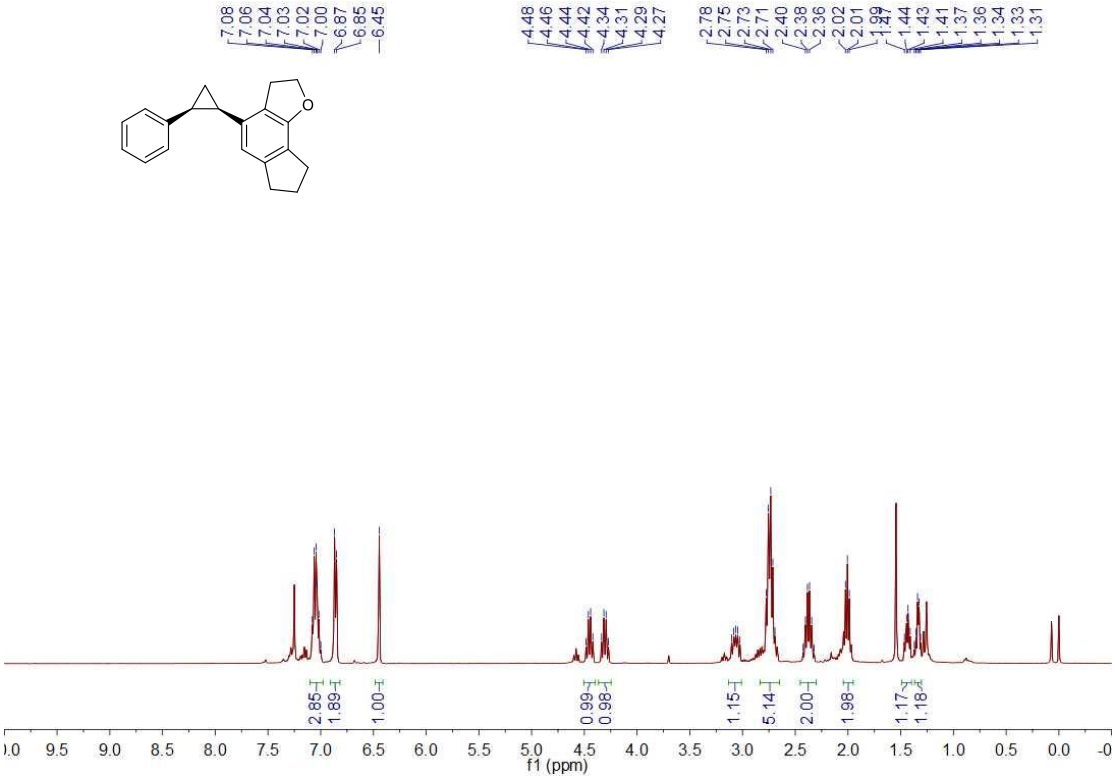
6-methyl-7-phenyl-4-(2-phenylcyclopropyl)-2,3-dihydrobenzofuran (3w)

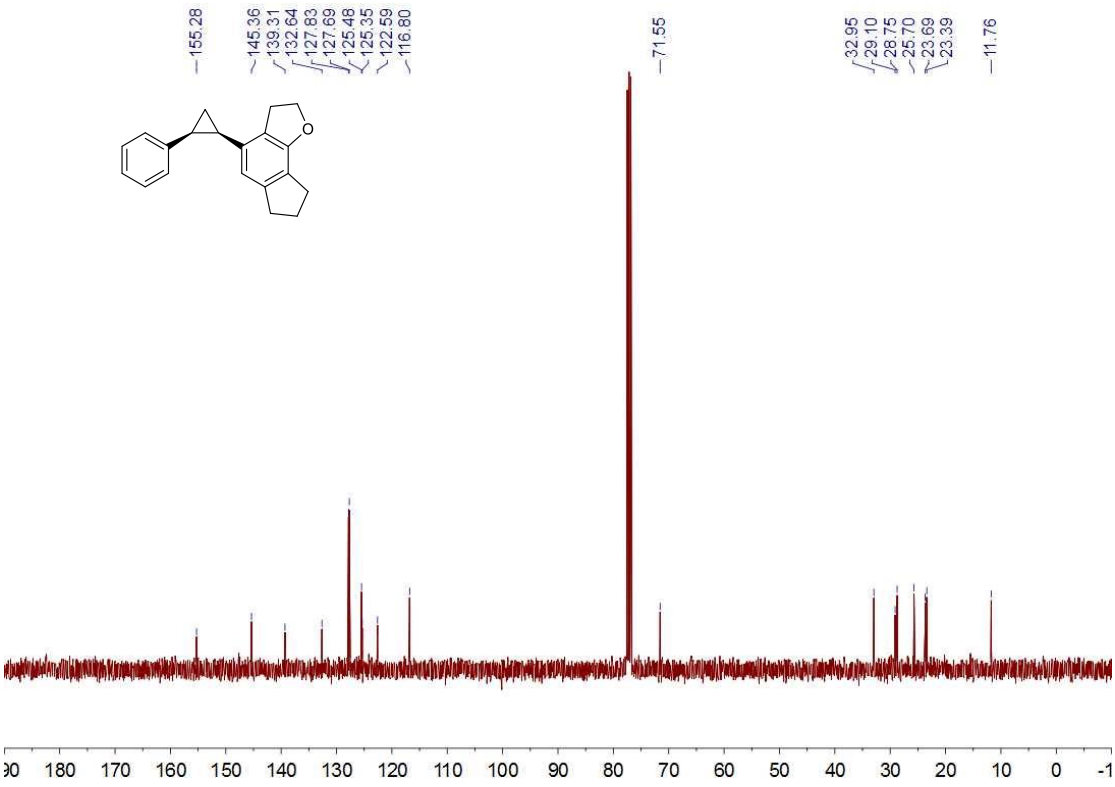


4-(2-(4-methoxyphenyl)cyclopropyl)-6-methyl-7-phenyl-2,3-dihydrobenzofuran (3x)

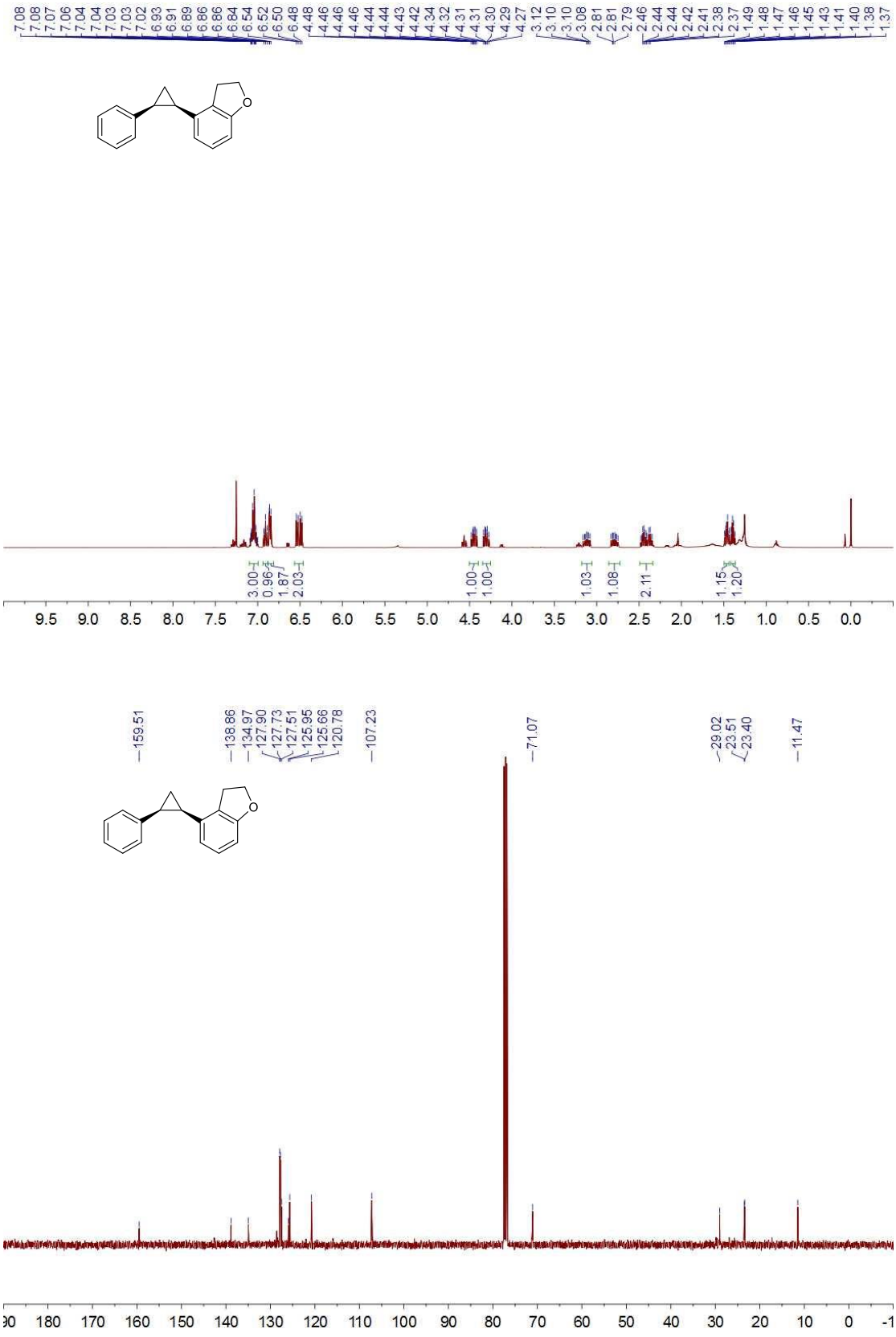


4-((1R,2S)-2-phenylcyclopropyl)-3,6,7,8-tetrahydro-2H-indeno[4,5-b]furan (3y)

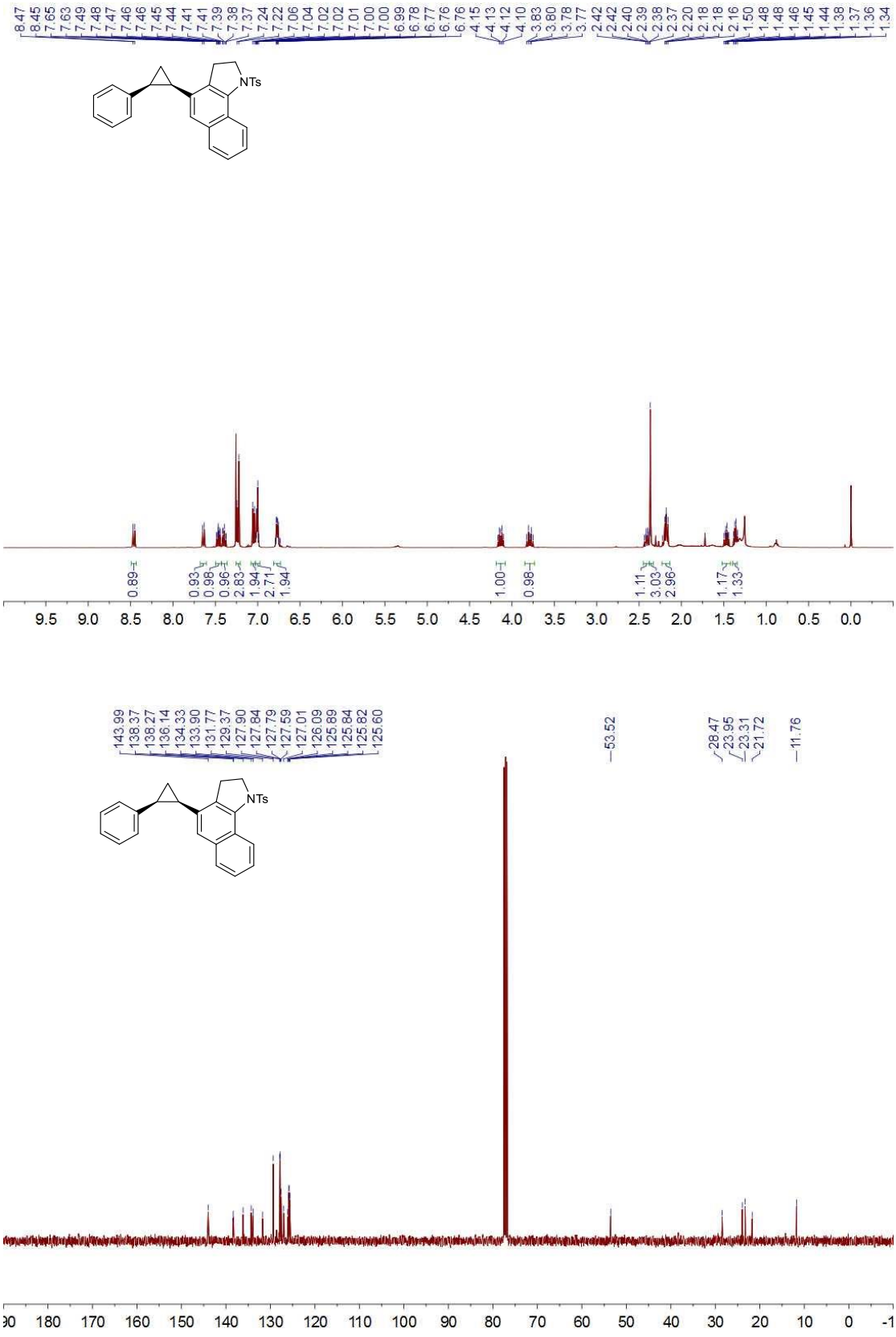




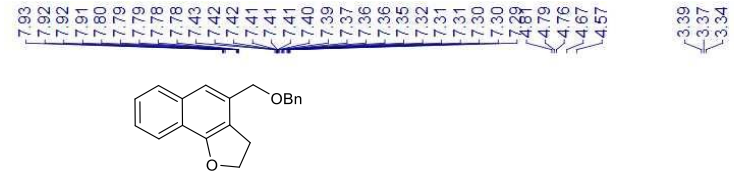
4-(2-phenylcyclopropyl)-2,3-dihydrobenzofuran (3z)

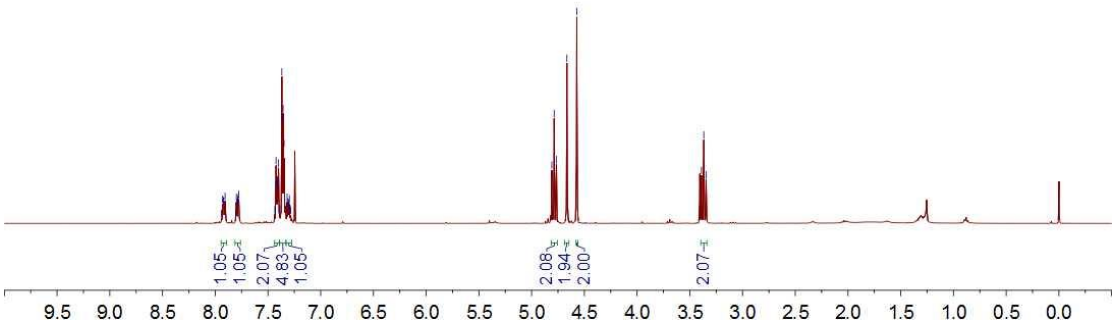


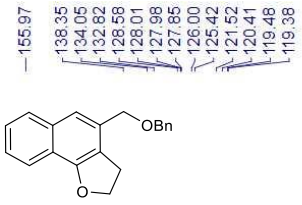
4-(2-phenylcyclopropyl)-1-tosyl-2,3-dihydro-1H-benzo[g]indole (3aa)

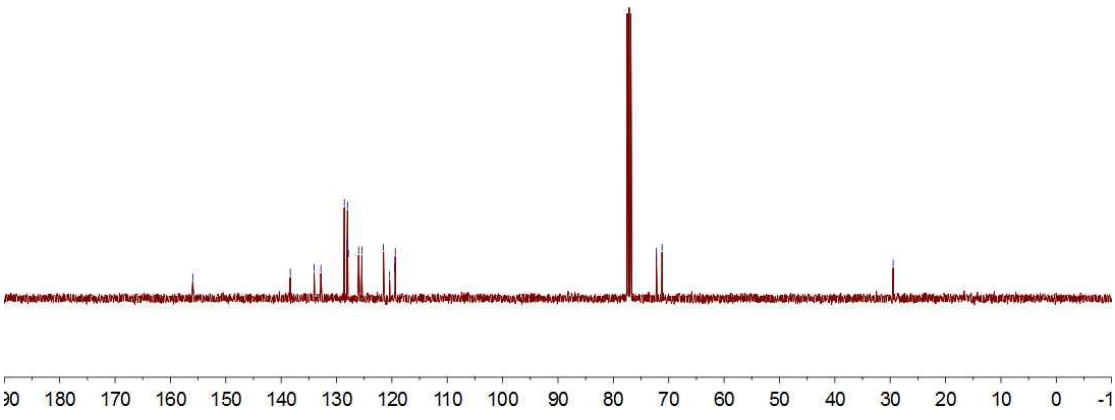


4-((benzyloxy)methyl)-2,3-dihydronaphtho[1,2-b]furan (5a)

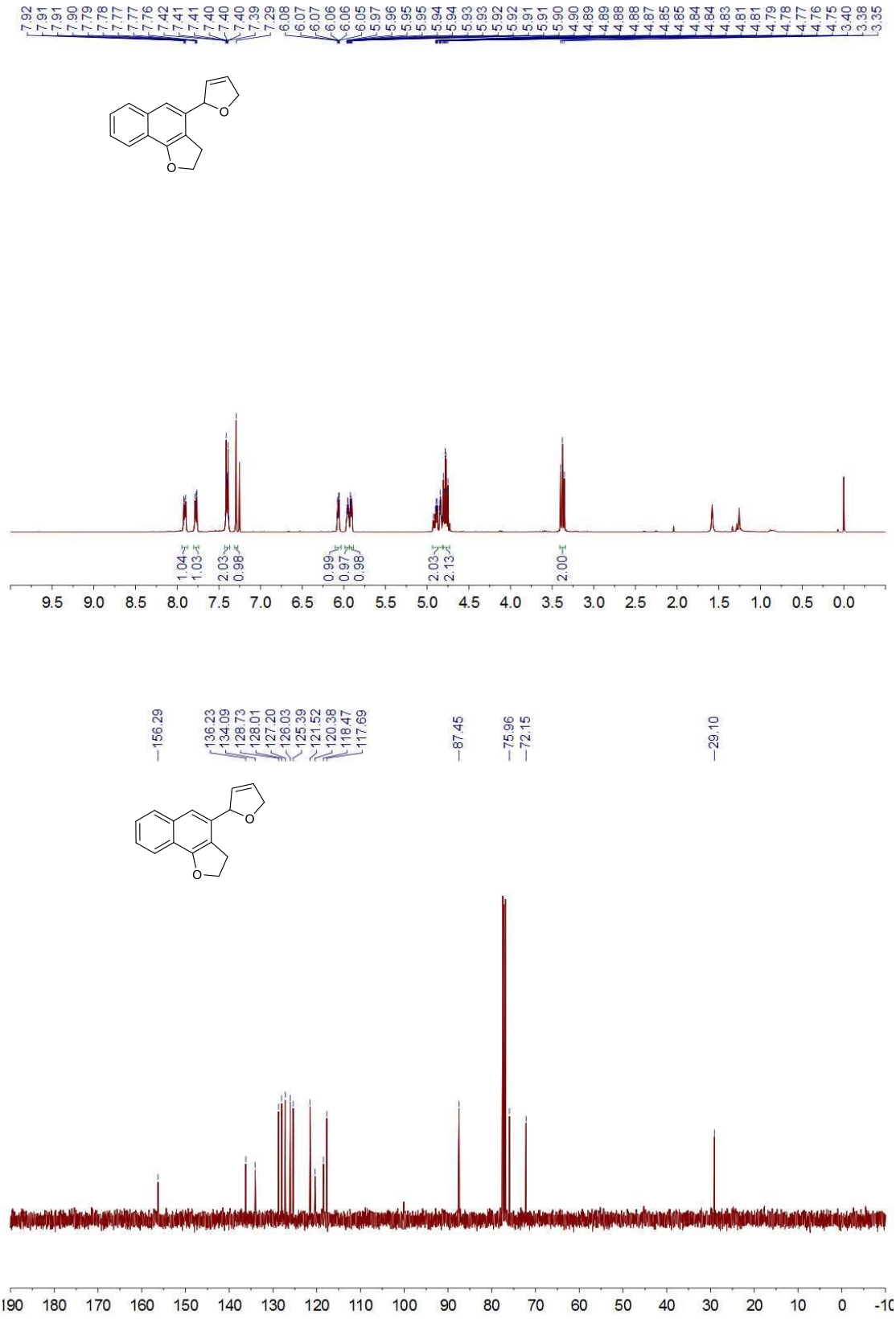


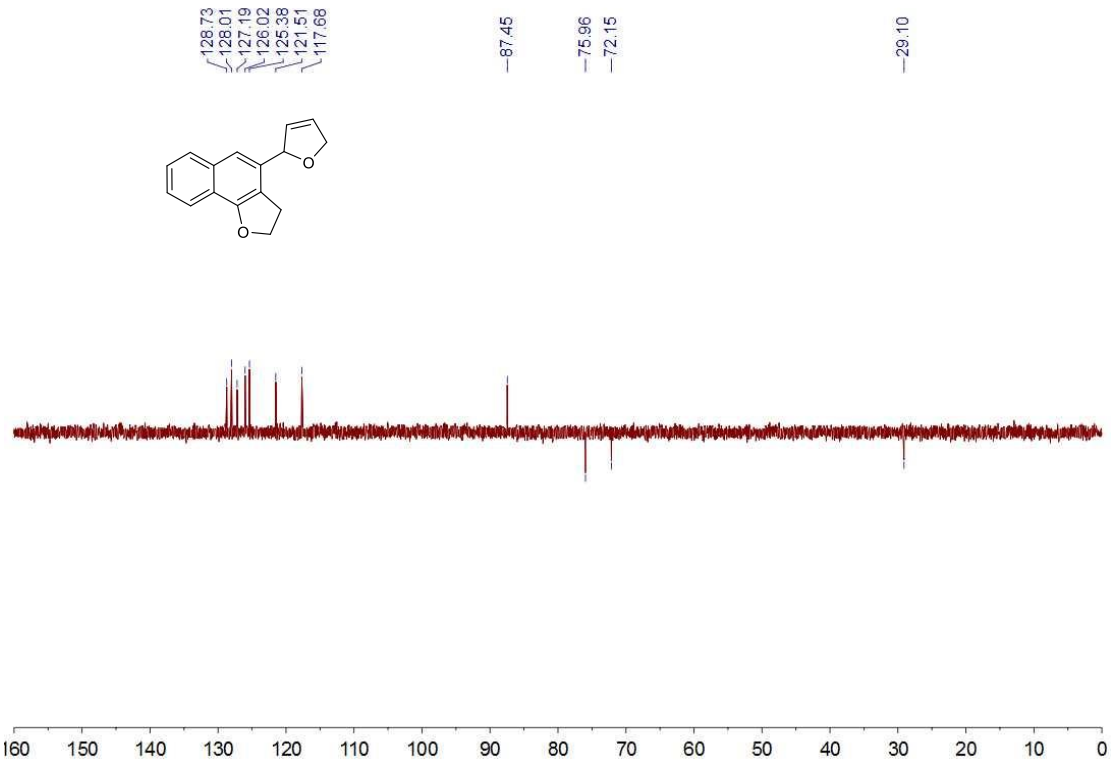


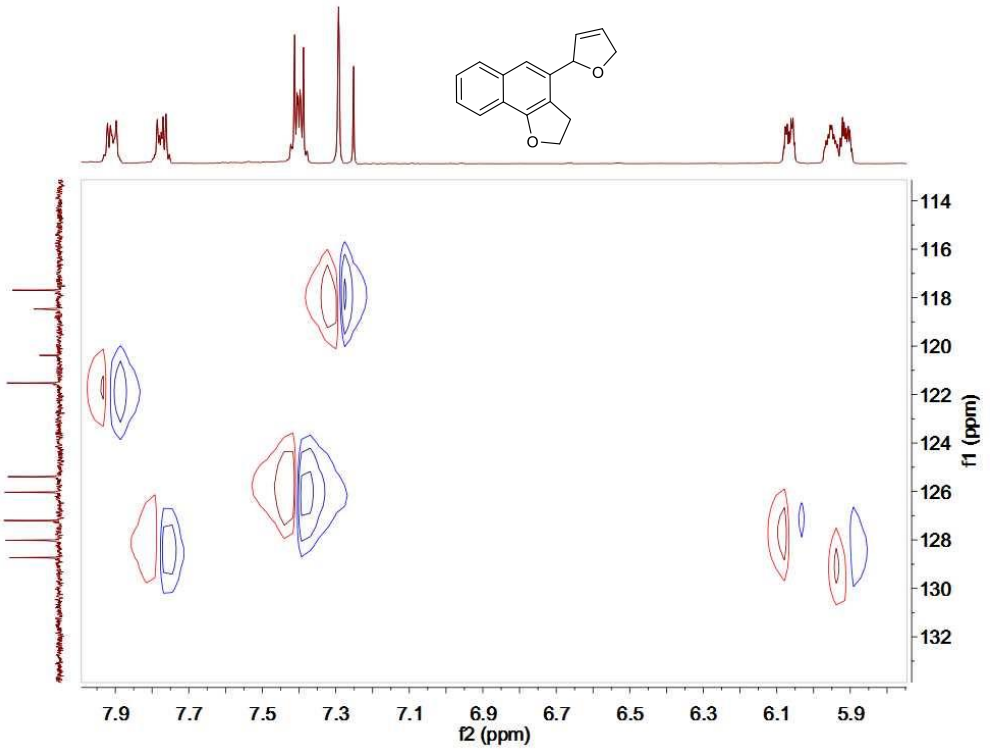




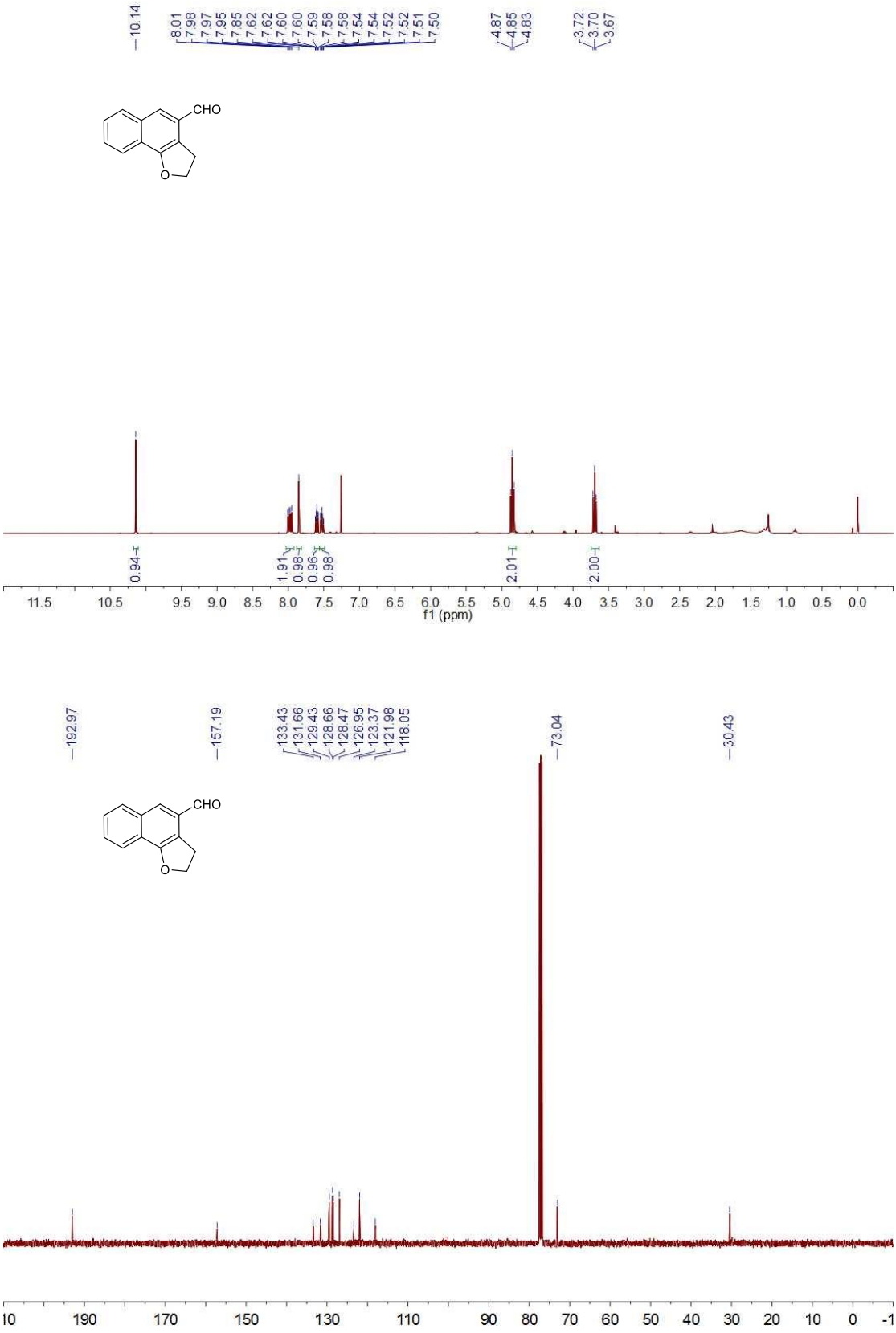
4-(2,5-dihydrofuran-2-yl)-2,3-dihydronaphtho[1,2-b]furan (5b)



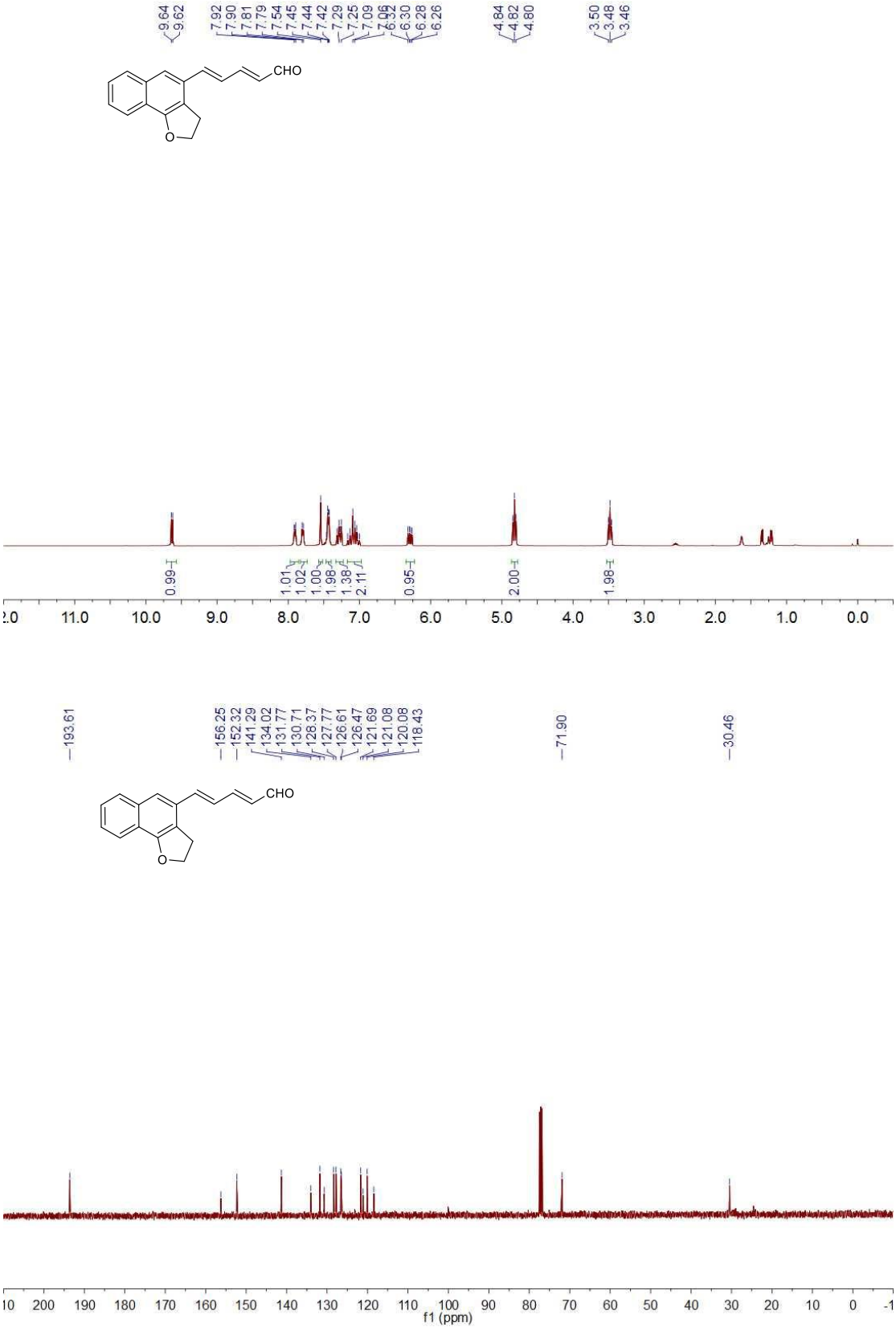

128.73
128.01
127.19
126.02
125.38
121.51
117.68
87.45
75.96
72.15
29.10
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


114
116
118
120
122
124
126
128
130
132
f1 (ppm)
7.9
7.7
7.5
7.3
7.1
6.9
6.7
6.5
6.3
6.1
5.9
f2 (ppm)

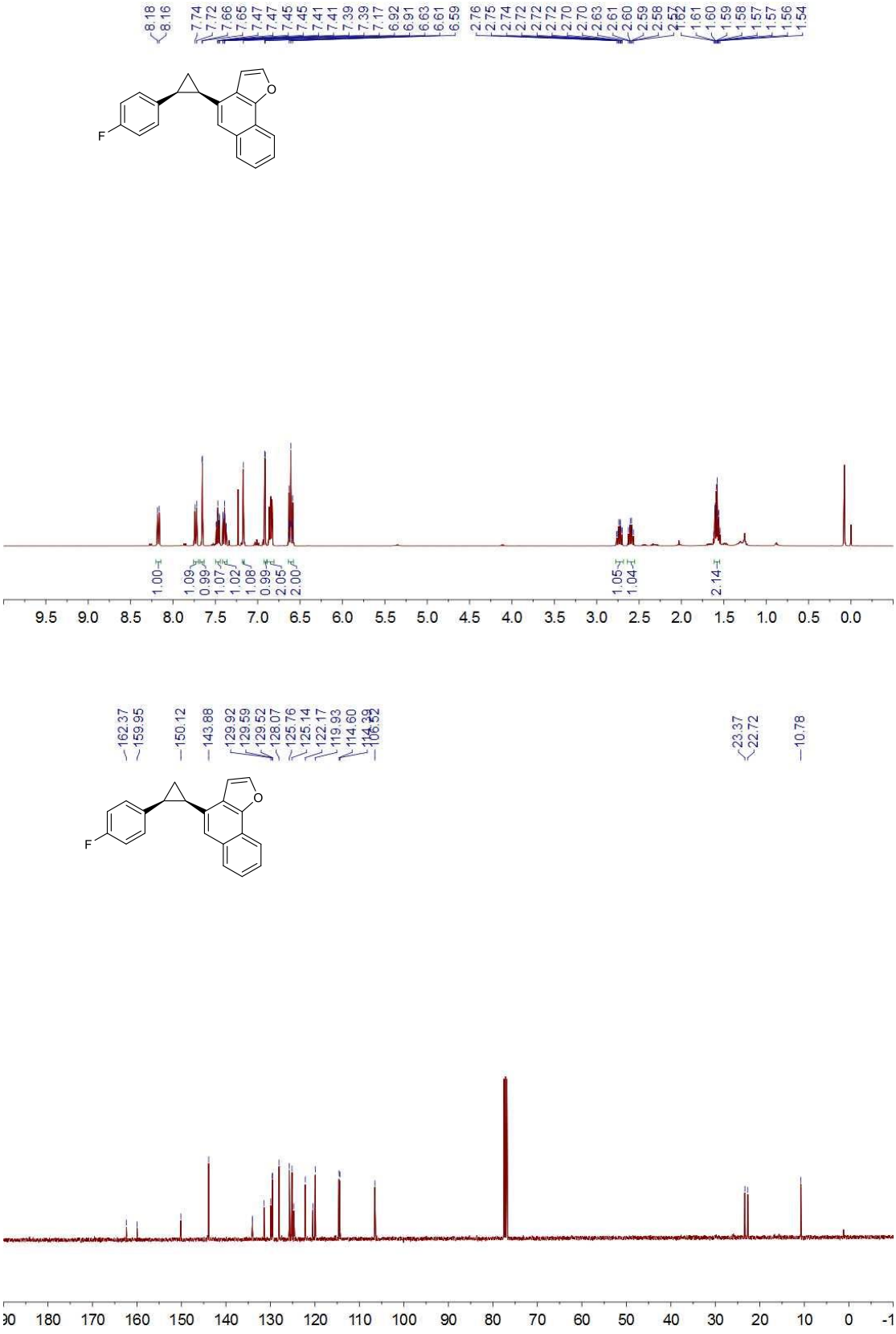
2,3-dihydronaphtho[1,2-b]furan-4-carbaldehyde (5c)



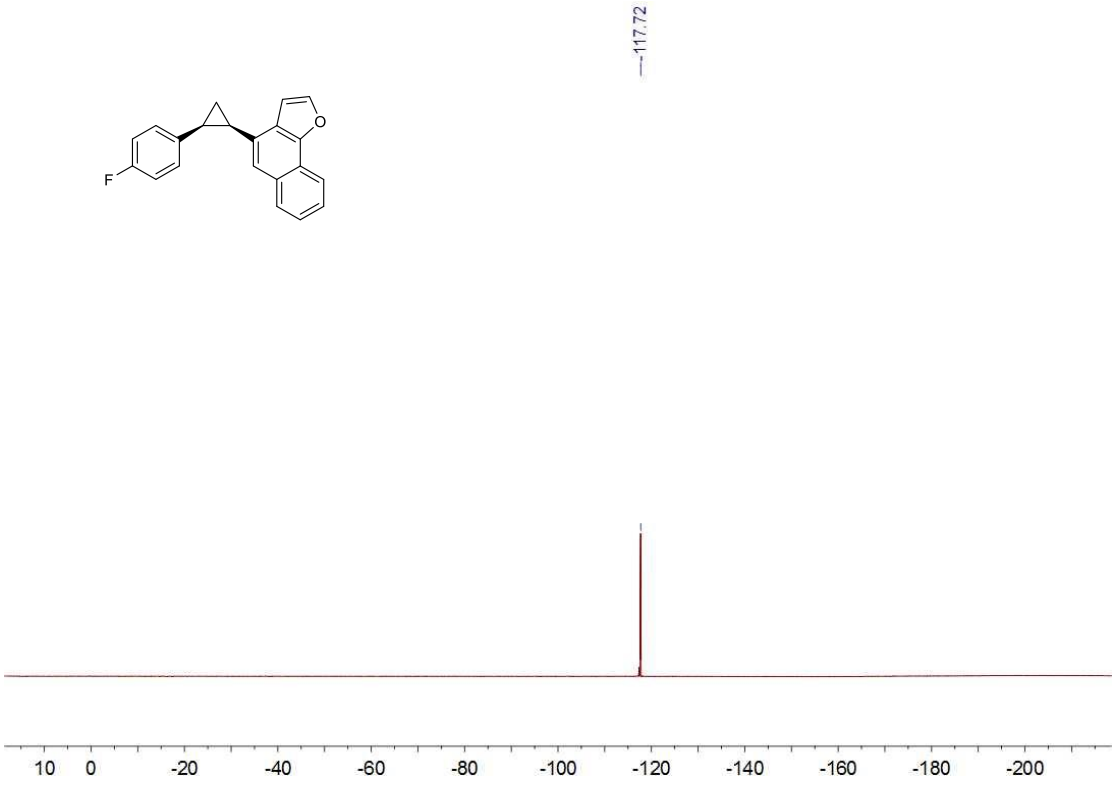
(2E,4E)-5-(2,3-dihydronaphtho[1,2-b]furan-4-yl)penta-2,4-dienal (5d)



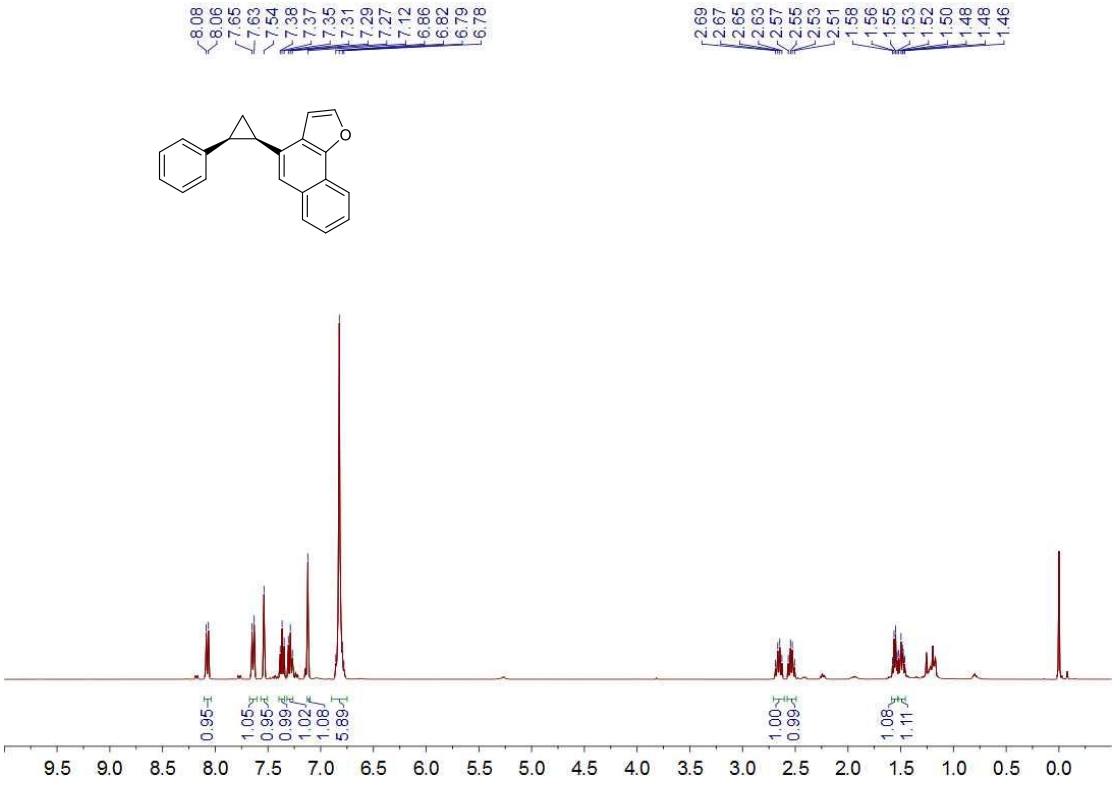
4-(2-(4-fluorophenyl)cyclopropyl)naphtho[1,2-b]furan (6a)

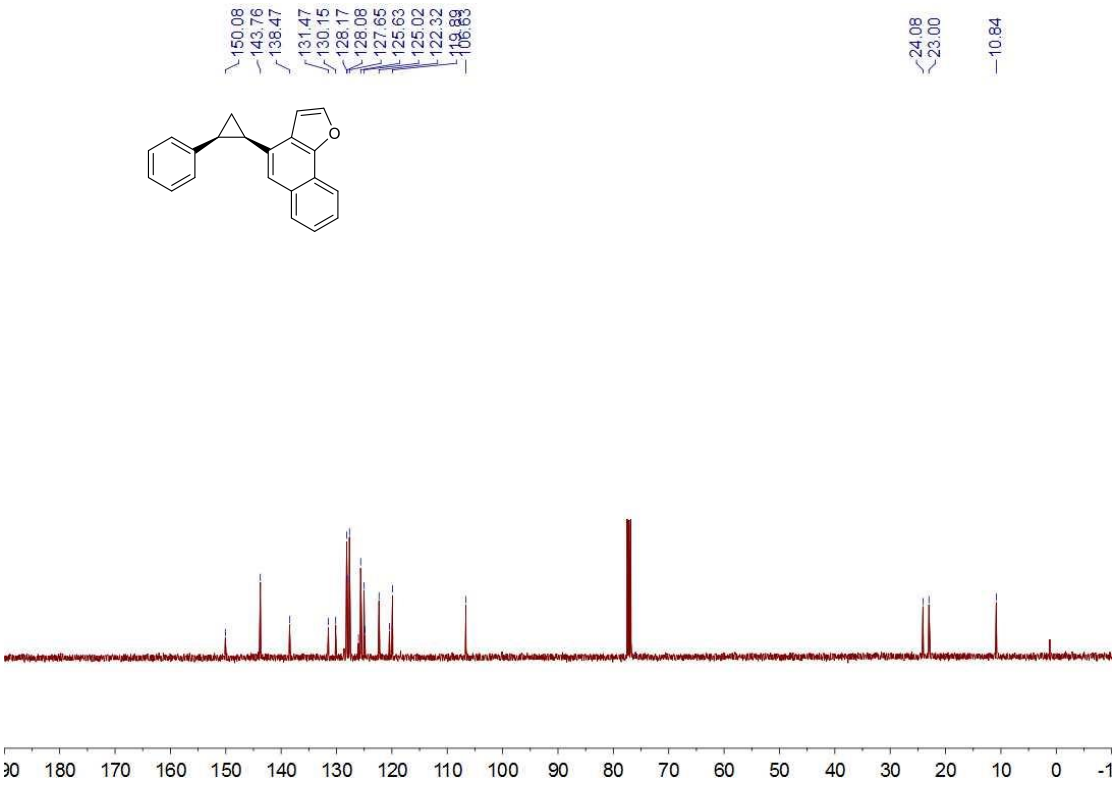


F
O

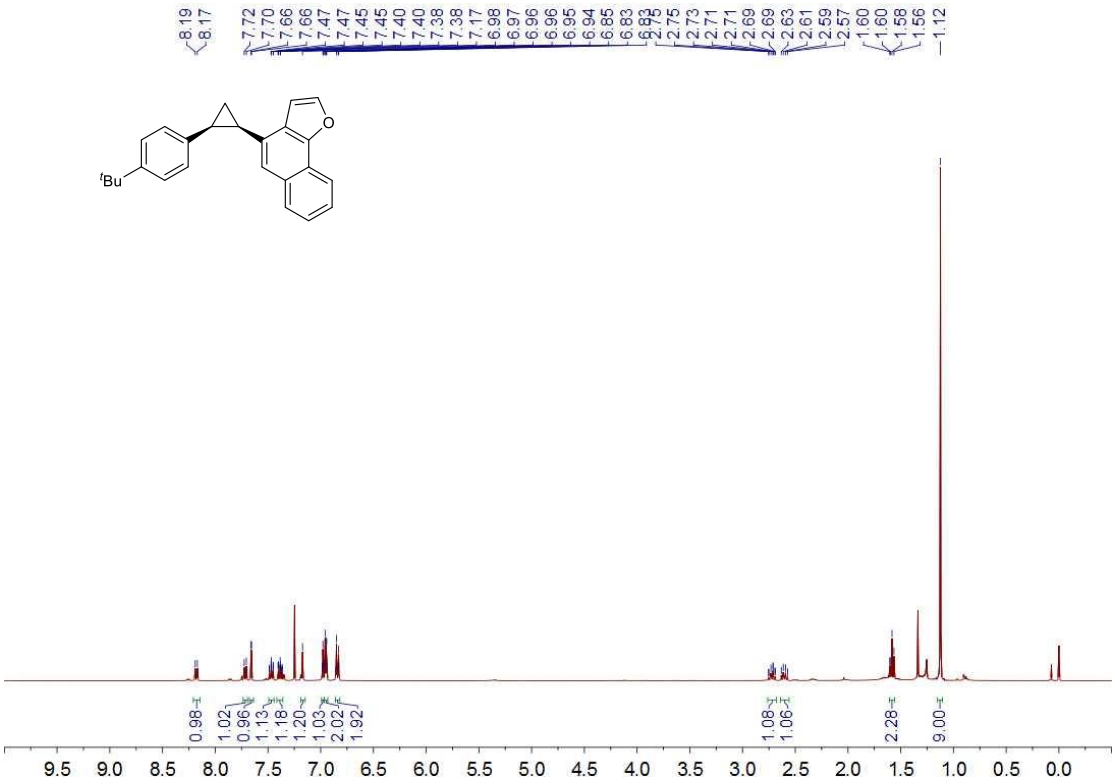

117.72
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200

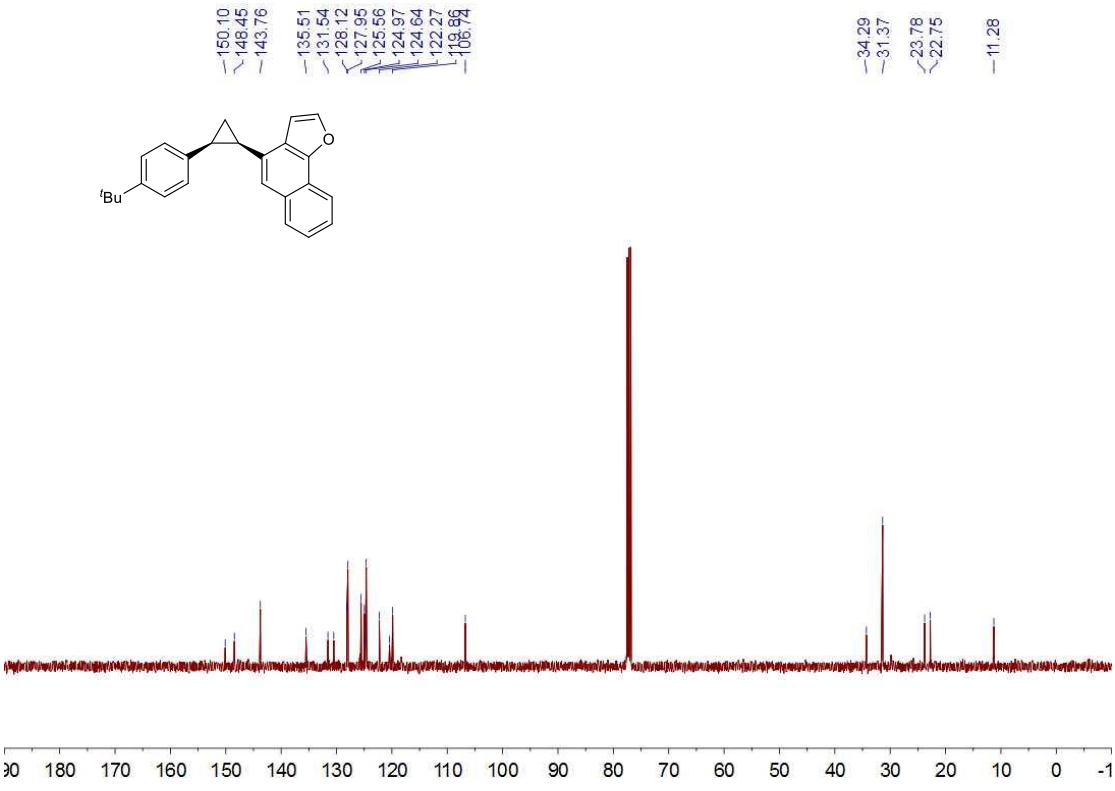
4-(2-phenylcyclopropyl)naphtho[1,2-b]furan (6h)



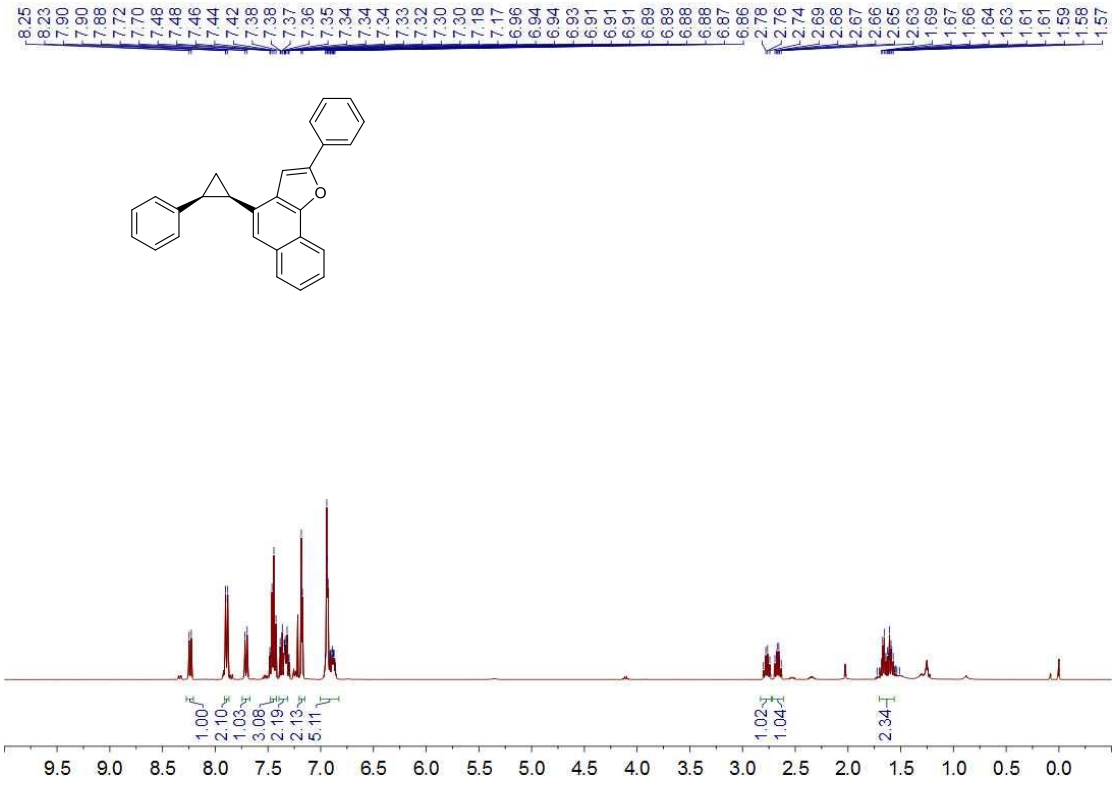


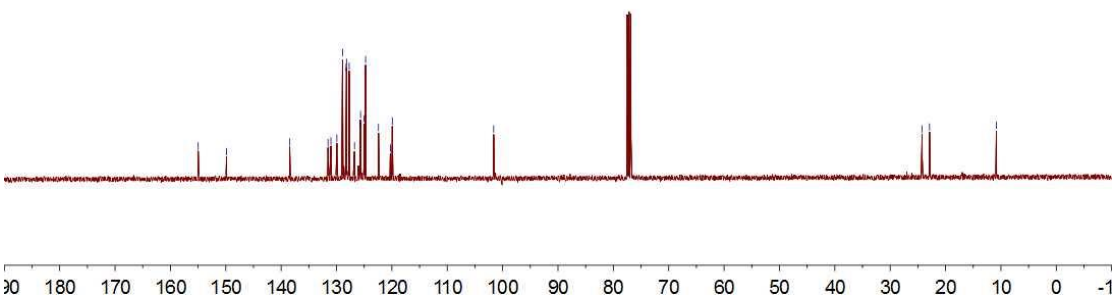
4-(2-(4-(tert-butyl)phenyl)cyclopropyl)naphtho[1,2-b]furan (6j)



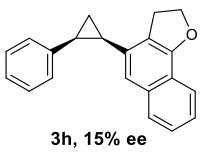


2-phenyl-4-(2-phenylcyclopropyl)naphtho[1,2-b]furan (6v)

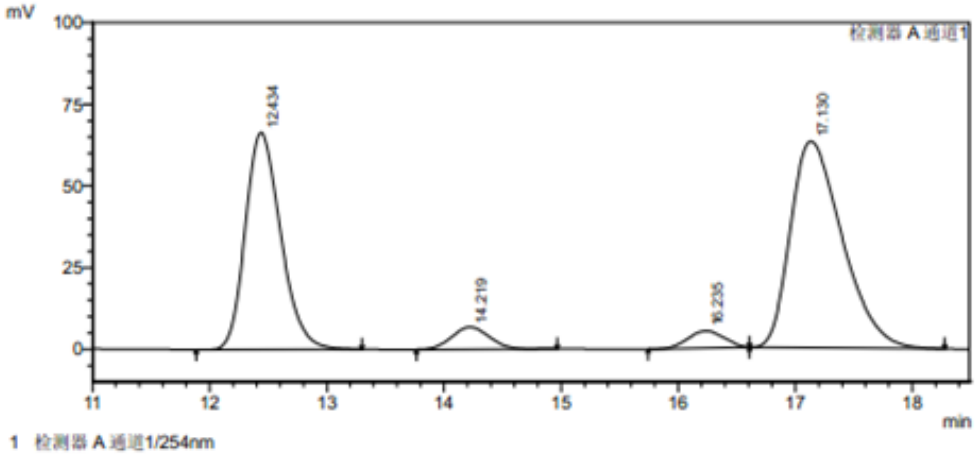




7. Chiral HPLC Traces



3h, 15% ee

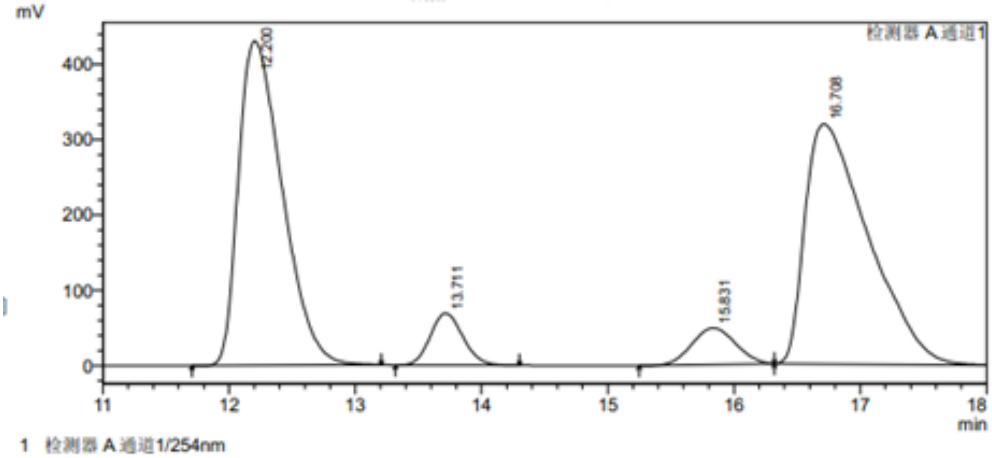


1 检测器 A 通道1/254nm

峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	12.434	1399391	66448	38.767	46.899
2	14.219	149782	6741	4.149	4.758
3	16.235	113074	5253	3.132	3.708
4	17.130	1947506	63242	53.951	44.636
总计		3609753	141684	100.000	100.000



1 检测器 A 通道1/254nm

峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	12.200	10409624	430901	43.528	49.701
2	13.711	1241716	69025	5.192	7.962
3	15.831	1164952	48492	4.871	5.593
4	16.708	11098574	318571	46.409	36.745
总计		23914866	866990	100.000	100.000

8. X-Ray diffraction analysis of compound 3a.

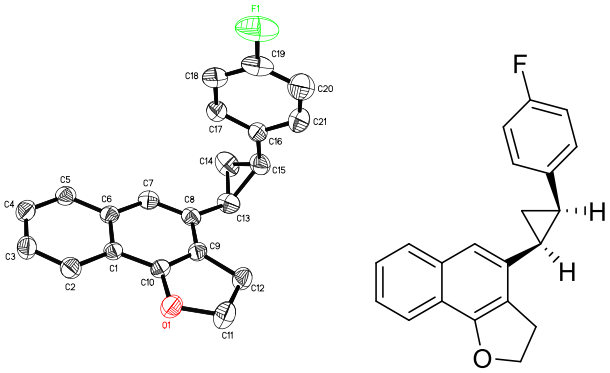
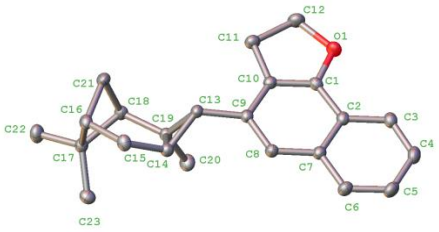


Table 1 Crystal data and structure refinement for **3a**

CCDC Number	1519965	
Identification code	cd16107	
Empirical formula	C21 H17 F O	
Formula weight	304.35	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 13.585(4) Å	α= 90 °.
	b = 12.569(3) Å	β= 106.741(6) °.
	c = 9.741(3) Å	γ = 90 °.
Volume	1592.9(7) $Å^3$	
Z	4	
Density (calculated)	1.269 Mg/m^3	
Absorption coefficient	0.084 mm^{-1}	
F(000)	640	
Crystal size	0.210 x 0.170 x 0.110 mm^3	
Theta range for data collection	2.253 to 25.496 °	
Index ranges	-16<=h<=16, -15<=k<=10, -10<=l<=11	
Reflections collected	8863	
Independent reflections	2960 [R(int) = 0.0678]	
Completeness to theta = 25.242 °	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.5821	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2960 / 0 / 208	
Goodness-of-fit on F^2	0.984	
Final R indices [I>2sigma(I)]	R1 = 0.0562, wR2 = 0.1286	
R indices (all data)	R1 = 0.1216, wR2 = 0.1552	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.175 and -0.144 e.$Å^{-3}$	

9. X-Ray diffraction analysis of compound 3s.



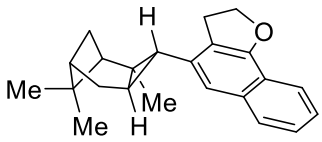


Table 1 Crystal data and structure refinement for **3s**.

CCDC Number	1519966	
Identification code	dm16314	
Empirical formula	C23 H26 O	
Formula weight	318.44	
Temperature	130 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 12.3103(16) Å	α= 90 °.
	b = 20.299(3) Å	β= 95.884(3) °.
	c = 6.9248(9) Å	γ = 90 °.
Volume	1721.3(4) $Å^3$	
Z	4	
Density (calculated)	1.229 Mg/m^3	
Absorption coefficient	0.073 mm^{-1}	
F(000)	688	
Crystal size	0.15 x 0.1 x 0.05 mm^3	
Theta range for data collection	1.663 to 30.492 °	
Index ranges	-17<=h<=16, -28<=k<=28, -9<=l<=9	
Reflections collected	17008	
Independent reflections	5226 [R(int) = 0.0408]	
Completeness to theta = 25.242 °	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7461 and 0.6831	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5226 / 0 / 220	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2sigma(I)]	R1 = 0.0487, wR2 = 0.1184	
R indices (all data)	R1 = 0.0754, wR2 = 0.1330	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.330 and -0.214 e.$Å^{-3}$	