



Supporting Information

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**Intramolecular carbolithiation of alkyne:
unprecedented *anti* selectivity**

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Materials and methods

THF was dried from sodium/benzophenone. All reagents were of reagent grade and were used as such or distilled prior to use. Reactions were monitored by TLC carried out on 0.25 mm E. Merck 5735 Kieselgel silica gel coated aluminium plates (60 F254) using UV light as visualizing agent and 7% ethanolic phosphomolybdic acid and heat as developing agents or by GC 24-m HP-methyl silicon capillary column. E. Merck silica gel (60, particle size 0.04-0.063 mm) was used for flash chromatography. ¹H and ¹³C NMR spectra were recorded at room temperature on a Bruker Avance DMX300 spectrometer at 300 MHz and 75 MHz respectively and calibrated using residual undeuterated solvent as an internal reference. The solvent was deuteriochloroform or deuterobenzen. The mass spectra were obtained on a JEOL AX500 apparatus or an Ati Unicam Automass 150 System 2, under electron impact conditions (EI) at 70 eV ionizing potential.

Synthesis and data of compounds **1**, **2** and **2D**

1-Bromo-2-(4,4-diethoxybut-2-ynyloxy)benzene **1**

To a solution of 4,4-diethoxybut-2-yn-1-ol¹ (8.21 g, 52 mmol), 2-bromophenol (6.18 mL, 1.0 eq., 52 mmol) and triphenylphosphine (13.63 g, 1.0 eq., 52 mmol) in 300 mL of THF at 0°C under argon was added dropwise diisopropylazodicarboxylate (10.30 mL, 1.0 eq., 52 mmol). The solution was warmed to room temperature, stirred for 3h and washed by adding NaOH solution 0.4 M (100 mL). The mixture was diluted by Et₂O (150 mL) and washed again by NaOH solution 0.4 M (2 x 100 mL). The combined organic layers were dried over anhydrous MgSO₄ and concentrated. Pentane (300 mL) was added to the residue to precipitate triphenylphosphine oxide. After filtration, the resulting brown liquid was purified by column chromatography (30% ethyl acetate in cyclohexane) to give the pure product **1** (14.97 g, 92%) as a yellow liquid.

¹H NMR (CDCl₃) δ 1.20 (t, 6H, *J* = 7.2 Hz); 3.55 (qd, 2H, *J* = 7.2 Hz, *J* = 9.4 Hz); 3.68 (qd, 2H, *J* = 7.2 Hz, *J* = 9.4 Hz); 4.83 (d, 2H, *J* = 1.1 Hz); 5.28 (t, 1H, *J* = 1.1 Hz); 6.88 (td, 1H, *J* = 7.5 Hz, *J* = 1.5 Hz); 7.07 (dd, 1H, *J* = 7.5 Hz, *J* = 1.5 Hz); 7.27 (td, 1H, *J* = 7.5 Hz, *J* = 1.5 Hz); 7.55 (dd, 1H, *J* = 7.5 Hz, *J* = 1.5 Hz). ¹³C NMR (CDCl₃) δ 15.2; 54.1; 61.0; 79.7; 83.7; 91.4; 112.5; 114.4; 123.1; 128.7; 133.8; 154.2. EI-MS: *m/z* 313 (M⁺, 21); 311 (M⁺, 21); 268 (34); 188 ([M-OEt]⁺, 27); 160 ([M-(OEt)₂]⁺, 68); 131 ([M-CH(OEt)₂]⁺, 62); 85 (85); 68 (100).

(*E*)-3-(2,2-Diethoxyethylidene)-2,3-dihydrobenzofuran **2** and **2D**

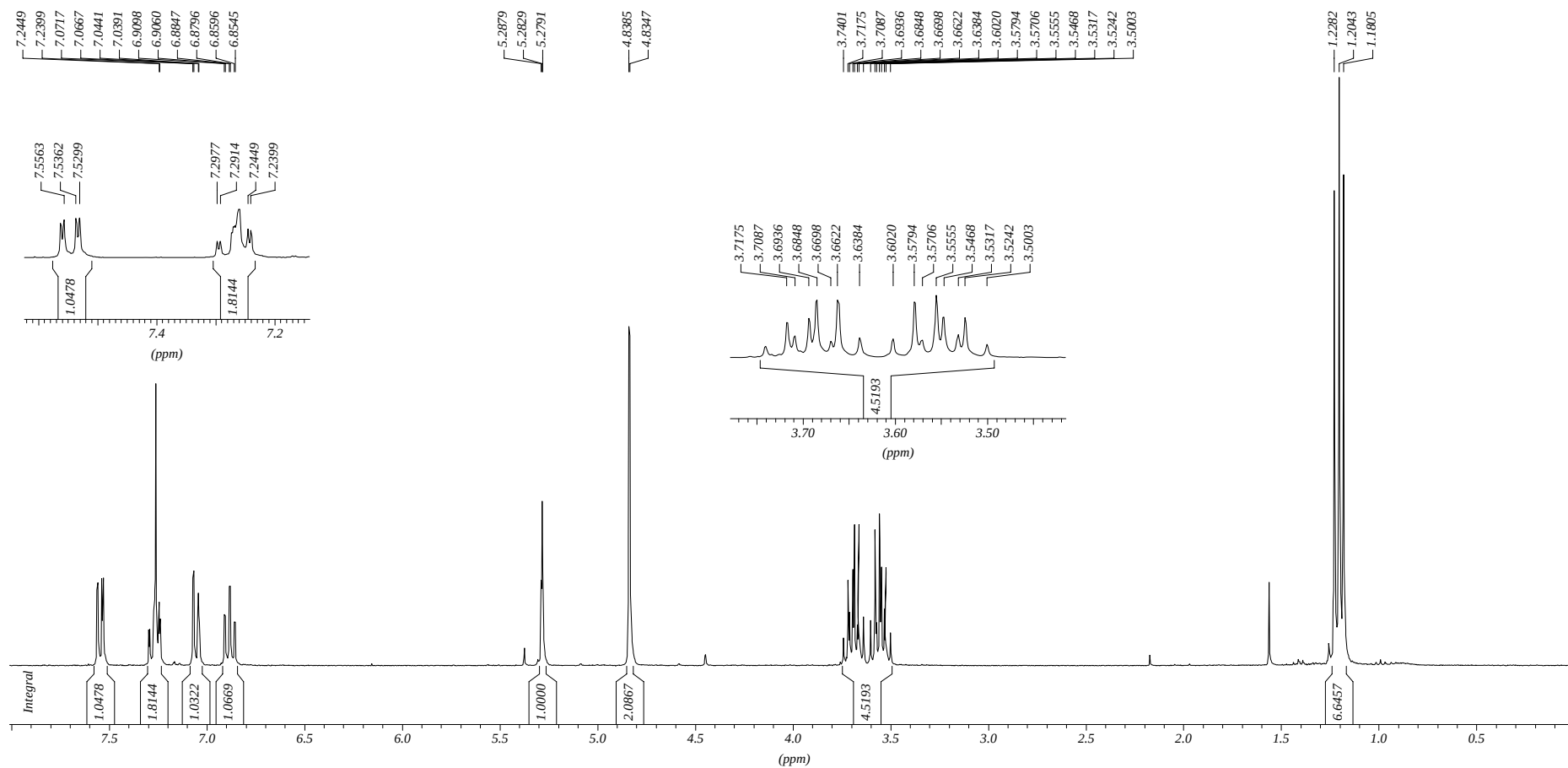
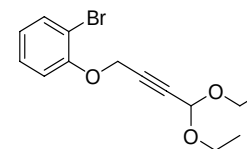
To a solution of the acetal **1** (0.313 g, 1.0 mmol) in anhydrous THF (5 mL) at -78°C under argon atmosphere was added a solution of *n*-butyllithium (2.37 M in hexane, 0.51 mL, 1.2 eq., 1.2 mmol). After 15 min of stirring, the mixture was deuterolysed with EtOD (0.6 mL). After 15 min of stirring, water (5 mL) was added. The aqueous phase was separated and extracted with Et₂O (3 x 5 mL). The combined organic phases were dried over anhydrous magnesium sulfate and concentrated. The residue was purified by column chromatography (10% ethyl acetate in cyclohexane) to provide a mixture **2** and **2D** (0.197 g, 84%, *H/D* = 66:34) as an orange liquid.

2: ¹H NMR (CDCl₃) δ 1.23 (t, 6H, *J* = 7.2 Hz); 3.58 (qd, 2H, *J* = 7.2 Hz, *J* = 9.4 Hz); 3.71 (qd, 2H, *J* = 7.2 Hz, *J* = 9.4 Hz); 5.10 (d, 2H, *J* = 1.1 Hz); 5.55 (m, 2H); 6.87 (d, 1H, *J* = 7.9 Hz); 6.94 (t, 1H, *J* = 7.9 Hz); 7.22 (td, 1H, *J* = 1.2 Hz, *J* = 7.9 Hz); 7.62 (d, 1H, *J* = 7.9 Hz). ¹H NMR (C₆D₆) 1.12 (t, 6H, *J* = 7.2 Hz); 3.45 (qd, 2H, *J* = 7.2 Hz, *J* = 9.4 Hz); 3.59 (qd, 2H, *J* = 7.2 Hz, *J* = 9.4 Hz); 4.63 (dd, 2H, *J* = 1.5 Hz, *J* = 2,3 Hz); 5.43 (dt, 1H, *J* = 2.3 Hz, *J* = 5.6 Hz); 5.56 (dt, 1H, *J* = 1.5 Hz, *J* = 5.6 Hz); 6.77 (td, 1H, *J* = 1.5 Hz, *J* = 7.6 Hz); 6.82 (d, 1H, *J* = 7.6 Hz); 6.95 (td, 1H, *J* = 1.5 Hz, *J* = 7.6 Hz); 7.86 (d, 1H, *J* = 7.6 Hz). ¹³C NMR (CDCl₃) δ 15.7; 60.7; 75.6; 98.1; 111.0; 116.1; 121.2; 124.3; 126.2; 131.3; 139.8; 165.4. EI-MS: *m/z* 234 (M⁺, 1); 188 ([M-OEt]⁺, 80); 160 ([M-(OEt)₂]⁺, 21); 131 ([M-CH(OEt)₂]⁺, 100).

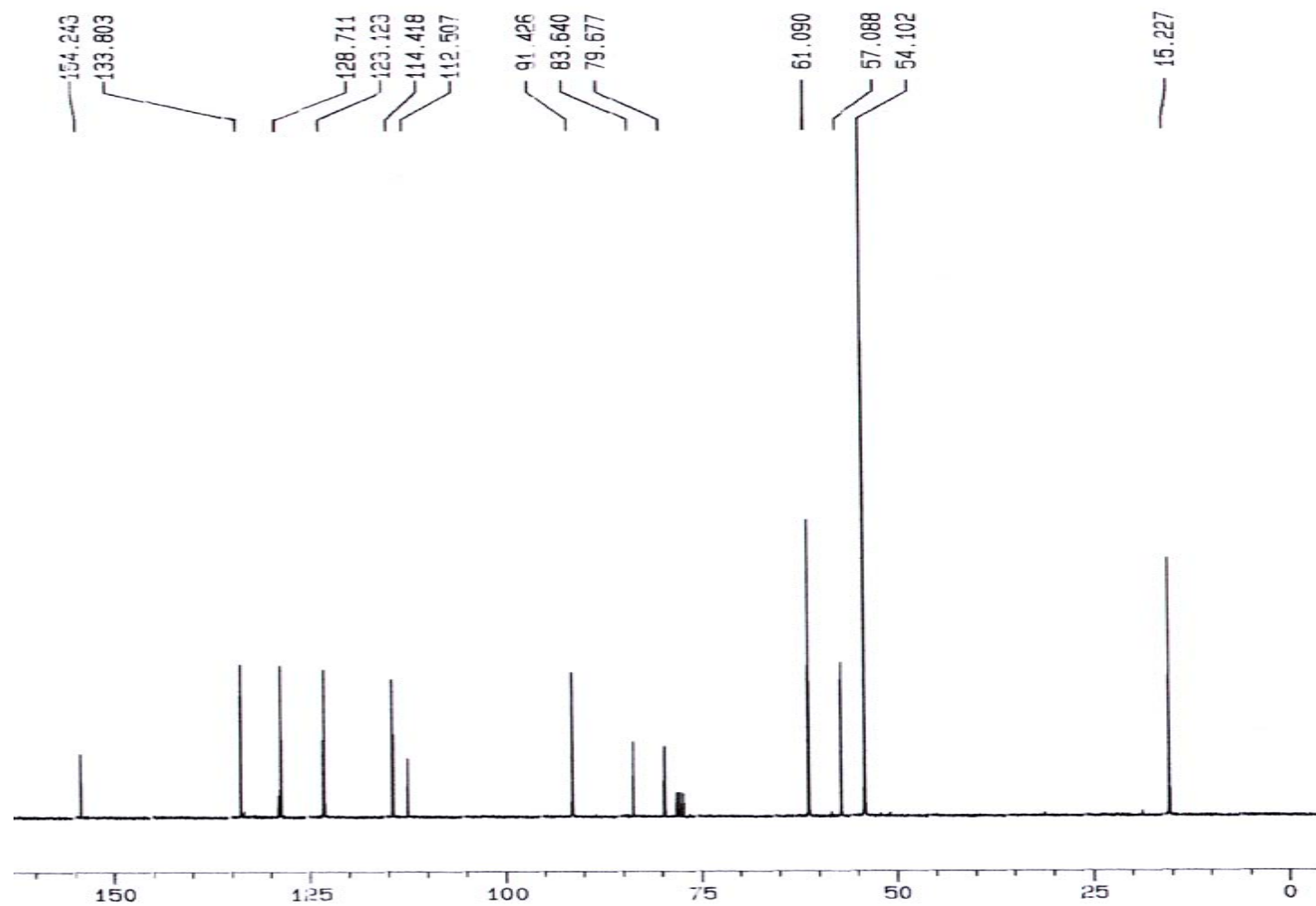
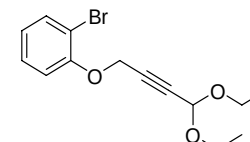
2D: ¹H NMR (C₆D₆) δ 1.12 (t, 6H, *J* = 7.2 Hz); 3.45 (qd, 2H, *J* = 7.2 Hz, *J* = 9.4 Hz); 3.61 (qd, 2H, *J* = 7.2 Hz, *J* = 9.4 Hz); 4.63 (d, 2H, *J* = 1.5 Hz); 5.56 (s, 1H); 6.77 (td, 1H, *J* = 1.5 Hz, *J* = 7.6 Hz); 6.83 (d, 1H, *J* = 7.6 Hz); 6.95 (td, 1H, *J* = 1.5 Hz, *J* = 7.6 Hz); 7.88 (d, 1H, *J* = 7.6 Hz). EI-MS: *m/z* 235 (M⁺, 1); 189 ([M-OEt]⁺, 80); 161 ([M-(OEt)₂]⁺, 21); 132 ([M-CH(OEt)₂]⁺, 100).

¹ Le Strat, F.; Maddaluno J. *Org. Lett.* **2002**, 4, 2791.

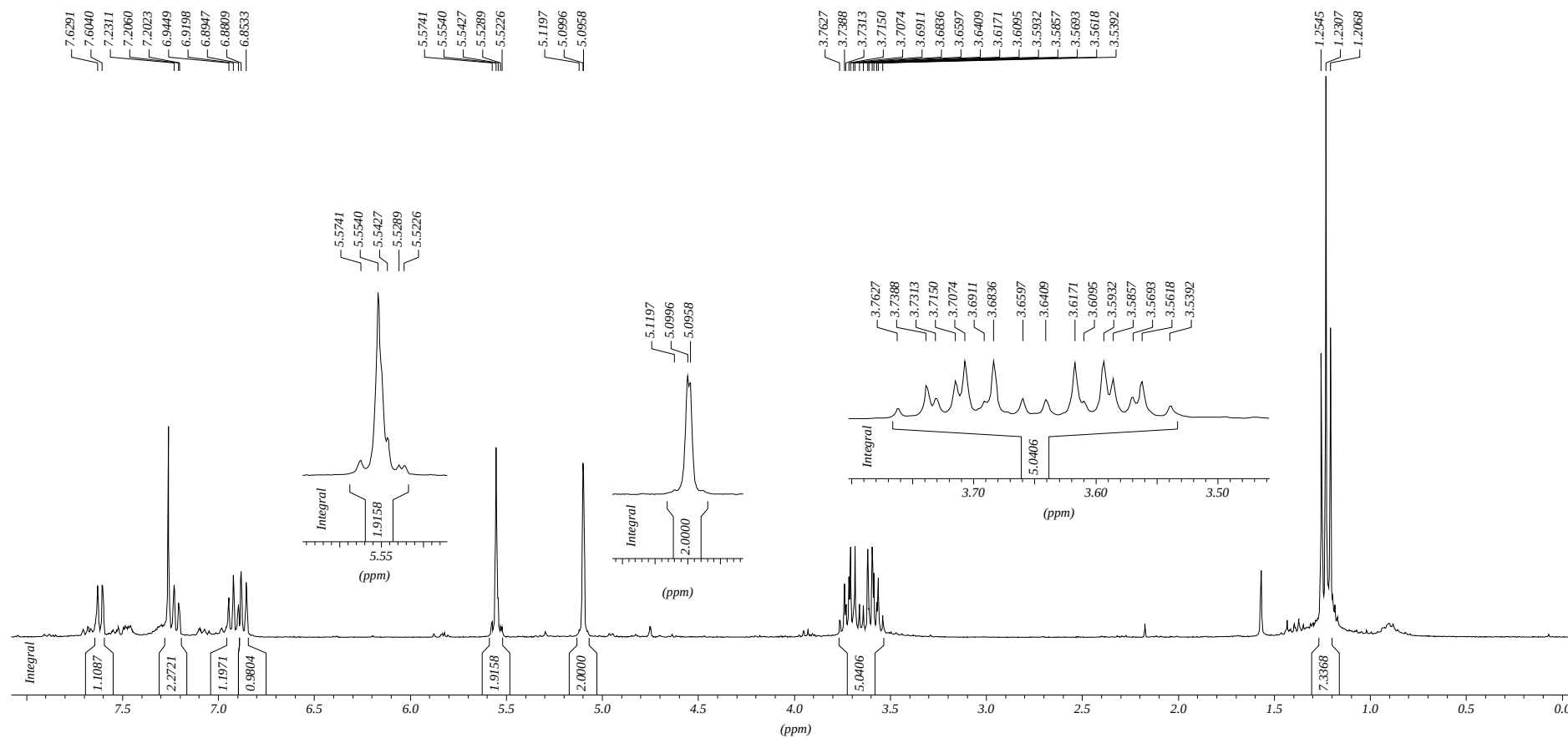
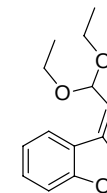
^1H NMR spectrum (CDCl_3) of compound **1**



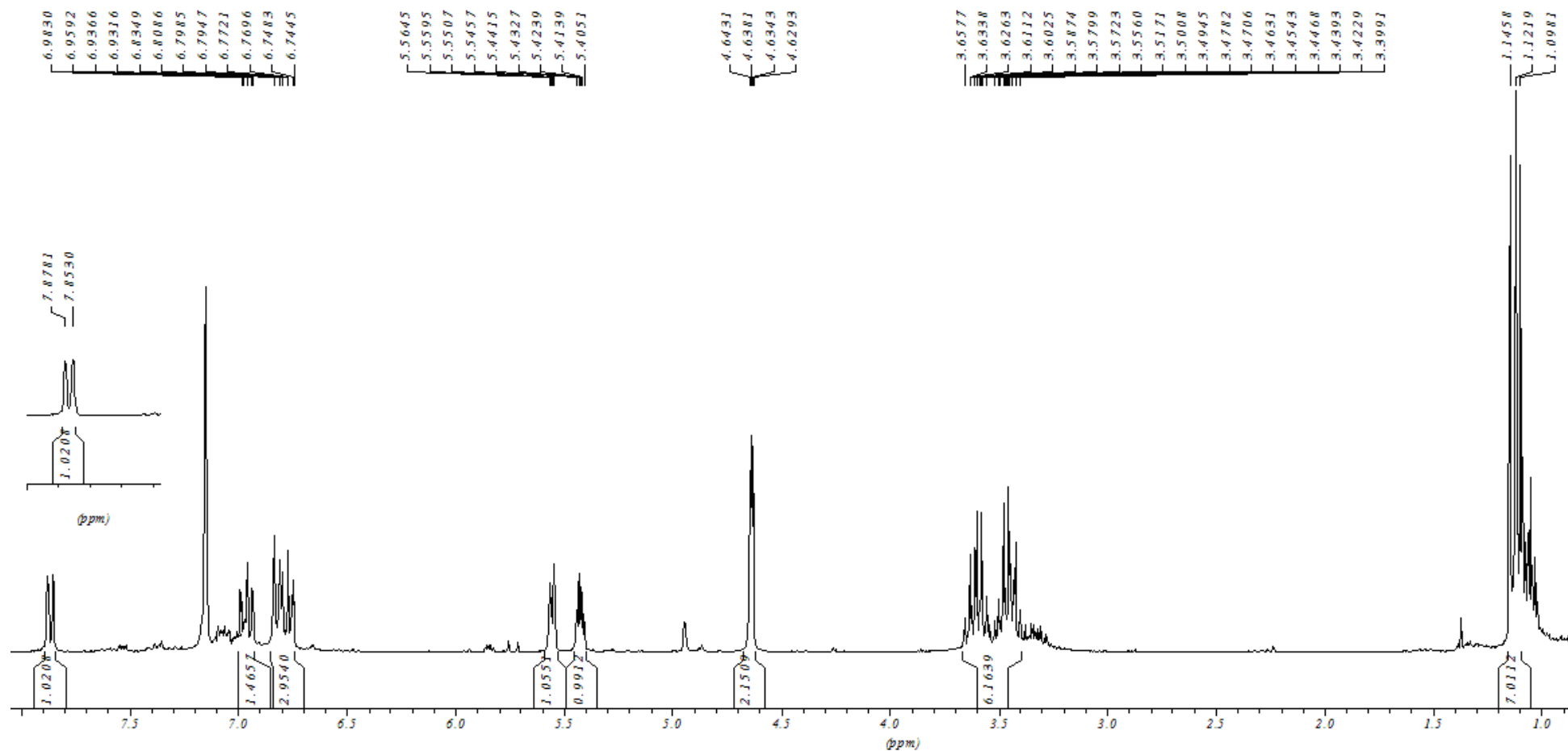
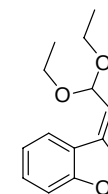
^{13}C NMR spectrum (CDCl_3) of compound **1**



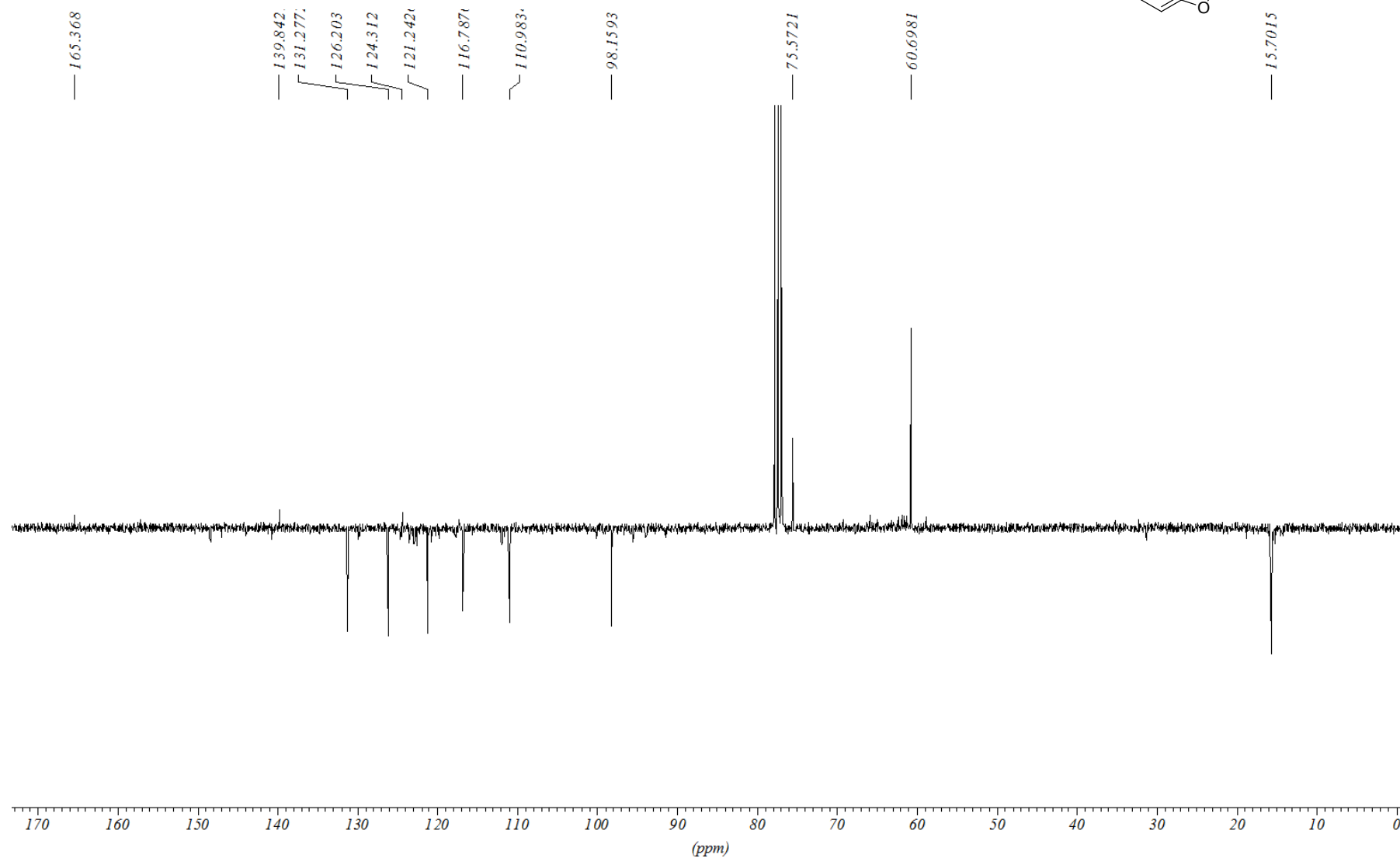
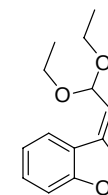
^1H NMR spectrum (CDCl_3) of compound 2

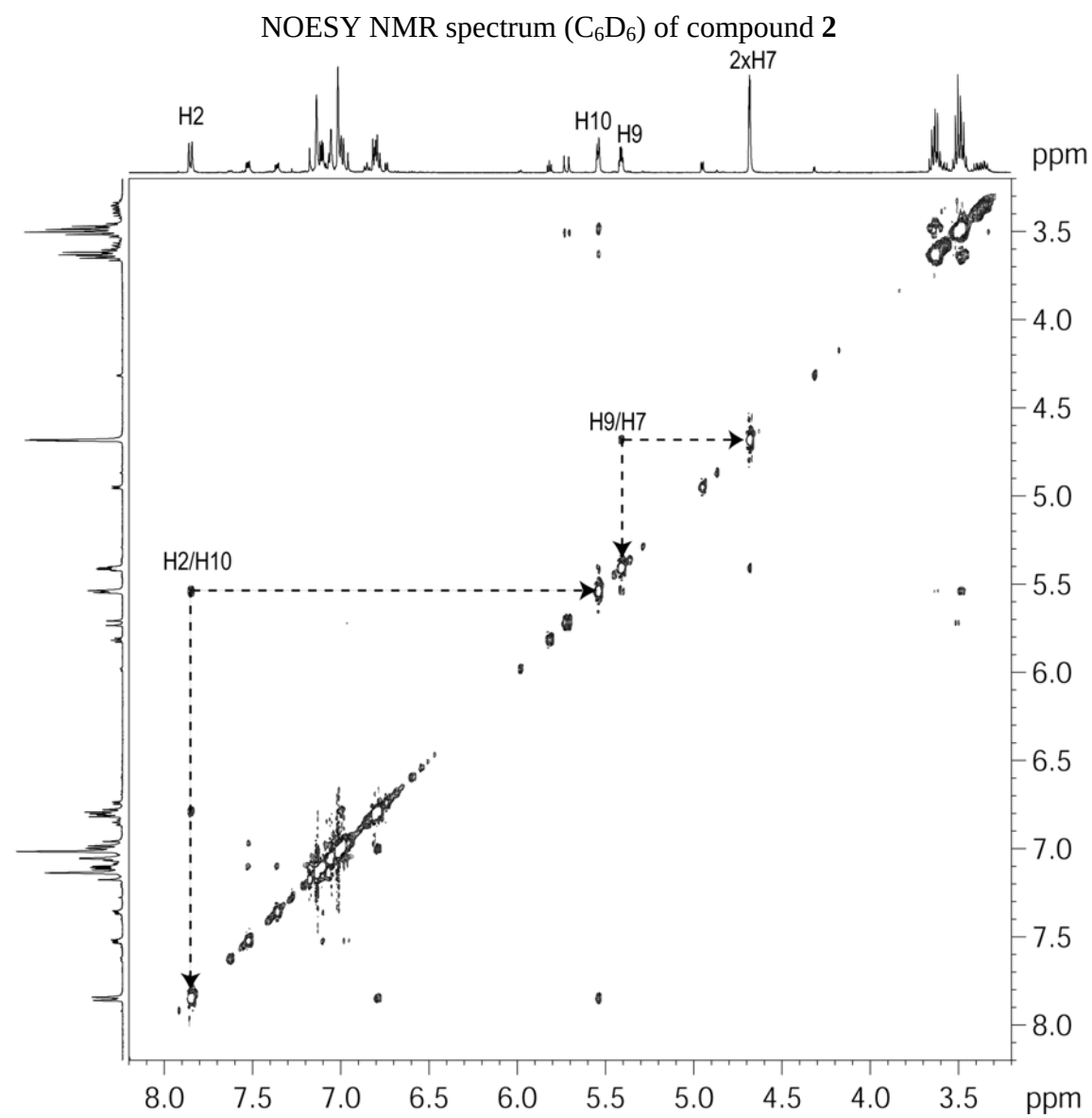


^1H NMR spectrum (C_6D_6) of compound 2



^{13}C NMR spectrum (CDCl_3) of compound 2





^1H NMR spectrum (C_6D_6) of compound **2D**

