Supporting Information

Microwave Assisted Domino Heck Cyclization and Alkynylation: Synthesis of Alkyne Substituted Dihydrobenzofurans

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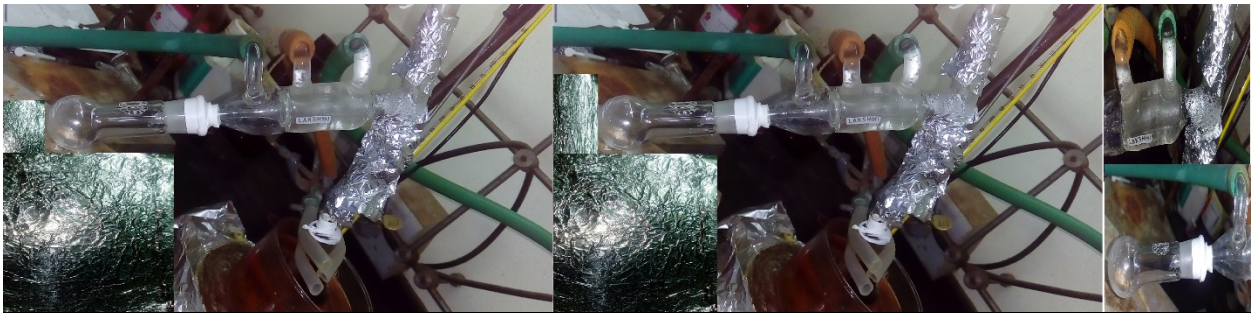
Experimental

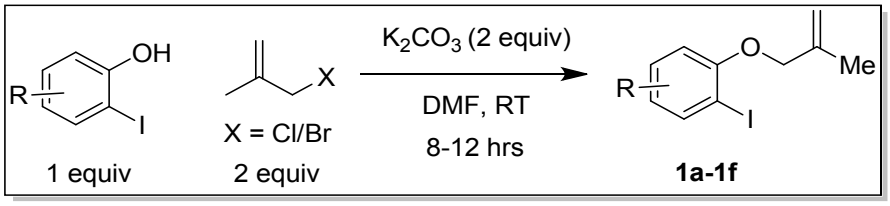
General: IR spectra were recorded on a Bruker Tensor 37 (FTIR) spectrophotometer. ^{1}H NMR spectra were recorded on Bruker Avance 400 (400 MHz) spectrometer at 295 K in $CDCl_3$; chemical shifts (δ ppm) and coupling constants (Hz) are reported in standard fashion with reference to either internal standard tetramethylsilane (TMS) (δ_H =0.00 ppm) or $CHCl_3$ (δ_H = 7.25 ppm). ^{13}C NMR spectra were recorded on Bruker Avance 400 (100 MHz) spectrometer at RT in $CDCl_3$; chemical shifts (δ ppm) are reported relative to $CHCl_3$ [δ_C = 77.00 ppm (central line of triplet)]. In the ^{13}C NMR, the nature of carbons (C, CH, CH_2 and CH_3) was determined by recording the DEPT-135 spectra, and is given in parentheses and noted as s = singlet (for C), d = doublet (for CH), t = triplet (for CH_2) and q = quartet (for CH_3). In the ^{1}H-NMR, the following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet, qui =quintet, sept = septet, dd = doublet of doublet, m = multiplet and br. s = broad singlet. The assignment of signals was confirmed by ^{1}H, ^{13}C CPD and DEPT spectra. High-resolution mass spectra (HR-MS) were recorded on an Agilent 6538 UHD Q-TOF electron spray ionization (ESI) mode and atmospheric pressure chemical ionization (APCI) modes. The microwave irradiation experiments were carried out in a dedicated CEM-Discover monomode microwave apparatus, operating at a frequency of 2.45 GHz with continuous irradiation power from 0 to 300 W and utilization of the standard absorbance level of 100 W. The reactions

were carried out in 10 mL glass tubes, sealed with Teflon septum and placed in the microwave cavity. The reactions were irradiated at the required set temperature for the stipulated time and then cooled to ambient temperature with air jet cooling. Reactions were monitored by TLC on silica gel using a combination of hexane and ethyl acetate as eluents. Reactions were generally run under argon or a nitrogen atmosphere. Solvents were distilled prior to use; petroleum ether with a boiling range of 60 to 80 °C was used. $Pd_2(dba)_3$, and Potassium Carbonate were purchased from Sigma-Aldrich and used as received. Orthoiodophenols, halo-alkenes and acetylenes were purchased from TCI/local sources and used as received. Acme's silica gel (60–120 mesh) was used for column chromatography (approximately 20 g per one gram of crude material).

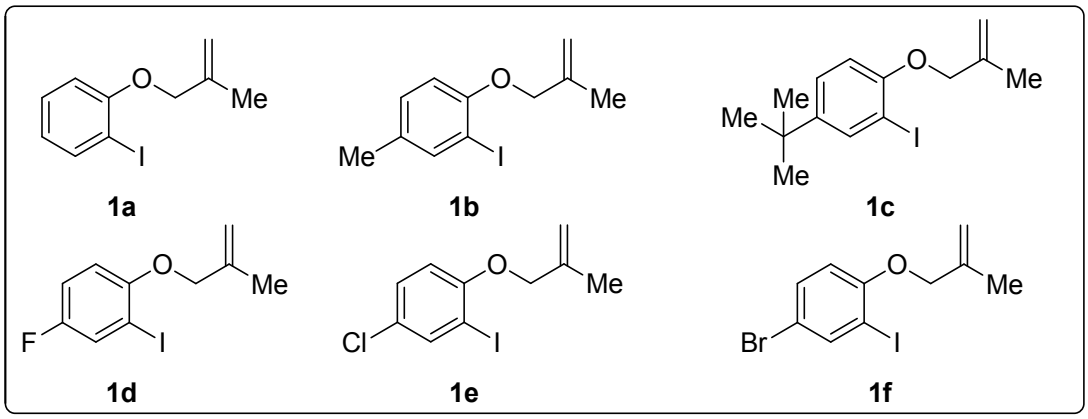
General procedure for the solvent Recyclization: A solvent recovery system is a process that takes useful raw materials and solvent back out of the medium. The recovery of solvents from reaction mixture can be achieved with a variety of techniques. A common one is distillation system. Here, we have recycled the solvent by using a vacuum and fractional distillation glassware apparatus, in which we have chosen long neck, inlet-outlets [for ice water circulation] and Vacuum nob containing 200 mm three-way condenser [see the picture down], and two 5 mL round bottomed flasks. The process involves, initially, the reaction mixture was transferred to magnetic stir bar containing 5 mL RBF from the microwave reactor vessel. Now to the three-way condenser, one way was connected to reaction mixture containing RBF and second way was connected to the Thermometer or Blocked with stopper, third way was connected to the receiver. After proper setup, the RBF containing reaction mixture was dipped into the oil bath and started stirring, then after by applying the heat (around 100 °C) and proper vacuum, the solvent was condensed by using ice water circulation and collected in to the recovery 5 mL RBF.



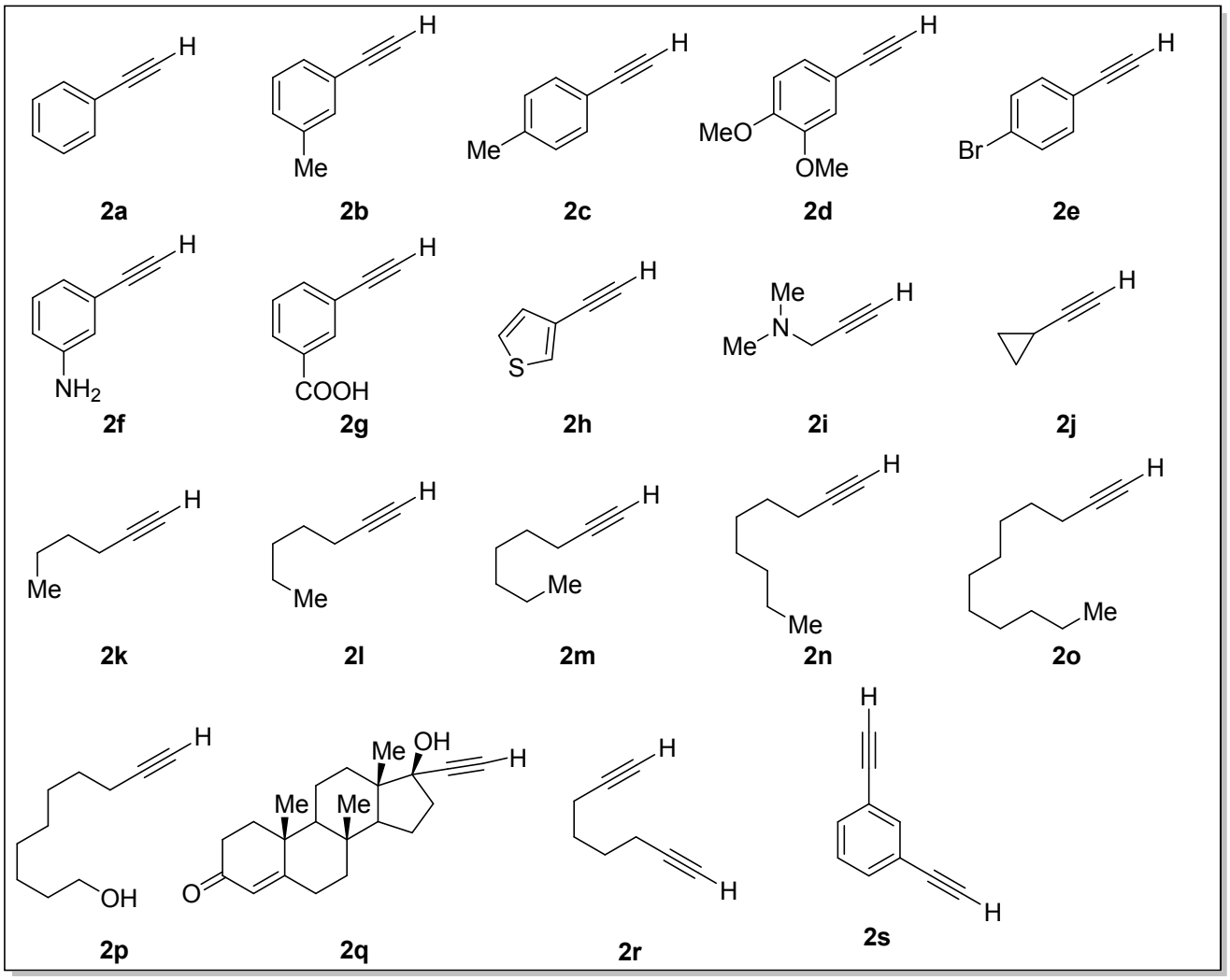
S1-Scheme: General Procedure for the synthesis of *ortho*-iodophenyl allyl ethers.



S1-Table: The following *ortho*-iodophenyl allyl ethers are known in the literature.



S2-Table: The following acetylenes are commercially available.



Single Crystal X-Ray of compound **3bd:**

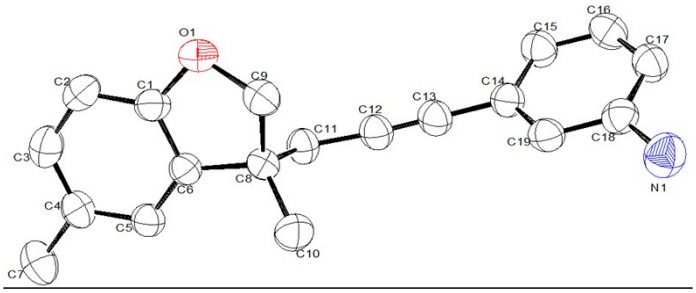


Table 1 Crystal data and structure refinement for .

Identification code	exp_8633
Empirical formula	$C_{19}H_{19}NO$

Formula weight	369.82
Temperature/K	293
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.0947(4)
b/Å	5.86763(14)
c/Å	18.4634(5)
α/°	90
β/°	97.511(3)
γ/°	90
Volume/Å^3	1513.87(7)
Z	3
ρ_{calc}g/cm^3	1.2169
μ/mm^{-1}	0.581
F(000)	593.7
Crystal size/mm^3	0.04 × 0.03 × 0.02
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.66 to 139.8
Index ranges	$-16 \leq h \leq 17$, $-3 \leq k \leq 7$, $-21 \leq l \leq 22$
Reflections collected	4979
Independent reflections	2797 [R_{int} = 0.0402, R_{sigma} = 0.0473]
Data/restraints/parameters	2797/0/192
Goodness-of-fit on F^2	1.063
Final R indexes [I>=2σ (I)]	R_1 = 0.0572, wR_2 = 0.1560
Final R indexes [all data]	R_1 = 0.0823, wR_2 = 0.1692
Largest diff. peak/hole / e Å^{-3}	0.31/-0.31

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for exp_8633. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	7664.2(13)	1264(3)	3072.6(10)	55.0(5)
C5	7356.6(17)	6045(4)	4227.2(13)	46.1(6)
C6	7747.5(16)	4430(4)	3814.7(12)	40.6(6)
C17	13583.0(18)	-946(5)	3404.2(14)	50.0(6)
C18	13204.2(17)	1144(4)	3163.3(13)	44.6(6)
C19	12363.2(16)	1871(4)	3411.1(13)	44.8(6)
C9	8579.9(18)	2347(5)	3023.6(13)	48.0(6)
C12	10256.3(18)	1961(5)	4239.6(14)	48.4(6)
C14	11900.7(17)	529(4)	3877.6(13)	44.9(6)
C1	7169.8(18)	2773(4)	3456.0(13)	45.5(6)
C4	6373.1(18)	6022(5)	4278.1(13)	48.3(6)
C8	8768.3(16)	3978(4)	3677.3(13)	40.6(6)
C13	11003.3(18)	1299(5)	4091.9(14)	48.5(6)
C11	9295.0(17)	2723(5)	4350.7(13)	46.2(6)

C2	6197.9(19)	2689(5)	3489.2(15)	55.6(7)
C16	13129.6(19)	-2268(5)	3868.5(15)	54.4(7)
N1	13668.4(16)	2524(4)	2705.9(13)	59.9(6)
C3	5816.9(19)	4335(5)	3902.1(15)	55.6(7)
C10	9314.2(19)	6099(5)	3499.7(17)	58.7(7)
C15	12287.1(19)	-1573(5)	4105.7(15)	53.2(7)
C7	5934(2)	7772(6)	4729.7(15)	64.9(8)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for exp_8633. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O1	54.6(10)	43.6(11)	66.3(11)	-3.4(9)	5.3(9)	-15.5(9)
C5	46.4(13)	41.7(15)	48.0(13)	2.5(11)	-1.8(10)	-2.0(11)
C6	40.2(12)	35.5(13)	44.8(12)	1.9(10)	0.7(9)	2.5(10)
C17	44.8(13)	50.4(16)	54.3(15)	7.1(12)	4.5(11)	-0.5(12)
C18	41.8(12)	44.3(15)	45.9(13)	-1.7(11)	-1.1(10)	0.7(11)
C19	43.7(13)	37.0(13)	50.6(13)	3.5(11)	-5.4(10)	1.2(11)
C9	49.9(14)	44.9(15)	49.1(14)	3.6(12)	6.3(11)	-0.3(11)
C12	46.2(14)	46.5(15)	50.7(14)	6.3(12)	-0.2(11)	3.0(12)
C14	41.9(12)	43.8(14)	47.2(13)	2.6(11)	-0.6(10)	-1.8(11)
C1	48.1(13)	37.7(14)	49.9(13)	-2.2(11)	3.6(11)	-1.5(11)
C4	48.6(14)	50.7(16)	45.5(13)	9.3(12)	5.7(10)	4.3(12)
C8	40.8(12)	33.7(13)	47.0(13)	2.6(10)	4.5(10)	1(1)
C13	46.4(14)	47.7(15)	50.0(14)	5.5(12)	0.5(11)	1.2(12)
C11	42.2(13)	48.8(15)	46.9(13)	4.4(11)	3.8(10)	3.7(12)
C2	47.7(14)	51.8(17)	66.2(17)	-11.8(13)	3.8(12)	-6.8(14)
C16	57.5(15)	41.7(15)	63.2(16)	12.4(13)	4.6(13)	6.3(13)
N1	53.9(13)	60.7(16)	65.0(14)	-0.2(12)	8.1(11)	10.8(12)
C3	41.9(13)	66.0(19)	59.3(16)	-2.4(13)	7.8(12)	5.8(14)
C10	52.7(15)	45.2(16)	77.8(19)	-3.2(13)	7.0(13)	10.2(14)
C15	52.8(14)	48.3(16)	58.9(16)	4.9(13)	9.4(12)	8.0(13)
C7	62.5(17)	74(2)	58.6(16)	18.7(16)	11.1(13)	-2.1(15)

Table 4 Bond Lengths for exp_8633.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C9	1.452(3)	C12	C13	1.187(3)
O1	C1	1.378(3)	C12	C11	1.466(3)
C5	C6	1.375(3)	C14	C13	1.446(3)
C5	C4	1.402(3)	C14	C15	1.391(4)
C6	C1	1.381(3)	C1	C2	1.380(3)

C6	C8	1.517(3)	C4	C3	1.391(4)
C17	C18	1.387(4)	C4	C7	1.506(4)
C17	C16	1.374(4)	C8	C11	1.548(3)
C18	C19	1.392(3)	C8	C10	1.521(4)
C18	N1	1.393(3)	C2	C3	1.382(4)
C19	C14	1.390(3)	C16	C15	1.380(4)
C9	C8	1.536(3)			

Table 5 Bond Angles for exp_8633.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	O1	C9	105.31(18)	C2	C1	C6	122.0(2)
C4	C5	C6	120.1(2)	C3	C4	C5	118.1(2)
C1	C6	C5	119.8(2)	C7	C4	C5	120.8(2)
C8	C6	C5	132.1(2)	C7	C4	C3	121.1(2)
C8	C6	C1	108.0(2)	C9	C8	C6	99.80(18)
C16	C17	C18	120.6(2)	C11	C8	C6	108.34(18)
C19	C18	C17	118.3(2)	C11	C8	C9	110.5(2)
N1	C18	C17	121.1(2)	C10	C8	C6	114.2(2)
N1	C18	C19	120.6(2)	C10	C8	C9	112.4(2)
C14	C19	C18	121.2(2)	C10	C8	C11	111.1(2)
C8	C9	O1	106.71(19)	C14	C13	C12	177.3(3)
C11	C12	C13	174.5(3)	C8	C11	C12	112.8(2)
C13	C14	C19	119.4(2)	C3	C2	C1	117.3(2)
C15	C14	C19	119.5(2)	C15	C16	C17	121.4(2)
C15	C14	C13	121.1(2)	C2	C3	C4	122.6(2)
C6	C1	O1	113.1(2)	C16	C15	C14	119.0(3)
C2	C1	O1	124.8(2)				

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for exp_8633.

Atom	*x*	*y*	*z*	U(eq)
H5	7745.5(17)	7154(4)	4472.9(13)	55.3(7)
H17	14148.5(18)	-1456(5)	3250.3(14)	60.0(8)
H19	12105.9(16)	3280(4)	3261.8(13)	53.8(7)
H9a	9082.9(18)	1212(5)	3042.9(13)	57.6(8)
H9b	8558.6(18)	3184(5)	2568.5(13)	57.6(8)
H11a	8919.5(17)	1411(5)	4459.2(13)	55.4(7)
H11b	9344.8(17)	3735(5)	4769.4(13)	55.4(7)
H2	5814.7(19)	1569(5)	3243.6(15)	66.7(8)
H16	13396.0(19)	-3661(5)	4026.1(15)	65.3(8)
H1a	13936(14)	1680(4)	2410(8)	71.8(8)

H1b	13250(3)	3390(30)	2461(9)	71.8(8)
H3	5162.8(19)	4314(5)	3929.5(15)	66.8(9)
H10a	8960(7)	6883(19)	3095(7)	88.0(11)
H10b	9399(13)	7086(16)	3918(4)	88.0(11)
H10c	9929(6)	5666(5)	3374(11)	88.0(11)
H15	11982.1(19)	-2495(5)	4413.6(15)	63.8(8)
H7a	6178(12)	7570(20)	5236(2)	97.3(12)
H7b	6093(13)	9272(6)	4576(8)	97.3(12)
H7c	5251(3)	7590(20)	4665(9)	97.3(12)

Experimental

Single crystals of $C_{19}H_{19}NO$ **[exp_8633]** were **[]**. A suitable crystal was selected and **[]** on a **SuperNova, Dual, Cu at zero, Eos** diffractometer. The crystal was kept at 293 K during data collection. Using Olex2 [1], the structure was solved with the SIR2004 [2] structure solution program using Direct Methods and refined with the olex2.refine [3] refinement package using Gauss-Newton minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Burla, M.C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G.L., De Caro, L., Giacovazzo, C., Polidori, G., Siliqi, D., Spagna, R. (2007). J. Appl. Cryst. 40, 609-613.
3. Bourhis, L.J., Dolomanov, O.V., Gildea, R.J., Howard, J.A.K., Puschmann, H. (2015). Acta Cryst. A71, 59-75.

Crystal structure determination of [exp_8633]

Crystal Data for $C_{19}H_{19}NO$ (M =369.82 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 14.0947(4) Å, b = 5.86763(14) Å, c = 18.4634(5) Å, β = 97.511(3)°, V = 1513.87(7) Å^3, Z = 3, T = 293 K, μ(Cu Kα) = 0.581 mm^{-1}, $Dcalc$ = 1.2169 g/cm^3, 4979 reflections measured (9.66° ≤ 2Θ ≤ 139.8°), 2797 unique (R_{int} = 0.0402, R_{sigma} = 0.0473) which were used in all calculations. The final R_1 was 0.0572 (I>=2u(I)) and wR_2 was 0.1692 (all data).

Refinement model description

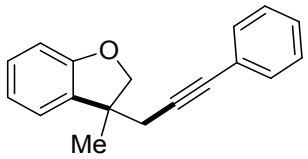
Number of restraints - 0, number of constraints - 31.

Details:
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups, All N(H,H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2.a Rotating group:
 N1(H1a,H1b)
2.b Secondary CH2 refined with riding coordinates:
 C9(H9a,H9b), C11(H11a,H11b)
2.c Aromatic/amide H refined with riding coordinates:
 C5(H5), C17(H17), C19(H19), C2(H2), C16(H16), C3(H3), C15(H15)
2.d Idealised Me refined as rotating group:
 C10(H10a,H10b,H10c), C7(H7a,H7b,H7c)

This report has been created with Olex2, compiled on 2016.02.19 svn.r3266 for OlexSys. Please let us know if there are any errors or if you would like to have additional feature

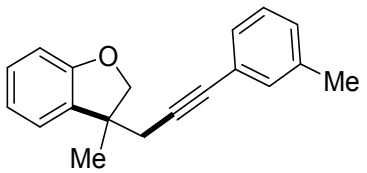
GP (General procedure for the synthesis of Dihydrobenzofurans): To an oven dried 10 mL glass tube sealed withteflon septum was equipped with a magnetic stir bar, were added *ortho*-iodoaryl allyl ether **1** (68.2-82.5 mg, 0.25 mmol), acetylene **2** (40.9-202.1 mg, 0.62 mmol), followed by $Pd_2(dba)_3$ (2.28 mg, 1 mol%), K_2CO_3 (138.6 mg, 1 mmol) and solvent DMF (0.5mL), at room temperature under inert atmosphere.

The resultant reaction mixture was subjected to microwave irradiation at 100 °C for 15 min (at 80 °C, for 20 min; in the case of **3ae, 3be, 3fa** & **3fc**), 300 W, closed vessel. Progress of the reaction was monitored by TLC till the reaction is completed. The mixture was cooled to room temperature, quenched with aqueous $NaHCO_3$ solution and extracted with ethyl acetate (3 × 20 mL). The organic layers were washed with saturated NaCl solution, dried (Na_2SO_4) and filtered. Evaporation of the solvent(s) under reduced pressure and purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate), furnished the dihydrobenzofurans **3** (89–99%) as oil/solid.



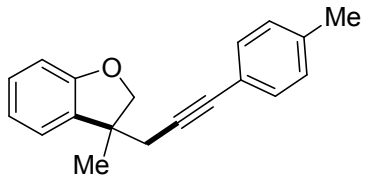
3aa

3-methyl-3-(3-phenylprop-2-ynyl)-2,3-dihydro-1-benzofuran (3aa): GP was carried out with 1-iodo-2-[(2-methylprop-2-enyl)oxy]benzene **1a** (68.2 mg, 0.25 mmol), ethynylbenzene **2a** (63.7 mg, 0.62 mmol), $Pd_2(dba)_3$ (2.28 mg, 1 mol%), K_2CO_3 (138.6 mg, 1 mmol) and DMF (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the dihydrobenzofuran **3aa** (60.5 mg, 98%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2a**)=0.9, R_f(**3aa**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3293, 2922, 2850, 2859, 1720, 1599, 1465, 1324, 1228, 978, 749, 636 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ= 7.40–7.37 (m, 2H, Ar–H), 7.30–7.28 (m, 3H, Ar–H), 7.25–7.23 (dd, J = 8.31, 1.95 Hz, 1H, Ar–H), 7.19–7.14 (dt, J = 7.83, 1.47 Hz, 1H, Ar–H), 6.92–6.88 (dt, J = 7.33, 0.97 Hz, 1H, Ar–H), 6.82 (d, J = 7.82 Hz, 1H, Ar–H), 4.55 (d, J = 8.80 Hz, 1H, –OCH_2–), 4.25–4.22 (d, J = 8.80 Hz, 1H, –OCH_2–), 2.68 (s, 2H, –C–CH_2–), 1.54 (s, 3H, –C–CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 159.4 (s, Ar–C), 134.0 (s, Ar–C), 131.6 (d, 2 × Ar–CH), 128.5 (d, Ar–CH), 128.2 (d, 2 × Ar–CH), 127.8 (d, Ar–CH), 123.5 (s, Ar–C), 123.0 (d, Ar–CH), 120.5 (d, Ar–CH), 109.8 (d, Ar–CH), 86.6 (s, Ar–*C*–C–), 82.4 (s, Ar–C–*C*–), 82.3 (t, –OCH_2–), 45.3 (s, –C–), 31.5 (t, –CH_2–), 24.2 (q, –CH_3). HR-MS (APCI+) m/z calculated for $[C_{18}H_{16}O]^+$=$[M+H]^+$: 249.1274; found 249.1274.



3ab

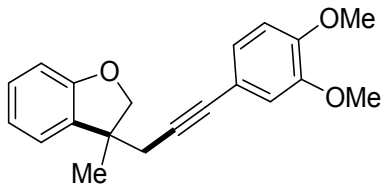
3-methyl-3-[3-(3-methylphenyl)prop-2-ynyl]-2,3-dihydro-1-benzofuran (3ab): GP was carried out with 1-iodo-2-[(2-methylprop-2-enyl)oxy]benzene **1a** (68.2 mg, 0.25 mmol), 1-ethynyl-3-methylbenzene **2b** (71.9 mg, 0.62 mmol), $Pd_2(dba)_3$ (0) (2.28 mg, 1 mol%), K_2CO_3 (138.6 mg, 1 mmol) and DMF (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 98:2) furnished the dihydrobenzofuran **3ab** (64.6 mg, 99%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2b**)=0.9, R_f(**3ab**)=0.8, UV detection IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3056, 2957, 2840, 2300, 1603, 1488, 1225, 1114, 1068, 980, 750, 696 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ= 7.24–7.14 (m, 5H, Ar–H), 7.10–7.09 (d, 1H, J = 8.31 Hz, Ar–H), 6.92–6.88 (m, 1H, Ar–H), 6.83–6.81 (d, J = 7.83 Hz, 1H, Ar–H), 4.56–4.53 (d, J = 8.80 Hz, 1H, –OCH_2–), 4.23 (d, J = 8.80 Hz, 1H, –OCH_2–), 2.67 (s, 2H, –C–CH_2–), 2.31 (s, 3H, Ar–CH_3), 1.53 (s, 3H, –C–CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 159.4 (s, Ar–C), 137.9 (s, Ar–C), 134.1 (s, Ar–C), 132.2 (d, Ar–CH), 128.6 (d, Ar–CH), 128.5 (d, Ar–CH), 128.1 (d, Ar–CH), 123.3 (s, Ar–C), 122.9 (d, Ar–CH), 120.5 (d, Ar–CH), 109.8 (d, Ar–CH), 86.2 (s, Ar–*C*–C–), 82.6 (s, Ar–C–*C*–), 82.3 (t, –OCH_2–), 45.3 (s, –C–), 31.5 (t, –CH_2–), 24.2 (q, –CH_3), 21.2 (q, Ar–CH_3).- HR-MS (APCI+) m/z calculated for $[C_{19}H_{18}O]^+$=$[M+H]^+$: 295.1431; found 295.1434.



3ac

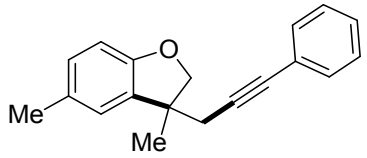
3-methyl-3-[3-(4-methylphenyl)prop-2-ynyl]-2,3-dihydro-1-benzofuran (3ac): GP was carried out with 1-iodo-2-[(2-methylprop-2-enyl)oxy]benzene **1a** (68.2 mg, 0.25 mmol), 1-ethynyl-4-methylbenzene **2c** (71.9 mg, 0.62 mmol), $Pd_2(dba)_3$ (2.28 mg, 1 mol%), K_2CO_3 (138.6 mg, 1 mmol) and DMF (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the dihydrobenzofuran **3ac** (65.4 mg, 97%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2c**)=0.9, R_f(**3ac**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3032, 2920, 2880, 2869, 1724, 1581, 1476, 1335, 1239, 978, 749, 647 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ= 7.29 (s, 1H, Ar–H), 7.27 (s, 1H, Ar–H), 7.27–7.22 (m, 1H, Ar–H), 7.18–7.14 (m, 1H, Ar–H), 7.11 (s, 1H, Ar–H), 7.09 (s, 1H, Ar–H), 6.92–6.88 (m, 1H, Ar–H), 6.82 (d, J = 8.31 Hz, 1H, Ar–H), 4.55 (d, J = 8.80 Hz, 1H, –OCH_2–), 4.24–4.22 (d, J = 8.80 Hz, 1H, –OCH_2–), 2.67 (s, 2H, –C–CH_2–), 2.34 (s, 3H, Ar–CH_3), 1.54 (s, 3H, –C–CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 159.4 (s, Ar–C), 137.9 (s, Ar–C), 134.1 (s, Ar–C), 131.5 (d, 2 × Ar–CH), 129.0 (d, 2 × Ar–CH), 128.5 (d, Ar–CH), 123.0 (d, Ar–CH), 120.5 (d, Ar–CH), 120.4 (s, Ar–C), 109.8 (d, Ar–CH), 85.8 (s, Ar–*C*–C–), 82.5 (s, Ar–C–*C*–), 82.3 (t, –

OCH_2–), 45.3 (s, –C–), 31.6 (t, –CH_2–), 24.2 (q, –CH_3), 21.4 (q, Ar–CH_3). HR-MS (APCI+) m/z calculated for $[C_{19}H_{18}O]^+$=$[M+H]^+$: 262.1358; found 262.1360.



3ad

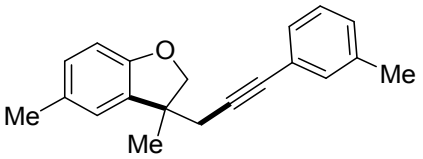
3-[3-(3,4-dimethoxyphenyl)prop-2-ynyl]-3-methyl-2,3-dihydro-1-benzofuran (3ad): GP was carried out with 1-iodo-2-[(2-methylprop-2-enyl)oxy]benzene **1a** (68.2 mg, 0.25 mmol), 4-ethynyl-1,2-dimethoxybenzene **2d** (100.4 mg, 0.62 mmol), $Pd_2(dba)_3$ (2.28 mg, 1 mol%), K_2CO_3 (138.6 mg, 1 mmol) and DMF (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 92:8) furnished the dihydrobenzofuran **3ad** (74.1 mg, 97%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 92:8), R_f(**2d**)=0.6, R_f(**3ad**)=0.5, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3054, 2956, 2850, 2852, 1730, 1589, 1445, 1320, 1238, 974, 746, 646 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ= 7.23–7.21 (dd, 5H, J = 8.32, 0.98 Hz, Ar–H), 7.17–7.13 (dt, 1H, J = 7.34, 1.47 Hz, Ar–H), 6.99–6.96 (dd, 1H, J = 8.32, 1.96 Hz, Ar–H), 6.91–6.86 (m, 2H, Ar–H), 6.81 (d, 1H, J = 7.83 Hz, Ar–H), 6.77 (d, 1H, J = 8.32, Hz, Ar–H), 4.55 (d, J = 8.81 Hz, 1H, –OCH_2–), 4.23 (d, J = 9.29 Hz, 1H, –OCH_2–), 3.87 (s, 3H, Ar–OCH_3), 3.86 (s, 3H, Ar–OCH_3), 2.86 (s, 2H, –C–CH_2–), 1.53 (s, 3H, –C–CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 159.4 (s, Ar–C), 149.1 (s, Ar–C), 148.5 (s, Ar–C), 134.1 (s, Ar–C), 128.5 (d, Ar–CH), 124.7 (d, Ar–CH), 123.0 (d, Ar–CH), 120.5 (d, Ar–CH), 115.7 (s, Ar–C), 114.3 (d, Ar–CH), 110.9 (d, Ar–CH), 109.8 (d, Ar–CH), 85.0 (s, Ar–*C*–C–), 82.4 (s, Ar–C–*C*–), 82.3 (t, –OCH_2–), 55.8 (q, 2 × Ar–OCH_3), 45.3 (s, –C–), 31.5 (t, –CH_2–), 24.3 (q, –CH_3). HR-MS (APCI+) m/z calculated for $[C_{20}H_{20}O_3]^+$=$[M+H]^+$: 309.1486; found 309.1485.



3ba

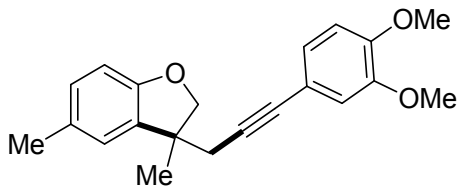
3,5-dimethyl-3-(3-phenylprop-2-ynyl)-2,3-dihydro-1-benzofuran (3ba): GP was carried out with 2-iodo-4-methyl-1-[(2-methylprop-2-enyl)oxy]benzene **1b** (72 mg, 0.25 mmol), ethynylbenzene **2a** (63.7 mg,

0.62 mmol), $Pd_2(dba)_3$ (2.28 mg, 1 mol%), K_2CO_3 (138.6 mg, 1 mmol) and DMF (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the dihydrobenzofuran **3ba** (64.1 mg, 98%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2a**)=0.9, R_f(**3ba**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3052, 2956, 2860, 2849, 1726, 1580, 1475, 1334, 1238, 968, 739, 646 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ= 7.41–7.38 (m, 2H, Ar–H), 7.28 (m, 3H, Ar–H), 7.03 (s, 1H, Ar–H), 6.96 (d, J = 6.85 Hz, 1H, Ar–H), 6.72 (d, J = 7.82 Hz, 1H, Ar–H), 4.54 (d, J = 8.80 Hz, 1H, –OCH_2–), 4.21 (d, J = 8.80 Hz, 1H, –OCH_2–), 2.67 (s, 2H, –C–CH_2–), 2.31 (s, 3H, Ar–CH_3), 1.52 (s, 3H, –C–CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 157.3 (s, Ar–C), 134.0 (s, Ar–C), 131.6 (d, 3 × Ar–CH), 129.8 (s, Ar–C), 128.9 (d, Ar–CH), 128.2 (d, 2 × Ar–CH), 127.8 (d, Ar–CH), 123.5 (d, Ar–CH), 109.3 (d, Ar–CH), 86.8 (s, Ar–*C*–C–), 82.5 (s, Ar–C–*C*–), 82.4 (t, –OCH_2–), 45.3 (s, –C–), 31.5 (t, –CH_2–), 24.1 (q, –CH_3), 20.9 (q, Ar–CH_3). HR-MS (APCI+) m/z calculated for $[C_{19}H_{18}O]^+$=$[M+H]^+$: 263.1431; found 263.1469.



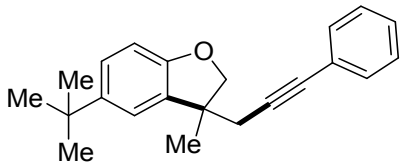
3bb

3,5-dimethyl-3-[3-(3-methylphenyl)prop-2-ynyl]-2,3-dihydro-1-benzofuran (3bb): GP was carried out with 2-iodo-4-methyl-1-[(2-methylprop-2-enyl)oxy]benzene **1b** (72 mg, 0.25 mmol), 1-ethynyl-3-methylbenzene **2b** (71.9 mg, 0.62 mmol), $Pd_2(dba)_3$ (2.28 mg, 1 mol%), K_2CO_3 (138.6 mg, 1 mmol) and DMF (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the dihydrobenzofuran **3bb** (65.5 mg, 95%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2b**)=0.9, R_f(**3bb**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}= 2952, 2860, 2839, 1726, 1596, 1466, 1334, 1226, 968, 739, 639 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ= 7.32–7.27 (m, 3H, Ar–H), 7.19 (d, 1H, J = 6.85 Hz, Ar–H), 7.12 (s, 1H, Ar–H), 7.05 (d, 1H, J = 8.31 Hz, Ar–H), 6.80 (d, J = 7.83 Hz, 1H, Ar–H), 4.62 (d, J = 8.80 Hz, 1H, –OCH_2–), 4.30 (d, J = 8.80 Hz, 1H, –OCH_2–), 2.75 (s, 2H, –C–CH_2–), 2.41 (s, 3H, Ar–CH_3), 2.40 (s, 3H, Ar–CH_3), 1.61 (s, 3H, –C–CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 157.3 (s, Ar–C), 137.9 (s, Ar–C), 134.1 (s, Ar–C), 132.2 (d, Ar–CH), 129.8 (s, Ar–C), 128.9 (d, Ar–CH), 128.7 (d, Ar–CH), 128.6 (d, Ar–CH), 128.1 (d, Ar–CH), 123.5 (d, Ar–CH), 123.3 (s, Ar–C), 109.3 (d, Ar–CH), 86.4 (s, Ar–*C*–C–), 82.5 (s, Ar–C–*C*–), 82.4 (t, –OCH_2–), 45.3 (s, –C–), 31.5 (t, –CH_2–), 24.1 (q, –CH_3), 21.2 (q, Ar–CH_3), 20.9 (q, Ar–CH_3).-HR-MS (APCI+) m/z calculated for $[C_{20}H_{20}O]^+$=$[M+H]^+$: 277.1587; found 277.1589.



3bd

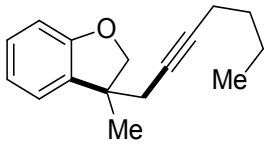
3-[3-(3,4-dimethoxyphenyl)prop-2-ynyl]-3,5-dimethyl-2,3-dihydro-1-benzofuran (3bd): GP was carried out with 2-iodo-4-methyl-1-[(2-methylprop-2-enyl)oxy]benzene **1b** (72 mg, 0.25 mmol), 4-ethynyl-1,2-dimethoxybenzene **2d** (100.4 mg, 0.62 mmol), $Pd_2(dba)_3$ (2.28 mg, 1 mol%), K_2CO_3 (138.6 mg, 1 mmol) and DMF (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 98:2) furnished the dihydrobenzofuran **3bd** (77.2 mg, 96%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**2d**)=0.6, R_f(**3bd**)=0.5, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3253, 2960, 2830, 2829, 1730, 1589, 1469, 1326, 1238, 976, 748, 666 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ= 7.02 (s, 1H, Ar–H), 7.00–6.97 (dd, 1H, J = 8.32, 1.95 Hz, Ar–H), 6.96–6.94 (d, 1H, J = 7.83 Hz, Ar–H), 6.88 ((d, 1H, J = 1.96 Hz, Ar–H), 6.78 (d, 1H, J = 8.32 Hz, Ar–H), 6.70 (d, 1H, J = 8.31, Hz, Ar–H), 4.53 (d, J = 8.81 Hz, 1H, –OCH_2–), 4.20 (d, J = 8.80 Hz, 1H, –OCH_2–), 3.89 (s, 3H, Ar–OCH_3), 3.86 (s, 3H, Ar–OCH_3), 2.85 (s, 2H, –C–CH_2–), 2.30 (s, 3H, Ar-CH_3) 1.51 (s, 3H, –C–CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 157.3 (s, Ar–C), 149.1 (s, Ar–C), 148.5 (s, Ar–C), 134.0 (s, Ar–C), 129.7 (s, Ar–C), 128.9 (d, Ar–CH), 124.6 (d, Ar–CH), 123.5 (d, Ar–CH), 115.7 (s, Ar–C), 114.3 (d, Ar–CH), 110.9 (d, Ar–CH), 109.3 (d, Ar–CH), 85.1 (s, Ar–*C*–C–), 82.4 (t, –OCH_2–), 82.3 (s, Ar–C–*C*–), 55.8 (q, 2 × Ar–OCH_3), 45.3 (s, –C–), 31.5 (t, –CH_2–), 24.3 (q, –CH_3), 20.9 (q, Ar–CH_3). HR-MS (APCI+) m/z calculated for $[C_{20}H_{20}O_3]^+$=$[M+H]^+$: 323.1642; found 323.1647.



3ca

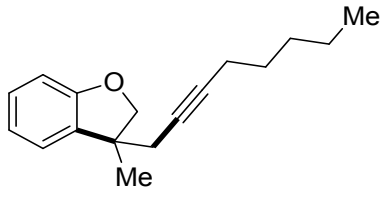
5-tert-butyl-3-methyl-3-(3-phenylprop-2-ynyl)-2,3-dihydro-1-benzofuran (3ca): GP was carried out with 4-tert-butyl-2-iodo-1-[(2-methylprop-2-enyl)oxy]benzene **1c** (82.5 mg, 0.25 mmol), ethynylbenzene **2a** (63.7 mg, 0.62 mmol), $Pd_2(dba)_3$ (2.28 mg, 1 mol%), K_2CO_3 (138.6 mg, 1 mmol) and DMF (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the dihydrobenzofuran **3ca** (72.2 mg, 95%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2a**)=0.8, R_f(**3ca**)=0.7, UV detection].- IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3233, 2953, 2860, 2849, 1730, 1589, 1466, 1323, 1229, 972, 742, 698, 636 cm^{-1}. ^1H

NMR ($CDCl_3$, 400 MHz): δ= 7.41–7.39 (m, 2H, Ar–H), 7.30–7.27 (m, 5H, Ar–H), 7.19 (dd, J = 8.32, 2.45 Hz, 1H, Ar–H), 6.75 (d, J = 8.81 Hz, 1H, Ar–H), 4.52 (d, J = 8.81 Hz, 1H, –OCH_2–), 4.24–4.21 (d, J = 8.81 Hz, 1H, –OCH_2–), 2.69 (s, 2H, –C–CH_2–), 1.55 (s, 3H, –C–CH_3), 1.29 (s, 9H, Ar–C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 157.2 (s, Ar–C), 143.6 (s, Ar–C), 133.6 (s, Ar–C), 131.6 (d, 2 × Ar–CH), 128.2 (d, 2 × Ar–CH), 127.8 (d, Ar–CH), 125.4 (d, Ar–CH), 123.5 (s, Ar–C), 119.8 (d, Ar–CH), 108.9 (d, Ar–CH), 86.9 (s, Ar–*C*–C–), 82.6 (t, –OCH_2–), 82.4 (s, Ar–C–*C*–), 45.4 (s, –C–), 34.4 (s, –*C*–), 31.5 (t, –CH_2–), 23.9 (q, –CH_3). HR-MS (APCI+) m/z calculated for $[C_{22}H_{24}O]^+$=$[M+H]^+$: 305.1900; found 305.1907.



3ak

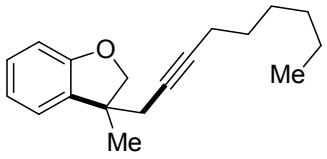
3-hept-2-ynyl-3-methyl-2,3-dihydro-1-benzofuran (3ak): GP was carried out with 1-iodo-2-[(2-methylprop-2-enyl)oxy]benzene **1a** (68.2 mg, 0.25 mmol), hex-1-yne **2k** (51 mg, 0.62 mmol), $Pd_2(dba)_3$ (2.28 mg, 1 mol%), K_2CO_3 (138.6 mg, 1 mmol) and DMF (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the dihydrobenzofuran **3ak** (54.8 mg, 98%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2k**)=0.9, R_f(**3ak**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3250, 2953, 2856, 2869, 1724, 1530, 1466, 1325, 1228, 976, 740, 631 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ= 7.17–7.12 (m, 2H, Ar–H), 6.90–6.86 (dt, J = 7.32, 0.98 Hz, 1H, Ar–H), 6.79 (d, J = 7.82, Hz, 1H, Ar–H), 4.49 (d, J = 8.80 Hz, 1H, –OCH_2–), 4.18 (d, J = 8.80 Hz, 1H, –OCH_2–), 2.43 (m, 2H, –C–CH_2–), 2.18–2.14 (m, 2H,), 1.48–1.33 (m, 2H,), 1.45 (s, 3H, –C–CH_3), 0.92–0.89 (m, 2H,), 0.91 (t, J = 8.80 Hz, 3H, –CH_2–CH_2–CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 159.4 (s, Ar–C), 134.3 (s, Ar–C), 128.3 (d, Ar–CH), 122.8 (d, Ar–CH), 120.4 (d, Ar–CH), 109.7 (d, Ar–CH), 82.3 (s, Ar–*C*–C–), 82.2 (t, –OCH_2–), 76.5 (s, Ar–C–*C*–), 45.1 (s, –C–), 31.0 (t, CH_2), 30.9 (t, CH_2), 24.3 (q, CH_3), 21.8 (t, CH_2), 18.3 (t, CH_2), 13.6 (q, CH_3). HR-MS (APCI+) m/z calculated for $[C_{16}H_{20}O]^+$=$[M+H]^+$: 229.1587; found 229.1585.



3al

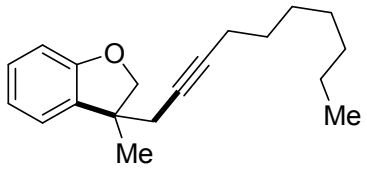
3-methyl-3-oct-2-ynyl-2,3-dihydro-1-benzofuran (3al): GP was carried out with 1-iodo-2-[(2-methylprop-2-enyl)oxy]benzene **1a** (68.2 mg, 0.25 mmol), hept-1-yne **2l** (59.5 mg, 0.62 mmol), $Pd_2(dba)_3$

(2.28 mg, 1 mol%), K_2CO_3 (138.6 mg, 1 mmol) and DMF (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the dihydrobenzofuran **3al** (58.2 mg, 97%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2l**)=0.9, R_f(**3al**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3250, 2960, 2830, 2869, 1730, 1590, 1463, 1323, 1229, 979, 745, 646 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ= 7.16–7.11 (m, 2H, Ar–H), 6.89–6.85 (dt, J = 7.33, 0.98 Hz, 1H, Ar–H), 6.78 (d, J = 8.31 Hz, 1H, Ar–H), 4.48 (d, J = 8.80 Hz, 1H, –OCH_2–), 4.17 (d, J = 8.80 Hz, 1H, –OCH_2–), 2.42 (m, 2H, –C–CH_2–), 2.16–2.11 (m, 2H,), 1.44 (s, 3H, –C–CH_3), 1.36–1.26 (m, 4H), 0.92–0.87 (m, 2H,), 0.89 (t, J = 8.80 Hz, 3H, –CH_2–CH_2–CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 159.4 (s, Ar–C), 134.3 (s, Ar–C), 128.3 (d, Ar–CH), 122.8 (d, Ar–CH), 120.4 (d, Ar–CH), 109.7 (d, Ar–CH), 82.4 (s, Ar–*C*–C–), 82.3 (t, –OCH_2–), 76.5 (s, Ar–C–*C*–), 45.2 (s, –C–), 31.0 (t, CH_2), 30.9 (t, CH_2), 28.6 (t, CH_2), 24.3 (q, CH_3), 22.2 (t, CH_2), 18.6 (t, CH_2), 14.0 (q, CH_3). HR-MS (APCI+) m/z calculated for $[C_{17}H_{22}O]^+$=$[M+H]^+$: 243.1751; found 243.1743.



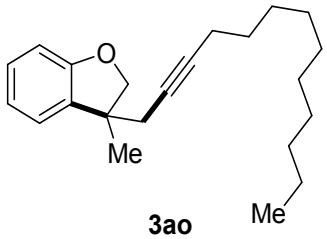
3am

3-methyl-3-non-2-ynyl-2,3-dihydro-1-benzofuran (3am): GP was carried out with 1-iodo-2-[(2-methylprop-2-enyl)oxy]benzene **1a** (68.2 mg, 0.25 mmol), oct-1-yne **2m** (65.7 mg, 0.62 mmol), $Pd_2(dba)_3$ (2.28 mg, 1 mol%), K_2CO_3 (138.6 mg, 1 mmol) and DMF (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the dihydrobenzofuran **3am** (62.8 mg, 99%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2m**)=0.9, R_f(**3am**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3250, 2962, 2860, 2846, 1731, 1610, 1464, 1321, 1229, 979, 745, 666 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ= 7.16–7.10 (m, 2H, Ar–H), 6.88–6.85 (dt, J = 7.33, 0.97 Hz, 1H, Ar–H), 6.78 (d, J = 7.82 Hz, 1H, Ar–H), 4.49–4.46 (d, J = 8.80 Hz, 1H, –OCH_2–), 4.17 (d, J = 8.80 Hz, 1H, –OCH_2–), 2.42 (m, 2H, –C–CH_2–), 2.16–2.12 (m, 2H,), 1.48–1.24 (m, 6H), 1.44 (s, 3H, –C–CH_3), 0.90–0.87 (m, 2H,), 0.89 (t, J = 8.80 Hz, 3H, –CH_2–CH_2–CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 159.4 (s, Ar–C), 134.3 (s, Ar–C), 128.3 (d, Ar–CH), 122.8 (d, Ar–CH), 120.4 (d, Ar–CH), 109.7 (d, Ar–CH), 82.4 (s, Ar–*C*–C–), 82.3 (t, –OCH_2–), 76.5 (s, Ar–C–*C*–), 45.2 (s, –C–), 31.3 (t, CH_2), 30.9 (t, CH_2), 28.9 (t, CH_2), 28.5 (t, CH_2), 24.3 (q, CH_3), 22.6 (t, CH_2), 18.7 (t, CH_2), 14.0 (q, CH_3). HR-MS (APCI+) m/z calculated for $[C_{18}H_{24}O]^+$=$[M+H]^+$: 257.1900; found 257.1896.



3an

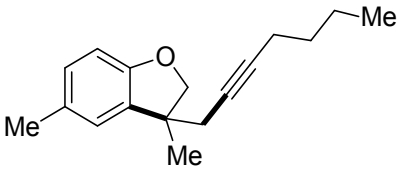
3-dec-2-ynyl-3-methyl-2,3-dihydro-1-benzofuran (3an): GP was carried out with 1-iodo-2-[(2-methylprop-2-enyl)oxy]benzene **1a** (68.2 mg, 0.25 mmol), non-1-yne **2n** (76.8 mg, 0.62 mmol), $Pd_2(dba)_3$ (2.28 mg, 1 mol%), K_2CO_3 (138.6 mg, 1 mmol) and DMF (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the dihydrobenzofuran **3an** (64.9 mg, 97%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2n**)=0.9, R_f(**3an**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3233, 2961, 2950, 2850, 1721, 1589, 1455, 1334, 1230, 980, 750, 640 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ= 7.17–7.12 (m, 2H, Ar–H), 6.89–6.86 (dt, J = 7.83, 0.98 Hz, 1H, Ar–H), 6.79 (d, J = 7.83 Hz, 1H, Ar–H), 4.48 (d, J = 8.81 Hz, 1H, –OCH_2–), 4.17 (d, J = 8.81 Hz, 1H, –OCH_2–), 2.43 (m, 2H, –C–CH_2–), 2.17–2.13 (m, 2H,), 1.51–1.28 (m, 8H), 1.45 (s, 3H, –C–CH_3), 0.91–0.88 (m, 2H,), 0.90 (t, J = 8.80 Hz, 3H, –CH_2–CH_2–CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 159.4 (s, Ar–C), 134.3 (s, Ar–C), 128.3 (d, Ar–CH), 122.8 (d, Ar–CH), 120.4 (d, Ar–CH), 109.7 (d, Ar–CH), 82.4 (s, Ar–*C*–C–), 82.2 (t, –OCH_2–), 76.5 (s, Ar–C–*C*–), 45.1 (s, –C–), 31.8 (t, CH_2), 30.9 (t, CH_2), 29.0 (t, CH_2), 28.8 (t, CH_2), 28.7 (t, CH_2), 24.3 (q, CH_3), 22.6 (t, CH_2), 18.6 (t, CH_2), 14.1 (q, CH_3). HR-MS (APCI+) m/z calculated for $[C_{22}H_{24}O]^+$=$[M+H]^+$: 271.2056; found 271.2062.



3ao

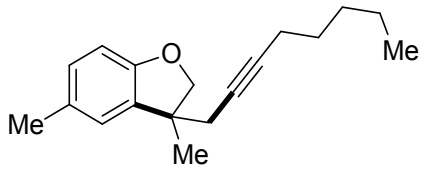
3-methyl-3-tridec-2-ynyl-2,3-dihydro-1-benzofuran (3ao): GP was carried out with 1-iodo-2-[(2-methylprop-2-enyl)oxy]benzene **1a** (68.2 mg, 0.25 mmol), dodec-1-yne **2o** (102.9 mg, 0.62 mmol), $Pd_2(dba)_3$ (2.28 mg, 1 mol%), K_2CO_3 (138.6 mg, 1 mmol) and DMF (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the dihydrobenzofuran **3ao** (78.4 mg, 98%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2o**)=0.9, R_f(**3ao**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}= 2960, 2950, 2850, 1721, 1593, 1466, 1325, 1229, 972, 742, 633 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ= 7.17–

7.11 (m, 2H, Ar–H), 6.89–6.85 (dt, J = 7.84, 0.98 Hz, 1H, Ar–H), 6.79 (d, J = 7.83 Hz, 1H, Ar–H), 4.48 (d, J = 8.80 Hz, 1H, –OCH_2–), 4.17 (d, J = 8.80 Hz, 1H, –OCH_2–), 2.43 (t, J = 3.92 Hz, 2H, –C–CH_2–), 2.17–2.12 (m, 2H,), 1.49–1.27 (m, 14H), 1.45 (s, 3H, –C–CH_3), 0.90–0.87 (m, 2H,), 0.89 (t, J = 8.80 Hz, 3H, –CH_2–CH_2–CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 159.5 (s, Ar–C), 134.4 (s, Ar–C), 128.4 (d, Ar–CH), 122.9 (d, Ar–CH), 120.4 (d, Ar–CH), 109.7 (d, Ar–CH), 82.5 (s, Ar–*C*–C–), 82.3 (t, –OCH_2–), 76.6 (s, Ar–C–*C*–), 45.2 (s, –C–), 31.9 (t, CH_2), 30.9 (t, CH_2), 29.6 (t,2 × CH_2), 29.3 (t, CH_2), 29.2 (t, CH_2), 29.0 (t, CH_2), 28.8 (t, CH_2), 24.3 (q, CH_3), 22.7 (t, CH_2), 18.7 (t, CH_2), 14.1 (q, CH_3). HR-MS (APCI+) m/z calculated for $[C_{22}H_{32}O]^+$=$[M+H]^+$: 313.2526; found 313.2527.



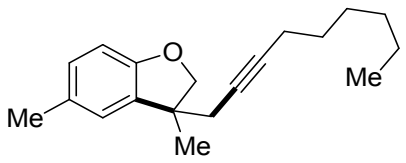
3bk

3-hept-2-ynyl-3,5-dimethyl-2,3-dihydro-1-benzofuran (3bk): GP was carried out with 2-iodo-4-methyl-1-[(2-methylprop-2-enyl)oxy]benzene **1b** (72 mg, 0.25 mmol), hex-1-yne **2k** (51 mg, 0.62 mmol), $Pd_2(dba)_3$ (2.28 mg, 1 mol%), K_2CO_3 (138.6 mg, 1 mmol) and DMF (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the dihydrobenzofuran **3ak** (59.2 mg, 98%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2k**)=0.9, R_f(**3ak**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3250, 2958, 2851, 2840, 1730, 1569, 1435, 1324, 1238, 979, 750, 652 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ= 6.95 (s, 1H, Ar–H), 6.93 (d, J = 7.82 Hz, 1H, Ar–H), 6.68 (d, J = 7.83, Hz, 1H, Ar–H), 4.45 (d, J = 8.81 Hz, 1H, –OCH_2–), 4.15 (d, J = 8.80 Hz, 1H, –OCH_2–), 2.41 (t, J = 4.40 Hz, 2H, –C–CH_2–), 2.29 (s, 3H, Ar–CH_3), 2.18–2.14 (m, 2H), 1.48–1.34 (m, 2H), 1.45 (s, 3H, –C–CH_3), 0.92–0.89 (m, 2H), 0.91 (t, J = 8.80 Hz, 3H, –CH_2–CH_2–CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 157.3 (s, Ar–C), 134.3 (s, Ar–C), 129.6 (s, Ar–C), 128.7 (d, Ar–CH), 123.4 (d, Ar–CH), 109.2 (d, Ar–CH), 82.4 (t, –OCH_2–), 82.3 (s, Ar–*C*–C–), 76.6 (s, Ar–C–*C*–), 45.2 (s, –C–), 31.0 (t, CH_2), 30.8 (t, CH_2), 24.2 (q, CH_3), 21.6 (t, CH_2), 20.8 (q, Ar–CH_3), 18.3 (t, CH_2), 13.6 (q, CH_3). HR-MS (APCI+) m/z calculated for $[C_{17}H_{22}O]^+$=$[M+H]^+$: 244.1743; found 244.1740.



3bl

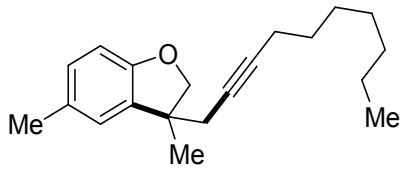
3,5-dimethyl-3-oct-2-ynyl-2,3-dihydro-1-benzofuran (3bl): GP was carried out with 2-iodo-4-methyl-1-[(2-methylprop-2-enyl)oxy]benzene **1b** (72 mg, 0.25 mmol), hept-1-yne **2l** (59.5 mg, 0.62 mmol), $Pd_2(dba)_3$ (2.28 mg, 1 mol%), K_2CO_3 (138.6 mg, 1 mmol) and DMF (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the dihydrobenzofuran **3bl** (62.7 mg, 98%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2l**)=0.9, R_f(**3bl**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3250, 2962, 2851, 2869, 1730, 1562, 1464, 1332, 1230, 962, 752, 662 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ= 6.95 (s, 1H, Ar–H), 6.93 (d, J = 7.83 Hz, 1H, Ar–H), 6.67 (d, J = 8.31, Hz, 1H, Ar–H), 4.45 (d, J = 8.81 Hz, 1H, –OCH_2–), 4.14 (d, J = 8.81 Hz, 1H, –OCH_2–), 2.40 (t, J = 3.91 Hz, 2H, –C–CH_2–), 2.28 (s, 3H, Ar–CH_3), 2.17–2.12 (m, 2H), 1.50–1.25 (m, 6H), 1.43 (s, 3H, –C–CH_3), 0.91–0.88 (t, J = 14.18, 7.34 Hz, 3H, –CH_2–CH_2–CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 157.3 (s, Ar–C), 134.3 (s, Ar–C), 129.6 (s, Ar–C), 128.7 (d, Ar–CH), 123.4 (d, Ar–CH), 109.2 (d, Ar–CH), 82.4 (t, –OCH_2–), 82.3 (s, Ar–*C*–C–), 76.6 (s, Ar–C–*C*–), 45.2 (s, –C–), 31.0 (t, CH_2), 30.8 (t, CH_2), 28.7 (t, CH_2), 24.2 (q, CH_3), 22.2 (t, CH_2), 20.8 (q, Ar–CH_3), 18.6 (t, CH_2), 14.0 (q, CH_3). HR-MS (APCI+) m/z calculated for $[C_{18}H_{24}O]^+$=$[M+H]^+$: 257.1900; found 257.1902.



3bm

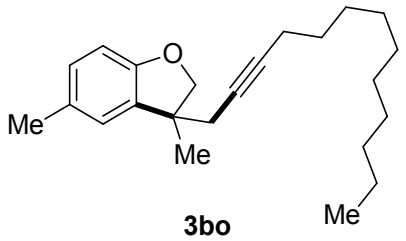
3,5-dimethyl-3-non-2-ynyl-2,3-dihydro-1-benzofuran (3bm): GP was carried out with 2-iodo-4-methyl-1-[(2-methylprop-2-enyl)oxy]benzene **1b** (72 mg, 0.25 mmol), oct-1-yne **2m** (65.7 mg, 0.62 mmol), $Pd_2(dba)_3$ (2.28 mg, 1 mol%), K_2CO_3 (138.6 mg, 1 mmol) and DMF (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the dihydrobenzofuran **3bm** (66.3 mg, 99%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2m**)=0.9, R_f(**3bm**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3250, 2968, 2851, 2839, 1742, 1602, 1485, 1364, 1302, 982, 762, 662 cm^{-1}. ^1H NMR ($CDCl_3$, 400

MHz): δ= 6.95 (s, 1H, Ar–H), 6.93 (d, J = 8.31 Hz, 1H, Ar–H), 6.68 (d, J = 7.83, Hz, 1H, Ar–H), 4.46 (d, J = 8.80 Hz, 1H, –OCH_2–), 4.15 (d, J = 8.80 Hz, 1H, –OCH_2–), 2.41 (t, J = 3.92 Hz, 2H, –C–CH_2–), 2.29 (s, 3H, Ar–CH_3), 2.18–2.13 (m, 2H), 1.50–1.26 (m, 8H), 1.43 (s, 3H, –C–CH_3), 0.91–0.88 (t, J = 13.69, 6.36 Hz, 3H, –CH_2–CH_2–CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 157.3 (s, Ar–C), 134.3 (s, Ar–C), 129.6 (s, Ar–C), 128.7 (d, Ar–CH), 123.4 (d, Ar–CH), 109.2 (d, Ar–CH), 82.4 (s, Ar–*C*–C–), 82.3 (t, –OCH_2–), 76.6 (s, Ar–C–*C*–), 45.2 (s, –C–), 31.3 (t, CH_2), 30.8 (t, CH_2), 28.9 (t, CH_2), 28.5 (t, CH_2), 24.2 (q, CH_3), 22.5 (t, CH_2), 20.8 (q, Ar–CH_3), 18.7 (t, CH_2), 14.0 (q, CH_3). HR-MS (APCI+) m/z calculated for $[C_{19}H_{26}O]^+$=$[M+H]^+$: 271.2056; found 271.2059.



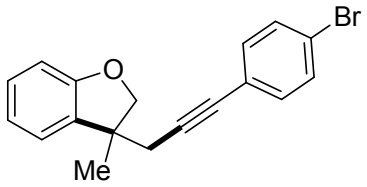
3bn

3-dec-2-ynyl-3,5-dimethyl-2,3-dihydro-1-benzofuran (3bn): GP was carried out with 2-iodo-4-methyl-1-[(2-methylprop-2-enyl)oxy]benzene **1b** (72 mg, 0.25 mmol), non-1-yne **2n** (76.8 mg, 0.62 mmol), $Pd_2(dba)_3$ (2.28 mg, 1 mol%), K_2CO_3 (138.6 mg, 1 mmol) and DMF (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the dihydrobenzofuran **3bn** (69.5 mg, 98%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2n**)=0.9, R_f(**3bn**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}= 2961, 2951, 2851, 2853, 1721, 1590, 1466, 1325, 1229, 979, 745, 637 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ= 6.96 (s, 1H, Ar–H), 6.93 (d, J = 8.80 Hz, 1H, Ar–H), 6.68 (d, J = 7.83, Hz, 1H, Ar–H), 4.46 (d, J = 8.80 Hz, 1H, –OCH_2–), 4.15 (d, J = 8.80 Hz, 1H, –OCH_2–), 2.41 (t, J = 3.92 Hz, 2H, –C–CH_2–), 2.29 (s, 3H, Ar–CH_3), 2.17–2.13 (m, 2H), 1.52–1.29 (m, 10H), 1.44 (s, 3H, –C–CH_3), 0.91–0.88 (t, J = 13.69, 6.36 Hz, 3H, –CH_2–CH_2–CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 157.3 (s, Ar–C), 134.3 (s, Ar–C), 129.6 (s, Ar–C), 128.7 (d, Ar–CH), 123.4 (d, Ar–CH), 109.2 (d, Ar–CH), 82.4 (t, –OCH_2–), 82.3 (s, Ar–*C*–C–), 76.6 (s, Ar–C–*C*–), 45.2 (s, –C–), 31.8 (t, CH_2), 30.8 (t, CH_2), 29.0 (t, CH_2), 28.8 (t, CH_2), 28.7 (t, CH_2), 24.2 (q, CH_3), 22.6 (t, CH_2), 20.9 (q, Ar–CH_3), 18.7 (t, CH_2), 14.1 (q, CH_3). HR-MS (APCI+) m/z calculated for $[C_{20}H_{28}O]^+$=$[M+H]^+$: 285.2213; found 285.2215.



3bo

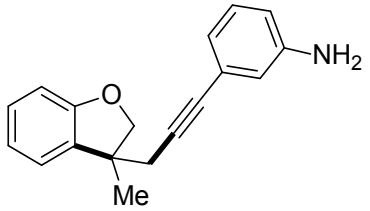
3,5-dimethyl-3-tridec-2-ynyl-2,3-dihydro-1-benzofuran (3bo): GP was carried out with 2-iodo-4-methyl-1-[(2-methylprop-2-enyl)oxy]benzene **1b** (72 mg, 0.25 mmol), dodec-1-yne **2o** (102.9 mg, 0.62 mmol), $Pd_2(dba)_3$ (2.28 mg, 1 mol%), K_2CO_3 (138.6 mg, 1 mmol) and DMF (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the dihydrobenzofuran **3bo** (79.3 mg, 98%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2o**)=0.9, R_f(**3bo**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3260, 2958, 2952, 2852, 1724, 1560, 1465, 1364, 1298, 971, 741, 633 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ= 6.95 (s, 1H, Ar–H), 6.93 (d, J = 7.83 Hz, 1H, Ar–H), 6.67 (d, J = 7.82, Hz, 1H, Ar–H), 4.45 (d, J = 8.81 Hz, 1H, –OCH_2–), 4.14 (d, J = 8.80 Hz, 1H, –OCH_2–), 2.41 (t, J = 4.40 Hz, 2H, –C–CH_2–), 2.29 (s, 3H, Ar–CH_3), 2.17–2.12 (m, 2H), 1.51–1.27 (m, 14H), 1.43 (s, 3H, –C–CH_3), 0.90–0.86 (m, 2H), 0.88 (t, J = 13.69, 6.35 Hz, 3H, –CH_2–CH_2–CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 157.3 (s, Ar–C), 134.3 (s, Ar–C), 129.6 (s, Ar–C), 128.7 (d, Ar–CH), 123.4 (d, Ar–CH), 109.2 (d, Ar–CH), 82.4 (t, –OCH_2–), 82.3 (s, Ar–*C*–C–), 76.6 (s, Ar–C–*C*–), 45.2 (s, –C–), 31.9 (t, CH_2), 30.8 (t, CH_2), 29.6 (t, CH_2), 29.5 (t, CH_2), 29.3 (t, CH_2), 29.1 (t, CH_2), 29.0 (t, CH_2), 28.8 (t, CH_2), 24.2 (q, CH_3), 22.7 (t, CH_2), 20.9 (q, Ar–CH_3), 18.7 (t, CH_2), 14.1 (q, CH_3). –HR-MS (APCI+) m/z calculated for $[C_{23}H_{34}O]^+$=$[M+H]^+$: 327.2682; found 327.2680.



3ae

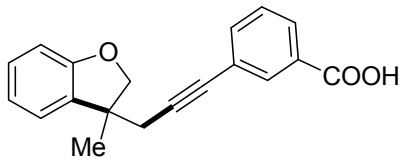
3-[3-(4-bromophenyl)prop-2-ynyl]-3-methyl-2,3-dihydro-1-benzofuran (3ae): GP was carried out with 1-iodo-2-[(2-methylprop-2-enyl)oxy]benzene **1a** (68.2 mg, 0.25 mmol), 1-bromo-4-ethynylbenzene **2e** (112.2 mg, 0.62 mmol), $Pd_2(dba)_3$ (2.28 mg, 1 mol%), K_2CO_3 (138.6 mg, 1 mmol) and DMF (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the dihydrobenzofuran **3ae** (74.6 mg, 92%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2e**)=0.9, R_f(**3ae**)=0.8, UV detection]. IR (MIR-ATR,

4000–600 cm^{-1}): ν_{max}=3053, 2957, 2865, 2852, 1732, 1583, 1464, 1344, 1248, 969, 749, 646 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ= 7.43–7.40 (m, 2H, Ar–H), 7.23–7.14 (m, 4H, Ar–H), 6.92–6.88 (m, 1H, Ar–H), 6.82 (d, 1H, J = 7.83 Hz, Ar–H), 4.53 (d, J = 8.80 Hz, 1H, –OCH_2–), 4.24–4.21 (d, J = 8.80 Hz, 1H, –OCH_2–), 2.66 (s, 2H, –C–CH_2–), 1.52 (s, 3H, –C–CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 159.4 (s, Ar–C), 133.8 (s, Ar–C), 133.0 (d, 2 × Ar–CH), 131.5 (d, 2 × Ar–CH), 128.6 (d, Ar–CH), 122.9 (d, Ar–CH), 122.4 (s, Ar–C), 122.0 (s, Ar–C), 120.6 (d, Ar–CH), 109.8 (d, Ar–CH), 88.0 (s, Ar–*C*–C–), 82.2 (t, –OCH_2–), 81.5 (s, Ar–C–*C*–),45.3 (s, –C–), 31.6 (t, –CH_2–), 24.2 (q, –CH_3). HR-MS (APCI+) m/z calculated for $[C_{19}H_{18}O]^+$=$[M+H]^+$: 326.0306; found 326.0312.



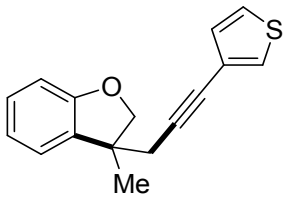
3af

3-[3-(3-methyl-2,3-dihydro-1-benzofuran-3-yl)prop-1-ynyl]aniline (3af): GP was carried out with 1-iodo-2-[(2-methylprop-2-enyl)oxy]benzene **1a** (68.2 mg, 0.25 mmol), 3-ethynylaniline **2f** (72.5 mg, 0.62 mmol), $Pd_2(dba)_3$ (2.28 mg, 1 mol%), K_2CO_3 (138.6 mg, 1 mmol) and DMF (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 96:4) furnished the dihydrobenzofuran **3af** (61.1 mg, 94%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 93:7), R_f(**2f**)=0.7, R_f(**3af**)=0.6, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3411, 3223, 2960, 2890, 2860, 1723, 1589, 1469, 1325, 1223, 979, 759, 646 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ= 7.24–7.22 (dd, J = 7.33, 0.98 Hz, 1H, Ar–H), 7.18–7.14 (dt, 1H, J = 7.83, 1.47 Hz, Ar–H), 7.07 (t, 1H, J = 15.65, Hz, Ar–H), 6.92–6.88 (dt, J = 7.34, 0.98 Hz, 1H, Ar–H), 6.81 (m, 2H, Ar–H), 6.71 (t, 1H, J = 3.91 Hz, Ar–H), 6.62–6.60 (m, 1H, Ar–H), 4.54 (d, J = 8.81 Hz, 1H, –OCH_2–), 4.22 (d, J = 8.80 Hz, 1H, –OCH_2–), 3.65 (bs, 2H, Ar–NH_2), 2.66 (s, 2H, –C–CH_2–), 1.52 (s, 3H, –C–CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 159.4 (s, Ar–C), 146.2 (s, Ar–C), 134.1 (s, Ar–C), 129.2 (d, Ar–CH), 128.5 (d, Ar–CH), 124.2 (s, Ar–C), 123.0 (d, Ar–CH), 122.0 (d, Ar–CH), 120.5 (d, Ar–CH), 117.9 (d, Ar–CH), 114.9 (d, Ar–CH), 109.8 (d, Ar–CH), 86.0 (s, Ar–*C*–C–), 82.6 (s, Ar–C–*C*–), 82.3 (t, –OCH_2–), 45.3 (s, –C–), 31.5 (t, –CH_2–), 24.2 (q, –CH_3).- HR-MS (APCI+) m/z calculated for $[C_{18}H_{17}NO]^+$=$[M+H]^+$: 264.1383; found 264.1386.



3ag

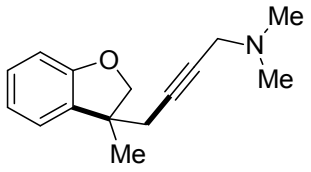
3-[3-(3-methyl-2,3-dihydro-1-benzofuran-3-yl)prop-1-ynyl]benzoic acid (3ag): GP was carried out 1-iodo-2-[(2-methylprop-2-enyl)oxy]benzene **1a** (68.2 mg, 0.25 mmol), 3-ethynylbenzoic acid **2g** (89.6 mg, 0.62 mmol), $Pd_2(dba)_3$ (2.28 mg, 1 mol%), K_2CO_3 (138.6 mg, 1 mmol) and DMF (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the dihydrobenzofuran **3ag** (68.5 mg, 94%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2g**)=0.4, R_f(**3ag**)=0.3, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}= 3456, 2996, 2953, 2864, 2639, 1826, 1696, 1566, 1434, 1326, 999, 789, 669 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ= 8.13 (s, 1H, Ar–H), 8.03 (d, 1H, J = 7.83 Hz, Ar–H), 7.60 (d, 1H, J = 7.34 Hz, Ar–H), 7.41 (t, 1H, J = 15.65, 7.83 Hz, Ar–H), 7.23 (m, 1H, Ar–H), 7.19–7.16 (m, 1H, Ar–H), 6.92 (m, 1H, Ar–H), 6.84 (d, 1H, J = 7.82 Hz, Ar–H), 4.56 (d, J = 8.80 Hz, 1H, –OCH_2–), 4.25 (d, J = 8.80 Hz, 1H, –OCH_2–), 2.70 (s, 2H, –C–CH_2–), 1.55 (s, 3H, –C–CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 171.4 (s, Ar–CO), 159.4 (s, Ar–C), 136.6 (s, Ar–C), 133.8 (s, Ar–C), 133.3 (d, Ar–CH), 129.5 (s, Ar–C), 129.4 (d, Ar–CH), 128.6 (d, Ar–CH), 128.5 (d, Ar–CH), 124.1 (s, Ar–C), 122.9 (d, Ar–CH), 120.6 (d, Ar–CH), 109.9 (d, Ar–CH), 88.0 (s, Ar–*C*–C–), 82.2 (t, –OCH_2–), 81.4 (s, Ar–C–*C*–), 45.3 (s, –C–), 31.5 (t, –CH_2–), 24.2 (q, –CH_3). HR-MS (APCI+) m/z calculated for $[C_{20}H_{20}O]^+$=$[M+H]^+$: 292.1099; found 292.1102.



3ah

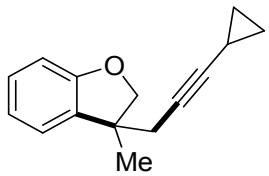
3-methyl-3-(3-thien-3-ylprop-2-ynyl)-2,3-dihydro-1-benzofuran (3ah): GP was carried out with 1-iodo-2-[(2-methylprop-2-enyl)oxy]benzene **1a** (68.2 mg, 0.25 mmol), 3-ethynylthiophene **2h** (66.9 mg, 0.62 mmol), $Pd_2(dba)_3$ (2.28 mg, 1 mol%), K_2CO_3 (138.6 mg, 1 mmol) and DMF (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 98:2) furnished the dihydrobenzofuran **3ah** (56.7 mg, 90%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**2h**)=0.8, R_f(**3ah**)=0.7, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3200, 2961, 2950, 2860, 1722, 1605, 1466, 1325, 1229, 976, 742, 646 cm^{-1}. ^1H NMR ($CDCl_3$,

400 MHz): δ= 7.36 (d, J = 8.31 Hz, 1H, Ar–H), 7.25–7.21 (m, 2H, Ar–H), 7.18–7.14 (m, 1H, Ar–H), 7.06–7.05 (dd, J = 4.90, 0.98 Hz, 1H, Ar–H), 6.90 (t, J = 15.16, 7.33 Hz, 1H, Ar–H), 6.80 (d, J = 7.83 Hz, 1H, Ar–H), 4.53 (d, J = 8.80 Hz, 1H, –OCH_2–), 4.20 (d, J = 8.80 Hz, 1H, –OCH_2–), 2.66 (s, 2H, –C–CH_2–), 1.52 (s, 3H, –C–CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 159.4 (s, Ar–C), 134.0 (s, Ar–C), 129.9 (d, Ar–CH), 128.5 (d, Ar–CH), 128.0 (d, Ar–CH), 125.1 (d, Ar–CH), 122.9 (d, Ar–CH), 122.4 (s, Ar–C), 120.5 (d, Ar–CH), 109.8 (d, Ar–CH), 86.2 (s, Ar–*C*–C–), 82.2 (t, –OCH_2–), 77.5 (s, Ar–C–*C*–), 42.2 (s, –C–), 31.5 (t, –CH_2–), 24.2 (q, –CH_3). HR-MS (APCI+) m/z calculated for $[C_{16}H_{14}OS]^+$=$[M+H]^+$: 255.2830; found 255.2836.



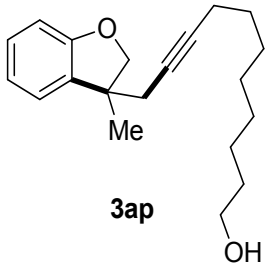
3ai

N,N-dimethyl-N-[4-(3-methyl-2,3-dihydro-1-benzofuran-3-yl)but-2-ynyl]amine (3ai): GP was carried out with 1-iodo-2-[(2-methylprop-2-enyl)oxy]benzene **1a** (68.2 mg, 0.25 mmol), N,N-dimethyl-N-prop-2-ynylamine **2i** (51.4 mg, 0.62 mmol), $Pd_2(dba)_3$ (2.28 mg, 1 mol%), K_2CO_3 (138.6 mg, 1 mmol) and DMF (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 70:30) furnished the dihydrobenzofuran **3ai** (51.1 mg, 90%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 60:40), R_f(**2i**)=0.3, R_f(**3ai**)=0.2, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3293, 2960, 2860, 2861, 1733, 1605, 1489, 1332, 1262, 989, 769, 663 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ= 7.15–7.10 (m, 2H, Ar–H), 6.88–6.85 (m, 1H, Ar–H), 6.78 (d, J = 7.82, Hz, 1H, Ar–H), 4.50 (d, J = 8.80 Hz, 1H, –OCH_2–), 4.18 (d, J = 8.80 Hz, 1H, –OCH_2–), 3.21 (t, 2H, J = 3.91 Hz, –C–CH_2–), 2.50–2.48 (m, 2H, N–CH_2–C), 2.22 (s, 6H, N(CH_3)$_2$), 1.45 (s, 3H, –C–CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 159.4 (s, Ar–C), 134.0 (s, Ar–C), 128.5 (d, Ar–CH), 122.8 (d, Ar–CH), 120.5 (d, Ar–CH), 109.8 (d, Ar–CH), 82.1 (t, –OCH_2–), 81.8 (s, Ar–*C*–C–), 76.8 (s, Ar–C–*C*–), 48.0 (t, CH_2), 43.9 (t, 2 × CH_2), 45.1 (s, –C–), 30.8 (t, CH_2), 24.6 (q, CH_3). HR-MS (APCI+) m/z calculated for $[C_{15}H_{19}NO]^+$=$[M+H]^+$: 230.1539; found 230.1740.



3aj

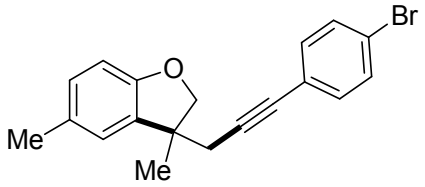
3-(3-cyclopropylprop-2-ynyl)-3-methyl-2,3-dihydro-1-benzofuran (3aj): GP was carried out with 1-iodo-2-[(2-methylprop-2-enyl)oxy]benzene **1a** (68.2 mg, 0.25 mmol), ethynylcyclopropane **2j** (40.9 mg, 0.62 mmol), $Pd_2(dba)_3$ (2.28 mg, 1 mol%), K_2CO_3 (138.6 mg, 1 mmol) and DMF (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the dihydrobenzofuran **3aj** (49.9 mg, 96%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2j**)=0.9, R_f(**3aj**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}= 2968, 2950, 2853, 2860, 1730, 1562, 1475, 1332, 1232, 932, 742, 631 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ= 7.15–7.11 (m, 2H, Ar–H), 6.89–6.85 (dt, J = 7.83, 0.98 Hz, 1H, Ar–H), 6.78 (d, J = 8.30, 0.98 Hz, 1H, Ar–H), 4.45 (d, J = 8.80 Hz, 1H, –OCH_2–), 4.16 (d, J = 8.80 Hz, 1H, –OCH_2–), 2.39 (d, 2H, J = 1.96 Hz, –C–CH_2–), 1.43 (s, 3H, –CH_3), 1.22–1.15 (m, 1H, –CH), 0.73–0.67 (m, 2H, –CH–CH_2), 0.62–0.56 (m, 2H, –CH–CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 159.4 (s, Ar–C), 134.2 (s, Ar–C), 128.4 (d, Ar–CH), 122.9 (d, Ar–CH), 120.4 (d, Ar–CH), 109.6 (d, Ar–CH), 85.4 (s, Ar–*C*–C–), 82.2 (t, –OCH_2–), 71.9 (s, Ar–C–*C*–), 45.1 (s, –C–), 30.9 (t, CH_2), 24.2 (q, CH_3), 8.0 (t, 2 × CH_2), -0.53 (s, 1C). HR-MS (APCI+) m/z calculated for $[C_{15}H_{16}O]^+$=$[M+H]^+$: 213.1274; found 213.1275.



3ap

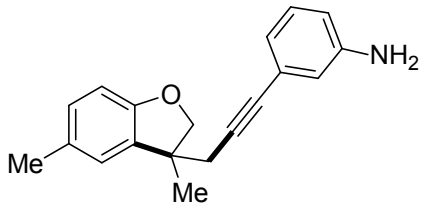
11-(3-methyl-2,3-dihydro-1-benzofuran-3-yl)undec-9-yn-1-ol (3ap): GP was carried out with 1-iodo-2-[(2-methylprop-2-enyl)oxy]benzene **1a** (68.2 mg, 0.25 mmol), dec-9-yn-1-ol **2p** (95.5 mg, 0.62 mmol), $Pd_2(dba)_3$ (2.28 mg, 1 mol%), K_2CO_3 (138.6 mg, 1 mmol) and DMF (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 70:30) furnished the dihydrobenzofuran **3ap** (71 mg, 96%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 73:27), R_f(**2p**)=0.7, R_f(**3ap**)=0.6, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3456, 3294, 2965, 2855, 2850, 1721, 1589, 1466, 1326, 1229, 989, 756, 656 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ= 7.15–7.10 (m, 2H, Ar–H), 6.88–6.84 (m, 1H, Ar–H), 6.77 (d, J = 7.83 Hz, 1H, Ar–H), 4.47 (d, J = 8.81 Hz, 1H, –OCH_2–), 4.16 (d, J = 8.81 Hz, 1H, –OCH_2–), 3.63 (t, J = 13.2, 6.36 Hz, 2H, HO–CH_2–), 2.41 (s, 2H, –C–CH_2–), 2.15–2.11 (m, 2H), 1.59–1.31 (m, 13H), 1.43 (s, 3H, –C–CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 159.4 (s, Ar–C), 134.3 (s, Ar–C), 128.3 (d, Ar–CH), 122.8 (d, Ar–CH), 120.4 (d, Ar–CH), 109.7 (d, Ar–CH), 82.3 (s, Ar–*C*–C–), 82.2 (t, –OCH_2–), 76.6 (s, Ar–C–*C*–), 63.0 (t, CH_2), 45.2 (s, –C–), 32.7 (t, CH_2),

30.9 (t, CH_2), 29.3 (t,2 × CH_2), 29.0 (t, CH_2), 28.9 (t, CH_2), 28.7 (t, CH_2), 25.7 (t, CH_2), 24.3 (q, CH_3), 18.6 (t, CH_2). HR-MS (APCI+) m/z calculated for $[C_{20}H_{28}O_2]^+$=$[M+H]^+$: 301.2162; found 301.2163.



3be

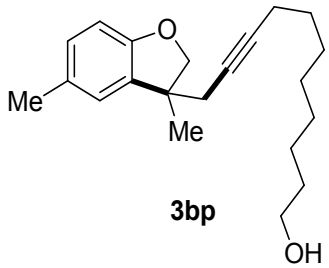
3-[3-(4-bromophenyl)prop-2-ynyl]-3,6-dimethyl-2,3-dihydro-1-benzofuran (3be): GP was carried out with 2-iodo-4-methyl-1-[(2-methylprop-2-enyl)oxy]benzene **1b** (72 mg, 0.25 mmol), 1-bromo-4-ethynylbenzene **2e** (112.2 mg, 0.62 mmol), $Pd_2(dba)_3$ (2.28 mg, 1 mol%), K_2CO_3 (138.6 mg, 1 mmol) and DMF (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the dihydrobenzofuran **3be** (81.6 mg, 96%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2e**)=0.9, R_f(**3be**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}= 2962, 2861, 2842, 1732, 1600, 1476, 1345, 1238, 979, 759, 669 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ= 7.42–7.40 (m, 2H, Ar–H), 7.24–7.22 (m, 3H, Ar–H), 6.99–6.94 (m, 2H, Ar–H), 6.79–6.69 (d, 1H, J = 8.31 Hz, Ar–H), 4.51 (d, J = 8.81 Hz, 1H, –OCH_2–), 4.21–4.18 (d, J = 8.80 Hz, 1H, –OCH_2–), 2.64 (s, 2H, –C–CH_2–), 2.29 (s, 3H, Ar–CH_3), 1.50 (s, 3H, –C–CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 157.3 (s, Ar–C), 133.8 (s, Ar–C), 133.0 (d, 2 × Ar–CH), 131.5 (d, 2 × Ar–CH), 129.8 (s, Ar–C), 129.0 (d, Ar–CH), 123.4 (d, Ar–CH), 122.0 (s, Ar–C), 109.4 (d, Ar–CH), 88.1 (s, Ar–*C*–C–), 82.3 (t, –OCH_2–), 81.4 (s, Ar–C–*C*–), 45.3 (s, –C–), 31.5 (t, –CH_2–), 20.9 (q, Ar–CH_3).-HR-MS (APCI+) m/z calculated for $[C_{20}H_{20}O]^+$=$[M+H]^+$: 340.0463; found 340.0466.



3bf

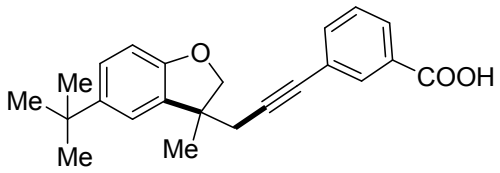
3-[3-(3,5-dimethyl-2,3-dihydro-1-benzofuran-3-yl)prop-1-ynyl]aniline (3bf): GP was carried out with 2-iodo-4-methyl-1-[(2-methylprop-2-enyl)oxy]benzene **1b** (72 mg, 0.25 mmol), 3-ethynylaniline **2f** (72.5 mg, 0.62 mmol), $Pd_2(dba)_3$ (2.28 mg, 1 mol%), K_2CO_3 (138.6 mg, 1 mmol) and DMF (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 97:3) furnished the dihydrobenzofuran **3bf** (63.4 mg, 92%) as a light yellow oily compound, [TLC control

(petroleum ether/ethyl acetate 96:4), R_f(**2f**)=0.9, R_f(**3bf**)=0.8, UV detection].–IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3412, 3224, 2961, 2891 2861, 1733, 1569, 1479, 1365, 1224, 980, 760, 645 cm^{-1}. cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ= 7.07 (t, J = 15.65, 7.82 Hz, 1H, Ar–H), 7.02 (s, 1H, Ar–H), 6.95 (d, 1H, J = 9.29, Hz, Ar–H), 6.80 (d, J = 7.82, Hz, 1H, Ar–H), 6.71 (s, 1H, Ar–H), 6.69 (s, 1H, Ar–H), 6.61 (m, 1H, Ar–H), 4.52 (d, J = 8.80 Hz, 1H, –OCH_2–), 4.20 (d, J = 8.80 Hz, 1H, –OCH_2–), 3.65 (bs, 2H, Ar–NH_2), 2.64 (s, 2H, –C–CH_2–), 2.30 (s, 3H, Ar–CH_3), 1.50 (s, 3H, –C–CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 157.3 (s, Ar–C), 146.2 (s, Ar–C), 134.1 (s, Ar–C), 129.8 (s, Ar–C), 129.2 (d, Ar–CH), 128.9 (d, Ar–CH), 124.2 (s, Ar–C), 123.5 (d, Ar–CH), 122.0 (d, Ar–CH), 117.9 (d, Ar–CH), 114.9 (d, Ar–CH), 109.3 (d, Ar–CH), 86.1 (s, Ar–*C*–C–), 82.6 (s, Ar–C–*C*–), 82.4 (t, –OCH_2–), 45.3 (s, –C–), 31.4 (t, –CH_2–), 24.1 (q, –CH_3), 20.9 (q, Ar–CH_3).-HR-MS (APCI+) m/z calculated for $[C_{19}H_{19}NO]^+$=$[M+H]^+$: 277.1500; found 277.1509. Melting point = 84–86 °C.



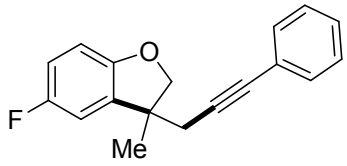
3bp

11-(3,5-dimethyl-2,3-dihydro-1-benzofuran-3-yl)undec-9-yn-1-ol (3bp): GP was carried out with 2-iodo-4-methyl-1-[(2-methylprop-2-enyl)oxy]benzene **1b** (72 mg, 0.25 mmol), dec-9-yn-1-ol **2p** (95.5 mg, 0.62 mmol), $Pd_2(dba)_3$ (2.28 mg, 1 mol%), K_2CO_3 (138.6 mg, 1 mmol) and DMF (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 80:20) furnished the dihydrobenzofuran **3bp** (75.6 mg, 97%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 74:26), R_f(**2p**)=0.7, R_f(**3bp**)=0.6, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3411, 2956, 2856, 2861, 1731, 1592, 1469, 1335, 1262, 968, 765, 626 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ= 6.94–6.91 (m, 2H, Ar–H), 6.66 (d, J = 7.83 Hz, 1H, Ar–H), 4.45 (d, J = 8.81 Hz, 1H, –OCH_2–), 4.13 (d, J = 8.80 Hz, 1H, –OCH_2–), 3.63 (t, J = 13.2, 6.36 Hz, 2H, HO–CH_2–), 2.40 (s, 2H, –C–CH_2–), 2.28 (s, 3H, Ar–CH_3), 2.16–2.12 (m, 2H), 1.66 (bs, 1H, –OH), 1.57–1.31 (m, 12H), 1.42 (s, 3H, –C–CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 157.3 (s, Ar–C), 134.3 (s, Ar–C), 129.7 (s, Ar–C), 128.7 (d, Ar–CH), 123.4 (d, Ar–CH), 109.2 (d, Ar–CH), 82.3 (t, –OCH_2–), 82.2 (s, Ar–*C*–C–), 76.7 (s, Ar–C–*C*–), 63.0 (t, CH_2), 45.2 (s, –C–), 32.7 (t, CH_2), 30.8 (t, CH_2), 29.3 (t, CH_2), 29.1 (t, CH_2), 28.9 (t, CH_2), 28.7 (t, CH_2), 25.7 (t, CH_2), 24.2 (q, CH_3), 20.9 (q, CH_3), 18.6 (t, CH_2). HR-MS (APCI+) m/z calculated for $[C_{21}H_{30}O_2]^+$=$[M+H]^+$: 315.2319; found 315.2319.



3cg

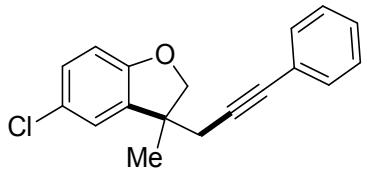
3-[3-(6-tert-butyl-3-methyl-2,3-dihydro-1-benzofuran-3-yl)prop-1-ynyl]benzoic acid (3cg): GP was carried out with 4-tert-butyl-2-iodo-1-[(2-methylprop-2-enyl)oxy]benzene **1c** (82.5 mg, 0.25 mmol), 1-3-ethynylbenzoic acid **2g** (89.6 mg, 0.62 mmol), $Pd_2(dba)_3$ (2.28 mg, 1 mol%), K_2CO_3 (138.6 mg, 1 mmol) and DMF (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the dihydrobenzofuran **3cg** (65.5 mg, 95%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2s**)=0.4, R_f(**3cg**)=0.3, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}= 3458, 2990, 2950, 2863, 2632, 1824, 1697, 15667, 1435, 13267, 988, 792, 673 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ= 8.15 (s, 1H, Ar–H), 8.04 (d, 1H, J = 7.82 Hz, Ar–H), 7.62 (d, 1H, J = 7.33 Hz, Ar–H), 7.42 (t, 1H, J = 15.65, 7.82 Hz, Ar–H), 7.25 (m, 1H, Ar–H), 7.21–7.19 (m, 1H, Ar–H), 6.76 (m, 1H, J = 8.32 Hz, Ar–H), 4.52 (d, J = 8.80 Hz, 1H, –OCH_2–), 4.24 (d, J = 8.80 Hz, 1H, –OCH_2–), 2.70 (s, 2H, –C–CH_2–), 1.56 (s, 3H, –C–CH_3), 1.30 (s, 9H, Ar–C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 171.3 (s, Ar–CO), 157.1 (s, Ar–C), 143.7 (s, Ar–C), 136.6 (d, Ar–CH), 133.4 (s, Ar–C), 133.3 (d, Ar–CH), 129.5 (s, Ar–C), 129.4 (d, Ar–CH), 128.5 (d, Ar–CH), 125.5 (d, Ar–CH), 124.2 (s, Ar–C), 119.8 (d, Ar–CH), 109.0 (d, Ar–CH), 88.3 (s, Ar–*C*–C–), 82.6 (t, –OCH_2–), 81.3 (s, Ar–C–*C*–), 45.4 (s, –C–), 34.4 (s, –C–), 31.7 (t, 3 × –C–CH_3), 31.6 (t, –CH_2–), 23.9 (q, –CH_3). HR-MS (APCI+) m/z calculated for $[C_{20}H_{20}O]^+$=$[M+H]^+$: 348.1725; found 348.1729.



3da

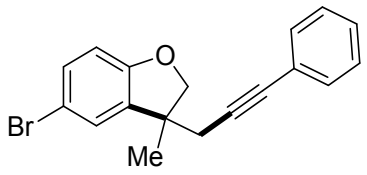
5-fluoro-3-methyl-3-(3-phenylprop-2-ynyl)-2,3-dihydro-1-benzofuran (3da): GP was carried out with 4-fluoro-2-iodo-1-[(2-methylprop-2-enyl)oxy]benzene **1d** (73 mg, 0.25 mmol), ethynylbenzene **2a** (63.7 mg, 0.62 mmol), $Pd_2(dba)_3$ (2.28 mg, 1 mol%), K_2CO_3 (138.6 mg, 1 mmol) and DMF (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the dihydrobenzofuran **3da** (63.8 mg, 96%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2a**)=0.9, R_f(**3da**)=0.8, UV detection]. IR (MIR-ATR, 4000–600

cm^{-1}): ν_{max}=3056, 2942, 2858, 2850, 1766, 1530, 1485, 1344, 1237, 969, 749, 656 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ= 7.40–7.37 (m, 2H, Ar–H), 7.30–7.29 (m, 3H, Ar–H), 6.96–6.93 (dd, J = 7.83, 2.93 Hz, 1H, Ar–H), 6.87–6.81 (m, 1H, Ar–H), 6.73–6.70 (dd, J = 8.80, 3.90 Hz, 1H, Ar–H), 4.53 (d, J = 8.80 Hz, 1H, –OCH_2–), 4.27–4.24 (d, J = 8.81 Hz, 1H, –OCH_2–), 2.68 (s, 2H, –C–CH_2–), 1.52 (s, 3H, –C–CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 158.7 (s, Ar–C), 156.4 (s, Ar–C), 155.3 (s, Ar–C), 135.4 (s, Ar–C), 131.6 (d, Ar–CH), 128.3 (d, Ar–CH), 128.0 (d, Ar–CH), 123.3 (s, Ar–C), 114.5 (d, Ar–CH), 110.2 (d, Ar–CH), 110.0 (d, Ar–CH), 109.9 (d, Ar–CH), 86.1 (s, Ar–*C*–C–), 82.8 (t, –OCH_2–), 82.7 (s, Ar–C–*C*–), 45.7 (s, –C–), 31.3 (t, –CH_2–), 24.1 (q, Ar–CH_3). HR-MS (APCI+) m/z calculated for $[C_{19}H_{18}O]^+$=$[M+H]^+$: 266.1107; found 266.1110.



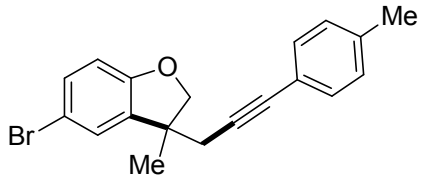
3ea

5-chloro-3-methyl-3-(3-phenylprop-2-ynyl)-2,3-dihydro-1-benzofuran (3ea): GP was carried out 4-chloro-2-iodo-1-[(2-methylprop-2-enyl)oxy]benzene **1e** (76.7 mg, 0.25 mmol), ethynylbenzene **2a** (63.7 mg, 0.62 mmol), $Pd_2(dba)_3$ (2.28 mg, 1 mol%), K_2CO_3 (138.6 mg, 1 mmol) and DMF (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the dihydrobenzofuran **3ea** (67.5 mg, 97%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2a**)=0.8, R_f(**3ea**)=0.7, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3051, 2963, 2861, 2859, 1746, 1590, 1479, 1336, 1234, 972, 742, 652 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ= 7.40–7.37 (m, 2H, Ar–H), 7.30–7.28 (m, 3H, Ar–H), 7.19 (d, J = 2.45 Hz, 1H, Ar–H), 7.12–7.09 (m, 1H, Ar–H), 6.73 (d, J = 8.31 Hz, 1H, Ar–H), 4.56 (d, J = 8.80 Hz, 1H, –OCH_2–), 4.26–4.24 (d, J = 8.81 Hz, 1H, –OCH_2–), 2.67 (s, 2H, –C–CH_2–), 1.51 (s, 3H, –C–CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 158.1 (s, Ar–C), 135.9 (s, Ar–C), 131.6 (d, 2 × Ar–CH), 128.4 (d, Ar–CH), 128.3 (d, 2 × Ar–CH), 128.0 (d, Ar–CH), 125.2 (s, Ar–C), 123.4 (d, Ar–CH), 123.3 (s, Ar–C), 110.8 (d, Ar–CH), 86.0 (s, Ar–*C*–C–), 82.9 (t, –OCH_2–), 82.8 (s, Ar–C–*C*–), 45.6 (s, –C–), 31.4 (t, –CH_2–), 24.1 (q, Ar–CH_3). HR-MS (APCI+) m/z calculated for $[C_{19}H_{18}O]^+$=$[M+H]^+$: 282.0811; found 282.0822.



3fa

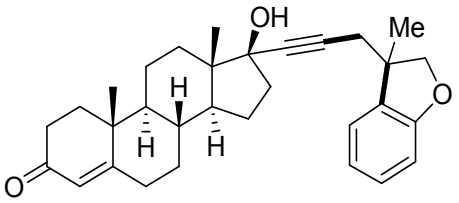
5-bromo-3-methyl-3-(3-phenylprop-2-ynyl)-2,3-dihydro-1-benzofuran (3fa): GP was carried out with 4-bromo-2-iodo-1-[(2-methylprop-2-enyl)oxy]benzene **1f** (88.2 mg, 0.25 mmol), ethynylbenzene **2a** (63.7 mg, 0.62 mmol), $Pd_2(dba)_3$ (2.28 mg, 1 mol%), K_2CO_3 (138.6 mg, 1 mmol) and DMF (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the dihydrobenzofuran **3fa** (74.1 mg, 91%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2a**)=0.9, R_f(**3fa**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3063, 2958, 2861, 2842, 1736, 1570, 1465, 1234, 1248, 998, 769, 666 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ= 7.40–7.38 (m, 2H, Ar–H), 7.33 (d, 1H, J = 2.45, Ar–H), 7.30–7.29 (m, 3H, Ar–H), 7.26–7.24 (m, 1H, Ar–H), 6.69 (d, J = 8.82 Hz, 1H, Ar–H), 4.53 (d, J = 8.81 Hz, 1H, –OCH_2–), 4.24 (d, J = 8.80 Hz, 1H, –OCH_2–), 2.66 (s, 2H, –C–CH_2–), 1.51 (s, 3H, –C–CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 158.6 (s, Ar–C), 136.4 (s, Ar–C), 131.6 (d, 2 × Ar–CH), 131.3 (d, Ar–CH), 128.3 (d, 2 × Ar–CH), 128.0 (d, Ar–CH), 126.3 (s, Ar–C), 123.2 (s, Ar–C), 112.3 (s, Ar–C), 111.4 (d, Ar–CH), 86.0 (s, Ar–*C*–C–), 82.8 (s, Ar–C–*C*–), 82.7 (t, –OCH_2–), 45.6 (s, –C–), 31.5 (t, –CH_2–), 24.1 (q, Ar–CH_3). HR-MS (APCI+) m/z calculated for $[C_{19}H_{18}O]^+$=$[M+H]^+$: 326.0306; found 326.0310.



3fc

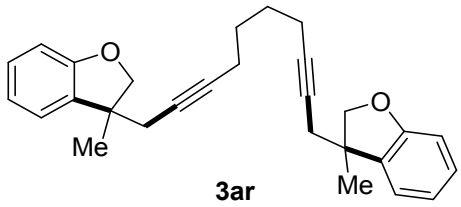
5-bromo-3-methyl-3-[3-(4-methylphenyl)prop-2-ynyl]-2,3-dihydro-1-benzofuran (3fc): GP was carried out with 4-bromo-2-iodo-1-[(2-methylprop-2-enyl)oxy]benzene **1f** (88.2 mg, 0.25 mmol), 1-ethynyl-3-methylbenzene **2c** (71.9 mg, 0.62 mmol), $Pd_2(dba)_3$ (2.28 mg, 1 mol%), K_2CO_3 (138.6 mg, 1 mmol) and DMF (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the dihydrobenzofuran **3fc** (76.5 mg, 90%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2c**)=0.7, R_f(**3fc**)=0.6, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}= 2952, 2861, 2849, 1728, 1596, 1476, 1344, 1227, 968, 749, 649 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ= 7.33–7.32 (d, 1H, J = 2.45 Hz, Ar–H), 7.29–7.25 (m,

1H, Ar–H), 7.23 (d, 1H, J = 1.95 Hz, Ar–H), 7.10 (d, 1H, J = 7.83 Hz, Ar–H), 6.68 (d, J = 8.32 Hz, 1H, Ar–H), 4.54 (d, J = 8.80 Hz, 1H, –OCH_2–), 4.25 (d, J = 9.29 Hz, 1H, –OCH_2–), 2.65 (s, 2H, –C–CH_2–), 2.33 (s, 3H, Ar–CH_3), 1.50 (s, 3H, –C–CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 158.7 (s, Ar–C), 138.0 (s, Ar–C), 136.5 (s, Ar–C), 131.5 (d, Ar–CH), 131.3 (d, Ar–CH), 129.0 (d, Ar–CH), 126.3 (d, Ar–CH), 120.2 (s, Ar–C), 112.3 (s, Ar–C), 111.4 (d, Ar–CH), 85.2 (s, Ar–*C*–C–), 82.9 (s, Ar–C–*C*–), 82.8 (t, –OCH_2–), 45.6 (s, –C–), 31.5 (t, –CH_2–), 24.1 (q, –CH_3), 21.4 (q, Ar–CH_3). HR-MS (APCI+) m/z calculated for $[C_{20}H_{20}O]^+$=$[M+H]^+$: 340.0463; found 340.0472.

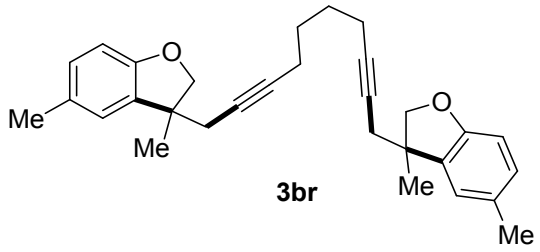


3aq

(8R,9S,10R,13S,14S,17S)-17-hydroxy-10,13-dimethyl-17-(3-((S)-3-methyl-2,3-dihydrobenzofuran-3-yl)prop-1-yn-1-yl)-6,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-1H-cyclopenta[a]phenanthren-3(2H)-one (3aq): GP was carried out with 1-iodo-2-[(2-methylprop-2-enyl)oxy]benzene **1a** (68.2 mg, 0.25 mmol), ethesterone **2q** (202 mg, 0.62 mmol), $Pd_2(dba)_3$ (2.28 mg, 1 mol%), K_2CO_3 (138.6 mg, 1 mmol) and DMF (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 80:20 to 70:30) furnished the dihydrobenzofuran **3aq** (105 mg, 93%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 70:30), R_f(**2q**)=0.3, R_f(**3aq**)=0.3, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}= 3456, 2972, 2961, 2940, 2860, 1722, 1583, 1476, 1324, 1239, 982, 792, 663 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ= 7.14–7.09 (m, 2H, Ar–H), 6.87–6.83 (t, J = 14.67, 7.33 Hz, 1H, Ar–H), 6.76 (d, J = 7.83 Hz, 1H, Ar–H), 5.76 (s, 1H) 4.50 (dd, J = 8.80, 0.98 Hz, 1H, –OCH_2–), 4.19 (d, J = 8.80 Hz, 1H, –OCH_2–), 2.59–2.47 (m, 2H,), 2.44–2.30 (m, 2H,), 2.17–2.13 (m, 1H,), 2.06–1.94 (m, 3H,), 1.83–1.67 (m, 4H,), 1.63–1.48 (m, 10H,), 1.45–1.37 (m, 4H,), 1.42 (s, 3H, –C–CH_3), 1.34–1.24 (m, 3H,), 1.18 (m, 3H,), 1.11–0.81 (m, 7H,). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 199.6 (Ar–CO), 171.3 (s Ar–C), 159.5 (s, Ar–C), 133.6 (s, Ar–C), 128.5 (d, 2 × Ar–CH), 123.8 (d, Ar–CH), 122.7 (d, 2 × Ar–CH), 120.5 (d, 2 × Ar–CH), 109.7 (d, 2 × Ar–CH), 85.5 (s, 2 × Ar–*C*–C–), 82.9 (s, 2 × Ar–*C*–C–), 81.9 (t, –OCH_2–), 79.7 (s, Ar–C), 53.3 (d, 2 × –C), 49.8 (s, –C–), 49.7 (s, –C–), 46.6 (s, 2 × –C–), 45.4 (s, 2 × –C–), 39.0 (s, 2 × –C–), 36.1 (q, CH_3), 35.6 (t, CH_2), 33.9 (t, CH_2), 32.7 (t, CH_2), 32.3 (t, CH_2), 31.4 (t, CH_2), 30.7 (t, CH_2), 33.6 (t, CH_2), 25.4 (t, 2 × CH_2), 22.9 (t, CH_2), 20.6 (t, CH_2), 17.3 (t, CH_2), 13.7 (q, CH_3). 12.7 (q, CH_3). HR-MS (APCI+) m/z calculated for $[C_{22}H_{32}O]^+$=$[M+H]^+$: 459.2894; found 459.2888.

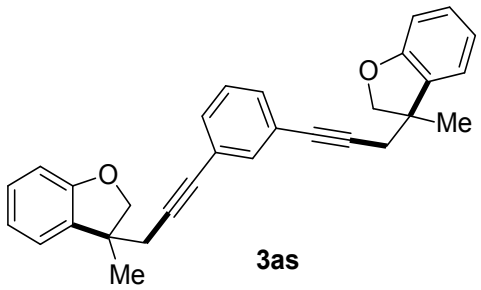


3-methyl-3-[10-(3-methyl-2,3-dihydro-1-benzofuran-3-yl)deca-2,8-diynyl]-2,3-dihydro-1-benzofuran (3ar): GP was carried out with 1-iodo-2-[(2-methylprop-2-enyl)oxy]benzene **1a** (68.2 mg, 0.25 mmol), octa-1,7-diyne **2r** (14 mg, 0.125 mmol), $Pd_2(dba)_3$ (2.28 mg, 1 mol%), K_2CO_3 (138.6 mg, 1 mmol) and DMF (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the dihydrobenzofuran **3ar** (43.6 mg, 91%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2r**)=0.9, R_f(**3ar**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3210, 2953, 2852, 2861, 1734, 1532, 1446, 1425, 1328, 1076, 965, 730, 661 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ= 7.15–7.10 (m, 2H, Ar–H), 6.88–6.84 (dt, J = 8.80, 0.97 Hz, 1H, Ar–H), 6.78 (d, J = 7.82, Hz, 1H, Ar–H), 4.47 (d, J = 8.80 Hz, 1H, –OCH_2–), 4.17 (d, J = 8.81 Hz, 1H, –OCH_2–), 2.43 (q, J = 6.36, 1.92 Hz, 2H, –C–CH_2–), 2.19–2.14 (m, 2H,), 1.60–1.50 (m, 4H,), 1.44 (s, 3H, –C–CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 159.4 (s, Ar–C), 134.2 (s, Ar–C), 128.4 (d, Ar–CH), 122.8 (d, Ar–CH), 120.4 (d, Ar–CH), 109.7 (d, Ar–CH), 82.2 (t, –OCH_2–), 81.8 (s, Ar–*C*–C–),76.9 (s, Ar–C–*C*–), 45.1 (s, –C–), 30.9 (t, CH_2), 24.4 (q, CH_3), 18.2 (t, CH_2). HR-MS (APCI+) m/z calculated for $[C_{16}H_{20}O]^+$=$[M+H]^+$: 398.5440; found 398.2339.



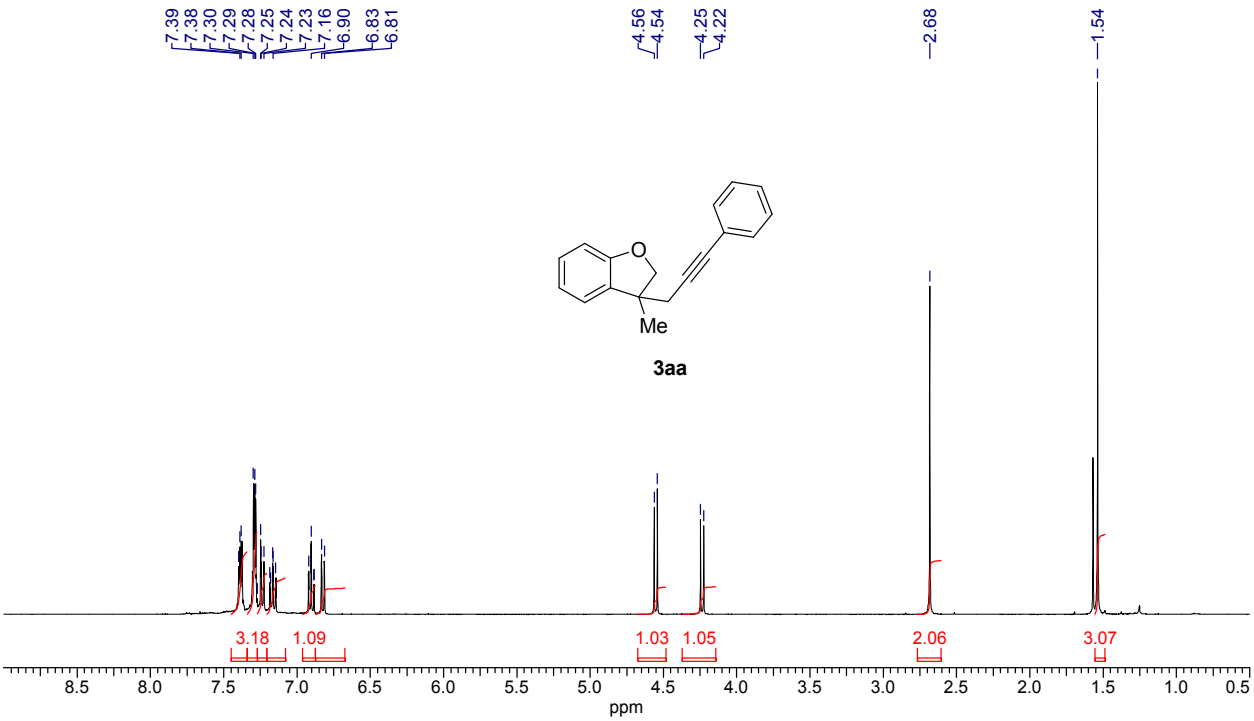
3-[10-(3,5-dimethyl-2,3-dihydro-1-benzofuran-3-yl)deca-2,8-diynyl]-3,5-dimethyl-2,3-dihydro-1-benzofuran (3br): GP was carried out with 2-iodo-4-methyl-1-[(2-methylprop-2-enyl)oxy]benzene **1b** (72 mg, 0.25 mmol), octa-1,7-diyne **2r** (15 mg, 0.125 mmol), $Pd_2(dba)_3$ (2.28 mg, 1 mol%), K_2CO_3 (138.6 mg, 1 mmol) and DMF (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) furnished the dihydrobenzofuran **3br** (48.7 mg, 92%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2r**)=0.9, R_f(**3br**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3210, 2968, 2831, 2820, 1760, 1560, 1445, 1334, 1240, 982, 752, 682 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ= 6.93 (s, 1H, Ar–H), 6.91 (s, 1H, Ar–H), 6.68 (d, J = 7.83 Hz, 1H, Ar–H), 4.45 (d, J = 8.81 Hz, 1H, –OCH_2–), 4.14 (d, J = 8.80 Hz, 1H, –OCH_2–), 2.41 (dd,

J = 5.86, 1.95 Hz, 2H), 2.28 (s, 3H, Ar–CH_3), 2.21–2.16 (m, 2H), 1.42 (s, 3H, –C–CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 157.3 (s, Ar–C), 134.2 (s, Ar–C), 129.6 (s, Ar–C), 128.7 (d, Ar–CH), 123.4 (d, Ar–CH), 109.2 (d, Ar–CH), 82.3 (t, –OCH_2–), 82.2 (s, Ar–*C*–C–), 81.8 (s, Ar–C–*C*–), 45.2 (s, –C–), 31.0 (t, CH_2), 30.8 (t, CH_2), 24.3 (q, CH_3), 20.8 (q, Ar–CH_3), 18.3 (t, CH_2). HR-MS (APCI+) m/z calculated for $[C_{17}H_{22}O]^+$=$[M+Na]^+$: 427.5972; found 449.2436.

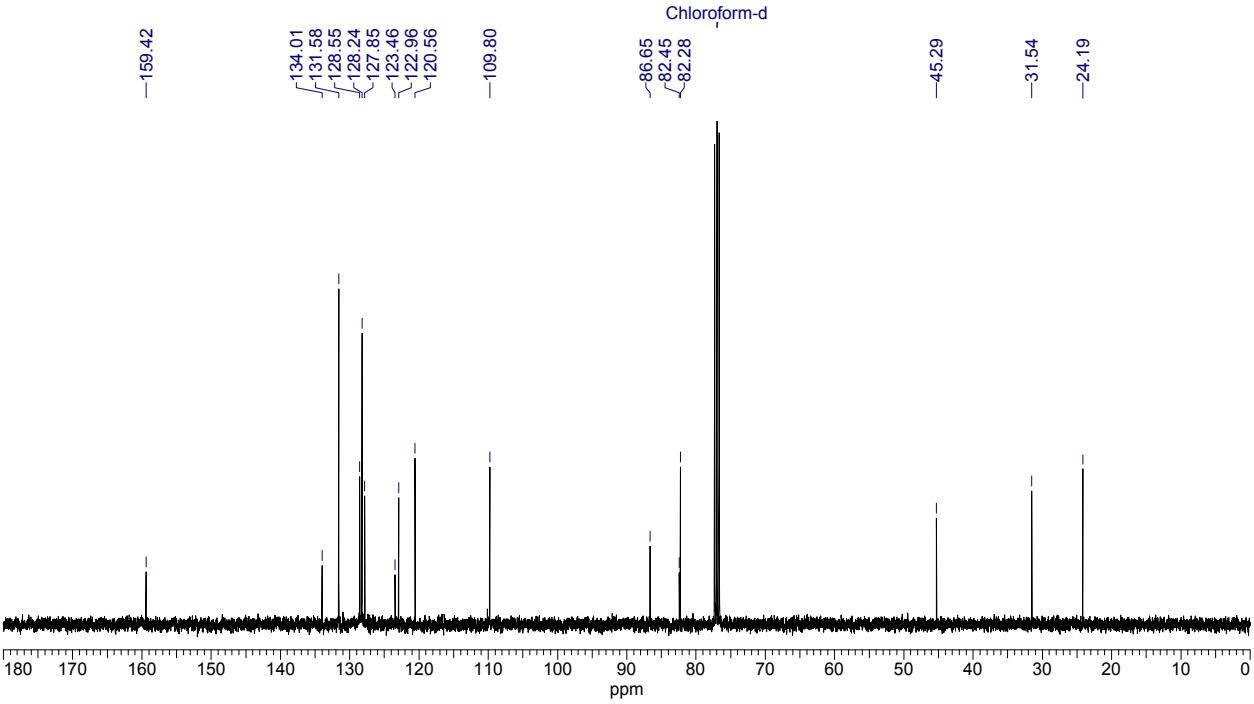


3as

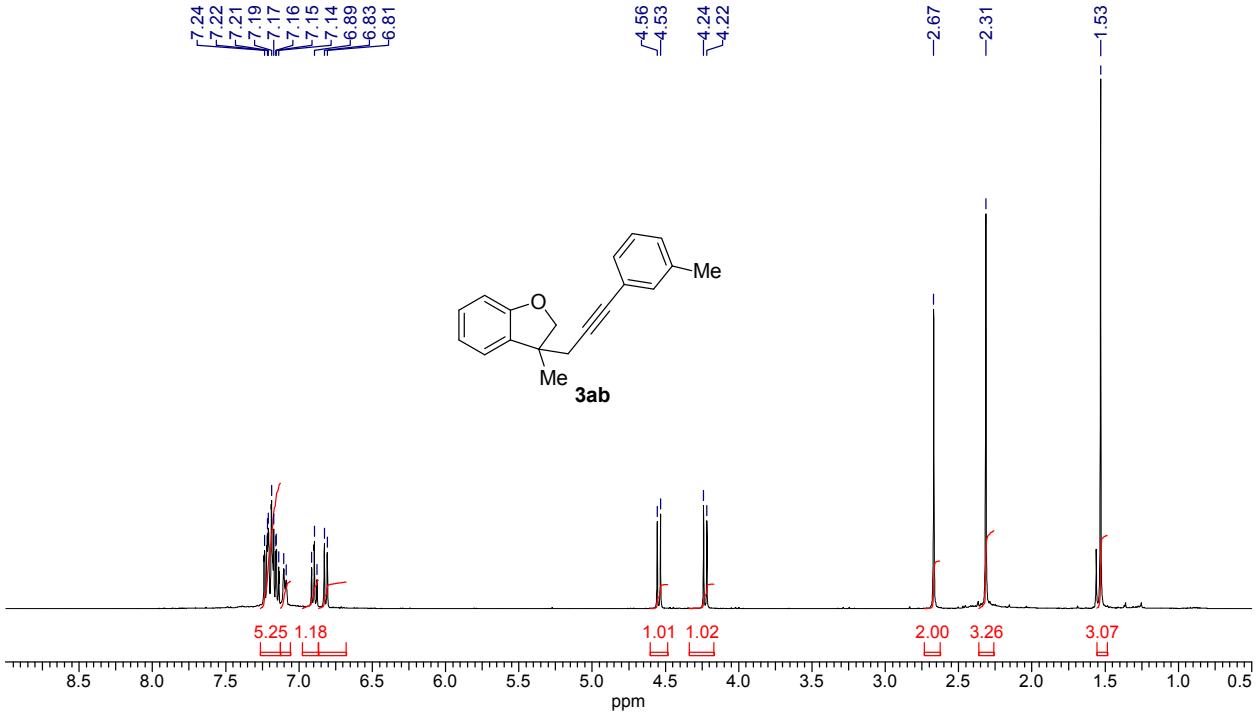
3-methyl-3-(3-{3-[3-(3-methyl-2,3-dihydro-1-benzofuran-3-yl)prop-1-ynyl]phenyl}prop-2-ynyl)-2,3-dihydro-1-benzofuran (3as): GP was carried out with 1-iodo-2-[(2-methylprop-2-enyl)oxy]benzene **1a** (68.2 mg, 0.25 mmol), 1,3-diethynylbenzene **2s** (16 mg, 0.125 mmol), $Pd_2(dba)_3$ (2.28 mg, 1 mol%), K_2CO_3 (138.6 mg, 1 mmol) and DMF (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 98:2) furnished the dihydrobenzofuran **3as** (48 mg, 94%) as a light yellow oily compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2s**)=0.6, R_f(**3as**)=0.4, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=3030, 2967, 2852, 2333, 1672, 1462, 1235, 1214, 1038, 970, 730, 682 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ= 7.16–7.14 (m, 1H, Ar–H), 7.10–7.07 (m, 2H, Ar–H), 7.05–7.00 (m, 1H, Ar–H), 6.78–6.74 (dt, J = 8.30, 0.98 Hz, 1H, Ar–H), 6.68 (d, J = 7.82 Hz, 1H, Ar–H), 4.39 (d, J = 8.80 Hz, 1H, –OCH_2–), 4.09 (d, J = 8.80 Hz, 1H, –OCH_2–), 2.53 (s, 2H, –C–CH_2–), 1.39 (s, 3H, –C–CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ= 159.4 (s, Ar–C), 134.6 (d, Ar–CH), 133.9 (s, Ar–C), 131.0 (d, Ar–CH), 128.6 (d, Ar–CH), 128.3 (d, Ar–CH), 123.7 (s, Ar–C), 122.9 (d, Ar–CH), 120.6 (d, Ar–CH), 109.8 (d, Ar–CH), 87.3 (s, Ar–*C*–C–), 82.2 (t, –OCH_2–), 81.7 (s, Ar–C–*C*–),45.3 (s, –C–), 31.5 (t, –CH_2–), 24.2 (q, –CH_3). HR-MS (APCI+) m/z calculated for $[C_{19}H_{18}O]^+$=$[M+H]^+$: 419.5336; found 419.5226.



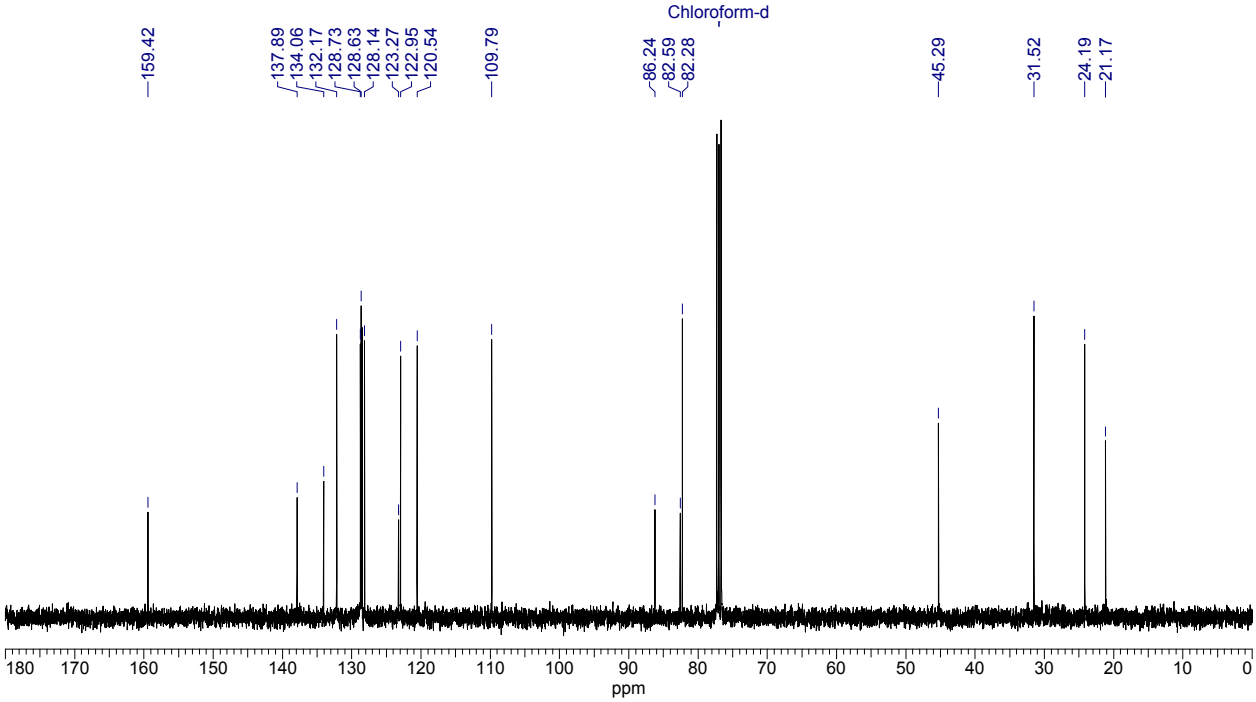
^{1}H-NMR (400 MHz) spectrum of **3aa** in $CDCl_3$



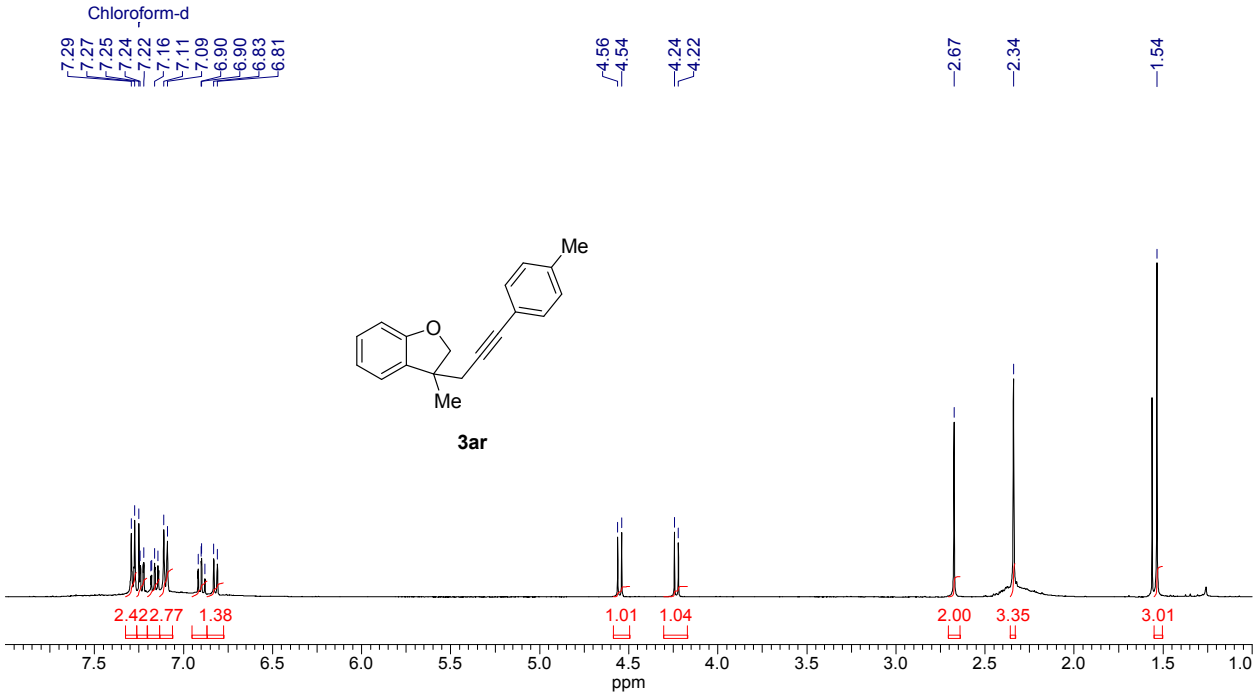
^{13}C-NMR (100 MHz) spectrum of **3aa** in $CDCl_3$



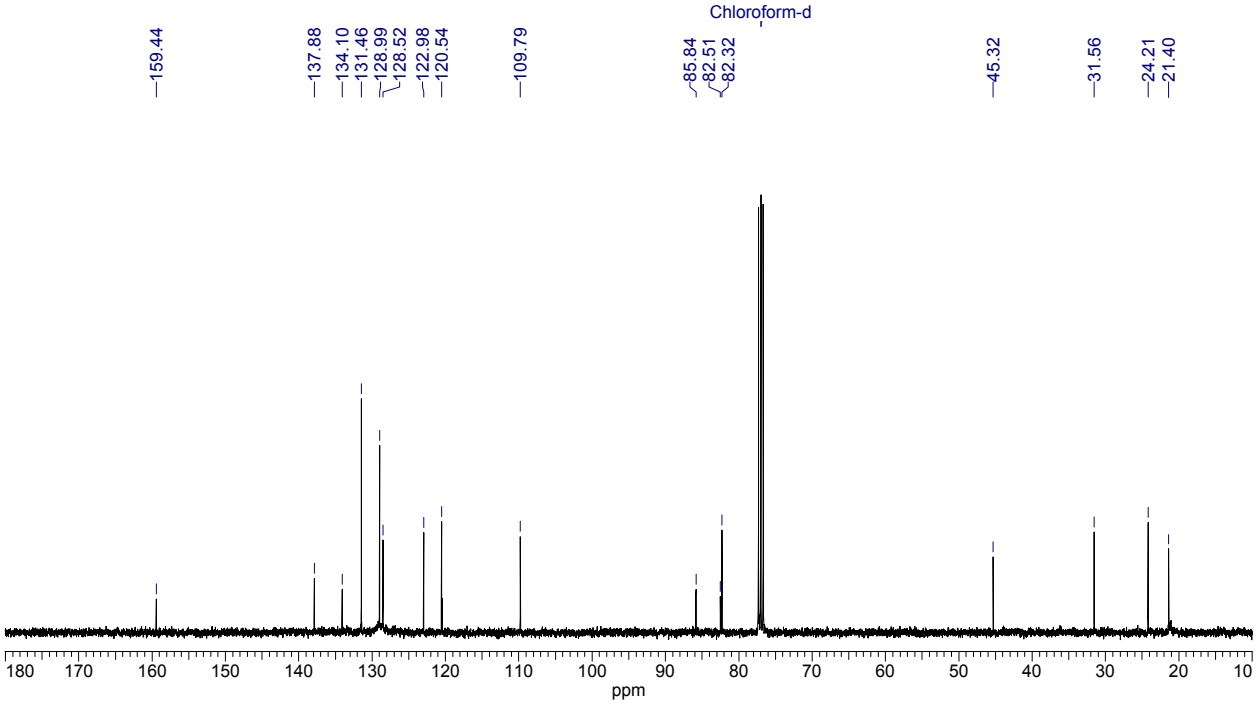
^{1}H-NMR (400 MHz) spectrum of **3ab** in $CDCl_3$



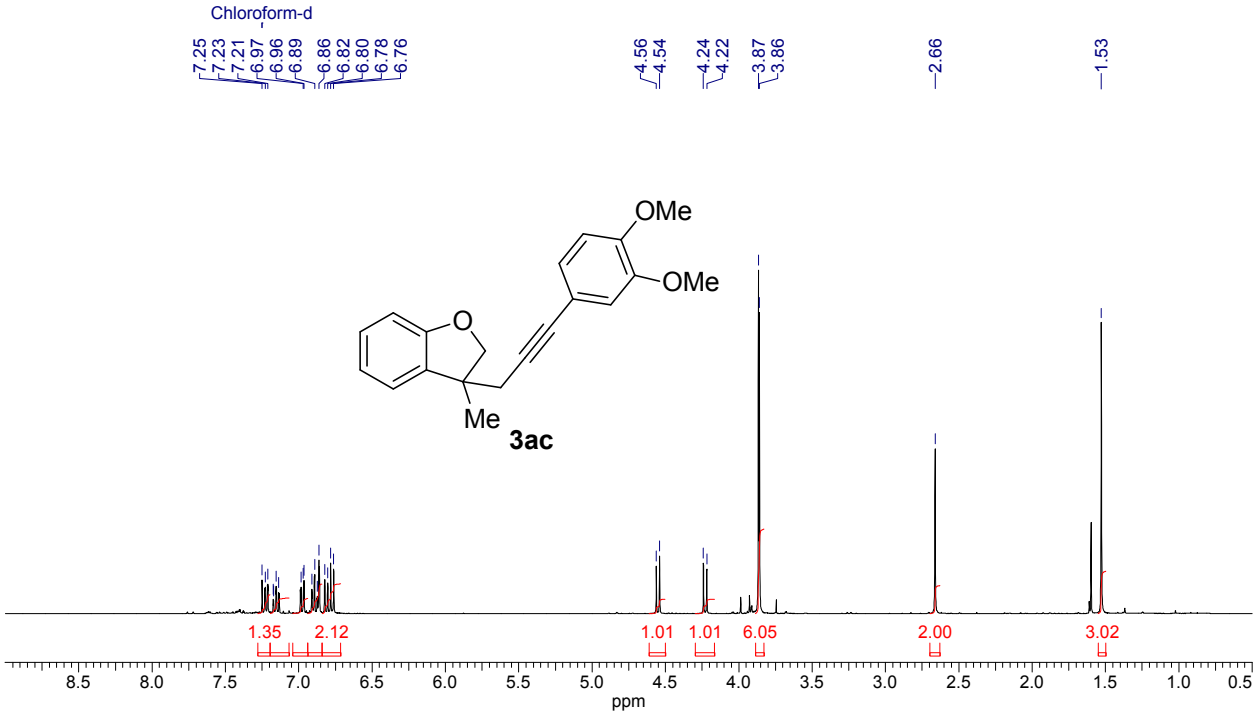
^{13}C-NMR (100 MHz) spectrum of **3ab** in $CDCl_3$



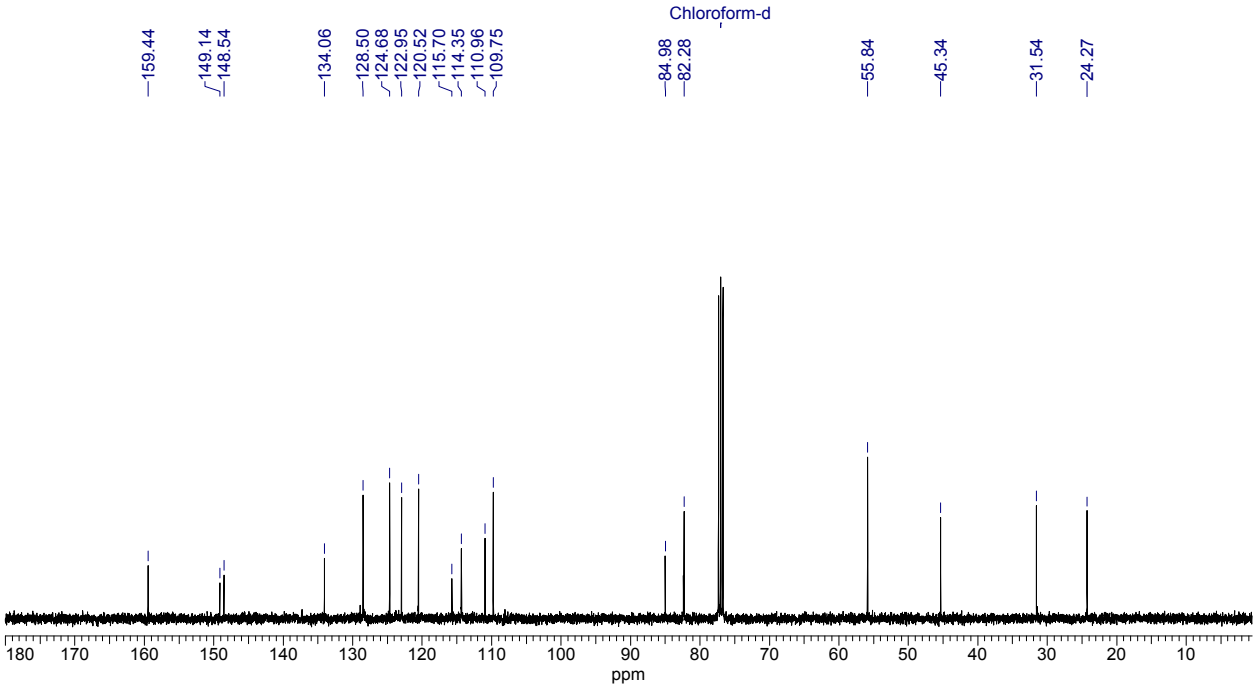
^{1}H-NMR (400 MHz) spectrum of **3ac** in $CDCl_3$



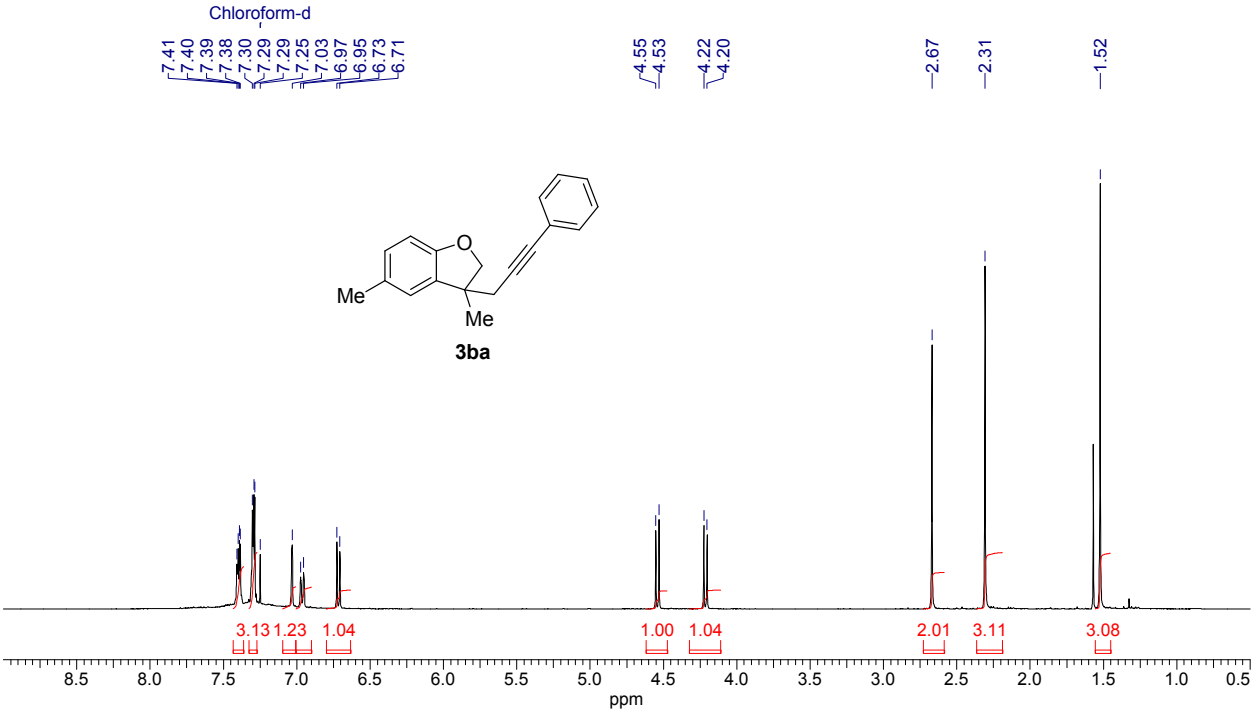
^{13}C-NMR (100 MHz) spectrum of **3ac** in $CDCl_3$



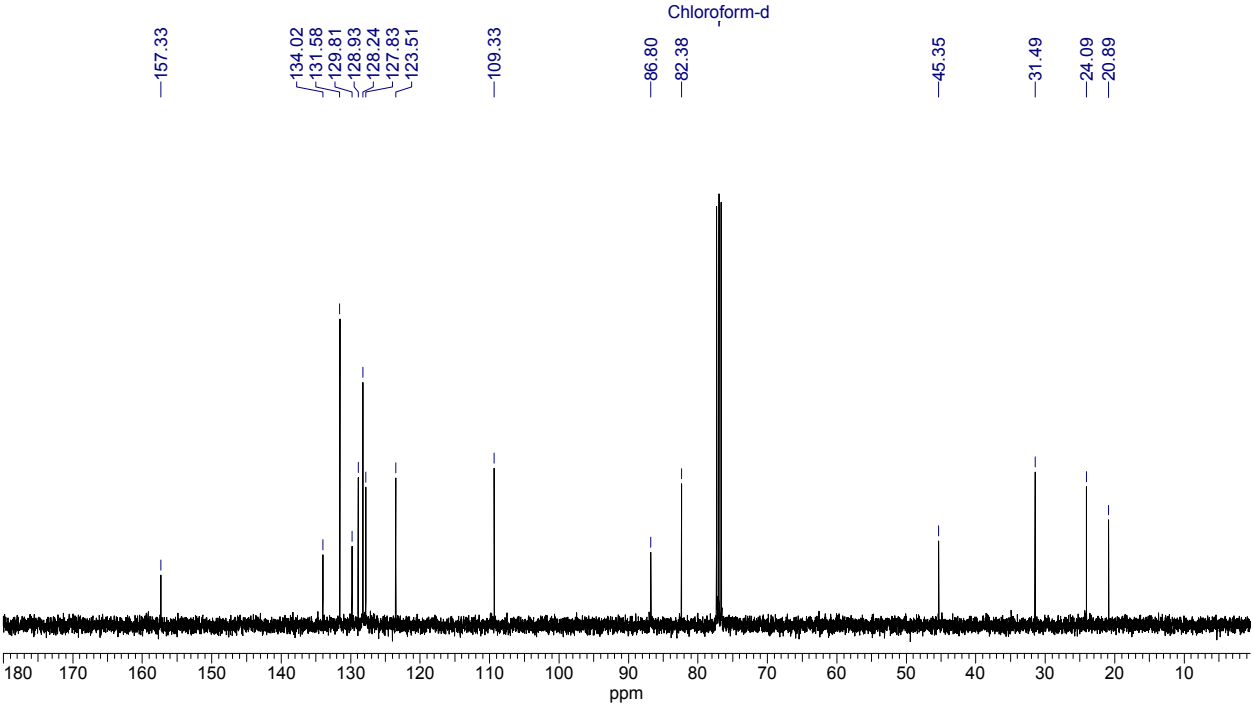
^{1}H-NMR (400 MHz) spectrum of **3ad** in $CDCl_3$



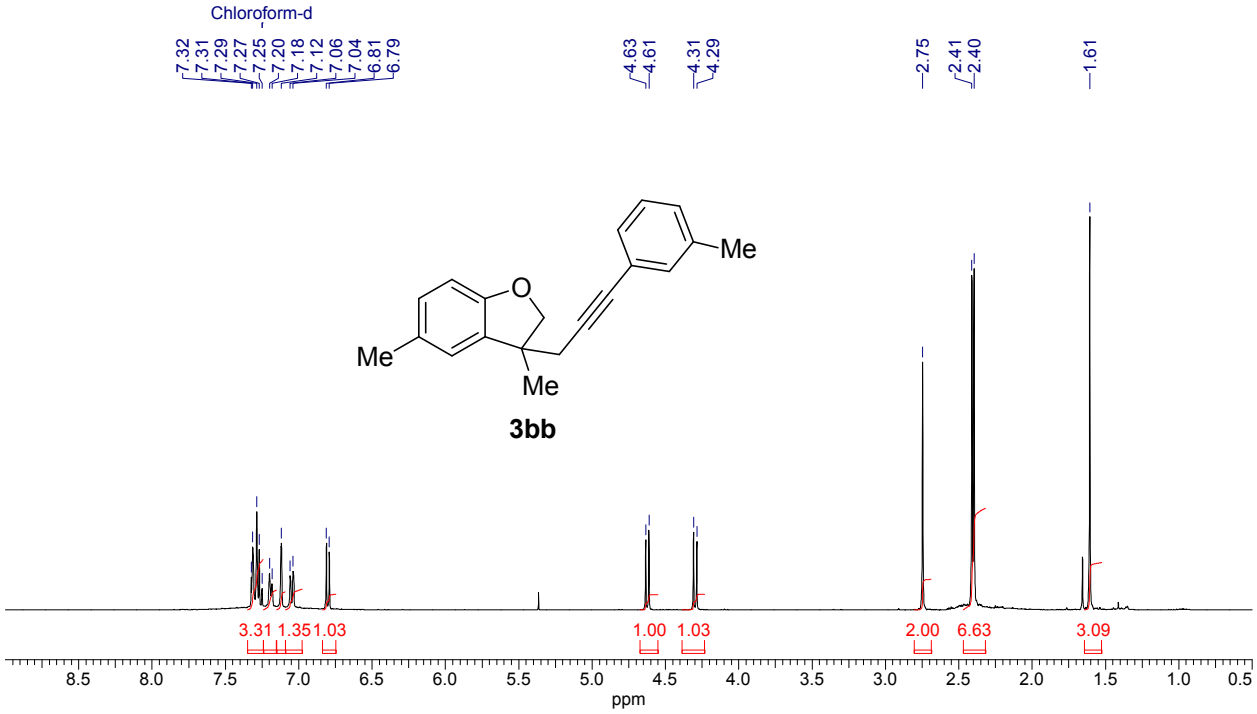
^{13}C-NMR (100 MHz) spectrum of **3ad** in $CDCl_3$



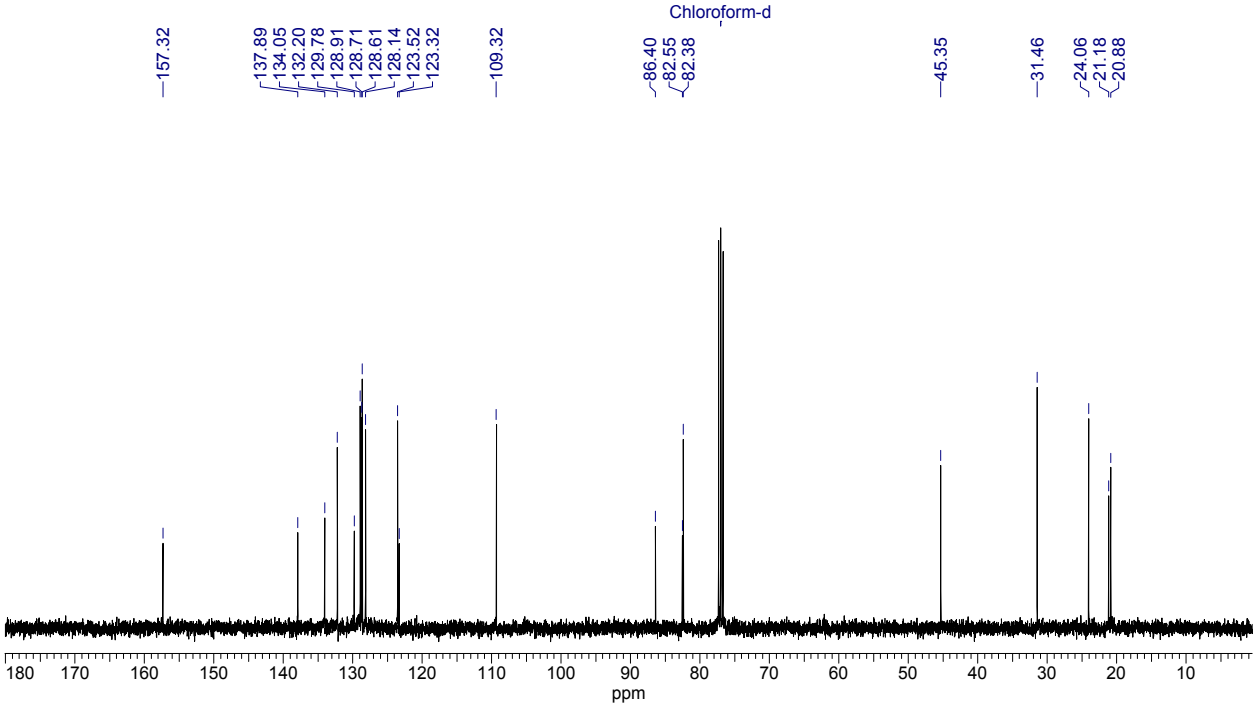
^{1}H-NMR (400 MHz) spectrum of **3ba** in $CDCl_3$



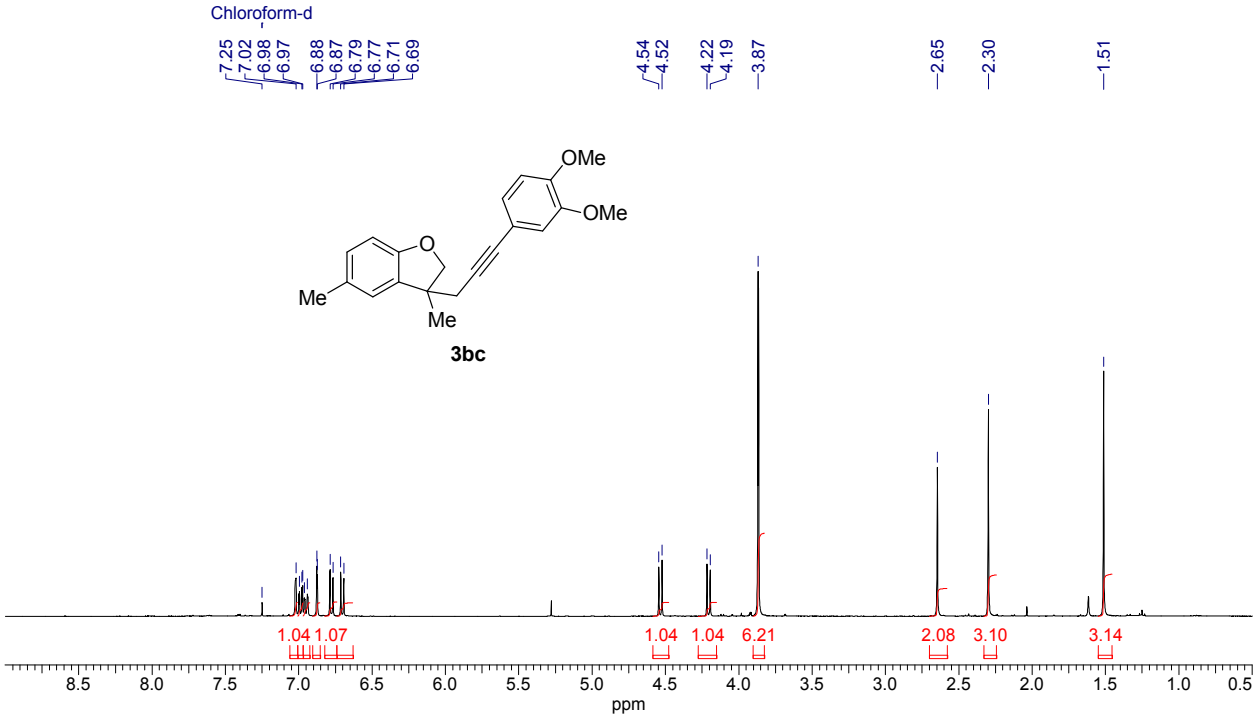
^{13}C-NMR (100 MHz) spectrum of **3ba** in $CDCl_3$



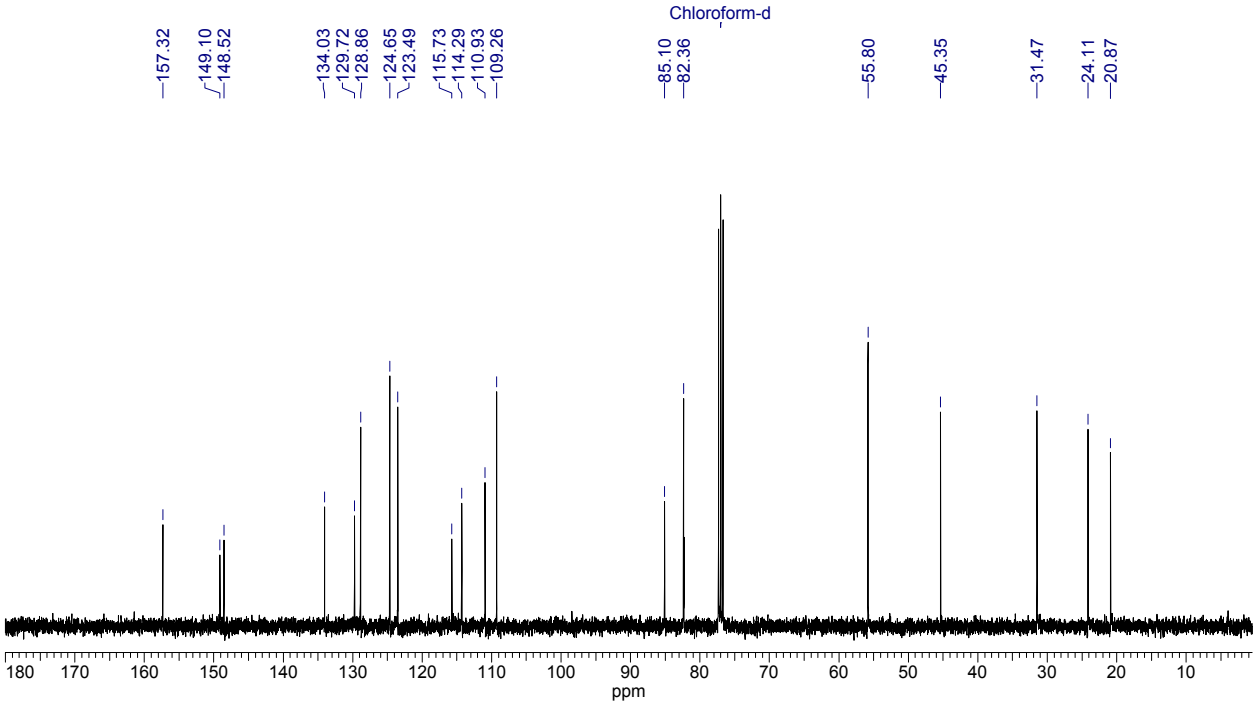
^{1}H-NMR (400 MHz) spectrum of **3bb** in $CDCl_3$



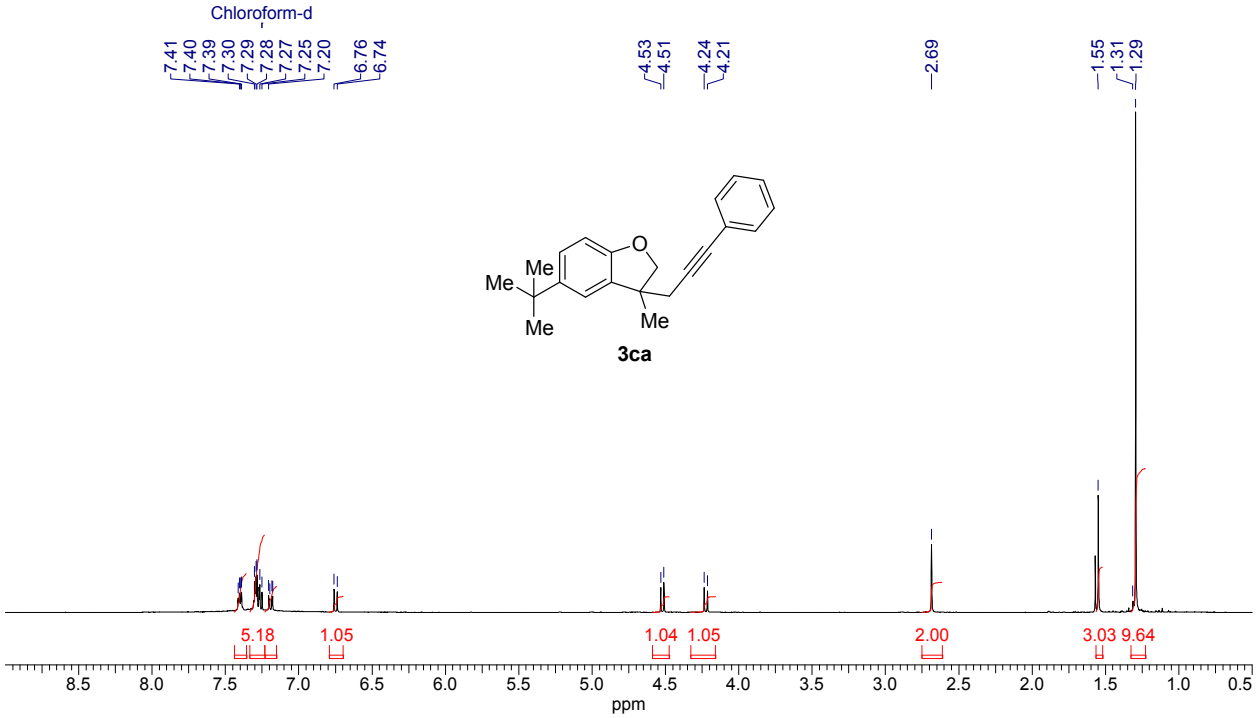
^{13}C-NMR (100 MHz) spectrum of **3bb** in $CDCl_3$



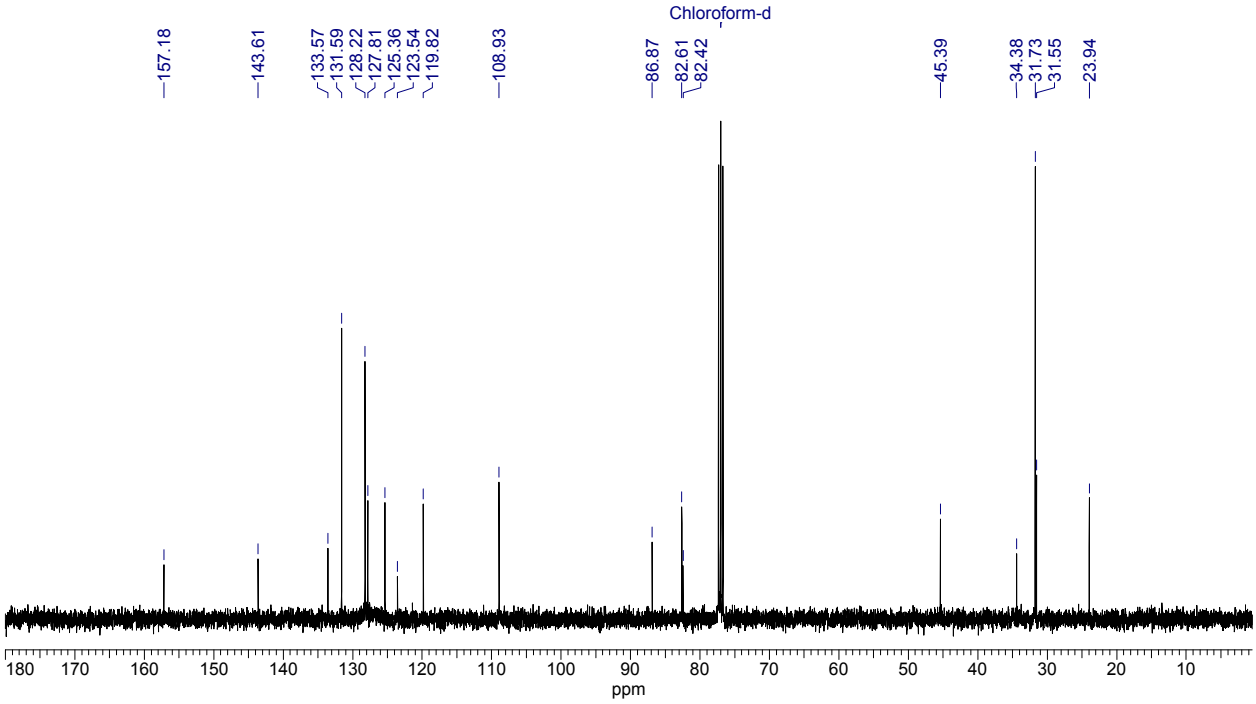
^{1}H-NMR (400 MHz) spectrum of **3bd** in $CDCl_3$



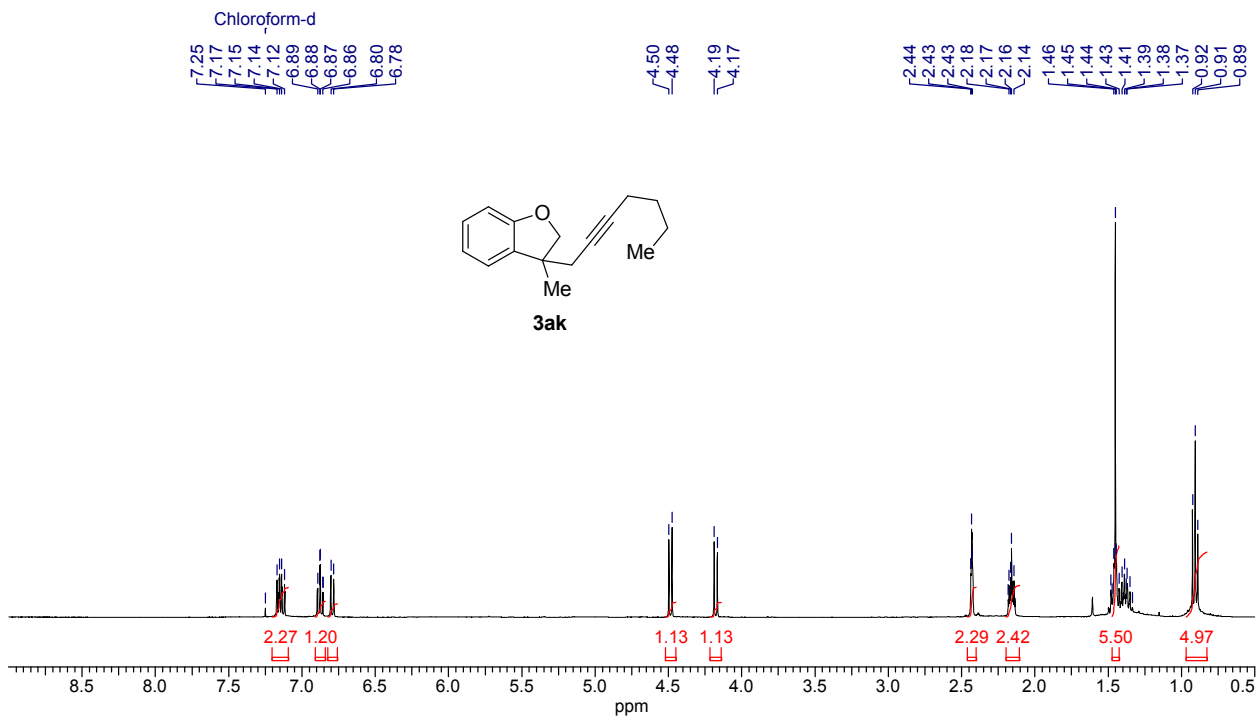
^{13}C-NMR (100 MHz) spectrum of **3bd** in $CDCl_3$



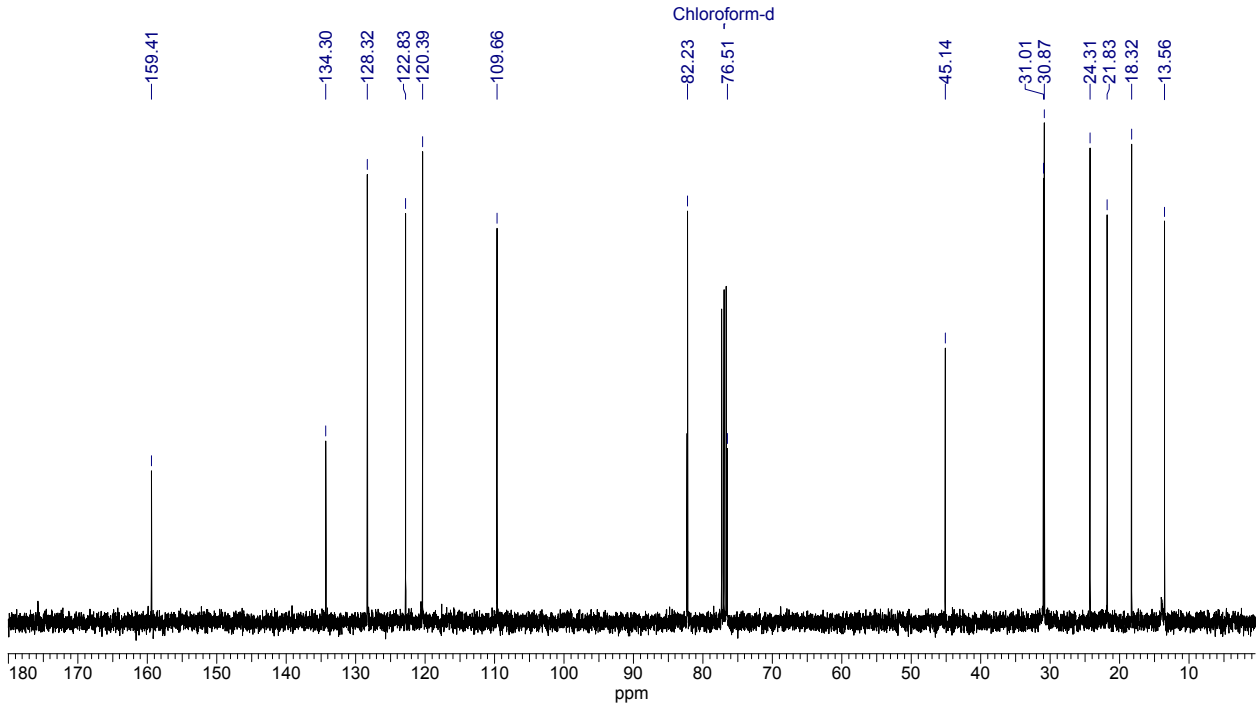
^{1}H-NMR (400 MHz) spectrum of **3ca** in $CDCl_3$



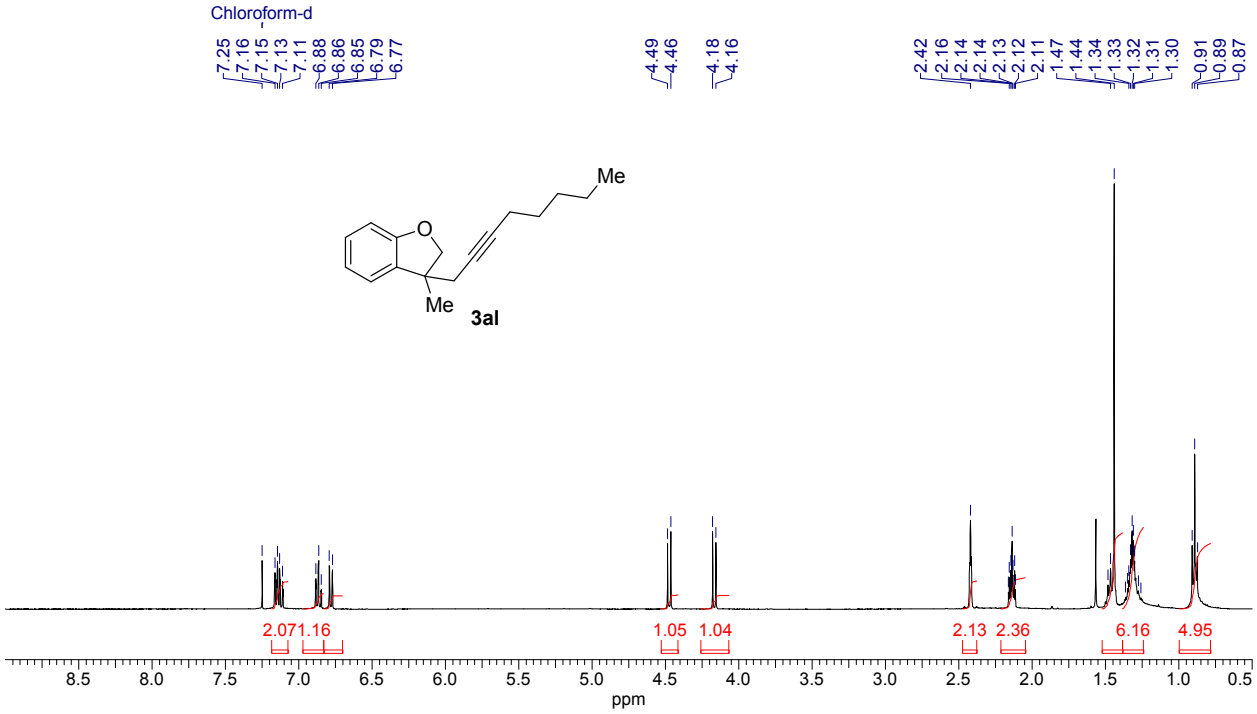
^{13}C-NMR (100 MHz) spectrum of **3ca** in $CDCl_3$



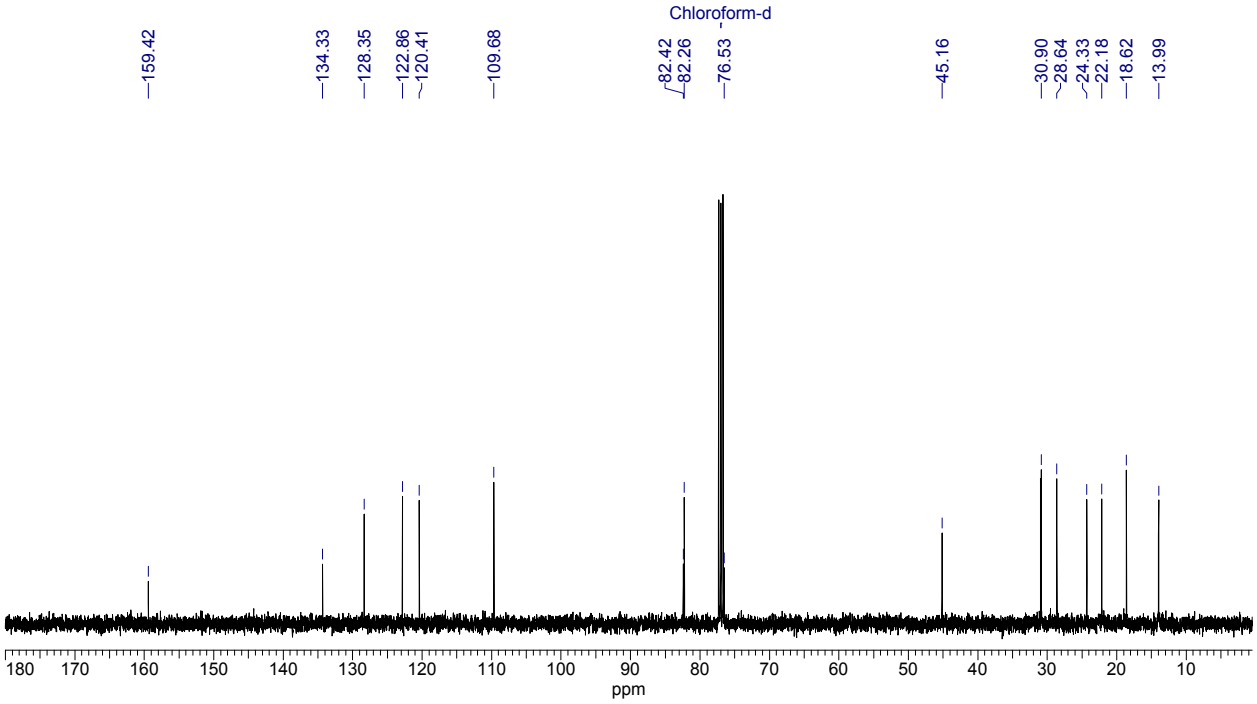
^{1}H-NMR (400 MHz) spectrum of **3ak** in $CDCl_3$



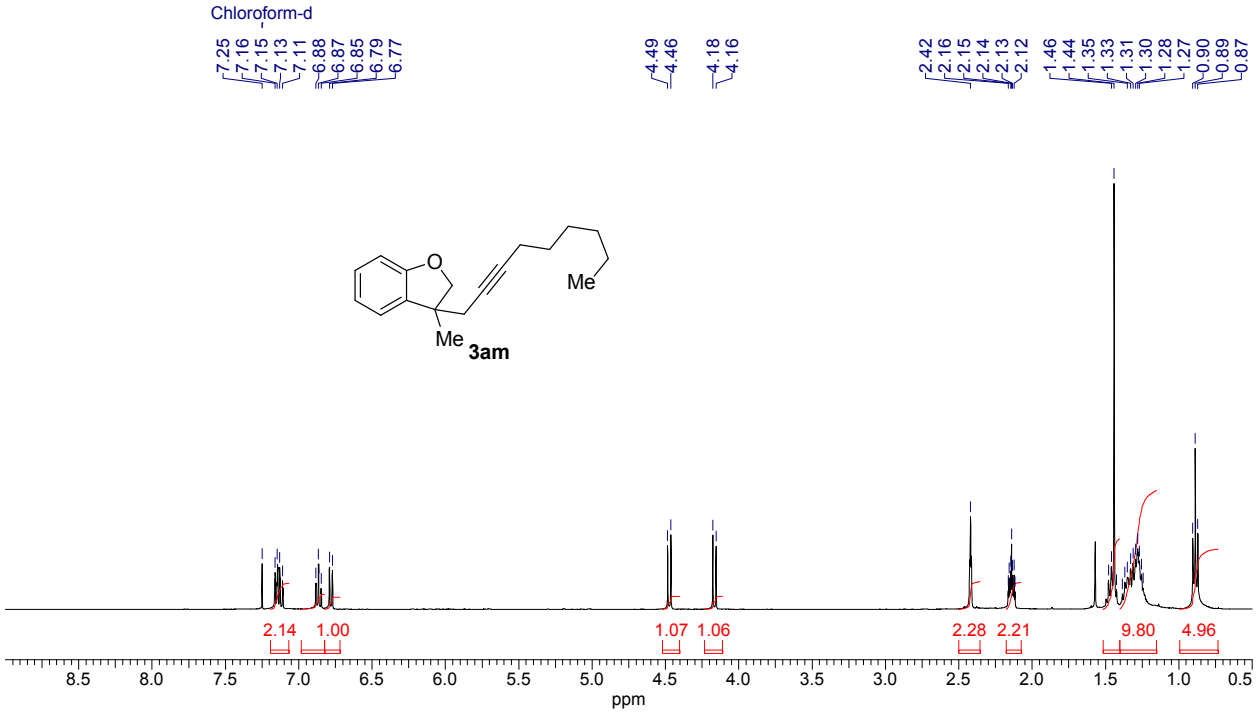
^{13}C-NMR (100 MHz) spectrum of **3ak** in $CDCl_3$



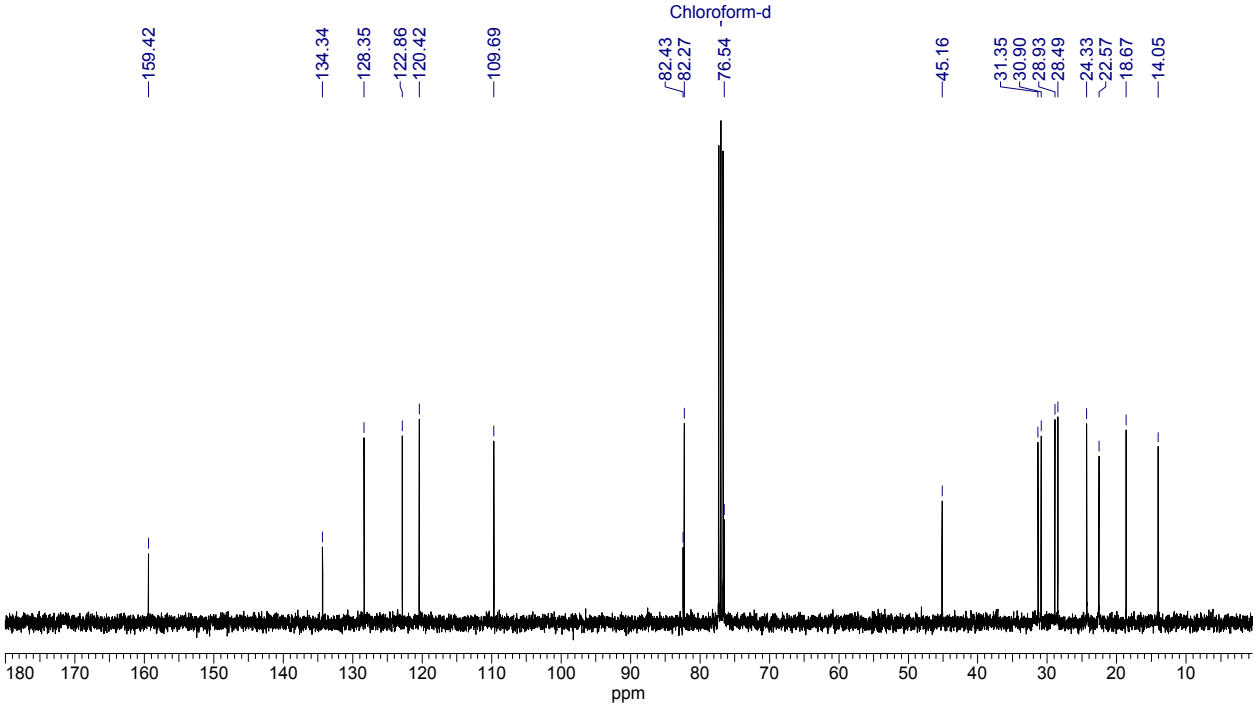
^{1}H-NMR (400 MHz) spectrum of **3al** in $CDCl_3$



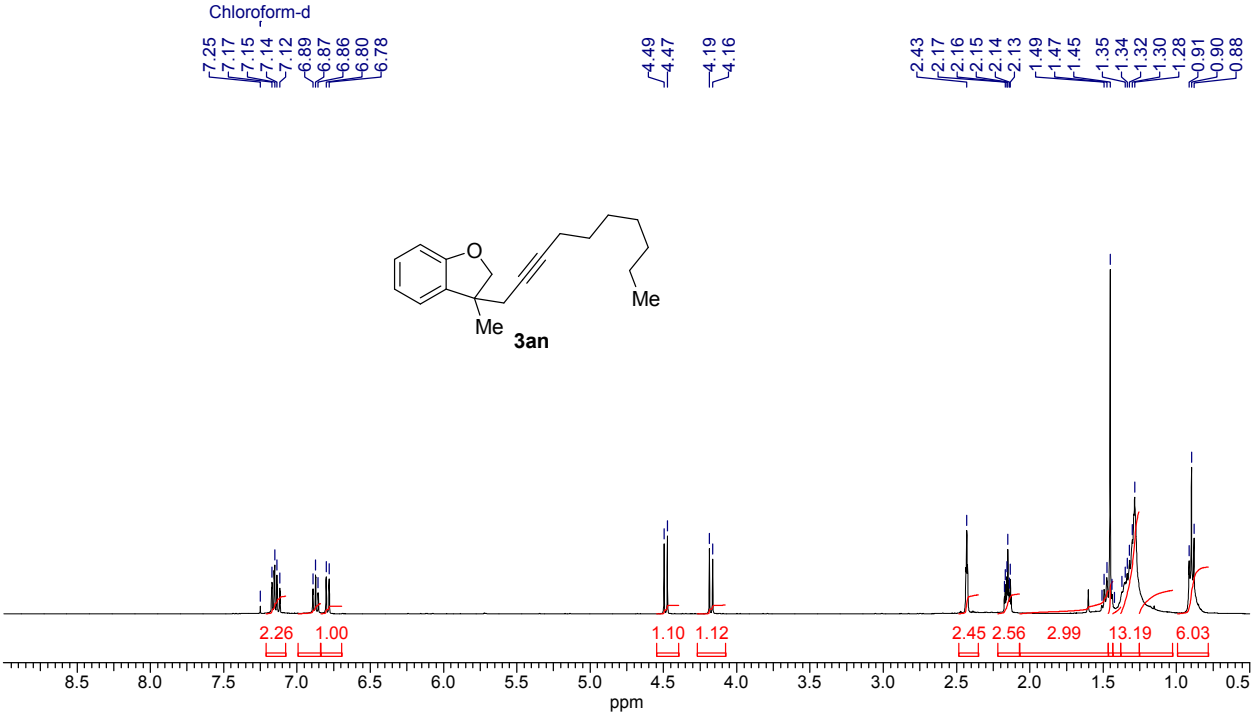
^{13}C-NMR (100 MHz) spectrum of **3al** in $CDCl_3$



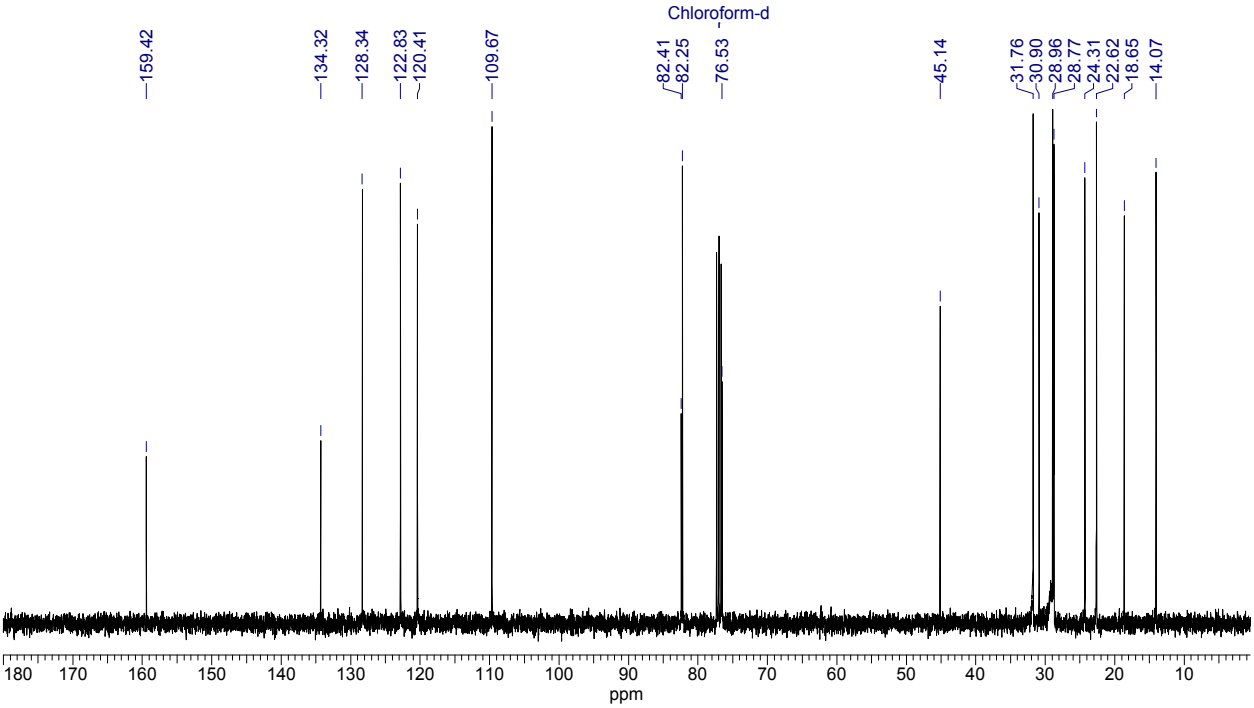
^{1}H-NMR (400 MHz) spectrum of **3am** in $CDCl_3$



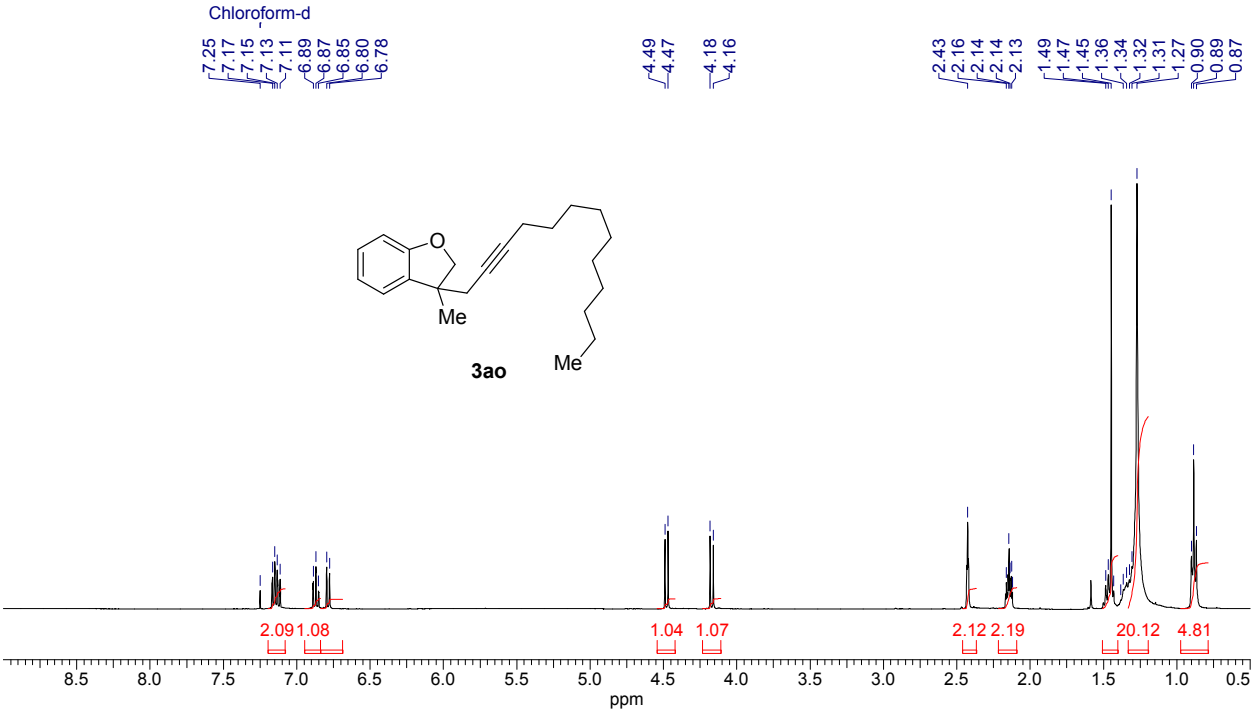
^{13}C-NMR (100 MHz) spectrum of **3am** in $CDCl_3$



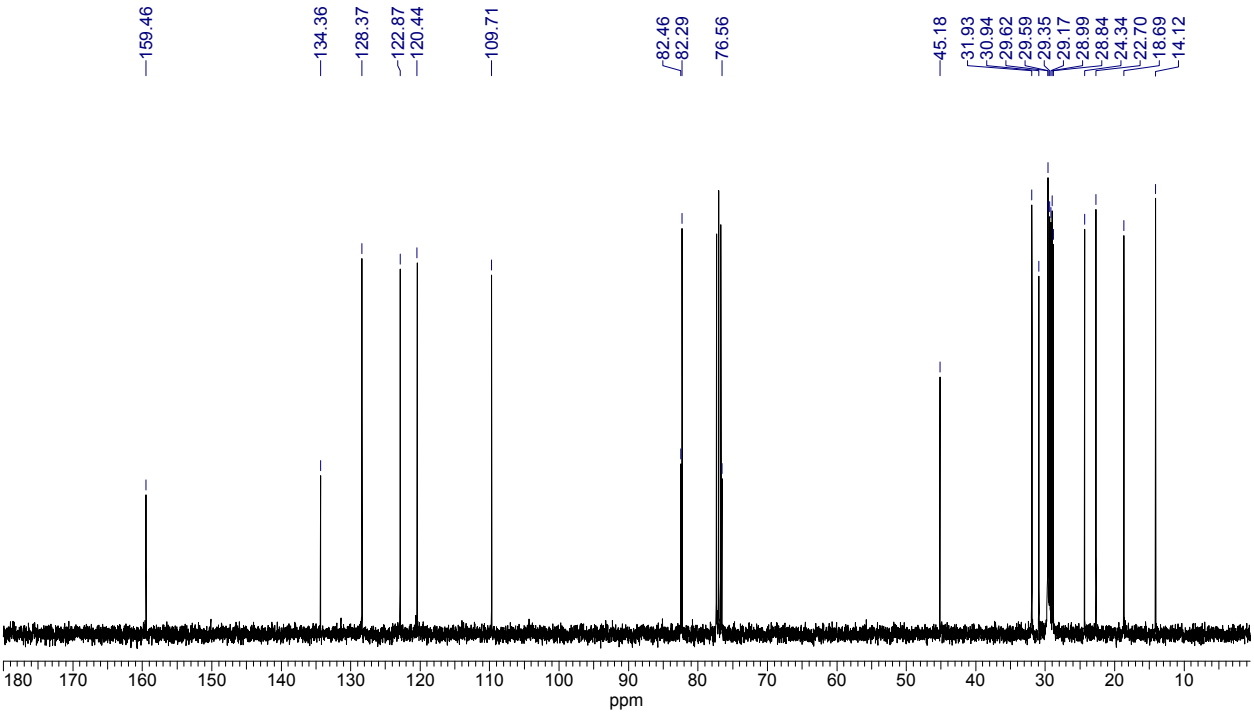
^{1}H-NMR (400 MHz) spectrum of **3an** in $CDCl_3$



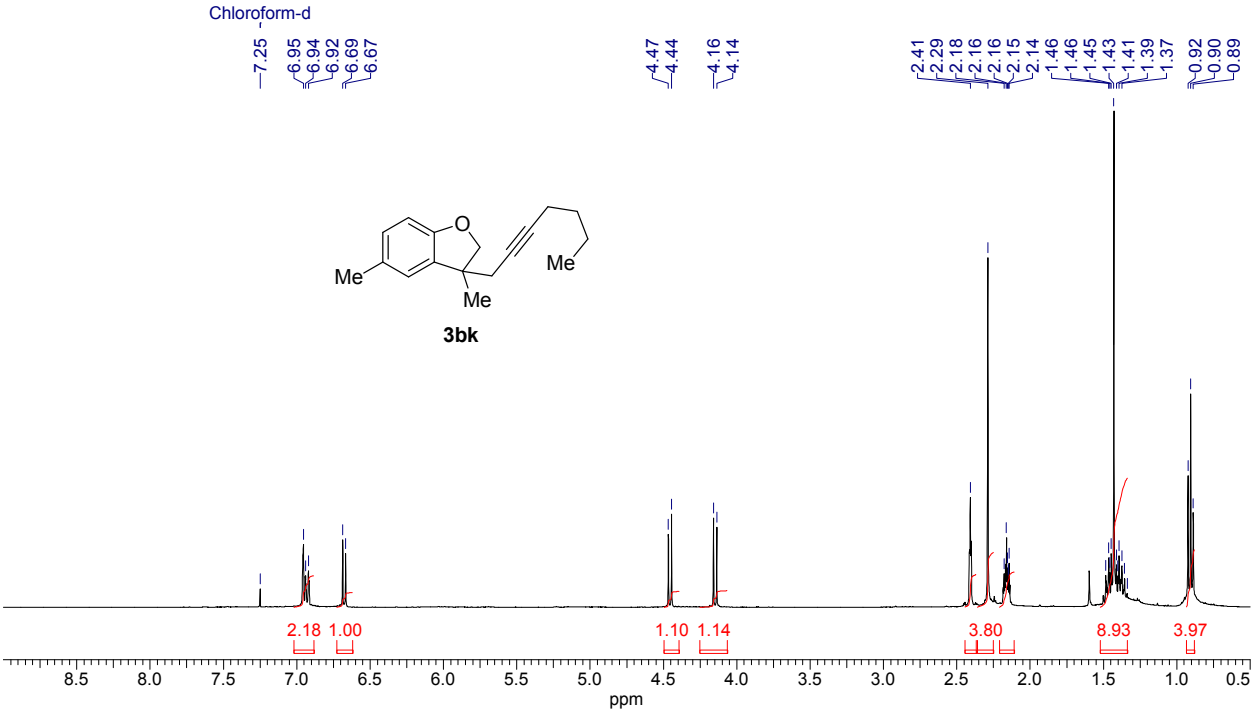
^{13}C-NMR (100 MHz) spectrum of **3an** in $CDCl_3$



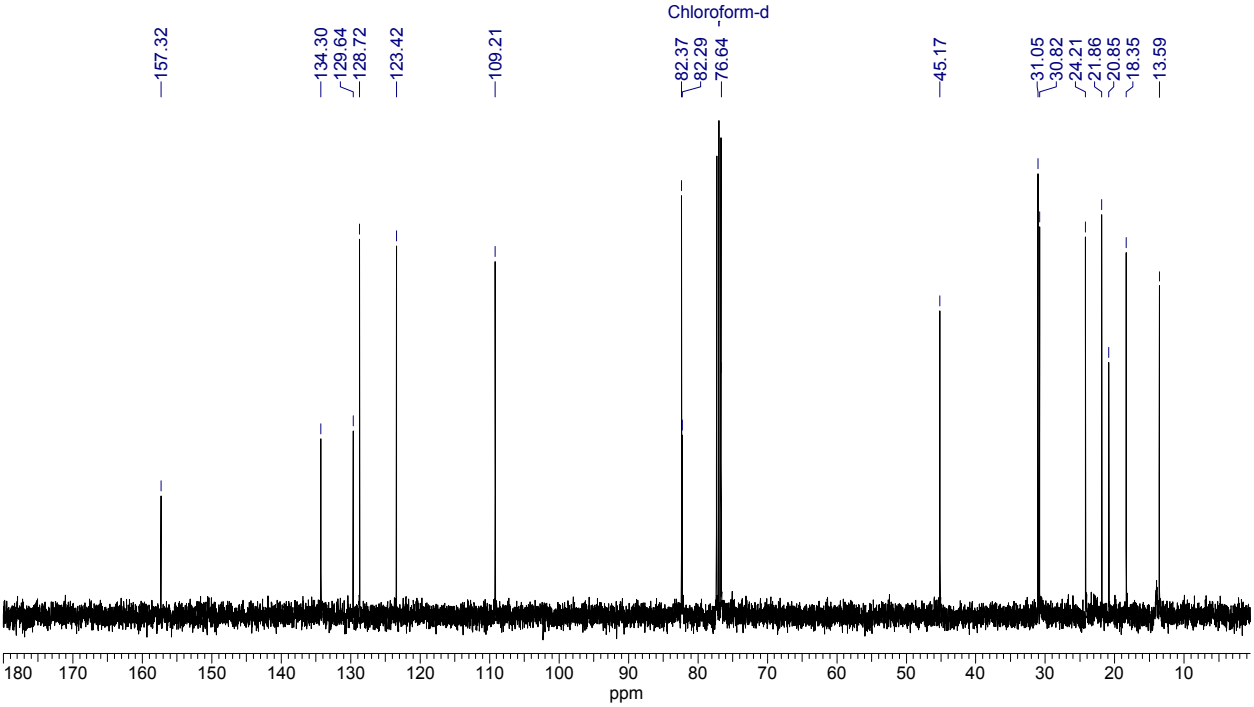
^{1}H-NMR (400 MHz) spectrum of **3ao** in $CDCl_3$



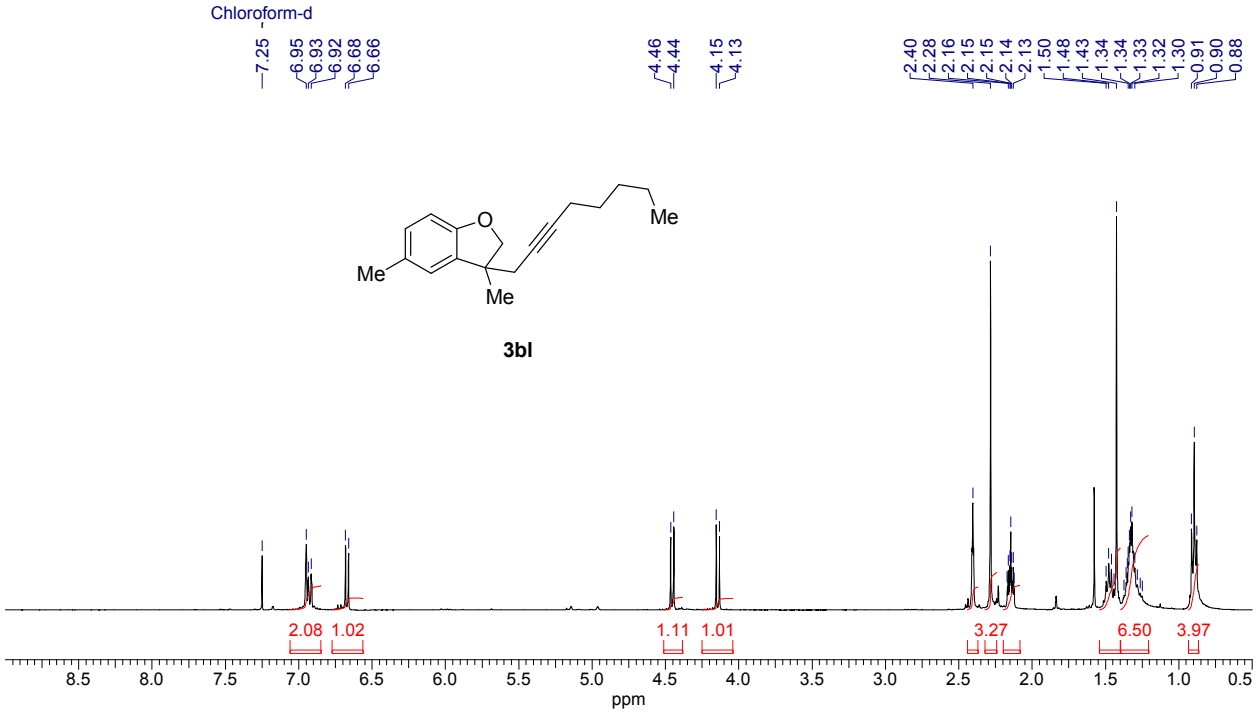
^{13}C-NMR (100 MHz) spectrum of **3ao** in $CDCl_3$



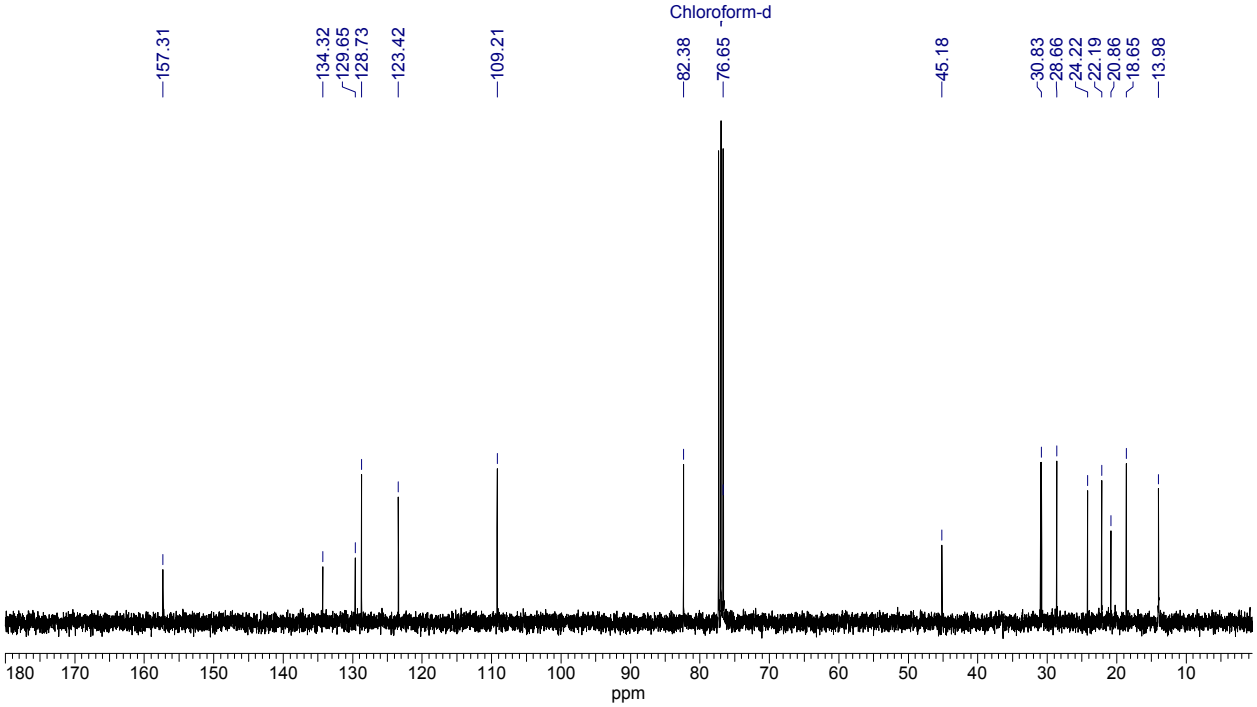
^{1}H-NMR (400 MHz) spectrum of **3bk** in $CDCl_3$



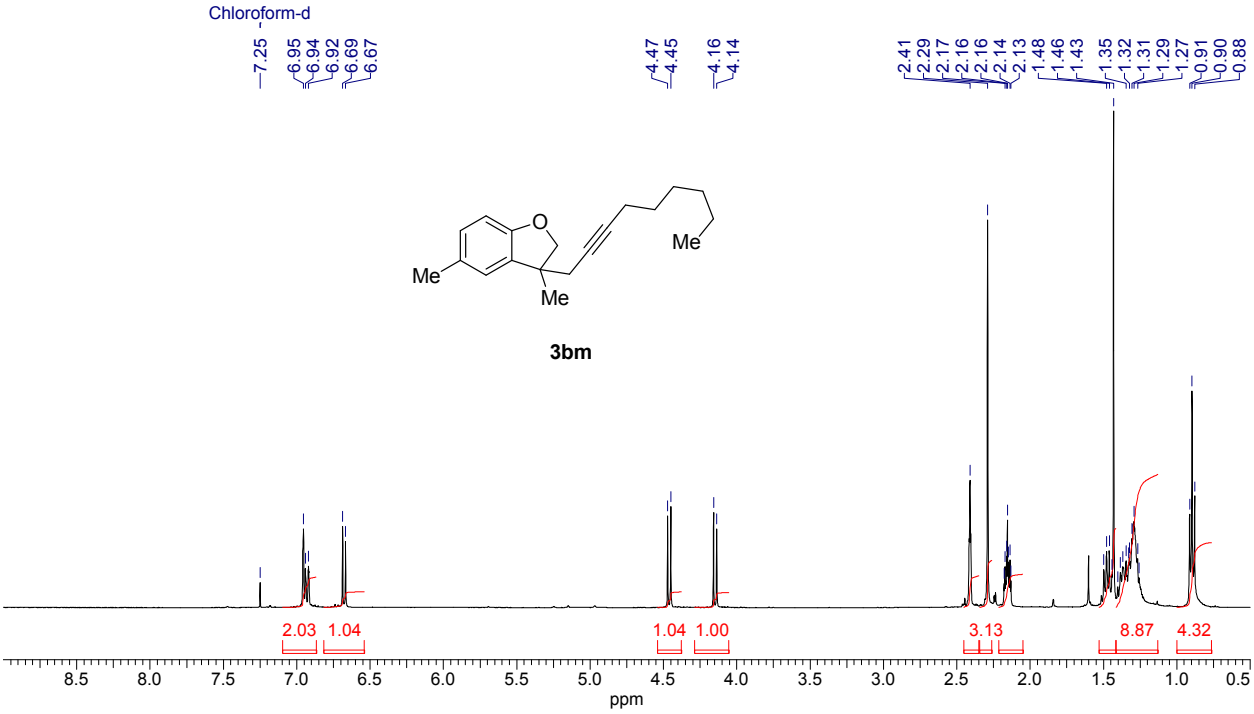
^{13}C-NMR (100 MHz) spectrum of **3bk** in $CDCl_3$



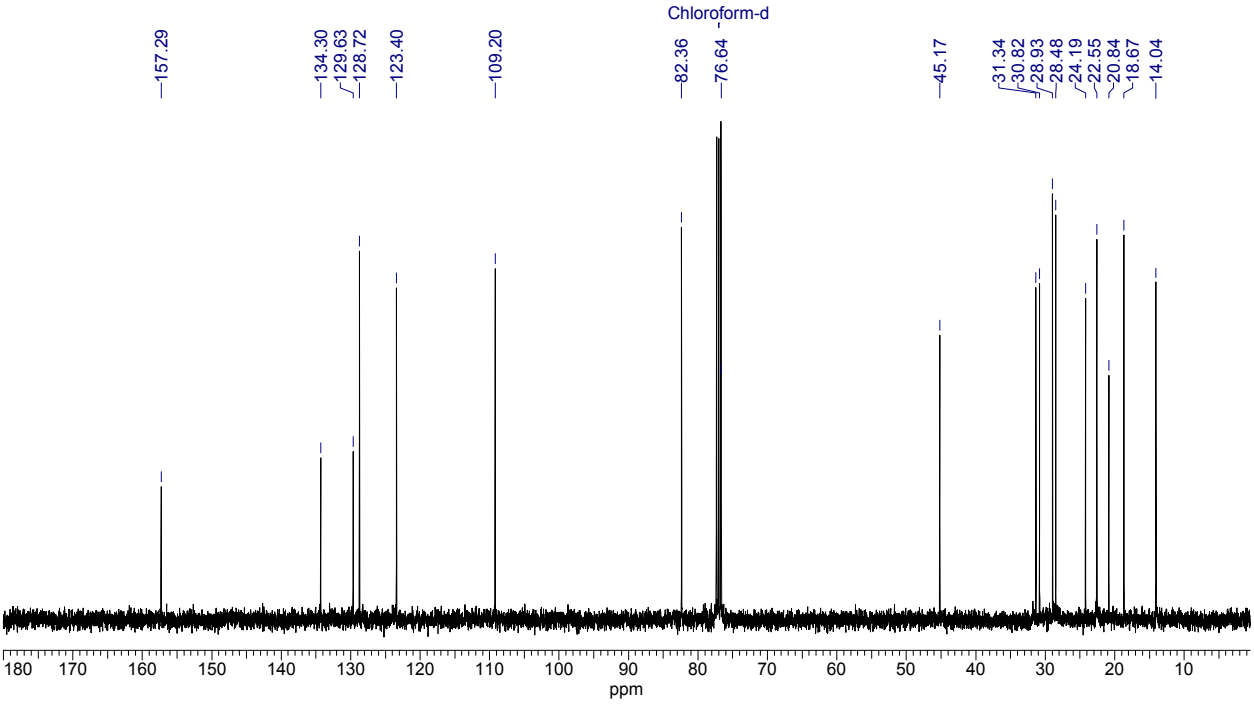
^{1}H-NMR (400 MHz) spectrum of **3bl** in $CDCl_3$



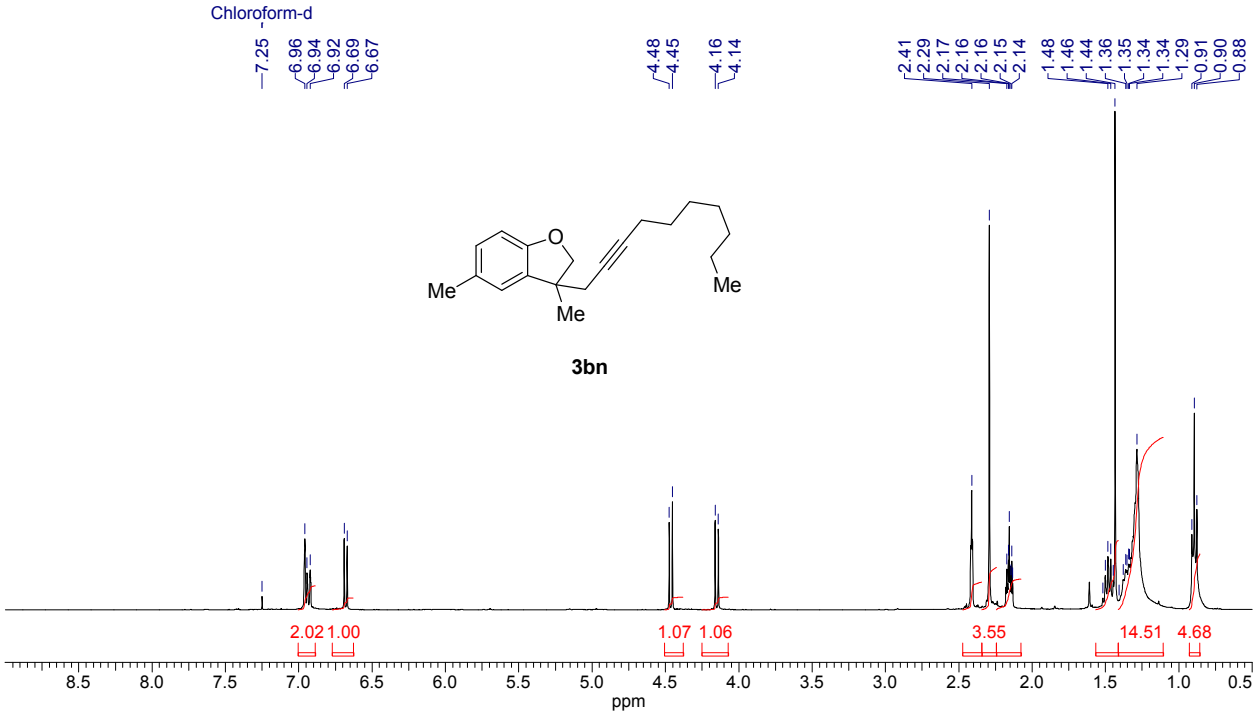
^{13}C-NMR (100 MHz) spectrum of **3bl** in $CDCl_3$



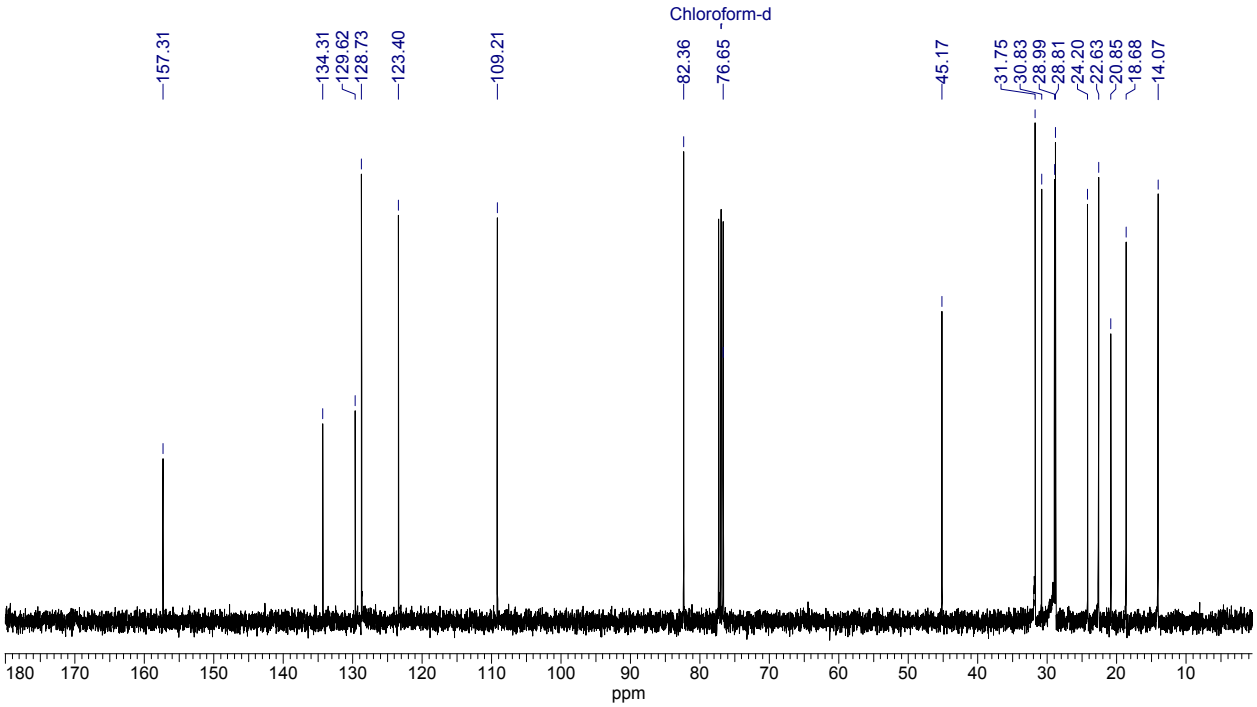
^{1}H-NMR (400 MHz) spectrum of **3bm** in $CDCl_3$



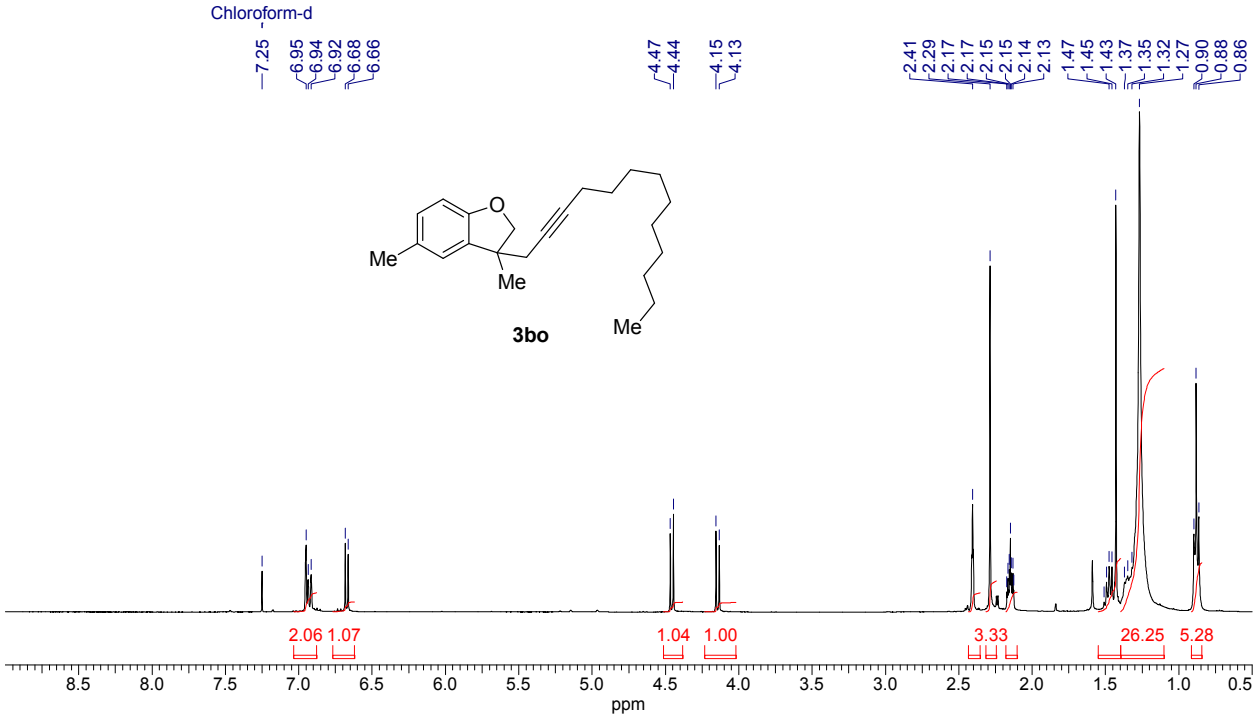
^{13}C-NMR (100 MHz) spectrum of **3bm** in $CDCl_3$



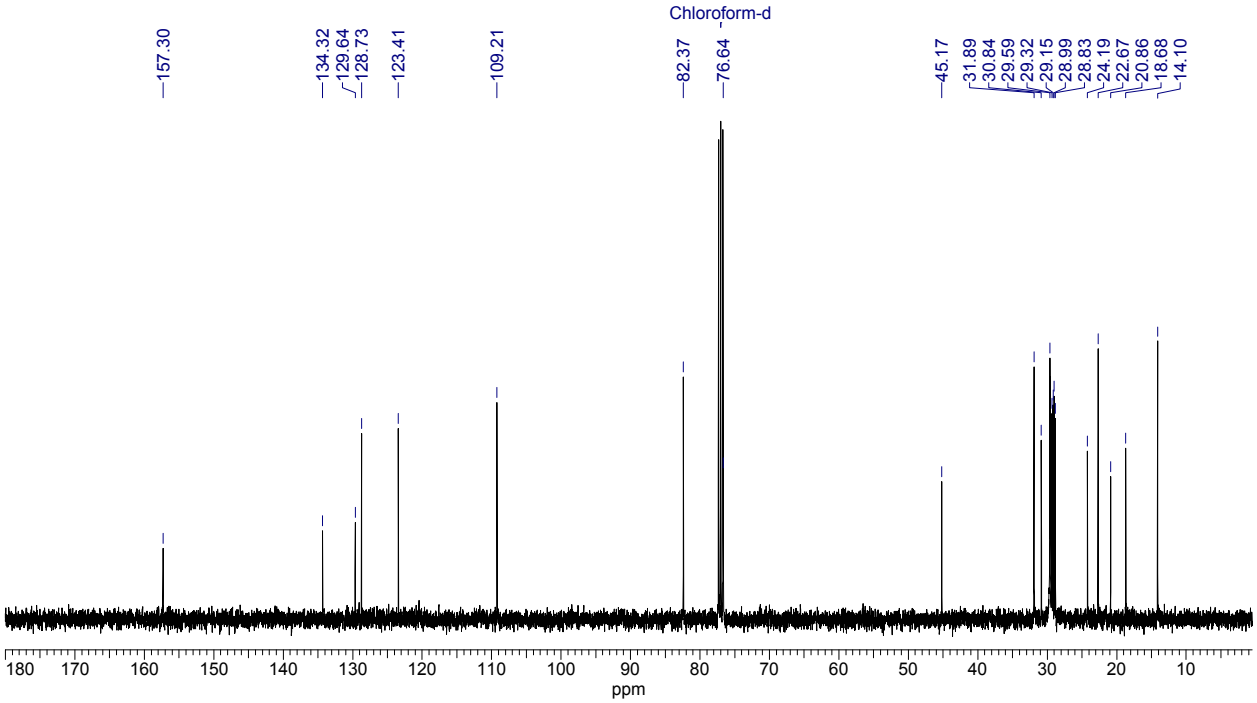
^{1}H-NMR (400 MHz) spectrum of **3bn** in $CDCl_3$



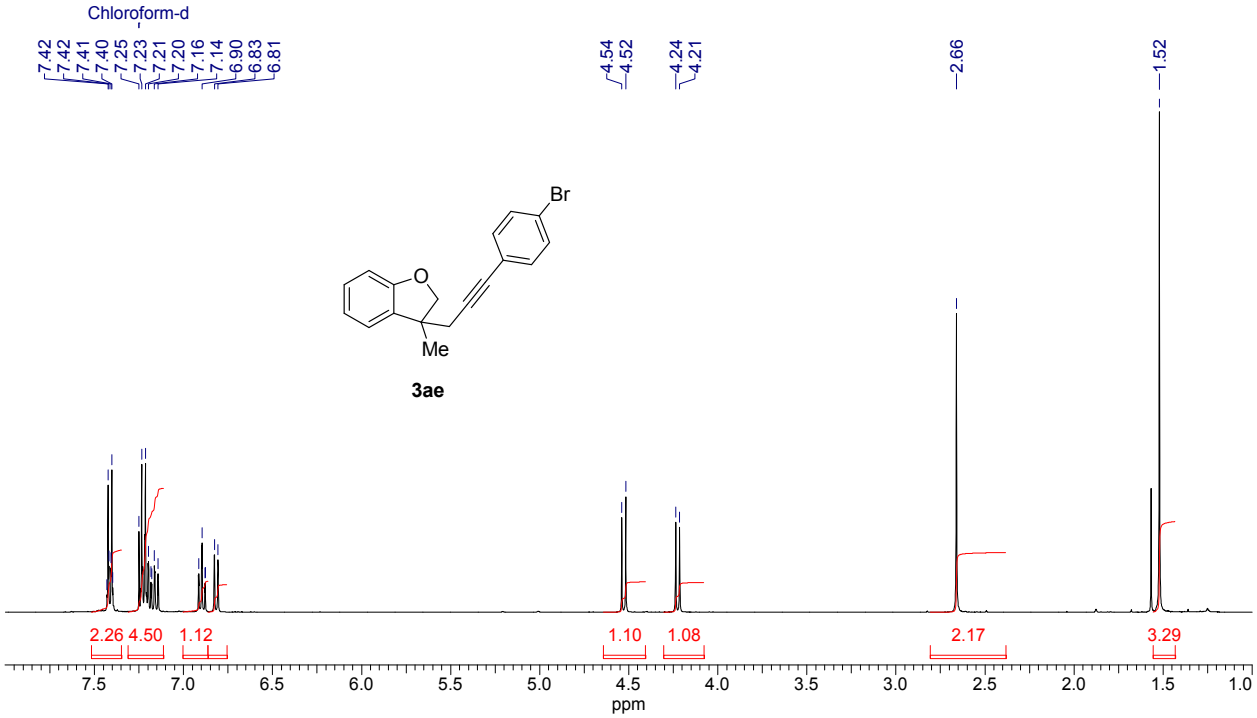
^{13}C-NMR (100 MHz) spectrum of **3bn** in $CDCl_3$



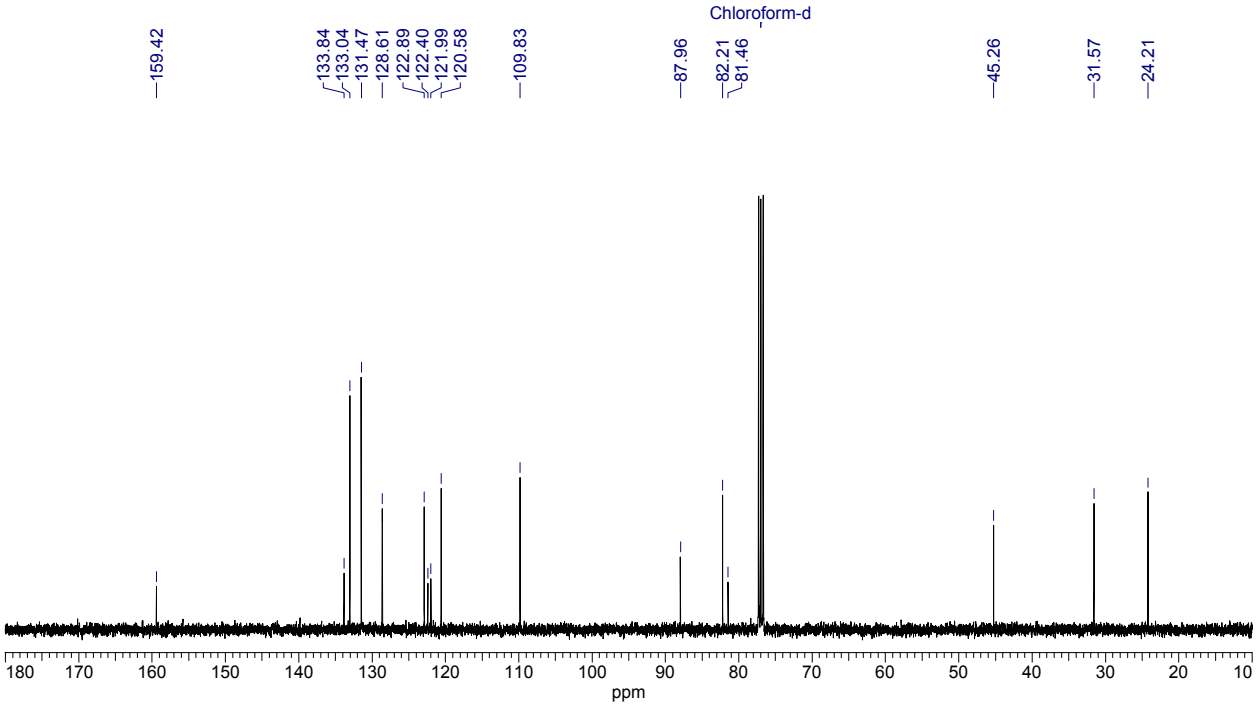
^{1}H-NMR (400 MHz) spectrum of **3bo** in $CDCl_3$



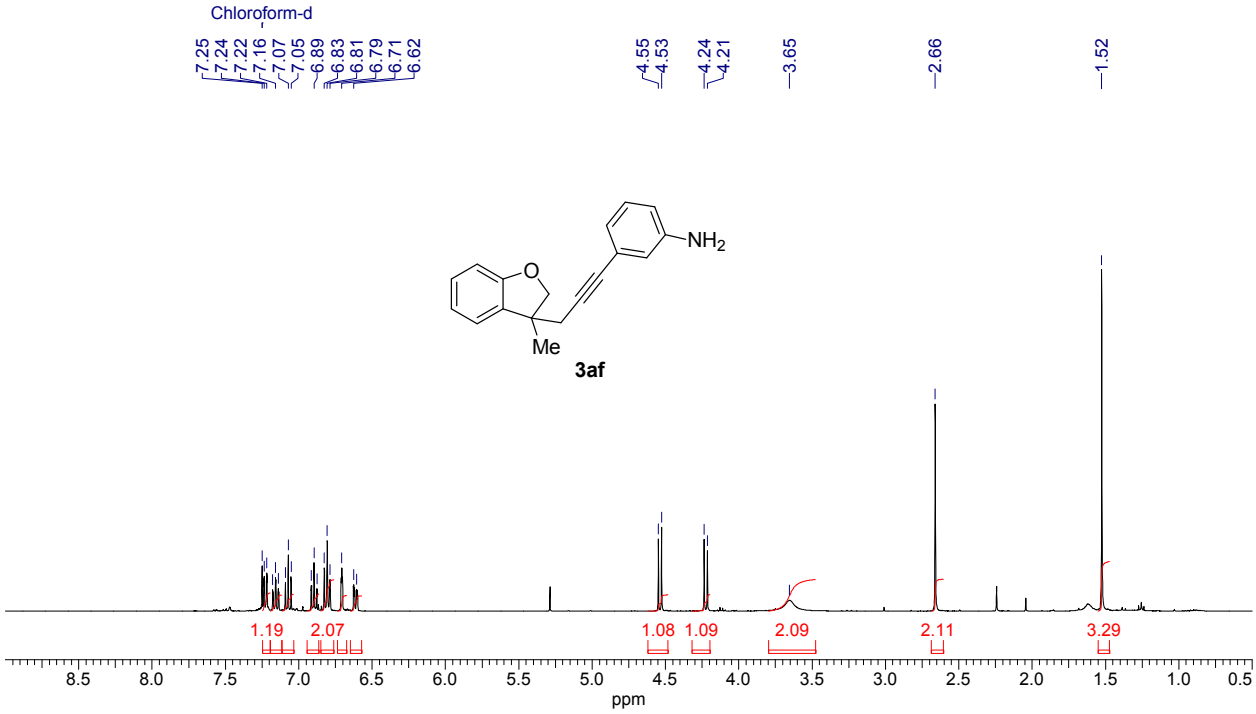
^{13}C-NMR (100 MHz) spectrum of **3bo** in $CDCl_3$



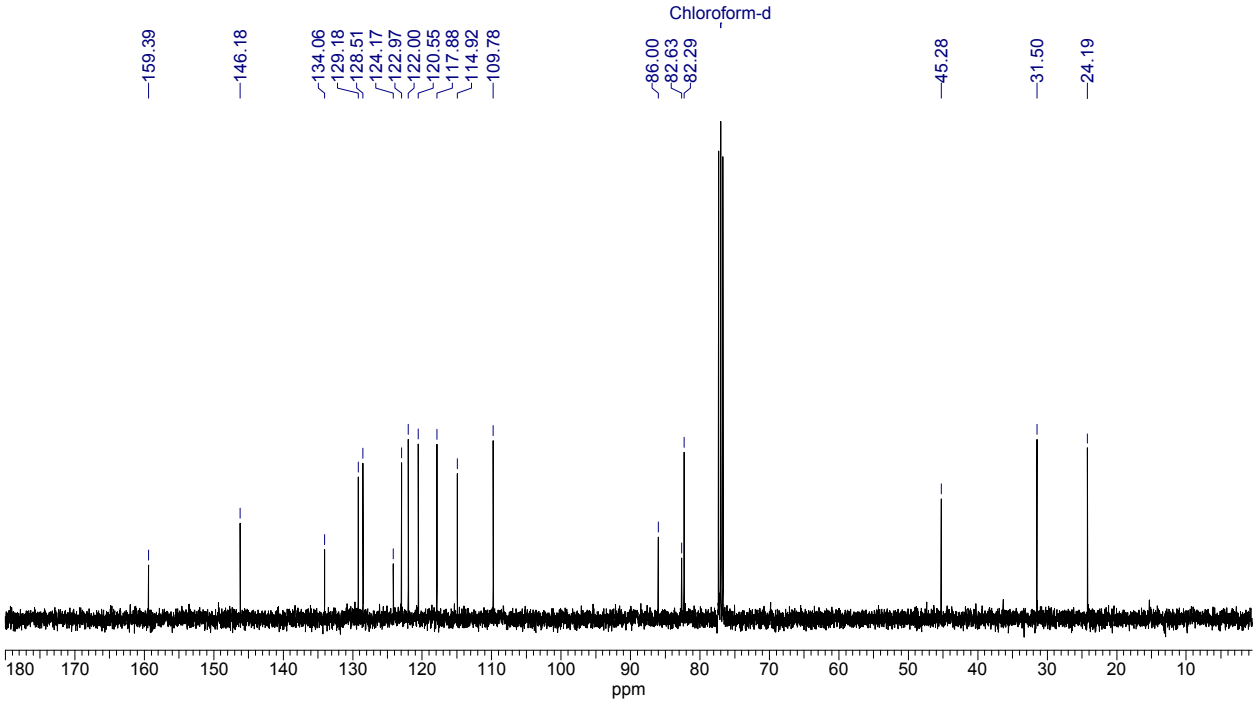
^{1}H-NMR (400 MHz) spectrum of **3ae** in $CDCl_3$



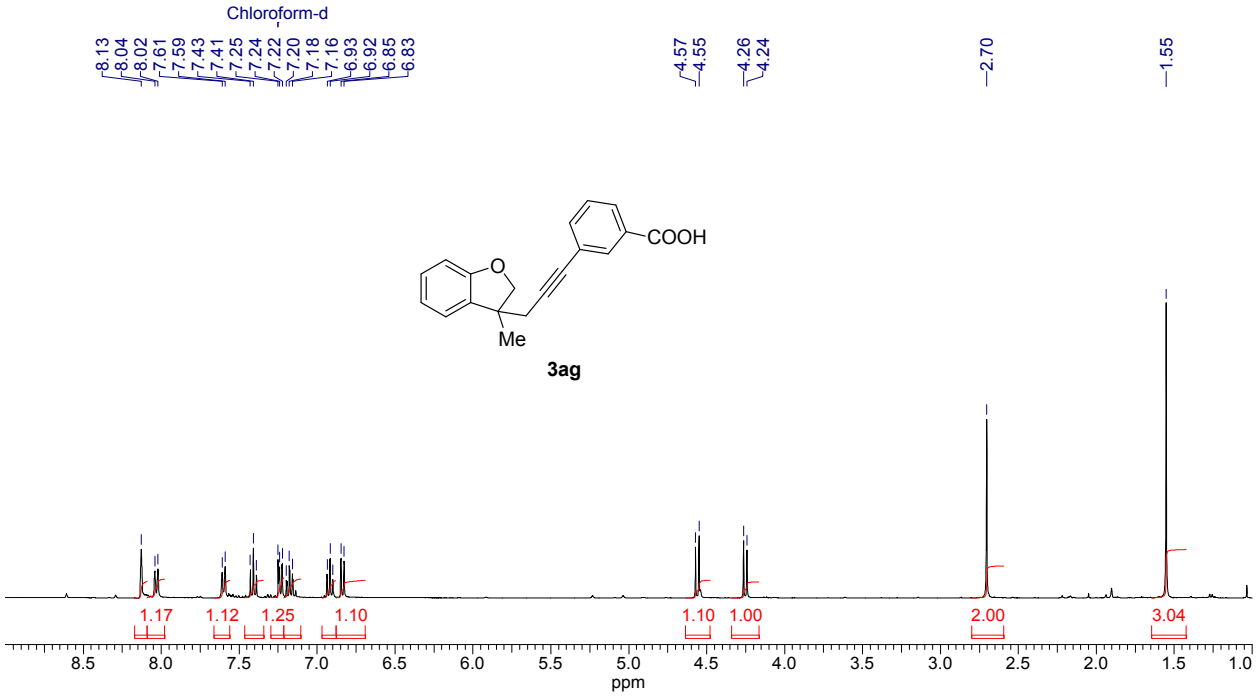
^{13}C-NMR (100 MHz) spectrum of **3ae** in $CDCl_3$



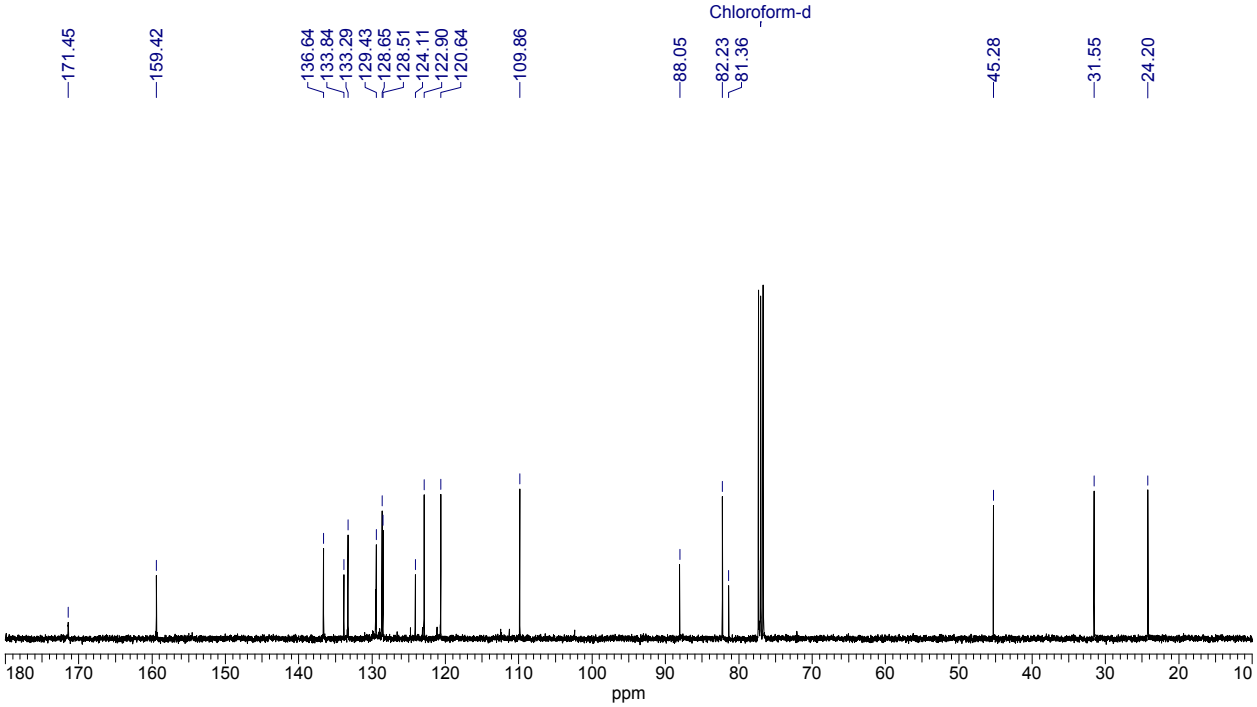
^{1}H-NMR (400 MHz) spectrum of **3af** in $CDCl_3$



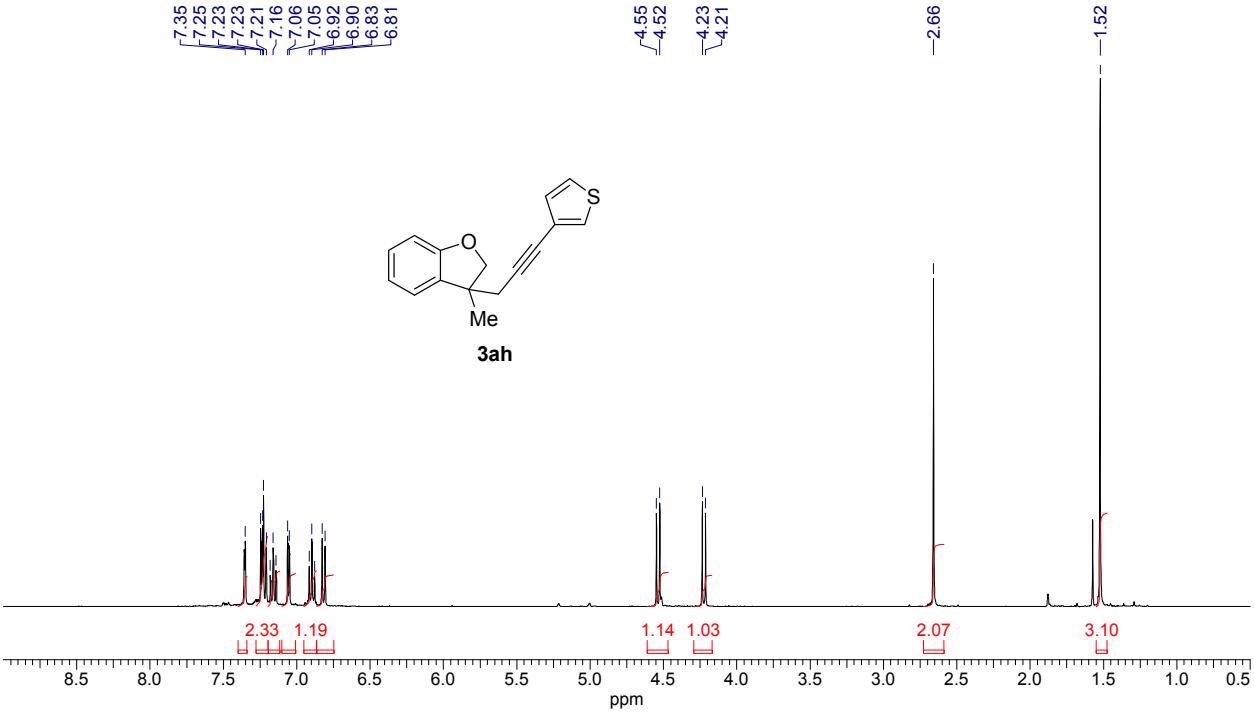
^{13}C-NMR (100 MHz) spectrum of **3af** in $CDCl_3$



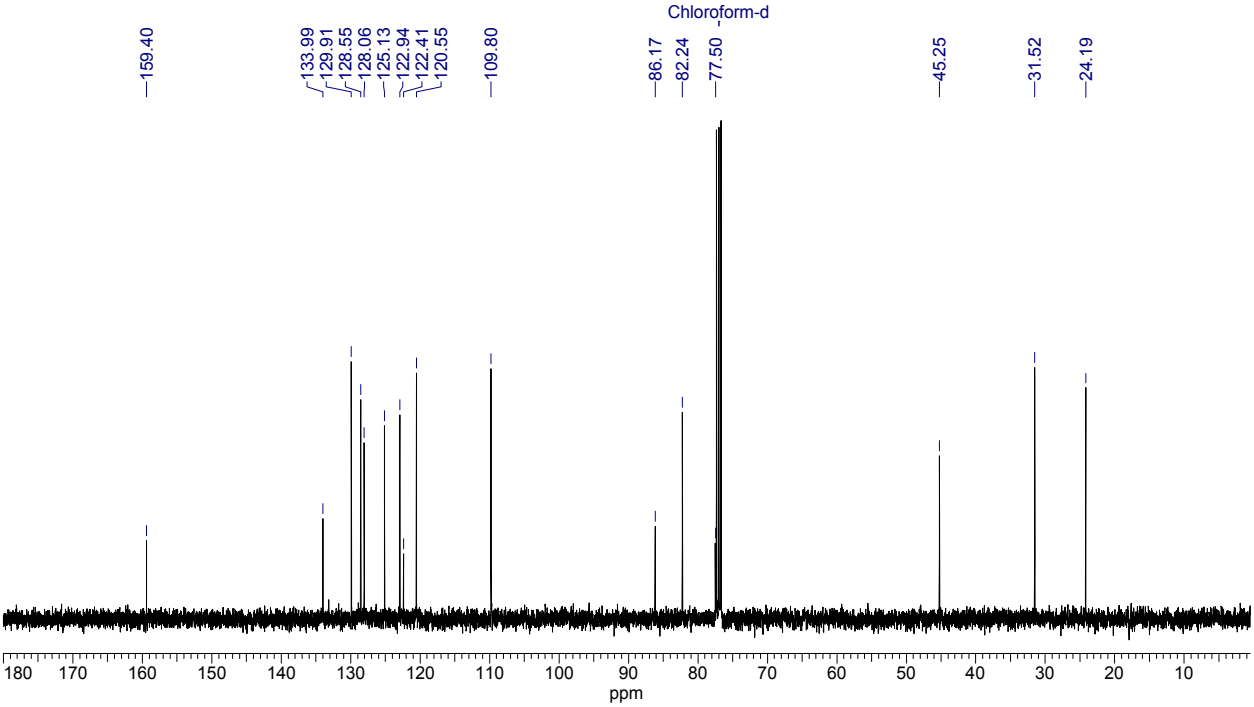
^{1}H-NMR (400 MHz) spectrum of **3ag** in $CDCl_3$



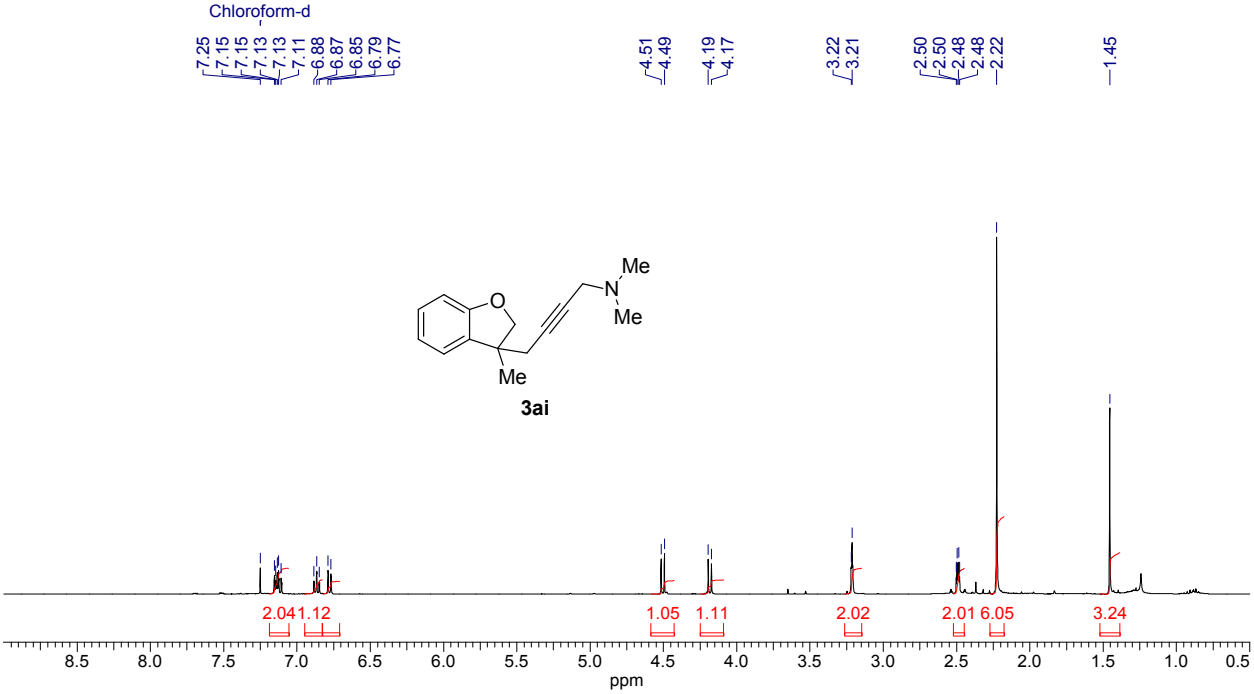
^{13}C-NMR (100 MHz) spectrum of **3ag** in $CDCl_3$



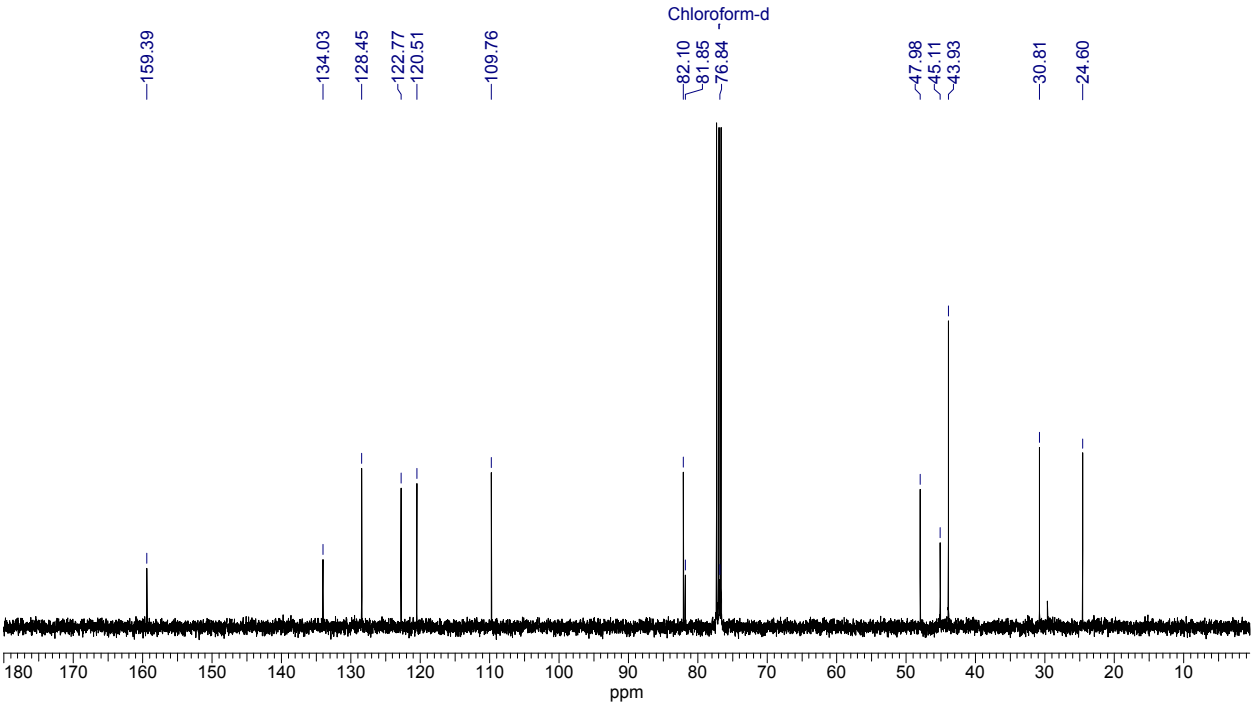
^{1}H-NMR (400 MHz) spectrum of **3ah** in $CDCl_3$



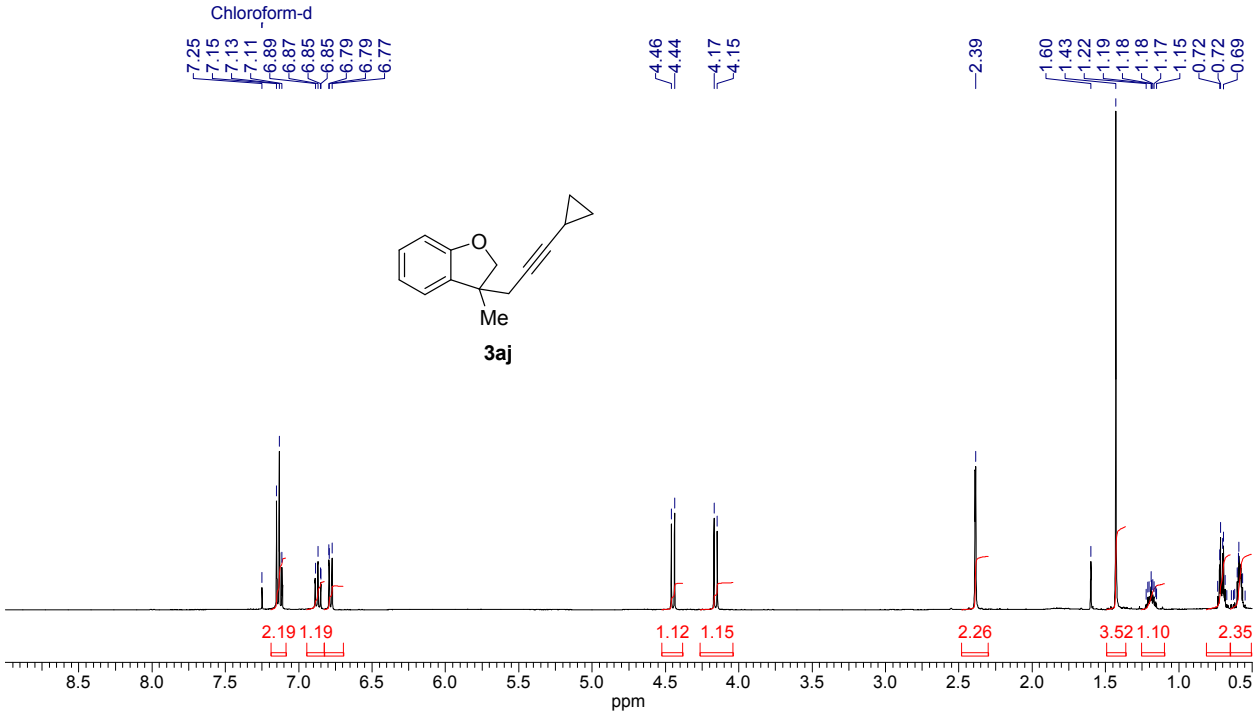
^{13}C-NMR (100 MHz) spectrum of **3ah** in $CDCl_3$



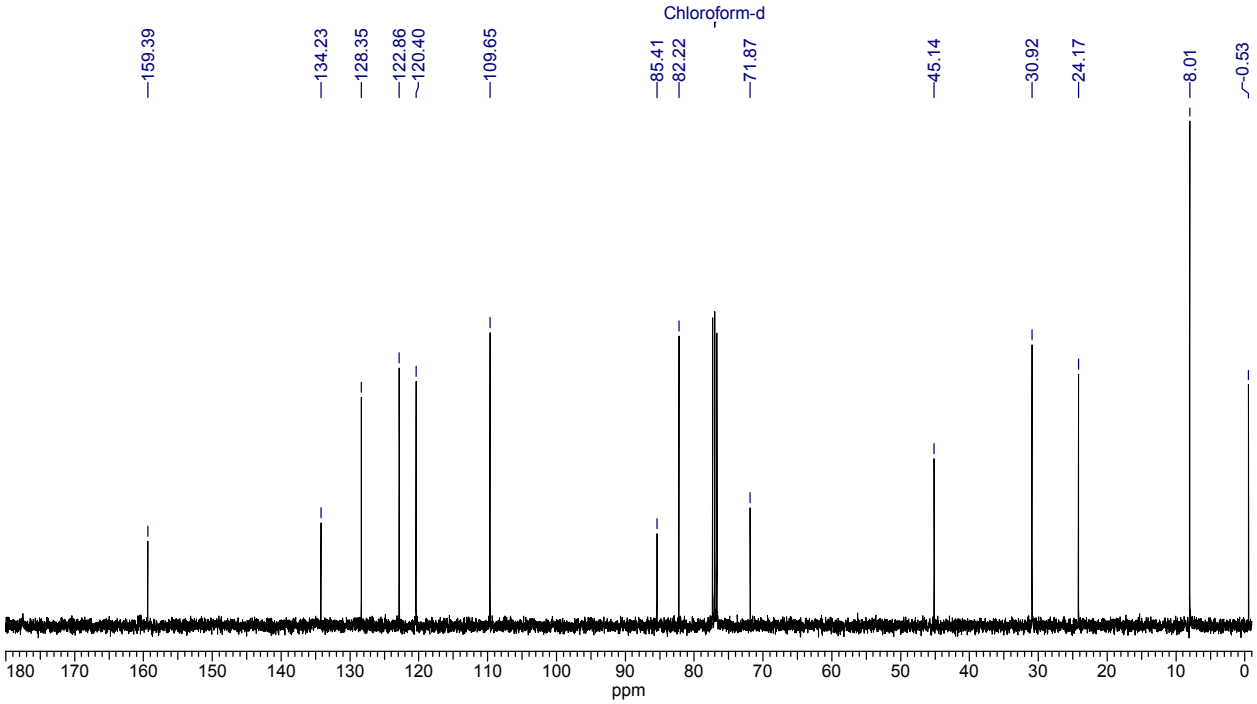
^{1}H-NMR (400 MHz) spectrum of **3ai** in $CDCl_3$



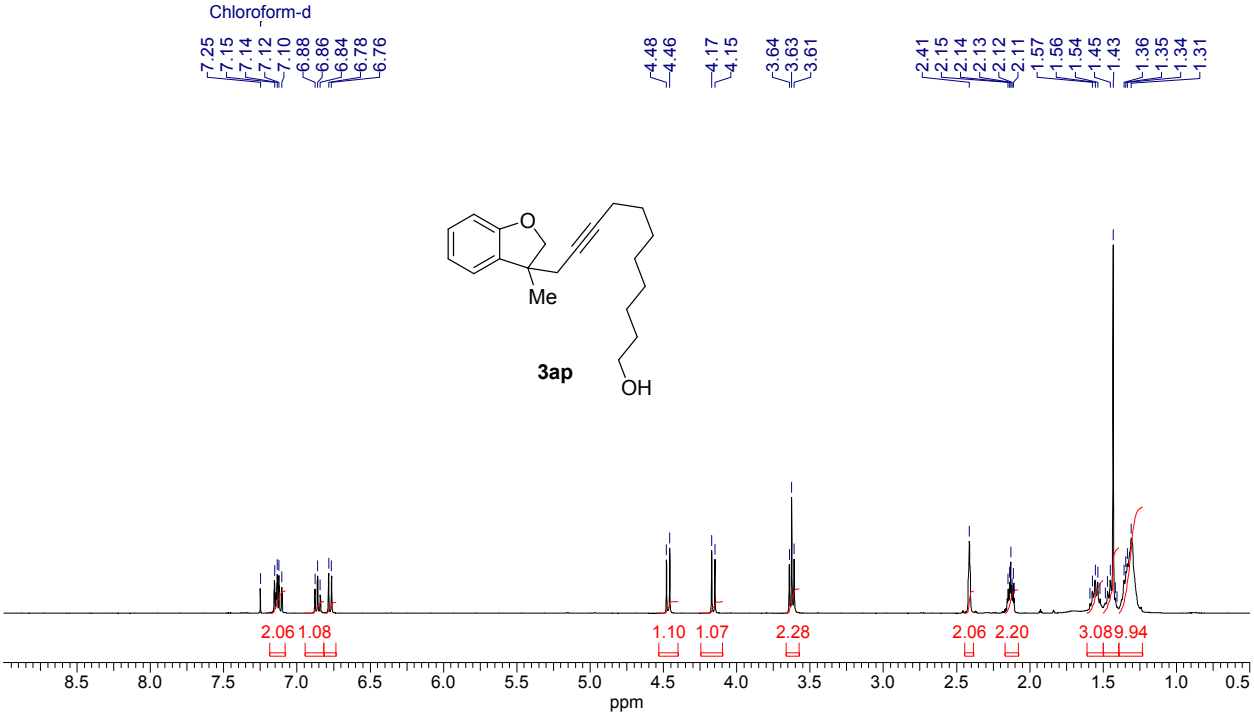
^{13}C-NMR (100 MHz) spectrum of **3ai** in $CDCl_3$



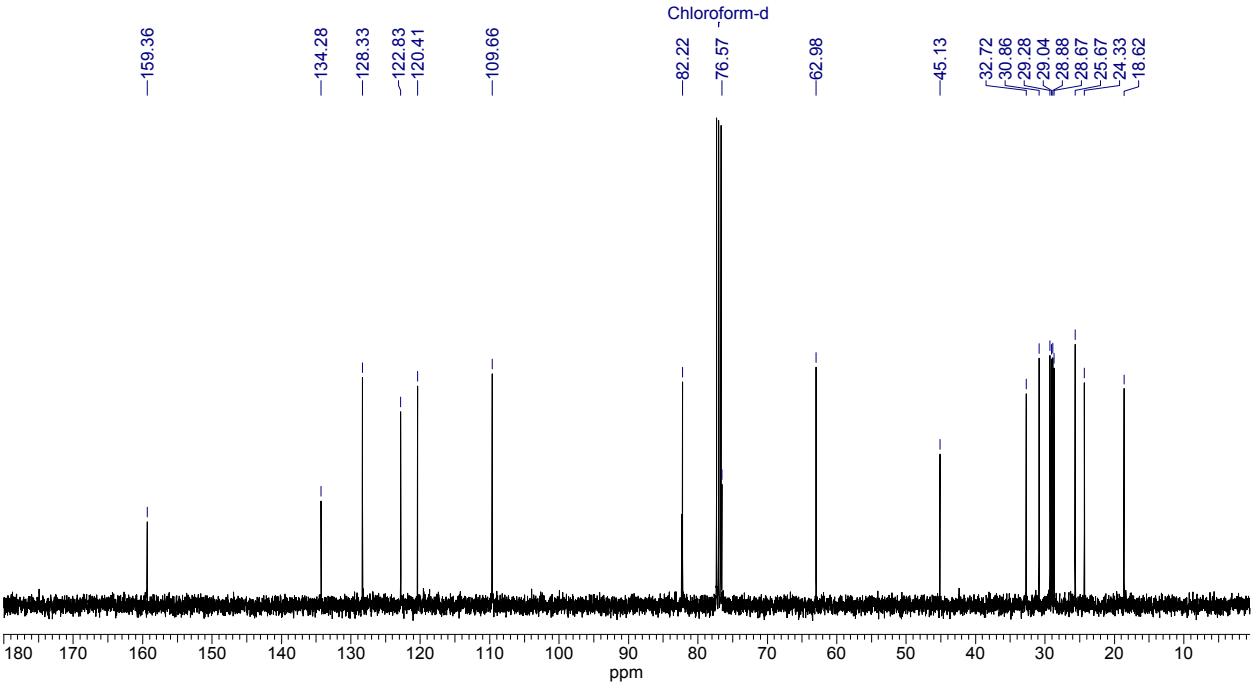
^{1}H-NMR (400 MHz) spectrum of **3aj** in $CDCl_3$



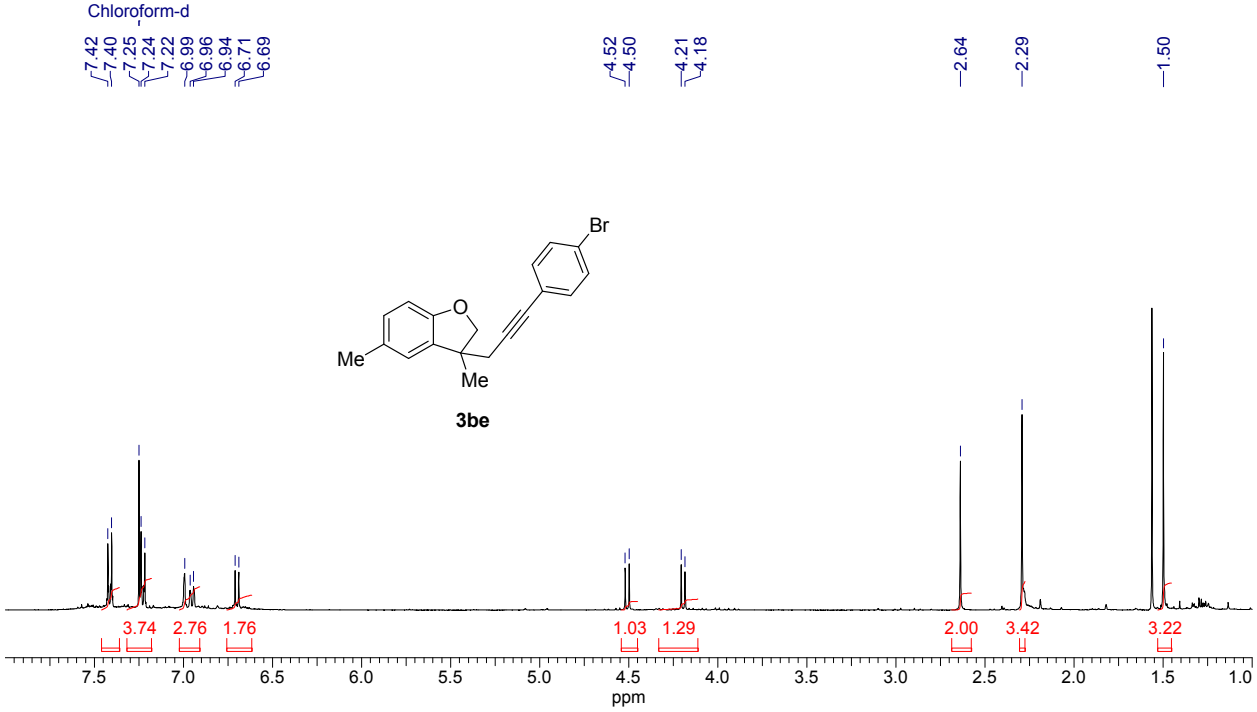
^{13}C-NMR (100 MHz) spectrum of **3aj** in $CDCl_3$



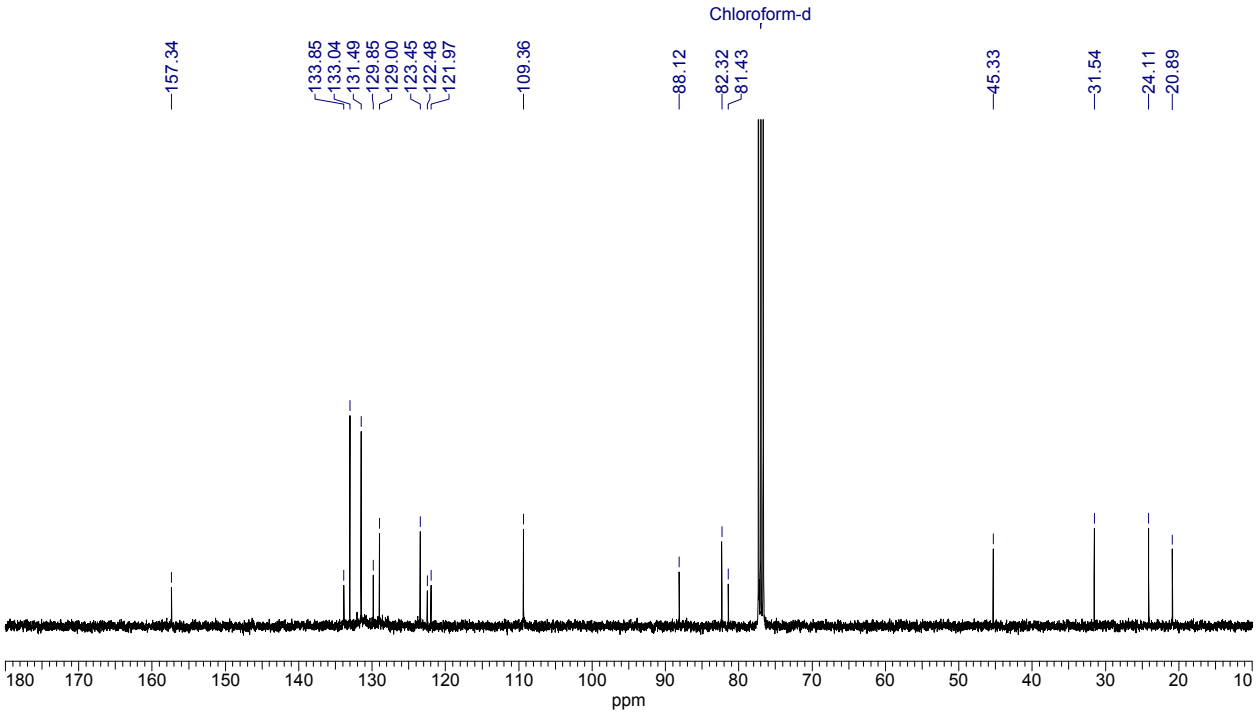
^{1}H-NMR (400 MHz) spectrum of **3ap** in $CDCl_3$



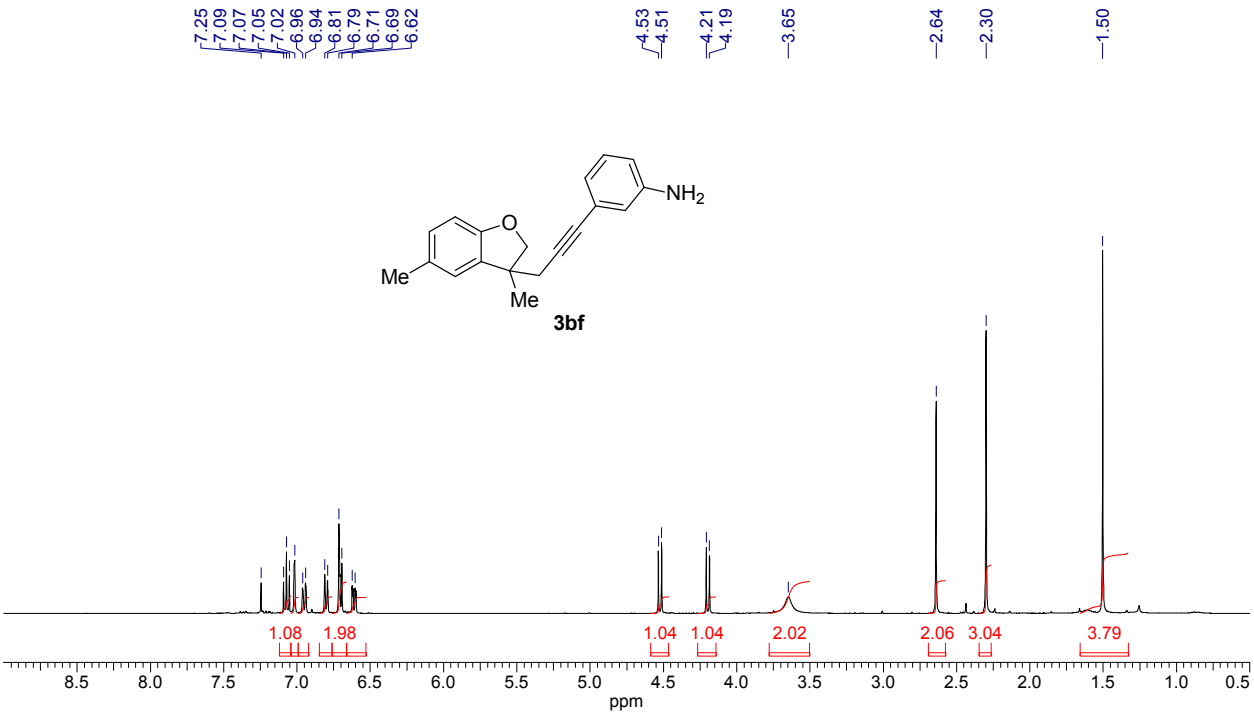
^{13}C-NMR (100 MHz) spectrum of **3ap** in $CDCl_3$



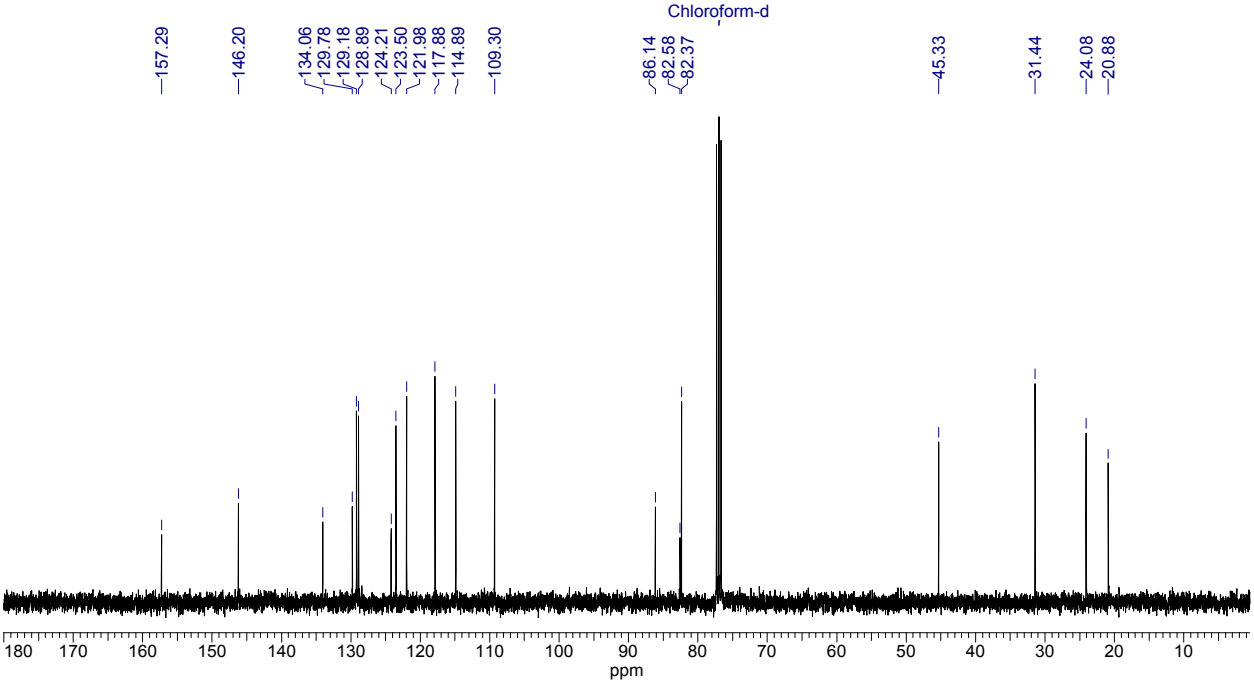
^{1}H-NMR (400 MHz) spectrum of **3be** in $CDCl_3$



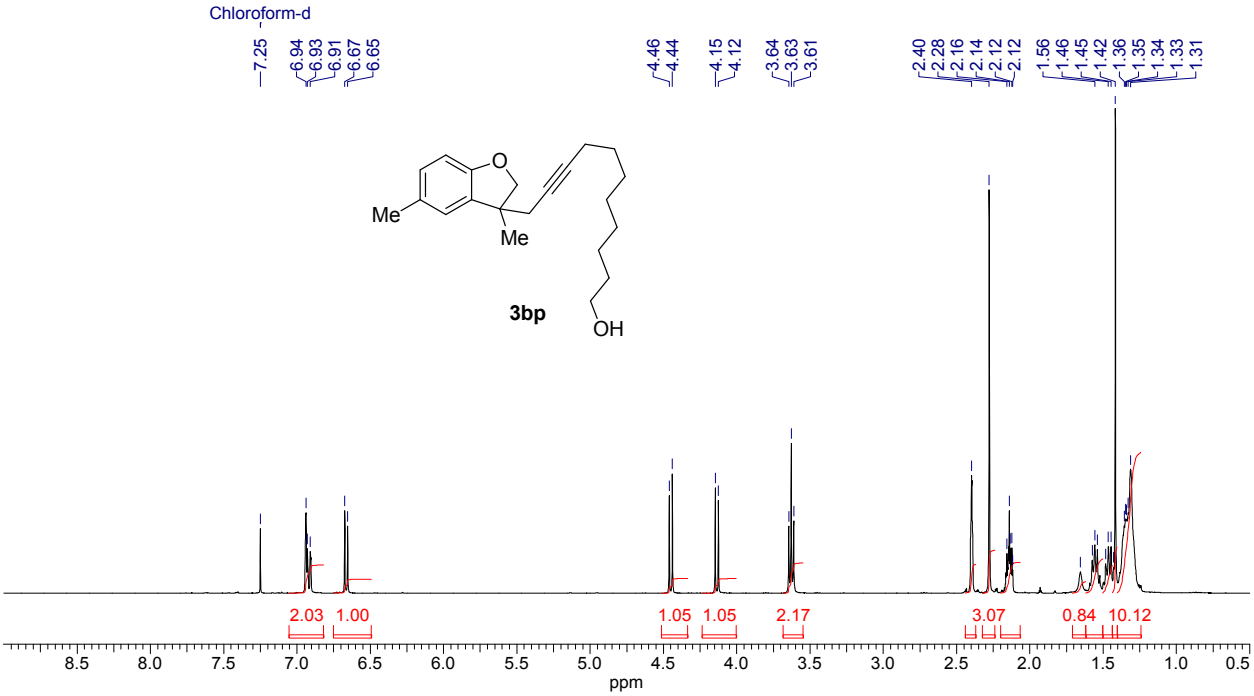
^{13}C-NMR (100 MHz) spectrum of **3be** in $CDCl_3$



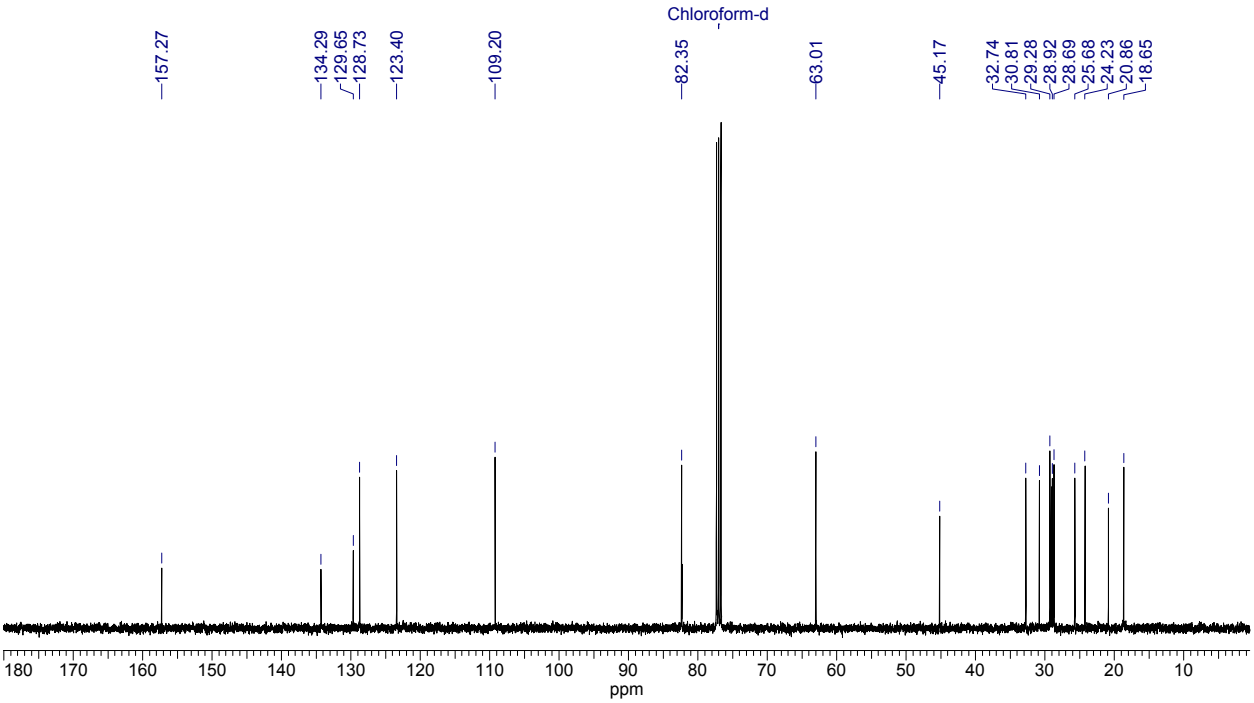
^{1}H-NMR (400 MHz) spectrum of **3bf** in $CDCl_3$



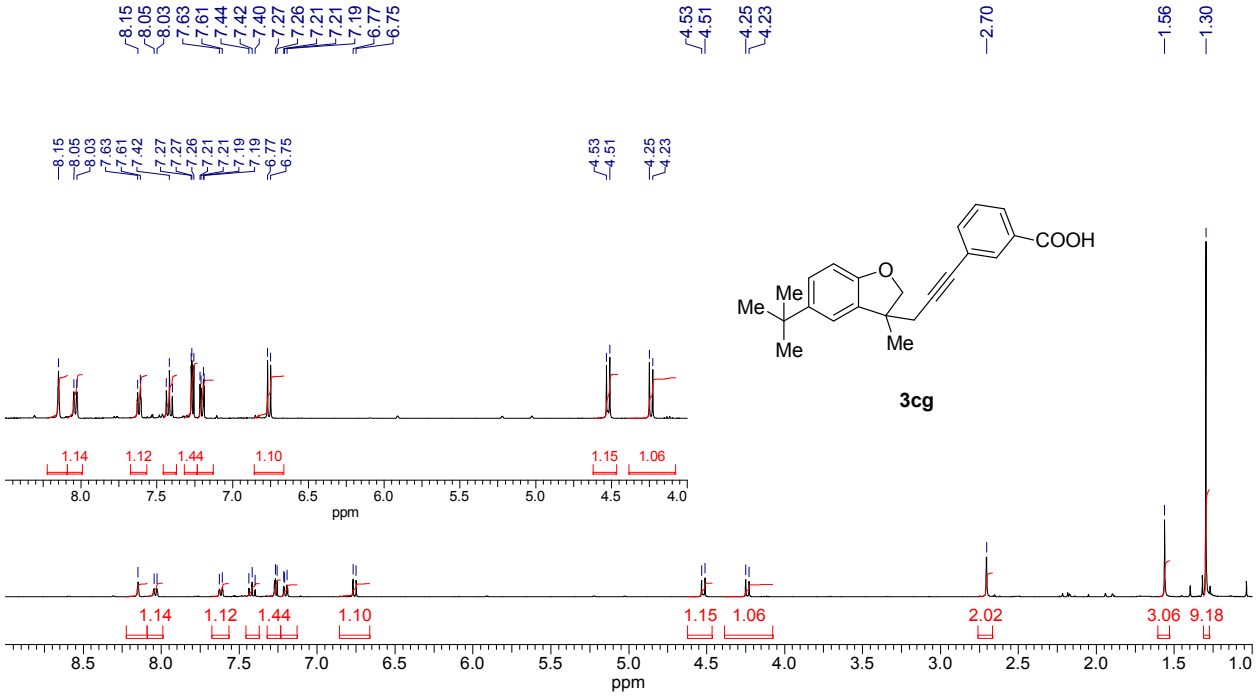
^{13}C-NMR (100 MHz) spectrum of **3bf** in $CDCl_3$



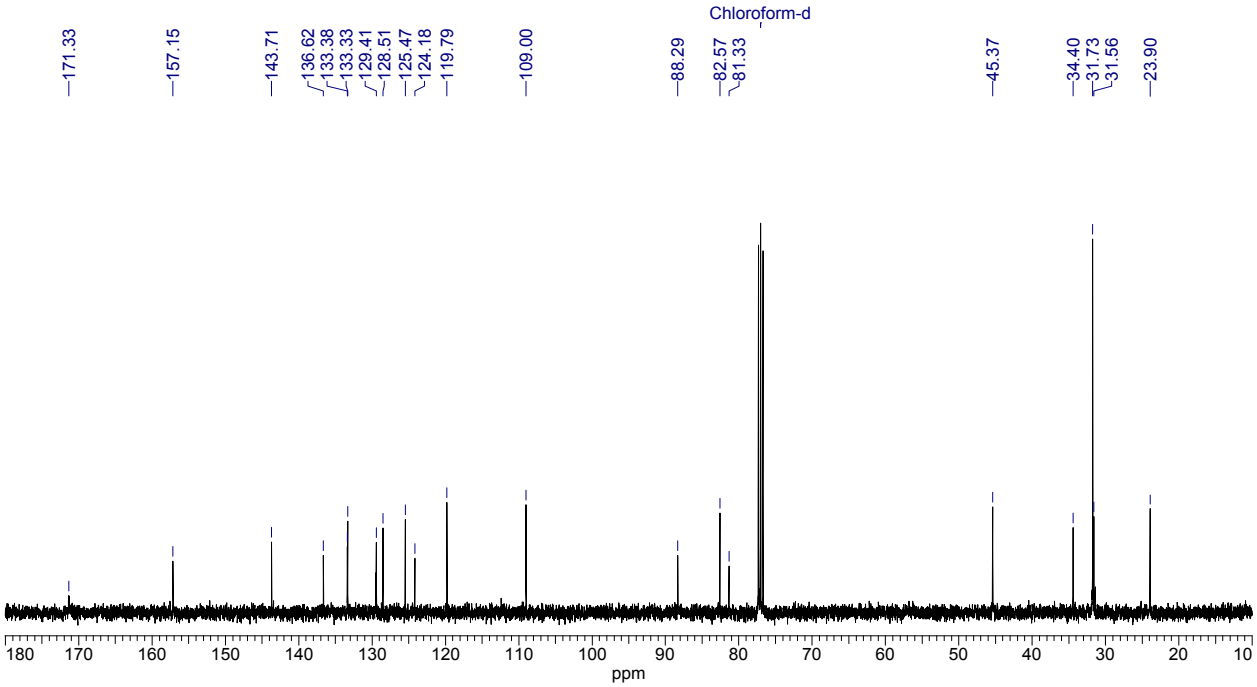
^{1}H-NMR (400 MHz) spectrum of **3bp** in $CDCl_3$



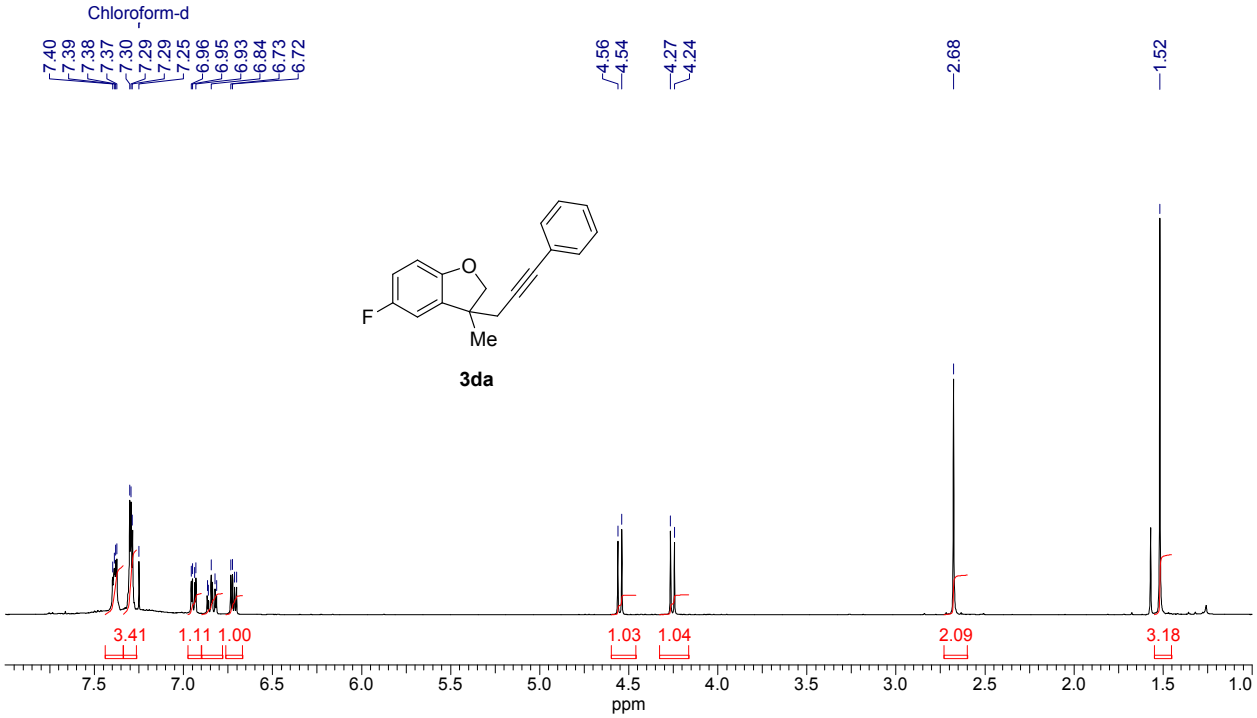
^{13}C-NMR (100 MHz) spectrum of **3bp** in $CDCl_3$



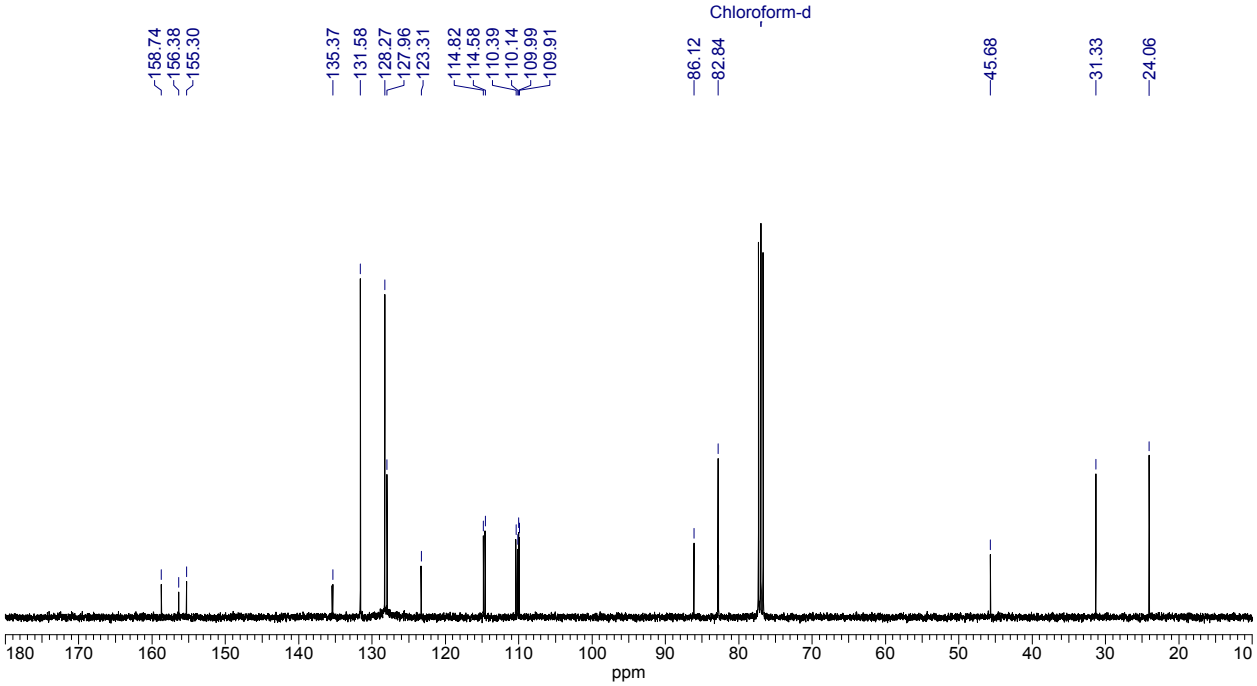
^{1}H-NMR (400 MHz) spectrum of **3cg** in $CDCl_3$



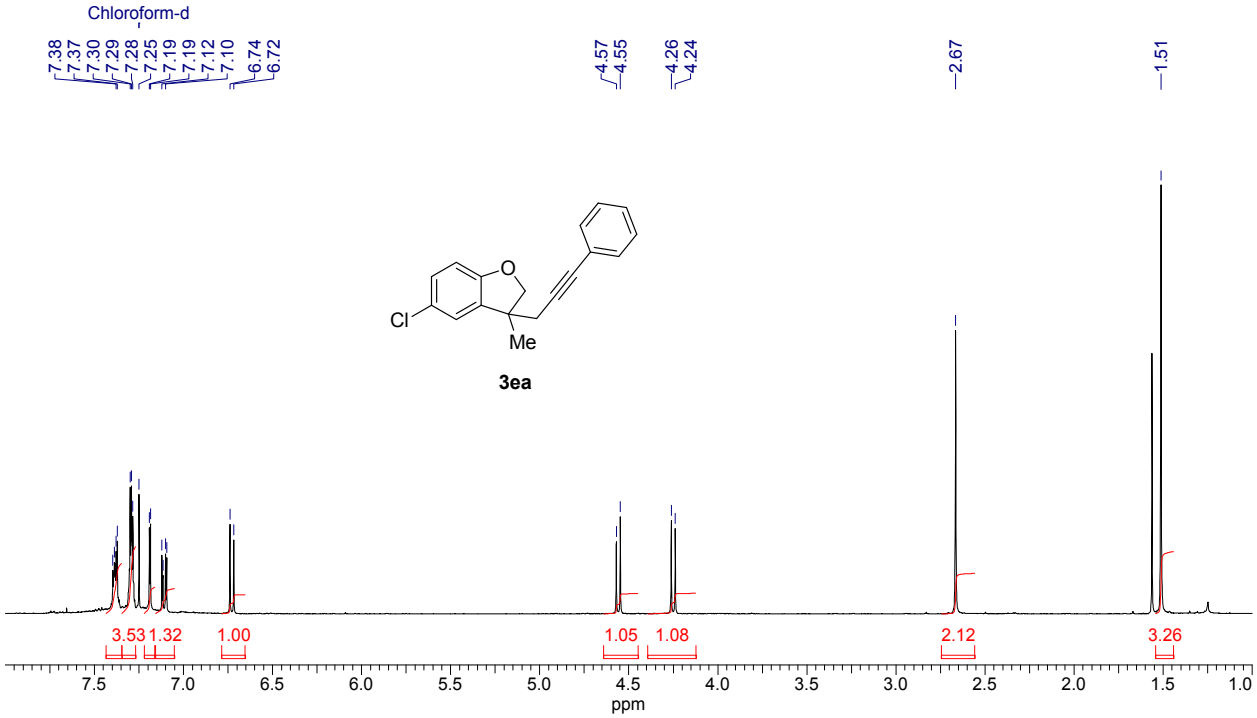
^{13}C-NMR (100 MHz) spectrum of **3cg** in $CDCl_3$



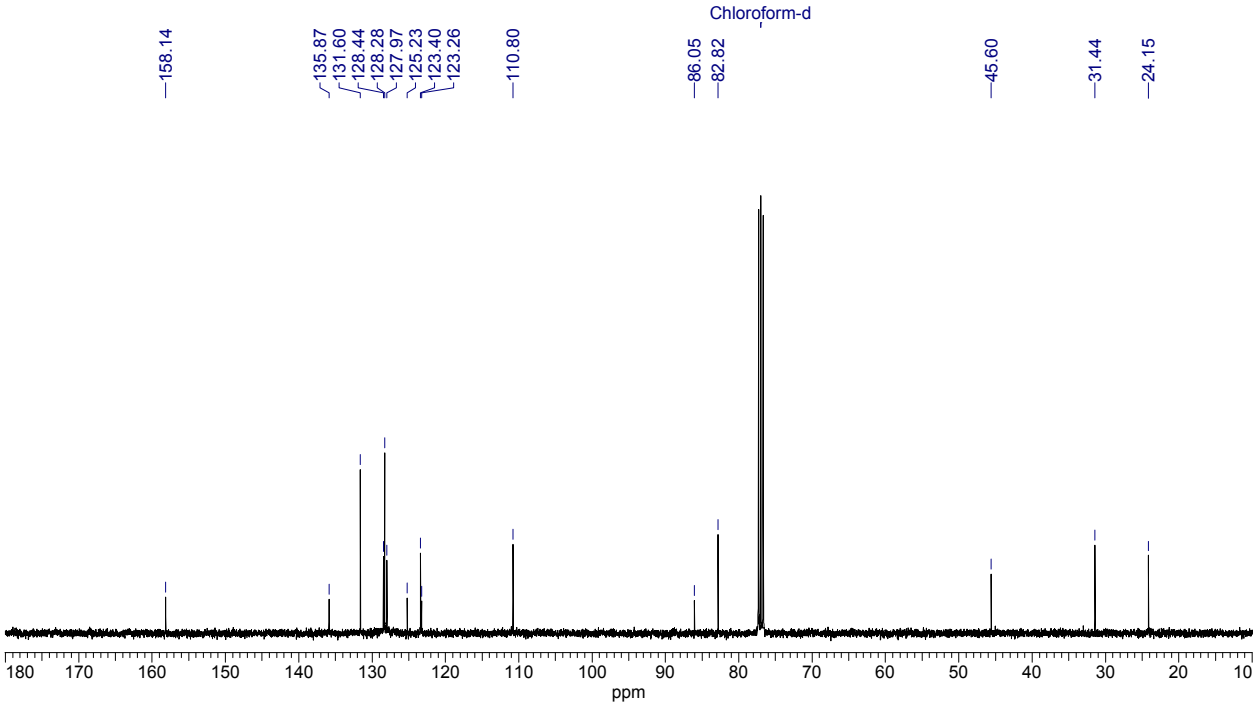
^{1}H-NMR (400 MHz) spectrum of **3da** in $CDCl_3$



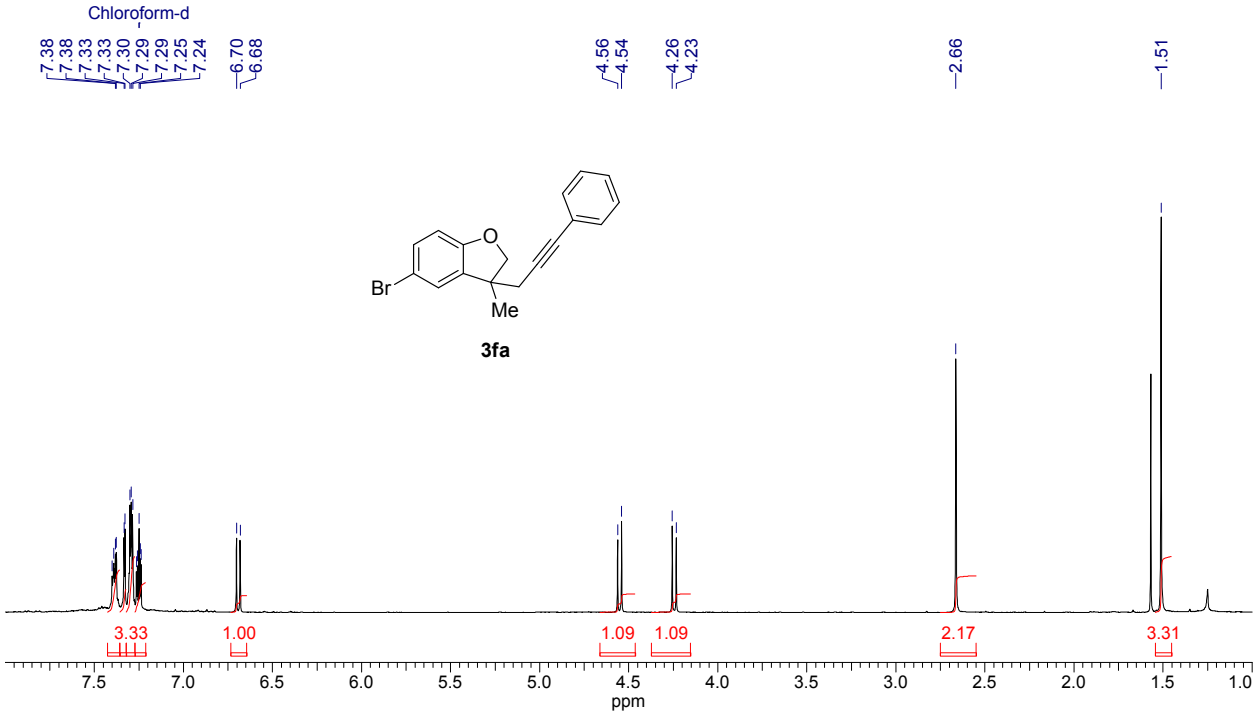
^{13}C-NMR (100 MHz) spectrum of **3da** in $CDCl_3$



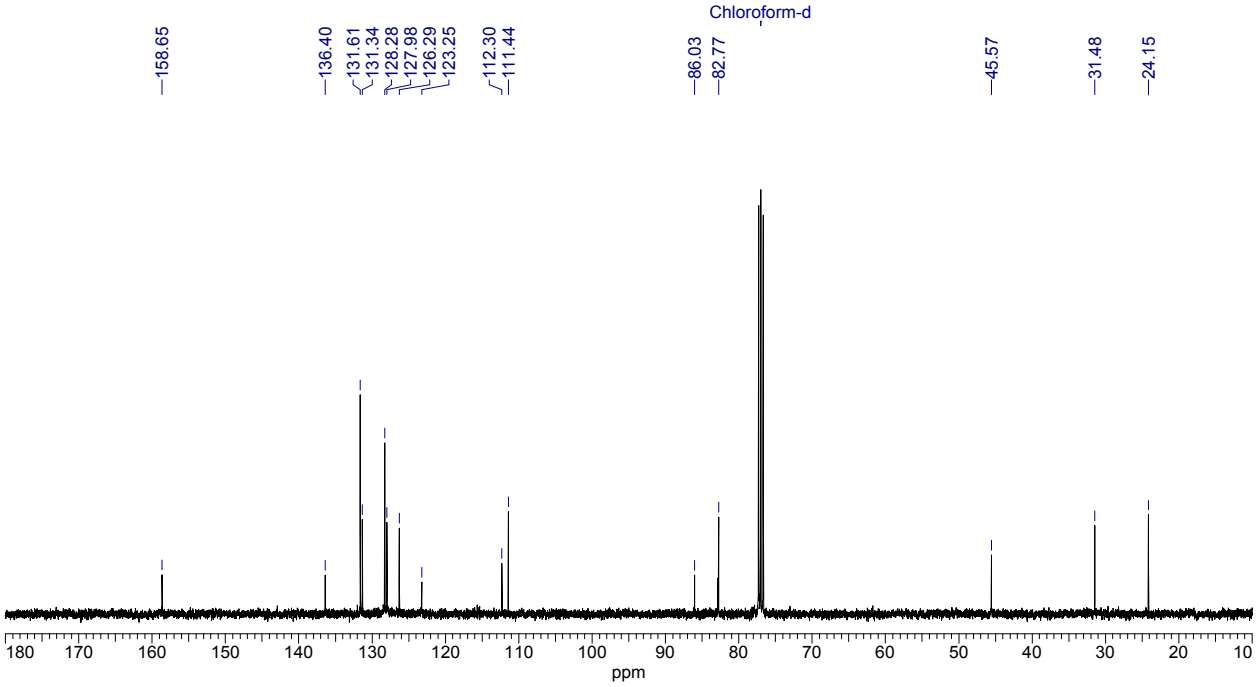
^{1}H-NMR (400 MHz) spectrum of **3ea** in $CDCl_3$



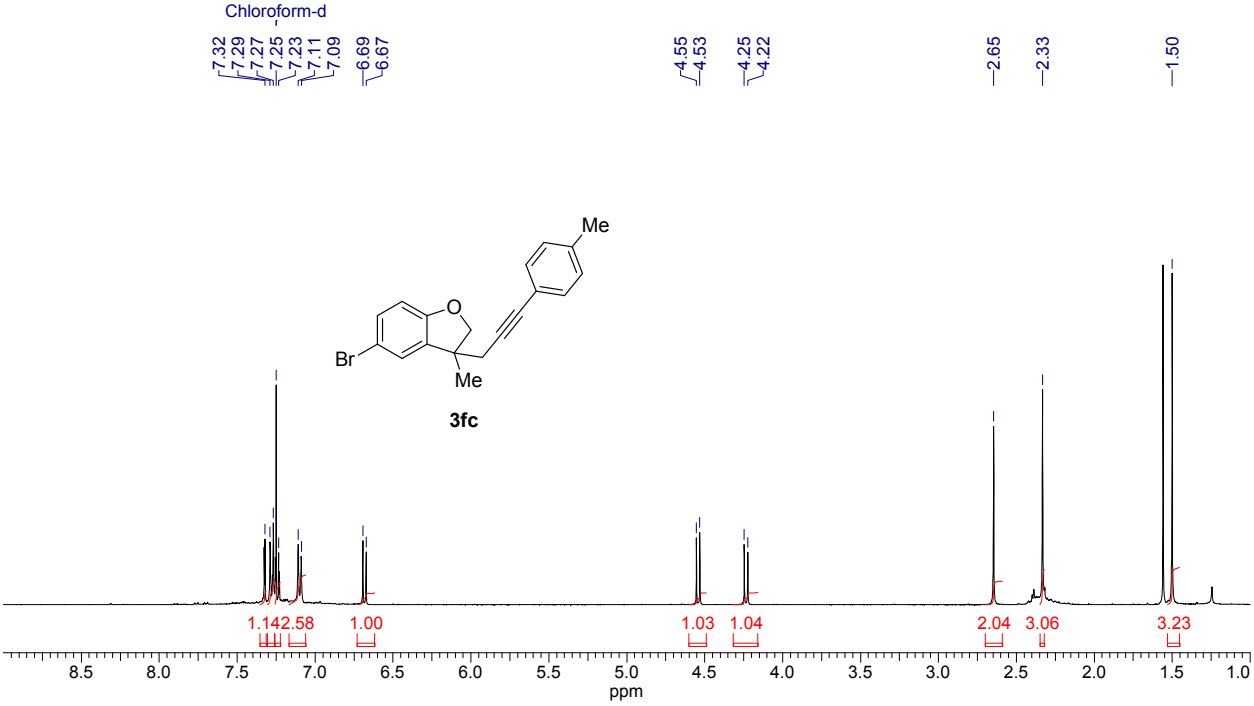
^{13}C-NMR (100 MHz) spectrum of **3ea** in $CDCl_3$



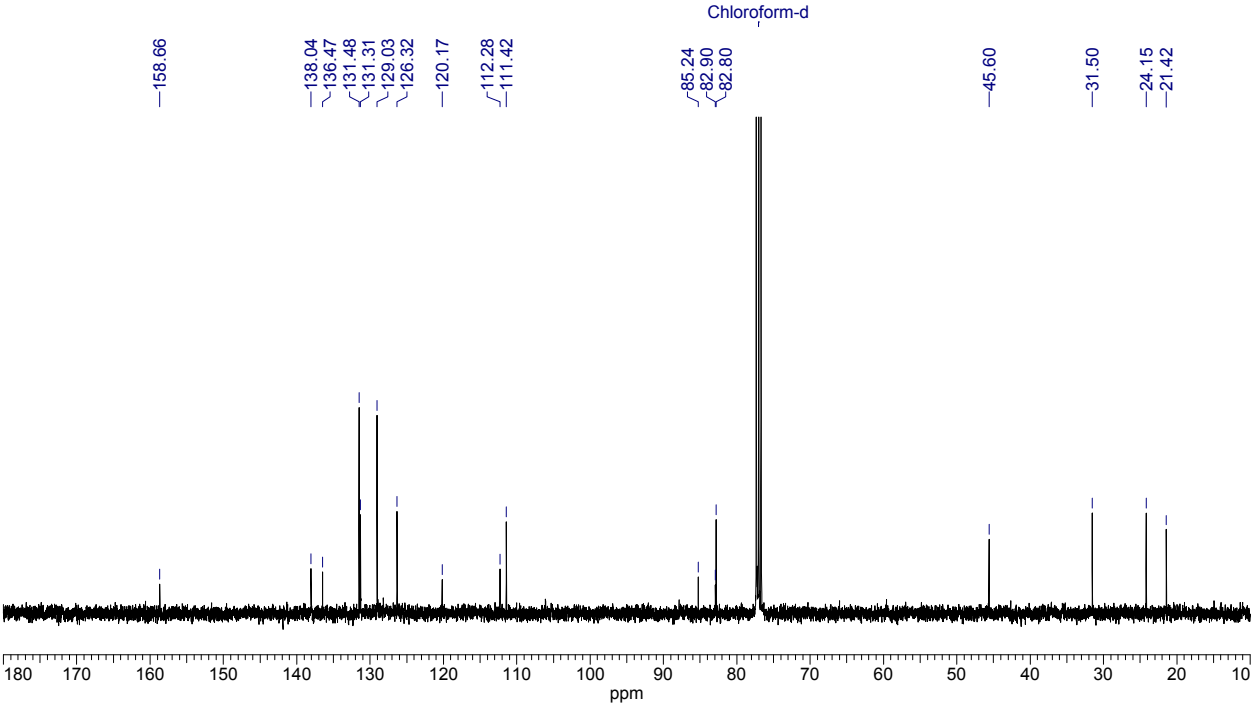
^{1}H-NMR (400 MHz) spectrum of **3fa** in $CDCl_3$



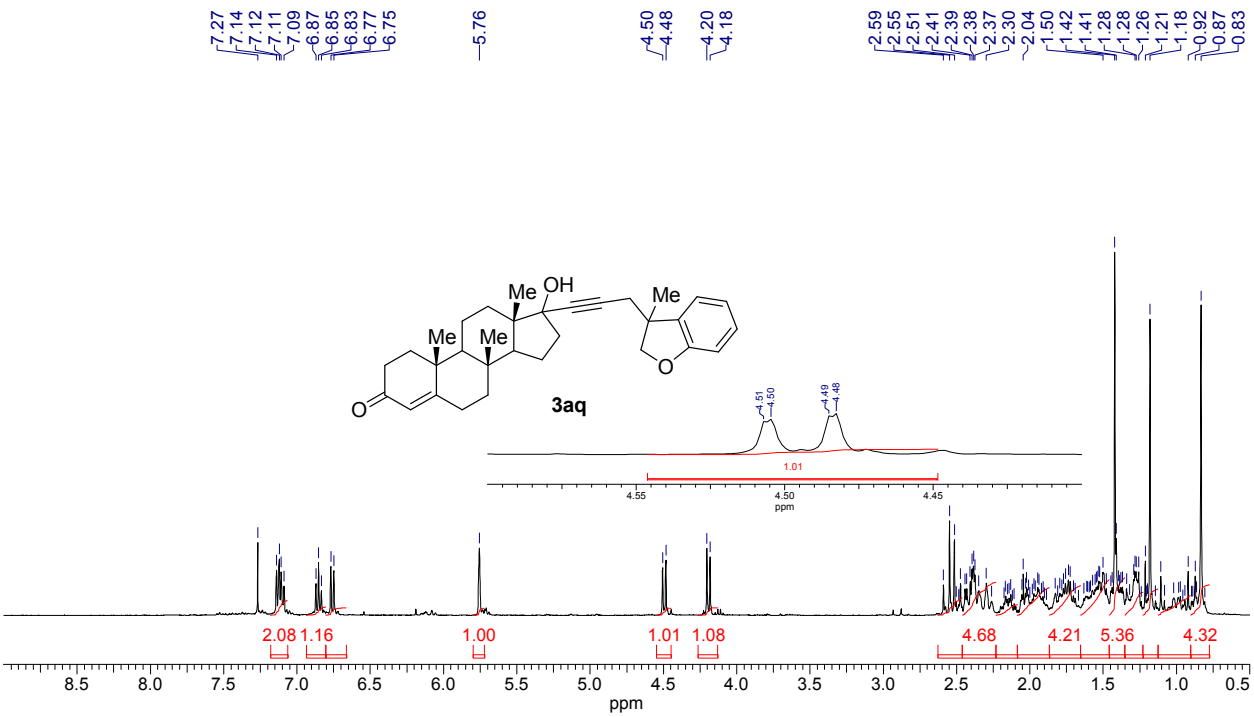
^{13}C-NMR (100 MHz) spectrum of **3fa** in $CDCl_3$



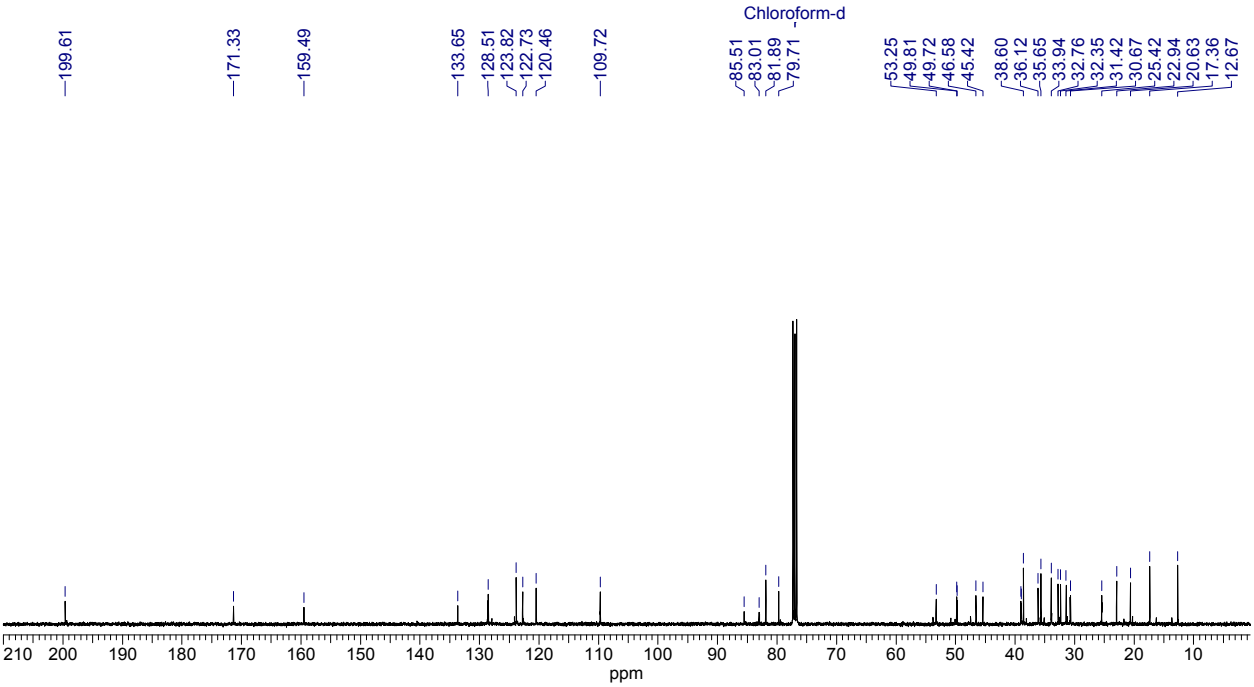
^{1}H-NMR (400 MHz) spectrum of **3fc** in $CDCl_3$



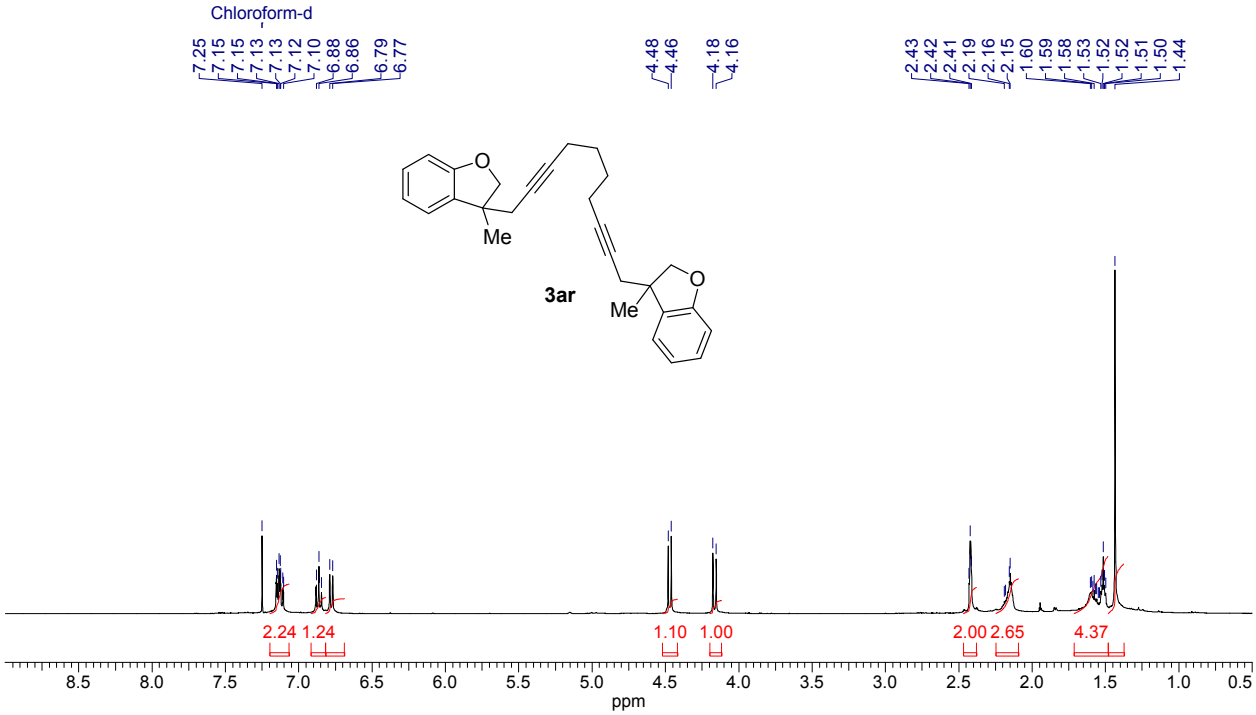
^{13}C-NMR (100 MHz) spectrum of **3fc** in $CDCl_3$



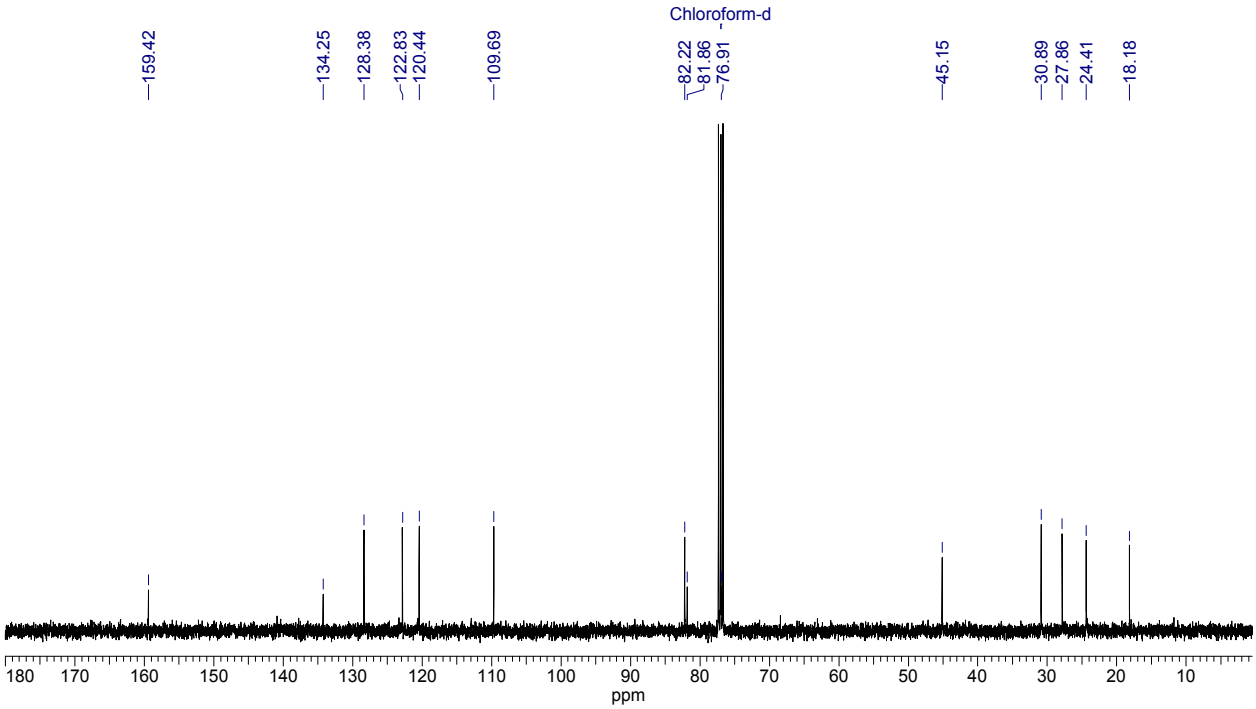
^{1}H-NMR (400 MHz) spectrum of **3aq** in $CDCl_3$



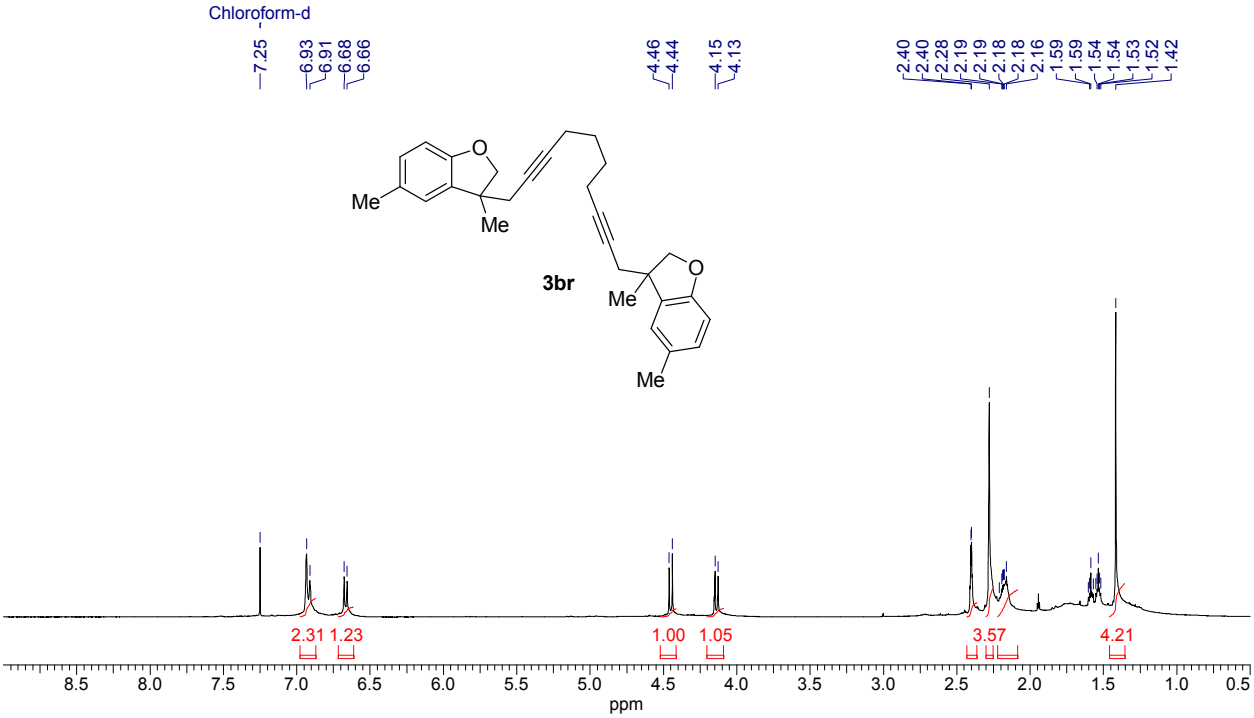
^{13}C-NMR (100 MHz) spectrum of **3aq** in $CDCl_3$



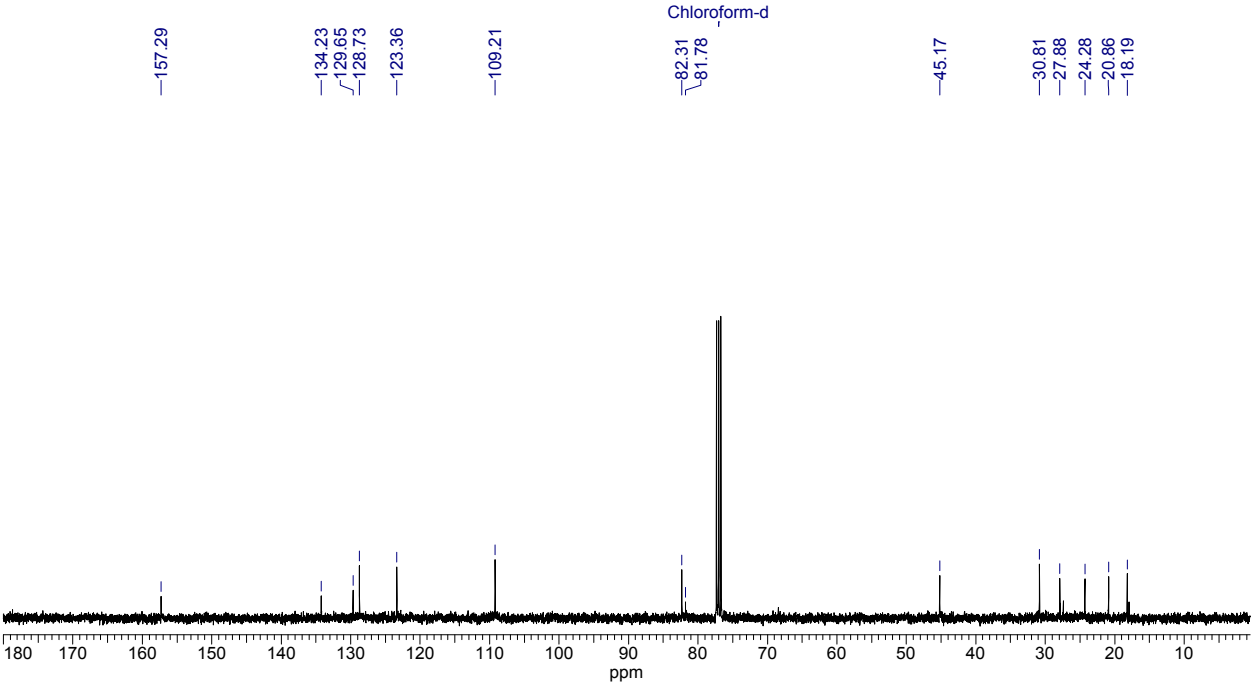
^{1}H-NMR (400 MHz) spectrum of **3ar** in $CDCl_3$



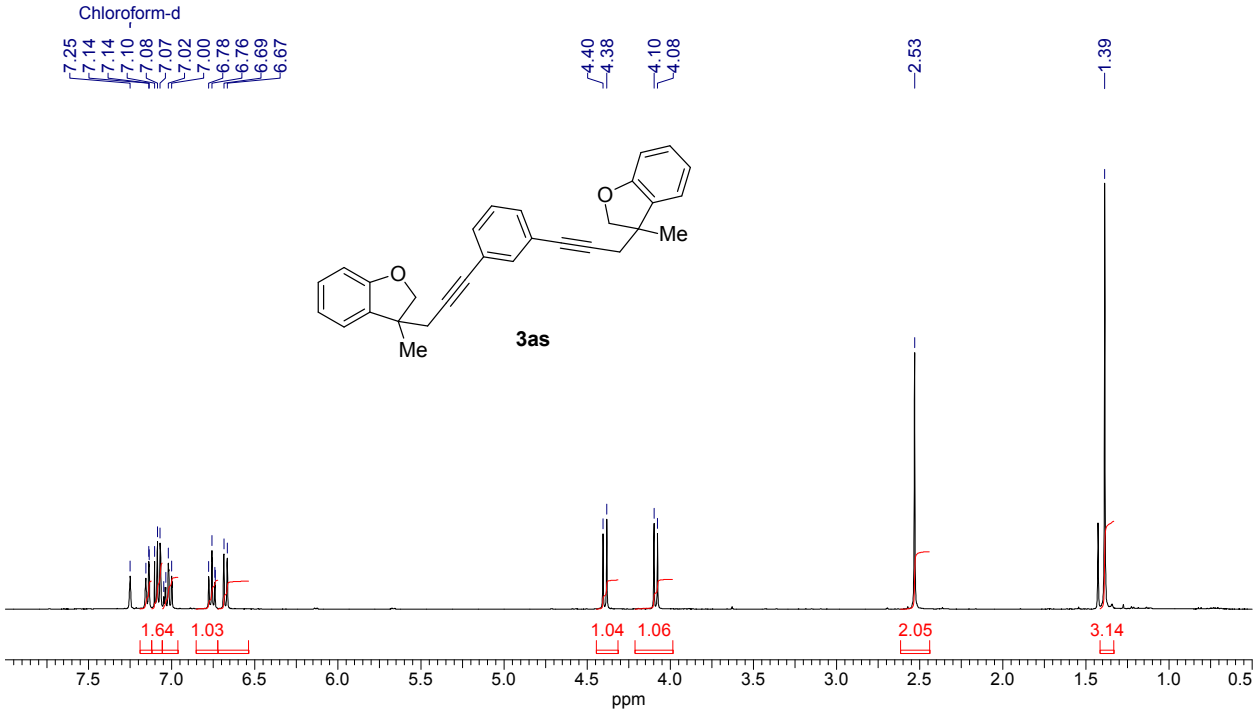
^{13}C-NMR (100 MHz) spectrum of **3ar** in $CDCl_3$



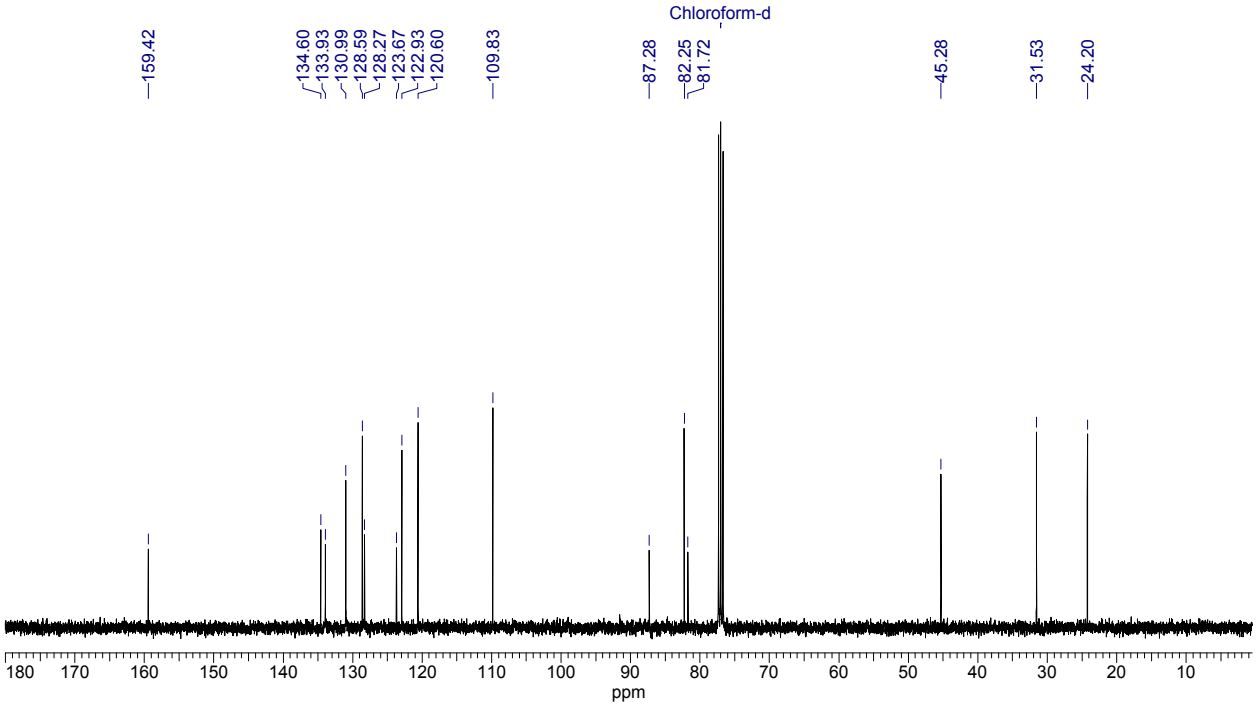
^{1}H-NMR (400 MHz) spectrum of **3br** in $CDCl_3$



^{13}C-NMR (100 MHz) spectrum of **3br** in $CDCl_3$



^{1}H-NMR (400 MHz) spectrum of **3as** in $CDCl_3$



^{13}C-NMR (100 MHz) spectrum of **3as** in $CDCl_3$