Electrochemical Synthesis of 2-Alkyl-4-phenylalkan-2-ols *via* Cathodic Reductive Coupling of Alkynes with Unactivated Aliphatic Ketones.

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Supporting Information

Experimental:

General methods:

IR spectra were recorded on a Bruker Tensor 37 (FTIR) spectrophotometer. ^{1}H NMR spectra were recorded on Bruker Advance 400 (400 MHz) and 600 (600 MHz) spectrometers at 295 K in $CDCl_3$; chemical shifts (δ ppm) and coupling constants (Hz) are reported in standard fashion concerning either internal standard tetramethylsilane (TMS) (δH = 0.00 ppm) or $CDCl_3$ (δH = 7.26 ppm). $^{13}C\{^{1}H\}$ NMR spectra were recorded on Bruker Advance 400 (100 MHz) and 600 (151 MHz) spectrometers at RT in $CDCl_3$. Chemical shifts (δ ppm) are reported relative to $CDCl_3$ [δ = 77.16 ppm (central line of the triplet)]. In the $^{13}C\{^{1}H\}$ 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, $^{13}C\{^{1}H\}$ CPD, and DEPT spectra. High-resolution mass spectra (HRMS) were recorded on an Agilent 6538 UHD Q-TOF electron spray ionization (ESI) mode and atmospheric pressure chemical ionization (APCI) modes. Melting points are recorded using Tempo and Mettler FP1 melting point apparatus in capillary tubes and are uncorrected. A single crystal of **3eg** was selected and mounted on an Oxford SuperNova, Dual, Cu at zero, Eos diffractometer. The crystal was kept at 298 K during data collection. Using Olex2, the structure was solved with the olex2.solve structure solution program using direct methods and refined with the olex2. refinement package using Gauss−Newton minimization. Electrolysis reactions were conducted using ElectraSyn 2.0 Package supply purchased from IKA Instruments. Reactions were monitored by TLC on silica gel using a combination of hexane and ethyl acetate as eluents. Solvents were distilled before use; petroleum ether the boiling range of 60−80 °C was used. Cyclic voltammetry (CV) analysis was performed on ElectraSyn 2.0 Package, using a glassy carbon electrode as working electrode, a platinum electrode as counter electrode and Ag/AgCl electrode as a reference electrode. Cyclic voltammogram was recorded at 200 mV/s scan rate. Alkynes, aliphatic ketones, DMF, DCM, TBAI were purchased from Sigma-Aldrich/Avra/BLD/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 Preparation of *tert*-Alcohols (GP): It was carried out with terminal acetylene **1** (0.98 mmol, 1 equiv), alkyl ketone **2** (3.91 mmol, 4 equiv), TBAI (0.01 M) in 8 mL DMF was added to an ElectraSyn vial (10 mL) with a magnetic stirring bar. The ElectraSyn vial cap equipped with anode (Zinc) and cathode (Graphite) were inserted into the mixture. The reaction mixture was electrolyzed at ambient temperature under a constant current of 15 mA for 9 h to 12 h. After electrolysis, the ElectraSyn vial cap was removed, electrodes were rinsed with DCM (1 mL) and the mixture was poured into aqueous NH_4Cl solution (40 mL) and extracted with DCM (3 × 10 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. Evaporation of the solvent(s) under reduced pressure and purification of the residue by silica gel column chromatography using petroleum ether/ethyl acetate as the eluent furnished the desired product *tert*-alcohol **3** (up to 92% yields).

Photographic guide for electrochemical reaction:

Left: Select New "Experiment" **Middle:** Select "Constant Current" **Right:** Select "15 mA"

Left: Reference electrode chose "No" **Middle:** Select "Time" **Right:** Select "9 hours"

Left: Select "0.98 mmol" **Middle:** Alternate the polarity Chose "No" **Right:** Select "Start the experiment"

Cyclic Voltammograms:

The cyclic voltammetry (CV) studies were carried out to further investigate the reaction mechanism, and below Figure 1S shows the cyclic voltammetry (CV) curves with 0.01 M $LiClO_4$ solution in DMF as a background. The voltammogram was obtained at a scan rate of 200 mV/s with Pt electrode as a counter electrode, Ag/AgCl as a reference electrode, and glassy carbon electrode as a working electrode. Within the scanning window (–2.2 to 0.5 V), the CV of acetone **2a** displayed reduction peak at -0.93 V *vs* Ag/AgCl (curve 1). When testing phenylacetylene **1a**, a reduction peak was seemed at -1.19 V *vs* Ag/AgCl in curve 2, signifying that the reduction of phenylacetylene required a strong reduction potential. The mixture of Phenylacetylene (**1a**) and acetone (**2a**) showed two reduction signals at -1.19 V and -0.97 V *vs* Ag/AgCl, responding to two reduction processes in electrolysis (curve 3). After adding $ZnCl_2$, the reduction peaks were appeared in the range of -0.88 V to 0.02 V (curve 4). On the basis of above results, we hypothesised that acetone may produce ketyl radicals *in-situ* by cathodic reduction and further activate alkynes in the presence of zinc salts.

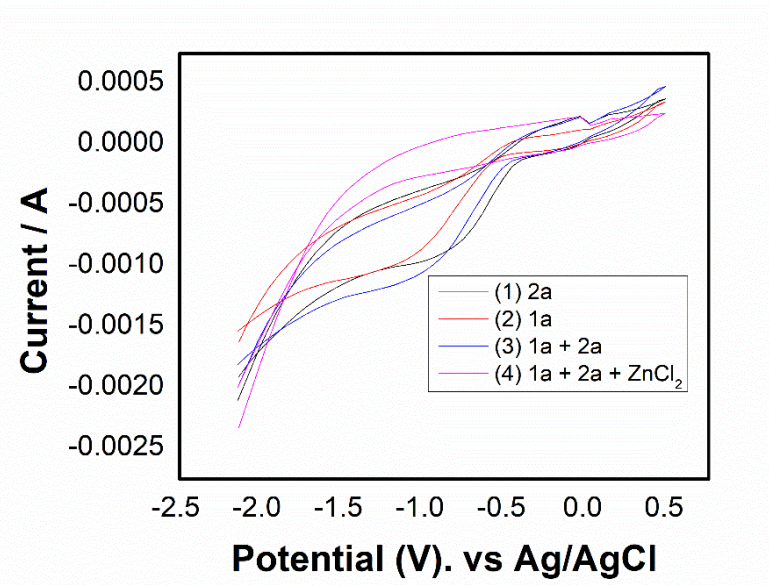
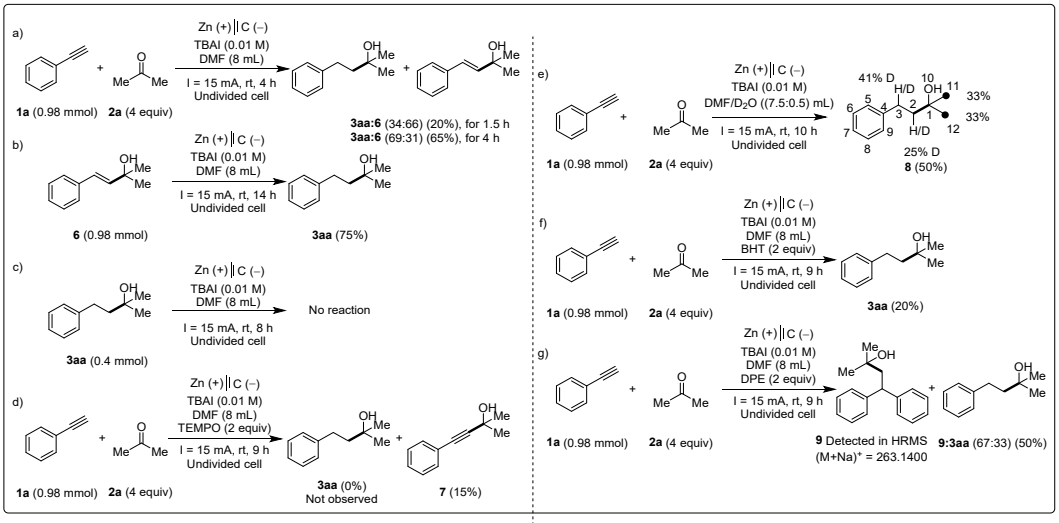


Figure S1. Cyclic voltammograms of reactants and their mixtures in 0.01 M $LiClO_4$ solution in DMF at room temperature: a) Acetone **2a** (0.04 M); b) Phenylacetylene **1a** (0.01 M); c) Phenylacetylene **1a** (0.01 M) + acetone **2a** (0.04 M); d) Phenylacetylene **1a** (0.01 M) + acetone **2a** (0.04 M) + $ZnCl_2$ (0.01M). The voltammogram was obtained at a scan rate of 200 mV/s with Pt electrode as a counter electrode, Ag/AgCl as a reference electrode, and glassy carbon electrode as a working electrode.

Scheme S1: Control experiments.

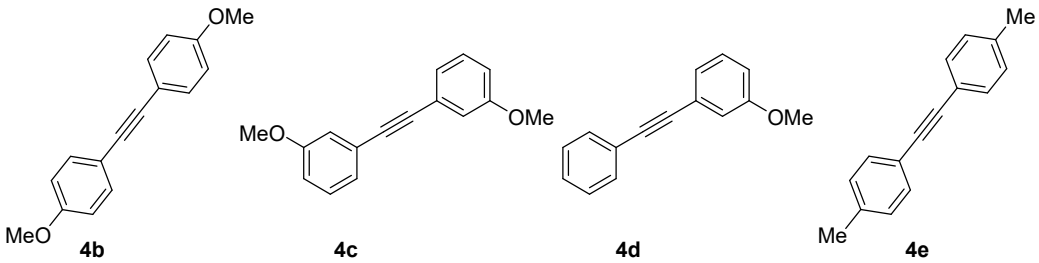


Reaction conditions: a) The reaction was carried out with phenylacetylene **1a** (100 mg, 0.98 mmol), acetone **2a** (227.5 mg, 3.91 mmol), and TBAI (29 mg, 0.01 M), in DMF (8 mL) for 1.5 h and 4 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished the mixture of product **6** & **3aa** in 20% and 65% respectively, as a yellow liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection]. b) The reaction was carried out with (*E*)-2-methyl-4-phenylbut-3-en-2-ol **6** (159 mg, 0.98 mmol), TBAI (29 mg, 0.01 M) in DMF (8

mL) for 14 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished the product **3aa** (120 mg, 75%), as an orange liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection]. c) The reaction was carried out with 2-methyl-4-phenylbutan-2-ol **3aa** (40 mg, 0.4 mmol) TBAI (29 mg, 0.01 M) in DMF (8 mL) for 8 h. d) The reaction was carried out with phenylacetylene **1a** (100 mg, 0.98 mmol), acetone **2a** (227.47 mg, 3.91 mmol), TBAI (29 mg, 0.01 M), and TEMPO (2 equiv., 306 mg) in DMF (8 mL) for 9 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished the product 2-methyl-4-phenylbut-3-yn-2-ol **7** (23 mg, 15%) as a yellow liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection]. e) The reaction was carried out with phenylacetylene **1a** (100 mg, 0.98 mmol), acetone **2a** (227.5 mg, 3.91 mmol), and TBAI (29 mg, 0.01 M), in DMF/D_2O (7.5/0.5 mL) for 10 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished product **8** (82.3 mg, 50%) as a yellow liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection]. The deuteration percentage is confirmed by ^{1}H NMR. f) The reaction was carried out with phenylacetylene **1a** (100 mg, 0.98 mmol), acetone **2a** (227.5 mg, 3.91 mmol), and TBAI (29 mg, 0.01 M), and BHT (2 equiv., 432 mg) in DMF (8 mL) for 9 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished the product **3aa** (32 mg, 20%) as a yellow liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection]. g) The reaction was carried out with phenylacetylene **1a** (100 mg, 0.98 mmol), acetone **2a** (227.5 mg, 3.91 mmol), and TBAI (29 mg, 0.01 M), and DPE (2 equiv., 353 mg) in DMF (8 mL) for 9 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished the product **9:3aa** (67:33) in 50% yield as a yellow liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection].

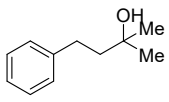
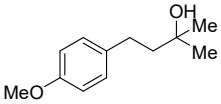
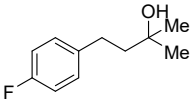
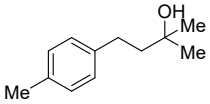
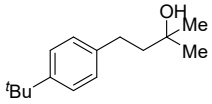
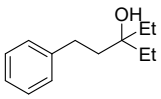
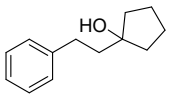
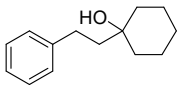
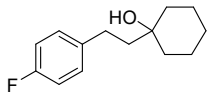
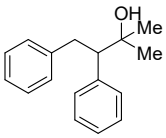
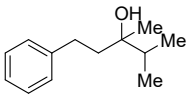
The substituted diphenylacetylenes **4b-4e** are prepared from previous literature reports as shown in the Table-1S.[1,2]

Table-1S. Previously reported diphenylacetylenes **4**.

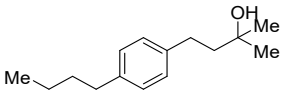


The following Products **3aa**, **3ca**, **3da**, **3ga**, **3ac**, **3af**, **3ag**, and **3dg** are known in the literature as shown in Table-2S.[3–7]

Table-2S. The reported compounds of *tert*-alcohols **3**.

 **3aa** (85%)	 **3ca** (70%)	 **3da** (80%)	 **3fa** (83%)
 **3ga** (70%)	 **3ac** (80%)	 **3af** (75%)	 **3ag** (75%)
 **3dg** (76%)	 **3pa** (25%)	 **3ad** (60%)	

Characterization of compounds:

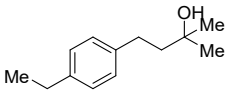


4-(4-Butylphenyl)-2-methylbutan-2-ol (3ba):

GP was carried out with 1-butyl-4-ethynylbenzene **1b** (155.0 mg, 0.98 mmol), acetone **2a** (227.1 mg, 3.91 mmol), and TBAI (29 mg, 0.01 M) in DMF (8 mL) for 9 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished the product **3ba** (177.0 mg, 82%), as a yellow liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection].

The gram scale synthesis of 3ba: It was carried out with 4-butyl phenylacetylene (3.16 mmol, 0.5 g), acetone (12.64 mmol, 4 equiv., 0.74 g), TBAI (0.01 M) in 10 mL DMF for 36 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished the product **3ba** (0.56 g, 80%), as a yellow liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection].

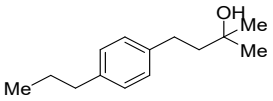
IR: (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3372, 2927, 2862, 1459, 1372, 1204, 1144, 919, 822 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.13 (s, 4H), 2.71 – 2.66 (m, 2H), 2.63 – 2.58 (t, 2H , *J* = 8 Hz), 1.82 – 1.78 (m, 2H), 1.64 (m, 3H), 1.42 (m, 2H), 1.30 (s, 6H), 0.95 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C{H} NMR** (151 MHz, $CDCl_3$) δ = 140.4, 139.7, 128.5 (2 × Ar–CH), 128.2 (2 × Ar–CH), 71.0, 45.9, 35.3, 33.8, 30.4, 29.4 (2 × CH_3), 22.5, 14.1 ppm. **HRMS:** *m/z* calcd for $C_{15}H_{24}KO^+$ $[M+K]^+$: 259.1459, found: 259.1458.



4-(4-Ethylphenyl)-2-methylbutan-2-ol (3ea)

GP was carried out with 1-ethyl-4-ethynylbenzene **1e** (127.6 mg, 0.98 mmol), acetone **2a** (227.1 mg, 3.91 mmol), and TBAI (29 mg, 0.01 M) in DMF (8 mL) for 9 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished the product **3ea** (173.4 mg, 92%) as an orange liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection].

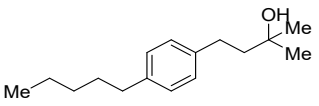
IR: (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3374, 2964, 1513, 1457, 1371, 1204, 1143, 917, 823 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.14 (s, 4H), 2.72 – 2.66 (m, 2H), 2.63 (t, *J* = 7.6 Hz, 2H), 1.84 – 1.75 (m, 2H), 1.53 (s, 1H), 1.30 (s, 6H), 1.24 (t, *J* = 7.6 Hz, 3H) ppm. **^{13}C{H} NMR** (151 MHz, $CDCl_3$) δ = 141.7, 139.8, 128.3 (2 × Ar–CH), 128.0 (2 × Ar–CH), 71.1, 45.9, 30.4, 29.4 (2 × CH_3), 28.5, 15.8 ppm. **HRMS (ESI):** *m/z* calcd for $C_{13}H_{24}NO^+$ $[M+NH_4]^+$: 210.1852, found: 210.1857.



2-Methyl-4-(4-propylphenyl)butan-2-ol (3ha)

GP was carried out with 1-ethynyl-4-propylbenzene **1h** (141.3 mg, 0.98 mmol), acetone **2a** (227.1 mg, 3.91 mmol), and TBAI (29 mg, 0.01 M) in DMF (8 mL) for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished the product **3ha** (161.7 mg, 80%) as a pale-yellow liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection].

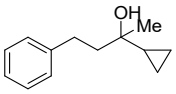
IR: (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3373, 2960, 2929, 1513, 1459, 1373, 1205, 1145, 919, 809 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.18 – 7.05 (m, 4H), 2.73 – 2.63 (m, 2H), 2.58 – 2.53 (m, 2H), 1.83 – 1.75 (m, 2H), 1.68 – 1.58 (m, 2H), 1.29 (s, 6H), 1.26 (s, 1H), 0.94 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C{H} NMR** (151 MHz, $CDCl_3$) δ = 140.2, 139.8, 128.6 (2 × Ar–CH), 128.3 (2 × Ar–CH), 71.1, 45.9, 37.8, 30.4, 29.4 (2 × CH_3), 24.7, 14.1 ppm. **HRMS:** *m/z* calcd for $C_{14}H_{22}KO^+$ $[M+K]^+$: 245.1302, found: 245.1300.



2-Methyl-4-(4-pentylphenyl)butan-2-ol (3ia)

GP was carried out with 1-ethynyl-4-pentylbenzene **1i** (168.8 mg, 0.98 mmol), acetone **2a** (227.1 mg, 3.91 mmol), and TBAI (29 mg, 0.01 M) in DMF (8 mL) for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished the product **3ia** (172.3 mg, 75%) as a light-yellow liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection].

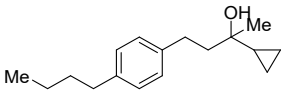
IR: (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3372, 2926, 2860, 1513, 1458, 1372, 1205, 1141, 918, 824, 758 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.18 – 7.06 (m, 4H), 2.74 – 2.64 (m, 2H), 2.58 (t, *J* = 8Hz, 2H), 1.84 – 1.76 (m, 2H), 1.67 – 1.55 (m, 3H), 1.39 – 1.32 (m, 4H), 1.30 (s, 6H), 0.91 (t, *J* = 6.9 Hz, 3H) ppm. **^{13}C{H} NMR** (151 MHz, $CDCl_3$) δ = 140.4, 139.7, 128.5 (2 × Ar–CH), 128.3 (2 × Ar–CH), 71.1, 45.9, 35.6, 31.7, 31.4, 30.4, 29.4 (2 × CH_3), 22.7, 14.1 ppm. **HRMS:** *m/z* calcd for $C_{16}H_{30}NO^+$ $[M+NH_4]^+$: 252.2322 , found: 252.2325.



2-Cyclopropyl-4-phenylbutan-2-ol (3ab)

GP was carried out with phenylacetylene **1a** (100 mg, 0.98 mmol), 1-cyclopropylethan-1-one **2b** (329.4 mg, 3.91 mmol), and TBAI (29 mg, 0.01 M) in DMF (8 mL) for 9 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished the product **3ab** (149.0 mg, 80%) as a light-yellow liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection].

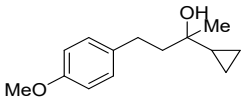
IR: (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3444, 2932, 1453, 1374, 1029, 917, 866, 748, 700 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.32 – 7.24 (m, 2H), 7.23 – 7.14 (m, 3H), 2.76 (td, *J* = 7.4, 3.5 Hz, 2H), 1.90 – 1.76 (m, 2H), 1.21 (s, 1H), 1.16 (s, 3H), 0.95 (tt, *J* = 8.3, 5.7 Hz, 1H), 0.46 – 0.26 (m, 4H) ppm. **^{13}C{H} NMR** (151 MHz, $CDCl_3$) δ = 142.8, 128.5 (2 × Ar–CH), 128.4 (2 × Ar–CH), 125.7, 71.1, 45.1, 30.5, 25.9, 21.2, 0.7, 0.6 ppm. **HRMS (ESI):** *m/z* calcd for $C_{13}H_{22}NO^+$ $[M+NH_4]^+$: 208.1696, found: 208.1701.



4-(4-Butylphenyl)-2-cyclopropylbutan-2-ol (3bb)

GP was carried out with 1-butyl-4-ethynylbenzene **1b** (155.1 mg, 0.98 mmol), 1-cyclopropylethan-1-one **2b** (329.4 mg, 3.91 mmol), and TBAI (29 mg, 0.01 M) in DMF (8 mL) for 9 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished the product **3bb** (193.2 mg, 80%) as a yellow liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection].

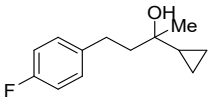
IR: (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3449, 2928, 2861, 1456, 1373, 1104, 1026, 923, 822 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.18 – 7.06 (m, 4H), 2.74 (td, *J* = 7.3, 2.8 Hz, 2H), 2.58 (t, *J* = 8 Hz, 2H), 1.90 – 1.78 (m, 2H), 1.67 – 1.53 (m, 3H), 1.40 – 1.31 (m, 2H), 1.18 (s, 3H), 1.07 (s, 1H), 1.02 – 0.95 (m, 1H), 0.93 (t, *J* = 7.3 Hz, 3H), 0.47 – 0.25 (m, 4H) ppm. **^{13}C{H} NMR** (151 MHz, $CDCl_3$) δ = 140.4, 139.9, 128.5 (2 × Ar–CH), 128.3 (2 × Ar–CH), 71.2, 45.2, 35.3, 33.9, 30.1, 26.0, 22.5, 21.2, 14.1, 0.8, 0.6 ppm. **HRMS (ESI):** *m/z* calcd for $C_{17}H_{30}NO^+$ $[M+NH_4]^+$: 264.2322, found: 264.2329.



2-Cyclopropyl-4-(4-methoxyphenyl)butan-2-ol (3cb)

GP1 was carried out with 1-ethynyl-4-methoxybenzene **1c** (129.5 mg, 0.98 mmol), 1-cyclopropylethan-1-one **2b** (329.4 mg, 3.91 mmol), and TBAI (29 mg, 0.01 M) in DMF (8 mL) for 9 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished the product **3cb** (161.9 mg, 75%) as a light-yellow liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection].

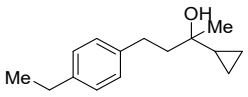
IR: (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3426, 2944, 1511, 1457, 1245, 1176, 1035, 924, 824 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.13 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 2.78 – 2.63 (m, 2H), 1.86 – 1.76 (m, 2H), 1.26 (s, 1H), 1.17 (s, 3H), 1.04 – 0.89 (m, 1H), 0.48 – 0.26 (m, 4H) ppm. **^{13}C{H} NMR** (151 MHz, $CDCl_3$) δ = 157.8, 134.9, 129.3 (2 × Ar–CH), 113.9 (2 × Ar–CH), 71.2, 55.4, 45.4, 29.6, 26.0, 21.2, 0.8, 0.6 ppm. **HRMS (ESI):** *m/z* calcd for $C_{14}H_{24}NO_2^+$ $[M+NH_4]^+$: 238.1802, found: 238.1805.



2-Cyclopropyl-4-(4-fluorophenyl)butan-2-ol (3db)

GP was carried out with 1-ethynyl-4-fluorobenzene **1d** (117.7 mg, 0.98 mmol), 1-cyclopropylethan-1-one **2b** (329.4 mg, 3.91 mmol), and TBAI (29 mg, 0.01 M) in DMF (8 mL) for 9 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished the product **3db** (153.1 mg, 75%) as a pale-yellow liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection].

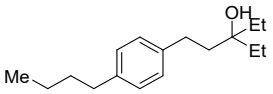
IR: (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3442, 2930, 1508, 1374, 1220, 1157, 1097, 1025, 921, 827 cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.21 – 7.12 (m, 2H), 7.01 – 6.89 (m, 2H), 2.81 – 2.68 (m, 2H), 1.86 – 1.76 (m, 2H), 1.25 (s, 1H), 1.17 (s, 3H), 0.96 (ddt, *J* = 14.1, 8.3, 5.6 Hz, 1H), 0.47 – 0.27 (m, 4H) ppm. **^{13}C{H} NMR** (151 MHz, $CDCl_3$) δ = 161.3 (d, *J* = 243.1 Hz), 138.4 (d, *J* = 2.9 Hz), 129.7 (d, *J* = 7.9 Hz, 2 × Ar–CH), 115.2 (d, *J* = 20.8 Hz, 2 × Ar–CH), 71.1, 45.2, 29.7, 26.0, 21.2, 0.8, 0.6 ppm. **^{19}F NMR** (565 MHz, $CDCl_3$) δ = –118.01 (s). **HRMS (ESI):** *m/z* calcd for $C_{13}H_{25}FN_2O^{2+}$ $[M+2(NH_4)]^{+2}$: 122.0970, found: 122.0964.



2-Cyclopropyl-4-(4-ethylphenyl)butan-2-ol (3eb)

GP was carried out with 1-ethyl-4-ethynylbenzene **1e** (127.6 mg, 0.98 mmol), 1-cyclopropylethan-1-one **2b** (329.4 mg, 3.91 mmol), and TBAI (29 mg, 0.01 M) in DMF (8 mL) for 9 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished the product **3db** (186.1 mg, 87%) as a colorless liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection].

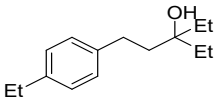
IR: (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3445, 2960, 1513, 1453, 1373, 1103, 1032, 922, 823 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.24 – 7.09 (m, 4H), 2.77 (td, *J* = 7.3, 3.0 Hz, 2H), 2.65 (q, *J* = 7.6 Hz, 2H), 1.93 – 1.79 (m, 2H), 1.42 (s, 1H), 1.26 (t, *J* = 7.6 Hz, 3H), 1.20 (s, 3H), 0.99 (tt, *J* = 8.3, 5.9 Hz, 1H), 0.51 – 0.28 (m, 4H) ppm. **^{13}C{H} NMR** (151 MHz, $CDCl_3$) δ = 141.7, 139.9, 128.4 (2 × Ar–CH), 127.9 (2 × Ar–CH), 71.2, 45.2, 30.1, 28.5, 25.9, 21.2, 15.8, 0.7, 0.6 ppm. **HRMS (ESI):** *m/z* calcd for $C_{15}H_{22}NaO^{+}$ $[M+Na]^{+}$: 241.1563, found: 241.1568.



1-(4-Butylphenyl)-3-ethylpentan-3-ol (3bc)

GP was carried out with 1-butyl-4-ethynylbenzene **1b** (155.1 mg, 0.98 mmol), pentan-3-one **2c** (336.8 mg, 3.91 mmol), and TBAI (29 mg, 0.01 M) in DMF (8 mL) for 10 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished the product **3bc** (206.9 mg, 85%) as a light-yellow liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection].

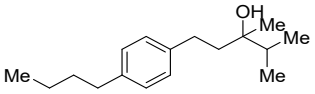
IR: (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3408, 2931, 1513, 1456, 1379, 1126, 926, 822 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.16 – 7.07 (m, 4H), 2.65 – 2.54 (m, 4H), 1.77 – 1.68 (m, 2H), 1.63 – 1.51 (m, 6H), 1.36 (dq, *J* = 14.6, 7.3 Hz, 3H), 0.92 (q, *J* = 7.4 Hz, 9H) ppm. **^{13}C{H} NMR** (151 MHz, $CDCl_3$) δ = 140.4, 139.9, 128.6 (2 × Ar–CH), 128.3 (2 × Ar–CH), 74.7, 40.6, 35.4, 33.9, 31.1 (2 × CH_2), 29.6, 22.5, 14.1, 7.9 (2 × CH_3) ppm. **HRMS:** *m/z* calcd for $C_{17}H_{28}KO^+$ $[M+K]^+$: 287.1772, found: 287.1773.



3-Ethyl-1-(4-ethylphenyl)pentan-3-ol (3ec)

GP was carried out with 1-ethyl-4-ethynylbenzene **1e** (127.6 mg, 0.98 mmol), pentan-3-one **2c** (336.8 mg, 3.91 mmol), and TBAI (29 mg, 0.01 M) in DMF (8 mL) for 10 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished the product **3ec** (155.5 mg, 72%) as a light-yellow liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection].

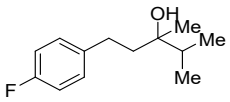
IR: (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3424, 2959, 1512, 1455, 1379, 1129, 1042, 963, 820 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.13 (s, 4H), 2.65 – 2.57 (m, 4H), 1.77 – 1.68 (m, 2H), 1.54 (q, *J* = 7.5 Hz, 4H), 1.29 (s, 1H), 1.23 (t, *J* = 7.6 Hz, 3H), 0.90 (t, *J* = 7.5 Hz, 6H) ppm. **^{13}C{H} NMR** (151 MHz, $CDCl_3$) δ = 141.8, 140.0, 128.4 (2 × Ar–CH), 128.0 (2 × Ar–CH), 74.8, 40.6, 31.1 (2 × CH_2), 29.6, 28.6, 15.8, 7.9 (2 × CH_3) ppm. **HRMS:** *m/z* calcd for $C_{15}H_{24}KO^+$ $[M+K]^+$: 259.1459, found: 259.1460.



1-(4-Butylphenyl)-3,4-dimethylpentan-3-ol (3bd)

GP was carried out with 1-butyl-4-ethynylbenzene **1b** (155.1 mg, 0.98 mmol), 3-methylbutan-2-one **2d** (336.8 mg, 3.91 mmol), and TBAI (29 mg, 0.01 M) in DMF (8 mL) for 9 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished the product **3bd** (158.2 mg, 65%) as a light-yellow liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection].

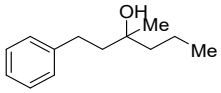
IR: (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3449, 2941, 1513, 1458, 1376, 1184, 1090, 921, 823, 752 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.18 – 7.06 (m, 4H), 2.72 – 2.62 (m, 2H), 2.58 (t, *J* = 8 Hz, 2H), 1.82 – 1.69 (m, 3H), 1.63 – 1.54 (m, 2H), 1.41 – 1.31 (m, 2H), 1.26 (s, 1H), 1.17 (s, 3H), 1.00 – 0.88 (m, 9H) ppm. **^{13}C{H} NMR** (151 MHz, $CDCl_3$) δ = 140.4, 140.0, 128.6 (2 × Ar–CH), 128.3 (2 × Ar–CH), 74.9, 41.9, 37.1, 35.4, 33.9, 29.6, 23.2, 22.5, 17.7, 17.1, 14.1 ppm. **HRMS (ESI):** *m/z* calcd for $C_{17}H_{28}NaO^+$ $[M+Na]^+$: 271.2032, found: 271.2043.



1-(4-Fluorophenyl)-3,4-dimethylpentan-3-ol (3dd)

GP was carried out with 1-ethynyl-4-fluorobenzene **1d** (117.7 mg, 0.98 mmol), 3-methylbutan-2-one **2d** (336.8 mg, 3.91 mmol), and TBAI (29 mg, 0.01 M) in DMF (8 mL) for 9 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished the product **3dd** (113.3 mg, 55%) as a colorless liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection].

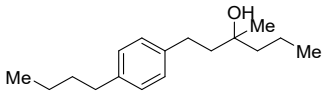
IR: (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3428, 2964, 1602, 1509, 1459, 1376, 1221, 1157, 1084, 829, 766 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.18 – 7.12 (m, 2H), 6.96 (ddd, *J* = 10.9, 5.8, 2.6 Hz, 2H), 2.74 – 2.60 (m, 2H), 1.78 – 1.70 (m, 3H), 1.71 (s, 1H), 1.25 (s, 1H), 1.16 (s, 3H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.92 (d, *J* = 6.9 Hz, 3H) ppm. **^{13}C{H} NMR** (151 MHz, $CDCl_3$) δ = 161.3 (d, *J* = 243.2 Hz), 138.5 (d, *J* = 3.2 Hz), 129.8 (d, *J* = 7.7 Hz, 2 × Ar–CH), 115.2 (d, *J* = 20.8 Hz, 2 × Ar–CH), 74.8, 41.9, 37.1, 29.2, 23.1, 17.7, 17.1 ppm. **^{19}F NMR** (565 MHz, $CDCl_3$) δ = –117.99 (s). **HRMS:** *m/z* calcd for $C_{13}H_{19}FNaO^+$ $[M+Na]^+$: 233.1312, found: 233.1333.



3-Methyl-1-phenylhexan-3-ol (3ae)

GP was carried out with phenylacetylene **1a** (100 mg, 0.98 mmol), pentan-2-one **2e** (336.8 mg, 3.91 mmol), and TBAI (29 mg, 0.01 M) in DMF (8 mL) for 10 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished the product **3ae** (150.6 mg, 80%) as a yellow liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection].

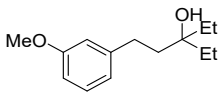
IR: (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3392, 2953, 1704, 1454, 1374, 1272, 1139, 929, 743, 698 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.34 – 7.27 (m, 2H), 7.25 – 7.16 (m, 3H), 2.75 – 2.65 (m, 2H), 1.84 – 1.73 (m, 2H), 1.56 – 1.49 (m, 2H), 1.41 (ddt, *J* = 9.1, 7.1, 4.6 Hz, 2H), 1.25 (s, 3H), 0.97 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C{H} NMR (**151 MHz, $CDCl_3$) δ = 142.7, 128.5 (2 × Ar–CH), 128.4 (2 × Ar–CH), 125.8, 72.8, 44.4, 43.8, 30.4, 26.9, 17.3, 14.8 ppm. **HRMS:** *m/z* calcd for $C_{13}H_{20}KO^+$ $[M+K]^+$: 231.1146, found: 231.1134.



1-(4-Butylphenyl)-3-methylhexan-3-ol (3be)

GP was carried out with 1-butyl-4-ethynylbenzene **1b** (155.0 mg, 0.98 mmol), pentan-2-one **2e** (336.8 mg, 3.91 mmol), and TBAI (29 mg, 0.01 M) in DMF (8 mL) for 10 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished the product **3be** (199.6 mg, 82%) as a colorless liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection].

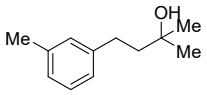
IR: (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3385, 2931, 1513, 1457, 1374, 1140, 932, 821, 638 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.17 – 7.08 (m, 4H), 2.69 – 2.63 (m, 2H), 2.62 – 2.56 (m, 2H), 1.81 – 1.73 (m, 2H), 1.65 – 1.55 (m, 2H), 1.55 – 1.48 (m, 2H), 1.44 – 1.30 (m, 5H), 1.24 (s, 3H), 0.95 (q, *J* = 15.3, 7.4 Hz, 6H) ppm. **^{13}C{H} NMR** (151 MHz, $CDCl_3$) δ = 140.4, 139.8, 128.5, 128.3, 72.9, 44.5, 43.9, 35.3, 33.8, 30.0, 27.0, 22.5, 17.3, 14.8, 14.1 ppm. **HRMS:** *m/z* calcd for $C_{17}H_{28}KO^+$ $[M+K]^+$: 287.1772, found: 287.1774.



3-Ethyl-1-(3-methoxyphenyl)pentan-3-ol (3kc)

GP was carried out with 1-ethynyl-3-methoxybenzene **1k** (129.5 mg, 0.98 mmol), pentan-3-one **2c** (336.8 mg, 3.91 mmol), and TBAI (29 mg, 0.01 M) in DMF (8 mL) for 10 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished the product **3kc** (163.4 mg, 75%) as a pale-yellow liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection].

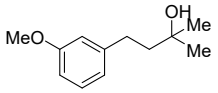
IR: (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3438, 2941, 1595, 1454, 1258, 1154, 1042, 927, 778, 694 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.21 (t, J = 7.8 Hz, 1H), 6.85 – 6.78 (m, 1H), 6.78 – 6.70 (m, 2H), 3.80 (s, 3H), 2.66 – 2.58 (m, 2H), 1.77 – 1.70 (m, 2H), 1.55 (q, J = 7.5 Hz, 4H), 1.26 (s, 1H), 0.91 (t, J = 7.5 Hz, 6H) ppm. **^{13}C{H} NMR** (151 MHz, $CDCl_3$) δ = 159.8, 144.6, 129.5, 120.9, 114.3, 111.1, 74.7, 55.3, 40.4, 31.1 (2 × CH_2), 30.1, 7.9 (2 × CH_3) ppm. **HRMS:** *m/z* calcd for $C_{14}H_{22}KO_2^+$ $[M+K]^+$: 261.1251, found: 261.1238.



2-Methyl-4-(m-tolyl)butan-2-ol (3ja)

GP was carried out with 1-ethynyl-3-methylbenzene **1j** (113.8 mg, 0.98 mmol), acetone **2a** (227.1 mg, 3.91 mmol), and TBAI (29 mg, 0.01 M) in DMF (8 mL) for 10 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished the product **3ja** (131.0 mg, 75%) as a light-yellow liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection].

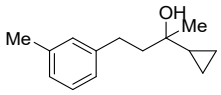
IR: (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3372, 2965, 1606, 1463, 1372, 1206, 1139, 918, 772, 697 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.20 (t, J = 7.5 Hz, 1H), 7.10 – 6.97 (m, 3H), 2.76 – 2.63 (m, 2H), 2.35 (s, 3H), 1.88 – 1.74 (m, 2H), 1.58 (s, 1H), 1.31 (s, 6H) ppm. **^{13}C{H} NMR** (100 MHz, $CDCl_3$) δ = 142.6, 138.0, 129.3, 128.4, 126.6, 125.4, 71.0, 45.9, 30.8, 29.4 (2 × CH_3), 21.5 ppm. **HRMS (ESI):** *m/z* calcd for $C_{12}H_{22}NO^+$ $[M+NH_4]^+$: 196.1696, found: 196.1701.



4-(3-Methoxyphenyl)-2-methylbutan-2-ol (3ka)

GP was carried out with 1-ethynyl-3-methoxybenzene **1k** (129.5 mg, 0.98 mmol), acetone **2a** (227.1 mg, 3.91 mmol), and TBAI (29 mg, 0.01 M) in DMF (8 mL) for 10 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished the product **3ka** (133.3 mg, 70%) as a yellow liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection].

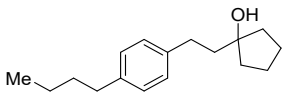
IR: (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3396, 2962, 1594, 1466, 1371, 1256, 1151, 1044, 917, 775, 693 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.20 (t, *J* = 7.8 Hz, 1H), 6.83 – 6.78 (m, 1H), 6.78 – 6.70 (m, 2H), 3.80 (s, 3H), 2.74 – 2.64 (m, 2H), 1.82 – 1.76 (m, 2H), 1.43 (s, 1H), 1.29 (s, 6H) ppm. **^{13}C{H} NMR** (151 MHz, $CDCl_3$) δ = 159.7, 144.3, 129.4, 120.8, 114.1, 111.1, 70.9, 55.2, 45.6, 30.9, 29.4 (2 × CH_3) ppm. **HRMS:** *m/z* calcd for $C_{12}H_{22}NO_2^+$ $[M+NH_4]^+$: 212.1645, found: 212.1618.



2-Cyclopropyl-4-(m-tolyl)butan-2-ol (3jb)

GP was carried out with 1-ethynyl-3-methylbenzene **1j** (113.8 mg, 0.98 mmol), 1-cyclopropylethan-1-one **2b** (329.4 mg, 3.44 mmol), and TBAI (29 mg, 0.01 M) in DMF (8 mL) for 9 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished the product **3jb** (160.2 mg, 80%) as a yellow liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection].

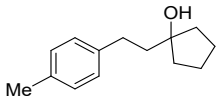
IR: (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3444, 2929, 1604, 1456, 1374, 1102, 1031, 918, 780, 698 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.21 (t, *J* = 7.5 Hz, 1H), 7.07 – 7.02 (m, 3H), 2.76 (td, *J* = 7.3, 3.2 Hz, 2H), 2.36 (s, 3H), 1.95 – 1.76 (m, 2H), 1.29 (s, 1H), 1.20 (s, 3H), 0.99 (tt, *J* = 8.2, 5.9 Hz, 1H), 0.56 – 0.25 (m, 4H) ppm. **^{13}C{H} NMR** (151 MHz, $CDCl_3$) δ = 142.8, 137.9, 129.3, 128.4, 126.5, 125.4, 71.1, 45.2, 30.4, 25.9, 21.5, 21.2, 0.7, 0.6 ppm. **HRMS (ESI):** *m/z* calcd for $C_{14}H_{20}NaO^+$ $[M+Na]^+$: 227.1406, found: 227.1414.



1-(4-Butylphenethyl)cyclopentan-1-ol (3bf)

GP was carried out with 1-butyl-4-ethynylbenzene **1b** (155.1 mg, 0.98 mmol), cyclopentanone **2f** (328.9 mg, 3.91 mmol), and TBAI (29 mg, 0.01 M) in DMF (8 mL) for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished the product **3bf** (169.0 mg, 70%) as a yellow liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection].

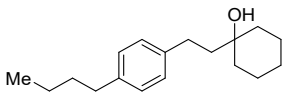
IR: (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3385, 2937, 1711, 1512, 1451, 1206, 1093, 1023, 954, 823, 655 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.16 – 7.07 (m, 4H), 2.78 – 2.69 (m, 2H), 2.58 (t, *J* = 8 Hz, 2H), 1.93 – 1.87 (m, 2H), 1.87 – 1.80 (m, 2H), 1.70 – 1.55 (m, 8H), 1.42 – 1.30 (m, 3H), 0.93 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C{H} NMR** (151 MHz, $CDCl_3$) δ = 140.4, 139.9, 128.6 (2 × Ar–CH), 128.3 (2 × Ar–CH), 82.7, 43.7, 39.9 (2 × CH_2), 35.3, 33.9, 30.9, 23.9 (2 × CH_2), 22.5, 14.1 ppm. **HRMS:** *m/z* calcd for $C_{17}H_{26}KO^+$ $[M+K]^+$: 285.1615, found: 285.1618.



1-(4-Methylphenethyl)cyclopentan-1-ol (3ff)

GP was carried out with 1-ethynyl-4-methylbenzene **1f** (113.8 mg, 0.98 mmol), cyclopentanone **2f** (328.9 mg, 3.91 mmol), and TBAI (29 mg, 0.01 M) in DMF (8 mL) for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished the product **3ff** (156.2 mg, 78%) as a white solid, mp = 51–53 °C [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection].

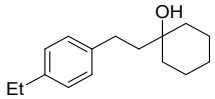
IR: (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3381, 2945, 1514, 1448, 1209, 1090, 1026, 953, 808, 758, 651 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.17 – 7.06 (m, 4H), 2.78 – 2.70 (m, 2H), 2.33 (s, 3H), 1.93 – 1.87 (m, 2H), 1.87 – 1.78 (m, 2H), 1.74 – 1.60 (m, 6H), 1.39 (s, 1H) ppm. **^{13}C{H} NMR** (151 MHz, $CDCl_3$) δ = 139.6, 135.2, 129.1 (2 × Ar–CH), 128.2 (2 × Ar–CH), 82.5, 77.1, 76.9, 43.7, 39.8 (2 × CH_2), 30.8, 23.8 (2 × CH_2), 21.0 ppm. **HRMS:** *m/z* calcd for $C_{14}H_{20}KO^+$ $[M+K]^+$: 243.1146, found: 243.1143.



1-(4-Butylphenethyl)cyclohexan-1-ol (3bg)

GP was carried out with 1-butyl-4-ethynylbenzene **1b** (155.1 mg, 0.98 mmol), cyclohexanone **2g** (383.8 mg, 3.91 mmol), and TBAI (29 mg, 0.01 M) in DMF (8 mL) for 10 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished the product **3bg** (204.2 mg, 80%) as a light-yellow liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection].

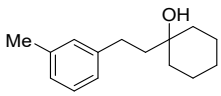
IR: (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3409, 2929, 1513, 1258, 1011, 786, 688 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.17 – 7.04 (m, 4H), 2.73 – 2.62 (m, 2H), 2.58 (t, *J* = 8 Hz, 2H), 1.79 – 1.71 (m, 2H), 1.66 (s, 1H), 1.64 – 1.56 (m, 5H), 1.50 (dt, *J* = 17.4, 7.2 Hz, 4H), 1.45 – 1.26 (m, 5H), 0.92 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C{H} NMR** (151 MHz, $CDCl_3$) δ = 140.4, 140.0, 128.6 (2 × Ar–CH), 128.3 (2 × Ar–CH), 71.6, 44.5, 37.6 (2 × CH_2), 35.3, 33.9, 29.1, 25.9, 22.5 (2 × CH_2), 22.4, 14.1 ppm. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{28}NaO^+$ $[M+Na]^+$: 283.2032, found: 283.2037.



1-(4-Ethylphenethyl)cyclohexan-1-ol (3eg)

GP was carried out with 1-ethyl-4-ethynylbenzene **1e** (127.6 mg, 0.98 mmol), cyclohexanone **2g** (383.8 mg, 3.91 mmol), and TBAI (29 mg, 0.01 M) in DMF (8 mL) for 10 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished the product **3eg** (159.4 mg, 70%) as a white solid, mp = 50–52 °C [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection].

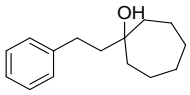
IR: (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3363, 2925, 1512, 1449, 1304, 1172, 1031, 811, 656 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.23 – 7.08 (m, 4H), 2.75 – 2.68 (m, 2H), 2.64 (t, *J* = 7.6 Hz, 2H), 1.81 – 1.75 (m, 2H), 1.69 – 1.58 (m, *J* = 13.5, 5.2 Hz, 5H), 1.57 – 1.43 (m, *J* = 18.4, 8.5 Hz, 5H), 1.37 (s, 1H), 1.26 (t, *J* = 7.6 Hz, 3H) ppm. **^{13}C{H} NMR** (151 MHz, $CDCl_3$) δ = 141.6, 140.1, 128.4 (2 × Ar–CH), 127.9 (2 × Ar–CH), 71.6, 44.4, 37.5 (2 × CH_2), 29.0, 28.5, 25.9, 22.3 (2 × CH_2), 15.7 ppm. **HRMS (ESI):** *m/z* calcd for $C_{16}H_{24}KO^+$ $[M+K]^+$: 271.1459, found: 271.1460.



1-(3-Methylphenethyl)cyclohexan-1-ol (3jg)

GP was carried out with 1-ethynyl-3-methylbenzene **1j** (113.8 mg, 0.98 mmol), cyclohexanone **2g** (383.8 mg, 3.91 mmol), and TBAI (29 mg, 0.01 M) in DMF (8 mL) for 10 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished the product **3jg** (149.8 mg, 70%) as a colorless liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection].

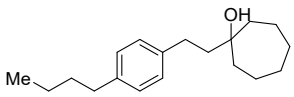
IR: (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3395, 2926, 1605, 1449, 1257, 1169, 966, 783, 698 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.18 (t, *J* = 7.5 Hz, 1H), 7.07 – 6.96 (m, 3H), 2.70 – 2.63 (m, 2H), 2.33 (s, 3H), 1.80 – 1.70 (m, 2H), 1.66 – 1.57 (m, 5H), 1.55 – 1.44 (m, 5H), 1.29 (s, 1H) ppm. **^{13}C{H} NMR** (151 MHz, $CDCl_3$) δ =142.9, 138.1, 129.3, 128.4, 126.6, 125.5, 71.6, 44.5, 37.6 (2 × CH_2), 29.4, 25.9, 22.4 (2 × CH_2), 21.5 ppm. **HRMS:** *m/z* calcd for $C_{15}H_{22}KO^+$ $[M+K]^+$: 257.1302, found: 257.1300.



1-Phenethylcycloheptan-1-ol (3ah)

GP was carried out with phenylacetylene **1a** (100 mg, 0.98 mmol), cycloheptanone **2h** (439.3 mg, 3.91 mmol), and TBAI (29 mg, 0.01 M) in DMF (8 mL) for 10 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished the product **3ah** (153.9 mg, 72%) as a light-yellow liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection].

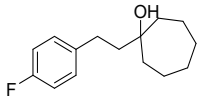
IR: (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3396, 2923, 1454, 1198, 1045, 906, 845, 747, 701 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.31 – 7.25 (m, 2H), 7.24 – 7.15 (m, 3H), 2.79 – 2.63 (m, 2H), 1.81 – 1.75 (m, 2H), 1.74 – 1.70 (m, 4H), 1.68 (s, 1H), 1.66 – 1.58 (m, 4H), 1.57 – 1.50 (m, 2H), 1.47 – 1.38 (m, 2H) ppm. **^{13}C{H} NMR** (151 MHz, $CDCl_3$) δ = 142.9, 128.6 (2 × Ar–CH), 128.5 (2 × Ar–CH), 125.8, 75.7, 45.6, 41.4 (2 × CH_2), 30.0, 29.9 (2 × CH_2), 22.6 (2 × CH_2) ppm. **HRMS:** *m/z* calcd for $C_{15}H_{22}KO^+$ $[M+K]^+$: 257.1302, found: 257.1301.



1-(4-Butylphenethyl)cycloheptan-1-ol (3bh)

GP was carried out with 1-butyl-4-ethynylbenzene **1b** (155.1 mg, 0.98 mmol), cycloheptanone **2h** (439.3 mg, 3.91 mmol), and TBAI (29 mg, 0.01 M) in DMF (8 mL) for 10 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished the product **3bh** (201.7 mg, 75%) as a yellow liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection].

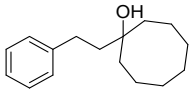
IR: (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3398, 2923, 1512, 1455, 1199, 1119, 1050, 836, 757 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.16 – 7.07 (m, 4H), 2.72 – 2.63 (m, 2H), 2.58 (t, *J* = 8 Hz, 2H), 1.80 – 1.75 (m, 2H), 1.74 – 1.69 (m, 4H), 1.66 – 1.47 (m, 8H), 1.45 – 1.30 (m, 4H), 1.26 (s, 1H), 0.93 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C{H} NMR** (151 MHz, $CDCl_3$) δ = 140.4, 140.0, 128.6 (2 × Ar–CH), 128.3 (2 × Ar–CH), 75.7, 45.6, 41.4 (2 × CH_2), 35.4, 33.9, 29.9, (2 × CH_2) 29.5, 22.6 (2 × CH_2), 22.5, 14.1 ppm. **HRMS:** *m/z* calcd for $C_{19}H_{30}KO^+$ $[M+K]^+$: 313.1928, found: 313.1930.



1-(4-Fluorophenethyl)cycloheptan-1-ol (3dh)

GP was carried out with 1-ethynyl-4-fluorobenzene **1d** (117.7 mg, 0.98 mmol), cycloheptanone **2h** (439.3 mg, 3.91 mmol), and TBAI (29 mg, 0.01 M) in DMF (8 mL) for 10 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished the product **3dh** (162.1 mg, 70%) as a pale-yellow liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection].

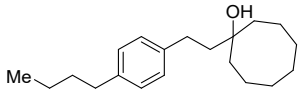
IR: (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3416, 2924, 1509, 1455, 1222, 958, 903, 832, 760 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.18 – 7.12 (m, 2H), 6.99 – 6.93 (m, 2H), 2.72 – 2.64 (m, 2H), 1.78 – 1.72 (m, 2H), 1.72 – 1.67 (m, 5H), 1.65 – 1.54 (m, 5H), 1.45 – 1.38 (m, 2H), 1.25 (s, 1H) ppm. **^{13}C{H} NMR** (151 MHz, $CDCl_3$) δ = 161.2 (d, *J* = 264.5 Hz), 138.5 (d, *J* = 3.2 Hz), 129.8 (d, *J* = 7.7 Hz, 2 × Ar–CH), 115.2 (d, *J* = 20.9 Hz, 2 × Ar–CH), 75.6, 45.7, 41.4 (2 × CH_2), 29.9 (2 × CH_2), 29.2, 22.6 (2 × CH_2) ppm. **^{19}F NMR** (565 MHz, $CDCl_3$) δ = –118.04 (s). **HRMS (ESI):** *m/z* calcd for $C_{15}H_{29}FN_2O^{2+}$ $[M+2(NH_4)]^{+2}$: 136.1126, found: 136.1115.



1-Phenethylcyclooctan-1-ol (3ai)

GP was carried out with phenylacetylene **1a** (100 mg, 0.98 mmol), cyclooctanone **2i** (494.2 mg, 3.91 mmol), and TBAI (29 mg, 0.01 M) in DMF (8 mL) for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished the product **3ai** (136.5 mg, 60%) as a colorless liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection].

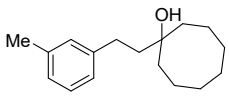
IR: (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3405, 2920, 1698, 1601, 1454, 1019, 896, 750, 700 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.32 – 7.26 (m, 2H), 7.23 – 7.15 (m, 3H), 2.75 – 2.66 (m, 2H), 1.87 – 1.79 (m, 2H), 1.79 – 1.73 (m, 2H), 1.72 – 1.56 (m, 10H), 1.55 (s, 1H), 1.45 – 1.39 (m, 2H) ppm. **^{13}C{H} NMR** (151 MHz, $CDCl_3$) δ = 143.1, 128.5 (4 × Ar–CH), 125.8, 75.0, 43.7, 36.5 (2 × CH_2), 29.9, 28.4 (2 × CH_2), 25.2, 22.5 (2 × CH_2) ppm. **HRMS (ESI):** *m/z* calcd for $C_{16}H_{24}NaO^+$ $[M+Na]^+$: 255.1719, found: 255.1727.



1-(4-Butylphenethyl)cyclooctan-1-ol (3bi)

GP was carried out with 1-butyl-4-ethynylbenzene (155.1 mg, 0.98 mmol), cyclooctanone **2i** (494.2 mg, 3.91 mmol), and TBAI (29 mg, 0.01 M) in DMF (8 mL) for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished the product **3bi** (197.9 mg, 70%) as a colorless liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection].

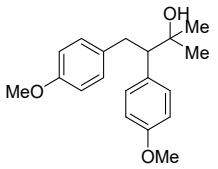
IR: (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3390, 2919, 1513, 1456, 1017, 953, 894, 818, 757 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.15 – 7.07 (m, 4H), 2.71 – 2.63 (m, 2H), 2.57 (t, *J* = 8 Hz, 2H), 1.87 – 1.78 (m, 2H), 1.77 – 1.72 (m, 2H), 1.71 – 1.52 (m, 12H), 1.47 – 1.39 (m, 2H), 1.38 – 1.31 (m, 2H), 1.17 (s, 1H), 0.92 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C{H} NMR** (151 MHz, $CDCl_3$) δ = 140.4, 140.1, 128.6 (2 × Ar–CH), 128.4 (2 × Ar–CH), 75.0, 43.8 (2 × CH_2), 36.5 (2 × CH_2), 35.4, 33.9, 29.4, 28.4 (2 × CH_2), 25.2, 22.5 (2 × CH_2), 14.1 ppm. **HRMS (ESI):** *m/z* calcd for $C_{20}H_{32}KO^+$ $[M+K]^+$: 327.2085, found: 327.2088.



1-(3-Methylphenethyl)cyclooctan-1-ol (3ji)

GP was carried out with 1-ethynyl-3-methylbenzene (113.8 mg, 0.98 mmol), cyclooctanone **2i** (494.2 mg, 3.91 mmol), and TBAI (29 mg, 0.01 M) in DMF (8 mL) for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished the product **3bi** (144.9 mg, 60%) as a colorless liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection].

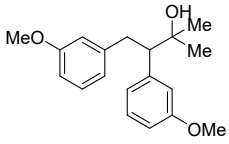
IR: (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3399, 2918, 1606, 1457, 1076, 1015, 955, 893, 782, 698 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.18 (t, *J* = 7.5 Hz, 1H), 7.07 – 6.96 (m, 3H), 2.71 – 2.61 (m, 2H), 2.33 (s, 3H), 1.86 – 1.79 (m, 2H), 1.78 – 1.71 (m, 3H), 1.70 – 1.54 (m, 10H), 1.45 – 1.40 (m, 2H) ppm. **^{13}C{H} NMR** (151 MHz, $CDCl_3$) δ = 142.9, 138.1, 129.3, 128.4, 126.6, 125.5, 75.0, 43.8, 36.4 (2 × CH_2), 29.8, 28.4 (2 × CH_2), 25.2, 22.5 (2 × CH_2), 21.5 ppm. **HRMS (ESI):** *m/z* calcd for $C_{17}H_{26}KO^+$ $[M+K]^+$: 285.1615, found: 285.1617.



3,4-bis(4-methoxyphenyl)-2-methylbutan-2-ol (5ba)

GP was carried out with 1,2-bis(4-methoxyphenyl)ethyne (233 mg, 0.98 mmol), acetone **2a** (227.1 mg, 3.91 mmol), and TBAI (29 mg, 0.01 M) in DMF (8 mL) for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished the product **5ba** (88 mg, 30%) as a colorless liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection].

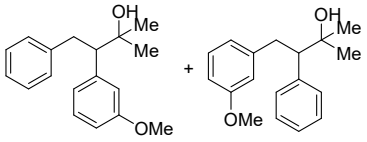
IR: (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3445, 2940, 1510, 1243, 1034, 827 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.13 – 7.08 (m, 2H), 6.92 – 6.86 (m, 2H), 6.81 – 6.75 (m, 2H), 6.70 – 6.63 (m, 2H), 3.76 (s, 3H), 3.70 (s, 3H), 3.20 (dd, *J* = 13.6, 3.0 Hz, 1H), 2.92 (dd, *J* = 13.5, 11.7 Hz, 1H), 2.82 (dd, *J* = 11.6, 3.0 Hz, 1H), 1.44 (s, 1H), 1.25 (s, 6H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ = 158.3, 157.5, 133.4, 132.7, 130.7 (2 × Ar–CH), 129.8 (2 × Ar–CH), 113.5 (2 × Ar–CH), 113.5 (2 × Ar–CH), 73.1, 58.7, 55.2, 55.2, 35.4, 28.2, 27.9 ppm. **HRMS (ESI):** *m/z* calcd for $C_{19}H_{24}KO_3^+$ $[M+K]^+$: 339.1357, found: 339.1366.



3,4-bis(3-methoxyphenyl)-2-methylbutan-2-ol (5ca)

GP was carried out with 1,2-bis(3-methoxyphenyl)ethyne (233 mg, 0.98 mmol), acetone **2a** (227.1 mg, 3.91 mmol), and TBAI (29 mg, 0.01 M) in DMF (8 mL) for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished the product **5ba** (59 mg, 20%) as a colorless liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection].

IR: (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3435, 2962, 1595, 1259, 1157, 1046, 697 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.16 (t, *J* = 7.9 Hz, 1H), 7.04 (t, *J* = 7.9 Hz, 1H), 6.80 (d, *J* = 7.7 Hz, 1H), 6.77 – 6.69 (m, 2H), 6.65 – 6.57 (m, 2H), 6.56 – 6.49 (m, 1H), 3.76 (s, 3H), 3.66 (s, 3H), 3.24 (dd, *J* = 13.6, 3.1 Hz, 1H), 3.05 – 2.93 (m, 1H), 2.91 – 2.83 (m, 1H), 1.46 (s, 1H), 1.26 (d, *J* = 8.5 Hz, 6H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ = 159.4 (2 × Ar–CH), 142.8, 142.5, 129.0 (2 × Ar–CH), 122.3, 121.4, 115.9, 114.6, 111.7, 111.2, 73.0, 59.1, 55.3, 55.1, 36.3, 28.4, 28.2 ppm. **HRMS (ESI):** *m/z* calcd for $C_{19}H_{24}NaO_3^+$ $[M+Na]^+$: 323.1618, found: 323.1627.

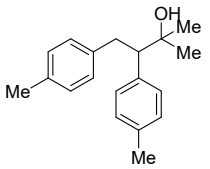


3-(3-methoxyphenyl)-2-methyl-4-phenylbutan-2-ol (5da) & 4-(3-methoxyphenyl)-2-methyl-3-phenylbutan-2-ol (5da')

GP was carried out with 1-methoxy-3-(phenylethynyl)benzene (204 mg, 0.98 mmol), acetone **2a** (227.1 mg, 3.91 mmol), and TBAI (29 mg, 0.01 M) in DMF (8 mL) for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished the product **5ba** (58 mg, 22%) as a colorless liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection].

IR: (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3424, 2966, 1596, 1453, 1259, 1156, 1046, 751, 701 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$, mixture of **5da** & **5da'**) δ = 7.26 – 7.08 (m, 8H), 7.06 – 6.97 (m, 3H), 6.81 – 6.67 (m, 2H), 6.59 (dd, *J* = 8.1, 2.2 Hz, 2H), 6.49 (t, *J* = 4 Hz, 1H), 3.74 (s, 2H), 3.62 (s, 3H), 3.26 (dd, *J* = 13.5, 2.6 Hz, 2H), 3.01 (dd, *J* = 14.3, 10.6 Hz, 2H), 2.93 – 2.85

(m, 2H), 1.38 (s, 1H), 1.27 (s, 2H), 1.26 (s, 3H), 1.25 (s, 2H), 1.24 (s, 3H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ = 159.3 (2 × Ar–CH), 142.9, 142.5, 141.2, 140.9, 129.8, 128.9, 129.0, 128.9, 128.1 (2 × Ar–CH), 126.7, 125.7, 122.3, 121.4, 115.9, 114.6, 111.6, 111.2, 73.1, 73.0, 59.3, 59.2, 55.2, 55.1, 36.3, 36.2, 28.5, 28.4, 28.1, 27.9 ppm. **HRMS (ESI):** *m/z* calcd for $C_{18}H_{22}NaO_2^+$ $[M+Na]^+$: 293.1512, found: 293.1525.



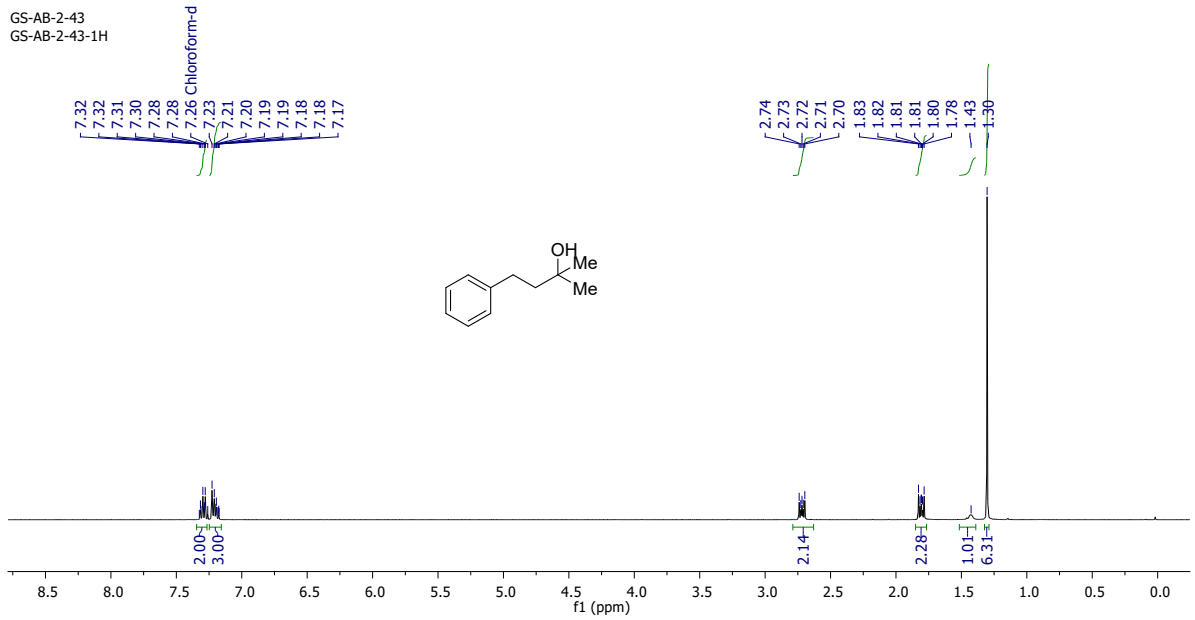
2-methyl-3,4-di-p-tolylbutan-2-ol (5ea)

GP was carried out with 1,2-di-*p*-tolylethyne (202 mg, 0.98 mmol), acetone **2a** (227.1 mg, 3.91 mmol), and TBAI (29 mg, 0.01 M) in DMF (8 mL) for 12 h. Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05) furnished the product **5ba** (79 mg, 30%) as a colorless liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *Rf* = 0.20, UV detection].

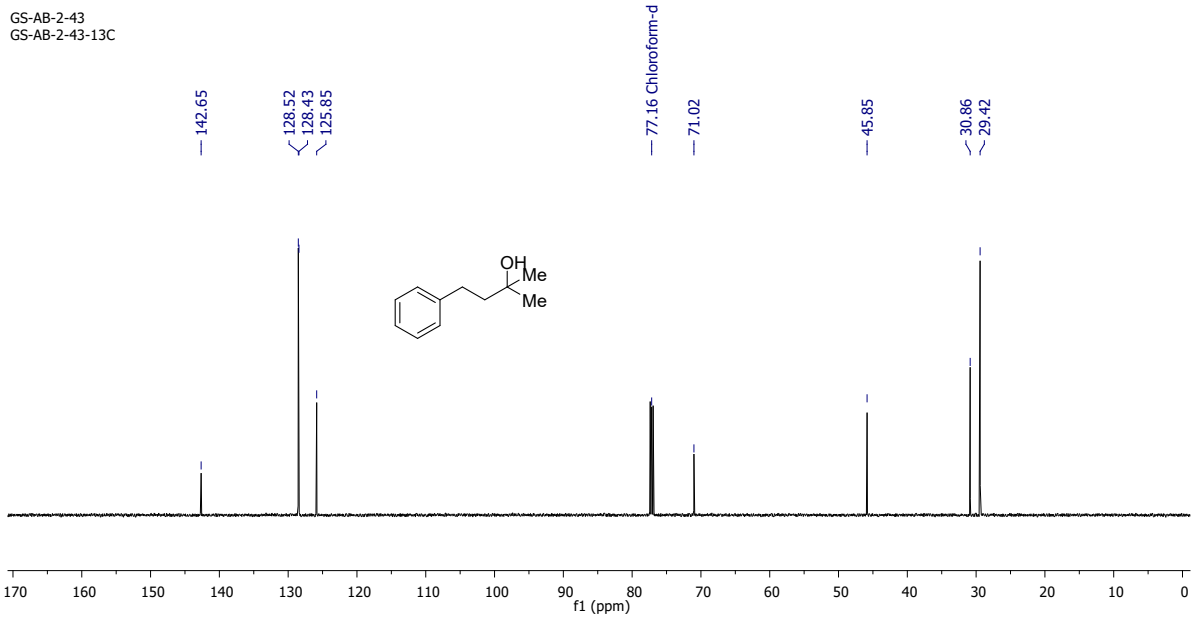
IR: (MIR-ATR, 4000–600 cm^{-1}) ν_{max} = 3423, 2967, 2929, 1512, 1453, 1372, 1123, 809 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.08 (dd, *J* = 19.9, 8.0 Hz, 4H), 6.93 (q, *J* = 8.1 Hz, 4H), 3.24 (dd, *J* = 13.6, 3.0 Hz, 1H), 3.06 – 2.94 (m, 1H), 2.93 – 2.85 (m, 1H), 2.30 (s, 3H), 2.23 (s, 3H), 1.49 (s, 1H), 1.27 (d, *J* = 4.8 Hz, 6H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ = 138.2, 137.6, 136.1, 134.9, 129.7, 128.8, 128.8, 128.8, 73.1, 58.9, 35.7, 28.2, 27.9, 21.1, 21.0 ppm. **HRMS (ESI):** *m/z* calcd for $C_{19}H_{24}NaO^+$ $[M+Na]^+$: 291.1719, found: 291.1732.

NMR Spectra:

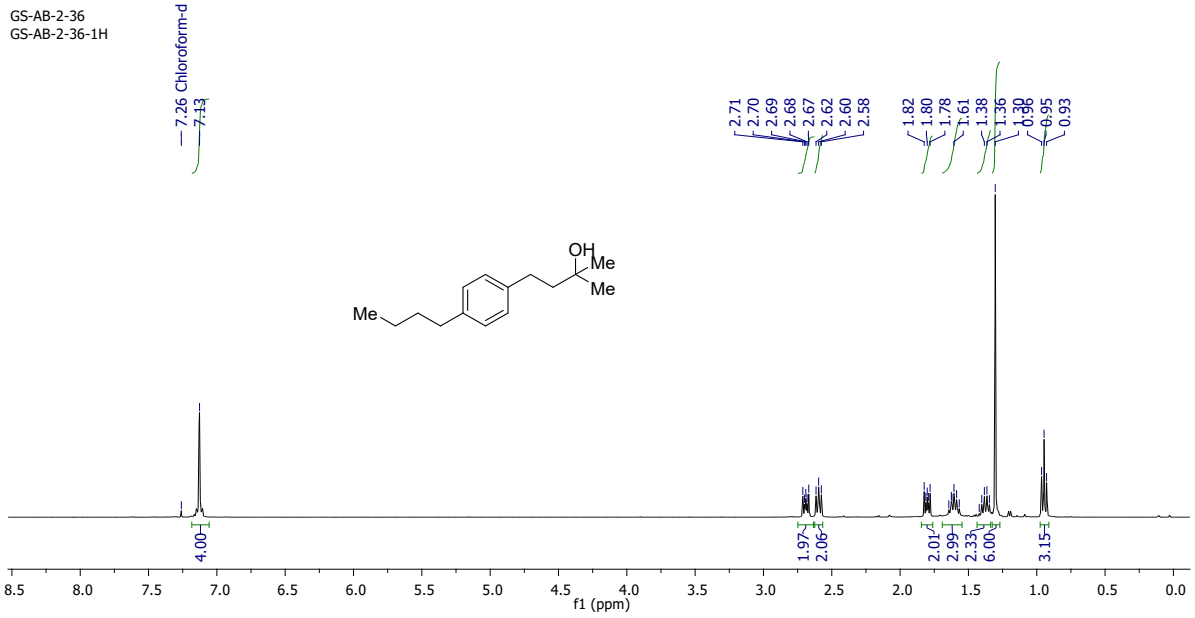
^{1}H-NMR (400 MHz) spectrum of **3aa** in $CDCl_3$



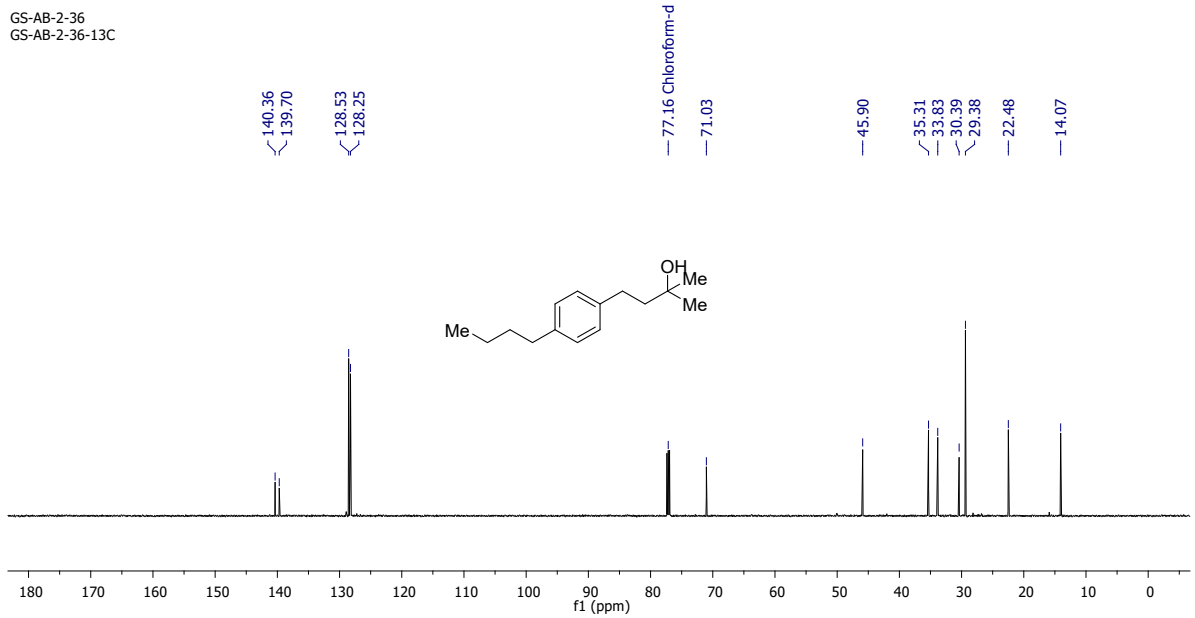
^{13}C{^{1}H}-NMR (100 MHz) spectrum of **3aa** in $CDCl_3$



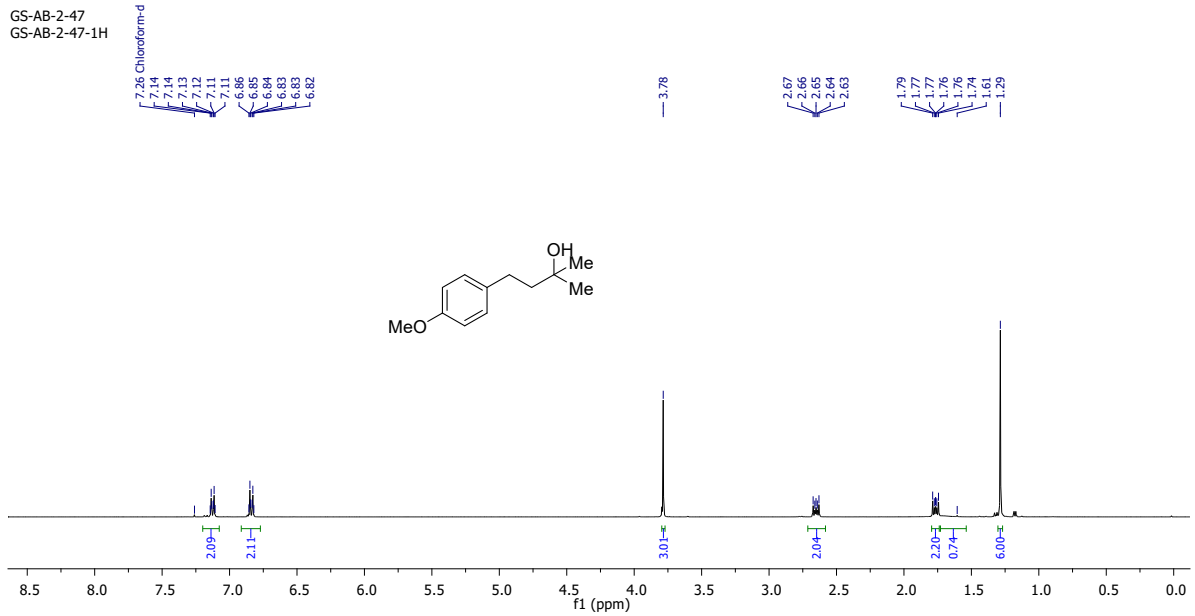
^{1}H-NMR (400 MHz) spectrum of **3ba** in $CDCl_3$



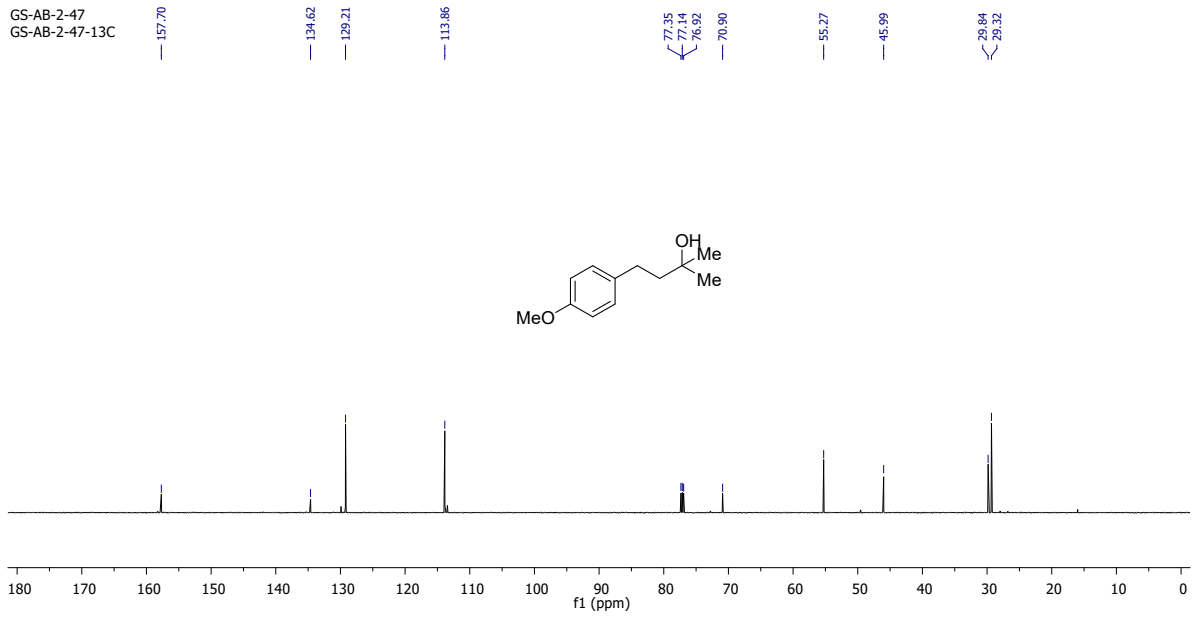
^{13}C{^{1}H}-NMR (151 MHz) spectrum of **3ba** in $CDCl_3$



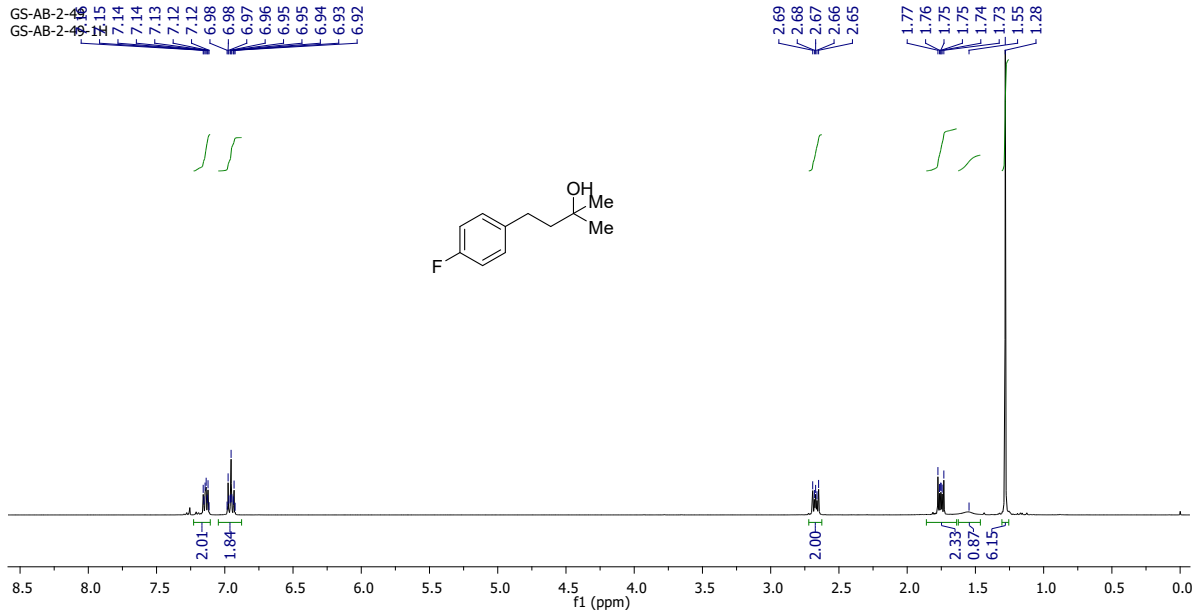
^{1}H-NMR (400 MHz) spectrum of **3ca** in $CDCl_3$



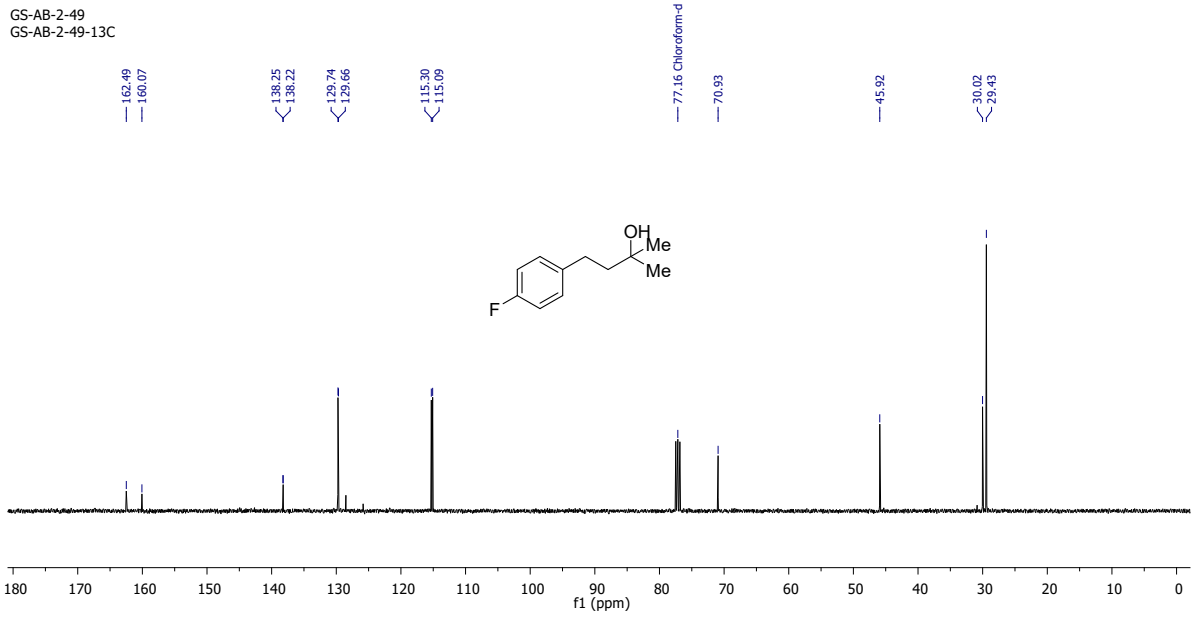
^{13}C{^{1}H}-NMR (151 MHz) spectrum of **3ca** in $CDCl_3$



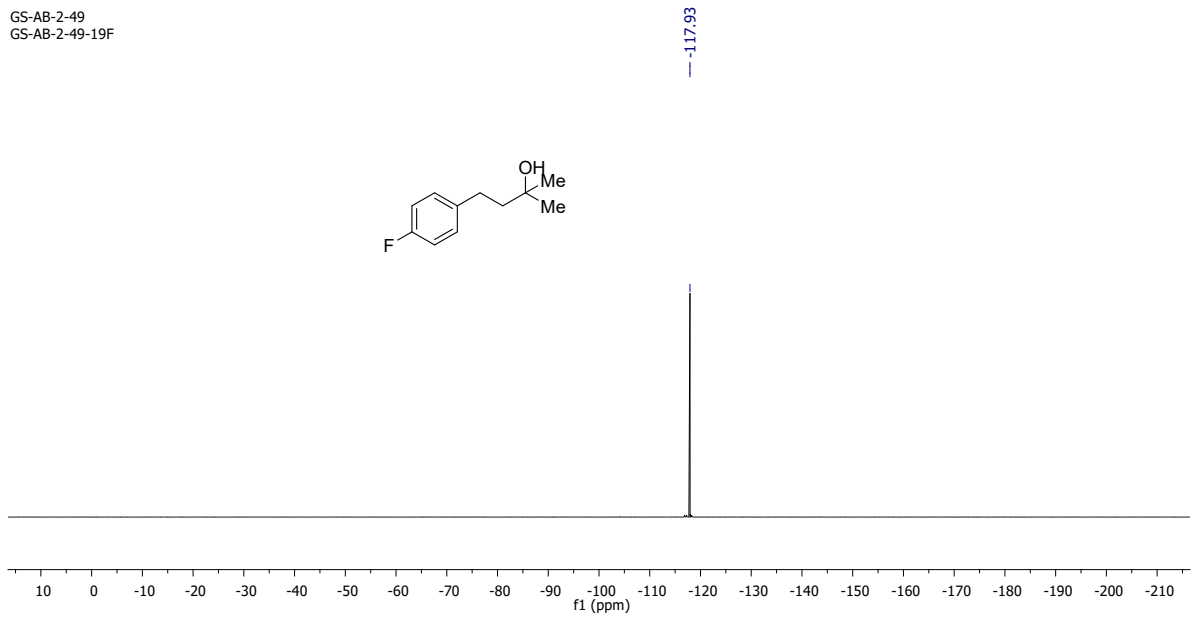
^{1}H-NMR (400 MHz) spectrum of **3da** in $CDCl_3$



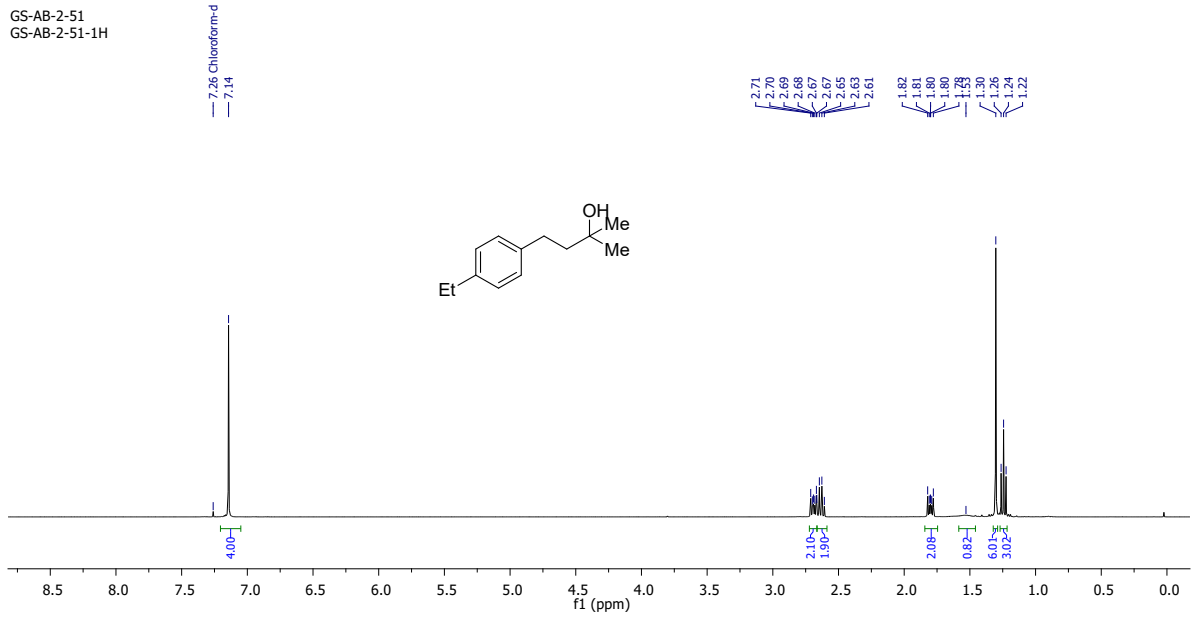
^{13}C{^{1}H}-NMR (100 MHz) spectrum of **3da** in $CDCl_3$



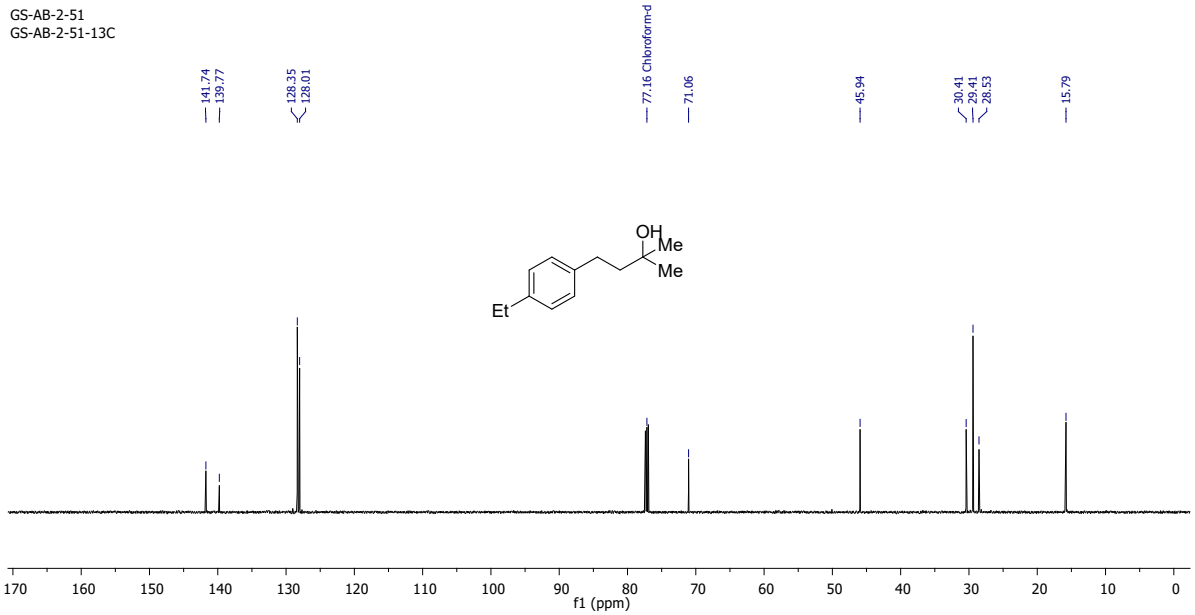
^{19}F-NMR (565 MHz) spectrum of **3da** in $CDCl_3$



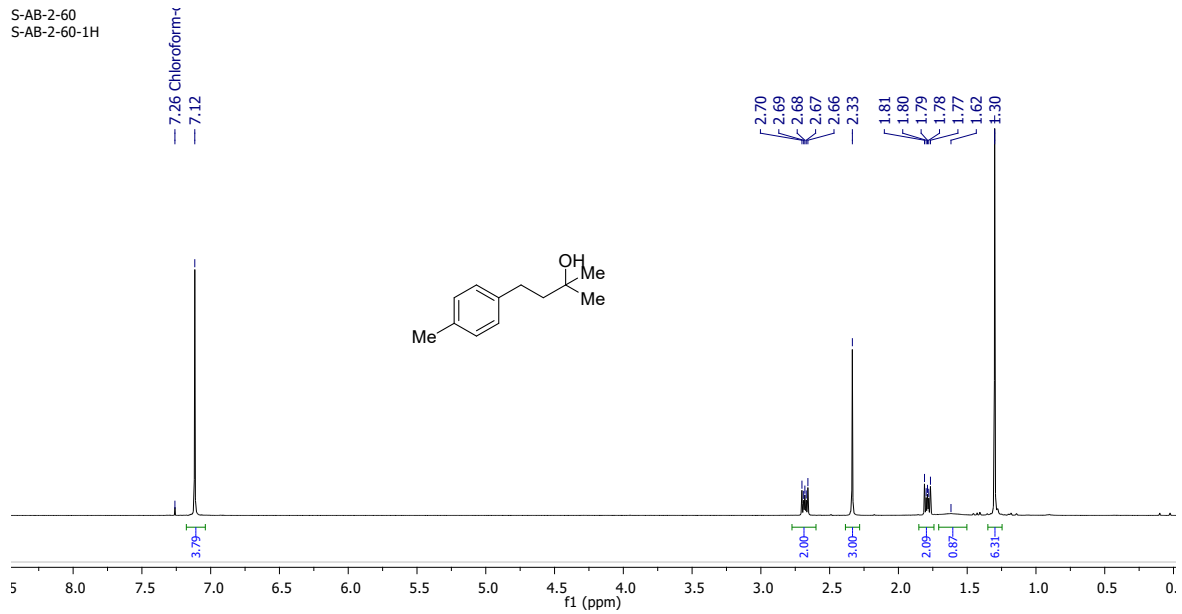
^{1}H-NMR (400 MHz) spectrum of **3ea** in $CDCl_3$



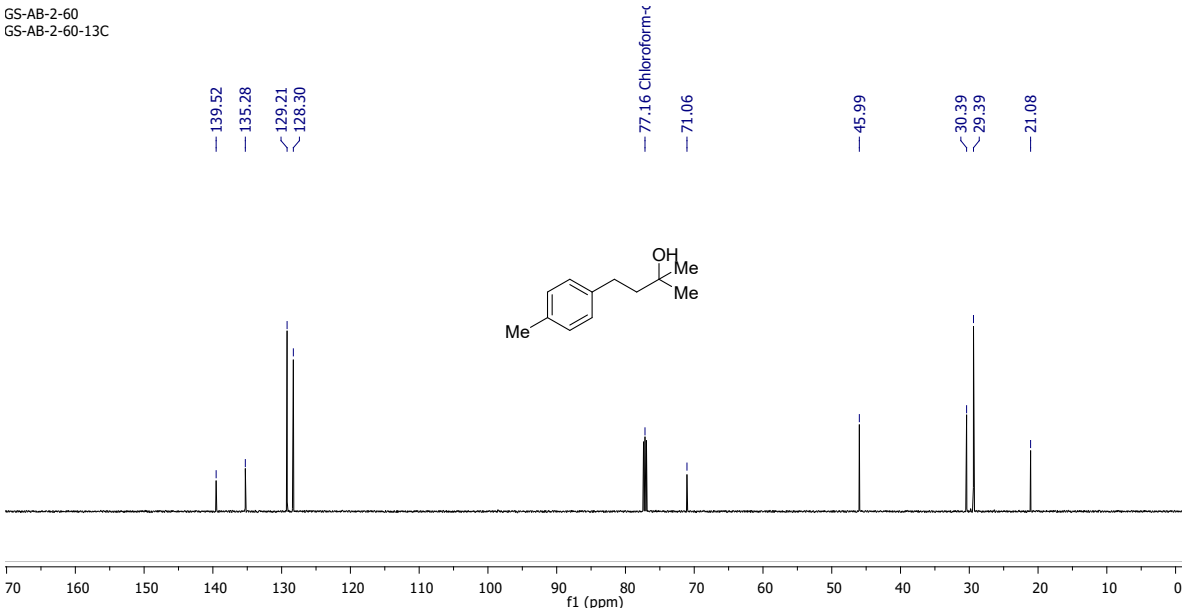
^{13}C{^{1}H}-NMR (151 MHz) spectrum of **3ea** in $CDCl_3$



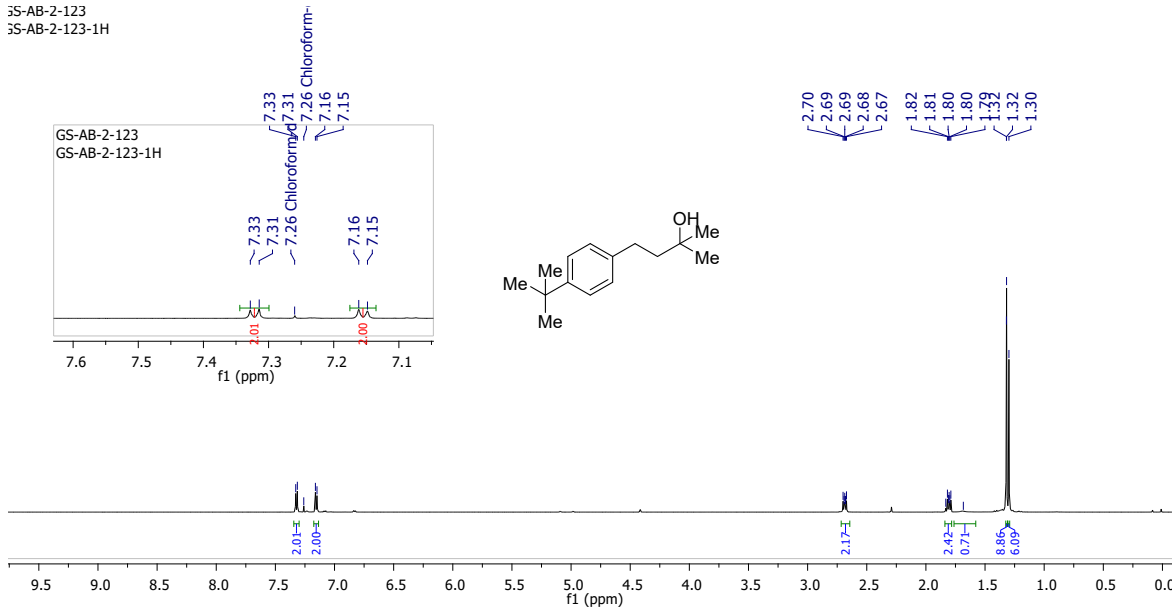
^{1}H-NMR (400 MHz) spectrum of **3fa** in $CDCl_3$



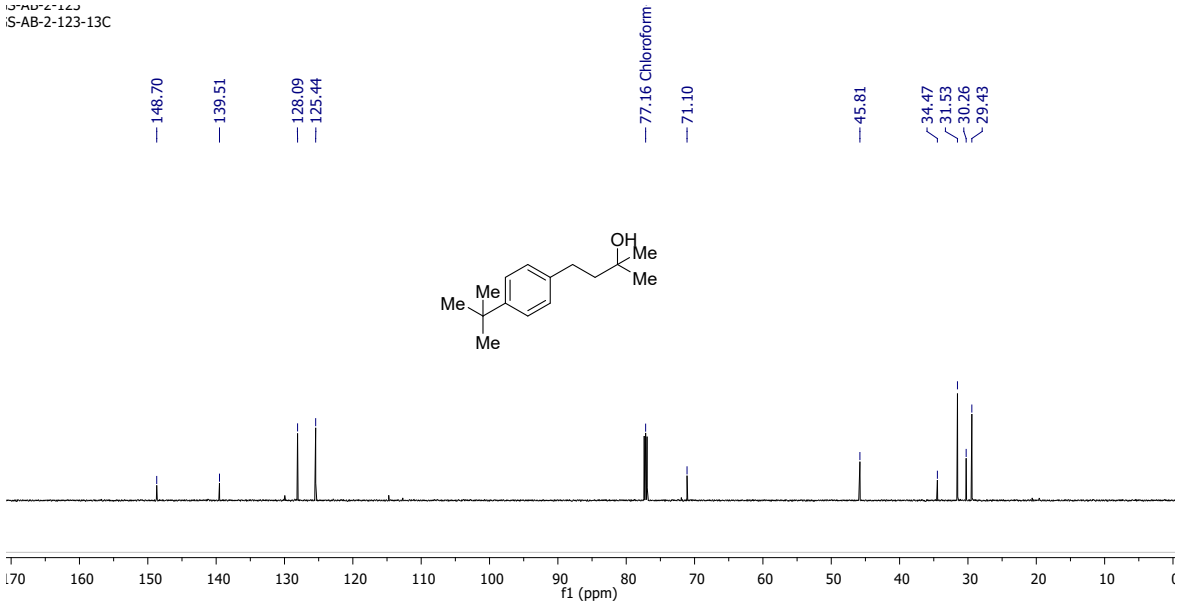
^{13}C{^{1}H}-NMR (151 MHz) spectrum of **3fa** in $CDCl_3$



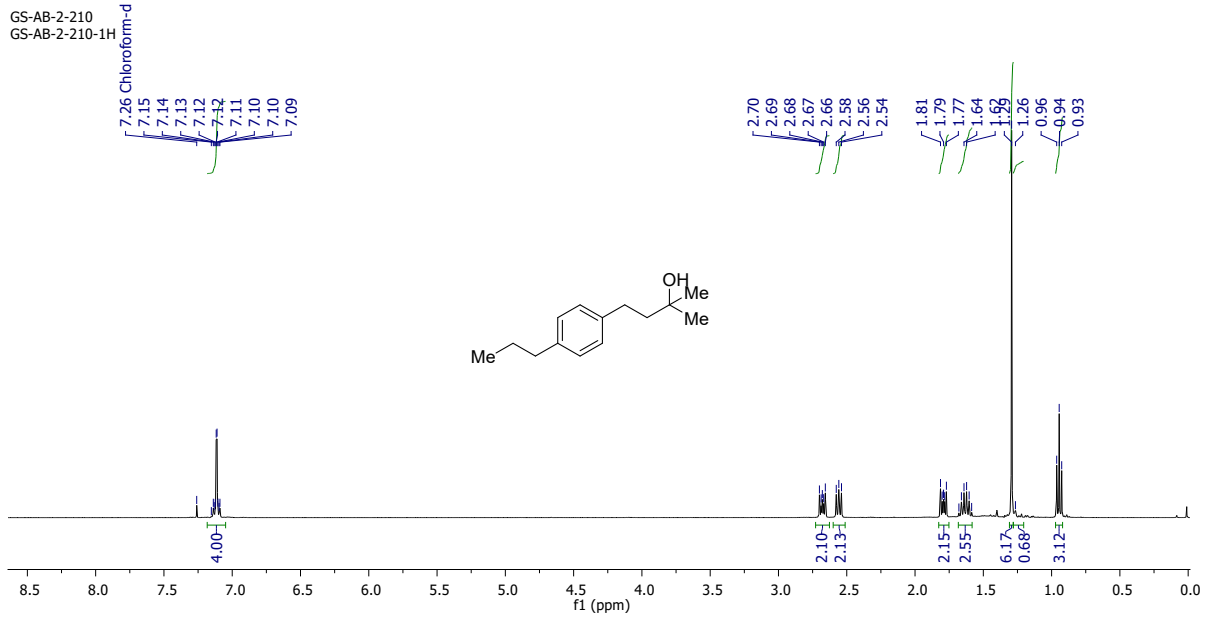
^{1}H-NMR (600 MHz) spectrum of **3ga** in $CDCl_3$



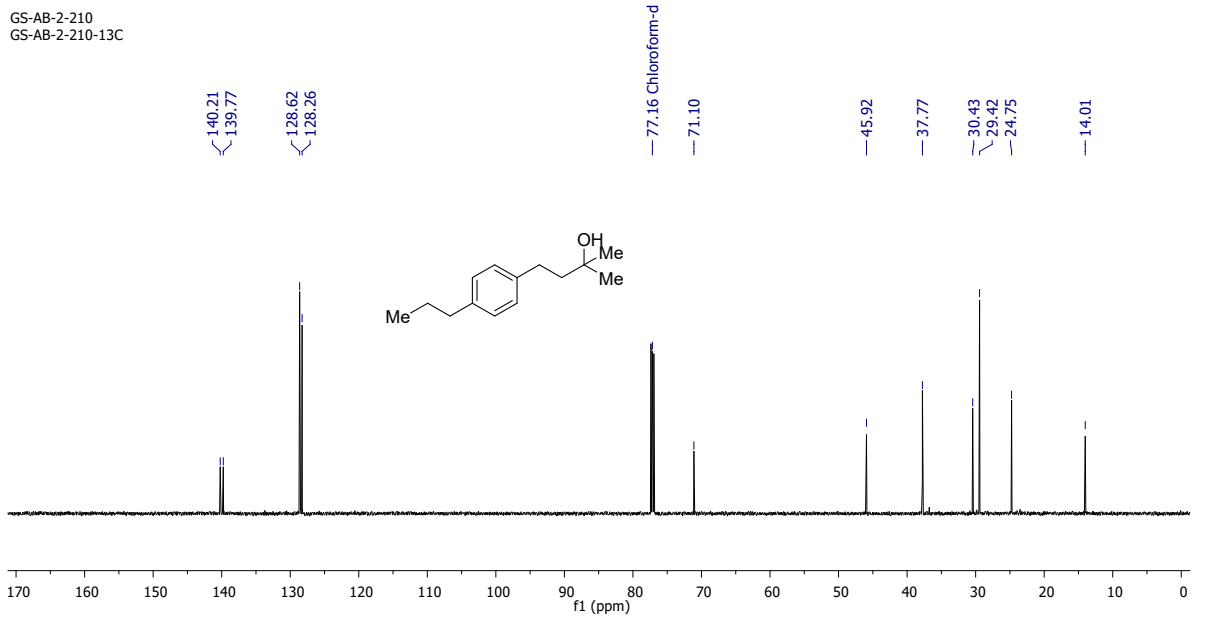
^{13}C{^{1}H}-NMR (151 MHz) spectrum of **3ga** in $CDCl_3$



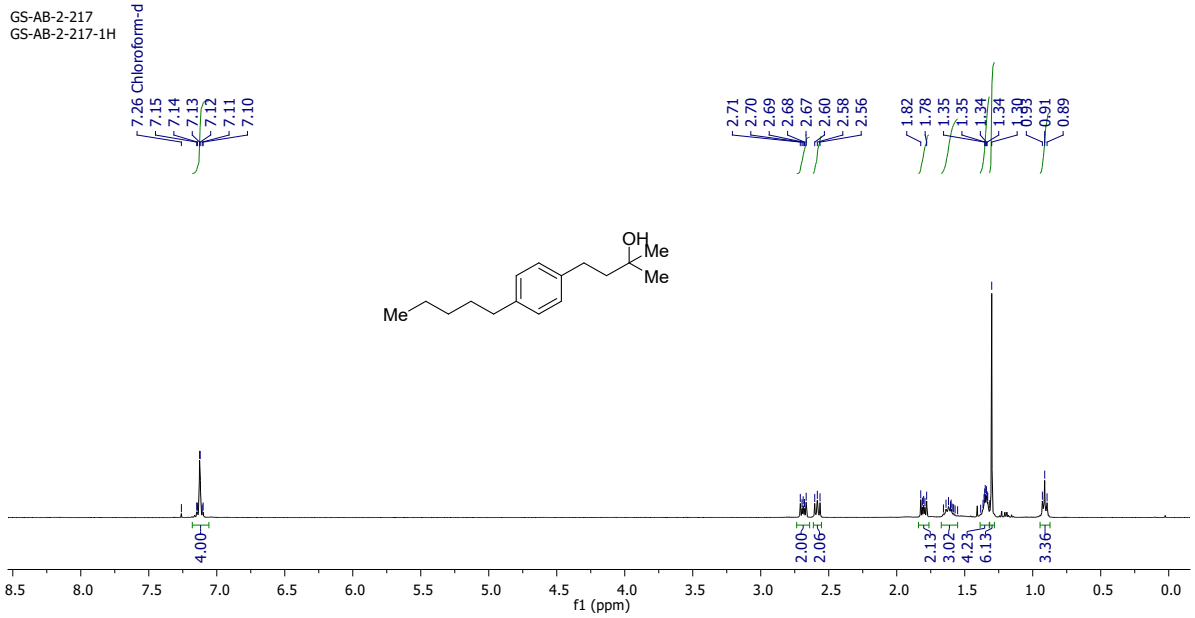
^{1}H-NMR (400 MHz) spectrum of **3ha** in $CDCl_3$



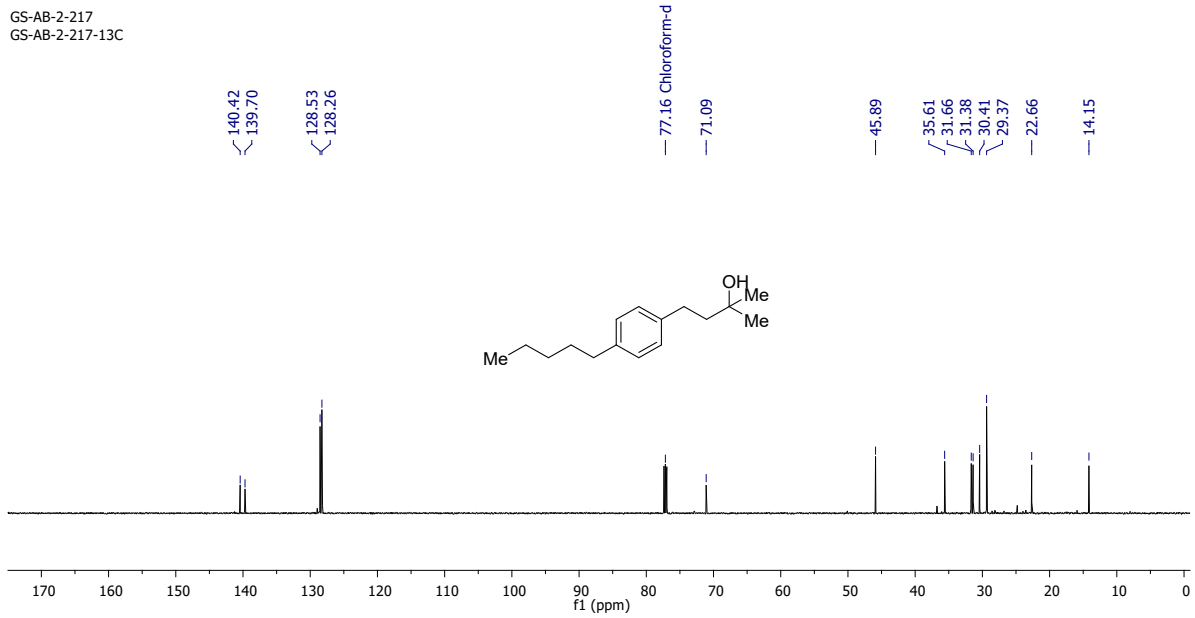
^{13}C{^{1}H}-NMR (151 MHz) spectrum of **3ha** in $CDCl_3$



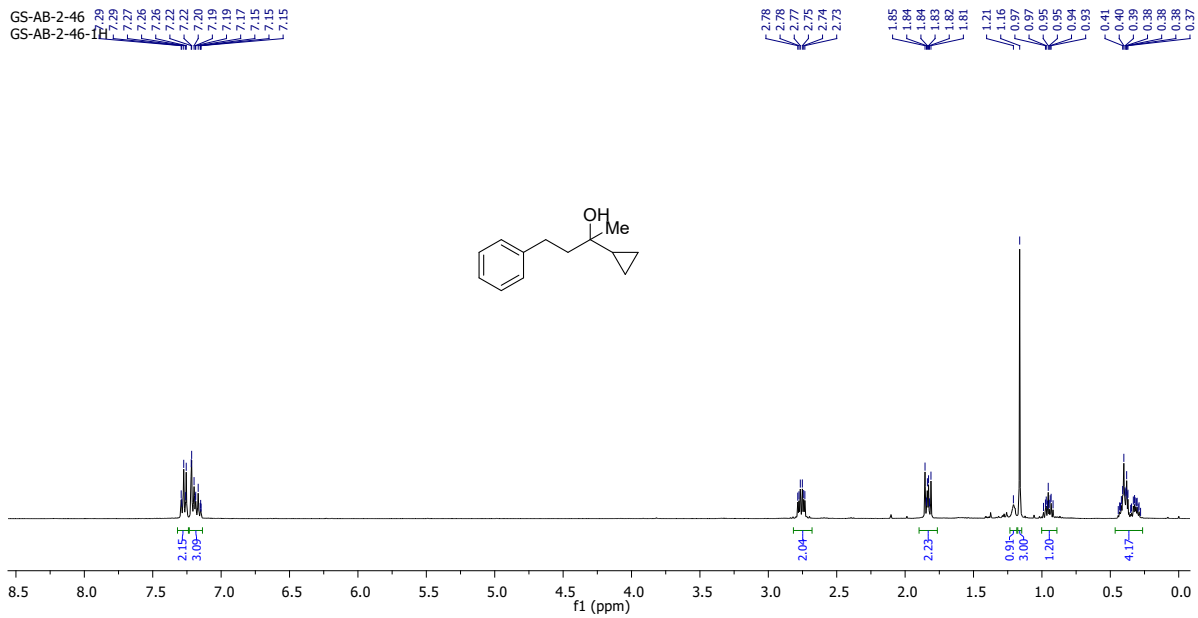
^{1}H-NMR (400 MHz) spectrum of **3ia** in $CDCl_3$



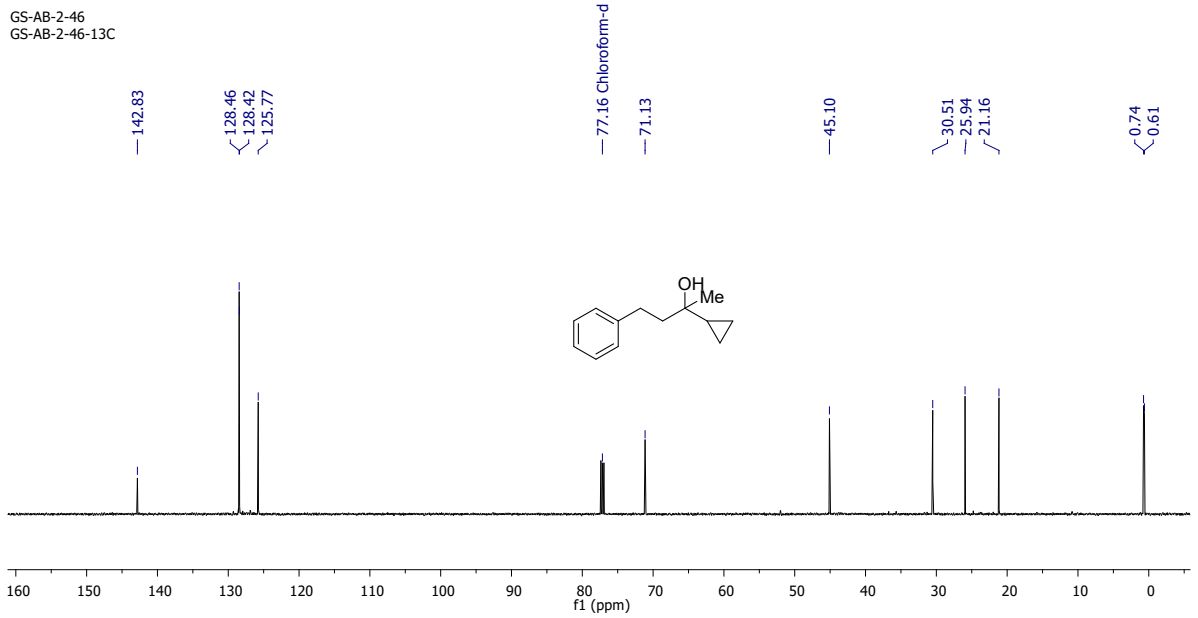
^{13}C{^{1}H}-NMR (151 MHz) spectrum of **3ia** in $CDCl_3$



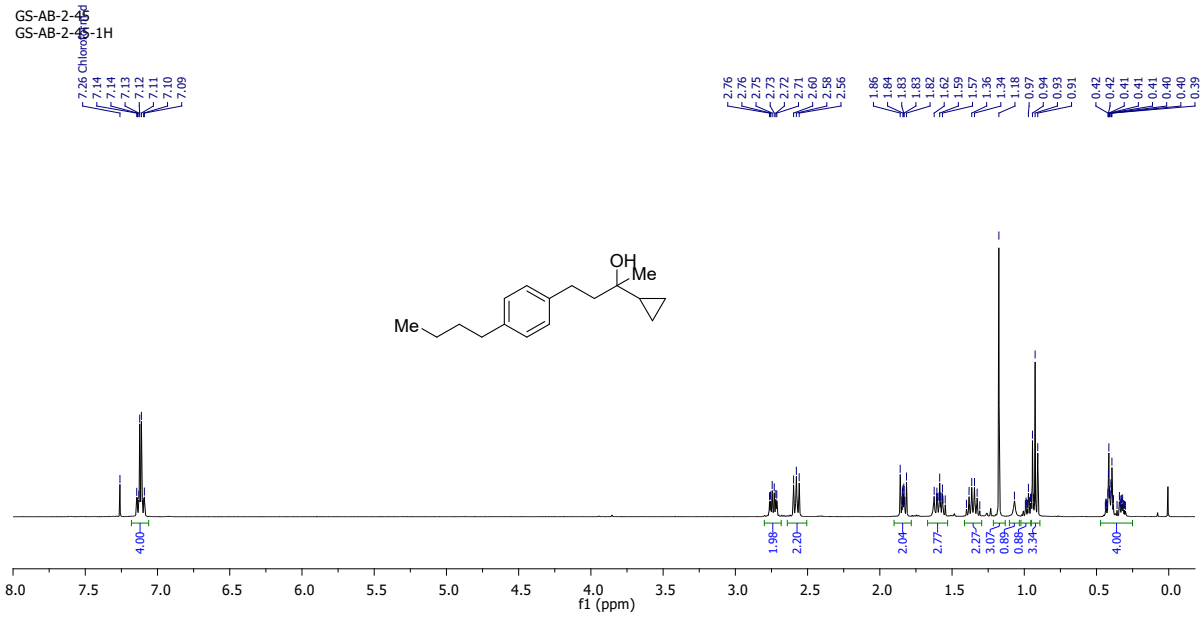
^{1}H-NMR (400 MHz) spectrum of **3ab** in $CDCl_3$



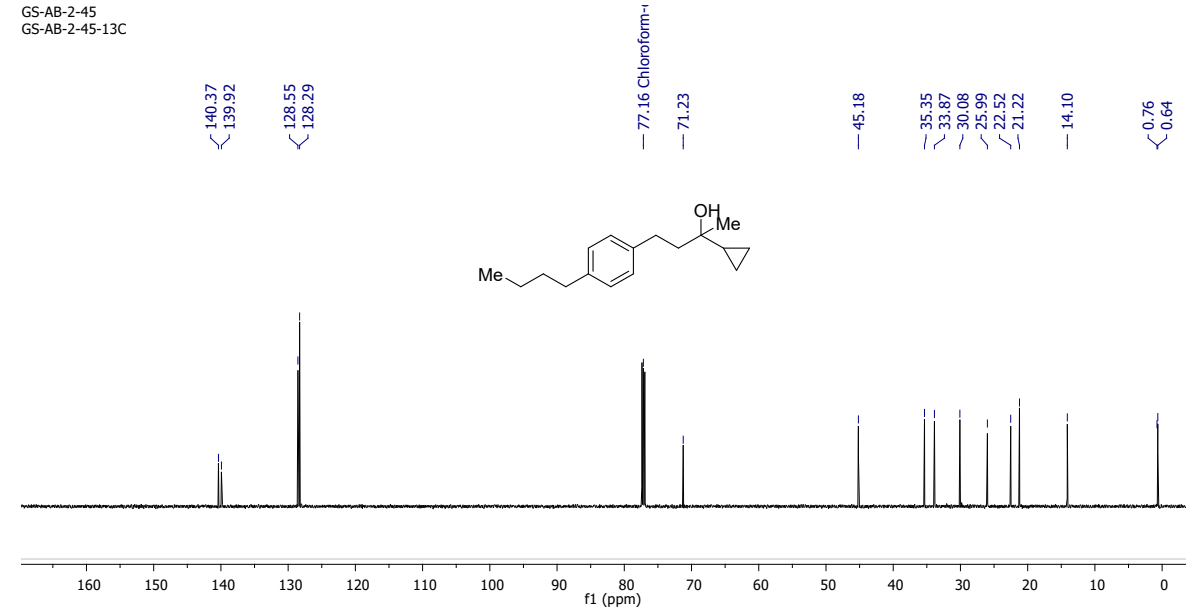
^{13}C{^{1}H}-NMR (151 MHz) spectrum of **3ab** in $CDCl_3$



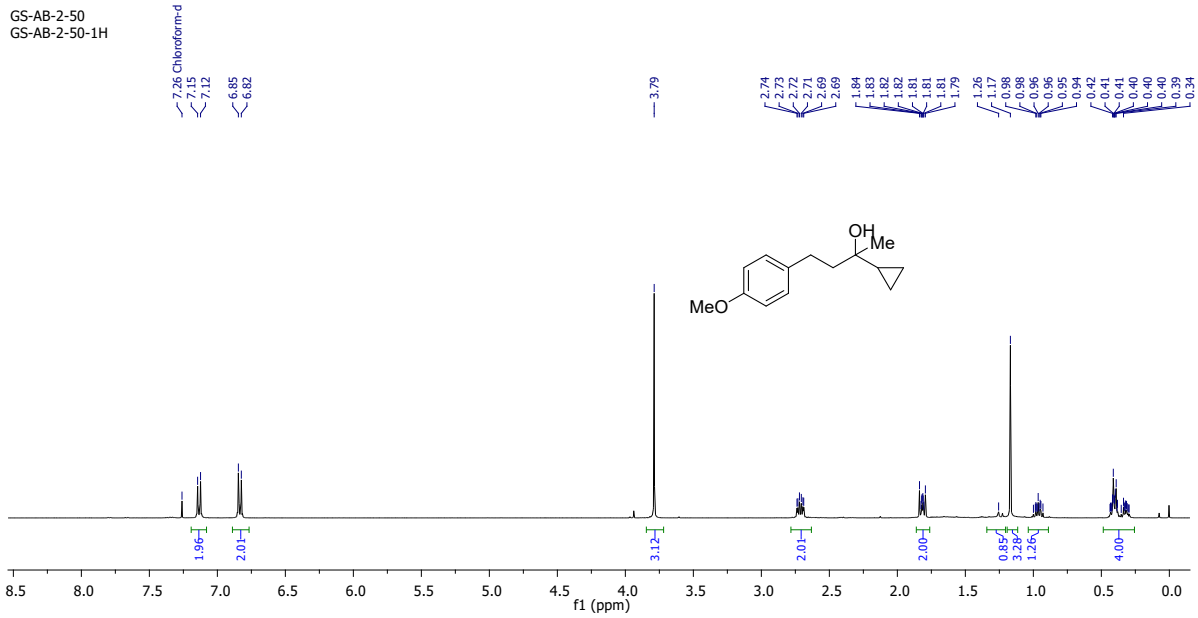
^{1}H-NMR (400 MHz) spectrum of **3bb** in $CDCl_3$



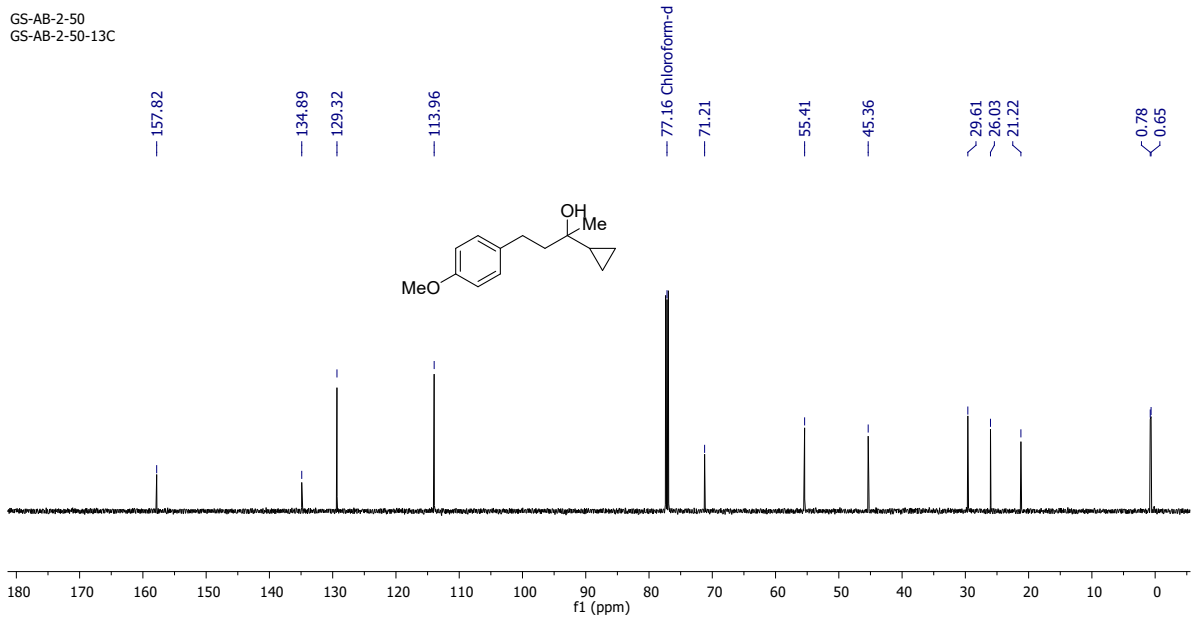
^{13}C{^{1}H}-NMR (151 MHz) spectrum of **3bb** in $CDCl_3$



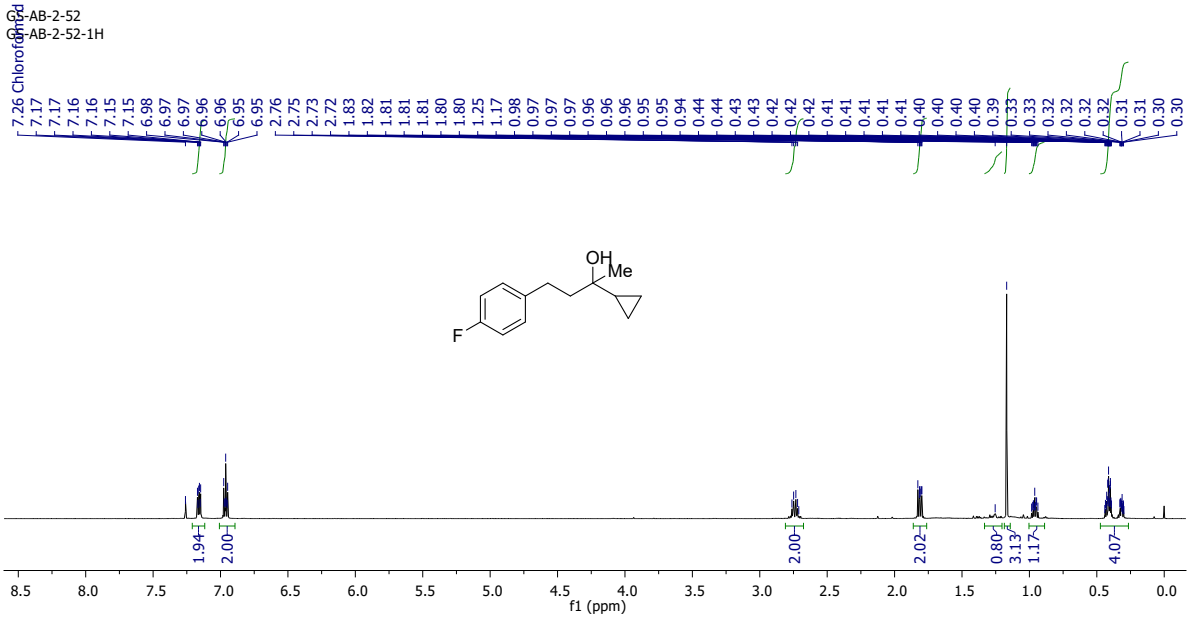
^{1}H-NMR (400 MHz) spectrum of **3cb** in $CDCl_3$



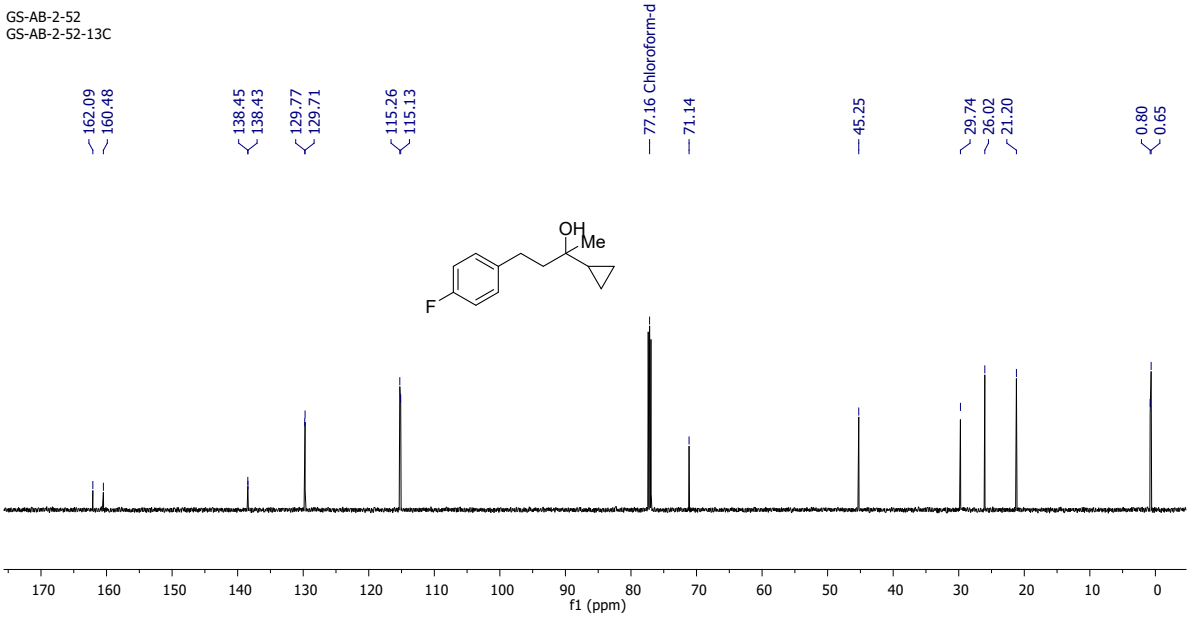
^{13}C{^{1}H}-NMR (151 MHz) spectrum of **3cb** in $CDCl_3$



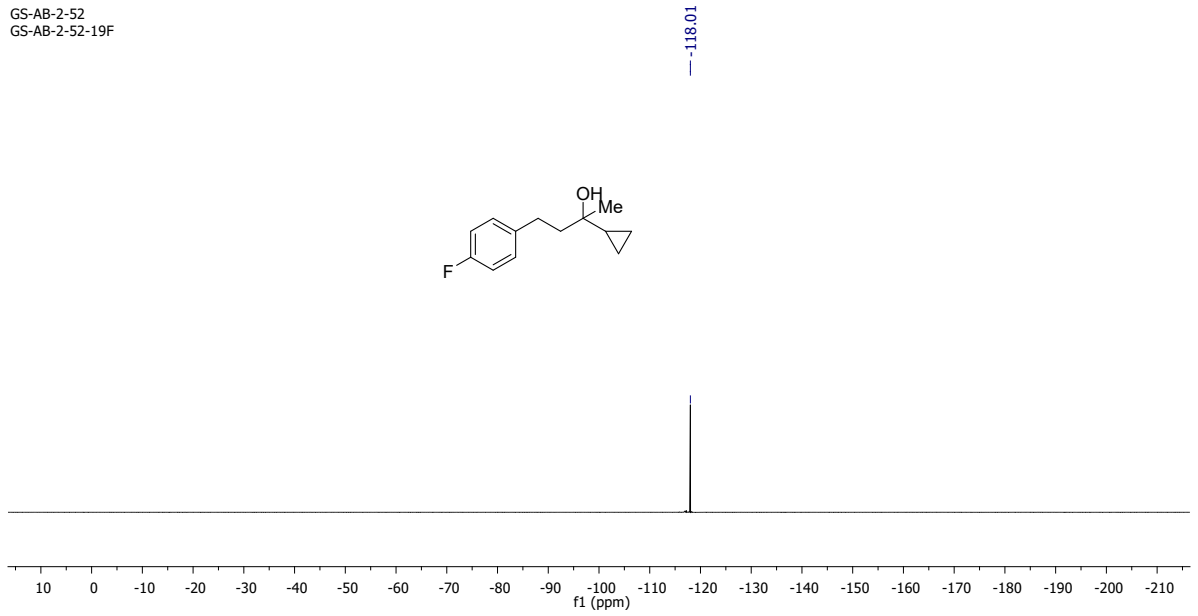
^{1}H-NMR (600 MHz) spectrum of **3db** in $CDCl_3$



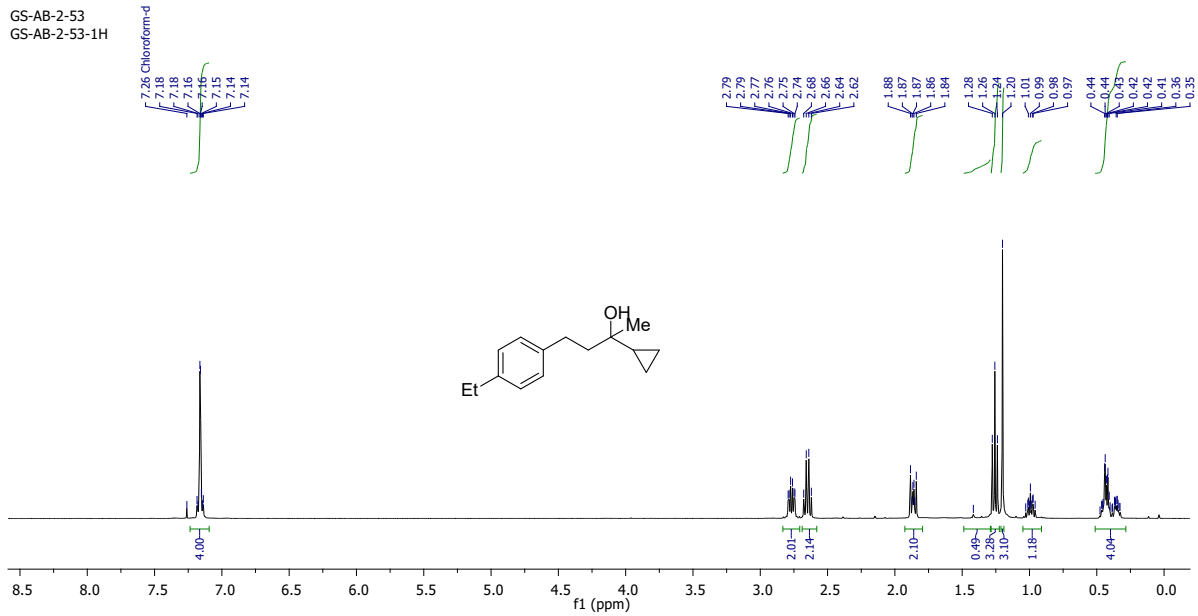
^{13}C{^{1}H}-NMR (151 MHz) spectrum of **3db** in $CDCl_3$



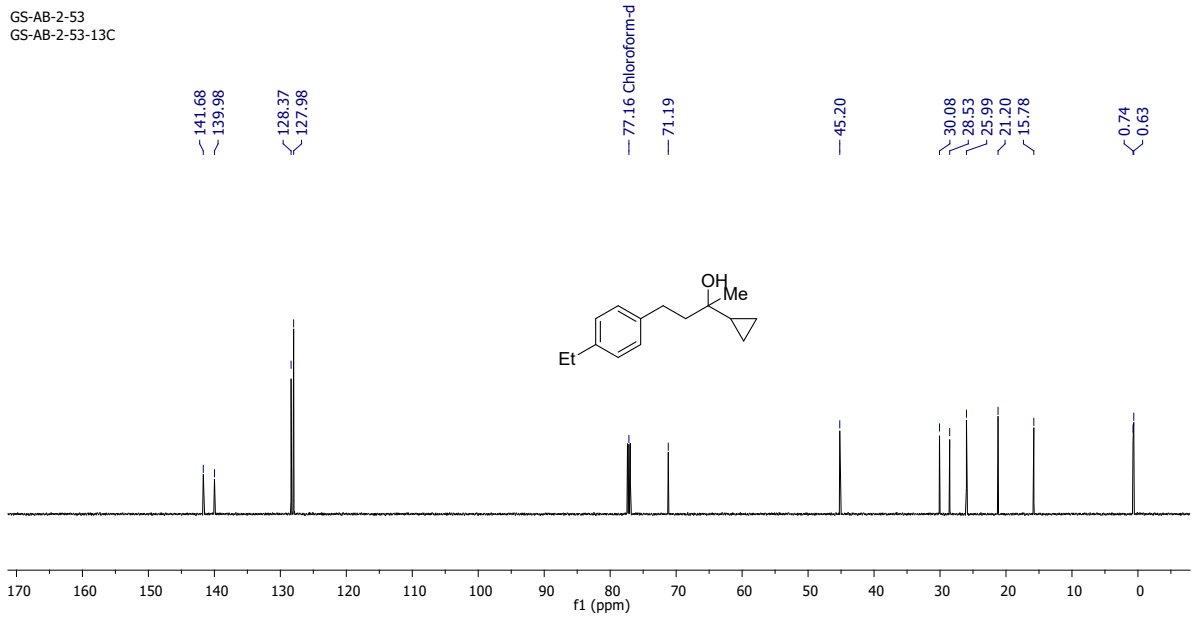
^{19}F-NMR (565 MHz) spectrum of **3db** in $CDCl_3$



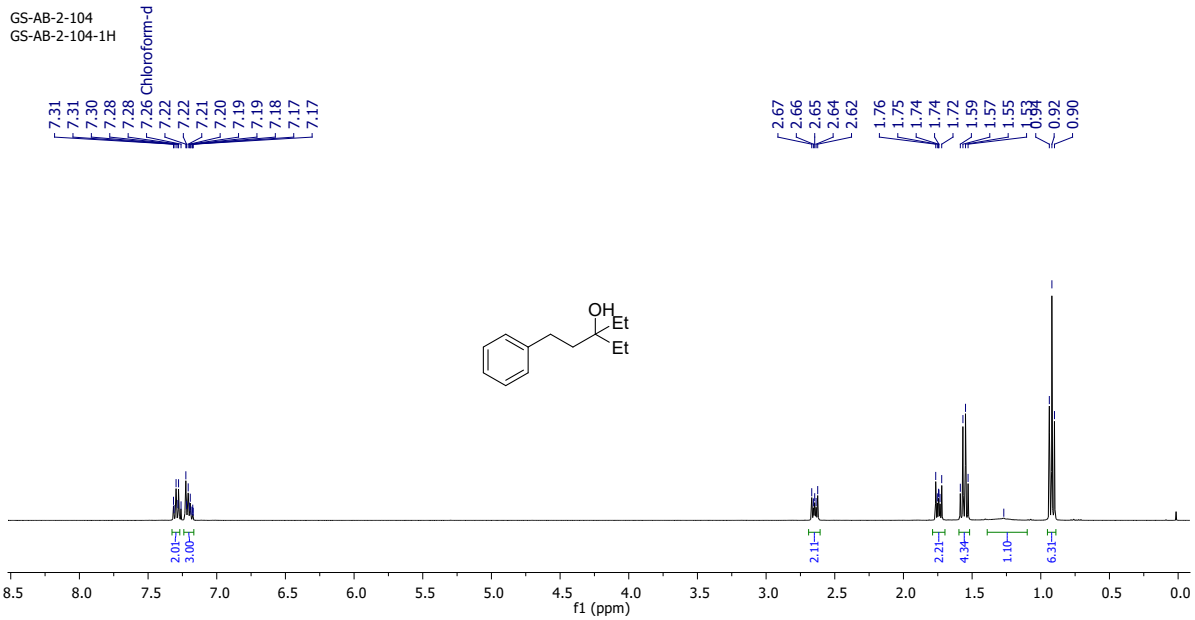
^{1}H-NMR (400 MHz) spectrum of **3eb** in $CDCl_3$



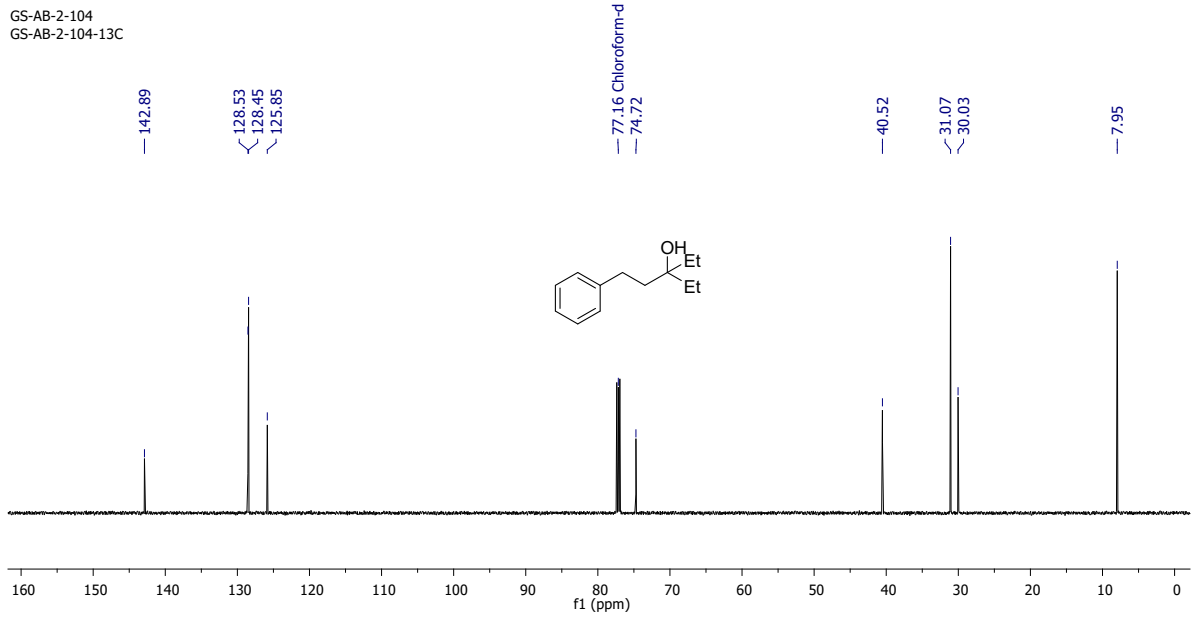
^{13}C{^{1}H}-NMR (151 MHz) spectrum of **3eb** in $CDCl_3$



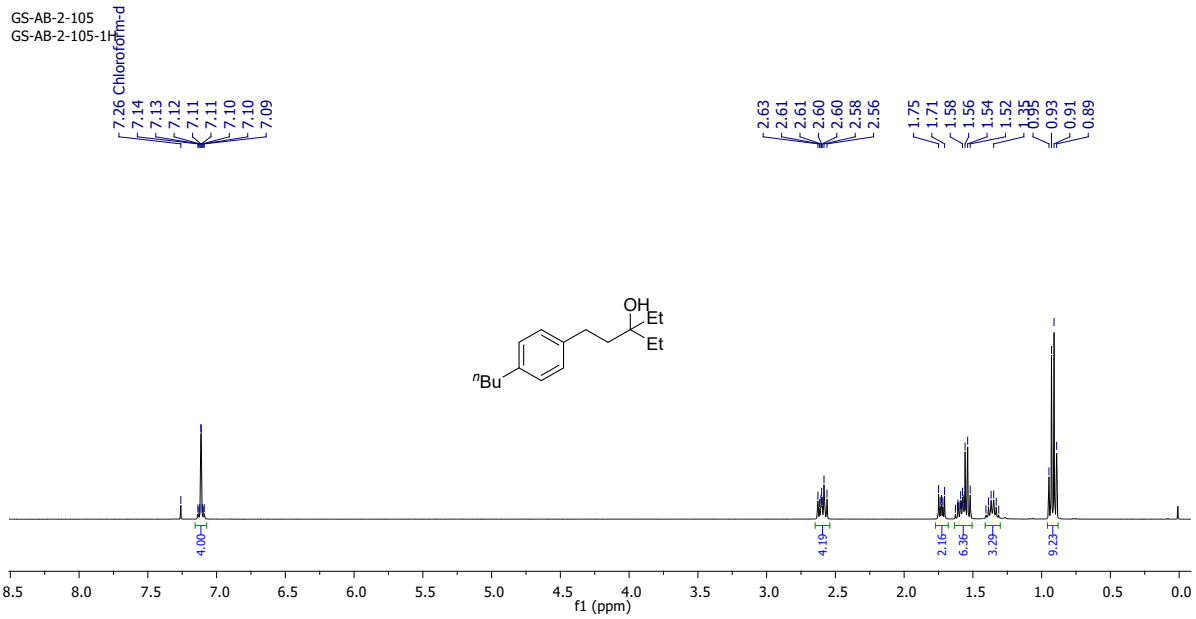
^{1}H-NMR (400 MHz) spectrum of **3ac** in $CDCl_3$



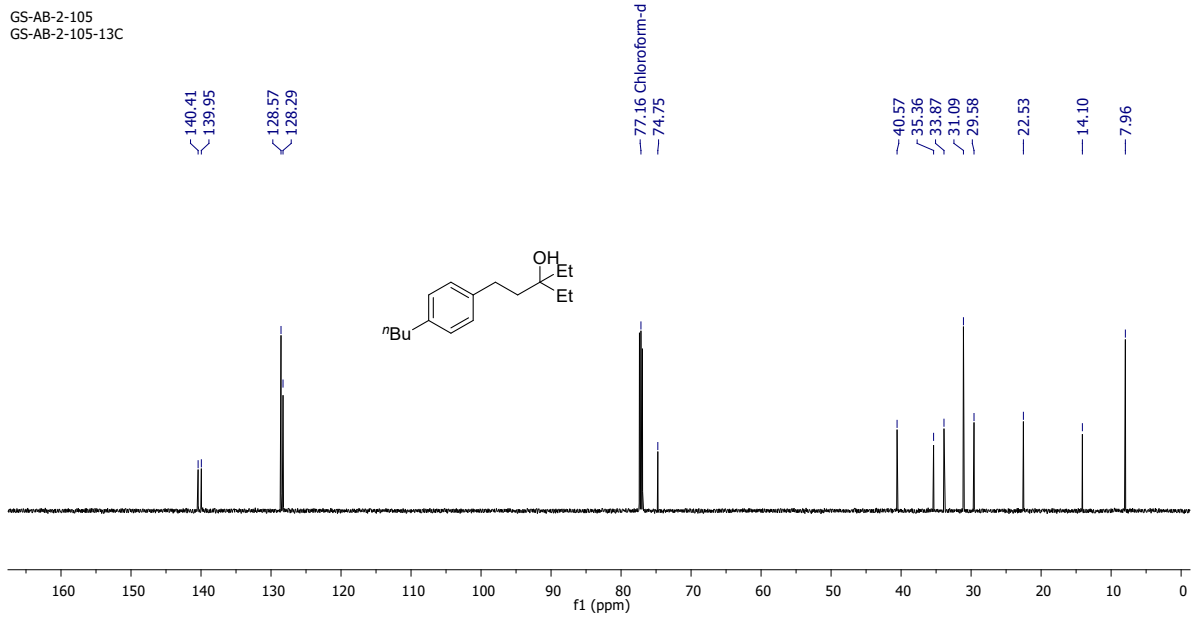
^{13}C{^{1}H}-NMR (151 MHz) spectrum of **3ac** in $CDCl_3$



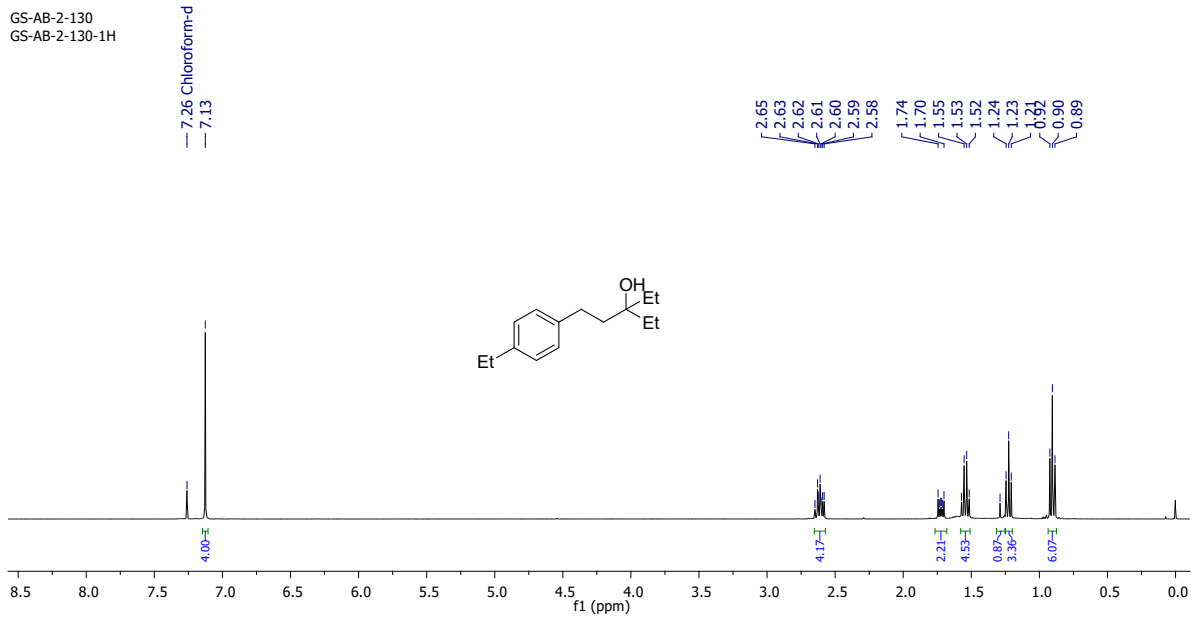
^{1}H-NMR (400 MHz) spectrum of **3bc** in $CDCl_3$



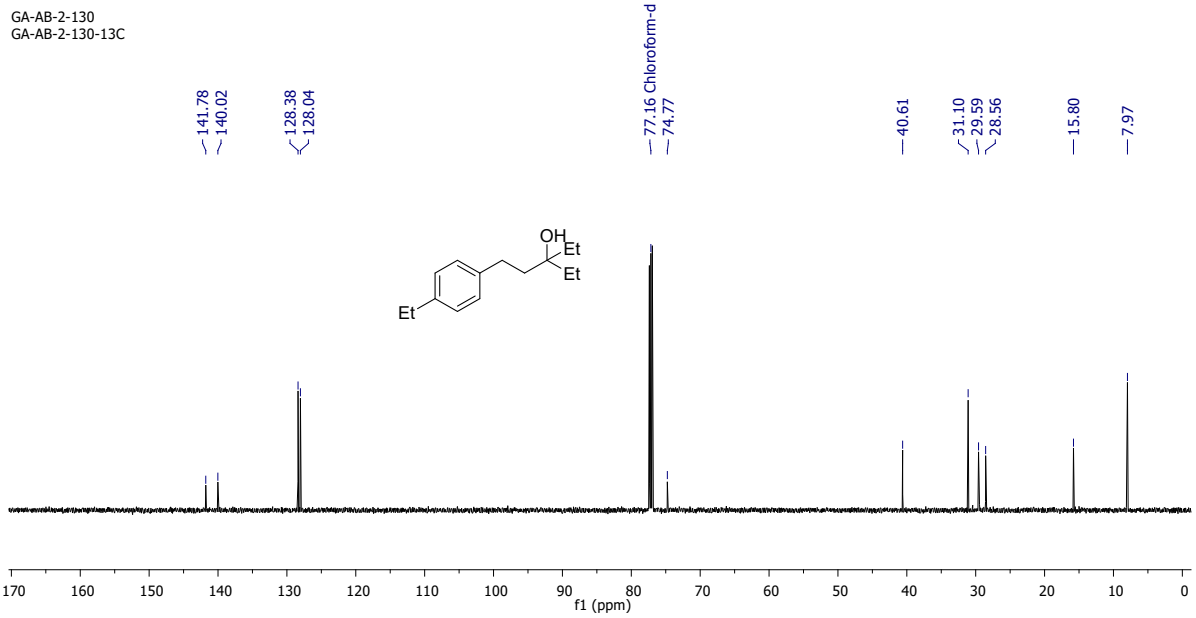
^{13}C{^{1}H}-NMR (151 MHz) spectrum of **3bc** in $CDCl_3$



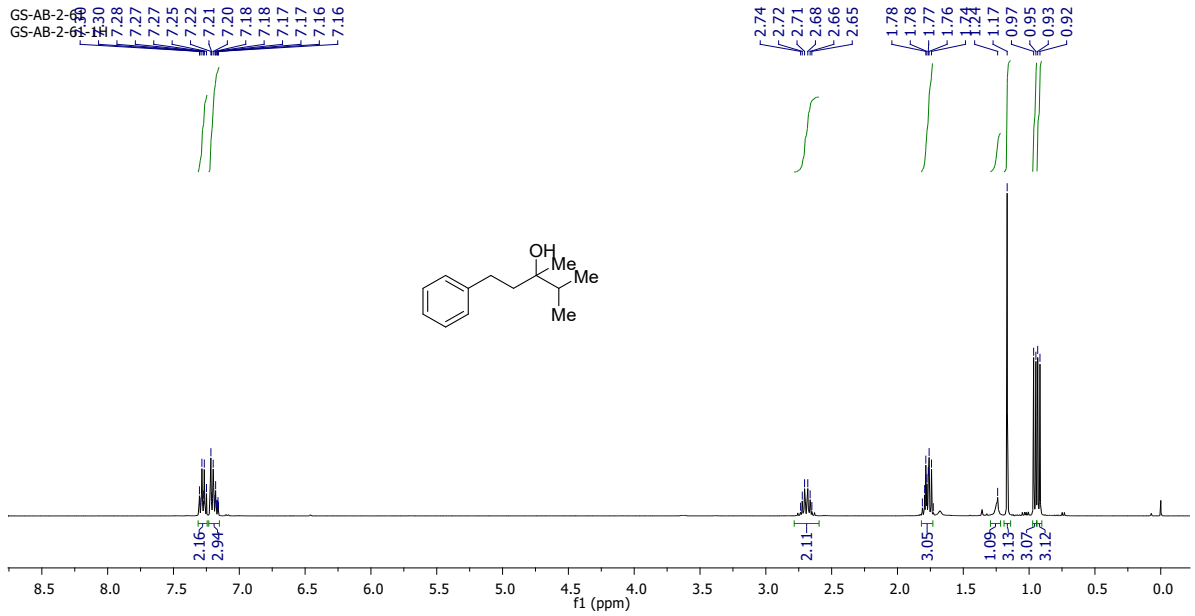
^{1}H-NMR (400 MHz) spectrum of **3ec** in $CDCl_3$



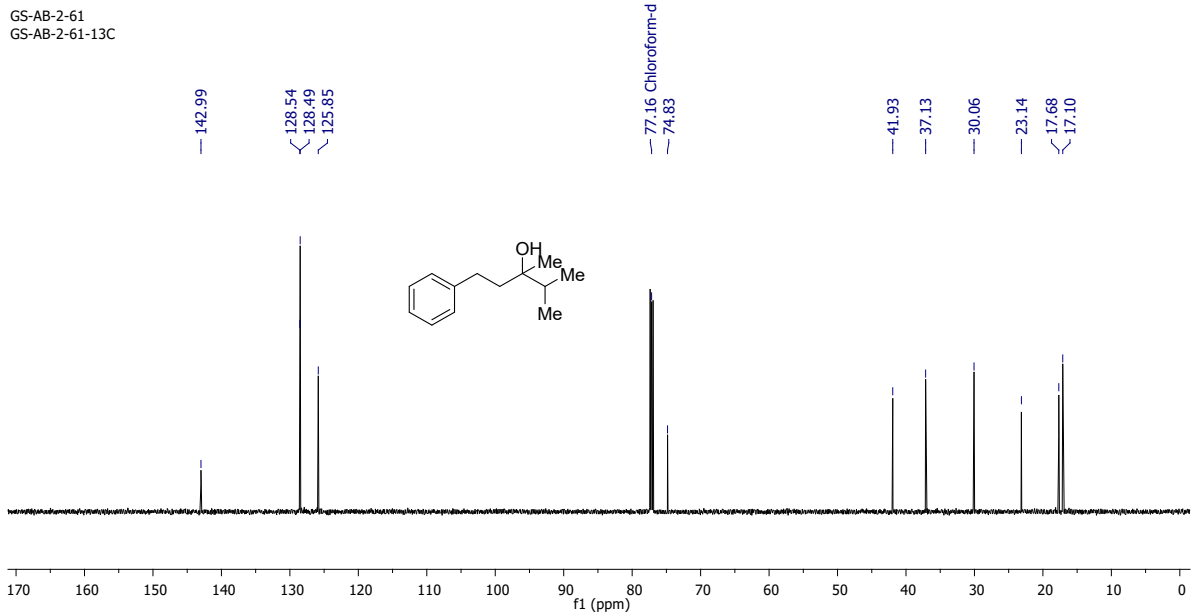
^{13}C{^{1}H}-NMR (151 MHz) spectrum of **3ec** in $CDCl_3$



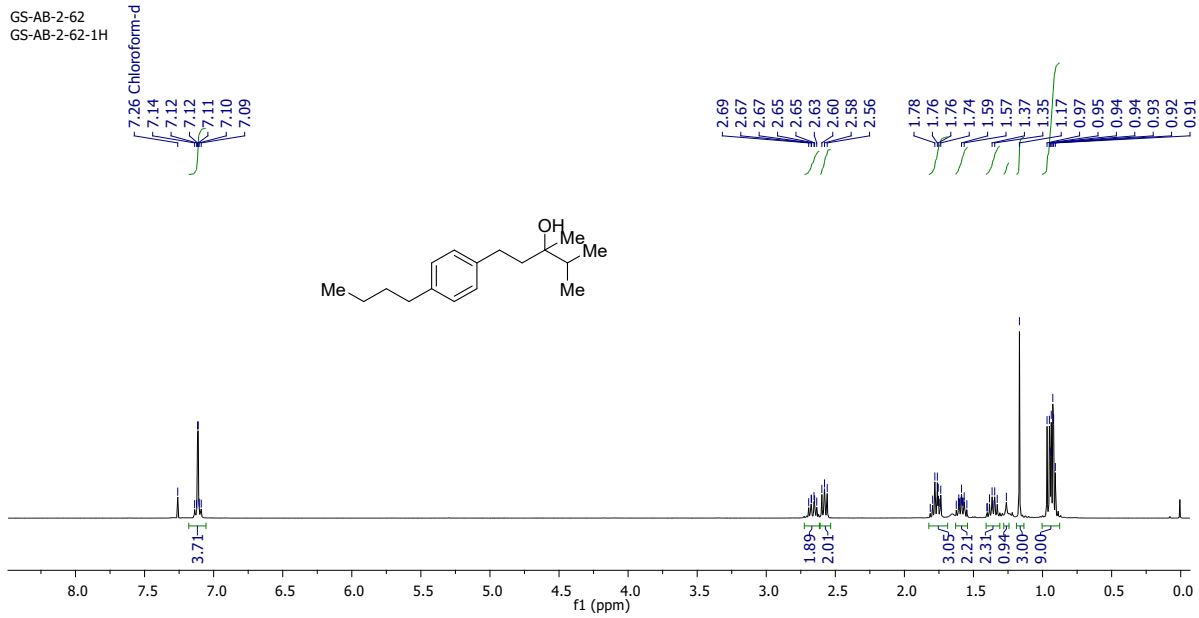
^{1}H-NMR (400 MHz) spectrum of **3ad** in $CDCl_3$



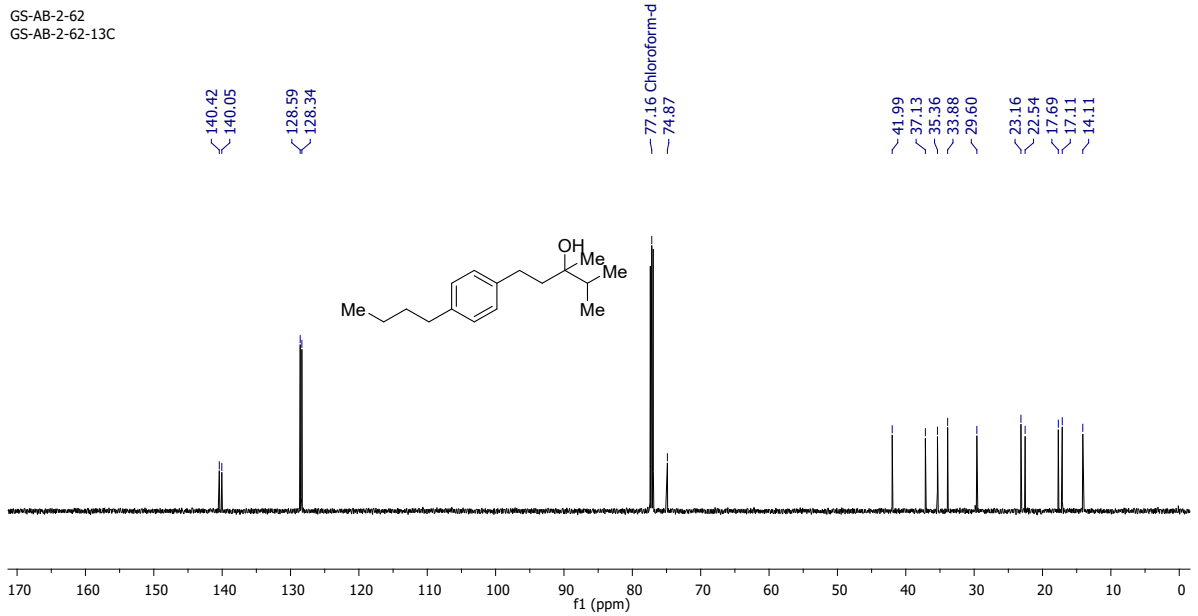
^{13}C{^{1}H}-NMR (151 MHz) spectrum of **3ad** in $CDCl_3$



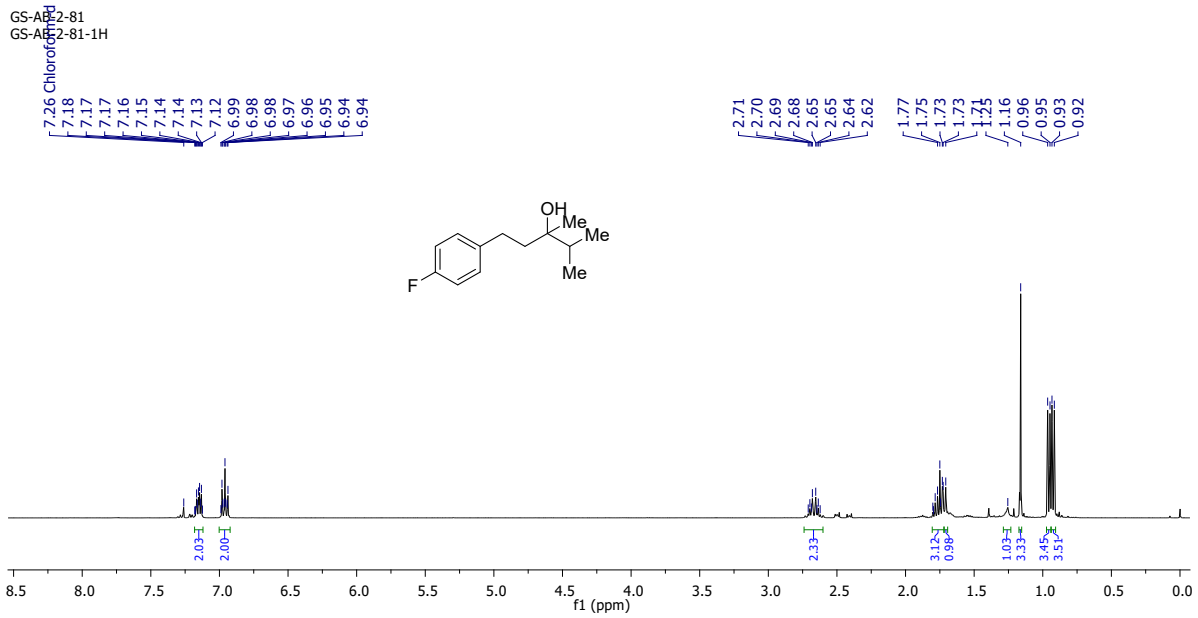
^{1}H-NMR (400 MHz) spectrum of **3bd** in $CDCl_3$



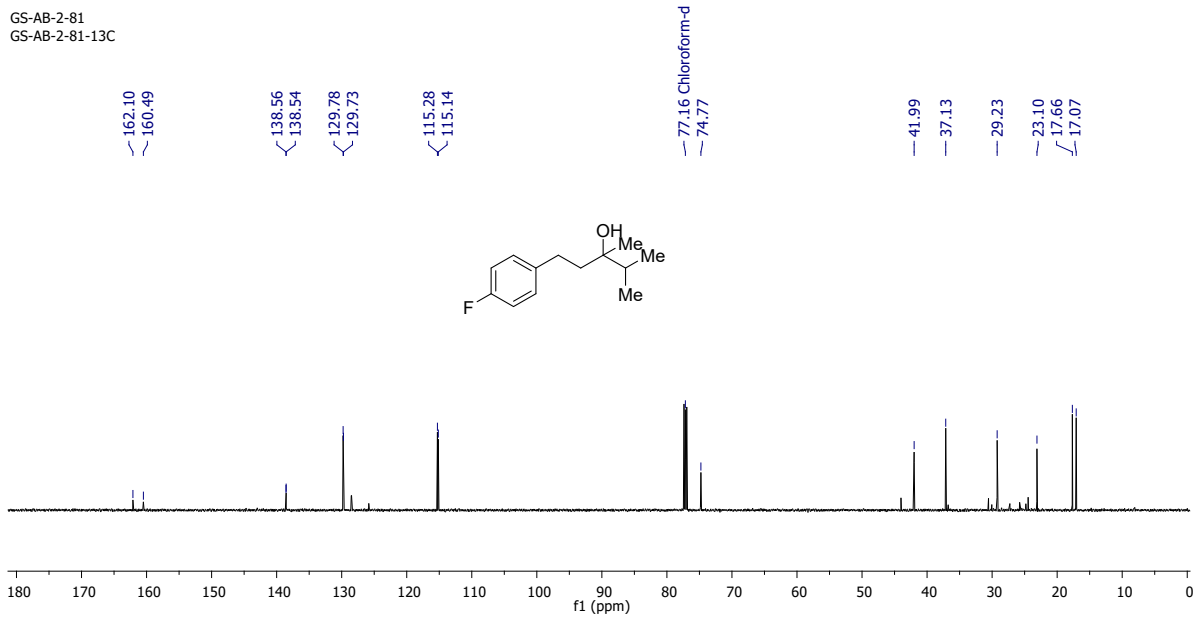
^{13}C{^{1}H}-NMR (151 MHz) spectrum of **3bd** in $CDCl_3$



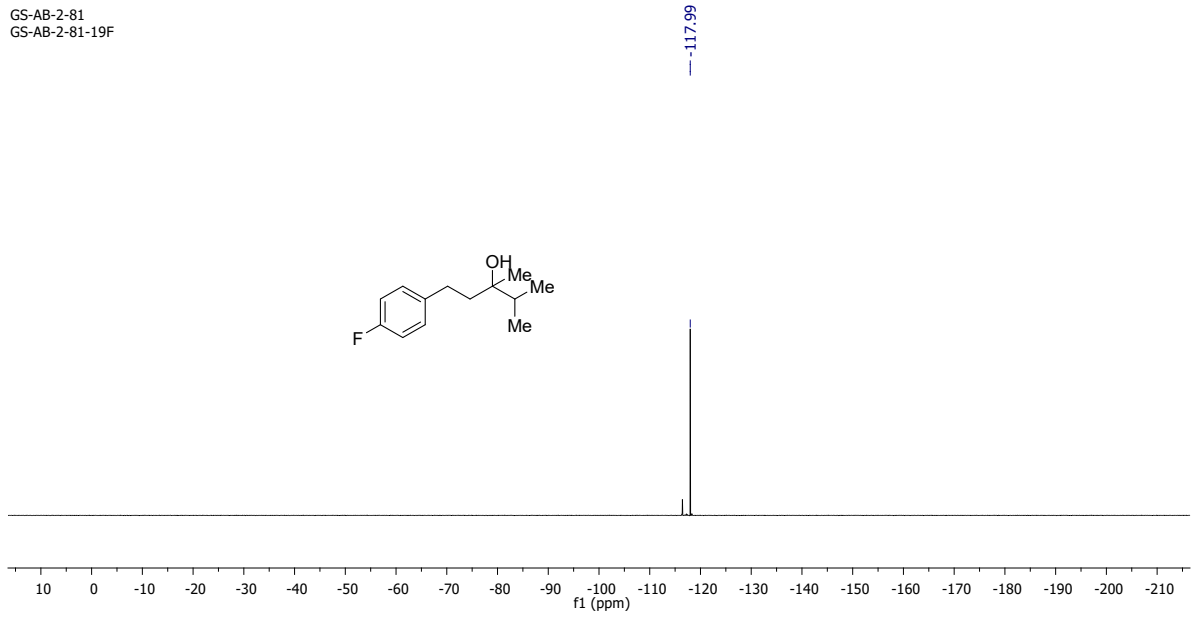
^{1}H-NMR (400 MHz) spectrum of **3dd** in $CDCl_3$



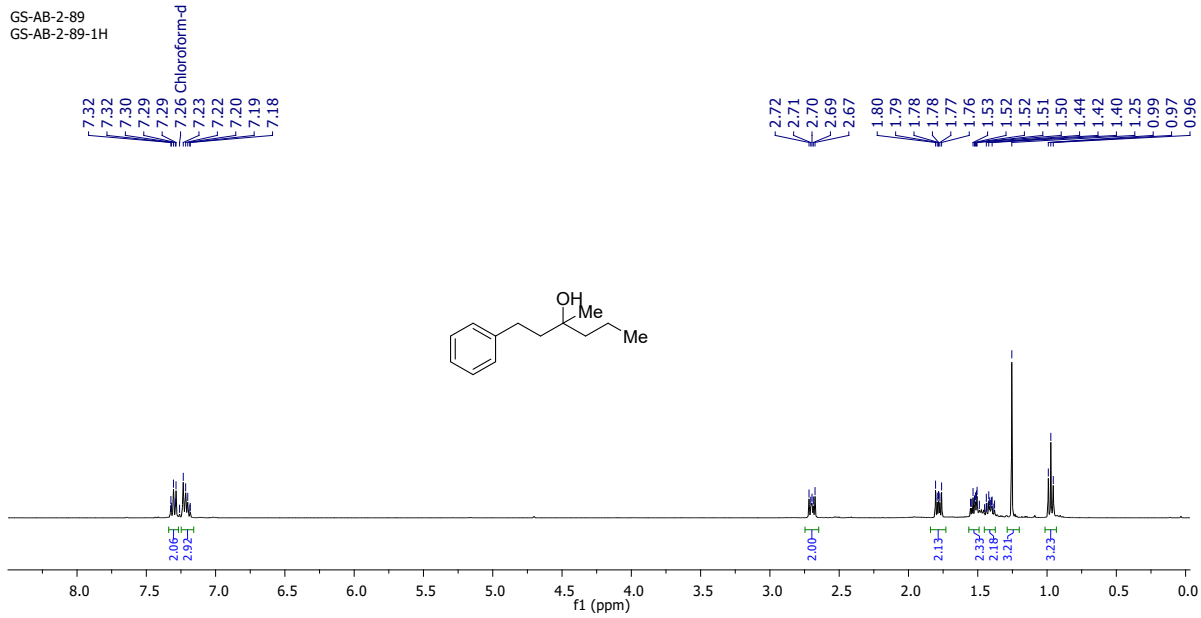
^{13}C{^{1}H}-NMR (151 MHz) spectrum of **3dd** in $CDCl_3$



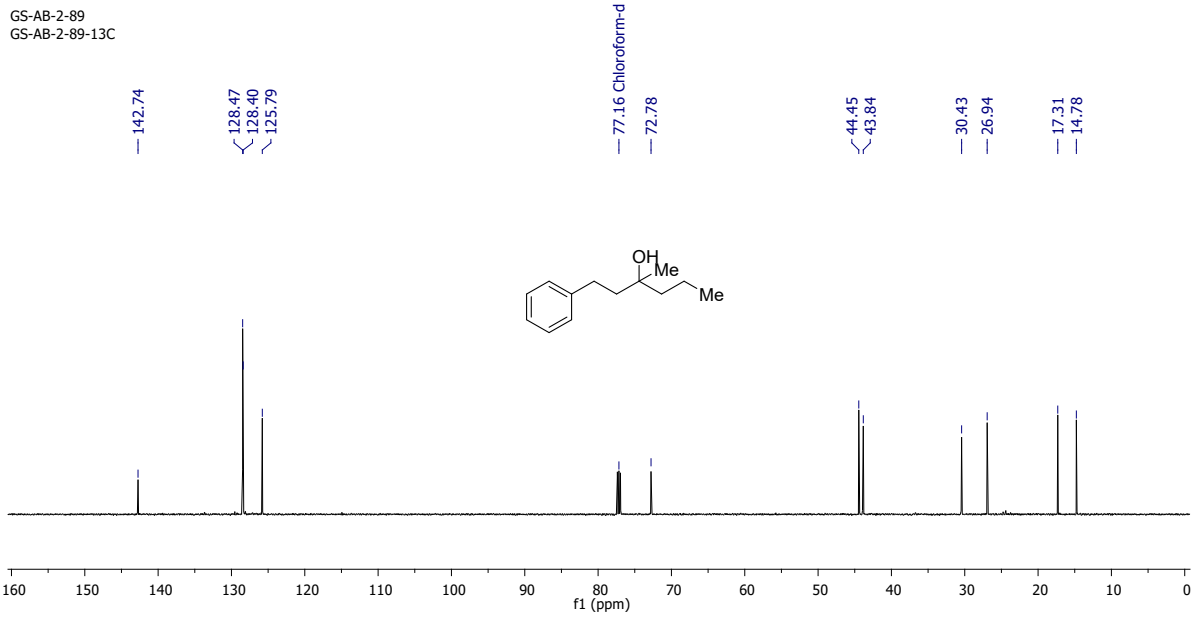
^{19}F-NMR (565 MHz) spectrum of **3dd** in $CDCl_3$



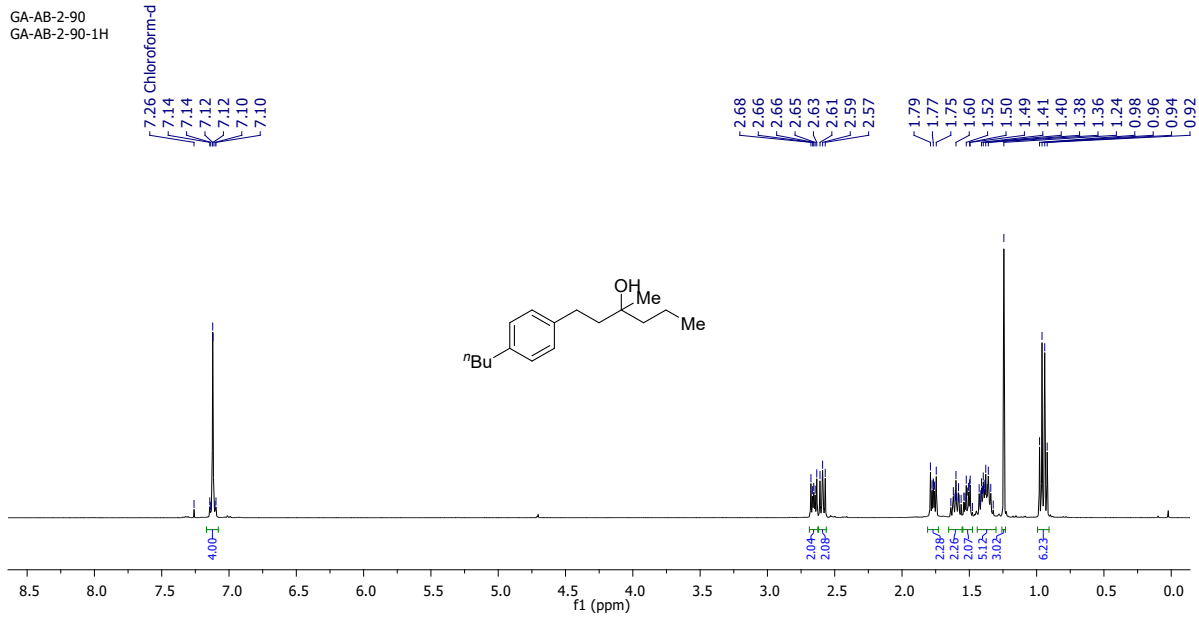
^{1}H-NMR (400 MHz) spectrum of **3ae** in $CDCl_3$



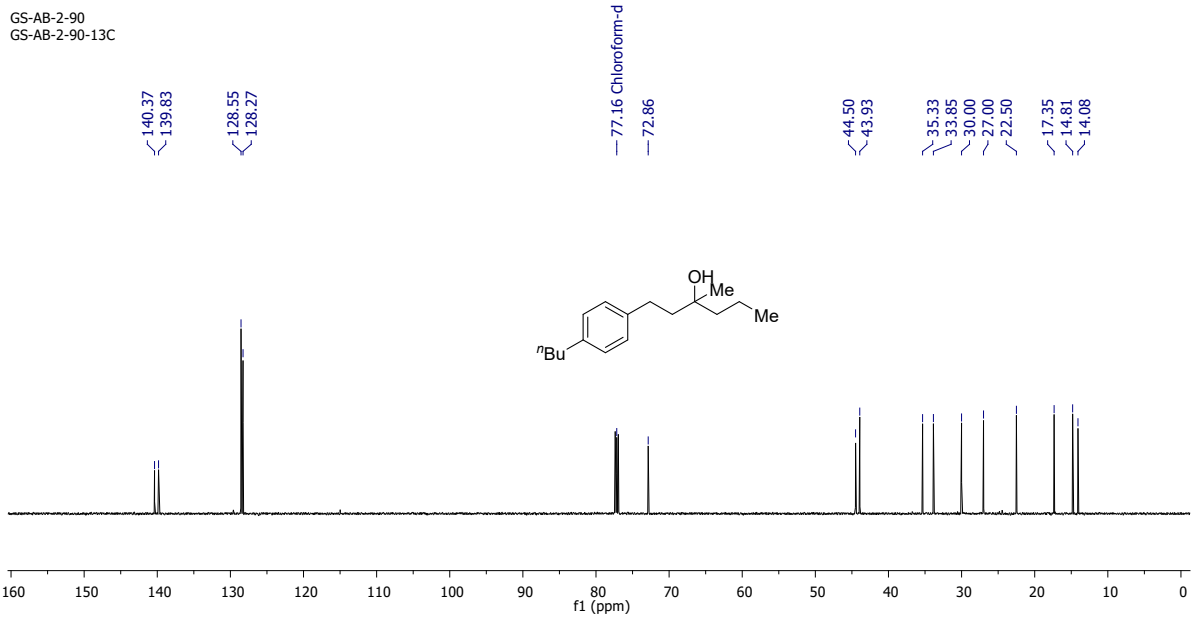
^{13}C{^{1}H}-NMR (151 MHz) spectrum of **3ae** in $CDCl_3$



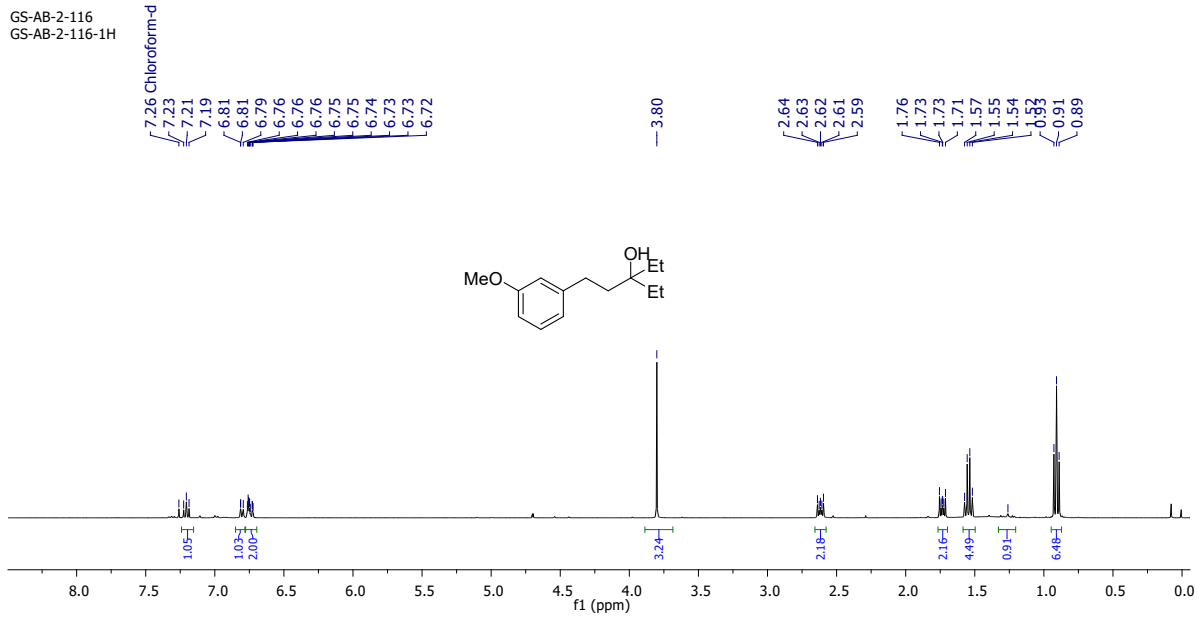
^{1}H-NMR (400 MHz) spectrum of **3be** in $CDCl_3$



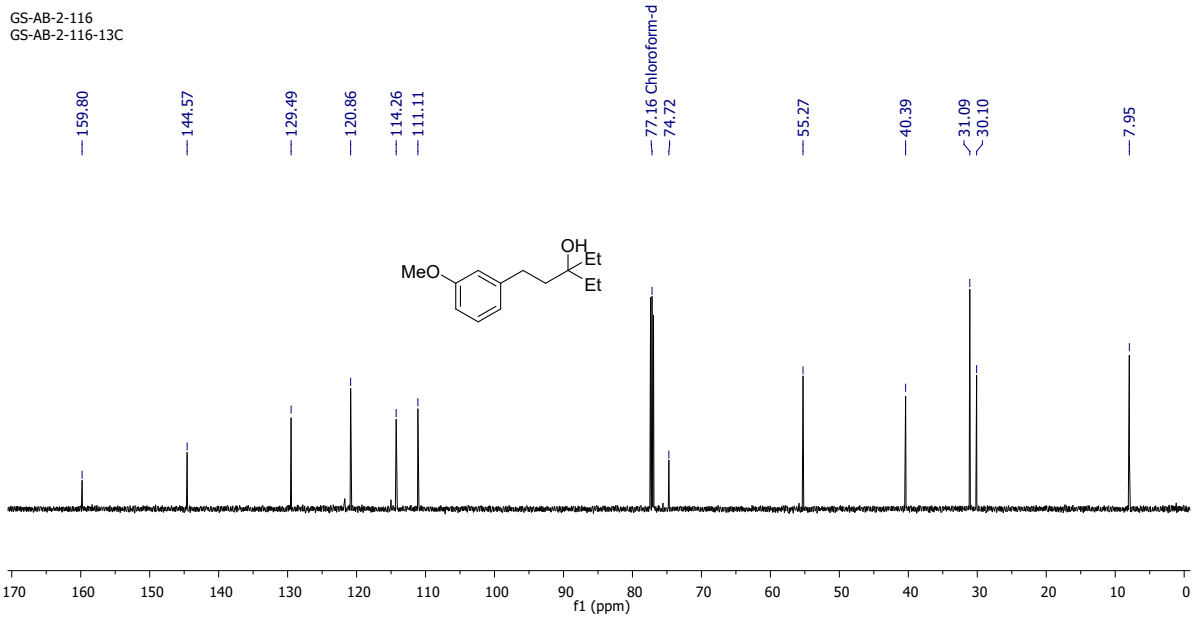
^{13}C{^{1}H}-NMR (151 MHz) spectrum of **3be** in $CDCl_3$



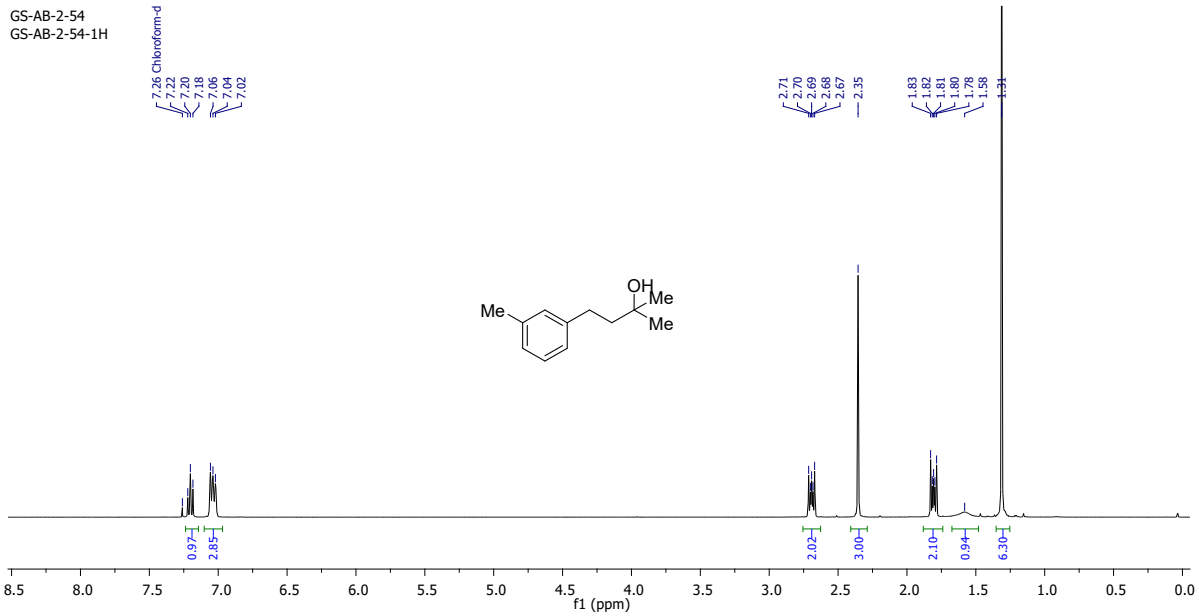
^{1}H-NMR (400 MHz) spectrum of **3kc** in $CDCl_3$



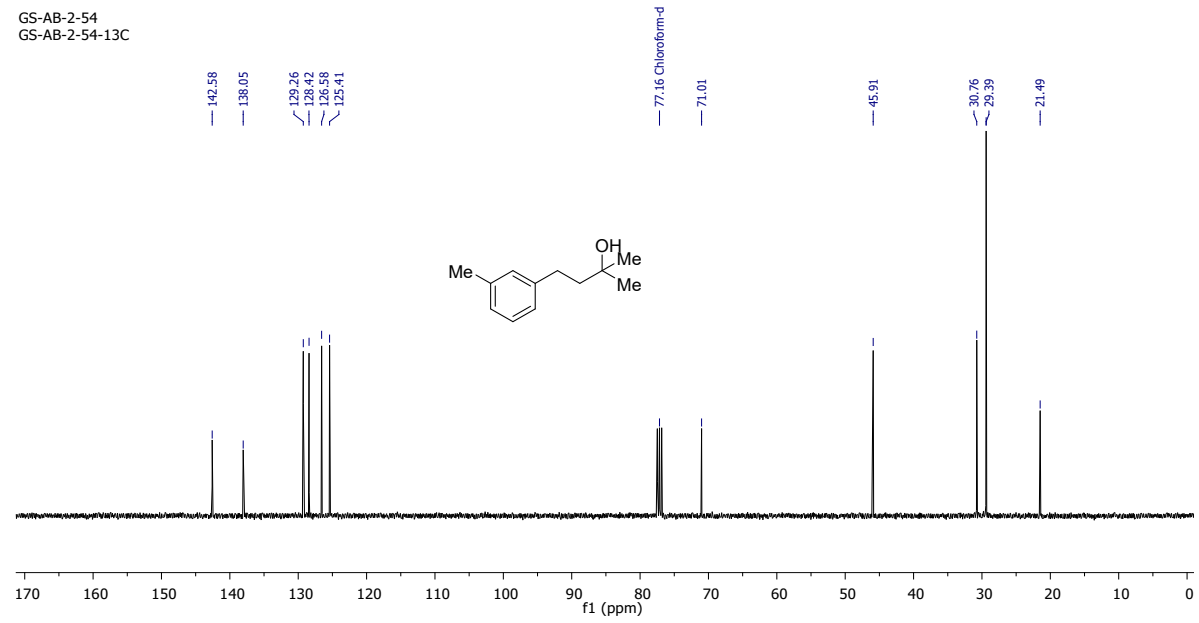
^{13}C{^{1}H}-NMR (151 MHz) spectrum of **3kc** in $CDCl_3$



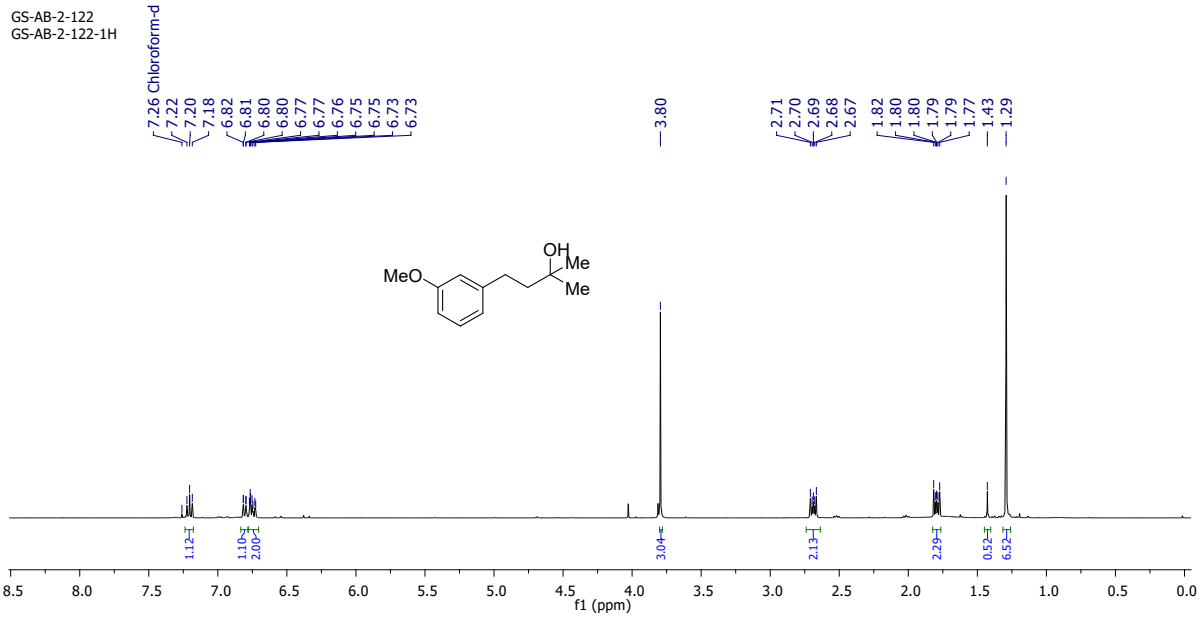
^{1}H-NMR (400 MHz) spectrum of **3ja** in $CDCl_3$



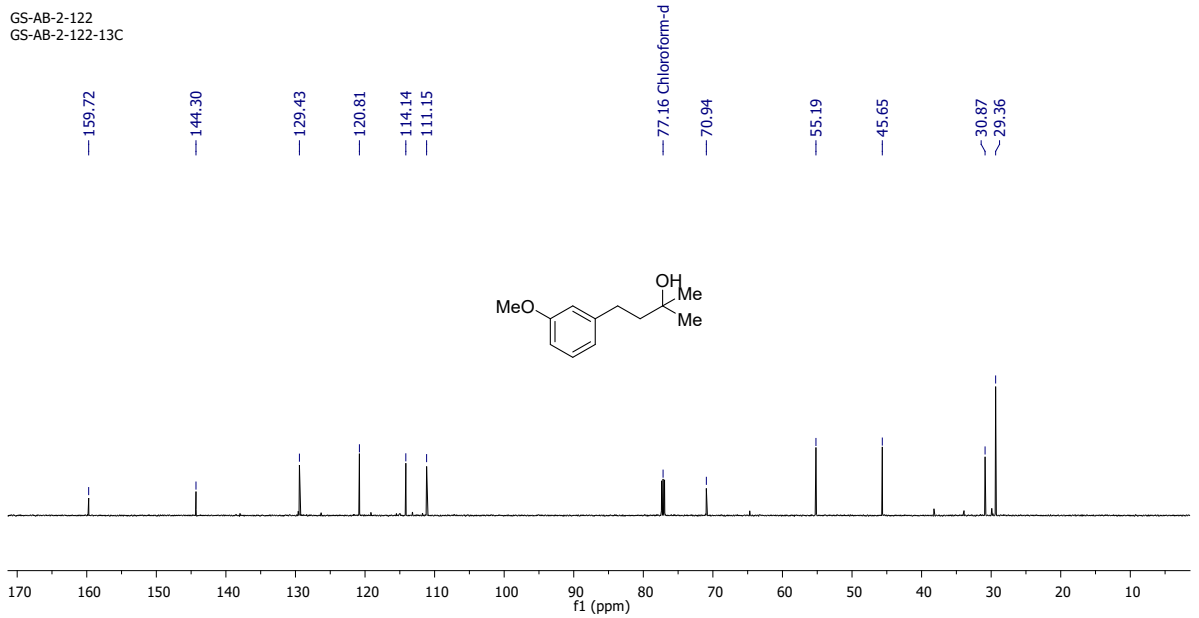
^{13}C{^{1}H}-NMR (100 MHz) spectrum of **3ja** in $CDCl_3$



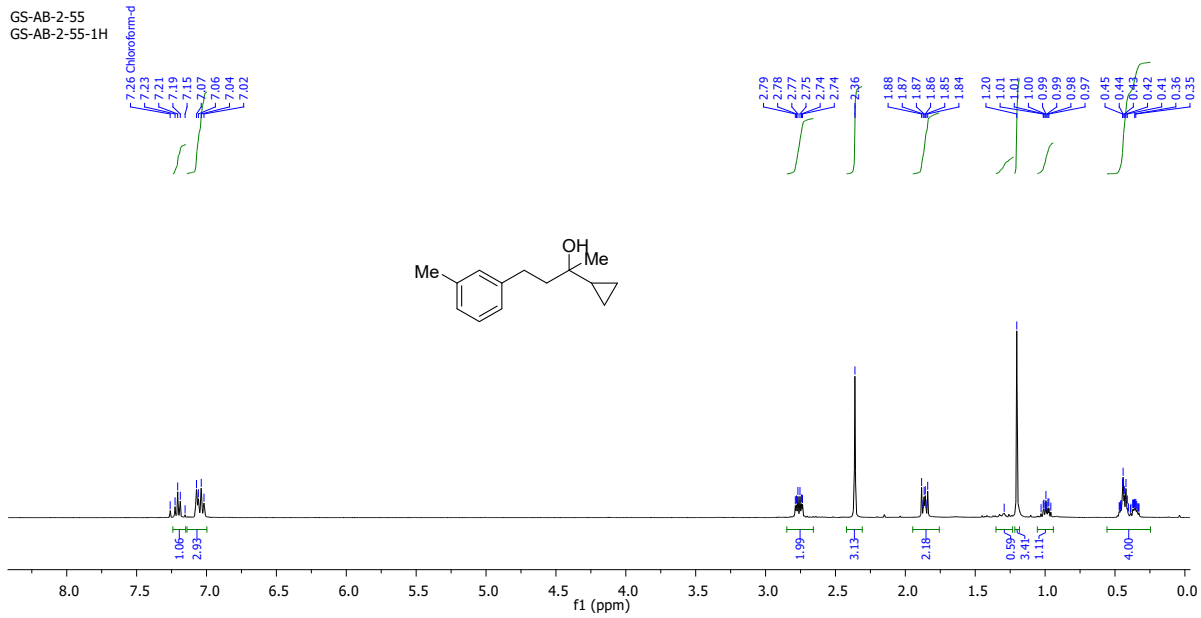
^{1}H-NMR (400 MHz) spectrum of **3ka** in $CDCl_3$



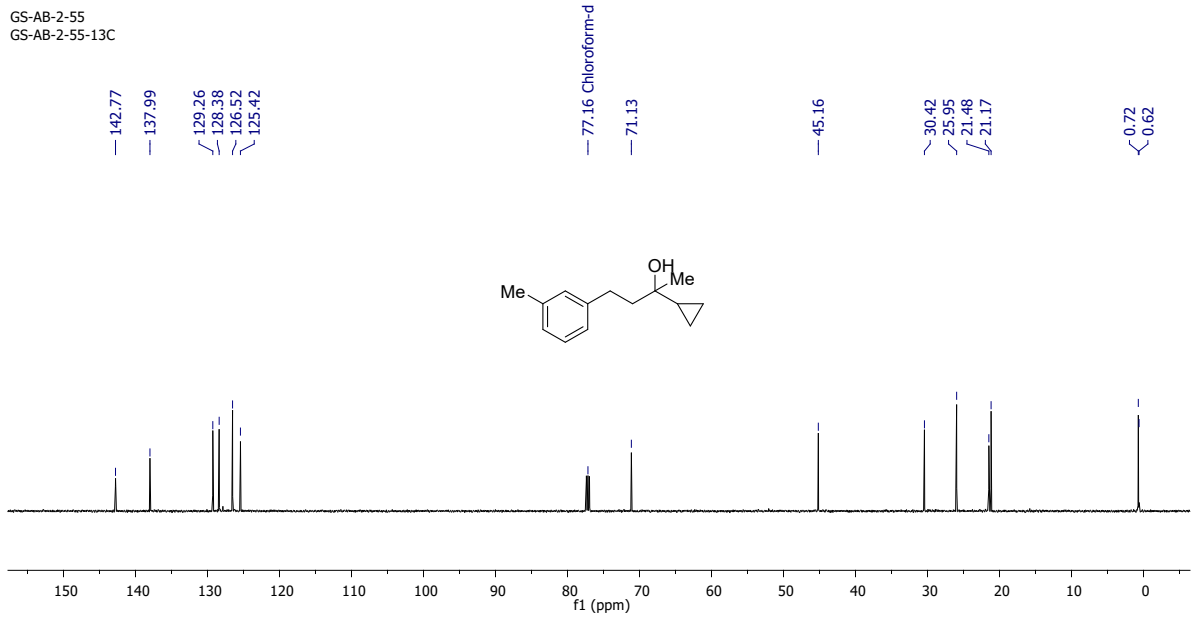
^{13}C{^{1}H}-NMR (151 MHz) spectrum of **3ka** in $CDCl_3$



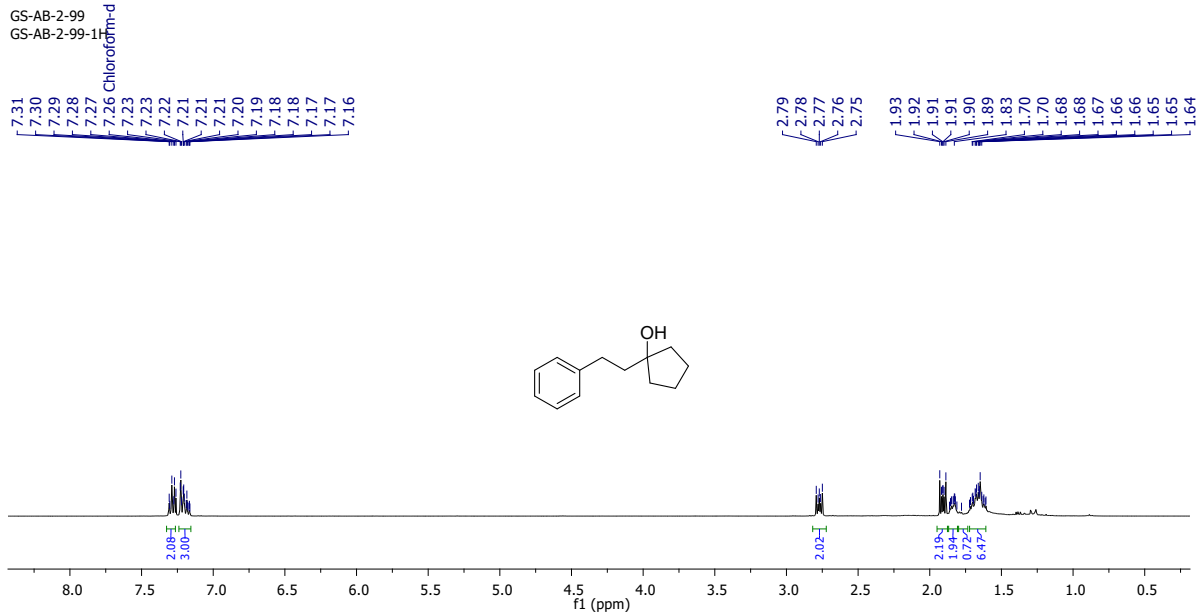
^{1}H-NMR (400 MHz) spectrum of **3jb** in $CDCl_3$



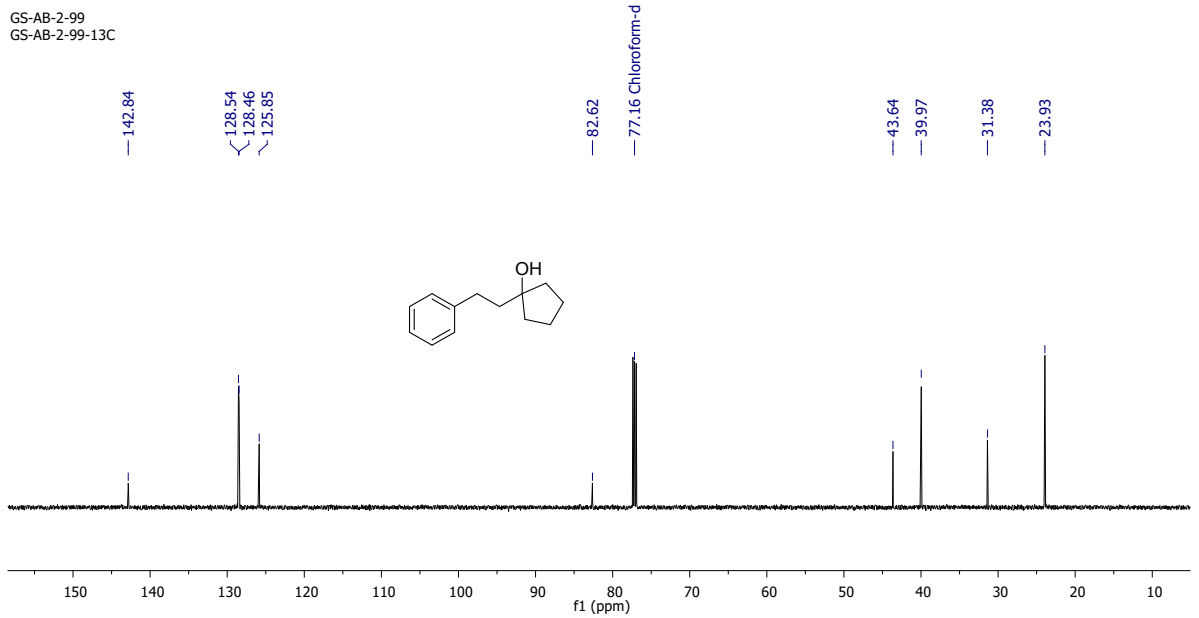
^{13}C{^{1}H}-NMR (151 MHz) spectrum of **3jb** in $CDCl_3$



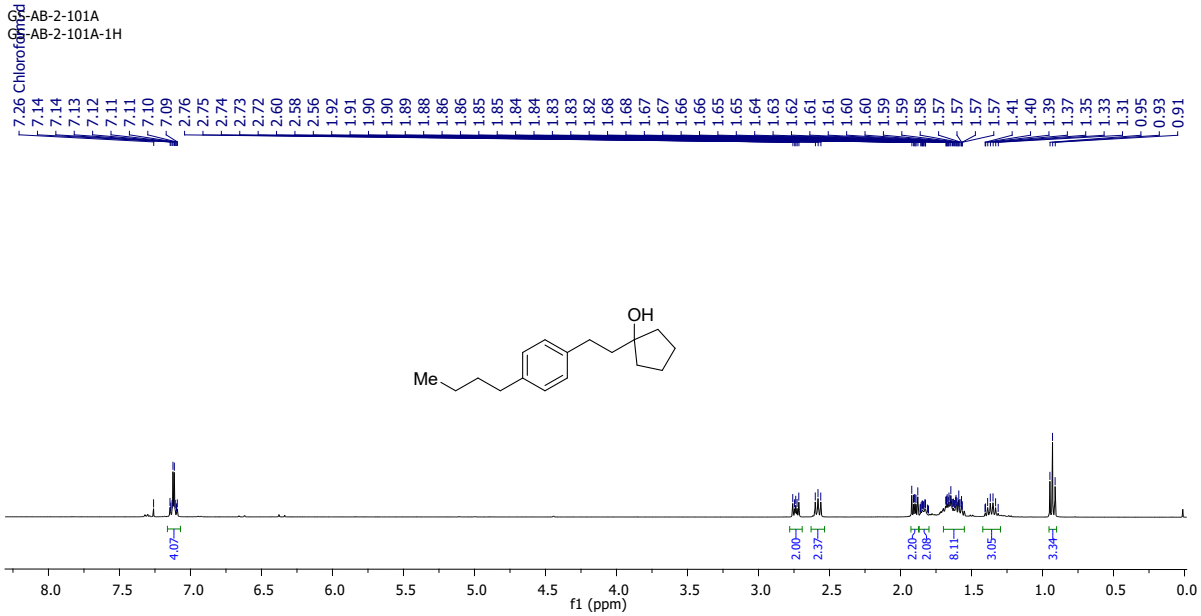
^{1}H-NMR (400 MHz) spectrum of **3af** in $CDCl_3$



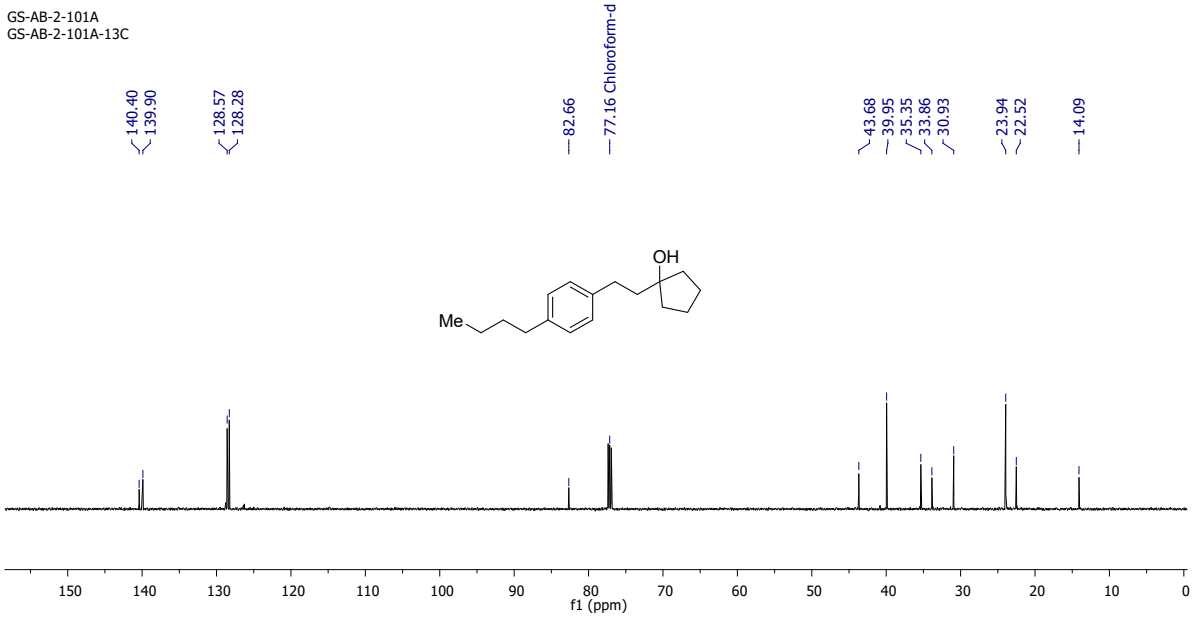
^{13}C{^{1}H}-NMR (151 MHz) spectrum of **3af** in $CDCl_3$



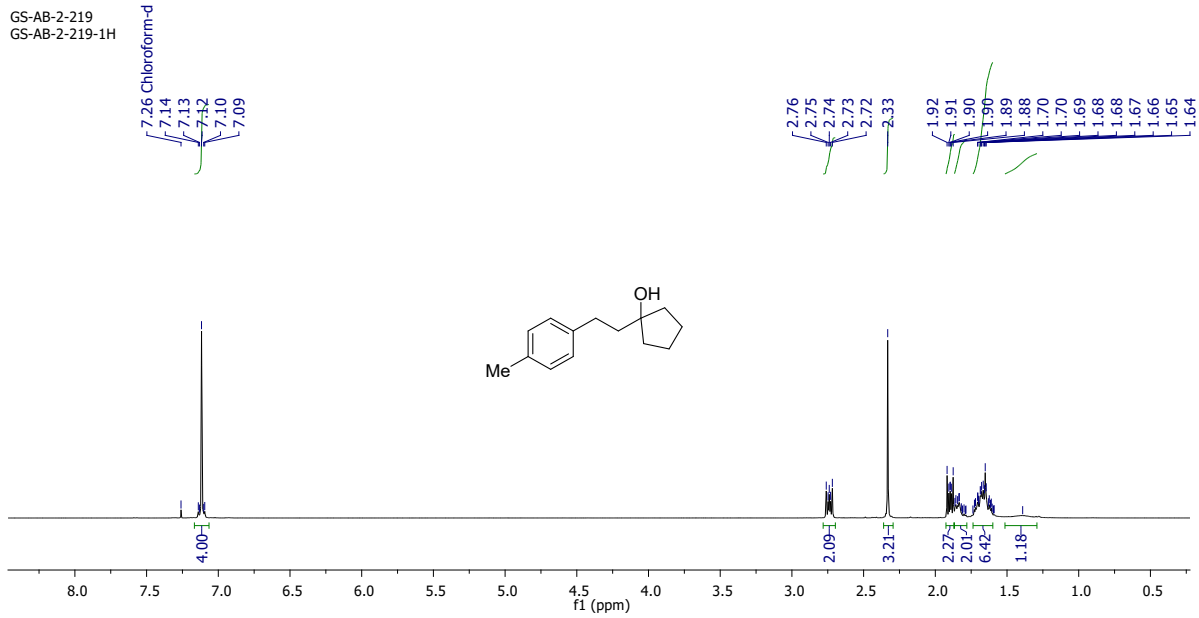
^{1}H-NMR (400 MHz) spectrum of **3bf** in $CDCl_3$



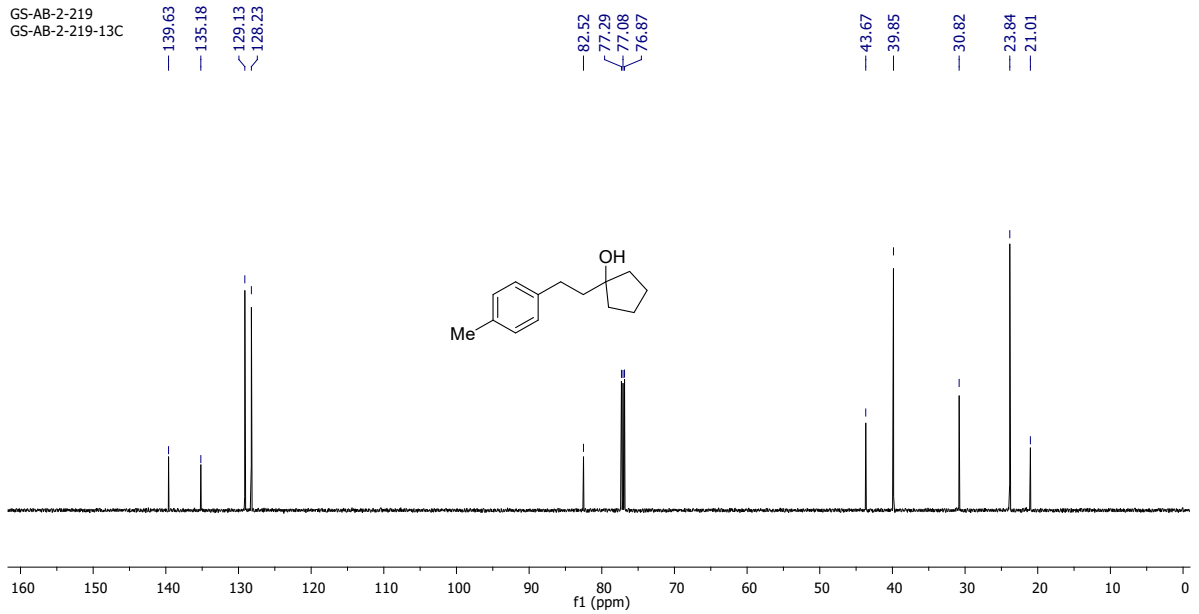
^{13}C{^{1}H}-NMR (151 MHz) spectrum of **3bf** in $CDCl_3$



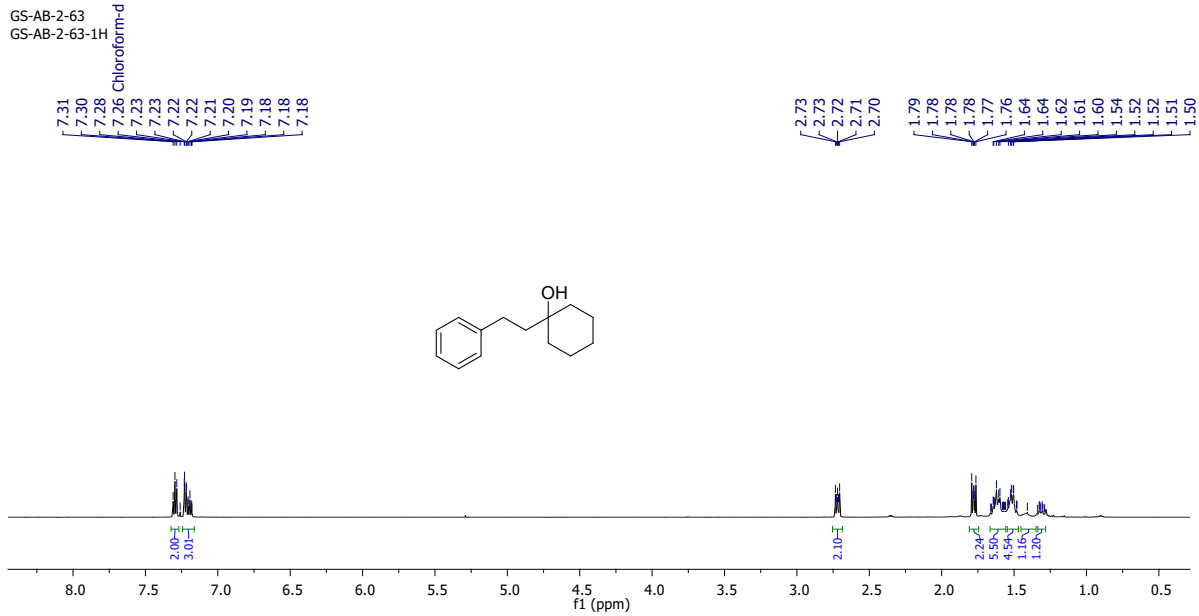
^{1}H-NMR (400 MHz) spectrum of **3ff** in $CDCl_3$



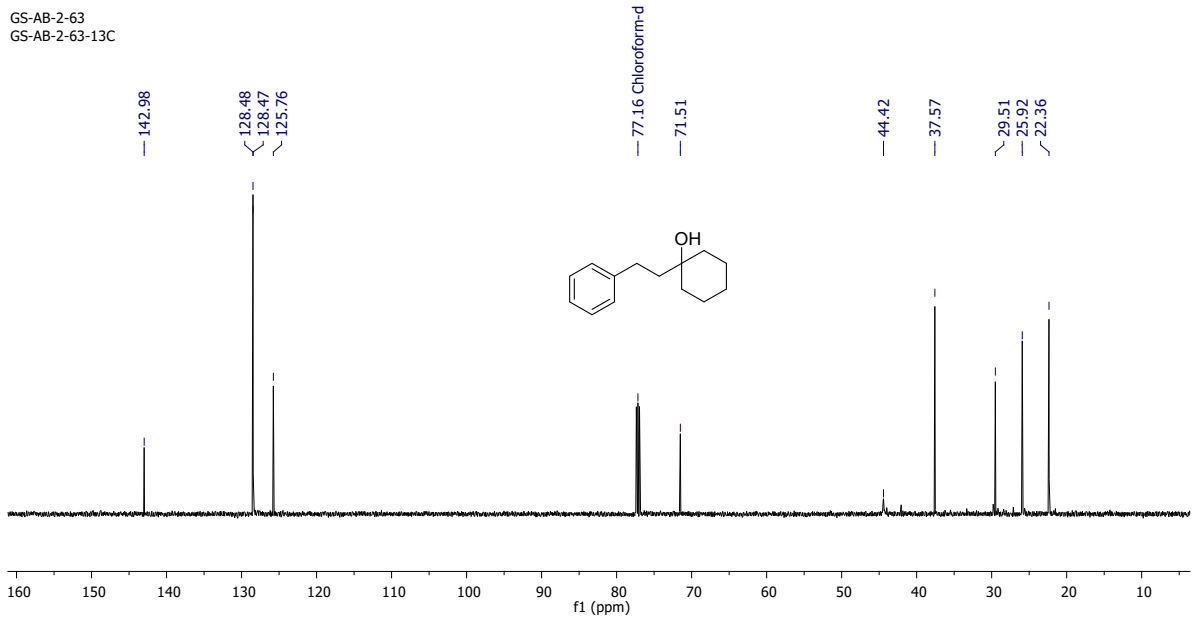
^{13}C{^{1}H}-NMR (151 MHz) spectrum of **3ff** in $CDCl_3$



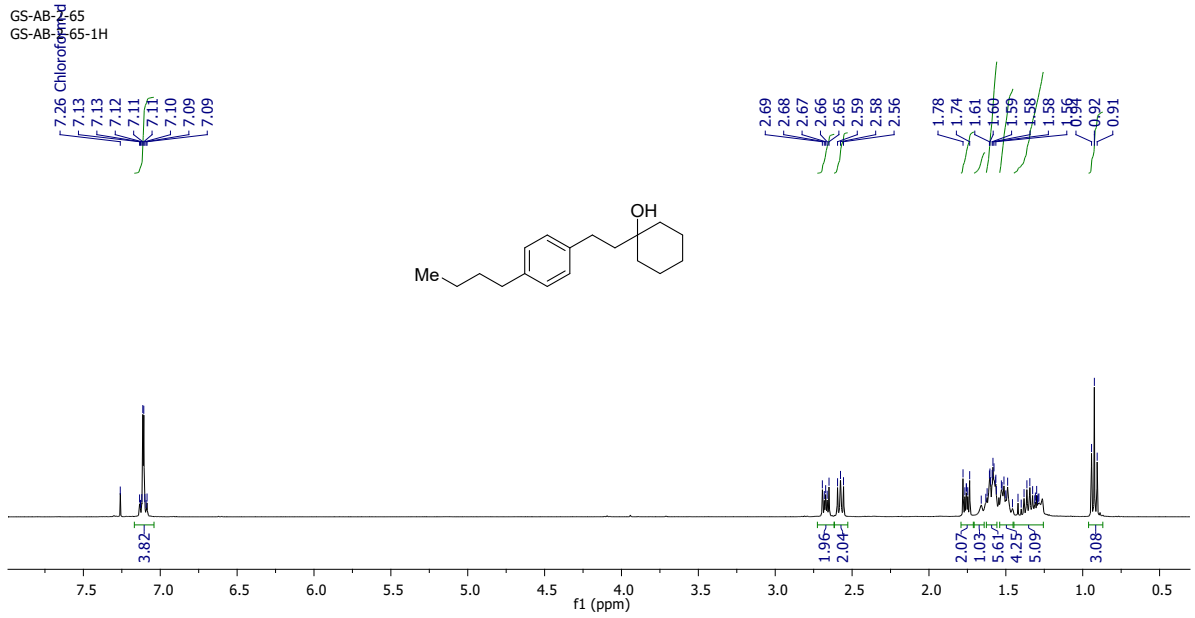
^{1}H-NMR (600 MHz) spectrum of **3ag** in $CDCl_3$



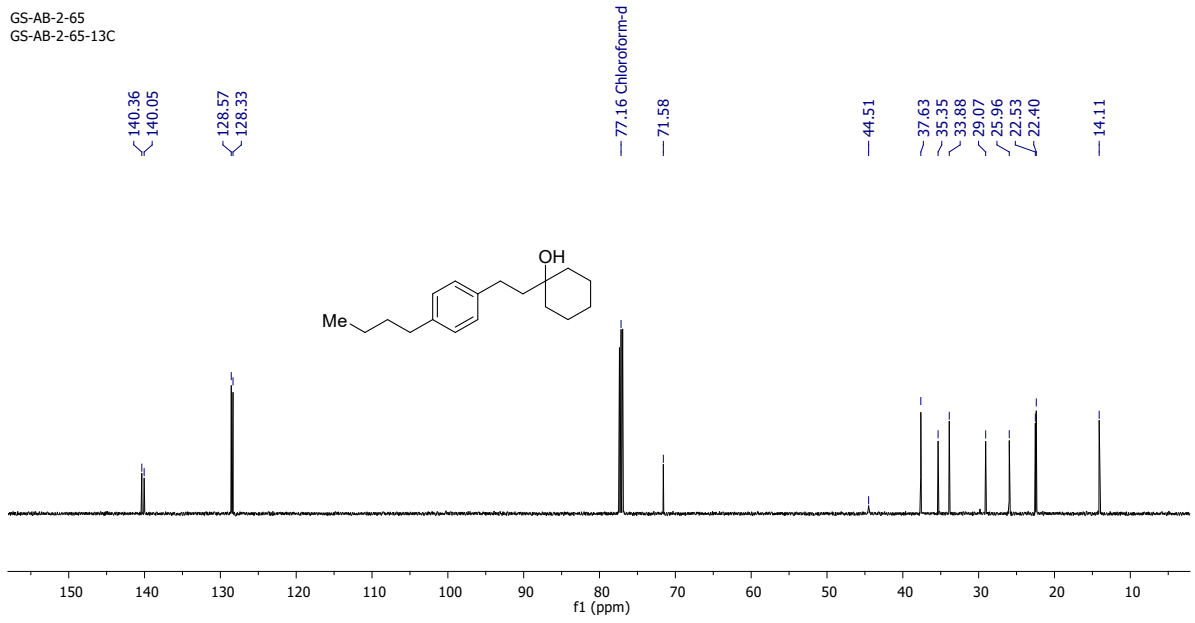
^{13}C{^{1}H}-NMR (151 MHz) spectrum of **3ag** in $CDCl_3$



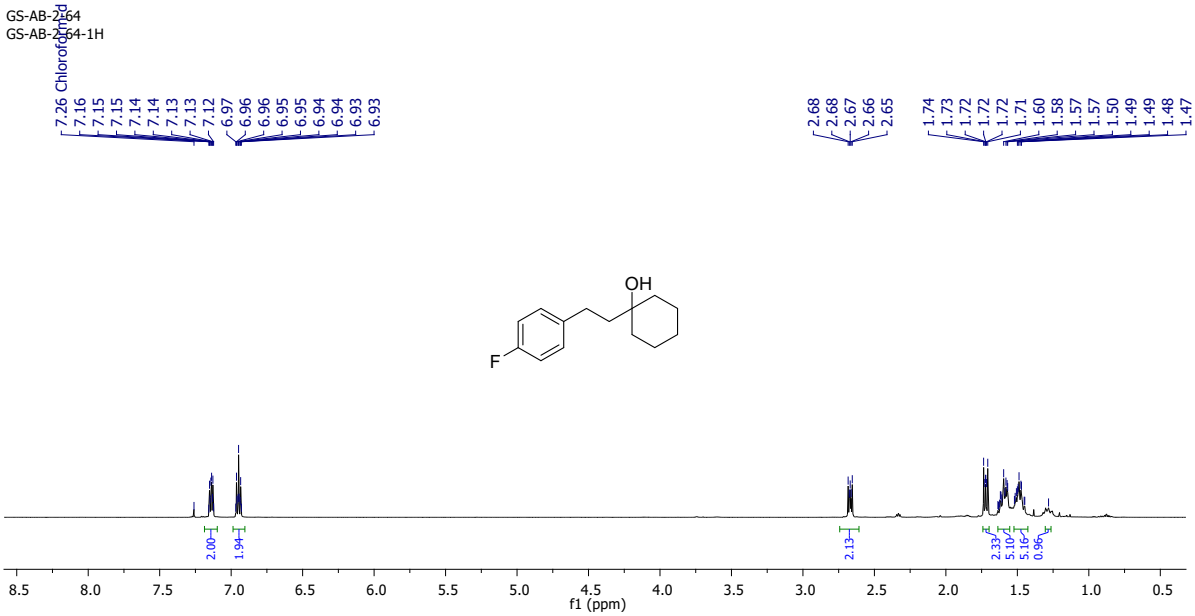
^{1}H-NMR (400 MHz) spectrum of **3bg** in $CDCl_3$



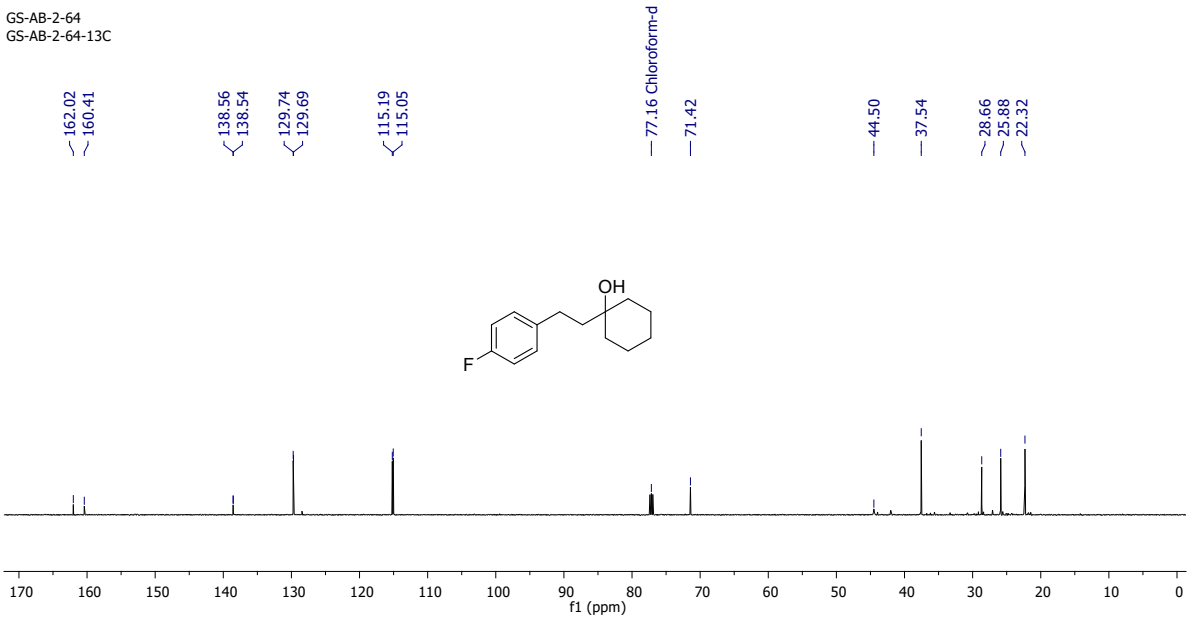
^{13}C{^{1}H}-NMR (151 MHz) spectrum of **3bg** in $CDCl_3$



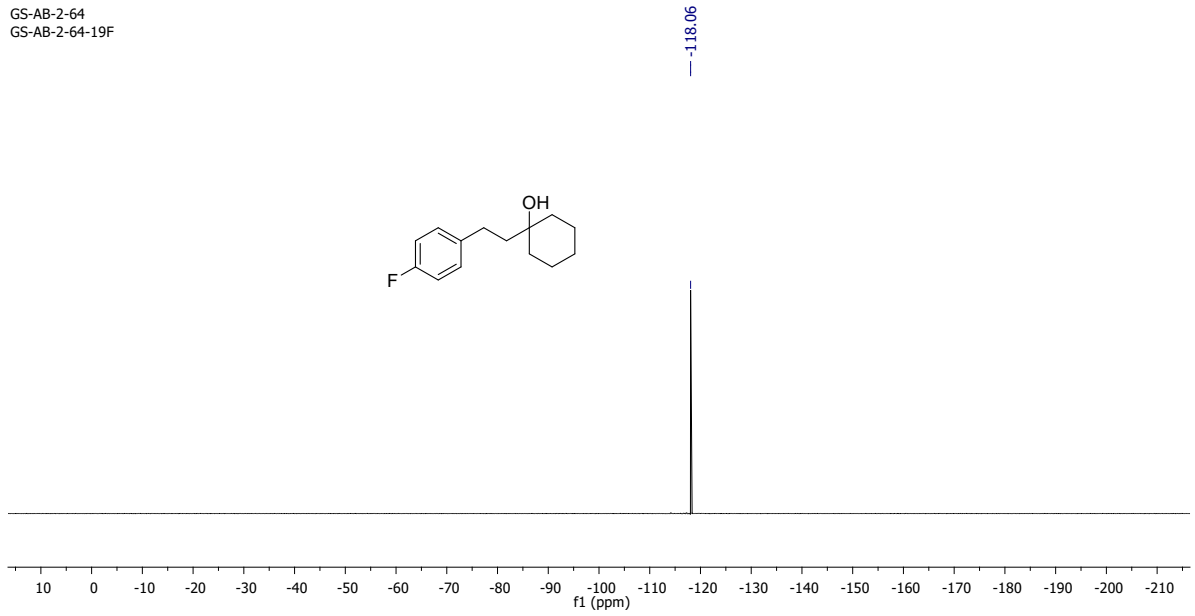
^{1}H-NMR (600 MHz) spectrum of **3dg** in $CDCl_3$



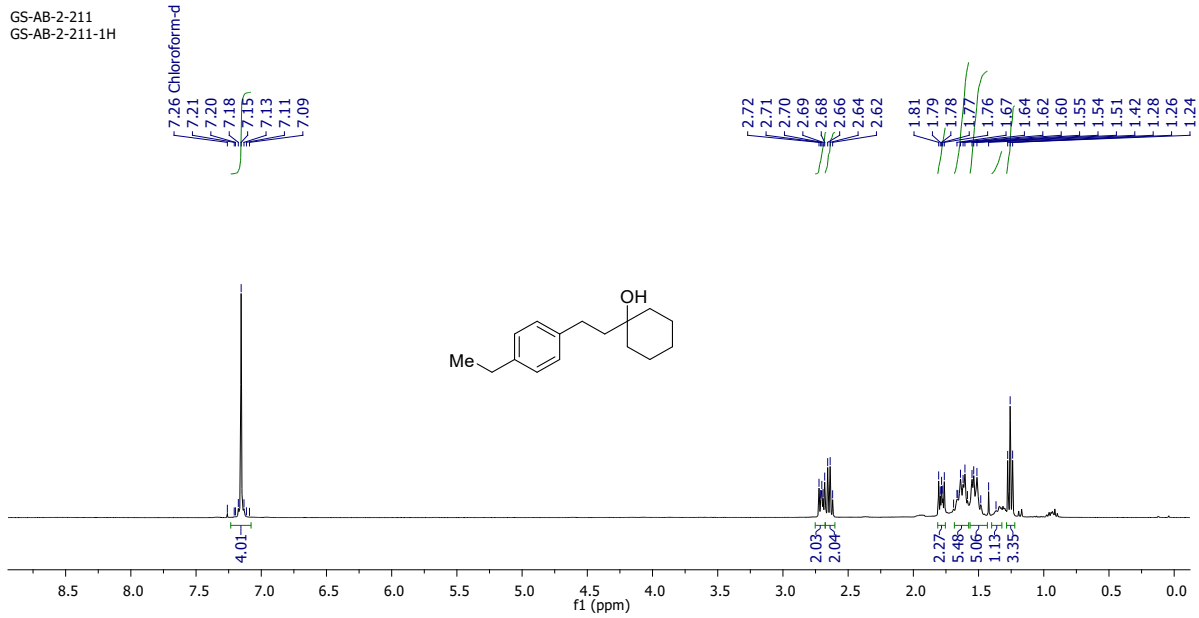
^{13}C{^{1}H}-NMR (151 MHz) spectrum of **3dg** in $CDCl_3$



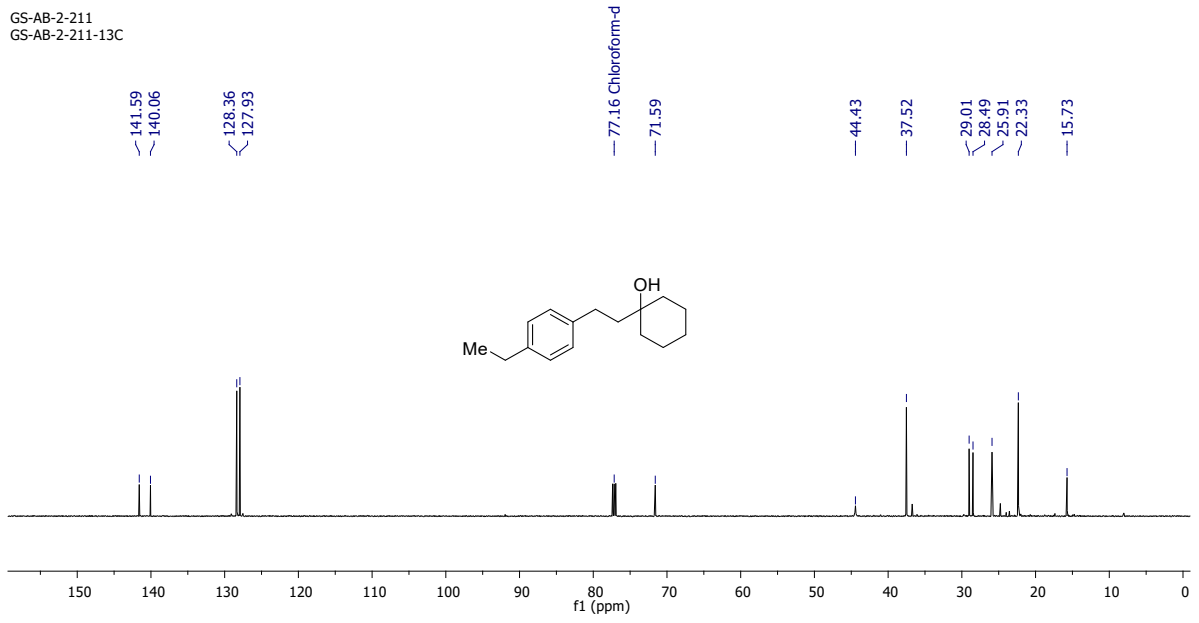
^{19}F-NMR (565 MHz) spectrum of **3dg** in $CDCl_3$



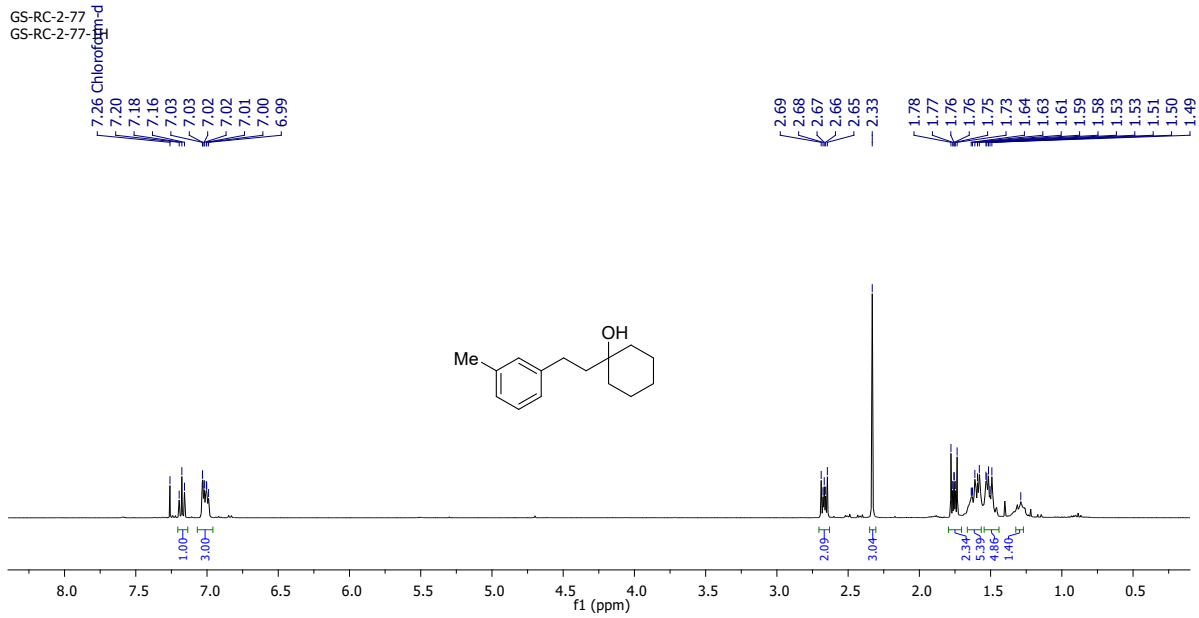
^{1}H-NMR (400 MHz) spectrum of **3eg** in $CDCl_3$



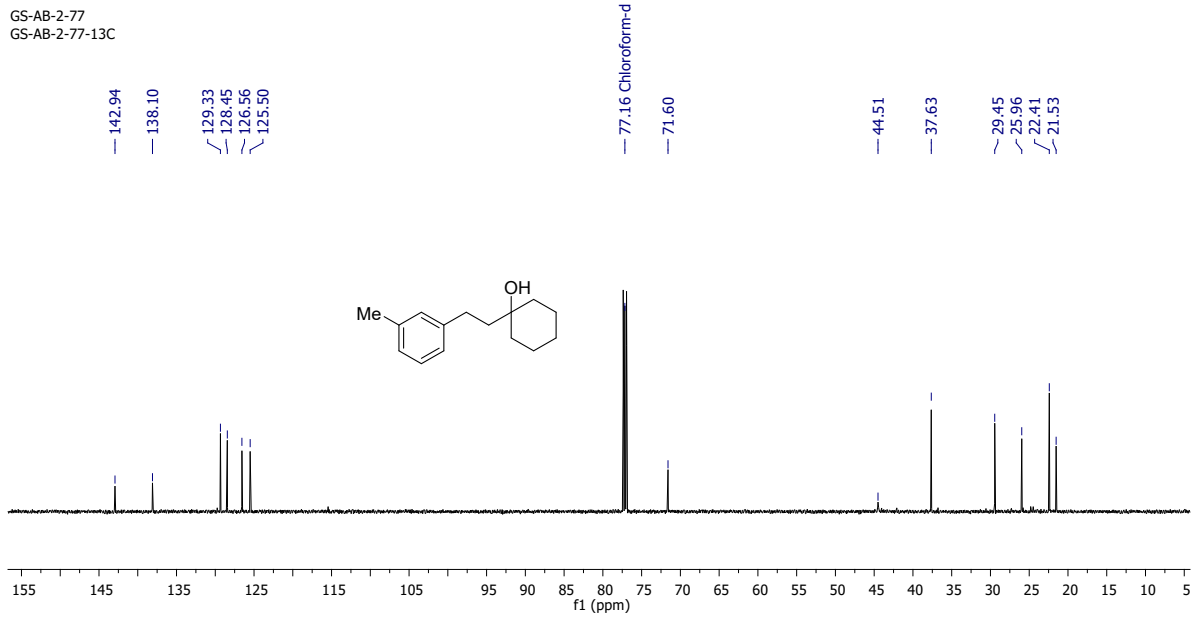
^{13}C{^{1}H}-NMR (151 MHz) spectrum of **3eg** in $CDCl_3$



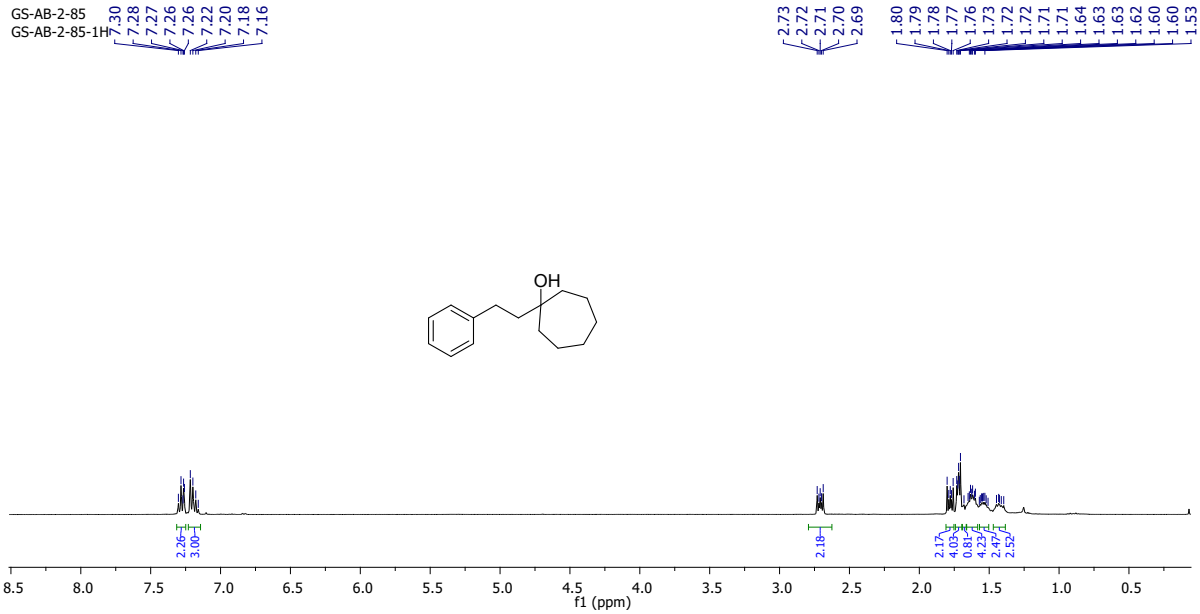
^{1}H-NMR (400 MHz) spectrum of **3jg** in $CDCl_3$



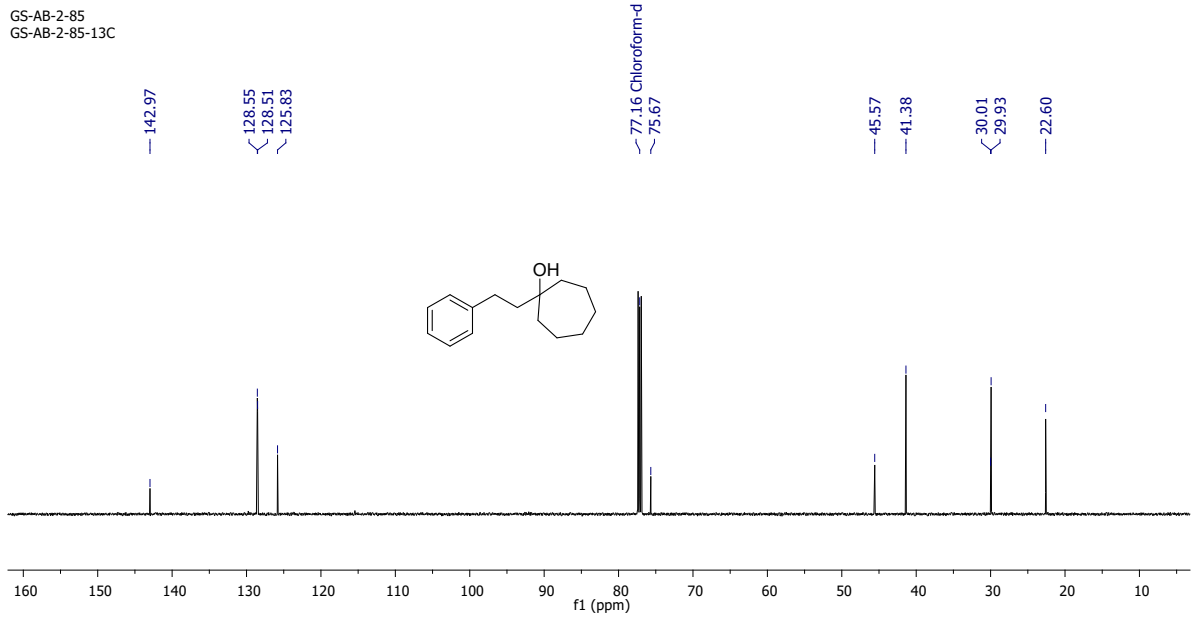
^{13}C{^{1}H}-NMR (151 MHz) spectrum of **3jg** in $CDCl_3$



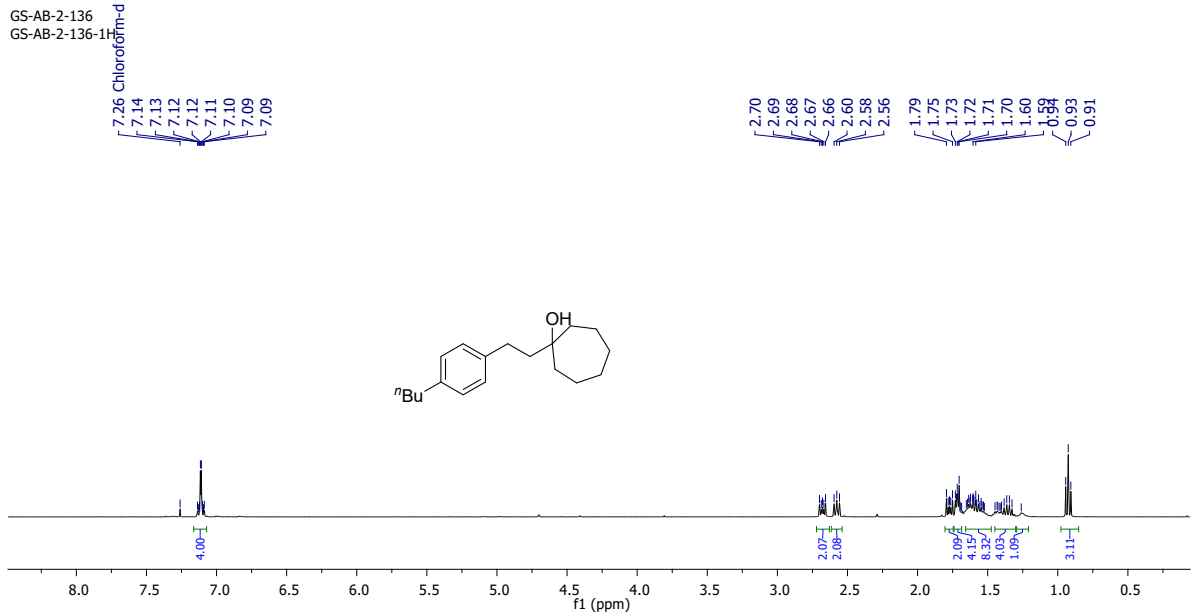
^{1}H-NMR (400 MHz) spectrum of **3ah** in $CDCl_3$



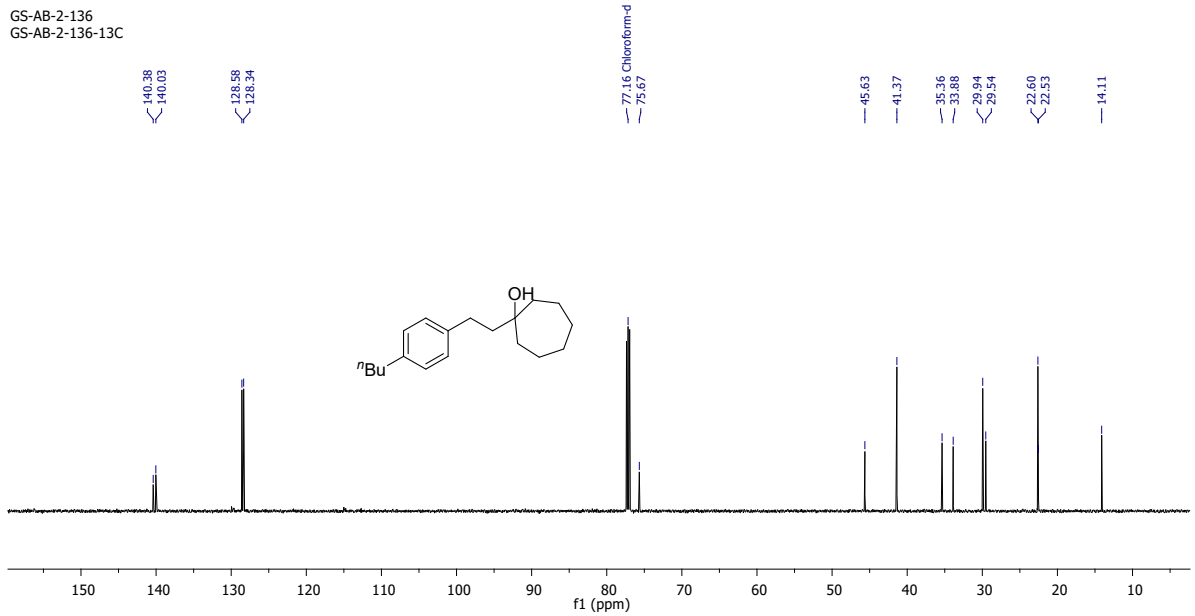
^{13}C{^{1}H}-NMR (151 MHz) spectrum of **3ah** in $CDCl_3$



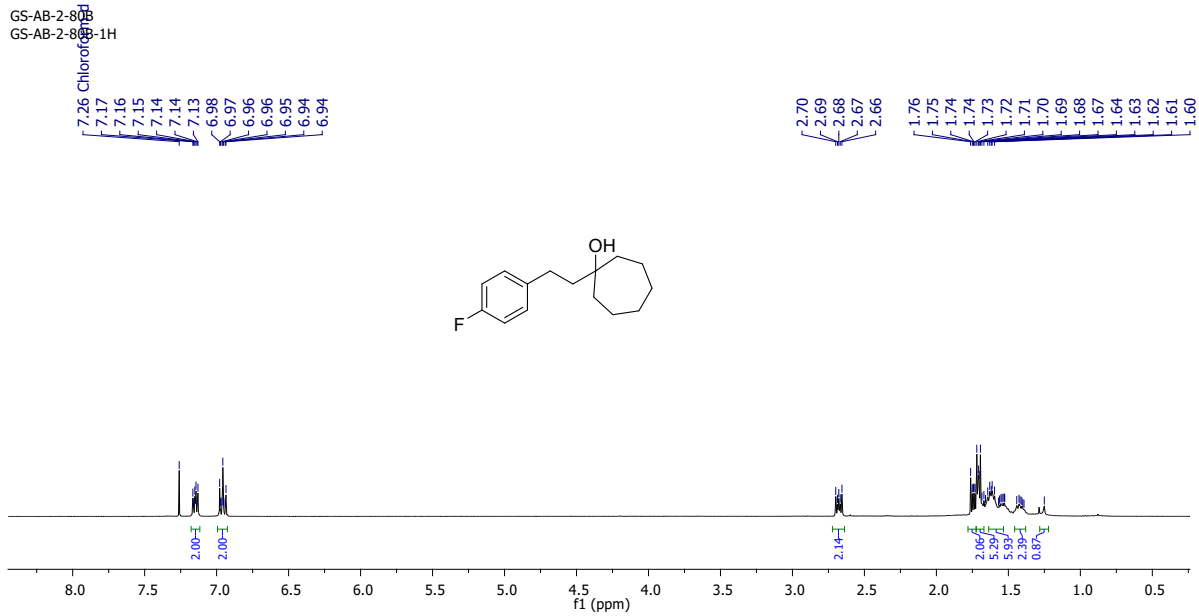
^{1}H-NMR (400 MHz) spectrum of **3bh** in $CDCl_3$



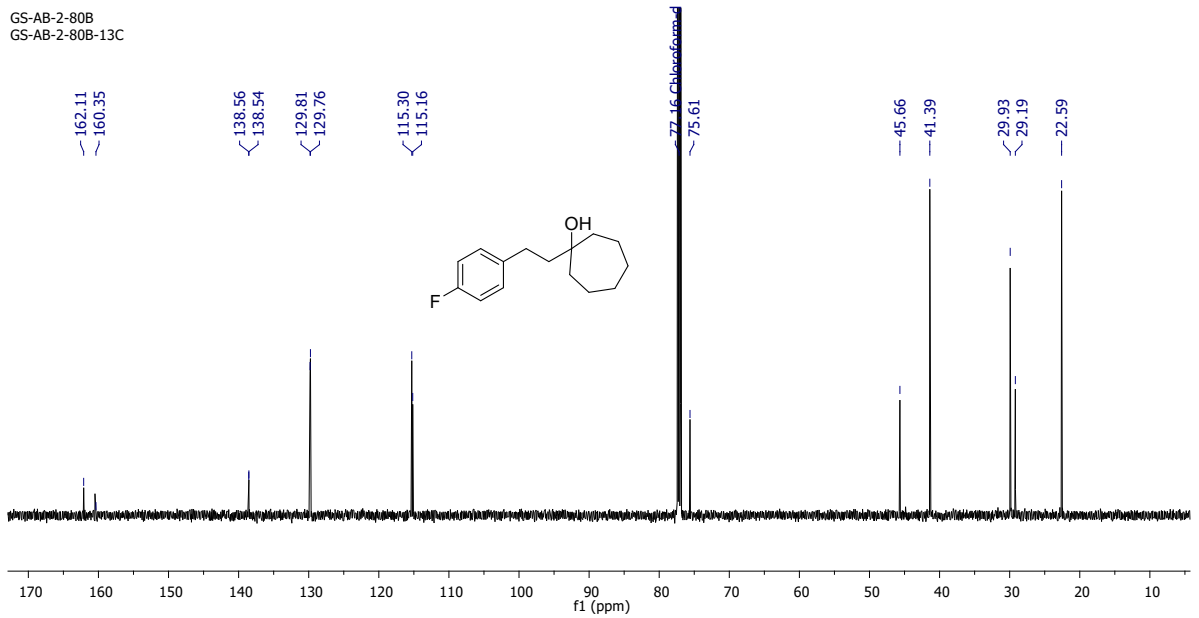
^{13}C{^{1}H}-NMR (151 MHz) spectrum of **3bh** in $CDCl_3$



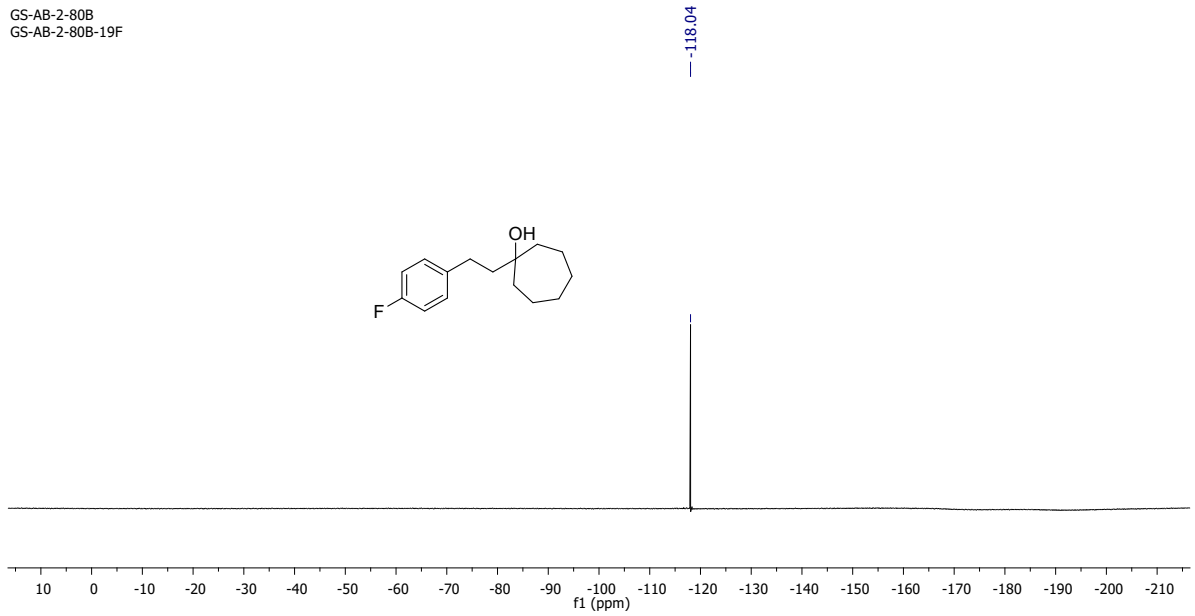
^{1}H-NMR (400 MHz) spectrum of **3dh** in $CDCl_3$



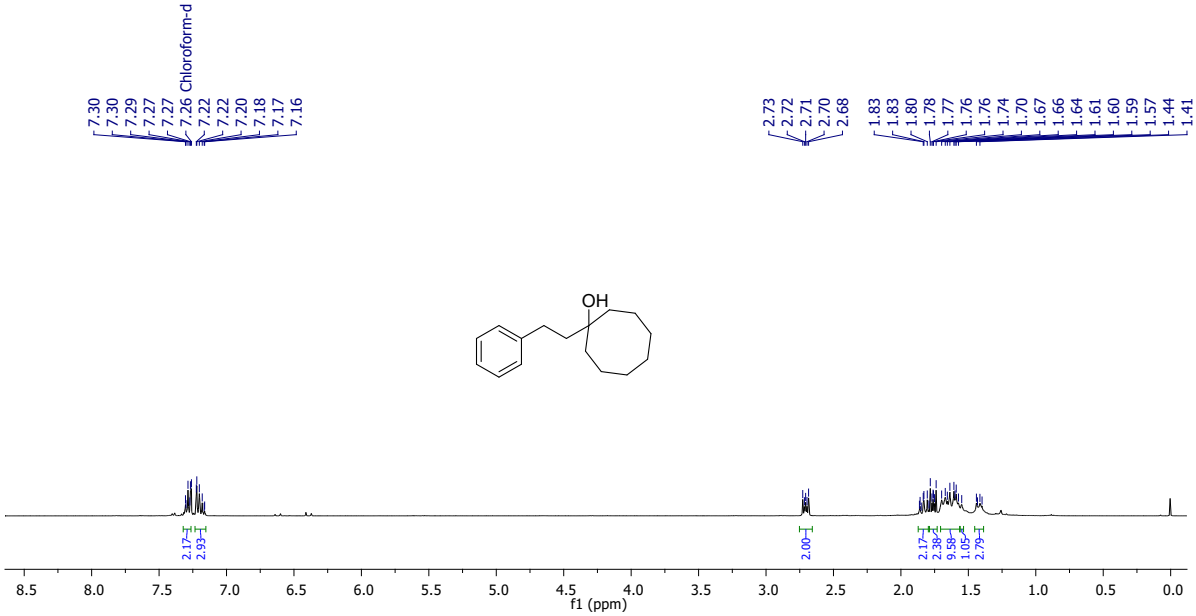
^{13}C{^{1}H}-NMR (151 MHz) spectrum of **3dh** in $CDCl_3$



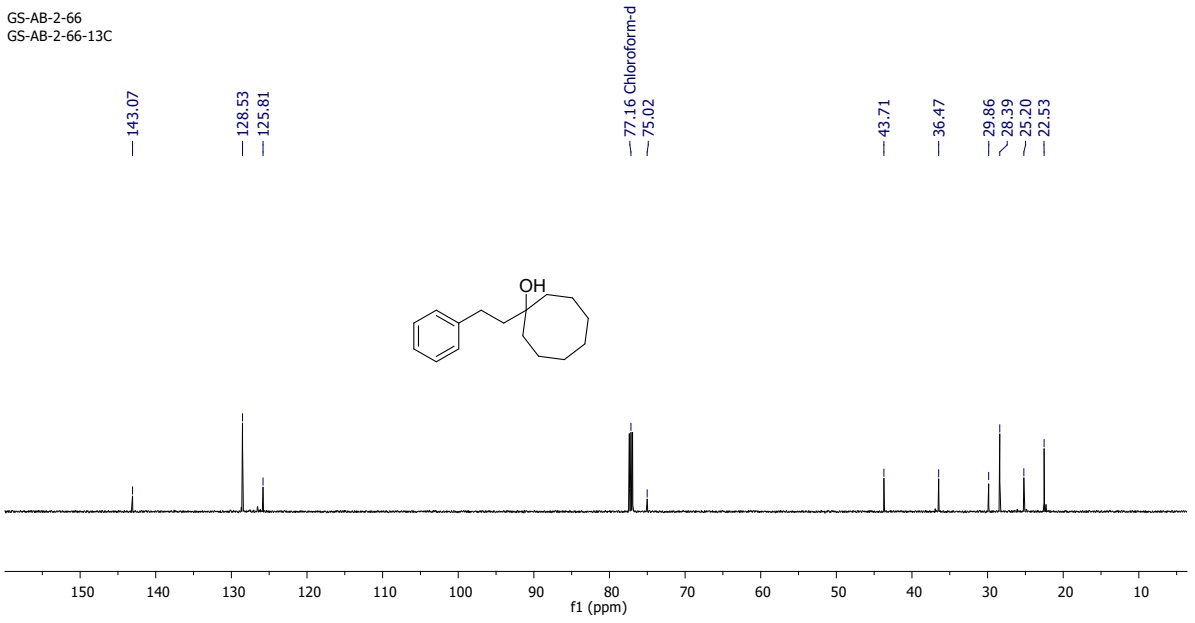
^{19}F-NMR (565 MHz) spectrum of **3dh** in $CDCl_3$



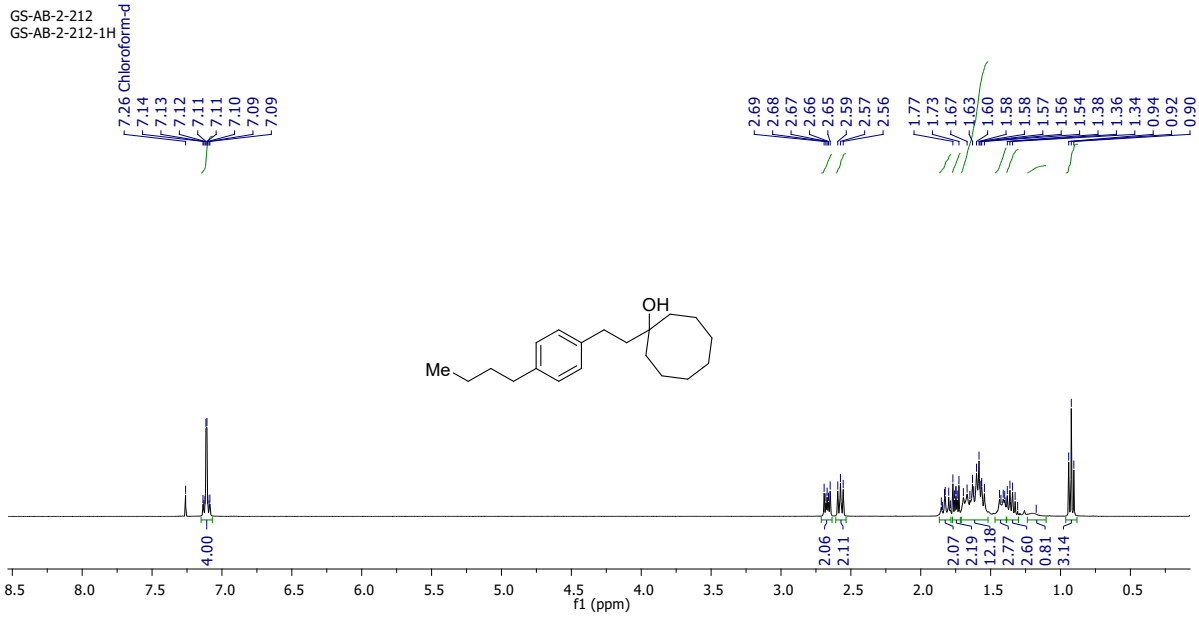
^{1}H-NMR (400 MHz) spectrum of **3ai** in $CDCl_3$



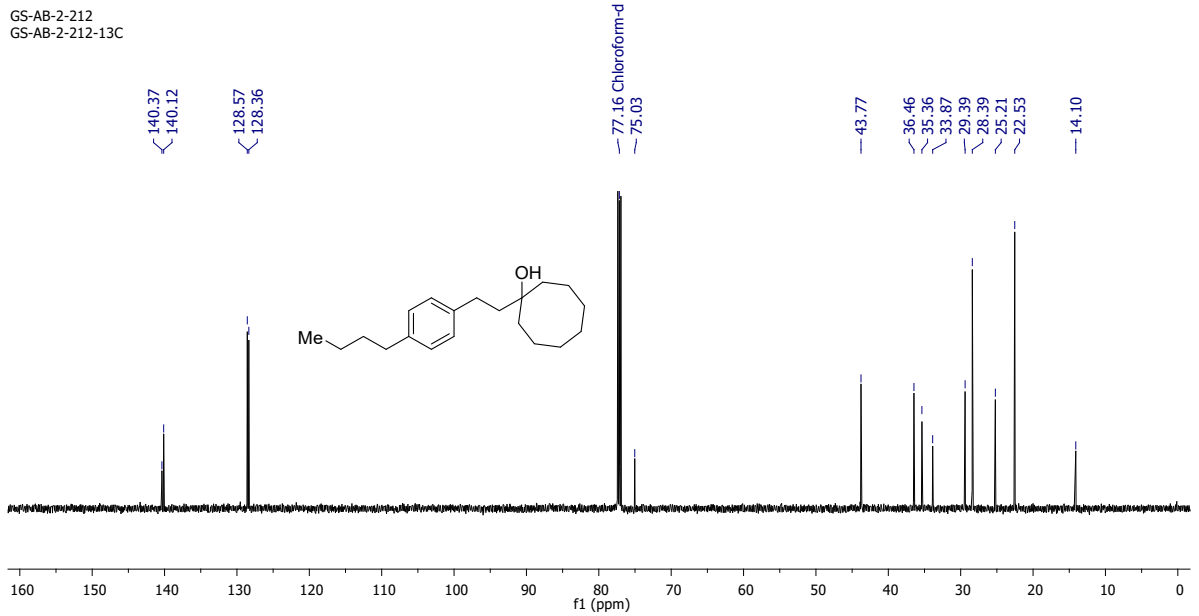
^{13}C{^{1}H}-NMR (151 MHz) spectrum of **3ai** in $CDCl_3$



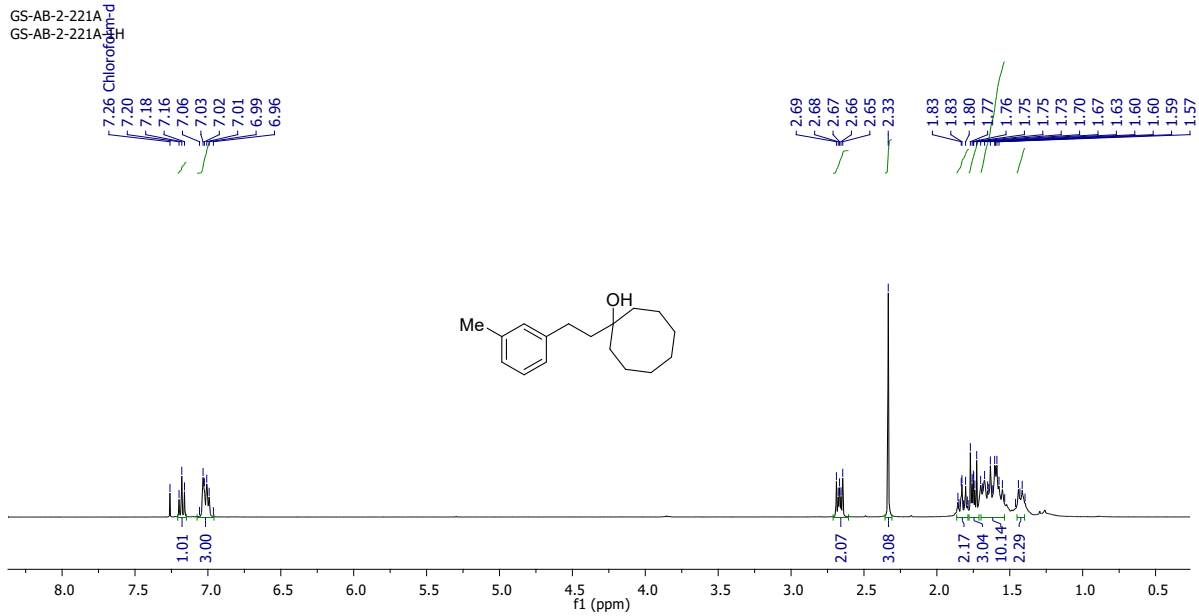
^{1}H-NMR (400 MHz) spectrum of **3bi** in $CDCl_3$



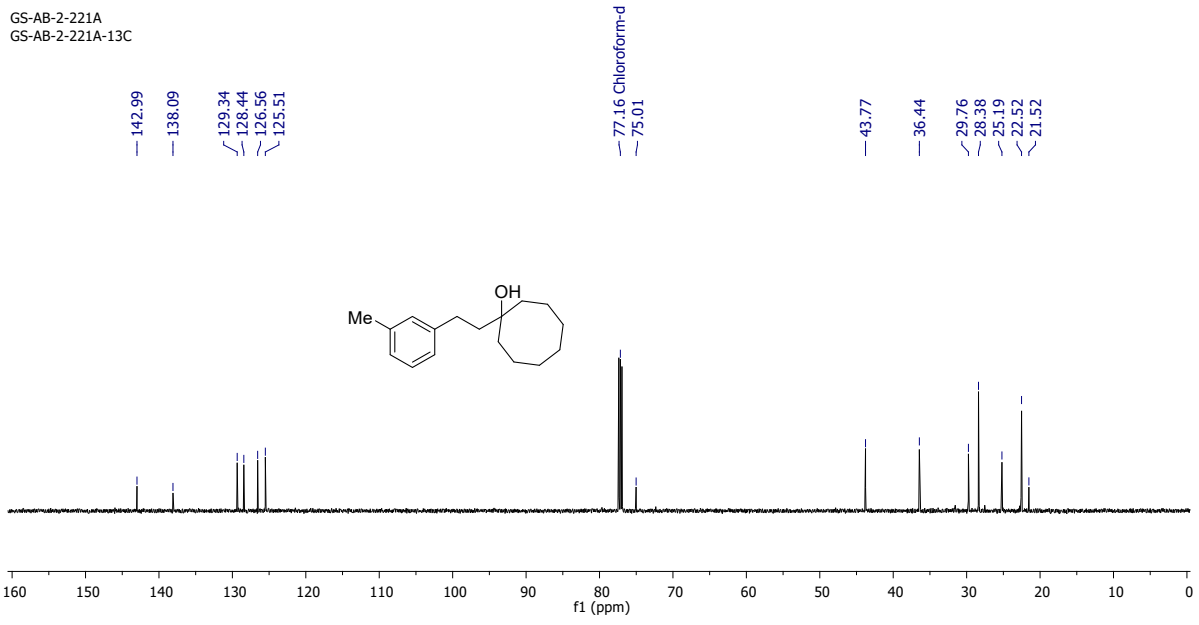
^{13}C{^{1}H}-NMR (151 MHz) spectrum of **3bi** in $CDCl_3$



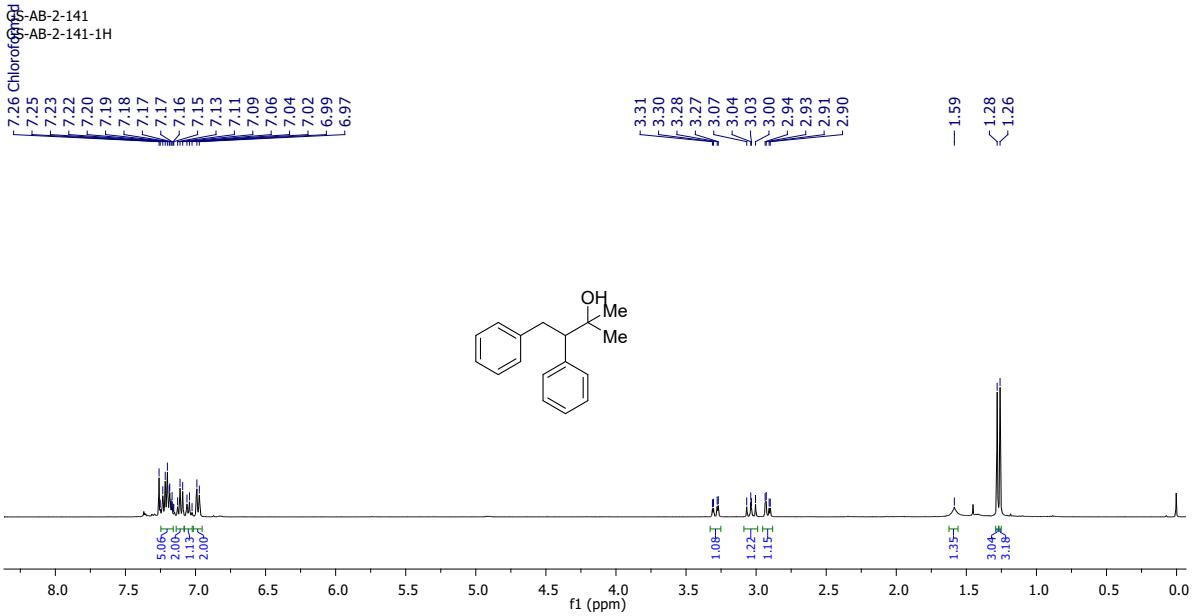
^{1}H-NMR (400 MHz) spectrum of **3ji** in $CDCl_3$



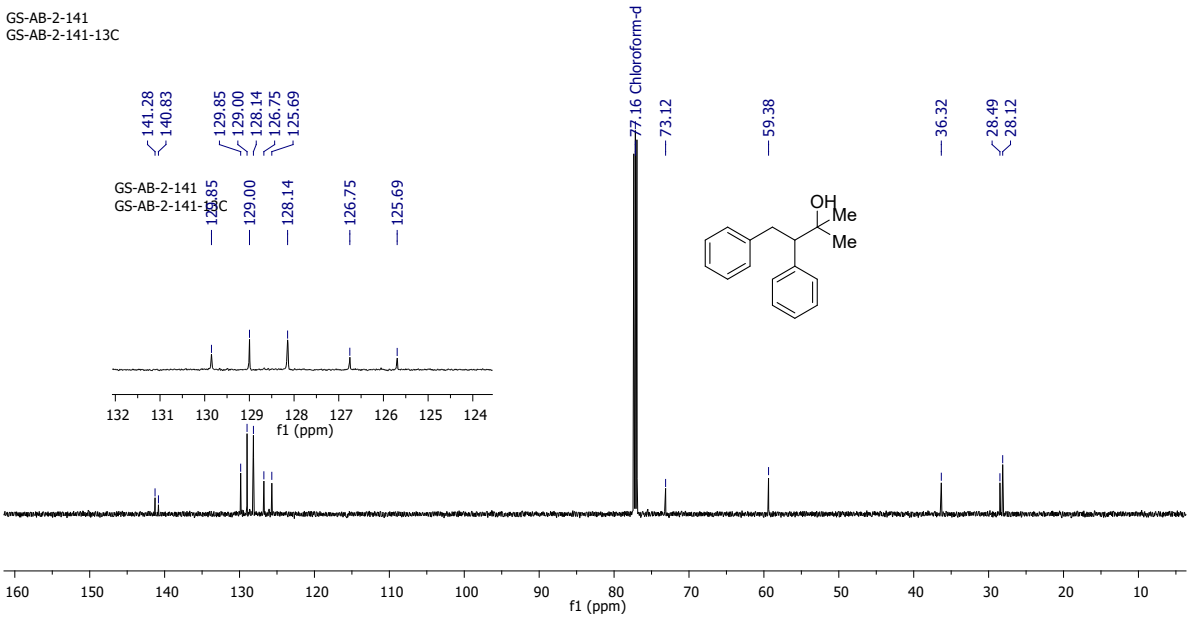
^{13}C{^{1}H}-NMR (151 MHz) spectrum of **3ji** in $CDCl_3$



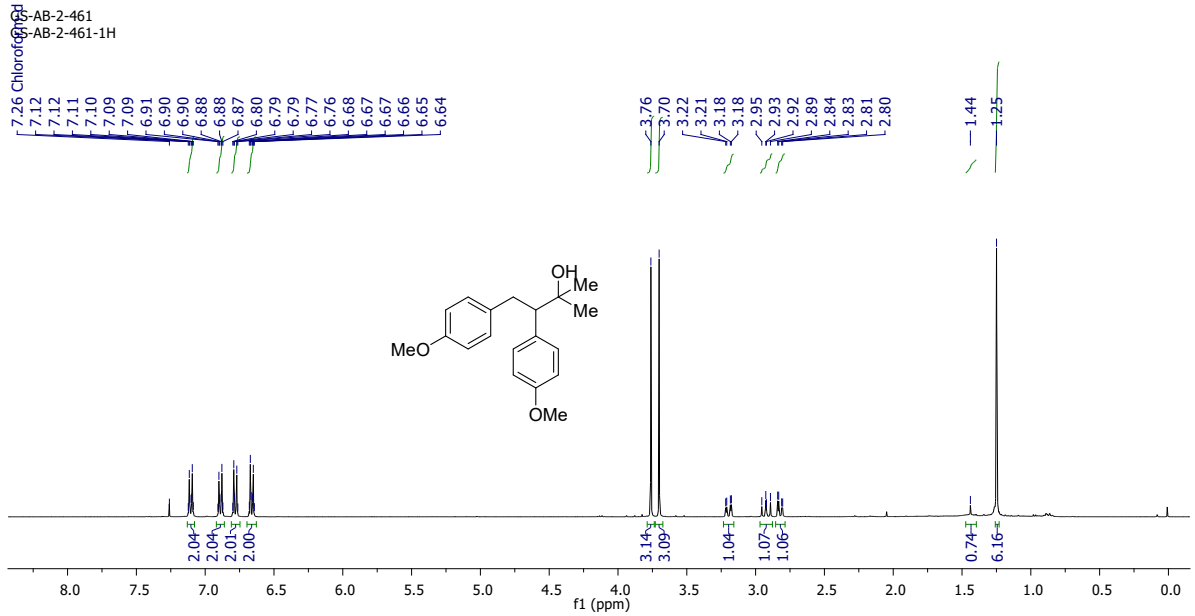
^{1}H-NMR (400 MHz) spectrum of **5aa** in $CDCl_3$



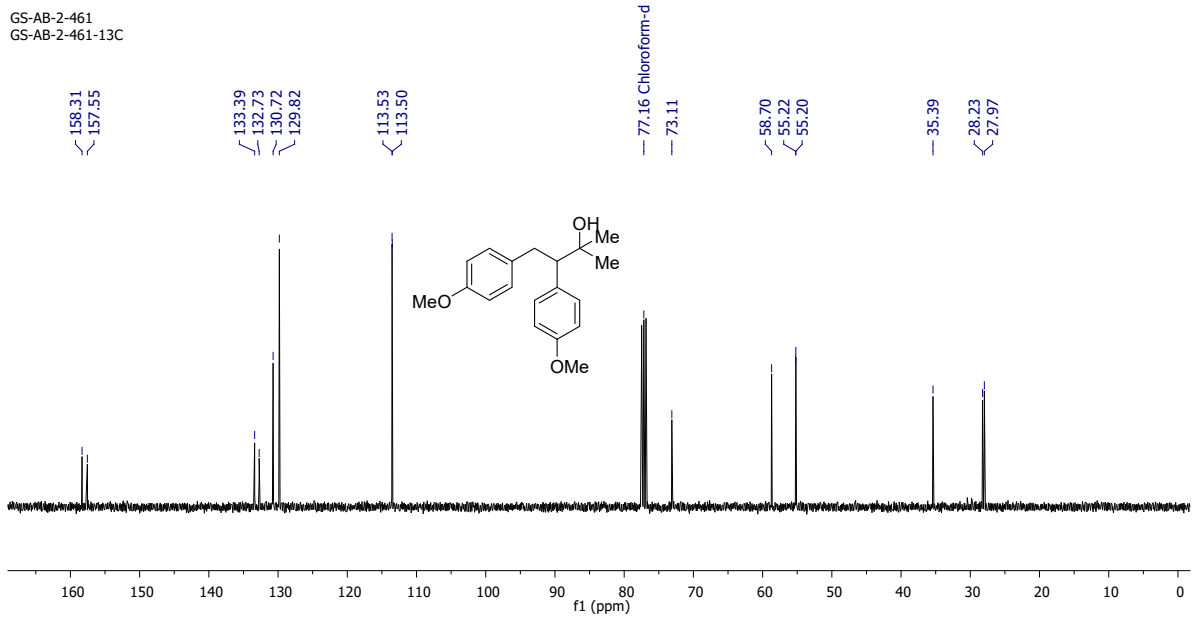
^{13}C{^{1}H}-NMR (151 MHz) spectrum of **5aa** in $CDCl_3$



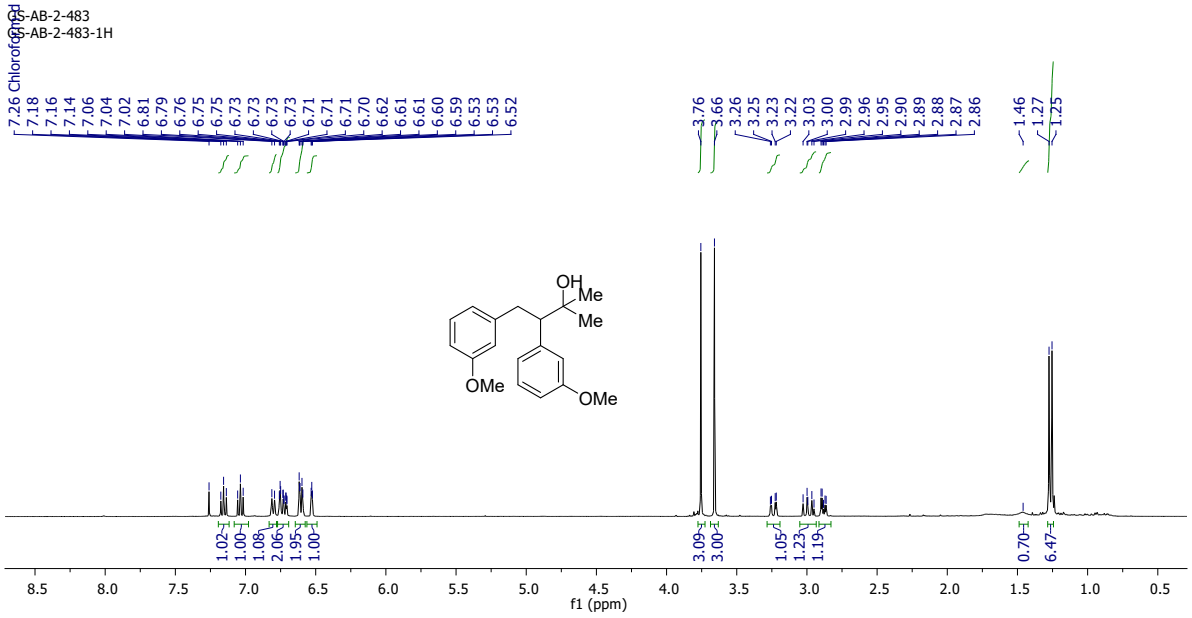
^{1}H-NMR (400 MHz) spectrum of **5ba** in $CDCl_3$



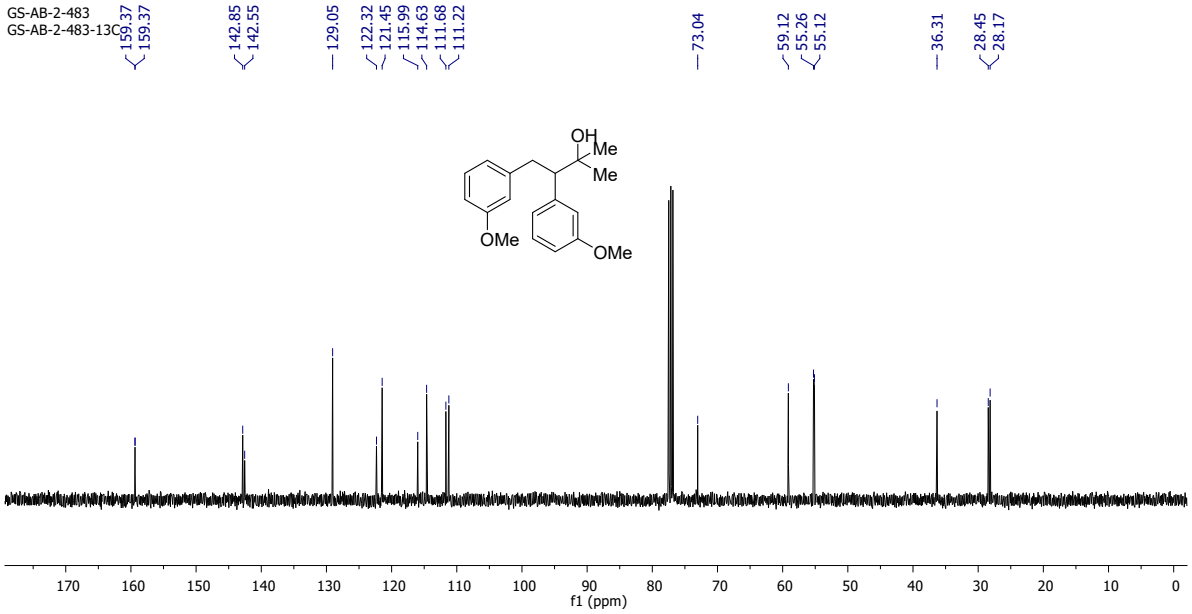
^{13}C{^{1}H}-NMR (101 MHz) spectrum of **5ba** in $CDCl_3$



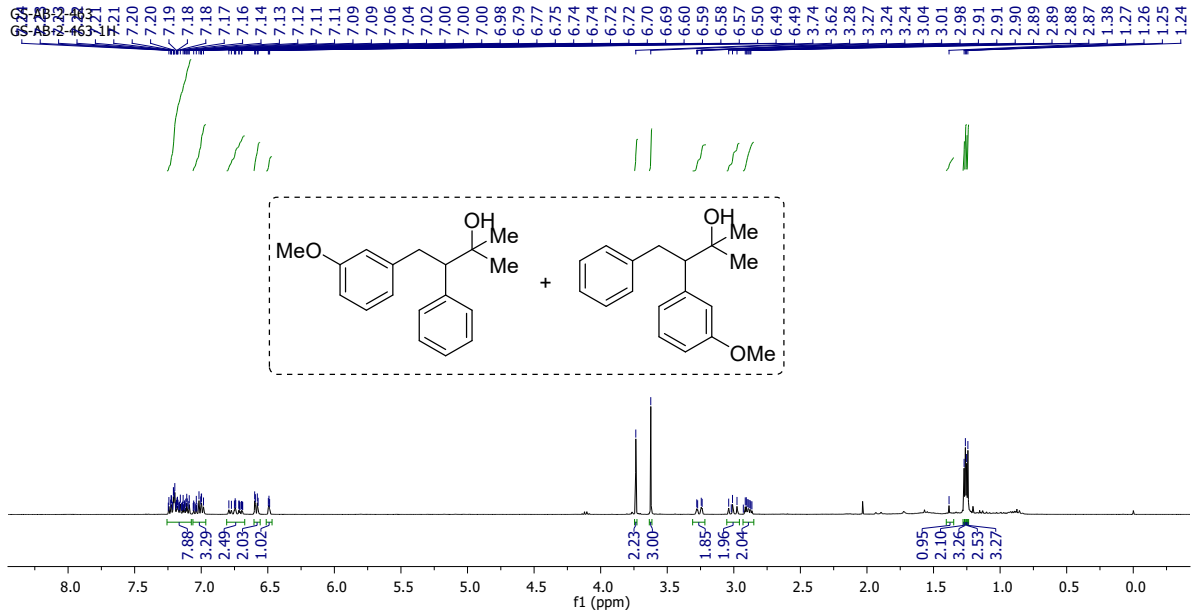
^{1}H-NMR (400 MHz) spectrum of **5ca** in $CDCl_3$



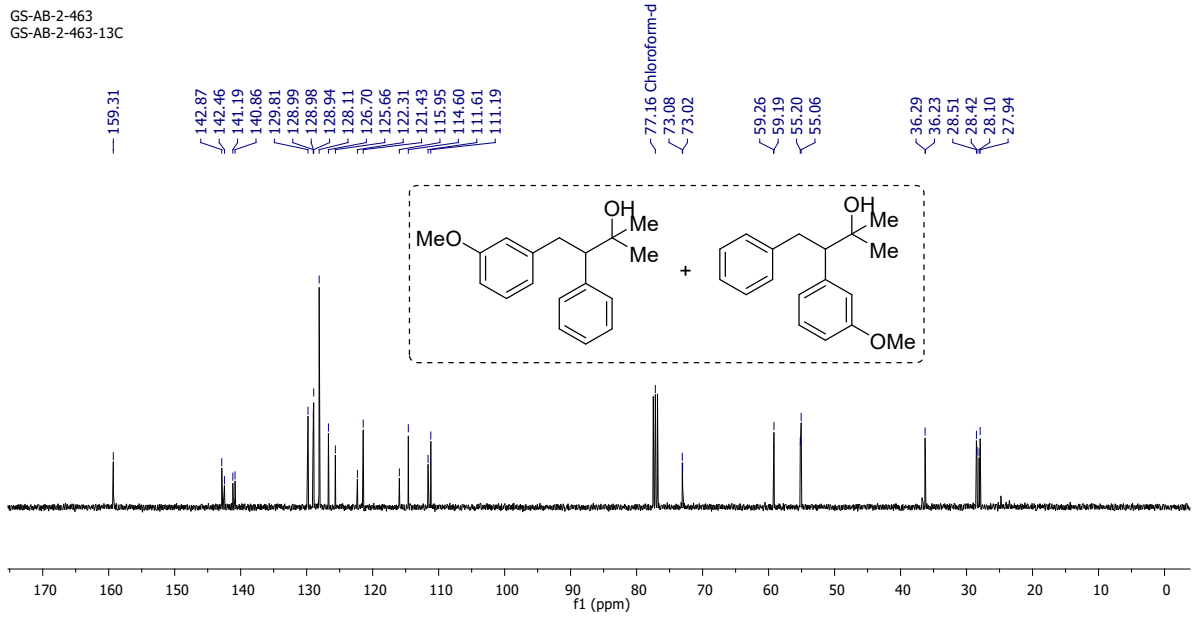
^{13}C{^{1}H}-NMR (101 MHz) spectrum of **5ca** in $CDCl_3$



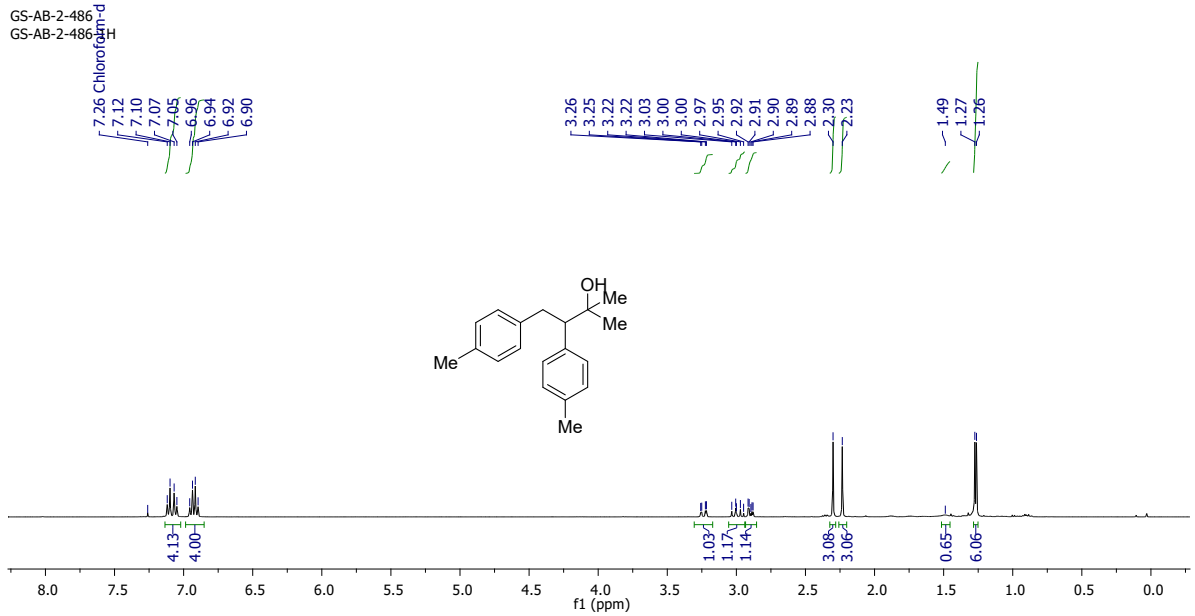
^{1}H-NMR (400 MHz) spectrum of **5da** in $CDCl_3$



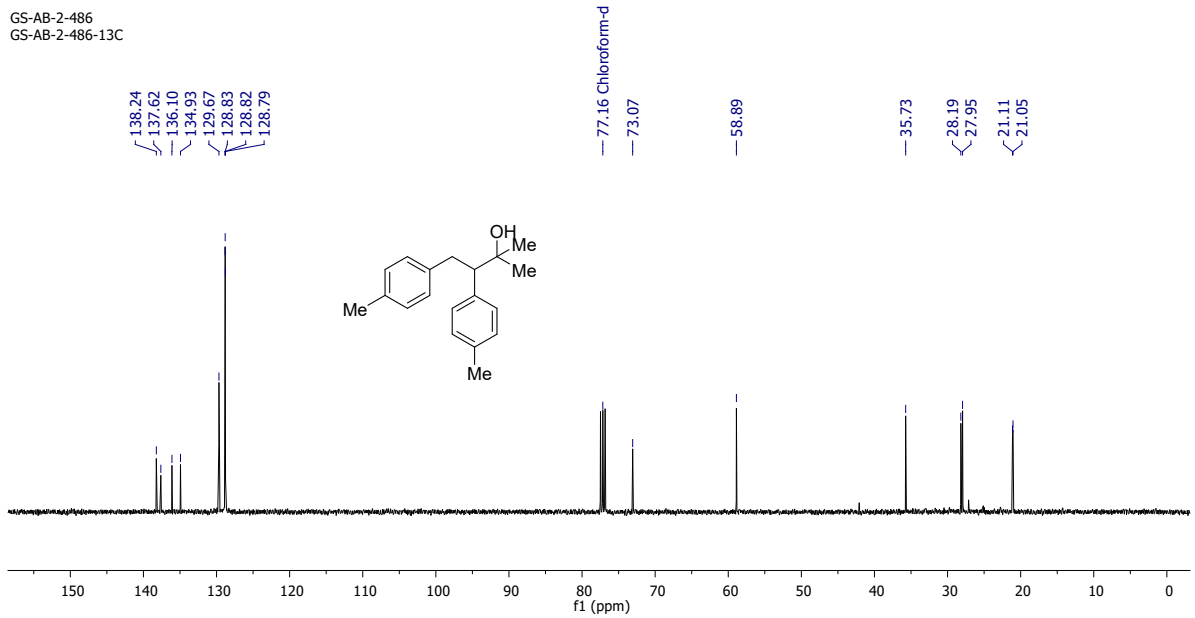
^{13}C{^{1}H}-NMR (101 MHz) spectrum of **5da** in $CDCl_3$



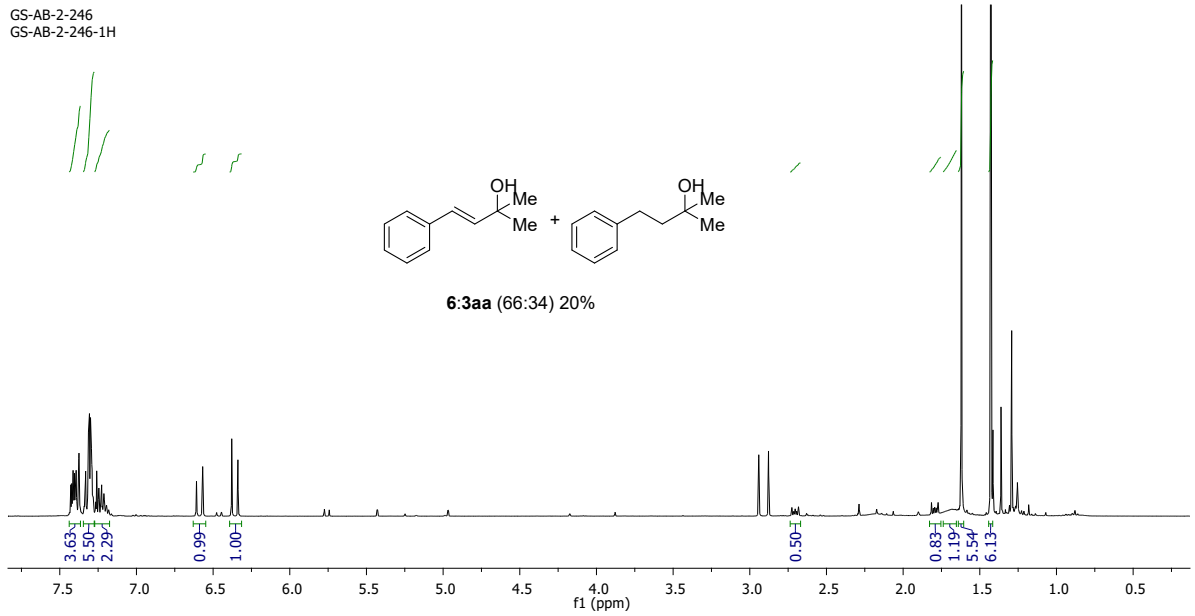
^{1}H-NMR (400 MHz) spectrum of **5ea** in $CDCl_3$



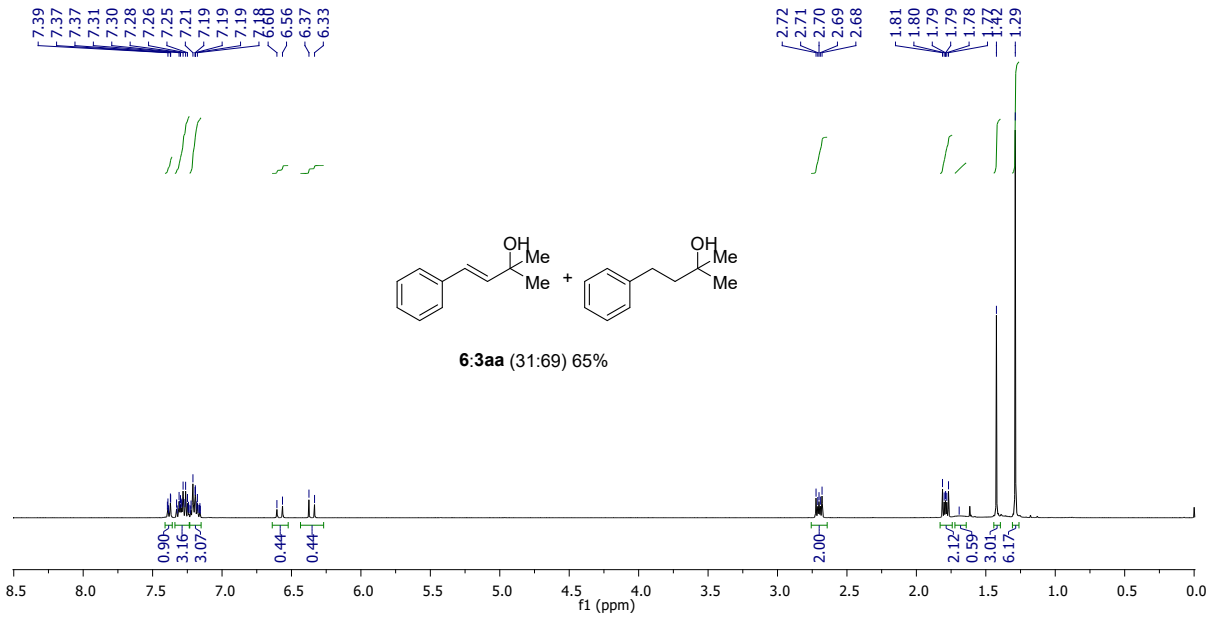
^{13}C{^{1}H}-NMR (101 MHz) spectrum of **5ea** in $CDCl_3$



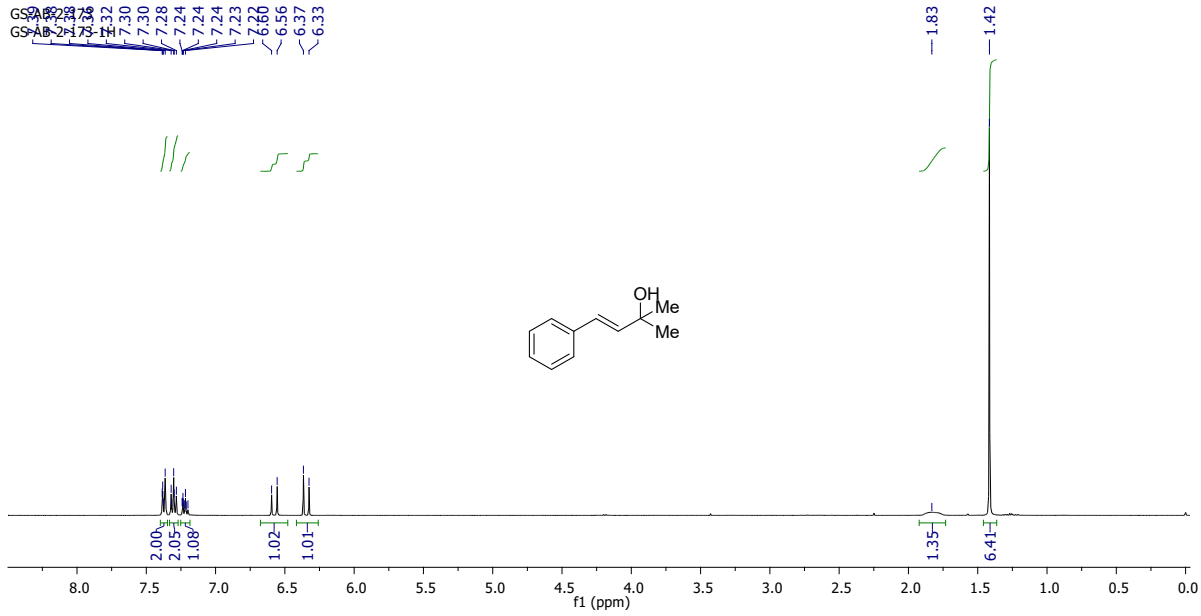
^{1}H-NMR (400 MHz) spectrum of mixture of **6** & **3aa** after 1.5 h in $CDCl_3$



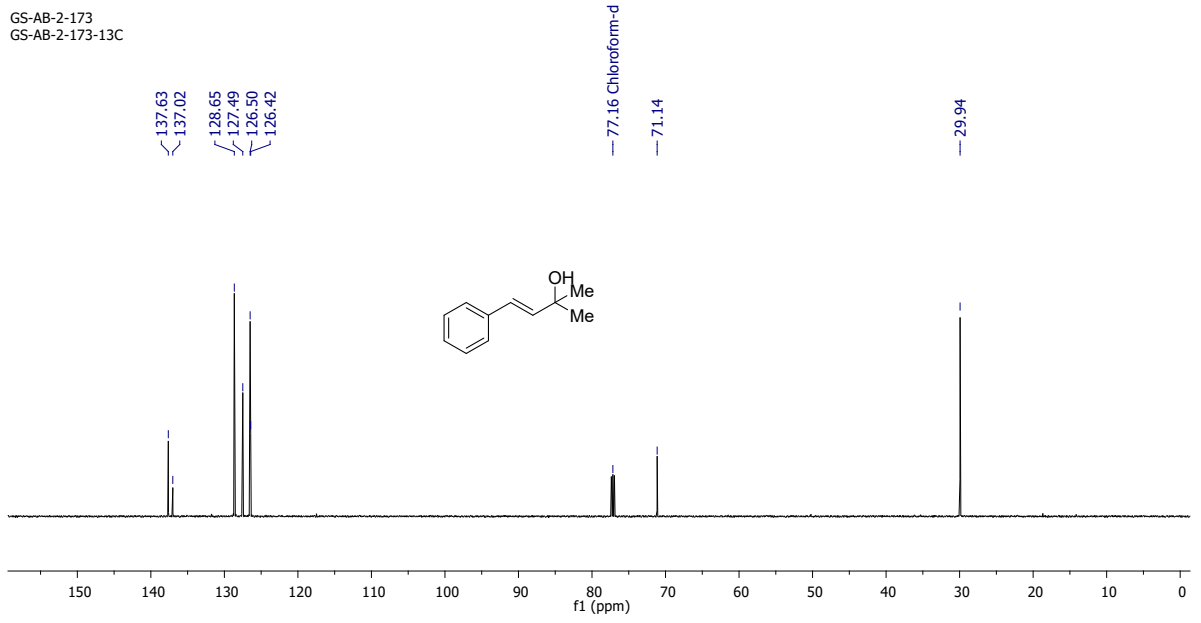
^{1}H-NMR (400 MHz) spectrum of mixture of **6** & **3aa** after 4 h in $CDCl_3$



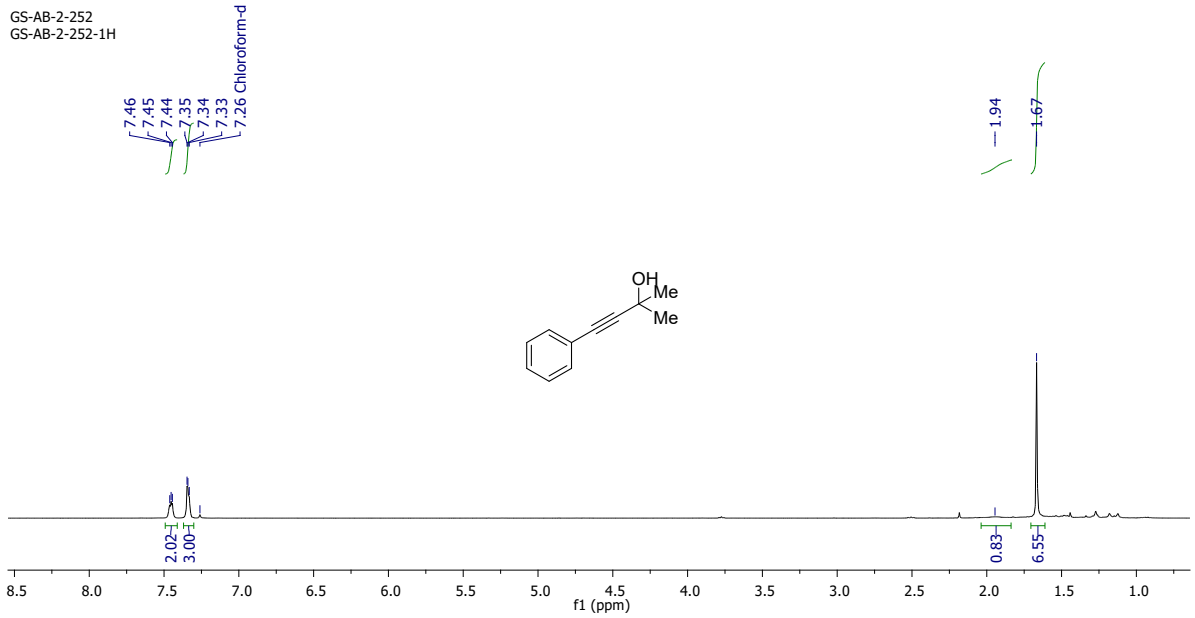
^{1}H-NMR (400 MHz) spectrum of **6** in $CDCl_3$



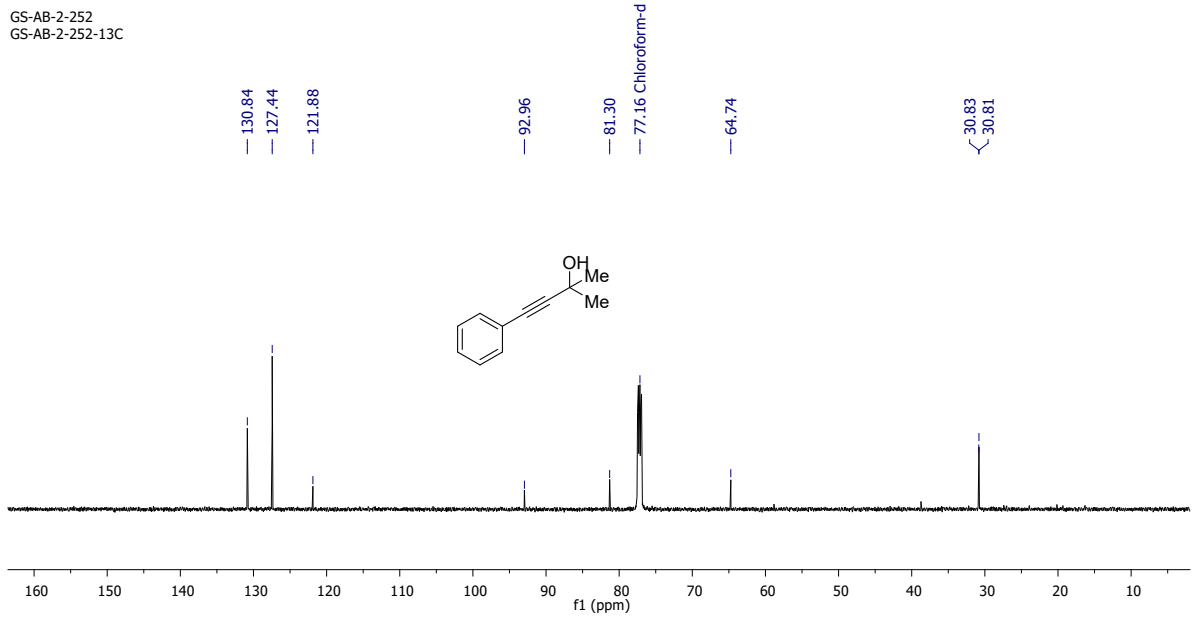
^{13}C{^{1}H}-NMR (151 MHz) spectrum of **6** in $CDCl_3$



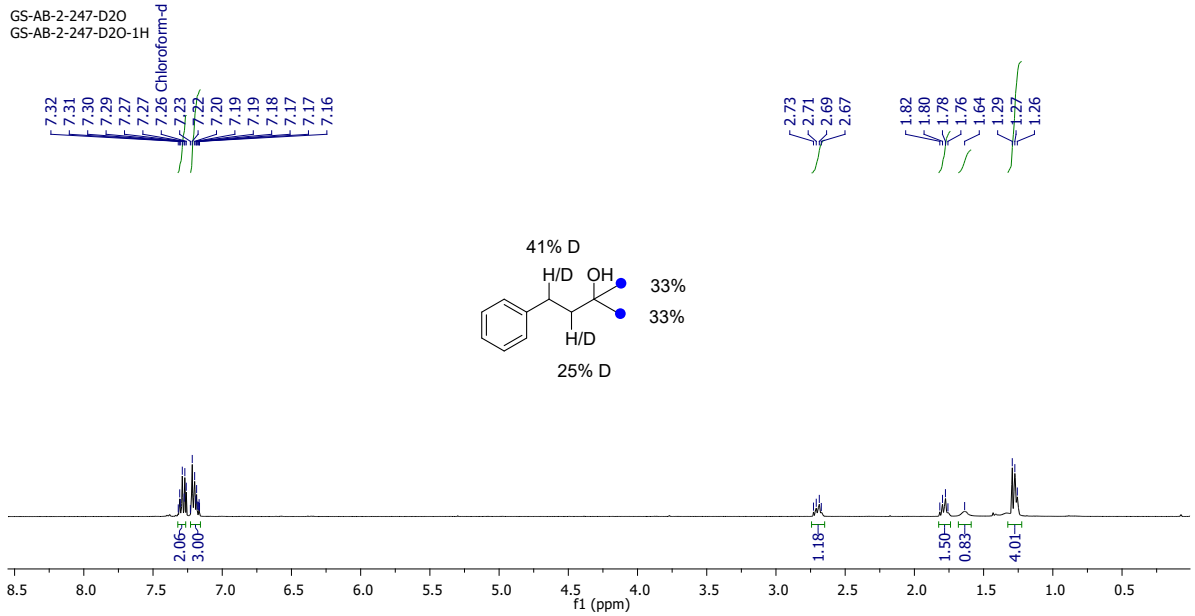
^{1}H-NMR (400 MHz) spectrum of **7** in $CDCl_3$



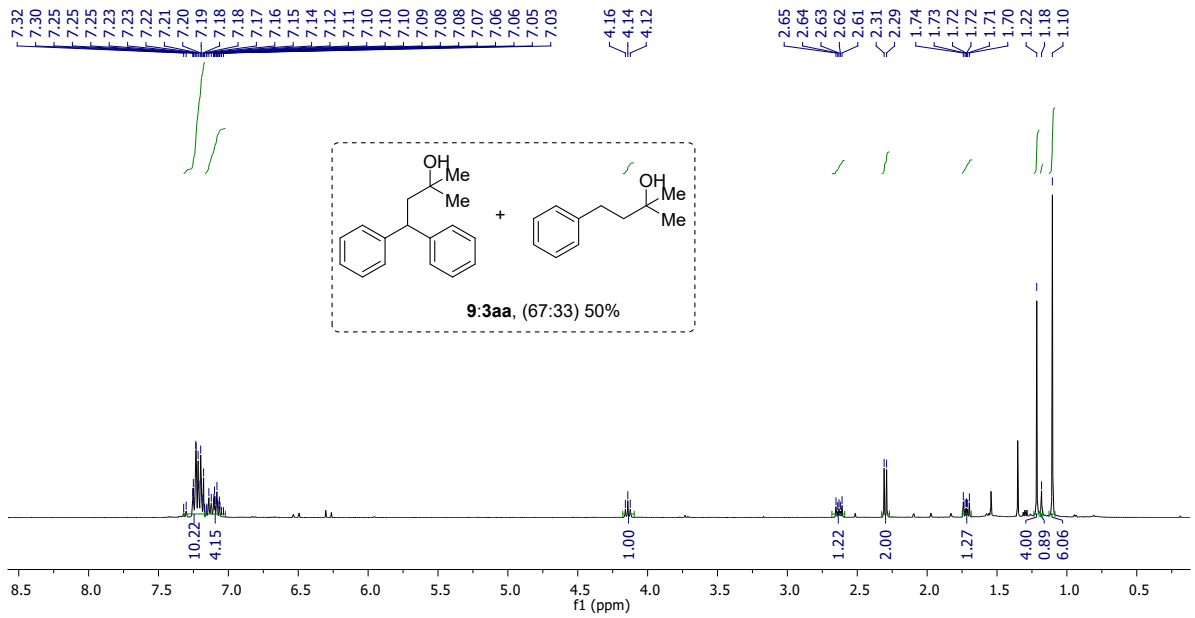
^{13}C{^{1}H}-NMR (151 MHz) spectrum of **7** in $CDCl_3$



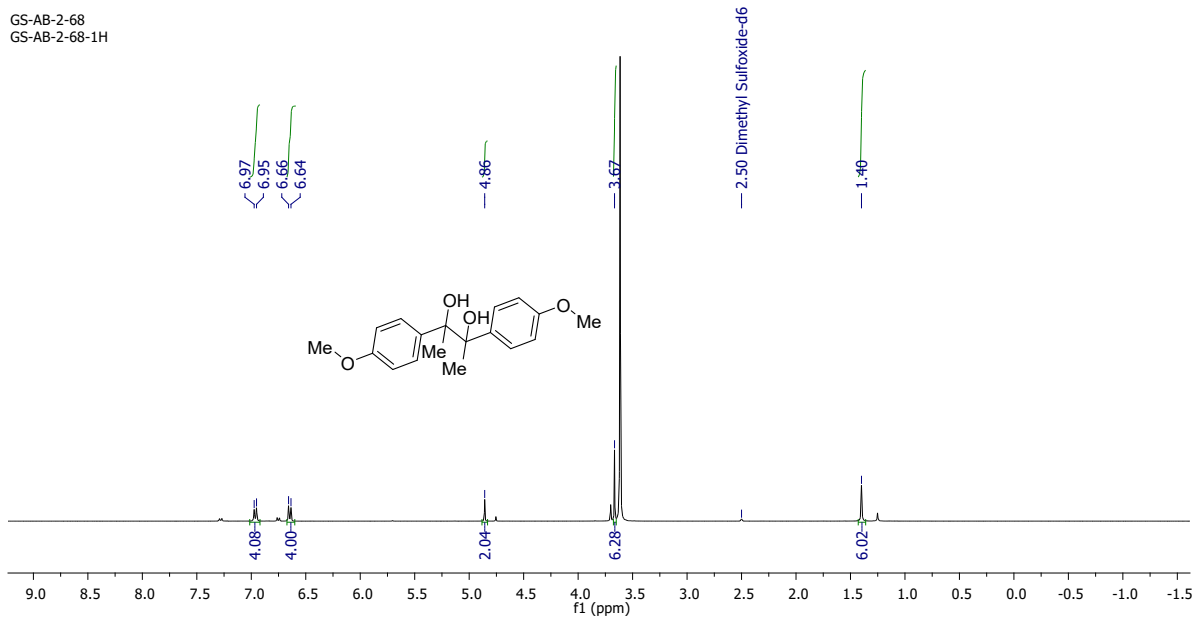
^{1}H-NMR (400 MHz) spectrum of **8** in $CDCl_3$



^{1}H-NMR (400 MHz) spectrum of **9** in $CDCl_3$



^{1}H-NMR (400 MHz) spectrum of Pinacol product **10** in DMSO-d_6



Crystal structure data:

X-Ray crystal structure of compound **3ff**: Crystal of compound **3ff** were obtained by dissolving the product in CH_2Cl_2/CH_3CN mixture and allowing the solvent to slowly evaporate at room temperature. A suitable crystal was selected and mounted onto the cryoloop on a Bruker APEX-II CCD diffractometer. The crystal was kept at 273.15 K during data collection. Using Olex2,[8] the structure was solved with the SHELXT[9] structure solution program using Intrinsic Phasing and refined with the SHELXL[10] refinement package using Least Squares minimisation.[11,12]

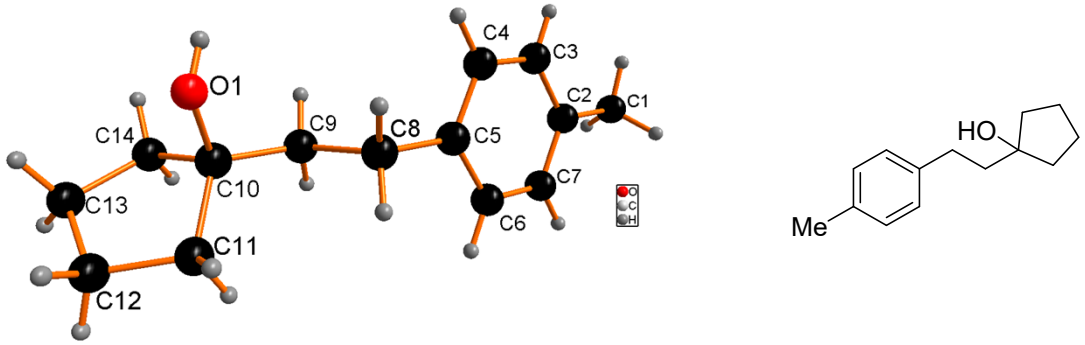


Figure S2: ORTEP diagram of compound **3ff** with ellipsoid shown at the 50% contour percent probability level (**CCDC**-2237742).

Table 3S: Crystal data and structure refinement for **3ff** (**CCDC**-2237742).

Table 3S: Crystal data and structure refinement for 3ff.	
Identification code	**3ff**
Empirical formula	$C_{14}H_{20}O$
Formula weight	204.30
Temperature/K	298
Crystal system	tetragonal
Space group	$I4_1/a$
a/Å	19.065(2)
b/Å	19.065(2)
c/Å	13.900(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	5052.3(15)
Z	16
ρ_{calc}g/cm^3	1.074
μ/mm^{-1}	0.065
F(000)	1792.0
Crystal size/mm^3	0.362 × 0.205 × 0.153
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.626 to 54.204
Index ranges	$-23 \leq h \leq 23$, $-23 \leq k \leq 24$, $-17 \leq l \leq 17$
Reflections collected	21267
Independent reflections	2790 [R_{int} = 0.0790, R_{sigma} = 0.0489]
Data/restraints/parameters	2790/0/142
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0574, wR_2 = 0.1467
Final R indexes [all data]	R_1 = 0.1108, wR_2 = 0.1756
Largest diff. peak/hole / e Å^{-3}	0.17/-0.19

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