Electronic Supplementary Material (ESI) for ChemComm.
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Cobalt catalysed [1,2]-Wittig rearrangement of ethers to secondary alcohols

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General methods

All reactions were performed in nitrogen atmosphere MBRAUN glove box. All chemicals were purchased from Acros, Sigma Aldrich, Alfa-aesar, Himedia. Chemicals are used without further purification. Dry solvents were prepared according to standard procedures. Infrared (IR) spectra were recorded in Perkin-Elmer FT-IR and Thermo-Nicolet FT-IR spectrophotometers. High-resolution mass spectra (HRMS) were obtained on Bruker micrOTOFQ II Spectrometer and are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion $[M+Na]^+$, $[M+H]^+$. Nuclear magnetic resonance spectra (^1H NMR and ^{13}C NMR) were recorded at Bruker AV-400 (^1H at 400 MHz, ^{13}C at 100.6 MHz). ^1H NMR chemical shifts are referenced in parts per million (ppm) with respect to tetramethyl silane (TMS, δ 0.00 ppm) and ^{13}C $\{^1H\}$ NMR chemical shifts are referenced in parts per million (ppm) with respect to $CDCl_3$ (δ 77.160 ppm). Coupling constants are reported in Hertz (Hz). ^1H NMR spectroscopy abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublets; dt, doublet of triplets; dq, doublet of quartets; td, triplet of doublets; qd, quartets of doublets; ddd, doublets of doublets of doublets; m, multiplet; br, broad.

General procedure for synthesis of secondary alcohols:

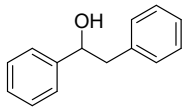
To an oven-dried vial, catalyst **1** (5 mol %), ether (1 mmol), and KO^{t}Bu (40 mol %) were added under nitrogen and allowed to stir for five minutes, and during this period, the color of reaction mixture turned from dark blue to light black. After the color change, diethylsilane (4 mmol) was added to the reaction mixture; the vial was sealed and allowed to stir at 100 °C in a preheated oil bath for 12 hours. After cooling the reaction mixture to room temperature, internal standard (benzene, 1 mmol) was added into the reaction mixture, and the conversion of ether was calculated using GC analysis. Further, the crude reaction mixture was quenched with (1 M) ethereal HCl, and water (2 mL) was added. The resulted reaction mixture was extracted with dichloromethane (3 × 10 mL). The combined organic layer was washed with brine and dried over anhydrous sodium sulfate. The solvents were removed under reduced pressure, and the resulted residue was purified by column chromatography over silica gel (100-200 mesh) using hexane/ethyl acetate (97:3) as an eluent.

Attempts were made by HMQC and HMBC spectroscopic technique to identify the structures of differently substituted ethers. Because of indistinguishable ortho protons in compounds **2j** and **2k,** it is difficult to assign the exact structure of compounds. Compounds **2l**, **2m,** and **2n** are formed as a mixture of isomers. However, secondary alcohol products **2o**, **2p**, **2q**, **2r**, and

2s are previously reported in the literature. The reference for reported compounds are cited in the Supporting Information. Hence, based on reported literature reports, structure was assigned for compounds **2o-2s**. In accordance with the reactivity pattern observed in these reactions, a similar structure is also assigned products **2j** and **2k**.

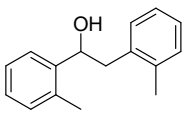
Spectral data of secondary alcohols:

1,2-Diphenylethan-1-ol (2a):[1] Purified by silica-gel column chromatography using hexane and ethyl acetate (97:3) as an eluent. Isolated as colorless liquid. Yield: 172 mg, 86%. IR



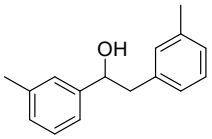
(DCM): 3366, 2979, 2855, 2833, 1645, 1461, 1209, 1177, 738, 700 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.37-7.36 (m, 4H, ArC*H*), 7.33-7.29 (m, 3H, ArC*H*), 7.27-7.25 (m, 1H, ArC*H*), 7.22-7.19 (m, 2H, ArC*H*), 4.91-4.88 (m, 1H, C*H*), 3.08-2.97 (m, 2H, CH_2), 1.97 (s, 1H, O*H*). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 143.9, 138.1, 129.6, 128.6, 128.5, 127.7, 126.7, 126.0, 75.4, 46.1.

1,2-Di-o-tolylethan-1-ol (2b): Purified by silica-gel column chromatography using hexane and ethyl acetate (97:3) as an eluent. Isolated as colorless liquid. Yield: 108 mg, 47%. IR (DCM):



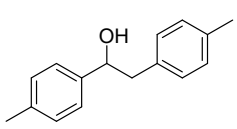
3323, 2924, 2851, 1675, 1494, 1264, 1183, 738 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.18-7.07 (m, 4H, ArC*H*), 7.03-6.93 (m, 4H, ArC*H*), 4.76-4.13 (m, 1H, C*H*), 2.93-2.78 (m, 2H, CH_2), 2.28 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 1.93 (s, 1H, O*H*). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 143.9, 138.2, 138.1, 130.3, 128.5, 128.3, 127.4, 126.5, 126.5, 122.9, 75.3, 46.1, 21.5, 21.4. HRMS (ESI) M/Z calcd for $C_{16}H_{18}O$ $(M+Na)^+$ 249.1250, found: 249.1278

1,2-Di-m-tolylethan-1-ol (2c): Purified by silica-gel column chromatography using hexane and ethyl acetate (97:3) as an eluent. Isolated as colorless liquid. Yield:



156 mg, 69%. IR (DCM): 3353, 2976, 2875, 1694, 1446, 1289, 1123, 784 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.66-7.63 (m, 1H, ArC*H*), 7.35-7.31 (m, 1H, ArC*H*), 7.25-7.18 (m, 6H, ArC*H*), 5.21-5.18 (t, *J* = 4 Hz, 1H, C*H*), 3.07-3.05 (d, *J* = 8 Hz, 2H, CH_2), 2.38 (s, 1H, CH_3), 2.30 (s, 1H, CH_3), 2.03 (s, 1H, O*H*). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 142.3, 136.8, 136.4, 134.5, 130.4, 130.3, 127.3, 126.8, 126.4, 126.0, 125.5, 70.6, 42.2, 19.6, 19.0. HRMS (ESI) M/Z calcd for $C_{16}H_{18}O$ $(M+Na)^+$ 249.1250, found: 249.1271

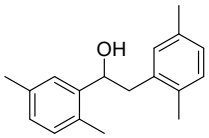
1,2-Di-p-tolylethan-1-ol (2d): Purified by silica-gel column chromatography using hexane and ethyl acetate (97:3) as an eluent. Isolated as colorless liquid. Yield: 179 mg, 79%. IR



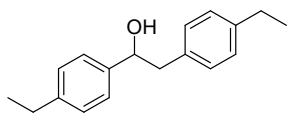
(DCM): 3349, 2942, 2881, 1676, 1436, 1283, 796 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.26-7.24 (m, 2H, ArC*H*), 7.16-7.14 (m, 2H, ArC*H*),

7.12-7.08 (m, 4H, ArC*H*), 4.85-4.82 (m, 1H, C*H*), 3.02-2.89 (m, 2H, CH_2), 2.35 (s, 1H, CH_3), 2.32 (s, 1H, CH_3), 1.75 (s, 1H, O*H*). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 144.0, 137.3, 136.2, 135.15, 129.4, 129.3, 129.1, 125.9, 75.3, 45.7, 21.2, 21.1. HRMS (ESI) M/Z calcd for $C_{16}H_{18}O$ $(M+Na)^+$ 249.1250, found: 249.1268

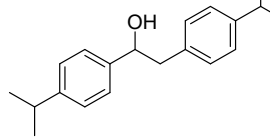
1,2-Bis(2,5-dimethylphenyl)ethan-1-ol (2e): Purified by silica-gel column chromatography using hexane and ethyl acetate (97:3) as an eluent. Isolated as colorless liquid. Yield: 179 mg, 70%. IR (DCM): 3342, 3123, 2942, 2856, 1674, 1433, 1232, 845, 838, 726 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.46 (s, 1H, ArC*H*), 7.12-7.00 (m, 5H, ArC*H*), 5.16-5.12 (m, 1H, C*H*), 3.03-2.91 (m, 2H, CH_2), 2.40 (s, 3H, CH_3), 2.35 (s, 6H, 2CH_3), 2.30 (s, 3H, CH_3), 1.92 (m, 1H, O*H*), $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 142.1, 136.2, 135.8, 135.5, 133.6, 131.1, 131, 130.4, 130.2, 128, 127.5, 125.9, 70.5, 40.2, 21.1, 20.9, 19.2, 18.6. HRMS (ESI) M/Z calcd for $C_{18}H_{22}O$ $(M+Na)^+$ 277.1563, found: 277.1550.



1,2-Bis(4-ethylphenyl)ethan-1-ol (2f): Purified by silica-gel column chromatography using hexane and ethyl acetate (97:3) as an eluent. Isolated as colorless liquid. Yield: 178 mg, 70%. IR (DCM): 3347, 3178, 3063, 2969, 2858, 1634, 1446, 1235, 841, 730, 710 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.23-7.21 (m, 2H, ArC*H*), 7.12-7.10 (m, 2H, ArC*H*), 7.07 (s, 1H, ArC*H*), 4.78-4.75 (m, 1H, C*H*), 2.95-2.82 (m, 2H, CH_2), 2.60-2.52 (m, 4H, 2CH_2), 1.18-1.14 (m, 6H, 2CH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 143.6, 142.5, 141.2, 135.4, 129.4, 128.0, 127.9, 125.9, 75.2, 45.7, 28.6, 28.5, 15.6, 15.6. HRMS (ESI) M/Z calcd for $C_{18}H_{22}O$ $(M+Na)^+$ 277.1563, found: 277.1557.



1,2-Bis(4-isopropylphenyl)ethan-1-ol (2g): Purified by silica-gel column chromatography using hexane and ethyl acetate (97:3) as an eluent. Isolated as colorless liquid. Yield: 183 mg, 64%. IR (DCM): 3367, 3178, 3043, 2942, 2876, 1672, 1467, 1234, 938, 821, 746 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.27-7.25 (m, 2H, ArC*H*), 7.18-7.15 (m, 2H, ArC*H*), 7.11(s, 4H, ArC*H*), 4.80-4.77 (m, 1H, C*H*), 2.97-2.79 (m, 4H, C*H*, CH_2), 1.86 (s, 1H, O*H*), 1.88 (s, 12H, 4CH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 141.4, 129.3, 126.6, 126.5, 125.8, 72.5, 45.7, 33.8, 33.7. HRMS (ESI) M/Z calcd for $C_{20}H_{26}O$ $(M+Na)^+$ 305.1876, found: 305.1882.



1,2-Bis(4-(tert-butyl)phenyl)ethan-1-ol (2h): Purified by silica-gel column chromatography using hexane and ethyl acetate (97:3) as an eluent. Isolated as colorless liquid. Yield: 222 mg, 71%. IR (DCM): 3356, 3178, 3093, 2956, 2865, 1671, 1492, 1232, 978, 890, 767 cm^{-1}. ^1H NMR (400

MHz, $CDCl_3$): δ 7.32-7.26 (m, 6H, ArC*H*), 7.13-7.11 (m, 2H, ArC*H*), 4.79-4.75 (m, 1H, C*H*), 2.96-2.80 (m, 2H, CH_2), 1.89 (s, 1H, O*H*), 1.25-1.24 (m, 18H, 6CH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ150.5, 149.4, 141.1, 135.4, 129.1, 125.6, 125.5, 125.4, 75.1, 45.4, 34.5, 34.4, 31.4. HRMS (ESI) M/Z calcd for $C_{22}H_{30}O$ $(M+Na)^+$ 333.2189, found: 333.2183.

1,2-Bis(4-isobutylphenyl)ethan-1-ol (2i): Purified by silica-gel column chromatography using hexane and ethyl acetate (97:3) as an eluent. Isolated as colorless liquid. Yield: 209 mg, 67%. IR (DCM): 3344, 3156, 3067, 2942, 2887, 1649, 1467, 1261, 976, 878, 798 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.31-7.28 (m, 2H, ArC*H*), 7.16-7.10 (m, 6H, ArC*H*), 4.90-4.87 (m, 1H, C*H*), 3.06-2.95 (m, 2H, CH_2), 2.52-2.47 (m, 4H, CH_2), 1.93-1.85 (m, 3H, 2C*H,* O*H*), 0.95-0.97 (d, 12H, 4CH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 141.2, 141.0, 139.9, 135.3, 129.2, 129.2, 129.1, 125.7, 75.2, 45.7, 45.1, 30.2, 30.2, 22.4, 22.3. HRMS (ESI) M/Z calcd for $C_{22}H_{30}O$ $(M+Na)^+$ 333.2189, found: 333.2215.

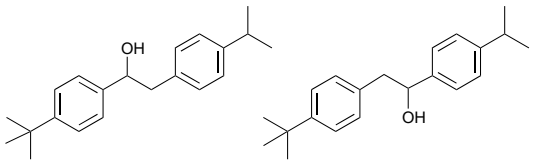
1-(4-Isopropylphenyl)-1-phenylethan-1-ol (2j): Purified by silica-gel column chromatography using hexane and ethyl acetate (97:3) as an eluent. Isolated as colorless liquid. Yield: 196 mg, 81%. IR (DCM): 3365, 3189, 2989, 2874, 1650, 1423, 1232, 967, 878, 760 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.44-7.39 (m, 3H, ArC*H*), 7.36-7.30 (m, 2H, ArC*H*), 7.28-7.26 (m, 1H, ArC*H*), 7.25-7.19 (m, 3H, ArC*H*), 4.94-4.91 (m, 1H, C*H*), 3.10-2.92 (m, 3H, C*H,* CH_2), 2.12 (s, 1H, O*H*), 1.32-1.30 (d, 6H, 2CH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 147.2, 114.0, 135.4, 129.4, 128.4, 127.5, 126.6, 125.9, 75.3, 45.8, 33.7, 24.0. HRMS (ESI) M/Z calcd for $C_{17}H_{20}O$ $(M+Na)^+$ 263.1406, found: 263.1379.

1-(4-(Tert-butyl)phenyl)-1-phenylethan-1-ol (2k): Purified by silica-gel column chromatography using hexane and ethyl acetate (97:3) as an eluent. Isolated as colorless liquid. Yield: 224 mg, 88%. IR (DCM): 3356, 3143, 3033, 2955, 2847, 1676, 1454, 1238, 834, 844, 709 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.41-7.37 (m, 3H, ArC*H*), 7.37-7.35 (m, 3H, ArC*H*), 7.32-7.27 (m, 1H, ArC*H*), 7.19-7.16 (m, 2H, ArC*H*), 4.91-4.87 (m, 1H, C*H*), 3.05-2.90 (m, 2H, CH_2), 2.02 (s, 1H, O*H*), 1.33 (s, 9H, 3CH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 149.6, 144.1, 135.1, 129.5, 129.2, 128.5, 127.6, 125.9, 125.7, 125.6, 125.4, 75.3, 45.7, 34.5, 31.4. HRMS (ESI) M/Z calcd for $C_{18}H_{22}O$ $(M+Na)^+$ 277.1563, found: 277.1553.

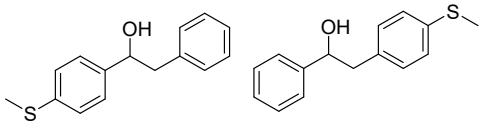
1-(4-Isopropylphenyl)-2-(p-tolyl)ethan-1-ol and 2-(4-isopropylphenyl)-1-(p-tolyl)ethan-1-ol (2l): Purified by silica-gel column chromatography using hexane and ethyl acetate (97:3) as an eluent. Isolated

as colorless liquid. Compound isolated was mixture of product (39:61), Yield: 202 mg, 79%. IR (DCM): 3331, 3167, 3031, 2987, 2841, 1684, 1432, 1298, 956, 845, 750 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.32-7.23 (m, 3H, ArC*H*), 7.18-7.16 (m, 3H, ArC*H*), 7.12 (s, 1H, ArC*H*), 4.87-4.82 (m, 1H, C*H*), 3.03-2.88 (m, 3H, CH_2, C*H*), 2.36, 2.34 (s, 3H, CH_3), 1.25-1.24 (d, *j* = 4 Hz, 6H, 2CH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 148.3, 147.2, 141.4, 141.1, 137.3, 136.2, 135.6, 135.3, 129.5, 129.4, 129.3, 129.1, 126.7, 126.5, 126.0, 125.9, 73.35, 75.26, 45.8, 45.6, 33.9, 33.8, 24.1, 21.2, 21.1. HRMS (ESI) M/Z calcd for $C_{18}H_{23}O$ (M) 255.1749, found: 255.1766.

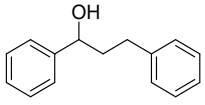
2-(4-(Tert-butyl)phenyl)-1-(4-isopropylphenyl)ethan-1-ol and 1-(4-(tert-butyl)phenyl)-2-(4-isopropylphenyl)ethan-1-ol (2m): Purified by silica-gel column chromatography using hexane and ethyl acetate (97:3) as an eluent. Isolated as colorless liquid. Compound isolated was mixture of product (83:17), Yield: 220 mg, 74%. IR (DCM): 3298, 3044, 2894, 2815, 1675, 1424, 1244, 956, 845, 728 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.42-7.34 (m, 4H, ArC*H*), 7.26-7.20 (m, 4H, ArC*H*), 4.89-4.85 (m, 1H, C*H*), 3.03-2.91 (m, 3H, CH_2, C*H*), 1.92 (s, 1H, O*H*), 1.29-1.26 (m, 6H, 2CH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 150.6, 149.5, 148.3, 147.2, 141.2, 135.8, 141.2, 135.8, 135.4, 129.5, 129.2, 126.7, 126.6, 126.0, 125.7, 125.6, 125.4, 75.2, 75.2, 45.7, 45.6, 34.6, 34.5, 39.9, 33.8, 31.5, 24.1. ESI mass for $C_{21}H_{29}O$, 297.1680.



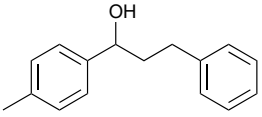
1-(4-(Methylthio)phenyl)-2-phenylethan-1-ol and 2-(4-(methylthio)phenyl)-1-phenylethan-1-ol (2n): Purified by silica-gel column chromatography using hexane and ethyl acetate (97:3) as an eluent. Isolated as colorless liquid. Compound isolated was mixture of product (64:36), Yield: 184 mg, 75%. IR (DCM): 3389, 3167, 3098, 2964, 2851, 1678, 1432, 1241, 987, 843, 744 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.40-7.20 (m, 9H, ArC*H*), 7.14-7.12 (m, 1H, ArC*H*), 4.91-4.87 (m, 1H, C*H*), 3.04-2.99 (m, 2H, CH_2), 2.51, 2.49 (s, 3H, SCH_3), 2.01 (s, 1H, O*H*). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 134.7, 140.7, 137.8, 136.4, 134.9, 130.11, 129.5, 128.5, 128.4, 127.6, 127.0, 126.9, 126.7, 126.6, 126.4, 125.9, 75.3, 74.9, 46.0, 45.4, 16.0, 15.9. ESI mass for $C_{15}H_{17}OS$, 245.1302.



1,3-Diphenylpropan-1-ol (2o): Purified by silica-gel column chromatography using hexane and ethyl acetate (97:3) as an eluent. Isolated as colorless liquid. Yield: 188 mg, 88%. IR (DCM): 3376, 3154, 3078, 2967, 2871, 1689, 1478, 1231, 978, 728 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.42-7.05 (m, 10H, ArC*H*), 4.94-4.90 (m, 1H, C*H*), 3.09-2.96 (m, 2H, CH_2), 2.42-2.40 (m, 2H, CH_2), 2.13 (s, 1H, O*H*). $^{13}C\{^1H\}$ NMR

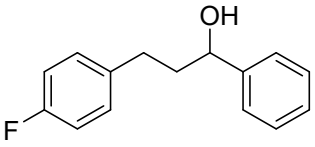


(100.6 MHz, $CDCl_3$): δ 143.9, 138.2, 138.1, 138.0, 130.3, 129.5, 128.5, 128.4, 128.4, 128.3, 128.3, 127.6, 127.4, 126.6, 126.5, 125.9, 123.0, 75.3, 46.1, 21.4. HRMS (ESI) M/Z calcd for $C_{15}H_{16}O$ $(M+Na)^+$ 235.1093, found: 235.1100.



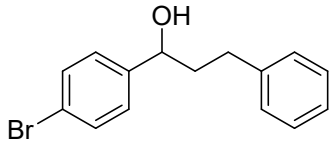
3-Phenyl-1-(p-tolyl)propan-1-ol (2p):[2] Purified by silica-gel column chromatography using hexane and ethyl acetate (97:3) as an eluent. Isolated as colorless liquid. Yield: 122 mg, 53%. IR (DCM): 3276, 3054, 3028, 2927, 2861, 1649, 1428, 1251, 989, 741 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.18-7.03 (m, 9H, ArC*H*), 4.51-4.48 (t, 1H, *J* = 4Hz, C*H*), 2.65-2.48 (m, 2H, CH_2), 2.23 (s, 1H, CH_3), 2.05 (s, 1H, O*H*), 2.03-21.84 (m, 2H, CH_2). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 141.9, 141.6, 137.3, 129.2, 128.5, 128.4, 128.4, 126.0, 125.9, 125.8, 73.7, 40.4, 31.2, 21.2,

3-(4-Fluorophenyl)-1-phenylpropan-1-ol (2q):[3] Purified by silica-gel column chromatography using hexane and ethyl acetate (97:3) as an eluent. Isolated as colorless liquid.



Yield: 110 mg, 47%. IR (DCM): 3166, 3154, 3038, 2965, 2856, 1643, 1443, 1241, 981, 745 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.41-7.30 (m, 5H, ArC*H*), 7.18-7.15 (m, 2H, ArC*H*), 7.01-6.97 (m, 2H, ArC*H*), 4.71-4.68 (m, 1H, C*H*), 2.79-2.63 (m, 2H, CH_2), 2.18-1.97 (m, 3H, CH_2, O*H*). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 162.5, 160.0, 144.4, 137.4, 137.3, 129.8, 129.7, 128.5, 127.7, 125.9, 115.2, 115.0, 73.7, 40.5, 31.2.

1-(4-Bromophenyl)-3-phenylpropan-1-ol (2r):[2] Purified by silica-gel column chromatography using hexane and ethyl acetate (97:3) as an eluent. Isolated as colorless liquid. Yield: 126 mg, 43%. IR (DCM): 3173, 3151, 3028, 2993, 2870, 1675, 1623, 1413, 1229, 991, 776 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): ^1H NMR (400 MHz, $CDCl_3$): δ 7.39-7.29 (m, 7H, ArC*H*), 7.06-7.04 (d, 2H, *J* = 8 Hz, ArC*H*), 4.66-4.63 (m, 1H, C*H*), 2.73-2.57 (m, 2H, CH_2), 2.14-1.93 (m, 2H, CH_2), 1.85 (s, 1H, O*H*). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 144.4, 140.8, 131.5, 130.3, 128.6, 127.8, 125.9, 119.6, 73.7, 40.3, 31.5.

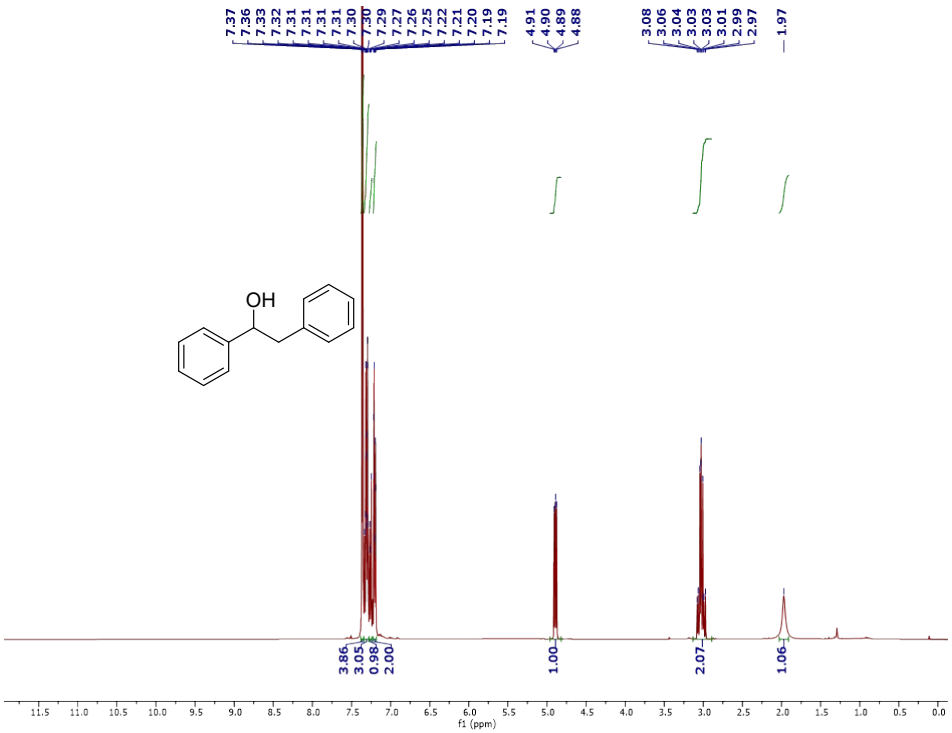


1-Phenylhexan-1-ol (2s):[4] Purified by silica-gel column chromatography using hexane and ethyl acetate (97:3) as an eluent. Isolated as colorless liquid. Yield: 101 mg, 56%. IR (DCM): 3161, 3057, 3033, 2933, 2865, 2860, 1643, 1633, 1421, 1409, 1226, 1174, 981, 823 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.34-7.33 (m, 4H, ArC*H*), 7.28-7.25 (m, 1H, ArC*H*), 4.66-4.63 (m, 1H, C*H*), 1.85-1.66 (m, 3H, CH_2, C*H*), 1.43-1.37 (m, 1H, C*H*), 1.30-1.27 (m, 4H, CH_2), 0.88-0.85 (m, 3H, *J*

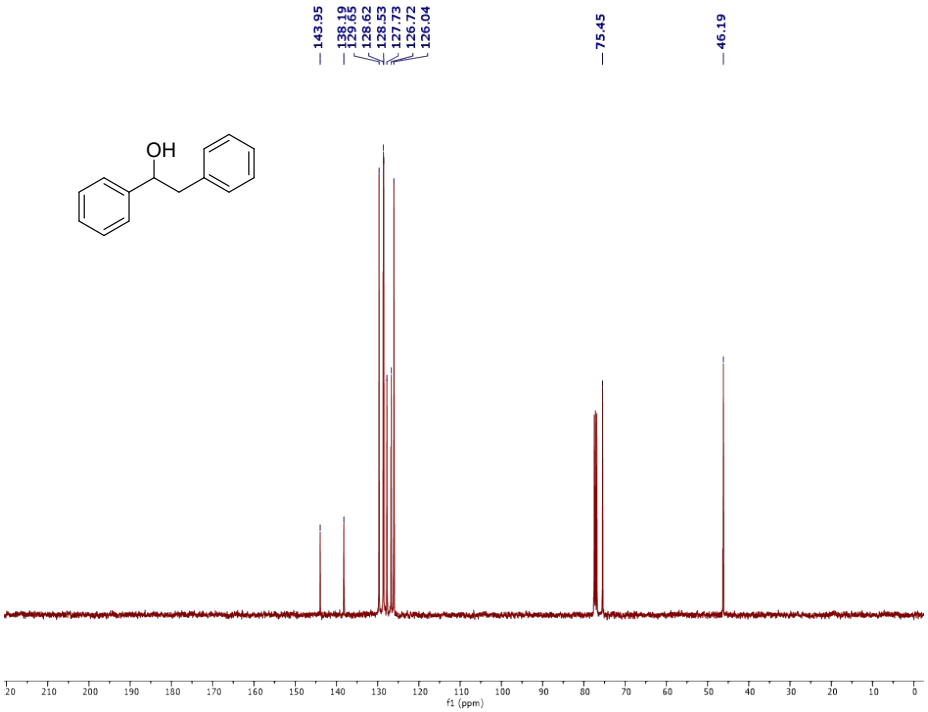
= 4 Hz, CH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 145.0, 128.5, 127.5, 126.0, 74.8, 39.1, 31.8, 25.6, 22.6, 14.1.

NMR spectra of secondary alcohols:

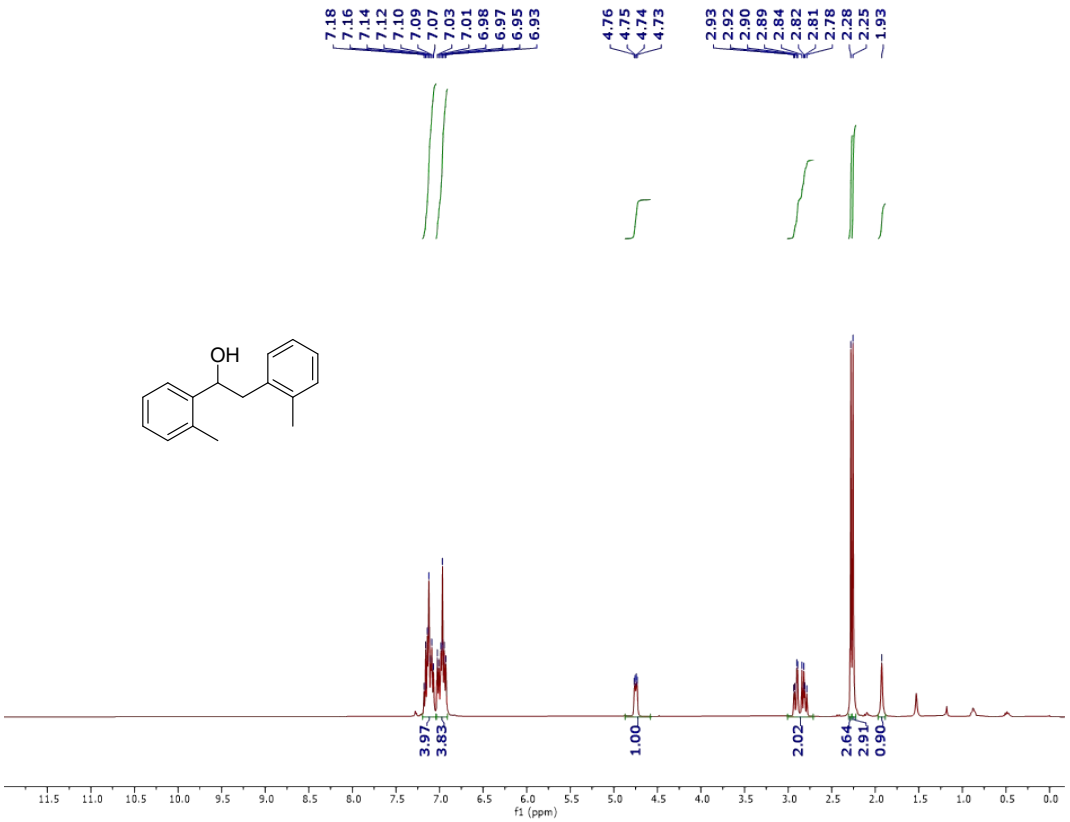
^1H NMR spectrum of 1,2-diphenylethan-1-ol (**2a**, 400 MHz, $CDCl_3$):



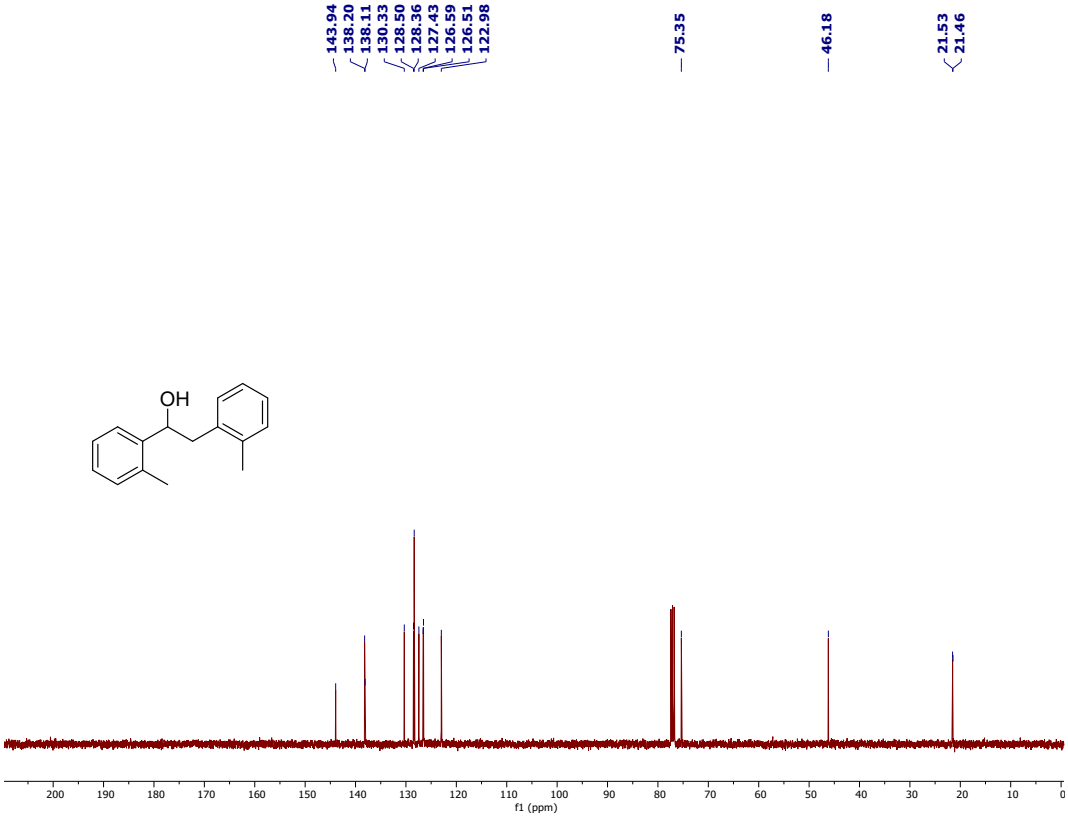
$^{13}C\{^1H\}$ NMR spectrum of 1,2-diphenylethan-1-ol (**2a**, 101 MHz, $CDCl_3$):



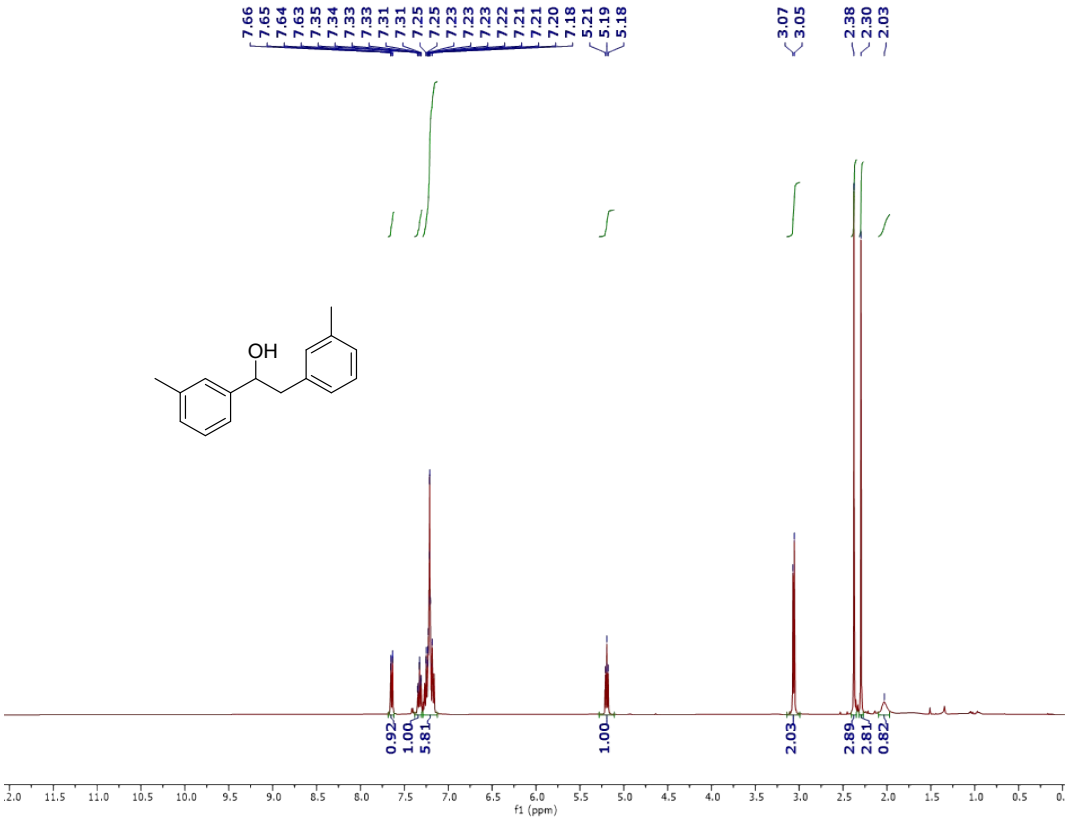
^{1}H NMR spectrum of 1,2-di-o-tolylethan-1-ol (**2b**, 400 MHz, $CDCl_3$):



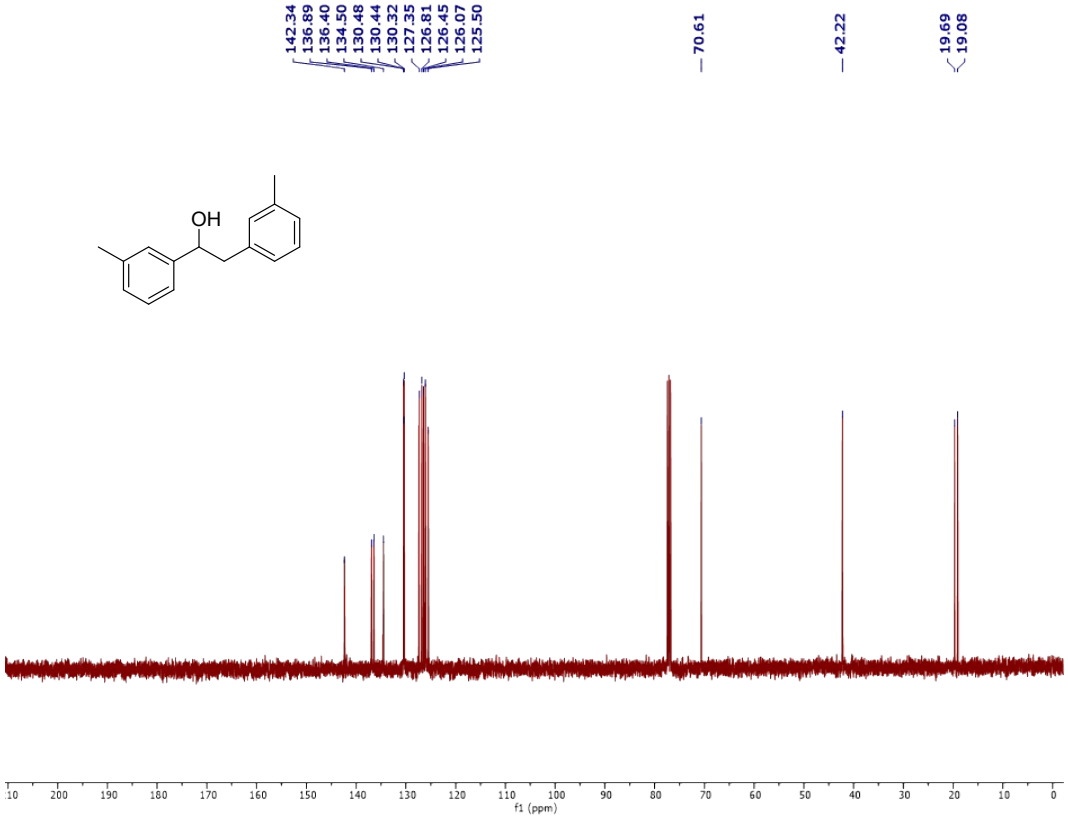
^{13}C{^{1}H} NMR spectrum of 1,2-di-o-tolylethan-1-ol (**2b**, 101 MHz, $CDCl_3$):



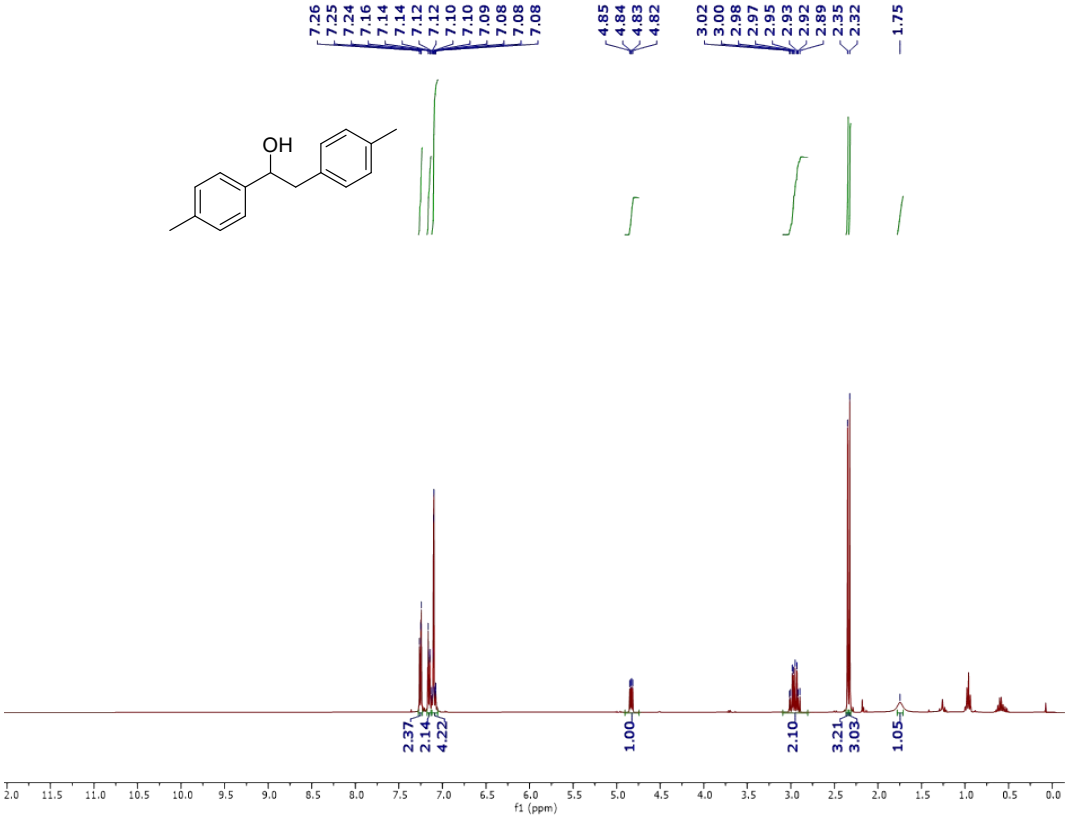
^{1}H NMR spectrum of 1,2-di-*m*-tolylethan-1-ol (**2c**, 400 MHz, $CDCl_3$):



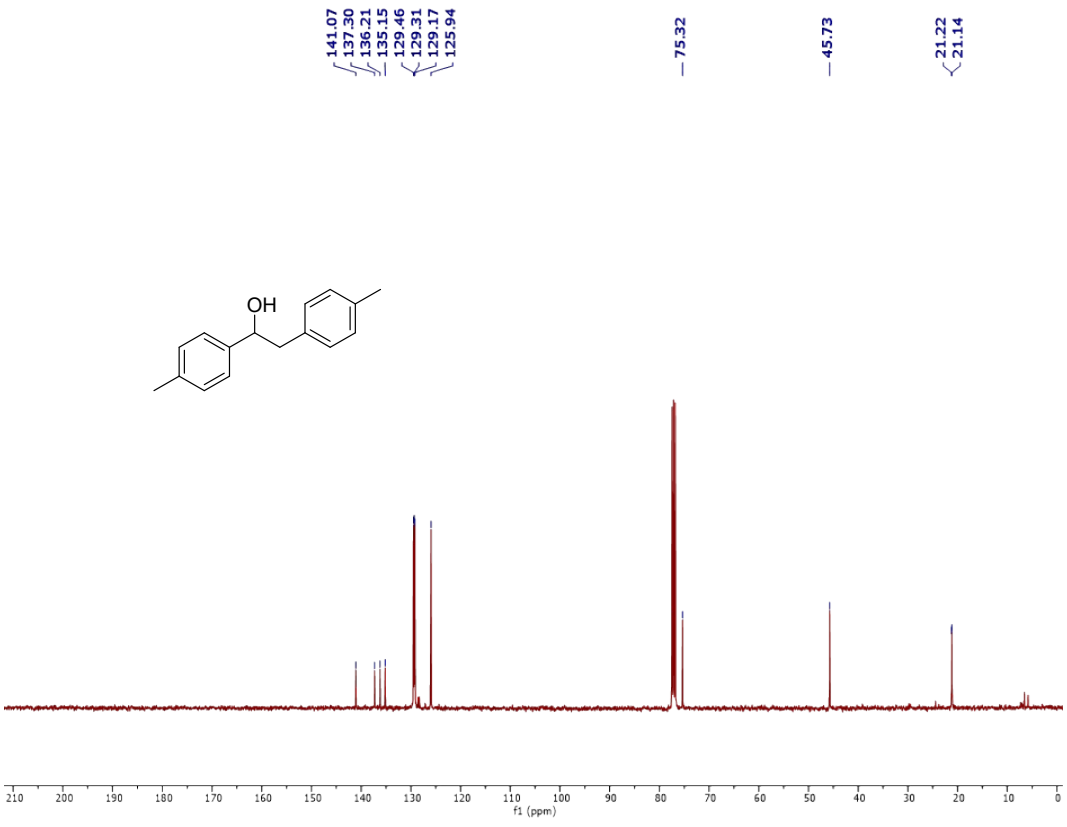
$^{13}C\{^{1}H\}$ NMR spectrum of 1,2-di-*m*-tolylethan-1-ol (**2c**, 101 MHz, $CDCl_3$):



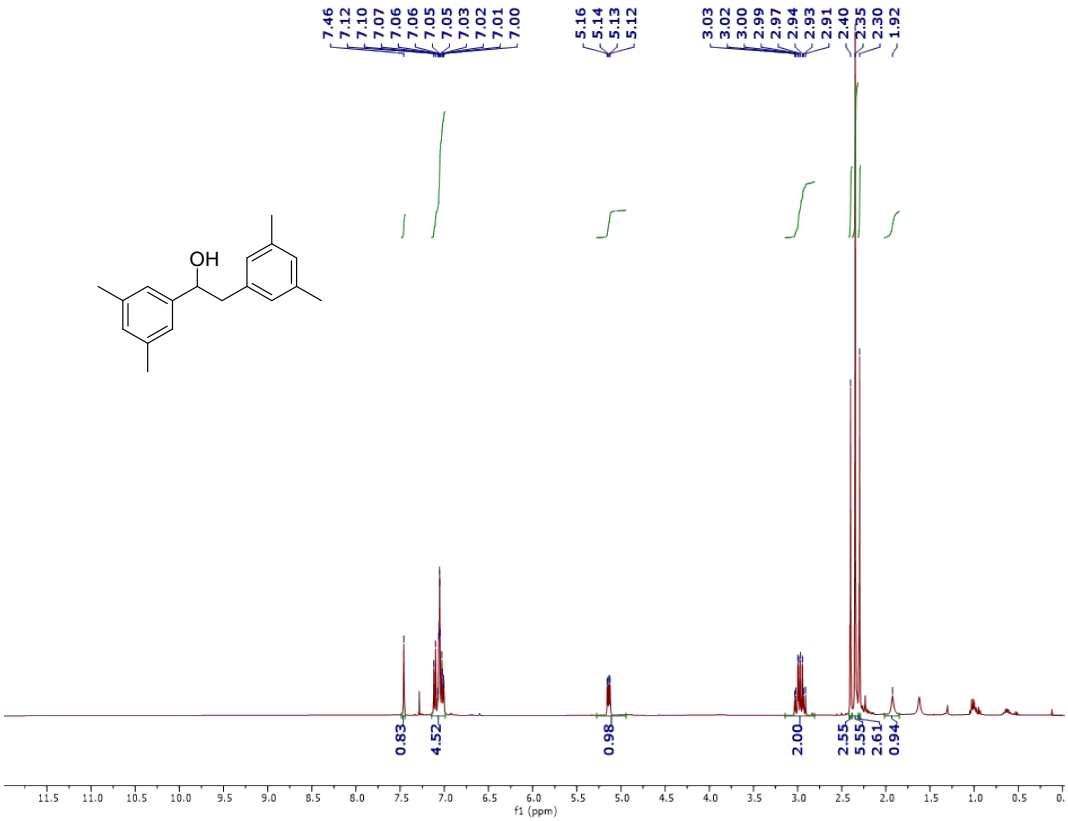
^{1}H NMR spectrum of 1,2-di-*p*-tolylethan-1-ol (**2d**, 400 MHz, $CDCl_3$):



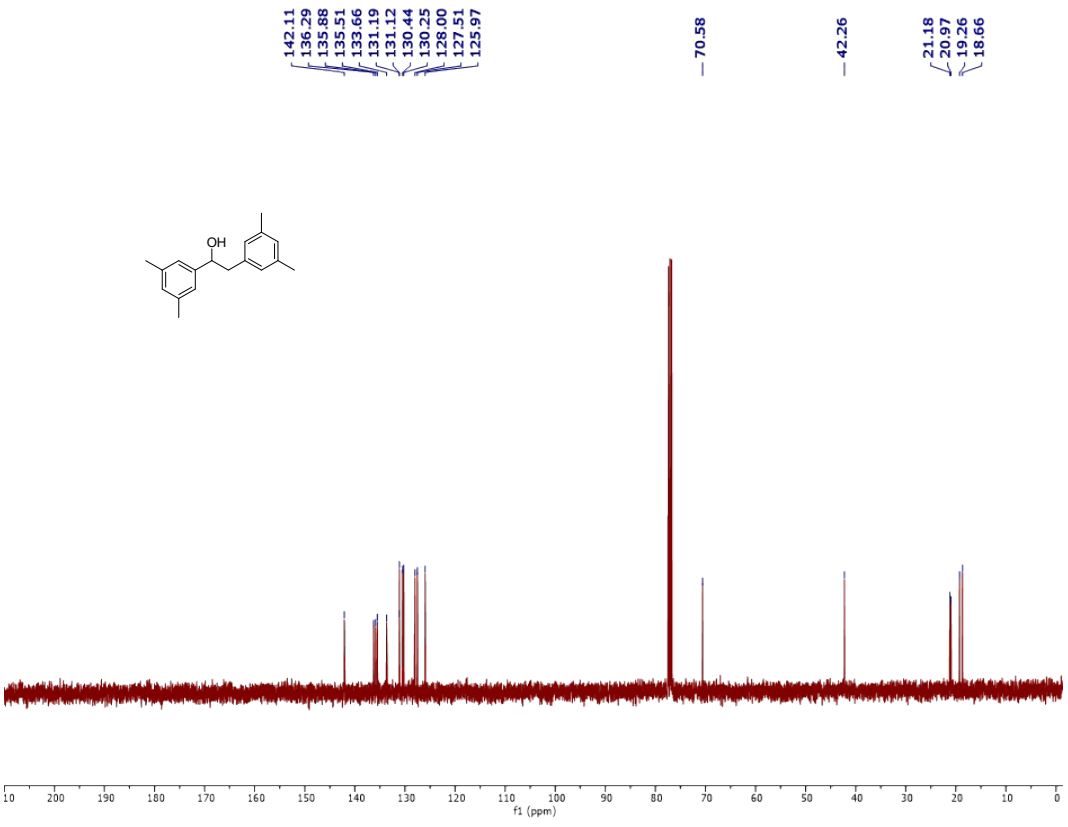
^{13}C{^{1}H} NMR spectrum of 1,2-di-*p*-tolylethan-1-ol (**2d**, 101 MHz, $CDCl_3$):



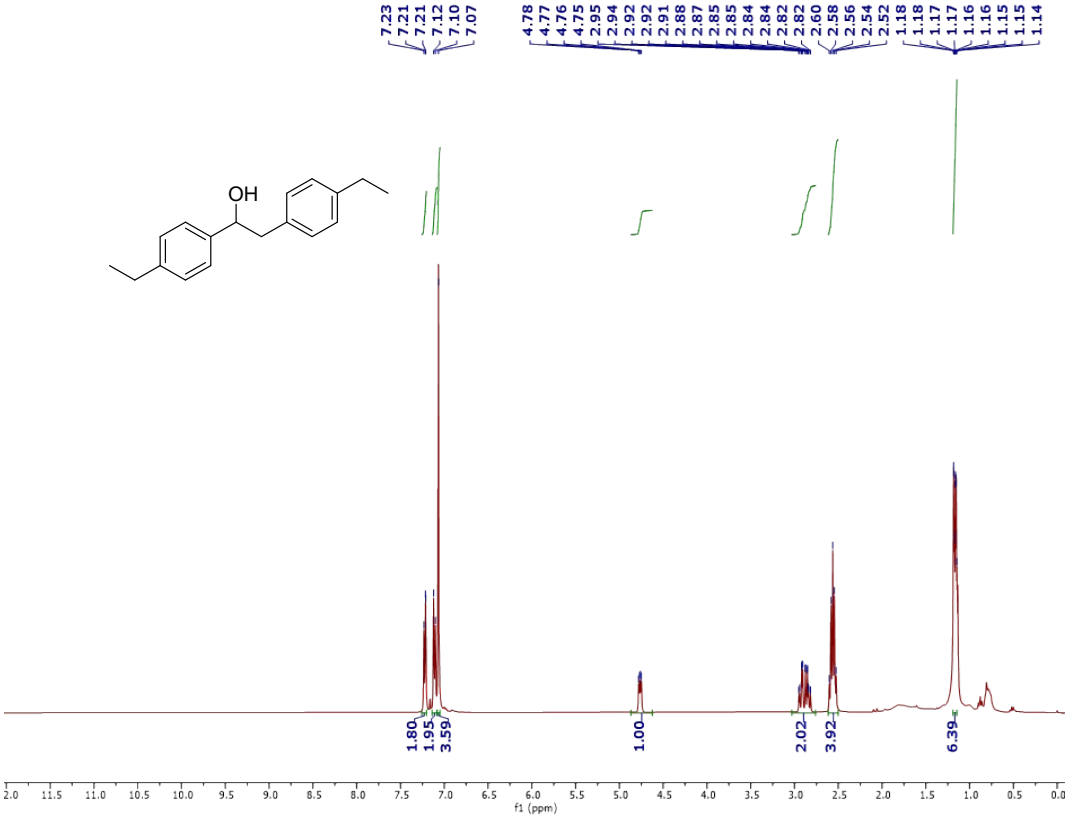
^{1}H NMR spectrum of 1,2-bis(2,5-dimethylphenyl)ethan-1-ol (**2e**, 400 MHz, $CDCl_3$):



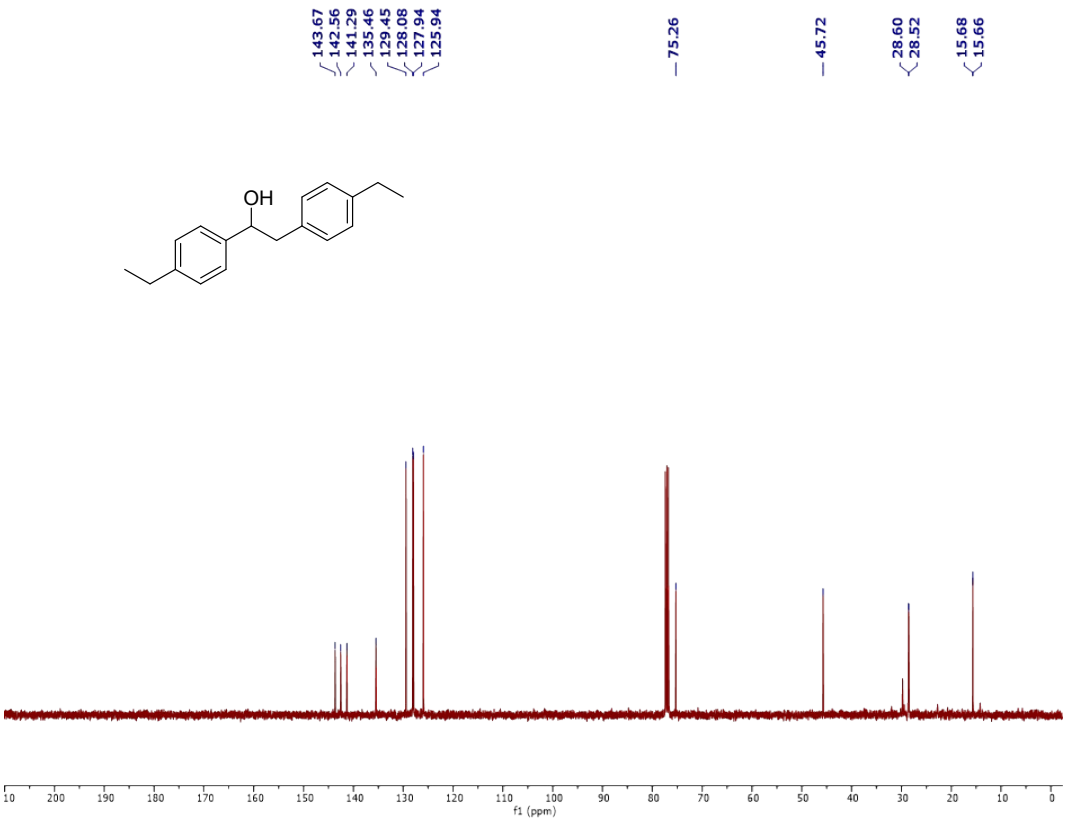
^{13}C{^{1}H} NMR spectrum of 1,2-bis(2,5-dimethylphenyl)ethan-1-ol (**2e**, 101 MHz, $CDCl_3$):



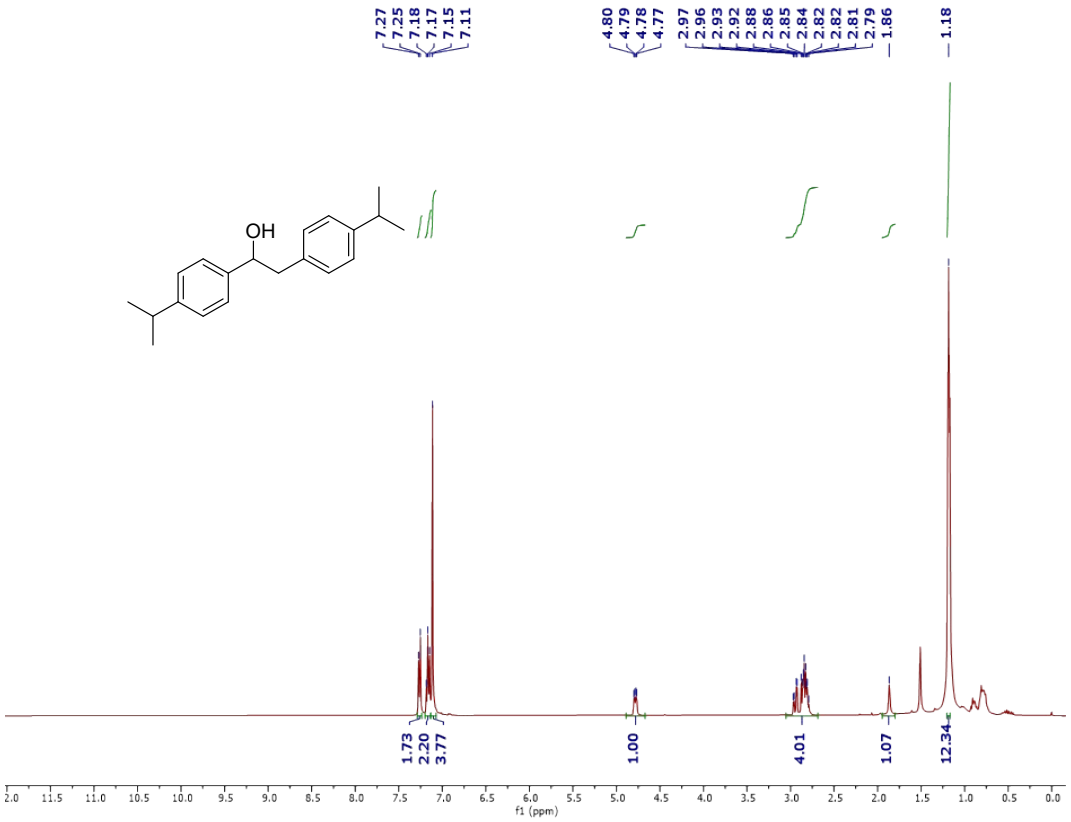
^{1}H NMR spectrum of 1,2-bis(4-ethylphenyl)ethan-1-ol (**2f**, 400 MHz, $CDCl_3$):



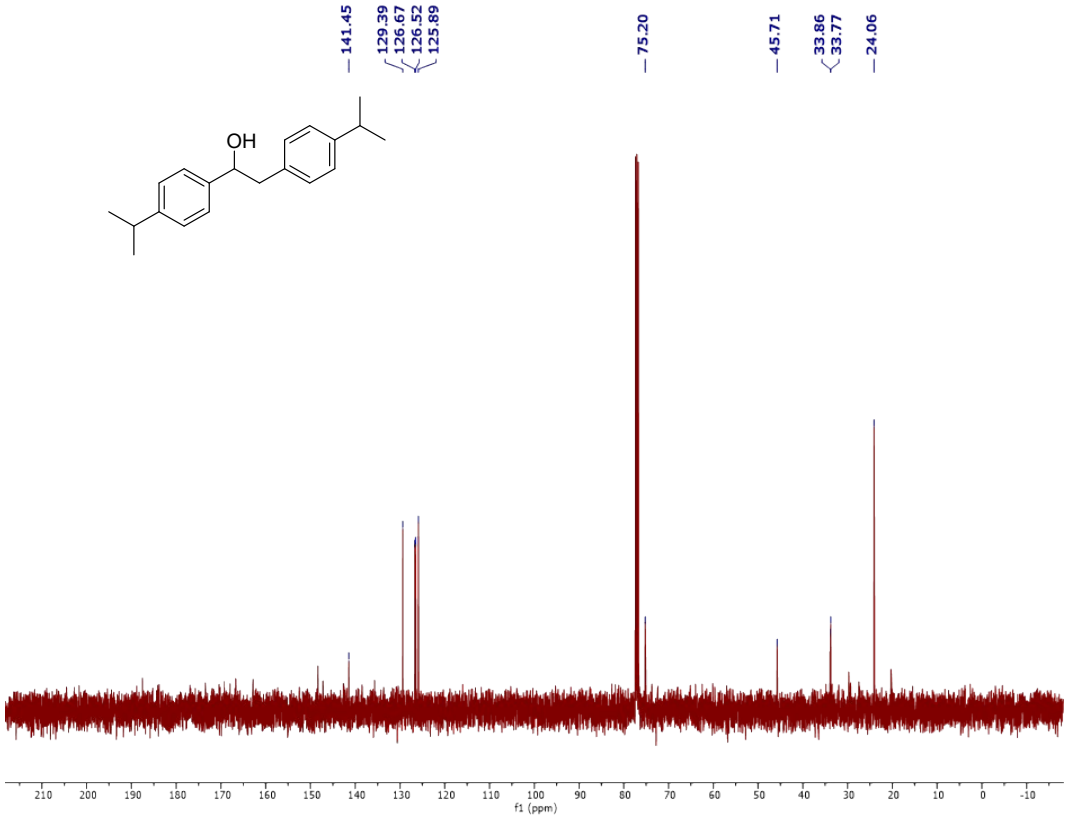
^{13}C{^{1}H} NMR spectrum of 1,2-bis(4-ethylphenyl)ethan-1-ol (**2f**, 101 MHz, $CDCl_3$):



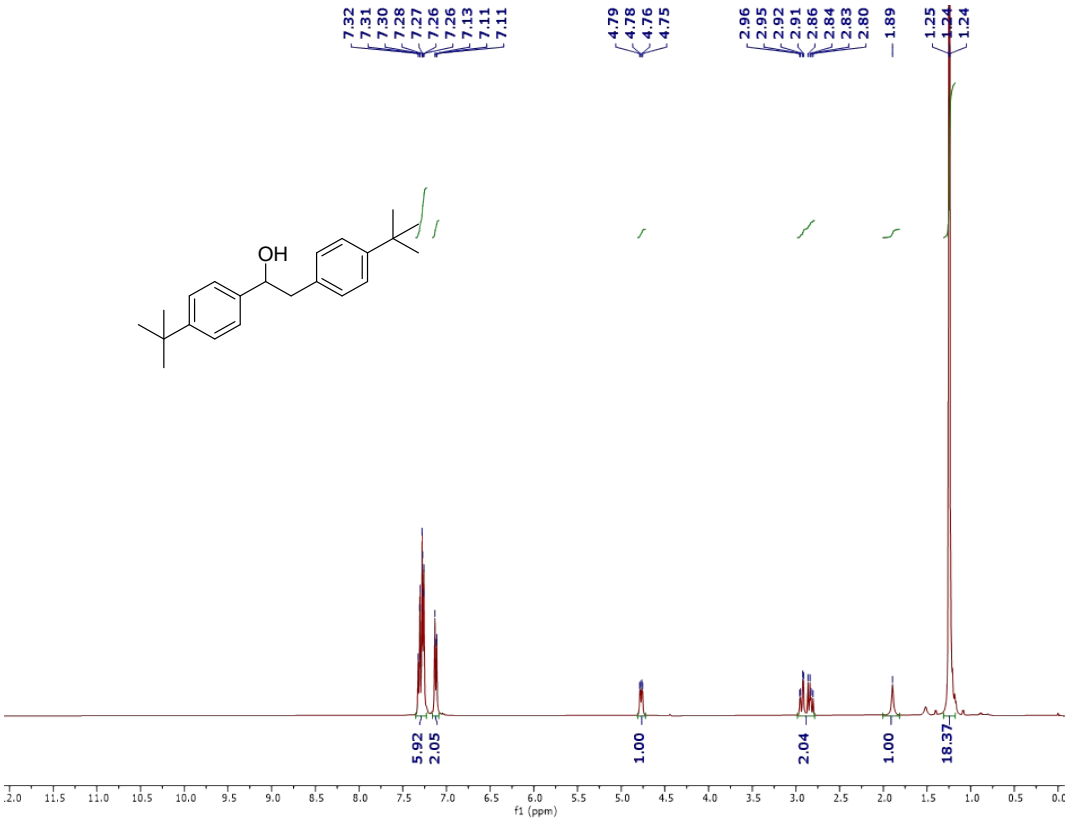
^{1}H NMR spectrum of 1,2-bis(4-isopropylphenyl)ethan-1-ol (**2g**, 400 MHz, $CDCl_3$):



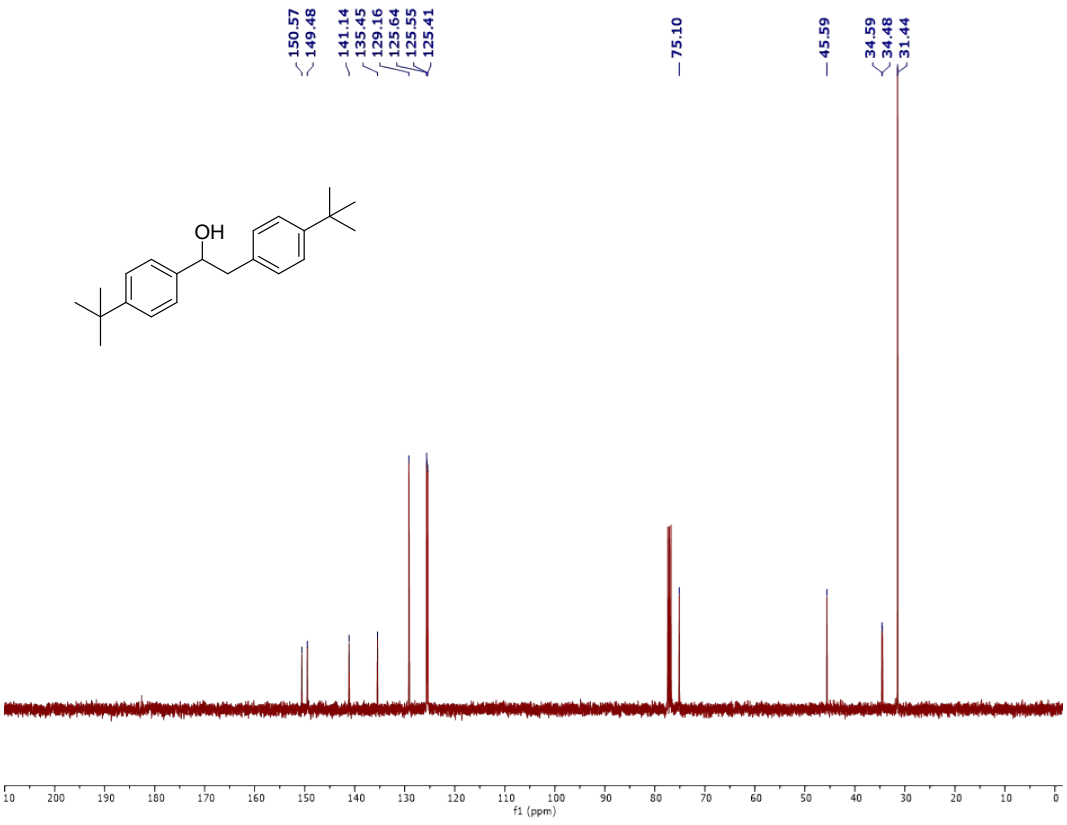
^{13}C{^{1}H} NMR spectrum of 1,2-bis(4-isopropylphenyl)ethan-1-ol (**2g**, 101 MHz, $CDCl_3$):



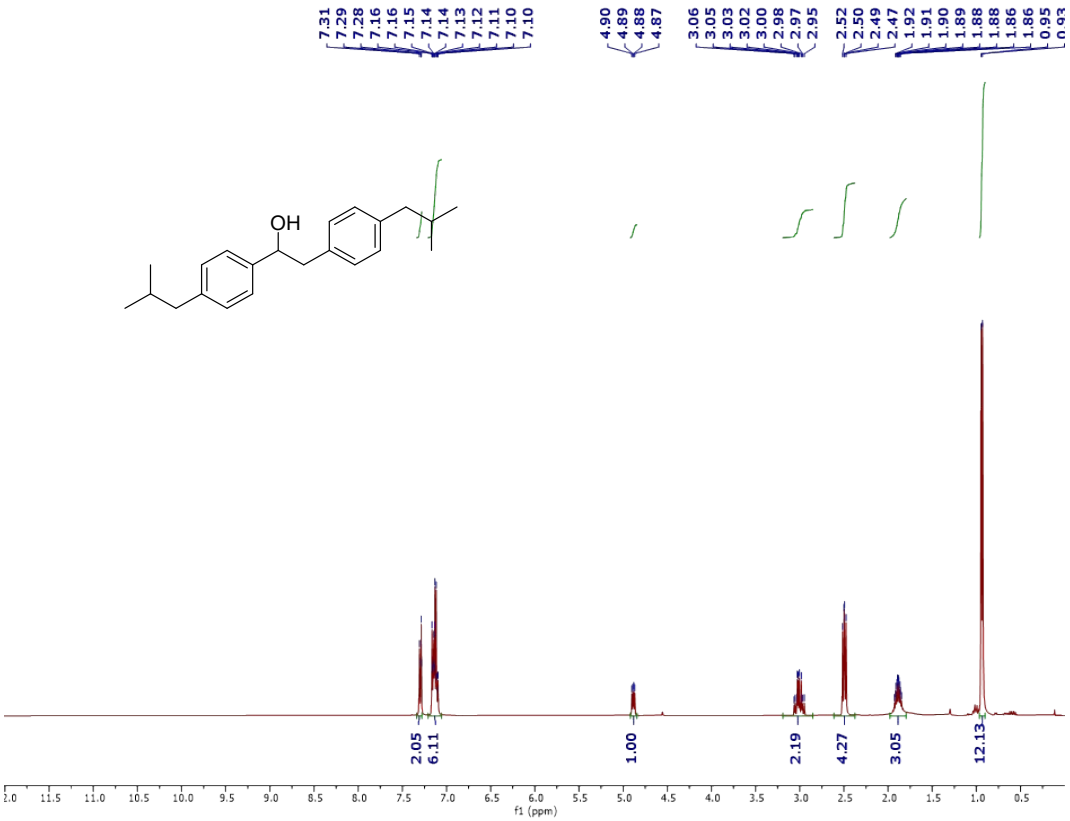
^{1}H NMR spectrum of 1,2-bis(4-(tert-butyl)phenyl)ethan-1-ol (**2h**, 400 MHz, $CDCl_3$):



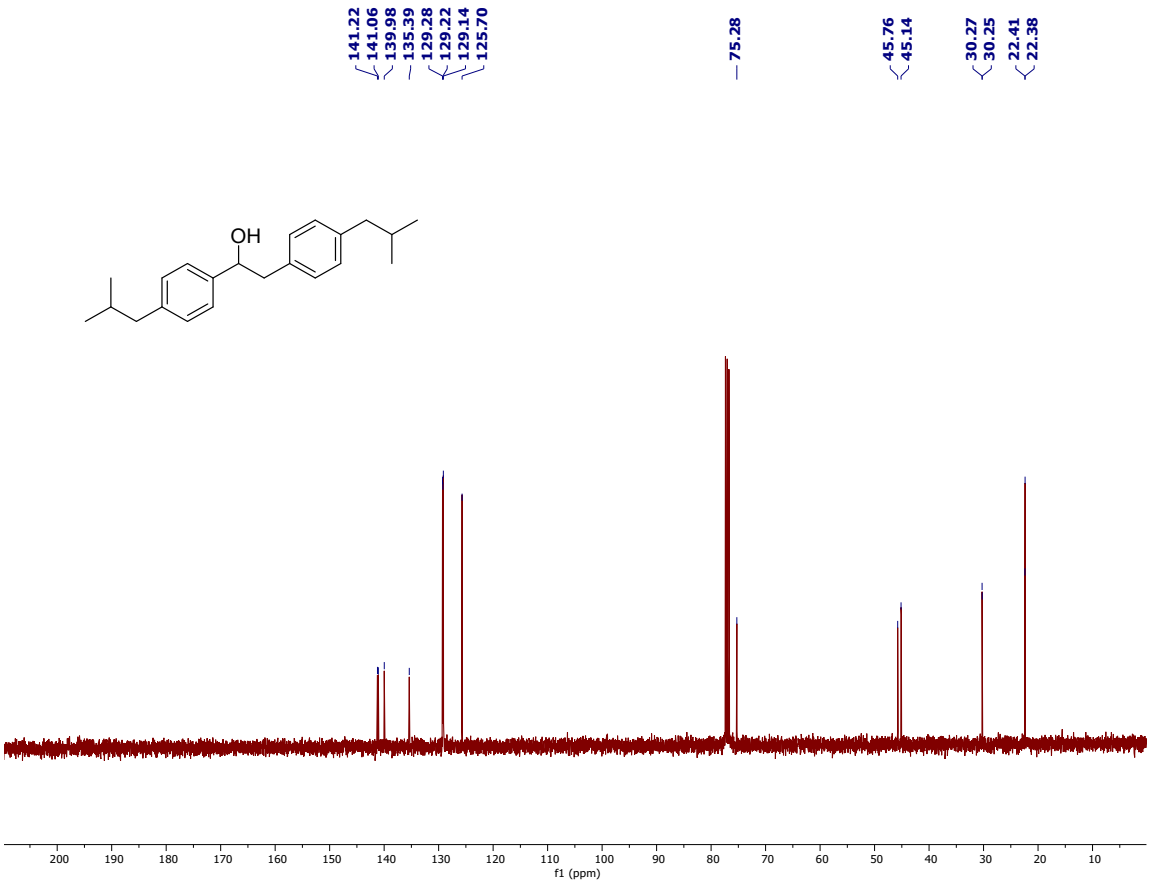
^{13}C{^{1}H} NMR spectrum of 1,2-bis(4-(tert-butyl)phenyl)ethan-1-ol (**2h**, 101 MHz, $CDCl_3$):



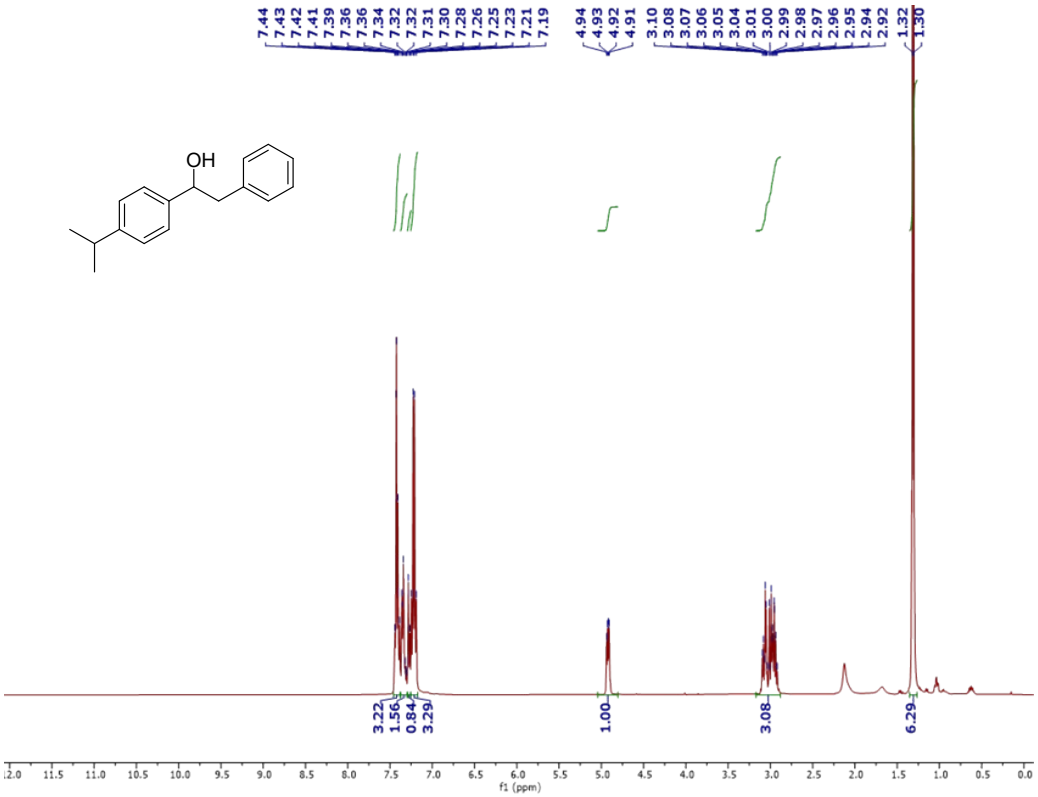
^{1}H NMR spectrum of 1,2-bis(4-isobutylphenyl)ethan-1-ol (**2i**, 400 MHz, $CDCl_3$):



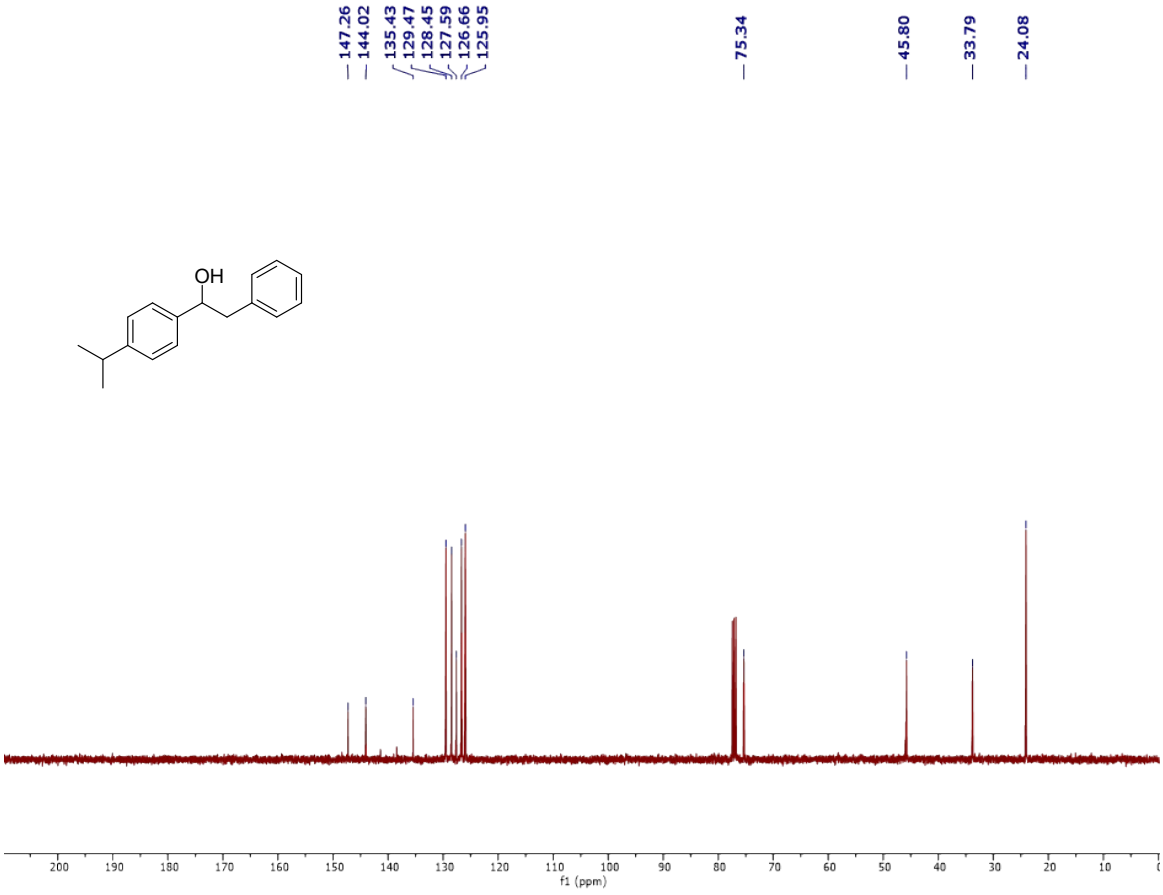
^{13}C{^{1}H} NMR spectrum of 1,2-bis(4-isobutylphenyl)ethan-1-ol (**2i**, 101 MHz, $CDCl_3$):



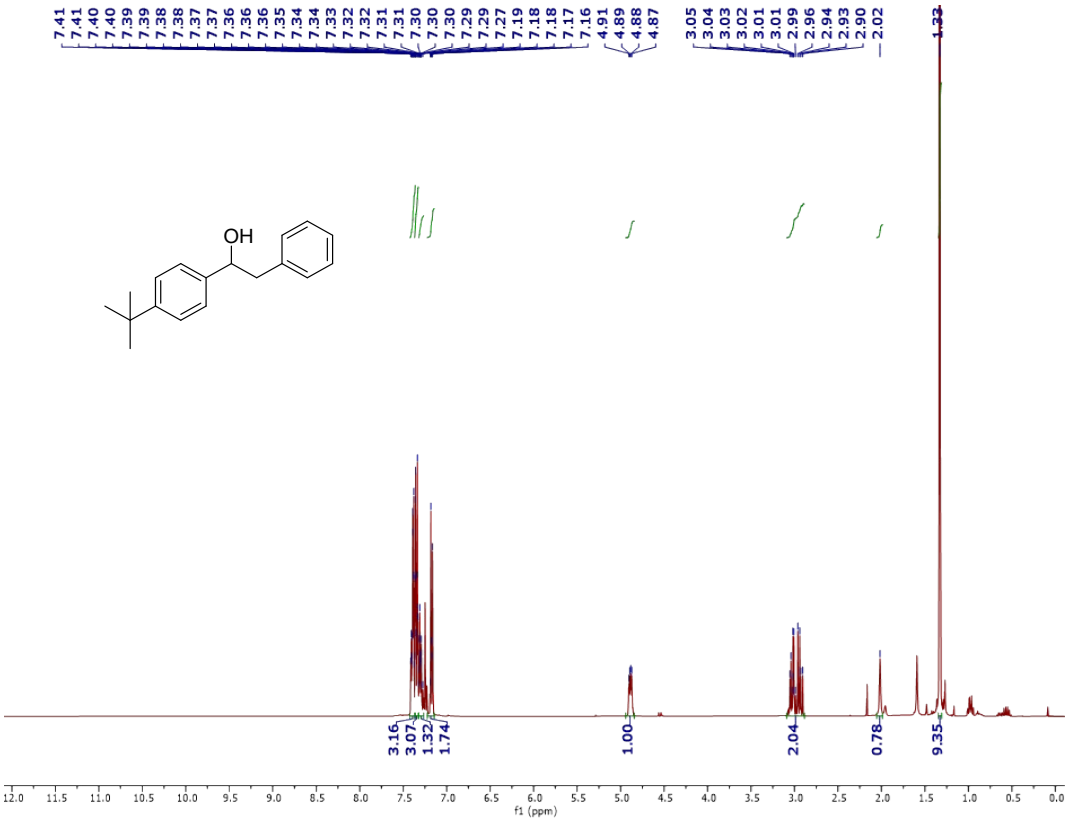
^{1}H NMR spectrum of 2-(4-isopropylphenyl)-1-phenylethan-1-ol (**2j**, 400 MHz, $CDCl_3$):



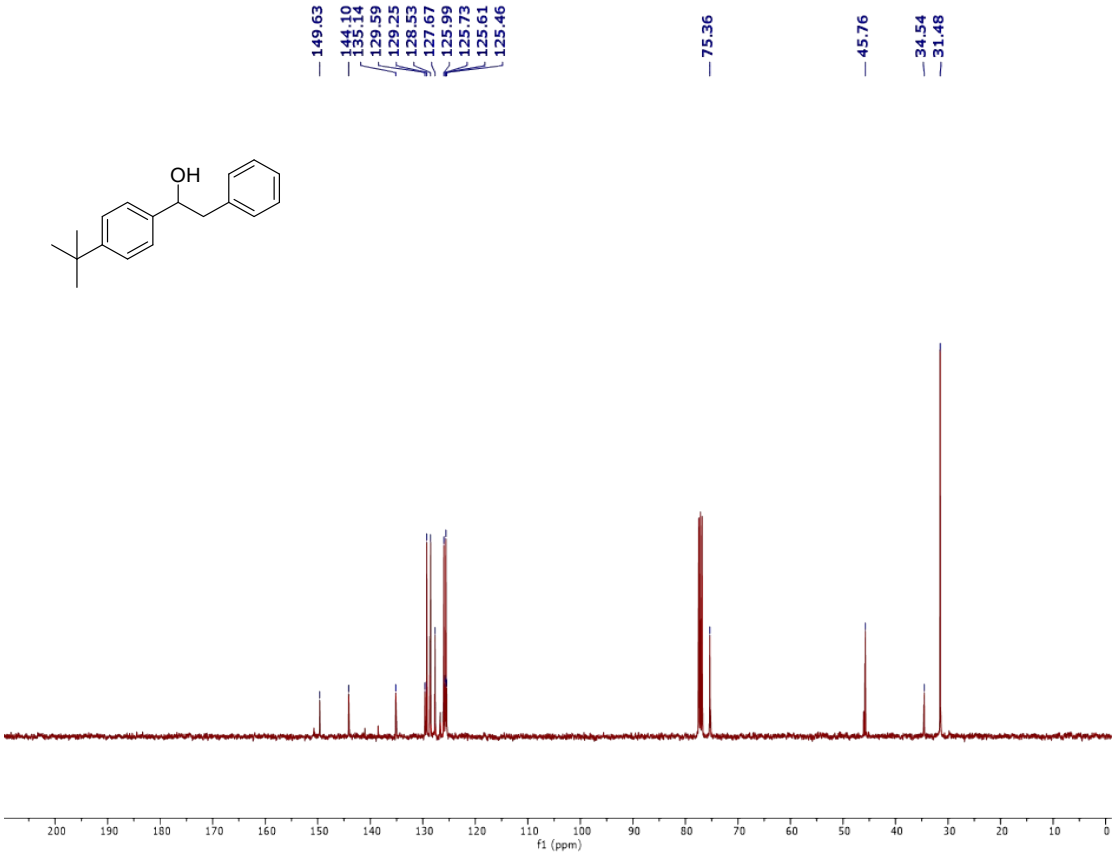
^{13}C{^{1}H} NMR spectrum of 2-(4-isopropylphenyl)-1-phenylethan-1-ol (**2j**, 101 MHz, $CDCl_3$):



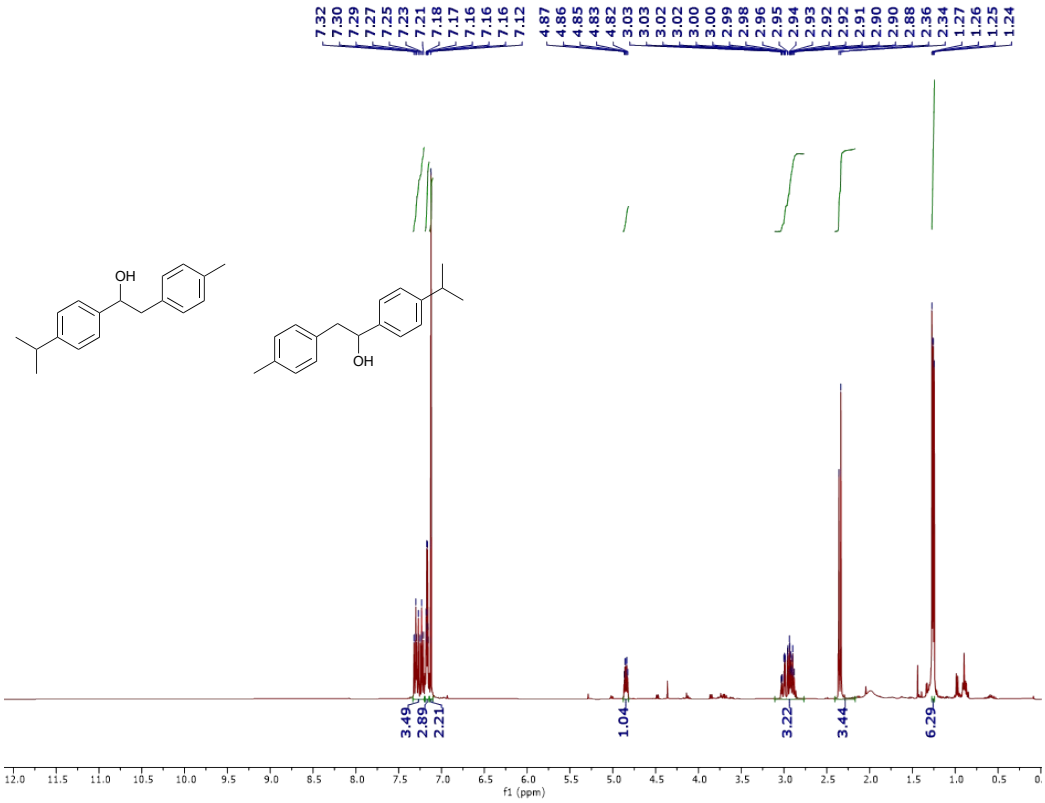
^{1}H NMR spectrum of 2-(4-(*tert*-butyl)phenyl)-1-phenylethan-1-ol (**2k**, 400 MHz, $CDCl_3$):



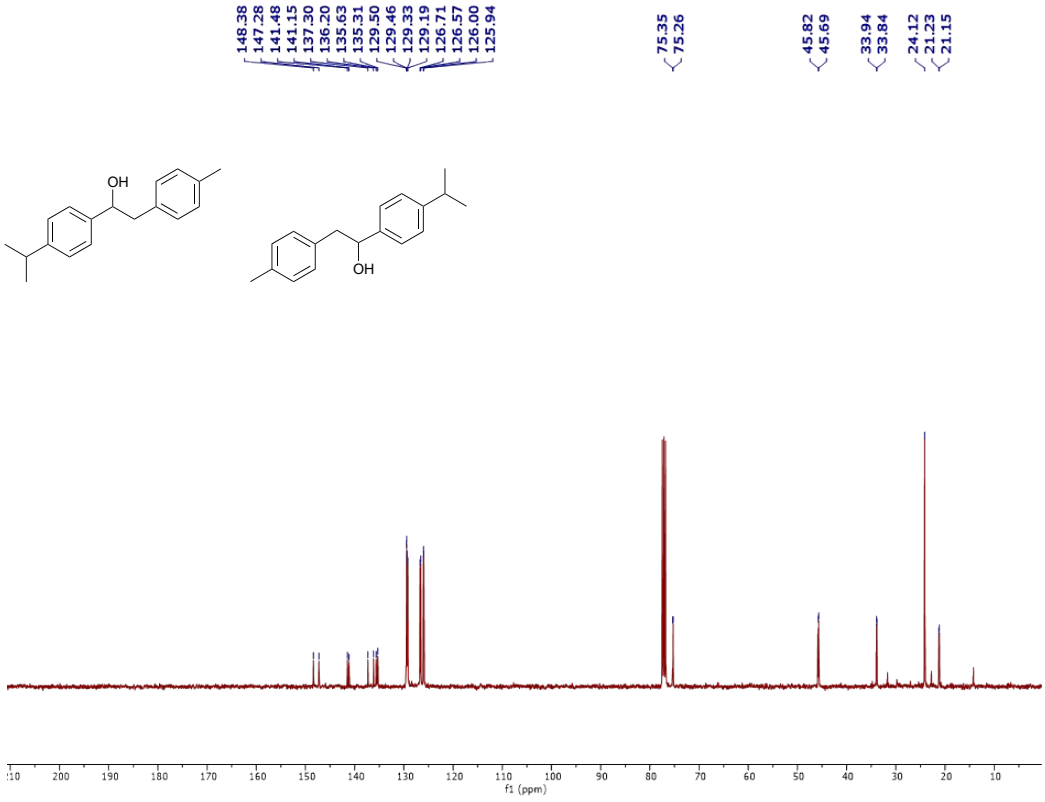
^{13}C{^{1}H} NMR spectrum of 2-(4-(*tert*-butyl)phenyl)-1-phenylethan-1-ol (**2k**, 101 MHz, $CDCl_3$):



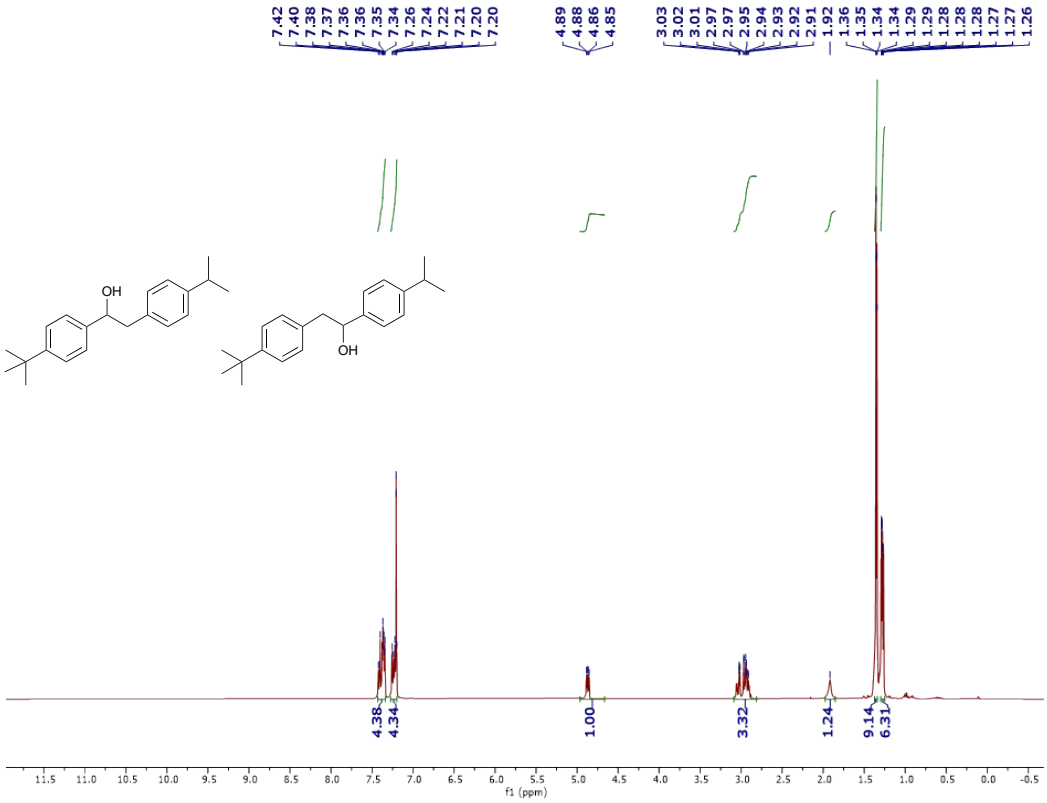
^{1}H NMR spectrum of 2-(4-isopropylphenyl)-1-(*p*-tolyl)ethan-1-ol and 1-(4-isopropylphenyl)-2-(p-tolyl)ethan-1-ol (**2l**, 400 MHz, $CDCl_3$):



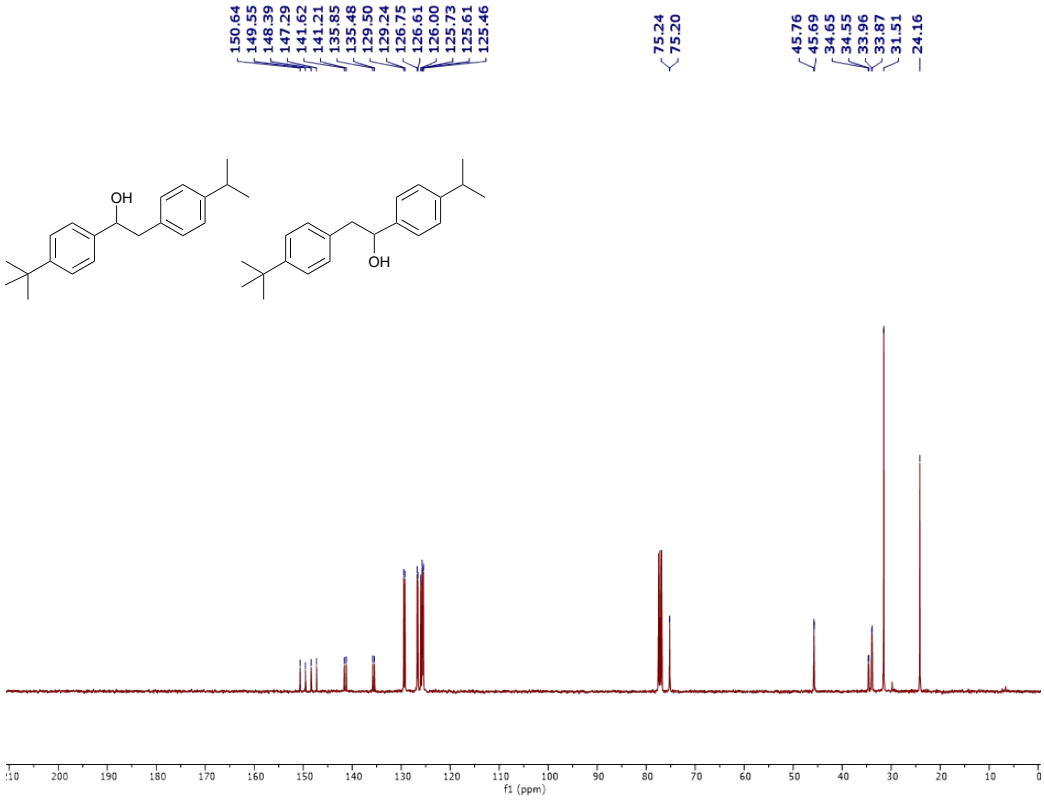
^{13}C{^{1}H} NMR spectrum of 2-(4-isopropylphenyl)-1-(*p*-tolyl)ethan-1-ol and 1-(4-isopropylphenyl)-2-(*p*-tolyl)ethan-1-ol (**2l**, 101 MHz, $CDCl_3$):



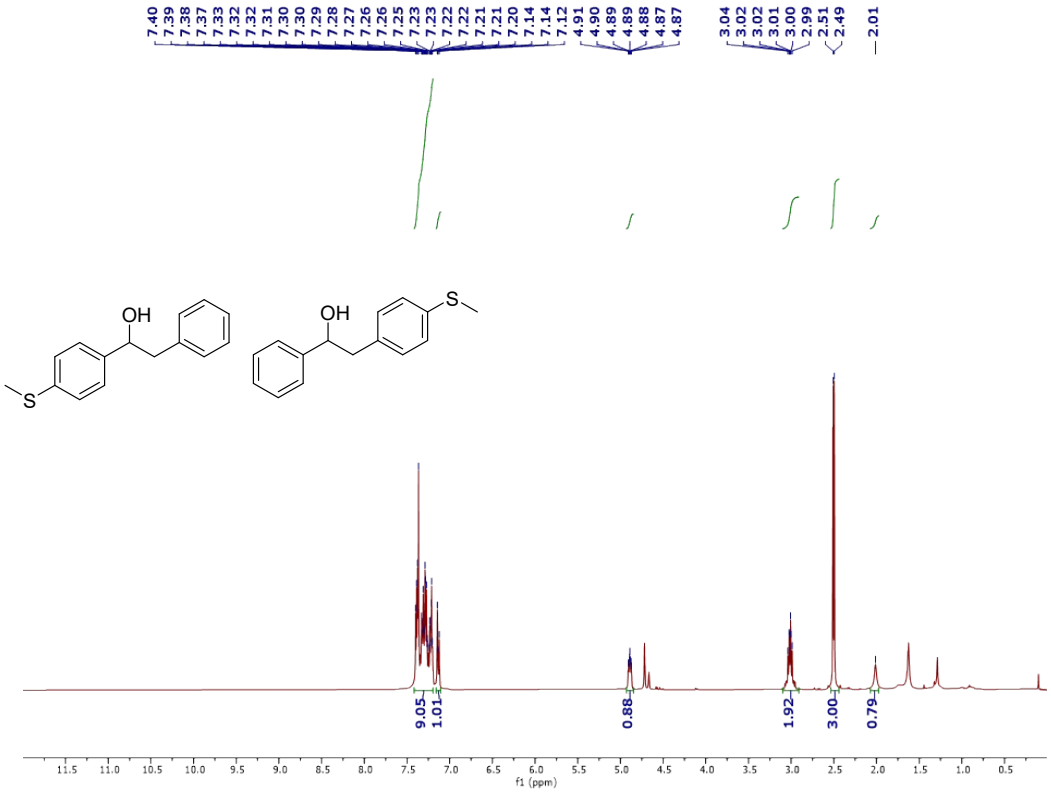
^{1}H NMR spectrum of 2-(4-(tert-butyl)phenyl)-1-(4-isopropylphenyl)ethan-1-ol and 1-(4-(tert-butyl)phenyl)-2-(4-isopropylphenyl)ethan-1-ol (**2m**, 400 MHz, $CDCl_3$):



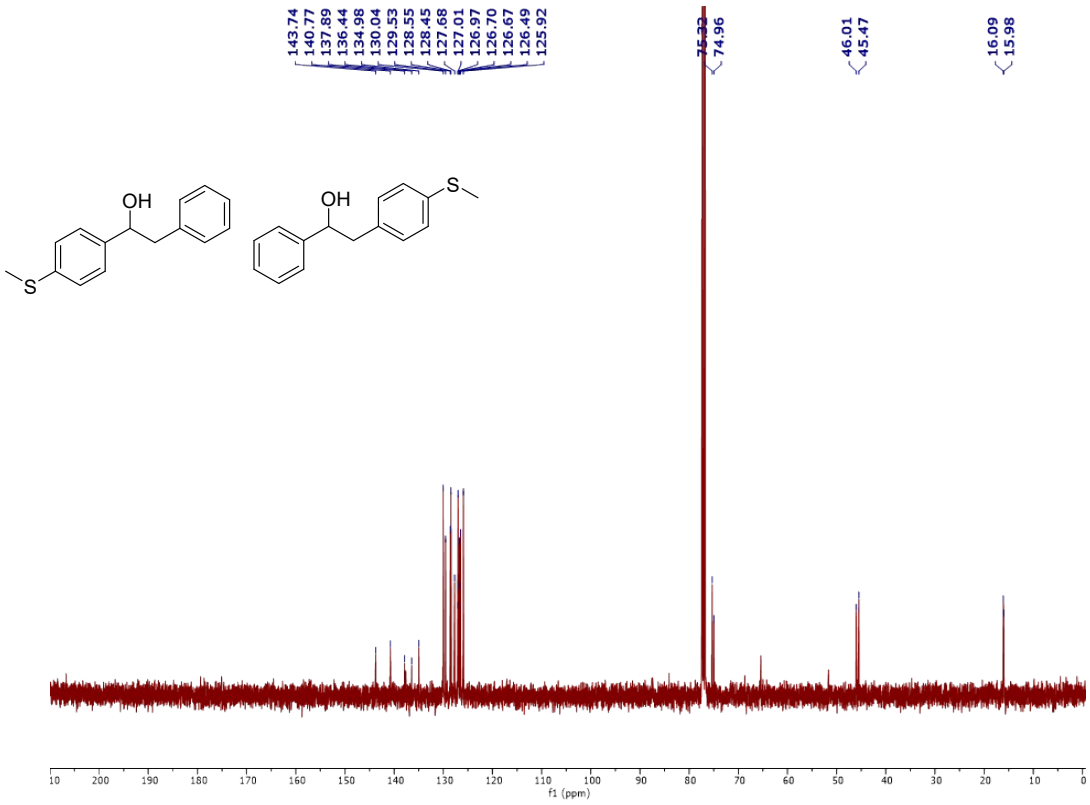
^{13}C{^{1}H} NMR spectrum of -(4-(tert-butyl)phenyl)-1-(4-isopropylphenyl)ethan-1-ol and 1-(4-(tert-butyl)phenyl)-2-(4-isopropylphenyl)ethan-1-ol (**2m**, 101 MHz, $CDCl_3$):



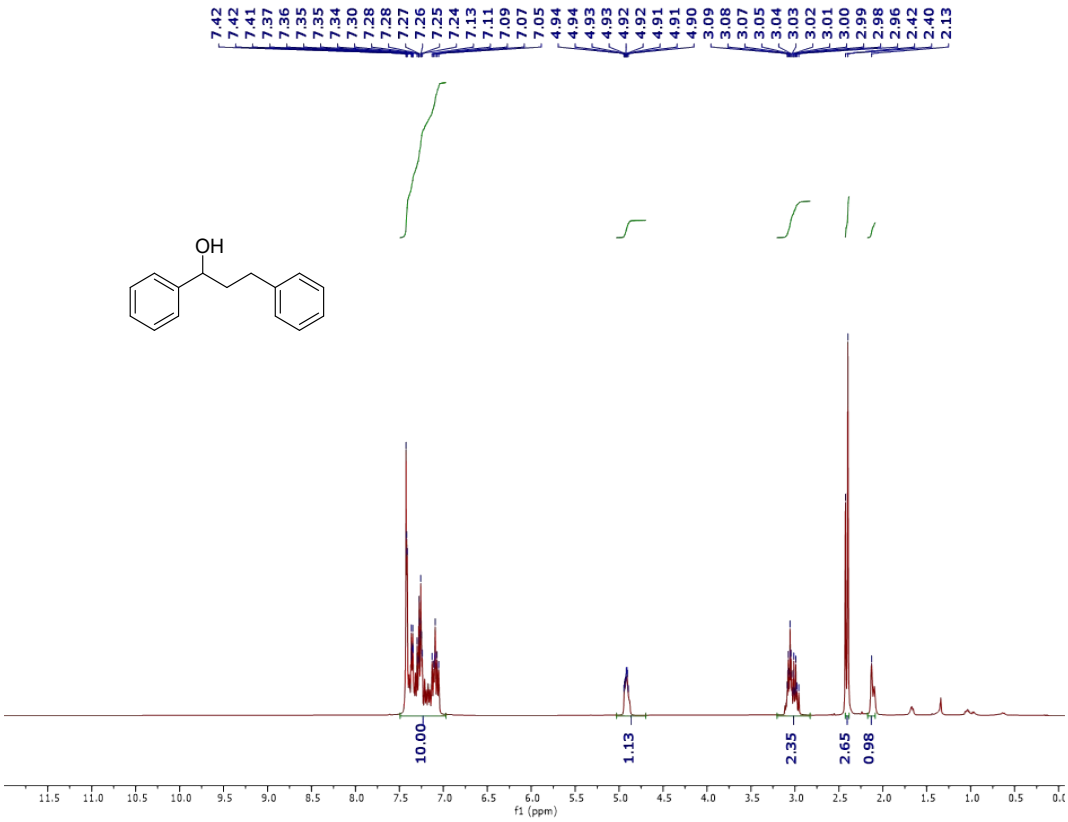
^{1}H NMR spectrum of 2-(4-(methylthio)phenyl)-1-phenylethan-1-ol and 1-(4-(methylthio)phenyl)-2-phenylethan-1-ol (**2n**, 400 MHz, $CDCl_3$):



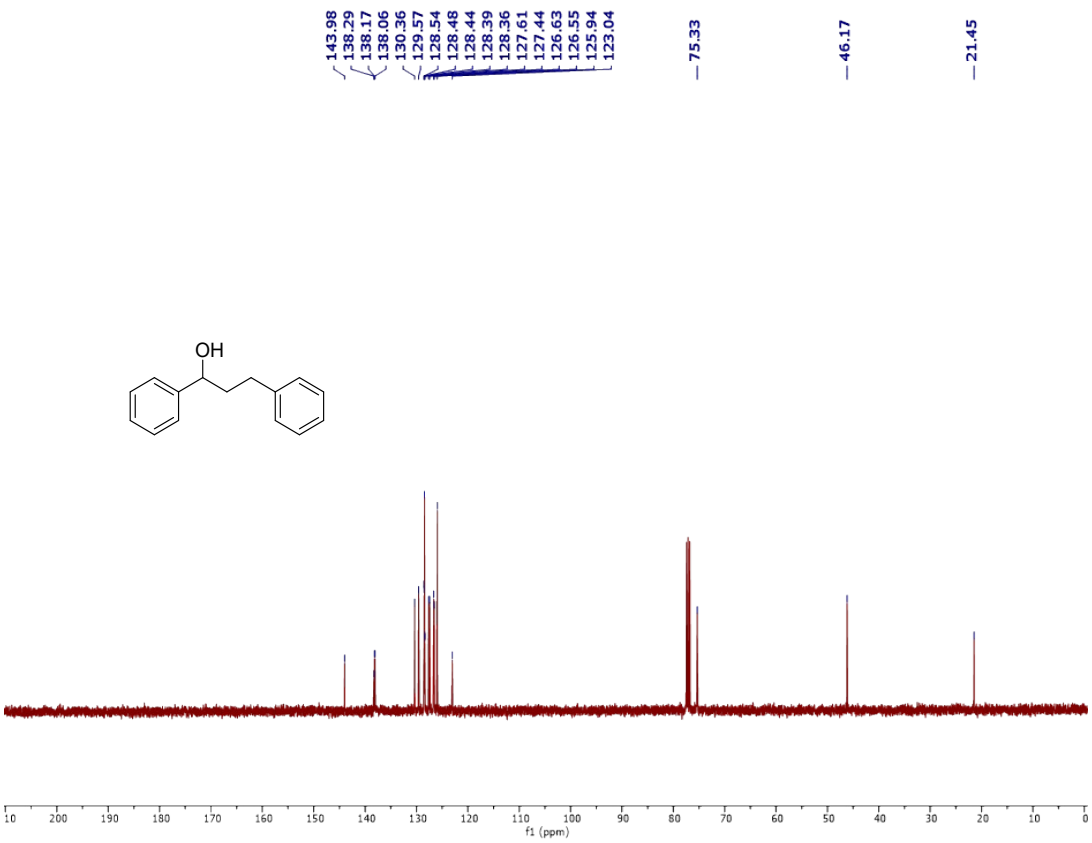
^{13}C{^{1}H} NMR spectrum of 2-(4-(methylthio)phenyl)-1-phenylethan-1-ol and 1-(4-(methylthio)phenyl)-2-phenylethan-1-ol (**2n**, 101 MHz, $CDCl_3$):



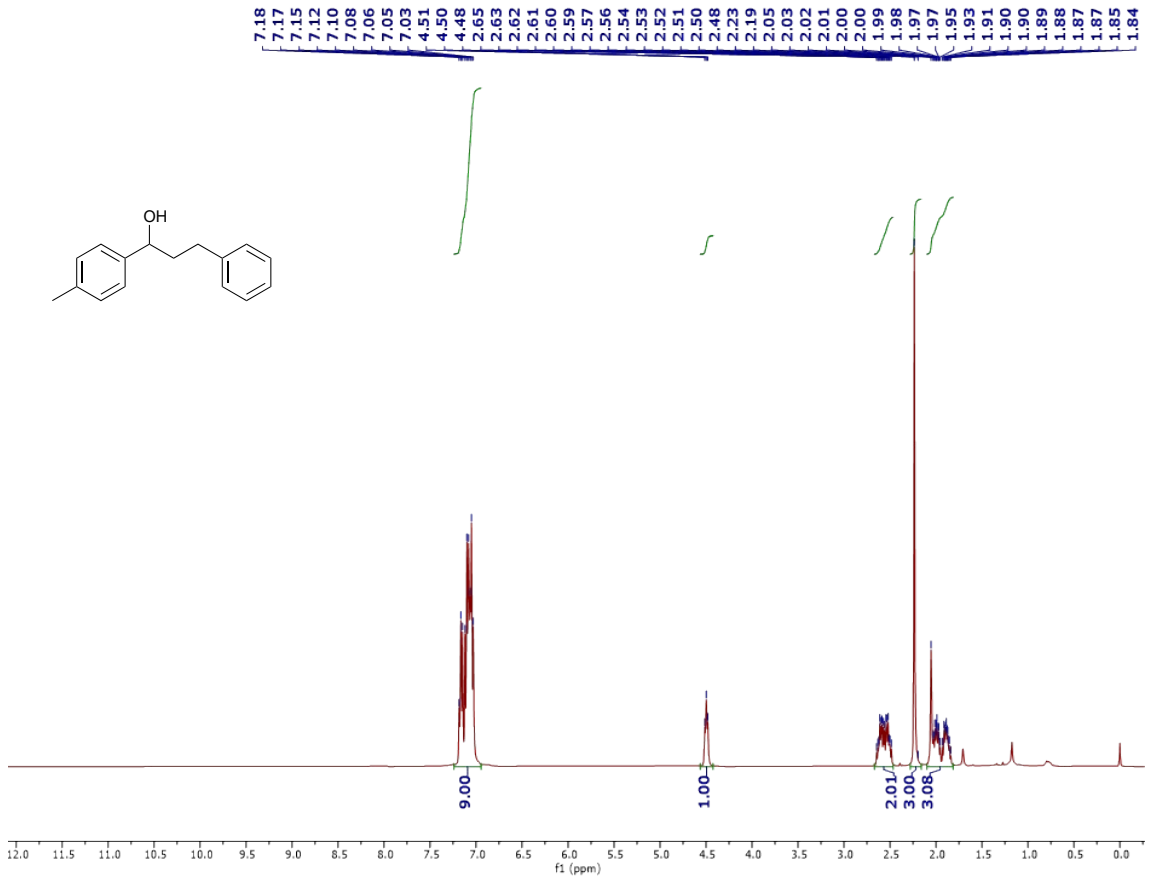
^{1}H NMR spectrum of 1,3-diphenylpropan-1-ol (**2o**, 400 MHz, $CDCl_3$):



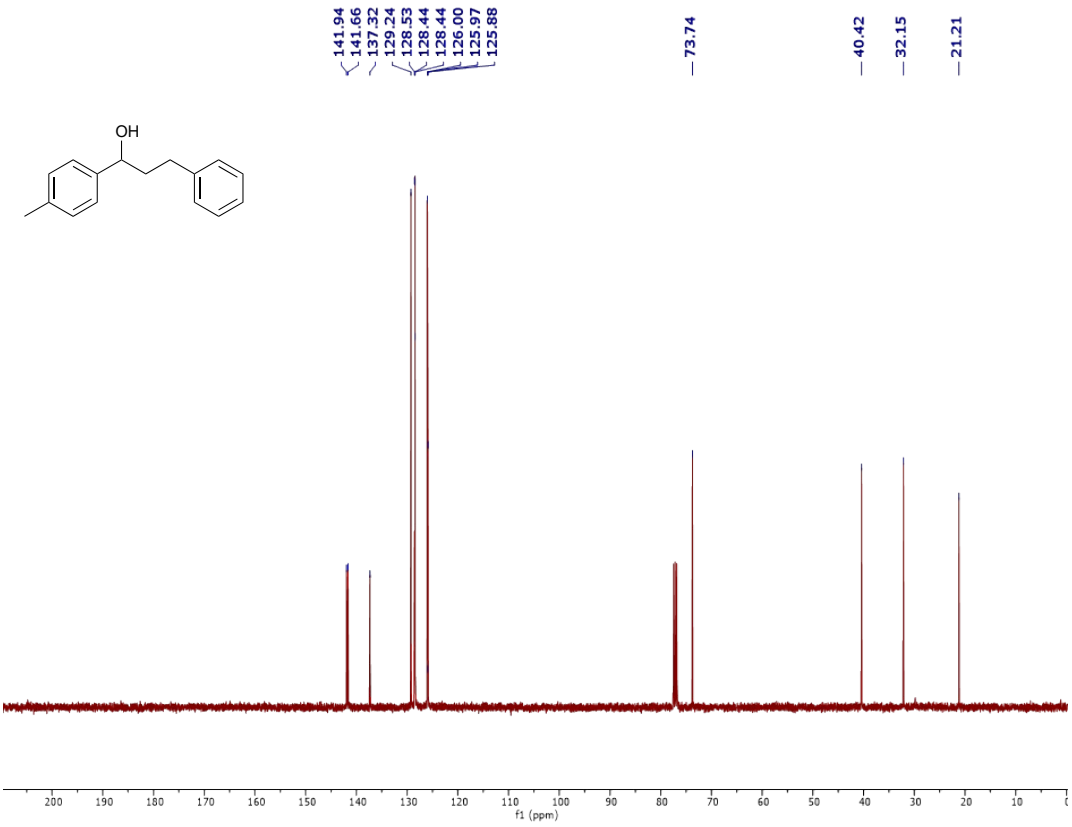
^{13}C{^{1}H} NMR spectrum of 1,3-diphenylpropan-1-ol (**2o**, 101 MHz, $CDCl_3$):



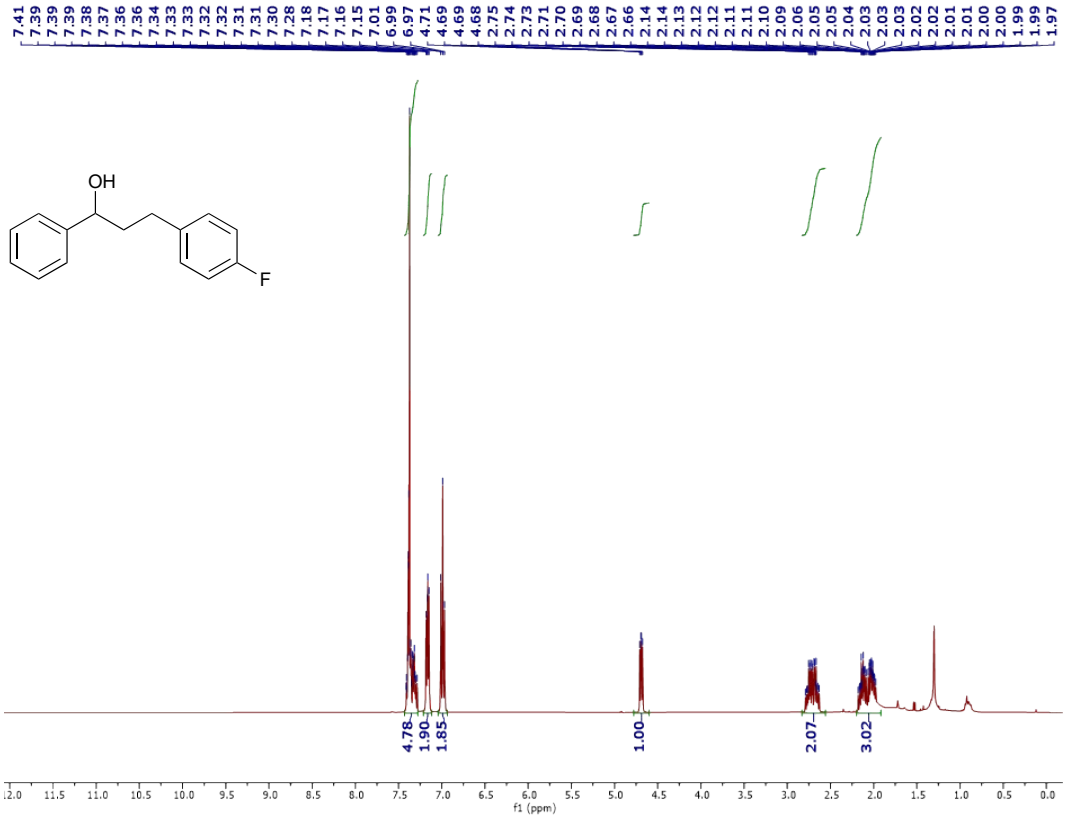
^{1}H NMR spectrum of 3-phenyl-1-(p-tolyl)propan-1-ol (**2p**, 400 MHz, $CDCl_3$):



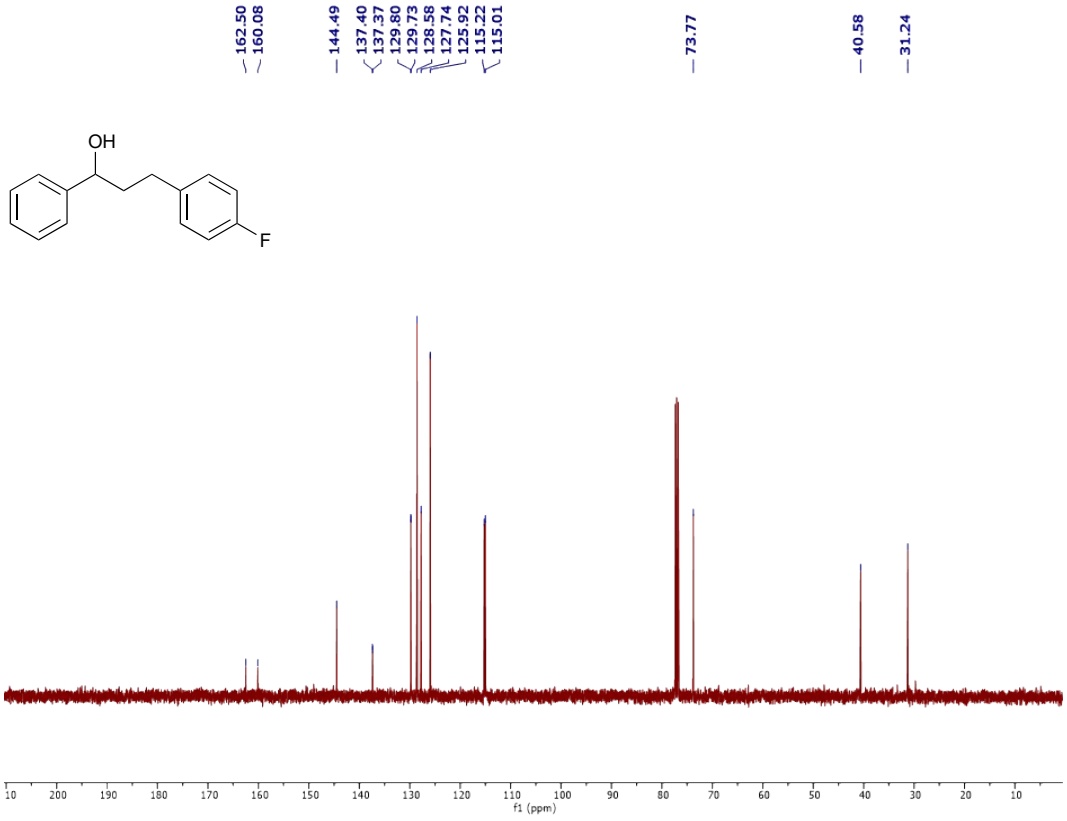
^{13}C{^{1}H} NMR spectrum of 3-phenyl-1-(p-tolyl)propan-1-ol (**2p**, 101 MHz, $CDCl_3$):



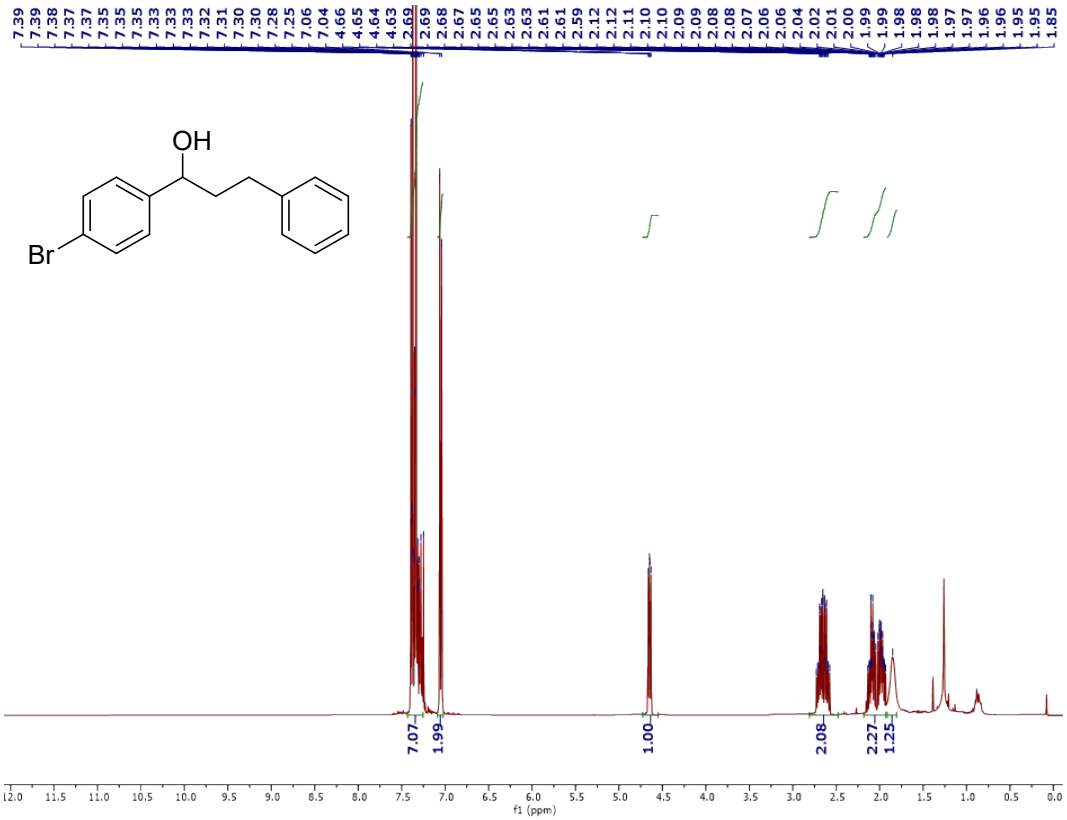
^{1}H NMR spectrum of 3-(4-fluorophenyl)-1-phenylpropan-1-ol (**2q**, 400 MHz, $CDCl_3$):



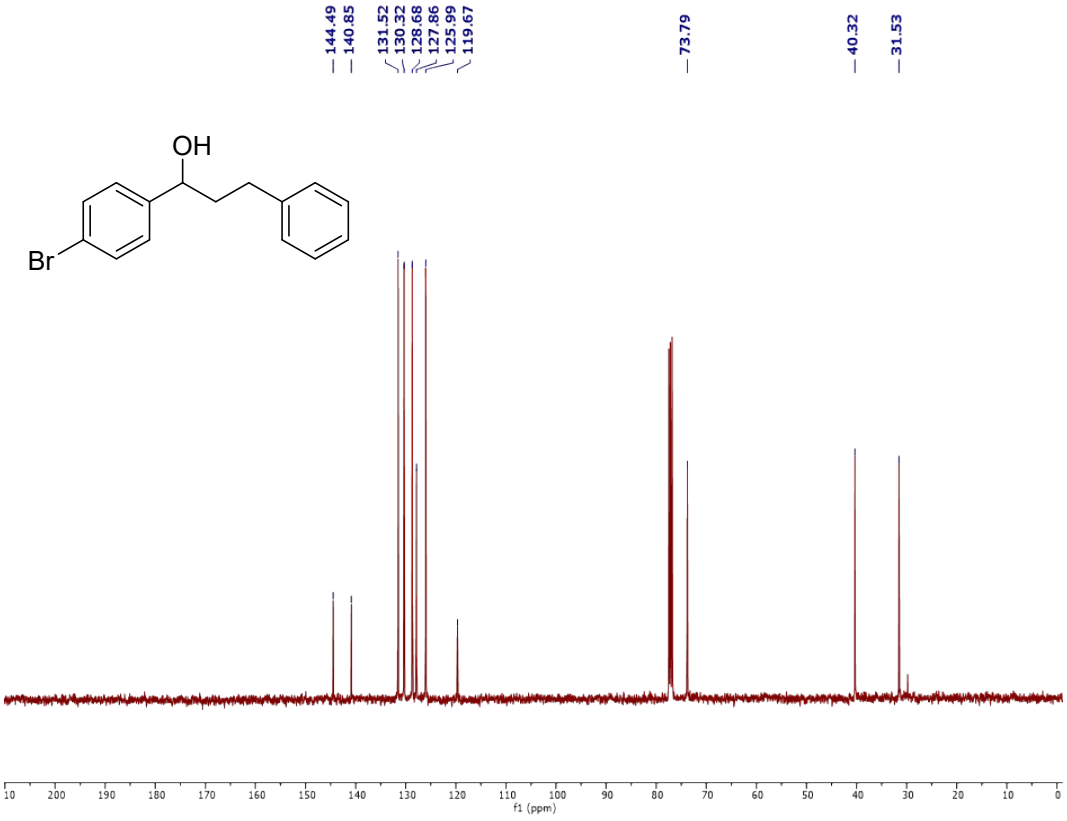
^{13}C{^{1}H} NMR spectrum of 3-(4-fluorophenyl)-1-phenylpropan-1-ol (**2q**, 101 MHz, $CDCl_3$):



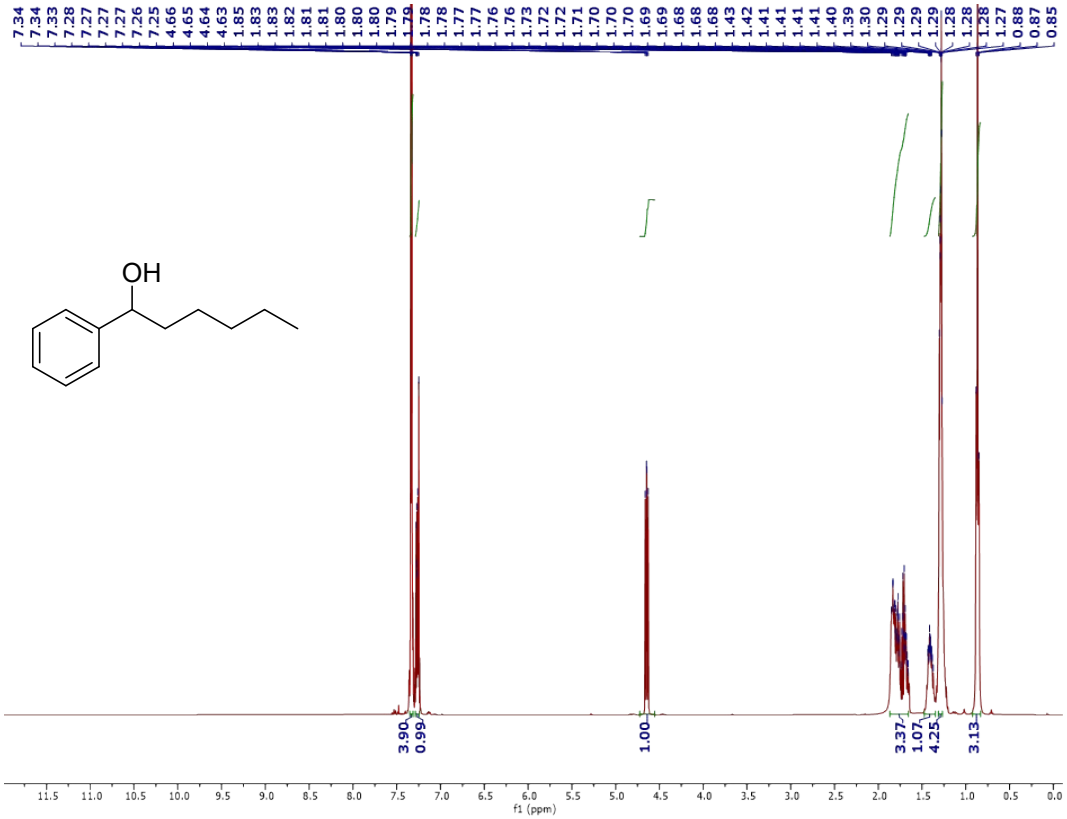
^{1}H NMR spectrum of 1-(4-bromophenyl)-3-phenylpropan-1-ol (**2r**, 400 MHz, $CDCl_3$):



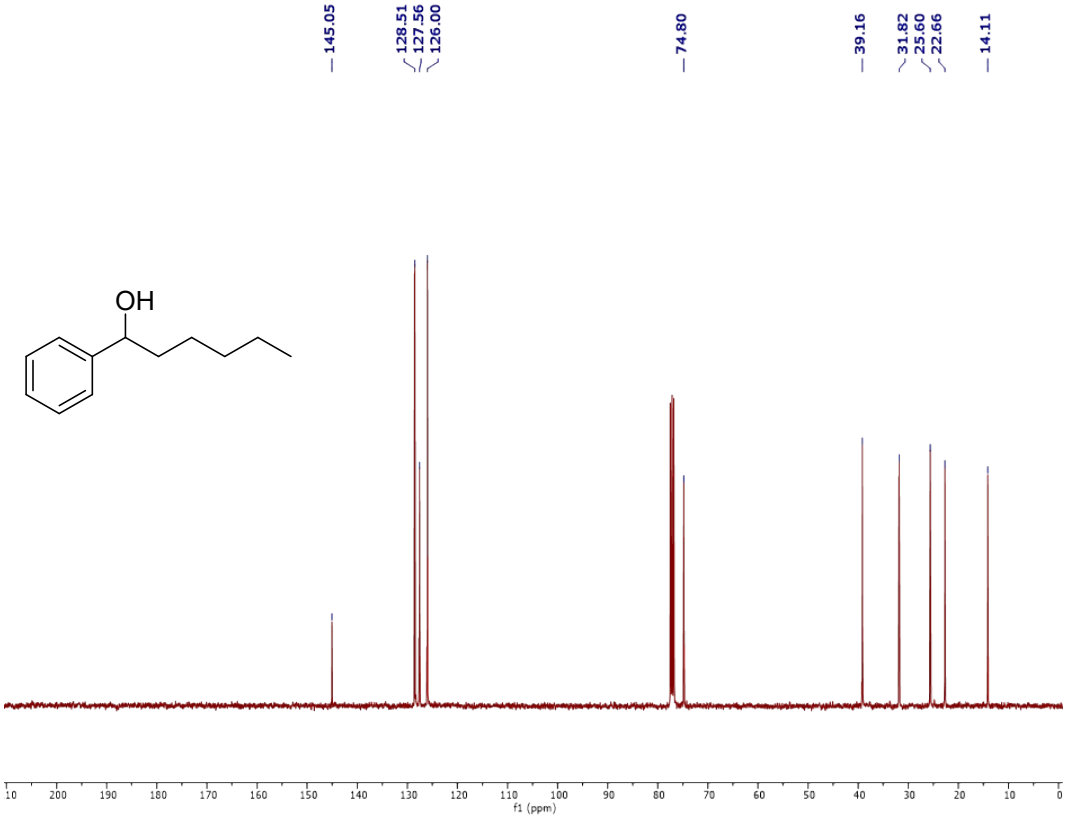
^{13}C{^{1}H} NMR spectrum of 1-(4-bromophenyl)-3-phenylpropan-1-ol (**2r**, 101 MHz, $CDCl_3$):



^{1}H NMR spectrum of 1-phenylhexan-1-ol (**2s**, 400 MHz, $CDCl_3$):



^{13}C{^{1}H} NMR spectrum of 1-phenylhexan-1-ol (**2s**, 101 MHz, $CDCl_3$):



Mercury poisoning experiment for detection of homogeneous pathway for synthesis of secondary alcohol from ether (Scheme 2a):

Under the nitrogen atmosphere of glove box, catalyst **1** (5 mol %), benzyl ether (1 mmol), KO^{t}Bu (40 mol %), diethylsilane (4 mmol), Hg (10 mmol) were charged into oven-dried teflon sealed vial. Then the reaction mixture was heated at 100 °C for 12 hours. After cooling the reaction mixture to room temperature, HCl in diethyl ether (1 M) was added to the reaction mixture and allowed to stir at room temperature for two hours. The reaction mixture was decanted from mercury, and water (2 mL) was added. The resulted reaction mixture was extracted with dichloromethane (3 × 10 mL). The combined organic layer was washed with brine dried over anhydrous sodium sulfate. The solvents were removed under reduced pressure, and the resulted residue was purified by column chromatography over silica gel (100-200 mesh) using hexane/ethyl acetate (97:3) as an eluent.

Experiment to verify involvement of radical intermediate for synthesis of secondary alcohol from ether (Scheme 2b):

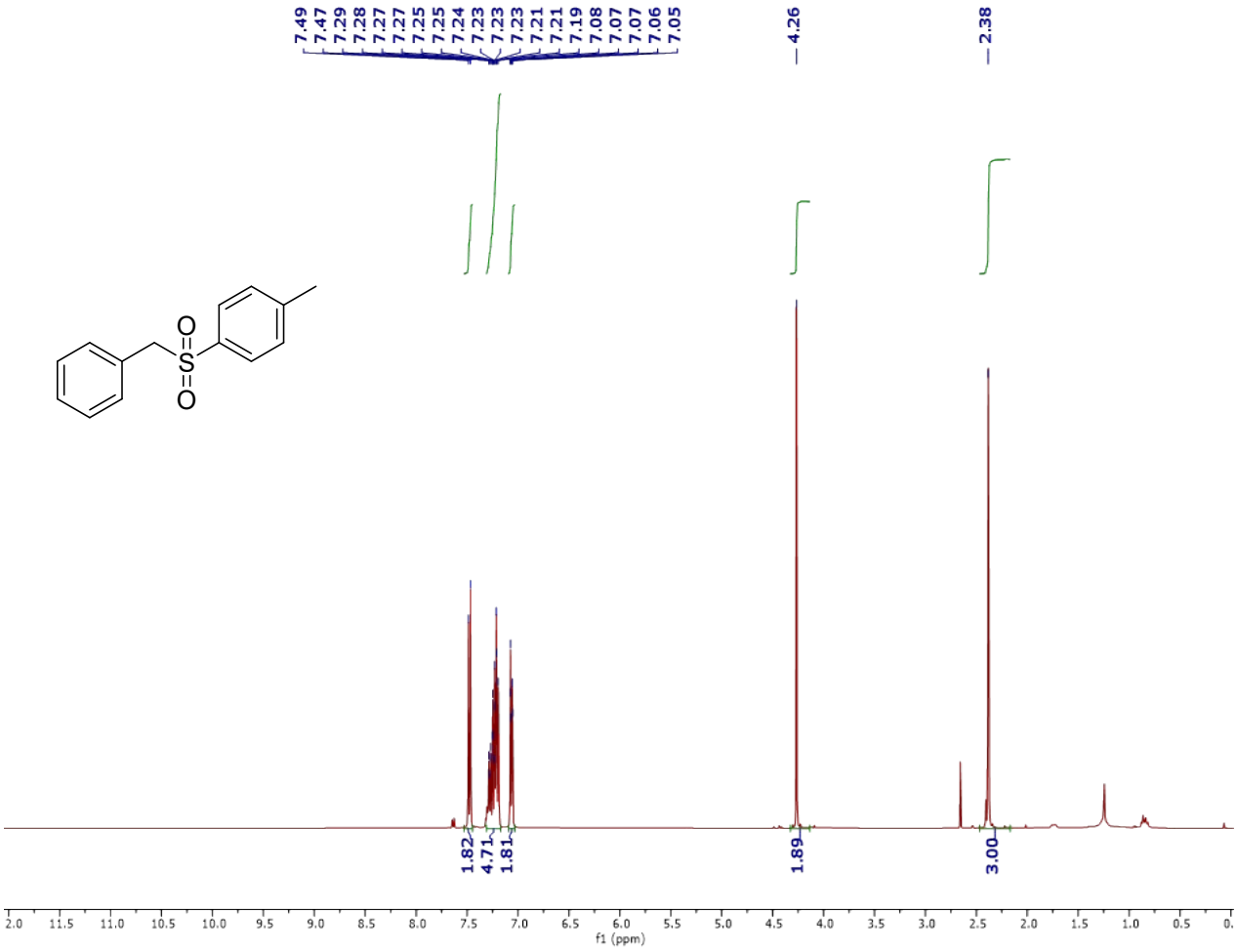
To an oven-dried teflon sealed vial, catalyst **1** (5 mol %), benzyl ether (1 mmol), KO^{t}Bu (40 mol %), diethylsilane (4 mmol), TEMPO (2 equiv), and toluene (2 mL) were charged under the nitrogen atmosphere, and the reaction mixture allowed stir at 100 °C in a preheated oil bath for 12 hours. After cooling the reaction mixture to room temperature, the solvent was removed under reduced pressure. HCl in diethyl ether (1 M) was added to reaction mixture and allowed to stir at room temperature for 2 hours. Water (2 mL) was added. The resulted reaction mixture was extracted with dichloromethane (3 × 10 mL). The combined organic layer was washed with brine and dried over anhydrous sodium sulfate. The solvents were removed under reduced pressure, and the resulted residue was purified by column chromatography over silica gel (100-200 mesh) using hexane/ethyl acetate (97:3) as an eluent.

Experiment to trap benzyl radical intermediate during cleavage of ether to secondary alcohol (Scheme 2c):

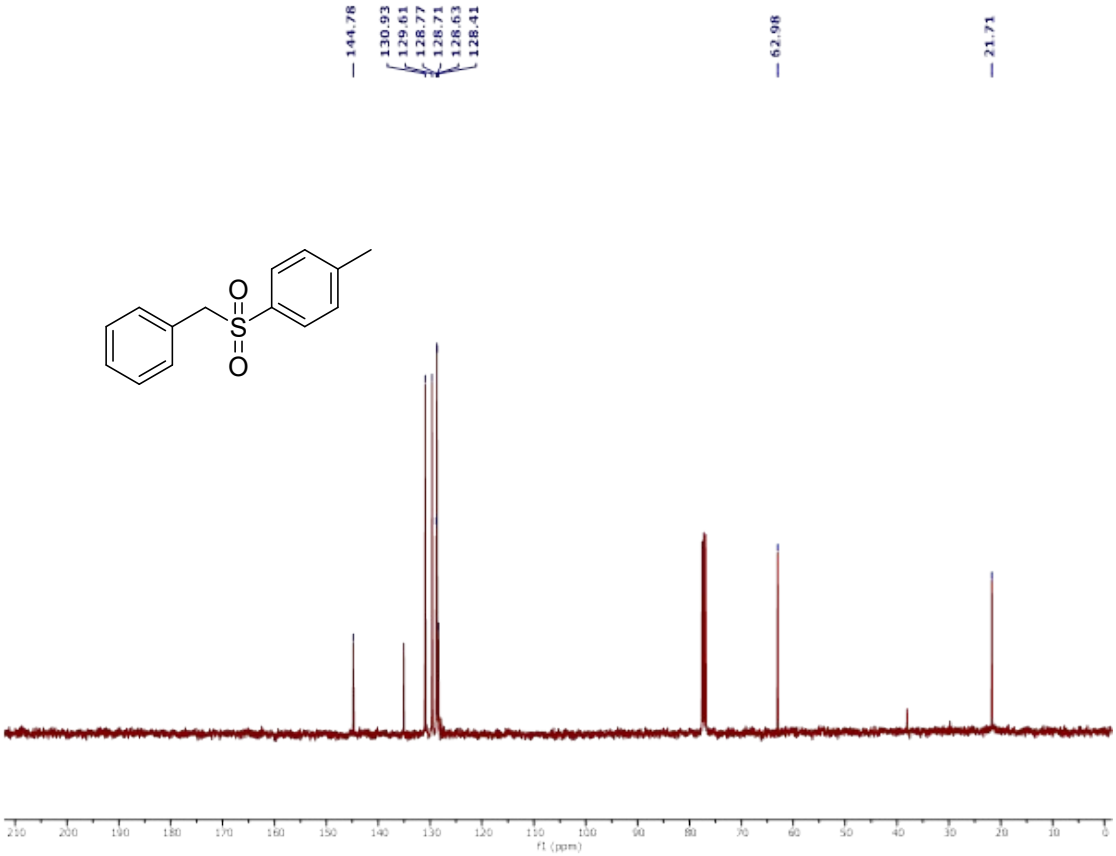
To an oven-dried teflon sealed vial, catalyst **1** (5 mol %), benzyl ether (1 mmol), KO^{t}Bu (40 mol %), diethylsilane (4 mmol), sodium p-toluenesulfinate (1 mmol), and toluene (2 mL) were charged under the nitrogen atmosphere, and the reaction mixture was allowed stir at 100 °C in a pre-heated oil bath for 2 hours. After cooling the reaction mixture to room temperature, the solvent was removed under reduced pressure. The final reaction mixture was purified by column chromatography using silica gel (100-200 mesh, hexane/EtOAc (88:12)).

1-(Benzylsulfonyl)-4-methylbenzene (3a): Isolated as white solid. Yield: 34 mg 13%. IR (DCM): 3167, 2956, 2862, 2358, 1692, 1474, 1227, 861,714 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.47 (m, *J* = 8 Hz, 2H, ArC*H*), 7.21-7.19 (m, 5H, ArC*H*), 7.08-7.05 (m, 2H, ArC*H*), 4.26 (s, 2H, CH_2), 2.38 (s, 3H, CH_3). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$): δ 144.7, 130.9, 129.6, 128.7, 128.7, 128.6, 128.4,62.9, 21.7.

^{1}H NMR spectrum of 1-(benzylsulfonyl)-4-methylbenzene (**3a**, 400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR spectrum of 1-(benzylsulfonyl)-4-methylbenzene (**3a**, 101 MHz, $CDCl_3$)

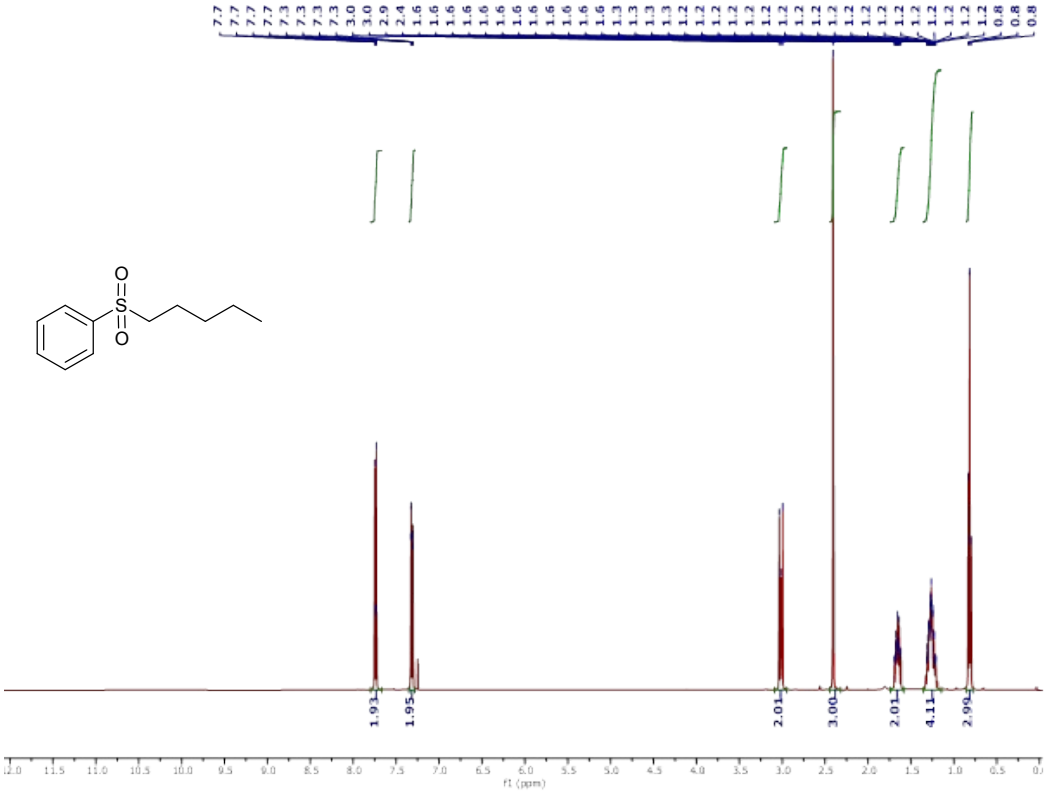


Experiment to trap radical intermediate from cleavage of (pentyloxy)methyl) benzene to secondary alcohol (Scheme 2d):

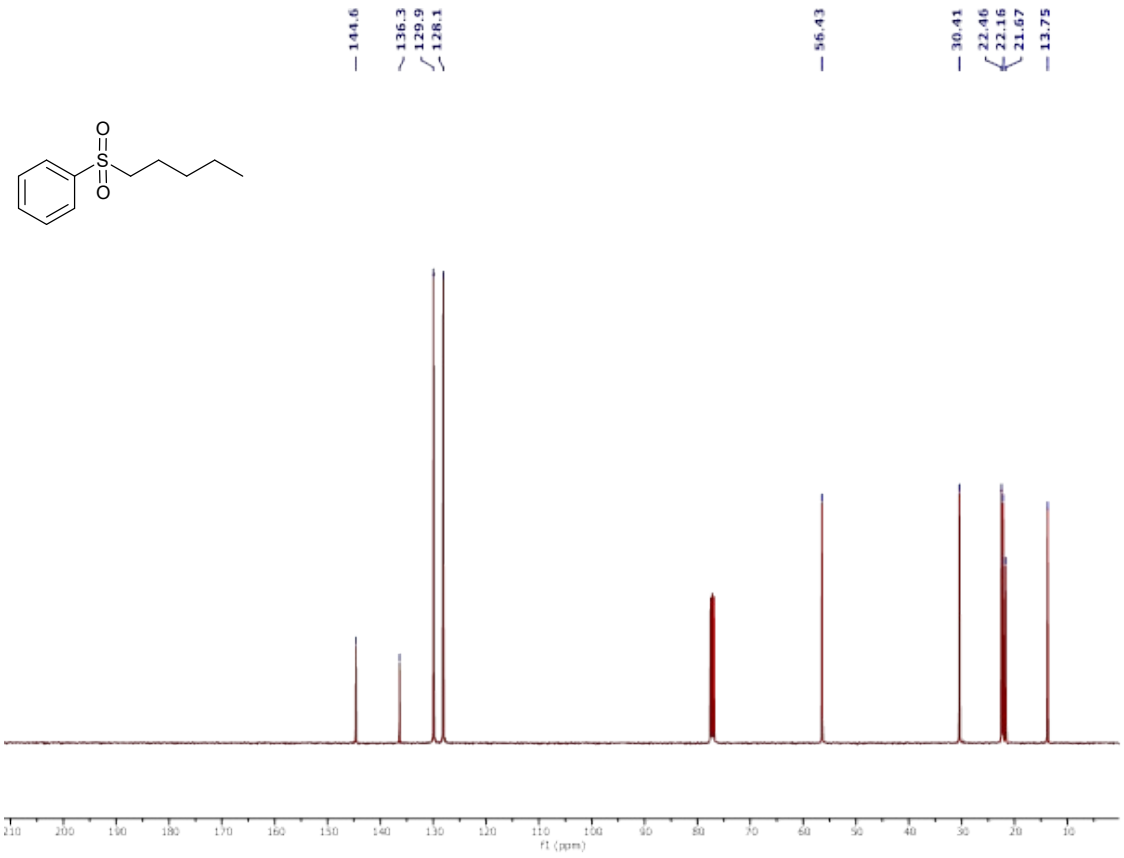
To an oven-dried teflon sealed vial, catalyst **1** (5 mol %), (pentyloxy)methyl)benzene (1 mmol), KO^{t}Bu (40 mol %), diethylsilane (4 mmol), *p*-toluene, sodium p-toluenesulfinate (1 mmol), and toluene (2 mL) were charged under the nitrogen atmosphere, and the reaction mixture was allowed to stir at 100 °C in a pre-heated oil bath for 2 hours. After cooling the reaction mixture to room temperature, the solvent was removed under reduced pressure. The reaction mixture was purified by column chromatography using silica gel (100-200 mesh, hexane/EtOAc (95:5).

1-Methyl-4-(pentylsulfonyl)benzene (3b): Isolated as colorless liquid. Yield: 54 mg 23%. IR (DCM): 3125, 3055, 2943, 2845, 2291, 1656, 1389, 1237, 853, 756, 714 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75-7.73 (m, 2H, ArC*H*), 7.33-7.30 (m, 2H, ArC*H*), 3.04-2.99 (m, 2H, CH_2), 2.41 (s, 3H, CH_3), 1.69-1.62 (m, 2H, CH_2), 1.31-1.21 (m, 4H, 2CH_2), 0.83-0.80 (t, J = 8 Hz, 3H, CH_3). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$): δ 144.6, 136.3, 129.9, 128.1, 56.4, 30.4, 22.4, 22.1, 21.6, 13.7.

^{1}H NMR spectrum of 1-methyl-4-(pentylsulfonyl)benzene (**3b**, 400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR spectrum of 1-methyl-4-(pentylsulfonyl)benzene (**3b**, 101 MHz, $CDCl_3$)

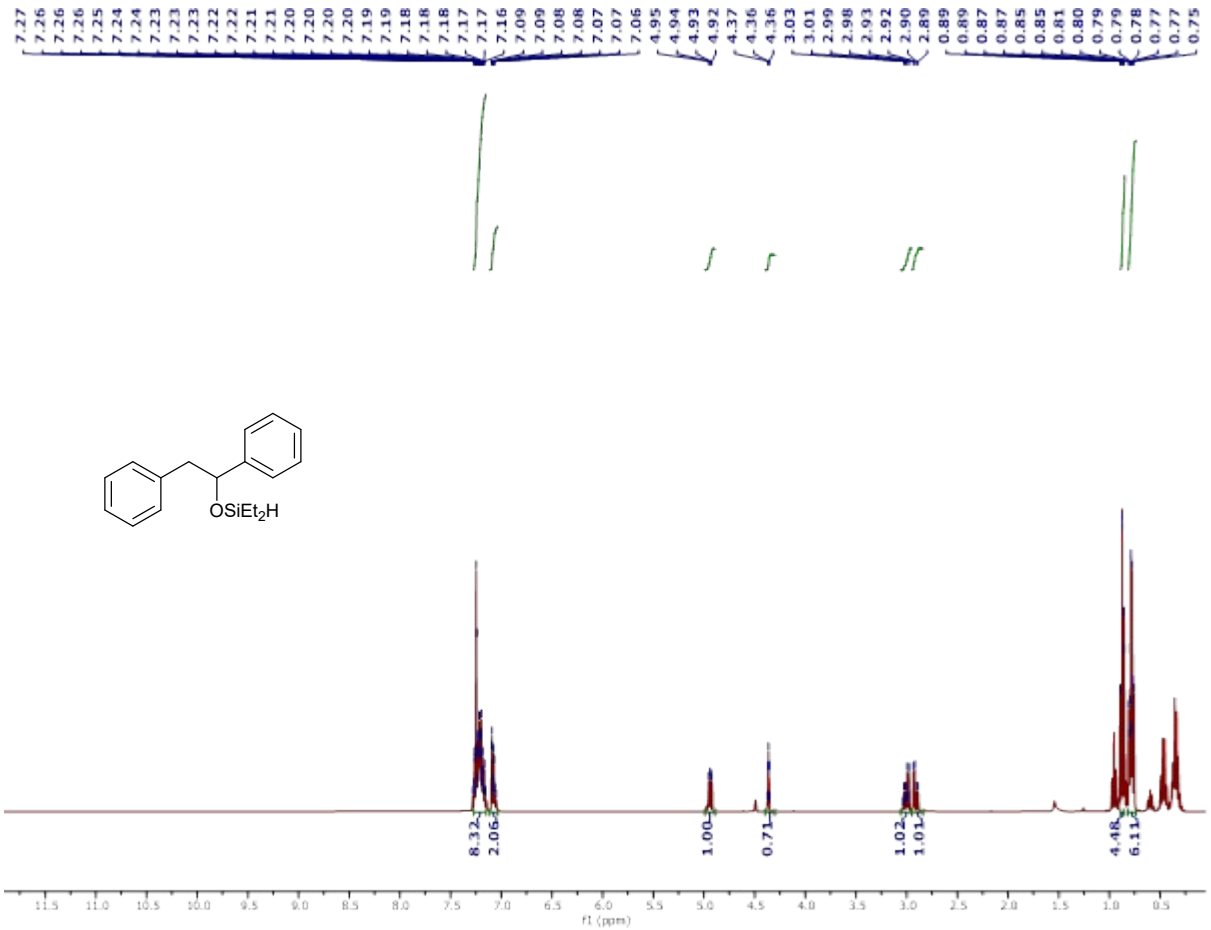


Experiment to verify involvement of alkoxy diethylsilylether as reaction intermediate:

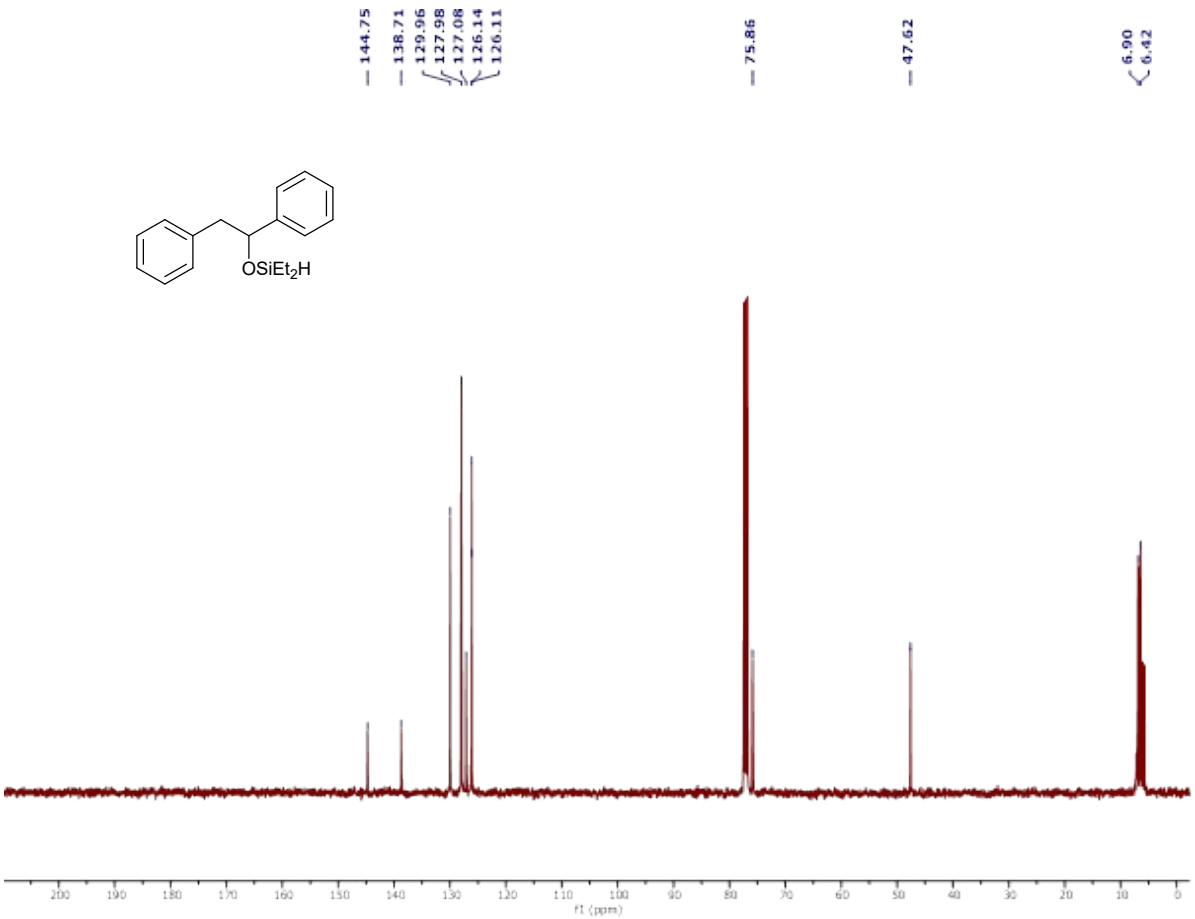
Under the nitrogen atmosphere of glove box, catalyst **1** (5 mol %), benzyl ether (1 mmol), KO^{t}Bu (40 mol %), diethylsilane (4 mmol) were charged into oven-dried teflon sealed vial. Then the reaction mixture was heated at 100 °C for 12 hours. After cooling the reaction mixture to room temperature, the reaction mixture was purified by column chromatography using silica gel (100-200 mesh, hexane/EtOAc (99:1).

(1,2-Diphenylethoxy)diethylsilane (4): Isolated as colorless liquid. Yield: 274 mg (96%). IR (DCM): 3177, 3066, 3045, 2993, 2867, 2344, 2277, 1664, 1647, 1237, 1177, 956, 756, 728 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.16 (m, 8H, ArC*H*), 7.09-7.05 (m, 2H, ArC*H*), 4.95-4.92 (m, 1H, C*H*), 4.37-4.35 (m, 1H, Si*H*), 3.04-2.98 (m, 1H, C*H*), 2.93-2.89 (m, 1H, C*H*), 0.89-0.85 (m, 4H, 2CH_2), 0.81-0.75 (m, 6H, 2CH_3). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 144.7, 138.7, 129.9, 127.9, 127.0, 126.1, 126.1, 75.8, 47.6, 6.9, 6.4.

^{1}H NMR spectrum of (1,2-diphenylethoxy)diethylsilane (**4**, 400 MHz, $CDCl_3$)



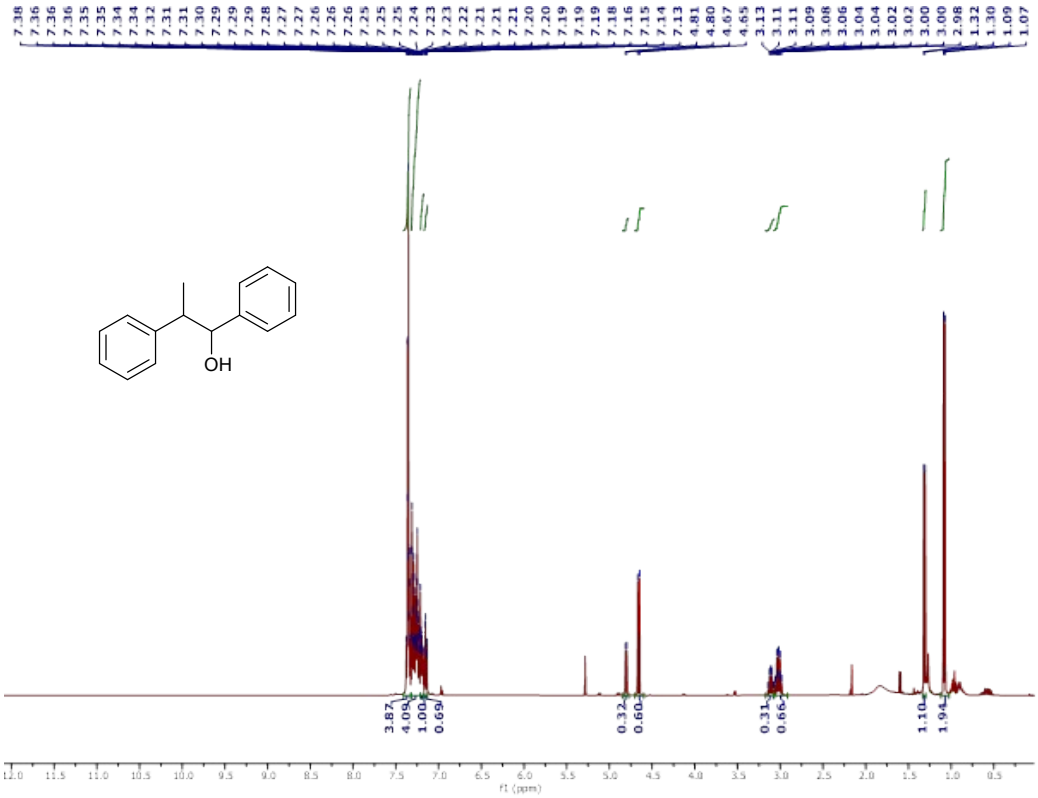
$^{13}C\{^{1}H\}$ NMR spectrum of (1,2-diphenylethoxy)diethylsilane (**4**, 101 MHz, $CDCl_3$)



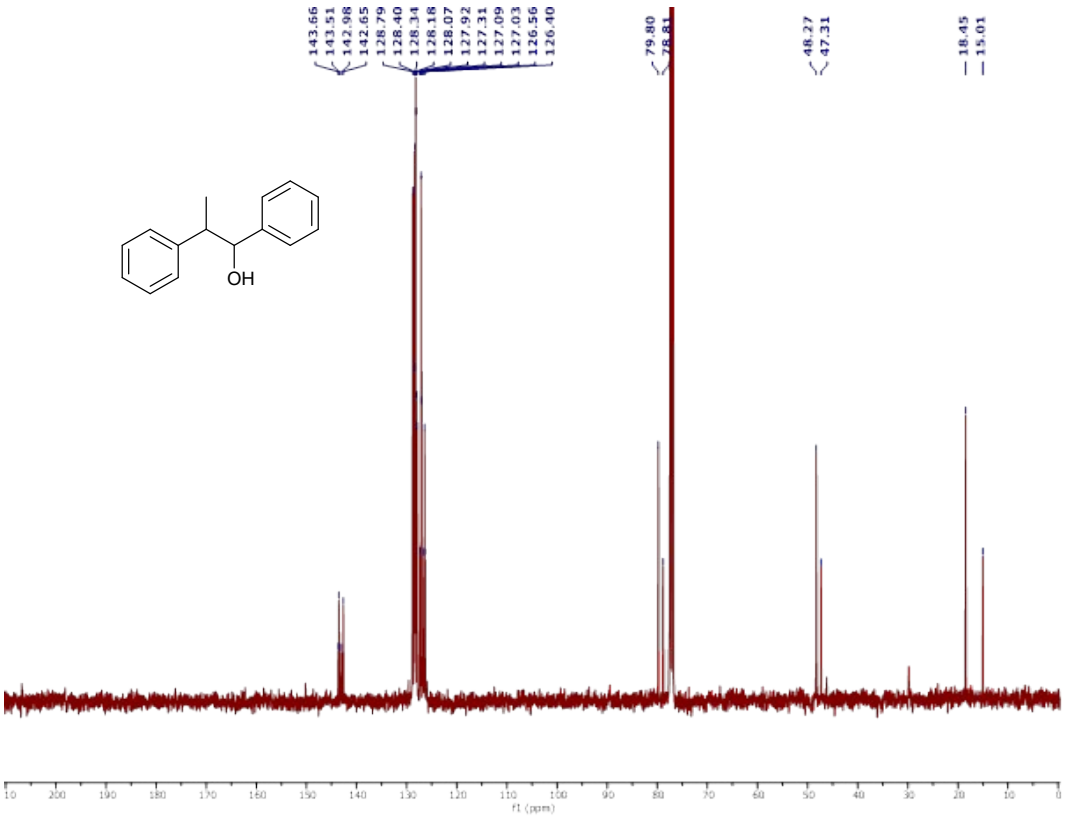
Experiment to verify effect of C-O bond cleavage on secondary ether: To an oven-dried teflon sealed vial, catalyst **1** (5 mol %), 1-(benzyloxy)ethyl)benzene (1 mmol), KO^{t}Bu (40 mol %), diethylsilane (4 mmol) were charged under the nitrogen atmosphere, and the reaction mixture allowed to stir at 100 °C in a preheated oil bath for 12 hours. After cooling the reaction mixture to room temperature, the solvent was removed under reduced pressure. HCl in diethyl ether (1 M) was added to reaction mixture and allowed to stir at room temperature for 2 hours. Water (2 mL) was added. The resulted reaction mixture was extracted with dichloromethane (3 × 10 mL). The combined organic layer was washed with brine and dried over anhydrous sodium sulfate. The solvents were removed under reduced pressure, and the resulted residue was purified by column chromatography over silica gel (100-200 mesh) using hexane/ethyl acetate (97:3) as an eluent. **1,2-Diphenylpropan-1-ol** Isolated as colorless liquid. Yield: 60 mg (28%). IR (DCM): 3466, 3123, 3040, 2947, 2876, 1654, 1626, 1246, 1073, 921, 856, 743 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.34 (m, 4H, ArC*H*), 7.32-7.23 (m, 4H, ArC*H*), 7.22-7.18 (m, 1H, ArC*H*), 7.16-7.13 (m, 1H, ArC*H*), 4.81-4.80 (d, *J* = 4 Hz, 1H, C*H*), 4.67-4.65 (d, *J* = 8 Hz, 1H, C*H*), 3.13-3.08 (m, 1H, C*H*), 3.04-2.98 (m, 1H, C*H*), 1.32-1.30 (d, *J* = 8 Hz, 1H, C*H*), 1.09-1.07 (d,

J = 8 Hz, 1H, CH_2). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 143.6, 143.5, 142.9, 142.6, 128.7, 128.4, 128.3, 128.1, 128.0, 127.9, 127.3, 127.0, 126.5, 126.4, 79.8, 78.8,48.2, 47.3, 18.4, 15.0.

^1H NMR spectrum of 1,2-diphenylpropan-1-ol (**5**, 400 MHz, $CDCl_3$)



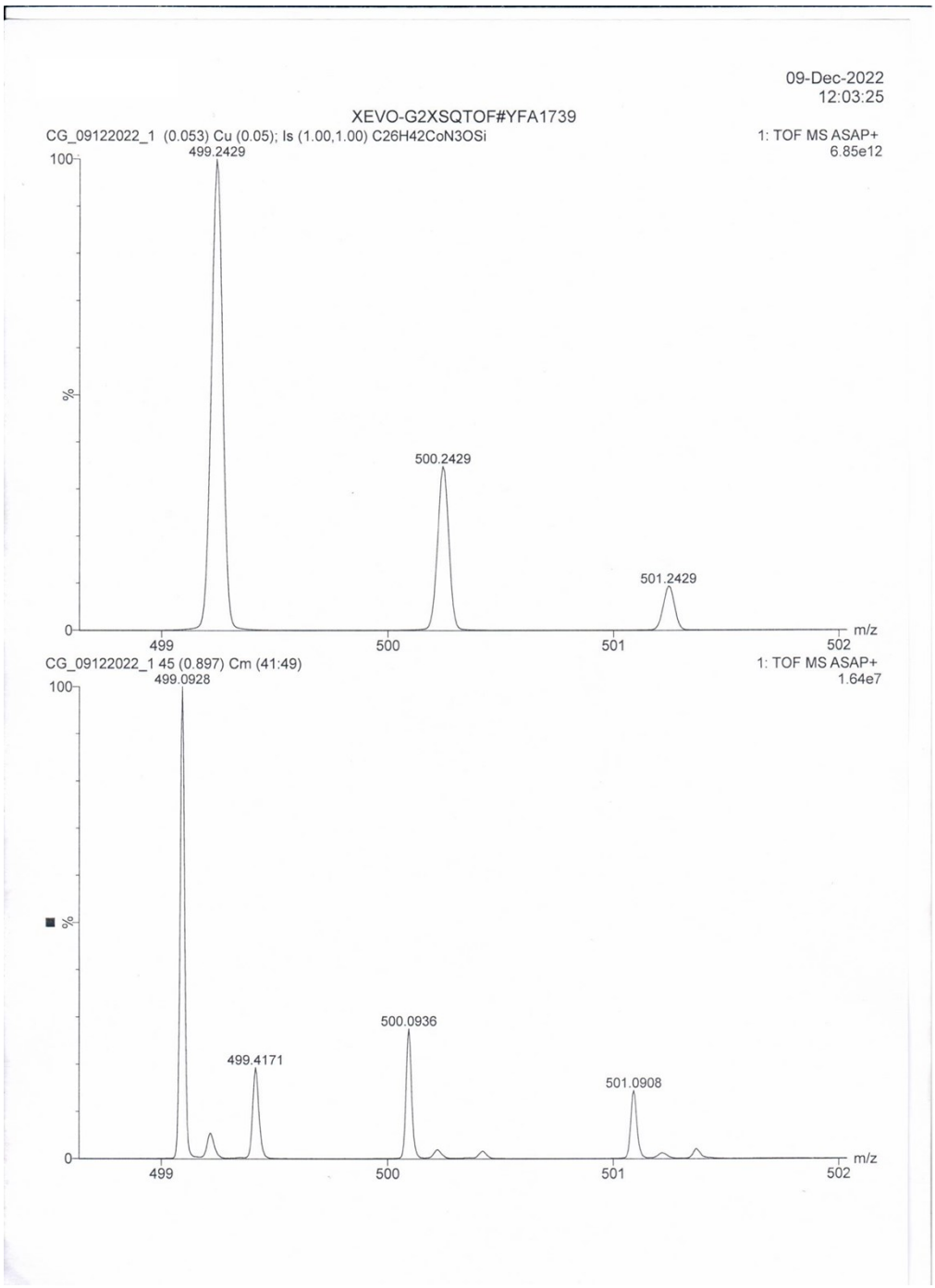
$^{13}C\{^{1}H\}$ NMR spectrum of 1,2-diphenylpropan-1-ol (**5**, 101 MHz, $CDCl_3$)



Experiment to verify effect of C-O bond cleavage on tertiary ether:

Under the nitrogen atmosphere of glove box, catalyst **1** (5 mol %), 2-(benzyloxy)pentan-2-yl)benzene (1 mmol), KO^{t}Bu (40 mol %), diethylsilane (4 mmol), Hg (10 mmol) were charged into oven-dried teflon sealed vial. Then the reaction mixture was heated at 100 °C for 12 hours. After cooling the reaction mixture to room temperature, the solvent was removed under reduced pressure. HCl in diethyl ether (1 M) was added to reaction mixture and allowed to stir at room temperature for 2 hours. Water (2 mL) was added. The resulted reaction mixture was extracted with dichloromethane (3 × 10 mL). The combined organic layer was washed with brine and dried over anhydrous sodium sulfate. The solvents were removed under reduced pressure, and the resulted residue was purified by column chromatography over silica gel (100-200 mesh) using hexane/ethyl acetate (97:3) as an eluent.

Solid state ESI mass spectrum of reaction mixture:



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