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Nickel-catalyzed desulfonylative olefination of β-hydroxysulfones

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Supplementary information

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1. General considerations

1.1 General experimental details

Unless otherwise indicated, reactions were conducted under an atmosphere of nitrogen in 8 mL screw capped vials that were oven dried (120 °C). Column chromatography was either performed manually using Silicycle F60 40−63 μm silica gel or by using a Combiflash Rf+ automated chromatography system with commercially available Biotage normal-phase Silica Flash columns (35−70 μm). Analytical thin layer chromatography (TLC) was conducted with aluminum-backed EMD Millipore Silica Gel 60 F254 pre-coated plates. Unless otherwise noted, visualization of developed plates was performed under UV light (254 nm) and/or using $KMnO_4$ stain.

1.2 Instrumentation

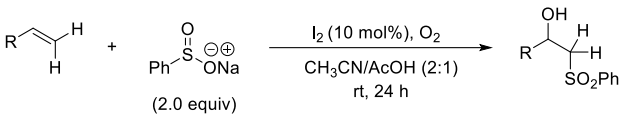
^1H NMR and ^{13}C NMR were recorded on a Bruker AVANCE 400 MHz spectrometer. ^1H NMR spectra were internally referenced to the residual solvent signal (e.g., $CDCl_3$ = 7.27 ppm). ^{13}C NMR spectra were internally referenced to the residual solvent signal (e.g., $CDCl_3$ = 77.00 ppm). Data for ^1H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet), coupling constant (Hz), integration. NMR yields for optimization studies were obtained by ^1H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. GC data was obtained via a 5-point calibration curve using FID analysis on an Agilent Technologies 7890B GC with a 30 m x 0.25 mm HP-5 column. Accurate mass data (EI) was obtained from an Agilent 5977A GC/MSD using MassWorks 4.0 from CERNO Bioscience.[1]

1.3 Materials

Organic solvents were purified by rigorous degassing with nitrogen before passing through a PureSolv solvent purification system. Low water content was confirmed by Karl Fischer titration (<20 ppm for all solvents). Unless otherwise noted, starting materials were obtained commercially from Sigma Aldrich, Alfa Aesar or Combi-Blocks and used as received. $Ni(cod)_2$ was purchased from Sigma Aldrich. $NiBr_2$·glyme (97% purity) was purchased from Sigma Aldrich. Granulated Mn was purchased from Alfa Aesar (99.6% purity, < 10 micron). ICy•HBF_4 was synthesized according to the literature, as were other NHC ligands.[2]

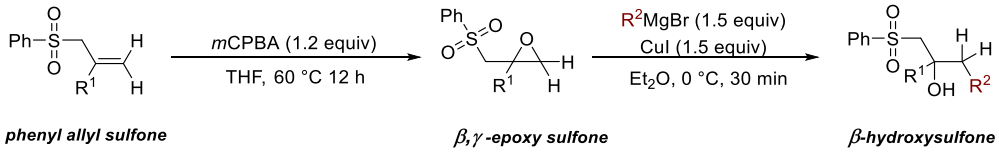
2. Synthesis of starting materials

General Protocol A: Hydroxysulfonylation from olefins



β-Hydroxysulfones (**S1-S7, S11**) were prepared from the corresponding olefins according to a literature procedure.[3] An oven-dried 10 mL round bottom flask was equipped with a magnetic stir bar. To this round bottom flask was added olefin starting material (1.0 equivalents, 0.6 mmol), benzene sulfinic acid sodium salt (2.0 equivalents, 1.2 mmol), and I_2 (0.1 equivalents, 0.06 mmol). CH_3CN (2 mL) and AcOH (1 mL) were subsequently added to the reaction vessel and the reaction was left to stir under open air conditions for 20 h at room temperature. Upon completion of the reaction, the solution was quenched with sat. $Na_2S_2O_3$ (aq) and diluted with 5 mL of EtOAc. The organic layer was separated before being washed twice with sat. $NaHCO_3$ (aq) and once with NaCl (aq). The solution was dried over $MgSO_4$, filtered via suction filtration and the solvent was removed *in vacuo* to reveal crude product. The crude product was subsequently dissolved in dichloromethane – a small amount of SiO_2 was added to the resulting solution and the solvent was once more removed *in vacuo*. The resulting solid was loaded directly on to a 10 g Biotage SNAP silica-packed column and purified on a CombiFlash Rf+ automated chromatography instrument using a mixture of ethyl acetate and hexanes.

General Protocol B: Synthesis of β-hydroxysulfones through an epoxide intermediate

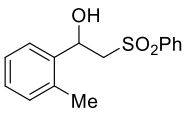


β-Hydroxysulfones **1**, **36**, **S8-S10**, and **S12-S20** were prepared from the corresponding phenyl allyl sulfones according to a literature procedure.[4] An oven-dried 10 mL round bottom flask was equipped with a magnetic stir bar. To this round bottom flask was added phenyl allyl sulfone (1.0 equivalents, 1.0 mmol) and anhydrous THF (2 mL). *m*-Chloroperbenzoic acid (*mCPBA*; 1.2 equivalents, 1.2 mmol) was dissolved in anhydrous THF (5 mL) and added dropwise to the phenyl allyl sulfone solution over a period of two minutes while stirring. The reaction mixture was subsequently capped and allowed to stir for 12 h

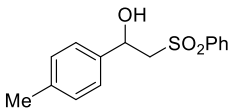
at 60 ˚C. After 12 h, the solution was allowed to come to room temperature before being passed through a short plug composed of SiO_2 and celite in a 50:50 mixture. Solvent was removed *in vacuo* to reveal crude β,γ-epoxy sulfone that was carried forward without further purification.

To the crude β,γ-epoxy sulfone was added anhydrous Et_2O (5 mL) and copper iodide (*CuI*; 1.5 equivalents, 1.5 mmol). The resulting mixture was cooled over ice to 0 ˚C and a solution of Grignard reagent (1.5 equivalents, 1.5 mmol) in anhydrous Et_2O (5 mL) was added dropwise over a period of two minutes while stirring *(Grignard reagents were purchased commercially or prepared in situ via the addition of organobromide and Mg).* The resulting solution was allowed to come to room temperature while stirring for an additional 30 minutes, after which it was quenched with sat. NH_4Cl (aq) and extracted into dichloromethane (10 mL). The organic phase was separated and washed twice with 1.0 M HCl and once with NaCl (aq) before being dried over Na_2SO_4. This mixture was filtered via suction filtration and solvent was evaporated *in vacuo* to reveal crude product. The crude product was subsequently dissolved in dichloromethane – a small amount of SiO_2 was added to the resulting solution and the solvent was once more removed *in vacuo*. The resulting solid was loaded directly on to a 10 g Biotage SNAP silica-packed column and purified on a CombiFlash Rf+ automated chromatography instrument using a mixture of ethyl acetate and hexanes.

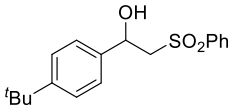
2.1 Starting materials and characterization data



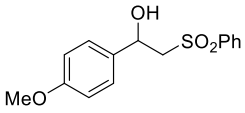
1-(2-Methylphenyl)-2-(phenylsulfonyl)-ethan-1-ol (S1) was prepared from *2-methylstyrene* and *benzene sulfinic acid sodium salt* according to General Protocol A. Column chromatography was performed using a gradient of 1→20% ethyl acetate in hexanes to afford product as a yellow liquid (126 mg, 76% yield). Characterization data matched those previously reported.[3] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.96-7.93 (m, 2H), 7.70-7.67 (m, 1H), 7.61-7.57 (m, 2H), 7.47-7.42 (m, 1H), 7.18-7.13 (m, 2H), 7.05-7.01 (m, 1H), 5.45-5.39 (m, 1H), 3.39-3.32 (m, 1H), 3.23-3.21 (m, 1H), 2.09 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 139.1, 138.8, 138.6, 133.7, 130.1, 129.7, 129.3, 128.0, 126.3, 125.0, 64.7, 62.3, 18.9.



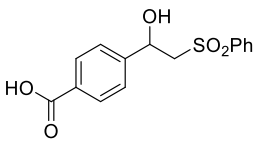
1-(4-Methylphenyl)-2-(phenylsulfonyl)-ethan-1-ol (S2) was prepared from *4-methylstyrene* and *benzene sulfinic acid sodium salt* according to General Protocol A. Column chromatography was performed using a gradient of 1→20% ethyl acetate in hexanes to afford product as a yellow liquid (137 mg, 83% yield). Characterization data matched those previously reported.[3] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.93-7.90 (m, 2H), 7.68-7.54 (m, 3H), 7.42-7.38 (m, 2H), 7.13-7.08 (m, 2H), 5.24-5.21 (m, 1H), 3.48-3.44 (m, 2H), 2.33 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 139.3, 138.1, 137.3, 133.8, 129.3, 129.2, 127.5, 125.2, 67.8, 63.1, 21.2.



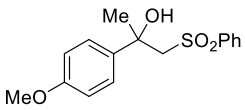
1-(4-Tertbutylphenyl)-2-(phenylsulfonyl)-ethan-1-ol (S3) was prepared from *4-tertbutylstyrene* and *benzene sulfinic acid sodium salt* according to General Protocol A. Column chromatography was performed using a gradient of 1→20% ethyl acetate in hexanes to afford product as a yellow liquid (162 mg, 85% yield). Characterization data matched those previously reported.[3] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.95-7.92 (m, 2H), 7.68-7.63 (m, 1H), 7.56-7.54 (m, 2H), 7.34-7.31 (m, 2H), 7.23-7.19 (m, 2H), 5.26-5.21 (m, 1H), 3.53-3.49 (m, 1H), 3.39-3.37 (m, 1H), 1.28 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): 151.6, 138.8, 138.5, 137.4, 134.1, 129.2, 127.7, 125.3, 68.3, 63.0, 34.2, 31.8.



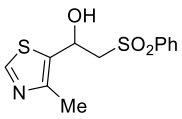
1-(4-Methoxyphenyl)-2-(phenylsulfonyl)-ethan-1-ol (S4) was prepared *from 4-methoxystyrene* and *benzene sulfinic acid sodium salt* according to General Protocol A. Column chromatography was performed using a gradient of 1→20% ethyl acetate in hexanes to afford product as a yellow liquid (130 mg, 74% yield). Characterization data matched those previously reported.[3] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.94-7.92 (m, 2H), 7.69-7.66 (m, 1H), 7.57-7.53 (m, 2H), 7.22-7.17 (m, 2H), 6.87-6.81 (m, 2H), 5.29-5.23 (m, 1H), 3.77 (s, 3H), 3.51-3.48 (m, 1H), 3.34-3.32 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): 159.3, 139.0, 134.2, 132.4, 129.2, 127.9, 126.8, 114.0, 67.0, 63.8, 55.3.



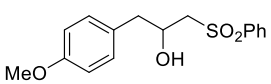
1-(4-Carbonic acid phenyl)-2-(phenylsulfonyl)-ethan-1-ol (S5) was prepared from *4-vinylbenzoic acid* and *benzene sulfinic acid sodium salt* according to General Protocol A. Column chromatography was performed using a gradient of 1→20% ethyl acetate in hexanes to afford product as a yellow liquid (133 mg, 74% yield). Characterization data matched those previously reported.[3] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.94-7.91 (m, 4H), 7.68-7.59 (m, 1H), 7.57-7.54 (m, 2H), 7.38-7.36 (m, 2H), 5.23-5.18 (m, 1H), 4.90 (br, 1H), 3.71-3.65 (m, 1H), 3.54-3.52 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): 169.3, 148.4, 141.2, 134.8, 133.6, 130.7, 129.9, 128.7, 127.1, 69.6, 64.1.



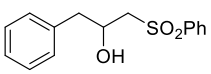
1-(4-Methoxyphenyl)-1-methyl-2-(phenylsulfonyl)-ethan-1-ol (S6) was prepared from *α-methylstyrene* and *benzene sulfinic acid sodium salt* according to General Protocol A. Column chromatography was performed using a gradient of 1→20% ethyl acetate in hexanes to afford product as a yellow liquid (145 mg, 79% yield). Characterization data matched those previously reported.[5] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.91-7.89 (m, 2H), 7.40-7.37 (m, 2H), 7.30-7.24 (m, 2H), 6.95-6.88 (m, 3H), 3.79 (s, 3H), 2.47 (s, 3H), 1.24-1.20 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): 159.5, 146.8, 141.6, 130.2, 129.4, 127.0, 120.6, 113.8, 58.4, 55.0, 21.8, 18.2.



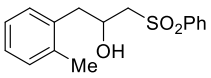
1-(4-Methyl-5-vinylthiazyl)-2-(phenylsulfonyl)-ethan-2-ol (S7) was prepared from *4-methyl-5-vinylthiazole* and *benzene sulfinic acid sodium salt* according to General Protocol A. Column chromatography was performed using a gradient of 1→20% ethyl acetate in hexanes to afford product as an off-white liquid (64 mg, 36% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.99-7.97 (m, 2H), 7.47-7.45 (m, 2H), 6.99-6.96 (m, 2H), 2.68-2.66 (m, 1H), 2.54 (s, 3H), 1.70-1.64 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): 146.8, 143.2, 141.7, 128.3, 127.0, 125.0, 119.7, 29.0, 23.5, 14.1. **Accurate mass (EI)**: Theoretical: 283.0337. Found: 283.0329. Spectral Accuracy: 97.8%. **FT-IR**: *v* (cm^{-1}) 3413, 3180, 1505, 1375, 882.



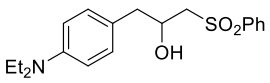
1-(4-Methoxyphenyl)-3-(phenylsulfonyl)propan-2-ol (1) was prepared from *allyl phenyl sulfone* and *4-methoxyphenylmagnesium bromide* according General Protocol B. Column chromatography was performed using a gradient of 1→20% ethyl acetate in hexanes to afford product as an off-white liquid (98 mg, 32% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.91-7.89 (m, 2H), 7.39-7.37 (m, 2H), 7.30-7.24 (m, 2H), 6.95-6.88 (m, 3H), 3.79 (s, 3H), 3.73-3.67 (m, 1H), 2.54-2.43 (m, 2H), 1.24-1.20 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): 159.5, 146.8, 141.6, 130.2, 129.4, 127.0, 120.6, 113.8, 58.4, 55.1, 21.8, 18.2. **Accurate mass (EI)**: Theoretical: 306.0926. Found: 306.0921. Spectral Accuracy: 97.0%. **FT-IR**: *v* (cm^{-1}) 3593, 2935, 1589, 1513, 1312, 1109, 978.



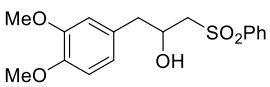
1-Phenyl-3-(phenylsulfonyl)propan-2-ol (36) was prepared from *allyl phenyl sulfone* and *phenylmagnesium bromide* according to General Protocol B. Column chromatography was performed using a gradient of 1→15% ethyl acetate in hexanes to afford product as a yellow liquid (81 mg, 29% yield). Characterization data matched those previously reported.[6] **^{1}H NMR** (400 MHz, $CDCl_3$): 7.92-7.90 (m, 2H), 7.40-7.38 (m, 3H), 7.29-7.27 (m, 2H), 7.25-7.17 (m, 3H), 3.68-3.65 (m, 1H), 2.71-2.67 (m, 2H), 1.92-1.85 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): 146.8, 141.7, 141.6, 130.2, 128.4, 128.3, 127.0, 125.8, 62.3, 34.1, 32.0.



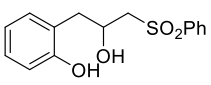
1-(2-Methylphenyl)-3-(phenylsulfonyl)propan-2-ol (S8) was prepared from *allyl phenyl sulfone* and *2-methylphenylmagnesium bromide* according to General Protocol B. Column chromatography was performed using a gradient of 1→15% ethyl acetate in hexanes to afford product as a yellow liquid (104 mg, 36% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.92-7.90 (m, 2H), 7.41-7.36 (m, 2H), 7.26-7.24 (m, 2H), 7.19-7.15 (m, 3H), 2.71-2.67 (m, 1H), 2.47 (s, 3H), 2.38-2.36 (m, 2H), 1.92-1.85 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): 146.8, 141.7, 141.6, 130.2, 129.3, 128.4, 128.3, 127.0, 126.3, 125.8, 62.3, 34.1, 32.0, 21.8. **Accurate mass (EI)**: Theoretical: 290.0977. Found: 290.0979. Spectral Accuracy: 98.8%. **FT-IR**: *v* (cm^{-1}) 3631, 2913, 1577, 1521, 1317, 1103, 875.



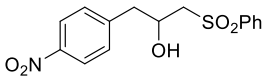
1-(4-Diethylaminophenyl)-3-(phenylsulfonyl)propan-2-ol (S9) was prepared from *allyl phenyl sulfone* and *4-diethylaminophenyl magnesium bromide* according to General Protocol B. Column chromatography was performed using a gradient of 1→30% ethyl acetate in hexanes to afford product as a yellow liquid (145.8 mg, 42% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.04-8.02 (m, 2H), 7.53-7.50 (m, 3H), 7.37-7.32 (m, 2H), 6.84-6.78 (m, 2H), 3.58-3.56 (m, 2H), 3.45-3.41 (m, 4H), 2.60 (m, 1H), 2.36 (m, 2H), 1.26-1.23 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): 146.8, 141.6, 130.2, 129.8, 129.7, 128.8, 128.0, 127.0, 125.9, 113.3, 50.7, 45.2, 21.8, 20.2, 12.3. **Accurate mass (EI)**: Theoretical: 347.1555. Found: 347.1552. Spectral Accuracy: 96.4%. **FT-IR**: *v* (cm^{-1}) 3614, 3108, 2880, 2640, 1595, 1532, 1318, 1103. **mp:** 128-131 °C.



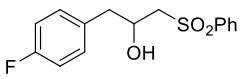
1-(3,4-Dimethoxyphenyl)-3-(phenylsulfonyl)propan-2-ol (S10) was prepared from *allyl phenyl sulfone* and *3,4-dimethoxyphenylmagnesium bromide* according to General Protocol B. Column chromatography was performed using a gradient of 1→15% ethyl acetate in hexanes to afford product as a white solid (81 mg, 24% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.92-7.88 (m, 2H), 7.46-7.37 (m, 5H), 6.98-6.96 (m, 1H), 3.95 (s, 3H), 3.93 (s, 3H), 3.73-3.68 (m, 2H), 2.78-2.75 (m, 1H), 1.24-1.20 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): 154.4, 149.5, 146.8, 141.6, 130.2, 130.0, 127.0, 126.9, 110.3, 108.8, 58.3, 56.1, 55.9, 21.7, 18.2. **Accurate mass (EI)**: Theoretical: 336.1031. Found: 336.1028. Spectral Accuracy: 98.4%. **FT-IR**: *v* (cm^{-1}) 3519, 2875, 1630, 1495, 1330, 1075, 984, 973. **mp:** 141-143 °C.



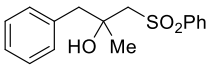
1-(2-Hydroxyphenyl)-3-(phenylsulfonyl)propan-2-ol (S11) prepared from *2-hydroxyallylbenzene* and *benzene sulfinic acid sodium salt* according to a modified General Protocol A, running the reaction for 40 h at 60 ˚C. Column chromatography was performed using a gradient of 1→20% ethyl acetate in hexanes to afford product as an off-white liquid (109 mg, 62% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.91-7.88 (m, 2H), 7.40-7.37 (m, 2H), 7.17-7.13 (m, 3H), 6.77-6.74 (m, 2H), 3.80-3.74 (m, 1H), 2.47-2.46 (m, 2H), 1.27-1.23 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): 154.3, 146.9, 141.5, 130.2, 129.7, 129.4, 129.1, 127.0, 125.4, 116.7, 58.8, 21.8, 17.9. **Accurate mass (EI)**: Theoretical: 292.0769. Found: 292.0764. Spectral Accuracy: 98.8%. **FT-IR**: *v* (cm^{-1}) 3630, 3401, 2970, 1845, 1603, 1540, 1321, 1146.



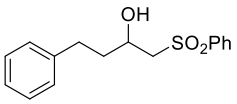
1-(4-Nitrophenyl)-3-(phenylsulfonyl)propan-2-ol (S12) was prepared from *allyl phenyl sulfone* and *4-nitrophenylmagnesium bromide* according to General Protocol B. Column chromatography was performed using a gradient of 1→35% ethyl acetate in hexanes to afford product as a yellow liquid (103 mg, 32% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.22-8.18 (m, 2H), 7.94-7.90 (m, 3H), 7.58-7.55 (m, 1H), 7.43-7.39 (m, 3H), 4.52 (s, 2H), 3.48 (s, 1H), 2.49-2.44 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): 147.6, 146.8, 144.8, 141.6, 130.2, 129.9, 127.0, 124.0, 50.7, 30.9, 21.8. **Accurate mass (EI)**: Theoretical: 321.0671. Found: 321.0670. Spectral Accuracy: 97.9% **FT-IR**: *v* (cm^{-1}) 3580, 2840, 1628, 1525, 1507, 1321, 1156.



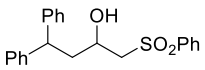
1-(4-Fluorophenyl)-3-(phenylsulfonyl)propan-2-ol (S13) was prepared from *allyl phenyl sulfone* and *4-fluorophenylmagnesium bromide* according to General Protocol B. Column chromatography was performed using a gradient of 1→15% ethyl acetate in hexanes to afford product as a yellow liquid (65 mg, 22% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.94-7.92 (m, 2H), 7.43-7.40 (m, 2H), 7.37-7.32 (m, 3H), 7.16-7.12 (m, 1H), 7.09-7.04 (m, 1H), 3.76-3.71 (m, 1H), 2.50 (s, 2H),1.27-1.23 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): 164.0, 161.6, 146.8, 141.6, 130.0 (t), 127.0, 124.0, 123.9, 115.4, 115.1, 58.4, 21.8, 18.2. **Accurate mass (EI)**: Theoretical: 294.0726. Found: 294.0718. Spectral Accuracy: 97.5%. **FT-IR**: *v* (cm^{-1}) 3530, 2860, 1645, 1585, 1385, 1330, 1075.



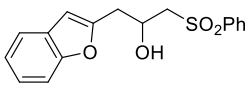
2-Methyl-1-phenyl-3-(phenylsulfonyl)propan-2-ol (S14) was prepared from *2-methylallyl phenyl sulfone* and *phenylmagnesium bromide* according to General Protocol B. Column chromatography was performed using a gradient of 1→20% ethyl acetate in hexanes to afford product as a yellow liquid (104 mg, 36% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.93-7.91 (m, 2H), 7.71-7.69 (m, 1H), 7.62-7.58 (m, 2H), 7.32-7.29 (m, 2H), 7.23-7.18 (m, 3H), 2.70-2.65 (m, 2H), 2.42 (m, 2H), 1.28-1.25 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 144.2, 138.6, 134.3, 129.3, 128.3, 128.2, 127.8, 125.5, 67.7, 31.4, 28.8, 15.6. **Accurate mass (EI)**: Theoretical: 290.0977. Found: 209.0972. Spectral Accuracy: 98.4%. **FT-IR**: *v* (cm^{-1}) 3680, 2895, 1590, 1504, 1315, 1083.



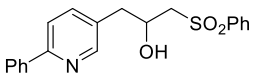
1-Phenyl-4-(phenylsulfonyl)butan-3-ol (S15) was prepared from *allyl phenyl sulfone* and *benzylmagnesium bromide* according to General Protocol B. Column chromatography was performed using a gradient of 1→20% ethyl acetate in hexanes to afford product as a colourless liquid (122 mg, 42% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.95-7.92 (m, 2H), 7.44-7.40 (m, 3H), 7.32-7.28 (m, 2H), 7.22-7.18 (m, 3H), 3.71-3.68 (m, 2H), 2.94 (m, 1H), 2.73-2.70 (m, 2H), 1.94-1.87 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): 146.8, 141.6, 130.2, 129.2, 128.4, 128.3, 127.0, 125.8, 62.2, 34.0, 32.0, 21.8. **Accurate mass (EI)**: Theoretical: 290.0977. Found: 290.0971. Spectral Accuracy: 97.3%. **FT-IR**: *v* (cm^{-1}) 3548, 2870, 1585, 1508, 1380, 1130, 1010.



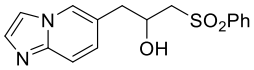
1,1-Diphenyl-4-(phenylsulfonyl)butan-3-ol (S16) was prepared from *allyl phenyl sulfone* and *diphenylmethylmagnesium bromide* according to General Protocol B. Column chromatography was performed using a gradient of 1→15% ethyl acetate in hexanes to afford product as a beige solid (139 mg, 38% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.84-7.82 (m, 2H), 7.33-7.08 (m, 13H), 3.89-3.80 (m, 1H), 3.43-3.40 (m, 2H), 1.74-1.66 (m, 1H), 0.95-0.90 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): 146.8, 141.6, 141.1, 130.2, 128.9, 128.5, 128.4, 128.3, 128.2, 127.5, 127.0, 126.0, 58.4, 41.9, 21.7, 18.2. **Accurate mass (EI)**: Theoretical: 366.1290. Found: 366.1283. Spectral Accuracy: 98.8%. **FT-IR**: *v* (cm^{-1}) 3640, 3580, 2975, 1630, 1550, 1504, 1318, 1105, 970. **mp:** 106-108 °C.



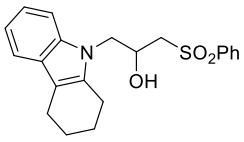
1-(2-Benzofuranyl)-3-(phenylsulfonyl)propan-2-ol (S17) was prepared from *allyl phenyl sulfone* and *2-benzofuranylmagnesium bromide* according to General Protocol B. Column chromatography was performed using a gradient of 1→20% ethyl acetate in hexanes to afford product as a yellow liquid (97 mg, 31% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.90-7.88 (m, 2H), 7.74-7.61 (m, 2H), 7.59-7.47 (m, 3H), 7.38-7.32 (m, 3H), 3.96-3.90 (m, 1H), 3.19-3.15 (m, 2H), 1.12-1.11 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): 156.2, 152.7, 147.8, 141.6, 129.6, 129.2, 126.7, 126.1, 124.4, 123.6, 117.7, 112.7, 58.9, 21.7, 18.5. **Accurate mass (EI)**: Theoretical: 316.0769. Found: 316.0764. Spectral Accuracy: 97.8%. **FT-IR**: *v* (cm^{-1}) 3570, 3100, 3044, 1480, 1360, 856.



1-[5-(2-Phenylpyridyl)]-3-(phenylsulfonyl)propan-2-ol (S18) was prepared from *allyl phenyl sulfone* and *2-phenylpyridyl-5-magnesium bromide* according to General Protocol B. Column chromatography was performed using a gradient of 1→20% ethyl acetate in hexanes to afford product as an off-white liquid (127 mg, 36% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.82-8.69 (m, 1H), 8.14-7.81 (m, 5H), 7.73-7.61 (m, 1H), 7.56-7.37 (m, 6H), 3.53-3.50 (m, 2H), 1.82-1.78 (m, 1H), 1.04-1.01 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): 157.0, 149.0, 146.8, 141.6, 137.5, 130.2, 129.2, 128.8, 128.7, 127.0, 126.0, 122.3, 120.9, 46.9, 26.0, 11.6. **Accurate mass (EI)**: Theoretical: 353.1086. Found: 353.1083. Spectral Accuracy: 98.0%. **FT-IR**: *v* (cm^{-1}) 3493, 3090, 1824, 1578, 1462, 740.

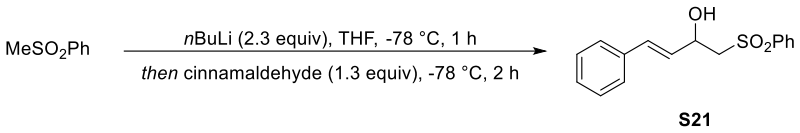


1-[Imidazo(1,2-α)pyridine]-3-(phenylsulfonyl)propan-2-ol (S19) was prepared from *allyl phenyl sulfone* and *chloroimidazo[1,2-α]pyridin-6-ylmagnesium* according to General Protocol B. Column chromatography was performed using a gradient of 1→20% ethyl acetate in hexanes to afford product as a yellow liquid (73 mg, 23% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.13 (s, 1H), 7.80-7.78 (m, 2H), 7.73-7.51 (m, 4H), 7.29-7.15 (m, 2H), 7.08-7.05 (m, 1H), 3.39-3.37 (m, 2H), 1.69-1.63 (m, 1H), 0.91-0.88 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): 146.8, 131.1, 130.1, 128.9, 128.2, 127.6, 125.7, 124.4, 121.9, 116.8, 114.5, 46.9, 25.9, 11.5. **Accurate mass (EI)**: Theoretical: 317.0960. Found: 317.0954. Spectral Accuracy: 97.3%. **FT-IR**: *v* (cm^{-1}) 3512, 3104, 2984, 1880, 1520, 1398, 813.



1-[*N*-(1,2,3,4-tetrahydrocarbazolyl)]-3-(phenylsulfonyl)propan-2-ol (S20) was prepared from *allyl phenyl sulfone* and *1,2,3,4-tetrahydrocarbazole* according to General Protocol B. Column chromatography was performed using a gradient of 1→25% ethyl acetate in hexanes to afford product as a yellow liquid (78 mg, 21% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.80-7.78 (m, 2H), 7.33-7.26 (m, 4H), 7.24-7.13 (m, 1H), 6.99-6.95 (m, 2H), 3.87-3.81 (m, 1H), 3.10-3.06 (m, 2H), 2.61-2.52 (m, 4H), 1.82-1.70 (m, 4H), 1.03-1.02 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): 146.8, 141.7, 135.7, 134.2, 130.2, 129.1, 127.8, 127.0, 120.9, 119.0, 117.7, 110.4, 66.4, 59.0, 23.3, 23.2, 23.1, 21.8, 18.7. **Accurate mass (EI)**: Theoretical: 369.1399. Found: 369.1398. Spectral Accuracy: 98.5%. **FT-IR**: *v* (cm^{-1}) 3510, 3468, 3120, 2943, 1494, 740.

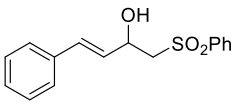
Preparation of allylhydroxysulfone **S21**



S21

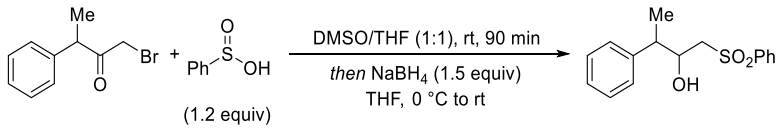
Compound **S21** was prepared according to a literature procedure.[7] An oven-dried 10 mL round-bottom flask was equipped with a magnetic stir bar. Phenylmethylsulfone (1.0 equivalent, 0.6 mmol) was added and dissolved in anhydrous THF (1 mL). This solution was cooled to -78 ˚C and *n*-BuLi (2.5 M in hexanes; 2.3 equivalents, 1.38 mmol) was added dropwise and the reaction was left to stir for 1 h. After 1 h had elapsed, a solution of cinnamaldehyde (1.3 equivalents, 0.78 mmol) in anhydrous THF (1 mL) was added dropwise and the reaction was left to stir for a further 2 h at -78 ˚C. Upon completion, the reaction was quenched with saturated NH_4Cl (aq) and extracted into EtOAc. The organic phase was separated, dried over $MgSO_4$ and filtered via suction filtration before solvents were removed in vacuo to reveal crude product. The crude product was subsequently dissolved in dichloromethane – a small amount of SiO_2 was added to the resulting solution and the solvent was once more removed *in vacuo*. The resulting

solid was loaded directly on to a 10 g Biotage SNAP silica-packed column and purified on a CombiFlash Rf+ automated chromatography instrument using a mixture of ethyl acetate and hexanes.



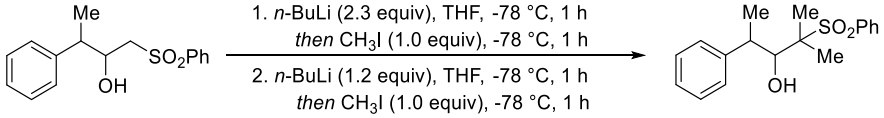
1-(Phenylsulfonyl)-4-phenyl-3-buten-2-ol (S21) was prepared from *2-methylsulfonylbenzene* and *cinnamaldehyde* according to the above literature procedure.[7] Column chromatography was performed using a gradient of 1→15% ethyl acetate in hexanes to afford product as a clear solid (64 mg, 37% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.89-7.87 (m, 2H), 7.69-7.65 (m, 1H), 7.58-7.56 (m, 2H), 7.39-7.37 (m, 2H), 7.33-7.31 (m, 2H), 7.24-7.20 (m, 1H), 6.67-6.62 (m, 1H), 6.34-6.26 (m, 1H), 4.24-4.22 (m, 1H), 2.41-2.38 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): 146.8, 141.6, 136.8, 135.3, 134.8, 130.2, 127.6, 127.1, 126.1, 125.3, 50.7, 19.6. **Accurate mass (EI)**: Theoretical: 288.0820. Found: 288.0821. Spectral Accuracy: 98.0%. **FT-IR**: *v* (cm^{-1}) 3640, 3130, 2960, 1670, 1480, 1230, 1054. **mp:** 79-81 °C.

<u>Preparation of hydroxysulfones to be used in the synthesis of trisubtituted olefins</u>



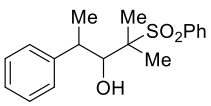
S22 **S23**

Step One: Preparation of hydroxysulfone **S23** was performed according to a literature procedure.[8] To an oven-dried 10 mL round bottom flask was added 1-bromo-3-phenyl-2-butanone (1.0 equivalent, 1.0 mmol) and phenyl sulfinic acid (1.2 equivalents, 1.2 mmol). A 1:1 mixture of DMSO/THF (1 mL: 1mL) was added to the solution before being capped and left to stir at room temperature for 90 minutes. The reaction mixture was subsequently diluted with EtOAc and passed through a small plug consisting of SiO_2 and celite in a 50:50 mixture. Solvent was removed *in vacuo* to reveal crude product that was carried forward without further purification. Anhydrous THF (3 mL) was added to the round bottom flask to dissolve the crude residue. The flask was cooled to 0 ˚C, after which $NaBH_4$ (1.5 equivalents, 1.5 mmol) was added. The reaction was allowed to stir for 1 h before being quenched with NH_4Cl, diluted with EtOAc and passed through a short plug consisting of SiO_2 and celite in a 50:50 mixture. Solvent was removed *in vacuo* to reveal crude hydroxysulfone **S23** that was carried forward without further purification.

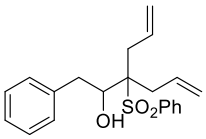


S23 **S24**

Step Two: Preparation of hydroxysulfone **S24** was performed according to a literature procedure.[9] Anhydrous THF (5 mL) was added to the round bottom flask to dissolve crude hydroxysulfone **S23**. The reaction mixture was brought to -78 ˚C and *n*-BuLi (2.5 M in hexanes; 2.3 equivalents, 2.3 mmol) was added dropwise. The reaction mixture was stirred for 1 h, after which CH_3I (1.0 M in hexanes; 1.0 equivalent, 1.0 mmol) was added dropwise. The reaction was stirred for another hour at -78 ˚C, after which a second portion of *n*-BuLi (2.5 M in hexanes, 1.2 equivalents, 1.2 mmol) was added dropwise. The reaction mixture was stirred at -78 ˚C for an hour, after which CH_3I (1.0 M in hexanes, 1.0 equivalent, 1.0 mmol) was added. The reaction was allowed to stir for another hour at -78 ˚C, at which time it was quenched with saturated NH_4Cl (aq) an extracted into dichloromethane. The organic phase was washed twice with sat. $NaHCO_3$ (aq) and once with sat. NaCl (aq) before being dried over $MgSO_4$. Solids were removed via suction filtration and the solvent was removed in vacuo to reveal crude product. The crude product was subsequently dissolved in dichloromethane – a small amount of SiO_2 was added to the resulting solution and the solvent was once more removed *in vacuo*. The resulting solid was loaded directly on to a 10 g Biotage SNAP silica-packed column and purified on a CombiFlash Rf+ automated chromatography instrument using a mixture of ethyl acetate and hexanes.

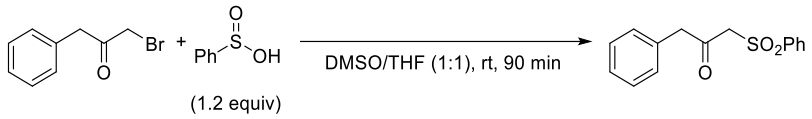


1,3,3-Trimethyl-1-(phenyl)-3-(phenylsulfonyl)propan-2-ol (S24) was prepared from *1-bromo-3-phenyl-2-butanone* according to the above procedure, dialkylating the resulting hydroxysulfone with CH_3I. Column chromatography was performed using a gradient of 1→20% ethyl acetate in hexanes to afford product as a yellow liquid (83 mg, 26% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.95-7.92 (m, 2H), 7.43-7.41 (m, 2H), 7.32-7.30 (m, 1H), 7.29-7.28 (m, 1H), 7.26-7.24 (m, 1H), 7.23-7.21 (m, 1H), 7.20-7.19 (m, 1H), 7.18-7.16 (m, 1H), 3.53-3.42 (m, 1H), 2.68-2.64 (m, 1H), 2.50 (m, 3H), 0.94-0.91 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): 146.8, 144.2, 141.7, 130.2, 129.2, 128.3, 127.8, 127.0, 126.3, 125.5, 68.0, 28.8, 25.7, 21.8, 16.1, 15.6. **Accurate mass (EI)**: Theoretical: 318.1290. Found: 318.1288. Spectral Accuracy: 97.3%. **FT-IR**: *v* (cm^{-1}) 3540, 2880, 1589, 1504, 1310, 1150, 975, 890.



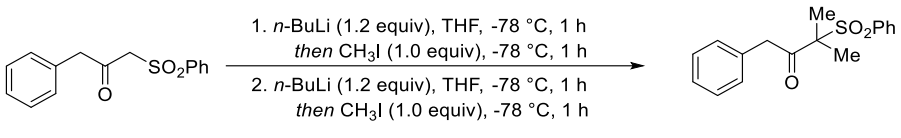
1-Phenyl-3,3-(Diprop-2-ene)-3-(phenylsulfonyl)propan-2-ol (S25) was prepared from *1-bromo-3-phenyl-2-propanone* according to the above procedure, dialkylating the resulting hydroxysulfone with allyl bromide rather than methyl iodide.[10] Column chromatography was performed using a gradient of 1→25% ethyl acetate in hexanes to afford product as a colourless liquid (78 mg, 22% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.91-7.89 (m, 2H), 7.40-7.36 (m, 2H), 7.26-7.25 (m, 4H), 7.19-7.15 (m, 2H), 6.01-5.93 (m, 2H), 5.29-5.10 (m, 4H), 3.65-3.62 (m, 2H), 2.70-2.66 (m, 4H), 1.90-1.85 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): 146.8, 141.7, 141.5, 137.2, 130.1, 128.6, 126.9, 125.7, 125.4, 115.1, 62.0, 34.0, 32.0, 21.7. **Accurate mass (EI)**: Theoretical: 356.1446. Found: 356.1449. Spectral Accuracy: 98.6%. **FT-IR**: *v* (cm^{-1}) 3630, 3240, 3200, 2830, 1660, 1318, 1120, 980, 940.

Preparation of hydroxysulfones to be used in the synthesis of tetrasubstituted olefins



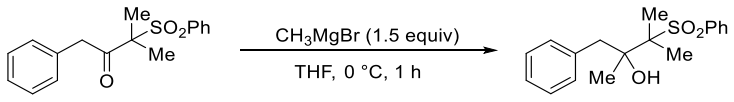
S26 **S27**

Step One: Preparation of ketosulfone **S27** was performed according to a literature procedure.[8] To an oven-dried 10 mL round bottom flask was added 1-bromo-3-phenyl-2-propanone (1.0 equivalent, 1.0 mmol) and phenyl sulfinic acid (1.2 equivalents, 1.2 mmol). A 1:1 mixture of DMSO/THF (1 mL: 1mL) was added to the solution before being capped and left to stir at room temperature for 90 minutes. The reaction mixture was subsequently diluted with EtOAc and passed through a small plug consisting of SiO_2 and celite in a 50:50 mixture. Solvent was removed *in vacuo* to reveal crude product that was carried forward without further purification.



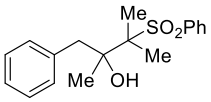
S27 **S28**

Step Two: Preparation of ketosulfone **S28** was performed according to a literature procedure.[9] Anhydrous THF (5 mL) was added to a 10 mL round bottom flask to dissolve crude ketosulfone **S27**. The reaction mixture was brought to -78 ˚C and *n*-BuLi (2.5 M in hexanes; 1.2 equivalents, 1.2 mmol) was added dropwise. The reaction mixture was stirred for 1 h, after which CH_3I (1.0 M in hexanes; 1.0 equivalent, 1.0 mmol) was added dropwise. The reaction was stirred for another hour at -78 ˚C, after which a second portion of *n*-BuLi (2.5 M in hexanes, 1.2 equivalents, 1.2 mmol) was added dropwise. The reaction mixture was stirred at -78 ˚C for an hour, after which CH_3I (1.0 M in hexanes, 1.0 equivalent, 1.0 mmol) was added. The reaction was allowed to stir for another hour at -78 ˚C, at which time it was quenched with saturated NH_4Cl (aq) an extracted into dichloromethane. The resulting organic phase was passed through a small plug consisting of SiO_2 and celite in a 50:50 mixture. Solvent was removed in vacuo to reveal crude product that was carried forward without further purification.



S28 **S29**

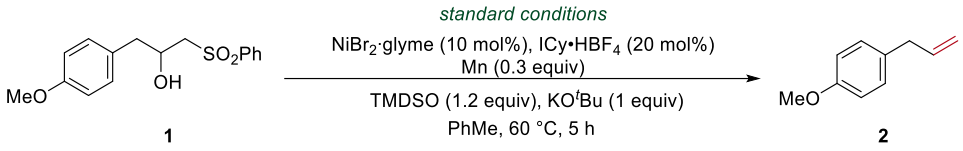
Step Three: Preparation of hydroxysulfone **S29** was performed according to a literature procedure.[11] Anhydrous THF (5 mL) was added to a 10 mL round bottom flask to dissolve crude ketosulfone **S28**. The reaction mixture was cooled to 0 °C and CH_3MgBr (1.0 M in hexanes; 1.5 equivalents, 1.5 mmol) was added dropwise. The reaction mixture was stirred for 1 h, after which it was quenched with saturated NH_4Cl (aq) an extracted into dichloromethane. The organic phase was washed twice with sat. $NaHCO_3$ (aq) and once with sat. NaCl (aq) before being dried over $MgSO_4$. Solids were removed via suction filtration and the solvent was removed *in vacuo* to reveal crude product. The crude product was subsequently dissolved in dichloromethane – a small amount of SiO_2 was added to the resulting solution and the solvent was once more removed *in vacuo*. The resulting solid was loaded directly on to a 10 g Biotage SNAP silica-packed column and purified on a CombiFlash Rf+ automated chromatography instrument using a mixture of ethyl acetate and hexanes.



2,3,3-Trimethyl-1-(phenyl)-3-(phenylsulfonyl)propan-2-ol (S29) was prepared from *1-bromo-3-phenyl-2-butanone* according to the above procedure. Column chromatography was performed using a gradient of 1→25% ethyl acetate in hexanes to afford product as a clear liquid (76.4 mg, 24% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.91-7.89 (m, 2H), 7.49-7.46 (m, 2H), 7.39-7.31 (m, 2H), 7.25-7.18 (m, 4H), 2.49 (s, 3H), 2.15 (s, 2H), 0.91 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): 146.8, 141.7, 131.5, 130.2, 130.0, 127.0, 126.9, 122.5, 66.3, 24.8, 23.9, 23.1, 22.3, 21.8. **Accurate mass (EI)**: Theoretical: 318.1290. Found: 318.1294. Spectral Accuracy: 98.7%. **FT-IR**: *v* (cm^{-1}) 3560, 2830, 1559, 1480, 1316, 1130, 980, 910.

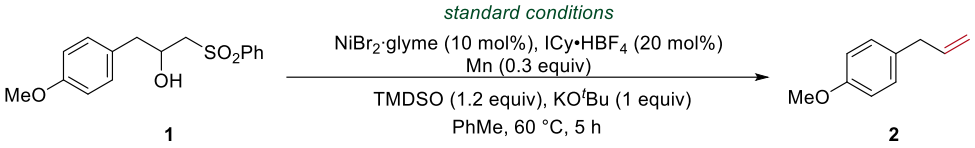
3. Control reactions and optimization

General Protocol C: Olefination of hydroxysulfones



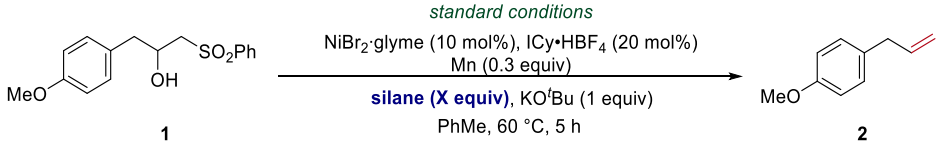
Optimization reactions were performed on *1-(4-methoxyphenyl)-3-(phenylsulfonyl)propan-2-ol* **(1).** An oven-dried 8 mL screw-top test tube is equipped with a magnetic stir bar. To this vial is added hydroxysulfone **(1)** (1 equivalent, 0.20 mmol), $NiBr_2$·glyme (0.10 equivalent, 0.02 mmol), ICy•HBF_4 (0.20 equivalent, 0.04 mmol), potassium *tert*-butoxide (*KO^{t}Bu*; 1.0 equivalent, 0.20 mmol) and Mn (0.3 equivalent, 0.06 mmol). To the resulting mixture is added anhydrous toluene (0.8 mL) followed by 1,1,3,3-tetramethyldisiloxane (*TMDSO*; 1.2 equivalents, 0.24 mmol). The reaction vessel is quickly sealed with a Teflon-septa equipped cap, purged with N_2 (g) and left to stir inside of a mineral-oil bath at 650 RPM for 5 hours at 60 °C. After 5 hours, the reaction vessel is allowed to cool to room temperature before being opened to the atmosphere. The reaction solution is filtered through a short plug composed of a 50:50 mixture of SiO_2 and celite before 100 µL of 0.1 M 1,3,5-trimethoxybenzene in toluene is added to act as an internal standard. Solvent is removed *in vacuo*, yielding crude product which is subsequently dissolved in 0.75 mL of $CDCl_3$ before being submitted for NMR analysis. All yields are obtained via ^{1}H-NMR, setting the integral value of the peak corresponding to the three methoxy protons on product **2** (-OC**H**$_3$) at 3.92 ppm to 3.00 and referencing it with respect to the peak at 6.08 ppm for 1,3,5-trimethoxybenzene.

Supplementary Table S1. Control Experiments



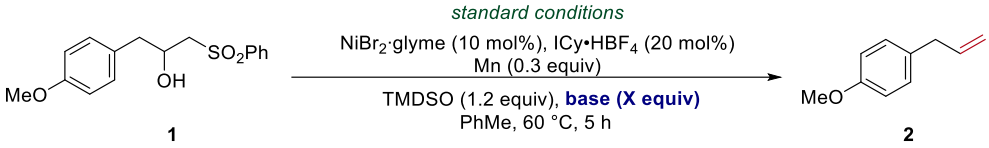
entry	deviation from standard conditions	yield, 2 [%]
1	none	76
2	no $NiBr_2$·glyme	0
3	no Mn	13
4	$Ni(cod)_2$ *instead of* $NiBr_2$·*glyme + Mn*	75
5	no TMDSO	0
6	no KO^tBu	0
7	no $ICy•HBF_4$	9

Supplementary Table S2. Effect of varying the silane



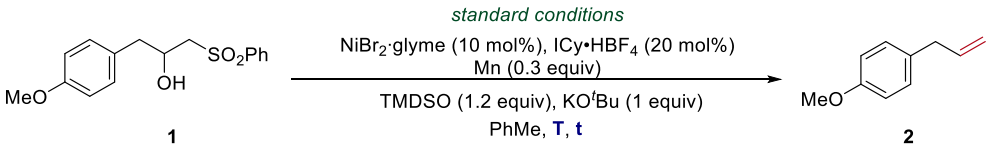
entry	silane	yield, 2 [%]
1	TMDSO (1.2 equiv)	76
2	Et_3SiH (2.4 equiv)	51
3	Ph_3SiH (2.4 equiv)	32
4	PHMS	6
5	$(EtO)_3SiH$ (2.4 equiv)	56
6	TMDSO (0.5 equiv)	46
7	TMDSO (1.0 equiv)	68
8	TMDSO (2.0 equiv)	74

Supplementary Table S3. Effect of varying the base



entry	base	yield, 2 [%]
1	KO^{t}Bu (1.0 equiv)	76
2	NaO^{t}Bu (1.0 equiv)	11
3	LiO^{t}Bu (1.0 equiv)	14
4	KF (1.0 equiv)	8
5	CsF (1.0 equiv)	0
6	KHMDS (1.0 equiv)	4
7	NaOH (1.0 equiv)	0
8	KOH (1.0 equiv)	0

Supplementary Table S4. Effect of varying time, temperature



entry	time	Temperature	yield, 2 [%]
1	5 h	60 °C	76
2	7 h	60 °C	71
3	3 h	60 °C	45
4	1 h	60 °C	19
5	5 h	100 °C	51
6	5 h	50 °C	73
7	5 h	40 °C	46
8	5 h	25 °C	27
9	16 h	25 °C	71

Supplementary Table S5. Effect of varying ligand

entry	ligand (mol %)	yield, 2 [%]
1	ICy•HBF$_4$ (20 mol%)	76
2	ICy•HBF$_4$ (10 mol%)	31
3	IPr•HCl (20 mol%)	27
4	IMes•HCl (20 mol%)	16
5	SIPr•HCl (20 mol%)	3
6	PCy$_3$ (20 mol%)	24
7	PPh$_3$ (20 mol%)	0
8	dcype (20 mol%)	0
9	dppe (20 mol%)	0
10	Xantphos (20 mol%)	11
11	1,10-phenanthroline (20 mol%)	0
12	bipyridine (20 mol%)	0

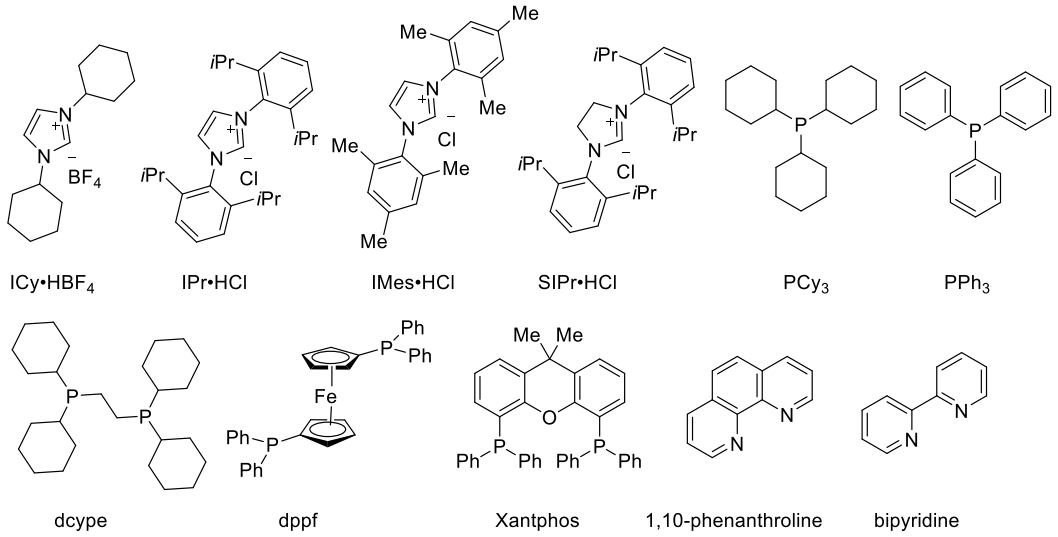
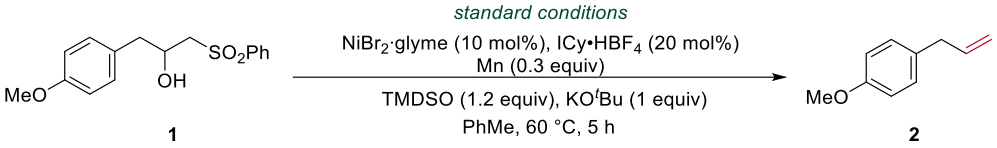


Figure S1. Structures of ligands used in this optimization

4. Substrate scope

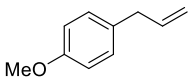
4.1 General Procedures

General Protocol C: Olefination of hydroxysulfones

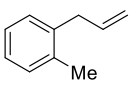


An oven-dried 8 mL screw-top test tube is equipped with a magnetic stir bar. To this vial is added hydroxysulfone (1 equivalent, 0.20 mmol), $NiBr_2$·glyme (0.10 equivalent, 0.02 mmol), ICy•HBF_4 (0.20 equivalent, 0.04 mmol), potassium *tert*-butoxide (*KO^{t}Bu*; 1.0 equivalent, 0.20 mmol) and Mn (0.3 equivalent, 0.06 mmol). To the resulting mixture is added anhydrous toluene (0.8 mL) followed by 1,1,3,3-tetramethyldisiloxane (*TMDSO*; 1.2 equivalents, 0.24 mmol). The reaction vessel is quickly sealed with a Teflon-septa equipped cap, purged with N_2 (g) and left to stir inside of a mineral-oil bath at 650 RPM for 5 hours at 60 °C. After 5 hours, the reaction vessel is allowed to cool to room temperature before being opened to the atmosphere. The crude reaction solution is diluted with EtOAc and passed through a short plug consisting of SiO_2 and celite in a 50:50 mixture. Solvent is evacuated *in vacuo* and the resulting residue is dissolved in dichloromethane. A small amount of SiO_2 is added to the resulting solution and the solvent is subsequently removed *in vacuo*. The resulting solid is loaded directly on to a 10 g Biotage SNAP silica-packed column and purified on a CombiFlash Rf+ automated chromatography instrument using a mixture of ethyl acetate in hexanes.

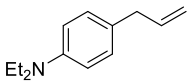
4.2. Reaction products and characterization data



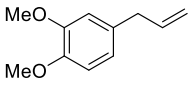
4-Methoxyallylbenzene (2) was prepared according to General Protocol C. Column chromatography was performed using a gradient of 1→15% ethyl acetate in hexanes to afford product as a yellow liquid (21.4 mg, 76% yield). Characterization data matched those previously reported.[12] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.30-7.28 (m, 2H), 7.04-7.02 (m, 2H), 6.21-6.11 (m, 1H), 5.30-5.24 (m, 2H), 3.92 (s, 3H), 3.53-3.51 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): 157.9, 137.7, 131.8, 129.3, 115.2, 113.7, 54.9, 39.2.



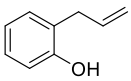
2-Methylallylbenzene (3) was prepared according to General Protocol C. Column chromatography was performed using a gradient of 1→15% ethyl acetate in hexanes to afford product as a yellow liquid (30 mg, 86% yield). Characterization data matched those previously reported.[13] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.23-7.20 (m, 4H), 6.08-5.98 (m, 1H), 5.16-5.04 (m, 2H), 3.46-3.44 (m, 2H), 2.37 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 138.1, 136.6, 136.3, 130.1, 129.1, 126.3, 126.0, 115.6, 37.7, 19.3.



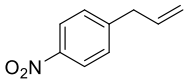
4-Diethylaminoallylbenzene (4) was prepared according to General Protocol C. Column chromatography was performed using a gradient of 1→15% ethyl acetate in hexanes to afford product as a yellow liquid (25.7 mg, 68% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.32-7.29 (m, 2H), 7.23-7.19 (m, 2H), 6.02-5.95 (m, 1H), 5.12-5.06 (m, 2H), 3.41-3.39 (m, 2H), 2.69-2.64 (q, *J* = 8.8 Hz, 4H), 1.14-1.10 (t, *J* = 6.4 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): 140.0, 137.4, 128.5, 128.4, 126.0, 115.7, 44.0, 40.2, 15.3. **Accurate mass (EI)**: Theoretical: 189.1517. Found: 189.1519. Spectral Accuracy: 98.4%. **FT-IR**: *v* (cm^{-1}) 3160, 3120, 3080, 2940, 1740, 1504, 1470, 1155, 930, 840.



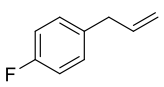
3,4-Dimethoxyallylbenzene (5) was prepared according to General Protocol C. Column chromatography was performed using a gradient of 1→15% ethyl acetate in hexanes to afford product as a yellow liquid (27.6 mg, 77% yield). The reaction was scaled up to use 1 g starting material *(2.98 mmol)*, 92.4 mg $NiBr_2$·glyme, 192 mg ICy•HBF_4, 49.5 mg Mn, 336 mg KO^{t}Bu and 561 µL TMDSO in 10 mL PhMe to reveal the same product (340 mg, 64%). Characterization data matched those previously reported.[13] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.83-6.81 (m, 1H), 6.75-6.72 (m, 2H), 6.02-5.92 (m, 1H), 5.12-5.05 (m, 2H), 3.88 (s, 3H), 3.87 (s, 3H), 3.36-3.34 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): 148.8, 147.3, 137.6, 132.6, 120.3, 115.5, 111.8, 111.2, 55.9, 55.7, 39.7.



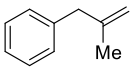
2-Hydroxyallylbenzene (6) was prepared according to General Protocol C. Column chromatography was performed using a gradient of 1→25% ethyl acetate in hexanes to afford product as a yellow liquid (21.7 mg, 81% yield). Characterization data matched those previously reported.[14] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.19-7.14 (m, 2H), 6.95-6.83 (m, 2H), 6.11-6.01 (m, 1H), 5.22-5.17 (m, 2H), 3.47-3.44 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): 154.0, 136.4, 130.4, 127.9, 125.3, 120.9, 116.4, 115.8, 35.0.



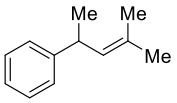
4-Nitroallylbenzene (7) was prepared according to General Protocol C. Column chromatography was performed using a gradient of 1→15% ethyl acetate in hexanes to afford product as a yellow liquid (18.3 mg, 56% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.96-7.94 (m, 2H), 7.25-7.23 (m, 2H), 5.99-5.88 (m, 1H), 5.11-5.04 (m, 2H), 3.43-3.41 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): 167.1, 145.5, 136.4, 129.7, 128.6, 128.1, 116.6, 52.0, 40.1. **Accurate mass (EI)**: Theoretical: 163.0633. Found: 163.0634. Spectral Accuracy: 97.9%. **FT-IR**: *v* (cm^{-1}) 3190, 3110, 2975, 1610, 1529, 1510, 1498, 1340, 1310, 1240, 1085.



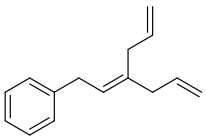
4-Fluoroallylbenzene (8) was prepared according to General Protocol C. Column chromatography was performed using a gradient of 1→15% ethyl acetate in hexanes to afford product as a yellow liquid (17.4 mg, 64% yield). Characterization data matched those previously reported.[13] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.18-7.14 (m, 2H), 7.02-6.97 (m, 2H), 6.01-5.91 (m, 1H), 5.12-5.06 (m, 2H), 3.39-3.36 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): 162.6, 160.2, 137.3, 135.6, 135.5, 130.0, 129.9, 115.5 (t), 39.3.



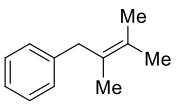
2-Methyl-3-phenylpropene (9) was prepared according to General Protocol C. Column chromatography was performed using a gradient of 1→15% ethyl acetate in hexanes to afford product as a yellow liquid (19.3 mg, 73% yield). Characterization data matched those previously reported.[15] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.36-7.32 (m, 2H), 7.28-7.24 (m, 3H), 4.88-4.78 (m, 2H), 3.38 (s, 2H), 1.74-1.73 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 145.1, 139.7, 128.9, 128.2, 126.0, 111.9, 44.7, 22.0.



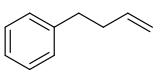
1,1,3-Trimethyl-3-phenylpropene (10) was prepared according to General Protocol C. Column chromatography was performed using a gradient of 1→15% ethyl acetate in hexanes to afford product as a yellow liquid (22.7 mg, 71% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.30-7.26 (m, 2H), 7.21-7.18 (m, 3H), 5.45-5.42 (m, 1H), 4.16-4.14 (m, 1H), 2.38 (m, 3H), 1.78-1.77 (m, 3H), 1.72-1.71 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 137.8, 136.4, 129.0, 128.2, 125.3, 123.6, 25.7, 21.4, 17.8. **Accurate mass (EI)**: Theoretical: 160.1252. Found: 160.1248. Spectral Accuracy: 98.1%. **FT-IR**: *v* (cm^{-1}) 3120, 3100, 2930, 1580, 1520, 1305, 1040.



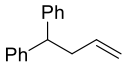
1,1-Diprop-2-ene-3-phenylpropene (11) was prepared according to General Protocol C. Column chromatography was performed using a gradient of 1→15% ethyl acetate in hexanes to afford product as a yellow liquid (30.1 mg, 76% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.30-7.18 (m, 5H), 6.08-5.89 (m, 1H), 5.37-5.31 (m, 2H), 5.16-5.07 (m, 4H), 3.95-3.93 (m, 4H), 3.41-3.38 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): 140.0, 137.4, 134.2, 128.5, 128.4, 126.0, 119.1, 115.7, 40.2, 32.8 **Accurate mass (EI)**: Theoretical: 198.1409. Found: 198.1408. Spectral Accuracy: 97.2%. **FT-IR**: *v* (cm^{-1}) 3230, 3190, 3140, 2980, 2830, 1630, 1504, 1480, 1210, 1150.



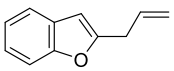
1,1,2-Trimethyl-1-phenylpropene (12) was prepared according to General Protocol C. Column chromatography was performed using a gradient of 1→15% ethyl acetate in hexanes to afford product as a yellow liquid (18.6 mg, 58% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.33-7.29 (m, 2H), 7.24-7.18 (m, 3H), 2.71-2.65 (m, 2H), 1.69-1.66 (m, 6H), 1.29-1.25 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 138.1, 136.6, 136.3, 130.1, 129.1, 126.3, 126.0, 123.4, 37.7, 21.1, 20.3, 19.3. **Accurate mass (EI)**: Theoretical: 160.1252. Found: 160.1251. Spectral Accuracy: 98.8%. **FT-IR**: *v* (cm^{-1}) 3110, 3090, 3040, 2805, 1605, 1530, 1230, 1140.



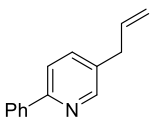
4-Phenylbutene (13) was prepared according to General Protocol C. Column chromatography was performed using a gradient of 1→15% ethyl acetate in hexanes to afford product as a yellow liquid (14.8 mg, 56% yield). Characterization data matched those previously reported.[16] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.37-7.33 (m, 2H), 7.26-7.23 (m, 3H), 5.98-5.87 (m, 1H), 5.15-5.04 (m, 2H), 2.80-2.76 (m, 2H), 2.47-2.42 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): 141.8, 138.1, 128.4, 128.3, 125.8, 114.9, 35.5, 35.4.



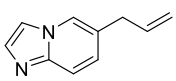
4,4-Diphenylbutene (14) was prepared according to General Protocol C. Column chromatography was performed using a gradient of 1→15% ethyl acetate in hexanes to afford product as a yellow liquid (25.4 mg, 61% yield). Characterization data matched those previously reported.[17] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.40-7.33 (m, 8H), 7.29-7.28 (m, 1H), 7.26-7.25 (m, 1H), 5.88-5.78 (m, 1H), 5.17-5.04 (m, 2H), 4.14-4.10 (m, 1H), 2.95-2.91 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): 144.5, 136.8, 128.4, 127.9, 126.2, 116.3, 51.2, 39.9.



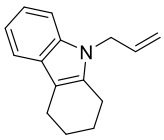
2-(2-Allyl)benzofuran (15) was prepared according to General Protocol C. Column chromatography was performed using a gradient of 1→10% ethyl acetate in hexanes to afford product as a yellow liquid (23.1 mg, 73% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.72-7.53 (m, 2H), 7.38-7.26 (m, 1H), 6.95-6.91 (m, 1H), 6.84-6.79 (m, 1H), 6.07-5.99 (m, 1H), 5.17-5.11 (m, 2H), 3.44-3.35 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): 154.8, 144.9, 143.8, 138.2, 131.9, 124.2, 122.7, 121.2, 115.5, 113.9, 39.8. **Accurate mass (EI)**: Theoretical: 158.0732. Found: 158.0728. Spectral Accuracy: 98.0%. **FT-IR**: *v* (cm^{-1}) 3181, 3010, 2948, 2840, 1610, 1484, 1093.



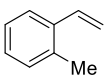
2-Phenyl-5-allylpyridine (16) was prepared according to General Protocol C. Column chromatography was performed using a gradient of 1→15% ethyl acetate in hexanes to afford product as a yellow liquid (28.8 mg, 69% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.44-8.40 (m, 2H), 7.50-7.46 (m, 1H), 7.32-7.25 (m, 1H), 7.23-7.07 (m, 4H), 6.01-5.93 (m, 1H), 5.10-5.05 (m, 2H), 3.39-3.38 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): 150.2, 146.8, 139.9, 137.4, 136.4, 133.1, 128.5, 128.4, 126.0, 123.1, 115.7, 40.2. **Accurate mass (EI)**: Theoretical: 195.1048. Found: 195.1042. Spectral Accuracy: 98.6%. **FT-IR**: *v* (cm^{-1}) 3073, 3040, 2847, 2744, 1610, 1584, 764.



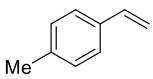
6-Allylimidazo[1,2-*α*]pyridine (17) was prepared according to General Protocol C. Column chromatography was performed using a gradient of 1→10% ethyl acetate in hexanes to afford product as a clear liquid (19.7 mg, 62% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.22 (s, 1H), 7.69-7.65 (m, 1H), 7.62-7.60 (m, 2H), 7.18-7.16 (m, 1H), 5.89-5.81 (m, 1H), 5.05-4.95 (m, 2H), 2.10-2.06 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): 143.8, 139.2, 134.4, 125.8, 123.6, 120.6, 118.2, 114.0, 112.7, 33.4. **Accurate mass (EI)**: Theoretical: 159.0922. Found: 159.0921. Spectral Accuracy: 97.8%. **FT-IR**: *v* (cm^{-1}) 3018, 2947, 2759, 1674, 1304, 840.



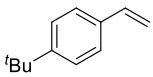
***N*-Allyl-1,2,3,4-tetrahydrocarbazole (18)** was prepared according to General Protocol C. Column chromatography was performed using a gradient of 1→15% ethyl acetate in hexanes to afford product as a yellow liquid (17.5 mg, 41% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.55-7.53 (m, 1H), 7.33-7.7.30 (m, 2H), 7.19-7.15 (m, 1H), 6.13-6.07 (m, 1H), 5.18-5.12 (m, 2H), 3.51-3.49 (m, 2H), 2.80-2.77 (m, 4H), 2.01-1.94 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): 137.5, 135.6, 133.3, 120.9, 119.7, 119.2, 118.1, 116.6, 110.8, 108.1, 33.9, 23.7, 21.0. **Accurate mass (EI)**: Theoretical: 213.1517. Found: 213.1513. Spectral Accuracy: 98.3%. **FT-IR**: *v* (cm^{-1}) 3149, 3008, 2810, 2746, 1510, 1473, 776.



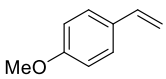
2-Methylstyrene (19) was prepared according to General Protocol C. Column chromatography was performed using a gradient of 1→15% ethyl acetate in hexanes to afford product as a yellow liquid (17.5 mg, 74% yield). Characterization data matched those previously reported.[18] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.65-7.63 (m, 1H), 7.34-7.28 (m, 3H), 7.14-7.07 (m, 1H), 5.82-5.78 (m, 1H), 5.46-5.43 (m, 1H), 2.51 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 136.8, 135.2, 134.8, 130.1, 127.6, 126.0, 125.3, 115.0, 19.6.



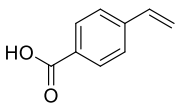
4-Methylstyrene (20) was prepared according to General Protocol C. Column chromatography was performed using a gradient of 1→15% ethyl acetate in hexanes to afford product as a yellow liquid (16.8 mg, 71% yield). Characterization data matched those previously reported.[19] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.58-7.55 (m, 2H), 7.39-7.37 (m, 2H), 6.99-6.92 (m, 1H), 5.99-5.94 (m, 1H), 5.47-5.44 (m, 1H), 2.59 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 137.4, 136.7, 134.8, 129.1, 126.1, 112.5, 21.1.



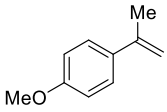
4-Tertbutylstyrene (21) was prepared according to General Protocol C. Column chromatography was performed using a gradient of 1→15% ethyl acetate in hexanes to afford product as a yellow liquid (23.1 mg, 72% yield). The reaction was repeated on the corresponding β-ketosulfone to reveal the same product (22.8 mg, 67%). Characterization data matched those previously reported.[20] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.67 (m, 4H), 7.05-6.98 (m, 1H), 6.05-6.01 (m, 1H), 5.52-5.49 (m, 1H), 1.65 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): 150.7, 136.6, 134.8, 126.0, 125.4, 112.9, 34.5, 31.3.



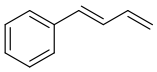
4-Methoxystyrene (22) was prepared according to General Protocol C. Column chromatography was performed using a gradient of 1→15% ethyl acetate in hexanes to afford product as a yellow liquid (20.1 mg, 75% yield). The reaction was repeated on the corresponding β-ketosulfone to reveal the same product (21.8 mg, 71%). Characterization data matched those previously reported.[18] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.14-7.12 (m, 2H), 6.88-6.85 (m, 2H), 6.03-5.93 (m, 1H), 5.11-5.05 (m, 2H), 3.81 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 158.5, 130.7, 130.3, 126.8, 123.4, 113.8, 55.2.



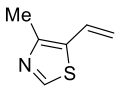
4-Vinylbenzoic acid (23) was prepared according to General Protocol C. Column chromatography was performed using a gradient of 1→15% ethyl acetate in hexanes to afford product as a yellow liquid (18.7 mg, 63% yield). Characterization data matched those previously reported.[21] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.11-8.07 (m, 2H), 7.53-7.50 (m, 2H), 6.82-6.75 (m, 1H), 5.93-5.89 (m, 1H), 5.44-5.42 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): 171.8, 142.8, 135.9, 130.6, 128.3, 126.2, 117.0.



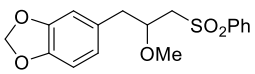
2-Methyl-2-(4-methoxyphenyl)ethene (24) was prepared according to General Protocol C. Column chromatography was performed using a gradient of 1→15% ethyl acetate in hexanes to afford product as a yellow liquid (18.8 mg, 63% yield). Characterization data matched those previously reported.[22] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.46-7.43 (m, 2H), 6.91-6.89 (m, 2H), 5.33-5.32 (m, 1H), 5.03 (m, 1H), 3.84 (s, 3H), 2.17 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 159.1, 142.5, 133.8, 126.6, 113.5, 110.6, 55.2, 21.9.



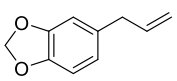
1,3-(Butadien-1-yl)benzene (25) was prepared according to General Protocol C. Column chromatography was performed using a gradient of 1→15% ethyl acetate in hexanes to afford product as a yellow liquid (17.8 mg, 68% yield). Characterization data matched those previously reported.[23] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.31-7.28 (m, 2H), 6.88-6.84 (m, 3H), 6.40-6.35 (m, 1H), 6.29-5.96 (m, 2H), 5.40-5.35 (m, 1H), 5.26-5.23 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): 158.5, 133.8, 130.8, 130.3, 126.8, 123.4, 118.5, 113.9.



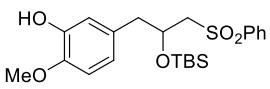
4-Methyl-5-vinylthiazole (26) was prepared according to General Protocol C. Column chromatography was performed using a gradient of 1→15% ethyl acetate in hexanes to afford product as a clear liquid (19.5 mg, 78% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.55 (s, 1H), 6.83-6.77 (m, 1H), 5.50-5.47 (m, 1H), 5.28-5.26 (m, 1H), 2.47 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 150.2, 149.7, 130.9, 126.5, 116.2, 15.2. **Accurate mass (EI)**: Theoretical: 125.0299. Found: 125.0297. Spectral Accuracy: 97.9%. **FT-IR**: *v* (cm^{-1}) 3085, 2840, 1765, 1648, 1473, 810.



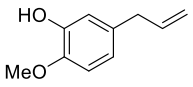
1-(1,3-Benzodioxol-5-yl)-3-(phenylsulfonyl)propan-2-ol methyl ether (32) was prepared according to General Protocol A. The resulting hydroxysulfone was *O*-methylated according to a literature procedure.[27] Column chromatography was performed using a gradient of 1→15% ethyl acetate in hexanes to afford product as a yellow liquid (44.1 mg, 22% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.91-7.88 (m, 2H), 7.39-7.37 (m, 3H), 6.83-6.75 (m, 3H), 5.93-5.89 (m, 2H), 4.54 (s, 2H), 3.70-3.65 (m, 1H), 2.46 (s, 3H), 1.22-1.18 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): 147.7, 146.8, 141.6, 134.8, 130.2, 126.9, 121.4, 120.5, 107.8, 100.9, 71.6, 65.1, 58.3, 21.8, 18.2. **Accurate mass (EI)**: Theoretical: 334.0934. Found: 334.0936. Spectral Accuracy: 97.6%. **FT-IR**: *v* (cm^{-1}) 3150, 3080, 2870, 1630, 1500, 1480, 1465, 1330, 1040.



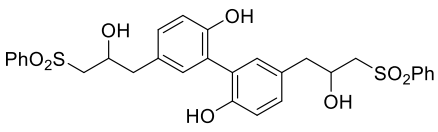
Safrole (33) was prepared according to General Protocol C. Column chromatography was performed using a gradient of 1→15% ethyl acetate in hexanes to afford product as a colourless liquid (24.6 mg, 76% yield). Characterization data matched those previously reported.[24] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.77-6.75 (m, 1H), 6.71-6.70 (m, 1H), 6.67-6.64 (m, 1H), 6.00- 5.90 (m, 3H), 5.11-5.06 (m, 2H), 3.33-3.31 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): 147.6, 145.8, 137.6, 133.8, 121.3, 115.7, 109.1, 108.1, 100.8, 39.9.



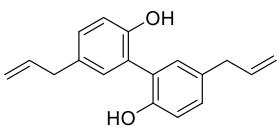
1-(3-Methoxyphenol)-3-(phenylsulfonyl)propan-2-ol tertbutyl dimethyl silyl ether (34) was prepared according to the General Protocol A. The resulting hydroxysulfone was *O*-silylated according to a literature procedure.[31] Column chromatography was performed using a gradient of 1→15% ethyl acetate in hexanes to afford product as an off-white liquid (60.2 mg, 23% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.94-7.92 (m, 2H), 7.43-7.40 (m, 2H), 7.32-7.28 (m, 2H), 6.96-6.91 (m, 2H), 3.82 (s, 3H), 3.74-3.64 (m, 2H), 2.50 (m, 2H), 2.44-2.34 (m, 1H), 0.94-0.91 (m, 9H), 0.11-0.09 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): 159.5, 146.8, 141.6, 130.2, 129.5, 129.4, 127.0, 126.6, 120.6, 113.8, 63.6, 55.0, 26.0, 25.6, 21.7, -3.7, -5.0. **Accurate mass (EI)**: Theoretical: 436.1740. Found: 436.1746. Spectral Accuracy: 97.7%. **FT-IR**: *v* (cm^{-1}) 3640, 2910, 1730, 1570, 1505, 1315, 1134, 1060.



Chavibetol (35) was prepared according to General Protocol C. Column chromatography was performed using a gradient of 1→15% ethyl acetate in hexanes to afford product as a yellow liquid (22.6 mg, 69% yield). Characterization data matched those previously reported.[24] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.89-6.87 (m, 1H), 6.73-6.70 (m, 2H), 6.02-5.95 (m, 1H), 5.58 (s, 1H), 5.13-5.07 (m, 2H), 3.89 (s, 3H), 3.36-3.34 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): 146.4, 143.8, 137.8, 131.9, 121.1, 115.5, 114.2, 111.1, 55.8, 39.8.



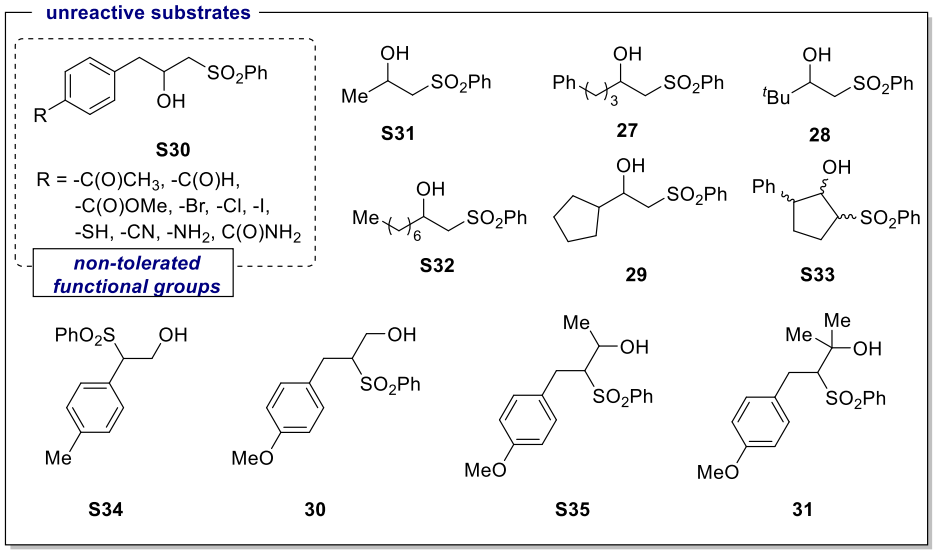
6,6'-Dihydroxy-[1,1'-biphenyl]-α3,α3'-bis(3-phenylsulfonyl-propan-2-ol) (36) was prepared according to a modified General Protocol A, employing 4 equivalents of *benzene sulfinic acid salt* instead of 2 equivalents. Column chromatography was performed using a gradient of 1→15% ethyl acetate in hexanes to afford product as a colourless liquid (94.3 mg, 27% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.99-7.96 (m, 4H), 7.46-7.43 (m, 4H), 7.32-7.27 (m, 5H), 7.00-6.91 (m, 3H), 5.34-5.30 (m, 4H), 3.85-3.82 (m, 2H), 1.33-1.29 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): 155.6, 146.9, 141.4, 130.2, 129.6, 129.5, 129.3, 126.9, 120.5, 115.3, 58.6, 21.7, 17.8. **Accurate mass (EI)**: Theoretical: 582.1422. Found: 582.1422. Spectral Accuracy: 97.6%. **FT-IR**: *v* (cm^{-1}) 3590, 3485, 2940, 1630, 1550, 1520, 1310, 1145.



Magnolol (37) was prepared according to General Protocol C. Column chromatography was performed using a gradient of 1→15% ethyl acetate in hexanes to afford product as a yellow liquid (30.9 mg, 58% yield). Characterization data matched those previously reported.[25] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.16-7.09 (m, 4H), 6.98-6.94 (m, 2H), 6.03-5.93 (m, 2H), 5.13-5.06 (m, 4H), 3.39-3.37 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): 151.1, 137.5, 133.2, 131.2, 130.0, 123.7, 116.6, 115.8, 39.3.

5. Troubleshooting

Multiple compounds were observed to be unreactive upon subjection to General Protocol C (Supporting Figure S2). The olefination reaction failed to tolerate electrophilic functionalities such as ketones, aldehydes, and esters, in each case leading to partial reduction and a complex mixture of resultant species. Other functional groups that could not be tolerated included bromides, chlorides and iodides, leading to protodehalogenation in each case. The presence of thiols, nitriles, unprotected amines and amides appeared to shut down reactivity, leading to the recovery of starting materials (**S30**). The olefination reaction failed to afford product in the absence of a nearby π-electron system (**S31, S32, 27-29**). Internal cyclic alkenes could not be formed (**29**), even when in proximity to a nearby π-electron system (**S33**). Switching the position of the -OH and -SO_2Ph groups on the β-hydroxysulfone, as in compounds **S34** and **30**, formed compounds that failed to react upon subjection to General Protocol C, even upon increasing the substitution of the hydroxide group (**S35**, **31**).



Supporting Figure S2. Troublesome substrates in this olefination reaction

We found this reaction to be fairly general, with the exceptions of the limitations noted in Supporting Figure S2 (above). However, some modifications to the procedure can be made to achieve a higher yield for problematic substrates. In the case of moderate yields, we found that they may be increased by:

i. Utilizing $Ni(cod)_2$ in lieu of $NiBr_2$·glyme + Mn

ii. Employ more rigorous anhydrous conditions (*i.e*. attempt the reaction inside of a glovebox)

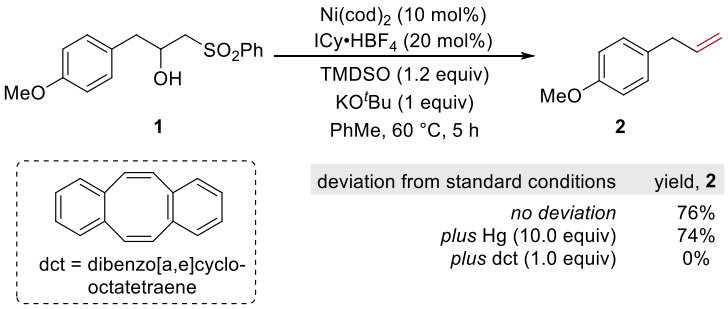
iii. Increasing reaction time from 5 h to 10 h

iv. Increasing reaction temperature from 60 °C to 110 °C

6. Mechanism: Experimental information

6.1. Control experiments to test for homogeneous or heterogeneous catalysis

To gain information as to the nature of the active catalyst in this olefination reaction, we subjected substrate **1** to General Protocol C upon introducing either Hg (a known poison for heterogeneous catalysts) or dct (a known poison for homogeneous catalysts) as a drop-in additive. $Ni(cod)_2$ was employed as the catalyst rather than the combination of $NiBr_2$·glyme and Mn, as it was found that Mn caused a heterogenous reaction mixture to form. Employing Hg as a drop-in additive led to the recovery of product **2** in yields reflective of the optimized reaction conditions, while employing dct as a drop-in additive led to complete reaction inhibition – both results suggest that the olefination reaction proceeds via homogeneous catalysis (Supporting Figure S3).

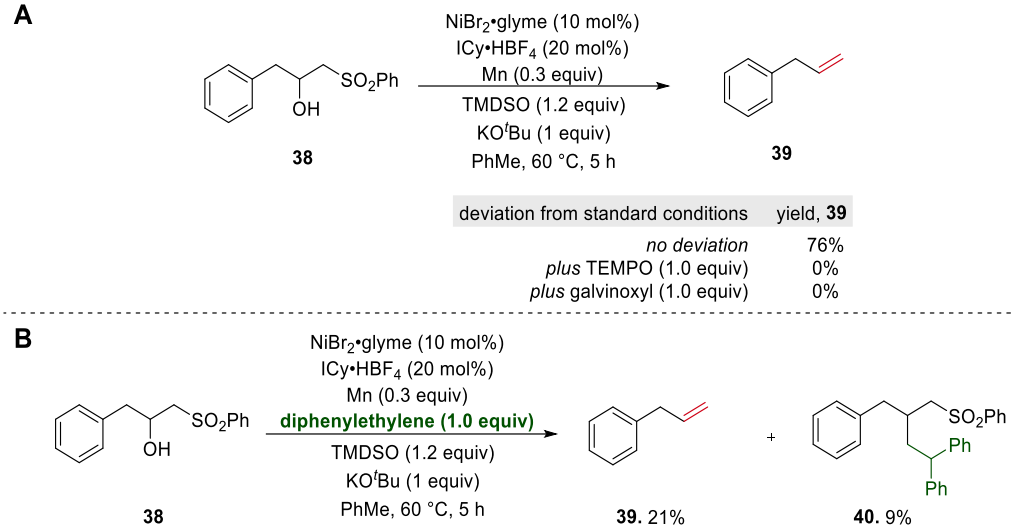


Supporting Figure S3. Investigating the nature of the active catalyst

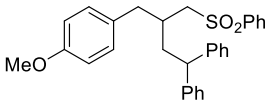
6.2. Control experiments to test for radical reactivity

To determine whether a radical species was formed over the course of the olefination reaction, a series of experiments was performed on compound **38** using different radical scavenging reagents. It was found that formation of product **39** was inhibited when employing 1.0 equivalent of either TEMPO or galvinoxyl as a drop-in additive (Supporting Figure S4A). When using diphenylethylene as a drop-in additive, the yield of expected product **39** was suppressed, and radical-trapped product **40** was

recovered in a low yield (Supporting Figure S4B). Each of these results suggest the involvement of a radical species in this olefination reaction.



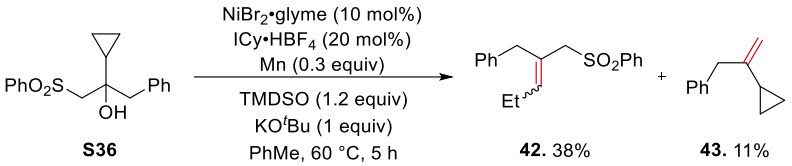
Supporting Figure S4. The effect of radical-trapping reagents on the olefination protocol



1,1-Diphenyl-3-(4-methoxytolyl)-4-phenylsulfone (40) was prepared according to a modified General Protocol C, employing 1.0 equivalent diphenylethylene as an additive. Column chromatography was performed using a gradient of 1→15% ethyl acetate in hexanes to afford product as a white solid (8.5 mg, 9% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.95-7.92 (m, 2H), 7.41-7.38 (m, 2H), 7.32-7.28 (m, 7H), 7.24-7.20 (m, 6H), 6.99-6.91 (m, 2H), 4.00 (s, 1H), 3.53-3.49 (m, 2H), 2.51-2.48 (m, 2H), 1.89-1.83 (m, 1H), 1.08-1.05 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): 159.5, 146.7, 141.6, 141.1, 130.2, 129.4, 128.9, 128.4, 127.0, 126.0, 120.6, 113.8, 41.9, 26.0, 21.7, 11.6, 11.5. **Accurate mass (EI)**: Theoretical: 470.1916. Found: 470.1908. Spectral Accuracy: 98.7%. **FT-IR**: *v* (cm^{-1}) 3030, 3010, 2945, 1610, 1550, 1465, 1310, 1180, 985. **mp:** 147-151 °C.

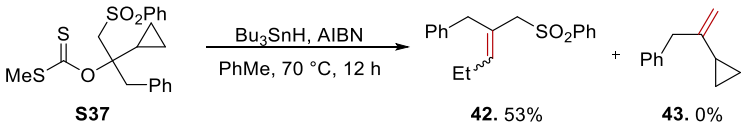
6.3. Experiments investigating the possibility of cyclopropyl ring-opening

To further investigate whether a radical species was formed over the course of this reaction, cyclopropane-bearing substrate **S36** was prepared. Subjecting this species to General Protocol C afforded a mixture of products with the ring-opened product **42** being obtained as the major product and ring-closed product **43** being the minor (Supporting Figure S5).



Supporting Figure S5. Subjecting compound **S36** to the general reaction conditions

To determine how substrate **S36** would react in traditional radical chemistry, the corresponding xanthate ester, **S37**, was prepared and subjected to radical-initiated Barton McCombie deoxygenation conditions (Supporting Figure S6),[26] revealing ring-opened product **42** without observation of ring-closed product **43**. The discrepancy between the product ratio obtained upon employing purely radical Barton McCombie conditions and our nickel-catalyzed conditions suggests that the nickel-catalyzed reaction is proceeding through a different mechanism.



Supporting Figure S6. Subjecting xanthate ester **S37** to Barton-McCombie conditions

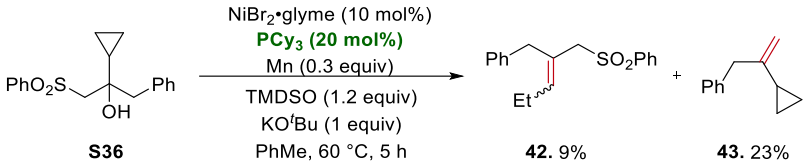
Barton McCombie reaction protocol

This procedure was adapted from the literature.[26] To an oven-dried 8 mL screw-top test tube is added a magnetic stir bar and 0.2 mmol of xanthate ester **S37**, prepared by reacting the corresponding alcohol and 1-(methyldithiocarbonyl)imidazole according to a literature procedure.[27] The reaction vessel is brought inside of a glovebox and charged with 0.2 mmol Bu_3SnH, 0.2 mmol AIBN, and 0.6 mL anhydrous PhMe. The reaction vessel is sealed and brought outside of the glovebox before being left to stir at 650 RPM for 12 h at 70 °C. The resulting reaction solution is quenched with 5 mL of distilled water and diluted in 10 mL of EtOAc. It is washed twice with saturated $NaHCO_3$ and once with saturated NaCl (aq)

before being dried over $MgSO_4$ and filtered via suction filtration. Solvent is evacuated *in vacuo* to reveal product that is subsequently analyzed by ^{1}H-NMR, revealing the formation of ring-opened product **42** (53% yield).

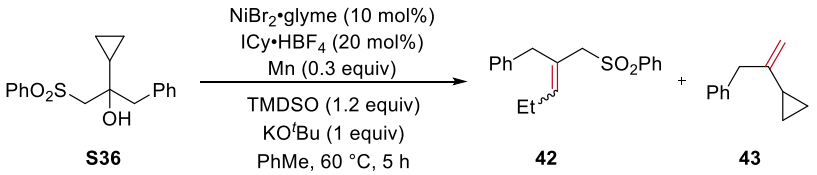
6.4. Experiments investigating the possibility of ligand-dependence upon product distribution

Seeking to further differentiate between the possibility of ligand-dependence upon the ratio of ring-opened to ring-closed product, the olefination reaction of substrate **S36** was performed using an alternative ligand, PCy_3, instead of ICy•HBF_4. This reaction once more revealed a mixture of products **42** and **43**, this time however with the major product being the ring-closed product **43** (Supporting Figure S7). The dependence of product distribution on the identity of the ligand suggests an organonickel species is likely formed in the reaction, and the resulting organonickel intermediate has different behaviour than an alkyl radical.

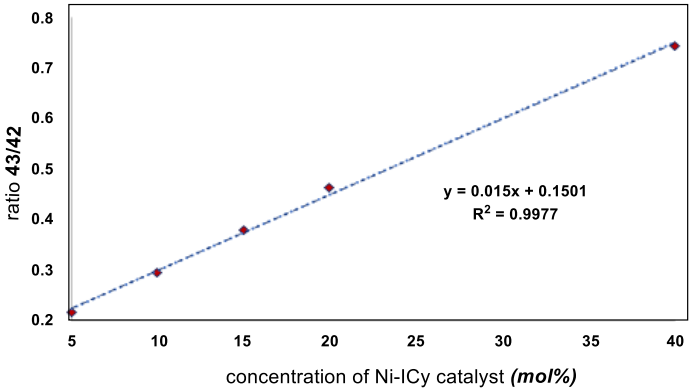


Supporting Figure S7. Subjecting compound **S36** to modified general reaction conditions, employing PCy_3 instead of ICy•HBF_4

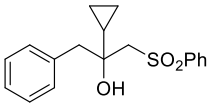
To further investigate the dependence of this reaction on the catalyst, we conducted a series of reactions with varied catalyst concentration. A significant linear relationship between the ratio of products **43**/**42** and catalyst concentration was observed, providing further evidence to suggest the presence of an organonickel intermediate at a key-step in this transformation (Supporting Figure S8).[28]



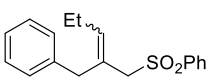
entry	deviation from standard conditions	yield, **42**	yield, **43**
1	$NiBr_2$·glyme (5%), ICy•HBF_4 (10%)	23%	5%
2	$NiBr_2$·glyme (10%), ICy•HBF_4 (20%)	38%	11%
3	$NiBr_2$·glyme (15%), ICy•HBF_4 (30%)	42%	16%
4	$NiBr_2$·glyme (20%), ICy•HBF_4 (40%)	43%	20%
5	$NiBr_2$·glyme (40%), ICy•HBF_4 (80%)	43%	32%



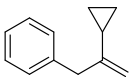
Supporting Figure S8. Investigating the dependence of product distribution on catalyst concentration



2-Cyclopropyl-1-phenyl-3-(phenylsulfonyl)propan-2-ol (S36) was prepared according to a literature procedure.[29] To an oven-dried 10 mL round-bottom flask was added a magnetic stir bar, β-ketosulfone **S22** (1.0 equiv, 1.0 mmol), anhydrous $CeCl_3$ (1.5 equiv, 1.5 mmol) and anhydrous THF (5 mL). The reaction mixture was cooled to 0 ˚C, at which point cyclopropylmagensium bromide (1.5 equiv, 1.5 mmol) was added dropwise. The reaction mixture was allowed to come to room temperature and stirred for an additional 8 h before being quenched with NH_4Cl (aq) and extracted into dichloromethane. The organic phase was separated and washed with $NaHCO_3$ (aq) twice and once with NaCl (aq) before being dried over Na_2SO_4. The resulting mixture was filtered via suction filtration. Solvent is evacuated *in vacuo* and the resulting residue is dissolved in dichloromethane. A small amount of SiO_2 is added to the resulting solution and the solvent is subsequently removed *in vacuo*. The resulting solid is loaded directly on to a 10 g Biotage SNAP silica-packed column and purified on a CombiFlash Rf+ automated chromatography instrument using a gradient of 1→15% ethyl acetate in hexanes to afford product as a dark yellow liquid (136 mg, 43% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.92-7.88 (m, 2H), 7.40-7.37 (m, 2H), 7.35-7.31 (m, 4H), 7.26-7.22 (m, 2H), 3.32-3.30 (m, 2H), 2.53-2.47 (m, 1H), 2.46-2.43 (m, 1H), 2.10-1.78 (m, 2H), 1.34-1.25 (m, 1H), 0.75-0.33 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): 146.8, 141.6, 137.8, 130.2, 129.0, 128.2, 127.0, 125.2, 67.7, 21.8, 21.4, 21.3, 13.4, 2.7. **Accurate mass (EI)**: Theoretical: 316.1133. Found: 316.1127. Spectral Accuracy: 98.2%. **FT-IR**: *v* (cm^{-1}) 3530, 2930, 1578, 1530, 1500, 1320, 1010, 760, 740.



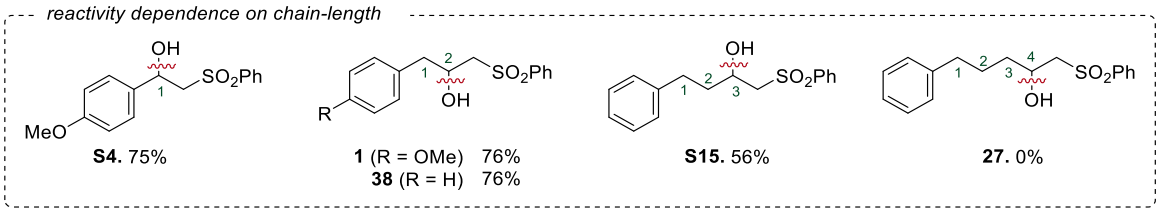
3-Ethyl-1-phenyl-2-(phenylsulfonyl)pent-2-ene (42) was prepared from **S36** according to General Protocol C. A ~1:1 mixture of diastereomers was observed, from which a single diastereomer was isolated via column chromatography and used for characterization. Column chromatography was performed using a gradient of 1→15% ethyl acetate in hexanes to afford product as an off-white liquid (10.2 mg, 19% yield), which was confirmed to be the Z diastereomer by NoE. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.93-7.90 (m, 2H), 7.41-7.38 (m, 2H), 7.31-7.27 (m, 2H), 7.22-7.1 7 (m, 4H), 6.02-5.92 (m, 1H), 3.52-3.48 (m, 2H), 3.39-3.38 (m, 2H), 1.83-1.75 (m, 2H), 1.03-0.99 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 146.8, 141.7, 140.0, 137.4, 130.2, 128.5, 128.4, 127.0, 126.0, 115.7, 40.2, 26.0, 21.8, 11.6. **Accurate mass (EI)**: Theoretical: 300.1184 Found: 300.1177. Spectral Accuracy: 97.4%. **FT-IR**: *v* (cm^{-1}) 3120, 3100, 2935, 1740, 1520, 1500, 1310, 1145.



2-Cyclopropyl-3-phenylpropene (43) was prepared from **S36** according to General Protocol C. Column chromatography was performed using a gradient of 1→15% ethyl acetate in hexanes to afford product as a yellow liquid (3.5 mg, 11% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.37-7.32 (m, 2H), 7.29-7.23 (m, 3H), 5.18-5.09 (m, 2H), 3.48-3.37 (m, 2H), 2.70-2.49 (m, 2H), 2.16-1.89 (m, 1H), 0.82-0.40 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): 140.0, 137.4, 128.6, 128.4, 126.0, 115.7, 40.2, 35.7, 19.0, 14.4. **Accurate mass (EI)**: Theoretical: 158.1096. Found: 158.1089. Spectral Accuracy: 97.6%. **FT-IR**: *v* (cm^{-1}) 3120, 3100, 2860, 1520, 1505, 1340, 1110, 940, 770, 730.

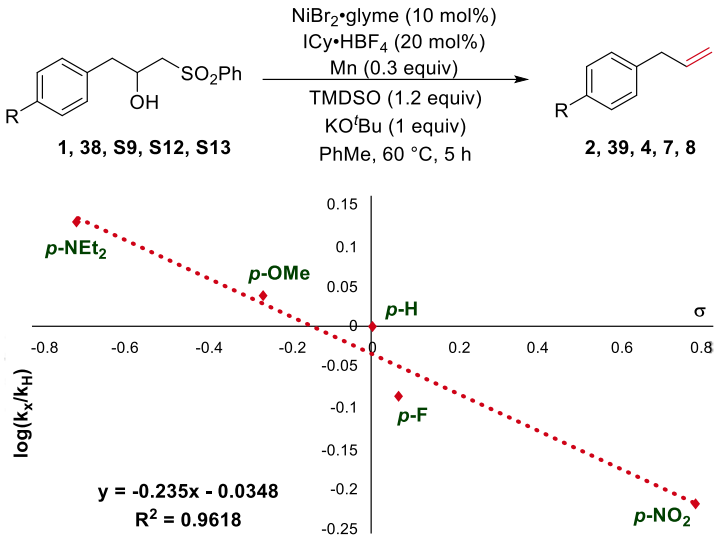
6.5. Experiments investigating the effect of the aryl ring on reaction outcome

While studying this reaction, we became interested in the requirement of a nearby, but not necessarily conjugated, π-electron system relative to the C(sp^3)–O bond (Supporting Figure S9). Specifically, we noted that while benzyl (**S4**) and homobenzyl (**1**, **38**) C(sp^3)–O bond-bearing β-hydroxysulfones afforded high yields, placing the target C–O bond three-carbons away from the π-system led to lower yields. For instance, β-hydroxysulfone **S15** reacts to provide the corresponding olefin in only a 56% yield. Moreover, placing the target C–O bond four-carbons away from the π-system failed to afford olefin product (**27**).



Supporting Figure S9. Effect of chain length on reactivity

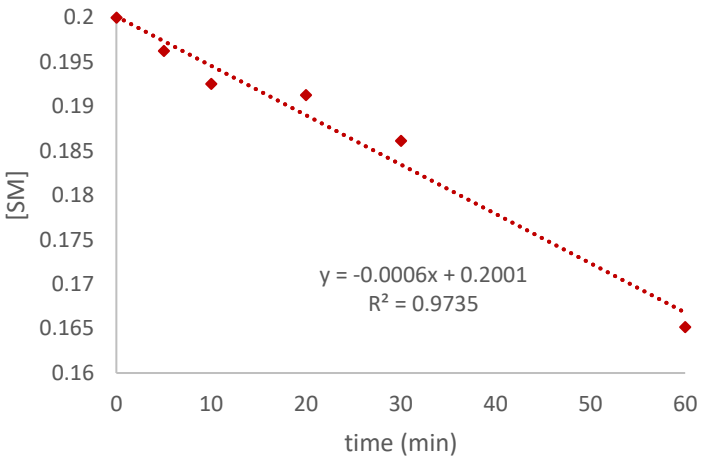
Seeking to confirm the relationship between the distant π-electron system and reaction outcome, we conducted a Hammett study. Substrates **1**, **38**, **S9**, **S12** and **S13**, varying only in their *p*-substituent, were subjected to General Protocol C to form products **2**, **39**, **4**, **7** and **8**. The initial-rates method was used to obtain rate constant values. Plotting the log of the rate constant (normalized with respect to that of the substrate lacking a *p*-substitutent) vs. the Hammett parameter for each substituent allowed us to demonstrate a linear relationship ($R^2 > 0.96$) which provides evidence that suggests involvement of the π-system in achieving reactivity (Supporting Figure S10).



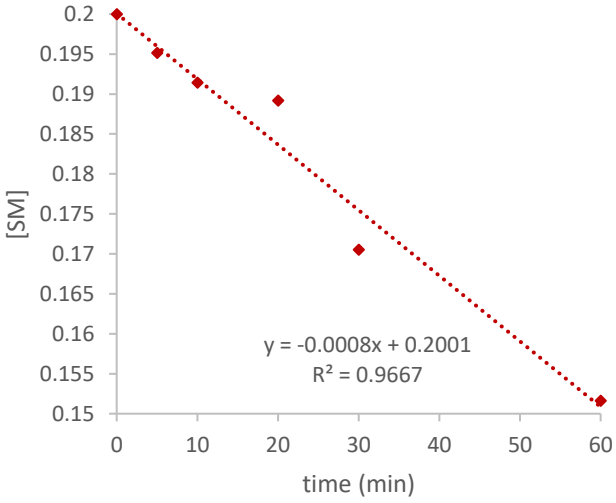
Supporting Figure S10. Investigating the effects of *p*-substitution on reactivity

Procedure for obtaining Hammett plot data

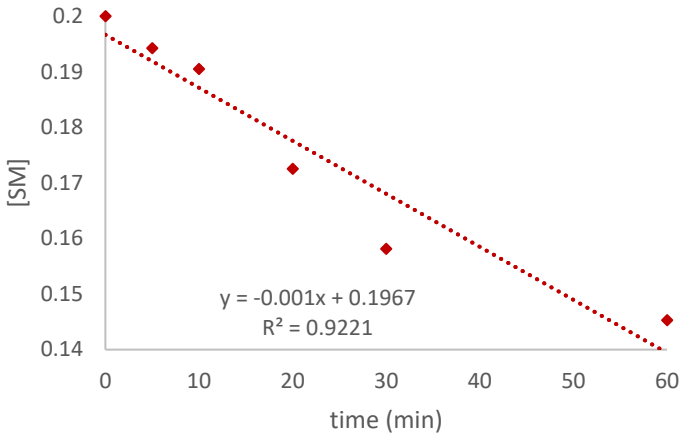
To five separate reaction vials was added 0.2 mmol substrate, 0.02 mmol $NiBr_2$•glyme, 0.04 mmol ICy•HBF_4, 0.06 mmol Mn, 0.24 mmol TMDSO and 0.2 mmol KO^{t}Bu. 0.8 mL PhMe was added to each of the reaction vials and they were placed in an oil bath at 70 °C. Each vial was quenched with 0.4 mmol TBAF (as a 1.0 mol/L solution in hexanes) at a variable amount of time: 5 min, 10 min, 20 min, 30 min or 60 min. Upon quenching, the reaction was left to stir at 60 °C for an additional 2 hours. The subsequent solution was washed three times with $NaHCO_3$ (aq) and once with saturated NaCl (aq) before being filtered through a silica-celite (50:50 mixture) plug into a round bottom flask. Solvent was removed *in vacuo* to reveal crude product. Yields were obtained via ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard and used to create Supporting Figures S11-S15, where [SM] = 1 – [P]. The slopes of these plots represent the reaction rate (dP/dt), which is proportional to the rate constant (k_X). Comparing the rate of a given substrate (k_X) to that of the unsubstituted substrate (k_H) provides the relative rate constant (k_X/k_H). The log of the k_X/k_H value for each substrate was taken and plotted against the corresponding σ value to generate a Hammett plot with a rho (ρ) value equal to -0.235 and an R^2 value of 0.9618.



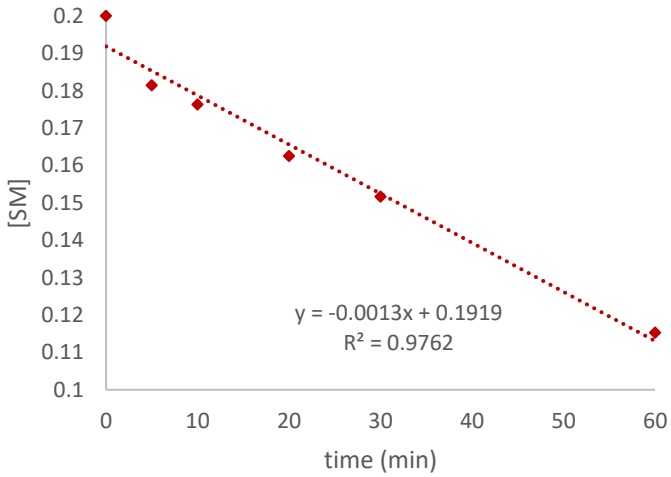
Supporting Figure S11. Initial reaction progress for *p*-NO_2 substituted alcohol **(S12)**



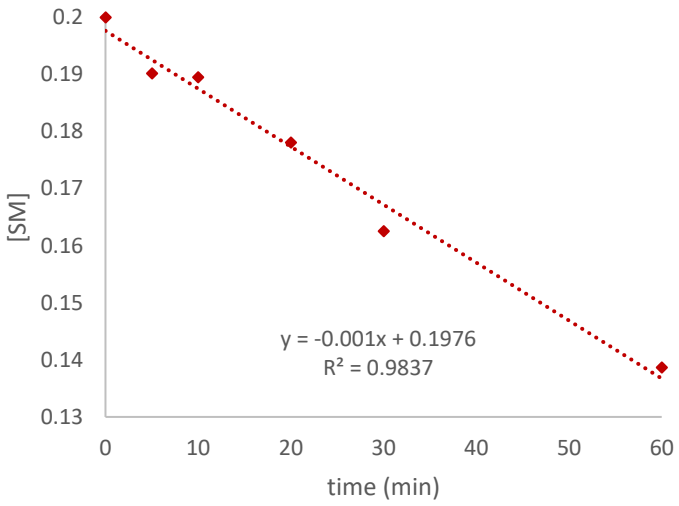
Supporting Figure S12. Initial reaction progress for *p*-F substituted alcohol **(S13)**



Supporting Figure S13. Initial reaction progress for unsubstituted alcohol **(38)**



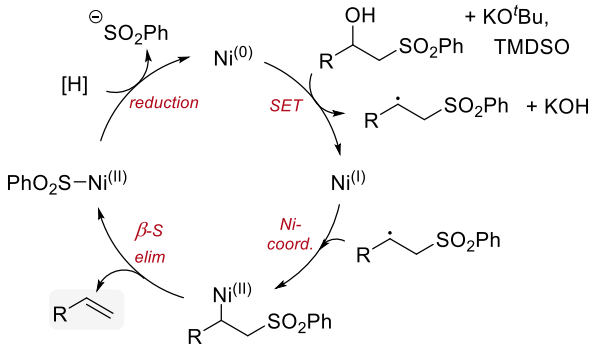
Supporting Figure S14. Initial reaction progress for *p*-NEt_2 substituted alcohol **(S9)**



Supporting Figure S15. Initial reaction progress for *p*-OMe substituted alcohol **(1)**

6.6. Proposed reaction mechanism

While mechanistic investigations are still in the preliminary stage, we propose a tentative mechanistic cycle for this transformation (Supporting Figure S16). A Ni^0 catalyst may first participate alongside the TMDSO and KO^{t}Bu in a single-electron transfer event with the β-hydroxysulfone substrate, generating a carbon-centered radical that proceeds to coordinate with the Ni catalyst. β-Sulfone elimination then occurs, generating olefin product alongside a Ni^{II}-catalyst that is reduced to re-form the active catalyst alongside hydroxide and sulfoxide salts.



Supporting Figure S16. Tentative reaction mechanism

Notably, while there is strong mechanistic evidence for the formation of the intermediate carbon-centered radical, we lack evidence regarding the details of the C–O bond cleavage step that must lead to this species. It is difficult to envision how a Ni^0 catalyst can induce radical fragmentation of a secondary alcohol given the high bond strength. Further, there appears to a key role of KO^{t}Bu and TMDSO in the radical forming step, though the specific details are unclear. Previous reports of chemistry utilizing alkoxides and silanes have shown that a plethora of reactive species, including radicals, hydrides, and radical anions, may be present. There is likely an interaction between one of these species with the Ni catalyst. Further studies are necessary before a conclusive mechanistic hypothesis can be proposed.

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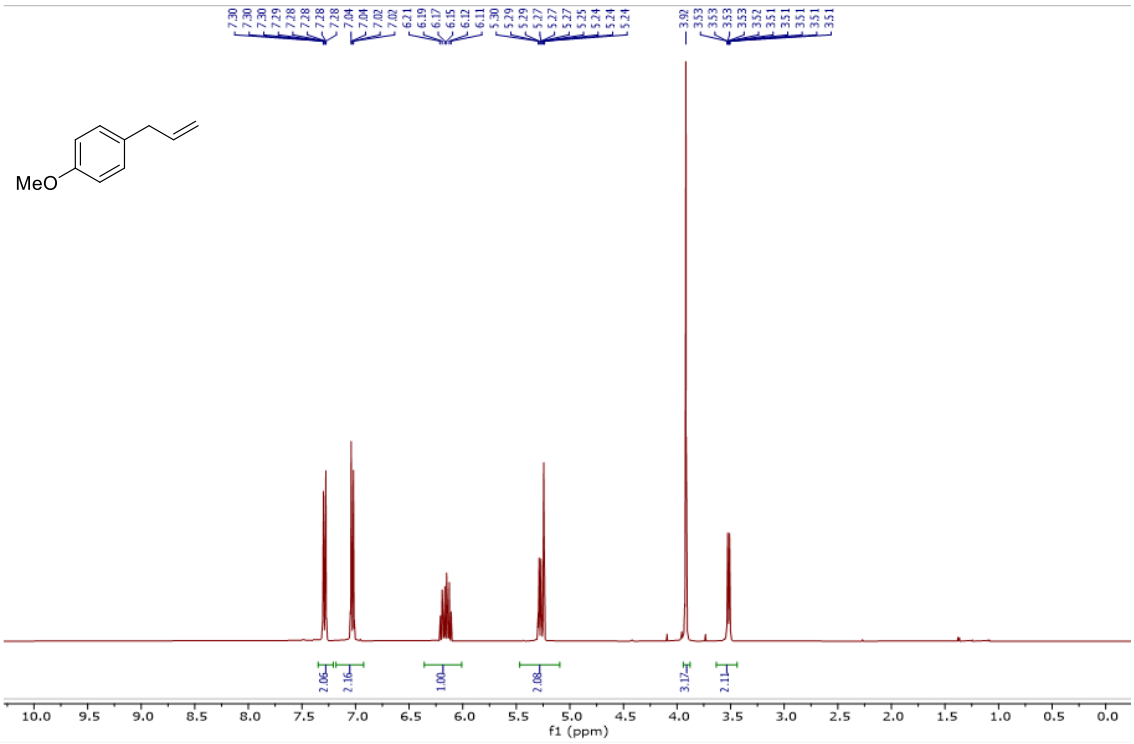
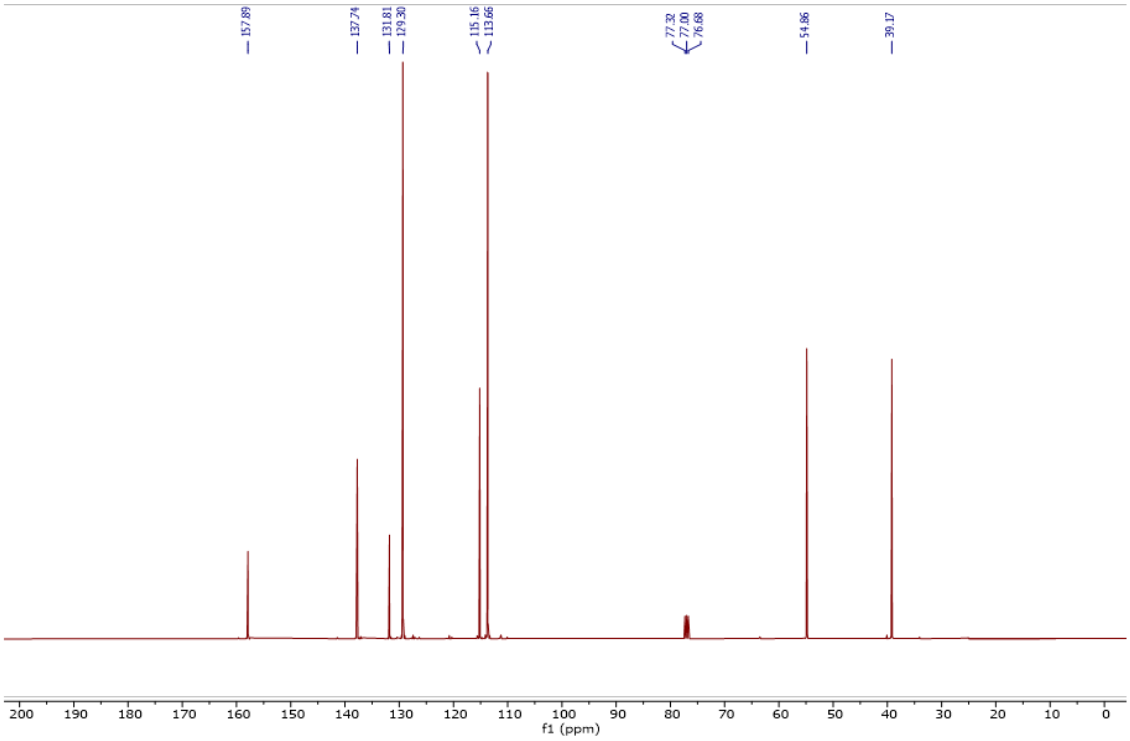
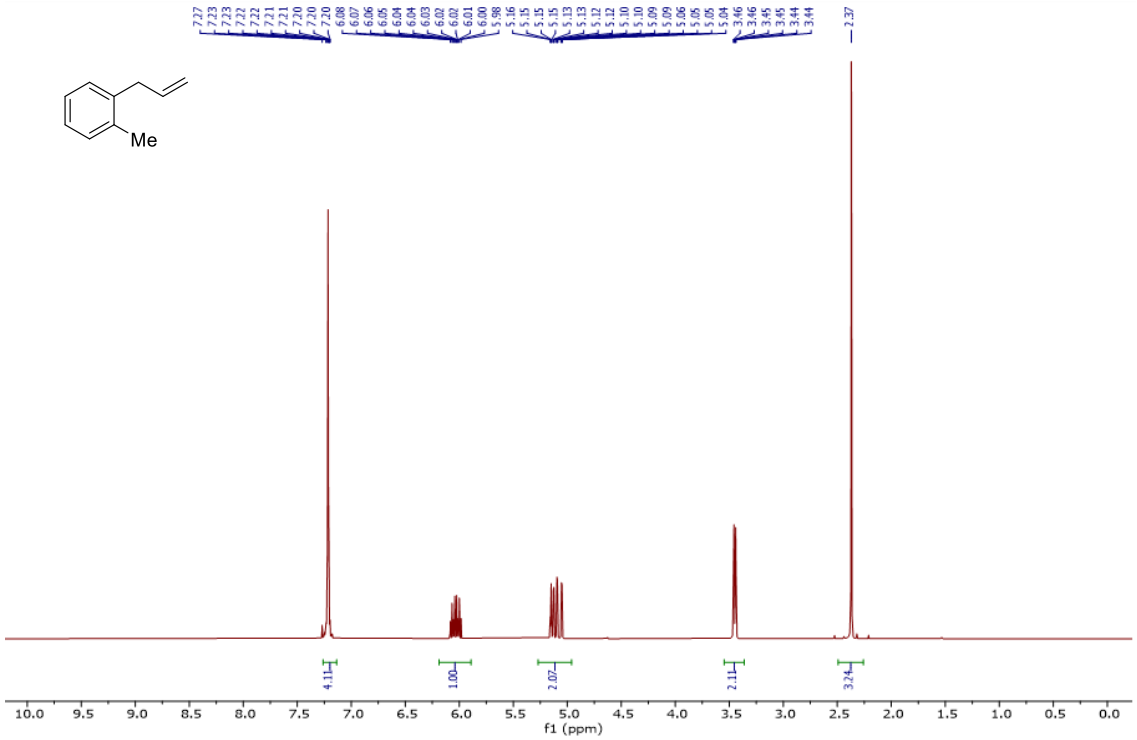
8. NMR Spectra

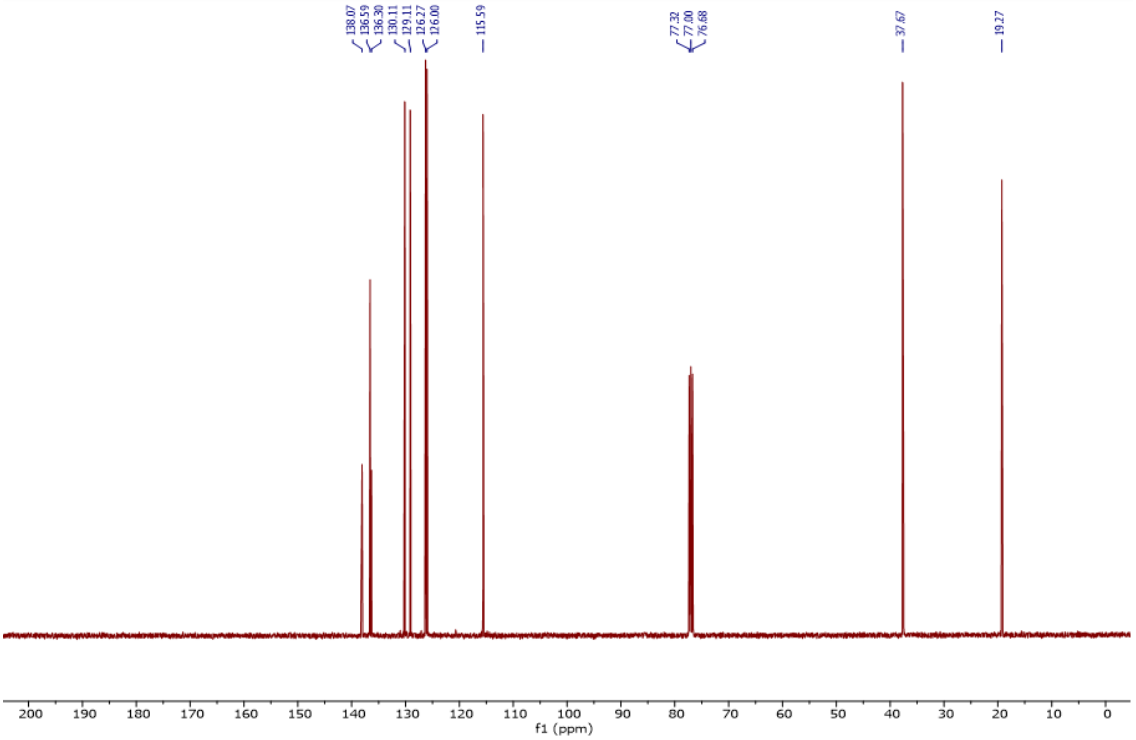
4-Methoxyallylbenzene **2** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



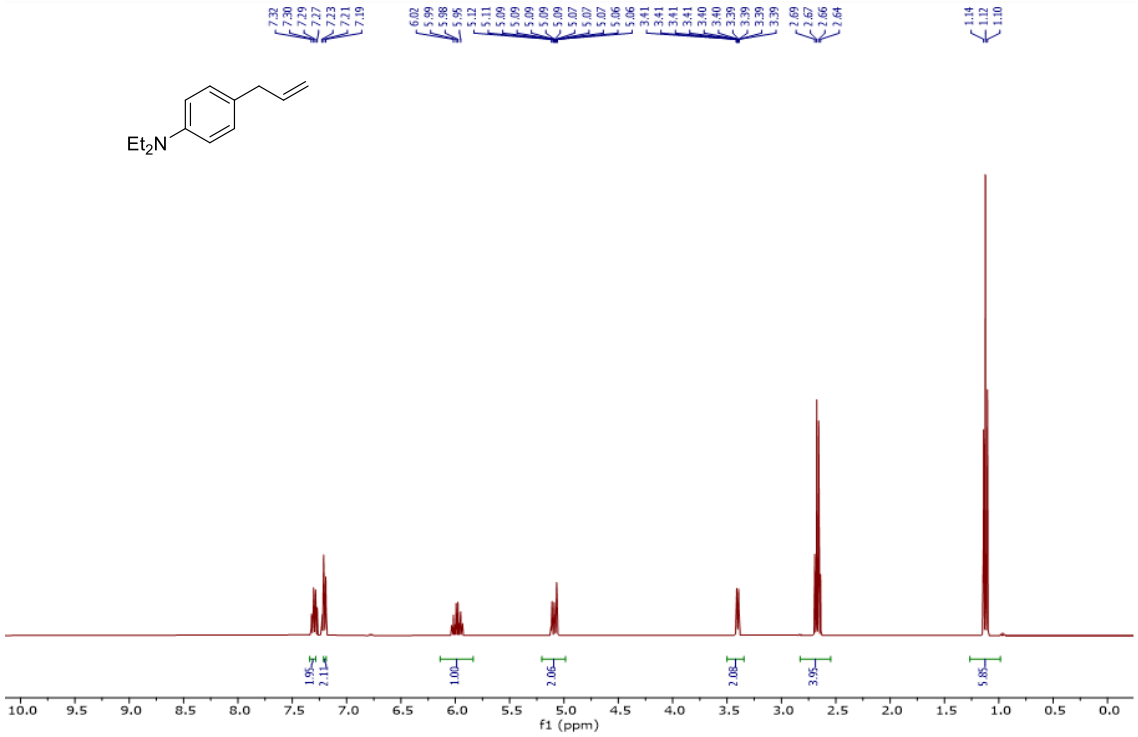


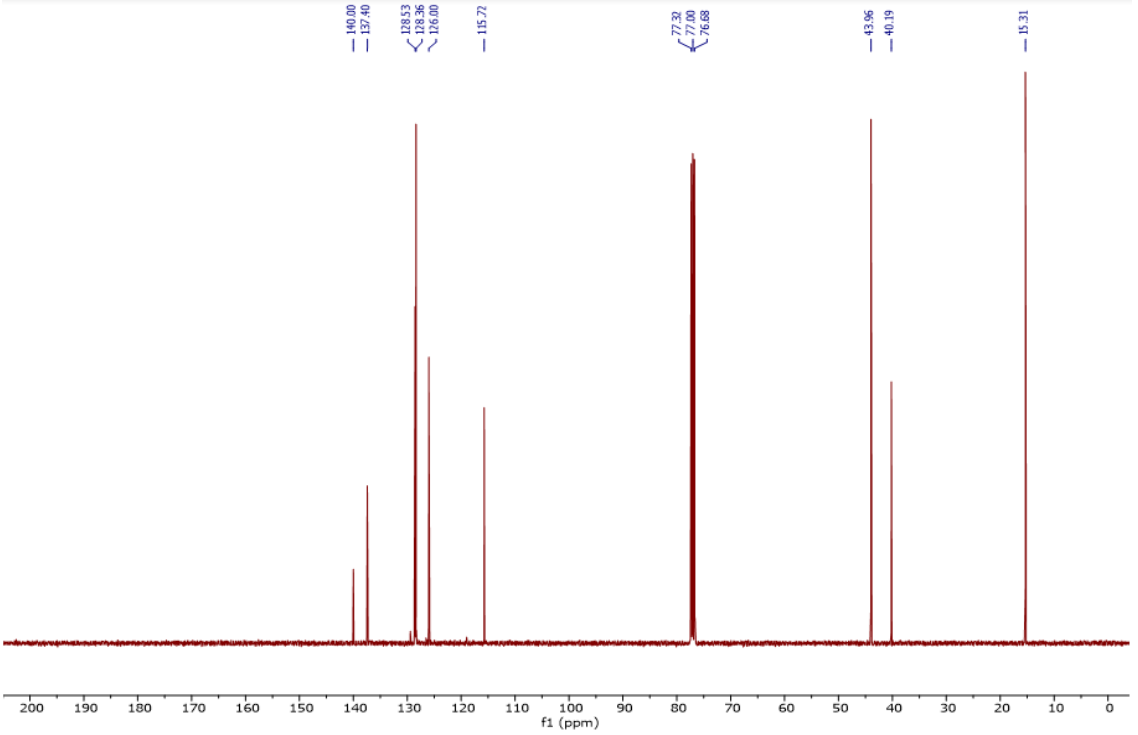
2-Methylallylbenzene **3** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



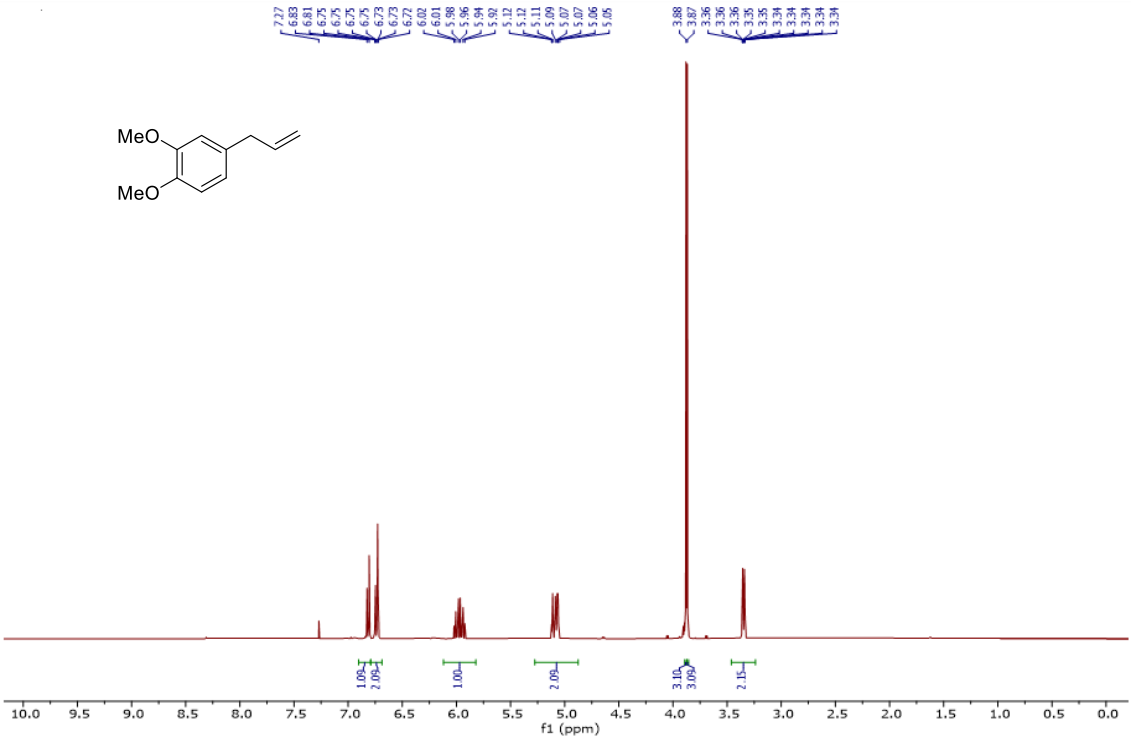


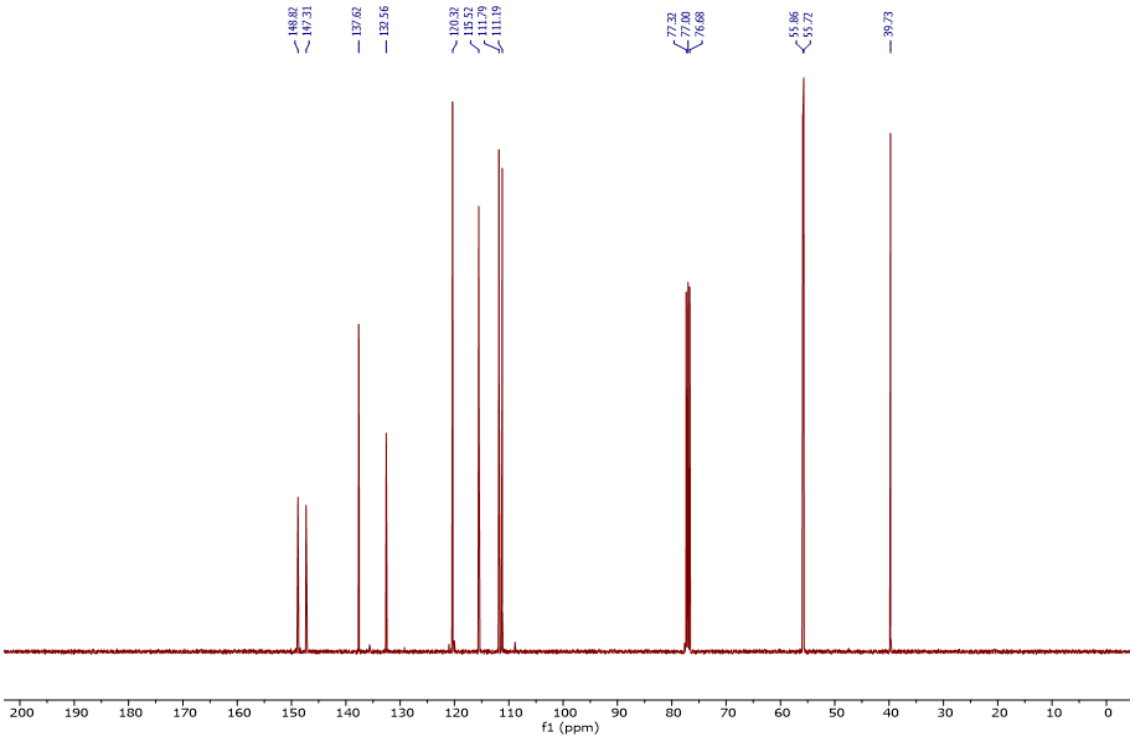
4-Diethylamino allylbenzene **4** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



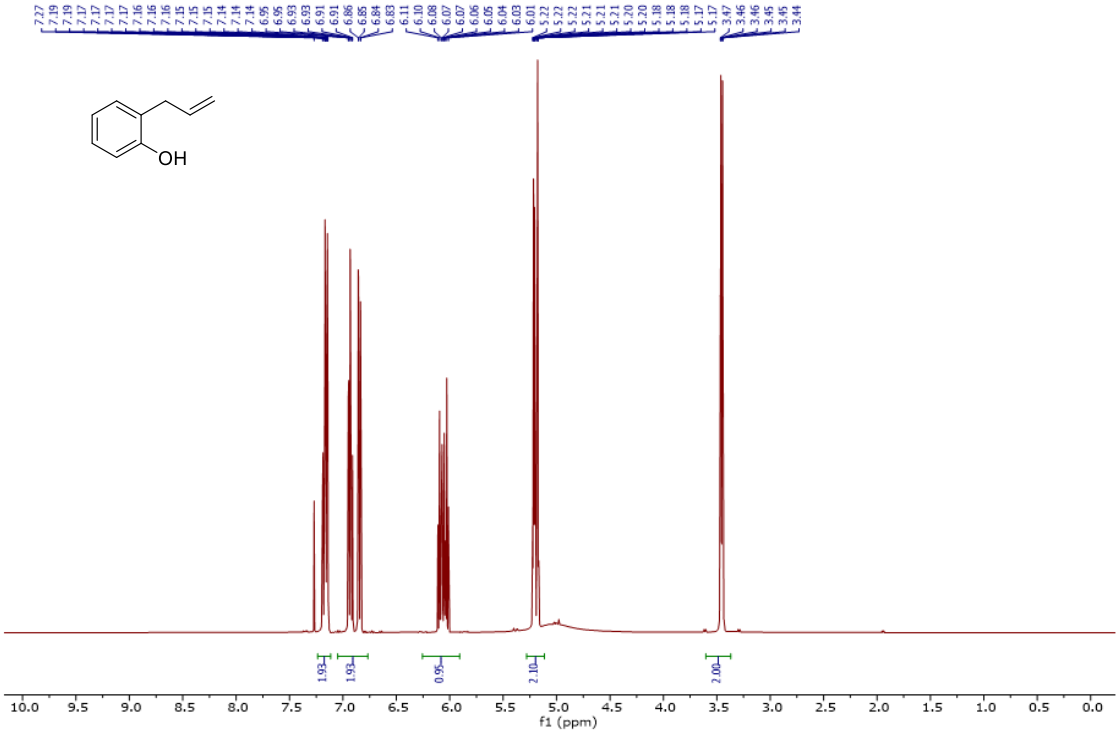


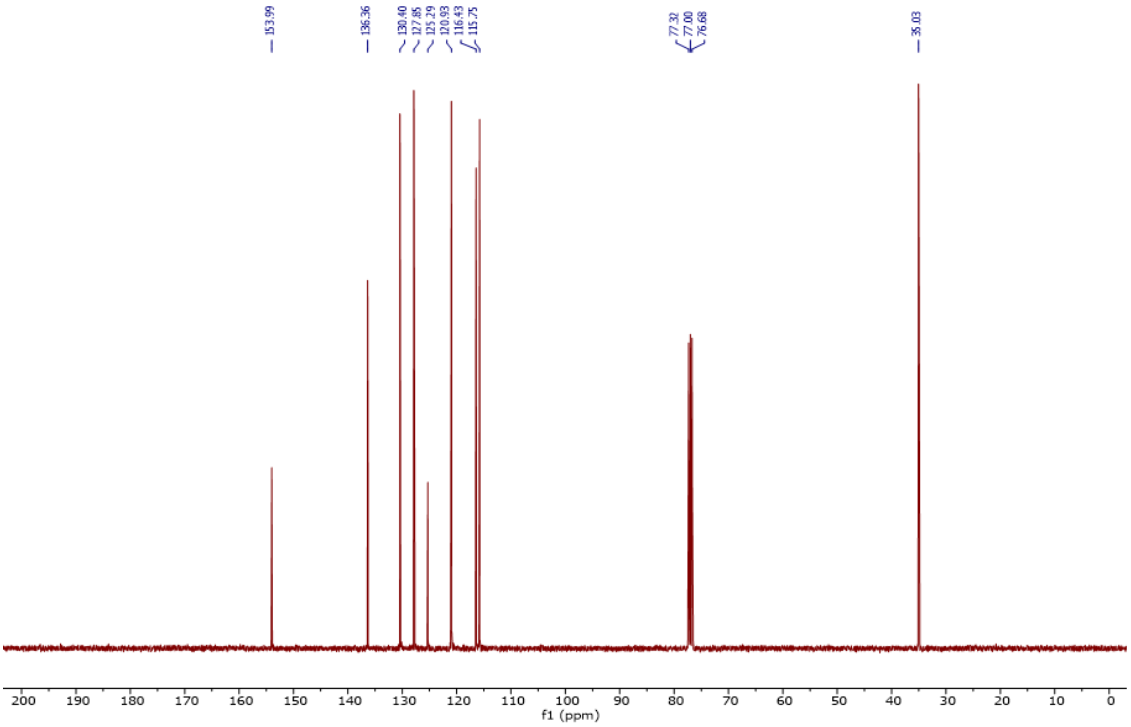
3,4-Dimethoxyallylbenzene **5** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



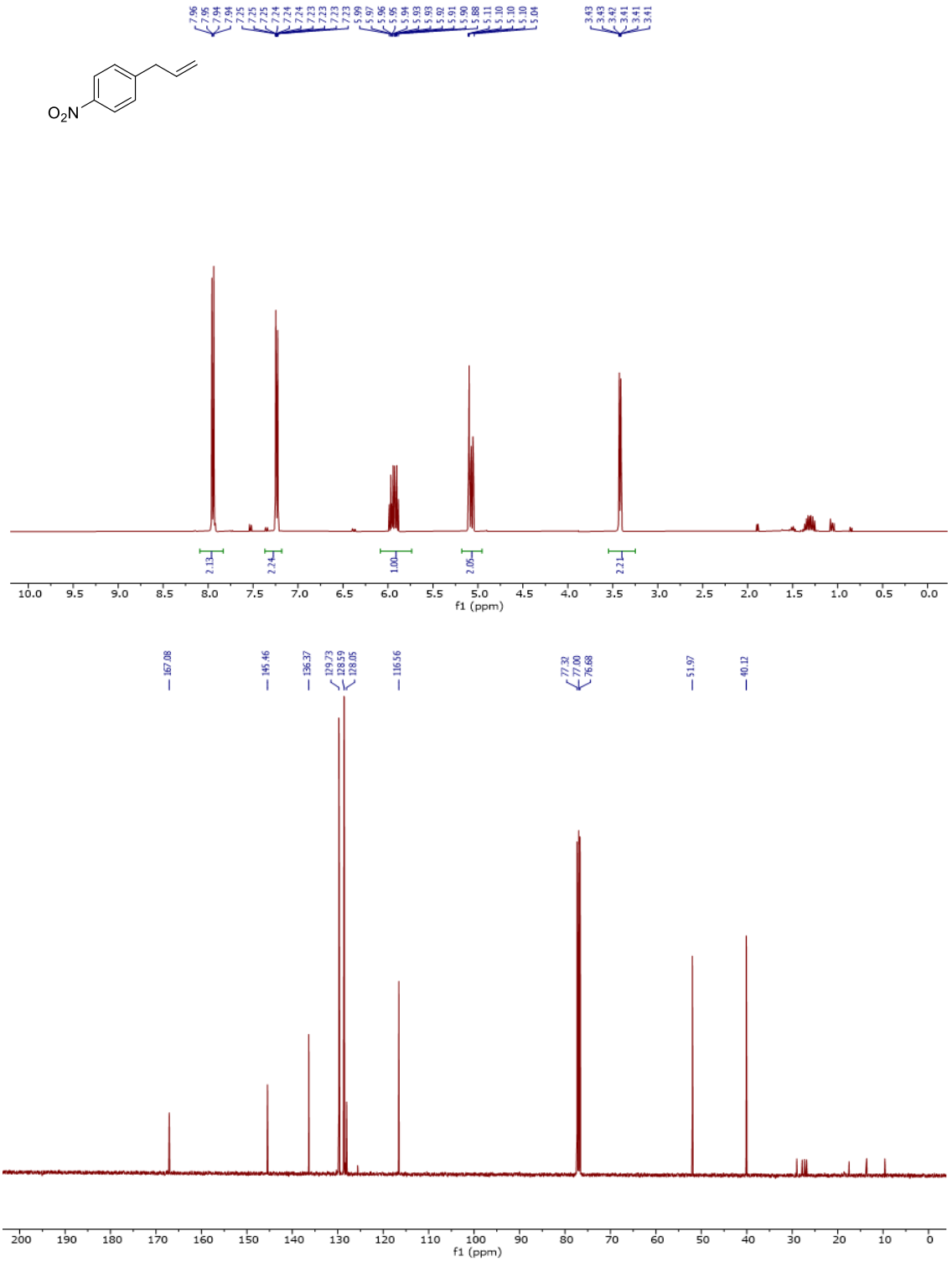


4-Hydroxyallylbenzene **6** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

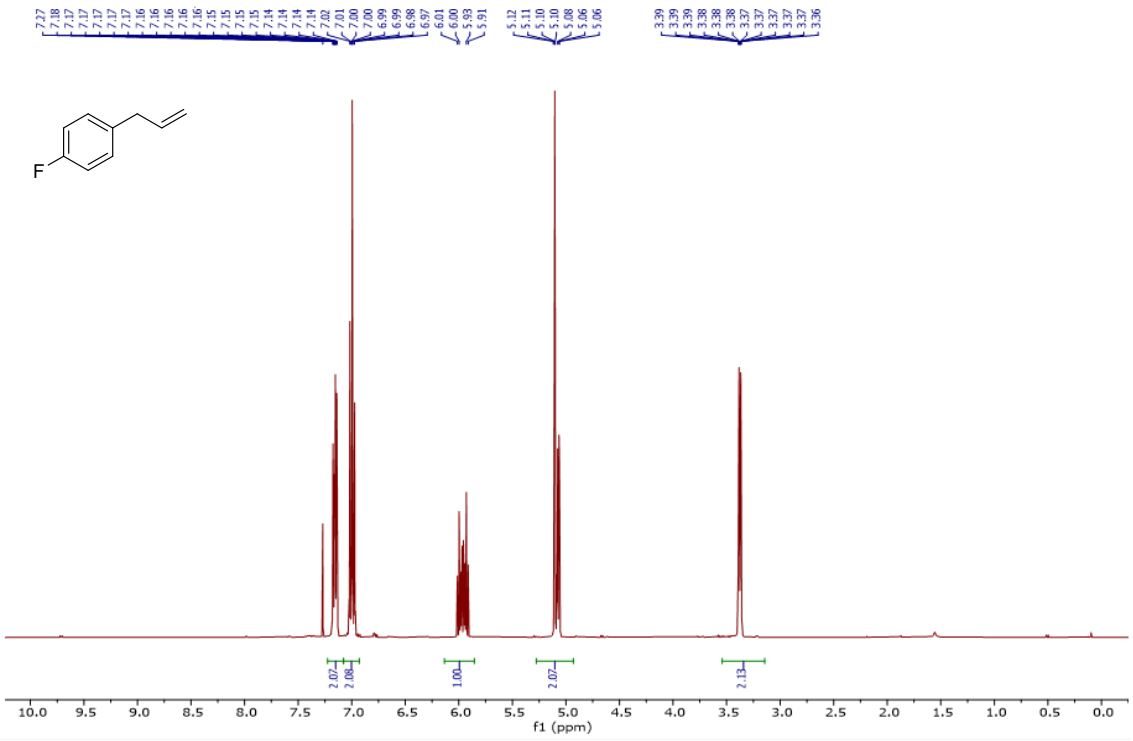


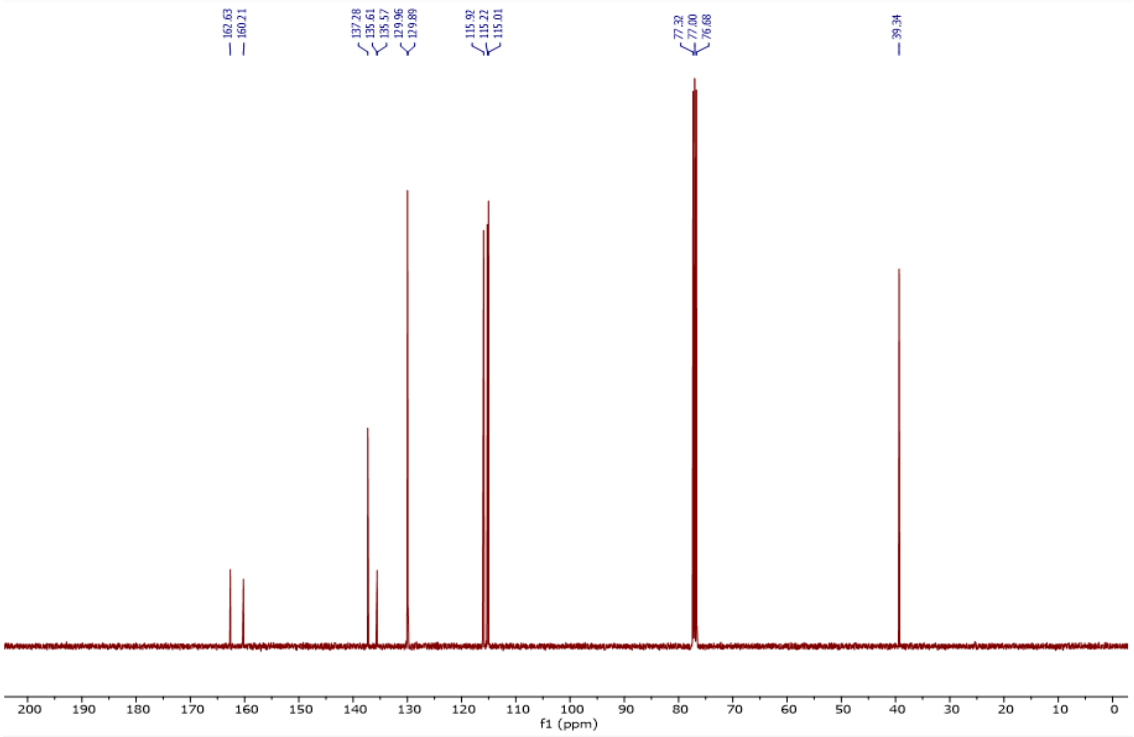


4-Nitroallylbenzene **7** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

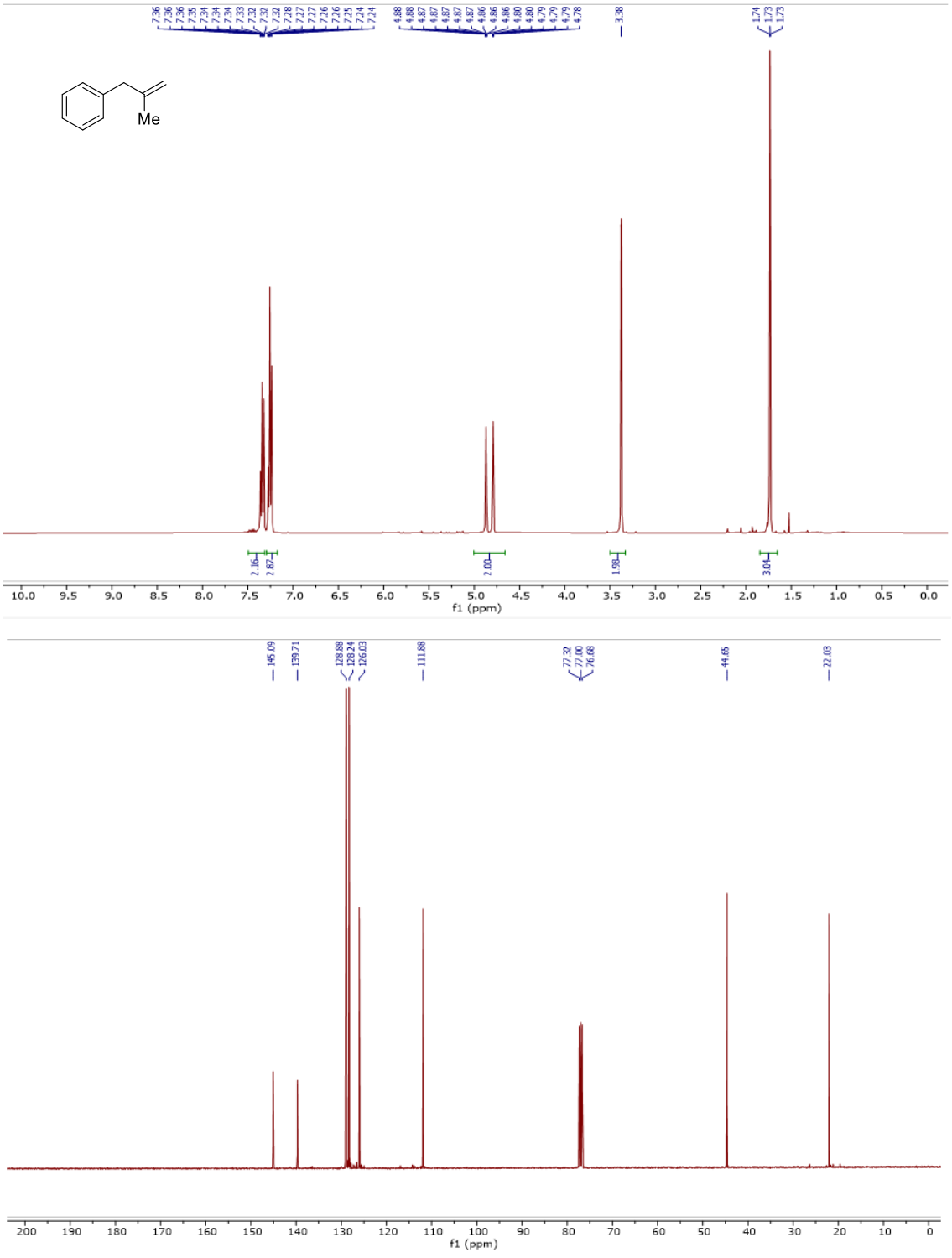


4-Fluoroallylbenzene **8** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

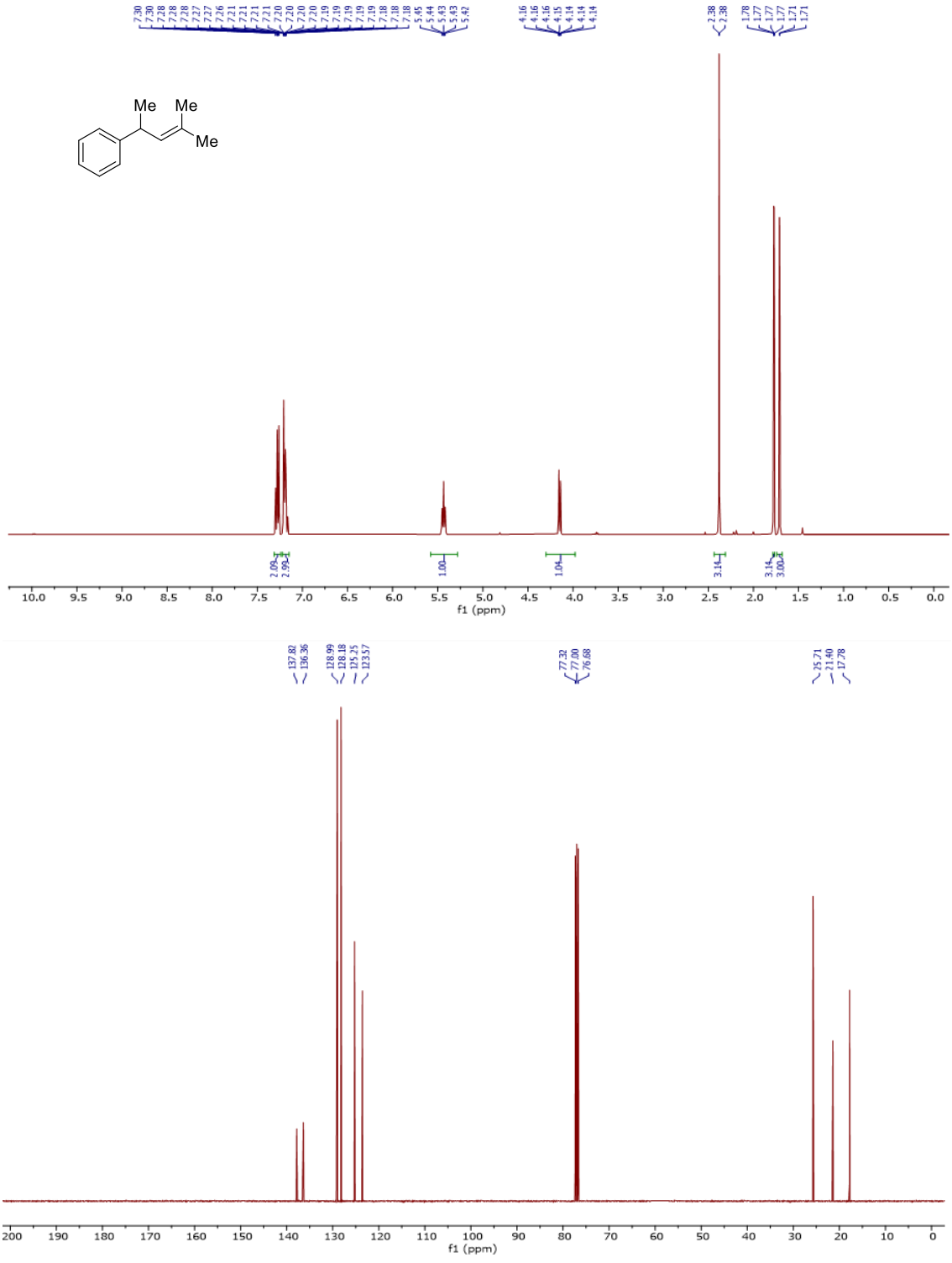




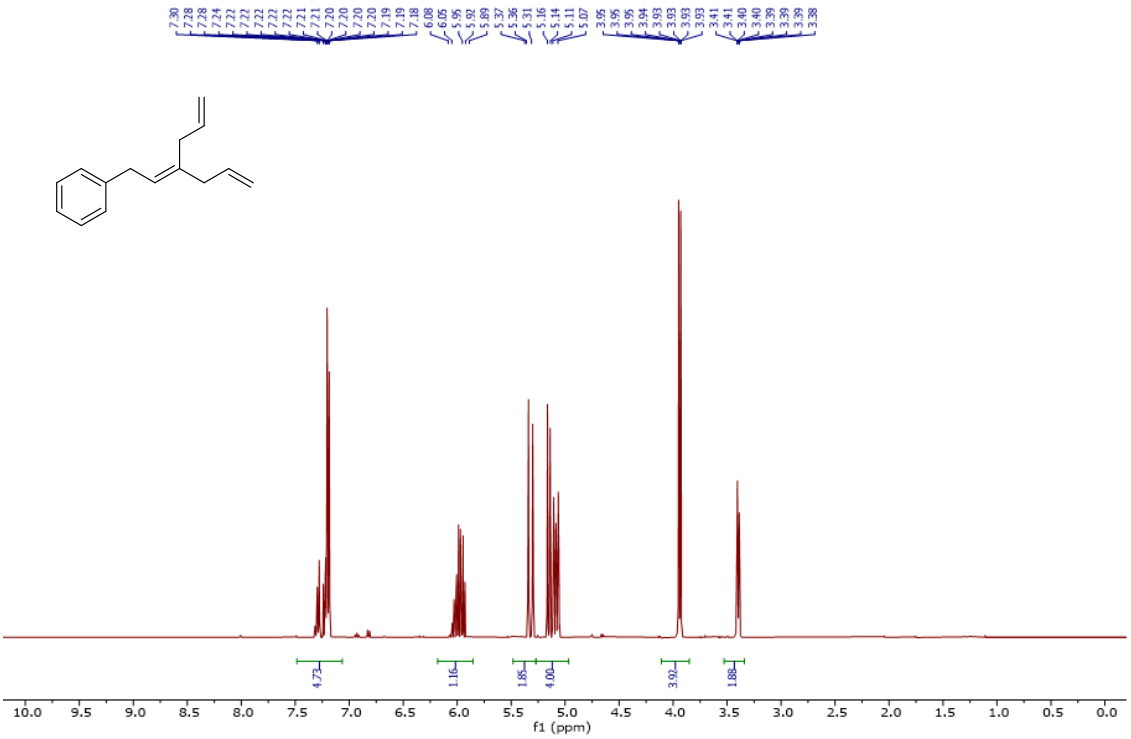
2-Methyl-3-phenylpropene **9** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

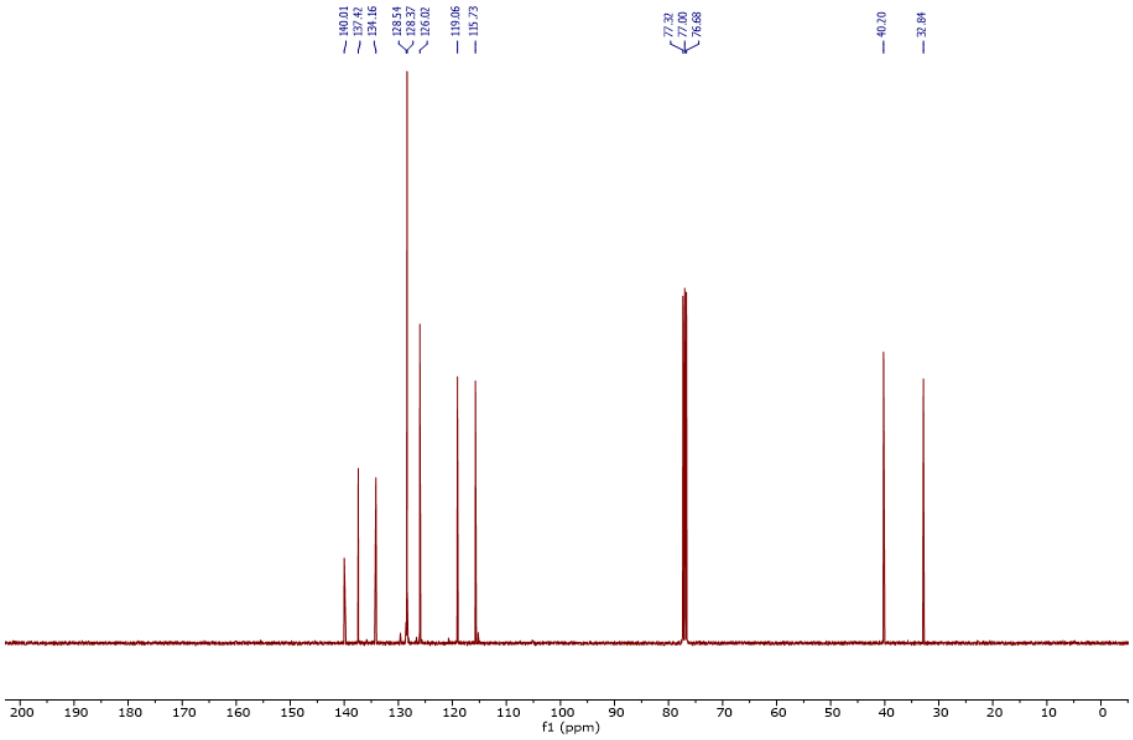


1,1,3-Trimethyl-3-phenylpropene **10** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

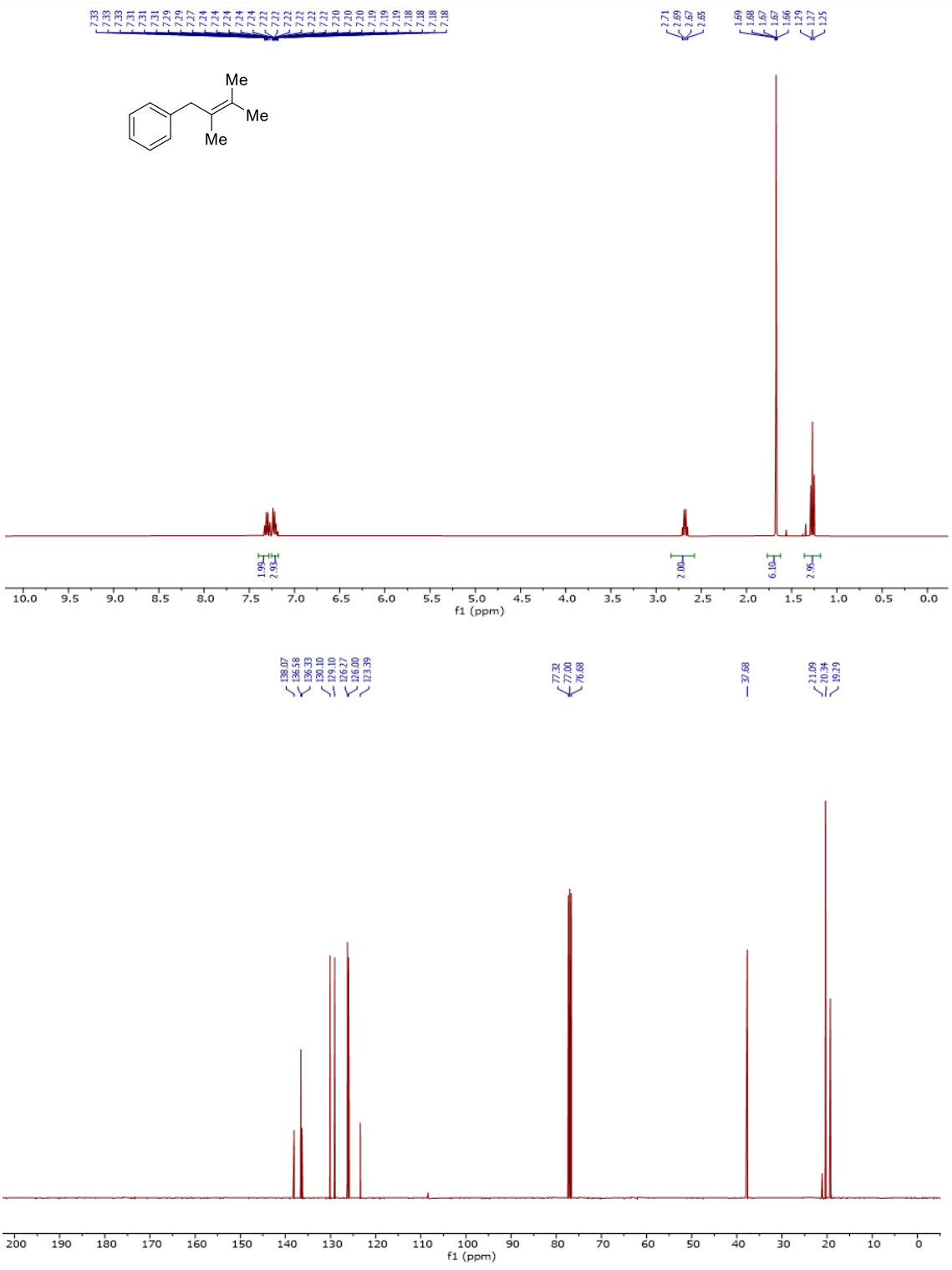


1,1-Diprop-2-ene-3-phenylpropene **11** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

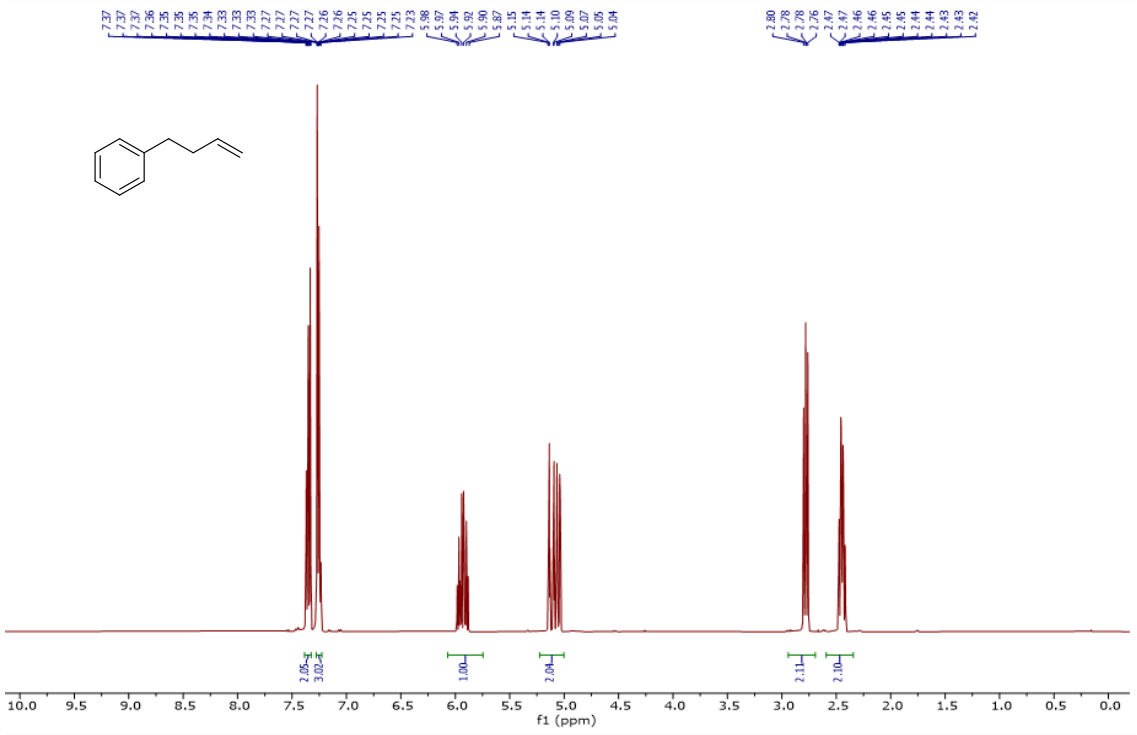


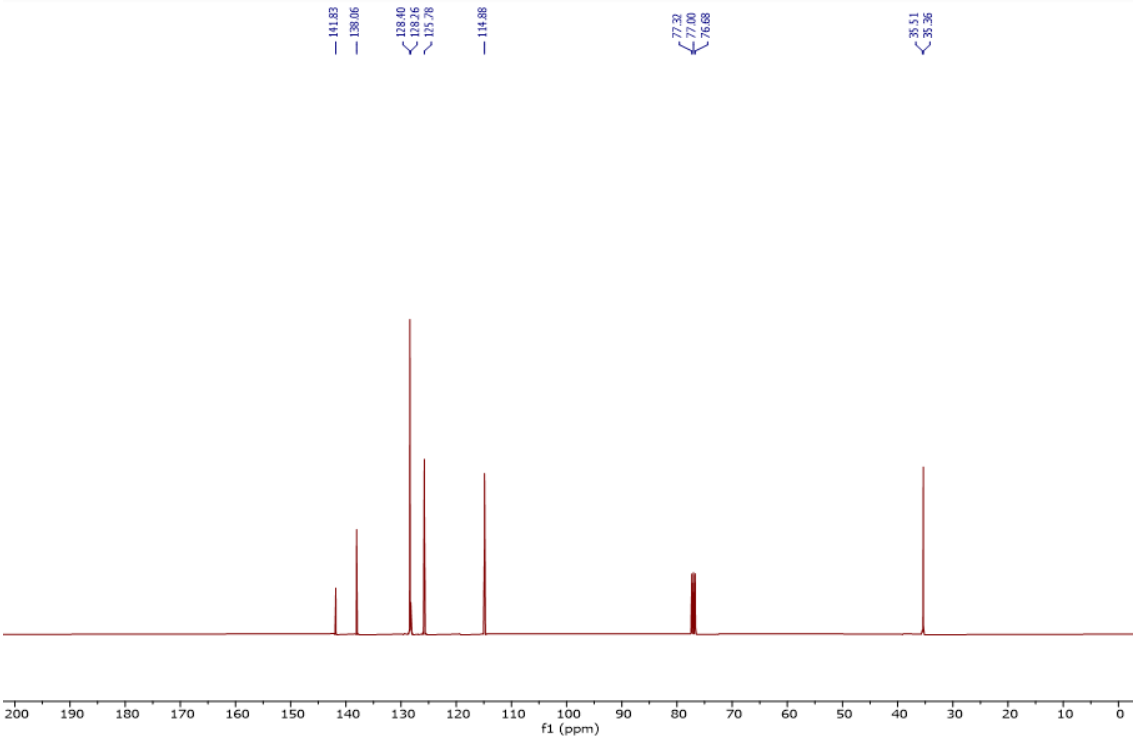


1,1,2-Trimethyl-1-phenylpropene **12** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

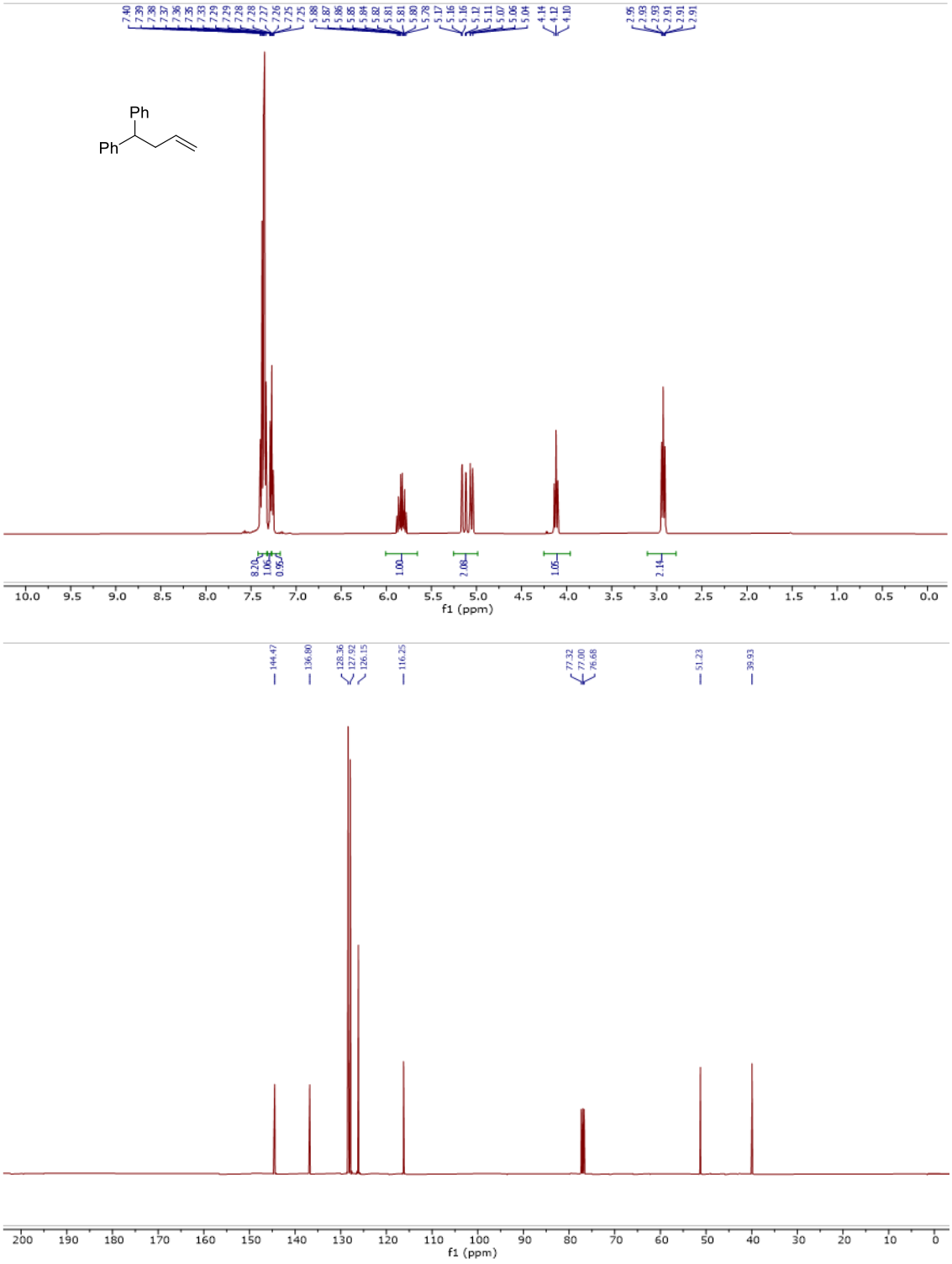


4-Phenylbutene **13** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

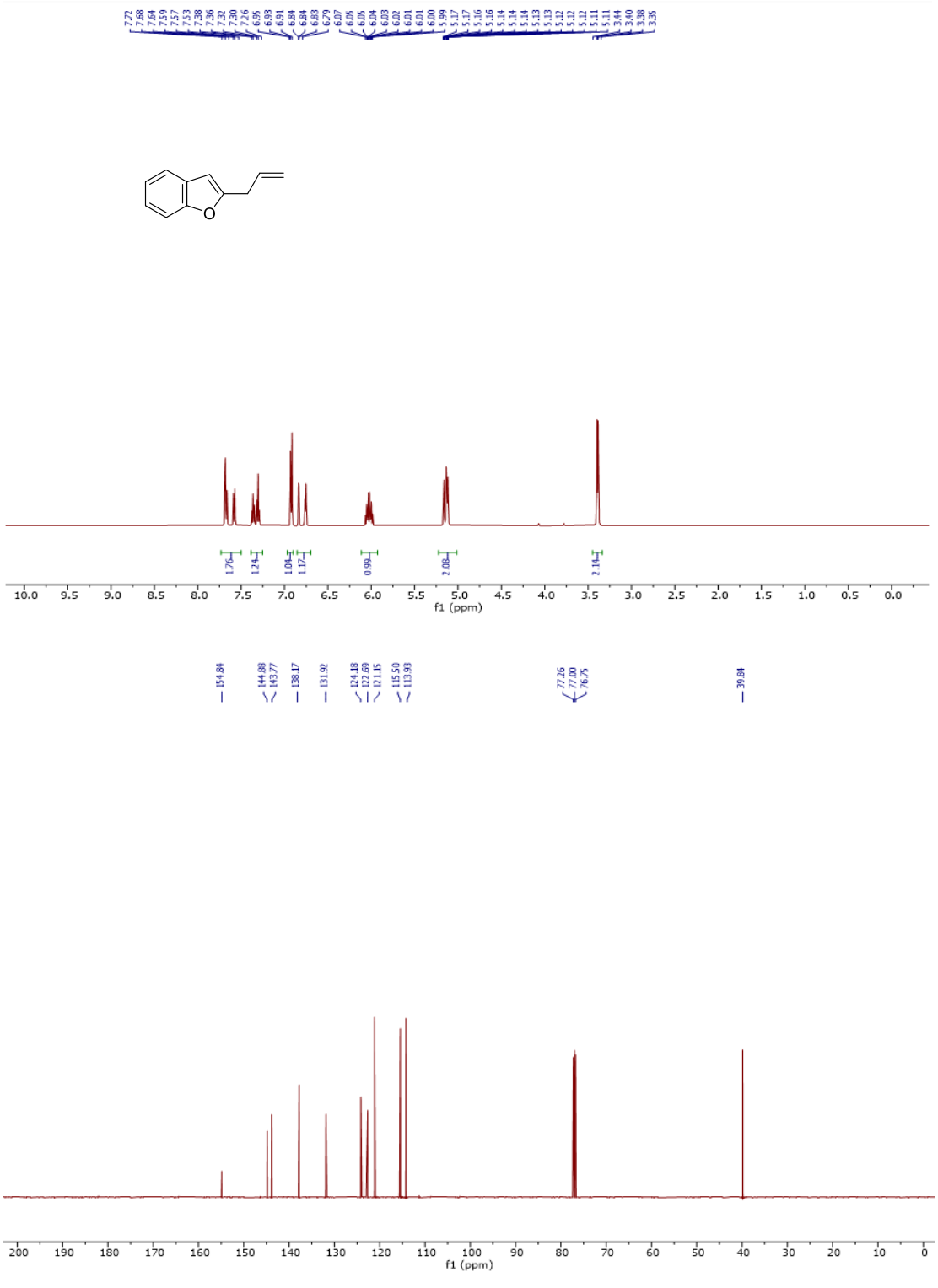




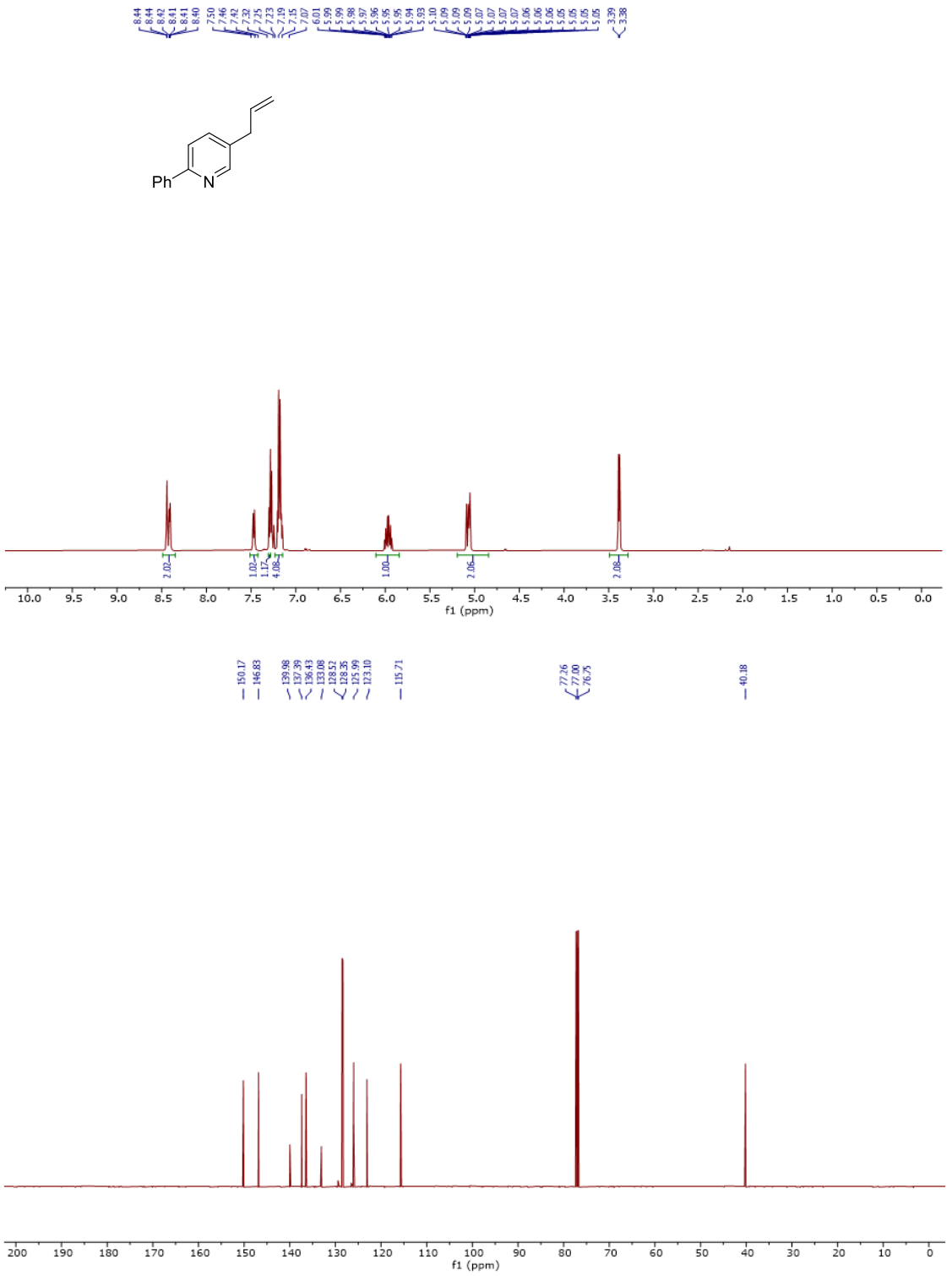
4,4-Diphenylbutene **14** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



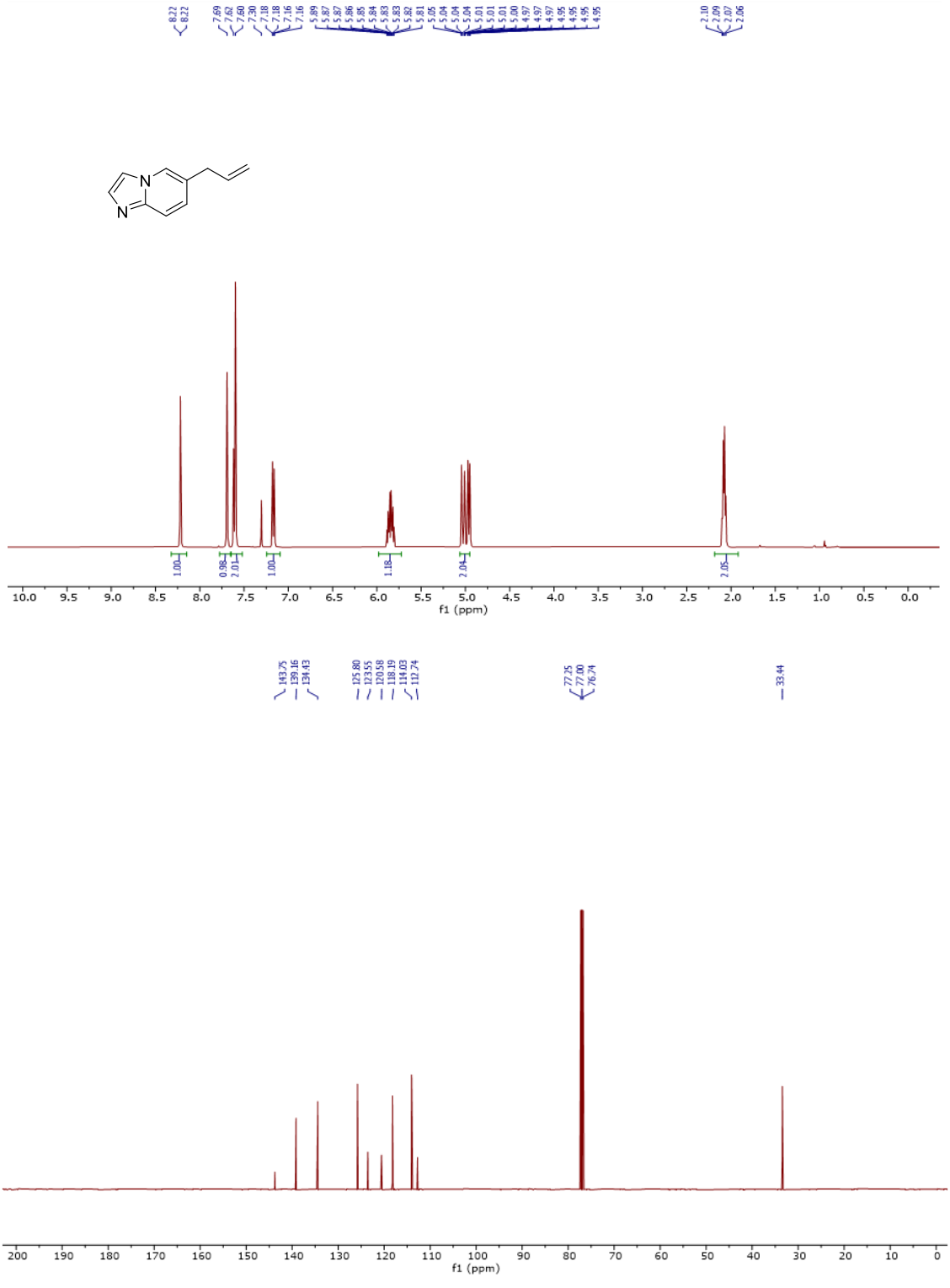
2-(2-Allyl)benzofuran **15** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



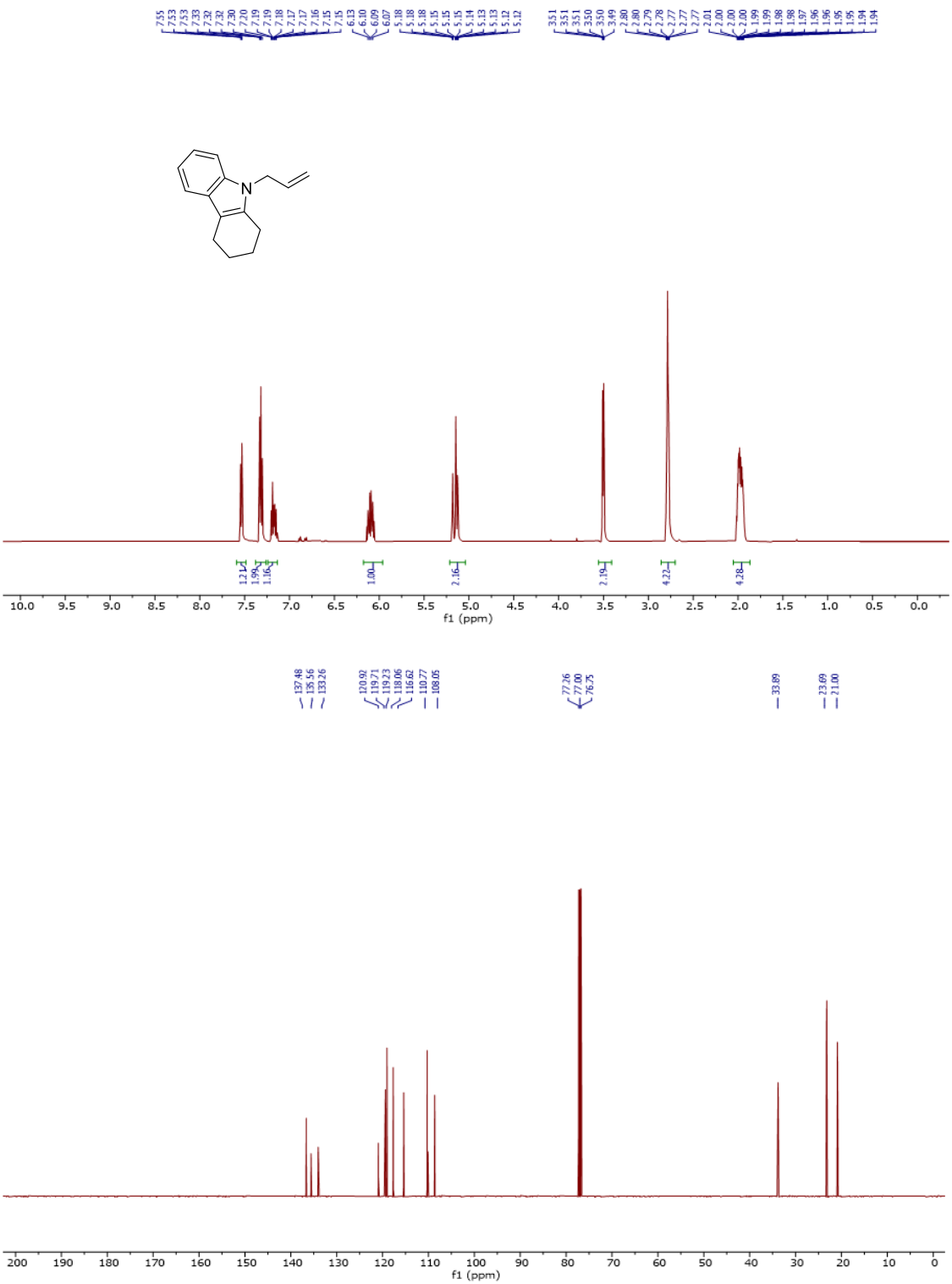
2-Phenyl-5-allylpyridine **16** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



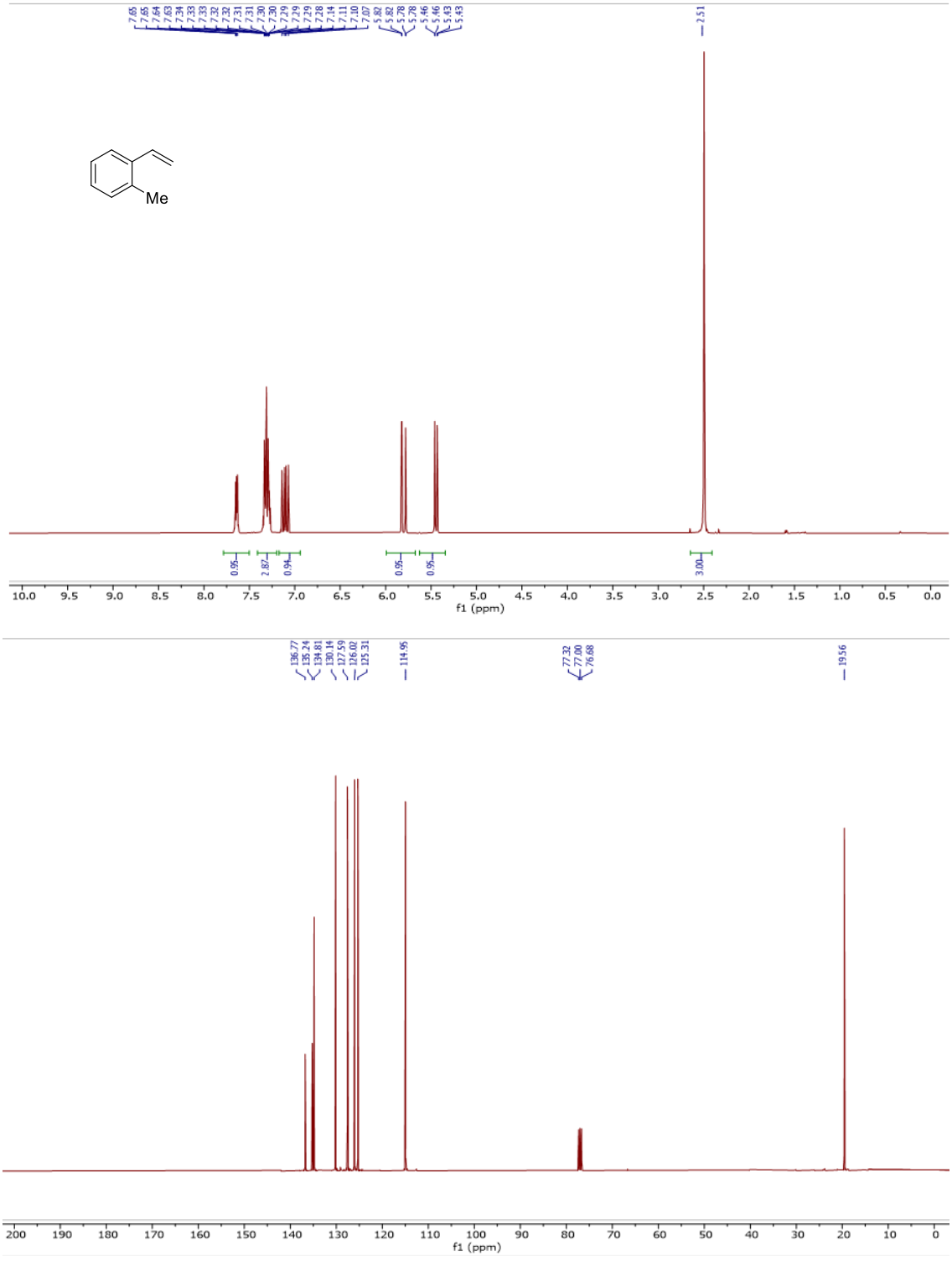
6-Allylimidazo[1,2-α]pyridine **17** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



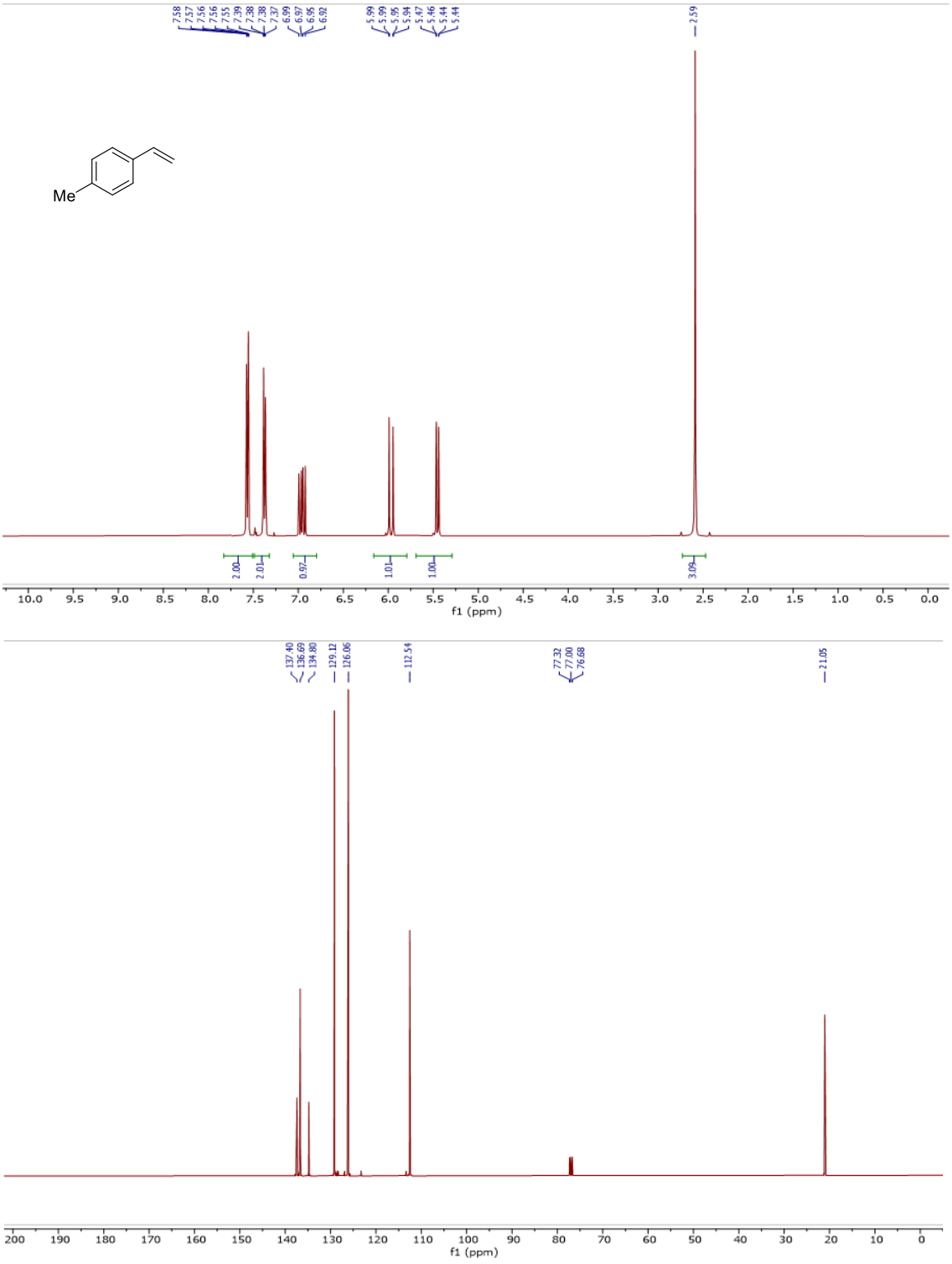
N-Allyl-1,2,3,4-tetrahydrocarbazole **18** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



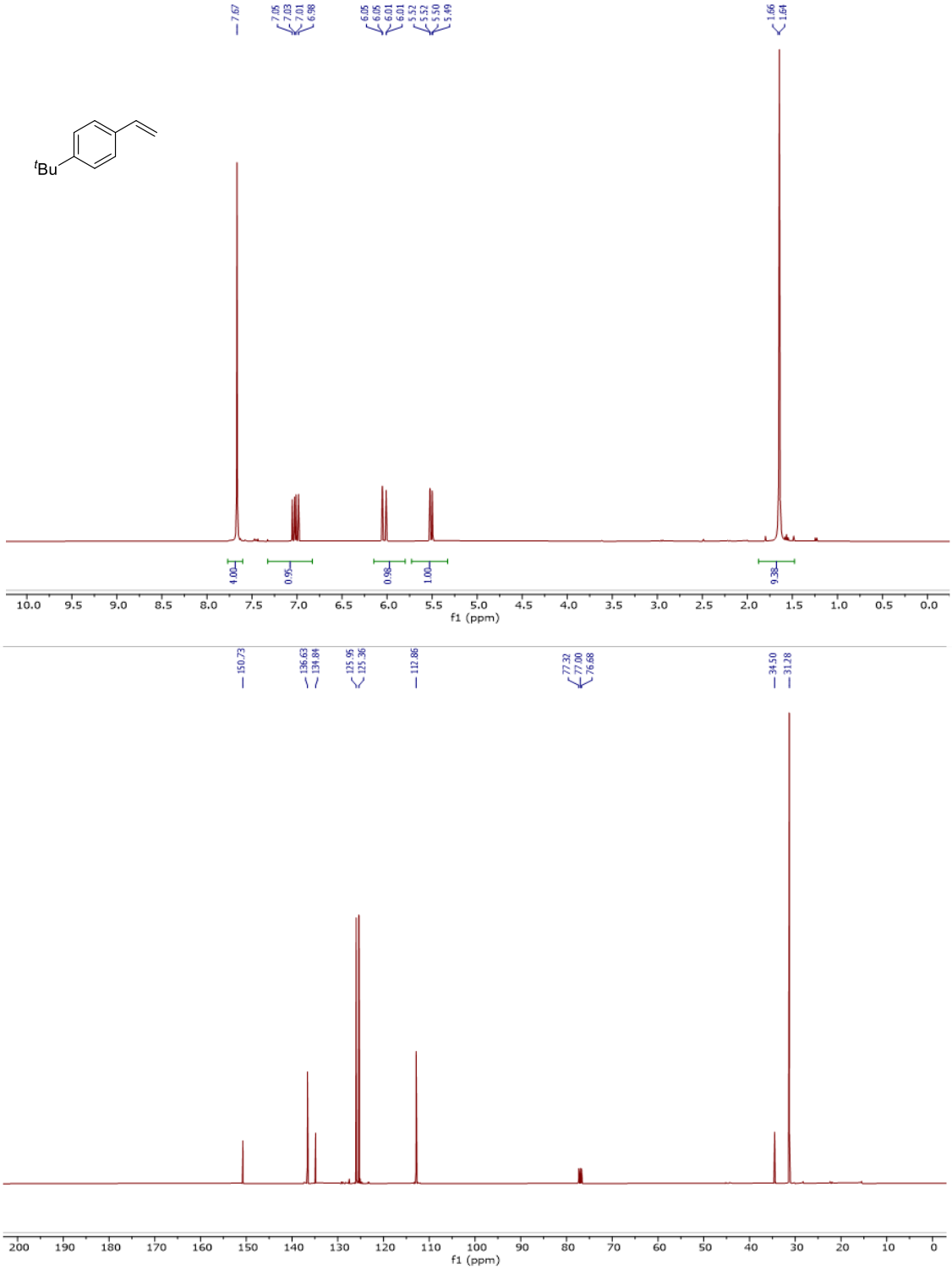
2-Methylstyrene **19** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



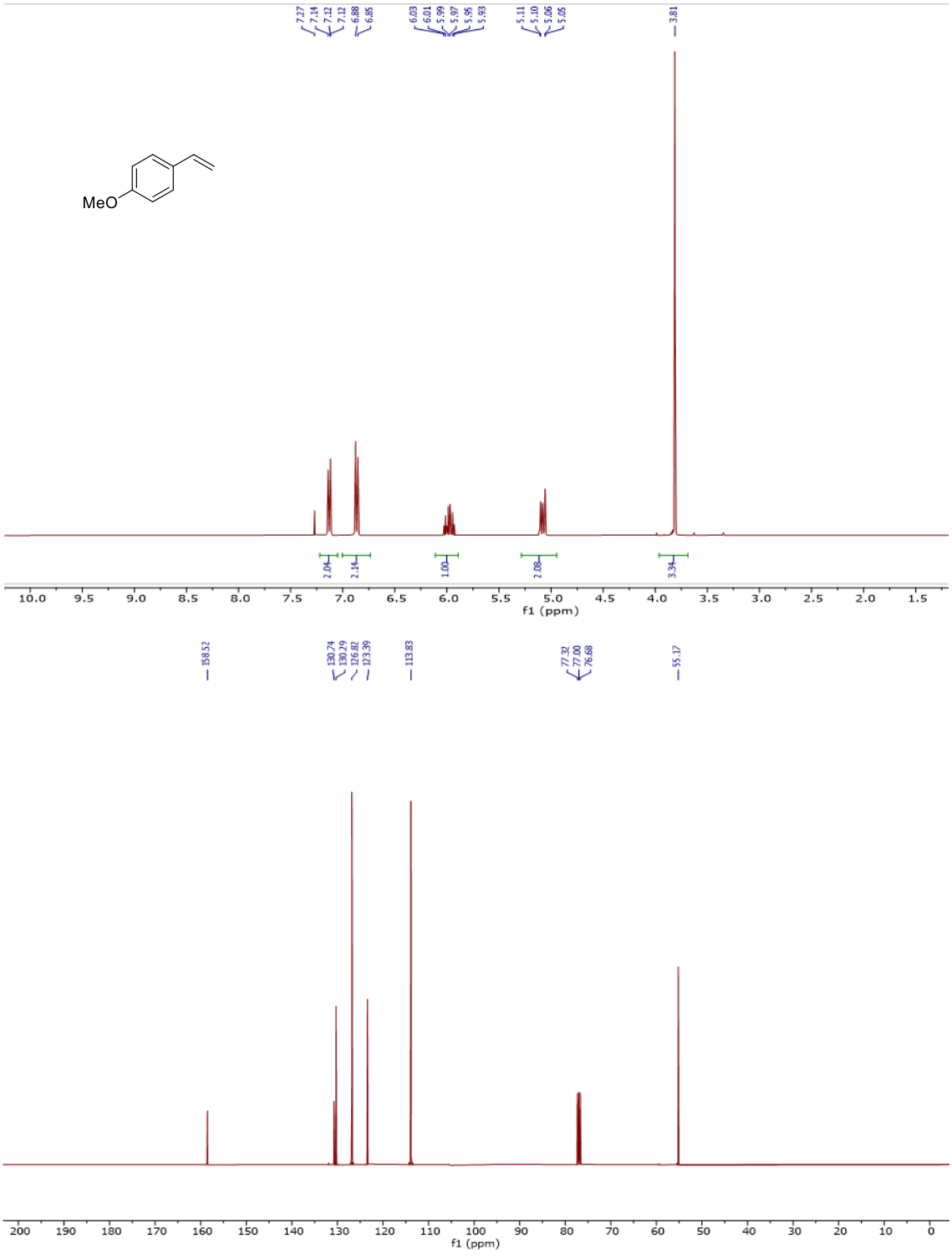
4-Methylstyrene **20** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



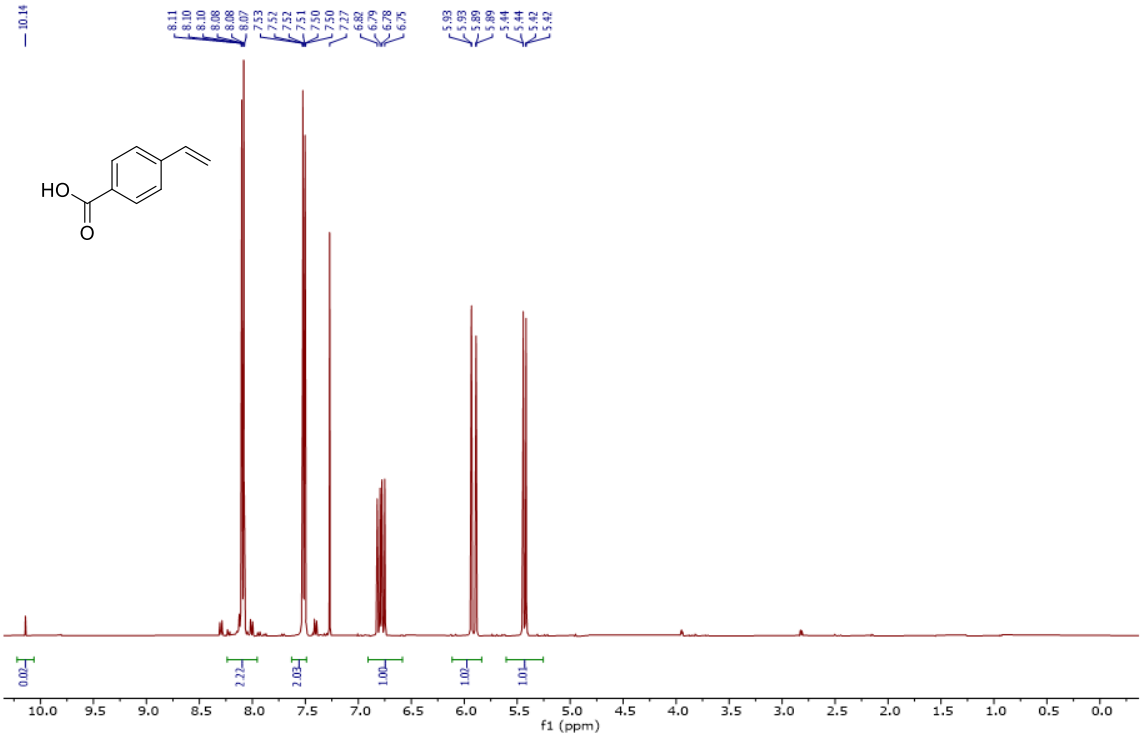
4-Tertbutylstyrene **21** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

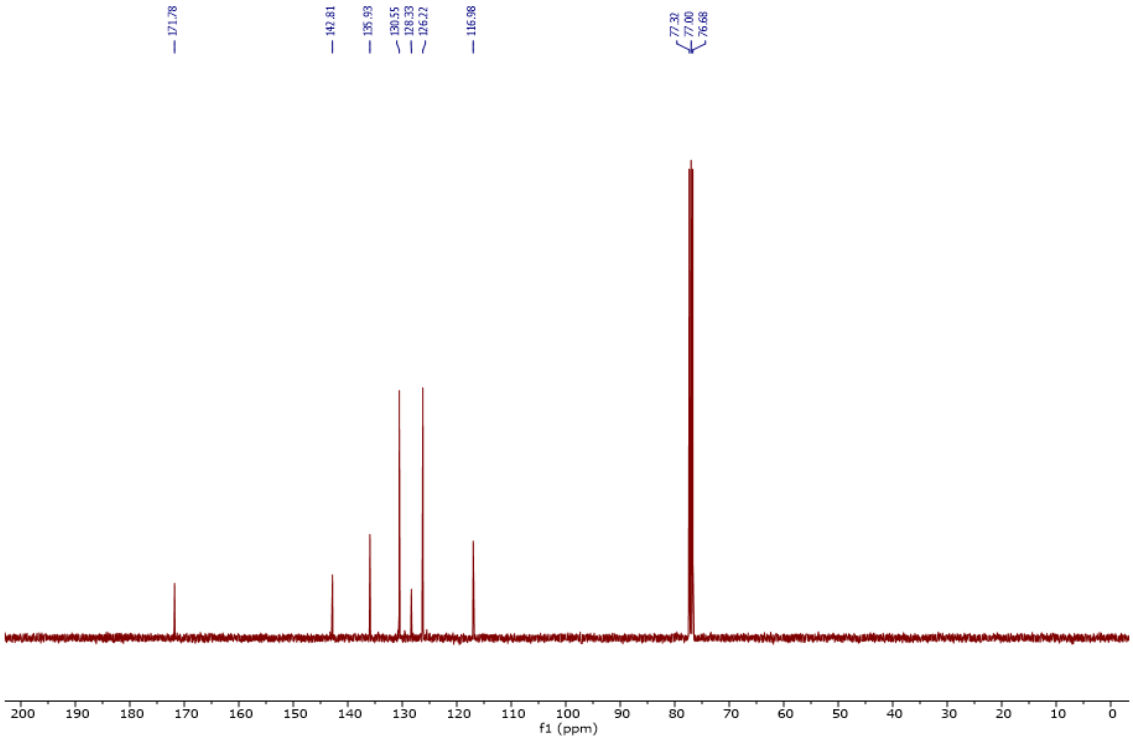


4-Methoxystyrene **22** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

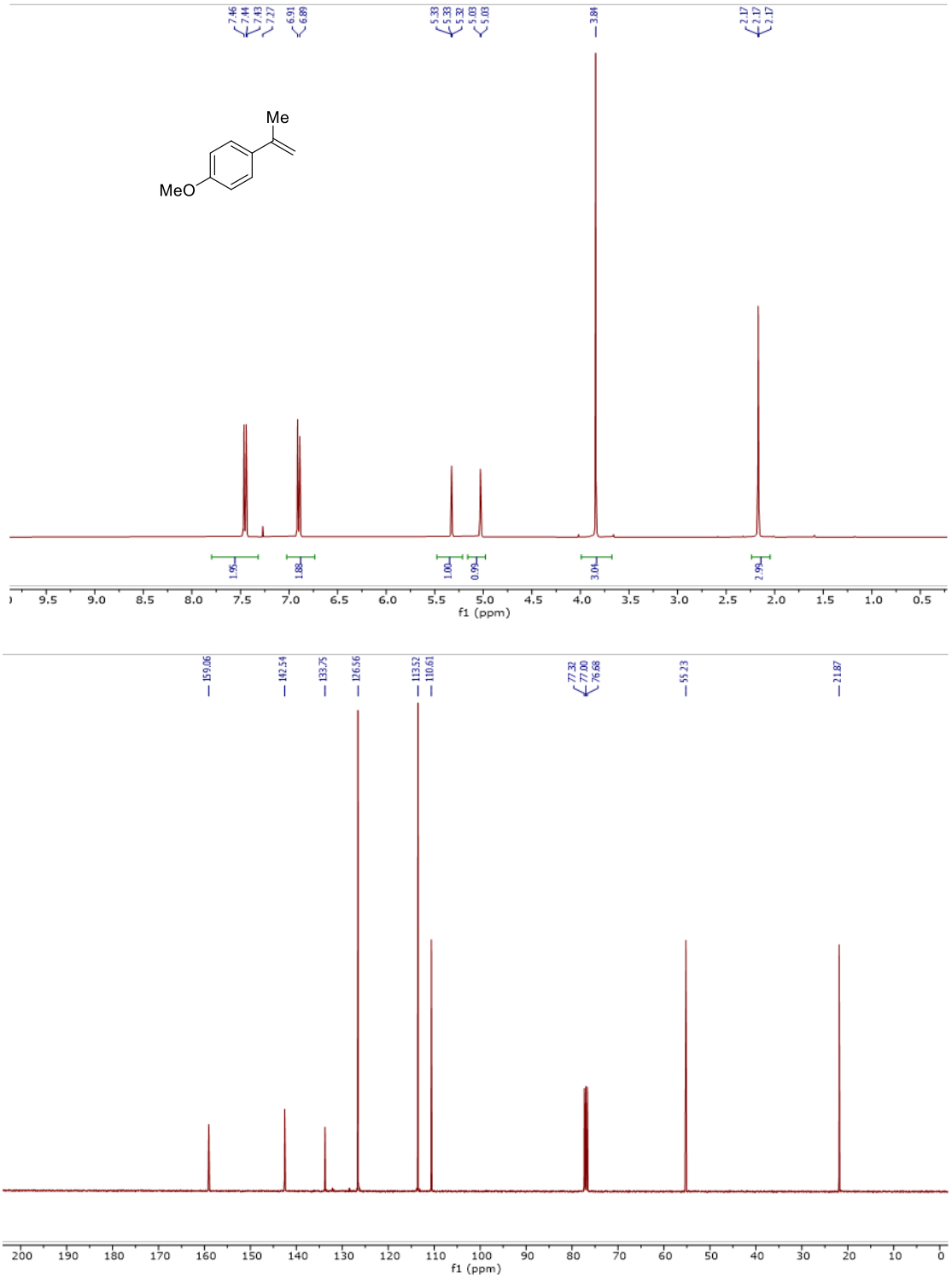


4-Vinylbenzoic acid **23** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

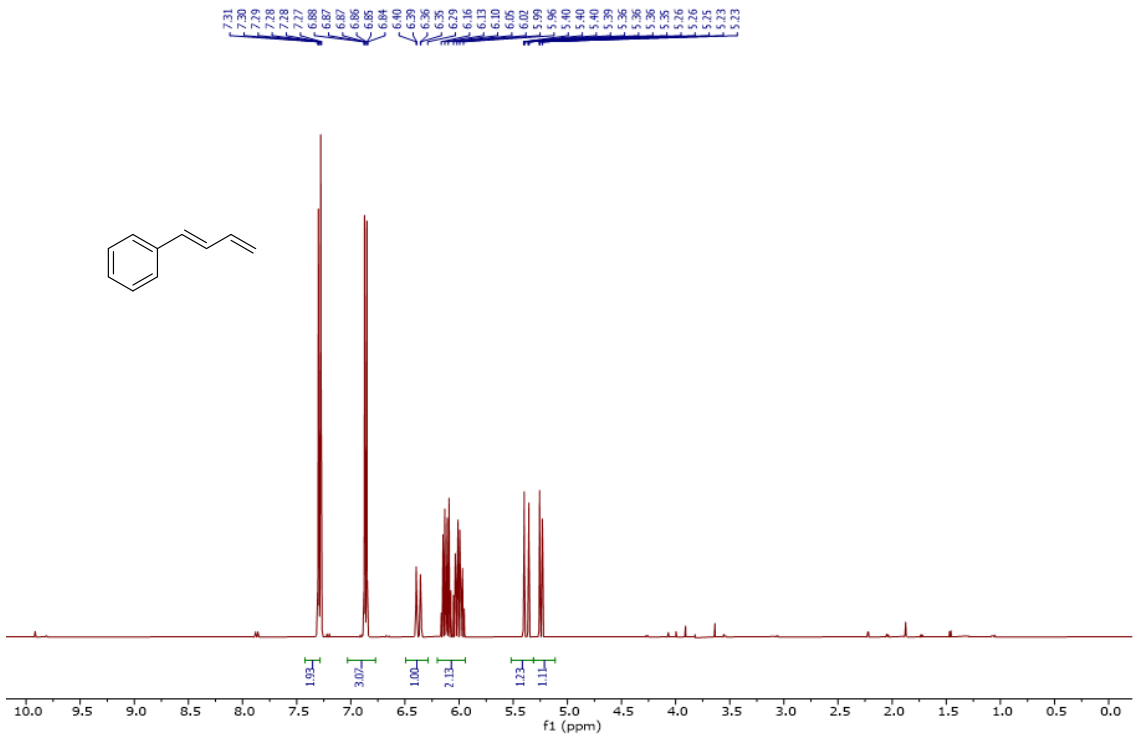


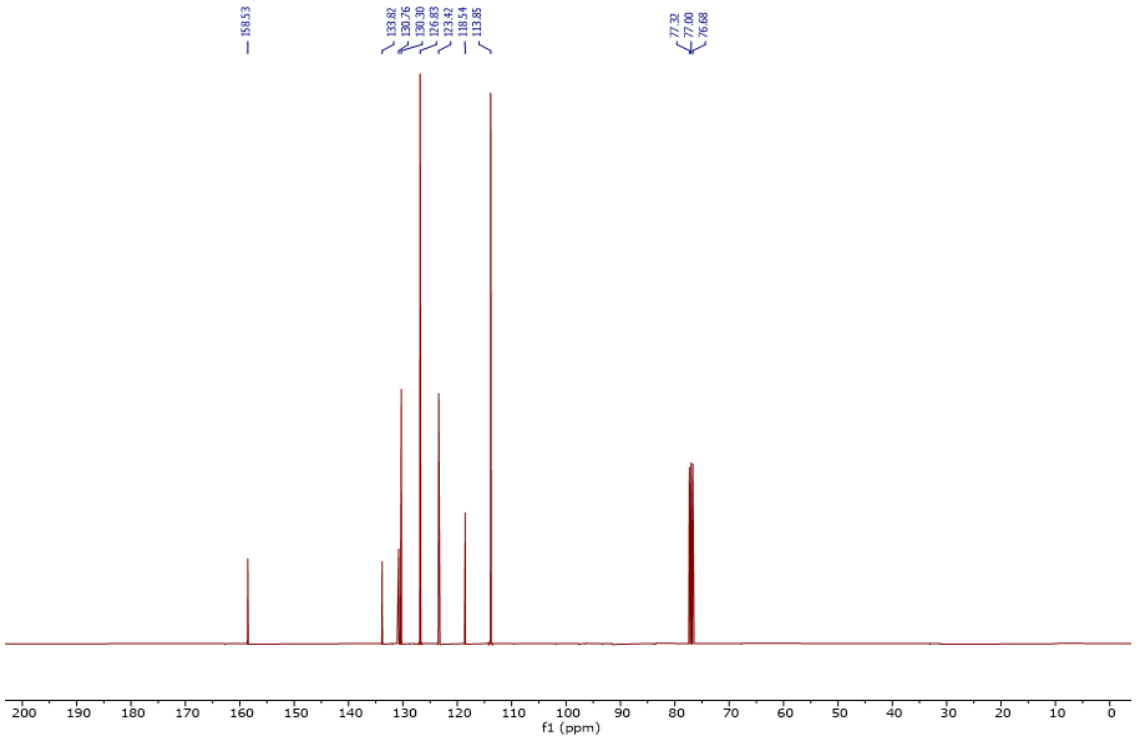


2-Methyl-2-(4-methoxyphenyl)ethene **24** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

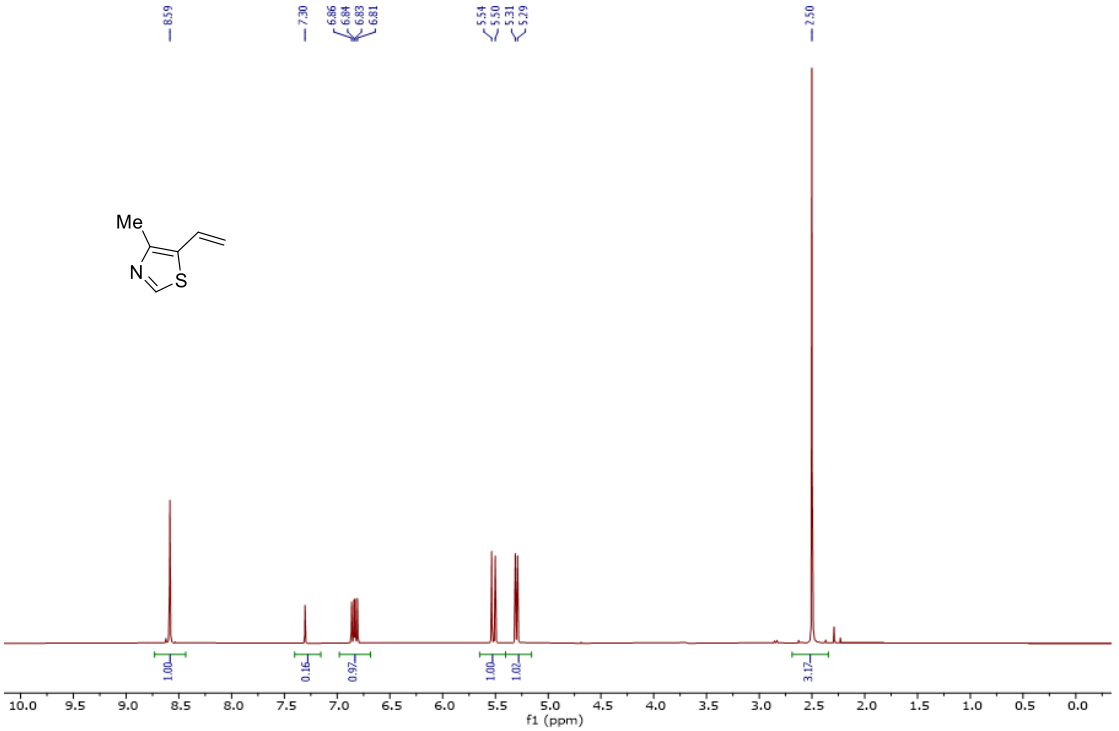


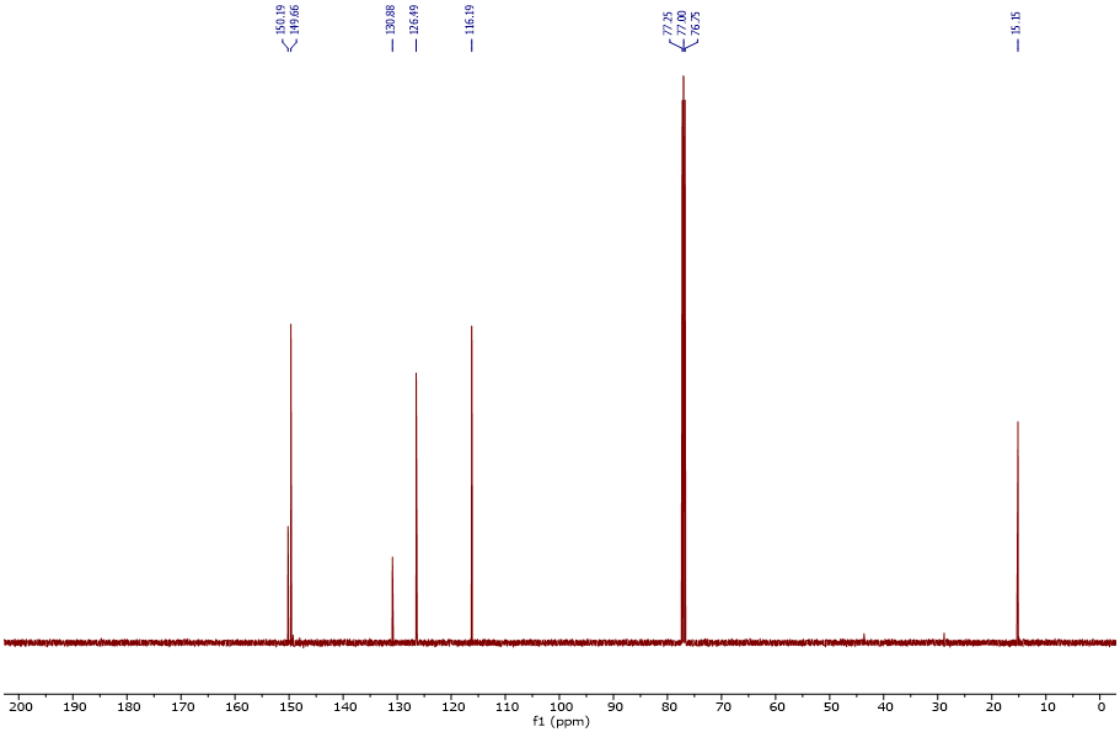
1,3-(Butadien-1-yl)benzene **25** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



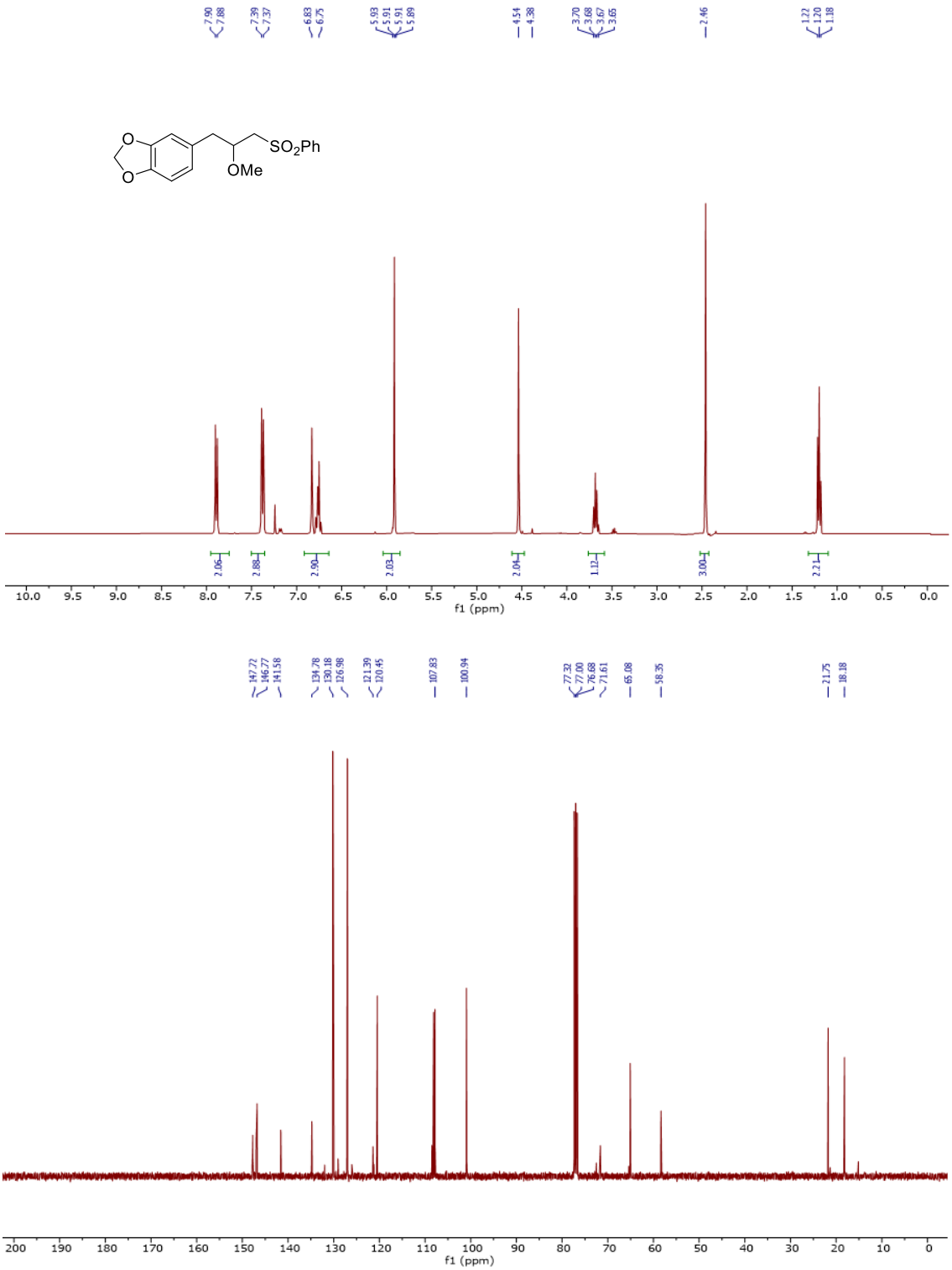


4-Methyl-5-vinylthiazole **26** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

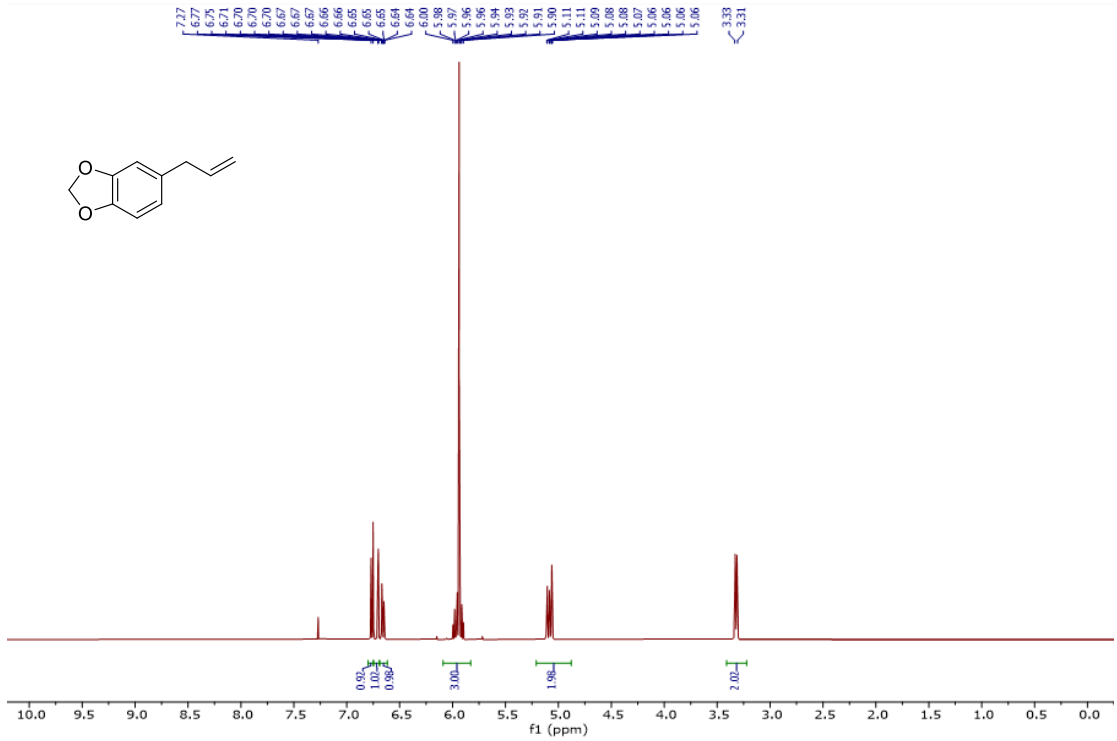


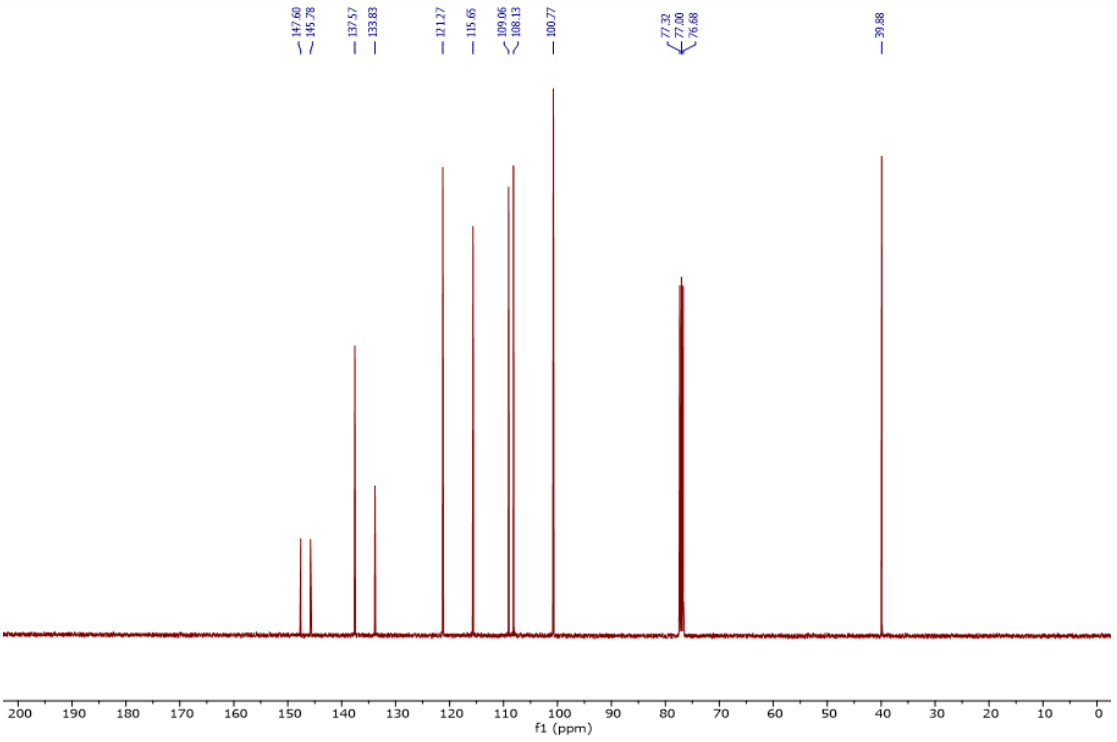


1-(1,3-Benzodioxol-5-yl)-3-(phenylsulfonyl)propan-2-ol methyl ether **32** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

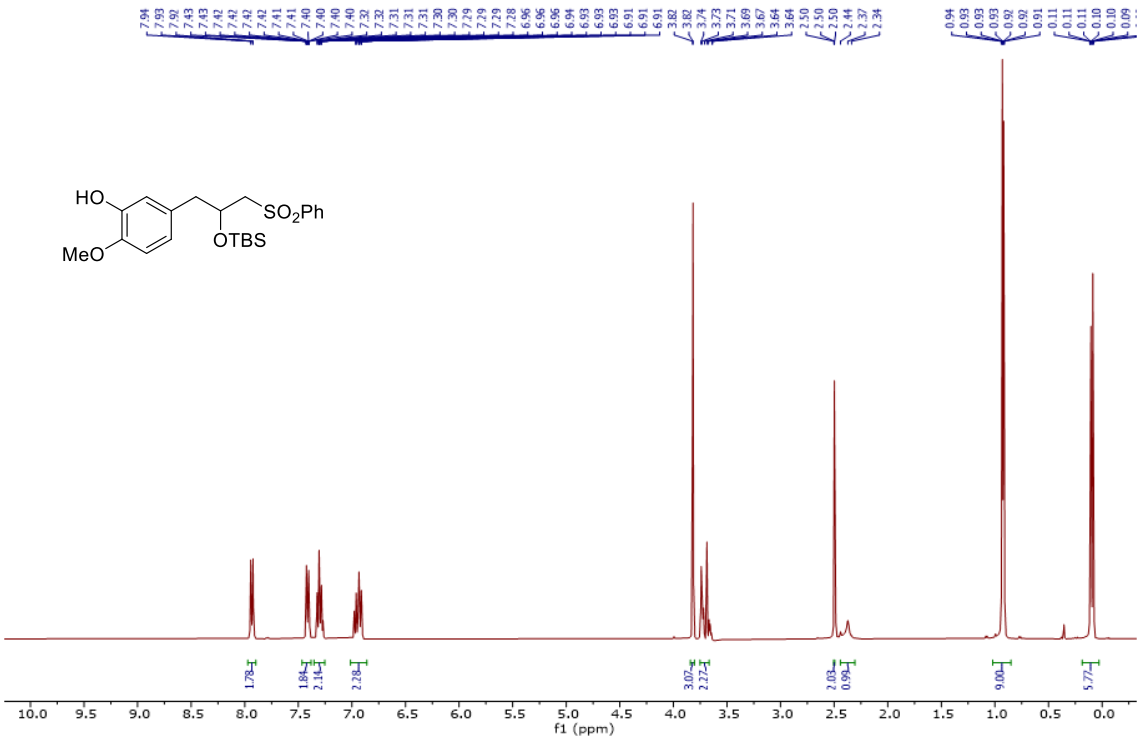


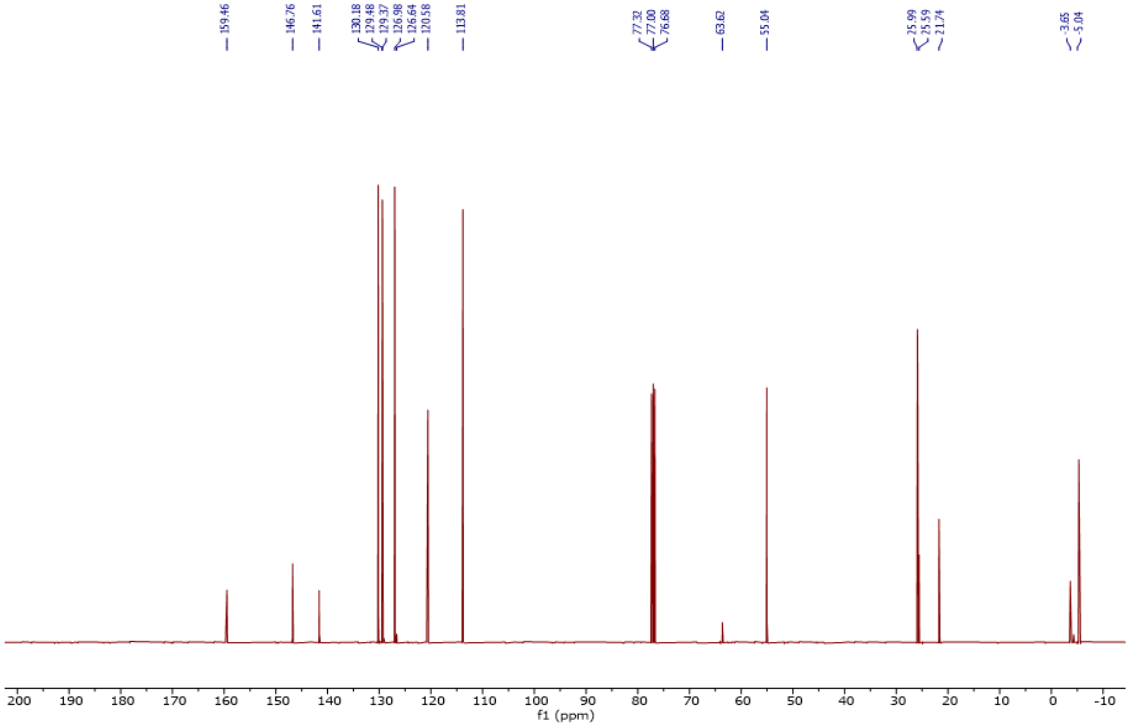
Safrole **33** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



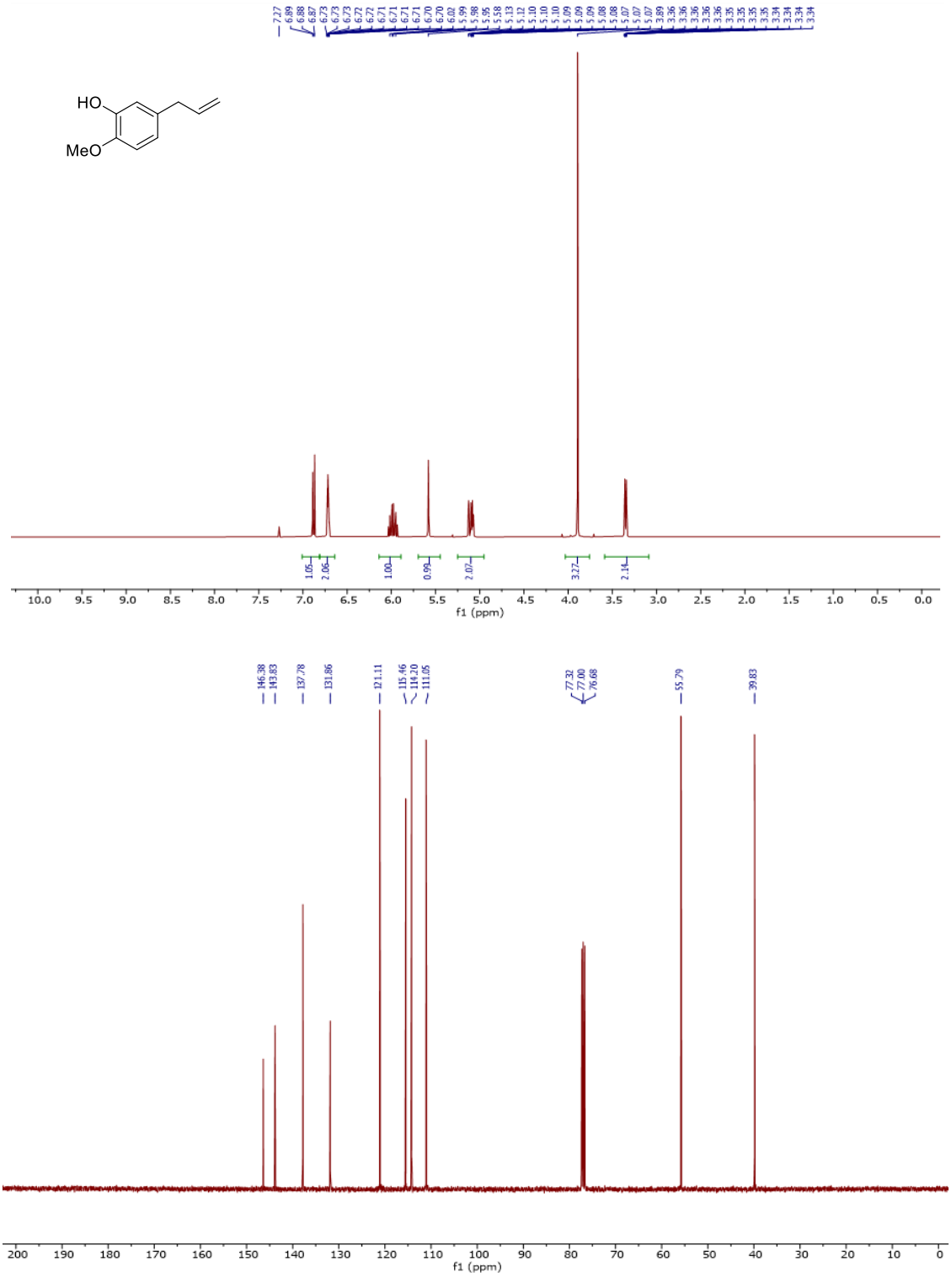


1-(3-Methoxyphenol)-3-(phenylsulfonyl)propan-2-ol tertbutyl dimethyl silyl ether **34** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

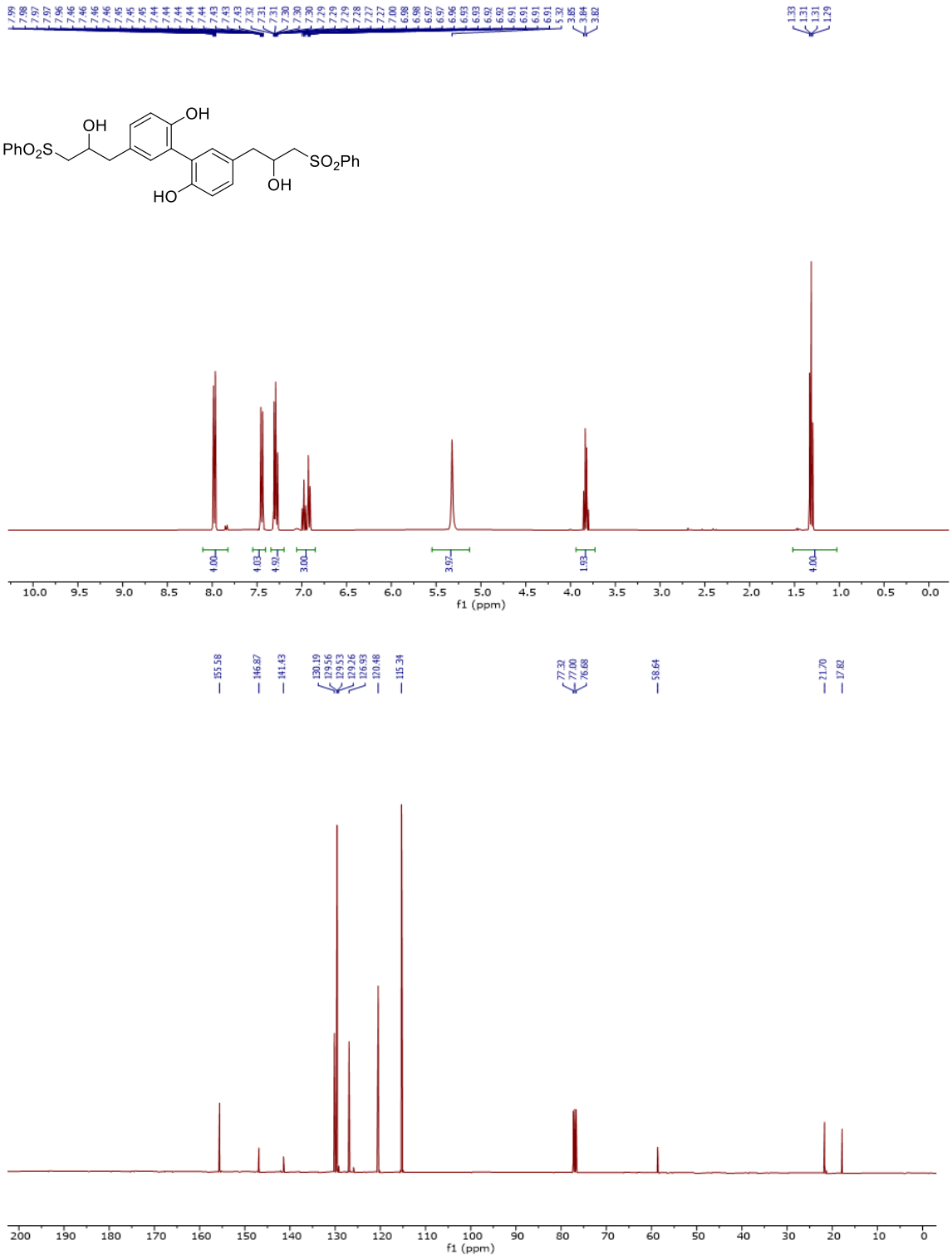




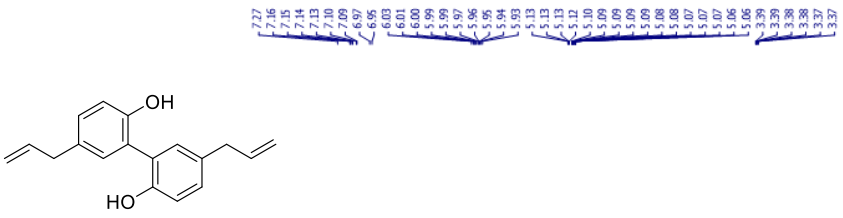
Chavibetol **35** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

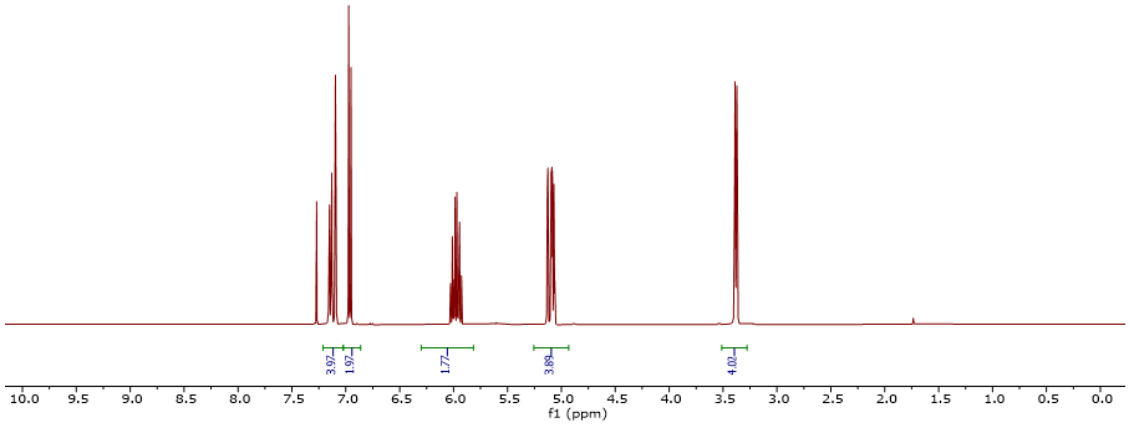


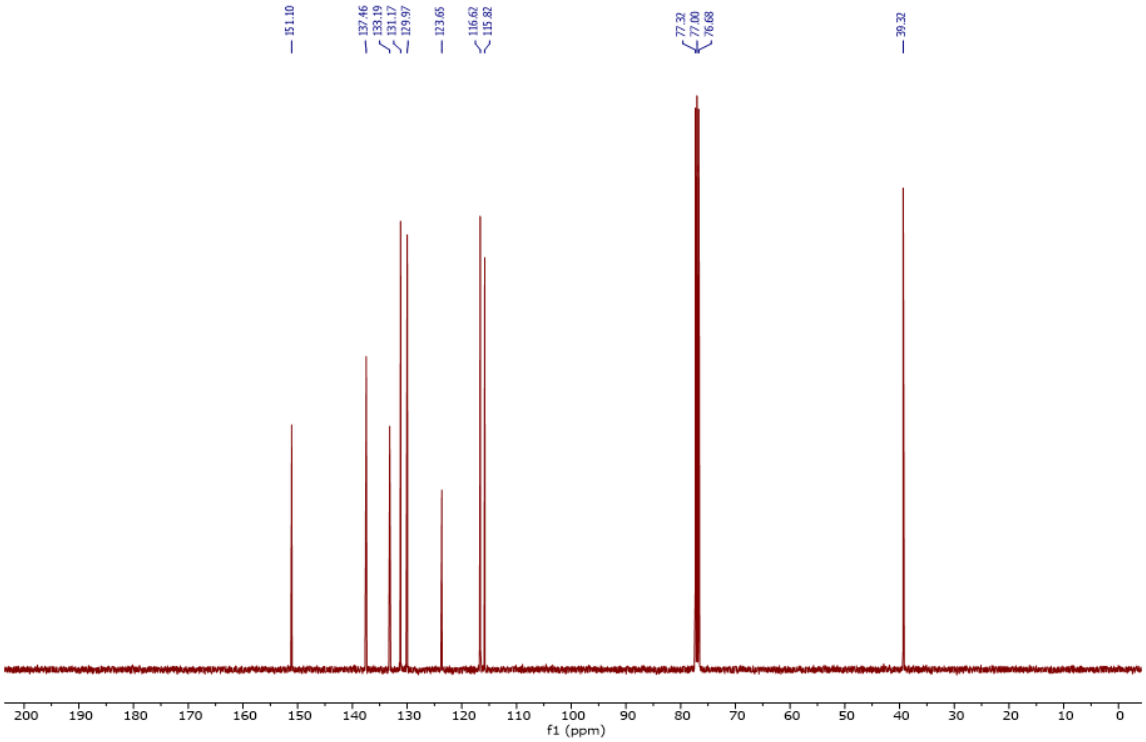
6,6’-Dihydroxy-[1,1’-biphenyl]-α3,α3’-bis(3-phenylsulfonyl-propan-2-ol) **36** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



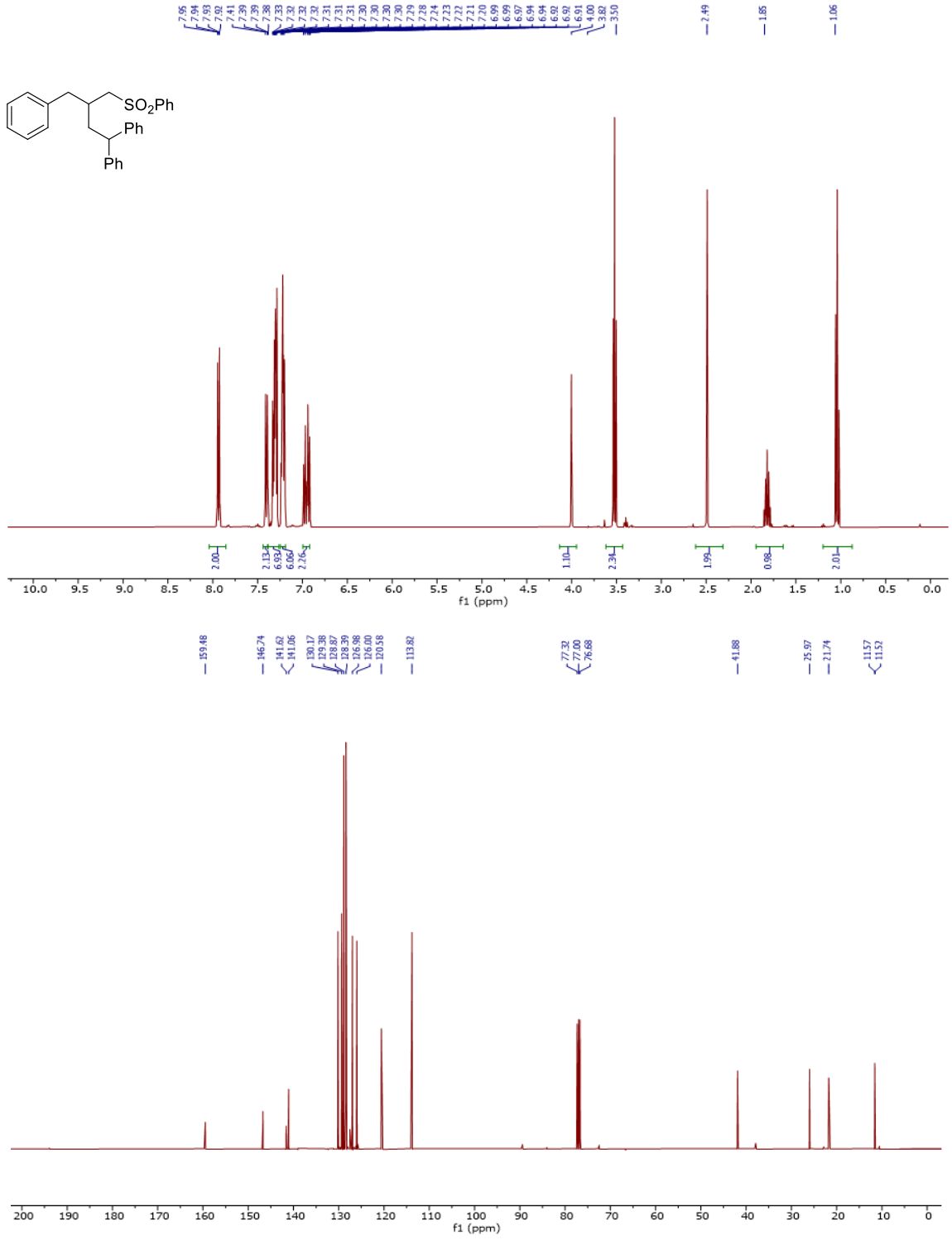
Magnolol **37** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



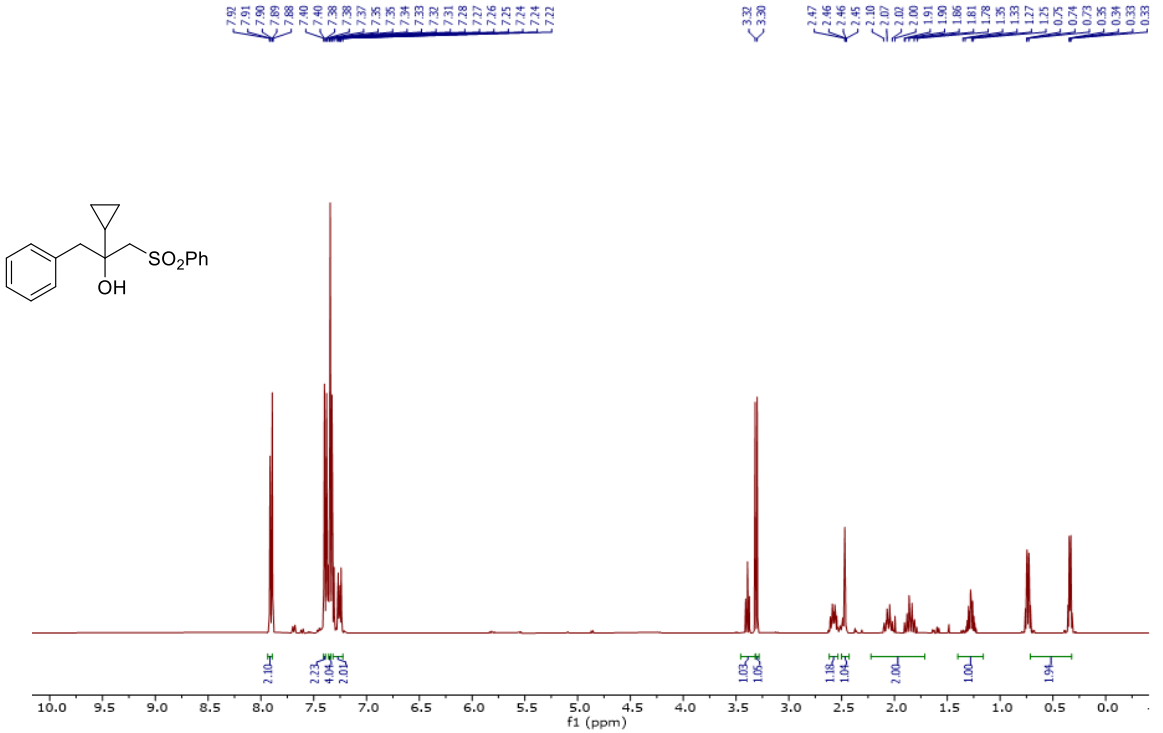


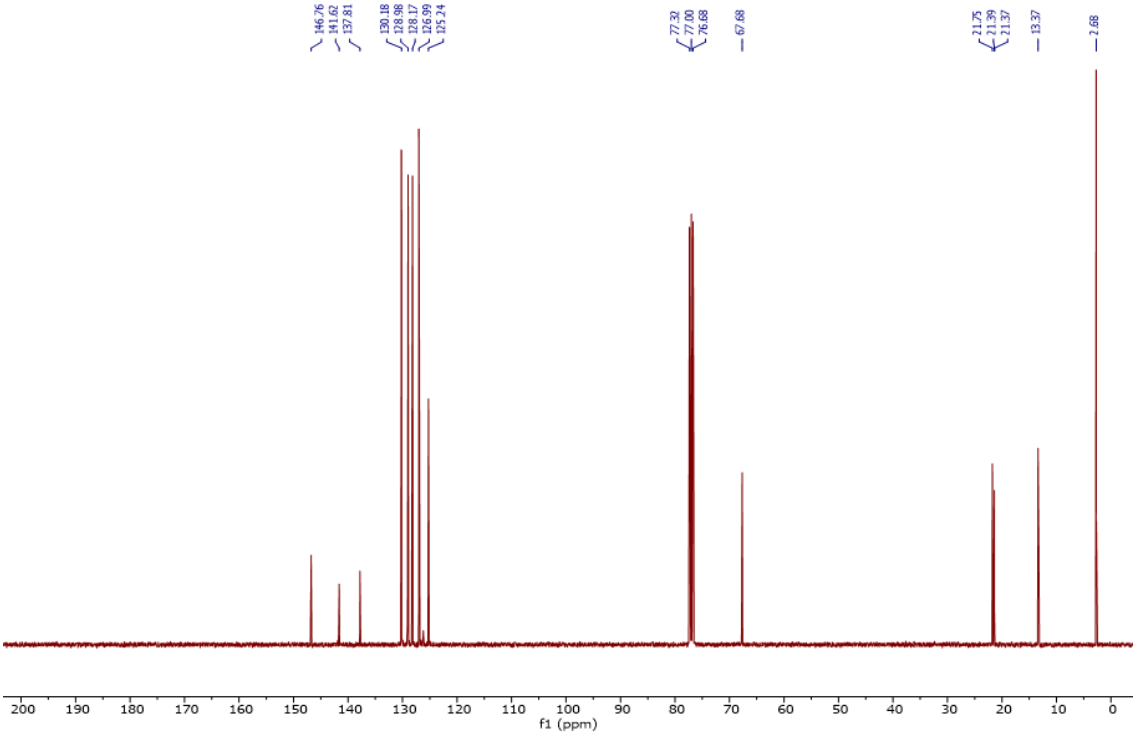


1,1-Diphenyl-3-(4-methoxytolyl)-4-phenylsulfone **40** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

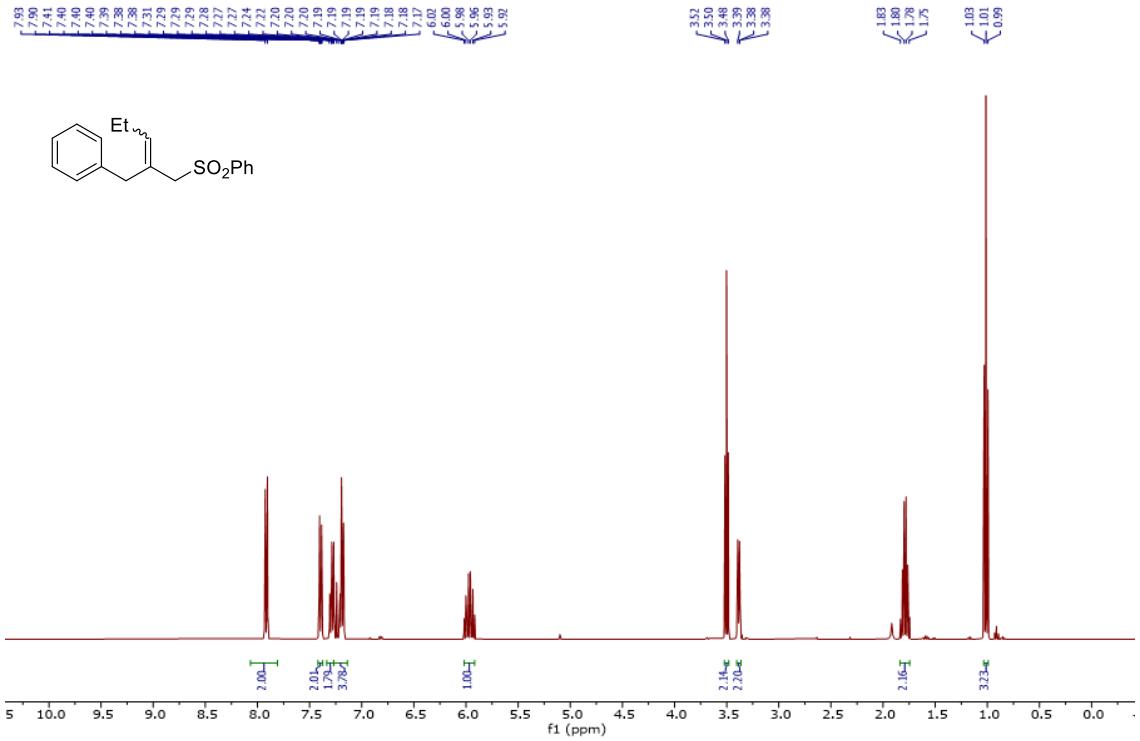


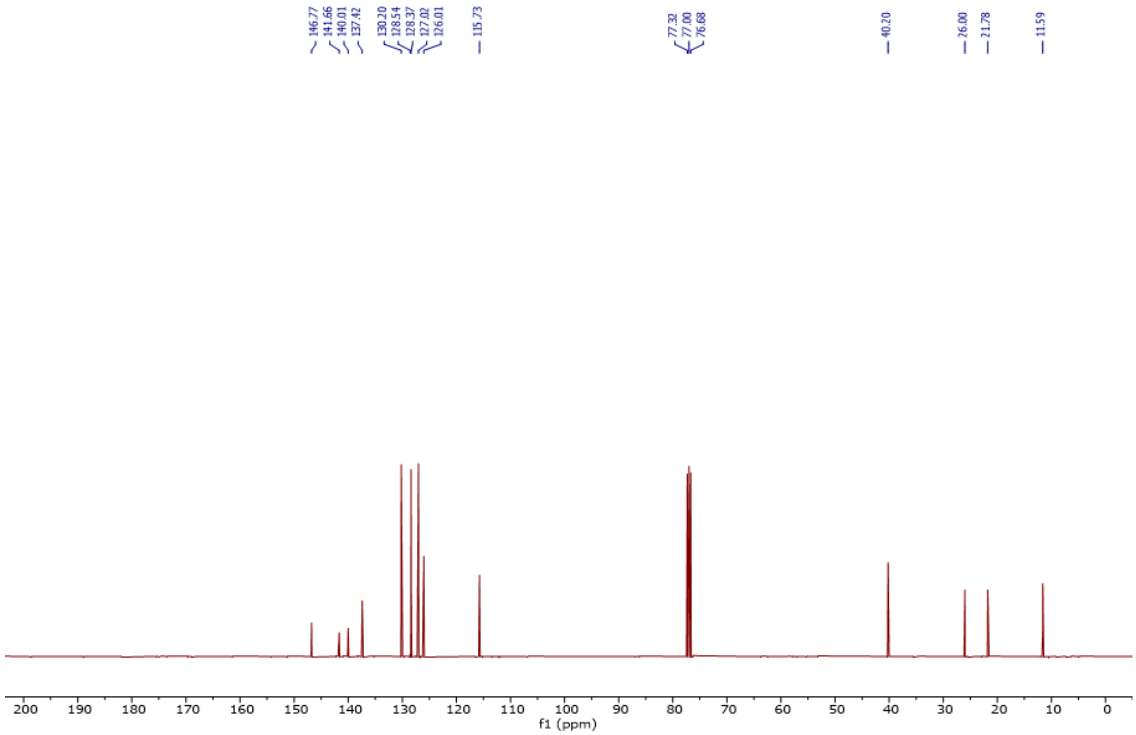
2-Cyclopropyl-1-phenyl-3-(phenylsulfonyl)propan-2-ol **S38** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



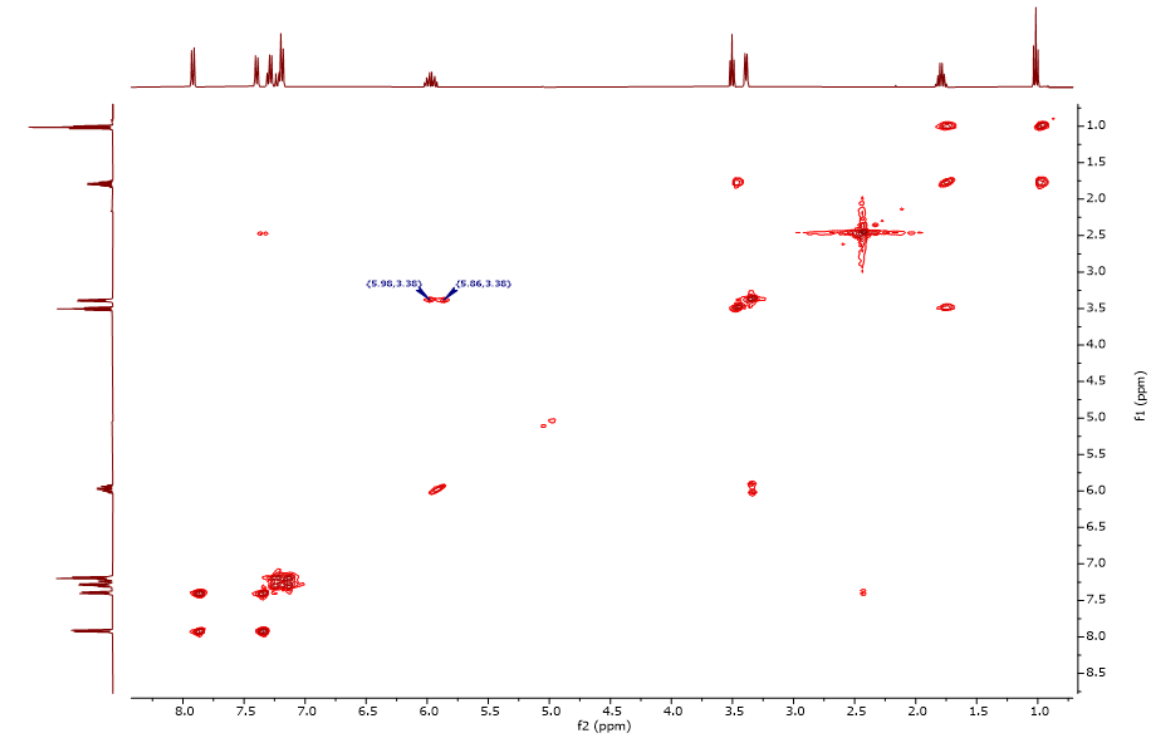


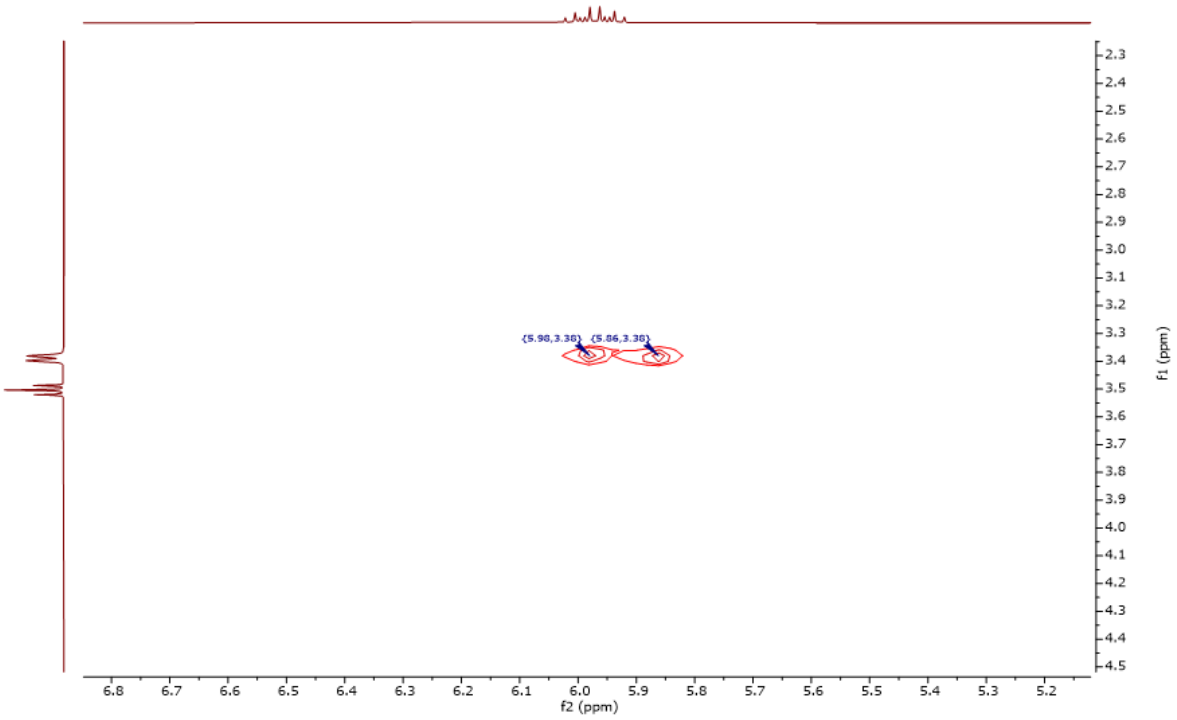
3-Ethyl-1-phenyl-2-(phenylsulfonyl)pent-2-ene **42** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



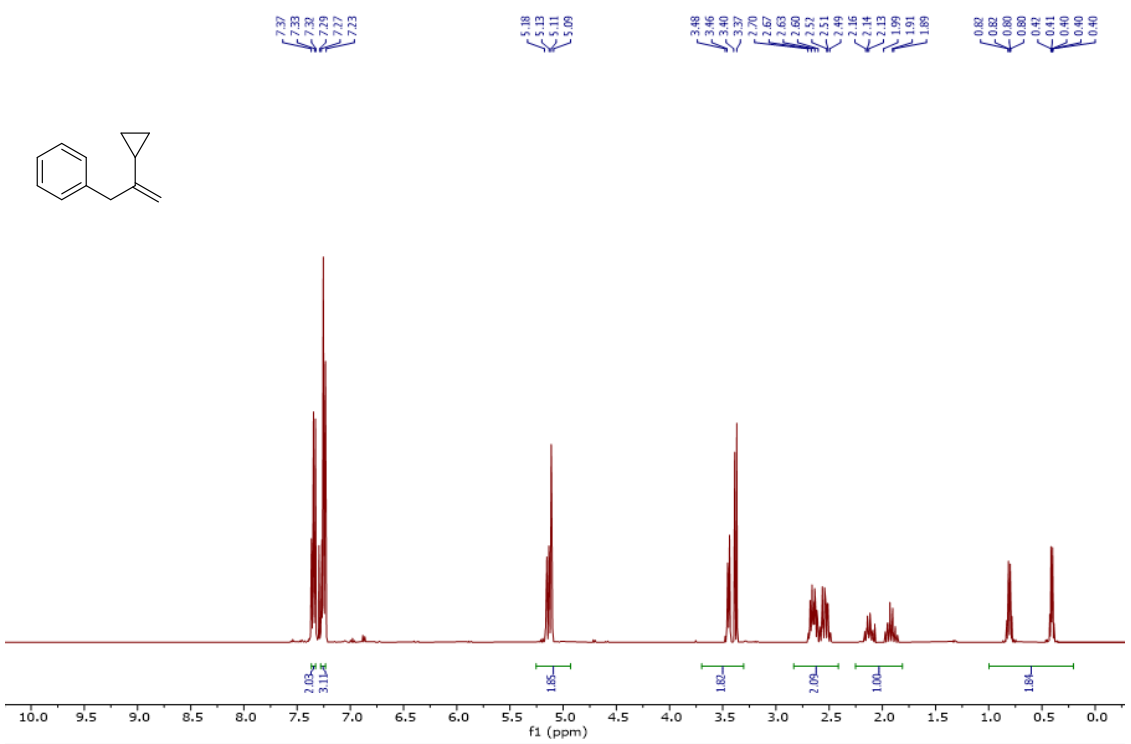


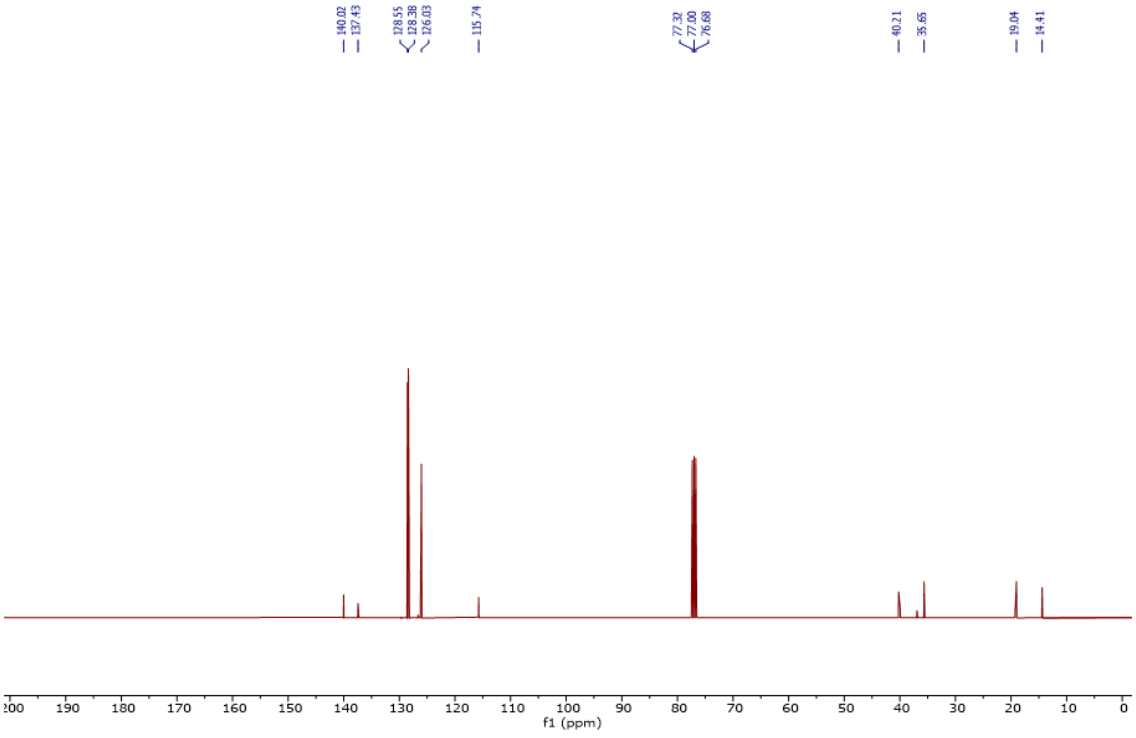
^{1}H-COSY



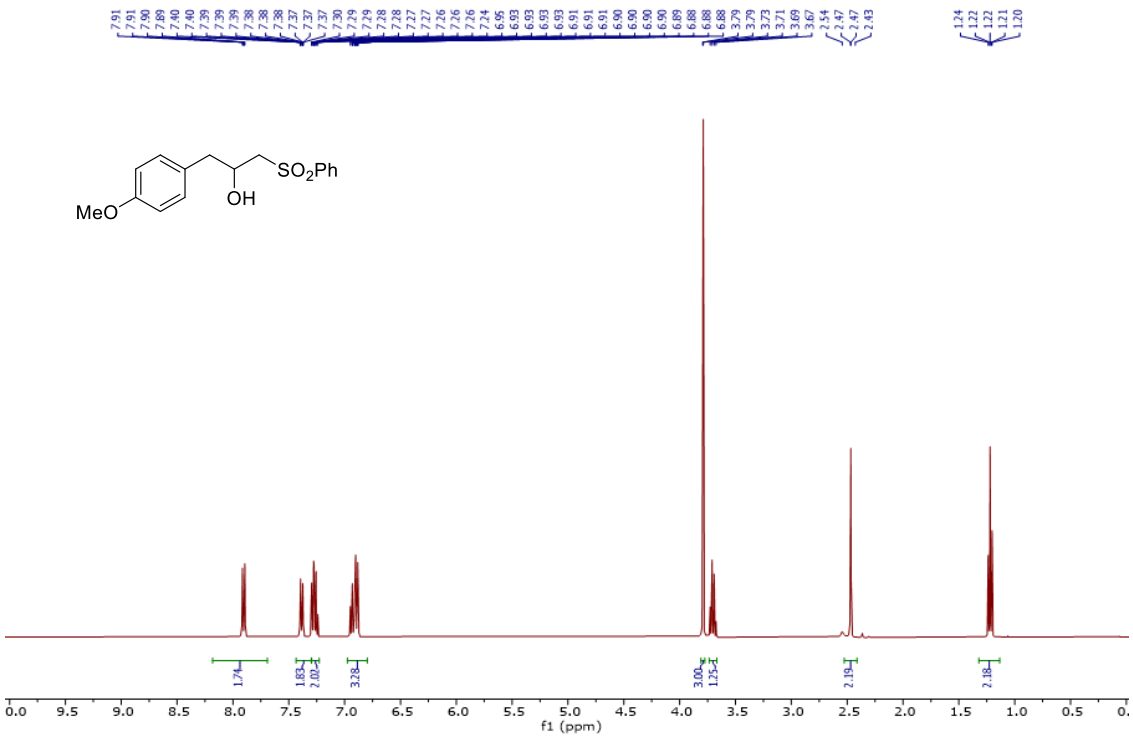


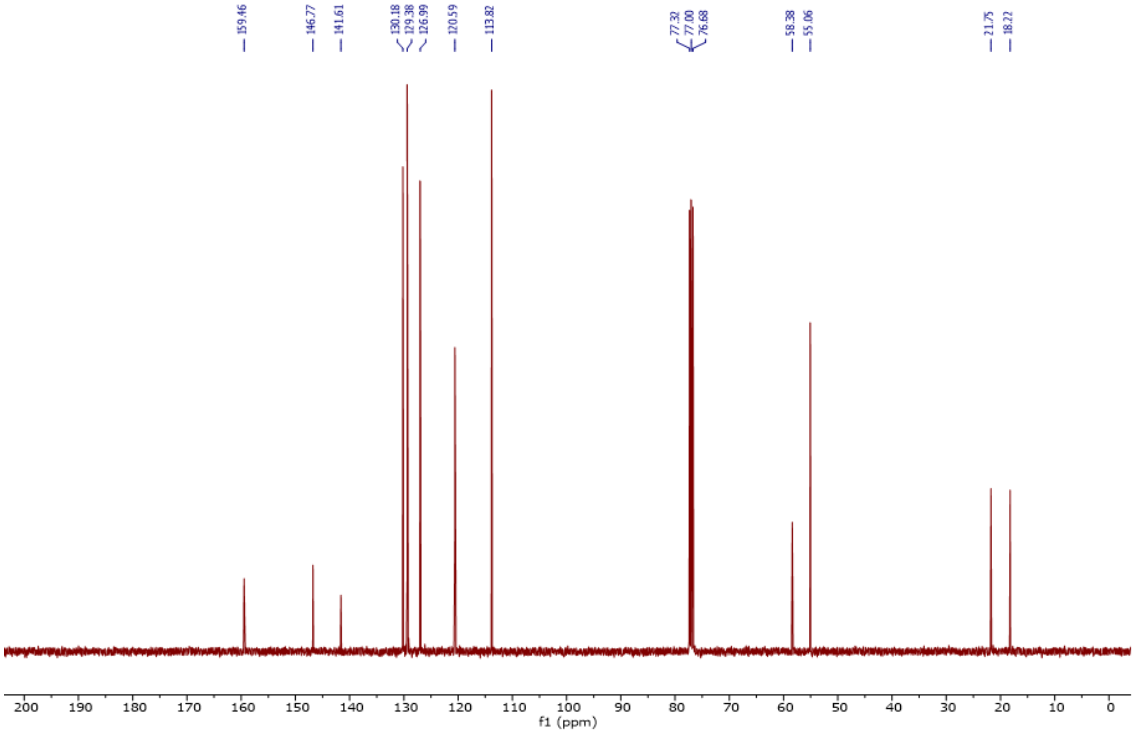
2-Cyclopropyl-3-phenylpropene **43** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



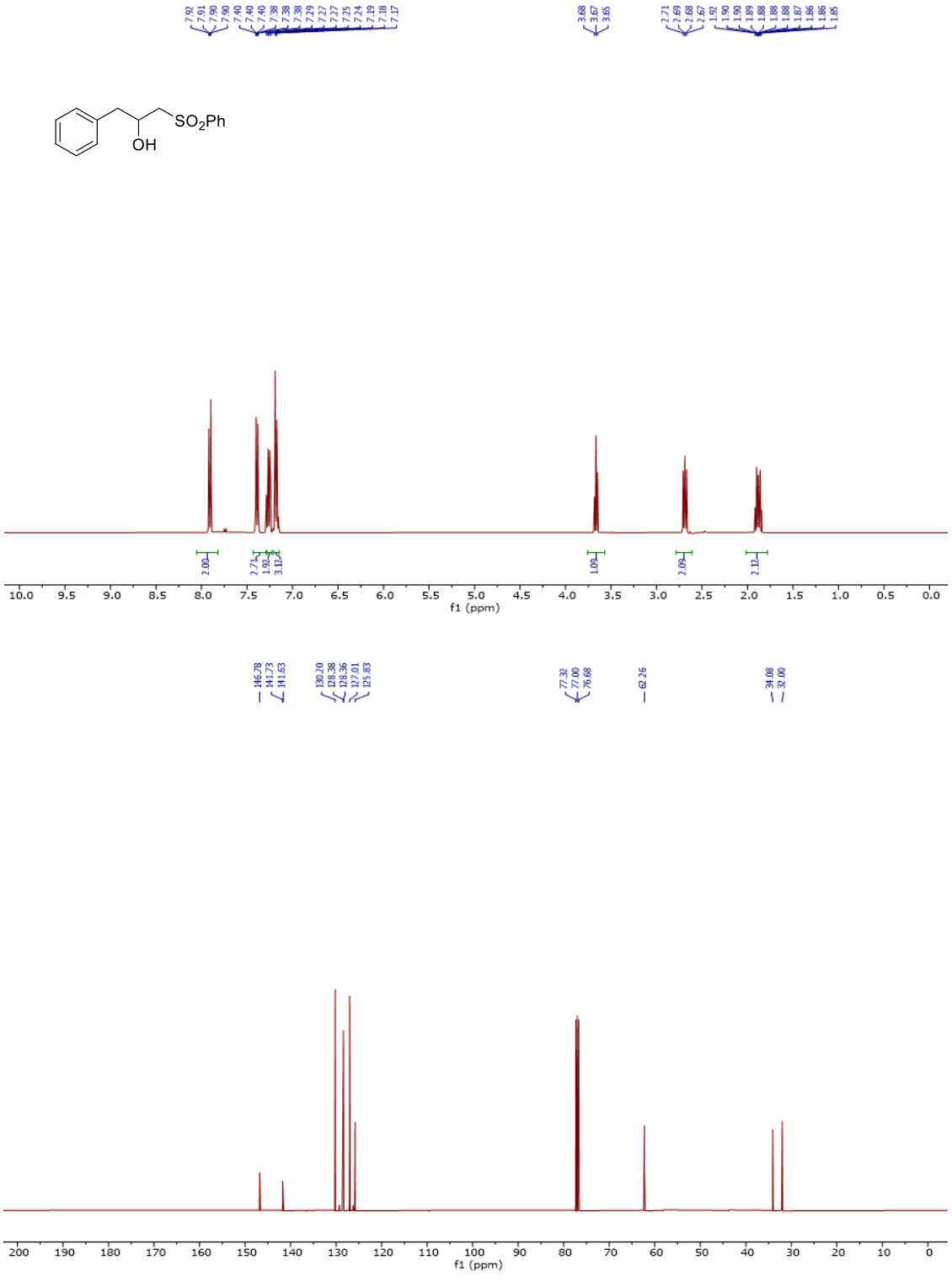


1-(4-Methoxyphenyl)-3-(phenylsulfonyl)propan-2-ol **1** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

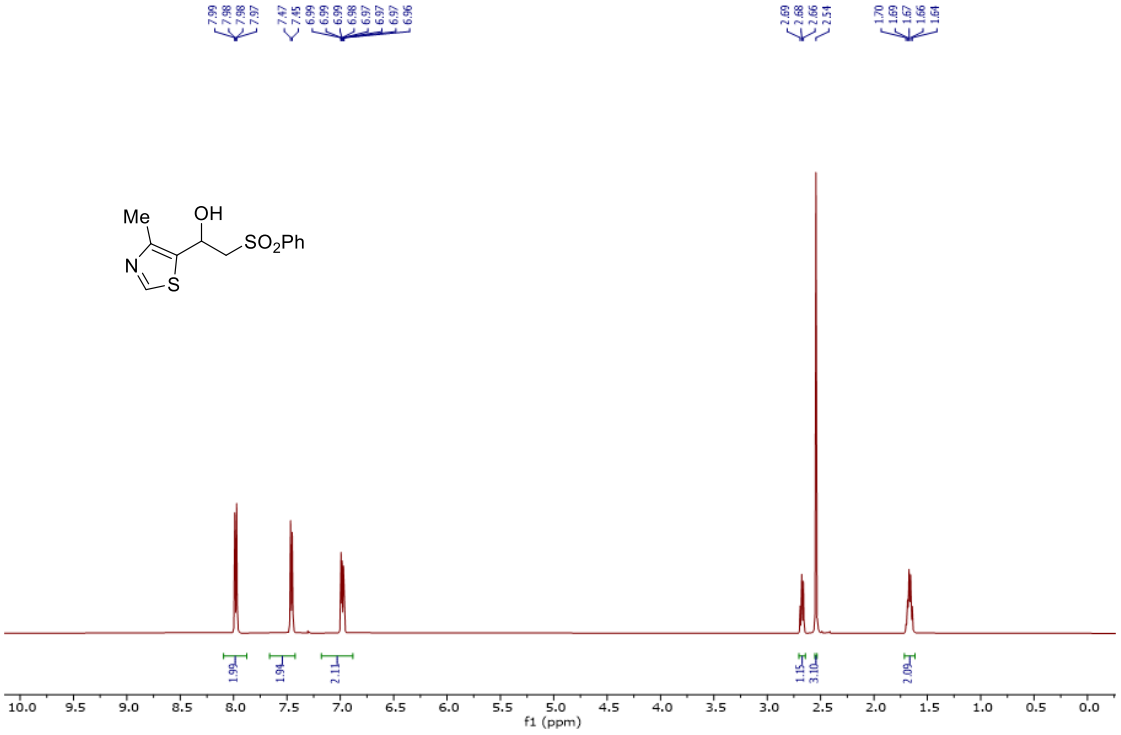


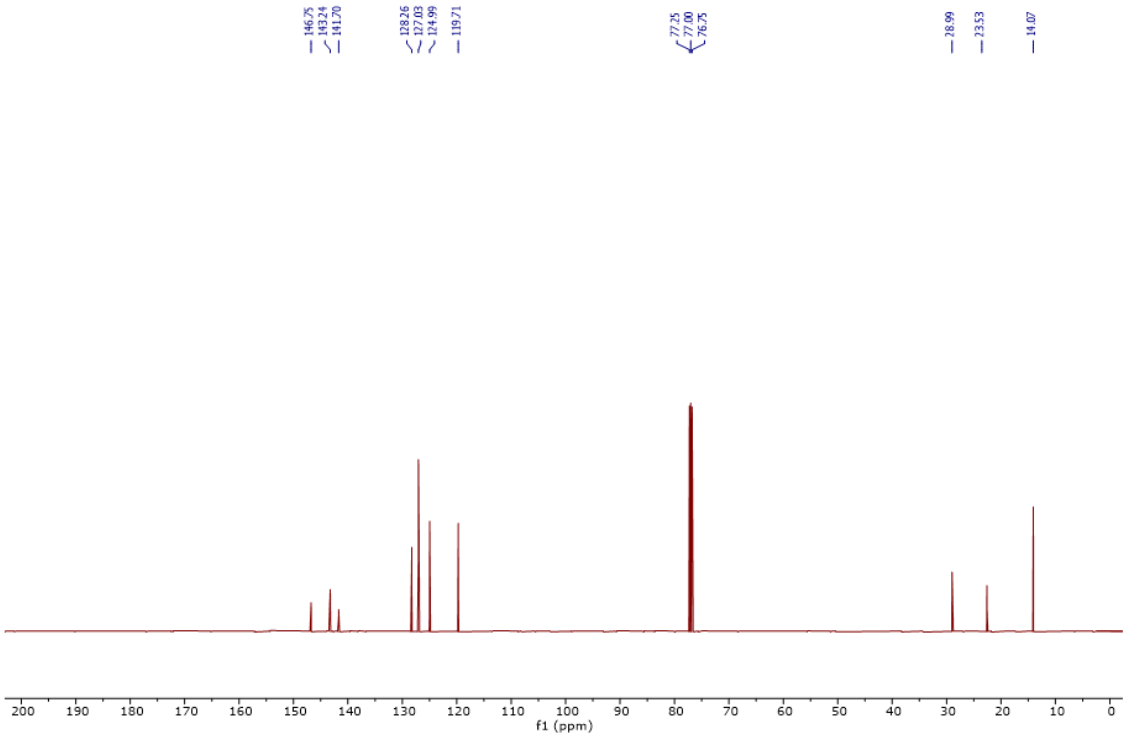


1-Phenyl-3-(phenylsulfonyl)propan-2-ol **38** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

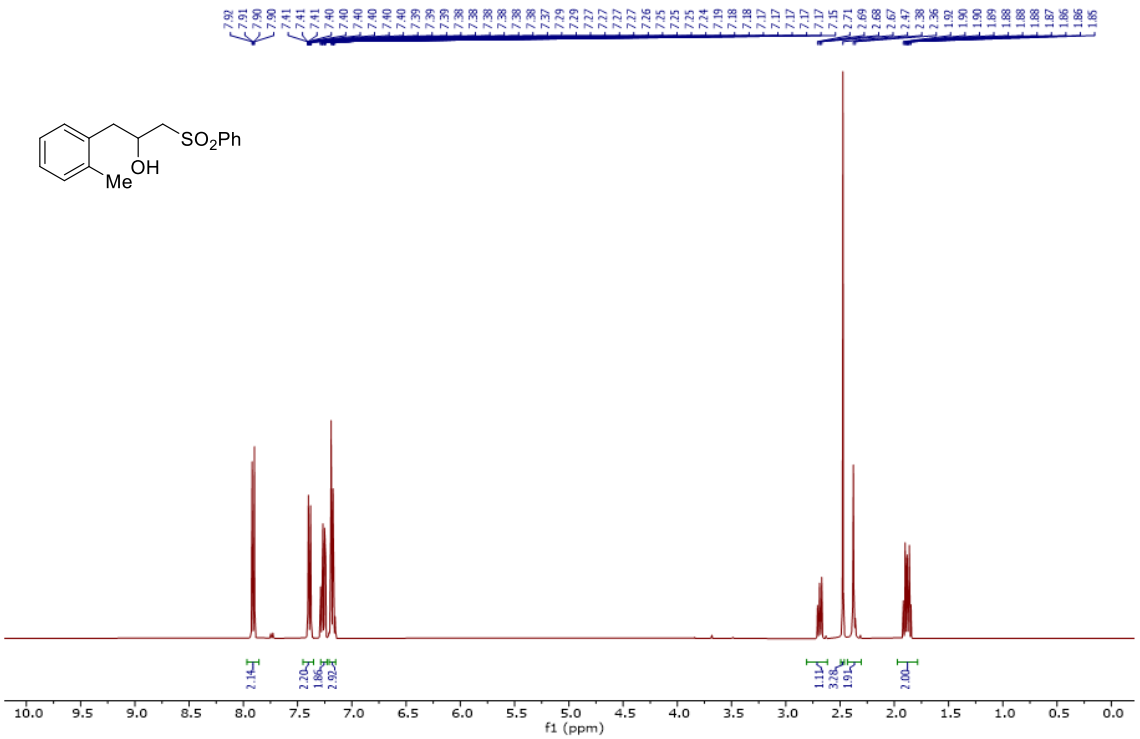


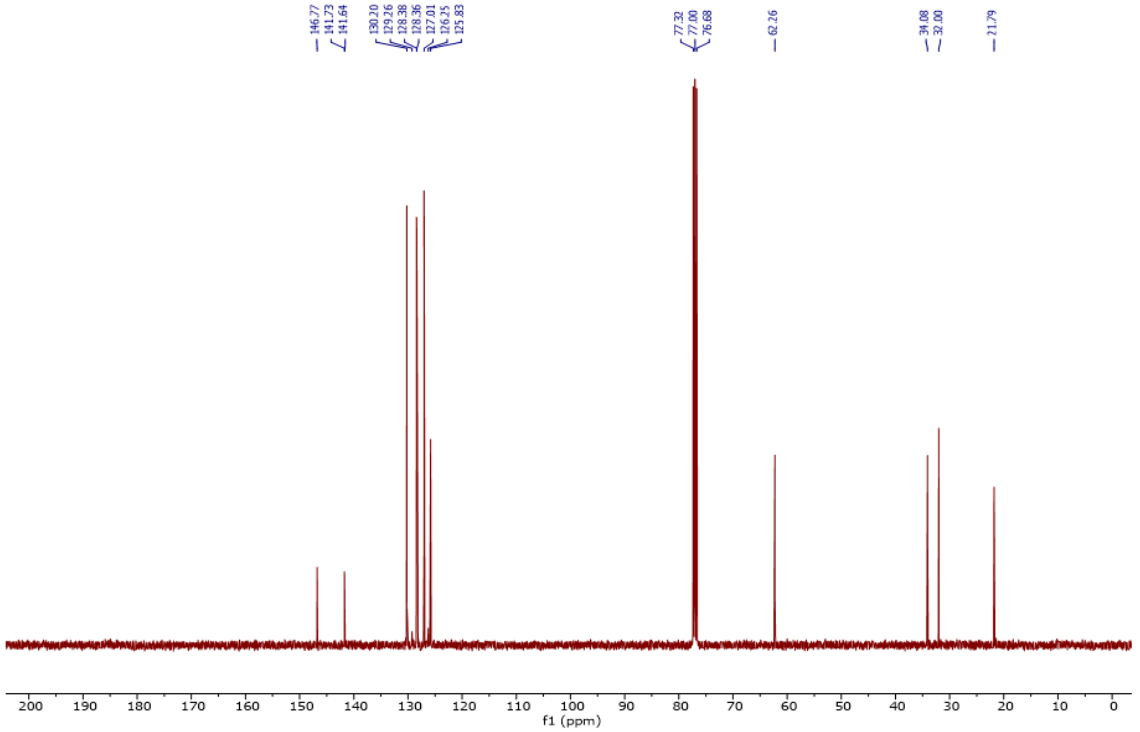
1-(4-Methyl-5-vinylthiazyl)-2-(phenylsulfonyl)ethan-2-ol **S7** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



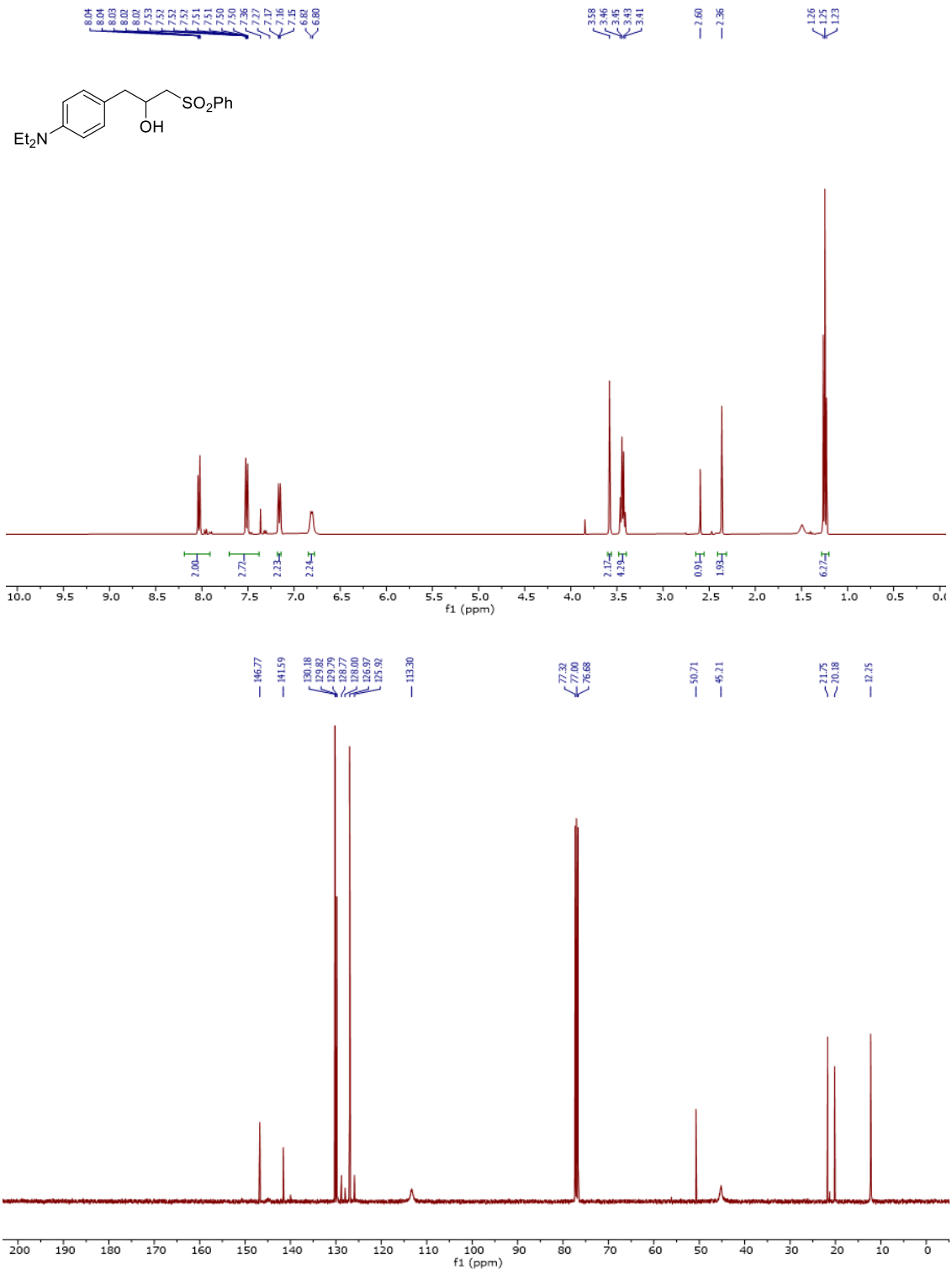


1-(2-Methylphenyl)-3-(phenylsulfonyl)propan-2-ol **S8** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

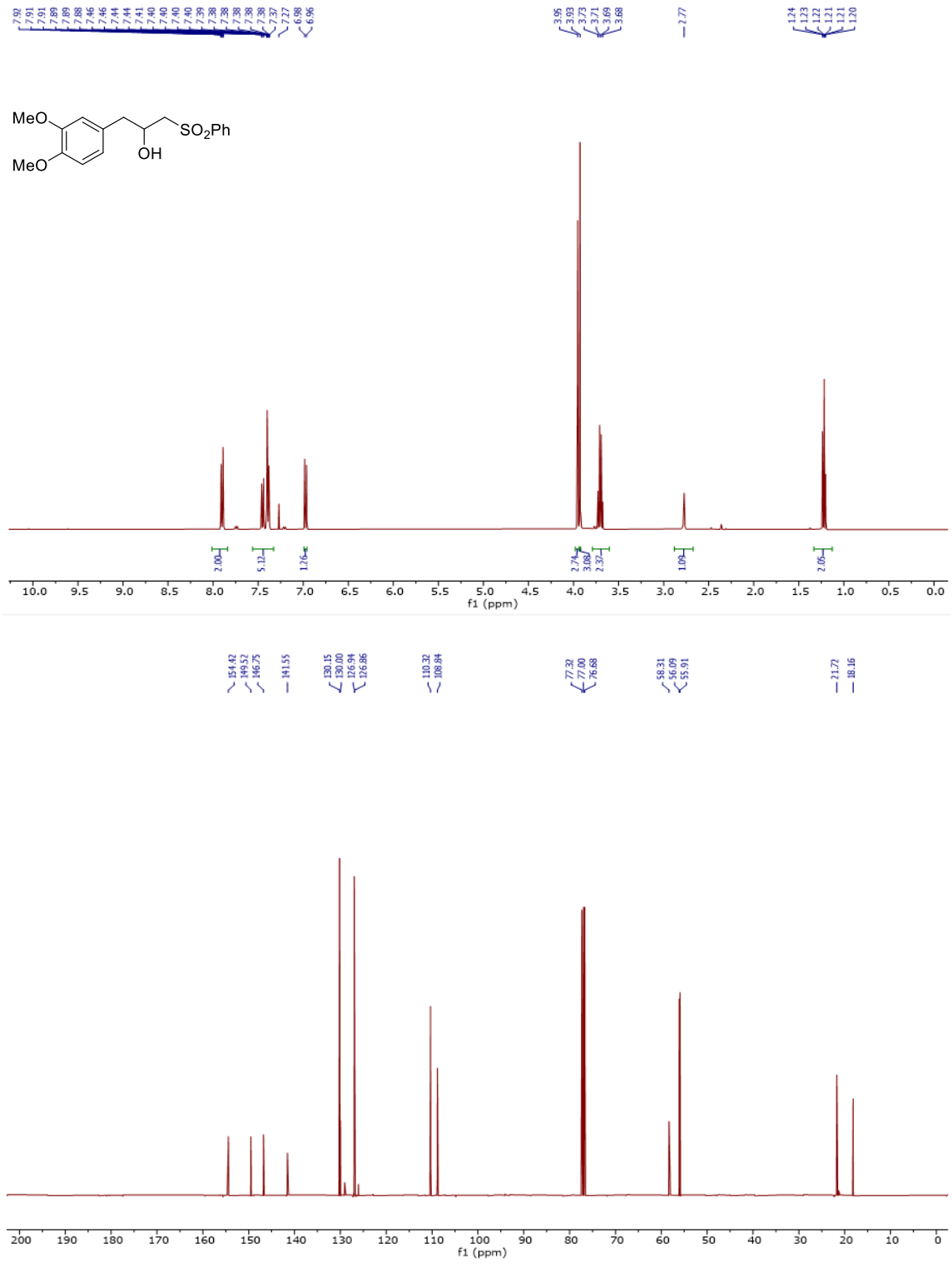




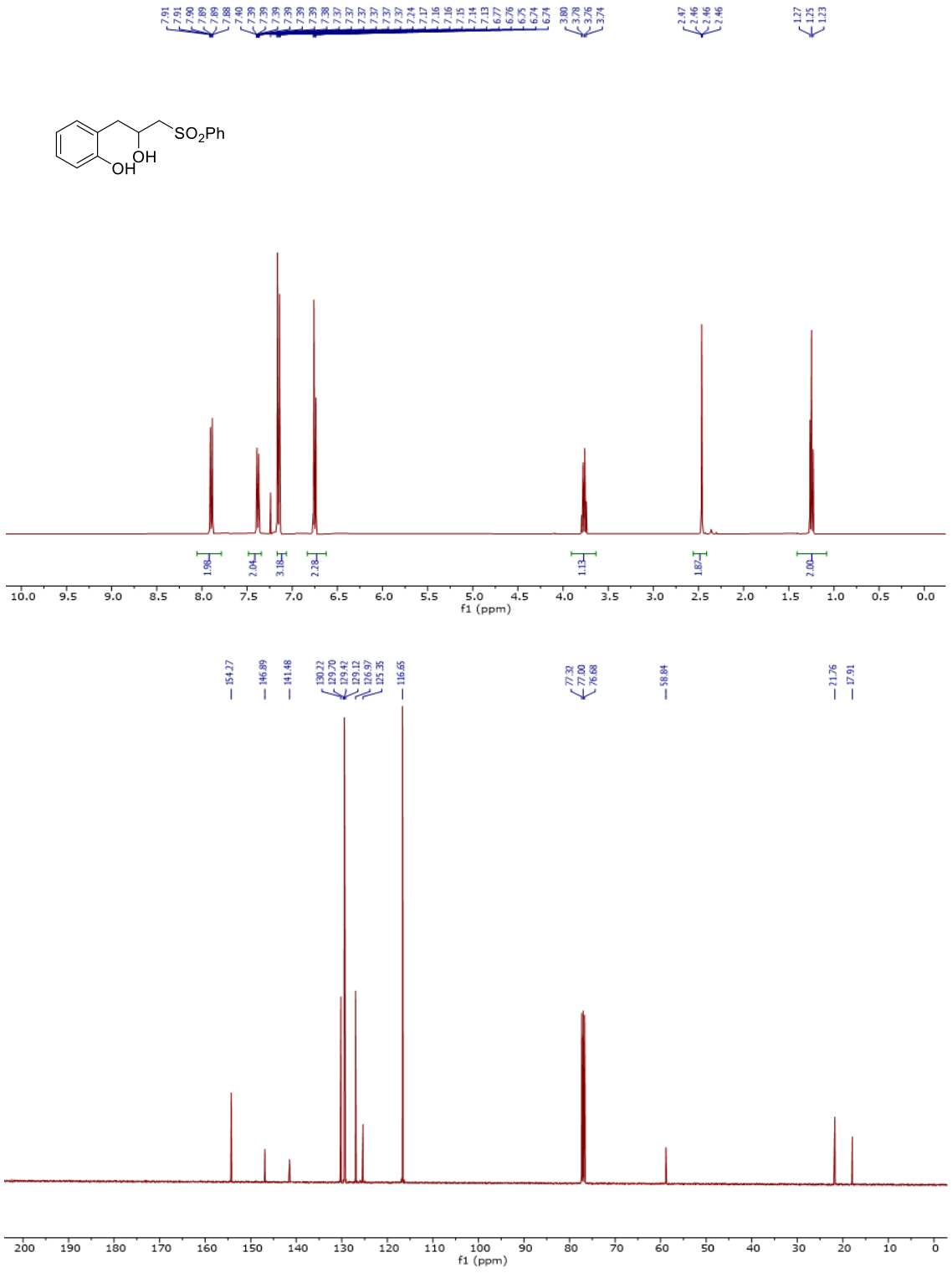
1-(4-Diethylaminophenyl)-3-(phenylsulfonyl)propan-2-ol **S9** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



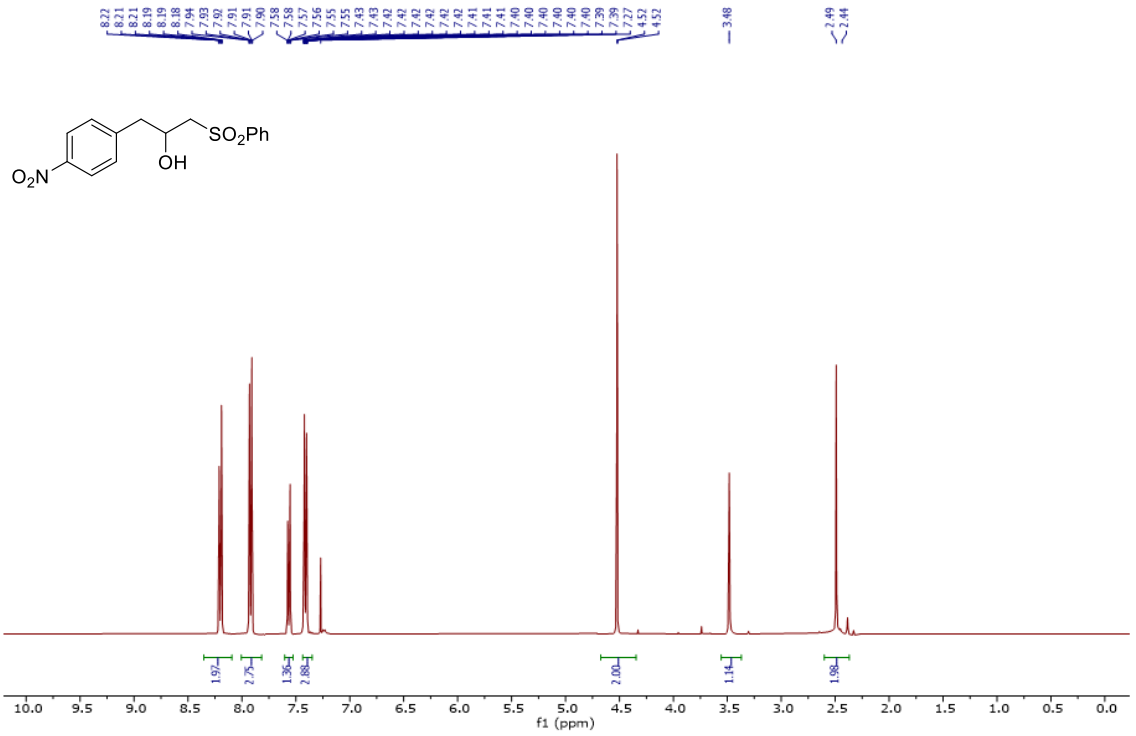
1-(3,4-Dimethoxyphenyl)-3-(phenylsulfonyl)propan-2-ol) **S10** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

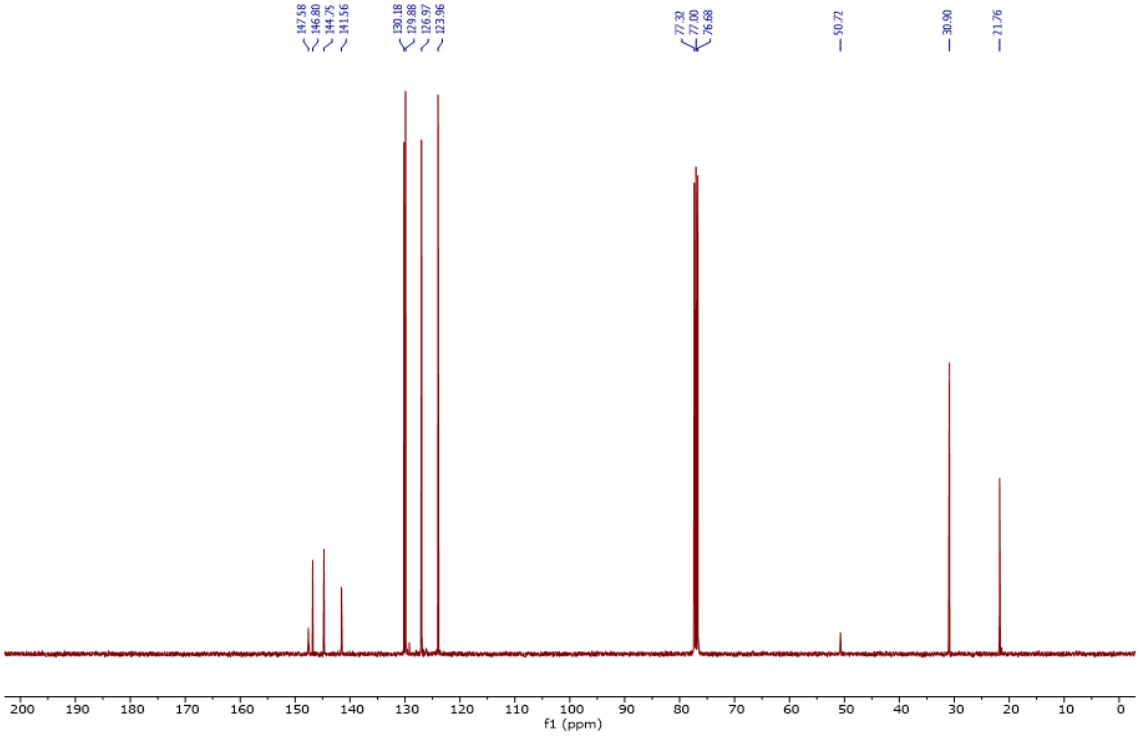


1-(2-Hydroxyphenyl)-3-(phenylsulfonyl)propan-2-ol **S11** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

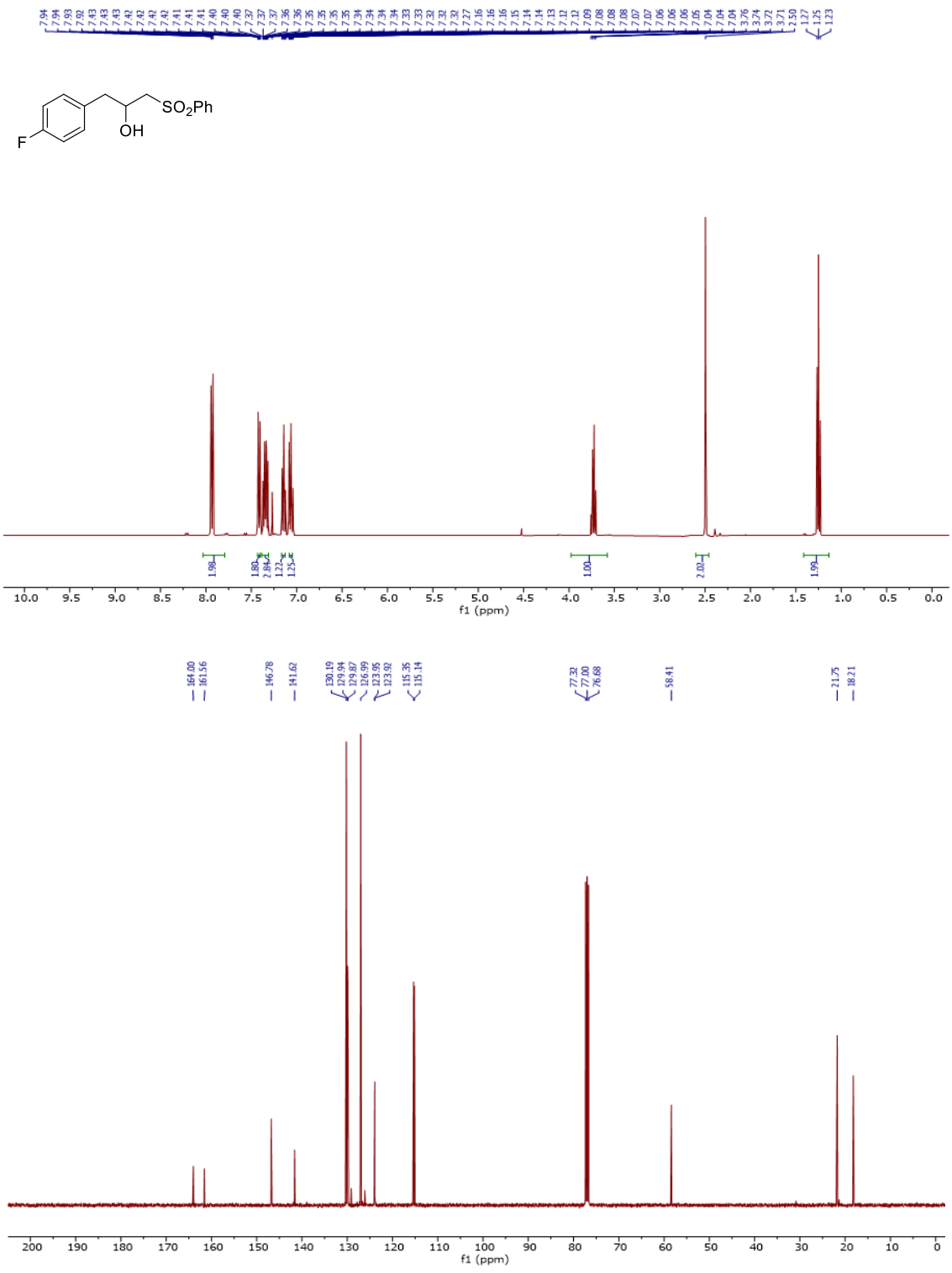


1-(4-Nitrophenyl)-3-(phenylsulfonyl)propan-2-ol **S12** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

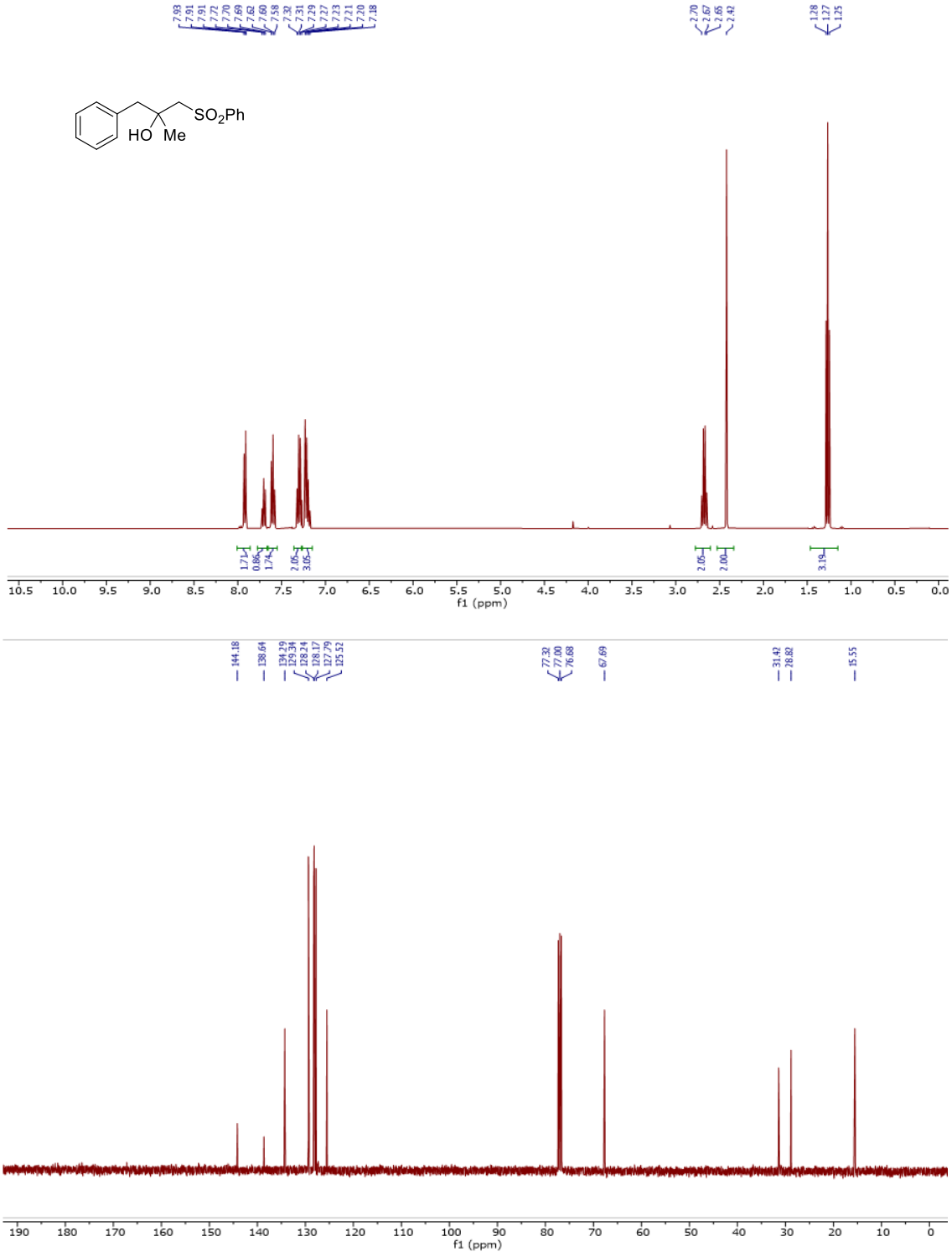




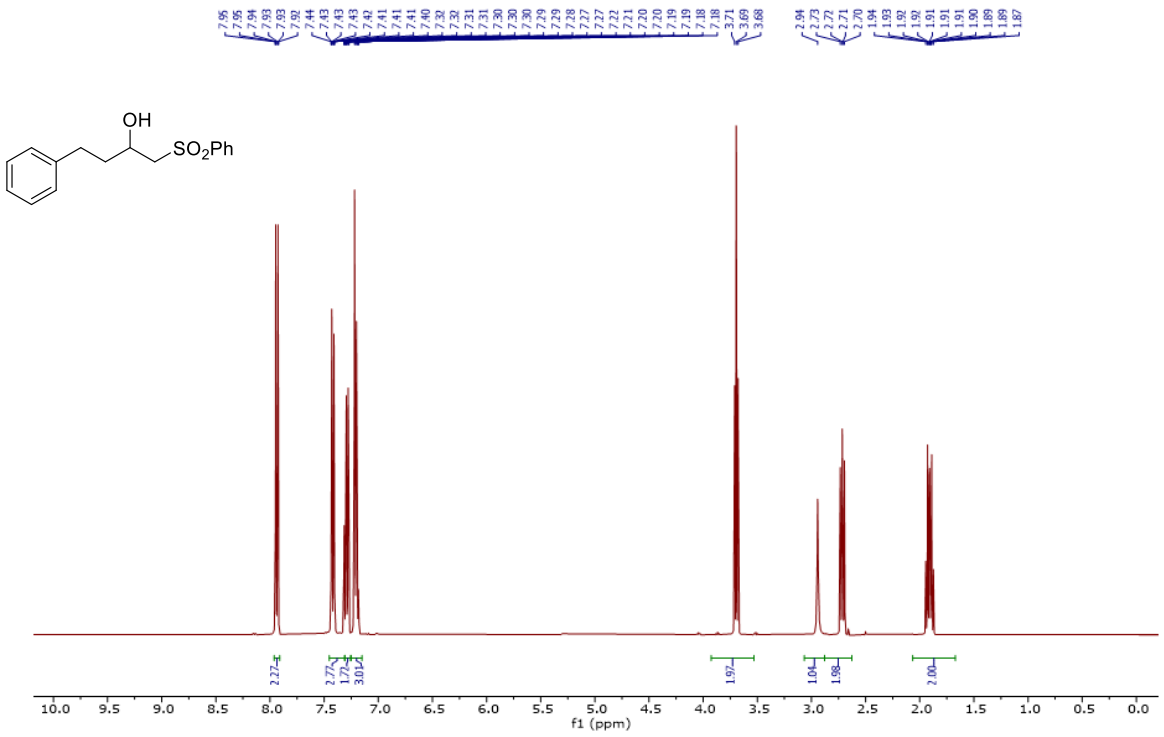
1-(4-Fluorophenyl)-3-(phenylsulfonyl)propan-2-ol **S13** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

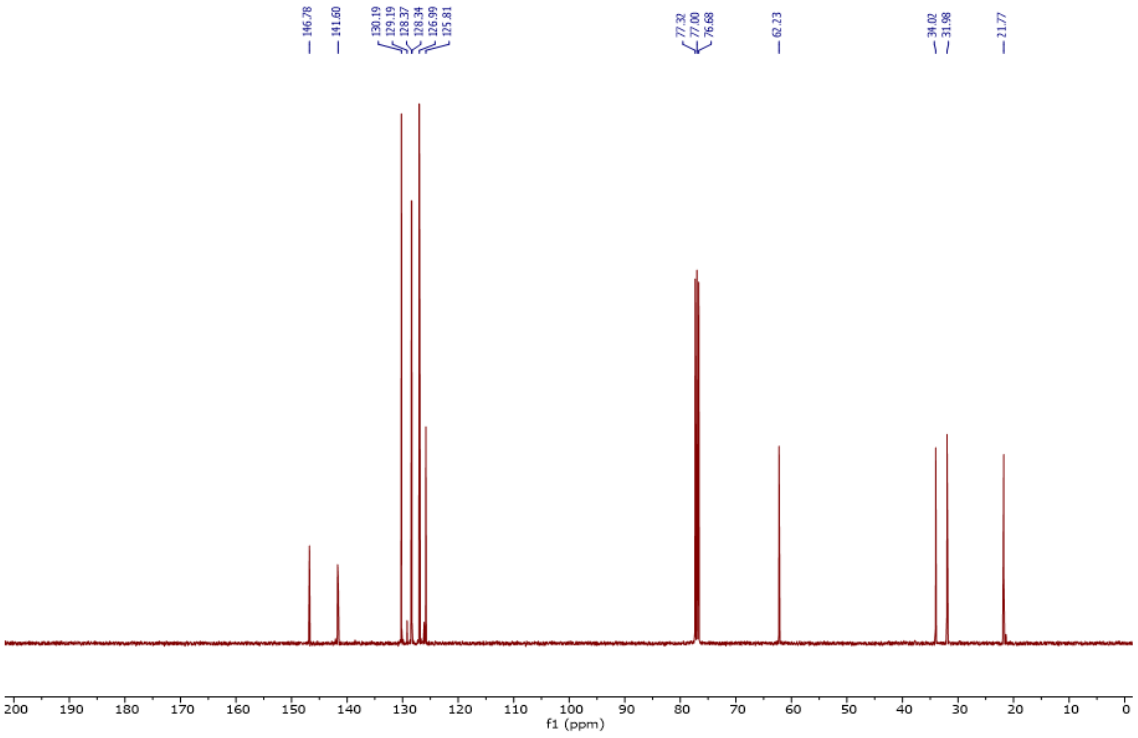


2-Methyl-1-phenyl-3-(phenylsulfonyl)propan-2-ol **S14** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

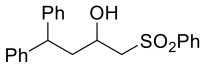


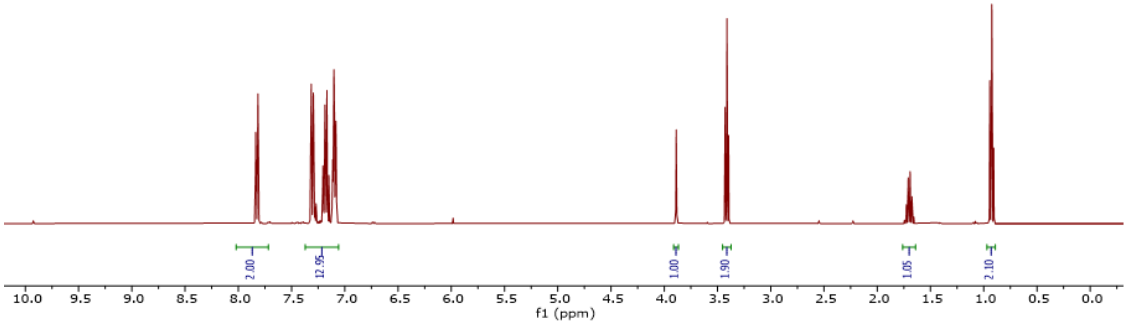
1-Phenyl-4-(phenylsulfonyl)butan-3-ol **S15** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

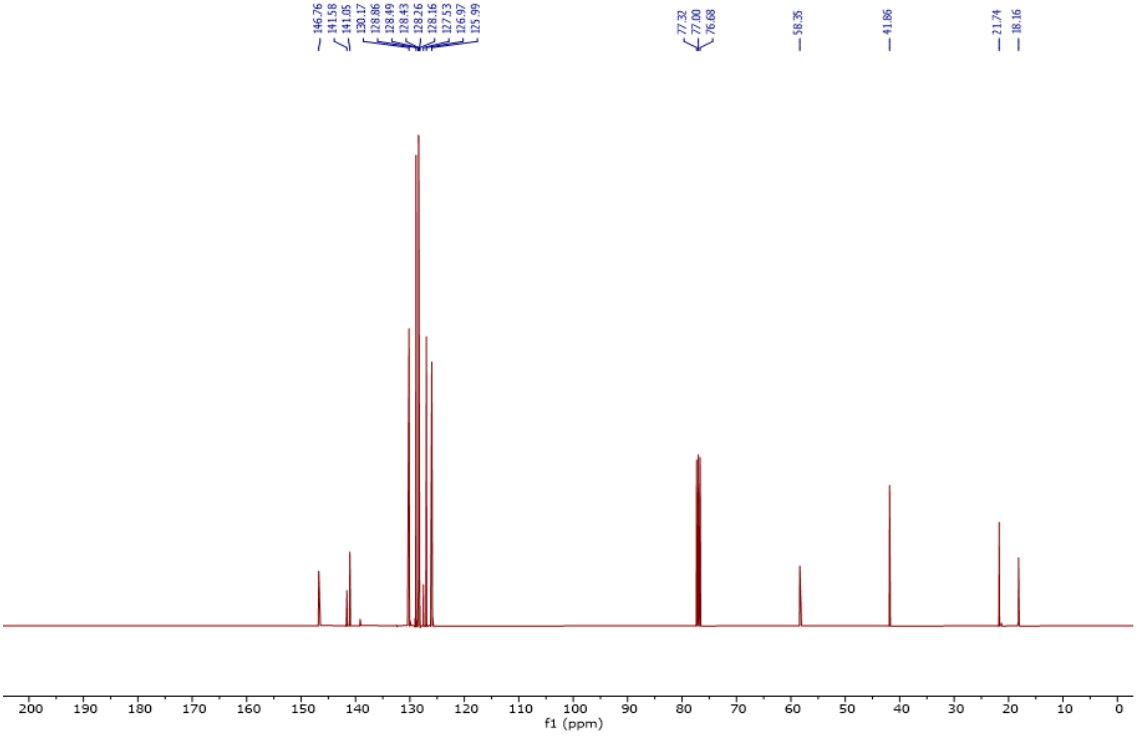




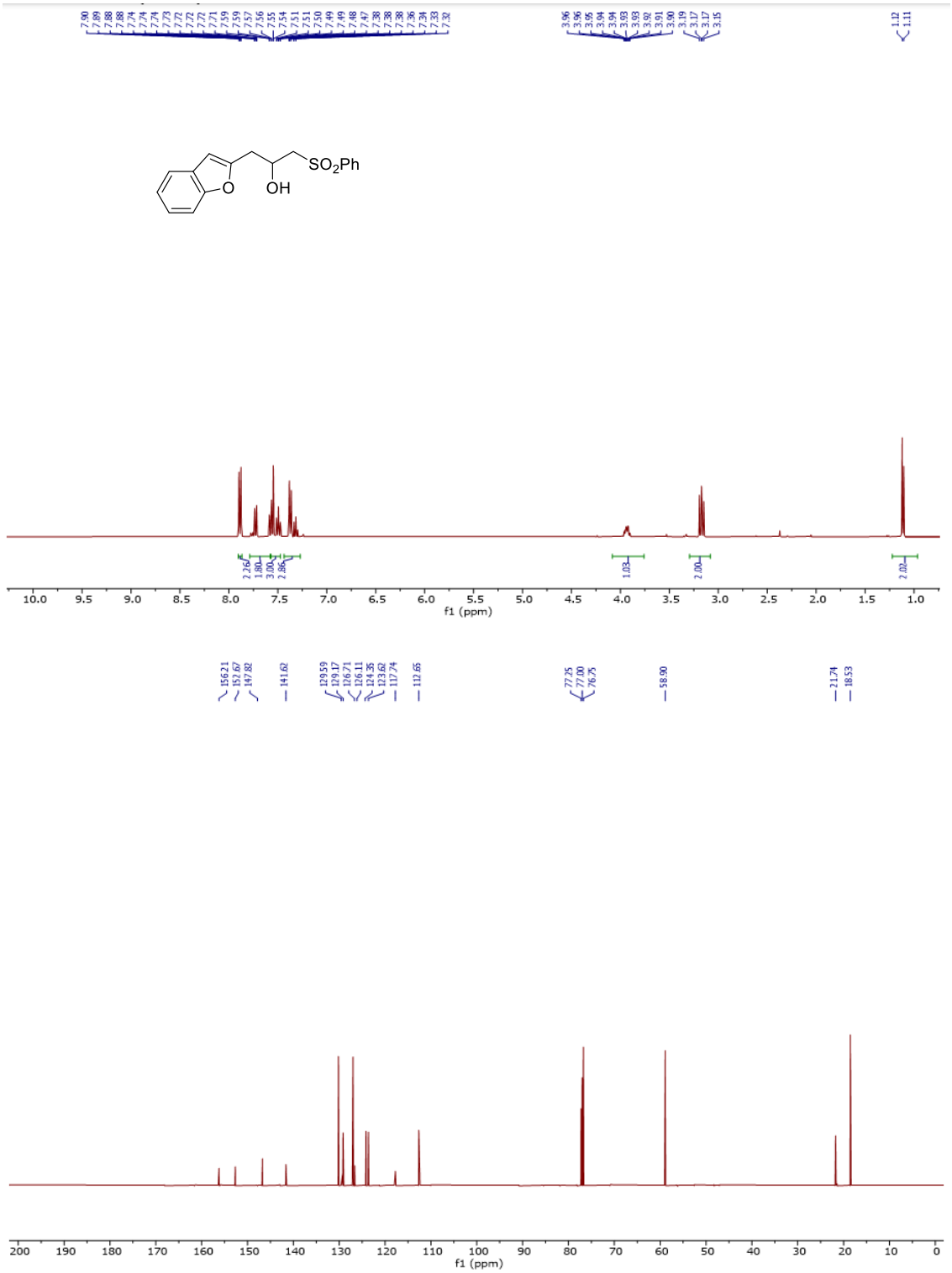
1,1-Diphenyl-4-(phenylsulfonyl))-butan-3-ol **S16** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



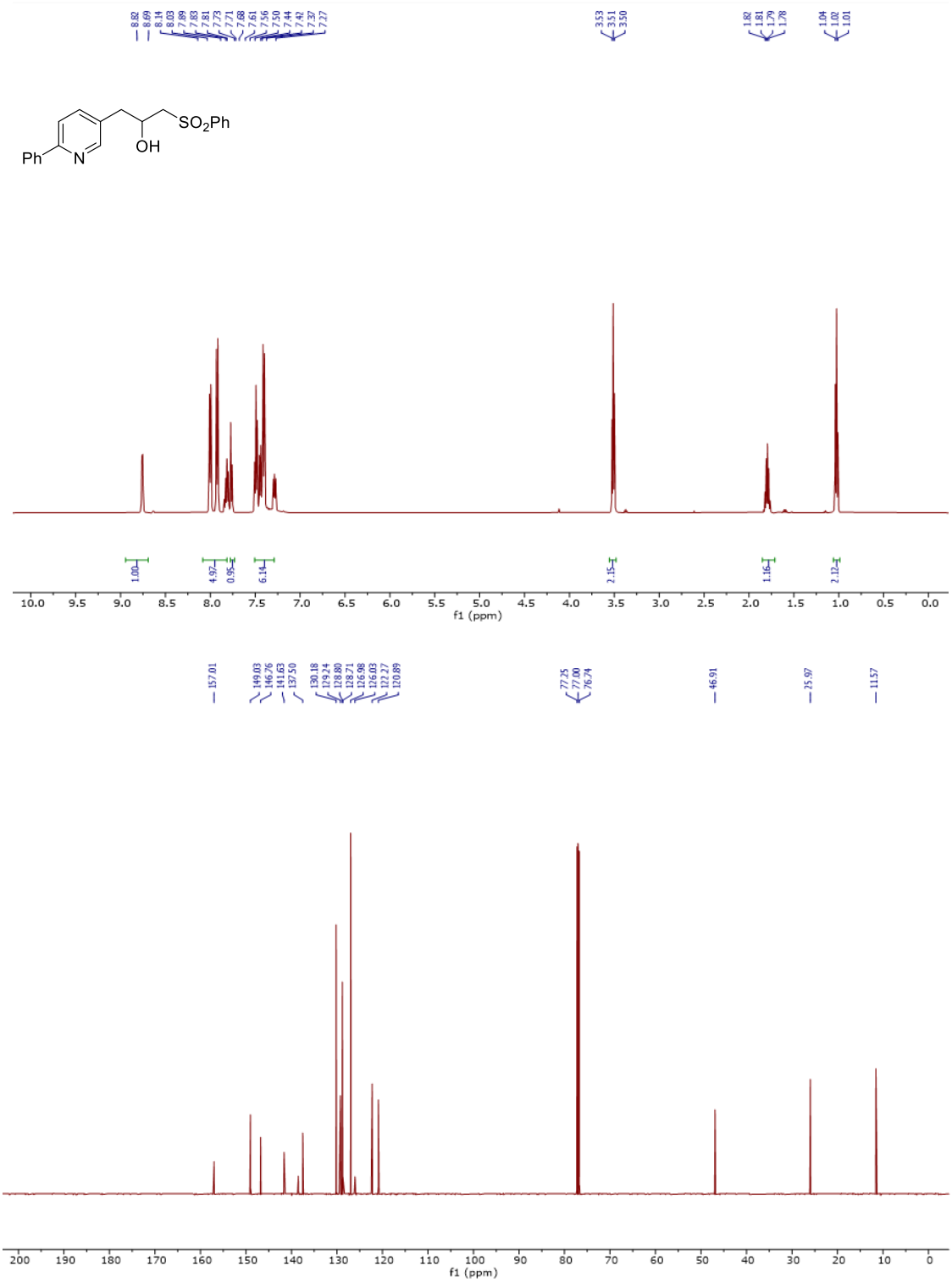




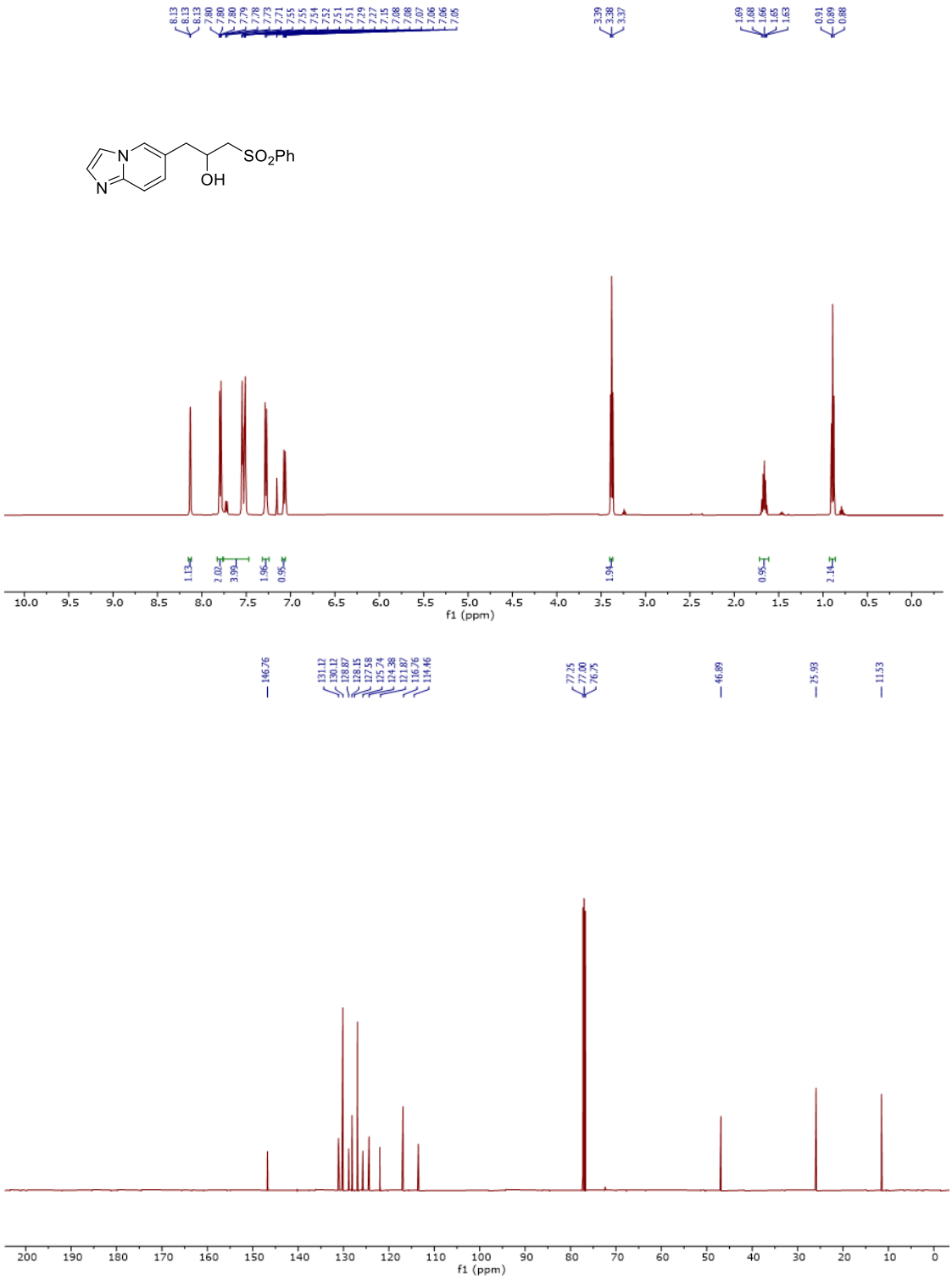
1-(2-Benzofuranyl)-3-(phenylsulfonyl)propan-2-ol **S17** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



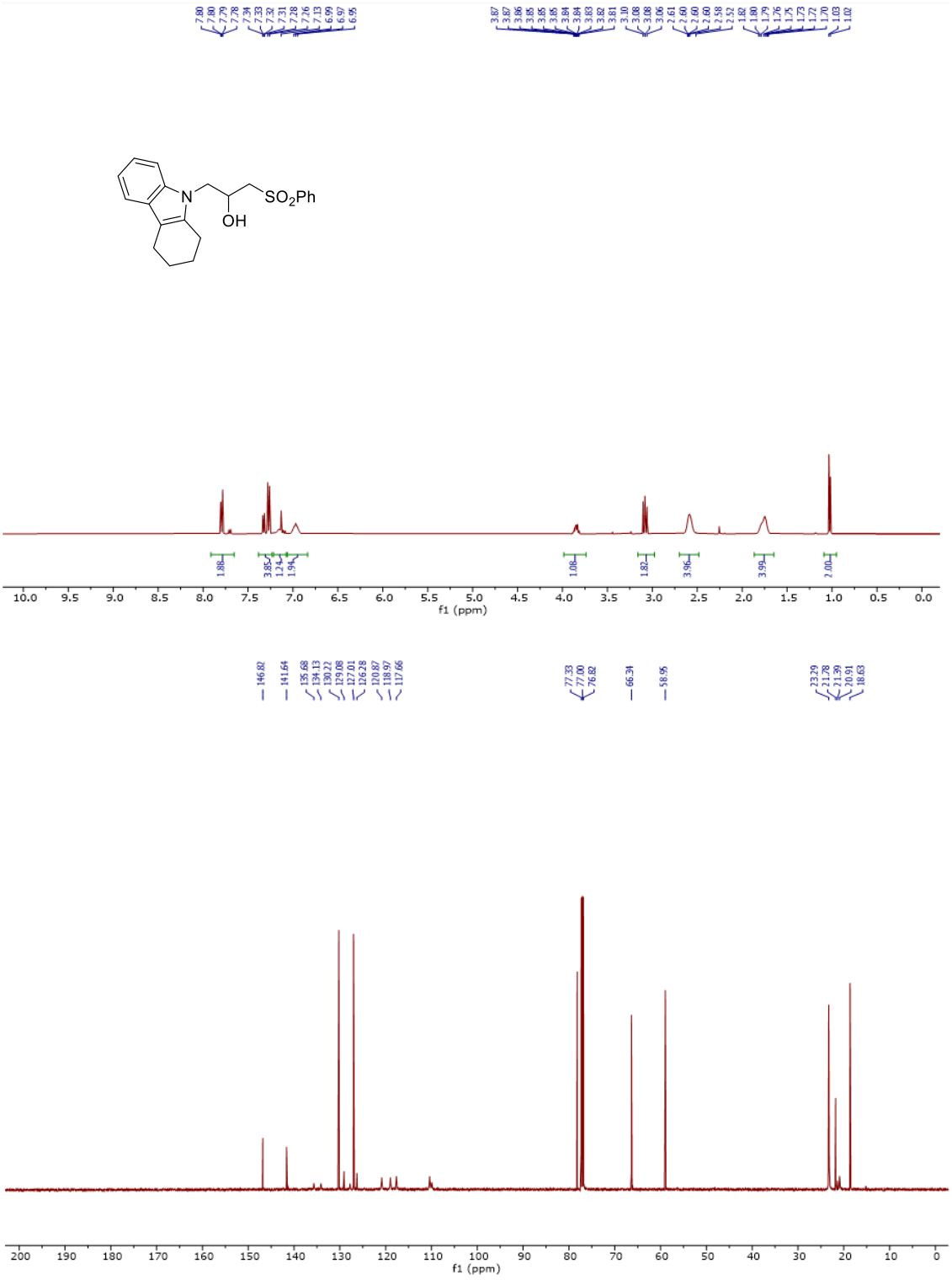
1-[4-(2-Phenylpyridyl)]-3-(phenylsulfonyl)propan-2-ol **S18** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



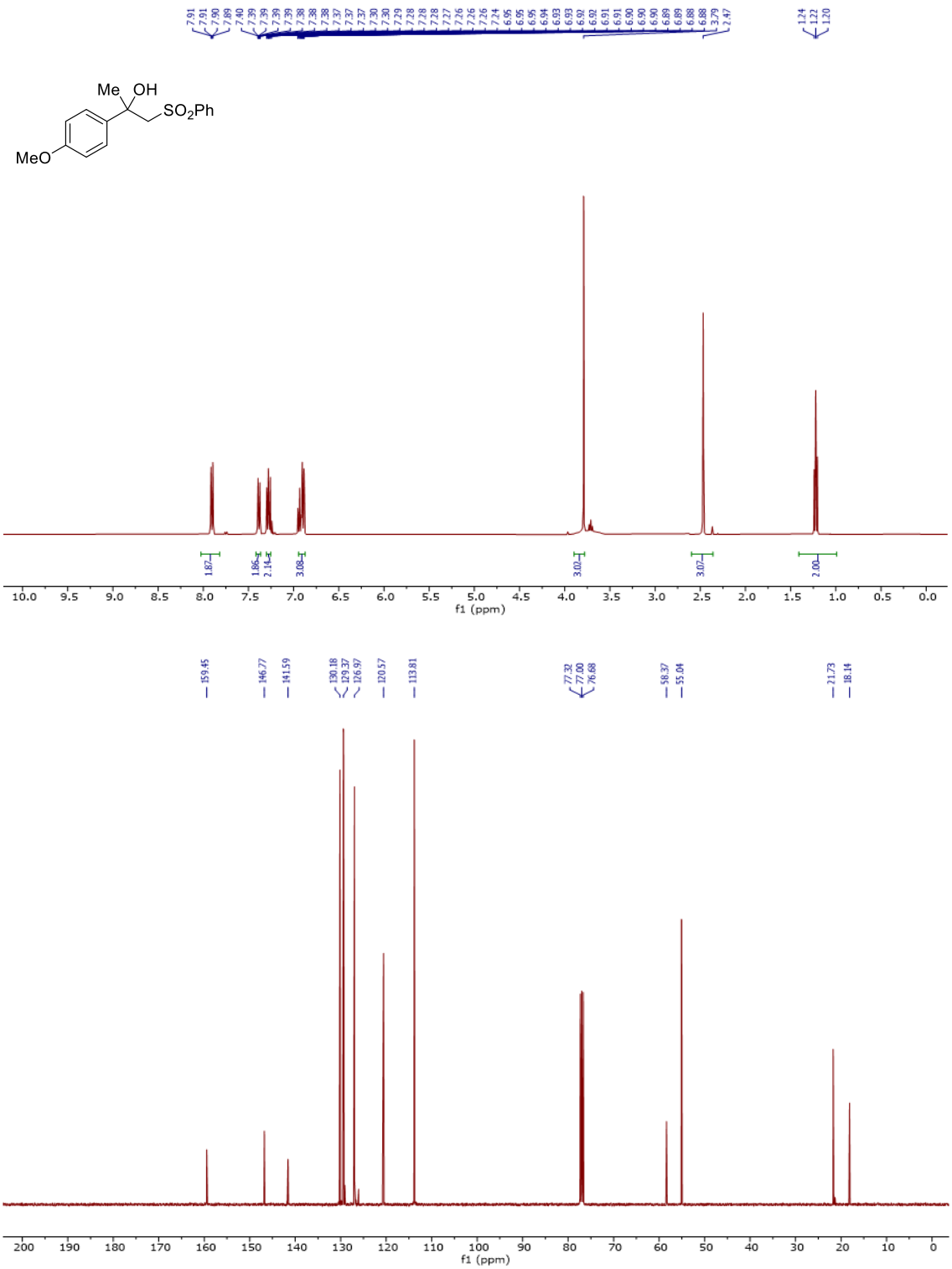
1-[Imidazo(1,2-α)pyridine]-3-(phenylsulfonyl)propan-2-ol **S19** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



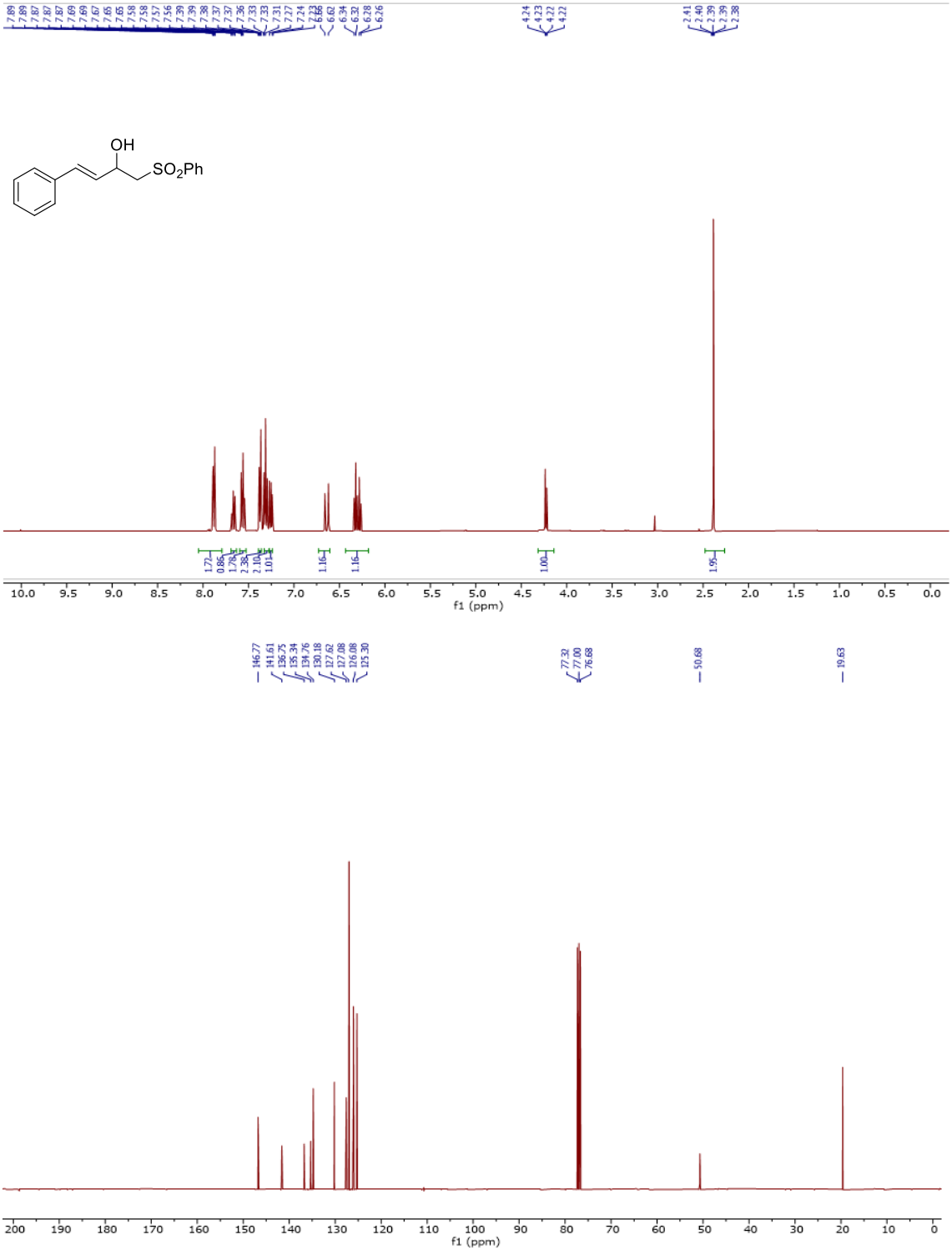
1-[*N*-(1,2,3,4-tetrahydrocarbazolyl)]-3-(phenylsulfonyl)propan-2-ol **S20** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



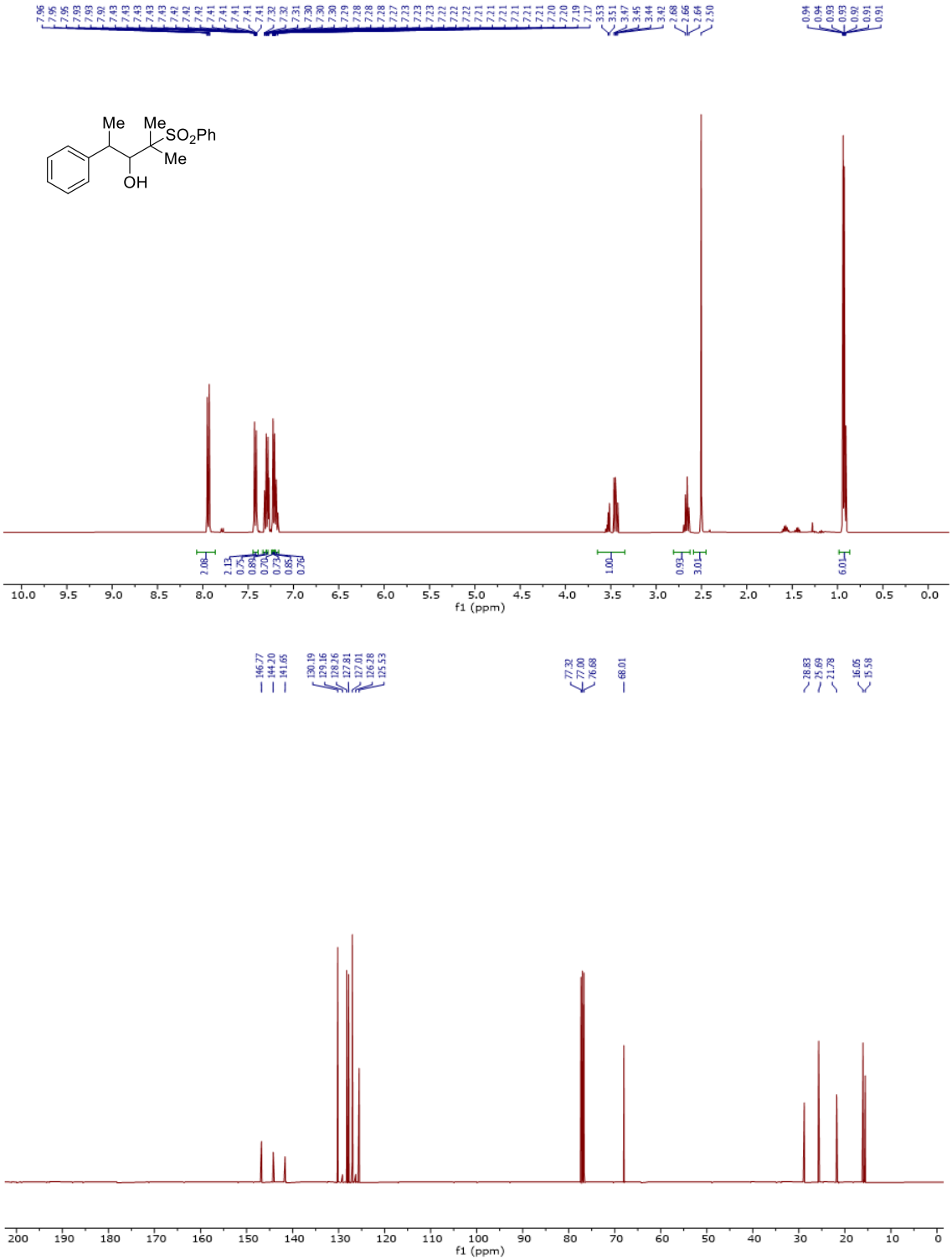
1-(4-Methoxyphenyl)-1-methyl-2-(phenylsulfonyl)-ethan-1-ol **S6** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



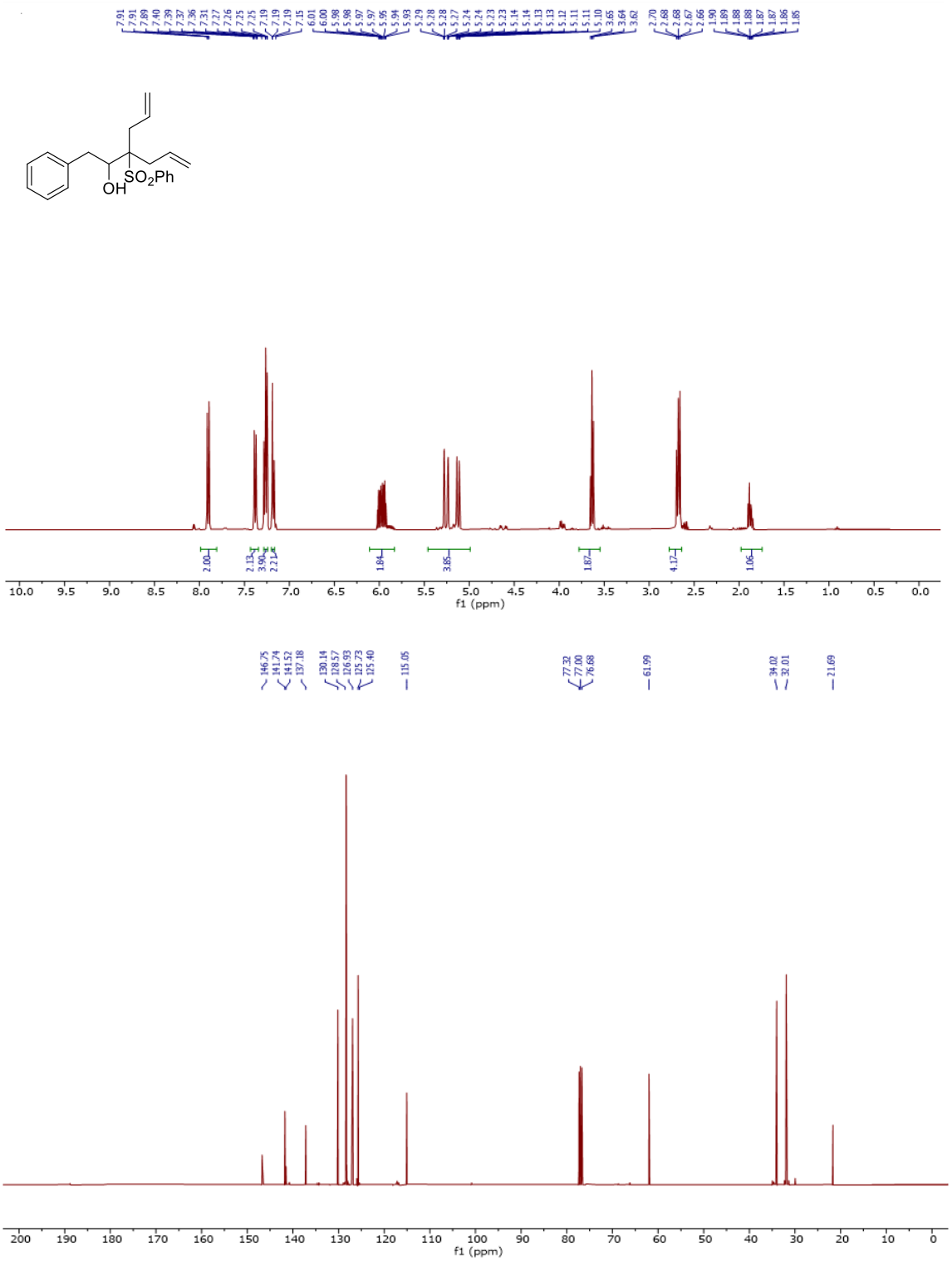
1-(Phenylsulfonyl)-4-phenyl-3-buten-2-**S21** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



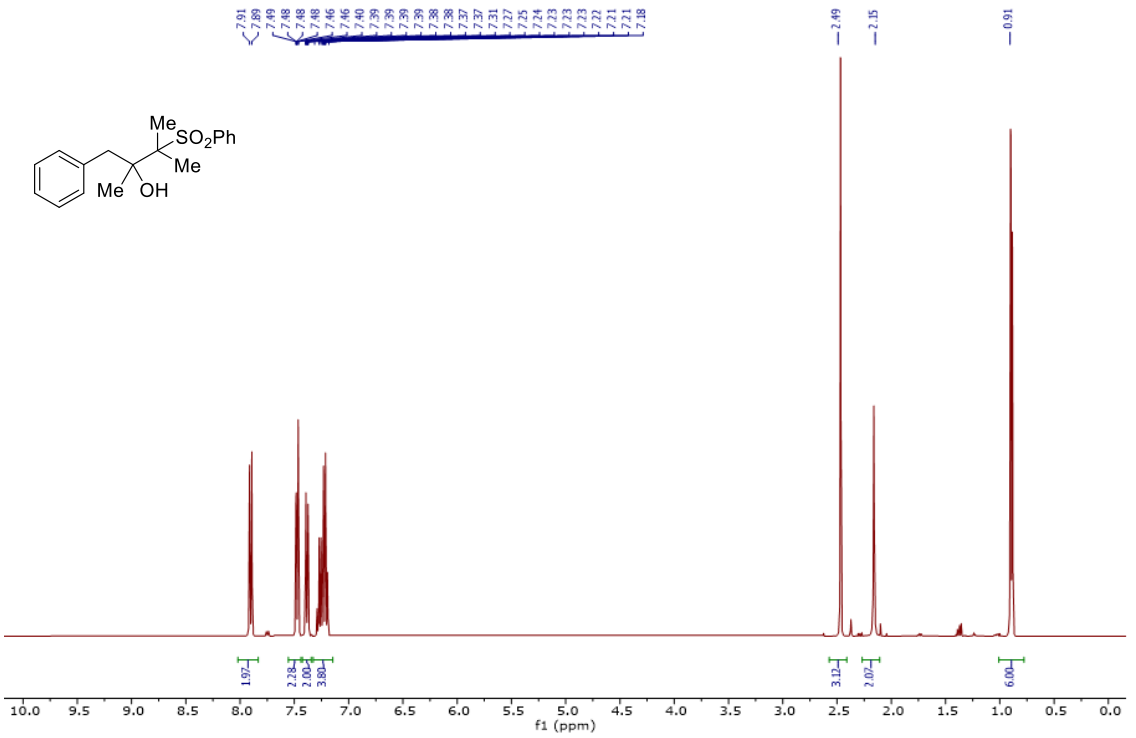
1,3,3-Trimethyl-1-(phenyl)-3-(phenylsulfonyl)propan-2-ol **S24** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)

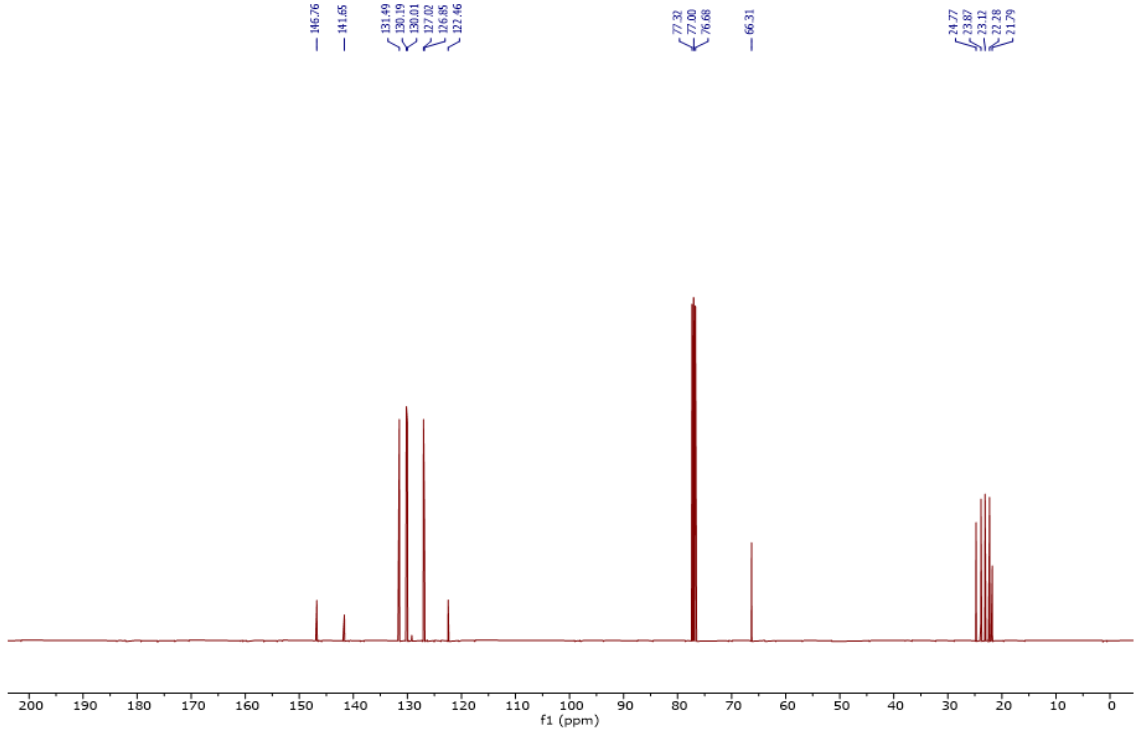


1-Phenyl-3,3-(Diprop-2-ene)-3-(phenylsulfonyl)propan-2-ol **S25** ($CDCl_3$, 400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR)

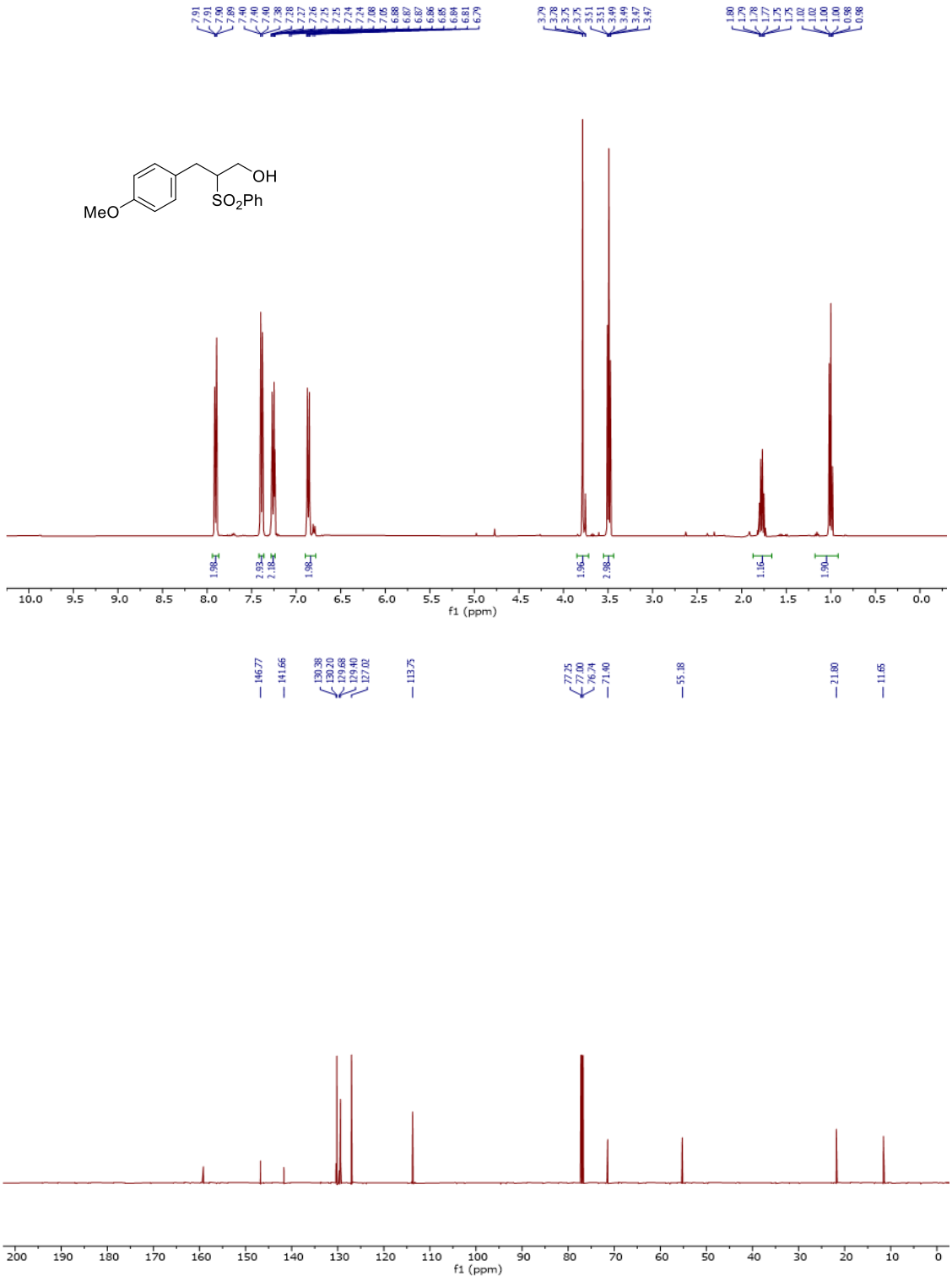


2,3,3-Trimethyl-1-(phenyl)-3-(phenylsulfonyl)propan-2-ol **S29** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)





1-(4-Methoxyphenyl)-2-(phenylsulfonyl)propan-1-ol **30** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)



1-(4-Methoxyphenyl)-3,3-dimethyl-2-(phenylsulfonyl)propan-1-ol **31** ($CDCl_3$, 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR)