Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Materials for

Pd-catalyzed allylative dearomatisation using Grignard reagents

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1. General experimental information

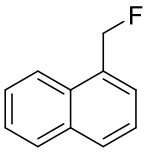
All reactions using oxygen- and/or moisture-sensitive materials were carried out with anhydrous solvents under a nitrogen atmosphere using standard Schlenk techniques. Flash column chromatography was performed using Merck 60 Å 230–400 mesh silica gel. Thin layer chromatography was performed using 0.25 mm E. Merck silica plates (60F-254). The products were visualized by phosphomolybdic acid (PMA) and KMnO4 staining. NMR data was collected on Varian VXR400 (1H at 400 MHz; 13C at 100.58 MHz) equipped with a 5 mm z-gradient broadband probe. Chemical shifts are reported in parts per million (ppm) relative to residual solvent peak ($CDCl_3$, 1H: 7.26 ppm; 13C: 77.16 ppm. CD_2Cl_2, 1H: 5.32 ppm; 13C: 53.84 ppm). Coupling constants are reported in Hertz. Multiplicity is reported with the usual abbreviations (s: singlet, bs: broad singlet, d: doublet, t: triplet, m: multiplet). Exact mass spectra were recorded on a LTQ Orbitrap XL apparatus with ESI ionization, and exact masses are given for previously unreported compounds. Enantiomeric excesses were determined by Chiral HPLC analysis using a Shimadzu LC-10ADVP HPLC equipped with a Shimadzu SPD-M10AVP diode array detector.

2. Chemicals

Unless otherwise indicated, reagents and substrates were purchased from commercial sources and used as received. Solvents not required to be dry were purchased as technical grade and used as received. Dry solvents were freshly collected from a dry solvent purification system prior to use. Inert atmosphere experiments were performed with standard Schlenk techniques with dried (P2O5) nitrogen gas. Grignard reagents were purchased from Sigma-Aldrich. 1-(Chloromethyl)naphthalene, 1-(Bromomethyl)naphthalene and 4-Methyl-1-(Chloromethyl)naphthalene were purchased from Sigma-Aldrich, other benzylic (**1ac, 1b-1t, 5a, 5b**) substrates were prepared following literature methods, characterization is reported only for the target halide, *R*-MOP was prepared following a reported procedure.[1] All reported compounds were characterized by 1H and 13C NMR and compared with literature data. All new compounds were fully characterized by 1H and 13C NMR and HRMS techniques.

3. Synthesis of Starting Materials

1-(Fluoromethyl)naphthalene (1ac)[2]



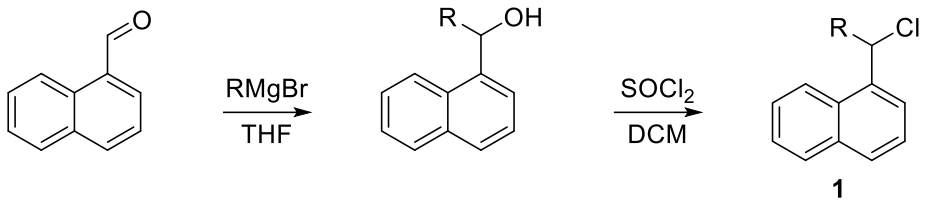
Following a literature procedure.[2] 1-bromomethylnaphthalene (500 mg, 2.27 mmol) and tert-butanol coordinated tetrabutylammonium fluoride (2.54 g, 4.54 mmol, 2.0 equiv.) in acetonitrile (0.1 M substrate concentration) was heated at reflux for 2h, then cooled to room temperature. The solvent was removed in vacuo, the residue redissolved in DCM and filtered through a plug of silica eluting with diethyl ether gave the product (340 mg, 2.11 mmol, 93%) as a colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, *J*=8.1 Hz, 1H), 7.98 (t, *J*=7.6 Hz, 2H), 7.38-7.79 (m, 4 H), 5.92 (d, *J*=48 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 133.69 (d, *J*=1.5 Hz), 131.79 (d, *J*=15.3 Hz), 131.40 (d, *J*=2.0 Hz), 129.91 (d, *J*=3.4 Hz), 128.70, 126.90 (d, *J*=8.5 Hz), 126.77 (d, *J*=1.2 Hz), 126.15, 125.22 (d, *J*=1.8 Hz), 123.59, 83.37 (d, *J*=165.6 Hz),.

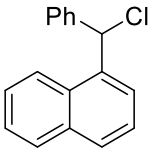
^{19}F NMR (377 MHz, $CDCl_3$): δ -205.8(d, J=48 Hz).

3.1. General procedure for the synthesis of benzyl substituted compound



Synthesis of **1-chloro(phenyl)methyl-naphthalene** (**1b**) given as example.[3] Following a literature procedure,[4] in a dried two-necked round bottom flask, under inert atmosphere, to a solution of 1-naphthaldehyde (2.34 g, 15.0 mmol, 1 equiv.) in dry THF (15mL) was added, drop wise, PhMgBr (22.5 mL 1M in THF, 1.5 eq), the mixture was stirred until reaction completion, then quenched by adding a saturated solution of NH_4Cl. The was extracted with ethyl acetate, the organic phases were washed with water and twice with brine, then dried over Na_2SO_4. The crude was used without further purification in the next step.

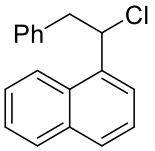
Following a literature procedure,[5] In a dried two-necked round bottom flask, under inert atmosphere, to a solution of 1-Hydroxy(phenyl)methyl-naphthalene (2.34 g, 10.0 mmol, 1 equiv.) in dry DCM (50 mL) at 0 ℃, SOCl2 (2.0 equiv) was slowly added, the mixture was stirred for 2 h at 0 ℃. After the reaction was completed, diluted aqueous sodium bicarbonate was slowly added to quench the reaction. Then, Et_2O was added, the mixture was washed with diluted aqueous sodium bicarbonate for several times until the pH of the aqueous layer was higher than 7. Then the organic layer was washed with brine and dried over Na_2SO_4, filtered and concentrated under reduced pressure. To the crude compound was then added hexane (10 ml), the insoluble residue was filtered off and the solvent removed to give **1b** as a slightly yellow solid, 2.43 g (96% yield). The spectral properties are in accordance with the one reported in literature.



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12-8.03 (m, 1 H), 7.94-7.81 (m, 2H) 7.61 (d, *J*=6.90 Hz, 1H), 7.55-7.42 (m, 5H), 7.40-7.29 (m, 3H), 6.90 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 140.42, 136.03, 133.93, 130.44, 129.27, 128.93, 128.56, 128.07, 128.00, 126.84, 126.50, 125.85, 125.20, 123.72, 61.74.

1-(1'-chloro-2'-phenylethyl)-naphthalene (**1c**)[6]

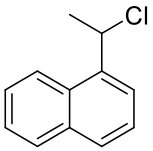


Following the general procedure (employing BnMgBr), compound **1c** was obtained as a white solid (93% yield). The spectral properties are in accordance with the one reported in literature.

^{1}H NMR (400 MHz, $CDCl_3$): δ : 3.52–3.66 (m, 2H), 5.88 (t, *J*=7.0 Hz, 1H), 7.19–7.33 (m, 5H), 7.44–7.60 (m, 3H), 7.73 (d, *J*=6.8 Hz, 1H), 7.83 (d, *J*=8.4 Hz, 1H), 7.89 (d, *J*=8.4 Hz, 1H), 8.16 (d, *J*=8.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ : 44.8, 60.4, 122.7, 124.8, 125.2, 125.7, 126.5, 126.8, 128.3, 129.0, 129.1, 129.3, 130.3, 133.8, 136.4, 137.8.

1-(1'-chloroethyl)-naphthalene (**1d**)[6]

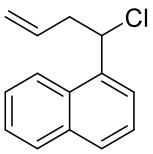


Following the general procedure (employing MeMgBr), compound **1d** was obtained as a slightly yellow oil (87% yield). The spectral properties are in accordance with the one reported in literature.

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.06 (d, *J*=6.7 Hz, 3H), 5.91 (q, *J*=6.7 Hz, 1H), 7.46–7.54 (m, 2H), 7.56–7.62 (m, 1H), 7.72 (d, *J*=6.7 Hz, 1H), 7.83 (d, *J*=7.9 Hz, 1H), 7.89 (d, *J*=7.9 Hz, 1H), 8.19 (d, *J*=8.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 24.9, 54.4, 122.9, 123.4, 125.1, 125.7, 126.3, 128.8, 129.0, 130.3, 133.7, 137.4.

1-(1'-chloro-3'-butenyl)-naphthalene (**1e**)[7]

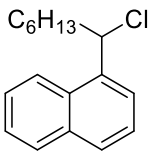


Following the general procedure (employing allylMgBr), compound **1e** was obtained as a slightly yellow sticky oil (79% yield). The spectral properties are in accordance with the one reported in literature.

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.03–3.07 (m, 2 H), 5.08–5.26 (m, 2 H), 5.64–5.76 (m, 1 H), 5.90 (m, 1 H), 7.45–7.62 (m, 3 H), 7.70 (d, *J*=7.4 Hz, 1 H), 7.79–7.92 (m, 2 H), 8.14 (d, *J*=8.1 Hz, 1 H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 42.8, 58.6, 118.9, 122.8, 124.6, 125.2, 125.8, 126.5, 129.0, 129.1, 130.4, 133.8, 134.2, 136.3.

1-(1'-chloroheptyl)-naphthalene (**1f**)



Following the general procedure (employing hexylMgBr), compound **1f** was obtained as a slightly yellow oil (90% yield).

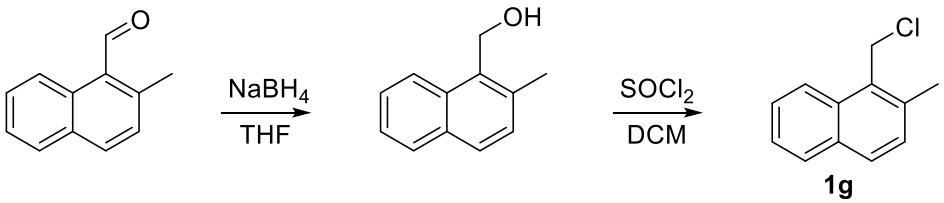
^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86 (t, *J*=7.7 Hz, 3H), 1.20-1.50 (m, 8H), 2.20-2.39 (m, 2H), 5.67 (t, *J*=7.0 Hz, 1H), 7.44-7.52 (m, 2H), 7.56 (t, *J*=7.9 Hz, 1H), 7.68 (d, *J*=6.5 Hz, 1H), 7.80 (d, *J*=8.2 Hz, 1H), 7.87 (d, *J*=7.9 Hz, 1H), 8.15 (d, *J*=8.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 139.78, 136.54, 133.18, 131.68, 131.58, 129.07, 128.40, 128.00, 127.16, 59.92 (broad signal), 41.39, 34.31, 31.44, 30.03, 25.23, 16.71.

MS (HRMS - ESI): Calc. for $C_{17}H_{21}Cl$ $[M+1]^+$ 261.1332, found 261.1335.

3.2 Synthesis of ring substituted compounds

1-chloromethyl-2-Methylnaphthalene (1g)[8]



1g

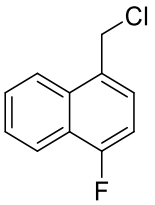
Following a literature procedure.[9] $NaBH_4$ (2.223 g, 58.751 mmol, 5.000 equiv.) was added to a solution of 2-methyl-1-naphthaldehyde (2.000 g, 11.750 mmol, 1.000 equiv.) in THF/EtOH (1:1 mixture 12mL) at room temperature. The mixture was stirred for 30 min and quenched with cold water. The pH was adjusted to 5−6, and the solution was stirred for 15 min. The mixture was extracted with Et_2O, and the combined organic extracts were dried ($MgSO_4$) and evaporated. The crude product was purified by column chromatography, silica gel, 3:10 EtOAc/hexane to give the alcohol as a white solid (60% yield).

Following a literature procedure.[5] In a dried two-necked round bottom flask, under inert atmosphere, to a solution of 2-methyl-1-hydroxymethyl-naphthalene (900.0 mg, 5.226 mmol, 1.000 equiv) in dry DCM (26 mL) at 0°C, $SOCl_2$ (0.758 mL, 10.451 mmol, 2.000 equiv) was slowly added, the mixture was stirred for 2 h at 0°C. After the reaction was completed, diluted aqueous sodium bicarbonate was slowly added to quench the reaction. Then, Et_2O was added, the mixture was washed with diluted aqueous sodium bicarbonate for several times until the pH of the aqueous layer was larger than 7. Then the organic layer was washed with brine and dried over Na_2SO_4, filtered and concentrated under reduced pressure to give the target product as a slightly sticky oil (94% yield).). The spectral properties are in accordance with the one reported in literature.

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.60 (s, 3H), 5.09 (s, 2H), 7.31 (d, *J*=8.3 Hz, 1H), 7.45 (t, *J*=7.5 Hz, 1H), 7.57 (t, *J*=7.5 Hz, 1H), 7.74 (d, *J*=8.2 Hz, 1H), 7.82 (d, *J*=8.2 Hz, 1H), 8.09 (d, *J*=8.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 135.44, 132.51, 131.64, 129.94, 129.23, 129.02, 128.66, 126.88, 125.14, 122.94, 39.94, 19.69.

1-chloromethyl-4-Fluoronaphthalene (1s)[10]

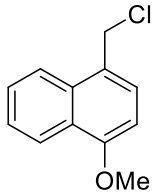


Following the procedure for the synthesis of **1g**, **1s** was obtained as a white solid (66% isolated yield from the starting aldehyde). The mass analysis is in line with the one reported in literature.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.00 (s, 2H), 7.08 (t, *J*=8.3 Hz, 1H), 7.45 (t, *J*=8.3 Hz, 1H), 7.59 (t, *J*=7.4 Hz, 1H), 7.65 (t, *J*=7.4 Hz, 1H), 8.14 (t, *J*=9.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ159.42 (d, *J*=254.3 Hz), 132.48 (d, *J*=4.9 Hz), 129.07 (d, *J*=4.5 Hz), 127.70 (d, *J*=8.9 Hz), 127.68, 126.47 (d, *J*=2.1 Hz), 124.23 (d, *J*=16.3 Hz), 123.77 (d, *J*=3.0 Hz), 121.41 (d, *J*=5.7 Hz), 108.79 (d, *J*=20.4 Hz), 44.10.

^{19}F NMR (377 MHz, $CDCl_3$): δ -120.63**1-chloromethyl-4-Methoxynaphthalene** (**1t**)



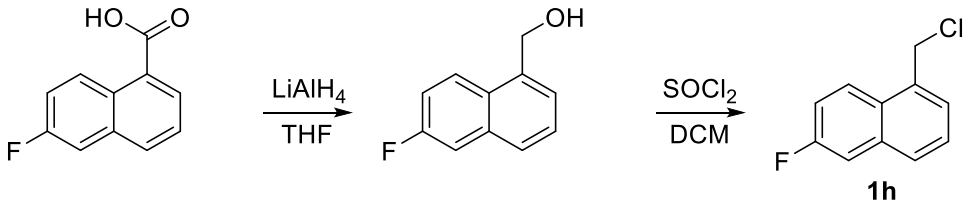
Following the procedure for the synthesis of **1g**, **1t** was obtained as a white solid (74% isolated yield from the starting aldehyde).

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.01 (s, 3H), 5.03 (s, 2H), 6.74 (d, *J*=7.9 Hz, 1H), 7.45 (d, *J*=7.9 Hz, 1H), 7.51-7.56 (m, 1H), 7.60-7.65 (m, 1H), 8.10 (d, *J*=8.4 Hz, 1H), 8.33 (d, *J*=8.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 156.56, 132.03, 128.26, 127.21, 126.11, 125.47, 125.11, 123.52, 122.79, 102.93, 55.58, 45.11.

MS (HRMS - ESI): Calc. for $C_{12}H_{11}ClO$ $[M+1]^+$ 207.0498, found 207.0511.

1-chloromethyl-6-Fluoronaphthalene (**1h**)



1h

Following a modified literature procedure.[11] In a dried round bottom flask, under N_2 atmosphere, 6-Fluoro-1-naphthoic acid (0.250 g, 1.315 mmol, 1.000 equiv.) was dissolved in dry THF (5.5 mL), the mixture was cooled to 0°C and a 1M solution in THF of $LiAlH_4$ (2.2 mL, 2.169 mmol, 1.650 equiv.) was added slowly. The reaction was then allowed to reach r.t. and stirred overnight. The mixture was then cooled with an ice/water bath and quenched with 5 mL of water, acidified with concentrated HCl and extracted with Et_2O (3x10 mL). The combined organic phases where dried on $MgSO_4$ and evaporated to give the crude compound as a white solid, which was used in the next step without further purification.

Following a literature procedure.[5] In a dried two-necked round bottom flask, under inert atmosphere, the crude from the previous step was dissolved in dry DCM (7 mL) and the solution was cooled with an ice/water bath. Then, $SOCl_2$ (2.0 equiv) was slowly added, the mixture was stirred for 2 h at 0 °C. After the reaction was completed, diluted aqueous sodium bicarbonate was slowly added to quench the reaction. Then, Et_2O was added, the mixture was washed with diluted aqueous sodium bicarbonate for several times until the pH of the aqueous layer was higher than 7. Then the organic layer was washed with brine and dried over Na_2SO_4, filtered and concentrated under reduced pressure. To the crude compound was then added hexane (10 ml), the insoluble residue was filtered off and the solvent removed to give **1h** as a white solid, 0.175 g (62% yield).

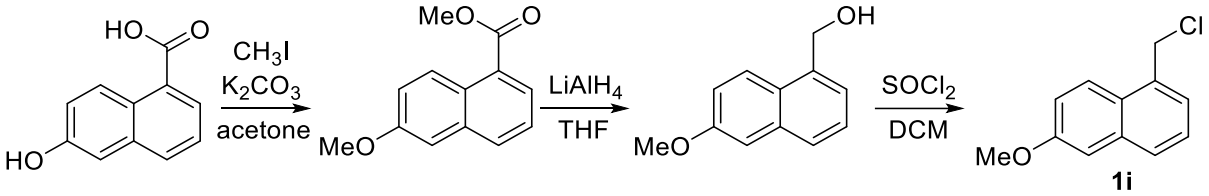
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.03 (s, 2H), 7.34-7.53 (m, 4H), 7.80 (d, *J*=8.1 Hz, 1H), 8.16 (dd, J_1=5.3 Hz J_2=9.2, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 160.63 (d, *J*=246.4 Hz), 134.99 (d, *J*=9.1 Hz), 133.29 (d, *J*=1.0 Hz), 129.14 (d, *J*=5.1 Hz), 128.11 (broad), 126.92 (d, *J*=2.7 Hz), 126.49 (broad), 126.29 (d, *J*=8.9 Hz), 116.91 (d, *J*=25.1 Hz), 11.85 (d, *J*=20.1 Hz), 44.46.

^{19}F NMR (377 MHz, $CDCl_3$): δ -114.65

MS (HRMS - ESI): Calc. for $C_{11}H_8ClF$ $[M+1]^+$ 194.0299, found 194.0302.

1-chloromethyl-6-Methoxylnaphthalene (**1i**)



Following a literature procedure.[12] 6-hydroxy-1-naphthoic acid (2.5 g, 13.28 mmol, 1 equiv.), K_2CO_3 (5.5 g, 39.85 mmol, 3 equiv.) and MeI (2.5 mL, 39.85 mmol, 3 equiv.) were dissolved in 30 mL of acetone and the mixture was heated to 50°C overnight. The salts were then filtered off and washed with acetone, the solvent of the filtrate was evaporated, the residue partitioned in H_2O and DCM (20-20 mL), the phases were separated and the aqueous one extracted once again, then the organic phases were dried over Na_2SO_4. The product was used in the next step without further purification.

Following a literature procedure.[11] A solution of methyl 6-methoxy-1-naphthoate (4.32 g, 20 mmol) in THF (40 mL) was added dropwise under an nitrogen atmosphere to a suspension of $LiAlH_4$ (1.14 g, 30.0 mmol) in dry THF (30 mL) at 0°C. After complete addition, the mixture was warmed to 25°C and was then stirred for 2 h at 25°C. Then the mixture was cooled to 0°C and was poured into 40 mL 2 M HCl, the mixture was evaporated to remove THF and the residue was mixed with 30 mL H_2O. The mixture was extracted with CH_2Cl_2 (30 mL × 3), the combined extracts were washed with saturated brine (15 mL × 3) and dried over $MgSO_4$. After the solvent was evaporated, the crude product was used for next reaction without purification (95% yield).

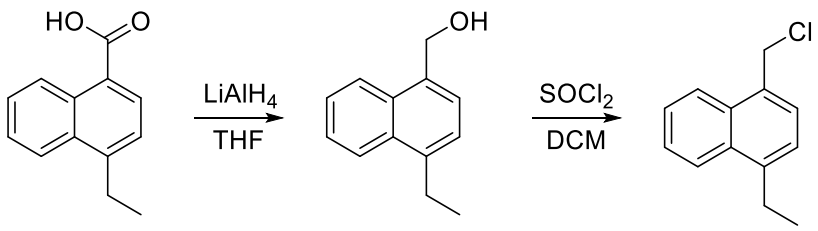
The crude from the reduction step was subjected to the general procedure for halogenation with $SOCl_2$, yielding, after purification with column chromatography (silica gel, pentane/EtOAc 98/2) **1j**, as a white solid, in 90% overall yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.93 (s, 3H), 5.02 (s, 2H), 7.19 (d, *J*=2.7 Hz, 1H), 7.24-7.29 (m, 1H), 7.36-7.42 (m, 2H), 7.72-7.77 (m, 1H), 8.06 (d, *J*=9.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 157.68, 135.35, 133.01, 128.66, 126.51, 125.92, 125.44, 125.21, 119.30, 106.80, 55.34, 44.64.

MS (HRMS - ESI): Calc. for $C_{12}H_{11}ClO$ $[M+1]^+$ 207.0498, found 207.0510.

1-chloromethyl-4-Ethylnaphthalene (**1k**)



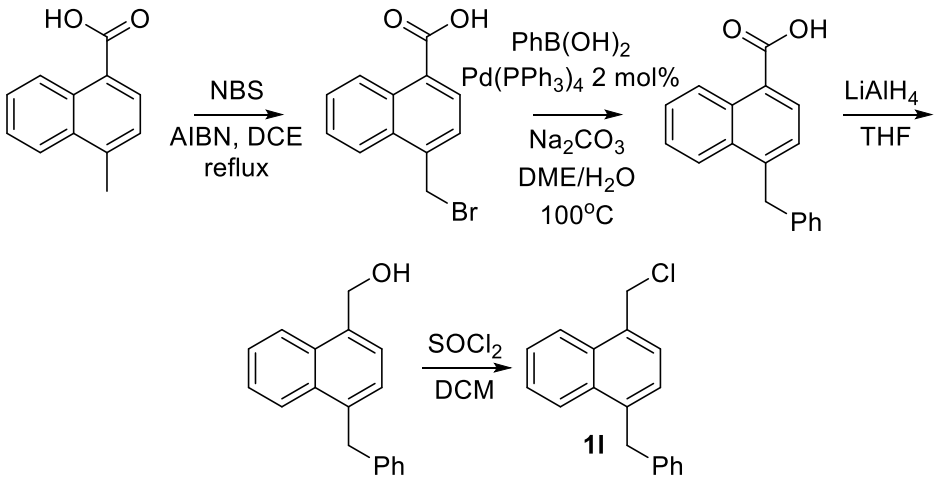
In a dried two-necked round bottom flask, under inert atmosphere, a solution of 4-ethyl-1-naphthoic Acid (2.000 g, 9.988 mmol, 1.000 eq) in dry THF (20 ml) was added dropwise to a solution of $LiAlH_4$ (16.5 mL, 16.480 mmol, 1.650 eq) in dry THF at 0 °C. The resulting solution was allowed to warm to r.t. and stirred for 16 h, the reaction was quenched by the addition of aq. 1 M KOH (40 mL) dropwise at 0 °C. Et_2O (60 mL) was then added and the mixture stirred for 30 min at r.t., the layers separated and the aqueous layer extracted with Et_2O (2x50 mL). The combined organic layers were washed with aq. 1 M HCl (50 mL), then brine (50 mL) dried over $MgSO_4$ and concentrated in vacuo to give the product, which was used in the next step without further purification.

In a dried two-necked round bottom flask, under inert atmosphere, to a solution of 4-ethyl-1-hydroxymethyl-naphthalene (1762.4 mg, 9.462 mmol, 1.000 eq) in dry DCM at 0 ℃, $SOCl_2$ (1.4 mL, 18.925 mmol, 2.000 eq) was slowly added, the mixture was stirred for 5 h at 0 ℃. After the reaction was completed, diluted aqueous sodium bicarbonate was slowly added to quench the reaction. Then, Et_2O was added, the mixture was washed with diluted aqueous sodium bicarbonate for several times until the pH of the aqueous layer was larger than 7. Then the organic layer was washed with brine and dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude was subjected to column chromatography (silica gel, pentane) and **1l** was obtained as a white solid, in 73% overall yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.38 (t, *J*=7.5 Hz, 3H), 3.11 (q, *J*=7.5 Hz, 2H), 5.04 (s, 2H), 7.29 (d, *J*=7.3 Hz, 1H), 7.45 (d, *J*=7.3 Hz, 1H), 7.53-7.62 (m, 2H), 8.11 (d, *J*=8.0 Hz, 1H), 8.18 (d, *J*=8.1 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 142.29, 132.32, 131.39, 131.14, 127.69, 126.24, 125.97, 124.60, 124.40, 124.31, 44.96, 26.07, 14.97.

MS (HRMS - ESI): Calc. for $C_{13}H_{13}Cl$ $[M+1]^+$ 205.0706, found 205.0708.**1-chloromethyl-4-Benzylnaphthalene** (**1l**)



A mixture of 4-methyl-1-naphthoic acid (5.0 g, 26.8 mmol, 1.0 equiv.), NBS (5.0 g, 28.2 mmol, 1.05 equiv.), and AIBN (2 mol%) in DCE (100 mL) was refluxed for 3 h. The reaction mixture was concentrated in vacuo and dissolved in EtOAc. The organic solution was washed with water and brine and dried ($MgSO_4$). The crude was used in the next step without further purification.

To a solution of benzyl bromide (1.06 g, 4.0 mmol, 1.0 equiv.) in 1,2-dimethoxyethane (8 mL) and water (4 mL) was added boronic acid (586 mg, 4.8 mmol, 1.2 equiv.), sodium carbonate (890 mg, 8.4 mmol, 2.1 equiv.) and Tetrakis(triphenylphosphine) palladium (2 mol%). The mixture was vacuum flushed with nitrogen and then heated to 100 ° C overnight. The solvent was removed and the residue used in the next step without further purification.

In a dried round bottom flask, under N_2 atmosphere, 4-Bn-1-naphthoic acid (1.045 g, 3.983 mmol, 1.000 eq) was dissolved in dry THF (16.6 mL), the mixture was cooled to 0°C and $LiAlH_4$ (6.6 mL, 6.572 mmol, 1.650 eq) in THF was added slowly and the reaction was then allowed to reach r.t. and stirred overnight. Water (10 mL) was added, then HCl (6 M) until the aqueous phase reached pH lower than 7. The organic phase was separated, dried over ($MgSO_4$) and concentrated on vacuo. The crude was then purified by column chromatography, silica gel, pentane/EtOAc 7/3.

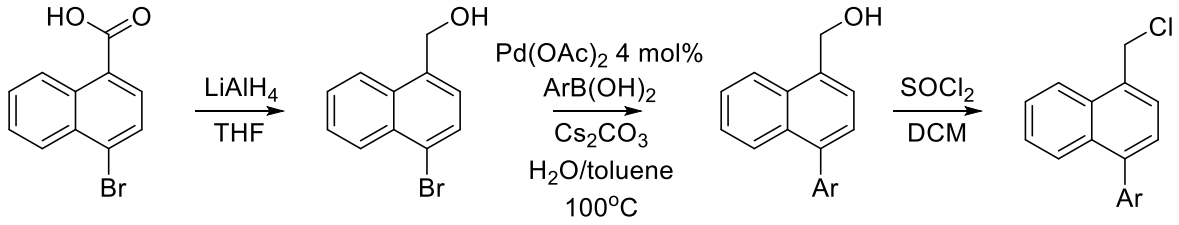
In a dried two-necked round bottom flask, under inert atmosphere, to a solution of the alcohol (426 mg, 1.7 mmol, 1.000 eq) in dry DCM (10 mL) at 0 °C, $SOCl_2$ (0.25 mL, 3.430 mmol, 2.000 eq) was slowly added, the mixture was stirred for 2 h at 0 °C. After the reaction was completed, diluted aqueous sodium bicarbonate was slowly added to quench the reaction. Then, Et_2O was added, the mixture was washed with diluted aqueous sodium bicarbonate for several times until the pH of the aqueous layer was larger than 7. Then the organic layer was washed with brine and dried over Na_2SO_4, filtered and concentrated under reduced pressure to give the target product, which was purified by column chromatography, silica gel, pentane/EtOAc 9/1.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.46 (s, 2H), 5.06 (s, 2H), 7.18-7.32 (m, 6H), 7.45-7.64 (m, 3H), 8.07 (d, *J*=8.4 Hz, 1H), 8.19 (d, *J*=8.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 140.19, 138.60, 132.62, 131.93, 131.51, 128.76, 128.53, 127.48, 126.75, 126.39, 126.23, 126.21, 125.14, 124.32, 44.79, 39.17.

MS (HRMS - ESI): Calc. for $C_{18}H_{15}Cl$ $[M+1]^+$ 267.0862, found 267.0864.

3.2.1 Synthesis of *p*-aryl compounds



Synthesis of **1m** (Ar=Ph - **1-chloromethyl-4-Phenylnaphthalene**) is given as an example.[13] Following a modified literature procedure,[14] In a dried round bottom flask, under N_2 atmosphere, 4-Bromo-1-naphthoic acid (15.065 g, 60.000 mmol, 1.000 eq) was dissolved in dry THF (250.0 mL) , to the mixture LiAlH4 (99.0 mL, 99.000 mmol, 1.650 eq) in THF was added slowly and the reaction was then heated to reflux overnight. The mixture was allowed to cool to r.t. and quenched by slow addition of ice cold water. Then the aqueous phase was acidified by addition of 6M HCl and extracted with Et_2O (3x100 mL). Then the organic layer was washed with brine and dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude was subjected to column chromatography (silica gel, pentane/ EtOAc 9:1 to 7:3) to give the alcohol as a white solid in 69% yield.

Under N_2 atmosphere, 4-bromo-1-hydroxymethyl-naphthalene (1.000 g, 4.218 mmol, 1.000 eq) was dissolved in toluene (29.5 mL) and an aqueous 2.0 M Cs_2CO_3 (13.5 mL, 26.993 mmol, 6.400 eq) solution was added. Phenyl boronic acid (1.029 g, 8.435 mmol, 2.000 eq) was dissolved in EtOH (13.5

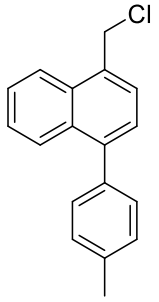
mL) and added to the mixture. Then TBAB (Tetrabutylammonium bromide) (1.360 g, 4.218 mmol, 1.000 eq) was added to the reaction mixture. The mixture was deoxygenated under reduced pressure and flushed with nitrogen. After repeating this cycle several times, $Pd(OAc)_2$ (0.038 g, 0.169 mmol, 0.040 eq) was added and the resulting suspension was heated under reflux for 8 h. After cooling, ethyl acetate (10 mL) and water (10 mL) were added and the organic phase was separated. The water phase was extracted with ethyl acetate (2x10 mL). The combined organic phases were washed with brine, dried over Na2SO4, filtered over a short plug of celite, and evaporated under reduced pressure. The crude was subjected to column chromatography (silica gel, pentane/ EtOAc 9:1) to give the alcohol as a white solid in 90% yield.

In a dried two-necked round bottom flask, under inert atmosphere, to a solution of 1-hydroxymethyl-4-phenyl-naphthalene (888.0 mg, 3.790 mmol, 1.000 eq) in dry DCM (19.0 mL) at 0 ℃, $SOCl_2$ (0.550 mL, 7.580 mmol, 2.000 eq) was slowly added, the mixture was stirred for 2 h at 0 ℃. After the reaction was completed, diluted aqueous sodium bicarbonate was slowly added to quench the reaction. Then, Et_2O was added, the mixture was washed with diluted aqueous sodium bicarbonate for several times until the pH of the aqueous layer was larger than 7. Then the organic layer was washed with brine and dried over Na_2SO_4, filtered and concentrated under reduced pressure to give the target product. The crude was subjected to column chromatography (silica gel, pentane) to give **1m** as a sticky oil in 90% yield. The spectral properties are in accordance with the one reported in literature.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.10 (s, 2H), 7.37 (d, *J*=7.1 Hz, 1H), 7.41-7.52 (m, 6), 7.57 (d, *J*=7.1 Hz, 1H), 7.61 (t, *J*=8.5 Hz, 1H), 7.93 (d, *J*=8.5 Hz, 1H), 8.21 (d, *J*=8.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 144.72, 143.04, 135.04, 134.89, 134.03, 132.67, 130.95, 130.13, 129.91, 129.75, 129.23, 128.96, 128.85, 126.53, 47.38.

1-chloromethyl-4-(*p*-Methyl-Phenyl)naphthalene (**1n**)[15]

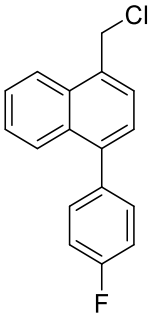


Following the general procedure for the synthesis of *p*-aryl compounds, compound **1o** was obtained as a white solid in 67% yield (from 4-bromo-1-hydroxymethyl-naphthalene). The spectral properties are in accordance with the one reported in literature.

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.46 (s, 3H), 5.11 (s, 2H), 7.31 (d, *J*=7.3 Hz, 1H), 7.34-7.39 (m, 3H), 7.44-7.50 (m, 1H), 7.55-7.64 (m, 2H), 7.96 (d, *J*=8.4 Hz, 1H), 8.21 (d, *J*=8.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 142.08, 137.44, 137.22, 132.32, 132.16, 131.38, 129.89, 129.00, 127.30, 127.16, 126.51, 126.26, 126.09, 123.85, 44.78, 21.24.

1-chloromethyl-4-(*p*-Fluoro-Phenyl)naphthalene (**1o**)



Following the general procedure for the synthesis of *p*-aryl compounds, compound **1p** was obtained as a white solid in 67% yield (from 4-bromo-1-hydroxymethyl-naphthalene).

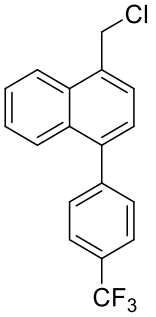
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.09 (s, 2H), 7.17 (t, *J*=8.5 Hz, 2H), 7.34 (d, *J*=7.3 Hz, 1H), 7.38-7.44 (m, 2H), 7.48 (t, *J*=7.5 Hz, 1H), 7.56 (d, *J*=7.3 Hz, 1H), 7.62 (t, *J*=7.5 Hz, 1H), 7.87 (d, *J*=8.5 Hz, 1H), 8.21 (d, *J*=8.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.04 (d, *J*=246.6 Hz), 143.59, 138.94 (d, *J*=3.3 Hz), 135.27, 134.91, 134.20 (d, *J*=8.0 Hz), 134.04, 129.85, 129.48, 129.31, 129.18, 129.05, 128.99, 126.62, 117.91 (d, *J*=21.4 Hz),, 47.28.

^{19}F NMR (377 MHz, $CDCl_3$): δ -115.00.

MS (HRMS - ESI): Calc. for $C_{17}H_{12}ClF$ $[M+1]^+$ 271.0612, found 271.0626.

1-chloromethyl-4-(*p*-TrifluoroMethyl-Phenyl)naphthalene (**1p**)



Following the general procedure for the synthesis of *p*-aryl compounds, compound **1q** was obtained as a white solid in 59% yield (from 4-bromo-1-hydroxymethyl-naphthalene).

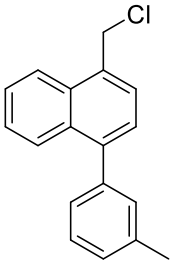
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.11 (s, 2H), 7.37 (d, *J*=7.3 Hz, 1H), 7.48-7.53 (m, 1H), 7.57-7.67 (m, 4H), 7.76 (d, *J*=8.1 Hz, 2H), 7.84 (d, *J*=8.5 Hz, 1H), 8.24 (d, *J*=8.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$):[i] δ 144.09, 140.44, 133.24, 131.87, 131.37, 130.35, 129.90, 127.14, 126.84, 126.60, 126.57, 126.39, 125.35, 125.31, 125.27, 125.24, 124.07, 44.49.

^{19}F NMR (377 MHz, $CDCl_3$): δ -62.45.

MS (HRMS - ESI): Calc. for $C_{18}H_{12}ClF_3$ $[M+1]^+$ 3210.0580, found 321.0584.**1-chloromethyl-4-(*m*-Methyl-Phenyl)naphthalene** (**1q**)

[i] High signal splitting from C-F coupling is present in the carbon NMR.



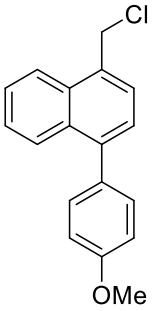
Following the general procedure for the synthesis of *p*-aryl compounds, compound **1r** was obtained as a white solid in 71% yield (from 4-bromo-1-hydroxymethyl-naphthalene).

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.43 (s, 3H), 5.09 (s, 2H), 7.22-7.28 (m, 3H), 7.33-7.40 (m, 2H), 7.46 (t, *J*=7.7 Hz, 1H), 7.54-7.63 (m, 2H), 7.94 (d, *J*=8.7 Hz, 1H), 8.20 (d, *J*=8.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 142.22, 140.33, 137.93, 132.27, 132.26, 131.36, 130.70, 128.19, 128.15, 127.26, 127.19, 127.11, 126.53, 126.21, 126.12, 123.85, 44.77, 21.50.

MS (HRMS - ESI): Calc. for $C_{18}H_{15}Cl$ $[M+1]^+$ 267.0862, found 267.0865.

1-chloromethyl-4-(*m*-Methoxy-Phenyl)naphthalene (**1r**)



Following the general procedure for the synthesis of *p*-aryl compounds, compound **1s** was obtained as a white solid in 80% yield (from 4-bromo-1-hydroxymethyl-naphthalene).

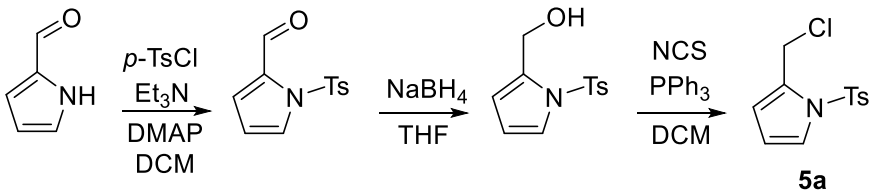
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.90 (s, 3H), 5.11 (s, 2H), 7.02-7.07 (m, 2H), 7.37 (d, *J*=7.3 Hz, 1H), 7.39-7.43 (m, 2H), 7.46-7.52 (m, 1H), 7.57 (d, *J*=7.3 Hz, 1H), 7.60-7.65 (m, 1H), 7.98 (d, *J*=8.4 Hz, 1H), 8.22 (d, *J*=8.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.13, 141.77, 132.73, 132.44, 132.07, 131.43, 131.11, 127.34, 127.15, 126.53, 126.31, 126.11, 123.89, 113.78, 55.38, 44.81.

MS (HRMS - ESI): Calc. for $C_{18}H_{15}Cl$ $[M+1]^+$ 283.0811, found 283.0813.

3.3 Synthesis of heteroaromatic compounds

2-chloromethyl-tosyl-pyrrole (5a)[16]



5a

Under N_2 atmosphere, p-TsCl (3.813 g, 20.00 mmol, 2 equiv.), Et_3N (4.2 ml, 30.00 equiv.) and DMAP (5 mol%) were added to a solution of pyrrole-2-carboxaldehyde in 50 mL of dry DCM at 0°C. The mixture

was stirred for 24 h at r.t., then quenched with NH_4Cl and extracted with DCM (3x30 mL). The combined organic phases were dried over Na2SO4 and the crude was purified by column chromatography (silica gel, pentane/DCM 3:1) to give the product as a white solid (90% yield).

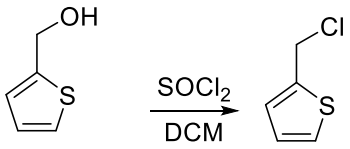
In a dry round bottom flask, under N_2 atm, $NaBH_4$ (0.355 g, 9.39 mmol, 1.5 equiv) was dissolved in 40 mL of dry MeOH. The aldehyde (1.56 g, 6.26 mmol, 1.0 equiv.) was dissolved in 40 ml of dry MeOH and added to the first solution. The mixture was stirred at r.t. until completion. The reaction was quenched with 20 mL of water and the methanol evaporated, then the aqueous phase was extracted with DCM (3x30 mL). The combined organic phases were dried over Na2SO4 and the crude was purified by column chromatography (silica gel, pentane/DCM 8:2) to give the product as a white solid (96% yield).

Into a flame-dried flask with a stirring bar was added the alcohol (1.5 g, 6.00 mmol, 1 equiv.). Dichloromethane (40 mL) was added to the flask under inert atmosphere. The reaction mixture was cooled to 0 °C. Triphenylphosphine (3.15 g, 12.00 mmol, 2 equiv.) was added to the flask. N-Chlorosuccinimide (1.36 g, 10.20 mmol, 1.7 equiv.) was then added slowly to the flask at 0 °C. The reaction mixture was stirred approximately for 20 min at 0 °C. Upon completion of reaction, the reaction mixture was diluted with water and extracted with ethyl acetate (3x30 mL). The organic layer was washed with brine and dried over sodium sulfate to give crude product which was purified by column chromatography (silica gel, pentane/DCM 3:1) to give the product as a white solid (86% yield). The spectral properties are in accordance with the one reported in literature.

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3H), 4.48 (s, 2H), 6.23-6.26 (m, 1H), 6.35-6.38 (m, 1H), 7.28-7.33 (m, 3H), 7.78 (d, *J*=8.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 145.21, 135.88, 130.39, 129.92, 127.31, 124.41, 116.96, 111.67, 37.30, 21.64.

2-chloromethyl-thiophene (5b)[17]



To a solution of $SOCl_2$ (1.5 mL, 21.00 mmol, 2.1 equiv.) in dry DCM (15.0 mL) was added a solution of the alcohol (1.142 g, 10.00 mmol, 1.0 equiv.) in dry THF (8.0 mL) dropwise at 0°C. The reaction mixture was stirred for 30 min at r.t. The resulting reaction mixture was quenched with $NaHCO_3$ and extracted with DCM. The crude product was distilled by vacuum distillation to get a colorless oil (88% yield). The spectral properties are in accordance with the one reported in literature.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (dd, J_1 = 5.1 Hz, J_2 = 1.2 Hz, 1H), 7.07 (dd, J_1 = 3.5 Hz, J_2 = 1.2 Hz, 1H), 6.94 (dd, J_1 = 5.1 Hz, J_2 = 3.5 Hz, 1H), 4.80 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 140.21, 127.82, 127.03 (two overlapping signals), 40.5.

4. General Procedures for the palladium catalyzed allylative deazomatisation.

4.1 General procedure for the Pd-catalyzed allylative dearomatisation with Grignard reagents (A)

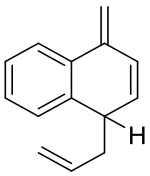
To an oven dried Schlenk, under N_2 atmosphere, were added the substrate (0.3 mmol, 1.0 equiv.) and $Pd(PPh_3)_4$ (0.003 mmol, 1 mol%), then dry 2-Me-THF (1 mL) was added and the mixture was stirred for 5 minutes. Allyl Magnesium Bromide (0.375 mL, 1M in Et_2O, 1.25 equiv.) was added in one go and the mixture stirred at r.t. until completion (TLC checks – 15 minutes). After complete consumption of the substrate, pentane (20 mL) was added to precipitate out the salts and the suspension was filtered over celite. Evaporation of the solvent yielded the crude dearomatised product, which was then purified by column chromatography (silica gel or alumina as stationary phase) using pentane or a mixture of pentane and EtOAc as an eluent.

4.2 General procedure for the acid catalyzed rearomatisation (B)

To an oven dried Schlenk, under N_2 atmosphere, were added the substrate (0.3 mmol, 1.0 equiv.) and $Pd(PPh_3)_4$ (0.003 mmol, 1 mol%), then dry 2-Me-THF (1 mL) was added and the mixture was stirred for 5 minutes. Allyl Magnesium Bromide (0.375 mL, 1M in Et_2O, 1.25 equiv.) was added in one go and the mixture stirred at r.t. until completion (TLC checks – 15 minutes). After complete consumption of the substrate, *p*-TsOH-H_2O (0.6 mmol, 2 equiv.) was added and the mixture was stirred for an additional 10 minutes. Then, a saturated solution of $NaHCO_3$ (10 mL) was added, and the aqueous phase was extracted with Et_2O (3x10 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated under reduced pressure to give the crude rearomatised compound, which was then purified by column chromatography (silica gel) using pentane or a mixture of pentane and EtOAc as an eluent.

5 Characterization of products

1-allyl-4-methylene-1,4-dihydronaphthalene (**2a**)[18]

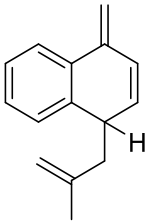


The compound was synthesized using the general procedure A, the crude compound was purified by column chromatography (basic alumina) using pentane as eluent, giving **2a** as a colorless oil (97% yield, 53 mg). The spectral properties are in accordance with the one reported in literature.

^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.39-2.47 (m, 1H), 2.52-5.60 (m, 1H), 3.67-3.73 (m, 1H), 4.95-5.04 (m, 3H), 5.64-5.78 (m, 2H), 5.98-6.03 (m, 1H), 6.49 (dd, J_1=10.0 Hz, J_2=1.5 Hz, 1H), 7.22-7.29 (m, 1H), 7.30-7.33 (m, 2H), 7.75 (d, J=7.4 Hz, 1H).

^{13}C NMR (101 MHz, CD_2Cl_2): δ 137.98, 137.96, 135.33, 132.06, 130.67, 128.82, 128.38, 127.77, 126.22, 123.13, 116.60, 108.50, 42.68, 40.30.

1-(2-methylallyl)-4-methylene-1,4-dihydronaphthalene (**2ad**)



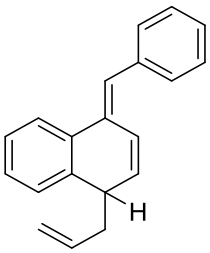
The compound was synthesized using a modification to the general procedure A, employing 1.5 equiv. of Grignard, the crude compound was purified by column chromatography (basic alumina) using pentane as eluent, giving **2d** as a colorless oil (90% yield, 53 mg).

^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.79 (s, 3H), 2.20-2.29 (m, 1H), 2.50-5.56 (m, 1H), 3.72-3.79 (m, 1H), 4.67-4.69 (m, 1H), 4.81-4.85 (m, 1H), 5.03-5.06 (m, 1H), 5.67 (s, 1H), 6.03 (ddq, J_1=0.7 Hz, J_2=4.5 Hz, J_3=10.1 Hz, 1H), 6.46 (d, J= 10.1 Hz, 1H) 7.22-7.32 (m, 3H), 7.76 (d, J=7.5 Hz, 1H).

^{13}C NMR (101 MHz, CD_2Cl_2): δ 143.08, 138.62, 137.95, 131.79, 130.81, 128.47, 128.24, 127.71, 126.18, 123.20, 112.59, 108.45, 47.68, 38.65, 22.16.

MS (HRMS - ESI): Calc. for $C_{15}H_{16}$ $[M+1]^+$ 197.1325, found 197.1324.

(*E*)-1-allyl-4-benzylidene-1,4-dihydronaphthalene (**2b**)



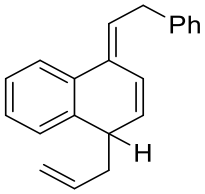
The compound was synthesized using the general procedure A, the crude compound was purified by column chromatography (basic alumina) using pentane as eluent, giving **2b** as a colorless oil (85% yield, 66 mg). Analysis of NOESY spectrum confirms the geometry of the external double bond (see below for spectrum).

^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.42-2.51 (m, 1H), 2.52-2.61 (m, 1H), 3.67-3.75 (m, 1H), 4.98-5.05 (m, 2H), 5.72-5.84 (m, 1H), 6.16 (ddd, J_1=1.5 Hz, J_2=4.8 Hz, J_3=10.2 Hz , 1H), 6.97 (d, J=10.2 Hz, 1H), 7.18 (s, 1H), 7.24-7.48 (m, 8H), 7.85-7.90 (m, 1H).

^{13}C NMR (101 MHz, CD_2Cl_2): δ 138.44, 137.66, 135.45, 133.78, 133.76, 133.56, 132.39, 131.25, 129.41, 128.45, 128.17, 127.23, 126.70, 126.32, 124.63, 122.62, 122.60, 116.65, 42.93, 40.78.

MS (HRMS - ESI): Calc. for $C_{21}H_{18}$ $[M-1]^+$ 259,14813 found 259.14823.

(E)-1-allyl-4-(2-phenylethylidene)-1,4-dihydronaphthalene (**2c**)



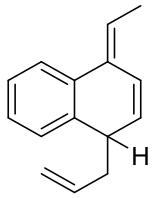
The compound was synthesized using the general procedure A, the crude compound was purified by column chromatography (basic alumina) using pentane as eluent, giving **2c** as a colorless oil (77% yield, 63 mg). Analysis of NOESY spectrum confirms the geometry of the external double bond (see below for spectrum).

^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.38-2.47 (m, 1H), 2.49-2.57 (m, 1H), 3.65-3.73 (m, 3H), 4.95-5.04 (m, 2H), 5.68-5.81 (m, 1H), 6.12 (ddd, J_1=1.8 Hz, J_2=4.6 Hz, J_3=10.3 Hz , 1H), 6.25-6.35 (m, 1H), 6.97 (dt, J_1=1.0 Hz, J_2=10.3 Hz, 1H), 7.18-7.35 (m, 8H), 7.65-7.71 (m, 1H).

^{13}C NMR (101 MHz, CD_2Cl_2): δ 140.93, 137.53, 135.53, 133.61, 131.27, 129.43, 128.46, 128.41, 128.33, 126.82, 126.15, 125.97, 123.26, 122.54, 122.43, 116.50, 42.88, 40.50, 33.68.

MS (HRMS - ESI): Calc. for $C_{21}H_{20}$ $[M-1]^+$ 271.1565, found 271.1561.

(*E*)-1-allyl-4-ethylidene-1,4-dihydronaphthalene (**2d**)



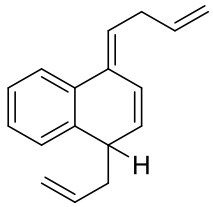
The compound was synthesized using the general procedure A, the crude compound was purified by column chromatography (basic alumina) using pentane as eluent, giving **2d** as a colorless oil (90% yield, 53 mg). Analysis of NOESY spectrum confirms the geometry of the external double bond (see below for spectrum).

^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.95 (d, *J*= 7.3 Hz, 3H), 2.36-2.46 (m, 1H), 2.48-2.57 (m, 1H), 3.63-3.70 (m, 1H), 4.97-5.05 (m, 2H), 5.71-5.84 (m, 1H), 6.03-6.09 (m, 1H), 6.24 (q, *J*= 7.3 Hz, 1H), 6.79 (d, *J*= 10.1 Hz, 1H), 7.18-7.31 (m, 3H), 7.63-7.70 (m, 1H).

^{13}C NMR (101 MHz, CD_2Cl_2): δ 137.18, 135.72, 133.83, 130.47, 130.05, 128.39, 126.56, 126.15, 123.17, 122.19, 118.60, 116.43, 43.07, 40.44, 13.11.

MS (HRMS - ESI): Calc. for $C_{15}H_{16}$ $[M-1]^+$ 195.1252, found 195.1258.

(*E*)-1-allyl-4-(but-3-en-1-ylidene)-1,4-dihydronaphthalene (**2e**)



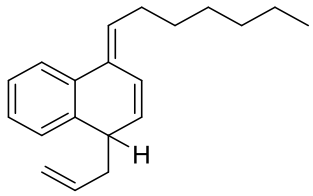
The compound was synthesized using the general procedure A, the crude compound was purified by column chromatography (basic alumina) using pentane as eluent, giving **2e** as a colorless oil (93%, 62 mg) yield). Analysis of NOESY spectrum confirms the geometry of the external double bond (see below for spectrum).

^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.36-2.45 (m, 1H), 2.48-2.56 (m, 1H), 3.09-3.15 (m, 2H), 3.63-3.71 (m, 1H), 4.97 (t, *J*=1.2 Hz, 1H), 4.99-5.02 (m, 1H), 5.06 (dq, J_1=1.6 Hz J_2=10.0 Hz, 1H), 5.14 (dq, J_1=1.6 Hz J_2=17.1 Hz, 1H), 5.70-5.81 (m, 1H), 5.90-6.00 (m, 1H), 6.08 (ddd, J_1=1.8 Hz, J_2=4.6 Hz, J_3=10.2 Hz, 1H), 6.15 (tq, J_1=1.5 Hz J_2=7.6 Hz, 1H), 6.74 (dt, J_1=1.2 Hz J_2=10.2 Hz, 1H), 7.20-7.30 (m, 3H), 7.68-7.73 (m, 1H).

^{13}C NMR (101 MHz, CD_2Cl_2): δ 137.45, 136.55, 135.57, 133.60, 130.84, 130.55, 128.34, 126.77, 126.16, 123.20, 122.38, 121.00, 116.47, 114.87, 42.91, 40.44, 31.78.

MS (HRMS - ESI): Calc. for $C_{17}H_{18}$ $[M-1]^+$ 221.1409, found 221.1324.

(*E*)-1-allyl-4-heptylidene-1,4-dihydronaphthalene (**2f**)



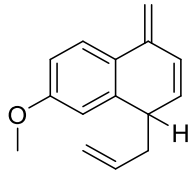
The compound was synthesized using the general procedure A, the crude compound was purified by column chromatography (basic alumina) using pentane as eluent, giving **2f** as a colorless oil (95% yield, 76 mg). Analysis of NOESY spectrum confirms the geometry of the external double bond (see below for spectrum).

^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.93 (t, *J*=6.8 Hz, 3H), 1.28-1.85 (m, 8H), 2.31-2.57 (m, 4H), 3.61-3.70 (m, 1H), 4.94-5.06 (m, 2H), 5.68-5.84 (m, 1H), 6.04 (ddd, J_1=1.8 Hz, J_2=4.7 Hz, J_3=10.3 Hz, 1H), 6.19 (t, J_1=7.6 Hz, 1H), 6.76 (d, J_1=10.3 Hz, 1H), 7.20-7.30 (m, 3H), 7.66-7.73 (m, 1H).

^{13}C NMR (101 MHz, CD_2Cl_2): δ 137.31, 135.69, 133.94, 130.01, 129.62, 128.34, 126.52, 126.09, 124.98, 123.57, 122.26, 116.39, 43.02, 40.44, 31.80, 29.78, 29.06, 27.63, 22.68, 13.88.

MS (HRMS - ESI): Calc. for $C_{20}H_{26}$ $[M-1]^+$ 265.2035, found 265.2038.

1-allyl-6-methoxy-4-methylene-1,4-dihydronaphthalene (**2i**)



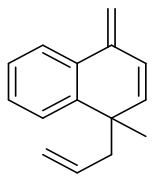
The compound was synthesized using the general procedure A, the crude compound was purified by column chromatography (basic alumina) using pentane/1% EtOAc as eluent, giving **2i** as a colorless oil (97% yield, 62 mg).

^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.40-2.49 (m, 1H), 2.53-2.60 (m, 1H), 3.64-3.69 (m, 1H), 3.83 (s, 3H), 4.92-4.94 (m, 1H), 4.97-5.03 (m, 2H), 5.54 (s, 1H), 5.67-5.78 (m, 1H), (ddd, J_2=0.8 Hz J_1= 4.3 Hz, J_2= 10.0 Hz, 1H), 6.43-6.47 (m, 1H), 6.79-6.86 (m, 2H), 7.69 (d, *J*=8.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.35, 139.49, 137.66, 135.34, 130.35, 128.94, 125.02, 124.66, 116.63, 112.94, 112.41, 106.77, 55.15, 42.66, 40.55.

MS (HRMS - ESI): Calc. for $C_{15}H_{16}O$ $[M-1]^+$ 211.1201, found 211.1204.

1-allyl-1-methyl-4-methylene-1,4-dihydronaphthalene (**2j**)[15]

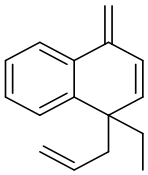


The compound was synthesized using the general procedure A, the crude compound was purified by column chromatography (basic alumina) using pentane as eluent, giving **2j** as a colorless oil (90% yield, 53 mg). The spectral properties are in accordance with the one reported in literature for crude mixtures.

^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.40 (s, 3H), 2.34-2.42 (m, 1H), 2.57-2.64 (m, 1H), 4.83-4.92 (m, 2H), 5.02 (d, *J*=0.9 Hz, 1H), 5.42-5.53 (m, 1H), 5.66 (s, 1H), 5.69-5.73 (m, 1H), 6.42 (d, *J*= 10.1 Hz, 1H), 7.20-7.26 (m, 1H), 7.32 (td, J_1= 1.4 Hz, J_2= 7.2, 1H), 7.42 (dd, J_1= 1.4 Hz, J_2= 7.8 Hz, 1H), 7.77 (dd, J_1= 1.4 Hz, J_2= 7.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 141.92, 137.80, 136.35, 134.19, 131.48, 128.12, 127.29, 126.64, 126.08, 123.23, 117.12, 108.97, 48.77, 40.72, 30.28.

1-allyl-1-ethyl-4-methylene-1,4-dihydronaphthalene (**2k**)



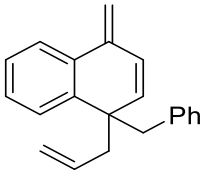
The compound was synthesized using the general procedure A, the crude compound was purified by column chromatography (basic alumina) using pentane as eluent, giving **2k** as a colorless oil (90% yield, 57 mg).

^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.57 (t, *J*=7.4 Hz, 3H), 1.61-1.72 (m, 1H), 1.89-2.00 (m, 1H), 2.36-2.44 (m, 1H), 2.60-2.70 (m, 1H), 4.81-4.93 (m, 2H), 5.00-5.05 (m, 1H), 5.42-5.53 (m, 1H), 5.56-5.61 (m, 1H), 5.67 (s, 1H), 6.55 (d, *J*=10.0 Hz, 1H), 7.21-7.27 (m, 1H), 7.30-7.39 (m, 2H), 7.80 (dd, J_1= 1.4 Hz, J_2= 8.0 Hz, 1H),

^{13}C NMR (101 MHz, $CDCl_3$): δ 139.84, 138.04, 134.91, 134.85, 132.84, 129.11, 128.10, 126.42, 125.88, 122.93, 116.46, 108.55, 48.10, 45.50, 35.79, 8.74.

MS (HRMS - ESI): Calc. for $C_{16}H_{18}$ $[M-1]^+$ 209.1323, found 209.1325. Main mass signal after fragmentation (loss of allyl). **MS (HRMS - ESI):** Calc. for $C_{13}H_{13}$ $[M]^+$ 169.1017, found 169.1007.

1-allyl-1-benzyl-4-methylene-1,4-dihydronaphthalene (2l)

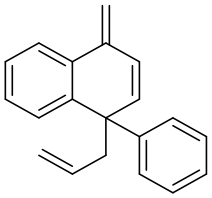


The compound was synthesized using the general procedure A, the crude compound was purified by column chromatography (basic alumina) using pentane as eluent, giving **2l** as a colorless oil (89% yield, 73 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.44-2.52 (m, 1H), 2.81-2.88 (m, 1H), 2.94 (d, *J*= 13.2 Hz, 1H), 3.12 (d, *J*= 13.2 Hz, 1H), 4.84-4.96 (m, 3H), 5.41-5.53 (m, 2H), 5.64 (d, *J*= 10.1 Hz, 1H), 6.39 (d, *J*= 10.1 Hz, 1H), 6.82-6.87 (m, 2H), 7.02-7.13 (m, 3H), 7.19-7.25 (m, 1H), 7.31-7.37 (m, 1H), 7.48 (dd, J_1= 1.4 Hz, J_2= 8.0 Hz, 1H), 7.68 (dd, J_1= 1.4 Hz, J_2= 8.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 139.59, 137.47, 137.44, 134.57, 134.07, 132.64, 130.46, 128.86, 128.43, 127.81, 127.40, 126.97, 126.13, 125.97, 123.14, 117.15, 108.99, 50.01, 46.66, 45.82.Main mass signal after fragmentation (loss of allyl and loss of benzyl). **MS (HRMS - ESI):** Calc. for $C_{18}H_{15}$ $[M]^+$ 231.1174, found 231.1166. **MS (HRMS - ESI):** Calc. for $C_{14}H_{13}$ $[M]^+$ 181.1017, found 181.1009.

1-allyl-4-methylene-1-phenyl-1,4-dihydronaphthalene (**2m**) [15]

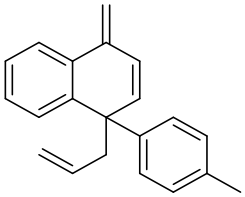


The compound was synthesized using the general procedure A, the crude compound was purified by column chromatography (basic alumina) using pentane/1% EtOAc as eluent, giving **2m** as a colorless oil (75% yield, 58 mg). The spectral properties are in accordance with the one reported in literature for crude mixtures.

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.91-3.02 (m, 1H), 3.05-3.16 (m, 1H), 4.87-5.01 (m, 2H), 5.13 (s, 1H), 5.45-5.60 (m, 1H), 5.68-5.79 (m, 2H), 6.52 (d, *J*= 9.9 Hz, 1H), 6.97-7.04 (m, 1H), 7.17-7.24 (m, 3H), 7.26-7.34 (m, 4H), 7.77-7.84 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 147.52, 141.18, 137.39, 135.05, 134.25, 131.58, 129.16, 128.30, 128.21, 127.45, 127.10, 126.20, 126.08, 122.87, 117.61, 109.76, 48.91, 44.99.

MS (HRMS - ESI): Calc. for $C_{20}H_{18}$ $[M+1]^+$ 259.1481, found 259.1483.**1-allyl-4-methylene-1-(4'-methylphenyl)-1,4-dihydronaphthalene** (**2n**)[15]

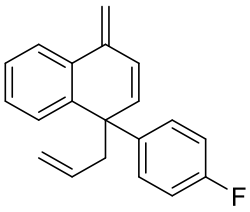


The compound was synthesized using the general procedure A, the crude compound was purified by column chromatography (basic alumina) using pentane/1% EtOAc as eluent, giving **2n** as a colorless oil (80% yield, 69 mg). The spectral properties are in accordance with the one reported in literature for crude mixtures.

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.30 (s, 3H), 2.90-2.97 (m, 1H), 3.03-3.11 (m, 1H), 4.86-4.98 (m, 2H), 5.10 (s, 1H), 5.44-5.56 (m, 1H), 5.67-5.75 (m, 2H), 6.49 (d, *J*= 9.9 Hz, 1H), 6.98-7.03 (m, 1H), 7.09 (d, *J*= 8.2 Hz, 2H), 7.14-7.20 (m, 4H), 7.76-7.81 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 144.61, 141.34, 137.47, 135.74, 135.25, 134.32, 131.55, 129.07, 128.98, 128.17, 127.28, 126.93, 125.98, 122.83, 117.48, 109.56, 48.57, 45.04, 20.90.

Main mass signal after fragmentation (loss of allyl). **MS (HRMS - ESI):** Calc. for $C_{18}H_{15}$ $[M]^+$ 231.1174, found 231.1168.**1-allyl-4-methylene-1-(4'-fluorophenyl)-1,4-dihydronaphthalene** (**2o**)



The compound was synthesized using the general procedure A, the crude compound was purified by column chromatography (basic alumina) using pentane/1% EtOAc as eluent, giving **2o** as a colorless oil (75% yield, 62 mg).

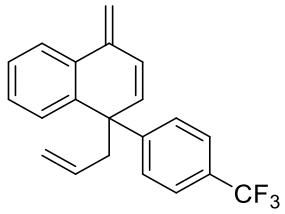
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.88-2.95 (m, 1H), 3.02-3.10 (m, 1H), 4.87-4.98 (m, 2H), 5.12 (s, 1H), 5.43-5.55 (m, 1H), 5.65-5.70 (m, 1H), 5.75 (s, 1H), 6.50 (d, *J*= 9.9 Hz, 1H), 6.92-7.00 (m, 3H), 7.14-7.20 (m, 2H), 7.22-7.28 (m, 2H), 7.76-7.81 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 161.18 (d, *J*= 245.4 Hz), 143.33 (d, *J*= 3.3 Hz), 140.93, 137.23, 134.78, 133.95, 131.53, 129.57, 129.01 (d, *J*= 2.3 Hz), 128.94, 128.23, 127.20, 126.18, 125.77, 122.94, 117.75, 11497 (d, *J*= 21.1 Hz), 109.99, 48.40, 45.21.

^{19}F NMR (377 MHz, $CDCl_3$): δ -117.01 --- -116.94 (m).

MS (HRMS - ESI): Calc. for $C_{20}H_{18}$ $[M+1]^+$ 277.1314, found 277.1289.

Main mass signal after fragmentation (loss of allyl). **MS (HRMS - ESI):** Calc. for $C_{17}H_{12}F$ $[M]^+$ 235.0933, found 235.0919.**1-allyl-4-methylene-1-(4'-trifluoromethyl-phenyl)-1,4-dihydronaphthalene** (**2p**)[15]



The compound was synthesized using the general procedure A, the crude compound was purified by column chromatography (basic alumina) using pentane/2% EtOAc as eluent, giving **2p** as a colorless oil (67% yield, 65 mg). The spectral properties are in accordance with the one reported in literature for crude mixtures.

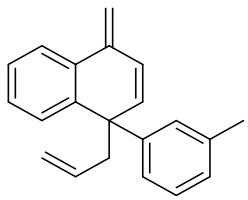
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.91-2.99 (m, 1H), 3.06-3.13 (m, 1H), 4.89-4.99 (m, 2H), 5.14 (s, 1H), 5.42-5.55 (m, 1H), 5.66 (d, *J*= 10.0 Hz, 1H), 5.77 (s, 1H), 6.53 (d, *J*= 10.0 Hz, 1H), 6.91-6.96 (m, 1H), 7.15-7.24 (m, 2H), 7.40 (d, *J*= 8.4 Hz, 2H), 7.52 (d, *J*= 8.4 Hz, 2H), 7.78-7.83 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$)[ii]: δ 151.54, 140.20, 137.02, 133.98, 133.58, 131.62, 130.47, 128.97, 128.34, 128.24, 128.10, 127.81, 127.75, 127.71, 126.66, 126.44, 125.25, 125.21, 125.18, 125.14, 123.06, 118.03, 110.44, 48.97, 44.88.

^{19}F NMR (377 MHz, $CDCl_3$): δ -62.47.

Main mass signal after fragmentation (loss of allyl). **MS (HRMS - ESI):** Calc. for $C_{18}H_{12}F_3$ $[M]^+$ 285.0891, found 285.0894.

1-allyl-4-methylene-1-(3'-methylphenyl)-1,4-dihydronaphthalene (**2q**)



[ii] High signal splitting from C-F coupling is present in the carbon NMR.

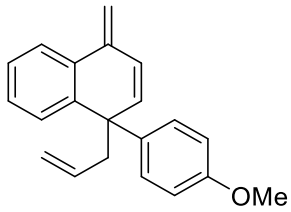
The compound was synthesized using the general procedure A, the crude compound was purified by column chromatography (basic alumina) using pentane/1% EtOAc as eluent, giving **2q** as a colorless oil (80% yield, 69 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.29 (s, 3H), 2.89-2.96 (m, 1H), 3.03-3.10 (m, 1H), 4.85-4.96 (m, 2H), 5.10 (s, 1H), 5.43-5.55 (m, 1H), 5.67-5.72 (m, 1H), 5.73 (s, 1H), 6.49 (d, *J*= 9.9 Hz, 1H), 6.96-7.02 (m, 2H), 7.06-7.11 (m, 2H), 7.12-7.19 (m, 3H), 7.75-7.80 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 147.43, 141.28, 137.80, 137.47, 135.15, 134.31, 131.54, 129.14, 128.24, 128.17, 128.12, 127.01, 126.98, 126.00, 124.46, 122.82, 117.49, 109.58, 48.82, 45.09, 21.63.

Main mass signal after fragmentation (loss of allyl). **MS (HRMS - ESI):** Calc. for $C_{18}H_{15}$ $[M]^+$ 231.1174, found 231.1168.

1-allyl-4-methylene-1-(4'-methoxyphenyl)-1,4-dihydronaphthalene (**2r**) [15]



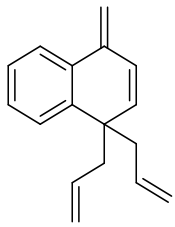
The compound was synthesized using the general procedure A, the crude compound was purified by column chromatography (basic alumina) using pentane/5% EtOAc as eluent, giving **2r** as a colorless oil (80% yield, 69 mg). The spectral properties are in accordance with the one reported in literature for crude mixtures.

^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.89-2.97 (m, 1H), 3.05-3.13 (m, 1H), 3.76 (s, 3H), 4.86-4.98 (m, 2H), 5.12 (s, 1H), 5.45-5.56 (m, 1H), 5.70 (d, *J*= 10.0 Hz, 1H), 5.76 (s, 1H), 6.51 (d, *J*= 10.0 Hz, 1H), 6.79-6.84 (m, 2H), 6.99-7.04 (m, 1H), 7.15-7.22 (m, 4H), 7.77-7.82 (m, 1H).

^{13}C NMR (101 MHz, CD_2Cl_2): δ 141.45, 139.67, 137.49, 135.31, 134.46, 131.47, 131.11, 128.98, 128.28, 128.08, 126.78, 125.95, 122.81, 117.13, 113.47, 109.40, 55.13, 48.16, 44.93.

MS (HRMS - ESI): Calc. for $C_{20}H_{18}$ $[M+1]^+$ 289.1586, found 289.1583.

1,1-diallyl-4-methylene-1,4-dihydronaphthalene (2s)



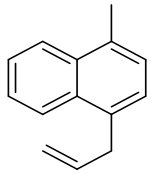
The compound was synthesized using a modification to the general procedure A, employing 2.5 equivalent of Grignard, the crude compound was purified by column chromatography (basic alumina) using pentane as eluent, giving **2s** as a colorless oil (80% yield, 53 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.39-2.46 (m, 2H), 2.62-2.70 (m, 2H), 4.83-4.91 (m, 4H), 5.06 (s, 1H), 5.41-5.53 (m, 2H), 5.64-5.69 (m, 2H), 6.51 (d, *J*= 10.3 Hz, 1H), 7.21-7.26 (m, 1H), 7.31-7.36 (m, 1H), 7.40 (dd, J_1= 1.3 Hz, J_2= 8.0 Hz, 1H), 7.78 (dd, J_1= 1.3 Hz, J_2= 8.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 139.70, 137.80, 134.59, 134.48, 132.42, 128.73, 128.06, 126.72, 126.04, 123.00, 116.82, 108.87, 47.45, 44.78.

MS (HRMS - ESI): Calc. for $C_{17}H_{18}$ $[M-1]^+$ 221.1409, found 221.1324.

1-allyl-4-methyl-naphthalene (**4a**)[8]

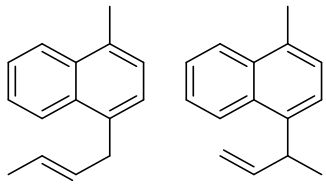


The compound was synthesized using the general procedure B, the crude compound was purified by column chromatography (silica gel) using pentane as eluent, giving **4a** as a colorless oil (90% yield, 50 mg). The spectral properties are in accordance with the one reported in literature.

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.67 (s, 3H), 3.79-3.83 (m, 2H), 5.05-5.12 (m, 2H), 6.05-6.16 (m, 2H), 7.12-7.28 (m, 2H), 7.48-7.55 (m, 2H), 7.99-8.06 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 139.90, 136.90, 135.60, 134.67, 129.01, 128.66, 128.08, 127.99, 127.42, 127.25, 118.62, 39.91, 22.09.

1-(2'-butenyl)-4-methyl-naphthalene (**4ab**) + **1-(1'-Methylallyl)-4-methyl-naphthalene** (**4ac**)[8]

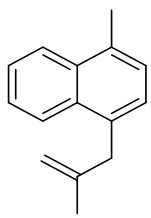


The compound was synthesized using a modification of the general procedure B, employing 1.5 equiv. of Grignard reagent, the crude compound was purified by column chromatography (silica gel) using pentane as eluent, giving **4ab** and **4ac** as a colorless oil (86% yield, 50 mg). The spectral properties are in accordance with the one reported in literature.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.51 (d, *J*=7.0 Hz, 3H minor), 1.83 (d, *J*=5.4 Hz, 3H major), 2.69 (s, 3H major + minor), 3.80-3.87 (m, 2H major + minor), 4.30 (q, *J*=6.6 Hz, 1H minor), 5.11-5.17 (m, 2H minor), 5.60-5.74 (m, 2H major), 6.13-6.23 (m, 1H minor), 7.27 (s, 2H major), 7.31 (s, 2H minor), 7.50-7.58 (m, 2H major + minor), 8.01-8.10 (m, 2H major + 1H minor), 8.15-8.21 (m, 1H minor)

^{13}C NMR (101 MHz, $CDCl_3$): δ 143.13, 139.61, 135.32, 133.03, 132.99, 132.68, 132.67, 132.11, 131.49, 129.15, 126.43, 126.39, 125.44, 125.42, 125.38, 125.36, 125.23, 124.95, 124.85, 124.83, 124.49, 124.04, 123.37, 113.53, 37.76, 30.66, 20.28, 19.53, 19.45, 13.02.

1-(2'-methyl-allyl)-4-methyl-naphthalene (**4ad**) [8]

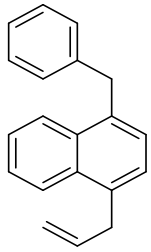


The compound was synthesized using a modification of the general procedure B, employing 1.5 equiv. of Grignard reagent, the crude compound was purified by column chromatography (silica gel) using pentane as eluent, giving **4ad** as a colorless oil (89% yield, 52 mg). The spectral properties are in accordance with the one reported in literature.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.78 (s, 3H), 2.69 (s, 3H), 3.76 (s, 2H), 4.63 (s, 1H), 4.86 (s, 1H), 7.21-7.29 (m, 2H), 7.46-7.55 (m, 2H), 8.00 -8.06 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 144.85, 133.85, 132.95, 132.93, 132.46, 126.90, 126.24, 125.31, 125.27, 124.88, 124.68, 112.07, 41.53, 22.78, 19.47.

1-allyl-4-benzylnaphthalene (**4b**)[8]

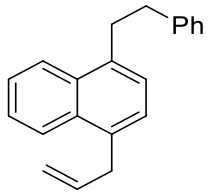


The compound was synthesized using the general procedure B, the crude compound was purified by column chromatography (silica gel) using pentane as eluent, giving **4b** as a colorless oil (81% yield, 63 mg). The spectral properties are in accordance with the one reported in literature.

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.85 (d, *J*=6.3 Hz, 2H), 4.44 (s, 2H), 5.08-5.16 (m, 2H), 6.07-6.19 (m, 1H), 7.15-7.32 (m, 7H), 7.42-7.53 (m, 2H), 8.03 (d, *J*=8.2 Hz, 1H), 8.07 (d, *J*=8.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 140.78, 137.11, 135.33, 135.08, 132.46, 132.42, 128.75, 128.45, 127.20, 126.03, 126.02, 125.63, 125.50, 124.99, 124.72, 116.18, 39.12, 37.37.

1-allyl-4-(2'-phenyl-ethyl)-naphthalene (**4c**)

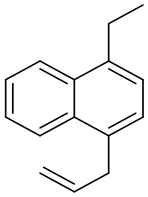


The compound was synthesized using the general procedure B, the crude compound was purified by column chromatography (silica gel) using pentane as eluent, giving **4c** as a colorless oil (76% yield, 62 mg). Mass has been reported for the dearomatised compound.

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.06 (t, *J*=7.8 Hz, 2H), 3.37 (t, *J*=7.8 Hz, 2H), 3.84 (d, *J*=6.3 Hz, 2H), 5.07-5.15 (m, 2H), 6.07-6.19 (m, 1H), 7.20-7.29 (m, 5H), 7.30-7.36 (m, 2H), 7.53-7.55 (m, 2H), 8.06-8.17 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 144.75, 139.83, 139.21, 137.27, 135.03, 134.78, 131.10, 131.09, 128.72, 128.67, 128.44, 128.19, 128.07, 127.56, 126.97, 118.75, 40.01, 39.84, 37.82.

1-allyl-4-Ethyl-naphthalene (**4d**)

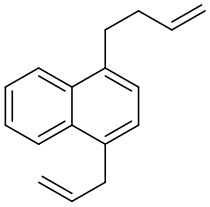


The compound was synthesized using the general procedure B, the crude compound was purified by column chromatography (silica gel) using pentane as eluent, giving **4d** as a colorless oil (88% yield, 52 mg). Mass has been reported for the dearomatised compound.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.30-1.56 (m, 3H), 3.10-3.21 (m, 2H), 3.83-3.91 (m, 2H), 5.11-5.21 (m, 2H), 6.10-6.25 (m, 1H), 7.30-7.36 (m, 2H), 7.51-7.60 (m, 2H), 8.06-8.17 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 138.99, 137.24, 134.19, 132.26, 132.12, 126.14, 126.14, 125.33, 125.33, 125.32, 124.78, 124.64, 124.40, 116.02, 37.35, 25.91, 15.09.

1-allyl-4-(but-3'-enyl)-naphthalene (**4e**)

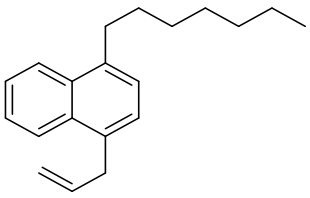


The compound was synthesized using the general procedure B, the crude compound was purified by column chromatography (silica gel) using pentane as eluent, giving **4e** as a colorless oil (90% yield, 64 mg). Mass has been reported for the dearomatised compound.

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.25 (q, *J*= 8.1 Hz, 2H), 3.17 (t, *J*= 8.1 Hz, 2H), 3.84 (d, *J*= 6.3 Hz, 2H), 5.02-5.16 (m, 4H), 5.92-6.03 (m, 1H), 6.08-6.19 (m, 1H), 7.28 (s, 2H), 7.49-7.56 (m, 2H), 8.05-8.11 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 141.00, 139.83, 139.30, 137.13, 135.00, 134.84, 128.66, 128.39, 128.07, 128.01, 127.47, 127.06, 118.73, 117.53, 40.00, 37.51, 35.17.

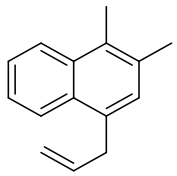
1-allyl-4-heptyl-naphthalene (**4f**)



The compound was synthesized using the general procedure B, the crude compound was purified by column chromatography (silica gel) using pentane as eluent, giving **4f** as a colorless oil (92% yield, 73 mg). Mass has been reported for the dearomatised compound.

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91 (t, *J*= 6.7 Hz, 3H), 1.23-1.51 (m, 8H), 1.76 (quint, *J*= 8.0 Hz, 2H), 3.05 (t, *J*= 7.5 Hz, 2H), 3.83 (d, *J*= 6.2 Hz, 2H), 5.05-5.17 (m, 2H), 6.05-6.21 (m, 1H), 7.27 (s, 2H), 7.46-7.57 (m, 2H), 8.02-8.13 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 137.76, 137.24, 134.14, 132.30, 132.23, 126.00, 125.62, 125.26, 125.25, 124.74, 124.58, 116.01, 37.35, 33.17, 31.90, 30.94, 29.86, 29.25, 22.71, 14.14.**1-allyl-4-isobutyl-naphthalene** (**4g**) [8]

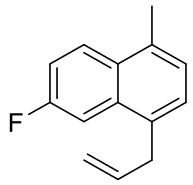


The compound was synthesized using the general procedure B, the crude compound was purified by column chromatography (silica gel) using pentane as eluent, giving **4g** as a colorless oil (78% yield, 46 mg). The spectral properties are in accordance with the one reported in literature.

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.48 (s, 3H), 2.59 (s, 3H), 3.80 (d, *J*= 6.3 Hz, 2H), 5.06-5.15 (m, 2H), 6.04-6.20 (m, 1H), 7.18 (s, 1H), 7.40-7.55 (m, 2H), 7.98-8.09 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 137.34, 133.40, 133.22, 132.80, 130.66, 129.83, 129.64, 125.40, 124.44, 124.39, 124.36, 115.92, 37.22, 20.76, 14.52.

4-allyl-6-fluoro-1-methylnaphthalene (**4h**)



The compound was synthesized using the general procedure B, the crude compound was purified by column chromatography (silica gel) using pentane as eluent, giving **4h** as a colorless oil (91% yield, 55 mg)

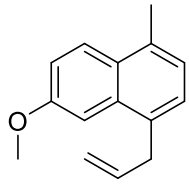
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.66 (s, 3H), 3.73 (d, *J*= 6.2 Hz, 2H), 5.04-5.14 (m, 2H), 6.02-6.13 (m, 1H), 7.18-7.31 (m, 3H), 7.63 (dd, J_1= 2.6 Hz, J_2= 11.3 Hz, 1H), 8.00 (dd, J_1= 5.8 Hz, J_2= 9.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 161.18 (d, *J*= 244.7 Hz), 139.38, 136.42 (d, *J*= 5.4 Hz), 135.88 (d, *J*= 1.4 Hz), 132.63 (d, *J*= 1.2 Hz), 129.88 (d, *J*= 8.7 Hz), 129.79, 128.29 (d, *J*= 2.3 Hz), 118.96, 118.01 (d, *J*= 24.9 Hz), 110.90 (d, *J*= 20.9 Hz), 39.94, 22.18.

^{19}F NMR (377 MHz, $CDCl_3$): δ -114.93 --- -114.84 (m)

MS (HRMS - ESI): Calc. for $C_{14}H_{13}F$ $[M+1]^+$ 200.1001, found 200.1013.

4-allyl-6-methoxy-1-methylnaphthalene (**4i**)

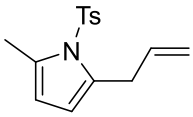


The compound was synthesized using the general procedure B, the crude compound was purified by column chromatography (silica gel) using pentane/2% EtOAc as eluent, giving **4i** as a colorless oil (96% yield, 61 mg). Mass has been reported for the dearomatised compound.

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.69 (s, 3H), 3.81 (d, *J*= 6.3 Hz, 2H), 3.96 (s, 3H), 5.14-5.21 (m, 2H), 6.09-6.21 (m, 1H), 7.16 (d, *J*= 7.2 Hz, 1H), 7.22-7.27 (m, 2H), 7.37 (d, *J*= 2.5 Hz, 1H), 7.98 (d, *J*= 9.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.93, 139.82, 135.98, 135.63, 135.62, 130.99, 129.35, 129.06, 126.93, 120.03, 118.63, 106.28, 57.89, 40.38, 22.13.

2-allyl-1,4-dimethylnaphthalene (**7a**)[16]

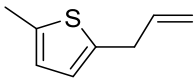


The compound was synthesized using the general procedure B, the crude compound was purified by column chromatography (silica gel) using pentane/5% EtOAc as eluent, giving **7k** as a white solid (88% yield, 73 mg).

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.37 (s, 3H), 2.40 (s, 3H), 3.56 (d, *J*= 6.7 Hz, 2H), 5.04-5.14 (m, 2H), 5.85-6.02 (m, 3H), 7.28 (d, *J*= 8.0 Hz, 2H), 7.54 (d, *J*= 8.0 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 144.42, 137.45, 135.23, 135.13, 132.74, 129.93, 126.12, 116.75, 111.96, 111.39, 33.40, 21.57, 15.58.

2-allyl-1,4-dimethylnaphthalene (**7b**) [16]

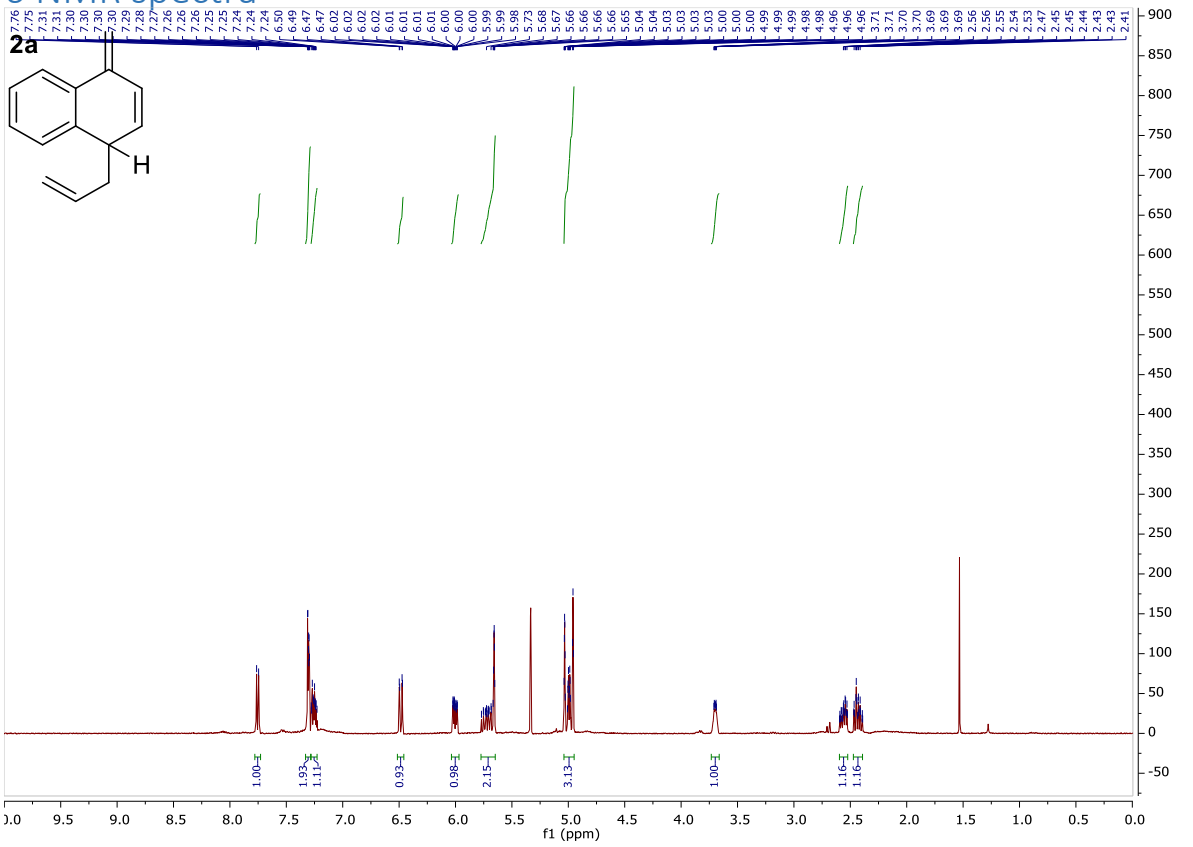


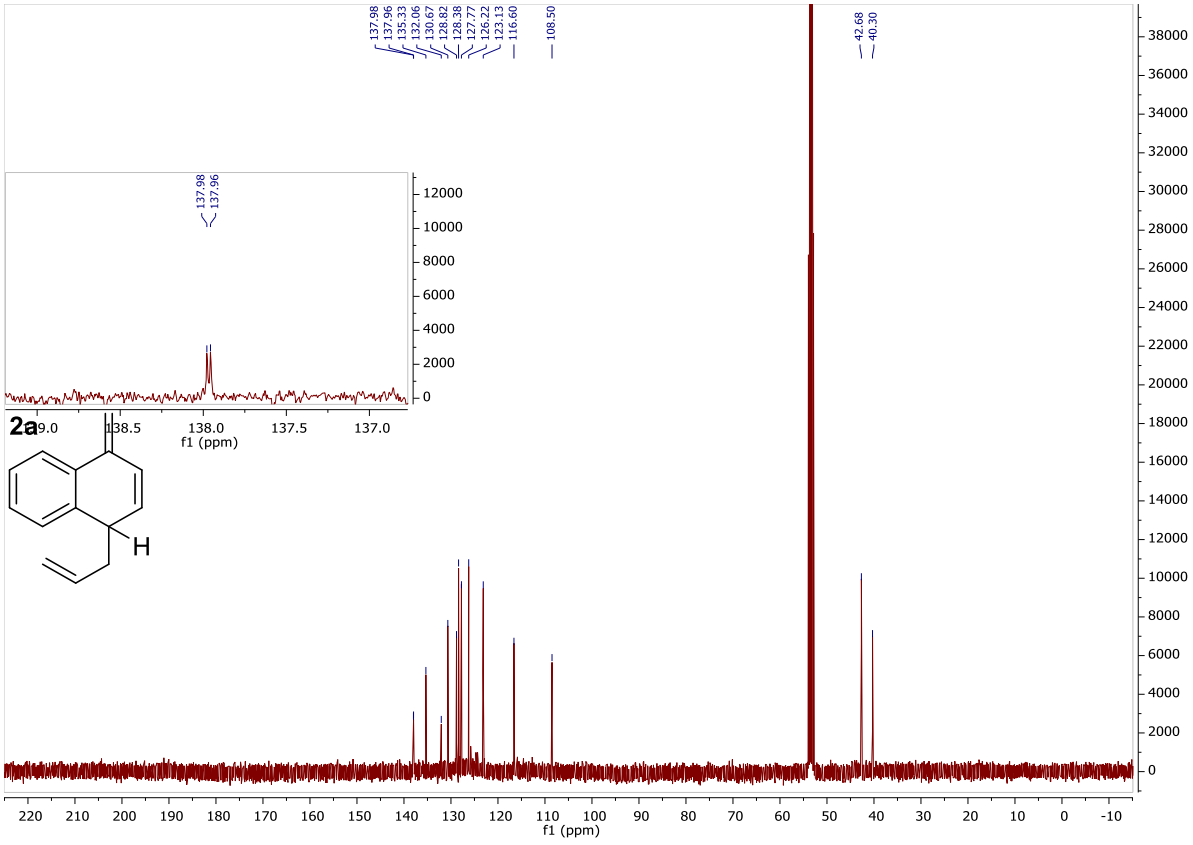
The compound was synthesized using the general procedure B, the crude compound was purified by column chromatography (silica gel) using pentane as eluent, giving **7k** as a colorless oil (67% yield, 28 mg)

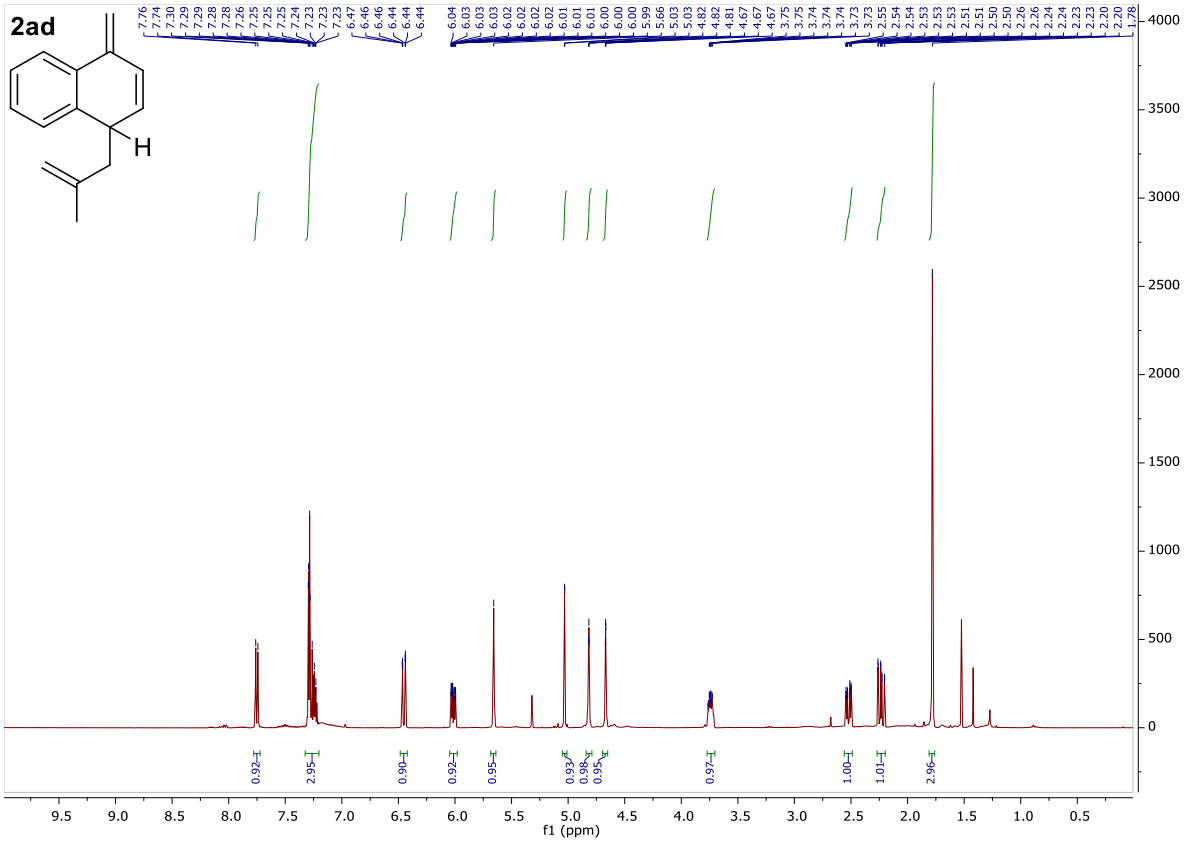
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.43 (s, 3H), 3.49 (d, *J*= 6.6 Hz, 2H), 5.04-5.17 (m, 2H), 5.91-6.03 (m, 1H), 6.57 (s, 2H).

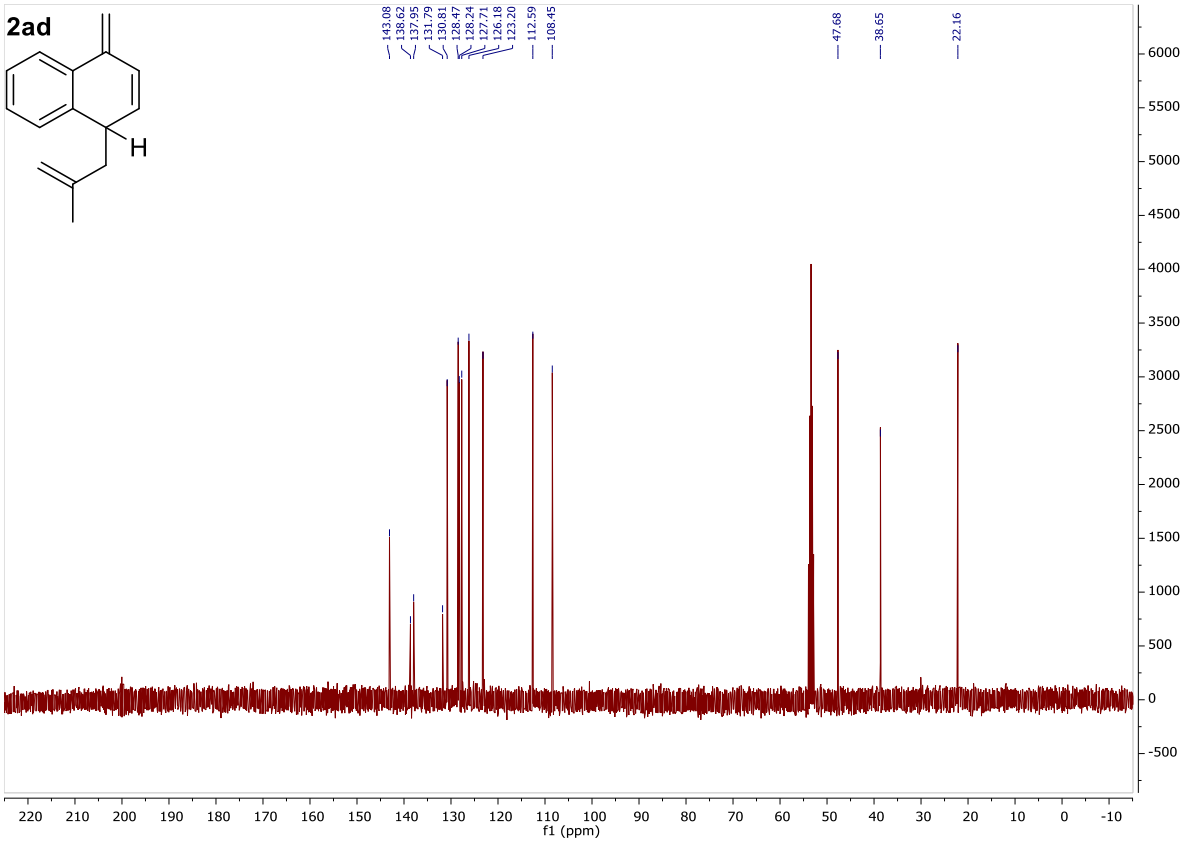
^{13}C NMR (101 MHz, $CDCl_3$): δ 13C NMR (101 MHz, cdcl3) δ 140.56, 138.03, 136.73, 124.78, 124.29, 115.93, 34.37, 15.29.

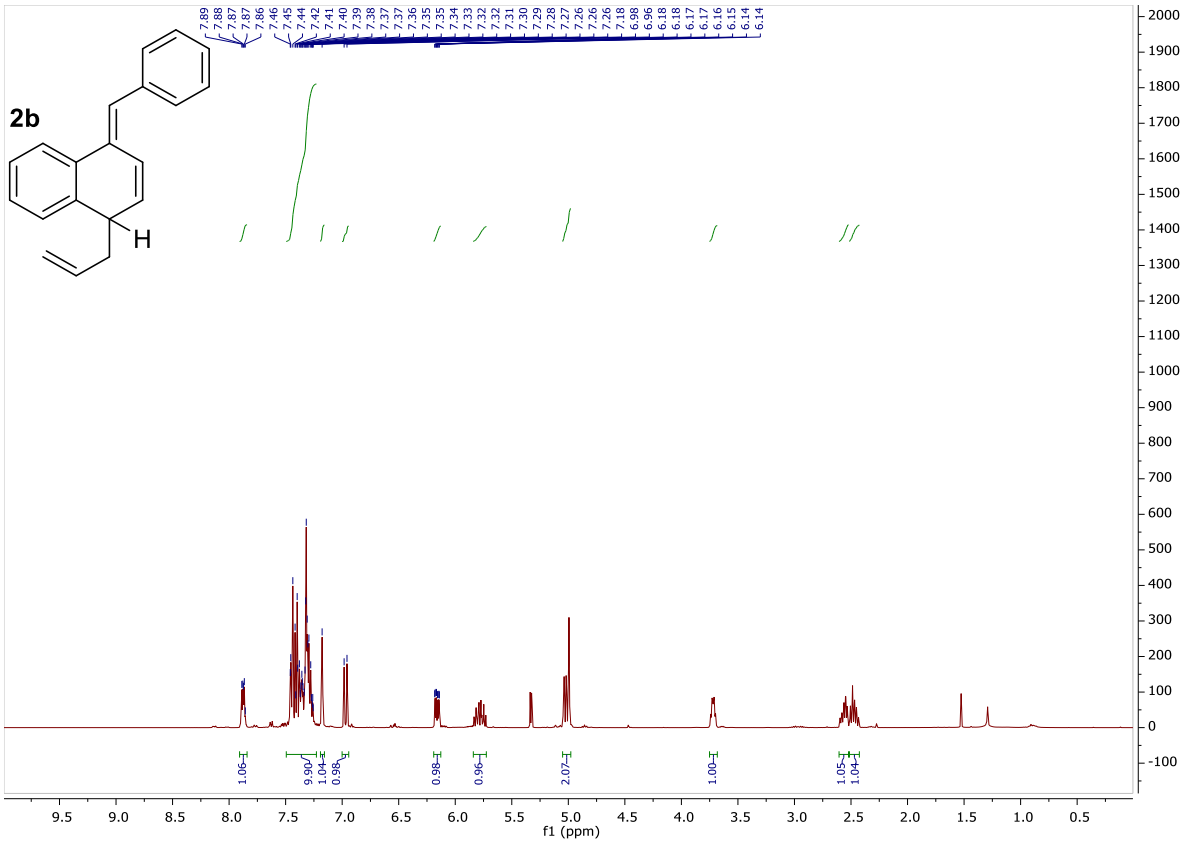
6 NMR spectra

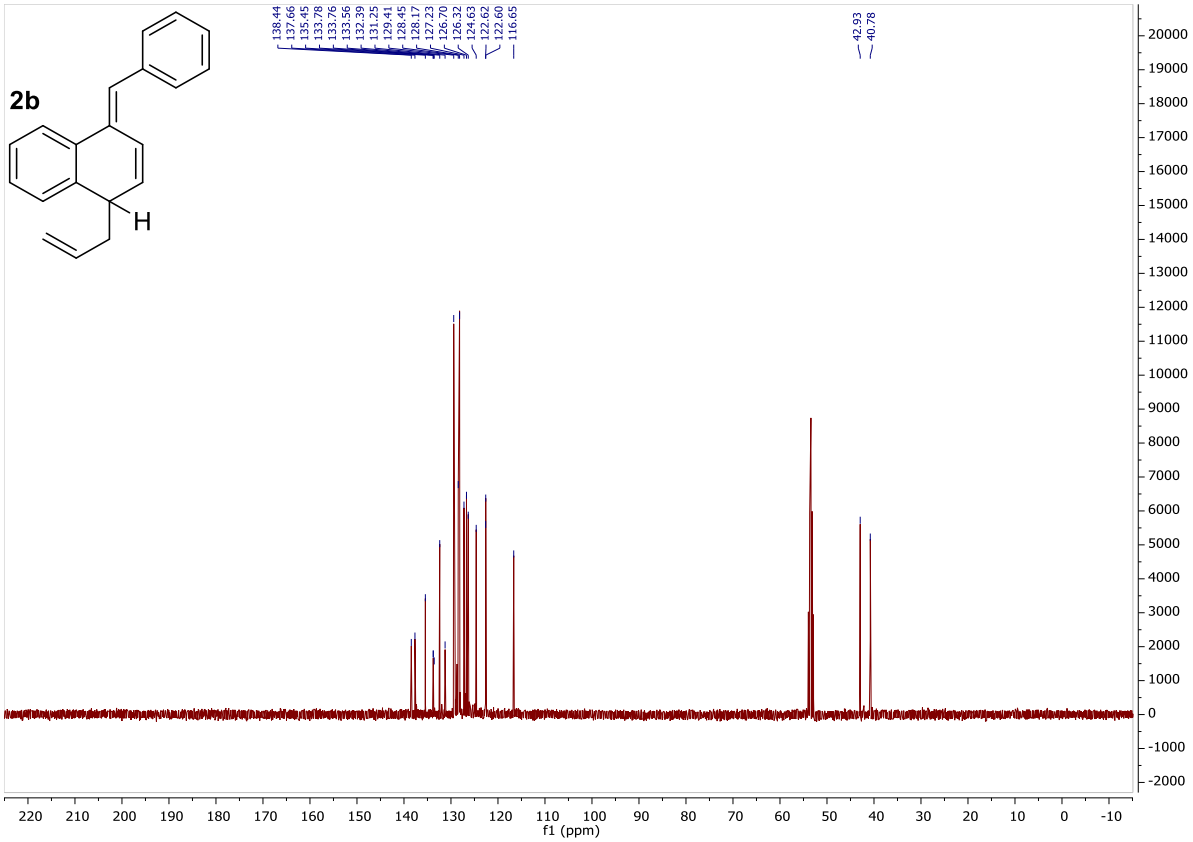


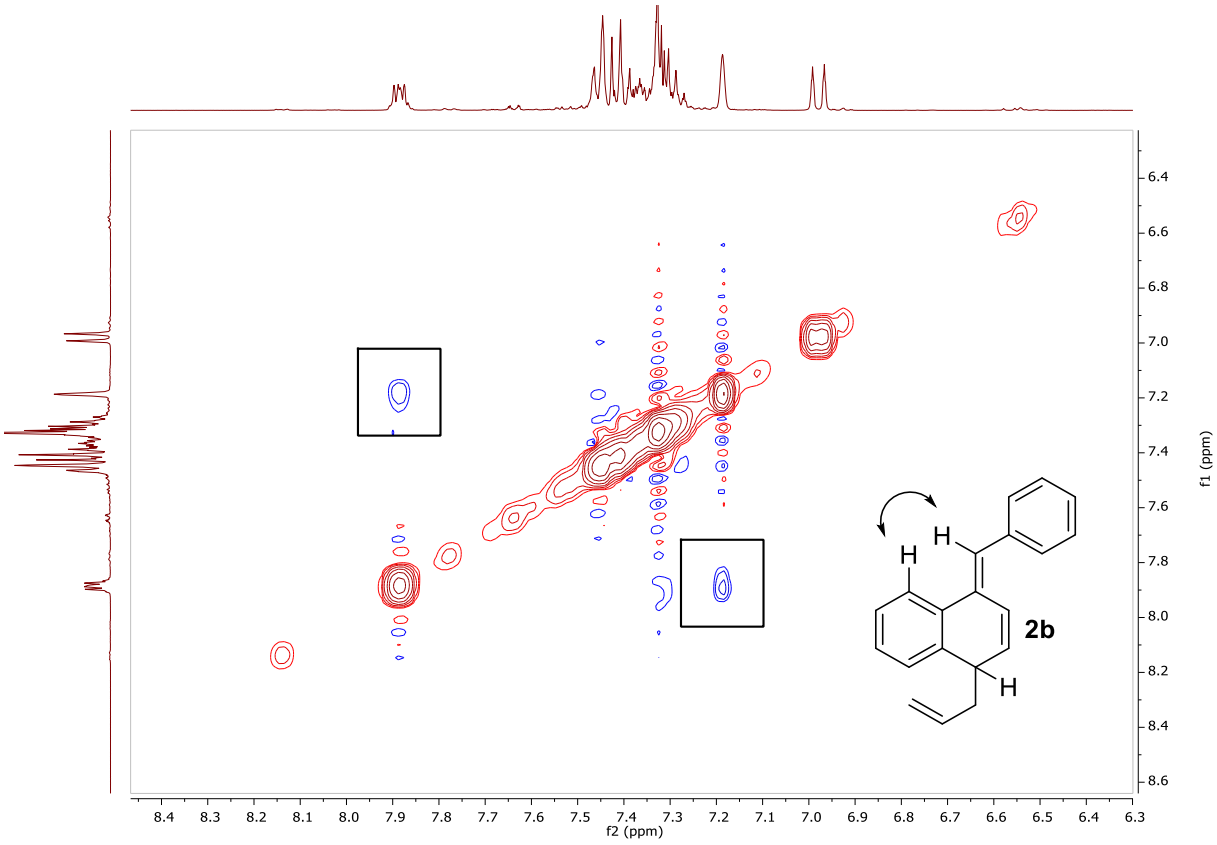


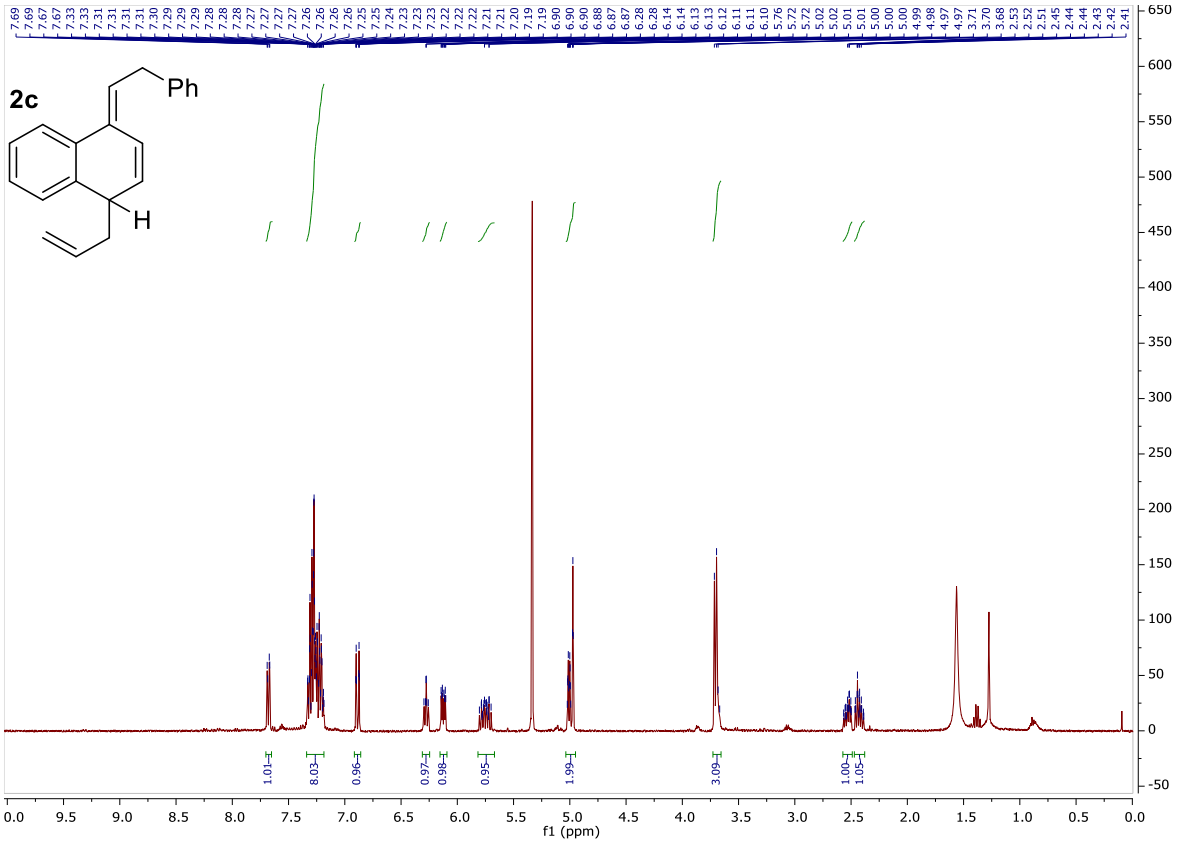

2ad
H
f1 (ppm)

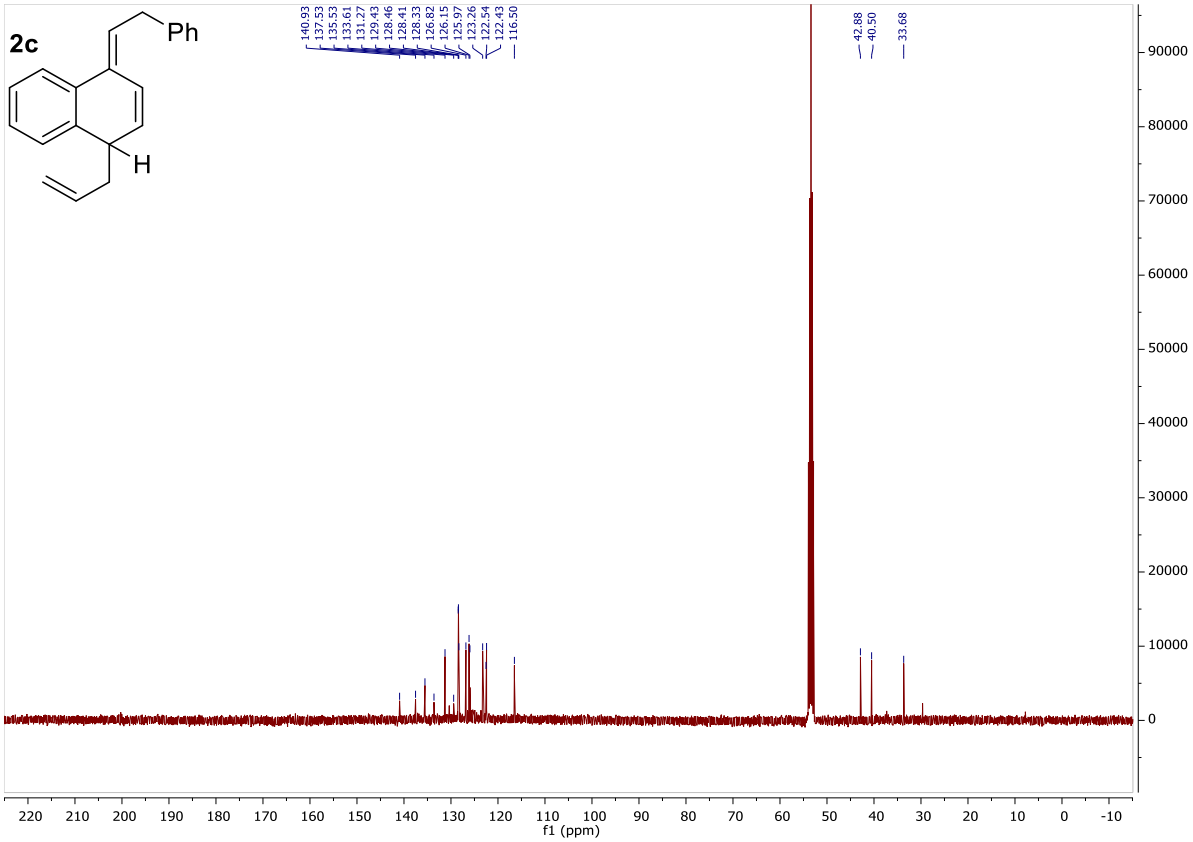

2ad
H
143.08
136.62
137.95
131.79
130.81
128.47
128.24
127.71
126.18
123.20
112.59
108.45
47.68
38.65
22.16
f1 (ppm)

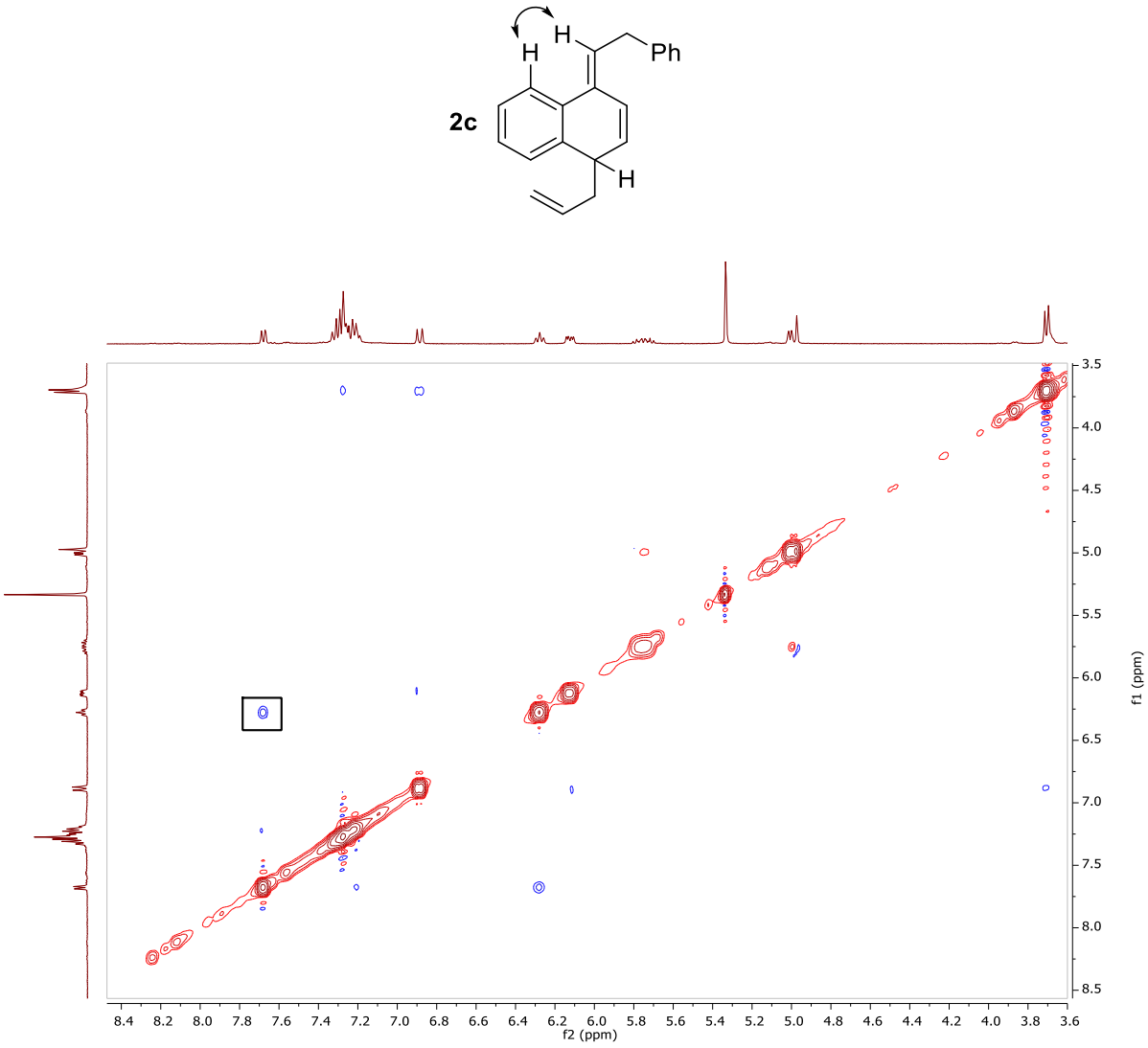

2b
H
f1 (ppm)

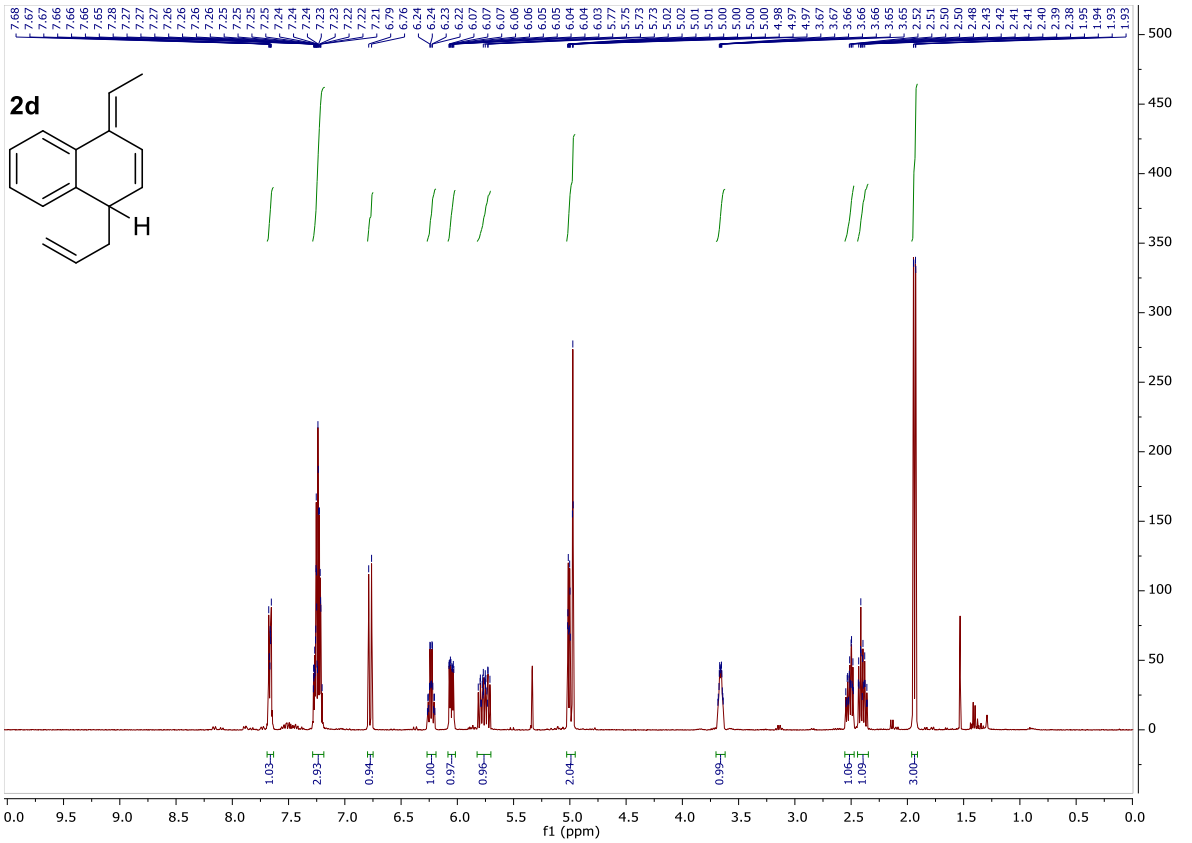

2b
H
f1 (ppm)

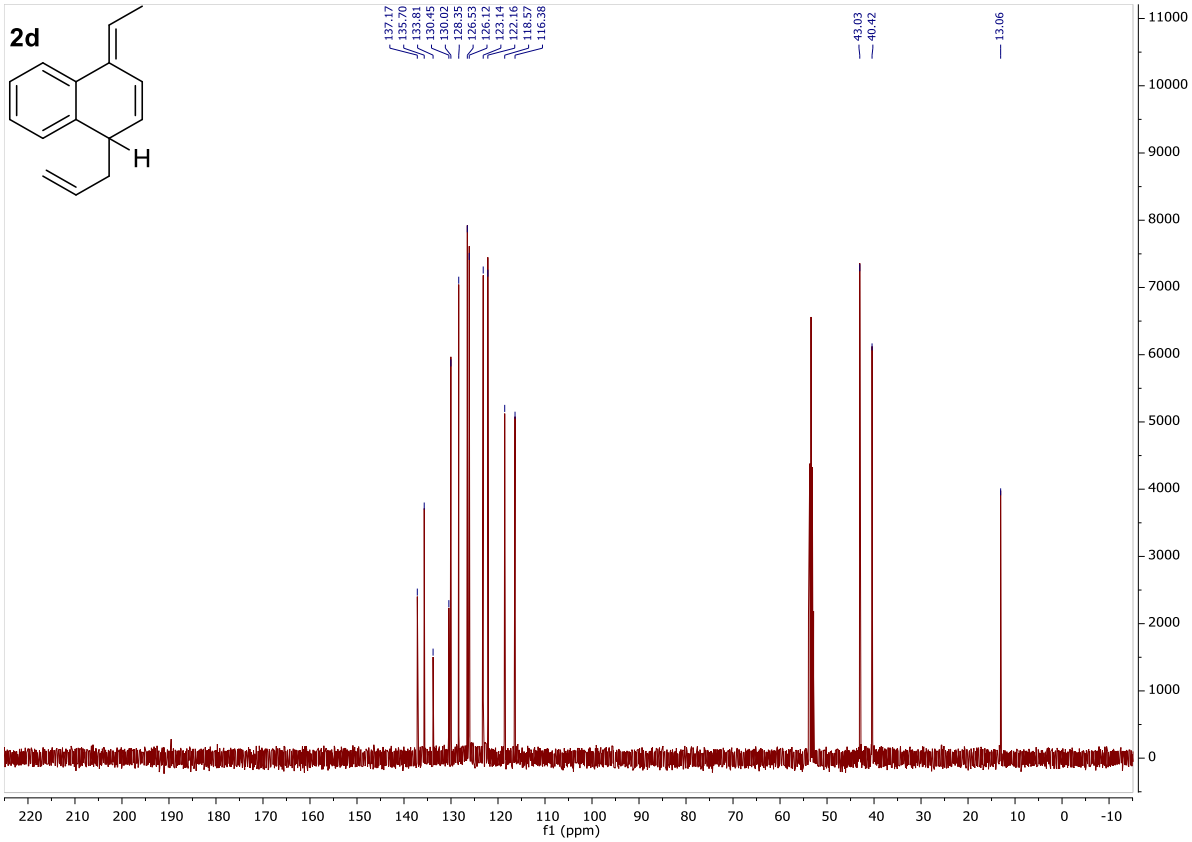

f1 (ppm)
f2 (ppm)
H
H
H
2b

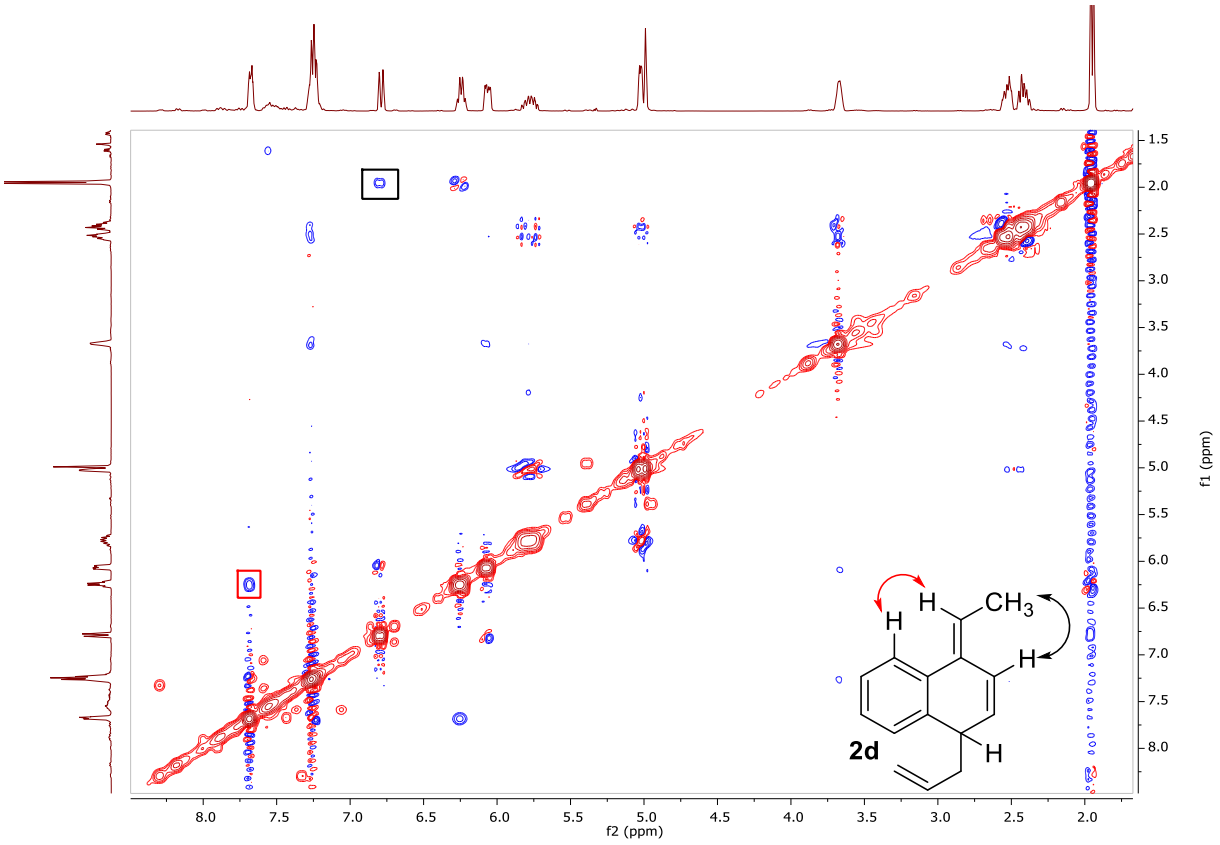

2c
Ph
H
f1 (ppm)

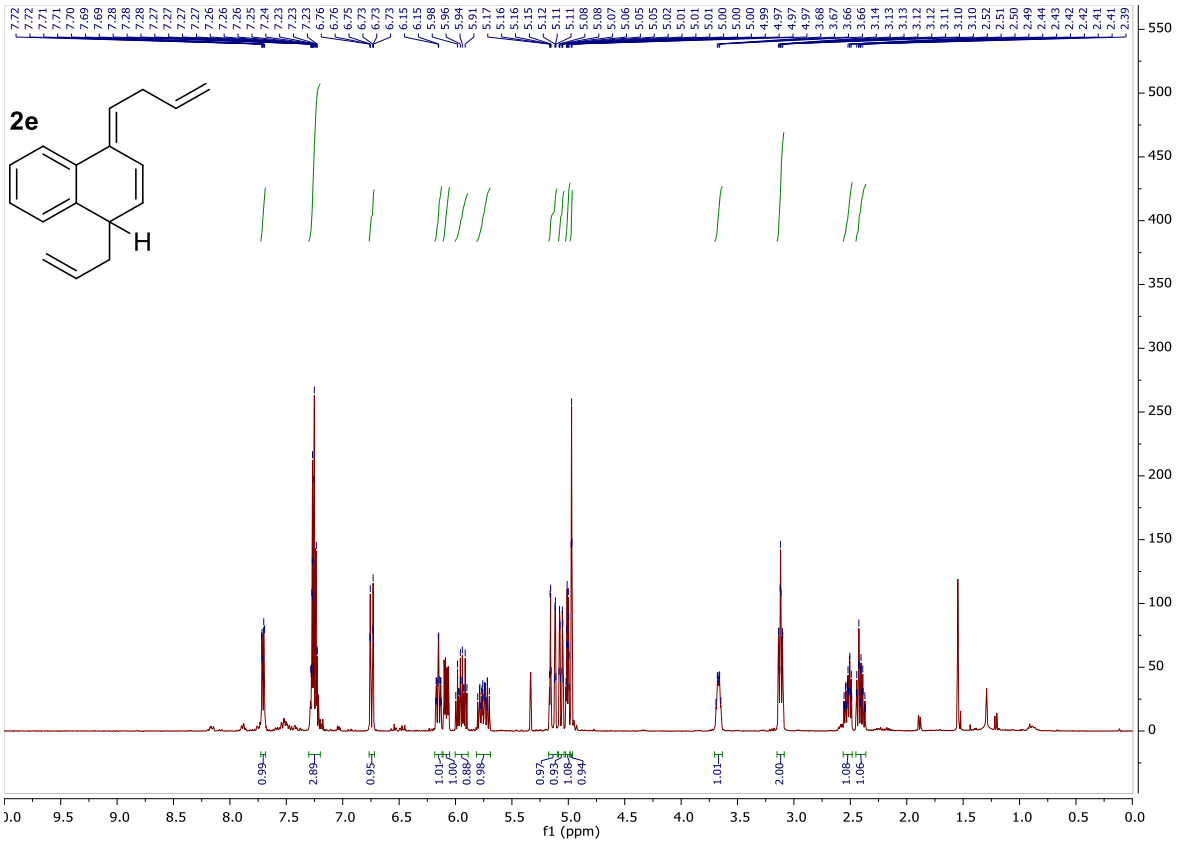

2c
Ph
H
f1 (ppm)

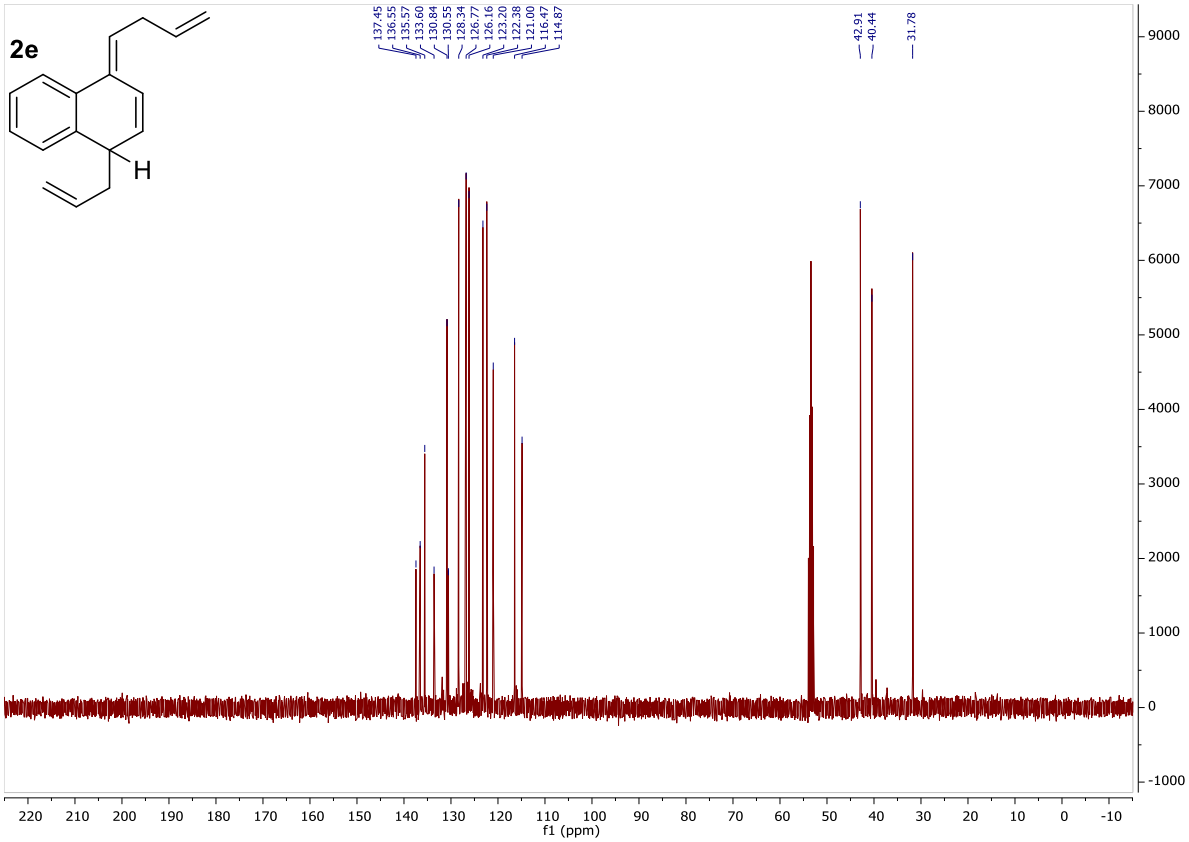

2c
H
H
Ph
H
f2 (ppm)
f1 (ppm)

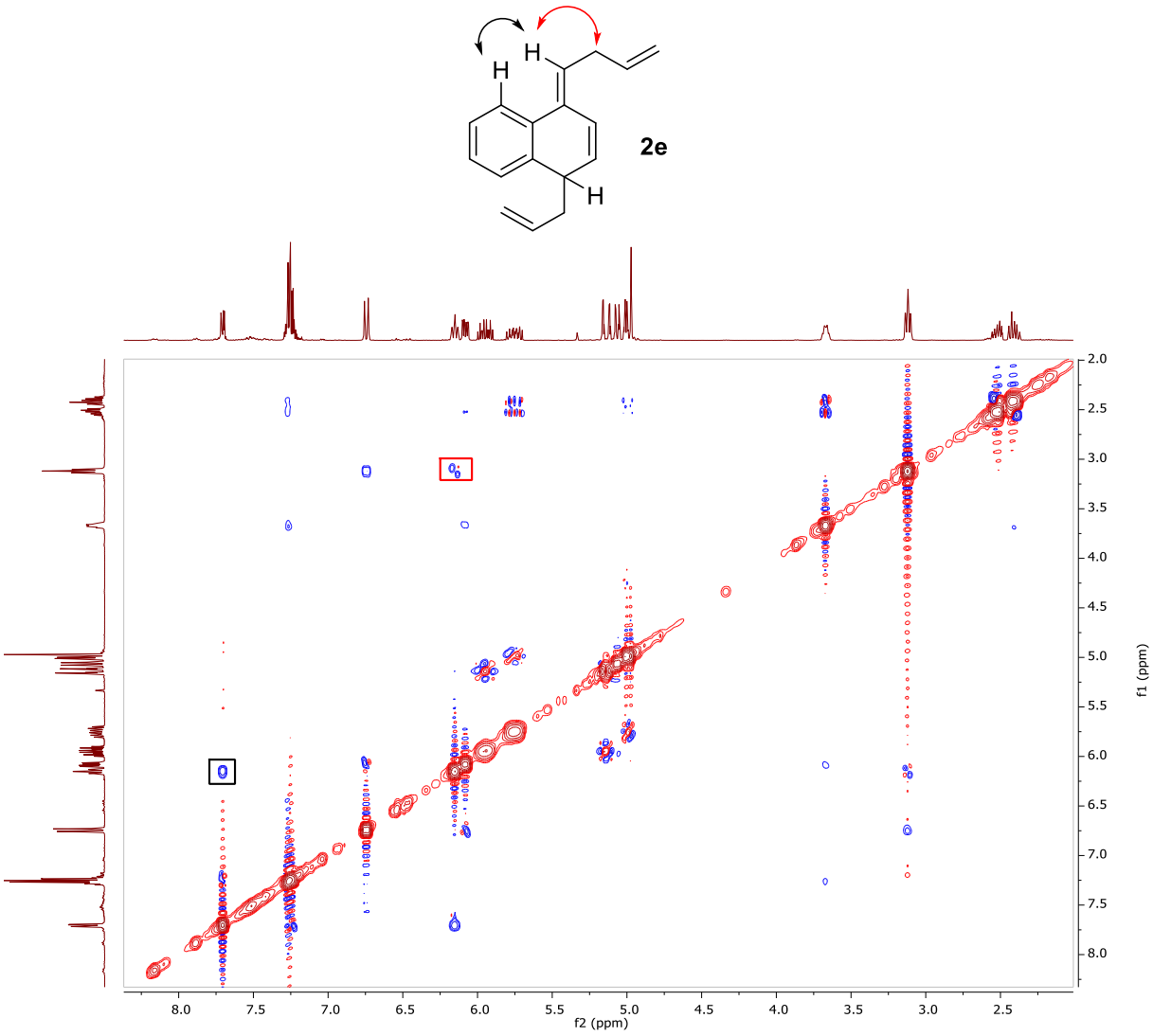

2d
H
f1 (ppm)

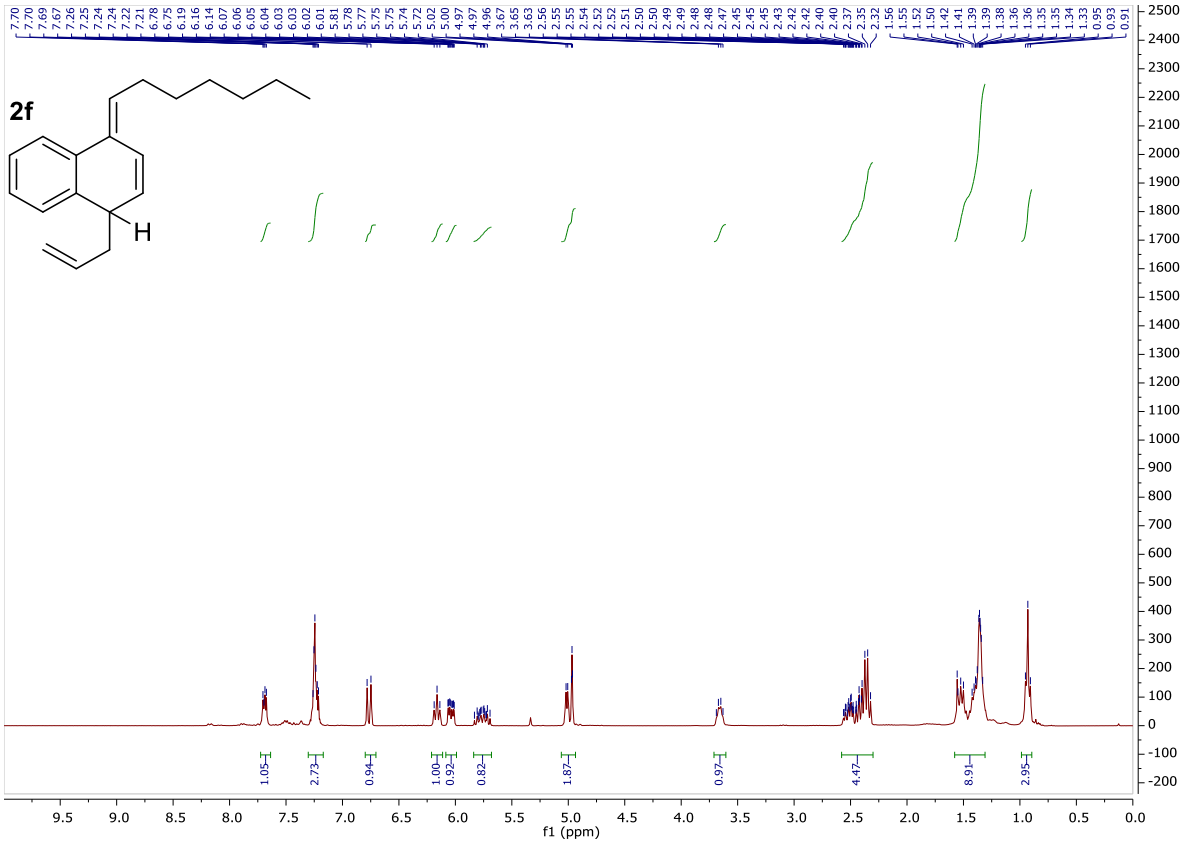

2d
H
137.17
135.70
133.81
130.45
130.02
128.35
126.53
126.12
123.14
122.16
118.57
116.38
43.03
40.42
13.06
f1 (ppm)

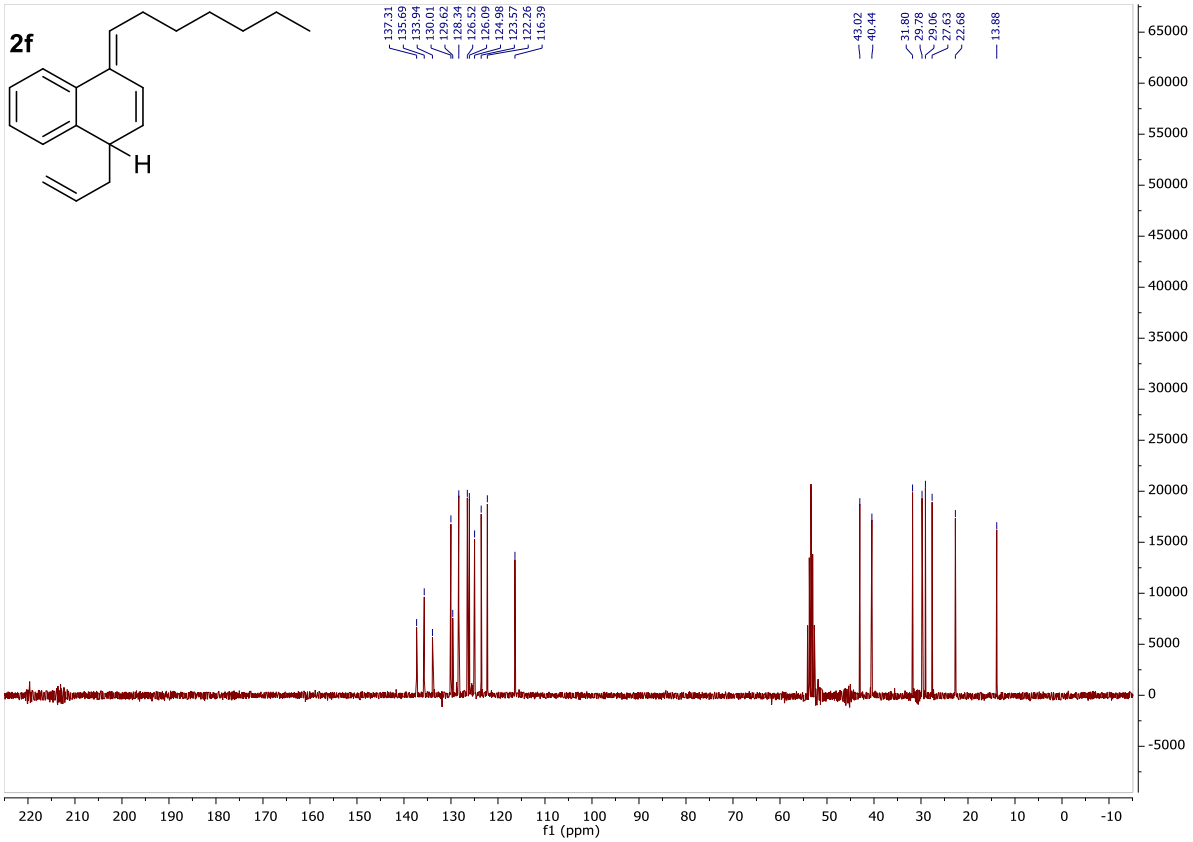

f2 (ppm)
f1 (ppm)
H
CH3
H
H
H
2d

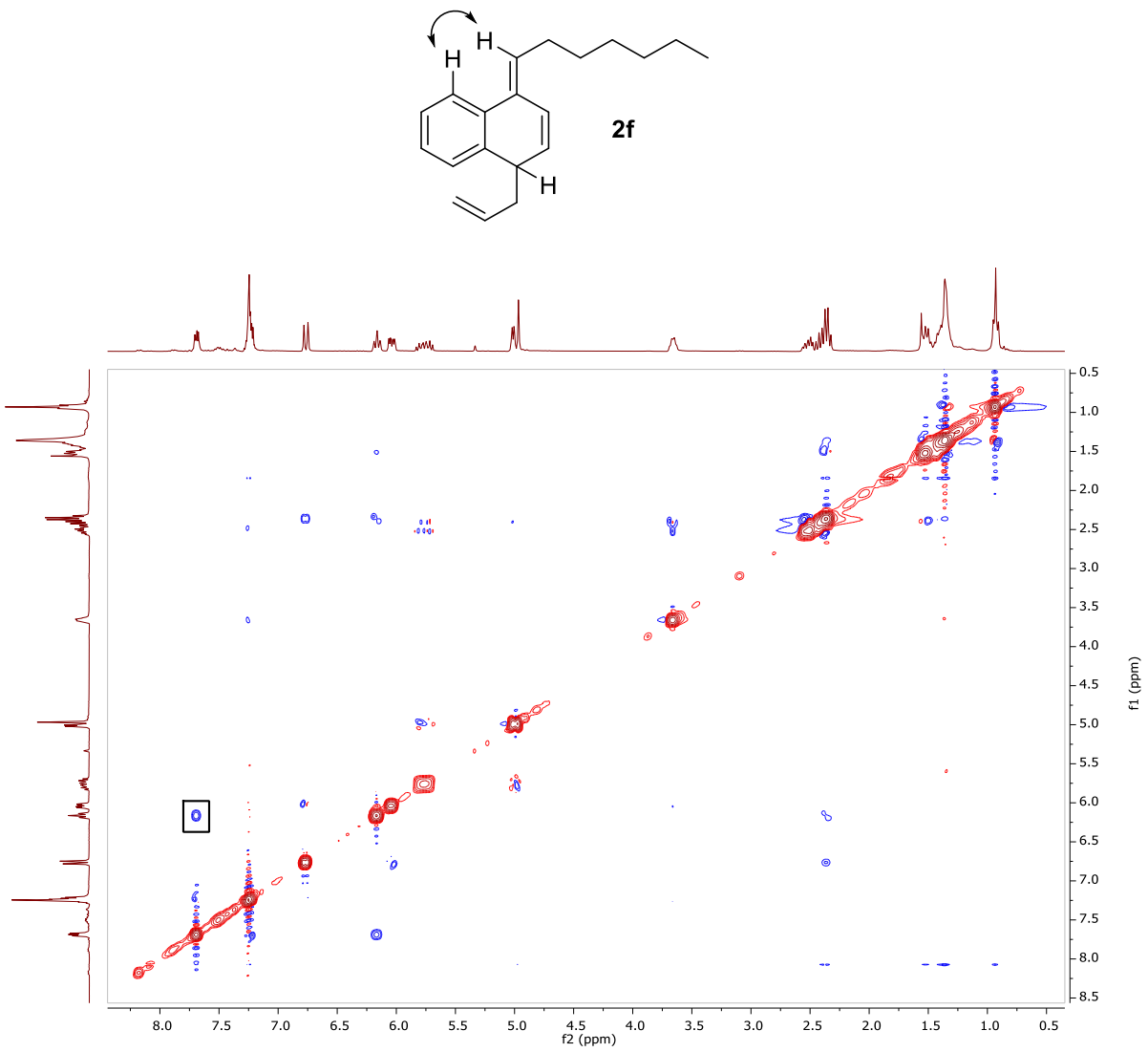

2e
H
f1 (ppm)

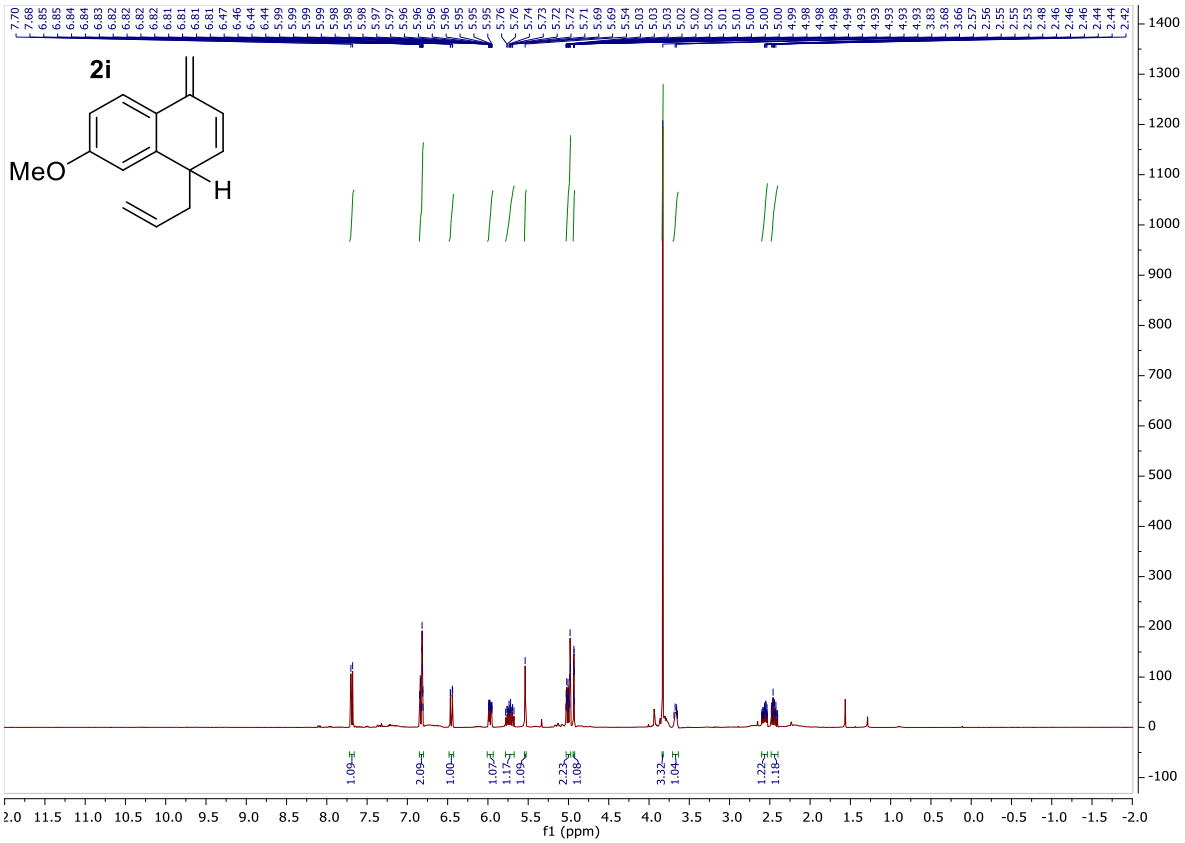

2e
H
f1 (ppm)

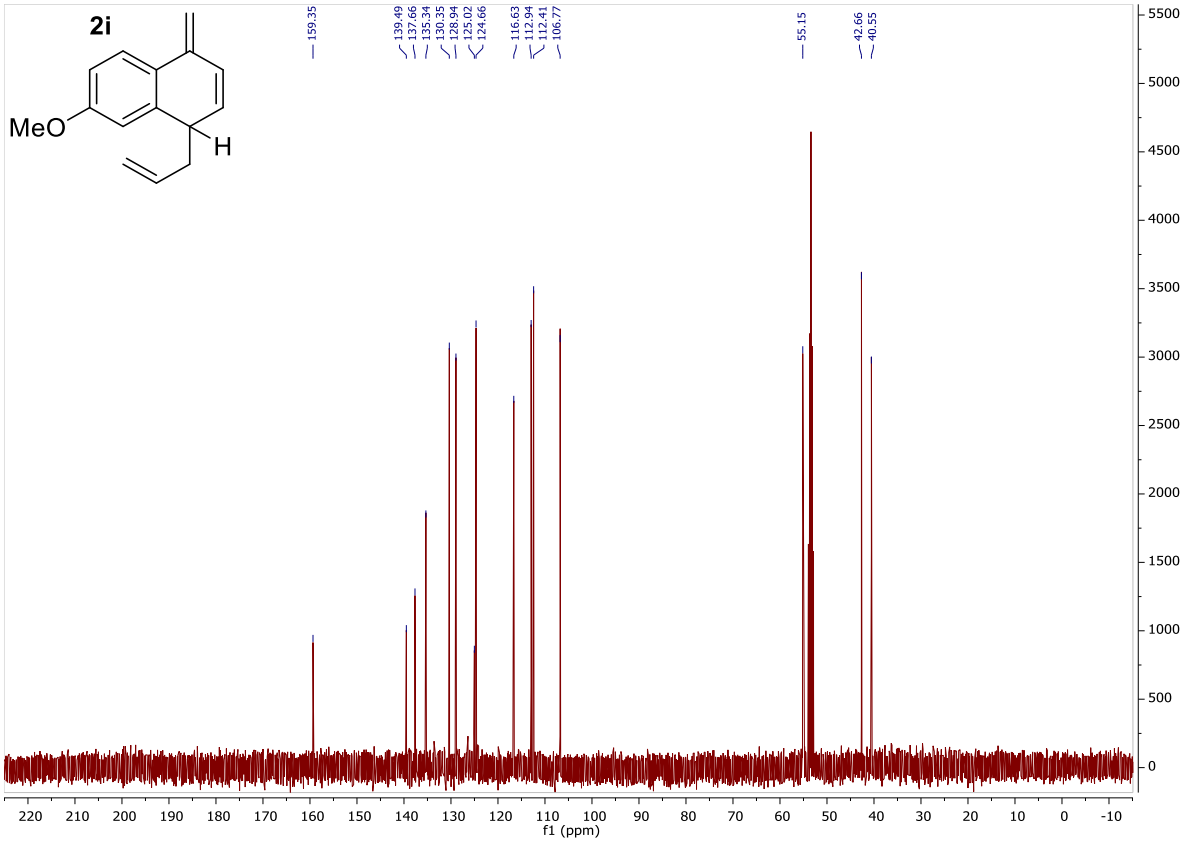

H
H
H
2e
f2 (ppm)
f1 (ppm)

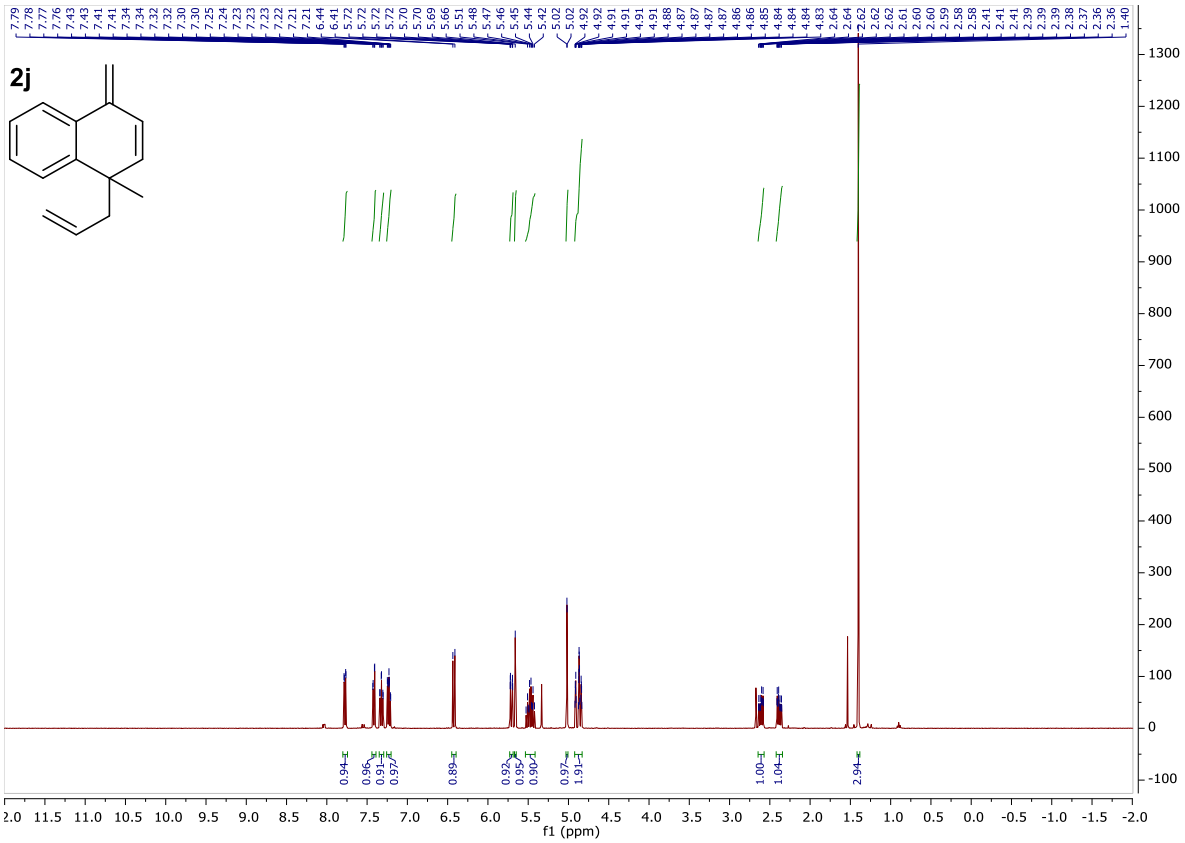

2f
H
f1 (ppm)

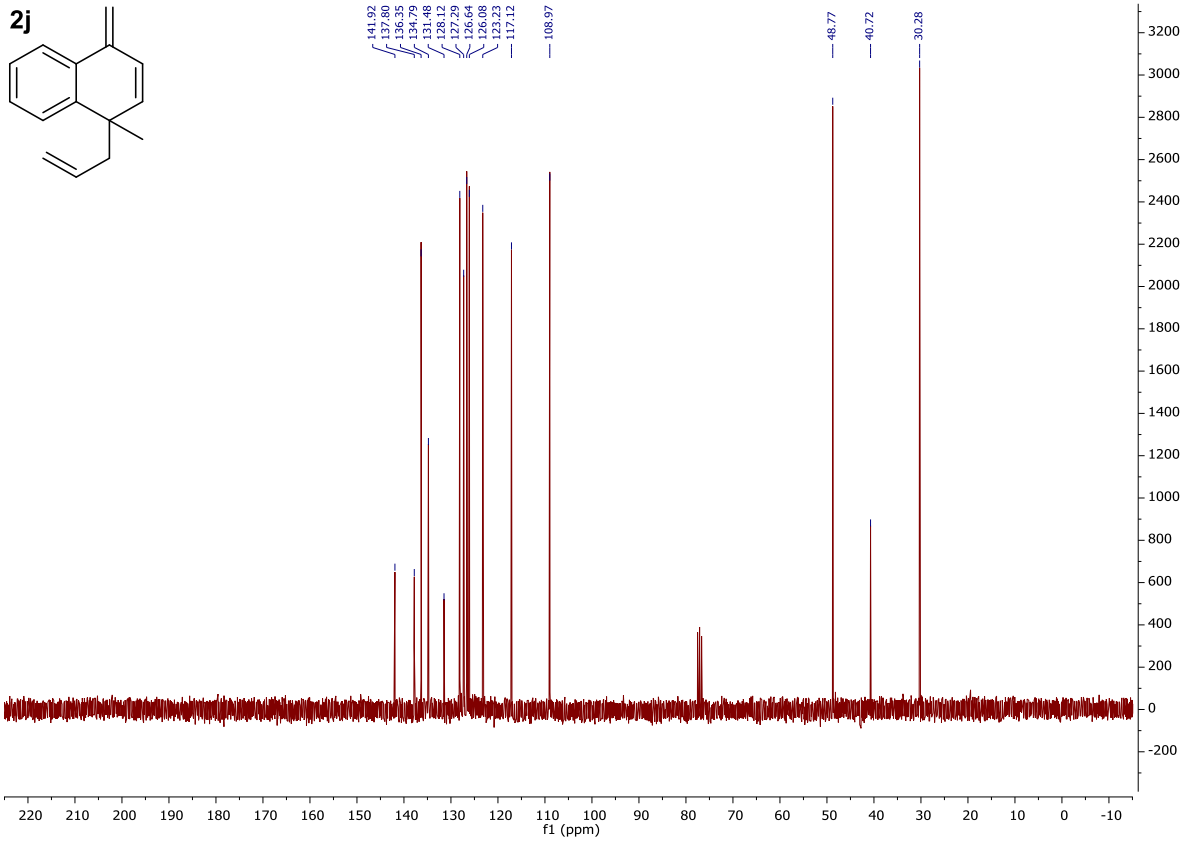

2f
H
f1 (ppm)

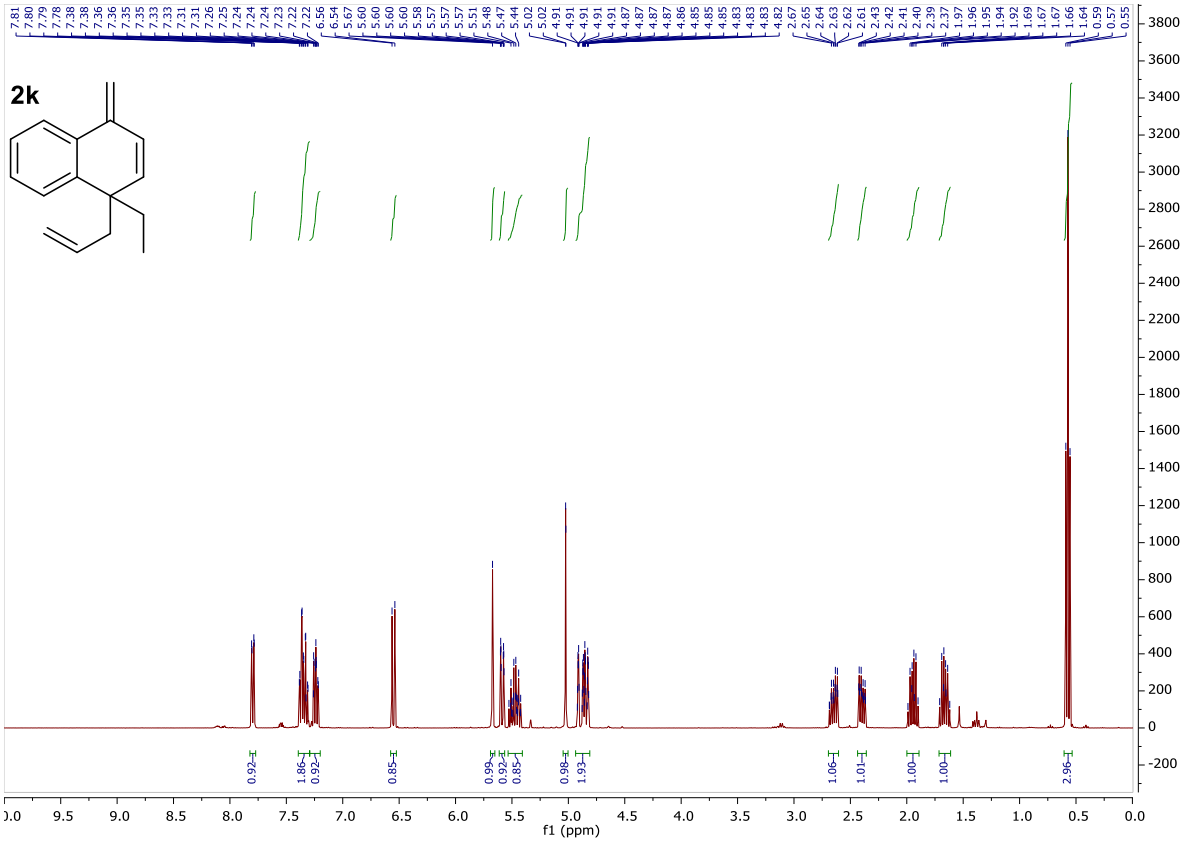

H
H
H
2f
f2 (ppm)
f1 (ppm)

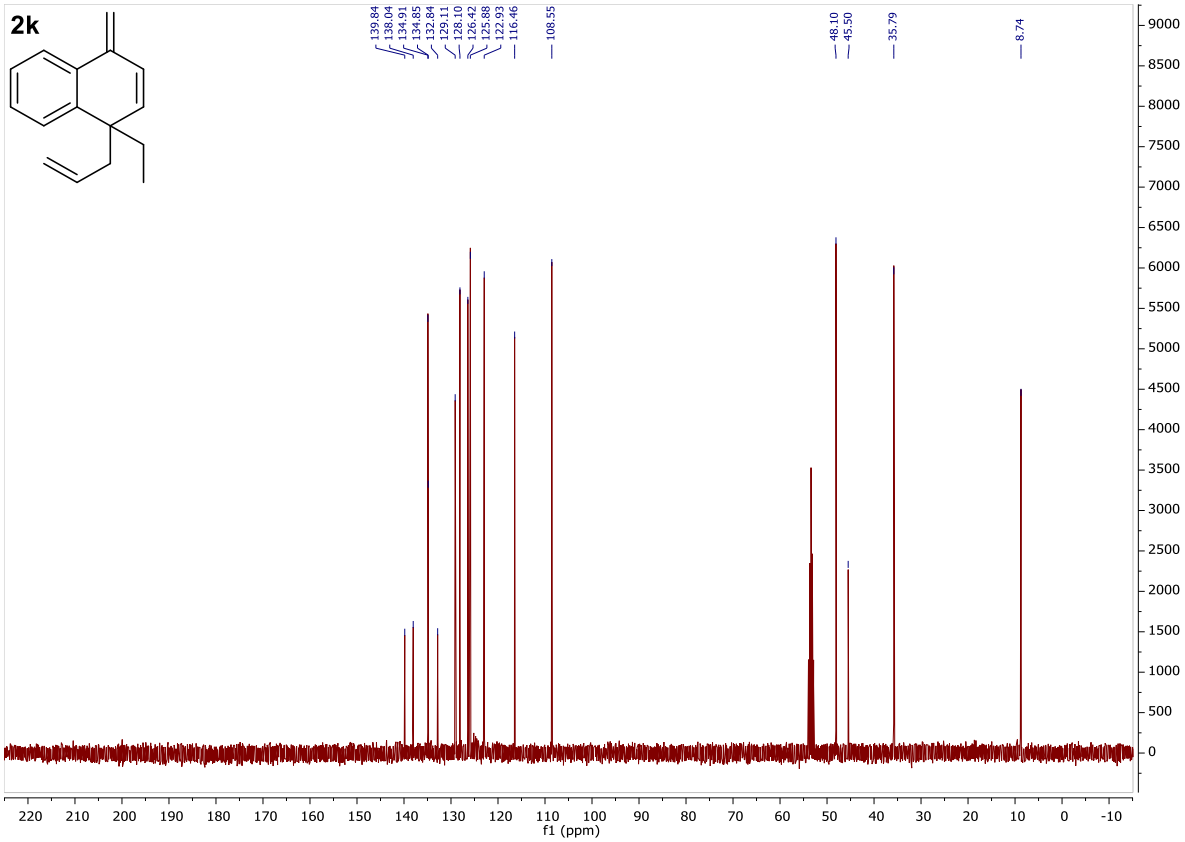

2i
MeO
H
f1 (ppm)

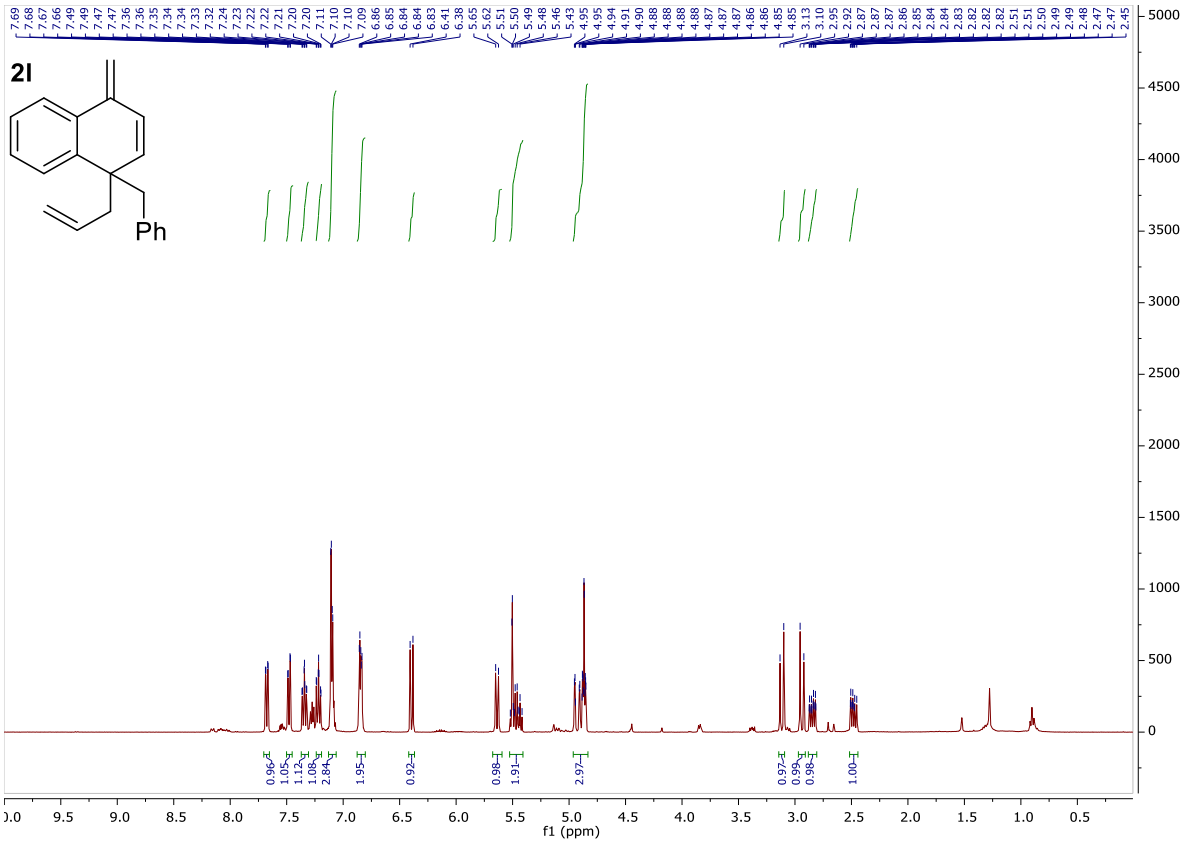

2i
MeO
H
159.35
139.49
137.66
135.34
130.35
128.94
125.02
124.66
116.63
112.94
112.41
106.77
55.15
42.66
40.55
f1 (ppm)

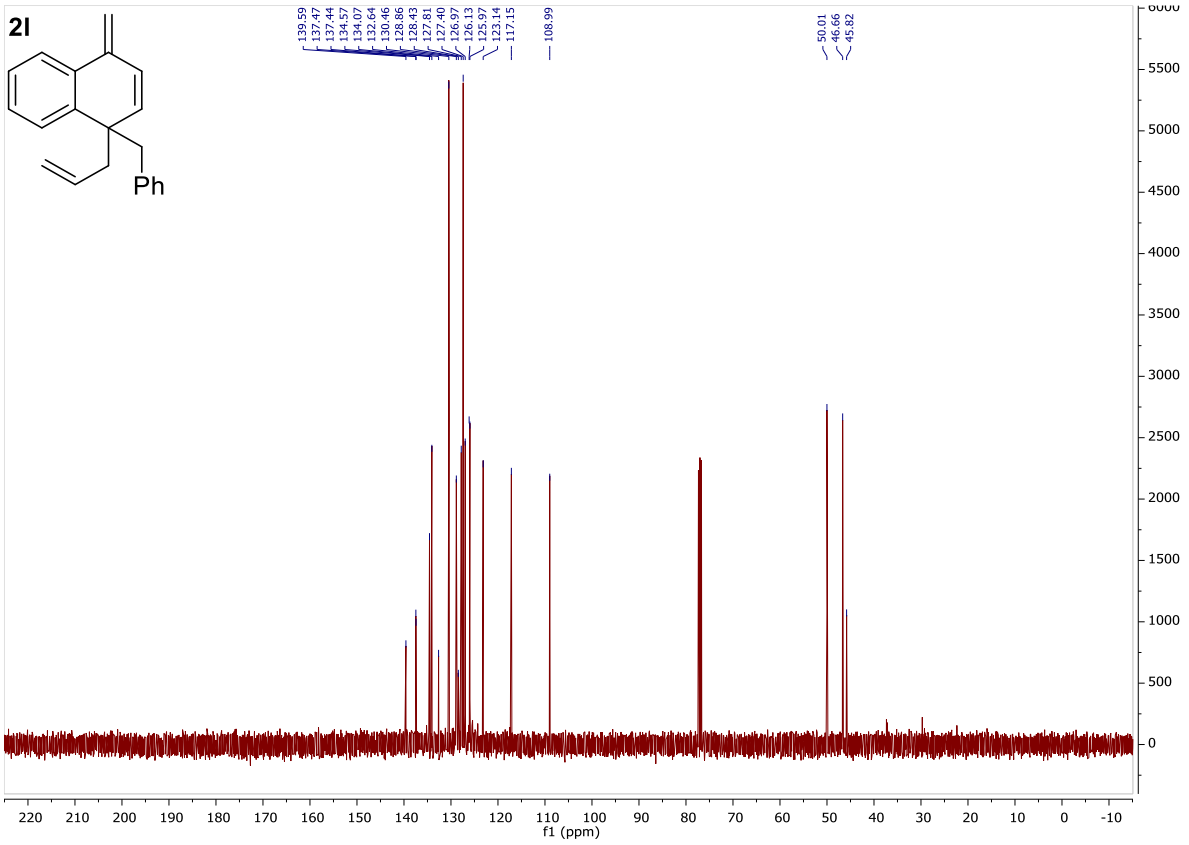

2j
f1 (ppm)

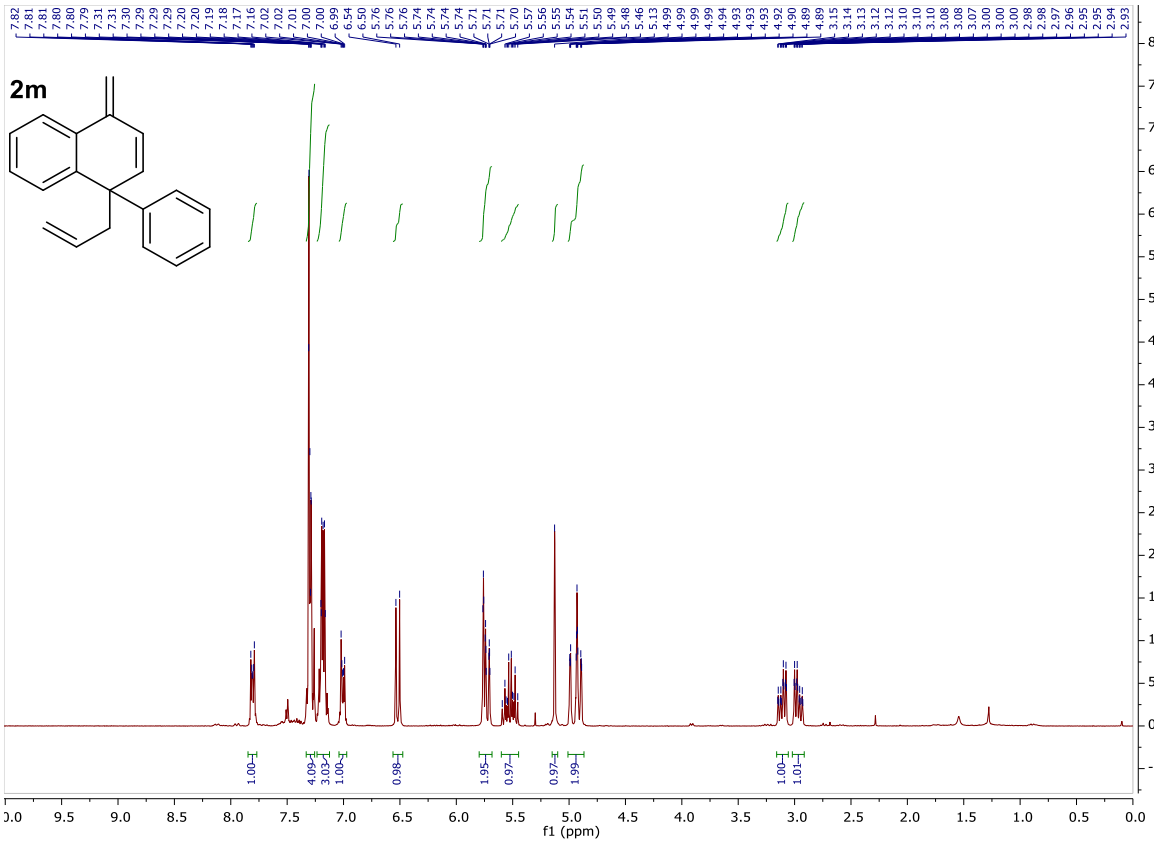

2j
141.92
137.80
136.35
134.79
131.48
128.12
127.29
126.64
126.08
123.23
117.12
108.97
48.77
40.72
30.28
f1 (ppm)

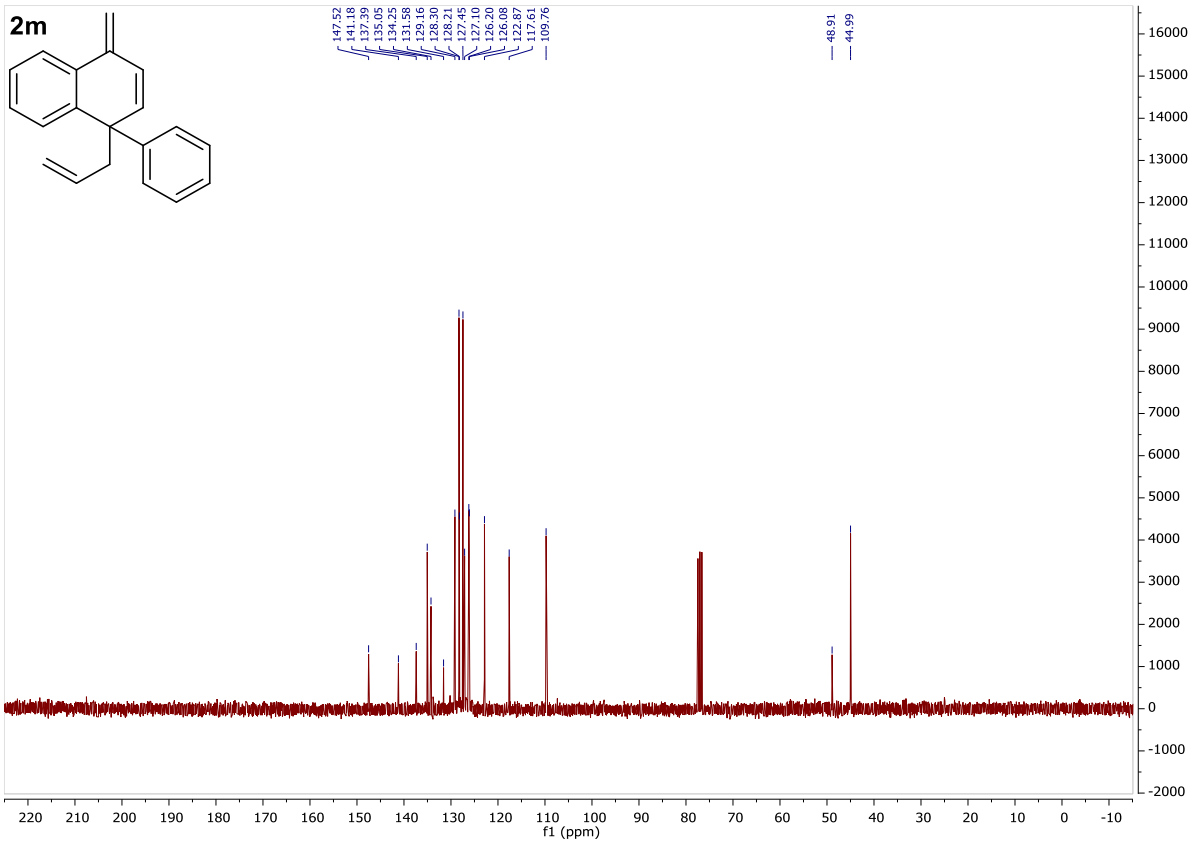

2k
f1 (ppm)

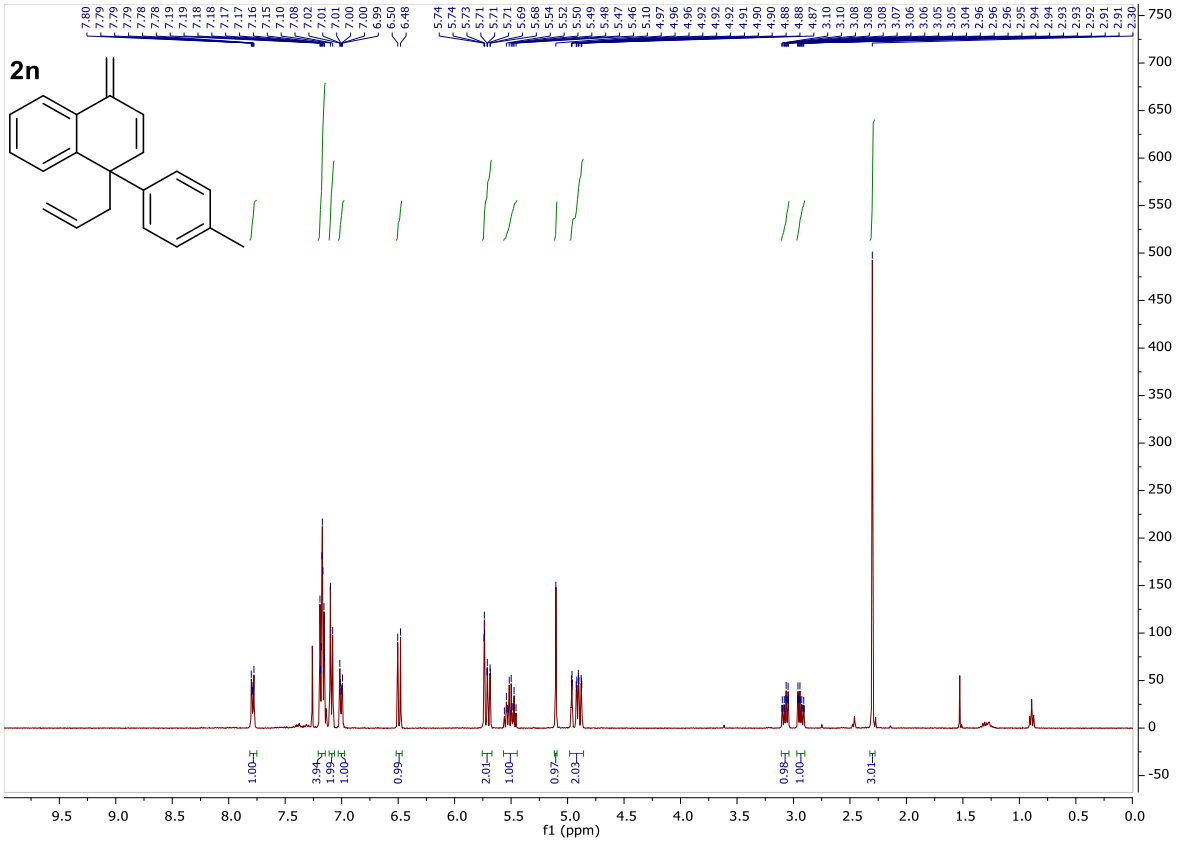

2k
f1 (ppm)

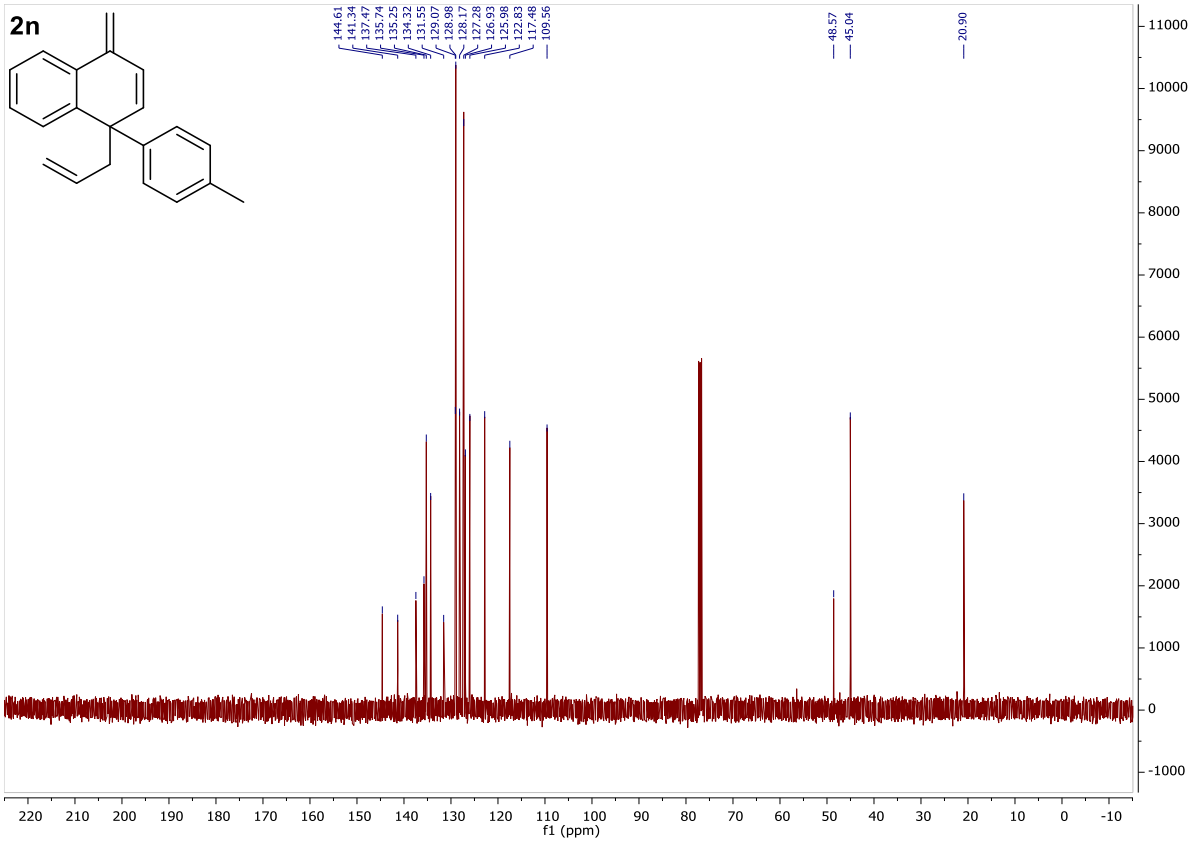

2l
Ph
f1 (ppm)

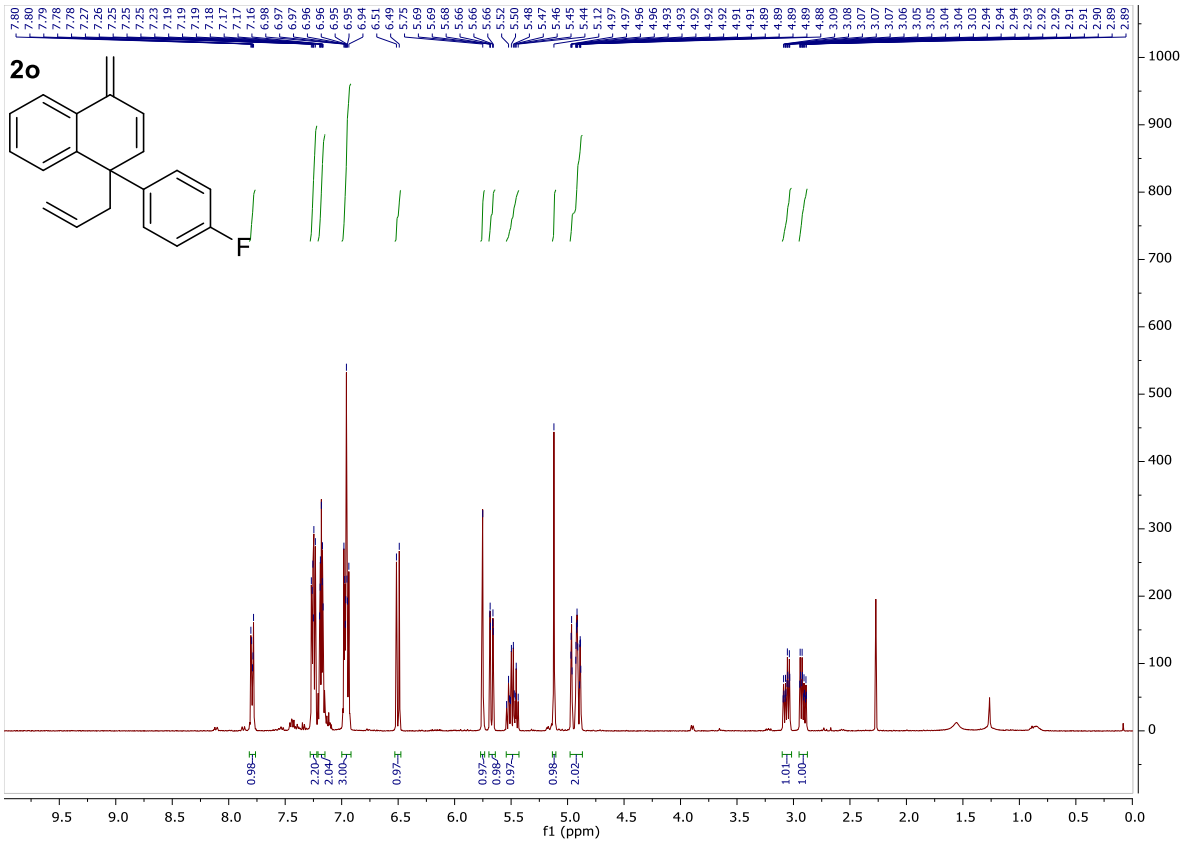

2l
Ph
f1 (ppm)

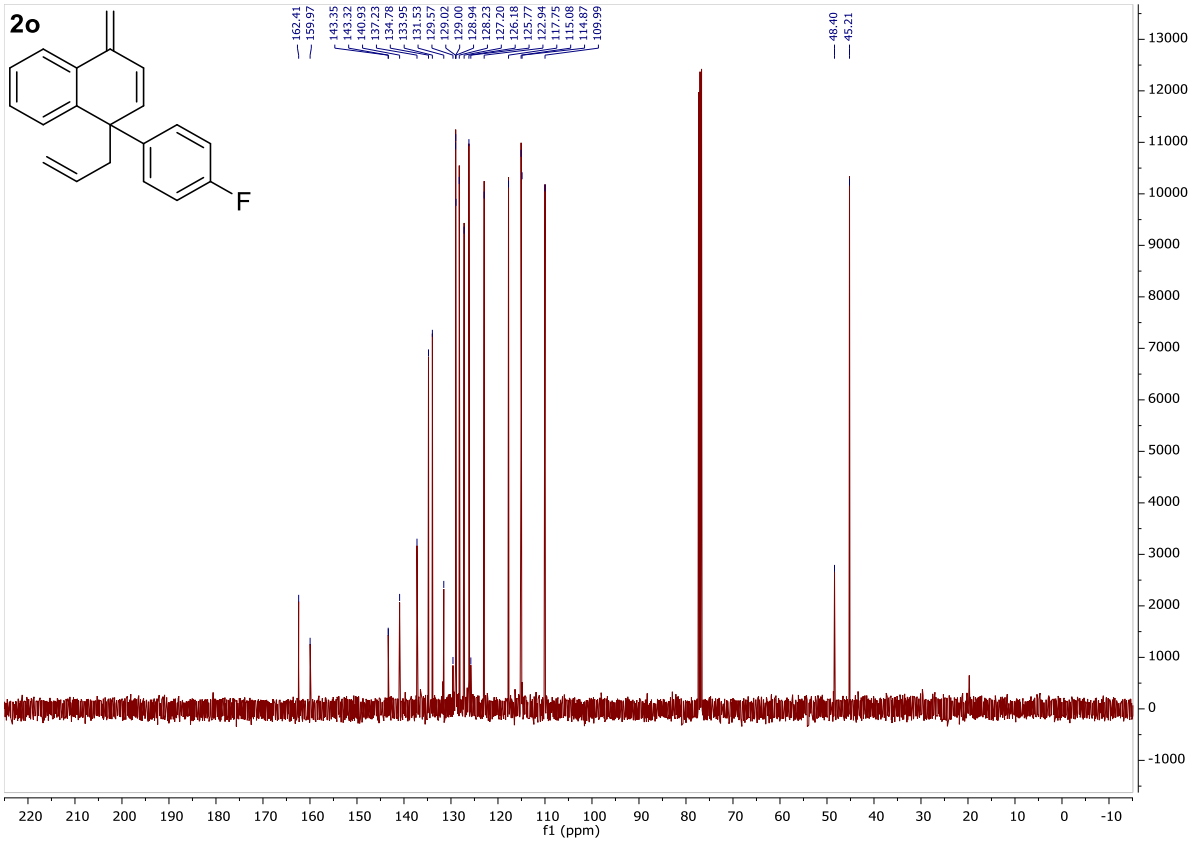

2m
f1 (ppm)

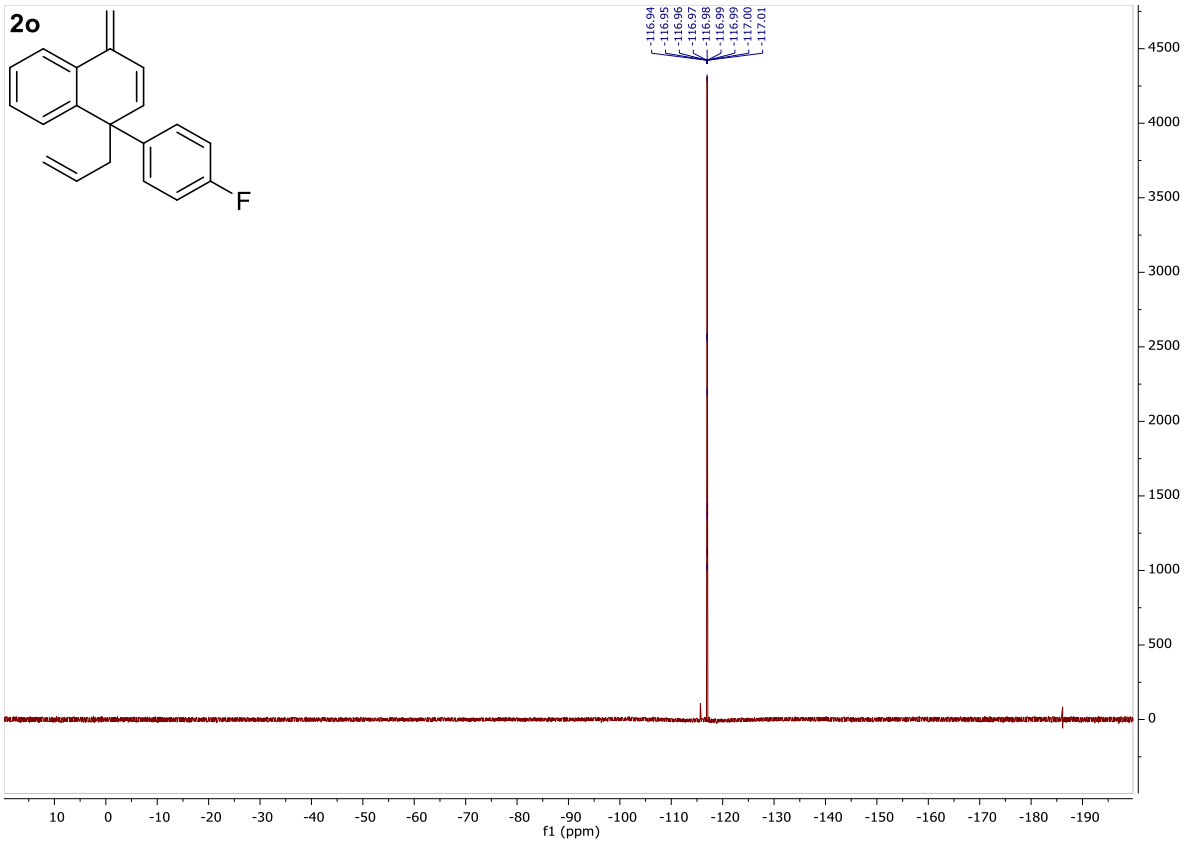

2m
f1 (ppm)

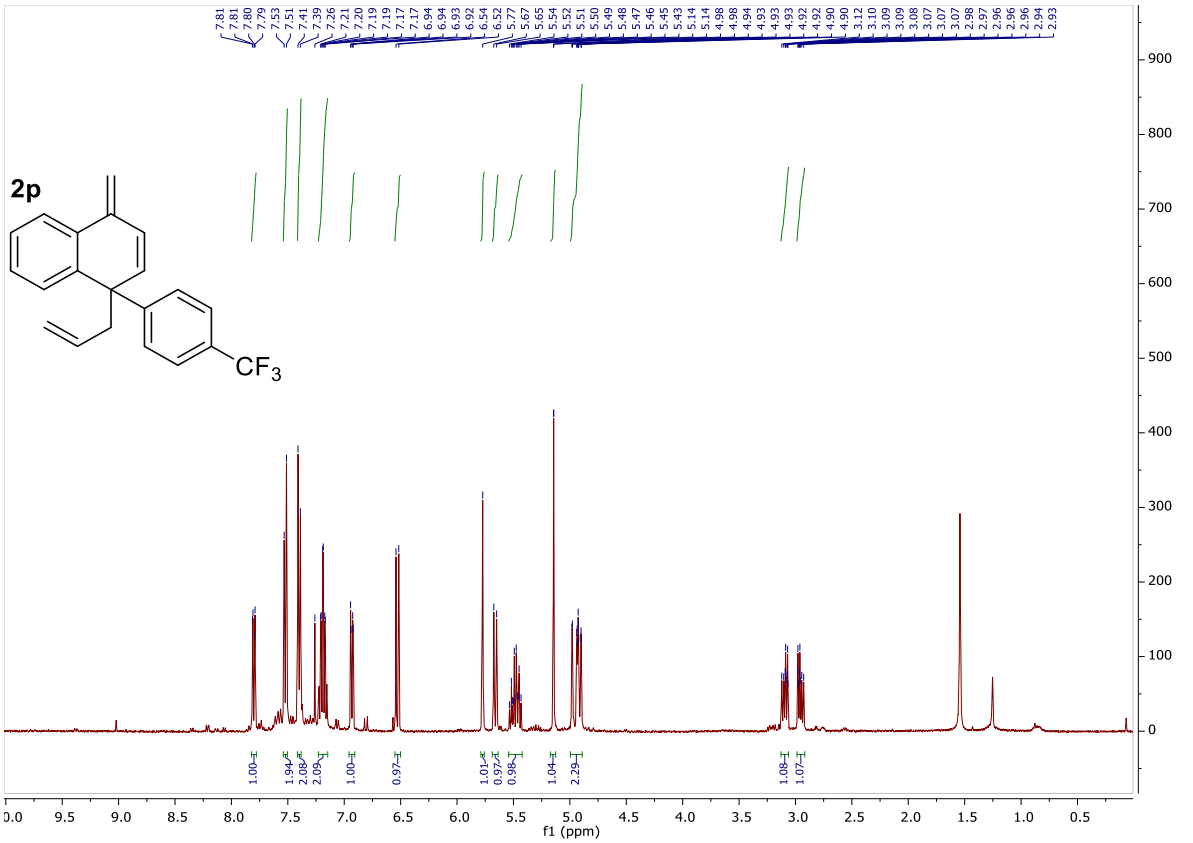

2n
f1 (ppm)

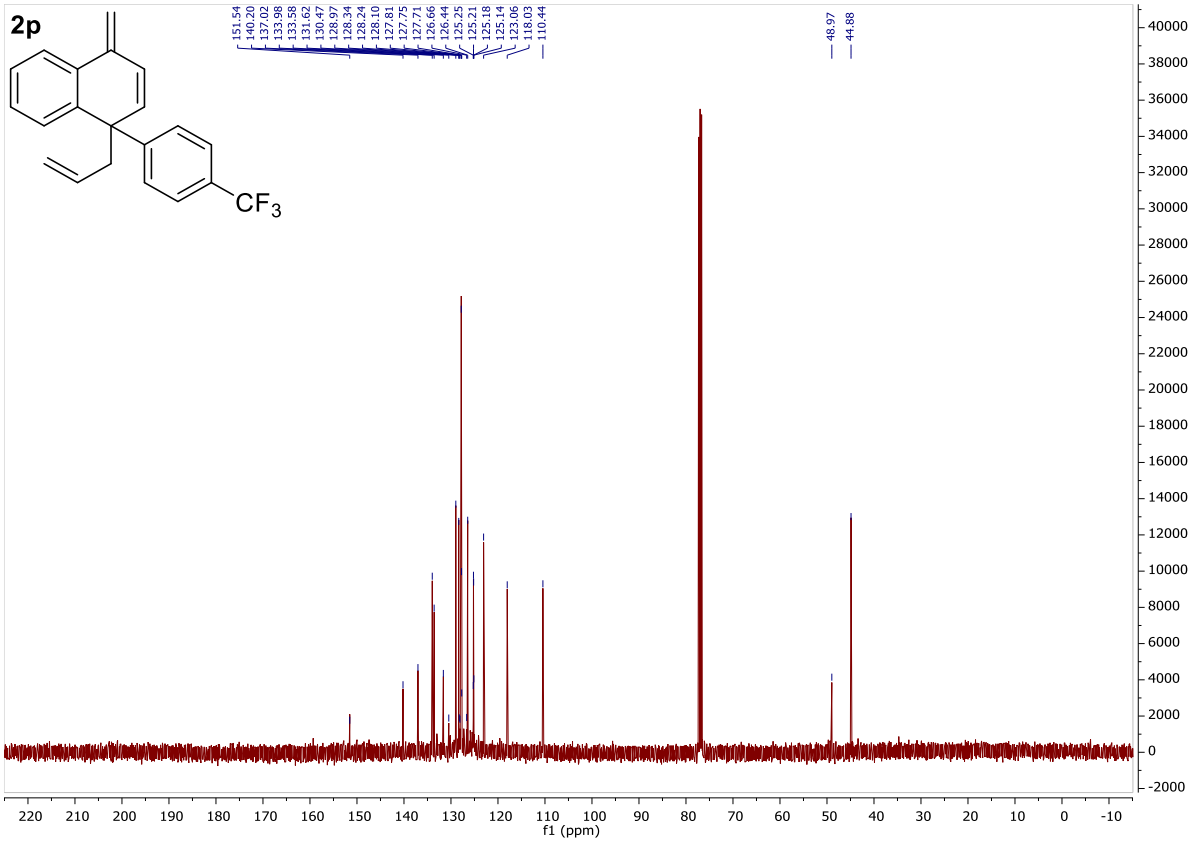

2n
f1 (ppm)

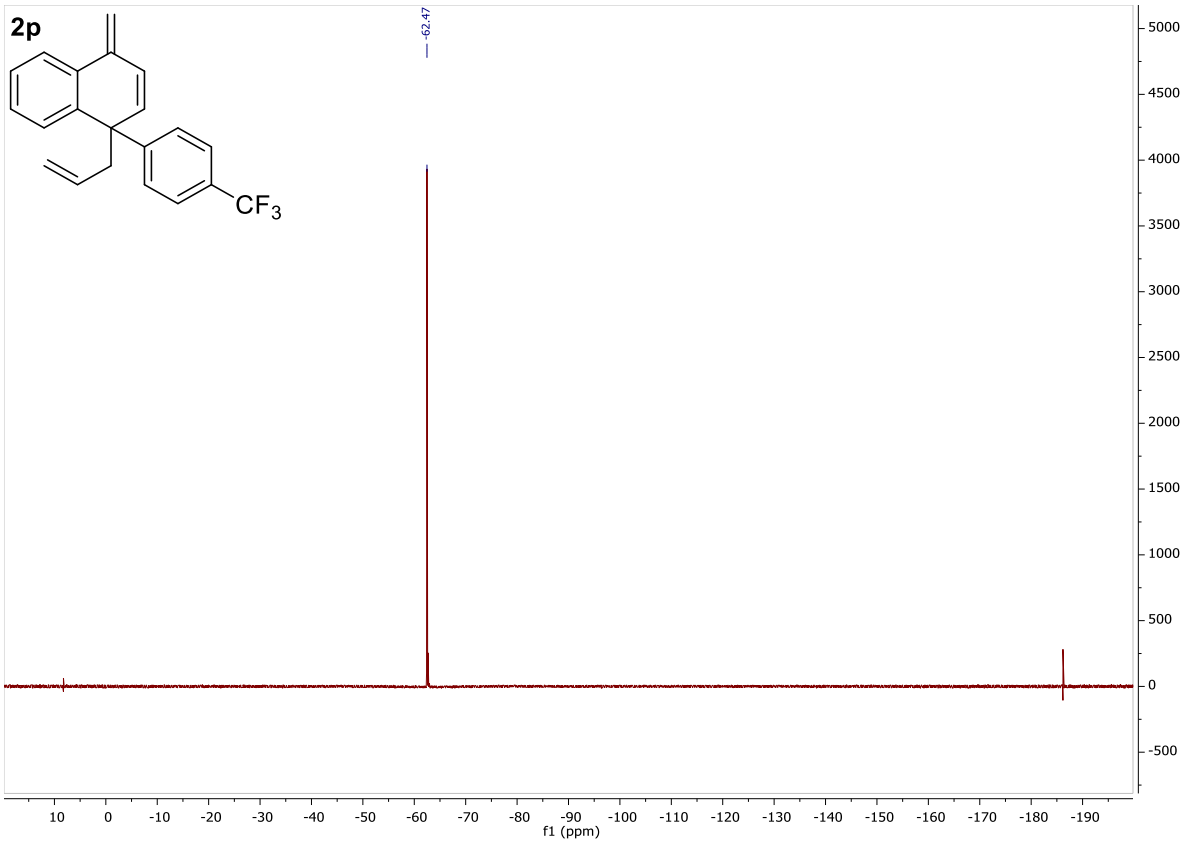

2o
F
f1 (ppm)

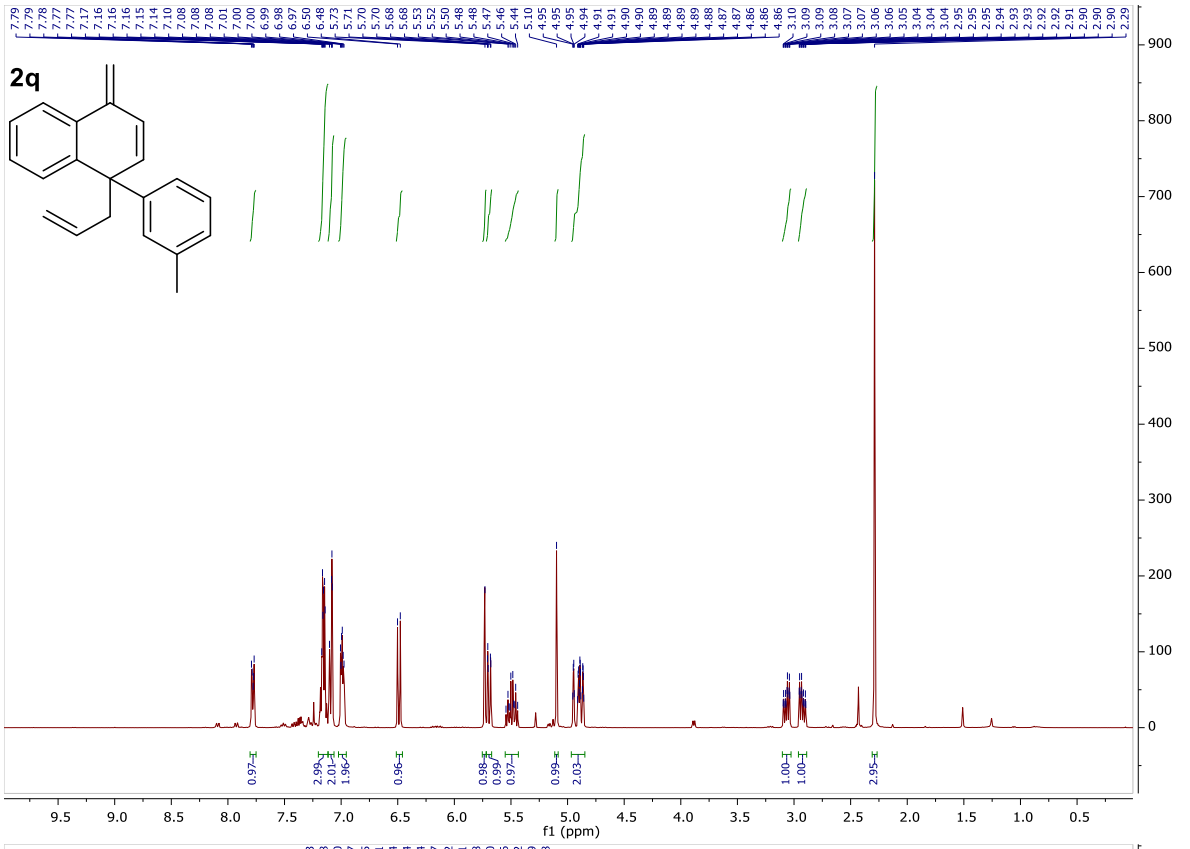

2o
F
f1 (ppm)

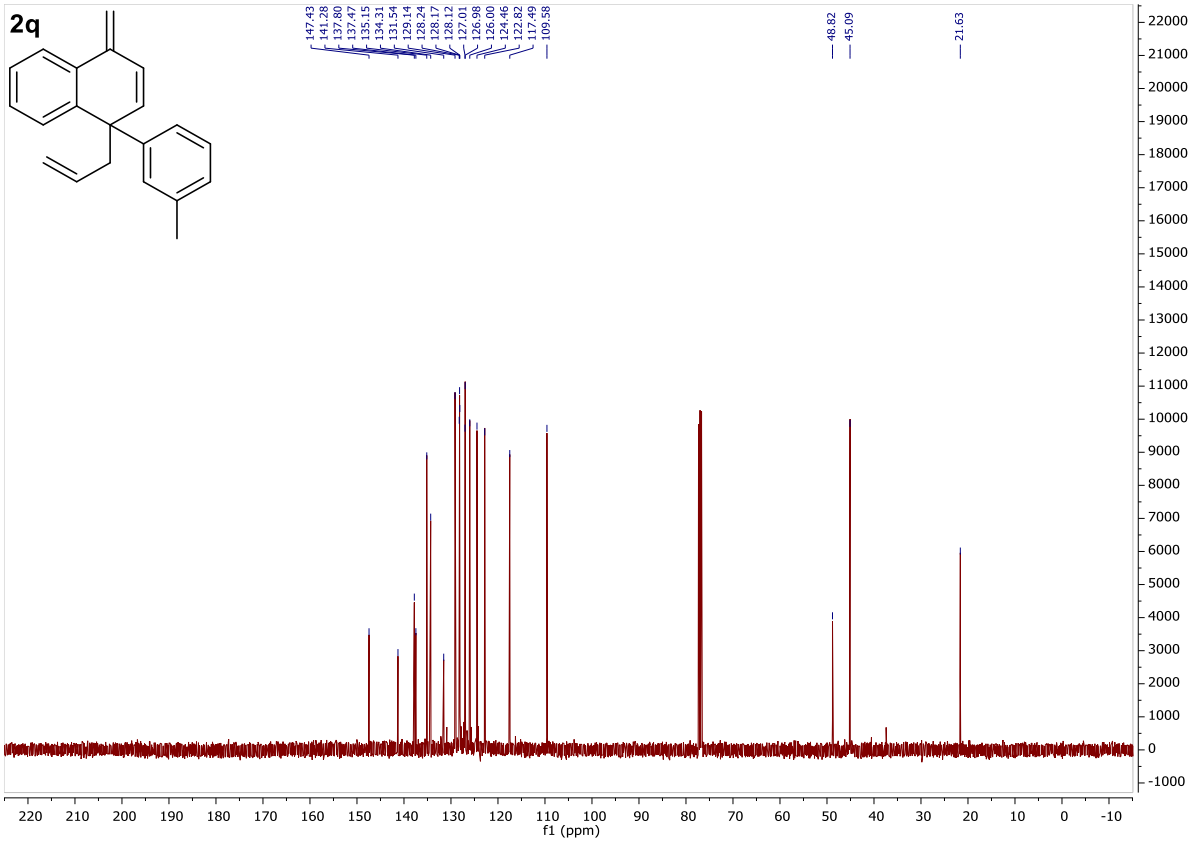

2o
F
-116.94
-116.95
-116.96
-116.97
-116.98
-116.99
-116.99
-117.00
-117.01
4500
4000
3500
3000
2500
2000
1500
1000
500
0
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

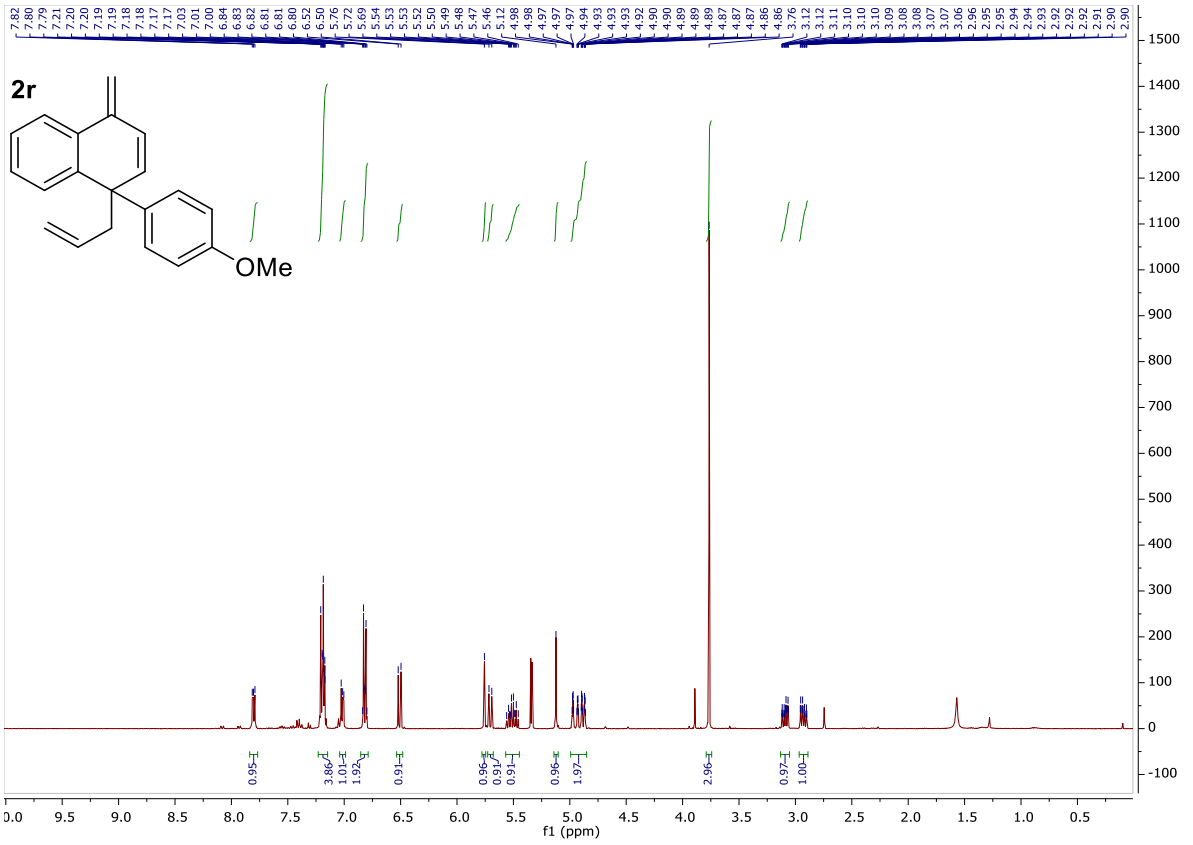

2p
CF3
f1 (ppm)

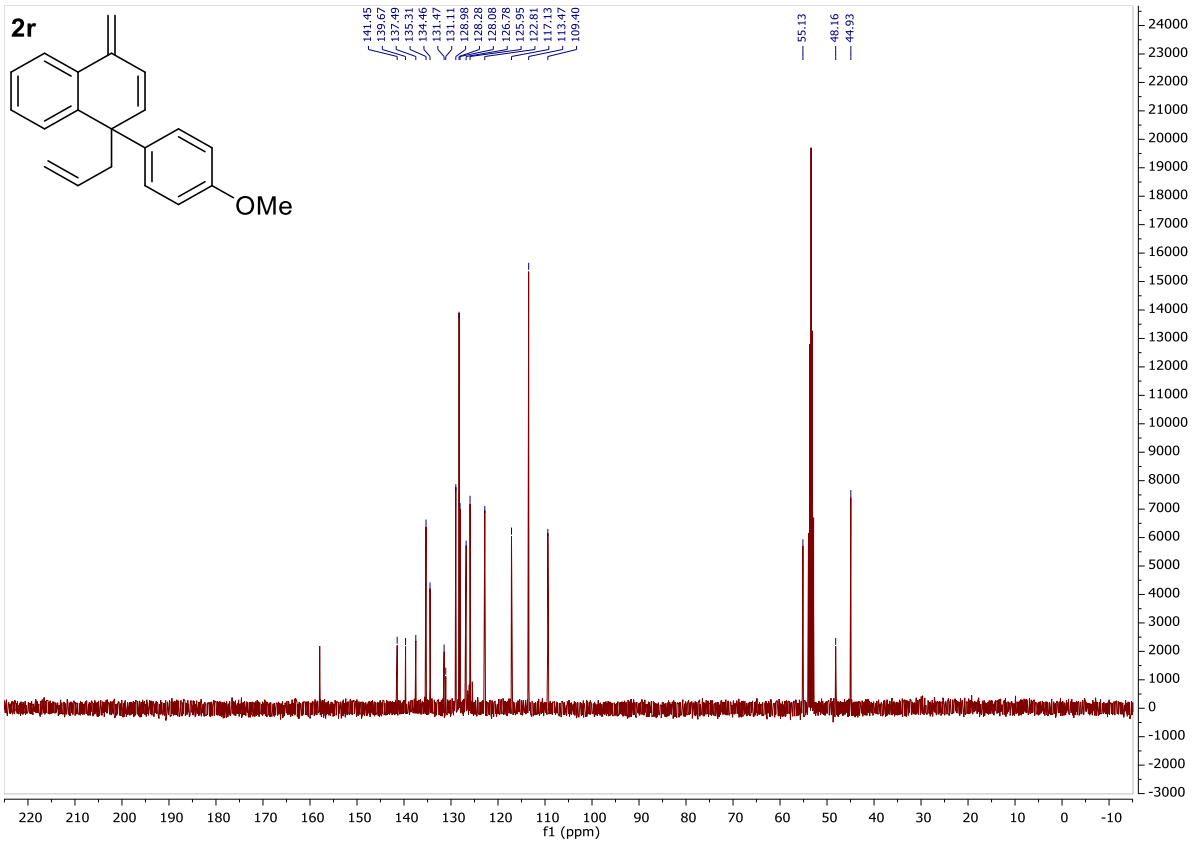

2p
CF3
f1 (ppm)

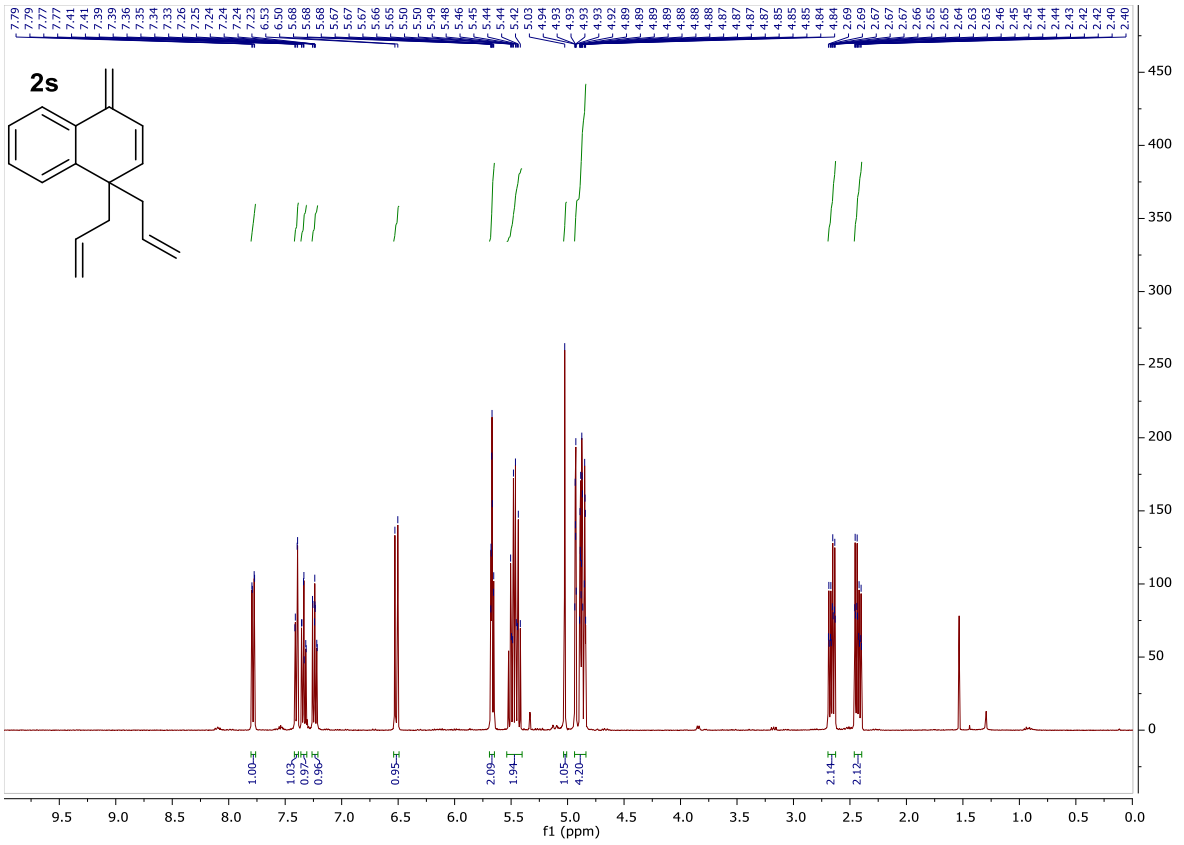

2p
-62.47
CF3
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

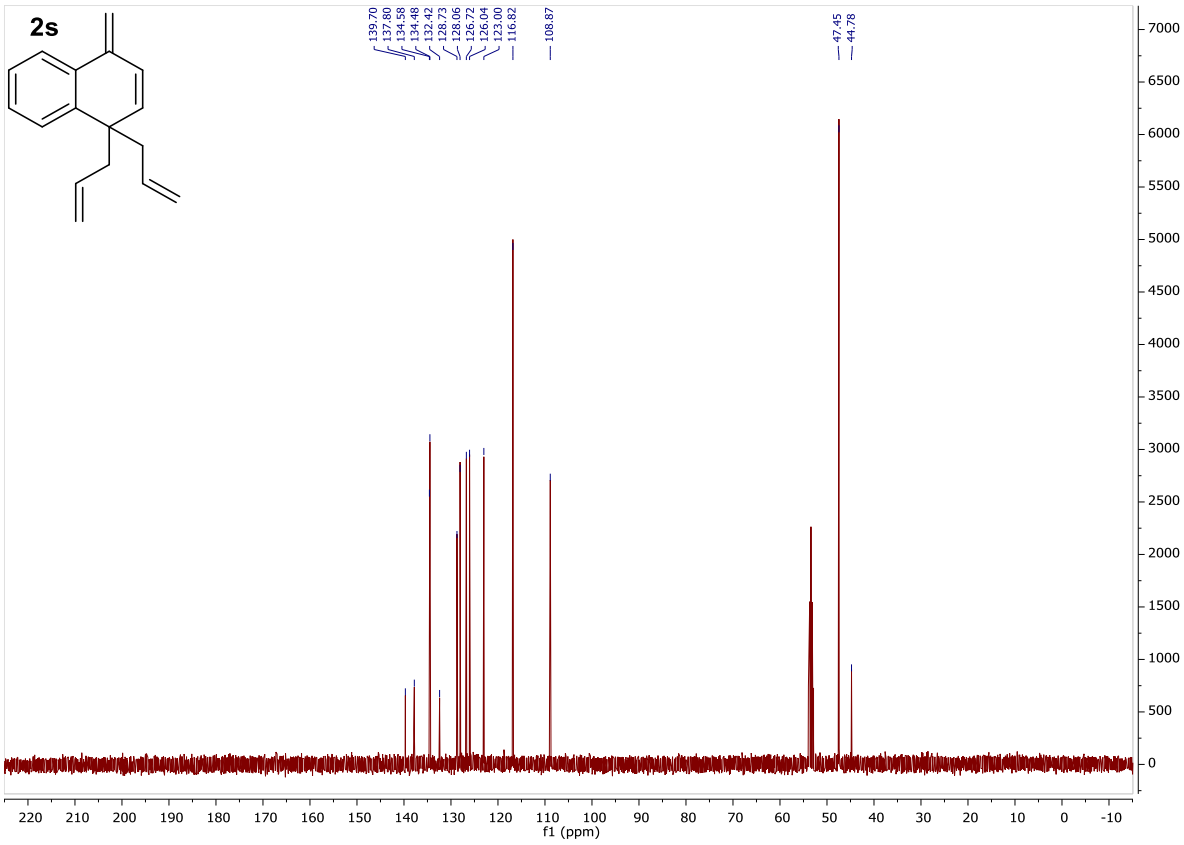

2q
f1 (ppm)

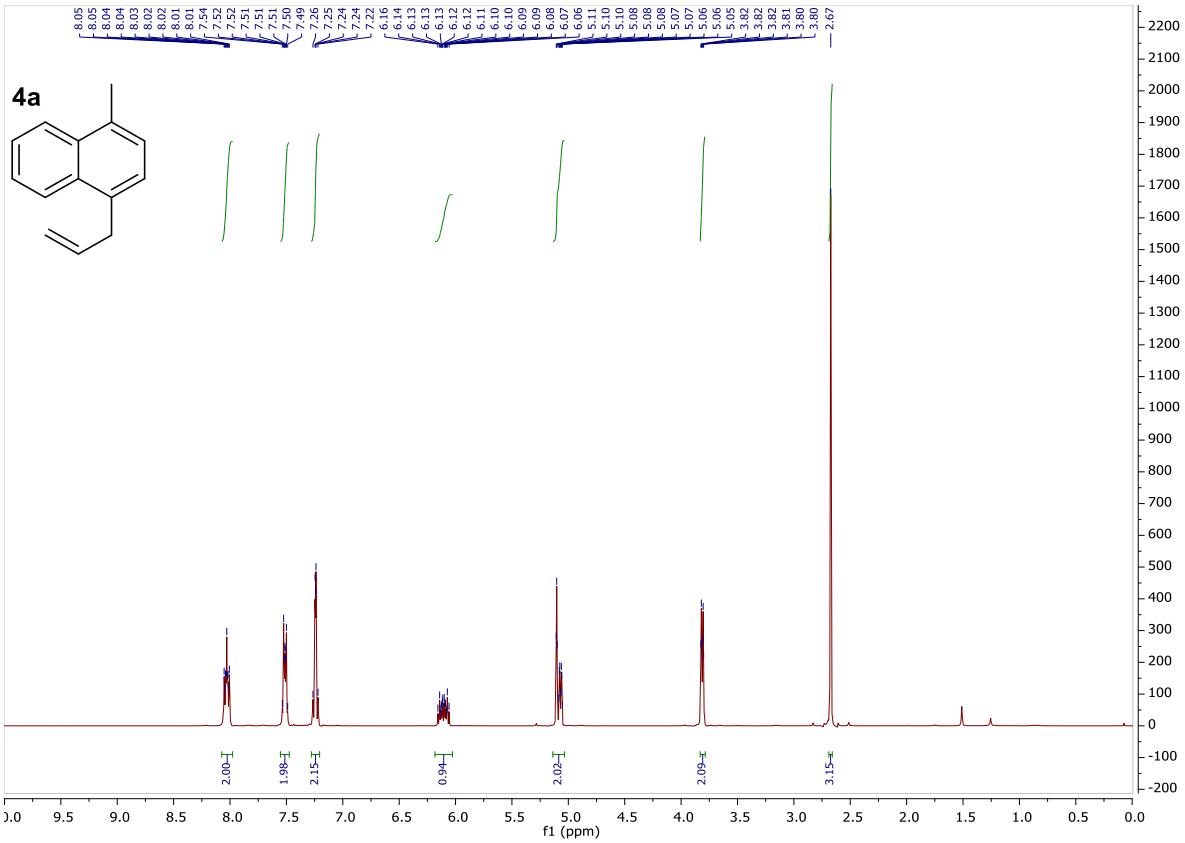

2q
f1 (ppm)

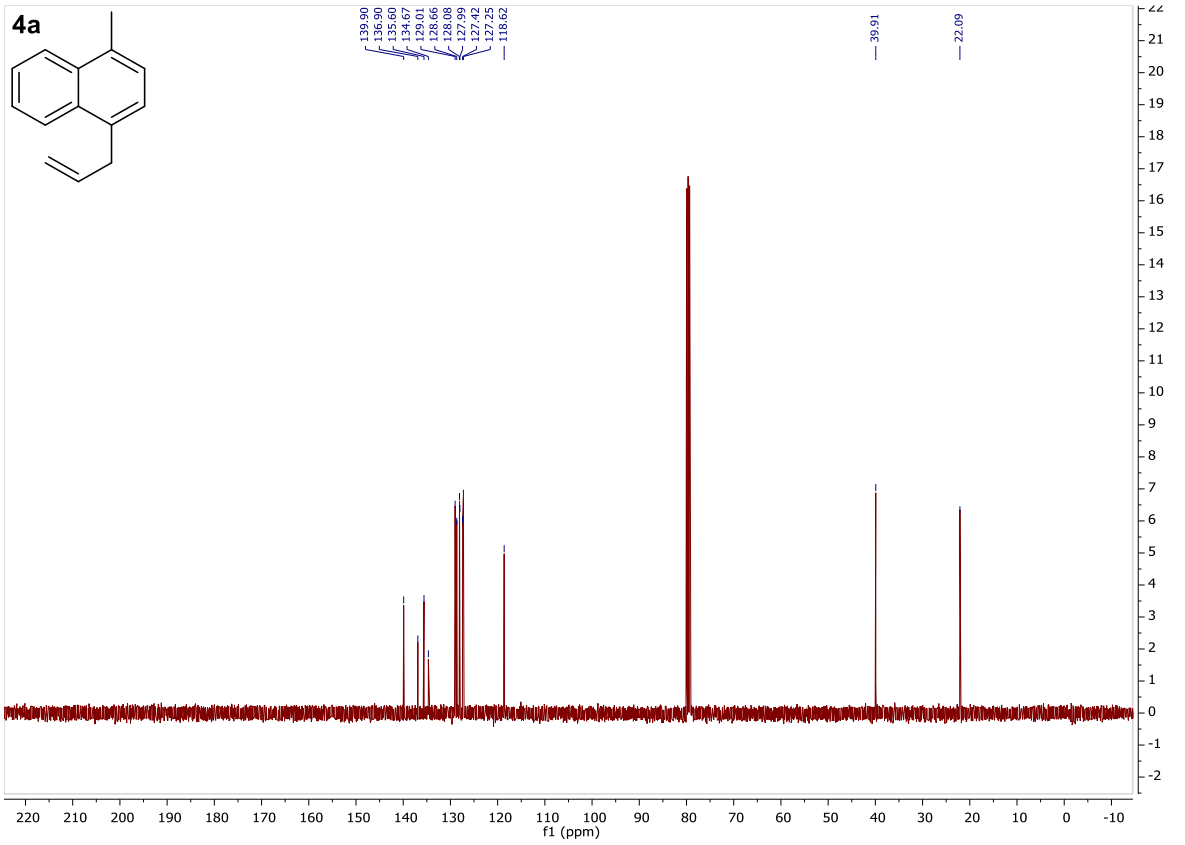

2r
OMe
f1 (ppm)

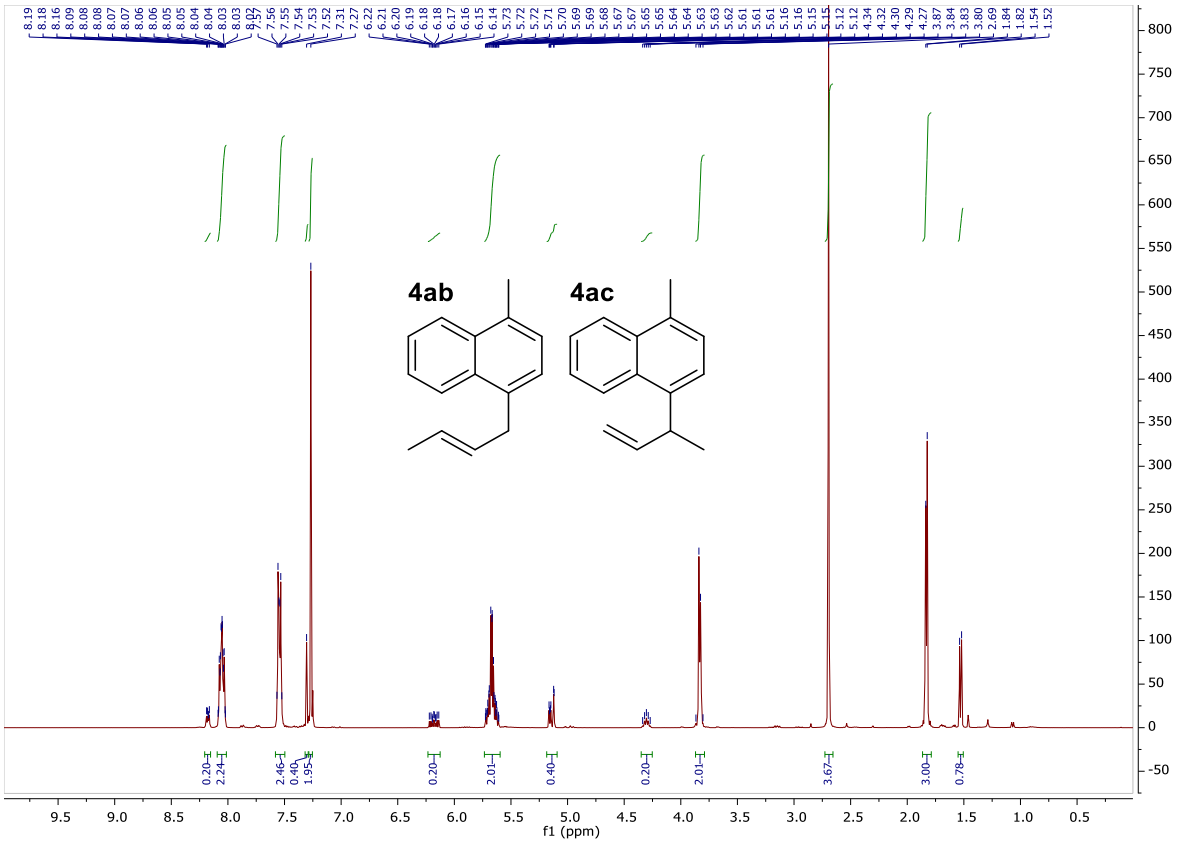

2r
OMe
141.45
139.67
137.49
135.31
134.46
131.47
131.11
128.98
128.28
128.08
126.78
125.95
122.81
117.13
113.47
109.40
55.13
48.16
44.93
f1 (ppm)

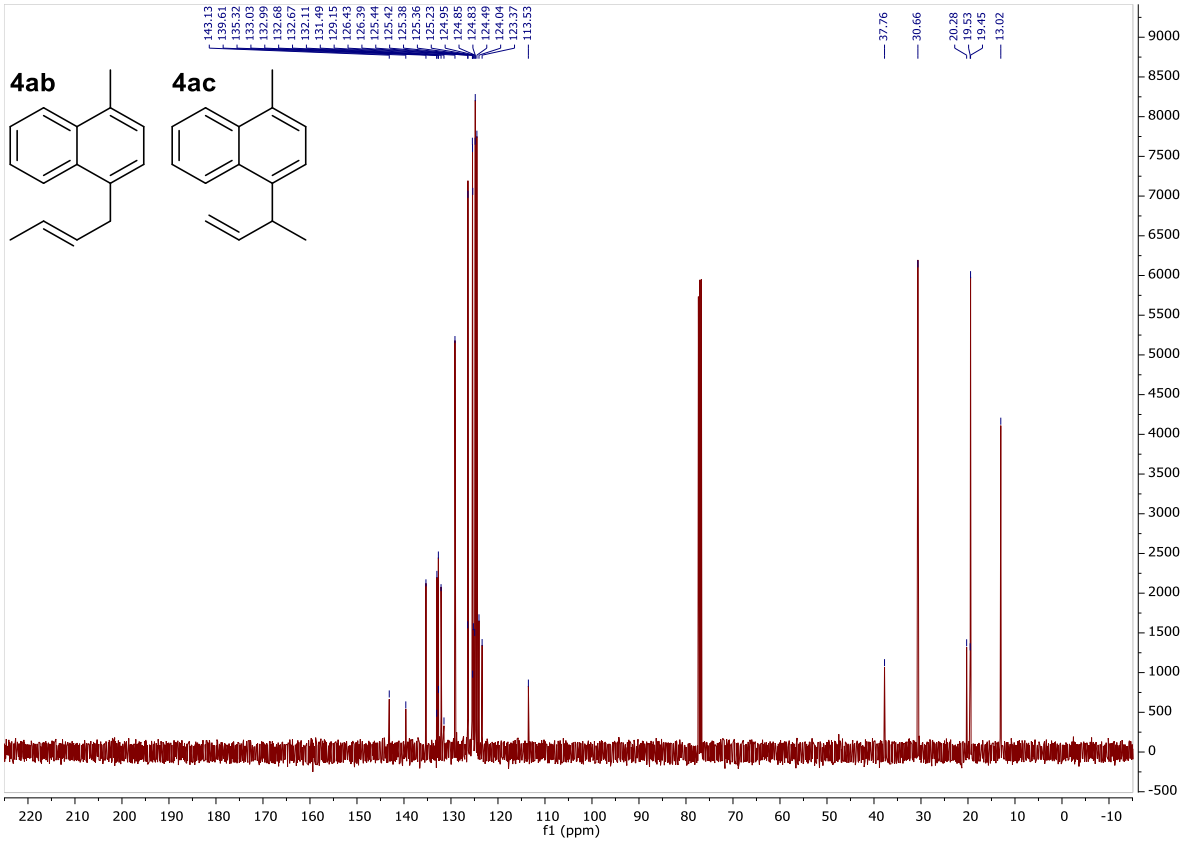

2s
f1 (ppm)

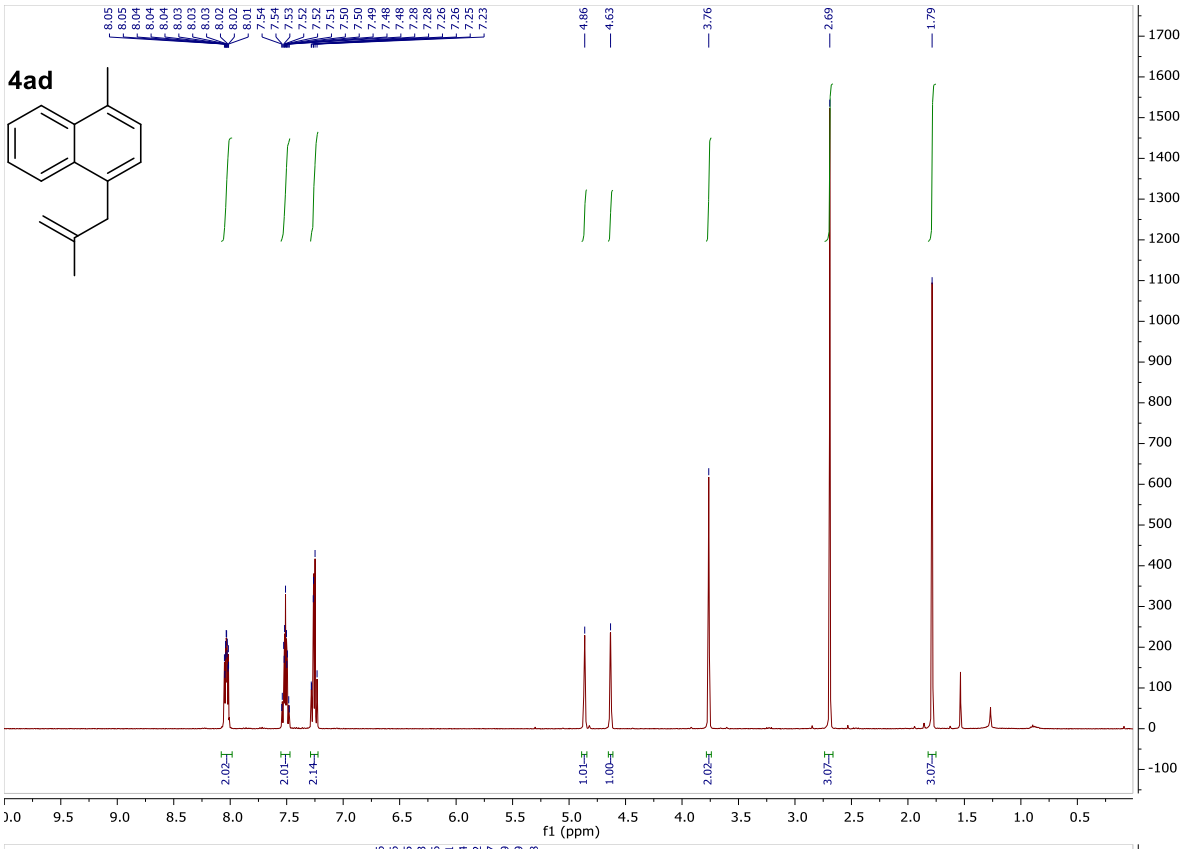

2s
f1 (ppm)

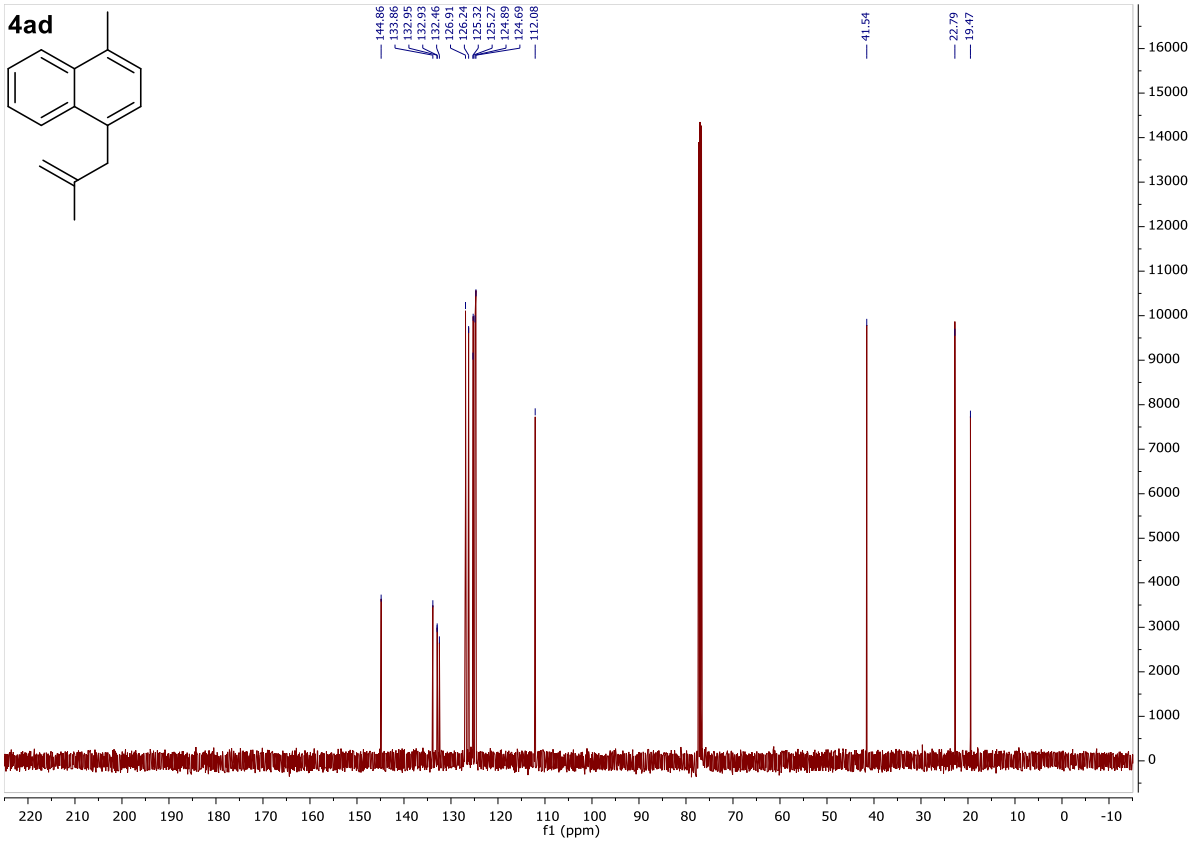

4a
8.05
8.05
8.04
8.04
8.04
8.03
8.02
8.02
8.01
8.01
7.54
7.52
7.52
7.51
7.51
7.51
7.50
7.49
7.26
7.25
7.24
7.24
7.22
6.16
6.14
6.13
6.13
6.13
6.12
6.12
6.11
6.10
6.10
6.09
6.09
6.08
6.07
6.06
5.11
5.10
5.10
5.08
5.08
5.07
5.07
5.06
5.06
5.05
3.82
3.82
3.81
3.80
3.80
2.67
2.00
1.98
2.15
0.94
2.02
2.09
3.15
f1 (ppm)

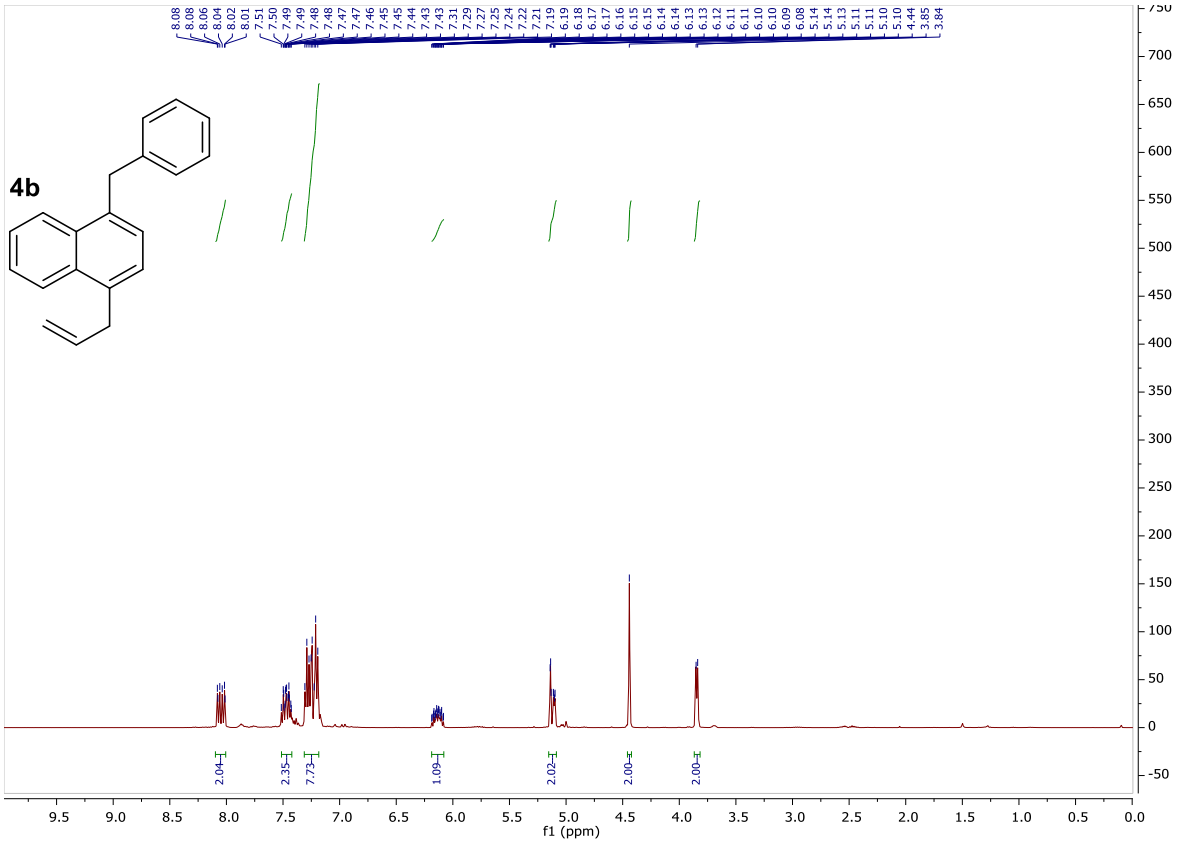

4a
139.90
136.90
135.60
134.67
129.01
128.66
128.08
127.99
127.42
127.25
118.62
39.91
22.09
f1 (ppm)

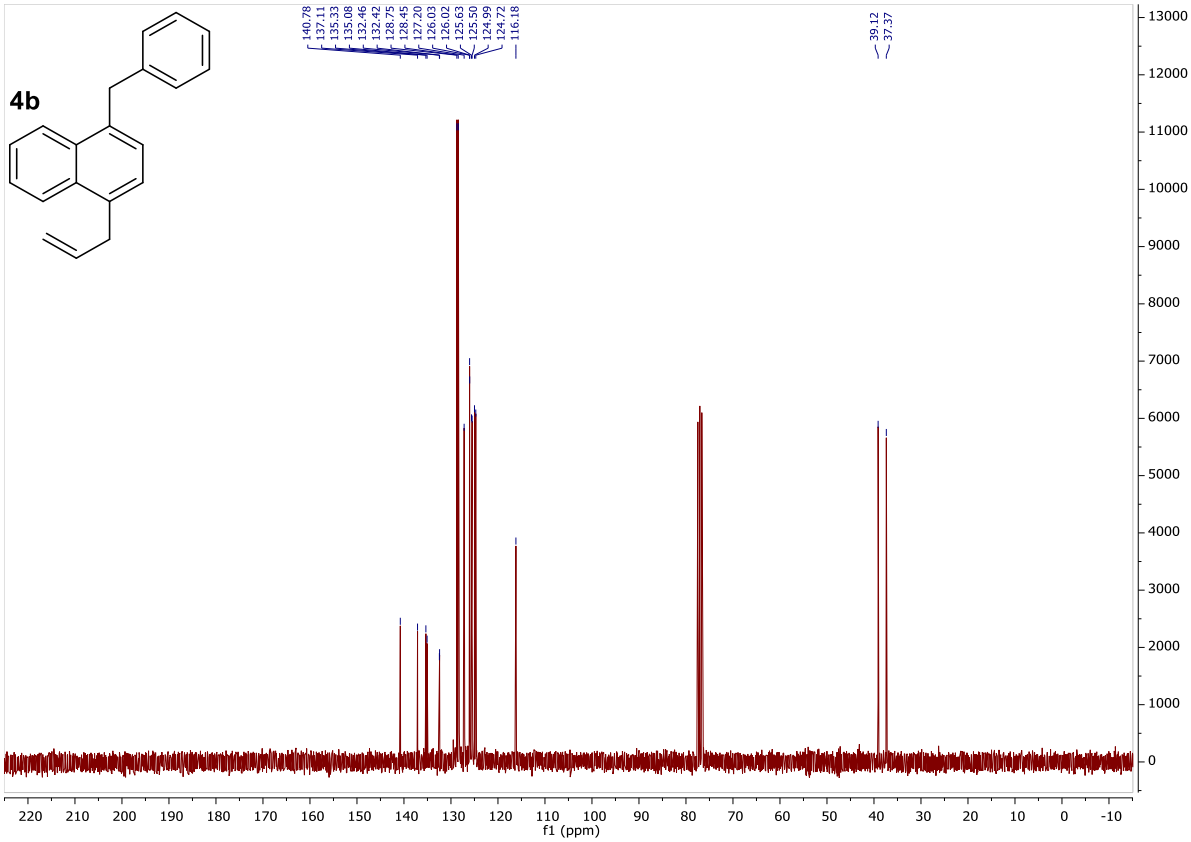

4ab
4ac
f1 (ppm)

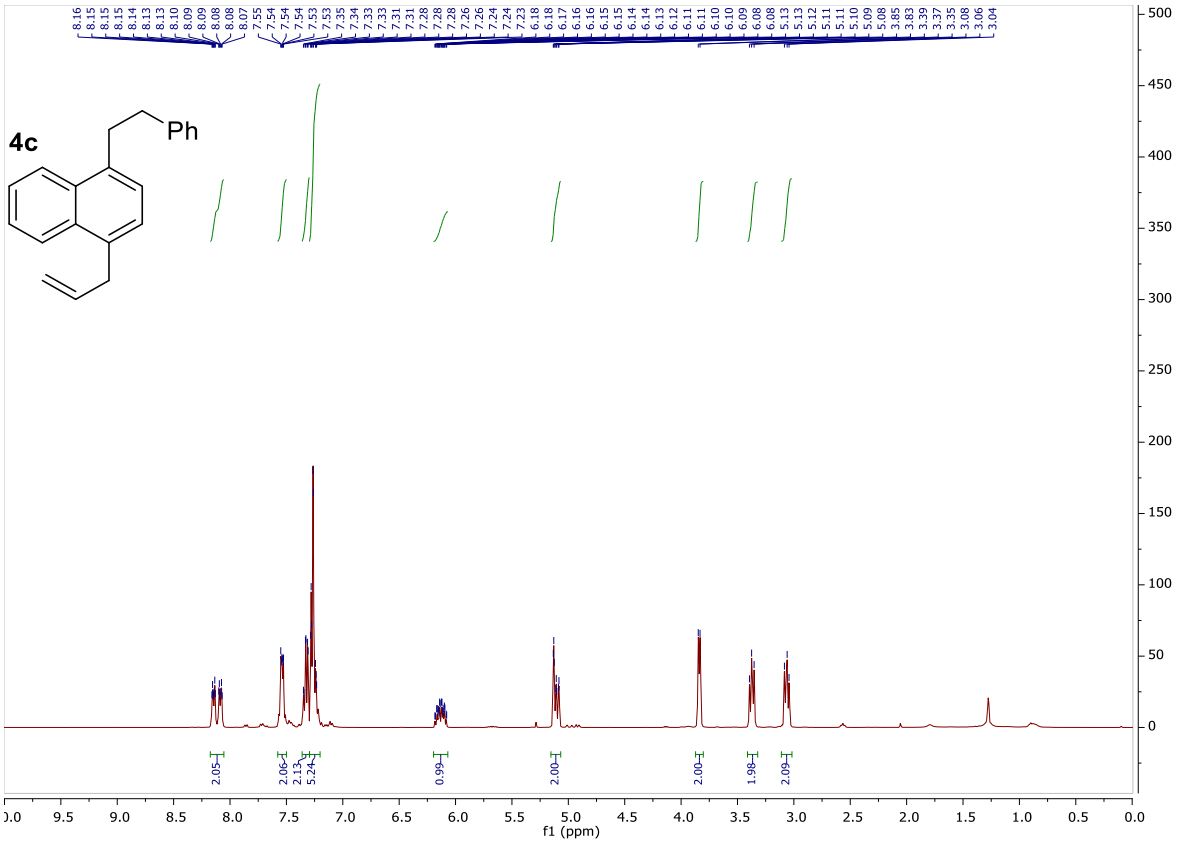

4ab
4ac
f1 (ppm)

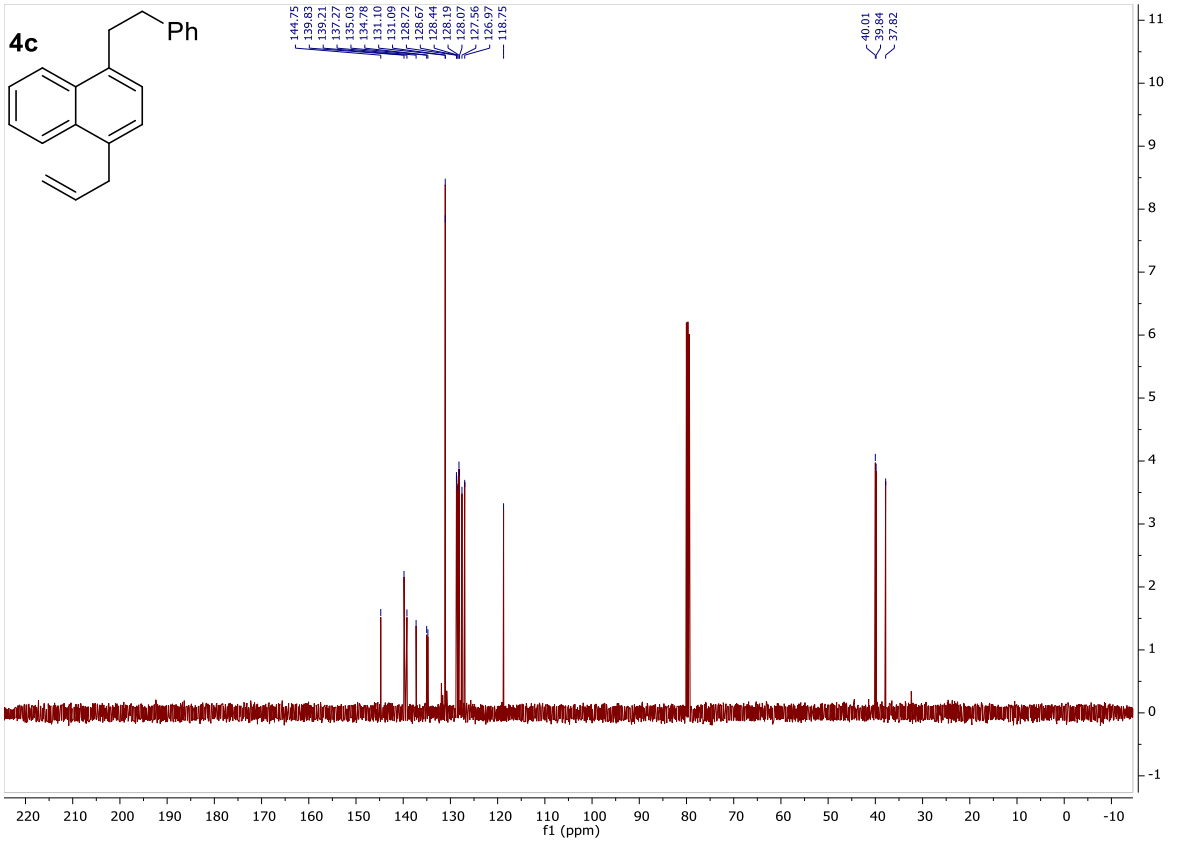

4ad
8.05
8.05
8.04
8.04
8.04
8.03
8.03
8.03
8.02
8.02
8.01
7.54
7.54
7.53
7.52
7.52
7.51
7.50
7.50
7.49
7.48
7.48
7.28
7.28
7.26
7.26
7.25
7.23
4.86
4.63
3.76
2.69
1.79
2.02
2.01
2.14
1.01
1.00
2.02
3.07
3.07
f1 (ppm)

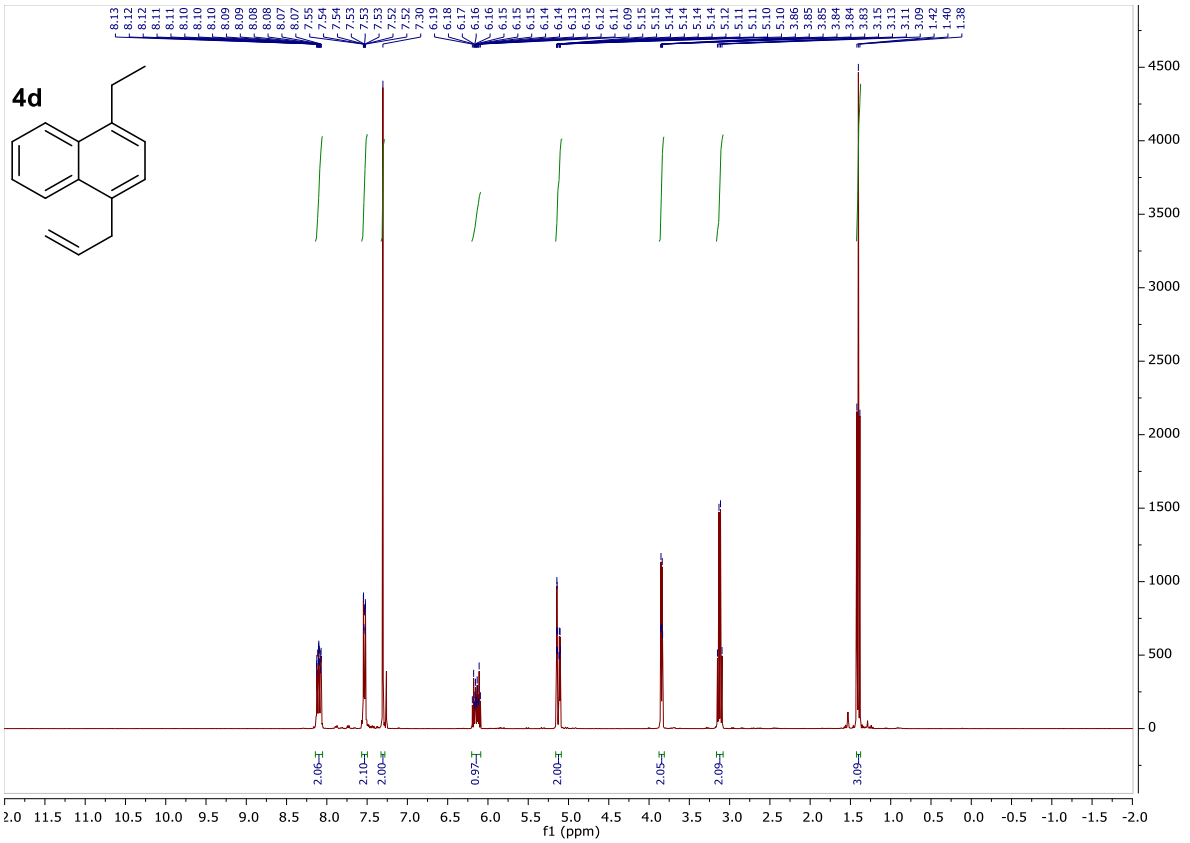

4ad
144.86
133.86
132.95
132.93
132.46
126.91
126.24
125.32
125.27
124.89
124.69
112.08
41.54
22.79
19.47
f1 (ppm)

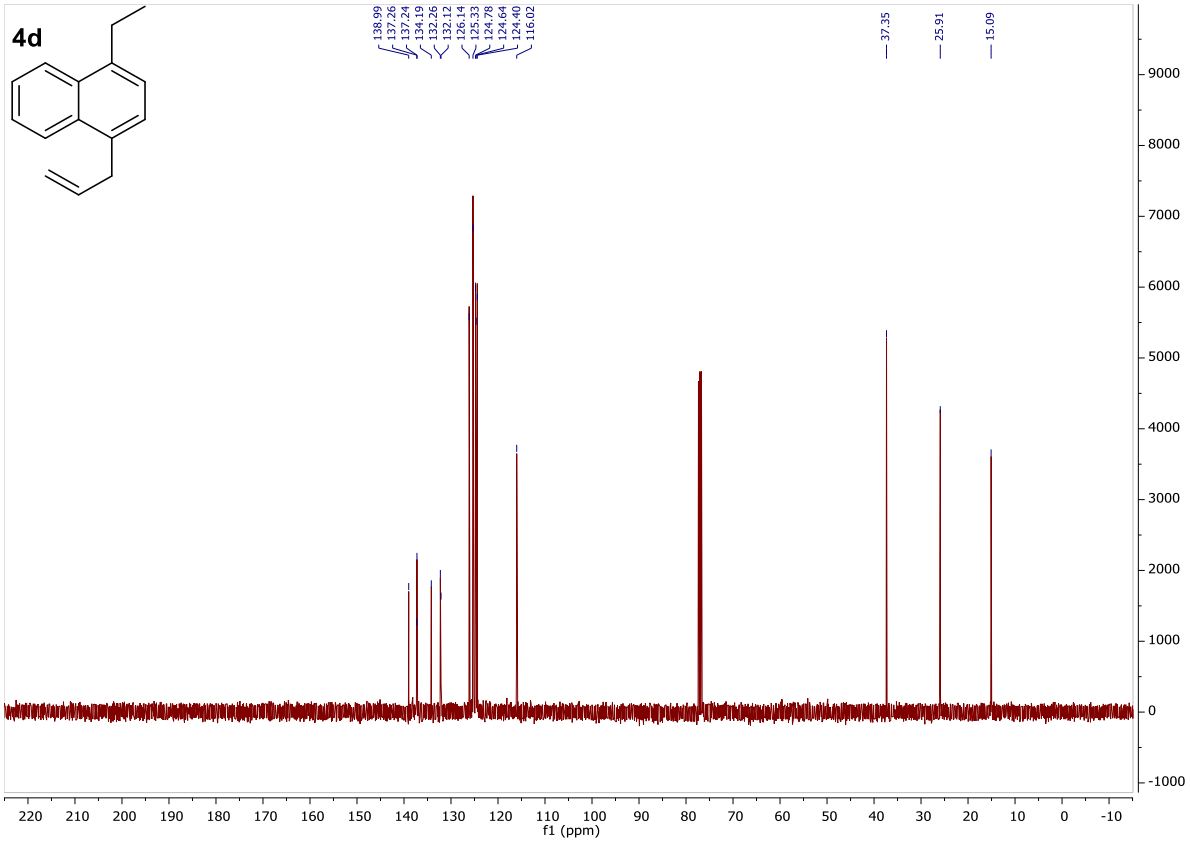

4b
8.08
8.08
8.06
8.04
8.02
8.01
7.51
7.50
7.49
7.49
7.48
7.48
7.47
7.47
7.46
7.45
7.45
7.44
7.43
7.43
7.31
7.29
7.27
7.25
7.24
7.22
7.21
7.19
6.19
6.18
6.17
6.17
6.16
6.15
6.15
6.14
6.14
6.13
6.13
6.12
6.11
6.11
6.10
6.10
6.09
6.08
5.14
5.14
5.13
5.11
5.11
5.10
4.44
3.85
3.84
2.04
2.35
7.73
1.09
2.02
2.00
2.00
f1 (ppm)

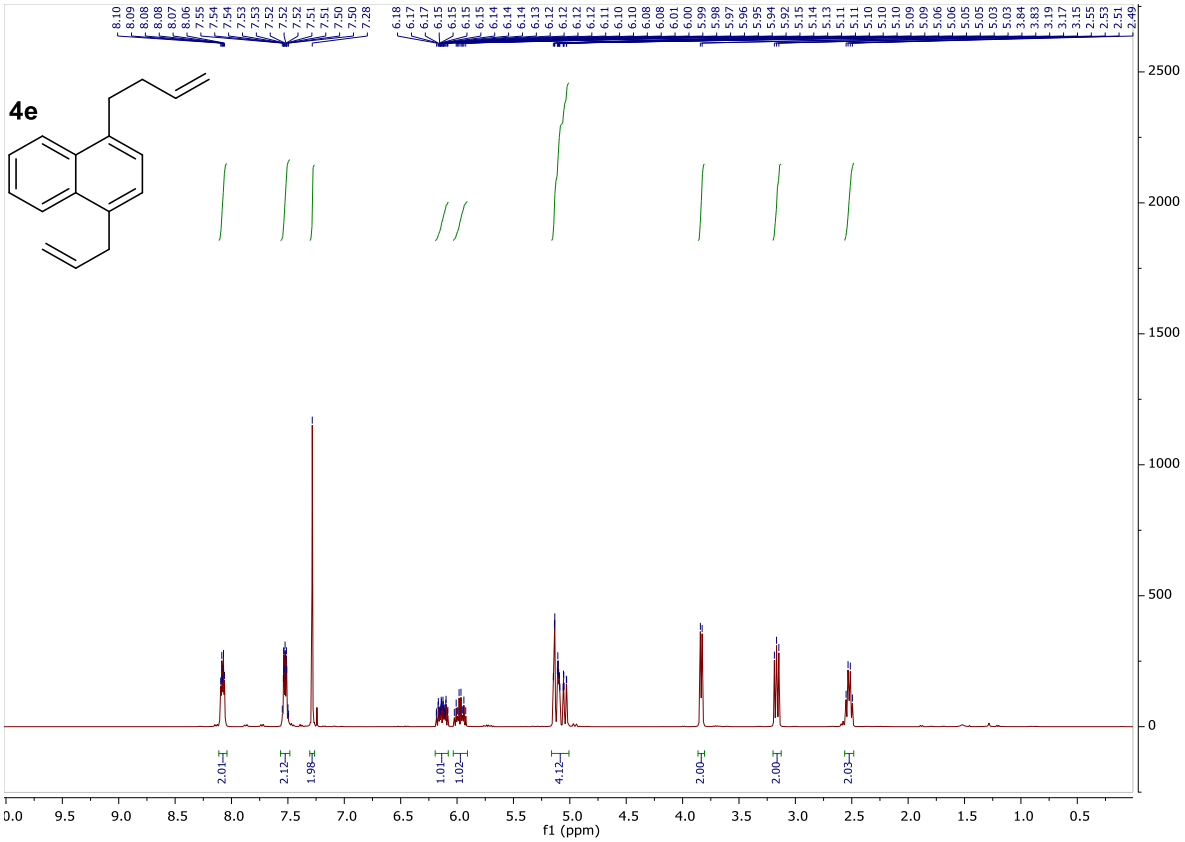

4b
140.78
137.11
135.33
135.08
132.46
132.42
128.75
128.45
127.20
126.03
126.02
125.63
125.50
124.99
124.72
116.18
39.12
37.37
f1 (ppm)

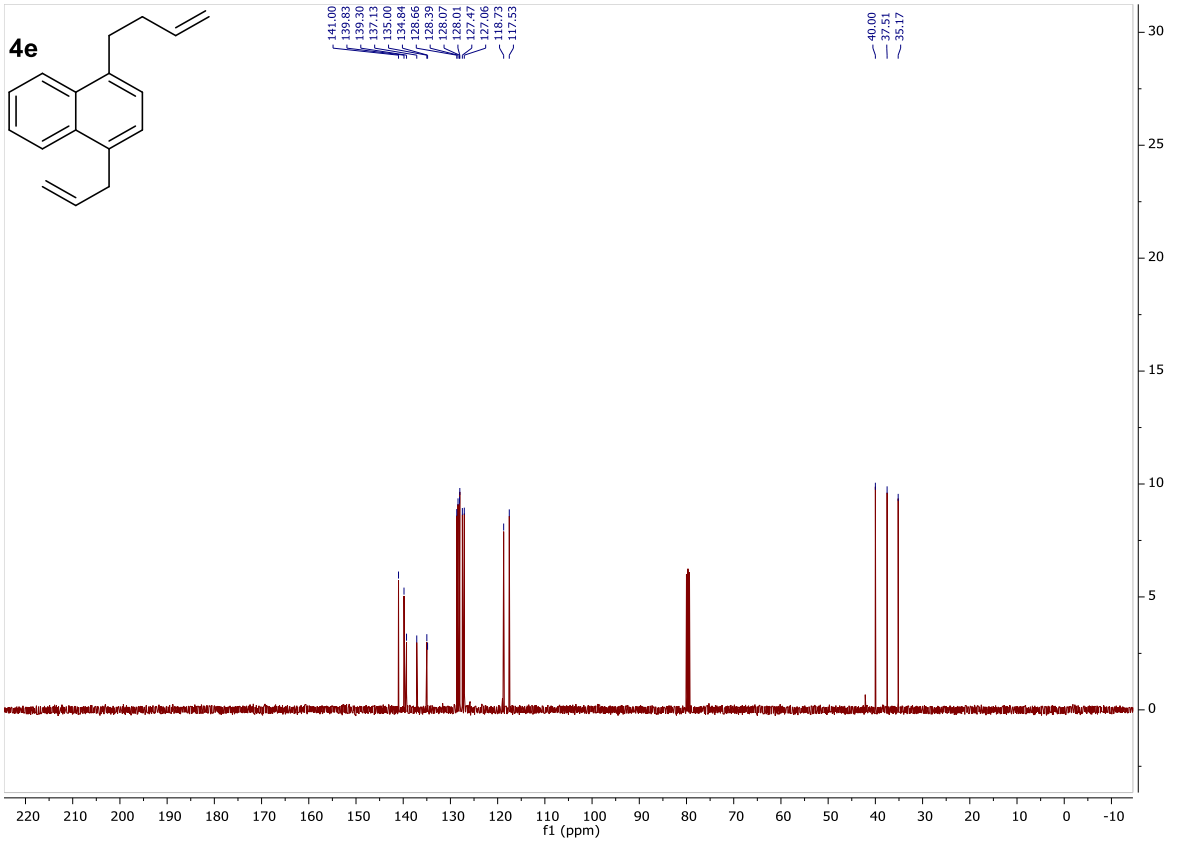

4c
Ph
f1 (ppm)

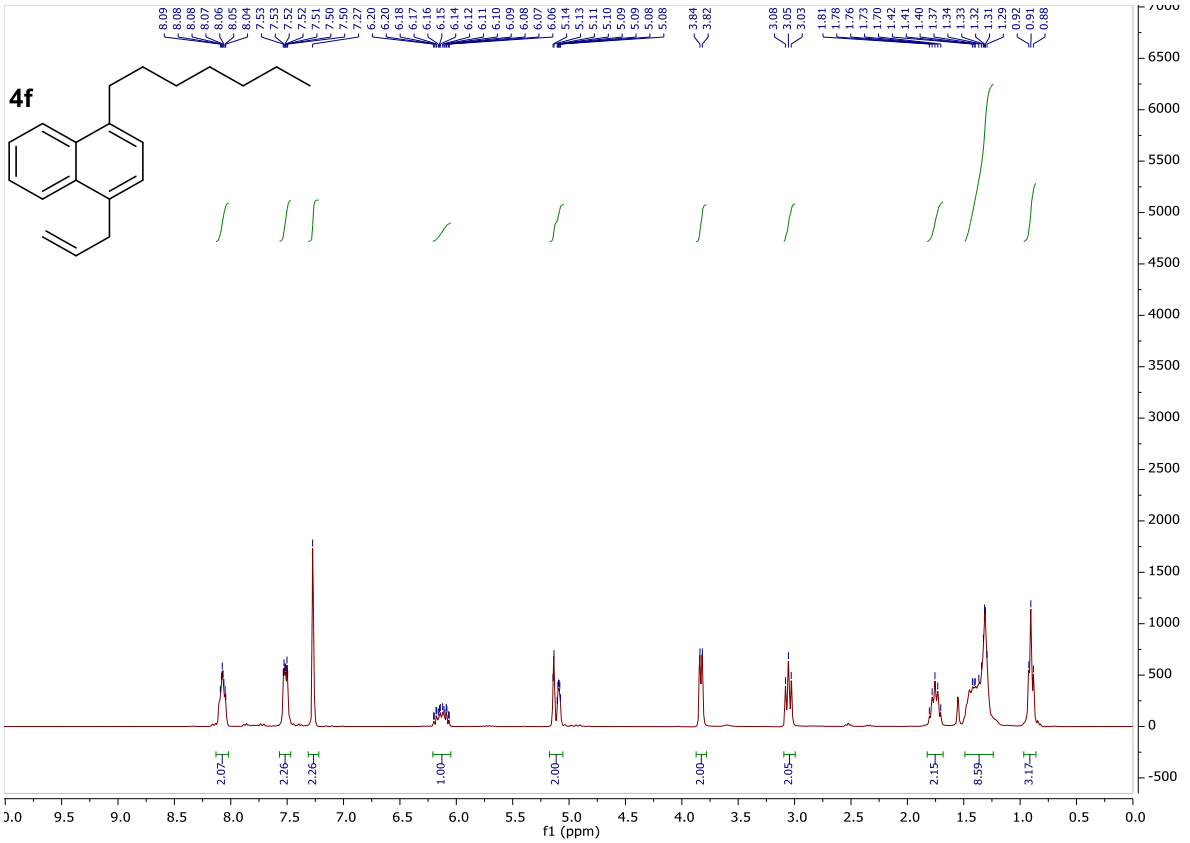

4c
Ph
f1 (ppm)

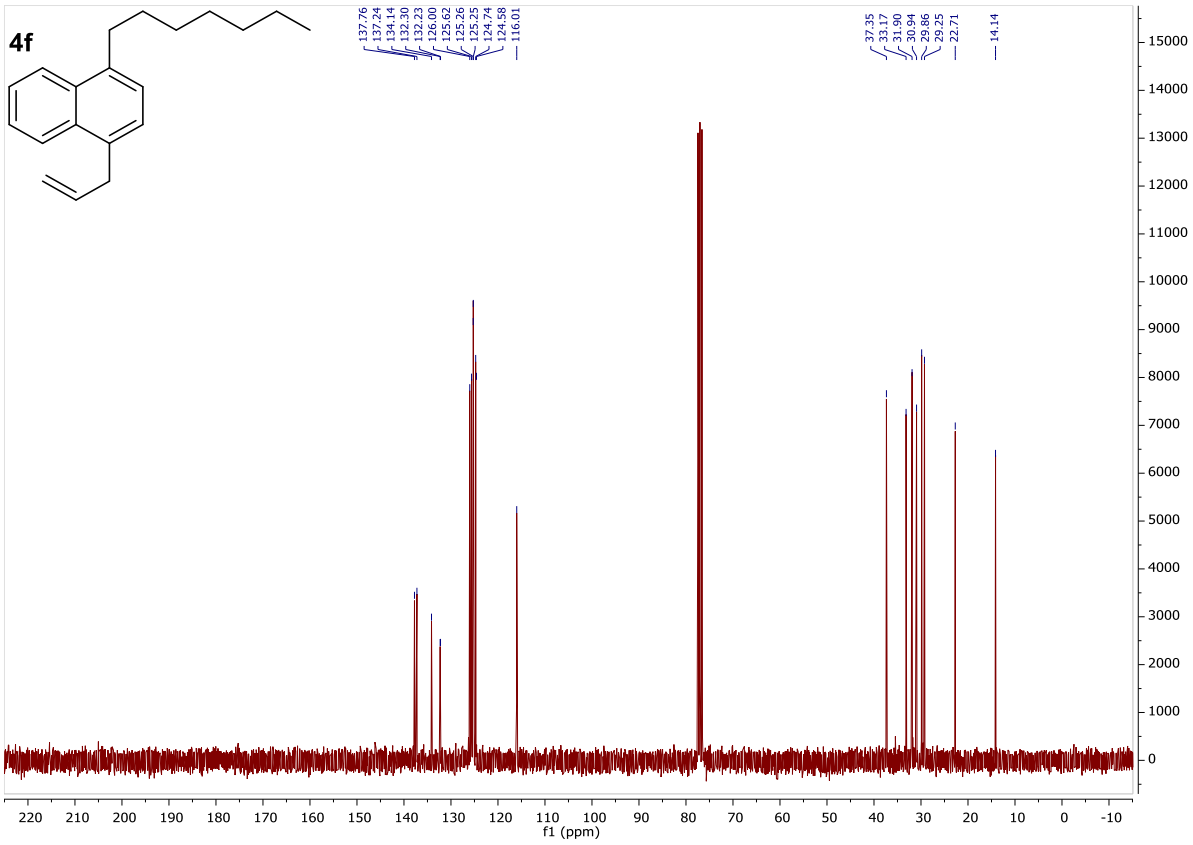

4d
f1 (ppm)

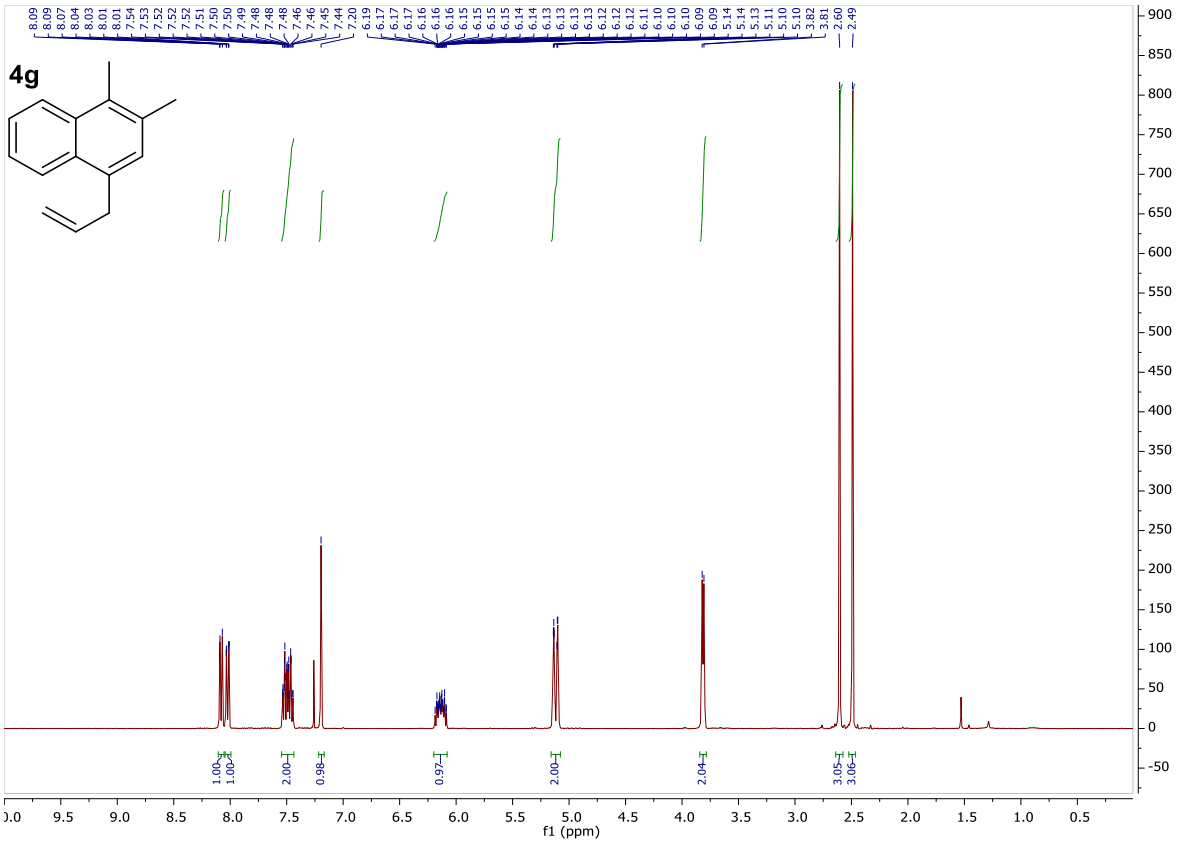

4d
f1 (ppm)

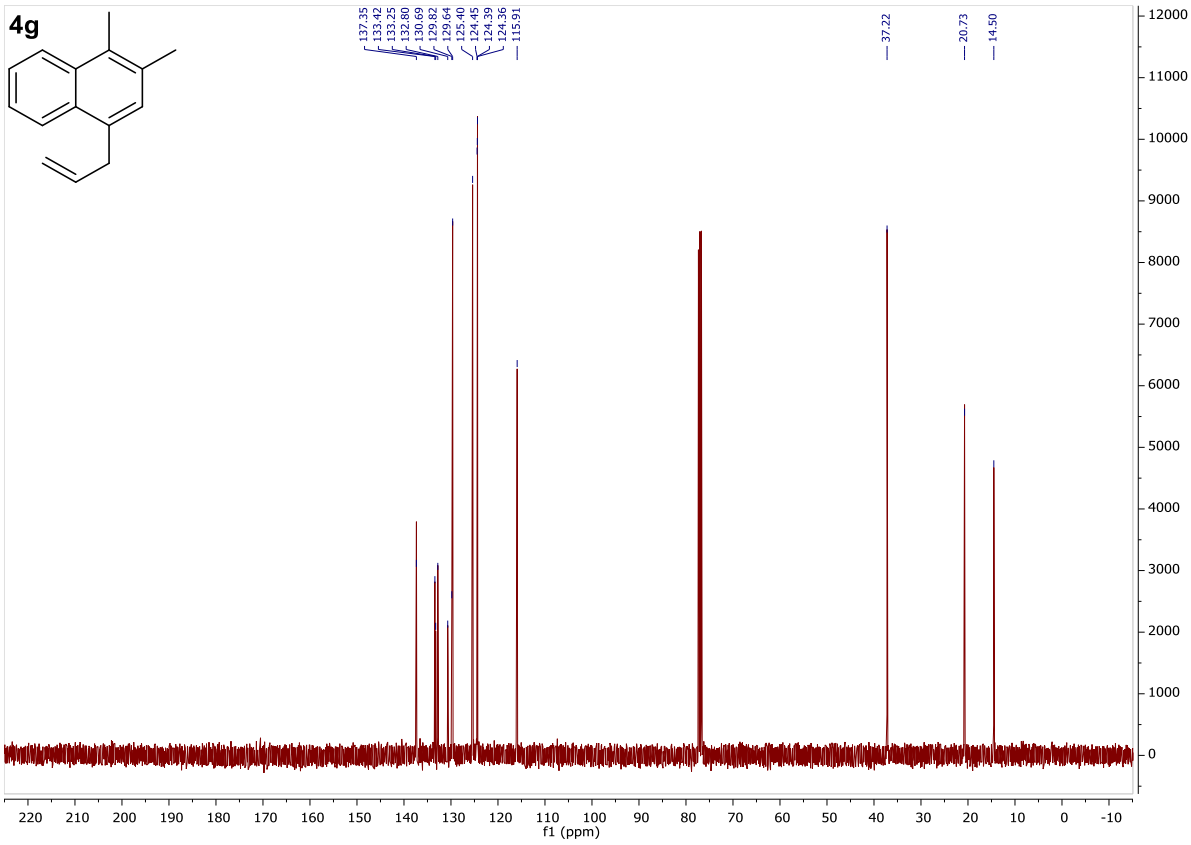

4e
f1 (ppm)

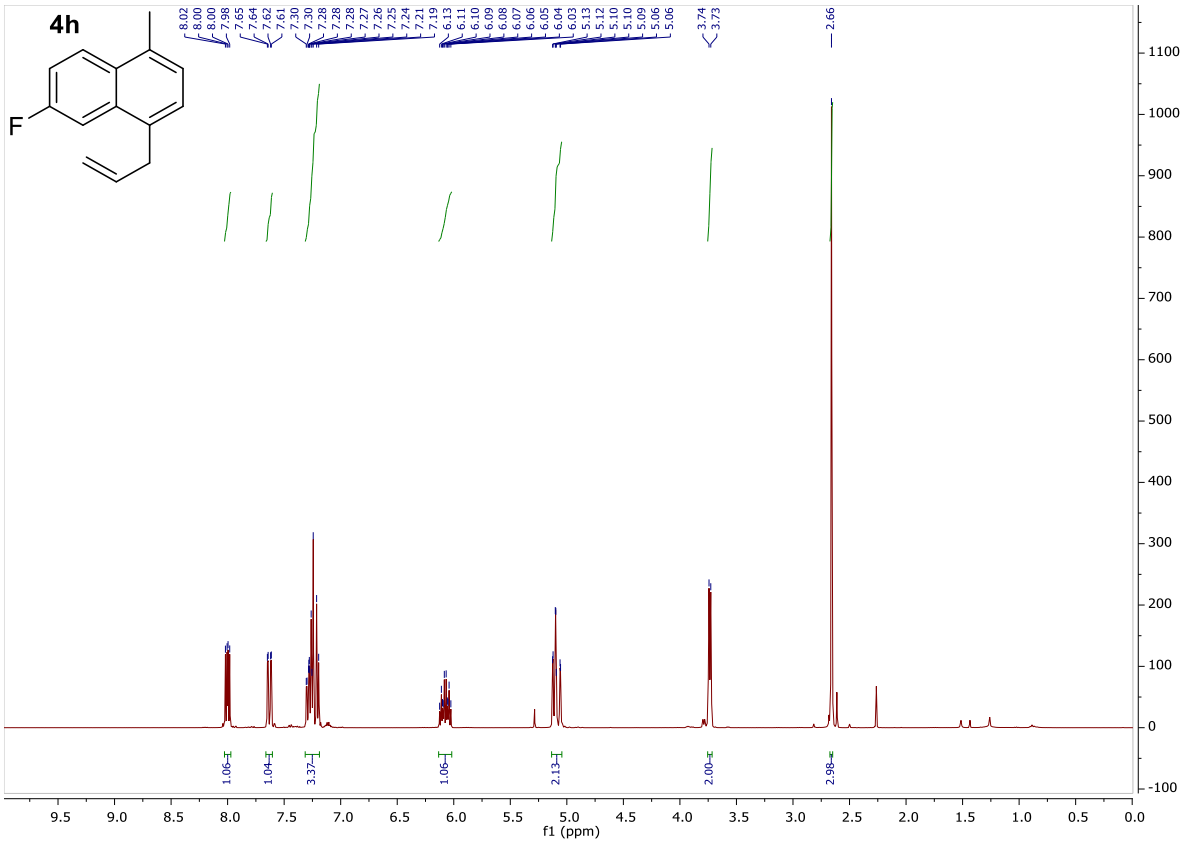

4e
f1 (ppm)

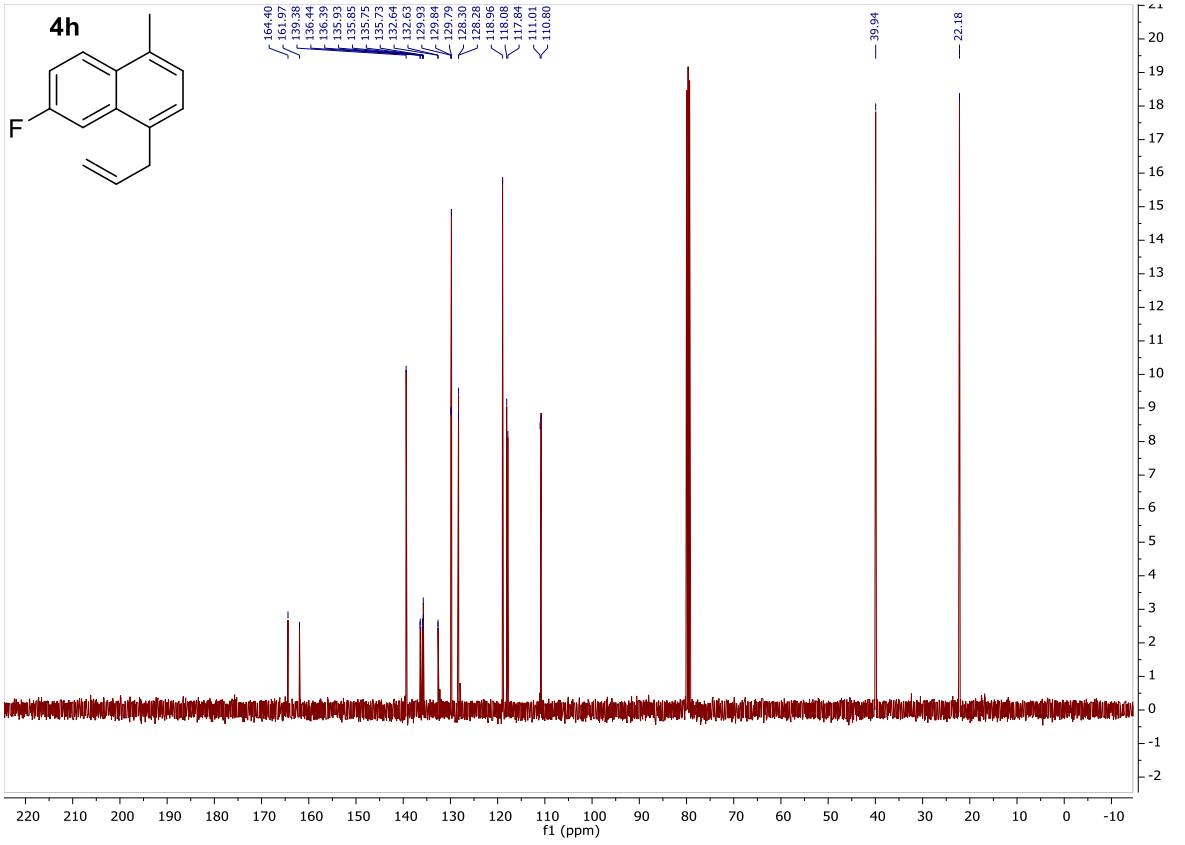

4f
8.09
8.08
8.08
8.07
8.06
8.05
8.04
7.53
7.52
7.52
7.51
7.50
7.50
7.27
6.20
6.18
6.17
6.16
6.15
6.14
6.12
6.11
6.10
6.09
6.08
6.07
6.06
5.14
5.13
5.11
5.10
5.09
5.09
5.08
5.08
3.84
3.82
3.08
3.05
3.03
1.81
1.78
1.76
1.73
1.70
1.42
1.41
1.40
1.37
1.34
1.33
1.32
1.31
1.29
0.92
0.91
0.88
2.07
2.26
2.26
1.00
2.00
2.00
2.05
2.15
8.59
3.17
f1 (ppm)

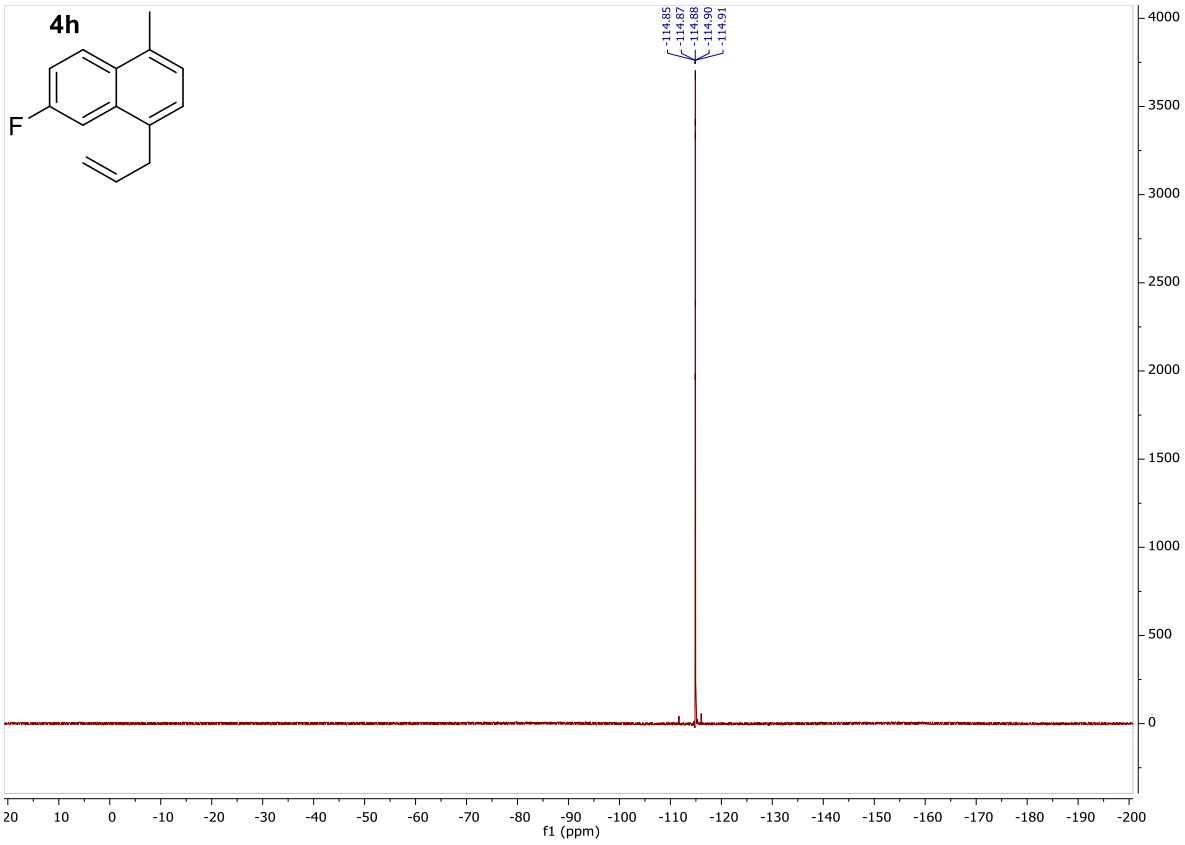

4f
137.76
137.24
134.14
132.30
132.23
126.00
125.62
125.26
125.25
124.74
124.58
116.01
37.35
33.17
31.90
30.94
29.86
29.25
22.71
14.14
f1 (ppm)

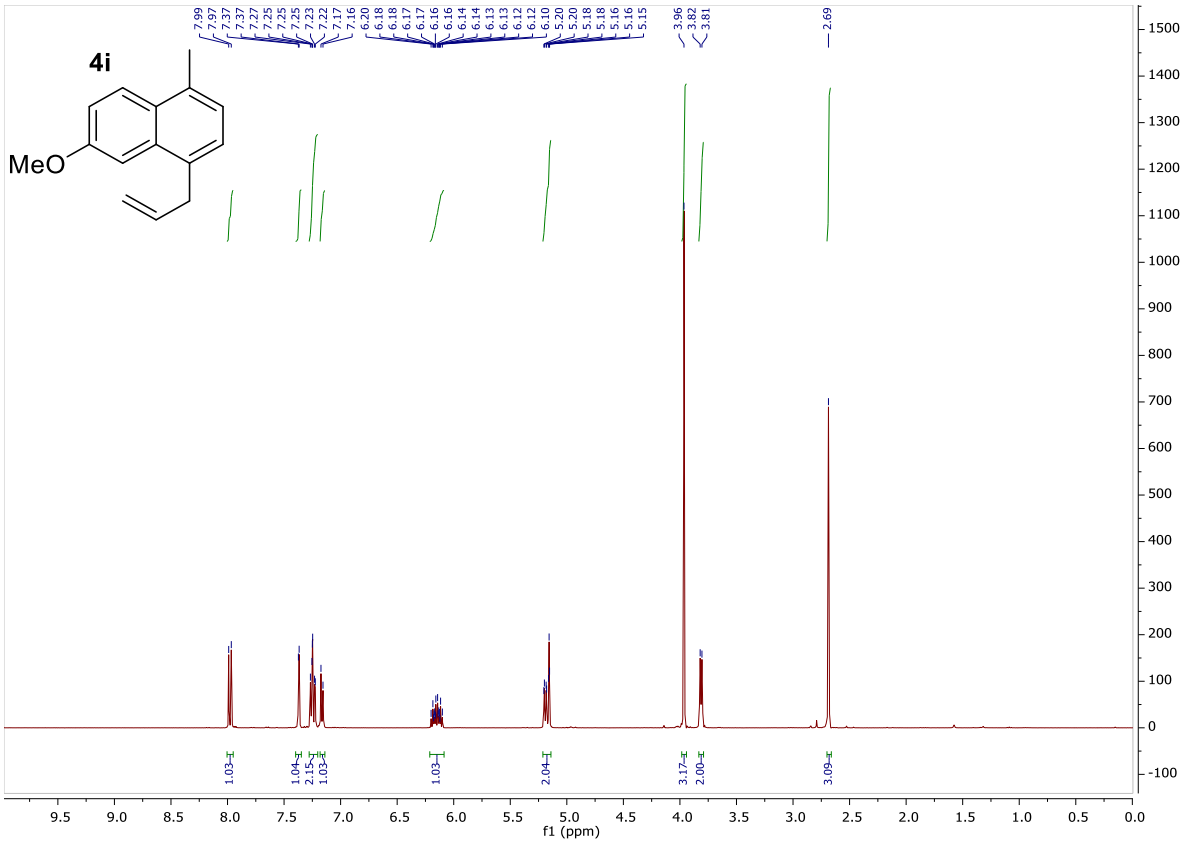

4g
f1 (ppm)

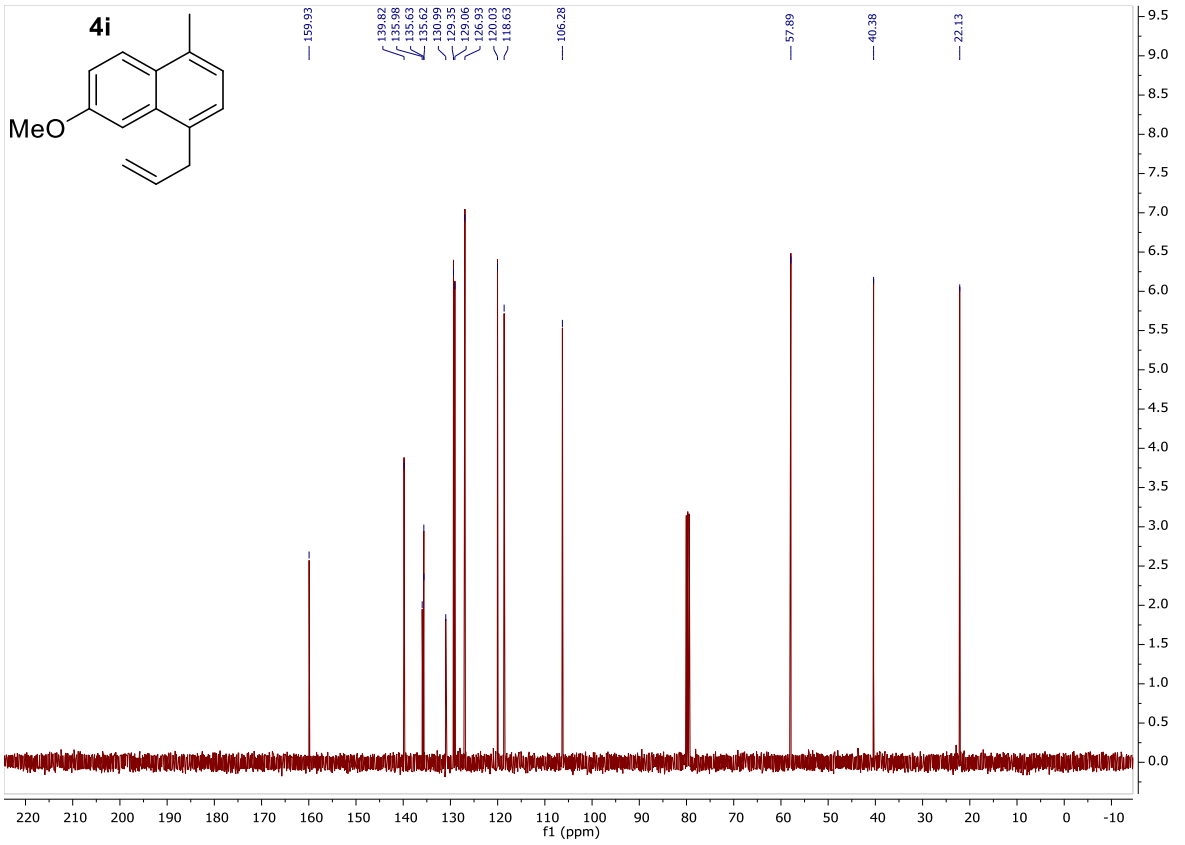

4g
f1 (ppm)

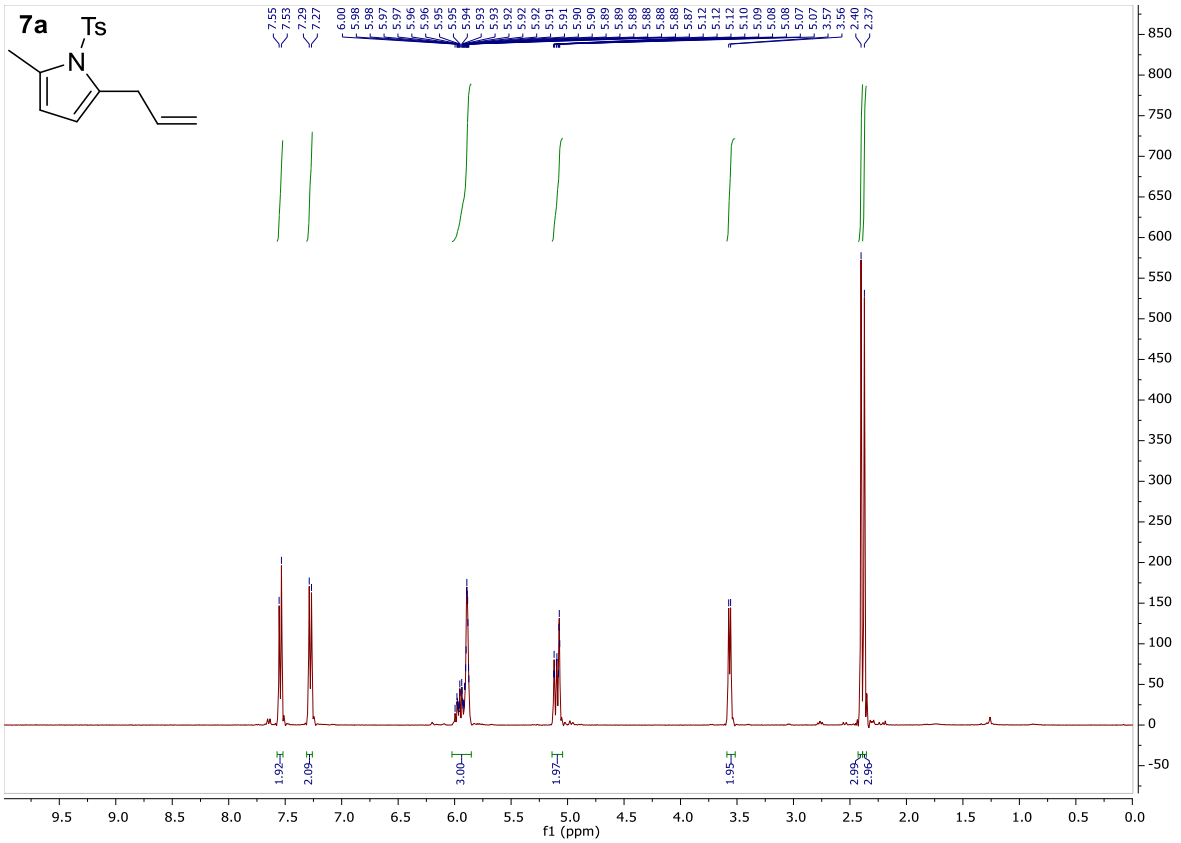

4h
F
8.02
8.00
8.00
7.98
7.65
7.64
7.62
7.61
7.30
7.30
7.28
7.28
7.28
7.27
7.26
7.25
7.24
7.21
7.19
6.13
6.11
6.10
6.09
6.08
6.07
6.06
6.05
6.04
6.03
5.13
5.12
5.10
5.10
5.09
5.06
5.06
3.74
3.73
2.66
1.06
1.04
3.37
1.06
2.13
2.00
2.98
f1 (ppm)

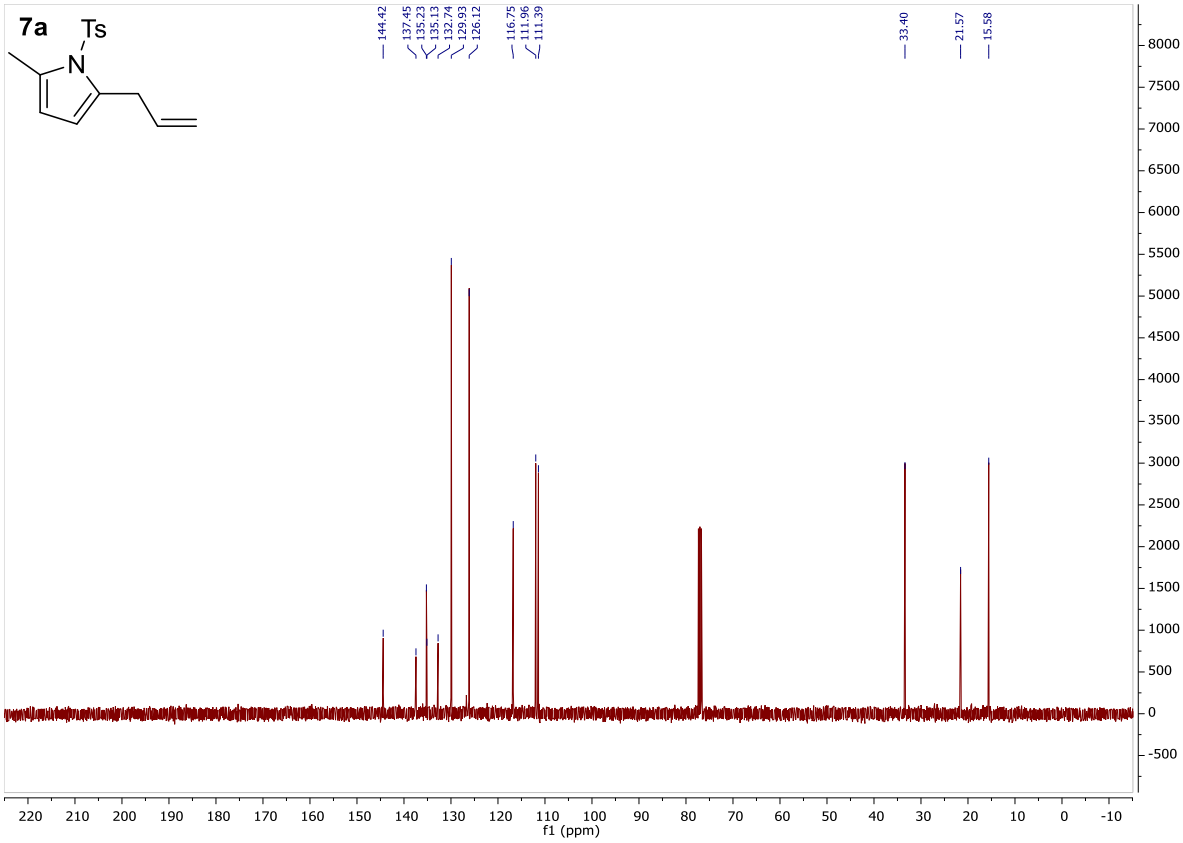

4h
F
164.40
161.97
139.38
136.39
135.85
135.75
135.73
132.64
132.63
129.93
129.84
129.79
128.30
128.28
118.96
118.08
117.84
111.01
110.80
39.94
22.18
f1 (ppm)

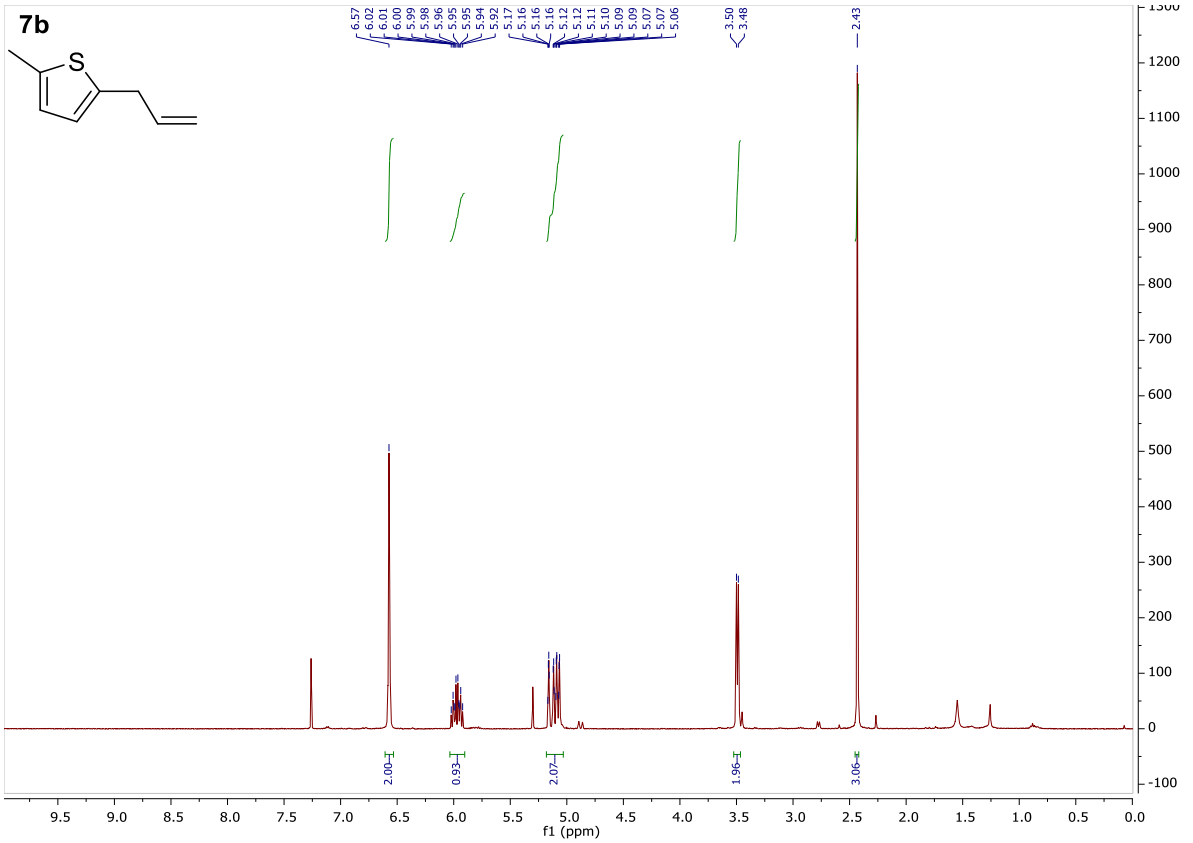

4h
F
-114.85
-114.87
-114.88
-114.90
-114.91
4000
3500
3000
2500
2000
1500
1000
500
0
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

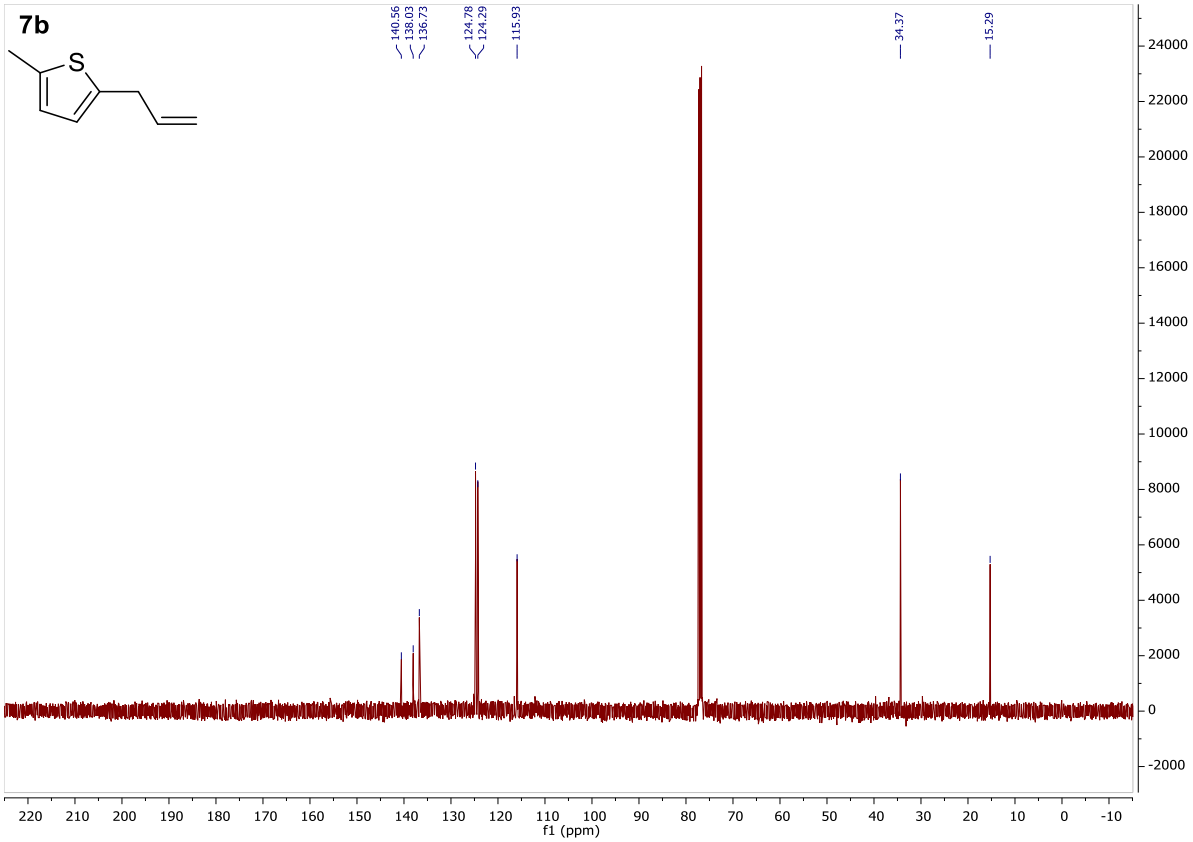

4i
MeO
7.99
7.97
7.37
7.37
7.27
7.25
7.25
7.25
7.23
7.22
7.17
7.16
6.20
6.18
6.18
6.17
6.17
6.16
6.16
6.14
6.13
6.13
6.12
6.12
6.10
5.20
5.20
5.18
5.18
5.16
5.16
5.15
3.96
3.82
3.81
2.69
1.03
1.04
2.15
1.03
1.03
2.04
3.17
2.00
3.09
f1 (ppm)


4i
MeO
159.93
139.82
135.98
135.63
135.62
130.99
129.35
129.06
126.93
120.03
118.63
106.28
57.89
40.38
22.13
f1 (ppm)


7a
Ts
N
f1 (ppm)


7a
Ts
N
f1 (ppm)


7b
S
6.57
6.02
6.01
6.00
5.99
5.98
5.96
5.95
5.95
5.94
5.92
5.17
5.16
5.16
5.12
5.12
5.11
5.10
5.09
5.09
5.07
5.07
5.06
3.50
3.48
2.43
2.00
0.93
2.07
1.96
3.06
f1 (ppm)


7b
S
140.56
138.03
136.73
124.78
124.29
115.93
34.37
15.29
f1 (ppm)

7 References

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