

Electronic Supporting Information for

Diastereoselective Bicyclization of Enynols *via* Gold Catalysis

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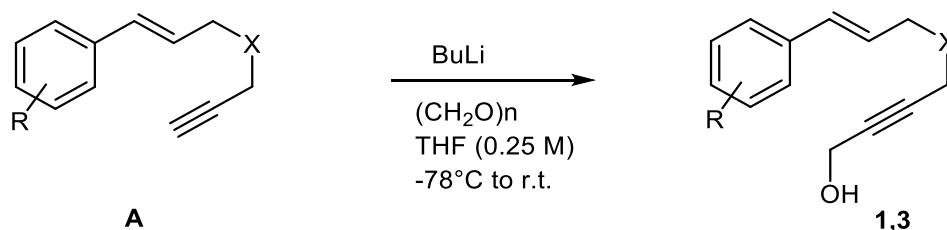
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General Remarks and Materials

All chemicals those syntheses are not reported hereafter were purchased from commercial sources and used as received. ^1H , ^{13}C , ^{31}P NMR spectra were recorded at 300 K on a Bruker 400 MHz or Bruker 300 MHz spectrometers using solvents as internal standards (7.26 ppm for ^1H NMR and 77.00 ppm for ^{13}C NMR for CDCl_3) ^{19}F -NMR spectra were recorded in CDCl_3 at 298 K on a JEOL 600 spectrometer. The terms m, s, d, t, q and quint represent multiplet, singlet, doublet, triplet, quadruplet and quintuplet respectively, and the term brs means a broad signal. LC-MS were recorded on an Agilent LQ Mass Spectrometer (ESI source). Chromatographic purifications were performed under gradient using a Combiflash® system and prepacked disposable silica cartridges. The synthesis of enynes **A** (see **GP-1**) and substituted acetates **B** (see **GP-2**) was carried out following known procedures.^[1,2] Substituted *N*-cinnamyl-4-methylbenzenesulfonamides **C** (see **GP-3**) were prepared according to a previously employed protocol.^[3] Gold complexes **B**, **C** and **E** were obtained following published procedures.^[4,5,6] CCDC 1941564-1941565 contain the crystallographic data for products **4a** and **2g**, respectively.

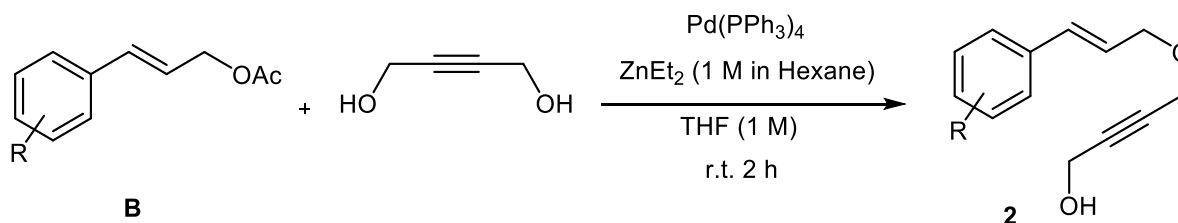
Synthesis of reagents

General Procedure for synthesis of enynols (GP-1)



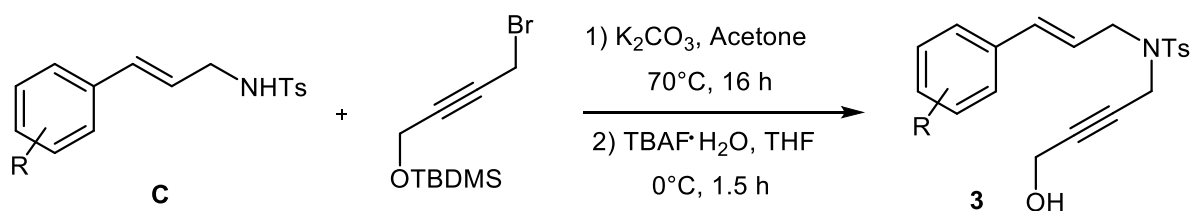
A solution of the desired enyne **A** (1 equiv.) in THF (0.25 M) was cooled to -78°C and then BuLi (1.6 M in hexane, 1.3 equiv.) was added dropwise under a N₂ atmosphere. After 1 hour, paraformaldehyde (3 equiv.) was added and the mixture was stirred overnight at room temperature. Upon complete conversion, a saturated solution of NH₄Cl (30 mL) was added and the resulting mixture was extracted with EtOAc (3 x 20 mL). The combined organic phases were dried over anhydrous Na₂SO₄, concentrated under reduced pressure and purified by column chromatography (eluent: gradient hexane/ethyl acetate).

General Procedure for synthesis of enynols (GP-2)



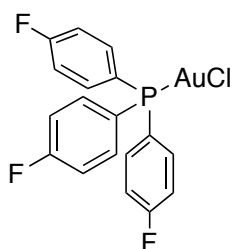
To a solution of but-2-yne-1,4-diol (5 equiv.) in THF, Et₂Zn (0.9 M in hexane, 0.5 equiv.) was added dropwise. The resulting mixture was stirred until it turned cloudily white (30 min). At this point the desired acetate **B** (1 equiv.) and Pd(PPh₃)₄ (5 mol%) were then added and the reaction was stirred overnight at room temperature. Upon complete conversion, the mixture was concentrated and carefully purified by column chromatography (eluent: gradient hexane/ethyl acetate).

General Procedure for synthesis of enynols (GP-3)



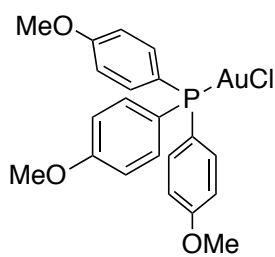
The desired cinnamyl-benzensulphonamide **C** (1 equiv.) was dissolved in acetone and then K_2CO_3 (2 equiv.) was added. After 15 minutes, ((4-bromobut-2-yn-1-yl)oxy)(tert-butyl)dimethylsilane (1.5 equiv.) was syringed and the resulting mixture was stirred overnight at $70^\circ C$. Upon complete conversion, the reaction was diluted with water and the solution was extracted with EtOAc (3 x 30 mL). The combined organic phases were dried over anhydrous Na_2SO_4 , filtered and concentrated under reduced pressure. The crude was dissolved in THF (0.4 M), cooled at $0^\circ C$ and subsequently $TBAF \cdot H_2O$ (1.3 equiv.) was added to the mixture. The reaction was stirred for 1.5 hours. Upon complete conversion, the reaction was diluted with a saturated solution of NH_4Cl and extracted with EtOAc (3 x 20 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 , concentrated under reduced pressure and purified by column chromatography (eluent: gradient hexane/ethyl acetate).

Gold catalyst B



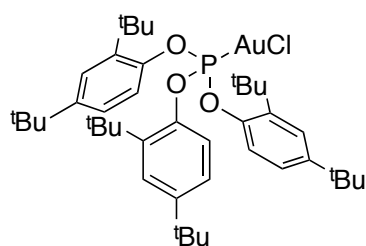
Complex **B** has been prepared following the reported procedure.^[4] Spectra correspond to the literature.^[4] ^{31}P NMR (162 MHz, CDCl_3) δ 30.8.

Gold catalyst C



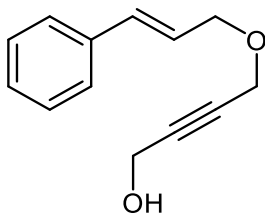
Complex **B** has been prepared following the reported procedure.^[5] Spectra correspond to the literature.^[5] ^{31}P NMR (162 MHz, CDCl_3) δ 29.3.

Gold catalyst E



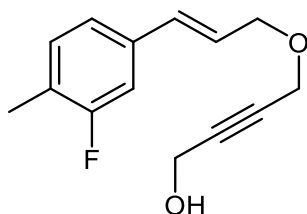
Complex **E** has been prepared following the reported procedure.^[6] Spectra correspond to the literature.^[6] ^{31}P NMR (162 MHz, CDCl_3) δ 100.8.

4-(cinnamyloxy)but-2-yn-1-ol (**1a**)



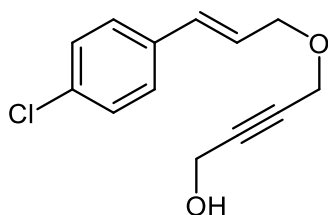
1a was isolated following the reported procedure.^[2] Spectra correspond to the literature.^[2] **¹H NMR** (300 MHz, CDCl₃) δ 7.43 – 7.27 (m, 5H), 6.66 (d, *J* = 16.0 Hz, 1H), 6.30 (dt, *J* = 15.9, 6.2 Hz, 1H), 4.35 (s, 2H), 4.26 – 4.24 (m, 4H).

(*E*)-4-[(3-(3-fluoro-4-methylphenyl)allyl)oxy]but-2-yn-1-ol (**1b**)



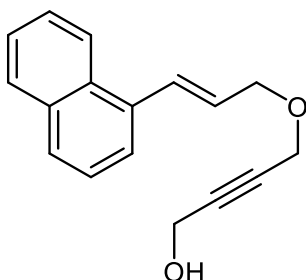
1b was isolated following procedure **GP-2** using but-2-yne-1,4-diol (925 mg, 10.8 mmol) and (*E*)-3-(3-fluoro-4-methylphenyl)allyl acetate (448 mg, 2.1 mmol). Purification by column chromatography afforded **1b** (39%, 196 mg, 0.8 mmol) as a brown oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.13 – 7.01 (m, 3H), 6.56 (d, *J* = 15.9 Hz, 1H), 6.22 (dt, *J* = 15.9, 6.1 Hz, 1H), 4.32 (s, 2H), 4.23 – 4.20 (m, 4H), 2.25 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 161.5 (d, ¹*J*_{C-F} = 244.2 Hz, C_q), 136.2 (d, ⁴*J*_{C-F} = 7.8 Hz, C_q), 132.2 (d, ⁸*J*_{C-F} = 2.2 Hz, CH), 131.5 (d, ⁵*J*_{C-F} = 5.3 Hz, CH), 125.4 (CH), 124.4 (d, ³*J*_{C-F} = 17.6 Hz, C_q), 122.1 (d, ⁷*J*_{C-F} = 3.2 Hz, CH), 112.6 (d, ²*J*_{C-F} = 22.8 Hz, CH), 84.9 (C_q), 81.6 (C_q), 70.2 (CH₂), 57.5 (CH₂), 51.1 (CH₂), 14.4 (d, ⁶*J*_{C-F} = 3.6 Hz, CH₃). **¹⁹F NMR** (565 MHz, CDCl₃) δ -117.7. **LC-MS** calcd for C₁₄H₁₅FNaO₂ [M+Na]⁺ 257.10, found 257.19.

(E)-4-[(3-(4-chlorophenyl)allyl)oxy]but-2-yn-1-ol (1c)



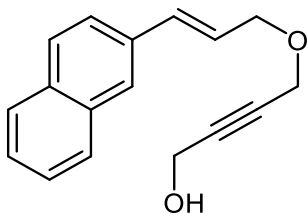
1c was isolated following procedure **GP-2** using but-2-yne-1,4-diol (851 mg, 9.9 mmol) and (*E*)-3-(4-chlorophenyl)allyl acetate (417 mg, 1.9 mmol). Purification by column chromatography afforded **1c** (54%, 255 mg, 1.1 mmol) as a pale yellow oil. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.33 – 7.26 (m, 4H), 6.59 (d, $J = 16.0$ Hz, 1H), 6.25 (dt, $J = 15.9, 6.0$ Hz, 1H), 4.33 (t, $J = 1.8$ Hz, 2H), 4.24 (t, $J = 1.8$ Hz, 2H), 4.21 (dd, $J = 6.1, 1.4$ Hz, 2H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 135.0 (C_q), 133.5 (C_q), 131.9 (CH), 128.8 (CH), 127.7 (CH), 125.8 (CH), 84.8 (C_q), 81.7 (C_q), 70.2 (CH_2), 57.5 (CH_2), 51.2 (CH_2). **LC-MS** calcd for $\text{C}_{13}\text{H}_{13}\text{ClNaO}_2$ $[\text{M}+\text{Na}]^+$ 259.05, found 259.12.

(E)-4-[(3-(naphthalen-1-yl)allyl)oxy]but-2-yn-1-ol (1d)



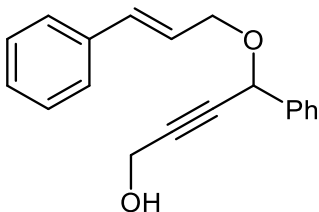
1d was isolated following procedure **GP-2** using but-2-yne-1,4-diol (1040 mg, 12.0 mmol) and (*E*)-3-(4-chlorophenyl)allyl acetate (550 mg, 2.4 mmol). Purification by column chromatography afforded **1d** (32%, 200 mg, 0.8 mmol) as a yellow oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.12 (d, $J = 7.8$ Hz, 1H), 7.86 (d, $J = 7.1$ Hz, 1H), 7.79 (d, $J = 8.2$ Hz, 1H), 7.61 (d, $J = 7.2$ Hz, 1H), 7.54 – 7.45 (m, 3H), 7.41 (d, $J = 15.8$ Hz, 1H), 6.31 (dt, $J = 15.7, 6.1$ Hz, 1H), 4.35 – 4.31 (m, 6H), 2.10 (s, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 134.3 (C_q), 133.6 (C_q), 131.1 (C_q), 130.5 (CH), 128.6 (CH), 128.3 (CH), 128.2 (CH), 126.1 (CH), 125.8 (CH), 125.6 (CH), 124.0 (CH), 123.8 (CH), 85.0 (C_q), 81.6 (C_q), 70.6 (CH_2), 57.6 (CH_2), 51.0 (CH_2). **LC-MS** calcd for $\text{C}_{17}\text{H}_{16}\text{NaO}_2$ $[\text{M}+\text{Na}]^+$ 245.10, found 245.16.

(E)-4-[(3-(naphthalen-2-yl)allyl)oxy]but-2-yn-1-ol (1e)



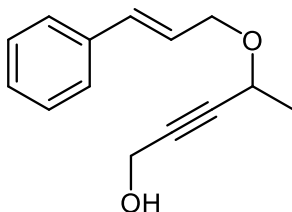
1e was isolated following procedure **GP-2** using but-2-yne-1,4-diol (732 mg, 8.5 mmol) and (*E*)-3-(naphthalen-2-yl)allyl acetate (385 mg, 1.7 mmol). Purification by column chromatography afforded **1e** (43%, 184 mg, 0.7 mmol) as a pale yellow wax. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.82 – 7.74 (m, 4H), 7.61 (dd, J = 8.6, 1.7 Hz, 1H), 7.49 – 7.42 (m, 2H), 6.81 (d, J = 16.0 Hz, 1H), 6.41 (dt, J = 15.8, 6.2 Hz, 1H), 4.36 – 4.27 (m, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 134.0 (C_q), 133.6 (C_q), 133.5 (CH), 133.1 (C_q), 128.3 (CH), 128.0 (CH), 127.7 (CH), 126.7 (CH), 126.3 (CH), 126.0 (CH), 125.5 (CH), 123.5 (CH), 84.8 (C_q), 81.8 (C_q), 70.5 (CH_2), 57.5 (CH_2), 51.2 (CH_2). **LC-MS** calcd for $\text{C}_{17}\text{H}_{16}\text{NaO}_2$ $[\text{M}+\text{Na}]^+$ 275.10, found 275.19.

4-(cinnamyloxy)-4-phenylbut-2-yn-1-ol (1f)



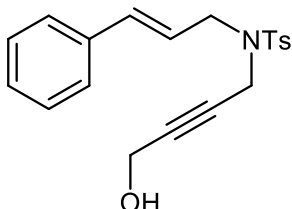
1f was isolated following procedure **GP-1** using (*E*)-(1-(cinnamyloxy)prop-2-yn-1-yl)benzene (500 mg, 2.0 mmol) and paraformaldehyde (181 mg, 6.0 mmol). Purification by column chromatography afforded **1f** (40 %, 224 mg, 0.8 mmol) as a pale yellow oil. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.57 – 7.54 (m, 2H), 7.45 – 7.28 (m, 8H), 6.68 (d, J = 16.0 Hz, 1H), 6.35 (dt, J = 15.9, 6.2 Hz, 1H), 5.32 (s, 1H), 4.38 (s, 2H), 4.35 – 4.29 (m, 2H), 1.96 (s, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 138.4 (C_q), 136.6 (C_q), 133.4 (CH), 128.7 (CH), 128.6 (CH), 128.6 (CH), 127.9 (CH), 127.5 (CH), 126.6 (CH), 125.4 (CH), 86.1 (C_q), 83.5 (C_q), 70.7 (CH_2), 69.0 (CH), 51.0 (CH_2). **LC-MS** calcd for $\text{C}_{14}\text{H}_{16}\text{NaO}_2$ $[\text{M}+\text{Na}]^+$ 301.12 found 301.16.

4-(cinnamyloxy)pent-2-yn-1-ol (**1g**)



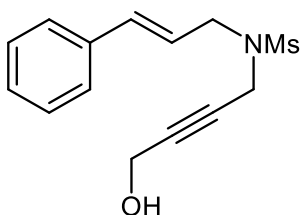
1g was isolated following procedure **GP-1** using (*E*)-(3-(but-3-yn-2-yloxy)prop-1-en-1-yl)benzene (432 mg, 2.3 mmol) and paraformaldehyde (209 mg, 7.0 mmol). Purification by column chromatography afforded **1g** (36%, 183 mg, 0.8 mmol) as a pale yellow oil. $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.43 – 7.26 (m, 5H), 6.66 (d, $J = 15.9$ Hz, 1H), 6.43 (dt, $J = 15.9, 6.0$ Hz, 1H), 4.42 (ddd, $J = 12.4, 5.7, 1.5$ Hz, 1H), 4.35 – 4.31 (m, 3H), 4.16 (ddd, $J = 12.4, 6.7, 1.3$ Hz, 1H), 1.87 (s, 1H), 1.50 (d, $J = 6.6$ Hz, 3H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 136.6 (C_q), 133.0 (CH), 128.6 (CH), 127.8 (CH), 126.5 (CH), 125.5 (CH), 85.6 (C_q), 83.3 (C_q), 69.3 (CH_2), 64.5 (CH), 51.1 (CH_2), 22.1 (CH_3). **LC-MS** calcd for $\text{C}_{14}\text{H}_{16}\text{NaO}_2$ $[\text{M}+\text{Na}]^+$ 239,11, found 239.15.

N-cinnamyl-*N*-(4-hydroxybut-2-yn-1-yl)-4-methylbenzenesulfonamide (**3a**)



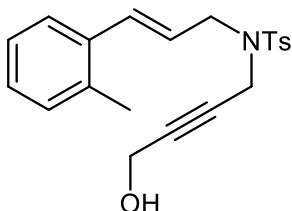
3a was isolated following procedure **GP-1** using *N*-cinnamyl-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (2.83 g, 8.7 mmol) and paraformaldehyde (784 mg, 26.1 mmol). Purification by column chromatography afforded **3a** (60 %, 1.86 g, 8.7 mmol) as a white solid. **M. p.** = (75 – 78) °C $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.77 (d, $J = 8.2$ Hz, 2H), 7.33 – 7.24 (m, 7H), 6.56 (d, $J = 15.8$ Hz, 1H), 6.08 (dt, $J = 15.7, 6.8$ Hz, 1H), 4.13 (s, 2H), 4.00 – 3.98 (m, 4H), 2.44 (s, 3H), 1.43 (brs, 1H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 143.7 (C_q), 136.2 (C_q), 136.1 (C_q), 134.8 (CH), 129.5 (CH), 128.7 (CH), 128.1 (CH), 128.0 (CH), 126.5 (CH), 123.0 (CH), 83.9 (C_q), 78.7 (C_q), 50.8 (CH_2), 48.9 (CH_2), 36.2 (CH_2), 21.5 (CH_3). **LC-MS** calcd for $\text{C}_{20}\text{H}_{21}\text{NNaO}_3\text{S}$ $[\text{M}+\text{Na}]^+$ 378.11, found 378.13.

***N*-cinnamyl-*N*-(4-hydroxybut-2-yn-1-yl)methanesulfonamide (3b)**



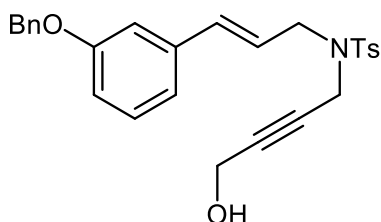
3b was isolated following procedure **GP-1** using *N*-cinnamyl-*N*-(prop-2-yn-1-yl)methanesulfonamide (500 mg, 2.0 mmol) and paraformaldehyde (180 mg, 6.0 mmol). Purification by column chromatography afforded **3b** (40 %, 224 mg, 0.8 mmol) as a white solid. **M. p.** = (91 – 95) °C. **¹H NMR** (300 MHz, CDCl₃) δ 7.41 – 7.26 (m, 5H), 6.65 (d, *J* = 15.8 Hz, 1H), 6.17 (dt, *J* = 15.8, 6.8 Hz, 1H), 4.32 (t, *J* = 1.7 Hz, 2H), 4.14 (t, *J* = 1.8 Hz, 2H), 4.05 (d, *J* = 6.8 Hz, 2H), 2.99 (s, 3H). **¹³C NMR** (75 MHz, CDCl₃) δ 136.0 (C_q), 135.0 (CH), 128.7 (CH), 128.2 (CH), 126.6 (CH), 122.9 (CH), 84.4 (C_q), 79.3 (C_q), 51.0 (CH₂), 48.9 (CH₂), 38.7 (CH₃), 36.1 (CH₂). **LC-MS** calcd for C₁₄H₁₇NNaO₃S [M+Na]⁺ 302.08, found 302.15.

***(E)*-*N*-(4-hydroxybut-2-yn-1-yl)-4-methyl-*N*-(3-(*o*-tolyl)allyl)benzenesulfonamide (3c)**



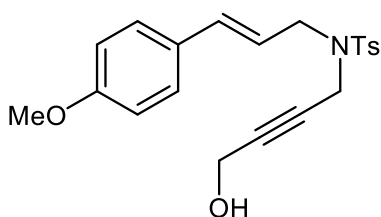
3c was isolated following procedure **GP-1** using *(E)*-4-methyl-*N*-(prop-2-yn-1-yl)-*N*-(3-(*o*-tolyl)allyl)benzenesulfonamide (399 mg, 1.2 mmol) and paraformaldehyde (106 mg, 3.5 mmol). Purification by column chromatography afforded **3c** (42%, 189 mg, 0.5 mmol) as a yellow solid. **M. p.** = (76 – 79) °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.37 – 7.32 (m, 3H), 7.18 – 7.12 (m, 3H), 6.79 (d, *J* = 15.7 Hz, 1H), 5.95 (dt, *J* = 15.6, 6.8 Hz, 1H), 4.15 (t, *J* = 1.9 Hz, 2H), 4.02 – 4.00 (m, 4H), 2.44 (s, 3H), 2.31 (s, 3H), 1.40 (brs, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 143.7 (C_q), 136.1 (C_q), 135.5 (C_q), 135.2 (C_q), 133.0 (CH), 130.4 (CH), 129.5 (CH), 128.0 (2CH), 126.2 (CH), 125.8 (CH), 124.2 (CH), 83.9 (C_q), 78.7 (C_q), 50.8 (CH₂), 49.1 (CH₂), 36.2 (CH₂), 21.5 (CH₃), 19.8 (CH₃). **LC-MS** calcd for C₂₁H₂₃NNaO₃S [M+Na]⁺ 392.13, found 392.20

(E)-N-[3-(3-(benzyloxy)phenyl)allyl]-N-(4-hydroxybut-2-yn-1-yl)-4-methylbenzenesulfonamide (3d)



3d was isolated following procedure **GP-3** using (*E*)-*N*-(3-(3-(benzyloxy)phenyl)allyl)-4-methylbenzenesulfonamide (879 mg, 2.2 mmol) and ((4-bromobut-2-yn-1-yl)oxy)(tert-butyl)dimethylsilane (880 mg, 3.3 mmol). Purification by column chromatography afforded **3d** (20%, 201 mg, 0.4 mmol) as a white solid. **M. p.** = (82 – 85) °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.45 – 7.35 (m, 5H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.23 (t, *J* = 7.9 Hz, 1H), 6.96– 6.87 (m, 3H), 6.53 (d, *J* = 15.8 Hz, 1H), 6.07 (dt, *J* = 15.7, 6.8 Hz, 1H), 5.06 (s, 2H), 4.13 (s, 2H), 4.00 – 3.97 (m, 4H), 2.43 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 159.1 (C_q), 143.7 (C_q), 137.6 (C_q), 136.9 (C_q), 136.2 (C_q), 134.7 (CH), 129.7 (CH), 129.5 (CH), 128.6 (CH), 128.1 (CH), 128.0 (CH), 127.5 (CH), 123.4 (CH), 119.5 (CH), 114.6 (CH), 112.9 (CH), 83.9 (C_q), 78.7 (C_q), 70.0 (CH₂), 50.8 (CH₂), 48.8 (CH₂), 36.3 (CH₂), 21.6 (CH₃). **LC-MS** calcd for C₂₇H₂₇NNaO₄S [M+Na]⁺ 484.15 found 484.19

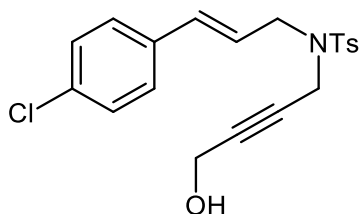
(E)-N-(4-hydroxybut-2-yn-1-yl)-N-(3-(4-methoxyphenyl)allyl)-4-methylbenzenesulfonamide (3e)



3e was isolated following procedure **GP-3** using (*E*)-*N*-(3-(4-methoxyphenyl)allyl)-4-methylbenzenesulfonamide (293 mg, 0.9 mmol) and ((4-bromobut-2-yn-1-yl)oxy)(tert-butyl)dimethylsilane (364 mg, 1.4 mmol). Purification by column chromatography afforded **3e** (33%, 120 mg, 0.3 mmol) as a white solid. **M. p.** = (83 – 87) °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.52 (d, *J* = 15.8 Hz, 1H), 5.95 (dt, *J* = 15.7, 6.9 Hz, 1H), 4.15 (s, 2H), 4.03 – 3.97 (m, 4H), 3.83 (s, 3H), 2.46 (s, 3H), 1.32 (brs, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 159.6 (C_q), 143.6 (C_q), 136.3 (C_q), 134.4 (CH), 129.4

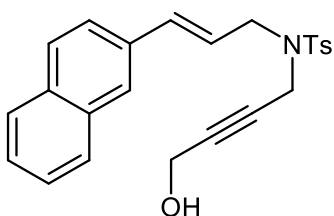
(CH), 128.9 (C_q), 128.0 (CH), 127.8 (CH), 120.6 (CH), 114.1 (CH), 83.8 (C_q), 78.8 (C_q), 55.3 (CH₃), 50.8 (CH₂), 49.0 (CH₂), 36.1 (CH₂), 21.5 (CH₃). **LC-MS** calcd for C₂₁H₂₃NNaO₄S [M+Na]⁺ 408.20, found 408.17.

(E)-N-(3-(4-chlorophenyl)allyl)-N-(4-hydroxybut-2-yn-1-yl)-4-methylbenzenesulfonamide (3f)



3f was isolated following procedure **GP-3** using (*E*)-*N*-(3-(4-chlorophenyl)allyl)-4-methylbenzenesulfonamide (413 mg, 1.3 mmol) and ((4-bromobut-2-yn-1-yl)oxy)(tert-butyl)dimethylsilane (505 mg, 1.9 mmol). Purification by column chromatography afforded **3f** (31%, 155 mg, 0.4 mmol) as a white solid. **M. p.** = (73 – 76) °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.29 – 7.24 (m, 4H), 6.52 (d, *J* = 15.8 Hz, 1H), 6.07 (dt, *J* = 15.8, 6.7 Hz, 1H), 4.13 (t, *J* = 1.7 Hz, 2H), 4.01 (t, *J* = 1.8 Hz, 2H), 3.98 (d, *J* = 5.8 Hz, 2H), 2.44 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 143.7 (C_q), 136.2 (C_q), 134.6 (C_q), 133.8 (C_q), 133.4 (CH), 129.5 (CH), 128.8 (CH), 128.0 (CH), 127.7 (CH), 123.9 (CH), 83.9 (C_q), 78.6 (C_q), 50.8 (CH₂), 48.7 (CH₂), 36.4 (CH₂), 21.5 (CH₃). **LC-MS** calcd for C₂₀H₂₀ClNNaO₃S [M+Na]⁺ 412.08, found 412.14.

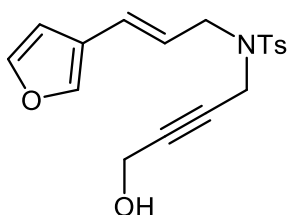
(E)-N-(4-hydroxybut-2-yn-1-yl)-4-methyl-N-(3-(naphthalen-2-yl)allyl)benzenesulfonamide (3g)



3g was isolated following procedure **GP-3** using (*E*)-4-methyl-*N*-(3-(naphthalen-2-yl)allyl)benzenesulfonamide (610 mg, 1.8 mmol) and ((4-bromobut-2-yn-1-yl)oxy)(tert-butyl)dimethylsilane (714 mg, 2.7 mmol). Purification by column chromatography afforded **3g** (18%, 175 mg, 0.3 mmol) as a yellow solid. **M. p.** = (78 – 81) °C. **¹H NMR** (300 MHz, CDCl₃) δ 7.81 – 7.77 (m, 5H), 7.69 (s, 1H), 7.55 – 7.52 (m, 1H), 7.48 – 7.44 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.73 (d, *J* =

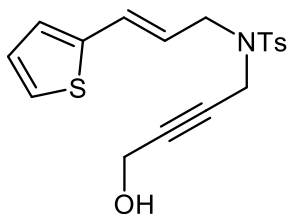
15.8 Hz, 1H), 6.21 (dt, $J = 15.8, 6.8$ Hz, 1H), 4.17 (t, $J = 1.7$ Hz, 2H), 4.05 – 4.02 (m, 4H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.7 (C_q), 136.3 (C_q), 134.9 (CH), 133.5 (C_q), 133.5 (C_q), 133.2 (C_q), 129.5 (CH), 128.4 (CH), 128.0 (CH), 128.0 (CH), 127.7 (CH), 126.8 (CH), 126.4 (CH), 126.2 (CH), 123.4 (CH), 123.4 (CH), 84.0 (C_q), 78.7 (C_q), 50.8 (CH_2), 49.0 (CH_2), 36.3 (CH_2), 21.5 (CH_3). LC-MS calcd for $\text{C}_{24}\text{H}_{23}\text{NNaO}_3\text{S}$ [$\text{M}+\text{Na}$] $^+$ 428.13, found 428.18.

(*E*)-*N*-(3-(furan-3-yl)allyl)-*N*-(4-hydroxybut-2-yn-1-yl)-4-methylbenzenesulfonamide (3h)



3h was isolated following procedure **GP-1** using (*E*)-*N*-(3-(furan-3-yl)allyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (270 mg, 0.9 mmol) and paraformaldehyde (77 mg, 2.6 mmol). Purification by column chromatography afforded **3h** (30 %, 88 mg, 0.2 mmol) as a yellow solid. **M. p.** = (85 – 89) °C. ^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, $J = 8.3$ Hz, 2H), 7.38 (d, $J = 16.2$ Hz, 2H), 7.32 (d, $J = 8.1$ Hz, 2H), 6.47 (s, 1H), 6.43 (d, $J = 15.8$ Hz, 1H), 5.80 (dt, $J = 15.6, 6.8$ Hz, 1H), 4.12 (s, 2H), 3.99 (s, 2H), 3.92 (d, $J = 6.5$ Hz, 2H), 2.43 (s, 3H), 1.29 (brs, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.7 (CH), 143.7 (C_q), 140.9 (CH), 136.2 (C_q), 129.4 (CH), 128.0 (CH), 124.6 (CH), 123.3 (C_q), 122.6 (CH), 107.5 (CH), 83.8 (C_q), 78.7 (C_q), 50.8 (CH_2), 48.7 (CH_2), 36.1 (CH_2), 21.5 (CH_3). LC-MS calcd for $\text{C}_{18}\text{H}_{19}\text{NNaO}_4\text{S}$ [$\text{M}+\text{Na}$] $^+$ 368.09, found 368.17.

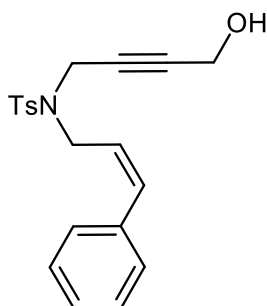
(*E*)-*N*-(4-hydroxybut-2-yn-1-yl)-4-methyl-*N*-(3-(thiophen-2-yl)allyl)benzenesulfonamide (3i)



3i was isolated following procedure **GP-1** using (*E*)-4-methyl-*N*-(prop-2-yn-1-yl)-*N*-(3-(thiophen-2-yl)allyl)benzenesulfonamide (292 mg, 0.9 mmol) and paraformaldehyde (79 mg, 2.6 mmol). Purification by column chromatography afforded **3i** (37%, 118 mg, 0.3 mmol) as a yellow solid. **M. p.** = (79 – 82) °C. ^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, $J = 8.3$ Hz, 2H), 7.32 (d, $J = 8.1$ Hz, 2H),

7.18 – 7.16 (m, 1H), 6.96 – 6.94 (m, 2H), 6.69 (d, $J = 15.6$ Hz, 1H), 5.89 (dt, $J = 15.5, 6.8$ Hz, 1H), 4.13 (s, 2H), 4.00 (t, $J = 1.8$ Hz, 2H), 3.95 (d, $J = 6.6$ Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.8 (C_q), 141.1 (C_q), 136.1 (C_q), 129.5 (CH), 128.0 (CH), 127.8 (CH), 127.5 (CH), 126.4 (CH), 124.9 (CH), 122.5 (CH), 83.9 (C_q), 78.7 (C_q), 50.8 (CH_2), 48.7 (CH_2), 36.3 (CH_2), 21.6 (CH_3). LC-MS calcd for $\text{C}_{18}\text{H}_{19}\text{NNaO}_3\text{S}_2$ $[\text{M}+\text{Na}]^+$ 384.07, found 384.11

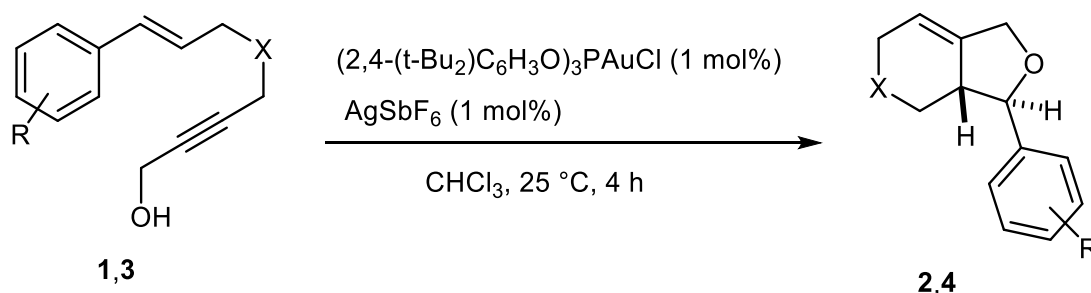
(Z)-N-(4-hydroxybut-2-yn-1-yl)-4-methyl-N-(3-phenylallyl)benzenesulfonamide (3j)



3j was isolated following procedure **GP-1** using (Z)-4-methyl-N-(3-phenylallyl)-N-(prop-2-yn-1-yl)benzenesulfonamide (498 mg, 1.53 mmol) and paraformaldehyde (137 mg, 4.59 mmol). Purification by column chromatography afforded **3j** (38%, 207 mg, 0.581 mmol) as a yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.73 (d, $J = 8.3$ Hz, 2H), 7.30 (m, 7H), 6.72 (d, $J = 11.6$ Hz, 1H), 5.64 (dt, $J = 11.6, 6.9$ Hz, 1H), 4.15 (dd, $J = 6.9, 1.5$ Hz, 2H), 4.10 (s, 2H), 3.72 (s, 2H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.7 (C_q), 136.2 (C_q), 135.9 (C_q), 134.0 (CH), 129.5 (CH), 128.9 (CH), 128.2 (CH), 127.8 (CH), 127.3 (CH), 126.1 (CH), 83.9 (C_q), 78.2 (C_q), 50.4 (CH_2), 44.1 (CH_2), 36.4 (CH_2), 21.5 (CH_3). LC-MS calcd for $\text{C}_{20}\text{H}_{21}\text{NNaO}_3\text{S}$ $[\text{M}+\text{Na}]^+$ 378.11, found 378.20.

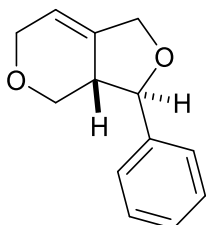
Synthesis of products

Catalytic Synthesis of 2 and 4 (GP-4)



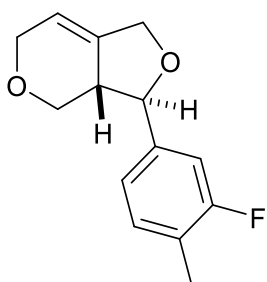
$(2,4-(t\text{-Bu}_2)\text{C}_6\text{H}_3\text{O})_3\text{PAuCl}$ (1.8 and 1.2 mg for reagents **1** and **3**, respectively, 1 mol%) was dissolved in 1.0 mL of freshly degassed CHCl_3 under N_2 in a 10 mL two-necked round bottom flask. The substrate (0.2 mmol and 0.14 mmol for reagents **1** and **3**, respectively, 1 equiv.) and AgSbF_6 (a tip of a spatula) were then added and the mixture was stirred at room temperature. The reaction was monitored by TLC. Upon complete conversion, the solution was diluted with DCM (5 mL) and purified by column chromatography (eluent: gradient hexane/ethyl acetate).

3-phenyl-3,3a,4,6-tetrahydro-1H-furo[3,4-c]pyran (**2a**)



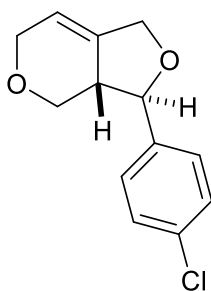
The procedure **GP-4** was followed using **1a** (40.4 mg, 0.20 mmol). Purification by column chromatography (eluent: gradient hexane/ethyl acetate.) yielded **2a** as a pale yellow oil (56%, 22.2 mg, 0.11 mmol, *d.r.* > 25:1). $R_f = 0.45$ (eluent: Hexane/ethyl acetate = 8:2). $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.40 – 7.33 (m, 5H), 5.65 (s, 1H), 4.73 (d, $J = 12.4$ Hz, 1H), 4.48 (d, $J = 12.5$ Hz, 1H), 4.35 (d, $J = 9.9$ Hz, 1H), 4.29 – 4.22 (m, 1H), 4.16 – 4.11 (m, 2H), 3.34 (t, $J = 10.1$ Hz, 1H), 2.79 (brs, 1H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 140.4 (C_q), 138.8 (C_q), 128.6 (CH), 128.1 (CH), 126.0 (CH), 116.2 (CH), 83.4 (CH), 69.7 (CH_2), 65.9 (CH_2), 64.3 (CH_2), 46.5 (CH). **LC-MS** calcd for $\text{C}_{13}\text{H}_{14}\text{NaO}_2$ $[\text{M}+\text{Na}]^+$ 225.09, found 225.12.

3-(3-fluoro-4-methylphenyl)-3,3a,4,6-tetrahydro-1H-furo[3,4-c]pyran (2b)



The procedure **GP-4** was followed using **1b** (46.8 mg, 0.20 mmol). Purification by column chromatography (eluent: gradient hexane/ethyl acetate.) yielded **2b** as a pale yellow oil (33%, 16.4 mg, 0.07 mmol, *d.r.* > 25:1). $R_f = 0.41$ (eluent: Hexane/ethyl acetate = 8:2). $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.19 – 7.13 (m, 1H), 7.05 – 6.97 (m, 2H), 5.63 (s, 1H), 4.68 (d, $J = 12.3$ Hz, 1H), 4.44 (d, $J = 12.6$ Hz, 1H), 4.27 (d, $J = 9.8$ Hz, 1H), 7.21 – 7.07 (m, 3H), 3.30 (t, $J = 10.1$ Hz, 1H), 2.70 (brs, 1H), 2.27 (s, 3H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 161.4 (d, $^1J_{\text{C-F}} = 245.0$ Hz, C_q), 140.3 (d, $^4J_{\text{C-F}} = 7.2$ Hz, C_q), 138.5 (C_q), 131.6 (d, $^5J_{\text{C-F}} = 5.4$ Hz, CH), 124.5 (d, $^3J_{\text{C-F}} = 17.3$ Hz, C_q), 121.2 (d, $^7J_{\text{C-F}} = 3.3$ Hz, CH), 116.4 (CH), 112.5 (d, $^2J_{\text{C-F}} = 23.1$ Hz, CH), 82.6 (d, $^8J_{\text{C-F}} = 1.6$ Hz, CH), 69.7 (CH_2), 65.8 (CH_2), 64.3 (CH_2), 46.6 (CH), 14.4 (d, $^6J_{\text{C-F}} = 3.5$ Hz, CH_3). $^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -117.0. **LC-MS** calcd for $\text{C}_{14}\text{H}_{15}\text{FNaO}_2$ $[\text{M}+\text{Na}]^+$ 257.10 found 257.12.

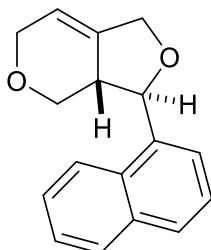
3-(4-chlorophenyl)-3,3a,4,6-tetrahydro-1H-furo[3,4-c]pyran (2c)



The procedure **GP-4** was followed using **1c** (47.3 mg, 0.20 mmol). Purification by column chromatography (eluent: gradient hexane/ethyl acetate.) yielded **2c** as a colourless oil (51%, 23.7 mg, 0.10 mmol, *d.r.* > 25:1). $R_f = 0.30$ (eluent: Hexane/ethyl acetate = 8:2). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.34 (d, $J = 8.6$ Hz, 2H), 7.28 (d, $J = 8.5$ Hz, 2H), 5.64 (s, 1H), 4.69 (d, $J = 12.6$ Hz, 1H), 4.45 (d, $J = 12.6$ Hz, 1H), 4.29 (d, $J = 9.9$ Hz, 1H), 4.25 – 4.20 (m, 1H), 4.146 – 4.06 (m, 2H), 3.30 (t, $J = 10.2$ Hz, 1H), 2.69 (brs, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 139.0 (C_q), 138.4 (C_q), 133.7 (C_q), 128.8

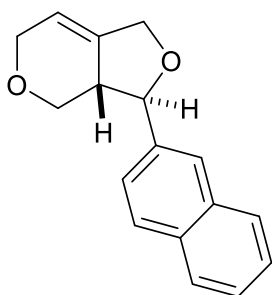
(CH), 127.3 (CH), 116.5 (CH), 82.7 (CH), 69.8 (CH₂), 65.7 (CH₂), 64.3 (CH₂), 46.7 (CH). **LC-MS** calcd for C₁₃H₁₃ClNaO₂ [M+Na]⁺ 259,05 found 259.09.

3-(naphthalen-1-yl)-5-tosyl-1,3,3a,4,5,6-hexahydrofuro[3,4-c]pyridine (**2d**)



The procedure **GP-4** was followed using **1d** (50.4 mg, 0.20 mmol). Purification by column chromatography (eluent: gradient hexane/ethyl acetate.) yielded **2d** as a white solid (40 %, 20.2 mg, 0.08 mmol, *d.r.* > 25:1). **M. p.** = (98 – 100) °C. **R_f** = 0.35 (eluent: Hexane/ethyl acetate = 8:2). **¹H NMR** (300 MHz, CDCl₃) δ 8.09 – 8.05 (m, 1H), 7.90 – 7.87 (m, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.69 (d, *J* = 7.1 Hz, 1H), 7.55 – 7.47 (m, 3H), 5.70 (bs, 1H), 5.08 (d, *J* = 10.0 Hz, 1H), 4.83 – 4.78 (m, 1H), 4.61 – 4.56 (m, 1H), 4.31 – 4.09 (m, 3H), 3.42 (t, *J* = 10.2 Hz, 1H), 3.12 (brs, 1H). **¹³C NMR** (75 MHz, CDCl₃) δ 139.0 (C_q), 135.3 (C_q), 133.9 (C_q), 131.3 (C_q), 128.9 (CH), 128.8 (CH), 126.2 (CH), 125.7 (CH), 125.5 (CH), 123.6 (CH), 123.3 (CH), 116.3 (CH), 80.6 (CH), 69.6 (CH₂), 66.5 (CH₂), 64.5 (CH₂), 45.4 (CH). **LC-MS** calcd for C₁₇H₁₆NaO₂ [M+Na]⁺ 275.10, found 275.14.

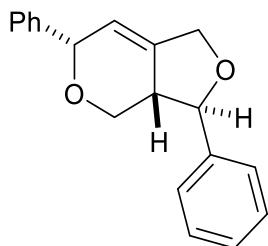
3-(naphthalen-2-yl)-3,3a,4,6-tetrahydro-1H-furo[3,4-c]pyran (**2e**)



The procedure **GP-4** was followed using **1e** (50.4 mg, 0.20 mmol). Purification by column chromatography (eluent: gradient hexane/ethyl acetate.) yielded **2e** as a white solid (64%, 32.8 mg, 0.13 mmol, *d.r.* > 25:1). **M. p.** = (82 – 85) °C. **R_f** = 0.30 (eluent: Hexane/ethyl acetate = 8:2). **¹H NMR** (400 MHz, CDCl₃) δ 7.88 – 7.81 (m, 4H), 7.51 – 7.46 (m, 3H), 5.66 (s, 1H), 4.77 (d, *J* = 12.5

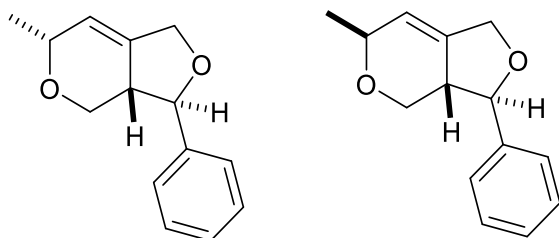
Hz, 1H), 4.55 – 4.49 (m, 2H), 4.28 – 4.13 (m, 3H), 3.38 (t, $J = 10.1$ Hz, 1H), 2.86 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 138.8 (C_q), 137.9 (C_q), 133.3 (C_q), 133.3 (C_q), 128.5 (CH), 128.0 (CH), 127.7 (CH), 126.2 (CH), 126.0 (CH), 125.0 (CH), 123.8 (CH), 116.3 (CH), 83.6 (CH), 69.9 (CH_2), 66.0 (CH_2), 64.4 (CH_2), 46.6 (CH). LC-MS calcd for $\text{C}_{17}\text{H}_{16}\text{NaO}_2$ $[\text{M}+\text{Na}]^+$ 275.10, found 275.12.

3,6-diphenyl-3,3a,4,6-tetrahydro-1H-furo[3,4-c]pyran (2f)



The procedure **GP-4** was followed using **1f** (55.6 mg, 0.20 mmol). Purification by column chromatography (eluent: gradient hexane/ethyl acetate.) yielded **2f** as a yellow oil (55 %, 30.6 mg, 0.11 mmol, *d.r.* > 25:1). $R_f = 0.55$ (eluent: Hexane/ethyl acetate = 8:2). ^1H NMR (300 MHz, CDCl_3) δ 7.40 – 7.30 (m, 10H), 5.68 (s, 1H), 5.13 (s, 1H), 4.77 (d, $J = 12.8$ Hz, 1H), 4.52 (d, $J = 12.7$ Hz, 1H), 4.41 (d, $J = 9.8$ Hz, 1H), 4.27 (dd, $J = 10.5, 5.6$ Hz, 1H), 3.62 (t, $J = 10.2$ Hz, 1H), 2.95 (brs, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ 140.8 (C_q), 140.2 (C_q), 139.4 (C_q), 128.7 (CH), 128.6 (CH), 128.2 (CH), 128.1 (CH), 127.2 (CH), 126.0 (CH), 119.8 (CH), 83.4 (CH), 76.3 (CH), 69.7 (CH_2), 67.0 (CH_2), 46.6 (CH). LC-MS calcd for $\text{C}_{19}\text{H}_{18}\text{NaO}_2$ $[\text{M}+\text{Na}]^+$ 301.12, found 301.16.

6-methyl-3-phenyl-3,3a,4,6-tetrahydro-1H-furo[3,4-c]pyran (2g)

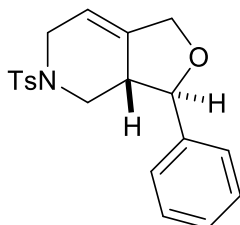


da + db

The procedure **GP-4** was followed using **1g** (43.3 mg, 0.20 mmol). Purification by column chromatography (eluent: gradient hexane/ethyl acetate) yielded **2g** as a pale yellow oil (31%, 13.0 mg, 0.06 mmol, *d.r.* \approx 2:1). $R_f = 0.6$ (eluent: Hexane/ethyl acetate = 8:2). ^1H NMR (400 MHz, CDCl_3) δ 7.40 – 7.33 (m, 10H, *da + db*) 5.62 – 5.60 (m, 1H, *da*), 5.57 – 5.56 (m, 1H, *db*), 4.75 – 4.71 (m, 1H,

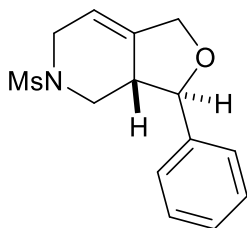
da), 4.70 – 4.68 (m, 1H, *db*), 4.50 – 4.47 (m, 1H, *da*), 4.46 – 4.44 (m, 1H, *db*), 4.41 – 4.38 (m, 1H, *da*), 4.35 (d, $J = 9.9$ Hz, 1H, *da*), 4.34 (d, $J = 9.9$ Hz, 1H, *db*), 4.25 – 2.20 (m, 1H, *db*), 4.13 (dd, $J = 10.5, 5.7$ Hz, 1H, *da*), 3.91 (dd, $J = 10.7, 5.9$ Hz, 1H, *db*), 3.50 – 3.47 (m, 1H, *da*), 3.45 – 3.40 (m, 1H, *db*), 2.83 – 2.76 (m, 1H, *da*), 2.72 – 2.71 (m, 1H, *db*), 1.33 – 1.29 (m, 3H, *db*), 1.31 – 1.27 (m, 3H, *da*). ^{13}C NMR (101 MHz, CDCl_3) δ 140.5 (C_q , *da*), 140.4 (C_q , *db*), 139.3 (C_q , *da*), 138.9 (C_q , *db*), 128.6 (CH, *da*), 128.6 (CH, *db*), 128.1 (CH, *da,db*), 126.0 (CH, *da*), 126.0 (CH, *db*), 121.3 (CH, *da*), 121.0 (CH, *db*), 83.5 (CH, *da*), 83.3 (CH, *db*), 69.9 (CH, *da*), 69.7 (CH, *db*), 69.5 (CH_2 , *da*), 67.6 (CH_2 , *db*), 66.5 (*da*), 60.4 (*db*), 46.5 (CH, *da*), 46.5 (CH, *db*), 21.3 (CH_3 , *da*), 20.0 (CH_3 , *db*). LC-MS calcd for $\text{C}_{14}\text{H}_{16}\text{NaO}_2$ $[\text{M}+\text{Na}]^+$ 239.10 found 239.16.

3-phenyl-5-tosyl-1,3,3a,4,5,6-hexahydrofuro[3,4-c]pyridine (4a)



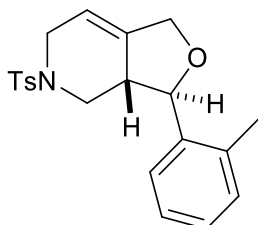
The procedure **GP-4** was followed using **3a** (49.8 mg, 0.14 mmol). Purification by column chromatography (eluent: gradient hexane/ethyl acetate) yielded **4a** as a wax (71%, 35.5 mg, 0.09 mmol, *d.r.* > 25:1). $R_f = 0.31$ (eluent: Hexane/ethyl acetate = 7:3). ^1H NMR (300 MHz, CDCl_3) δ 7.65 (d, $J = 8.2$ Hz, 2H), 7.38–7.31 (m, 7H), 5.53 (s, 1H), 4.66 (d, $J = 12.8$ Hz, 1H), 4.37 (d, $J = 12.8$ Hz, 1H), 4.22 (d, $J = 9.8$ Hz, 1H), 4.11 (d, $J = 16.6$ Hz, 1H), 4.02 (dd, $J = 11.1, 5.7$ Hz, 1H), 3.24 (d, $J = 16.8$ Hz, 1H), 2.79 (brs, 1H), 2.43 (s, 3H), 2.27 (t, $J = 10.6$ Hz, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ 143.7 (C_q), 130.0 (C_q), 139.4 (C_q), 133.5 (C_q), 129.8 (CH), 128.7 (CH), 128.5 (CH), 127.5 (CH), 126.2 (CH), 113.0 (CH), 84.1 (CH), 69.5 (CH_2), 47.3 (CH), 44.5 (CH_2), 44.3 (CH_2), 21.6 (CH_3). LC-MS calcd for $\text{C}_{20}\text{H}_{21}\text{NNaO}_3\text{S}$ $[\text{M}+\text{Na}]^+$ 378.11, found 378.17.

5-(methylsulfonyl)-3-phenyl-1,3,3a,4,5,6-hexahydrofuro[3,4-c]pyridine (**4b**)



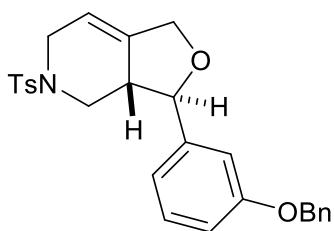
The procedure **GP-4** was followed using **3b** (55.9 mg, 0.20 mmol). Purification by column chromatography (eluent: gradient hexane/ethyl acetate) yielded **4b** as a white solid (45 %, 25.1 mg, 0.09 mmol, *d.r.* > 25:1). **M. p.** = (116 – 119)°C. **R_f** = 0.27 (eluent: Hexane/ethyl acetate = 7:3). **¹H NMR** (400 MHz, CDCl₃) δ 7.40 – 7.30 (m, 5H), 5.62 (s, 1H), 4.72 (d, *J* = 12.9 Hz, 1H), 4.46 (d, *J* = 12.9 Hz, 1H), 4.31 (d, *J* = 9.7 Hz, 1H), 4.11 (d, *J* = 17.0 Hz, 1H), 3.98 (dd, *J* = 11.5, 5.6 Hz, 1H), 3.60 (d, *J* = 17.1 Hz, 1H), 2.80 – 2.74 (m, 4H), 2.64 (t, *J* = 10.0 Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 140.3 (C_q), 139.4 (C_q), 128.8 (CH), 128.4 (CH), 126.0 (CH), 113.2 (CH), 84.1 (CH), 69.6 (CH₂), 47.5 (CH), 44.3 (CH₂), 44.1 (CH₂), 36.0 (CH₃). **LC-MS** calcd for C₁₄H₁₇NNaO₃S [M+Na]⁺ 302.08, found 302.21.

3-(*o*-tolyl)-5-tosyl-1,3,3a,4,5,6-hexahydrofuro[3,4-c]pyridine (**4c**)



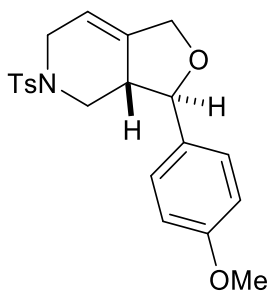
The procedure **GP-4** was followed using **3c** (51.7 mg, 0.14 mmol). Purification by column chromatography (eluent: gradient hexane/ethyl acetate) yielded **4c** as a white solid (87%, 44.3 mg, 0.12 mmol, *d.r.* > 25:1). **M. p.** = (120 – 124) °C. **R_f** = 0.33 (eluent: Hexane/ethyl acetate = 7:3). **¹H NMR** (400 MHz, CDCl₃) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.46 – 7.44 (m, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.30 – 7.18 (m, 3H), 5.55 (s, 1H), 4.67 (d, *J* = 13.0 Hz, 1H), 4.49 (d, *J* = 10.0 Hz, 1H), 4.39 (d, *J* = 12.9 Hz, 1H), 4.15 (d, *J* = 16.7 Hz, 1H), 4.04 (dd, *J* = 11.1, 5.6 Hz, 1H), 3.27 (d, *J* = 16.8 Hz, 1H), 2.94 (brs, 1H), 2.46 (s, 3H), 2.33 (s, 3H), 2.29 (t, *J* = 10.7 Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 143.7 (C_q), 140.2 (C_q), 136.8 (C_q), 135.9 (C_q), 133.6 (C_q), 130.7 (CH), 129.8 (CH), 128.2 (CH), 127.5 (CH), 126.5 (CH), 126.1 (CH), 112.9 (CH), 80.8 (CH), 69.3 (CH₂), 46.5 (CH), 44.7 (CH₂), 44.3 (CH₂), 21.5 (CH₃), 19.3 (CH₃). **LC-MS** calcd for C₂₁H₂₃NNaO₃S [M+Na]⁺ 392.13, found 392.18.

3-(3-(benzyloxy)phenyl)-5-tosyl-1,3,3a,4,5,6-hexahydrofuro[3,4-c]pyridine (4d)



The procedure **GP-4** was followed using **3d** (64.6 mg, 0.14 mmol). Purification by column chromatography (eluent: gradient hexane/ethyl acetate) yielded **4d** as a white solid (64%, 41.5 mg, 0.09 mmol, *d.r.* > 25:1). **M. p.** = (134 – 137) °C. **R_f** = 0.38 (eluent: Hexane/ethyl acetate = 7:3). **¹H NMR** (400 MHz, CDCl₃) δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.48 – 7.28 (m, 8H), 6.99 – 6.91 (m, 3H), 5.52 (s, 1H), 5.09 (s, 2H), 4.66 (d, *J* = 12.8 Hz, 1H), 4.37 (d, *J* = 12.8 Hz, 1H), 4.19 (d, *J* = 9.8 Hz, 1H), 4.11 (d, *J* = 16.8 Hz, 1H), 4.03 (dd, *J* = 11.1, 5.7 Hz, 1H), 3.23 (d, *J* = 16.7 Hz, 1H), 2.78 (brs, 1H), 2.43 (s, 3H), 2.26 (t, *J* = 10.6 Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 159.2 (C_q), 143.8 (C_q), 141.2 (C_q), 139.9 (C_q), 136.9 (C_q), 133.5 (C_q), 129.8 (CH), 129.8 (CH), 128.7 (CH), 128.1 (CH), 127.7 (CH), 127.5 (CH), 118.7 (CH), 114.5 (CH), 113.0 (CH), 112.8 (CH), 83.9 (CH), 70.1 (CH₂), 69.6 (CH₂), 47.4 (CH), 44.6 (CH₂), 44.3 (CH₂), 21.6 (CH₃). **LC-MS** calcd for C₂₇H₂₇NNaO₄S [M+Na]⁺ 484.16, found 484.19.

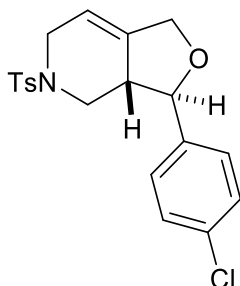
3-(4-methoxyphenyl)-5-tosyl-1,3,3a,4,5,6-hexahydrofuro[3,4-c]pyridine (4e)



The procedure **GP-4** was followed using **3e** (53.9 mg, 0.14 mmol). Purification by column chromatography (eluent: gradient hexane/ethyl acetate) yielded **4e** as a white solid (92%, 50.1 mg, 0.13 mmol, *d.r.* > 25:1). **M. p.** = (126 – 128) °C. **R_f** = 0.27 (eluent: Hexane/ethyl acetate = 7:3). **¹H NMR** (400 MHz, CDCl₃) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 5.51 (s, 1H), 4.63 (d, *J* = 12.8 Hz, 1H), 4.34 (d, *J* = 12.9 Hz, 1H), 4.15 (d, *J* = 10.0 Hz, 1H), 4.12 – 4.08 (m, 1H), 3.99 (dd, *J* = 11.1, 5.7 Hz, 1H), 3.83 (s, 3H), 3.24 (d, *J* = 16.7 Hz, 1H), 2.78 (brs, 1H), 2.43 (s, 3H), 2.24 (t, (*J* = 10.0 Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃)

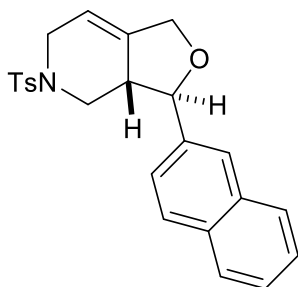
δ 159.8 (C_q), 143.7 (C_q), 140.1 (C_q), 133.6 (C_q), 131.2 (C_q), 129.8 (CH), 127.6 (CH), 127.5 (CH), 114.1 (CH), 112.9 (CH), 83.8 (CH), 69.4 (CH₂), 55.4 (CH₃), 47.0 (CH), 44.5 (CH₂), 44.3 (CH₂), 21.5 (CH₃). **LC-MS** calcd for C₂₁H₂₃NNaO₄S [M+Na]⁺ 408.12, found 408.17.

3-(4-chlorophenyl)-5-tosyl-1,3,3a,4,5,6-hexahydrofuro[3,4-c]pyridine (**4f**)



The procedure **GP-4** was followed using **3f** (54.6 mg, 0.14 mmol). Purification by column chromatography (eluent: gradient hexane/ethyl acetate) yielded **4f** as a white solid (71%, 39.0 mg, 0.01 mmol, *d.r.* > 25:1). **M. p.** = (140 – 144) °C. **R_f** = 0.28 (eluent: Hexane/ethyl acetate = 7:3). **¹H NMR** (400 MHz, CDCl₃) δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 5.56 (s, 1H), 4.69 – 4.64 (m, 1H), 4.41 – 4.37 (m, 1H), 4.21 (d, *J* = 9.8 Hz, 1H), 4.16 – 4.11 (m, 1H), 4.02 (dd, *J* = 11.1, 5.7 Hz, 1H), 3.30 – 3.24 (m, 1H), 2.74 (brs, 1H), 2.46 (s, 3H), 2.32 – 2.27 (m, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 143.8 (C_q), 139.6 (C_q), 138.1 (C_q), 134.1 (C_q), 133.6 (C_q), 129.8 (CH), 128.92 (CH), 127.5 (2CH), 113.3 (CH), 83.3 (CH), 69.6 (CH₂), 47.5 (CH), 44.4 (CH₂), 44.3 (CH₂), 21.6 (CH₃). **LC-MS** calcd for C₂₀H₂₀ClNNa₂O₃S [M+Na]⁺ 412.08, found 412.13.

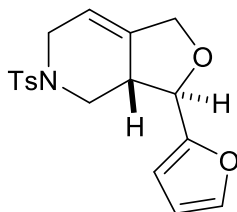
3-(naphthalen-2-yl)-5-tosyl-1,3,3a,4,5,6-hexahydrofuro[3,4-c]pyridine (**4g**)



The procedure **GP-4** was followed using **3g** (56.8 mg, 0.14 mmol). Purification by column chromatography (eluent: gradient hexane/ethyl acetate) yielded **4g** as a white solid (63%, 36.5 mg,

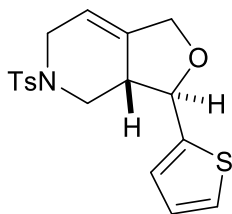
0.09 mmol, *d.r.* > 25:1). **M.p.** = (177 – 180) °C. **R_f** = 0.27 (eluent: Hexane/ethyl acetate = 7:3). **¹H NMR** (400 MHz, CDCl₃) δ 7.90 – 7.84 (m, 3H), 7.78 (s, 1H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.52 – 7.55 (m, 3H), 7.32 (d, *J* = 8.3 Hz, 2H), 5.57 (s, 1H), 4.72 (d, *J* = 12.9 Hz, 1H), 4.45 – 4.41 (m, 1H), 4.39 (d, *J* = 9.8 Hz, 1H), 4.17 – 4.11 (m, 1H), 4.04 (dd, *J* = 11.2, 5.7 Hz, 1H), 3.32 – 3.26 (m, 1H), 2.88 (s, 1H), 2.43 (s, 3H), 2.35 (t, *J* = 10.0 Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 143.7 (C_q), 140.0 (C_q), 136.8 (C_q), 133.7 (C_q), 133.5 (C_q), 133.3 (C_q), 129.8 (CH), 128.7 (CH), 128.0 (CH), 127.8 (CH), 127.5 (CH), 126.3 (CH), 126.2 (CH), 125.4 (CH), 123.8 (CH), 113.1 (CH), 84.3 (CH), 69.7 (CH₂), 47.3 (CH), 44.6 (CH₂), 44.3 (CH₂), 21.6 (CH₃). **LC-MS** calcd for C₂₄H₂₃NNaO₃S [M+Na]⁺ 428.13, found 428.16.

3-(furan-2-yl)-5-tosyl-1,3,3a,4,5,6-hexahydrofuro[3,4-c]pyridine (**4h**)



The procedure **GP-4** was followed using **3h** (48.4 mg, 0.14 mmol). Purification by column chromatography (eluent: gradient hexane/ethyl acetate) yielded **4h** as a white solid (68%, 34.5 mg, 0.10 mmol, *d.r.* > 25:1). **M.p.** = (149 – 152) °C. **R_f** = 0.27 (eluent: Hexane/ethyl acetate = 7:3). **¹H NMR** (400 MHz, CDCl₃) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.45 – 7.44 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.44 (s, 1H), 5.52 (s, 1H), 4.56 (d, *J* = 12.9 Hz, 1H), 4.30 (d, *J* = 12.9 Hz, 1H), 4.19 (d, *J* = 10.0 Hz, 1H), 4.12 (d, *J* = 16.7 Hz, 1H), 4.03 (dd, *J* = 11.2, 5.7 Hz, 1H), 3.23 (d, *J* = 16.8 Hz, 1H), 2.82 (brs, 1H), 2.43 (s, 3H), 2.18 (t, *J* = 10.0 Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 143.9 (CH), 143.8 (C_q), 140.2 (CH), 139.7 (C_q), 133.5 (C_q), 129.8 (CH), 127.5 (CH), 123.9 (C_q), 113.1 (CH), 108.5 (CH), 76.3 (CH), 69.2 (CH₂), 45.7 (CH), 44.6 (CH₂), 44.3 (CH₂), 21.6 (CH₃). **LC-MS** calcd for C₁₈H₁₉NNaO₄S [M+Na]⁺ 368.09, found 368.13.

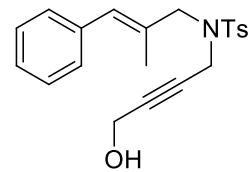
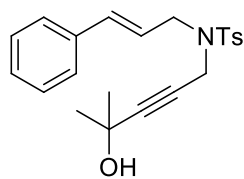
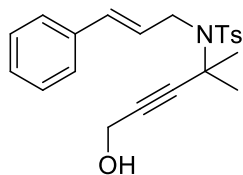
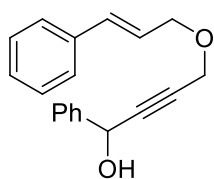
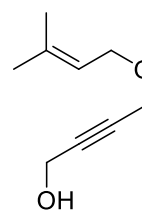
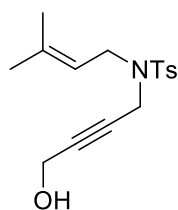
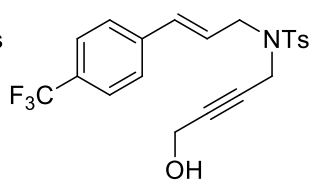
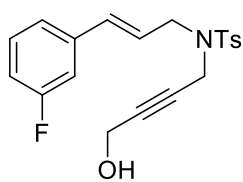
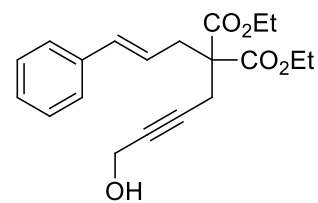
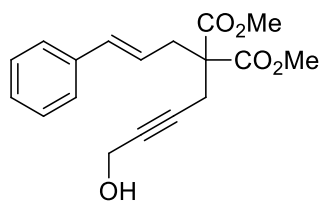
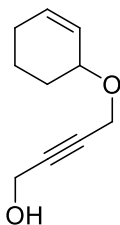
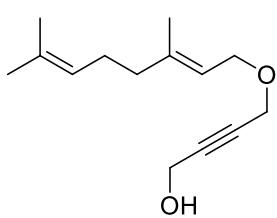
3-(thiophen-2-yl)-5-tosyl-1,3,3a,4,5,6-hexahydrofuro[3,4-c]pyridine (4i)



The procedure **GP-4** was followed using **3i** (50.6 mg, 0.14 mmol). Purification by column chromatography (eluent: gradient hexane/ethyl acetate) yielded **4i** as a pale yellow solid (68%, 36.1 mg, 0.10 mmol, *d.r.* > 25:1). **M. p.** = (132 – 135) °C. **R_f** = 0.24 (eluent: Hexane/ethyl acetate = 7:3). **¹H NMR** (400 MHz, CDCl₃) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.33 – 7.31 (m, 3H), 7.03 – 6.99 (m, 2H), 5.52 (s, 1H), 4.61 (d, *J* = 12.9 Hz, 1H), 4.48 (d, *J* = 9.8 Hz, 1H), 4.33 (d, *J* = 12.9 Hz, 1H), 4.15 – 4.07 (m, 2H), 3.24 (d, *J* = 16.9 Hz, 1H), 2.90 (s, 1H), 2.43 (s, 3H), 2.25 (t, *J* = 10.0 Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 143.80 (C_q), 142.38 (C_q), 139.3 (C_q), 133.6 (C_q), 129.8 (CH), 127.5 (CH), 126.8 (CH), 125.8 (CH), 125.2 (CH), 113.4 (CH), 79.5 (CH), 69.4 (CH₂), 47.4 (CH), 44.5 (CH₂), 44.3 (CH₂), 21.6 (CH₃). **LC-MS** calcd for C₁₈H₁₉NNaO₃S₂ [M+Na]⁺ 384.07, found 384.11.

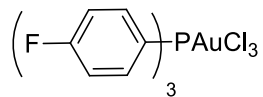
Scope limitations

List of unsuccessful substrates

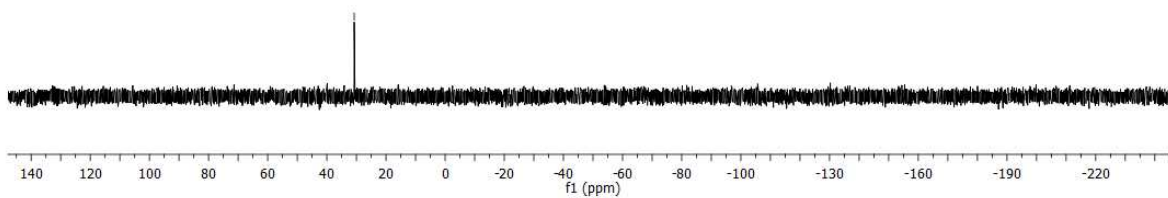


Copies of NMR spectra

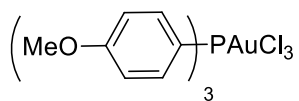
—30.8



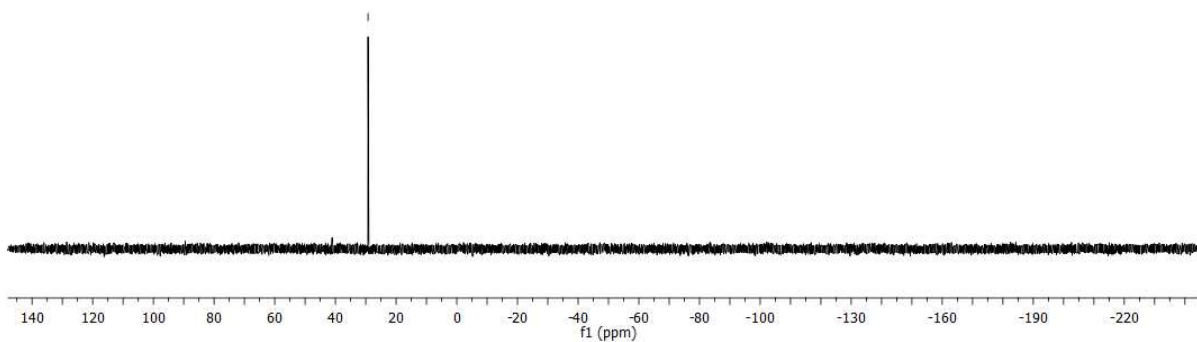
Gold catalyst **B** (162 MHz, CDCl₃)

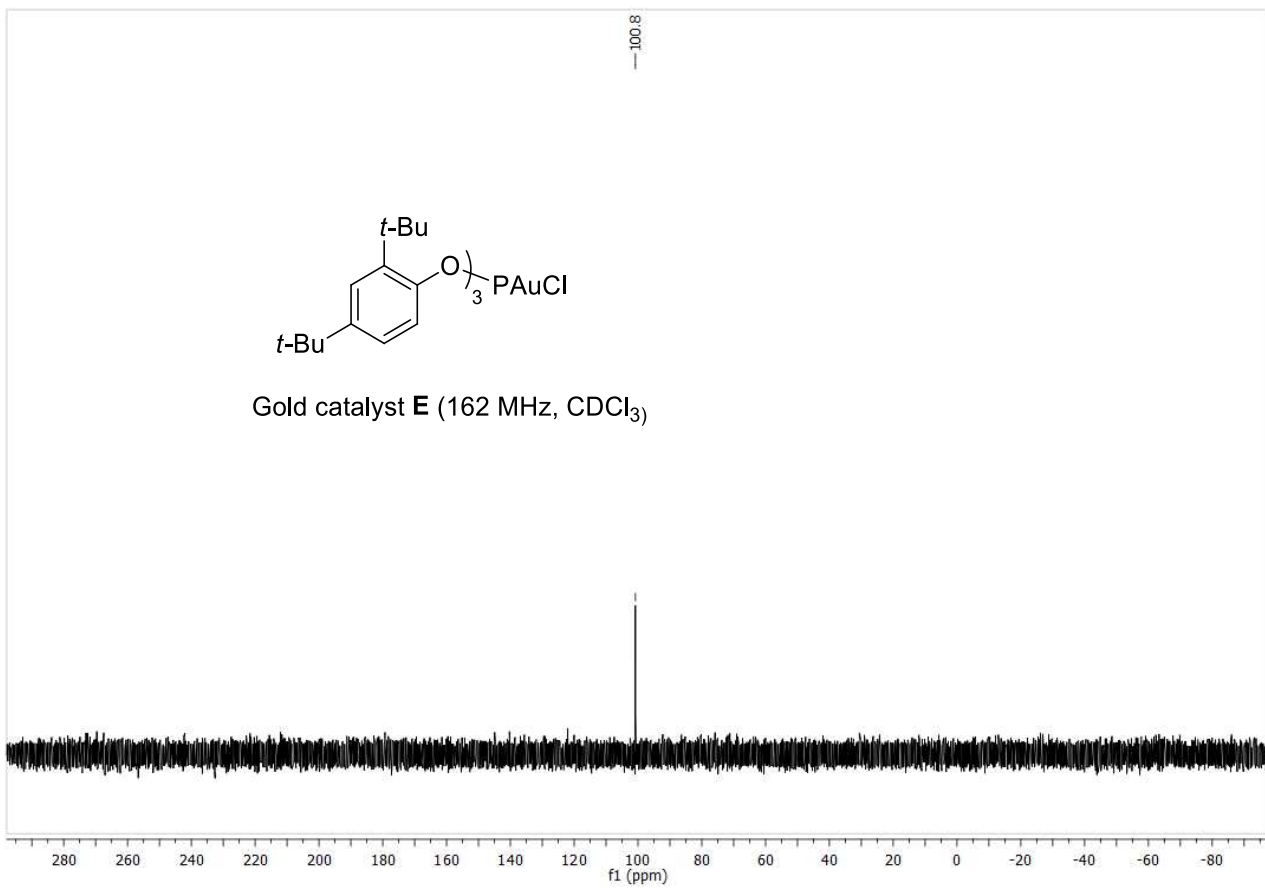


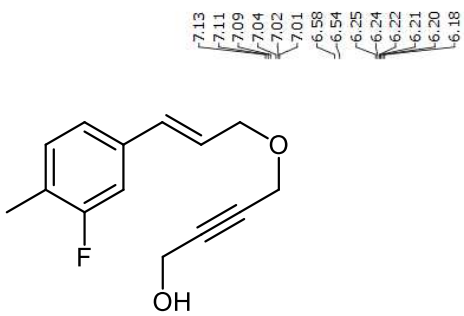
—29.3



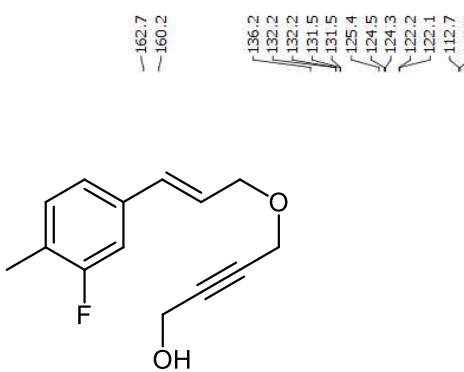
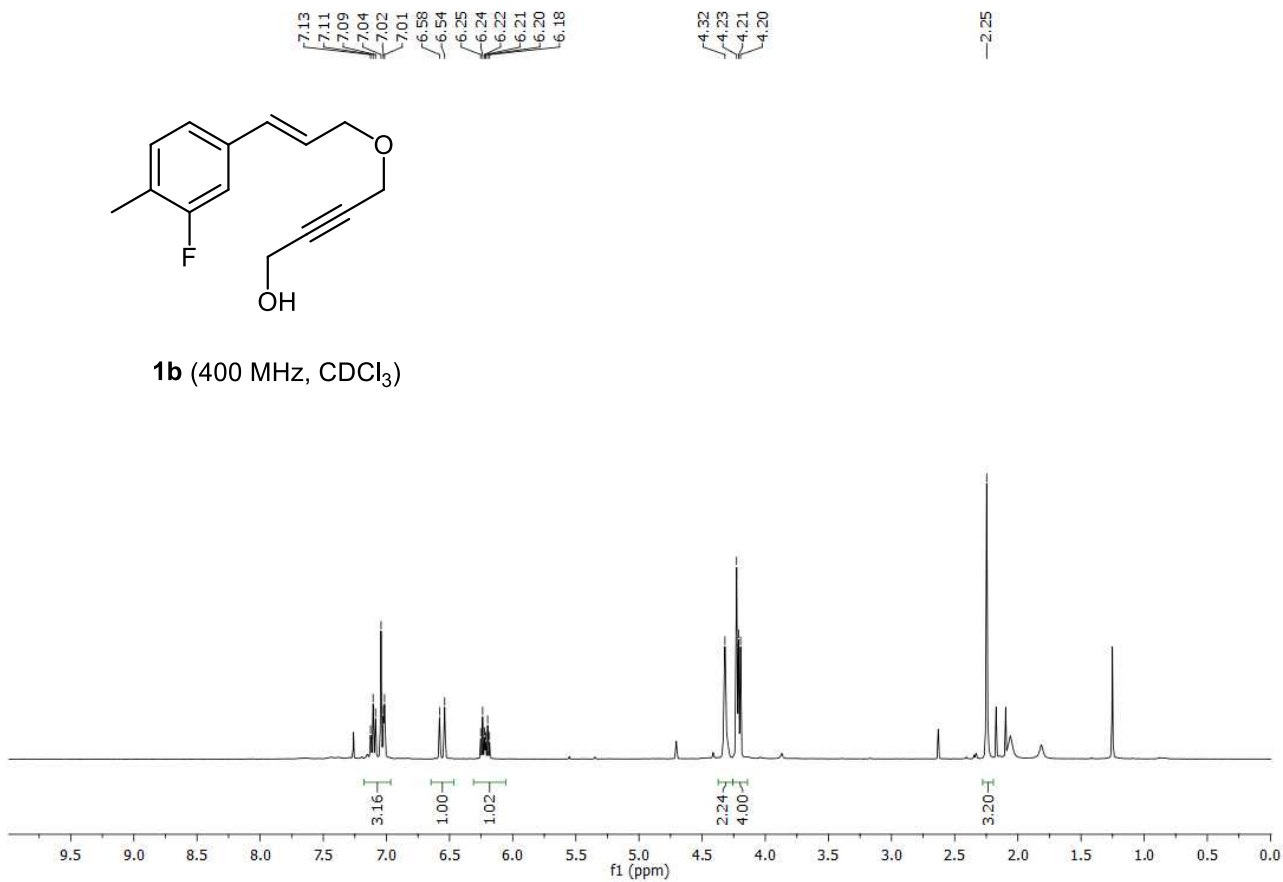
Gold catalyst **C** (162 MHz, CDCl₃)



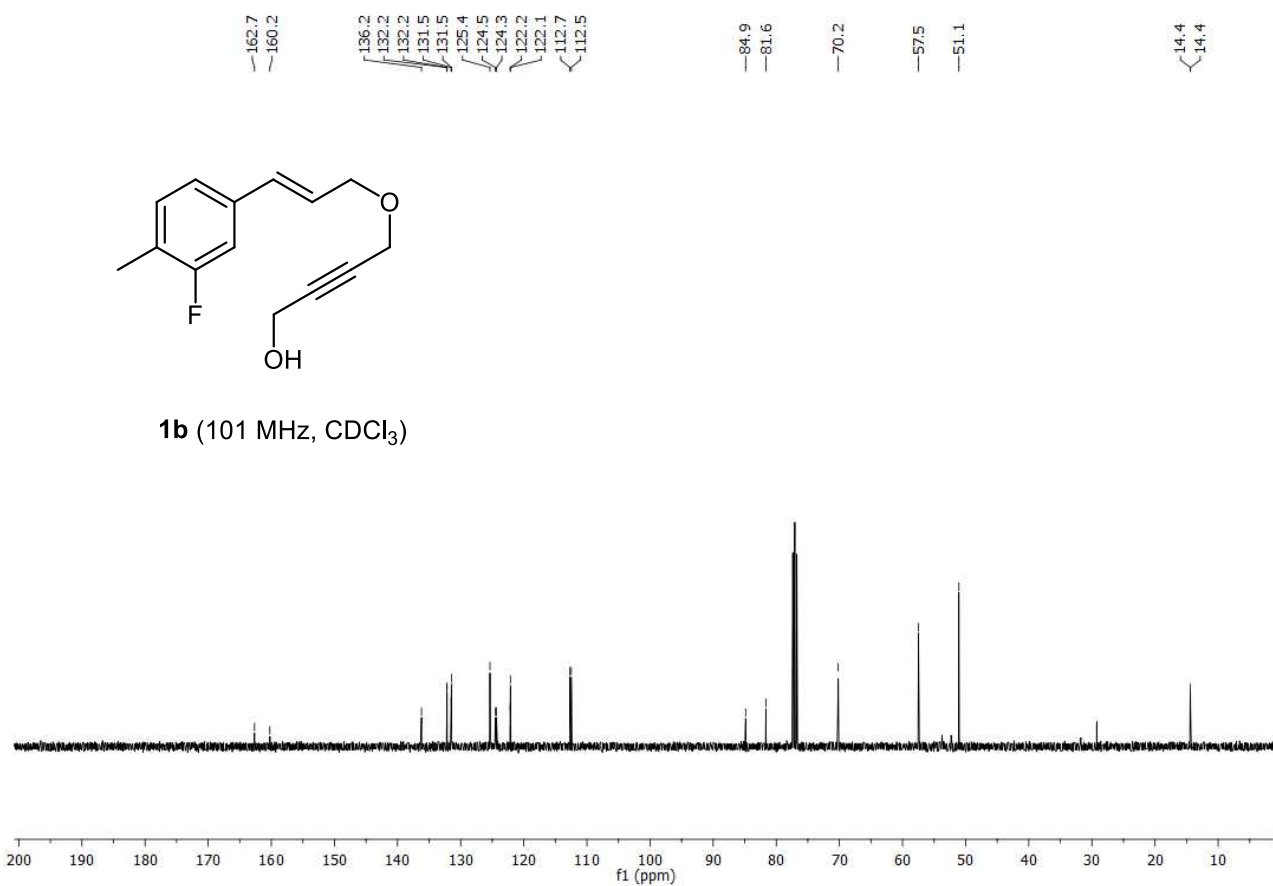


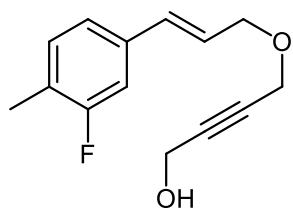


1b (400 MHz, CDCl₃)

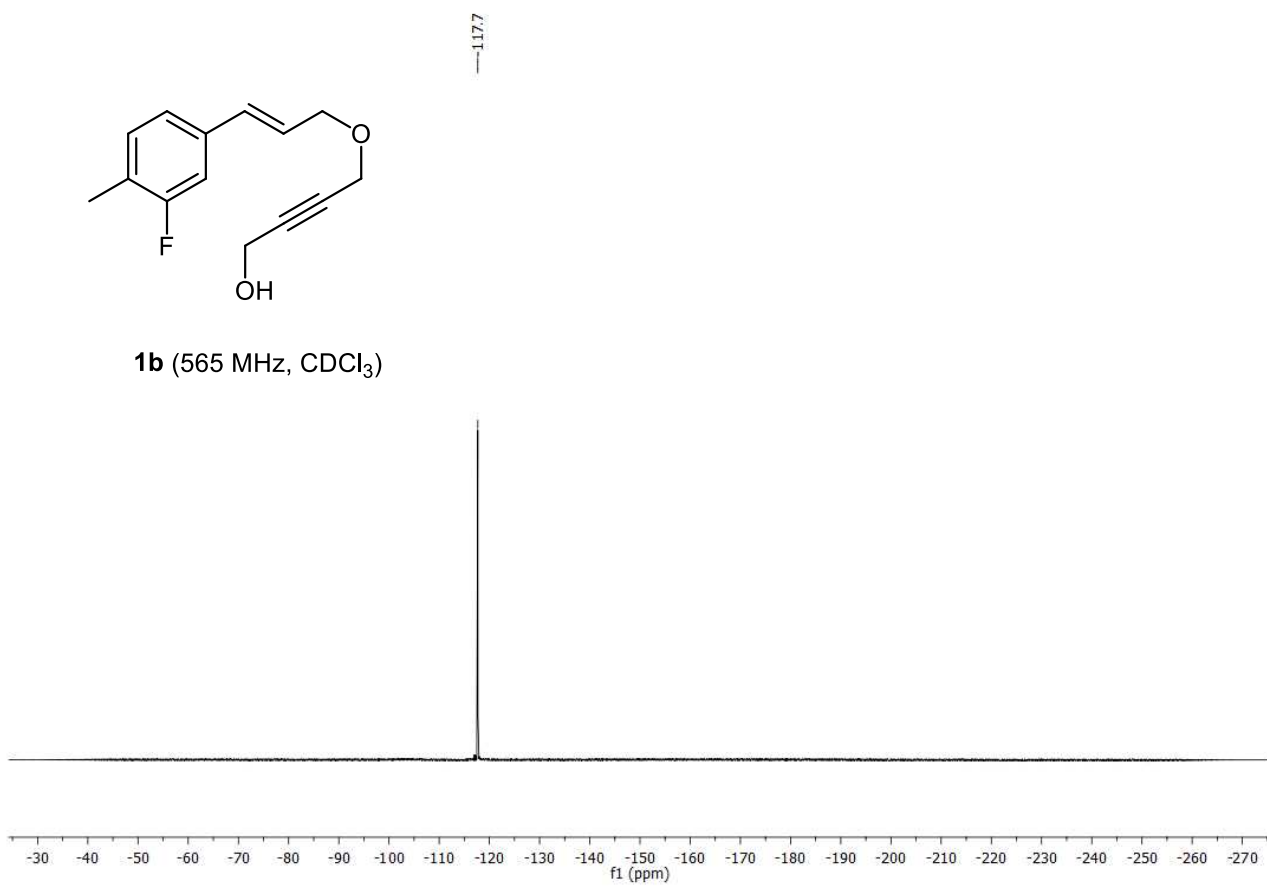


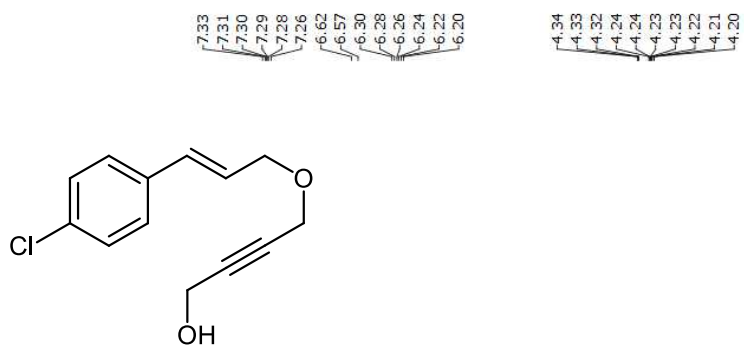
1b (101 MHz, CDCl₃)



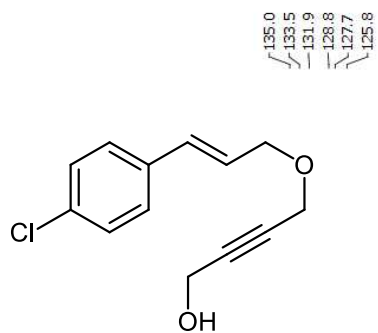
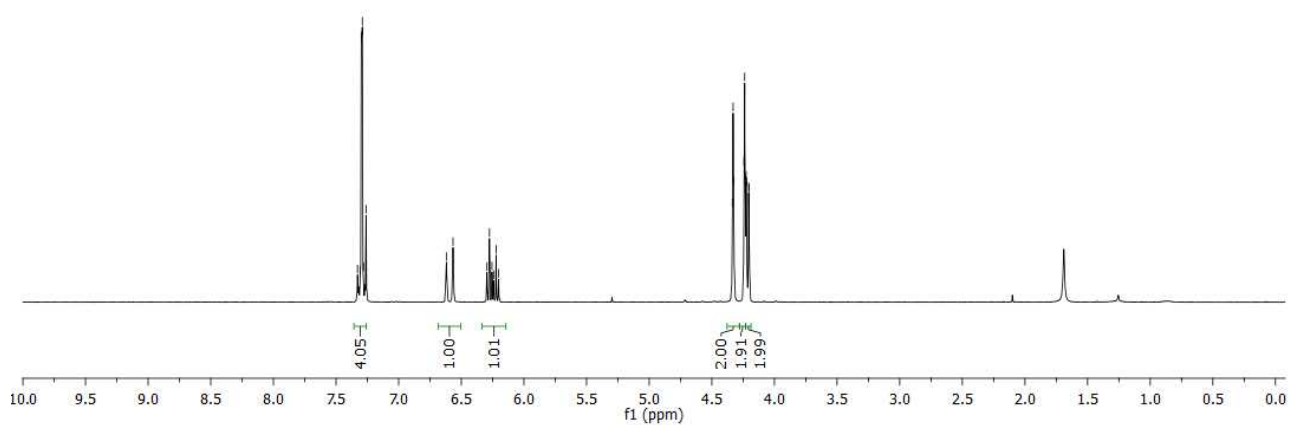


1b (565 MHz, CDCl₃)

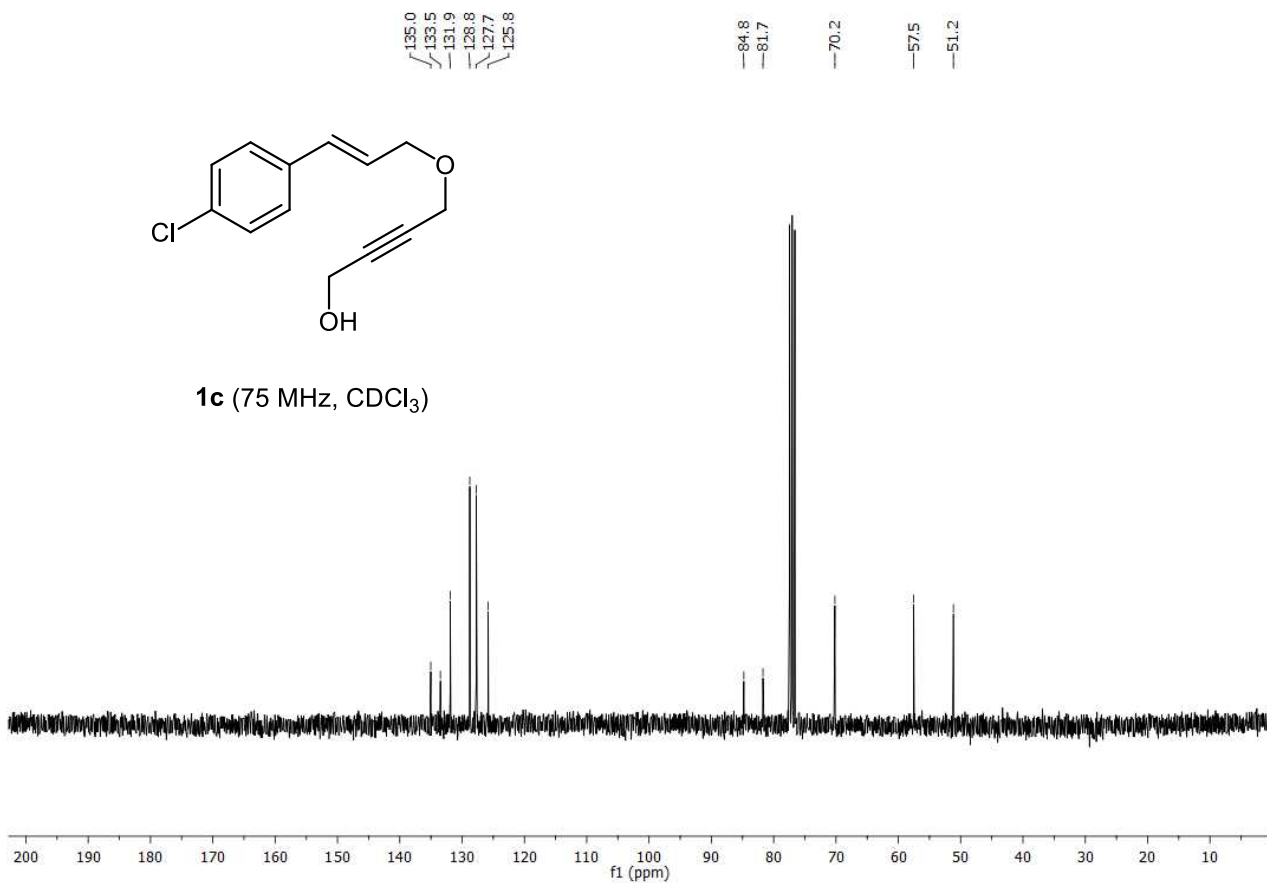




1c (300 MHz, CDCl₃)



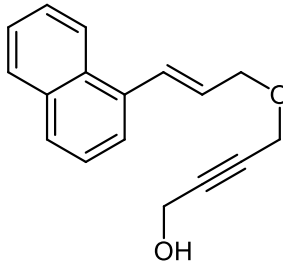
1c (75 MHz, CDCl₃)



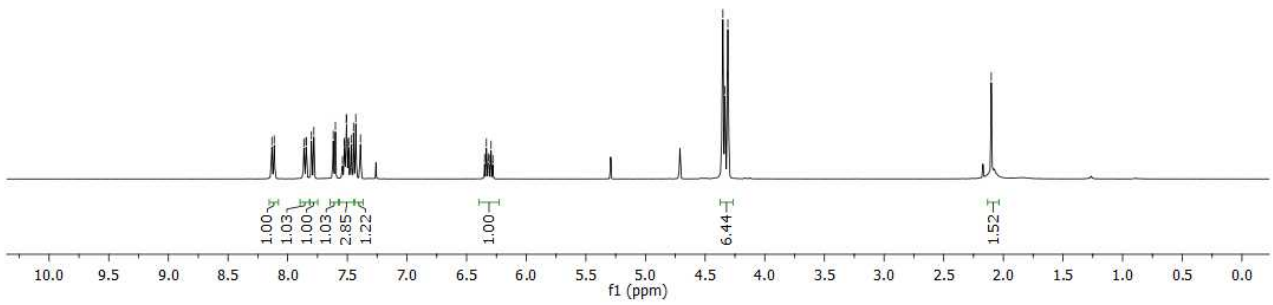
8.13
8.11
7.86
7.85
7.84
7.80
7.78
7.62
7.60
7.54
7.53
7.52
7.51
7.51
7.49
7.49
7.47
7.45
7.39
6.35
6.33
6.32
6.31
6.29
6.28

4.35
4.33
4.31
4.31

2.10

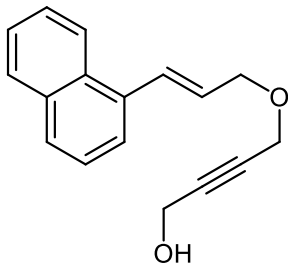


1d (400 MHz, CDCl₃)

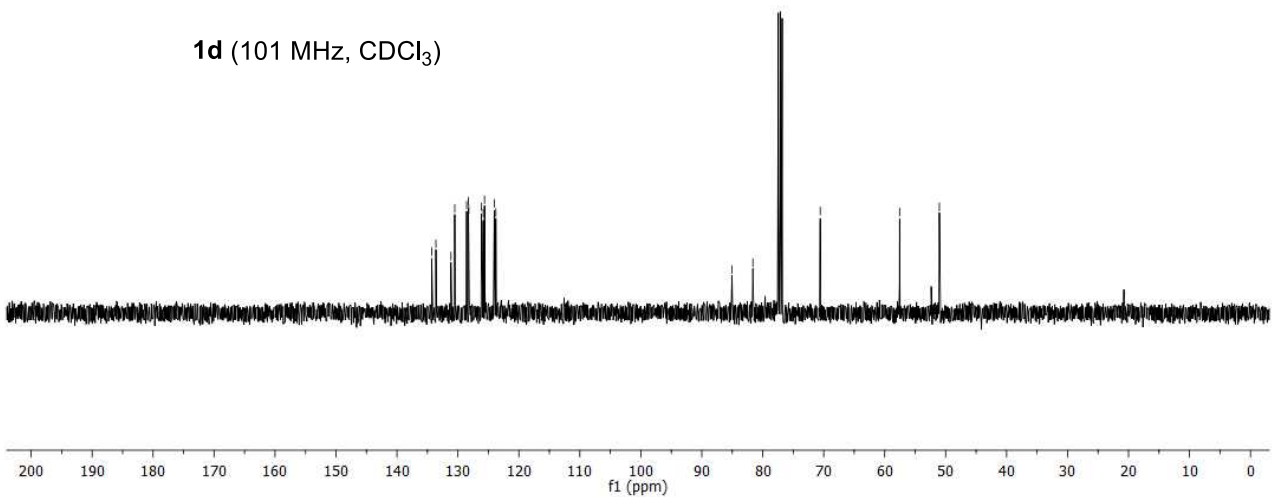


134.3
133.6
131.1
130.5
128.6
128.3
128.2
126.1
125.8
125.6
124.0
123.8

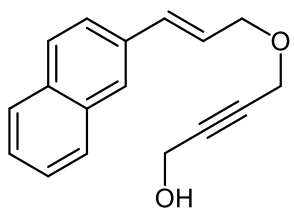
85.0
81.6
70.6
57.6
51.0



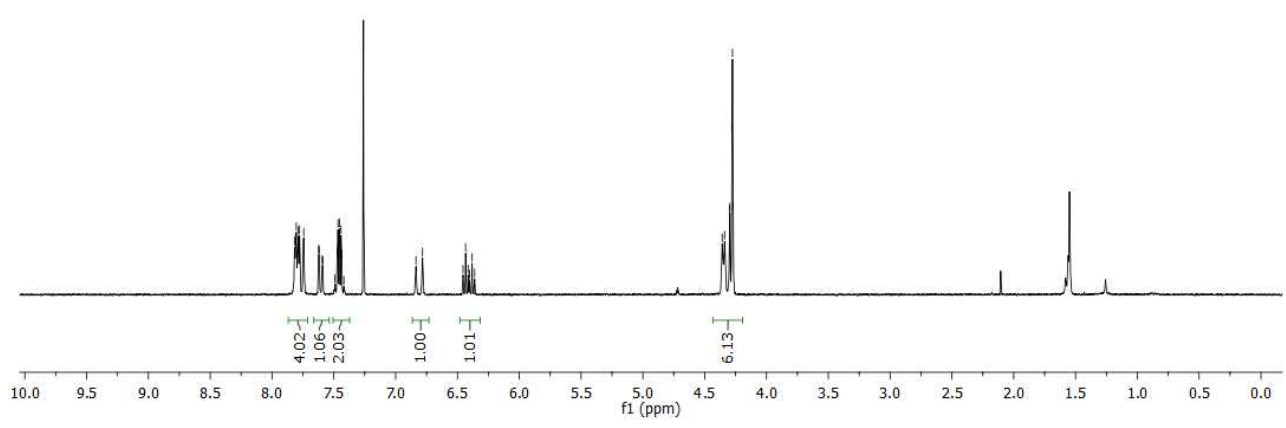
1d (101 MHz, CDCl₃)



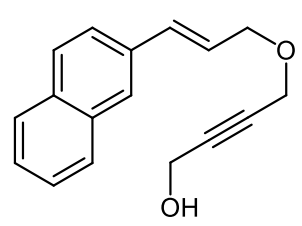
7.82 7.80 7.79 7.78 7.74 7.62 7.62 7.59 7.49 7.47 7.47 7.45 7.44 7.42 6.84 6.78 6.45 6.43 6.41 6.40 6.38 6.36 4.36 4.34 4.30 4.30 4.28 4.28 4.27



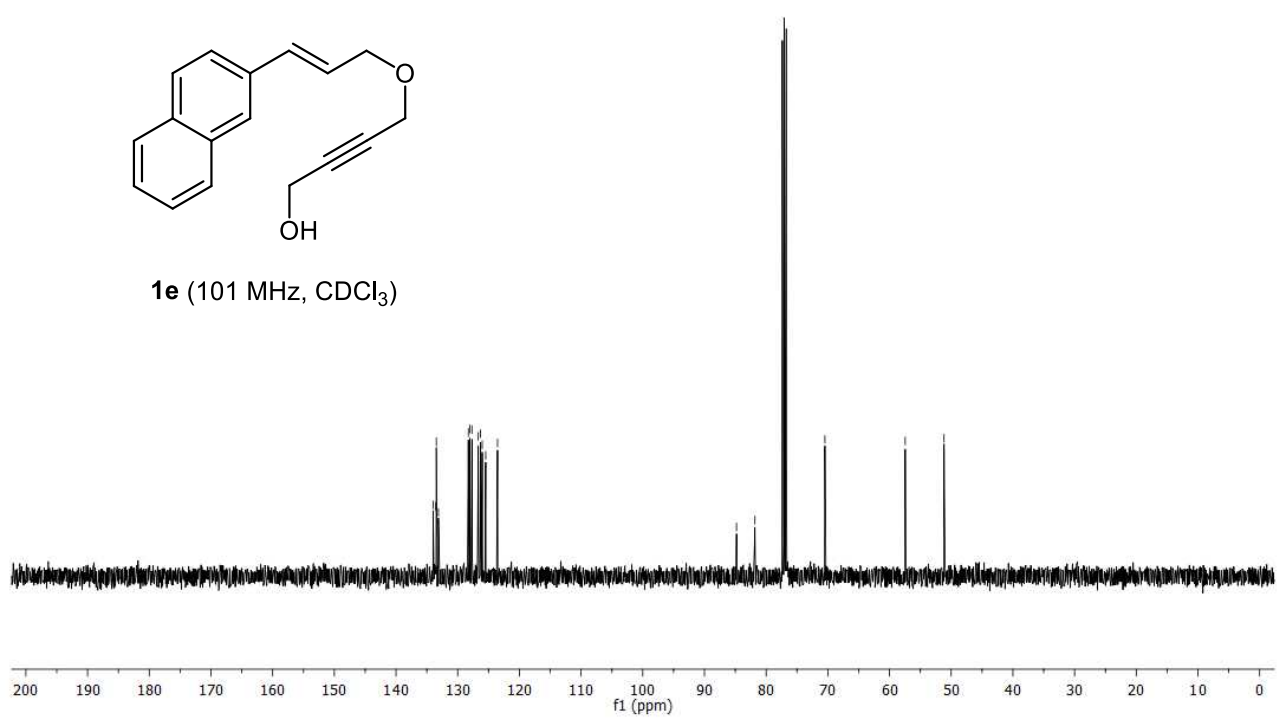
1e (300 MHz, CDCl₃)



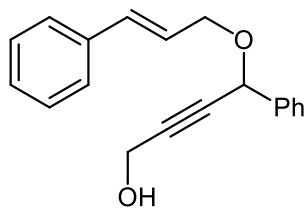
134.0 133.6 133.5 133.1 128.3 128.0 127.7 126.7 126.3 126.0 125.5 123.5 -84.8 -81.8 -70.5 -57.5 -51.2



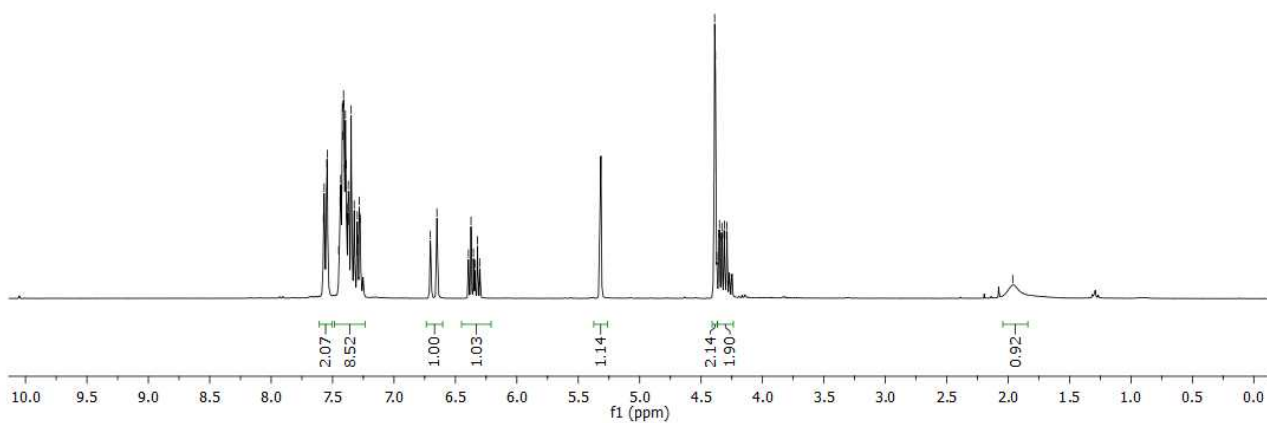
1e (101 MHz, CDCl₃)



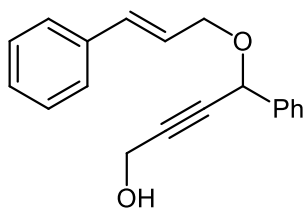
7.57
7.55
7.54
7.44
7.43
7.42
7.41
7.41
7.40
7.40
7.39
7.38
7.37
7.37
7.37
7.35
7.32
7.32
6.78
6.65
6.39
6.37
6.35
6.34
6.32
6.30
-5.32
4.39
4.38
4.37
4.35
4.35
4.34
4.33
4.31
4.31
4.29
4.29
-1.96



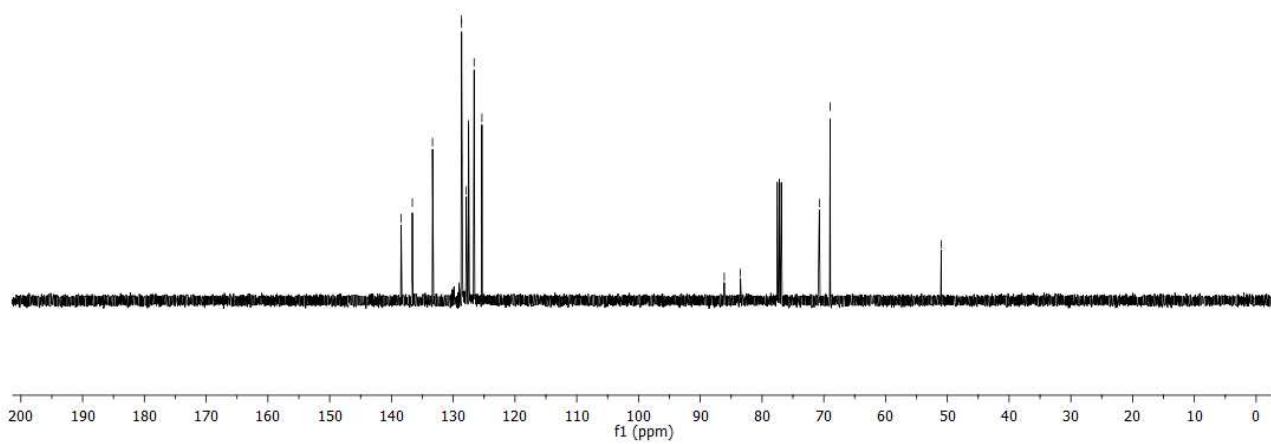
1f (300 MHz, CDCl₃)



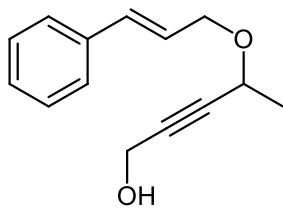
138.4
136.6
133.4
128.7
128.6
128.6
127.9
127.5
126.6
125.4
86.1
83.5
70.7
69.0
51.0



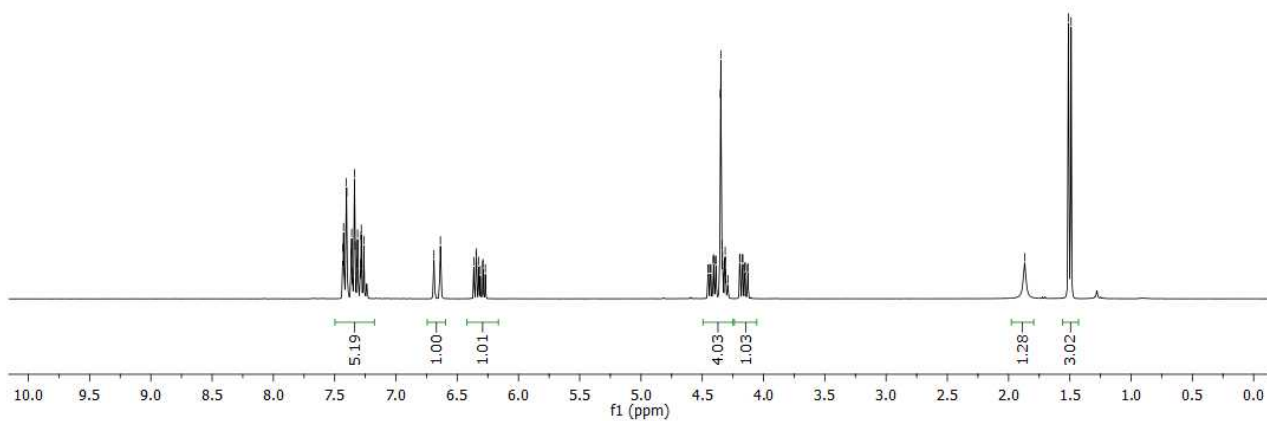
1f (101 MHz, CDCl₃)



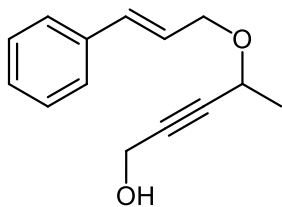
7.43 7.43 7.42 7.40 7.40 7.37 7.36 7.35 7.34 7.33 7.32 7.31 7.29 7.29 7.28 7.26 6.69 6.64 6.36 6.35 6.34 6.32 6.31 6.29 6.27 4.45 4.43 4.43 4.41 4.41 4.39 4.39 4.35 4.35 4.34 4.34 4.32 4.31 4.19 4.19 4.17 4.17 4.15 4.15 4.13 4.13 1.51 1.49



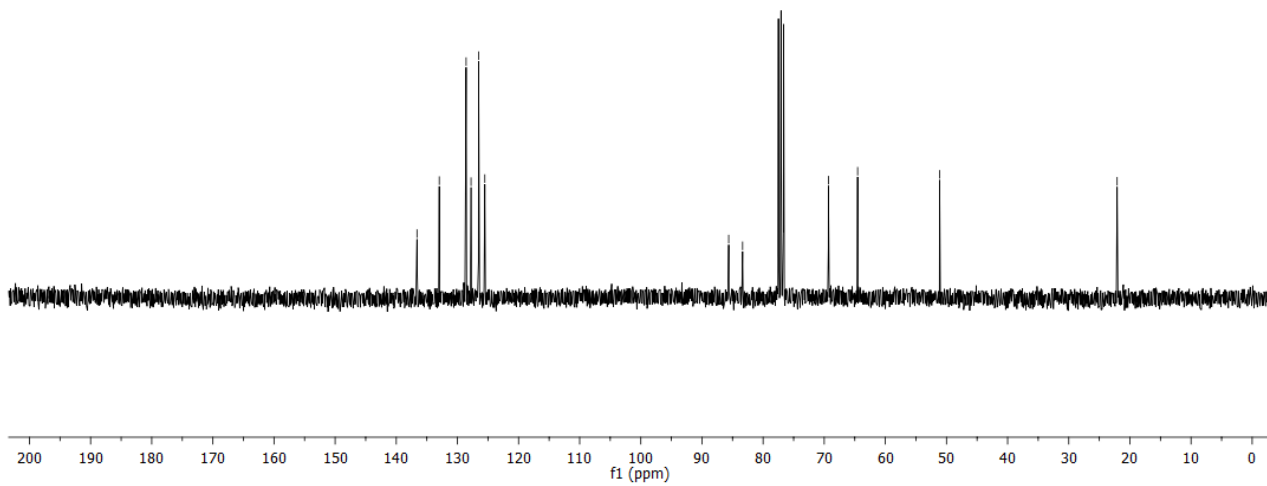
1g (300 MHz, CDCl₃)

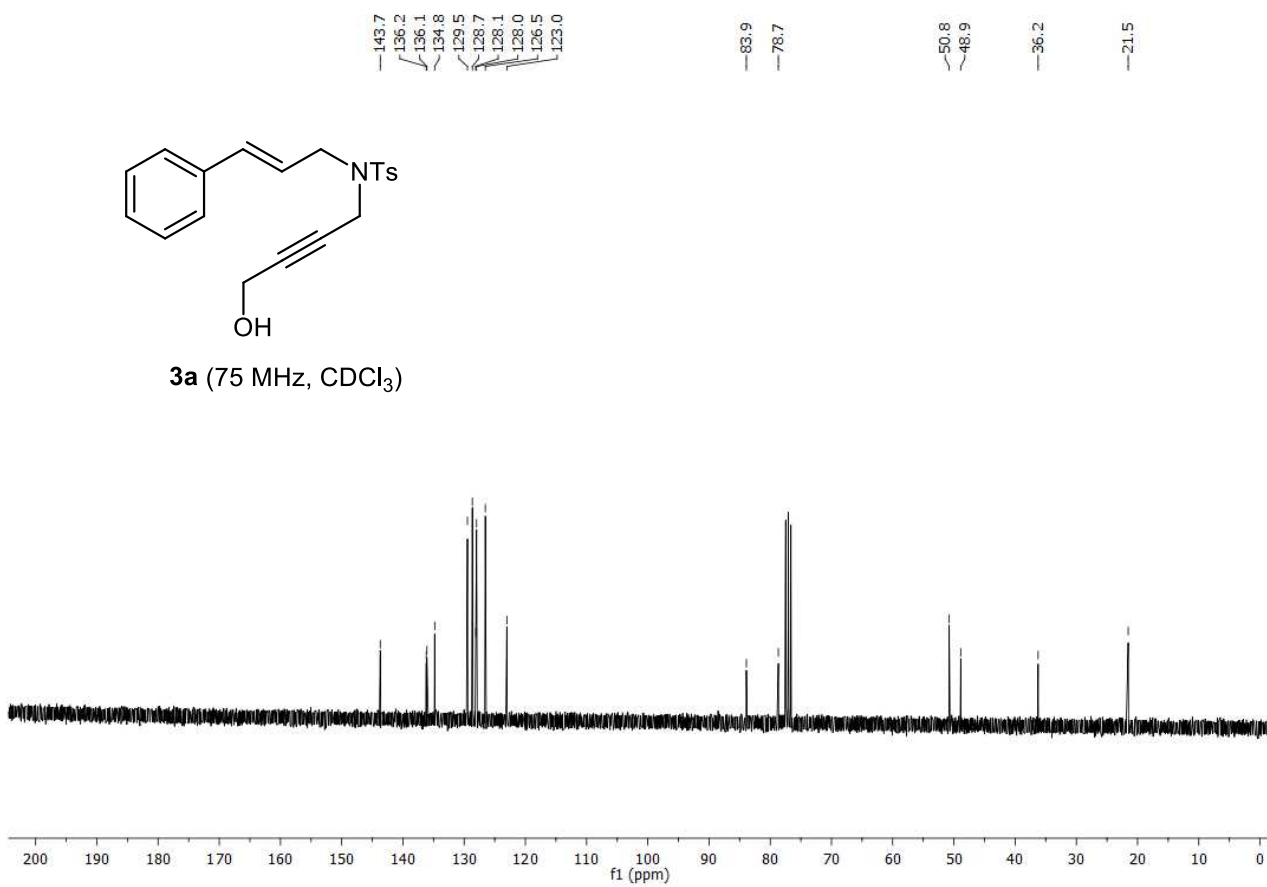
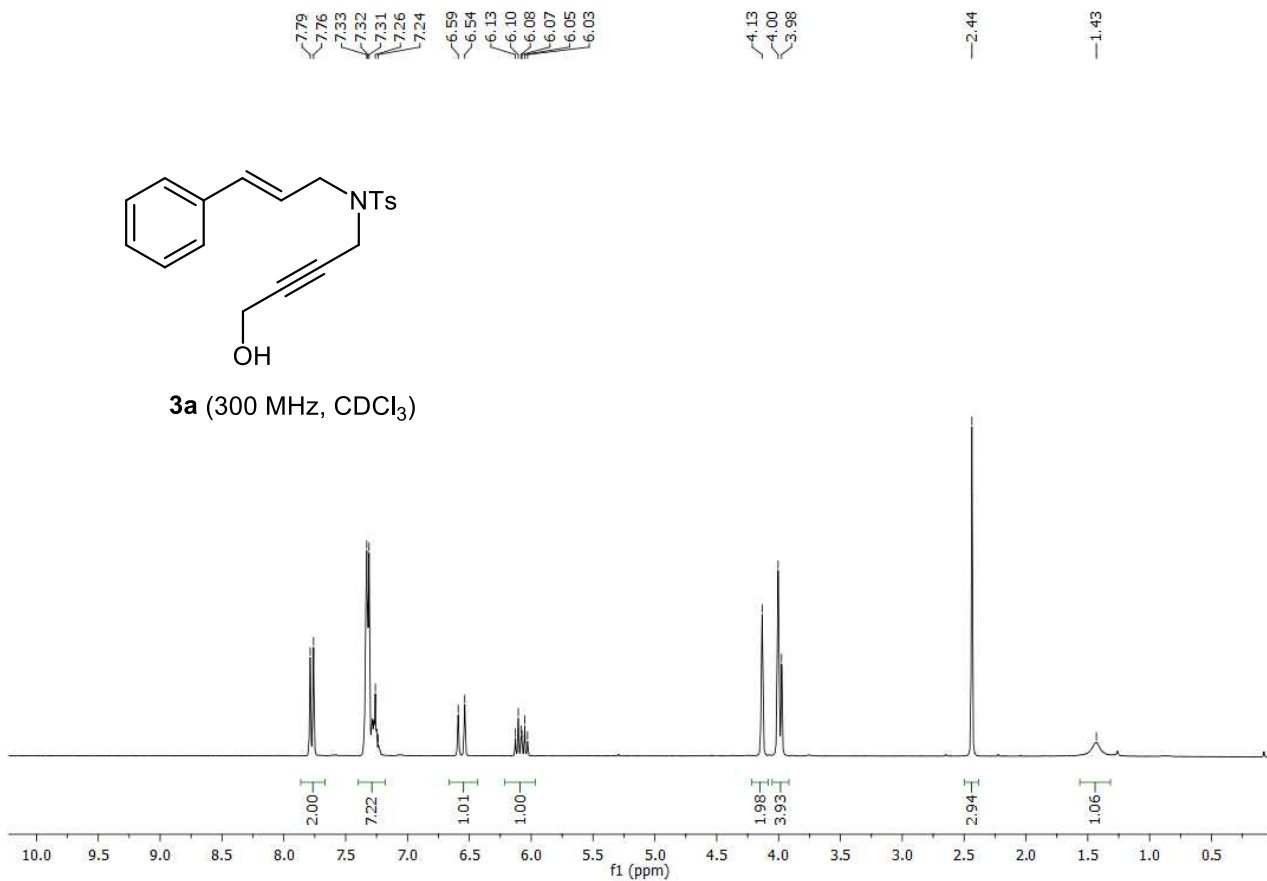


136.6 133.0 128.6 127.8 126.5 125.5 85.6 83.3 69.3 64.5 51.1 22.1

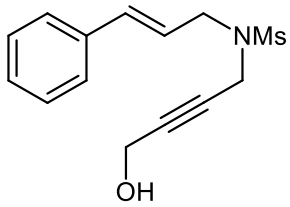


1g (75 MHz, CDCl₃)

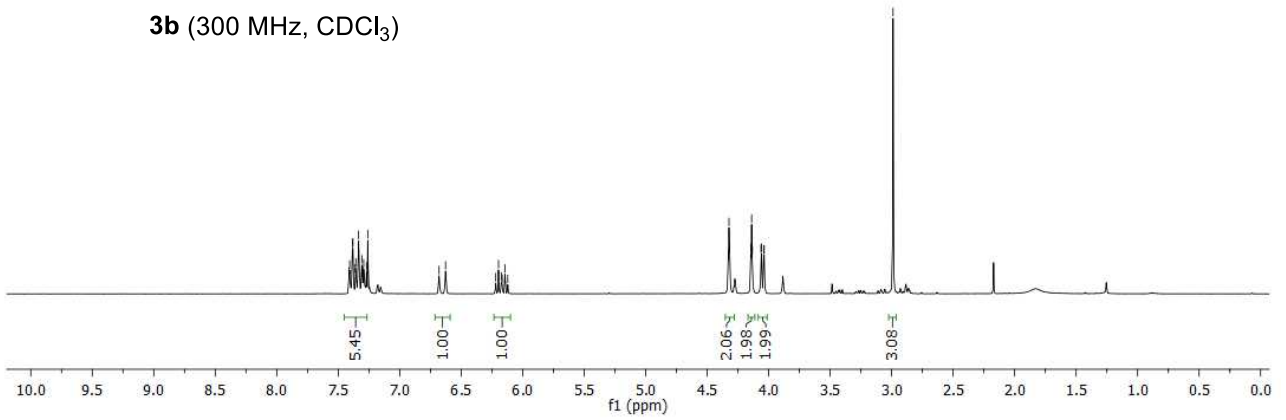




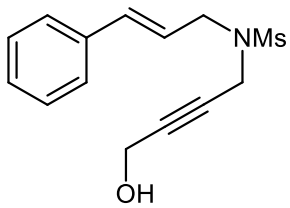
7.41, 7.38, 7.36, 7.33, 7.30, 7.29, 7.27, 7.26, 6.68, 6.63, 6.22, 6.20, 6.17, 6.14, 6.12, 4.33, 4.32, 4.32, 4.14, 4.14, 4.13, 4.06, 4.06, 4.04, 4.04, -2.99



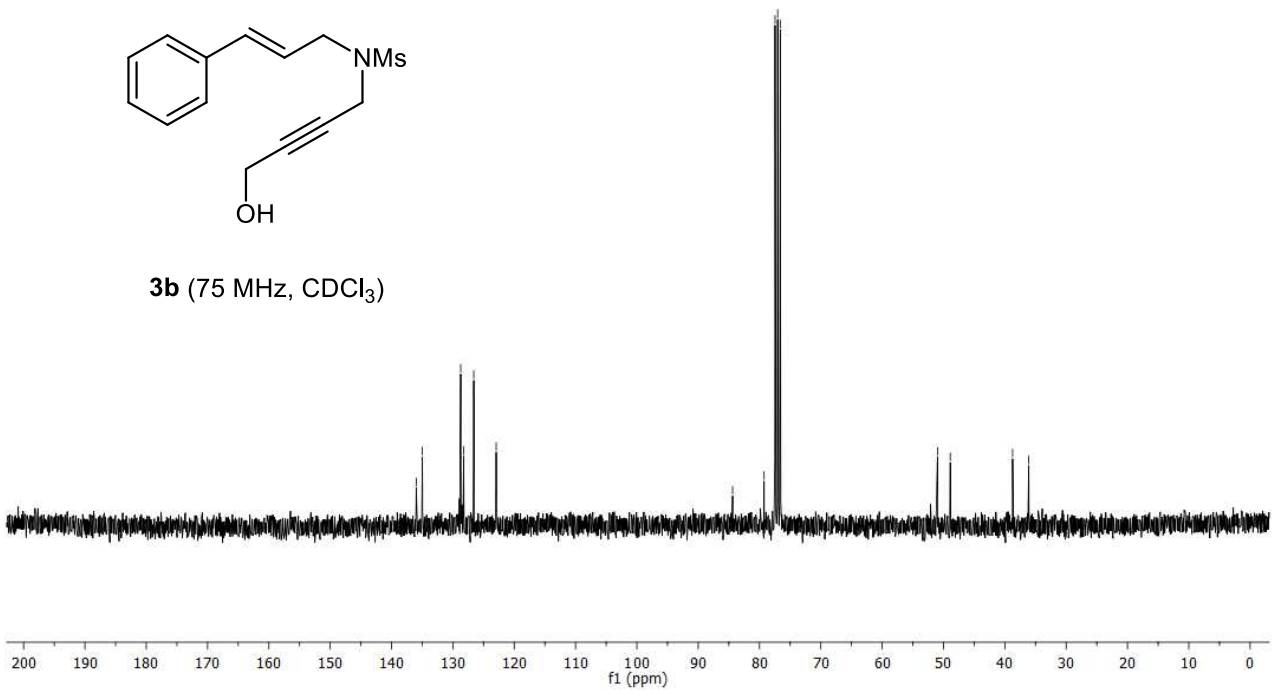
3b (300 MHz, CDCl₃)

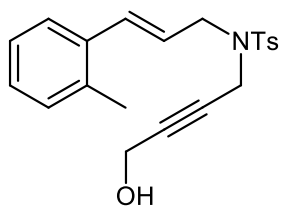


136.0, 135.0, 128.7, 128.2, 126.6, 122.9, 84.4, 79.3, 77.5, 77.0, 76.6, 51.0, 48.9, 38.7, 36.1

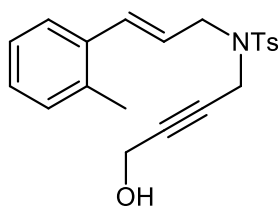
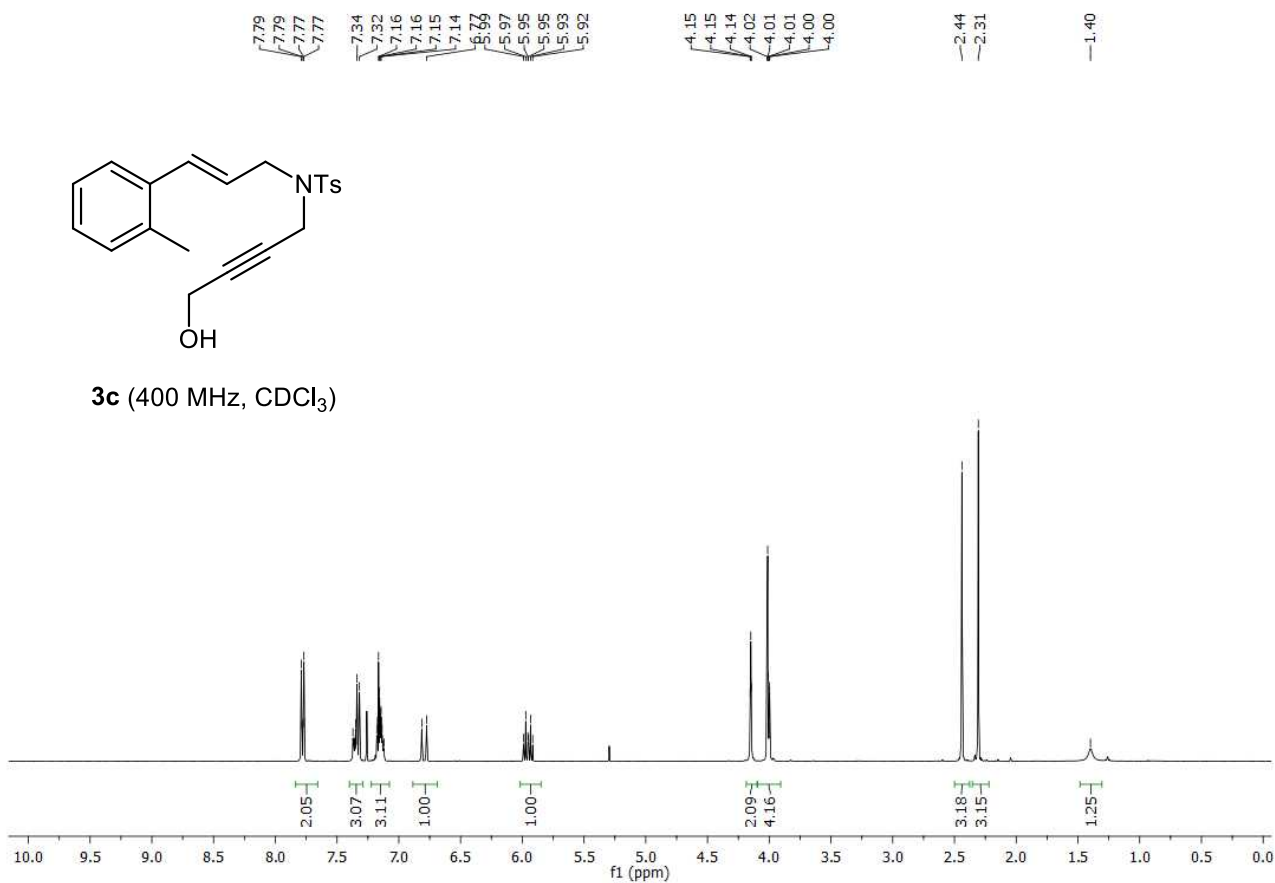


3b (75 MHz, CDCl₃)

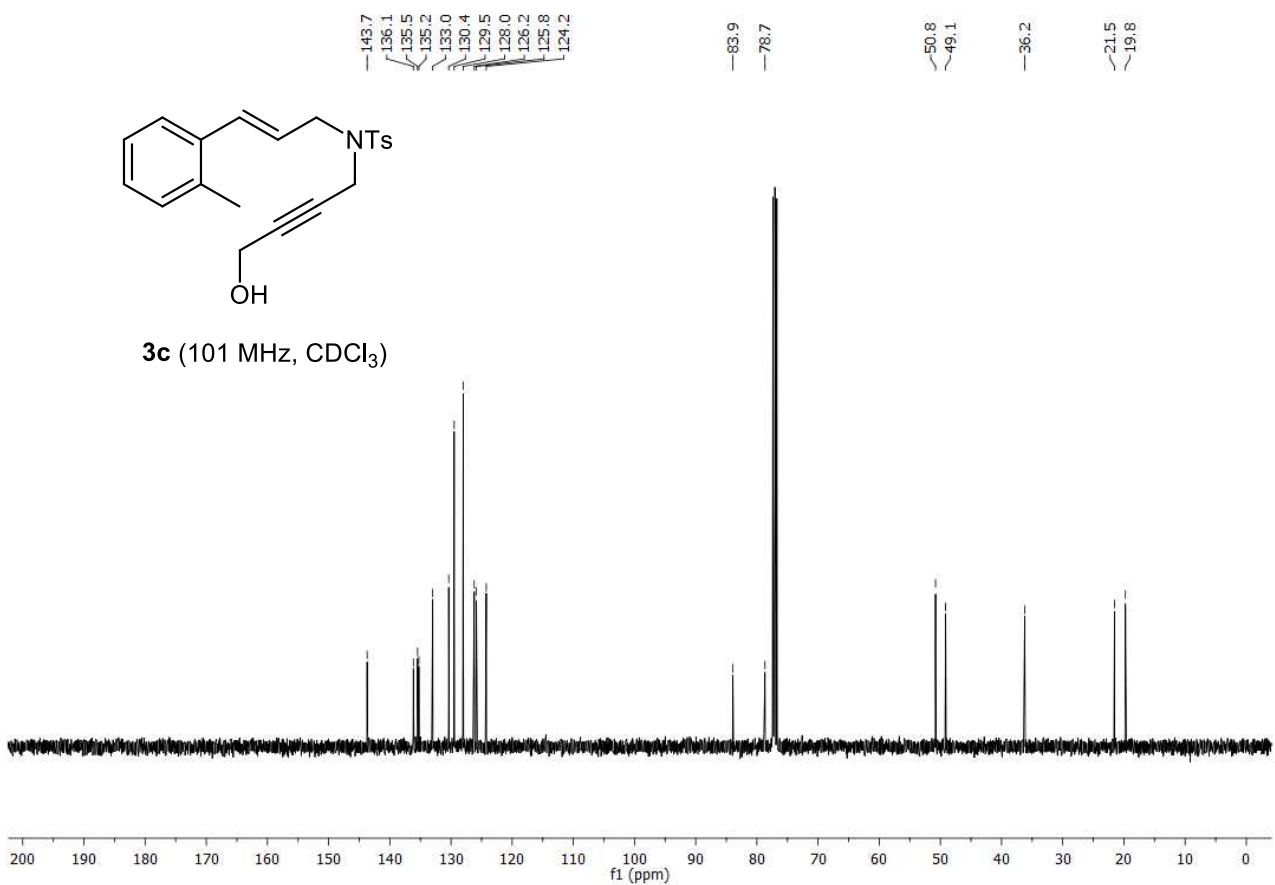




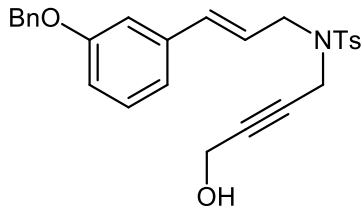
3c (400 MHz, CDCl₃)



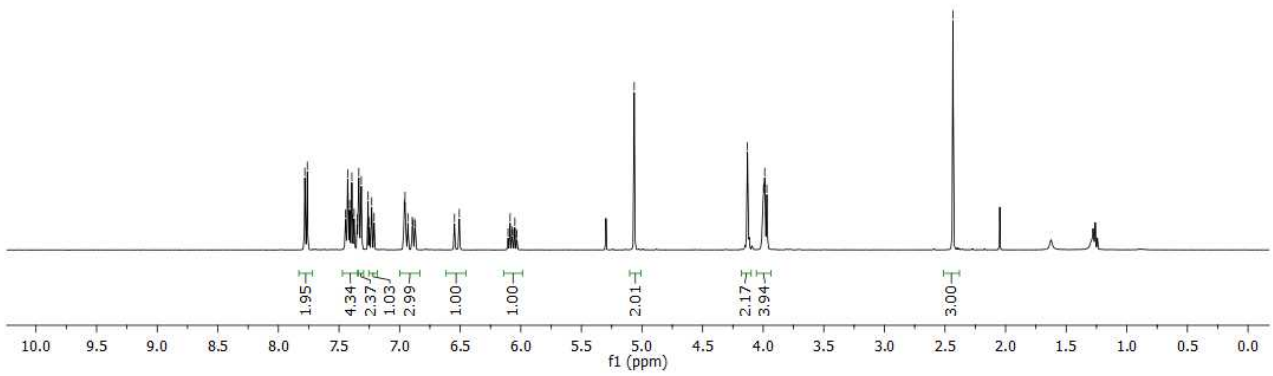
3c (101 MHz, CDCl₃)



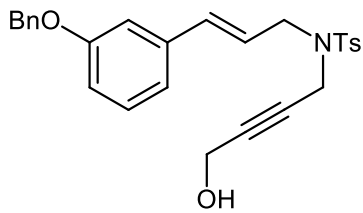
7.78
7.76
7.45
7.43
7.41
7.39
7.39
7.37
7.35
7.34
7.32
7.26
7.25
7.23
7.21
6.96
6.96
6.93
6.90
6.89
6.88
6.87
6.55
6.51
6.11
6.09
6.07
6.07
6.05
6.03
— 5.06
4.13
4.00
3.99
3.97
— 2.43



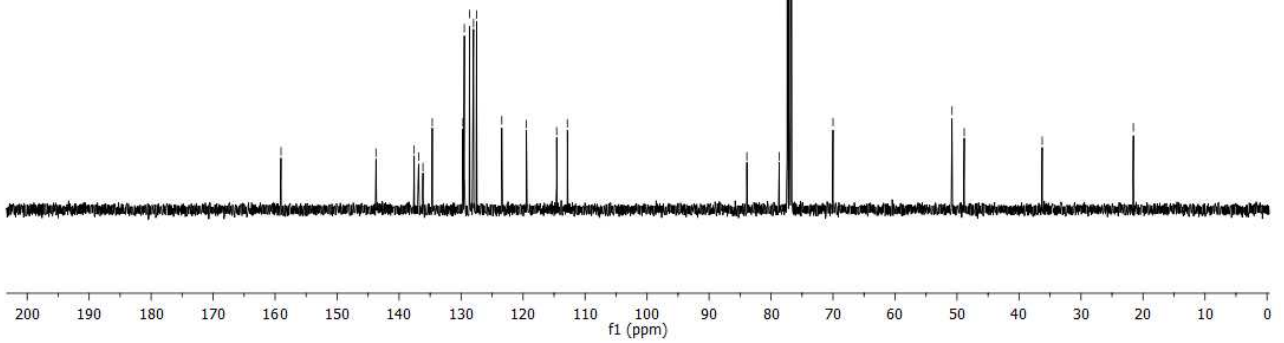
3d (400 MHz, CDCl₃)

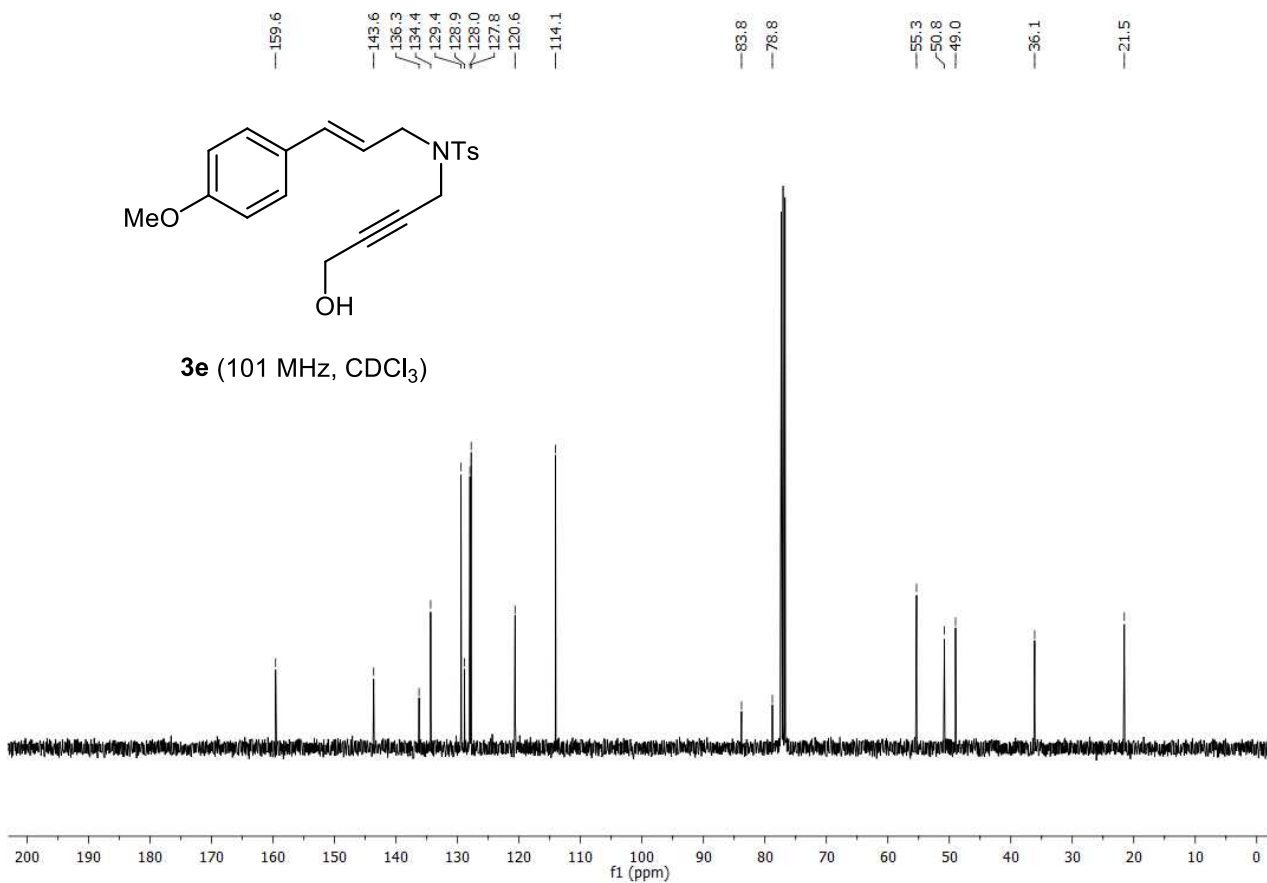
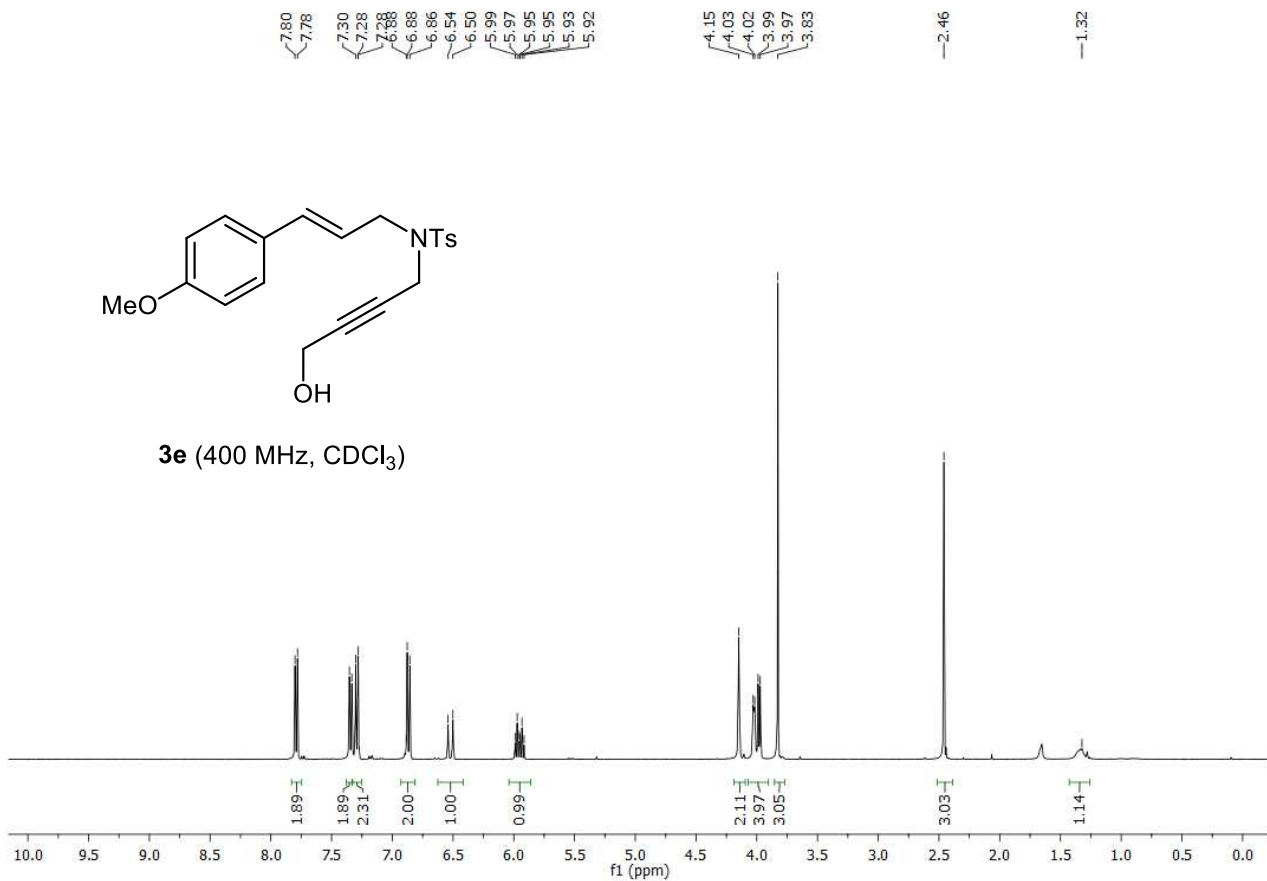


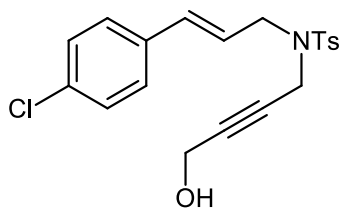
— 159.1
143.7
137.6
136.9
136.2
134.6
129.7
129.5
128.6
128.1
128.0
127.5
123.4
119.5
114.6
112.9
— 83.9
— 78.7
— 70.0
— 50.8
— 48.8
— 36.3
— 21.6



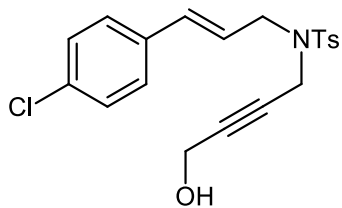
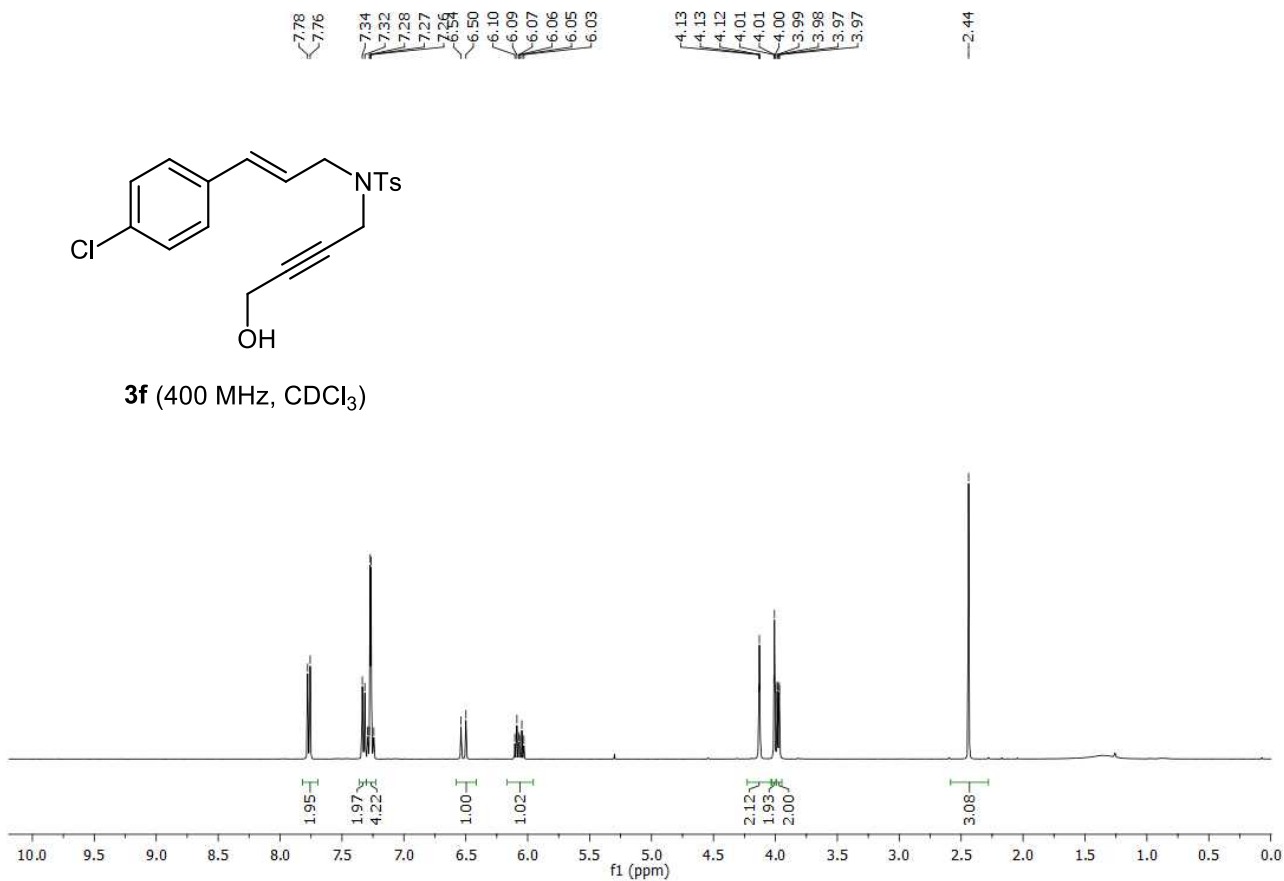
3d (101 MHz, CDCl₃)



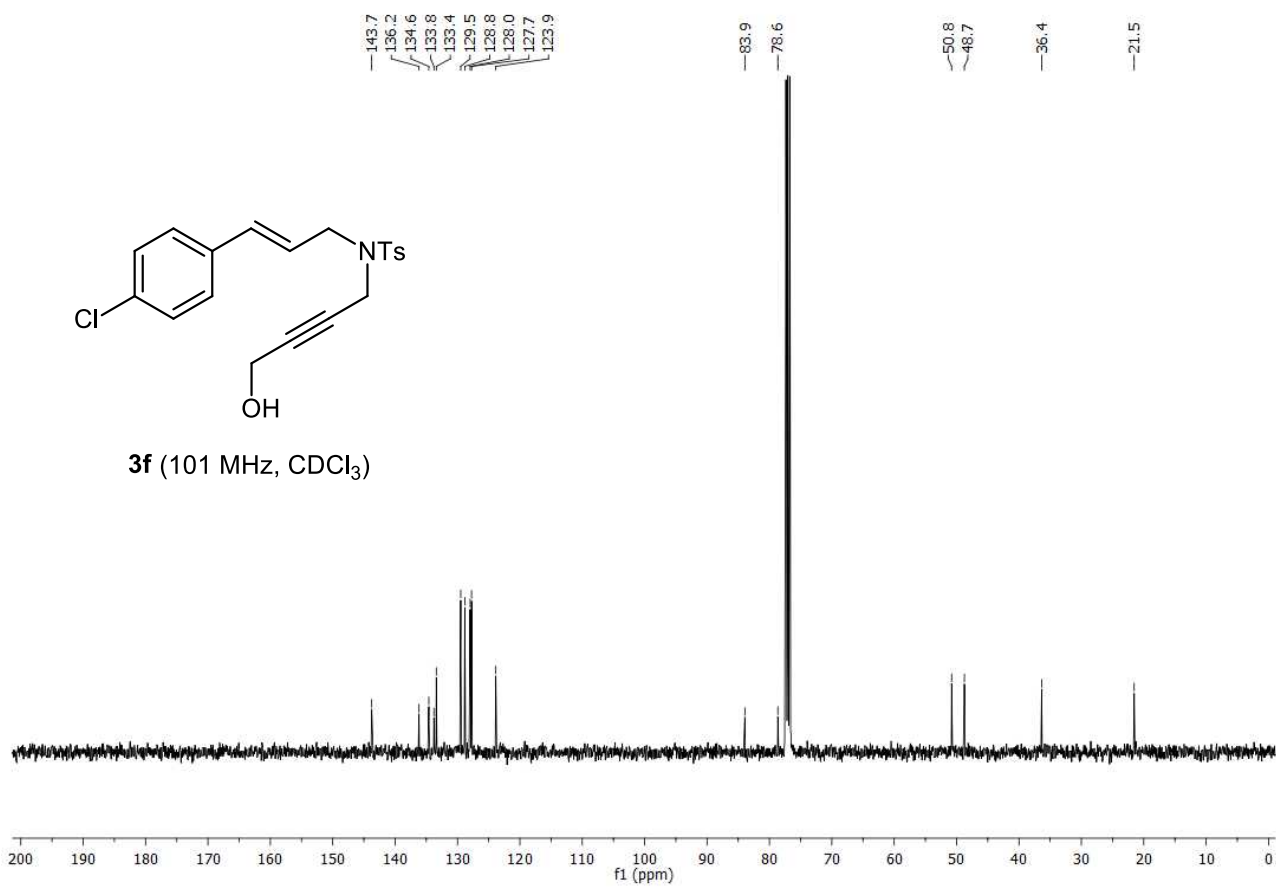


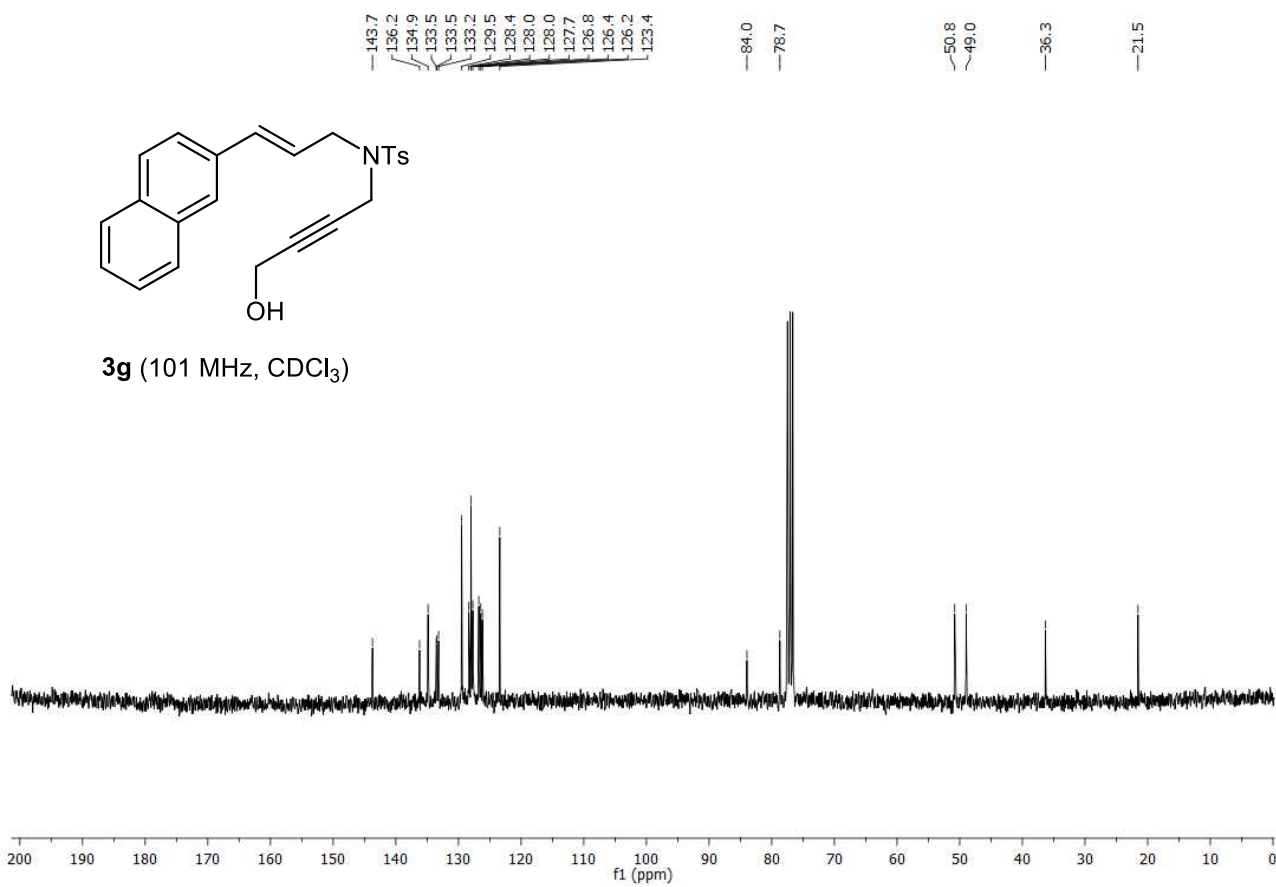
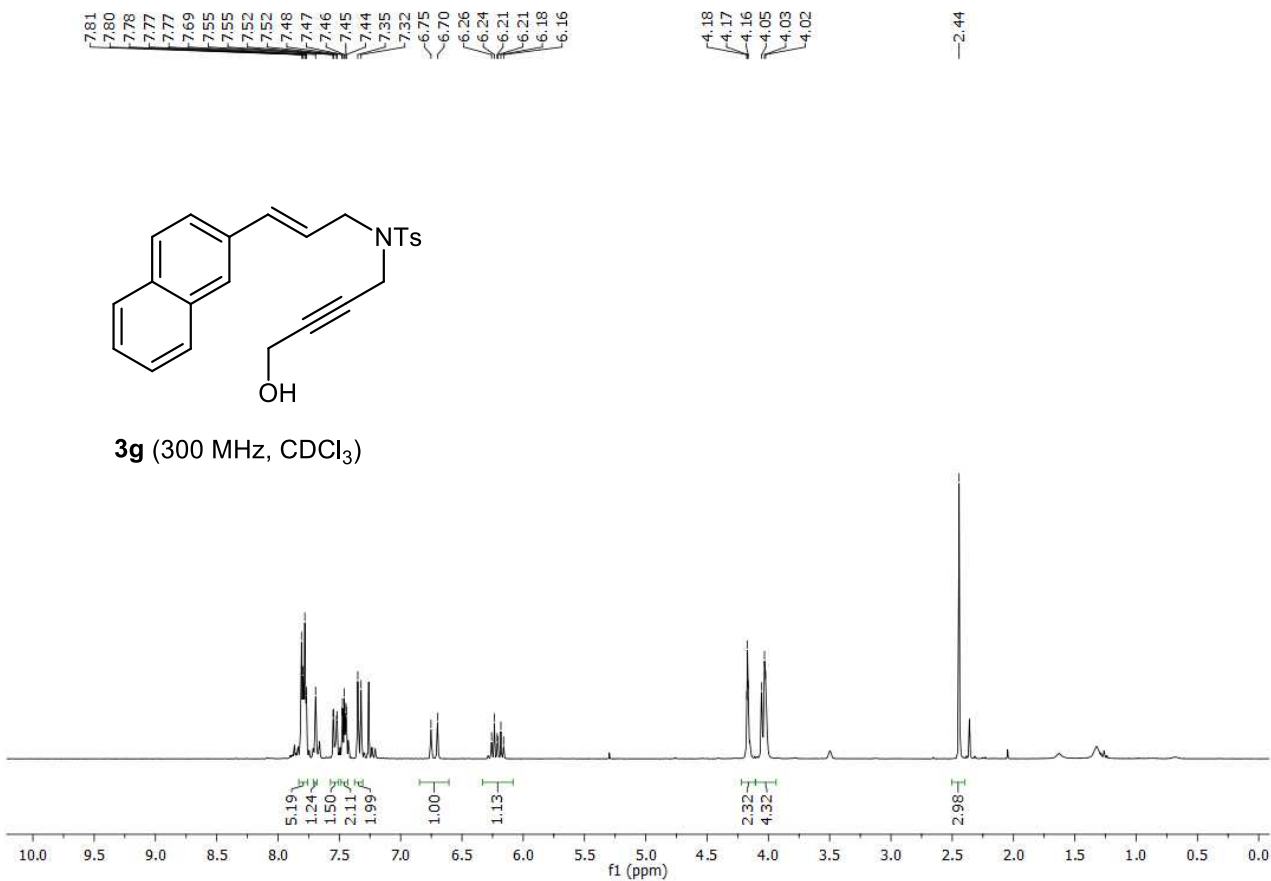


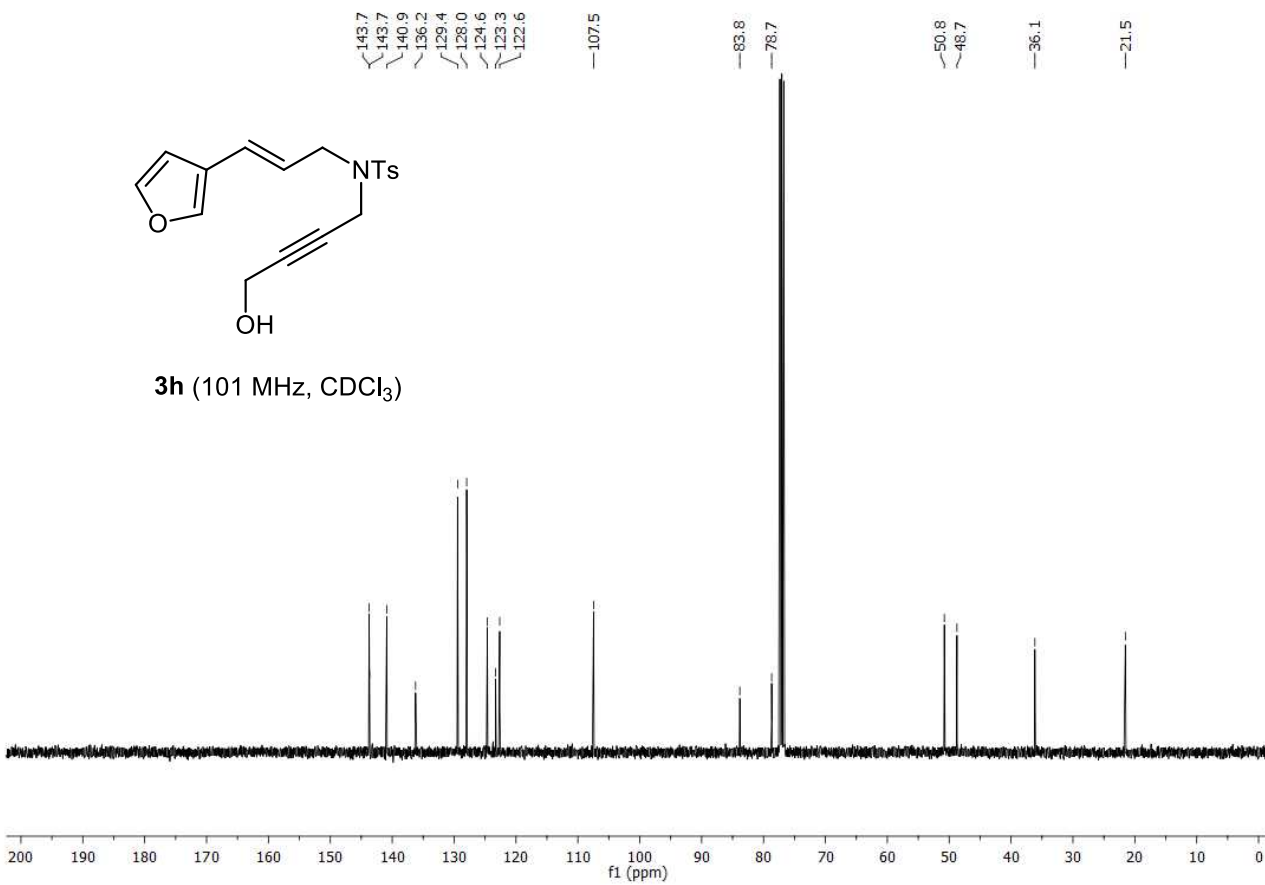
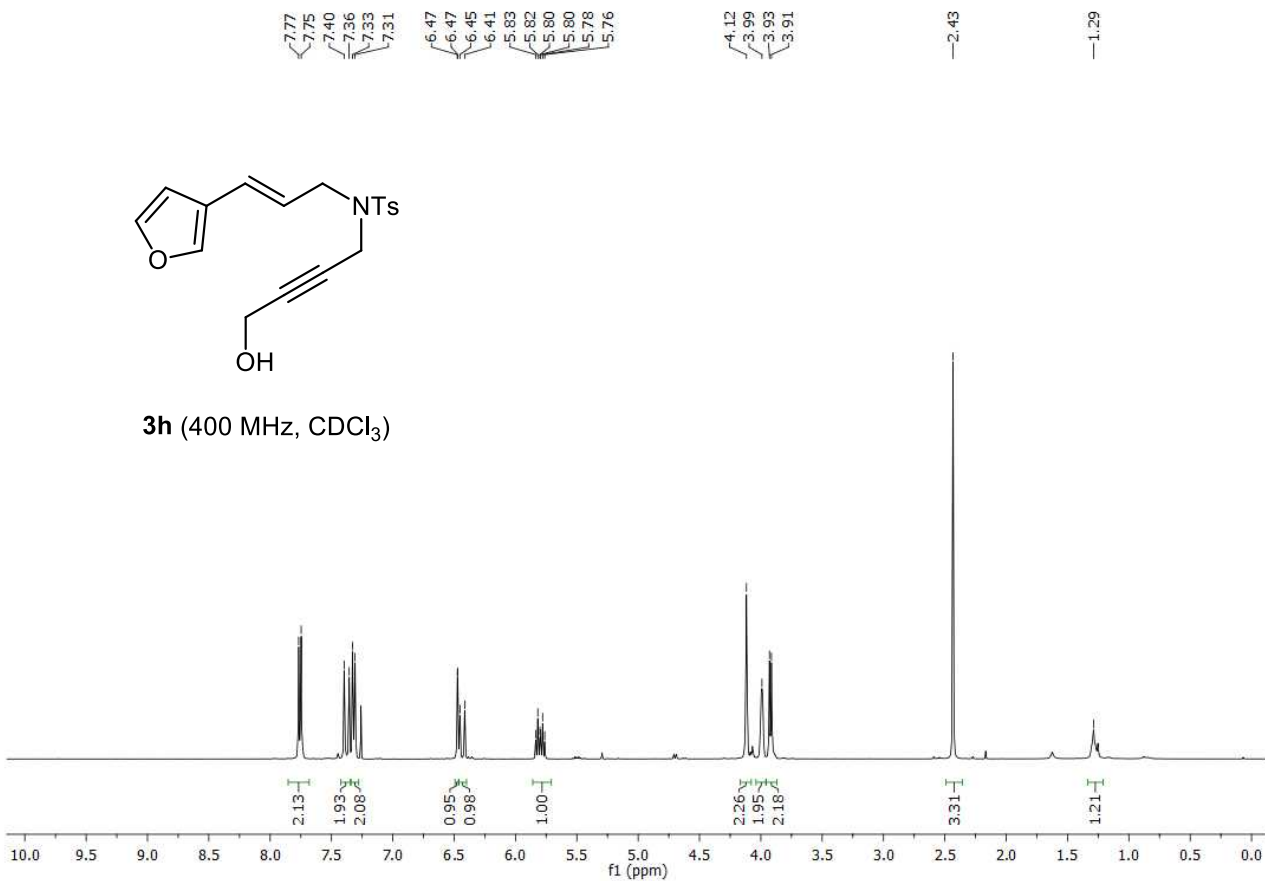
3f (400 MHz, CDCl₃)

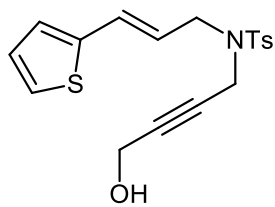


3f (101 MHz, CDCl₃)

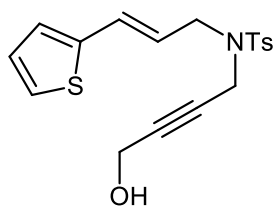
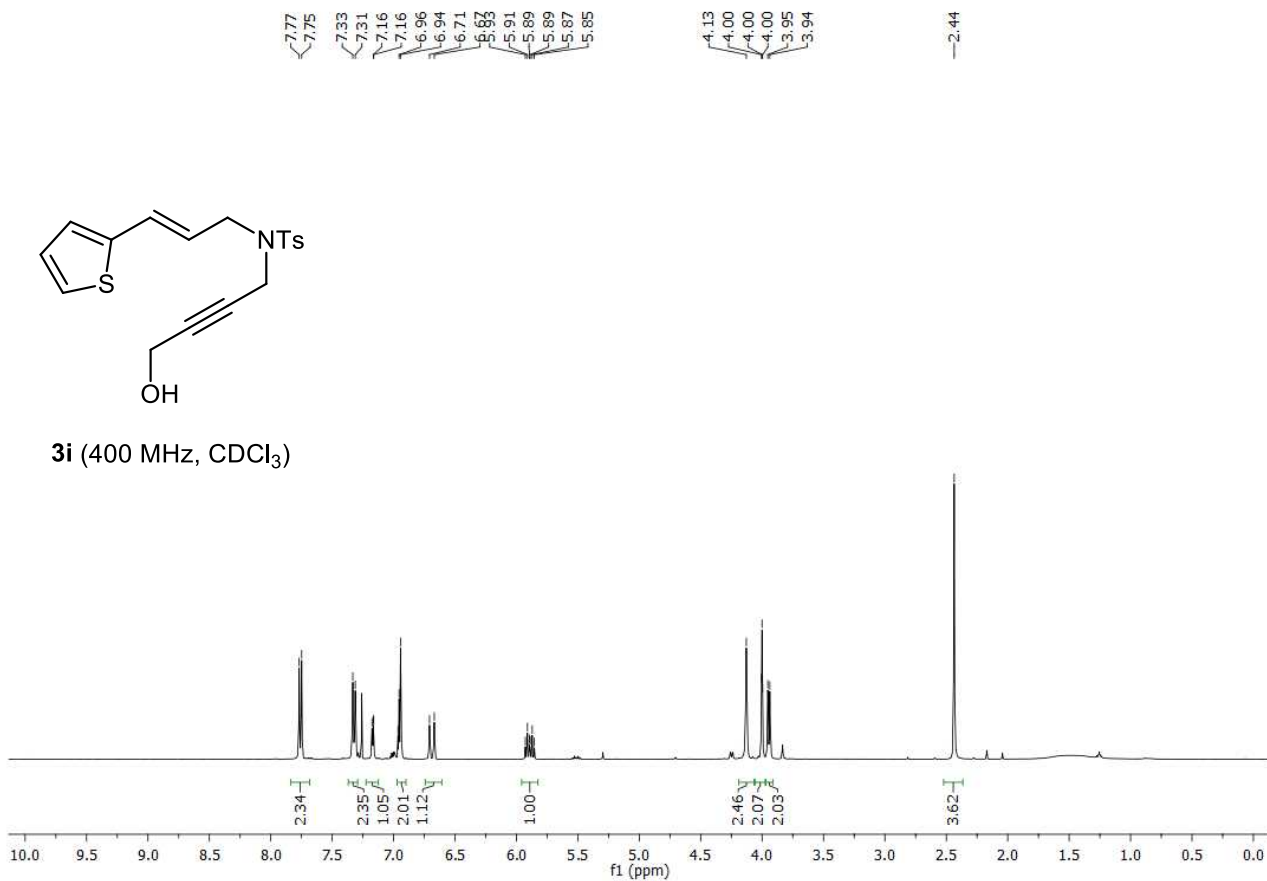




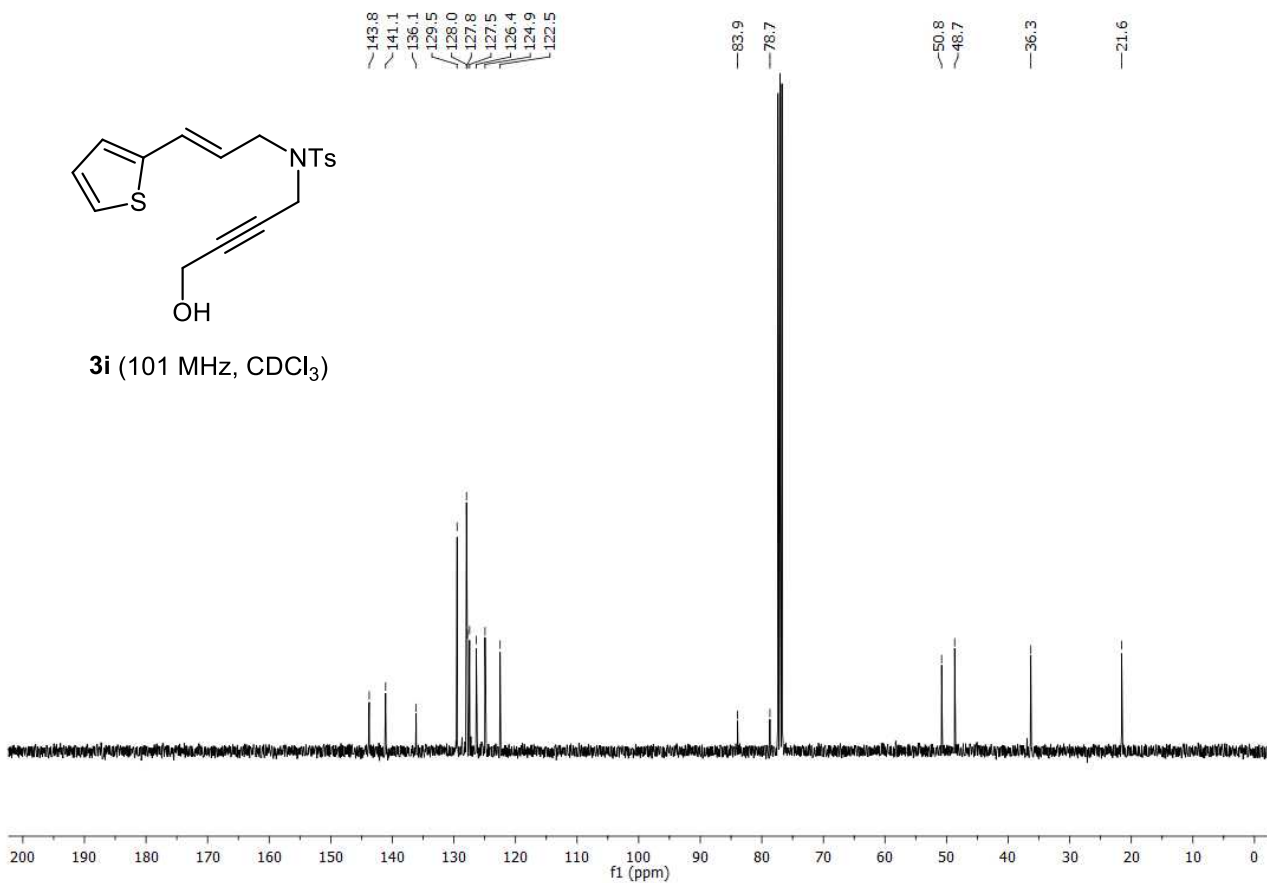


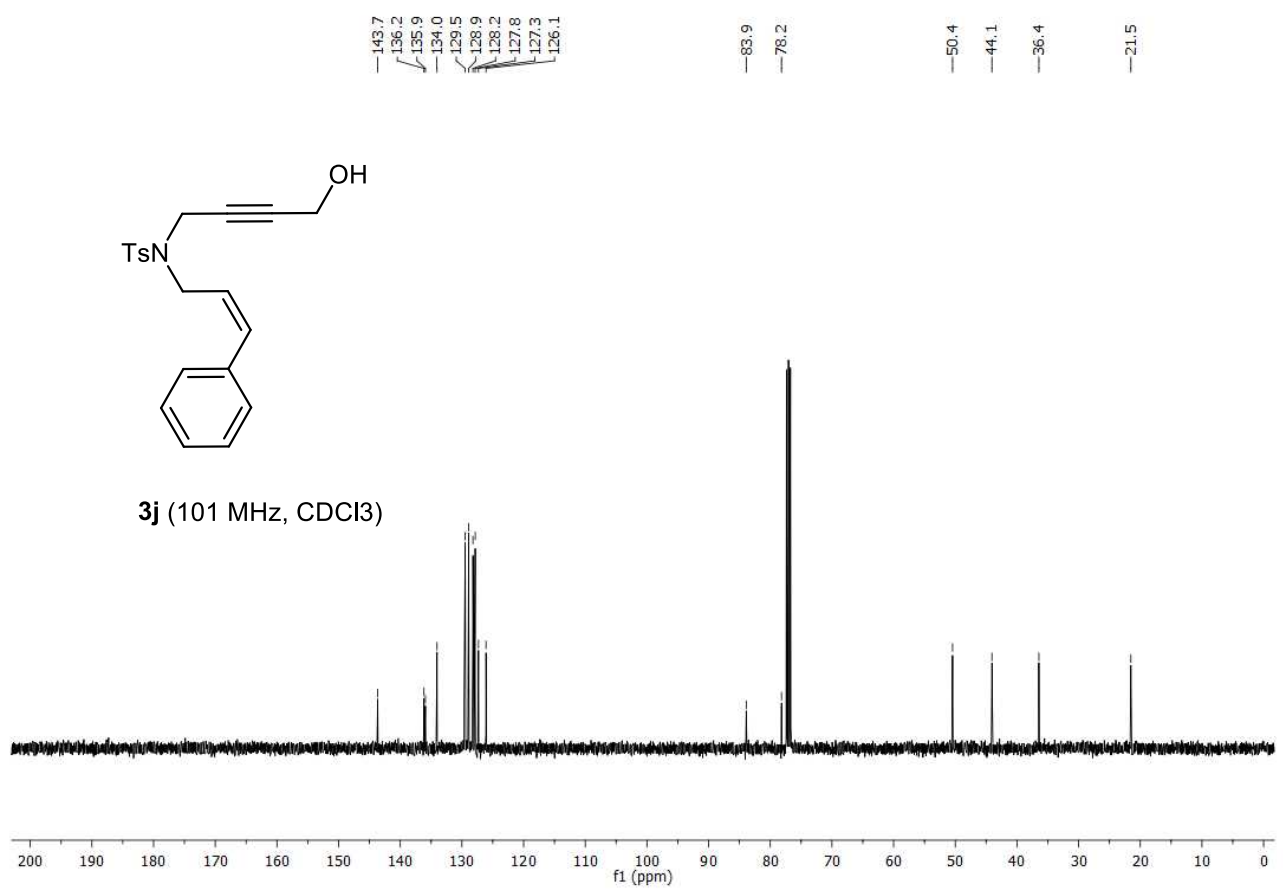
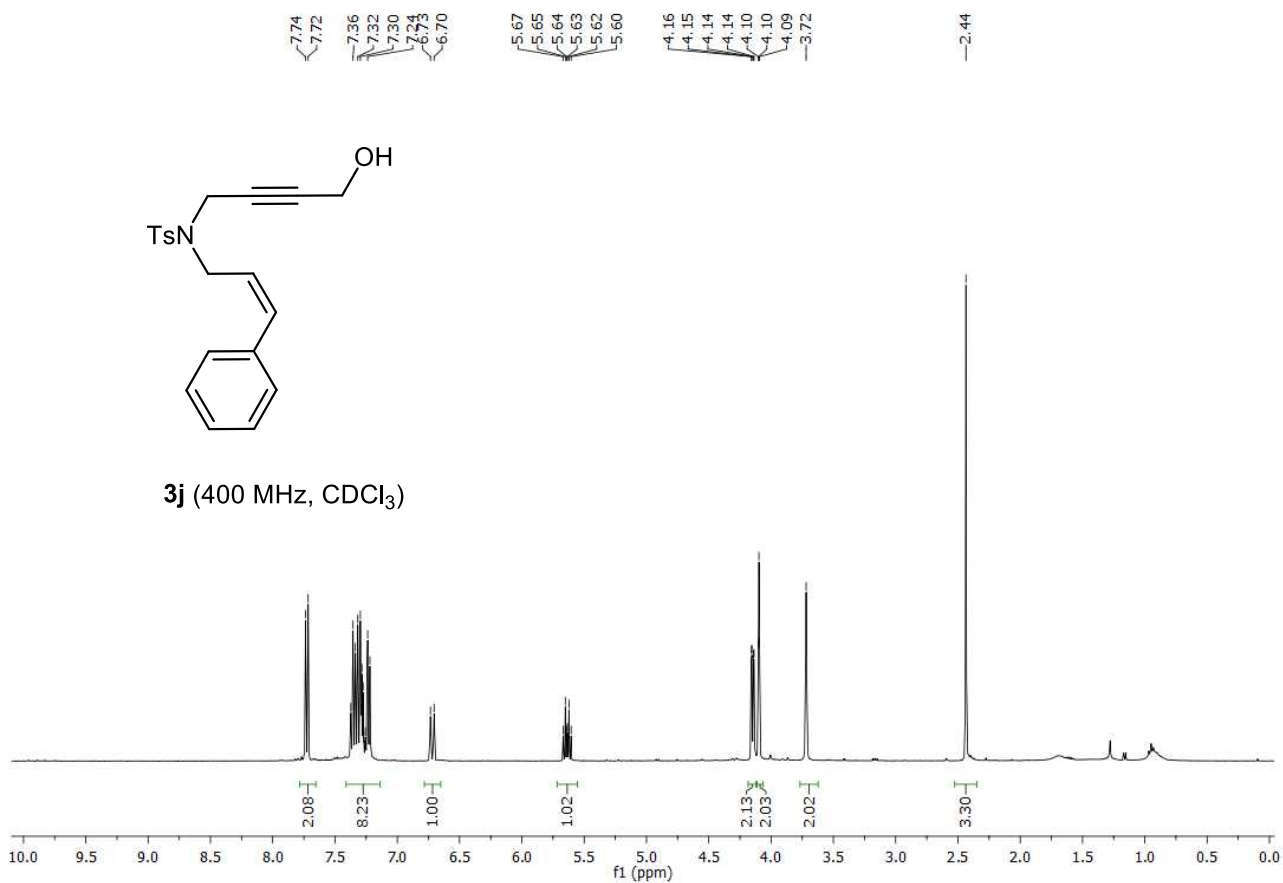


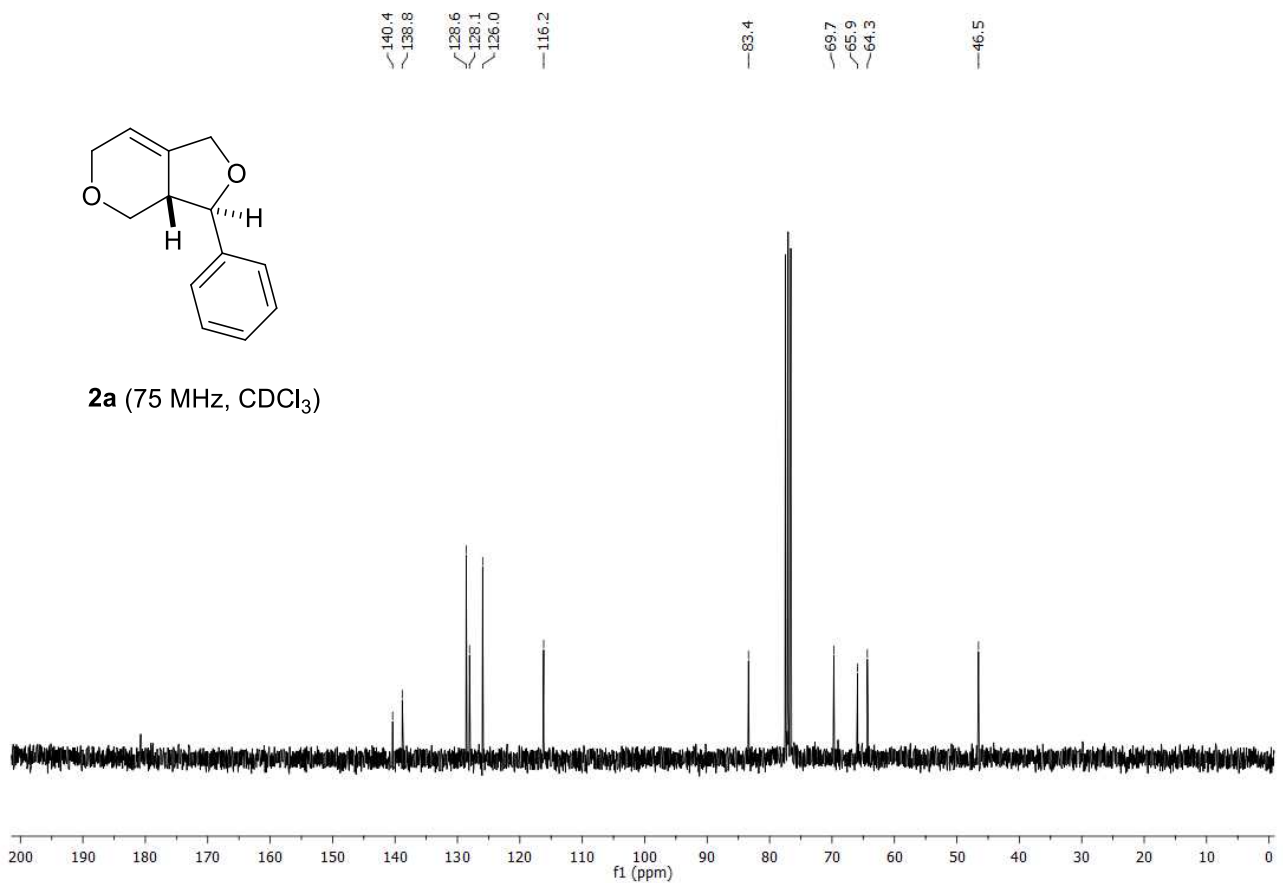
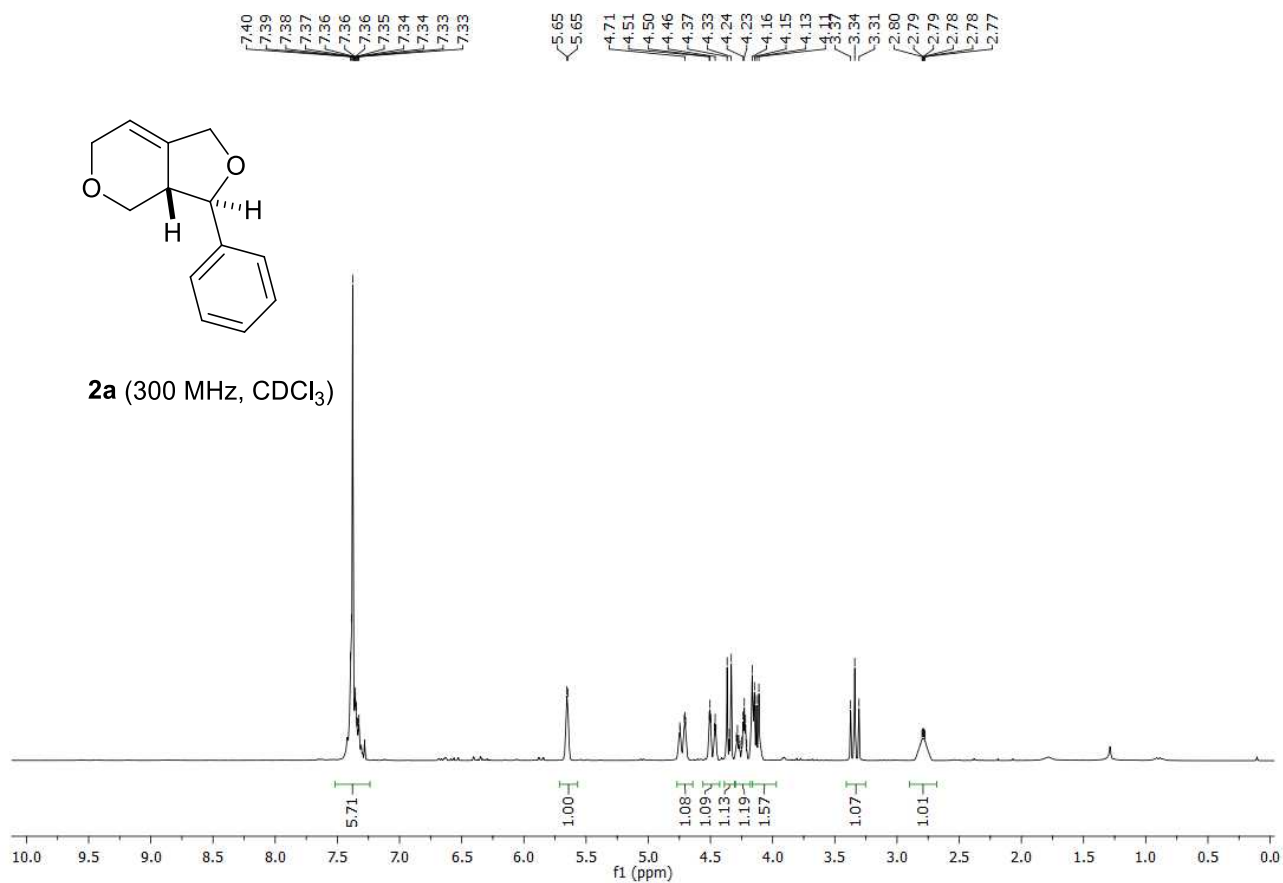
3i (400 MHz, CDCl₃)

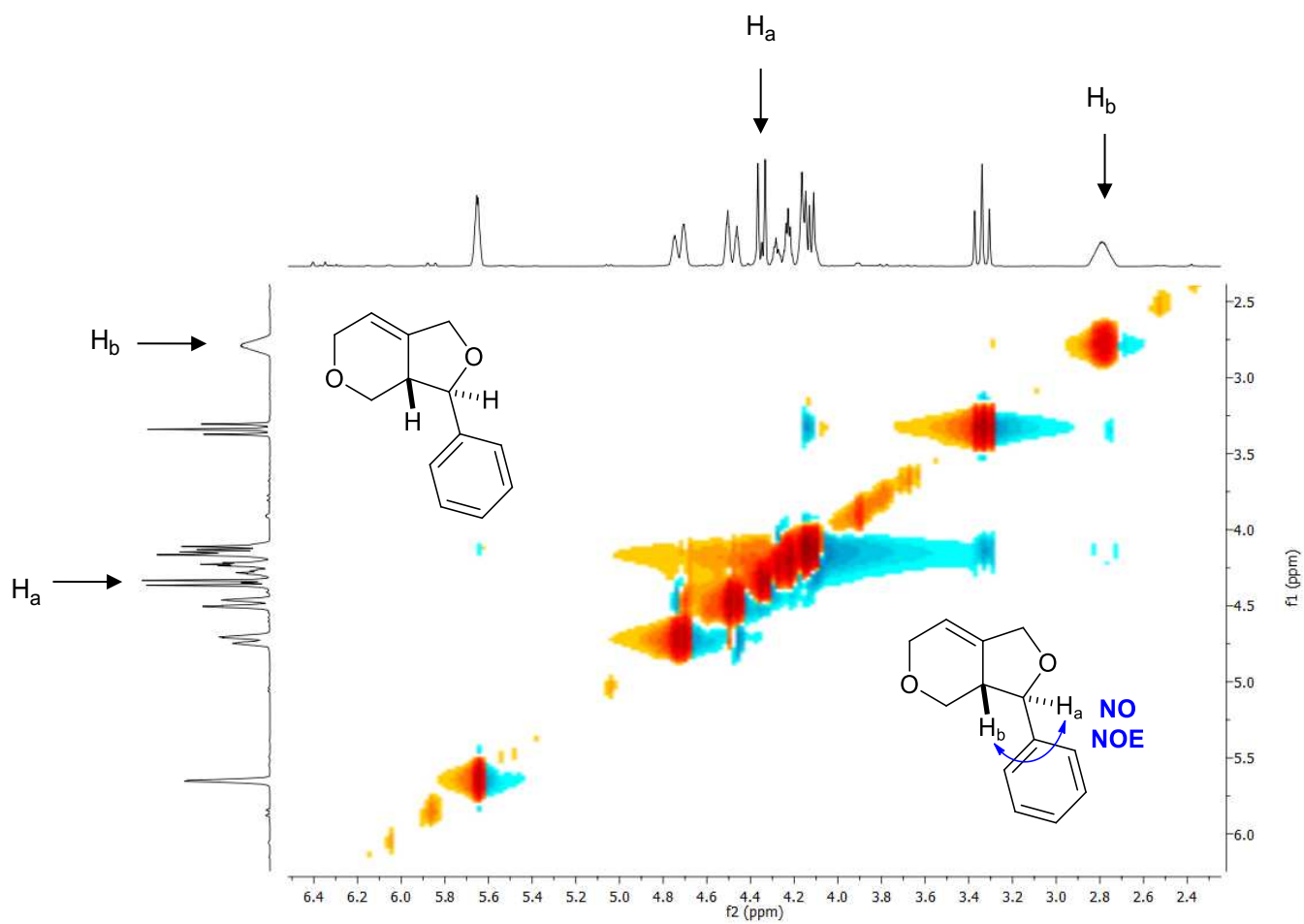


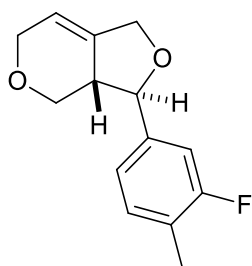
3i (101 MHz, CDCl₃)



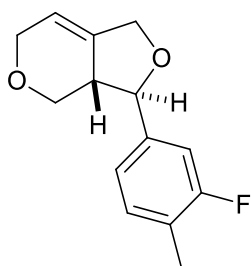
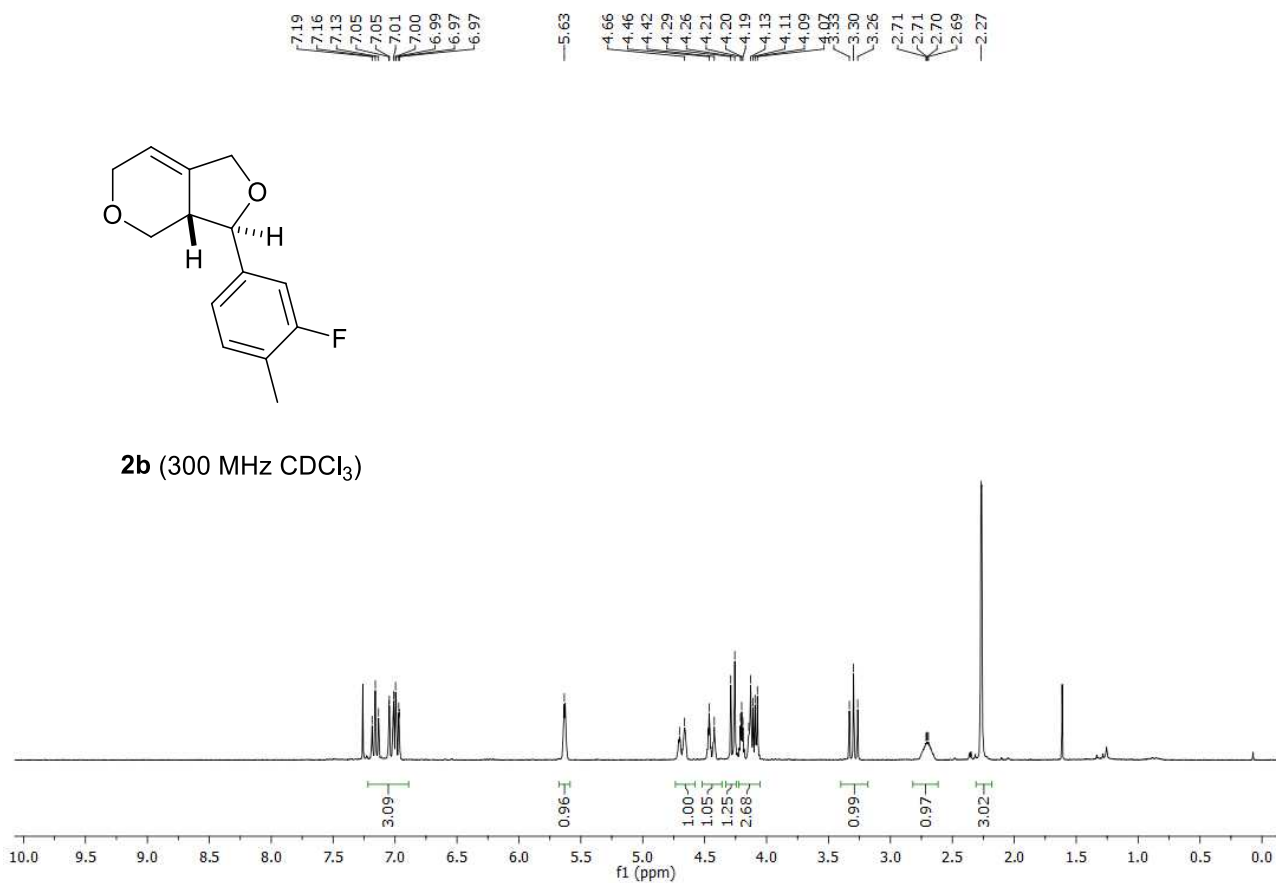




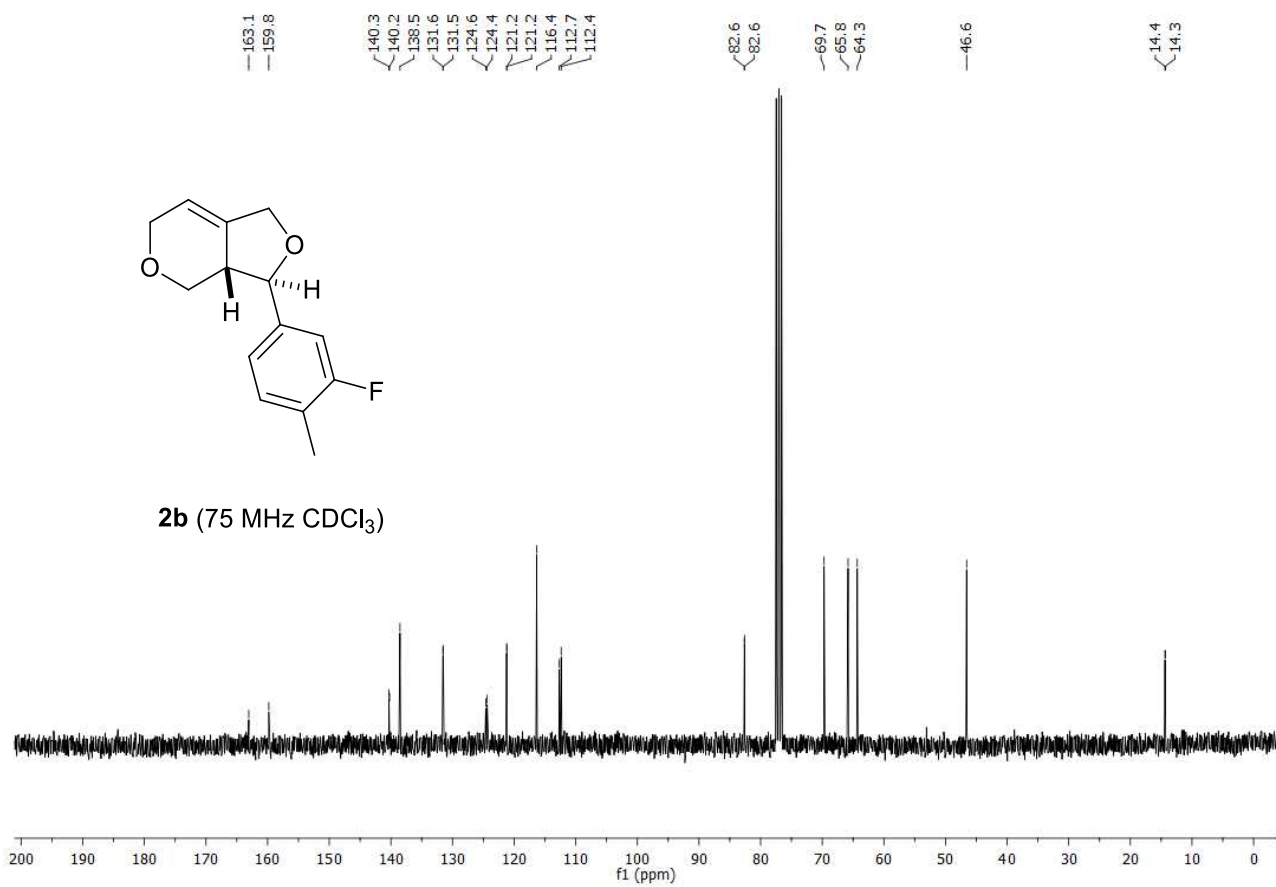


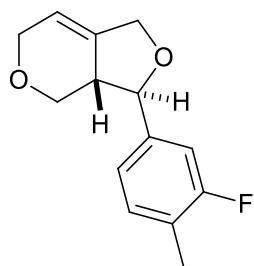


2b (300 MHz CDCl₃)

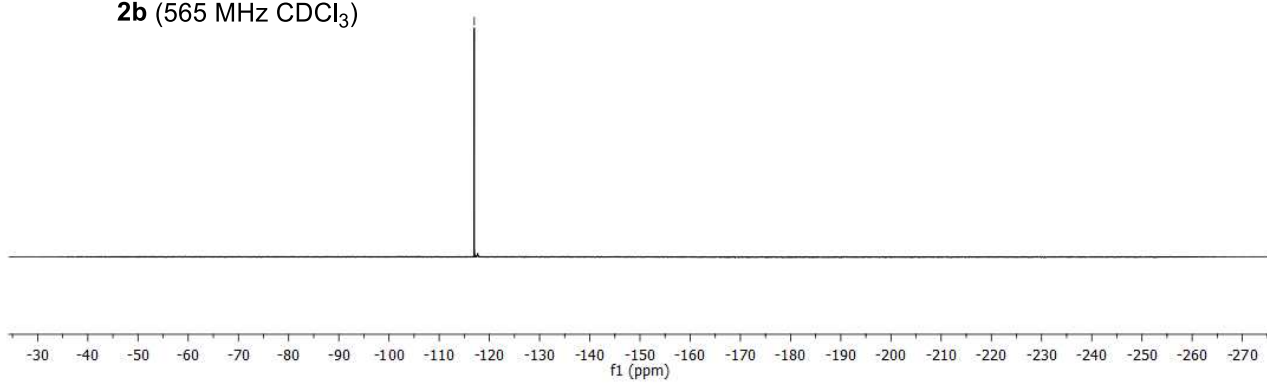


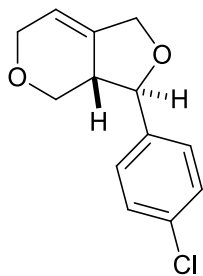
2b (75 MHz CDCl₃)



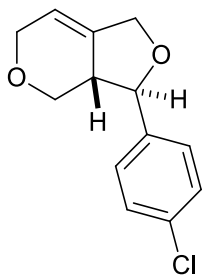
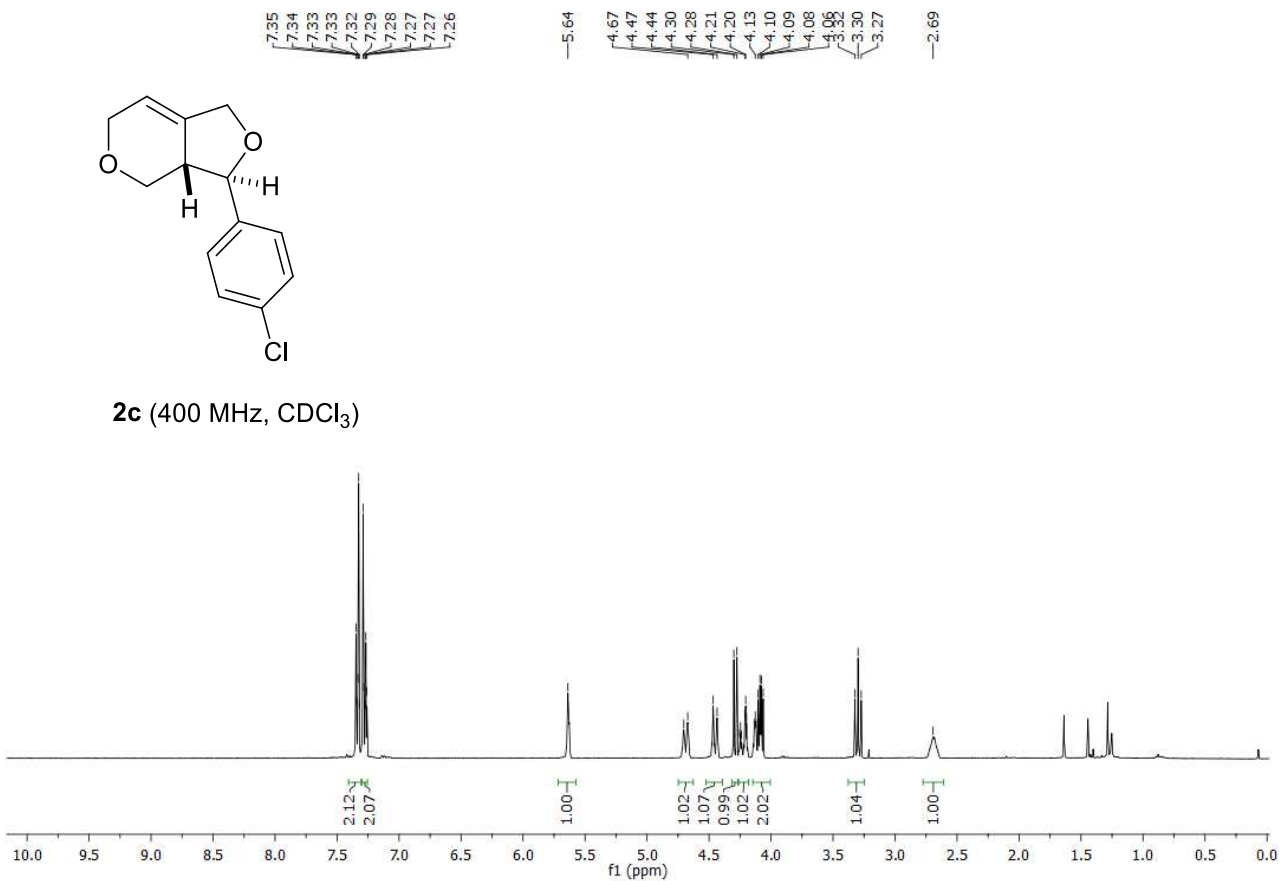


2b (565 MHz CDCl₃)

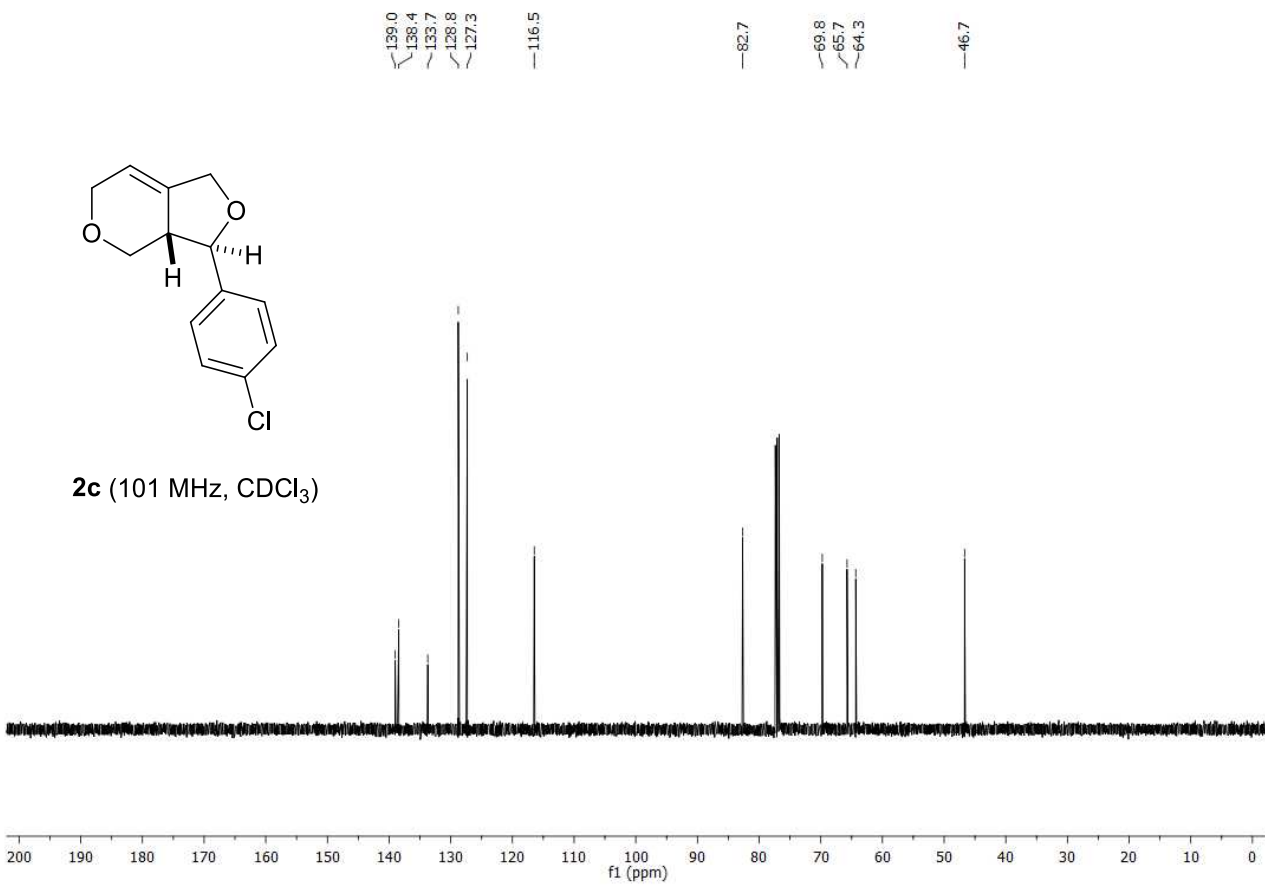




2c (400 MHz, CDCl₃)

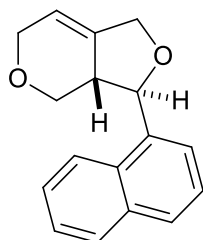


2c (101 MHz, CDCl₃)

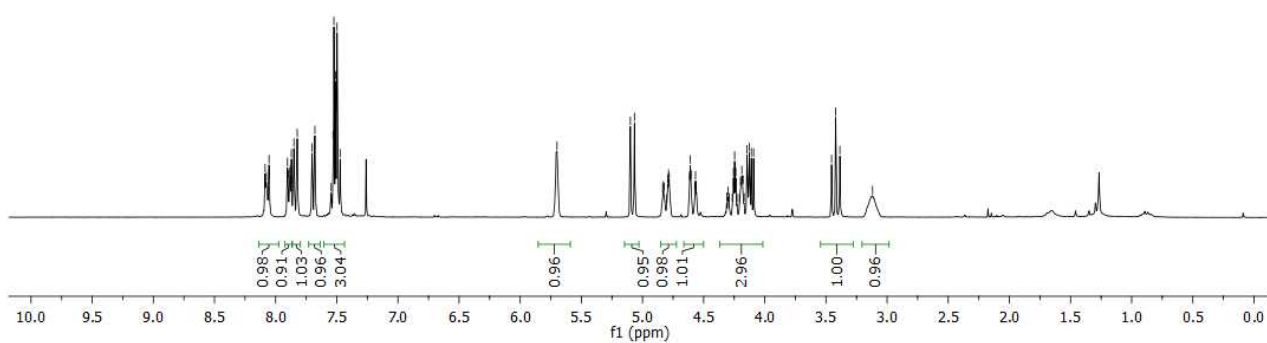


8.09
8.08
8.05
7.90
7.90
7.88
7.88
7.87
7.85
7.82
7.70
7.68
7.55
7.53
7.52
7.51
7.50
7.47

5.70
5.10
5.07
4.79
4.61
4.26
4.25
4.24
4.19
4.14
4.13
4.11
3.98
3.45
3.42
3.39
3.12



2d (300 MHz, CDCl₃)



139.0
135.3
133.9
131.3
128.9
128.8
126.2
125.7
125.5
123.6
123.3
116.3

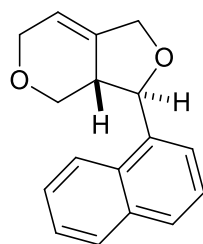
80.6

69.6

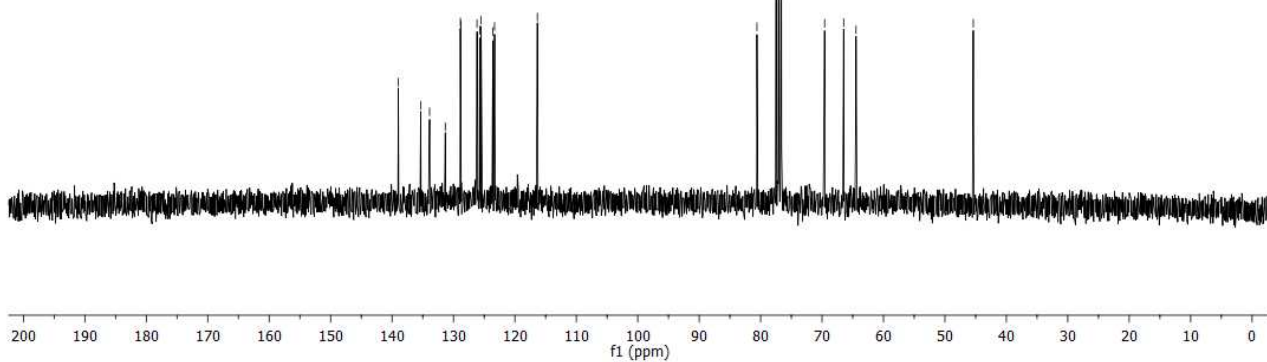
66.5

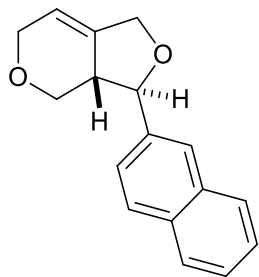
64.5

45.4

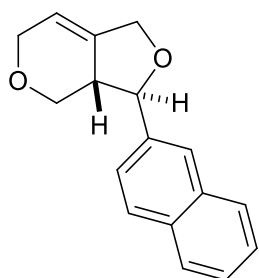
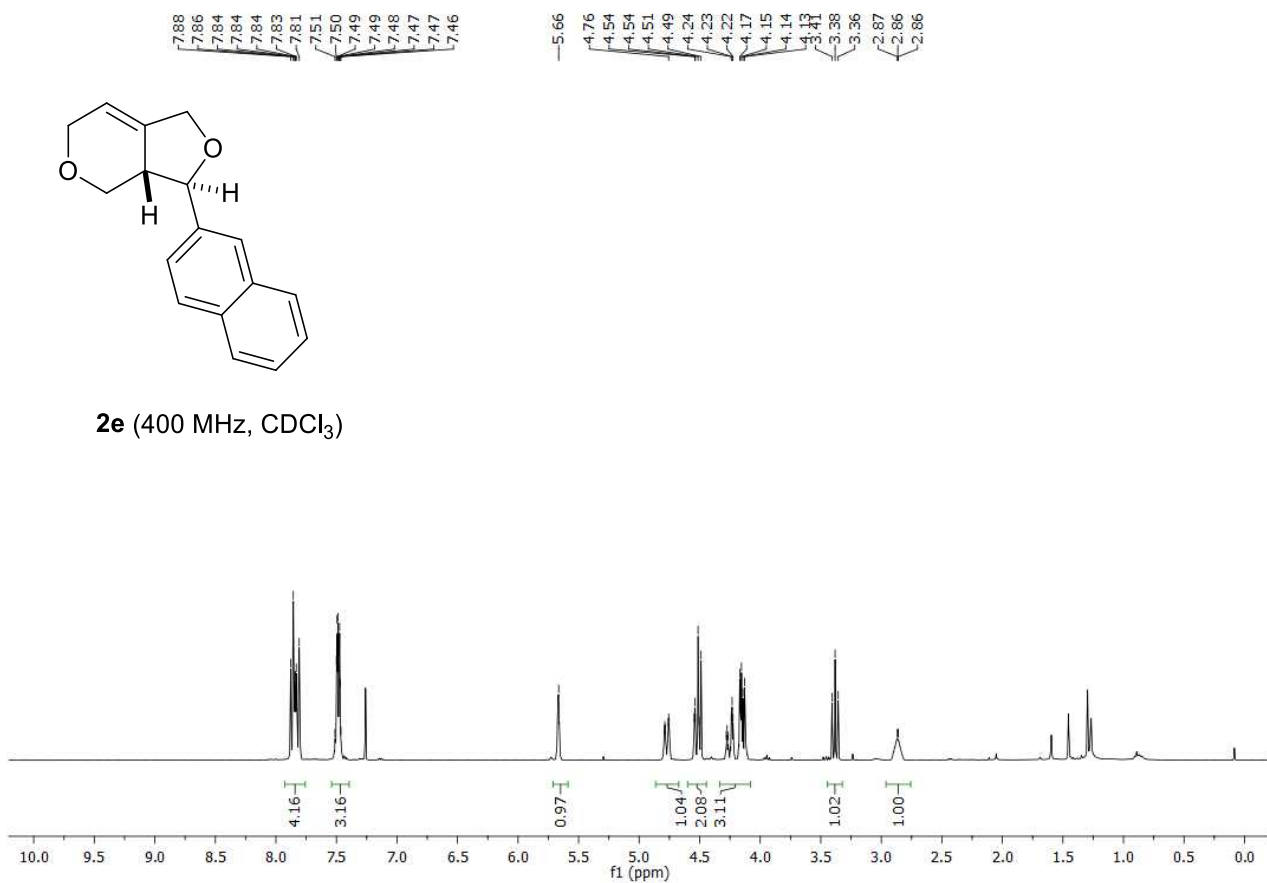


2d (75 MHz, CDCl₃)

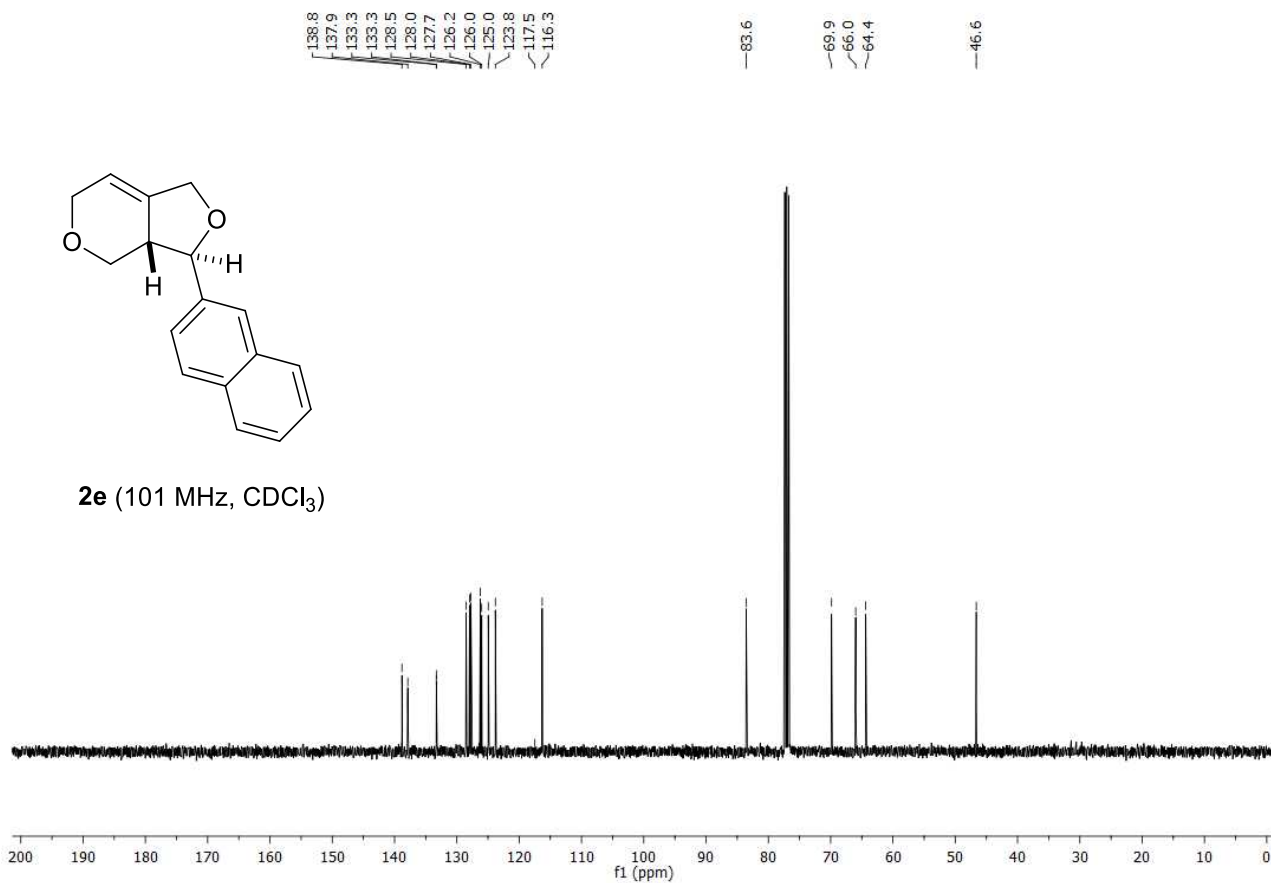


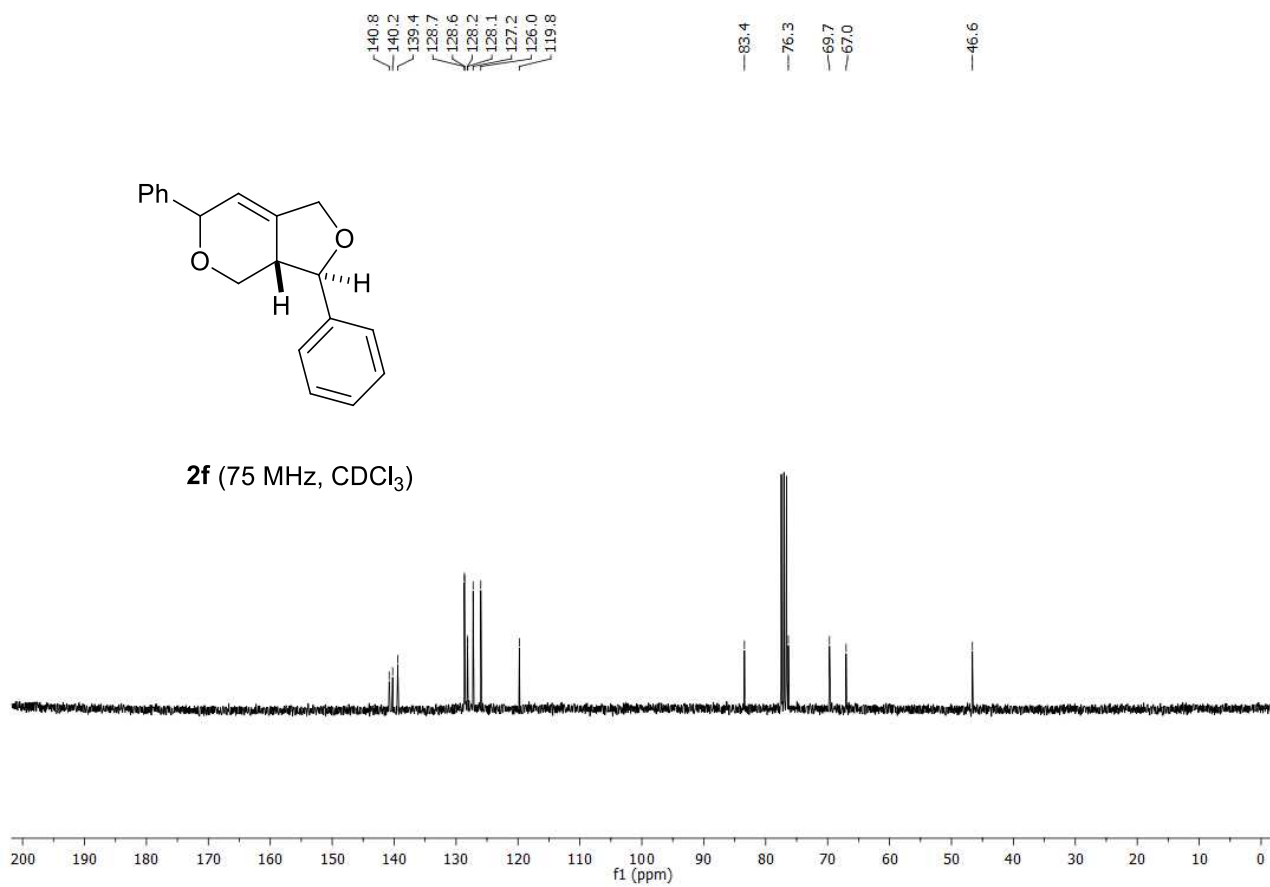
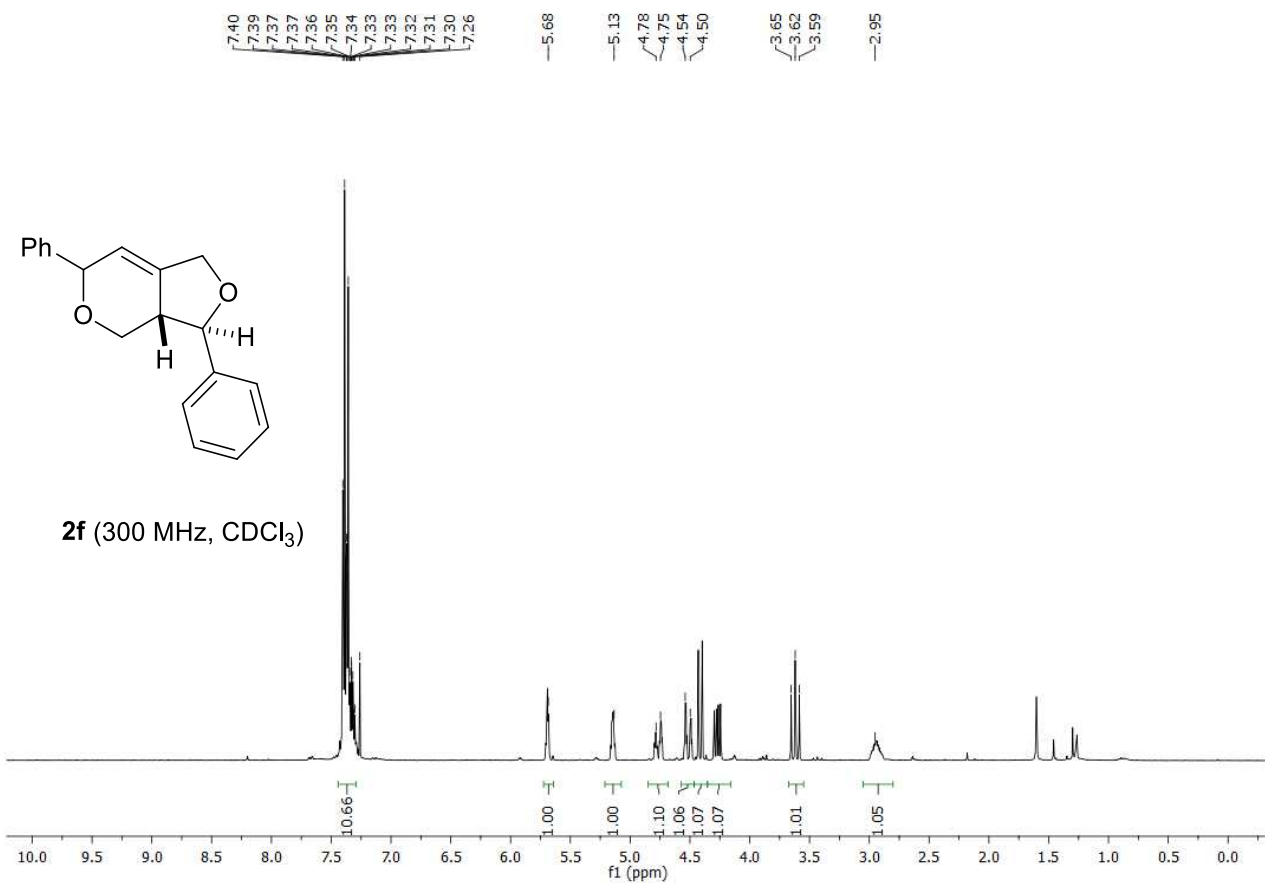


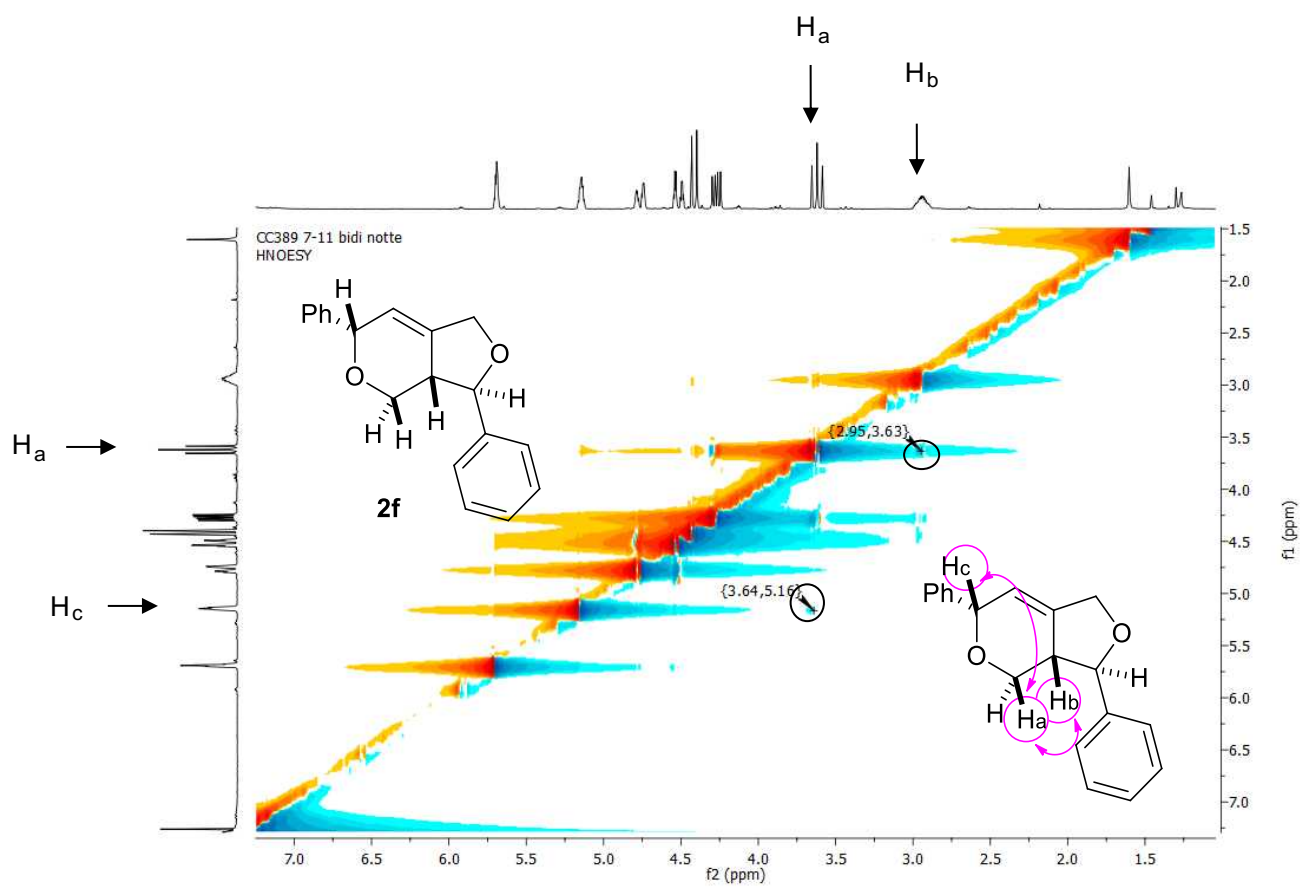
2e (400 MHz, CDCl₃)

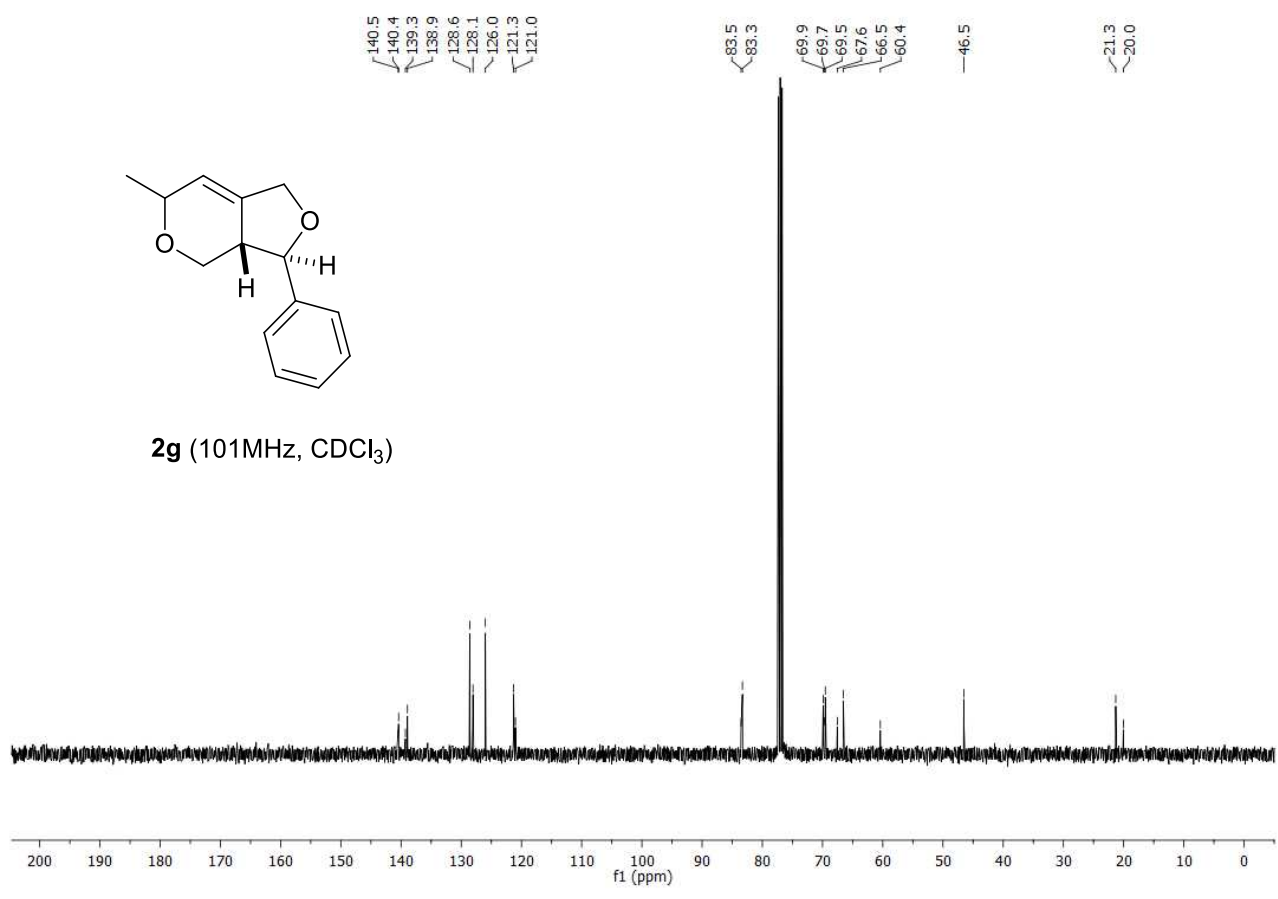
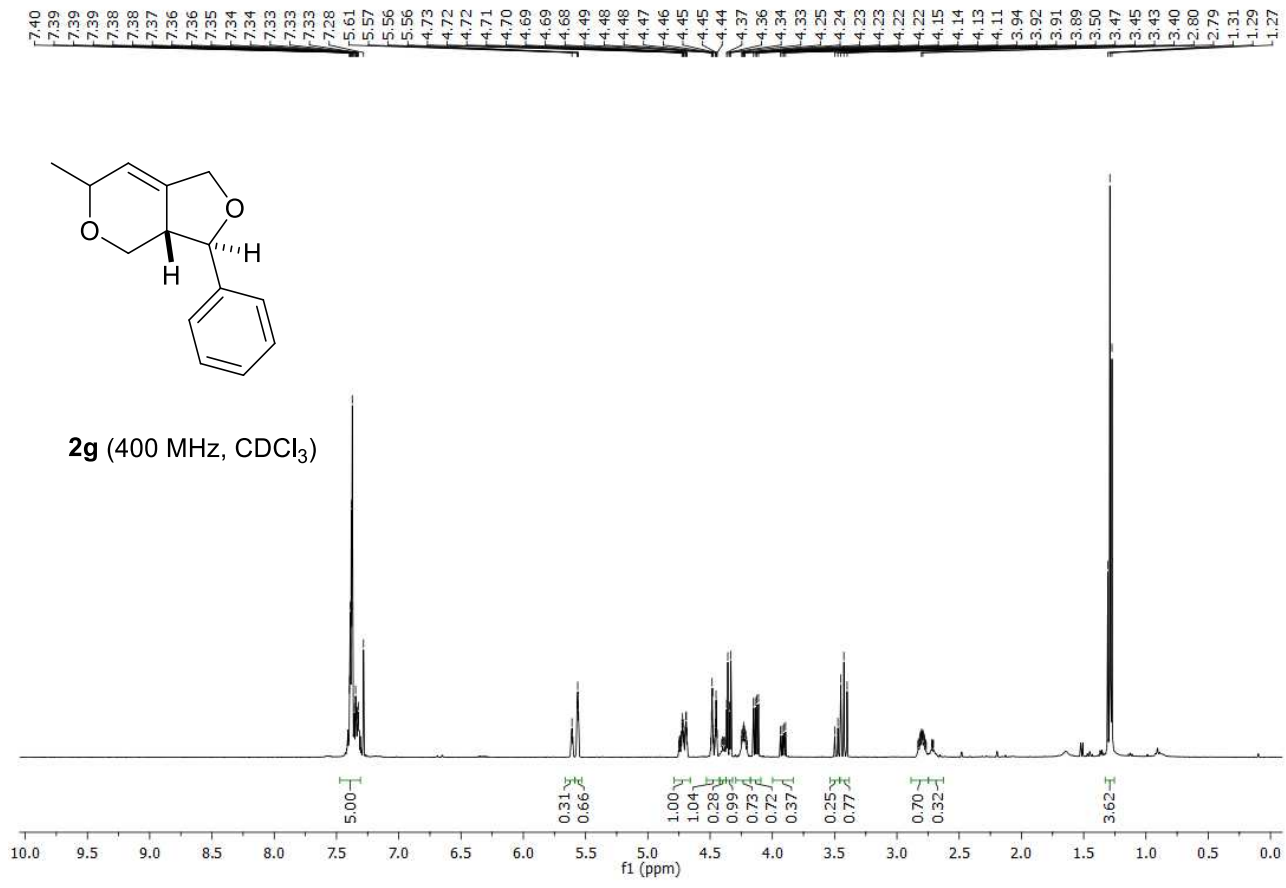


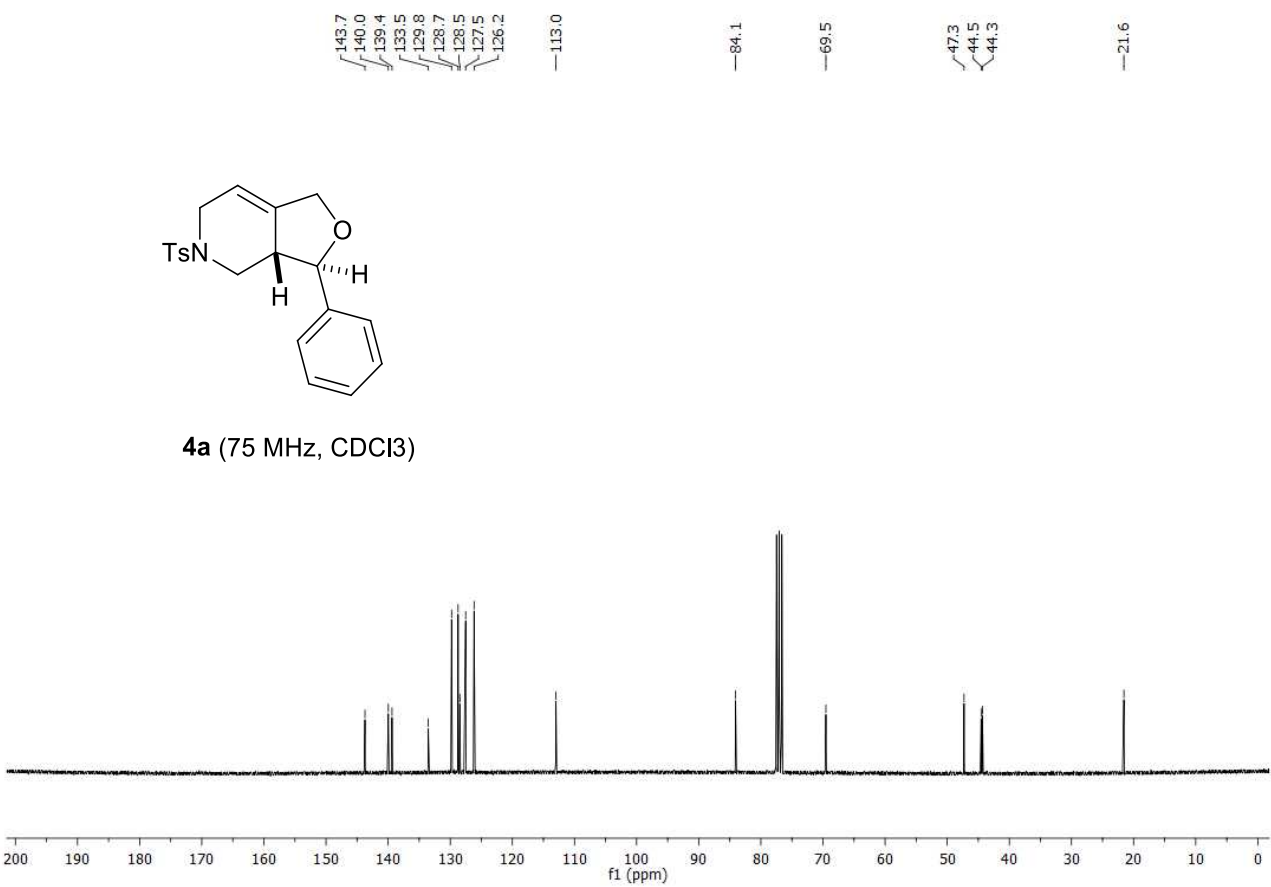
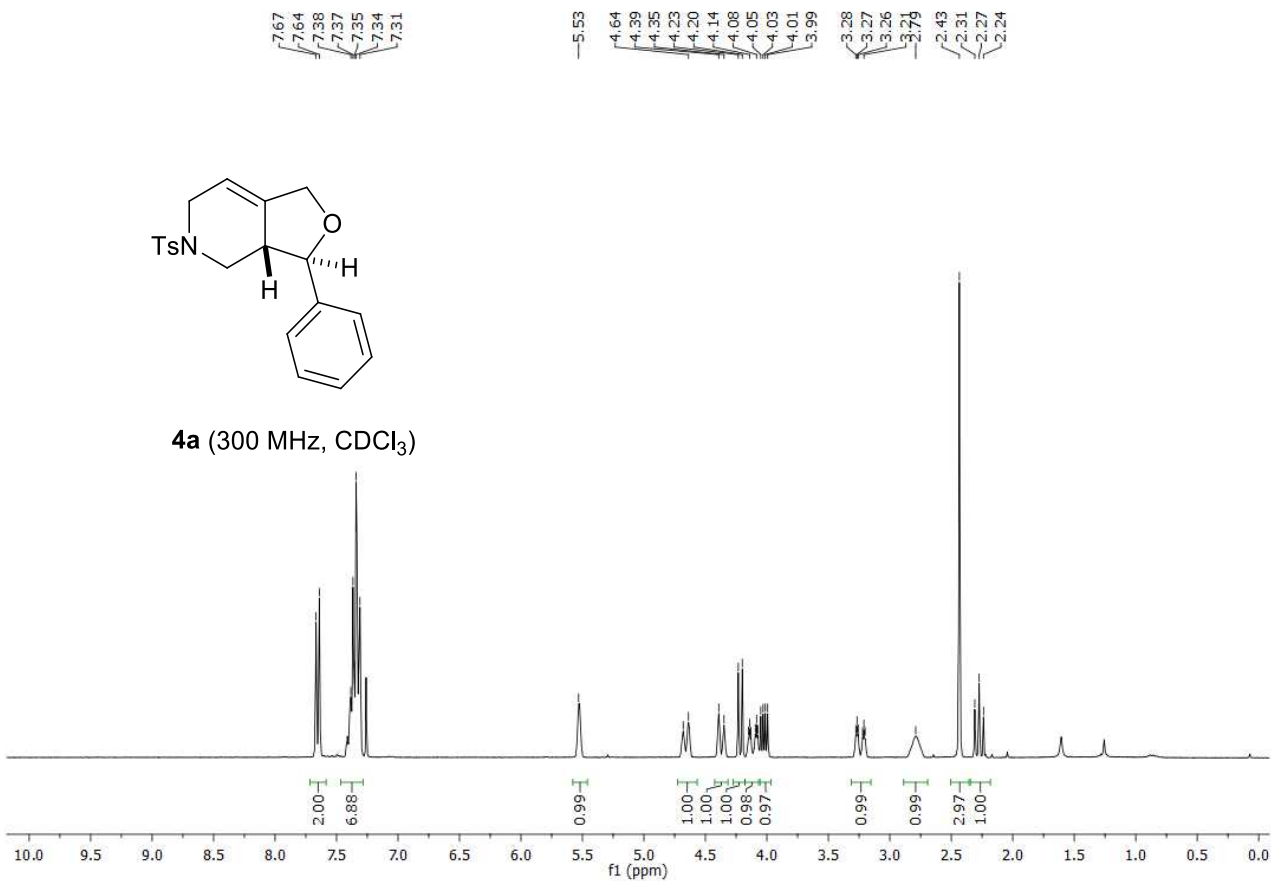
2e (101 MHz, CDCl₃)

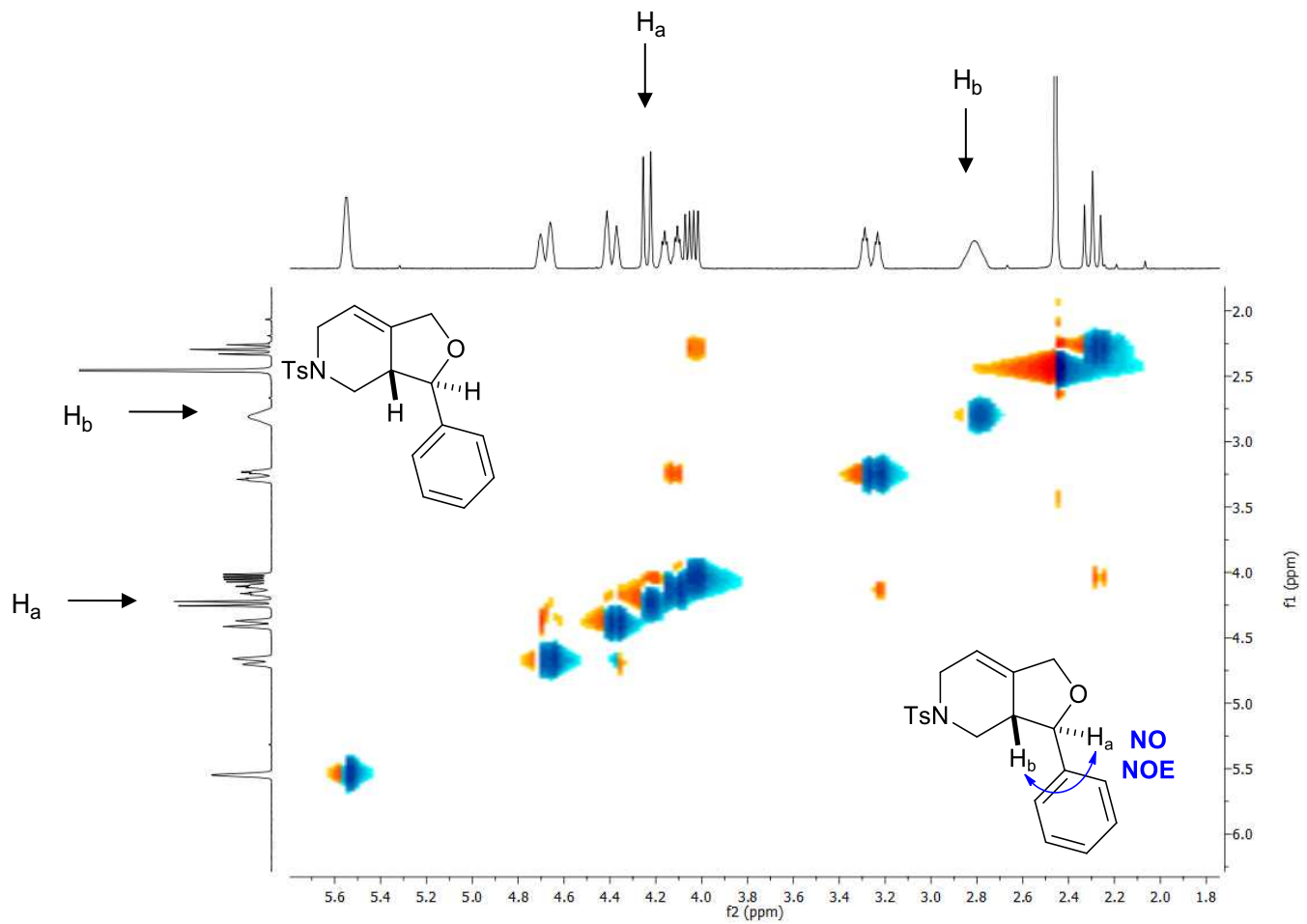


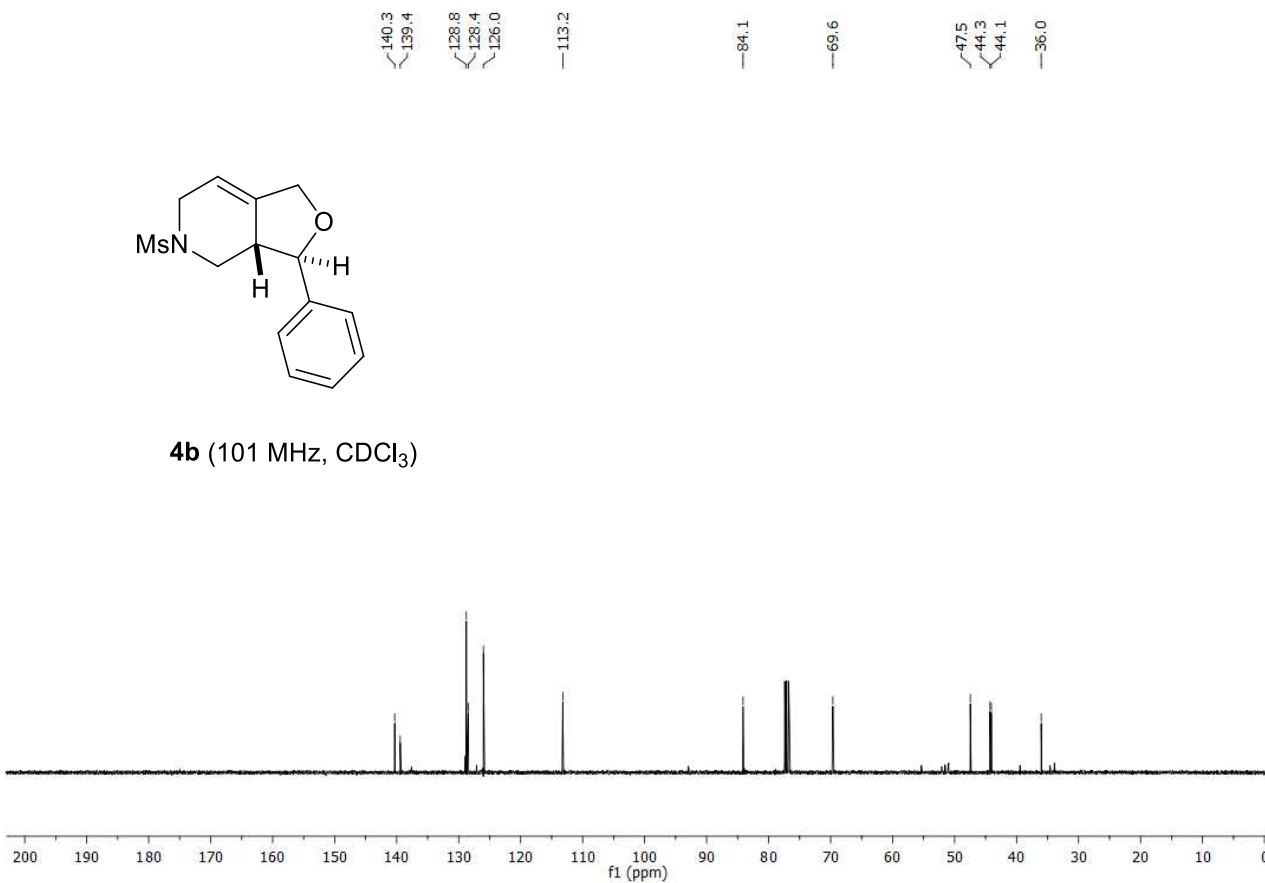
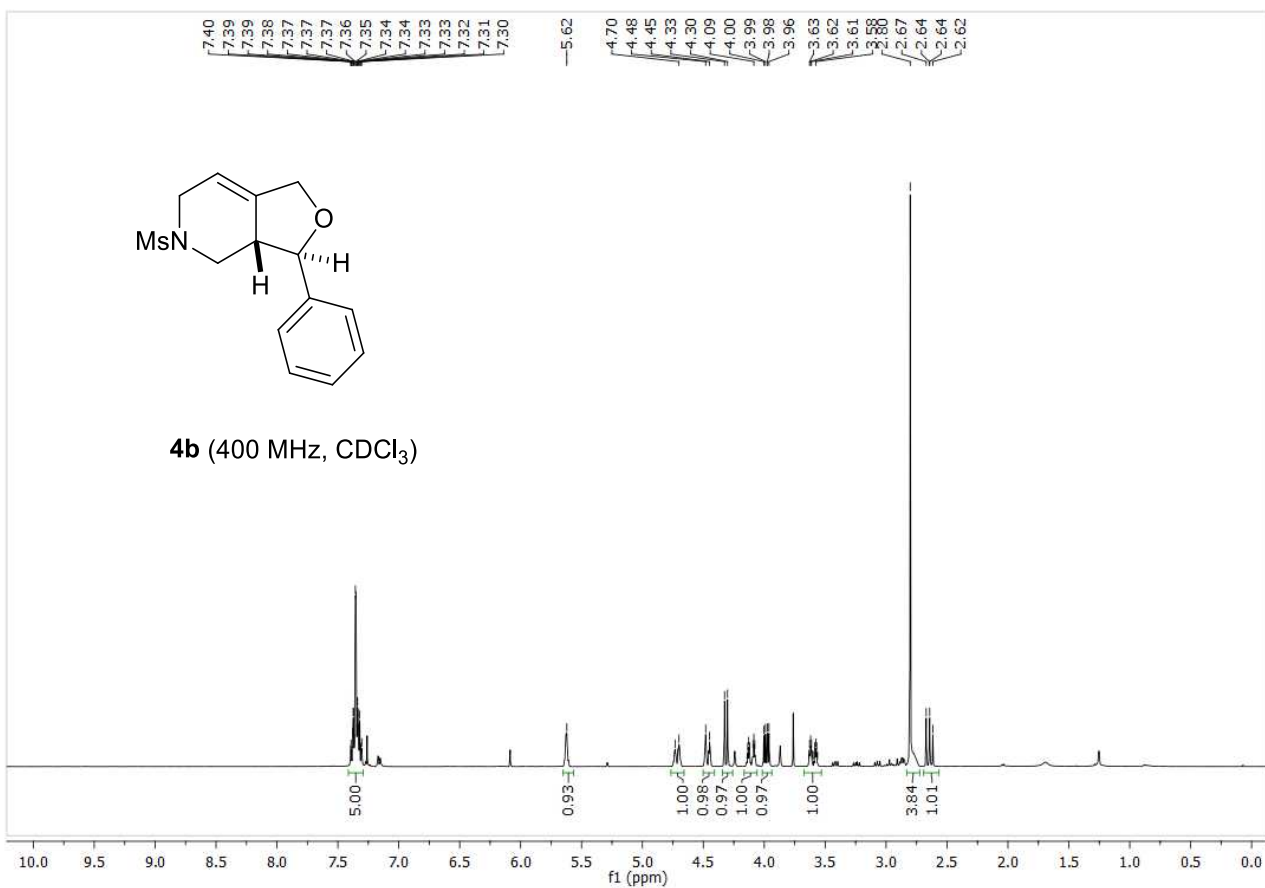




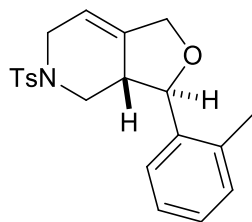




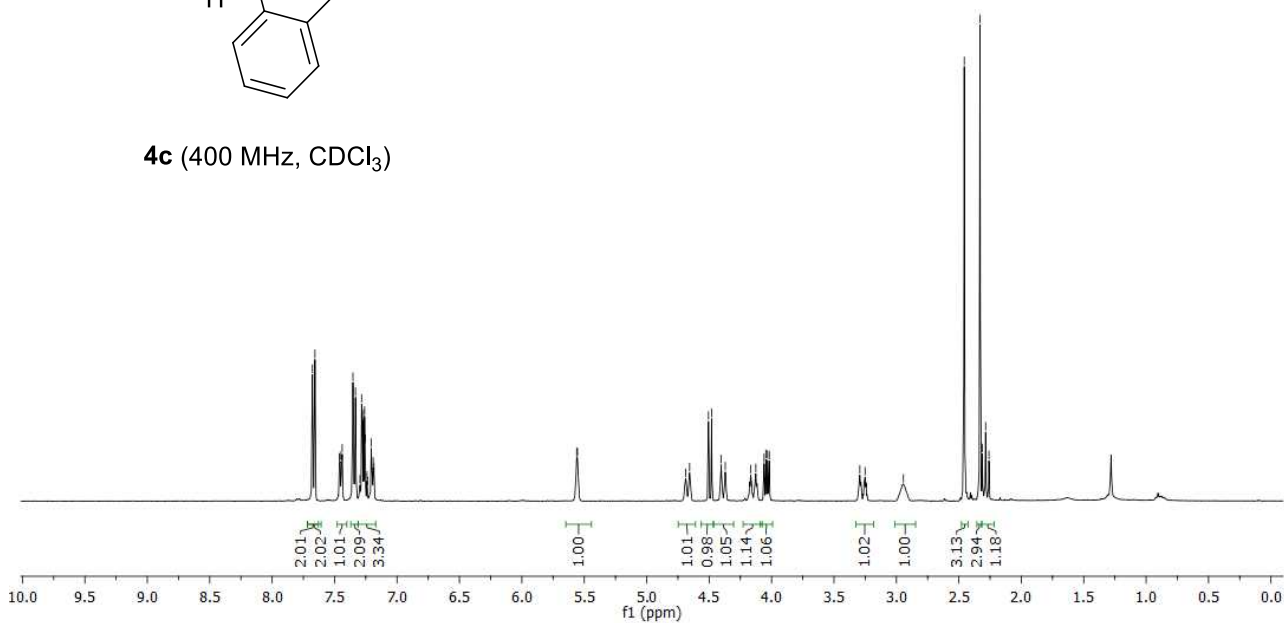




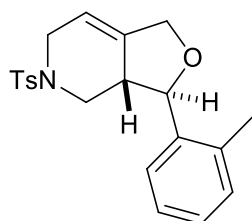
7.68
7.66
7.46
7.45
7.44
7.35
7.33
7.30
7.28
7.28
7.27
7.26
7.25
7.24
7.24
7.21
7.19
7.18
5.56
5.55
4.69
4.66
4.51
4.48
4.40
4.37
4.17
4.13
4.06
4.05
4.03
4.02
3.29
3.25
2.94
2.46
2.33
2.31
2.29
2.26



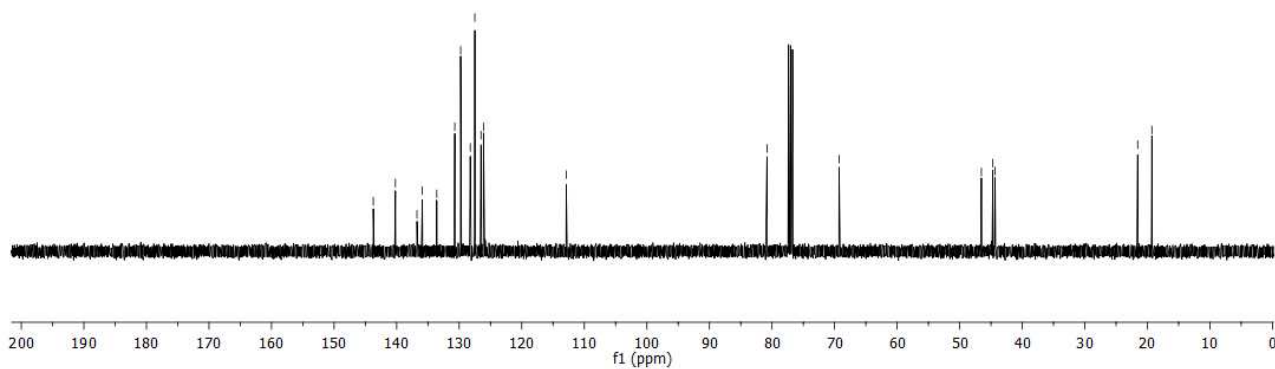
4c (400 MHz, CDCl₃)



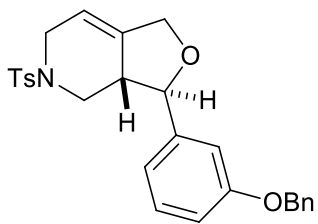
143.7
140.2
136.8
135.9
133.6
130.7
129.8
128.2
127.5
126.5
126.1
112.9
80.8
69.3
46.5
44.7
44.3
21.5
19.3



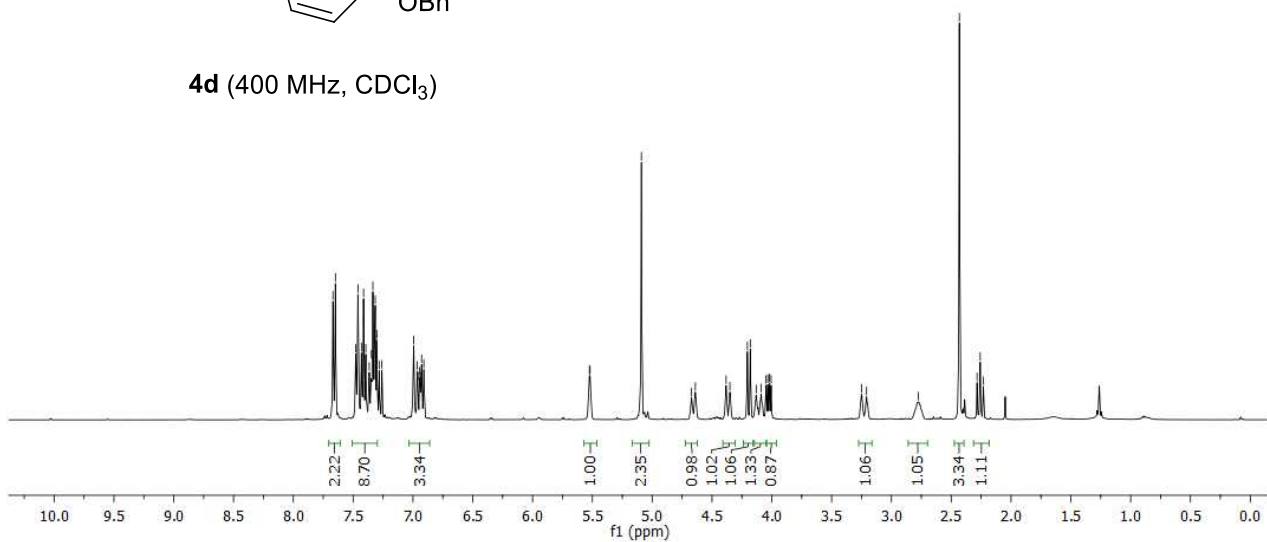
4c (101 MHz, CDCl₃)



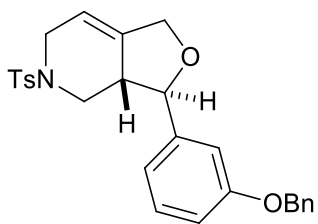
7.67
7.65
7.48
7.46
7.43
7.41
7.39
7.37
7.35
7.34
7.32
7.32
7.30
7.28
7.26
6.99
6.96
6.96
6.94
6.94
6.93
6.91
5.52
5.52
-5.09
4.64
4.38
4.35
4.20
4.18
4.05
4.03
4.02
3.01
3.03
3.21
-2.78
2.43
2.28
2.26
2.23



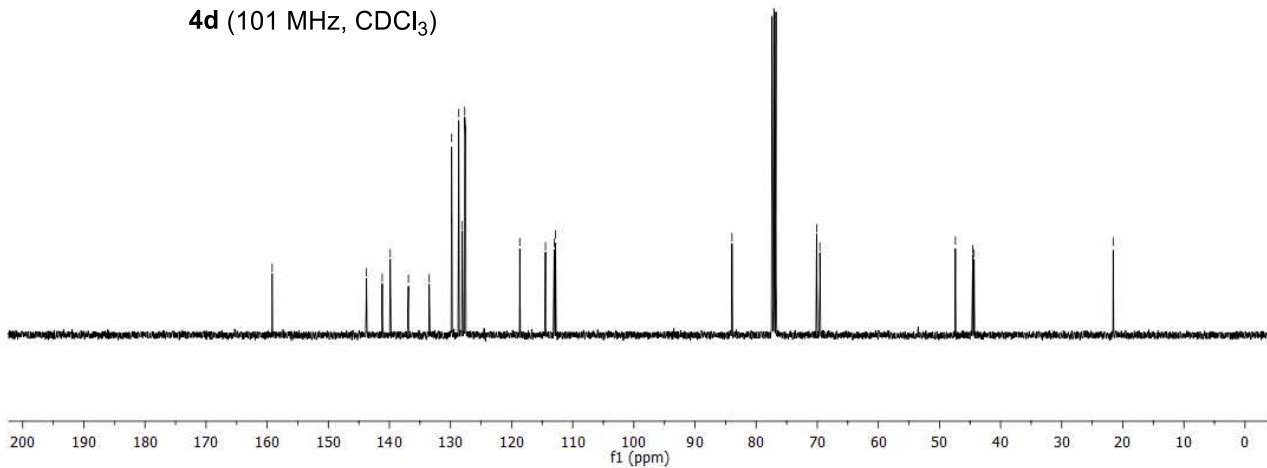
4d (400 MHz, CDCl₃)

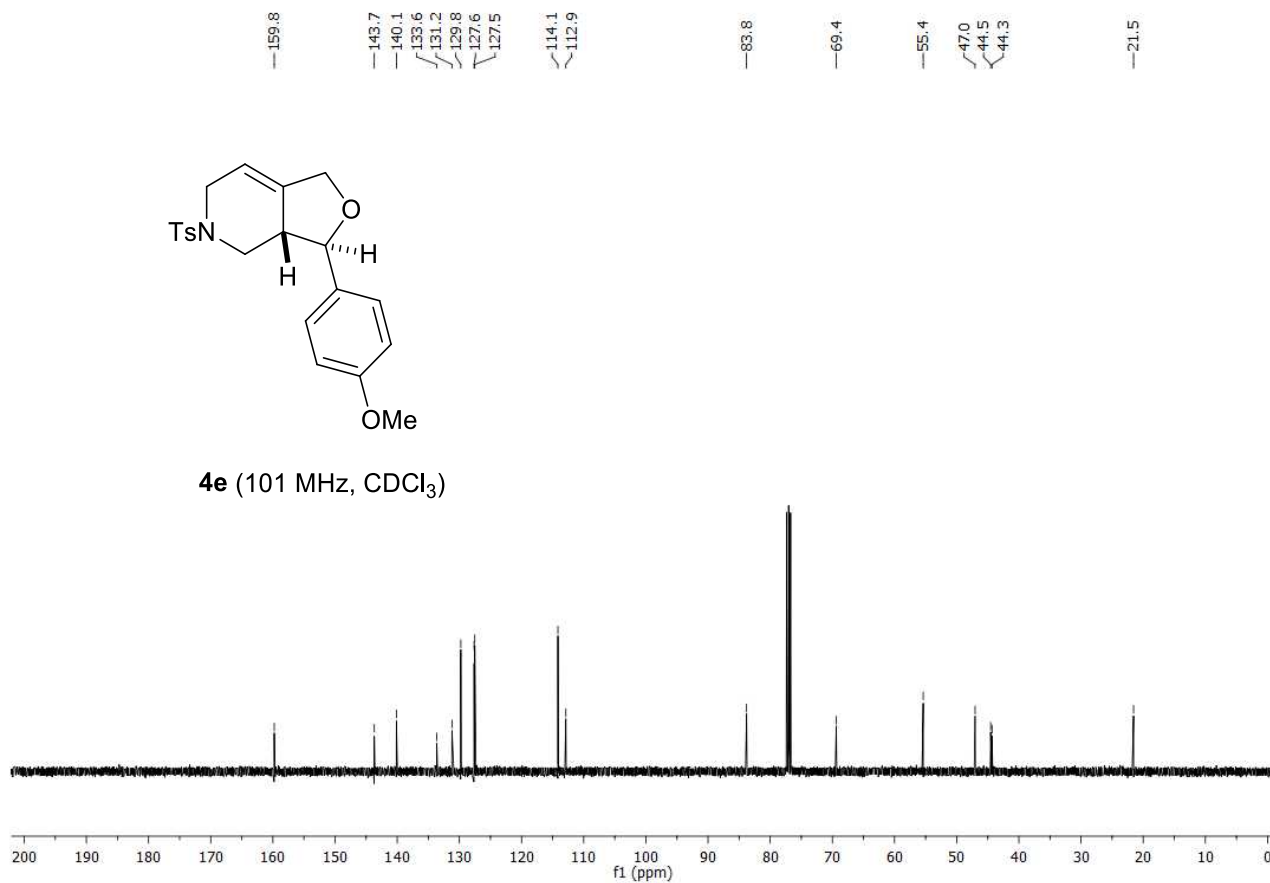
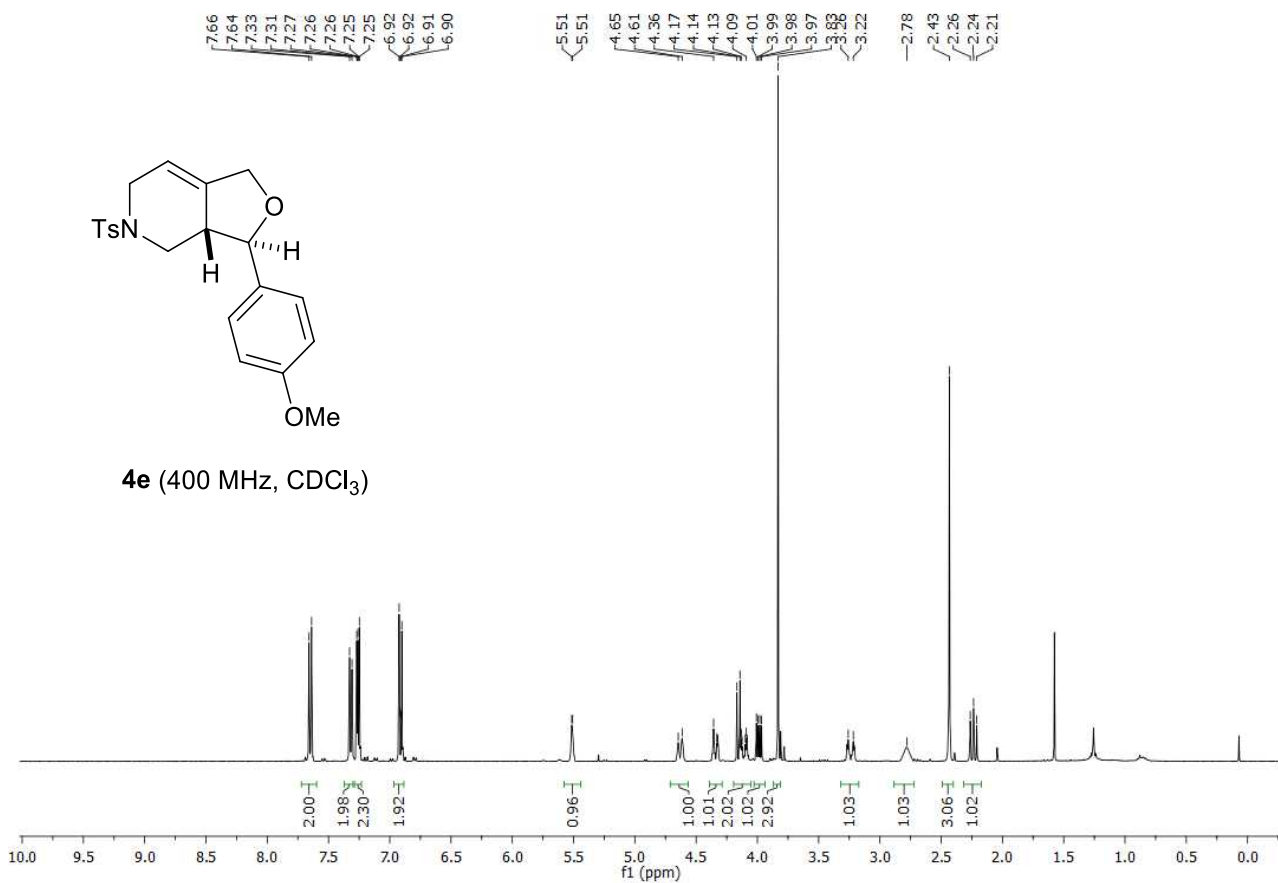


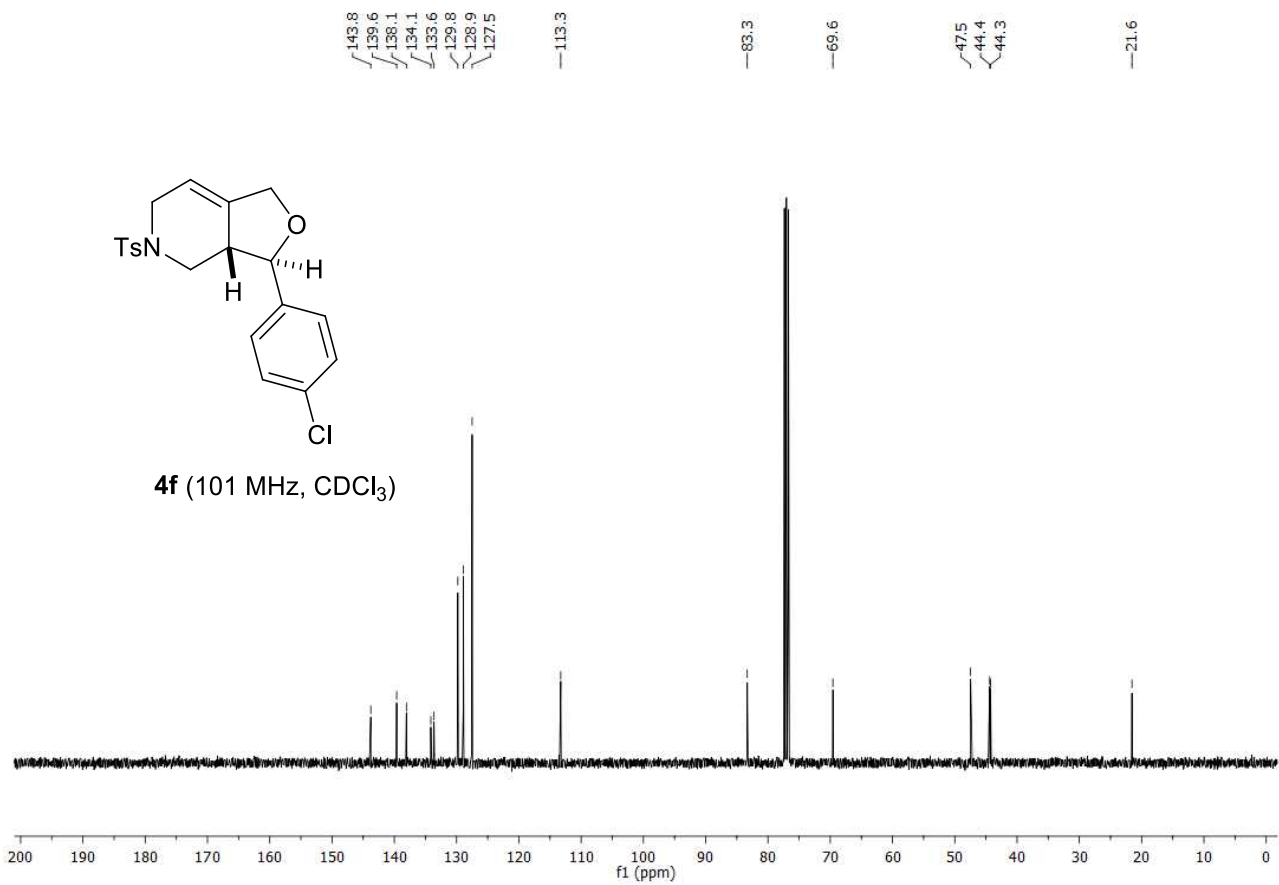
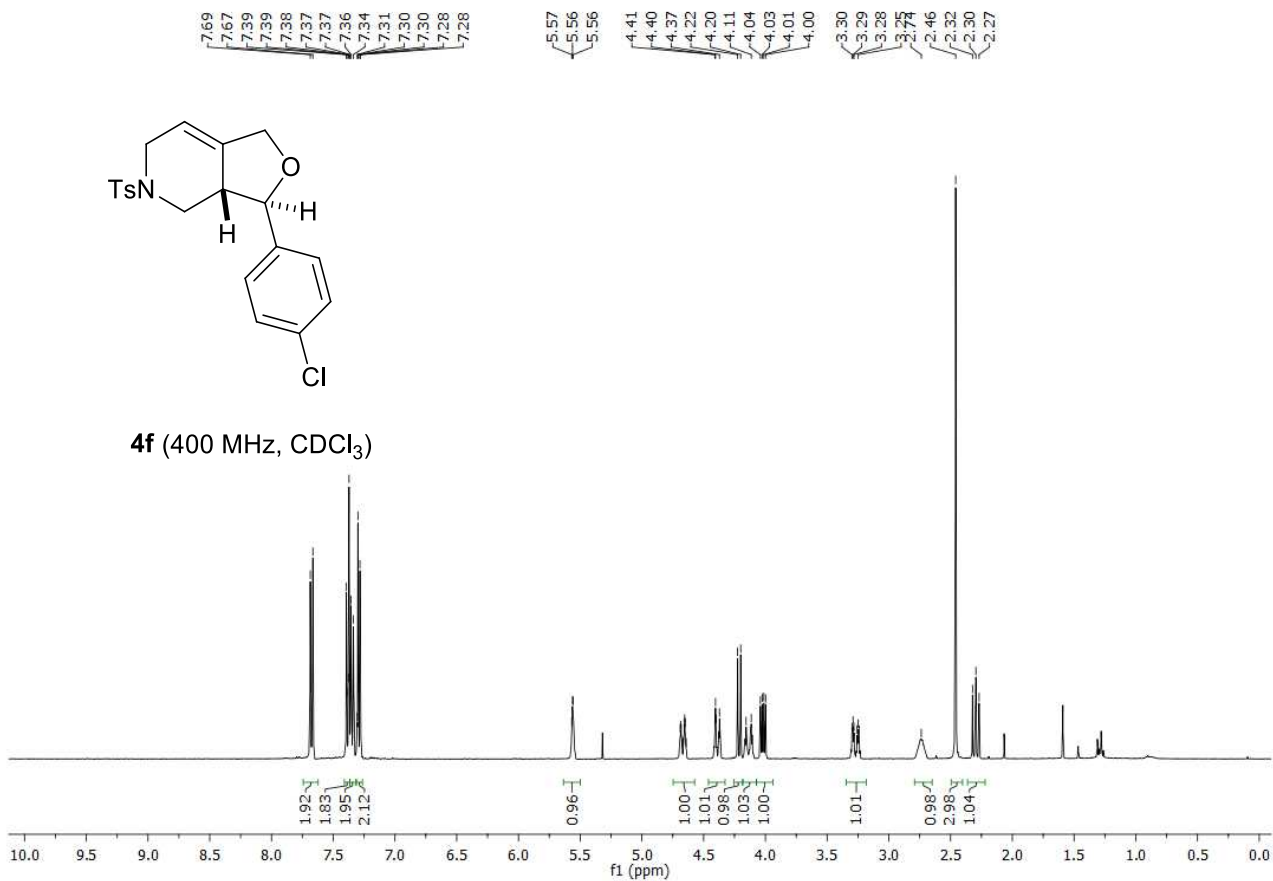
159.2
143.8
141.2
139.9
136.9
133.5
129.8
129.8
128.7
128.1
127.7
127.5
118.7
114.5
113.0
112.8
-83.9
70.1
69.6
47.4
44.6
44.3
-21.6

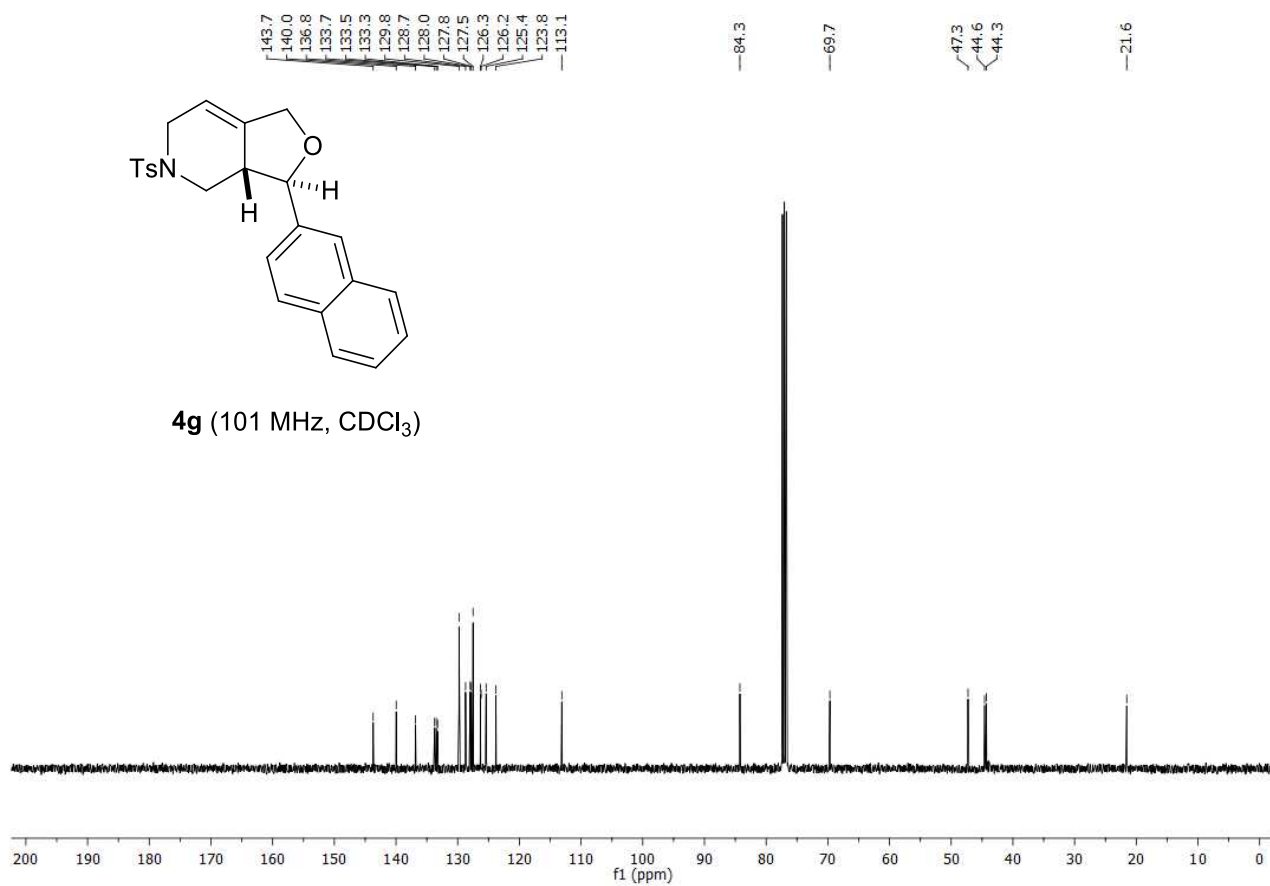
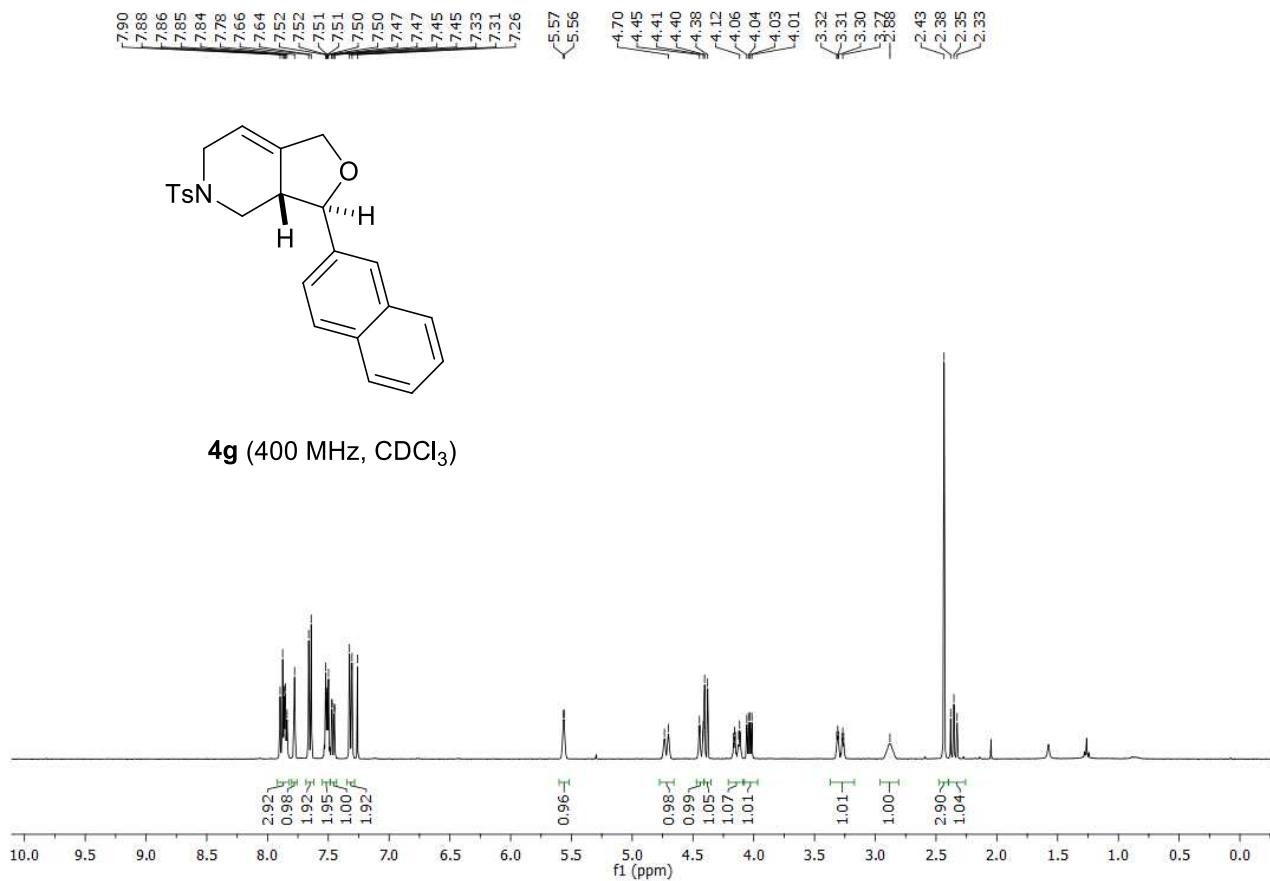


4d (101 MHz, CDCl₃)



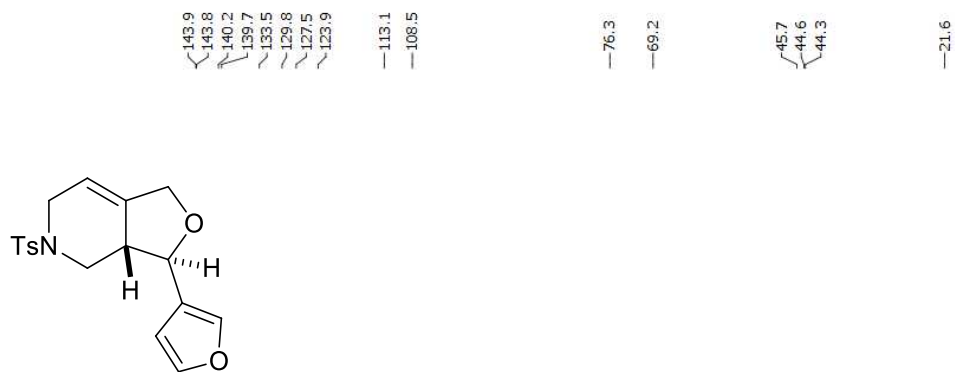
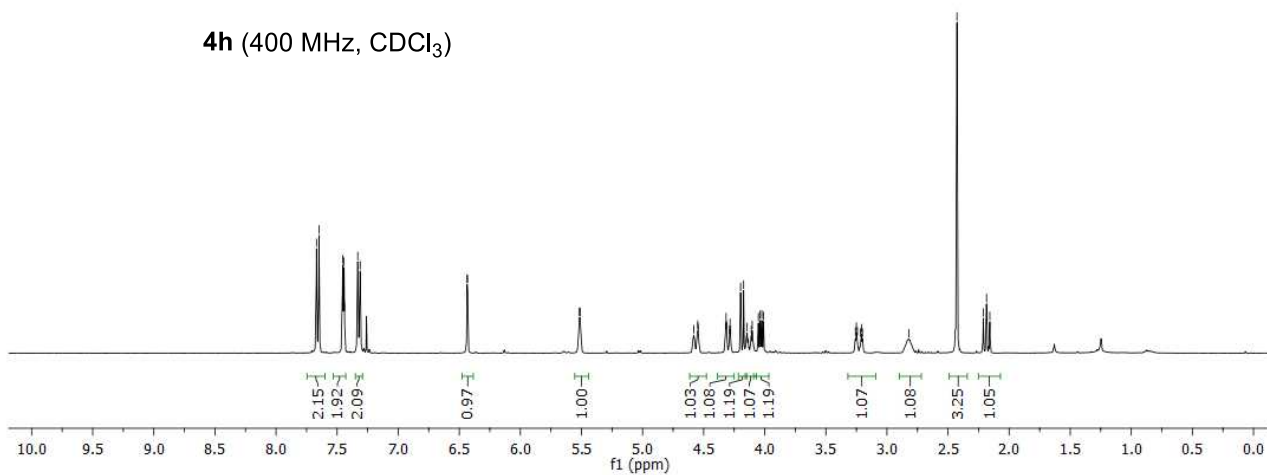




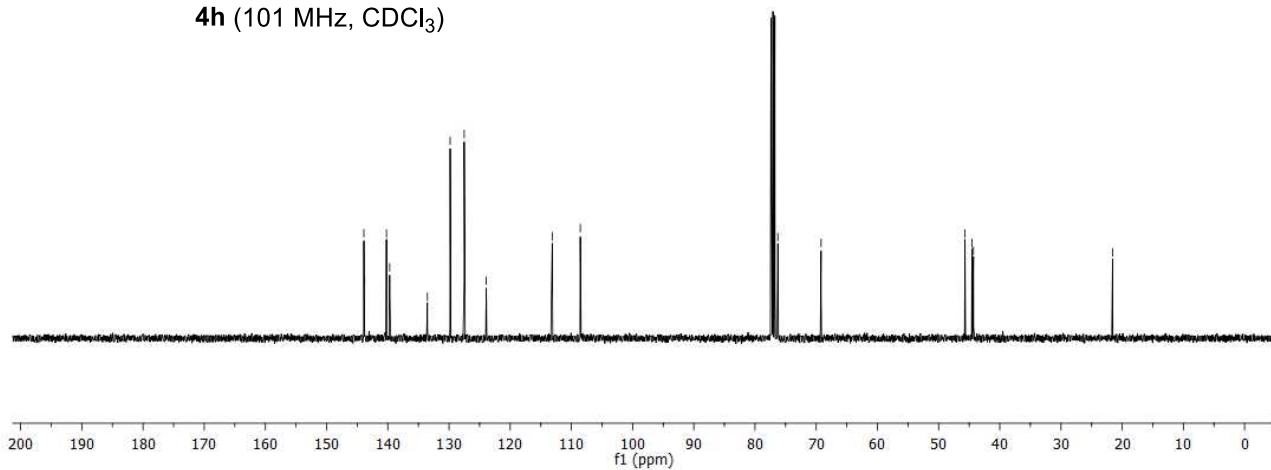




4h (400 MHz, CDCl₃)

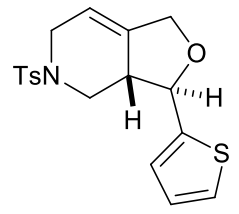


4h (101 MHz, CDCl₃)

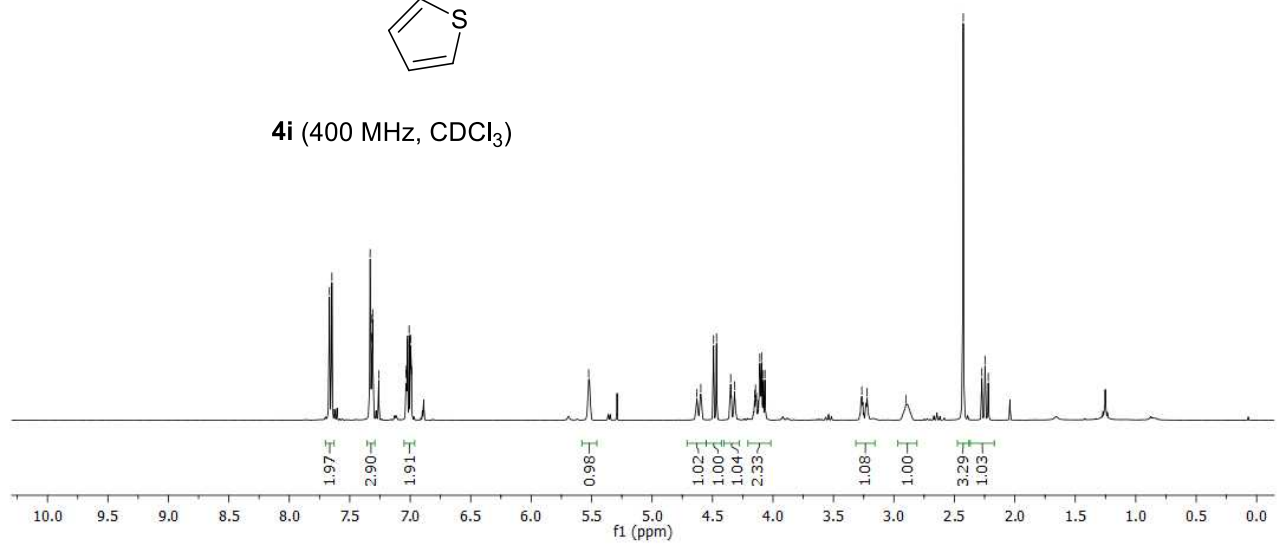


7.67
7.65
7.33
7.32
7.32
7.31
7.26
7.03
7.03
7.02
7.01
7.00
6.99

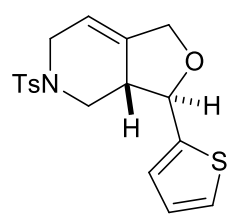
5.52
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4.60
4.49
4.47
4.35
4.32
4.15
4.14
4.11
4.10
4.09
4.08
4.07
3.22
2.90
2.43
2.27
2.25
2.22



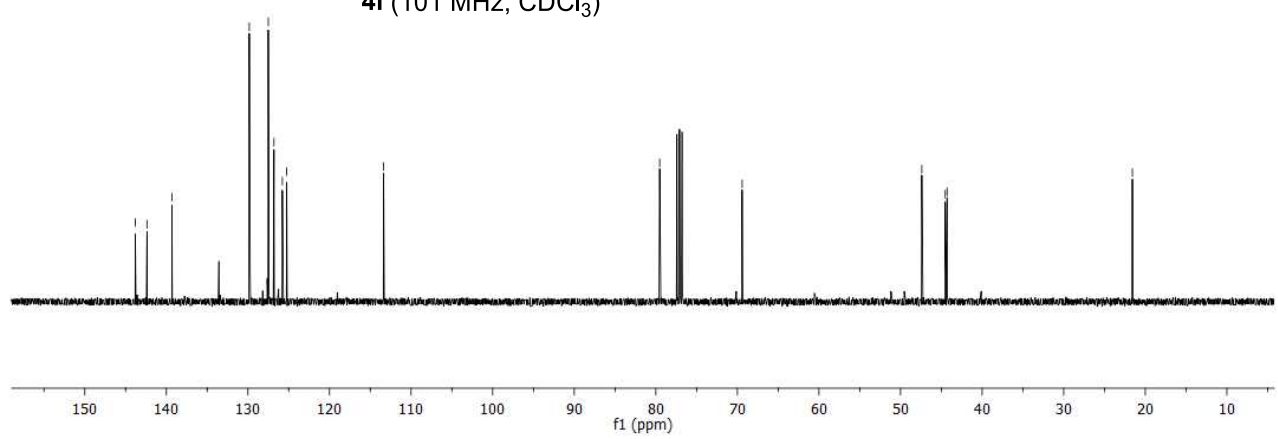
4i (400 MHz, CDCl₃)



143.8
142.4
139.3
129.8
127.5
126.8
125.8
125.2
113.4
79.5
69.4
47.4
44.5
44.3
21.6



4i (101 MHz, CDCl₃)



Crystallographic data

X-ray crystallography. A summary of data collection and structure refinement for **4a** and **2e** is reported in Table 1. Single crystal data were collected with *Bruker D8 Venture PhotonII* area detector diffractometer. Complete datasets were obtained by merging several series of exposure frames.^[7] An absorption correction was applied with the program SADABS.^[8] The structure were solved with ShelxT^[9] and refined on F^2 with full-matrix least squares (ShelxL),^[10] using the Olex2 software package.^[11] Non hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed at their calculated positions.

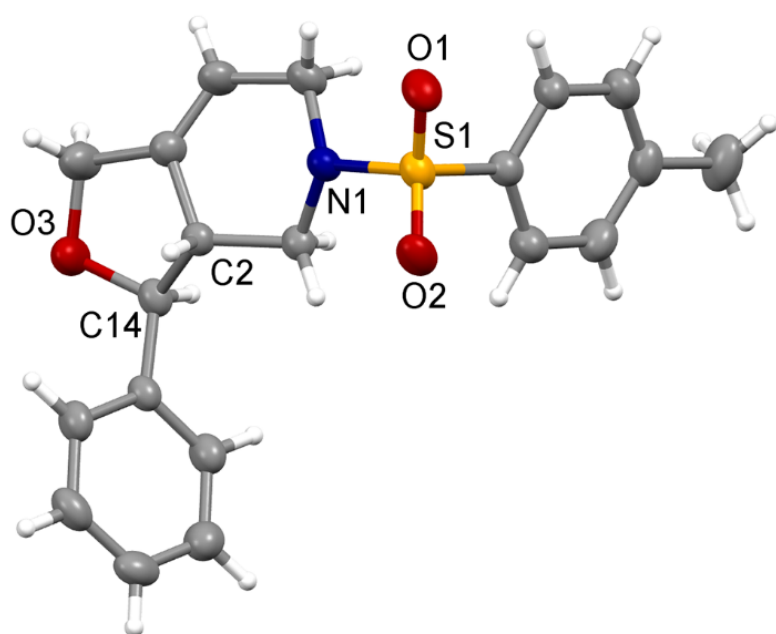


Figure 1. Asymmetric unit of **4a** with thermal ellipsoids depicted at the 30% probability level. C(14) and C(2) are stereocenters and in the asymmetric unit they exhibit S and R chirality, respectively. The space group is centrosymmetric ($C2/c$), hence the centrosymmetrically related molecular structure is also present.

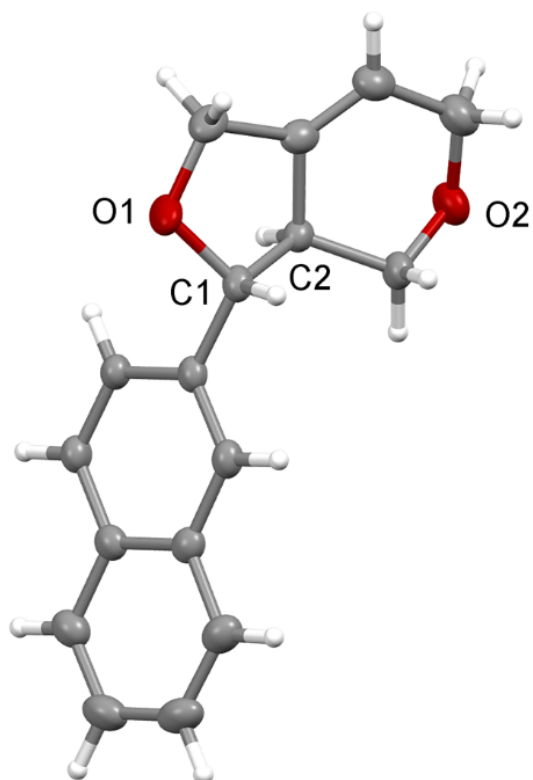


Figure 2. Asymmetric unit of **2e** with thermal ellipsoids depicted at the 30% probability level. C(1) and C(2) are stereocenters and in the asymmetric unit they exhibit R and S chirality, respectively. The space group is chiral $P2_12_12_1$ and, in the crystal, the compound is enantiopure.

Table 1. Crystal data and structure refinement for **4a** and **2e**

	4a	2e
Empirical formula	C ₂₀ H ₂₁ NO ₃ S	C ₁₇ H ₁₆ O ₂
Formula weight	355.44	252.30
Temperature/K	270	200
Crystal system	monoclinic	orthorhombic
Space group	C2/c	P2 ₁ 2 ₁ 2 ₁
a/Å	33.942(4)	7.3872(2)
b/Å	11.5163(11)	10.8747(3)
c/Å	9.4629(9)	16.4977(4)
α /°	90	90
β /°	99.030(4)	90
γ /°	90	90
Volume/Å ³	3653.1(6)	1325.32(6)
Z	8	4
$\rho_{\text{calc}}/\text{cm}^3$	1.293	1.264
μ/mm^{-1}	0.195	0.648
F(000)	1504.0	536.0
Crystal size/mm ³	0.22 × 0.06 × 0.06	0.27 × 0.22 × 0.08
Radiation	MoK α (λ = 0.71073)	CuK α (λ = 1.54184)
2 Θ range for data collection/°	5.888 to 51.43	10.726 to 149.024
Index ranges	-41 ≤ h ≤ 38, -14 ≤ k ≤ 14, -11 ≤ l ≤ 11	-9 ≤ h ≤ 9, -13 ≤ k ≤ 13, -20 ≤ l ≤ 20
Reflections collected	19589	40279
Independent reflections	3460 [R _{int} = 0.0991, R _{sigma} = 0.0607]	2682 [R _{int} = 0.0208, R _{sigma} = 0.0084]
Data/restraints/parameters	3460/0/228	2682/0/172
Goodness-of-fit on F ²	1.031	1.059
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0516, wR ₂ = 0.1011	R ₁ = 0.0306, wR ₂ = 0.0833
Final R indexes [all data]	R ₁ = 0.1147, wR ₂ = 0.1309	R ₁ = 0.0307, wR ₂ = 0.0835
Largest diff. peak/hole / e Å ⁻³	0.19/-0.23	0.29/-0.16
Flack parameter	-	0.04(2)

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