Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Ir-Catalyzed Ring-Opening of Oxa(aza)benzonorbornadienes with Water or Alcohols

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1. Experimental Procedures

General Experimental. Unless otherwise noted, reactions were carried out in single-neck or two-neck flask round bottomed flasks, with magnetic stirring. Air- or water-sensitive liquids and solutions were transferred *via* syringe. Organic solutions were concentrated by rotary evaporation at 23–40 °C under 40 Torr (house vacuum). Analytical thin layer chromatography (TLC) was performed with Silicycle normal phase glass plates (0.25 mm, 60-A pore size, 230-400 mesh). Visualization was done under a 254 nm UV light source.

Materials. Unless otherwise stated, all starting materials, catalysts, and solvents were commercially available and were used as purchased. Super anhydrous solvent 1,4-dioxane, THF, CH_3CN, toluene and DMF were used without any pretreatment. Water was used as a solvent by deionization. Flash column chromatography was performed using the indicated solvent system on Qingdao-Haiyang silica gel (200−300 mesh). Oxa(aza)bicyclic alkenes[1] were prepared according to literature procedures.

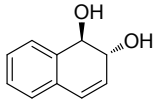
Instrumentation. Proton nuclear magnetic resonance spectra (^{1}H NMR) spectra and carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded at 23 °C with a Varian Mercury NMR spectrometer. Recorded shifts for protons are reported in parts per million (δ scale) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvents ($CHCl_3$: δ 7.26, CD_2HOD: δ 3.30). Chemical shifts for carbon resonances are reported in parts per million (δ scale) downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$: δ 77.0, CD_3OD: δ 49.2). Data are represented as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), and coupling constant (*J*, Hz). HRMS (ion trap) were obtained from mass spectrometer (ESI) and MS were recorded using EI at 70 eV. Melting points were recorded on an electrothermal digital melting point apparatus and were uncorrected.

The general procedure (A) for iridium-catalyzed ring-opening of oxa(aza)benzonorbornadienes (1a–1k) with water: All experiments were carried out under air. $[Ir(COD)Cl]_2$ (1.4–3.4 mg, 1–2.5 mol%), TBAI (74 mg, 1 equiv.), oxa(aza)benzonorbornadienes (**1a–k**), (0.2 mmol), 1,4-dioxane (2.0 mL) and water (1.0 mL) were simultaneously added to a 10.0 mL round-bottomed flask. After the mixture was stirred at 80 ^{o}C in oil bath for 30 min until it was completed as judged by thin-layer chromatography. After cooling to the room temperature, the mixture was extracted three times with ethyl acetate (3×10 mL) and combined organic layer, and saturated brine to wash. The combined organic layer was dried over Na_2SO_4, and volatiles were removed under reduced pressure. The residue was purified by column chromatography (200–300 mesh silica gels) to obtain the desired products **3**.

The general procedure (B) for iridium-catalyzed ring-opening of oxa(aza)benzonorbornadienes (1a–1k) with alcohol nucleophiles: All experiments were carried out under air. $[Ir(COD)Cl]_2$ (1.4–3.4 mg, 1–2.5 mol%), TBAI (74 mg, 1 equiv.), oxa(aza)benzonorbornadienes (**1a–k**), (0.2 mmol), alcohol nucleophiles (1.0 mL) were simultaneously added to a 10.0 mL round-bottomed flask. After the mixture was stirred at 80 ^{o}C in oil bath for 30 min until it was completed as judged by thin-layer chromatography. After cooling to the room temperature, the reaction mixture was concentrated in vacuo and the solvents were removed, the crude mixture was purified by flash chromatography(Silica Gel: 200-300 mesh) to afford the desired product **5**.

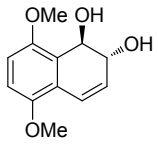
The procedure (C) for synthesis of 6: The substrate ((1*R**, 2*R**)-*tert*-butyl-2-hydroxy-1,2-dihydronaphthalen-1-yl)carbamate (0.2 mmol) **3f** was added to a flame-dried 10.0 mL round-bottomed flask. The flask was sealed under nitrogen and CH_2Cl_2 (1.0 mL) was added. $BF_3{\cdot}OEt_2$ (20 mol%, 5.7 mg) in CH_2Cl_2 (1.0 mL) was dropped to mixture using syringe. The mixture was stirred at room temperature for 10 h. After completion the reaction mixture was concentrated in vacuo and the solvents were removed, the crude mixture was purified by flash chromatography(Silica Gel: 200-300 mesh) to afford the desired product **6**.

2. Characterization data of 3a–k, 5a–q and 6



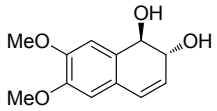
3a

(1*R,2*R**)-1,2-Dihydronaphthalene-1,2-diol (3a).** Following the general procedure (**A**), **3a** was obtained as a white solid (32.1 mg, 99%). m.p. 118–120 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.56 – 7.40 (m, 1H), 7.30 – 7.13 (m, 2H), 7.13 – 7.02 (m, 1H), 6.37 (dd, J = 9.8, 2.2 Hz, 1H), 5.89 (dd, J = 9.8, 2.4 Hz, 1H), 5.44 (br. d, J = 4.4 Hz 1H), 5.17 (br. 1H), 4.55 (d, J = 10.2 Hz, 1H), 4.24 (d, J = 10.2 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 138.6, 133.3, 132.9, 127.7, 127.6, 126.73, 126.2, 125.8, 74.1, 72.6. HRMS *m/z* (EI) [M – H]$^-$ calcd for $C_{10}H_9O_2$: 161.0603, found: 161.0606.



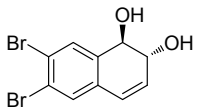
3b

(1*R,2*R**)-5,8-Dimethoxy-1,2-dihydronaphthalene-1,2-diol (3b).** Following the general procedure (**A**), **3b** was obtained as a yellow oil (43.9 mg, 99%). ^{1}H NMR (600 MHz, CD_3OD) δ 7.00 (d, J = 9.9 Hz, 1H), 6.88 (s, 2H), 6.05 (ddd, J = 9.8, 5.5, 1.1 Hz, 1H), 5.05 – 4.96 (m, 1H), 4.18 (dd, J = 5.5, 2.0 Hz, 1H), 3.82 (s, 3H), 3.78 (s, 3H). ^{13}C NMR (150 MHz, CD_3OD) δ 153.9, 151.39, 126.9, 124.9, 124.2, 123.1, 112.9, 112.6, 68.8, 66.5, 56.8, 56.7. HRMS *m/z* (EI) [M – H]$^-$ calcd for $C_{12}H_{13}O_4$: 221.0814, found: 211.0815.



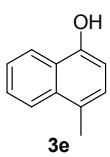
3c

(1*R,2*R**)-6,7-Dimethoxy-1,2-dihydronaphthalene-1,2-diol (3c).** Following the general procedure (**A**), **3c** was obtained as a white solid (35.5 mg, 80%). m.p. 103–105 °C. ^{1}H NMR (600 MHz, CD_3OD) δ 7.14 (s, 1H), 6.73 (s, 1H), 6.35 (dd, J = 9.8, 2.1 Hz, 1H), 5.81 (dd, J = 9.8, 2.7 Hz, 1H), 4.62 (d, J = 9.8 Hz, 1H), 4.31 (dt, J = 9.8, 2.4 Hz, 1H), 3.84 (s, 3H), 3.79 (s, 3H). ^{13}C NMR (150 MHz, CD_3OD) δ 150.0, 149.9, 131.4, 129.9, 128.4, 127.2, 111.9, 111.4, 75.7, 74.2, 56.8, 56.7. HRMS *m/z* (EI) [M – H]$^-$ calcd for $C_{12}H_{13}O_4$: 221.0814, found: 211.0816.



3d

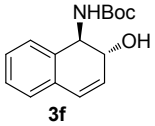
(1*R,2*R**)-6,7-Dibromo-1,2-dihydronaphthalene-1,2-diol (3d).** Following the general procedure (**A**), **3d** was obtained as a white solid (51.4 mg, 81%). m.p. 113–115 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.71 (s, 1H), 7.47 (s, 1H), 6.35 (dd, J = 9.8, 2.2 Hz, 1H), 5.97 (dd, J = 9.8, 2.4 Hz, 1H), 4.49 (dd, J = 10.5, 0.8 Hz, 1H), 4.21 (dt, J = 3.9, 2.3 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 140.0, 135.5, 134.2, 130.9, 130.7, 124.7, 122.7, 122.3, 73.1, 71.7. HRMS *m/z* (EI) [M – H]$^-$ calcd for $C_{10}H_7Br_2O_2$: 316.8813, found: 316.8813.



3e

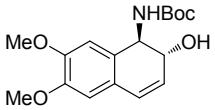
4-Methylnaphthalen-1-ol (3e). Following the general procedure (**A**), **3e** was obtained as a yellow oil (31.0 mg, 98%). ^{1}H NMR (600 MHz, CD_3OD) δ 8.29 – 8.15 (m, 1H), 7.84 (dd, J = 4.7, 3.6 Hz, 1H), 7.48 – 7.41 (m, 1H), 7.39 (t, J =

7.5 Hz, 1H), 7.06 (dd, *J* = 7.5, 0.5 Hz, 1H), 6.71 (dd, *J* = 7.6, 1.8 Hz, 1H), 2.51 (d, *J* = 4.6 Hz, 3H). ^{13}C NMR (150 MHz, CD_3OD) δ 153.0, 135.0, 127.7, 127.0, 126.7, 125.9, 125.4, 125.0, 123.8, 108.6, 19.0. HRMS *m/z* (EI) $[M - H]^-$ calcd for $C_{11}H_9O$: 157.0653, found: 157.0658.



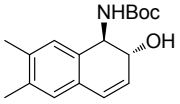
3f

***Tert*-butyl ((1*R**,2*R**)-2-hydroxy-1,2-dihydronaphthalen-1-yl)carbamate (3f).** Following the general procedure (**A**), **3f** was obtained as a white solid (49.6 mg, 95%). m.p. 145–147 °C. ^{1}H NMR (500 MHz, CD_3OD) δ 7.29 – 7.22 (m, 1H), 7.23 – 7.16 (m, 2H), 7.08 (dd, *J* = 5.6, 3.1 Hz, 1H), 6.45 (dd, *J* = 9.8, 2.0 Hz, 1H), 5.95 (dd, *J* = 9.8, 2.7 Hz, 1H), 4.79 (d, *J* = 10.6 Hz, 1H), 4.38 (d, *J* = 10.6 Hz, 1H), 1.47 (d, *J* = 17.3 Hz, 9H). ^{13}C NMR (125 MHz, CD_3OD) δ 159.0, 136.6, 134.4, 132.4, 130.0, 129.0, 128.9, 127.8, 127.0, 80.5, 71.7, 58.0, 29.0. HRMS *m/z* (EI) $[M + Na]^+$ calcd for $C_{15}H_{19}NNaO_3$: 284.1263, found: 284.1258.



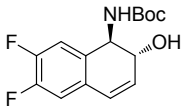
3g

***Tert*-butyl ((1*R**,2*R**)-2-hydroxy-6,7-dimethoxy-1,2-dihydronaphthalen-1-yl)carbamate (3g).** Following the general procedure (**A**), **3g** was obtained as a oil liquid (54.6 mg, 85%). ^{1}H NMR (600 MHz, CD_3OD) δ 6.85 (s, 1H), 6.73 (s, 1H), 6.38 (dd, *J* = 9.8, 1.4 Hz, 1H), 5.85 (dd, *J* = 9.8, 2.9 Hz, 1H), 4.71 (d, *J* = 10.1 Hz, 1H), 4.34 (d, *J* = 10.0 Hz, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 1.48 (s, 9H). ^{13}C NMR (150 MHz, CD_3OD) δ 158.9, 150.0, 149.9, 130.0, 129.3, 128.8, 127.5, 112.2, 111.8, 80.5, 71.5, 57.7, 56.8, 56.7, 29.0. HRMS *m/z* (EI) $[M + Na]^+$ calcd for $C_{17}H_{23}NNaO_5$: 344.1474, found: 344.1467.



3h

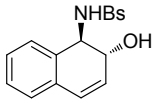
***Tert*-butyl ((1*R**,2*R**)-2-hydroxy-6,7-dimethyl-1,2-dihydronaphthalen-1-yl)carbamate (3h).** Following the general procedure (**A**), **3h** was obtained as a white solid (55.0 mg, 95%). m.p. 194–196 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 6.98 (d, *J* = 8.9 Hz, 1H), 6.87 (d, *J* = 12.9 Hz, 2H), 6.30 (dd, *J* = 9.8, 1.7 Hz, 1H), 5.82 (dd, *J* = 9.8, 2.0 Hz, 1H), 5.09 (d, *J* = 6.2 Hz, 1H), 4.58 (t, *J* = 10.1 Hz, 1H), 4.40 – 4.21 (m, 1H), 2.18 (s, 3H), 2.16(s, 3H), 1.46 (s, 9H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 156.2, 134.9, 134.7, 133.3, 132.3, 130.4, 127.4 126.8, 126.2, 77.6, 69.3, 56.3, 28.3, 19.5, 18.8. HRMS *m/z* (EI) $[M + Na]^+$ calcd for $C_{17}H_{23}NNaO_3$: 312.1576, found: 312.1569.



3i

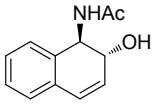
***Tert*-butyl ((1*R**,2*R**)-6,7-difluoro-2-hydroxy-1,2-dihydronaphthalen-1-yl)carbamate (3i).** Following the general procedure (**A**), **3i** was obtained as a white solid (38.6 mg, 65%). m.p. 179–181 °C. ^{1}H NMR (600 MHz, CD_3OD) δ 7.08 (dd, *J* = 10.9, 8.1 Hz, 1H), 7.03 (dd, *J* = 10.7, 7.9 Hz, 1H), 6.39 (dd, *J* = 9.9, 2.0 Hz, 1H), 6.00 (dd, *J* = 9.9, 2.6 Hz, 1H), 4.71 (d, *J* = 10.7 Hz, 1H), 4.38 (d, *J* = 10.7 Hz, 1H), 1.49 (s, 9H). ^{13}C NMR (150 MHz, CD_3OD) δ 158.8, 151.9,

151.8, 151.6, 151.5, 150.2, 150.1, 149.9, 149.8, 134.3, 133.7, 131.7, 127.0, 116.6, 116.6, 116.5, 116.4, 80.8, 71.0, 57.4, 29.0. ^{19}F NMR (565 MHz, CD_3OD) δ -141.5, -141.6, -143.2, -143.2. HRMS *m/z* (EI) $[M + Na]^+$ calcd for $C_{15}H_{17}F_2NNaO_3$: 320.1074, found: 320.1069.



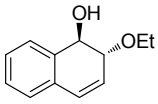
3j

4-Bromo-*N*-((1*R,2*R**)-2-hydroxy-1,2-dihydronaphthalen-1-yl)benzenesulfonamide (3j).** Following the general procedure (**A**), **3j** was obtained as a white solid (72.7 mg, 96%). m.p. 172–174 °C. ^{1}H NMR (600 MHz, CD_3OD) δ 7.79 (d, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.07 (dd, *J* = 14.1, 7.4 Hz, 2H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.52 (d, *J* = 9.7 Hz, 1H), 5.95 (dd, *J* = 9.7, 4.0 Hz, 1H), 4.43 (d, *J* = 6.8 Hz, 1H), 4.33 – 4.19 (m, 1H). ^{13}C NMR (150 MHz, CD_3OD) δ 142.8, 134.7, 134.1, 133.4, 130.2, 130.1, 130.0, 129.6, 129.1, 129.0, 128.1, 70.5, 59.7. HRMS *m/z* (EI) $[M + Na]^+$ calcd for $C_{16}H_{14}BrNNaO_3S$: 401.9775, found: 401.9770.



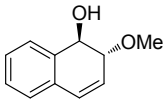
3k

***N*-((1*R**,2*R**)-2-hydroxy-1,2-dihydronaphthalen-1-yl)acetamide (3k).** Following the general procedure (**A**), **3k** was obtained as a oil liquid (36.5 mg, 90%). ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.05 (d, *J* = 8.6 Hz, 1H), 7.26 – 7.14 (m, 2H), 7.15 – 7.06 (m, 2H), 6.44 (dd, *J* = 9.8, 1.8 Hz, 1H), 5.94 (dd, *J* = 9.8, 2.7 Hz, 1H), 5.19 (br. 1H), 4.93 (t, *J* = 9.5 Hz, 1H), 4.29 (d, *J* = 10.2 Hz, 1H), 1.94 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 170.1, 135.7, 133.2, 133.1, 127.9, 127.8, 127.1, 126.7, 126.5, 69.2, 54.9, 23.3. HRMS *m/z* (EI) $[M + Na]^+$ calcd for $C_{12}H_{13}NNaO_2$: 226.0844, found: 226.0839.



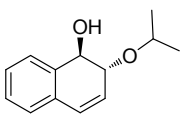
5a

(1*R,2*R**)-2-Ethoxy-1,2-dihydronaphthalen-1-ol (5a).** Following the general procedure (**B**), **5a** was obtained as a oil liqiud (37.6 mg, 99%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.3 Hz, 1H), 7.33 – 7.14 (m, 2H), 7.14 – 6.98 (m, 1H), 6.42 (dd, *J* = 9.9, 2.1 Hz, 1H), 6.00 (dd, *J* = 9.9, 2.3 Hz, 1H), 4.90 (d, *J* = 10.5 Hz, 1H), 4.18 (dt, *J* = 10.5, 2.2 Hz, 1H), 3.77 (dq, *J* = 9.4, 7.0 Hz, 1H), 3.58 (dq, *J* = 9.4, 7.0 Hz, 1H), 3.03 (br., 1H), 1.26 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 136.0, 131.9, 127.9, 127.8, 127.7, 127.6, 126.1, 124.9, 80.7, 72.4, 64.6, 15.4. HRMS *m/z* (EI) $[M + Na]^+$ calcd for $C_{12}H_{14}NaO_2$: 213.0891, found: 213.0886.



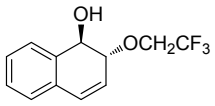
5b

(1*R,2*R**)-2-Methoxy-1,2-dihydronaphthalen-1-ol (5b).** Following the general procedure (**B**), **5b** was obtained as a oil liqiud (34.5 mg, 98%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.1 Hz, 1H), 7.29 – 7.16 (m, 2H), 7.10 – 6.98 (m, 1H), 6.43 (dd, *J* = 9.9, 1.9 Hz, 1H), 6.01 (dd, *J* = 9.9, 2.3 Hz, 1H), 4.89 (d, *J* = 10.2 Hz, 1H), 4.09 (dt, *J* = 10.2, 2.2 Hz, 1H), 3.46 (s, 3H), 3.31 (br., 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 135.9, 131.8, 128.2, 127.8, 127.6, 126.7, 126.1, 125.1, 82.1, 72.1, 56.6. HRMS *m/z* (EI) $[M - H]^-$ calcd for $C_{11}H_{11}O_2$: 175.0759, found: 175.0760.



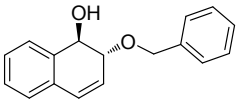
5c

(1*R,2*R**)-2-Isopropoxy-1,2-dihydronaphthalen-1-ol (5c).** Following the general procedure (**B**), **5c** was obtained as a oil liquid (37.1 mg, 91%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.3 Hz, 1H), 7.30 – 7.17 (m, 2H), 7.08 – 6.99 (m, 1H), 6.39 (dd, *J* = 9.9, 2.2 Hz, 1H), 5.95 (dd, *J* = 9.9, 2.2 Hz, 1H), 4.86 (d, *J* = 10.8 Hz, 1H), 4.24 (dt, *J* = 10.8, 2.2 Hz, 1H), 3.91 – 3.73 (m, 1H), 2.78 (s, 1H), 1.24 (d, *J* = 6.2 Hz, 3H), 1.21 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 136.0, 132.1, 129.3, 127.7, 127.7, 127.6, 126.1, 124.8, 78.7, 72.8, 70.9, 23.3, 22.1. HRMS *m/z* (EI) $[M + Na]^+$ calcd for $C_{13}H_{16}NaO_2$: 227.1048, found: 227.1044.



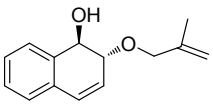
5d

(1*R,2*R**)-2-(2,2,2-Trifluoroethoxy)-1,2-dihydronaphthalen-1-ol (5d).** Following the general procedure (**B**), **5d** was obtained as a oil liquid (43.4 mg, 89%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.3 Hz, 1H), 7.32 – 7.19 (m, 2H), 7.16 – 7.03 (m, 1H), 6.48 (dd, *J* = 9.9, 2.0 Hz, 1H), 5.94 (dd, *J* = 9.9, 2.4 Hz, 1H), 4.96 (dd, *J* = 9.8, 2.6 Hz, 1H), 4.38 (dt, *J* = 9.9, 2.2 Hz, 1H), 4.03 (q, *J* = 8.6 Hz, 2H), 2.60 (d, *J* = 3.9 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 135.4, 131.7, 129.2, 128.3, 128.1, 126.5, 125.9, 125.2, 123.8 (q, *J* = 277.3 Hz), 83.0, 72.8, 67.0 (q, *J* = 34.0 Hz). ^{19}F NMR (565 MHz, $CDCl_3$) δ -74.41. HRMS *m/z* (EI) $[M - H]^-$ calcd for $C_{12}H_{10}F_3O_2$: 243.0633, found: 243.0632.



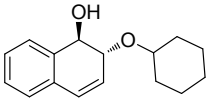
5e

(1*R,2*R**)-2-(Benzyloxy)-1,2-dihydronaphthalen-1-ol (5e).** Following the general procedure (**B**), **5e** was obtained as a oil liquid (44.3 mg, 88%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.1 Hz, 1H), 7.36 (dt, *J* = 13.0, 7.3 Hz, 4H), 7.29 (t, *J* = 7.1 Hz, 1H), 7.26 – 7.18 (m, 2H), 7.09 – 7.03 (m, 1H), 6.44 (dd, *J* = 9.9, 2.0 Hz, 1H), 6.03 (dd, *J* = 9.9, 2.3 Hz, 1H), 4.96 (d, *J* = 10.2 Hz, 1H), 4.76 (d, *J* = 11.8 Hz, 1H), 4.61 (d, *J* = 11.8 Hz, 1H), 4.32 (dt, *J* = 10.2, 2.2 Hz, 1H), 2.68 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.0, 135.9, 131.9, 128.5, 128.3, 127.9, 127.9, 127.9, 127.8, 127.4, 126.2, 125.1, 80.4, 72.6, 71.3. HRMS *m/z* (EI) $[M + Na]^+$ calcd for $C_{17}H_{16}NaO_2$: 275.1048, found: 275.1043.



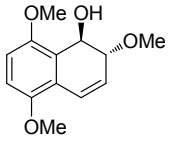
5f

(1*R,2*R**)-2-((2-Methylallyl)oxy)-1,2-dihydronaphthalen-1-ol (5f).** Following the general procedure (**B**), **5f** was obtained as a oil liquid (37.2 mg, 86%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 – 7.49 (m, 1H), 7.27 – 7.20 (m, 2H), 7.07 (dd, *J* = 7.2, 1.4 Hz, 1H), 6.44 (dd, *J* = 9.9, 2.1 Hz, 1H), 6.02 (dd, *J* = 9.9, 2.4 Hz, 1H), 5.03 (dd, *J* = 1.9, 0.9 Hz, 1H), 4.98 – 4.89 (m, 2H), 4.24 (dt, *J* = 10.3, 2.2 Hz, 1H), 4.13 (d, *J* = 12.5 Hz, 1H), 4.02 (d, *J* = 12.5 Hz, 1H), 1.81 – 1.78 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.1, 135.9, 131.9, 128.2, 127.9, 127.7, 127.5, 126.2, 125.1, 112.8, 80.2, 73.2, 72.6, 19.6. HRMS *m/z* (EI) $[M - 3H]^-$ calcd for $C_{14}H_{13}O_2$: 213.0916, found: 213.0917.



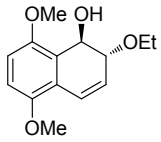
5g

(1*R,2*R**)-2-(Cyclohexyloxy)-1,2-dihydronaphthalen-1-ol (5g).** Following the general procedure (**B**), **5g** was obtained as a oil liquid (39.5 mg, 81%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.3 Hz, 1H), 7.23 (tdd, *J* = 15.0, 10.6, 4.2 Hz, 2H), 7.08 – 7.03 (m, 1H), 6.39 (dd, *J* = 9.9, 2.2 Hz, 1H), 5.97 (dd, *J* = 9.9, 2.1 Hz, 1H), 4.87 (d, *J* = 10.9 Hz, 1H), 4.29 (dt, *J* = 10.9, 2.1 Hz, 1H), 3.55 – 3.42 (m, 1H), 2.75 (s, 1H), 2.00 – 1.92 (m, 2H), 1.80 – 1.73 (m, 2H), 1.63 – 1.50 (m, 1H), 1.46 – 1.36 (m, 1H), 1.34 – 1.17 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 136.0, 132.1, 129.6, 127.7, 127.6, 127.5, 126.0, 124.7, 78.7, 72.9, 33.6, 32.4, 25.6, 24.3, 24.2. HRMS *m/z* (EI) $[M - H]^-$ calcd for $C_{16}H_{19}O_2$: 243.1385, found: 243.1390.



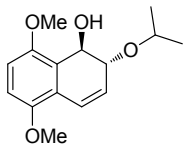
5h

(1*R,2*R**)-2,5,8-Trimethoxy-1,2-dihydronaphthalen-1-ol (5h).** Following the general procedure (**B**), **5h** was obtained as a oil liquid (46.7 mg, 99%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.03 (d, *J* = 10.0 Hz, 1H), 6.77 (s, 2H), 6.09 (dd, *J* = 10.0, 4.8 Hz, 1H), 5.16 (t, *J* = 3.3 Hz, 1H), 4.04 (dd, *J* = 4.5, 3.3 Hz, 1H), 3.82 (s, 3H), 3.78 (s, 3H), 3.43 (s, 3H), 2.60 (d, *J* = 4.3 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.5, 149.9, 124.1, 123.9, 123.5, 121.33, 111.5, 111.1, 76.9, 64.9, 56.3, 56.1, 55.9. HRMS *m/z* (EI) $[M + Na]^+$ calcd for $C_{13}H_{16}NaO_4$: 259.0946, found: 259.0942.



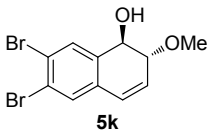
5i

(1*R,2*R**)-2-Ethoxy-5,8-dimethoxy-1,2-dihydronaphthalen-1-ol (5i).** Following the general procedure (**B**), **5i** was obtained as a oil liquid (50.0 mg, 99%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.01 (d, *J* = 10.0 Hz, 1H), 6.77 (s, 2H), 6.07 (dd, *J* = 10.0, 4.8 Hz, 1H), 5.16 (d, *J* = 2.9 Hz, 1H), 4.20 – 4.06 (m, 1H), 3.83 (s, 3H), 3.78 (s, 3H), 3.71 (tt, *J* = 14.1, 7.1 Hz, 1H), 3.66 – 3.57 (m, 1H), 2.58 (br., 1H), 1.19 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.5, 149.9, 124.8, 124.1, 122.9, 121.5, 111.4, 110.9, 75.7, 65.6, 64.1, 56.1, 55.9, 15.6. HRMS *m/z* (EI) $[M + Na]^+$ calcd for $C_{14}H_{18}NaO_4$: 273.1103, found: 273.1097.



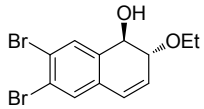
5j

(1*R,2*R**)-2-Isopropoxy-5,8-dimethoxy-1,2-dihydronaphthalen-1-ol (5j).** Following the general procedure (**B**), **5j** was obtained as a oil liquid (47.5 mg, 90%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.97 (dd, *J* = 9.9, 0.6 Hz, 1H), 6.76 (s, 2H), 6.02 (dd, *J* = 9.9, 4.8 Hz, 1H), 5.11 (s, 1H), 4.18 (dd, *J* = 5.7, 2.2 Hz, 1H), 3.95 – 3.89 (m, 1H), 3.83 (s, 3H), 3.78 (s, 3H), 2.58 (br., 1H), 1.19 (d, *J* = 2.3 Hz, 3H), 1.18 (d, *J* = 2.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.6, 149.9, 125.6, 124.1, 122.4, 121.6, 111.4, 110.9, 73.7, 70.2, 66.5, 56.1, 56.0, 22.9, 22.6. HRMS *m/z* (EI) $[M + Na]^+$ calcd for $C_{15}H_{20}NaO_4$: 287.1259, found: 287.1256.



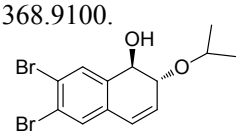
5k

(1*R,2*R**)-6,7-Dibromo-2-methoxy-1,2-dihydronaphthalen-1-ol (5k).** Following the general procedure (**B**), **5k** was obtained as a white solid (59.1 mg, 89%). m.p. 114–116 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.72 (s, 1H), 7.54 (s, 1H), 6.47 (dd, *J* = 9.9, 1.6 Hz, 1H), 6.13 (dd, *J* = 9.9, 2.6 Hz, 1H), 5.81 (d, *J* = 6.0 Hz, 1H), 4.73 – 4.55 (m, 1H), 3.98 (dt, *J* = 9.6, 2.2 Hz, 1H), 3.40 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 139.4, 133.4, 130.9, 130.9, 130.6, 125.6, 122.5, 122.1, 80.5, 70.2, 56.6. HRMS *m/z* (EI) $[M - H]^-$ calcd for $C_{11}H_9Br_2O_2$: 330.8969, found: 330.8970.



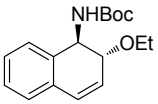
5l

(1*R,2*R**)-6,7-Dibromo-2-ethoxy-1,2-dihydronaphthalen-1-ol (5l).** Following the general procedure (**B**), **5l** was obtained as a white solid (62.3 mg, 90%). m.p. 112–114 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.29 (s, 1H), 6.32 (dd, *J* = 9.9, 2.1 Hz, 1H), 6.09 (dd, *J* = 9.9, 1.9 Hz, 1H), 4.81 (d, *J* = 11.1 Hz, 1H), 4.14 (dt, *J* = 11.1, 2.1 Hz, 1H), 3.79 (dq, *J* = 9.2, 7.0 Hz, 1H), 3.58 (tt, *J* = 14.0, 4.8 Hz, 1H), 2.87 (s, 1H), 1.28 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 136.7, 132.7, 130.7, 130.3, 130.1, 126.0, 123.7, 123.6, 80.4, 71.9, 64.9, 15.5. HRMS *m/z* (EI) $[M + Na]^+$ calcd for $C_{12}H_{12}Br_2NaO_2$: 368.9102, found: 368.9100.



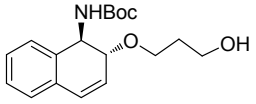
5m

(1*R,2*R**)-6,7-Dibromo-2-isopropoxy-1,2-dihydronaphthalen-1-ol (5m).** Following the general procedure (**B**), **5m** was obtained as a white solid (63.3 mg, 88%). m.p. 86–88 °C ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 0.7 Hz, 1H), 7.29 (s, 1H), 6.29 (dd, *J* = 9.9, 2.3 Hz, 1H), 6.03 (dd, *J* = 9.9, 2.0 Hz, 1H), 4.76 (d, *J* = 11.2 Hz, 1H), 4.20 (dt, *J* = 11.2, 2.2 Hz, 1H), 3.92 – 3.75 (m, 1H), 2.75 (s, 1H), 1.25 (d, *J* = 6.2 Hz, 3H), 1.22 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 136.8, 132.9, 131.7, 130.6, 130.1, 125.7, 123.6, 123.5, 78.2, 72.1, 71.1, 23.3, 22.0. HRMS *m/z* (EI) $[M - H]^-$ calcd for $C_{12}H_{12}Br_2O_2$: 345.9204, found: 345.8538.



5n

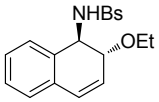
***Tert*-butyl ((1*R**,2*R**)-2-ethoxy-1,2-dihydronaphthalen-1-yl)carbamate (5n).** Following the general procedure (**B**), **5n** was obtained as a oil liquid (52.6 mg, 91%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 1H), 7.26 – 7.20 (m, 2H), 7.09 (dd, *J* = 6.9, 1.7 Hz, 1H), 6.56 (d, *J* = 9.7 Hz, 1H), 6.06 (dd, *J* = 9.6, 4.2 Hz, 1H), 5.09 – 4.88 (m, 1H), 4.62 (d, *J* = 7.8 Hz, 1H), 4.10 (t, *J* = 4.7 Hz, 1H), 3.84 – 3.57 (m, 2H), 1.46 (s, 9H), 1.19 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.4, 134.1, 132.0, 129.6, 128.2, 128.1, 127.0, 126.6, 79.6, 75.6, 64.2, 51.7, 28.4, 15.6. HRMS *m/z* (EI) $[M + Na]^+$ calcd for $C_{17}H_{23}NNaO_3$: 312.1576, found: 312.1573.



5o

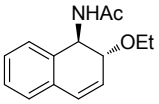
***Tert*-butyl ((1*R**,2*R**)-2-(3-hydroxypropoxy)-1,2-dihydronaphthalen-1-yl)carbamate (5o).** Following the general procedure (**B**), **5o** was obtained as a white solid (51.1 mg, 80%). m.p. 100–102 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 1H), 7.25 – 7.17 (m, 2H), 7.10 – 7.05 (m, 1H), 6.53 (d, *J* = 9.7 Hz, 1H), 6.04 (dd, *J* = 9.7, 3.8 Hz, 1H), 5.01

(t, J = 7.5 Hz, 1H), 4.75 (s, 1H), 4.22 – 4.06 (m, 1H), 3.79 (dt, J = 10.8, 7.1 Hz, 2H), 3.68 (t, J = 5.3 Hz, 2H), 2.44 (s, 1H), 1.88 – 1.73 (m, 2H), 1.45 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.6, 133.9, 132.0, 129.6, 128.2, 127.7, 126.9, 126.4, 79.8, 76.5, 66.7, 60.9, 51.8, 32.4, 28.3. HRMS *m/z* (EI) $[M + Na]^+$ calcd for $C_{18}H_{25}NNaO_4$: 342.1681, found: 342.1679.



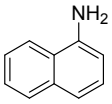
5p

4-Bromo-*N*-((1*R,2*R**)-2-ethoxy-1,2-dihydronaphthalen-1-yl)benzenesulfonamide (5p).** Following the general procedure (**B**), **5p** was obtained as a oil liquid (74.9 mg, 92%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 – 7.70 (m, 2H), 7.69 – 7.52 (m, 2H), 7.22 (td, J = 7.5, 1.2 Hz, 1H), 7.12 (td, J = 7.5, 1.3 Hz, 1H), 7.07 (d, J = 7.4 Hz, 1H), 6.98 (d, J = 7.5 Hz, 1H), 6.55 (d, J = 9.7 Hz, 1H), 6.01 (dd, J = 9.7, 4.2 Hz, 1H), 4.81 (d, J = 7.7 Hz, 1H), 4.55 (dd, J = 8.1, 5.7 Hz, 1H), 4.12 – 3.96 (m, 1H), 3.57 – 3.42 (m, 2H), 1.04 (t, J = 7.0 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 140.0, 132.7, 132.2, 131.9, 129.7, 128.8, 128.3, 128.0, 127.5, 127.2, 125.9, 75.6, 64.5, 55.3, 15.3. HRMS *m/z* (EI) $[M + Na]^+$ calcd for $C_{18}H_{18}BrNNaO_3S$: 430.0088, found: 430.0085.



5q

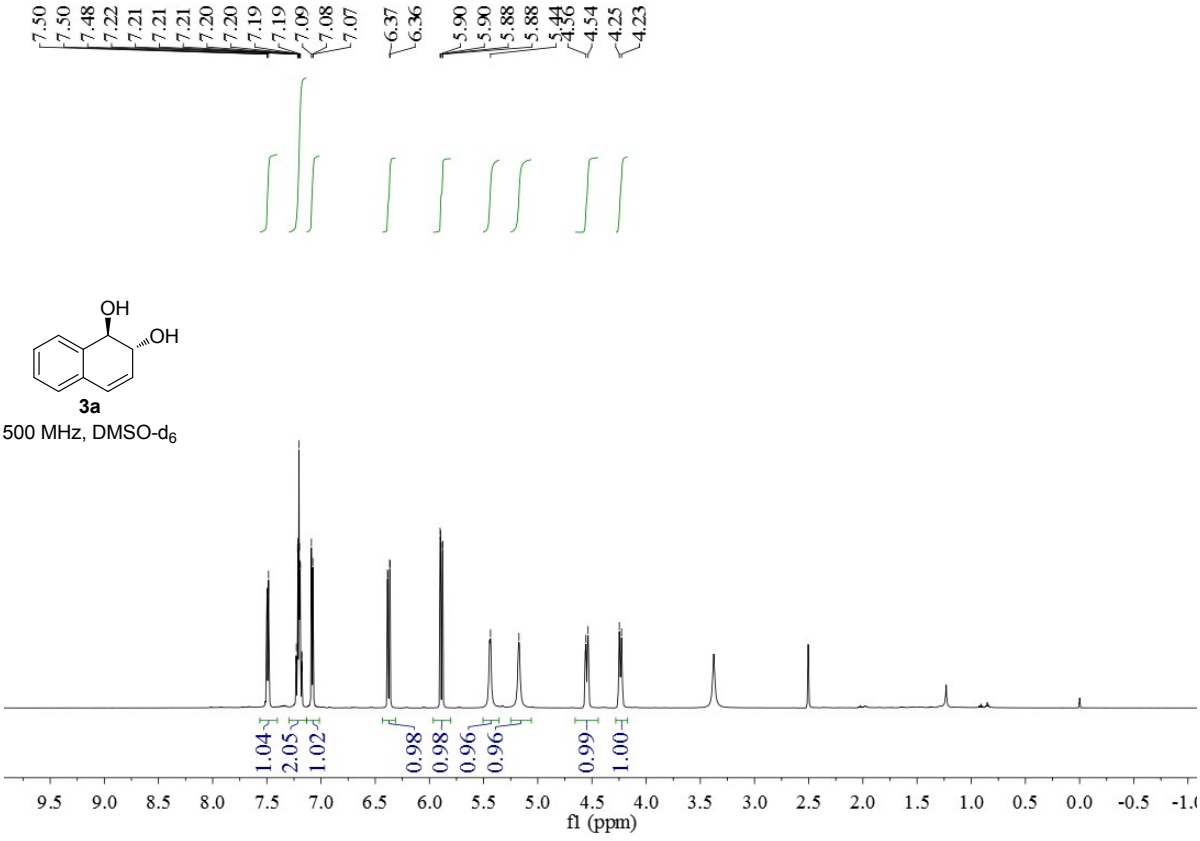
***N*-((1*R**,2*R**)-2-Ethoxy-1,2-dihydronaphthalen-1-yl)acetamide (5q).** Following the general procedure (**B**), **5q** was obtained as a oil liquid (43.5 mg, 94%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 – 7.16 (m, 3H), 7.08 (d, J = 7.2 Hz, 1H), 6.56 (d, J = 9.7 Hz, 1H), 6.01 (dd, J = 9.7, 4.5 Hz, 1H), 5.84 (s, 1H), 5.27 (dd, J = 8.1, 5.1 Hz, 1H), 4.04 (t, J = 4.7 Hz, 1H), 3.71 – 3.58 (m, 2H), 1.91 (s, 3H), 1.14 (t, J = 7.0 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.6, 133.4, 131.9, 129.7, 128.5, 128.3, 128.2, 127.0, 126.2, 74.5, 64.0, 50.1, 23.1, 15.5. HRMS *m/z* (EI) $[M + Na]^+$ calcd for $C_{14}H_{17}NNaO_2$: 254.1157, found: 254.1150.

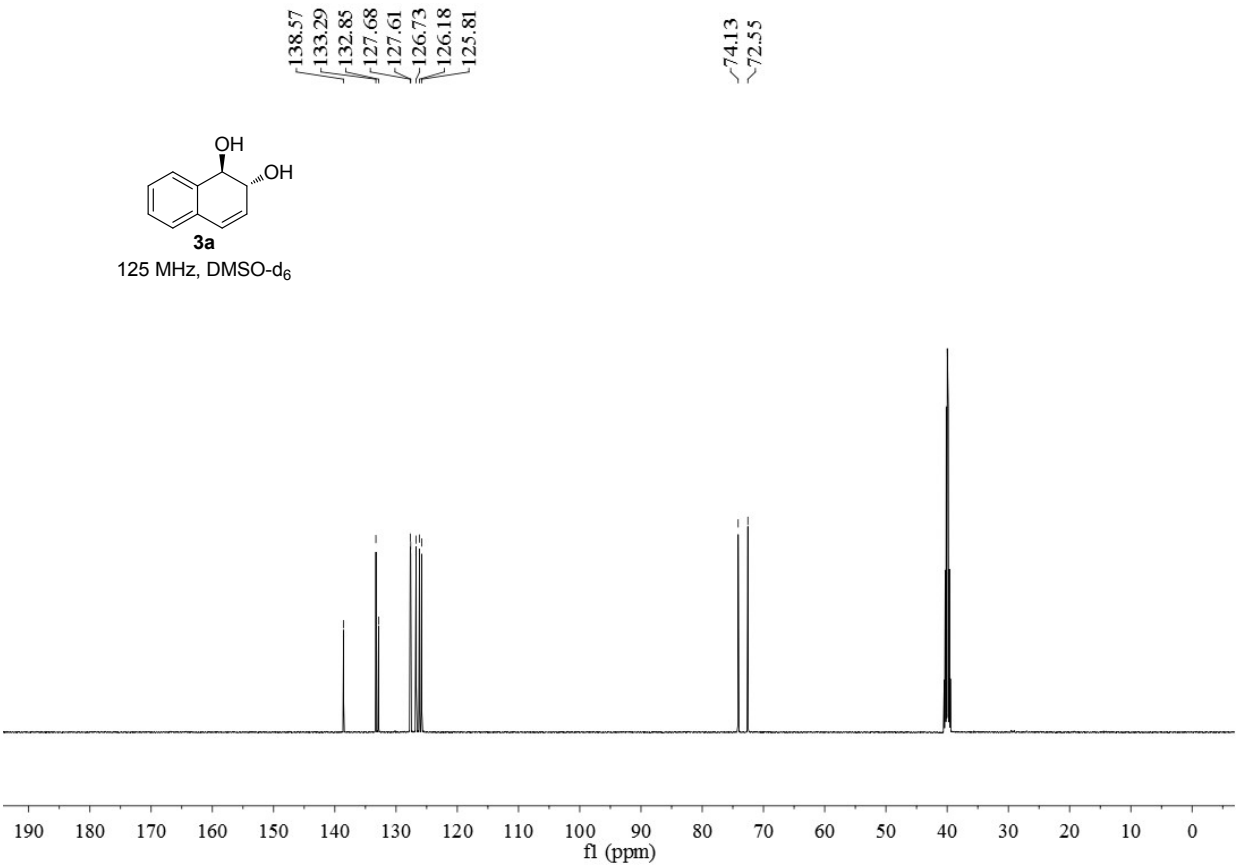


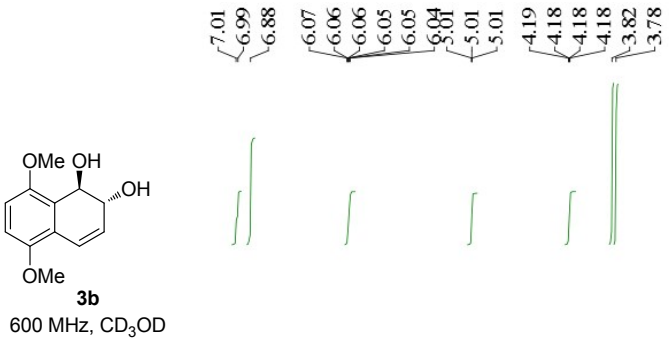
6

Naphthalen-1-amine1 (6). Following the general procedure (**C**), **6** was obtained as a red solid (16.6 mg, 58%). m.p. 48–50 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (td, J = 6.6, 2.2 Hz, 2H), 7.51 – 7.41 (m, 2H), 7.34 – 7.24 (m, 2H), 6.78 (dd, J = 6.9, 1.2 Hz, 1H). HRMS *m/z* (EI) $[M + H]^+$ calcd for $C_{10}H_{10}N$: 144.0813, found: 144.0808.

3. Copies of ^{1}H, ^{13}C and ^{19}F NMR spectra of **3a–k**, **5a–q** and ^{19}F NMR spectra for **3i** and **5d**

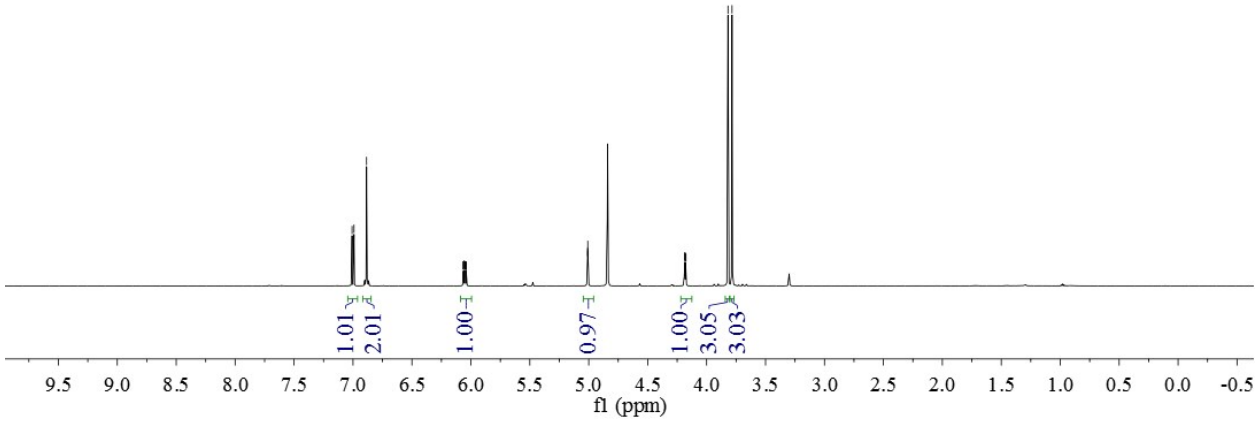


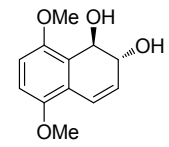




3b

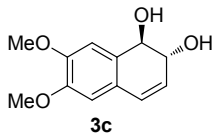
600 MHz, CD_3OD





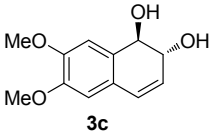
3b

150 MHz, CD_3OD



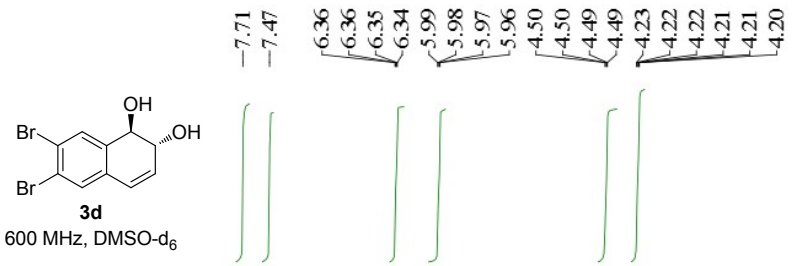
3c

600 MHz, CD_3OD



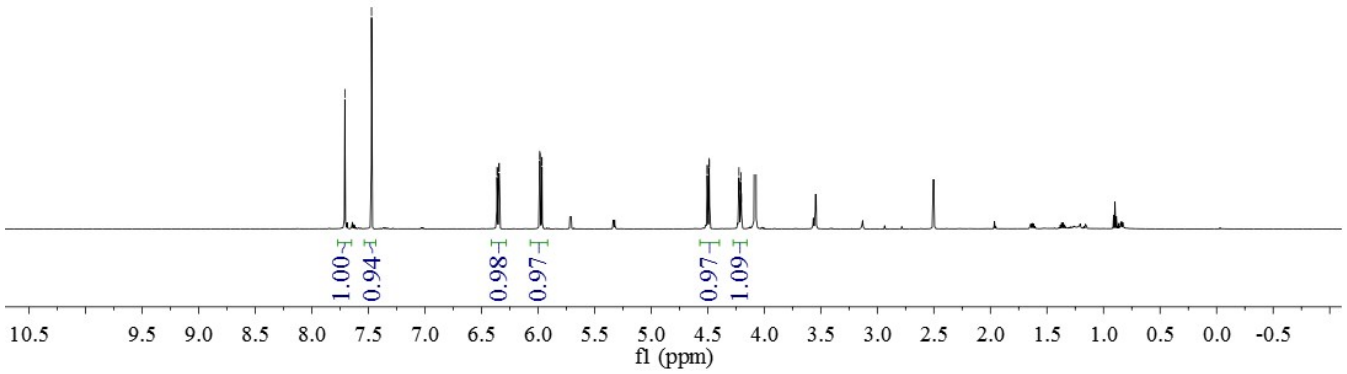
3c

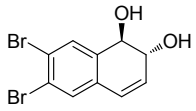
150 MHz, CD_3OD



3d

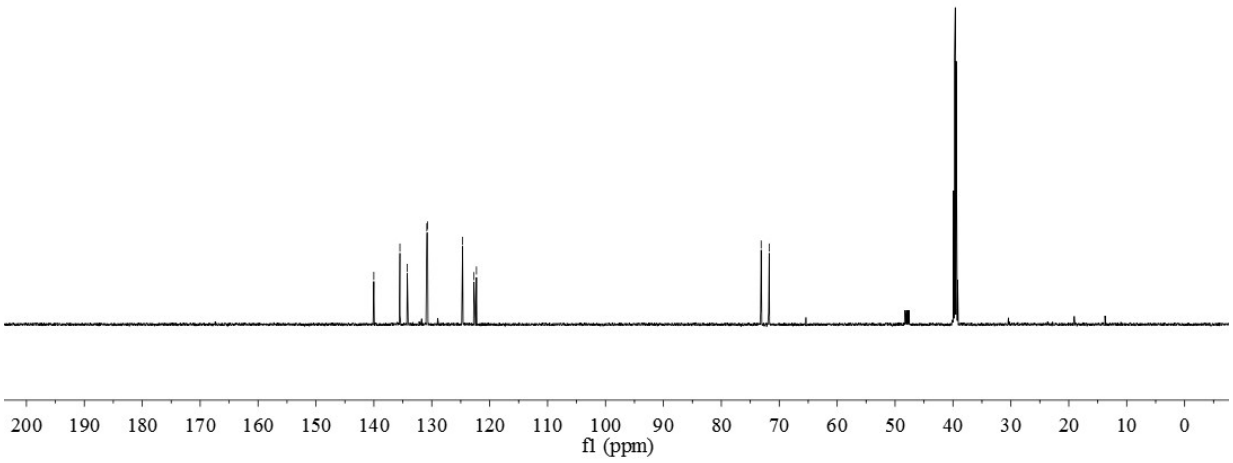
600 MHz, DMSO-d_6

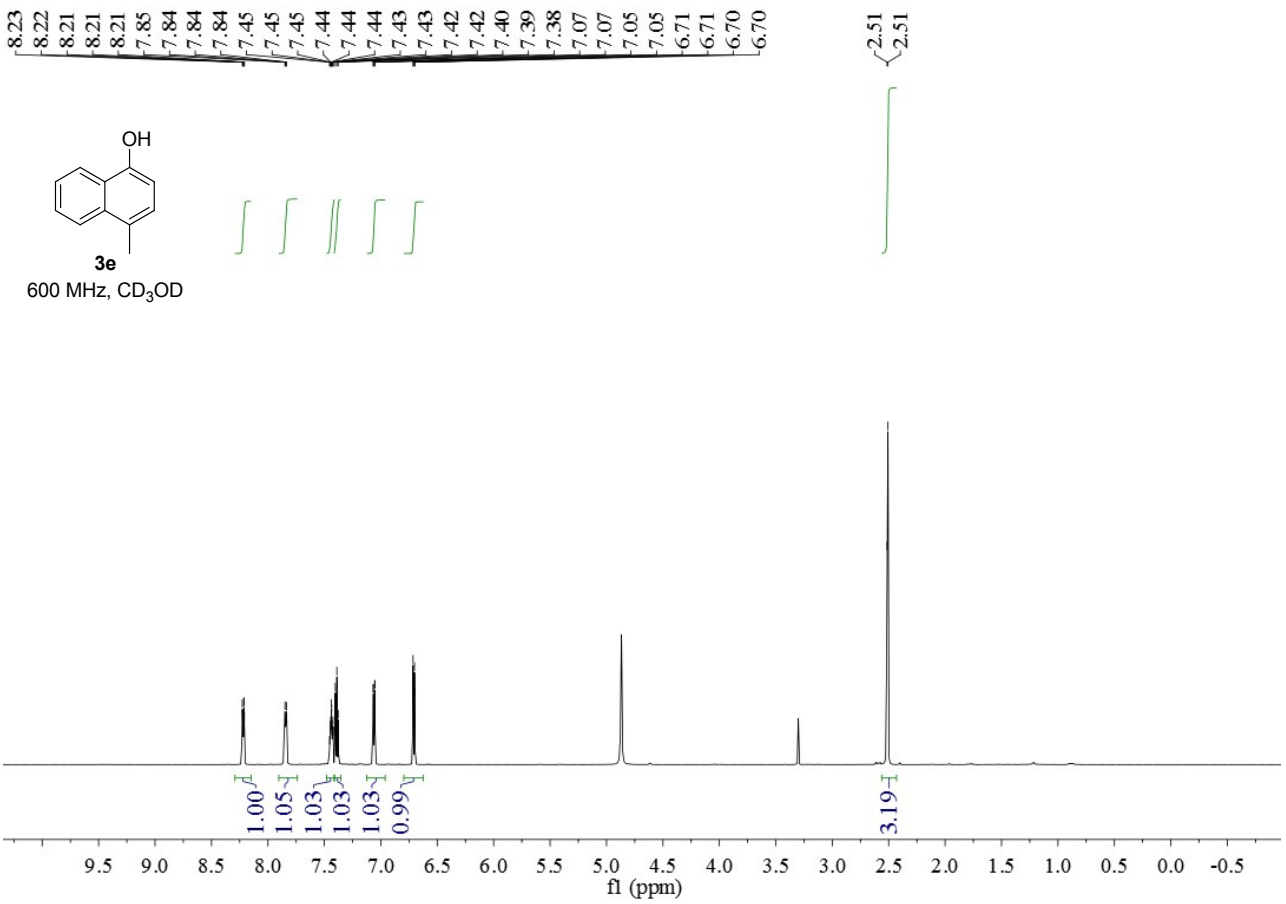


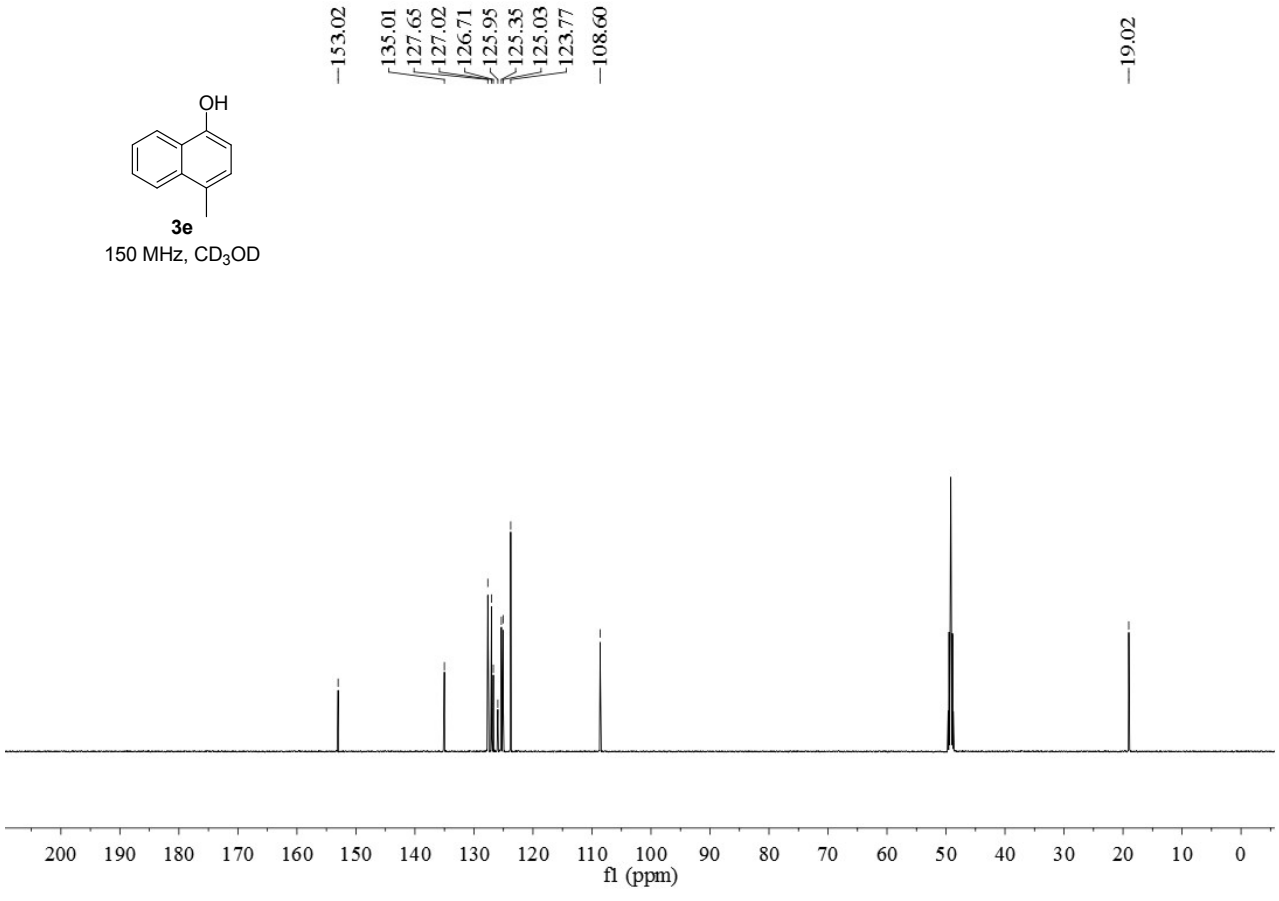


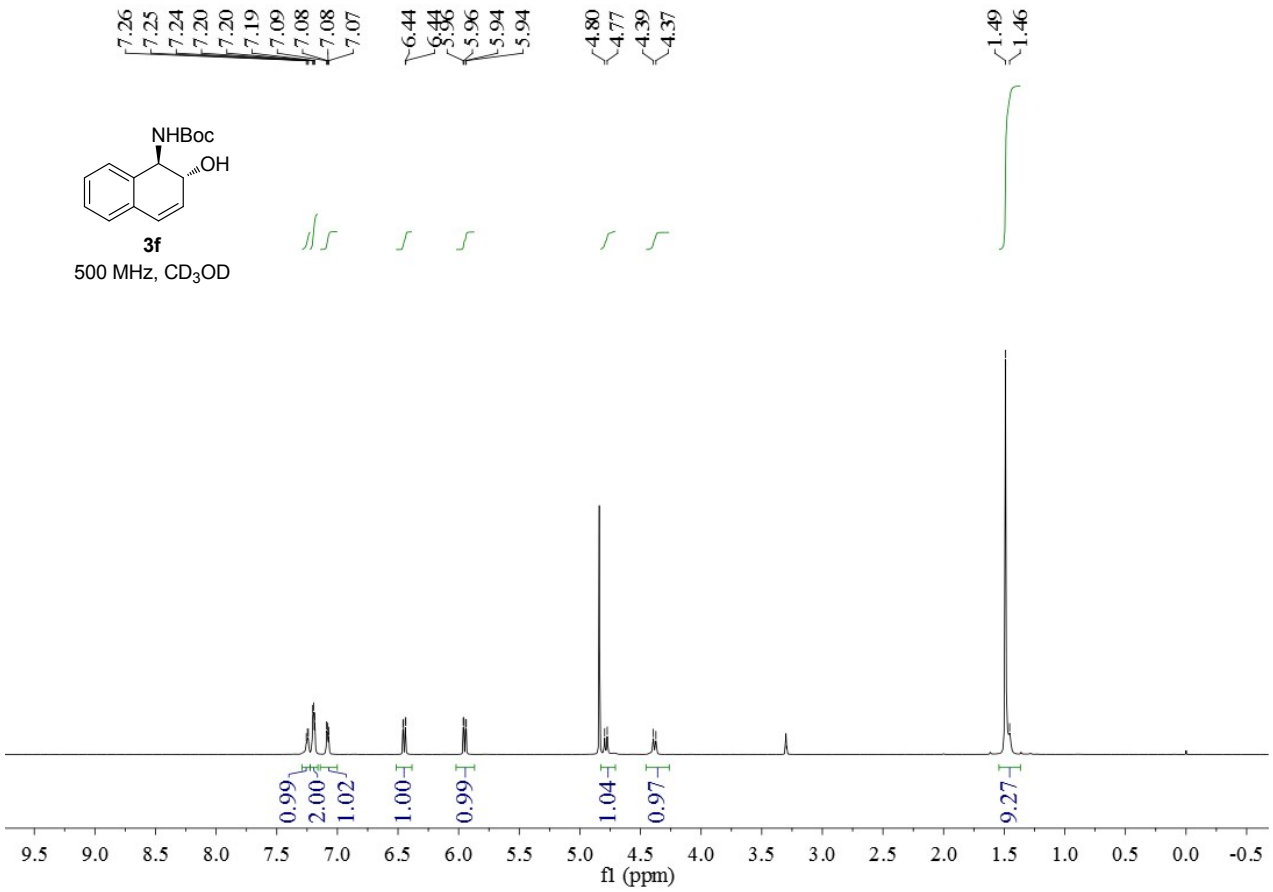
3d

150 MHz, DMSO-d_6

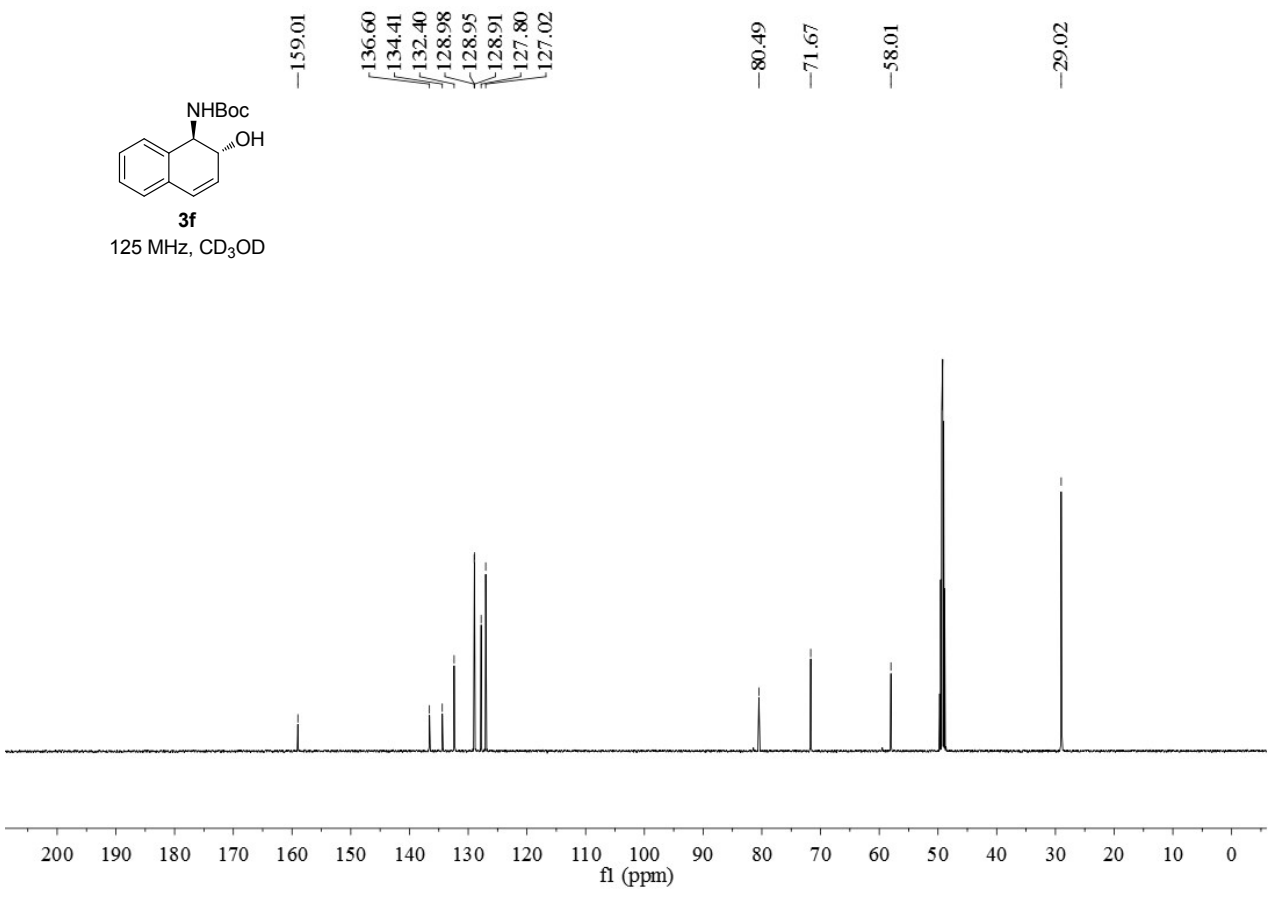



8.23
8.22
8.21
8.21
8.21
7.85
7.84
7.84
7.84
7.45
7.45
7.44
7.44
7.44
7.43
7.43
7.42
7.42
7.40
7.39
7.38
7.07
7.07
7.05
7.05
6.71
6.71
6.70
6.70
2.51
2.51
OH
3e
600 MHz, CD3OD
1.00
1.05
1.03
1.03
1.03
0.99
3.19
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

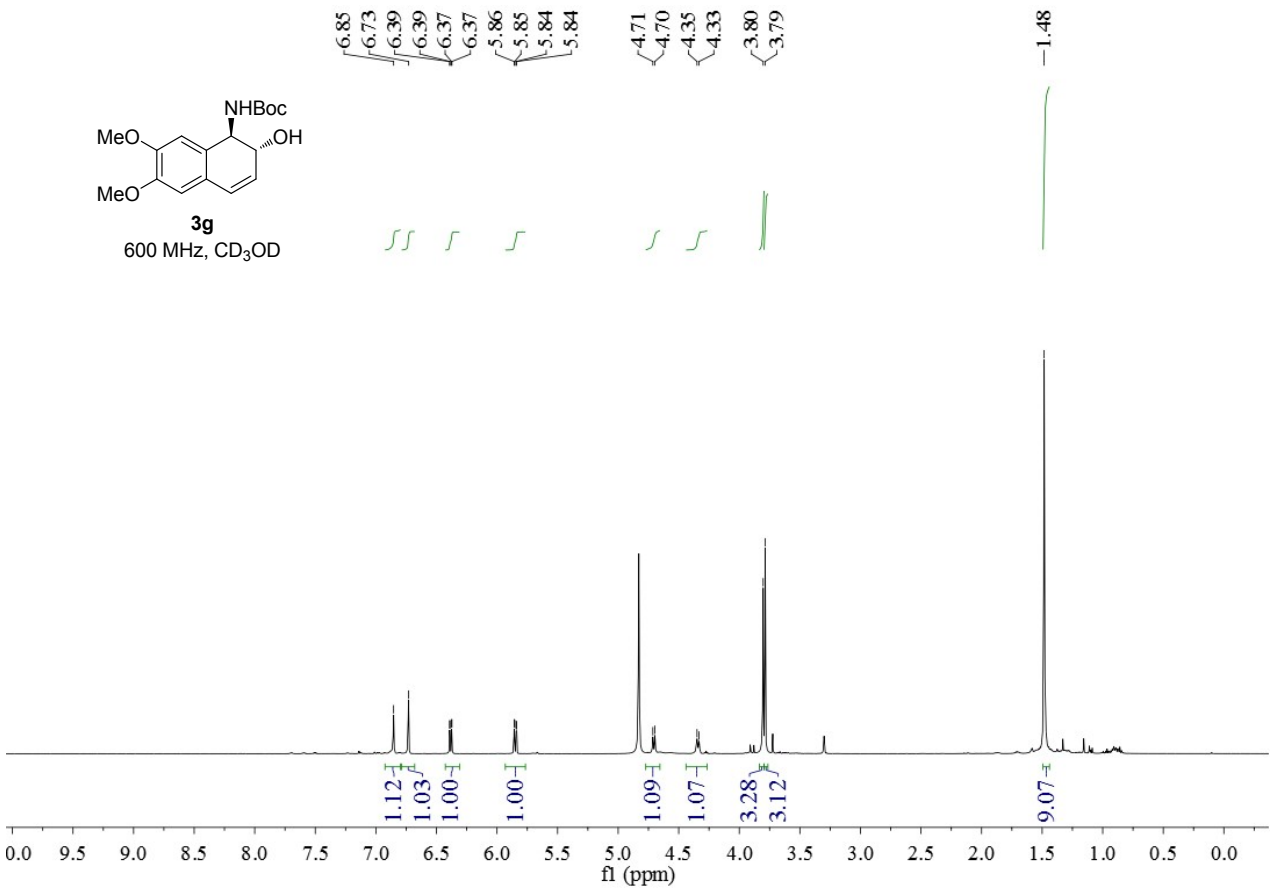

153.02
135.01
127.65
127.02
126.71
125.95
125.35
125.03
123.77
108.60
19.02
OH
3e
150 MHz, CD3OD
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



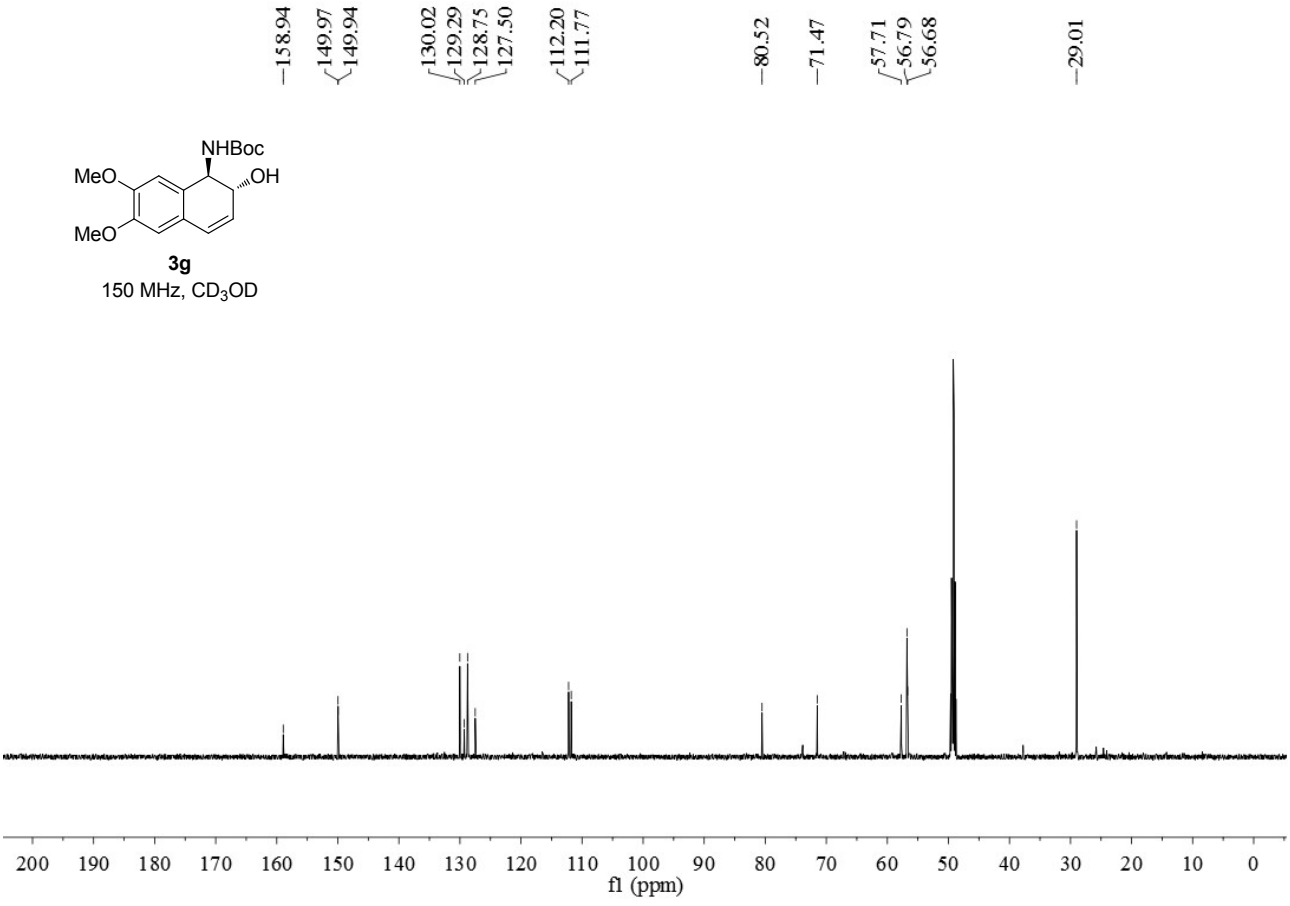
3f
500 MHz, CD_3OD



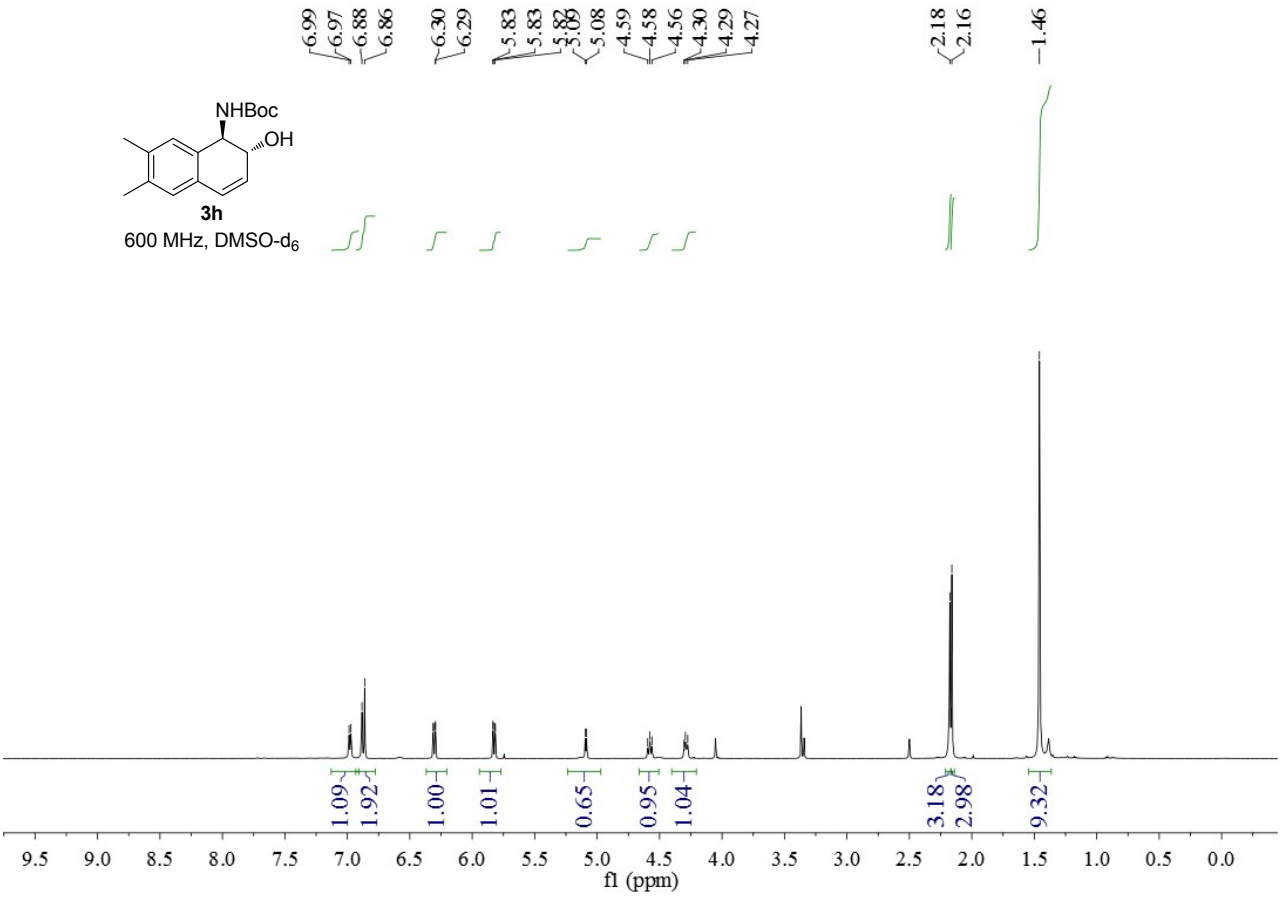
3f
125 MHz, CD_3OD

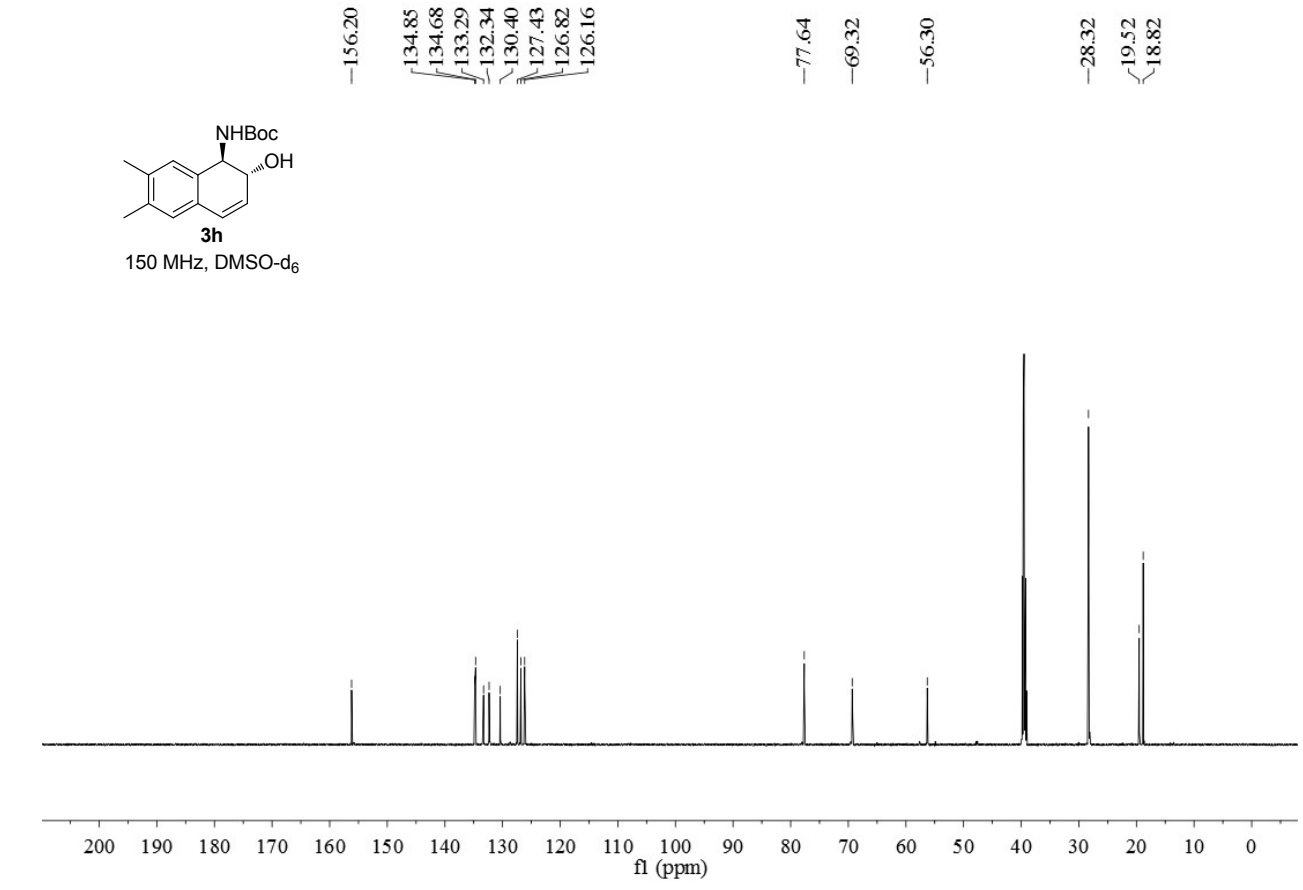


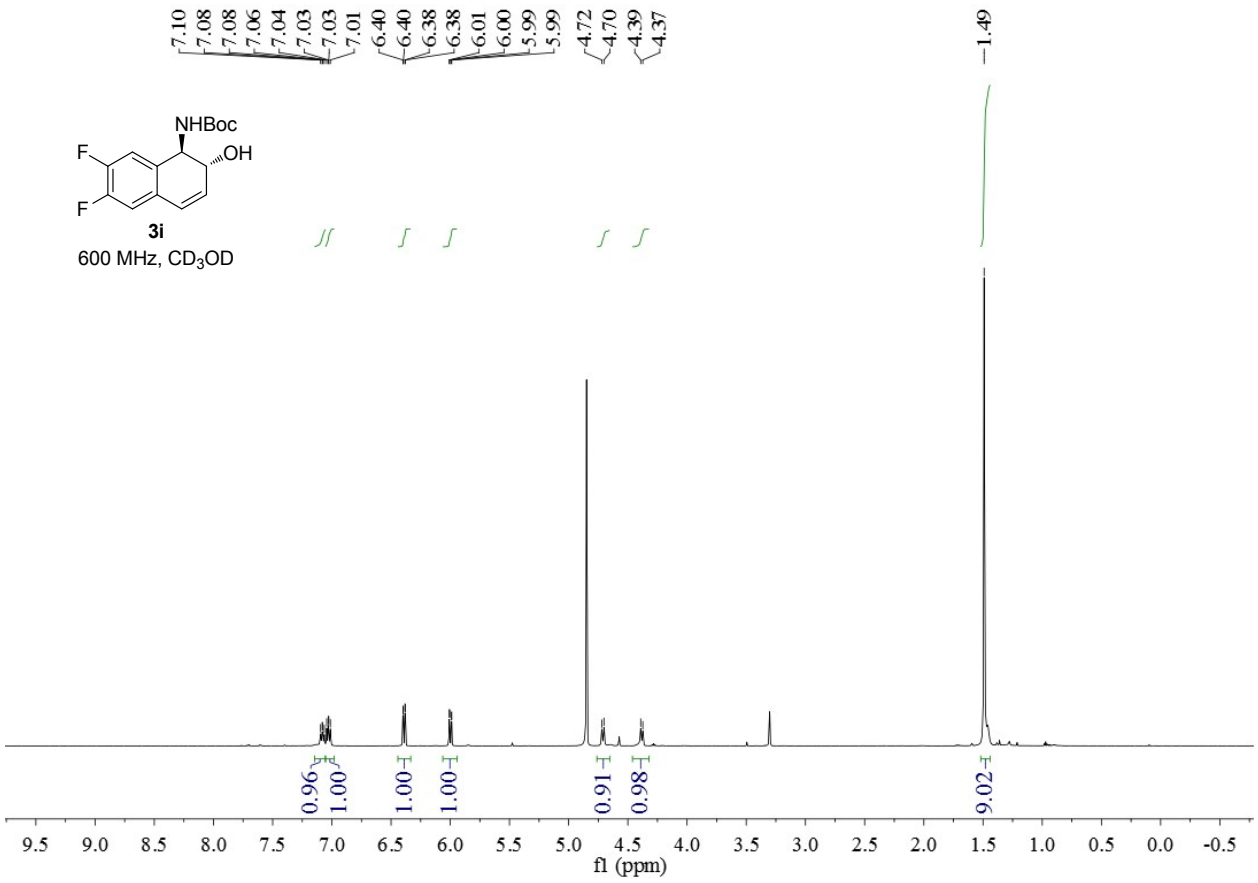
3g
600 MHz, CD_3OD

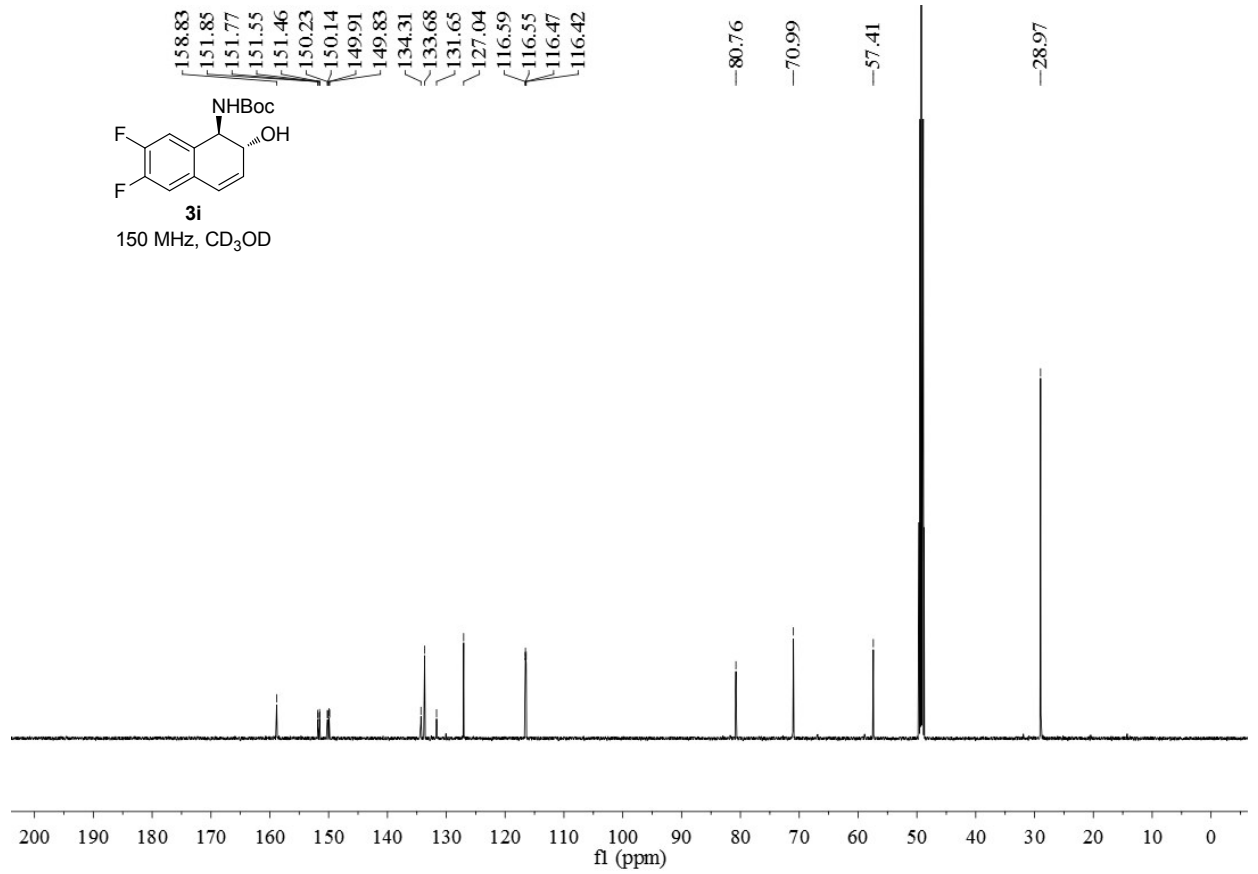


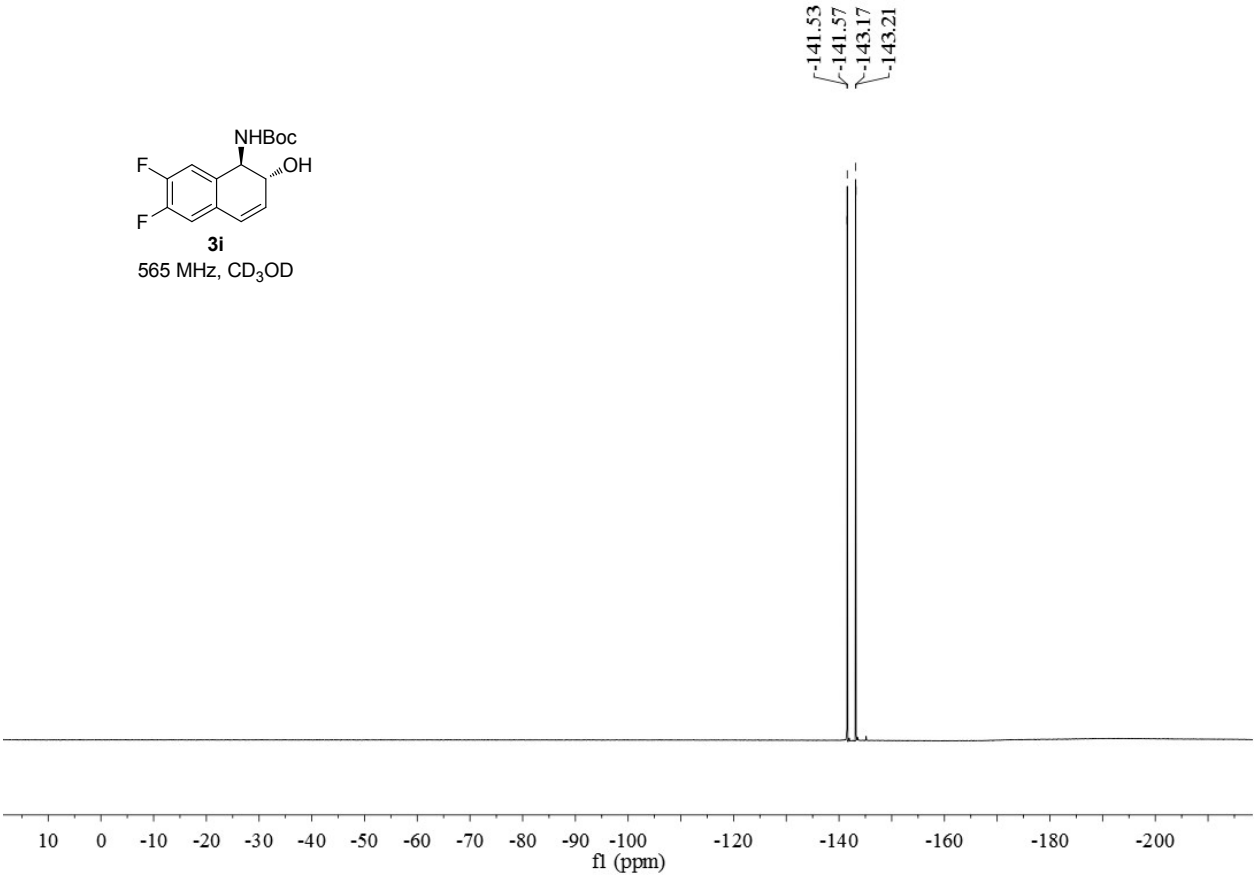
3g
150 MHz, CD_3OD

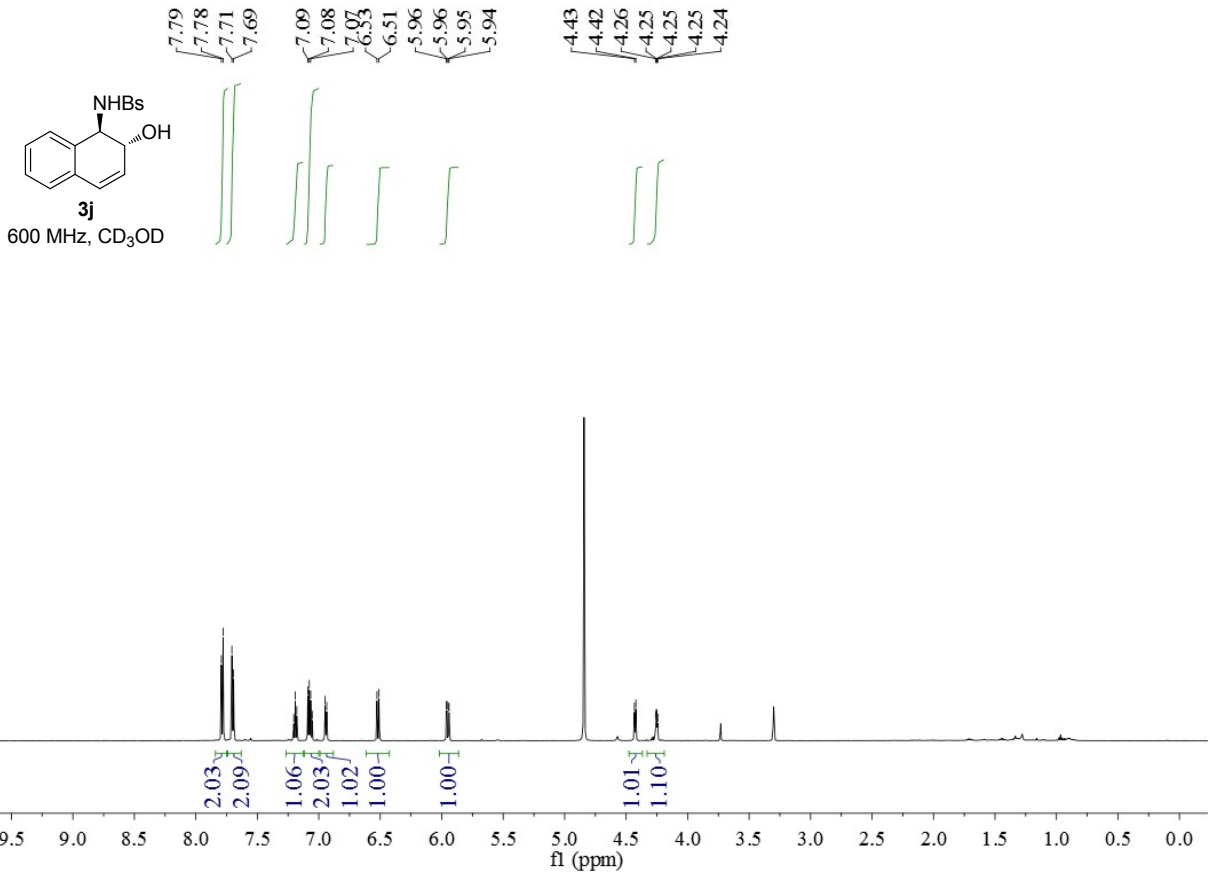

NHBoc
OH
3h
600 MHz, DMSO-d6
6.99
6.97
6.88
6.86
6.30
6.29
5.83
5.83
5.08
4.59
4.58
4.56
4.30
4.29
4.27
2.18
2.16
1.46
1.09
1.92
1.00
1.01
0.65
0.95
1.04
3.18
2.98
9.32
f1 (ppm)

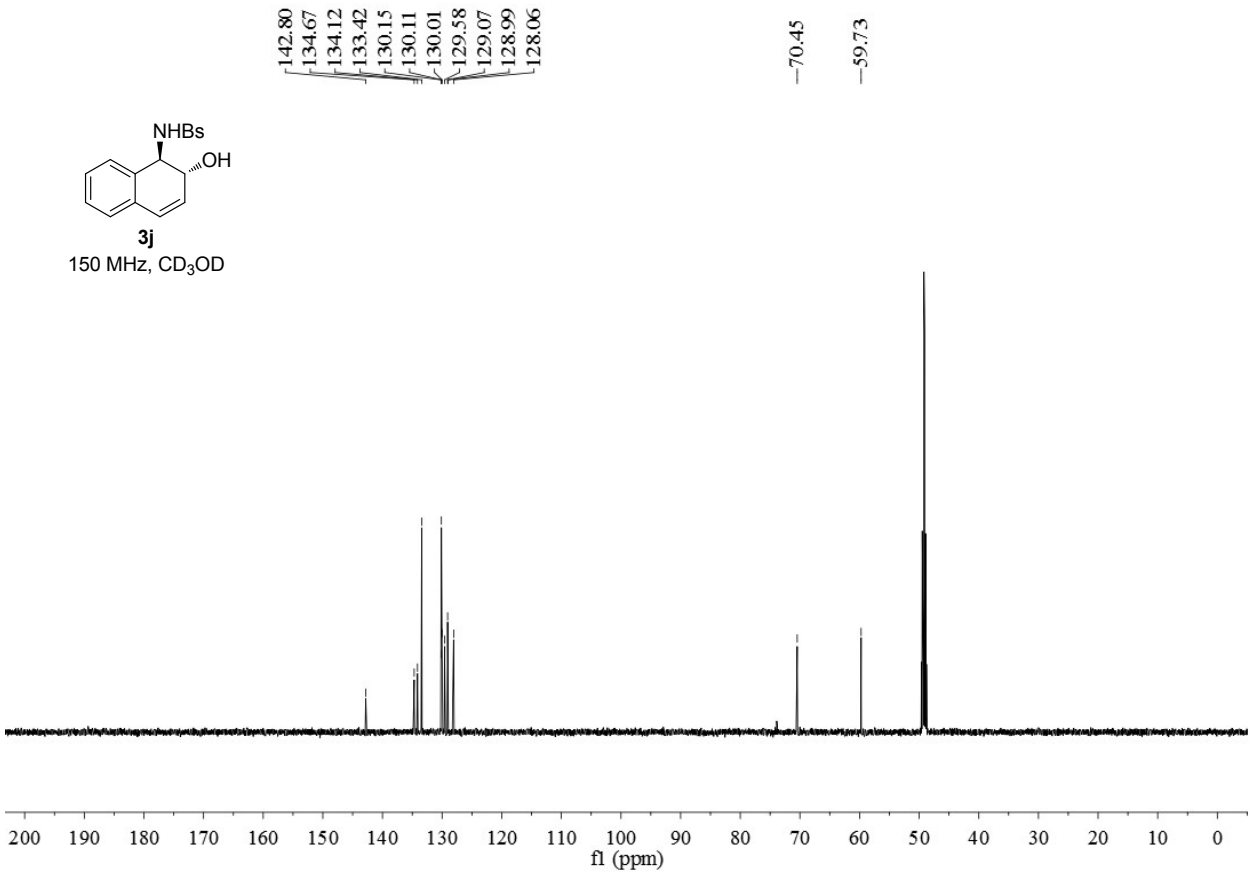

NHBoc
OH
3h
150 MHz, DMSO-d6
156.20
134.85
134.68
133.29
132.34
130.40
127.43
126.82
126.16
77.64
69.32
56.30
28.32
19.52
18.82
f1 (ppm)

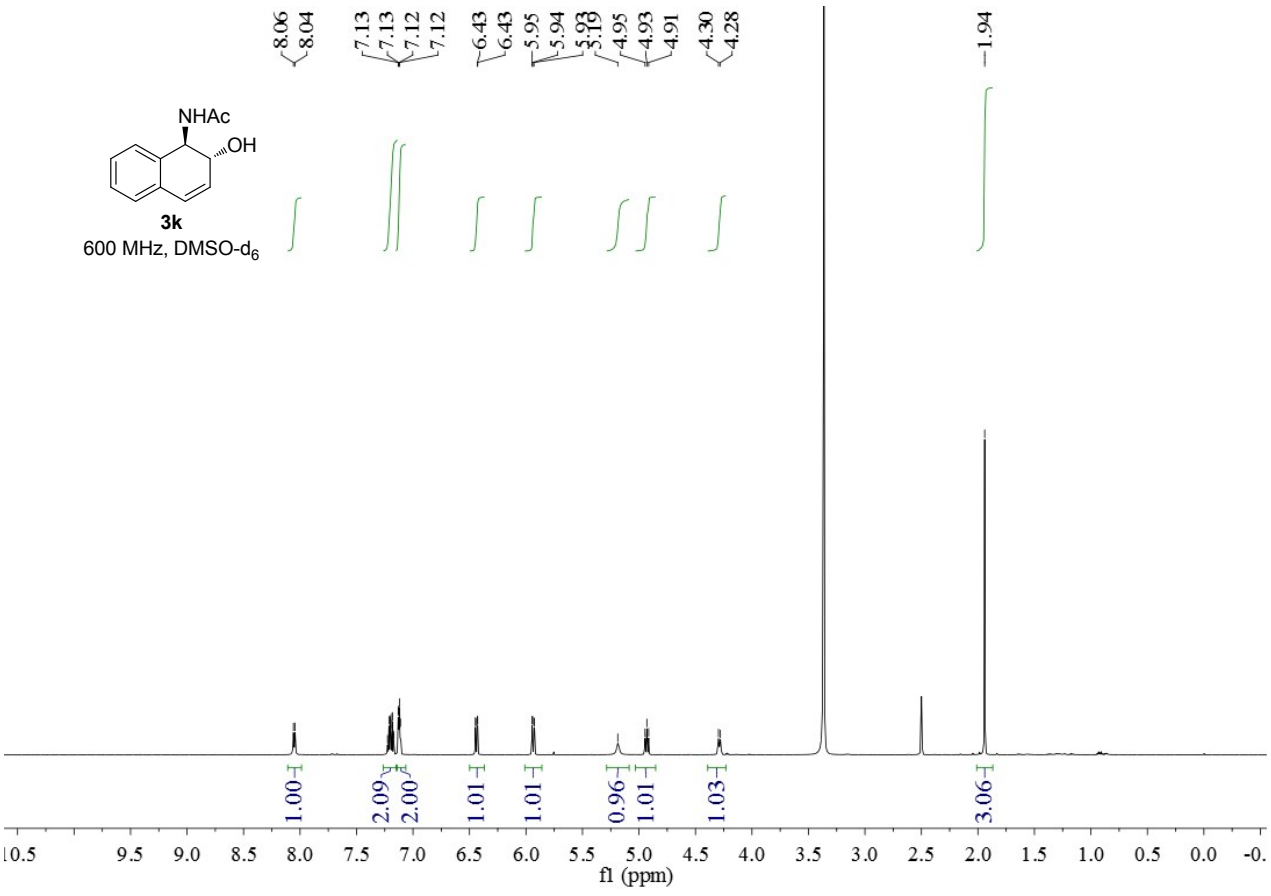

7.10
7.08
7.08
7.06
7.04
7.03
7.03
7.01
6.40
6.40
6.38
6.38
6.01
6.00
5.99
5.99
4.72
4.70
4.39
4.37
1.49
NHBoc
F
OH
F
3i
600 MHz, CD3OD
0.96
1.00
1.00
1.00
0.91
0.98
9.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

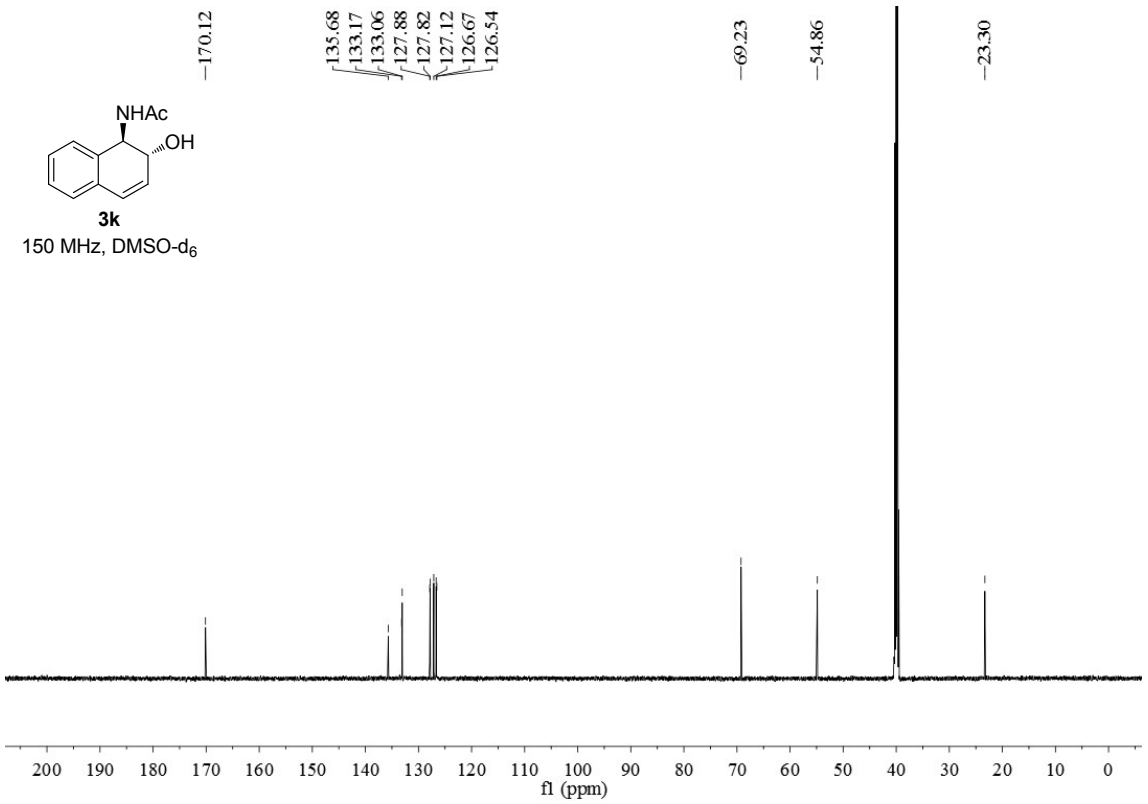

158.83
151.85
151.77
151.55
151.46
150.23
150.14
149.91
149.83
134.31
133.68
131.65
127.04
116.59
116.55
116.47
116.42
80.76
70.99
57.41
28.97
NHBoc
F
OH
F
3i
150 MHz, CD3OD
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

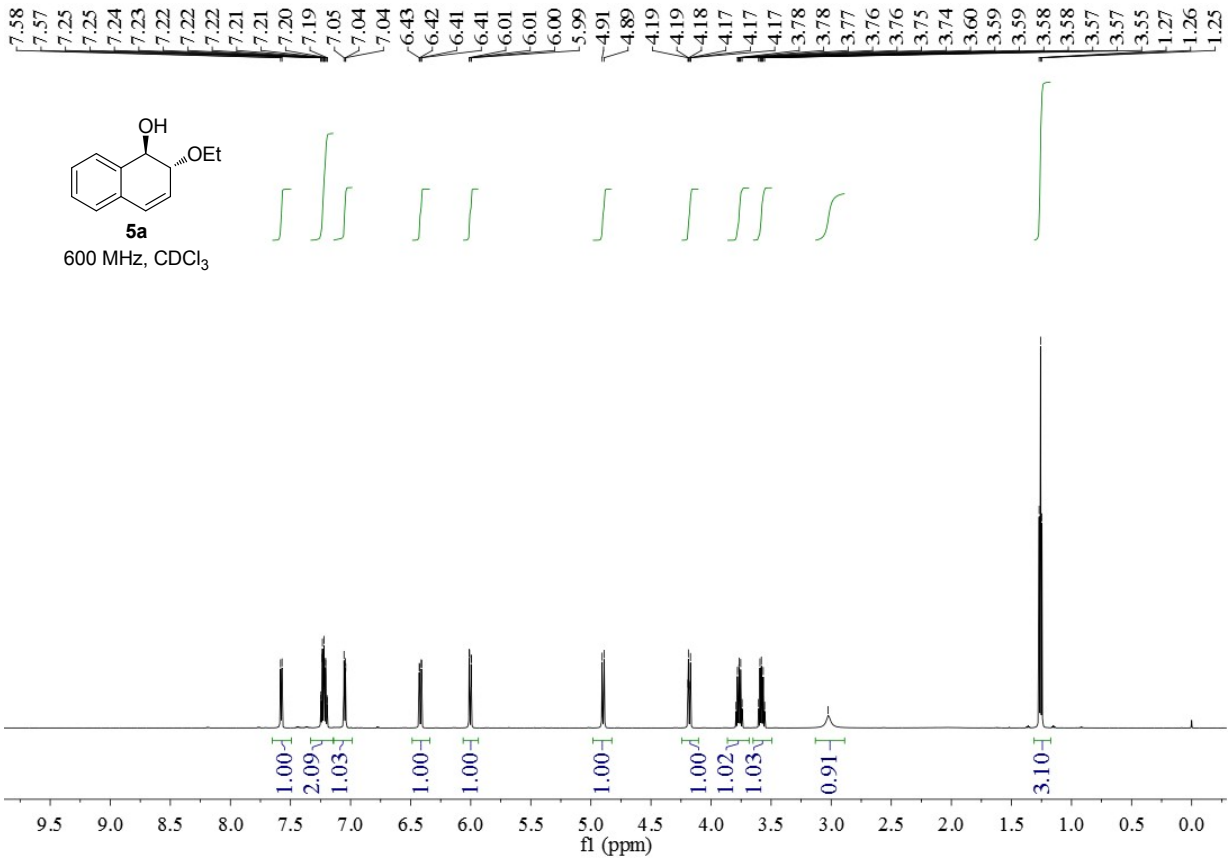

-141.53
-141.57
-143.17
-143.21
NHBoc
OH
F
F
3i
565 MHz, CD3OD
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

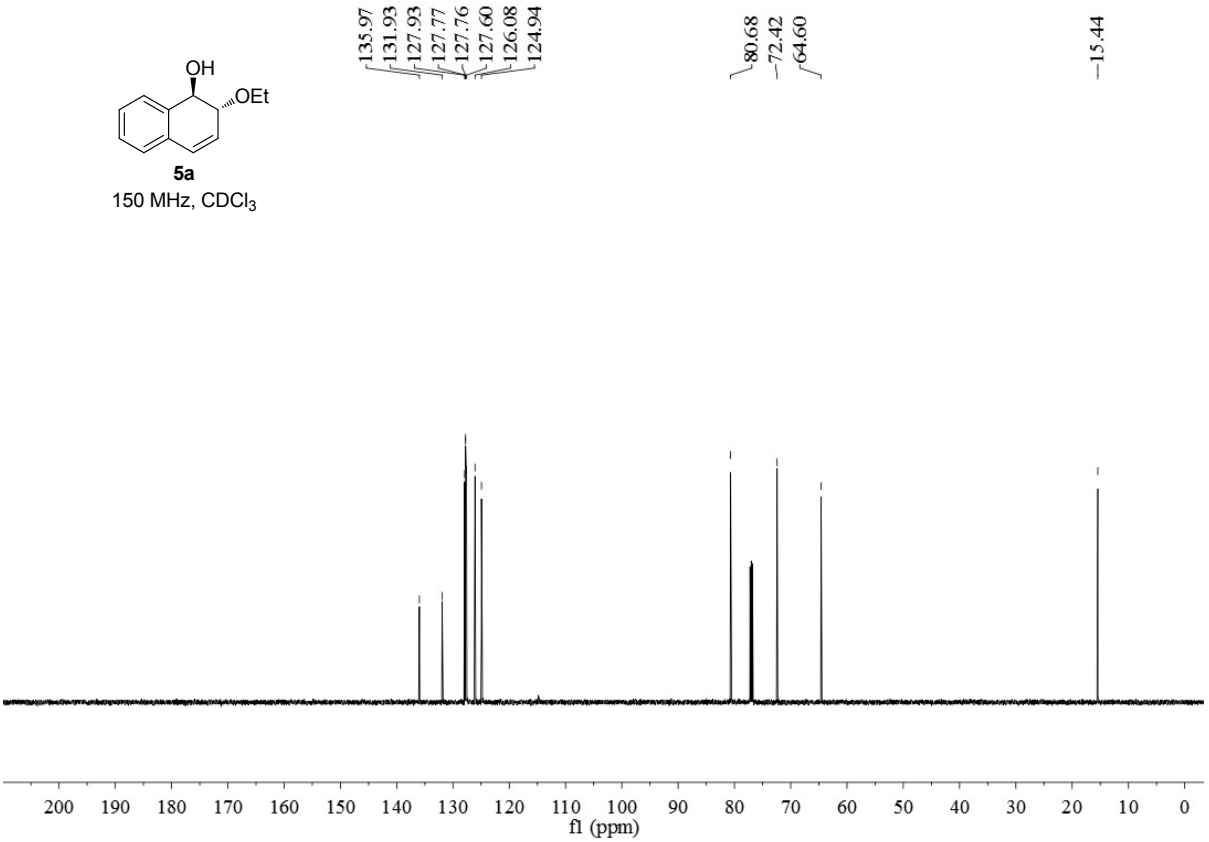

7.79
7.78
7.71
7.69
7.09
7.08
7.07
6.53
6.51
5.96
5.96
5.95
5.94
4.43
4.42
4.26
4.25
4.25
4.25
4.24
NHBs
OH
3j
600 MHz, CD3OD
2.03
2.09
1.06
2.03
1.02
1.00
1.00
1.01
1.10
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

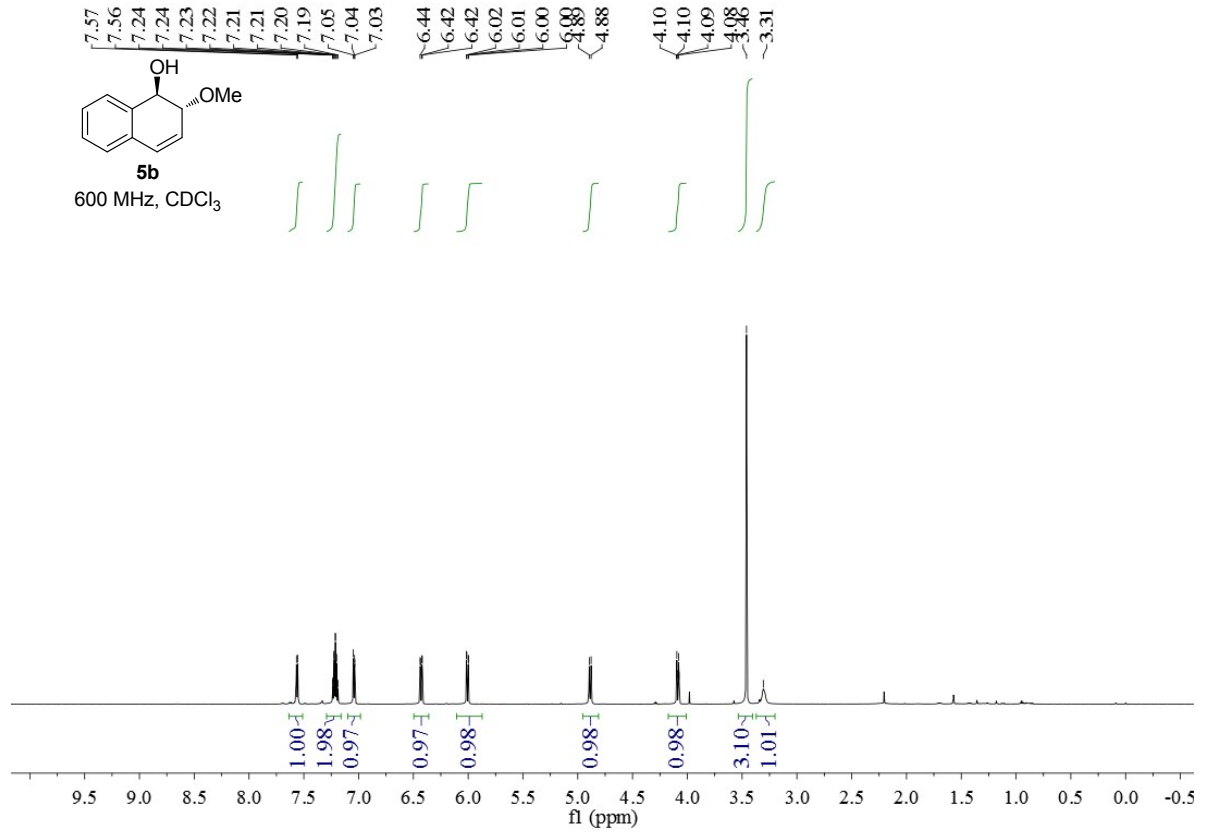

142.80
134.67
134.12
133.42
130.15
130.11
130.01
129.58
129.07
128.99
128.06
70.45
59.73
NHBs
OH
3j
150 MHz, CD3OD
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

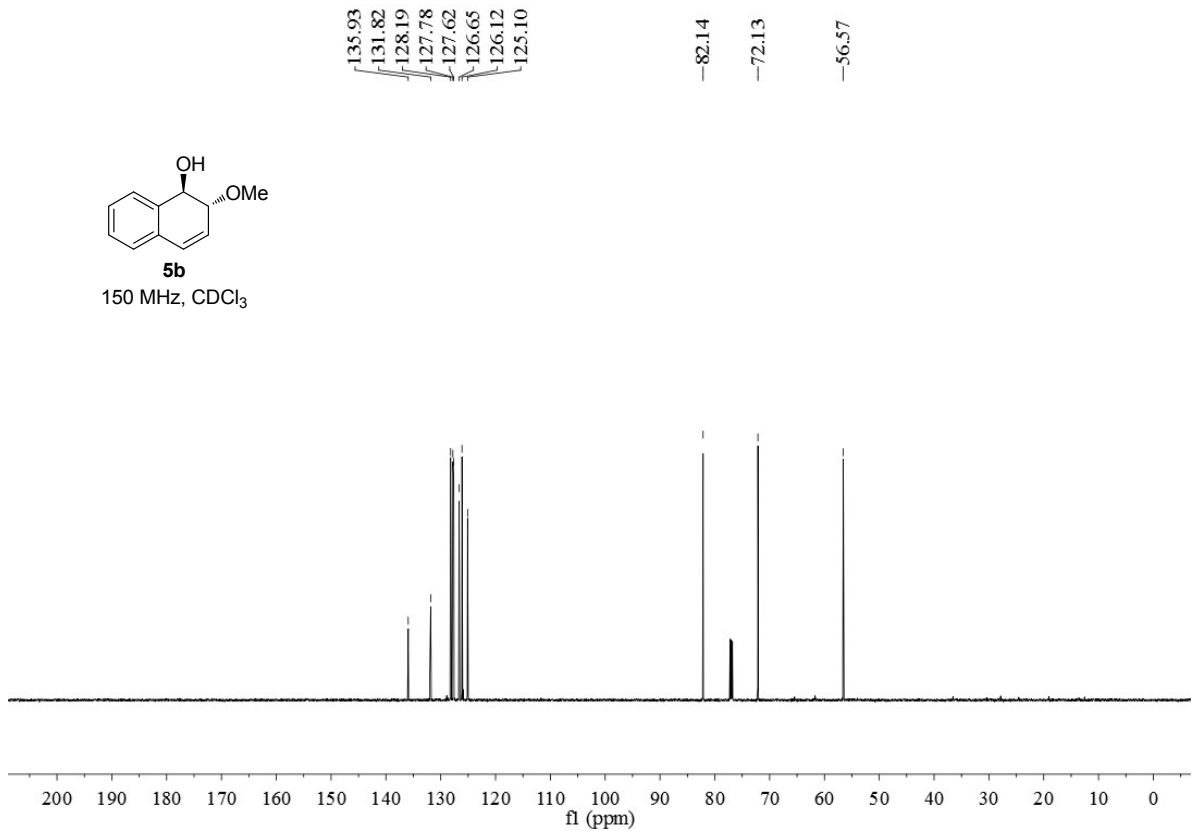

8.06
8.04
7.13
7.13
7.12
7.12
6.43
6.43
5.95
5.94
5.93
5.19
4.95
4.93
4.91
4.30
4.28
1.94
NHAc
OH
3k
600 MHz, DMSO-d6
1.00
2.09
2.00
1.01
1.01
0.96
1.01
1.03
3.06
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

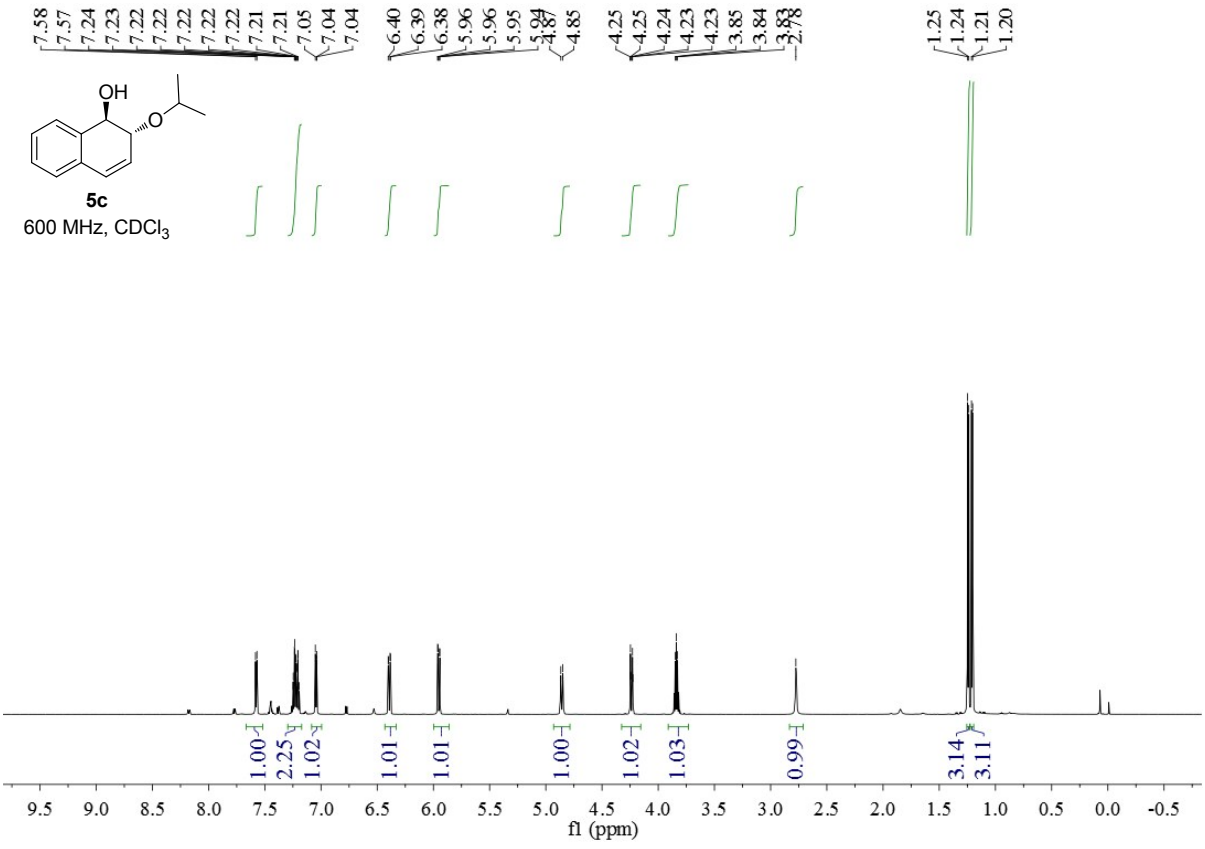

170.12
135.68
133.17
133.06
127.88
127.82
127.12
126.67
126.54
69.23
54.86
23.30
NHAc
OH
3k
150 MHz, DMSO-d6
fl (ppm)

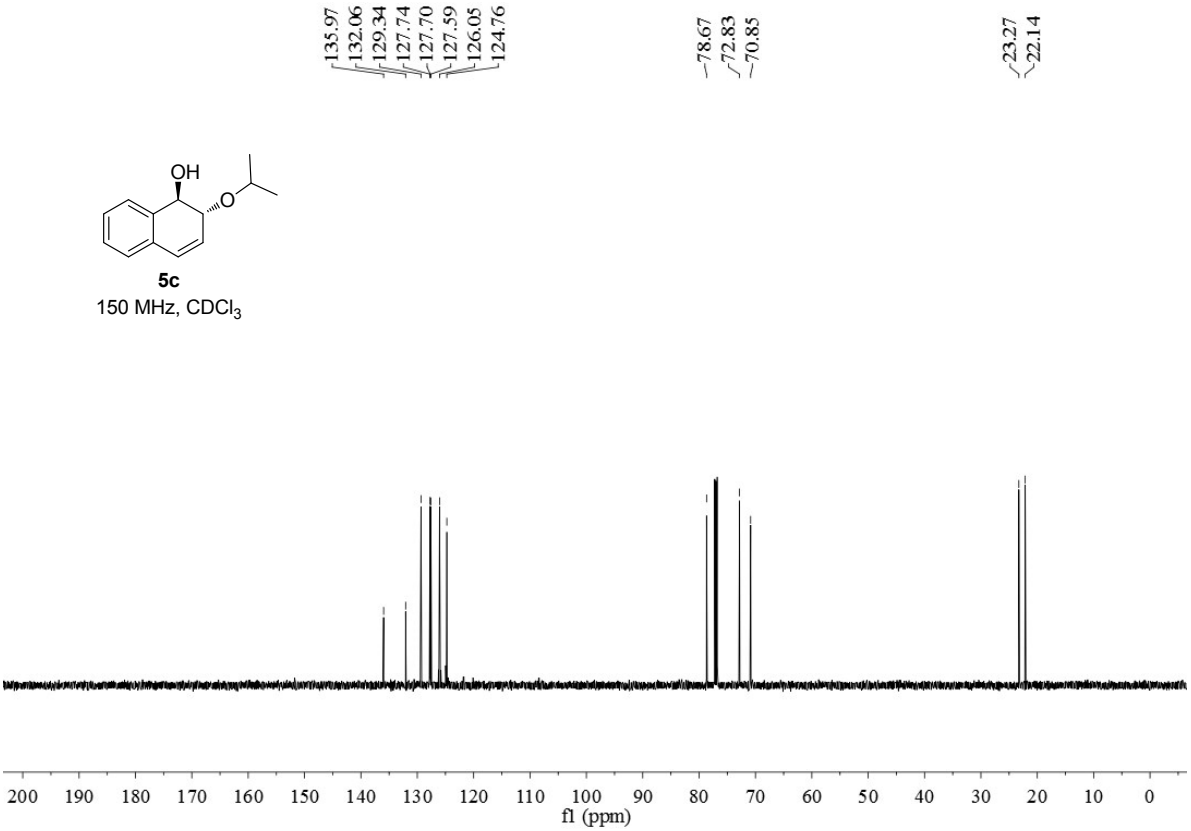

OH
OEt
5a
600 MHz, CDCl3
1.00
2.09
1.03
1.00
1.00
1.00
1.00
1.02
1.03
0.91
3.10
fl (ppm)

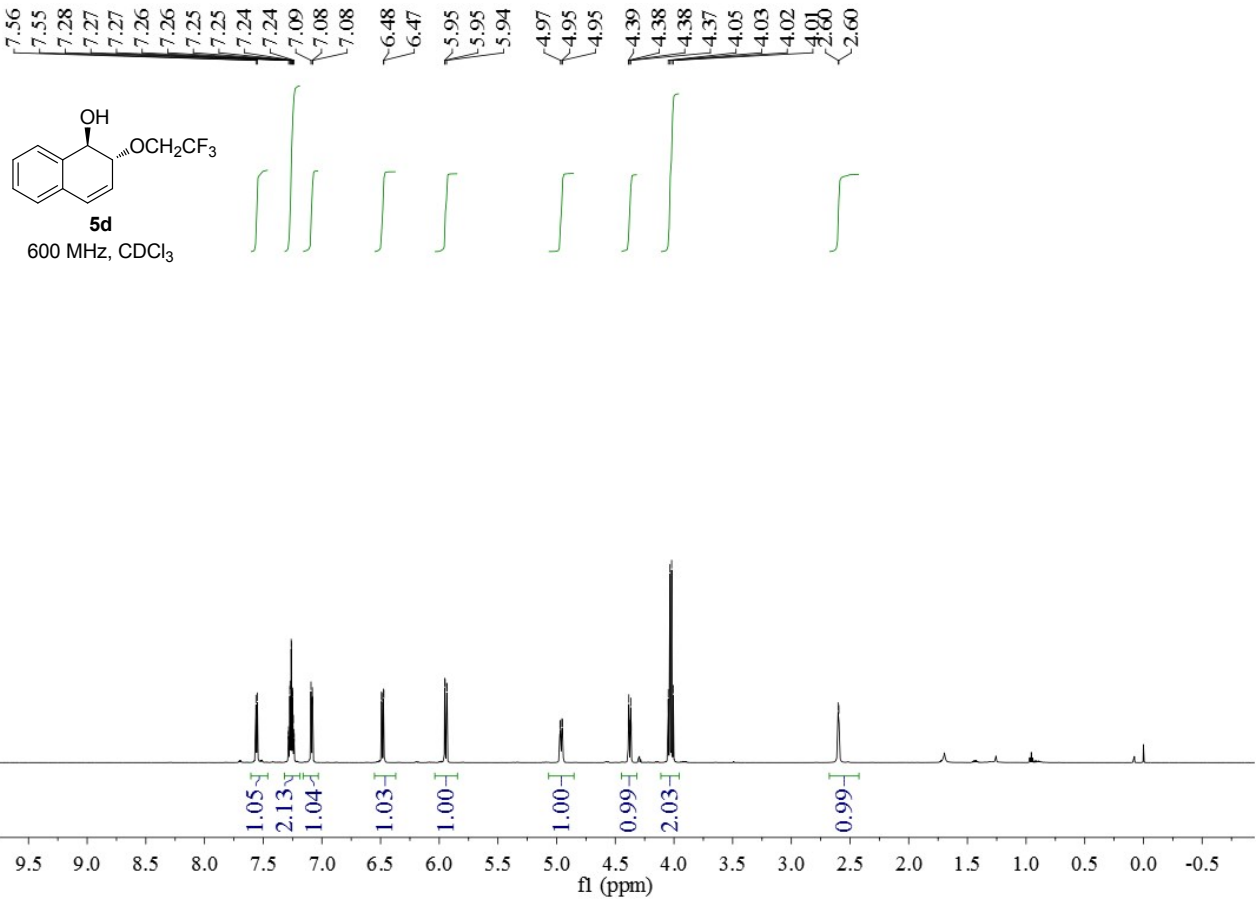

OH
OEt
5a
150 MHz, CDCl3
135.97
131.93
127.93
127.77
127.76
127.60
126.08
124.94
80.68
72.42
64.60
15.44
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

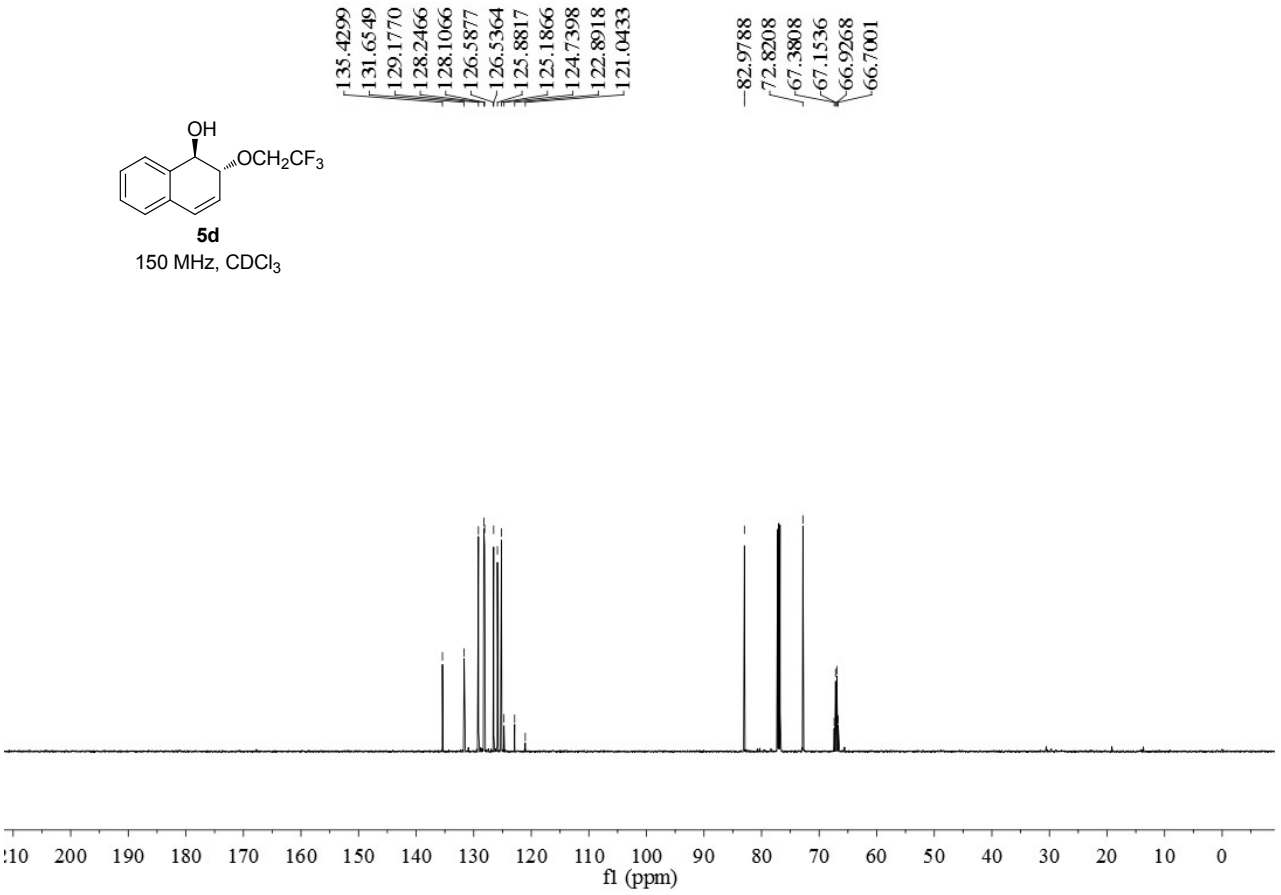

7.57
7.56
7.24
7.24
7.23
7.22
7.21
7.21
7.20
7.19
7.05
7.04
7.03
6.44
6.42
6.42
6.02
6.01
6.00
4.89
4.88
4.10
4.10
4.09
4.08
3.46
3.31
OH
OMe
5b
600 MHz, CDCl3
1.00
1.98
0.97
0.97
0.98
0.98
0.98
3.10
1.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


135.93
131.82
128.19
127.78
127.62
126.65
126.12
125.10
82.14
72.13
56.57
OH
OMe
5b
150 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.58
7.57
7.24
7.23
7.22
7.22
7.22
7.22
7.22
7.21
7.21
7.05
7.04
7.04
6.40
6.39
6.38
5.96
5.96
5.95
4.87
4.85
4.25
4.25
4.24
4.23
4.23
3.85
3.84
3.83
2.78
1.25
1.24
1.21
1.20
OH
O
5c
600 MHz, CDCl3
1.00
2.25
1.02
1.01
1.01
1.00
1.02
1.03
0.99
3.14
3.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


135.97
132.06
129.34
127.74
127.70
127.59
126.05
124.76
78.67
72.83
70.85
23.27
22.14
OH
O
5c
150 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.56
7.55
7.28
7.27
7.27
7.26
7.26
7.25
7.25
7.24
7.24
7.09
7.08
7.08
6.48
6.47
5.95
5.95
5.94
4.97
4.95
4.95
4.39
4.38
4.38
4.37
4.05
4.03
4.02
4.01
2.00
2.60
OH
OCH2CF3
5d
600 MHz, CDCl3
1.05
2.13
1.04
1.03
1.00
1.00
0.99
2.03
0.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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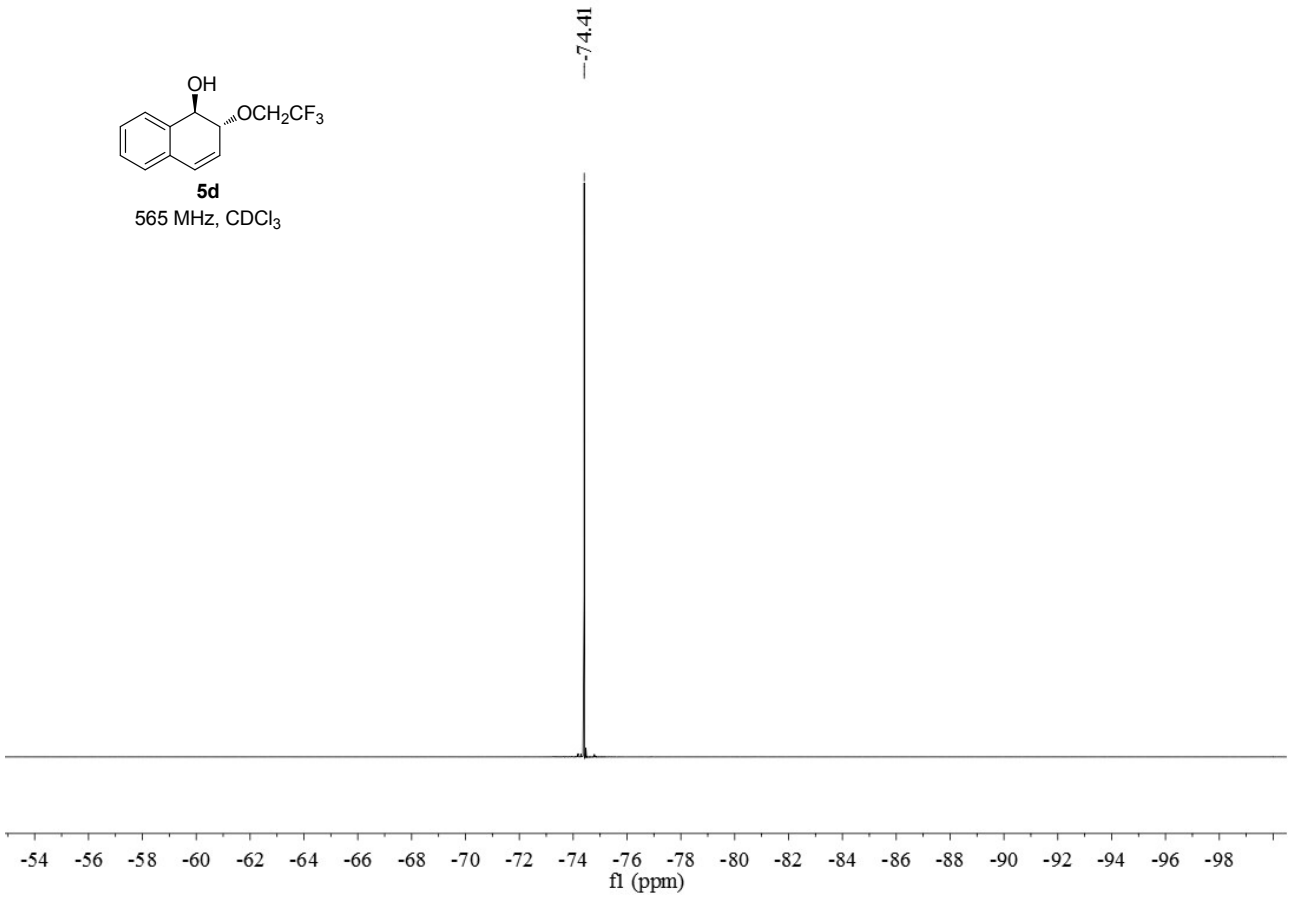
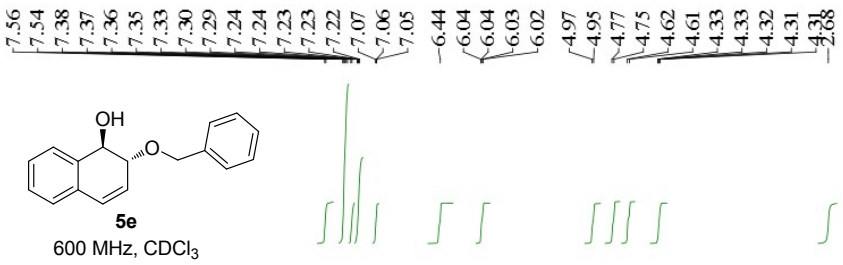
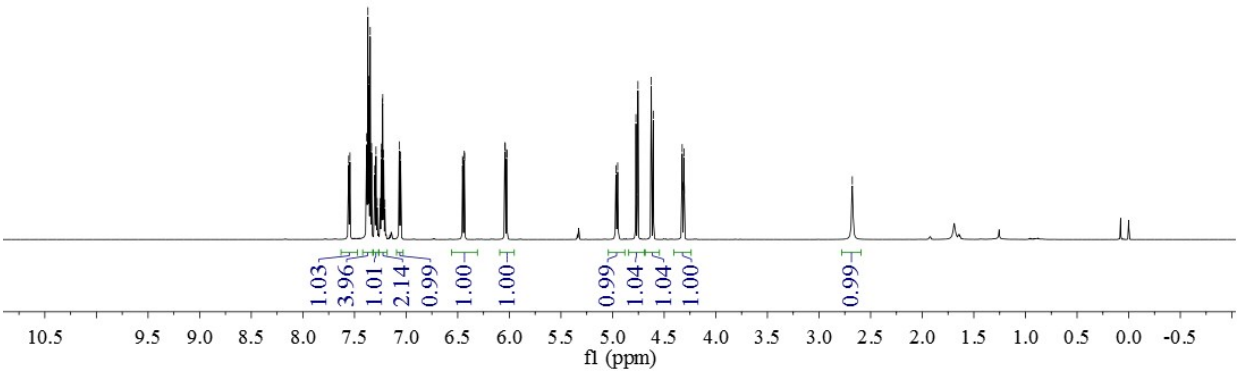
131.6549
129.1770
128.2466
128.1066
126.5877
126.5364
125.8817
125.1866
124.7398
122.8918
121.0433
82.9788
72.8208
67.3808
67.1536
66.9268
66.7001
OH
OCH2CF3
5d
150 MHz, CDCl3
f1 (ppm)

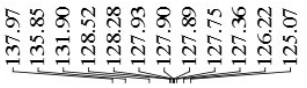

-74.41
OH
OCH2CF3
5d
565 MHz, CDCl3
f1 (ppm)

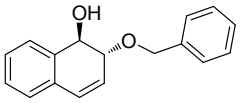


5e

600 MHz, $CDCl_3$

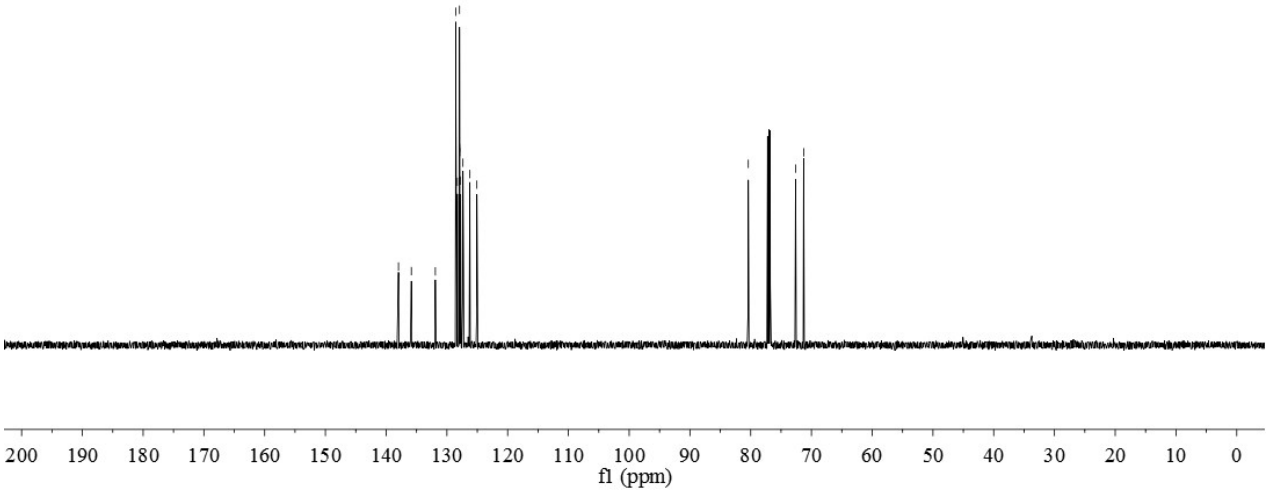


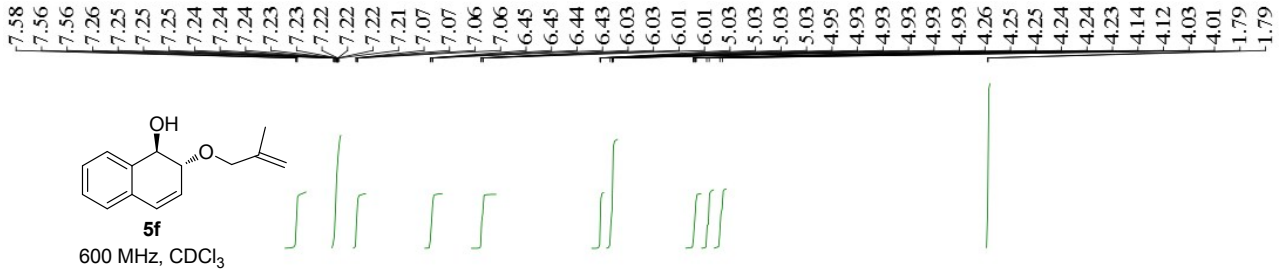




5e

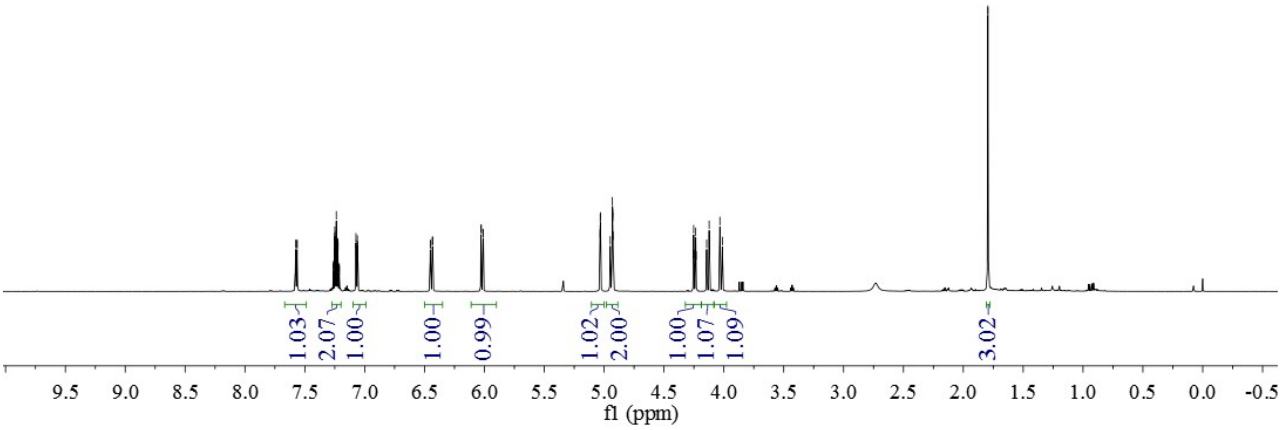
150 MHz, $CDCl_3$

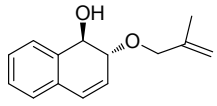




5f

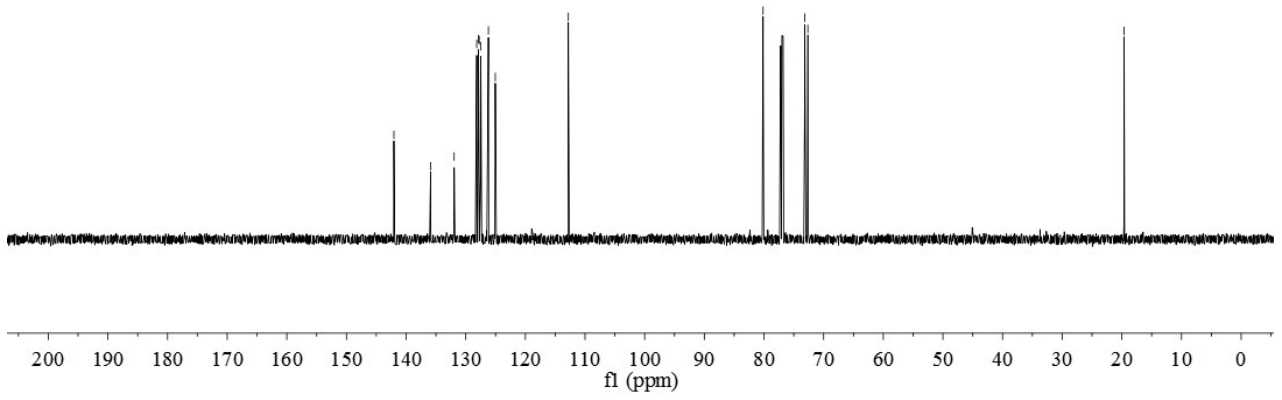
600 MHz, $CDCl_3$

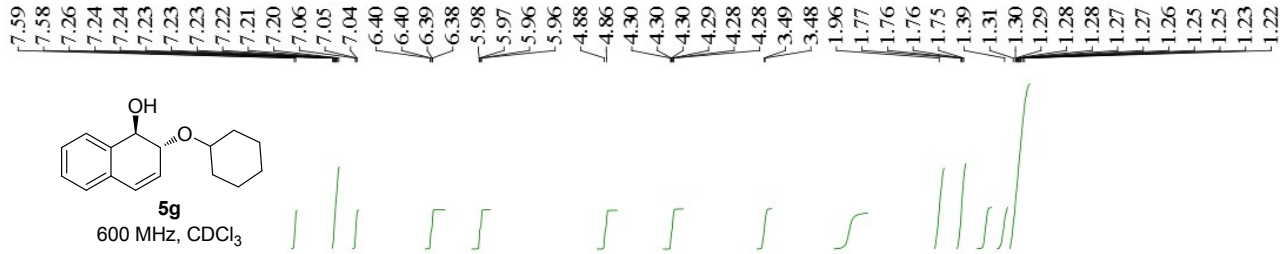




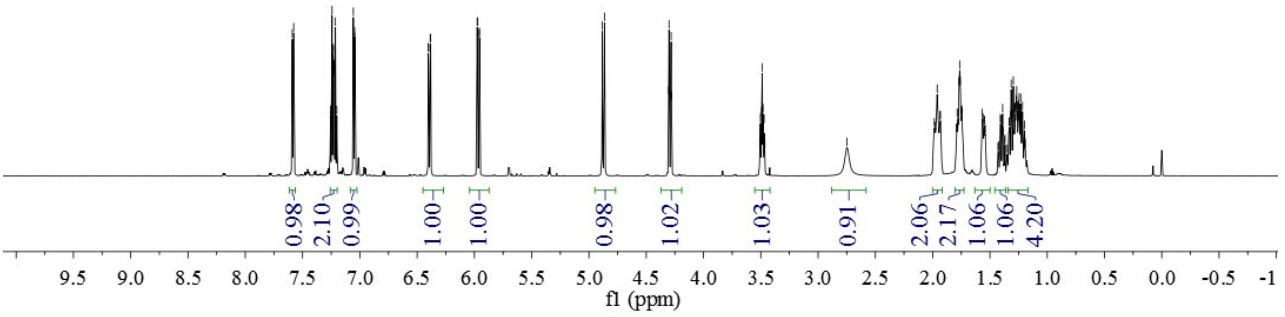
5f

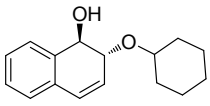
150 MHz, $CDCl_3$



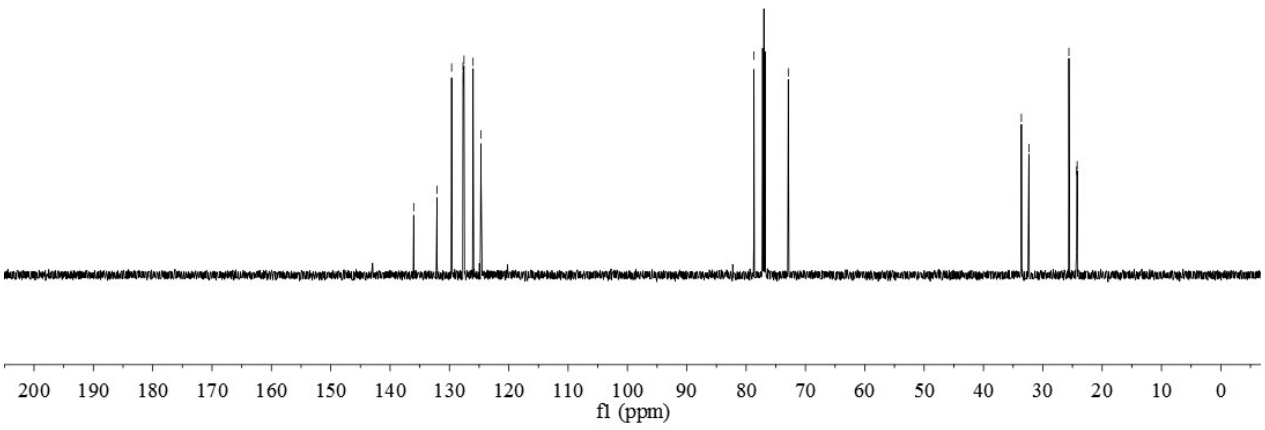


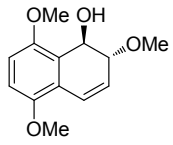
5g
600 MHz, $CDCl_3$





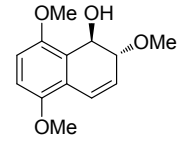
5g
150 MHz, $CDCl_3$





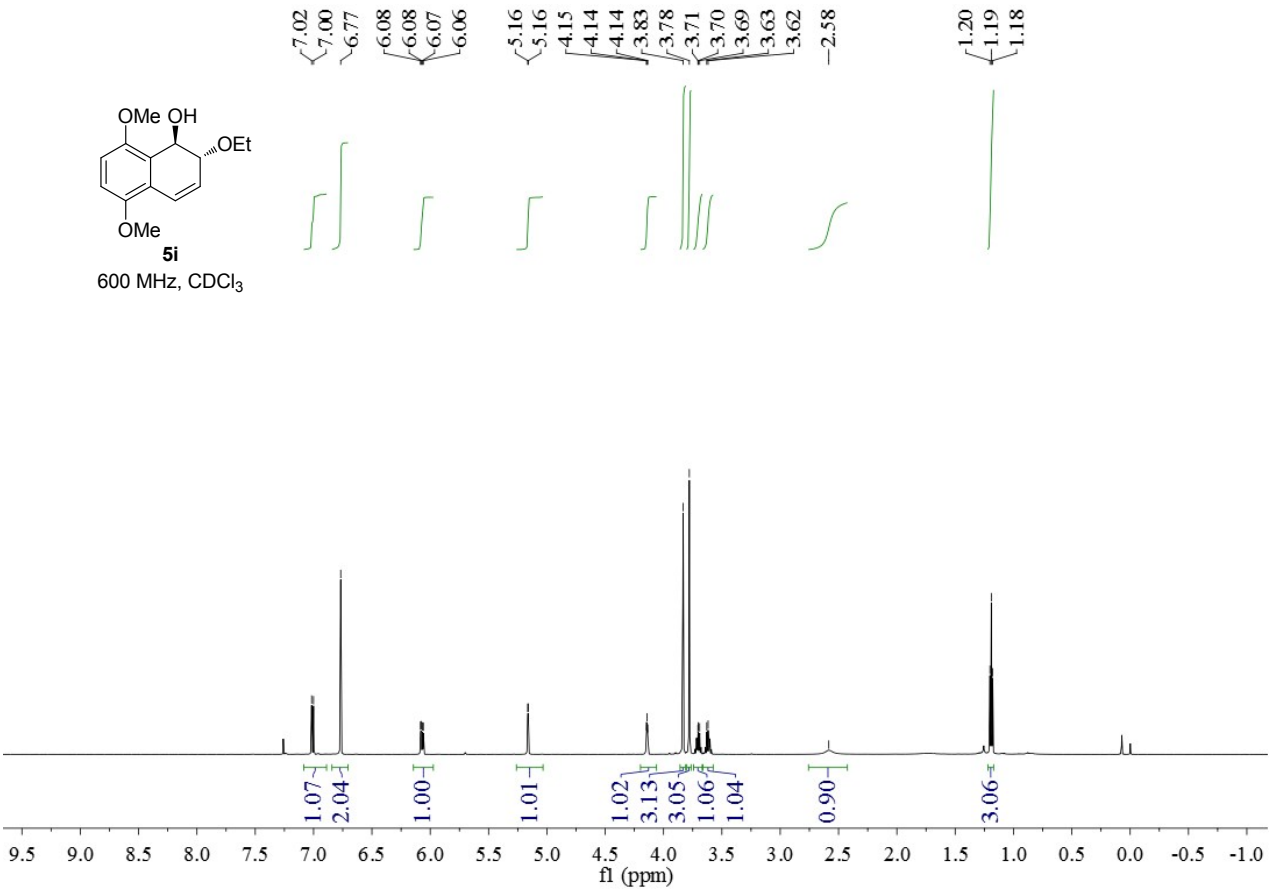
5h

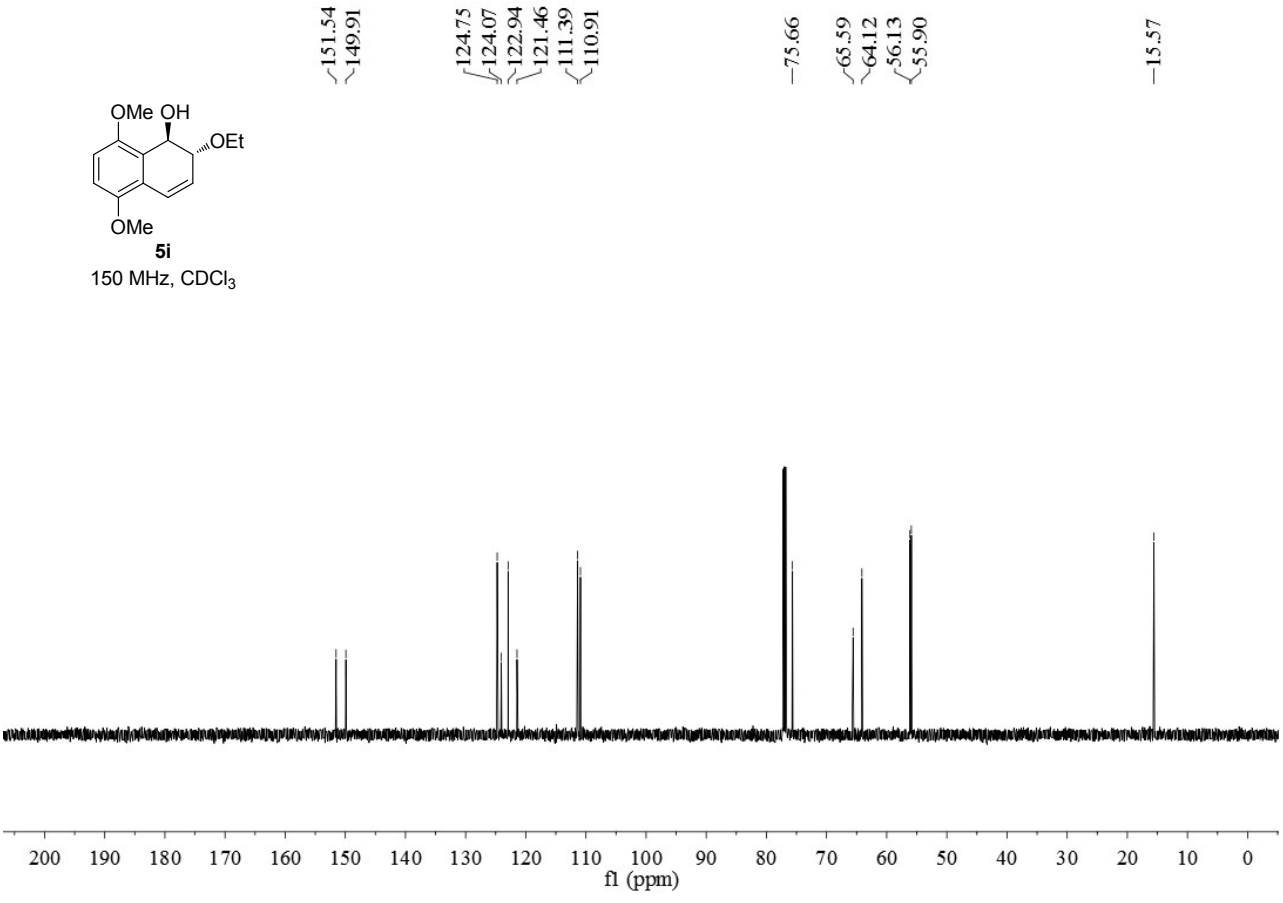
600 MHz, $CDCl_3$

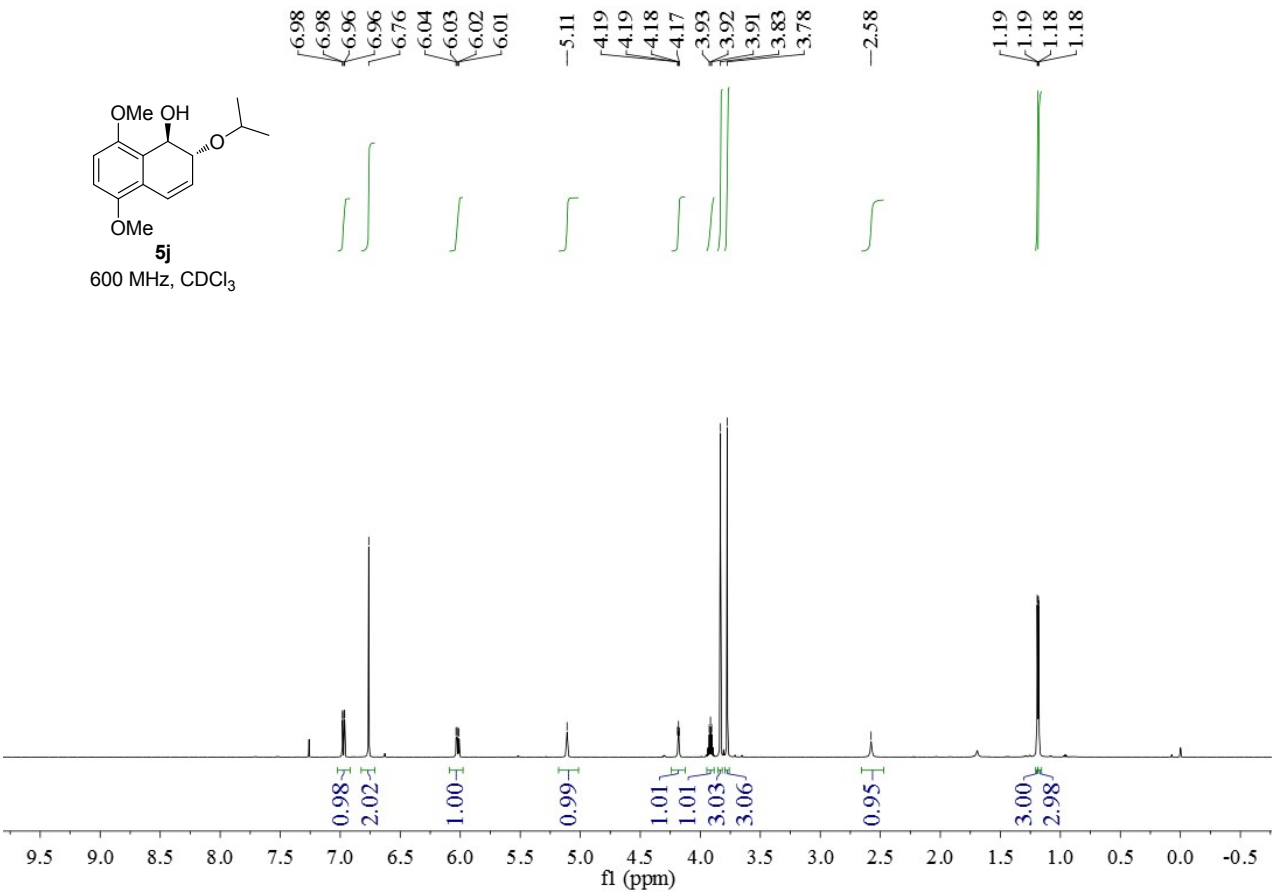


5h

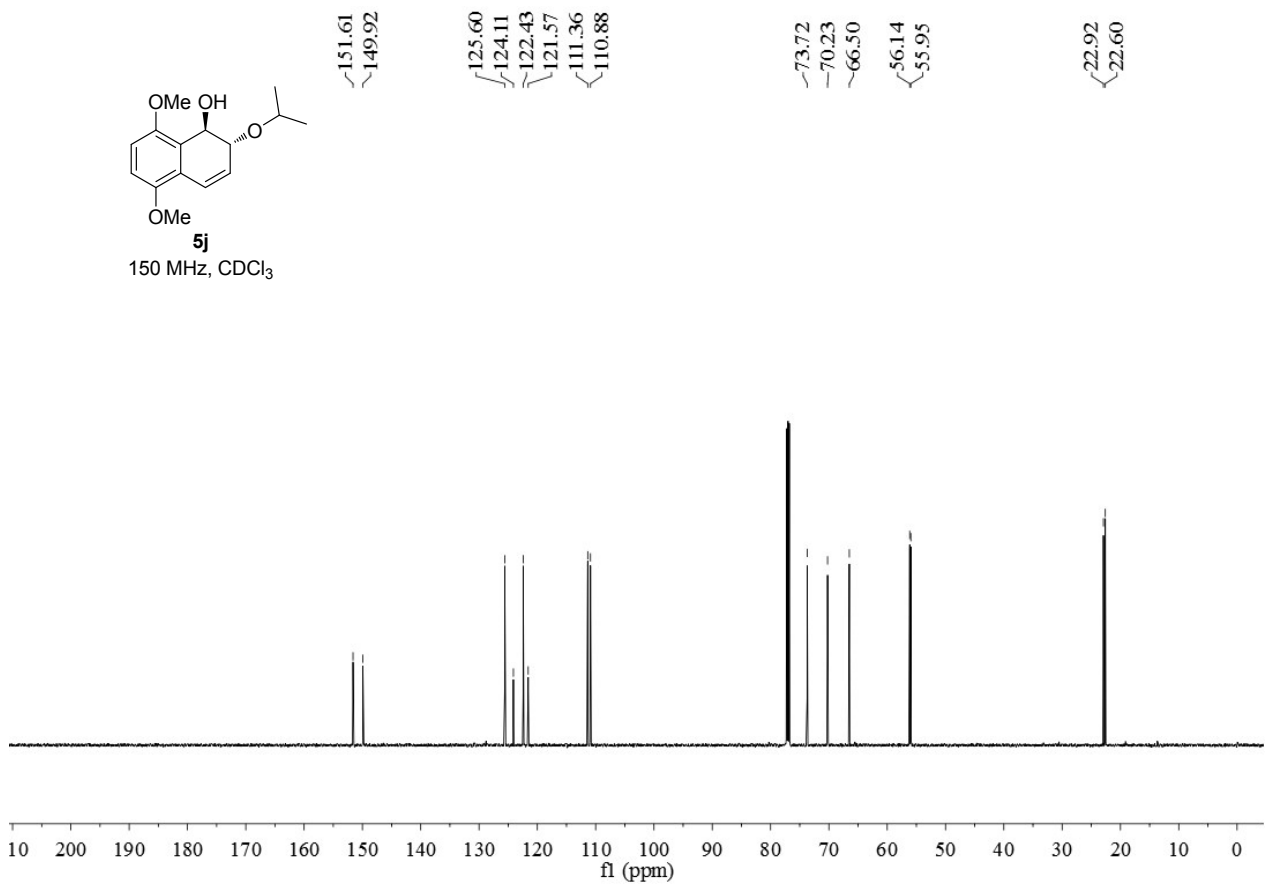
150 MHz, $CDCl_3$


7.02
7.00
6.77
6.08
6.08
6.07
6.06
5.16
5.16
4.15
4.14
4.14
3.83
3.78
3.71
3.70
3.69
3.63
3.62
2.58
1.20
1.19
1.18
OMe OH
OEt
OMe
5i
600 MHz, CDCl3
1.07
2.04
1.00
1.01
1.02
3.13
3.05
1.06
1.04
0.90
3.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

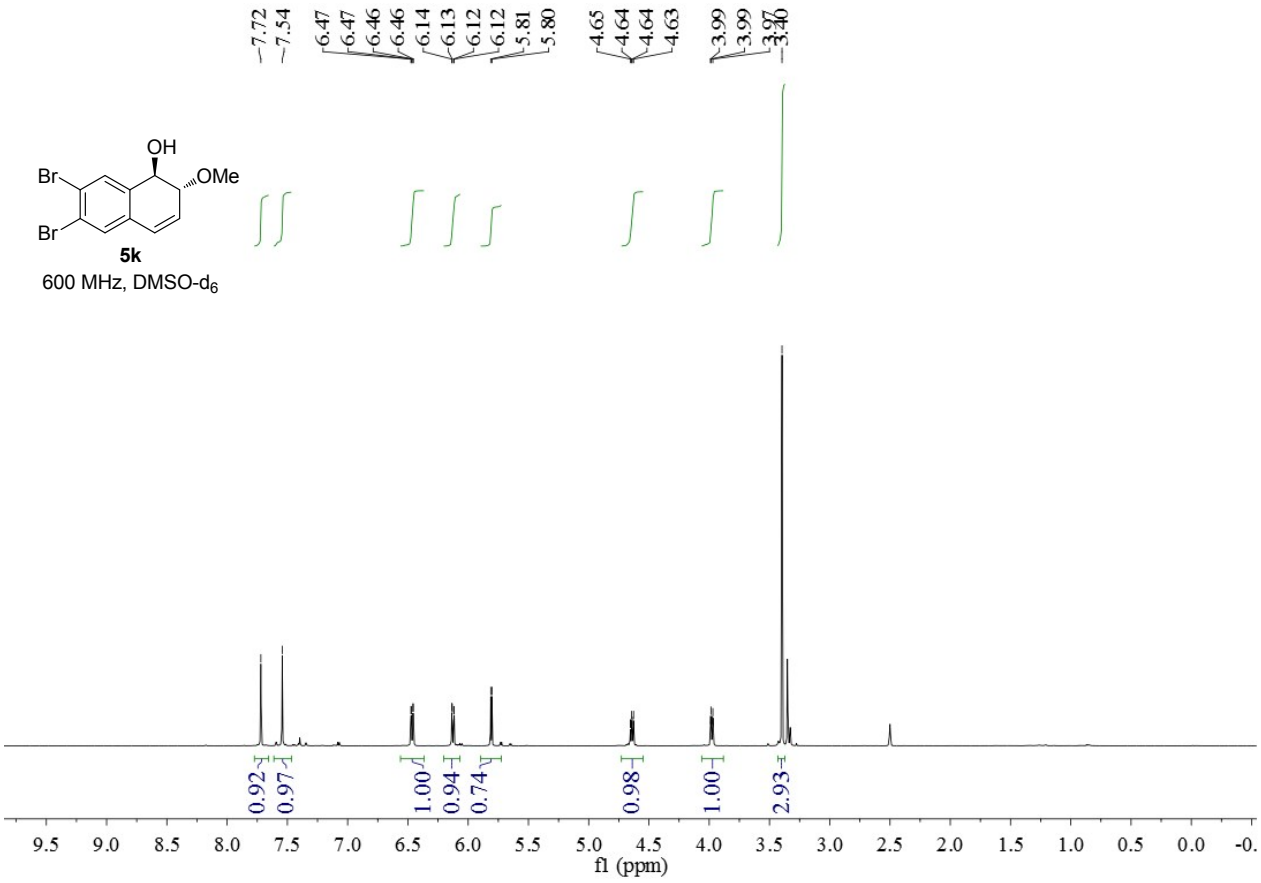

151.54
149.91
124.75
124.07
122.94
121.46
111.39
110.91
75.66
65.59
64.12
56.13
55.90
15.57
OMe OH
OEt
OMe
5i
150 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

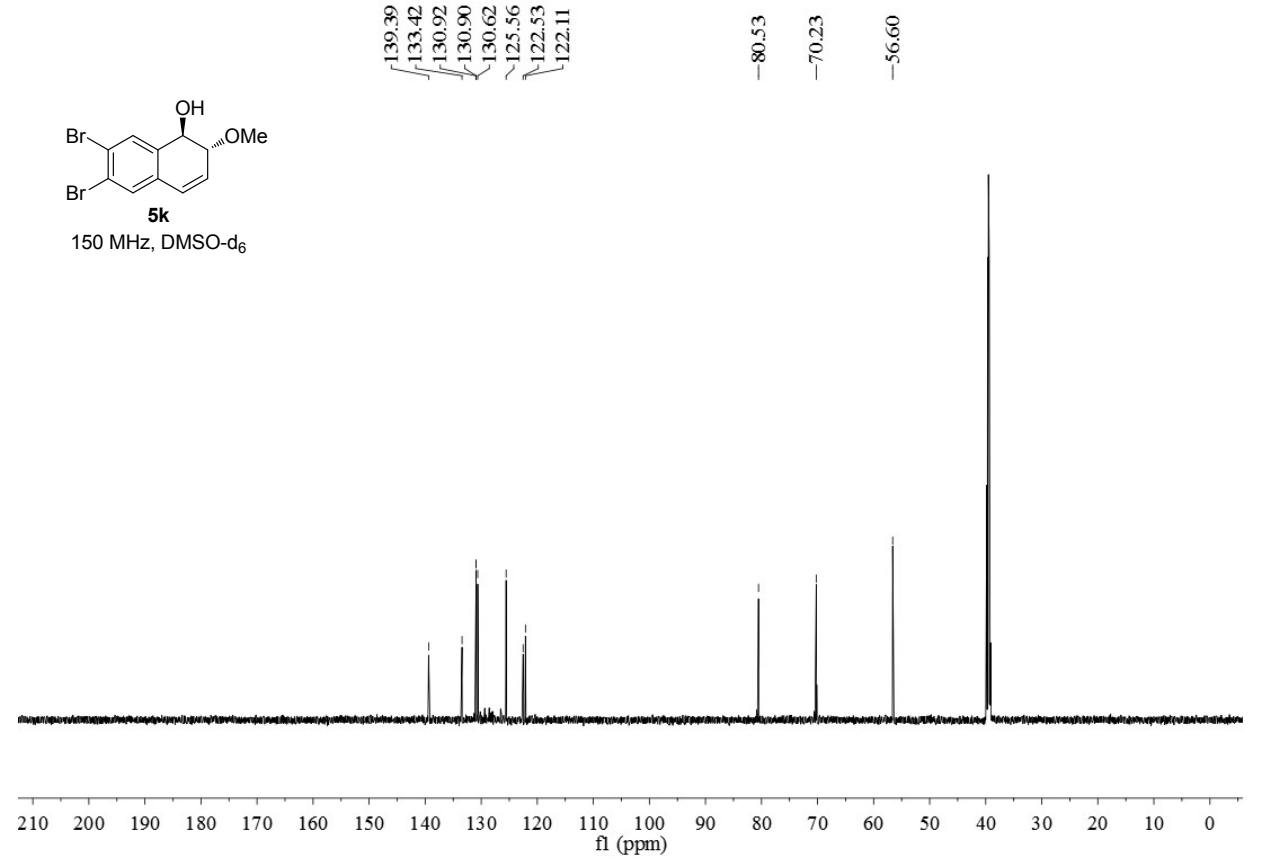


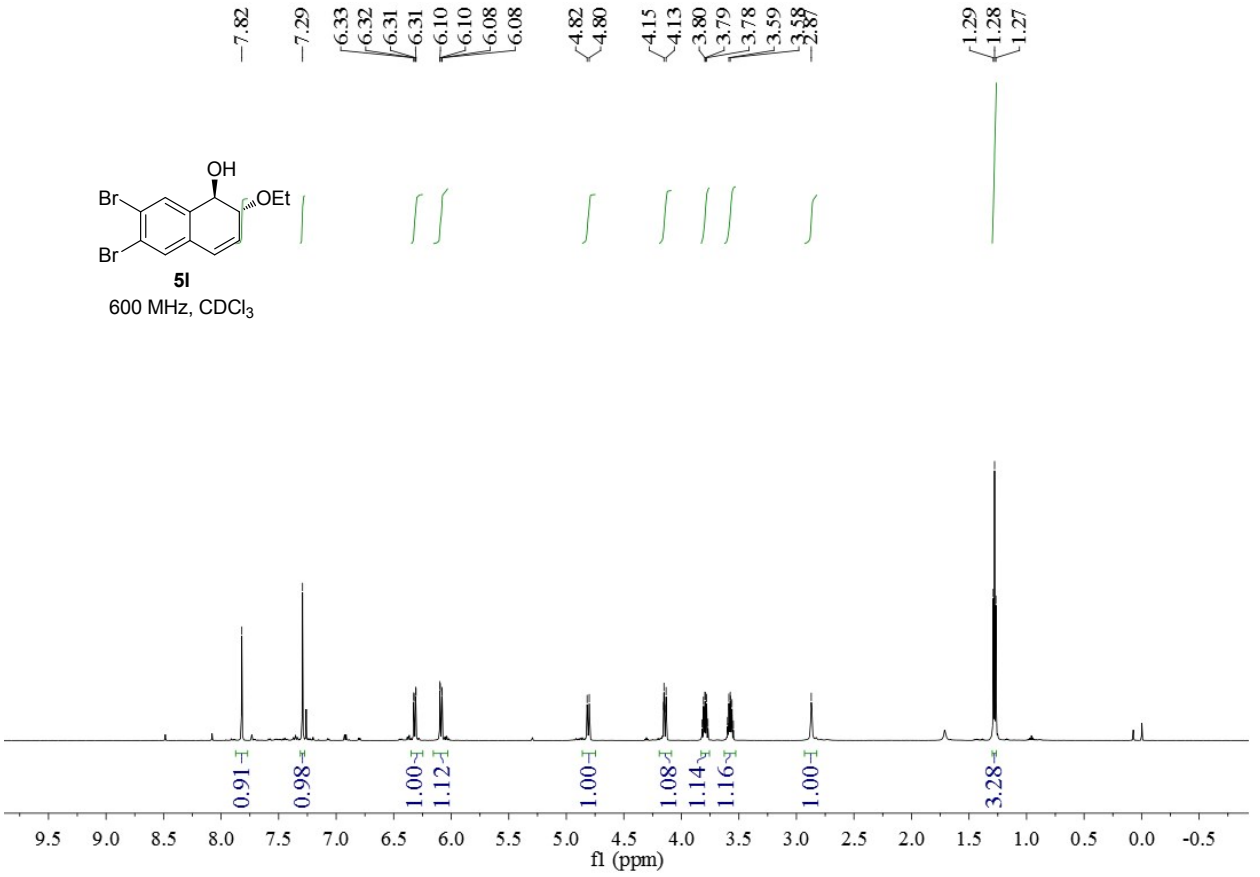
5j
600 MHz, $CDCl_3$



5j
150 MHz, $CDCl_3$

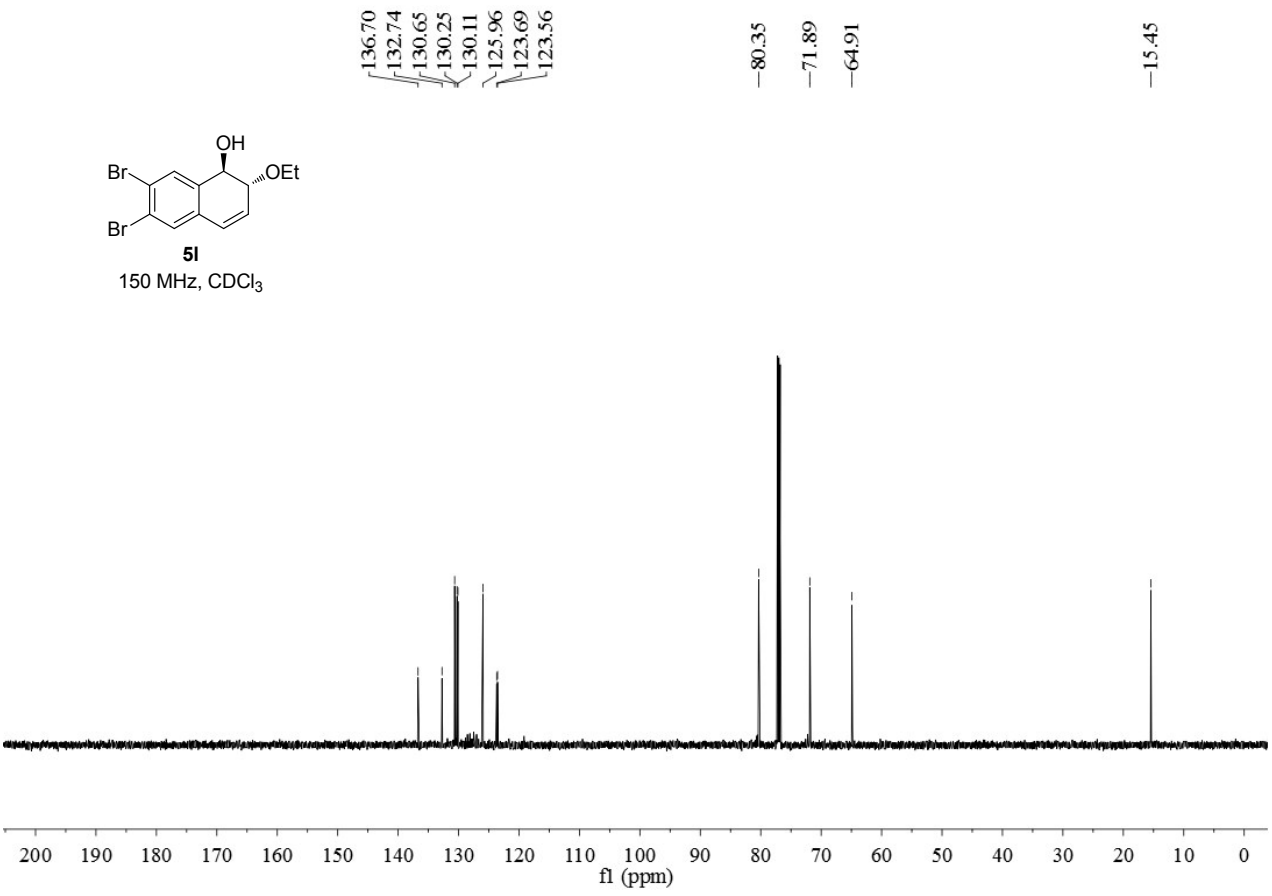

7.72
7.54
6.47
6.47
6.46
6.46
6.14
6.13
6.12
6.12
5.81
5.80
4.65
4.64
4.64
4.63
3.99
3.99
3.97
3.40
OH
Br
OMe
Br
5k
600 MHz, DMSO-d6
0.92
0.97
1.00
0.94
0.74
0.98
1.00
2.93
f1 (ppm)


139.39
133.42
130.92
130.90
130.62
125.56
122.53
122.11
80.53
70.23
56.60
OH
Br
OMe
Br
5k
150 MHz, DMSO-d6
f1 (ppm)



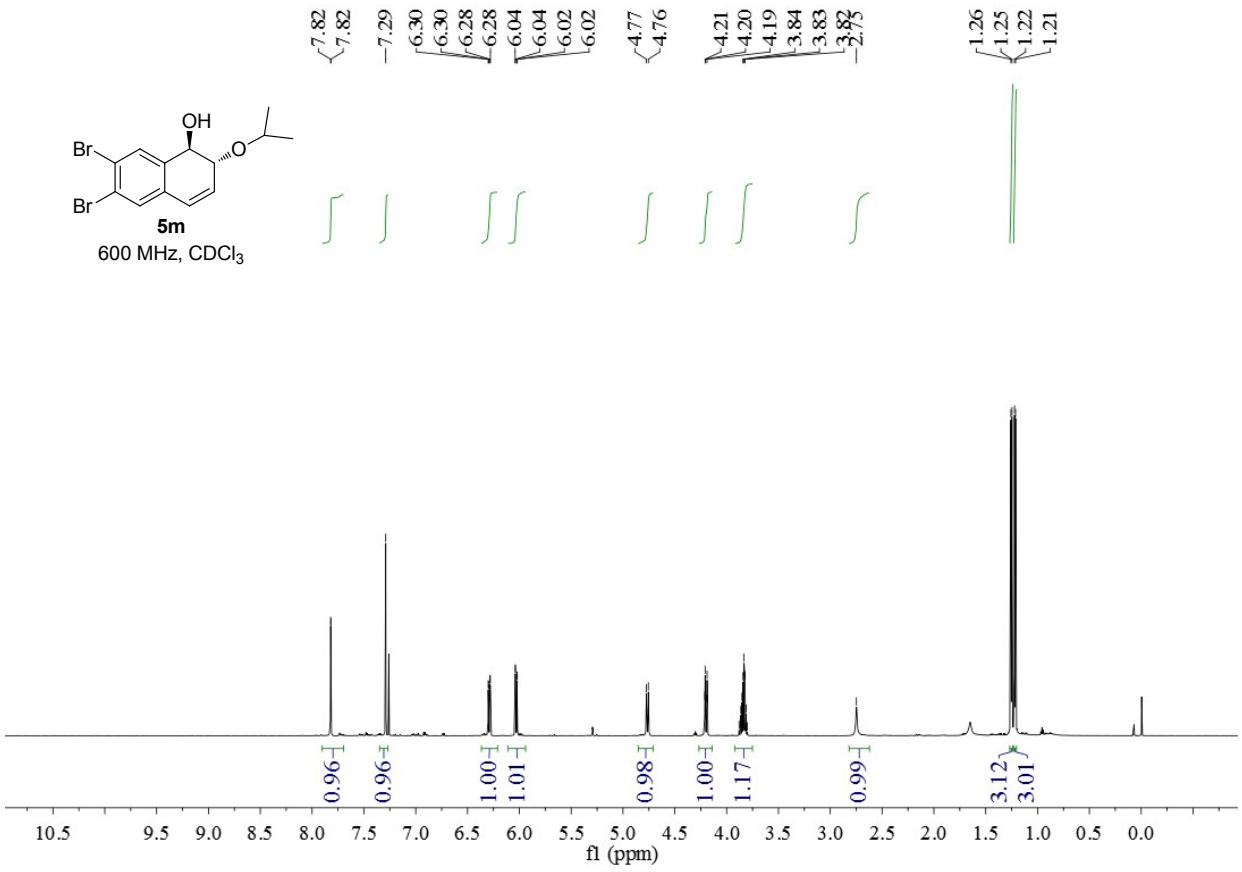
5l

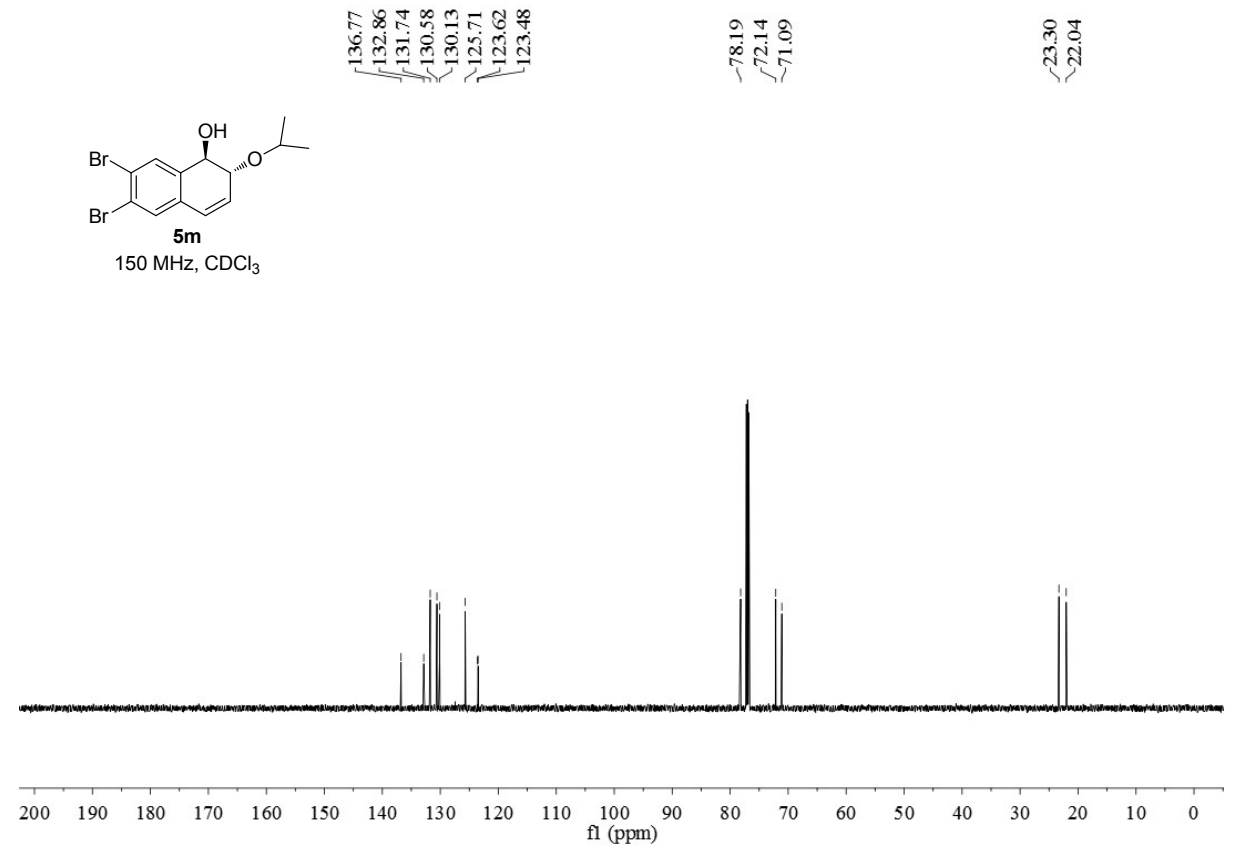
600 MHz, $CDCl_3$

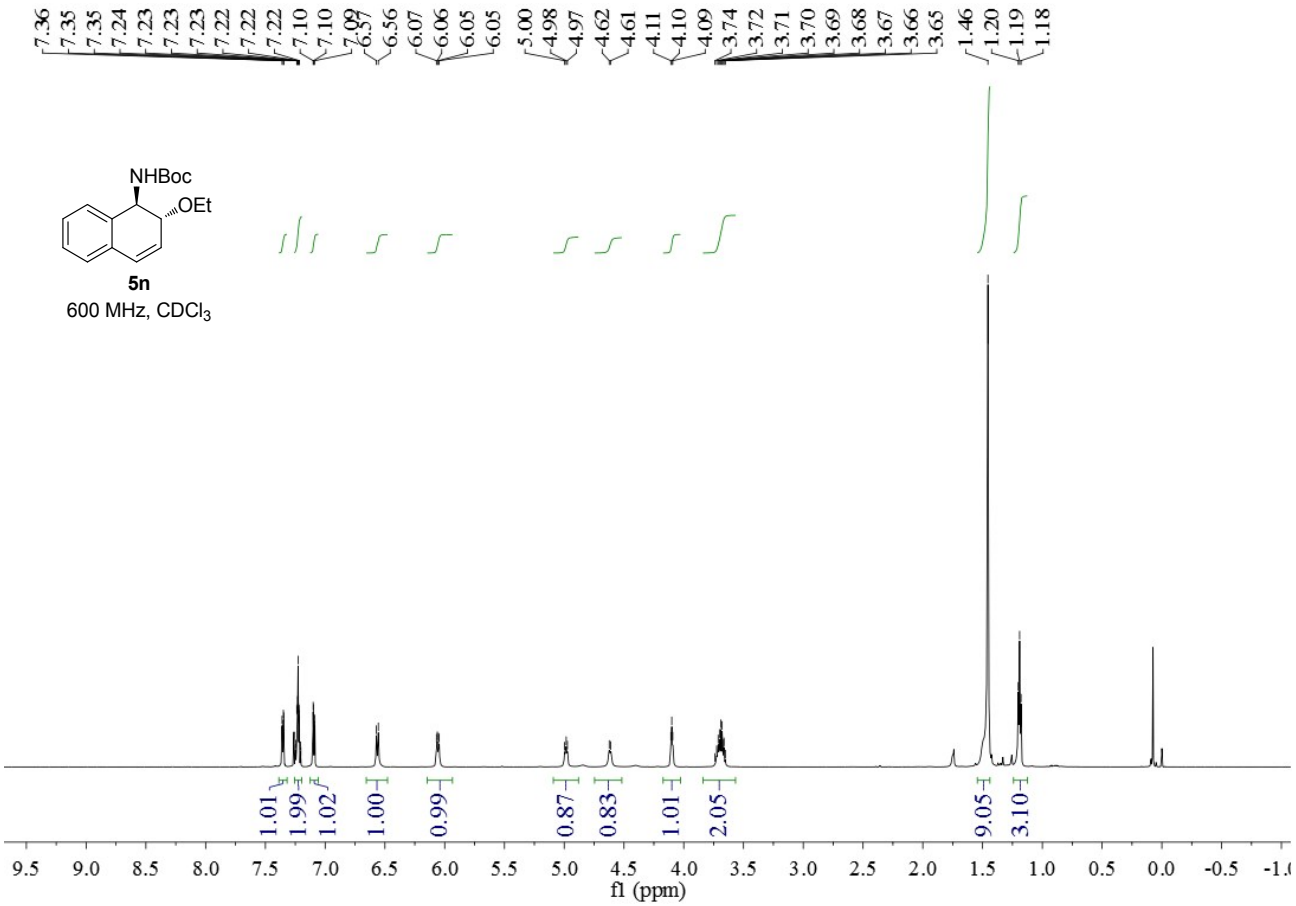


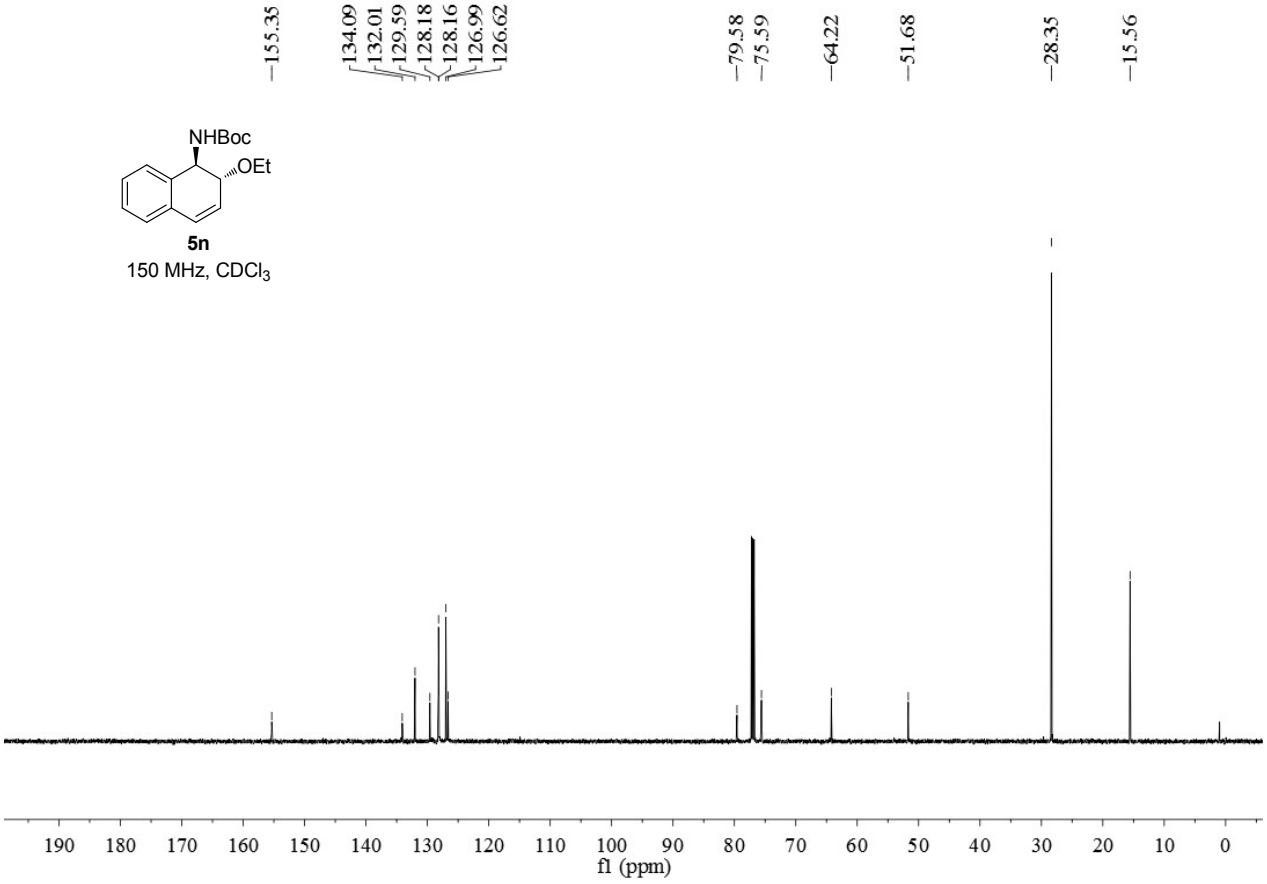
5l

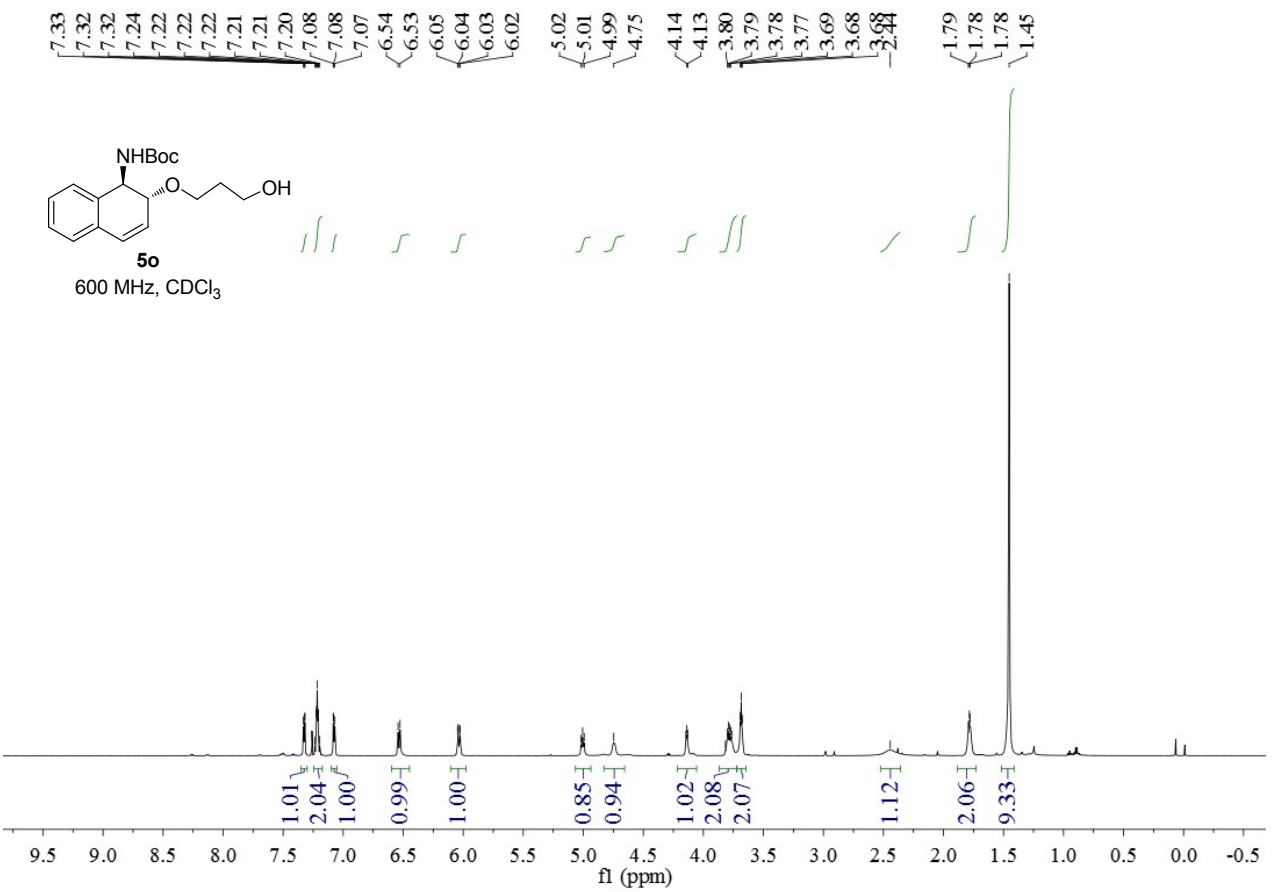
150 MHz, $CDCl_3$

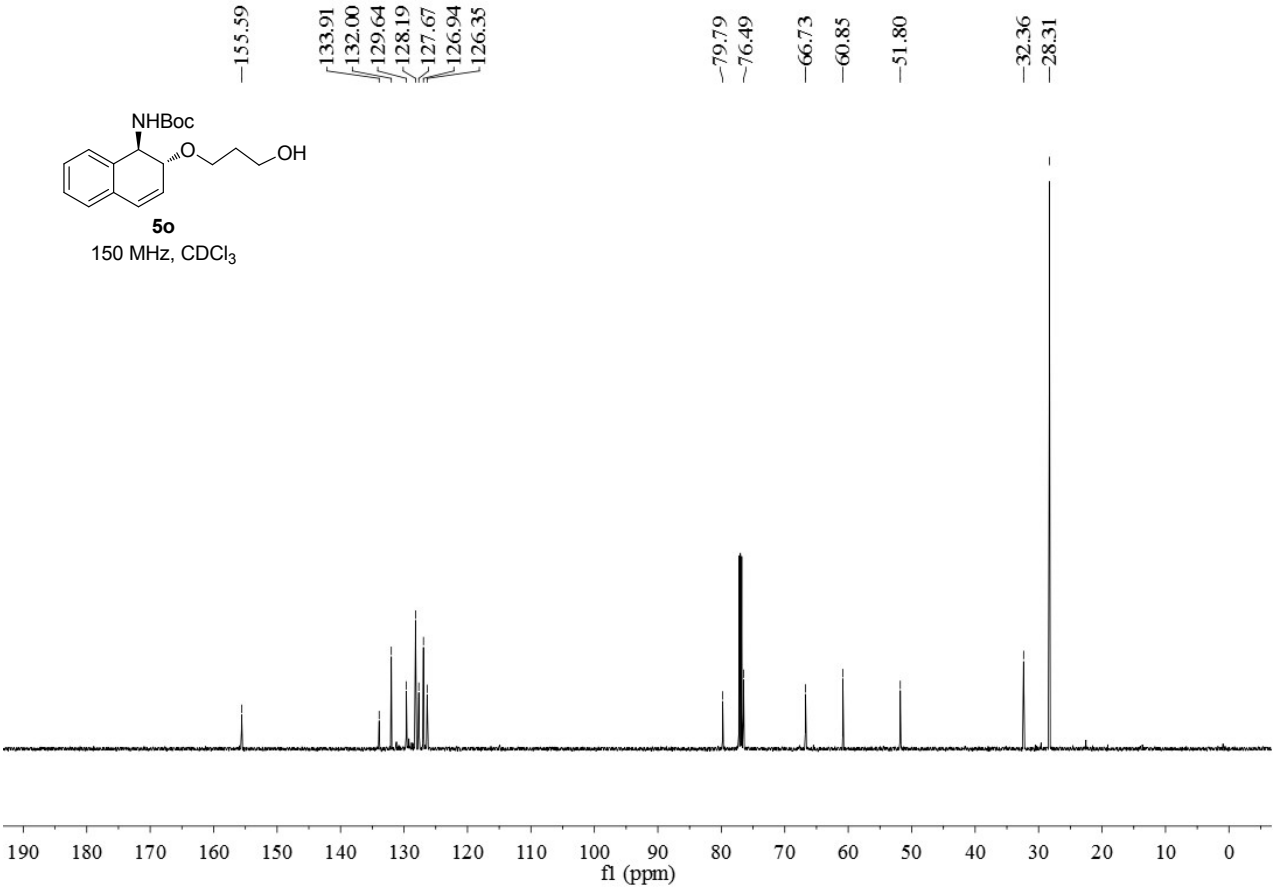

7.82
7.82
7.29
6.30
6.30
6.28
6.28
6.04
6.04
6.02
6.02
4.77
4.76
4.21
4.20
4.19
3.84
3.83
3.82
2.75
1.26
1.25
1.22
1.21
OH
Br
Br
O
5m
600 MHz, CDCl3
0.96
0.96
1.00
1.01
0.98
1.00
1.17
0.99
3.12
3.01
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

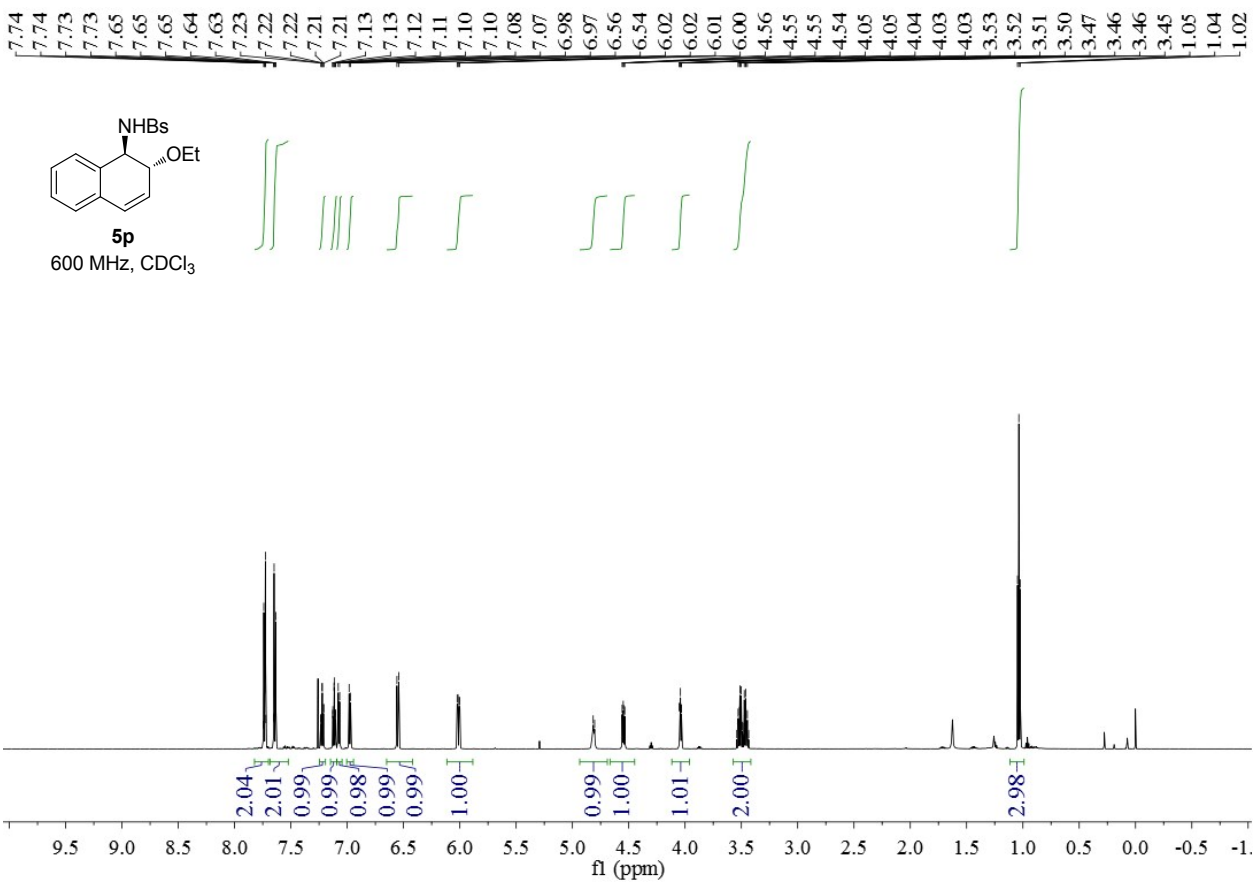

136.77
132.86
131.74
130.58
130.13
125.71
123.62
123.48
78.19
72.14
71.09
23.30
22.04
OH
Br
Br
O
5m
150 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

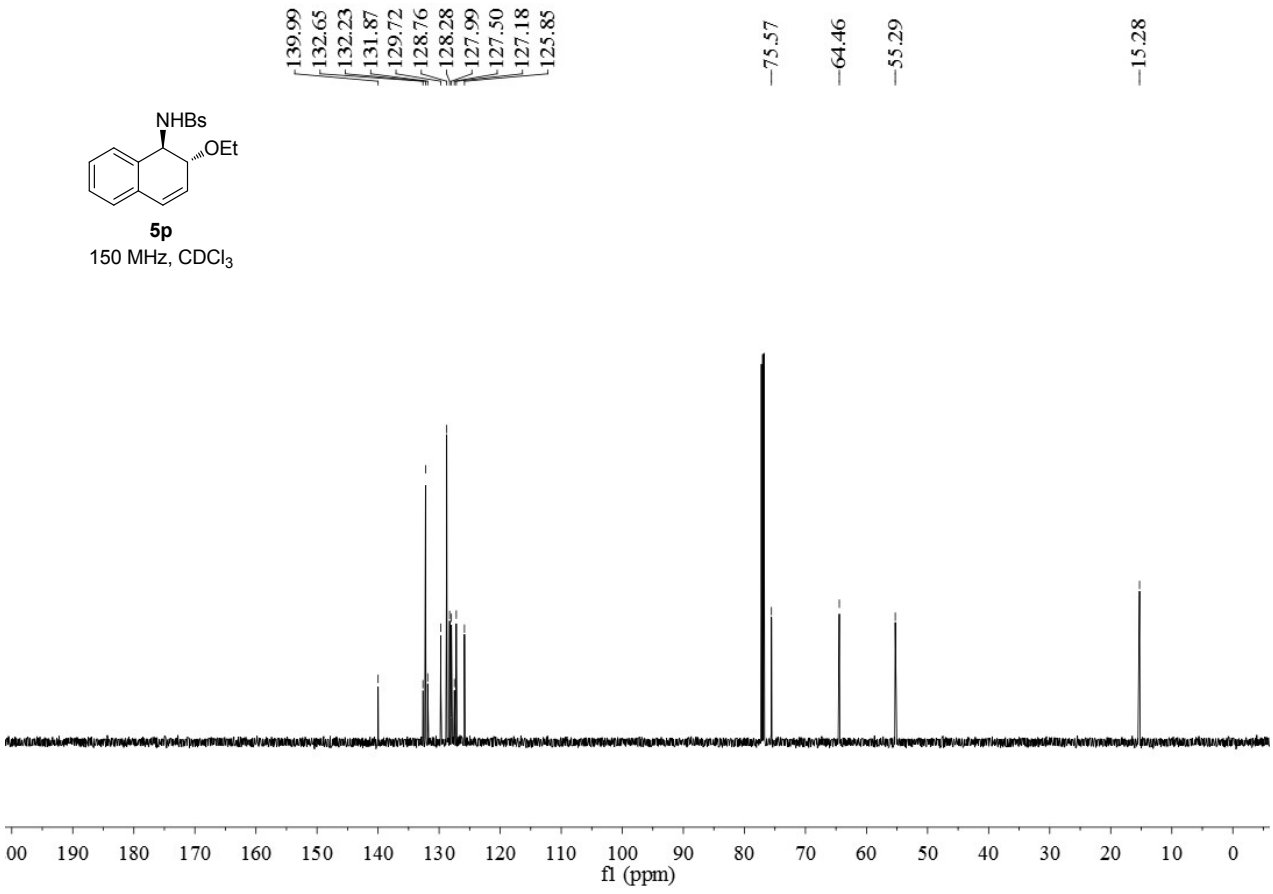

NHBoc
OEt
5n
600 MHz, CDCl3
7.36
7.35
7.35
7.24
7.23
7.23
7.23
7.22
7.22
7.22
7.10
7.10
7.09
6.57
6.56
6.07
6.06
6.06
6.05
6.05
5.00
4.98
4.97
4.62
4.61
4.11
4.10
4.09
3.74
3.72
3.71
3.70
3.69
3.68
3.67
3.66
3.65
1.46
1.20
1.19
1.18
1.01
1.99
1.02
1.00
0.99
0.87
0.83
1.01
2.05
9.05
3.10
f1 (ppm)

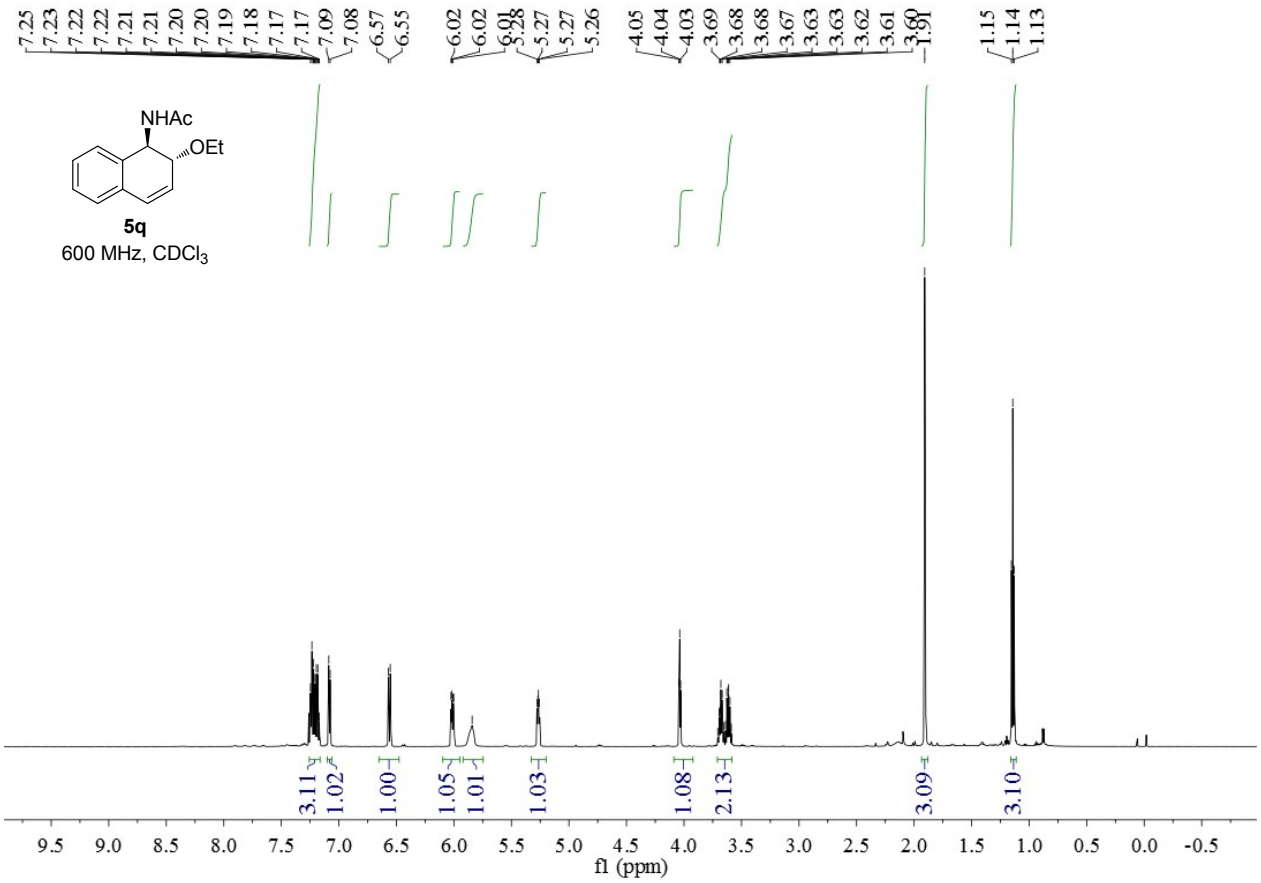

NHBoc
OEt
5n
150 MHz, CDCl3
155.35
134.09
132.01
129.59
128.18
128.16
126.99
126.62
79.58
75.59
64.22
51.68
28.35
15.56
f1 (ppm)

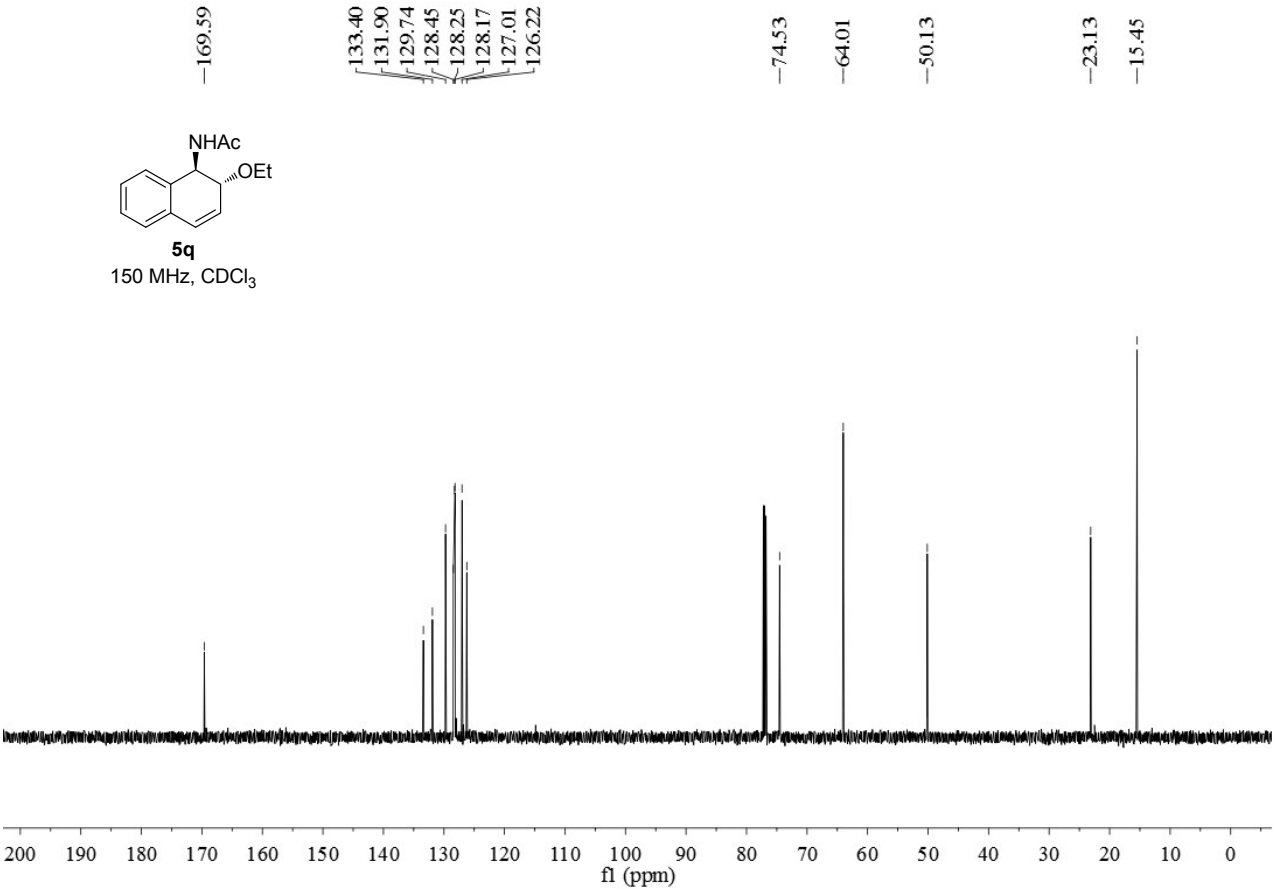

NHBoc
O
OH
5o
600 MHz, CDCl3
fl (ppm)

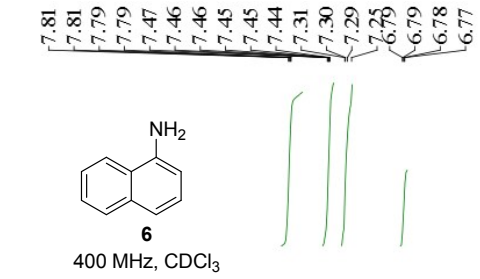

NHBoc
O
OH
5o
150 MHz, CDCl3
fl (ppm)


NHBs
OEt
5p
600 MHz, CDCl3
fl (ppm)


NHBs
OEt
5p
150 MHz, CDCl3
fl (ppm)

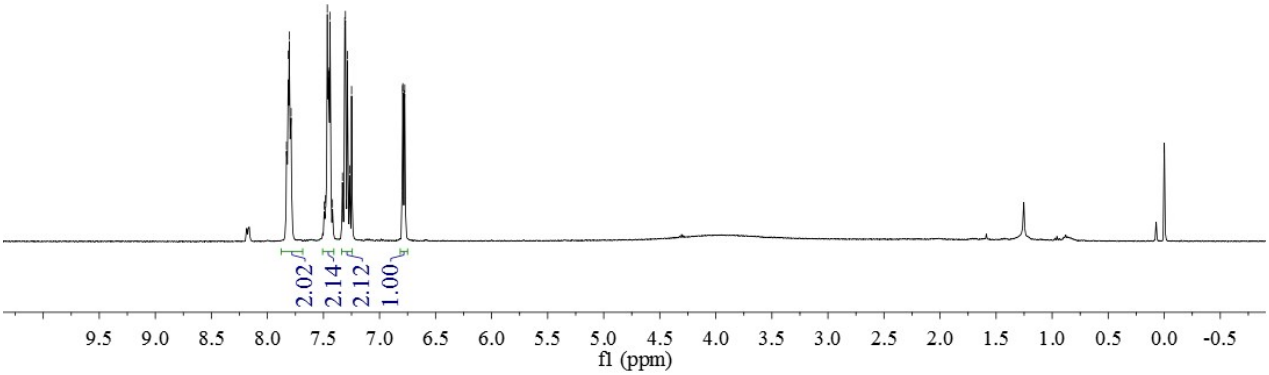

NHAc
OEt
5q
600 MHz, CDCl3
f1 (ppm)


NHAc
OEt
5q
150 MHz, CDCl3
f1 (ppm)



6

400 MHz, $CDCl_3$



4. References

1 (a) E. Wolthuis, *J. Org. Chem*., 1961, **26**, 2215; (b) H. Hart, C. Lai, G. C. Nwokogu, S. Shamouilian, *Tetrahedron* 1987, **43**, 5203; (c) G. Stork, E. E. van Tamelen, L. J. Friedman, A. W. Burgstahler, *J. Am. Chem. Soc.*, 1953, **75**, 384; (d) D. B. Millward, G. Sammis, R. M. Waymouth, *J. Org. Chem*., 2000, **65**, 3902; (e) M. Lautens, K. Fagnou,; V. Zunic, *Org. Lett.*, 2002, **4**, 3465.

2. A. L. Silberstein, S. D. Ramgren, N. K. Garg, *Org. Lett.*, 2012, **14**, 3796.