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Supporting Information

Platinum-Catalyzed *syn*-Stereocontrolled Ring-Opening of Oxabicyclic Alkenes with Sodium Arylsulfinates

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1. General information

Unless otherwise indicated, all reagents were purchased from commercial suppliers and used without further purification. DME was distilled from sodium benzophenone ketyl and CH_3OH, CH_3CH_2OH, *i*-PrOH was distilled from magnesium. Super dry solvent 1,4-dioxane were used without any pretreatment. All flasks were flame-dried under a stream of nitrogen and cooled to room temperature before use. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 400/500/600 MHz and 100/125/150 MHz at 25 ^oC in $CDCl_3$, respectively. Spectral data are reported as follows: chemical shift (δ, ppm); multiplicity (s-singlet, d-doublet, t-triplet, q-quadruplet, m-multiplet); coupling constants (*J*, Hz) and number of protons. HRMS (ion trap) were obtained from mass spectrometer (ESI) and MS were recorded using EI at 70 eV. Enantiomeric excesses were determined with a Chiralcel OD-H column eluted with a mixture of hexane and *i*-propanol (hexane/*i*-propanol 90:10, 1.0 mL/min, λ =254 nm). Melting points were uncorrected.

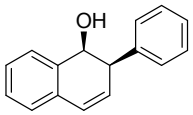
2. General Procedure for the Preparation of Sodium Sulfinates (2b–2f and 2h–2m)[1]

4-Fluorobenzenesulfinic acid sodium salt (**2b**) was prepared by heating 2.5 g of sodium sulfite, 2.06 g of 4-fluorobenzenesulphonyl chloride, and 1.68 g of sodium bicarbonate in 9.6 mL of water at 70–80 ^oC for 4 h. After cooling to room temperature, water was removed under vacuum and the residue was extracted by ethanol, recrystallization as a white solid, the yield was 67% (1.34 g). Similarly, other sodium arenesulfinates (**2c–2f and 2h–2m**) was prepared from their corresponding sulphonyl chlorides.

Oxabenzonorbornadienes (**1a–1e**) were prepared according to the literature procedures.[2]

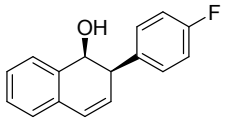
General Procedure for Platinum-Catalyzed *syn*-Stereocontrolled Ring-Opening of Oxabenzonorbornadienes (1a–1e) with Sodium Arylsulfinates. All experiments were carried out under the N_2 atmosphere. [Pt(COD)Cl_2] (3.7 mg, 5 mol %) and PPh_3 (6.8 mg, 10 mol %) were simultaneously added to a 10.0 mL round-bottomed flask, followed by the addition of CH_3OH (3 mL). After the mixture was stirred for about 30 min, oxabenzonorbornadienes (**1a**–**1e**) (0.2 mmol), sodium arylsulfinates (3 equiv, 0.6 mmol) and $AgSbF_6$ (3 mol%) were put into the reaction system. The mixture was stirred at 70 °C for 15 h. After cooling to the room temperature, the mixture should be concentrated through vacuum evaporation to remove solvent, and the residue was purified by column chromatography (200–300 mesh silica gels) to obtain the desired products **3** or **4**.

3. Analytical data of products.



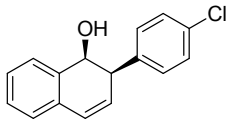
3aa *(1S*,2R*)-2-Phenyl-1,2-dihydronaphthalen-1-ol (**3aa**).*[5a]

Prepared according to general procedure. Colorless oil (35.9 mg, 81% yield). R_f = 0.25 on silica gel (ethyl acetate/petroleum ether 1:20, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28–7.19 (m, 6H), 7.19–7.15 (m, 2H), 7.11–7.07 (m, 1H), 6.63 (dd, *J* = 9.6, 2.0 Hz, 1H), 6.05 (dd, *J* = 9.6, 4.0 Hz, 1H), 4.85 (t, *J* = 6.7 Hz, 1H), 3.79 (ddd, *J* = 6.0, 4.0, 2.1 Hz, 1H), 1.43 (d, *J* = 7.9 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 137.8, 136.1, 132.7, 129.7, 129.3, 128.7, 128.4, 128.3, 128.1, 127.5, 126.8, 126.4, 71.4, 47.4. MS (EI) *m/z*: [M − 3H]$^-$ calcd for $C_{16}H_{11}O$, 219.08; found 219.04.



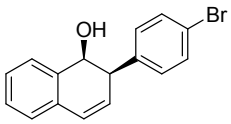
3ab

(1S,2R*)-2-(4-Fluorophenyl)-1,2-dihydronaphthalen-1-ol* ***(3ab)***.[5a] Prepared according to general procedure. A white solid (34.6 mg, 72% yield). mp 85–86 °C. R_f = 0.13 on silica gel (ethyl acetate/petroleum ether 1:20, v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29–7.15 (m, 6H), 6.94 (t, *J* = 8.6 Hz, 2H), 6.65 (dd, *J* = 9.6, 1.8 Hz, 1H), 6.04 (dd, *J* = 9.6, 4.1 Hz, 1H), 4.87 (d, *J* = 6.0 Hz, 1H), 3.80–3.78 (m, 1H), 1.18 (d, *J* = 6.4 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 163.3 (d, $^1J_{C\text{-}F}$ = 243.8 Hz), 161.7, 136.3, 133.6(d, $^4J_{C\text{-}F}$ = 3 Hz), 132.8, 131.1, 129.9, 128.7, 128.6, 128.5, 126.7(d, $^3J_{C\text{-}F}$ = 15 Hz), 115.8, 115.6(d, $^2J_{C\text{-}F}$ = 21.0 Hz), 71.6, 46.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.4. MS (EI) *m/z*: $[M - 3H]^-$ calcd for $C_{16}H_{10}FO$, 237.07; found 237.23.



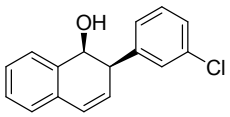
3ac

(1S,2R*)-2-(4-Chlorophenyl)-1,2-dihydronaphthalen-1-ol* ***(3ac)***.[5a] Prepared according to general procedure. A white solid (44.2 mg, 87% yield). mp 113–114 °C. R_f = 0.13 on silica gel (ethyl acetate/petroleum ether 1:20, v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26–7.16 (m, 5H), 7.13–7.08 (m, 3H), 6.63 (d, *J* = 9.6 Hz, 1H), 6.00 (dd, *J* = 9.6, 4.0 Hz, 1H), 4.83 (d, *J* = 4.0 Hz, 1H), 3.75 (s, 1H), 1.41 (s, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 136.3, 136.0, 133.2, 132.5, 130.7, 129.3, 128.7, 128.5, 128.5, 128.2, 126.6, 126.5, 71.3, 46.7. MS (EI) *m/z*: $[M + Na]^+$ calcd for $C_{16}H_{13}ClONa$, 279.07; found 279.13.



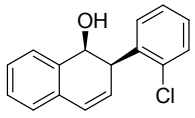
3ad

(1S,2R*)-2-(4-Bromophenyl)-1,2-dihydronaphthalen-1-ol* (***3ad***).[5a] Prepared according to general procedure. Colorless oil (37.1 mg, 62% yield). R_f = 0.13 on silica gel (ethyl acetate/petroleum ether 1:20, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.39 (m, 2H), 7.35–7.25 (m, 3H), 7.19–7.15 (m, 1H), 7.13 (d, *J* = 8.3 Hz, 2H), 6.71 (dd, *J* = 9.6, 1.9 Hz, 1H), 6.07 (dd, *J* = 9.6, 4.1 Hz, 1H), 4.91 (d, *J* = 5.9 Hz, 1H), 3.84–3.79 (m, 1H), 1.52 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 136.8, 135.9, 132.4, 131.6, 131.0, 129.1, 128.5, 128.4, 128.2, 126.5, 126.5, 121.3, 71.2, 46.8. MS (EI) *m/z*: [M – 3H]$^-$ calcd for $C_{16}H_{10}BrO$, 297.00; found 297.46.



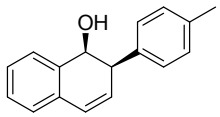
3ae

(1S,2R*)-2-(3-Chlorophenyl)-1,2-dihydronaphthalen-1-ol* (***3ae***).[5a] Prepared according to general procedure. Colorless oil (46.1 mg, 90% yield). R_f = 0.21 on silica gel (ethyl acetate/petroleum ether 1:20, v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29–7.15 (m, 6H), 6.94 (t, *J* = 8.6 Hz, 2H), 6.65 (dd, *J* = 9.6, 1.8 Hz, 1H), 6.04 (dd, *J* = 9.6, 4.1 Hz, 1H), 4.87 (d, *J* = 6.0 Hz, 1H), 3.80–3.78 (m, 1H), 1.18 (t, *J* = 6.4 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.9, 135.4, 133.9, 131.9, 129.3, 129.0, 128.4, 128.1, 128.1, 127.8, 127.1, 127.0, 126.3, 126.1, 70.8, 46.7. MS (EI) *m/z*: [M – 3H]$^-$ calcd for $C_{16}H_{10}ClO$, 253.04; found 253.70.



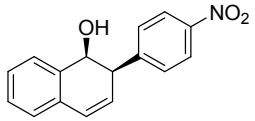
3af

(1S,2R*)-2-(2-Chlorophenyl)-1,2-dihydronaphthalen-1-ol* ***(3af)***.[5a] Prepared according to general procedure. Colorless oil (42.5 mg, 83% yield). R_f = 0.19 on silica gel (ethyl acetate/petroleum ether 1:20, v/v). ^{1}H NMR (500 MHz, $CDCl_3$)δ 7.36 (dd, *J* = 7.4, 1.9 Hz, 1H), 7.34–7.25 (m, 3H), 7.25–7.14 (m, 4H), 7.13 (d, *J* = 7.4 Hz, 1H), 6.67 (dd, *J* = 9.6, 2.7 Hz, 1H), 5.97 (dd, *J* = 9.6, 2.5 Hz, 1H), 4.82 (d, *J* = 5.0 Hz, 1H), 4.42 (dt, *J* = 5.3, 2.8 Hz, 1H), 1.48 (s, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 137.5, 135.8, 134.8, 132.8, 131.6, 130.2, 129.7, 129.5, 129.1, 129.0, 128.7, 128.6, 127.6, 127.4, 69.9, 44.7. MS (EI) *m/z*: $[M - 3H]^-$ calcd for $C_{16}H_{10}ClO$,253.04; found 253.13.



3ag

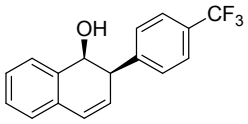
(1S,2R*)-2-(4-Methylphenyl)-1,2-dihydronaphthalen-1-ol* ***(3ag)***.[5a] Prepared according to general procedure. Colorless oil (39.1 mg, 83% yield). R_f = 0.20 on silica gel (ethyl acetate/petroleum ether 1:20, v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (d, *J* = 7.3 Hz, 1H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.16–7.13 (m, 1H), 7.08–7.01 (m, 5H), 6.60 (d, *J* = 9.6 Hz, 1H), 6.02 (dd, *J* = 9.6, 4.1 Hz, 1H), 4.83 (d, *J* = 5.6 Hz, 1H), 3.74 (s, 1H), 2.23 (s, 3H), 1.40 (s, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 136.7, 135.8, 134.0, 132.3, 129.5, 129.0, 128.8, 127.9, 127.7, 127.60, 126.3, 126.0, 71.0, 46.5, 20.7. MS (EI) *m/z*: $[M - 3H]^-$ calcd for $C_{17}H_{13}O$, 233.10; found 233.16.



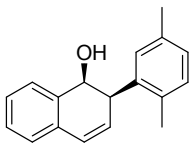
3ah

(1S,2R*)-2-(4-Nitrophenyl)-1,2-dihydronaphthalen-1-ol* ***(3ah)***.[19] Prepared according to general procedure. A pale yellow solid (21.3 mg, 40% yield). mp 122.3–123.6 °C. R_f = 0.3 on silica gel (ethyl acetate/petroleum ether 1:5,

v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.7 Hz, 2H), 7.41 (d, *J* = 8.7 Hz, 2H), 7.28 (dt, *J* = 24.6, 6.2 Hz, 3H), 7.17 (d, *J* = 6.9 Hz, 1H), 6.73 (dd, *J* = 9.6, 2.0 Hz, 1H), 6.04 (dd, *J* = 9.6, 3.8 Hz, 1H), 4.90 (d, *J* = 5.2 Hz, 1H), 3.92 (dd, *J* = 6.8, 4.7 Hz, 1H), 1.54 (s, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 147.3, 146.5, 135.6, 132.1, 130.2, 129.0, 128.8, 128.5, 128.1, 126.8, 126.7, 123.6, 71.2, 58.5, 47.3. MS (EI) *m/z*: [M – 3H]$^-$ calcd for $C_{16}H_{10}NO_3$, 264.08; found 264.05.

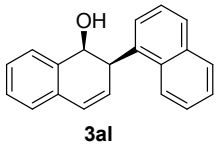


3ai *(1S*,2R*)-2-(4-Trifluoromethylphenyl)-1,2-dihydronaphthalen-1-ol (**3ai**).*[13f] Prepared according to general procedure. A white solid (38.9 mg, 67% yield). mp 112–114 °C. R_f = 0.11 on silica gel (ethyl acetate/petroleum ether 1:20, v/v).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.27–7.17 (m, 3H), 7.12 (d, *J* = 7.2 Hz, 1H), 6.67 (dd, *J* = 9.6, 1.5 Hz, 1H), 6.02 (dd, *J* = 9.6, 3.8 Hz, 1H), 4.85 (d, *J* = 5.7 Hz, 1H), 3.84 (s, 1H), 1.46 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.1, 136.4, 133.0, 130.3, 130.2, 129.5 (q, $^2J_{C\text{-}F}$ = 30.0 Hz), 129.4, 129.3, 129.0, 127.4, 127.3(q, $^1J_{C\text{-}F}$ = 271.3 Hz), 126.1, 126.0(q, $^3J_{C\text{-}F}$ = 3.7 Hz), 72.0, 47.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.51. MS (EI) *m/z*: [M – 3H]$^-$ calcd for $C_{17}H_{10}F_3O$, 287.06; found 287.08.



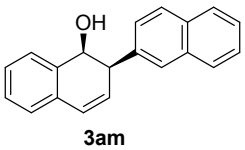
3aj *(1S*,2R*)-2-(2,5-Dimethylphenyl)-1,2-dihydronaphthalen-1-ol (**3aj**).*[2h] Prepared according to general procedure. Colorless oil (39.0 mg, 78%

yield). R_f = 0.27 on silica gel (ethyl acetate/petroleum ether 1:20, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 9.8, 7.3 Hz, 2H), 7.17 (d, *J* = 7.2 Hz, 1H), 7.10 (d, *J* = 7.3 Hz, 1H), 7.03 (d, *J* = 6.9 Hz, 2H), 6.92 (d, *J* = 7.3 Hz, 1H), 6.63 (dd, *J* = 9.6, 2.5 Hz, 1H), 5.98 (dd, *J* = 9.6, 2.7 Hz, 1H), 4.66 (d, *J* = 5.0 Hz, 1H), 4.07 (dt, *J* = 5.3, 2.8 Hz, 1H), 2.28 (s, 3H), 2.19 (s, 3H), 1.48 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 136.1, 135.2, 134.7, 132.8, 131.9, 130.0, 129.9, 129.4, 128.1, 127.4, 127.3, 127.2, 127.1, 126.0, 68.8, 42.8, 20.3, 18.7. MS (EI) *m/z*: $[M - 3H]^-$ calcd for $C_{18}H_{15}O$, 247.11; found 247.21.



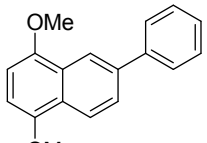
3al

(1S,2R*)-1',2'-Dihydro-[1,2']binaphthalenyl-1'-ol* ***(3al)***.[10c] Prepared according to general procedure. Colorless oil (29.9 mg, 55% yield). R_f = 0.22 on silica gel (ethyl acetate/petroleum ether 1:20, v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.4 Hz, 1H), 7.82–7.79 (m, 1H), 7.70 (t, *J* = 7.8 Hz, 1H), 7.47–7.35 (m, 4H), 7.25 (ddd, *J* = 7.2, 6.4, 2.4 Hz, 2H), 7.19–7.16 (m, 1H), 7.14–7.12 (m, 1H), 6.70 (dt, *J* = 7.8, 3.9 Hz, 1H), 6.10 (dd, *J* = 9.6, 2.5 Hz, 1H), 4.82 (d, *J* = 4.9 Hz, 1H), 4.70 (s, 1H), 1.42 (s, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 135.5, 135.1, 134.4, 132.9, 132.2, 130.6, 129.5, 129.1, 128.6, 128.4, 128.3, 128.2, 127.3, 127.1, 126.7, 126.0, 125.9, 123.4, 70.6, 43.1. MS (EI) *m/z*: $[M + CH_3]^+$ calcd for $C_{21}H_{19}O$, 287.15; found 287.06.



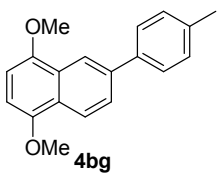
3am

(1S,2R*)-1,2-Dihydro-[2,2'-binaphthalen]-1-ol (**3am**).*[5a] Prepared according to general procedure. Colorless oil (26.1 mg, 48% yield). R_f = 0.22 on silica gel (ethyl acetate/petroleum ether 1:20, v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82–7.76 (m, 4H), 7.48–7.43 (m, 2H), 7.36–7.30 (m, 3H), 7.24 (ddd, *J* = 22.5, 14.4, 6.8 Hz, 2H), 6.77 (dd, *J* = 9.6, 2.0 Hz, 1H), 6.22 (dd, *J* = 9.6, 4.0 Hz, 1H), 5.01 (d, *J* = 5.9 Hz, 1H), 4.04 (ddd, *J* = 6.0, 4.0, 2.1 Hz, 1H), 1.53 (s, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 136.1, 135.3, 133.4, 132.8, 132.7, 129.5, 128.4, 128.4, 128.3, 128.1, 127.8, 127.6, 127.3, 126.7, 126.5, 126.1, 125.8, 71.3, 47.5. MS (EI) *m/z*: [M – 3H]$^-$ calcd for $C_{20}H_{13}O$, 269.10; found 268.88.



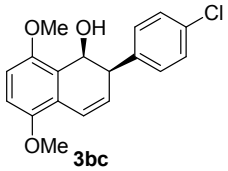
4ba

*1,4-Dimethoxy-6-phenylnaphthalene (**4ba**).*[13a] Prepared according to general procedure. White solid (50.2 mg, 95% yield). mp 87.2–87.8 °C. R_f = 0.2 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.40 (d, *J* = 1.8 Hz, 1H), 8.23 (d, *J* = 8.7 Hz, 1H), 7.72 (ddd, *J* = 8.3, 7.5, 1.4 Hz, 3H), 7.45–7.42 (m, 2H), 7.34–7.31 (m, 1H), 6.69–6.65 (m, 2H), 3.94 (d, *J* = 1.8 Hz, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 150.3, 150.1, 141.9, 139.1, 129.3, 128.1, 127.8, 127.2, 126.0, 125.9, 123.0, 120.4, 104.2, 103.9, 56.4, 56.3. MS (EI) *m/z*: [M – CH_3]$^-$ calcd for $C_{17}H_{13}O_2$, 249.08; found 248.52.



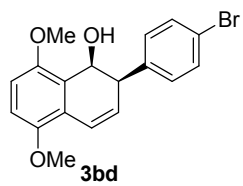
4bg

*1,4-Dimethoxy-6-(p-tolyl)naphthalene (**4bg**)*. Prepared according to general procedure. A white solid (56.8 mg, 90% yield). mp 113.2–114.4 °C. R_f =0.23 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 1.6 Hz, 1H), 8.27 (d, *J* = 8.7 Hz, 1H), 7.78 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 6.71 (q, *J* = 8.3 Hz, 2H), 3.98 (t, *J* = 3.4 Hz, 6H), 2.43 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.1, 149.9, 138.8, 138.7, 137.4, 129.9, 127.7, 127.0, 125.6, 122.8, 119.8, 104.0, 103.5, 56.13, 21.5. HRMS (ESI-ion trap) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{19}O_2$, 279.1386; found 279.1375.



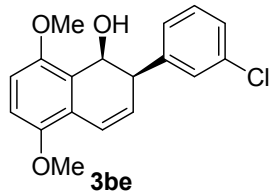
3bc

(1S,2R*)-2-(4-Chlorophenyl)-5,8-dimethoxy-1,2-dihydronaphthalen-1-ol (**3bc**)*[5a]. Prepared according to general procedure. A white solid (50.8 mg, 80% yield). mp 115.6–117.2 °C. R_f = 0.3 on silica gel (ethyl acetate/petroleum ether 1:5, v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (d, *J* = 9.2 Hz, 4H), 7.01 (dd, *J* = 9.8, 3.2 Hz, 1H), 6.74 (q, *J* = 9.0 Hz, 2H), 6.00–5.97 (m, 1H), 4.98 (d, *J* = 4.2 Hz, 1H), 3.75 (d, *J* = 8.3 Hz, 6H), 3.69–3.66 (m, 1H), 1.15 (p, *J* = 9.0 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 149.6, 148.7, 138.1, 131.7, 129.5, 127.5, 127.4, 123.2, 121.3, 121.2, 110.5, 110.0, 63.3, 55.2, 55.1, 45.6. MS (EI) *m/z*: $[M - 3H]^-$ calcd for $C_{18}H_{14}ClO_3$, 313.06; found 313.14.



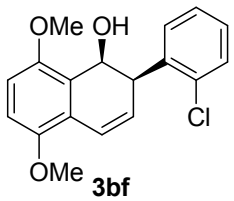
3bd

(1S,2R*)-2-(4-Bromophenyl)-5,8-dimethoxy-1,2-dihydronaphthalen-1-ol* ***(3bd)***.[5a] Prepared according to general procedure. A white solid (28.8 mg, 40% yield). mp 91.6–93.8 °C. R_f = 0.29 on silica gel (ethyl acetate/petroleum ether 1:5, v/v).^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45–7.41 (m, 2H), 7.24–7.21 (m, 2H), 7.03–6.99 (m, 1H), 6.77 –6.72 (m, 2H), 5.98 (ddd, *J* = 9.8, 2.2, 1.6 Hz, 1H), 4.99 (d, *J* = 4.1 Hz, 1H), 3.75 (d, *J* = 8.1 Hz, 6H), 3.67–3.65 (m, 1H), 1.53 (s, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 150.6, 149.7, 139.6, 131.5, 130.9, 128.3, 124.2, 122.3, 122.2, 120.8, 111.5, 111.0, 64.2, 56.2, 56.1, 46.7. MS (EI) *m/z*: $[M - H]^-$ calcd for $C_{18}H_{16}BrO_3$, 359.02; found 359.01.



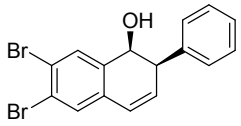
3be

(1S,2R*)-2-(3-Chlorophenyl)-5,8-dimethoxy-1,2-dihydronaphthalen-1-ol* ***(3be)***.[13f] Prepared according to general procedure. Colorless oil (57.9 mg, 92% yield). R_f = 0.24 on silica gel (ethyl acetate/petroleum ether 1:5, v/v). ^{1}H NMR (600 MHz, $CDCl_3$)δ 7.36 (s, 1H), 7.24 (d, *J* = 5.2 Hz, 2H), 7.22–7.19 (m, 1H), 7.02 (dd, *J* = 9.8, 3.2 Hz, 1H), 6.75 (q, *J* = 8.9 Hz, 2H), 6.02–5.99 (m, 1H), 5.02–5.00 (m, 1H), 3.75 (d, *J* = 5.9 Hz, 6H), 3.69–3.67 (m, 1H), 1.53 (s, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 150.9, 150.0, 143.0, 134.6, 130.0, 129.6, 128.3, 127.6, 127.4, 124.6, 122.7, 122.5, 111.8, 111.4, 64.5, 56.5, 56.4, 47.3. MS (EI) *m/z*: $[M + Na]^+$ calcd for $C_{18}H_{17}ClO_3Na$, 339.08; found 338.84.



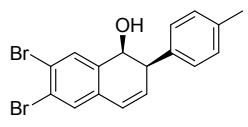
3bf

(1S,2R*)-2-(2-Chlorophenyl)-5,8-dimethoxy-1,2-dihydronaphthalen-1-ol* ***(3bf)***.[4b] Prepared according to general procedure. A white solid (55.4 mg, 92% yield). mp 98–99 °C. R_f = 0.3 on silica gel (ethyl acetate/petroleum ether 1:5, v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.42 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.30 (td, *J* = 7.5, 1.0 Hz, 1H), 7.25 – 7.22 (m, 1H), 7.11 (dd, *J* = 9.8, 3.2 Hz, 1H), 6.82 (q, *J* = 9.0 Hz, 2H), 6.07 – 6.04 (m, 1H), 5.23 (d, *J* = 4.2 Hz, 1H), 4.35 – 4.33 (m, 1H), 3.83 (d, *J* = 4.8 Hz, 6H), 1.59 (d, *J* = 33.7 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 150.8, 149.6, 137.9, 134.0, 131.4, 129.4, 128.6, 128.2, 126.8, 124.1, 122.2, 122.1, 111.5, 111.0, 61.6, 56.2, 56.1, 43.8. MS (EI) *m/z*: $[M - 3H]^-$ calcd for $C_{18}H_{14}ClO_3$, 313.06; found 313.14.



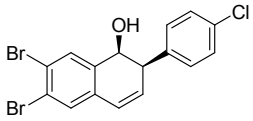
3ca

(1S,2R*)-6,7-Dibromo-2-phenyl-1,2-dihydronaphthalen-1-ol* ***(3ca)***.[5a] Prepared according to general procedure. Colorless oil (68.2 mg, 90% yield). R_f = 0.29 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.33 (d, *J* = 3.8 Hz, 1H), 7.23 (tt, *J* = 4.7, 3.6 Hz, 3H), 7.12–7.09 (m, 2H), 6.53 (dd, *J* = 9.6, 1.5 Hz, 1H), 6.14 (dd, *J* = 9.6, 4.8 Hz, 1H), 4.90 (t, *J* = 7.0 Hz, 1H), 3.76 (ddd, *J* = 6.5, 4.8, 1.6 Hz, 1H), 1.44 (d, *J* = 8.6 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 137.1, 135.6, 133.5, 131.8, 131.4, 130.8, 129.3, 128.9, 127.9, 126.4, 124.0, 123.6, 70.3, 46.7. MS (EI) *m/z*: $[M - H]^-$ calcd for $C_{16}H_{11}Br_2O$, 376.93; found 376.94.



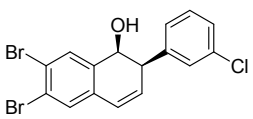
3cg

(1S,2R*)-6,7-Dibromo-2-(4-methylphenyl)-1,2-dihydronaphthalen-1-ol* ***(3cg)***[13f]. Prepared according to general procedure. A white solid (62.9 mg, 80% yield). mp 108–109 °C. R_f = 0.24 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 4.5 Hz, 1H), 7.45–7.39 (m, 1H), 7.16 (dd, *J* = 7.7, 1.8 Hz, 4H), 6.60–6.51 (m, 1H), 6.09 (td, *J* = 9.4, 3.3 Hz, 1H), 4.79–4.73 (m, 1H), 3.75–3.68 (m, 1H), 2.37 (s, 3H), 2.06 (t, *J* = 9.3 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 137.3, 137.1, 136.6, 133.4, 132.4, 131.2, 130.8, 129.7, 128.3, 125.9, 124.0, 123.5, 73.6, 49.5, 21.1. MS (EI) *m/z*: $[M - CH_3]^-$ calcd for $C_{16}H_{11}Br_2O$, 376.91; found 376.87.



3cc

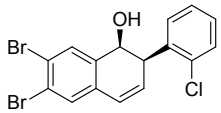
(1S,2R*)-6,7-Dibromo-2-(4-chlorophenyl)-1,2-dihydronaphthalen-1-ol* ***(3cc)***.[5a] Prepared according to general procedure. Colorless oil (69.87 mg, 85% yield). R_f = 0.3 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 9.5 Hz, 1H), 7.32 (d, *J* = 3.4 Hz, 1H), 7.02 (t, *J* = 6.0 Hz, 2H), 6.97 (d, *J* = 8.1 Hz, 2H), 6.50 (dd, *J* = 9.7, 1.1 Hz, 1H), 6.11 (dd, *J* = 9.7, 4.9 Hz, 1H), 4.87 (d, *J* = 6.7 Hz, 1H), 3.73–3.69 (m, 1H), 1.54–1.47 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 137.7, 137.3, 133.6, 132.2, 132.0, 131.4, 130.7, 129.6, 129.2, 126.2, 123.9, 123.5, 70.2, 46.2. MS (EI) *m/z*: $[M - H]^-$ calcd for $C_{16}H_{10}Br_2ClO$, 410.88; found 410.81.



3ce

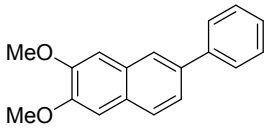
(1S,2R*)-6,7-Dibromo-2-(3-chlorophenyl)-1,2-dihydronaphthalen-1-ol* ***(3ce)***. Prepared according to general procedure. Colorless oil

(71.9 mg, 87% yield). R_f = 0.32 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 4.5 Hz, 1H), 7.35 (s, 1H), 7.21–7.12 (m, 4H), 7.02–6.98 (m, 1H), 6.55 (dd, *J* = 9.7, 1.5 Hz, 1H), 6.09 (dd, *J* = 9.7, 4.5 Hz, 1H), 4.86 (d, *J* = 6.3 Hz, 1H), 3.99 (t, *J* = 6.7 Hz, 1H), 3.73 (dd, *J* = 7.8, 3.1 Hz, 1H), 1.54 (t, *J* = 4.6 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 138.3, 136.7, 134.6, 133.1, 131.5, 131.0, 130.9, 130.0, 129.5, 128.0, 127.3, 127.0, 124.3, 123.8, 70.1, 46.5. HRMS (ESI-ion trap) *m/z*: $[M - 3H]^-$ calcd for $C_{16}H_8Br_2ClO$, 408.8628; found 408.8627.



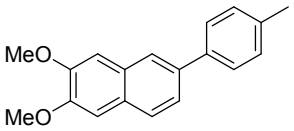
3cf

(1S,2R*)-6,7-Dibromo-2-(2-chlorophenyl)-1,2-dihydronaphthalen-1-ol (**3cf**)* Prepared according to general procedure. Colorless oil (64.4 mg, 78% yield). R_f = 0.32 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.37 (s, 1H), 7.21–7.14 (m, 4H), 6.57 (dd, *J* = 9.7, 2.3 Hz, 1H), 6.06 (dd, *J* = 9.7, 3.5 Hz, 1H), 4.85 (d, *J* = 5.3 Hz, 1H), 4.38 (dt, *J* = 5.7, 2.9 Hz, 1H), 1.53 (dd, *J* = 14.8, 6.3 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 135.8, 135.3, 134.3, 132.8, 132.6, 131.2, 131.0, 130.7, 129.7, 128.8, 127.2, 126.6, 124.6, 123.5, 68.4, 43.3. HRMS (ESI-ion trap) *m/z*: $[M - 3H]^-$ calcd for $C_{16}H_8Br_2ClO$, 408.8628; found 408.8632.



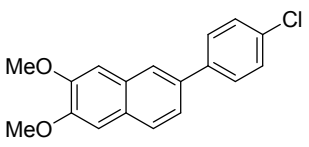
4da

6,7-Dimethoxy-2-phenyl-naphthalene ***(4da)***.[13a] Prepared according to general procedure. A white solid (49.6 mg, 88% yield). mp 121–122 °C. R_f = 0.35 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 1.5 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.63–7.60 (m, 2H), 7.52 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.38 (dd, *J* = 10.6, 4.8 Hz, 2H), 7.29–7.24 (m, 1H), 7.07 (d, *J* = 19.6 Hz, 2H), 3.93 (d, *J* = 1.2 Hz, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 149.9, 149.6, 141.4, 137.0, 129.5, 128.8, 128.4, 127.3, 127.1, 126.8, 124.4, 123.9, 106.6, 106.1, 55.9. MS (EI) *m/z*: $[M - H]^-$ calcd for $C_{18}H_{15}O_2$, 263.11; found 263.00.



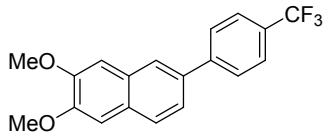
4dg

6,7-Dimethoxy-2-(4-methylphenyl)-naphthalene ***(4dg)***. Prepared according to general procedure. A white solid (47.8 mg, 86% yield). mp 136.2–137.3 °C. R_f = 0.36 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, *J* = 1.4 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.51 (ddd, *J* = 7.1, 4.2, 1.8 Hz, 3H), 7.20 (d, *J* = 7.9 Hz, 2H), 7.09 (s, 1H), 7.05 (s, 1H), 3.93 (d, *J* = 2.2 Hz, 6H), 2.33 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 150.4, 150.1, 139.1, 137.5, 137.4, 130.1, 130.1, 128.8, 127.7, 127.3, 124.6, 124.4, 107.1, 106.7, 56.5, 21.7. HRMS (ESI-ion trap) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{19}O_2$ 279.1386; found, 279.1375.



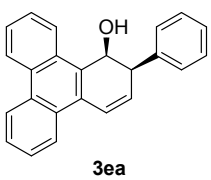
4dc

*6,7-Dimethoxy-2-(4-chlorophenyl)-naphthalene (**4dc**).* Prepared according to general procedure. A white solid (47.1 mg, 79% yield). mp 139–140 °C. R_f = 0.15 on silica gel (ethyl acetate/petroleum ether 1:10, v/v).^{1}H NMR (600 MHz, $CDCl_3$) δ 8.34 (d, *J* = 1.7 Hz, 1H), 8.17 (d, *J* = 8.7 Hz, 1H), 7.68 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.65–6.60 (m, 2H), 3.90 (d, *J* = 2.7 Hz, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 150.6, 150.4, 140.5, 136.4, 133.8, 130.1, 129.6, 129.2, 129.1, 127.6, 125.0, 124.2, 107.2, 106.7, 56.6, 56.5. HRMS (ESI-ion trap) *m/z*: $[M + 3H]^+$ calcd for $C_{18}H_{18}ClO_2$, 301.0998; found 301.1002.



4di

*6,7-Dimethoxy-2-(4-trifluoromethylphenyl)-naphthalene **(4di)*** Prepared according to general procedure. A white solid (36.5 mg, 55% yield). mp 113–114 °C. R_f = 0.3 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.72–7.60 (m, 6H), 7.49 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.08 (d, *J* = 15.6 Hz, 2H), 3.93 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.7(q, $^2J_{C\text{-}F}$ = 30Hz), 144.6, 135.1, 129.3, 129.1 (q, $^3J_{C\text{-}F}$ = 315Hz), 128.6, 127.1 (q, $^3J_{C\text{-}F}$ = 18Hz), 126.8, 125.5, 125.4 (q, $^4J_{C\text{-}F}$ = 4Hz), 124.5, 123.4, 123.2, 106.3, 105.7, 55.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.30. HRMS (ESI-ion trap) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{16}F_3O_2$, 333.1103; found 333.1094.

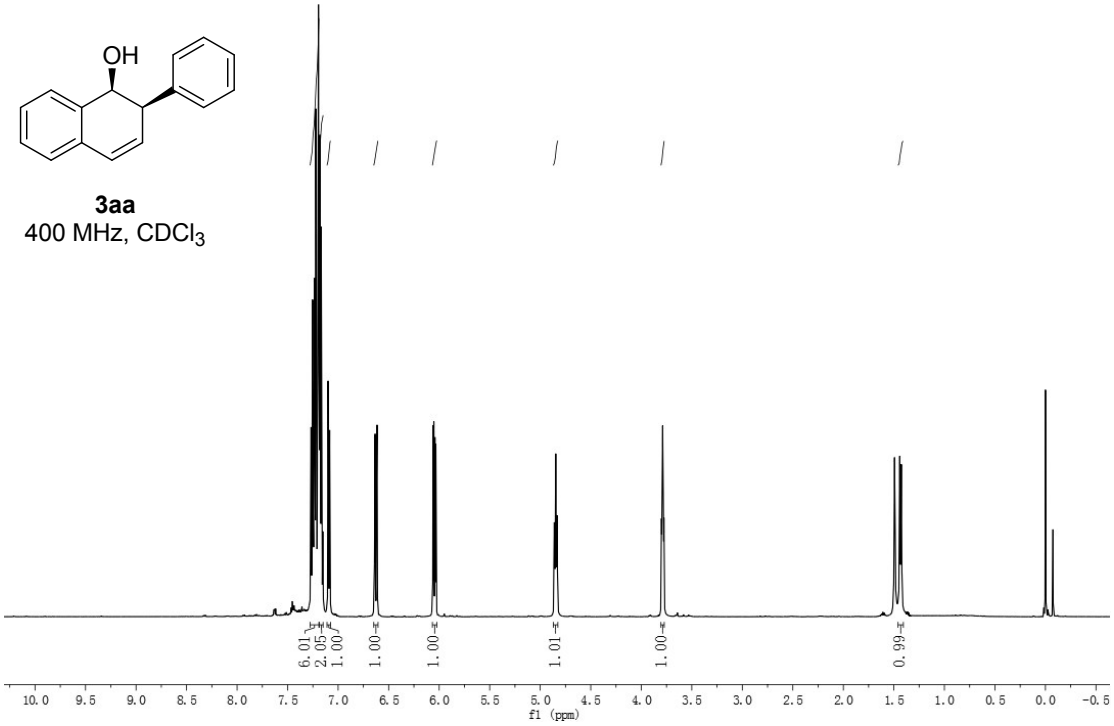


3ea

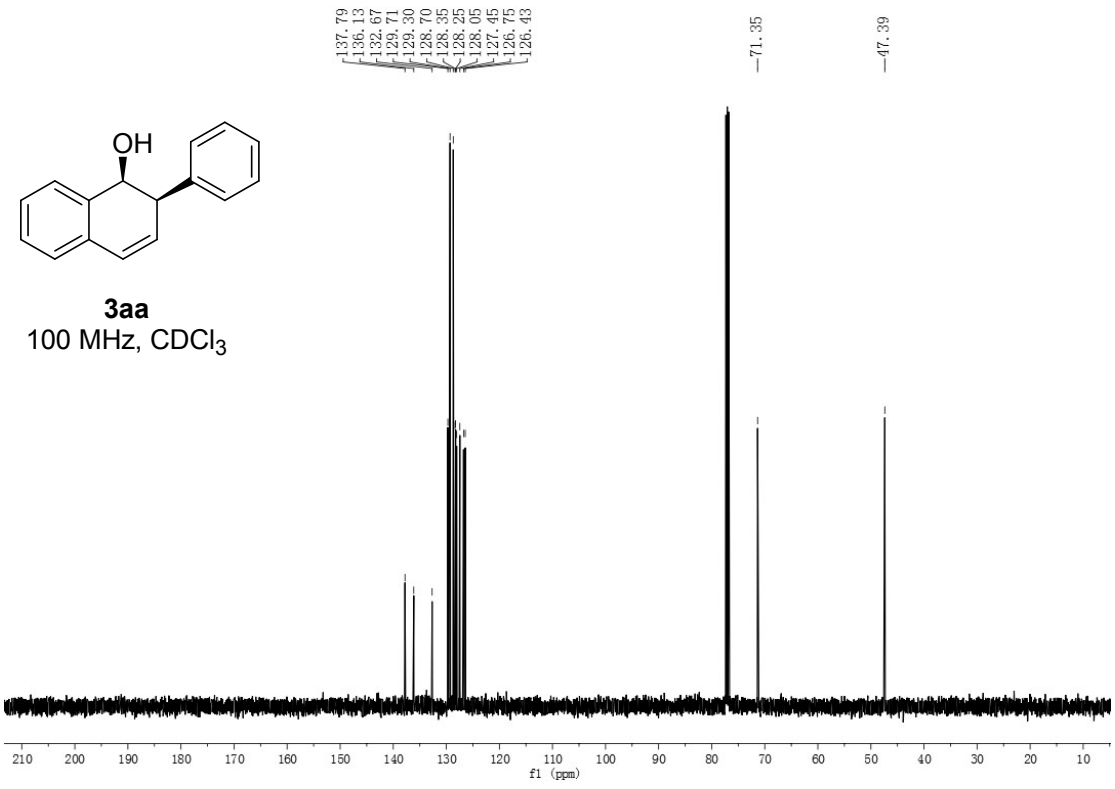
(1S,2R*)-2-Phenyl-1,2-dihydrotriphenylen-1-ol (**3ea**).*[5a]

Prepared according to general procedure. A white solid (26.4 mg, 41% yield). mp 156–158 °C. R_f = 0.23 on silica gel (ethyl acetate/petroleum ether 1:10, v/v). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.70–8.64 (m, 2H), 8.27–8.22 (m, 1H), 8.21–8.14 (m, 1H), 7.64–7.50 (m, 5H), 7.48–7.45 (m, 2H), 7.42–7.37 (m, 2H), 7.34–7.28 (m, 1H), 6.41 (ddd, *J* = 9.8, 2.3, 1.5 Hz, 1H), 5.36 (t, *J* = 4.7 Hz, 1H), 3.98–3.89 (m, 1H), 1.60 (d, *J* = 5.7 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 140.3, 131.1, 131.0, 130.8, 130.1, 129.4, 129.0, 128.9, 128.8, 127.6, 127.5, 127.2, 127.1, 126.8, 126.6, 124.3, 124.2, 124.0, 123.3, 123.2, 67.8, 48.2. MS (EI) *m/z*: $[M - 3H]^-$ calcd for $C_{24}H_{15}O$, 319.11; found 319.86.

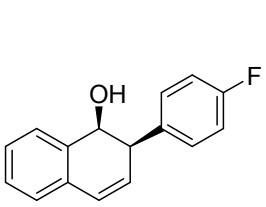
4. Copies of ^{1}H, ^{13}C and ^{19}F NMR spectra



3aa
400 MHz, $CDCl_3$

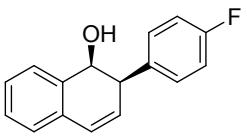


3aa
100 MHz, $CDCl_3$



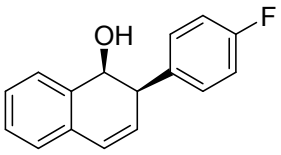
3ab

600MHZ, $CDCl_3$

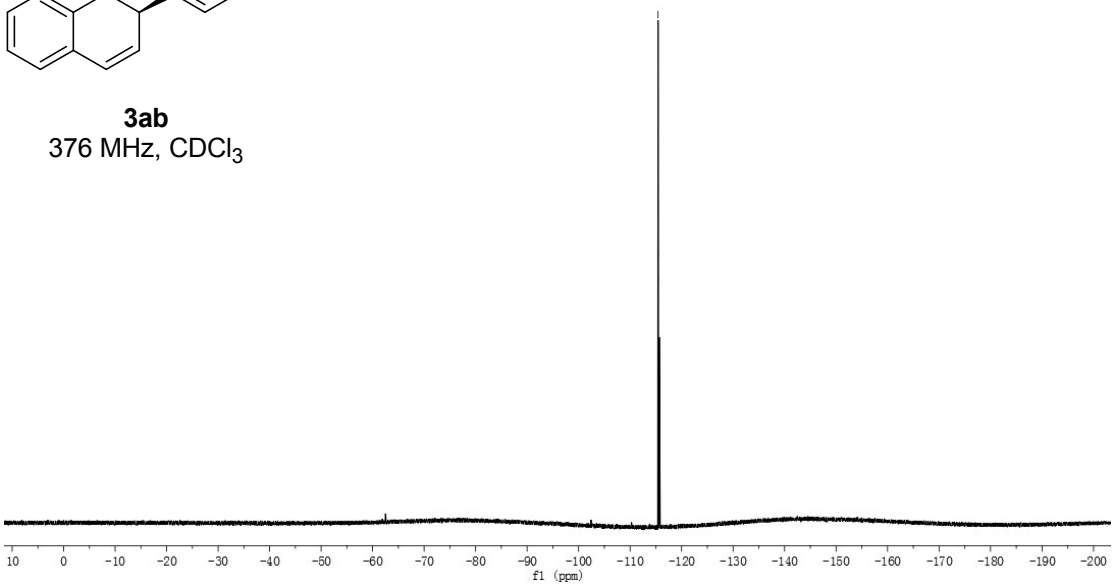


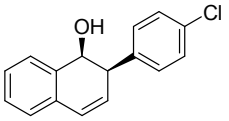
3ab

150 MHz, $CDCl_3$

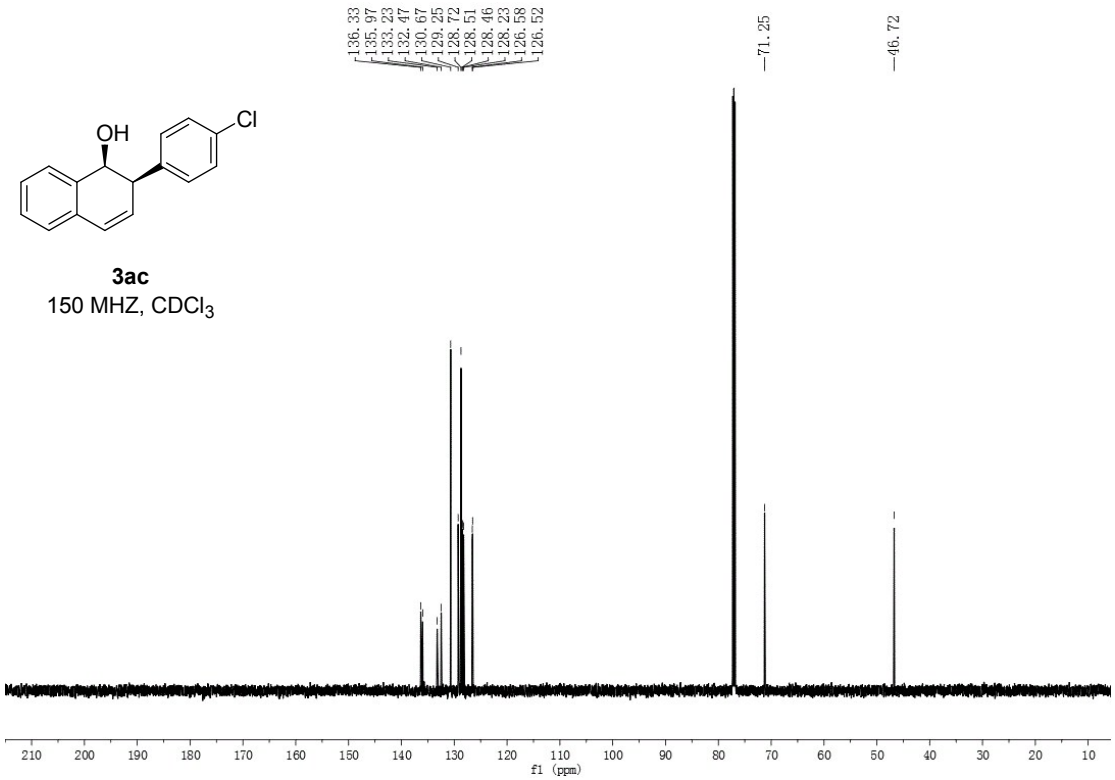


3ab
376 MHz, $CDCl_3$

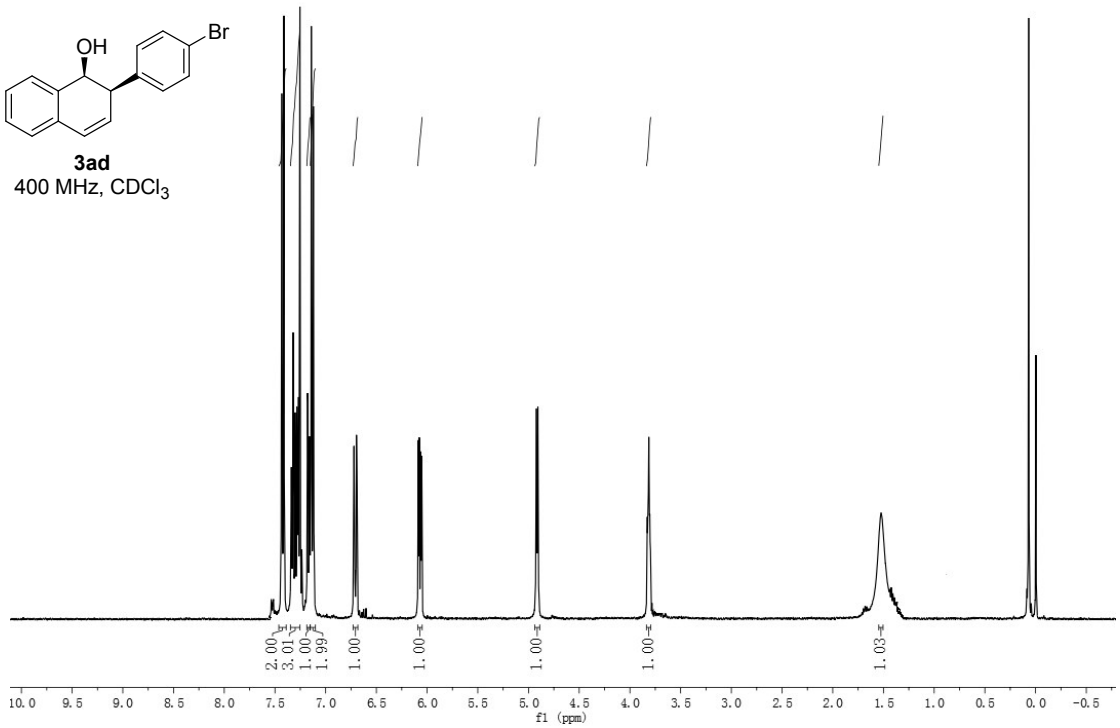




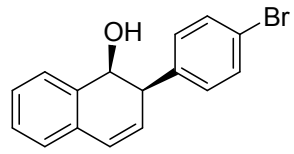
3ac
600 MHZ, $CDCl_3$



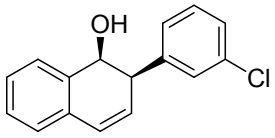
3ac
150 MHZ, $CDCl_3$



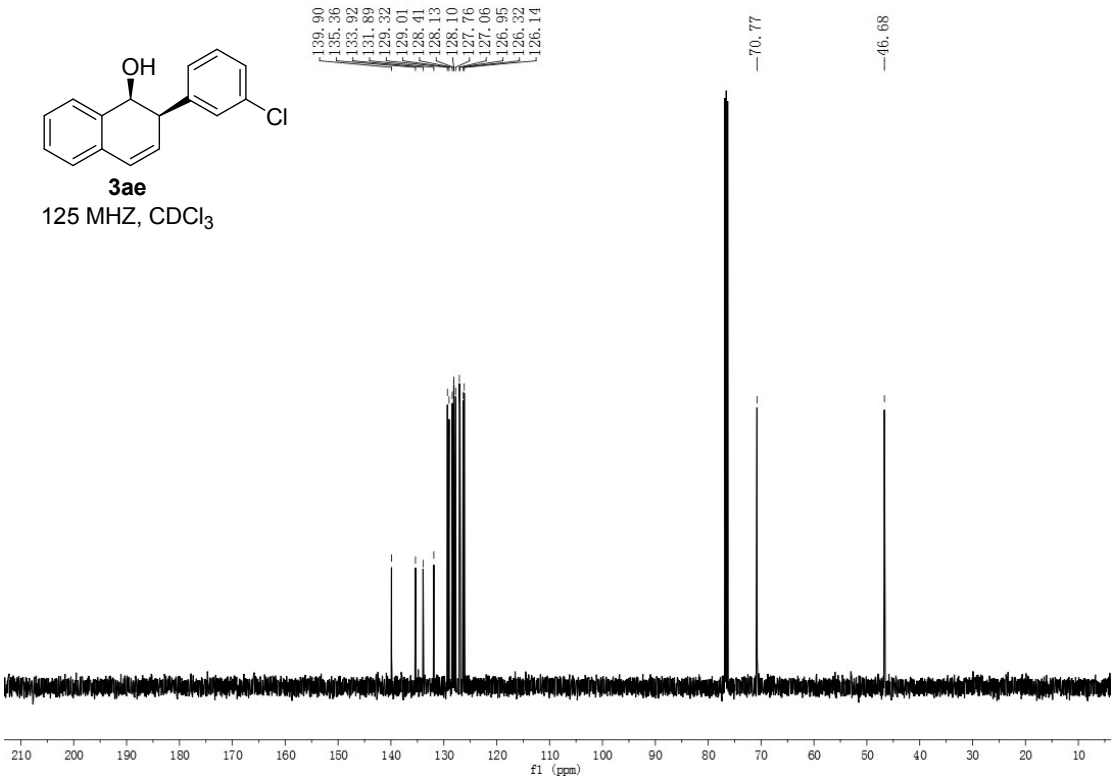
3ad
400 MHz, $CDCl_3$



3ad
100 MHz, $CDCl_3$

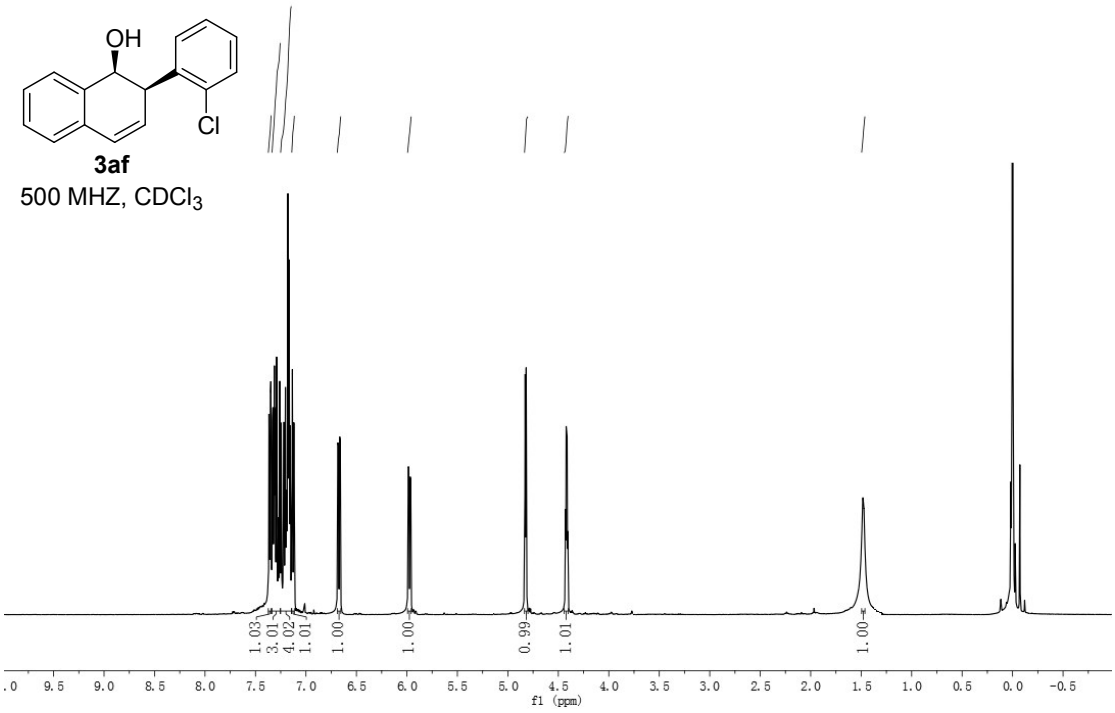


3ae
500 MHZ, $CDCl_3$



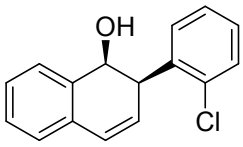
3ae

125 MHZ, $CDCl_3$



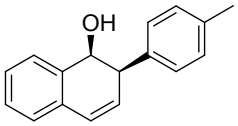
3af

500 MHZ, $CDCl_3$



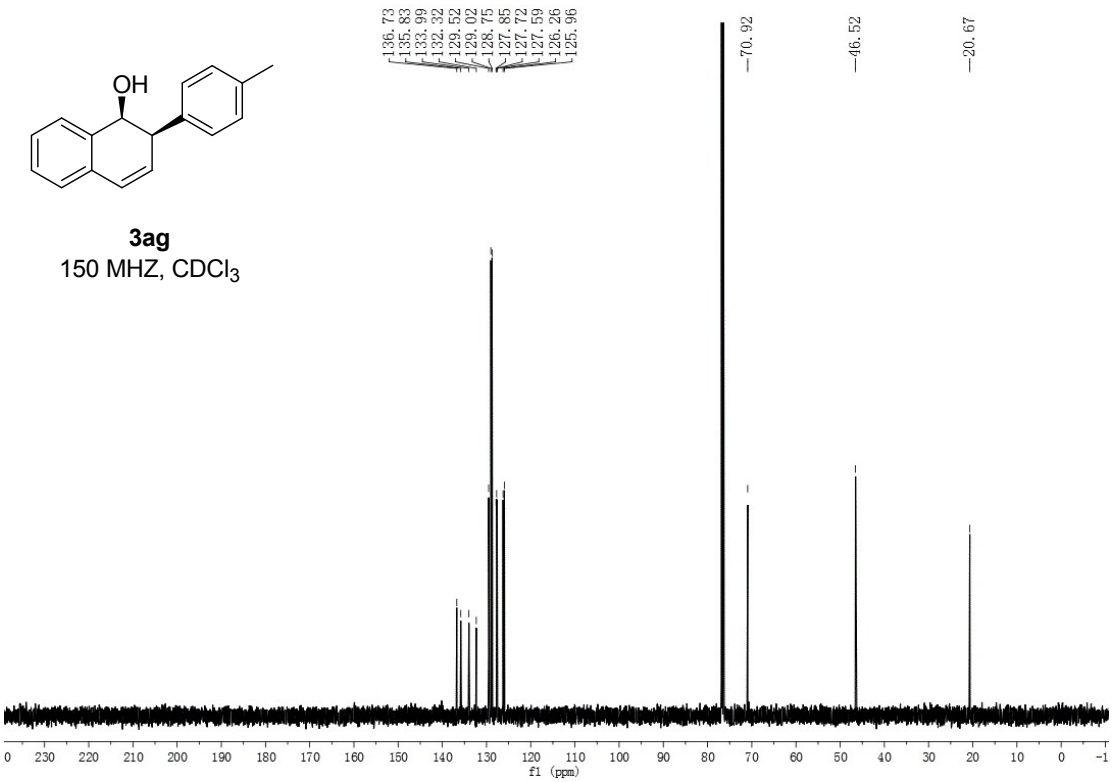
3af

125 MHZ, $CDCl_3$



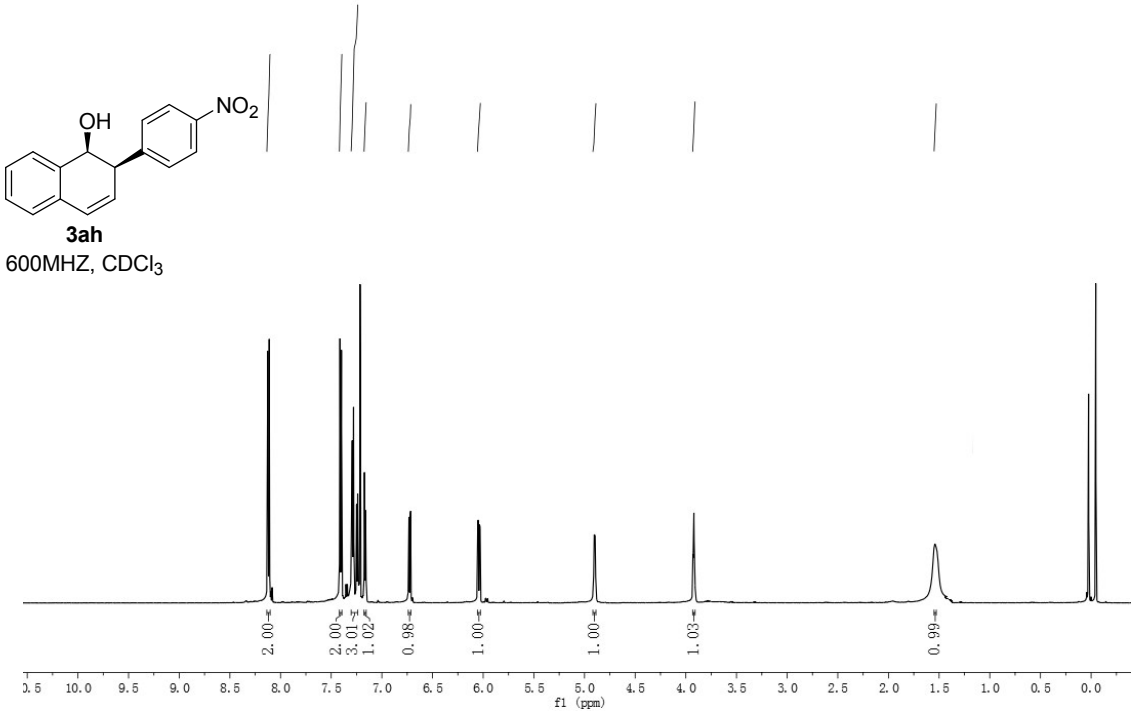
3ag

600 MHZ, $CDCl_3$



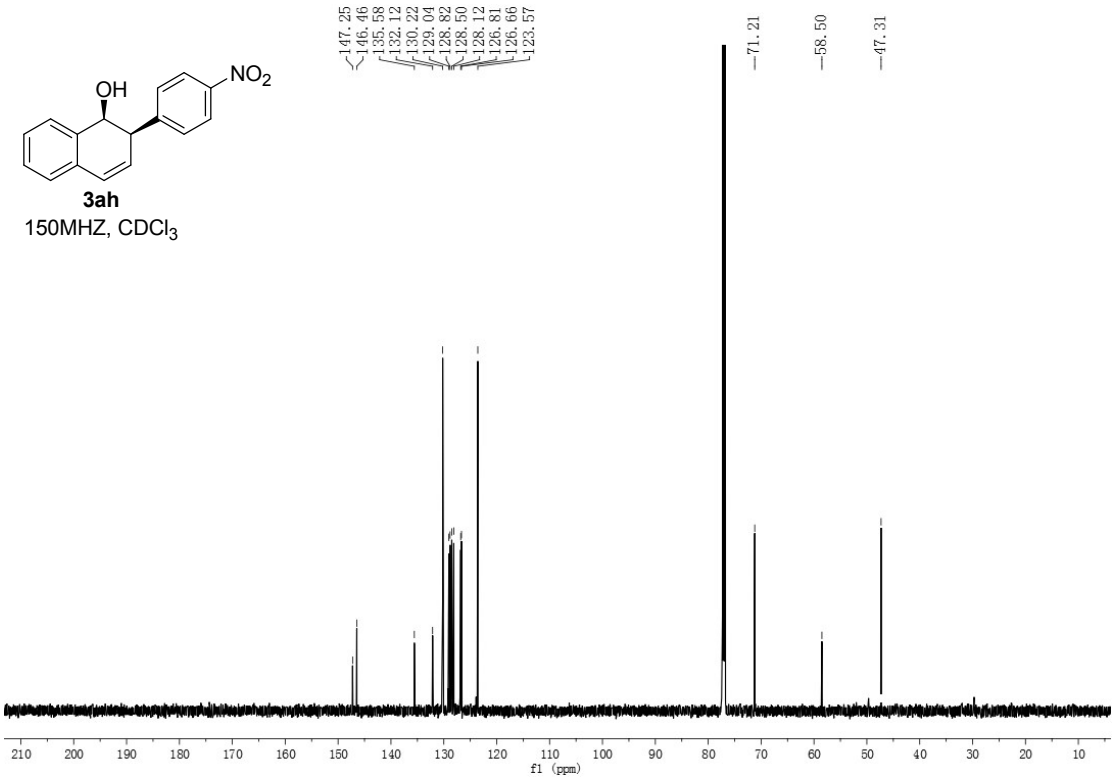
3ag

150 MHZ, $CDCl_3$



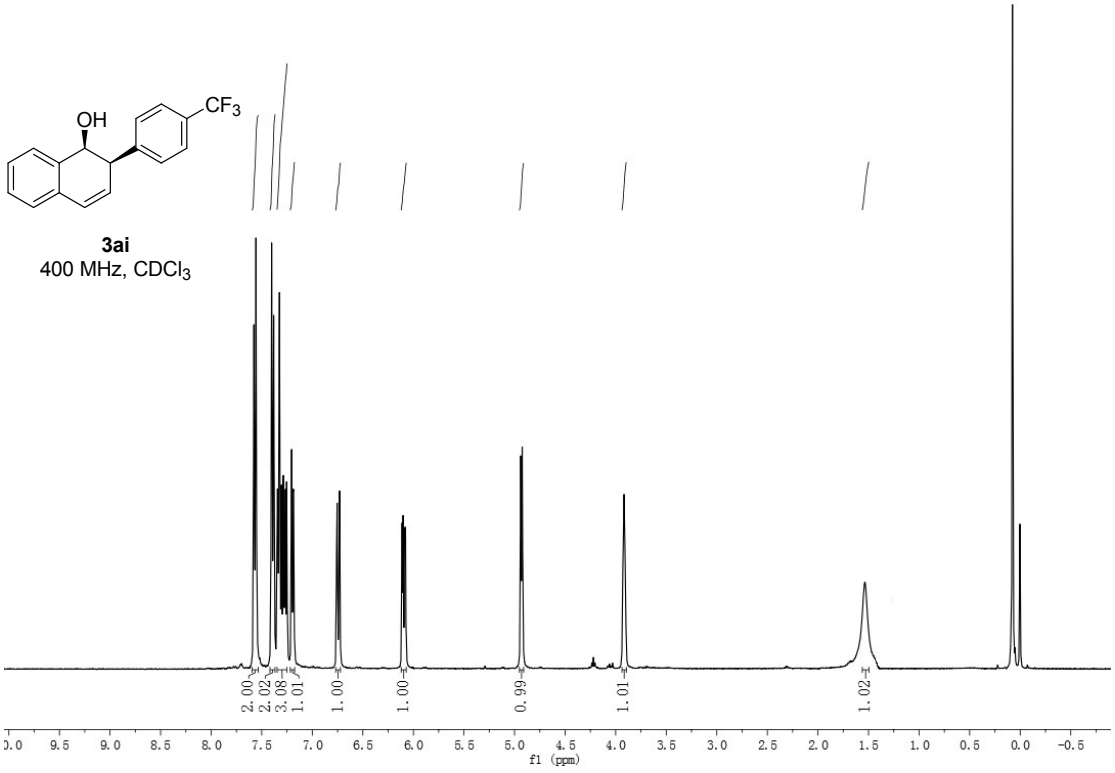
3ah

600MHZ, $CDCl_3$



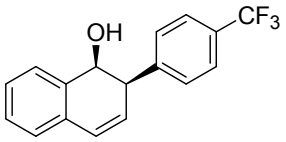
3ah

150MHZ, $CDCl_3$

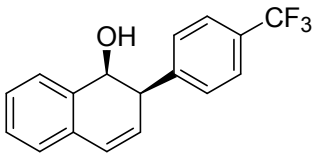


3ai

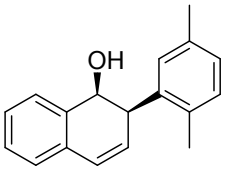
400 MHz, $CDCl_3$



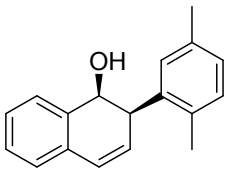
3ai
100 MHz, $CDCl_3$



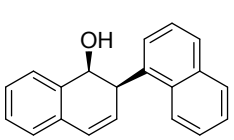
3ai
376 MHz, $CDCl_3$



3aj
400 MHz, $CDCl_3$

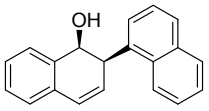


3aj
100 MHz, $CDCl_3$



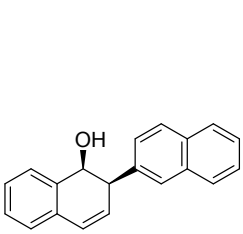
3al

600 MHz, $CDCl_3$

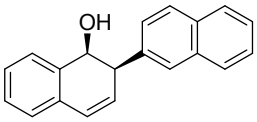


3al

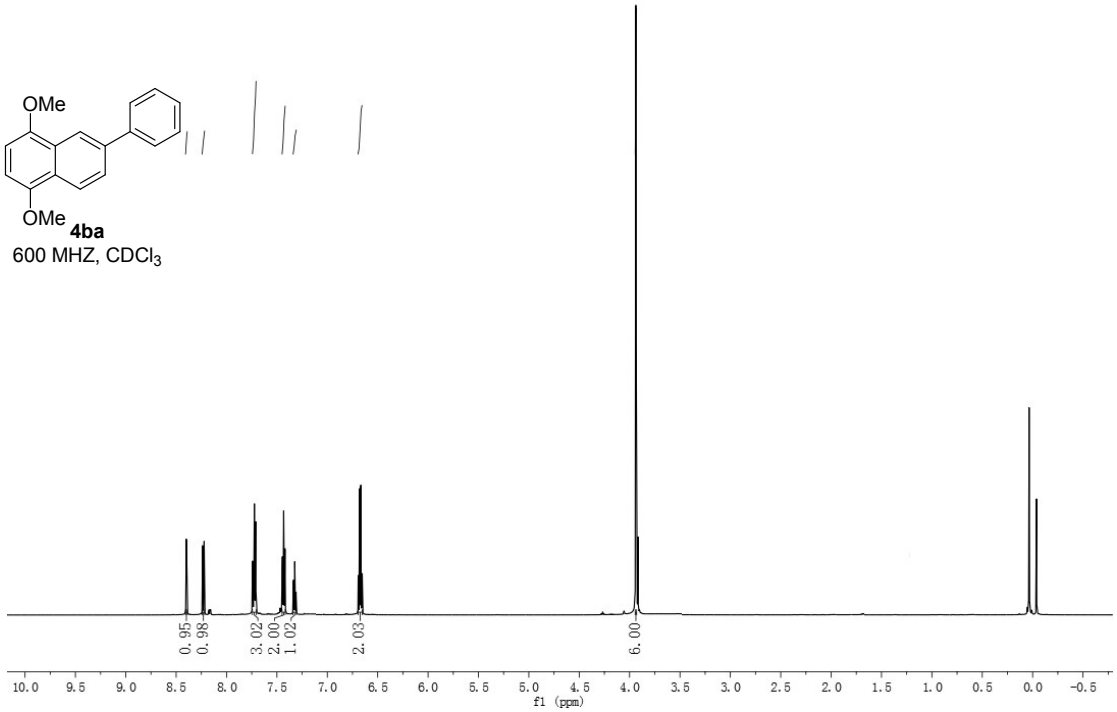
150 MHz, $CDCl_3$

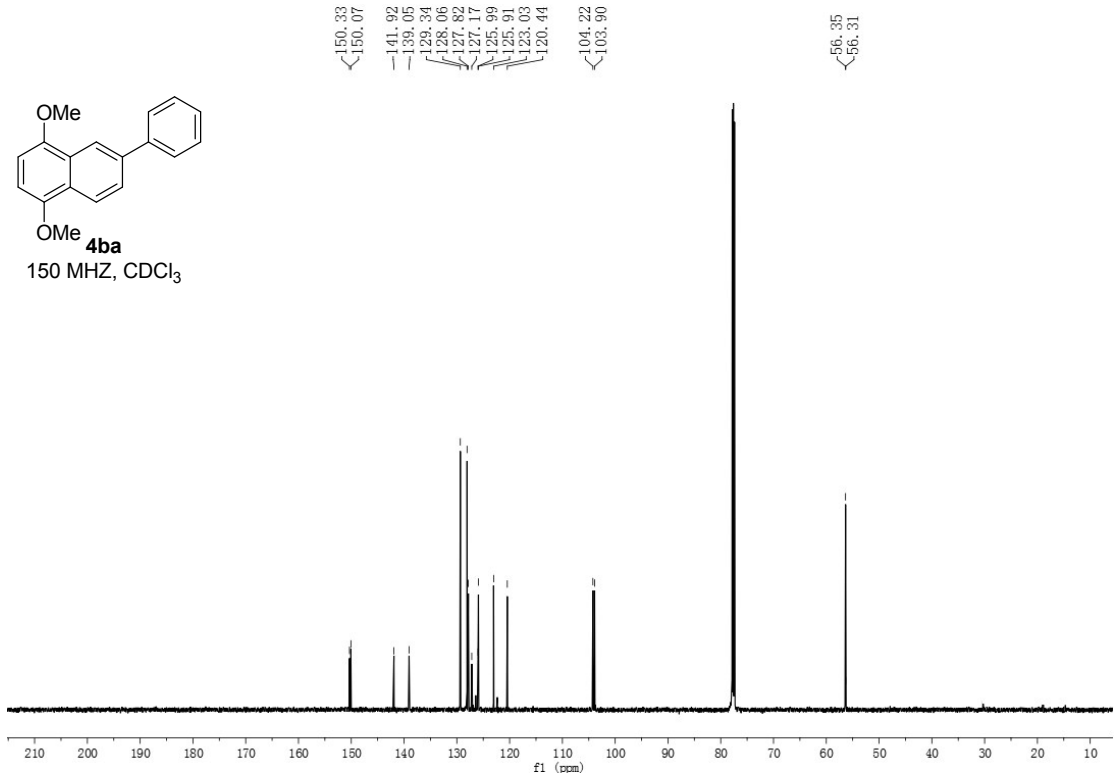


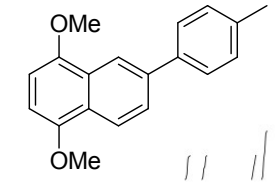
3am
600 MHz, $CDCl_3$



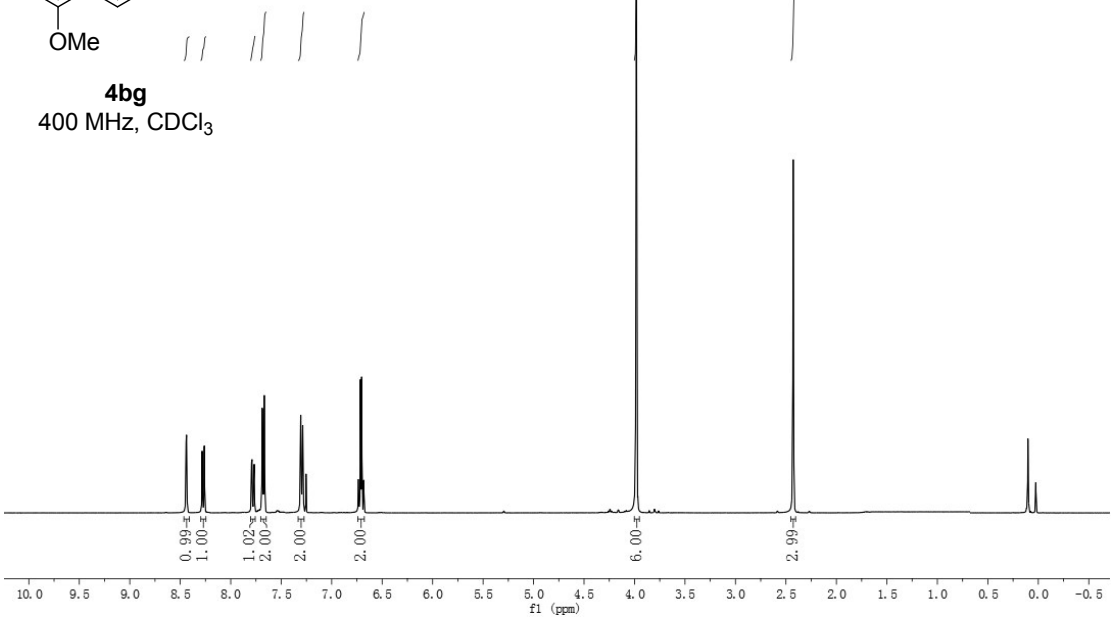
3am
150 MHz, $CDCl_3$

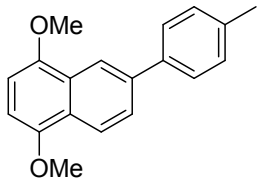

OMe
OMe
4ba
600 MHZ, CDCl3
0.95
0.98
3.02
2.00
1.02
2.03
6.00
f1 (ppm)


150.33
150.07
141.92
139.05
129.34
128.06
127.82
127.17
125.99
125.91
123.03
120.44
104.22
103.90
56.35
56.31
OMe
OMe
4ba
150 MHZ, CDCl3
f1 (ppm)

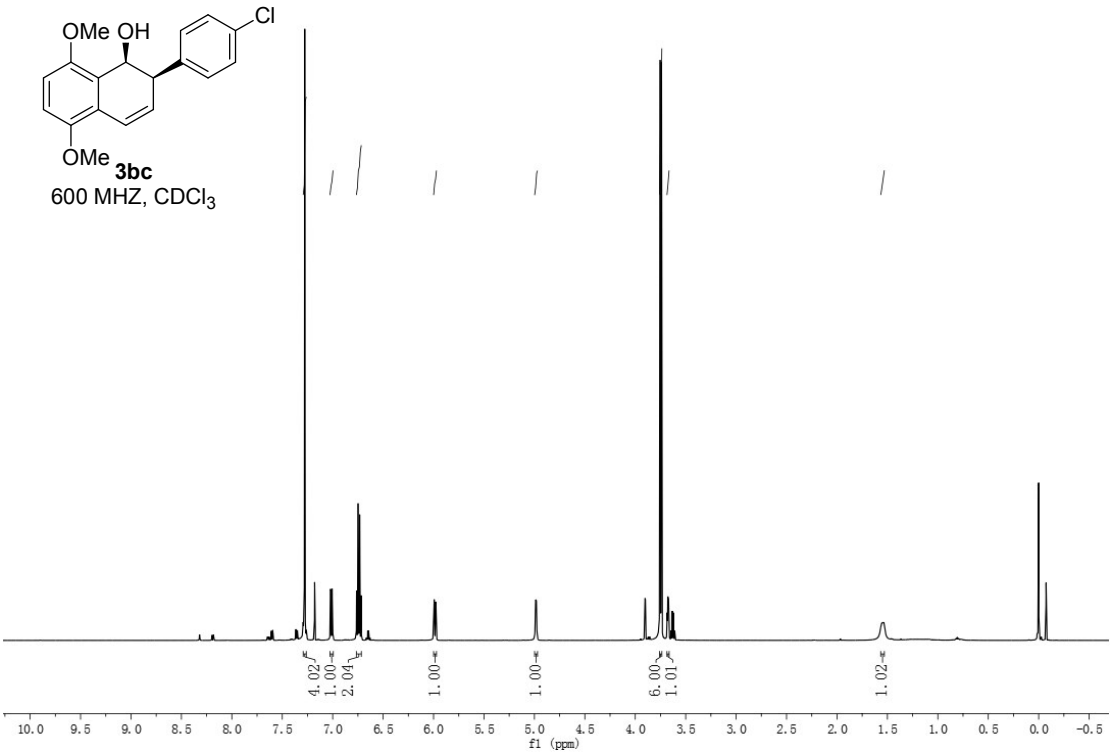


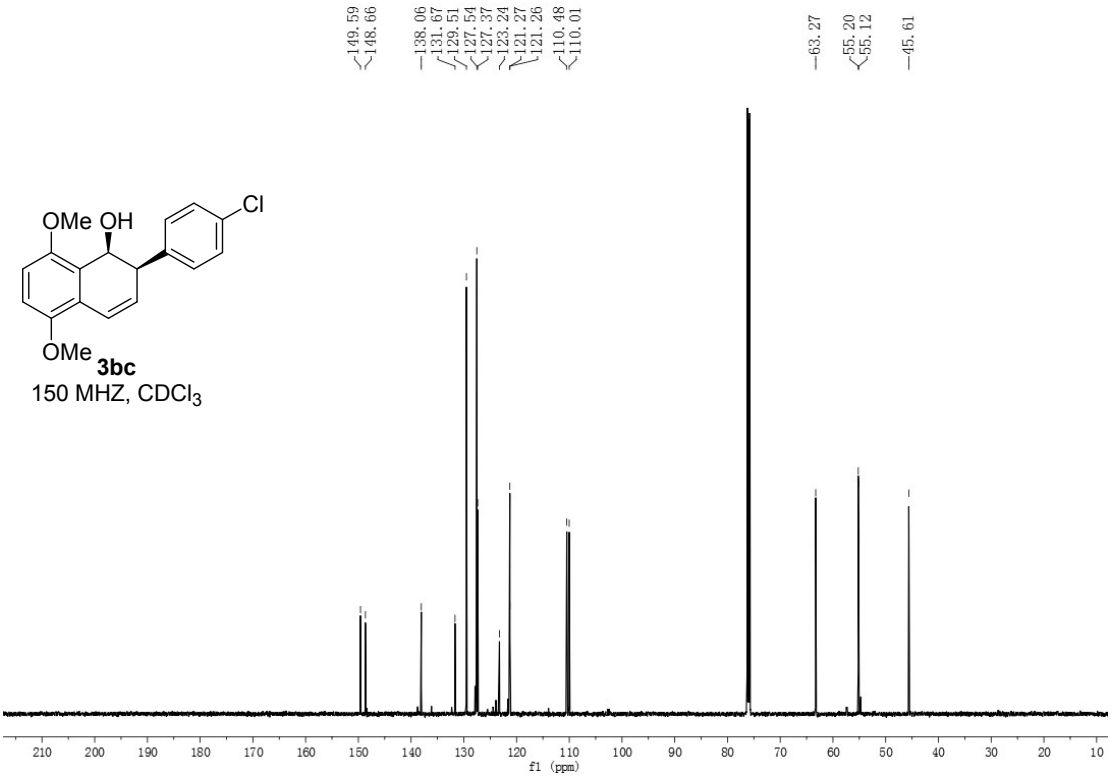
4bg
400 MHz, $CDCl_3$

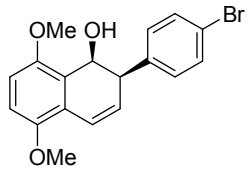




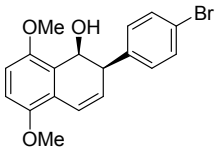
4bg
100 MHz, $CDCl_3$


OMe OH
Cl
OMe
3bc
600 MHZ, CDCl3
4.02
1.00
2.04
1.00
1.00
6.00
1.01
1.02
f1 (ppm)

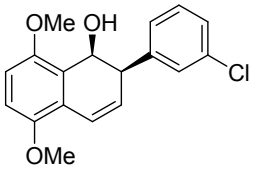

149.59
148.66
138.06
131.67
129.51
127.54
127.37
123.24
121.27
121.26
110.48
110.01
63.27
55.20
55.12
45.61
OMe OH
Cl
OMe
3bc
150 MHZ, CDCl3
f1 (ppm)



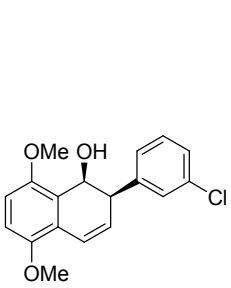
3bd
600 MHz, $CDCl_3$



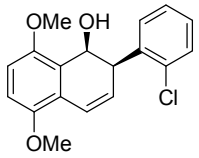
3bd
150 MHz, $CDCl_3$



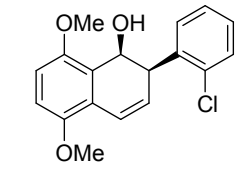
3be
600 MHz, $CDCl_3$



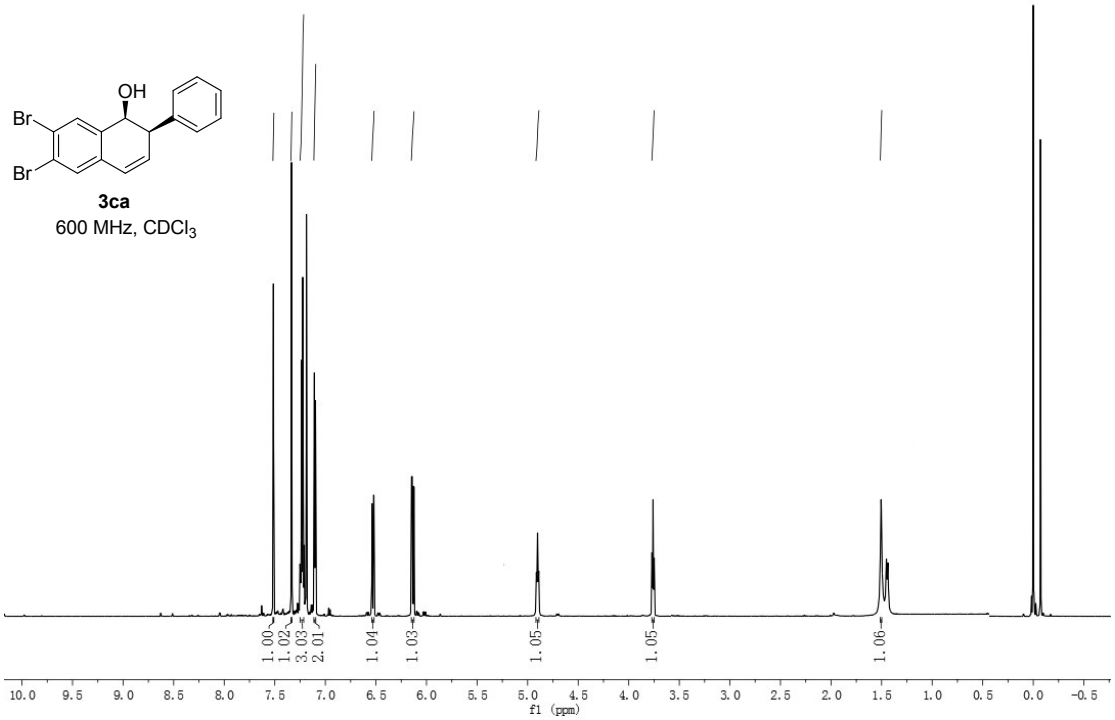
3be
150 MHz, $CDCl_3$



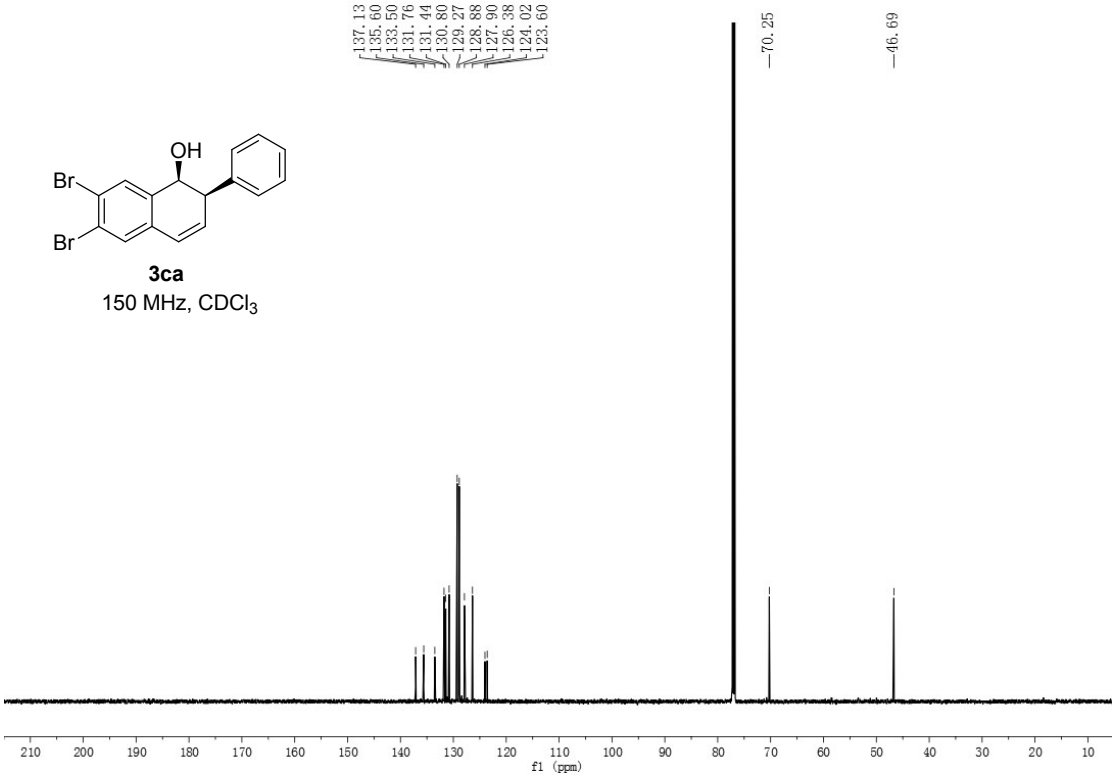
3bf
600 MHz, $CDCl_3$



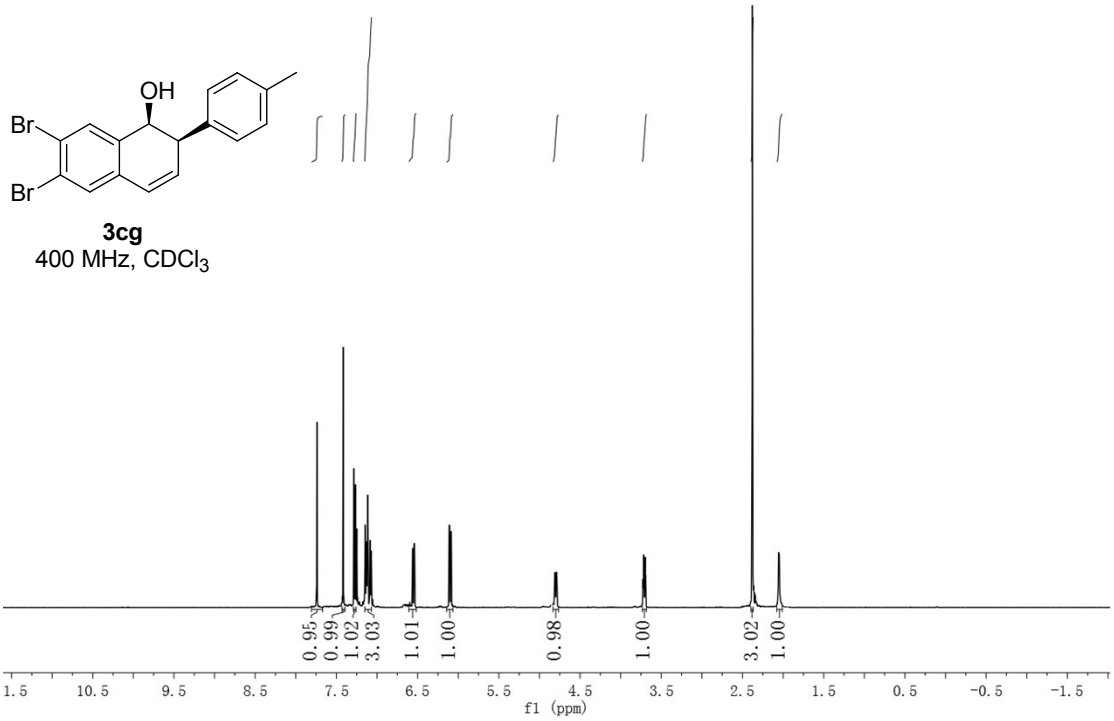
3bf
150 MHz, $CDCl_3$



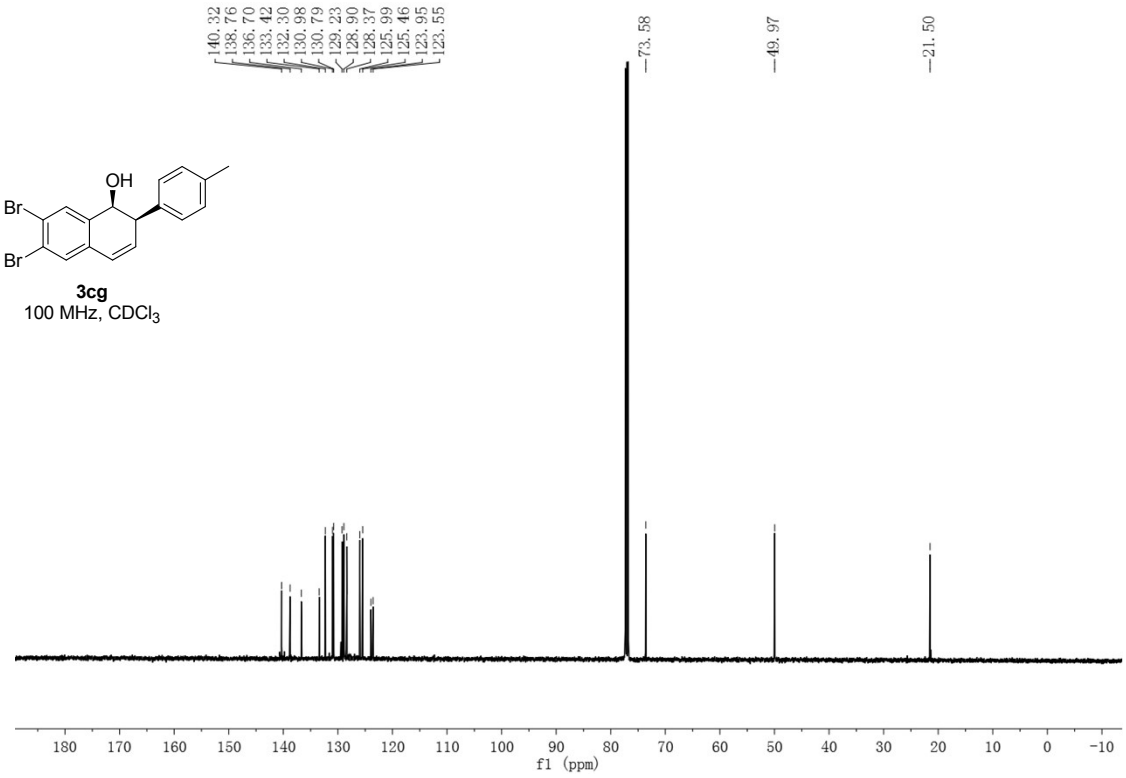
3ca
600 MHz, $CDCl_3$



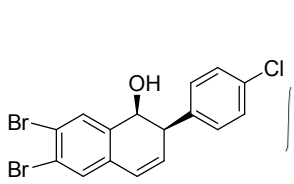
3ca
150 MHz, $CDCl_3$



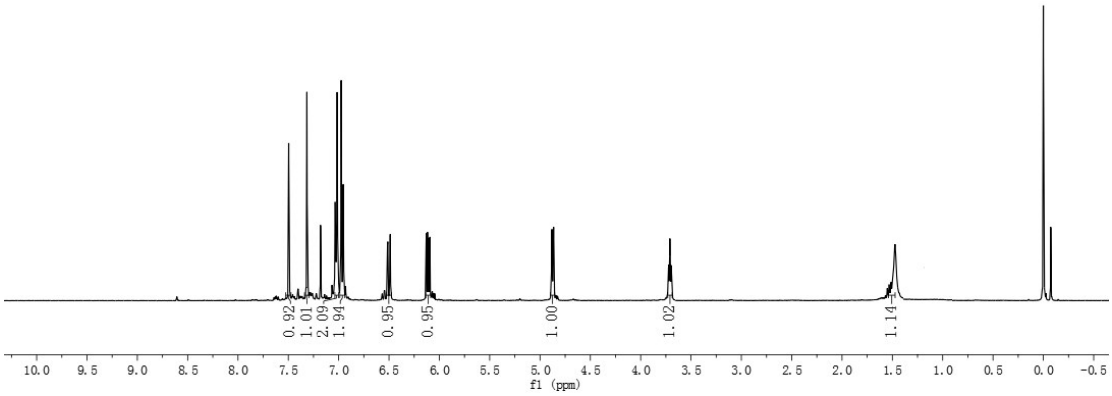
3cg
400 MHz, $CDCl_3$

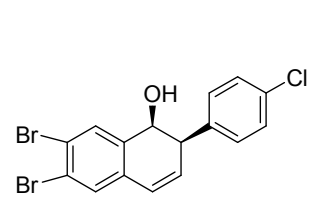


3cg
100 MHz, $CDCl_3$

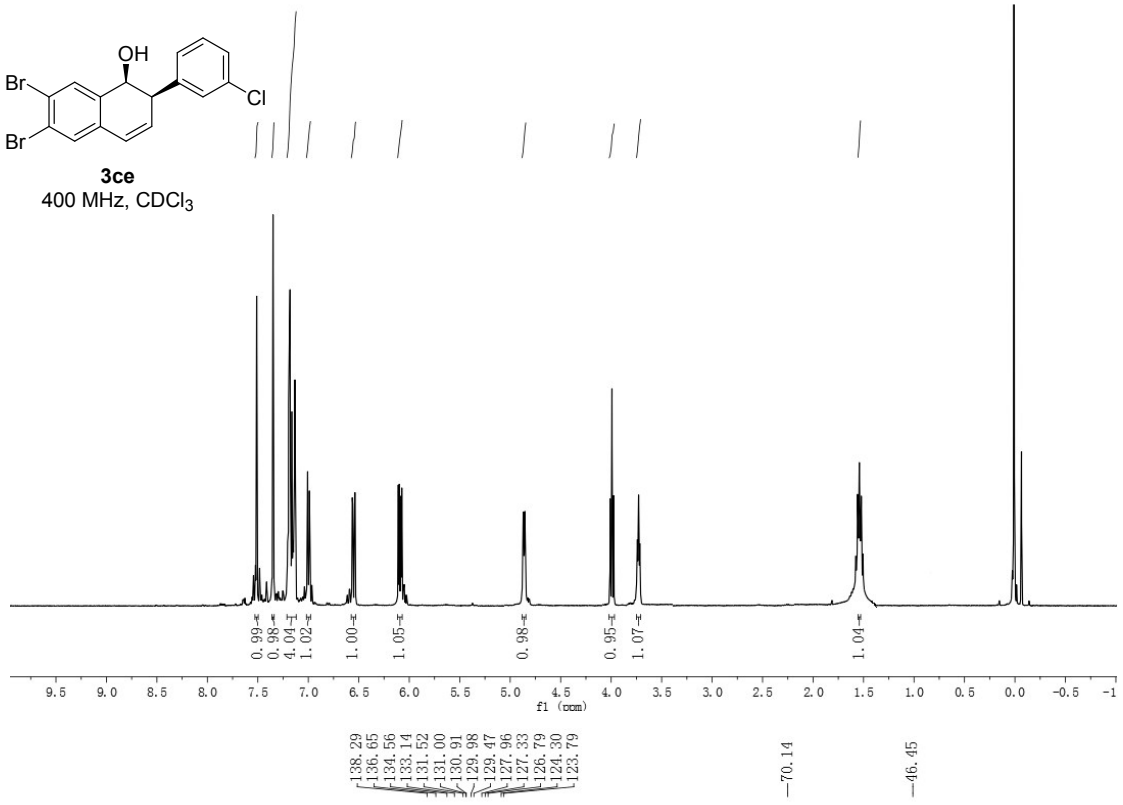


3cc
400 MHz, $CDCl_3$

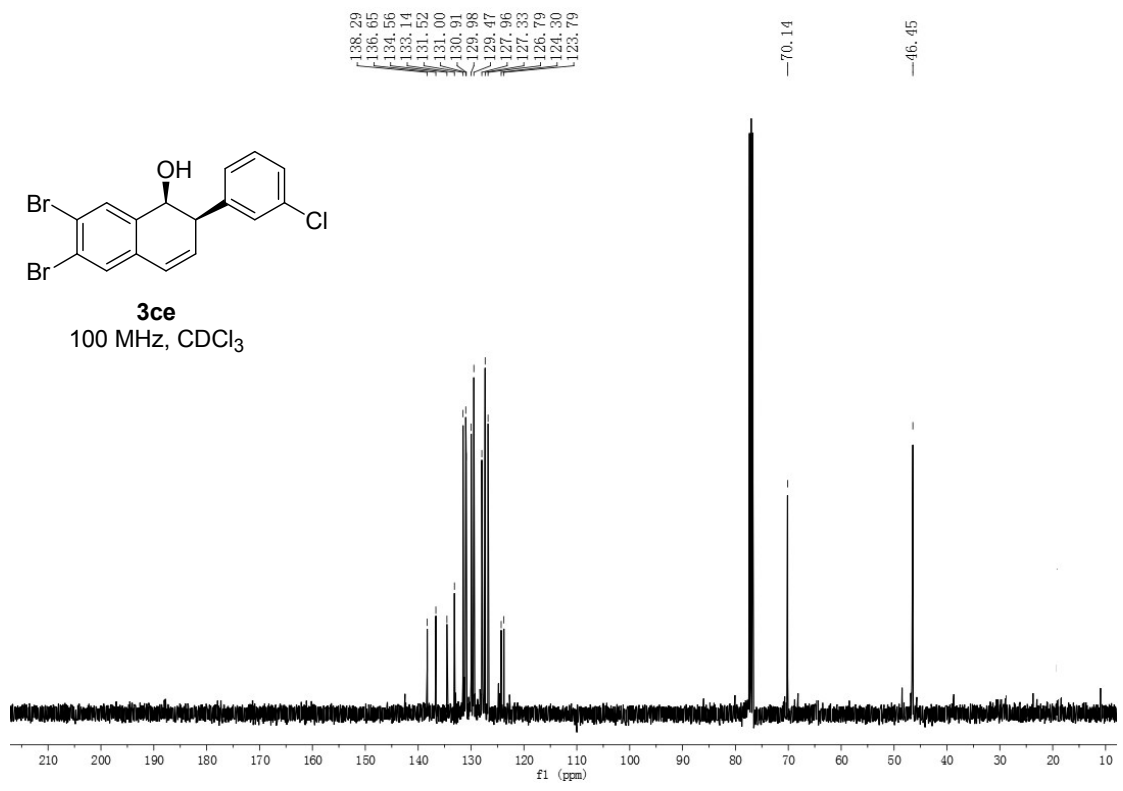




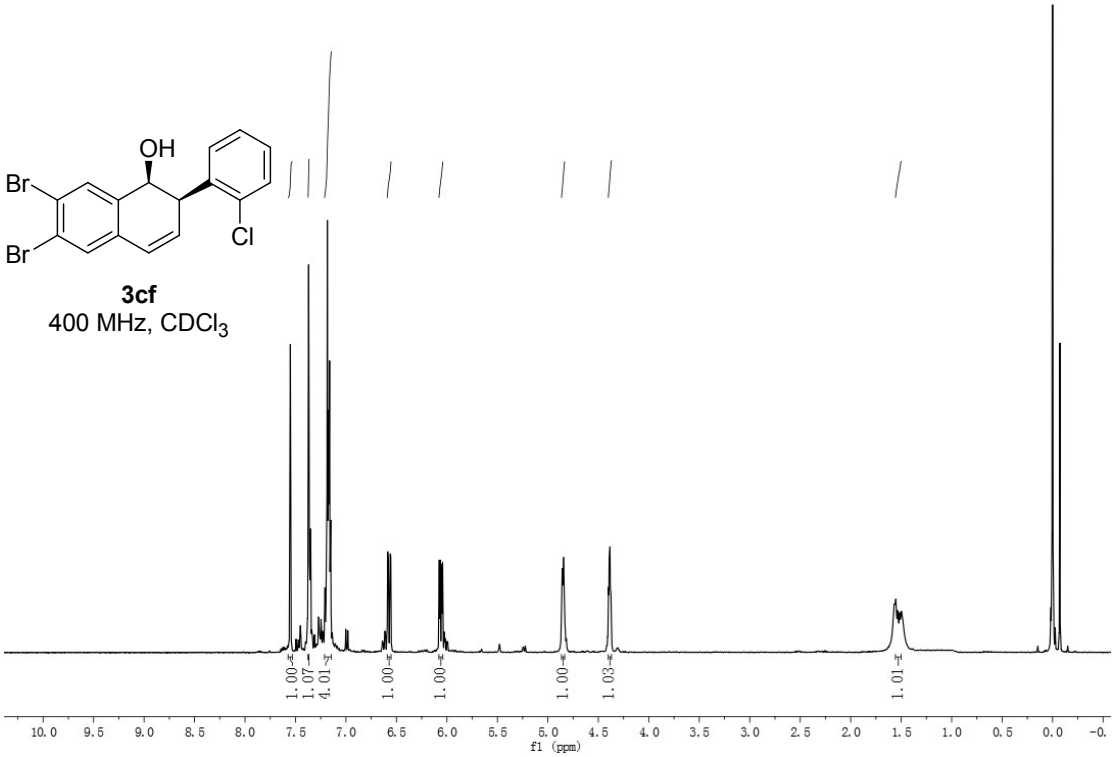
3cc
100 MHz, $CDCl_3$



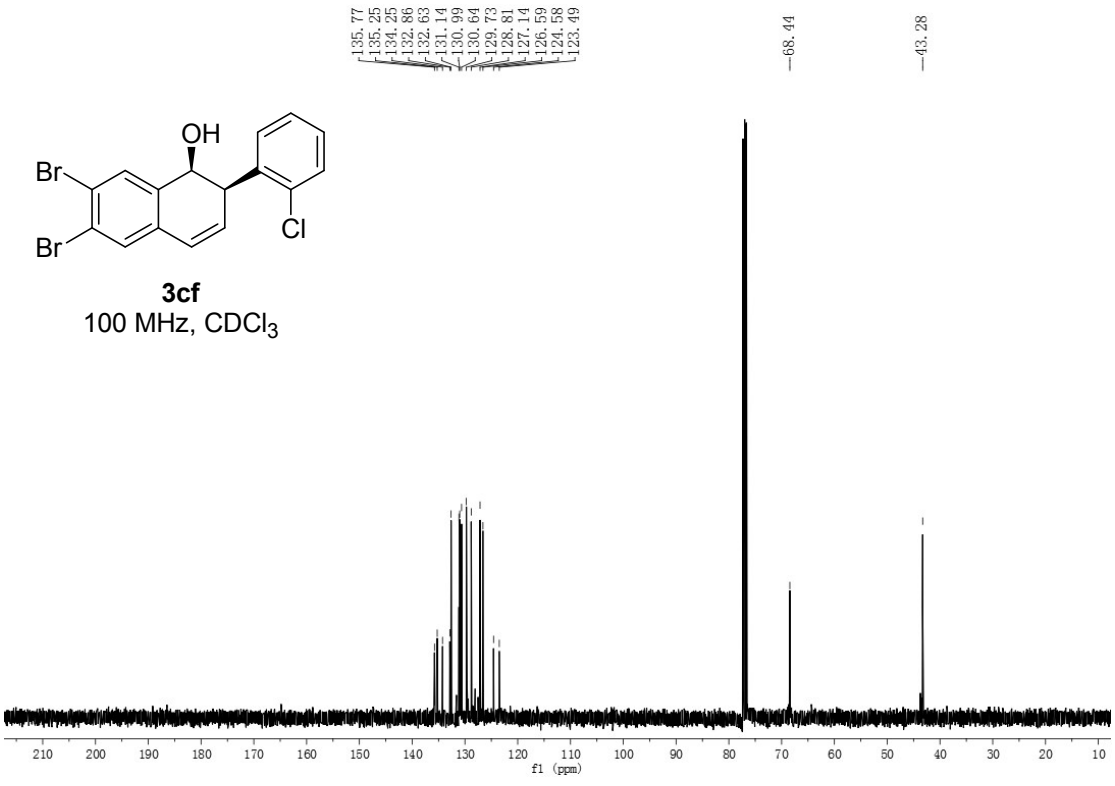
3ce
400 MHz, $CDCl_3$



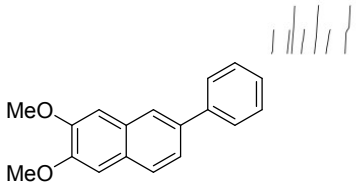
3ce
100 MHz, $CDCl_3$



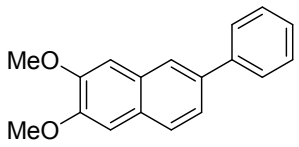
3cf
400 MHz, $CDCl_3$



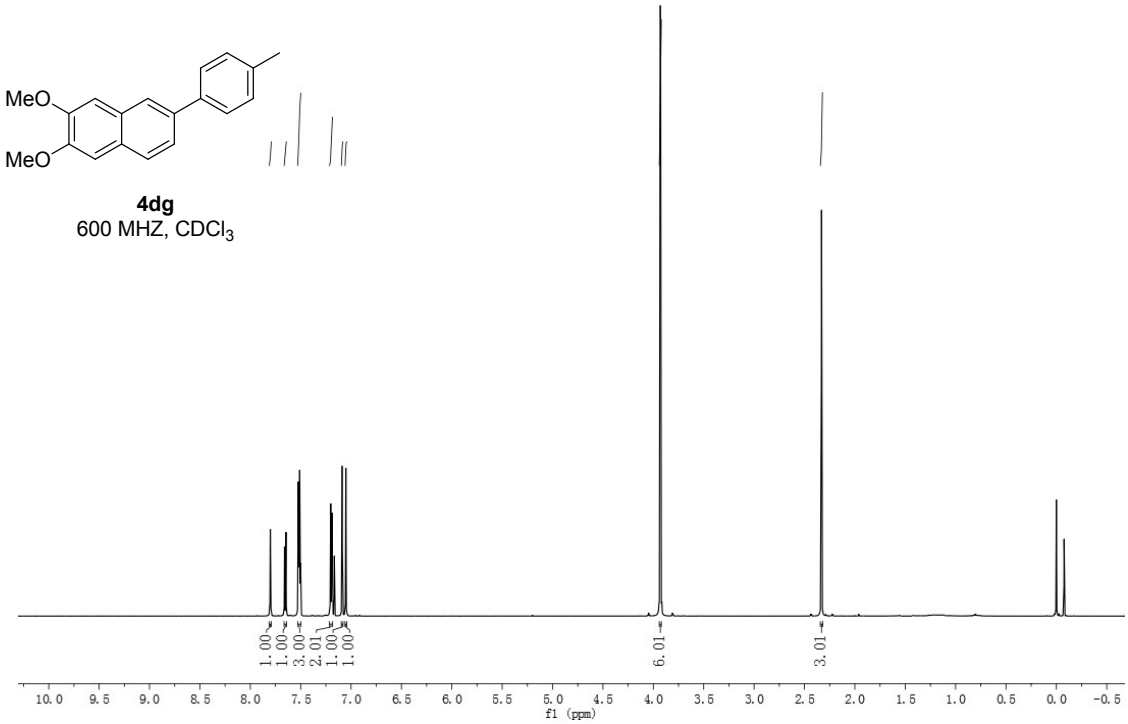
3cf
100 MHz, $CDCl_3$



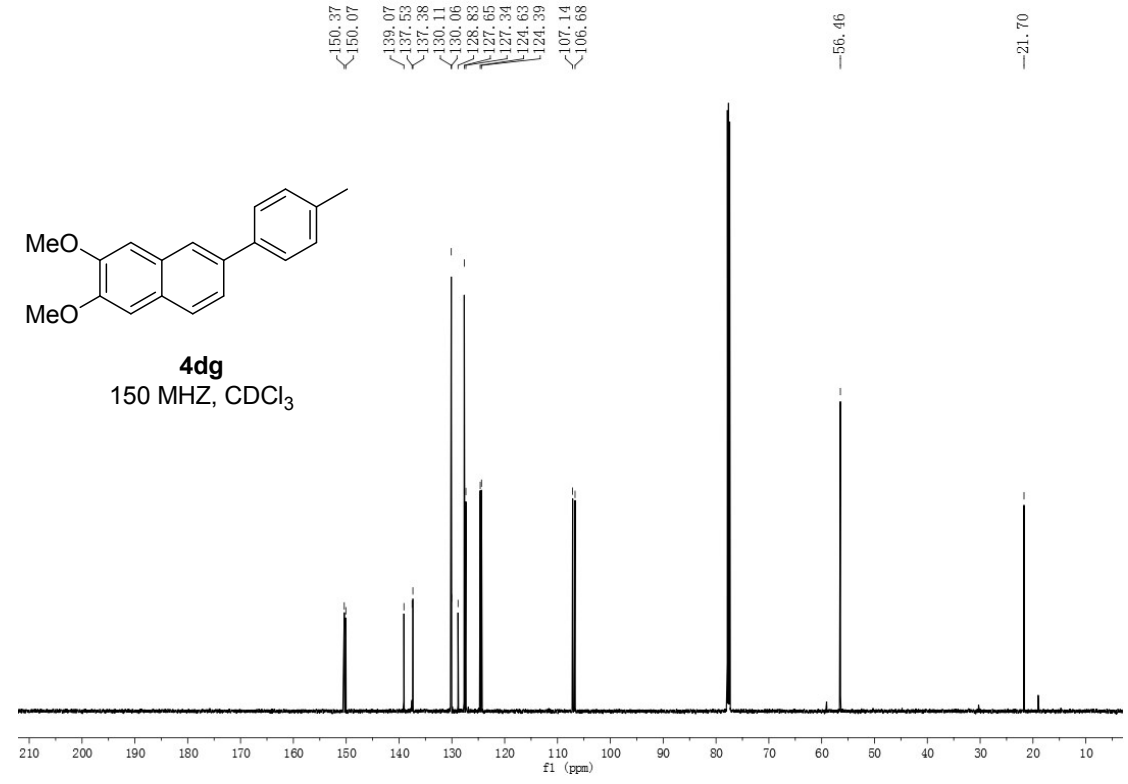
4da
500MHZ, $CDCl_3$



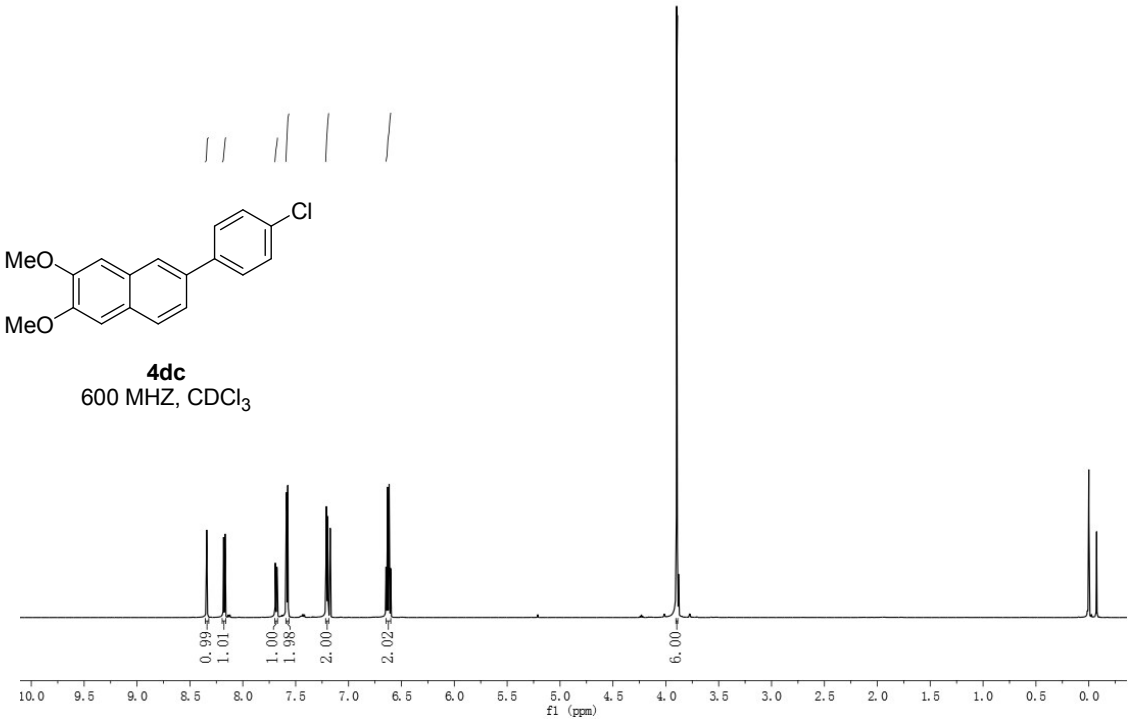
4da
125MHZ, $CDCl_3$



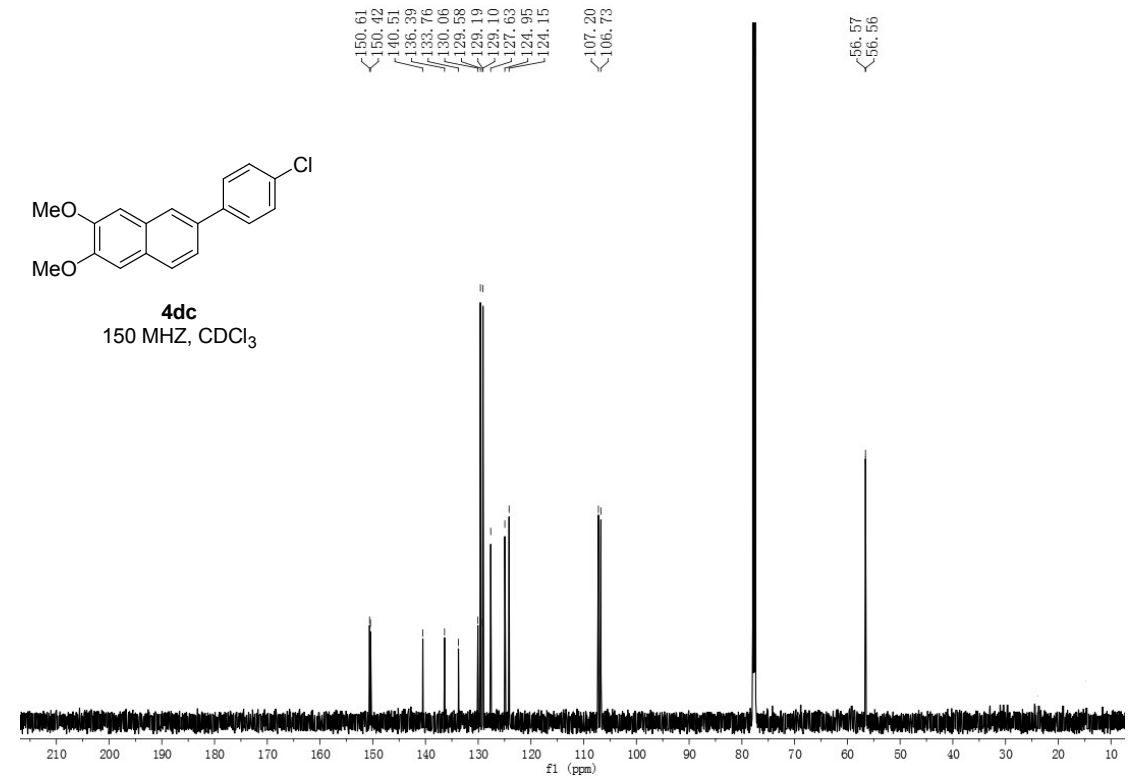
4dg
600 MHZ, $CDCl_3$



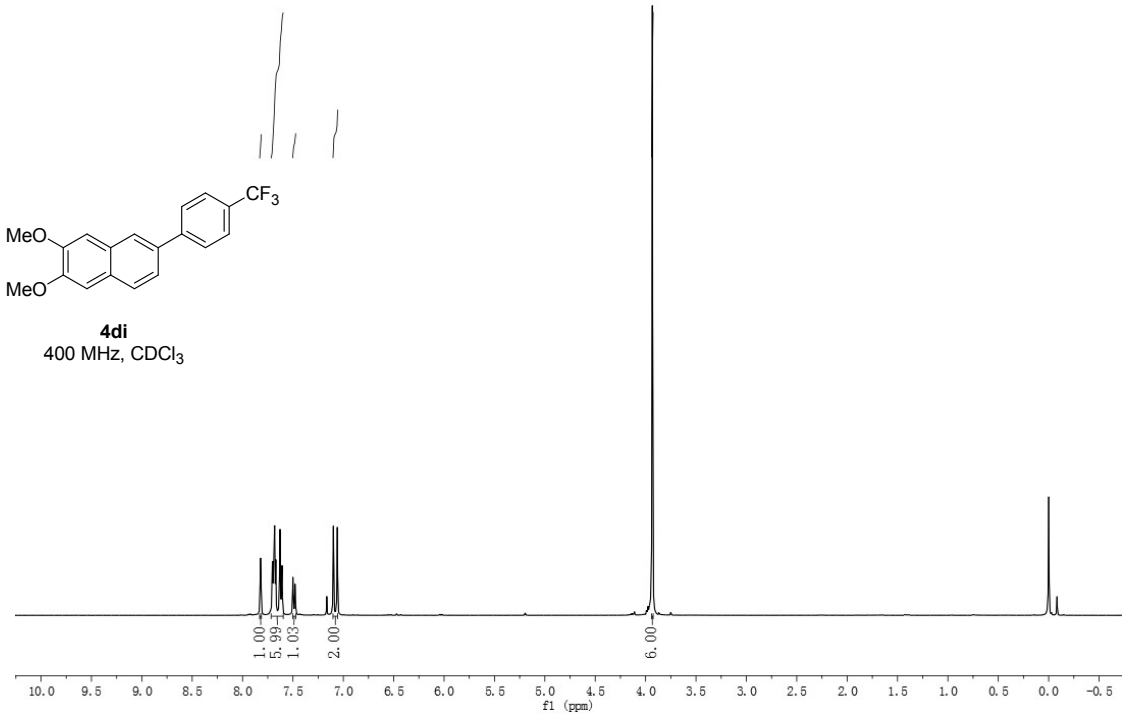
4dg
150 MHZ, $CDCl_3$



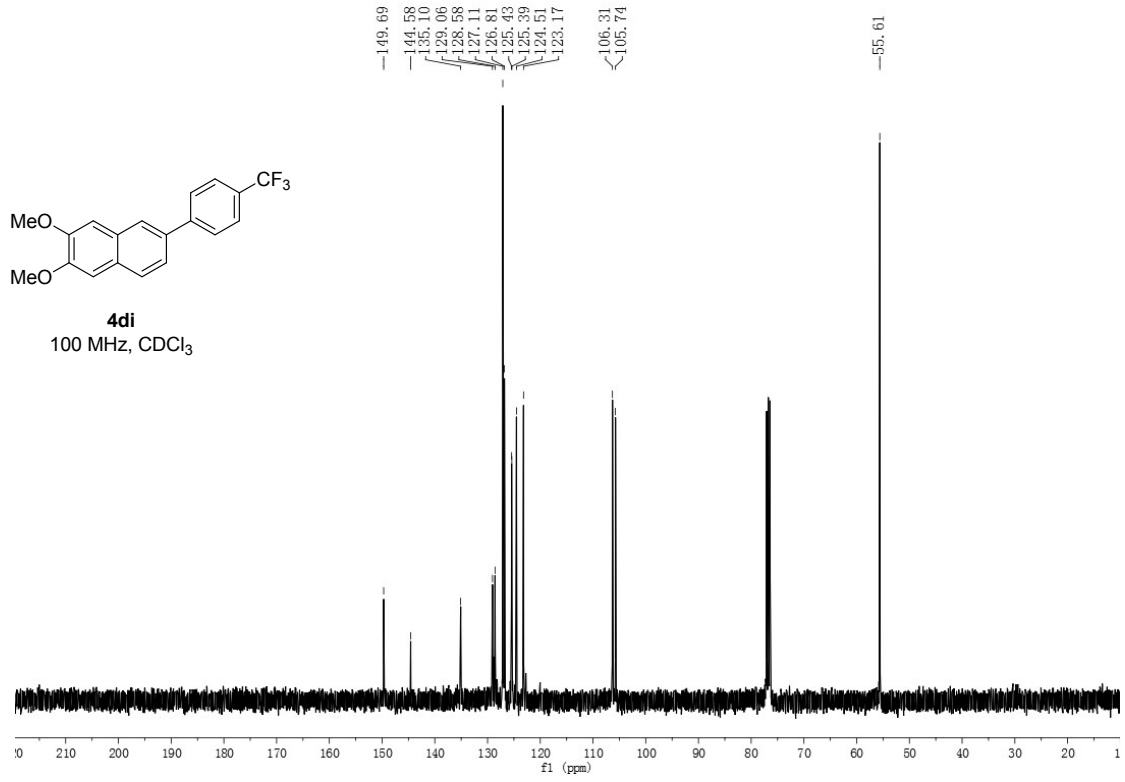
4dc
600 MHZ, $CDCl_3$



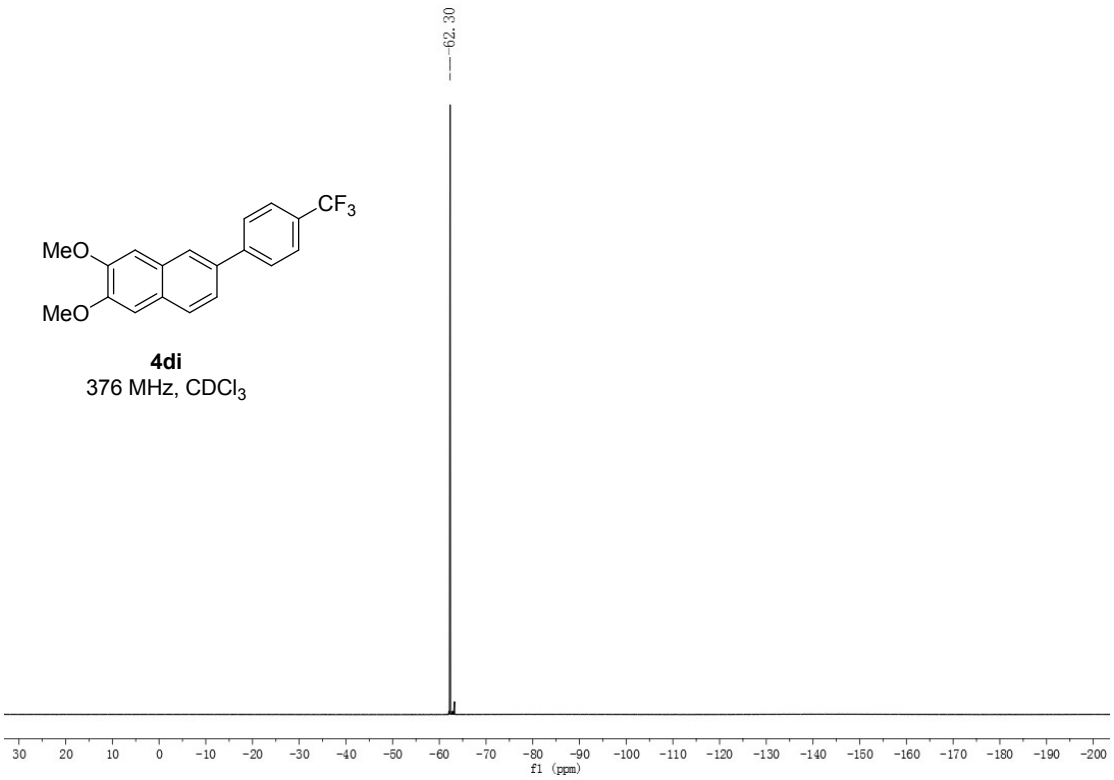
4dc
150 MHZ, $CDCl_3$



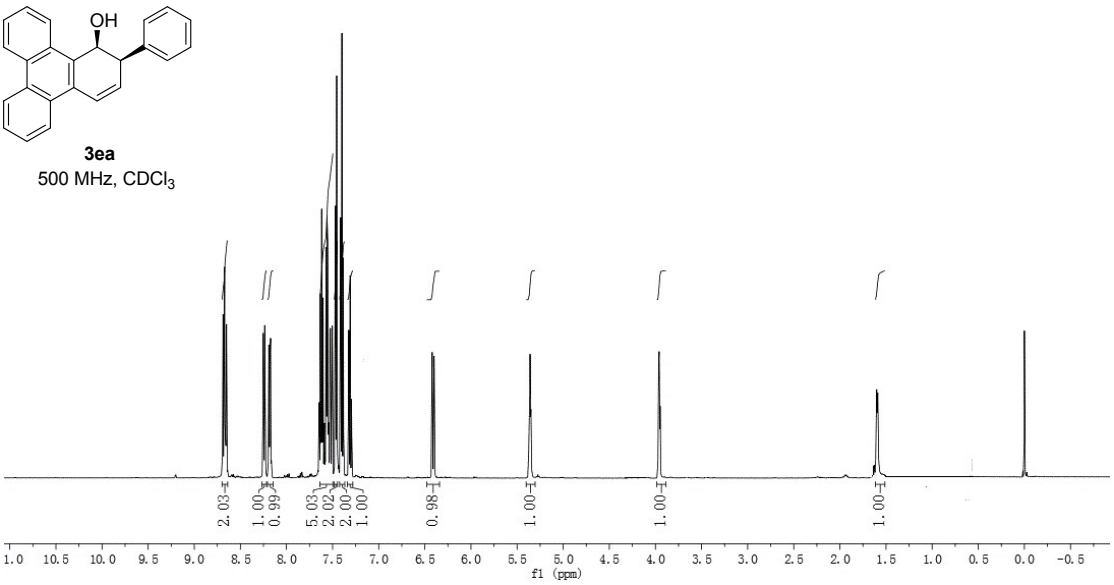
4di
400 MHz, $CDCl_3$



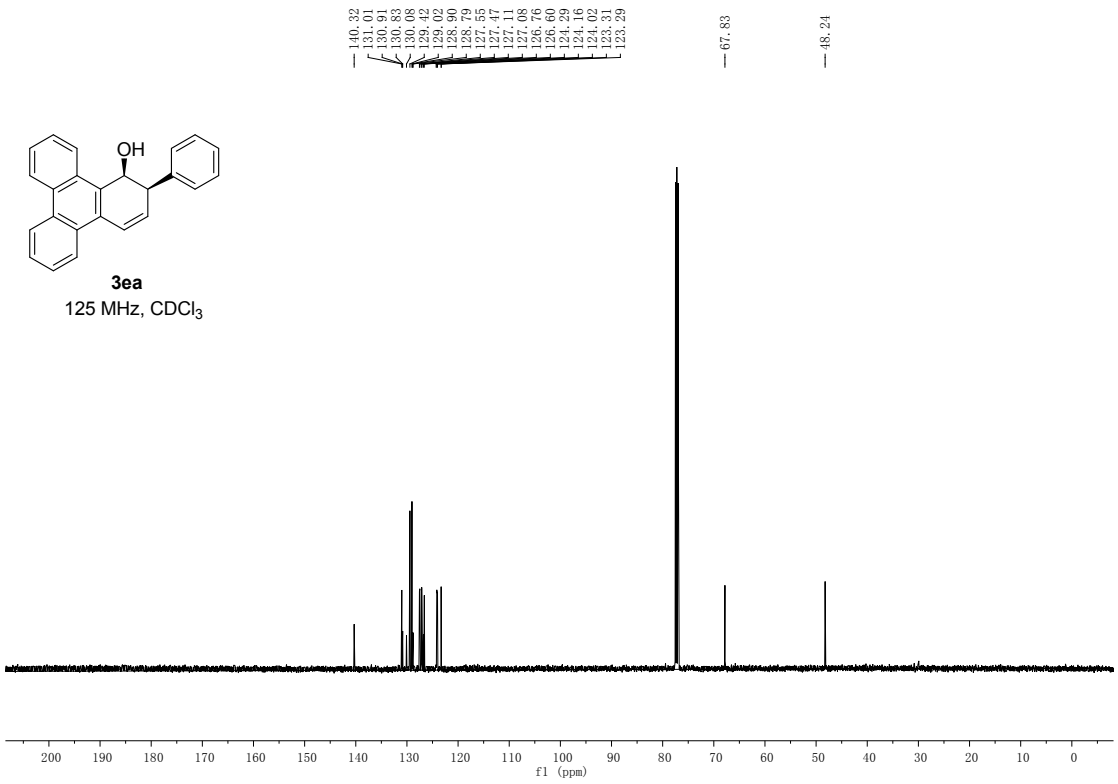
4di
100 MHz, $CDCl_3$



4di
376 MHz, $CDCl_3$

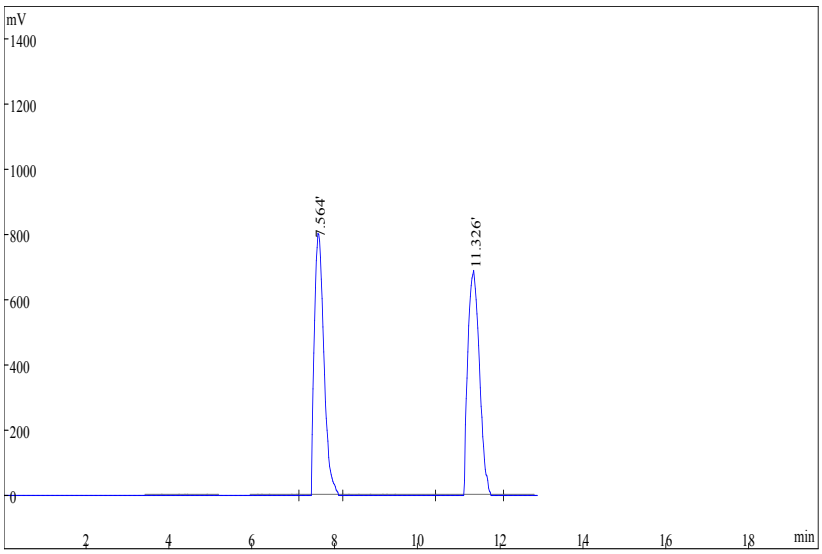


3ea
500 MHz, $CDCl_3$


140.32
131.01
130.91
130.83
130.08
129.42
129.02
128.90
128.79
127.55
127.47
127.11
127.08
126.76
126.60
124.29
124.16
124.02
123.31
123.29
67.83
48.24
OH
3ea
125 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)

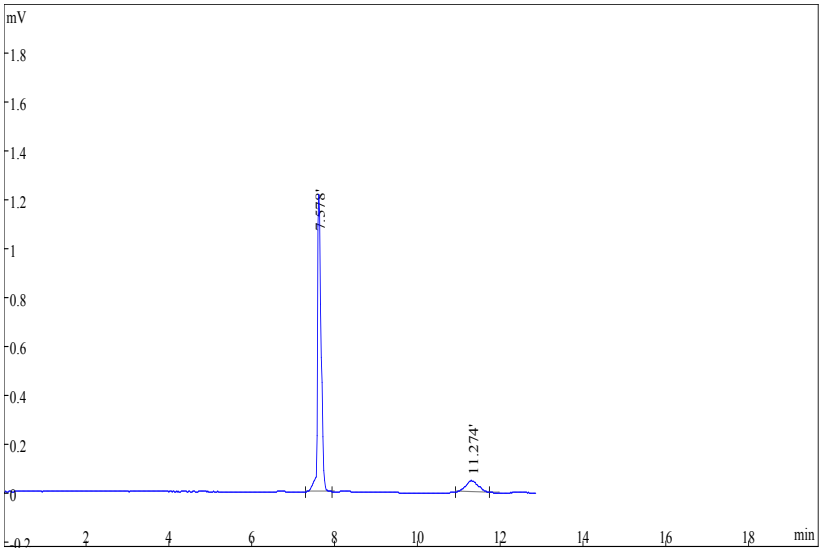
5. Copy of HPLC of 3aa

HPLC trace for racemic-**3aa**



Peak No.	Time (min)	Area (mV*s)	Area (%)
1	7.564	12964386	49.15
2	11.326	13410796	50.85

HPLC trace for enantioenriched-**3aa (*ee* = 75%)**



Peak No.	Time (min)	Area (mV*s)	Area (%)
1	7.578	7443	87.2
2	11.274	1092	12.8

6. References

1 L. Liu, Y. Chi, K. Jen, *J. Org. Chem*., 1980, **45***,* 406.
2 (a) W. M. Best, P. A. Collins, R. K. McCulloch, D. Wege, *Aust. J. Chem.*, 1982, **35**, 843; (b) H. Hart, C.-Y. Lai, G. C. Nwokogu, S. Shamouilian, *Tetrahedron,* 1987, **43**, 5203; (c) M. Lautens, K. Fagnou, D.-Q. Yang, *J. Am. Chem. Soc.,* 2003, **125**, 14884; (d) K. Villeneuve, W. Tam, *Organometallics,* 2007, **26**, 6082.