Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Iridium-Catalyzed Asymmetric Ring-Opening of Azabicyclic Alkenes with Alcohols

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Supporting Information

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1. General

All flasks were flame-dried under a stream of nitrogen and cooled before use. Solvents and solutions were transferred with syringes and cannulae using standard inert atmosphere techniques. NMR spectra were recorded at 400 MHz using a Varian INOVA NMR spectrometer with $CDCl_3$ as reference standard (δ 7.27 ppm) for ^1H NMR and (δ 77.23 ppm) for ^{13}C NMR. Spectral features are tabulated in the following order: Chemical shift (δ, ppm); number of protons; multiplicity (s-singlet, d-doublet, t-triplet, m-complex multiplet br-broad); coupling constants (*J*, Hz). IR spectra were obtained using a Nicolet DX FT-IR spectrometer as a KBr pellet or using a Perkin-Elmer Spectrum 1000 FT-IR spectrometer as a neat film on a NaCl plate. MS spectra were recorded on a Bruker esquire 6000 mass spectrometer (ESI). Optical rotations were measured on a Perkin-Elmer Model 243 Polarimeter using the sodium D line with spectra-grade $CHCl_3$ in a 1 dm cell. Melting points were taken on an XT_4 binocular micromelting point apparatus. HPLC analysis was performed on an Agilent 1100 Series HPLC with a Chiralcel AD column. Elemental analysis was conducted on a Thermo. Flash EA. TM. 1112. Crystal structure determination was carried out on a Bruker SMART-1000 X-ray diffraction apparatus.

Materials: DME was distilled from sodium benzophenone ketyl and stored. The THP, dioxane, toluene, and THF were distilled from sodium benzophenone ketyl immediately prior to use. CH_3CN was distilled from calcium hydride. DMF was dried over $MgSO_4$ and stored over activated molecular sieves. The *N*-protected azabenzonorbornadienes **1a**[1], **1b**[1], **1c**[2], **1d**[2] and $[Ir(COD)Cl]_2$ were prepared according to the reported procedure, respectively.[3]

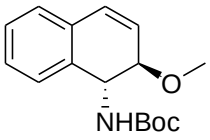
1. Lautens, M.; Fagnou, K.; Zunic, V. *Org. Lett.* **2002**, *4*, 3465-3468

2. Zunic, Y.-H.; Cho, V.; Senboku, H.; Olsen, M.; Lautens, M. *J. Am. Chem. Soc.* **2006**, *128*, 6837-6846.

3. Van der Ent, A.; Onderdelinden, A. L. *Inorg. Synth.* **1973**, *14*, 92-95.

2. Experimental procedures and characterization data

General procedure (I) for the asymmetric ring-opening of azabicyclic alkenes with various alcohols: A 5.0 mL round-bottomed flask fitted with a reflux condenser was flame-dried under a stream of nitrogen and cooled to room temperature. $[Ir(COD)Cl]_2$ (3.5 mg, 2.5 mol %) and (*S*)-BINAP (6.5 mg, 5.0 mol %) were simultaneously added and followed by the addition of anhydrous tetrahydrofuran (2.0 mL). After the mixture was stirred for about 20 min, azabicyclic alkene **1b** (59.4 mg, 0.20 mmol) was added and the resulting mixture was heated to reflux. On the first sign of reflux, alcohol nucleophile (5 equiv to **1b**) was added. Then the oil bath temperature was continuously increased to 80 ^{o}C until the reaction was completed as judged by thin layer chromatography. The solvent was removed in *vacuo* and the crude mixture was purified by column chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 10, v/v) to give the target product.

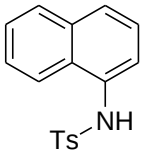


2a

(1*R*,2*R*)-[2-Methoxy-1,2-dihydro-naphthalen-1-yl]-carbamic acid *tert*-butyl ester (2a). Following the general procedure (**I**), **2a** was obtained as a white solid (25.0 mg, 50 %). R_f = 0.31 on silica gel (ethyl acetate : petroleum ether = 1 : 6, v/v). mp 69-70 °C. The ee was determined to be 63 % using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol = 95/5, 0.5 mL/min, λ = 254 nm); Retention times were 18.4 min (minor) and 20.7 min (major). $[\alpha]^{20}_{D}$ = -100.5 (*c* 1.00, $CHCl_3$). IR (film, cm^{-1}): 3448(w), 2973(w), 2928(w), 1703(s), 1489(m), 1366(m), 1274(w), 1160(w), 910(w), 750(w), 577(w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 2.4 Hz, 1H), 7.24-7.22 (m, 2H) , 7.10 (d, *J* = 2.4 Hz, 1H), 6.59 (dd, *J* = 9.6 Hz, 2.8Hz, 1H), 6.08 (dd, *J* = 9.6 Hz, 4.4 Hz, 1H), 4.98 (dd, *J* = 7.6 Hz, 4.8Hz, 1H), 4.62 (d, *J* = 8.0 Hz, 1H), 3.99 (t, *J* = 4.8 Hz, 1H), 3.46 (s, 3H), 1.44 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.3, 133.9, 131.9, 130.1, 129.0, 128.3, 127.1, 126.3, 125.8, 79.7, 76.6, 56.4, 51.1, 28.4. MS (ESI) calcd for $C_{16}H_{21}NO_3$ (M^+): 275.15; Found: 298.30 $(M+Na)^+$. Anal. Calcd. for $C_{16}H_{21}NO_3$: C, 69.79; H, 7.69; N, 5.09. Found: C, 69.78; H, 7.71; N, 5.07.

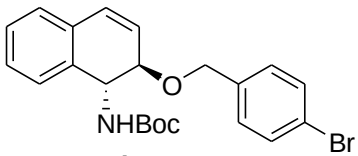
For the asymmetric ring-opening of *N*-Boc-azabenzonorbornadiene (**1a**), *N*-Ts-azabenzonorbornadiene (**1b**), *N*-Ns-azabenzonorbornadiene (**1c**), and *N*-Bs-azabenzonorbornadiene (**1d**) with alcohols and addition of **1a—1b** with thiols to afford the corresponding new compounds **2b, 3a—3l**, **4a—4c, 5a,** and **6a—6d,** respectively, are as the same as

above representative procedure.



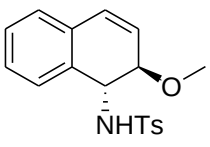
3fa

1-Naphthyltosylamine (3fa). 3fa was obtained as a light-brown solid and was purified by column chromatography (R_f = 0.22, ethyl acetate : petroleum ether = 1 : 4, v/v). mp 145-147 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.87-7.84 (m, 1H), 7.81-7.79 (m, 1H), 7.70 (dd, *J* = 2.4, 7.2 Hz, 1H), 7.65 (s, 1H), 7.63 (s, 1H), 7.46-7.40 (m, 2H), 7.38-7.33 (m, 2H), 7.16 (s, 1H), 7.13 (s, 1H), 7.11 (s, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 136.4, 134.3, 131.6, 129.7, 129.0, 128.5, 127.5, 127.3, 126.7, 126.4, 125.5, 122.8, 121.6, 21.6.



2b

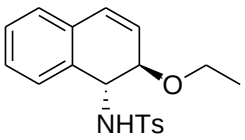
(1*R*,2*R*)-[2-(4-Bromobenzyloxy)-1,2-dihydro-naphthalen-1-yl]-carbamic acid *tert*-butyl ester (2b). Following the general procedure (**I**), **2b** was obtained as a white solid (27.5 mg, 32 %). R_f = 0.31 on silica gel (ethyl acetate : petroleum ether = 1 : 6, v/v). mp 96-98 °C. The ee was determined to be 75 % using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol = 95/5, 0.5 mL/min, λ = 254 nm); Retention times were 20.2 min (major) and 21.9 min (minor). $[\alpha]^{20}_D$ = -143.5 (*c* 1.00, $CHCl_3$). IR (film, cm^{-1}): 3339(w), 2962(w), 2926(w), 1714(s), 1488(m), 1366(w), 1248(w), 1170(s), 1081(w), 1012(w), 802(w), 747(w), 647(w). ^1H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 7.6 Hz, 2H), 7.38 (d, *J* = 5.6 Hz, 1H), 7.30-7.24 (m, 4H) , 7.15 (d, *J* = 6.4 Hz, 1H), 6.62 (d, *J* = 9.6 Hz, 1H), 6.05 (d, *J* = 9.6, 1H), 5.09 (t, *J* = 5.6 Hz, 1H), 4.70-4.65 (m, 3H), 4.20 (s, 1H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.4, 137.5, 133.8, 132.0, 131.4, 130.2, 129.6, 128.4, 128.3, 127.1, 126.3, 125.9, 121.5, 79.8, 75.3, 69.7, 51.7, 28.4. MS (ESI) calcd for $C_{22}H_{24}BrNO_3$ (M^+): 429.09; Found: 452.37 $(M+Na)^+$. Anal. Calcd. for $C_{22}H_{24}BrNO_3$: C, 61.40; H, 5.62; N, 3.25. Found: C, 61.36; H, 5.60; N, 3.25.



3a

(1*R*,2*R*)-*N*-(2-Methoxy-1,2-dihydronaphthalen-1-yl)-4-methylbenzenesulfonamide (3a).

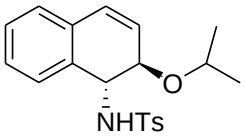
Following the general procedure (**I**), **3a** was obtained as a white solid (73.0 mg, 85 %). R_f = 0.25 on silica gel (ethyl acetate : petroleum ether = 1 : 6, v/v). mp 71-72 °C. The ee was determined to be 4 % using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol = 90/10, 0.5 mL/min, λ = 254 nm); Retention times were 52.9 min (major) and 58.0 min (minor). $[\alpha]^{20}_D$ = 10.6 (*c* 1.00, $CHCl_3$). IR (film, cm^{-1}): 3273(w), 3038(w), 2926(w), 2853(w), 1721(s), 1598(m), 1493(m), 1454(w), 1329(m), 1159(s), 1093(m), 970(m), 916(w), 813(m), 666(m), 571(m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8 Hz, 2H), 7.30 (d, *J* = 8.8 Hz, 2H), 7.22-7.18 (m, 1H), 7.07-7.04 (m, 2H), 6.60 (d, *J* = 8 Hz, 1H), 6.57 (d, *J* = 9.6 Hz, 1H), 6.03 (dd, *J* = 9.6 Hz, 4.8 Hz, 1H), 4.68 (d, *J* = 7.6 Hz, 1H), 4.49 (dd, *J* = 4.8 Hz, 7.6 Hz, 1H), 3.96 (t, *J* = 4.4 Hz, 1H), 3.25 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5, 137.7, 132.5, 131.7, 130.3, 129.6, 128.8, 128.3, 127.3, 125.0, 76.7, 56.5, 54.2, 21.6. MS (ESI) calcd for $C_{18}H_{19}NO_3S$ (M^+): 329.11; Found: 347.10 $(M+Na)^+$. Anal. Calcd. for $C_{18}H_{19}NO_3S$: C, 65.63; H, 5.81; N, 4.25; S, 9.73. Found: C, 65.66; H, 5.78; N, 4.23; S, 9.69.



3b

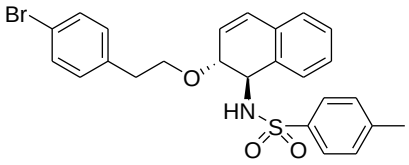
(1*R*,2*R*)-*N*-(2-Ethoxy-1,2-dihydronaphthalen-1-yl)-4-methylbenzenesulfonamide (3b).

Following the general procedure (**I**), **3b** was obtained as a white solid (61.7 mg, 90 %). R_f = 0.20 on silica gel (ethyl acetate : petroleum ether = 1 : 5, v/v). mp 146-148 °C. The ee was determined to be 1 % using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol = 90/10, 0.5 mL/min, λ = 254 nm); Retention times were 27.9 min (major) and 39.4 min (minor). $[\alpha]^{20}_D$ = -10.2 (*c* 1.00, $CHCl_3$). IR (film, cm^{-1}): 3273(w), 3040(w), 2967(w), 2924(m), 2853(w),1921(w), 1598(m), 1454(m), 1329(w), 1159(s), 1093(s), 968(m), 923(w), 813(m), 780(m), 737(m), 666(m), 547(m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.8 Hz, 2H), 7.21-7.15 (m, 1H), 7.08-7.03 (m, 2H), 6.85 (d, *J* = 7.6 Hz, 1H), 6.54 (d, *J* = 9.6 Hz, 1H), 6.00 (dd, *J* = 9.6 Hz, 4.8 Hz, 1H), 4.74 (d, *J* = 7.6 Hz, 1H), 4.49 (dd, *J* = 4.8 Hz, 7.6 Hz, 1H), 4.04 (t, *J* = 4.8 Hz, 1H), 3.49 (q, *J* = 7.2 Hz, 14 Hz, 2H), 2.44 (s, 3H) , 1.03 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5, 137.8, 132.7, 131.8, 129.8, 129.6, 128.7, 128.3, 128.2, 127.3, 127.2,125.8, 75.3, 64.5, 54.7, 21.6, 15.4. MS (ESI) calcd for $C_{19}H_{21}NO_3S$ (M^+): 343.12; Found: 366.40 $(M+Na)^+$. Anal. Calcd. for $C_{19}H_{21}NO_3S$: C, 66.45; H, 6.16; N, 4.08; S, 9.34. Found: C, 66.49; H, 6.14; N, 4.05; S, 9.30.



3c

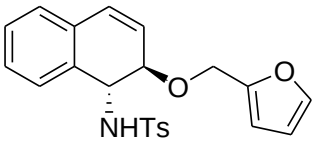
(1*R*,2*R*)-*N*-(2-Isopropoxy-1,2-dihydronaphthalen-1-yl)-4-methylbenzenesulfonamide (3c). Following the general procedure (**I**), **3c** was obtained as a white solid (53.6 mg, 75 %). R_f = 0.16 on silica gel (ethyl acetate : petroleum ether = 1 : 5, v/v). mp 121-123 °C. The ee was determined to be 12 % using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol = 90/10, 0.5 mL/min, λ = 254 nm); Retention times were 22.6min (minor) and 28.3 min (major). $[\alpha]^{20}_D$ = -23.5 (*c* 1.00, $CHCl_3$). IR (film, cm^{-1}): 3255(w), 3040(w), 2957(w), 2923(m), 2852(w),1727(w), 1598(w), 1495(m), 1462(w), 1288(w), 1185(w), 1161(s), 968(m), 776(m), 666(m), 568(w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8 Hz, 2H) , 7.20-7.16 (m, 1H), 7.05-7.02 (m, 2H), 6.82 (d, *J* = 7.6 Hz, 1H), 6.54 (d, *J* = 9.6 Hz, 1H), 5.96 (dd, *J* = 9.6 Hz, 4.8 Hz, 1H), 4.68 (d, *J* = 7.6 Hz, 1H), 4.43 (dd, *J* = 4.8 Hz, 7.6 Hz, 1H), 4.09 (t, *J* = 4.8 Hz, 1H), 3.75-3.72 (m, 1H), 2.44 (s, 3H) , 1.02 (dd, *J* = 2.4 Hz, 8.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5, 137.8, 132.7, 131.9, 129.7, 129.5, 128.6, 128.4, 128.2, 127.3, 127.2,126.4, 72.8, 70.3, 55.3, 22.5, 21.6. MS (ESI) calcd for $C_{20}H_{23}NO_3S$ (M^+): 357.14; Found: 380.46 $(M+Na)^+$. Anal. Calcd. for $C_{20}H_{23}NO_3S$: C, 67.20; H, 6.49; N, 3.92; S, 8.97. Found: C, 67.18; H, 6.50; N, 3.93; S, 8.95.



3d

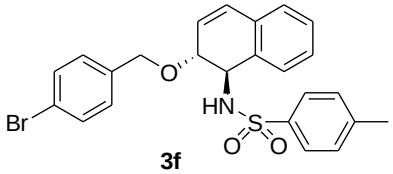
(1*R*,2*R*)-*N*-(2-(4-Bromophenethoxy)-1,2-dihydronaphthalen-1-yl)-4-methylbenzenesulfonamide (3d). Following the general procedure (**I**), **3d** was obtained as a white solid (74.5 mg, 75 %). R_f = 0.27 on silica gel (ethyl acetate : petroleum ether = 1 : 4, v/v). mp 163-164 °C. The ee was determined to be 30 % using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol = 85/15, 0.5 mL/min, λ = 254 nm); Retention times were 24.4 min (minor) and 36.3 min (major). $[\alpha]^{20}_D$ = -62.7 (*c* 1.00, $CHCl_3$). IR (film, cm^{-1}): 3273(w), 3033(w), 2957(s), 2279(w), 1727(m), 1598(w), 1488(m), 1455(w), 1331(m), 1160(s), 1093(s), 962(w), 813(m), 666(m), 547(m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 4H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 7.2 Hz, 2H), 6.97 (d, *J* = 8.4 Hz,

2H), 6.61 (d, *J* = 7.6 Hz, 1H), 6.56 (d, *J* = 9.6 Hz, 1H), 5.96 (dd, *J* = 4.8 Hz, 9.6 Hz, 1H), 4.58 (d, *J* = 7.6 Hz, 1H), 4.31 (dd, *J* = 4.0 Hz, 7.6 Hz, 1H), 4.07 (t, *J* = 4.4 Hz, 1H), 3.73-3.61 (m, 2H), 2.66 (t, *J* = 7.2 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.6, 137.9, 137.6, 132.3, 131.7, 131.3, 130.7, 130.3, 129.7, 128.8, 128.5, 128.3, 172.3, 127.2, 125.1, 120.0, 75.3, 69.5, 54.2, 35.7, 21.6. MS (ESI) calcd for $C_{25}H_{24}BrNO_3S$ (M^+): 497.07; Found: 520.16 $(M+Na)^+$. Anal. Calcd. for $C_{25}H_{24}BrNO_3S$: C, 60.24; H, 4.85; N, 2.81; S, 6.43. Found: C, 60.21; H, 4.87; N, 2.82; S, 6.40.



3e

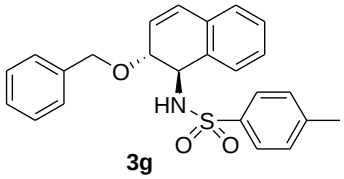
(1*R*,2*R*)-*N*-(2-(Furan-2-ylmethoxy)-1,2-dihydronaphthalen-1-yl)-4-methylbenzenesulfonamide (3e). Following the general procedure (**I**), **3e** was obtained as a white solid (40.5 mg, 51 %). R_f = 0.30 on silica gel (ethyl acetate : petroleum ether = 1 : 3, v/v). mp 123-124 °C. The ee was determined to be 94 % using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol = 85/15, 0.5 mL/min, λ = 254 nm); Retention times were 29.1 min (minor) and 33.3 min (major). $[\alpha]^{20}_D$ = -165 (*c* 1.00, $CHCl_3$). IR (film, cm^{-1}): 3269(w), 2926(w), 2854(w), 1715(m), 1598(w), 1503(w), 1454(m), 1331(m), 1159(s), 1069(m), 918(w), 815(m), 749(m), 665(m), 569(m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.37 (s, 1H), 7.30 (d, *J* = 8.0 Hz, 2H) , 7.18 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.2 Hz, 2H), 6.84 (d, *J* = 7.6 Hz, 1H), 6.56 (d, *J* = 9.6 Hz, 1H), 6.32 (s, 1H), 6.27 (s, 1H), 5.92 (dd, *J* = 4.8 Hz, 9.6 Hz, 1H), 4.51-4.46 (m, 2H), 4.43 (s, *J* = 8.0 Hz, 2H), 4.18 (s, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.3, 143.5, 142.9, 137.5, 132.5, 131.7, 130.2, 129.6 128.7, 128.4, 128.3, 127.4, 125.2, 110.3, 109.8, 74.4, 62.8, 54.7, 21.6. MS (ESI) calcd for $C_{22}H_{21}NO_4S$ (M^+): 395.12; Found: 518.51 $(M+Na)^+$. Anal. Calcd. for $C_{22}H_{21}NO_4S$: C, 66.82; H, 5.35; N, 3.54; S, 8.11. Found: C, 66.80; H, 5.34; N, 3.55; S, 8.08.



3f

(1*R*,2*R*)-*N*-(2-(4-Bromobenzyloxy)-1,2-dihydronaphthalen-1-yl)-4-methylbenzenesulfonamide (3f). Following the general procedure (**I**), **3f** was obtained as a white solid (53.5 mg, 55 %). R_f = 0.24 on silica gel (ethyl acetate : petroleum ether = 1 : 4, v/v). mp 132-134 °C. The ee was determined to be 92 % using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol = 85/15, 0.5 mL/min, λ = 254 nm); Retention times were 27.6 min (minor) and 38.6 min (major). $[\alpha]^{20}_D$ = -175 (*c* 1.00, $CHCl_3$).

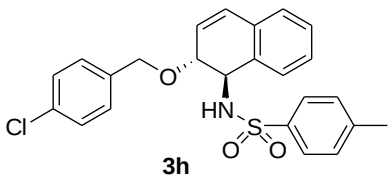
IR (film, cm^{-1}): 3275(w), 3034(w), 2925(w), 1721(m), 1597(w), 1487(m), 1454(w), 1330(m), 1159(s), 1093(s), 1070(s), 1011(m), 912(w), 811(m), 666(m), 570(m), 547(m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H) , 7.28 (d, *J* = 8.4 Hz, 2H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 3H), 7.09-7.06 (m, 1H), 6.73 (d, *J* = 7.6 Hz, 1H), 6.63 (d, *J* = 9.6 Hz, 1H), 6.00 (dd, *J* = 4.8 Hz, 9.6 Hz, 1H), 4.56-4.51 (m, 3H), 4.46 (t, *J* = 8.0 Hz, 1H), 4.17 (t, *J* = 4.8 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.6, 137.6, 137.2, 132.3, 131.7, 131.4, 130.5, 129.7 129.4, 129.0, 128.9, 128.5, 172.3, 127.2, 124.9, 121.6, 74.7, 70.1, 54.4, 21.6. MS (ESI) calcd for $C_{24}H_{22}BrNO_3S$ (M^+): 483.05; Found: 508.43 $(M+Na)^+$. Anal. Calcd. for $C_{24}H_{22}BrNO_3S$: C, 59.51; H, 4.58; N, 2.89; S, 6.62. Found: C, 59.53; H, 4.59; N, 2.89; S, 6.60.



3g

(1*R*,2*R*)-*N*-(2-Benzyloxy-1,2-dihydronaphthalen-1-yl)-4-methylbenzenesulfonamide (3g).

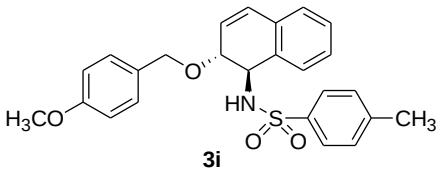
Following the general procedure (**I**), **3g** was obtained as a white solid (36.5 mg, 45 %). R_f = 0.25 on silica gel (ethyl acetate : petroleum ether = 1 : 4, v/v). mp 113-114 °C. The ee was determined to be 78 % using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol = 85/15, 0.5 mL/min, λ = 254 nm); Retention times were 26.4 min (minor) and 29.2 min (major). $[\alpha]^{20}_D$ = -135 (*c* 1.00, $CHCl_3$). IR (film, cm^{-1}): 3280(w), 3061(w), 2920(w), 1723(m), 1598(w), 1495(m), 1454(w), 1330(s), 1160(s), 1093(s), 966(w), 918(w), 813(m), 750(w), 698(w), 666(m), 569(m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.33-1.21 (m, 8H), 7.10 (d, *J* = 7.6 Hz, 2H), 6.79 (d, *J* = 7.2 Hz, 1H), 6.62 (d, *J* = 9.6 Hz, 1H), 6.00 (dd, *J* = 4.8 Hz, 9.6 Hz, 1H), 4.59-4.55 (m, 3H), 4.50 (t, *J* = 7.6 Hz, 1H), 4.18 (t, *J* = 4.8 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5, 138.1, 137.6, 132.5, 131.8, 130.3, 129.6, 128.8, 128.5, 128.4, 127.8, 127.7, 127.3, 127.2, 125.3, 74.5, 70.9, 54.5, 21.6. MS (ESI) calcd for $C_{24}H_{23}NO_3S$ (M^+): 405.14; Found: 428.64 $(M+Na)^+$. Anal. Calcd. for $C_{24}H_{23}NO_3S$: C, 71.09; H, 5.72; N, 3.45; S, 7.91. Found: C, 71.12; H, 5.74; N, 3.48; S, 7.89.



3h

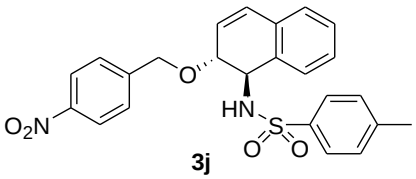
(1*R*,2*R*)-*N*-(2-(4-Chlorobenzyloxy)-1,2-dihydronaphthalen-1-yl)-4-methylbenzenesulfonamide

(3h). Following the general procedure (**I**), **3h** was obtained as a white solid (36.5 mg, 65 %). R_f = 0.22 on silica gel (ethyl acetate : petroleum ether = 1 : 4, v/v). mp 133-134 °C. The ee was determined to be 73 % using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol = 85/15, 0.5 mL/min, λ = 254 nm); Retention times were 25.4 min (minor) and 33.9 min (major). $[\alpha]^{20}_D$ = -135 (*c* 1.00, $CHCl_3$). IR (film, cm^{-1}): 3281(w), 2925(w), 1492(w), 1455(w), 1328(m), 1454(w), 1330(s), 1159(s), 1093(s), 1014(w), 812(m), 667(w), 666(m), 569(m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 7.2 Hz, 2H), 7.30-7.27 (m, 4H), 7.24 (t, *J* = 7.2 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.12-7.08 (m, 2H), 6.73 (d, *J* = 7.6 Hz, 1H), 6.62 (d, *J* = 9.6 Hz, 1H), 6.00 (dd, *J* = 4.8 Hz, 9.6 Hz, 1H), 4.53 (d, *J* = 7.6 Hz, 2H), 4.49 (t, *J* = 7.6 Hz, 1H), 4.17 (t, *J* = 7.6 Hz, 1H), 2.46 (s, 3H), 2.18 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.6, 137.6, 136.7, 133.4, 132.3, 131.7, 130.5, 129.7, 129.1, 128.9, 128.4, 128.5, 127.3, 127.2, 124.9, 74.7, 70.1, 54.4, 21.6. MS (ESI) calcd for $C_{24}H_{22}NO_3ClS$ (M^+): 439.10; Found: 462.58 $(M+Na)^+$. Anal. Calcd. for $C_{24}H_{22}NO_3ClS$: C, 65.52; H, 5.04; N, 3.18; S, 7.29. Found: C, 65.53; H, 5.02; N, 3.19; S, 7.26.



3i

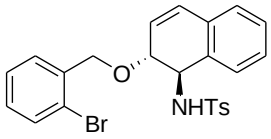
(1*R*,2*R*)-*N*-(2-(4-Methoxybenzyloxy)-1,2-dihydronaphthalen-1-yl)-4-methylbenzenesulfonamide (3i). Following the general procedure (**I**), **3i** was obtained as a white solid (27.9 mg, 32 %). R_f = 0.15 on silica gel (ethyl acetate : petroleum ether = 1 : 5, v/v). mp 83-84 °C. The ee was determined to be 82 % using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol = 85/15, 0.5 mL/min, λ = 254 nm); Retention times were 37.6 min (minor) and 40.8 min (major). $[\alpha]^{20}_D$ = -143 (*c* 1.00, $CHCl_3$). IR (film, cm^{-1}): 3276(w), 3035(w), 2925(w), 1724(w), 1612(w), 1514(w), 1454(w), 1329(m), 1248(m), 1159(s), 1094(m), 1034(m), 914(w), 8125(m), 664(m), 566(m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 9.6 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 6.76 (d, *J* = 7.2 Hz, 1H), 6.59 (d, *J* = 9.6 Hz, 1H), 5.96 (dd, *J* = 4.4 Hz, 9.6 Hz, 1H), 4.55-4.51 (m, 1H), 4.50-4.47 (m, 3H), 4.16 (s, 1H), 3.82 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 143.5, 137.7, 132.5, 131.8, 130.2, 130.1, 129.7, 129.5, 128.8, 128.5, 128.3, 127.3, 125.4, 113.7, 74.0, 70.6, 55.3, 54.4, 21.6. MS (ESI) calcd for $C_{25}H_{25}NO_4S$ (M^+): 435.15; Found: 458.45 $(M+Na)^+$. Anal. Calcd. for $C_{25}H_{25}NO_4S$: C, 68.94; H, 5.79; N, 3.22; S, 7.36. Found: C, 68.93; H, 5.77; N, 3.19; S, 7.34.



3j

(1*R*,2*R*)-*N*-(2-(4-Nitrobenzyloxy)-1,2-dihydronaphthalen-1-yl)-4-methylbenzenesulfonamide

(3j). Following the general procedure (**I**), **3j** was obtained as a white solid (54.1 mg, 60 %). R_f = 0.12 on silica gel (ethyl acetate : petroleum ether = 1 : 4, v/v). mp 190-191 °C. The ee was determined to be 60 % using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol = 90/10, 1.0 mL/min, λ = 254 nm); Retention times were 47.3 min (minor) and 54.6 min (major). $[\alpha]^{20}_D$ = -121 (*c* 1.00, $CHCl_3$). IR (film, cm^{-1}): 3282(w), 3045(w), 2925(w), 2854(w), 1958(w), 1519(w), 1397(w), 1344(s), 1161(s), 1092(m), 961(w), 814(m), 775(m), 667(m), 569(m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.30-7.27 (m, 3H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 3H), 6.70 (d, *J* = 7.6 Hz, 1H), 6.63 (d, *J* = 9.6 Hz, 1H), 5.98 (dd, *J* = 4.8 Hz, 9.6 Hz, 1H), 4.55-4.52 (m, 3H), 4.45 (t, *J* = 8.0 Hz, 1H), 4.16 (t, *J* = 4.8 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.6, 137.6, 136.7, 133.4, 132.3, 131.7, 130.5, 129.7, 129.1, 128.9, 128.4, 128.5, 127.3, 127.2, 124.9, 79.2, 71.9, 54.4, 24.3. MS (ESI) calcd for $C_{24}H_{22}N_2O_5S$ (M^+): 450.13; Found: 473.52 $(M+Na)^+$. Anal. Calcd. for $C_{24}H_{22}N_2O_5S$: C, 63.98; H, 4.92; N, 6.22; S, 7.12. Found: C, 63.95; H, 4.94; N, 6.19; S, 7.08.

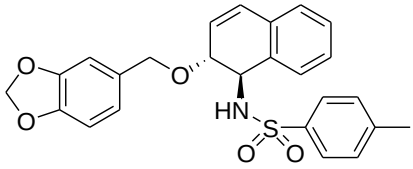


3k

(1*R*,2*R*)-*N*-(2-(2-Bromobenzyloxy)-1,2-dihydronaphthalen-1-yl)-4-methylbenzenesulfonamide

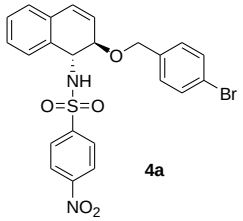
(3k). Following the general procedure (**I**), **3k** was obtained as a white solid (40.5 mg, 75 %). R_f = 0.10 on silica gel (ethyl acetate : petroleum ether = 1 : 8, v/v). mp 134-135 °C. The ee was determined to be 12 % using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol = 85/15, 0.5 mL/min, λ = 254 nm); Retention times were 46.7 min (minor) and 50.3 min (major). $[\alpha]^{20}_D$ = -23 (*c* 1.00, $CHCl_3$). IR (film, cm^{-1}): 3284(w), 3059(w), 2924(w), 1597(w), 1491(w), 1444(m), 1332(m), 1159(s), 1094(m), 928(w), 812(w), 664(m), 547(m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 1H) , 7.35(d, *J* = 4.8 Hz, 1H), 7.26-7.21 (m, 4H), 7.16-7.09 (m, 3H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.61 (d, *J* = 9.6 Hz, 1H), 6.05 (dd, *J* = 4.8 Hz, 9.6 Hz, 1H), 4.62 (s, 1H), 4.56 (s, 2H), 4.23 (t, *J* = 4.0 Hz, 1H), 2.40 (s, 3H), 2.34 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3, 137.5, 137.3, 132.7, 132.4,

131.8, 130.4, 129.6, 129.4, 129.0, 128.7, 128.4, 128.3, 127.3, 127.2， 125.0, 122.8, 121.4, 75.5, 70.2, 54.7, 21.6. MS (ESI) calcd for $C_{24}H_{22}BrNO_3S$ (M^+): 485.05; Found: 506.33 $(M+Na)^+$. Anal. Calcd. for $C_{24}H_{22}NBrO_3S$: C, 59.51; H, 4.58; N, 2.89; S, 6.62. Found: C, 59.54; H, 4.55; N, 2.88; S, 6.58.



3l

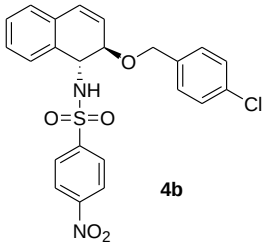
(1*R*,2*R*)-*N*-(2-(Benzo[d][1,3]dioxol-5-ylmethoxy)-1,2-dihydronaphthalen-1-yl)-4-methylbenzenesulfonamide (3l). Following the general procedure (**I**), **3l** was obtained as a white solid (72.6 mg, 45 %). R_f = 0.15 on silica gel (ethyl acetate : petroleum ether = 1 : 5, v/v). mp 63-64 °C. The ee was determined to be 88 % using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol = 85/15, 0.5 mL/min, λ = 254 nm); Retention times were 26.1 min (minor) and 35.5 min (major). $[\alpha]^{20}_D$ = -128 (*c* 1.00, $CHCl_3$). IR (film, cm^{-1}): 3268(w), 3059(w), 2957(w), 2924(w), 1597(w), 1454(w), 1329(m), 1161(s), 1093(s), 967(w), 916(w), 813(m), 752(m), 665(m), 548(m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H) , 7.21 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 7.6 Hz, 2H), 6.77-6.73 (m, 4H), 6.59 (d, *J* = 9.6 Hz, 1H), 5.98 (d, *J* = 4.4 Hz, 1H), 5.95 (s, 2H), 4.52 (s, 2H), 4.43 (s, 2H), 4.14 (s, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7, 143.2, 139.6, 133.7, 128.5, 127.9, 127.8, 126.4, 125.7, 124.9, 124.5, 124.4, 123.4, 123.3, 121.3, 117.6, 104.7, 104.1, 97.0, 70.1, 66.8, 50.5, 17.7. MS (ESI) calcd for $C_{25}H_{23}NO_5S$ (M^+): 449.13; Found: 472.33 $(M+Na)^+$. Anal. Calcd. for $C_{25}H_{23}NO_5S$: C, 66.80; H, 5.16; N, 3.12; S, 7.13. Found: C, 66.81; H, 5.15; N, 3.12; S, 7.16.



4a

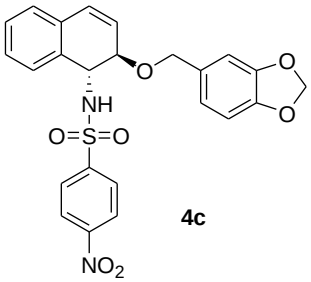
(1*R*,2*R*)-*N*-(2-(4-Bromobenzyloxy)-1,2-dihydronaphthalen-1-yl)-4-nitrobenzenesulfonamide (4a). Following the general procedure (**I**), **4a** was obtained as a white solid (77.3 mg, 75 %). R_f = 0.18 on silica gel (ethyl acetate : petroleum ether = 1 : 4, v/v). mp 166-167 °C. The ee was determined to be 10 % using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol = 80/20, 1.0 mL/min, λ = 254 nm); Retention times were 33.5 min (minor) and 50.1 min (major). $[\alpha]^{20}_D$ = -19 (*c* 1.00, $CHCl_3$). IR (film, cm^{-1}): 3274(w), 3059(w), 2925(w), 2854(m), 1724(m), 1605(w), 1530(s), 1487(w), 1455(w), 1348(s), 1288(m), 1164(m), 1092(m), 1073(m), 853(w), 811(w), 736(m), 615(m), 503(m). ^{1}H NMR

(400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.4 Hz, 2H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.26 (s, 1H), 7.15-7.11 (m, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.60 (d, *J* = 9.6 Hz, 1H), 5.99 (dd, *J* = 4.0 Hz, 3.6 Hz, 1H), 4.96 (d, *J* = 7.6 Hz, 1H), 4.65 (t, *J* = 7.2 Hz, 1H), 4.52 (d, *J* = 8.0 Hz, 1H), 4.36 (d, *J* = 9.6 Hz, 1H), 4.14 (t, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.8, 146.5, 136.7, 132.1, 131.9, 131.5, 130.3, 129.3, 129.1, 128.5, 128.2, 127.7, 127.4, 125.1, 124.1, 121.9, 75.5, 70.2, 55.8. MS (ESI) calcd for $C_{23}H_{19}N_2O_5BrS$ (M^+): 514.02; Found: 538.34 $(M+Na)^+$. Anal. Calcd. for $C_{23}H_{19}N_2O_5BrS$: C, 53.60; H, 3.72; N, 5.44; S, 6.22. Found: C, 53.62; H, 3.71; N, 5.44; S, 6.19.



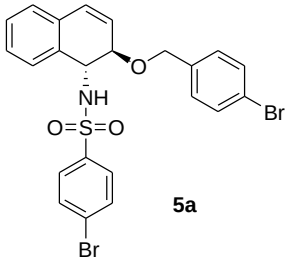
4b

(1*R*,2*R*)-*N*-(2-(4-Chlorobenzyloxy)-1,2-dihydronaphthalen-1-yl)-4-nitrobenzenesulfonamide (4b). Following the general procedure (**I**), **4b** was obtained as a white solid (61.1 mg, 65 %). R_f = 0.18 on silica gel (ethyl acetate : petroleum ether = 1 : 4, v/v). mp 173-174 °C. The ee was determined to be 16 % using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol = 80/20, 1.0 mL/min, λ = 254 nm); Retention times were 31.0 min (minor) and 42.7 min (major). $[\alpha]^{20}_D$ = -32 (*c* 1.00, $CHCl_3$). IR (film, cm^{-1}) 3283(w), 3104(w), 2919(w), 2852(w), 1728(w), 1605(w), 1530(s), 1492(w), 1454(w), 1348(s), 1164(s), 1091(m), 1014(w), 853(m), 813(m), 736(m), 558(m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, *J* = 4.8 Hz, 2H), 7.94 (d, *J* = 8.8 Hz, 2H), 7.36-7.24 (m, 4H), 7.14-1.10 (m, 3H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.60 (d, *J* = 9.6 Hz, 1H), 6.00 (dd, *J* = 9.6 Hz, 4.0 Hz, 1H), 4.85 (d, *J* = 8.4 Hz, 1H), 4.66 (t, *J* = 6.0 Hz, 1H), 4.53 (d, *J* = 12.0 Hz, 1H), 4.38 (d, *J* = 9.6 Hz, 1H), 4.15 (t, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.5, 136.1, 133.8, 132.1, 131.9, 130.3, 129.1, 128.9, 128.6, 128.5, 128.2, 127.7, 127.4, 125.1, 124.8, 124.1, 75.4, 70.1, 55.8. MS (ESI) calcd for $C_{23}H_{19}N_2O_5ClS$ (M^+): 470.07; Found:493.43 $(M+Na)^+$. Anal. Calcd. for $C_{23}H_{19}N_2O_5ClS$: C, 58.66; H, 4.07; N, 5.95; S, 6.81. Found: C, 58.67; H, 4.06; N, 5.94; S, 6.77.



4c

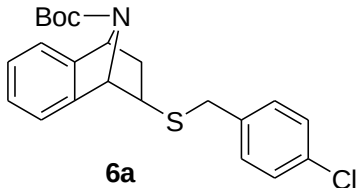
(1*R*,2*R*)-*N*-(2-(Benzo[d][1,3]dioxol-5-ylmethoxy)-1,2-dihydronaphthalen-1-yl)-4-nitrobenzenesulfonamide (4c). Following the general procedure (**I**), **4c** was obtained as a white solid (52.8 mg, 55 %). R_f = 0.15 on silica gel (ethyl acetate : petroleum ether = 1 : 5, v/v). mp 173-175 °C. The ee was determined to be 18 % using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol = 75/25, 1.0 mL/min, λ = 254 nm); Retention times were 38.6 min (major) and 53.7 min (minor). $[\alpha]^{20}_D$ = -28 (*c* 1.00, $CHCl_3$). IR (film, cm^{-1}): 3735(w), 3294(w), 2921(s), 1729(w), 1529(m), 1444(m), 1348(s), 1254(m), 1163(s), 1094(m), 1039(m), 929(w), 737(w), 615(w), 503(m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.21-7.10 (m, 4H), 6.72 (d, *J* = 8.0 Hz, 1H), 6.63-6.56 (m, 3H), 6.00 (d, *J* = 3.6 Hz, 1H), 5.98 (d, *J* = 4.0 Hz, 2H), 4.75-4.68 (m, 2H), 4.46 (d, *J* = 12.0 Hz, 1H), 4.27 (d, *J* = 12.0 Hz, 1H), 4.10 (t, *J* = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.7, 147.7, 147.3, 146.5, 132.6, 132.0, 131.2, 130.9, 129.9, 128.9, 128.5, 128.3, 127.5, 127.2, 125.6, 124.0, 121.3, 108.2, 101.2, 75.1, 70.6, 55.3. MS (ESI) calcd for $C_{24}H_{20}N_2O_7S$ (M^+): 480.10; Found: 503.76 $(M+Na)^+$. Anal. Calcd. for $C_{24}H_{20}N_2O_7S$: C, 59.99; H, 4.20; N, 5.83; S, 6.67. Found: C, 59.95; H, 4.19; N, 5.80; S, 6.63.



5a

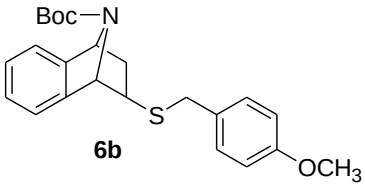
(1*R*,2*R*)-*N*-(2-(4-Bromobenzyloxy)-1,2-dihydronaphthalen-1-yl)-4-bromobenzenesulfonamide (5a). Following the general procedure (**I**), **5a** was obtained as a white solid (74.6 mg, 68 %). R_f = 0.15 on silica gel (ethyl acetate : petroleum ether = 1 : 5, v/v). mp 136-137 °C. The ee was determined to be 4 % using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol = 85/15, 1.0 mL/min, λ = 254 nm); Retention times were 16.7 min (minor) and 27.1 min (major). $[\alpha]^{20}_D$ = -17 (*c* 1.00, $CHCl_3$). IR (film, cm^{-1}): 3565(w), 3270(w), 2924(s), 2028(w), 1575(w), 1487(w), 1390(s), 1333(m), 1275(w), 1162(s), 1069(m), 1011(m), 819(m), 739(m), 610(m), 558(w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.28-7.25 (m, 2H), 7.12-7.07 (m, 3H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.60 (d, *J* = 9.6 Hz, 1H), 5.98 (dd, *J* = 9.6 Hz, 4.4 Hz, 1H), 4.63 (d, *J* = 8.0 Hz, 1H), 4.56-4.51 (m, 2H), 4.43 (d, *J* = 9.6 Hz, 1H), 4.13 (d, *J* = 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.7, 136.9, 132.3, 132.2, 131.7, 131.5, 130.5, 129.4, 129.0, 128.6, 128.5, 128.2, 127.7,

127.4, 124.9, 121.7, 74.9, 70.2, 54.9. MS (ESI) calcd for $C_{23}H_{19}NO_3Br_2S$ (M^+): 546.95; Found: 569.93 $(M+Na)^+$. Anal. Calcd. for $C_{23}H_{19}NO_3Br_2S$: C, 50.29; H, 3.49; N, 2.55; S, 5.84. Found: C, 50.32; H, 3.48; N, 2.51; S, 5.80.



6a

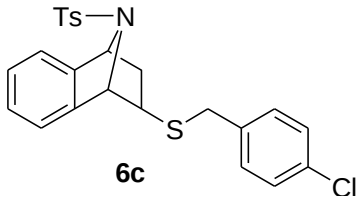
2-(4-Chloro-benzylsulfanyl)-1,2,3,4-tetrahydro-1,4-epiazano-naphthalene-9-carboxylic acid tert-butyl ester (6a). Following the general procedure (**I**), **6a** was obtained as a white solid (64.2 mg, 80 %). R_f = 0.25 on silica gel (ethyl acetate : petroleum ether = 1 : 15, v/v). mp 91-93 °C. The ee was determined to be 9 % using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol = 90/10, 0.5 mL/min, λ = 254 nm); Retention times were 12.2 min (minor) and 16.2 min (major). $[\alpha]^{20}_D$ = 9 (*c* 1.00, $CHCl_3$). IR (film, cm^{-1}): 3339(w), 2962(w), 2926(w), 1714(m), 1488(w), 1366(m), 1248(s), 1170(m), 1081(w), 802(s), 747(m), 693(w), 526(m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.26 (m, 4H), 7.20-7.12 (m, 4H), 5.14 (s, 1H), 4.76 (s, 1H), 3.88-3.78 (m, 2H), 2.60 (s, 1H), 1.87-1.84 (m, 1H), 1.78-1.75 (m, 1H), 1.40 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 145.0, 132.9, 130.9, 130.2, 128.8, 126.9, 126.7, 80.3, 65.6, 45.3, 36.4, 30.6, 29.7, 28.3. MS (ESI) calcd for $C_{22}H_{24}ClNO_2S$ (M^+): 401.12; Found: 424.23 $(M+Na)^+$. Anal. Calcd. for $C_{22}H_{24}ClNO_2S$: C, 65.74; H, 6.02; N, 3.48; S, 7.98 Found: C, 65.75; H, 5.99; N, 3.44; S, 7.90.



6b

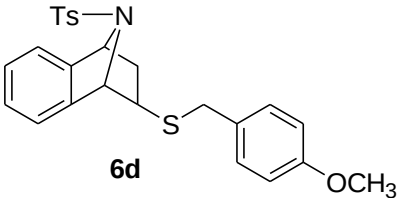
2-(4-Methoxy-benzylsulfanyl)-1,2,3,4-tetrahydro-1,4-epiazano-naphthalene-9-carboxylic acid tert-butyl ester (6b). Following the general procedure (**I**), **6b** was obtained as a white solid (65.1 mg, 82 %). R_f = 0.25 on silica gel (ethyl acetate : petroleum ether = 1 : 15, v/v). mp 85-87 °C. The ee was determined to be 8 % using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol = 90/10, 0.5 mL/min, λ = 254 nm); Retention times were 13.4 min (minor) and 15.2 min (major). $[\alpha]^{20}_D$ = 8 (*c* 1.00, $CHCl_3$). IR (film, cm^{-1}): 3339(w), 2962(w), 2926(w), 1714(m), 1488(w), 1366(m), 1248(s), 1170(m), 1081(w), 802(s), 747(m), 693(w), 526(m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.12 (m, 6H), 6.89-6.87 (m, 2H), 5.15-4.99 (m, 1H), 4.77 (s, 1H), 3.87-3.79 (m, 5H), 2.63 (s, 1H), 1.90-1.84 (m, 1H),

1.80-1.73 (m, 1H), 1.42 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 145.1, 145.0, 130.0, 129.9, 126.8, 126.6, 114.0, 80.2, 65.2, 60.0, 55.3, 45.2, 36.5, 35.9, 28.3. MS (ESI) calcd for $C_{23}H_{27}NO_3S$ (M^+): 397.17; Found: 420.25 $(M+Na)^+$. Anal. Calcd. for $C_{23}H_{27}NO_3S$: C, 69.49; H, 6.85; N, 3.52; S, 8.07. Found: C, 69.45; H, 6.83; N, 3.50; S, 8.17.



6c

2-(4-Chloro-benzylsulfanyl)-9-(toluene-4-sulfonyl)-1,2,3,4-tetrahydro-1,4-epiazano-naphthalene (6c). Following the general procedure (**I**), **6c** was obtained as a white solid (77.3 mg, 85 %). R_f = 0.25 on silica gel (ethyl acetate : petroleum ether = 1 : 15, v/v). mp 94-96 °C. The ee was determined to be 1 % using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol = 85/15, 0.5 mL/min, λ = 254 nm); Retention times were 35.4 min (major) and 41.9 min (minor). $[\alpha]^{20}_D$ = 1 (*c* 1.00, $CHCl_3$). IR (film, cm^{-1}): 2934(w), 2925(w), 1596(w), 1511(m), 1489(w), 1342(m), 1161(s), 1090(m), 1014(w), 971(s), 812(m), 693(w), 679(m), 604(m), 526(m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.26 (m, 6H), 6.91 (d, *J* = 4.0 Hz, 2H), 6.86 (s, 3H), 6.73 (d, *J* = 4.4 Hz, 1H), 5.00 (d, *J* = 4.4 Hz, 1H), 4.52 (s, 1H), 3.84 (d, *J* = 4.8 Hz, 2H), 2.51 (dd, *J* = 3.6 Hz, 8.0 Hz, 1H), 2.25 (s, 3H), 2.01-1.98 (m, 1H), 1.78-1.74 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.0, 142.9, 141.7, 136.9, 134.9, 132.9, 130.3, 128.9, 128.8, 127.9, 126.9, 126.7, 120.2, 120.1, 68.3, 63.1, 44.6, 36.7, 36.3, 21.4. MS (ESI) calcd for $C_{24}H_{22}ClNO_2S_2$ (M^+): 455.08; Found: 478.43 $(M+Na)^+$. Anal. Calcd. for $C_{24}H_{22}ClNO_2S_2$: C, 63.21; H, 4.86; N, 3.07; S, 14.06. Found: C, 63.23; H, 4.83; N, 3.08; S, 14.12.

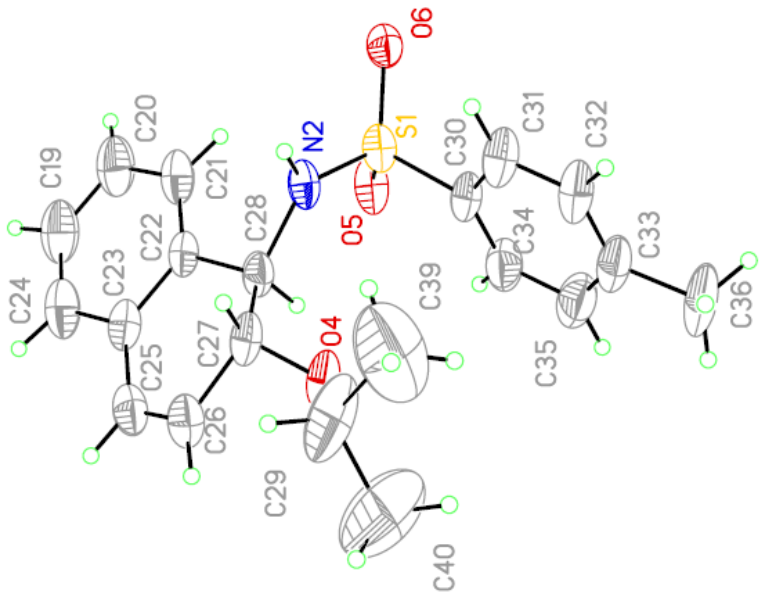


6d

2-(4-Methoxy-benzylsulfanyl)-9-(toluene-4-sulfonyl)-1,2,3,4-tetrahydro-1,4-epiazano-naphthalene (6d). Following the general procedure (**I**), **6d** was obtained as a white solid (79.3 mg, 88 %). R_f = 0.20 on silica gel (ethyl acetate : petroleum ether = 1 : 15, v/v). mp 102-103 °C. The ee was determined to be 5 % using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol = 85/15, 0.5 mL/min, λ = 254 nm); Retention times were 39.0 min (minor) and 48.1 min (major). $[\alpha]^{20}_D$ = 5 (*c* 1.00, $CHCl_3$). IR (film, cm^{-1}): 2933(w), 2925(w), 1669(w), 1511(m), 1460(w), 1342(m), 1161(s), 1089(m), 1031(w),

971(s), 813(m), 604(w), 558(m). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H) , 6.97 (d, *J* = 8.0 Hz, 2H), 6.87-6.85 (m, 5H), 6.75 (d, *J* = 4.0 Hz, 1H), 4. 98 (d, *J* = 3.6 Hz, 1H), 4.50 (s, 1H), 3.83 (d, *J* = 4.8 Hz, 2H), 3.80 (s, 3H), 2.55-2.52 (m, 1H), 2.25 (s, 3H), 2.00-1.96 (m, 1H), 1.78-1.73 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.7, 139.1, 138.9, 137.9, 131.0, 126.3, 126.1, 124.9, 123.9, 122.9, 122.7, 116.3, 116.2, 110.1, 64.4, 59.2, 51.4, 40.6, 32.7, 32.5, 17.5. MS (ESI) calcd for $C_{25}H_{25}NO_3S_2$ (M^+): 451.13; Found: 474.41 $(M+Na)^+$. Anal. Calcd. for $C_{25}H_{25}NO_3S_2$: C, 66.49; H, 5.58; N, 3.10; 14.20. Found: C, 66.55; H, 5.54; N, 3.12; 14.11.

3. Crystal structure and data of (1*R*,2*R*)-*N*-(-2-isopropoxy-1,2-dihydronaphthalen-1-yl)-4-methylbenzenesulfonamide (3c).



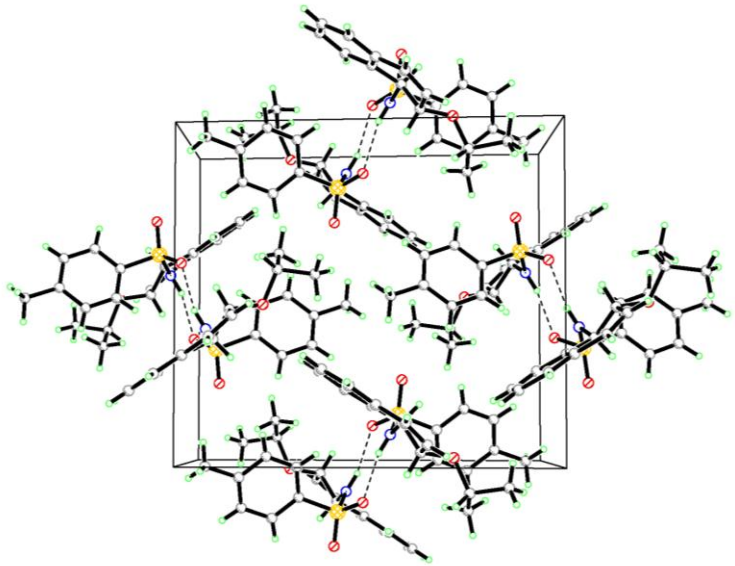


Table 1. Crystal data and structure refinement for 3c.

Identification code	3c
Empirical formula	$C_{20}H_{25}NO_3S$
Formula weight	359.47
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P21/c
Unit cell dimensions	a = 9.807(5) A alpha = 90 deg.
	b = 13.026(6) A beta = 96.029(8) de
	c = 14.561(7) A gamma = 90 deg.
Volume	1849.8(16) A^3

Z, Calculated density	4, 1.291 Mg/m^3
Absorption coefficient	0.193 mm^-1
F(000)	768
Crystal size	0.20 x 0.18 x 0.16 mm
Theta range for data collection	2.10 to 25.00 deg.
Limiting indices	-10<=h<=11, -15<=k<=15, -17<=l<=17
Reflections collected / unique	9163 / 3223 [R(int) = 0.1478]
Completeness to theta = 25.00	98.9 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3223 / 135 / 229
Goodness-of-fit on F^2	1.003
Final R indices [I >2 sigma (I)]	R1 = 0.0813, wR2 = 0.1339
R indices (all data)	R1 = 0.2585, wR2 = 0.1580
Largest diff. peak and hole	0.373 and -0.392 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 3c. U(eq) is defined as one third of the trace of the orthogonalzed Uij tensor.

	x	y	z	U(eq)
S(1)	4771(2)	3517(2)	825(1)	69(1)
O(4)	1681(5)	4748(3)	2233(3)	85(2)
O(5)	4463(4)	2452(3)	928(3)	85(2)
O(6)	5810(4)	3848(3)	132(3)	74(1)
N(2)	3410(5)	4093(3)	605(3)	68(2)
C(19)	66(10)	2195(6)	-1187(6)	113(3)
C(20)	1453(9)	2225(6)	-1268(5)	107(3)
C(21)	2077(8)	2763(5)	-603(5)	89(2)
C(22)	1344(7)	3238(5)	110(4)	63(2)
C(23)	-85(8)	3215(5)	201(5)	73(2)
C(24)	-686(8)	2672(5)	-480(5)	98(3)
C(25)	-846(7)	3734(5)	946(5)	81(2)
C(26)	-294(8)	4356(5)	1505(5)	81(2)
C(27)	1185(8)	4586(5)	1369(4)	73(2)
C(28)	2011(7)	3736(5)	887(4)	64(2)
C(29)	1340(12)	5762(6)	2627(6)	151(4)

C(30)	5252(7)	3969(5)	1886(4)	68(2)
C(31)	5852(7)	4908(5)	1933(5)	85(2)
C(32)	6319(7)	5237(6)	2742(5)	94(2)
C(33)	6206(8)	4598(7)	3494(5)	88(2)
C(34)	5144(7)	3330(5)	2627(5)	90(2)
C(35)	5599(8)	3657(7)	3450(5)	107(3)
C(36)	6782(8)	4943(6)	4382(4)	130(3)
C(39)	2550(12)	6302(8)	2629(8)	226(5)
C(40)	1053(14)	5591(7)	3622(6)	239(5)

Table 3. Bond lengths [A] and angles [deg] for 3c.

S(1)-O(5)	1.431(4)
S(1)-N(2)	1.536(5)
S(1)-O(6)	1.568(4)
S(1)-C(30)	1.675(6)
O(4)-C(27)	1.317(6)
O(4)-C(29)	1.492(8)
N(2)-C(28)	1.545(7)
N(2)-H(2C)	0.8600
C(19)-C(20)	1.378(10)
C(19)-C(24)	1.466(9)
C(19)-H(19A)	0.9300
C(20)-C(21)	1.295(8)
C(20)-H(20A)	0.9300
C(21)-C(22)	1.462(8)
C(21)-H(21A)	0.9300
C(22)-C(28)	1.405(7)
C(22)-C(23)	1.422(8)
C(23)-C(24)	1.307(8)
C(23)-C(25)	1.536(9)

C(24)-H(24A)	0.9300
C(25)-C(26)	1.233(7)
C(25)-H(25A)	0.9300
C(26)-C(27)	1.515(9)
C(26)-H(26A)	0.9300
C(27)-C(28)	1.579(8)
C(27)-H(27A)	0.9800
C(28)-H(28A)	0.9800
C(29)-C(39)	1.379(13)
C(29)-C(40)	1.521(11)
C(29)-H(29A)	0.9800
C(30)-C(31)	1.355(8)
C(30)-C(34)	1.376(8)
C(31)-C(32)	1.292(7)
C(31)-H(31A)	0.9300
C(32)-C(33)	1.389(9)
C(32)-H(32A)	0.9300
C(33)-C(35)	1.361(9)
C(33)-C(36)	1.428(8)
C(34)-C(35)	1.306(8)
C(34)-H(34A)	0.9300
C(35)-H(35A)	0.9300
C(36)-H(36A)	0.9600
C(36)-H(36B)	0.9600
C(36)-H(36C)	0.9600
C(39)-H(39A)	0.9600
C(39)-H(39B)	0.9600
C(39)-H(39C)	0.9600
C(40)-H(40A)	0.9600
C(40)-H(40B)	0.9600

C(40)-H(40C)	0.9600
O(5)-S(1)-N(2)	107.9(3)
O(5)-S(1)-O(6)	119.6(3)
N(2)-S(1)-O(6)	109.9(3)
O(5)-S(1)-C(30)	106.7(3)
N(2)-S(1)-C(30)	100.1(3)
O(6)-S(1)-C(30)	110.9(3)
C(27)-O(4)-C(29)	115.8(5)
S(1)-N(2)-C(28)	125.0(4)
S(1)-N(2)-H(2C)	117.5
C(28)-N(2)-H(2C)	117.5
C(20)-C(19)-C(24)	128.4(8)
C(20)-C(19)-H(19A)	115.8
C(24)-C(19)-H(19A)	115.8
C(21)-C(20)-C(19)	110.2(9)
C(21)-C(20)-H(20A)	124.9
C(19)-C(20)-H(20A)	124.9
C(20)-C(21)-C(22)	122.0(8)
C(20)-C(21)-H(21A)	119.0
C(22)-C(21)-H(21A)	119.0
C(28)-C(22)-C(23)	108.4(7)
C(28)-C(22)-C(21)	123.0(7)
C(23)-C(22)-C(21)	128.4(6)
C(24)-C(23)-C(22)	108.1(8)
C(24)-C(23)-C(25)	124.1(8)
C(22)-C(23)-C(25)	127.8(6)
C(23)-C(24)-C(19)	122.8(8)
C(23)-C(24)-H(24A)	118.6
C(19)-C(24)-H(24A)	118.6
C(26)-C(25)-C(23)	122.9(8)

C(26)-C(25)-H(25A)	118.5
C(23)-C(25)-H(25A)	118.5
C(25)-C(26)-C(27)	113.8(8)
C(25)-C(26)-H(26A)	123.1
C(27)-C(26)-H(26A)	123.1
O(4)-C(27)-C(26)	99.7(6)
O(4)-C(27)-C(28)	112.4(5)
C(26)-C(27)-C(28)	117.6(6)
O(4)-C(27)-H(27A)	108.9
C(26)-C(27)-H(27A)	108.9
C(28)-C(27)-H(27A)	108.9
C(22)-C(28)-N(2)	106.0(6)
C(22)-C(28)-C(27)	117.6(6)
N(2)-C(28)-C(27)	114.7(5)
C(22)-C(28)-H(28A)	105.8
N(2)-C(28)-H(28A)	105.8
C(27)-C(28)-H(28A)	105.8
C(39)-C(29)-O(4)	103.0(10)
C(39)-C(29)-C(40)	108.6(8)
O(4)-C(29)-C(40)	107.9(7)
C(39)-C(29)-H(29A)	112.3
O(4)-C(29)-H(29A)	112.3
C(40)-C(29)-H(29A)	112.3
C(31)-C(30)-C(34)	125.1(6)
C(31)-C(30)-S(1)	116.3(6)
C(34)-C(30)-S(1)	118.2(6)
C(32)-C(31)-C(30)	117.1(7)
C(32)-C(31)-H(31A)	121.5
C(30)-C(31)-H(31A)	121.5
C(31)-C(32)-C(33)	118.1(8)

C(31)-C(32)-H(32A)	121.0
C(33)-C(32)-H(32A)	121.0
C(35)-C(33)-C(32)	125.0(8)
C(35)-C(33)-C(36)	117.1(8)
C(32)-C(33)-C(36)	117.9(8)
C(35)-C(34)-C(30)	118.3(7)
C(35)-C(34)-H(34A)	120.8
C(30)-C(34)-H(34A)	120.8
C(34)-C(35)-C(33)	116.3(8)
C(34)-C(35)-H(35A)	121.9
C(33)-C(35)-H(35A)	121.9
C(33)-C(36)-H(36A)	109.5
C(33)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	109.5
C(33)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5
C(29)-C(39)-H(39A)	109.5
C(29)-C(39)-H(39B)	109.5
H(39A)-C(39)-H(39B)	109.5
C(29)-C(39)-H(39C)	109.5
H(39A)-C(39)-H(39C)	109.5
H(39B)-C(39)-H(39C)	109.5
C(29)-C(40)-H(40A)	109.5
C(29)-C(40)-H(40B)	109.5
H(40A)-C(40)-H(40B)	109.5
C(29)-C(40)-H(40C)	109.5
H(40A)-C(40)-H(40C)	109.5
H(40B)-C(40)-H(40C)	109.5

Symmetry transformations used to generate equivalent atoms:

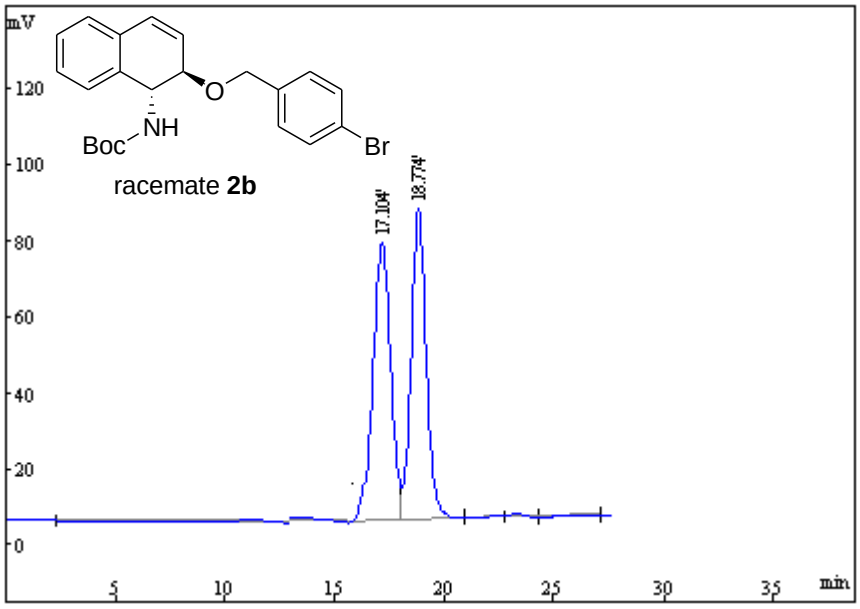
Table 4. Anisotropic displacement parameters (A^2 x 10^3) for 3c. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

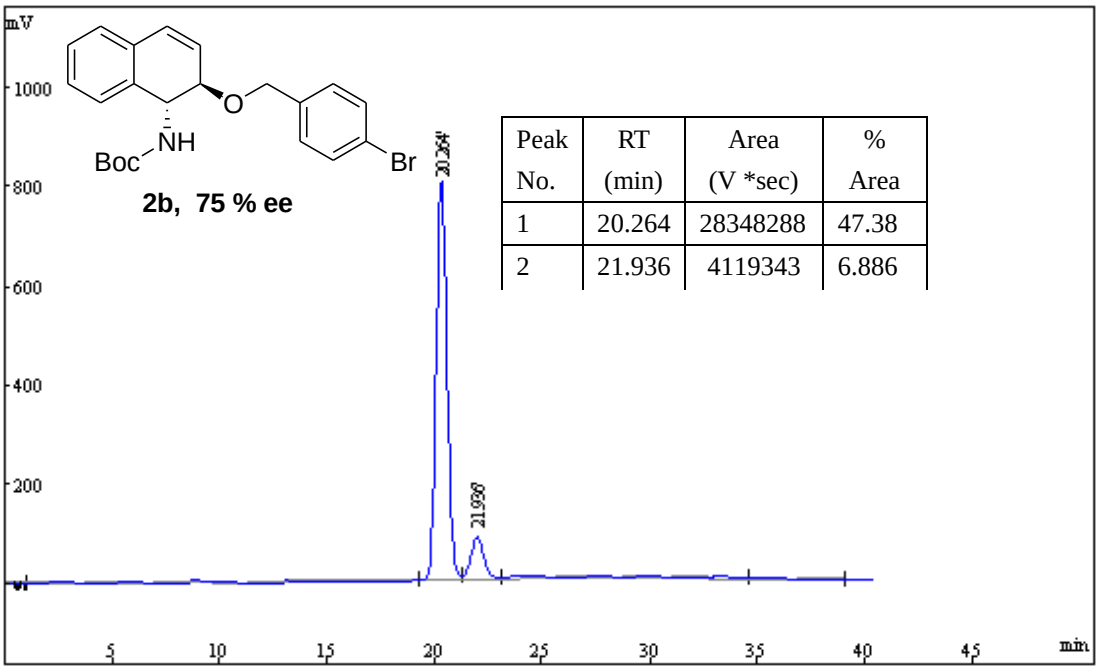
	U11	U22	U33	U23	U13	U12
S(1)	62(1)	67(1)	74(1)	-4(1)	-16(1)	5(1)
O(4)	91(4)	86(3)	70(3)	-5(3)	-36(3)	13(3)
O(5)	79(4)	63(3)	104(4)	-8(3)	-35(3)	6(3)
O(6)	57(3)	94(4)	68(3)	0(3)	-5(3)	6(3)
N(2)	54(4)	69(4)	76(4)	5(3)	-20(3)	13(3)
C(19)	111(6)	104(5)	111(6)	-26(4)	-46(6)	-5(6)
C(20)	101(6)	103(5)	106(5)	-32(4)	-37(5)	3(5)
C(21)	78(5)	95(5)	87(5)	-11(4)	-32(4)	-7(4)
C(22)	60(4)	66(4)	58(4)	-2(3)	-19(4)	-1(4)
C(23)	76(5)	65(4)	71(4)	5(3)	-25(4)	0(4)
C(24)	89(6)	90(5)	106(6)	-7(4)	-41(5)	-5(4)
C(25)	63(5)	85(5)	89(5)	12(4)	-19(4)	4(4)
C(26)	71(5)	82(5)	85(5)	-3(4)	-19(4)	11(4)
C(27)	77(5)	68(4)	65(4)	1(4)	-28(4)	15(4)
C(28)	55(4)	71(4)	62(4)	3(3)	-14(4)	15(4)
C(29)	248(11)	86(6)	100(5)	-46(5)	-73(7)	-34(6)
C(30)	68(5)	69(5)	60(4)	0(4)	-22(4)	12(4)
C(31)	95(5)	76(5)	76(5)	-5(4)	-33(4)	17(4)
C(32)	96(5)	96(5)	81(5)	-17(4)	-40(5)	10(4)
C(33)	85(5)	105(6)	66(4)	-10(5)	-29(4)	23(5)
C(34)	85(5)	94(5)	85(5)	5(4)	-24(5)	-19(4)
C(35)	109(6)	129(6)	75(5)	17(5)	-23(5)	-6(5)
C(36)	126(8)	160(7)	88(6)	-28(5)	-63(5)	29(6)
C(39)	181(10)	177(10)	309(11)	-128(9)	-28(9)	3(7)
C(40)	387(13)	194(9)	133(7)	-79(8)	10(9)	-40(9)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 3c.

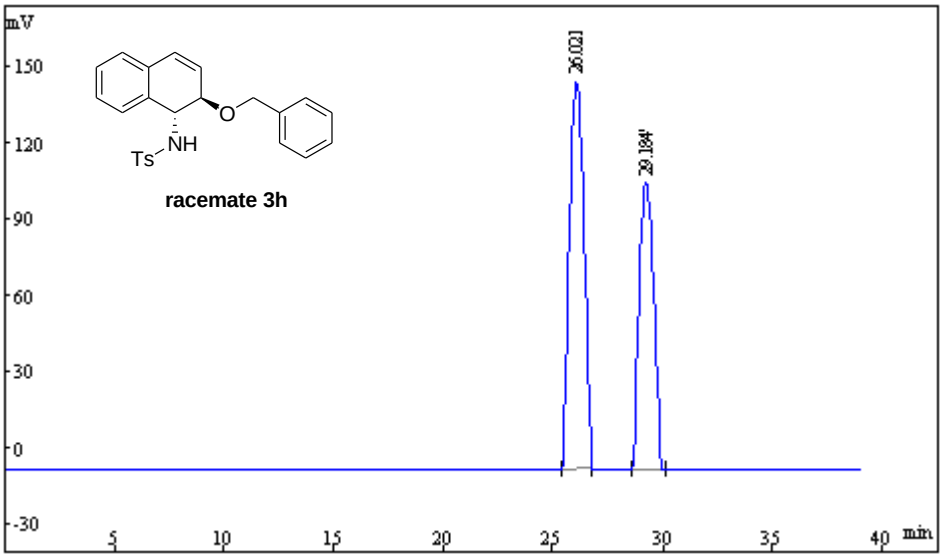
	x	y	z	U(eq)
H(2C)	3425	4654	294	82
H(19A)	-461	1824	-1640	135
H(20A)	1879	1905	-1732	128
H(21A)	3022	2848	-579	107
H(24A)	-1631	2585	-518	118
H(25A)	-1763	3571	976	97
H(26A)	-745	4656	1968	97
H(27A)	1222	5229	1023	87
H(28A)	2219	3199	1352	77
H(29A)	576	6103	2260	181
H(31A)	5925	5298	1405	102
H(32A)	6718	5883	2819	113
H(34A)	4756	2680	2544	108
H(35A)	5514	3269	3977	128
H(36A)	6371	4574	4853	195
H(36B)	6610	5664	4442	195
H(36C)	7753	4822	4448	195
H(39A)	2896	6229	2040	339
H(39B)	3210	6037	3103	339
H(39C)	2387	7014	2745	339
H(40A)	1870	5724	4028	358
H(40B)	770	4893	3698	358
H(40C)	338	6047	3769	358

4. The parties of the copies of HPLC of 2b, 3h and 3f.

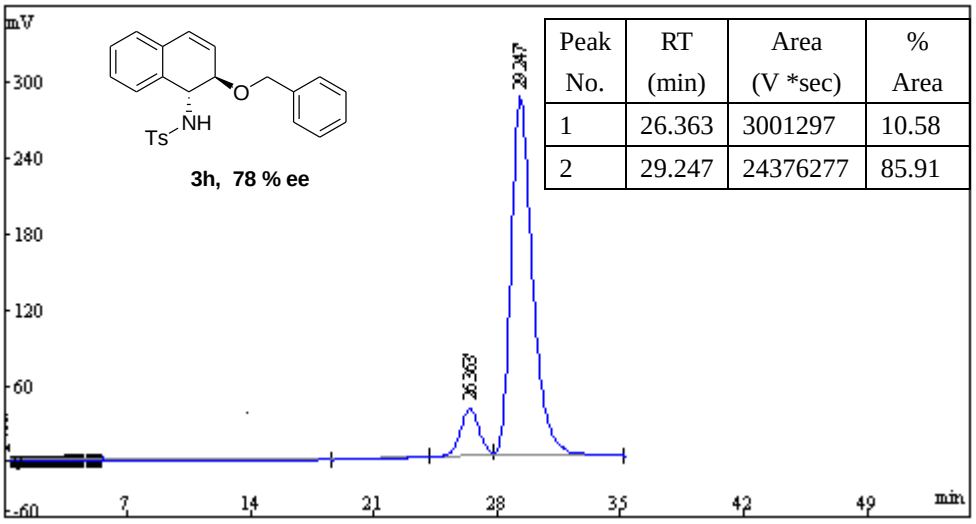




Peak No.	RT (min)	Area (V *sec)	% Area
1	20.264	28348288	47.38
2	21.936	4119343	6.886

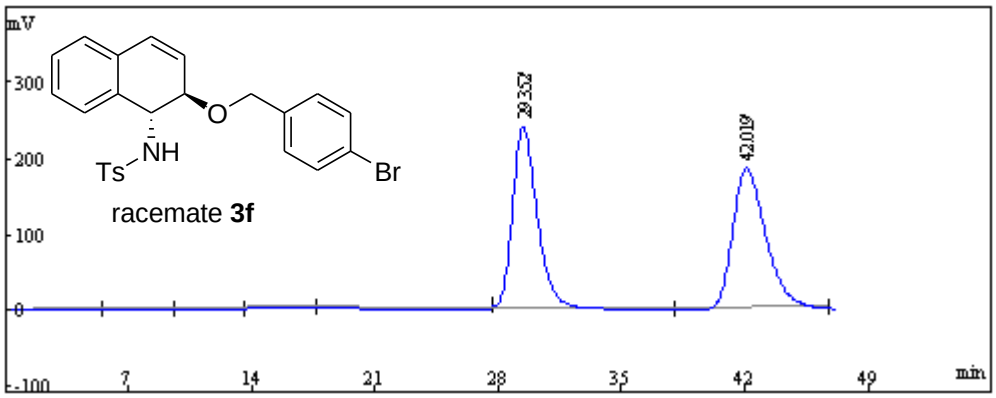


racemate 3h

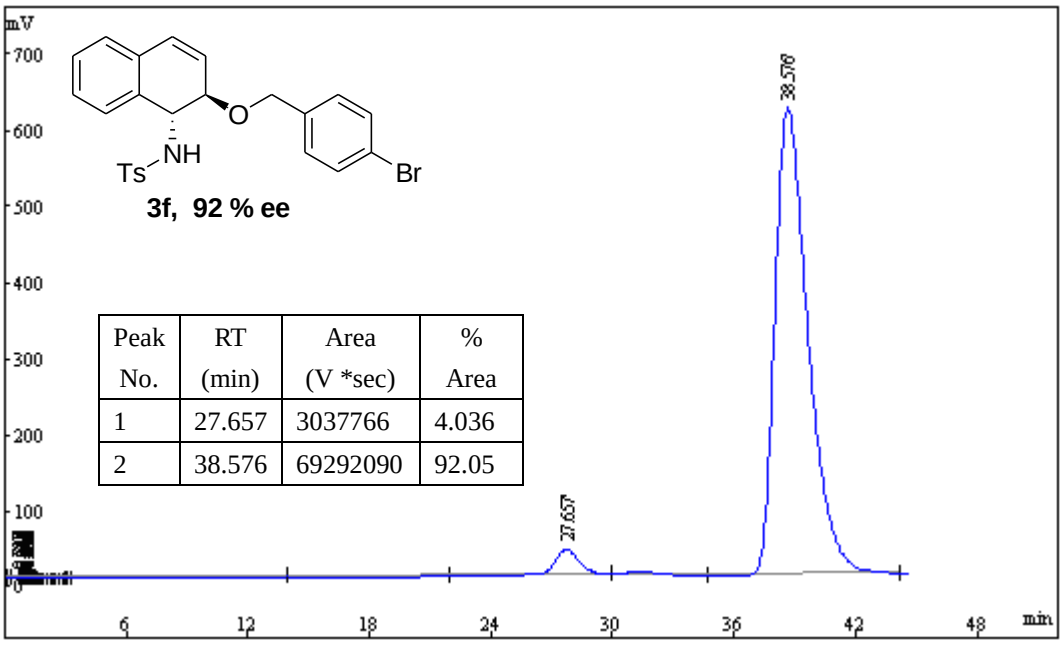


3h, 78 % ee

Peak No.	RT (min)	Area (V *sec)	% Area
1	26.363	3001297	10.58
2	29.247	24376277	85.91



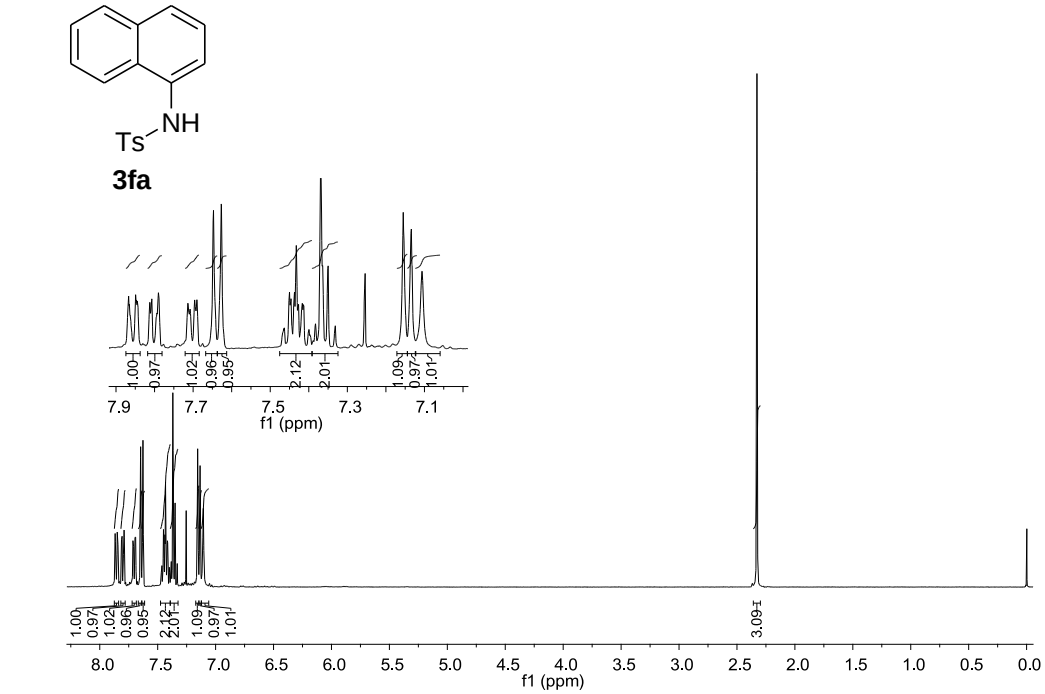
racemate **3f**

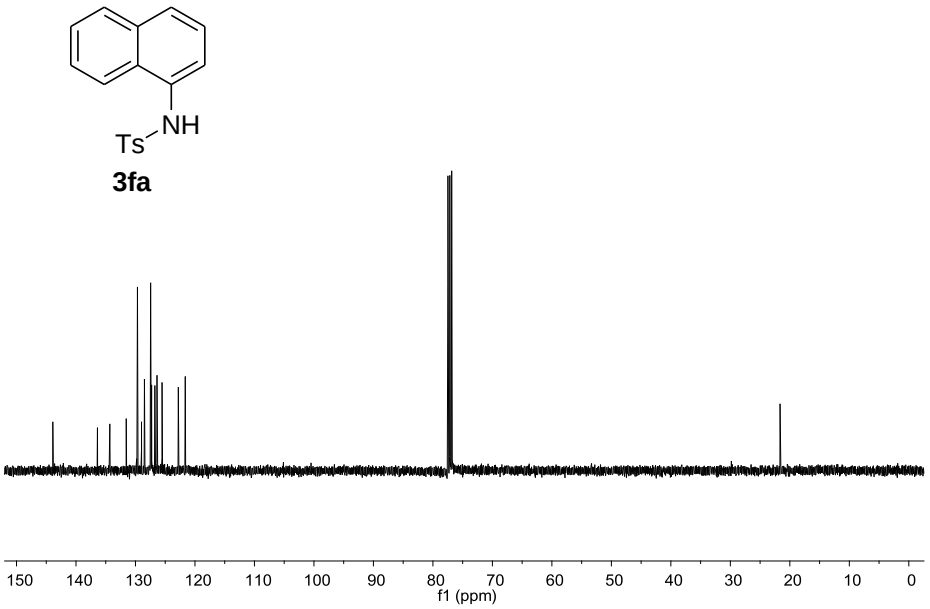


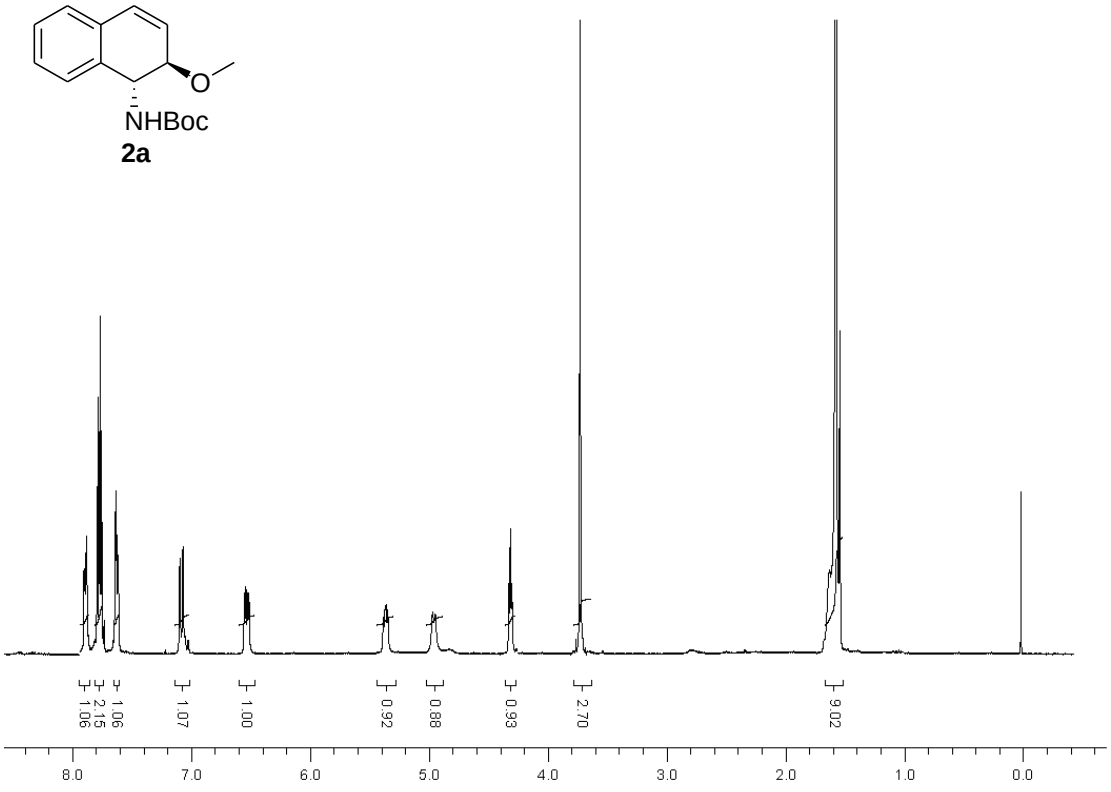
3f, 92 % ee

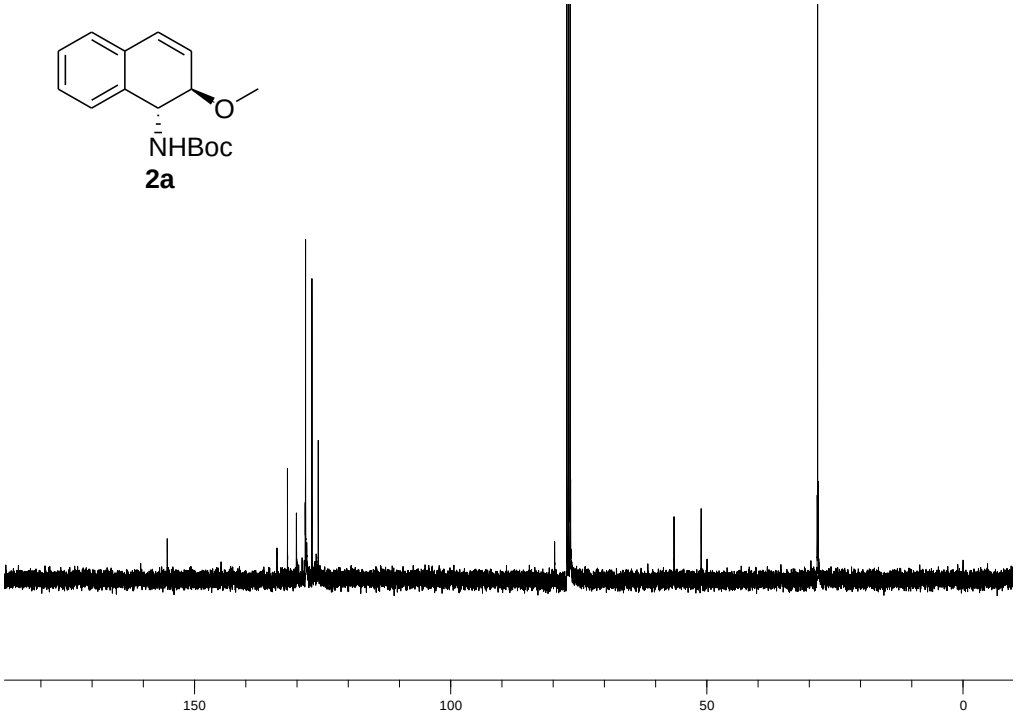
Peak No.	RT (min)	Area (V *sec)	% Area
1	27.657	3037766	4.036
2	38.576	69292090	92.05

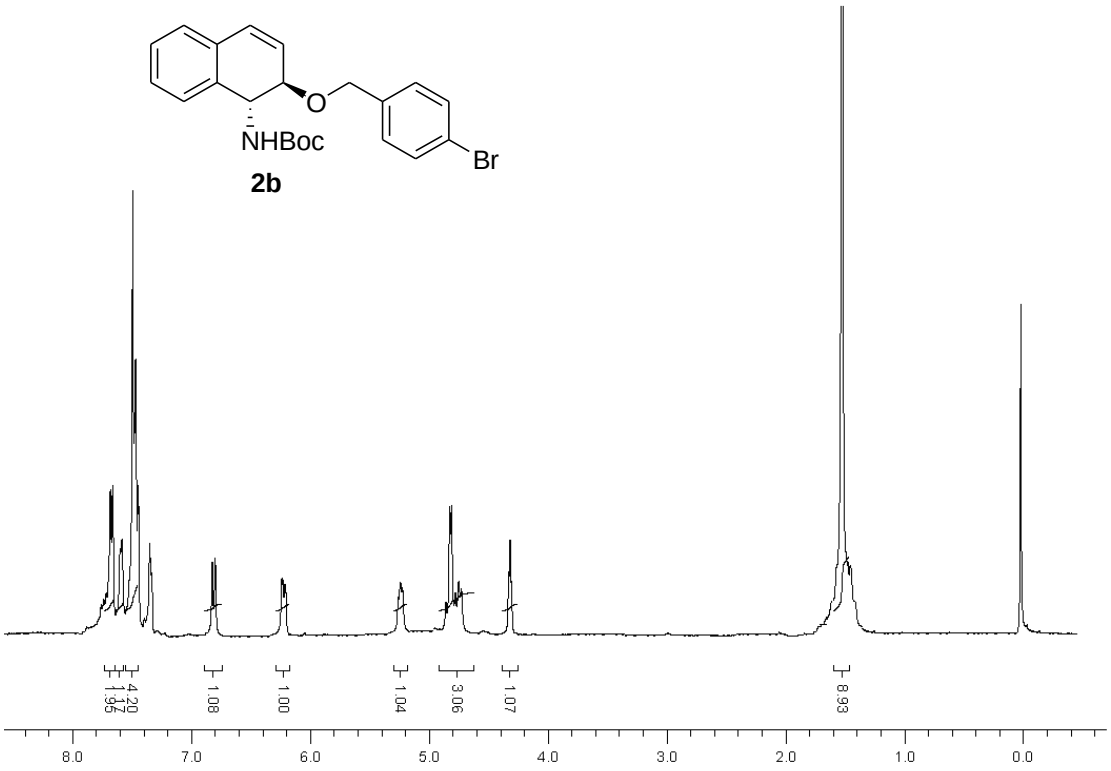
5. Copies of ^{1}H and ^{13}C NMR spectra of 3fa, 2a─2b, 3a─3l, 4a─4c, 5a and 6a─6d.

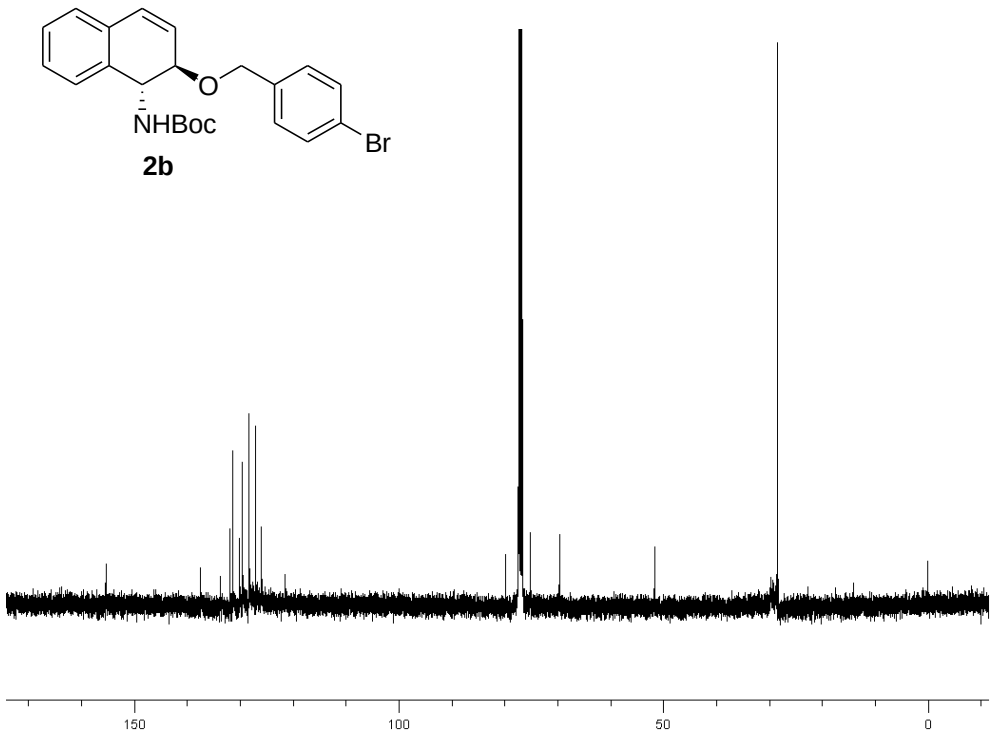


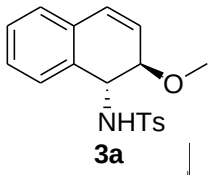












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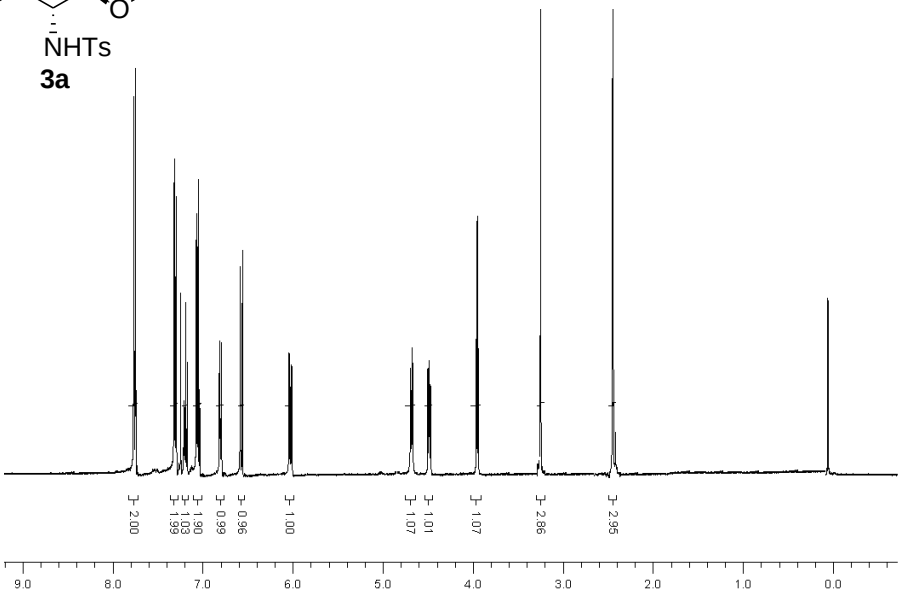

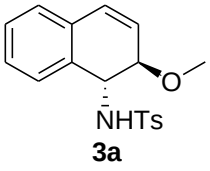

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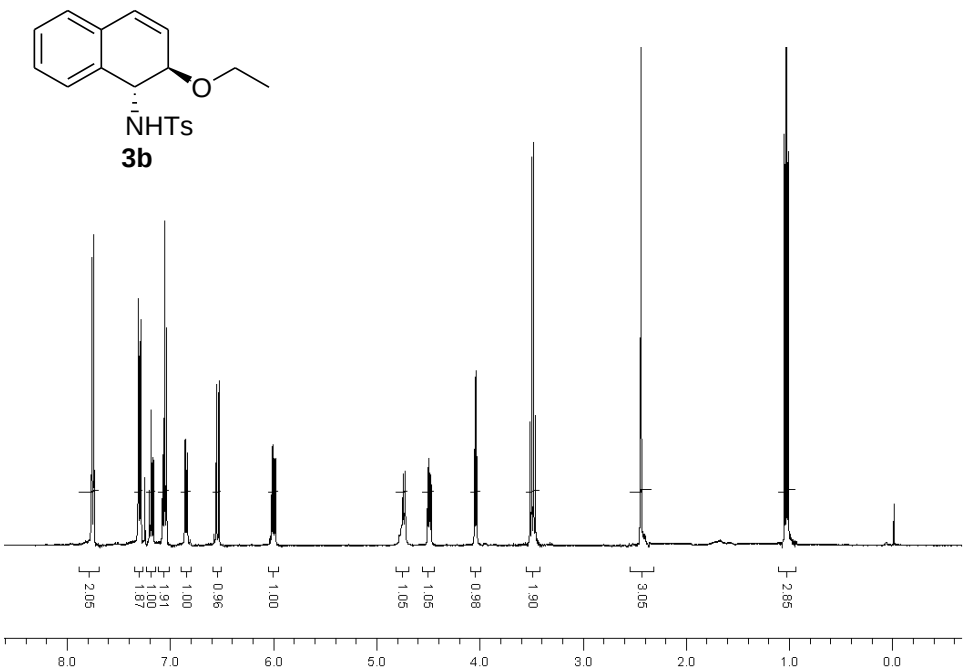

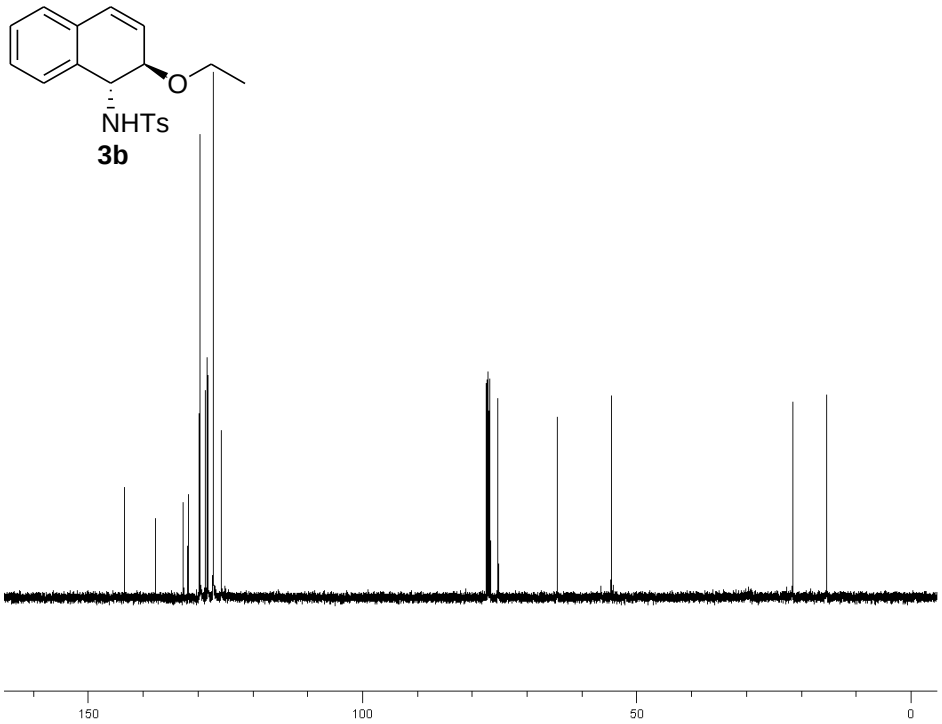

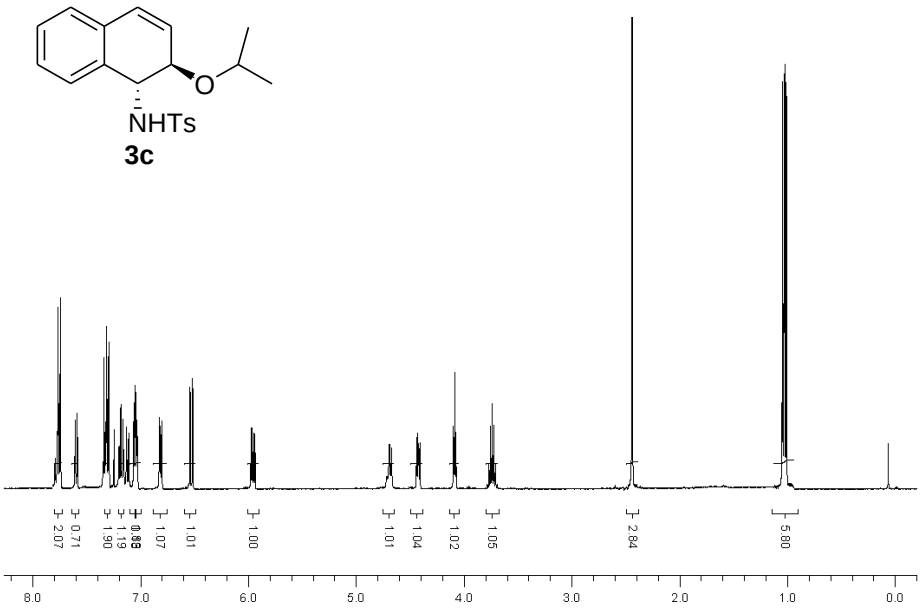

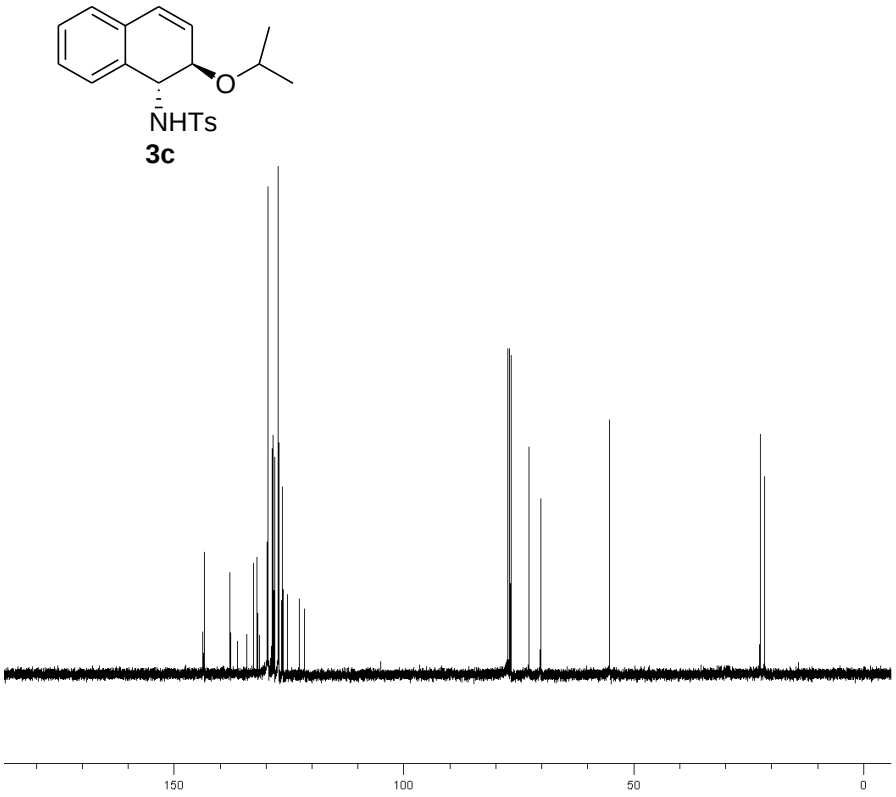

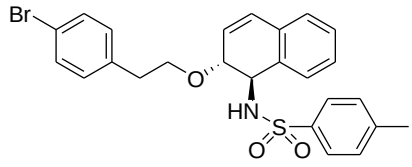

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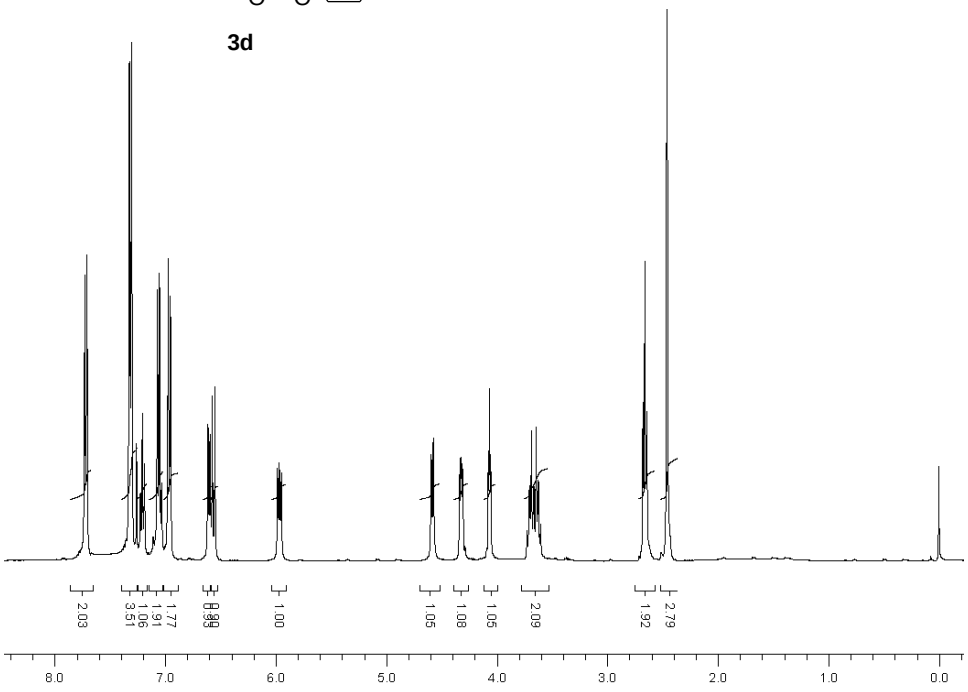

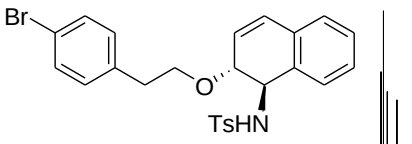

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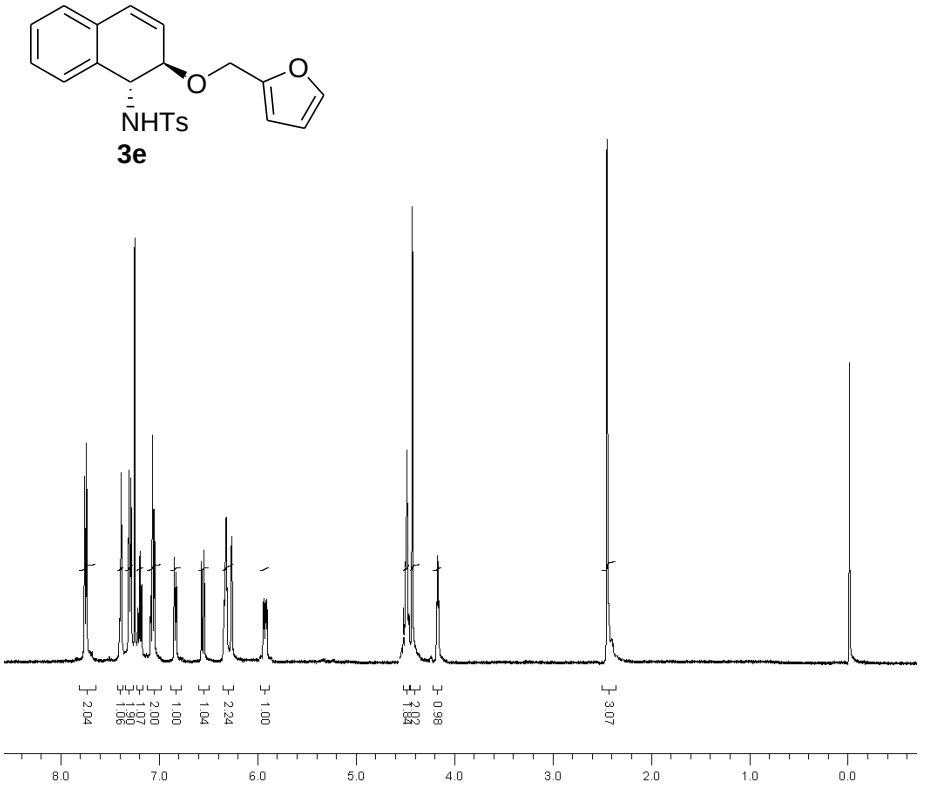

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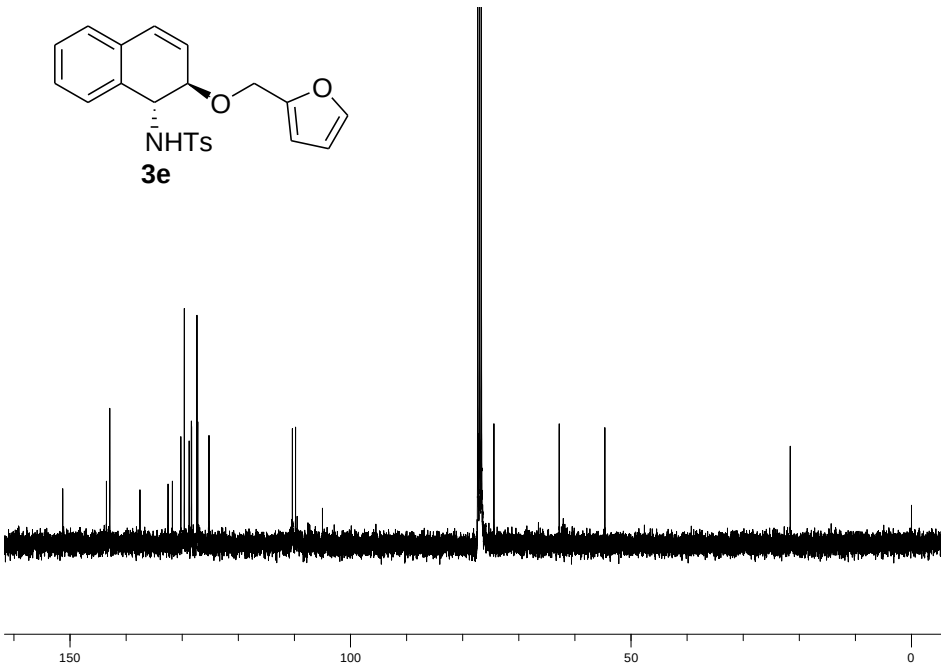

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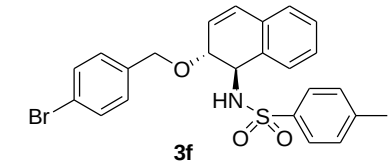

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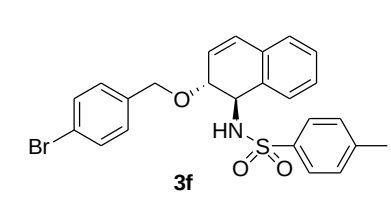

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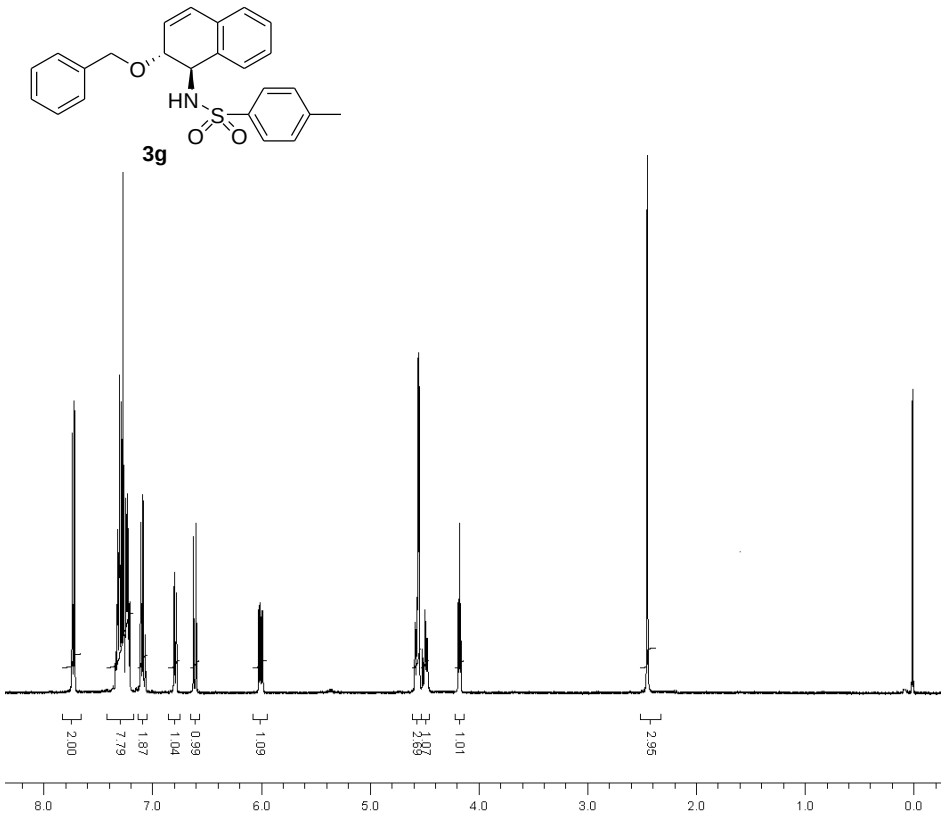

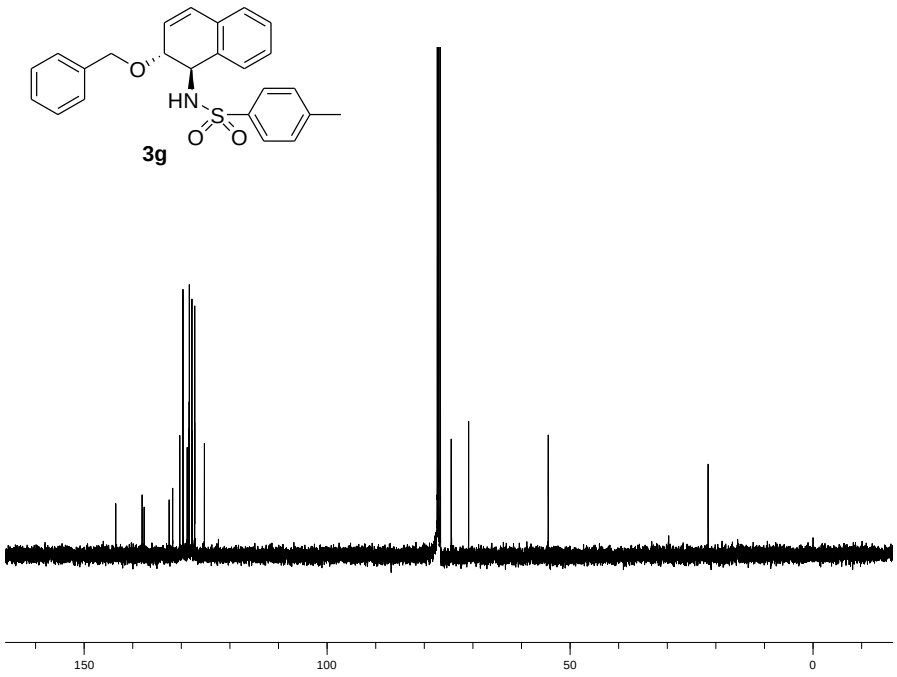

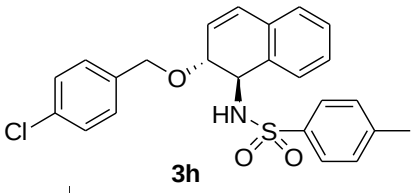

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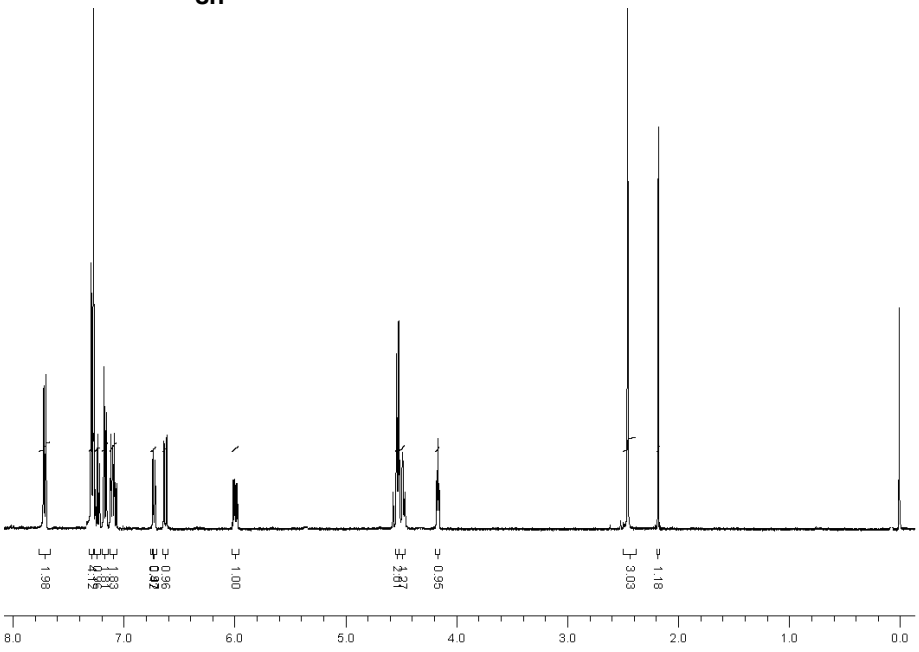

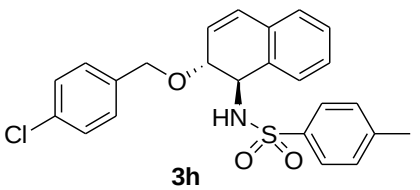

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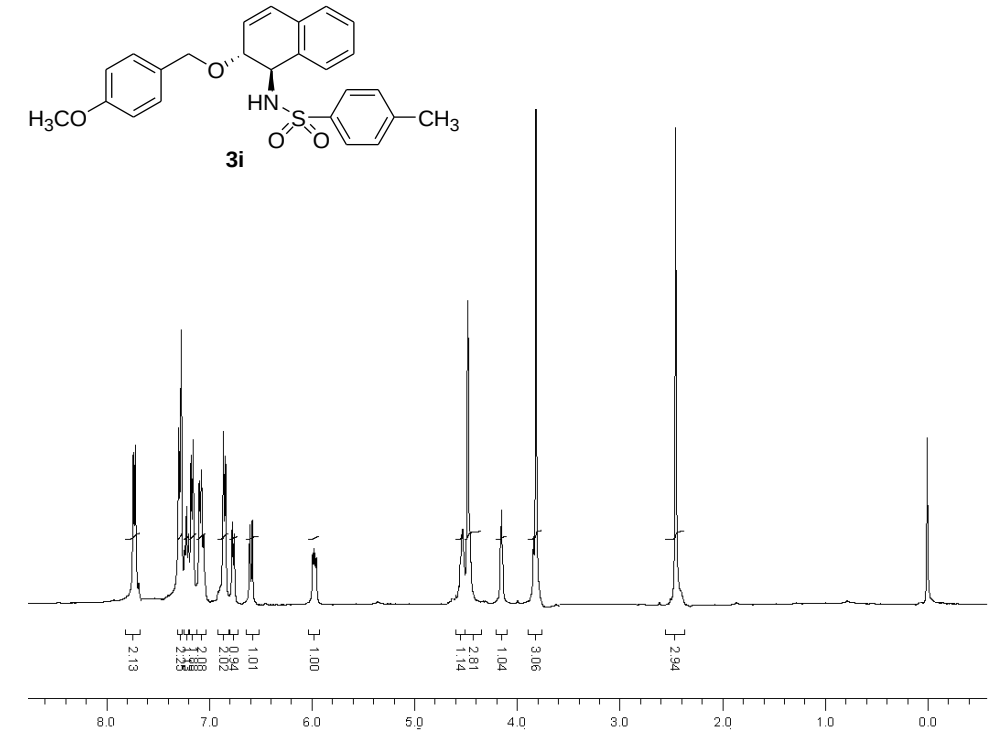

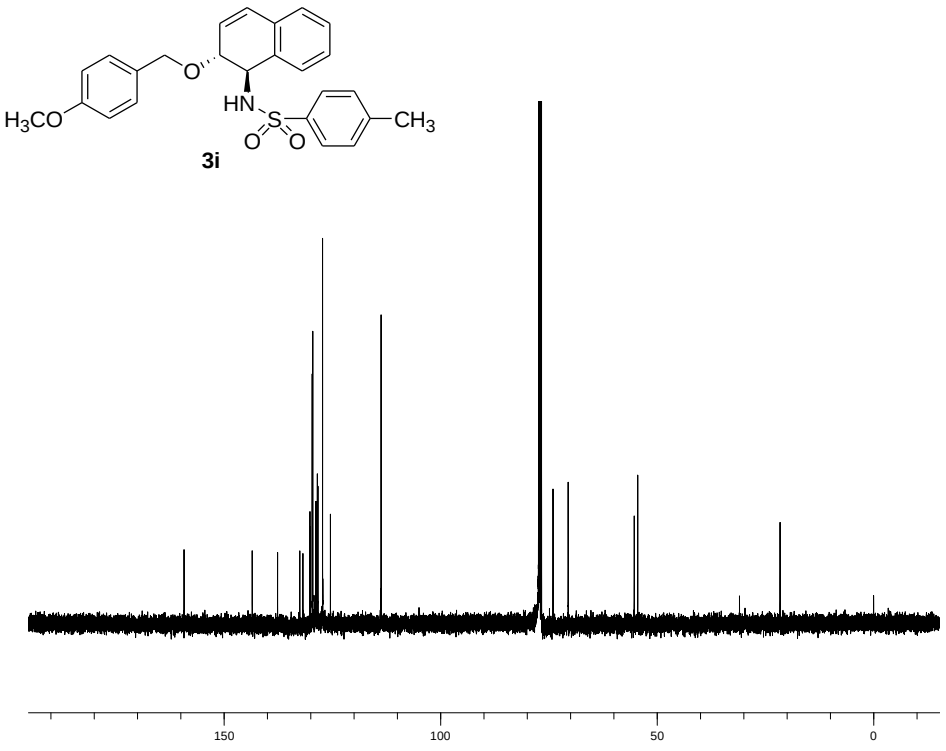

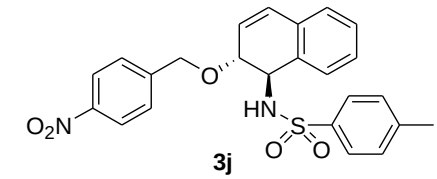

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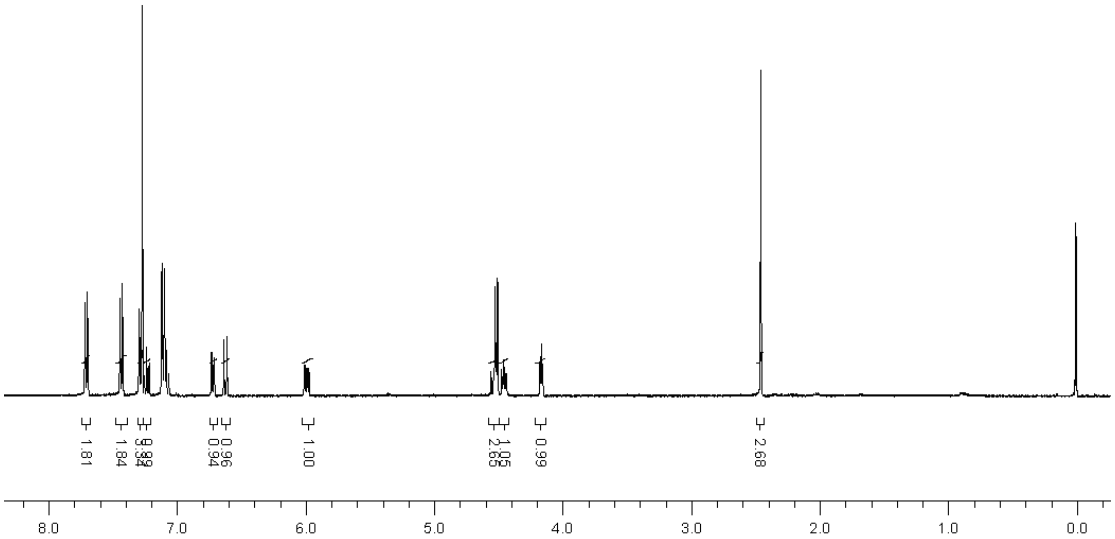

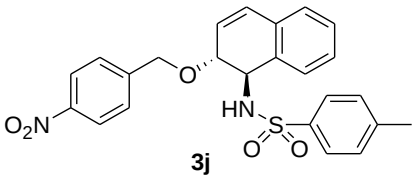

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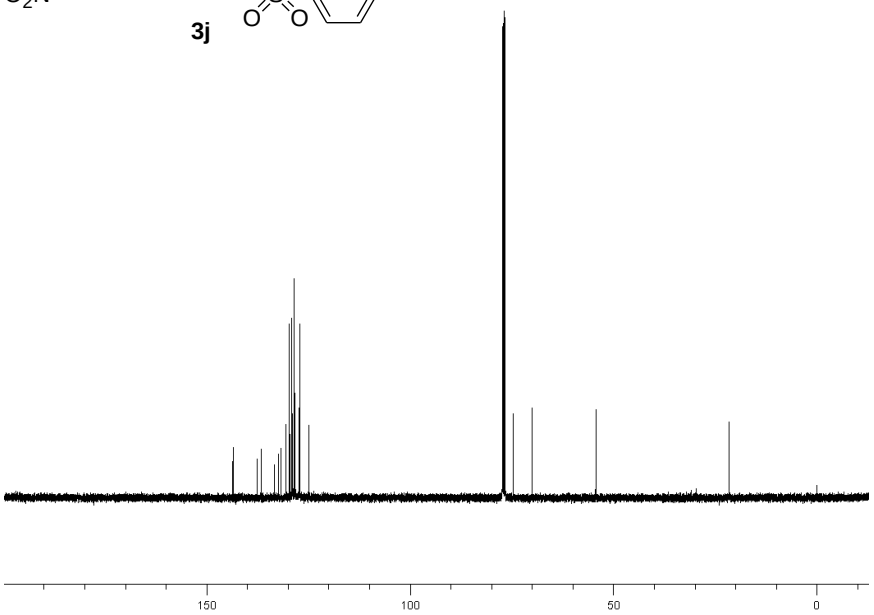

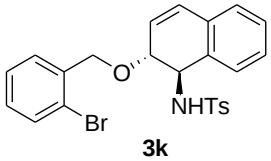

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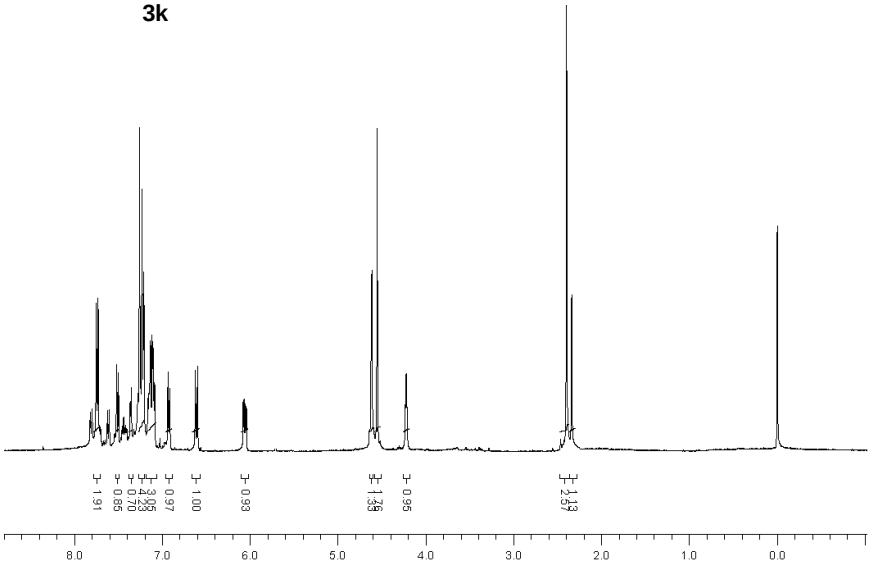

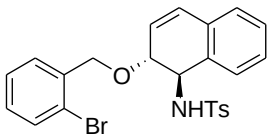

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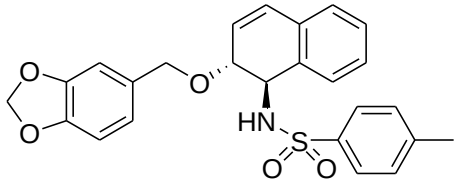

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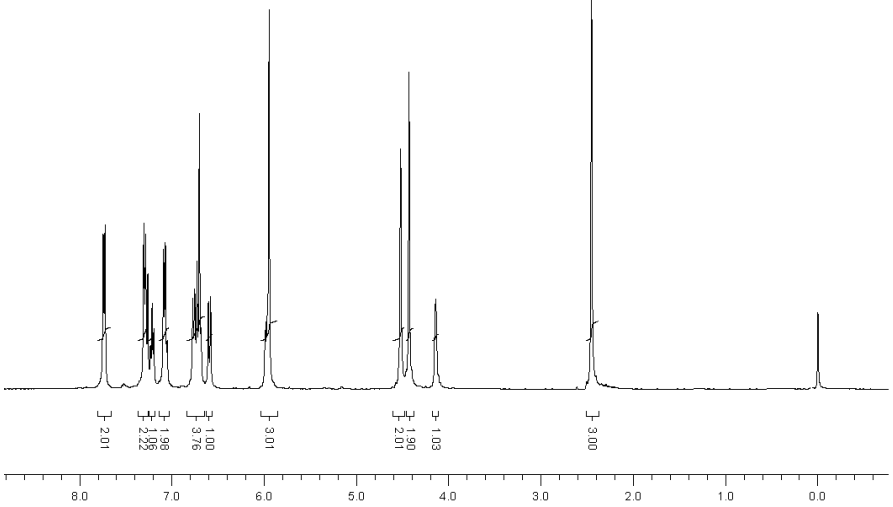

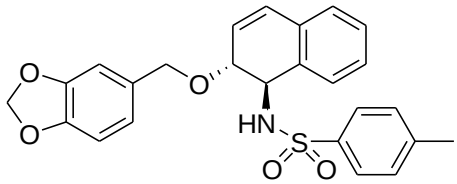

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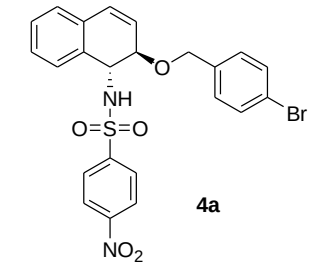

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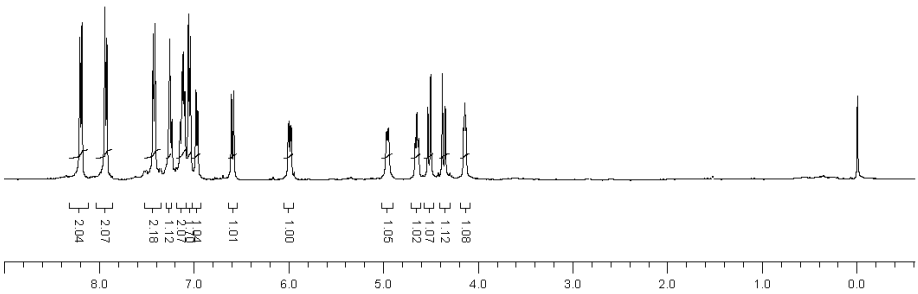

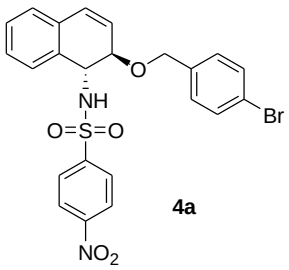

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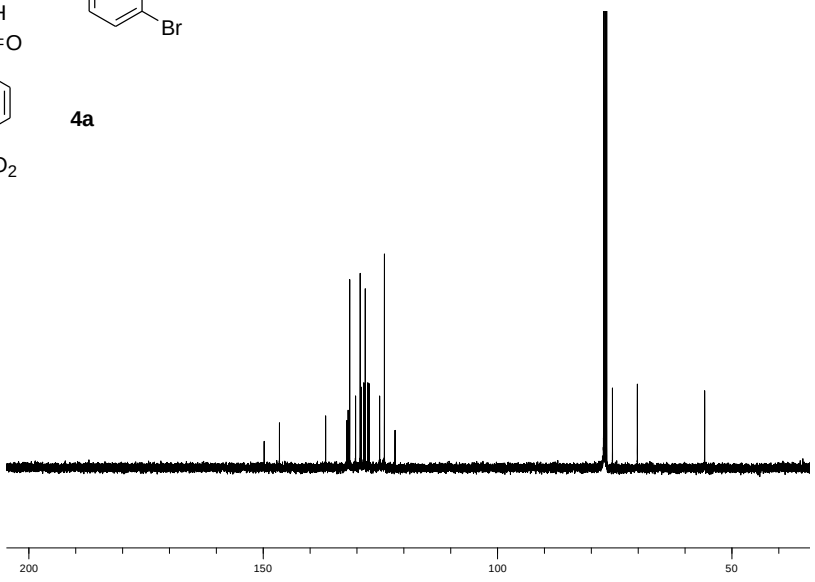

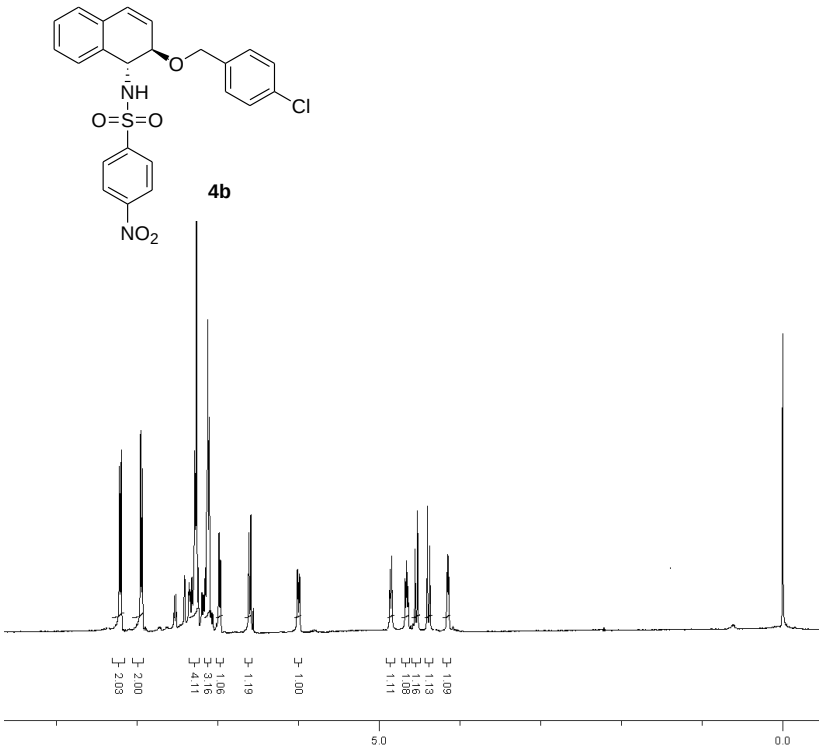

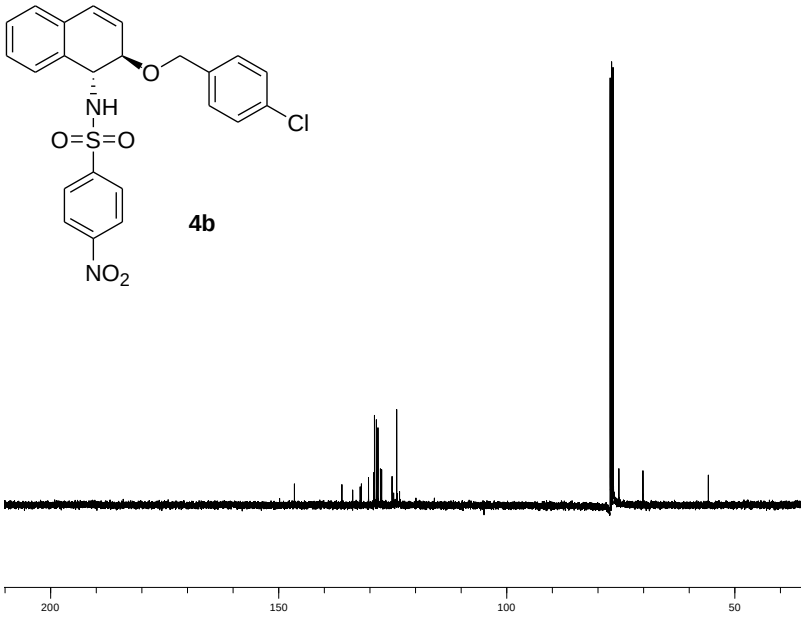

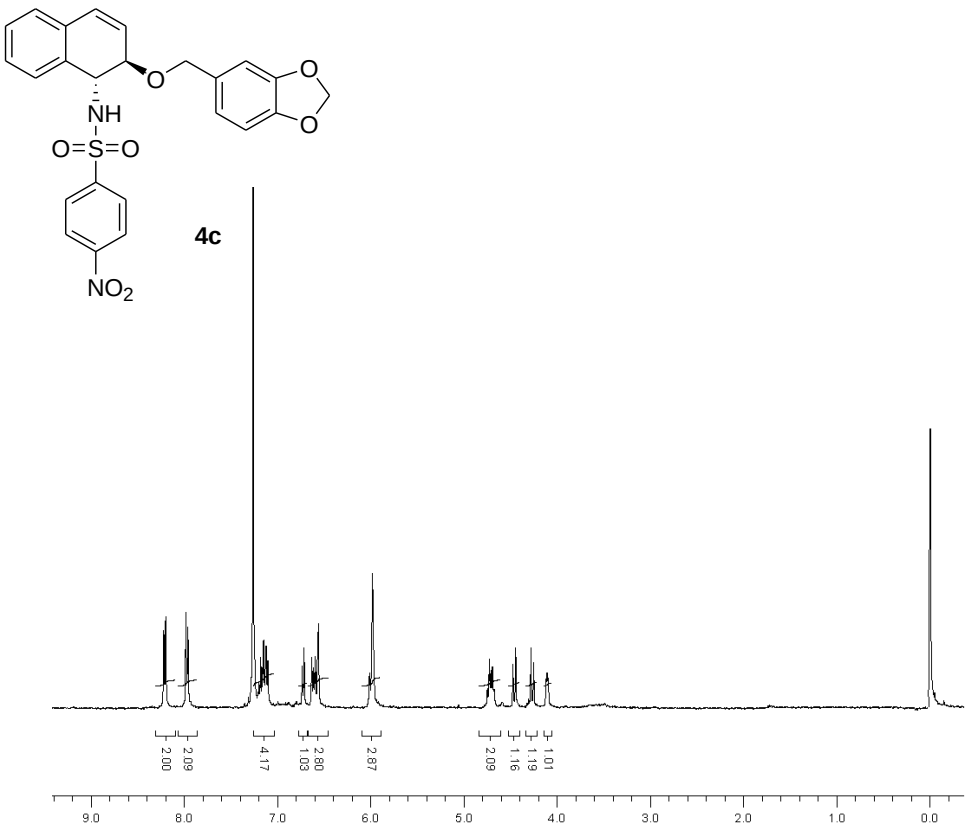

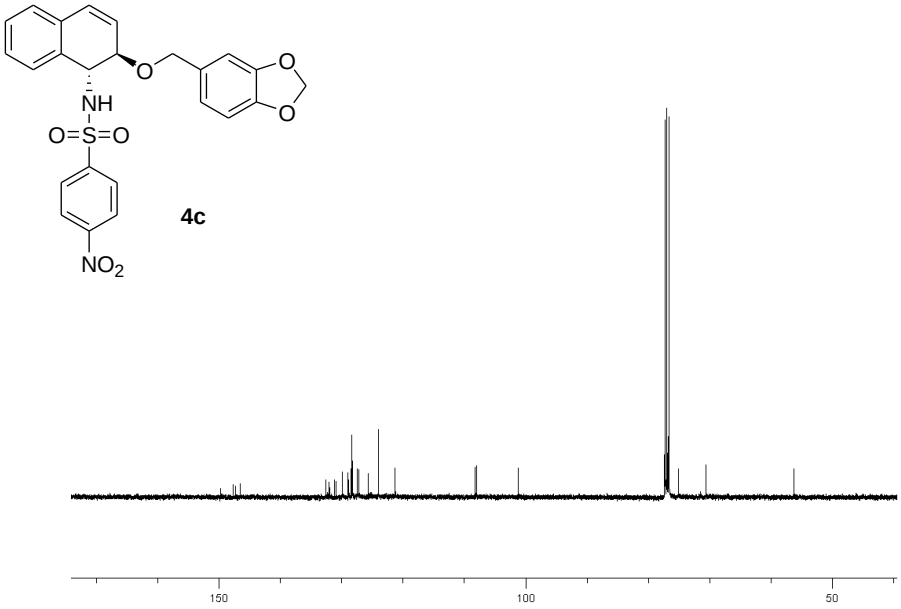

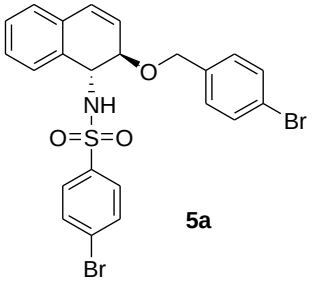

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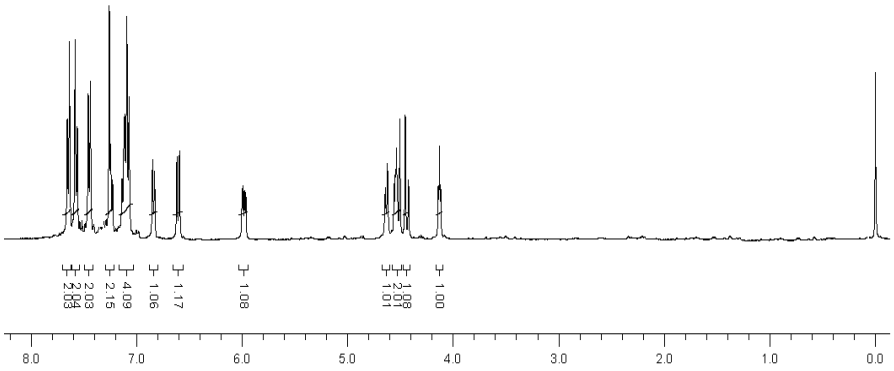

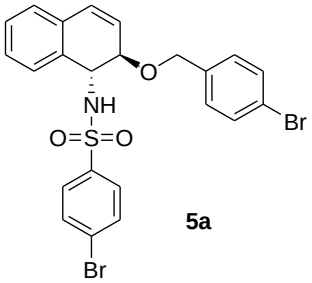

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