General Information: Starting materials, reagents, and solvents were purchased from commercial sources and used as received unless stated otherwise. Pyrrolidine, piperidine, morpholine, benzaldehyde, 2-chlorobenzaldehyde, 3-chlorobenzaldehyde, p-tolualdehyde, *p*-anisaldehyde and ethyl glyoxalate were distilled prior to use. 4-Chlorophenol was purified by Kugelrohr distillation. 4-Chlorobenzaldehyde was recrystallized from ethanol/H₂O. 2-Naphthol was recrystallized from toluene/ethanol. Microwave reactions were carried out in a CEM Discover reactor. Silicon carbide (SiC) passive heating elements were purchased from Anton Paar. Purification of reaction products was carried out by flash column chromatography using Sorbent Technologies Standard Grade silica gel (60 Å, 230–400 mesh). Analytical thin layer chromatography was performed on EM Reagent 0.25 Visualization was accomplished with UV light or mm silica gel 60 F_{254} plates. Dragendorff-Munier stains, followed by heating. Melting points were recorded on a Thomas Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on an ATI Mattson Genesis Series FT-Infrared spectrophotometer. Proton nuclear magnetic resonance spectra (¹H-NMR) were recorded on a Varian VNMRS-500 MHz or Varian VNMRS-400 MHz and chemical shifts are reported in ppm using the solvent as an internal standard (CDCl₃ at 7.26 ppm). Data are reported as app = apparent, s = singlet, d =doublet, t = triplet, q = quartet, m = multiplet, comp = complex, br = broad; coupling constant(s) in Hz. Proton-decoupled carbon nuclear magnetic resonance spectra (¹³C-NMR) were recorded on a Varian VNMRS-500 MHz or Varian VNMRS-400 MHz and chemical shifts are reported in ppm using the solvent as an internal standard (CDCl₃ at 77.0 ppm). Mass spectra were recorded on a Finnigan LCQ-DUO mass spectrometer. Ratios of diastereomeric products were determined by ¹H-NMR analysis of the crude reaction mixture.

General Procedure A for the Synthesis of Starting Materials:¹

A solution of the amine (7.5 mmol, 1 equiv), 2-naphthol (7.5 mmol, 1 equiv) and the aldehyde (9.75 mmol, 1.3 equiv) in the specified solvent (4 mL) was stirred at the given temperature. The reaction progress was monitored by TLC. When complete, the reaction mixture was allowed to cool to room temperature and the product was purified as specified.

General Procedure B for the Synthesis of Starting Materials:²

To a solution of the corresponding amine (7.5 mmol, 1 equiv) in ethanol (95%, 4 mL) cooled in an ice bath was added formaldehyde (7.5 mmol, 1 equiv, 37% water solution) dropwise. After a few minutes, a solution of the corresponding 2-naphthol (7.5 mmol, 1 equiv) in ethanol (95%, 3 mL) was added. The mixture was stirred at room temperature for 1 hour and the product was purified as specified.

General Procedure for the Redox-Neutral α,β-Difunctionalization of Amines:

A 10 mL microwave reaction tube was charged with a 10 x 8 mm SiC passive heating element, the 1-(aminomethyl)- β -naphthol or 2-(aminomethyl)-phenol (0.5 mmol, 1 equiv), toluene (2 mL) and the aldehyde (0.55 mmol, 1.1 equiv). The reaction tube was sealed with a Teflon-lined snap cap, and heated in a microwave reactor at 200 °C (200 W, 70–100 psi, for substrates containing a pyrrolidine moiety) or 250 °C (200W, 150–200 psi, for substrates containing piperidine/morpholine moieties) for 15 minutes. After cooling with compressed air flow, the solution was transferred to a 50 mL round-bottom flask. The solvent was then removed under reduced pressure and the residue was purified by silica gel chromatography.

Procedure for the One-pot Redox-Neutral *α*,β-Difunctionalization of Pyrrolidine:

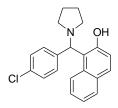
A 35 mL microwave reaction tube was charged with 4Å molecular sieves (200 wt%), 2-naphthol (5 mmol, 1 equiv), toluene (20 mL), benzaldehyde (10.5 mmol, 2.1 equiv) and pyrrolidine (5 mmol, 1 equiv). The mixture was stirred at room temperature for 5 hours at which time 2-naphthol was consumed as judged by TLC analysis. The stir bar was removed and a 10 x 18 mm SiC passive heating element was added. The reaction tube was sealed with a Teflon-lined snap cap, and heated in a microwave reactor at 200 °C (200 W, 110–130 psi) for 15 minutes. After cooling with compressed air flow, the solution was transferred to a 250 mL round-bottom flask. The solvent was then removed under reduced pressure and the residue was purified by silica gel chromatography.

Note: SiC passive heating elements must not be used in conjunction with stir bars; they may score glass and cause vessel failure.

1-(phenyl(pyrrolidin-1-yl)methyl)naphthalen-2-ol (2a): The title compound was synthesized following the general procedure A. Ethanol (95%) was used as the solvent and the reaction conducted under reflux. Upon completion, the reaction mixture was allowed to cool to room temperature. The resulting precipitate was filtered and washed with cold ethanol. After drying under high vacuum, the product was obtained as a white solid in 77% yield. Compound **2a** was previously reported and its published characterization data matched our own in

all respects.¹

1-((4-chlorophenyl)(pyrrolidin-1-yl)methyl)naphthalen-2-ol (2b): The title compound



299.9 $[M + H]^+$.

was synthesized following the general procedure A. Ethanol (95%) was used as the solvent and the reaction conducted under reflux. Upon completion, the reaction mixture was allowed to cool to room temperature. The solvent was then removed under reduced pressure. The residue was purified by silica gel chromatography, followed by recrystallization from hexanes/ethyl acetate. After drying under high vacuum, the product was

obtained as colorless crystals in 56% yield. Compound **2b** was previously reported and its published characterization data matched our own in all respects.³

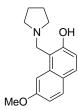
ethyl-2-(2-hydroxynaphthalen-1-yl)-2-(pyrrolidin-1-yl)acetate (2c): The title compound was synthesized following the general procedure A. Toluene was used as the solvent and the reaction conducted at room temperature. Upon completion, the solvent was removed under reduced pressure. The residue was purified

by silica gel chromatography. After drying under high vacuum, the product was obtained as a white solid in 48% yield (R_f = 0.26 in hexanes/ethyl acetate 85:15 v/v); mp: 93–95 °C; IR (KBr) 3054, 2980, 2876, 2819, 1736, 1622, 1596, 1522, 1470, 1418, 1369, 1349, 1326, 1270, 1242, 1210, 1187, 1138, 1022, 949, 911, 850, 828, 756 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) 12.08 (br s, 1H), 8.05 (d, *J* = 8.6 Hz, 1H), 7.77–7.73 (m, 1H), 7.70 (d, *J* = 8.9 Hz, 1H), 7.52–7.45 (m, 1H), 7.34–7.27 (m, 1H), 7.11 (d, *J* = 8.9 Hz, 1H), 4.91 (s, 1H), 4.18–4.05 (comp, 2H), 2.95–2.61 (comp, 4H), 1.96–1.86 (comp, 4H), 1.13 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 169.7, 156.8, 132.2, 130.5,

1-(pyrrolidin-1-ylmethyl)naphthalen-2-ol (2d): The title compound was synthesized following the general procedure B. Upon completion, the resulting precipitate was filtered and washed with cold ethanol, followed by recrystallization from ethanol. After drying under high vacuum, the product was obtained as colorless crystals in 56% yield. Compound 2d was previously reported and its published characterization data matched our own in all respects.²

128.7, 128.5, 126.7, 122.6, 121.7, 119.5, 110.5, 67.9, 61.2, 52.4, 23.5, 14.0; *m/z* (ESI-MS)

7-methoxy-1-(pyrrolidin-1-ylmethyl)naphthalen-2-ol (2e): The title compound was



synthesized following the general procedure B. Upon completion, the resulting precipitate was filtered and washed with cold ethanol, followed by recrystallization from ethanol. After drying under high vacuum, the product was obtained as colorless crystals in 65% yield ($R_f = 0.15$ in hexanes/ethyl acetate 20:80 v/v); mp: 118–121 °C; IR (KBr) 3061, 3031, 3004, 2964, 2873, 2829, 1624, 1518, 1490, 1471, 1390, 1340, 1314, 1265, 1229, 1133, 1060,

1028, 931, 839, 823, 809 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) 12.2 (br s, 1H), 7.66 (d, J = 8.9 Hz, 1H), 7.61 (d, J = 8.7 Hz, 1H), 7.10 (d, J = 2.4 Hz, 1H), 7.00–6.96 (comp, 2H), 4.23 (s, 2H), 3.93 (s, 3H), 2.82–2.71 (comp, 4H), 1.95–1.87 (comp, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 158.1, 157.2, 133.4, 130.2, 128.7, 123.6, 116.6, 113.9, 110.8, 100.7, 55.1, 54.2, 53.8, 23.6; m/z (ESI–MS) 258.0 [M + H]⁺.

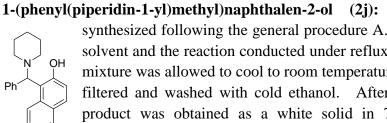
6-bromo-1-(pyrrolidin-1-ylmethyl)naphthalen-2-ol (2f): The title compound was synthesized following the general procedure B. Upon completion, the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography. After drying under high vacuum, the product was obtained as a yellow oil in 55% yield. Compound 2f was previously reported and its published characterization data matched our own in all respects.²

4-chloro-2-(phenyl(pyrrolidin-1-yl)methyl)phenol (2g): The title compound was synthesized following the general procedure A. Toluene was used as the ΟН solvent and the reaction conducted at 80 °C. Upon completion, the reaction mixture was allowed to cool to room temperature. Ph The solvent was then removed under reduced pressure. The residue was purified by silica gel ċι chromatography. After drying under high vacuum, the product was obtained as a yellow oil in 40% yield ($R_f = 0.38$ in hexanes/EtOAc 90:10 v/v); IR (KBr) 3061, 3028, 2972, 2877, 2821, 2681, 1605, 1583, 1478, 1453, 1385, 1255, 1168, 1108, 1033, 890, 817, 727, 698, 645 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) 12.45 (br s, 1H), 7.50–7.43 (m, 2H), 7.34–7.22 (comp, 3H), 7.07 (dd, J = 8.7, 2.6 Hz, 1H), 6.97 (d, J = 2.6 Hz, 1H), 6.82 (d, J =8.7 Hz, 1H), 4.34 (s, 1H), 2.63 (br s, 2H), 2.54–2.41 (m, 2H), 1.90–1.75 (comp, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 155.3, 141.3, 128.7, 128.1, 127.9(2), 127.8(8), 127.6, 123.4, 118.1, 75.1, 53.0, 23.3; m/z (ESI–MS) 287.9 [M + H]⁺.

4-methoxy-2-(phenyl(pyrrolidin-1-yl)methyl)phenol (2h): The title compound was synthesized following the general procedure A. Toluene was used as the ОН solvent and the reaction conducted at 80 °C. Upon completion, the reaction mixture was allowed to cool to room temperature. The solvent was then removed under reduced pressure. The residue was purified by silica gel ÓМе chromatography. After drying under high vacuum, the product was obtained as a yellow oil in 26% yield. Compound 2h was previously reported and its published

characterization data matched our own in all respects.³

2-(pyrrolidin-1-ylmethyl)phenol (2i): Compound 2i was synthesized according to a literature procedure,³ and its published characterization data matched our own in all respects.⁴ ОН



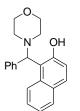
The title compound was synthesized following the general procedure A. Ethanol (95%) was used as the solvent and the reaction conducted under reflux. Upon completion, the reaction mixture was allowed to cool to room temperature. The resulting precipitate was filtered and washed with cold ethanol. After drying under high vacuum, the product was obtained as a white solid in 75% yield. Compound 2j was previously reported and its published characterization data matched our own in

all respects.³

4-chloro-2-(phenyl(piperidin-1-yl)methyl)phenol (2k): The title compound was synthesized following the general procedure A. Toluene was used as the solvent and the reaction conducted at 80 °C. Upon completion, the reaction mixture was allowed to cool to room temperature. The solvent was then removed under reduced pressure. The residue was purified by silica gel chromatography. After drying under high vacuum, the product was obtained as a colorless oil in 51% yield ($R_f = 0.49$ in hexanes/EtOAc 90:10 v/v); IR (KBr)

3061, 3028, 2937, 2855, 2809, 2678, 1604, 1581, 1480, 1453, 1389, 1256, 1167, 1108, 1032, 875, 812, 727, 699 644 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) 12.69 (br s, 1H), 7.48–7.24 (comp, 5H), 7.06 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.87 (d, *J* = 2.6 Hz, 1H), 6.80 (d, *J* = 8.6 Hz, 1H). 4.43 (s, 1H), 2.40 (br s, 4H), 1.72–1.31 (comp, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 155.8, 138.6, 128.8, 128.1(0), 128.0(7), 127.0, 123.3, 118.2, 76.0, 52.4, 25.9, 23.9; *m/z* (ESI-MS) $301.9 [M + H]^+$.

1-(morpholino(phenyl)methyl)naphthalen-2-ol (2l): The title compound was synthesized



following the general procedure A. Toluene was used as the solvent and the reaction conducted at 80 °C. Upon completion, the reaction mixture was allowed to cool to room temperature. The solvent was then removed under reduced pressure. The residue was purified by silica gel chromatography, followed by recrystallization from hexanes/ethyl acetate. After drying under high vacuum, the product was obtained as colorless crystals in 42% yield.

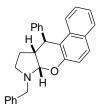
Compound **2l** was previously reported and its published characterization data matched our own in all respects.³

1-((*cis*-2,6-dimethylmorpholino)methyl)naphthalen-2-ol (2m): The title compound was synthesized following the general procedure B. Upon completion, the Me solvent was removed under reduced pressure. The residue was purified by ОН silica gel chromatography. After drying under high vacuum, the product was obtained as a colorless oil in 85% yield ($R_f = 0.28$ in hexanes/EtOAc 90:10 v/v); IR (KBr) 3055, 2973, 2934, 2856, 1622, 1599, 1522, 1469, 1413, 1369, 1320, 1264, 1236, 1143, 1083, 1000, 882. 816, 747, 706 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) 11.47 (br s, 1H), 7.84 (app d, J = 8.6 Hz, 1H), 7.79 (app d, J = 8.1 Hz, 1H), 7.73 (d, J = 8.8 Hz, 1H), 7.48 (app t, J = 7.5 Hz, 1H), 7.33 (app t, J = 7.5 Hz, 1H), 7.16 (d, J= 8.8 Hz, 1H), 4.11 (s, 2H), 3.82–3.73 (m, 2H), 2.91 (app d, J = 11.2 Hz, 2H), 1.95 (app t, J = 10.9 Hz, 2H), 1.19 (d, J = 6.3 Hz, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 156.1, 132.5, 129.2, 128.8, 128.4, 126.3, 122.4, 120.8, 119.0, 110.3, 71.5, 58.4, 56.2, 18.8; *m/z* (ESI-MS) 271.8 $[M + H]^{+}$.

1-(thiomorpholinomethyl)naphthalen-2-ol (2n): The title compound was synthesized following the general procedure B. Upon completion, the resulting precipitate was filtered and washed with cold ethanol, followed by recrystallization from acetone. After drying under high vacuum, the product was obtained as light yellow crystals in 82% yield ($R_f = 0.38$ in hexanes/ethyl acetate 85:15 v/v); mp: 156–158 °C; IR (KBr) 3056, 2970, 2915, 2838, 1621, 1597, 1518, 1471, 1362, 1298, 1238, 1161, 1127, 1100, 1007, 951, 814, 751, 710 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) 11.75 (br s, 1H), 7.81 (app d, *J* = 8.6 Hz, 1H), 7.77 (app d, *J* = 8.1 Hz, 1H), 7.71 (d, *J* = 8.8 Hz, 1H), 7.49–7.43 (m, 1H), 7.34–7.28 (m, 1H), 7.12 (d, *J* = 8.8 Hz, 1H), 4.15 (s, 2H), 3.03–2.70 (comp, 8H); ¹³C NMR (125 MHz, CDCl₃) δ 156.2, 132.6, 129.3, 128.8, 128.5, 126.4, 122.5, 120.8, 119.0, 110.3, 57.0, 54.5, 27.8; *m/z* (ESI–MS) 259.9 [M + H]⁺.

benzyl-4-((2-hydroxynaphthalen-1-yl)methyl)piperazine-1-carboxylate (20): The title compound was synthesized following the general procedure B. Upon completion, the resulting precipitate was filtered and washed with cold ethanol. After drying under high vacuum, the product was obtained as a white solid in 73% yield ($R_f =$ 0.37 in hexanes/ethyl acetate 70:30 v/v); mp: 103–104 °C; IR (KBr) 3061, 3029, 2954, 2900, 2853, 1698, 1622, 1599, 1521, 1458, 1429, 1361, 1325, 1290, 1269, 1234, 1133, 1086, 995, 939, 906, 816, 764, 741, 696 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) 11.61 (br s, 1H), 7.83–7.75 (comp, 2H), 7.71 (d, J = 8.8 Hz, 1H), 7.45 (app td, J = 6.8, 1.4 Hz, 1H), 7.40–7.28 (comp, 6H), 7.12 (d, J = 8.8 Hz, 1H), 5.15 (s, 2H), 4.19 (s, 2H), 3.91–3.39 (comp, 4H), 2.90–2.46 (br s, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 156.1, 155.0, 136.4, 132.6, 129.6, 128.9, 128.6, 128.5, 128.1, 127.9, 126.5, 122.7, 120.9, 119.1, 110.3, 67.4, 56.1, 52.4, 43.5; m/z (ESI–MS) 377.2 [M + H]⁺.

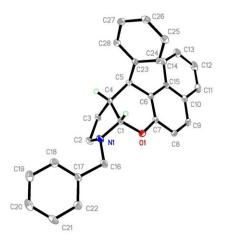
7a-trans-10a-trans-8-benzyl-11-phenyl-7a,8,9,10,10a,11-hexahydrobenzo[5,6]chromeno[



2,3-b]pyrrole (7a): Following the general procedure compound **7a** was obtained from the corresponding 1-(aminomethyl)- β -naphthol and benzaldehyde as an off-white solid in 81% yield ($R_f = 0.33$ in hexanes/ethyl ether 93:7 v/v); mp: 162–163 °C; IR (KBr) 3078, 3063, 2952, 2876, 2834, 1621, 1597, 1492, 1464, 1451, 1366, 1228, 1192, 1153, 1066, 1025, 958, 816, 749, 728, 700 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) 7.86–7.79

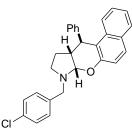
(comp, 2H), 7.68 (d, J = 8.4 Hz, 1H), 7.48–7.42 (comp, 2H), 7.41–7.35 (comp, 3H), 7.35–7.27 (comp, 5H), 7.26–7.19 (comp, 3H), 5.19 (d, J = 3.9 Hz, 1H), 4.64 (s, 1H), 4.37 (d, J = 13.5 Hz, 1H), 4.00 (d, J = 13.5 Hz, 1H), 3.08 (app td, J = 8.8, 5.5 Hz, 1H), 3.01 (app tdd, J = 9.9, 3.9, 1.7 Hz, 1H), 2.86–2.79 (m, 1H), 2.32–2.22 (m, 1H), 1.75 (app dtd, 12.6, 10.3, 5.5 Hz, 1H); ¹³C NMR (125 MHz, CDCl3) δ 152.9, 145.3, 139.1, 133.2, 129.2, 129.0, 128.7, 128.6, 128.4, 128.2, 127.6, 126.9, 126.4, 126.3, 122.8, 122.3, 118.8, 112.5, 89.6, 53.6, 49.4, 45.8, 41.3, 27.9; m/z (ESI–MS) 392.1 [M + H]⁺.

The title compound was further characterized by X-ray crystallography:



The requisite CIF has been deposited with the CCDC (deposition # 963306).

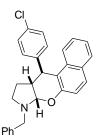
7a-trans-10a-trans-8-(4-chlorobenzyl)-11-phenyl-7a,8,9,10,10a,11-hexahydrobenzo[5,6]c



hromeno[2,3-b]pyrrole (7b): Following the general procedure compound 7b was obtained from the corresponding 1-(aminomethyl)-β-naphthol and 4-chlorobenzaldehyde as a colorless oil in 82% yield ($R_f = 0.33$ in hexanes/ethyl ether 93:7 v/v); IR (KBr) 3059, 3024, 2930, 2873, 2841, 1623, 1599, 1514, 1491, 1402, 1361, 1262, 1226, 1191, 1150, 1081, 1067, 1013, 966, 838, 813, 744, 702 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) 7.89–7.83 (comp, 2H), 7.73 (d, *J*

= 8.4 Hz, 1H), 7.44–7.35 (comp, 6H), 7.35–7.30 (comp, 3H), 7.29–7.22 (comp, 3H), 5.18 (d, J = 3.8 Hz, 1H), 4.68 (s, 1H), 4.34 (d, J = 13.7 Hz, 1H), 3.99 (d, J = 13.7 Hz, 1H), 3.12–2.99 (comp, 2H), 2.86–2.77 (m, 1H), 2.34–2.25 (m, 1H), 1.83–1.72 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 152.7, 145.2, 137.5, 133.1, 132.5, 129.8, 129.2, 129.0, 128.7, 128.4(2), 128.3(6), 127.6, 126.4(1), 126.3(8), 122.9, 122.3, 118.7, 112.5, 89.3, 52.9, 49.4, 45.8, 41.2, 27.8; m/z (ESI–MS) 426.1 [M + H]⁺.

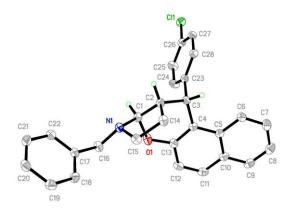
7a-trans-10a-trans-8-benzyl-11-(4-chlorophenyl)-7a,8,9,10,10a,11-hexahydrobenzo[5,6]c



hromeno[2,3-b]pyrrole (7c): Following the general procedure compound 7c was obtained from the corresponding 1-(aminomethyl)-β-naphthol and benzaldehyde as a colorless oil in 75% yield ($R_f = 0.29$ in hexanes/ethyl ether 93:7 v/v); IR (KBr) 3061, 3029, 2930, 2876, 2838, 1623, 1599, 1514, 1489, 1466, 1453, 1401, 1225, 1150, 1069, 1014, 966, 815, 745 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) 7.88–7.82 (comp, 2H), 7.65 (d, J = 8.4 Hz, 1H), 7.51–7.46 (comp, 2H), 7.45–7.39 (comp, 3H), 7.38–7.30 (comp, 3H),

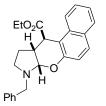
7.30–7.25 (comp, 2H), 7.20–7.14 (comp, 2H), 5.17 (d, J = 3.8 Hz, 1H), 4.62 (s, 1H), 4.39 (d, J = 13.5 Hz, 1H), 4.03 (d, J = 13.5 Hz, 1H), 3.11 (app td, J = 8.9, 5.6 Hz, 1H), 2.99 (app tdd, J = 10.0, 3.8, 1.7 Hz, 1H), 2.89–2.81 (m, 1H), 2.33–2.23 (m, 1H), 1.76 (app dtd, J = 12.6, 10.3, 5.6 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 152.8, 143.7, 138.9, 133.0, 132.1, 129.2(3), 129.2(2), 129.0, 128.8, 128.6, 128.5, 128.2, 126.9, 126.5, 123.0, 122.1, 118.9, 112.0, 89.3, 53.6, 49.3, 45.7, 40.7, 27.8; m/z (ESI–MS) 426.1 [M + H]⁺.

The title compound was further characterized by X-ray crystallography:



The requisite CIF has been deposited with the CCDC (deposition # 963308).

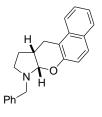
7a-trans-10a-trans-ethyl-8-benzyl-7a,8,9,10,10a,11-hexahydrobenzo[5,6]chromeno[2,3-b]



pyrrole-11-carboxylate (7d): Following the general procedure compound **7d** was obtained from the corresponding 1-(aminomethyl)-β-naphthol and benzaldehyde as a yellow oil in 72% yield ($R_f = 0.40$ in hexanes/ethyl acetate 85:15 v/v); IR (KBr) 3059, 3024, 2976, 2841, 1729, 1624, 1600, 1515, 1467, 1403, 1365, 1329, 1227, 1152, 1074, 1026, 970, 818, 747, 699 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) 7.93 (d, J = 8.5 Hz, 1H), 7.81–7.77 (m,

1H), 7.73 (d, J = 8.9 Hz, 1H), 7.51 (ddd, J = 8.5, 6.9, 1.3 Hz, 1H), 7.46–7.42 (m, 2H), 7.40–7.33 (comp, 3H), 7.32–7.26 (m, 1H), 7.16 (d, J = 8.9 Hz, 1H), 5.44 (d, J = 4.2 Hz, 1H), 4.33 (d, J = 13.4 Hz, 1H), 4.27 (d, J = 1.4 Hz, 1H), 4.17–4.07 (comp, 2H), 3.97 (d, J = 13.4 Hz, 1H), 3.11 (ddd, J = 9.8, 4.2, 1.6 Hz, 1H), 2.99 (td, J = 8.7, 5.6 Hz, 1H), 2.75–2.68 (m, 1H), 2.19–2.10 (m, 1H), 1.54 (app dtd, J = 12.6, 10.0, 5.5 Hz, 1H), 1.18 (t, J = 7.1 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 173.3, 152.8, 138.9, 133.2, 129.5, 129.1, 128.7, 128.5, 128.3, 127.0, 126.6, 123.0, 121.8, 119.2, 109.0, 90.2, 61.1, 53.6, 48.9, 41.5, 39.5, 27.1, 14.1; m/z (ESI–MS) 388.1 [M + H]⁺.

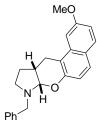
10a-*cis*-8-benzyl-7a,8,9,10,10a,11-hexahydrobenzo[5,6]chromeno[2,3-b]pyrrole (7e):



Following the general procedure compound **7e** was obtained from the corresponding 1-(aminomethyl)- β -naphthol and benzaldehyde as a colorless oil in 73% yield (R_f = 0.22 in hexanes/ethyl ether 93:7 v/v); IR (KBr) 3056, 3027, 2970, 2905, 2852, 1622, 1597, 1512, 1495, 1469, 1452, 1398, 1362, 1317, 1236, 1177, 1152, 1069, 930, 831, 814, 746, 726, 695 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) 7.89–7.83 (comp, 2H), 7.73 (d, *J* = 8.8 Hz, 1H),

7.59–7.49 (comp, 3H), 7.46–7.39 (comp, 3H), 7.38–7.32 (m, 1H), 7.22 (d, J = 8.8 Hz, 1H), 5.09 (d, J = 4.0 Hz, 1H), 4.36 (d, J = 13.4 Hz, 1H), 4.07 (d, J = 13.4 Hz, 1H), 3.26–3.06 (comp, 3H), 3.00–2.93 (m, 1H), 2.92–2.86 (m, 1H), 2.20–2.11 (m, 1H), 1.73 (app dtd, J = 12.5, 10.1, 6.1 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 151.9, 139.1, 133.1, 129.0, 128.7, 128.4, 128.2, 127.7, 126.9, 126.1, 122.9, 121.6, 119.2, 112.4, 91.3, 53.7, 49.7, 36.8, 27.9, 23.8; m/z (ESI–MS) 316.1 [M + H]⁺.

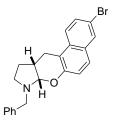
10a-cis-8-benzyl-2-methoxy-7a,8,9,10,10a,11-hexahydrobenzo[5,6]chromeno[2,3-b]pyrr



ole (7f): Following the general procedure compound 7f was obtained from the corresponding 1-(aminomethyl)-β-naphthol and benzaldehyde as a white solid in 68% yield ($R_f = 0.32$ in hexanes/ethyl acetate 85:15 v/v); mp: 98–100 °C; IR (KBr) 3086, 3029, 2997, 2942, 2909, 2874, 2839, 1621, 1513, 1494, 1422, 1365, 1316, 1221, 1175, 1152, 1135, 1080, 1037, 1028, 936, 838, 740, 697 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) 7.73 (d, J = 8.8 Hz, 1H), 7.64 (d, J = 8.8 Hz, 1H), 7.54–7.48 (m, 2H), 7.45–7.38 (m, 2H),

7.36–7.31 (m, 1H), 7.12 (d, J = 2.3 Hz, 1H), 7.10–7.04 (comp, 2H), 5.06 (d, J = 3.9 Hz, 1H), 4.35 (d, J = 13.3 Hz, 1H), 4.05 (d, J = 13.3 Hz, 1H), 3.97 (s, 3H), 3.21–3.14 (m, 1H), 3.14–3.02 (comp, 2H), 3.00–2.92 (m, 1H), 2.92–2.85 (m, 1H), 2.21–2.12 (m, 1H), 1.74 (app dtd, J = 12.5, 10.1, 6.1 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 158.1, 152.4, 139.1, 134.3, 129.9, 128.7, 128.2, 127.4, 126.9, 124.2, 116.6, 114.8, 111.3, 101.0, 91.1, 55.1, 53.7, 49.7, 36.7, 27.9, 24.0; m/z (ESI–MS) 346.2 [M + H]⁺.

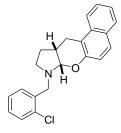
10a-cis-8-benzyl-3-bromo-7a,8,9,10,10a,11-hexahydrobenzo[5,6]chromeno[2,3-b]pyrrole



(**7g**): Following the general procedure compound **7g** was obtained from the corresponding 1-(aminomethyl)-β-naphthol and benzaldehyde as a white solid in 61% yield ($R_f = 0.43$ in hexanes/ethyl acetate 85:15 v/v); mp: 143–145 °C; IR (KBr) 3058, 3026, 2972, 2903, 2840, 1615, 1587, 1496, 1464, 1394, 1366, 1316, 1233, 1176, 1149, 1075, 1065, 973, 926, 878, 806, 781, 753, 699 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) 7.92 (s, 1H),

7.65 (d, J = 8.9 Hz, 1H), 7.59–7.51 (comp, 2H), 7.45 (app d, J = 7.5 Hz, 2H), 7.37 (app t, J = 7.5 Hz, 2H), 7.33–7.27 (m, 1H), 7.14 (d, J = 8.9 Hz, 1H), 5.03 (d, J = 3.8 Hz, 1H), 4.28 (d, J = 13.4 Hz, 1H), 4.00 (d, J = 13.4 Hz, 1H), 3.21–3.11 (m, 1H), 3.10–3.00 (comp, 2H), 2.97–2.88 (m, 1H), 2.87–2.79 (m, 1H), 2.17–2.06 (m, 1H), 1.71–1.59 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 152.2, 139.0, 131.7, 130.3, 130.2, 129.3, 128.7, 128.3, 126.9, 126.8, 123.5, 120.3, 116.6, 112.6, 91.4, 53.7, 49.7, 36.6, 27.8, 23.8; m/z (ESI–MS) 394.2 (⁷⁹Br) [M + H]⁺, 396.2 (⁸¹Br) [M + H]⁺.

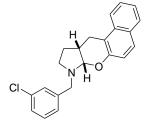
10a-cis-8-(2-chlorobenzyl)-7a,8,9,10,10a,11-hexahydrobenzo[5,6]chromeno[2,3-b]pyrrol



e (**7h**): Following the general procedure compound **7h** was obtained from the corresponding 1-(aminomethyl)-β-naphthol and 2-chlorobenzaldehyde as a yellow oil in 74% yield ($R_f = 0.40$ in hexanes/ethyl ether 90:10 v/v); IR (KBr) 3061, 2929, 2841, 1624, 1599, 1467, 1435, 1399, 1363, 1227, 1178, 1151, 1076, 926, 811, 746 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) 7.89–7.80 (comp, 2H), 7.71 (d, J = 8.8 Hz, 1H), 7.61–7.56 (m, 1H), 7.56–7.51 (m, 1H), 7.44 (dd, J = 7.8, 1.2 Hz, 1H),

7.42–7.37 (m, 1H), 7.30 (app td, J = 7.4, 1.2 Hz, 1H), 7.25 (app td, J = 7.6, 1.7 Hz, 1H), 7.19 (d, J = 8.8 Hz, 1H), 5.10 (d, J = 4.0 Hz, 1H), 4.48 (d, J = 14.5 Hz, 1H), 4.17 (d, J = 14.5 Hz, 1H), 3.27–3.18 (m, 1H), 3.17–3.07 (comp, 2H), 3.02–2.89 (comp, 2H), 2.19–2.09 (m, 1H), 1.74 (app dtd, J = 12.5, 10.1, 6.4 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 151.8, 136.8, 134.0, 133.1, 130.3, 129.4, 129.1, 128.4, 128.1, 127.7, 126.5, 126.1, 123.0, 121.7, 119.3, 112.4, 91.7, 50.9, 49.9, 36.8, 28.0, 23.8; m/z (ESI–MS) 350.2 [M + H]⁺.

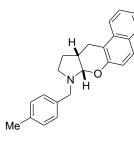
10a-cis-8-(3-chlorobenzyl)-7a,8,9,10,10a,11-hexahydrobenzo[5,6]chromeno[2,3-b]pyrrol



e (7i): Following the general procedure compound 7i was obtained from the corresponding 1-(aminomethyl)-β-naphthol and 3-chlorobenzaldehyde as a yellow oil in 72% yield ($R_f = 0.31$ in hexanes/ethyl ether 90:10 v/v); IR (KBr) 3061, 2929, 2844, 1624, 1599, 1575, 1514, 1468, 1434, 1399, 1362, 1228, 1178, 1150, 1075, 811, 746, 684 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) 7.87–7.79 (comp, 2H), 7.69 (d, J = 8.8 Hz, 1H), 7.55–7.46 (comp, 2H), 7.41–7.35 (m,

1H), 7.35–7.27 (comp, 3H), 7.15 (d, J = 8.8 Hz, 1H), 5.03 (d, J = 3.9 Hz, 1H), 4.29 (d, J = 13.7 Hz, 1H), 3.99 (d, J = 13.7 Hz, 1H), 3.24–3.16 (m, 1H), 3.15–3.08 (m, 1H), 3.05 (app td, J = 8.7, 6.3 Hz, 1H), 2.99–2.90 (m, 1H), 2.86–2.79 (m, 1H), 2.18–2.08 (m, 1H), 1.69 (app dtd, J = 12.5, 10.2, 6.2 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 151.7, 141.4, 134.1, 133.1, 129.5, 129.1, 128.7, 128.4, 127.7, 127.0, 126.7, 126.2, 123.0, 121.7, 119.1, 112.3, 91.3, 53.2, 49.7, 36.7, 27.9, 23.8; m/z (ESI–MS) 350.2 [M + H]⁺.

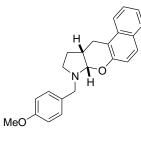
$10 a\ cis\ 8\ (4\ methylbenzyl)\ 7a\ ,8\ ,9\ ,10\ ,10\ a\ ,11\ hexahydrobenzo\ [5\ ,6\]chromeno\ [2\ ,3\ -b\]pyrrol$



e (7j): Following the general procedure compound 7j was obtained from the corresponding 1-(aminomethyl)-β-naphthol and *p*-tolualdehyde as a yellow oil in 74% yield ($R_f = 0.26$ in hexanes/ethyl ether 90:10 v/v); IR (KBr) 3051, 2920, 2843, 1624, 1599, 1514, 1467, 1399, 1228, 1177, 1151, 1075, 926, 810, 746 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) 7.90–7.82 (comp, 1H), 7.73 (d, *J* = 8.9 Hz, 1H), 7.60–7.52 (m, 1H), 7.46–7.38 (comp, 3H), 7.29–7.19 (comp,

3H), 5.08 (d, J = 3.9 Hz, 1H), 4.32 (d, J = 13.2 Hz, 1H), 4.03 (d, J = 13.2 Hz, 1H), 3.27–3.19 (m, 1H), 3.18–3.06 (comp, 2H), 3.01–2.92 (m, 1H), 2.92–2.86 (m, 1H), 2.44 (s, 3H), 2.20–2.11 (m, 1H), 1.73 (app dtd, J = 12.6, 10.1, 6.2 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 151.9, 136.4, 136.0, 133.1, 129.0, 128.9, 128.7, 128.4, 127.6, 126.1, 122.9, 121.6, 119.2, 112.3, 91.2, 53.4, 49.7, 36.7, 27.8, 23.8, 21.1; m/z (ESI–MS) 330.3 [M + H]⁺.

10a-cis-8-(4-methoxybenzyl)-7a,8,9,10,10a,11-hexahydrobenzo[5,6]chromeno[2,3-b]pyrr



ole (7k): Following the general procedure compound 7k was obtained from the corresponding 1-(aminomethyl)-β-naphthol and *p*-anisaldehyde as a white solid in 71% yield ($R_f = 0.32$ in hexanes/ethyl acetate 85:15 v/v); mp: 89–90 °C; IR (KBr) 3054, 3004, 2902, 2835, 1622, 1610, 1597, 1512, 1467, 1435, 1398, 1362, 1248, 1227, 1178, 1144, 1073, 1028, 929, 816, 769, 745 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) 7.89–7.79 (comp, 2H), 7.70 (d, *J* = 8.8 Hz,

1H), 7.56–7.49 (m, 1H), 7.45–7.35 (comp, 3H), 7.18 (d, J = 8.8 Hz, 1H), 6.98–6.90 (m, 2H), 5.04 (d, J = 3.9 Hz, 1H), 4.25 (d, J = 13.1 Hz, 1H), 3.97 (d, J = 13.1 Hz, 1H), 3.85 (s, 3H), 3.24–3.16 (m, 1H), 3.15–3.02 (comp, 2H), 2.98–2.89 (m, 1H), 2.89–2.82 (m, 1H), 2.18–2.09 (m, 1H), 1.70 (app dtd, J = 12.5, 10.1, 6.1 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 158.6, 151.9, 133.1, 131.1, 129.9, 129.0, 128.4, 127.6, 126.1, 122.9, 121.6, 119.2, 113.6, 112.4, 91.0, 55.2, 53.0, 49.6, 36.7, 27.8, 23.8; m/z (ESI–MS) 346.2 [M + H]⁺.

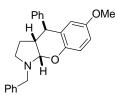
3a-trans-9a-trans-1-benzyl-6-chloro-4-phenyl-1,2,3,3a,4,9a-hexahydrochromeno[2,3-b]p



yrrole (71): Following the general procedure compound **71** was obtained from the corresponding 2-(aminomethyl)-phenol and benzaldehyde as a yellow oil in 79% yield (6.5:1 mixture of two diastereomers) ($R_f = 0.39$ in hexanes/ethyl ether 93:7 v/v); Characterization data of the major diastereomer: IR (KBr) 3083, 3061, 3027, 2932, 2878, 2842, 1598, 1579,

1482, 1453, 1363, 1220, 1194, 1156, 1093, 1029, 846, 816, 738, 700 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 7.44–7.38 (comp, 3H), 7.38–7.34 (comp, 3H), 7.34–7.31 (m, 1H), 7.31–7.26 (comp, 2H), 7.22 (dd, J = 8.6, 2.5 Hz, 1H), 7.20–7.13 (comp, 2H), 7.03 (d, J = 2.5 Hz, 1H), 6.97 (d, J = 8.6 Hz, 1H), 5.07 (d, J = 4.6 Hz, 1H), 4.24 (d, J = 13.7 Hz, 1H), 4.04–3.96 (comp, 2H), 3.02–2.78 (comp, 3H), 2.26–2.13 (m, 1H), 1.77–1.64 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 153.8, 143.9, 138.8, 129.8, 128.6, 128.5, 128.2(1), 128.1(8), 127.8, 126.9, 126.6, 125.8, 125.0, 118.1, 91.5, 53.7, 49.1, 45.5, 45.4, 28.1; m/z (ESI–MS) 376.1 [M + H]⁺

3a-trans-9a-trans-1-benzyl-6-methoxy-4-phenyl-1,2,3,3a,4,9a-hexahydrochromeno[2,3-b

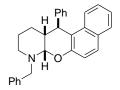


]pyrrole (7m): Following the general procedure compound **7m** was obtained from the corresponding 2-(aminomethyl)-phenol and benzaldehyde as a yellow oil in 60% (7.5:1 mixture of two diastereomers) ($R_f = 0.26$ in hexanes/ethyl ether 93:7 v/v); Characterization data of the major diastereomer: IR (KBr) 3081, 3060, 3027, 2934, 2832, 1601,

1494, 1453, 1362, 1272, 1208, 1150, 1041, 950, 875, 851, 739, 700 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 7.44–7.37 (comp, 3H), 7.37–7.31 (comp, 4H), 7.31–7.25 (comp, 2H), 7.24–7.19 (comp, 2H), 6.97 (d, J = 8.8 Hz, 1H), 6.84 (dd, J = 8.8, 3.0 Hz, 1H), 6.58 (d, J = 3.0 Hz, 1H), 5.02 (d, J = 4.9 Hz, 1H), 4.22 (d, J = 13.6 Hz, 1H), 4.03 (d, J = 13.6 Hz, 1H), 3.98 (d, J = 3.2 Hz, 1H), 3.74 (s, 3H), 2.98–2.80 (comp, 3H), 2.24–2.11 (m, 1H), 1.79–1.67 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 153.6, 149.0, 144.2, 139.0, 128.6, 128.5, 128.2, 128.0, 126.8, 126.4, 125.8, 117.5, 114.8, 113.7, 91.4, 55.5, 53.9, 49.3, 46.1, 45.9, 28.5; *m/z* (ESI–MS) 372.1 [M + H]⁺

9a-cis-1-benzyl-1,2,3,3a,4,9a-hexahydrochromeno[2,3-b]pyrrole (7n): Following the general procedure compound **7n** was obtained from the corresponding 2-(aminomethyl)-phenol and benzaldehyde as a colorless oil in 38% yield (R_f = 0.31 in hexanes/ethyl ether 90:10 v/v); IR (KBr) 3062, 3026, 2931, 2840, 1603, 1585, 1487, 1456, 1364, 1226, 1150, 1108, 895, 805, 753, 700 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) 7.48–7.43 (m, 2H), 7.42–7.37 (m, 2H), 7.34–7.29 (m, 1H), 7.24–7.18 (m, 1H), 7.15–7.10 (m, 1H), 6.98–6.91 (comp, 2H), 5.10 (d, *J* = 5.2 Hz, 1H), 4.22 (d, *J* = 13.4 Hz, 1H), 4.05 (d, *J* = 13.4 Hz, 1H), 3.04 (dd, *J* = 15.6, 5.9 Hz, 1H), 2.93–2.83 (comp, 2H), 2.77 (app td, *J* = 9.0, 5.0 Hz, 1H), 2.63 (dd, *J* = 15.6, 2.6 Hz, 1H), 2.10–2.00 (m, 1H), 1.65–1.56 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 155.3, 139.0, 129.1, 128.7, 128.2, 127.4, 126.8, 123.5, 120.5, 116.9, 93.0, 53.8, 49.8, 37.7, 28.3, 27.7; *m/z* (ESI–MS) 266.0 [M + H]⁺.

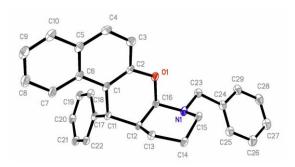
7a-trans-11a-trans-8-benzyl-12-phenyl-8,9,10,11,11a,12-hexahydro-7aH-benzo[5,6]chro



me no[2,3-b]pyridine (70): Following the general procedure compound 70 was obtained from the corresponding 1-(aminomethyl)- β -naphthol and benzaldehyde as an off-white solid in 75% yield ($R_f = 0.44$ in hexanes/ethyl ether 93:7 v/v); mp = 177–179 °C; IR (KBr) 3081, 3059, 3017, 2966, 2966, 2935, 2862, 1622, 1598, 1492, 1464, 1450, 1403, 1230,

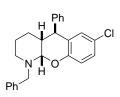
1148, 1083, 987, 843, 813, 749, 728, 700 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) 7.86–7.77 (comp, 2H), 7.57 (d, J = 7.8 Hz, 1H), 7.43–7.38 (comp, 2H), 7.37–7.26 (comp, 8H), 7.26–7.21 (m, 1H), 7.21–7.16 (comp, 2H), 5.01 (s, 1H), 4.48 (s, 1H), 4.12 (d, J = 13.9 Hz, 1H), 4.03 (d, J = 13.9 Hz, 1H), 2.83 (app td, J = 10.9, 4.4 Hz, 1H), 2.66–2.58 (m, 1H), 2.42–2.34 (m, 1H), 1.84–1.69 (comp, 3H), 1.65–1.53 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) 8 152.7, 145.8, 139.1, 133.2, 129.3, 128.9, 128.4(8), 128.4(7), 128.4, 128.2, 128.1, 126.8, 126.3(0), 126.2(5), 123.0, 122.7, 118.8, 112.1, 85.5, 59.0, 45.6, 44.0, 42.0, 25.8, 25.0; *m/z* (ESI–MS) 406.2 [M + H]⁺.

The title compound was further characterized by X-ray crystallography:



The requisite CIF has been deposited with the CCDC (deposition # 963307).

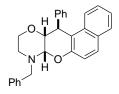
4a-trans-10a-trans-1-benzyl-7-chloro-5-phenyl-2,3,4,4a,5,10a-hexahydro-1H-chromeno[



2,3-b]pyridine (7p): Following the general procedure compound **7p** was obtained from the corresponding 2-(aminomethyl)-phenol and benzaldehyde as a yellow oil in 67% yield (7.5:1 mixture of two diastereomers) ($R_f = 0.46$ in hexanes/ethyl ether 93:7 v/v); Characterization data of the major diastereomer: IR (KBr) 3081, 3061,

3026, 2929, 2853, 1601, 1576, 1481, 1452, 1403, 1355, 1265, 1234, 1169, 1111, 977, 939, 851, 828, 815, 737, 700 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 7.36–7.29 (comp, 7H), 7.29–7.24 (comp, 2H), 7.20 (dd, J = 8.7, 2.6 Hz, 1H), 7.09–7.03 (comp, 2H), 7.00 (d, J = 2.6 Hz, 1H), 6.96 (d, J = 8.7 Hz, 1H), 4.84 (d, J = 2.1 Hz, 1H), 4.02 (d, J = 13.9 Hz, 1H), 3.99–3.92 (comp, 2H), 2.81–2.70 (m, 1H), 2.61–2.50 (m, 1H), 2.28–2.14 (m, 1H), 1.79–1.61 (comp, 3H); 1.60–1.42 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 153.6, 145.5, 138.9, 130.4, 128.4(3), 128.4(1), 128.3, 128.1, 128.0, 126.8, 126.4, 124.6, 122.9, 117.8, 86.2, 58.8, 48.1, 44.0, 41.5, 25.7, 24.8; m/z (ESI–MS) 390.1 [M + H]⁺.

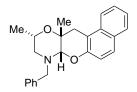
7a-trans-11a-trans-8-benzyl-12-phenyl-7a,8,9,10,11a,12-hexahydrobenzo[5,6]chromeno[



3,2-b][1,4]oxazine (7q): Following the general procedure compound 7q was obtained from the corresponding 1-(aminomethyl)- β -naphthol and benzaldehyde as a yellow oil in 40% yield (R_f = 0.20 in hexanes/ethyl ether 93:7 v/v); IR (KBr) 3060, 3025, 2962, 2908, 2851, 1624, 1600, 1515, 1493, 1467, 1450, 1404, 1346, 1227, 1127, 1099, 1066, 1014, 975,

835, 744, 699 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) 7.83–7.77 (comp, 2H), 7.58–7.53 (m, 1H), 7.43–7.38 (comp, 2H), 7.38–7.34 (comp, 2H), 7.34–7.28 (comp, 6H), 7.26–7.21 (comp, 3H), 4.87 (s, 1H), 4.83 (d, J = 1.9 Hz, 1H), 4.15–4.09 (comp, 2H), 4.03 (d, J = 13.6 Hz, 1H), 3.98–3.93 (m, 1H), 3.88 (app td, J = 11.7, 2.8 Hz, 1H), 3.08 (app td, J = 11.7, 3.7 Hz, 1H), 2.45–2.39 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 152.3, 142.0, 138.0, 132.8, 129.5, 129.2, 128.7(5), 128.7(3), 128.6(6), 128.4, 128.3, 127.1, 126.9, 126.4, 123.0, 122.7, 118.3, 111.1, 82.1, 76.4, 67.2, 58.4, 45.1, 43.5; m/z (ESI–MS) 408.1 [M + H]⁺.

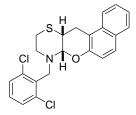
7a-cis-11a-cis-8-benzyl-10,11a-dimethyl-7a,8,9,10,11a,12-hexahydrobenzo[5,6]chromeno



[3,2-b][1,4]oxazine (7r): Following the general procedure compound 7r was obtained from the corresponding 1-(aminomethyl)- β -naphthol and benzaldehyde as a yellow oil in 65% yield (5:1 mixture of two diastereomers) (R_f = 0.37 in hexanes/ethyl ether 93:7 v/v); Characterization data of the major diastereomer: IR (KBr) 3061, 3026,

2972, 2932, 2896, 2845, 1626, 1602, 1470, 1401, 1263, 1231, 1109, 1070, 991, 912, 809, 745, 699 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 7.83–7.76 (comp, 2H), 7.70 (d, J = 8.8 Hz, 1H), 7.55–7.50 (comp, 3H), 7.46–7.39 (comp, 2H), 7.39–7.34 (comp, 2H), 7.20 (d, J = 8.8 Hz, 1H), 4.54 (s, 1H), 4.30–4.19 (m, 1H), 4.16 (d, J = 13.6 Hz, 1H), 3.95 (d, J = 13.6 Hz, 1H), 3.35 (d, J = 17.4 Hz, 1H), 3.00 (d, J = 17.4 Hz, 1H), 2.80 (app t, J = 11.1 Hz, 1H), 2.50 (dd, J = 11.1, 3.0 Hz, 1H), 1.67 (s, 3H), 1.09 (d, J = 6.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 151.3, 138.5, 132.6, 128.8(5), 128.7(9), 128.3, 127.5, 127.1, 126.1, 122.8, 121.8, 118.2, 113.5, 110.9, 87.5, 71.0, 69.5, 65.6, 58.1, 50.8, 36.1, 22.4; m/z (ESI–MS) 360.1 [M + H]⁺.

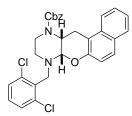
11-cis-8-(2,6-dichlorobenzyl)-7a,8,9,10,11a,12-hexahydrobenzo[5,6]chromeno[3,2-b][1,4]



thiazine (7s): Following the general procedure (reaction performed at 180 °C for 45 minutes) compound **7s** was obtained from the corresponding 1-(aminomethyl)- β -naphthol and 2,6-dichlorobenzaldehyde as a yellow oil in 53% yield (R_f = 0.59 in hexanes/ethyl acetate 85:15 v/v); IR (KBr) 3061, 2928, 2910, 2849, 1624, 1600, 1581, 1515, 1435, 1400, 1228, 1209, 1154, 1061, 986, 926, 888, 812,

768, 739 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) 7.81–7.76 (m, 1H), 7.74–7.66 (comp, 2H), 7.48 (app td, J = 6.8, 1.3 Hz, 1H), 7.37–7.29 (comp, 3H), 7.22–7.13 (comp, 2H), 4.91 (d, J = 1.3 Hz, 1H), 4.31 (d, J = 13.3 Hz, 1H), 4.24 (d, J = 13.3 Hz, 1H), 3.68–3.63 (m, 1H), 3.54 (app d, J = 17.5, 6.8 Hz, 1H), 3.36 (app td, J = 11.8, 2.7 Hz, 1H), 3.10 (app d, J = 17.5 Hz, 1H), 3.06–2.97 (m, 1H), 2.88 (app dt, J = 11.8, 3.2 Hz, 1H), 2.53 (app dt, J = 13.3, 2.7 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 150.9, 137.1, 134.3, 132.8, 129.1(1), 129.0(7), 128.5, 128.4, 128.2, 126.3, 123.2, 121.7, 119.0, 110.6, 85.6, 53.9, 45.2, 37.2, 28.9, 28.5; *m/z* (ESI–MS) 415.9 (³⁵Cl/³⁵Cl) [M + H]⁺, 417.9 (³⁵Cl/³⁷Cl) [M + H]⁺.

11-cis-benzyl-8-(2,6-dichlorobenzyl)-9,10,11a,12-tetrahydro-7aH-benzo[5,6]chromeno[2,



3-b]pyrazine-11(8H)-carboxylate (7t): Following the general procedure (reaction performed at 170 °C for 45 minutes) compound **7t** was obtained from the corresponding 1-(aminomethyl)- β -naphthol and 2,6-dichlorobenzaldehyde as a yellow oil in 58% yield (R_f = 0.21 in hexanes/ethyl acetate 90:10 v/v); IR (KBr) 3061, 3031, 2950, 2854, 2821, 1701, 1627, 1561, 1435, 1354, 1314, 1270, 1225, 1117, 1082, 968,

904, 811, 768, 746, 696 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) 7.82–7.73 (comp, 2H), 7.62 (d, J = 8.9 Hz, 1H), 7.53–7.46 (m, 1H), 7.44–7.29 (comp, 5H), 7.18–7.11 (m, 2H), 7.10–6.99 (comp, 2H), 5.20 (s, 2H), 4.86–4.78 (m, 1H), 4.60–4.49 (comp, 2H), 4.00–3.90 (m, 1H), 3.63 (app d, J = 12.6 Hz, 1H), 3.40 (dd, J = 15.6, 11.0 Hz, 1H), 3.35–3.25 (m, 1H), 3.12 (dd, J = 15.6, 6.4 Hz, 1H), 2.83–2.73 (m, 1H), 2.56 (app td, J = 11.9, 3.9 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 155.2, 148.8, 137.1, 136.3, 133.4, 132.5, 129.2, 128.8, 128.5, 128.4, 128.2,

128.1, 128.0, 127.8, 126.3, 123.4, 121.7, 118.3, 112.1, 87.0, 67.5, 50.8, 49.9, 49.0, 39.0, 21.0; *m*/*z* (ESI–MS) 533.0 (³⁵Cl/³⁵Cl) [M + H]⁺, 535.0 (³⁵Cl/³⁷Cl) [M + H]⁺.

Transformation of *N***,***O***-acetals:**

1-((1-benzylpyrrolidin-3-yl)methyl)naphthalen-2-ol (11): To a solution of 7e (0.25 mmol, 1 equiv) in dry THF (2.5 mL) cooled in an ice bath, LiAlH₄ (0.75 mmol, 3 equiv) was added in one portion. The resulting mixture was stirred at 0 °C for one hour, and then quenched with saturated aqueous NH₄Cl. The mixture was filtered through a short pad of celite and washed with EtOAc (6 x 5 mL). The filtrate was then washed with saturated aqueous NaHCO₃ (3 x 10 mL), and the combined organic layers were washed with water (40 mL), brine (40 mL),

To fin2), and the combined organic hayers were washed with wher (46 fin2), or the (46 fin2), and dried over anhydrous Na₂SO₄. Solvent was then removed under reduced pressure. The residue was purified by silica gel chromatography and the product isolated as a yellow oil in 69% yield ($R_f = 0.31$ in ethyl acetate); IR (KBr) 3060, 3026, 2955, 2873, 2814, 1623, 1595, 1514, 1454, 1437, 1354, 1265, 1242, 814, 748, 700 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) 9.51 (br s, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.66 (d, J = 8.8 Hz, 1H), 7.58–7.04 (comp, 8H), 4.07 (d, J = 12.5 Hz, 1H), 3.42 (d, J = 12.5 Hz, 1H), 3.27 (dd, J = 14.5, 6.7 Hz, 1H), 3.22–3.13 (m, 1H), 3.11–2.97 (m, 1H), 2.87–2.60 (comp, 2H), 2.51–2.22 (comp, 2H), 2.21–2.04 (m, 1H), 1.93–1.77 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 155.1, 137.1, 133.3, 129.3, 128.9, 128.5, 127.8, 127.5, 126.0, 122.5(4), 122.4(8), 119.6, 118.3, 60.1, 57.8, 50.2, 36.8, 30.6, 29.8; m/z (ESI–MS) 318.2 [M + H]⁺.

1-((1-benzyl-2-methylpyrrolidin-3-yl)methyl)naphthalen-2-ol (12): To a solution of **7e** (0.25 mmol, 1 equiv) in dry THF (2.5 mL) cooled in an ice bath, MeMgBr (0.5 mmol, 2 equiv, 3 molar solution in THF) was added. The resulting mixture was warmed up to room temperature and stirred for 30 minutes, then quenched with saturated aqueous NH_4Cl . The mixture was diluted with EtOAc (10 mL) and washed with saturated aqueous $NaHCO_3$ (3 x 10 mL).

^{Ph'} The combined aqueous layers were extracted with EtOAc (3 x 10 mL), and the combined organic layers were washed with water (40 mL), brine (40 mL), and dried over anhydrous Na₂SO₄. Solvent was then removed under reduced pressure. The residue was purified by silica gel chromatography and the product isolated as a yellow oil in 86% yield (3:1 mixture of two diastereomers) ($R_f = 0.44$ in ethyl acetate); IR (KBr) 3061, 3026, 2964, 2873, 2794, 1624, 1601, 1514, 1453, 1436, 1376, 1355, 1267, 1243, 1143, 812, 745, 700 cm⁻¹; ¹H NMR (Note: due to overlapping peaks, integration values of the diastereomers are reported together) (500 MHz, CDCl₃) 9.61 (br s, 1.03H), 7.95 (d, *J* = 8.6 Hz, 0.35H), 7.89 (d, *J* = 8.6 Hz, 1.04H), 7.81–7.73 (comp, 1.38H), 7.61 (d, *J* = 8.8 Hz, 1.02H), 7.57 (d, *J* = 8.8 Hz, 0.40H), 7.52–7.28 (comp, 9.89H), 7.12 (d, *J* = 8.8 Hz, 1.00H), 6.97 (d, *J* = 8.8 Hz, 0.32H), 4.15 (d, *J* = 12.7 Hz, 1.0H), 3.85 (d, *J* = 12.4 Hz, 0.34H), 3.66 (d, *J* = 12.4 Hz, 0.33H), 3.43 (d, *J* = 12.7 Hz, 1.03H), 3.29 (dd, *J* = 14.5, 7.4 Hz, 1.07H), 3.24–3.09 (comp, 1.79H), 2.90–2.82 (m, 1.03H), 2.81–2.69 (comp, 3.09H), 2.54–2.46 (m, 0.34H), 2.28–2.19 (m, 1.02H),

1.93 (ddd, J = 17.5, 12.5, 8.7 Hz, 0.35H), 1.71–1.51 (comp, 2.57H), 1.45 (d, J = 6.6 Hz, 3.07H), 1.15 (d, J = 6.3 Hz, 1.01H); ¹³C NMR of the diastereomers (125 MHz, CDCl₃) δ 153.9, 153.3, 137.7, 136.8, 134.1, 133.5, 129.6, 129.4, 129.0, 128.7, 128.5(0), 128.4(7), 128.4(3), 128.3, 127.6, 127.5, 127.4, 127.3, 125.9(0), 125.8(8), 122.9, 122.7, 122.4, 122.3, 119.7, 119.4, 118.7(4), 118.6(8), 63.3, 62.9, 57.7, 56.9, 51.8, 49.6, 44.2, 40.7, 29.8, 28.1, 26.7, 24.1, 14.2, 13.6; m/z (ESI–MS) 332.2 [M + H]⁺.

1-((1-benzyl-2-phenylpyrrolidin-3-yl)methyl)naphthalen-2-ol (13): The synthetic procedure followed was the same as for **12**. Compound **13** was obtained from **7e** and PhMgBr (1 molar solution in THF) as a yellow oil in 98% yield (3.5:1 mixture of two diastereomers) ($R_f = 0.41$ in hexanes/ethyl acetate 80:20 v/v); IR (KBr) 3060, 3028, 2960, 2871, 2795, 1625, 1601, 1584, 1514, 1494, 1453, 1436, 1358, 1265, 1239, 1143, 1068, 1028, 958, 907, 812, 747, 701 cm⁻¹; ¹H NMR (Note: due to overlapping peaks, integration values of the

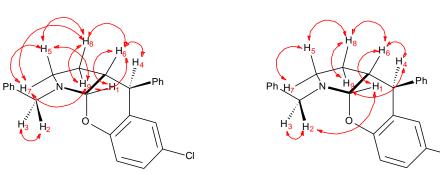
diastereomers are reported together) (500 MHz, CDCl₃) 7.80–7.66 (comp, 2.24H), 7.64–7.19 (comp, 19.25H), 7.04 (d, J = 8.8 Hz, 0.29H), 6.87 (d, J = 8.8 Hz, 1.00H), 6.11 (br s, 0.89H), 4.13 (d, J = 13.2 Hz, 0.24H), 3.93 (d, J = 6.9 Hz, 0.26H), 3.87 (d, J = 13.0 Hz, 0.95H), 3.35 (d, J = 7.1 Hz, 1.16H), 3.29–2.77 (comp, 5.26H), 2.72–2.55 (comp, 1.31H), 2.49 (app td, J = 8.7, 8.7 Hz, 1.06H), 2.34 (app td, J = 8.5, 8.5 Hz, 0.33H), 1.97–1.51 (comp, 2.76H); ¹³C NMR of the diastereomers (125 MHz, CDCl₃) δ 151.8, 151.2, 141.7, 138.9, 133.5, 133.3, 129.3, 129.2, 129.1, 129.0, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 127.7, 127.6, 127.5, 127.3, 127.1, 126.9, 126.1, 123.0, 122.9, 122.7, 118.8, 118.4, 117.8, 76.0, 72.5, 58.0, 51.9(2), 51.7(9), 49.5, 47.7, 42.4, 28.5, 28.0, 27.9, 26.2; m/z (ESI–MS) 394.2 [M + H]⁺.

2D-NMR Analysis for Compound 7l, Selected Interactions:





CI



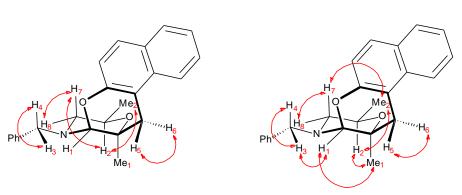
	¹ H NMR	shifts
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Protons	Chemical shifts (ppm)
H1	5.07
H2	4.24
H3, H4	4.04–3.96
H5, H6, H7	3.02–2.78
H8	2.26–2.13
H9	1.77–1.64

2D-NMR Analysis for Compound 7r, Selected Interactions:

GCOSY

NOESY

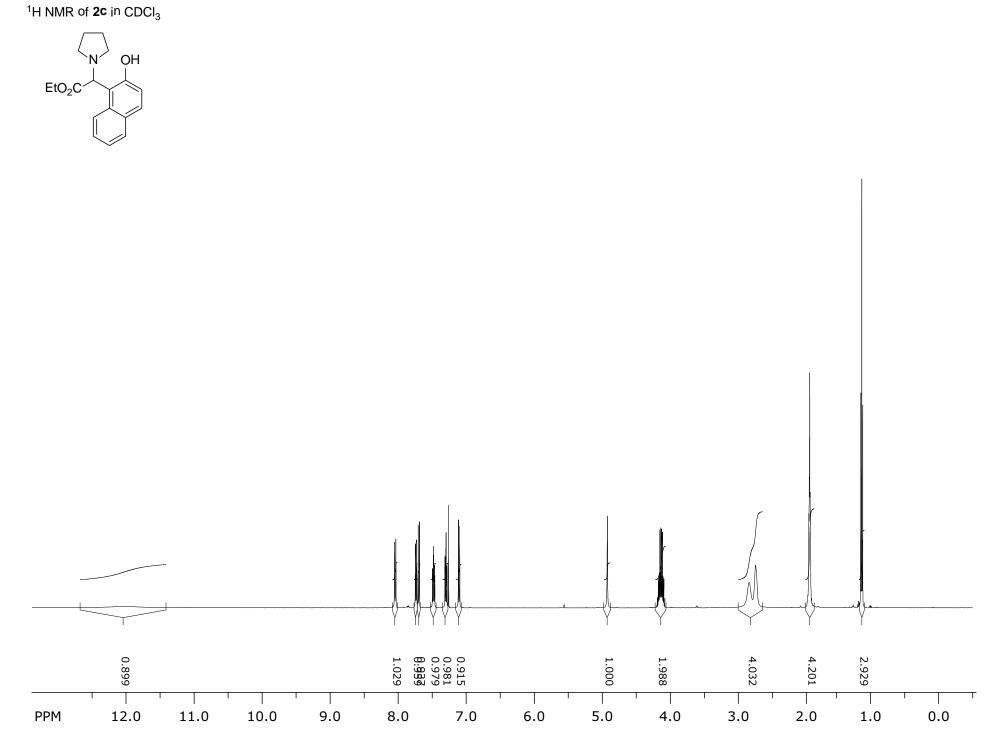


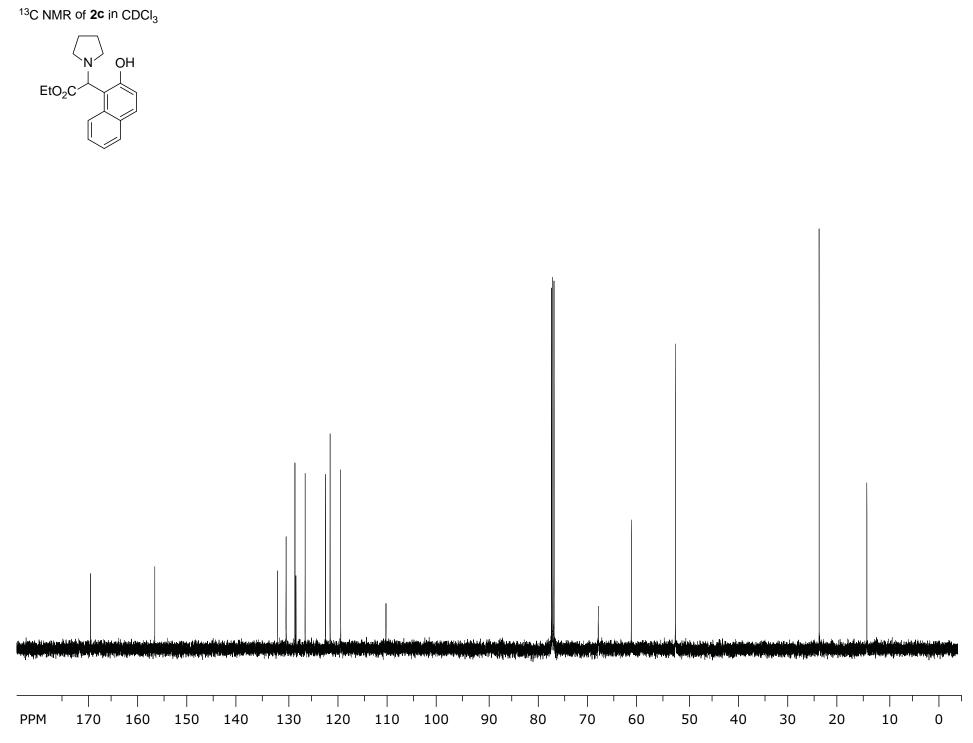
¹H NMR shifts

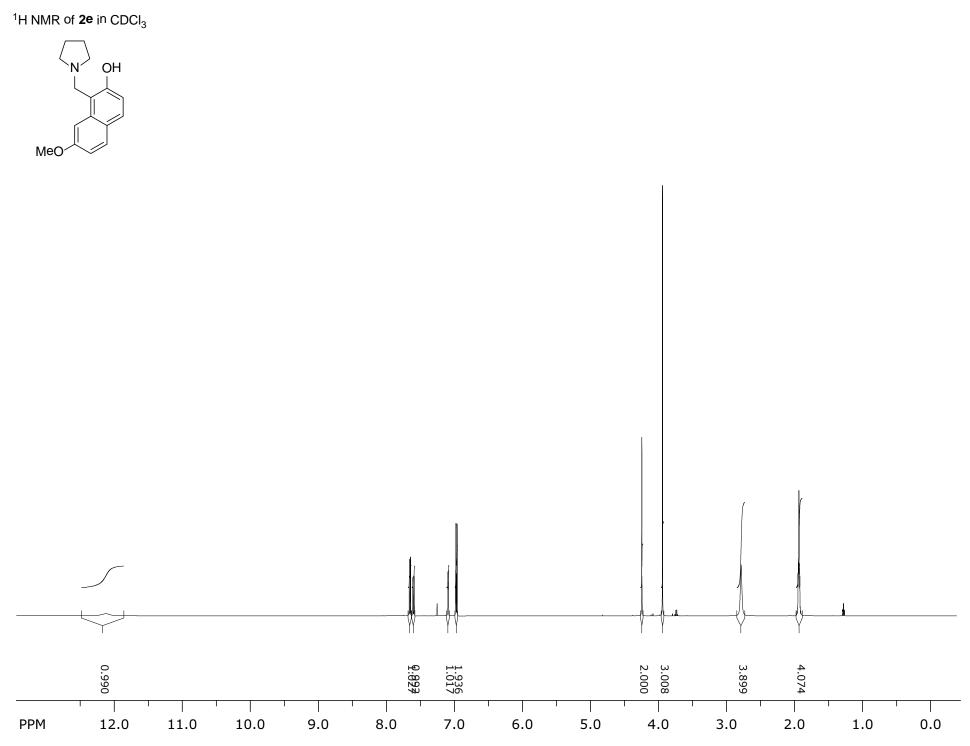
Protons	Chemical shifts (ppm)
H1	4.54
H2	4.30–4.19
НЗ	4.16
H4	3.95
H5, H6	3.35, 3.00
H7	2.80
H8	2.50
Me1	1.67
Me2	1.09

References:

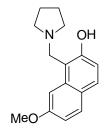
- (1) M. Periasamy, M. N. Reddy, S. Anwar, Tetrahedron: Asymmetry 2004, 15, 1809.
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- (3) M. L. Deb, S. S. Dey, I. Bento, M. T. Barros, C. D. Maycock, *Angew. Chem. Int. Ed.* **2013**, *52*, 9791.
- (4) A. K. Shaikh, A. J. A. Cobb, G. Varvounis, Org. Lett. 2012, 14, 584.

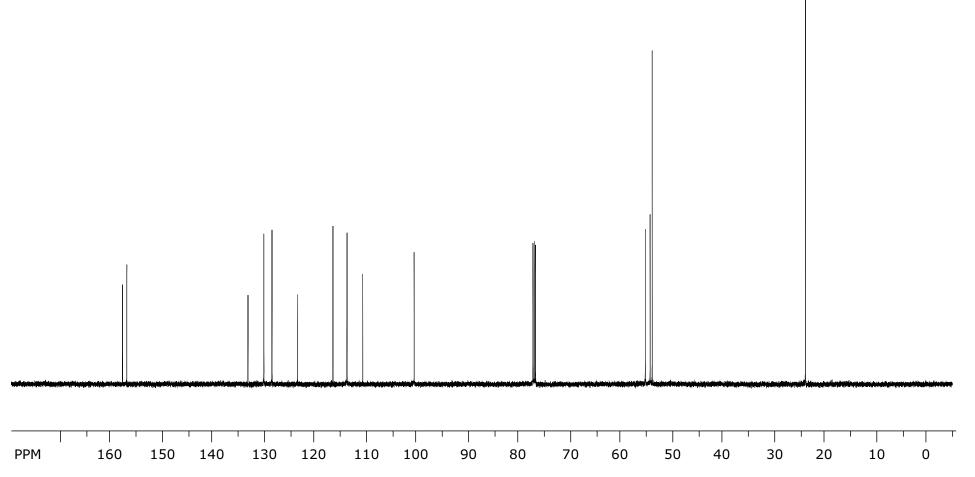




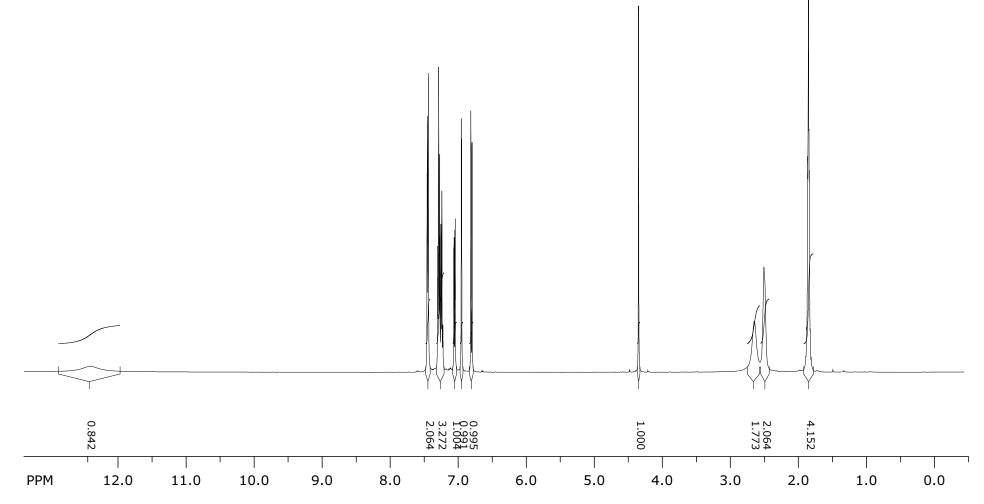


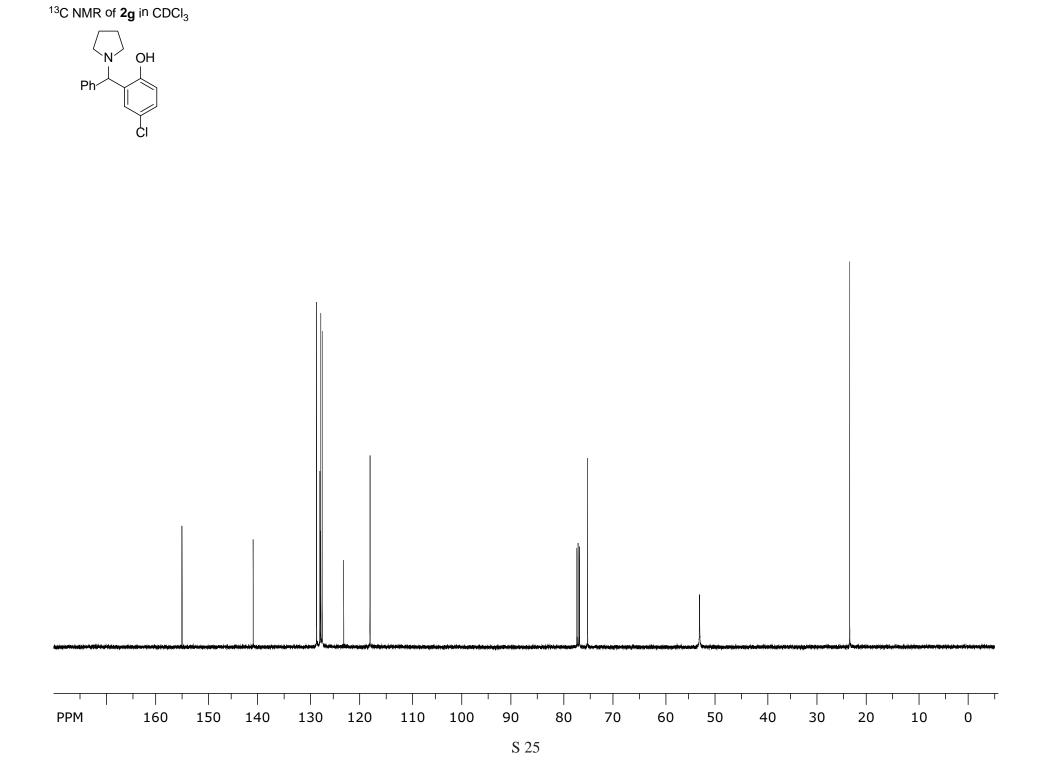
$^{\rm 13}{\rm C}$ NMR of ${\rm 2e}$ in ${\rm CDCI}_{\rm 3}$

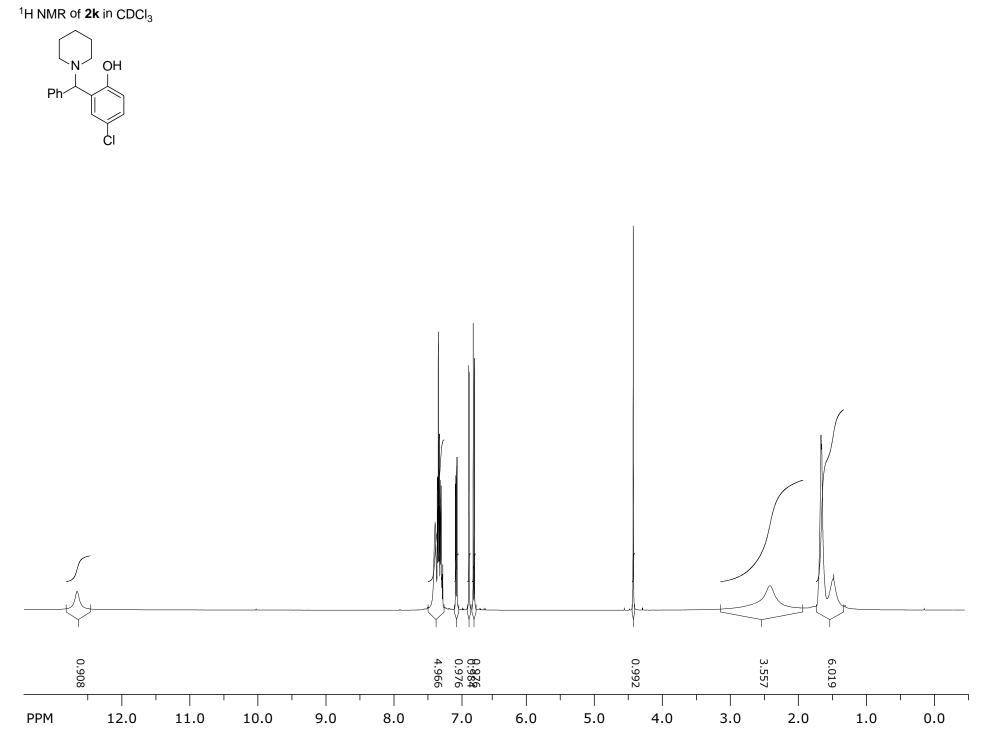


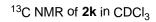


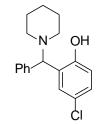


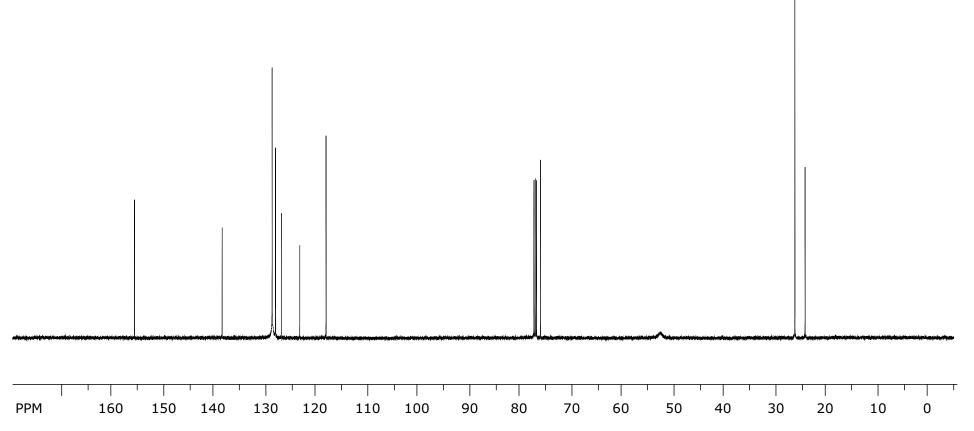


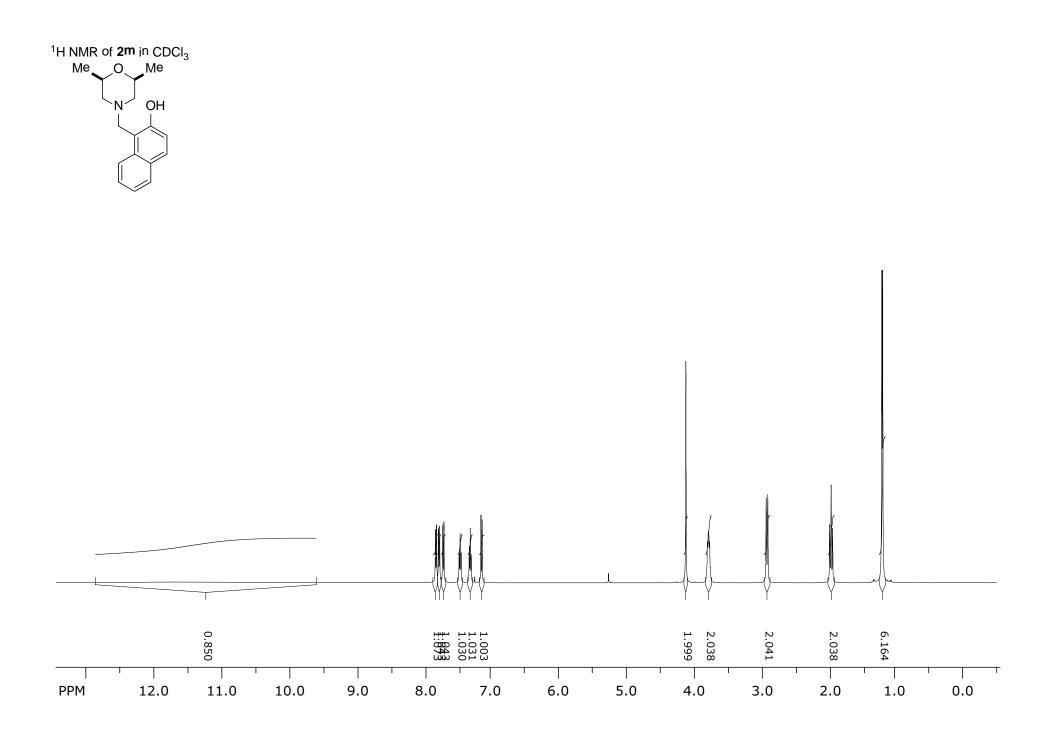


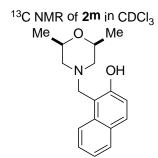


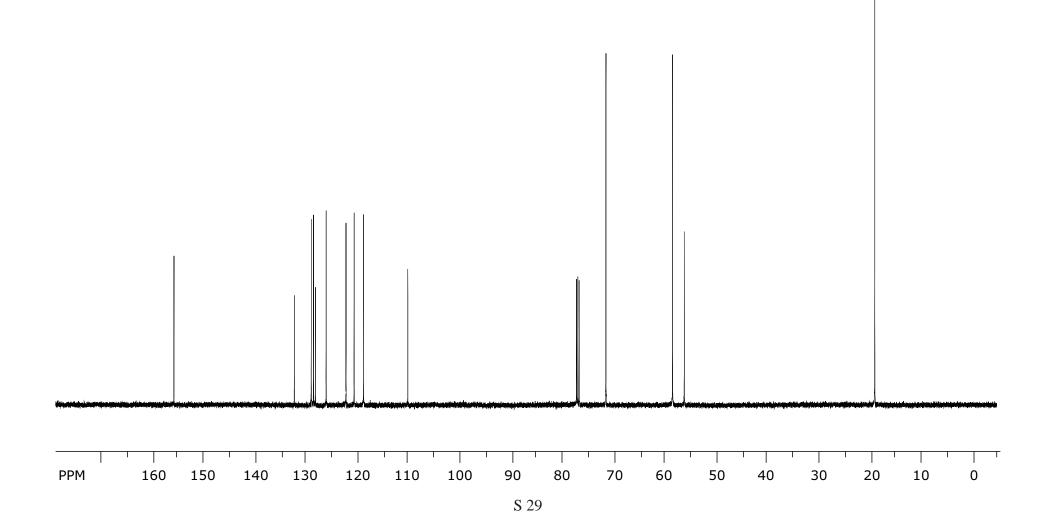


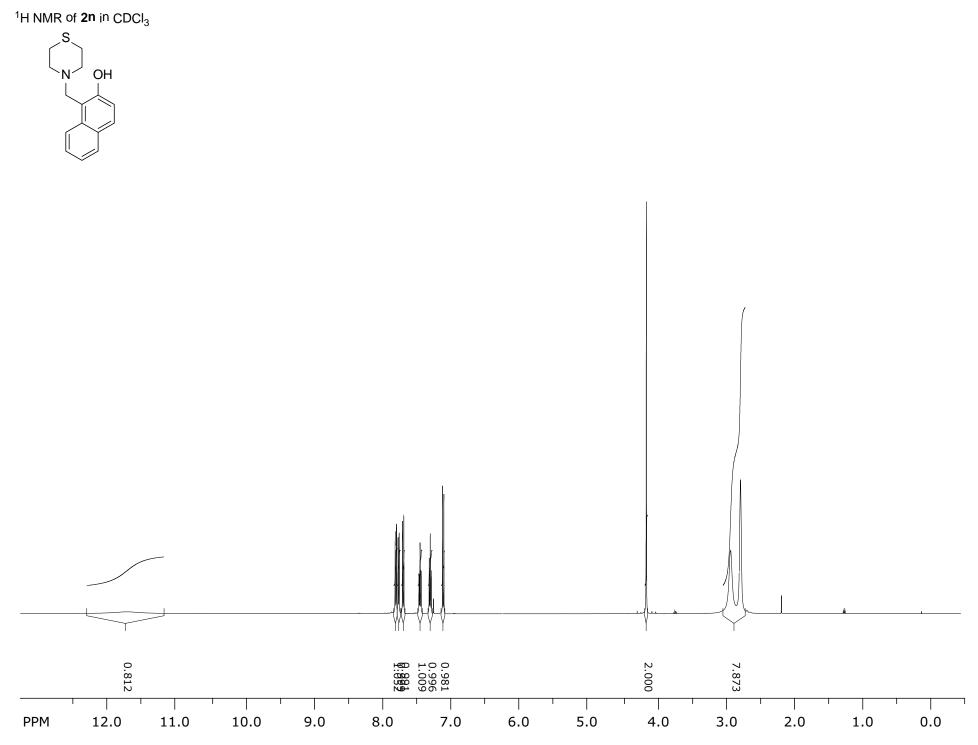




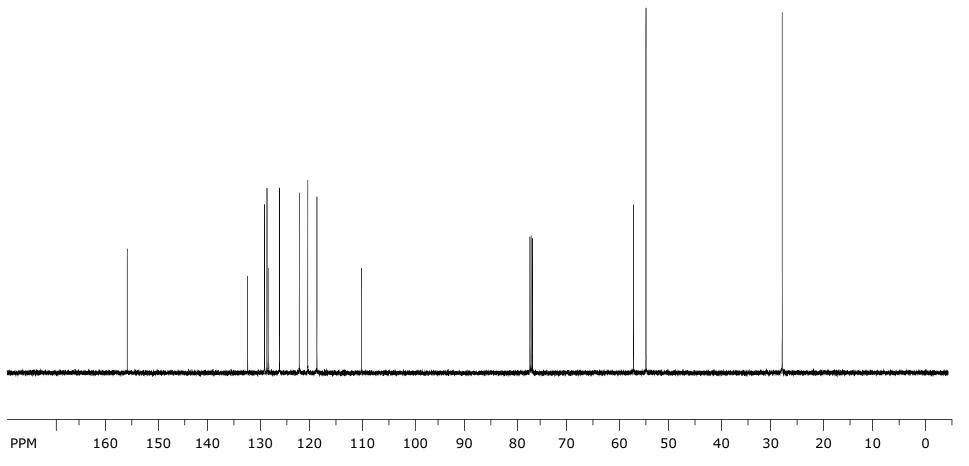


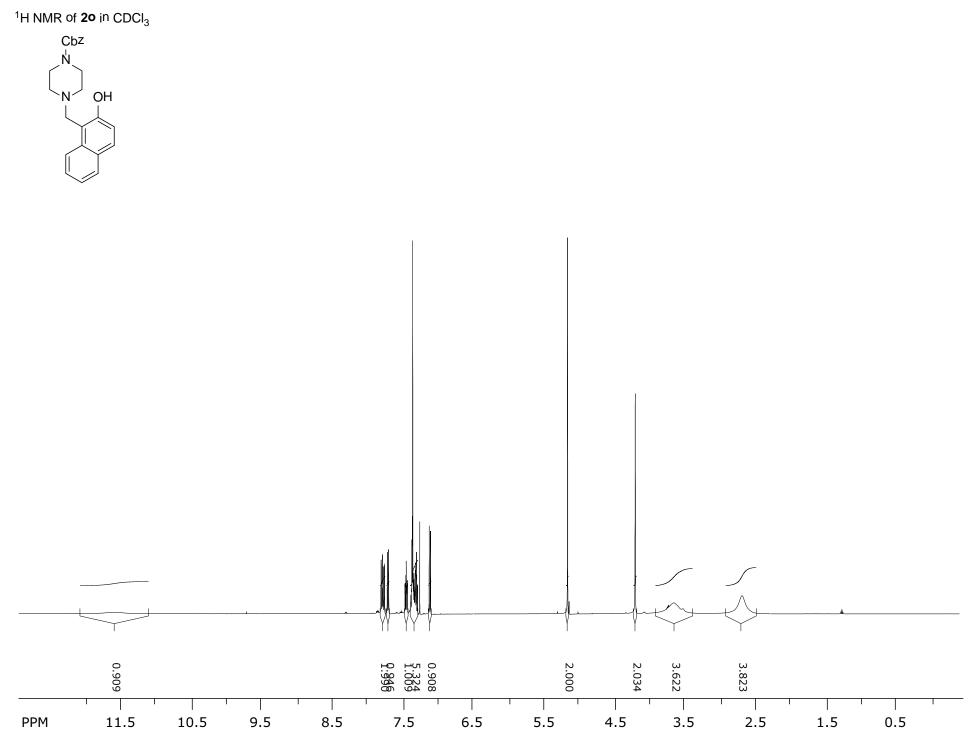


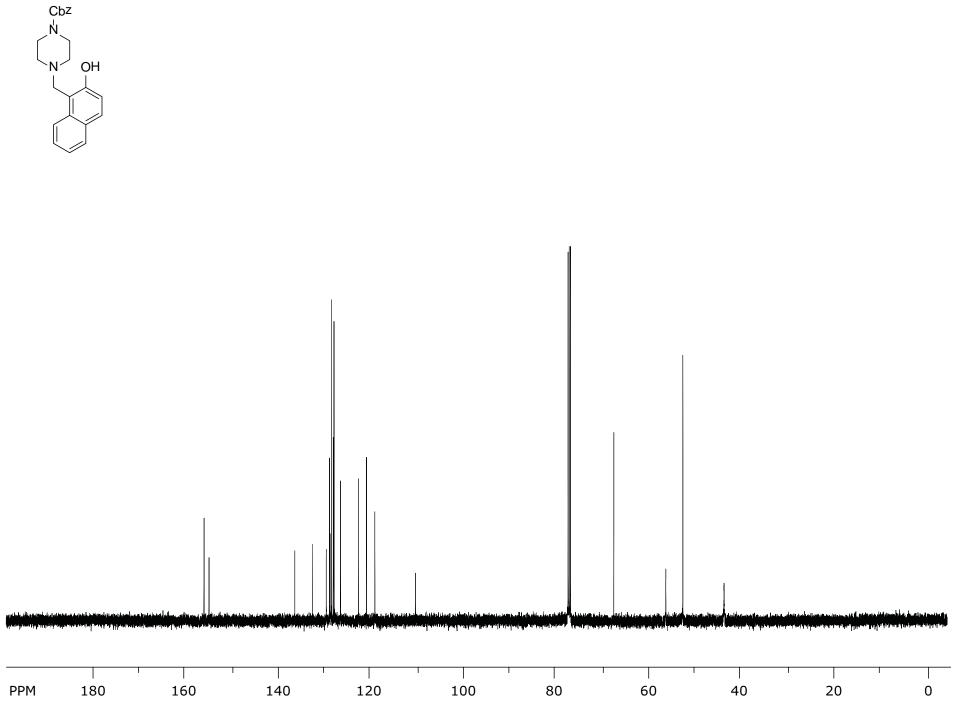




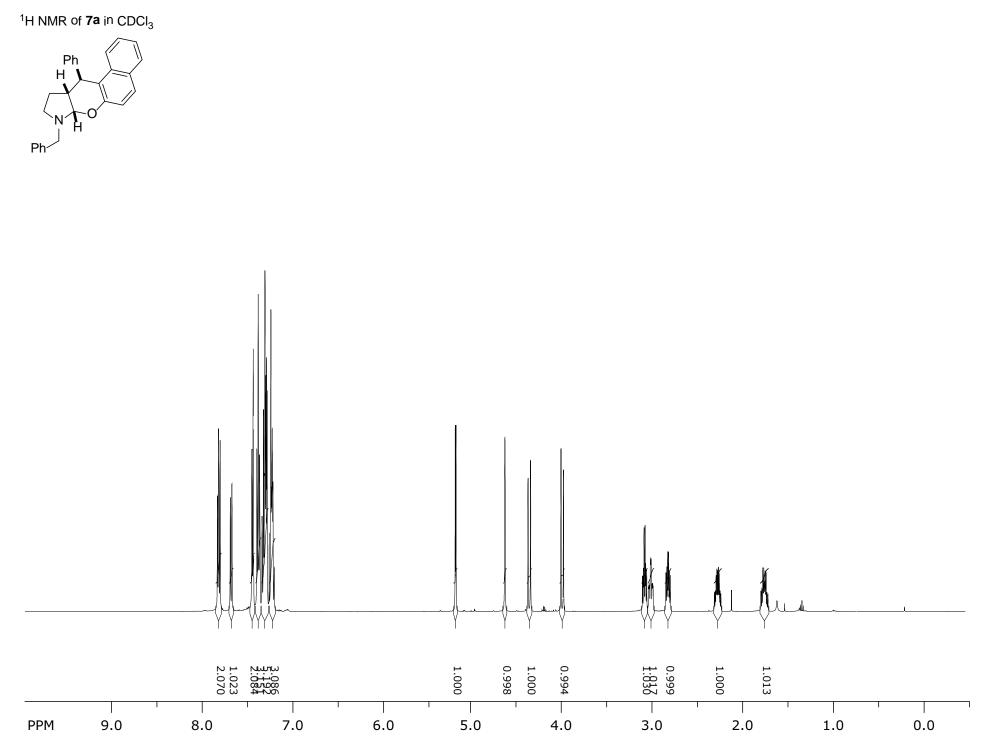


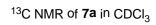


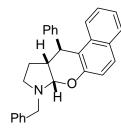


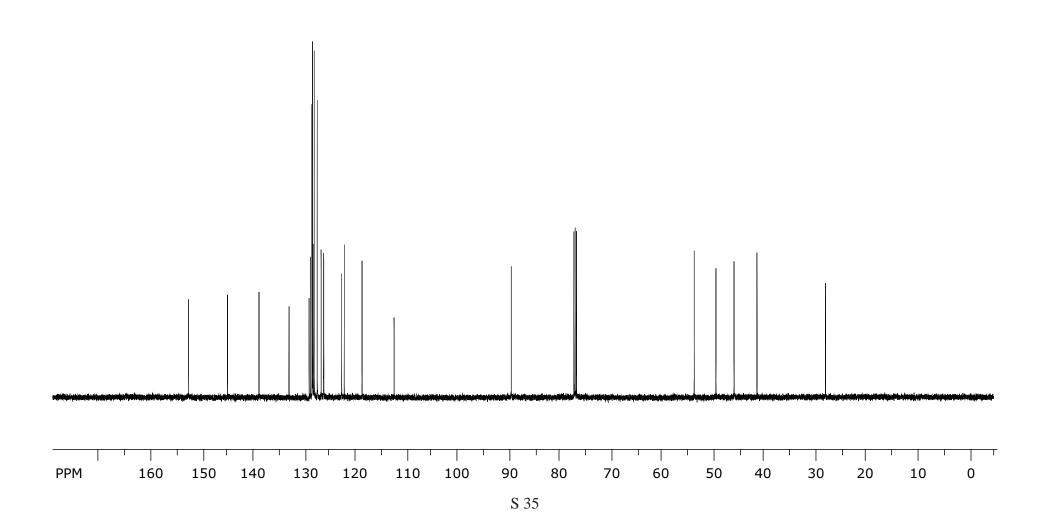


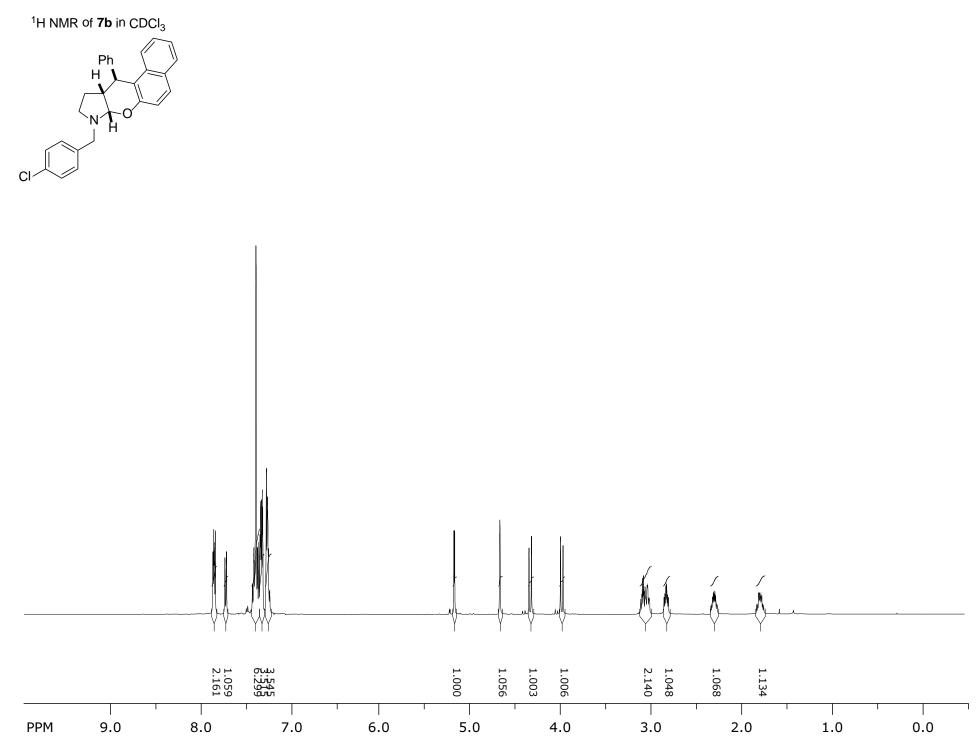
 $^{\rm 13}{\rm C}$ NMR of ${\bf 20}$ in ${\rm CDCI}_{\rm 3}$

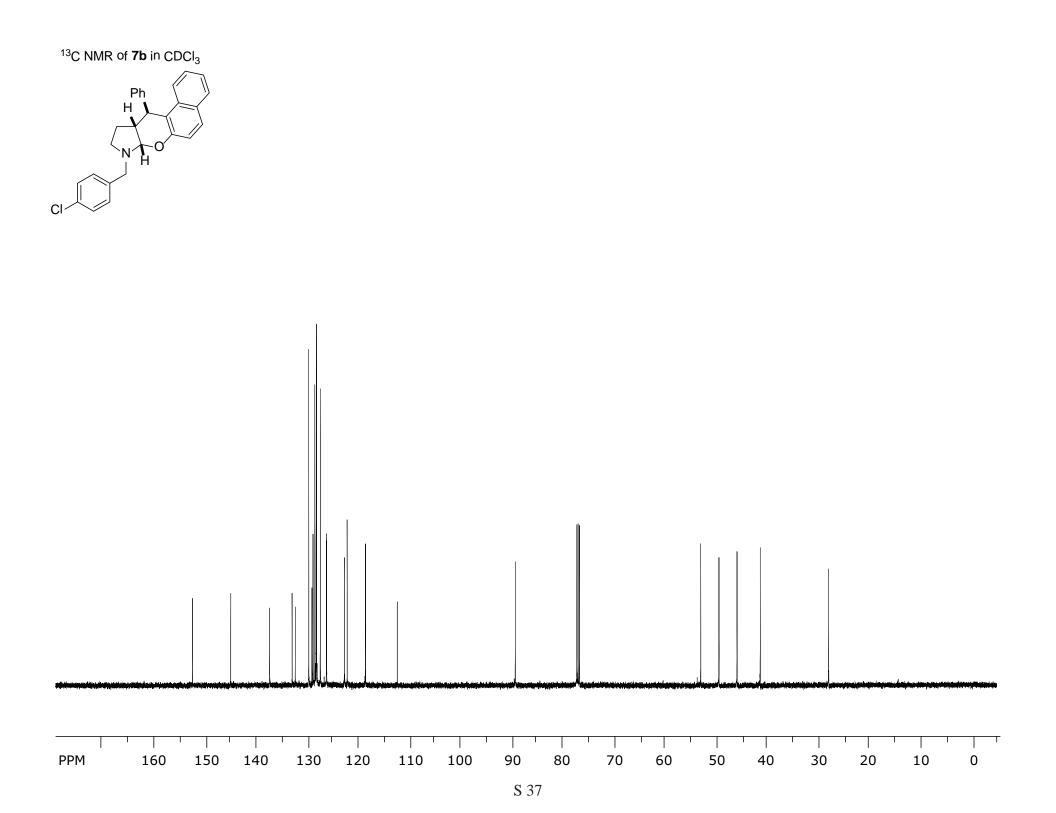


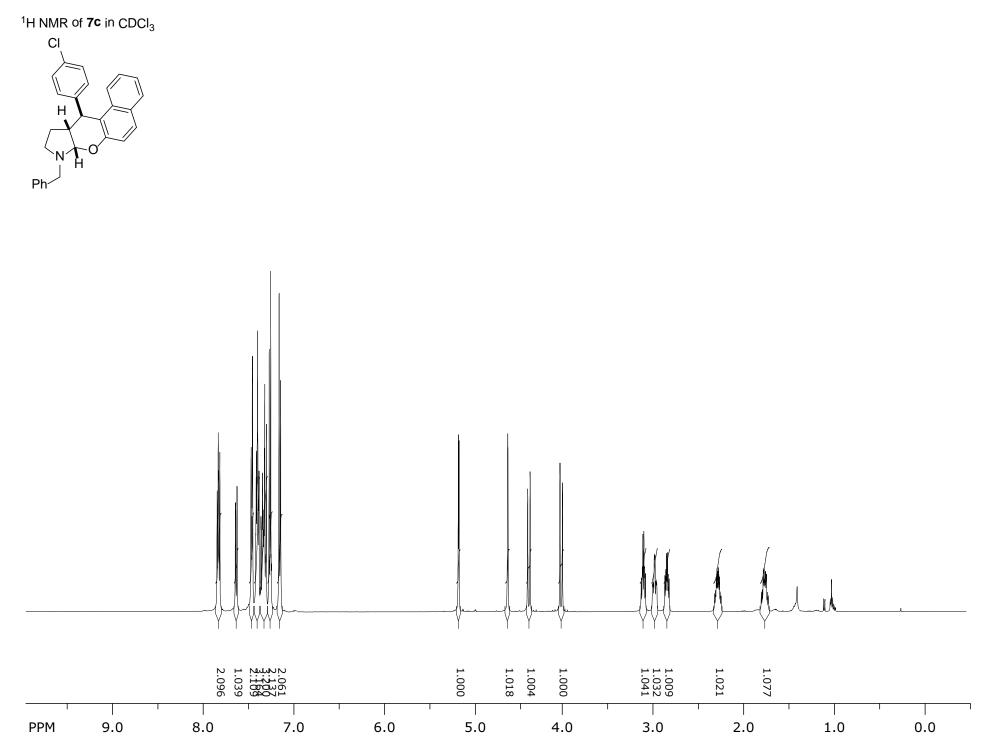


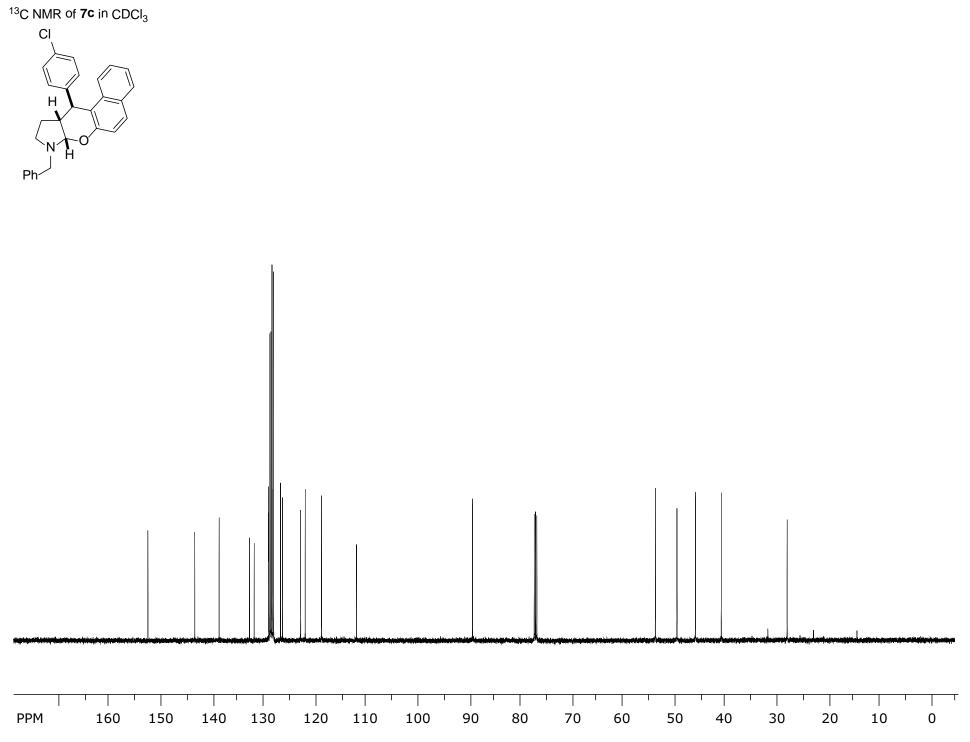




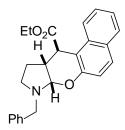


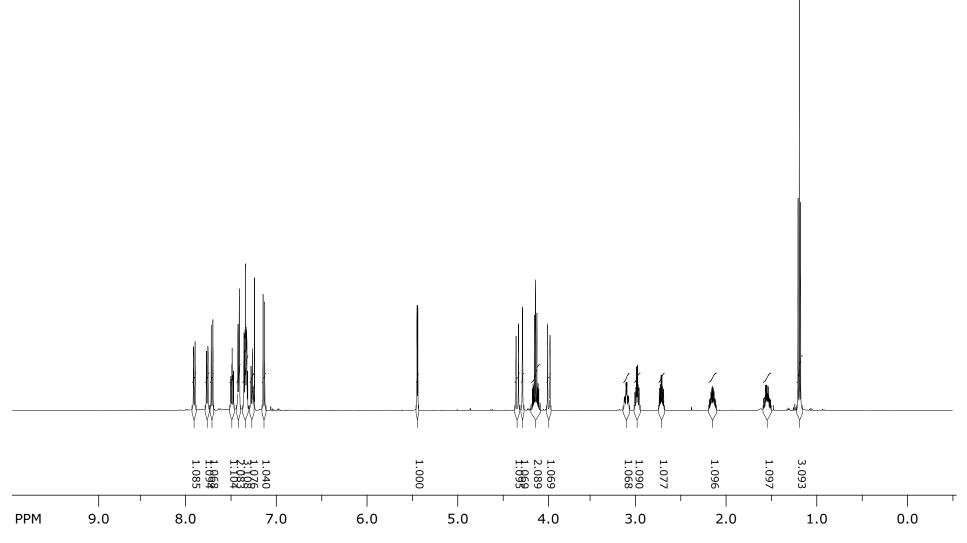


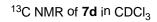


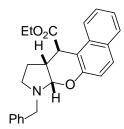


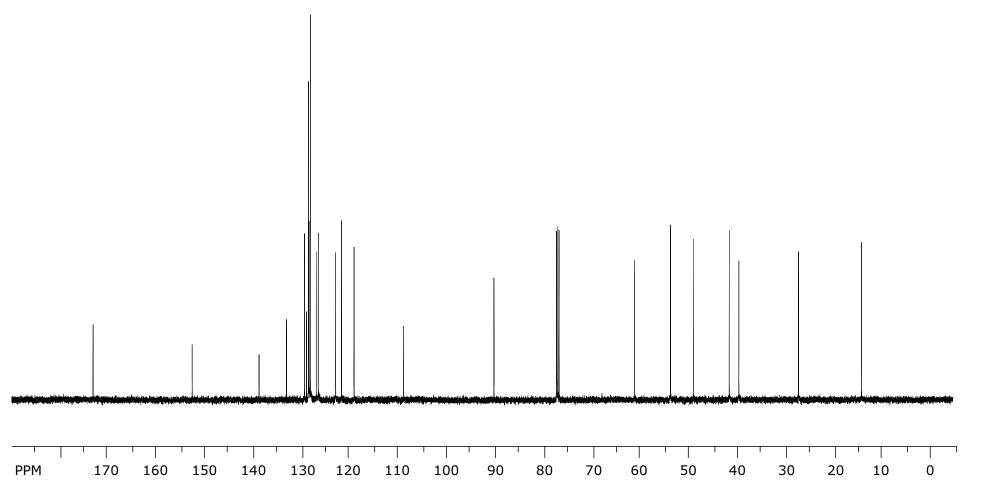
¹H NMR of **7d** in CDCl₃

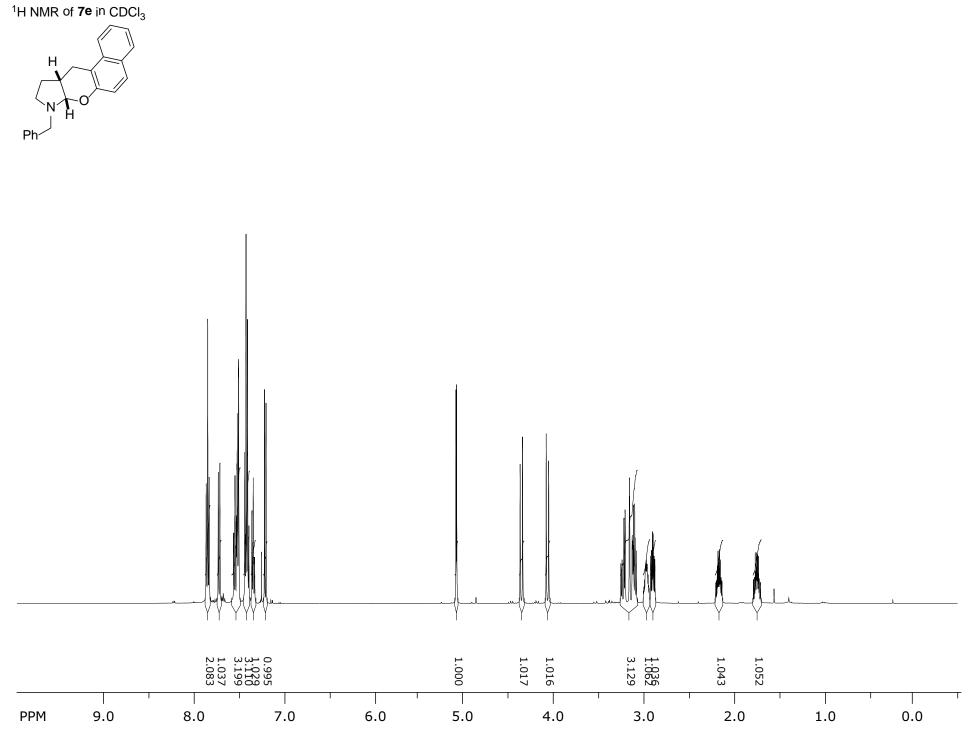


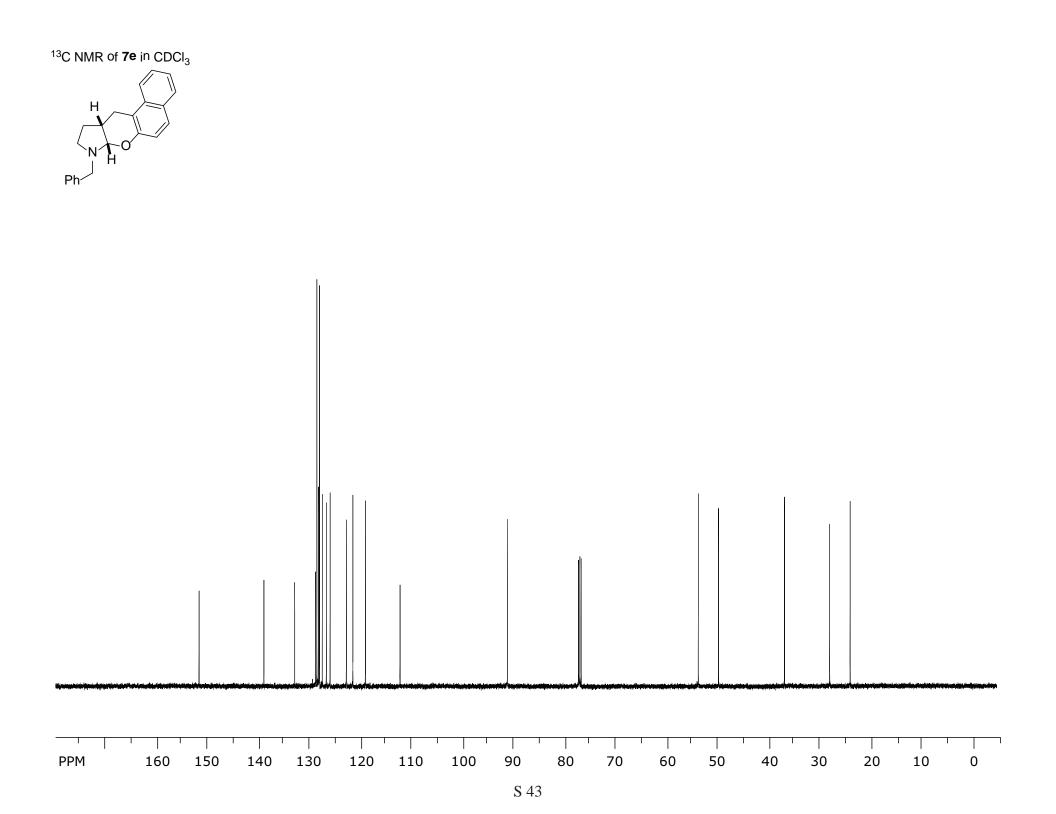


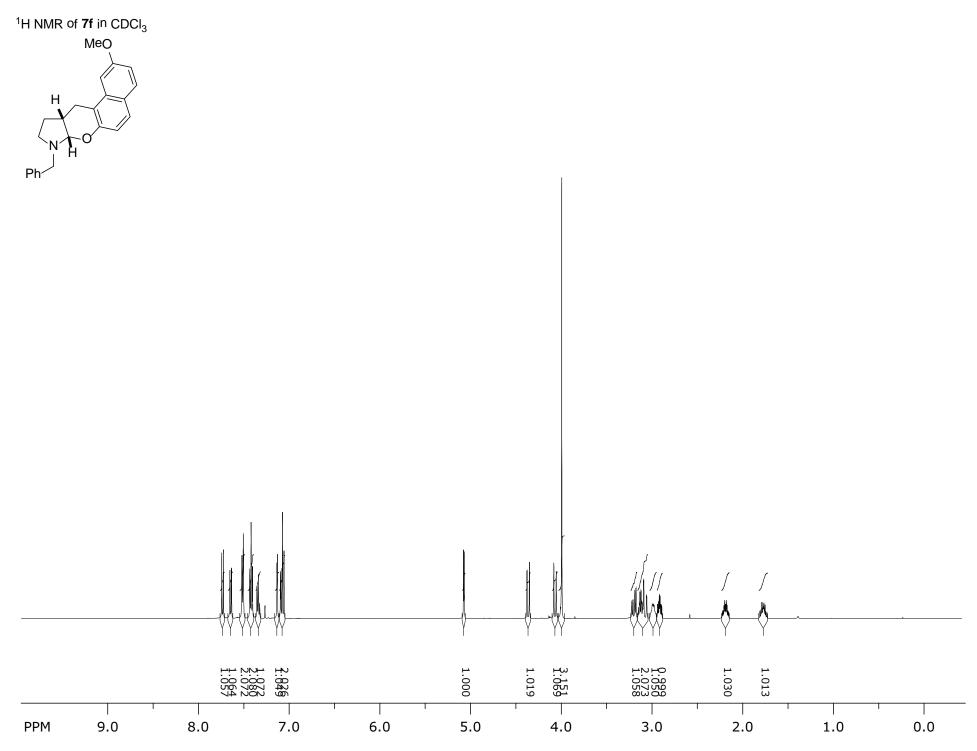


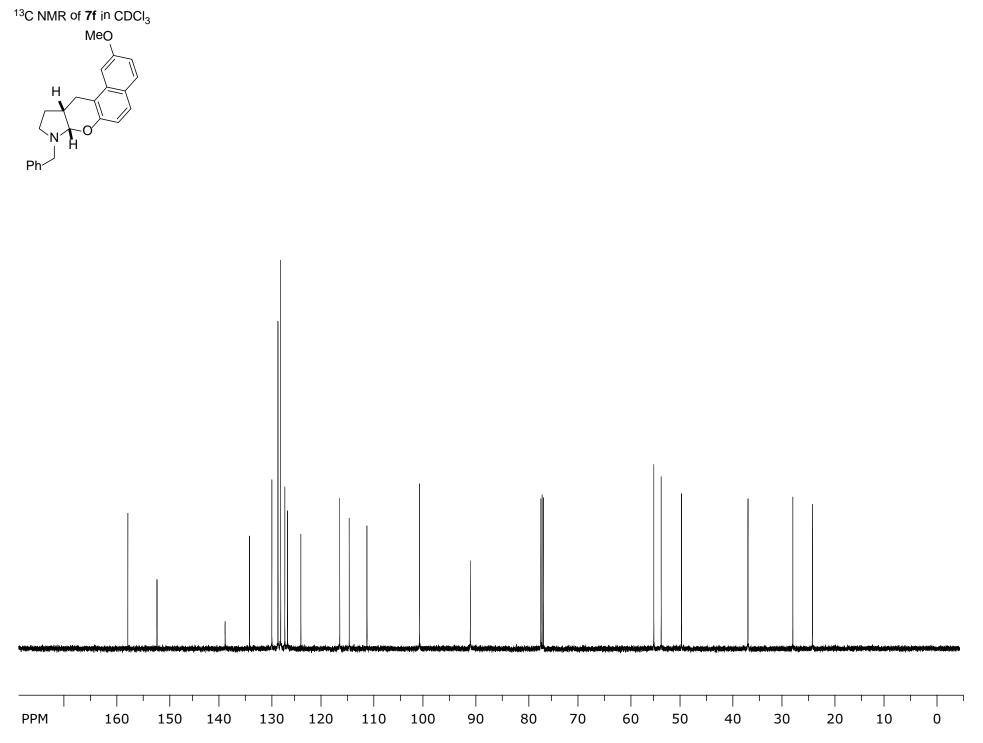


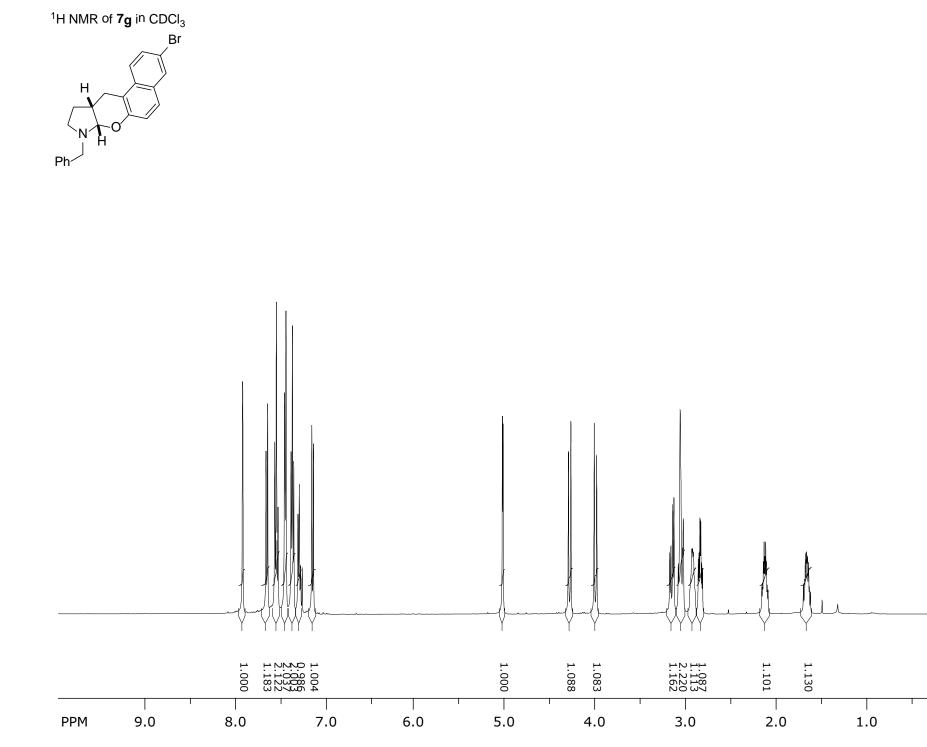




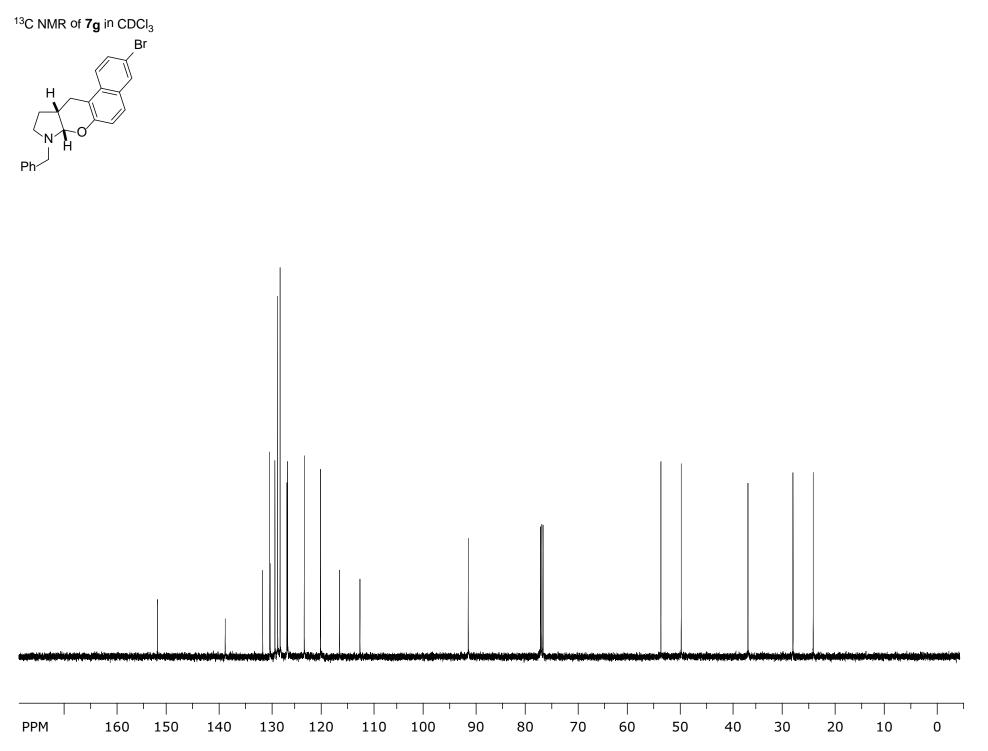


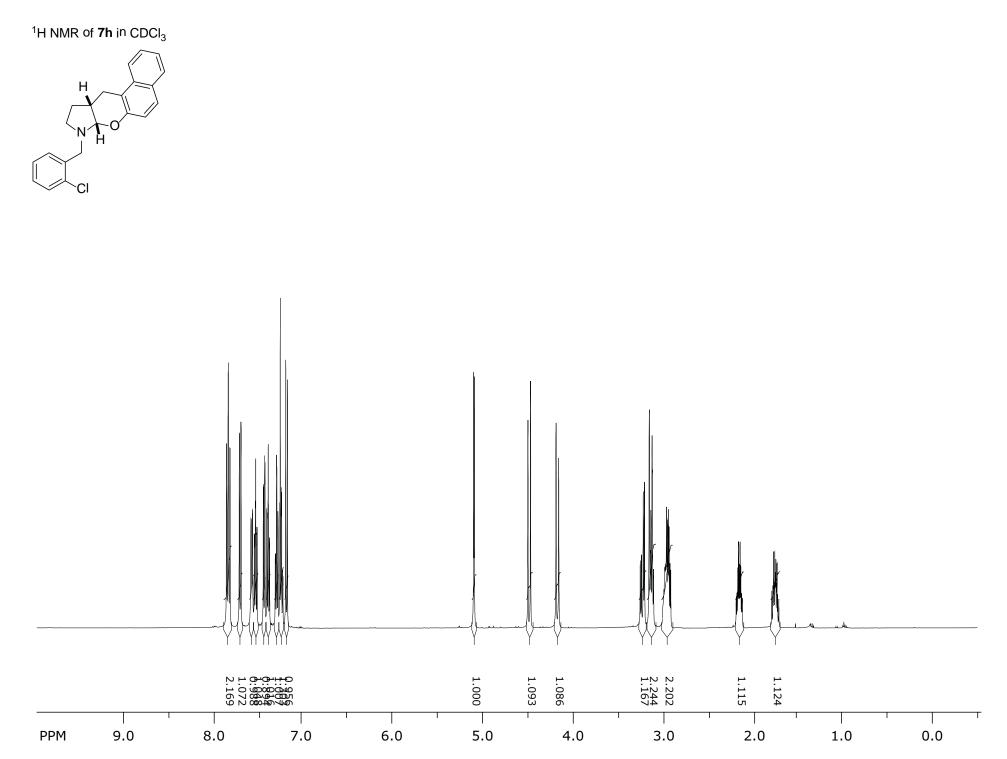


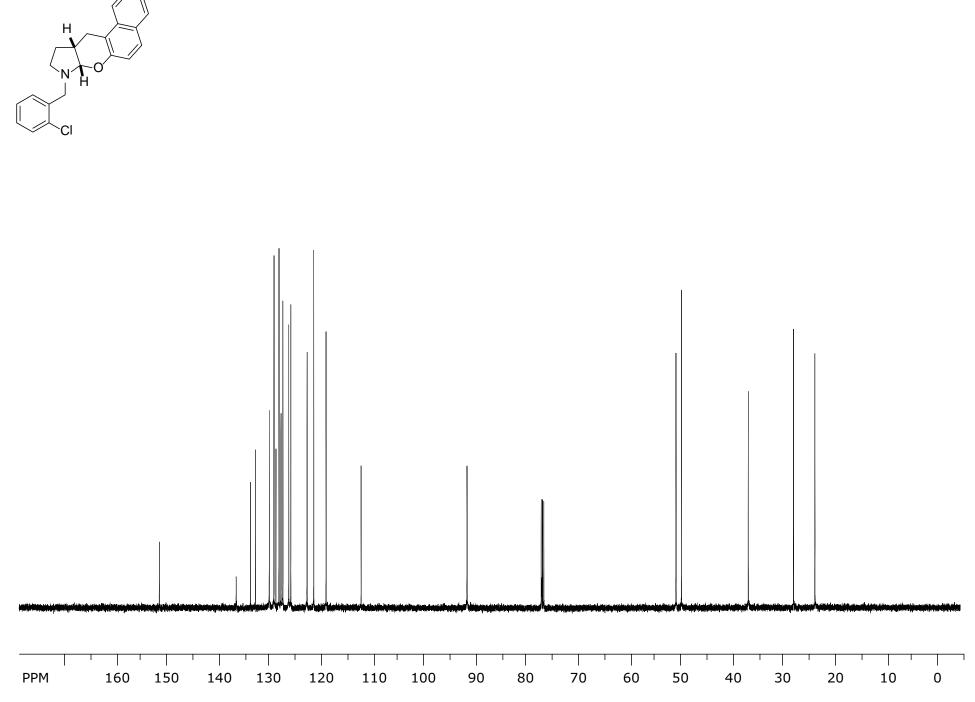




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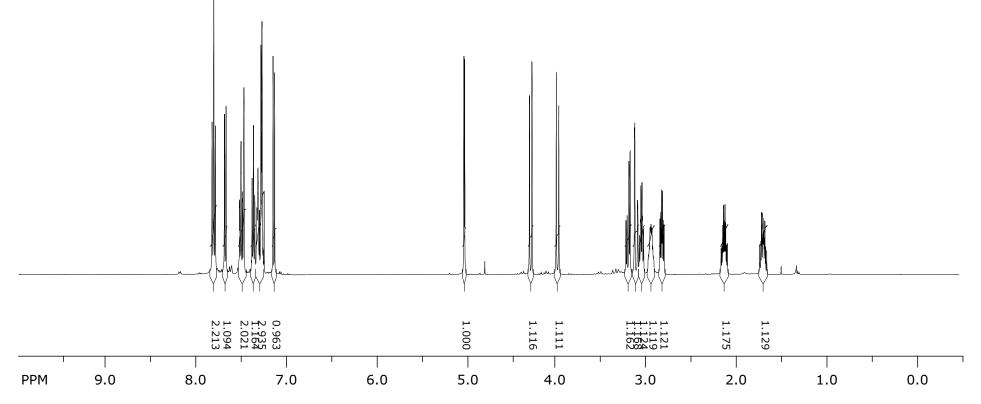


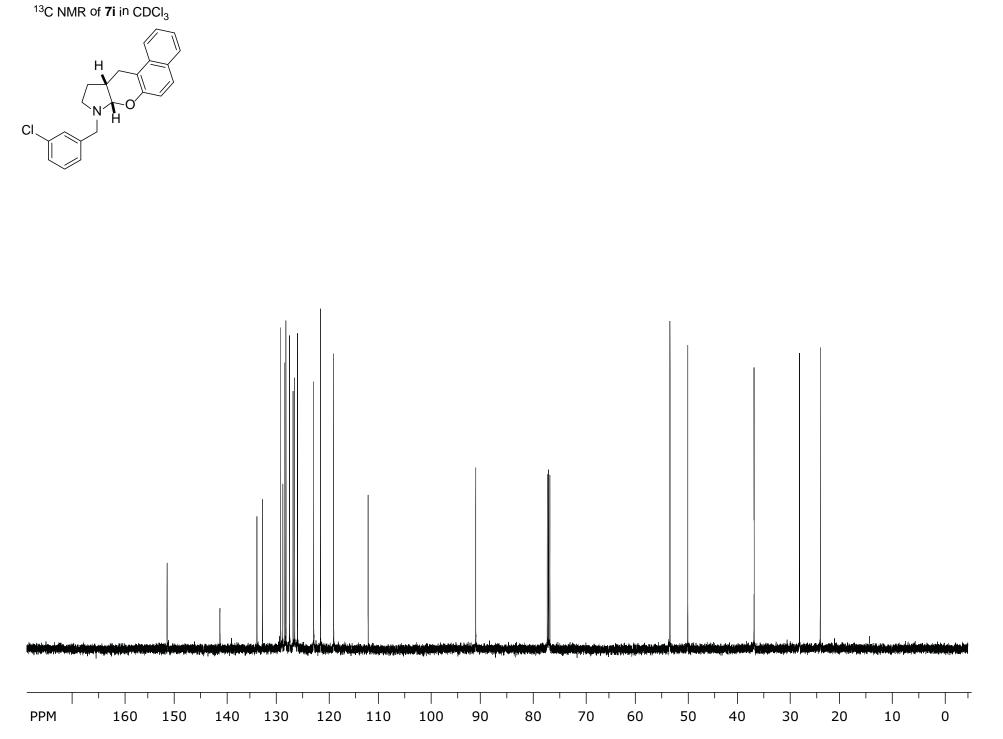


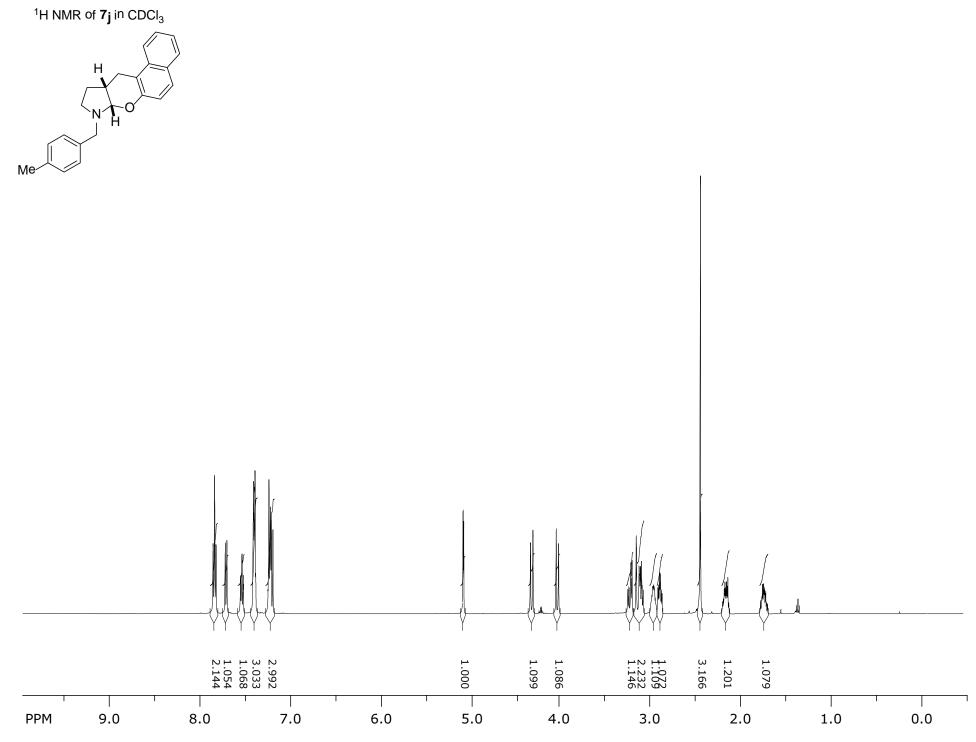


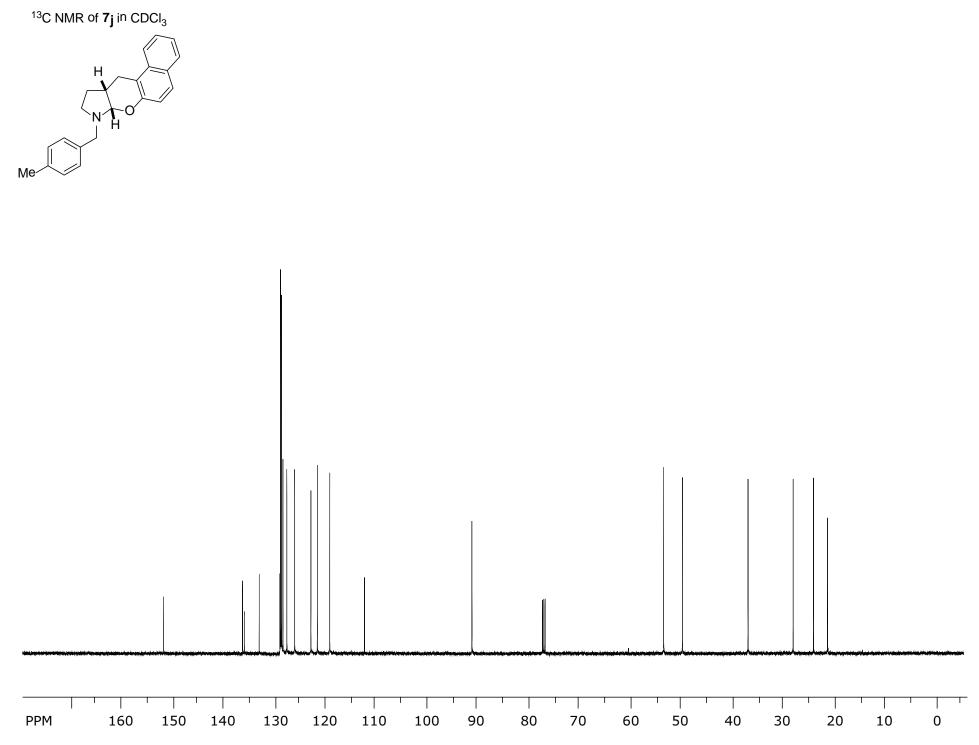
 $^{13}\mathrm{C}$ NMR of $\mathbf{7h}$ in CDCl_3

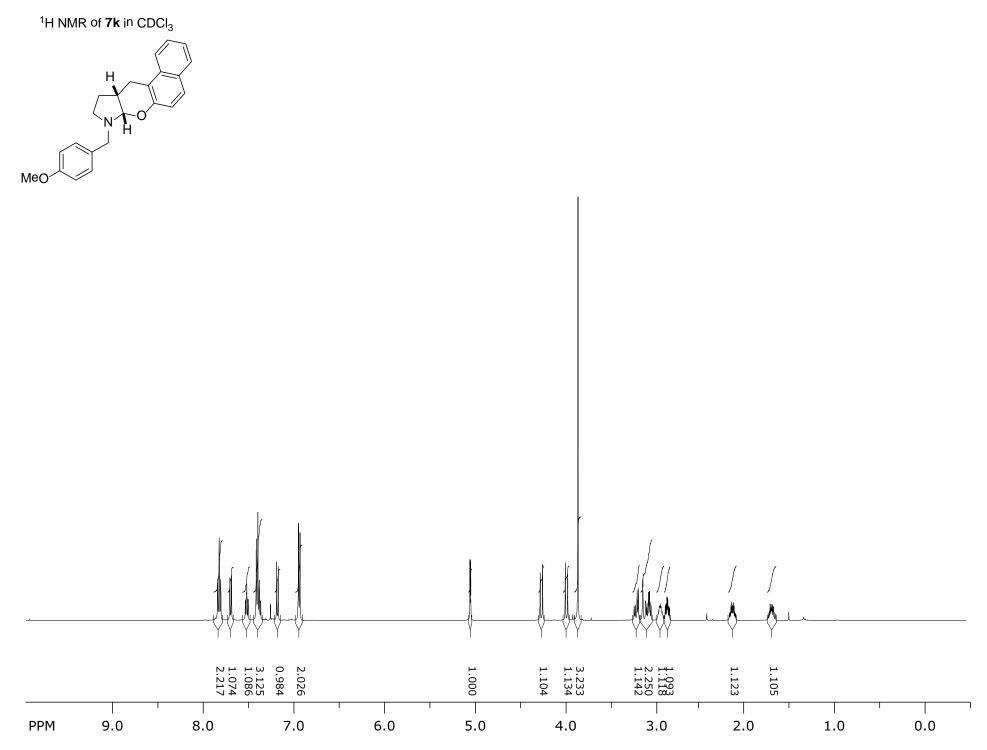


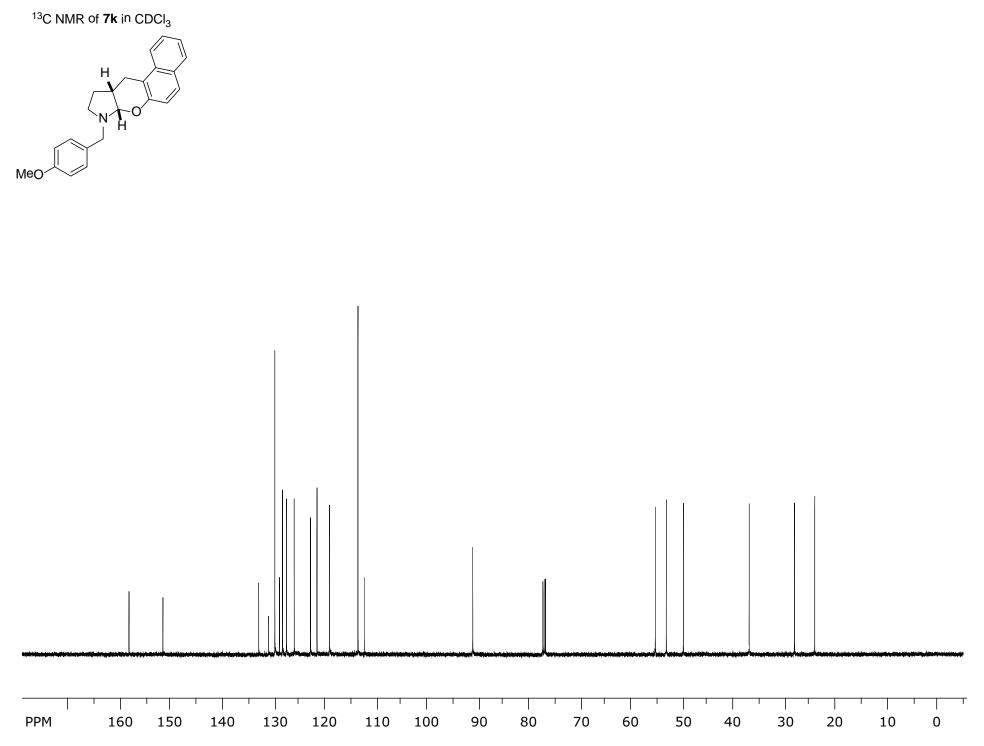


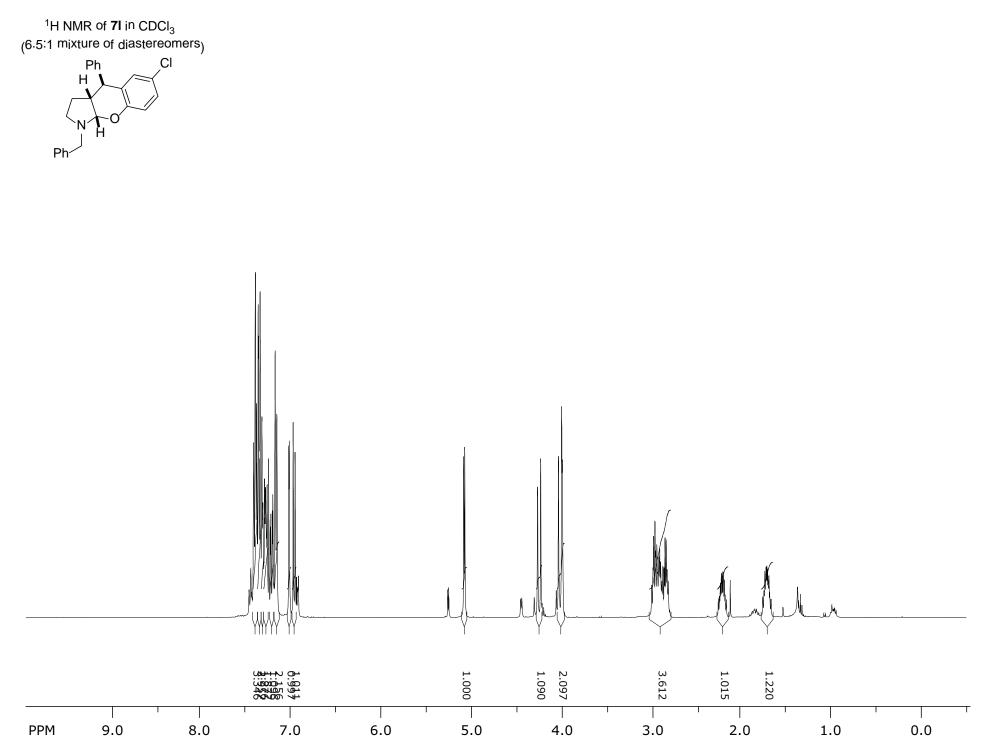


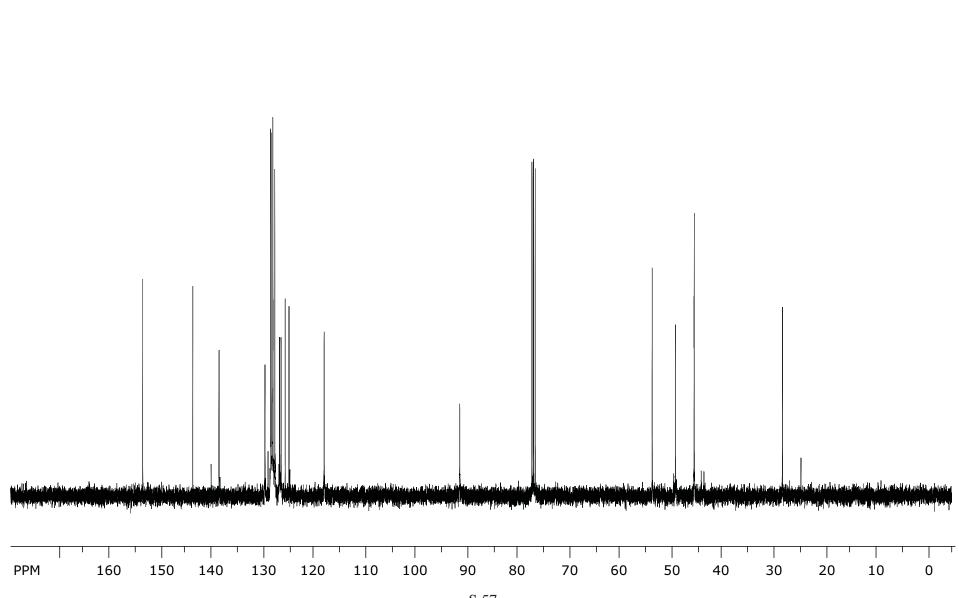




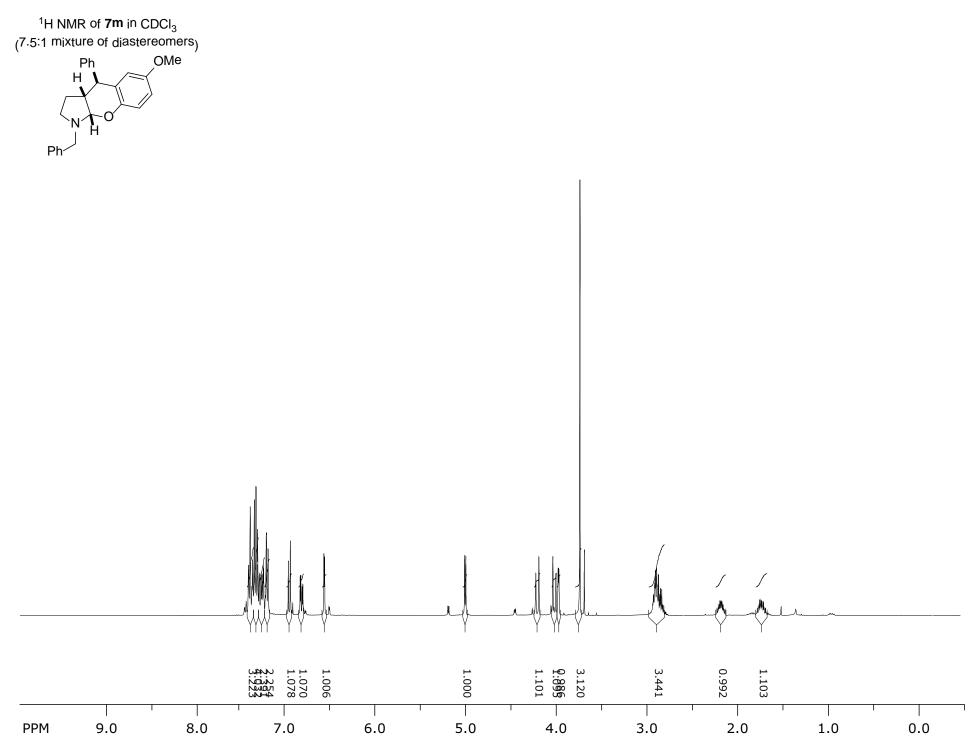


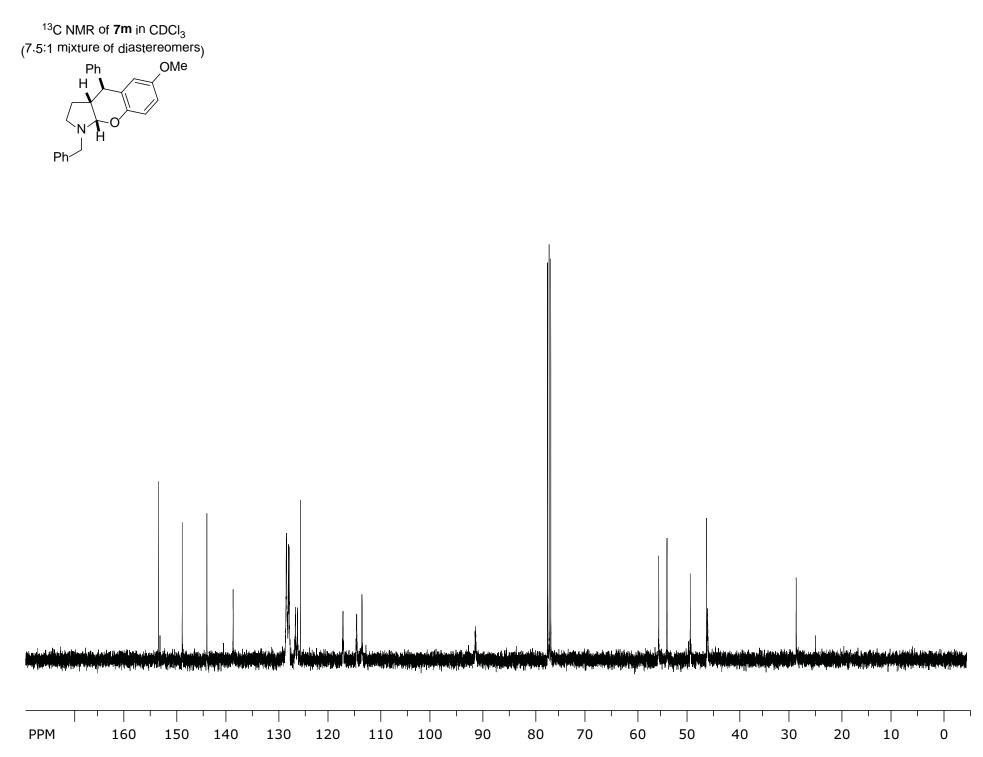




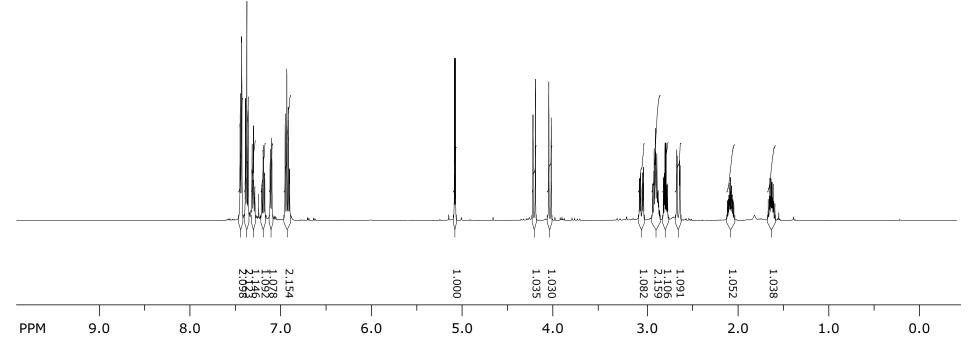


¹³C NMR of **7I** in CDCl₃ (6.5:1 mixture of diastereomers) Ph Cl Н Ph-

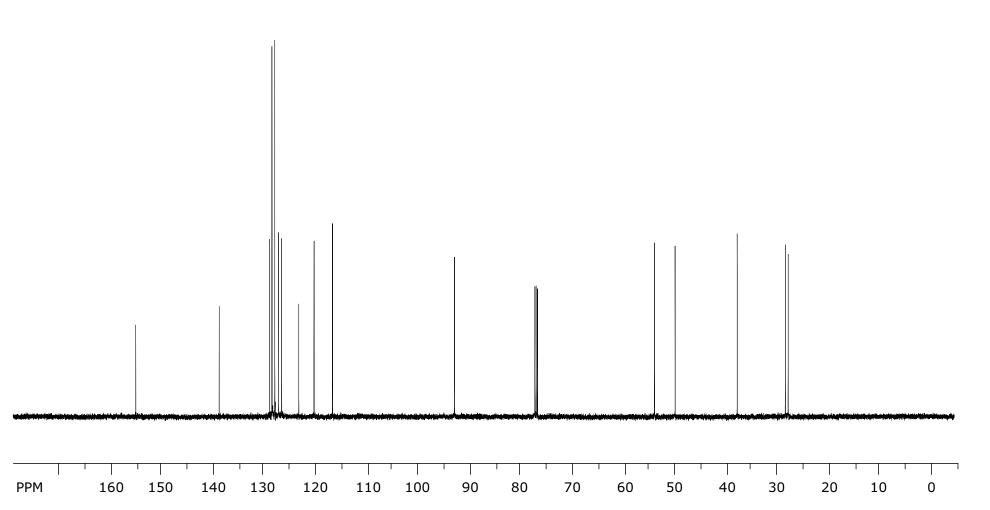


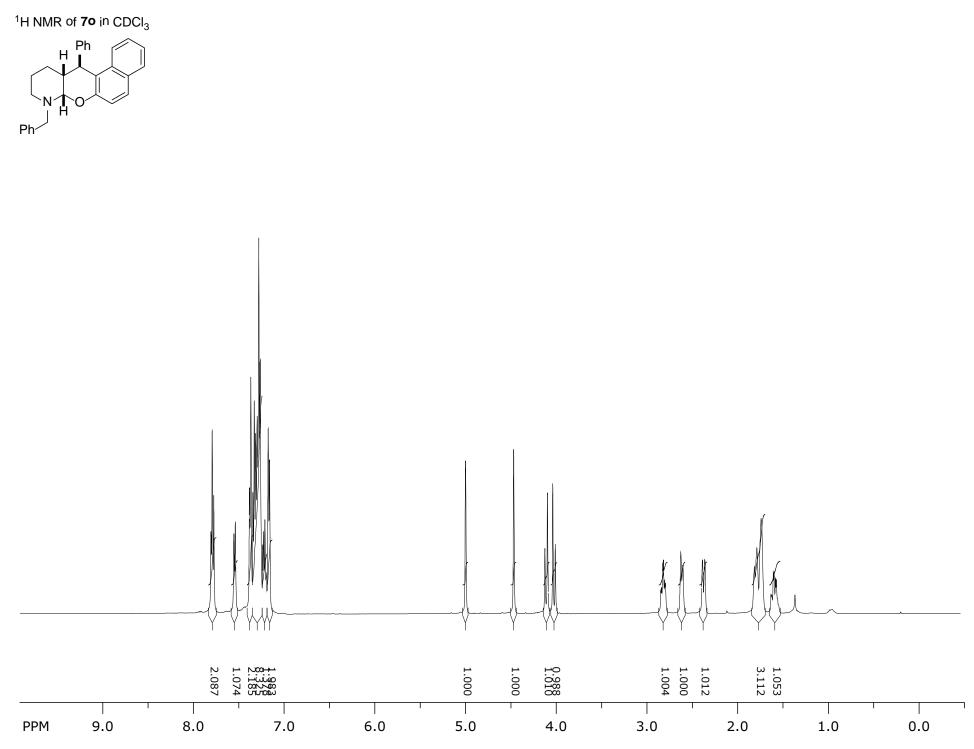


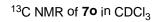


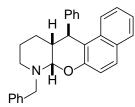


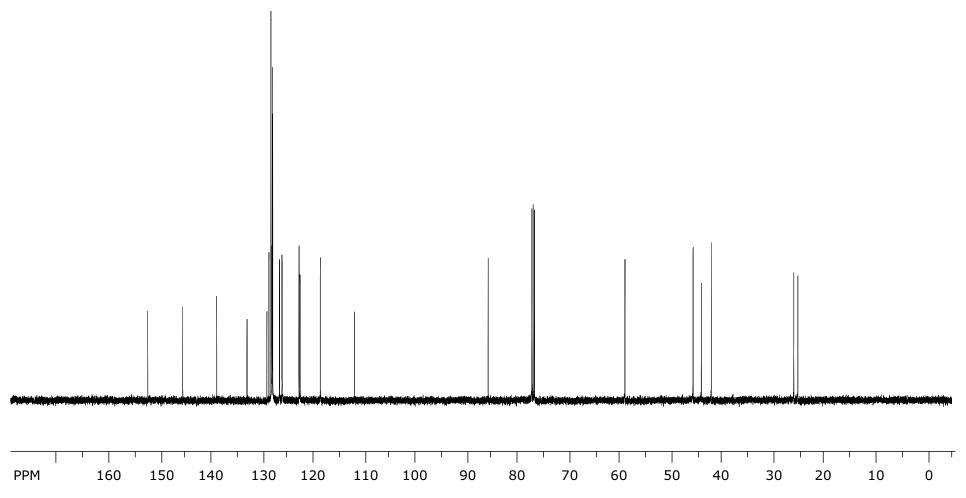


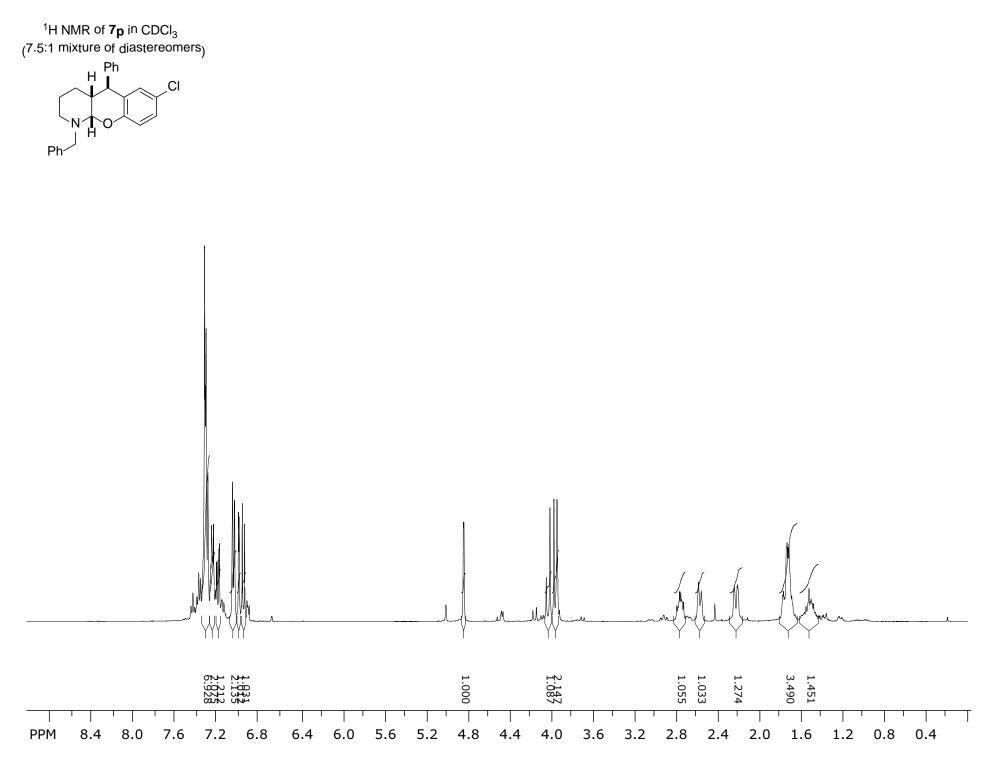


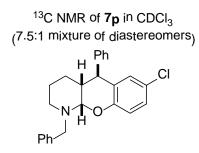


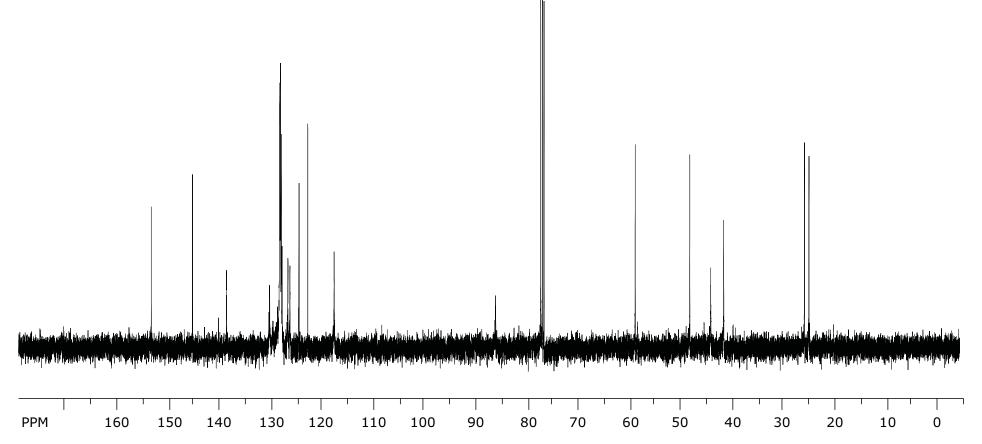


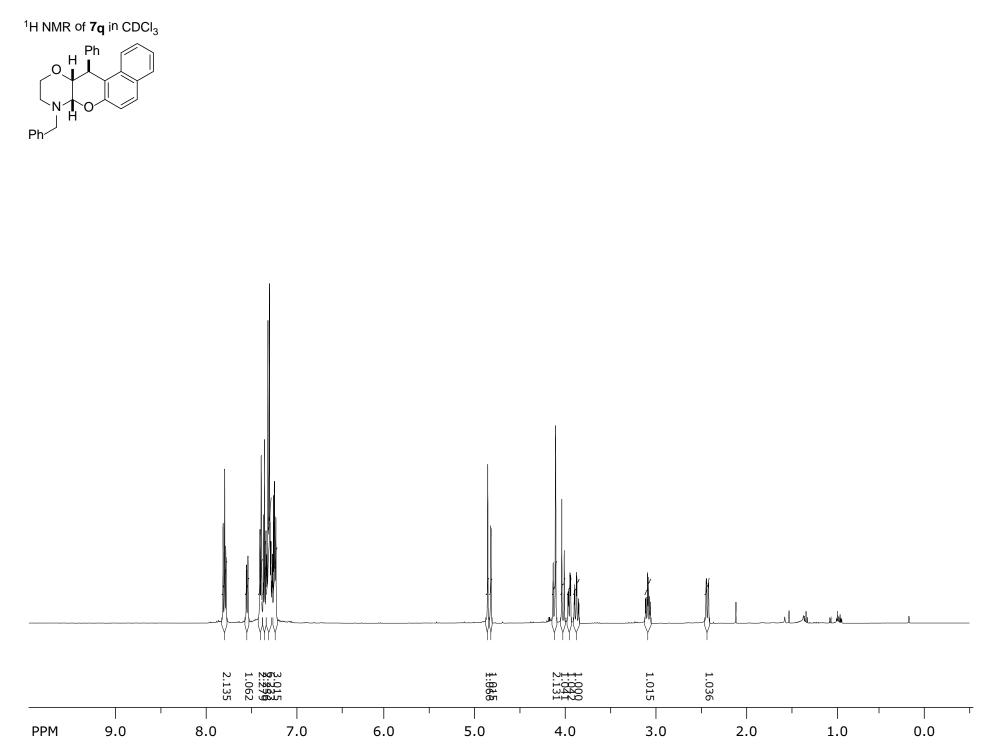


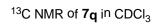


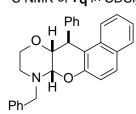


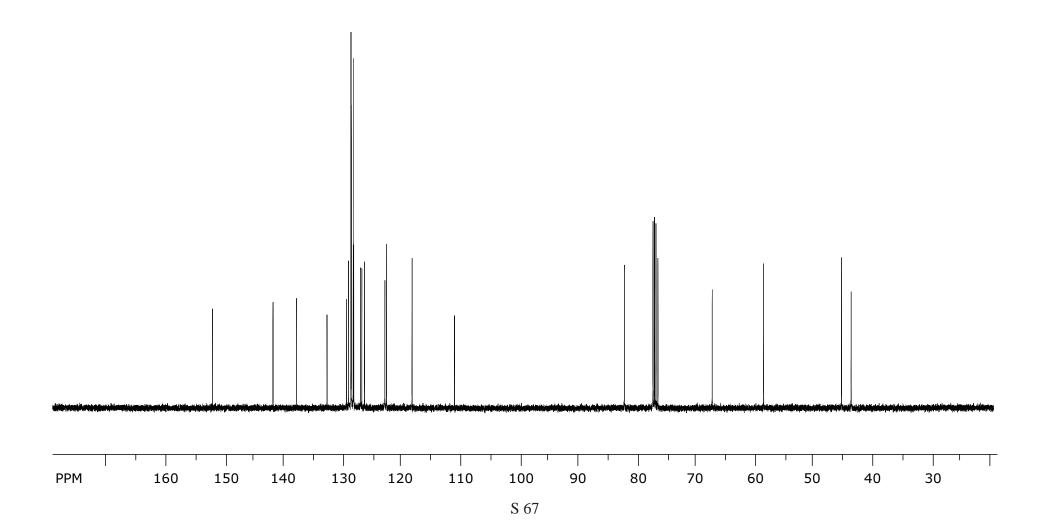


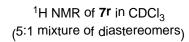


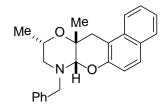


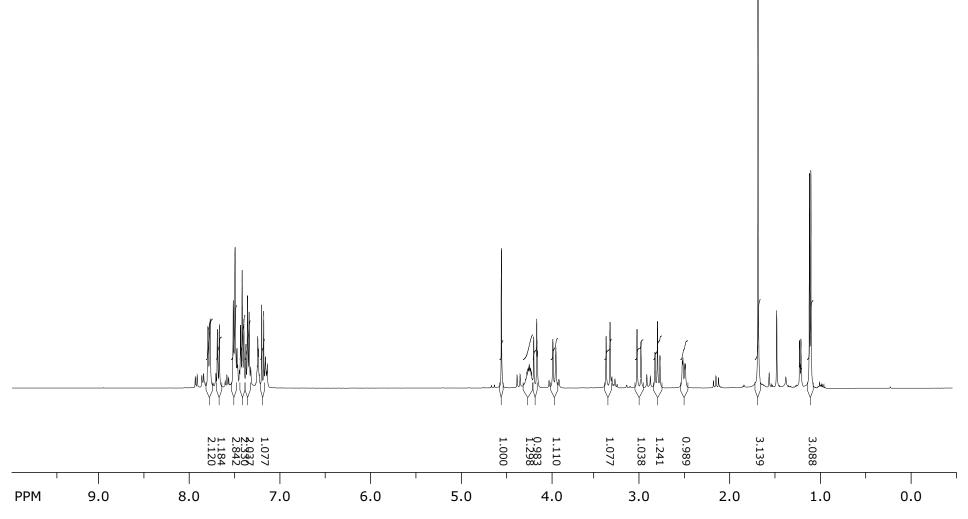


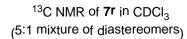


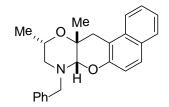


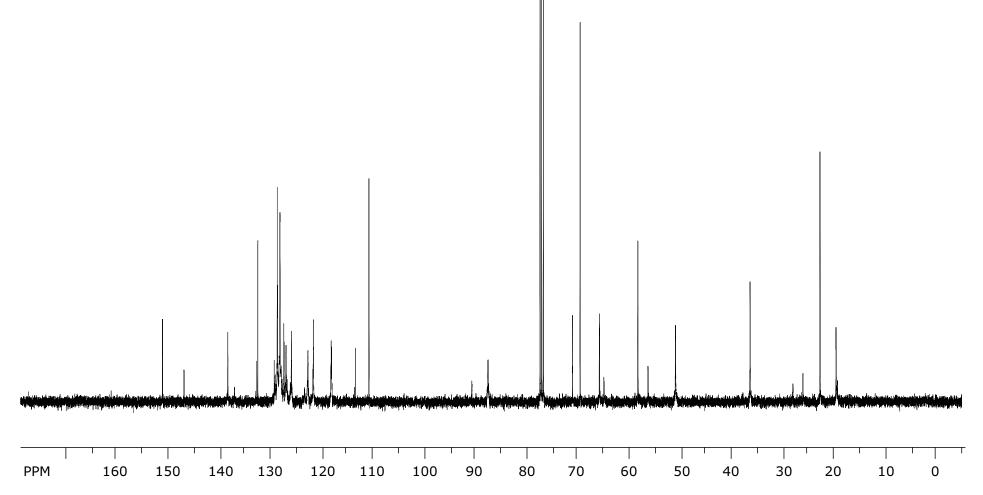


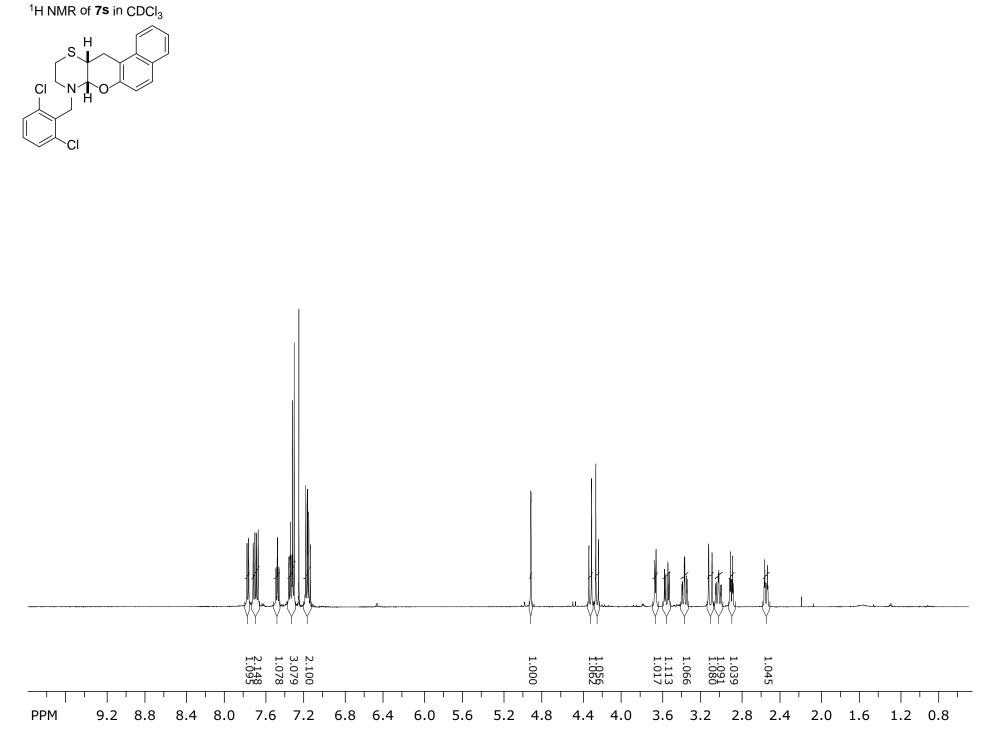




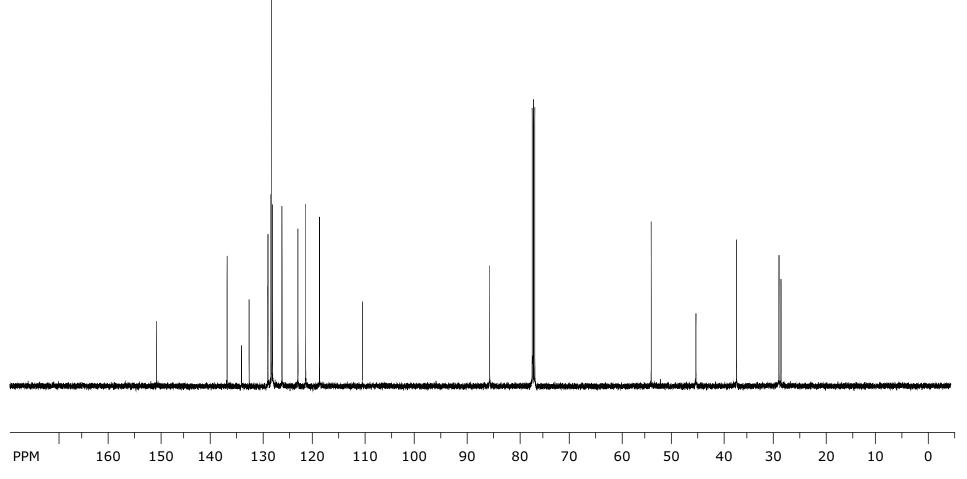


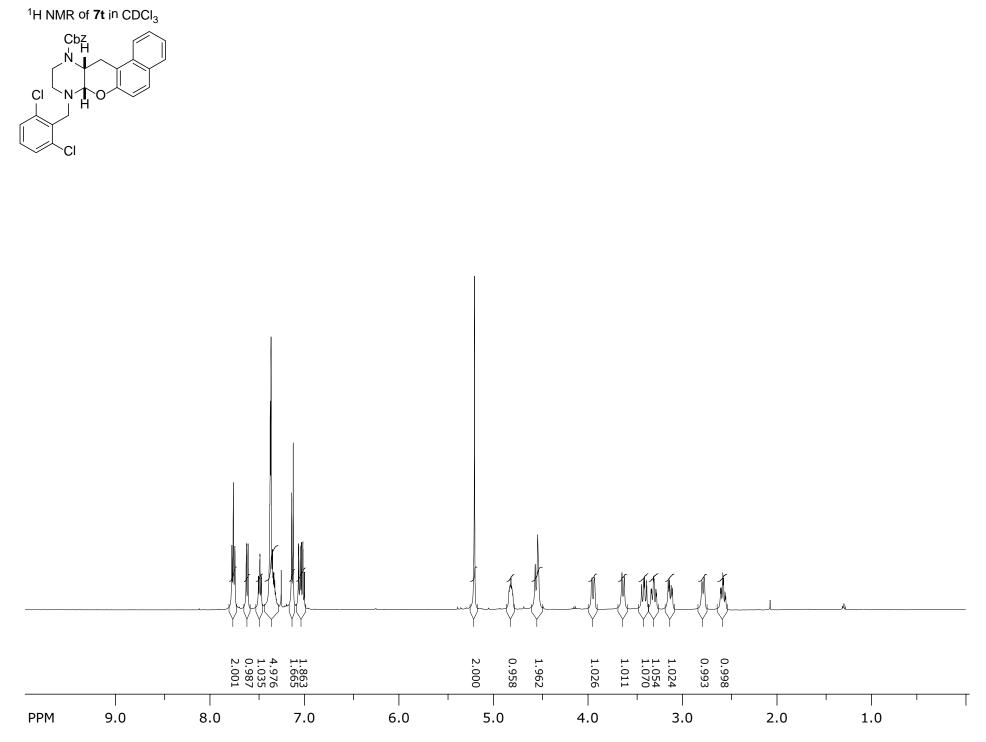


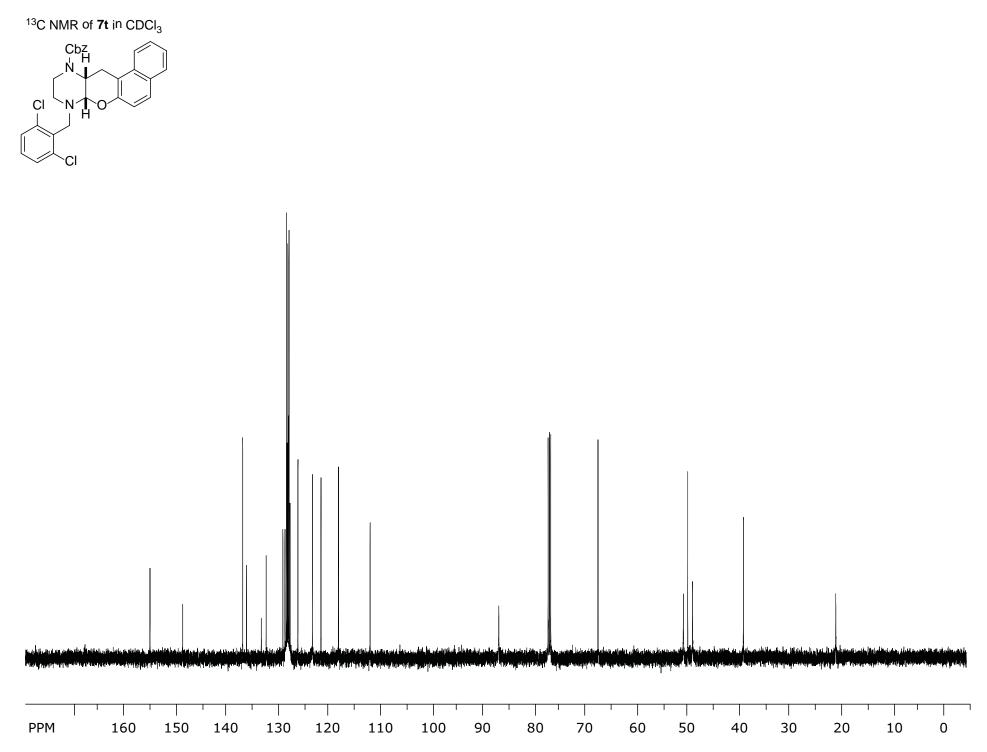


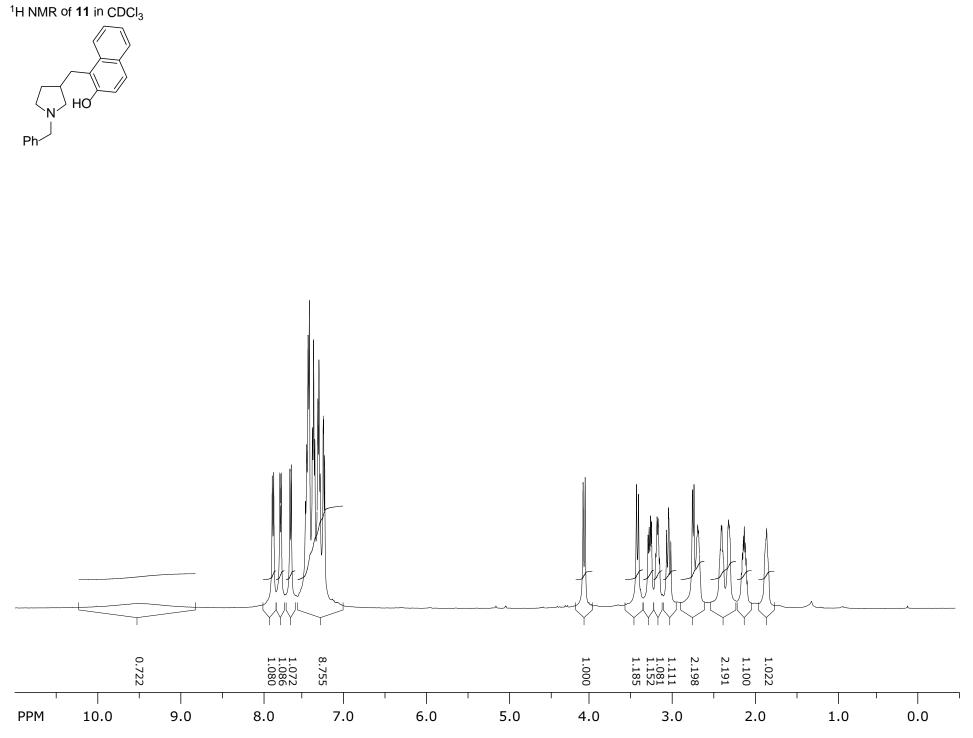


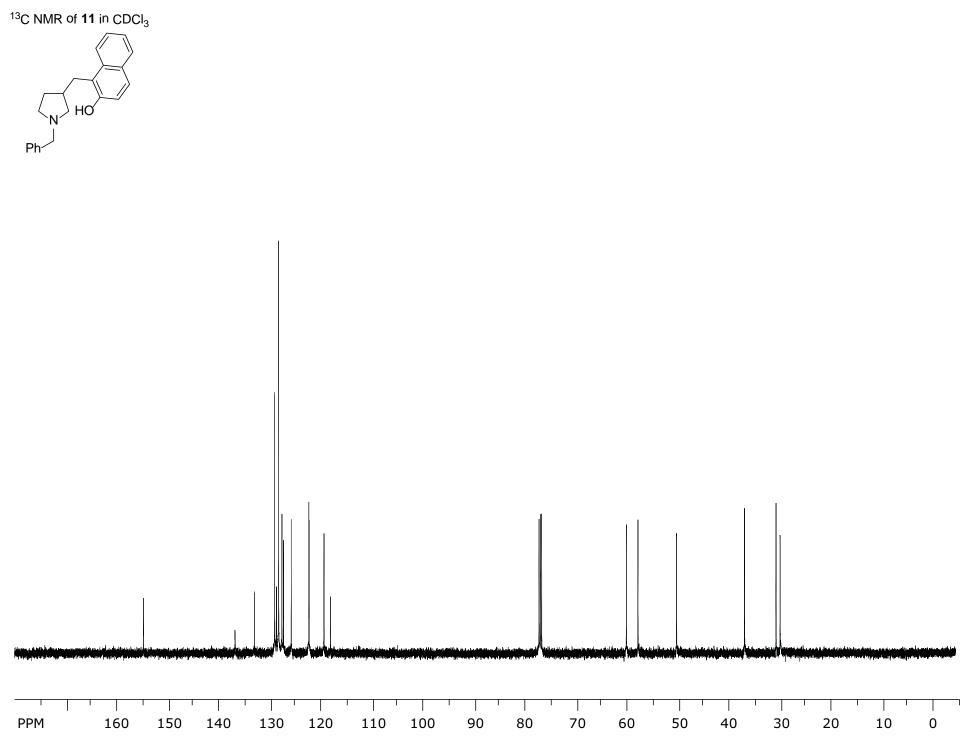


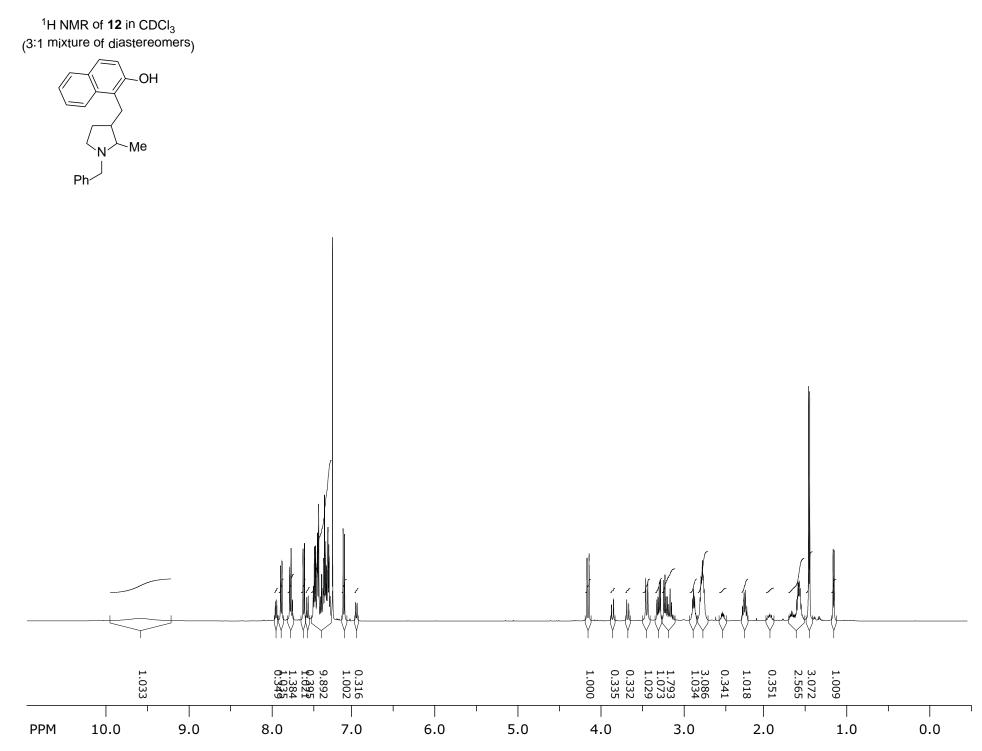


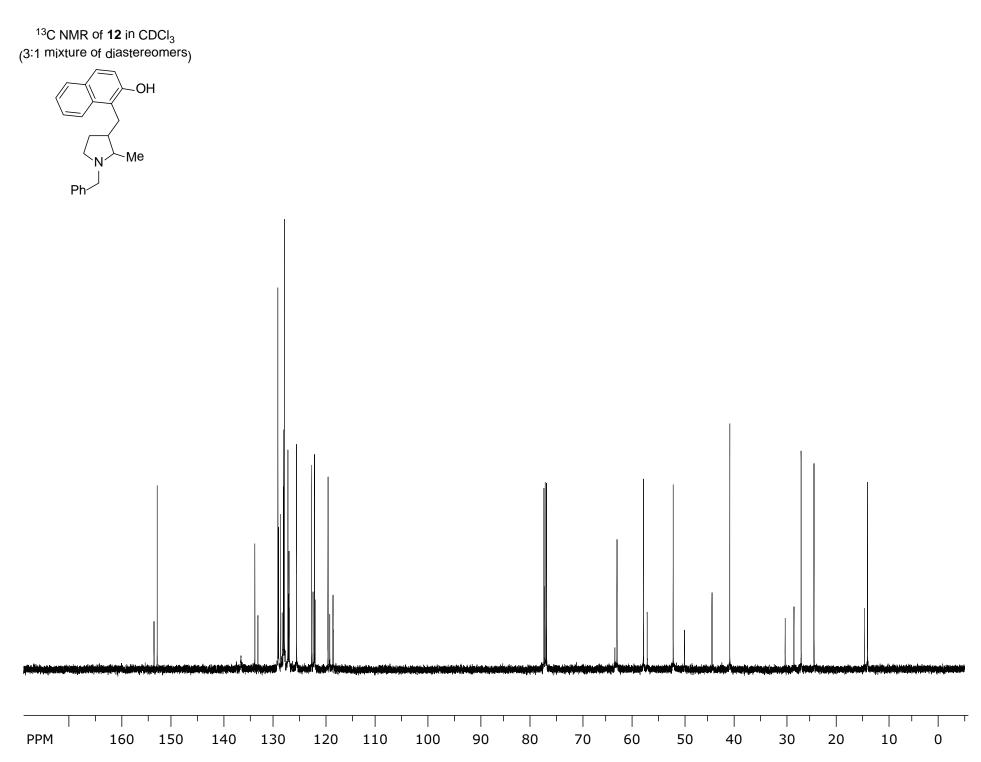


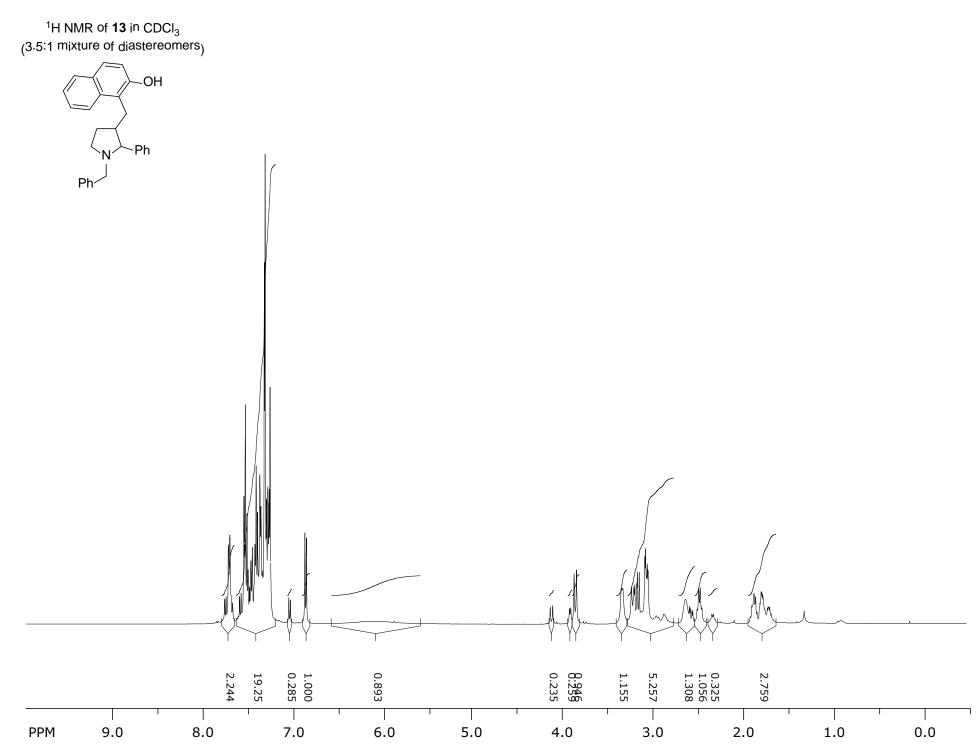


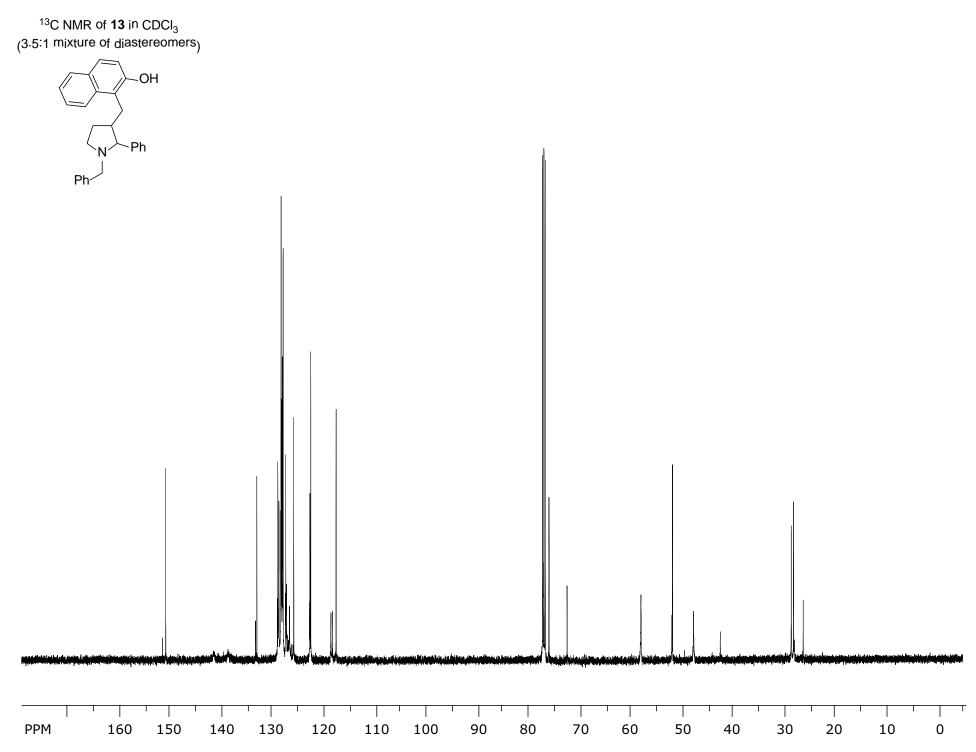


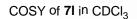


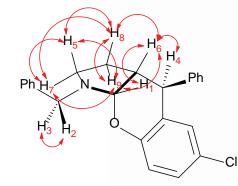


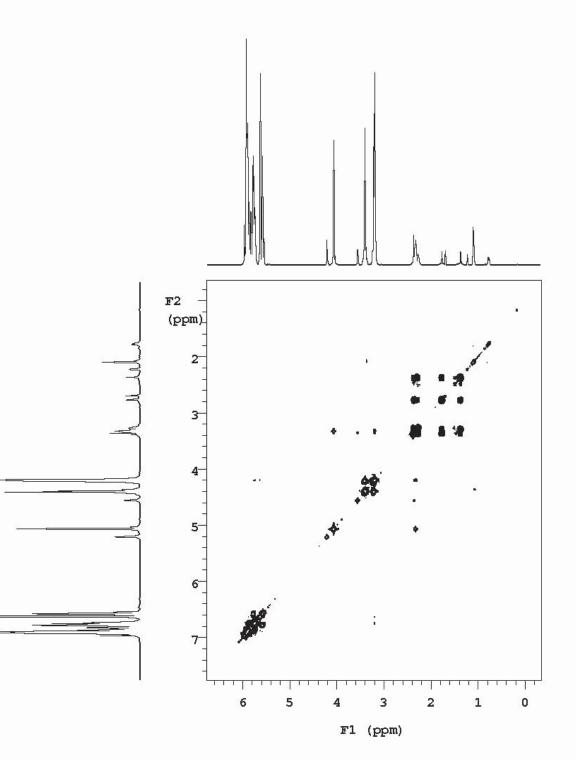


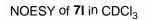


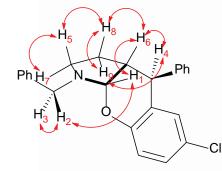


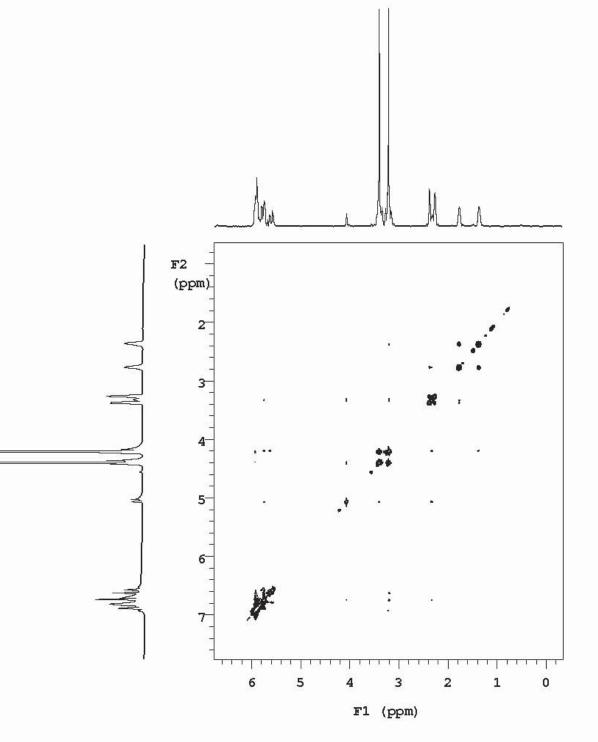


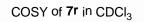




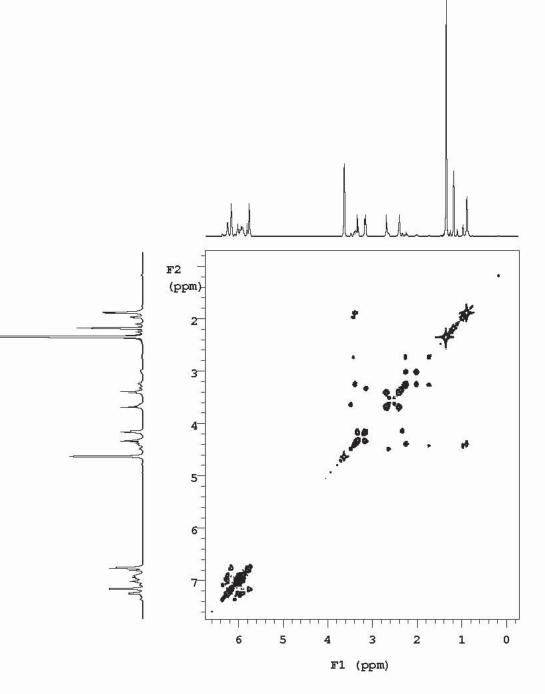








 H_{4} H_{7} Me H_{8} N H_{1} H_{2} H_{5} Me_{1}



NOESY of 7r in CDCl₃

