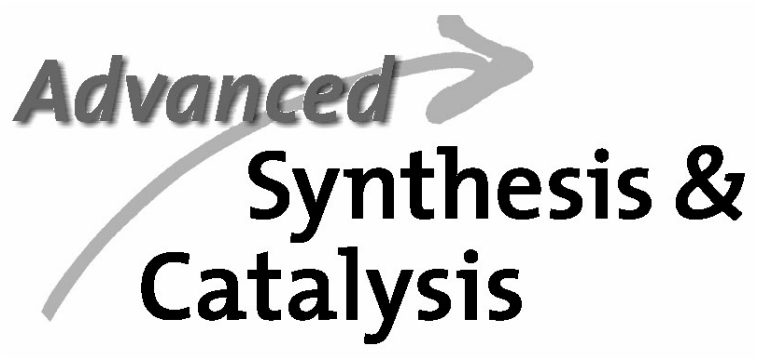

Supporting Information

Supporting Information for

New Pathway to *C*2-Symmetric Atropoisomeric Bipyridine *N,N'*-Dioxides and Solvent Effect in Enantioselective Allylation of Aldehydes

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Contents

1. General methods

All solvents unless otherwise stated were used as obtained. THF was distilled from sodium and benzophenone, and dichloromethane from CaH_2 under Ar. All other reagents were obtained from commercial sources.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400 (^{1}H at 400 MHz, ^{13}C at 100.6 MHz) as solutions in C_6D_6 or $CDCl_3$ with Me_4Si as an internal standard referenced to the residual solvent signal. Chemical shifts are given in δ-scale, coupling constants *J* are given in Hz. Melting points (uncorrected) were determined using a Kofler apparatus. Mass spectra were recorded on a ZAB-SEQ (VG-Analytical) instrument. Infrared spectra were recorded on a Bruker IFS 55 spectrometer as $CHCl_3$ solutions and are reported in wave numbers (cm^{-1}). Fluka 60 silica gel was used for flash chromatography. TLC was performed on silica gel 60 F_{254}-coated aluminum sheets (Merck). All reactions were carried out under an argon atmosphere using Schlenk-tube technique or in microwave reactor Biotage Initiator.

2. Synthesis of starting material

Hexadeca-1,7,9,15-tetrayne (1). To a suspension of CuI (448 mg, 2.35 mmol), $PdCl_2(MeCN)_2$ (300 mg, 1.16 mmol), PPh_3 (1.23 g, 4.7 mmol) in dry and degassed THF (300 mL) under atmosphere of argon was added 1,7-octadiyne (10 g, 94 mmol).[1] After cooling of the suspension to 0 °C a solution of I_2 (3 g, 11.8 mmol) in THF (7 mL) was added dropwise, followed by the addition of diisopropylamine (30 mL) and the reaction mixture was left stirring at 20 °C for 8 hours. Then it was diluted by water (50 mL) and diethylether (100 mL), the organic layer was separated, dried over $MgSO_4$, and filtrated over silica gel. Volatiles were removed under reduced pressure and the residue was filtered over a short pad of alumina (hexane). Once again volatiles were removed under reduced pressure and Kugelrohr distillation of the residue afforded 1.58 g (16 %) of the title compound as a colorless liquid: ^{1}H NMR (400 MHz, C_6D_6) δ 1.26-1.30 (m, 8H), 1.71-1.73 (m, 2H), 1.78-1.80 (m, 2H), 1.82-1.86 (m, 4H); ^{13}C NMR (100 MHz, C_6D_6) δ 18.7, 19.5, 28.3, 28.4, 67.8, 70.1, 78.3, 84.9. IR and EA data were in agreement with the previously published values.[2]

3. Synthesis of bis(tetrahydroisoquinolines)

General procedure for cyclotrimerization of hexadeca-1,7,9,15-tetrayne (1) with nitriles. To a solution of hexadeca-1,7,9,15-tetrayne **1** (200 mg, 0.95 mmol) in a dry nitrile (15 mL) or a solution of a nitrile (20 mmol) in dry and degassed THF in a vial was added $CpCo(CO)_2$ (34 mg, 0.16 mmol) under atmosphere of argon. Then the vial was placed into the microwave oven and irradiated for 30 min (300 W) (during the process temperature and pressure reached

200°C and 20 barr). Then nitrile was removed under reduced pressure and column chromatography of the residue on silica gel (solvent) afforded a product.

Bis-1,1'-(5,6,7,8-tetrahydro-3-methyl-isoquinoline) (3a). Acetonitrile (15 mL). Column chromatography silica gel (EtOAc) afforded 100 mg (36%) of the title compound as a pale yellow solid: m.p. 150 °C (EtOAc); ^{1}H NMR (400 MHz, C_6D_6) δ 1.45-1.47 (m, 8H), 2.42-2.43 (m, 4H), 2.48 (s, 6H), 2.58-2.62 (m, 4H), 6.57 (s, 2H); ^{13}C NMR (100 MHz, C_6D_6) δ 23.3 (2C), 24.0 (2C), 24.7 (2C), 26.7 (2C), 30.2 (2C), 123.1 (2C), 128.6 (2C), 147.2 (2C), 154.6 (2C), 158.9 (2C); IR ($CHCl_3$) ν 3047, 2942, 2879, 2853, 1587, 1552, 1432, 1378, 1299, 1159, 1001, 947, 855, 751, 719, 694, 669 cm^{-1} ; EI-MS m/z (% relative intensity) 292 (M^+, 100), 277 (12), 264 (42), 250 (10), 146 (12), 118 (10); HR-MS calculated for $C_{20}H_{24}N_2$ 292.19395, found 292.193461.

Bis-1,1'-(5,6,7,8-tetrahydro-3-phenylisoquinoline) (3b). Benzonitrile (15 mL). Column chromatography (3/1 hexane/Et_2O) afforded 202 mg (51%) of the title compound as a pale yellow solid: m.p. 193 °C (EtOAc); ^{1}H NMR (400 MHz, C_6D_6) δ 1.44-1.48 (m, 8H), 2.48-2.52 (m, 4H), 2.64-2.72 (m, 4H), 7.16- 7.20 (m, 2H), 7.27-7.32 (m, 6H), 8.20-8.22 (m, 4H); ^{13}C NMR (100 MHz, C_6D_6) δ 23.3 (2C), 24.1 (2C), 27.3 (2C), 30.6 (2C), 121.3 (2C), 128.6 (4C), 130.0 (2C), 130.2 (4C), 131.8 (2C), 141.8 (2C), 149.0 (2C), 154.8 (2C), 160.0 (2C); IR ($CHCl_3$) ν 3059, 2939, 2917, 2856, 2828, 1587, 1552, 1413, 1305, 1216, 1159, 1023, 859, 770, 688, 672, 612 cm^{-1} ; EI-MS m/z (% relative intensity) 416 (M^+, 100), 388 (20), 208 (22), 180 (7); HR-MS calculated for $C_{30}H_{28}N_2$ 416.22525, found 416.22416.

Bis-1,1'-{5,6,7,8-tetrahydro-3-[4-(trifluoromethyl)phenyl]-isoquinoline} (3c). 4-(Trifluoromethyl)benzonitrile (3.28 g, 19.2 mmol) and THF (12 mL). Column chromatography (3/1 hexane/Et_2O) afforded 249 mg (47%) of the title compound as a pale yellow solid: m.p. 290 °C (EtOAc); ^{1}H NMR (400 MHz, C_6D_6) δ 1.42-1.55 (m, 8H), 2.48-2.52 (m, 4H), 2.60-2.65 (m, 4H), 7.16- 7.18 (m, 2H), 7.48-7.50 (m, 4H), 7.80-8.02 (m, 4H); ^{13}C NMR (100 MHz, C_6D_6) δ 23.1 (2C), 23.8 (2C), 27.1 (2C), 30.4 (2C), 121.2 (2C), 126.4 (2C), 128.0 (4C), 130.9 (2C), 131.3 (2C), 132.1 (4C), 143.9 (2C), 148.6 (2C), 152.4 (2C), 159.0 (2C); IR ($CHCl_3$) ν 3050, 2942, 2863, 2828, 1615, 1577, 1454, 1429, 1324, 1156, 1115, 1068, 1014, 840, 817 cm^{-1} ; EI-MS m/z (% relative intensity) 552 (M^+, 100), 524 (20), 276 (15); HR-MS calculated for $C_{32}H_{26}N_2F_6$ 552.20002, found 552.200873.

Bis-1,1'-[5,6,7,8-tetrahydro-3-(4-methoxyphenyl)isoquinoline] (3d). 4-Methoxybenzonitrile (2.53 g, 19.2 mmol) and THF (12 mL). Column chromatography (3/1 hexane/Et_2O) afforded 228 mg (50%) of the title compound as a pale yellow solid: m.p. 231 °C (EtOAc); ^{1}H NMR (400 MHz, C_6D_6) δ 1.49-1.51 (m, 8H), 2.52-2.54 (m, 4H), 2.68-2.74 (m, 4H), 3.31 (s, 6H), 6.90- 6.93 (m, 4H), 7.32 (s, 2H), 8.19-8.22 (m, 4H); ^{13}C NMR (100 MHz, C_6D_6) δ 23.3 (2C), 24.1 (2C), 27.1 (2C), 30.6 (2C), 55.5 (2C), 114.9 (4C), 119.8 (2C), 129.2 (4C), 130.2 (2C), 133.6 (2C), 148.0 (2C), 153.8 (2C), 159.1 (2C), 161.4 (2C); IR ($CHCl_3$) ν 3100, 2933, 2860, 2834, 2217, 1603, 1555, 1511, 1410, 1372, 1308, 1254, 1210, 1172, 1023, 830, 681 cm^{-1} ; EI-MS m/z (% relative intensity) 476 (M^+, 85), 448 (14), 238 (16), 84 (100), 56 (15); HR-MS calculated for $C_{32}H_{32}N_2O_2$ 404.24638, found 476.245570.

Bis-1,1'-[5,6,7,8-tetrahydro-3-(3,4,5-trimethoxyphenyl)-isoquinoline] (3e). 3,4,5-Trimethoxybenzonitrile (3.7 g, 19.2 mmol) and THF (10 mL). Column chromatography (2/1 hexane/EtOAc) afforded 263 mg (46%) of the title compound as a pale yellow solid: m.p. 134 °C (EtOAc); ^{1}H NMR (400 MHz, C_6D_6) δ 1.50-1.52 (m, 8H), 2.53-2.56 (m, 4H), 2.60-2.80 (m, 4H), 3.43 (s, 12H), 3.88 (s, 6H), 7.43 (s, 2H), 7.55 (s, 4H); ^{13}C NMR (100 MHz, C_6D_6) δ 23.2 (2C), 23.9 (2C), 27.0 (2C), 30.5 (2C), 56.6 (2C), 61.2 (2C), 106.1 (4C), 120.5 (2C), 129.2 (4C), 130.7 (2C), 136.3 (2C), 141.2 (2C), 148.3 (2C), 154.4 (2C), 155.1 (2C), 159.2 (2C); IR ($CHCl_3$) ν 2999, 2932, 2828, 1742, 1581, 1546, 1501, 1419, 1375, 1337, 1248, 1232, 1118, 1001, 846, 764, 681 cm^{-1} ; EI-MS m/z (% relative intensity) 596 (M^+, 48), 476 (22), 416 (24); HR-MS calculated for $C_{36}H_{40}N_2O_6$ 596.28864, found 596.28664.

Bis-1,1'-[5,6,7,8-tetrahydro-3-(tetrahydrofuran-2-yl)isoquinoline] (3f). Hexadeca-1,7,9,15-tetrayne **1** (90 mg, 0.42 mmol), (*R*)-tetrahydrofuran-2-carbonitrile (1.0 g, 10.3 mmol), THF (3 mL), and $CpCo(CO)_2$ (16 mg, 0.08 mmol). Column chromatography (EtOAc) afforded 90 mg (48%) of the title compound as a pale yellow viscous liquid: ^{1}H NMR (400 MHz, C_6D_6) δ 1.44-1.64 (m, 12H), 2.04-2.08 (m, 2H), 2.17-2.22 (m, 2H), 2.48- 2.50 (m, 6H), 2.51-2.66 (m, 2H), 3.72-3.78 (m, 2H), 3.92-3.98 m (2H) 5.18 (t, J = 7.0 Hz, 2H), 7.36 (s, 2H); ^{13}C NMR (100 MHz, C_6D_6) δ 23.2 (2C), 24.0 (2C), 26.6 (2C), 26.9 (2C), 30.4 (2C), 33.9 (2C), 69.5 (2C), 82.4 (2C), 120.2 (2C), 130.3 (2C), 147.8 (2C), 158.5 (2C), 160.0 (2C); IR ($CHCl_3$) ν 2970, 2936, 2860, 1590, 1555, 1448, 1432, 1394, 1324, 1299, 1220, 1159, 1061, 1001, 916, 871, 748 cm^{-1} ; EI-MS m/z (% relative intensity) 404 (M^+, 100), 376 (18), 359 (78), 348 (18), 292 (16), 256 (22), 213 (10), 185 (14), 167 (14), 149 (22), 129 (20), 111 (18), 97 (30); HR-MS calculated for $C_{26}H_{32}N_2O_2$ 404.24638, found 404.24527.

Bis-1,1'-(5,6,7,8-tetrahydro-3-benzylisoquinoline) (3g). Hexadeca-1,7,9,15-tetrayne **1** (100 mg, 0.47 mmol), benzylcyanide (3 mL) and $CpCo(CO)_2$ (16 mg, 0.08 mmol). Column chromatography (hexane/EtOAc 3/1) afforded 72 mg (34%) of the title compound as a pale yellow solid: m.p. 163 °C (benzene); ^{1}H NMR (400 MHz, C_6D_6) δ 1.40-1.42 (m, 8H), 2.32-2.35 (m, 4H), 2.55-2.57 (m, 4H), 4.13 (s, 4H), 6.70 (s, 2H), 7.05-7.07 (m, 2H), 7.13-7.17 (m, 4H), 7.29-7.31 (m, 4H); ^{13}C NMR (100 MHz, C_6D_6) δ 23.2 (2C), 23.9 (2C), 26.8 (2C), 30.2 (2C), 45.4 (2C), 123.2 (2C), 126.9 (2C), 129.3 (4C), 129.7 (2C), 130.2 (4C), 141.7 (2C), 147.8 (2C), 157.5 (2C), 158.7 (2C); IR ($CHCl_3$) ν 3062, 3024, 2929, 2856, 1590, 1552, 1495, 1451, 1435, 1387, 1302, 1261, 1172, 1134, 1074, 1001, 944, 862, 741, 729, 700 cm^{-1}; FAB-MS m/z (% relative intensity) 445 ($M+H^+$, 100), 177 (6), 154 (10), 137 (10), 91 (7); HR-MS calculated for $C_{32}H_{33}N_2$ 445.26437, found 445.263659.

Bis-1,1'-(5,6,7,8-tetrahydro-3-cyclohexylisoquinoline) (3h). Hexadeca-1,7,9,15-tetrayne **1** (100 mg, 0.47 mmol), cyclohexanecarbonitrile (3 mL) and $CpCo(CO)_2$ (16 mg, 0.08 mmol). Column chromatography (hexane/EtOAc 3/1) afforded 42 mg (21%) of the title compound as a pale yellow solid: m.p. 156 °C (benzene); ^{1}H NMR (400 MHz, C_6D_6) δ 1.24-1.50 (m, 14H), 1.64-1.80 (m, 10H), 2.05-2.08 (m, 4H), 2.48-2.74 (m, 10H), 6.70 (s, 2H); ^{13}C NMR (100 MHz, C_6D_6) δ 23.4 (2C), 24.2 (2C), 27.0 (2C), 27.3 (2C), 27.8 (4C), 30.4 (2C), 34.0 (4C), 47.2 (2C), 121.1 (2C), 129.4 (2C), 147.3 (2C), 158.8 (2C), 162.6 (2C); IR ($CHCl_3$) ν 2923, 2847, 1584, 1552, 1444, 1432, 1394, 1349, 1261, 1156, 1014, 862 cm^{-1}; FAB-MS m/z (% relative intensity) 429 ($M+H^+$, 100), 373 (10), 137 (6); HR-MS calculated for $C_{30}H_{41}N_2$ 429.32697, found 429.32799.

Bis-1,1'-(5,6,7,8-tetrahydro-3-cyclopropylisoquinoline) (3i). Hexadeca-1,7,9,15-tetrayne **1** (100 mg, 0.47 mmol), cyclopropanecarbonitrile (3 mL) and $CpCo(CO)_2$ (16 mg, 0.08 mmol). Column chromatography (hexane/EtOAc 3/1) afforded 15 mg (9%) of the title compound as a pale yellow solid: m.p. 188 °C (benzene); ^{1}H NMR (400 MHz, C_6D_6) δ 0.77-0.79 (m, 4H), 1.22-1.24 (m, 4H), 1.43-1.45 (m, 8H), 1.85-1.87 (m, 2H), 2.42-2.56 (m, 8H), 6.66 (s, 2H); ^{13}C NMR (100 MHz, C_6D_6) δ 10.2 (4C), 17.8 (2C), 23.3 (2C), 24.1 (2C), 26.9 (2C), 30.2 (2C), 121.8 (2C), 137.1 (2C), 147.0 (2C), 158.6 (2C), 158.8 (2C); IR ($CHCl_3$) ν 3081, 3002, 2932, 2856, 2831, 1590, 1555, 1451, 1432, 1292, 1239, 1201, 1163, 1052, 1017, 998, 935, 871, 811 cm^{-1}; FAB-MS m/z (% relative intensity) 345 ($M+H^+$, 100), 177 (12), 154 (14), 137 (14); HR-MS calculated for $C_{24}H_{29}N_2$ 345.23307, found 345.23307.

4. Preparation of bipyridine *N,N'*-dioxides

General procedure for oxidation of bipyridines 3. To a solution of a bipyridine **3** (1.8 mmol) in dry dichloromethane (7 mL) cooled to 0 °C MCPBA (3.9 mmol) was added, then it was allowed to reach 20 °C and stirred for 1h. The reaction mixture was quenched with brine (7 mL) and extracted by dichloromethane (7 mL). The organic layer was separated, dried over $MgSO_4$, and volatiles were removed under reduced pressure. Column chromatography of the residue on alumina or silica gel afforded a product.

***rac*-Bis-1,1'-(5,6,7,8-tetrahydro-3-phenylisoquinoline)-*N,N'*-dioxide (4a).** Column chromatography on silica gel (EtOAc) afforded 330 mg (41%) of a colorless viscous liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.72-1.77 (m, 8H), 2.23- 2.81 (2H), 2.68-2.78 (m, 6H), 7.35-7.38 (m, 8H), 7.88- 7.91 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7 (2C), 21.8 (2C), 24.5 (2C), 28.5 (2C), 127.1 (2C), 127.8 (4C), 128.3 (2C), 129.1 (2C), 129.6 (4C), 132.7 (2C), 134.6 (2C), 136.4 (2C), 146.0 (2C); IR ($CHCl_3$) ν 2933, 2857, 1709, 1448, 1388, 1353, 1261, 1144, 1070, 956, 820, 774, 736 cm^{-1} ; HR-MS (ES+) calculated for $C_{30}H_{29}N_2O_2$ ($M+H^+$) 449.2229, found 449.2250.

***rac*-Bis-1,1'-[5,6,7,8-tetrahydro-3-(3,4,5-trimethoxyphenyl)-isoquinoline]-*N,N'*-dioxide (4b).** Column chromatography on silica gel (9/1 $CHCl_3$/2-propanol) afforded 249 mg (22%) of a colorless viscous liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.84-1.92 (m, 8H), 2.32- 2.37 (2H), 2.68-3.10 (m, 6H), 3.88 (s, 6H), 3.91 (s, 12H), 7.15 (s, 4H), 7.40 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4 (2C), 21.5 (2C), 25.4 (2C), 29.1 (2C), 56.6 (4C), 60.8 (2C), 77.2 (2C), 107.7 (4C), 126.3 (2C), 128.4 (2C), 135.9 (2C), 139.7 (2C), 142.2 (2C), 148.2 (2C), 153.1 (4C); IR ($CHCl_3$) ν 2932, 2855, 1584, 1509, 1463, 1428, 1386, 1341, 1247, 1125, 1006, 914, 754 cm^{-1} ; HR-MS (ES+) calculated for $C_{36}H_{41}N_2O_8$ ($M+H^+$) 629.2863, found 629.2872.

(*R,R,R*)-Bis-1,1'-[5,6,7,8-tetrahydro-3-(tetrahydrofuran-2-yl)isoquinoline]-*N,N'*-dioxide (4c) and (*S,R,R*)-bis-1,1'-[5,6,7,8-tetrahydro-3-(tetrahydrofuran-2-yl)isoquinoline]-*N,N'*-dioxide (4c). Column chromatography on alumina ($CHCl_3$) of a mixture of diastereoisomeric *N,N'*–dioxides afforded 376 mg (48%) of (*R,R,R*)-**4c** and 219 mg (28%) of (*S,R,R*)-**4c** as colorless solids. (*R,R,R*)-**4c**: m.p. decomposition >150 °C; $[\alpha]_D$ = +396° (c = 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.68-2.14 (m, 16H), 2.59-2.65 (m, 4H), 2.77-2.80 (m, 4H), 3.92- 3.97 (m, 2H), 4.09-4.14 (m, 2H), 5.37 (t, *J* = 6.8 Hz, 2H), 7.32 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8 (2C), 21.9 (2C), 24.3 (2C), 25.6 (2C), 28.7 (2C), 31.0 (2C), 69.1 (2C),

75.4 (2C), 122.4 (2C), 134.1 (2C), 136.2 (2C), 141.4 (2C), 150.1 (2C); IR ($CHCl_3$) ν 2978, 2934, 2862, 2223, 1685, 1547, 1445, 1402, 1351, 1326, 1260, 1209, 1064, 919, 730, 643 cm^{-1} ; FAB-MS m/z (% relative intensity) 459 ($M+Na^+$, 30), 437 ($M+H^+$, 100), 419 (26), 405 (6), 375 (10), 331 (7), 244 (15), 177 (6), 154 (14), 137 (14), 109 (9); HR-MS calculated for $C_{26}H_{32}N_2O_4$ 436.23621, found 436.23556. (*S,R,R*)-**(4c).** Column chromatography on alumina ($CHCl_3$) afforded 219 mg (28%) of a white viscous liquid: $[\alpha]_D$ = +95° (c = 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 1.69-1.91 (m, 12H), 1.97- 2.02 (2H), 2.18-2.23 (m, 2H), 2.52-2.83 (m, 8H), 3.92- 3.96 (m, 2H), 3.98- 4.14 (m, 2H), 5.38- 5.41 (m, 2H), 7.35 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5 (2C), 21.6 (2C), 25.1 (2C), 25.7 (2C), 28.9 (2C), 29.6 (2C), 31.8 (2C), 69.2 (2C), 75.1 (2C), 123.3 (2C), 134.2 (2C), 141.3 (2C), 151.9 (2C); IR ($CHCl_3$) ν 2978, 2934, 2862, 2223, 1685, 1547, 1445, 1402, 1351, 1326, 1260, 1209, 1064, 919, 730, 643 cm^{-1} ; FAB-MS m/z (% relative intensity) 459 ($M+Na^+$, 30), 437 ($M+H^+$, 100), 419 (26), 405 (6), 375 (10), 331 (7), 244 (15), 177 (6), 154 (14), 137 (14), 109 (9); HR-MS calculated for $C_{26}H_{32}N_2O_4$ 436.23621, found 436.23556.

(*S*)-(-)-Bis-1,1'-(5,6,7,8-tetrahydro-3-phenylisoquinoline)-*N,N'*-dioxide ((*S*)-(-)-4a) and (*R*)-(+)-bis-1,1'-(5,6,7,8-tetrahydro-3-phenylisoquinoline)-*N,N'*-dioxide ((*R*)-(+)-4a). Separation of racemic **4a** (200 mg, 0.44 mmol) was carried out by HPLC with a column with a chiral stationary phase (Chiralcel OD-H, 0.46 × 25 cm, 3/1 heptane/2-propanol, 0.7mL/min). It afforded 92 mg (46%) of (S)-(-)-**4a** and 86 mg (43%) of (*R*)-(+)-**4a**. Each enantiomer was obtained in >98% ee (t_S = 14 min, t_R = 48 min). The separated enantiomers were subjected to column chromatography on silica gel (EtOAc) prior to the use. **(*R*)-(+)-4a**: $[\alpha]_D$ = -183° (*c* = 0.5, $CHCl_3$).

(*S*)-(-)-Bis-1,1'-[5,6,7,8-tetrahydro-3-(3,4,5-trimethoxyphenyl)isoquinoline]-*N,N'*-dioxide ((*S*)-(-)-4b)) and (*R*)-(+)-Bis-1,1'-[5,6,7,8-tetrahydro-3-(3,4,5-trimethoxyphenyl)isoquinoline]-*N,N'*-dioxide ((*R*)-(+)-4b)). Separation of racemic **4b** (100 mg, 0.15 mmol) was carried out by HPLC with a column with a chiral stationary phase (Chiralpak OP(+),0.46 × 25 cm, methanol, 0.5 mL/min). It afforded 42 mg, (42%) of (*S*)-(-)-**4b** and 38 mg (38%) of (*R*)-(+)-**4b**. Each enantiomer was obtained in >98% ee (t_S = 11 min, t_R = 42 min). The separated enantiomers were subjected to column chromatography on silica gel ($CHCl_3$/2-propanol 9/1) prior to the use. $[\alpha]_D$ = -21° (*c* =0.5, $CHCl_3$).

5. Synthesis of compound 7

1-[5,6,7,8-Tetrahydro-3-(tetrahydrofuran-2-yl)isoquinolin-1-yl]isoquinoline. To a solution 1-(octa-1,7-diynyl)isoquinoline[3] (800 mg, 3.43 mmol) and (*R*)-tetrahydrofuran-2-carbonitrile (1.0 g, 10.3 mmol) in dry and degassed THF (15 mL) in a vial was added $CpCo(CO)_2$ (123 mg, 0.68 mmol) under atmosphere of argon. Then the vial was placed into the microwave oven and irradiated for 30 min (300 W) (during the process temperature and pressure reached 200°C and 20 barr). Then volatiles were removed under reduced pressure and column chromatography of the residue on silica gel (EtOAc) afforded 340 mg (30 %) of the title compound as a pale yellow liquid: ^{1}H NMR (400 MHz, C_6D_6) δ 1.35-1.66 (m, 6H), 2.08-2.16 (m, 2H), 2.49-2.53 (m, 4H), 3.72- 3.78 (m, 1H), 3.93-3.98 (m, 1H), 5.19 (t, *J* = 7.2 Hz, 1H), 7.11-7.15 (m, 1H), 7.21-7.25 (m, 2H), 7.42-7.44 (m, 2H), 7.90-7.93 (m,1H), 8.62 (d, *J* = 5.6 Hz, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 23.2, 23.9, 27.0, 30.6, 34.0, 69.9, 82.7, 121.5, 121.7, 128.3, 128.4, 129.3, 129.6, 129.9, 131.2, 132.2, 138.5, 143.8, 149.0, 157.9, 161.0, 161.8; IR ($CHCl_3$) ν 3007, 2943, 2865, 1629, 1622, 1592, 1555, 1499, 1457, 1430, 1387, 1308, 1255, 1148, 1061, 952, 870, 827 cm^{-1} ; EI-MS m/z (% relative intensity) 330 (M^+, 90), 329 (100), 302 (35), 284 (40), 274 (10), 257 (12); HR-MS calculated for $C_{22}H_{22}N_2O$ 330.17321, found 330.17239.

(*R*,*R*)-1-(5,6,7,8-Tetrahydro-3-(tetrahydrofuran-2-yl)isoquinolin-1-yl)isoquinoline-*N*,*N*'-dioxide ((*R*,*R*)-7) and (*S*,*R*)-1-(5,6,7,8-tetrahydro-3-(tetrahydrofuran-2-yl)isoquinolin-1-yl)isoquinoline-*N*,*N*'-dioxide ((*S*,*R*)-7). To a solution of 1-(5,6,7,8-tetrahydro-3-(tetrahydrofuran-2-yl)isoquinolin-1-yl)isoquinoline (360 mg, 1.1 mmol) (1.8 mmol) in dry dichloromethane (4.5 mL) cooled to 0 °C was added MCPBA (486 mg, 2.2 mmol), then it was allowed to reach 20 °C and stirred for 1h. The reaction mixture was quenched with brine (4.5 mL) and extracted by dichloromethane (5 mL). The organic layer was separated, dried over $MgSO_4$, and volatiles were removed under reduced pressure. Column chromatography of a mixture of diastereoisomeric *N*,*N*'–dioxides on silica gel (10/1 $CHCl_3$/2-propanol) afforded 64 mg (16%) of (*R,R*)-**7** and 16 mg (4%) of (*S,R*)-**7** as colorless viscous liquids. (*R,R*)-**7**: $[\alpha]_D$ = +298° (c = 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6) δ 1.74-2.15 (m, 8H), 2.51-2.64 (m, 2H), 2.83-2.86 (m, 2H), 3.93- 3.98 (m, 1H), 4.11-4.14 (m, 1H), 5.37 (t, *J* = 7.0 Hz, 1H), 7.18-7.21 (m, 1H), 7.41 (s, 1H), 7.52-7.57 (m, 2H), 7.74 (d, *J* = 7.2 Hz, 1H), 7.81-7.84 (m, 1H), 8.25 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 21.7, 21.9, 24.8, 25.7, 28.8, 31.2, 69.5, 75.7, 123.8, 123.9, 125.2, 127.8, 129.3, 129.3, 129.4, 130.8, 135.5, 137.7, 139.0, 139.9, 140.5, 151.6; IR ($CHCl_3$) ν 3057, 2931, 2845, 1401, 1324, 1262, 1219, 1139,

1072, 835, 761, 671 cm^{-1} ; FAB m/z (% relative intensity) 363 ($M+H^+$, 100), 347 (30), 329 (10), 301 (7), 274 (7), 163 (6), 147 (21), 131 (16), 119 (56), 109 (11), 101 (10), 93 (19), 85 (28), 69 (26); HR-MS calculated for $C_{22}H_{23}N_2O_3$ ($M+H^+$) 363.17087, found 363.17031. (*S,R*)-**7**: $[\alpha]_D$ = +13° (c = 0.5, $CHCl_3$); ^1H NMR (400 MHz, C_6D_6) δ 1.67-2.15 (m, 8H), 2.42-2.51 (m, 1H), 2.62-2.68 (m, 1H), 2.82-2.85 (m, 2H), 3.92- 3.98 (m, 1H), 4.11-4.15 (m, 1H), 5.37 (t, *J* = 6.4 Hz, 1H), 7.16-7.18 (m, 1H), 7.41 (s, 1H), 7.51-7.58 (m, 2H), 7.73 (d, *J* = 7.2 Hz, 1H), 7.82-7.85 (m, 1H), 8.26 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 21.7, 21.9, 25.0, 25.8, 28.8, 31.4, 69.5, 75.6, 123.8, 123.9, 125.2, 128.0, 129.3, 129.3, 129.5, 130.8, 135.2, 137.5, 138.0, 139.9, 140.5, 151.9; IR ($CHCl_3$) ν 3036, 2949, 2922, 2869, 2851, 1724, 1601, 1453, 1401, 1327, 1266, 1207, 1065, 878, 761, 699, 516 cm^{-1} ; FAB m/z (% relative intensity) 363 ($M+H^+$, 100), 347 (30), 329 (10), 301 (7), 274 (7), 163 (6), 147 (21), 131 (16), 119 (56), 109 (11), 101 (10), 93 (19), 85 (28), 69 (26); HR-MS calculated for $C_{22}H_{23}N_2O_3$ ($M+H^+$) 363.17087, found 363.17031.

6. Enantioselective allylation of benzaldehydes

General procedure for catalytic enantioselective allylation of benzaldehydes with allyltrichlorosilane. To a solution of **4** (0.01 mmol) in a solvent (1 mL) aldehyde (1 mmol), di(isopropyl)ethylamine (155 mg, 208 μL, 1.2 mmol), and allyl(trichloro)silane (210 mg, 170 μL, 1.2 mmol) were added at -40 or -78 °C and the reaction mixture was stirred for 1h. Then it was quenched with saturated aqueous $NaHCO_3$ (1 mL), the organic layer was separated and dried over $MgSO_4$. Yields and ees of homoallylalcohols **6** were determined by GC (HP-Chiral β, 30 m × 0.25 mm, oven: 80 °C for 15 min, then 1 °C/min to 150 °C, 5 min at that temperature). Spectral data of **6a-6c** were in agreement with the previously reported values.[2]

Allylation of benzaldehyde 5b catalyzed by (*S*)**-4a (Table 2 in the text)**

In CH_2Cl_2 at -78 °C: **(*R*)-(+)-1-phenyl-but-3-en-1-ol (6b)** (t_R = 57.90 min, t_S = 58.33 min), 55% ee (100% yield).

In MeCN at -40 °C: **(*R*)-(+)-6b**, 65% ee (100% yield).

In $CHCl_3$ at -40 °C: **(*R*)-(+)-6b**, 36% ee (100% yield).

In $EtNO_2$ at -78 °C: **(*R*)-(+)-6b**, 53% ee (71% yield).

In PhMe at -78 °C: **(*S*)-(-)-6b**, 83% ee (45% yield).

In PhF at -40 °C: **(*S*)-(-)-6b**, 78% ee (100% yield).

In PhCl at -40 °C: **(*S*)-(-)-6b**, 79% ee (100% yield).

In *m*-$C_6H_4F_2$ at -40 °C: **(*S*)-(-)-6b**, 73% ee (100% yield).

In C_7F_8 at -78 °C: **(*S*)-(-)-6b**, 50% ee (14% yield).

In $CFCl_3$ at -78 °C: **(*S*)-(-)-6b**, 40% ee (14% yield).

In pentane at -78 °C: **(*S*)-(-)-6b**, 44% ee (1% yield).

In THF at -78 °C: **(*S*)-(-)-6b**, 70% ee (100% yield).

In EtOAc at -78 °C: **(*S*)-(-)-6b**, 74% ee (100% yield).

In $MeOC_6F_5$/PhMe (3/1 mixture) at -78 °C: **(*S*)-(-)-6b**, 66% ee (10% yield).

Allylation of benzaldehyde 5b catalyzed by (*R,R,R*)**-4c (Table 2 in the text)**

In CH_2Cl_2 at -78 °C: **(*S*)-(-)-6b**, 59% ee (50% yield).

In MeCN at -40 °C: **(*S*)-(-)-6b**, 48% ee (100% yield).

In PhMe at -78 °C: no reaction

Allylation of benzaldehyde 5b catalyzed by (*S,R,R*)**-4c (Table 2 in the text)**

In CH_2Cl_2 at -78 °C: **(*R*)-(+)-6b**, 37% ee (44% yield).

In MeCN at -40 °C: **(*R*)-(+)-6b**, 63% ee (82% yield).

In PhMe at -78 °C: **(*S*)-(-)-6b**, 75% ee (10% yield).

Allylation of benzaldehydes 5a, 5b, and 5c catalyzed by (*R*)-4a (Table 3 in the text)

Aldehyde **5a** in MeCN at -40 °C: **(*S*)-(-)-1-(4-trifluoromethylphenyl)-but-3-en-1-ol (6a).** (t_R = 59.58 min, t_S = 61.09 min), 30% ee (100% yield).

Aldehyde **5a** in PhCl at -40 °C: **(*R*)-(+)-6a**, 61% ee (83% yield).

Aldehyde **5b** in MeCN at -40 °C: **(*S*)-(-)-1-phenyl-but-3-en-1-ol (6b).** (t_R = 57.90 min, t_S = 58.33 min), 65% ee (100% yield).

Aldehyde **5b** in PhCl at -40 °C: **(*R*)-(+)-6b**, 82% ee (100% yield).

Aldehyde **5c** in MeCN at -40 °C: **(*S*)-(-)-1-(4-methoxyphenyl)-but-3-en-1-ol (6c).** (t_R = 83.64 min, t_S = 84.26 min), 80% ee (100% yield).

Aldehyde **5c** in PhCl at -40 °C: **(*R*)-(+)-6c**, 60% ee (78% yield).

Allylation of benzaldehydes 5a, 5b, and 5c catalyzed by (*R*)-4b (Table 3 in the text)

Aldehyde **5a** in MeCN at -40 °C: **(*S*)-(-)-6a**, 7% ee (32% yield).

Aldehyde **5a** in PhCl at -40 °C: **(*R*)-(+)-6a**, 73% ee (90% yield).

Aldehyde **5b** in MeCN at -40 °C: **(*S*)-(-)-6b**, 52% ee (61% yield).

Aldehyde **5b** in PhCl at -40 °C: **(*R*)-(+)-6b**, 70% ee (100% yield).

Aldehyde **5c** in MeCN at -40 °C: **(*S*)-(-)-6c**, 68% ee (24% yield).

Aldehyde **5c** in PhCl at -40 °C: **(*R*)-(+)-6c**, 33% ee (96% yield).

Allylation of benzaldehydes 5a, 5b, and 5c catalyzed by (*R*,*R*,*R*,)-4c (Table 3 in the text)

Aldehyde **5a** in MeCN at -40 °C: **(*R*)-(+)- 6a,** 15% ee (82% yield).

Aldehyde **5a** in PhCl at -40 °C: 0% ee (0% yield).

Aldehyde **5b** in MeCN at -40 °C: **(*S*)-(-)-6b**, 48% ee (100% yield).

Aldehyde **5b** in PhCl at -40 °C: 0% ee (0% yield).

Aldehyde **5c** in MeCN at -40 °C: **(*S*)-(-)-6c**, 60% ee (100% yield).

Aldehyde **5c** in PhCl at -40 °C: 0% ee (0% yield).

Allylation of benzaldehydes 5a, 5b, and 5c catalyzed by (*S*,*R*,*R*,)-4c (Table 3 in the text)

Aldehyde **5a** in MeCN at -40 °C: **(*R*)-(+)-6a**, 16% ee (100% yield).

Aldehyde **5a** in PhCl at -40 °C: **(*S*)-(-)-6a**, 75% ee (40% yield).

Aldehyde **5b** in MeCN at -40 °C: **(*R*)-(+)-6b**, 46% ee (100% yield).

Aldehyde **5b** in PhCl at -40 °C: **(*S*)-(-)-6b**, 62% ee (100% yield).

Aldehyde **5c** in MeCN at -40 °C: **(*R*)-(+)-6c**, 0% ee (100% yield).

Aldehyde **5c** in PhCl at -40 °C: **(*S*)-(-)-6c**, 56% ee (47% yield).

7. X-ray data

Crystal data for (*R*,*R*,*R*)-**4c** $C_{26}H_{32}N_2O_4$, M = 436.54, orthorombic, *P* 2_1 2_1 2, *a* = 10.64500 (10) Å, *b* = 17.1630 (2) Å, *c* = 6.0859 (3) Å, *V* = 1111.91 (6) Å^3, *Z* = 2, D_x = 1.304 Mg m^{-3}. A colorless prism dimensions 0.5×0.4×0.2 mm was mounted on glass capillary with epoxy glue and measured at Nonius KappaCCD diffractometer by monochromatized Mo Kα radiation (λ=0.71073 Å) at 150 (2) K. An absorption was neglected (μ = 0.09 mm^{-1}); a total of 18533 measured reflections in the range *h* = −13 to 13, *k* = −22 to 22, *l* = −7 to 7 (θ_{max} = 27.5°), from which 2552 were unique (R_{int} = 0.030), 2450 observed according to the $I>2\sigma(I)$ criterion. The structure was solved by direct methods (SIR92)[4] and refined by full-matrix least squares based on F^2 (SHELXL97).[5] The hydrogen atoms were recalculated into idealised positions (riding model). The refinement converged (Δ/σ_{max}=0.001) to *R* = 0.031 for observed reflections and *wR* = 0.080, *S* = 1.08 for 145 parameters and all 2552 reflections. The final

difference map displayed no peaks of chemical significance ($\Delta\rho_{max}$ = 0.17 eÅ^{-3} , $\Delta\rho_{min}$ = −0.16 eÅ^{-3}).

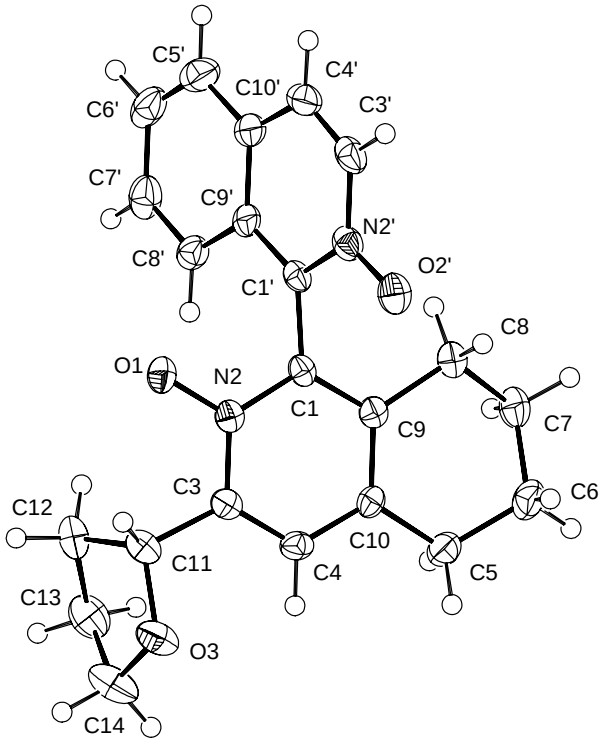

Figure 1. View on the molecule of **7** with atom numbering schema. The displacement ellipsoids are drawn on 50% probability level.

Crystal data for (*S*,*R*)-**7** $C_{22}H_{22}N_2O_3$, M = 362.42, monoclinic, *P* 2_1 , *a* = 9.381 (5) Å, *b* = 9.5083 (16) Å, *c* = 10.187 (6) Å, β = 97.72 (4)°, *V* = 900.4 (7) Å^3, *Z* = 2, D_x = 1.337 Mg m^{-3}. A prism dimensions 0.270×0.140×0.035 mm was mounted on glass capillary with epoxy glue and measured at Nonius KappaCCD diffractometer by monochromatized Mo Kα radiation (λ=0.71069 Å) at 150 (2) K. An absorption was neglected (μ = 0.09 mm^{-1}); a total of 12257 measured reflections in the range *h* = −11 to 11, *k* = −11 to 11, *l* = −12 to 12 (θ_{max} = 26.63°), from which 3744 were unique (R_{int} = 0.0392), 2483 observed according to the $I>2\sigma(I)$ criterion. The structure was solved by direct methods (SIR92)[4] and refined by full-matrix least squares based on F^2 (SHELXL97).[5] The hydrogen atoms were recalculated into idealised positions (riding model). The refinement converged (Δ/σ_{max}=0.002) to *R* = 0.0300 for observed reflections and *wR* = 0.0582, *S* = 0.867 for 244 parameters and all 3744 reflections. The final difference map displayed no peaks of chemical significance ($\Delta\rho_{max}$ = 0.128 eÅ^{-3} , $\Delta\rho_{min}$ = −0.142 eÅ^{-3}).

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 662246 and 662245 for (*R*,*R*,*R*)-**4c** and (*S*,*R*)-**7**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

8. NMR experiments

NMR spectra were recorded on a Bruker Avance II 500 spectrometer (499.8 MHz for ^{1}H). The spectra were referenced to a solvent signal (5.32 for dichloromethane and 7.24 for *para*-hydrogen of chlorobenzene). Temperature was calibrated with methanol.

Experiments in chlorobenzene-d_5. Complexation of compound **4a** with trichloroallylsilane in chlorobenzene was studied at -40 °C. (NMR charts are at the end of the file.)

Free N-oxide. Aromatic region: ten hydrogens of the phenyl groups (δ 7.47-7.54 and 8.12-8.16) and two hydrogens in the position 4 (H-4: δ 7.03 (2H)) of the tetrahydroisochinoline ring, signals of residual non-deuterated solvent. Aliphatic region: eight benzylic hydrogens (H-5 and H-8: δ 2.35-2.50 (2H), 2.60-2.75 (4H), 2.95-3.05 (2H)) and other eight aliphatic hydrogens (H-6 and H-7: δ 1.6-1.7 (8H)).

*N-oxide with allyl(trichloro)silane***.** Aromatic region: Adding of low amount (less then 1 equivalent) of the silane caused broadening of the lines and lowfield shift of the signal of H-4 (δ 7.09-7.13 (2H)). After adding more equivalents of the silane, the signals of phenyl groups became sharper and the signal of H-4 moved more to lower field (δ 7.14-7.30 (2H)). The lowfield shift of the H-4 is probably caused by bonding of the oxygen atom to silicon atom and lowering the electron density in the aromatic ring.

Double bond region: After adding of low amount of the silane new broad signals of the double bond of the allylsilane appeared (δ 5.3-5.4 and 6.1-6.3). When more equivalents of silane were added, sharp lines of the free silane appeared. By integrating the broad and sharp signals we could easily obtain the ratio of free and bound silane.

Aliphatic region: A small amount of added silane caused line broadening and shifting. First, a new resonance appeared (δ 3.3-3.5) (signal of a benzylic hydrogen of a complex *N*-oxide:silane 2:1). Adding more the silane caused decrease of intensity of the signal of 2:1 complex and increasing intensity of new resonance (δ 3.9-4.1) of a 1:1 complex. When 3

equivalents of silane were added, one equivalent was bound in the 1:1 complex and all the signals in aliphatic region became sharper. Adding more silane caused upfield shift of the signals of benzylic hydrogens (δ 3.6-3.7), line broadening and 1:2 complex formation.

Experiments in dichloromethane-d_2. Complexation of compound **4a** with trichloroallylsilane in dichloromethane was studied at -73 °C.

Free N-oxide. Aromatic region: ten hydrogens of the phenyl groups (δ 7.38-7.46 (6H) and 7.76-7.80 (4H)) and two hydrogens in the position 4 (H-4: δ 7.27 (2H)) of the tetrahydroisochinoline ring, chloroform from the solvent.

Aliphatic region: eight benzylic hydrogens (H-5 and H-8: δ 2.1-2.2 (2H), 2.45-2.55 (2H), 2.7-2.85 (4H)) and and other eight aliphatic hydrogens (H-6 and H-7: δ 1.6-1.8 (8H)).

N-oxide with allyl(trichloro)allylsilane. Aromatic region: low amount of the silane (less then 0.5 equivalent) caused line broadening and 0.2 ppm shift of H-4 resonance to lower field (δ 7.45-7.50). When 0.6 equivalent of the silane was added a signal of H-4 with intensity of 0.5 hydrogen appeared at 7.8 ppm and all the lines became narrower. After adding of more silane the intensity of the signal at 7.8 ppm increased. When 1 equivalent of silane was bound, the intensity of the H-4 signal close to 7.8 ppm was two hydrogens (indicting a 1:1 complex) and further silane addition caused gradual lowfield shift of this signal.

Double bond region: as in the case of chlorobenzene, we could easily obtain the ratio of free and bound silane by integrating the broad and sharp signals.

Aliphatic region: low amount of silane (less then 0.5 equivalent) caused sever line broadening. When 0.5 equivalent of silane was bound, the lines became narrow and a signal of benzylic hydrogen with 0.5 intensity appeared (δ 3.4). This indicates a 2:1 complex formation with the two *N*-oxide molecules unequivalently bound to the silane molecule. Further silane addition caused a 1:1 complex formation (the signal at 3.4 ppm increased its intensity to one. Adding excess of the silane cuased the signal move to higher field with further increasing intensity till the intensity of two hydrogens was reached (δ 2.9-3.0) indicating the formation of 1:2 complex.

9. References

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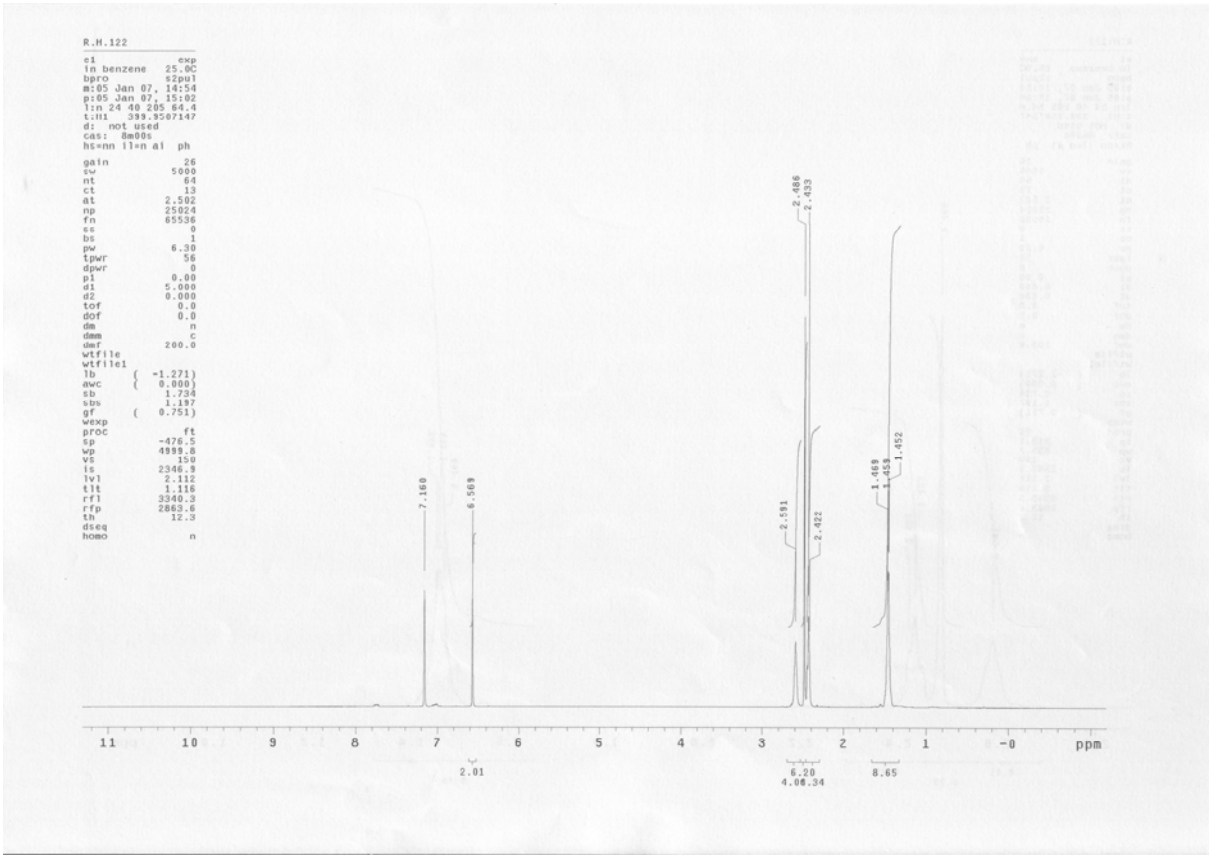
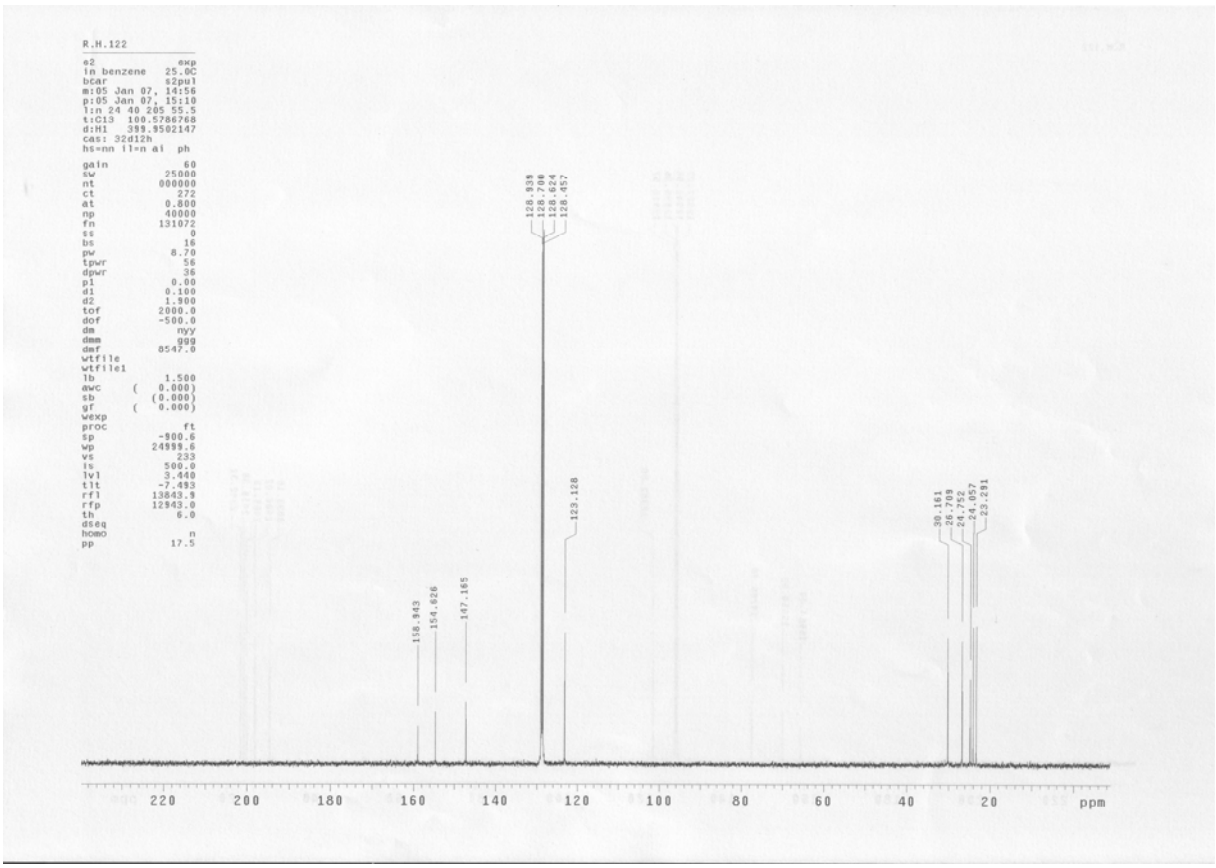
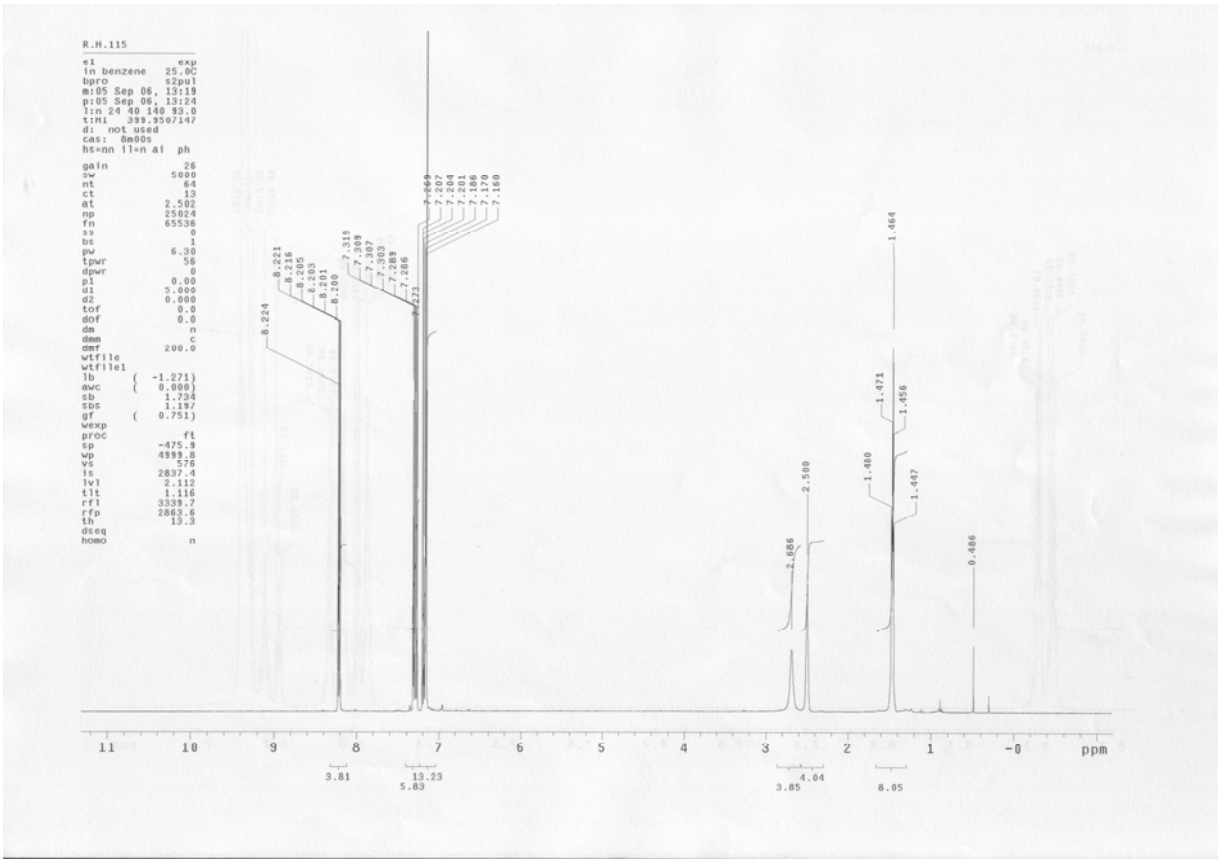
10. ^{1}H and ^{13}C NMR spectra

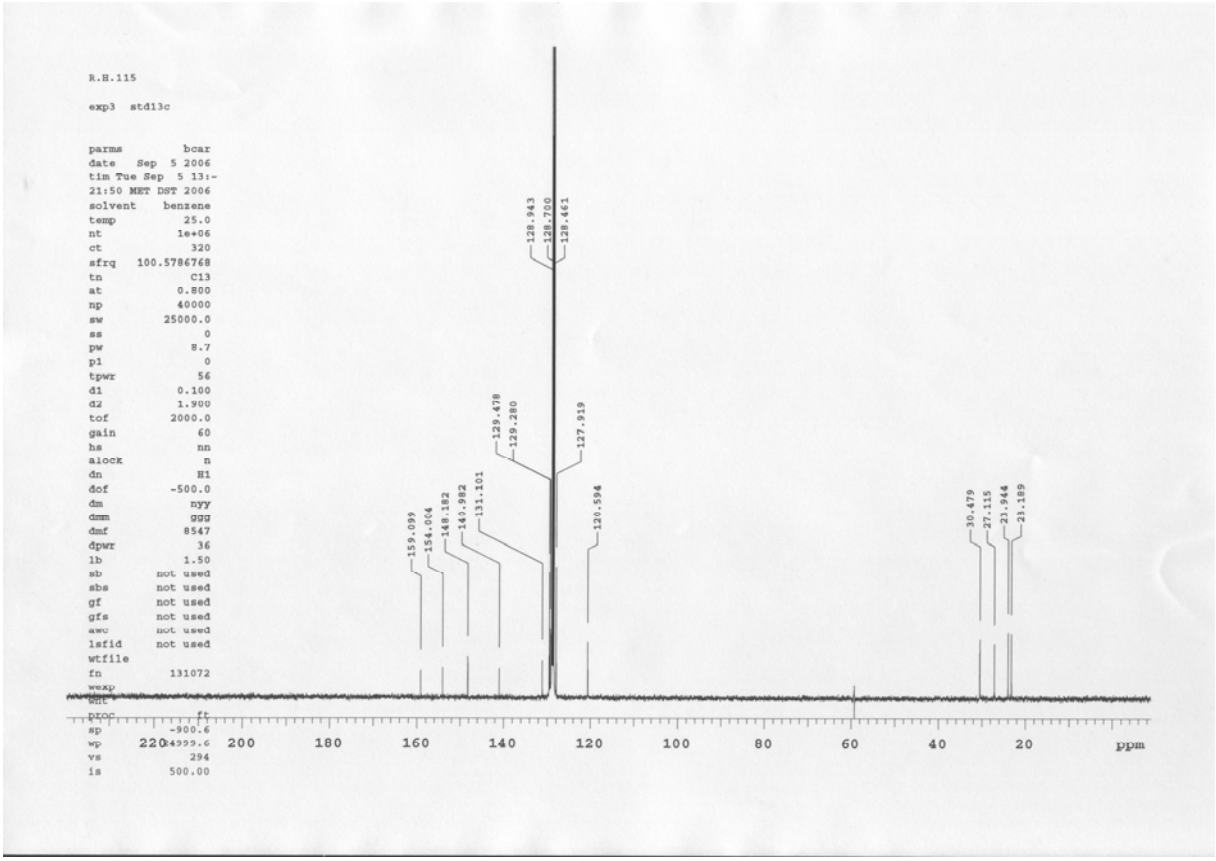
Bis-1,1'-(5,6,7,8-tetrahydro-3-methyl-isoquinoline) (3a)



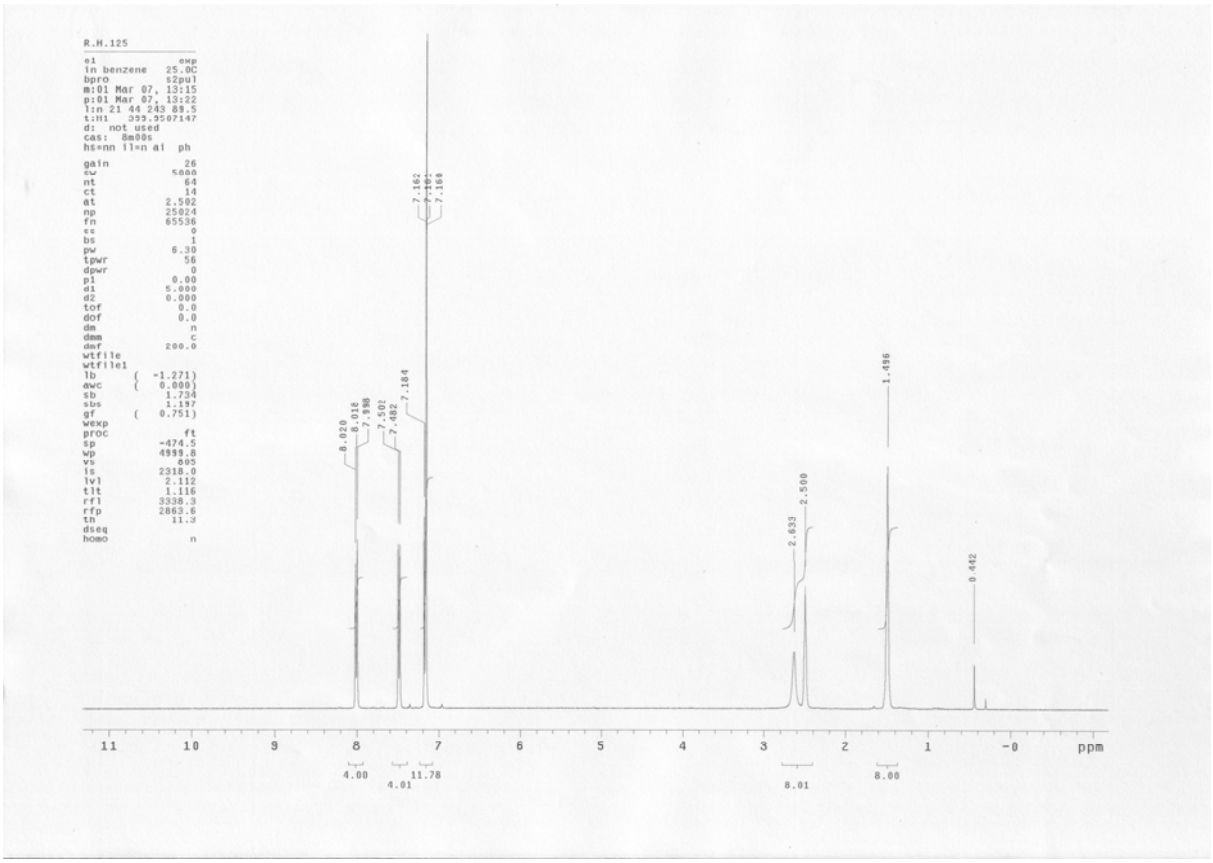


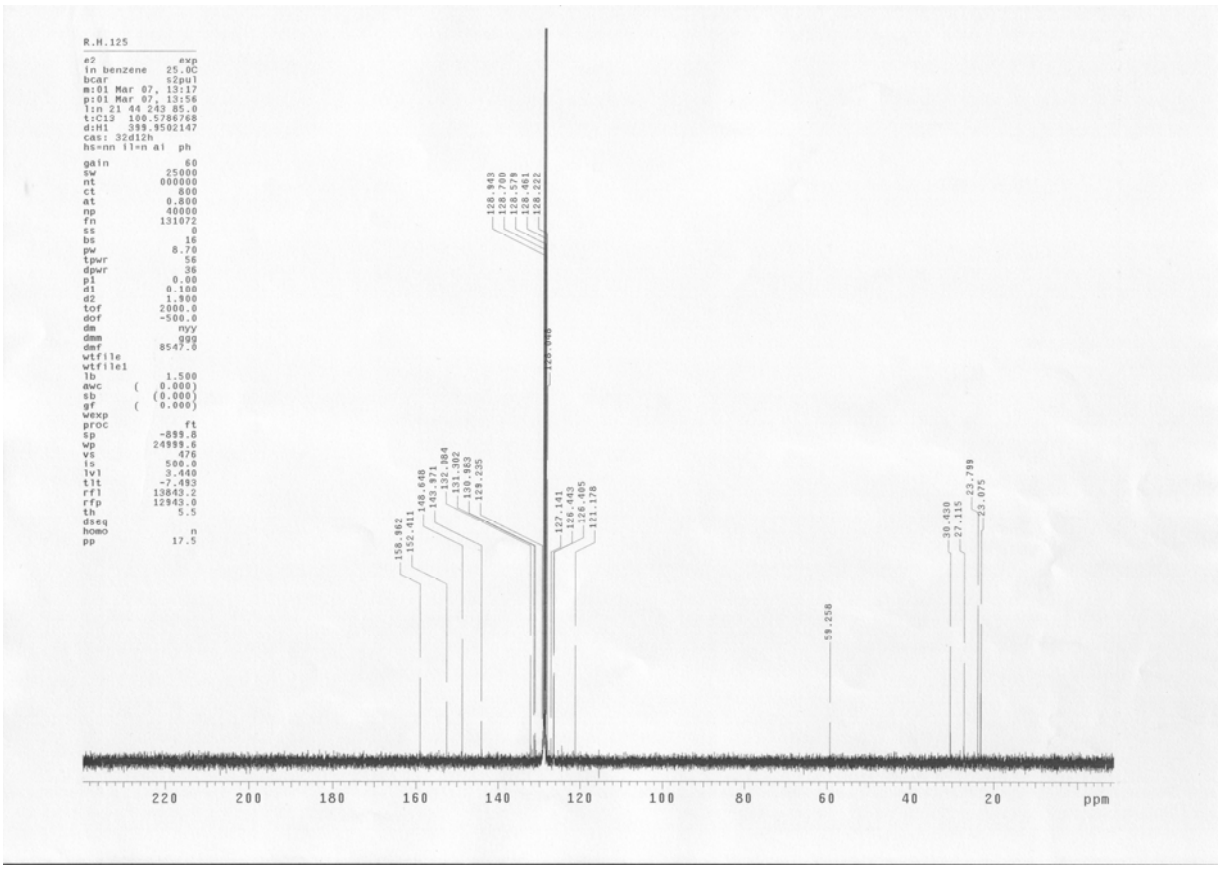
Bis-1,1'-(5,6,7,8-tetrahydro-3-phenyl-isoquinoline) (3b)



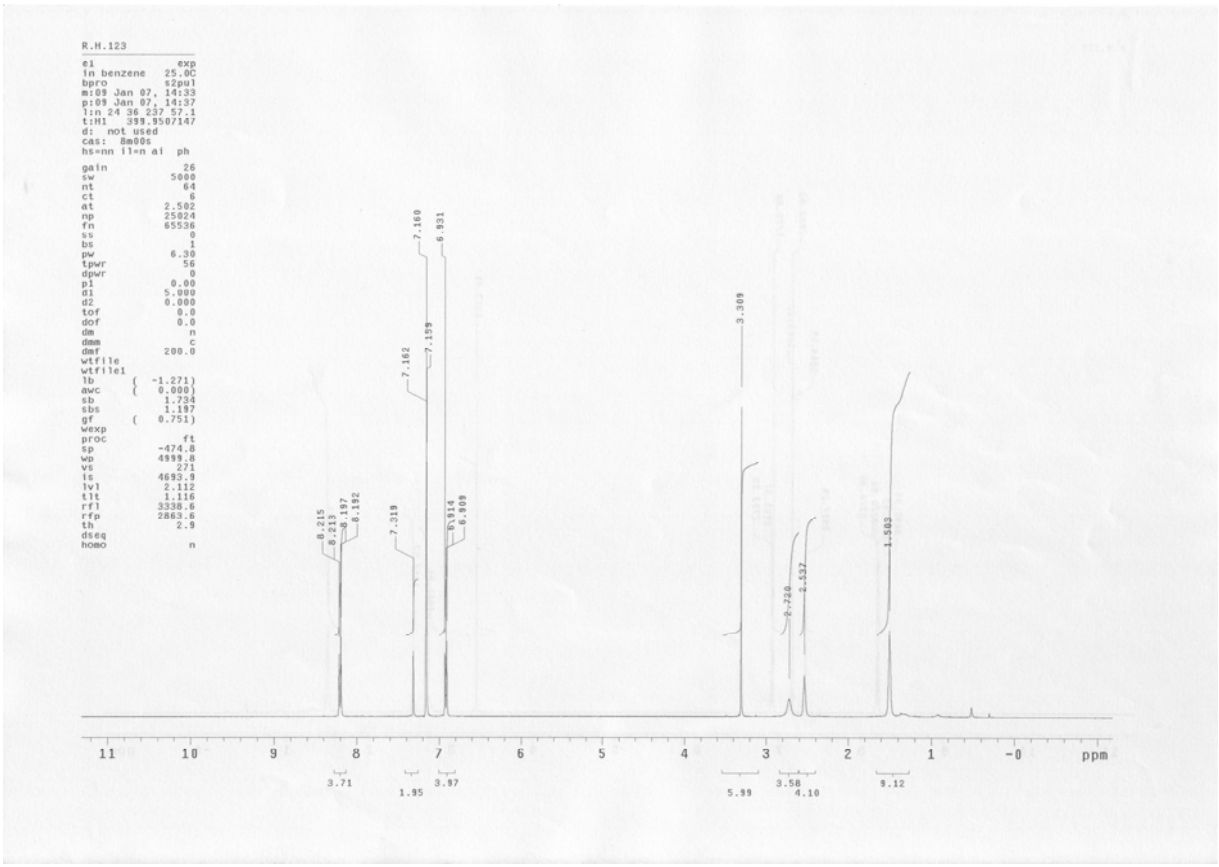


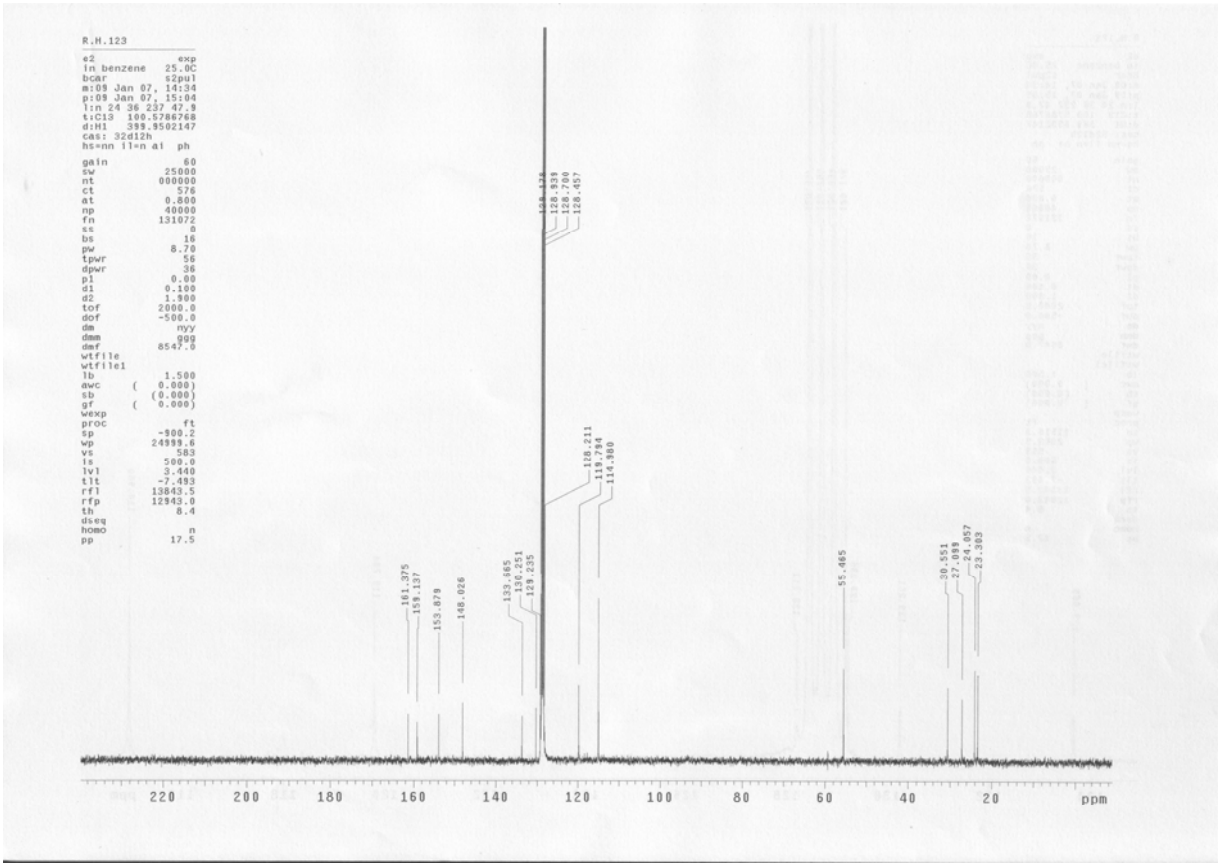
Bis-1,1'-(5,6,7,8-tetrahydro-3-(4-(trifluoromethyl)-phenyl)-isoquinoline) (3c)



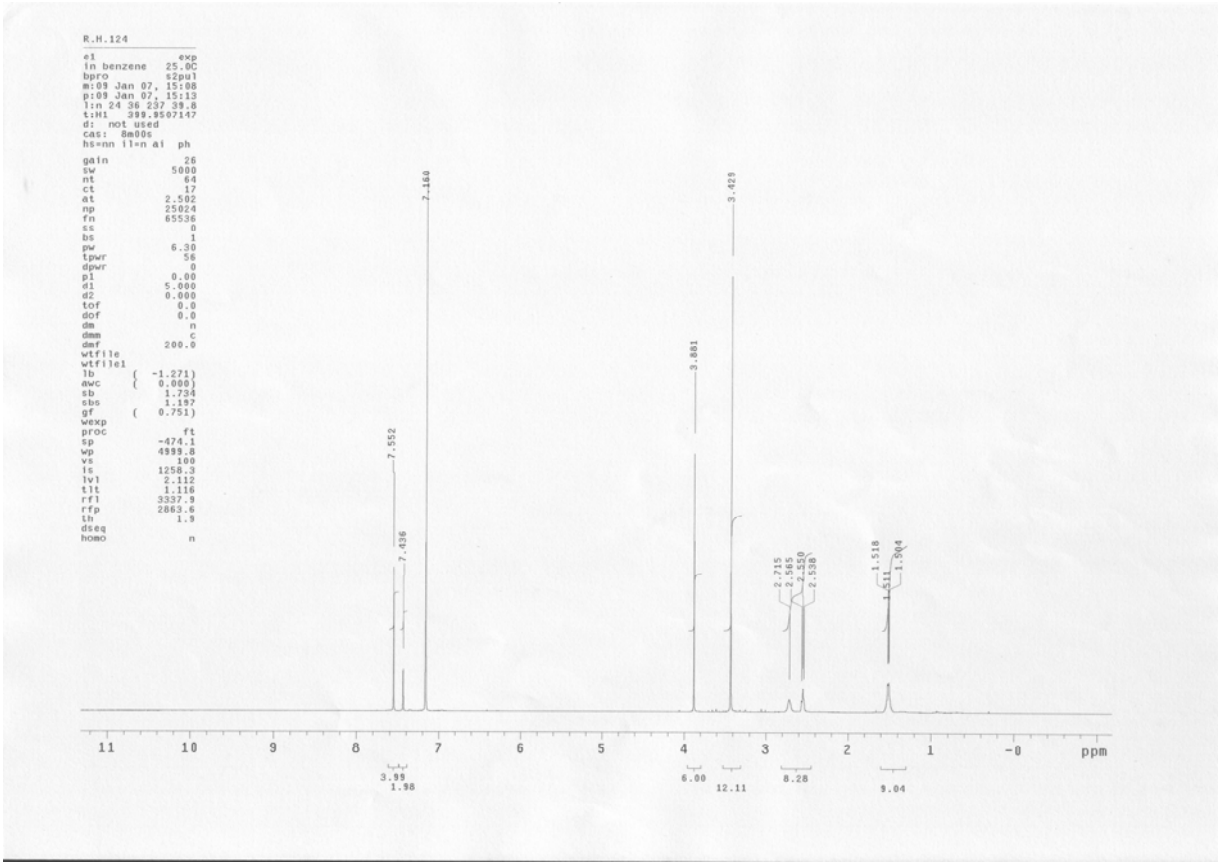


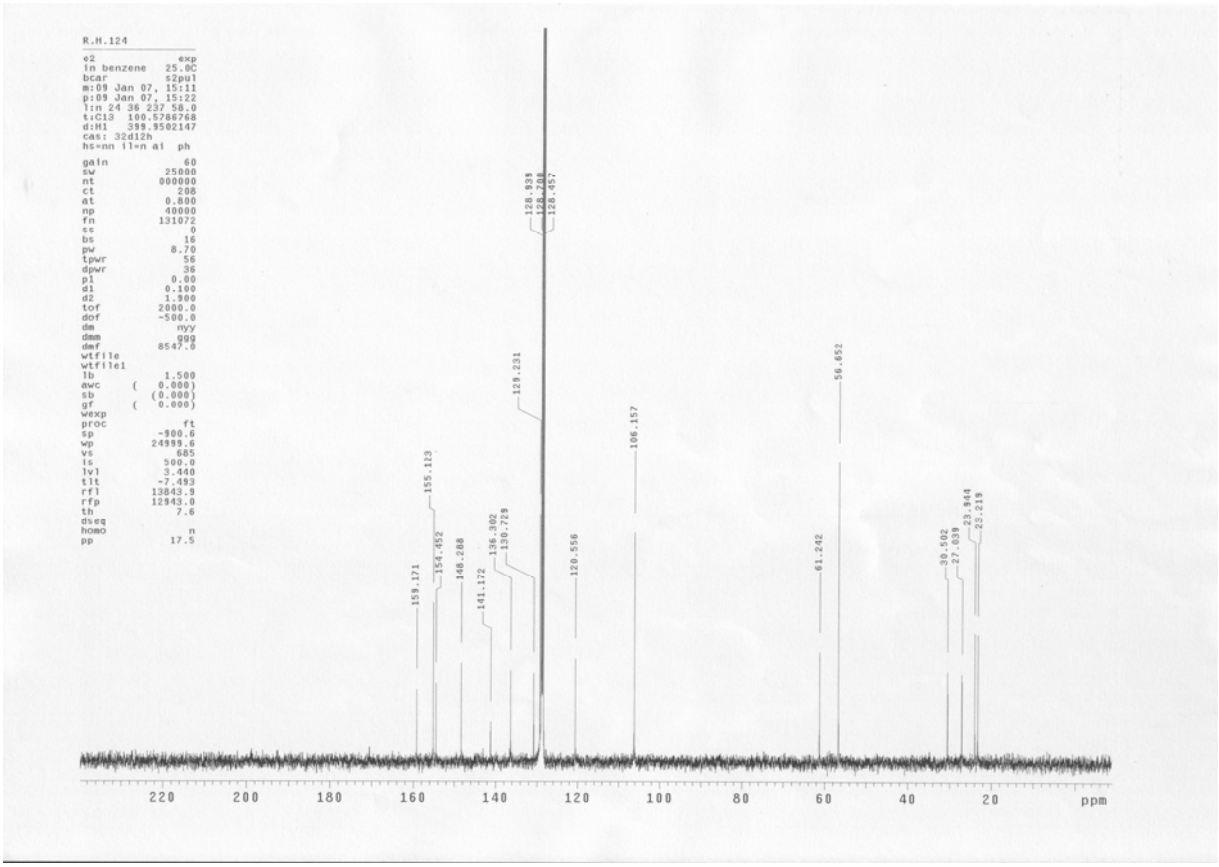
Bis-1,1'-(5,6,7,8-tetrahydro-3-(4-methoxyphenyl)-isoquinoline) (3d)



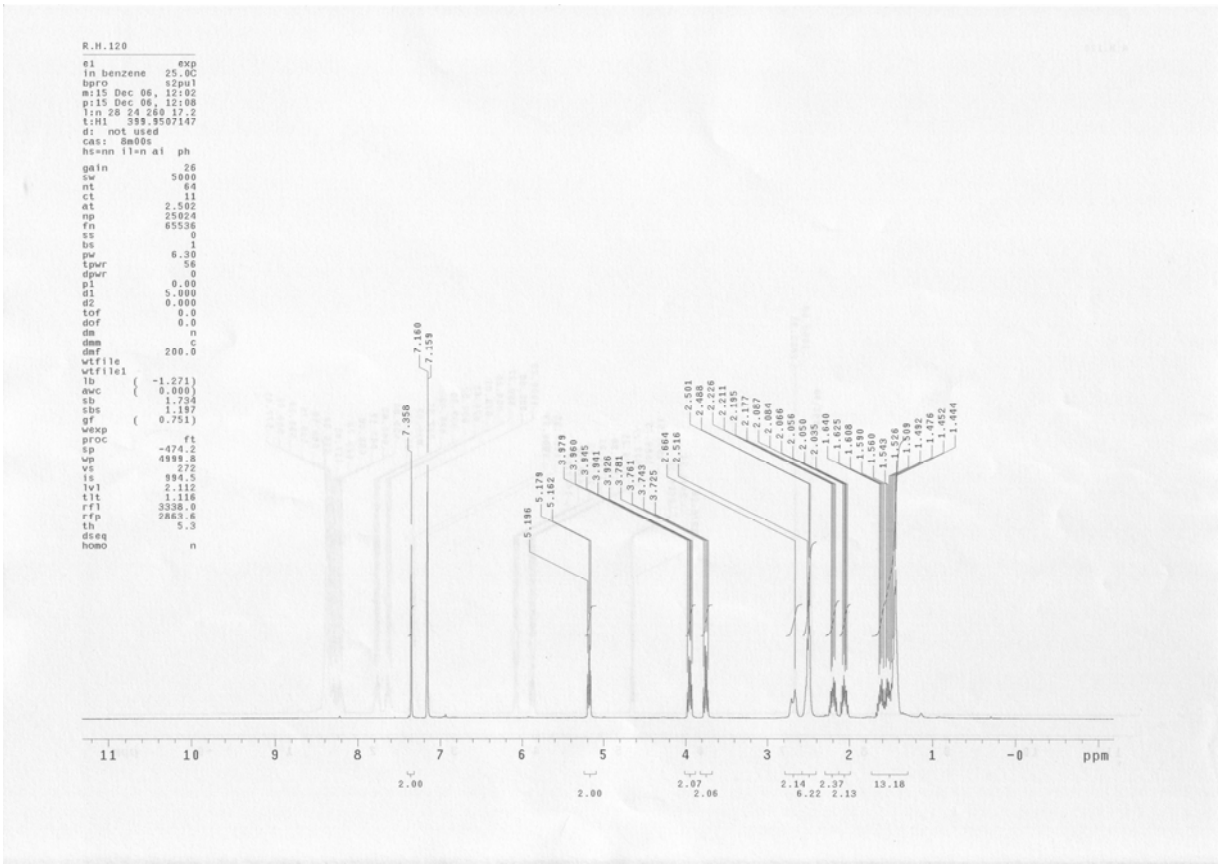


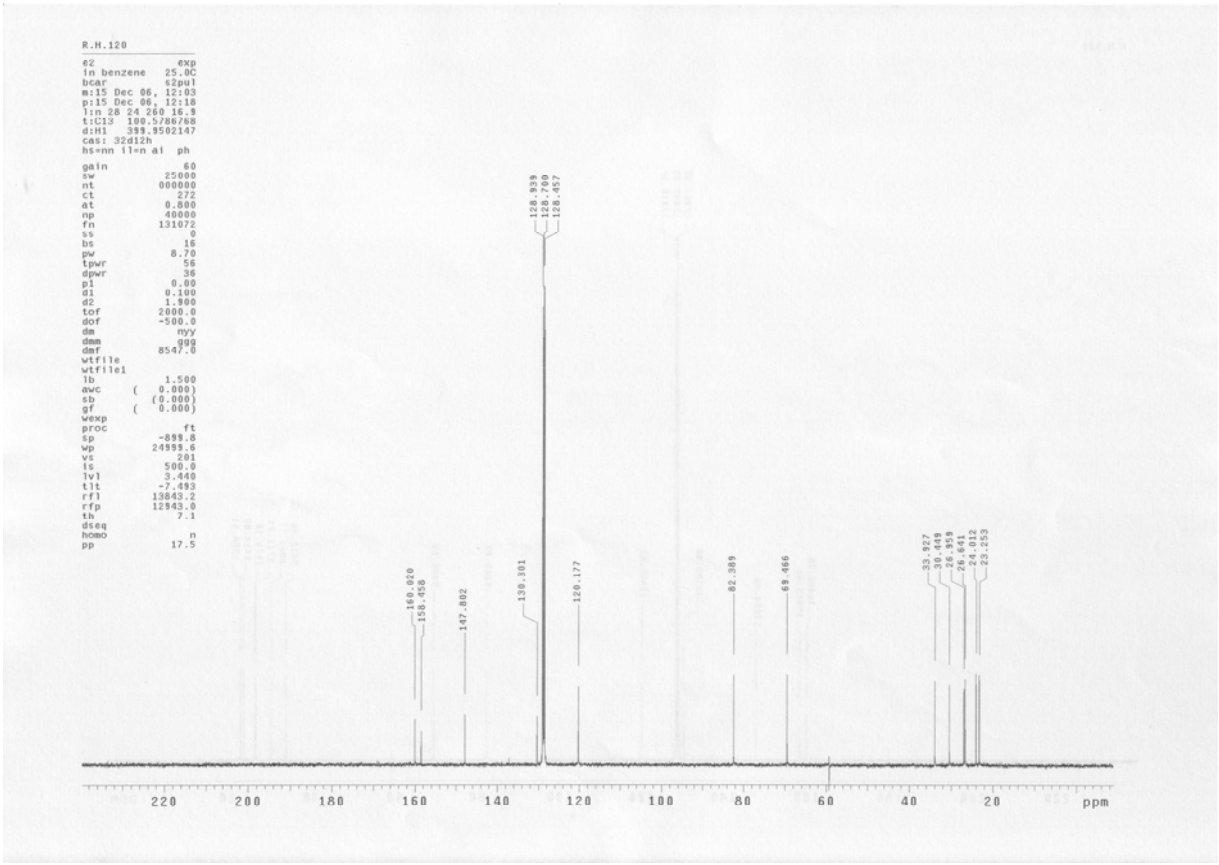
Bis-1,1'-(5,6,7,8-tetrahydro-3-(3,4,5-trimethoxyphenyl)-isoquinoline) (3e)



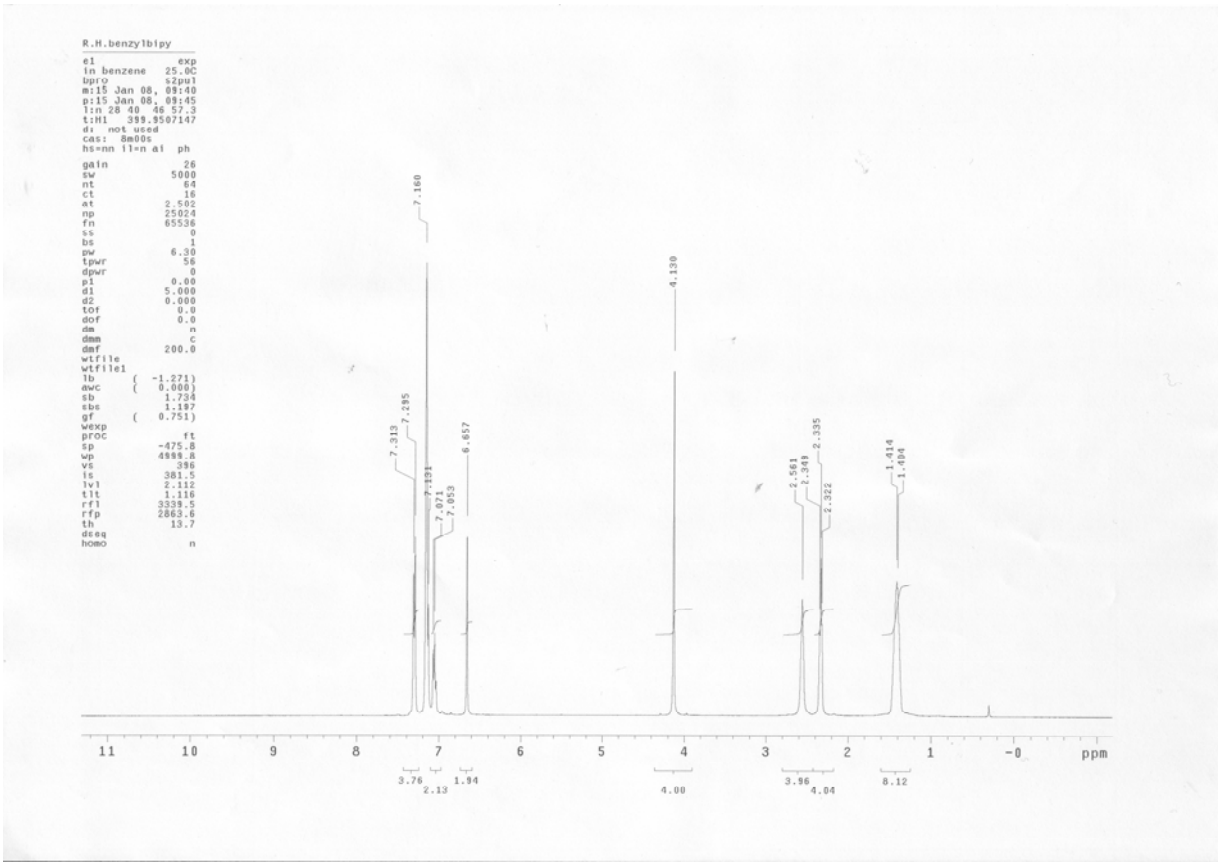


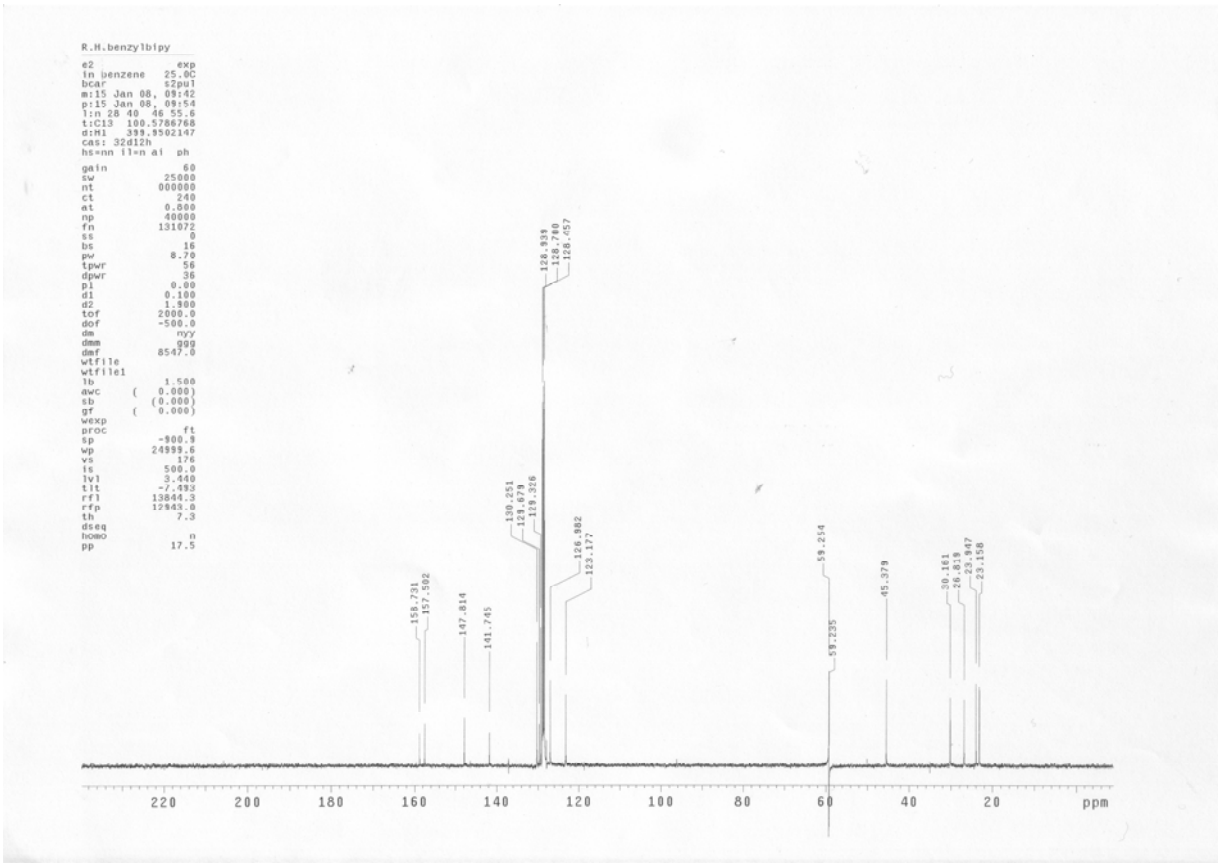
Bis-1,1'-(5,6,7,8-tetrahydro-3-(tetrahydrofuran-2-yl)-isoquinoline) (3f)



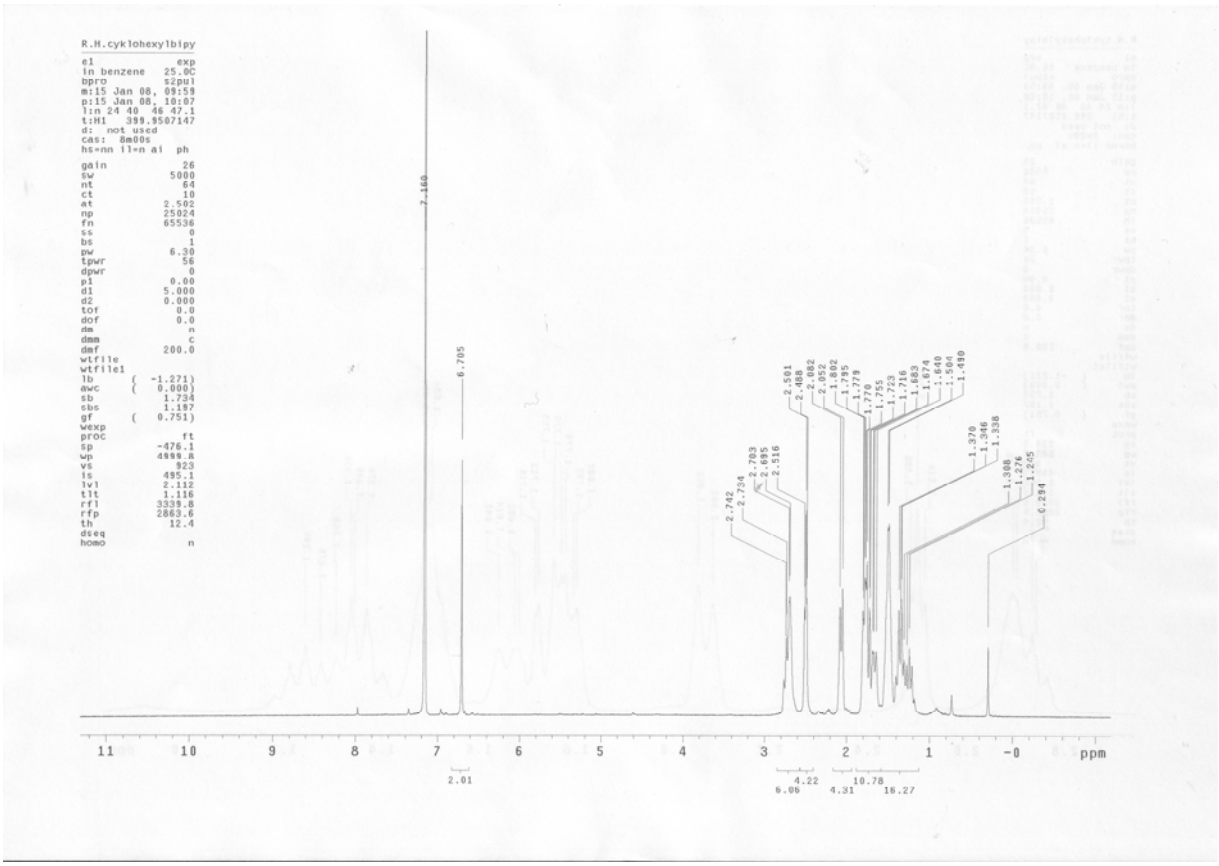


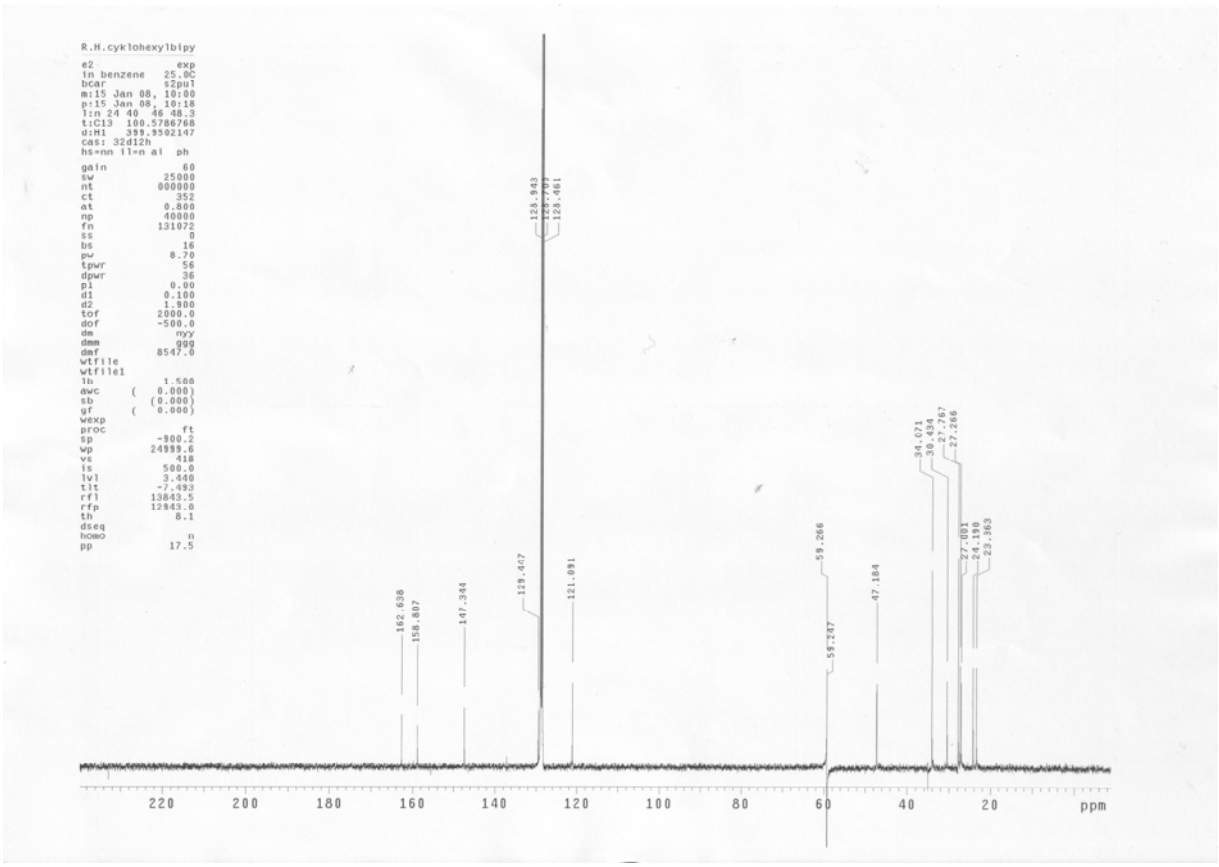
Bis-1,1'-(5,6,7,8-tetrahydro-3-cyclopropyl-isoquinoline) (3g)



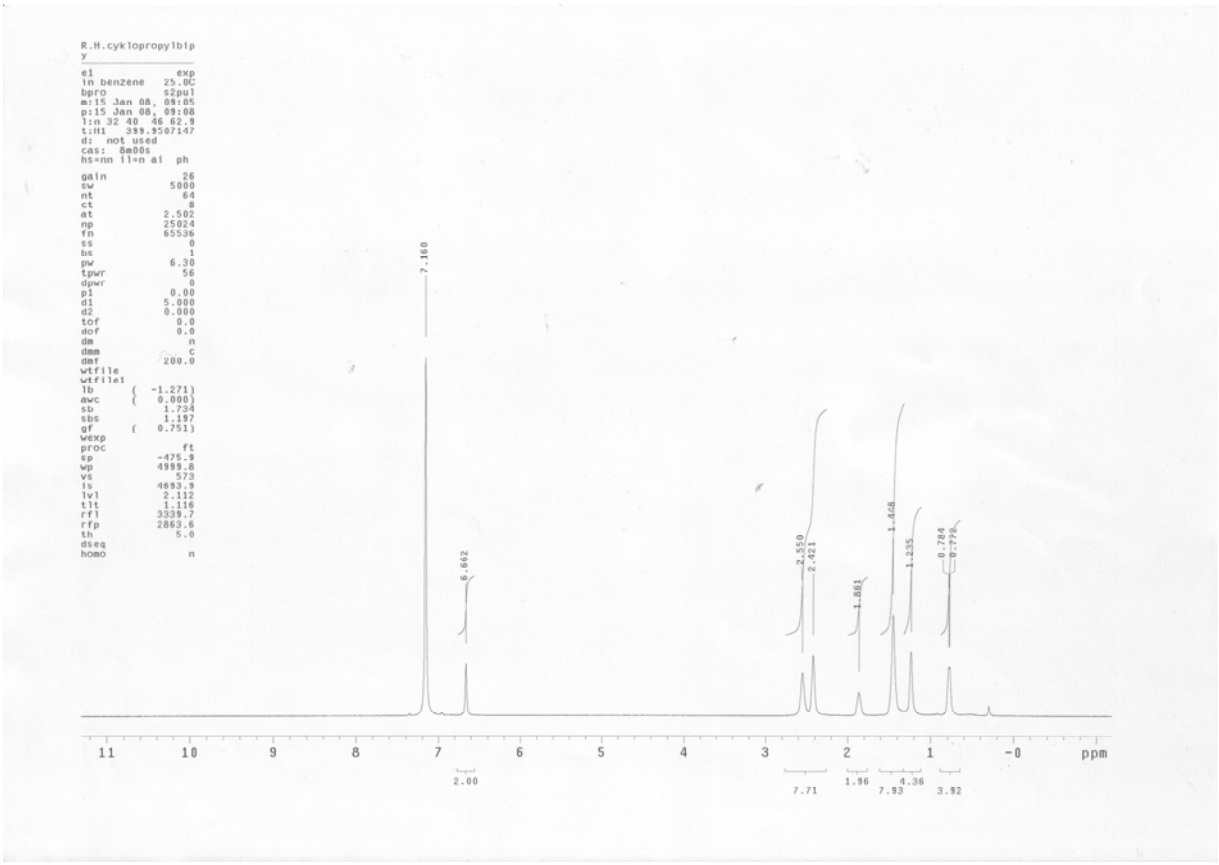


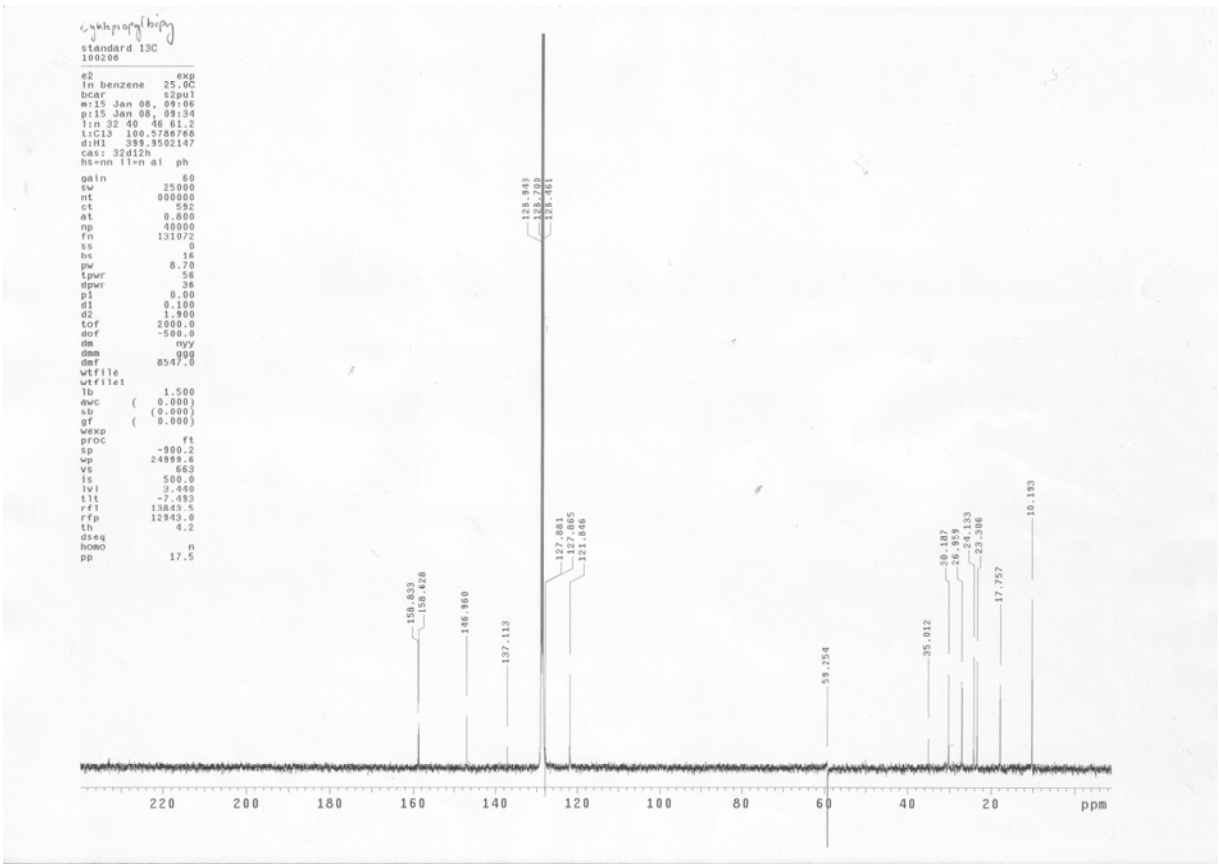
Bis-1,1'-(5,6,7,8-tetrahydro-3-cyclohexyl-isoquinoline) (3h)



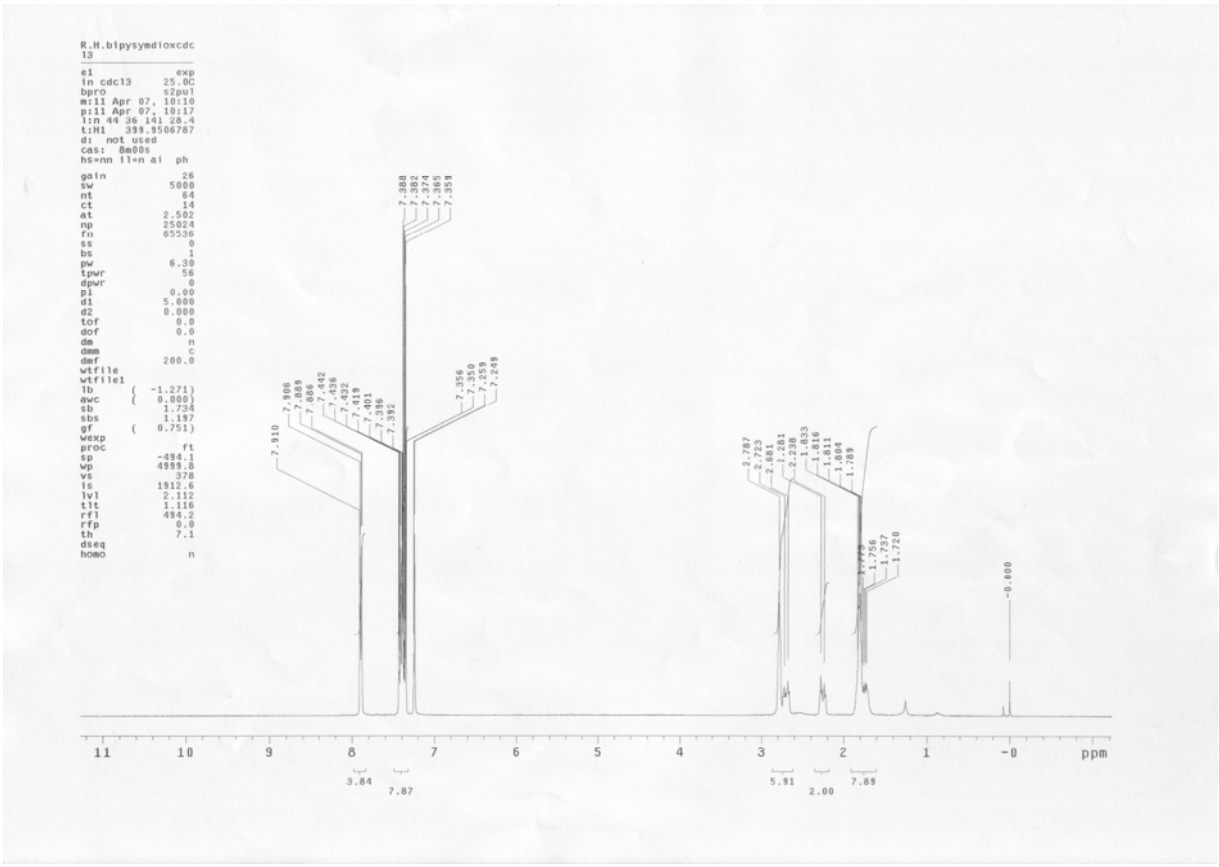


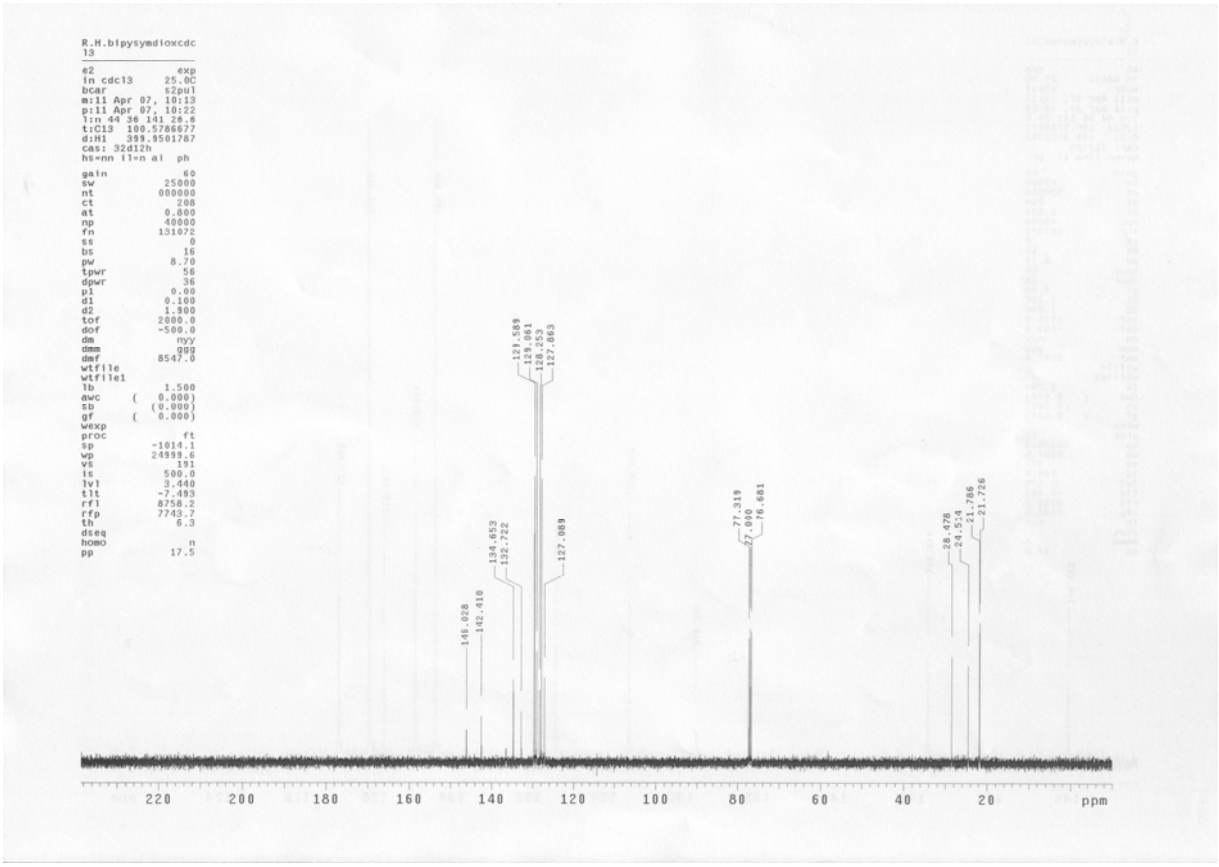
Bis-1,1'-(5,6,7,8-tetrahydro-3-benzyl-isoquinoline) (3i)



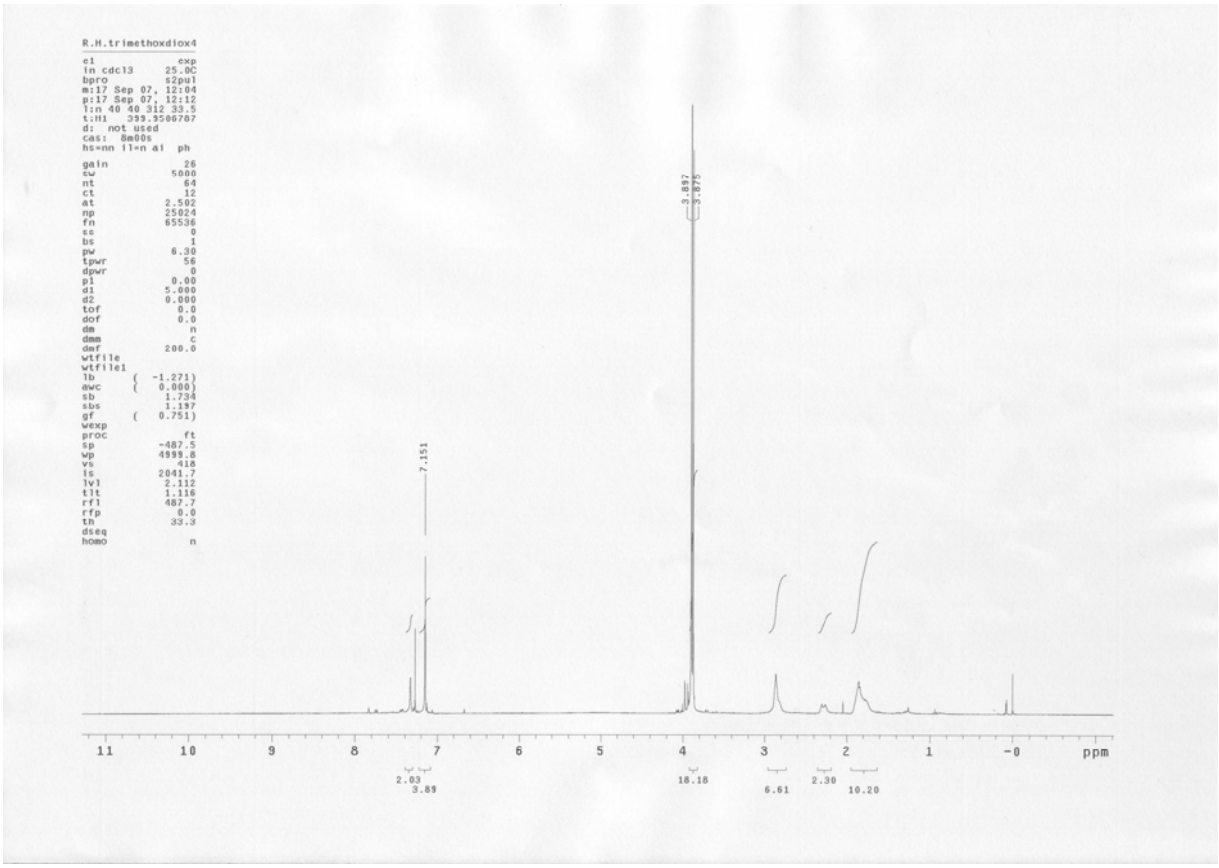


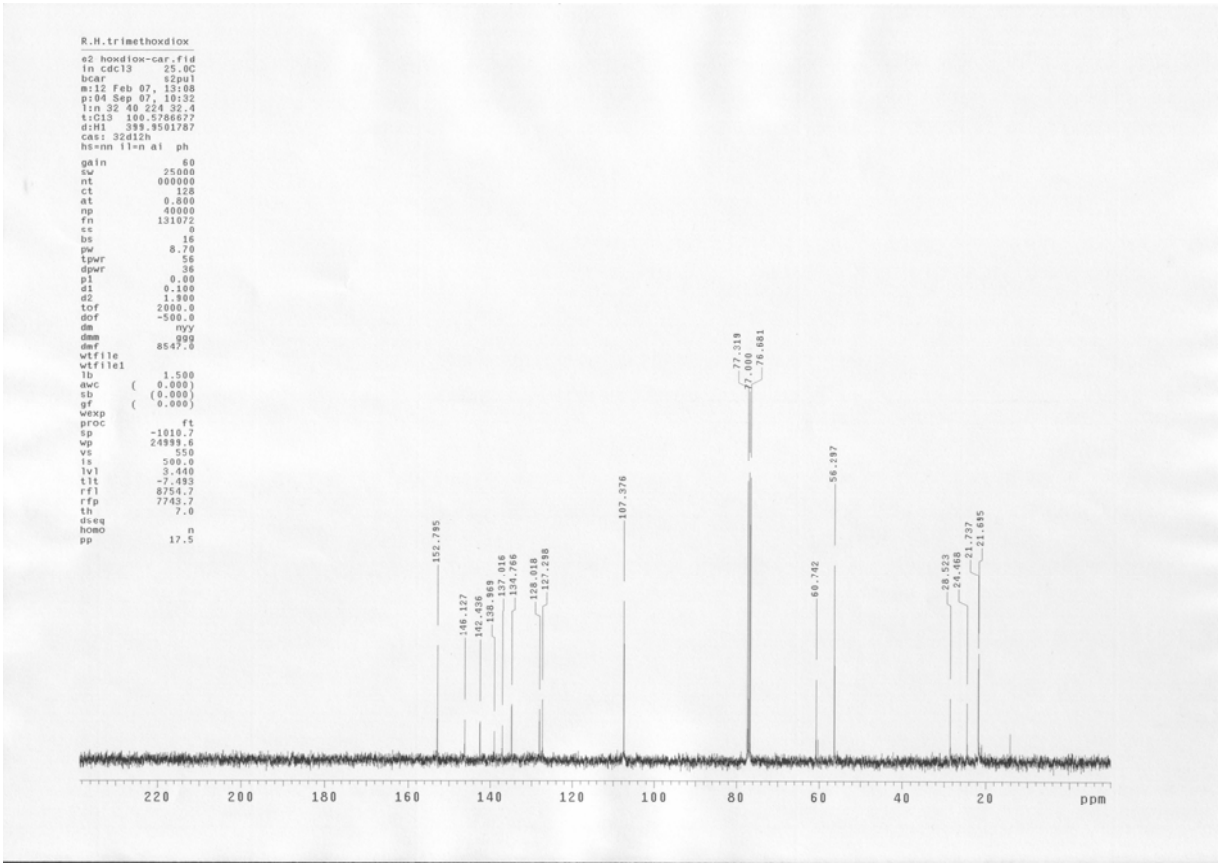
Bis-1,1'-(5,6,7,8-tetrahydro-3-phenyl-isoquinoline)-*N,N'*-dioxide (4a)



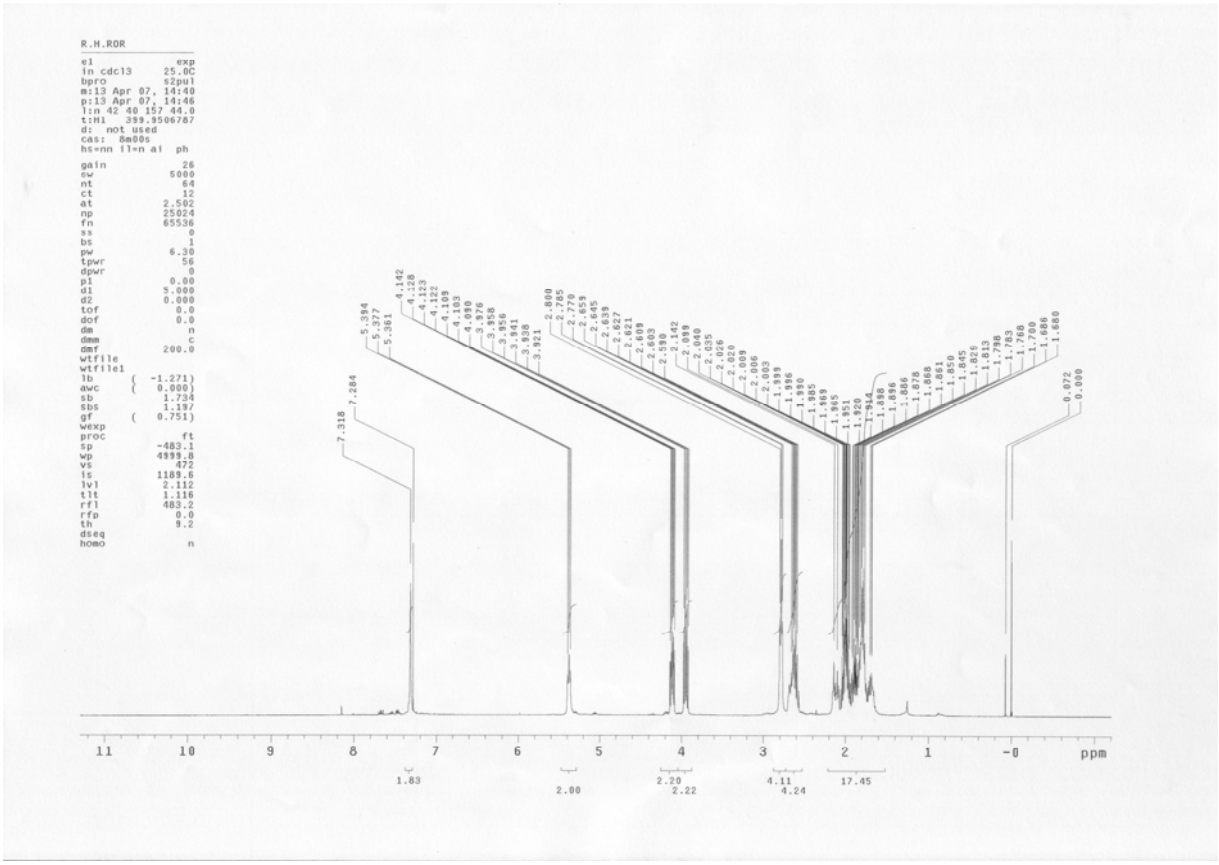


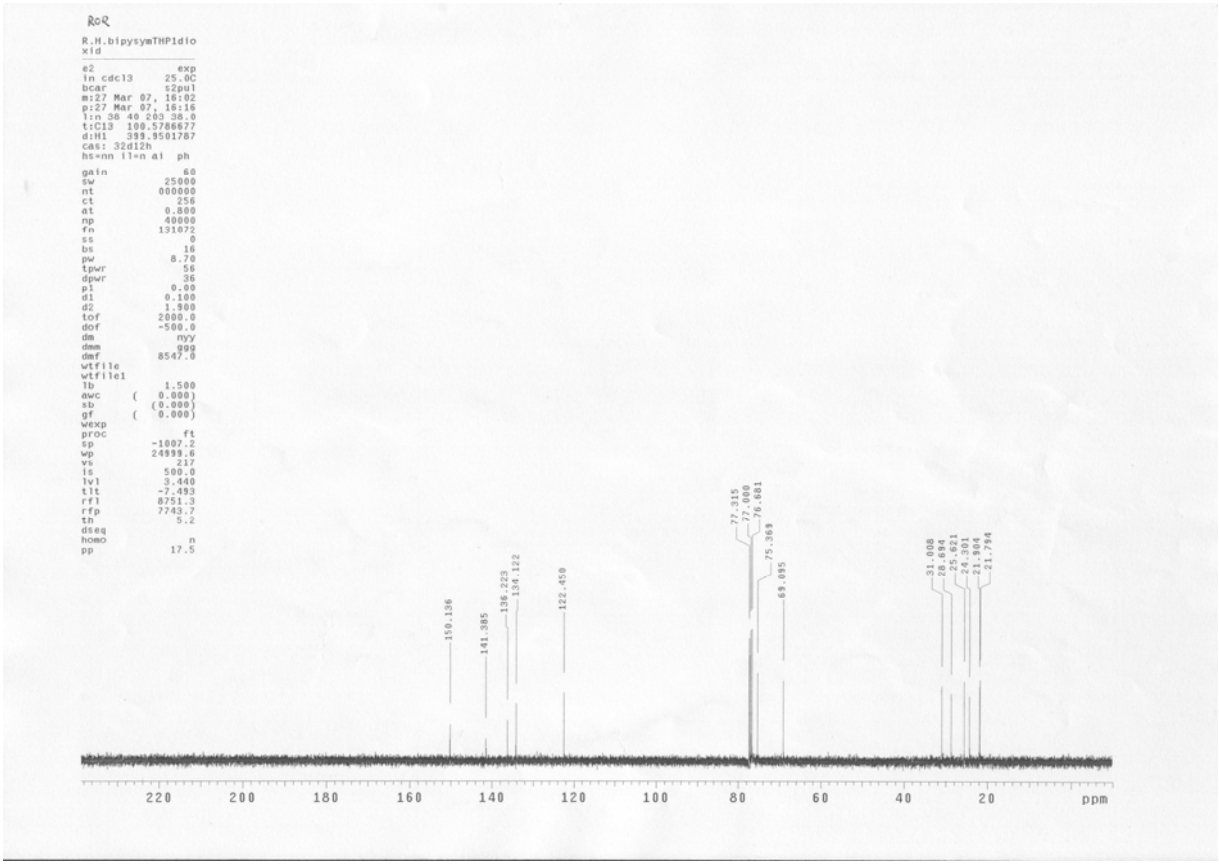
Bis-1,1'-(5,6,7,8-tetrahydro-3-(3,4,5-trimethoxyphenyl)-isoquinoline)-*N,N'*-dioxide (4b)



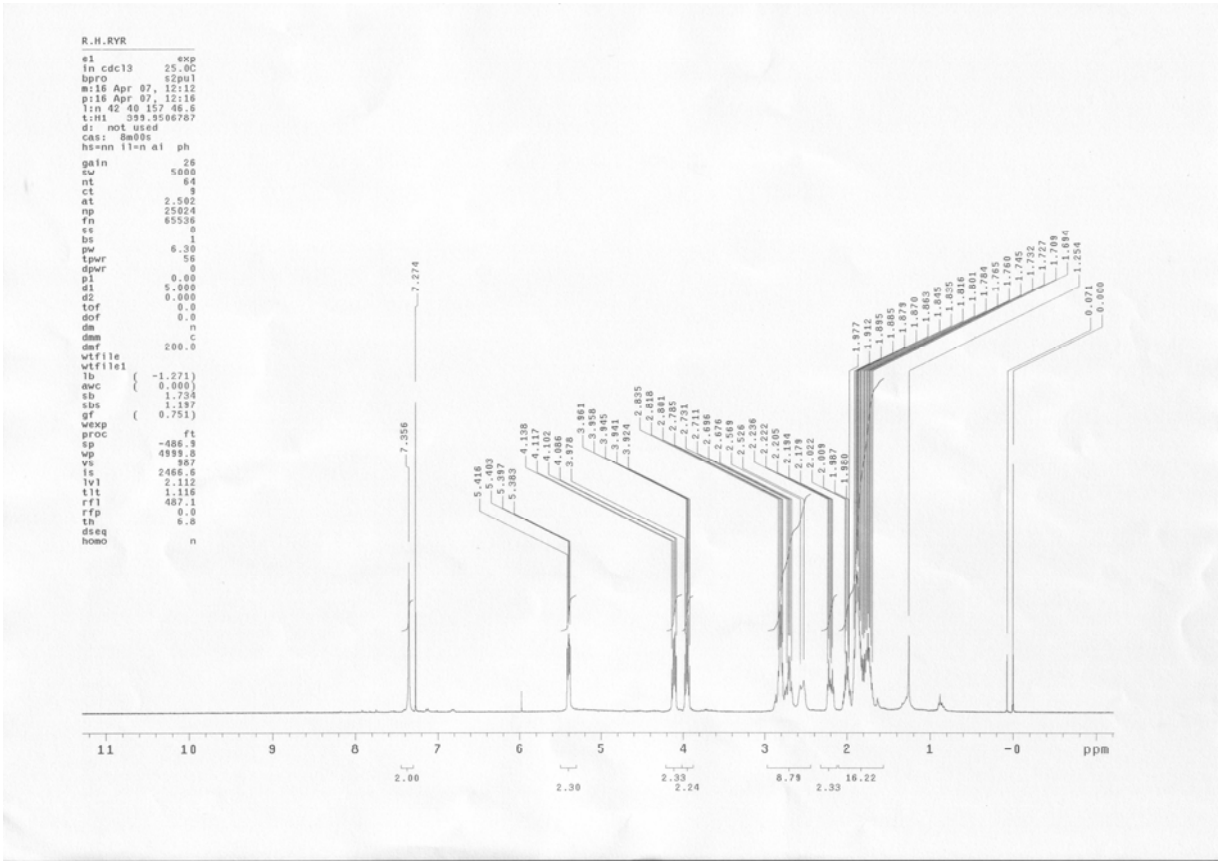


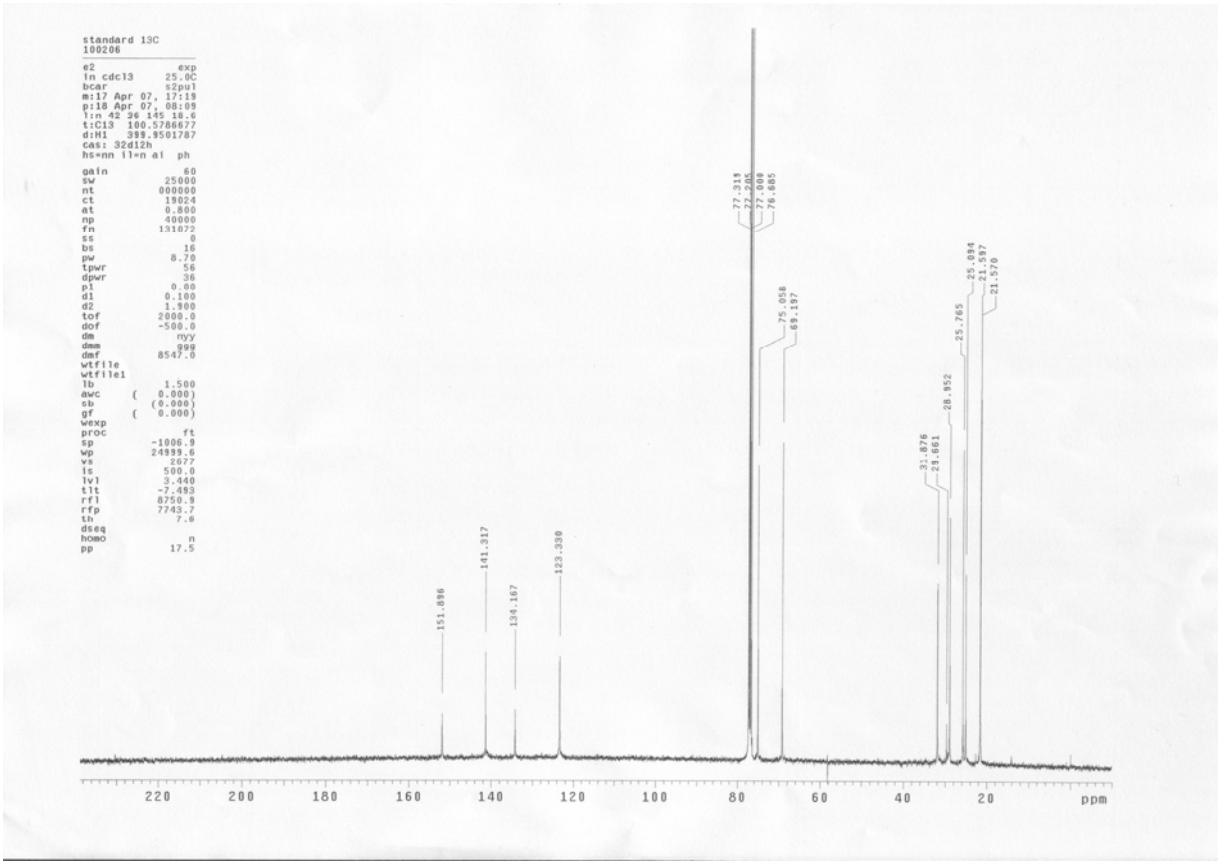
(*R*,*R*,*R*)-Bis-1,1'-[5,6,7,8-tetrahydro-3-(tetrahydrofuran-2-yl)-isoquinoline]-*N*,*N*'-dioxide (4c)

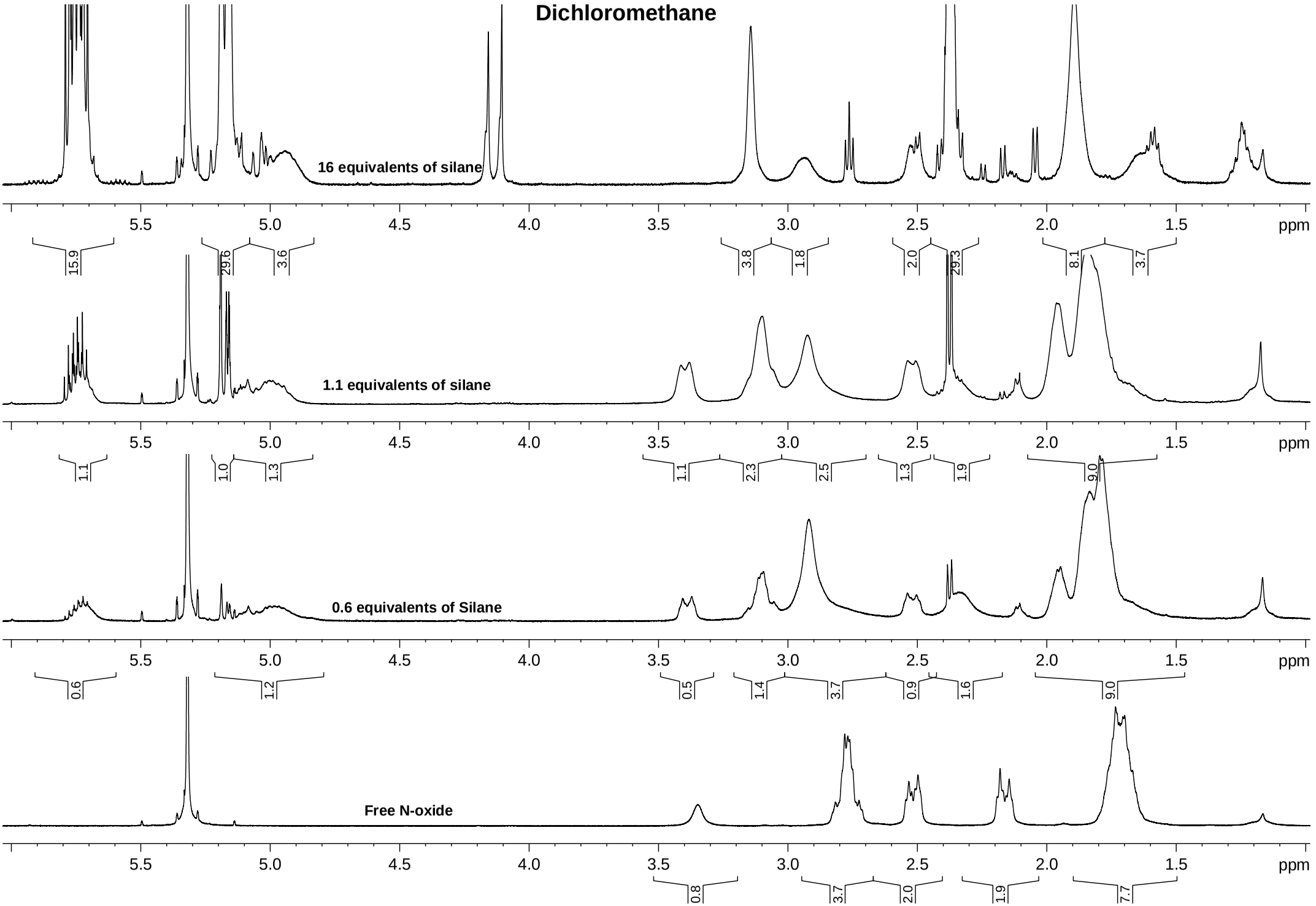


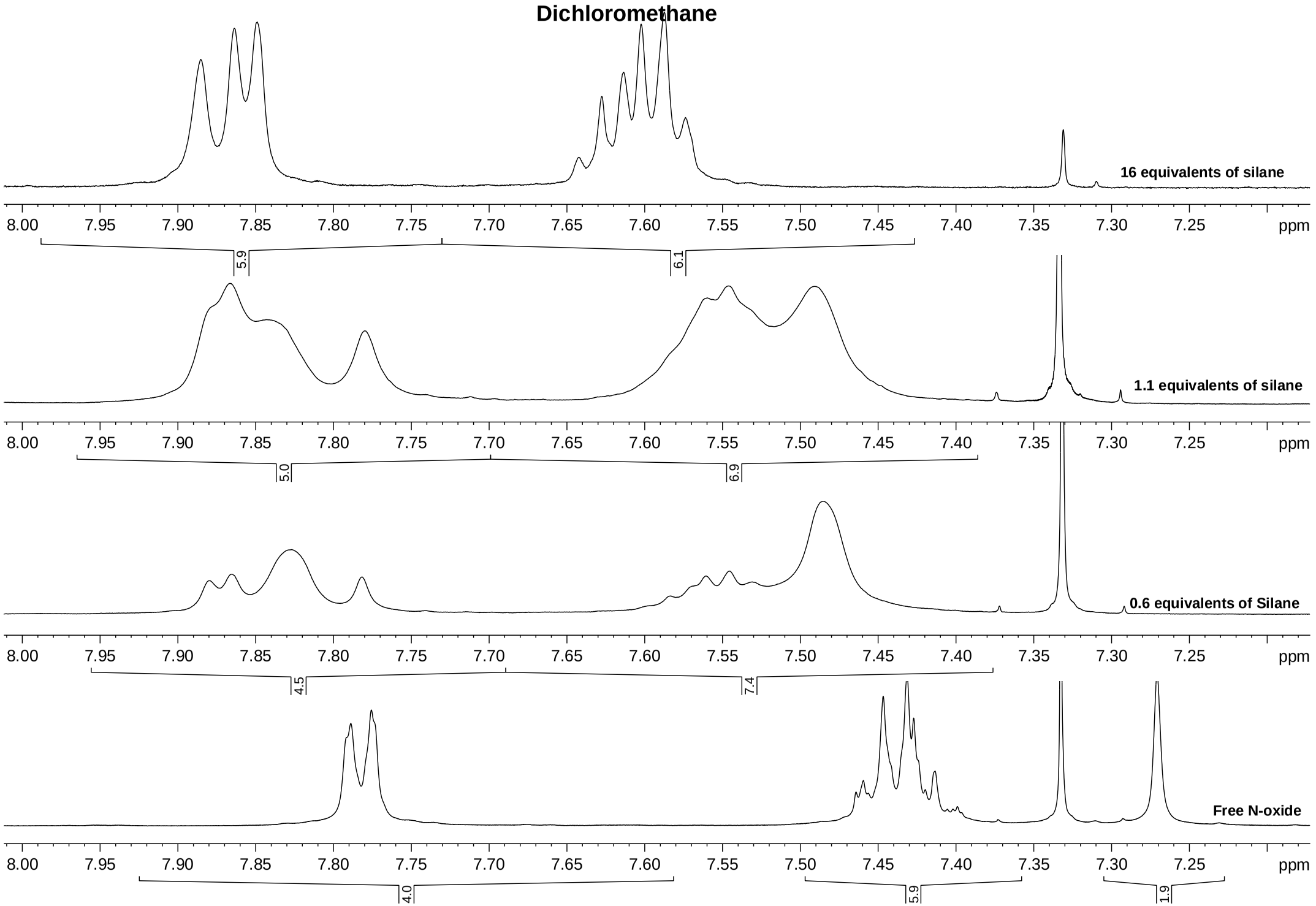


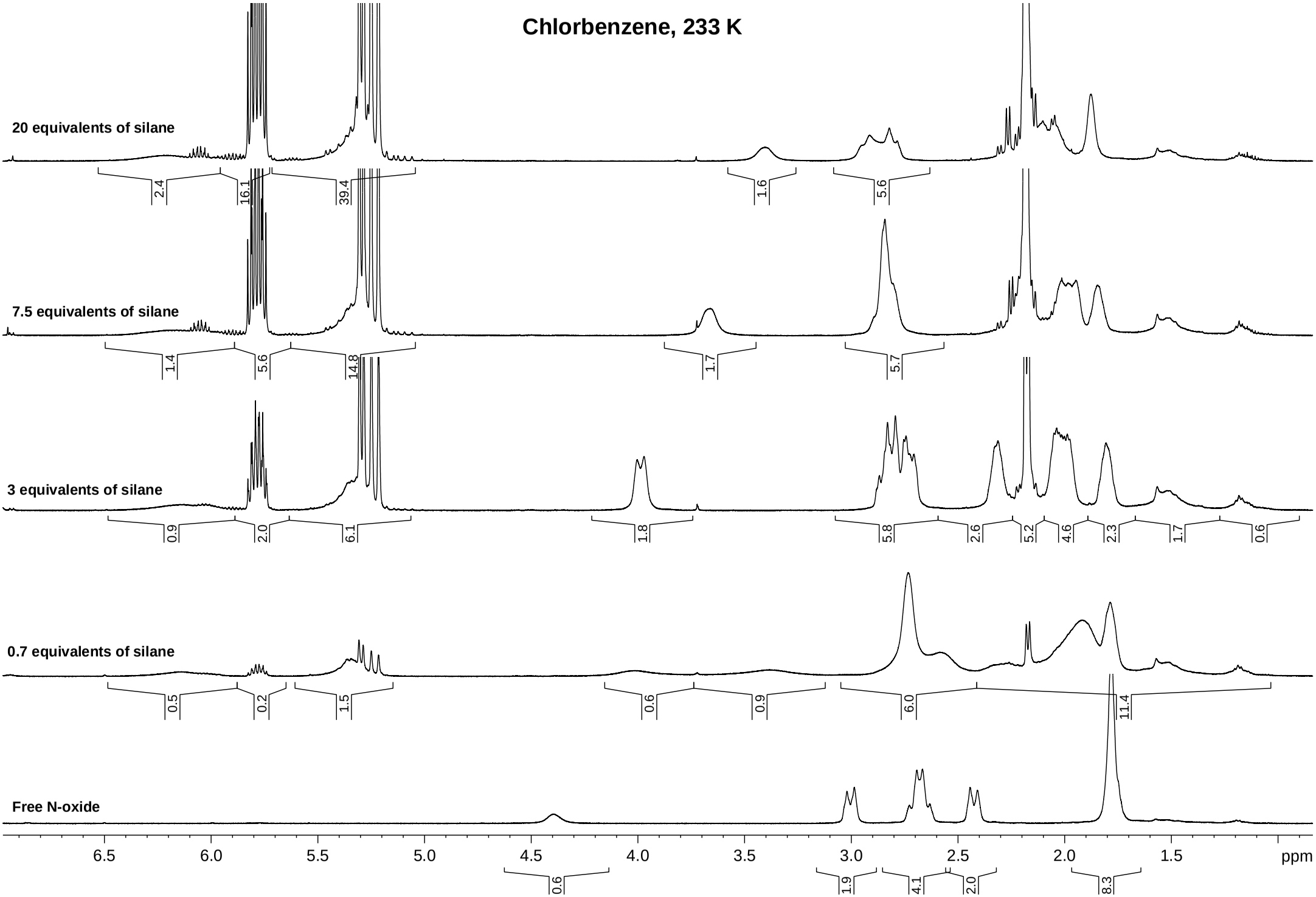
(*S,R,R*)-bis-1,1'-[5,6,7,8-tetrahydro-3-(tetrahydrofuran-2-yl)-isoquinoline]-*N,N'*-dioxide (4c)

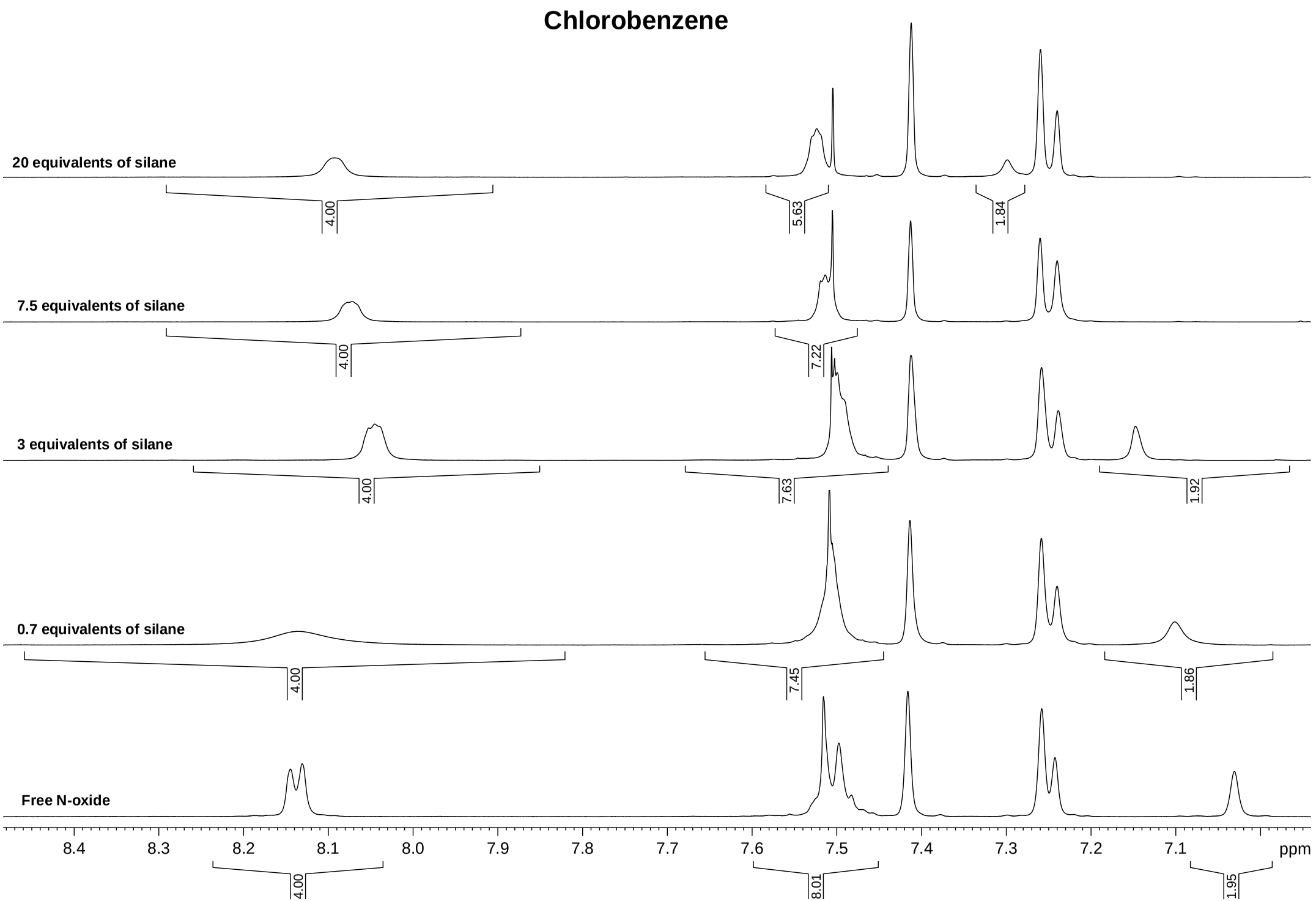





Dichloromethane
16 equivalents of silane
1.1 equivalents of silane
0.6 equivalents of Silane
Free N-oxide
ppm


Dichloromethane
16 equivalents of silane
1.1 equivalents of silane
0.6 equivalents of Silane
Free N-oxide
ppm
5.9
6.1
5.0
6.9
4.5
7.4
4.0
5.9
1.9


Chlorbenzene, 233 K
20 equivalents of silane
2.4
16.1
39.4
1.6
5.6
7.5 equivalents of silane
1.4
5.6
14.8
1.7
5.7
3 equivalents of silane
0.9
2.0
6.1
1.8
5.8
2.6
5.2
4.6
2.3
1.7
0.6
0.7 equivalents of silane
0.5
0.2
1.5
0.6
0.9
6.0
11.4
Free N-oxide
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
0.6
1.9
4.1
2.0
8.3


Chlorobenzene
20 equivalents of silane
4.00
5.63
1.84
7.5 equivalents of silane
4.00
7.22
3 equivalents of silane
4.00
7.63
1.92
0.7 equivalents of silane
4.00
7.45
1.86
Free N-oxide
4.00
8.01
1.95
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
ppm