Excess Substrate is a Spectator Ligand in a Rhodium Catalyzed Asymmetric [2+2+2] Cycloaddition of Alkenyl Isocyanates with Tolanes

Mark Emil Oinen, Robert T. Yu and Tomislav Rovis*
Department of Chemistry, Colorado State University
Fort Collins, Colorado 80523

Supporting Information

General Methods.

All reactions were carried out under an atmosphere of argon in oven dried glassware with magnetic stirring. Toluene was degassed with argon and passed through one column of neutral alumina and one column of Q5 reactant. Acetonitrile (certified ACS grade) and triethylamine (peptide synthesis grade) were purchased from Fisher Scientific and used without further purification. Column chromatography was performed on EM Science silica gel 60 (230-400 mesh). Thin layer chromatography was performed on EM Science 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light and $KMnO_4$ followed by heating. NMR data are reported as follows: chemical shift in parts per million (δ, ppm) from deuterated chloroform ($CDCl_3$) taken as 7.26 ppm (300 MHz) or 7.23 ppm (400 MHz), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), and coupling constant (Hz). ^{13}C NMR chemical shifts are reported in ppm from $CDCl_3$ taken as 77.0 ppm. Alkyne **2a** and pyridines **4a-e** were purchased from Aldrich Chemicals Co. and used without further purification. Alkynes **2b-n** were prepared via literature procedure.[1] Alkenyl isocyanates **2** and **5** are known compounds and can be synthesized by the procedure previously described.[2] $[Rh(C_2H_4)_2Cl]_2$ was purchased from Strem Chemical, Inc. and used without further purification. Ligand **L1** was prepared as described in the literature.[3]

General procedure A for the Rh-catalyzed [2+2+2] cycloaddition.

An oven-dried 10 mL round bottom flask was charged with $[Rh(C_2H_4)_2Cl]_2$ (0.03 eq, 0.0038 mmol) and the phosphoramidite ligand **L1** 3.9 mg (0.06 eq, 0.0077 mmol), and was fitted with an oven-dried reflux condenser in an inert atmosphere (N_2) glove box. A solution of alkyne (1.0 eq, 0.128 mmol) and isocyanate (1.5 eq, 0.193 mmol) in 3 ml of toluene was prepared. This solution was placed under an atmosphere of argon. The 3 mL solution of toluene was then added via syringe to the flask containing the rhodium catalyst. An additional 1 mL of toluene to rinse any remaining isocyanate and alkyne was used and added to the reaction. The resulting solution was heated to 110 °C in an oil bath, and maintained at this temperature for *ca.* 16 h. The reaction mixture was allowed to cool to 23 °C, concentrated *in vacuo*, and purified by flash column chromatography (gradient elution typically to 100% ethyl acetate). Evaporation of solvent afforded the analytically pure product.

General procedure B for the Rh-catalyzed [2+2+2] cycloaddition using additives.

An oven-dried 10 mL round bottom flask was charged with $[Rh(C_2H_4)_2Cl]_2$ (0.03 eq, 0.0038 mmol) and the phosphoramidite ligand **L1** 3.9 mg (0.06 eq, 0.0077 mmol), and was fitted with an oven-dried reflux condenser in an inert atmosphere (N_2) glove box. A solution of alkyne (1.0 eq, 0.128 mmol), isocyanate (1.5 eq, 0.193 mmol) and compound **4d** (1.0 eq, 0.128) in 3 mL of toluene was prepared. This solution was placed under an atmosphere of argon. The 3 mL solution of toluene was then added via syringe to the flask containing the rhodium catalyst. An additional 1 mL of toluene to rinse any remaining isocyanate and alkyne was used and added to the reaction. The resulting solution was heated to 110 °C in an oil bath, and maintained at this temperature for *ca.* 16 h. The reaction mixture was allowed to cool to 23 °C, concentrated *in vacuo*, and purified by flash column chromatography (gradient elution to typically 100% ethyl acetate). Evaporation of solvent afforded the analytically pure product.

Procedure for the competition experiments.

Diphenyl acetylene and bis(4-carboxyethyl phenyl) acetylene.

An oven-dried 10 mL round bottom flask was charged with $[Rh(C_2H_4)_2Cl]_2$ (0.03 eq, 0.0069 mmol) and the phosphoramidite ligand **L1** 3.9 mg (0.06 eq, 0.0138 mmol), and was fitted with an oven-dried reflux condenser in an inert atmosphere (N_2) glove box. A solution of alkyne **2a** (0.6 eq, 0.140 mmol), bis(4-carboxyethyl phenyl) acetylene **2f** (0.6 eq, 0.140 mmol) and 5-Isocyanato-pent-1-ene **1** (1.0 eq, 0.231 mmol) in 3 ml of toluene was prepared. This solution was placed under an atmosphere of argon. The 3 mL solution of toluene was then added via syringe to the flask containing the rhodium catalyst. An additional 1 ml of toluene to rinse any remaining isocyanate and alkyne was used and added to the reaction. The resulting solution was heated to 110 °C in an oil bath, and maintained at reflux for *ca.* 16 h. The reaction mixture was cooled to 23 °C, concentrated *in vacuo*, and purified by flash column chromatography (gradient elution typically 100% ethyl acetate). Evaporation of solvent afforded the analytically pure products **3a** and **3f** in 41% and 23% yields respectively.

5-Isocyanato pent-1-ene and 5-Isocyanato-2-methyl-pent-1-ene.

An oven-dried 10 mL round bottom flask was charged with $[Rh(C_2H_4)_2Cl]_2$ (0.03 eq, 0.0055 mmol) and the phosphoramidite ligand **L1** 3.9 mg (0.06 eq, 0.0110 mmol), and was fitted with an oven-dried reflux condenser in an inert atmosphere (N_2) glove box. A solution of alkyne **2a** (1.0 eq, 0.184 mmol), 5-Isocyanato pent-1-ene **1** (1.0 eq, 0.184 mmol) and 5-Isocyanato-2-methyl-pent-1-ene **1a** (1.0 eq, 0.184 mmol) in 3 ml of toluene was prepared. This solution was placed under an atmosphere of argon. The 3 mL solution of toluene was then added via syringe to the flask containing the rhodium catalyst. An additional 1 mL of toluene to rinse any remaining isocyanate and alkyne was used and added to the reaction. The resulting solution was heated to 110 °C in an oil bath, and maintained at reflux for *ca.* 16 h. The reaction mixture was cooled to 23 °C, concentrated *in vacuo*, and purified by flash column chromatography (gradient elution typically 100% ethyl acetate). Evaporation of solvent afforded the analytically pure products **3a** and **5a** in 44% and 49% yields respectively.

Procedure for the ^{19}F NMR experiments.

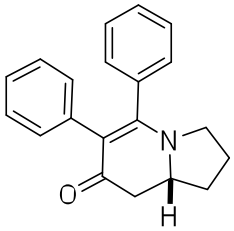
Procedure for monitoring the disappearance of Bis(3-fluorophenyl) acetylene 2n in the Rh-catalyzed [2+2+2] cycloaddition of 5-Isocyanato pent-1-ene without additive.

An oven-dried NMR tube was flushed with argon. In an inert atmosphere (N_2) glove box a 1 dram vial was charged with $[Rh(C_2H_4)_2Cl]_2$ (0.03 eq, 0.0055 mmol) and the phosphoramidite ligand **L1** 3.9 mg (0.06 eq, 0.0110 mmol), alkyne **2n** (1.0 eq, 0.184 mmol) and 1-Fluoronapthalene (10 μL, 0.077 mmol) as an internal standard. 0.250 mL of d_8-toluene was used to dissolve the rhodium precatalyst, ligand and alkyne, and the solution was transferred to the NMR tube. The reaction was placed in the NMR tube and inside the NMR and slowly heated over ten minutes to 90 °C. Data was collected without isocyanate at T=0. The NMR was removed and injected with 5-Isocyanato pent-1-ene **1** (1.0 eq, 0.184 mmol) in 0.150 ml of d_8-toluene. NMR spectra were subsequently taken at periods of 2 minutes.

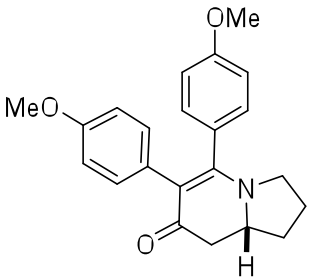
Procedure for monitoring the disappearance of Bis(3-fluorophenyl) acetylene 2n in the Rh-catalyzed [2+2+2] cycloaddition of 5-Isocyanato pent-1-ene with methyl nicotinate.

An oven-dried NMR tube was flushed with argon. In an inert atmosphere (N_2) glove box a 1 dram vial was charged with $[Rh(C_2H_4)_2Cl]_2$ (0.03 eq, 0.0055 mmol) and the phosphoramidite ligand **L1** 3.9 mg (0.06 eq, 0.0110 mmol), alkyne **2a** (1.0 eq, 0.187 mmol), methyl nicotinate (0.5 eq, 0.094 mmol) and 1-Fluoronapthalene (10 μL, 0.077 mmol) as an internal standard. 0.250 mL of d_8-toluene was used to dissolve the rhodium precatalyst, ligand, alkyne, and methyl nicotinate and the solution was transferred to the NMR tube. The reaction was placed in the NMR and slowly heated over ten minutes to 90 °C. Data was collected without isocyanate at T=0. The NMR tube was removed and injected with 5-Isocyanato pent-1-ene **1** (1.0 eq, 0.184 mmol) in 0.150 ml in d_8-toluene. NMR spectra were taken at periods of 2 minutes for the first 26 minutes and then 5 minutes for an additional 25 minutes until the reaction was greater than 80% conversion.

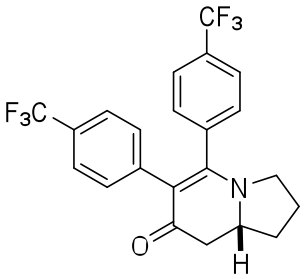
Characterization of new compounds.



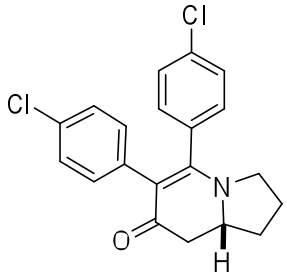
5,6-diphenyl-2,3,8,8a-tetrahydroindolizin-7(1*H*)-one (3a). The general procedure B yielded a light yellow solid (95% yield).. R_f = 0.13 (1:1 EtOAc/Hex); $[\alpha]_D^{20}$ = + 632 (c =1.5, THF); HPLC analysis – Chiracel OD-H column 80:20 hexane:iPrOH, 1.0 ml/min, Major: 12.1 minutes, Minor: 13.8 minutes, 230 nm detection light, *ee* = 93%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 – 7.30 (m, 5H), 7.00 (m, 2H), 6.88 – 6.94 (m, 3H), 4.14 (dddd, 1H, *J* = 6.8, 6.8, 6.8, 13.6 Hz), 3.40 (ddd, 1H, *J* = 4.0, 7.5, 11.5 Hz), 3.11 (ddd, 1H, *J* = 7.5, 7.5, 10.9 Hz), 2.67 (dd, 1H, *J* = 5.3, 15.6 Hz), 2.59 (dd, 1H, *J* = 5.3, 16.0 Hz), 2.35 (m, 1H), 1.94 – 2.03 (m, 1H), 1.73 – 1.93 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.9, 161.1, 136.7, 135.9, 132.2, 128.9, 128.2, 127.4, 125.3, 112.4, 57.8, 50.1, 42.1, 32.5, 24.4; IR (NaCl, $CDCl_3$) 1617, 1528, 1450, 1383, 1304, 1091 cm^{-1}; HRMS $[C_{20}H_{20}NO]^+$ calcd 290.1545; found 290.1545 (FAB+).



5,6-bis(4-methoxyphenyl)-2,3,8,8a-tetrahydroindolizin-7(1*H*)-one (3b). The general procedure B yielded a light yellow solid (93% yield). R_f = 0.21 (EtOAc); $[\alpha]_D^{20}$ = + 559 (c =1.5, THF); HPLC analysis – Chiracel AD-H column 80:20 hexane:iPrOH, 1.0 ml/min, Major: 12.1 minutes, Minor: 13.8 minutes, 230 nm detection light, *ee* = 91%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.54 – 7.20 (m, 8H), 4.11 (dddd, 1H, *J* = 6.5, 6.5, 6.5, 12.9 Hz), 3.71 (s, 3H), 3.65 (s, 3H), 3.43 (m, 1H), 3.10 (m, 1H), 2.64 (dd, 1H, *J* = 5.2, 15.8 Hz), 2.55 (dd, 1H, *J* = 4.5, 15.8 Hz), 2.31 (m, 1H), 1.91 – 2.01 (m, 1H), 1.71 – 1.90 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.9, 161.0, 159.8, 157.1, 133.0, 130.6, 129.3, 128.2, 113.6, 113.1, 111.8, 57.5, 55.3, 55.2, 50.3, 42.0, 32.3, 24.5; IR (NaCl, $CHCl_3$) 1598, 1521, 1440, 1301, 1030 cm^{-1}; HRMS $[C_{22}H_{24}NO_3]^+$ calcd 350.1756; found 350.1761 (FAB+).

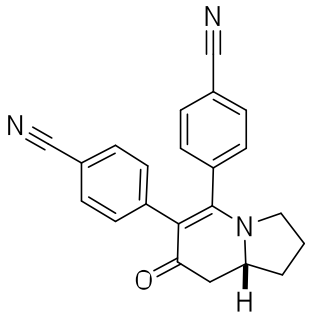


5,6-bis(4-trifluoromethylphenyl)-2,3,8,8a-tetrahydroindolizin-7(1*H*)-one (3c). The general procedure B with 4 eq. of benzonitrile yielded a dark yellow solid (74% yield). R_f = 0.20 (EtOAc); $[\alpha]_D^{20}$ = + 448 (c = 1.2, THF); HPLC analysis – Chiracel OD-H column 85:15 hexane:iPrOH, 1.0 ml/min, Major: 11.14 minutes, Minor: 12.53 minutes, 254 nm detection light, *ee* = 80%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.4 (m, 3H), 7.30 (d, 2H, *J* = 8 Hz), 7.14-7.06 (m, 1H), 7.02 (d, 2H, *J* = 8 Hz), 4.19 (dddd, 1H, *J* = 7.2, 7.2, 7.2, 14.4 Hz), 3.40 (ddd, 1H, *J* = 4.0, 7.2, 11.6 Hz), 3.12 (ddd, 1H, *J* = 7.6, 7.6, 10.8 Hz), 2.73-2.63 (m, 2H), 2.41 (m, 1H), 2.1-1.8 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.6, 159.4, 140.0, 138.0, 132.2, 131.5, 129.6 (m), 125.7 (m), 124.6, 111.6, 58.2, 50.3, 41.8, 32.5, 29.9, 24.5; IR (NaCl, $CHCl_3$) 2924, 1630, 1534, 1455, 1406,1325,1164,1066 cm^{-1}; HRMS $[C_{22}H_{18}F_6NO]^+$ calcd. 426.1214; found 426.1212 (ESI+).

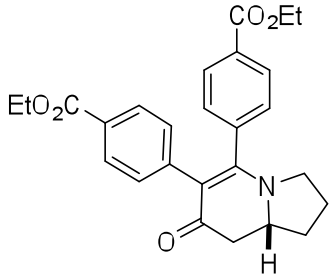


5,6-bis(4-chlorophenyl)-2,3,8,8a-tetrahydroindolizin-7(1*H*)-one (3d). The general procedure B yielded a light yellow solid (71% yield). R_f = 0.25 (EtOAc); $[\alpha]_D^{20}$ = + 591.0 (c = 1, THF); HPLC analysis – Chiracel OD-H column 80:20 hexane:iPrOH, 1.0 ml/min, Major: 12.5 minutes, Minor: 16.0 minutes, 254 nm detection light, *ee* = 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76 – 7.32 (m, 8H), 4.12 (dddd, 1H, *J* = 7.2, 7.2, 7.2,

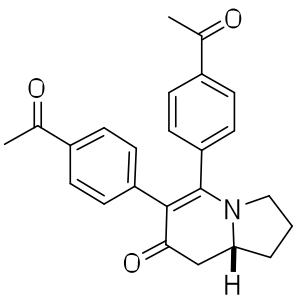
14.4 Hz), 3.39 (ddd, 1H, *J* = 4.3, 7.5, 11.5 Hz), 3.09 (ddd, 1H, *J* = 7.5, 7.5, 11.1 Hz), 2.63 (dd, 1H, *J* = 16.0, 16.0 Hz), 2.61 (dd, 1H, *J* = 6.6, 16.0 Hz), 2.35 (dddd, 1H, *J* = 4.3, 6.7, 6.7, 6.7 Hz), 1.95 – 2.04 (m, 1H), 1.73 – 1.93 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.5, 160.0, 135.3, 134.9, 133.9, 133.3, 131.2, 130.6, 130.3, 128.8, 127.8, 111.4, 57.9, 50.3, 41.7, 32.4, 24.4; IR (NaCl, $CHCl_3$) 1614, 1516, 1440, 1301, 1086 cm^{-1} ; HRMS $[C_{20}H_{18}Cl_2NO]^+$ calcd 358.0765; found 358.0755 (ESI+).



5,6-bis(4-cyanophenyl)-2,3,8,8a-tetrahydroindolizin-7(1*H*)-one (3e). The general procedure B yielded an orange solid (70% yield). R_f = 0.17 (EtOAc); $[\alpha]_D^{20}$ = + 403.6 (c = 0.8, THF); HPLC analysis – Chiracel AD-H column 80:20 hexane:iPrOH, 1.0 ml/min, Major: 34.06 minutes, Minor: 40.91 minutes, 254 nm detection light, *ee* = 62%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.62 (m, 1H), 7.48-7.40 (m, 1H), 7.30 (d, 2H, *J* = 8 Hz), 7.05-7.02 (m, 1H), 6.96 (d, 2H, *J* = 8 Hz), 4.17 (dddd, 1H, *J* = 8, 8, 8, 15.6 Hz), 3.39 (ddd, 1H, *J* = 4, 7.2, 11.2 Hz), 3.09 (ddd, 1H, *J* = 7.2, 7.2, 15.2 Hz), 2.70-2.60 (m, 2H), 2.45-2.35 (m, 1H), 2.09-1.76 (m, 1H); ^{13}C NMR δ (100 MHz, $CDCl_3$) 189.3, 158.9, 141.3, 139.6, 132.7, 132.5, 132.3, 131.4, 130.1, 129.8, 119.3, 117.9, 113.6, 111.3, 109.0, 58.2, 50.3, 41.6, 32.3, 24.5; IR (NaCl, $CHCl_3$) 2969, 2876, 2224, 1628, 1528, 1455,1301, 1127, 731 cm^{-1}; HRMS $[C_{22}H_{18}N_3O]^+$ calcd. 340.1372; found 340.1375 (ESI+).

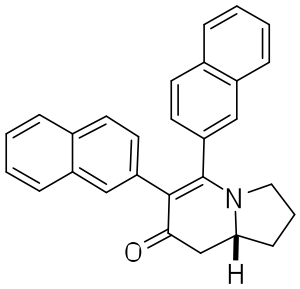


5,6-bis(4-carboethoxyphenyl)-2,3,8,8a-tetrahydroindolizin-7(1*H*)-one (3f). The general procedure B yielded a dark yellow solid (92% yield). R_f = 0.21 (EtOAc);; $[\alpha]_D^{20}$ = + 447.6 (c = 0.8, THF); HPLC analysis – Chiracel OD-H column 90:10 hexane:iPrOH, 1.0 ml/min, Major: 34.06 minutes, Minor: 40.91 minutes, 254 nm detection light, *ee* = 93%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, 1H, *J* = 6.8 Hz), 7.72 (d, 1H, *J* = 7.2 Hz), 7.63 (d, 2 H, *J* = 8.4 Hz), 7.31 (d, 1H, *J* = 6.8 Hz), 6.95 (d, 1H, *J* = 7.2 Hz), 6.91 (d, 1H, *J* = 8.4 Hz), 4.26 (q, 2, *J* = 9 Hz), 4.20 (q, 2H, *J* = 7.2 Hz), 4.11 (m, 1H) 3.33 (ddd, 1H, *J* = 4.2, 7.4, 11.5 Hz), 3.02 (ddd, 1H, *J* = 7.5, 7.5, 11 Hz), 2.59 (m, 2H), 2.30 (ddd, *J* = 6, 10.8, 17.3 Hz), 1.96-1.74 (m, 3H), 1.28 (t, 3H, *J* = 7.15 Hz), 1.24 (t, 3H, *J* = 7.15 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.4, 170.0, 166.9, 165.9, 160.0, 141.6, 139.8, 131.9, 131.1, 129.9, 129.5, 129.3, 129.1, 128.8, 127.2, 61.5, 60.8, 58.0, 50.2, 42.0, 32.5, 29.9, 24.5,14.5; IR (NaCl, $CHCl_3$) 2977, 2928, 2873, 1712, 1631, 1528, 1273, 1101, 1020 cm^{-1}; HRMS $[C_{26}H_{28}NO_5]^+$ calcd. 433.1889; found 433.1882 (ESI+).

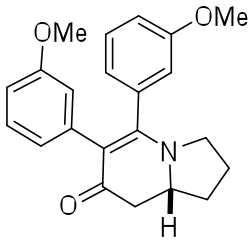


5,6-bis(4-acetylphenyl)-2,3,8,8a-tetrahydroindolizin-7(1*H*)-one (3g). The general procedure yielded a light yellow solid (95% yield). R_f = 0.13 (EtOAc); $[\alpha]_D^{20}$ = + 513.9 (c = 1.3, THF); HPLC analysis – Chiracel OD-H column 70:30 hexane:iPrOH, 1.0 ml/min, Major: 17.7 minutes, Minor: 23.3 minutes, 254 nm detection light, *ee* = 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (broad d, 1H, *J* = 7.0 Hz), 7.67 (broad d, 1H, *J* = 7.2 Hz), 7.59 (d, 2H, *J* = 8.3 Hz), 7.39 (broad d, 1H, *J* = 6.8 Hz), 7.03 (broad d, 1H, *J* = 7.5 Hz), 6.98 (d, 2H, *J* = 8.3 Hz), 4.17 (dddd, 1H, *J* = 7.0, 7.0, 7.0, 14.1 Hz), 3.40 (ddd, 1H, *J* = 4.3, 7.5, 11.6 Hz), 3.08 (ddd, 1H, *J* = 7.5, 7.5, 11.1 Hz), 2.67 (dd, 1H, *J* = 5.6, 15.3 Hz), 2.61 (dd, 1H, *J* = 6.1, 15.8 Hz), 2.52 (s, 3H), 2.44 (s, 3H), 2.38 (dddd, 1H, *J* = 4.3, 6.6, 6.6, 6.6 Hz), 2.01 (m, 1H), 1.75 – 1.96 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 197.4, 189.6, 159.9, 142.0, 140.0, 137.5, 134.1, 132.1, 129.6, 129.4, 128.8, 128.3, 127.7, 111.7, 58.1, 50.3,

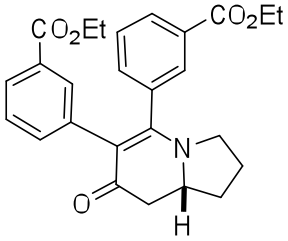
41.8, 32.4, 26.8, 26.7, 24.5; IR (NaCl, $CHCl_3$) 1680, 1619, 1521, 1429, 1301, 1040 cm^{-1}; HRMS $[C_{24}H_{24}NO_3]_+$ calcd 374.1756; found 374.1739 (ESI+).



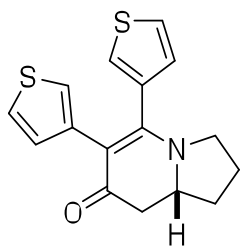
5,6-bis(naphthyl)-2,3,8,8a-tetrahydroindolizin-7(1*H*)-one (3h). The general procedure yielded a dark yellow solid (92% yield). R_f = 0.25 (EtOAc); $[\alpha]_D^{20}$ = + 428.8 (c = 1.2, THF); HPLC analysis – Chiracel AD-H column 80:20 hexane:iPrOH, 1.0 ml/min, Major: 15.0 minutes, Minor: 12.8 minutes, 254 nm detection light, *ee* = 91%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.8 – 7.0 (m, 14H), 4.25-4.10 (m, 1H), 3.5-3.25 (m, 1H), 3.2-3.0 (m, 1H), 2.76-2.5 (m, 2H), 2.38-2.27 (m, 1H), 1.98-1.6 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.2, 161.2, 133.4,131.7, 130.7, 128.8, 128.6, 128.4, 128.2, 127.9, 127.8, 127.4, 127.2, 127.0, 126.9, 126.7, 126.6, 126.4, 125.1, 124.9, 112.5, 58.0, 50.6, 42.1, 32.5, 24.4; IR (NaCl, $CHCl_2$) 3052, 2962, 2925, 2872, 1620, 1520, 1438, 1368, 1300, 1238, 746 cm^{-1}; HRMS $[C_{28}H_{23}NO]_+$ calcd 390.1780; found 390.1788 (ESI+)



5,6-bis(3-methoxyphenyl)-2,3,8,8a-tetrahydroindolizin-7(1*H*)-one (3i). The general procedure yielded a light yellow solid (93% yield). R_f = 0.21 (EtOAc); $[\alpha]_D^{20}$ = + 396.9 (c = 1.6, THF) HPLC analysis – Chiracel AD-H column 85:15 hexane:iPrOH, 1.0 ml/min, Major: 13.1 minutes, Minor: 14.4 minutes, 254 nm detection light, *ee* = 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.46 – 7.18 (m, 8H), 4.12 (dddd, 1H, *J* = 6.8, 6.8, 6.8, 13.6 Hz), 3.50 – 3.76 (m, 6H), 3.43 (m, 1H), 3.14 (ddd, 1H, *J* = 7.5, 7.5, 10.9 Hz), 2.65 (dd, 1H, *J* = 5.2, 15.7 Hz), 2.57 (dd, 1H, *J* = 5.3, 15.9 Hz), 2.34 (m, 1H), 1.94 – 2.03 (m, 1H), 1.73 – 1.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.9, 160.7, 159.4, 158.9, 138.2, 137.1, 129.4, 128.3, 124.8, 121.4, 117.2, 114.6, 111.8, 57.9, 55.4, 55.2, 50.1, 42.1, 32.5, 24.4; IR (NaCl, $CHCl_3$) 1614, 1521, 1460, 1419, 1312, 1045 cm^{-1}; HRMS $[C_{22}H_{23}NO_3]_+$ calcd 349.1678; found 349.1667 (ESI+).

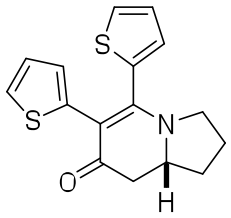


5,6-bis(3-carboethoxyphenyl)-2,3,8,8a-tetrahydroindolizin-7(1*H*)-one. (3j) The general procedure yielded a dark yellow solid (92% yield). R_f =0.20 (EtOAc); $[\alpha]_D^{20}$ = + 430.3 (c = 1.2, THF); HPLC analysis – Chiracel OD-H column 70:30 hexane:iPrOH, 1.0 ml/min, Major: 10.9 minutes, Minor: 14.0 minutes, 254 nm detection light, *ee* = 93%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.96 (m, 1H), 7.85 (d, 1H, *J* = 7.2 Hz), 7.65 – 7.63 (m, 1H), 7.60 (d, 1H, *J* = 7.2 Hz), 7.57-.7.53 (m, 1H), 7.40-7.32 (m, 1H), 7.18-7.05(m, 2H), 4.4-4.1(m, 5H), 3.5-3.25 (m, 1H), 3.2-3.0 (m, 1H), 2.673 (t, *J* = 6 Hz), 2.64-2.5 (m, 1H), 2.45-2.35 (m, 1H), 2.05-1.70 (m, 3H) 1.41-1.2 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.7, 166.9, 160.0, 136.7, 135.7, 133.7, 133.4, 133.1, 130.6, 130.0, 129.7, 128.7, 128.5, 127.6, 126.7, 111.7, 61.5, 60.7, 57.9, 50.1, 41.9, 32.4, 24.4, 14.4; IR (NaCl, $CHCl_3$) 3065, 2978, 2873, 2238, 1715, 1627, 1530, 1455, 1261 cm^{-1}; HRMS $[C_{26}H_{28}NO_5]^+$ calcd. 433.1889; found 433.1892 (ESI+).

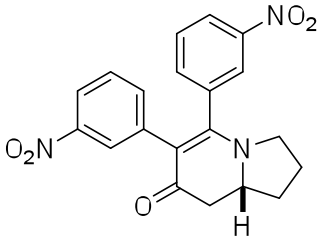


5,6-bis(3-thiophenyl)-2,3,8,8a-tetrahydroindolizin-7(1*H*)-one. (3k) The general procedure yielded an orange solid (94% yield). R_f = 0.30 (EtOAc); $[\alpha]_D^{20}$ = + 480 (c = 0.5, THF); HPLC analysis – Chiracel AD-H column 90:10 hexane:iPrOH, 1.0 ml/min, Major: 16.76 minutes, Minor: 17.93 minutes, 254 nm detection light, *ee* = 86%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19-7.12 (m 2H) 6.97-6.94 (m, 1H), 6.81 (d, 1H, *J* = 4.8 Hz), 6.77 (m, 1H), 6.63 (d, 1H, *J* = 4.8 Hz), 4.10 (dddd, 1H, *J* = 6.8,

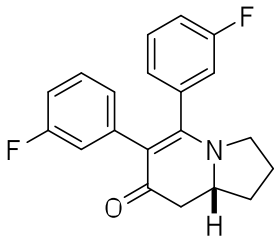
6.8, 6.8, 13.6 Hz), 3.55 (ddd, 1H, *J* = 7.2, 7.2, 12 Hz), 3.22 (ddd, 1H, *J* = 7.2, 7.2, 11.2 Hz), 2.67-2.54 (m, 2H), 2.36-2.28 (m, 1H), 2.04-1.71 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.2, 156.5 136.3 136.1 130.2 128.2, 127.1, 125.9, 123.1, 122.9, 107.46, 57.4, 50.5, 41.7, 32.0, 24.1; IR (NaCl, $CHCl_3$) 3093, 3964, 2877,1614, 1538, 1504, 1454, 1408, 1285, 770 cm^{-1}; HRMS $[C_{16}H_{16}NOS_2]^+$ calcd. 302.0668; found 302.0608 (ESI+).



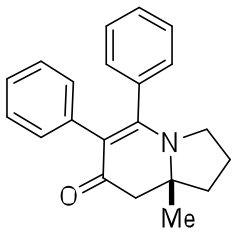
5,6-bis(2-thiophenyl)-2,3,8,8a-tetrahydroindolizin-7(1*H*)-one. (3l) The general procedure yielded an orange solid (91% yield). R_f = 0.30 (EtOAc); $[\alpha]_D^{20}$ = + 180 (c = 0.8, THF) HPLC analysis – Chiracel AS-H column 90:10 hexane:iPrOH, 1.0 ml/min, Major: 20.06 minutes, Minor: 24.84 minutes, 254 nm detection light, *ee* = 19%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, 1H, *J* = 5.2 Hz) 7.04 (d, 1H, *J* = 4.8 Hz), 6.99 (d, 1H, *J* = 3.2 Hz), 6.93 (t, 1H, *J* = 4 Hz), 6.73 (t, 1H, *J* = 4 Hz), 6.49 (d, 1H, *J* = 3.2 Hz), 4.14 (dddd, 1H, *J* = 6.4, 6.4, 6.4, 12.8 Hz), 3.70-3.65 (m, 1H), 3.31-3.28 (m, 1H), 2.69-2.55 (m, 2H), 2.34 (dddd, 1H, *J* = 6.8, 6.8, 6.8, 12.8 Hz), 2.05-1.75 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.1, 154.2, 138.2, 136.2, 130.3, 128.8, 127.1, 127.0, 125.8, 124.3, 113.6, 106.8, 57.3, 50.9, 41.9, 31.9, 24.5 IR (NaCl, $CHCl_3$) 3097, 2978, 2933, 2879, 1614, 1531, 1495, 1286 cm^{-1}; HRMS $[C_{16}H_{16}NOS_2]^+$ calcd. 302.0668; found 302.0594 (ESI+).



5,6-bis(3-nitrophenyl)-2,3,8,8a-tetrahydroindolizin-7(1*H*)-one.(3m) The general procedure yielded an orange solid (70% yield). R_f = 0.20 (EtOAc); $[\alpha]_D^{20}$ = + 353 (c = 1, THF); HPLC analysis – Chiracel AD-H column 80:20 hexane:iPrOH, 1.0 ml/min, Major: 18.6 minutes, Minor: 20.3 minutes, 254 nm detection light, *ee* = 86%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22-7.20 (m, 8H), 4.21 (m, 1H), 3.47-3.36 (m, 1H), 3.17-3.12 (m, 1H), 2.74-2.59 (m, 2H), 2.44-2.42 (m, 1H), 1.97-1.79 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.3, 158.3, 148.3, 136.6, 135.0, 132.2, 130.1, 128.6, 128.5, 126.9, 124.4, 124.0, 120.8, 120.7,111.1, 58.3, 50.3, 41.6, 32.4, 24.4; IR (NaCl, $CHCl_3$) 3081, 2963, 2925, 2873, 1628, 1578, 1532, 1451, 1348, 1310, 911 cm^{-1}; HRMS $[C_{20}H_{18}N3O5]^+$ calcd. 379.1168 Found 379.1170 (ESI+).

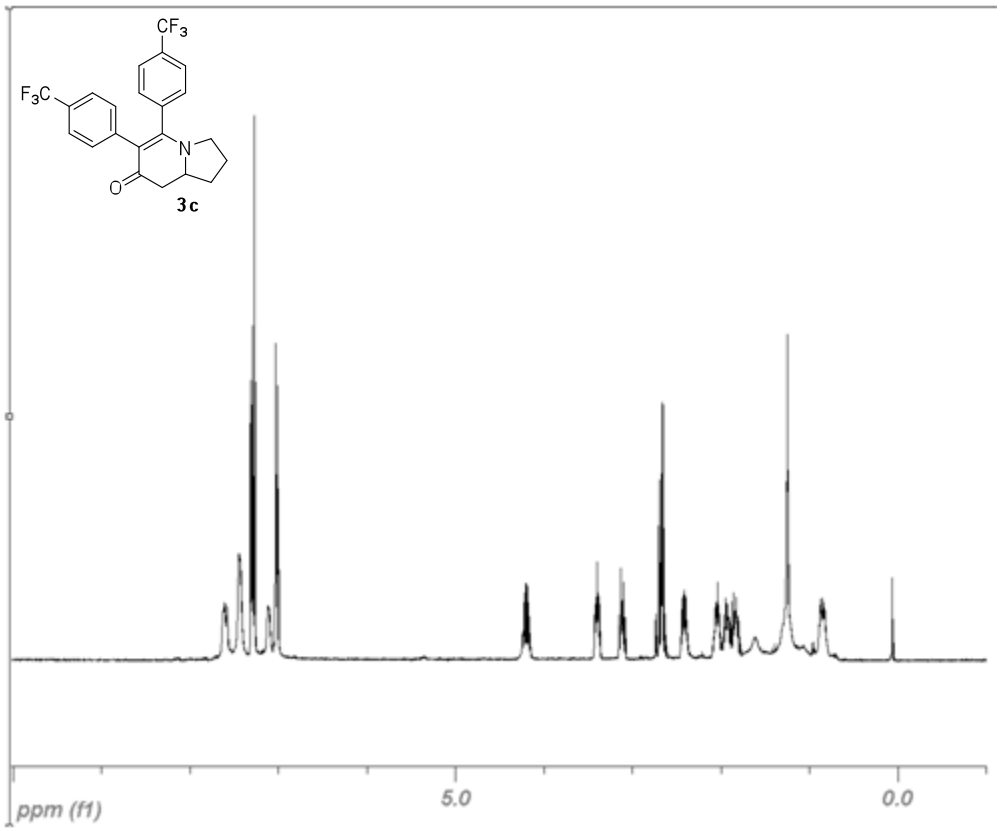


5,6-bis(3-fluorophenyl)-2,3,8,8a-tetrahydroindolizin-7(1*H*)-one.(3n) The general procedure yielded a yellow solid (80% yield). R_f = 0.30 (EtOAc); $[\alpha]_D^{20}$ = 535 (c = 0.85, THF); HPLC analysis – Chiracel AD-H column 80:20 hexane:iPrOH, 1.0 ml/min, Major: 7.56 minutes, Minor: 9.06 minutes, 254 nm detection light, *ee* = 93%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-6.80 (m, 6H), 6.82 (t, 1H, *J* = 6 Hz), 6.70 (t, 1H, *J* = 8.8 Hz), 4.10 (dddd, 1H, *J* = 6.8, 6.8, 6.8, 14 Hz), 3.38 (ddd, 1H, *J* = 4.4, 4.4, 7.6 Hz), 3.12 (ddd, 1H, *J* = 7.6, 7.6, 10.8 Hz), 2.67-2.53 (m, 2H), 2.38-2.30 (m, 1H), 2.03-1.72 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.9, 163.0 (d, $J_{C\text{-}F}$ = 249 Hz), 161 (d, $J_{C\text{-}F}$ = 246 Hz), 160.0, 133.6, 133.5, 132.4, 131.7, 131.3, 115.7, 114.5, 111.6, 57.7, 50.1, 41.9, 32.4, 24.4; IR (NaCl, $CHCl_3$) 2971, 2876, 1629, 1529, 1449, 1306, 1220 cm^{-1}; HRMS $[C_{20}H_{18}NOF_2]^+$ calcd. 326.1521 Found 326.1532 (ESI+).



5,6-diphenyl-8a-methyl-2,3,8,8a-tetrahydroindolizin-7(1*H*)-one (5a). The procedure for competition between isocyanates yielded a yellow solid (49% yield). R_f = 0.60 (EtOAc); $[\alpha]_D^{20}$ = 486 (c = 1.0, THF); HPLC analysis – Chiracel AD-H column 90:10 hexane:iPrOH, 1.0 ml/min, Major:

13.8 minutes, Minor: 13.2 minutes, 254 nm detection light, *ee* = 98%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.3-6.8 (m, 10H) 3.45 (m, 1H), 3.07 (m, 1H), 2.87 (d, 1H, *J* = 9 Hz), 2.49 (d, 1H, *J* = 9 Hz), 2.1-1.85 (m, 4H), 1.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.7, 159.6,136.7, 132.1, 131.9, 129.4, 129.2, 129.0, 128.2, 128.0, 127.4, 125.2, 111.6, 61.7, 50.8, 48.1, 40.2, 23.5, 22.0; (NaCl, $CHCl_3$) 3056, 2966, 2871, 1624, 1570, 1522, 1490, 1448, 1330, 1291, 697 cm^{-1}; HRMS $[C_{21}H_{22}NO]^+$ calcd. 304.1696 Found 304.1623 (ESI+).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F3C
N
O
3c
ppm (f1)
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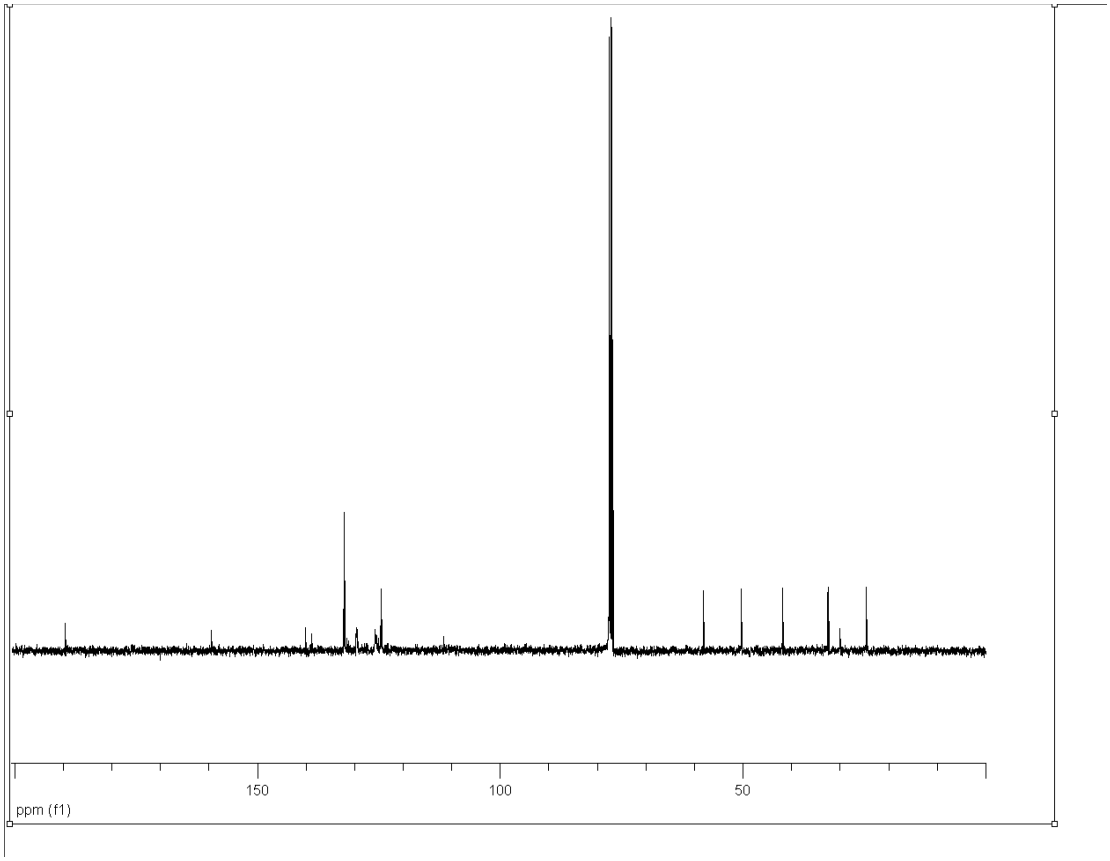
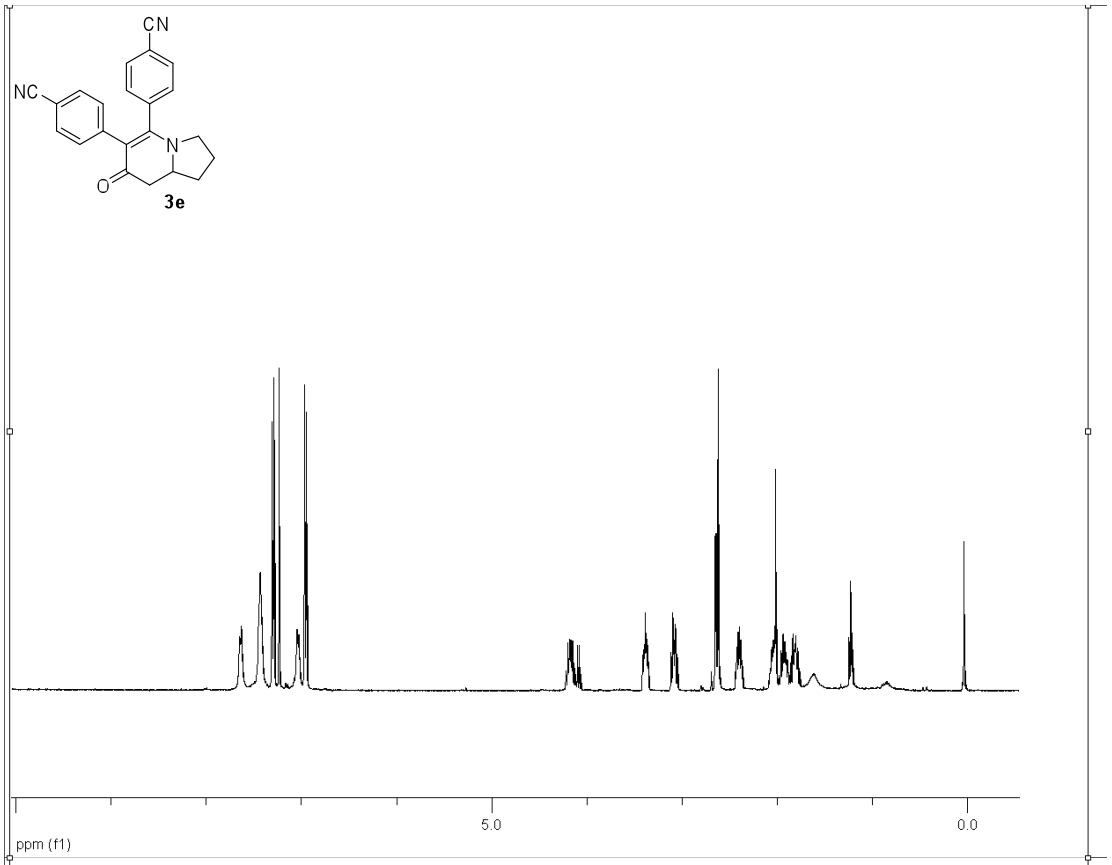
0.0


150
100
50
ppm (f1)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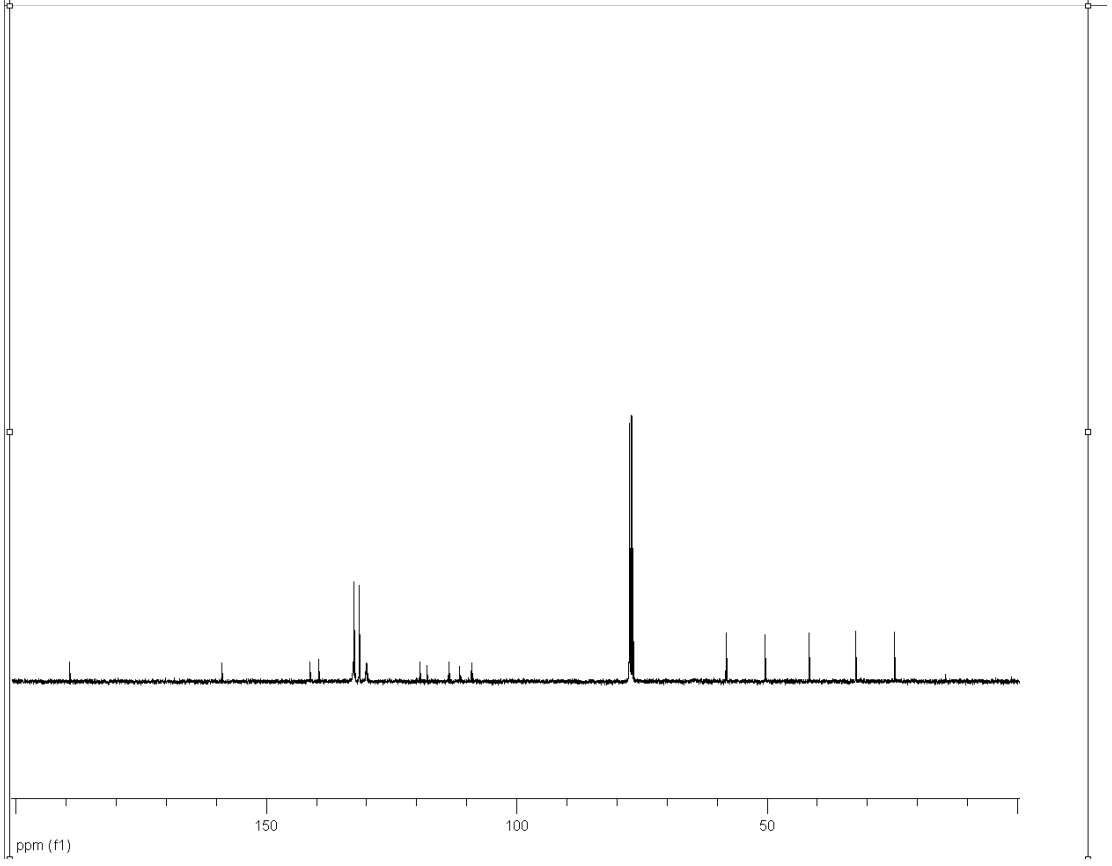
NC
N
O
3e
5.0
0.0
ppm (f1)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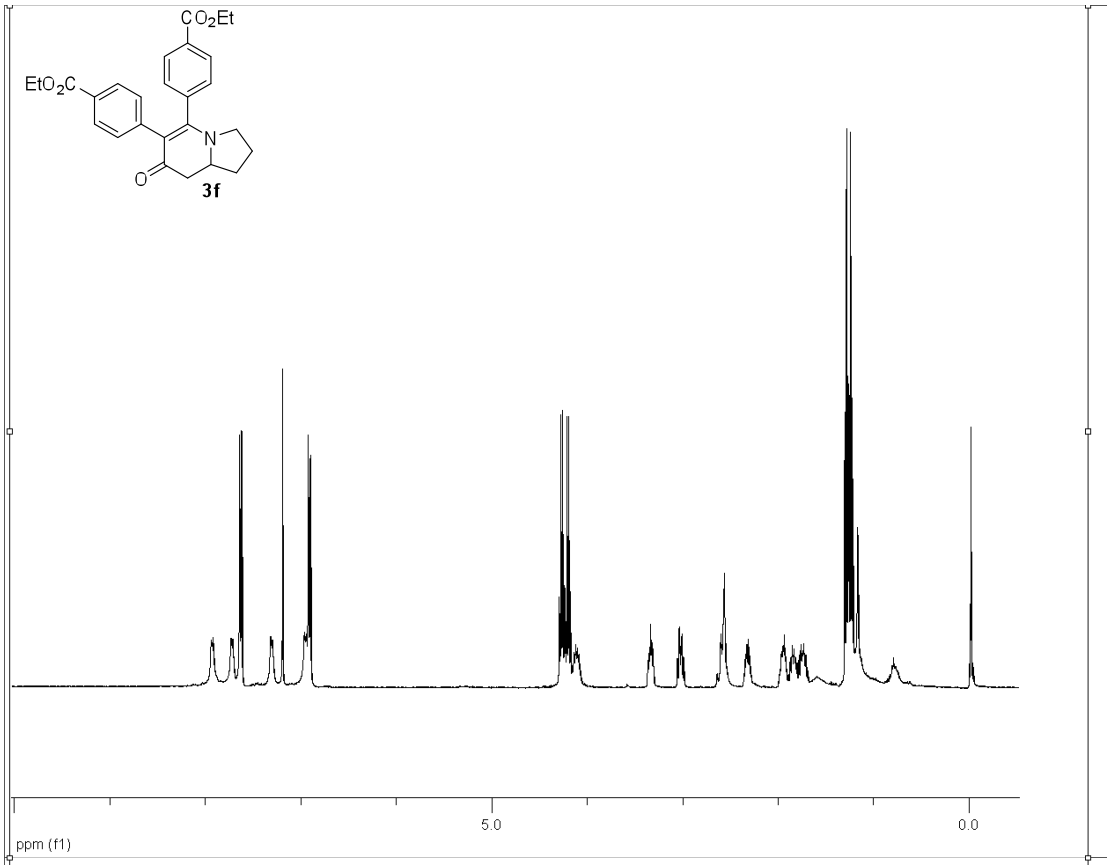
100
50
ppm (f1)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EtO2C
N
O
3f
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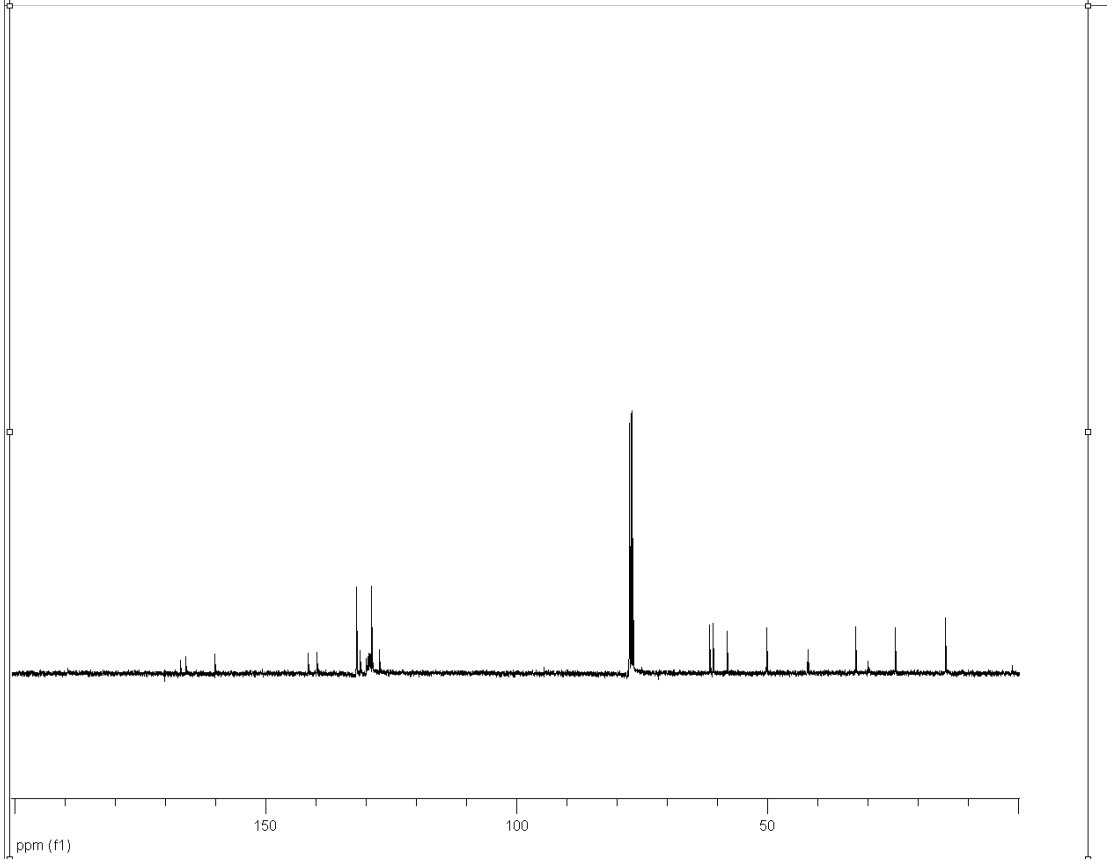
0.0
ppm (f1)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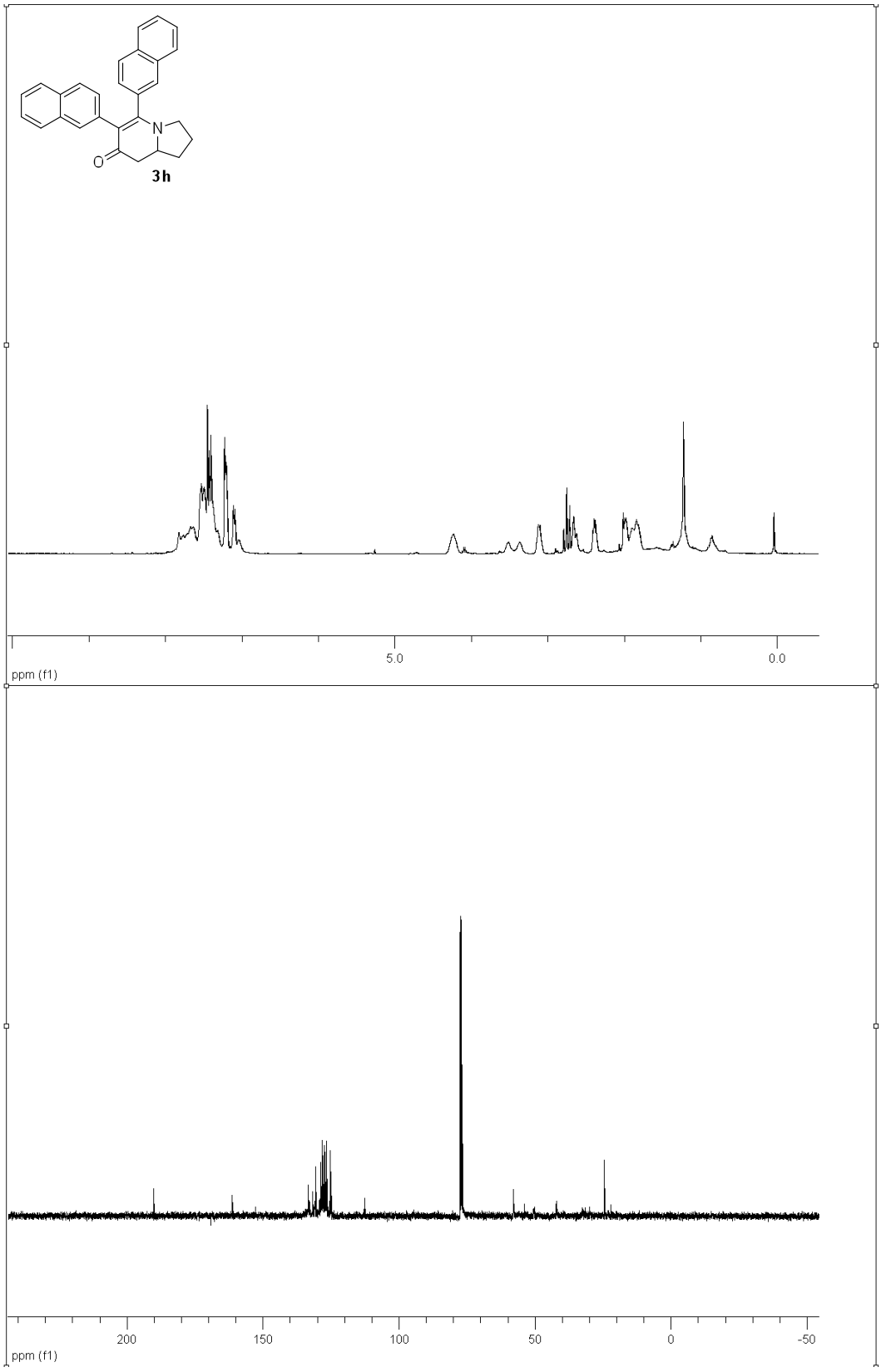
100
50
ppm (f1)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N
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150
100
50
0
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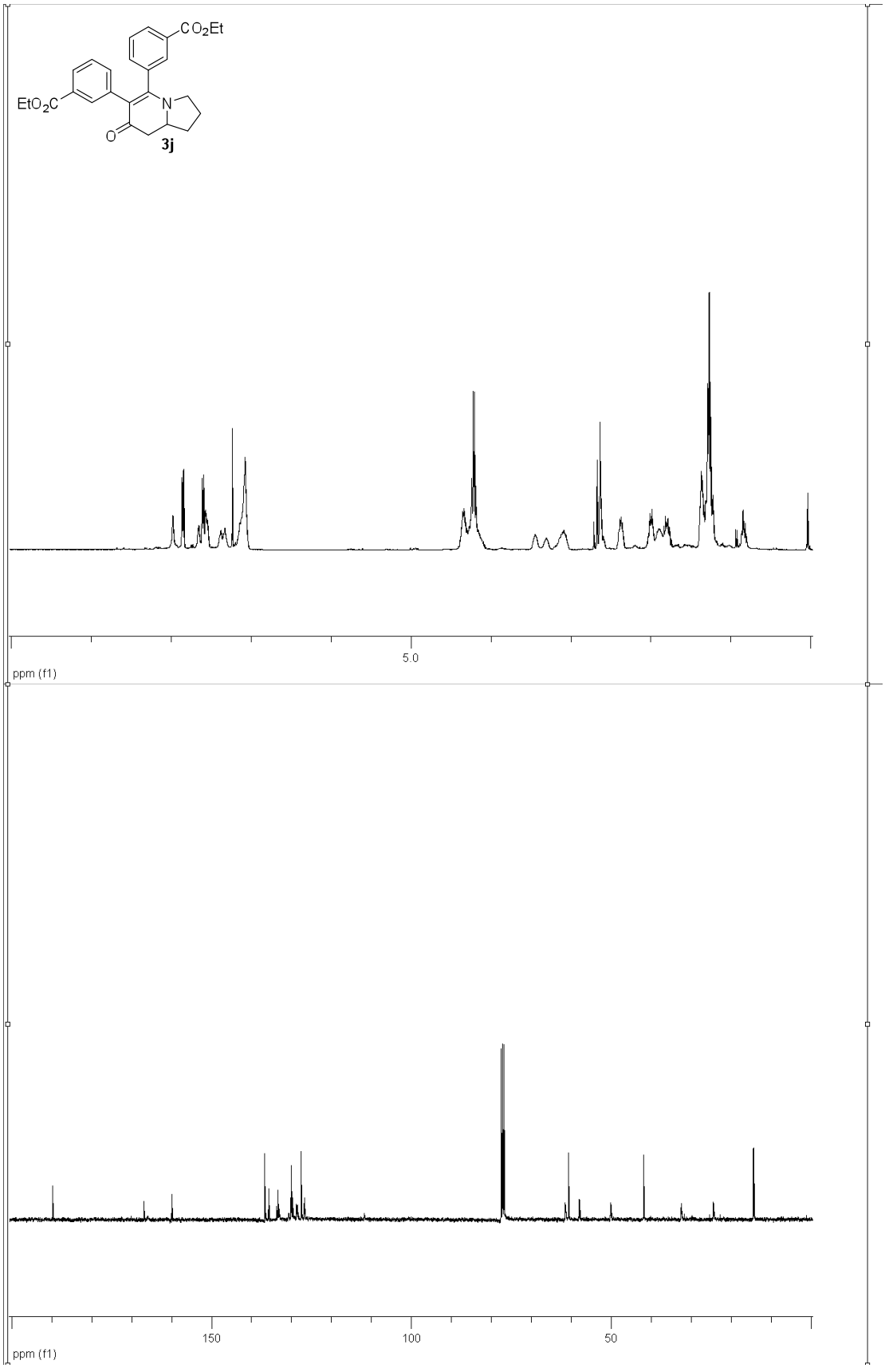
ppm (f1)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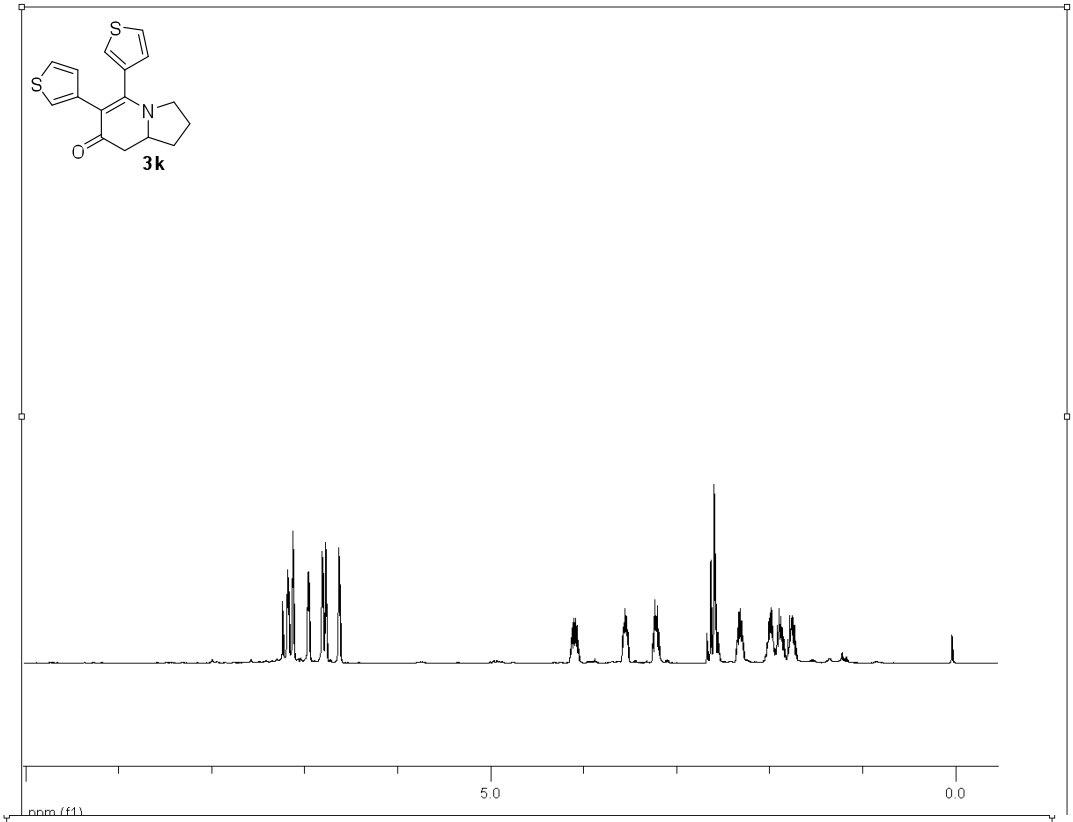
EtO2C
N
O
3j
5.0
ppm (f1)
150
100
50
ppm (f1)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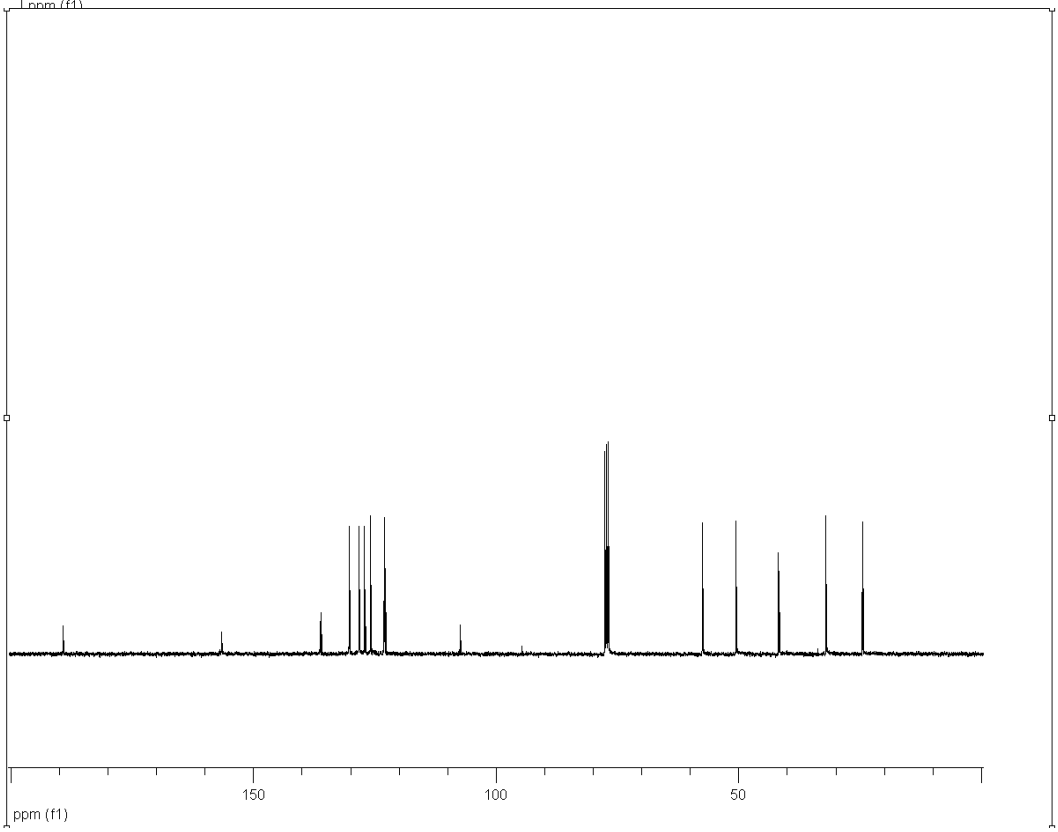
N
O
3k
5.0
0.0
ppm (f1)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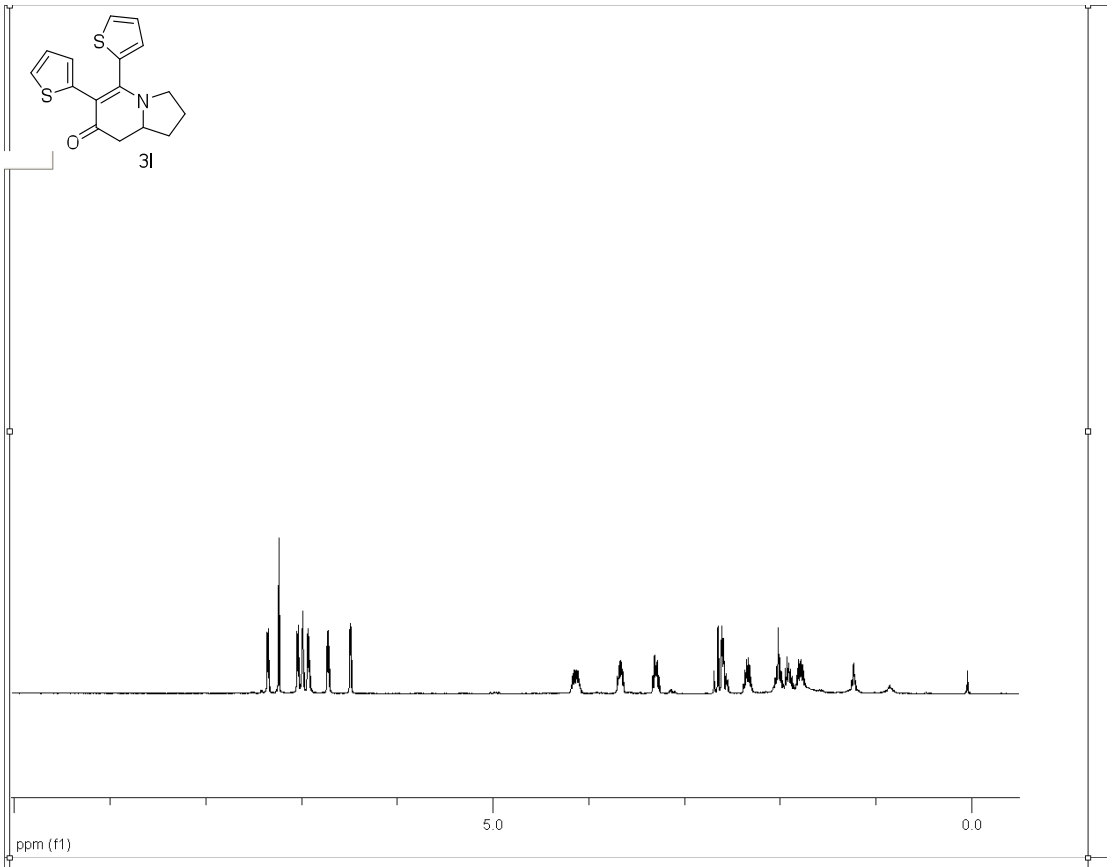
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N
O
3l
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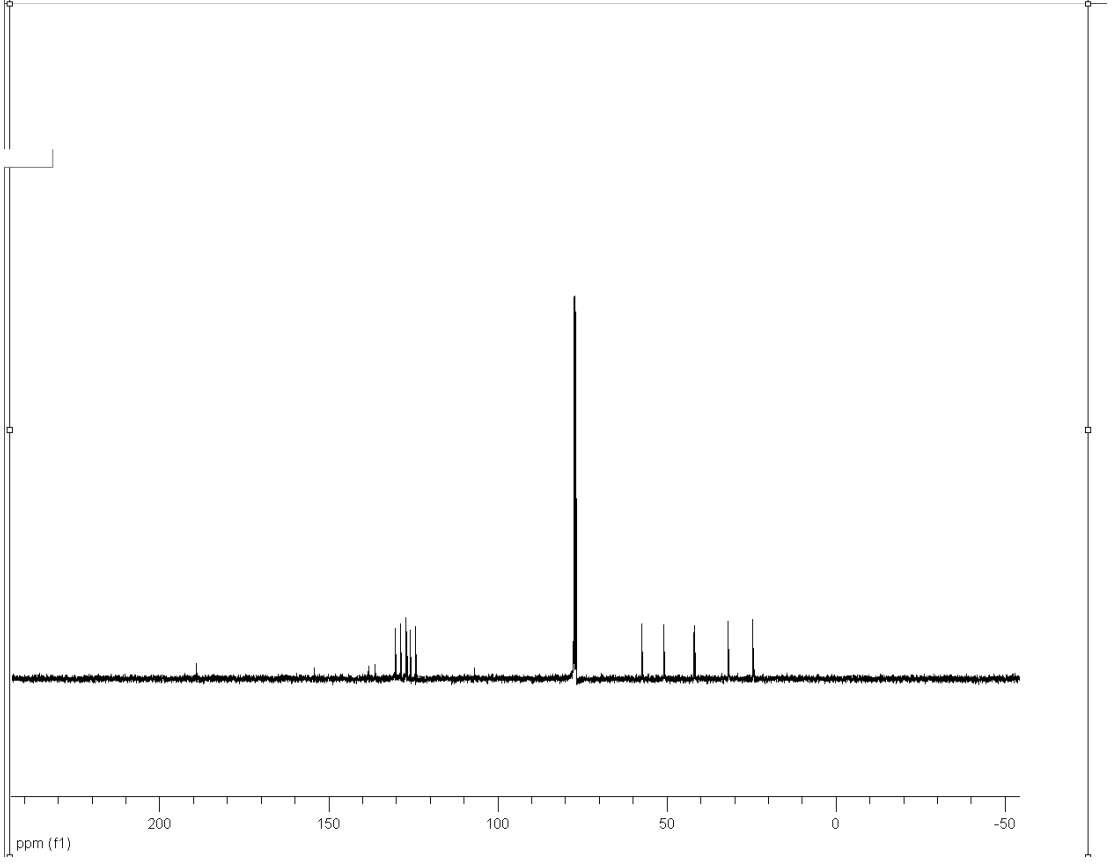
0.0
ppm (f1)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0
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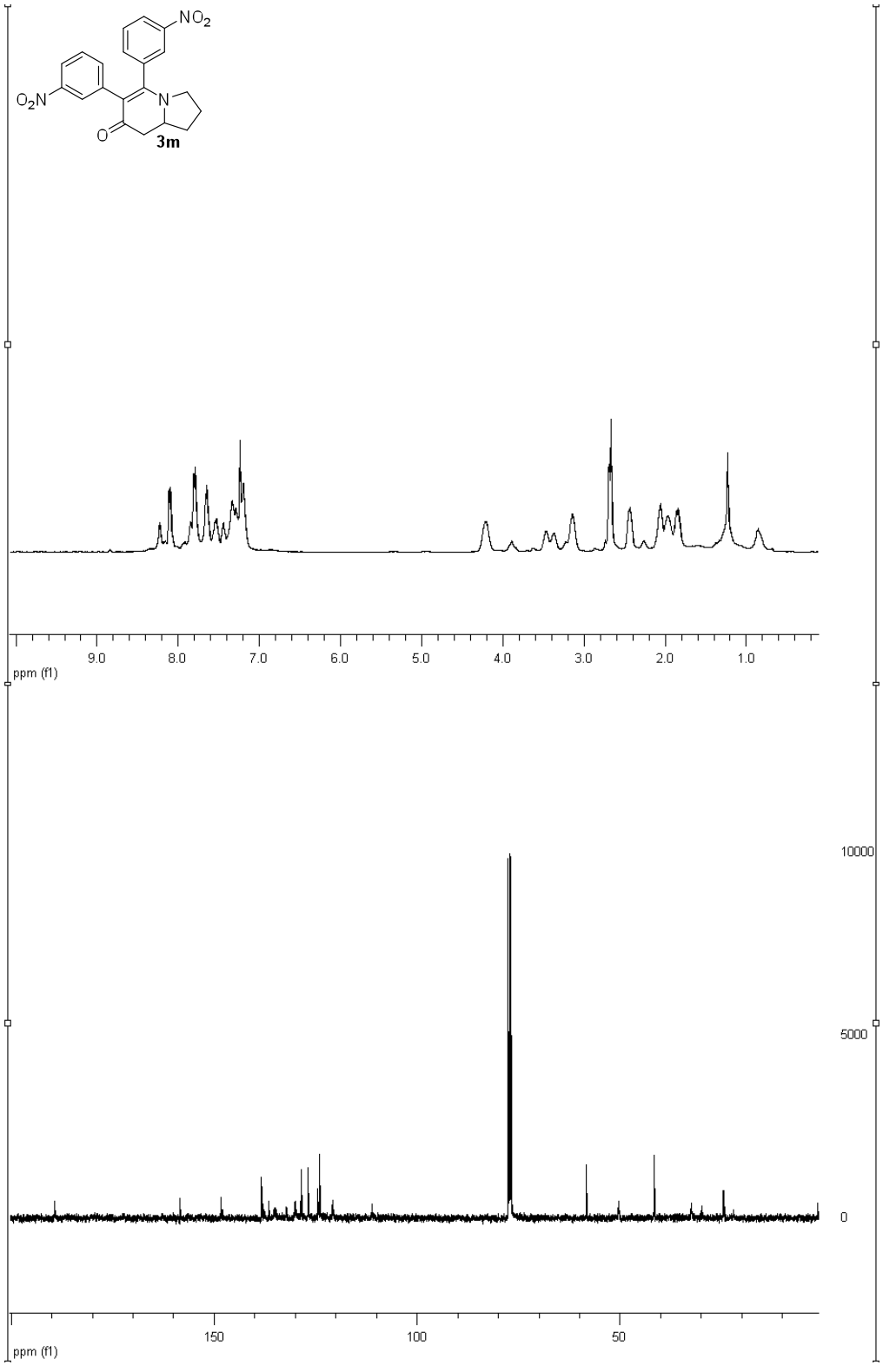
ppm (f1)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N
O
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8.0
7.0
6.0
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4.0
3.0
2.0
1.0
ppm (f1)
10000
5000
0
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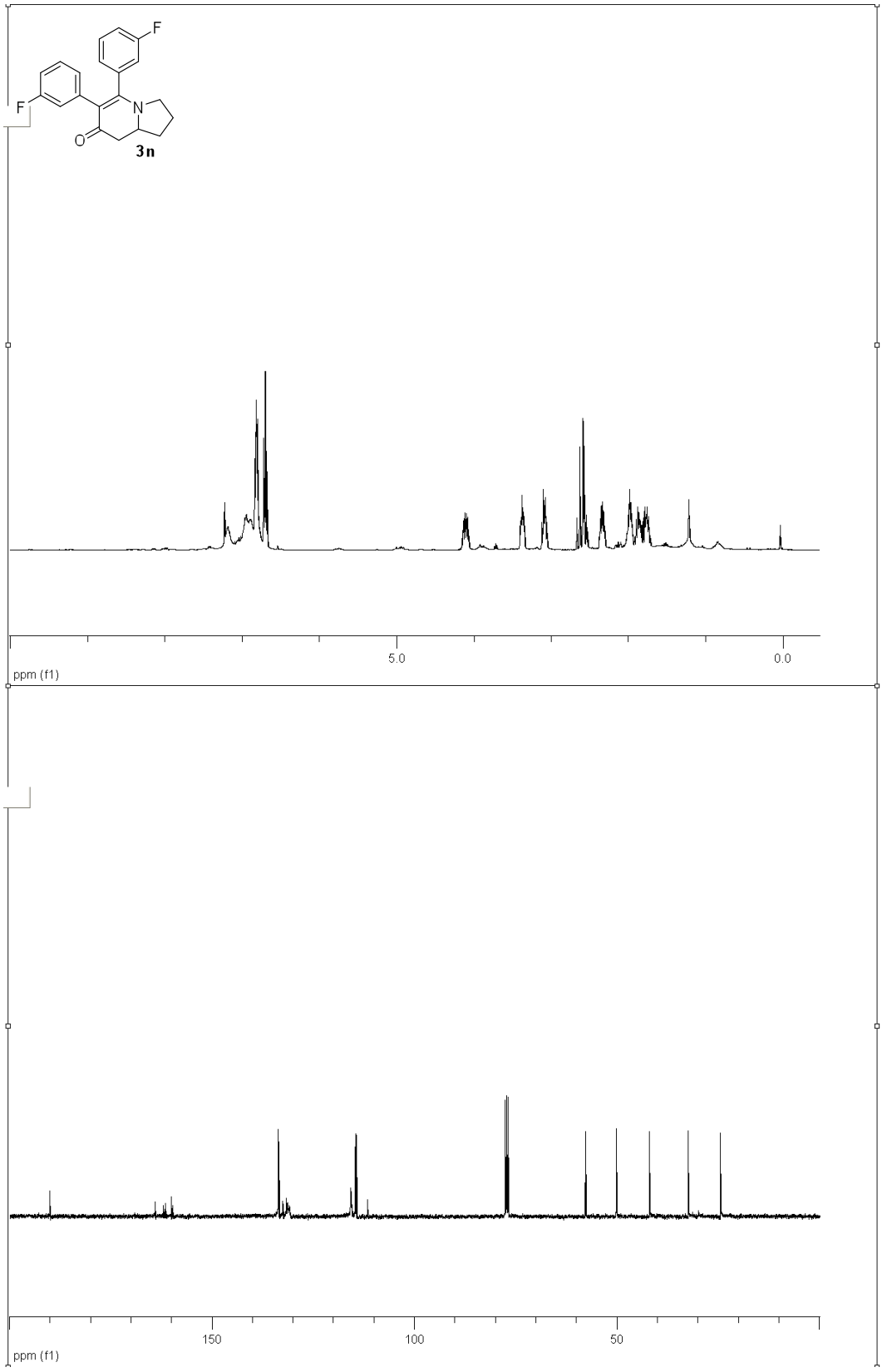
100
50
ppm (f1)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N
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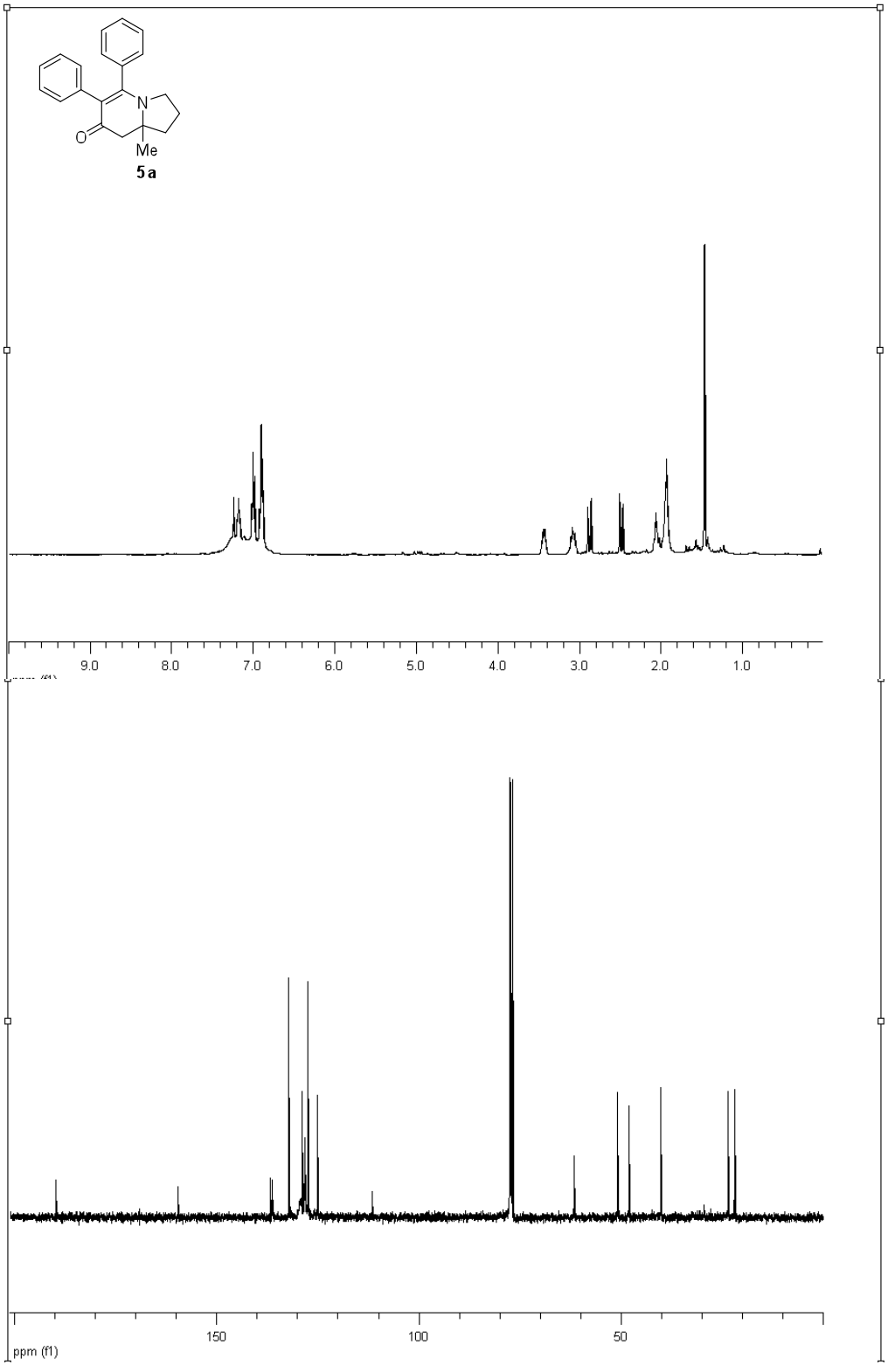
100
50
ppm (f1)



5a

X-ray Crystallographic Data

Table 1. Crystal data and structure refinement for **3d**.

Identification code	rovis51	
Empirical formula	C20 H17 Cl2 N O	
Formula weight	358.25	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	*a* = 12.5109(4) Å	α= 90°.
	b = 15.3410(5) Å	β= 90°.
	c = 17.9478(6) Å	γ = 90°.
Volume	3444.72(19) Å^3	
Z	8	
Density (calculated)	1.382 Mg/m^3	
Absorption coefficient	0.383 mm^{-1}	
F(000)	1488	
Crystal size	0.40 x 0.36 x 0.10 mm^3	
Theta range for data collection	1.75 to 33.21°.	
Index ranges	-15<=h<=19, -23<=k<=23, -27<=l<=27	
Reflections collected	30600	
Independent reflections	12520 [R(int) = 0.0490]	
Completeness to theta = 33.21°	99.5 %	
Absorption correction	None	
Max. and min. transmission	0.9627 and 0.8619	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12520 / 0 / 434	
Goodness-of-fit on F^2	1.013	
Final R indices [I>2sigma(I)]	R1 = 0.0501, wR2 = 0.1001	
R indices (all data)	R1 = 0.0897, wR2 = 0.1157	
Absolute structure parameter	0.00(4)	
Largest diff. peak and hole	0.440 and -0.284 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for rovis51. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	7426(2)	4014(1)	9078(1)	22(1)
C(2)	6930(2)	4828(1)	9055(1)	22(1)
C(3)	7564(2)	5654(1)	9025(1)	20(1)
C(4)	7489(2)	6220(1)	8420(1)	24(1)
C(5)	8067(2)	6985(1)	8406(1)	25(1)
C(6)	8797(2)	6648(1)	9614(1)	24(1)
C(7)	8701(2)	7198(1)	9006(1)	23(1)
C(8)	8232(2)	5868(1)	9620(1)	21(1)
C(9)	8960(2)	4305(1)	8224(1)	23(1)
C(10)	8565(2)	3920(1)	8876(1)	21(1)
C(11)	9278(2)	3416(1)	9297(1)	24(1)
C(12)	10338(2)	3317(1)	9083(1)	25(1)
C(13)	10690(2)	3714(1)	8437(1)	24(1)
C(14)	10010(2)	4206(1)	8002(1)	25(1)
C(15)	6822(2)	3256(1)	9324(1)	25(1)
C(16)	5159(2)	4145(2)	9077(1)	31(1)
C(17)	5651(2)	3411(2)	9506(1)	30(1)
C(18)	4125(2)	4502(2)	9409(2)	42(1)
C(19)	5255(2)	5741(2)	9180(1)	31(1)
C(20)	4105(2)	5428(2)	9130(2)	44(1)
C(21)	2533(2)	1276(1)	8764(1)	27(1)
C(22)	2268(2)	414(1)	8636(1)	25(1)
C(23)	3534(2)	1576(1)	8561(1)	25(1)
C(24)	4282(2)	1035(1)	8220(1)	21(1)
C(25)	3987(2)	161(1)	8094(1)	24(1)
C(26)	2987(2)	-152(1)	8305(1)	24(1)
C(27)	5328(2)	1382(1)	7971(1)	23(1)
C(28)	6293(2)	985(1)	8153(1)	21(1)
C(29)	7285(2)	1923(2)	7290(1)	34(1)
C(30)	6421(2)	2588(2)	7401(1)	36(1)
C(31)	5340(2)	2218(1)	7585(1)	30(1)

C(32)	8449(2)	2216(2)	7340(1)	39(1)
C(33)	9044(2)	1400(2)	7561(2)	45(1)
C(34)	8299(2)	985(2)	8137(2)	36(1)
C(35)	6352(2)	248(1)	8698(1)	19(1)
C(36)	6384(2)	429(1)	9455(1)	24(1)
C(37)	6379(2)	-611(1)	8457(1)	23(1)
C(38)	6459(2)	-250(1)	9969(1)	26(1)
C(39)	6445(2)	-1291(1)	8965(1)	24(1)
C(40)	6500(2)	-1096(1)	9713(1)	22(1)
Cl(1)	1004(1)	25(1)	8875(1)	37(1)
Cl(2)	9374(1)	8192(1)	9000(1)	35(1)
Cl(3)	6623(1)	-1950(1)	10348(1)	33(1)
Cl(4)	12026(1)	3599(1)	8170(1)	34(1)
N(1)	7233(2)	1238(1)	7871(1)	26(1)
N(2)	5866(2)	4921(1)	9069(1)	26(1)
O(1)	4535(2)	2645(1)	7442(1)	45(1)
O(2)	7205(2)	2526(1)	9412(1)	35(1)

Table 3. Bond lengths [Å] and angles [°] for rovis51.

C(1)-C(2)	1.396(3)	C(25)-C(26)	1.392(3)
C(1)-C(15)	1.454(3)	C(27)-C(28)	1.391(3)
C(1)-C(10)	1.478(3)	C(27)-C(31)	1.458(3)
C(2)-N(2)	1.339(3)	C(28)-N(1)	1.338(3)
C(2)-C(3)	1.495(3)	C(28)-C(35)	1.496(3)
C(3)-C(8)	1.394(3)	C(29)-N(1)	1.482(3)
C(3)-C(4)	1.395(3)	C(29)-C(30)	1.499(4)
C(4)-C(5)	1.378(3)	C(29)-C(32)	1.527(4)
C(5)-C(7)	1.377(3)	C(30)-C(31)	1.504(4)
C(6)-C(7)	1.384(3)	C(31)-O(1)	1.228(3)
C(6)-C(8)	1.390(3)	C(32)-C(33)	1.509(4)
C(7)-Cl(2)	1.742(2)	C(33)-C(34)	1.531(4)
C(9)-C(14)	1.381(3)	C(34)-N(1)	1.468(3)
C(9)-C(10)	1.401(3)	C(35)-C(37)	1.387(3)
C(10)-C(11)	1.401(3)	C(35)-C(36)	1.388(3)
C(11)-C(12)	1.389(3)	C(36)-C(38)	1.394(3)
C(12)-C(13)	1.381(3)	C(37)-C(39)	1.389(3)
C(13)-C(14)	1.380(3)	C(38)-C(40)	1.377(3)
C(13)-Cl(4)	1.748(2)	C(39)-C(40)	1.377(3)
C(15)-O(2)	1.229(3)	C(40)-Cl(3)	1.743(2)
C(15)-C(17)	1.520(4)		
C(16)-N(2)	1.482(3)	C(2)-C(1)-C(15)	119.6(2)
C(16)-C(17)	1.497(3)	C(2)-C(1)-C(10)	120.60(18)
C(16)-C(18)	1.526(4)	C(15)-C(1)-C(10)	119.82(18)
C(18)-C(20)	1.506(4)	N(2)-C(2)-C(1)	122.46(19)
C(19)-N(2)	1.486(3)	N(2)-C(2)-C(3)	115.97(18)
C(19)-C(20)	1.520(4)	C(1)-C(2)-C(3)	121.6(2)
C(21)-C(22)	1.383(3)	C(8)-C(3)-C(4)	119.30(19)
C(21)-C(23)	1.384(3)	C(8)-C(3)-C(2)	119.39(18)
C(22)-C(26)	1.384(3)	C(4)-C(3)-C(2)	121.30(19)
C(22)-Cl(1)	1.743(2)	C(5)-C(4)-C(3)	120.6(2)
C(23)-C(24)	1.392(3)	C(7)-C(5)-C(4)	119.37(19)
C(24)-C(25)	1.409(3)	C(7)-C(6)-C(8)	119.1(2)
C(24)-C(27)	1.482(3)	C(5)-C(7)-C(6)	121.43(19)

C(5)-C(7)-Cl(2)	118.77(16)	C(28)-C(27)-C(31)	119.2(2)
C(6)-C(7)-Cl(2)	119.78(17)	C(28)-C(27)-C(24)	122.52(18)
C(6)-C(8)-C(3)	120.15(19)	C(31)-C(27)-C(24)	118.0(2)
C(14)-C(9)-C(10)	122.0(2)	N(1)-C(28)-C(27)	123.15(18)
C(9)-C(10)-C(11)	117.3(2)	N(1)-C(28)-C(35)	115.04(19)
C(9)-C(10)-C(1)	120.24(19)	C(27)-C(28)-C(35)	121.79(19)
C(11)-C(10)-C(1)	122.40(19)	N(1)-C(29)-C(30)	110.9(2)
C(12)-C(11)-C(10)	121.2(2)	N(1)-C(29)-C(32)	102.0(2)
C(13)-C(12)-C(11)	119.3(2)	C(30)-C(29)-C(32)	118.6(2)
C(14)-C(13)-C(12)	121.3(2)	C(29)-C(30)-C(31)	114.86(19)
C(14)-C(13)-Cl(4)	119.34(18)	O(1)-C(31)-C(27)	124.0(2)
C(12)-C(13)-Cl(4)	119.40(18)	O(1)-C(31)-C(30)	119.4(2)
C(13)-C(14)-C(9)	118.9(2)	C(27)-C(31)-C(30)	116.5(2)
O(2)-C(15)-C(1)	124.4(2)	C(33)-C(32)-C(29)	104.0(2)
O(2)-C(15)-C(17)	119.3(2)	C(32)-C(33)-C(34)	102.8(2)
C(1)-C(15)-C(17)	116.19(19)	N(1)-C(34)-C(33)	102.9(2)
N(2)-C(16)-C(17)	111.38(19)	C(37)-C(35)-C(36)	119.64(18)
N(2)-C(16)-C(18)	102.79(19)	C(37)-C(35)-C(28)	120.96(18)
C(17)-C(16)-C(18)	114.7(2)	C(36)-C(35)-C(28)	119.41(17)
C(16)-C(17)-C(15)	113.75(19)	C(35)-C(36)-C(38)	120.06(18)
C(20)-C(18)-C(16)	102.9(2)	C(35)-C(37)-C(39)	120.66(19)
N(2)-C(19)-C(20)	102.14(19)	C(40)-C(38)-C(36)	119.04(19)
C(18)-C(20)-C(19)	105.2(2)	C(40)-C(39)-C(37)	118.70(18)
C(22)-C(21)-C(23)	119.4(2)	C(38)-C(40)-C(39)	121.88(19)
C(21)-C(22)-C(26)	121.0(2)	C(38)-C(40)-Cl(3)	119.53(16)
C(21)-C(22)-Cl(1)	120.25(18)	C(39)-C(40)-Cl(3)	118.59(15)
C(26)-C(22)-Cl(1)	118.77(17)	C(28)-N(1)-C(34)	126.75(18)
C(21)-C(23)-C(24)	121.70(19)	C(28)-N(1)-C(29)	120.7(2)
C(23)-C(24)-C(25)	117.5(2)	C(34)-N(1)-C(29)	112.1(2)
C(23)-C(24)-C(27)	120.71(18)	C(2)-N(2)-C(16)	120.50(18)
C(25)-C(24)-C(27)	121.7(2)	C(2)-N(2)-C(19)	127.12(18)
C(26)-C(25)-C(24)	121.3(2)	C(16)-N(2)-C(19)	111.85(18)
C(22)-C(26)-C(25)	119.04(19)		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for rovis51. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

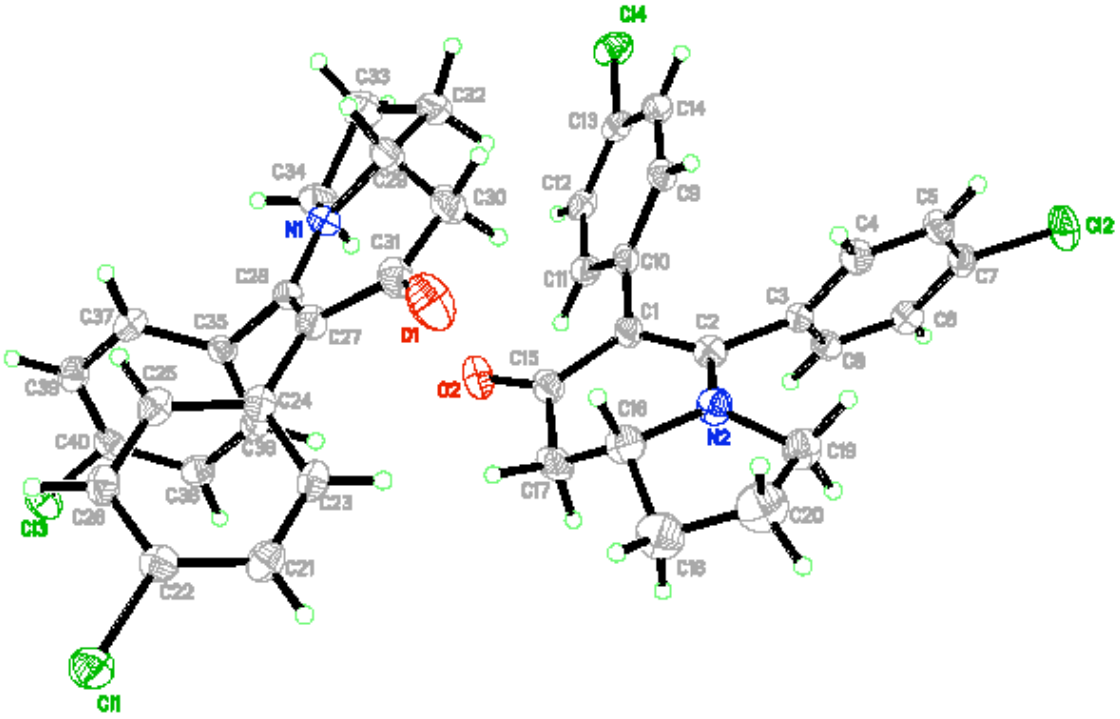
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	26(1)	19(1)	20(1)	-2(1)	-1(1)	-3(1)
C(2)	22(1)	24(1)	18(1)	0(1)	-4(1)	-2(1)
C(3)	21(1)	19(1)	21(1)	0(1)	1(1)	1(1)
C(4)	28(1)	24(1)	21(1)	0(1)	-4(1)	0(1)
C(5)	28(1)	22(1)	26(1)	6(1)	1(1)	2(1)
C(6)	19(1)	26(1)	26(1)	-3(1)	-3(1)	0(1)
C(7)	18(1)	18(1)	34(1)	-1(1)	5(1)	-1(1)
C(8)	21(1)	23(1)	19(1)	2(1)	-1(1)	0(1)
C(9)	28(1)	20(1)	20(1)	2(1)	-4(1)	-1(1)
C(10)	26(1)	16(1)	19(1)	-1(1)	-3(1)	-2(1)
C(11)	33(1)	22(1)	19(1)	0(1)	-1(1)	2(1)
C(12)	31(1)	23(1)	21(1)	-3(1)	-3(1)	6(1)
C(13)	24(1)	24(1)	25(1)	-7(1)	0(1)	1(1)
C(14)	31(1)	24(1)	20(1)	-2(1)	1(1)	-2(1)
C(15)	31(1)	24(1)	20(1)	-1(1)	-2(1)	-7(1)
C(16)	25(1)	36(1)	31(1)	-6(1)	-2(1)	-6(1)
C(17)	29(1)	33(1)	28(1)	-1(1)	2(1)	-13(1)
C(18)	26(2)	48(2)	53(2)	-2(1)	-2(1)	-5(1)
C(19)	26(1)	30(1)	37(1)	1(1)	-2(1)	4(1)
C(20)	25(2)	51(2)	56(2)	2(1)	-4(1)	7(1)
C(21)	27(1)	28(1)	27(1)	-6(1)	-4(1)	4(1)
C(22)	24(1)	29(1)	20(1)	0(1)	-3(1)	-2(1)
C(23)	29(1)	19(1)	26(1)	-2(1)	-5(1)	3(1)
C(24)	26(1)	20(1)	18(1)	2(1)	-6(1)	2(1)
C(25)	26(1)	22(1)	23(1)	0(1)	-4(1)	6(1)
C(26)	29(1)	19(1)	26(1)	1(1)	-5(1)	1(1)
C(27)	30(1)	20(1)	18(1)	3(1)	-3(1)	0(1)
C(28)	25(1)	20(1)	16(1)	-1(1)	2(1)	-2(1)
C(29)	48(2)	30(1)	24(1)	-1(1)	6(1)	-15(1)
C(30)	55(2)	27(1)	25(1)	6(1)	1(1)	-9(1)
C(31)	44(2)	25(1)	22(1)	5(1)	-6(1)	-4(1)

C(32)	48(2)	37(1)	33(1)	-8(1)	16(1)	-19(1)
C(33)	38(2)	44(1)	52(2)	-7(1)	19(1)	-12(1)
C(34)	24(1)	39(1)	44(1)	1(1)	11(1)	-2(1)
C(35)	17(1)	18(1)	21(1)	1(1)	3(1)	1(1)
C(36)	31(1)	21(1)	21(1)	-2(1)	1(1)	0(1)
C(37)	25(1)	25(1)	21(1)	-4(1)	-1(1)	5(1)
C(38)	32(1)	27(1)	20(1)	-1(1)	0(1)	-2(1)
C(39)	23(1)	20(1)	30(1)	-2(1)	-2(1)	4(1)
C(40)	15(1)	23(1)	28(1)	6(1)	1(1)	1(1)
Cl(1)	30(1)	42(1)	38(1)	-8(1)	6(1)	-7(1)
Cl(2)	30(1)	23(1)	52(1)	3(1)	-4(1)	-7(1)
Cl(3)	33(1)	29(1)	36(1)	13(1)	-4(1)	0(1)
Cl(4)	26(1)	44(1)	34(1)	-9(1)	1(1)	0(1)
N(1)	29(1)	24(1)	24(1)	1(1)	7(1)	-4(1)
N(2)	22(1)	26(1)	31(1)	-2(1)	-2(1)	-2(1)
O(1)	48(1)	38(1)	49(1)	23(1)	-12(1)	4(1)
O(2)	41(1)	21(1)	42(1)	4(1)	-2(1)	-6(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for rovis51.

	x	y	z	U(eq)
H(4)	7044	6081	8022	29
H(5)	8029	7353	7995	30
H(6)	9234	6798	10012	29
H(8)	8299	5489	10021	25
H(9)	8501	4637	7931	27
H(11)	9037	3143	9728	29
H(12)	10805	2987	9370	30
H(14)	10255	4467	7567	30
H(16)	5026	3955	8564	37
H(17A)	5254	2881	9404	36
H(17B)	5586	3533	10035	36
H(18A)	3510	4178	9233	51
H(18B)	4142	4483	9949	51
H(19A)	5415	6164	8794	37
H(19B)	5405	5997	9663	37
H(20A)	3641	5785	9437	53
H(20B)	3852	5450	8619	53
H(21)	2043	1651	8986	33
H(23)	3712	2155	8653	29
H(25)	4470	-215	7866	28
H(26)	2805	-732	8225	29
H(29)	7175	1646	6804	41
H(30A)	6360	2933	6951	43
H(30B)	6636	2977	7800	43
H(32A)	8700	2433	6864	47
H(32B)	8536	2668	7713	47
H(33A)	9733	1538	7778	54
H(33B)	9148	1017	7137	54
H(34A)	8378	356	8146	43
H(34B)	8435	1213	8632	43

H(36)	6356	1003	9620	29
H(37)	6352	-732	7949	28
H(38)	6481	-134	10477	32
H(39)	6452	-1867	8804	29



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