Superbase Promoted Synthesis of Dienamides as Useful Intermediates for the Synthesis of α-Ketoamides, γ-Lactams and Cyclic Iminoethers

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Materials and methods

All solvent were degassed before use in cross-coupling processes. Chromatographic separations were carried out under pressure on Merck silica gel 60 pretreated with Et_3N (1%) using flash-column techniques. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm silica gel coated aluminum plates (60 Merck F254) using UV light (254 nm) as visualizing agent and aqueous $KMnO_4$ or *p*-anisaldehyde ethanolic solution and heat as developing agents. All reactions involving air-sensitive reagents were performed under nitrogen in oven-dried glassware using syringe-septum cap technique. Anhydrous THF was freshly distilled under argon from Na/benzophenone ketyl prior to use. *n*BuLi (1.6 M solution in hexanes) was purchased from Aldrich. Potassium *tert*-butoxide was sublimed in vacuo (5.0 mmHg) prior to the reaction. Acetals **1** were purchased from Aldrich or synthesized from the corresponding aldehydes as previously reported.[1] Isocyanates were purchased from Aldrich and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature at 200 MHz and 50.2 MHz respectively and calibrated using residual undeuterated solvent as an internal reference. The solvent was $CDCl_3$ with a calibration at 7.26 ppm for ^{1}H spectra and 77.16 ppm for ^{13}C spectra. Chemical shifts (δ) are given in parts per million (ppm) and the coupling constants (*J*) in Hertz (Hz). The following abbreviations were used to designate the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, qt = quintet, m = multiplet, br = broad. The known products were characterized by comparing the ^{1}H NMR, ^{13}C NMR and melting points data with those reported in the literature. MS spectra were recorded at an ionizing voltage of 70 eV.

[1] J. Kang, G. J. Lim, S. K. Yoon, M. Y. Kim, *J. Org. Chem.*, 1995, **60**, 564-577.

General procedures

General procedure for the syntheses of pentadienamides 2. A solution of freshly sublimated *t*BuOK (5 mmol, 560 mg, 2.5 equiv.) in THF (7 mL) was cooled to –78 °C. 1,1-Diethoxybut-2-ene (2 mmol, 288 mg) in THF (2 mL) and *n*BuLi (1.6 M in hexanes, 5 mmol, 3.13 mL) were added in quick succession and the mixture was stirred for 2 h during which time the temperature was raised to –40 °C. Afterwards the reaction was cooled back to –78 °C and the appropriate isocyanate (2.2 mmol) in THF (2 mL) was added. After stirring the mixture at –78 °C for 2 h, a saturated NH_4Cl solution (10 mL) was added. The resulting mixture was extracted with Et_2O (3 x 10 mL), washed with water (10 mL) and brine (2 x 10 mL), and dried with anhydrous K_2CO_3. After filtration and evaporation of the solvent, the crude products were purified by flash column chromatography.

General procedure for the syntheses of α-ketoamides derivatives 3. A solution of the appropriate pentadienamide (0.5 mmol) in CH_2Cl_2/MeOH (3 mL) was stirred in the presence of *p*-toluenesulfonic acid monohydrate (0.5 mmol, 95 mg, 1 equiv.) and the reaction progress monitored by TLC. After 0.5 h the reaction was complete, the reaction was quenched with water. After extraction with CH_2Cl_2 (3 x 10 mL), the collected organic layers were washed with water (10 mL) and brine (2 x 10 mL), and dried with anhydrous K_2CO_3. After filtration and evaporation of the solvent, the crude products were purified by column flash chromatography.

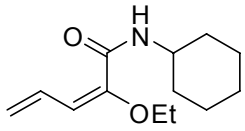
General procedure for the syntheses of *N*-aryl pyrrolidinones 4 and cyclic iminoethers 5. A 20-mL sealed tube fitted with a rubber septum cap and connected to a nitrogen filled balloon was charged with the appropriate pentadienamide (0.5 mmol) and cooled to 0°C. Then TFA (5 ml) was added dropwise, and the resulting mixture was stirred for 1 h. Afterwards the reaction was cooled back to 0 °C and a solution of NaOH (10%) was added, and the resulting mixture was extracted with several portions of Et_2O. The combined organic layers were washed twice with $NaHCO_3$, water and brine, and dried over anhydrous K_2CO_3. After filtration and evaporation of the solvent, the crude products were purified by column flash chromatography.

Experimental data

Spectroscopic data for pentadienamides **2**

(*E*)-*N*-cyclohexyl-2-ethoxypenta-2,4-dienamide **2a**.

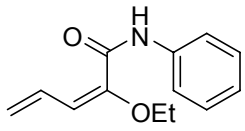
Purified by flash chromatography (Et_2O:petroleum ether 3:7, 1% Et_3N, R_f 0.45) to give **2a** as a colorless oil (356 mg, 79%).



^{1}H NMR (200 MHz, $CDCl_3$). δ ppm 7.69 (dt, *J* = 17.2, 10.7 Hz, 1H), 6.53 (br, 1H), 5.68 (d, *J* = 10.7 Hz, 1H), 5.19 (d, *J* = 17.2 Hz, 1H), 5.08 (d, *J* = 10.7 Hz, 1H), 3.83 (q, *J* = 6.9 Hz, 2H) superimposed to 3.92-3.78 (m, 1H), 2.00-1.82 (m, 2H), 1.79-1.54 (m, 4H), 1.36 (t, *J* = 6.9 Hz, 3H) superimposed to 1.27-1.07 (m, 4H). ^{13}C NMR (50.2 MHz, $CDCl_3$). δ 162.0 (s), 145.9 (s), 132.4 (d), 117.6 (t), 111.9 (d), 63.5 (t), 47.4 (d), 32.7 (t), 25.3 (t), 24.6 (t), 14.3 (q). MS *m/z* 223 (M^+, 26), 193 (100), 111 (98), 67 (50), 55 (39). Anal. Calcd for $C_{13}H_{21}NO_2$: C, 69.92; H, 9.48. Found C, 69.84; H, 9.29.

(*E*)-2-ethoxy-*N*-phenylpenta-2,4-dienamide **2b**.

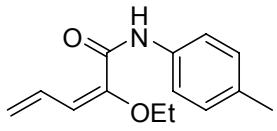
Purified by flash chromatography (CH_2Cl_2, 1% Et_3N, R_f 0.70) to give **2b** as a yellow oil (323 mg, 74%).



^{1}H NMR (200 MHz, $CDCl_3$). δ ppm 8.44 (br, 1H), 7.76 (dt, *J* = 17.2, 10.6 Hz, 1H), 7.66-7.56 (m, 2H), 7.41-7.30 (m, 2H), 7.20-7.06 (m, 1H), 5.84 (d, *J* = 10.6 Hz, 1H), 5.29 (d, *J* = 17.2 Hz, 1H), 5.20 (d, *J* = 10.6 Hz, 1H), 3.94 (q, *J* = 6.9 Hz, 2H), 1.45 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (50.2 MHz, $CDCl_3$). δ 160.8 (s), 145.3 (s), 137.2 (s), 132.1 (d), 128.8 (d), 124.2 (d), 119.9 (d), 118.9 (t), 113.4 (d), 63.9 (t), 14.5 (q). MS *m/z* 217 (M^+, 27), 188 (100), 120 (31), 77 (42), 55 (57). Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96. Found C, 71.44; H, 6.84.

(*E*)-2-ethoxy-*N*-*p*-tolylpenta-2,4-dienamide **2c**.

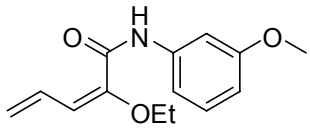
Purified by flash chromatography (Et_2O:petroleum ether 1:1, 1% Et_3N, R_f 0.50) to give **2c** as a yellow oil (328 mg, 71%).



^{1}H NMR (200 MHz, $CDCl_3$). δ ppm 8.40 (s, 1H), 7.78 (dt, *J* = 17.4, 10.3 Hz, 1H), 7.58-7.41 (m, 2H), 7.28-7.06 (m, 2H), 5.81 (d, *J* = 10.3 Hz, 1H), 5.28 (d, *J* = 17.4 Hz, 1H), 5.18 (d, *J* = 10.3 Hz, 1H), 3.91 (q, *J* = 6.9 Hz, 2H), 2.33 (s, 3H), 1.43 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (50.2 MHz, $CDCl_3$). δ 160.7 (s), 145.5 (s), 134.7 (s), 133.8 (s), 132.2 (d), 129.3 (d), 119.9 (d), 118.6 (t), 113.2 (d), 63.9 (t), 20.7 (q), 14.4 (q). MS *m/z* 231 (M^+, 44), 202 (100), 135 (37), 77 (53), 55 (39). Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41. Found C, 72.64; H, 6.99.

(*E*)-2-ethoxy-*N*-(3-methoxyphenyl)penta-2,4-dienamide **2d**.

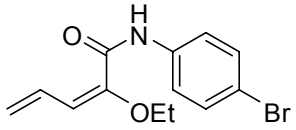
Purified by flash chromatography (CH_2Cl_2:petroleum ether 9:1, 1% Et_3N, R_f 0.50) to give **2d** as an orange oil (380 mg, 77%).



^{1}H NMR (200 MHz, $CDCl_3$). δ ppm 8.34 (br, 1H), 7.63 (dt, *J* = 17.0, 10.5 Hz, 1H), 7.33-7.26 (m, 1H), 7.18-7.04 (m, 1H), 6.99-6.91 (m, 1H), 6.60-6.53 (m, 1H), 5.70 (d, *J* = 10.5 Hz, 1H), 5.18 (d, *J* = 17.0 Hz, 1H), 5.07 (d, *J* = 10.5 Hz, 1H), 3.79 (q, *J* = 7.0 Hz, 2H), 3.69 (s, 3H), 1.31 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (50.2 MHz, $CDCl_3$). δ 160.8 (s), 159.9 (s), 145.3 (s), 138.4 (s), 132.1 (d), 129.4 (d), 118.8 (t), 113.3 (d), 112.0 (d), 110.2 (d), 105.4 (d), 63.9 (t), 55.1 (q), 14.4 (q). MS *m/z* 247 (M^+, 38), 218 (100), 153 (26), 77 (50), 55 (56). Anal. Calcd for $C_{14}H_{17}NO_3$: C, 68.00; H, 6.93. Found C, 67.96; H, 6.72.

(*E*)-*N*-(4-bromophenyl)-2-ethoxypenta-2,4-dienamide **2e**.

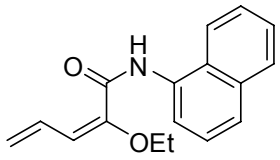
Purified by flash chromatography (Et_2O:petroleum ether 2:3, 1% Et_3N, R_f 0.65) to give **2e** as a brown oil (379 mg, 64%).



^{1}H NMR (200 MHz, $CDCl_3$). δ ppm 8.42 (br, 1H), 7.71 (dt, *J* = 17.0, 10.4 Hz, 1H) superimposed to 7.55-7.40 (m, 4H), 5.83 (d, *J* = 10.4 Hz, 1H), 5.30 (d, *J* = 17.0 Hz, 1H), 5.20 (d, *J* = 10.4 Hz, 1H), 3.93 (q, *J* = 6.9 Hz, 2H), 1.43 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (50.2 MHz, $CDCl_3$). δ 160.7 (s), 144.9 (s), 136.3 (s), 131.9 (d), 131.7 (d), 121.4 (d), 119.3 (t), 116.7 (s), 113.7 (d), 63.9 (t), 14.4 (q). MS *m/z* 295 (M^+, 68), 266 (100), 216 (49), 197 (28), 77 (43), 55 (61). Anal. Calcd for $C_{13}H_{14}BrNO_2$: C, 52.72; H, 4.76. Found C, 52.66; H, 4.59.

(*E*)-2-ethoxy-*N*-(naphthalen-1-yl)penta-2,4-dienamide **2f**.

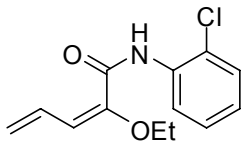
Purified by flash chromatography (Et_2O:petroleum ether 2:3, 1% Et_3N, R_f 0.60) to give **2f** as a yellow oil (385 mg, 72%).



^{1}H NMR (200 MHz, $CDCl_3$). δ ppm 8.96 (br, 1H), 8.15-8.08 (m, 1H), 7.87-7.72 (m, 1H) superimposed to 7.63 (dt, *J* = 16.1, 10.6 Hz, 1H), 7.68-7.60 (m, 1H) 7.50-7.40 (m, 4H), 5.84 (d, *J* = 10.6 Hz, 1H), 5.27 (d, *J* = 16.1 Hz, 1H), 5.16 (d, *J* = 10.6 Hz, 1H), 3.94 (q, *J* = 7.0 Hz, 2H), 1.45 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (50.2 MHz, $CDCl_3$). δ 168.8 (s), 161.1 (s), 145.5 (s), 133.9 (s), 132.2 (d), 131.7 (s), 128.7 (d), 126.5 (d), 126.1 (d), 125.7 (d), 125.2 (d), 120.0 (d), 119.5 (d), 119.1 (t), 113.6 (t), 64.0 (t), 14.6 (q). MS *m/z* 267 (M^+, 47), 238 (100), 143 (38), 115 (41), 69 (25). Anal. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41. Found C, 76.06; H, 6.29.

(*E*)-*N*-(2-chlorophenyl)-2-ethoxypenta-2,4-dienamide **2g**.

Purified by flash chromatography (Et_2O:petroleum ether 1:4, 1% Et_3N, R_f 0.70) to give **2g** as a colourless oil (362 mg, 72%).

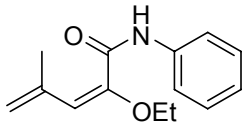


^{1}H NMR (200 MHz, $CDCl_3$). δ ppm 9.14 (br, 1H), 8.46 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.69 (dt, *J* = 17.1, 10.8 Hz, 1H), 7.35 – 7.13 (m, 2H), 7.09 – 6.80 (m, 1H), 5.79 (d, *J* = 10.8 Hz, 1H), 5.24 (ddd, *J* = 17.1, 2.0, 0.8 Hz, 1H), 5.14 (ddd, *J* = 10.1, 2.0, 0.8 Hz, 1H), 3.86 (q, *J* = 7.0 Hz, 2H), 1.38 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (50.2 MHz, $CDCl_3$). δ 160.6 (s), 145.2 (s), 134.3 (s), 131.9 (d), 128.8 (d), 127.5 (d), 124.3 (d), 122.8 (s), 120.7 (d), 119.3 (t), 114.0 (d), 64.1 (t), 14.4 (q). MS *m/z* 251 (M^+,

41), 222 (100), 224 (31), 154 (26), 127 (48), 69 (30). Anal. Calcd for $C_{13}H_{14}ClNO_2$: C, 62.03; H, 5.61. Found C, 62.00; H, 5.48.

(*E*)-2-ethoxy-4-methyl-*N*-phenylpenta-2,4-dienamide **2h**.

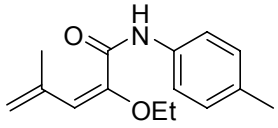
Purified by flash chromatography (CH_2Cl_2, 1% Et_3N, R_f 0.35) to give **2h** as a pale yellow oil (240 mg, 52%).



^{1}H NMR (200 MHz, $CDCl_3$). δ ppm 8.01 (br, 1H), 7.56-7.46 (m, 2H), 7.30-7.20 (m, 2H), 7.08-6.98 (m, 1H), 5.57 (s, 1H), 4.89 (d, *J* = 10.1 Hz, 2H), 3.79 (q, *J* = 6.9 Hz, 2H), 1.90 (s, 3H), 1.33 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (50.2 MHz, $CDCl_3$). δ 160.9 (s), 147.4 (s), 139.3 (s), 137.3 (s), 128.8 (d), 124.2 (d), 119.6 (d), 114.8 (t), 111.4 (d), 64.0 (t), 22.7 (q), 14.4 (q). MS *m/z* 231 (M^+, 20), 202 (100), 120 (29), 93 (28), 83 (39), 77 (33), 55 (41). Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41. Found C, 72.58; H, 7.15.

(*E*)-2-ethoxy-4-methyl-*N*-*p*-tolylpenta-2,4-dienamide **2i**.

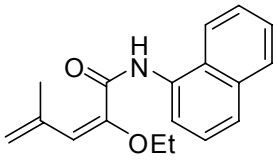
Purified by flash chromatography (Et_2O:petroleum ether 2:3, 1% Et_3N, R_f 0.60) to give **2i** as a pale yellow oil (289 mg, 59%).



^{1}H NMR (200 MHz, $CDCl_3$). δ ppm 8.11 (br, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 5.63 (s, 1H), 4.97 (d, *J* = 7.4 Hz, 2H), 3.85 (q, *J* = 6.9 Hz, 2H), 2.31 (s, 3H), 1.98 (s, 3H), 1.40 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (50.2 MHz, $CDCl_3$). δ 161.1 (s), 153.7 (s), 147.8 (s), 139.3 (s), 135.3 (s), 129.3 (d), 119.7 (d), 114.8 (t), 110.9 (d), 63.9 (t), 22.7 (q), 20.5 (q), 14.4 (q). MS *m/z* 245 (M^+, 31), 216 (100), 188 (10), 106 (28), 83 (57), 55 (24). Anal. Calcd for $C_{15}H_{19}NO_2$: C, 73.44; H, 7.81. Found C, 73.39; H, 7.64.

(*E*)-2-ethoxy-4-methyl-*N*-(naphthalen-1-yl)penta-2,4-dienamide **2j**.

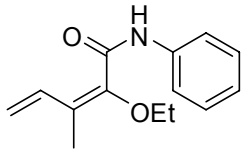
Purified by flash chromatography (Et_2O:petroleum ether 2:3, 1% Et_3N, R_f 0.50) to give **2j** as a yellow oil (382 mg, 68%).



^{1}H NMR (200 MHz, $CDCl_3$). δ ppm 8.70 (br, 1H), 8.31-8.15 (m, 1H), 7.99-7.74 (m, 1H), 7.70-7.52 (m, 4H), 7.58-7.32 (m, 1H), 5.69 (s, 1H), 5.03 (s, 2H), 3.86 (q, *J* = 6.9 Hz, 2H), 2.04 (s, 3H), 1.43 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (50.2 MHz, $CDCl_3$). δ 161.3 (q), 156.6 (q), 151.6 (q), 147.6 (q), 139.5 (q), 133.9 (q), 131.8 (d), 128.7 (d), 125.8 (d), 125.2 (d), 120.5 (d), 119.9 (d), 119.5 (d), 115.1 (t), 111.8 (d), 64.1 (t), 22.9 (q), 14.6 (q). MS *m/z* 281 (M^+, 67), 252 (73), 224 (31), 83 (100), 55 (49). Anal. Calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81. Found C, 76.58; H, 6.31.

(*E*)-2-ethoxy-3-methyl-*N*-phenylpenta-2,4-dienamide **2k**.

Purified by flash chromatography (Et_2O:petroleum ether 2:3, 1% Et_3N, R_f 0.60) to give **2k** as a white oil (300 mg, 65%).

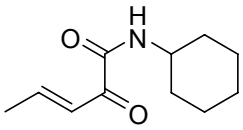


^{1}H NMR (200 MHz, $CDCl_3$). δ ppm 8.20 (br, 1H), 7.65 (dd, *J* = 17.5, 11.0 Hz, 1H), 7.58 – 7.47 (m, 2H), 7.37 – 7.17 (m, 3H), 5.41 (dd, *J* = 17.5, 1.4 Hz, 1H), 5.23 (dd, *J* = 11.0, 1.4 Hz, 1H), 3.77 (q, *J* = 7.1 Hz, 2H), 1.93 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (50.2 MHz, $CDCl_3$). δ 161.4 (s), 152.4 (s), 140.3 (s), 132.97 (s), 128.0 (d), 127.8 (d), 123.3 (d), 118.86 (t), 116.62 (d), 67.5 (t), 26.8 (q), 14.4 (q). MS *m/z* 231 (M^+, 20), 202 (100), 174 (10), 120 (15), 93 (28), 81 (31). Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41. Found C, 72.44; H, 7.29.

Spectroscopic data for α-ketoamides derivatives **3**

(*E*)-*N*-cyclohexyl-2-oxopent-3-enamide **3a**.

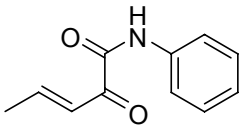
Purified by flash chromatography (Et_2O:petroleum ether 3:7, 1% Et_3N, R_f 0.40) to give **3a** as a colorless oil (91 mg, 93%).



^{1}H NMR (200 MHz, $CDCl_3$). δ ppm 7.41-7.24 (m, 1H), 7.14 (dd, *J* = 15.7, 1.4 Hz, 1H), 7.03 (br, 1H), 4.19-4.01 (m, 1H), 3.88-3.69 (m, 1H), 2.02 (dd, *J* = 6.8, 1.4 Hz, 3H), 1.99-1.87 (m, 4H), 1.82-1.60 (m, 6H), 1.45-1.31 (m, 4H), 1.33-1.12 (m, 6H). ^{13}C NMR (50.2 MHz, $CDCl_3$). δ 185.3 (s), 160.0 (s), 149.1 (d), 124.4 (d), 48.1 (d), 32.4 (t), 24.5 (t), 18.8 (q). MS *m/z* 195 (M^+, 8), 180 (12), 126 (15), 83 (72), 69 (100), 55 (58). Anal. Calcd for $C_{11}H_{17}NO_2$: C, 67.66; H, 8.78. Found C, 67.32; H, 8.75.

(*E*)-2-oxo-*N*-phenylpent-3-enamide **3b**.[2]

Purified by flash chromatography (CH_2Cl_2, 1% Et_3N, R_f 0.60) to give **3b** as a yellow oil (83 mg, 88%).

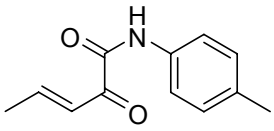


^{1}H NMR (200 MHz, $CDCl_3$). δ ppm 8.85 (br, 1H), 7.62-7.54 (m, 2H), 7.36-7.24 (m, 3H), 7.20 (dd, *J* = 15.4, 1.2 Hz, 1H), 7.12 (dq, *J* = 15.4, 6.5 Hz, 1H), 1.97 (dd, *J* = 6.5, 1.2 Hz, 3H). ^{13}C NMR (50.2 MHz, $CDCl_3$). δ 184.9 (s), 158.5 (s), 150.4 (d), 136.4 (s), 129.0 (d), 124.9 (d), 123.6 (d), 119.5 (d), 19.0 (q). MS *m/z* 189 (M^+, 16), 120 (27), 77 (43), 69 (100), 55 (16). Anal. Calcd for $C_{11}H_{11}NO_2$: C, 69.83; H, 5.86. Found C, 69.59; H, 5.72.

(*E*)-2-oxo-*N*-*p*-tolylpent-3-enamide **3c**.

Purified by flash chromatography (CH_2Cl_2, 1% Et_3N, R_f 0.70) to give **3c** as a yellow oil (85 mg, 84%).

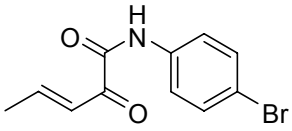
[2] M. S. Novikov, I. V. Voznyi, A. F. Khlebnikov, *J. Chem. Soc., Perkin Trans. 1*, 2002, 1628-1630.



^{1}H NMR (200 MHz, $CDCl_3$). δ ppm 8.89 (br, 1H), 7.59-7.51 (m, 2H), 7.41 (dd, *J* = 15.5, 1.2 Hz, 1H), 7.27 (dq, *J* = 15.5, 6.5 Hz, 1H), 7.22-7.14 (m, 2H), 2.34 (s, 3H), 2.05 (d, *J* = 6.5, 1.2 Hz, 3H). ^{13}C NMR (50.2 MHz, $CDCl_3$). δ 185.0 (s), 158.4 (s), 150.2 (d), 134.7 (s), 133.8 (s), 129.5 (d), 123.7 (d), 119.5 (d), 20.7 (q), 19.0 (q). MS *m/z* 203 (M^+, 22), 134 (31), 77 (32), 69 (100), 55 (57). Anal. Calcd for $C_{12}H_{13}NO_2$: C, 70.92; H, 6.45. Found C, 70.88; H, 6.17.

(*E*)-*N*-(4-bromophenyl)-2-oxopent-3-enamide **3e**.

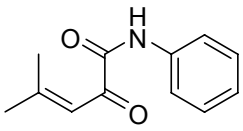
Purified by flash chromatography (CH_2Cl_2:petroleum ether 4:1, 1% Et_3N, R_f 0.70) to give **3e** as a brown oil (106 mg, 79%).



^{1}H NMR (200 MHz, $CDCl_3$). δ ppm 8.85 (br, 1H), 7.62-7.14 (m, 6H), 2.05 (dd, *J* = 6.7, 1.2 Hz, 3H). ^{13}C NMR (50.2 MHz, $CDCl_3$). δ 183.7 (s), 157.7 (s), 149.9 (d), 134.6 (s), 131.2 (d), 122.7 (d), 120.3 (d), 116.9 (s), 18.2 (q). MS *m/z* 268 (M^+, 57), 197 (12), 77 (64), 69 (100), 55 (28). Anal. Calcd for $C_{11}H_{10}BrNO_2$: C, 49.28; H, 3.76. Found C, 48.99; H, 3.66.

4-methyl-2-oxo-*N*-phenylpent-3-enamide **3h**.

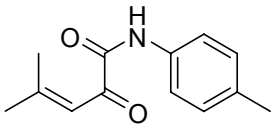
Purified by flash chromatography (CH_2Cl_2, 1% Et_3N, R_f 0.80) to give **3h** as a yellow oil (82 mg, 81%).



^{1}H NMR (200 MHz, $CDCl_3$). δ ppm 8.95 (br, 1H), 7.62-7.55 (m, 2H), 7.34-7.25 (m, 3H), 7.19-7.16 (m, 1H), 2.23 (d, *J* = 1.1 Hz, 3H), 2.01 (d, *J* = 1.2 Hz, 3H). ^{13}C NMR (50.2 MHz, $CDCl_3$). δ 185.1 (s), 165.9 (s), 159.2 (s), 136.5 (s), 128.9 (d), 124.8 (d), 119.4 (d), 116.5 (d), 28.6 (q), 21.7 (q). MS *m/z* 203 (M^+, 21), 120 (11), 83 (100), 77 (13), 55 (59). Anal. Calcd for $C_{12}H_{13}NO_2$: C, 70.92; H, 6.45. Found C, 70.87; H, 6.04.

4-methyl-2-oxo-*N*-p-tolylpent-3-enamide **3i**.

Purified by flash chromatography (CH_2Cl_2, 1% Et_3N, R_f 0.85) to give **3i** as a yellow oil (94 mg, 86%).

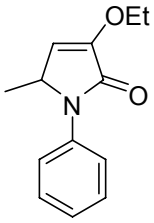


^{1}H NMR (200 MHz, $CDCl_3$). δ ppm 8.89 (br, 1H), 7.50-7.43 (m, 2H), 7.28-7.14 (m, 1H), 7.11-7.01 (m, 2H), 2.25 (s, 3H), 2.22 (d, J = 1.04 Hz, 3H), 2.00 (d, J = 1.04 Hz, 3H). ^{13}C NMR (50.2 MHz, $CDCl_3$). δ 185.3 (s), 165.6 (s), 159.0 (s), 134.5 (s), 134.0 (s), 129.4 (d), 119.4 (d), 116.6 (d), 28.6 (q), 21.7 (q), 20.7 (q). MS *m/z* 217 (M^+, 21), 134 (19), 83 (100), 77 (47), 55 (54). Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96. Found C, 71.48; H, 6.59.

Spectroscopic data for *N*-aryl pyrrolidinones **4**

3-ethoxy-5-methyl-1-phenyl-1*H*-pyrrol-2(5*H*)-one **4b**.

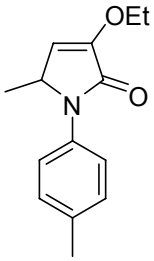
Purified by flash chromatography (Et_2O:petroleum ether 7:3, 1% Et_3N, R_f 0.50) to give **4b** as a yellow oil (98 mg, 91%).



^{1}H NMR (200 MHz, $CDCl_3$). δ ppm 7.36-7.20 (m, 4H), 7.12-7.02 (m, 1H), 5.70 (d, *J* = 1.9 Hz, 1H), 5.13 (qd, *J* = 6.2, 1.9 Hz, 1H), 4.04 (q, *J* = 7.0 Hz, 2H), 1.50 (t, *J* = 7.0 Hz, 3H), 1.40 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (50.2 MHz, $CDCl_3$). δ 156.1 (s), 148.6 (s), 146.1 (s), 128.2 (d), 123.6 (d), 123.2 (d), 111.5 (d), 78.7 (d), 66.6 (t), 20.9 (q), 14.0 (q). MS *m/z* 217 (M^+, 11), 202 (38), 174 (19), 120 (24), 83 (100), 77 (34). Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96. Found C, 71.46; H, 6.73.

3-ethoxy-5-methyl-1-*p*-tolyl-1*H*-pyrrol-2(5*H*)-one **4c**.

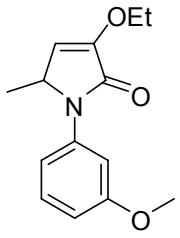
Purified by flash chromatography (Et_2O:petroleum ether 3:2, 1% Et_3N, R_f 0.45) to give **4c** as an orange oil (107 mg, 93%).



^{1}H NMR (200 MHz, $CDCl_3$). δ ppm 7.26-7.08 (m, 4H), 5.68 (d, *J* = 1.8 Hz, 1H), 5.18 (qd, *J* = 6.4, 1.9 Hz, 1H), 4.04 (q, *J* = 6.9 Hz, 2H), 2.32 (s, 3H), 1.47 (q, *J* = 6.9 Hz, 3H), 1.40 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (50.2 MHz, $CDCl_3$). δ 155.9 (s), 148.6 (s), 143.4 (s), 133.2 (s), 128.9 (d), 123.2 (d), 111.3 (d), 78.6 (d), 66.6 (t), 21.0 (q), 20.8 (q), 14.1 (q). MS *m/z* 231 (M^+, 15), 216 (33), 188 (27), 134 (49), 91 (100), 77 (64). Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41. Found C, 72.54; H, 7.08.

3-ethoxy-1-(3-methoxyphenyl)-5-methyl-1*H*-pyrrol-2(5*H*)-one **4d**.

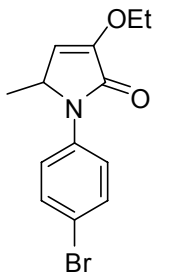
Purified by flash chromatography (Et_2O:petroleum ether 4:1, 1% Et_3N, R_f 0.40) to give **4d** as an orange oil (116 mg, 94%).



^{1}H NMR (200 MHz, $CDCl_3$). δ ppm 7.21-7.08 (m, 1H), 6.83-6.71 (m, 2H), 6.62-6.52 (m, 1H), 5.63 (d, *J* = 1.9 Hz, 1H), 5.06 (qd, *J* = 6.5, 1.9 Hz, 1H), 3.97 (q, *J* = 7.0 Hz, 2H), 3.71 (s, 3H), 1.41 (t, *J* = 7.0 Hz, 3H), 1.33 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (50.2 MHz, $CDCl_3$). δ 159.6 (s), 156.3 (s), 148.5 (s), 147.4 (s), 128.8 (d), 115.6 (d), 111.6 (d), 109.6 (d), 108.9 (d), 78.7 (d), 66.6 (t), 54.9 (q), 20.9 (q), 14.0 (q). MS *m/z* 247 (M^+, 7), 232 (15), 204 (31), 150 (42), 91 (100), 77 (58). Anal. Calcd for $C_{14}H_{17}NO_3$: C, 68.00; H, 6.93. Found C, 67.91; H, 6.90.

1-(4-bromophenyl)-3-ethoxy-5-methyl-1*H*-pyrrol-2(5*H*)-one **4e**.

Purified by flash chromatography (Et_2O:petroleum ether 4:1, 1% Et_3N, R_f 0.40) to give **4e** as a dark yellow oil (142 mg, 96%).

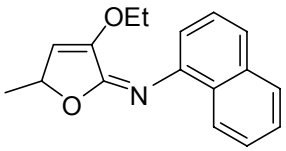


^{1}H NMR (200 MHz, $CDCl_3$). δ ppm 7.39 (d, *J* = 8.6 Hz, 2H), 7.13 (d, *J* = 8.6 Hz, 2H), 5.73 (d, *J* = 1.8 Hz, 1H), 5.14 (qd, *J* = 6.5, 1.8 Hz, 1H), 4.04 (q, *J* = 7.1 Hz, 2H), 1.50 (t, *J* = 7.1 Hz, 3H), 1.41 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (50.2 MHz, $CDCl_3$). δ 155.7 (s), 147.6 (s), 144.3 (s), 144.2 (s), 130.5 (d), 124.3 (d), 115.8 (d), 111.1 (d), 78.2 (d), 64.8 (t), 20.1 (q), 14.3 (q). MS *m/z* 296 (M^+, 45), 280 (29), 251 (100), 198 (17), 77 (50). Anal. Calcd for $C_{13}H_{14}BrNO_2$: C, 52.72; H, 4.76. Found C, 52.49; H, 4.61.

Spectroscopic data for cyclic iminoethers **5**

(*E*)-*N*-(3-ethoxy-5-methylfuran-2(5*H*)-ylidene)naphthalen-1-amine **5f**.

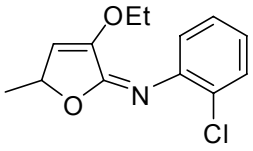
Purified by flash chromatography (EtOAc:petroleum ether 1:1, 1% Et_3N, R_f 0.50). Further recrystallization from Et_2O give **5f** as white crystals (108 mg, 81%).



^{1}H NMR (200 MHz, $CDCl_3$). δ ppm 8.13-7.94 (m, 1H), 7.75-7.69 (m, 1H), 7.53-7.45 (m, 1H), 7.42-7.28 (m, 3H), 7.18-7.10 (m, 1H), 5.63 (d, *J* = 1.9 Hz, 1H), 4.98 (qd, *J* = 6.4, 1.9 Hz, 1H), 3.96 (q, *J* = 7.0, 1H), 1.43 (t, *J* = 7.0 Hz, 1H), 1.24 (d, *J* = 6.4 Hz, 1H). ^{13}C NMR (50.2 MHz, $CDCl_3$). δ 155.6 (s), 147.6 (s), 142.4 (s), 133.1 (s), 126.8 (s), 126.7 (d), 124.7 (2C, d), 123.9 (d), 123.3 (d), 122.5 (d), 116.0 (d), 111.2 (d), 77.7 (d), 65.8 (t), 20.1 (q), 13.3 (q). MS *m/z* 267 (M^+, 100), 252 (34), 168 (76), 143 (27), 69 (91). Anal. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41. Found C, 76.11; H, 6.38. m.p. 102–103°C

(*E*)-2-chloro-*N*-(3-ethoxy-5-methylfuran-2(5*H*)-ylidene)aniline **5g**.

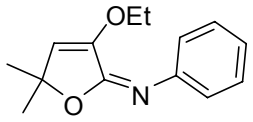
Purified by flash chromatography (Et_2O:petroleum ether 7:3, 1% Et_3N, R_f 0.40) to give **5g** as a yellow oil (110 mg, 88%).



^{1}H NMR (200 MHz, $CDCl_3$). δ 7.28 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.14-6.98 (m, 2H), 6.95-6.85 (m, 1H), 5.66 (d, *J* = 1.9 Hz, 1H), 5.02 (dq, *J* = 6.4, 1.9 Hz, 1H), 3.96 (q, *J* = 7.0 Hz, 2H), 1.40 (t, *J* = 7.0 Hz, 3H), 1.30 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (50.2 MHz, $CDCl_3$). 157.2 (s), 148.0 (s), 144.5 (s), 129.3 (d), 126.6 (d), 126.1 (s), 124.0 (d), 123.1 (d), 112.5 (d), 78.9 (d), 66.6 (t), 20.9 (q), 14.1 (q). MS *m/z* 251 (M^+, 18), 236 (91), 224 (31), 154 (36), 127 (20), 69 (100), 41 (39). Anal. Calcd for $C_{13}H_{14}ClNO_2$: C, 62.03; H, 5.61. Found C, 61.89; H, 5.55.

(*E*)-*N*-(3-ethoxy-5,5-dimethylfuran-2(5*H*)-ylidene)aniline **5h**.

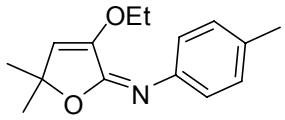
Purified by flash chromatography (Et_2O:petroleum ether 7:3, 1% Et_3N, R_f 0.55) to give **5h** as a yellow oil (109 mg, 95%).



^{1}H NMR (200 MHz, $CDCl_3$). δ ppm 7.27-7.06 (m, 5H), 5.59 (s, 1H), 3.90 (q, *J* = 7.0 Hz, 2H), 1.36 (s, 6H) superimposed to 1.36 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (50.2 MHz, $CDCl_3$). δ 155.8 (s), 147.5 (s), 146.1 (s), 128.2 (d), 123.6 (d), 123.4 (d), 115.9 (d), 85.7 (s), 66.4 (t), 27.3 (q), 14.0 (q). MS *m/z* 231 (M^+, 28), 216 (56), 188 (21), 120 (24), 83 (100), 55 (73). Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.70; H, 4.64. Found C, 72.66; H, 4.57.

(*E*)-*N*-(3-ethoxy-5,5-dimethylfuran-2(5*H*)-ylidene)-4-methylaniline **5i**.

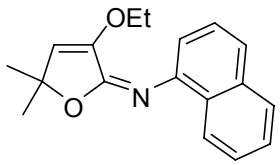
Purified by flash chromatography (Et_2O:petroleum ether 4:1, 1% Et_3N, R_f 0.70) to give **5i** as a pale yellow oil (113 mg, 92%).



^{1}H NMR (200 MHz, $CDCl_3$). δ ppm 7.30-7.00 (m, 4H), 5.68 (s, 1H), 4.00 (q, *J* = 7.1 Hz, 2H), 2.31 (s, 3H), 1.46 (s, 6H) superimposed to 1.46 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (50.2 MHz, $CDCl_3$). δ 155.5 (s), 147.6 (s), 143.4 (s), 133.1 (s), 128.8 (d), 123.4 (d), 115.6 (d), 85.6 (s), 66.4 (t), 27.4 (q), 20.8 (q), 14.1 (q). MS *m/z* 245 (M^+, 13), 230 (49), 202 (100), 134 (33), 91 (100), 77 (51). Anal. Calcd for $C_{15}H_{19}NO_2$: C, 73.44; H, 7.81. Found C, 73.06; H, 7.77.

(*E*)-*N*-(3-ethoxy-5,5-dimethylfuran-2(5*H*)-ylidene)naphthalen-1-amine **5j**.

Purified by flash chromatography (Et_2O:petroleum ether 1:1, 1% Et_3N, R_f 0.45). Further recrystallization from Et_2O give **5j** as white crystals (117 mg, 83%).

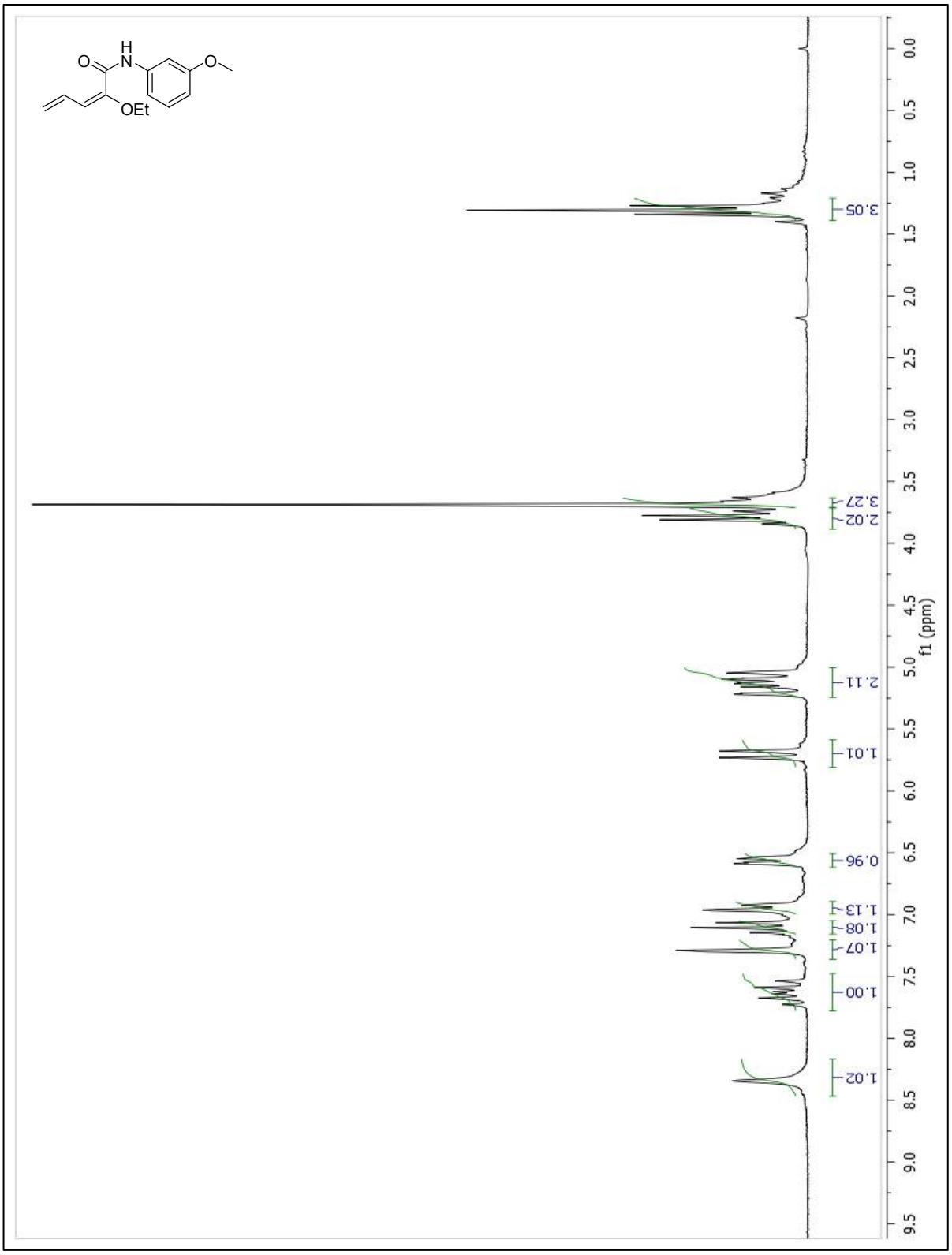


^{1}H NMR (200 MHz, $CDCl_3$). δ ppm 8.12-8.00 (m, 1H), 7.78-7.71 (m, 1H), 7.56-7.46 (m, 1H), 7.41-7.30 (m, 3H), 7.20-7.14 (m, 1H), 5.69 (s, 1H), 4.01 (q, *J* = 7.0 Hz, 2H), 1.47 (t, *J* = 7.0 Hz, 3H), 1.35 (s, 6H). ^{13}C NMR (50.2 MHz, $CDCl_3$). δ 156.1 (q), 147.4 (q), 143.4 (q), 133.9 (q), 128.5 (q), 127.9 (d), 127.5 (d), 125.6 (d), 124.7 (d), 124.3 (d), 123.3 (d), 117.1 (d), 116.5 (d), 85.6 (q), 66.4 (t), 27.3 (q), 14.2 (q). MS *m/z* 281 (M^+, 95), 266 (48), 252 (53), 83 (100), 55 (32). Anal. Calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81. Found C, 76.77; H, 6.29. m.p. 105−106°C

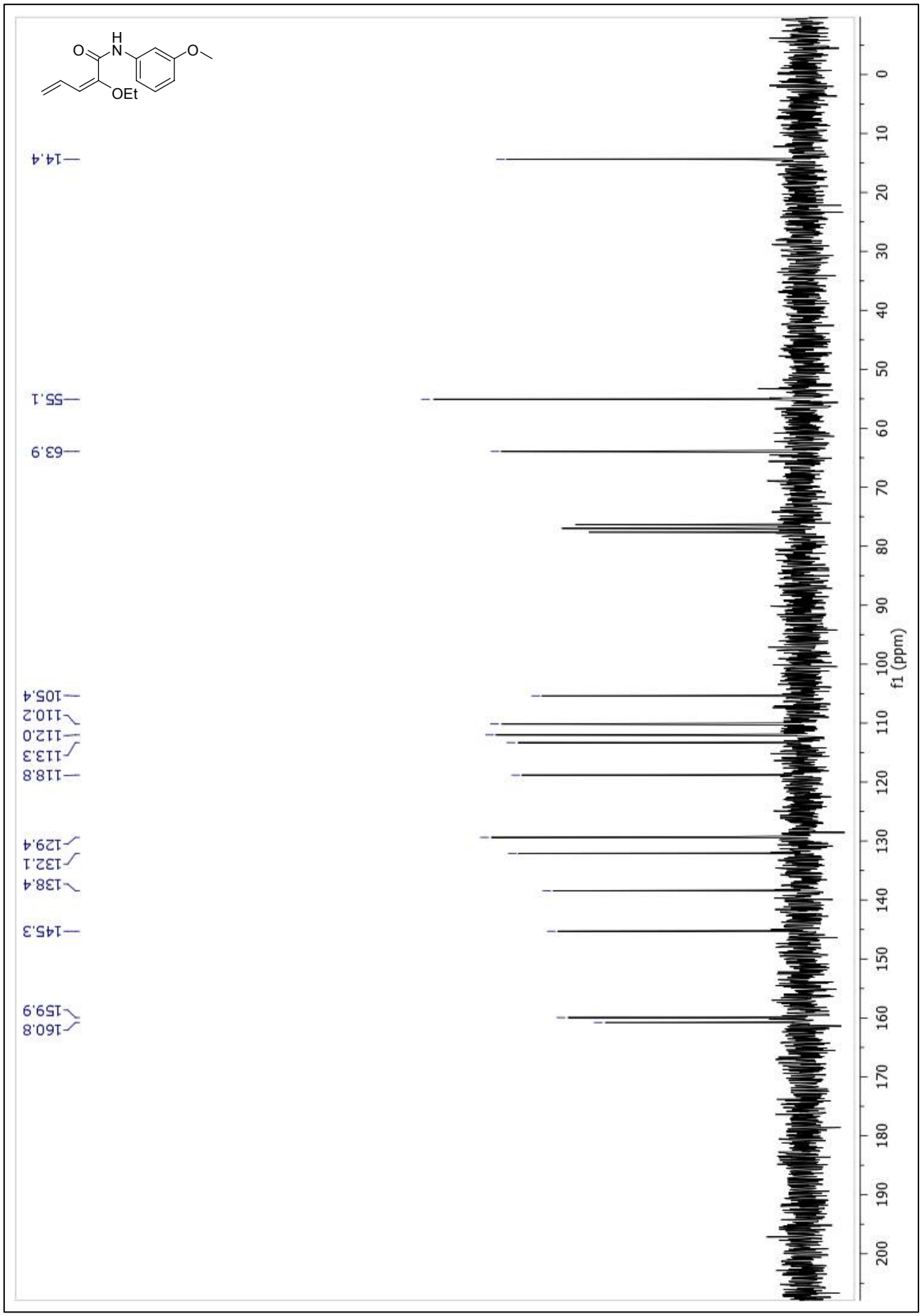
Copy of ^{1}H NMR and ^{13}C NMR spectra for new compounds

(*E*)-2-ethoxy-*N*-(3-methoxyphenyl)penta-2,4-dienamide **2d**.

^{1}H NMR ($CDCl_3$, 200 MHz)

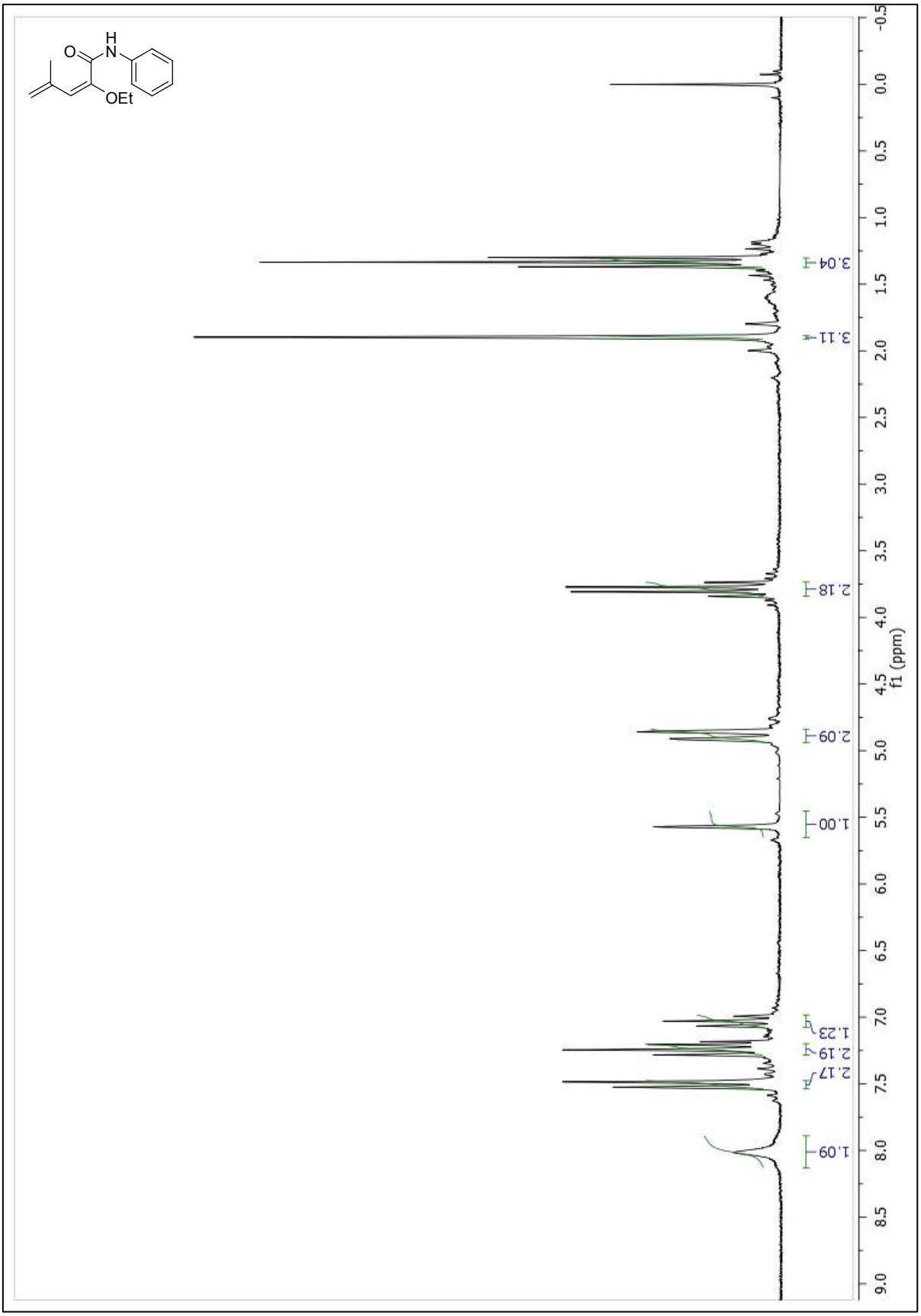


^{13}C NMR ($CDCl_3$, 50.2 MHz)

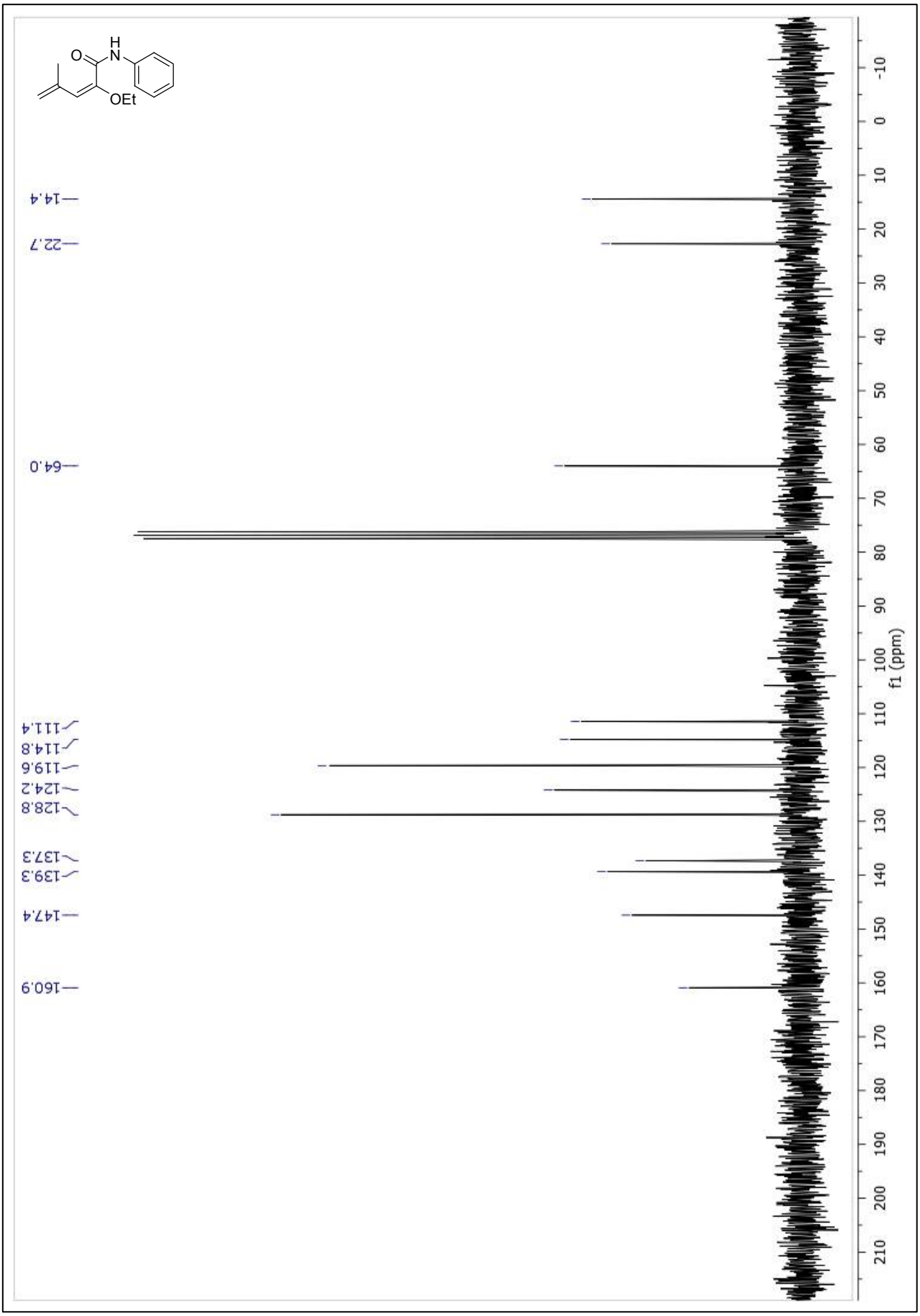


(*E*)-2-ethoxy-4-methyl-*N*-phenylpenta-2,4-dienamide **2h**.

^{1}H NMR ($CDCl_3$, 200 MHz)

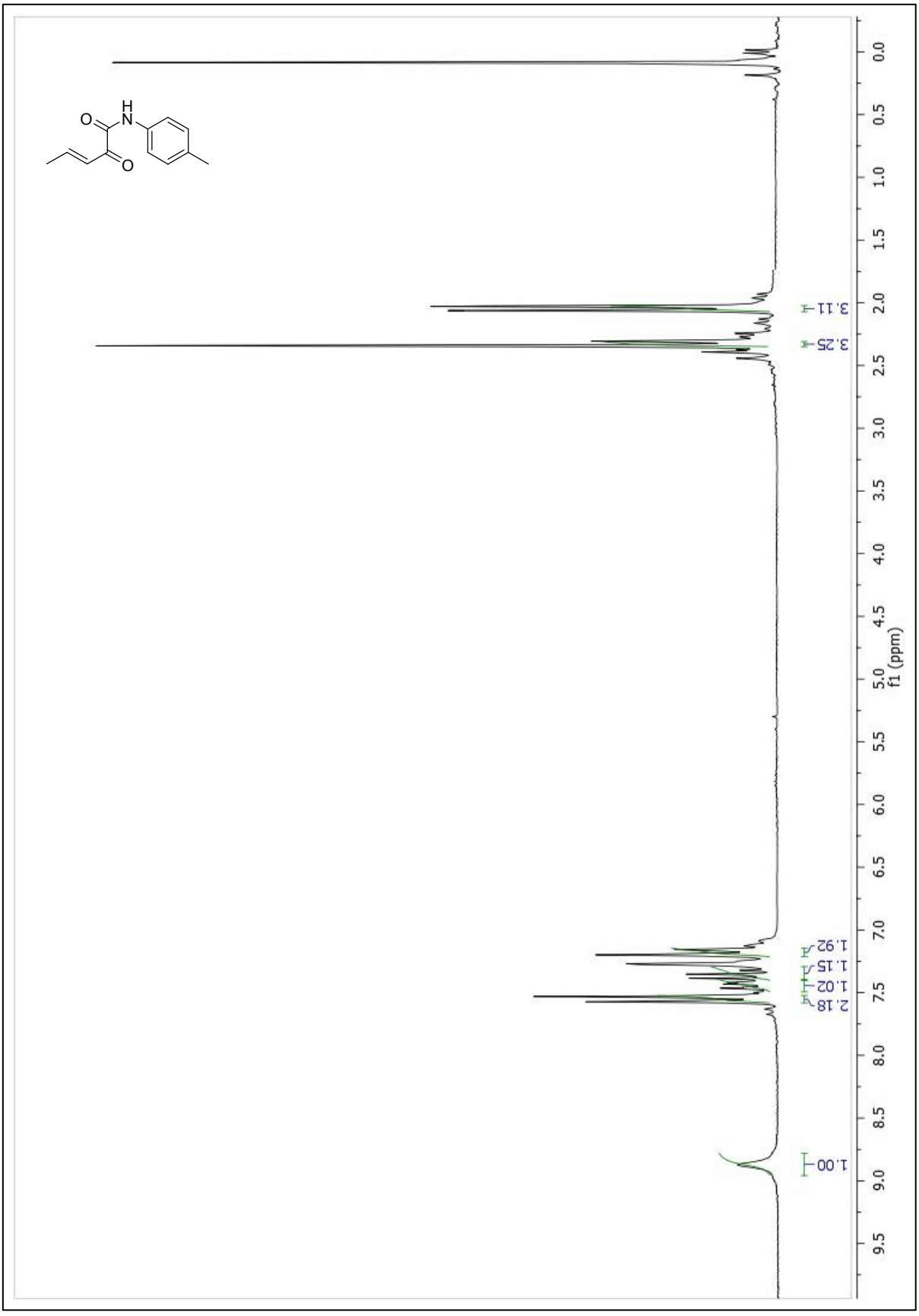


^{13}C NMR ($CDCl_3$, 50.2 MHz)

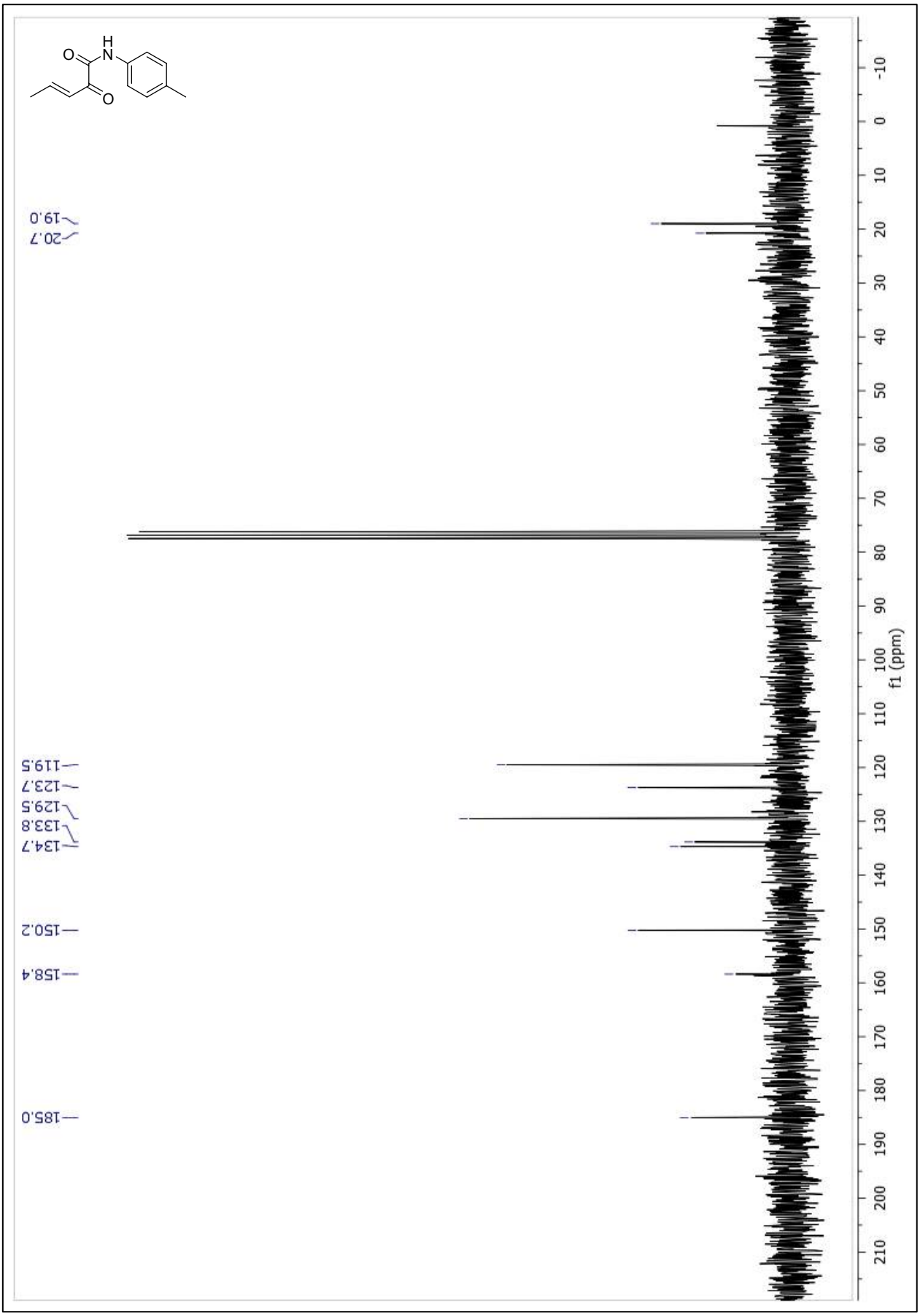


(*E*)-2-oxo-*N*-*p*-tolylpent-3-enamide **3c**.

^{1}H NMR ($CDCl_3$, 200 MHz)

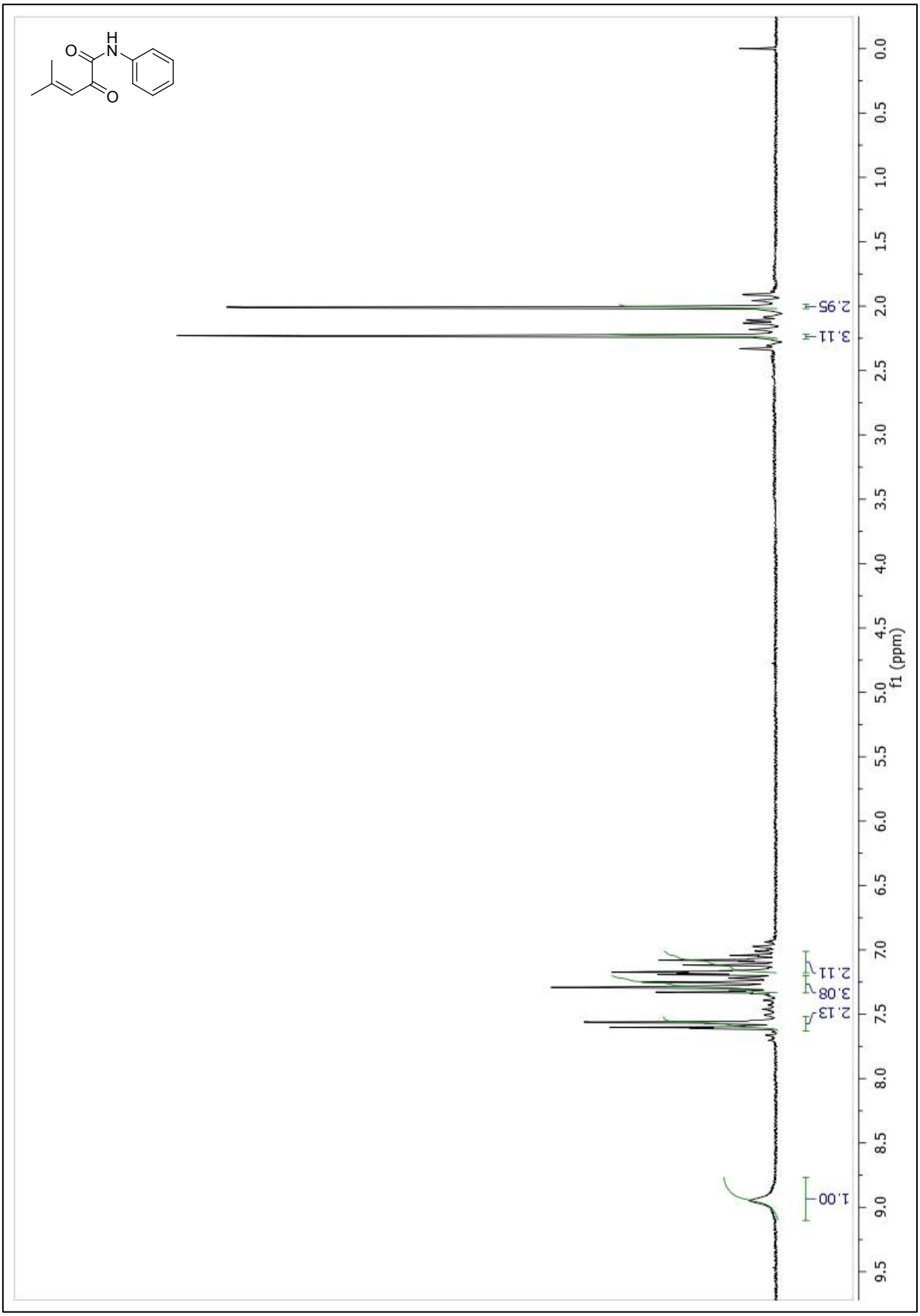


^{13}C NMR ($CDCl_3$, 50.2 MHz)

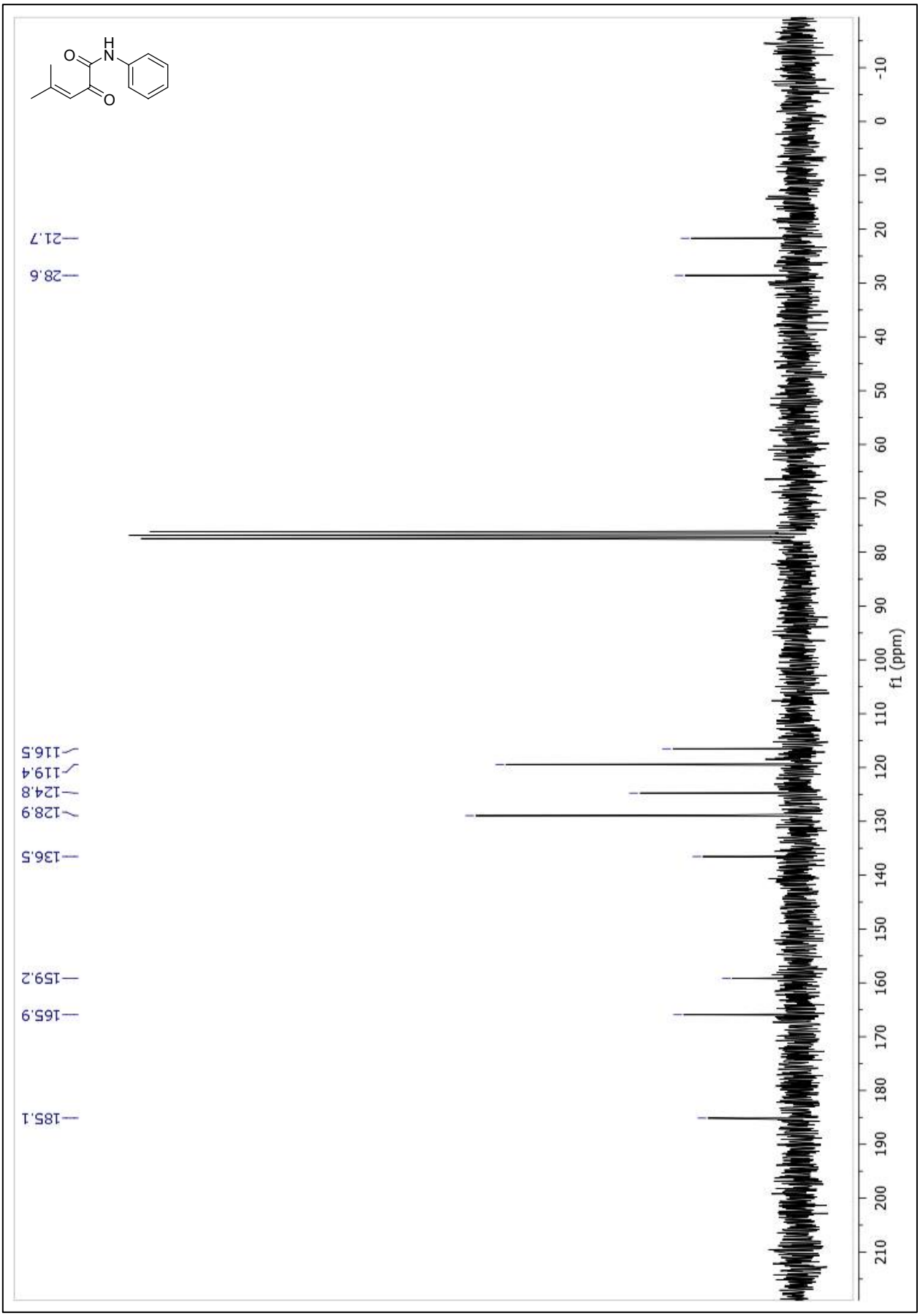


4-methyl-2-oxo-*N*-phenylpent-3-enamide **3h**.

^{1}H NMR ($CDCl_3$, 200 MHz)

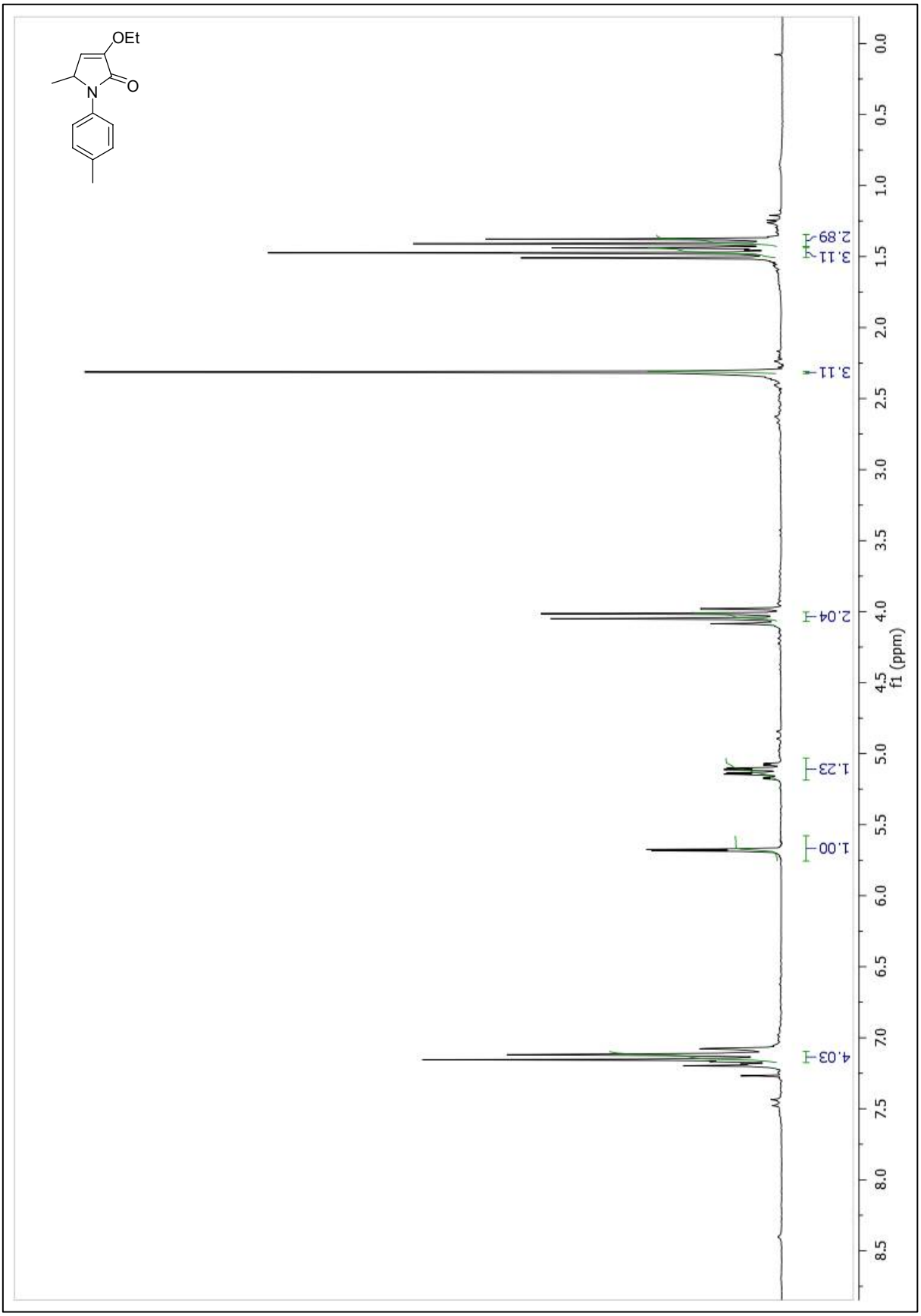


^{13}C NMR ($CDCl_3$, 50.2 MHz)

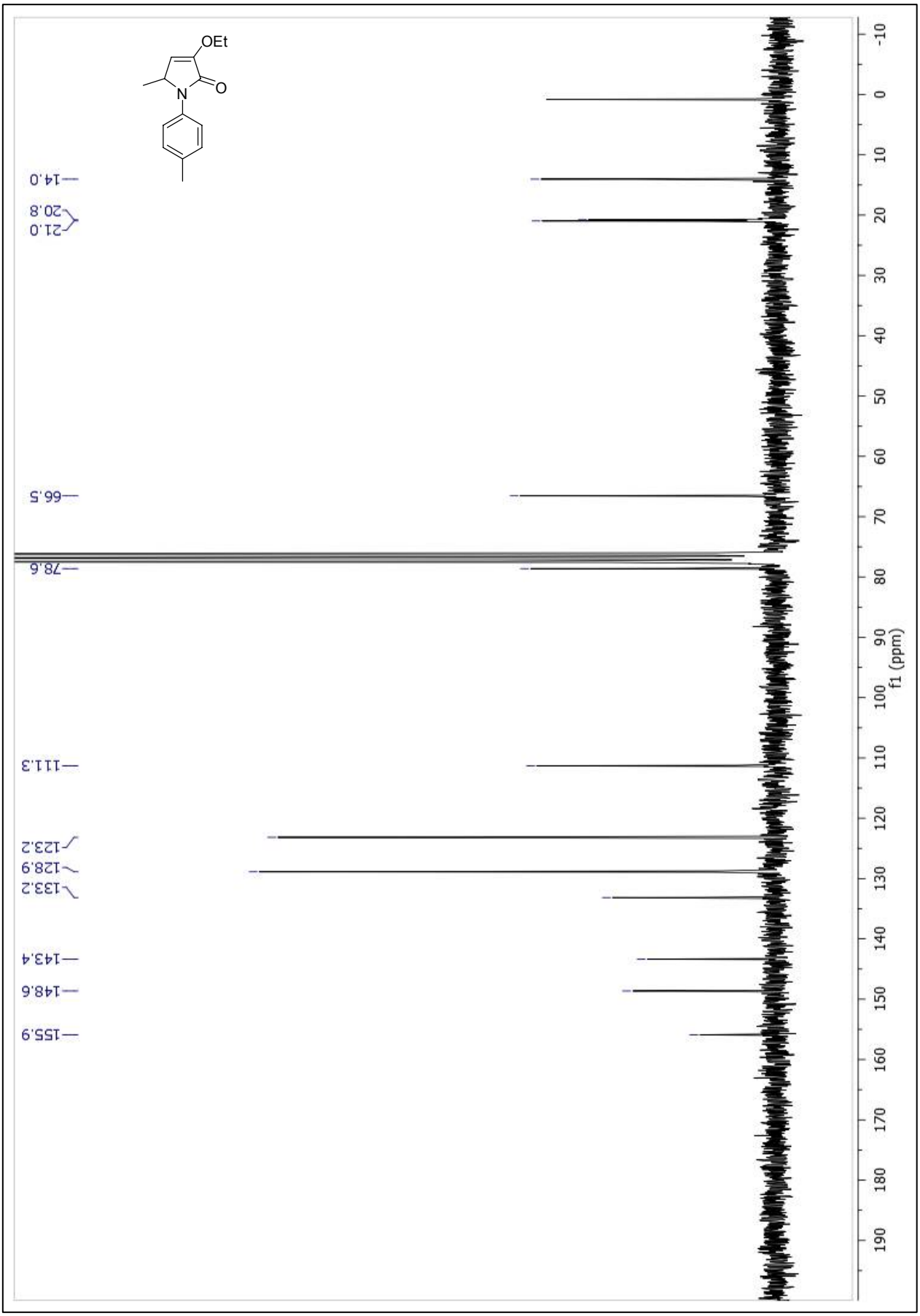


3-ethoxy-5-methyl-1-*p*-tolyl-1*H*-pyrrol-2(5*H*)-one **4c**.

^{1}H NMR ($CDCl_3$, 200 MHz)

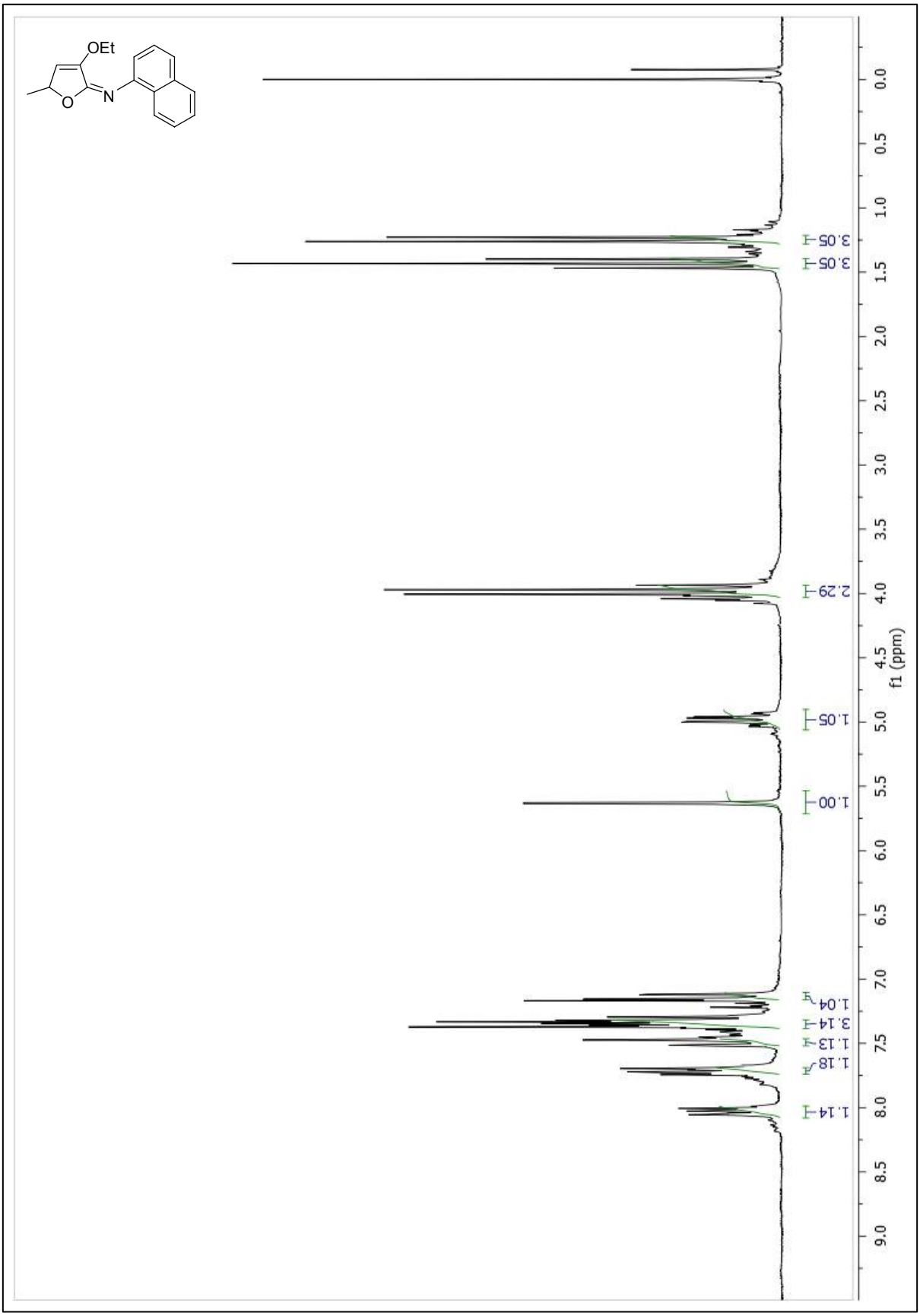


^{13}C NMR ($CDCl_3$, 50.2 MHz)

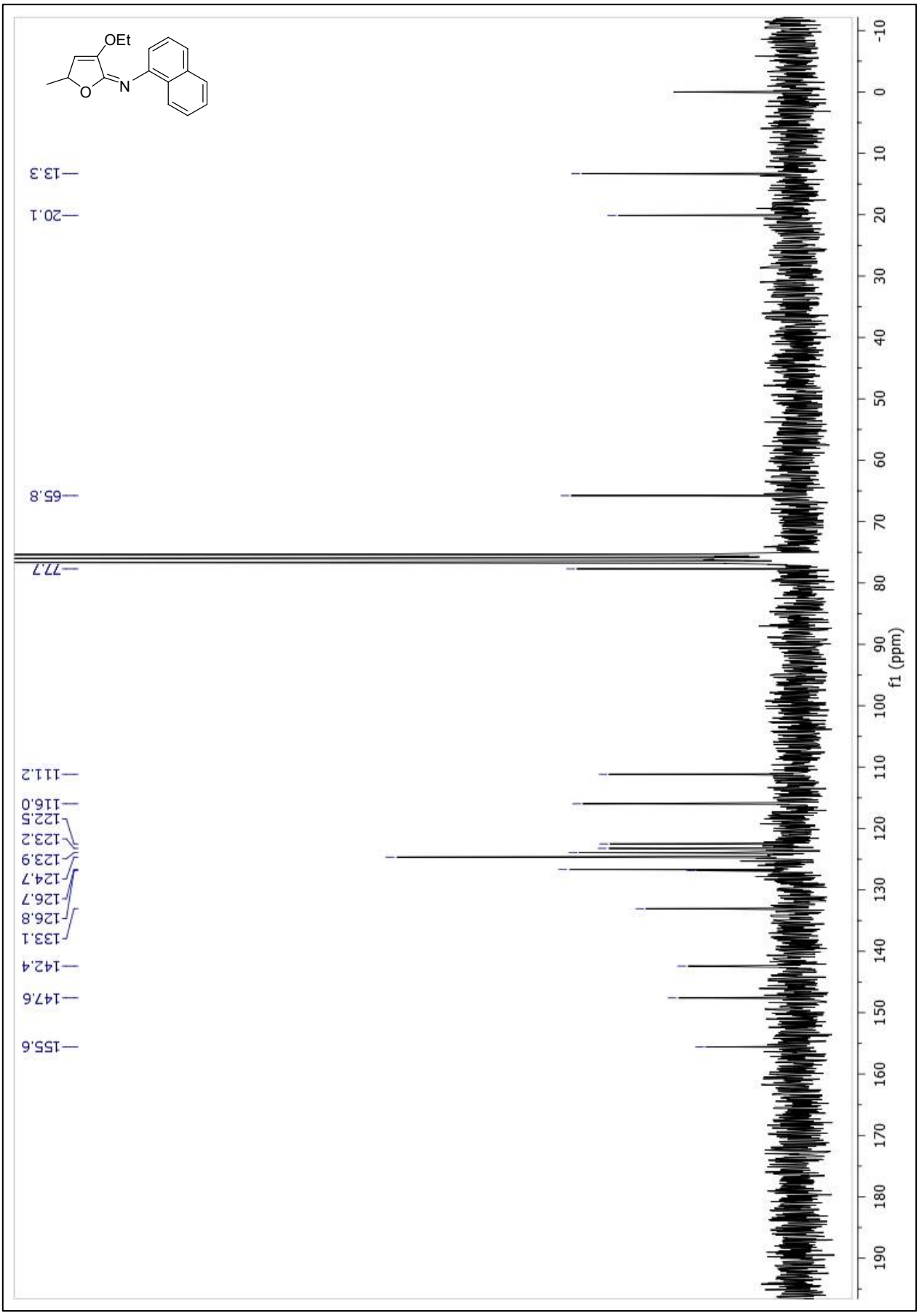


(*E*)-*N*-(3-ethoxy-5-methylfuran-2(5*H*)-ylidene)naphthalen-1-amine **5f**.

^{1}H NMR ($CDCl_3$, 200 MHz)

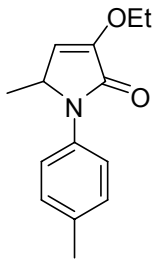


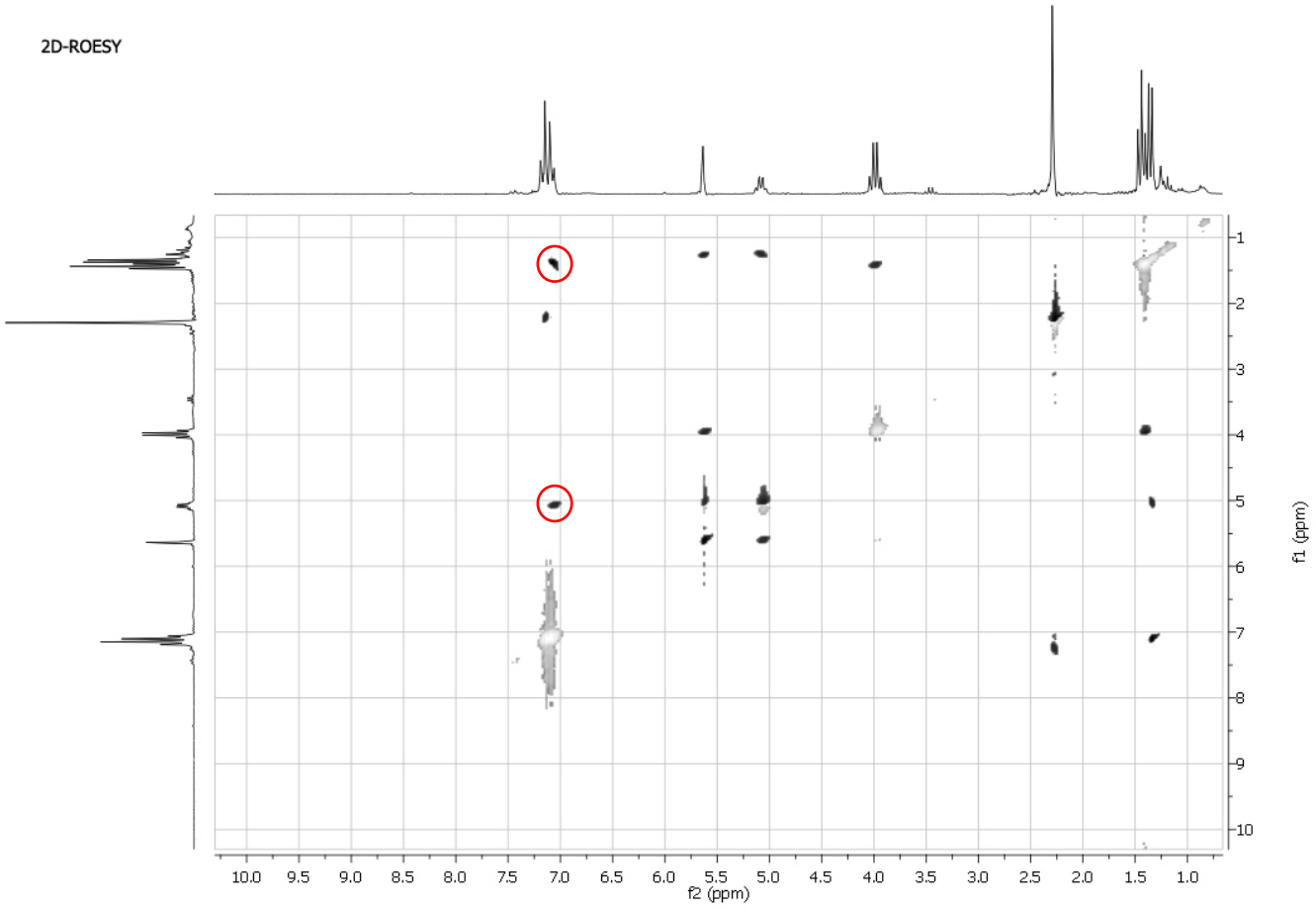
^{13}C NMR ($CDCl_3$, 50.2 MHz)



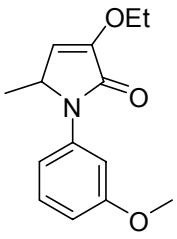
Copy of 2D-ROESY and 2D-NOESY spectra for compounds **4c**, **4d** and **5g**

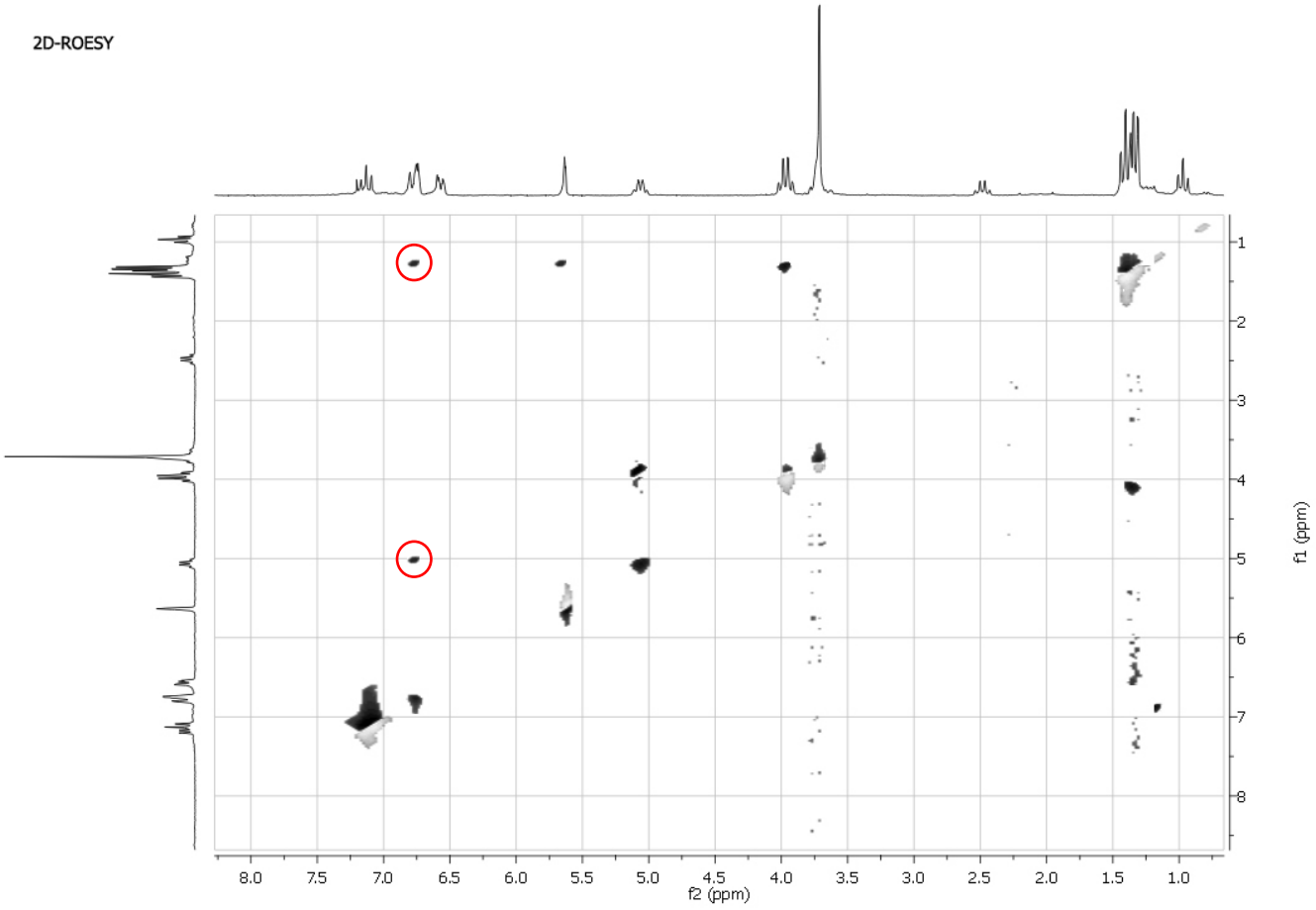
3-ethoxy-5-methyl-1-*p*-tolyl-1*H*-pyrrol-2(5*H*)-one **4c**.



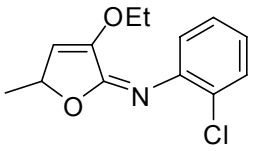


3-ethoxy-1-(3-methoxyphenyl)-5-methyl-1*H*-pyrrol-2(5*H*)-one **4d**.

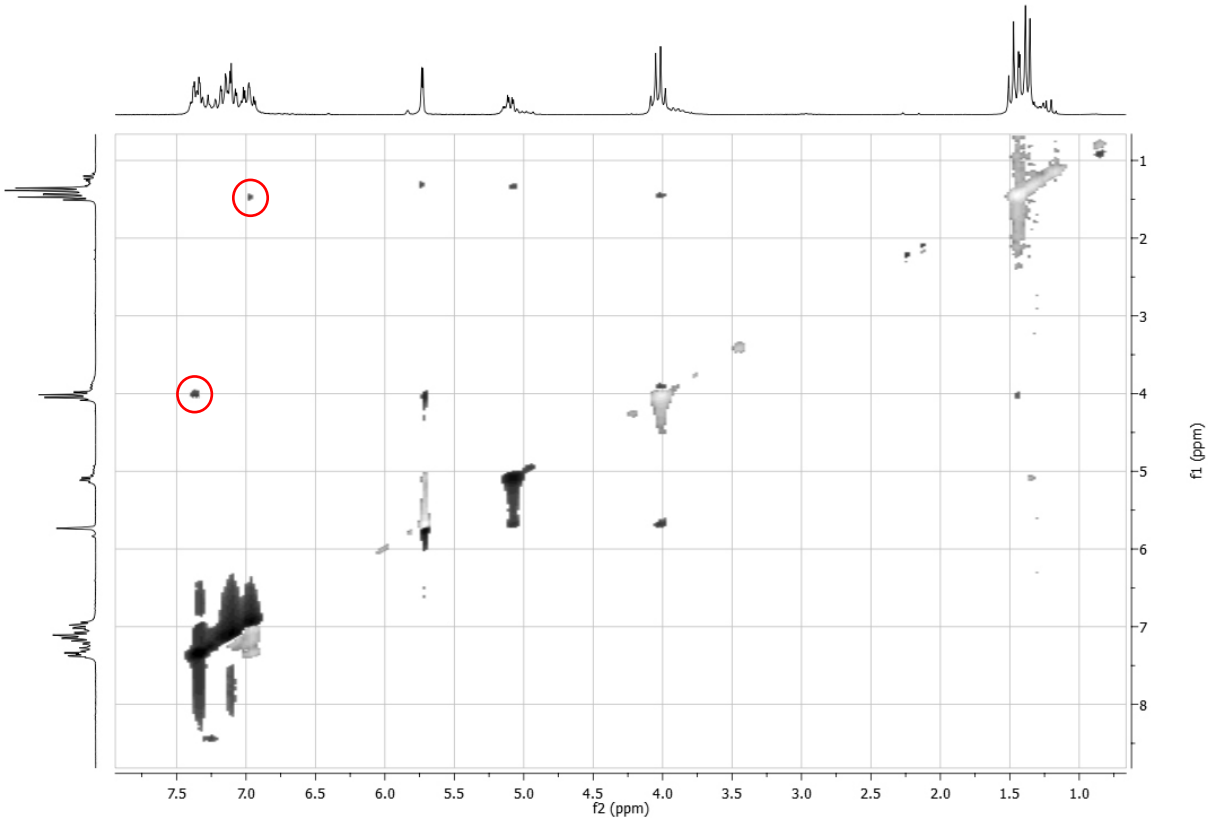




(*E*)-2-chloro-*N*-(3-ethoxy-5-methylfuran-2(5*H*)-ylidene)aniline **5g**.



2D-NOESY



X-ray crystal analyses

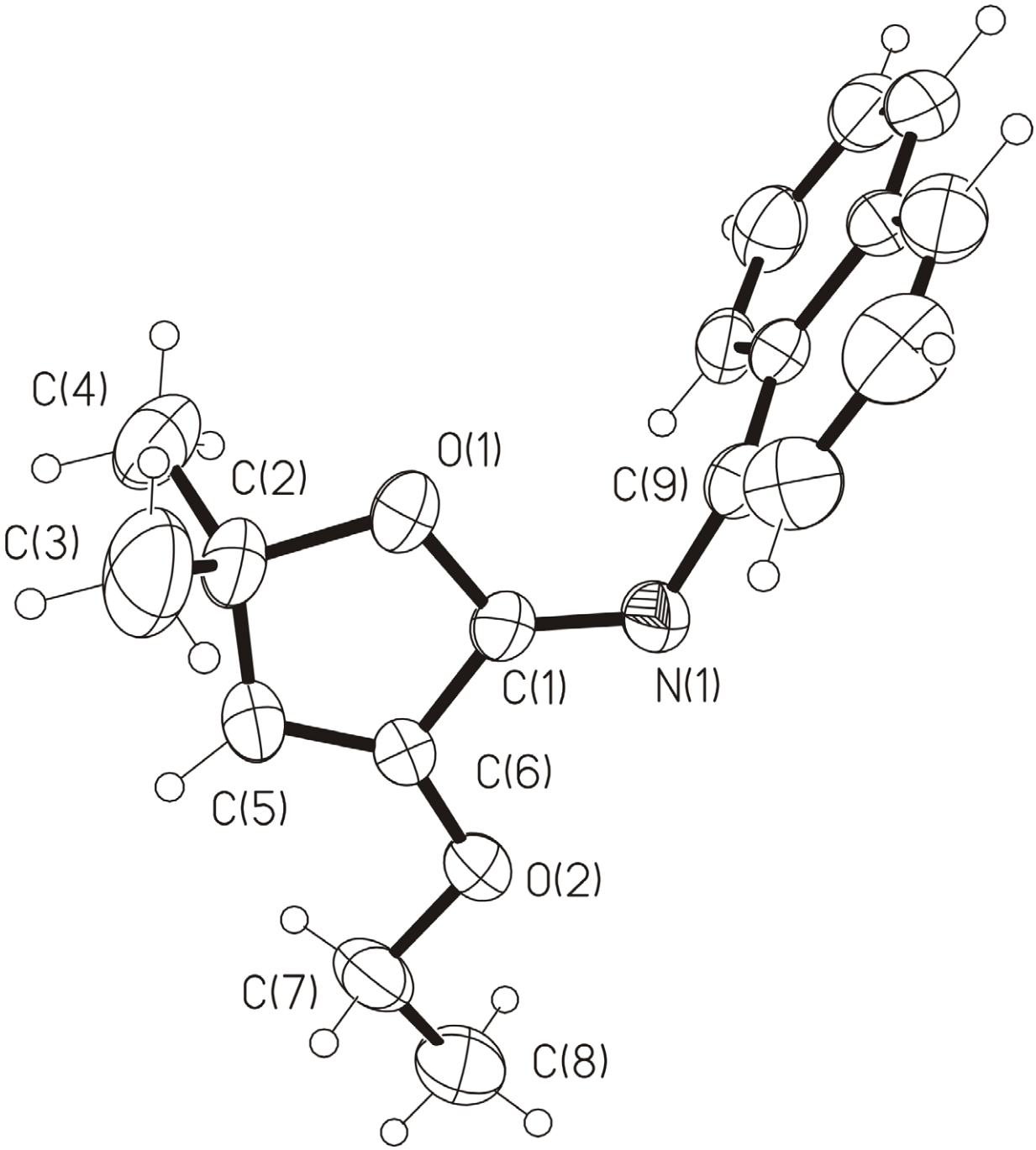
Compound **5j**: mol. formula $C_{18}H_{19}NO_2$, formula weight 281.34, monoclinic $P2_1/c$ space group, a= 14.009(6) Å, b= 8.4952(3) Å, c= 26.8703(12) Å, β= 97.117(4)°, V = 3171.3(2) $Å^3$, Z=8, d= 1.179g cm^{-3}, μ = 0.077 mm^{-1}, R1= 0.0427 for 2747 data with I>2σ(I), wR2 = 0.0773. Two molecules in the asymmetric unit. The C, N, and O atoms have been anisotropically refined. H atoms have been calculated and refined riding on the corresponding atom with U_{iso}. The asymmetric unit contains two molecules, A and B, with different conformation: in the molecule A the naphthalene moiety form an angle of 87° with the penta-atomic ring, in the other molecule B the angle value is 40°. This fact demonstrates the possibility of a free rotation around the N(1)-C(9) bond in the isolated molecule and therefore its single bond feature. The C(1)-N(1) bond values agree with a double bond value (1.263(2) Å av.), and the angle around N(1) is those of a sp^2 hybridization. The C(1)-O(1) and C(6)-O(2) bond values agree with a Csp^2–O distance (1.349(2) Å av), while the C(5)-C(6) corresponds to a double bond (1.318(2) Å av.).[3] The crystal packing shows only weak C–H··N and C–H··O intermolecular hydrogen bonds.[4]

Compound **5f**: mol. formula $C_{17}H_{17}NO_2$, formula weight 281.34, monoclinic $P2_1/n$ space group, a= 8.8274(5) Å, b= 13.2339(6) Å, c= 12.3855(7) Å, β= 103.267(6)°, V = 1408.27(13) $Å^3$, Z= 4, d= 1.261 g cm^{-3}, μ = 0.083 mm^{-1}, R1= 0.0634 for 2012 data with I>2σ(I), wR2 = 0.1687. One part of the molecule (penta-atomic ring) is disordered and isotropically refined. The other C, N, and O atoms have been anisotropically refined. The final Fourier difference-maps have shown the hydrogen atoms, however it was preferred to calculate and refine them riding on the corresponding atom with U_{iso}. Owing to the disorder of the molecule and to the great thermal motion the data have been collected at 153K. The disorder of the pentatomic ring may be described as a reflection with respect to the plane defined by the N(1), C(1) and C(6) atoms. The two pentatomic rings have an asymmetric carbon atom (C(2A) and C(2B)) and the two faced rings are enantiomerically related. The naphthalene moiety and the planes of the pentatomic ring form angles of 143° and 110° respectively (A ring, B ring). Also in **5f** C(1)-N(1) and C(5)-C(6) bonds are formal double bonds (1.247(4) Å and 1.35(1) Å av.), while C(1)-O(1) and C(6)-O(2) distances are in keeping with a Csp^2–O distance (1.413(6) Å av. and 1.321(4) Å, respectively). As in 5i the crystal structure shows only weak C–H··N and C–H··O intermolecular hydrogen bonds.[3]

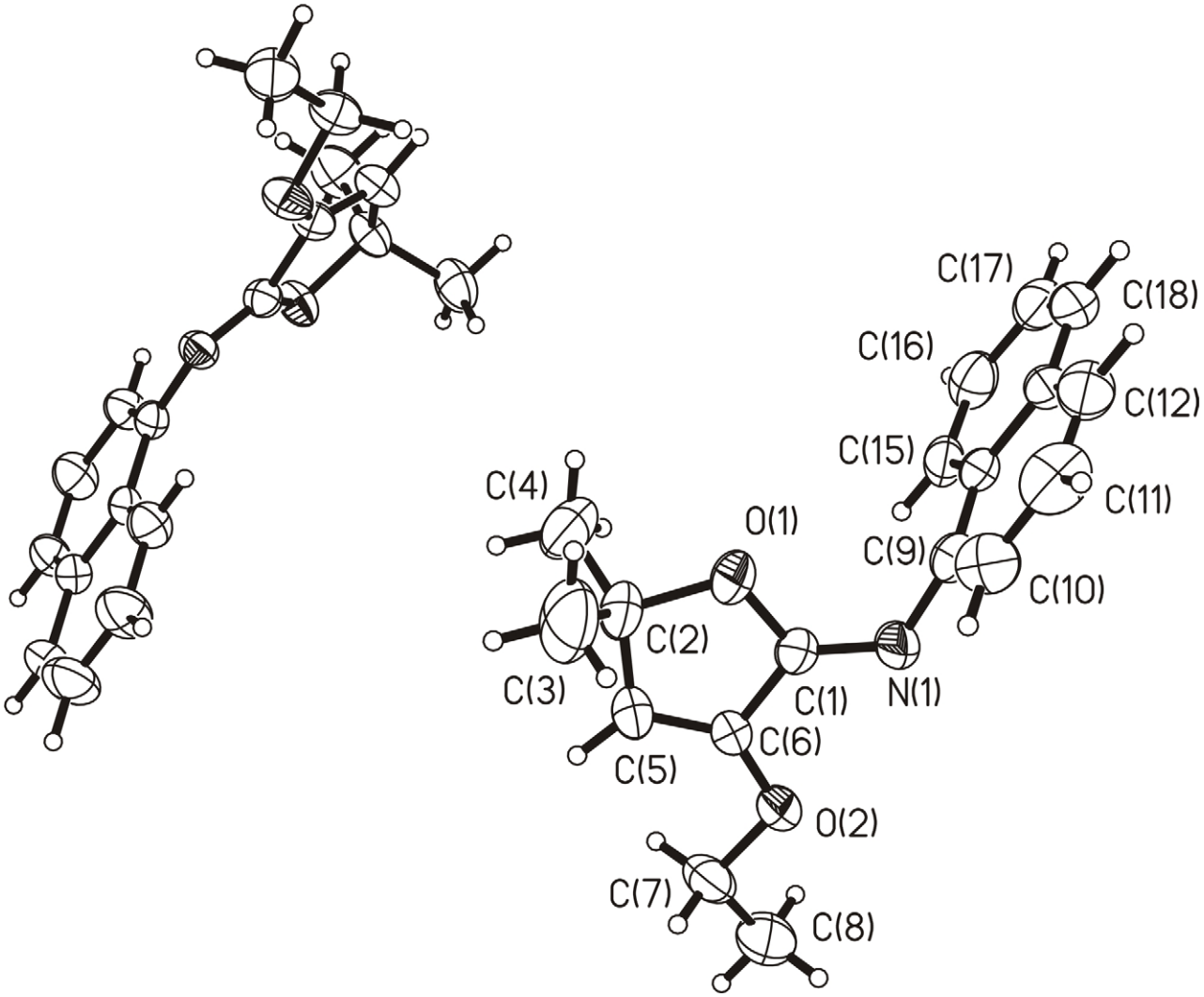
The both data sets have been collected on a Gemini R Ultra diffractometer with MoKα radiation (0.71073 Å) at 293K (**5j**) and at 153K (**5f**). The diffractometer is equipped with a N_2 cooling device. CrysAlisPro[Oxford-Diffraction Ltd,Yarnton, UK] package for data collection and resolution, and SHELXTL for refinement [M.Sheldrick (1997), SHELXTL, Version 5.1, Bruker AXS inc., Madison].

[3] F. H. Allen, O. Kennard, D. G. Watson, et al., *J. Chem. Soc., Perkin Trans. 2* 1987, S1.
[4] G. R. Desiraju, T. Steiner, *The Weak Hydrogen Bond*. Oxford University Press: 1998.

CIF files are deposited at Cambridge Crystallographic Database with CCDC 776929 (**5f**) and CCDC 776930 (**5j**).



ORTEP plot (thermal ellipsoids at 30% of probability) of **5j** (molecule A) showing the atom labeling.



ORTEP plot (thermal ellipsoids at 30% of probability) of **5j** (molecule A and B) showing the atom labeling.

Molecule A

N(1)-C(1)	1.2654(16)
N(1)-C(9)	1.4460(18)
O(1)-C(1)	1.3490(16)
O(1)-C(2)	1.4678(18)
O(2)-C(6)	1.3452(16)
O(2)-C(7)	1.4415(15)
C(1)-C(6)	1.4520(19)
C(2)-C(5)	1.485(2)
C(2)-C(4)	1.512(2)
C(2)-C(3)	1.520(2)
C(3)-H(3A)	0.9600
C(3)-H(3B)	0.9600
C(3)-H(3C)	0.9600
C(4)-H(4A)	0.9600
C(4)-H(4B)	0.9600
C(4)-H(4C)	0.9600
C(5)-C(6)	1.3079(18)
C(5)-H(5A)	0.9300
C(7)-C(8)	1.465(2)

C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(8)-H(8A)	0.9600
C(8)-H(8B)	0.9600
C(8)-H(8C)	0.9600
C(9)-C(10)	1.346(2)
C(9)-C(14)	1.3999(18)
C(10)-C(11)	1.398(2)
C(10)-H(10A)	0.9300
C(11)-C(12)	1.368(2)
C(11)-H(11A)	0.9300
C(12)-C(13)	1.413(2)
C(12)-H(12A)	0.9300
C(13)-C(18)	1.395(2)
C(13)-C(14)	1.4155(19)
C(14)-C(15)	1.4275(18)
C(15)-C(16)	1.367(2)
C(15)-H(15A)	0.9300
C(16)-C(17)	1.378(2)
C(16)-H(16A)	0.9300
C(17)-C(18)	1.335(2)
C(17)-H(17A)	0.9300
C(18)-H(18A)	0.9300

Molecule B

N(1')-C(1')	1.2611(15)
N(1')-C(9')	1.4105(15)
O(1')-C(1')	1.3615(14)
O(1')-C(2')	1.4788(14)
C(1')-C(6')	1.4683(17)
C(2')-C(5')	1.4840(17)
C(2')-C(3')	1.5173(18)
C(2')-C(4')	1.5216(18)
C(3')-H(3'A)	0.9600
C(3')-H(3'B)	0.9600
C(3')-H(3'C)	0.9600
C(4')-H(4'A)	0.9600
C(4')-H(4'B)	0.9600
C(4')-H(4'C)	0.9600
O(2')-C(6')	1.3418(15)
O(2')-C(7')	1.4410(14)
C(5')-C(6')	1.3281(16)
C(5')-H(5'A)	0.9300
C(7')-C(8')	1.4944(17)
C(7')-H(7'A)	0.9700
C(7')-H(7'B)	0.9700
C(8')-H(8'A)	0.9600
C(8')-H(8'B)	0.9600
C(8')-H(8'C)	0.9600
C(9')-C(10')	1.3737(17)
C(9')-C(14')	1.4309(16)
C(10')-C(11')	1.4027(18)
C(10')-H(10B)	0.9300
C(11')-C(12')	1.3522(18)
C(11')-H(11B)	0.9300
C(12')-C(13')	1.4012(18)
C(12')-H(12B)	0.9300
C(13')-C(18')	1.4140(18)
C(13')-C(14')	1.4153(17)
C(14')-C(15')	1.4028(17)

C(15')-C(16')	1.3630(18)
C(15')-H(15B)	0.9300
C(16')-C(17')	1.396(2)
C(16')-H(16B)	0.9300
C(17')-C(18')	1.344(2)
C(17')-H(17B)	0.9300
C(18')-H(18B)	0.9300

Molecule A

C(1)-N(1)-C(9)	119.87(13)
C(1)-O(1)-C(2)	109.10(13)
C(6)-O(2)-C(7)	113.61(12)
N(1)-C(1)-O(1)	123.77(15)
N(1)-C(1)-C(6)	127.46(15)
O(1)-C(1)-C(6)	108.78(13)
O(1)-C(2)-C(5)	102.80(12)
O(1)-C(2)-C(4)	107.84(14)
C(5)-C(2)-C(4)	112.54(17)
O(1)-C(2)-C(3)	106.93(16)
C(5)-C(2)-C(3)	113.31(16)
C(4)-C(2)-C(3)	112.63(15)
C(2)-C(3)-H(3A)	109.5
C(2)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	109.5
C(2)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5
C(2)-C(4)-H(4A)	109.5
C(2)-C(4)-H(4B)	109.5
H(4A)-C(4)-H(4B)	109.5
C(2)-C(4)-H(4C)	109.5
H(4A)-C(4)-H(4C)	109.5
H(4B)-C(4)-H(4C)	109.5
C(6)-C(5)-C(2)	110.48(14)
C(6)-C(5)-H(5A)	124.8
C(2)-C(5)-H(5A)	124.8
C(5)-C(6)-O(2)	133.43(15)
C(5)-C(6)-C(1)	108.76(15)
O(2)-C(6)-C(1)	117.81(13)
O(2)-C(7)-C(8)	108.64(13)
O(2)-C(7)-H(7A)	110.0
C(8)-C(7)-H(7A)	110.0
O(2)-C(7)-H(7B)	110.0
C(8)-C(7)-H(7B)	110.0
H(7A)-C(7)-H(7B)	108.3
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(10)-C(9)-C(14)	120.36(16)
C(10)-C(9)-N(1)	121.14(17)
C(14)-C(9)-N(1)	118.30(17)
C(9)-C(10)-C(11)	120.89(18)
C(9)-C(10)-H(10A)	119.6
C(11)-C(10)-H(10A)	119.6
C(12)-C(11)-C(10)	120.87(18)
C(12)-C(11)-H(11A)	119.6
C(10)-C(11)-H(11A)	119.6
C(11)-C(12)-C(13)	119.25(17)

C(11)-C(12)-H(12A)	120.4
C(13)-C(12)-H(12A)	120.4
C(18)-C(13)-C(12)	122.16(18)
C(18)-C(13)-C(14)	118.64(17)
C(12)-C(13)-C(14)	119.21(16)
C(9)-C(14)-C(13)	119.36(16)
C(9)-C(14)-C(15)	122.53(16)
C(13)-C(14)-C(15)	118.11(15)
C(16)-C(15)-C(14)	119.72(15)
C(16)-C(15)-H(15A)	120.1
C(14)-C(15)-H(15A)	120.1
C(15)-C(16)-C(17)	121.04(18)
C(15)-C(16)-H(16A)	119.5
C(17)-C(16)-H(16A)	119.5
C(18)-C(17)-C(16)	120.30(19)
C(18)-C(17)-H(17A)	119.8
C(16)-C(17)-H(17A)	119.8
C(17)-C(18)-C(13)	122.16(18)
C(17)-C(18)-H(18A)	118.9
C(13)-C(18)-H(18A)	118.9

Molecule B

C(1')-N(1')-C(9')	123.84(12)
C(1')-O(1')-C(2')	109.99(10)
N(1')-C(1')-O(1')	127.13(12)
N(1')-C(1')-C(6')	125.52(14)
O(1')-C(1')-C(6')	107.34(12)
O(1')-C(2')-C(5')	103.08(11)
O(1')-C(2')-C(3')	107.29(11)
C(5')-C(2')-C(3')	113.57(13)
O(1')-C(2')-C(4')	107.15(11)
C(5')-C(2')-C(4')	112.38(13)
C(3')-C(2')-C(4')	112.58(13)
C(2')-C(3')-H(3'A)	109.5
C(2')-C(3')-H(3'B)	109.5
H(3'A)-C(3')-H(3'B)	109.5
C(2')-C(3')-H(3'C)	109.5
H(3'A)-C(3')-H(3'C)	109.5
H(3'B)-C(3')-H(3'C)	109.5
C(2')-C(4')-H(4'A)	109.5
C(2')-C(4')-H(4'B)	109.5
H(4'A)-C(4')-H(4'B)	109.5
C(2')-C(4')-H(4'C)	109.5
H(4'A)-C(4')-H(4'C)	109.5
H(4'B)-C(4')-H(4'C)	109.5
C(6')-O(2')-C(7')	115.43(11)
C(6')-C(5')-C(2')	109.97(13)
C(6')-C(5')-H(5'A)	125.0
C(2')-C(5')-H(5'A)	125.0
C(5')-C(6')-O(2')	133.08(13)
C(5')-C(6')-C(1')	109.58(14)
O(2')-C(6')-C(1')	117.33(13)
O(2')-C(7')-C(8')	106.87(12)
O(2')-C(7')-H(7'A)	110.3
C(8')-C(7')-H(7'A)	110.3
O(2')-C(7')-H(7'B)	110.3
C(8')-C(7')-H(7'B)	110.3
H(7'A)-C(7')-H(7'B)	108.6
C(7')-C(8')-H(8'A)	109.5
C(7')-C(8')-H(8'B)	109.5
H(8'A)-C(8')-H(8'B)	109.5

C(7')-C(8')-H(8'C)	109.5
H(8'A)-C(8')-H(8'C)	109.5
H(8'B)-C(8')-H(8'C)	109.5
C(10')-C(9')-N(1')	124.48(12)
C(10')-C(9')-C(14')	118.63(13)
N(1')-C(9')-C(14')	116.75(13)
C(9')-C(10')-C(11')	121.08(14)
C(9')-C(10')-H(10B)	119.5
C(11')-C(10')-H(10B)	119.5
C(12')-C(11')-C(10')	120.92(15)
C(12')-C(11')-H(11B)	119.5
C(10')-C(11')-H(11B)	119.5
C(11')-C(12')-C(13')	120.52(14)
C(11')-C(12')-H(12B)	119.7
C(13')-C(12')-H(12B)	119.7
C(12')-C(13')-C(18')	121.33(15)
C(12')-C(13')-C(14')	119.43(14)
C(18')-C(13')-C(14')	119.24(15)
C(15')-C(14')-C(13')	118.33(13)
C(15')-C(14')-C(9')	122.25(13)
C(13')-C(14')-C(9')	119.42(14)
C(16')-C(15')-C(14')	120.92(14)
C(16')-C(15')-H(15B)	119.5
C(14')-C(15')-H(15B)	119.5
C(15')-C(16')-C(17')	120.26(16)
C(15')-C(16')-H(16B)	119.9
C(17')-C(16')-H(16B)	119.9
C(18')-C(17')-C(16')	120.80(16)
C(18')-C(17')-H(17B)	119.6
C(16')-C(17')-H(17B)	119.6
C(17')-C(18')-C(13')	120.44(15)
C(17')-C(18')-H(18B)	119.8
C(13')-C(18')-H(18B)	119.8

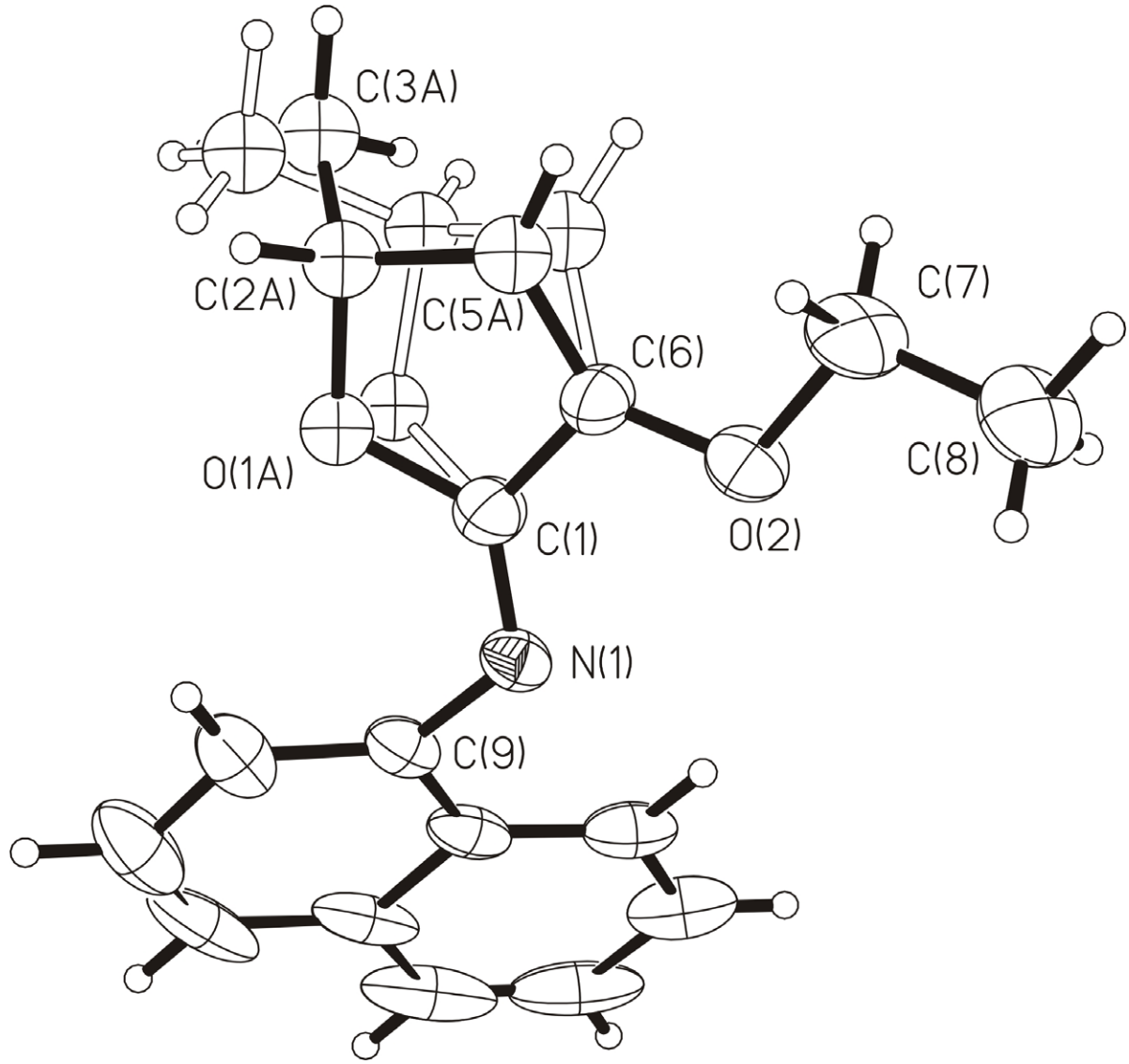


Figure 3. ORTEP plot (thermal ellipsoids at 30% of probability) of **5f** molecule showing the atom labeling. The two disordered rings are shown: the ring with open bonds corresponds to the occupancy factor 0.38 (ring B).

N(1)-C(1)	1.247(4)
N(1)-C(9)	1.424(4)
C(1)-O(1A)	1.378(5)
C(1)-O(1B)	1.448(6)
C(1)-C(6)	1.461(5)
O(1A)-C(2A)	1.475(6)
C(2A)-C(5A)	1.464(8)
C(2A)-C(3A)	1.477(9)
C(2A)-H(2AA)	0.9800
C(3A)-H(3AA)	0.9600
C(3A)-H(3AB)	0.9600
C(3A)-H(3AC)	0.9600
C(5A)-C(6)	1.316(6)
C(5A)-H(5AA)	0.9300
O(1B)-C(2B)	1.488(11)
C(2B)-C(5B)	1.494(13)

C(2B)-C(3B)	1.579(16)
C(2B)-H(2BA)	0.9800
C(3B)-H(3BA)	0.9600
C(3B)-H(3BB)	0.9600
C(3B)-H(3BC)	0.9600
C(5B)-C(6)	1.389(11)
C(5B)-H(5BB)	0.9300
C(6)-O(2)	1.321(4)
O(2)-C(7)	1.458(4)
C(7)-C(8)	1.421(5)
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(8)-H(8A)	0.9600
C(8)-H(8B)	0.9600
C(8)-H(8C)	0.9600
C(9)-C(10)	1.367(5)
C(9)-C(14)	1.410(5)
C(10)-C(11)	1.389(6)
C(10)-H(10A)	0.9300
C(11)-C(12)	1.334(7)
C(11)-H(11A)	0.9300
C(12)-C(13)	1.409(7)
C(12)-H(12A)	0.9300
C(13)-C(18)	1.392(8)
C(13)-C(14)	1.435(5)
C(14)-C(15)	1.398(5)
C(15)-C(16)	1.381(5)
C(15)-H(15A)	0.9300
C(16)-C(17)	1.423(8)
C(16)-H(16A)	0.9300
C(17)-C(18)	1.338(7)
C(17)-H(17A)	0.9300
C(18)-H(18A)	0.9300
C(1)-N(1)-C(9)	121.8(3)
N(1)-C(1)-O(1A)	124.7(3)
N(1)-C(1)-O(1B)	119.9(3)
O(1A)-C(1)-O(1B)	35.7(2)
N(1)-C(1)-C(6)	127.5(3)
O(1A)-C(1)-C(6)	106.3(3)
O(1B)-C(1)-C(6)	108.2(3)
C(1)-O(1A)-C(2A)	109.3(3)
C(5A)-C(2A)-O(1A)	103.9(5)
C(5A)-C(2A)-C(3A)	115.4(5)
O(1A)-C(2A)-C(3A)	108.3(5)
C(5A)-C(2A)-H(2AA)	109.7
O(1A)-C(2A)-H(2AA)	109.7
C(3A)-C(2A)-H(2AA)	109.7
C(2A)-C(3A)-H(3AA)	109.5
C(2A)-C(3A)-H(3AB)	109.5
H(3AA)-C(3A)-H(3AB)	109.5
C(2A)-C(3A)-H(3AC)	109.5
H(3AA)-C(3A)-H(3AC)	109.5
H(3AB)-C(3A)-H(3AC)	109.5
C(6)-C(5A)-C(2A)	109.8(5)
C(6)-C(5A)-H(5AA)	125.1
C(2A)-C(5A)-H(5AA)	125.1
C(1)-O(1B)-C(2B)	108.3(5)
O(1B)-C(2B)-C(5B)	103.6(8)
O(1B)-C(2B)-C(3B)	106.7(7)
C(5B)-C(2B)-C(3B)	118.3(8)
O(1B)-C(2B)-H(2BA)	109.3
C(5B)-C(2B)-H(2BA)	109.3

C(3B)-C(2B)-H(2BA)	109.3
C(2B)-C(3B)-H(3BA)	109.5
C(2B)-C(3B)-H(3BB)	109.5
H(3BA)-C(3B)-H(3BB)	109.5
C(2B)-C(3B)-H(3BC)	109.5
H(3BA)-C(3B)-H(3BC)	109.5
H(3BB)-C(3B)-H(3BC)	109.5
C(6)-C(5B)-C(2B)	110.9(8)
C(6)-C(5B)-H(5BB)	124.6
C(2B)-C(5B)-H(5BB)	124.6
C(5A)-C(6)-O(2)	129.7(4)
C(5A)-C(6)-C(5B)	35.3(4)
O(2)-C(6)-C(5B)	127.4(5)
C(5A)-C(6)-C(1)	110.6(4)
O(2)-C(6)-C(1)	118.4(3)
C(5B)-C(6)-C(1)	108.0(5)
C(6)-O(2)-C(7)	114.2(3)
C(8)-C(7)-O(2)	109.7(3)
C(8)-C(7)-H(7A)	109.7
O(2)-C(7)-H(7A)	109.7
C(8)-C(7)-H(7B)	109.7
O(2)-C(7)-H(7B)	109.7
H(7A)-C(7)-H(7B)	108.2
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(10)-C(9)-C(14)	119.9(3)
C(10)-C(9)-N(1)	122.5(3)
C(14)-C(9)-N(1)	117.4(3)
C(9)-C(10)-C(11)	121.0(4)
C(9)-C(10)-H(10A)	119.5
C(11)-C(10)-H(10A)	119.5
C(12)-C(11)-C(10)	121.0(5)
C(12)-C(11)-H(11A)	119.5
C(10)-C(11)-H(11A)	119.5
C(11)-C(12)-C(13)	121.1(4)
C(11)-C(12)-H(12A)	119.5
C(13)-C(12)-H(12A)	119.5
C(18)-C(13)-C(12)	123.1(5)
C(18)-C(13)-C(14)	118.3(5)
C(12)-C(13)-C(14)	118.6(4)
C(15)-C(14)-C(9)	123.0(3)
C(15)-C(14)-C(13)	118.5(4)
C(9)-C(14)-C(13)	118.5(4)
C(16)-C(15)-C(14)	121.6(4)
C(16)-C(15)-H(15A)	119.2
C(14)-C(15)-H(15A)	119.2
C(15)-C(16)-C(17)	118.7(5)
C(15)-C(16)-H(16A)	120.7
C(17)-C(16)-H(16A)	120.7
C(18)-C(17)-C(16)	120.4(5)
C(18)-C(17)-H(17A)	119.8
C(16)-C(17)-H(17A)	119.8
C(17)-C(18)-C(13)	122.5(5)
C(17)-C(18)-H(18A)	118.7
C(13)-C(18)-H(18A)	118.7