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# Supporting Information

## A Rare γ-Pyranopyrazole Skeleton: Design, One-Pot Synthesis and Computational study

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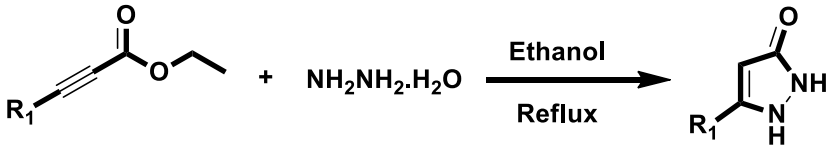
## 1. General Methods

All reagents were purchased from commercial suppliers (Aldrich and Merck) and they were used without further purification unless otherwise noted. The compounds were analyzed by Thermo Science ISQGC-MS and isolated by column chromatography using a hexane-ethyl acetate eluent. $^{1}H$ NMR and $^{13}C$ NMR were measured on a Varian VNMRJ 400 Nuclear Magnetic Resonance Spectrometer and chemical shifts were calibrated using residual solvents signals ($CDCl_3$: δ (H)= 7.26, δ (C)= 77) or TMS. Infrared spectra were obtained using a Perkin–Elmer Spectrum 100 by ATR method with neat samples. Melting points were determined by using an Electrothermal Melting Point Apparatus 9200. UV absorption spectra were measured on Shimadzu UV-2550 Spectrophotometer. All computations were carried out with the Gaussian 09 program package.[1] Fluorescence experiments were performed by using Varian Cary Eclipse Fluorescence spectrophotometer. Samples were contained in 10.0 mm path length quartz cuvettes (2.0 mL volume). Upon excitation at 250 nm, the emission spectra were integrated over the range 270 nm to 600 nm. The slit width was 10 nm for both excitation and emission. All measurements were conducted at least in triplicate.

## 2. Experimental Section

Alkynoic acid derivatives were synthesized by using literature methods.[2,3]

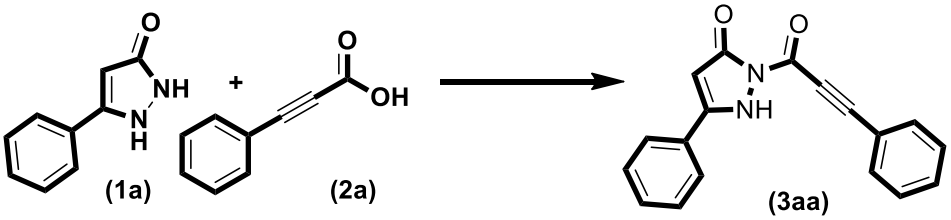
### a. General Method for Synthesis of Pyrazole Compounds




(1)

Pyrazole compounds were synthesized by using literature procedure. To a solution of ethyl alkynoate (10 mmol) in absolute ethanol (20 mL) 2 equivalents of hydrazine hydrate ($NH_2NH_2.H_2O$, 20 mmol 50-60 % in water) was added and solution stirred at reflux temperature for overnight. Then, the solution was cooled to room temperature and the resultant precipitate was filtered with cold ethanol (3 x 50mL). The obtained solid was dried under reduced pressure and used without further purification.

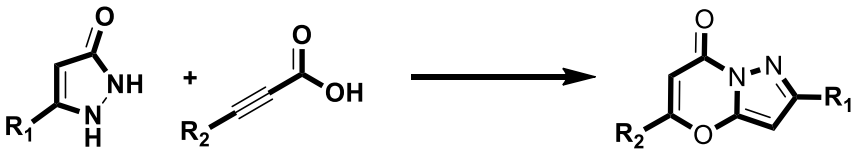
### b. Synthesis of compound (3aa)




(1a) (2a) (3aa)

To a solution of pyrazol compound (1a) (32 mg, 0.2 mmol) in tetrahydrofuran (2 mL) 1.2 equivalents of phenyl propiolic acid (2) (30 mg, 0.24 mmol) was added and solution stirred for a minute under argon atmosphere. Then, 0.3 equivalent of dimethylaminopyridine (DMAP) (7.3 mg, 0.06 mmol) and 1.2 equivalents of N,N'-dicyclohexylcarbodiimide (DCC) (49.5 mg, 0.24 mmol) were added successively. The progress of reaction was monitored by using thin layer chromatography. When all starting materials consumed the solvent was removed under reduced pressure and the product was isolated by using a short pad of silica as quick as possible.

### c. General Method for Synthesis of Flavone Compounds

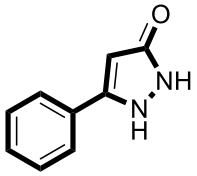



(1) (2) (6)

To a solution of pyrazol compound (1) (0.2 mmol) in tetrahydrofuran (2 mL) 1.2 equivalents of corresponding propiolic acid (2) (0.24 mmol) was added and solution stirred for a minute under argon atmosphere. Then, 0.3 equivalent of dimethylaminopyridine (DMAP) (7.3 mg, 0.06 mmol) and 1.2 equivalents of N,N'-dicyclohexylcarbodiimide (DCC) (49.5 mg, 0.24 mmol) were added successively. The progress of reaction was monitored by using thin layer chromatography. When all starting materials consumed 2 equivalents of $Cs_2CO_3$ (130.4 mg, 0.4 mmol) was added and the reaction was stirred completion of reaction. Then, solvent was removed under reduced pressure and the resultant residue extracted with dichloromethane (3 x 30 mL). Collected organic layers were dried over $Na_2SO_4$ and the solvent was evaporated under vacuo. The resultant residue was prufied by slica gel column chromatography.

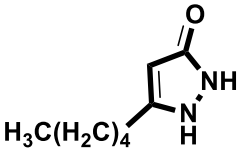
## 3. Characterization Data for Synthesized Compounds

***5-phenyl-1H-pyrazol-3(2H)-one, (2a)***



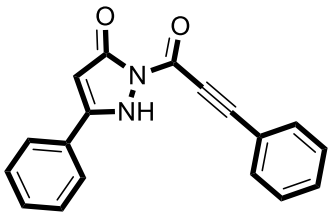

White solid (85 % yield). Mp: 250-252 ºC. $^{1}$H NMR (400 MHz, DMSO-$d_6$) δ (ppm): 11.16 (bs, 2H), 7.66 (d, J= 7.6 Hz, 2H), 7.38 (t, J=7.6 Hz, 2H), 7.28 (t, J= 7.6Hz, 1H), 5.89 (s, 1H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ (ppm): 166.2, 148.6, 135.7, 134.0, 132.5, 132.9, 129.7, 129.9, 92.0. MS (EI, *m/z*): 160 (100, $M^+$), 131 (22), 118 (7), 103 (86), 77 (48). IR (ATR, neat) cm$^{-1}$: υ 1618 [(C=O)], 1596, 1500 [(C=C, C=N)].

***5-pentyl-1H-pyrazol-3(2H)-one, (2b)***



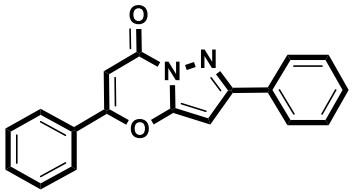

White solid (70 % yield). Mp: 200-202 ºC. $^{1}$H NMR (400 MHz, DMSO-$d_6$) δ (ppm): 10.37 (bs, 2H), 5.22 (s, 1H), 2.41 (t, J=7.6 Hz, 2H), 1.51 (pent, J= 7.6 Hz, 2H), 1.30-1.22 (m, 4H), 0.84 (t, J=6.8 Hz, 3H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ (ppm): 161.4, 144.8, 88.4, 31.2, 28.8, 26.0, 22.2, 14.3. MS (EI, *m/z*): 154 (13, $M^+$), 125 (4), 111 (25), 98 (100), 67 (9). IR (ATR, neat) cm$^{-1}$: υ 2989 [(C-H)], 1611 [(C=O)], 1543, 1499, 1455 [(C=C, C=N)].

***5-phenyl-2-(3-phenylpropioloyl)-1H-pyrazol-3(2H)-one, (3aa)***



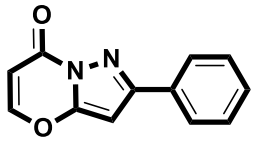

$^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm): 11.22 (bs, 1H), 7.65-7.62 (m, 4H), 7.52-7.34 (m, 6H), 6.55 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm): 155.6, 150.6, 144.5, 133.3, 131.1, 129.1, 129.0, 128.9, 128.7, 125.5, 119.1, 93.7, 89.3, 79.8. MS (EI, *m/z*): 288 (42, $M^+$), 259 (10), 232 (14), 206 (22), 193 (7), 129 (96), 116 (16), 102 (100), 89 (17), 77 (33). IR (ATR, neat) cm$^{-1}$: υ 2231 [(C≡C)], 1731 [(C=O)].

***2,5-diphenyl-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6aa)***



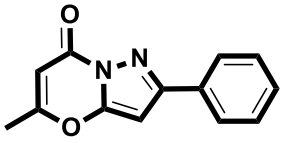
White solid (47.3 mg, 82 % yield). Mp: 200-202 ºC. $^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.02-7.99 (m, 2H), 7.89-7.87 (m, 2H), 7.63-7.54 (m, 3H), 7.49-7.41 (m, 3H), 6.56 (s, 1H), 6.55 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm): 162.3, 155.1, 154.3, 152.0, 132.5, 131.5, 129.7, 129.5, 128.7, 126.6, 126.4, 97.0, 87.2. MS (EI, *m/z*): 288 (3, M+), 260 (2), 231 (2), 203 (2), 155 (1), 129 (18), 102 (100), 77(17). IR (ATR, neat) $cm^{-1}$: υ 1718 [(C=O)], 1620, 1595, 1572 [(C=C, C=N)].

***2-phenyl-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6ab)***



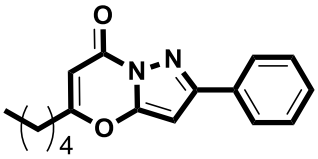
White solid (10.6 mg, 25 % yield). Mp: 153-155ºC. $^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.99 – 7.95 (m, 2H), 7.68 (d, *J*= 6.0 Hz, 1H), 7.48 – 7.41 (m, 3H), 6.49 (s, 1H), 6.17 (d, *J*= 6.0 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm): 155.0, 153.4, 153.1, 153.1, 131.3, 129.8, 128.7, 126.6, 100.1, 87.4. MS (EI, *m/z*): 212 (27, $M^+$), 184 (6), 155 (6), 128 (42), 102 (67), 76 (34), 54 (100). IR (ATR, neat) $cm^{-1}$: υ 1726 [(C=O)], 1610, 1595, 1574 [(C=C, C=N)].

***5-methyl-2-phenyl-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6ac)***



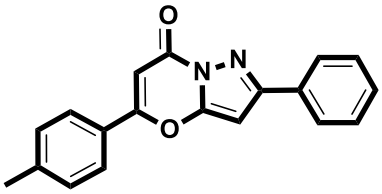
White solid (25.8 mg, 57 % yield). Mp: 142-144ºC. $^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.98 – 7.95 (m, 2H), 7.47 – 7.41 (m, 3H), 6.41 (s, 1H), 5.94 (s, 1H), 2.40 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm): 164.7, 154.8, 153.9, 152.3, 131.5, 129.6, 128.7, 126.6, 100.2, 86.7, 19.6. MS (EI, *m/z*): 226 (10, $M^+$), 197 (7), 155 (2), 141 (3), 127 (5), 102 (41), 76 (18), 53 (100). IR (ATR, neat) $cm^{-1}$: υ 1711 [(C=O)], 1624, 1594, 1573 [(C=C, C=N)].

***5-pentyl-2-phenyl-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6ad)***



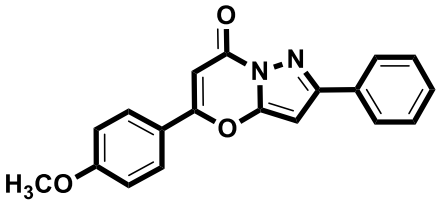
Bright solid (28.2 mg, 50 % yield). Mp: 111-113°C. $^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.98 – 7.95 (m, 2H), 7.47 – 7.40 (m, 3H), 6.41 (s, 1H), 5.92 (s, 1H), 2.61 (t, *J*= 7.6 Hz, 2H), 1.77 – 1.70 (m, 2H), 1.43 – 1.37 (m, 4H), 0.95 – 0.91 (m, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.4, 154.8, 154.1, 152.3, 131.5, 129.5, 128.6, 126.5, 99.3, 86.7, 33.2, 30.9, 26.1, 22.2, 13.8. MS (EI, *m/z*): 282 (23, $M^+$), 239 (3), 226 (8), 207 (10), 197 (100), 161 (11), 123 (15), 102 (41), 67 (100). IR (ATR, neat) $cm^{-1}$: υ 1718 [(C=O)], 1627, 1591, 1572 [(C=C, C=N)].

***2-phenyl-5-(p-tolyl)-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6ae)***



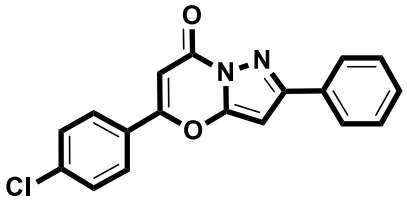
White solid (45.3 mg, 75 % yield). Mp: 233-235°C. $^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.01 - 7.98 (m, 2H), 7.77 - 7.74 (m, 2H), 7.48 – 7.40 (m, 3H), 7.34 (d, *J*= 8 Hz, 2H), 2.45 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm): 162.5, 155.0, 154.4, 152.0, 143.4, 131.5, 130.0, 129.6, 128.7, 126.6, 126.2, 96.1, 87.1, 21.6. MS (EI, *m/z*): 302 (14, $M^+$), 274 (10), 207 (12), 151 (6), 143 (45), 115 (95), 102 (100), 76 (41). IR (ATR, neat) $cm^{-1}$: υ 1717 [(C=O)], 1617, 1591, 1570 [(C=C, C=N)].

***5-(4-methoxyphenyl)-2-phenyl-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6af)***



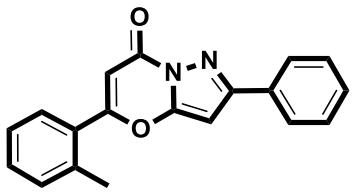
Light brown solid (45.8 mg, 72 % yield). Mp: 238-240°C. $^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.02 – 7.99 (m, 2H), 7.85 – 7.81 (m, 2H), 7.49 – 7.40 (m, 3H), 7.07 – 7.03 (m, 2H), 6.53 (s, 1H), 6.44 (s, 1H), 3.91 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm): 163.1, 162.3, 154.9, 152.0, 131.6, 129.6, 128.7, 126.6, 121.7, 114.7, 95.2, 87.0, 55.6. MS (EI, *m/z*): 318 (5, $M^+$), 275 (1), 247 (1), 159 (36), 132 (26), 117 (25), 102 (100), 89 (46), 76 (31). IR (ATR, neat) $cm^{-1}$: υ 1716 [(C=O)], 1640, 1605, 1572 [(C=C, C=N)].

***5-(4-chlorophenyl)-2-phenyl-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6ag)***



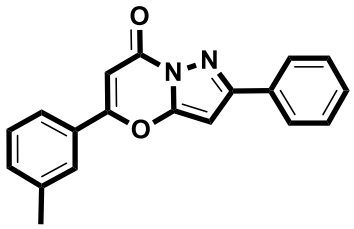

Pale yellow solid (49.0 mg, 76 % yield). Mp: 235-237°C. $^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm): : 8.00 – 7.97 (m, 2H), 7.82 – 7.79 (m, 2H), 7.54 – 7.52 (m, 2H), 7.48 – 7.42 (m, 3H), 6.54 (s, 1H), 6.50 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm): 161.1, 155.2, 154.0, 151.8, 138.9, 131.4, 129.7, 128.7, 127.9, 127.6, 126.6, 97.1, 87.3. MS (EI, *m/z*): 322 (3, $M^+$), 294 (2), 207 (5), 163 (10), 136 (28), 102 (100), 75 (31). IR (ATR, neat) $cm^{-1}$: υ 1716 [(C=O)], 1615, 1594, 1576 [(C=C, C=N)].

***2-phenyl-5-(o-tolyl)-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6ah)***



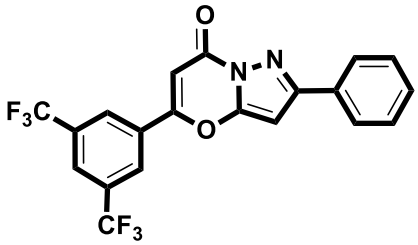

Bright solid (46.5 mg, 77 % yield). Mp: 135-137°C. $^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.01 – 7.98 (m, 2H), 7.55 – 7.53 (m, 1H), 7.47 – 7.42 (m, 3H), 7.36 – 7.33 (m, 2H), 6.50 (s, 1H), 6.24 (s, 1H), 2.51 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm): 164.4, 155.1, 154.1, 152.2, 136.9, 131.6, 131.5, 131.5, 130.2, 129.6, 129.2, 128.7, 126.6, 126.4, 101.4, 87.1, 20.5. MS (EI, *m/z*): 302 (18, $M^+$), 274 (9), 207 (2), 169 (2), 143 (74), 115 (100), 102 (54), 89 (51), 76 (13). IR (ATR, neat) $cm^{-1}$: υ 1726 [(C=O)], 1626, 1591, 1574 [(C=C, C=N)].

***2-phenyl-5-(m-tolyl)-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6ai)***



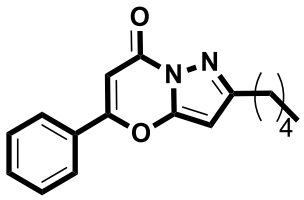

White solid (42.9 mg, 71 % yield). Mp: 208- 210°C. $^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.02 – 7.99 (m, 2H), 7.68 – 7.66 (m, 2H), 7.48 – 7.39 (m, 5H), 6.55 (s, 1H), 6.53 (s, 1H), 2. 47 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm): 162.5, 155.0, 154.4, 152.0, 139.2, 133.3, 131.5, 129.7, 129.4, 129.2, 128.7, 126.8, 126.6, 123.5, 96.8, 87.1, 21.2. MS (EI, *m/z*): 302 (24, $M^+$), 274 (26), 245 (4), 230 (5), 207 (17), 143 (100), 115 (80), 102 (60), 89 (23), 73 (36). IR (ATR, neat) $cm^{-1}$: υ 1711 [(C=O)], 1618, 1592, 1573 [(C=C, C=N)].

***5-(3,5-bis(trifluoromethyl)phenyl)-2-phenyl-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6aj)***



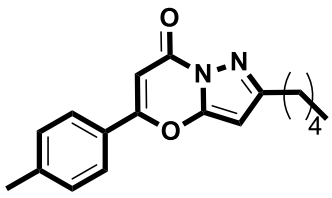
White solid (65.3 mg, 77 % yield). Mp: 241-243°C. $^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.31 (s, 2H), 8.10 (s, 1H), 8.01 – 7.99 (m, 2H), 7.50 – 7.43 (m, 3H), 6.67 (s, 1H), 6.65 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm): : 158.7, 155.6, 153.2, 151.5, 133.3, 133.0, 131.8, 130.0, 128.8, 126.7, 126.3, 125.7, 99.3, 87.8. MS (EI, *m/z*): 424 (13, $M^+$), 396 (16), 367 (2), 339 (2), 327 (5), 299 (9), 271 (14), 238 (8), 169 (23), 155 (6), 127 (9), 102 (100), 77 (21). IR (ATR, neat) $cm^{-1}$: υ 1734 [(C=O)], 1625, 1594, 1577 [(C=C, C=N)].

***2-pentyl-5-phenyl-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6ba)***



Light brown solid (26.5 mg, 47 % yield). Mp: 103-105°C. $^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.85 (d, *J*= 7.2 Hz, 2H), 7.60 – 7.52 (m, 3H), 6.48 (s, 1H), 6.05 (s, 1H), 2.76 (d, *J*= 7.8 Hz, 2H), 1.75 – 1.70 (m, 2H), 1.39 – 1.35 (m, 4H), 0.91 (t, *J*= 6.8 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm): 162.0, 158.7, 154.2, 151.4, 132.3, 129.6, 129.2, 126.3, 96.7, 88.8, 31.5, 29.2, 28.6, 22.4, 14.0. MS (EI, *m/z*): 282 (2, $M^+$), 239 (10), 226 (20), 214 (3), 197 (1), 147 (3), 129 (100), 102 (17), 76 (9). IR (ATR, neat) $cm^{-1}$: υ 1718 [(C=O)], 1621, 1590, 1576 [(C=C, C=N)].

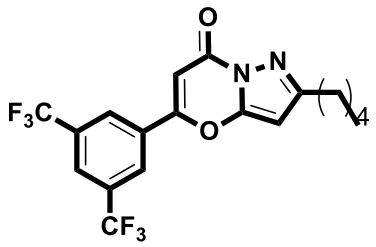
***2-pentyl-5-(p-tolyl)-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6be)***



Light brown solid (29.6 mg, 50 % yield). Mp: 110-112°C. $^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.75 – 7.72 (m, 2H), 7.33 (d, *J*= 8.0 Hz, 2H), 6.43 (s, 1H), 6.04 (s, 1H), 2.76 (t, *J*= 7.8 Hz, 2H), 2.45 (s, 3H), 1.77 – 1.69 (m, 2H), 1.39 – 1.34 (m, 4H), 0.90 (t, *J*= 7.0 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm): 162.2, 158.6, 154.4, 151.4, 143.2, 129.9, 126.7, 126.2, 95.9, 88.7, 31.4, 29.2, 28.6, 22.4, 21.6, 14.0. MS

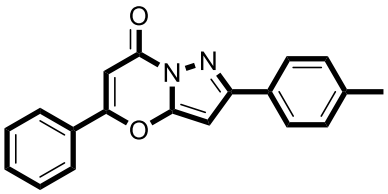
(EI, *m/z*): 296 (2, M+), 253 (12), 240 (21), 207 (3), 161 (3), 143 (100), 115 (34), 89 (9), 67 (5). IR (ATR, neat) $cm^{-1}$: υ 1710 [(C=O)], 1618, 1591 [(C=C, C=N)].

***5-(3,5-bis(trifluoromethyl)phenyl)-2-pentyl-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6bj)***



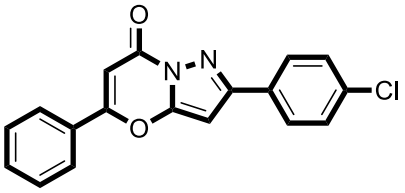
Bright solid (37.6 mg, 45 % yield). Mp: 163-165ºC. $^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm): : 8.28 (s, 2H), 8.09 (s, 1H), 6.61 (s, 1H), 6.16 (s, 1H), 2.78 (t, *J*= 7.8 Hz, 2H), 1.78 – 1.70 (m, 2H), 1.39 – 1.34 (m, 4H), 0.91 (t, *J*= 7.0 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm): 159.3, 158.5, 153.2, 151.0, 133.2, 132.9, 131.9, 126.2, 125.6, 121.3, 99.0, 89.5, 31.4, 29.2, 28.5, 22.4, 14.0. MS (EI, *m/z*): 418 (6, $M^+$), 399 (3), 389 (10), 374 (46), 362 (63), 350 (9), 333 (3), 283 (4), 265 (100), 237 (6), 213 (6), 187 (9), 169 (23), 136 (6), 67(48). IR (ATR, neat) $cm^{-1}$: υ 1718 [(C=O)], 1629, 1591 [(C=C, C=N)].

***5-phenyl-2-(p-tolyl)-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6ca)***



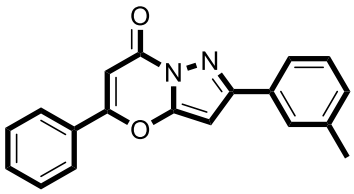
White solid (47.1 mg, 85 % yield). $^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.90-7.85 (m, 4H), 7.59-7.53 (m, 3H), 7.27-7.25 (m, 2H), 6.53 (s, 1H), 6.51 (s, 1H), 2.39 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm): 162.2, 155.2, 154.4, 139.8, 132.5, 132.3, 129.5, 129.4, 126.7, 126.3, 96.7, 87.0, 21.4. IR (ATR, neat) $cm^{-1}$: υ 1716 [(C=O)], 1615, 1595, [(C=C, C=N)].

***2-(4-chlorophenyl)-5-phenyl-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6da)***



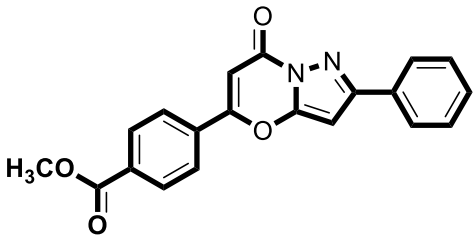
White solid (50.3 mg, 90 % yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.92-7.86 (m, 2H), 7.85-7.84 (m, 2H), 7.60-7.55 (m, 3H), 7.42-7.40 (m, 2H), 6.53 (s, 1H), 6.50 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm): 162.4, 154.2, 153.9, 135.7, 132.6, 130.0, 129.4, 129.3, 129.0, 127.8, 126.3, 96.9, 87.2. IR (ATR, neat) $cm^{-1}$: υ 1714 [(C=O)], 1620, 1593, [(C=C, C=N)].

***5-phenyl-2-(m-tolyl)-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6ea)***



White solid (42.9 mg, 76 % yield). $^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.89-7.86 (m, 3H), 7.74-7.72 (m, 1H), 7.59-7.53 (m, 3H), 7.36-7.32 (m, 1H), 7.24-7.22 (m, 1H) 6.53 (s, 2H), 2.41 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm): 162.3, 155.2, 154.3, 138.5, 132.5, 130.5, 129.3, 128.6, 127.1, 126.3, 123.8, 96.9, 87.2, 21.3 IR (ATR, neat) $cm^{-1}$: υ 1718 [(C=O)], 1615, 1595, [(C=C, C=N)].

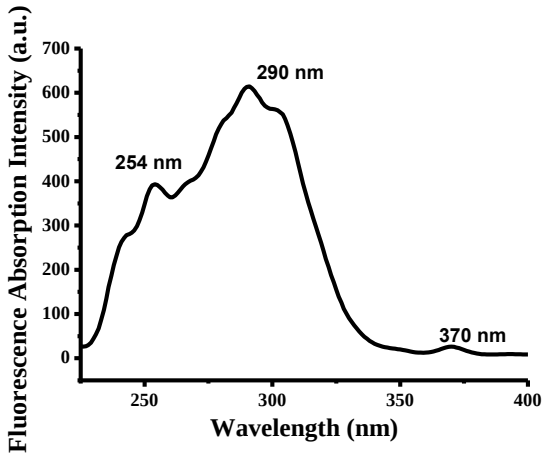
***methyl 4-(7-oxo-2-phenyl-7H-pyrazolo[5,1-b][1,3]oxazin-5-yl)benzoate, (6ak)***

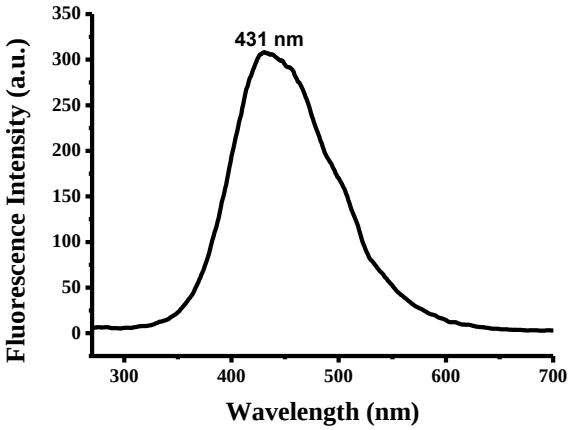


White solid (40.0 mg, 81 % yield). $^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.22-8.20 (m, 2H), 8.01-7.94 (m, 4H) 7.47-7.43 (m, 3H), 2.41 (s, 3H). 6.62 (s, 1H), 6.58 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm): 165.8, 161.0, 155.4, 153.9, 133.5, 133.4, 131.3, 130.4, 129.8, 128.8, 126.6, 126.3, 98.4, 87.4, 49.1

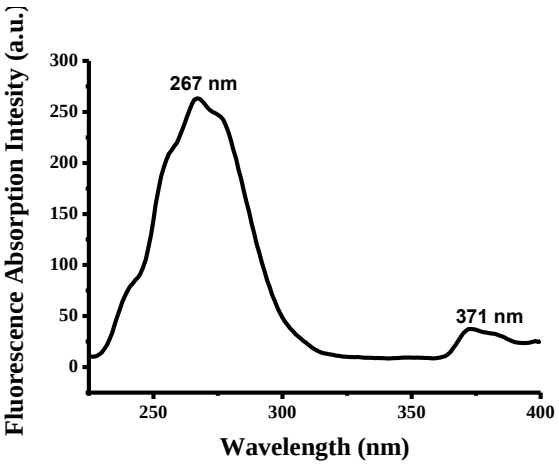
## 4. Fluorescence Absorption and Emission Spectrum of Synthesized Compounds

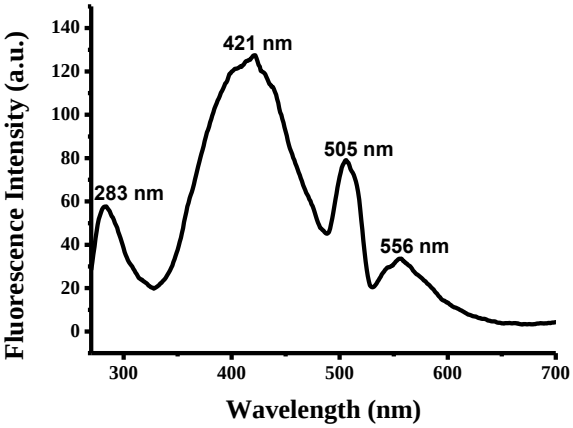
***2,5-diphenyl-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6aa)***



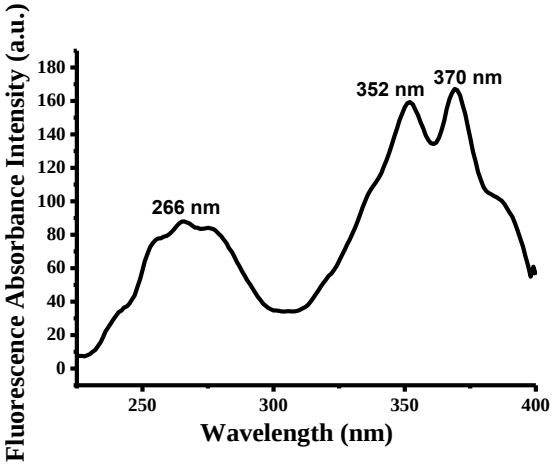



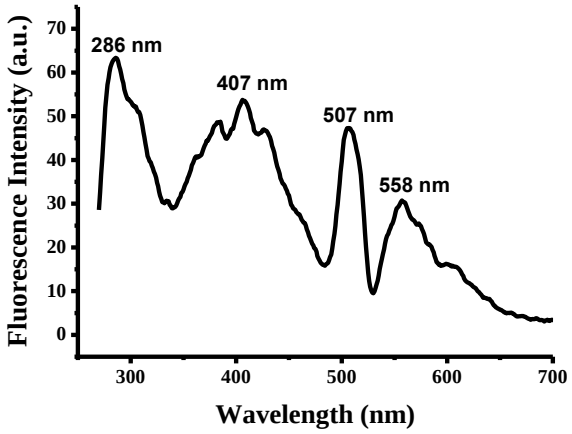

***2-phenyl-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6ab)***



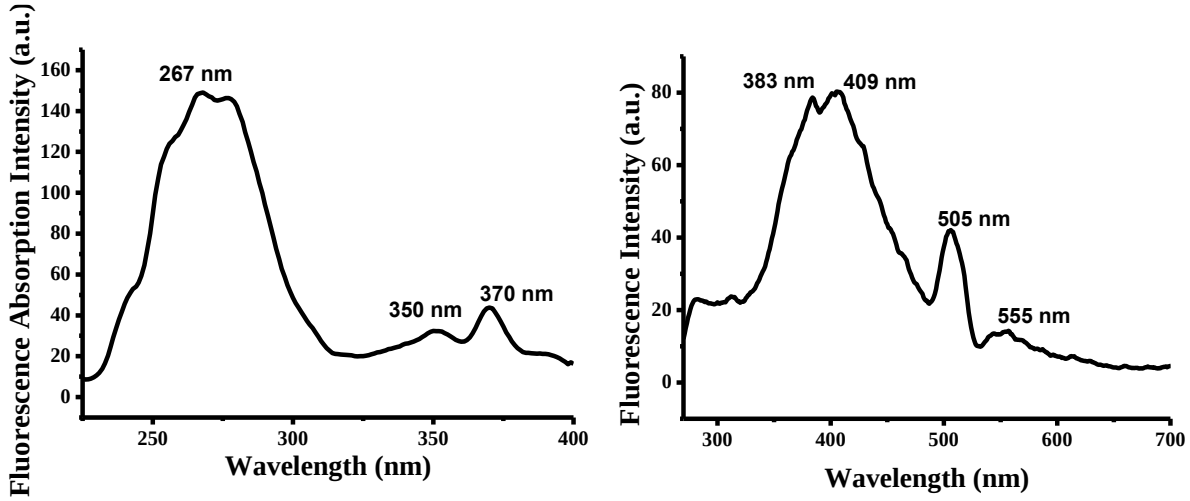




***5-methyl-2-phenyl-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6ac)***

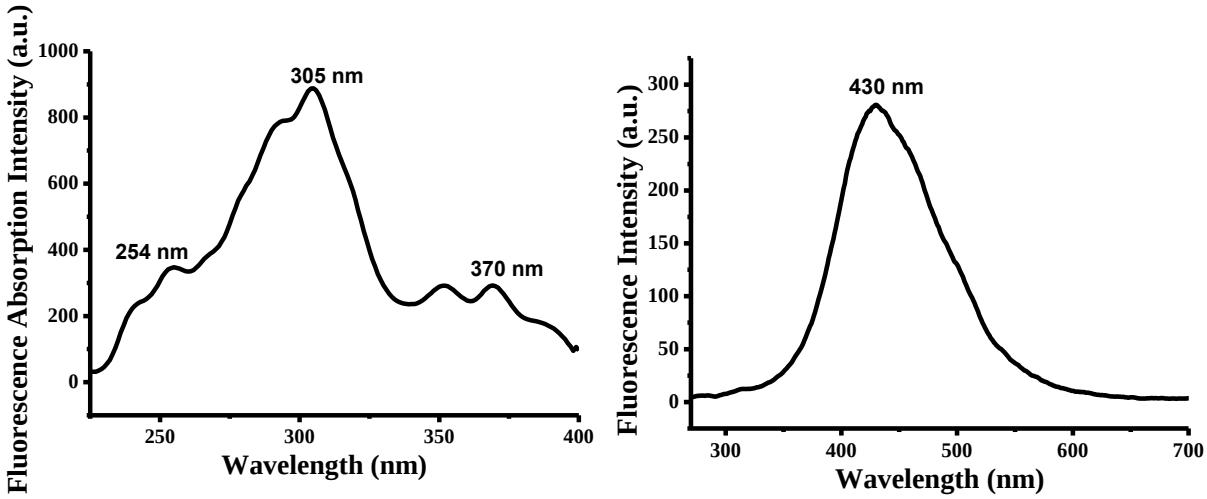


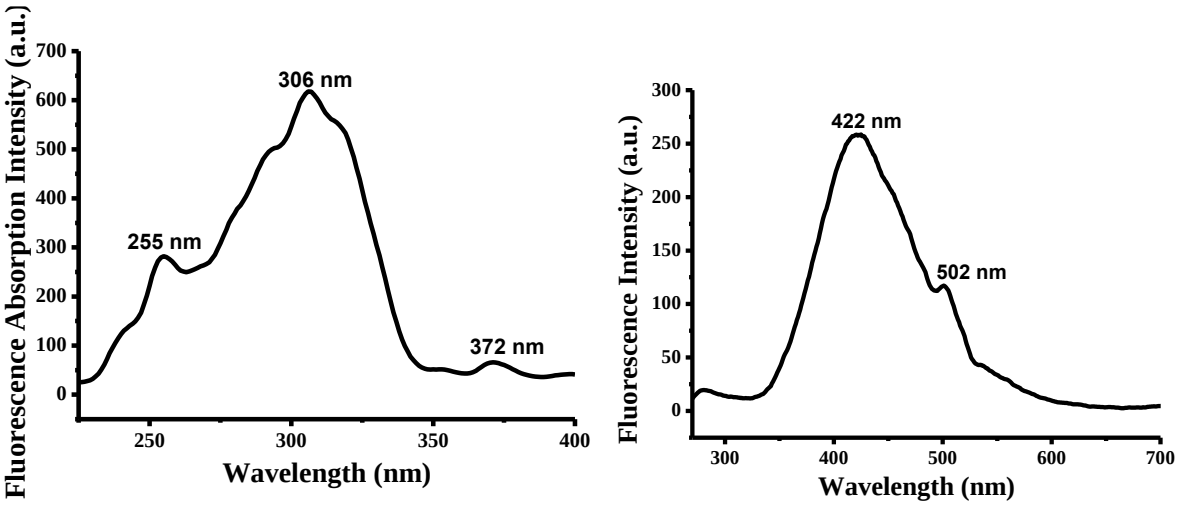
***5-butyl-2-phenyl-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6ad)***



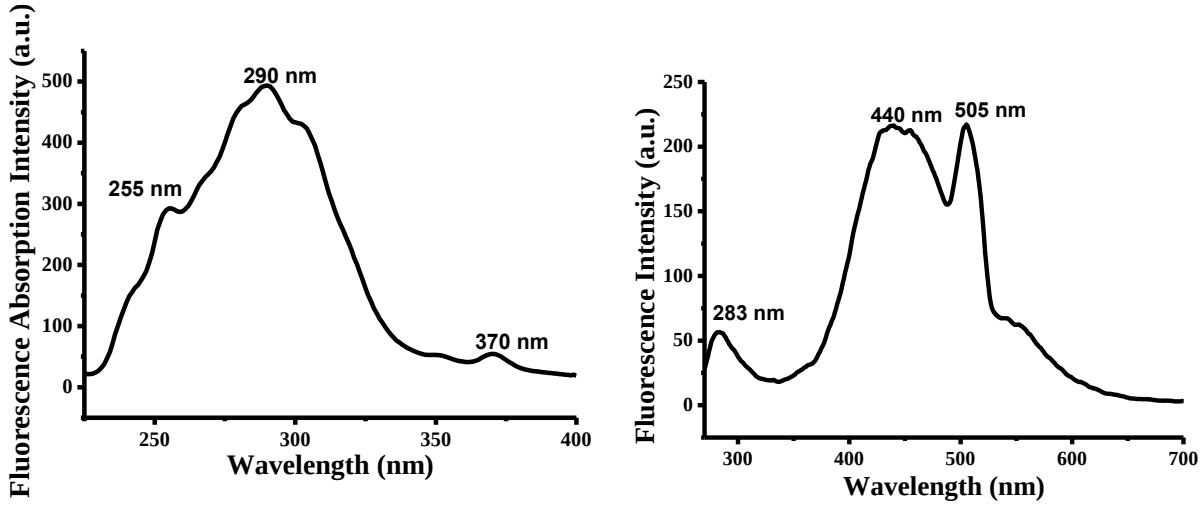

***2-phenyl-5-(p-tolyl)-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6ae)***



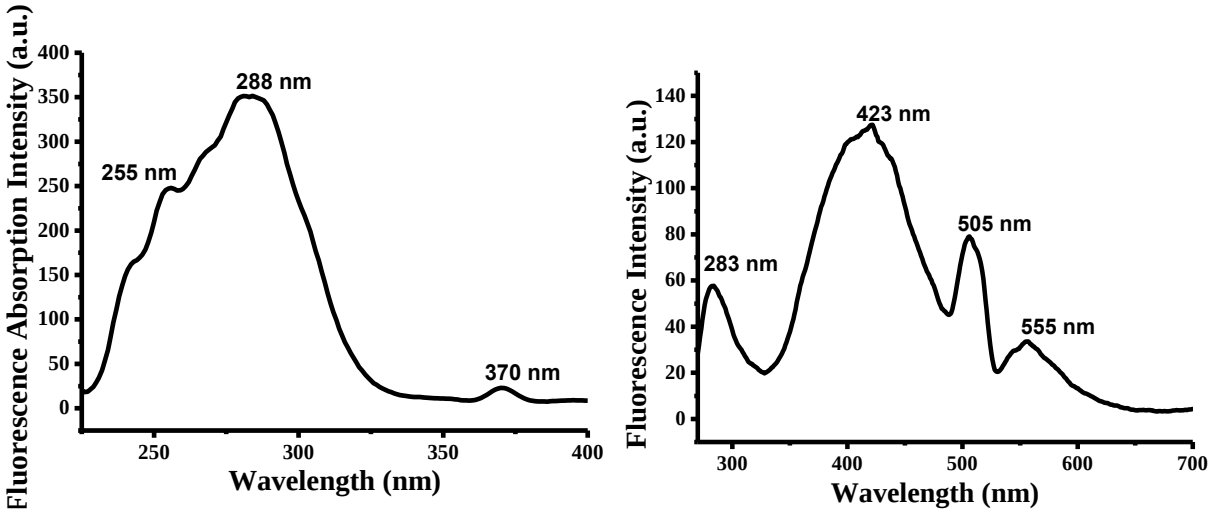

***5-(4-methoxyphenyl)-2-phenyl-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6af)***



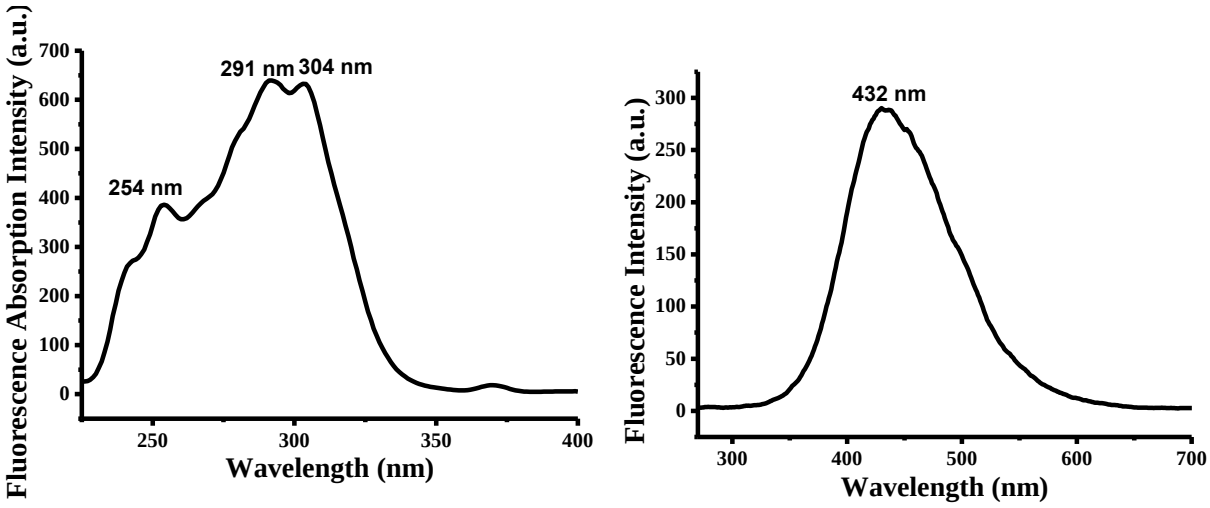
***5-(4-chlorophenyl)-2-phenyl-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6ag)***



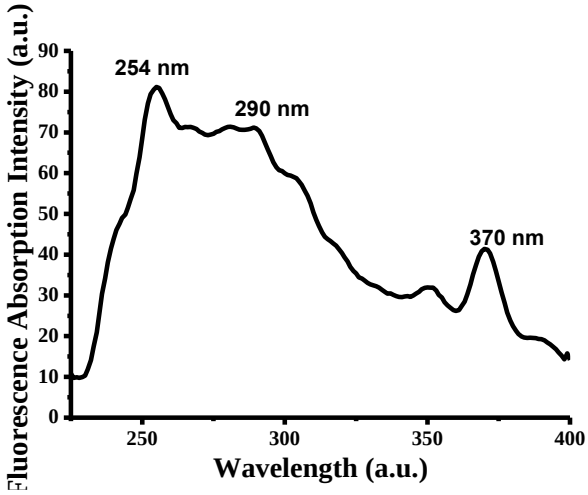

***2-phenyl-5-(o-tolyl)-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6ah)***

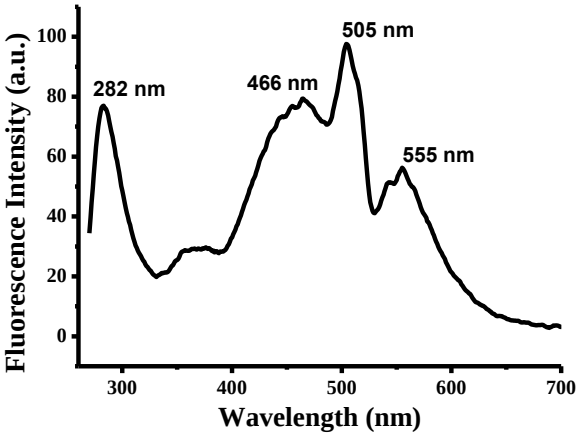



***2-phenyl-5-(m-tolyl)-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6ai)***

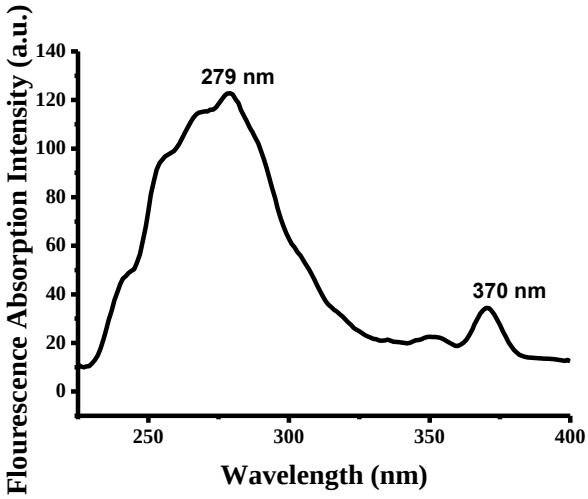


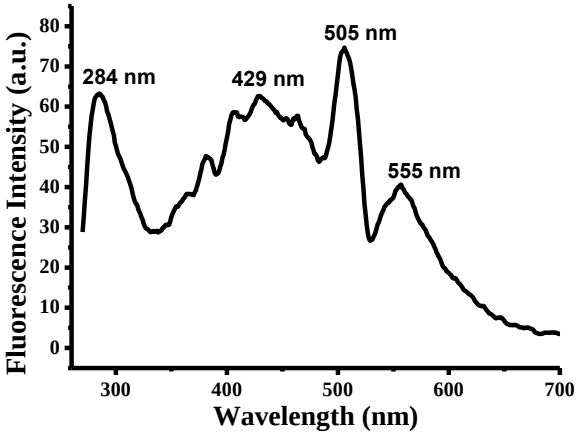
***5-(3,5-bis(trifluoromethyl)phenyl)-2-phenyl-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6aj)***



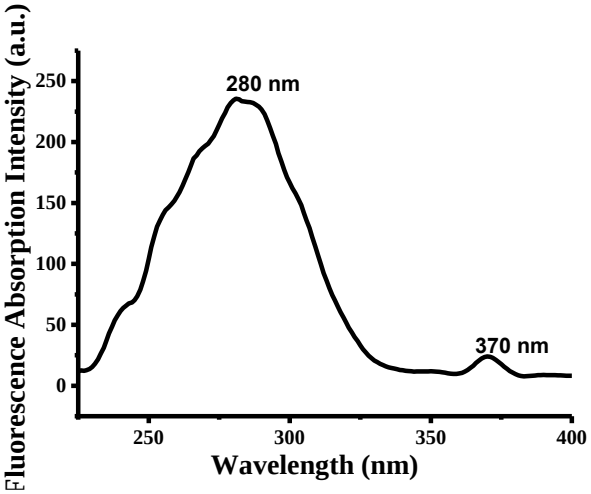



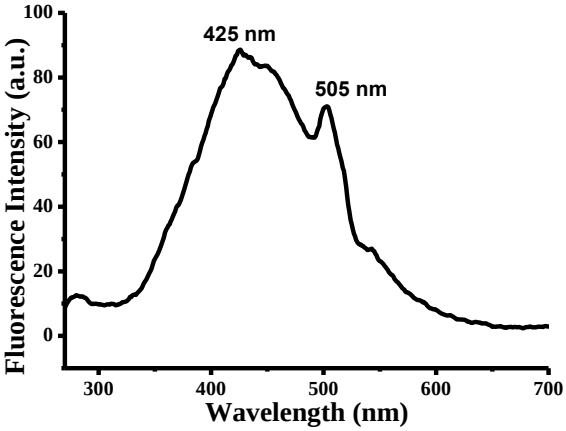

***2-pentyl-5-phenyl-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6ba)***



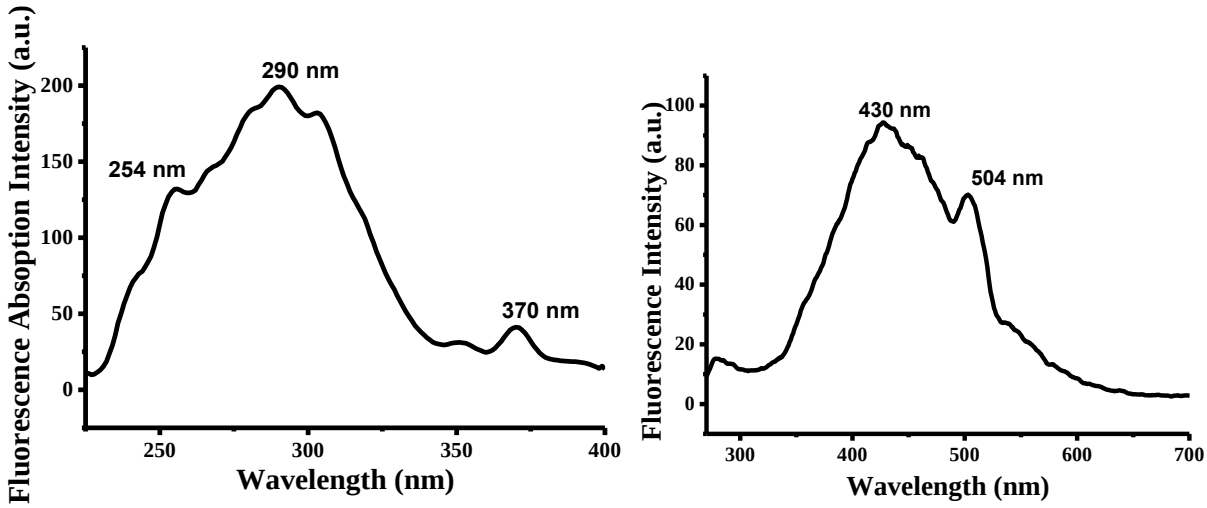




***2-pentyl-5-(p-tolyl)-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6be)***



***5-(3,5-bis(trifluoromethyl)phenyl)-2-pentyl-7H-pyrazolo[5,1-b][1,3]oxazin-7-one, (6bj)***




## 5. Determination of Quantum Yields and Extinction Coefficients

### Quantum Yield

Fluorescence quantum yields of synthesized compounds were determined by using optically matching solutions of Coumarin 102 ($\Phi_F$=0.76 in methanol) as a standard.[4] The quantum yield was calculated according to the equation;

$$\Phi_{F(X)} = \Phi_{F(S)} (A_S F_X / A_X F_S) (n_X / n_S)^2 \ldots [1]$$

Where $\Phi_F$ is the fluorescence quantum yield, A is the absorbance at the excitation wavelength, F is the area under the corrected emission curve, and n is the refractive index of the solvents used. Subscripts S and X refer to the standard and to the unknown, respectively.

### Extincton coefficient

Extincton coefficients of synthesized compounds were calculated by using absorption spectrum of compounds in the range of 1-5 µM concentration in dioxane solution. The extincton coefficient was calculated according to the equation;

$$A = \text{Ɛ} \times b \times c \ldots [2]$$

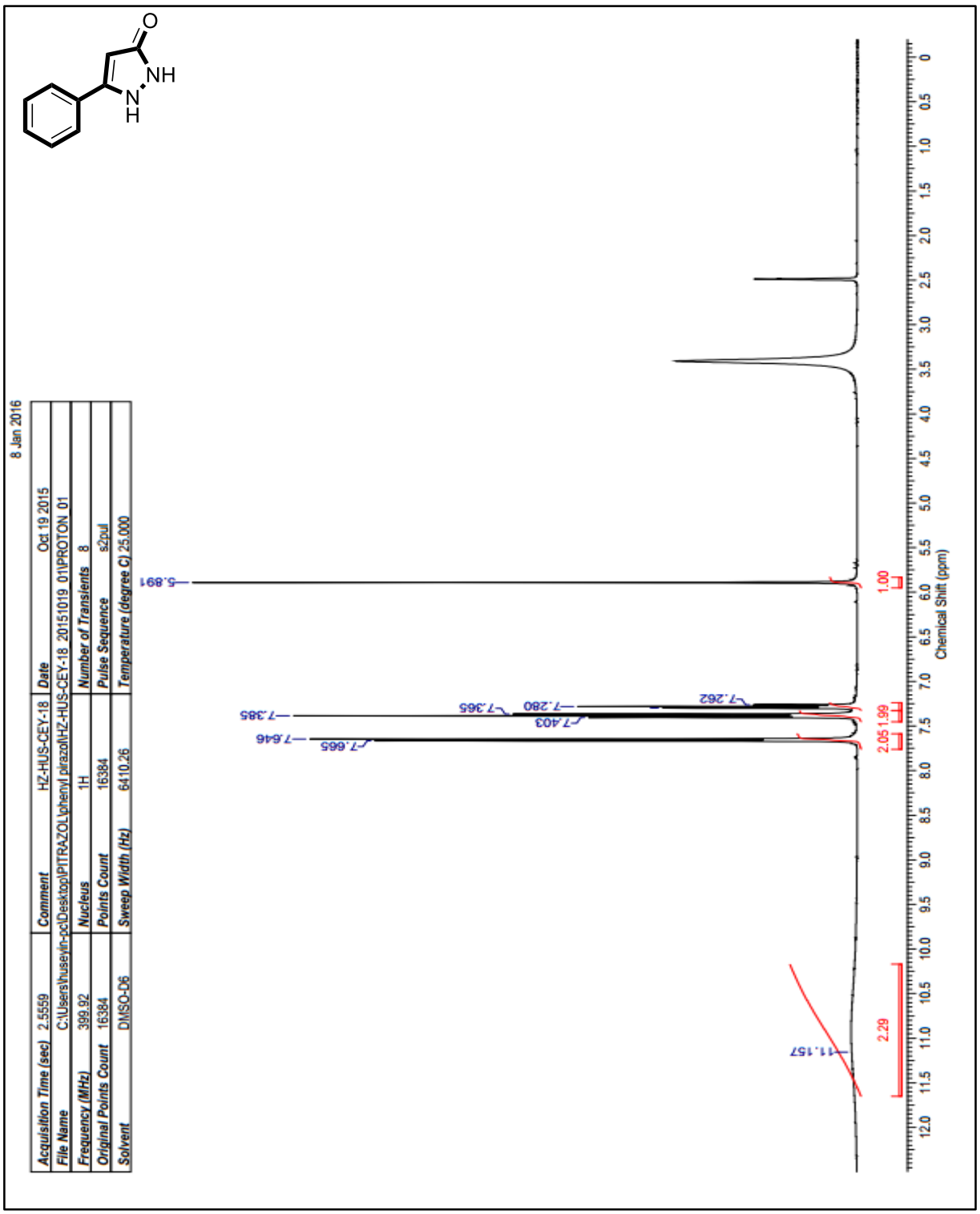
Where A is the absorbance, Ɛ is the extinction coefficient ($cm^{-1}$ $M^{-1}$), b is the path length of the sample (cm), and c is the concentration of measured compound (M)

**Table S1:** Absorption and Emission Data for of Pyranopyrazole Compounds

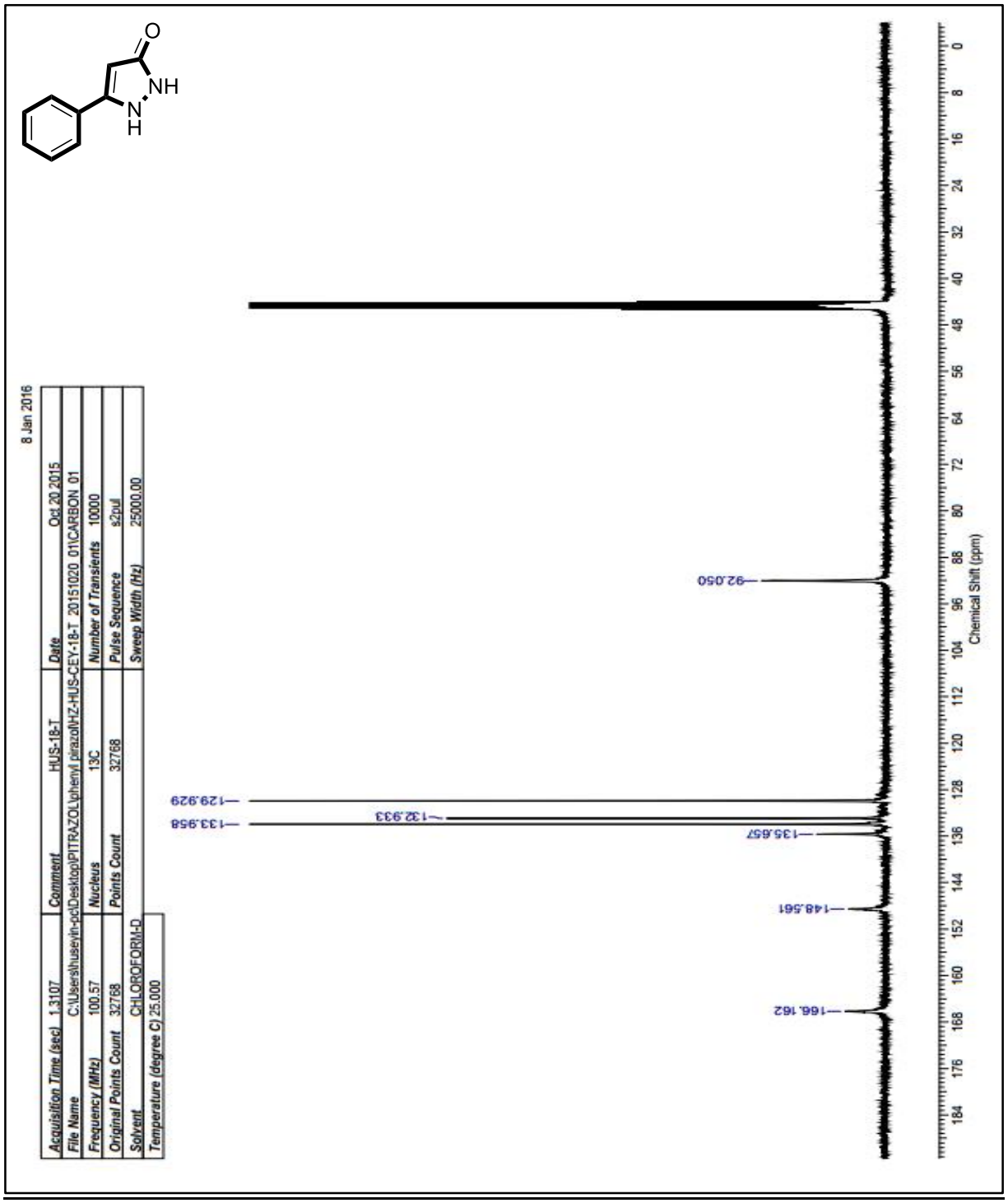
| | Absorption | | | | Emission | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Compounds** | **$\lambda_1$** | **$\lambda_2$** | **$\lambda_3$** | **$\varepsilon_{\lambda 2}$ ($10^6$ $M^{-1}cm^{-1}$)** | **$\lambda_1$** | **$\lambda_2$** | **$\lambda_3$** | **$\lambda_4$** | **$\Phi_F$** |
| **6aa** | 254 | 290 | 370 | 0.035 | - | 431 | - | - | 0.286 |
| **6ab** | 267 | - | 371 | 0.010 | 283 | 421 | 505 | 556 | 0.075 |
| **6ac** | 266 | 352 | 370 | 0.008 | 286 | 407 | 507 | 558 | 0.121 |
| **6ad** | 267 | 350 | 370 | 0.011 | 383 | 409 | 505 | 555 | 0.235 |
| **6ae** | 254 | 305 | 370 | 0.034 | - | 430 | - | - | 0.140 |
| **6af** | 255 | 306 | 372 | 0.104 | - | 422 | 505 | - | 0.184 |
| **6ag** | 255 | 290 | 370 | 0.032 | 283 | 440 | 505 | - | 0.242 |
| **6ah** | 255 | 288 | 370 | 0.037 | 283 | 423 | 505 | 555 | 0.136 |
| **6ai** | 254 | 291 | 304 | 0.027 | - | 432 | - | - | 0.124 |
| **6aj** | 255 | 290 | 370 | 0.012 | 283 | 440 | 505 | - | 0.058 |
| **6ba** | - | 279 | 370 | 0.012 | 284 | 429 | 505 | 555 | 0.033 |
| **6be** | - | 280 | 370 | 0.022 | - | 425 | 505 | - | 0.055 |
| **6bj** | 254 | 290 | 370 | 0.009 | - | 430 | 504 | - | 0.027 |

## 6. NMR Spectra for All Compounds

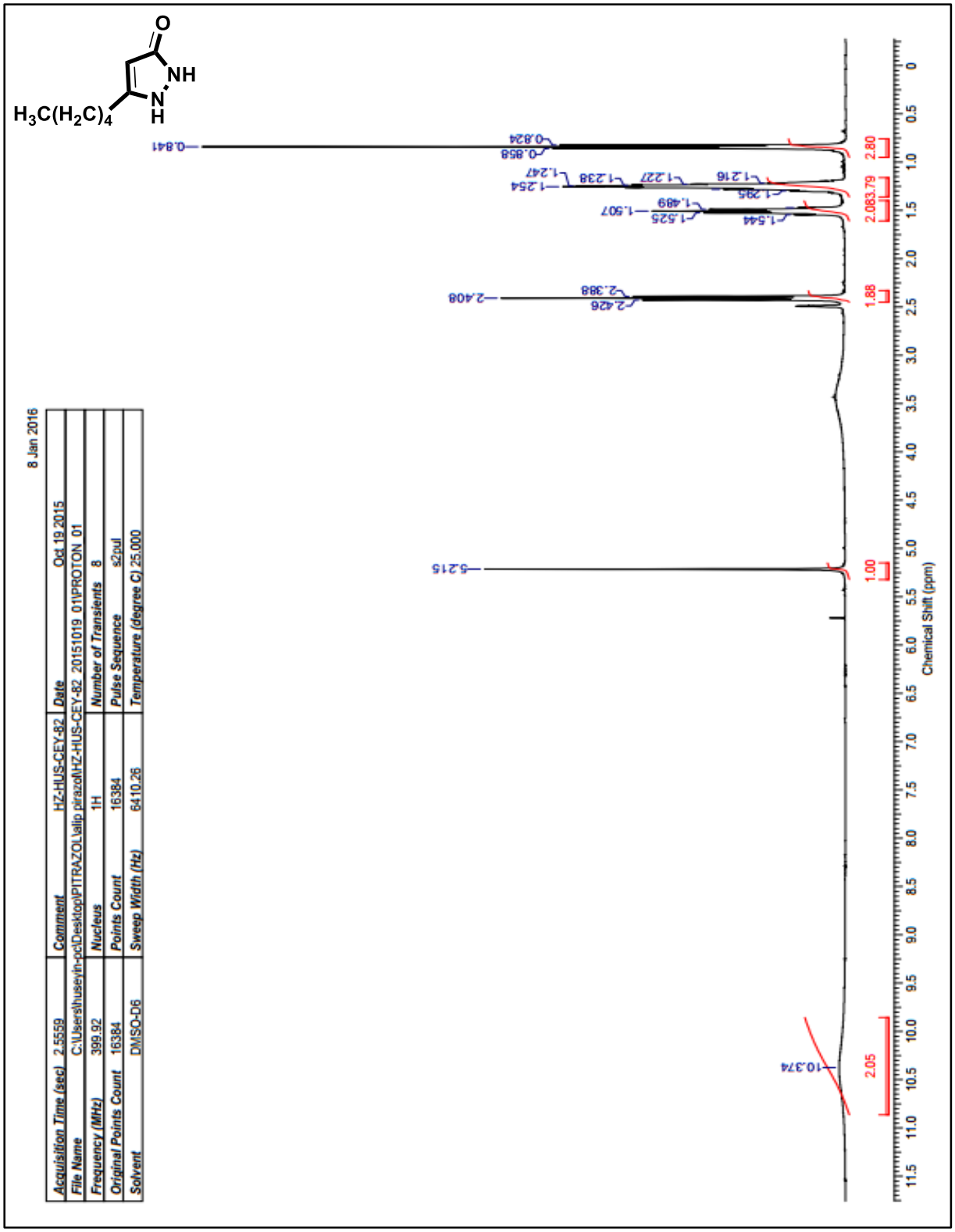
**$^1$H NMR Spectrum of 2a in DMSO-$d_6$:**



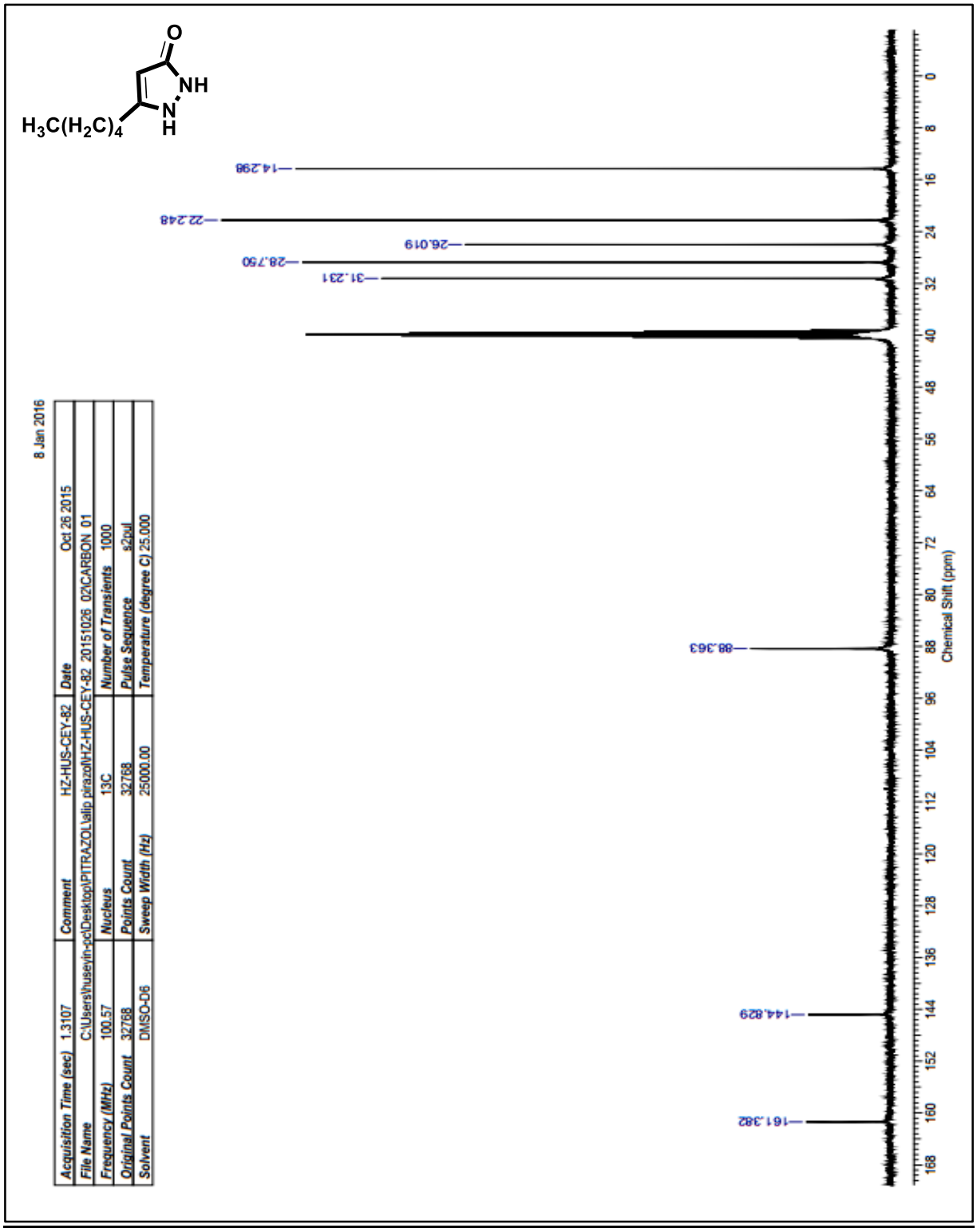
**$^{13}$C NMR Spectrum of 2a in DMSO-$d_6$:**



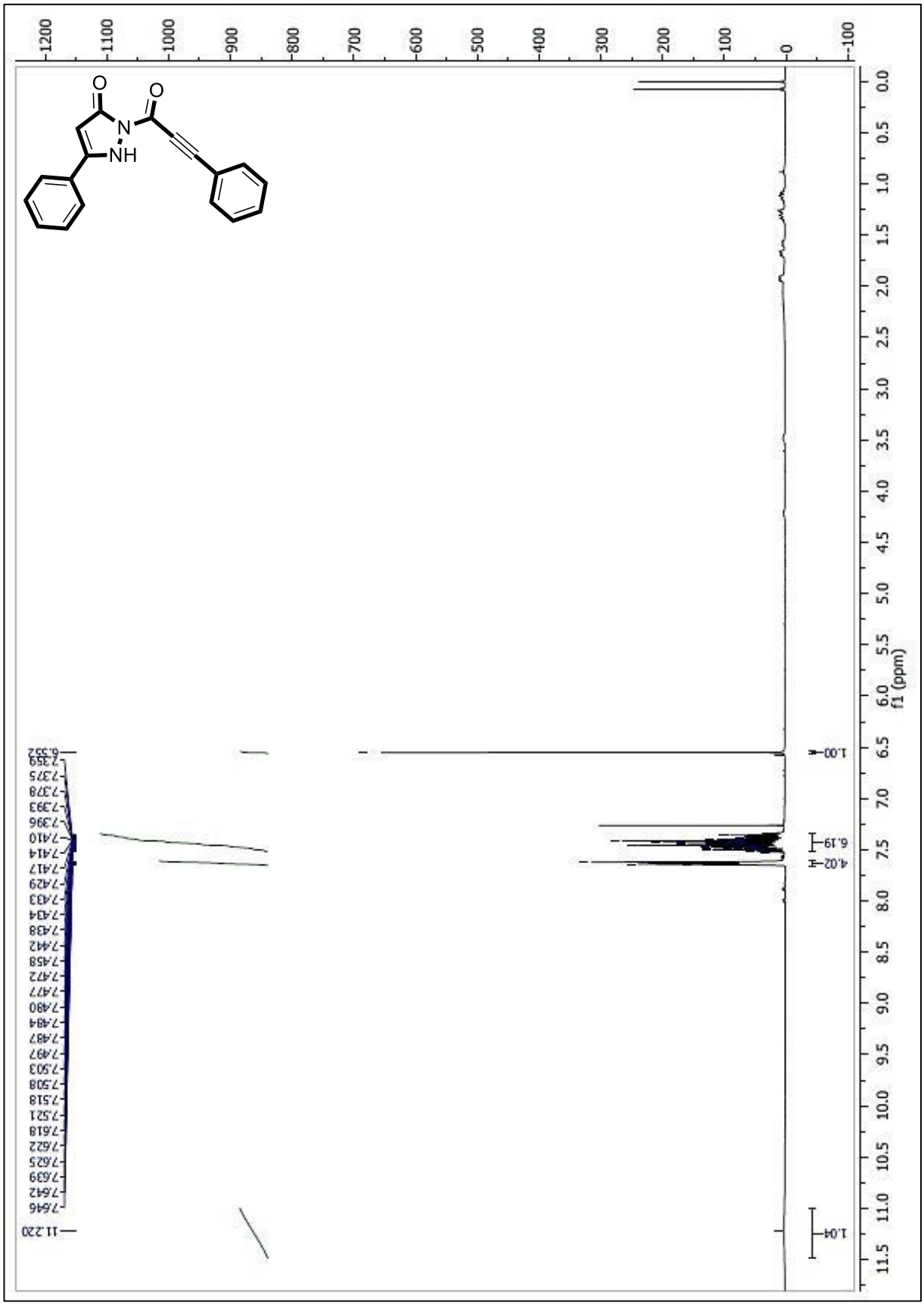
**$^{1}$H NMR Spectrum of 2b in DMSO-$d_6$:**



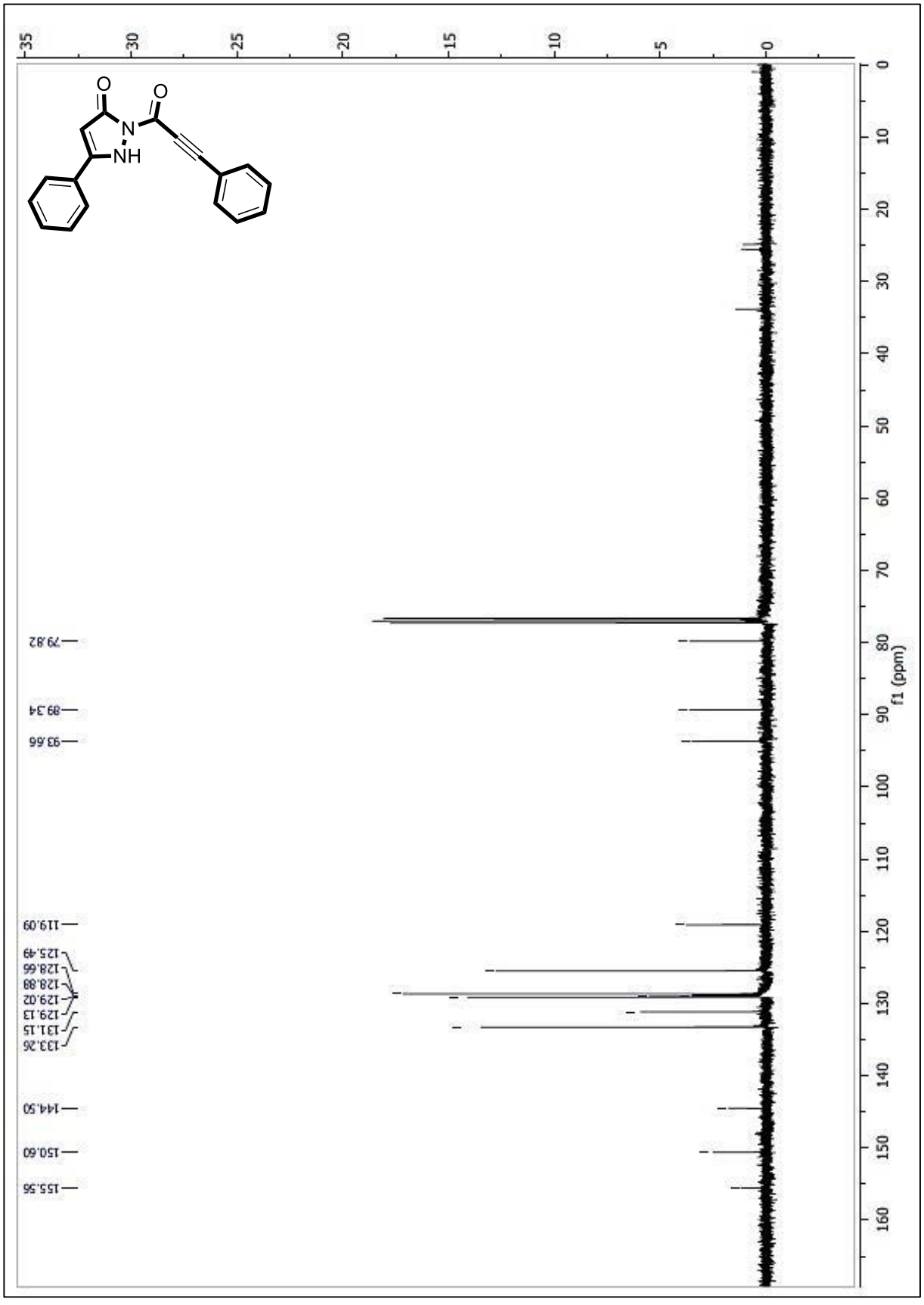
**$^{13}$C NMR Spectrum of 2b in DMSO-$d_6$:**



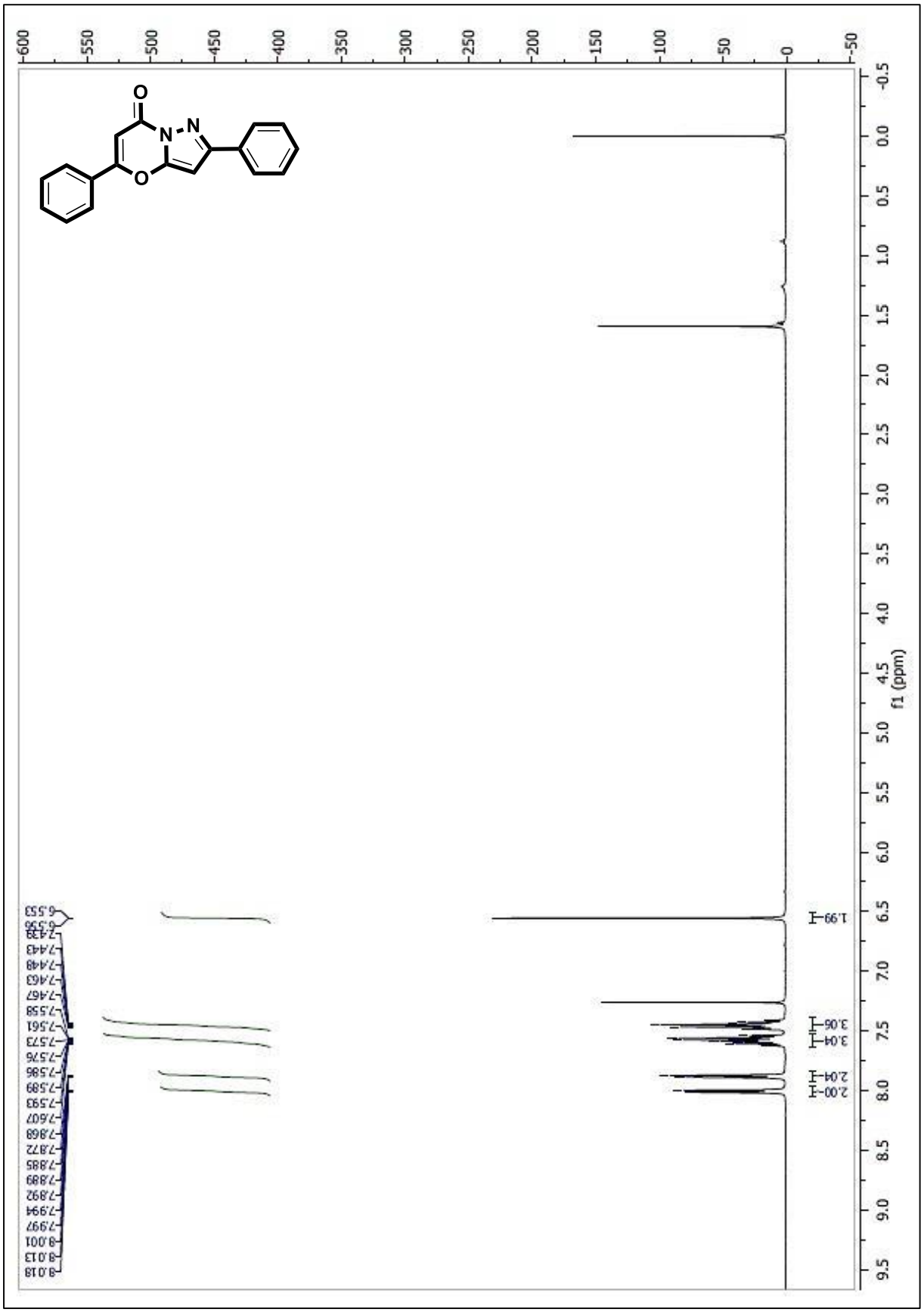
**$^{1}$H NMR Spectrum of 3aa in $CDCl_3$:**



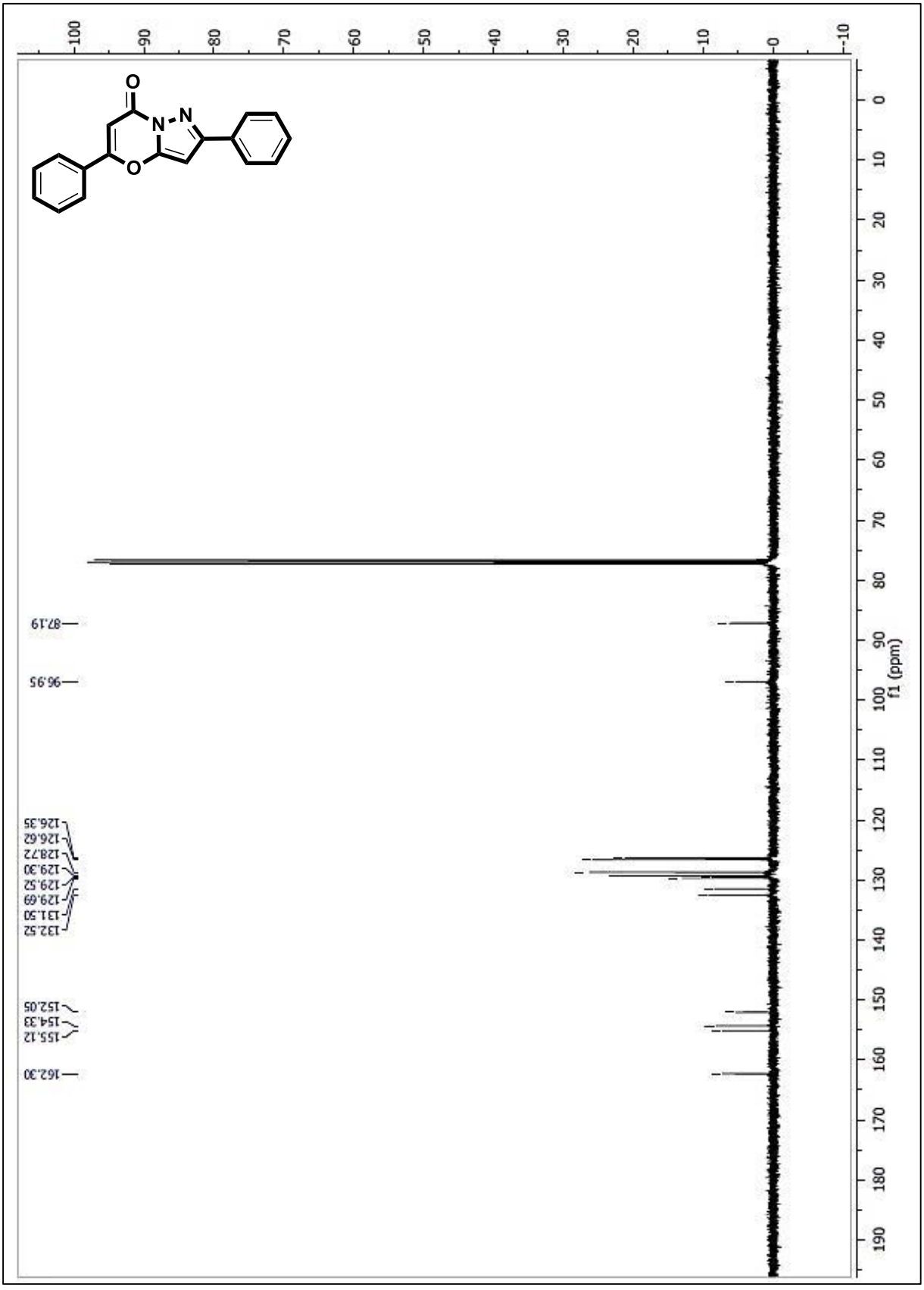
**$^{13}$C NMR Spectrum of 3aa in $CDCl_3$:**



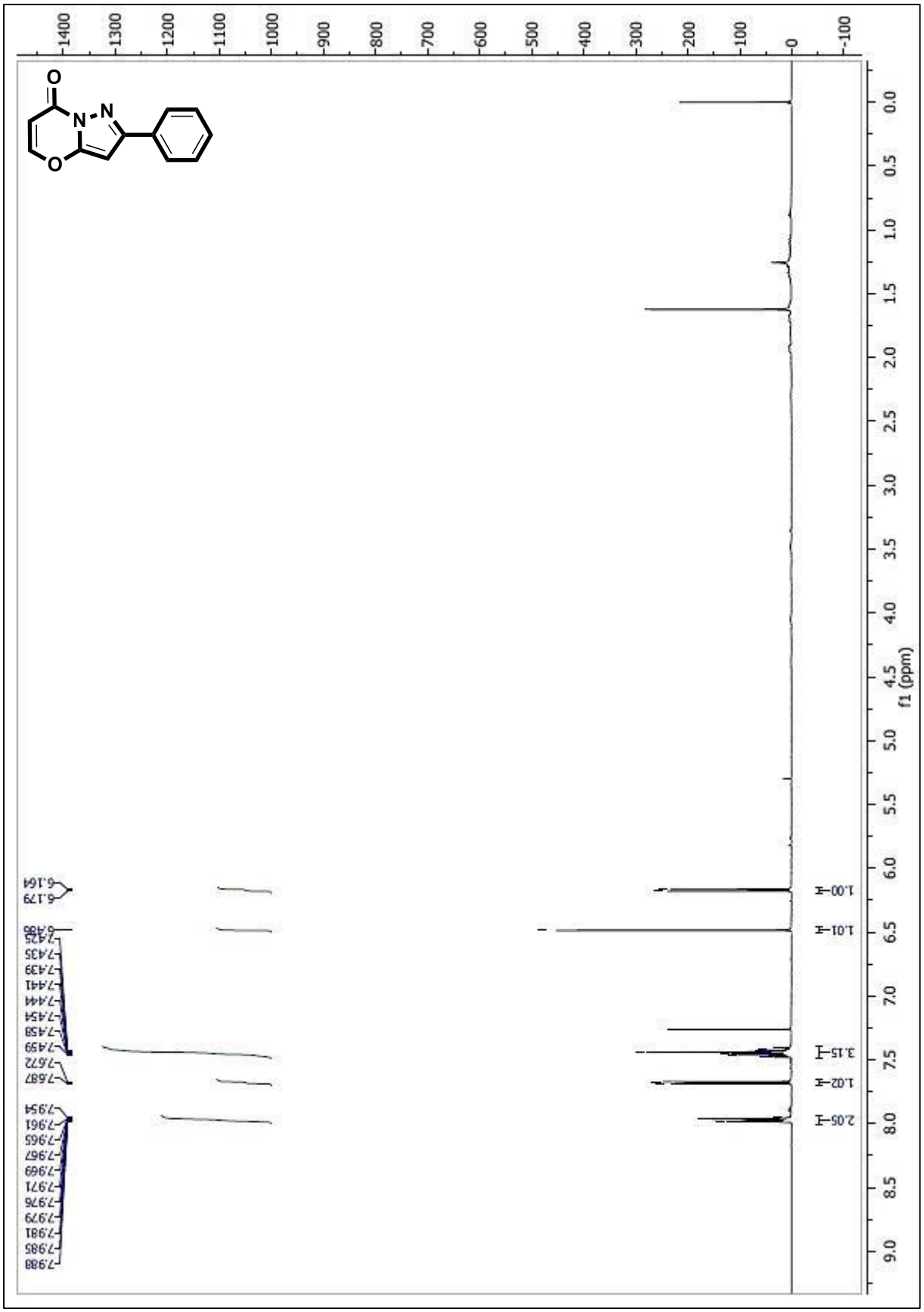
**$^1$H NMR Spectrum of 6aa in $CDCl_3$:**



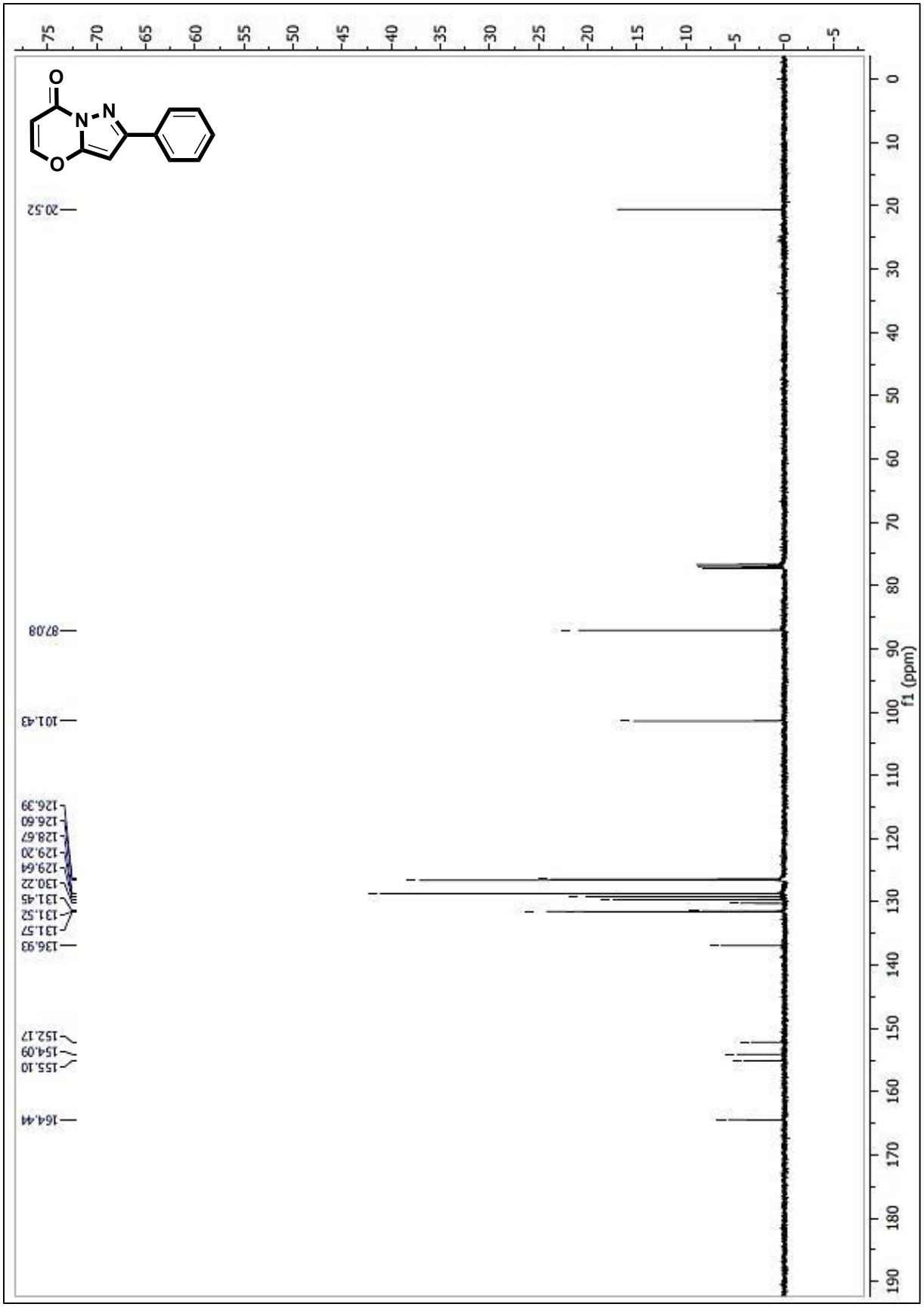
**$^{13}$C NMR Spectrum of 6aa in $CDCl_3$:**



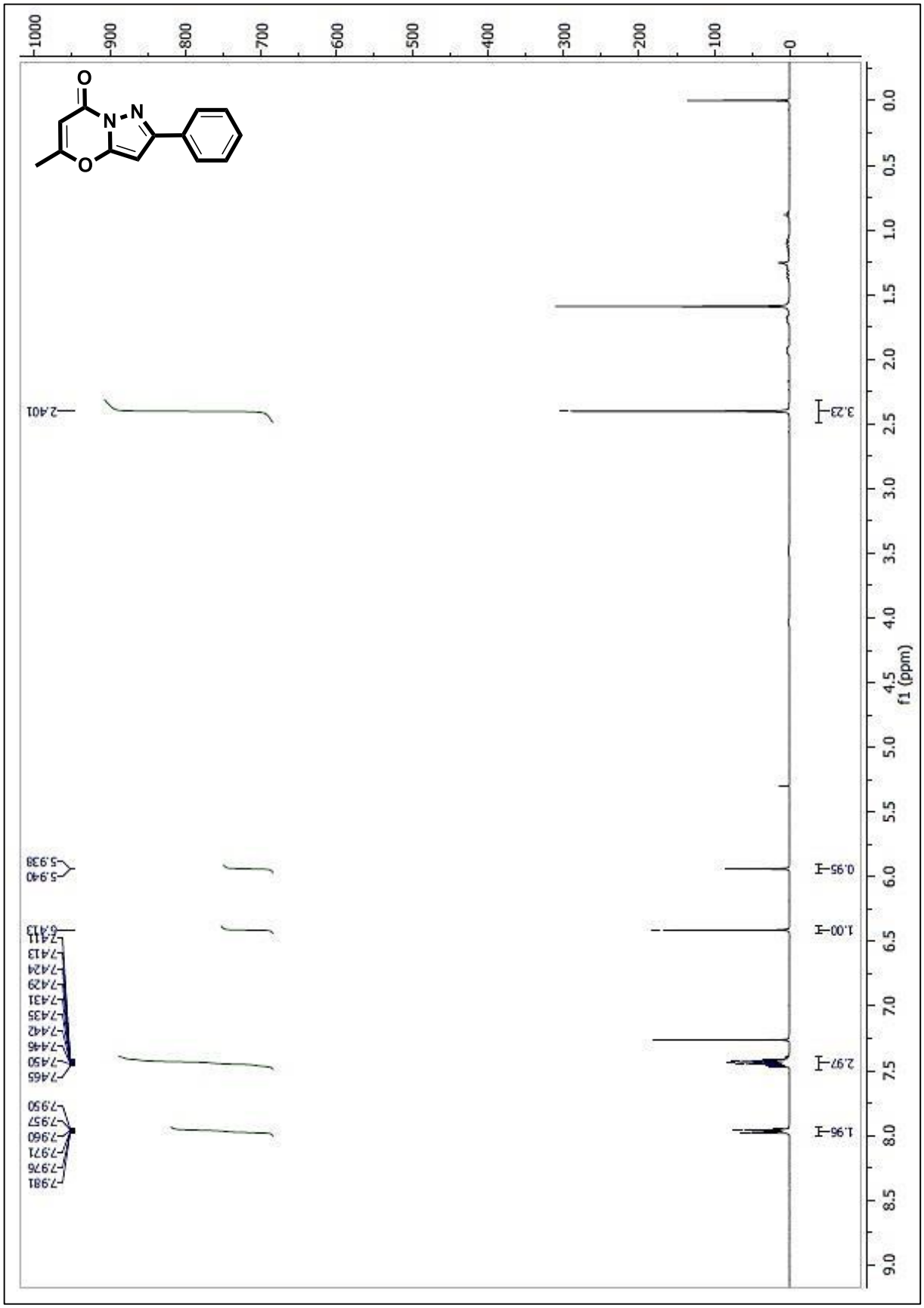
**$^1$H NMR Spectrum of 6ab in $CDCl_3$:**



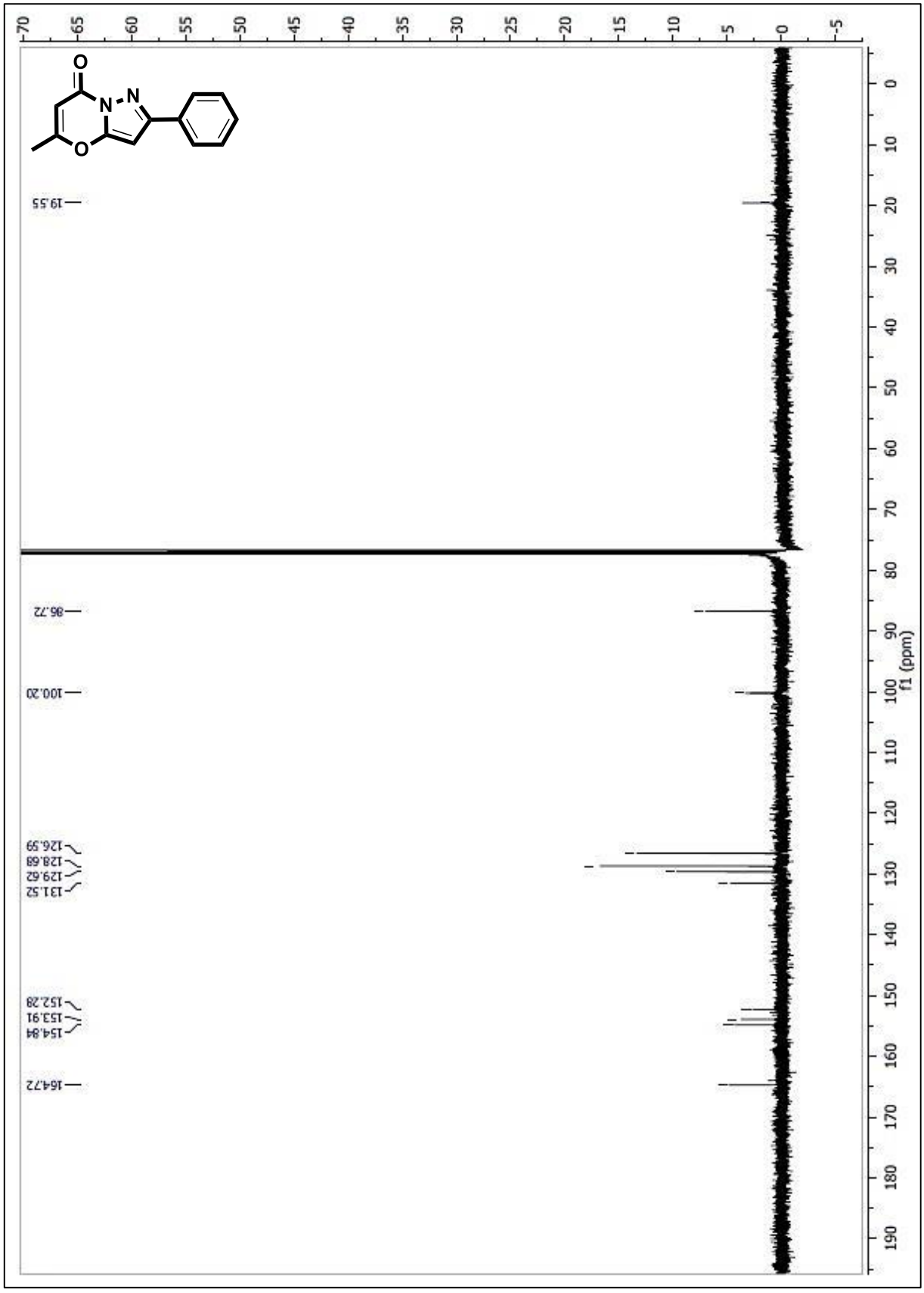
**$^{13}$C NMR Spectrum of 6ab in $CDCl_3$:**



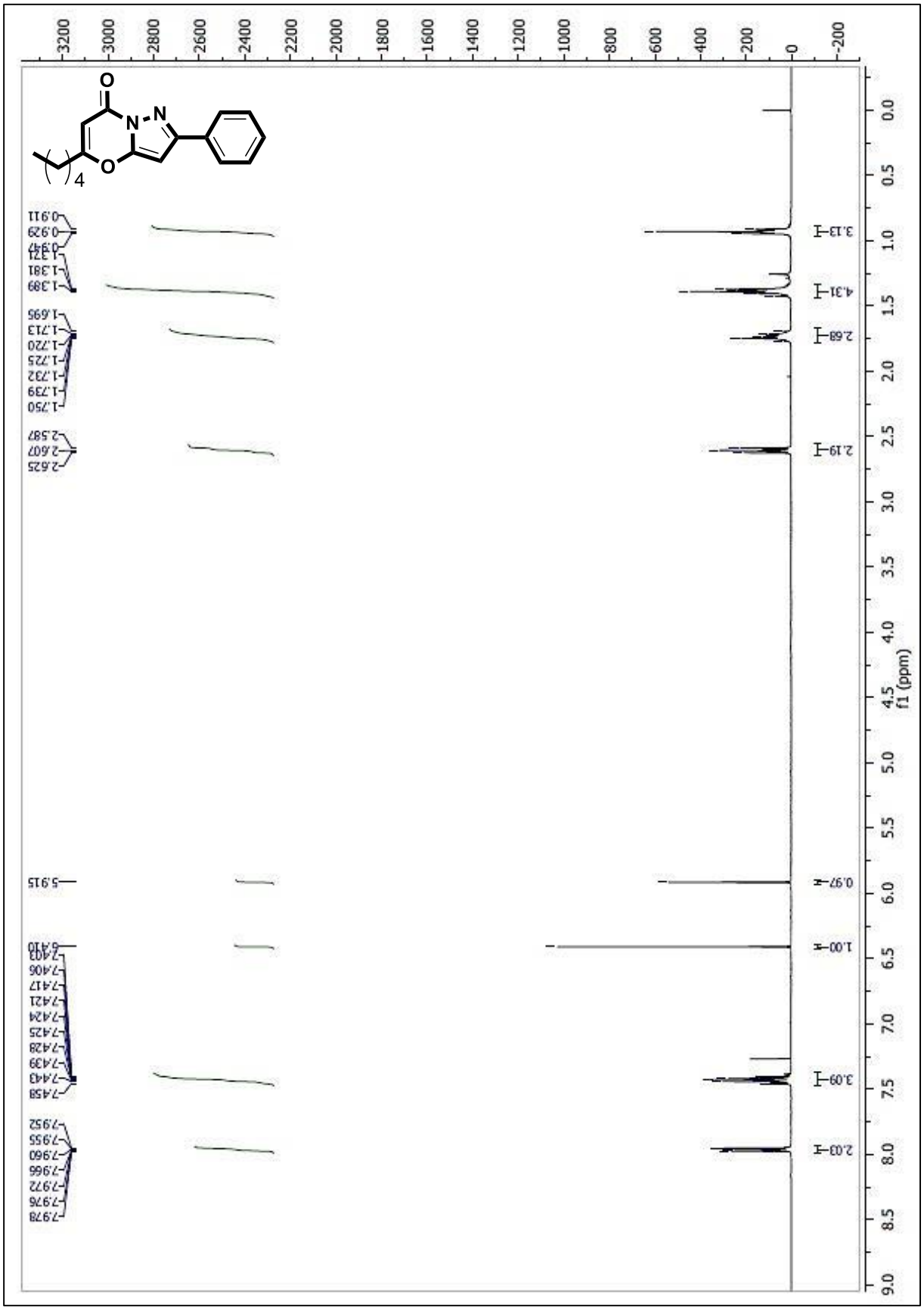
**$^1$H NMR Spectrum of 6ac in $CDCl_3$:**



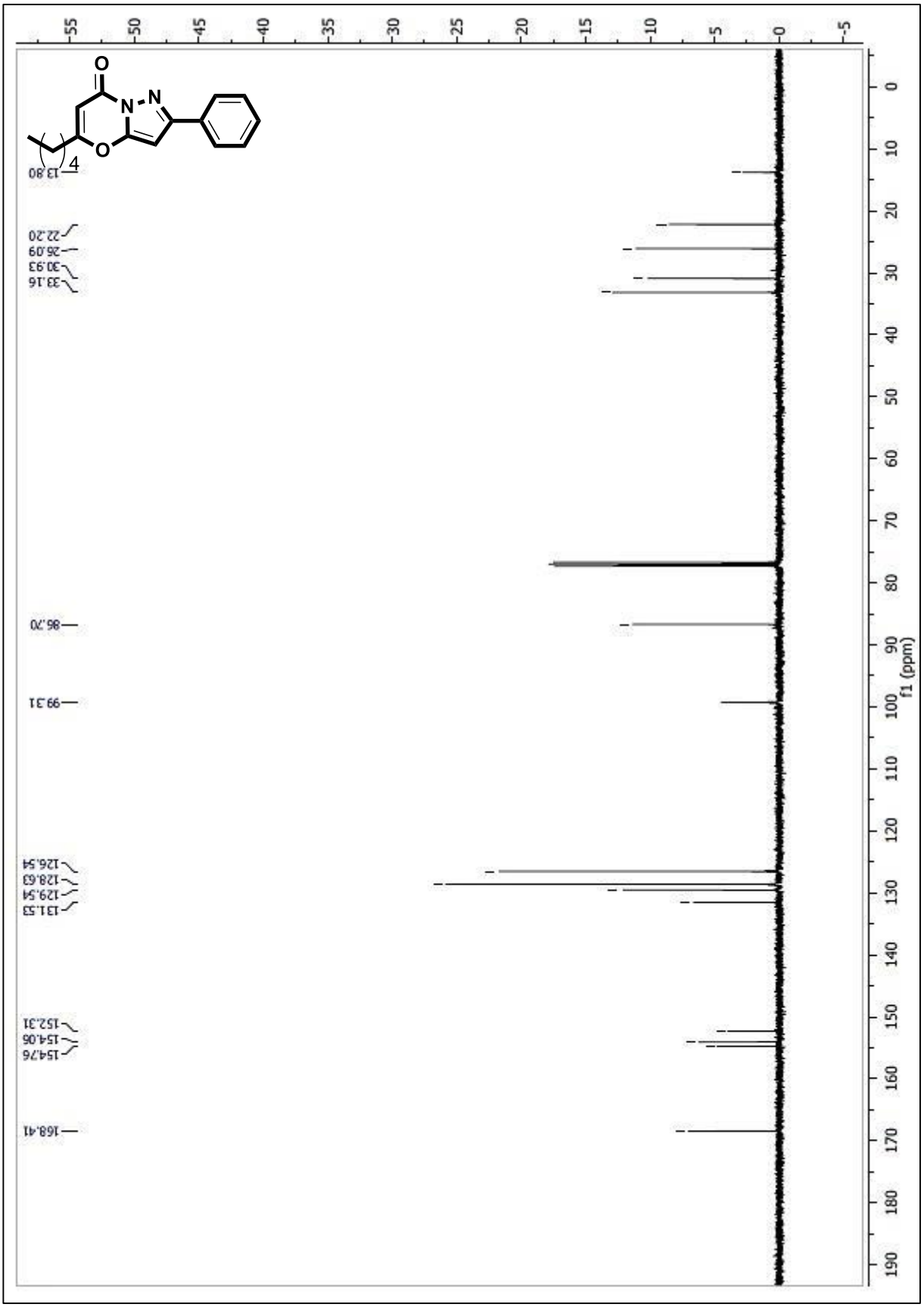
**$^{13}$C NMR Spectrum of 6ac in $CDCl_3$:**



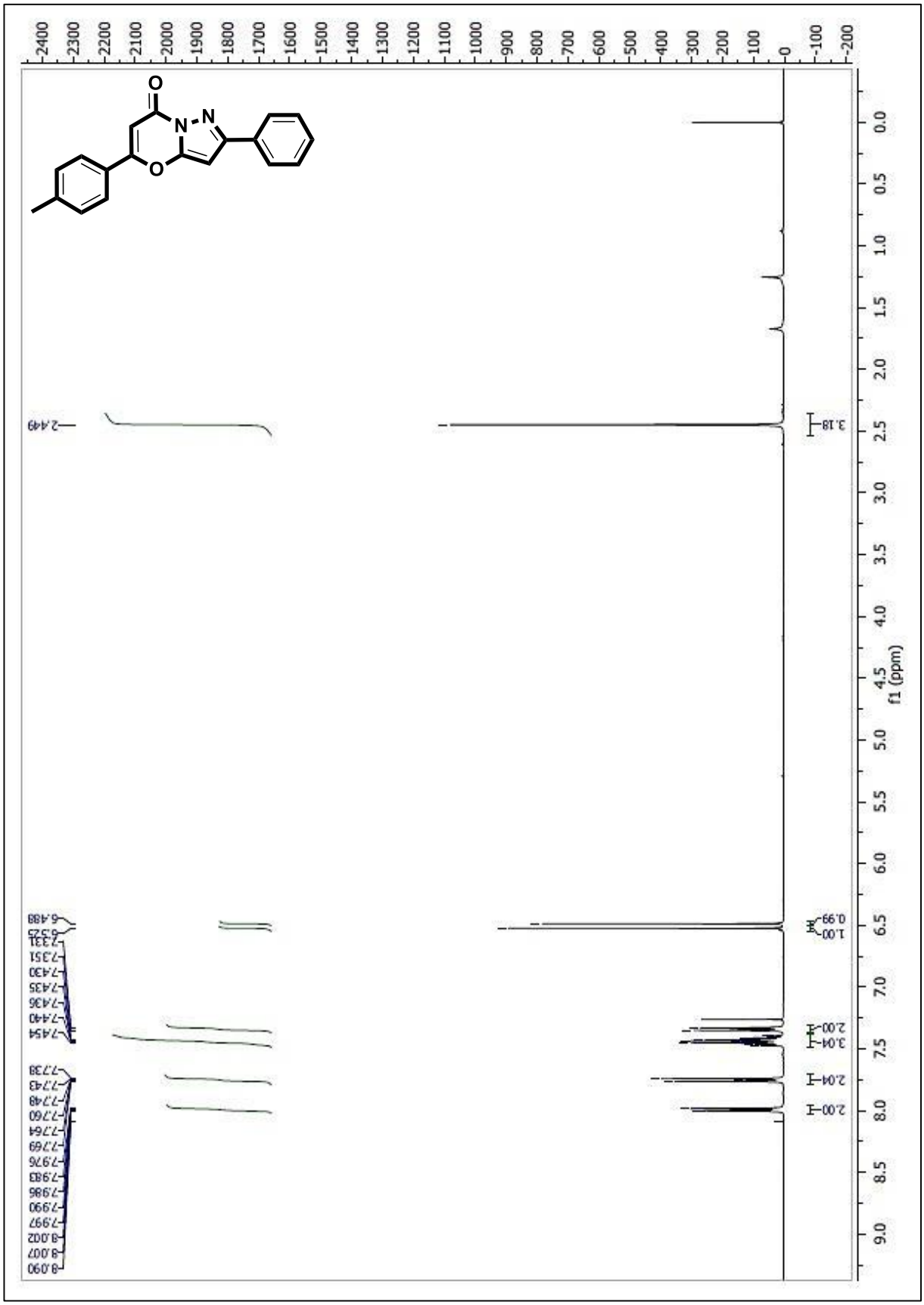
**$^1$H NMR Spectrum of 6ad in $CDCl_3$:**



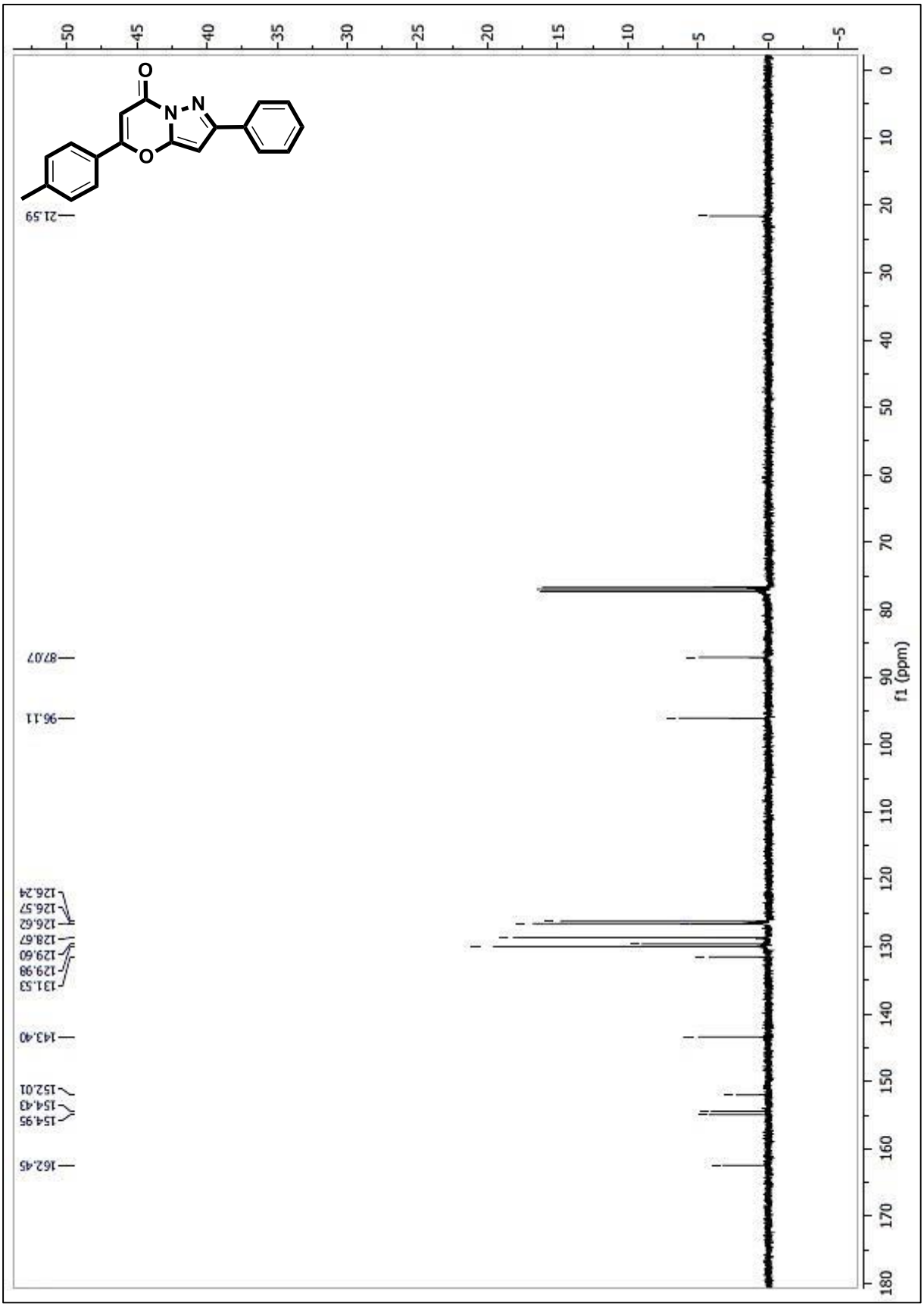
**$^{13}$C NMR Spectrum of 6ad in $CDCl_3$:**



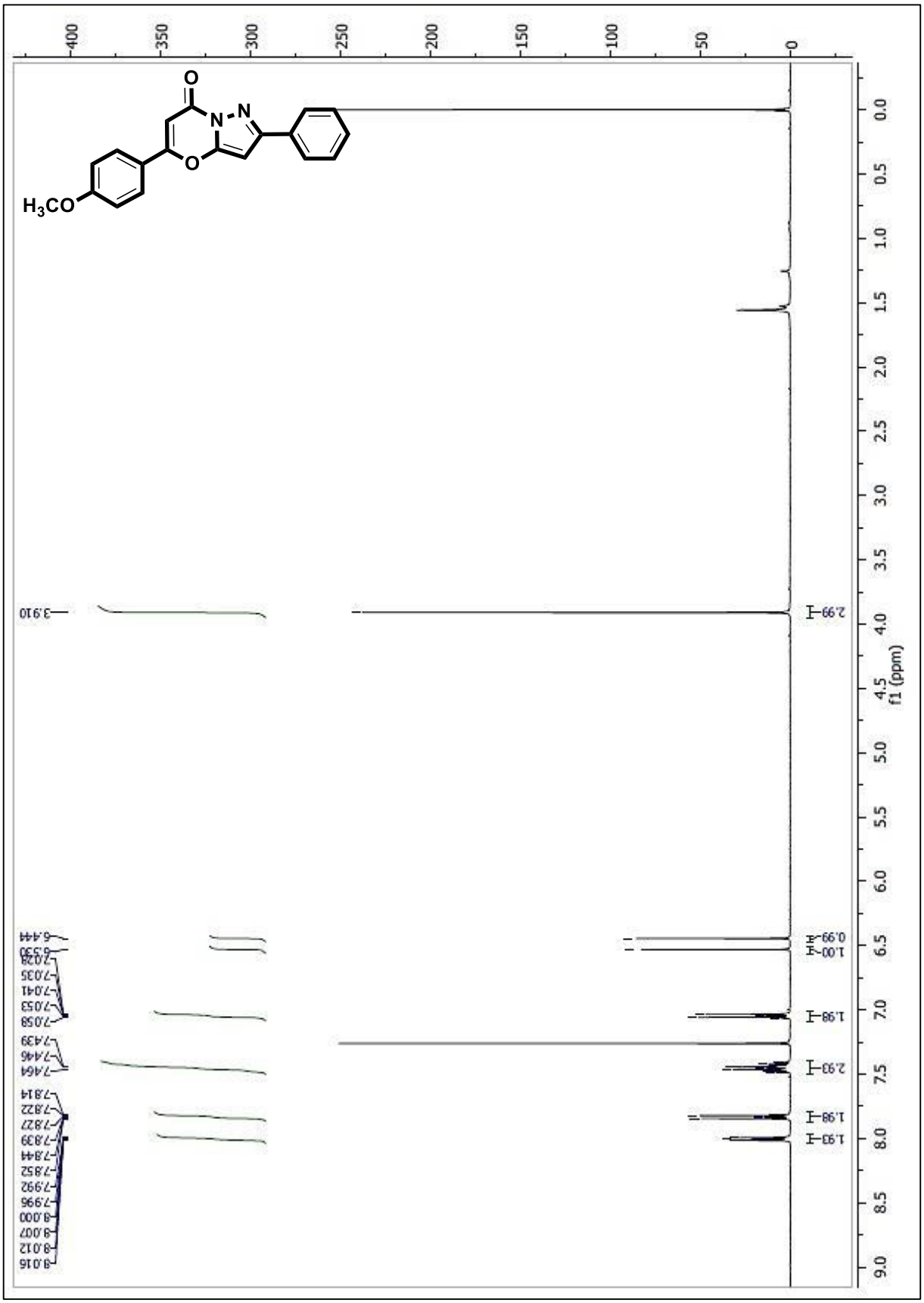
**$^{1}$H NMR Spectrum of 6ae in $CDCl_3$:**



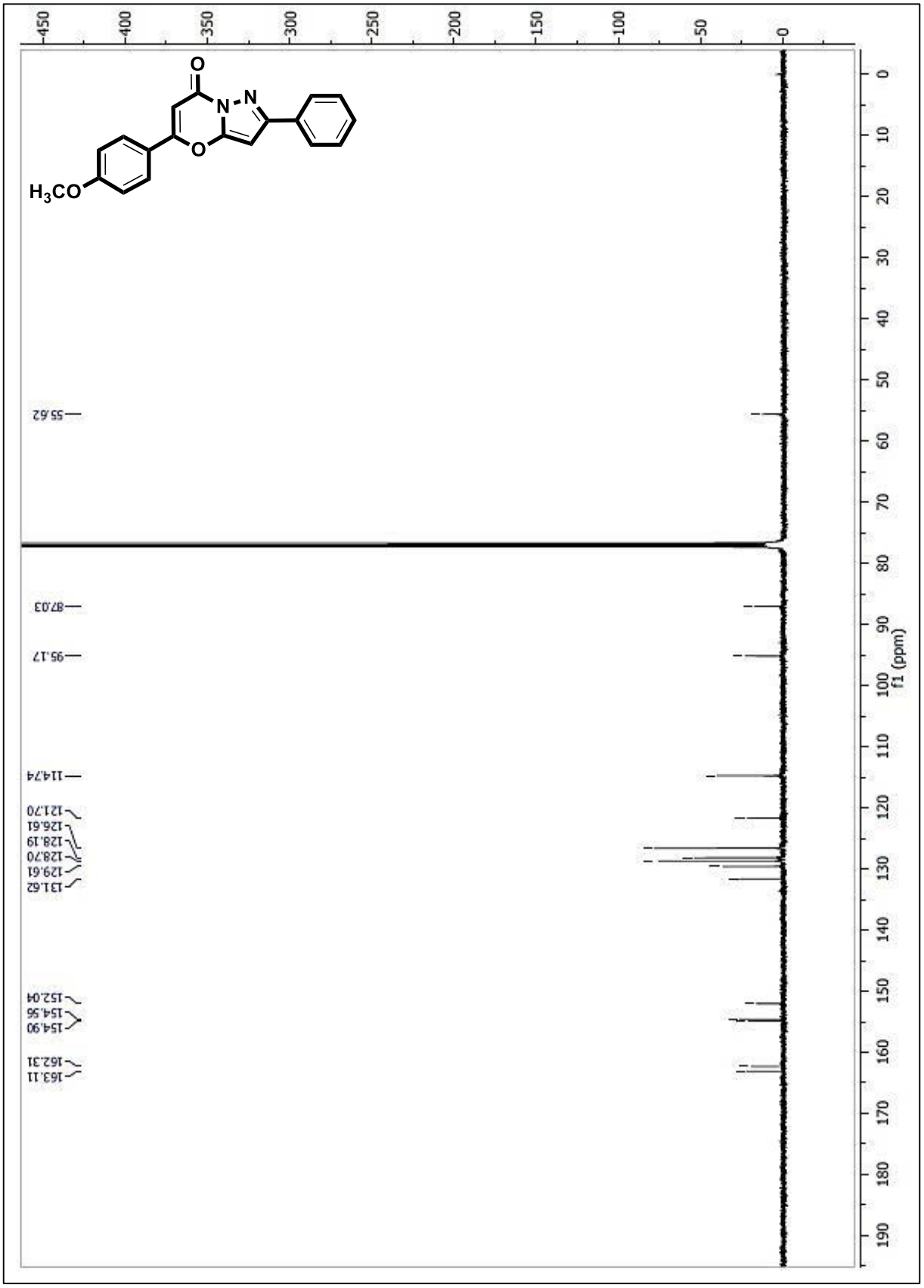
**$^{13}$C NMR Spectrum of 6ae in $CDCl_3$:**



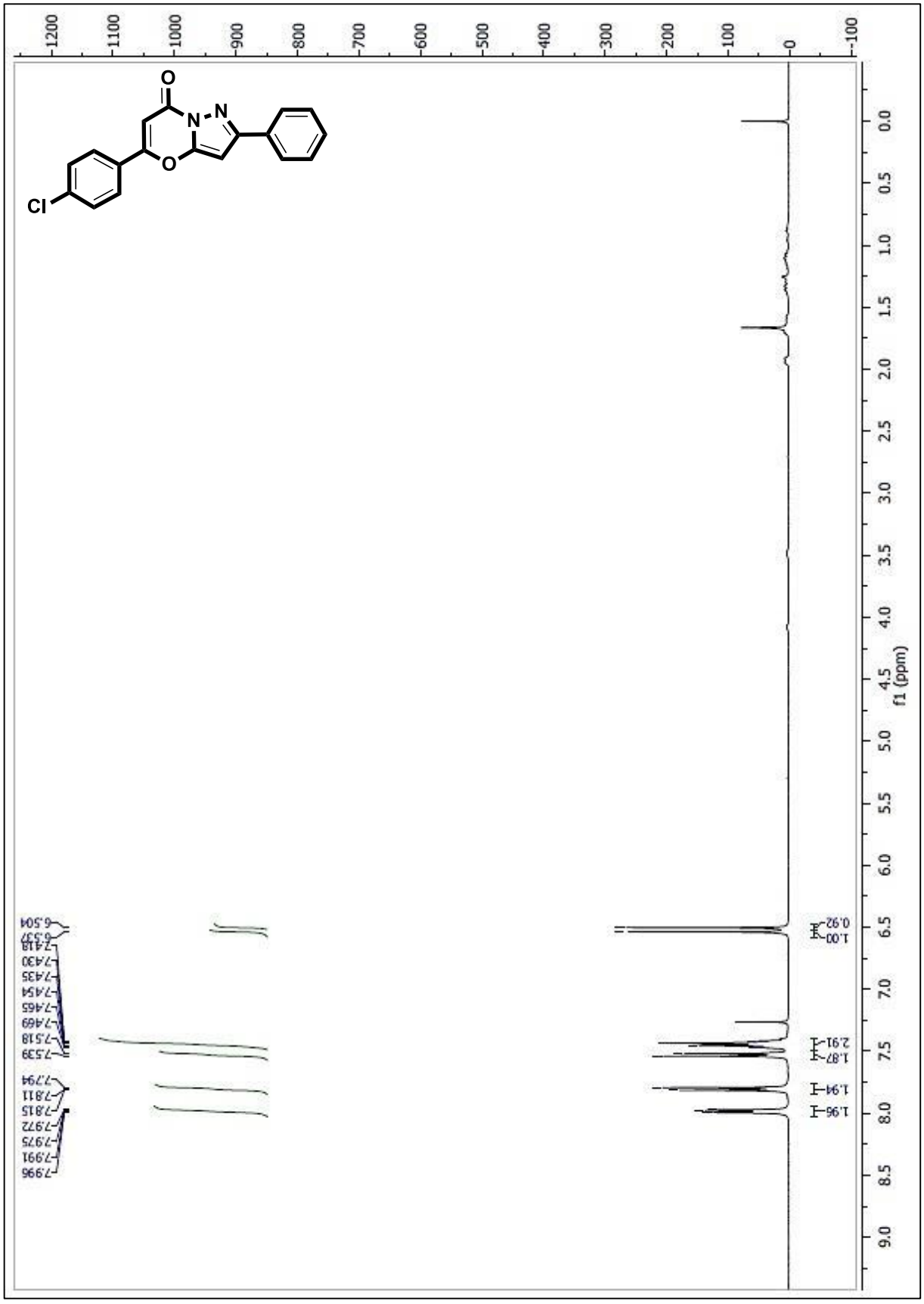
**$^{1}$H NMR Spectrum of 6af in $CDCl_3$:**



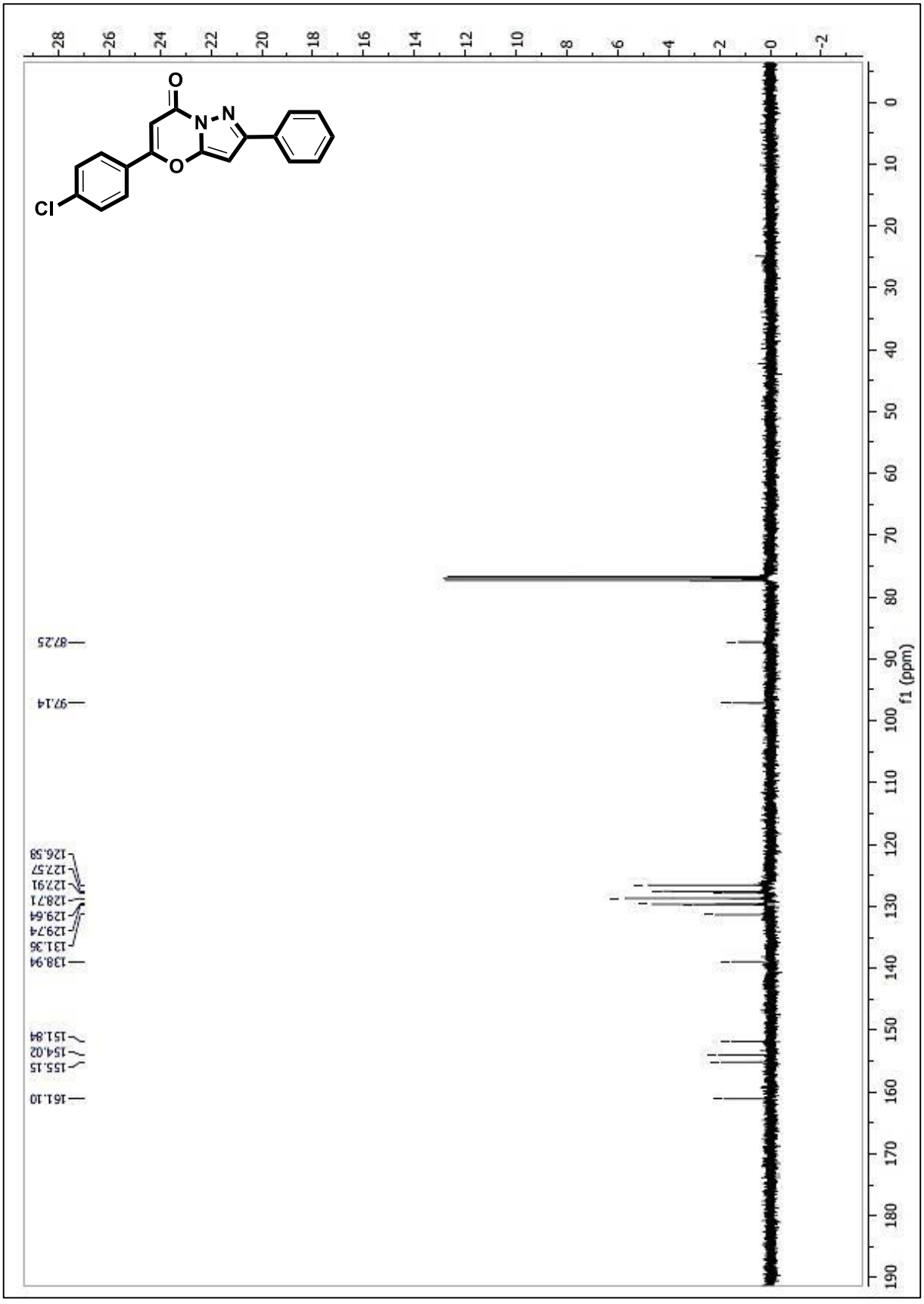
**$^{13}$C NMR Spectrum of 6af in $CDCl_3$:**



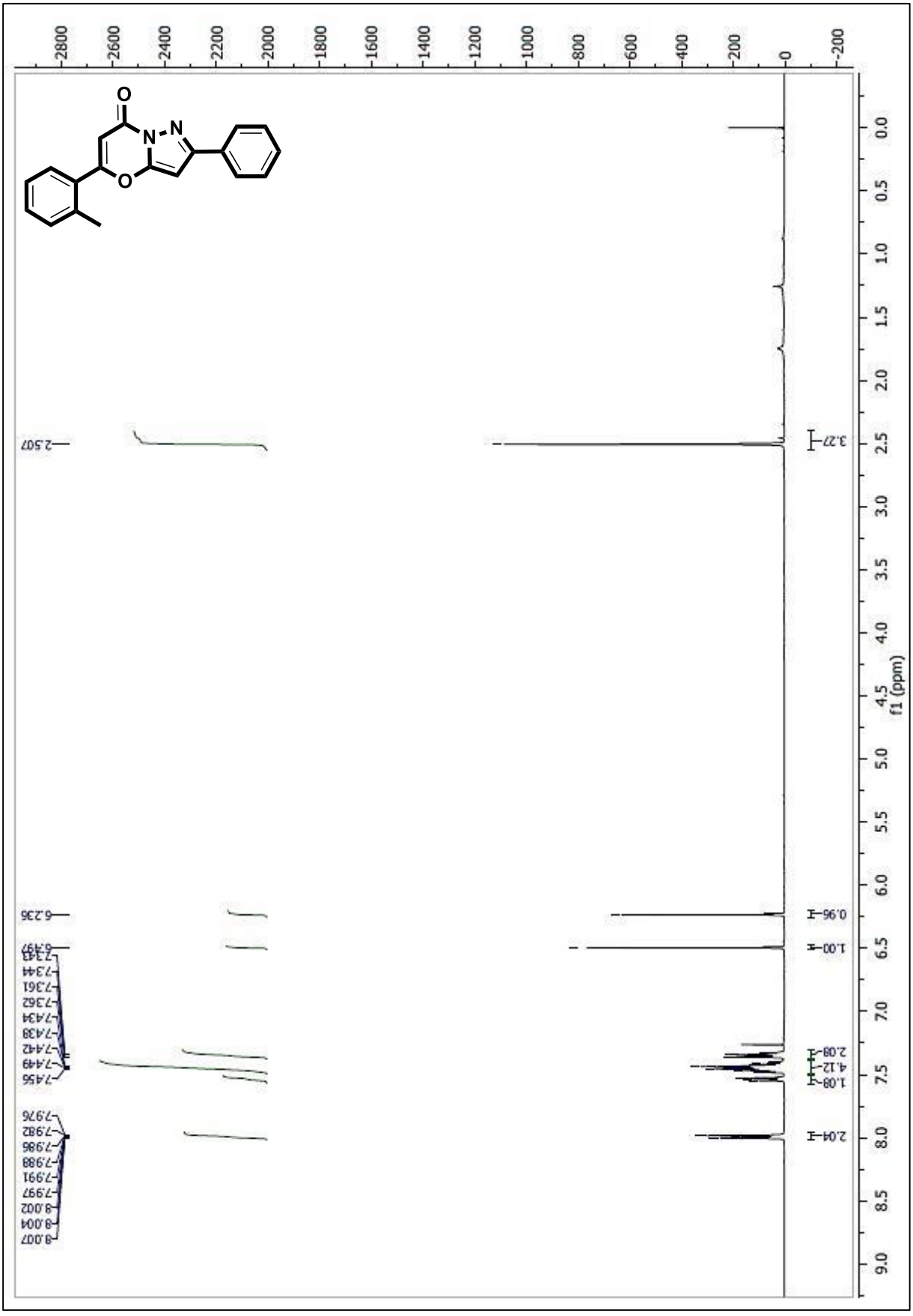
**$^1$H NMR Spectrum of 6ag in $CDCl_3$:**



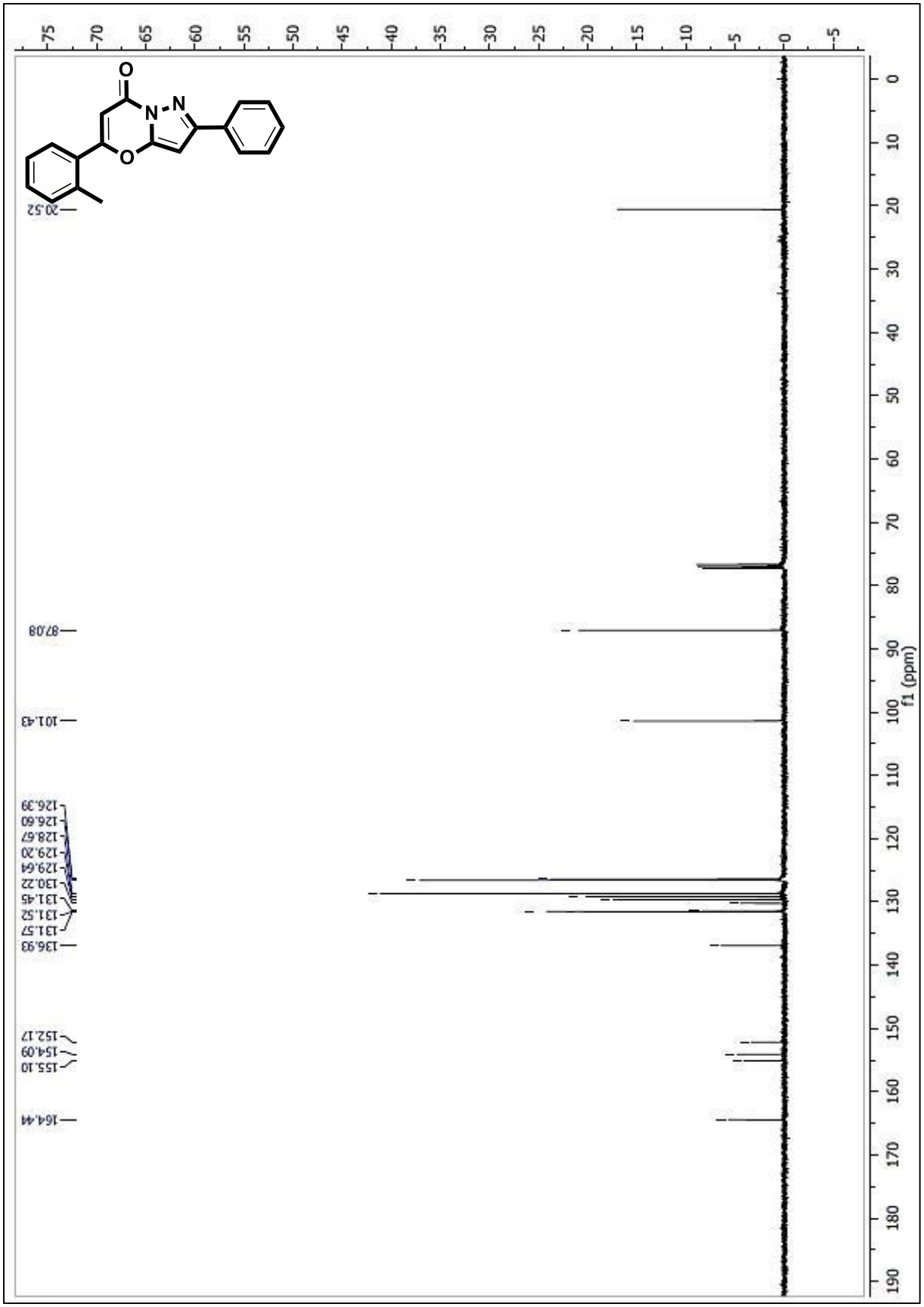
**$^{13}$C NMR Spectrum of 6ag in $CDCl_3$:**



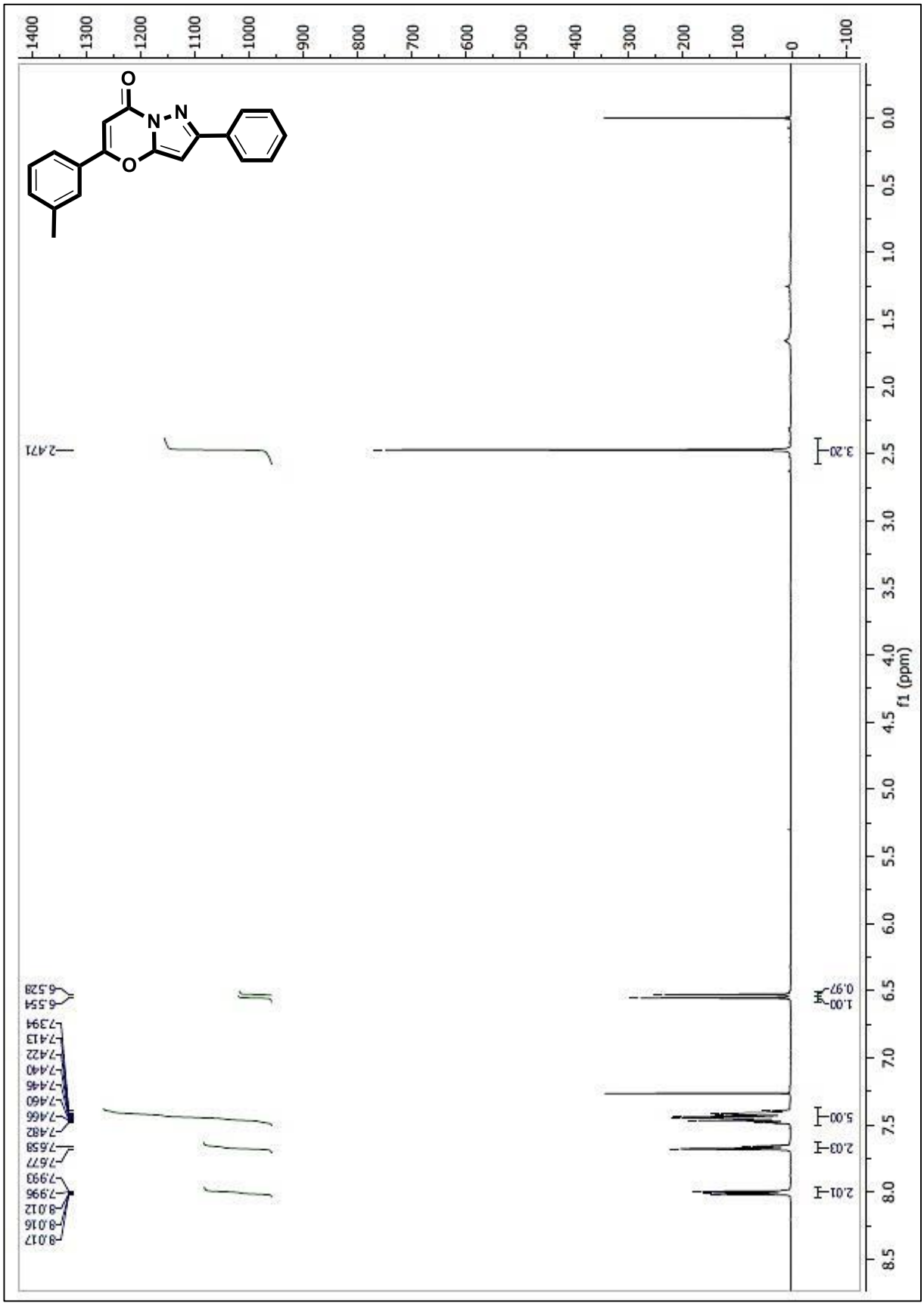
**$^1$H NMR Spectrum of 6ah in $CDCl_3$:**



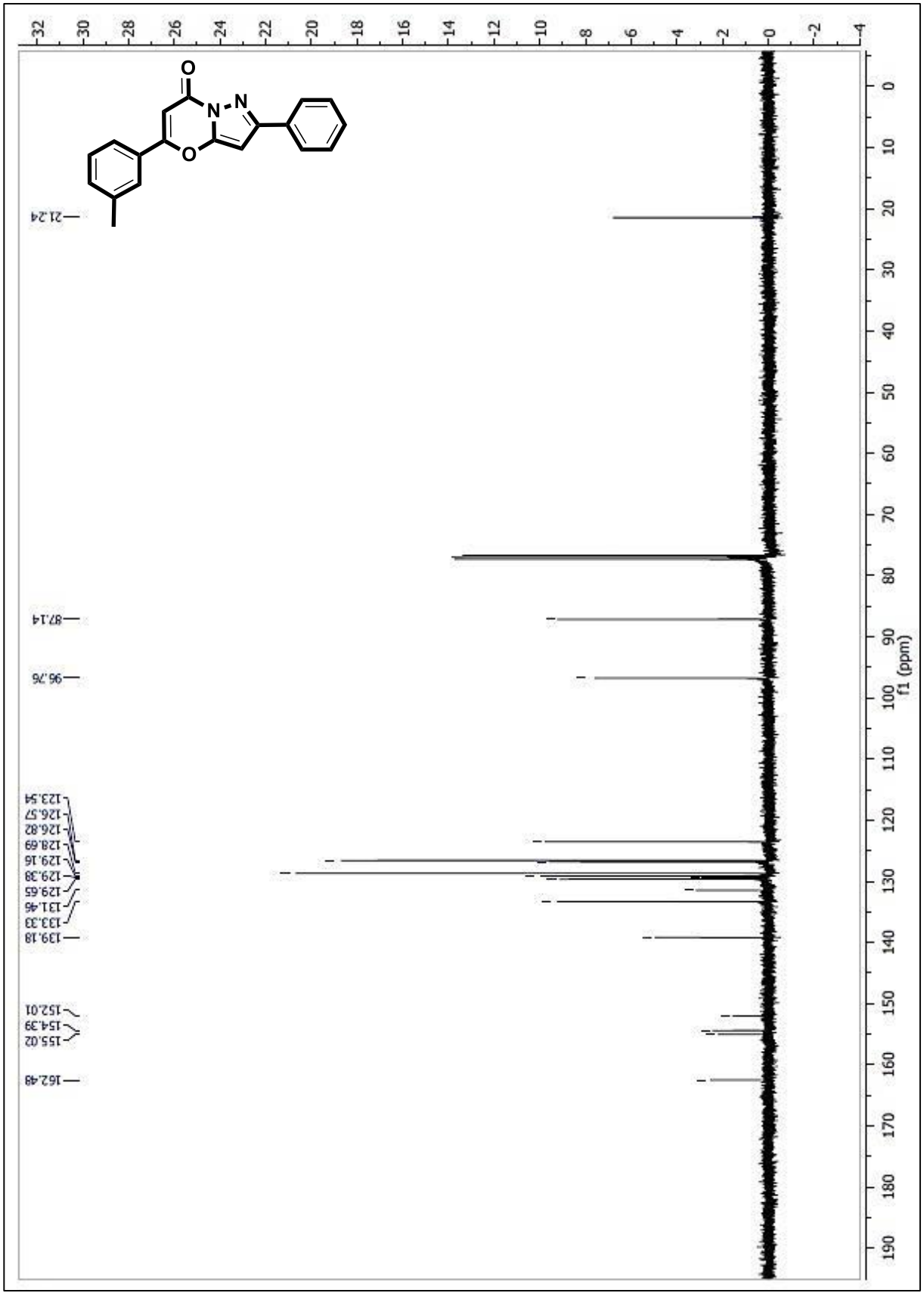
**$^{13}$C NMR Spectrum of 6ah in $CDCl_3$:**



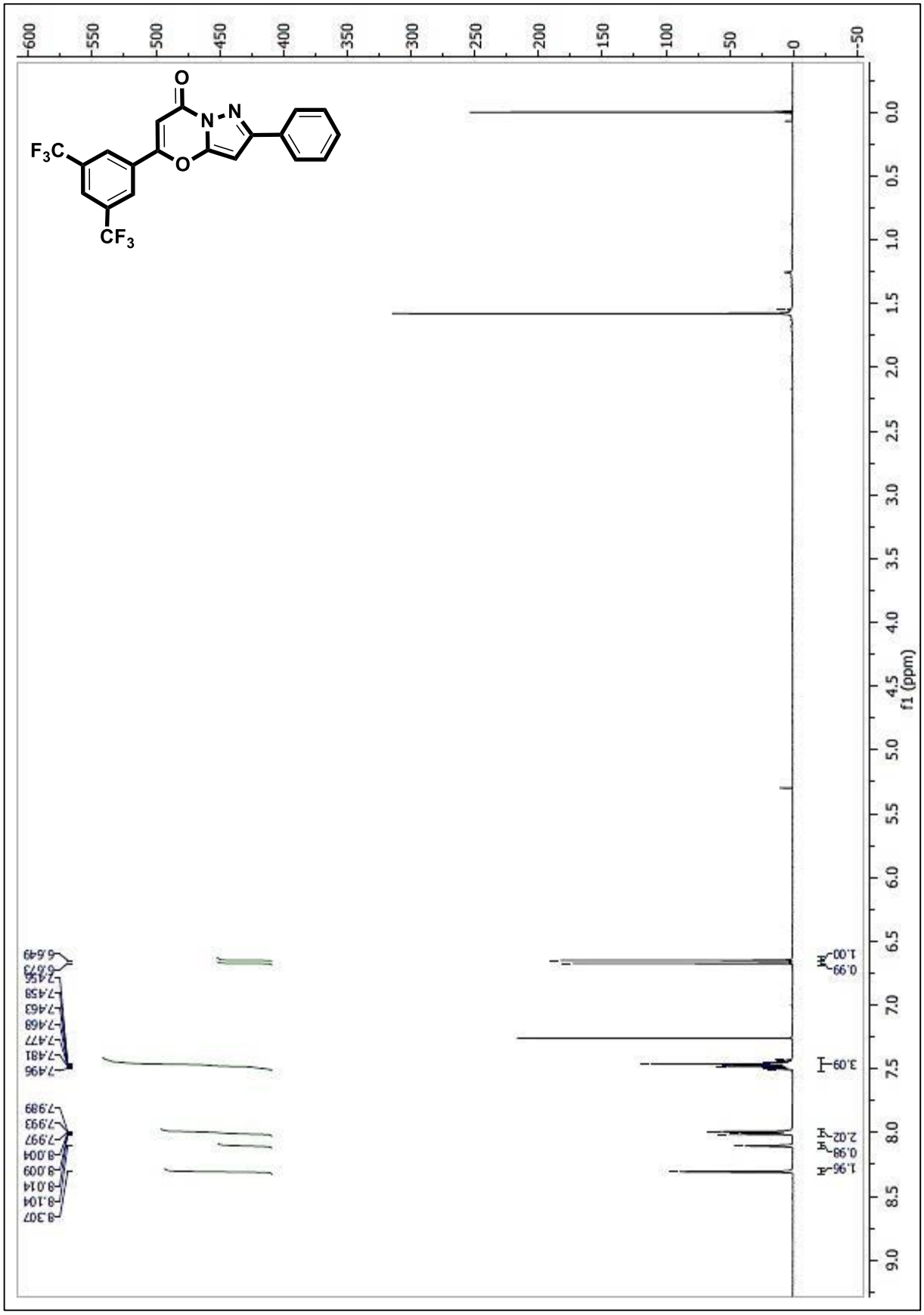
**$^1$H NMR Spectrum of 6ai in $CDCl_3$:**



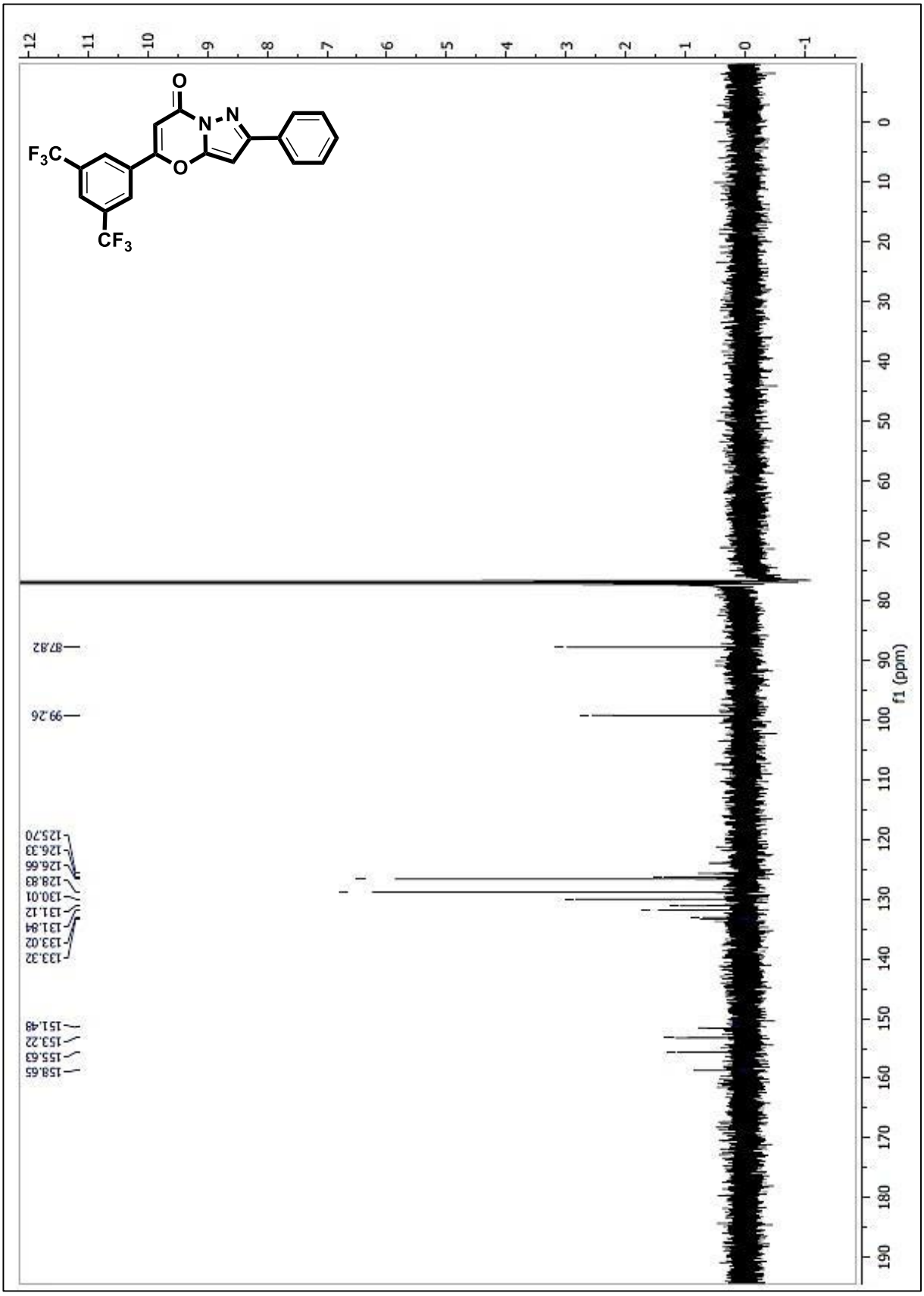
**$^{13}$C NMR Spectrum of 6ai in $CDCl_3$:**



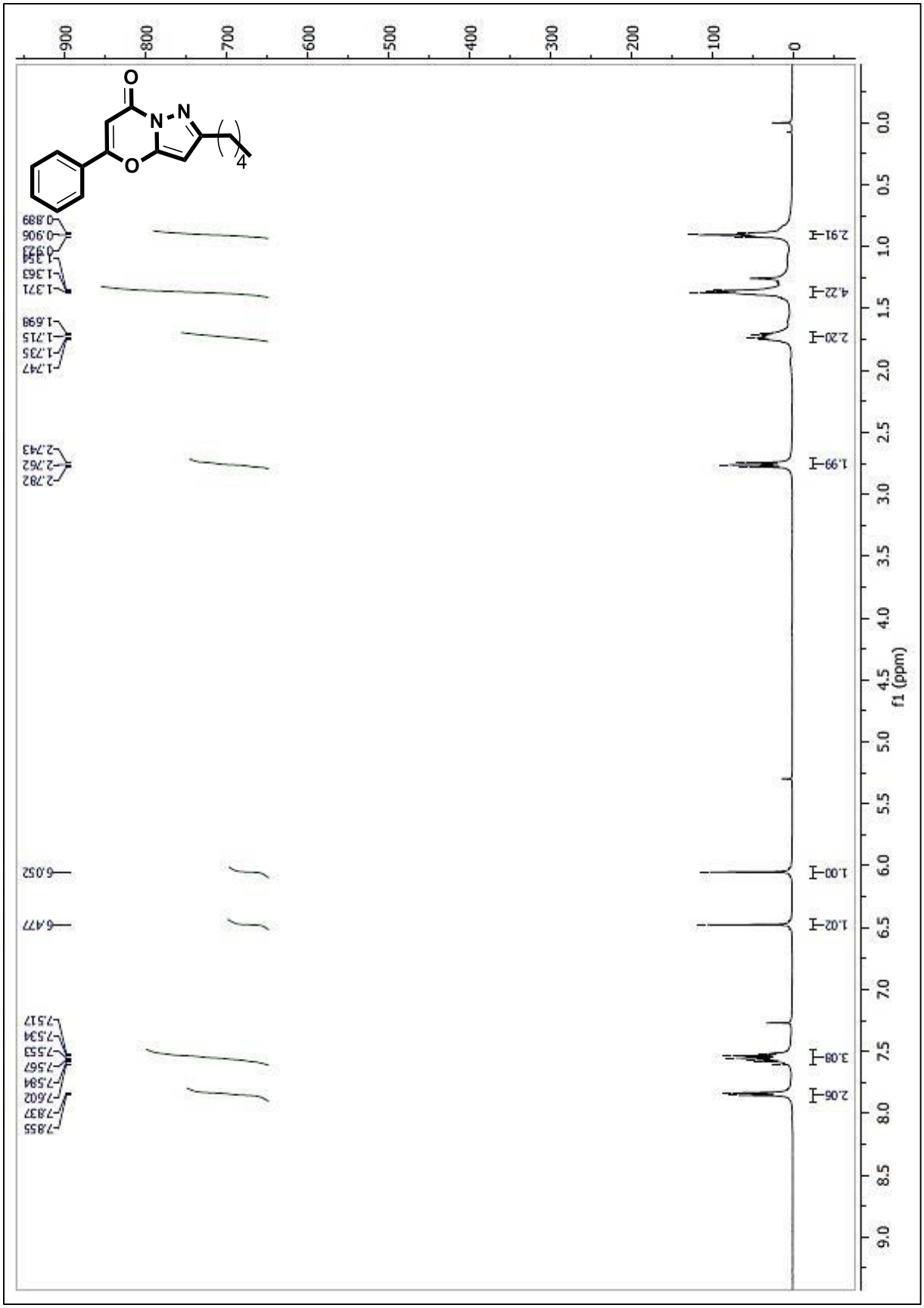
**$^{1}$H NMR Spectrum of 6aj in $CDCl_3$:**



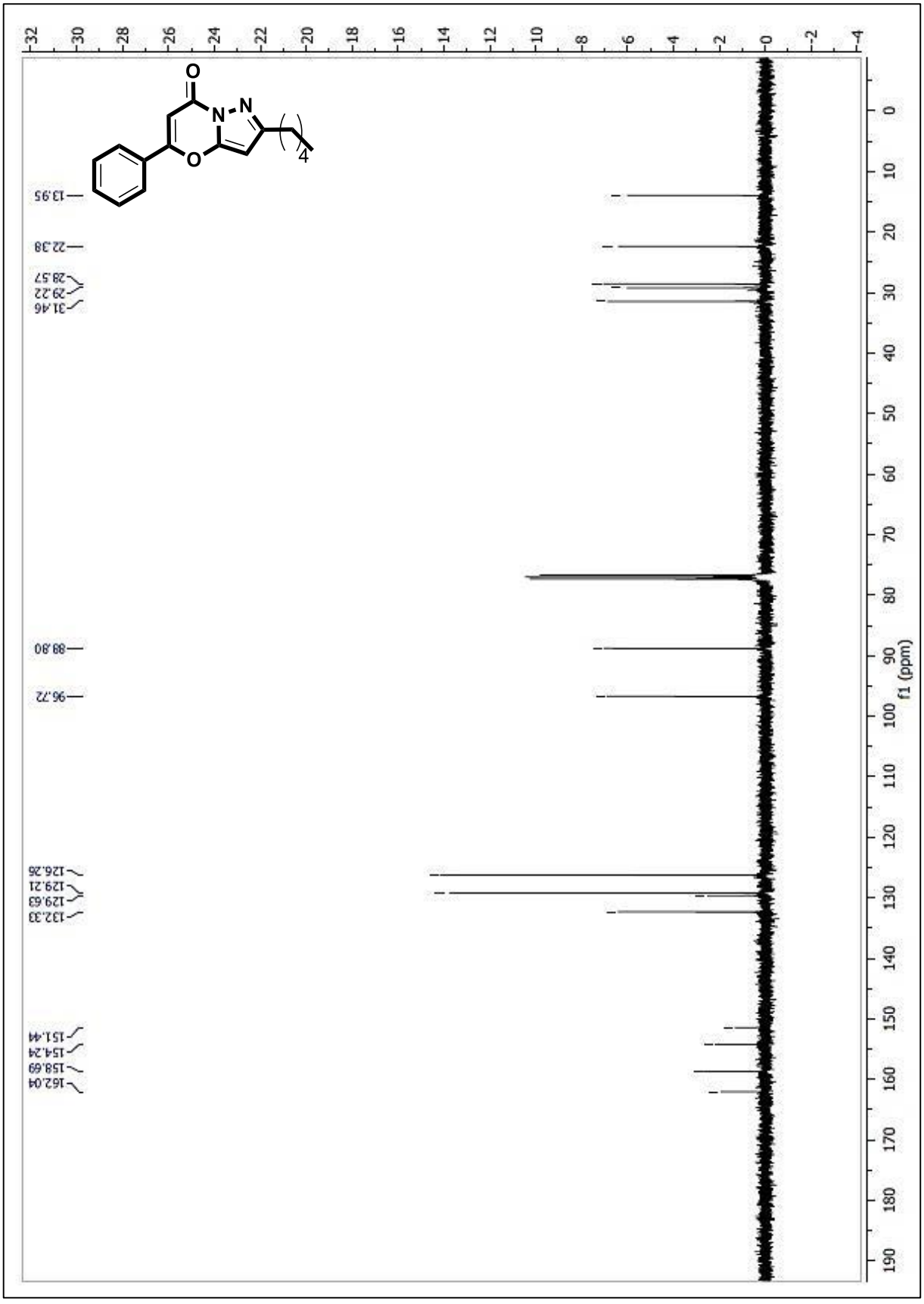
**$^{13}$C NMR Spectrum of 6aj in $CDCl_3$:**



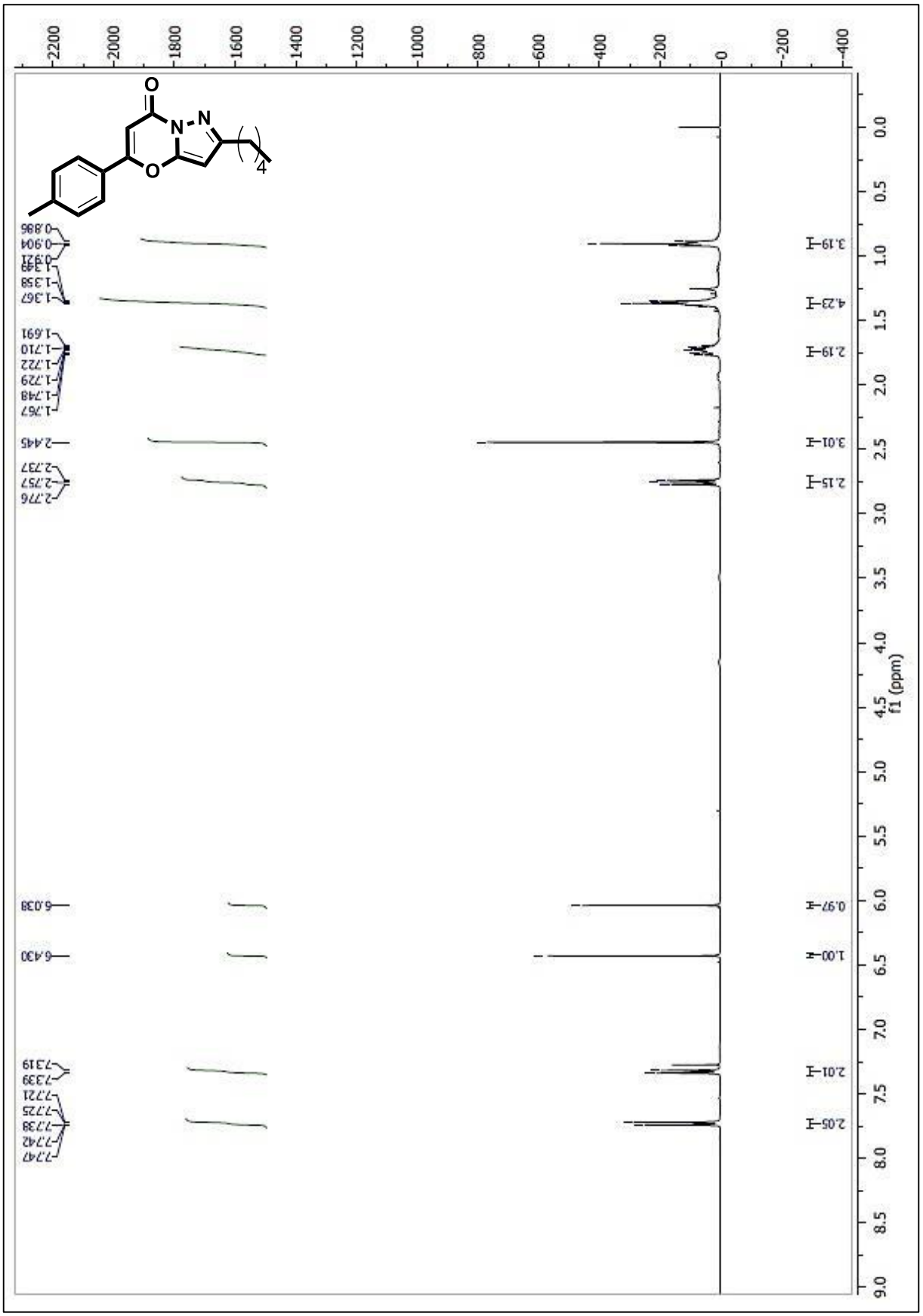
**$^1$H NMR Spectrum of 6ba in $CDCl_3$:**



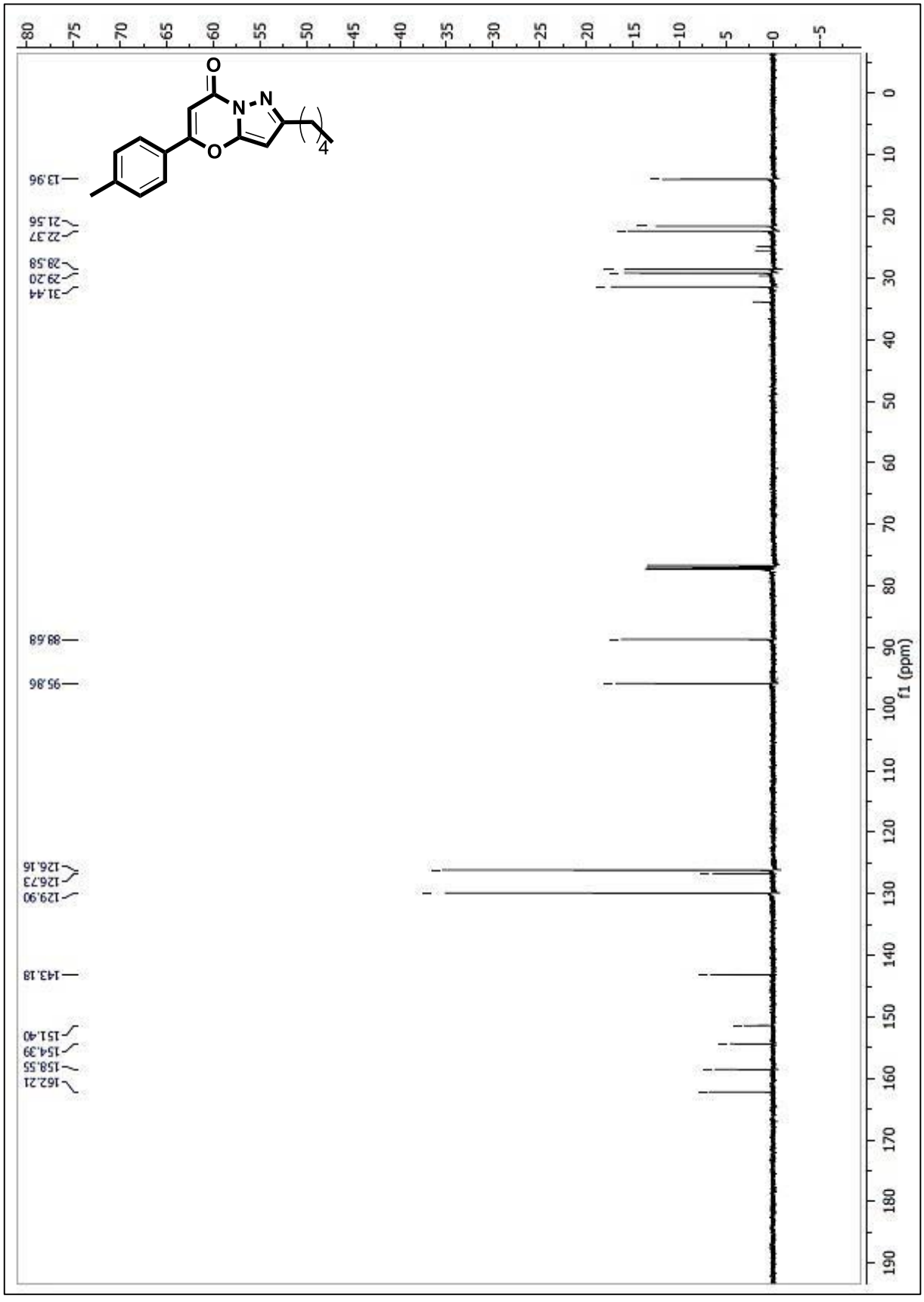
**$^{13}$C NMR Spectrum of 6ba in $CDCl_3$:**



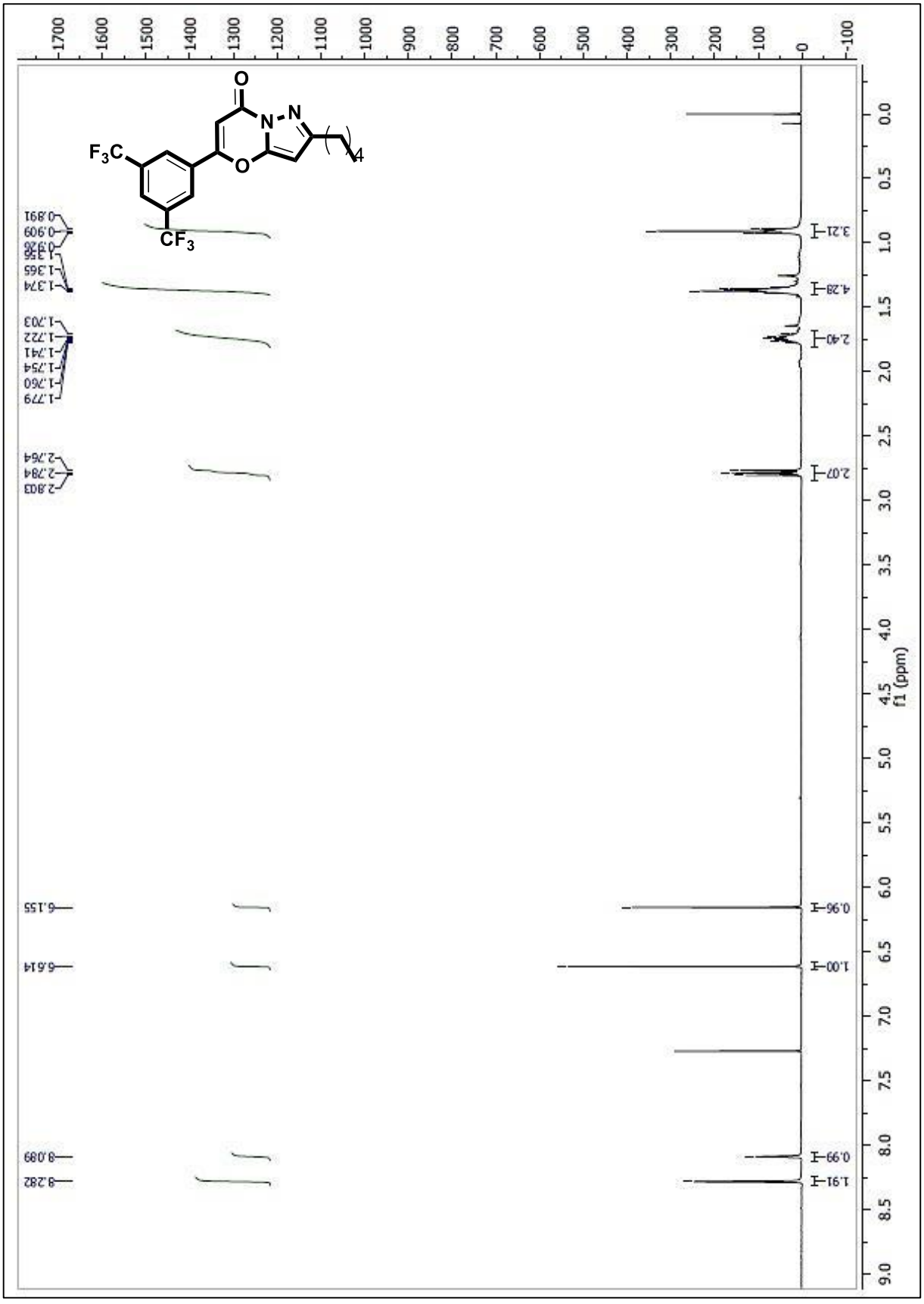
**$^1$H NMR Spectrum of 6be in $CDCl_3$:**



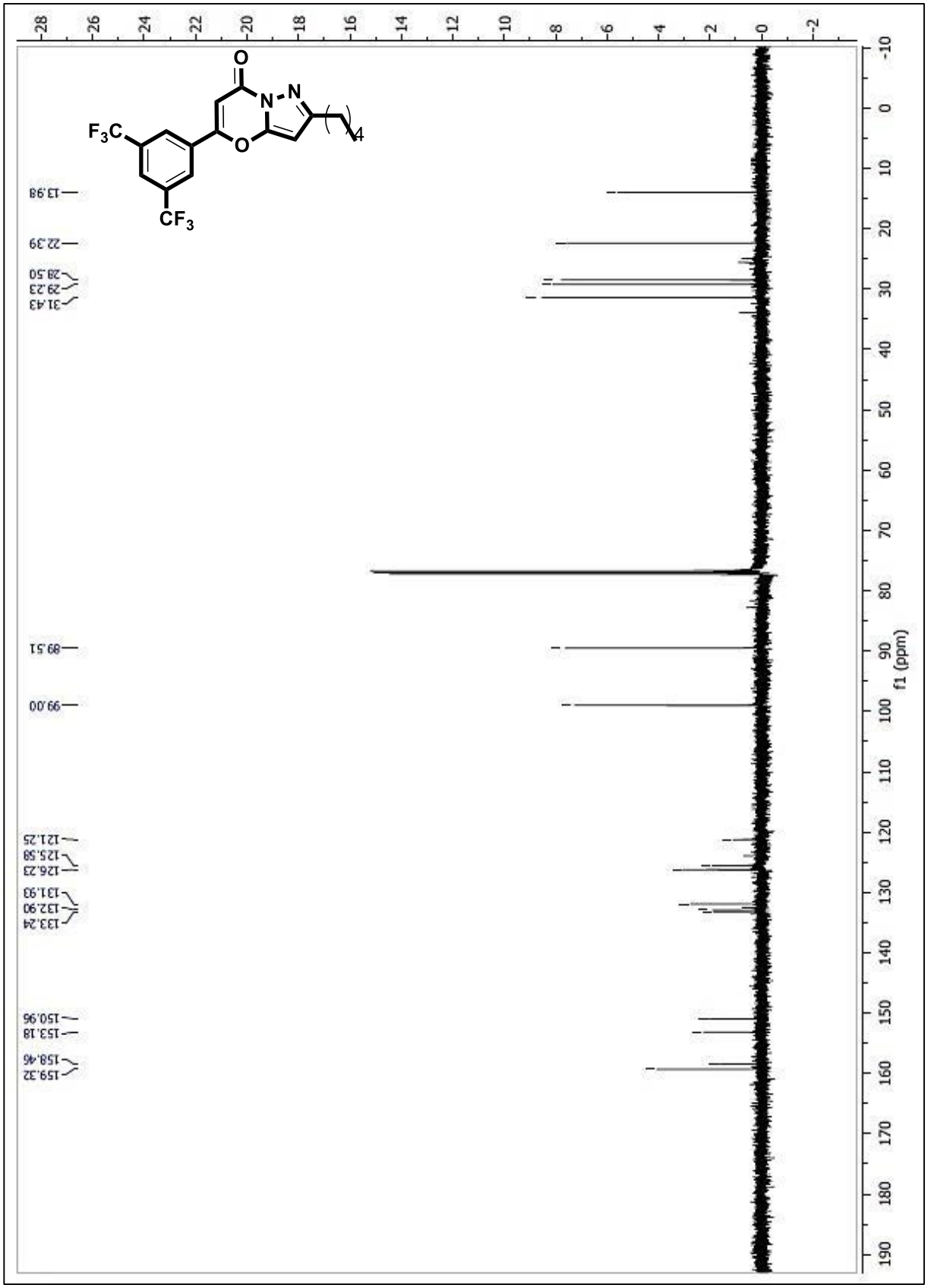
**$^{13}$C NMR Spectrum of 6be in $CDCl_3$:**



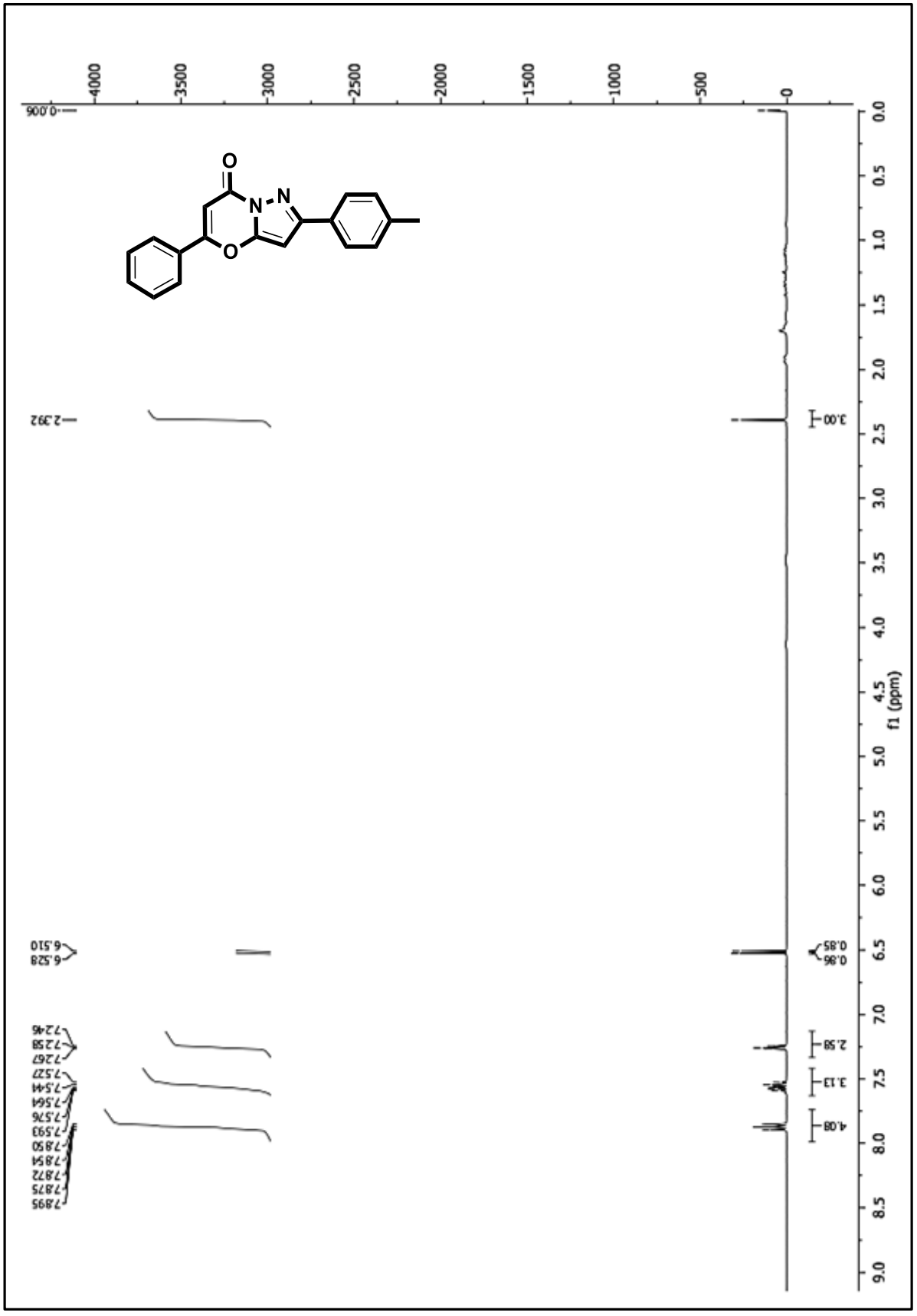
**$^{1}$H NMR Spectrum of 6bj in $CDCl_3$:**



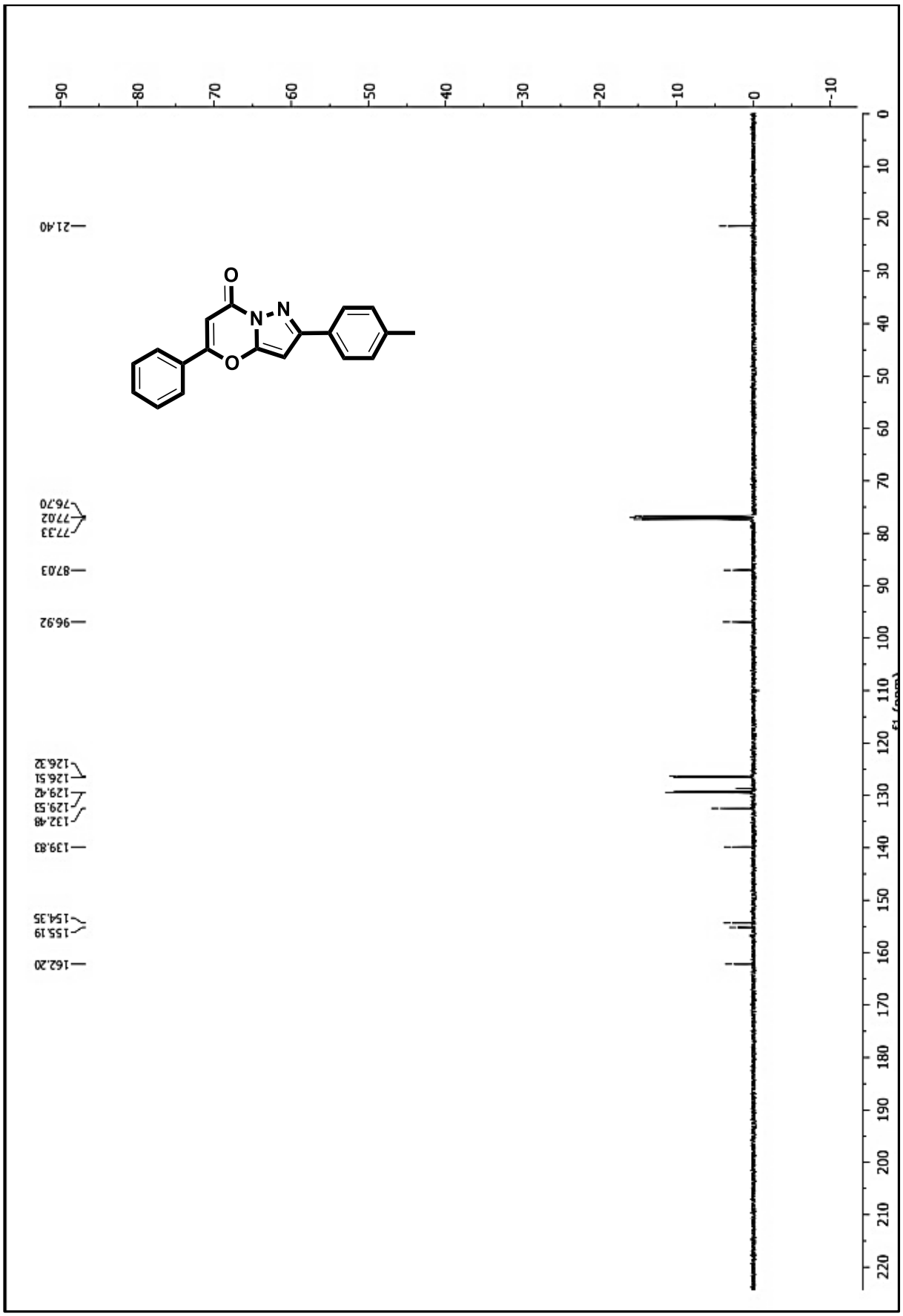
**$^{13}$C NMR Spectrum of 6bj in $CDCl_3$:**



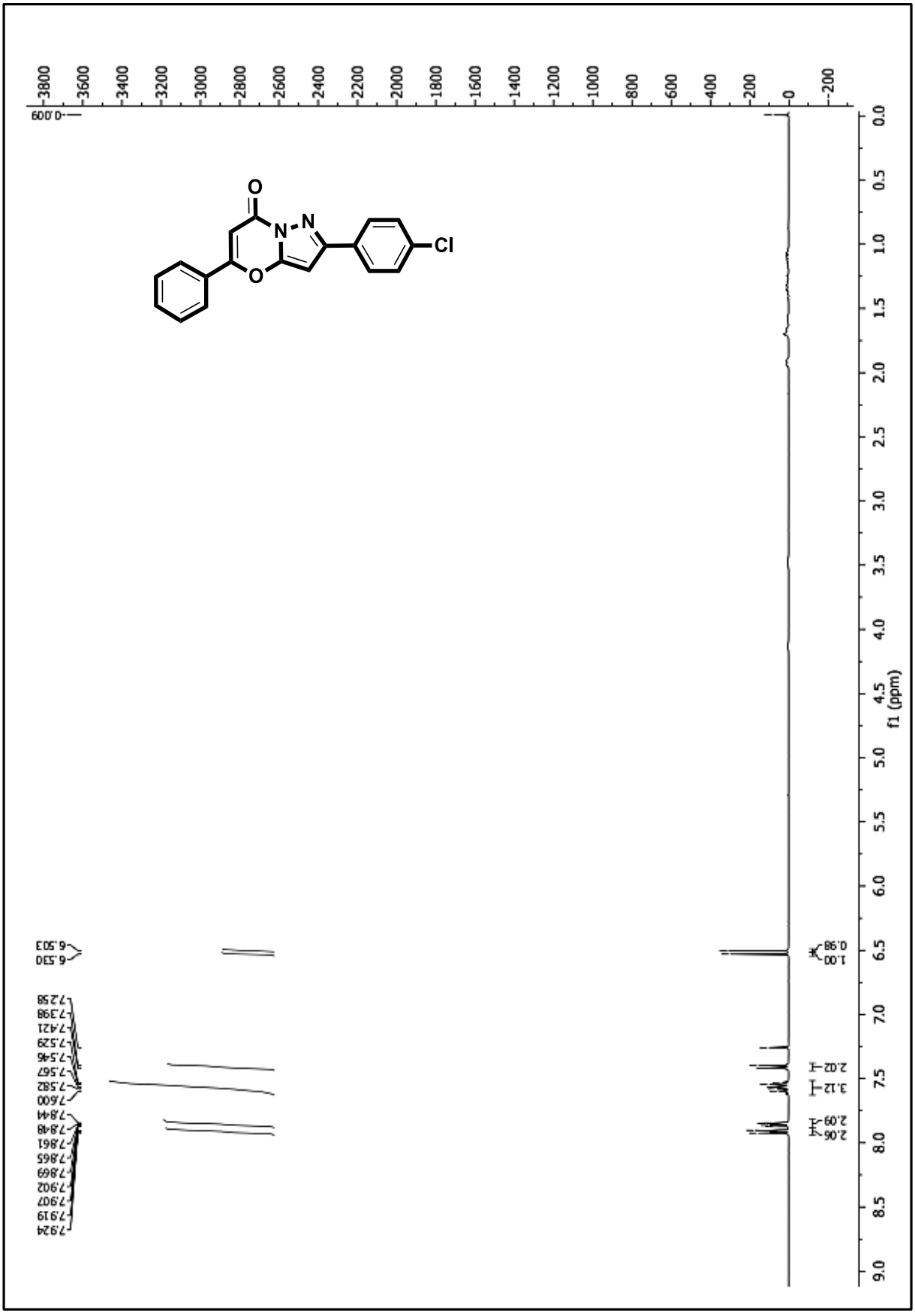
**$^{1}$H NMR Spectrum of 6ca in $CDCl_3$:**



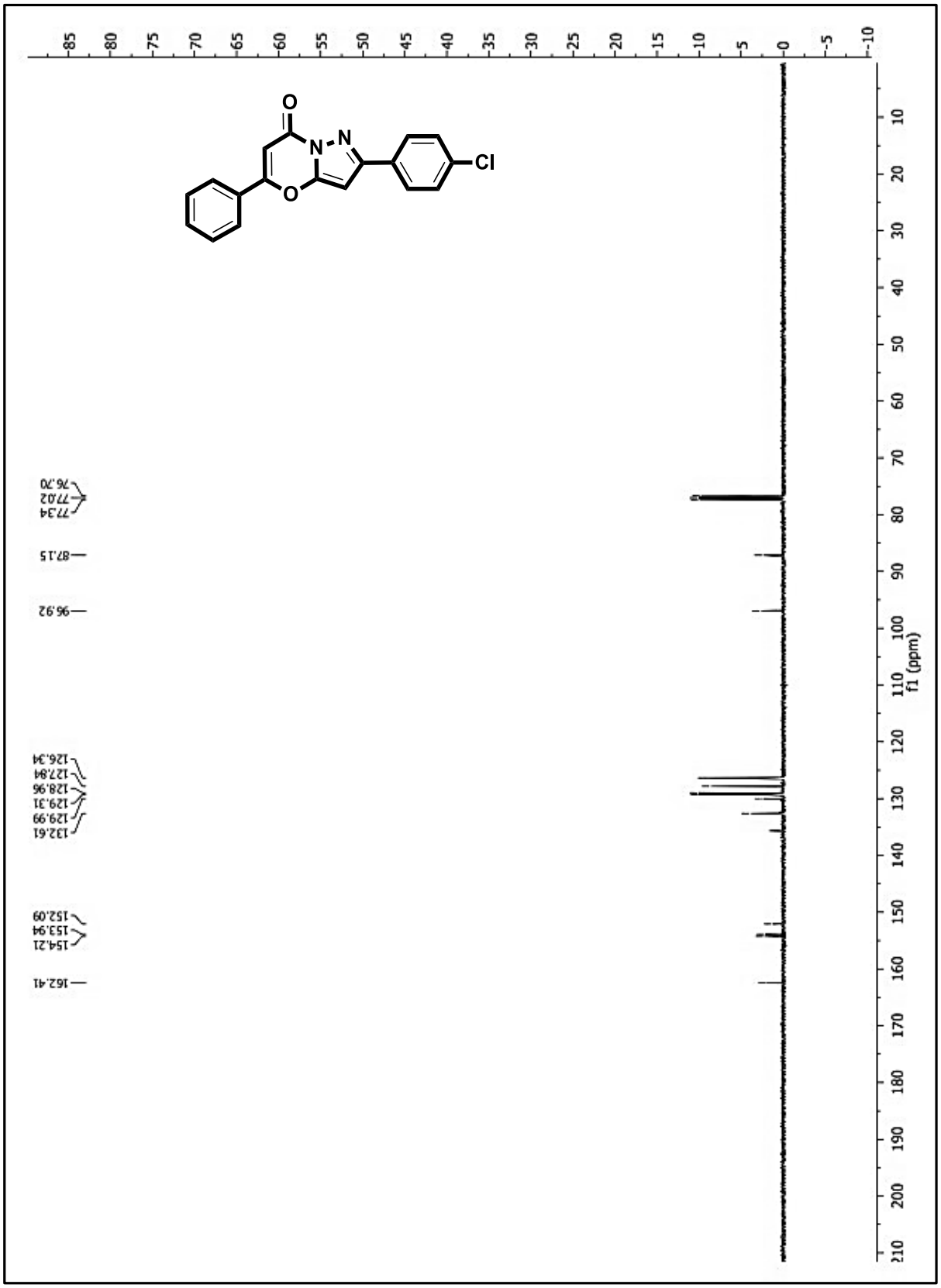
**$^{13}$C NMR Spectrum of 6ca in $CDCl_3$:**



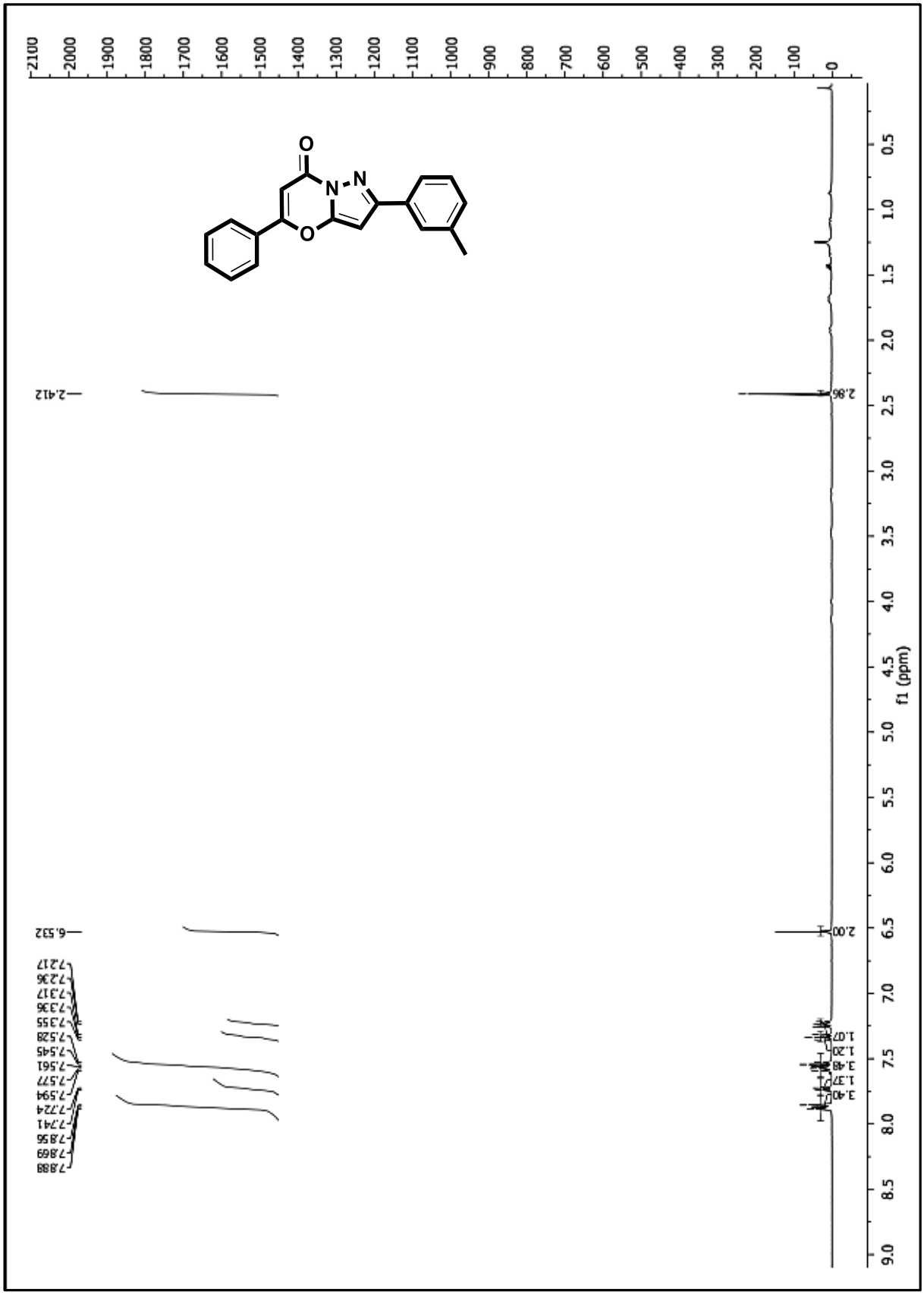
**$^{1}$H NMR Spectrum of 6da in $CDCl_3$:**



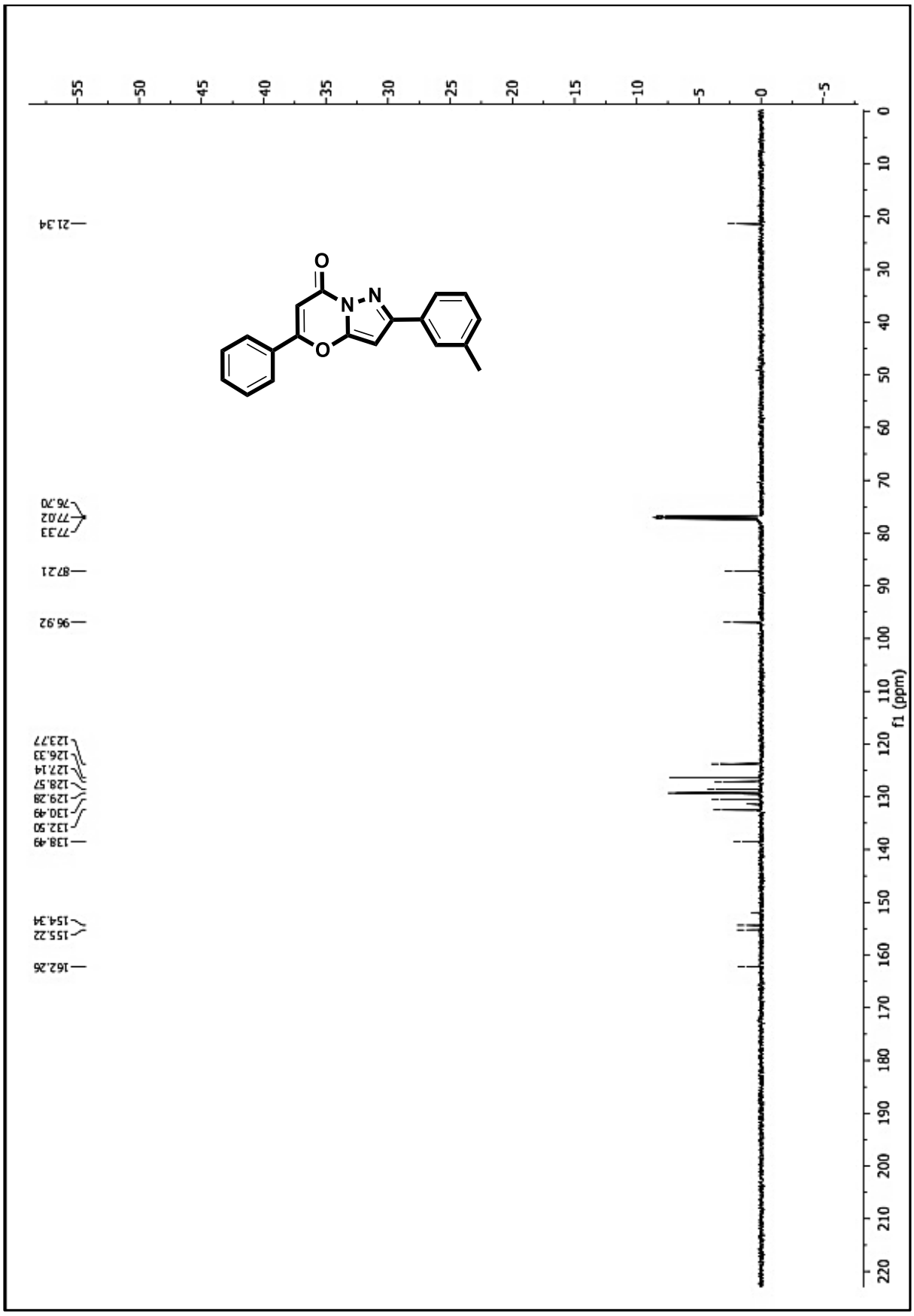
**$^{13}$C NMR Spectrum of 6da in $CDCl_3$:**



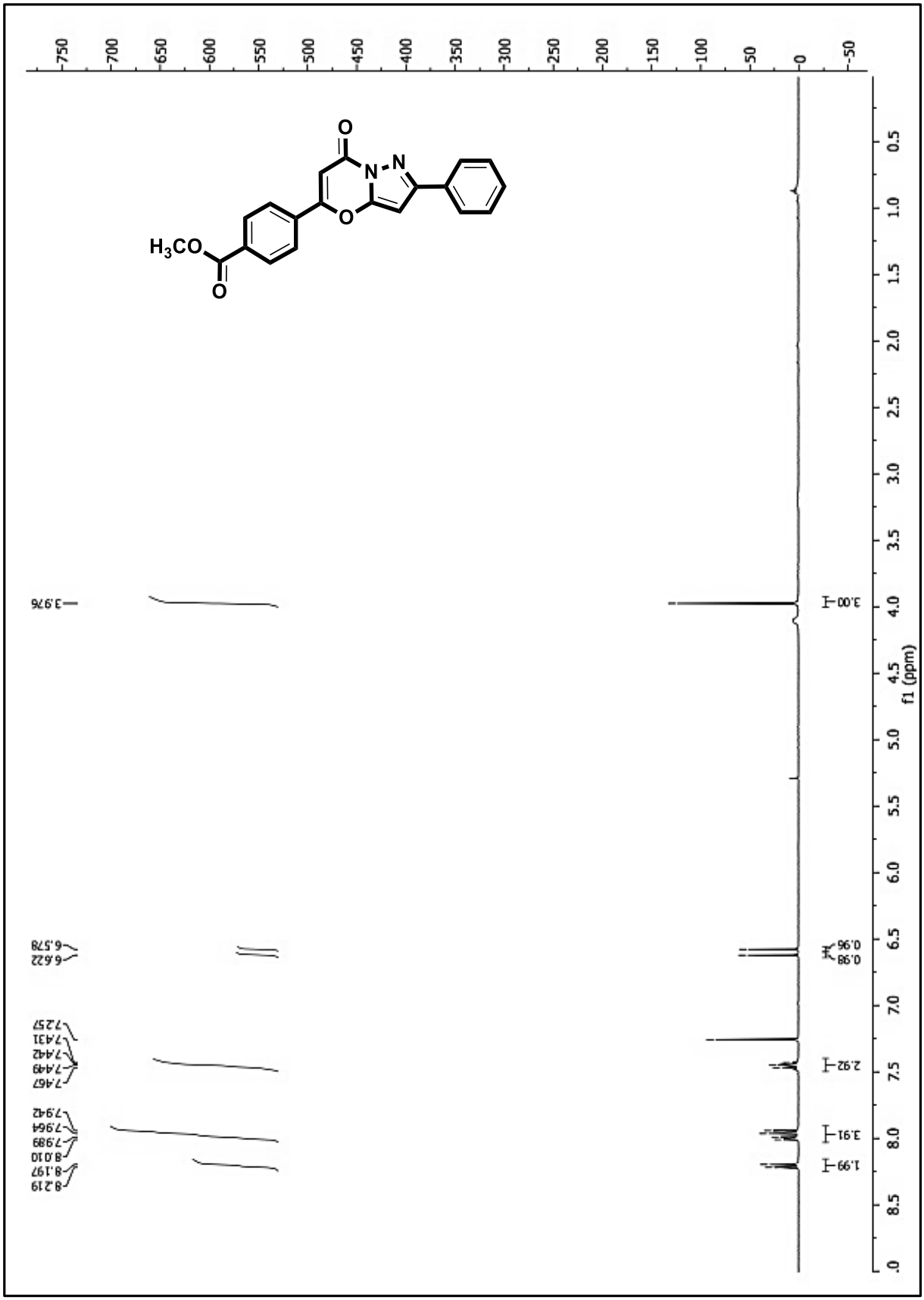
**$^{1}$H NMR Spectrum of 6ea in $CDCl_3$:**



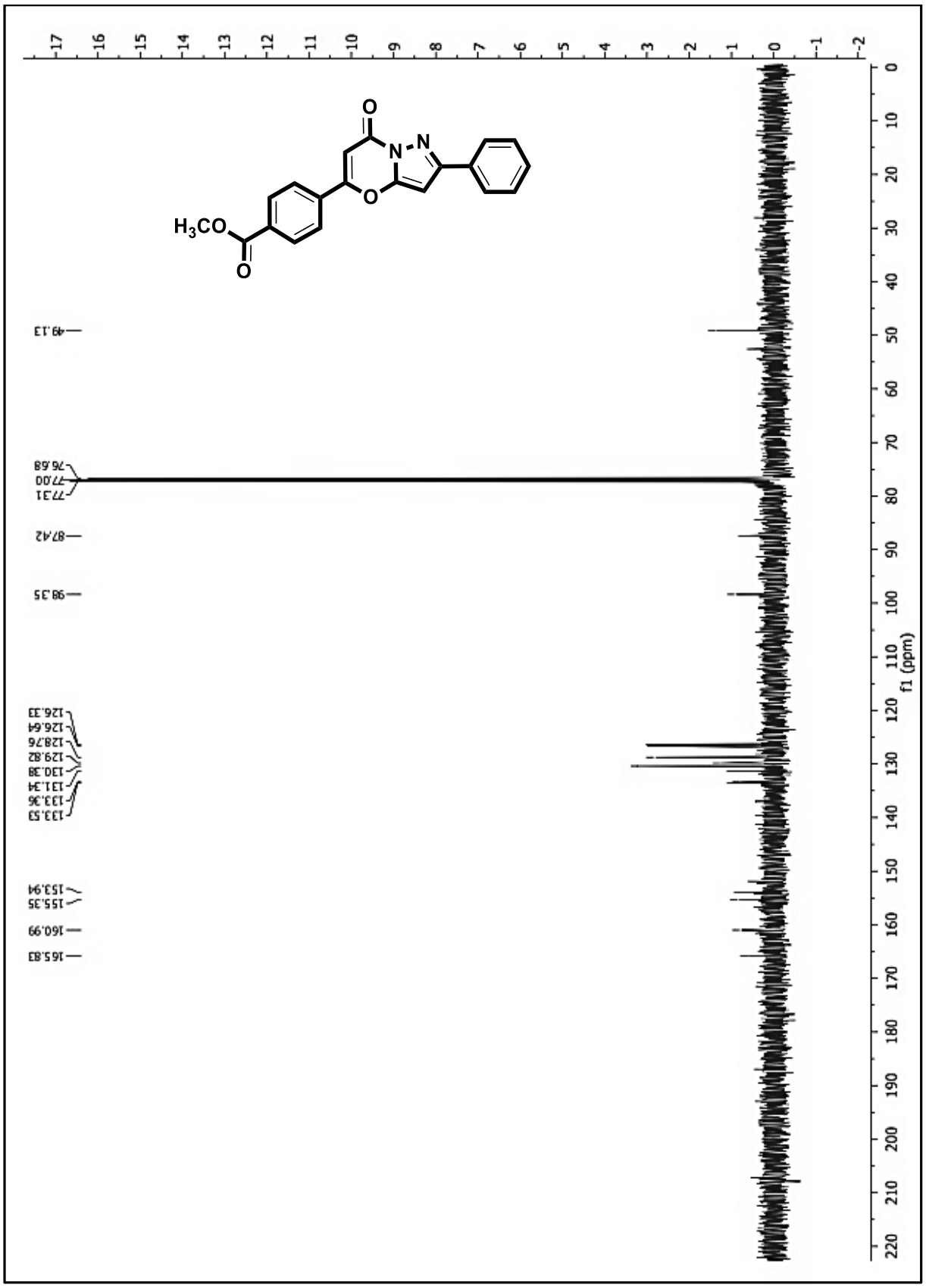
**$^{13}$C NMR Spectrum of 6ea in $CDCl_3$:**



**$^{1}$H NMR Spectrum of 6ak in $CDCl_3$:**



**$^{13}$C NMR Spectrum of 6ak in $CDCl_3$:**



## 7. Computational Studies

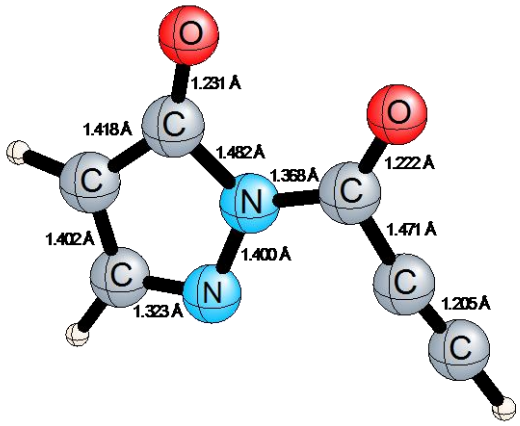



**Figure S1:** Selected interatomic distances (Å) for **3x (3cb)**.

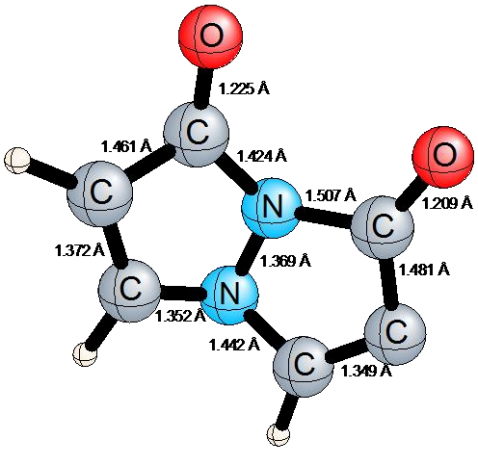



**Figure S2:** Selected interatomic distances (Å) for **4x**.

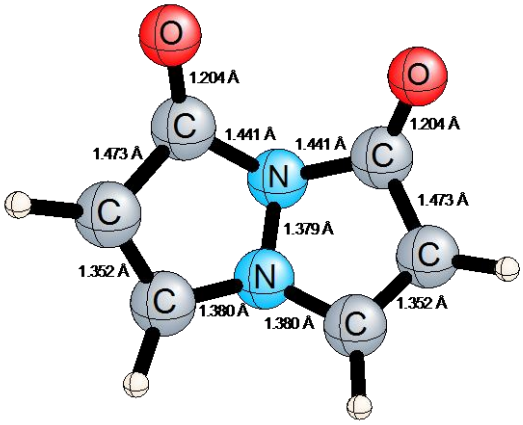



**Figure S3:** Selected interatomic distances (Å) for **7**.

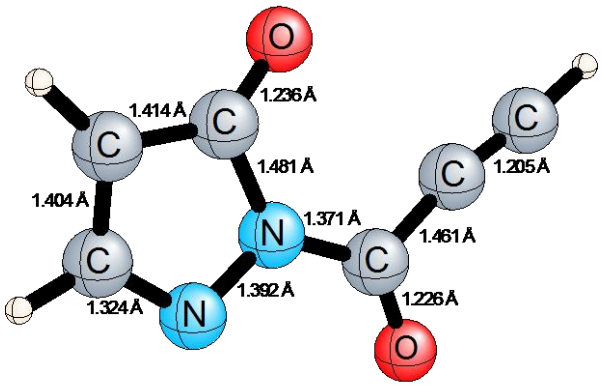



**Figure S4:** Selected interatomic distances (Å) for **3y**.

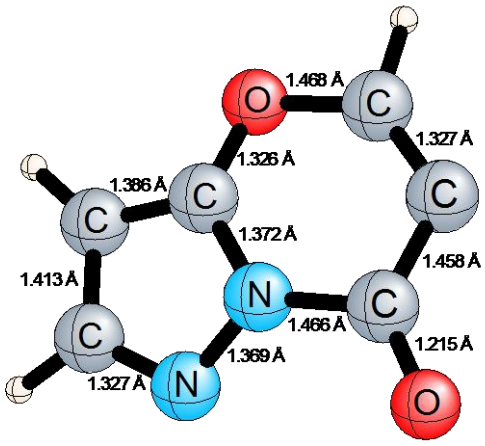



**Figure S5:** Selected interatomic distances (Å) for **4y**.

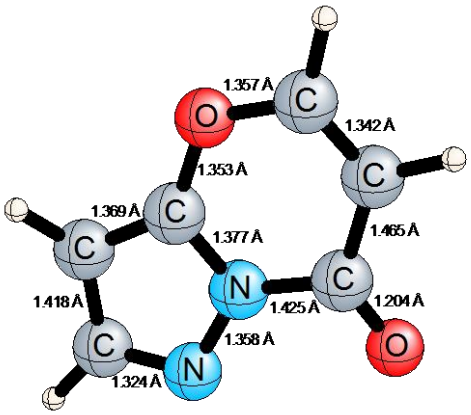



**Figure S6:** Selected interatomic distances (Å) for **6**.

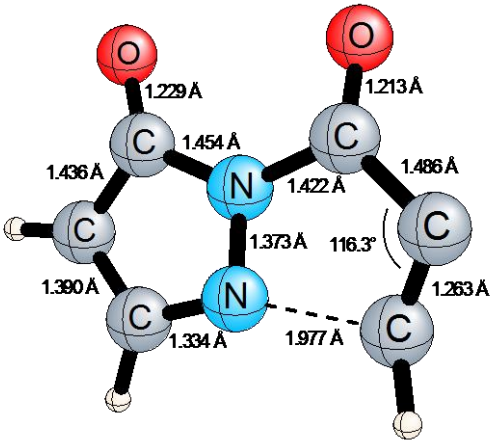



**Figure S7:** Selected interatomic distances (Å) for **3x/4x**.

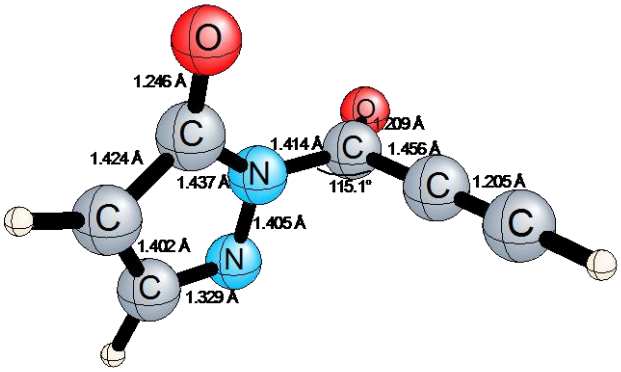



**Figure S8:** Selected interatomic distances (Å) for **3x/3y**.

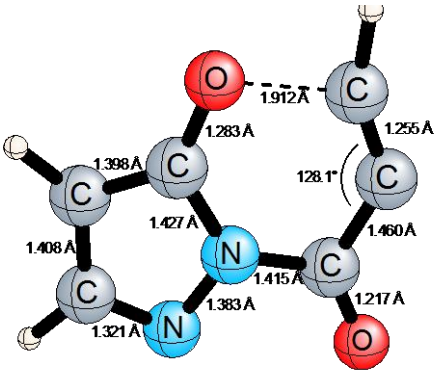



**Figure S9:** Selected interatomic distances (Å) for **3y/4y**.

## Computations at the B3LYP/6-311++G** level

**3x (R=H)**

-1 1

| | | | |
|---|---|---|---|
| C | -0.08172700 | 2.40515300 | 0.00000000 |
| C | 0.87355900 | 1.35668500 | 0.00000000 |
| N | 0.00000000 | 0.15894900 | 0.00000000 |
| C | -1.35357000 | 1.81425100 | 0.00000000 |
| N | -1.36039600 | 0.49129800 | 0.00000000 |
| O | 2.10388600 | 1.31657000 | 0.00000000 |
| H | -2.31054500 | 2.32593600 | 0.00000000 |
| C | 0.36564500 | -1.15966600 | 0.00000000 |
| O | 1.50824400 | -1.59339400 | 0.00000000 |
| C | -0.75616200 | -2.11140300 | 0.00000000 |
| C | -1.54145200 | -3.02481100 | 0.00000000 |
| H | -2.26767600 | -3.79894400 | 0.00000000 |
| H | 0.16619400 | 3.45461700 | 0.00000000 |

**4x (R=H)**

-1 1

| | | | |
|---|---|---|---|
| C | -2.09648500 | -0.54360900 | -0.12437400 |
| C | -1.31944300 | 0.68648800 | 0.01307900 |
| N | 0.01132600 | 0.22252000 | 0.22029600 |
| C | -1.22678600 | -1.60135800 | -0.03833300 |
| N | 0.02527900 | -1.14581200 | 0.19180900 |
| O | -1.67341800 | 1.85871100 | -0.01256800 |
| H | -1.40487500 | -2.66482100 | -0.11352200 |
| C | 1.43159700 | 0.67135400 | -0.00893800 |
| O | 1.68630200 | 1.85195900 | -0.05114800 |
| C | 2.26915900 | -0.54374000 | -0.13260400 |
| H | -3.16623400 | -0.57665700 | -0.25750600 |
| C | 1.38794500 | -1.56015600 | -0.03296200 |
| H | 1.53588000 | -2.63471200 | -0.05918700 |

**7 (R=H)**

0 1

| | | | |
|---|---|---|---|
| C | -2.12330800 | -0.53409900 | -0.11932800 |
| C | -1.34241400 | 0.70777000 | 0.00956100 |
| N | 0.00002800 | 0.23163500 | 0.22948700 |
| C | -1.28544900 | -1.59171400 | -0.03521900 |
| N | -0.00010300 | -1.14732800 | 0.19872800 |
| O | -1.67088100 | 1.86520400 | -0.03581800 |
| H | -1.47985800 | -2.65195300 | -0.09289100 |
| C | 1.34255500 | 0.70760200 | 0.00968700 |
| O | 1.67121000 | 1.86498200 | -0.03573300 |
| C | 2.12321800 | -0.53439300 | -0.11933000 |
| H | -3.19224800 | -0.55345300 | -0.24921900 |
| C | 1.28514100 | -1.59186200 | -0.03547900 |
| H | 1.47936600 | -2.65212600 | -0.09325200 |
| H | 3.19217000 | -0.55392400 | -0.24909700 |

**3y (R=H)**

-1 1

| | | | |
|---|---|---|---|
| C | -2.19601600 | -0.85700400 | 0.00028500 |
| C | -0.79348100 | -1.03274300 | -0.00020500 |
| N | -0.30921200 | 0.36686000 | -0.00025000 |
| C | -2.43477800 | 0.52645100 | 0.00071600 |
| N | -1.35255200 | 1.28896600 | 0.00057900 |
| O | -0.04318500 | -2.01483700 | -0.00114100 |
| H | -3.40111900 | 1.02015700 | 0.00114400 |
| C | 0.98430500 | 0.82143000 | -0.00035900 |
| O | 1.30642000 | 2.00458000 | -0.00097900 |
| C | 2.04155900 | -0.18633800 | 0.00036900 |
| C | 3.05595800 | -0.83585700 | 0.00115900 |
| H | 3.89672200 | -1.48348500 | 0.00195200 |
| H | -2.91441800 | -1.66102100 | -0.00022500 |

**4y (R=H)**

-1 1

| | | | |
|---|---|---|---|
| C | 1.97510600 | -0.89044600 | 0.00009700 |
| C | 0.58978300 | -0.84671300 | 0.00012800 |
| N | 0.21168600 | 0.47224200 | -0.00016500 |
| C | 2.34247200 | 0.47372400 | 0.00031000 |
| N | 1.30319800 | 1.29869400 | -0.00045100 |
| O | -0.29518600 | -1.83467000 | 0.00026600 |
| H | 3.34250500 | 0.88768100 | 0.00046000 |
| H | 2.59885900 | -1.76905200 | 0.00019800 |
| C | -1.18420200 | 0.91943400 | -0.00016700 |
| C | -2.16425600 | -0.16045200 | -0.00020900 |
| O | -1.38594600 | 2.11765600 | 0.00008000 |
| C | -1.69840600 | -1.40339000 | -0.00000500 |
| H | -2.25948600 | -2.33201900 | -0.00003800 |

**6 (R=H)**

0 1

| | | | |
|---|---|---|---|
| C | 1.98956500 | -0.90199800 | 0.00032700 |
| C | 0.62245300 | -0.83494700 | -0.00001700 |
| N | 0.25645400 | 0.49281300 | -0.00071400 |
| C | 2.37592100 | 0.46276900 | 0.00033900 |
| N | 1.34925300 | 1.29951600 | -0.00042500 |
| O | -0.30028000 | -1.82432600 | -0.00014100 |
| H | 3.37989100 | 0.86115800 | 0.00061300 |
| H | 2.60546000 | -1.78480600 | 0.00060700 |
| C | -1.09195700 | 0.95266800 | -0.00025500 |
| C | -2.02326700 | -0.17820100 | 0.00008900 |
| O | -1.38637300 | 2.12002100 | 0.00048700 |
| C | -1.60554400 | -1.45358100 | 0.00006600 |
| H | -2.25551300 | -2.31730700 | 0.00025200 |
| H | -3.07957700 | 0.04883100 | 0.00043700 |

**3x-TS-4x (R=H)**

-1 1

| | | | |
|---|---|---|---|
| C | -2.11987200 | -0.69293100 | -0.00019300 |
| C | -1.39040300 | 0.54408700 | -0.00007400 |
| N | -0.00680000 | 0.09636800 | 0.00022600 |
| C | -1.18588500 | -1.72221600 | 0.00016500 |
| N | 0.07073700 | -1.27451800 | 0.00050600 |
| O | -1.75054200 | 1.71892500 | -0.00040300 |
| H | -1.36217900 | -2.79107900 | 0.00055300 |
| C | 1.22579800 | 0.80593100 | 0.00014000 |
| O | 1.28468500 | 2.01723100 | 0.00040100 |
| C | 2.35467600 | -0.15991900 | -0.00043500 |
| H | -3.19621000 | -0.76830900 | -0.00015200 |
| C | 2.04442800 | -1.38379700 | -0.00042700 |
| H | 2.26524000 | -2.42972900 | -0.00056300 |

**3x-TS-3y (R=H)**

-1 1

| | | | |
|---|---|---|---|
| C | 2.21407200 | 0.26800700 | 0.44697600 |
| C | 1.04970300 | 0.88107800 | -0.09595800 |
| N | 0.25598300 | -0.25694600 | -0.46953400 |
| C | 1.98001400 | -1.11474100 | 0.45386200 |
| N | 0.80742300 | -1.48088200 | -0.05384300 |
| O | 0.67908200 | 2.05711300 | -0.27402700 |
| H | 2.64682000 | -1.89468800 | 0.80674700 |
| C | -1.15110500 | -0.22320200 | -0.60797900 |
| O | -1.73078700 | -0.33453300 | -1.66306700 |
| C | -1.88928800 | -0.05002400 | 0.63548400 |
| C | -2.49544800 | 0.10945000 | 1.66445200 |
| H | -3.01152600 | 0.25524000 | 2.58076900 |
| H | 3.08681700 | 0.80019300 | 0.79184800 |

**3y-TS-4y (R=H)**

-1 1

| | | | |
|---|---|---|---|
| C | 2.01203400 | -0.87039800 | -0.00000800 |
| C | 0.61503700 | -0.92803700 | 0.00001100 |
| N | 0.19605200 | 0.43607900 | -0.00002300 |
| C | 2.33016600 | 0.50154200 | -0.00003300 |
| N | 1.27705200 | 1.29915500 | -0.00002600 |
| O | -0.17452300 | -1.93869000 | 0.00010600 |
| H | 3.31714600 | 0.94870100 | -0.00005900 |
| H | 2.67348300 | -1.72156700 | -0.00000200 |
| C | -1.12377900 | 0.94598600 | -0.00001200 |
| C | -2.14857600 | -0.09340300 | -0.00013400 |
| O | -1.33555200 | 2.14486600 | 0.00010500 |
| C | -1.98946100 | -1.33818900 | -0.00003800 |
| H | -2.39428800 | -2.32818600 | 0.00000000 |

**3x (R=Methyl)**

-1 1

| | | | |
|---|---|---|---|
| C | -2.58098000 | 0.16499400 | -0.00006800 |
| C | -1.78676900 | -1.00816000 | -0.00004800 |
| N | -0.41828700 | -0.44072800 | 0.00006400 |
| C | -1.71550600 | 1.27365900 | 0.00001800 |
| N | -0.42911000 | 0.95955600 | 0.00009300 |
| O | -2.03835200 | -2.21341600 | -0.00010500 |
| C | 0.78176000 | -1.10301900 | 0.00006700 |
| O | 0.92906000 | -2.31789500 | 0.00008800 |
| C | 1.96401300 | -0.23498700 | 0.00002700 |
| C | 3.02755400 | 0.33287600 | -0.00001700 |
| H | -3.66010900 | 0.16693300 | -0.00014300 |
| C | -2.10252500 | 2.72365100 | 0.00001900 |
| H | -2.70259800 | 2.97379000 | 0.88251200 |
| H | -2.70229600 | 2.97387500 | -0.88265500 |
| H | -1.20484700 | 3.34633700 | 0.00020100 |
| C | 4.28030500 | 1.07396500 | -0.00009300 |
| H | 4.88282900 | 0.83197500 | -0.88234400 |
| H | 4.88227600 | 0.83305500 | 0.88283100 |
| H | 4.10375100 | 2.15485600 | -0.00079500 |

**4x (R=methyl)**

-1 1

| | | | |
|---|---|---|---|
| C | -0.17714900 | 2.09541500 | 0.08785300 |
| C | -1.36133500 | 1.25413500 | -0.02414800 |
| N | -0.82686800 | -0.04441900 | -0.22758800 |
| C | 0.93893900 | 1.29937400 | -0.00297300 |
| N | 0.54941100 | 0.01075600 | -0.21887400 |
| O | -2.55150400 | 1.54441200 | 0.01576100 |
| C | -1.21433400 | -1.46467100 | 0.02441600 |
| O | -2.38516400 | -1.76613500 | 0.09708300 |
| C | 0.02794300 | -2.25135000 | 0.12329400 |
| H | -0.20013100 | 3.16816700 | 0.20502800 |
| C | 1.02479800 | -1.34819900 | 0.00451100 |
| C | 2.37559600 | 1.70946500 | 0.08167300 |
| H | 2.43955300 | 2.79861500 | 0.10756600 |
| H | 2.94997300 | 1.34955100 | -0.77587100 |
| H | 2.85435700 | 1.31916000 | 0.98483000 |
| C | 2.50611500 | -1.57375400 | -0.00646700 |
| H | 2.67188100 | -2.64679500 | 0.08731000 |
| H | 3.02262800 | -1.07339000 | 0.82292800 |
| H | 2.97383500 | -1.22837500 | -0.93825700 |

**7 (R=methyl)**

0 1

| | | | |
|---|---|---|---|
| C | 0.07880800 | -2.11680700 | 0.09718900 |
| C | 1.31268800 | -1.33335800 | -0.00673700 |
| N | 0.83334800 | 0.00007400 | -0.23656400 |
| C | -0.99977900 | -1.30035000 | -0.00459000 |

| | | | |
|---|---|---|---|
| N | -0.55339000 | -0.00003700 | -0.22881100 |
| O | 2.47346400 | -1.65435600 | 0.06115400 |
| C | 1.31244400 | 1.33337600 | -0.00548000 |
| O | 2.47318500 | 1.65476000 | 0.06116000 |
| C | 0.07846400 | 2.11685100 | 0.09700500 |
| H | 0.06399100 | -3.18743300 | 0.21869900 |
| C | -0.99999600 | 1.30020900 | -0.00461700 |
| H | 0.06349700 | 3.18754400 | 0.21790800 |
| C | -2.45020300 | -1.64743700 | 0.04074100 |
| H | -2.55789400 | -2.72894000 | 0.11690100 |
| H | -2.96979900 | -1.31243900 | -0.86052400 |
| H | -2.94792500 | -1.19709600 | 0.90365600 |
| C | -2.45047300 | 1.64710700 | 0.04042500 |
| H | -2.55833200 | 2.72862400 | 0.11614500 |
| H | -2.94822400 | 1.19703300 | 0.90346600 |
| H | -2.96992100 | 1.31168100 | -0.86076200 |

**3y (R=methyl)**

-1 1

| | | | |
|---|---|---|---|
| C | 1.90904600 | -1.37763100 | 0.00007400 |
| C | 0.51502800 | -1.15802500 | 0.00004000 |
| N | 0.43797800 | 0.32034600 | -0.00006000 |
| C | 2.53622200 | -0.11631600 | -0.00003800 |
| N | 1.69888600 | 0.91004400 | -0.00008400 |
| O | -0.47589700 | -1.89862400 | 0.00009900 |
| C | -0.67583200 | 1.12462300 | 0.00003900 |
| O | -0.64108800 | 2.35190700 | 0.00012600 |
| C | -1.96531200 | 0.44994700 | -0.00000800 |
| C | -3.10513500 | 0.05813600 | -0.00003700 |
| H | 2.37297600 | -2.35179200 | -0.00005500 |
| C | 4.01097000 | 0.15931000 | -0.00004900 |
| H | 4.49549700 | -0.27434200 | -0.88257000 |
| H | 4.49547100 | -0.27419900 | 0.88255500 |
| H | 4.18377600 | 1.23774800 | -0.00013800 |
| C | -4.42724100 | -0.54715200 | -0.00007400 |
| H | -5.00235900 | -0.24699600 | -0.88284900 |
| H | -5.00239400 | -0.24704900 | 0.88269700 |
| H | -4.35161200 | -1.63972400 | -0.00010800 |

**4y (R=methyl)**

-1 1

| | | | |
|---|---|---|---|
| C | -1.35568400 | -1.45029400 | -0.00807100 |
| C | -0.12605300 | -0.81295600 | -0.00593000 |
| N | -0.35345300 | 0.53646600 | 0.00453700 |
| C | -2.28796700 | -0.38223600 | 0.00185000 |
| N | -1.69756600 | 0.80721800 | 0.00867000 |
| O | 1.09766400 | -1.32270300 | -0.01272100 |
| H | -1.53643300 | -2.51314400 | -0.01484300 |
| C | 0.71189900 | 1.53748200 | -0.00070500 |
| C | 2.06030200 | 0.98879600 | 0.00817200 |
| O | 0.37885300 | 2.70772600 | -0.01162400 |

| | | | |
|---|---|---|---|
| C | 2.19810100 | -0.33459900 | 0.00193500 |
| C | -3.78441900 | -0.47294100 | 0.00566400 |
| H | -4.15232500 | -1.01051800 | 0.88702300 |
| H | -4.15723100 | -1.00188100 | -0.87882300 |
| H | -4.20973800 | 0.53245800 | 0.01192200 |
| C | 3.45956300 | -1.14579400 | 0.00833400 |
| H | 4.30941500 | -0.46560900 | 0.02007600 |
| H | 3.52643700 | -1.79039900 | -0.87772600 |
| H | 3.51041400 | -1.80163000 | 0.88718800 |

**6 (R=methyl)**

0 1

| | | | |
|---|---|---|---|
| C | -1.38747200 | -1.44093900 | -0.00016900 |
| C | -0.17372500 | -0.81186300 | 0.00025400 |
| N | -0.39276500 | 0.54434100 | 0.00067200 |
| C | -2.32258300 | -0.36401800 | -0.00002000 |
| N | -1.72631100 | 0.82113300 | 0.00042000 |
| O | 1.07625000 | -1.32824500 | 0.00040200 |
| H | -1.57656400 | -2.50118500 | -0.00038700 |
| C | 0.64322900 | 1.51494500 | -0.00000100 |
| C | 1.95907700 | 0.87518100 | -0.00030800 |
| O | 0.43108100 | 2.70252900 | -0.00017700 |
| C | 2.13417200 | -0.46065100 | -0.00010700 |
| H | 2.81550100 | 1.53374800 | -0.00076400 |
| C | -3.81476200 | -0.45838400 | -0.00041900 |
| H | -4.17455900 | -0.99595500 | 0.88166300 |
| H | -4.17411600 | -0.99465900 | -0.88350200 |
| H | -4.24693900 | 0.54239400 | 0.00016400 |
| C | 3.43564900 | -1.18704400 | -0.00021900 |
| H | 4.26652400 | -0.48292600 | -0.00091000 |
| H | 3.51143200 | -1.82917400 | -0.88226800 |
| H | 3.51211000 | -1.82818100 | 0.88249900 |

**3x-TS-4x (R=methyl)**

-1 1

| | | | |
|---|---|---|---|
| C | -0.88231700 | 2.00887000 | -0.06462100 |
| C | -1.68148400 | 0.81554500 | -0.01364100 |
| N | -0.68521700 | -0.22726500 | 0.09444700 |
| C | 0.45461100 | 1.63113600 | 0.00589100 |
| N | 0.58485900 | 0.30217200 | 0.10979000 |
| O | -2.89702800 | 0.63485700 | -0.04612300 |
| C | -0.75990700 | -1.64984700 | 0.01886100 |
| O | -1.81875600 | -2.24362100 | 0.01543100 |
| C | 0.60654500 | -2.21553200 | -0.04805700 |
| H | -1.28088200 | 3.00907300 | -0.14694200 |
| C | 1.55166000 | -1.36495800 | -0.03428100 |
| C | 1.66374700 | 2.51841700 | 0.01935800 |
| H | 2.04989600 | 2.64912600 | 1.03666200 |
| H | 1.41463800 | 3.50664600 | -0.37388300 |
| H | 2.47074800 | 2.09873800 | -0.58821000 |
| C | 2.99103100 | -1.06590400 | -0.04494600 |

| | | | |
|---|---|---|---|
| H | 3.54961600 | -2.00491200 | -0.08478400 |
| H | 3.29092600 | -0.51942200 | 0.85500100 |
| H | 3.27052600 | -0.45985500 | -0.91334000 |

**3x-TS-3y (R=methyl)**

-1 1

| | | | |
|---|---|---|---|
| C | 1.96260200 | -0.03748900 | 1.10228000 |
| C | 0.84974200 | 0.84377100 | 1.03061300 |
| N | 0.46738600 | 0.74265100 | -0.35188900 |
| C | 2.08141500 | -0.66229800 | -0.15248500 |
| N | 1.18016300 | -0.25441300 | -1.04098300 |
| O | 0.25646200 | 1.57411600 | 1.84741100 |
| C | -0.85827300 | 0.97240700 | -0.80592500 |
| O | -1.17057800 | 1.90373000 | -1.51328000 |
| C | -1.83600000 | -0.00400300 | -0.36292600 |
| C | -2.63527800 | -0.81086000 | 0.04438600 |
| H | 2.57348000 | -0.18827000 | 1.97950100 |
| C | 3.10239000 | -1.67853300 | -0.57597900 |
| H | 2.85965000 | -2.05097000 | -1.57443400 |
| H | 3.13127200 | -2.52650300 | 0.11801700 |
| H | 4.11068400 | -1.24796100 | -0.60603700 |
| C | -3.57263300 | -1.79516200 | 0.56093500 |
| H | -3.54867900 | -1.80922200 | 1.65538600 |
| H | -3.31022900 | -2.79970100 | 0.21313900 |
| H | -4.59988200 | -1.58480200 | 0.24608400 |

**3y-TS-4y (R=methyl)**

-1 1

| | | | |
|---|---|---|---|
| C | 1.38784800 | -1.46666700 | 0.00025100 |
| C | 0.11830600 | -0.89086000 | 0.00007400 |
| N | 0.33866000 | 0.50140900 | -0.00027800 |
| C | 2.29357800 | -0.37963100 | -0.00002500 |
| N | 1.68888800 | 0.79661500 | -0.00031500 |
| O | -1.04882400 | -1.44287400 | 0.00008300 |
| H | 1.60006500 | -2.52417900 | 0.00039700 |
| C | -0.64450800 | 1.52745800 | 0.00003100 |
| C | -2.01721200 | 1.03800600 | -0.00001100 |
| O | -0.30754300 | 2.69856800 | 0.00027100 |
| C | -2.37882400 | -0.18020600 | 0.00002200 |
| C | 3.79184100 | -0.43988600 | -0.00000700 |
| H | 4.17065900 | -0.96764200 | 0.88289600 |
| H | 4.19910700 | 0.57323700 | -0.00040300 |
| H | 4.17065900 | -0.96832600 | -0.88249900 |
| C | -3.54295700 | -1.08778100 | -0.00010600 |
| H | -4.45989300 | -0.49498300 | 0.00009200 |
| H | -3.53540200 | -1.73642000 | 0.88132900 |
| H | -3.53553000 | -1.73600100 | -0.88185700 |

## 8. Proposed reaction mechanism

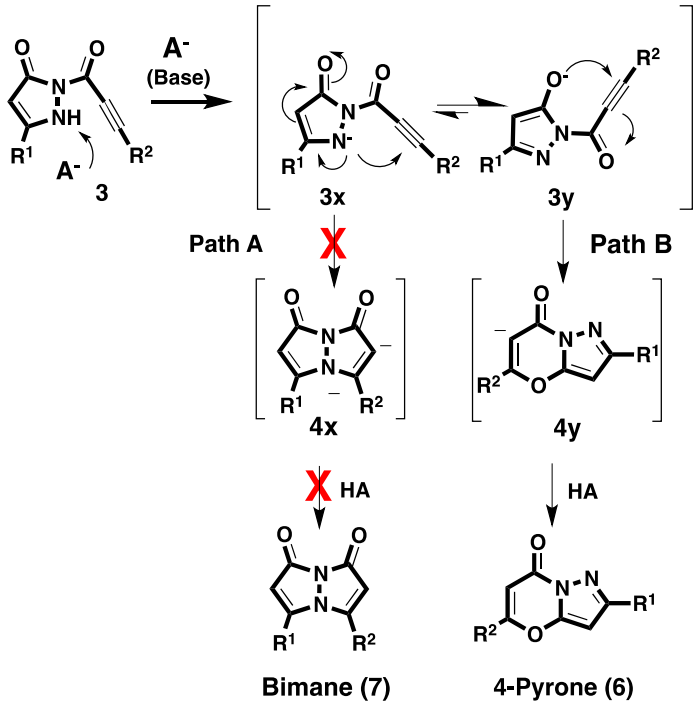



**Figure S10:** Proposed reaction mechanism

**Table S2: Reaction Energy, ΔG and k**

| entry | | b3lyp/6-311++g(d,p); **R=H** | | | |
|---|---|---|---|---|---|
| | | **E** | **ZPVE** | **H0** | **G(298 K)** |
| **1** | **3x** | -490,497161 | 0,079718 | -490,417443 | -490,451378 |
| **2** | **4x** | -490,483284 | 0,081786 | -490,401498 | -490,434161 |
| **3** | **7** | -491,084500 | 0,096160 | -490,988340 | -491,020752 |
| **4** | **3y** | -490,498685 | 0,079839 | -490,418846 | -490,452662 |
| **5** | **4y** | -490,484058 | 0,082513 | -490,401545 | -490,434728 |
| **6** | **6** | -491,084156 | 0,097388 | -490,986768 | -491,018471 |
| **7** | **3x-TS-4x** | -490,462776 | 0,079580 | -490,383196 | -490,416399 |
| **8** | **3x-TS-3y** | -490,4761204 | 0,078897 | -490,397223 | -490,430468 |
| **9** | **3y-TS-4y** | -490,4762131 | 0,080363 | -490,395850 | -490,428477 |
| | **Reaction Energy kcal/mol** | | **ΔG** | **k** | |
| **10** | 3x -> 3x-TS-4x | **21,49** | 21,95 | **5,04E-04** | |
| **11** | 4x -> 3x-TS-4x | 11,48 | 11,15 | 4,19E+04 | |
| **12** | 3x -> 3x-TS-3y | 12,69 | 13,12 | 1,49E+03 | |
| **13** | 3y -> 3x-TS-3y | 13,57 | 13,93 | 3,83E+02 | |
| **14** | 3y -> 3y-TS-4y | **14,43** | 15,18 | **4,65E+01** | |
| **15** | 4y -> 3y-TS-4y | 3,57 | 3,92 | 8,27E+09 | |
| | | **Reaction Barrier kcal/mol** | | | |
| | | **R=H** | **R=Methyl** | | |
| **16** | 3x -> 4x | 10,01 | 13,24 | | |
| **17** | 3x -> 3y | -0,88 | -1,49 | | |
| **18** | 3y-> 4y | 10,86 | 13,27 | | |

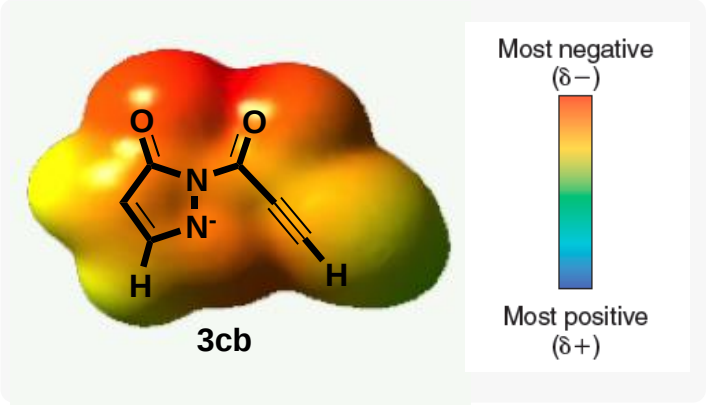



**Figure S11**: Electron density potential map of compound **3cb**

## 9. X-Ray Difraction Analysis

For the crystal structure determination, single-crystal of compound **6aa** was used for data collection on a four-circle Rigaku R-AXIS RAPID-S diffractometer (equipped with a two-dimensional area IP detector). Graphite-monochromated Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å) and oscillation scans technique with $\Delta w = 5^o$ for one image were used for data collection. The lattice parameters were determined by the least-squares methods on the basis of all reflections with $F^2 > 2\sigma(F^2)$. Integration of the intensities, correction for Lorentz and polarization effects and cell refinement was performed using CrystalClear (Rigaku/MSC Inc.,2005) software. [5] The structures were solved by direct methods using SHELXS-97 [6] and refined by a full-matrix least-squares procedure using the program SHELXL-97.[6] H atoms were positioned geometrically and refined using a riding model. The final difference Fourier maps showed no peaks of chemical significance. *Crystal data for* ***6aa***: $C_{18}H_{12}N_2O_2$, crystal system, space group: monoclinic, $P2_1/n$; (no:14); unit cell dimensions: $a$=4.7369(4), $b$=24.6856(22), $c$= 12.2902(13) Å, $\alpha$= 90, $\beta$ = 99.492(3), $\gamma$ = 90 º; volume: 1417.46(8) Å$^3$; Z = 4; calculated density: 1.35 g/cm$^3$; absorption coefficient: 0.090 mm$^{-1}$ ; $F$(000)= 600; $\theta$-range for data collection 2.9–28.2º ; refinement method: full matrix least-square on $F^2$; data/parameters: 3508/200; goodness-of-fit on $F^2$: 1.002; final $R$-indices [I > 2$\sigma$(I)]: $R_1$ = 0.045, w$R_2$ = 0.101; largest diff. peak and hole: 0.177 and -0.135 e Å$^{-3}$.

CCDC-1456335 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/ retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

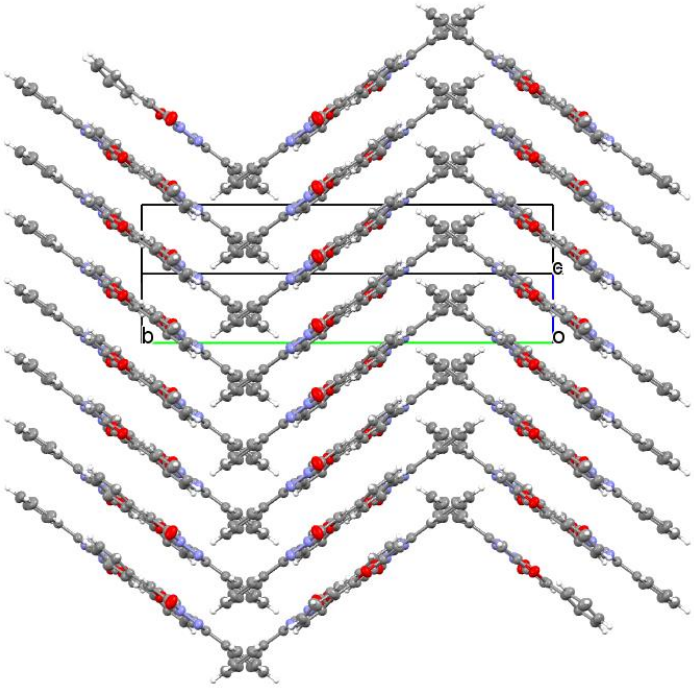



**Figure S11:** Packing diagram viewed dawn along the diagonal [101] axis

## SUPPLEMENTARY DATA for compound 6aa

Fractional atomic coordinates and isotropic temperature factors (Angstrom squared), with standard deviations in the least Significant digits in parentheses. For anisotropic atoms, the equivalent isotropic temperature factors are shown.

| | x/a | y/b | z/c | U |
|---|---|---|---|---|
| O(1) | 0.3538(2) | 0.4540(0) | 0.3289(1) | 0.04862 |
| O(2) | 0.6997(3) | 0.4280(1) | 0.0522(1) | 0.06562 |
| N(1) | 0.6551(3) | 0.4053(1) | 0.2284(1) | 0.04208 |
| N(2) | 0.8395(3) | 0.3621(1) | 0.2404(1) | 0.04735 |
| C(7) | 0.2785(3) | 0.4868(1) | 0.2379(1) | 0.03893 |
| C(1) | 0.0776(3) | 0.5294(1) | 0.2586(1) | 0.04013 |
| C(10) | 0.5413(3) | 0.4134(1) | 0.3214(1) | 0.04227 |
| C(8) | 0.3858(3) | 0.4787(1) | 0.1457(1) | 0.04327 |
| H(8) | 0.32631 | 0.50147 | 0.08601 | 0.05193 |

| | | | | |
|---|---|---|---|---|
| C(9) | 0.5889(4) | 0.4366(1) | 0.1331(1) | 0.04503 |
| C(12) | 0.8312(3) | 0.3444(1) | 0.3421(1) | 0.04579 |
| C(11) | 0.6475(4) | 0.3754(1) | 0.3966(1) | 0.05100 |
| H(11) | 0.60821 | 0.37078 | 0.46776 | 0.06119 |
| C(2) | -0.0481(3) | 0.5632(1) | 0.1735(1) | 0.04957 |
| H(2) | -0.00471 | 0.55873 | 0.10295 | 0.05948 |
| C(13) | 0.9984(3) | 0.2964(1) | 0.3844(2) | 0.04996 |
| C(6) | 0.0106(4) | 0.5373(1) | 0.3626(2) | 0.05728 |
| H(6) | 0.09211 | 0.51511 | 0.42045 | 0.06873 |
| C(3) | -0.2370(4) | 0.6032(1) | 0.1933(2) | 0.05603 |
| H(3) | -0.32170 | 0.62531 | 0.13581 | 0.06724 |
| C(4) | -0.3003(4) | 0.6105(1) | 0.2969(2) | 0.06215 |
| H(4) | -0.42736 | 0.63752 | 0.30987 | 0.07458 |
| C(18) | 1.1606(4) | 0.2685(1) | 0.3190(2) | 0.06503 |
| H(18) | 1.16825 | 0.28071 | 0.24793 | 0.07803 |
| C(14) | 0.9923(5) | 0.2777(1) | 0.4899(2) | 0.06998 |
| H(14) | 0.88570 | 0.29601 | 0.53537 | 0.08398 |
| C(5) | -0.1757(4) | 0.5778(1) | 0.3816(2) | 0.07097 |
| H(5) | -0.21724 | 0.58290 | 0.45223 | 0.08517 |
| C(16) | 1.3030(5) | 0.2043(1) | 0.4632(2) | 0.08486 |
| H(16) | 1.40448 | 0.17348 | 0.48947 | 0.10183 |
| C(17) | 1.3115(5) | 0.2228(1) | 0.3586(2) | 0.08174 |
| H(17) | 1.41973 | 0.20438 | 0.31384 | 0.09809 |
| C(15) | 1.1447(5) | 0.2316(1) | 0.5284(2) | 0.08502 |
| H(15) | 1.13862 | 0.21917 | 0.59940 | 0.10202 |

Vibration parameters (Angstrom squared) in the expression:-2(pi squared)(U11((h.a*)squared) + U22((k.b*)squared) + U33((l.c*)squared) + 2.U12.h.k.a*.b* + 2.U13.h.l.a*.c* + 2.U23.k.l.b*.c*)

| | U11 | U22 | U33 | U12 | U13 | U23 |
|---|---|---|---|---|---|---|
| O(1) | 0.0570(7) | 0.0496(7) | 0.0417(7) | 0.0123(6) | 0.0153(5) | 0.0110(5) |
| O(2) | 0.093(1) | 0.067(1) | 0.042(1) | 0.025(1) | 0.023(1) | 0.006(1) |
| N(1) | 0.0507(8) | 0.0387(7) | 0.0370(7) | 0.0053(6) | 0.0079(6) | 0.0011(6) |
| N(2) | 0.0559(8) | 0.0391(7) | 0.0455(8) | 0.0086(7) | 0.0040(6) | -.0006(6) |
| C(7) | 0.0398(8) | 0.0387(8) | 0.0373(9) | -.0033(7) | 0.0035(6) | 0.0047(7) |
| C(1) | 0.0363(8) | 0.0397(9) | 0.0447(9) | -.0036(7) | 0.0078(7) | 0.0010(7) |
| C(10) | 0.0458(9) | 0.0405(9) | 0.0407(9) | 0.0037(7) | 0.0080(7) | 0.0037(7) |
| C(8) | 0.0510(9) | 0.0421(9) | 0.0356(9) | 0.0038(8) | 0.0042(7) | 0.0050(7) |
| C(9) | 0.056(1) | 0.043(1) | 0.036(1) | 0.001(1) | 0.006(1) | 0.002(1) |
| C(12) | 0.0472(9) | 0.0408(9) | 0.0472(10) | -.0024(7) | 0.0011(7) | 0.0029(7) |
| C(11) | 0.058(1) | 0.054(1) | 0.043(1) | 0.009(1) | 0.012(1) | 0.011(1) |
| C(2) | 0.052(1) | 0.047(1) | 0.050(1) | 0.003(1) | 0.009(1) | 0.006(1) |
| C(13) | 0.0467(9) | 0.0400(9) | 0.0593(11) | -.0012(8) | -.0026(8) | 0.0052(8) |
| C(6) | 0.057(1) | 0.067(1) | 0.049(1) | 0.015(1) | 0.014(1) | 0.008(1) |
| C(3) | 0.052(1) | 0.047(1) | 0.068(1) | 0.003(1) | 0.007(1) | 0.007(1) |
| C(4) | 0.052(1) | 0.056(1) | 0.080(1) | 0.011(1) | 0.013(1) | -0.005(1) |
| C(18) | 0.065(1) | 0.052(1) | 0.074(1) | 0.009(1) | 0.003(1) | 0.002(1) |
| C(14) | 0.073(1) | 0.063(1) | 0.072(1) | 0.010(1) | 0.004(1) | 0.021(1) |
| C(5) | 0.068(1) | 0.086(1) | 0.062(1) | 0.023(1) | 0.022(1) | -0.002(1) |
| C(16) | 0.070(1) | 0.050(1) | 0.124(2) | 0.005(1) | -0.015(1) | 0.024(1) |
| C(17) | 0.076(1) | 0.051(1) | 0.112(2) | 0.020(1) | 0.001(1) | -0.001(1) |
| C(15) | 0.083(2) | 0.072(1) | 0.093(2) | 0.007(1) | -0.004(1) | 0.036(1) |

## Complete Listing of Torsion Angles

C(7) - O(1) - C(10) - N(1) 0.8

C(10) - O(1) - C(7) - C(1) -179.2

C(10) - O(1) - C(7) - C(8) 0.1

C(7) - O(1) - C(10) - C(11) -179.1

N(2) - N(1) - C(10) - O(1) 179.7

C(10) - N(1) - N(2) - C(12) 0.6

N(2) - N(1) - C(10) - C(11) -0.4

N(2) - N(1) - C(9) - O(2) -1.5

N(2) - N(1) - C(9) - C(8) 179.4

C(9) - N(1) - N(2) - C(12) -178.8

C(9) - N(1) - C(10) - O(1) -1.0

C(10) - N(1) - C(9) - O(2) 179.2

C(10) - N(1) - C(9) - C(8) 0.1

C(9) - N(1) - C(10) - C(11) 178.9

N(1) - N(2) - C(12) - C(11) -0.6

N(1) - N(2) - C(12) - C(13) 178.0

O(1) - C(7) - C(1) - C(2) -173.1

O(1) - C(7) - C(1) - C(6) 7.3

O(1) - C(7) - C(8) - H(8) 179.0

O(1) - C(7) - C(8) - C(9) -1.0

C(1) - C(7) - C(8) - H(8) -1.9

C(1) - C(7) - C(8) - C(9) 178.1

C(8) - C(7) - C(1) - C(2) 7.7

C(8) - C(7) - C(1) - C(6) -171.9

C(7) - C(1) - C(2) - H(2) -0.1

C(7) - C(1) - C(2) - C(3) 179.9

C(7) - C(1) - C(6) - H(6) -0.6

C(7) - C(1) - C(6) - C(5) 179.4

C(6) - C(1) - C(2) - H(2) 179.5

C(2) - C(1) - C(6) - H(6) 179.8

C(6) - C(1) - C(2) - C(3) -0.5

C(2) - C(1) - C(6) - C(5) -0.2

O(1) - C(10) - C(11) - C(12) 180.0

O(1) - C(10) - C(11) - H(11) 0.0

N(1) - C(10) - C(11) - C(12) 0.1

N(1) - C(10) - C(11) - H(11) -180.0

C(7) - C(8) - C(9) - O(2) -178.2

C(7) - C(8) - C(9) - N(1) 0.9

H(8) - C(8) - C(9) - O(2) 1.8

H(8) - C(8) - C(9) - N(1) -179.1

N(2) - C(12) - C(11) - C(10) 0.3

N(2) - C(12) - C(11) - H(11) -179.7

N(2) - C(12) - C(13) - C(18) -1.3

N(2) - C(12) - C(13) - C(14) 179.8

C(13) - C(12) - C(11) - C(10) -178.2

C(13) - C(12) - C(11) - H(11) 1.9

C(11) - C(12) - C(13) - C(18) 177.1

C(11) - C(12) - C(13) - C(14) -1.9

C(1) - C(2) - C(3) - H(3) -179.3

C(1) - C(2) - C(3) - C(4) 0.7

H(2) - C(2) - C(3) - H(3) 0.7

H(2) - C(2) - C(3) - C(4) -179.3

C(12) - C(13) - C(18) - H(18) 1.5

C(12) - C(13) - C(18) - C(17) -178.5

C(12) - C(13) - C(14) - H(14) -1.6

C(12) - C(13) - C(14) - C(15) 178.4

C(14) - C(13) - C(18) - H(18) -179.5

C(18) - C(13) - C(14) - H(14) 179.4

C(14) - C(13) - C(18) - C(17) 0.4

C(18) - C(13) - C(14) - C(15) -0.6

C(1) - C(6) - C(5) - C(4) 0.7

C(1) - C(6) - C(5) - H(5) -179.3

H(6) - C(6) - C(5) - C(4) -179.2

H(6) - C(6) - C(5) - H(5) 0.8

C(2) - C(3) - C(4) - H(4) 179.9

C(2) - C(3) - C(4) - C(5) -0.1

H(3) - C(3) - C(4) - H(4) -0.1

H(3) - C(3) - C(4) - C(5) 179.9

C(3) - C(4) - C(5) - C(6) -0.6

C(3) - C(4) - C(5) - H(5) 179.4

H(4) - C(4) - C(5) - C(6) 179.4

H(4) - C(4) - C(5) - H(5) -0.6

C(13) - C(18) - C(17) - C(16) -0.1

C(13) - C(18) - C(17) - H(17) 179.9

H(18) - C(18) - C(17) - C(16) 179.9

H(18) - C(18) - C(17) - H(17) -0.1

C(13) - C(14) - C(15) - C(16) 0.3

C(13) - C(14) - C(15) - H(15) -179.7

H(14) - C(14) - C(15) - C(16) -179.7

H(14) - C(14) - C(15) - H(15) 0.3

H(16) - C(16) - C(17) - C(18) 179.8

H(16) - C(16) - C(17) - H(17) -0.1

H(16) - C(16) - C(15) - C(14) -180.0

H(16) - C(16) - C(15) - H(15) 0.0

C(15) - C(16) - C(17) - C(18) -0.2

C(17) - C(16) - C(15) - C(14) 0.1

C(15) - C(16) - C(17) - H(17) 179.8

C(17) - C(16) - C(15) - H(15) -180.0

## Complete Listing of Torsion Angles (Angstroms)

O(1) - C(7) 1.377(2) O(1) - C(10) 1.353(2)

O(2) - C(9) 1.218(3) N(1) - N(2) 1.370(2)

N(1) - C(10) 1.357(3) N(1) - C(9) 1.395(2)

N(2) - C(12) 1.330(3) C(7) - C(1) 1.470(3)

C(7) - C(8) 1.332(3) C(1) - C(2) 1.391(3)

C(1) - C(6) 1.381(3) C(10) - C(11) 1.355(3)

C(8) - H(8) 0.930(2) C(8) - C(9) 1.441(3)

C(12) - C(11) 1.409(3) C(12) - C(13) 1.472(3)

C(11) - H(11) 0.930(2) C(2) - H(2) 0.930(2)

| | | | |
|---|---|---|---|
| C(2) - C(3) | 1.382(3) | C(13) - C(18) | 1.382(3) |
| C(13) - C(14) | 1.382(3) | C(6) - H(6) | 0.930(2) |
| C(6) - C(5) | 1.377(3) | C(3) - H(3) | 0.930(2) |
| C(3) - C(4) | 1.367(3) | C(4) - H(4) | 0.930(2) |
| C(4) - C(5) | 1.372(3) | C(18) - H(18) | 0.930(3) |
| C(18) - C(17) | 1.381(3) | C(14) - H(14) | 0.930(3) |
| C(14) - C(15) | 1.388(4) | C(5) - H(5) | 0.930(3) |
| C(16) - H(16) | 0.930(3) | C(16) - C(17) | 1.372(4) |
| C(16) - C(15) | 1.361(4) | C(17) - H(17) | 0.930(3) |
| C(15) - H(15) | 0.930(3) | | |

## Complete Listing of Torsion Angles (Degrees)

| | | | |
|---|---|---|---|
| C(7)-O(1)-C(10) | 117.7(2) | N(2)-N(1)-C(10) | 111.0(2) |
| N(2)-N(1)-C(9) | 125.0(2) | C(10)-N(1)-C(9) | 124.0(2) |
| N(1)-N(2)-C(12) | 103.9(2) | O(1)-C(7)-C(1) | 111.6(2) |
| O(1)-C(7)-C(8) | 121.3(2) | C(1)-C(7)-C(8) | 127.1(2) |
| C(7)-C(1)-C(2) | 120.5(2) | C(7)-C(1)-C(6) | 121.0(2) |
| C(2)-C(1)-C(6) | 118.4(2) | O(1)-C(10)-N(1) | 121.5(2) |
| O(1)-C(10)-C(11) | 129.9(2) | N(1)-C(10)-C(11) | 108.6(2) |
| C(7)-C(8)-H(8) | 118.2(2) | C(7)-C(8)-C(9) | 123.6(2) |
| H(8)-C(8)-C(9) | 118.2(2) | O(2)-C(9)-N(1) | 121.3(2) |
| O(2)-C(9)-C(8) | 126.8(2) | N(1)-C(9)-C(8) | 111.9(2) |
| N(2)-C(12)-C(11) | 112.6(2) | N(2)-C(12)-C(13) | 120.0(2) |
| C(11)-C(12)-C(13) | 127.4(2) | C(10)-C(11)-C(12) | 103.9(2) |
| C(10)-C(11)-H(11) | 128.1(2) | C(12)-C(11)-H(11) | 128.1(2) |

| | | | |
|---|---|---|---|
| C(1)-C(2)-H(2) | 119.8(2) | C(1)-C(2)-C(3) | 120.3(2) |
| H(2)-C(2)-C(3) | 119.8(2) | C(12)-C(13)-C(18) | 120.9(2) |
| C(12)-C(13)-C(14) | 120.5(2) | C(18)-C(13)-C(14) | 118.6(2) |
| C(1)-C(6)-H(6) | 119.6(2) | C(1)-C(6)-C(5) | 120.7(2) |
| H(6)-C(6)-C(5) | 119.7(2) | C(2)-C(3)-H(3) | 119.8(2) |
| C(2)-C(3)-C(4) | 120.4(2) | H(3)-C(3)-C(4) | 119.8(2) |
| C(3)-C(4)-H(4) | 120.1(2) | C(3)-C(4)-C(5) | 119.7(2) |
| H(4)-C(4)-C(5) | 120.1(3) | C(13)-C(18)-H(18) | 119.8(2) |
| C(13)-C(18)-C(17) | 120.5(3) | H(18)-C(18)-C(17) | 119.8(3) |
| C(13)-C(14)-H(14) | 119.9(2) | C(13)-C(14)-C(15) | 120.2(2) |
| H(14)-C(14)-C(15) | 119.9(3) | C(6)-C(5)-C(4) | 120.4(2) |
| C(6)-C(5)-H(5) | 119.8(3) | C(4)-C(5)-H(5) | 119.8(3) |
| H(16)-C(16)-C(17) | 120.3(3) | H(16)-C(16)-C(15) | 120.3(3) |
| C(17)-C(16)-C(15) | 119.5(3) | C(18)-C(17)-C(16) | 120.6(3) |
| C(18)-C(17)-H(17) | 119.7(3) | C(16)-C(17)-H(17) | 119.7(3) |
| C(14)-C(15)-C(16) | 120.7(3) | C(14)-C(15)-H(15) | 119.7(3) |
| C(16)-C(15)-H(15) | 119.7(3) | | |

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