Electronic Supporting Information

Waste minimized synthesis of pharmaceutically active compounds via heterogeneous manganese catalysed C–H oxidation in flow

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CONTENTS

General Remarks

Catalytic reactions were carried out in pre-dried 10 mL vials adapted with rubber septum when gas atmosphere was used. The substituted aminophenols (**1a-i**) substrates were prepared according to previously described procedures.[1], [2], [3] Other chemicals were obtained from commercial sources and were used without further purification unless noted otherwise. Yields refer to isolated compounds, estimated to be > 95% pure as determined by ^{1}H-NMR. TLC: Merck TLC Silica gel 60 F254, TLC plates; detection under UV light at 254 nm. Chromatography separations were carried out on Merck Geduran® Silica 60 (0.040–0.063 mm, 70–230 mesh ASTM). GLC analyses were performed by using Hewlett-Packard HP 5890 SERIES II equipped with a capillary column DB5MS (30 m, 0.32 mm), a FID detector and helium as gas carrier. GC-EIMS analyses were carried out by using a Hewlett-Packard HP 6890N Network GC system/5975 Mass Selective Detector equipped with an electron impact ionizer at 70 eV. NMR spectra in solution were recorded on a Bruker DRX-ADVANCE 400 MHz (^{1}H at 400 MHz and ^{13}C at 100.6 MHz). Elemental analysis of palladium content was carried out using an Agilent 4210 MP-AES instrument. Melting point were collected on a Barloworld Scientifc Stewart SMP3 micro melting point apparatus and are uncorrected. All IR spectra were recorded on a Bruker FT-IR Alpha device. The XRD patterns were collected in the on a PANalytical X'PERT PRO diffractometer, PW3050 goniometer, equipped with an X'Celerator detector by using the CuKα radiation. High resolution Transmission Electron Microscopy (HRTEM) was conducted on a JEOL JEM-2100F system electron microscope to observe the morphology and structure of the samples, before the experiments the samples were ground into powder and then dispersed in ethanol, the suspension was allowed to stand a while and then the supernatant was dropped onto the ultrathin carbon film.

General procedures for K-OMS-2 synthesis

A solution of 5.89 g of $KMnO_4$ in 100 mL of water was added to a solution of 8.8 g of $MnSO_4$-H_2O in 30 mL of water and 3 mL concentrated HNO_3. The solution was refluxed at 100 °C for 24 h, and the product was filtered, washed with distilled water (300 mL), and dried at 120 °C. The resulting material was further calcinated at 350 °C over a period of 4h. Finally, the black stony material was finely grounded using a mortar and filtered using size exclusion sieves yielding 13 g of K-OMS-2 catalyst. Powder X-ray diffraction data were collected (Fig S1) to confirm the structure of the material.

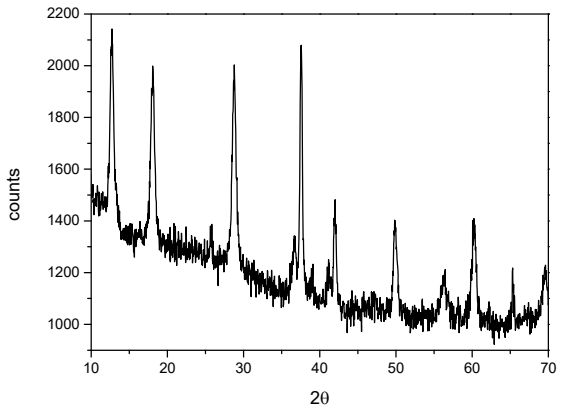


Figure S1. X-ray diffraction path for K-OMS-2

General procedures for batch reaction optimization for the synthesis of phenoxazinone derivatives

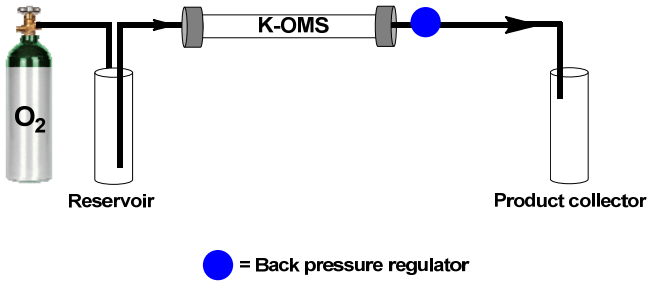
To a 10 mL vial were added the aminophenol substrate (1 mmol, 1 equiv.), the solvent 4 mL, and H_2O_2 30% w/w in H_2O (3.0 equiv), followed by K-OMS-2 62% w/w Mn-loading (1.6 mol%). The vial was capped with a septum and wrapped with Parafilm the vial was then equipped with O_2 balloon. The reaction mixture was stirred for the time and temperatures indicated in (**Table 1 in the main text**). The heterogeneous mixture was filtered over a short pad of silica eluting with the same solvent used in the reaction. The solvent was removed under reduced pressure to afford the products.

General procedures for catalyst/solvent recycle and reuse in batch

To a 10 mL vial were added the aminophenol substrate (0.109 g, 1 mmol, 1 equiv.), CPME(4 mL), and H_2O_2 30% w/w in H_2O (306 µL, 3 mmol, 3.0 equiv), followed by K-OMS-2 62% w/w Mn-loading (1.6 mol%, 1.37 mg). The vial was capped with a septum and wrapped with Parafilm the vial was then equipped with O_2 balloon. The reaction mixture was stirred for 2h at 27 °C. After the indicated reaction time, the heterogeneous catalyst was filtered over Büchner funnel and washed with CPME (2x5 mL). The heterogeneous catalyst was collected and dried at 120 °C over oxygen atmosphere for 2h. The organic phase was distilled under reduced pressure to afford the target compound (103 mg, 97 % yield) and the solvent recovered (98 % of the total amount) was dried by adding 100 mg of Na_2SO_4.

E-factor (considering aminophenol as substrate):{ [0.109 g $_{(aminophenol)}$ + 12 g $_{(CPME)}$ + 0.340 g $_{(H_2O_2)}$] – 0.103 g$_{(2\text{-aminophenoxazinone})}$ – 11.7 g$_{(CPME\ recovered)}$ } / 0.103 g $_{(2\text{-aminophenoxazinone})}$ = **6.2**

General continuous flow procedure (1 mmol of 2-aminophenol (1a) as starting material))



The reservoir was charged with 2 mL of CPME, the 2-aminophenol (**1a**) (0.109 g, 1 mmol,), followed by H_2O_2 (0.340 g, 306 µL, 3 mmol,) then the oxygen line has been set to the desired pressure and the reaction mixture started to flow through K-OMS-2 filled reactor (filled with 60 mg of K-OMS-2). Once the reagents reservoir has been completely emptied, the system has been rinsedwith CPME (2x2 mL). The product has been collected into the product reservoir. Then CPME was recovered *via* distillation under reduced pressure (98 % of the total amount, purity confirmed by ^{1}HNMR) to afford pure product (103 mg, 97 % yield).

E-factor (considering aminophenol as substrate):{ [0.109 g $_{(aminophenol)}$ + 5.1 g $_{(CPME)}$ + 0.340 g $_{(H_2O_2)}$] – 0.103 g $_{(2\text{-aminophenoxazinone})}$ – 5 g $_{(CPME\ recovered)}$ } / 0.103 g $_{(2\text{-aminophenoxazinone})}$ = **4.3**

Large scale continuous flow procedure (50 mmol of 2-aminophenol, 1a)

The reservoir was charged with 100 mL of CPME, 2-aminophenol (**1a**) (5.45 g, 50 mmol), followed by H_2O_2 (5.1 g, 4.6 mL, 150 mmol,) then the oxygen line has been set to 5 bar and the reaction mixture started to flow through K-OMS-2 filled reactor (60 mg of K-OMS-2) at flow rate of 0.1 mL/min with a residence time of 30 min. Once the reagents reservoir has been completely emptied, the system has been rinsed with CPME (2 x 5 mL). The product has been collected continuously into the product reservoir. The CPME was recovered *via* distillation under reduced pressure (98 % of the total amount, purity confirmed by ^{1}HNMR) to afford pure product (5.24 g, 99 % yield).

E-factor: { [5.45 g $_{(aminophenol)}$ + 94.6 g $_{(CPME)}$ + 5.1 g $_{(H_2O_2)}$] – 5.24 g $_{(2\text{-aminophenoxazinone})}$ – 92.7 g $_{(CPME\ recovered)}$ } / 5.24 g $_{(2\text{-aminophenoxazinone})}$ = **1.4**

Large scale continuous flow procedure (50 mmol of substituted aminophenols (1a-i), or phenylenediamines (1j or 1k) or pyrogallol (1l) as starting material)

The reservoir was charged with 4 mL of CPME, the substrates of choice (2 mmol), followed by H_2O_2 (0.239 g, 216µL, 6 mmol) then the oxygen line has been set to 5 bar and the reaction mixture started to flow through K-OMS-2 filled reactor (filled with 60 mg of K-OMS-2) at flow rate of 0.1 mL/min with a residence time of 30 min. Once the reagents reservoir has been completely emptied, the system has been rinsed with CPME (1 mL). Once the reagents reservoir has been emptied again, the subsequent aminophenol (2 mmol) has been charged as a 0.5 M solution of CPME. The products have been collected continuously into the product reservoir. The CPME was recovered *via* distillation under reduced pressure (98 % of the total amount, purity confirmed by ^{1}HNMR) to afford pure products. The distilled CPME has been continuously reused for the entire scope of the flow procedure.

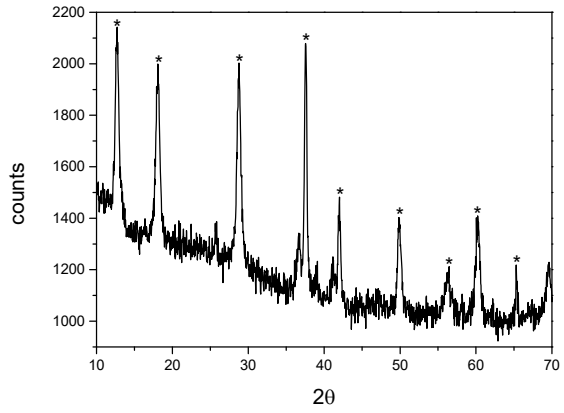
E-factor (considering the total mass of starting reagents and products synthesized):
E-factor = [86 g (CPME) + 7.06 g (starting materials) + 5.25 g (H_2O_2)] – [84.2 (CPME recovered) + 6.67 g (products 95-98 % range yield)]/ 6.67 g (products 95-98 % range yield)] = **1.12.**

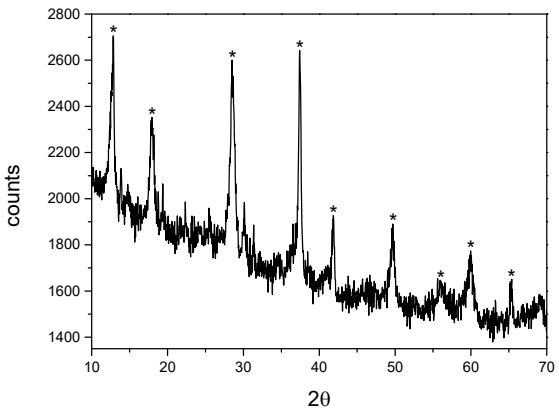
E-factor for literatures procedures:

Reference	Procedures	E-factor
ACS Sustainable Chem. Eng., 2019**, 74,** 4414-4419	According to the general procedure, the title compound was synthesized from 4,5-dimethoxy-2-nitrophenol (50.0 mg, 251 µmol) and palladium on activated charcoal (10 wt%, 5.00 mg, 4.70 µmol) in degassed MeOH (3 mL) as well as from 2-aminophenol (5, 109 mg, 1.00 mmol) and aqueous H_2O_2 solution (35%, 43.0 µL, 502 µmol) in degassed MeOH (3 mL). The crude product was recrystallized from water (5 mL) in order to obtain the product as a red solid (53.1 mg, 250 µmol, quant.)	**68**
*Tetrahedron Letters***,** 2015**, 56,** 6104–6107	To the solution of Buchwald product (200 mg) in methanol (5 ml) was added wet 10% Pd/C (10 mg) and the reaction mixture was stirred for 5 h under the pressure of hydrogen balloon. The reaction mixture was then filtered, washed the solids with EtOAc (210 ml), and the combined solvents were evaporated on a rotary evaporator under reduced pressure to get the crude product which was purified by column chromatography using EtOAc/Hexane (1:4) to get a red colored dye (60 mg, 0.28 mmol in caseof5A) and (56 mg, 0.26 mmol in case of5B).	**368**

XRD Analysis of the used K-OMS-2 after large scale flow procedures

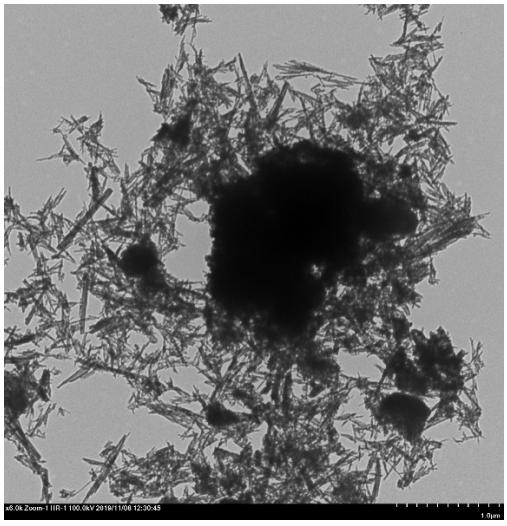
Powder X-ray diffraction data were collected after large scale flow procedure to analyze if changes occur onto the structure of the K-OMS-2 catalyst.



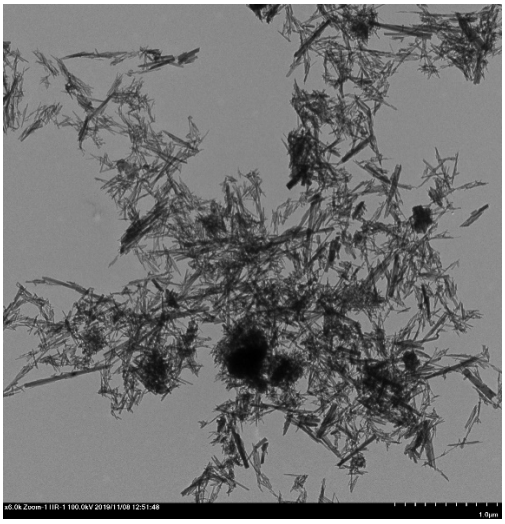


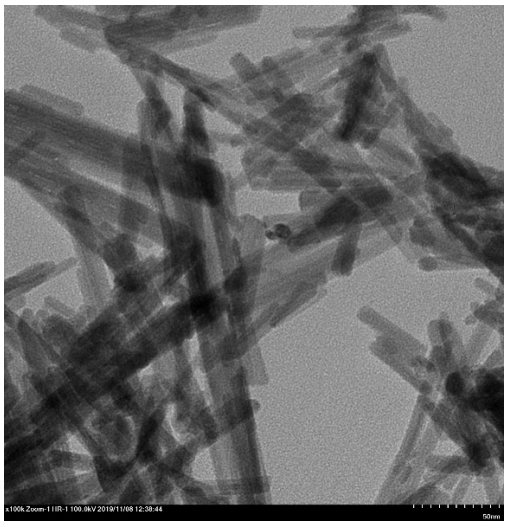
HRTEM Analysis of the used K-OMS-2 after large scale flow procedures

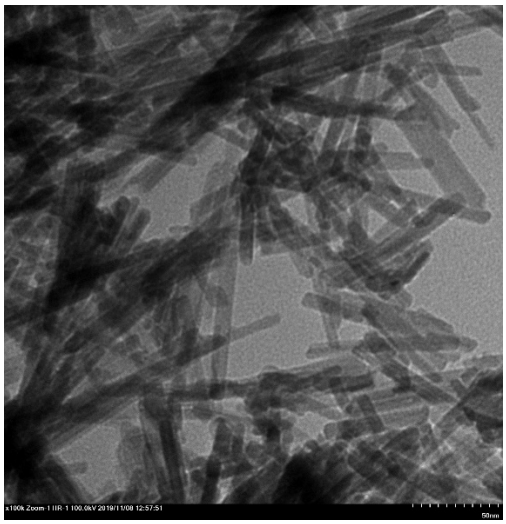
Fresh Catalyst



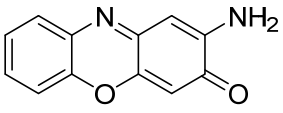
Used Catalyst



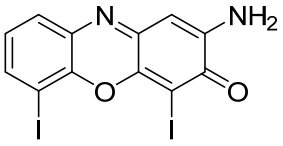




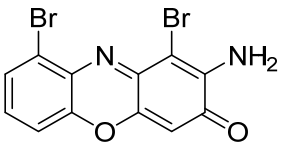
Spectral data for compounds 2a-l



2-amino-3H-phenoxazin-3-one (2a):[4] continuous flow procedure has been followed using 2-aminophenol (**1a**) (109 mg, 1 mmol) as substrate. Yield 97 % (103 mg). Red powder, m.p. = 255 – 257 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.70 (d, *J* = 7.6 Hz, 1H), 7.53 – 7.43 (m, 2H), 7.4 – 7.37 (m, 1H), 6.80 (s, 2H), 6.38 – 6.36 (m, 2H). **^{13}C NMR** (101 MHz, DMSO) δ 180.63, 149.29, 148.65, 147.78, 142.33, 134.13, 129.22, 128.38, 125.69, 116.35, 103.84, 98.76. **FT-IR**: 3432, 3407, 1604, 1580, 1472, 1420, 1278, 1121, 1106, 1054 cm^{-1}. **GC-EIMS** (m/z %): 212 (100), 185 (75), 157 (20), 144 (25), 129 (20), 102 (20), 76 (35).

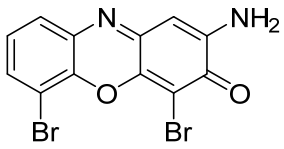


2-amino-4,6-diiodo-3H-phenoxazin-3-one (2b): continuous flow procedure has been followed using 2-amino-6-iodophenol (**1b**) (470 mg, 2 mmol) as substrate. Yield 98 % (454 mg). Red powder, m.p. = 257 – 260 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.96 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.73 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.23 (t, *J* = 7.9 Hz, 1H), 7.06 (s, 2H), 6.38 (s, 1H). **^{13}C NMR** (101 MHz, DMSO) δ 176.63, 151.13, 148.45, 146.57, 142.86, 138.32, 135.21, 128.37, 127.63, 98.37, 84.26, 81.52. **FT-IR**: 3401, 3375, 2915, 2832, 1693, 1174, 912, 742, 524 cm^{-1}. **GC-EIMS** (m/z %): 464 (100), 463 (35), 450 (50), 435 (25), 337 (65), 334 (20), 235 (25), 210 (55).

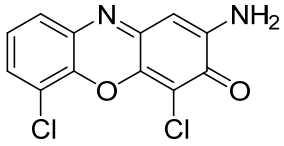


2-amino-1,9-dibromo-3H-phenoxazin-3-one (2c): continuous flow procedure has been followed using 2-amino-3-bromophenol (**1c**) (376 mg, 2 mmol) as substrate. Yield 97 % (359 mg). Red powder, decomposition occur at 287 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.83 (d, *J* = 2.1 Hz, 1H), 7.71 (d, *J* = 8.6 Hz, 1H), 7.59 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.10 (s, 2H), 6.39 (s, 1H). **^{13}C NMR** (101 MHz, DMSO) δ 178.00, 149.60, 146.30, 144.66, 142.99, 132.98, 130.21, 128.99, 121.91, 119.18, 103.25, 95.12. **FT-IR**: 3405, 3375, 3318, 2920, 2850, 1644, 1173, 909, 754,

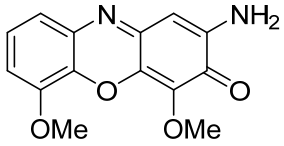
582 cm^{-1}. **GC-EIMS** (m/z %): 372 (49), 370 (100), 368 (50), 359 (30), 354 (45), 290 (65), 188 (55), 186 (54), 183 (25), 109 (20), 94 (80).



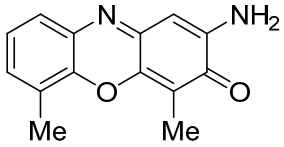
2-amino-4,6-dibromo-3H-phenoxazin-3-one (2d): continuous flow procedure has been followed using 2-amino-6-bromophenol (**1d**) (376 mg, 2 mmol) as substrate. Yield 98 % (363 mg). Red powder, decomposition occur at 275 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.80 – 7.73 (m, 2H), 7.38 (t, *J* = 7.9 Hz, 1H), 7.12 (s, 2H), 6.40 (s, 1H). **^{13}C NMR** (101 MHz, DMSO) δ 174.91, 148.07, 147.55, 146.55, 139.48, 135.51, 132.26, 127.82, 126.83, 109.25, 101.63, 98.09. **FT-IR**: 3403, 3375, 2915, 2844, 1644, 1170, 900, 752, 580 cm^{-1}. **GC-EIMS** (m/z %): 372 (48), 370 (100), 368 (52), 359 (45), 354 (65), 290 (80), 188 (35), 186 (54), 183 (25), 94 (75).



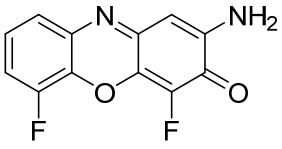
2-amino-4,6-dichloro-3H-phenoxazin-3-one(2e): continuous flow procedure has been followed using 2-amino-6-chlorophenol (**1e**) (288 mg, 2 mmol) as substrate. Yield 98 % (275 mg). Red powder, decomposition occur at 256 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.73 – 7.65 (m, 2H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.13 (s, 2H), 6.40 (s, 1H). **^{13}C NMR** (101 MHz, DMSO) δ 174.75, 147.86, 147.66, 144.40, 138.20, 135.42, 129.31, 127.34, 126.16, 120.27, 109.96, 97.95. **FT-IR**: 3407, 3390, 2902, 1670, 1170, 904, 748, 510 cm^{-1}. **GC-EIMS** (m/z %): 281 (100), 279 (64), 267 (75), 252 (65), 250 (45), 242 (25), 245 (50), 212 (20), 209 (75), 143 (40), 141 (25).



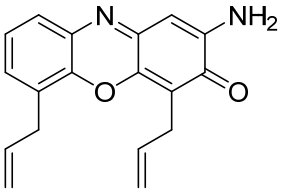
2-amino-4,6-dimethoxy-3H-phenoxazin-3-one (2f): continuous flow procedurehas been followed using 2-amino-6-methoxyphenol (**1f**) (278 mg, 2 mmol) as substrate. Yield 97 % (264 mg). Purple powder, m.p. = 250 – 253 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.33 – 7.28 (m, 2H), 7.20 – 7.17 (m, 1H), 6.81 (s, 2H), 6.29 (s, 1H), 3.96 (s, 3H), 3.89 (s, 3H). **^{13}C NMR** (101 MHz, DMSO) δ 176.42, 148.46, 147.58, 147.28, 137.62, 134.93, 134.69, 131.93, 124.68, 120.12, 111.85, 96.90, 60.21, 56.74. **FT-IR**: 3412, 3381, 2912, 2832, 1687, 1174, 1102, 909 cm^{-1}. **GC-EIMS** (m/z %): 272 (100), 258 (20), 244 (65), 243 (35), 230 (65), 223 (45), 212 (30), 210 (75).



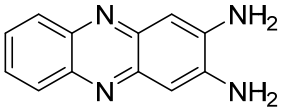
2-amino-4,6-dimethyl-3H-phenoxazin-3-one (2g):[5] continuous flow procedurehas been followed using 2-amino-6-methylphenol (**1g**) (246 mg, 2 mmol) as substrates. Yield 97 % (233 mg).Red powder, m.p. = 248 – 249 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ7.53 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.35 – 7.33 (m, 1H), 7.29 – 7.25 (m, 1H), 6.74 (s, 2H), 6.32 (s, 1H), 2.47 (s, 3H), 2.12 (s, 3H).**^{13}C NMR** (101 MHz, DMSO) δ180.35, 148.20, 147.14, 140.95, 139.60, 133.69, 130.16, 126.00, 125.37, 124.75, 111.64, 97.93, 14.85, 7.98. **FT-IR**: 3401, 3381, 2918, 2830, 1667, 1388,1102, 904 cm^{-1}. **GC-EIMS** (m/z %): 240 (100), 226 (30), 225 (80), 211 (65), 197 (25), 186 (20).



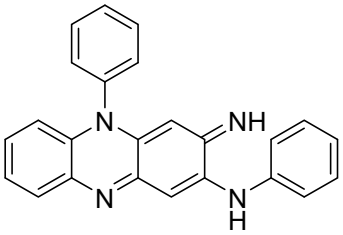
2-amino-4,6-difluoro-3H-phenoxazin-3-one (2h): continuous flow procedure has been followed using 2-amino-6-fluorophenol (**1h**) (254 mg, 2 mmol) as substrate. Yield 98 % (243 mg).Purple powder, decomposition occur at 256 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ7.58 (d, J = 8.0 Hz, 1H), 7.52 – 7.44 (m, 1H), 7.42 – 7.37 (m, 1H), 7.11 (s, 2H), 6.34 (s, 1H).**^{13}C NMR** (101 MHz, DMSO) δ172.85, (d, $^{2}J_{C–F}$ = 16 Hz, C_q), 149.76 (d, $^{1}J_{C–F}$ = 248 Hz, C_q), 147.82, 147.14 (d, $^{4}J_{C–F}$ = 2 Hz, C_q), 139.28 (d, $^{1}J_{C–F}$ = 252 Hz, C_q), 135.65, 132.63 (d, $^{3}J_{C–F}$ = 11 Hz, C_q), 130.05 (d, $^{3}J_{C–F}$ = 11 Hz, C_q), 125.22 (d, $^{3}J_{C–F}$ = 7 Hz, CH), 124.23, 115.84 (d, $^{2}J_{C–F}$ = 17 Hz, CH), 96.94.**^{19}F NMR**(101 MHz, DMSO) δ-137.49 (dd, J = 10.7, 5.6 Hz), -161.22. **FT-IR**: 3404, 3388, 2902, 1670, 1298, 901, 517 cm^{-1}. **GC-EIMS** (m/z %): 248 (100), 228 (45), 208 (65), 232 (25), 230 (40), 216 (20), 212 (40), 210 (25).



4,6-diallyl-2-amino-3H-phenoxazin-3-one (2i): continuous flow procedure has been followed using 2-amino-6-allylphenol (**1i**) (298 mg, 2 mmol) as substrate. Yield 93 % (272 mg).Red powder, m.p. = 258 – 260 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ7.59 (t, J = 4.8 Hz, 1H), 7.33 (d, J = 4.8 Hz, 2H), 6.78 (s, 2H), 6.57 – 6.45 (m, 3H), 6.35 (s, 1H), 6.30 (dd, J = 7.2, 2.0 Hz, 1H), 6.10 – 5.84 (m, 2H), 3.64 (d, J = 6.4 Hz, 1H), 3.41 (d, J = 6.6 Hz, 1H), 3.28 (d, J = 6.6 Hz, 2H).**^{13}C NMR** (101 MHz, DMSO) δ 179.60, 148.20, 147.26, 141.47, 137.83, 129.52, 127.54, 127.29, 125.12, 120.43, 117.88, 116.82, 115.84, 115.35, 113.47, 98.14, 33.36, 26.87.**FT-IR**: 3398, 3371, 3092, 1625, 1174, 1102, 842 cm^{-1}. **GC-EIMS** (m/z %): 292 (100), 290 (35), 276 (35), 274 (60), 260 (40), 254 (45), 210 (70), 196 (20).

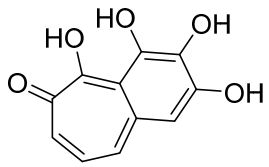


phenazine-2,3-diamine (2j):[6] continuous flow procedurehas been followed using benzene-1,2-diamine (**1j**) (216 mg, 2 mmol) as substrate. Yield 98 % (206 mg). Red powder, m.p. = 262 – 265 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.91 – 7.89 (m, 2H), 7.65 – 7.44 (m, 2H), 6.92 (s, 2H), 6.26 (s, 4H). **^{13}C NMR** (101 MHz, DMSO) δ 144.45, 142.45, 140.70, 128.28, 126.83, 102.58. **FT-IR**: 3310, 3155, 1630, 1532, 1372, 1240, 890, 835 cm^{-1}. **GC-EIMS** (m/z %): 211 (45), 210 (100), 186 (20), 115 (40), 102 (20), 74 (45).



3-imino-N,5-diphenyl-3,5-dihydrophenazin-2-amine (2k):[7] continuous flow procedure has been followed using 2-phenylamino-aniline (**1k**) (368 mg, 2 mmol) as substrate. Yield 98 % (354 mg). Deep red powder, decomposition occur at 265 °C. **^{1}H NMR** (400

MHz, DMSO-d_6) δ 7.67 (dd, *J* = 7.4, 2.0 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 2H), 7.57 – 7.50 (m, 1H), 7.41 – 7.34 (m, 2H), 7.25 – 7.11 (m, 4H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.72 – 6.66 (m, 2H), 6.60 (s, 2H), 6.48 – 6.42 (m, 2H), 5.23 (s, 1H). **^{13}C NMR** (101 MHz, DMSO) δ 152.82, 151.36, 150.29, 149.86, 137.30, 136.00, 134.66, 131.27, 130.93, 129.91, 128.99, 128.89, 127.96, 127.54, 123.21, 123.08, 121.15, 114.57, 99.38, 90.60. **FT-IR**: 3312, 3134, 1630, 1532, 1375, 1248, 835, 760 cm^{-1}. **GC-EIMS** (m/z %): 363 (64), 362 (100), 273 (20), 262 (25), 184 (22), 182 (25), 174 (34), 122 (35), 108 (42).



2,3,4,5-tetrahydroxy-6H-benzo[7]annulen-6-one (2l):[8] continuous flow procedure has been followed using benzene-1,2,3-triol (**1l**) (252 mg, 2 mmol) as substrate. Yield 95 % (209 mg). Orange powder, m.p. = 274 – 276. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.35 (d, *J* = 11.4 Hz, 1H), 7.07 (d, *J* = 9.4 Hz, 1H), 6.90 (s, 1H), 6.74 (dd, *J* = 11.4, 9.5 Hz, 1H). **^{13}C NMR** (101 MHz, DMSO) δ 182.65, 155.09, 152.17, 151.95, 135.11, 134.71, 133.40, 123.98, 116.91, 115.25, 110.64. **FT-IR**: 3416, 3322, 1626, 1590, 1423, 1378, 1237, 1065, 1036, 845, 802, 650 cm^{-1}. **GC-EIMS** (m/z %): 220 (100), 192 (45), 163 (20), 146 (25), 118 (35), 98 (45).

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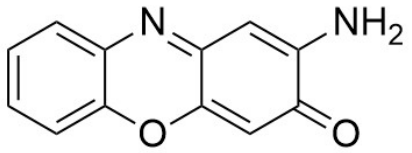
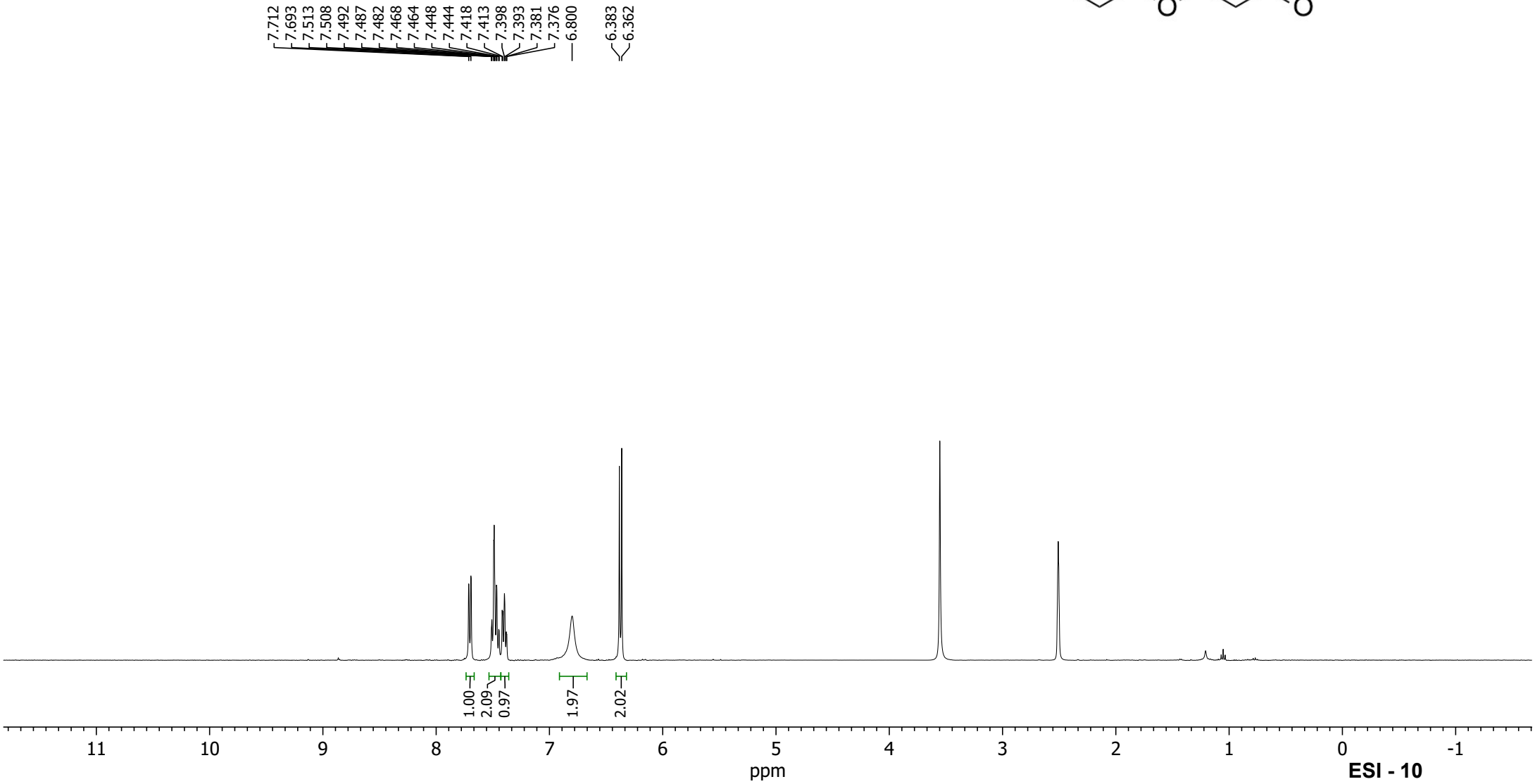
2-amino-3H-phenoxazin-3-one (2a)

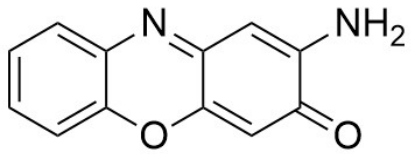
^{1}H-NMR (400 MHz)
DMSO-d_6

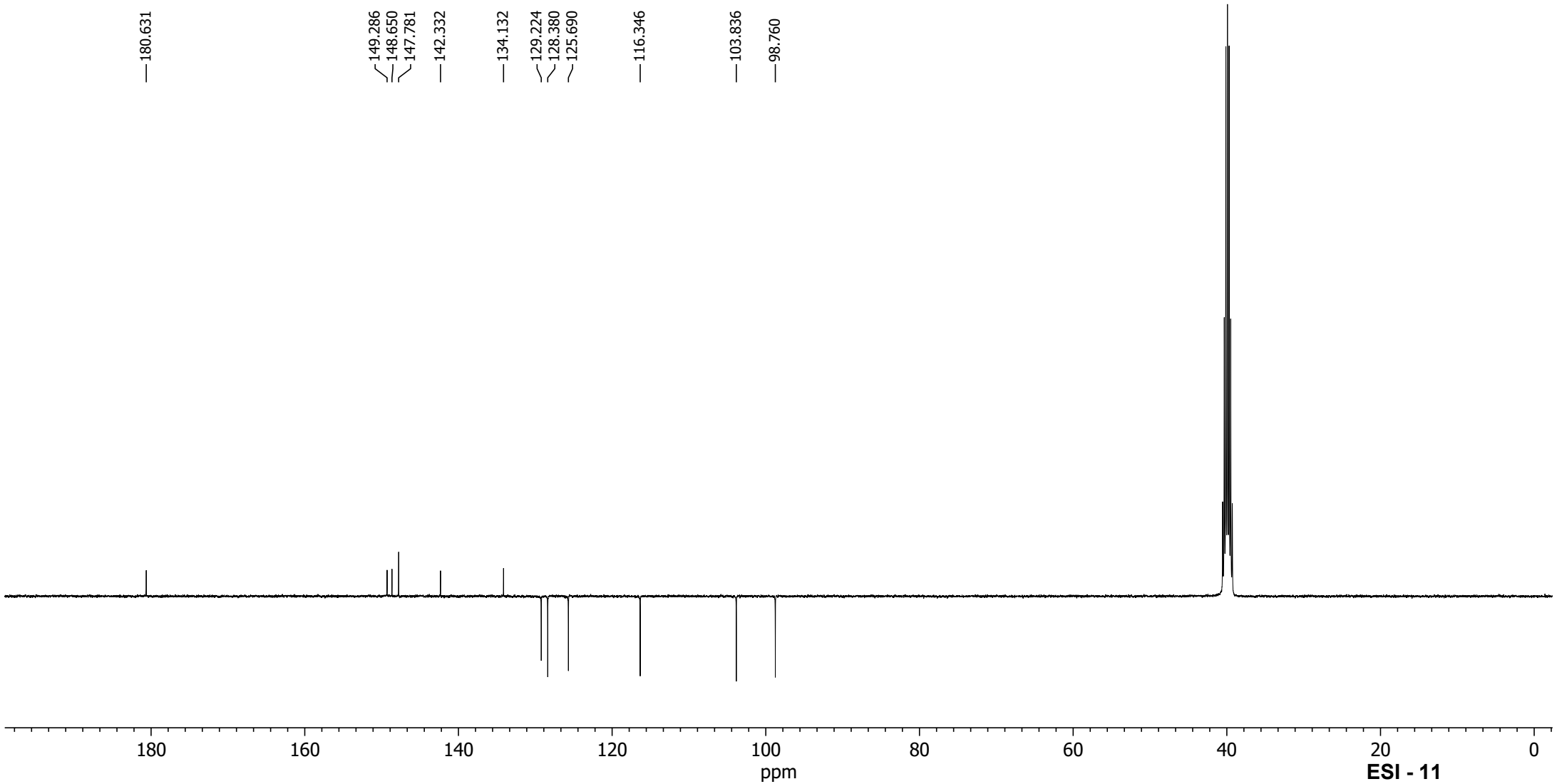




2-amino-3H-phenoxazin-3-one (2a)

^{13}C-NMR (100 MHz)
DMSO-d_6

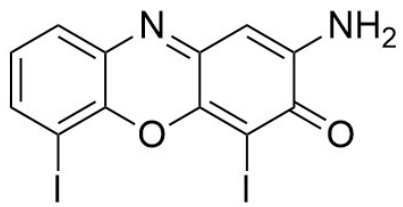


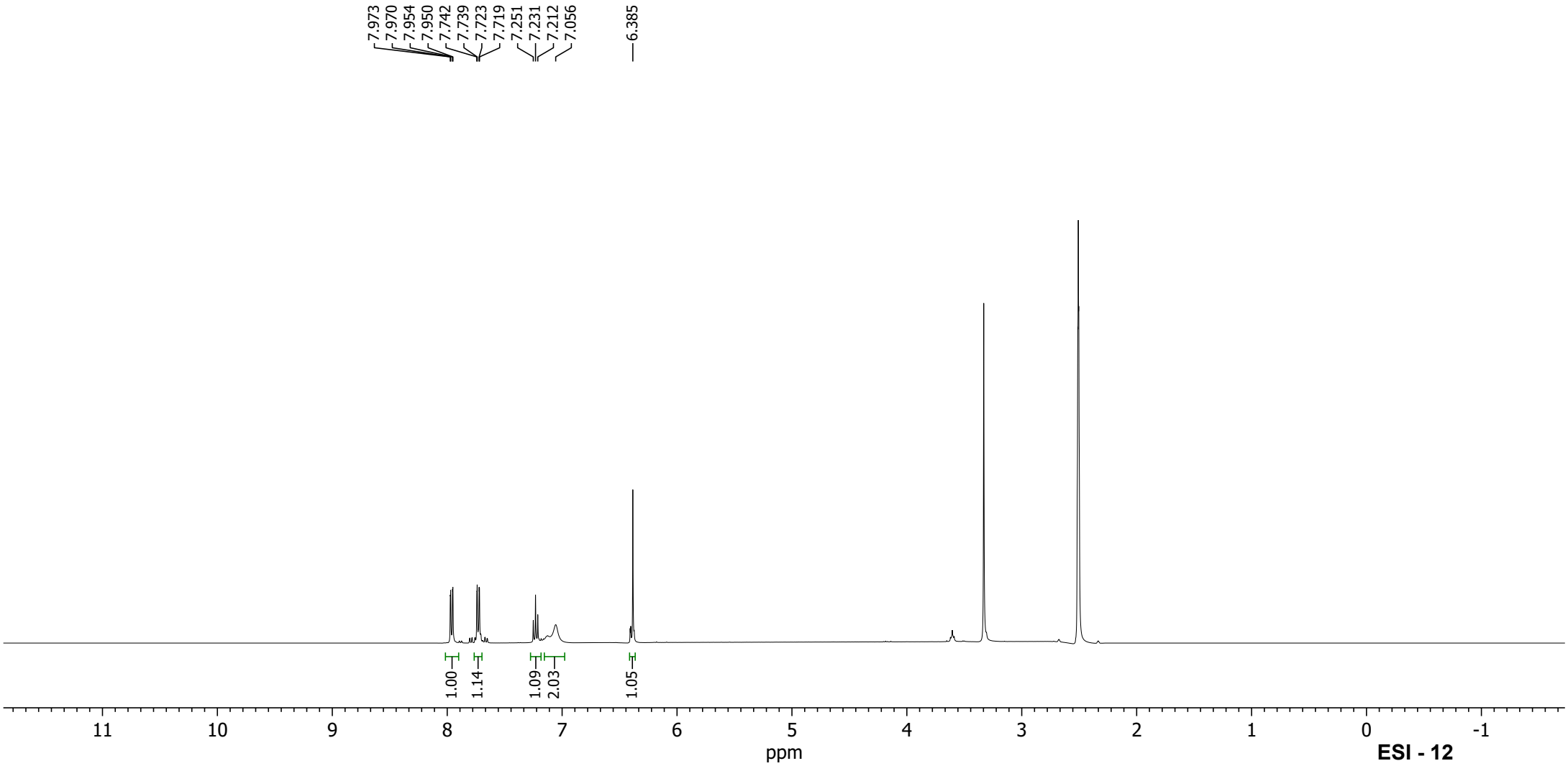


ESI - 11

2-amino-4,6-diiodo-3H-phenoxazin-3-one (2b)

^{1}H-NMR (400 MHz)
DMSO-d_6

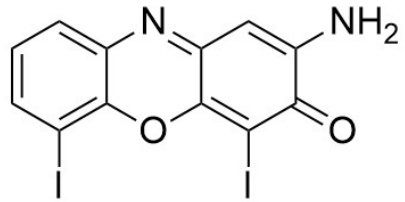


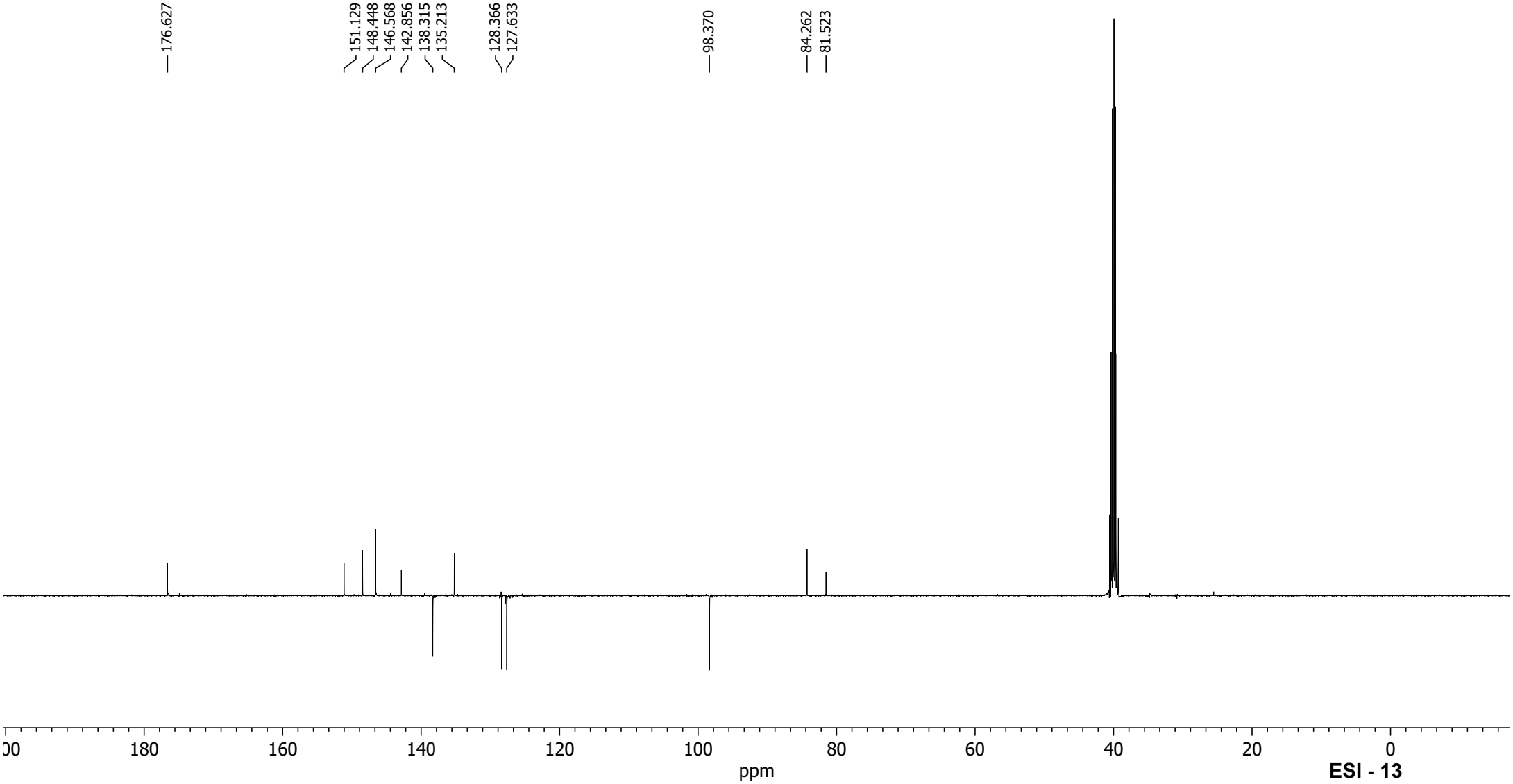


ESI - 12

2-amino-4,6-diiodo-3H-phenoxazin-3-one (2b)

^{13}C-NMR (100 MHz)
DMSO-d_6

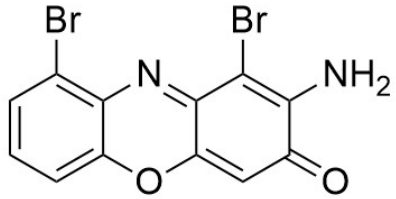


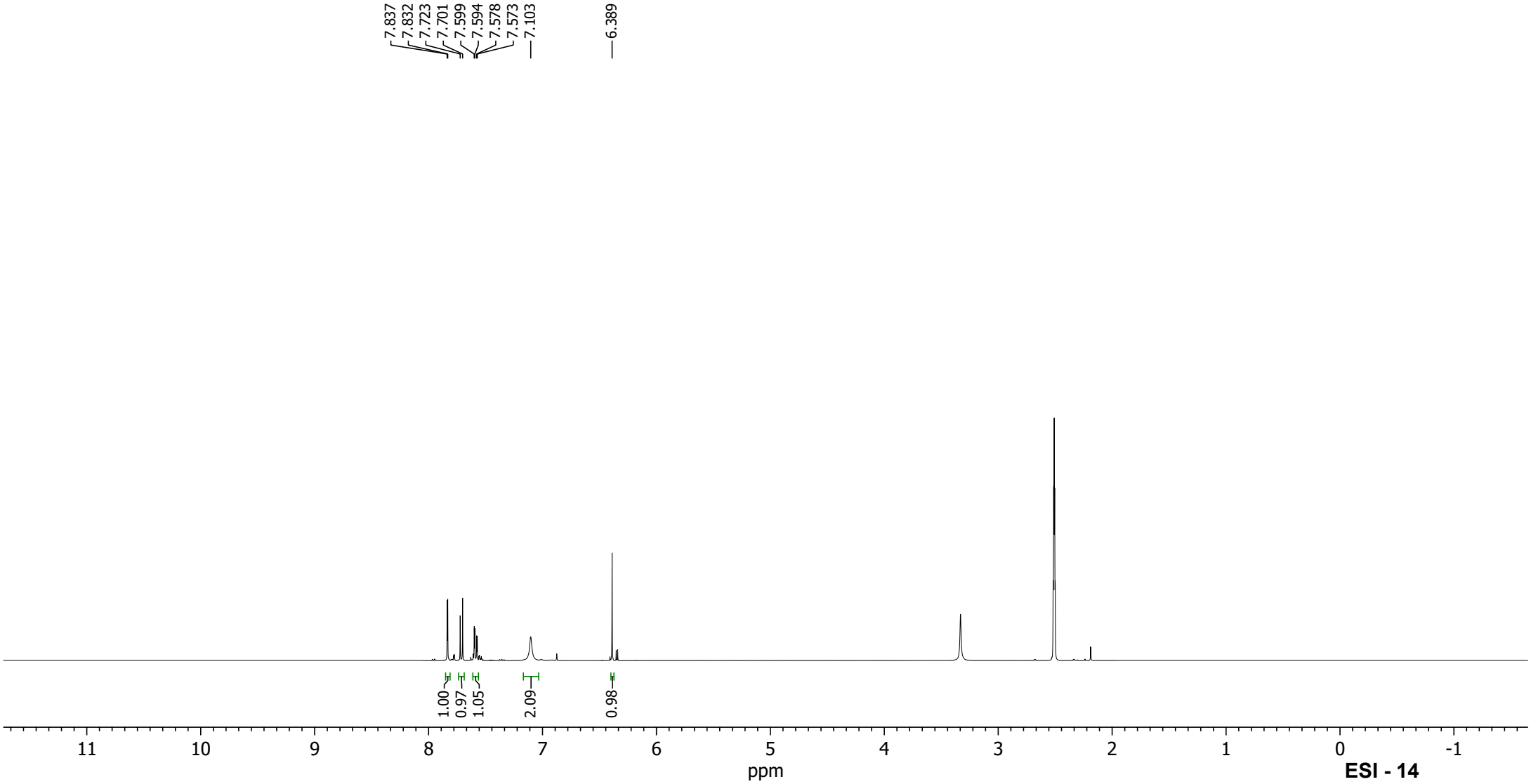


ESI - 13

2-amino-1,9-dibromo-3H-phenoxazin-3-one (2c)

^{1}H-NMR (400 MHz)
DMSO-d_6

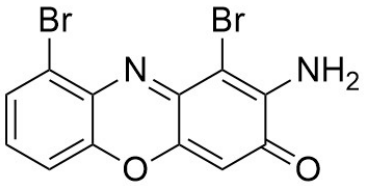




ESI - 14

2-amino-1,9-dibromo-3H-phenoxazin-3-one (2c)

^{13}C-NMR (100 MHz)
DMSO-d_6



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128.987
121.914
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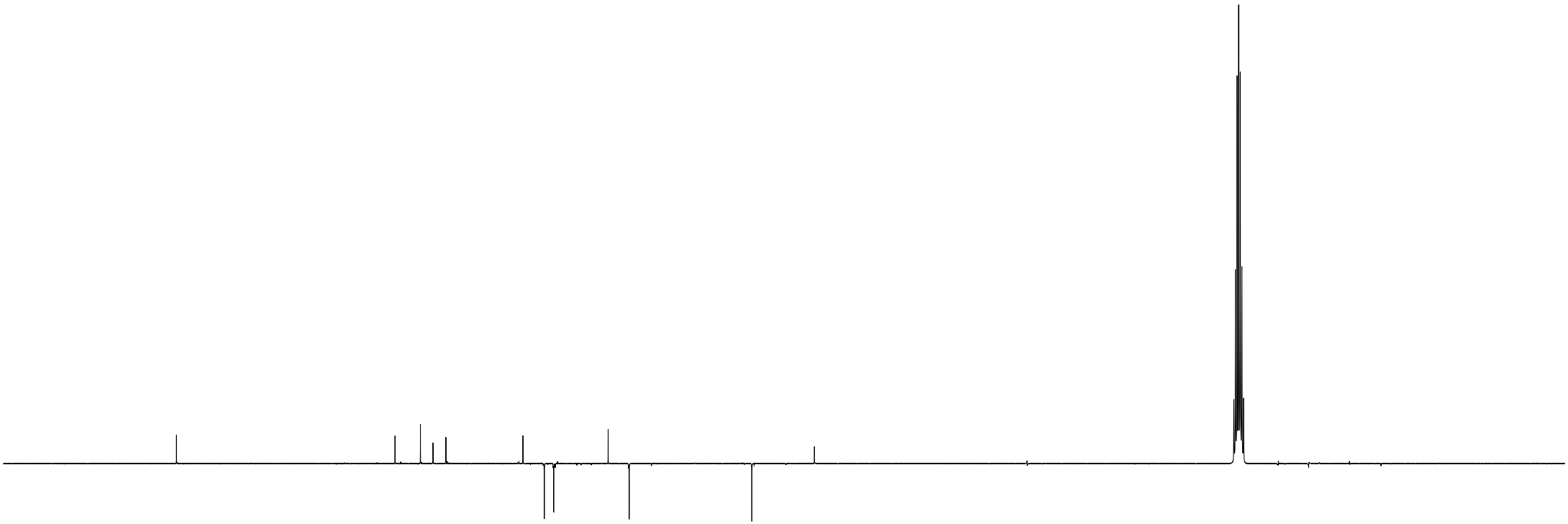
95.119



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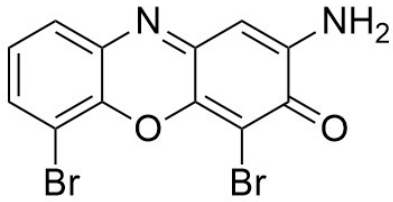
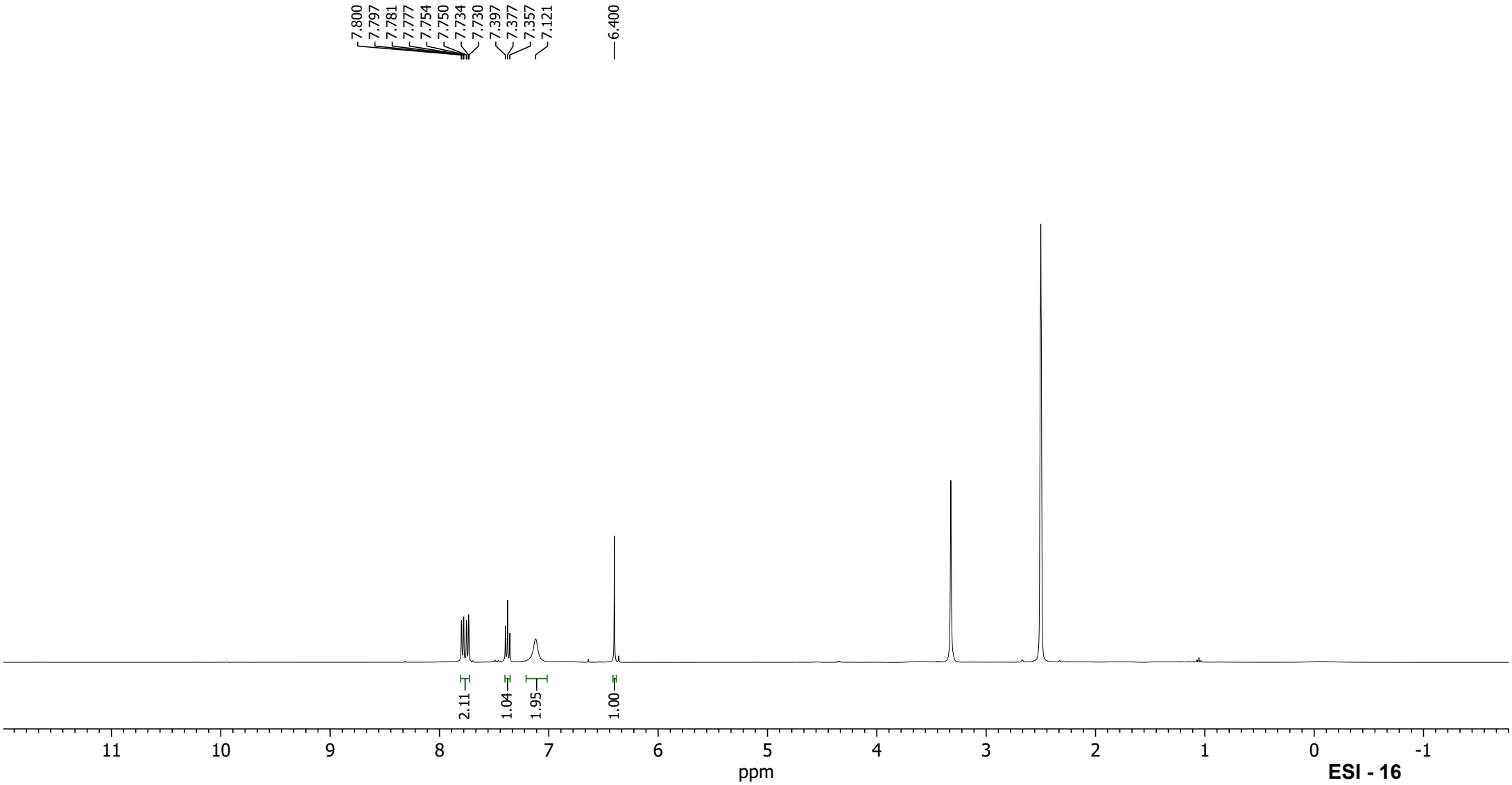
ppm

ESI - 15

2-amino-4,6-dibromo-3H-phenoxazin-3-one (2d)

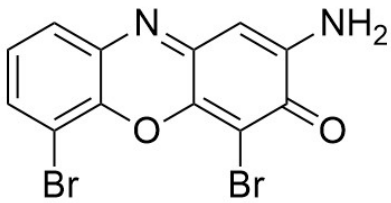
^{1}H-NMR (400 MHz)
DMSO-d_6

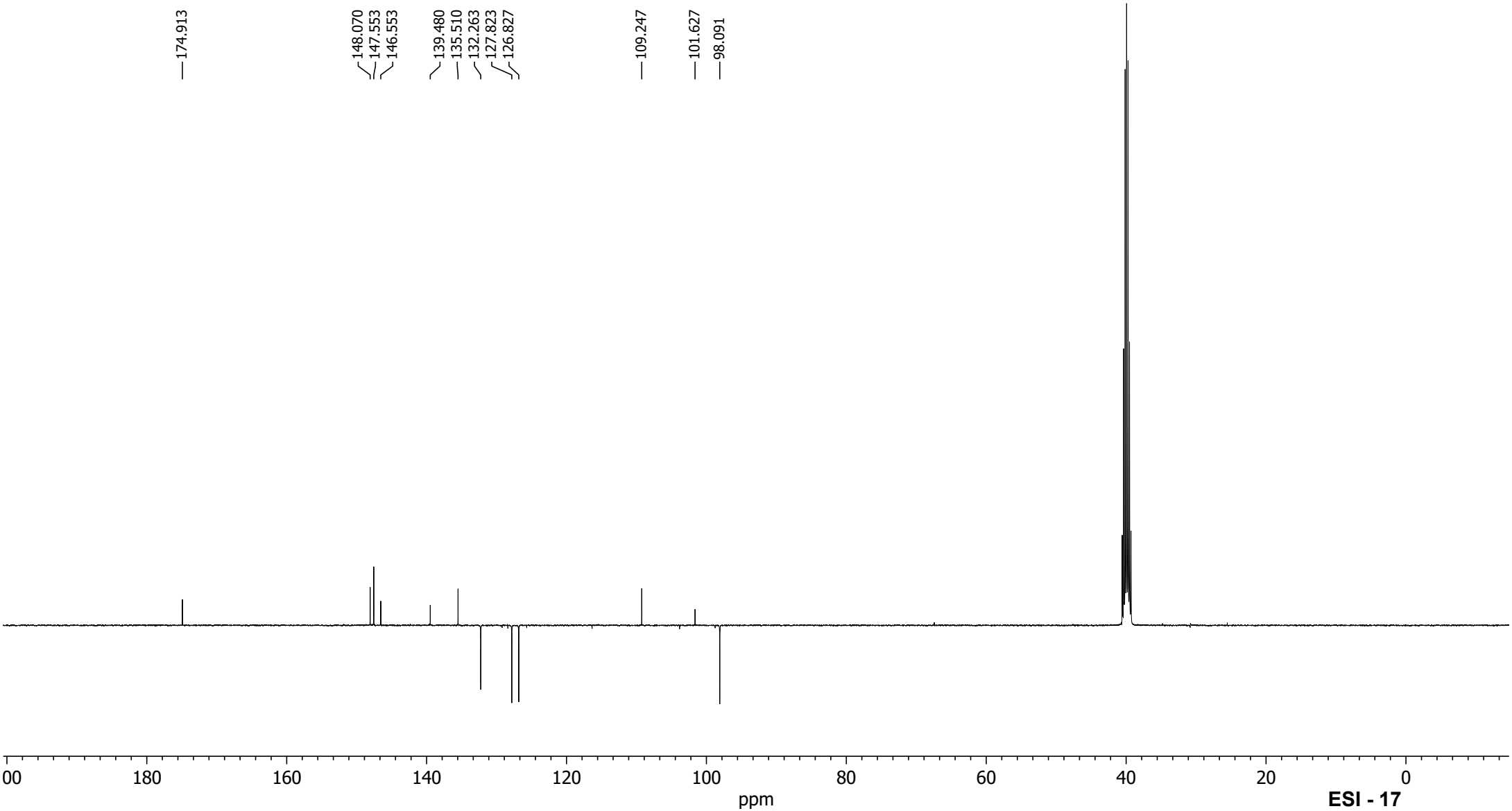




2-amino-4,6-dibromo-3H-phenoxazin-3-one (2d)

^{13}C-NMR (100 MHz)
DMSO-d_6

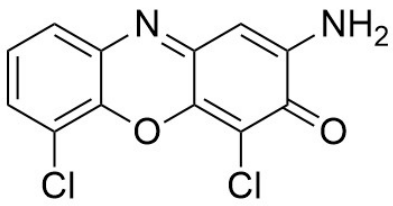


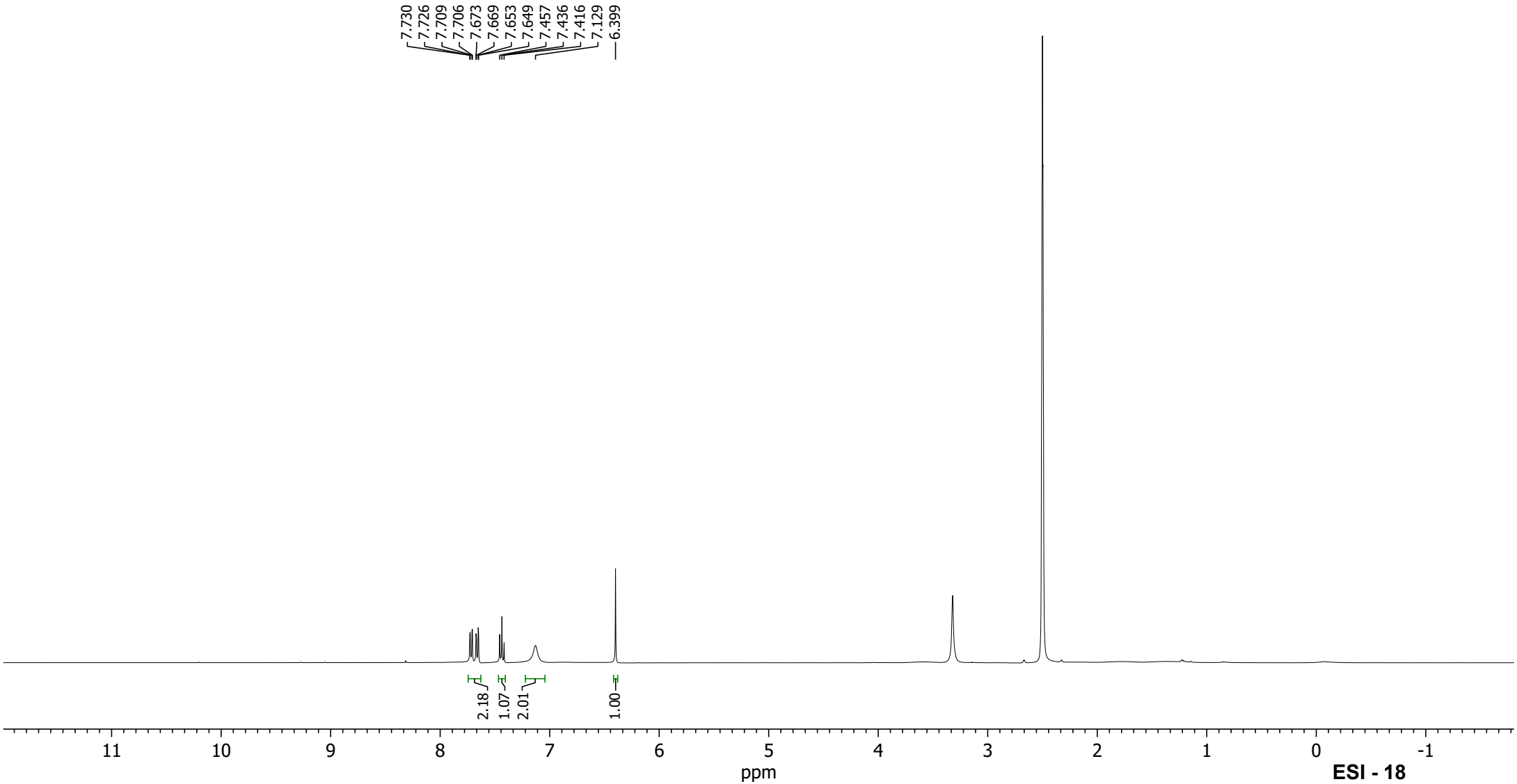


ESI - 17

2-amino-4,6-dichloro-3H-phenoxazin-3-one (2e)

^{1}H-NMR (400 MHz)
DMSO-d_6

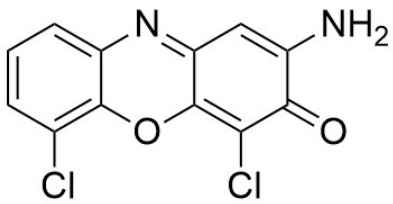


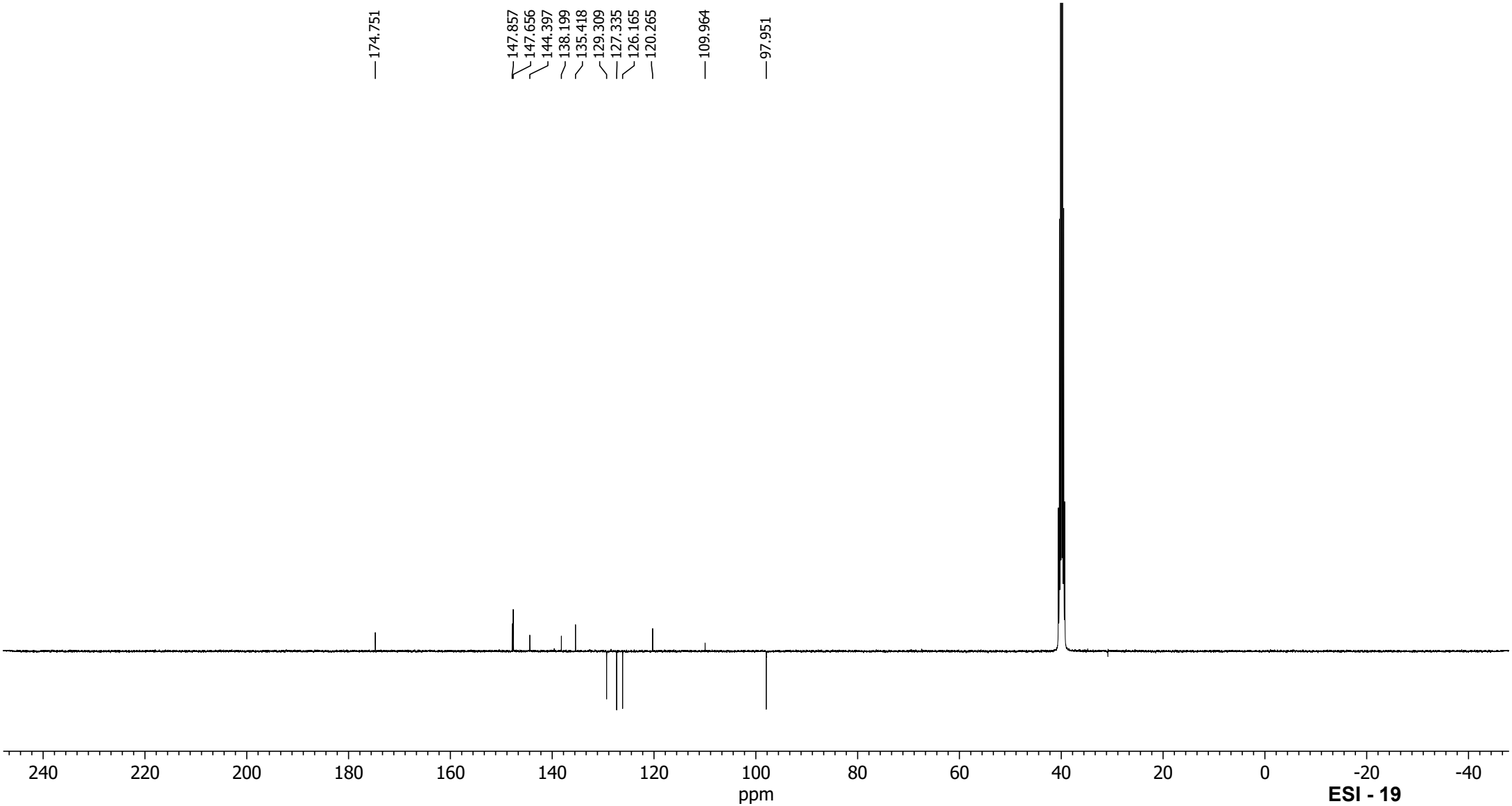


ESI - 18

2-amino-4,6-dichloro-3H-phenoxazin-3-one (2e)

^{13}C-NMR (100 MHz)
DMSO-d_6

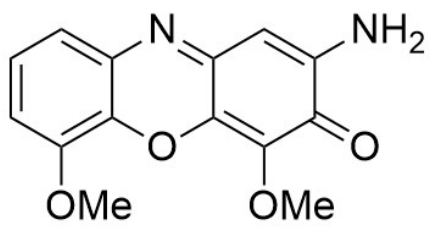


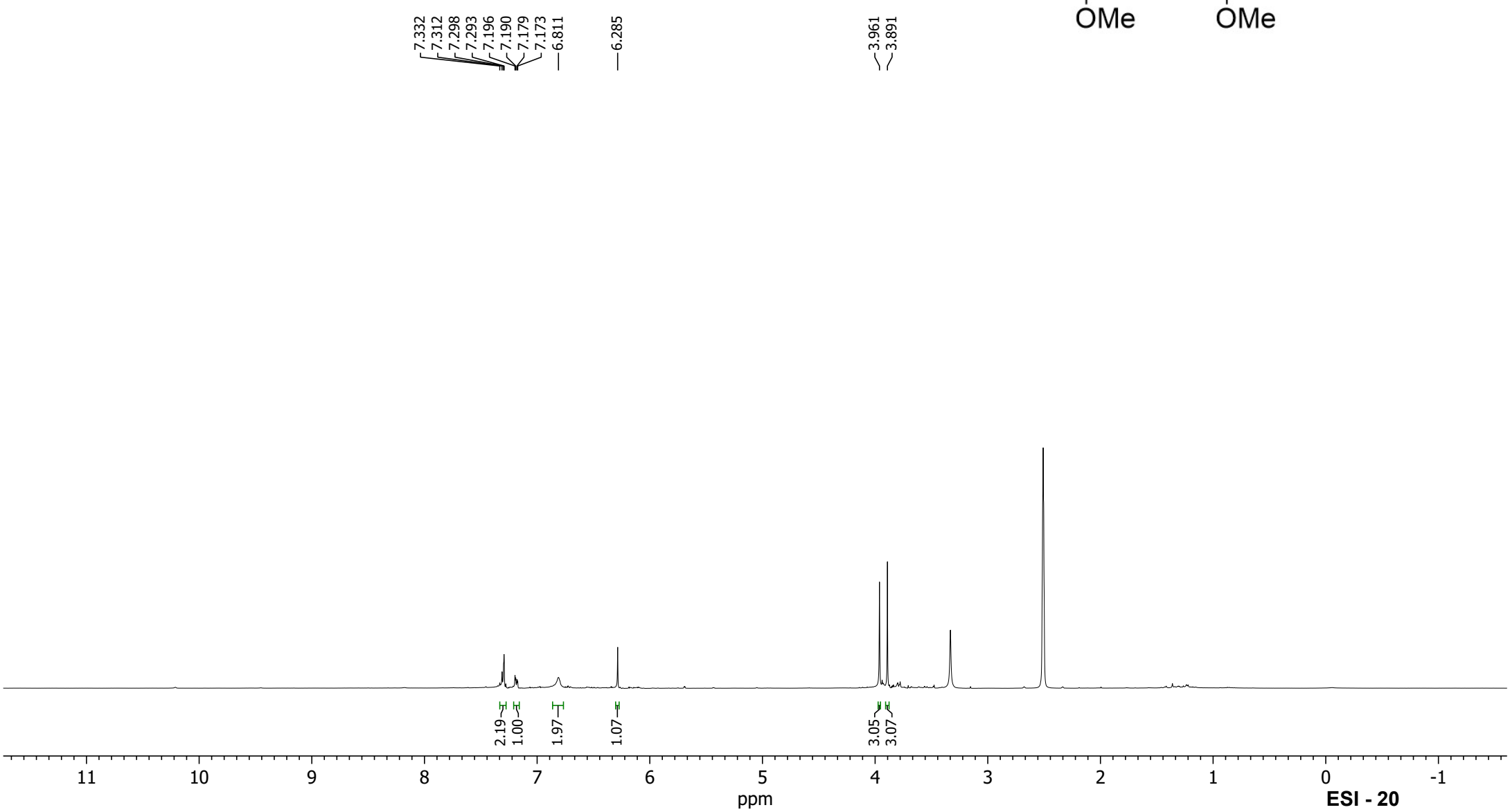


ESI - 19

2-amino-4,6-dimethoxy-3H-phenoxazin-3-one (2f)

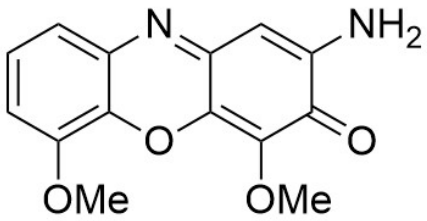
^{1}H-NMR (400 MHz)
DMSO-d_6

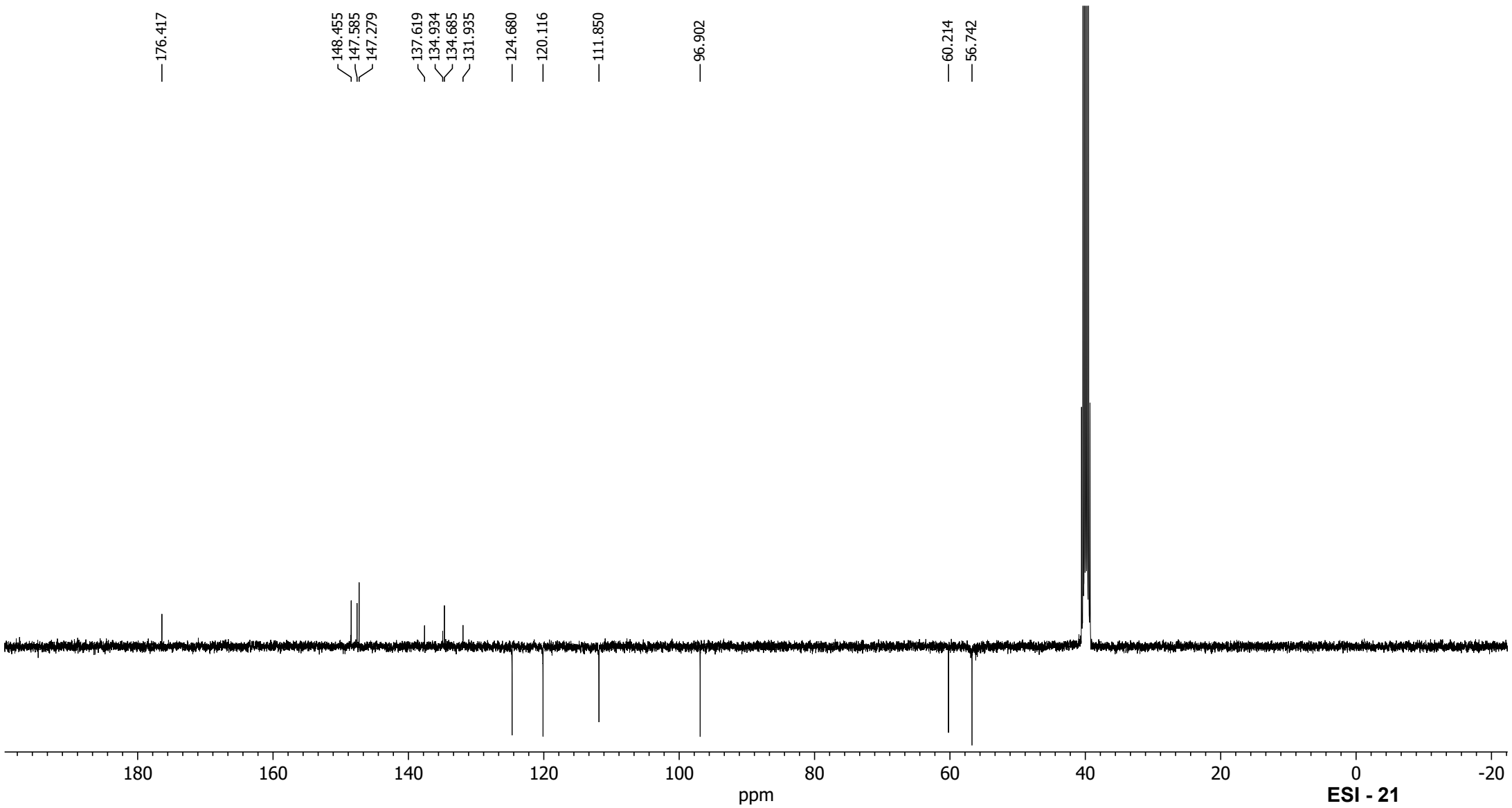




2-amino-4,6-dimethoxy-3H-phenoxazin-3-one (2f)

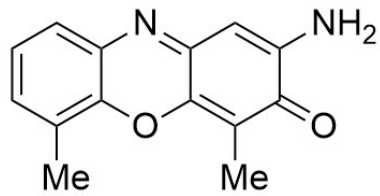
^{13}C-NMR (100 MHz)
DMSO-d_6

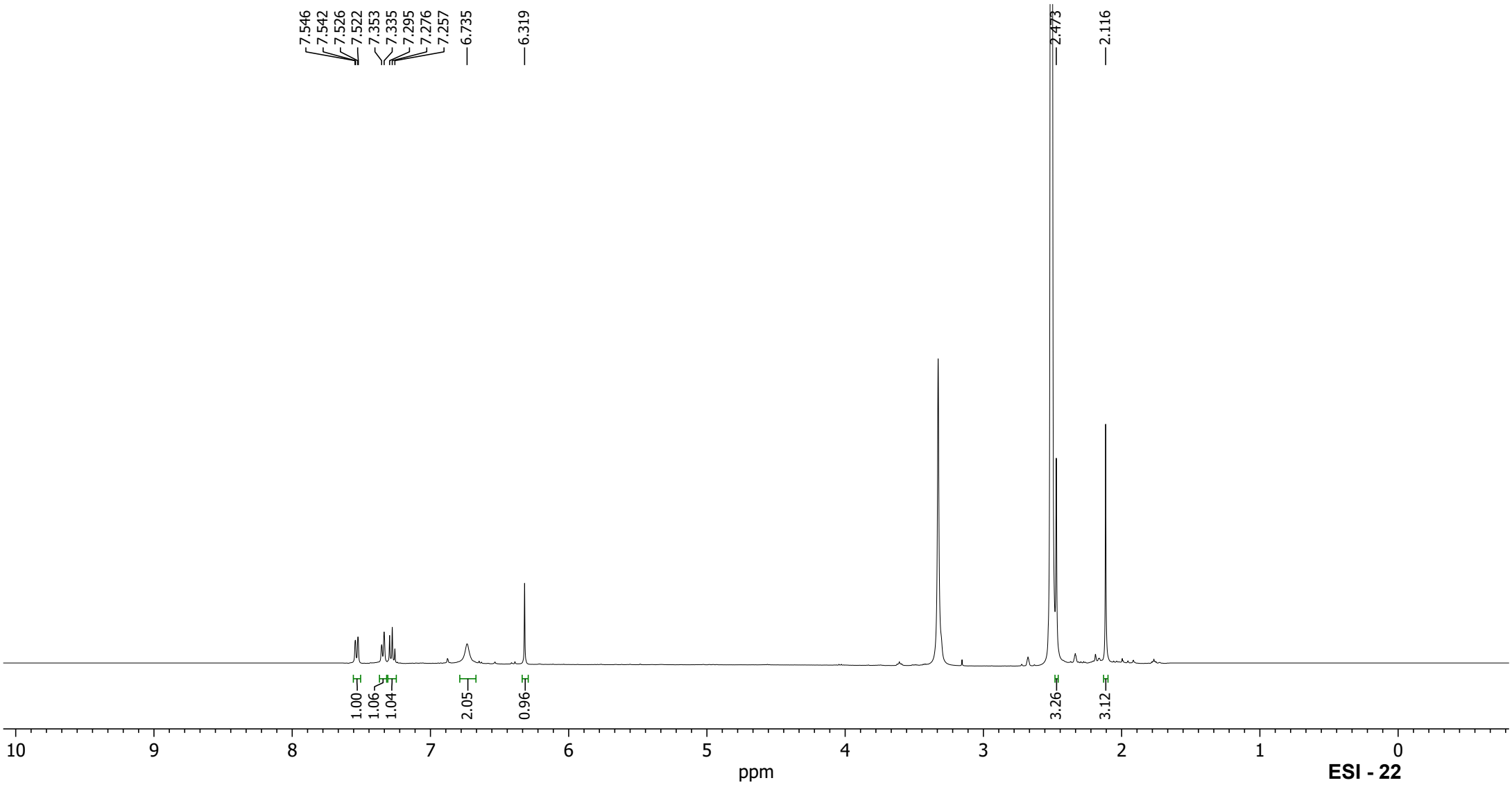




2-amino-4,6-dimethyl-3H-phenoxazin-3-one (2g)

^{1}H-NMR (400 MHz)
DMSO-d_6

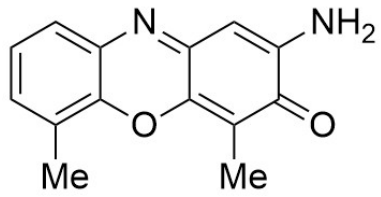


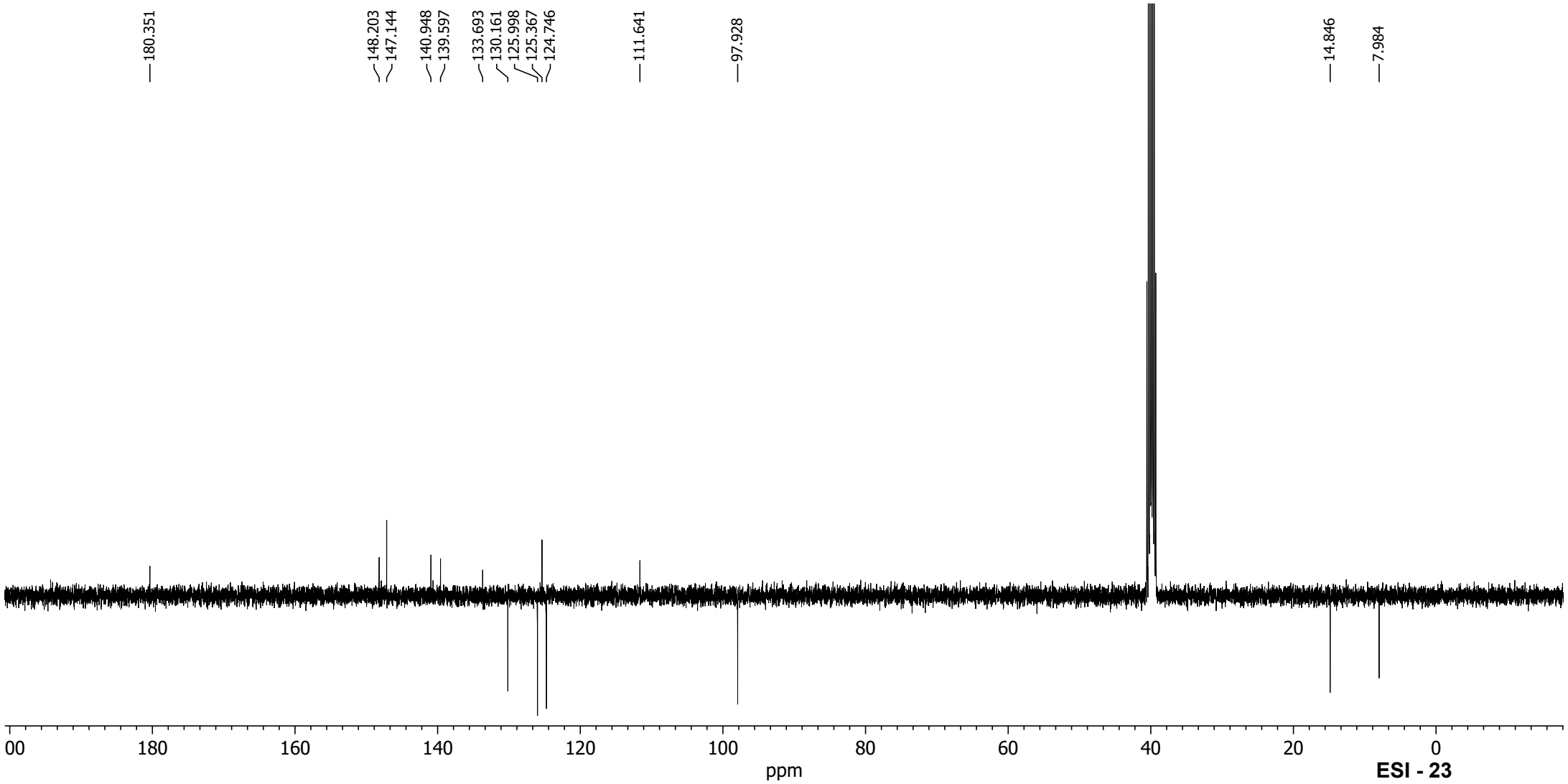


ESI - 22

2-amino-4,6-dimethyl-3H-phenoxazin-3-one (2g)

^{13}C-NMR (100 MHz)
DMSO-d_6

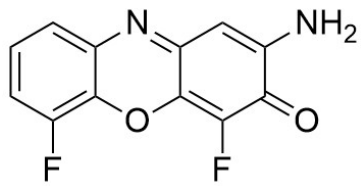


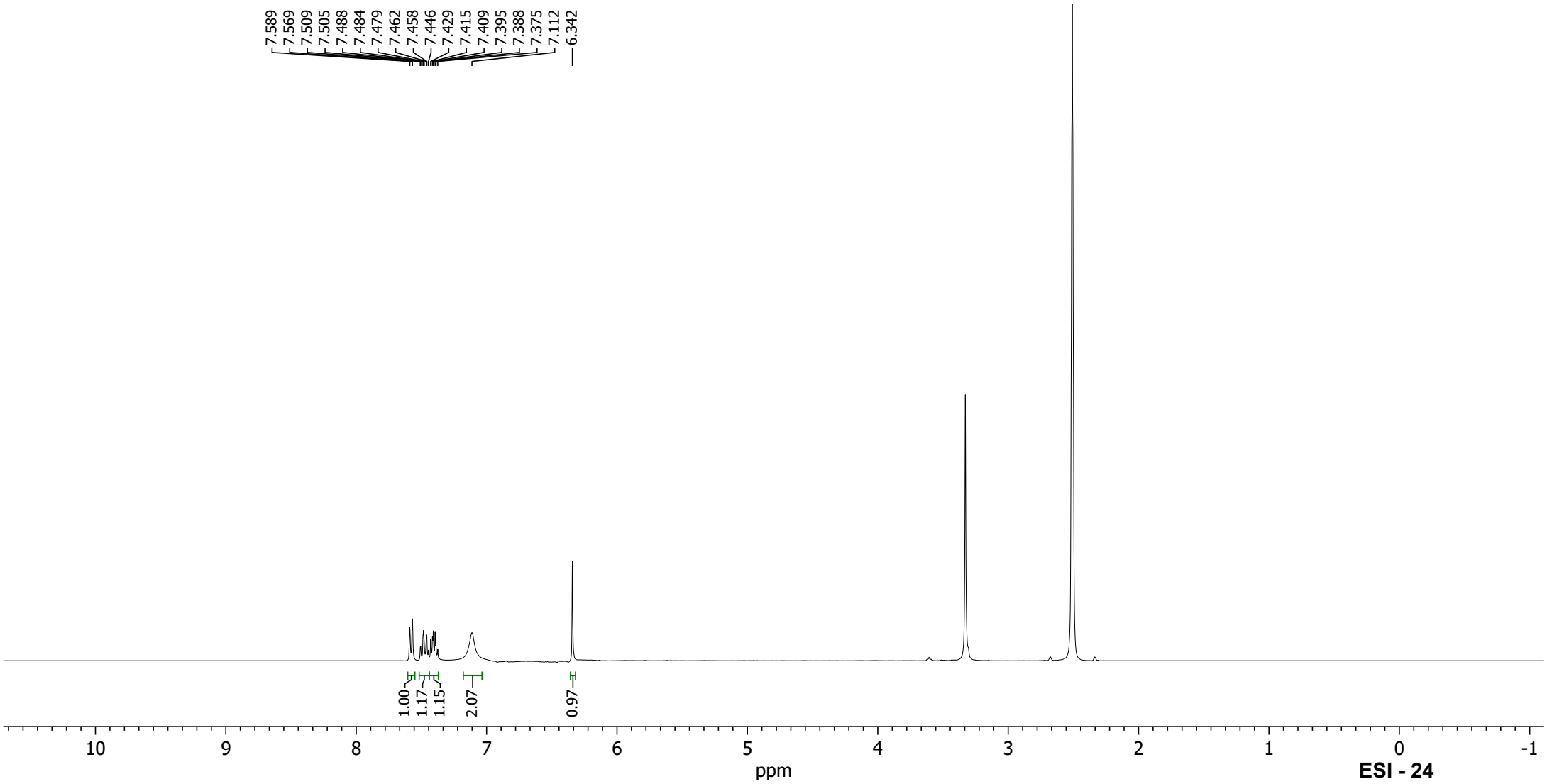


ESI - 23

2-amino-4,6-difluoro-3H-phenoxazin-3-one (2h)

^{1}H-NMR (400 MHz)
DMSO-d_6

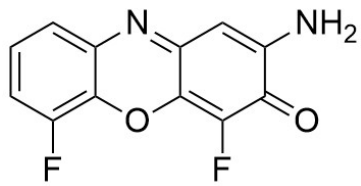


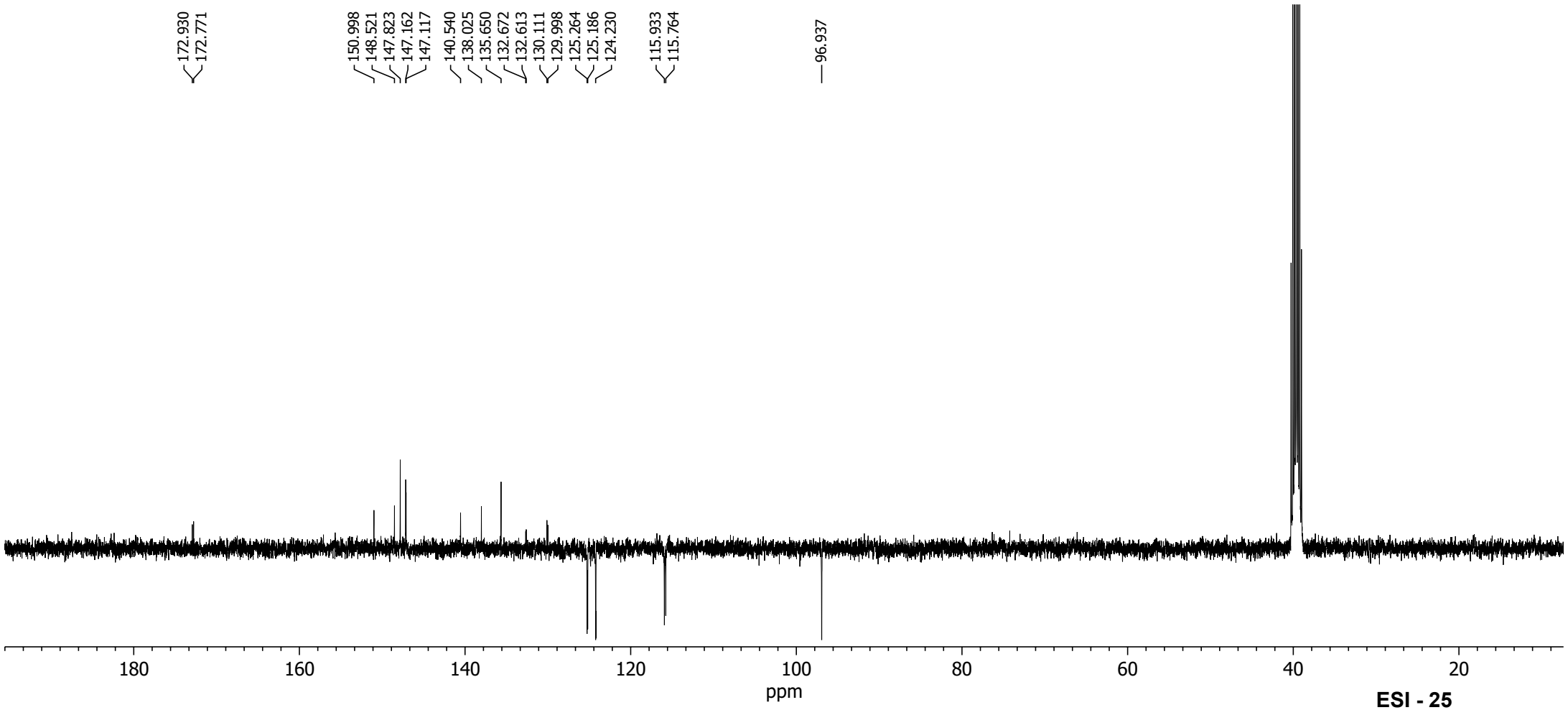


ESI - 24

2-amino-4,6-difluoro-3H-phenoxazin-3-one (2h)

^{13}C-NMR (100 MHz)
DMSO-d_6

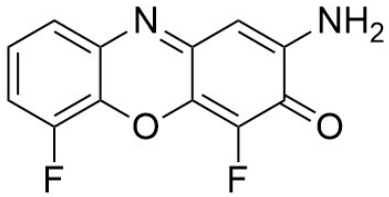




ESI - 25

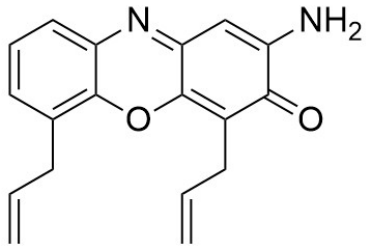
2-amino-4,6-difluoro-3H-phenoxazin-3-one (2h)

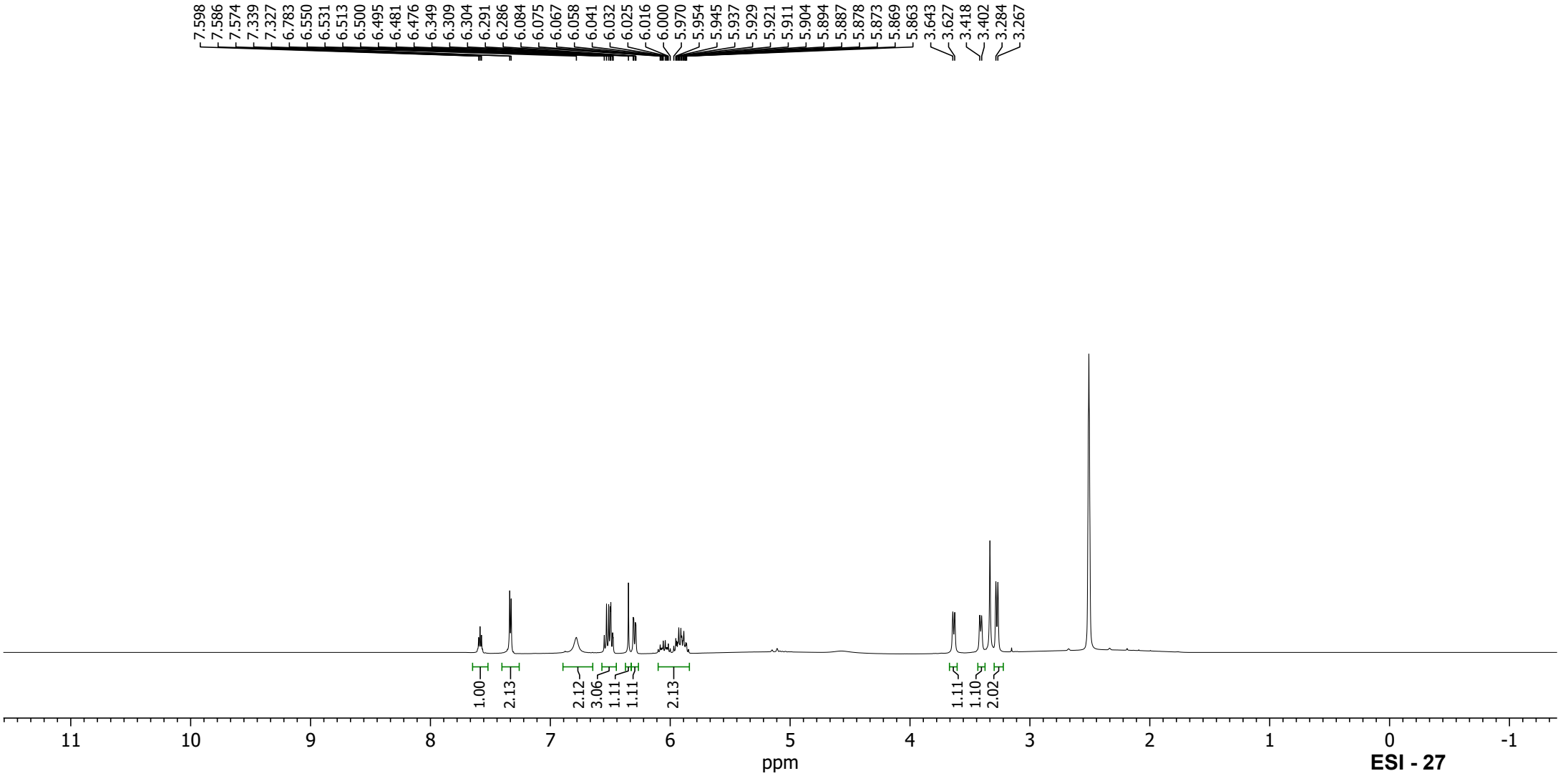
^{19}F-NMR (282 MHz)
DMSO-d_6



4,6-diallyl-2-amino-3H-phenoxazin-3-one (2i)

^{1}H-NMR (400 MHz)
DMSO-d_6

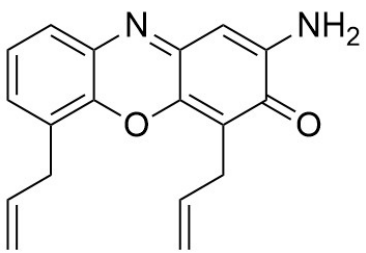


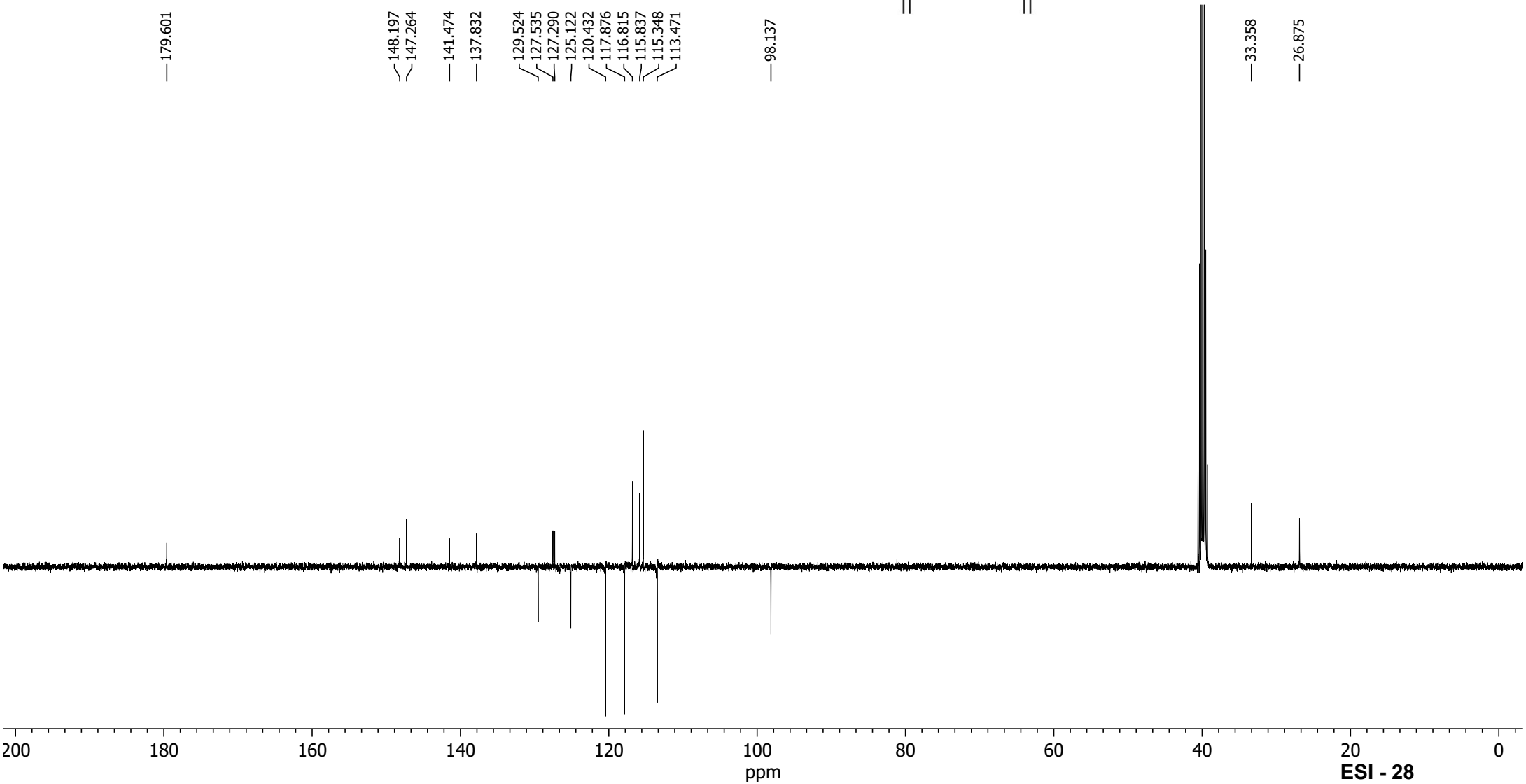


ESI - 27

4,6-diallyl-2-amino-3H-phenoxazin-3-one (2i)

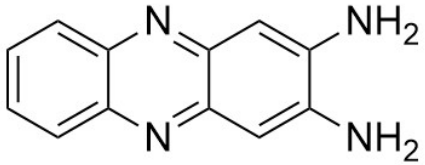
^{13}C-NMR (100 MHz)
DMSO-d_6

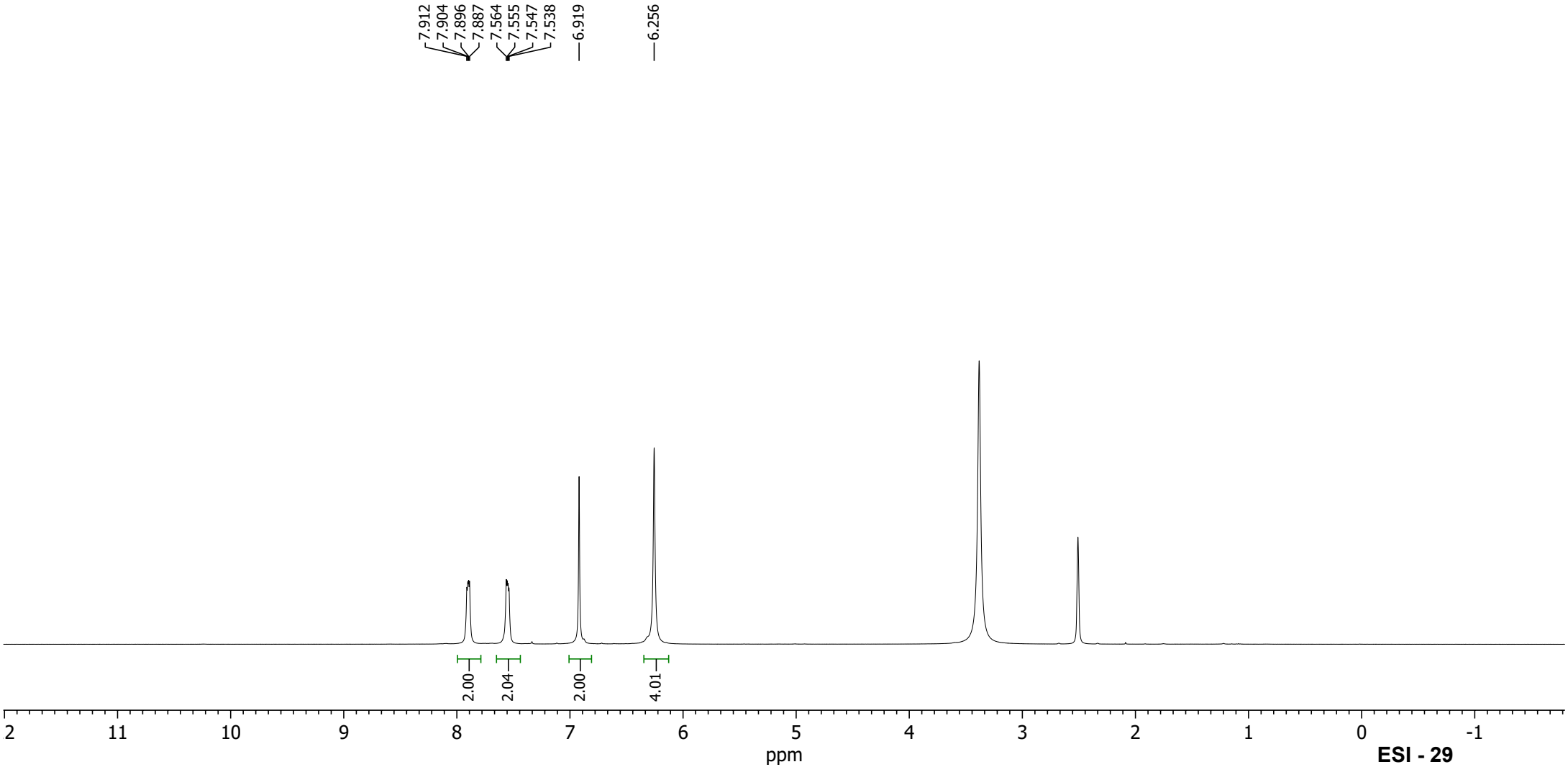




phenazine-2,3-diamine (2j)

^{1}H-NMR (400 MHz)
DMSO-d_6

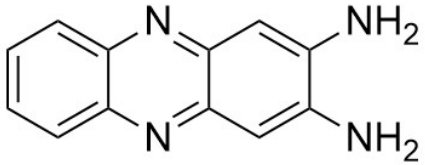


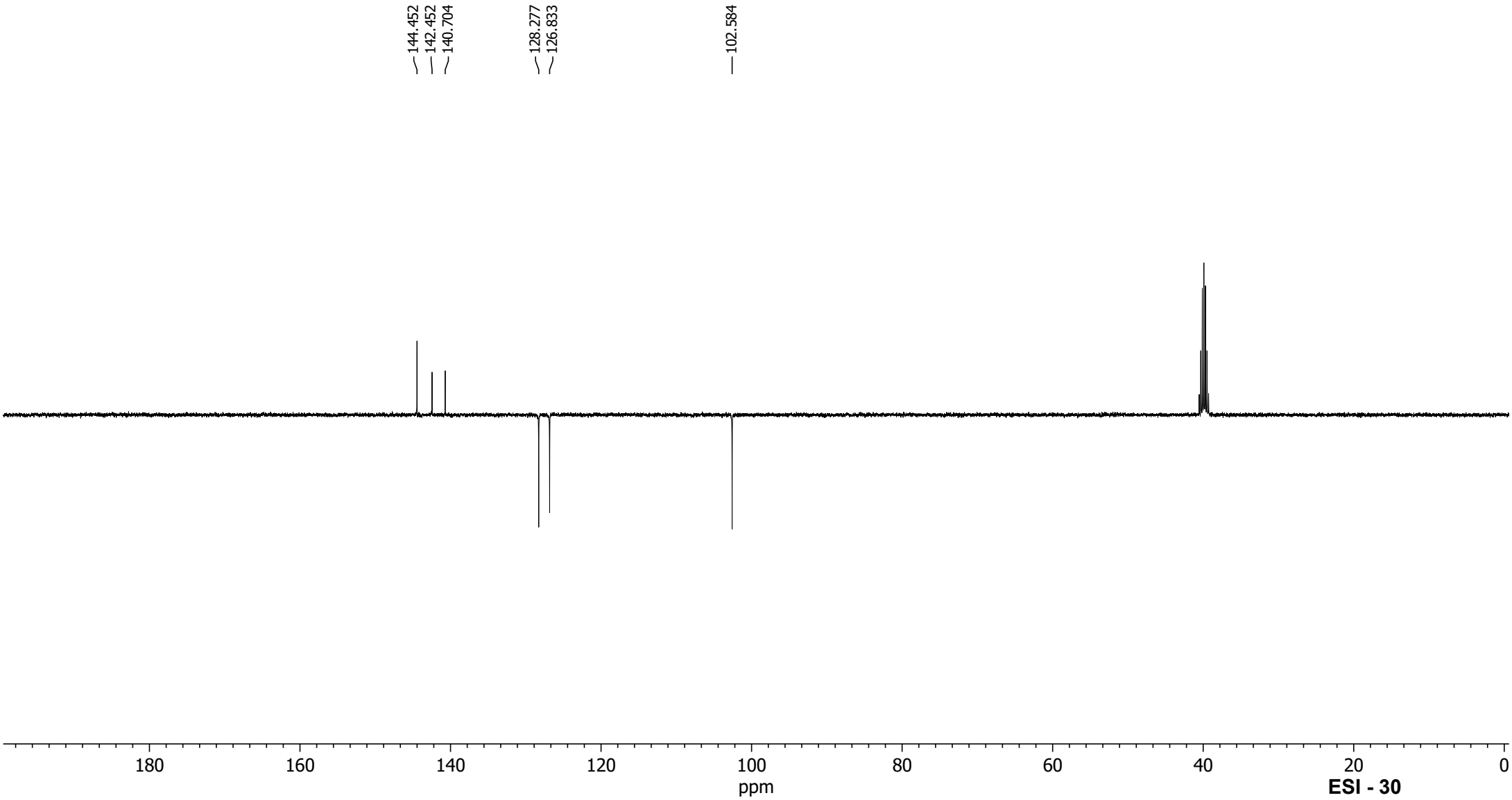


ESI - 29

phenazine-2,3-diamine (2j)

^{13}C-NMR (100 MHz)
DMSO-d_6

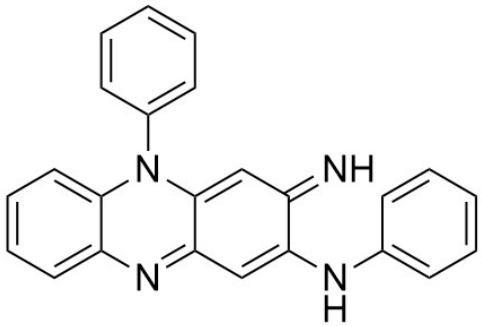


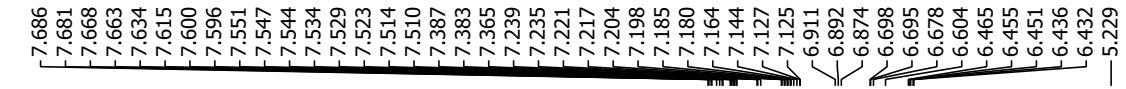


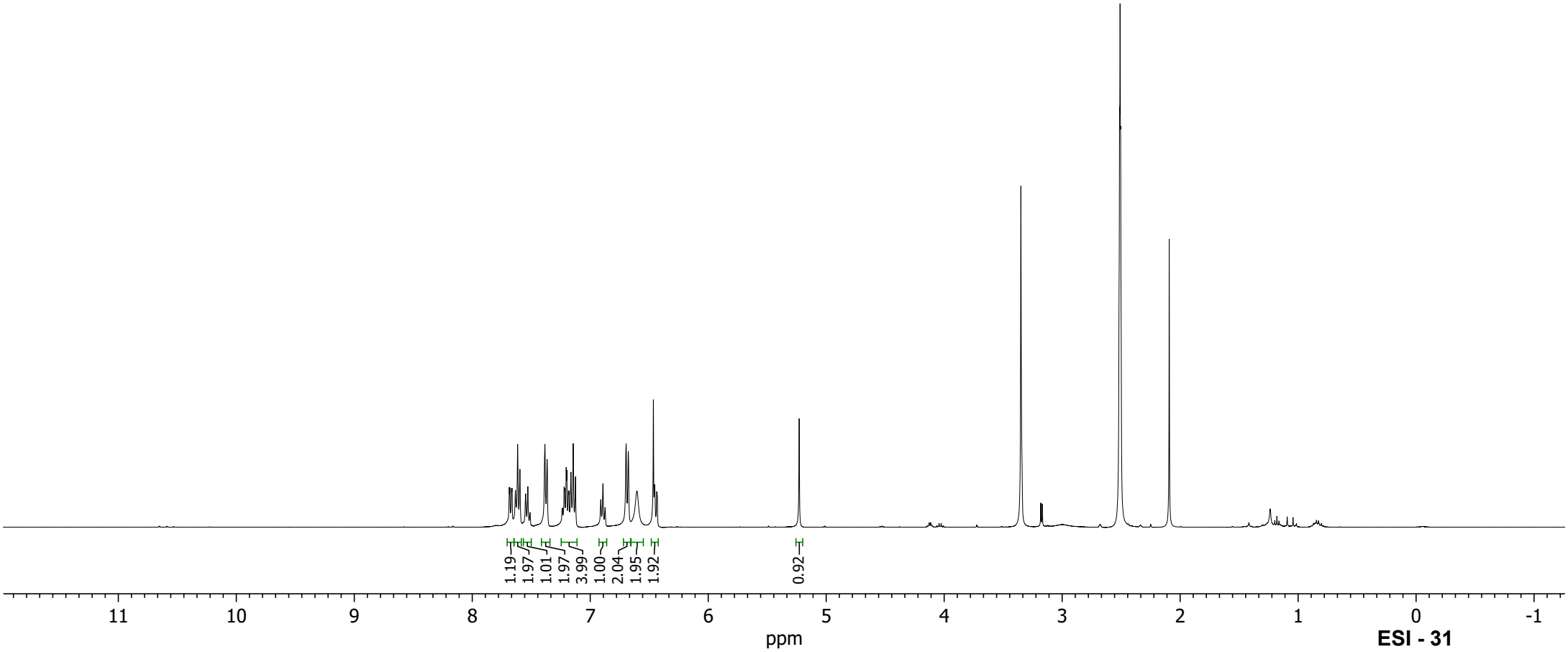
ESI - 30

3-imino-N,5-diphenyl-3,5-dihydrophenazin-2-amine (2k)

^{1}H-NMR (400 MHz)
DMSO-*d*6



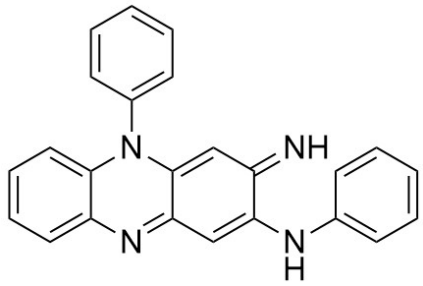


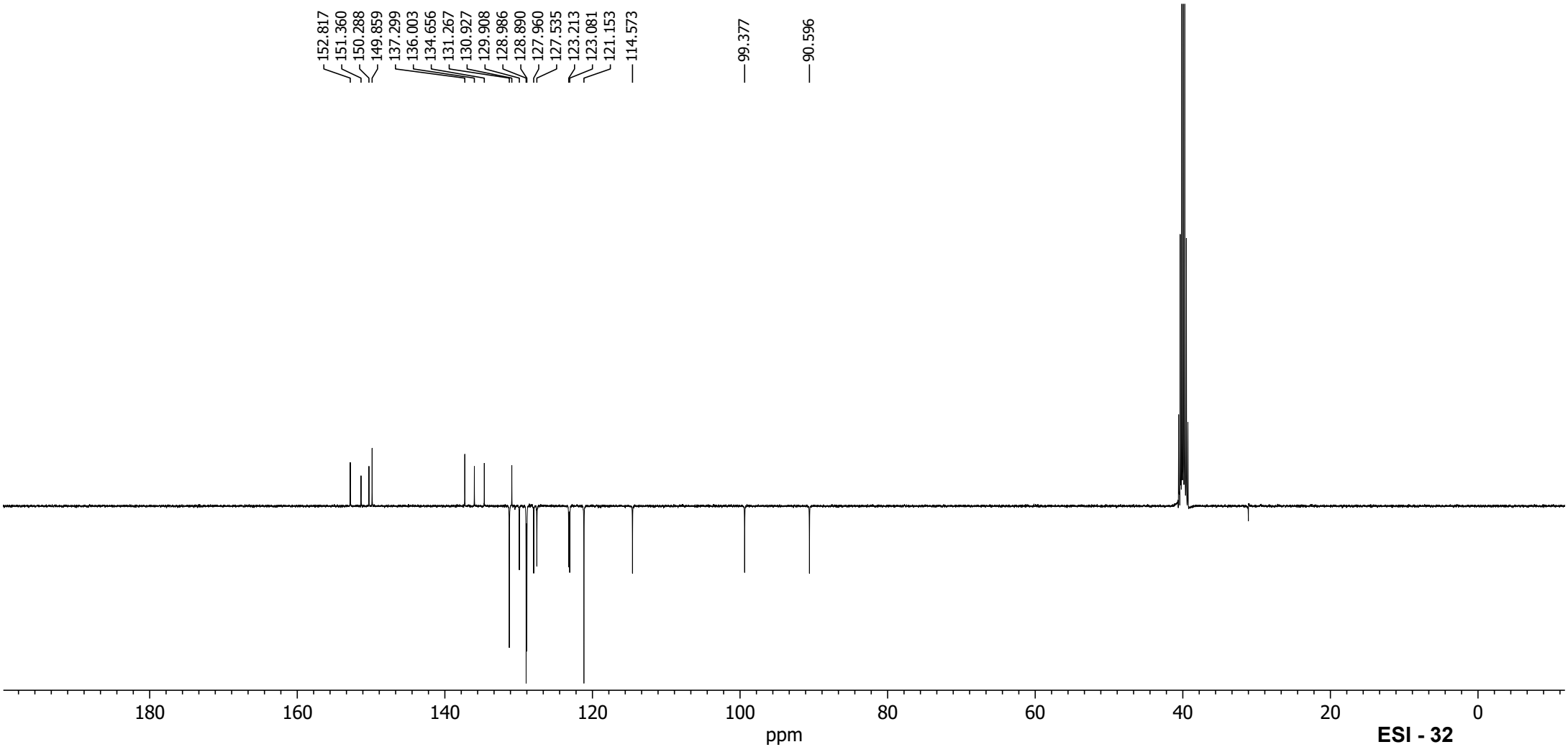


ESI - 31

3-imino-N,5-diphenyl-3,5-dihydrophenazin-2-amine (2k)

^{13}C-NMR (100 MHz)
DMSO-d_6

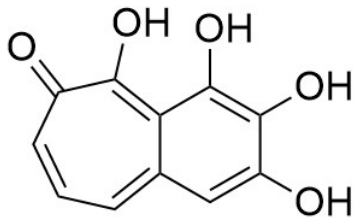


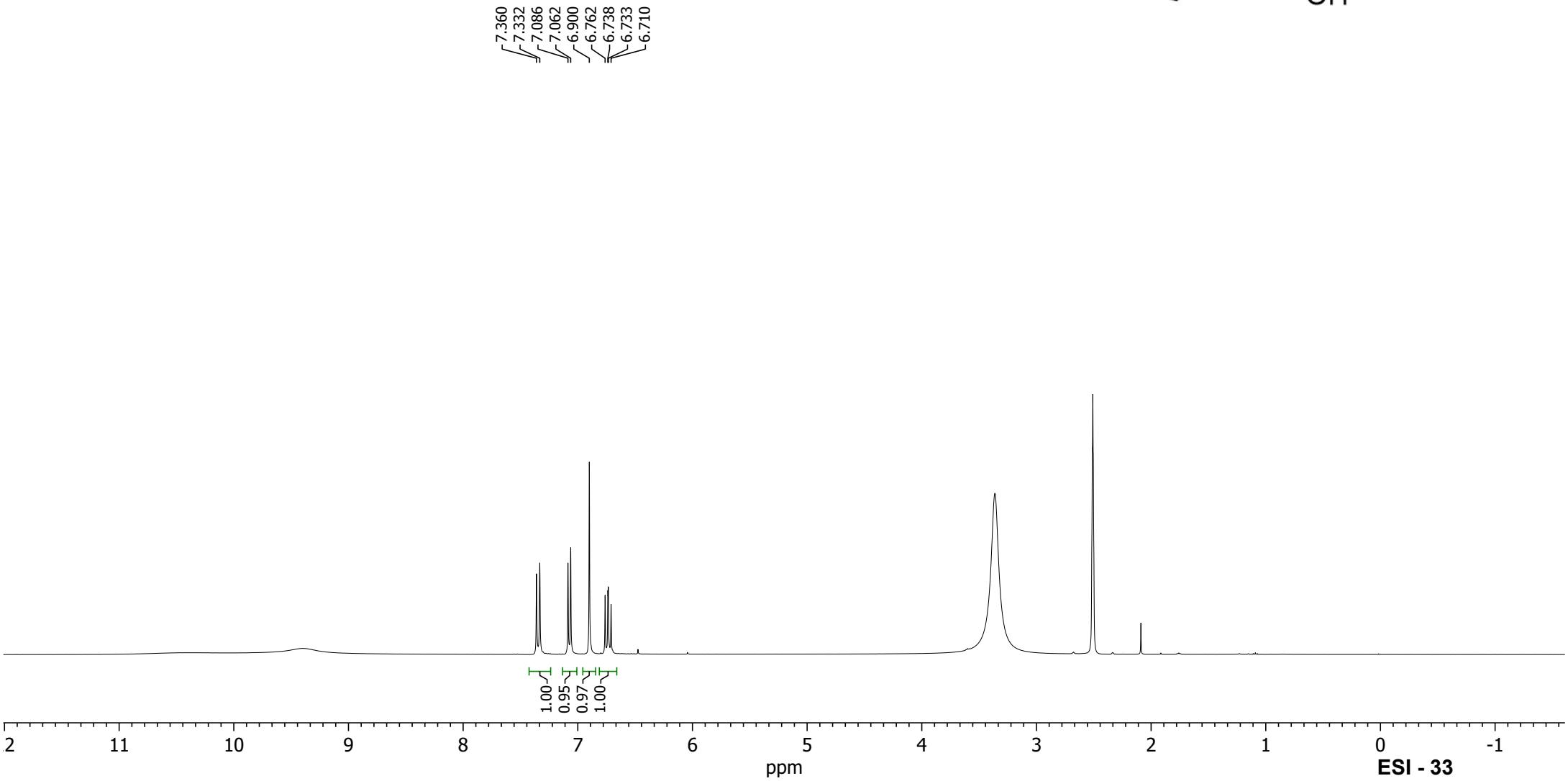


ESI - 32

2,3,4,5-tetrahydroxy-6H-benzo[7]annulen-6-one (2l)

^{1}H-NMR (400 MHz)
DMSO-d_6

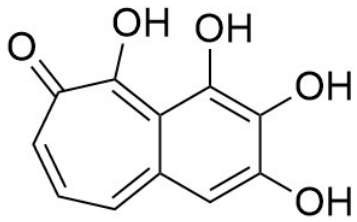




ESI - 33

2,3,4,5-tetrahydroxy-6H-benzo[7]annulen-6-one (2l)

^{13}C-NMR (100 MHz)
DMSO-d_6



182.651
155.091
152.168
151.950
135.111
134.714
133.400
123.979
116.915
115.252
110.642

240 220 200 180 160 140 120 100 80 60 40 20 0 -20 -40
ppm

ESI - 34