Electronic Supplementary Information

DABCO-mediated [3+3] cycloaddition of azomethine imines with *in situ* generated nitrile oxides from hydroximoyl chlorides

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Table of Contents

General methods Solvents were treated prior to use according to the standard methods. Other reagents were used as purchased without further purification. Reaction progress was monitored by thin-layer chromatography (TLC) on silica gel plates. Chromatographic purification was performed on silica gel columns (200-300 mesh size). Melting points were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz in $CDCl_3$ with chemical shift (δ) given in ppm relative to TMS as internal standard. Multiplicities were indicated, s (singlet), d (doublet), t (triplet), m (multiplet), dd (doublet of doublets), etc; coupling constant (*J*) were given in Hertz (Hz). High resolution mass spectra (HRMS) were recorded using electrospray ionization (ESI) and time-of-flight (TOF) mass analysis. The azomethine imines **1** and hydroximoyl chlorides **2** were prepared following the literature procedures.[1,2]

General procedure for the synthesis of product 3. To a solution of hydroximoyl chloride **2** (0.1 mmol) in chloroform (2.0 mL) was added DABCO (0.3 mmol) and azomethine imines **1** (0.15 mmol). The reaction mixture was stirred at 50 °C for 10 h. Upon completion of the reaction, water (5 mL) was added and the mixture was extracted with DCM (3 × 5 mL). The combined organic layers were dried and concentrated under reduced pressure followed by silica gel column chromatography purification (petroleum ether/ethyl acetate = 5:1-3:1) to a□ord the product **3**.

1,4-Diphenyl-7,8-dihydro-1H,6H-pyrazolo[1,2-d] [1,2,4,5] oxatriazin-6-one (**3a**). White solid (20 mg, 68% yield); mp 164-166 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.57 (m, 2H), 7.56-7.53 (m, 2H), 7.52-7.44 (m, 4H), 7.46-7.41 (m, 2H), 5.04 (s, 1H), 3.41 (ddd, *J* = 8.8, 5.2, 2.0

Hz, 1H), 2.98 (dt, *J* = 10.8, 9.2 Hz, 1H), 2.76-2.67 (m, 1H), 2.53 (ddd, *J* = 14.4, 8.8, 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 145.4, 132.9, 130.8, 130.4, 129.3, 129.0, 128.8, 128.6, 128.0, 95.1, 45.7, 29.6. HRMS (ESI) m/z calcd for $C_{17}H_{16}N_3O_2$ $[M + H]^+$ 294.1243; found 294.1262.

1-Phenyl-4-(o-tolyl)-7,8-dihydro-1H,6H-pyrazolo[1,2-d][1,2,4,5]oxatriazin-6-one (**3b**). White solid (18 mg, 57% yield); mp 179-180 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.55 (m, 2H), 7.50-7.40 (m, 5H), 7.28 (d, *J* = 8.0 Hz, 2H), 5.00 (s, 1H), 3.41 (ddd, *J* = 10.8, 8.8, 5.2 Hz, 1H), 2.98 (dt, *J* = 10.8, 9.2 Hz, 1H), 2.74-2.67 (m, 1H), 2.51 (ddd, *J* = 14.4, 8.8, 5.2 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 145.3, 141.0, 130.4, 130.0, 129.7, 129.3, 128.7, 128.6, 128.0, 95.1, 45.7, 29.7, 21.4. HRMS (ESI) m/z calcd for $C_{18}H_{18}N_3O_2$ $[M + H]^+$ 308.1399; found 308.1403.

1-Phenyl-4-(m-tolyl)-7,8-dihydro-1H,6H-pyrazolo[1,2-d][1,2,4,5]oxatriazin-6-one (**3c**). White solid (22 mg, 72% yield); mp 180-181 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.45 (m, 6H), 7.41-7.28 (m, 3H), 5.03 (s, 1H), 3.41 (ddd, *J* = 11.2, 9.2, 5.6 Hz, 1H), 2.98 (dt, *J* = 10.8, 9.2 Hz, 1H), 2.75-2.66 (m, 1H), 2.52 (ddd, *J* = 14.0, 8.8, 5.2 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 145.3, 141.0, 130.4, 130.0, 129.7, 129.3, 128.7, 128.6, 128.0, 95.1, 45.7, 29.7, 21.4. HRMS (ESI) m/z calcd for $C_{18}H_{18}N_3O_2$ $[M + H]^+$ 308.1399; found 308.1416.

1-Phenyl-4-(p-tolyl)-7,8-dihydro-1H,6H-pyrazolo[1,2-d][1,2,4,5]oxatriazin-6-one (**3d**). White solid (24 mg, 78% yield); mp 181-182 ºC^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.45 (m, 7H), 7.24 (d, *J* = 8.0 Hz, 2H), 5.02 (s, 1H), 3.39 (ddd, *J* = 10.8, 9.2, 5.2 Hz, 1H), 2.97 (dt, *J* = 10.8, 9.2 Hz, 1H), 2.73-2.65 (m, 1H), 2.51 (ddd, *J* = 14.4, 8.8, 5.6 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR

(100 MHz, $CDCl_3$) δ 168.3, 145.4, 140.6, 133.0, 130.8, 129.0, 128.8, 128.8, 128.4, 126.3, 95.1, 45.6, 29.7, 21.5. HRMS (ESI) m/z calcd for $C_{18}H_{17}N_3NaO_2$ $[M + Na]^+$ 330.1218; found 330.1242.

4-(4-Methoxyphenyl)-1-phenyl-7,8-dihydro-1H,6H-pyrazolo[1,2-d][1,2,4,5]oxatriazin-6-one (**3e**). White solid (27 mg, 82% yield); mp 171-172 ºC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.53-7.44 (m, 7H), 6.97-6.92 (m, 2H), 5.03 (s, 1H), 3.84 (s, 3H), 3.45-3.37 (m, 1H), 3.03-2.95 (m, 1H), 2.73-2.64 (m, 1H), 2.57-2.48 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 161.4, 145.1, 133.1, 132.9, 130.9, 130.8, 130.4, 130.0, 129.0, 129.0, 128.8, 121.5, 113.5, 95.0, 55.3, 45.4, 29.6. HRMS (ESI) m/z calcd for $C_{18}H_{18}N_3O_3$ $[M + H]^+$ 324.1348; found 324.1360.

4-(4-(Methylthio)phenyl)-1-phenyl-7,8-dihydro-1H,6H-pyrazolo[1,2-d][1,2,4,5]oxatriazin-6-one (**3f**). (26 mg, 76% yield); mp 175-176 ºC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.4 Hz, 2H), 7.50-7.40 (m, 5H), 7.33 (d, J = 8.4 Hz, 2H), 4.99 (s, 1H), 3.45-3.37 (m, 1H), 3.41 (ddd, J = 10.8, 9.2, 5.2 Hz, 1H), 3.03-2.93 (m, 1H), 2.75-2.66 (m, 1H), 2.54-2.48 (m, 1H), 2.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 145.3, 142.3, 130.4, 129.2, 129.1, 128.6, 128.0, 126.3, 94.8, 45.7, 29.6, 15.3. HRMS (ESI) m/z calcd for $C_{18}H_{18}N_3O_2S$ $[M + H]^+$ 340.1120; found 340.1116.

4-([1,1'-Biphenyl]-4-yl)-1-phenyl-7,8-dihydro-1H,6H-pyrazolo[1,2-d][1,2,4,5]oxatriazin-6-one (**3g**). White solid (21 mg, 57% yield); mp 174-175 ºC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.66-7.61 (m, 6H), 7.56-7.43 (m, 7H), 7.38 (t, J = 7.2 Hz, 1H), 5.07 (s, 1H), 3.44 (ddd, J = 10.8, 9.2, 5.6 Hz, 1H), 3.02 (dt, J = 11.2, 8.8 Hz, 1H), 2.77-2.68 (m, 1H), 2.55 (ddd, J = 14.8, 9.2, 6.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 145.2, 143.2, 140.4, 133.0, 130.8, 129.0, 129.0, 128.8, 128.8, 128.1, 127.7, 127.3, 126.8, 95.1, 45.6, 29.6. HRMS (ESI) m/z

calcd for $C_{23}H_{19}N_3NaO_2$ $[M + Na]^+$ 392.1375; found 392.1398.

4-(4-Bromophenyl)-1-phenyl-7,8-dihydro-1H,6H-pyrazolo[1,2-d][1,2,4,5]oxatriazin-6-one (**3h**). White solid (29 mg, 79% yield); mp 191-193 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.43 (m, 9H), 5.01 (s, 1H), 3.41 (ddd, *J* = 11.2, 9.2, 5.6 Hz, 1H), 2.99 (dt, *J* = 11.2, 8.8 Hz, 1H), 2.73-2.65 (m, 1H), 2.52 (ddd, *J* = 14.8, 8.8, 5.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 144.5, 132.7, 131.3, 131.0, 130.1, 129.1, 128.8, 128.2, 125.0, 95.1, 45.6, 29.5. HRMS (ESI) m/z calcd for $C_{17}H_{15}BrN_3O_2$ $[M + H]^+$ 372.0348; found 372.0378.

4-(3-Bromophenyl)-1-phenyl-7,8-dihydro-1H,6H-pyrazolo[1,2-d][1,2,4,5]oxatriazin-6-one (**3i**). White solid (30 mg, 80% yield); mp 192-194 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (t, *J* = 2.0 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.53-7.45 (m, 6H), 7.30 (t, *J* = 7.6 Hz, 1H), 5.01 (s, 1H), 3.41 (ddd, *J* = 10.8, 8.8, 5.6 Hz, 1H), 2.99 (dt, *J* = 10.8, 9.2 Hz, 1H), 2.74-2.65 (m, 1H), 2.52 (ddd, *J* = 14.4, 8.8, 5.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 144.1, 133.4, 132.6, 131.5, 131.2, 131.0, 129.5, 129.1, 128.8, 127.2, 122.0, 95.1, 45.7, 29.5. HRMS (ESI) m/z calcd for $C_{17}H_{14}BrN_3NaO_2$ $[M + Na]^+$ 394.0167; found 394.0185.

4-(3-Chlorophenyl)-1-phenyl-7,8-dihydro-1H,6H-pyrazolo[1,2-d][1,2,4,5]oxatriazin-6-one (**3j**). White solid (25 mg, 76% yield); mp 173-175 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (t, *J* = 2.0 Hz, 1H), 7.53-7.43 (m, 7H), 7.35 (t, *J* = 7.6 Hz, 1H), 5.01 (s, 1H), 3.41 (ddd, *J* = 10.8, 9.2, 5.6 Hz, 1H), 2.98 (dt, *J* = 10.4, 9.6 Hz, 1H), 2.74-2.65 (m, 1H), 2.52 (ddd, *J* = 14.8, 8.8, 5.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 144.2, 134.0, 132.6, 131.0, 130.9, 130.5, 129.2, 129.0, 128.8, 128.7, 126.8, 95.0, 45.6, 29.4. HRMS (ESI) m/z calcd for $C_{17}H_{14}ClN_3NaO_2$ $[M + Na]^+$ 350.0672; found 350.0685.

1-Phenyl-4-(4-(trifluoromethyl)phenyl)-7,8-dihydro-1H,6H-pyrazolo[1,2-

d][1,2,4,5]oxatriazin-6-one (**3k**). White solid (33 mg, 91% yield); mp 168-169 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 11.2, 8.4 Hz, 4H), 7.54-7.45 (m, 5H), 5.04 (s, 1H), 3.44 (ddd, *J* = 10.8, 8.8, 5.6 Hz, 1H), 3.01 (dt, *J* = 11.2, 8.8 Hz, 1H), 2.75-2.67 (m, 1H), 2.54 (ddd, *J* = 14.4, 8.8, 5.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 144.3, 132.8 (*J* = 1.4 Hz), 132.6, 132.2 (*J* = 32.4 Hz), 131.0, 129.1, 129.0, 128.9, 125.0 (*J* = 3.7 Hz), 123.9 (*J* = 271.1 Hz), 95.2, 45.7, 29.4. HRMS (ESI) m/z calcd for $C_{18}H_{15}F_3N_3O_2$ $[M + H]^+$ 362.1116; found 362.1108.

4-(4-Nitrophenyl)-1-phenyl-7,8-dihydro-1H,6H-pyrazolo[1,2-d][1,2,4,5]oxatriazin-6-one (**3l**). Yellow solid (26 mg, 78% yield); mp 184-185 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.8 Hz, 2H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.55-7.47 (m, 5H), 5.06 (s, 1H), 3.43 (ddd, *J* = 11.2, 9.2, 6.0 Hz, 1H), 3.06 (dt, *J* = 10.8, 9.2 Hz, 1H), 2.78-2.69 (m, 1H), 2.57 (ddd, *J* = 15.2, 9.2, 6.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 149.0, 143.7, 135.4, 132.4, 131.1, 129.6, 129.1, 128.8, 123.2, 95.2, 45.7, 29.3. HRMS (ESI) m/z calcd for $C_{17}H_{14}N_4NaO_4$ $[M + Na]^+$ 361.0913; found 361.0915.

4-(3,4-Dichlorophenyl)-1-phenyl-7,8-dihydro-1H,6H-pyrazolo[1,2-d][1,2,4,5]oxatriazin-6-one (**3m**). White solid (29 mg, 81% yield); mp 147-149 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 2.0 Hz, 1H), 7.54-7.45 (m, 6H), 7.41 (dd, *J* = 8.3, 2.1 Hz, 1H), 5.01 (s, 1H), 3.44 (ddd, *J* = 10.8, 8.8, 6.0 Hz, 1H), 3.01 (dt, *J* = 11.2, 8.8 Hz, 1H), 2.75-2.66 (m, 1H), 2.54 (ddd, *J* = 14.8, 8.8, 5.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 143.5, 134.8, 132.5, 132.5, 131.0, 130.4, 130.0, 129.2, 129.1, 128.8, 127.8, 95.1, 45.6, 29.4. HRMS (ESI) m/z calcd for $C_{17}H_{14}Cl_2N_3O_2$ $[M + H]^+$ 362.0463; found 362.0449.

4-(2,3-Dichlorophenyl)-1-phenyl-7,8-dihydro-1H,6H-pyrazolo[1,2-d][1,2,4,5]oxatriazin-6-

one (**3n**). White solid (20 mg, 55% yield); mp 165-166 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.53 (m, 3H), 7.52-7.45 (m, 3H), 7.39 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.29 (dd, *J* = 15.3, 7.5 Hz, 1H), 4.95 (s, 1H), 3.27-3.23 (m, 1H), 2.86-2.68 (m, 2H), 2.49-2.43 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 142.5, 133.1, 132.6, 132.2, 132.1, 131.0, 131.0, 129.2, 129.0, 129.0, 127.4, 95.3, 47.4, 30.1. HRMS (ESI) m/z calcd for $C_{17}H_{14}Cl_2N_3O_2$ $[M + H]^+$ 362.0463; found 362.0438.

1-(2-Chlorophenyl)-4-phenyl-7,8-dihydro-1H,6H-pyrazolo[1,2-d][1,2,4,5]oxatriazin-6-one (**3ba**). White solid (16 mg, 49% yield); mp 157-159 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.64 (m, 1H), 7.62-7.59 (m, 2H), 7.50-7.39 (m, 6H), 5.67 (s, 1H), 3.51-3.44 (m, 1H), 3.17-3.10 (m, 1H), 2.72-2.56 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 145.4, 134.3, 131.6, 130.8, 130.7, 130.6, 129.5, 129.3, 128.4, 128.1, 127.9, 89.9, 44.8, 29.7. HRMS (ESI) m/z calcd for $C_{17}H_{14}ClN_3NaO_2$ $[M + Na]^+$ 350.0672; found 350.0693.

1-(3-Chlorophenyl)-4-phenyl-7,8-dihydro-1H,6H-pyrazolo[1,2-d][1,2,4,5]oxatriazin-6-one (**3ca**). White solid (18 mg, 55% yield); mp 159-161 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.54 (m, 3H), 7.51-7.45 (m, 2H), 7.44-7.38 (m, 4H), 4.99 (s, 1H), 3.42 (ddd, *J* = 10.8, 9.2, 5.2 Hz, 1H), 2.96 (dt, *J* = 10.8, 9.2 Hz, 1H), 2.75-2.66 (m, 1H), 2.52 (ddd, *J* = 14.0, 8.8, 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 145.5, 135.0, 134.8, 131.0, 130.5, 130.3, 129.0, 128.9, 128.6, 128.0, 127.0, 94.1, 45.7, 29.5. HRMS (ESI) m/z calcd for $C_{17}H_{14}ClN_3NaO_2$ $[M + Na]^+$ 350.0672; found 350.0693.

1-(4-Chlorophenyl)-4-phenyl-7,8-dihydro-1H,6H-pyrazolo[1,2-d][1,2,4,5]oxatriazin-6-one (**3da**). White solid (20 mg, 60% yield); mp 158-159 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.55 (m, 2H), 7.51-7.45 (m, 4H), 7.44-7.40 (m, 2H), 7.38-7.34 (m, 1H), 4.95 (s, 1H), 3.27-

3.23 (m, 1H), 2.86-2.68 (m, 2H), 2.50-2.44 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 143.0, 134.1, 132.4, 131.4, 131.0, 131.0, 129.2, 129.0, 128.8, 128.7, 126.8, 95.3, 47.4, 30.2. HRMS (ESI) m/z calcd for $C_{17}H_{14}ClN_3NaO_2$ $[M + Na]^+$ 350.0672; found 350.0693.

1-(2-Bromophenyl)-4-phenyl-7,8-dihydro-1H,6H-pyrazolo[1,2-d][1,2,4,5]oxatriazin-6-one (**3ea**). White solid (17 mg, 47% yield); mp 165-167 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 7.6 Hz, 2H), 7.51-7.41 (m, 4H), 7.35 (td, *J* = 8.0, 2.0 Hz, 1H), 5.65 (s, 1H), 3.49 (dt, *J* = 11.2, 8.0 Hz, 1H), 3.21-3.14 (m, 1H), 2.75-2.61 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 145.4, 132.8, 132.5, 131.9, 131.1, 130.6, 129.3, 128.5, 128.4, 128.1, 124.3, 92.4, 44.7, 29.8. HRMS (ESI) m/z calcd for $C_{17}H_{14}BrN_3NaO_2$ $[M + Na]^+$ 394.0167; found 394.0160.

1-(4-Bromophenyl)-4-phenyl-7,8-dihydro-1H,6H-pyrazolo[1,2-d][1,2,4,5]oxatriazin-6-one (**3fa**). White solid (20 mg, 54% yield); mp 165-167 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.51-7.46 (m, 1H), 7.45-7.41 (m, 4H), 5.00 (s, 1H), 3.41 (ddd, *J* = 10.8, 9.2, 5.2 Hz, 1H), 2.95 (dt, *J* = 11.2, 8.8 Hz, 1H), 2.76-2.67 (m, 1H), 2.53 (ddd, *J* = 14.0, 8.8, 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 145.5, 132.3, 132.0, 130.5, 130.4, 129.1, 128.6, 128.1, 125.3, 94.3, 45.7, 29.6. HRMS (ESI) m/z calcd for $C_{17}H_{14}BrN_3NaO_2$ $[M + Na]^+$ 394.0167; found 394.0186.

1-(4-Fluorophenyl)-4-phenyl-7,8-dihydro-1H,6H-pyrazolo[1,2-d][1,2,4,5]oxatriazin-6-one (**3ga**). White solid (17 mg, 55% yield); mp 150-152 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.40 (m, 7H), 7.17 (t, *J* = 8.4 Hz, 2H), 5.02 (s, 1H), 3.40 (ddd, *J* = 10.8, 9.2, 5.2 Hz, 1H), 2.95 (dt, *J* = 10.8, 9.2 Hz, 1H), 2.76-2.67 (m, 1H), 2.52 (ddd, *J* = 14.0, 8.8, 4.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 164.2 (*J* = 248.6 Hz), 145.4, 130.8 (*J* = 8.8 Hz), 130.5, 129.1,

128.9 (*J* = 2.9 Hz), 128.6, 128.0, 116.2 (*J* = 21.9 Hz), 94.3, 45.7, 29.6. HRMS (ESI) m/z calcd for $C_{17}H_{14}FN_3NaO_2$ $[M + Na]^+$ 334.0968; found 334.1003.

4-Phenyl-1-(4-(trifluoromethyl)phenyl)-7,8-dihydro-1H,6H-pyrazolo[1,2-d][1,2,4,5]oxatriazin-6-one (**3ha**). White solid (22 mg, 62% yield); mp 148-150 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.58-7.55 (m, 2H), 7.52-7.41 (m, 3H), 5.09 (s, 1H), 3.42 (ddd, *J* = 10.8, 8.8, 5.2 Hz, 1H), 2.96 (dt, *J* = 10.8, 9.2 Hz, 1H), 2.78-2.69 (m, 1H), 2.54 (ddd, *J* = 14.0, 8.8, 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 145.6, 136.7, 132.9 (*J* = 32.7 Hz), 130.6, 129.4, 129.0, 128.6, 128.1, 126.0 (*J* = 3.6 Hz), 123.7 (*J* = 271.5 Hz), 94.1, 45.7, 29.5. HRMS (ESI) m/z calcd for $C_{18}H_{14}F_3N_3NaO_2$ $[M + Na]^+$ 384.0936; found 384.0967.

4-Phenyl-1-(p-tolyl)-7,8-dihydro-1H,6H-pyrazolo[1,2-d][1,2,4,5]oxatriazin-6-one (**3ia**). White solid (14 mg, 47% yield); mp 159-160 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.6 Hz, 2H), 7.49-7.40 (m, 5H), 7.30 (d, *J* = 7.6 Hz, 2H), 5.00 (s, 1H), 3.41 (ddd, *J* = 10.8, 9.2, 5.2 Hz, 1H), 2.98 (dt, *J* = 11.2, 8.8 Hz, 1H), 2.74-2.65 (m, 1H), 2.51 (ddd, *J* = 14.0, 8.8, 5.2 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 145.3, 141.0, 130.4, 130.0, 129.7, 129.3, 128.7, 128.6, 128.0, 95.1, 45.7, 29.7, 21.4. HRMS (ESI) m/z calcd for $C_{18}H_{18}N_3O_2$ $[M + H]^+$ 308.1399; found 308.1403.

1-(4-Methoxyphenyl)-4-phenyl-7,8-dihydro-1H,6H-pyrazolo[1,2-d][1,2,4,5]oxatriazin-6-one (**3ja**). White solid (18 mg, 55% yield); mp 151-153 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.50-7.40 (m, 5H), 6.98 (d, *J* = 8.8 Hz, 2H), 4.99 (s, 1H), 3.85 (s, 3H), 3.40 (ddd, *J* = 10.8, 9.2, 5.2 Hz, 1H), 2.97 (dt, *J* = 10.8, 9.2 Hz, 1H), 2.74-2.65 (m, 1H), 2.51 (ddd, *J* = 14.0, 8.8, 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 161.5, 145.2, 130.4, 130.1,

129.3, 128.6, 128.0, 125.0, 114.4, 94.8, 55.4, 45.7, 29.7. HRMS (ESI) m/z calcd for $C_{18}H_{18}N_3O_3$ $[M + H]^+$ 324.1348; found 324.1370.

4-Phenyl-1-(thiophen-2-yl)-7,8-dihydro-1H,6H-pyrazolo[1,2-d][1,2,4,5]oxatriazin-6-one (**3ka**). White solid (16 mg, 53% yield); mp 176-178 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.54 (m, 3H), 7.50-7.46 (m, 1H), 7.44-7.40 (m, 2H), 7.34 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.11 (dd, *J* = 5.2, 3.6 Hz, 1H), 5.10 (s, 1H), 3.55 (ddd, *J* = 10.8, 9.2, 5.2 Hz, 1H), 3.08 (dt, *J* = 11.2, 9.2 Hz, 1H), 2.78-2.68 (m, 1H), 2.54 (ddd, *J* = 14.4, 9.2, 5.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 145.4, 134.7, 130.5, 129.4, 129.3, 129.0, 128.6, 128.0, 126.9, 90.6, 45.9, 29.5. HRMS (ESI) m/z calcd for $C_{15}H_{13}N_3NaO_2S$ $[M + Na]^+$ 322.0626; found 322.0629.

1-Butyl-4-phenyl-7,8-dihydro-1H,6H-pyrazolo[1,2-d][1,2,4,5]oxatriazin-6-one (**3la**). White solid (14 mg, 52% yield); mp 147-149 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.43 (m, 3H), 7.44-7.37 (m, 2H), 4.20 (dd, *J* = 6.8, 2.8 Hz, 1H), 3.73 (td, *J* = 9.6, 3.6 Hz, 1H), 3.07-2.30 (m, 1H), 2.73 (ddd, *J* = 16.8, 11.2, 9.2 Hz, 1H), 2.54 (ddd, *J* = 12.0, 8.4, 3.6 Hz, 1H), 1.93-1.84 (m, 1H), 1.82-1.73 (m, 1H), 1.70-1.49 (m, 2H), 1.47-1.36 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 145.5, 130.2, 129.2, 128.6, 127.9, 93.4, 46.1, 30.3, 29.6, 25.4, 22.7, 13.9. HRMS (ESI) m/z calcd for $C_{15}H_{20}N_3O_2$ $[M + H]^+$ 274.1556; found 274.1579.

1-(4-Bromophenyl)-4-(4-methoxyphenyl)-7,8-dihydro-1H,6H-pyrazolo[1,2-d][1,2,4,5]oxatriazin-6-one (**3fe**). White solid (18 mg, 46% yield); mp 170-172 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 4.99 (s, 1H), 3.84 (s, 3H), 3.46-3.37 (m, 1H), 3.01-2.92 (m, 1H), 2.76-2.66 (m, 1H), 2.57-2.49 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 161.4, 145.2, 132.3, 132.3, 132.1, 130.4, 130.1, 128.3, 125.2, 121.3, 113.6, 94.2, 55.3, 45.4, 29.6. HRMS

(ESI) m/z calcd for $C_{18}H_{17}BrN_3O_3$ $[M + H]^+$ 402.0453; found 402.0473.

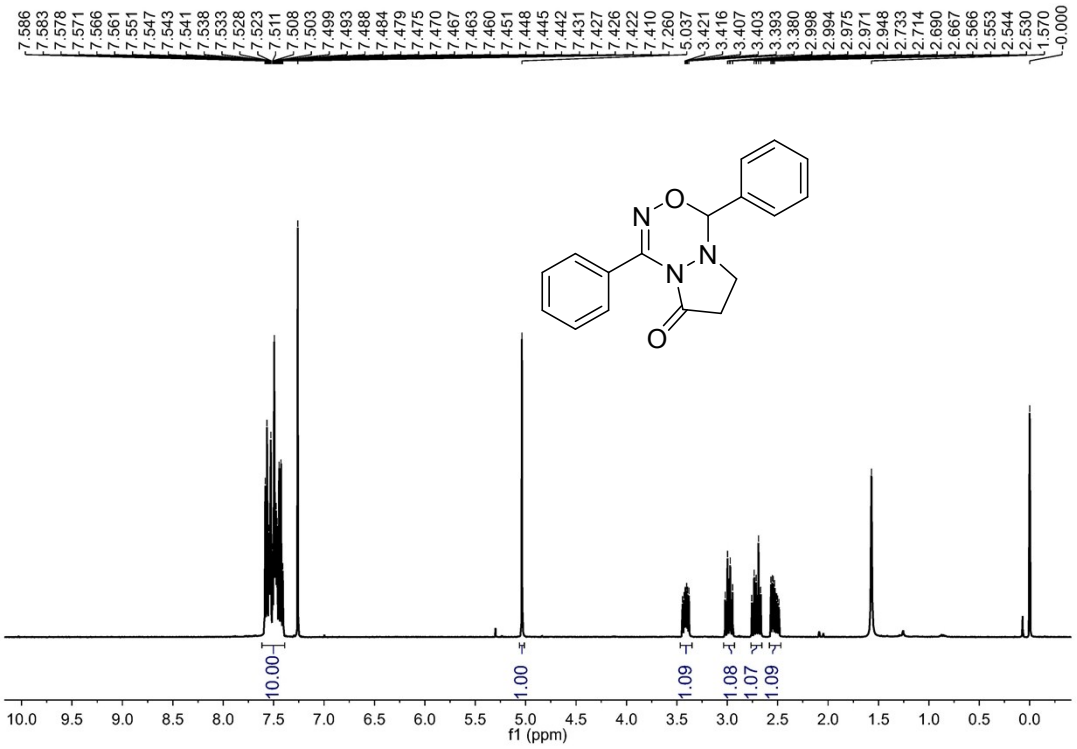
1-(4-Bromophenyl)-4-(4-(trifluoromethyl)phenyl)-7,8-dihydro-1H,6H-pyrazolo[1,2-d][1,2,4,5]oxatriazin-6-one (**3fk**). White solid (25 mg, 58% yield); mp 191-192 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 4H), 7.64 (*J* = 8.4 Hz, 2H), 7.41 (*J* = 8.4 Hz, 2H), 5.01 (s, 1H), 3.45 (ddd, *J* = 10.8, 9.2, 5.2 Hz, 1H), 3.00 (dt, *J* = 10.8, 9.2 Hz, 1H), 2.78-2.69 (m, 1H), 2.55 (ddd, *J* = 14.8, 9.2, 5.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 146.0, 144.4, 142.9, 133.2 (*J* = 30.8 Hz), 132.4, 131.6, 130.4, 129.0, 125.0 (*J* = 3.7 Hz), 124.0 (*J* = 271.1 Hz), 94.4, 45.8, 29.4. HRMS (ESI) m/z calcd for $C_{18}H_{14}BrF_3N_3O_2$ $[M + H]^+$ 440.0221; found 440.0244.

Procedure for the synthesis of 4. To a solution of **3fa** (37 mg, 0.10 mmol) in THF/H_2O (2 mL, 9:1) was added $Pd(PPh_3)_4$ (11 mg, 0.01 mmol), phenylboronic acid (25 mg, 0.20 mmol), and Na_2CO_3 (16 mg, 0.15 mmol). The resulting mixture was stirred at 80 °C for 10 h under N_2. Upon completion of the reaction, water (5 mL) was added and the mixture was extracted with DCM (3 × 5 mL). The combined organic layers were dried and concentrated under reduced pressure followed by silica gel column chromatography purification (petroleum ether/ethyl acetate = 5:1) to give the coupling product **4** (21 mg, 58% yield) as a white solid; mp 150-152 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.61-7.56 (m, 6H), 7.48-7.36 (m, 6H), 5.04 (s, 1H), 3.41 (ddd, *J* = 10.8, 8.8, 5.2 Hz, 1H), 2.98 (dt, *J* = 11.2, 8.8 Hz, 1H), 2.71-2.62 (m, 1H), 2.49 (ddd, *J* = 14.4, 9.2, 5.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 145.3, 143.6, 140.1, 131.7, 130.4, 129.3, 129.2, 128.9, 128.5, 128.0, 127.9, 127.7, 127.2, 94.8, 45.7, 29.6. HRMS (ESI) m/z calcd for $C_{23}H_{19}N_3NaO_2$ $[M + Na]^+$ 392.1375; found 392.1394.

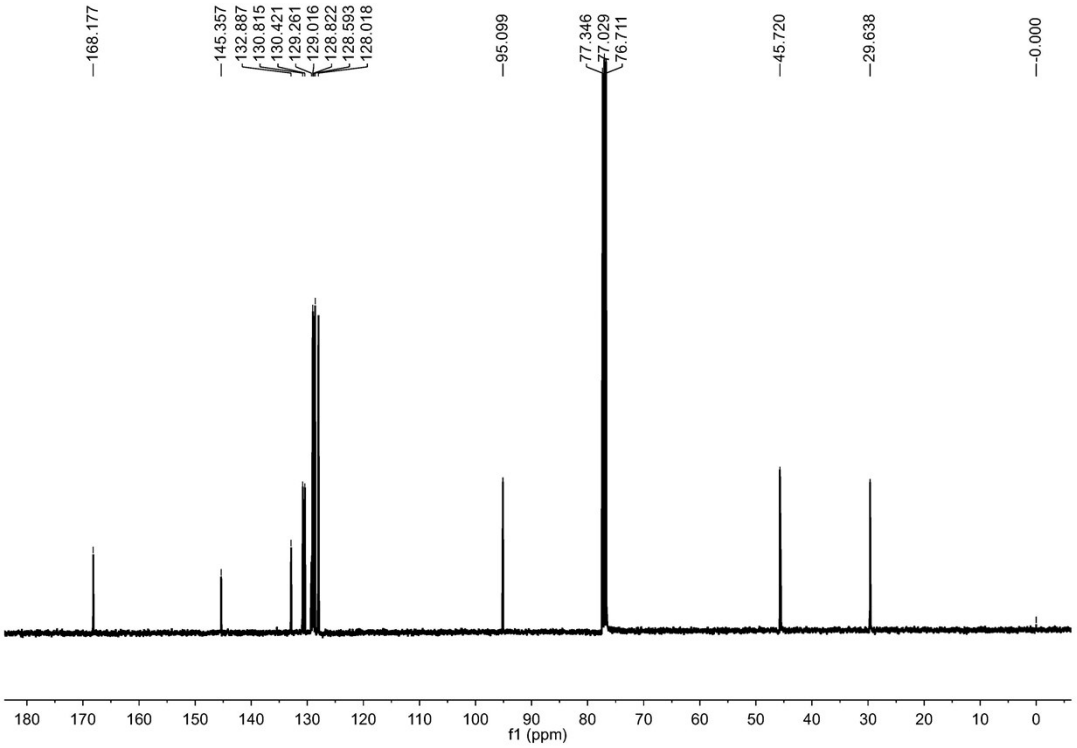
References

1. (a) R. Na, C. Jing, Q. Xu, H. Jiang, X. Wu, J. Shi, J. Zhong, M. Wang, D. Benitez and E. Tkatchouk, *J. Am. Chem. Soc.*, 2011, **133**, 13337; (b) S. E. Winterton, and J. M. Ready, *Org. Lett.*, 2016, **18**, 2608.

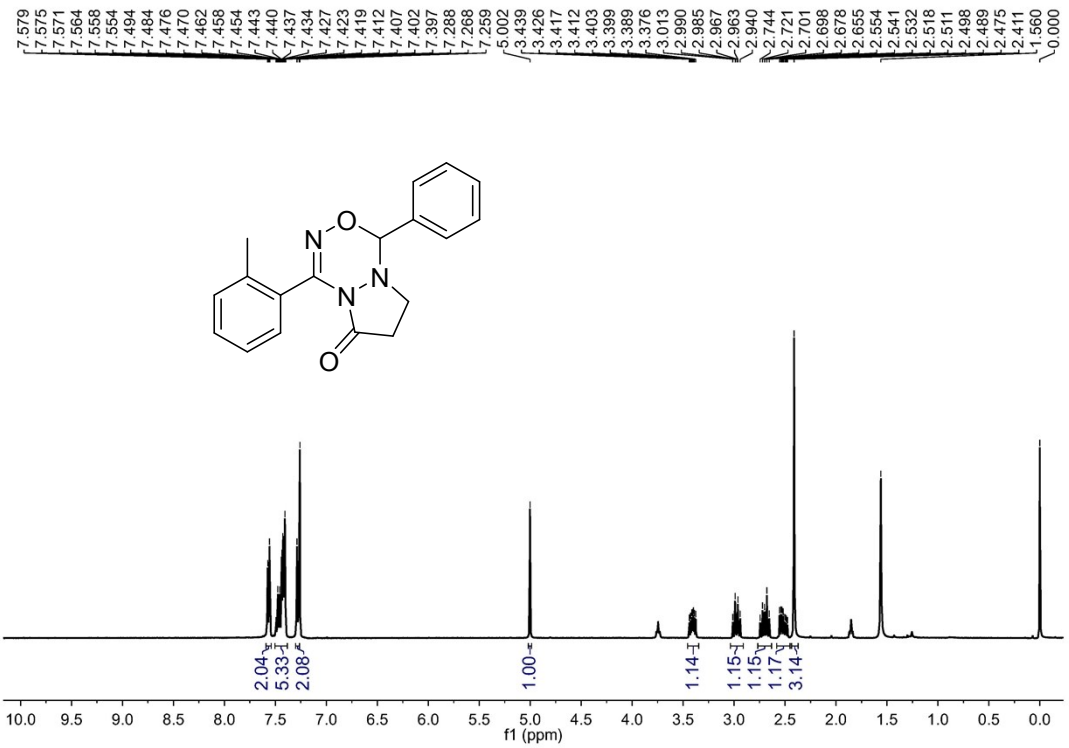
2. (a) L. Jiang, T. Gao, Z. Li, S. Sun, C. Kim, C. Huang, H. Guo, J. Wang and Y. Xing, *Tetrahedron Lett.*, 2016, **57**, 712; (b) L. F. Minuti, M. G. Memeo, S. Crespi and P. Quadrelli, *Eur. J. Org. Chem.*, 2016, 821.



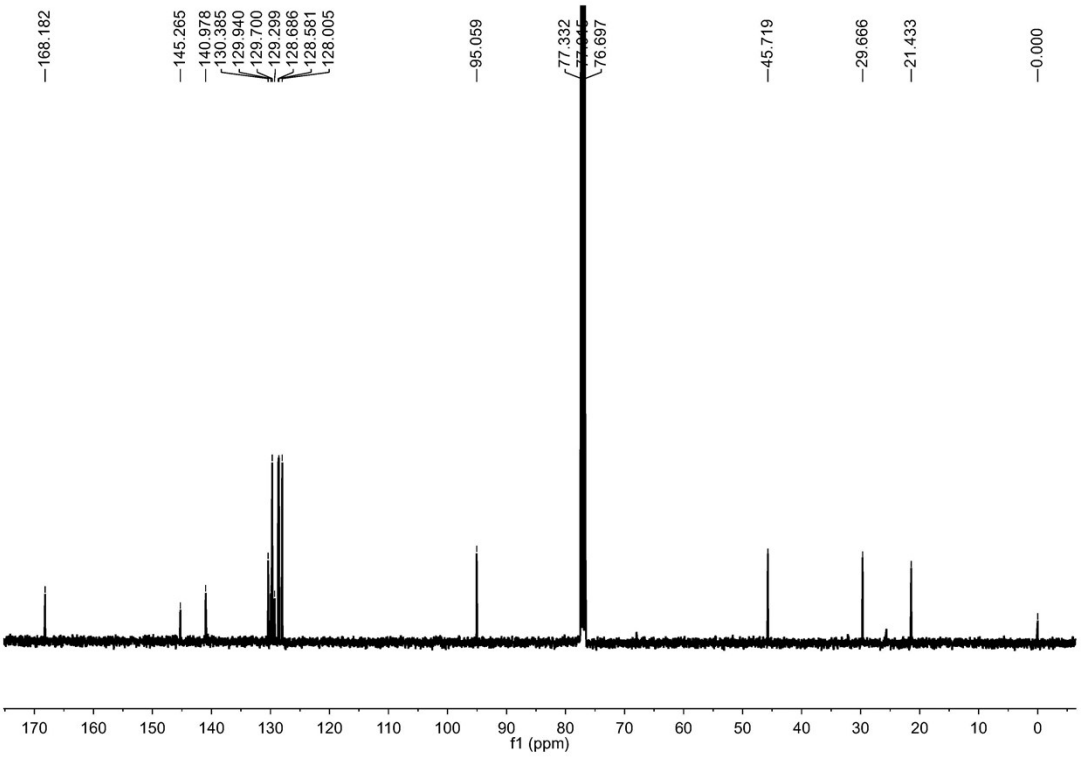
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3a**



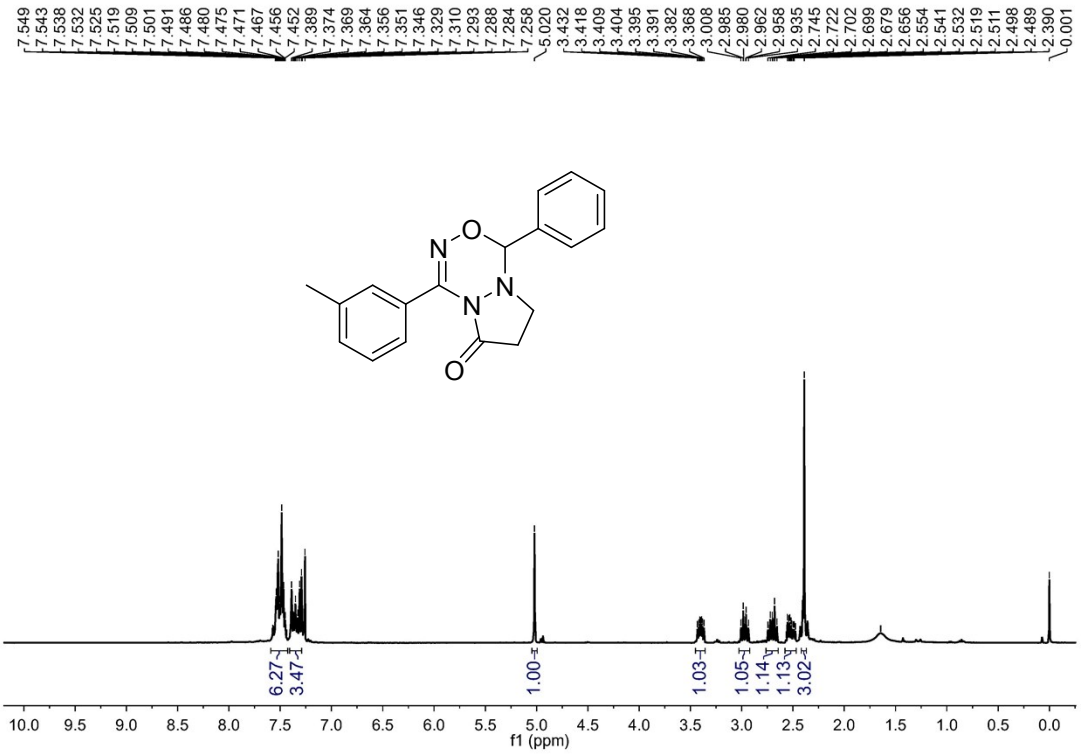
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3a**



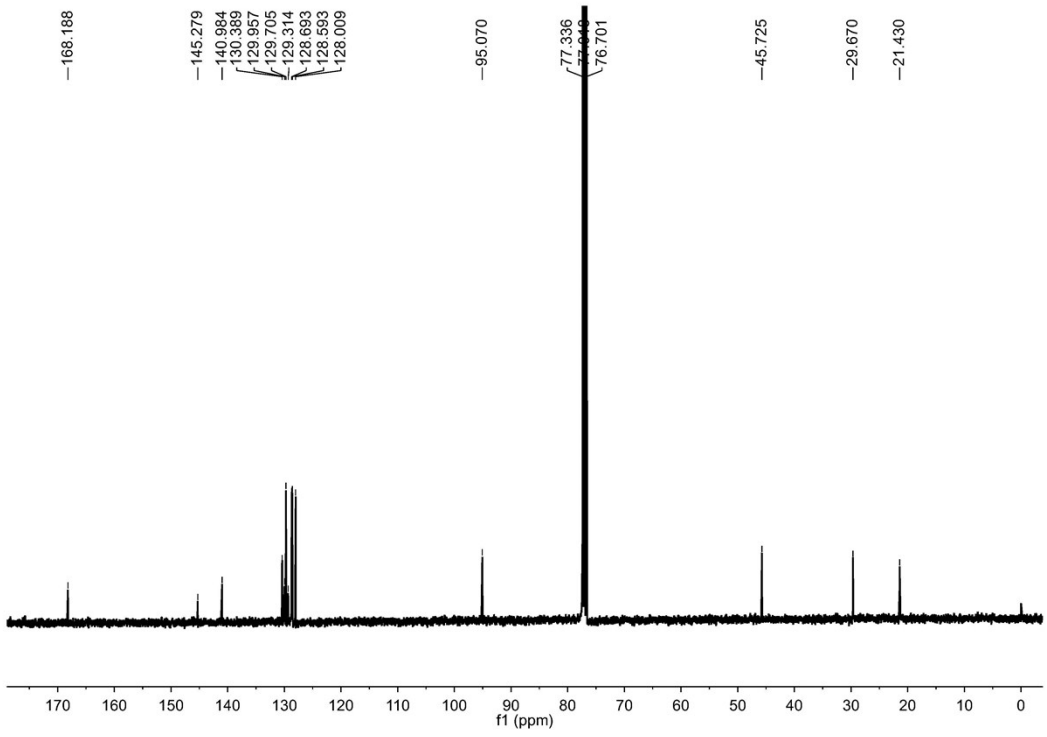
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3b**



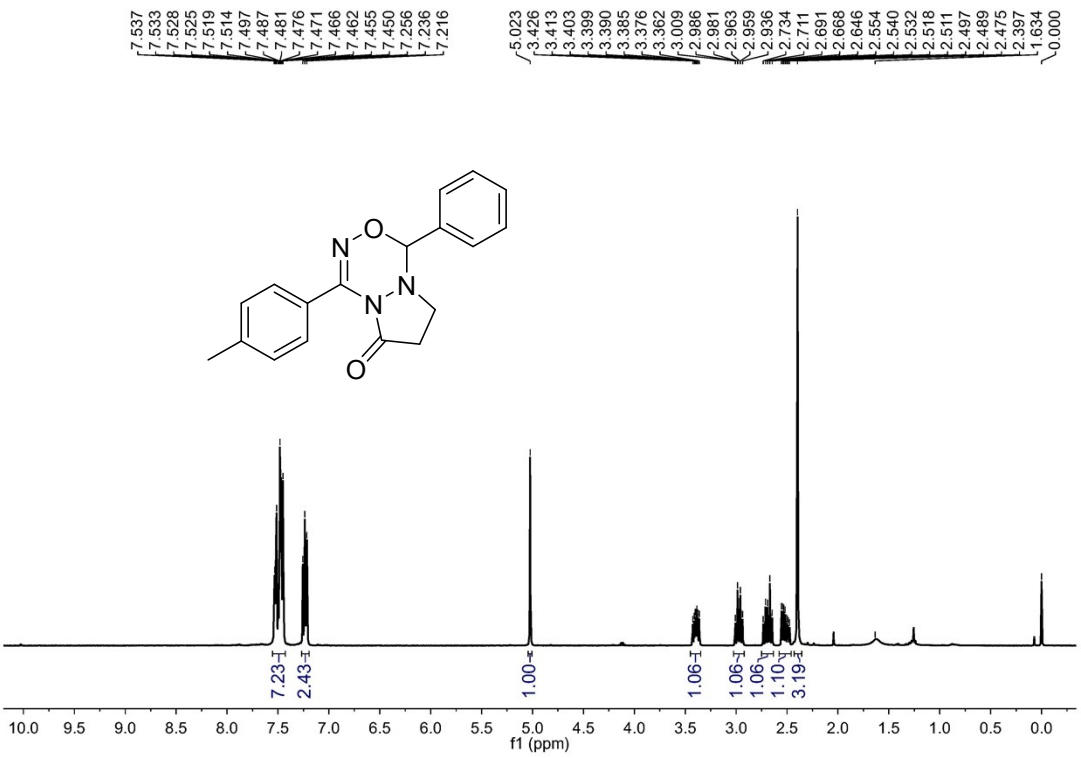
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3b**



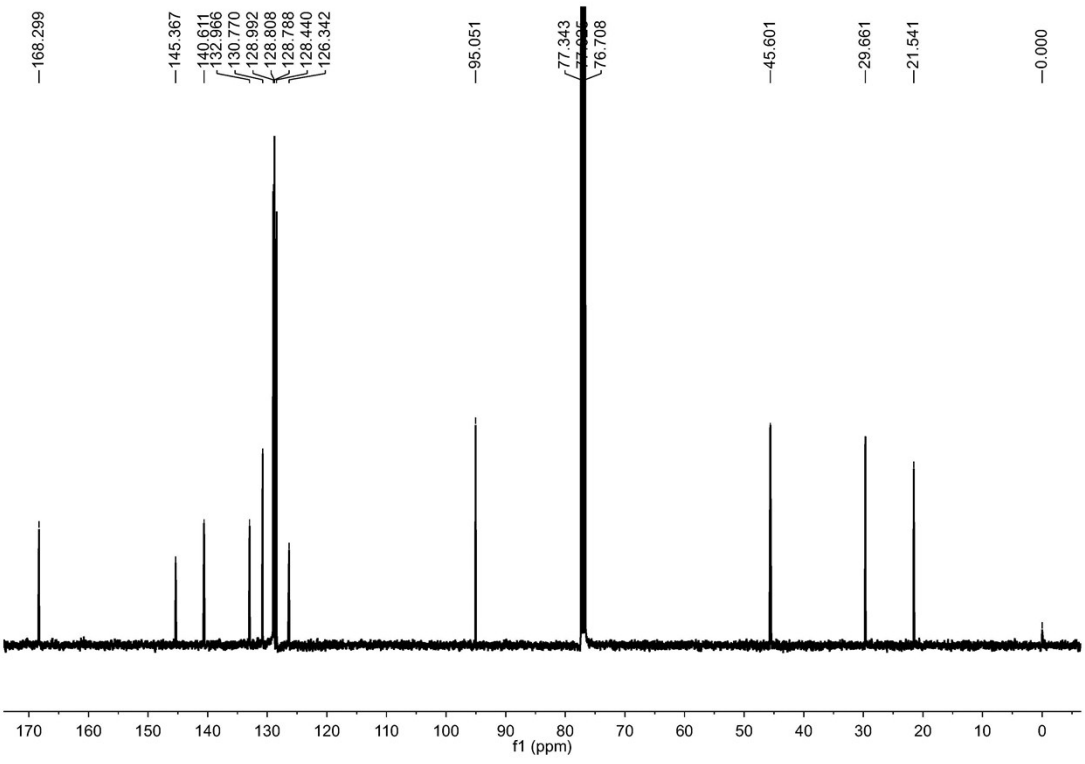
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3c**



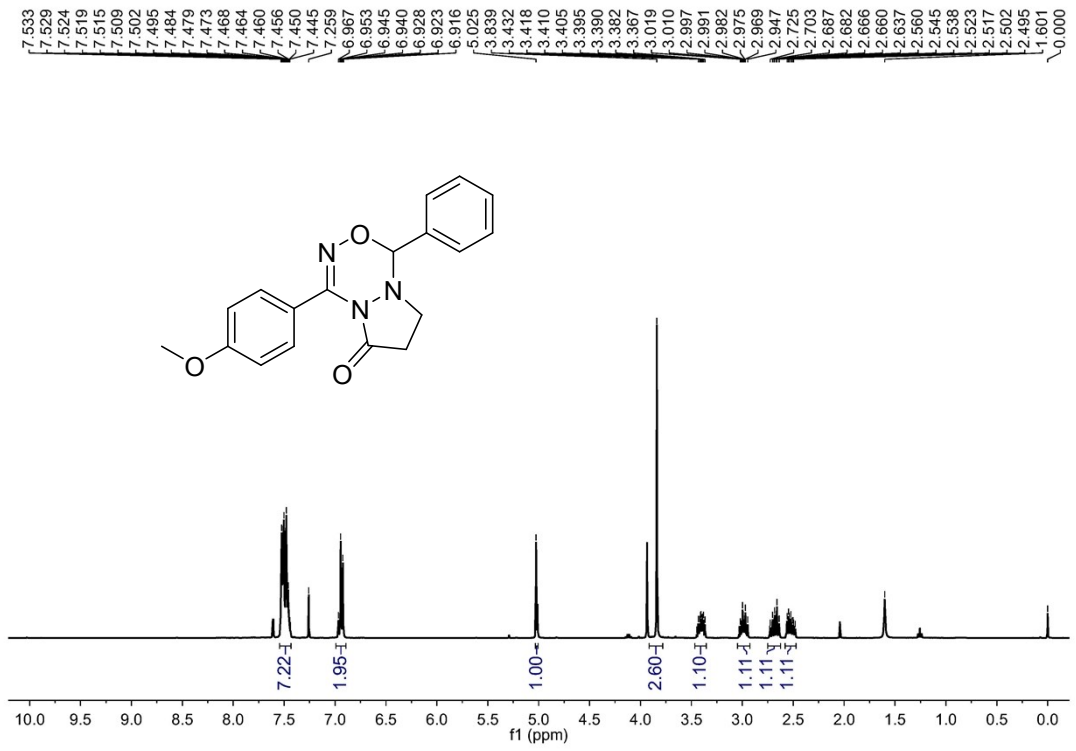
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3c**



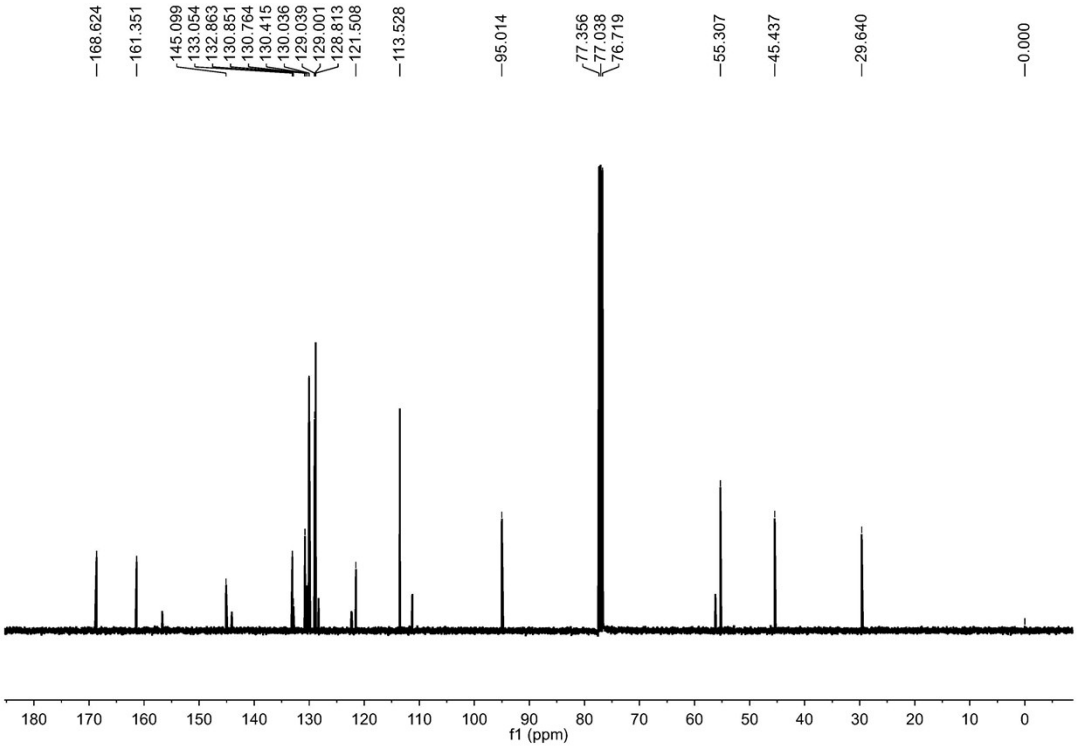
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3d**



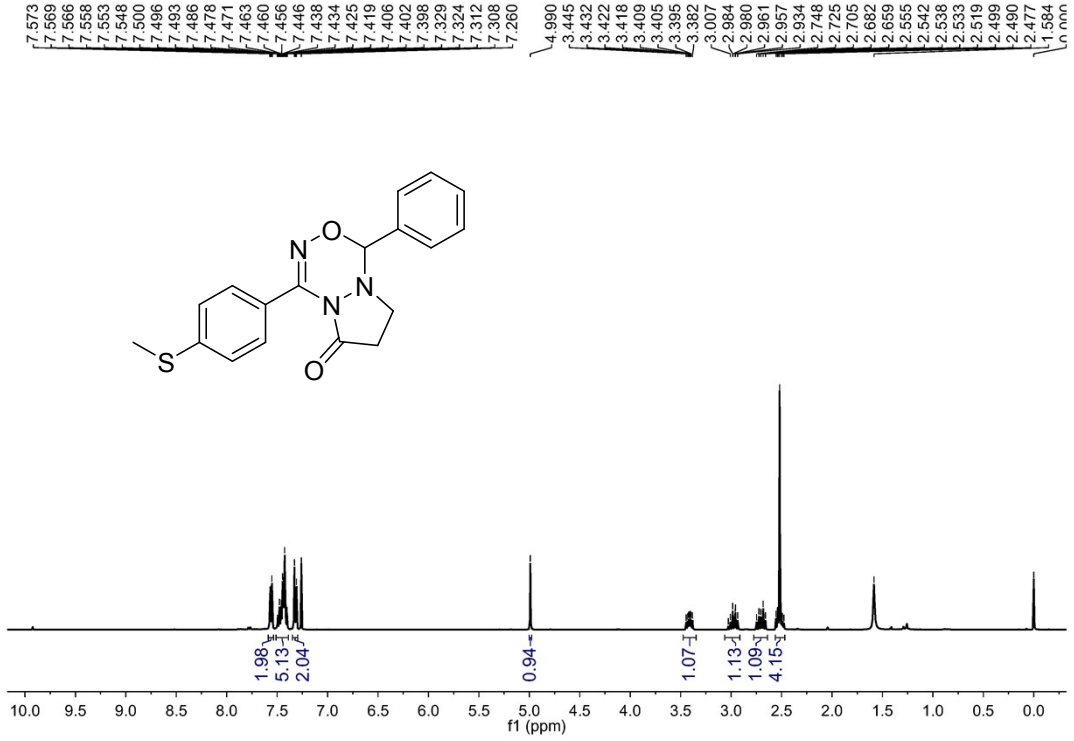
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3d**



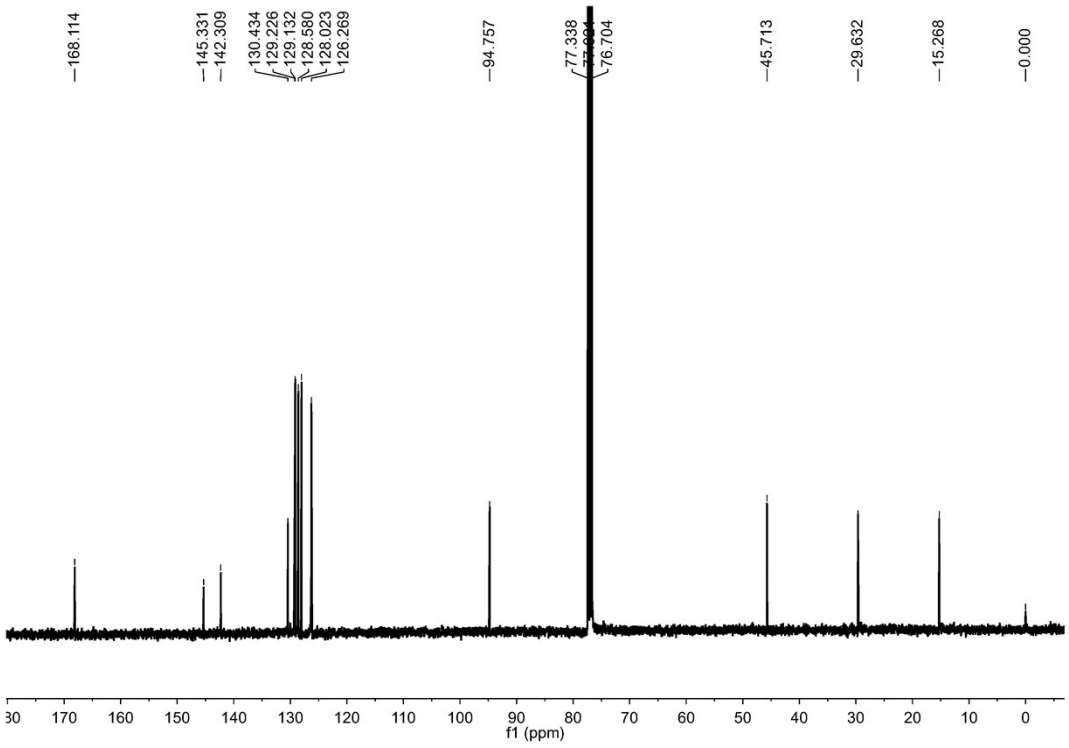
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3e**



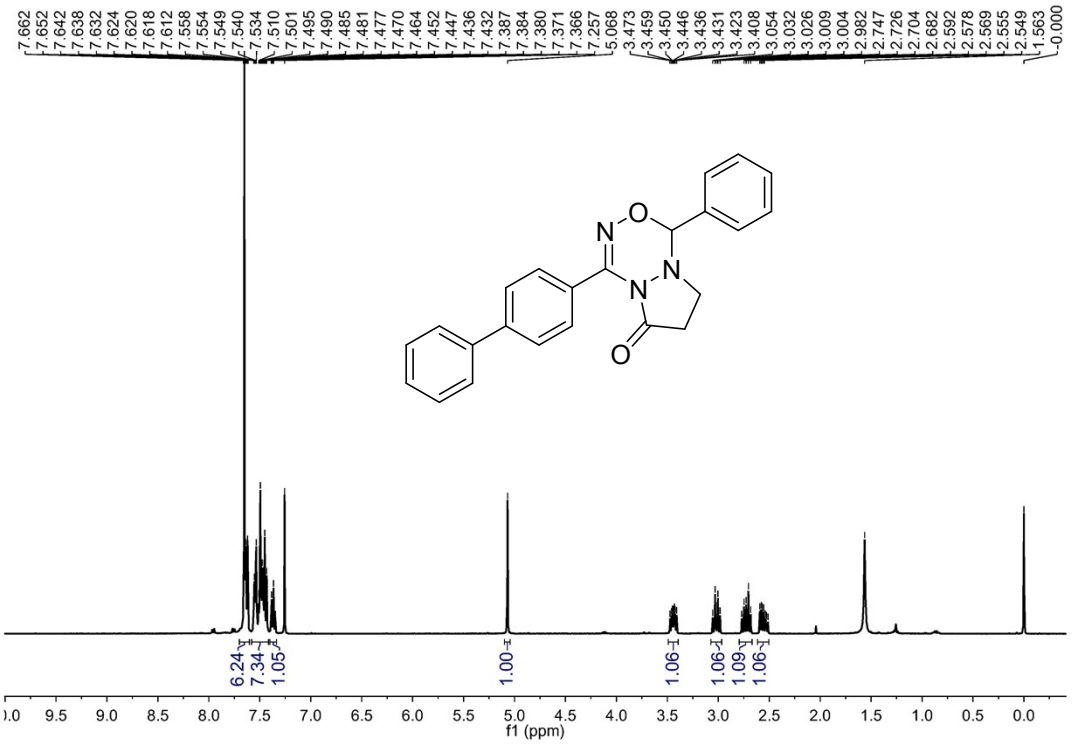
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3e**



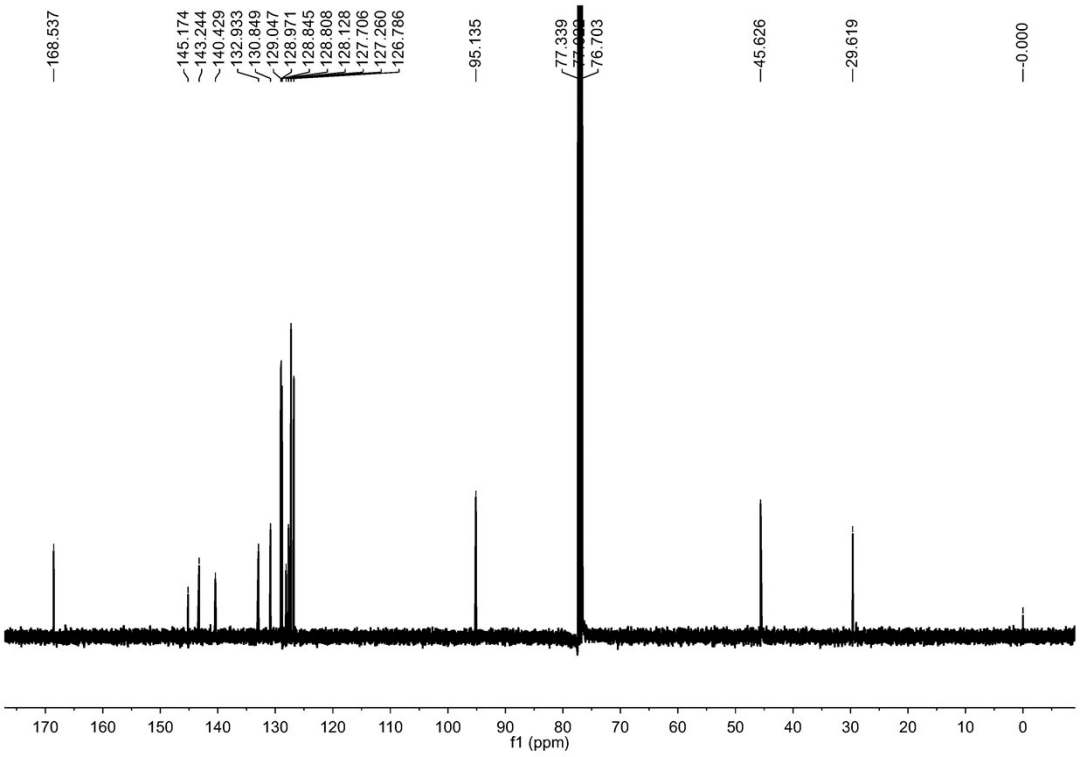
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3f**



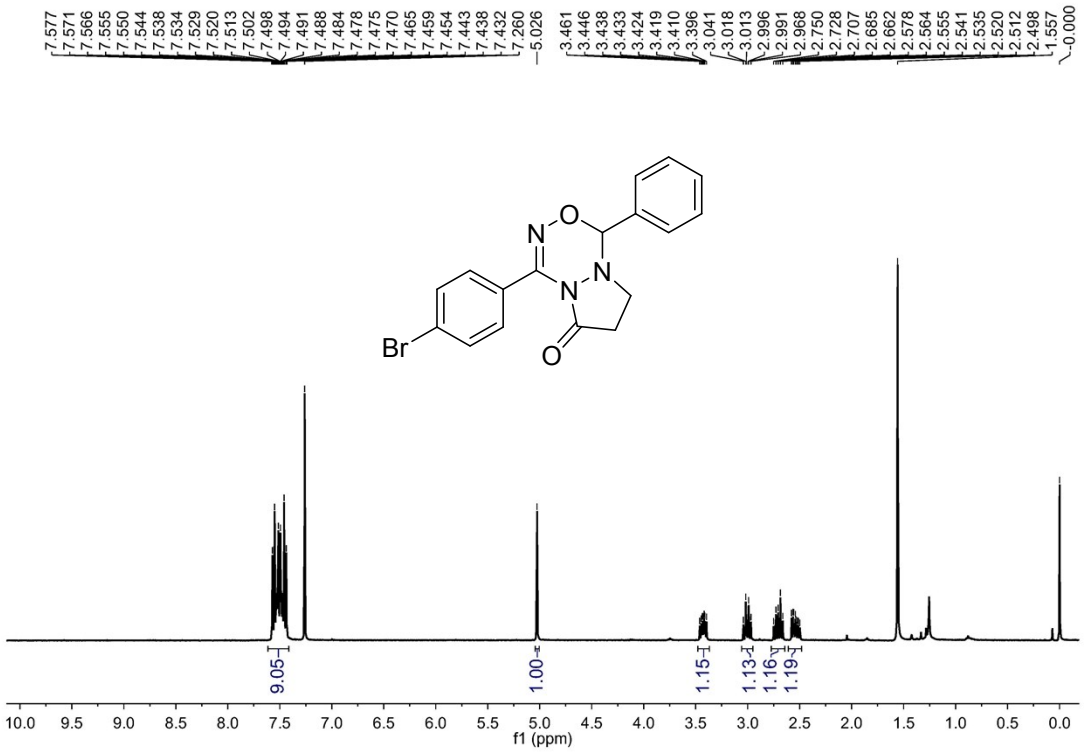
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3f**



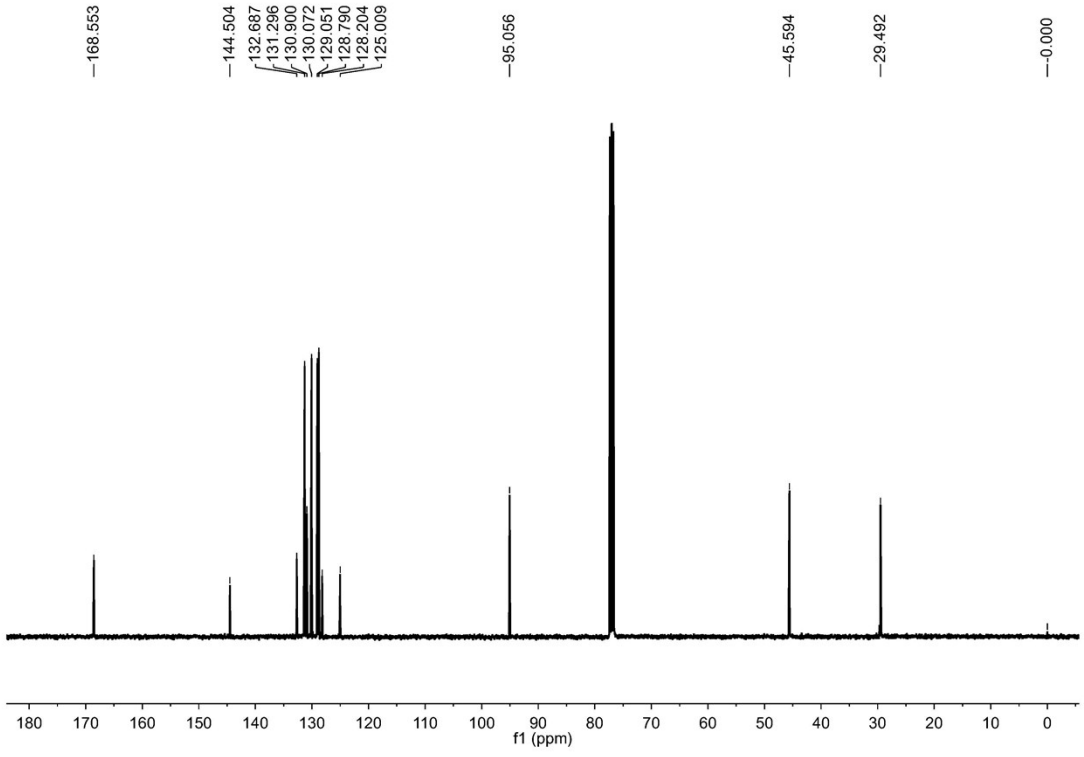
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3g**



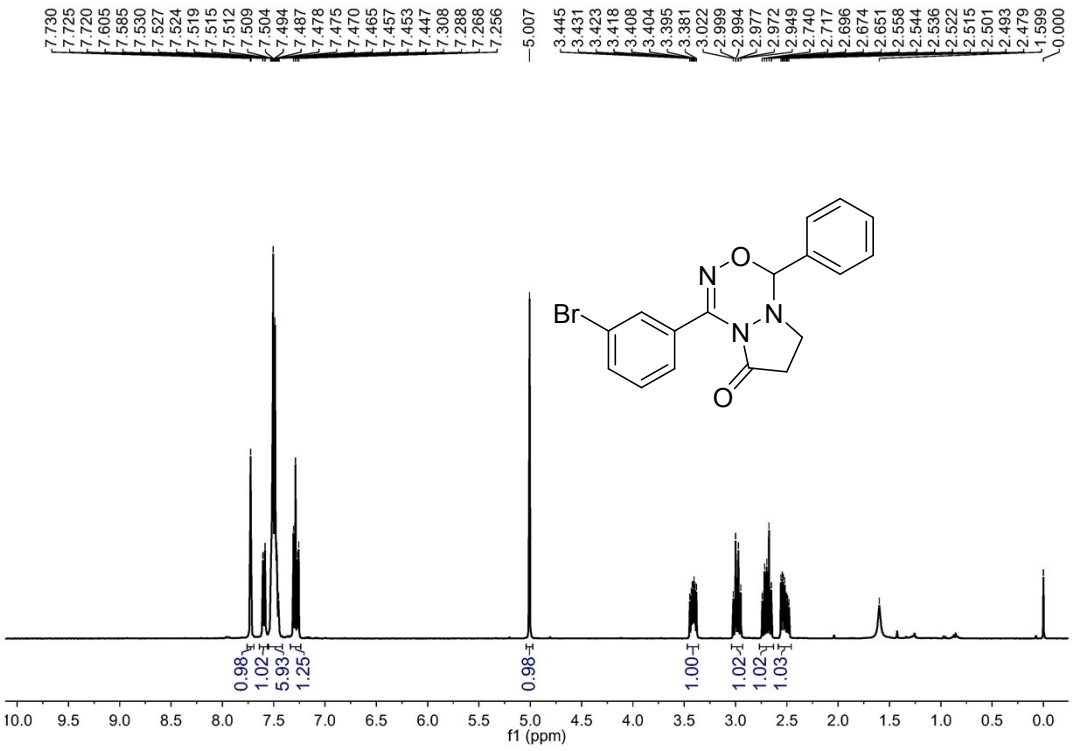
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3g**



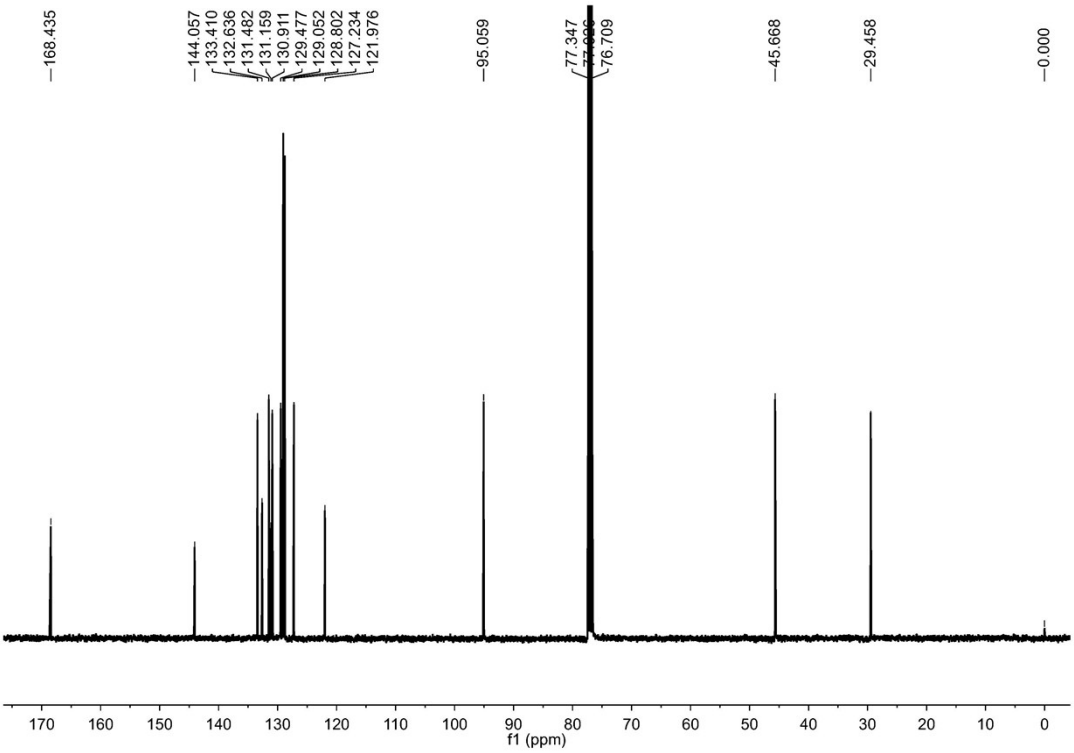
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3h**



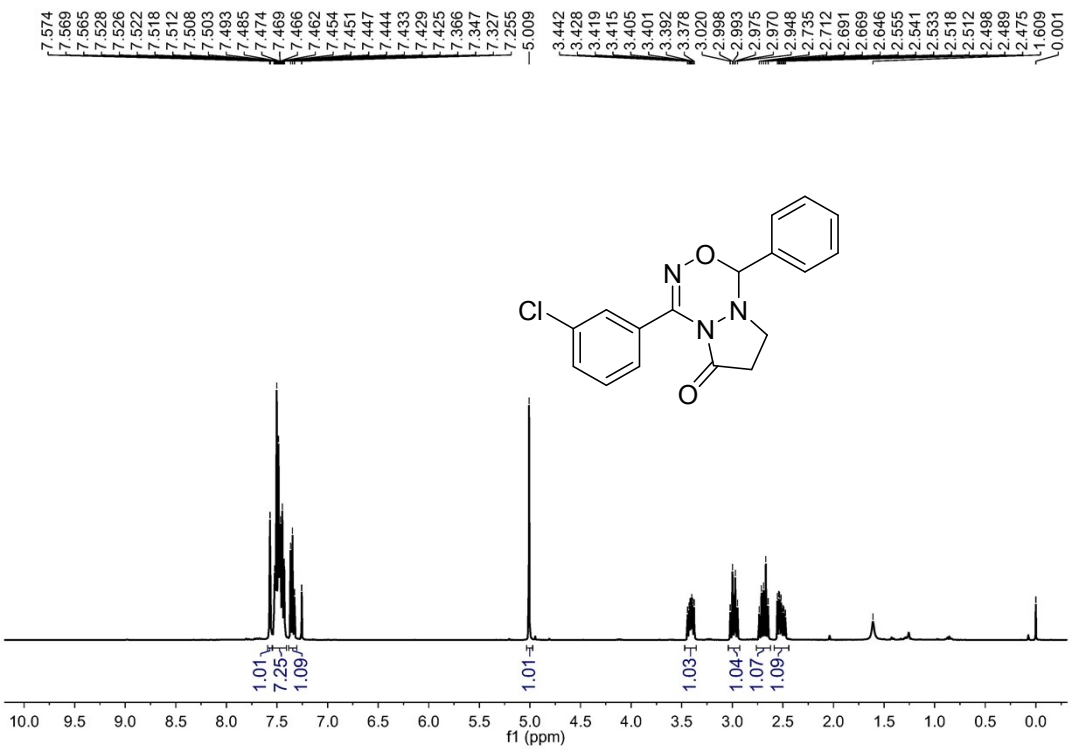
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3h**



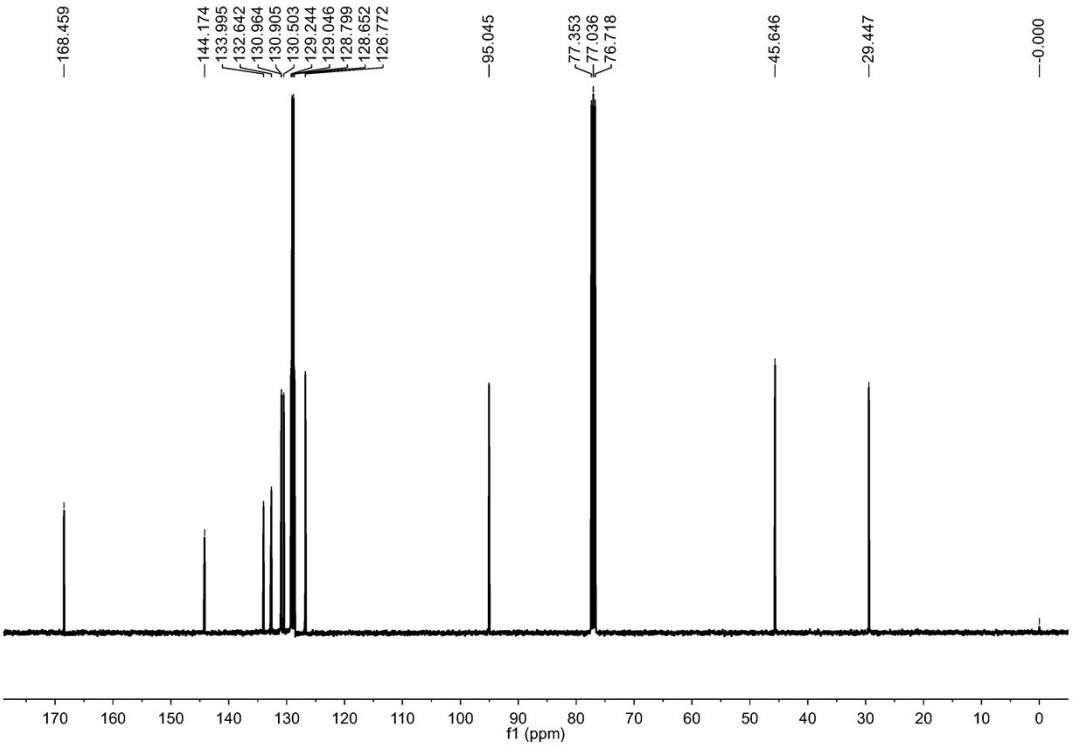
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3i**



^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3i**



^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3j**



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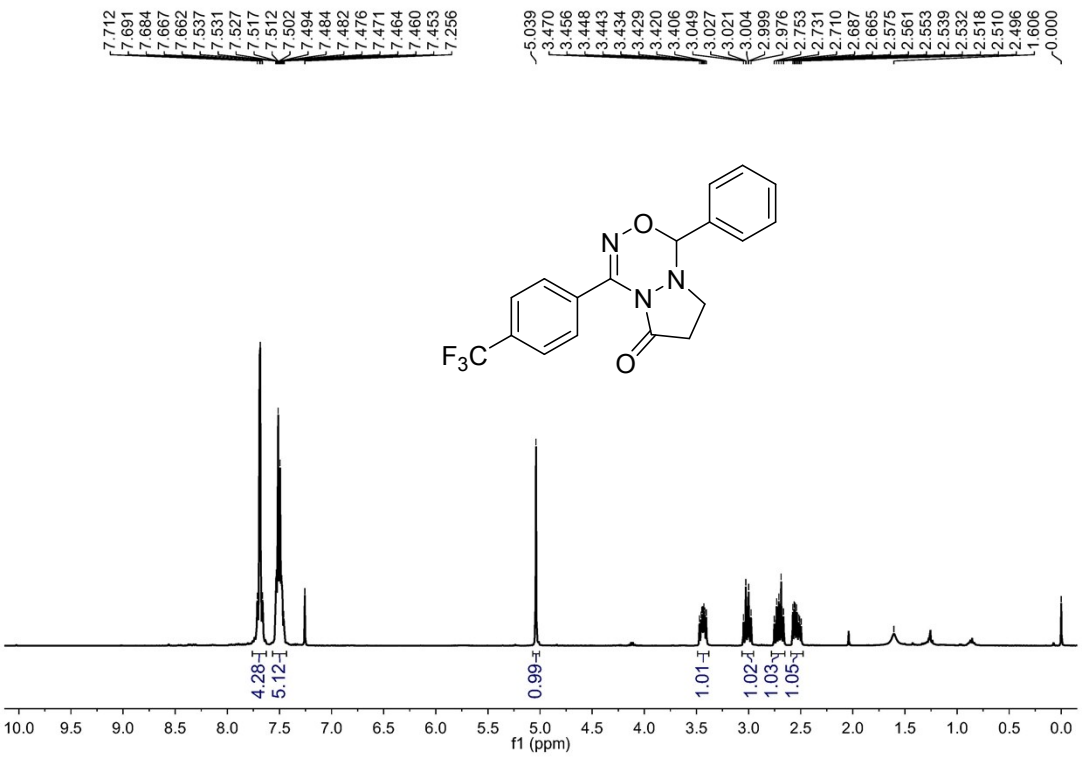
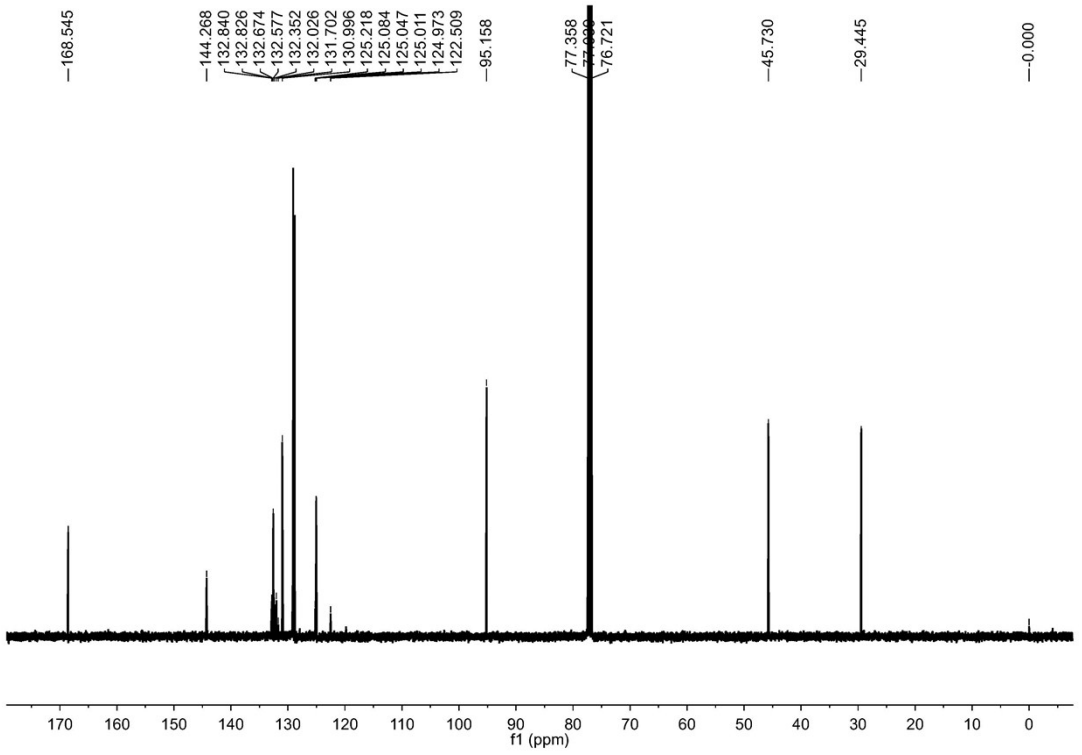
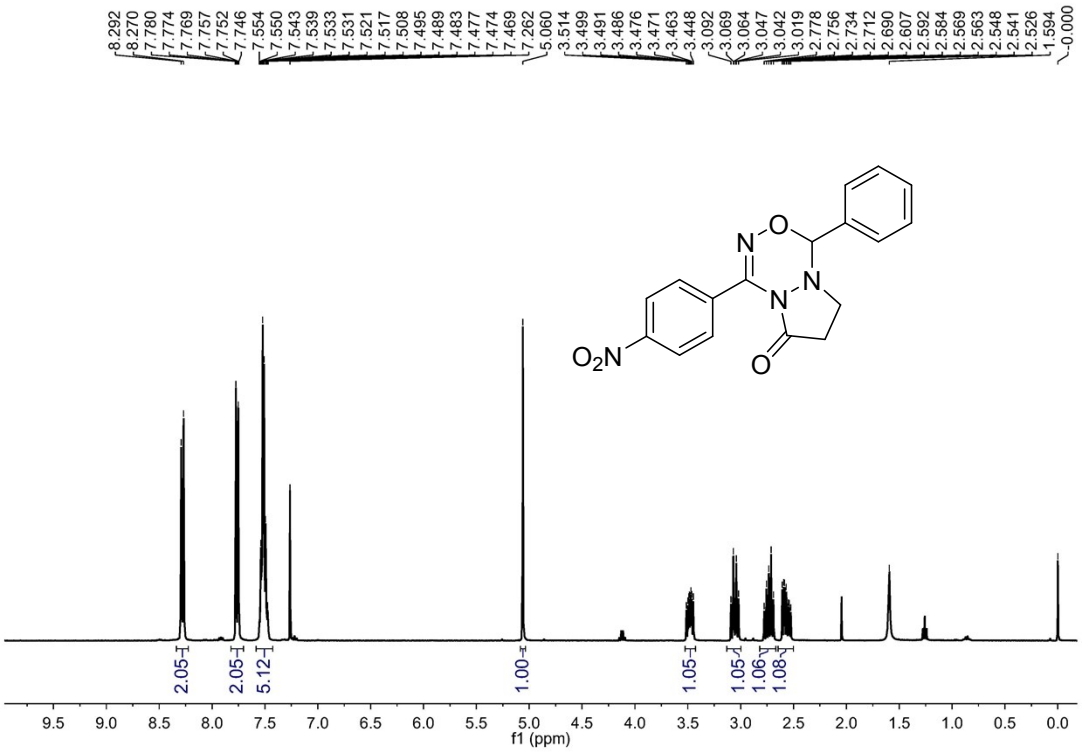


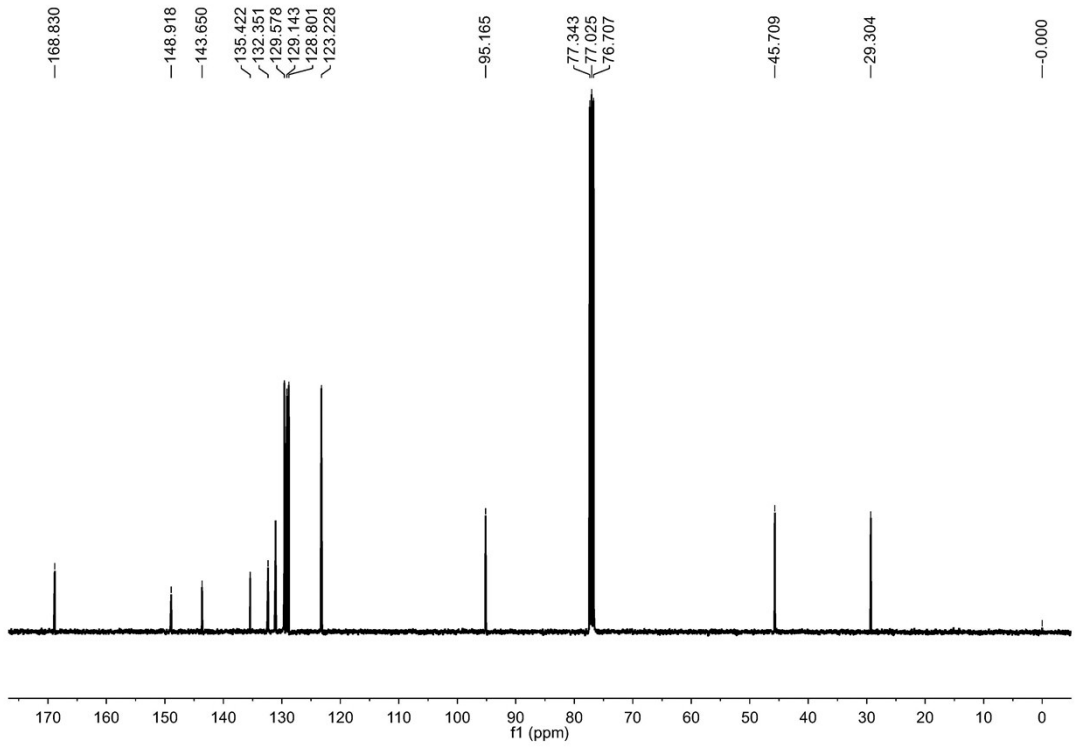
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3k**



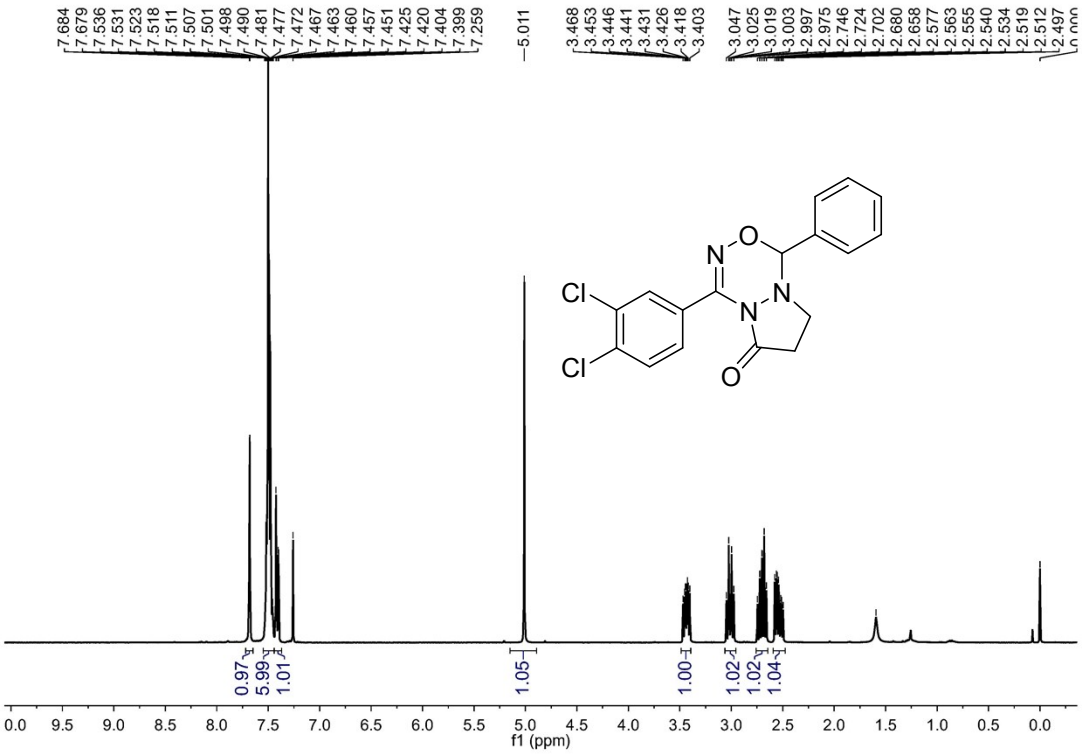
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3k**



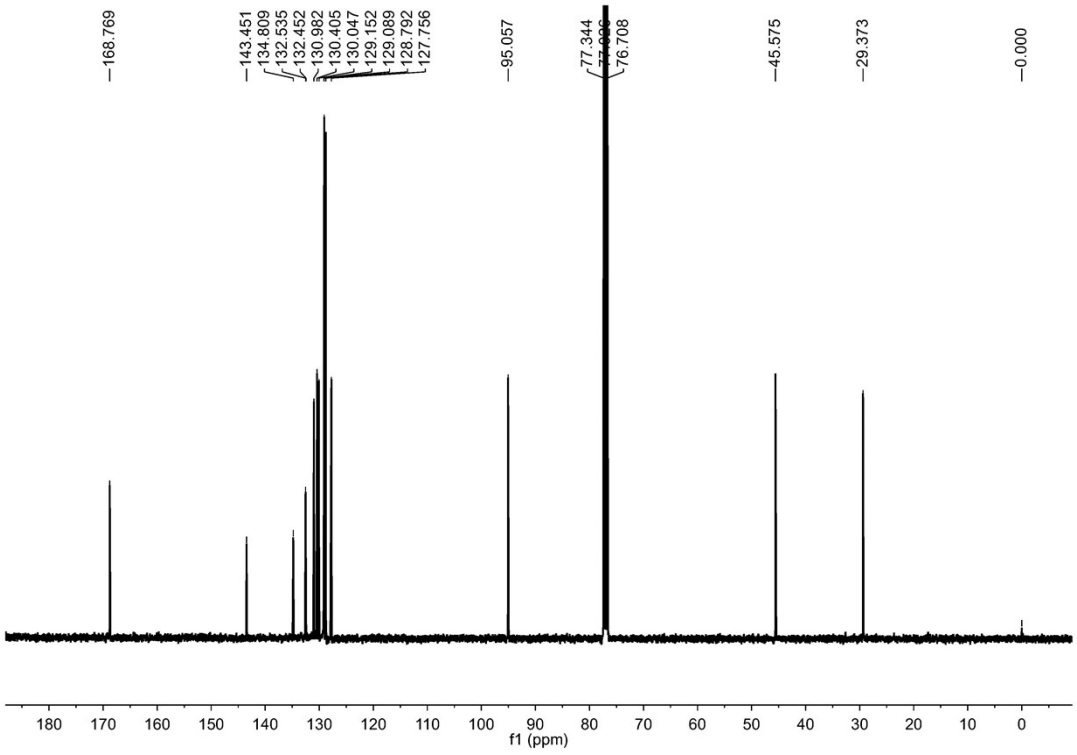
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3l**



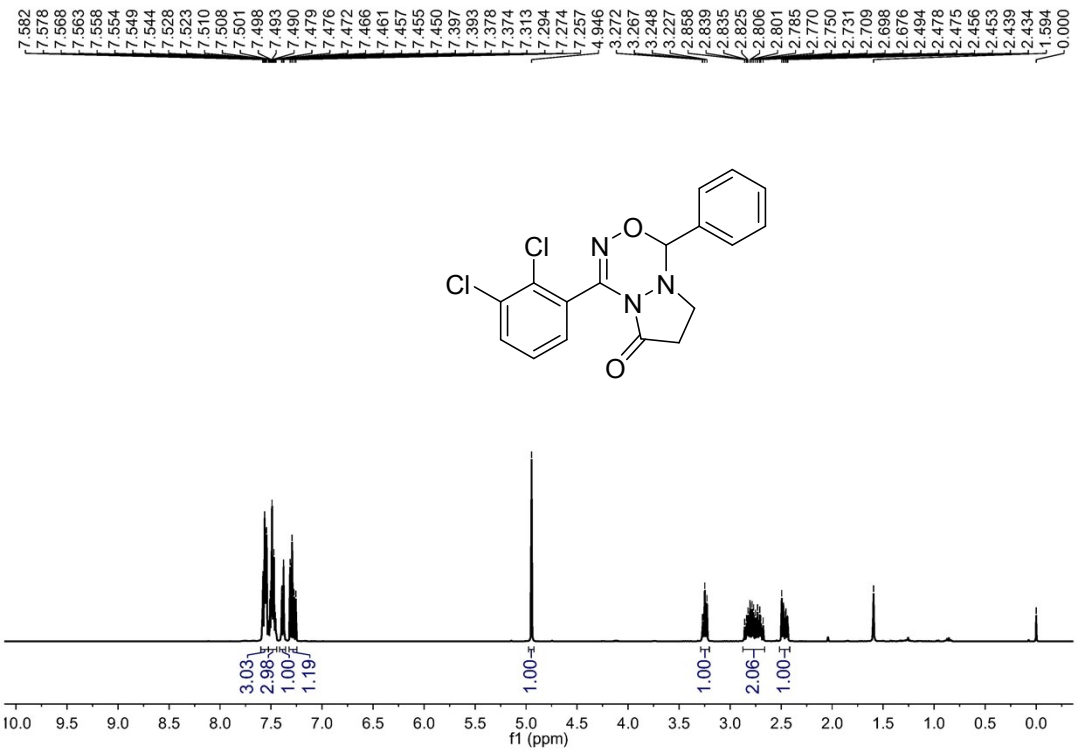
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3l**



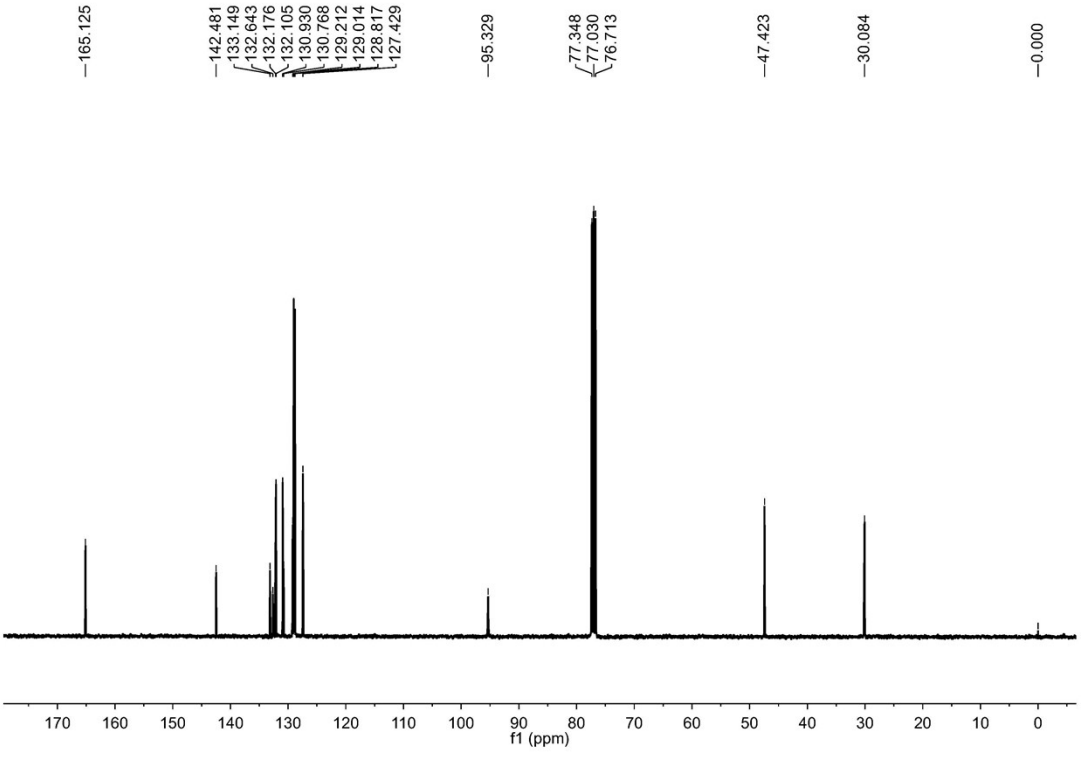
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3m**



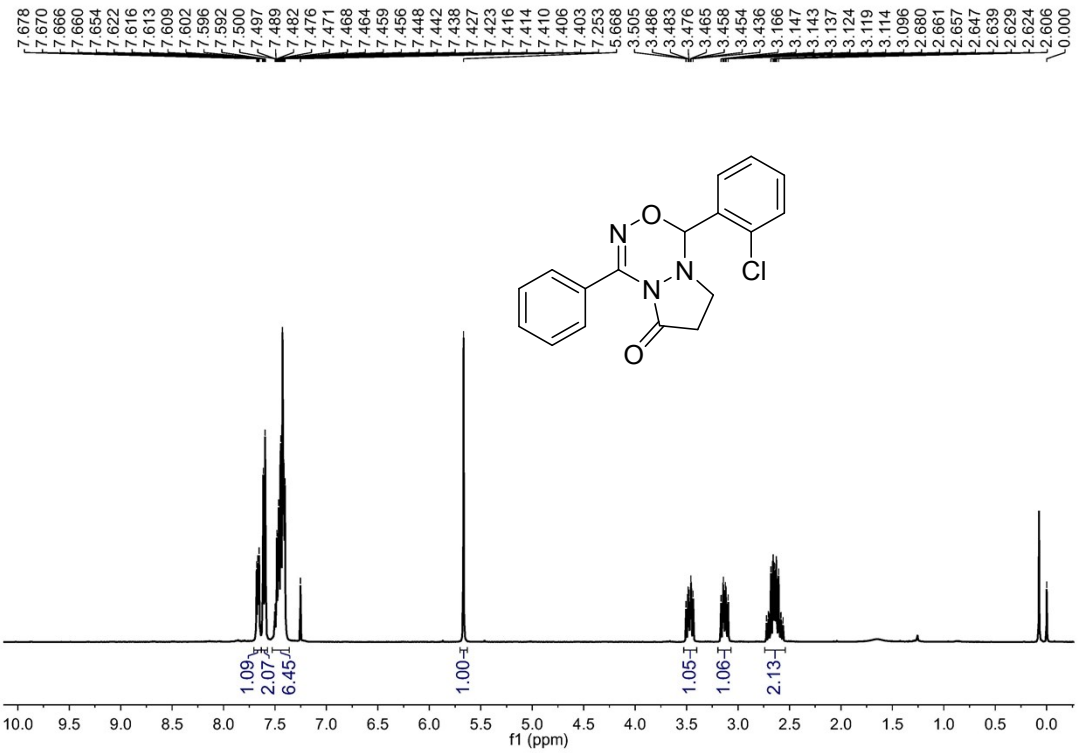
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3m**



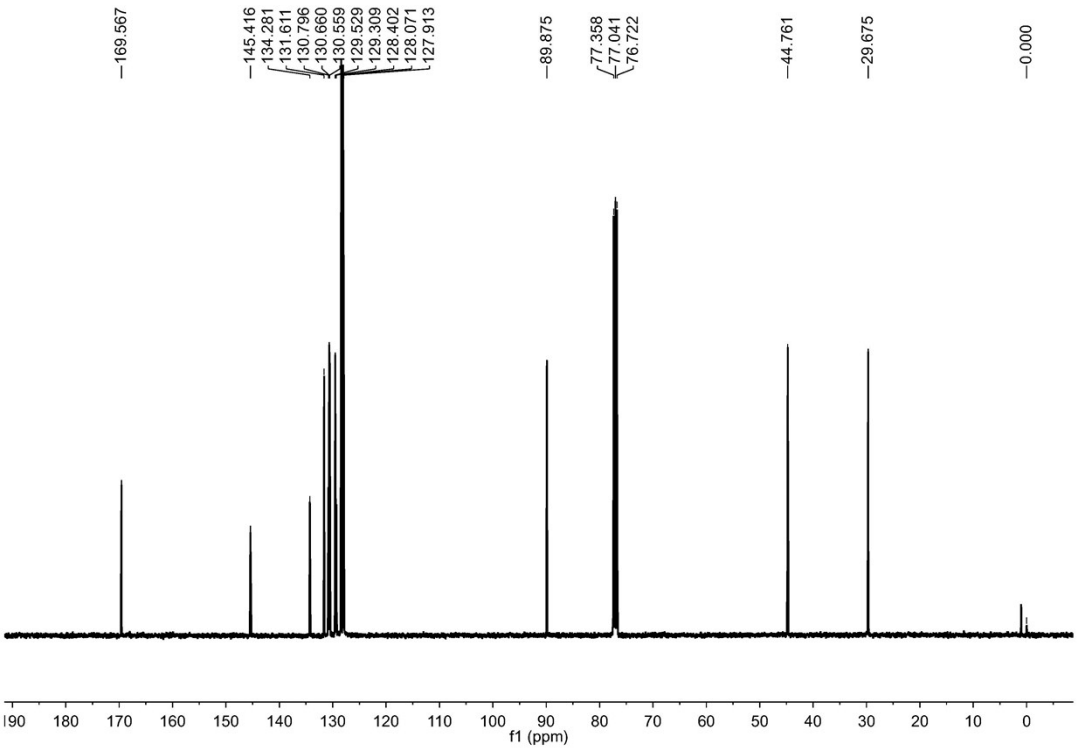
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3n**



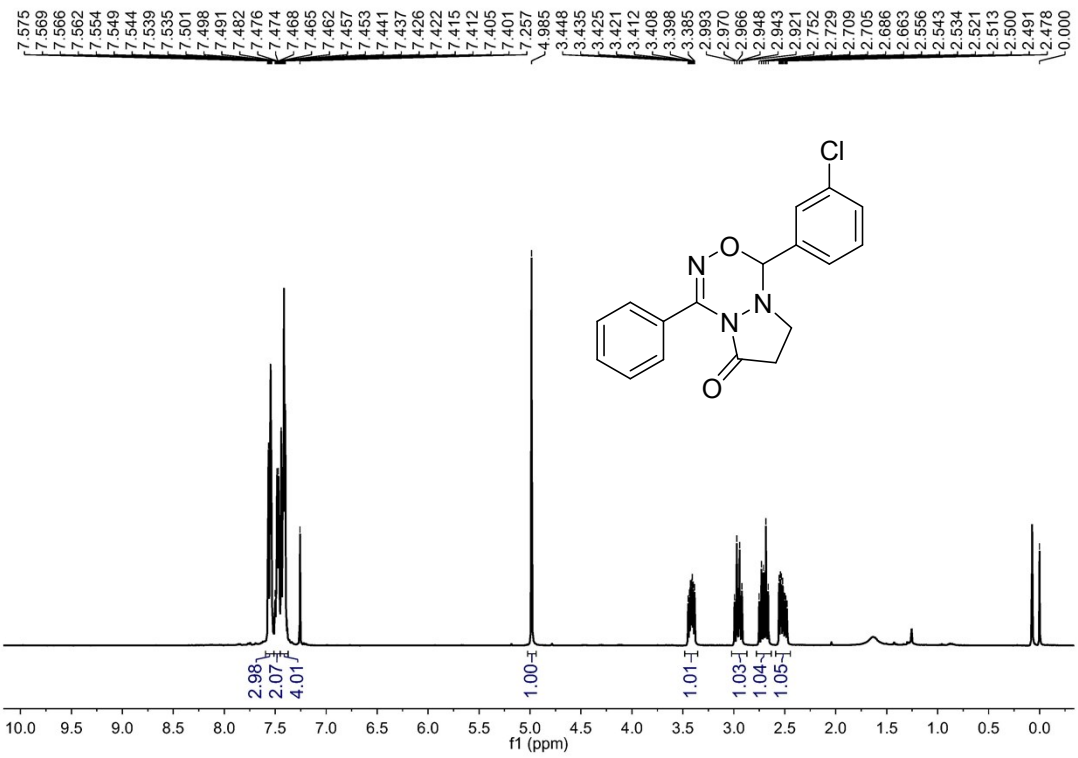
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3n**



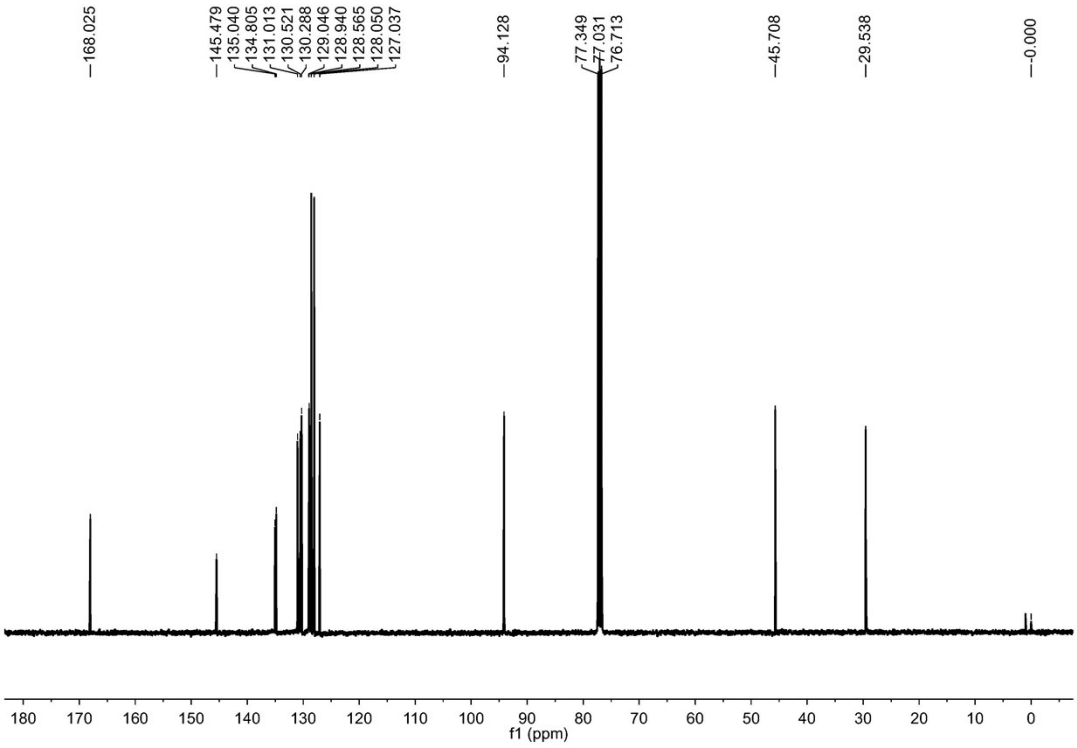
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3ba**



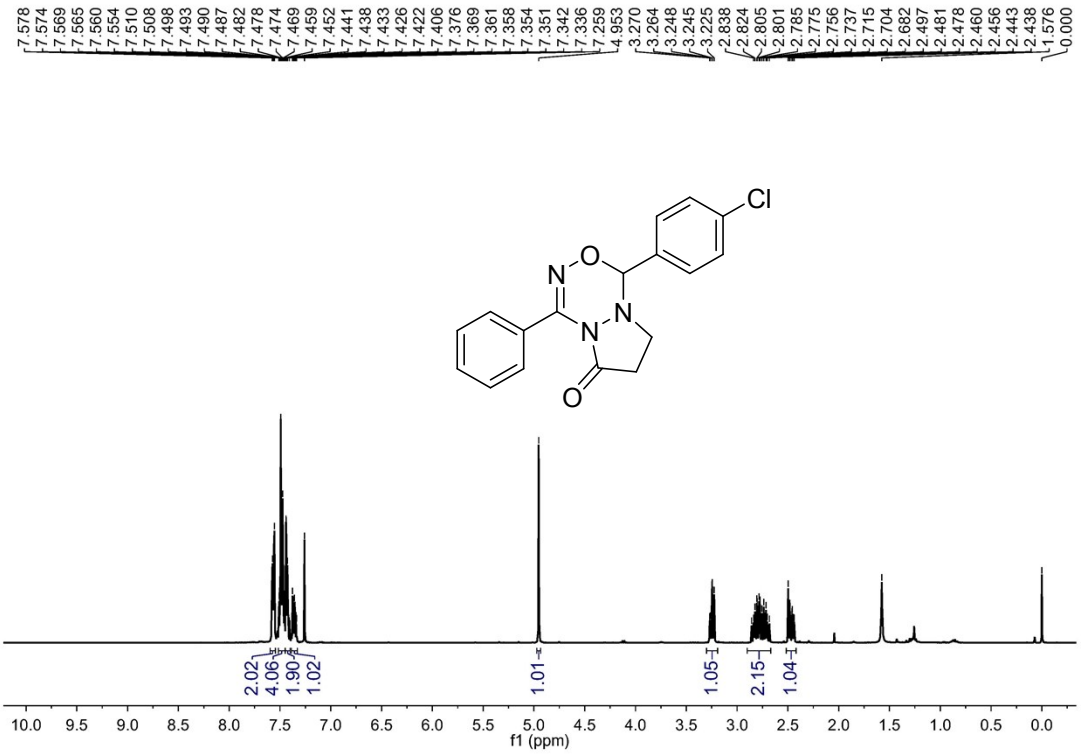
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3ba**



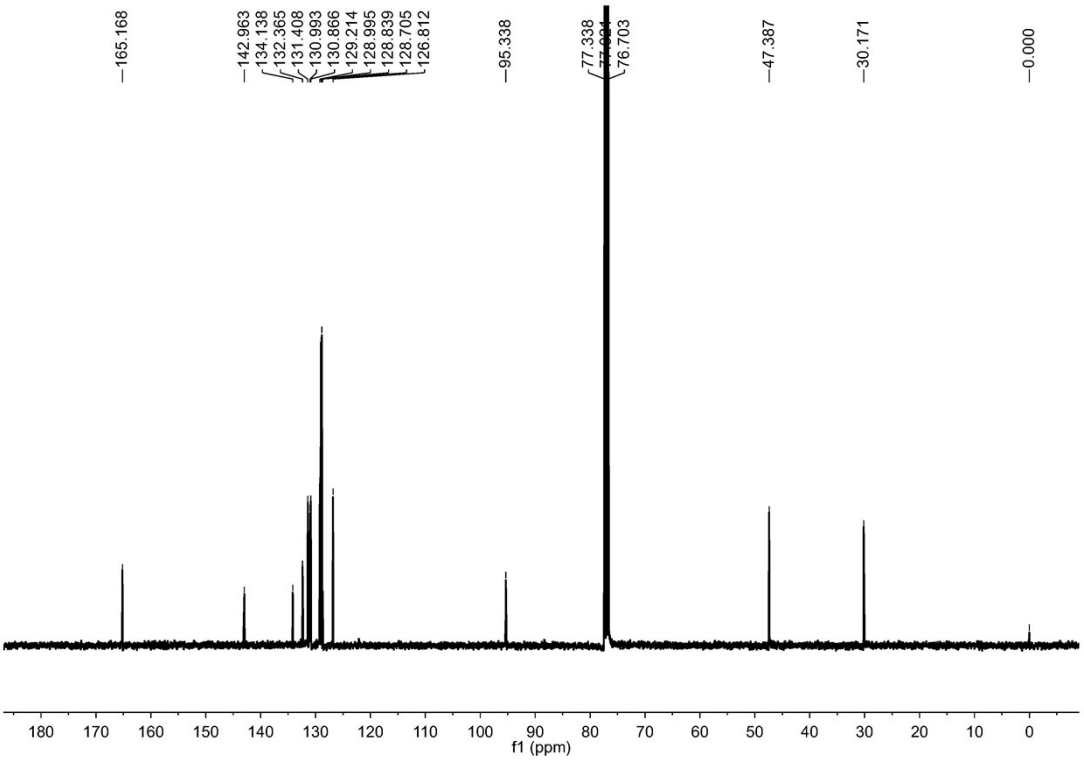
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3ca**



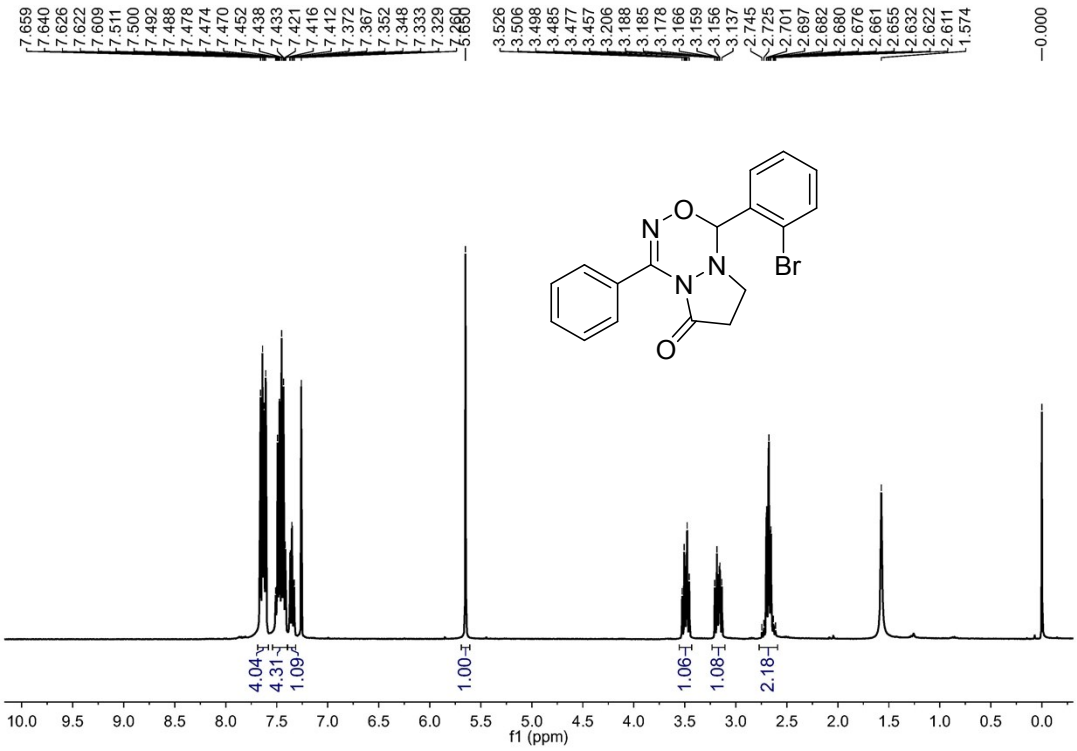
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3ca**



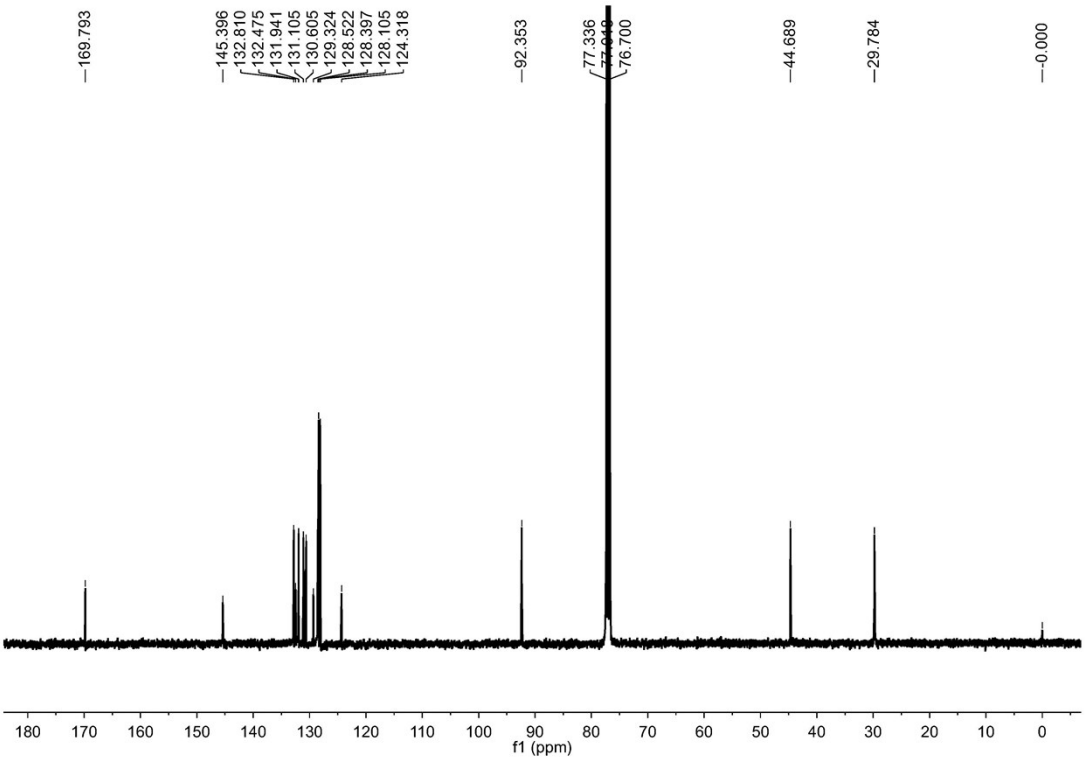
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3da**



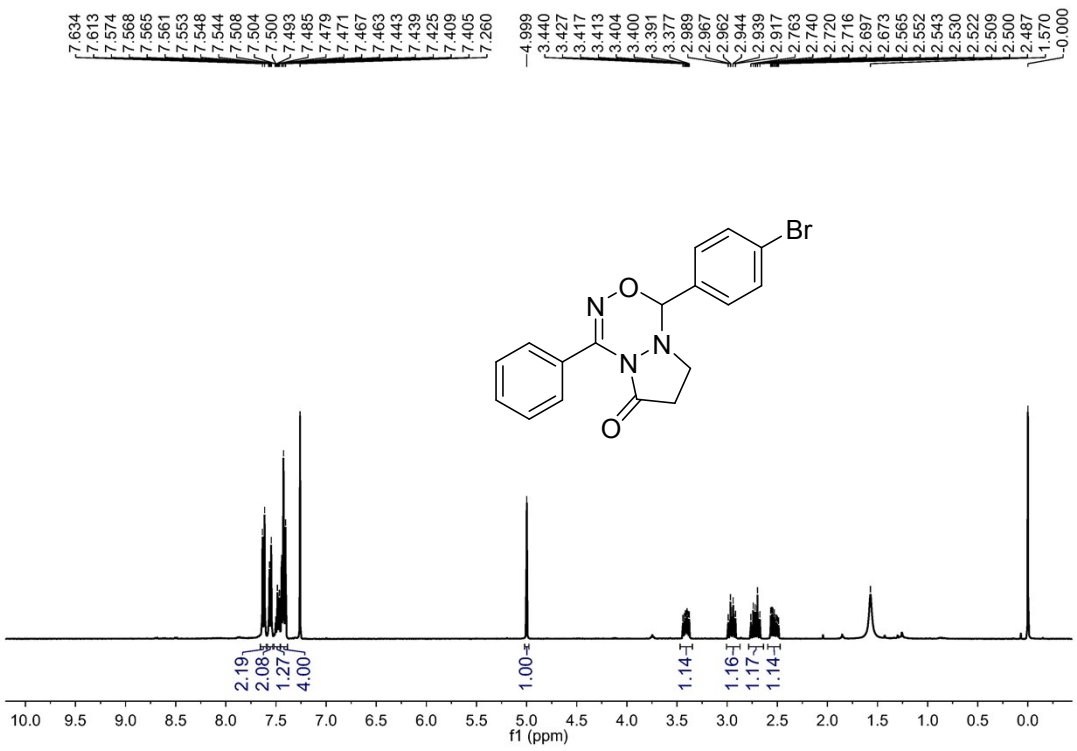
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3da**



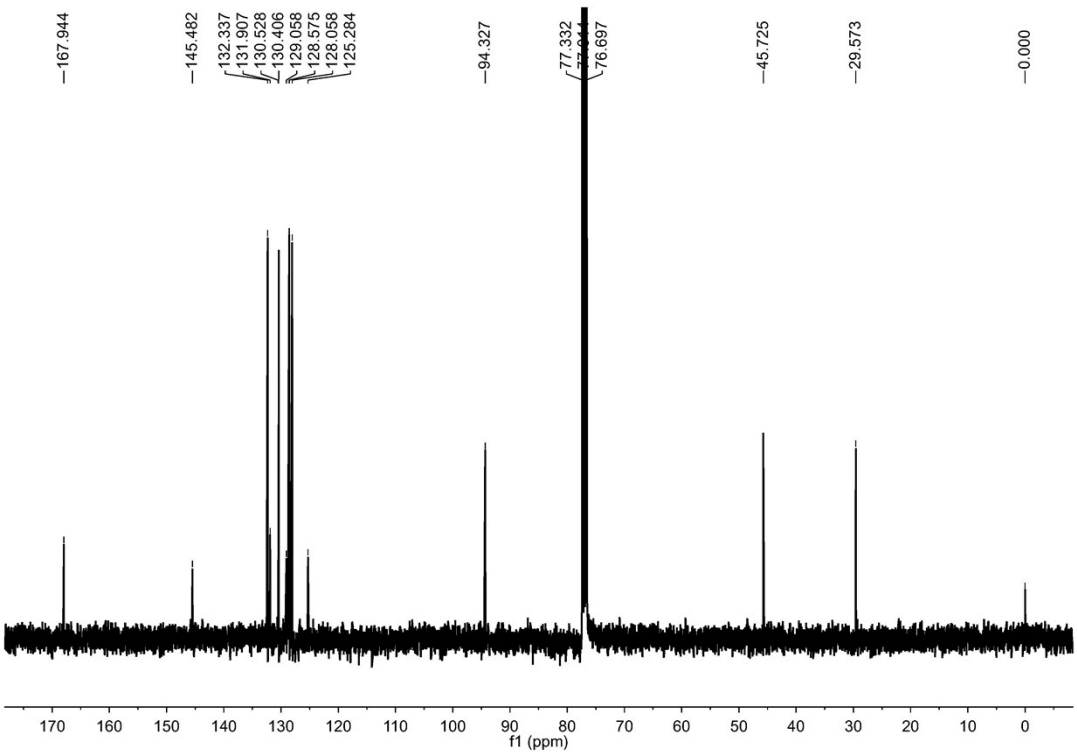
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3ea**



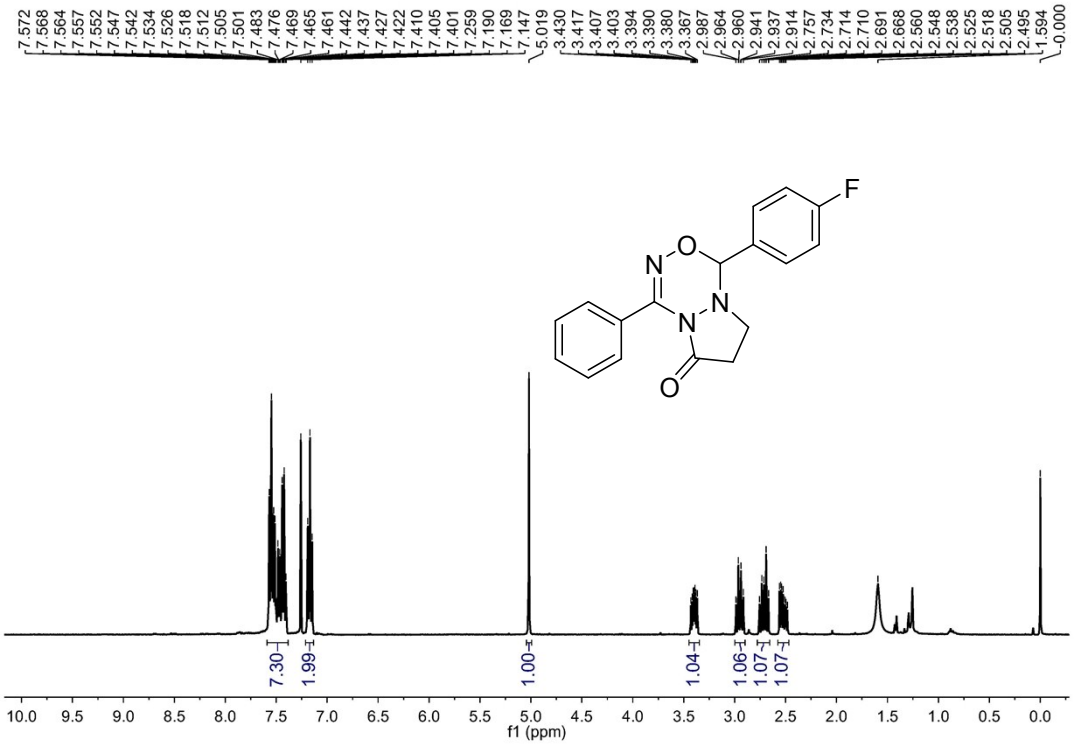
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3ea**



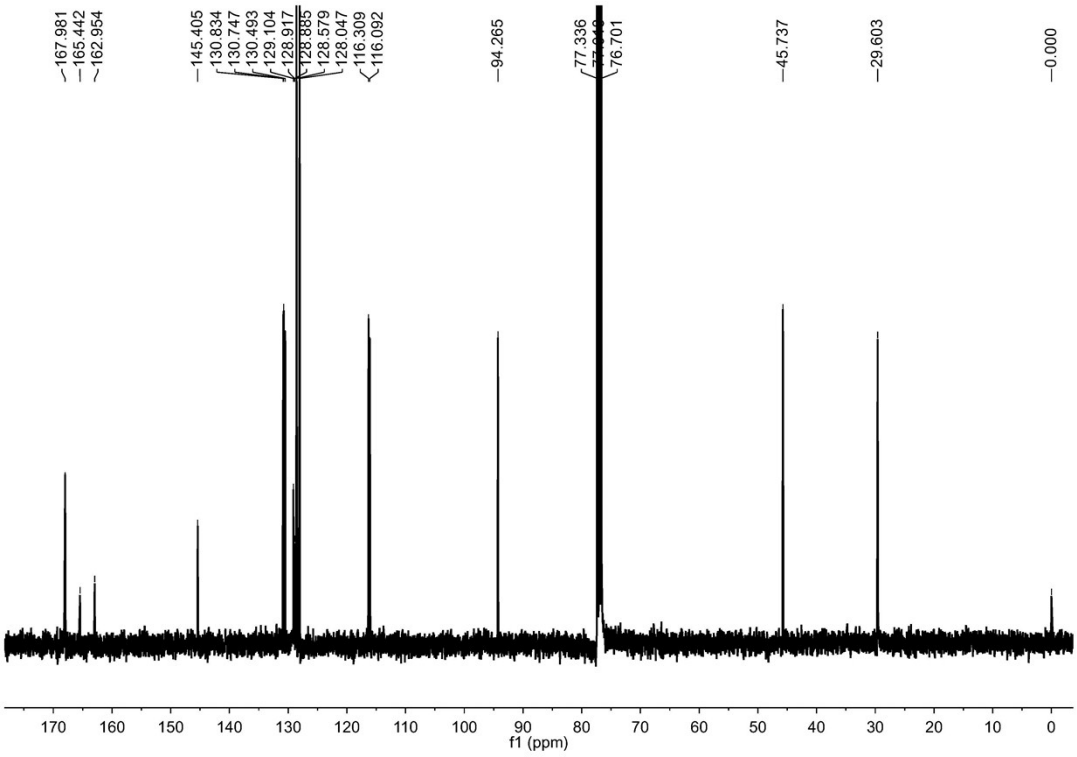
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3fa**



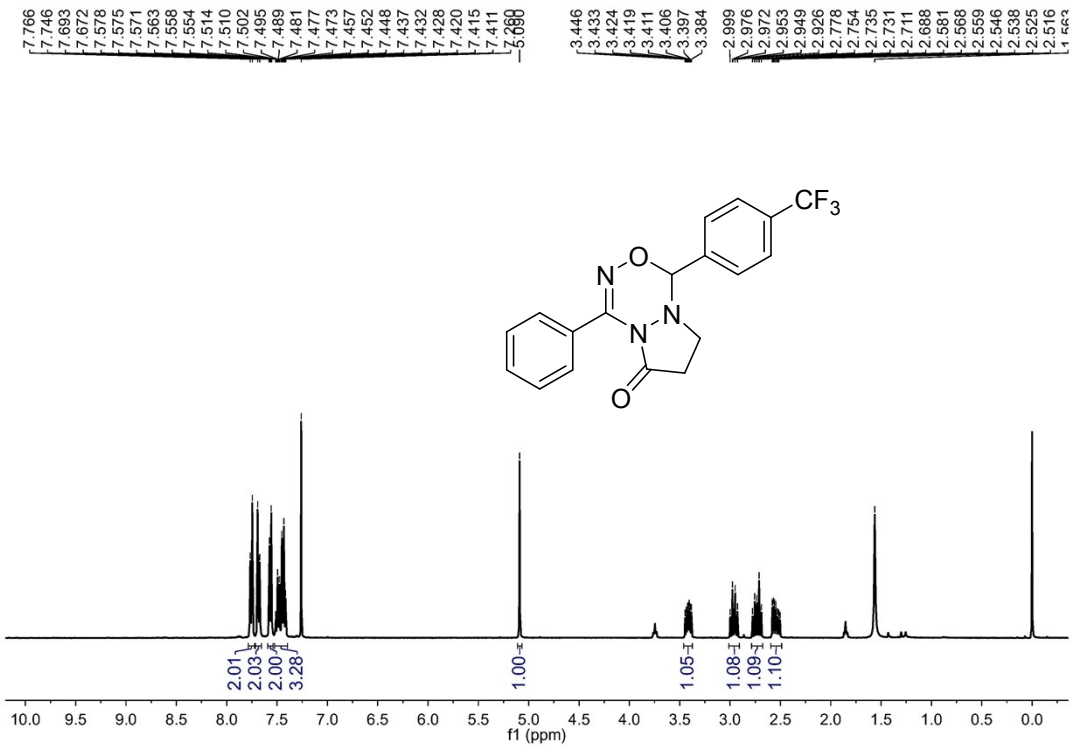
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3fa**



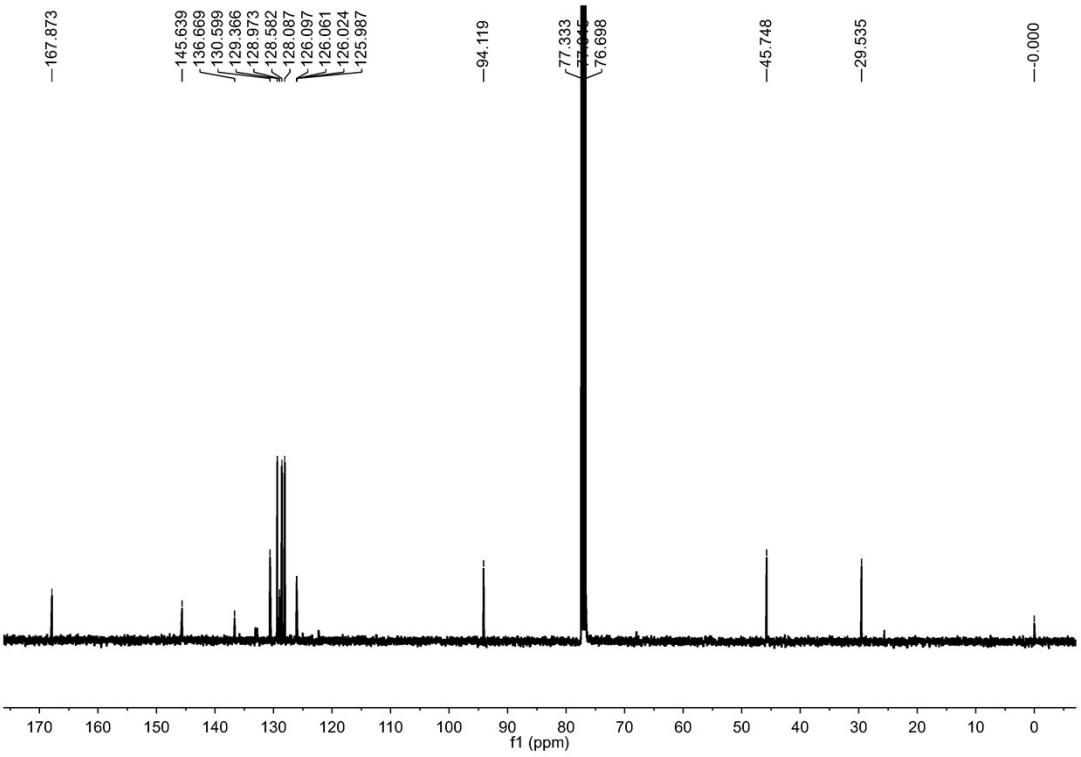
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3ga**



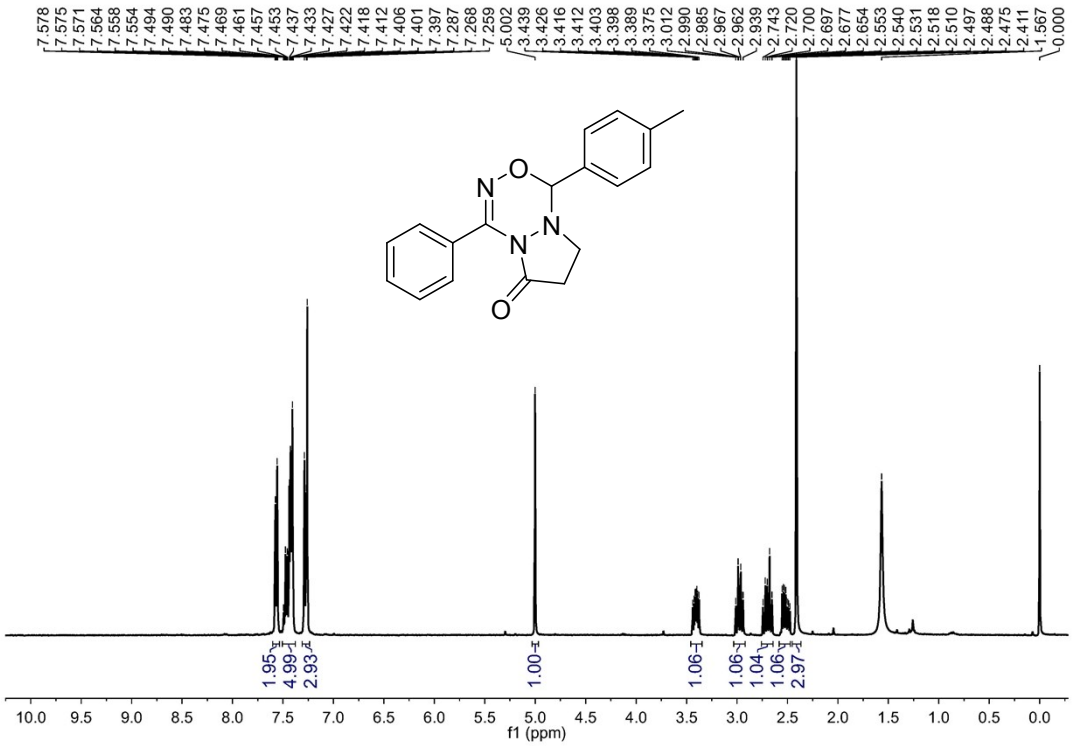
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3ga**



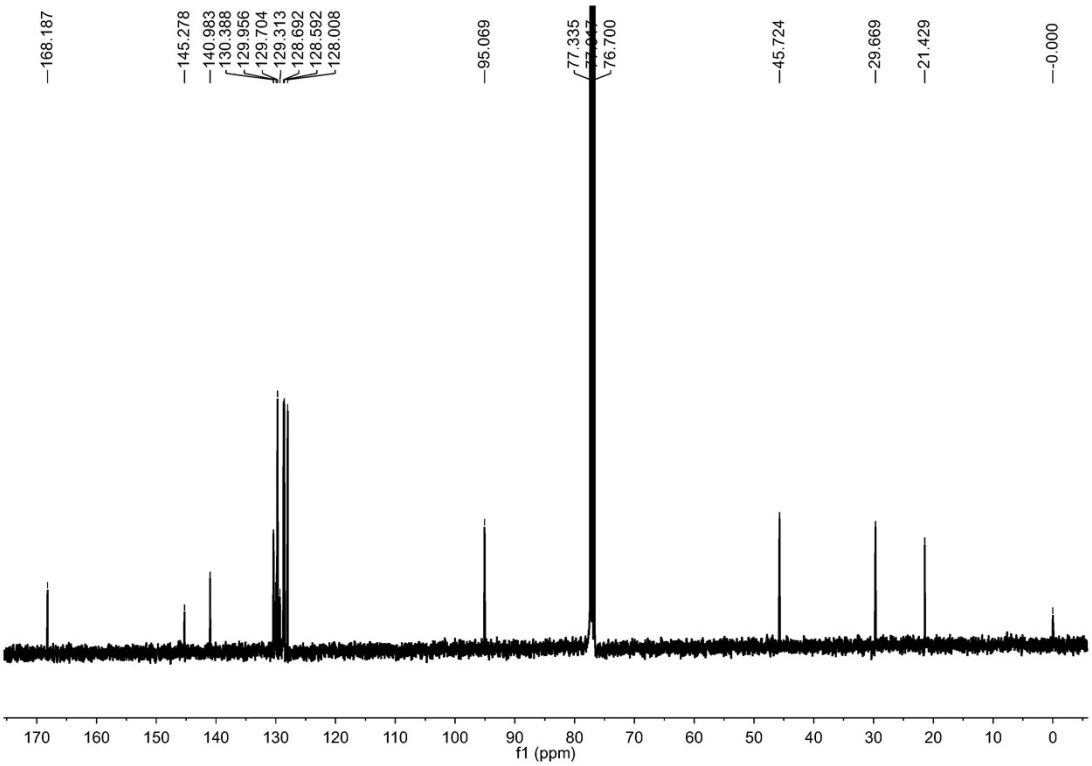
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3ha**



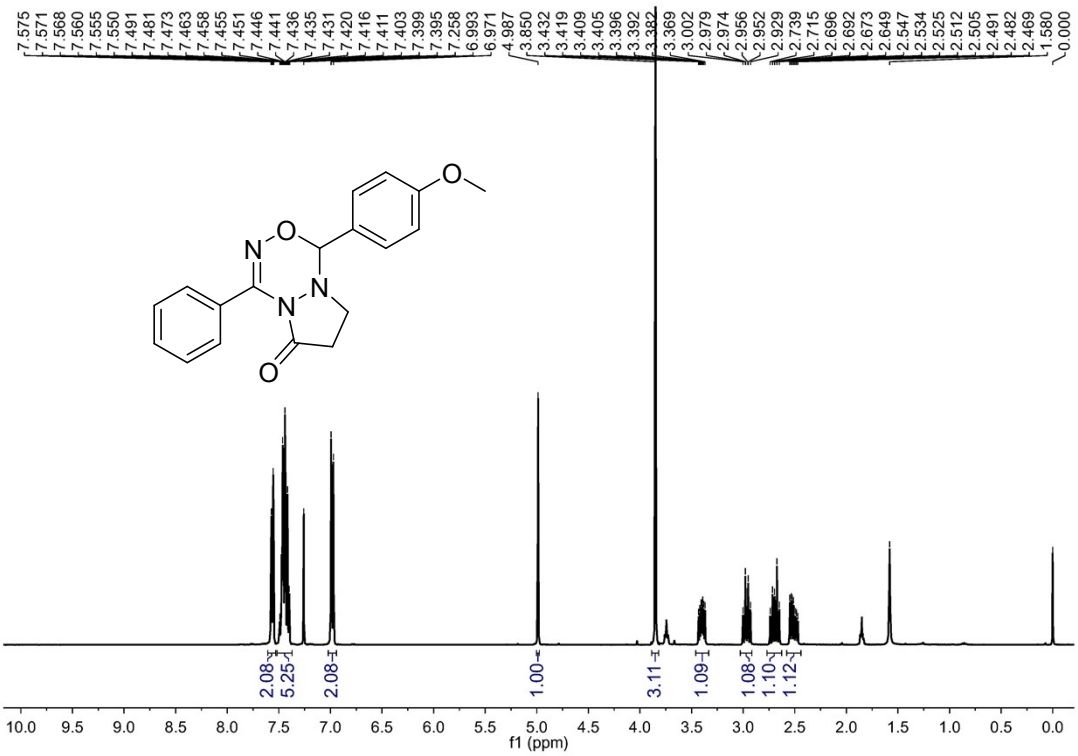
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3ha**



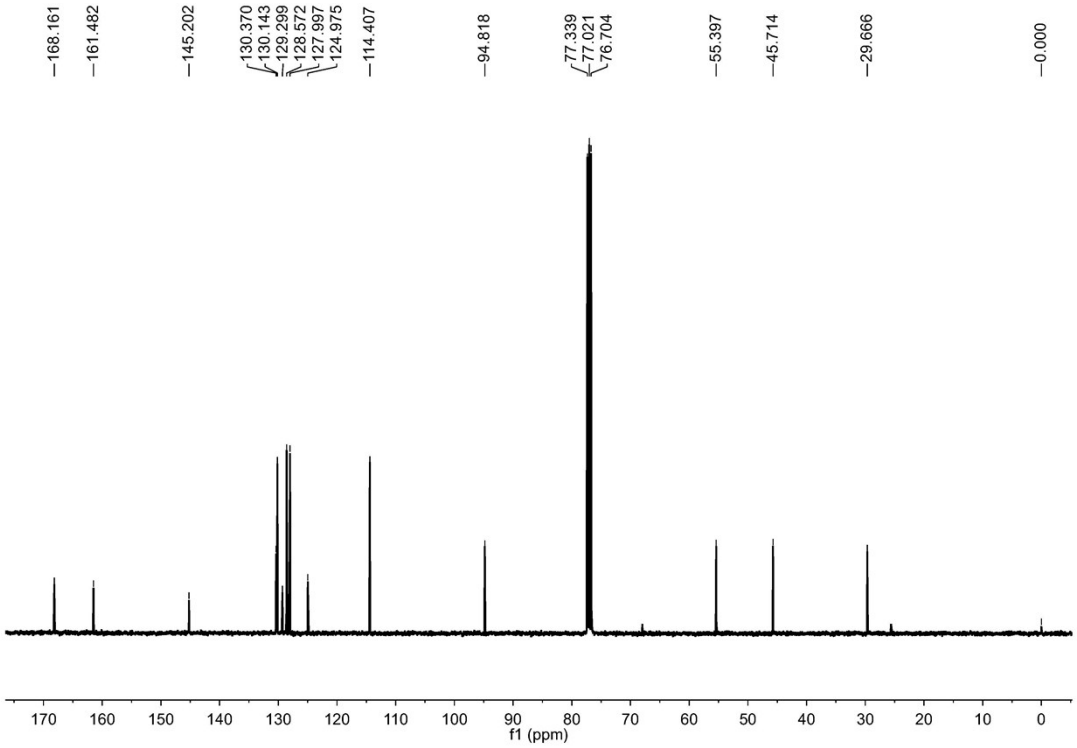
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3ia**



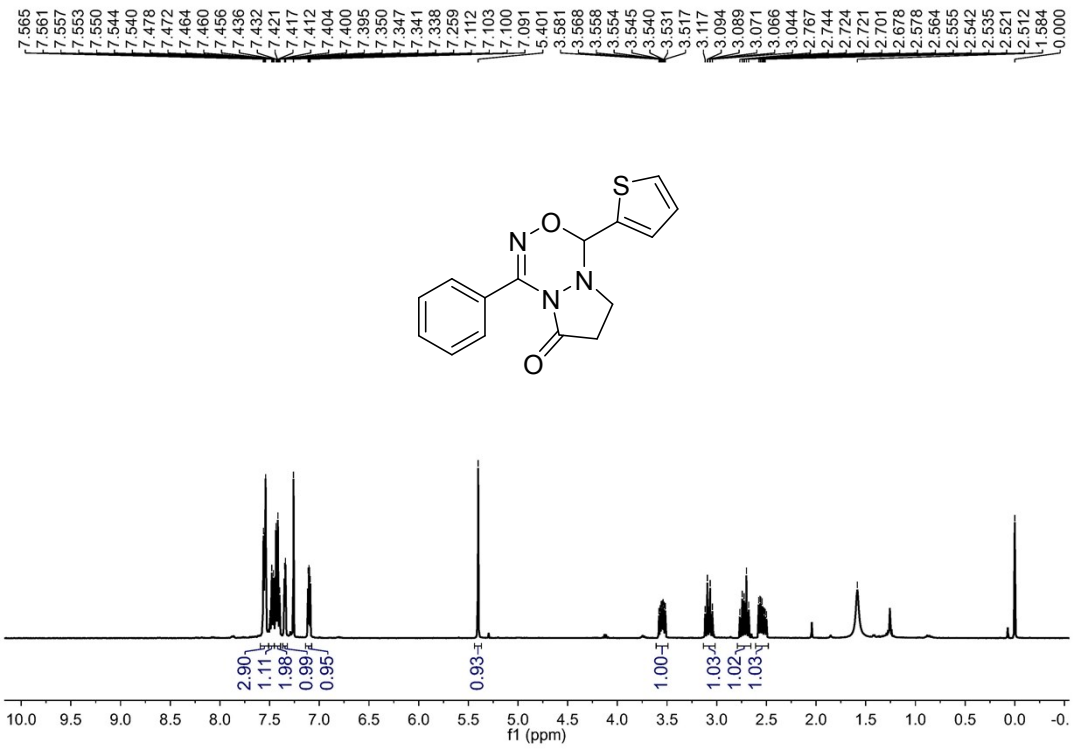
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3ia**



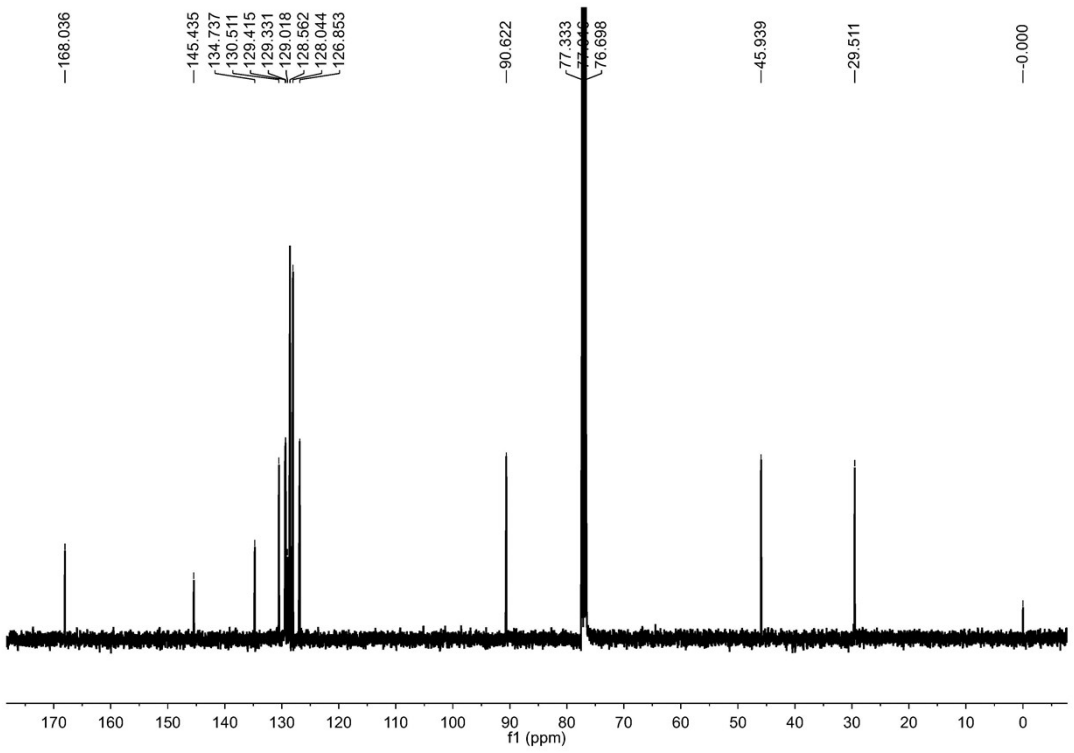
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3ja**



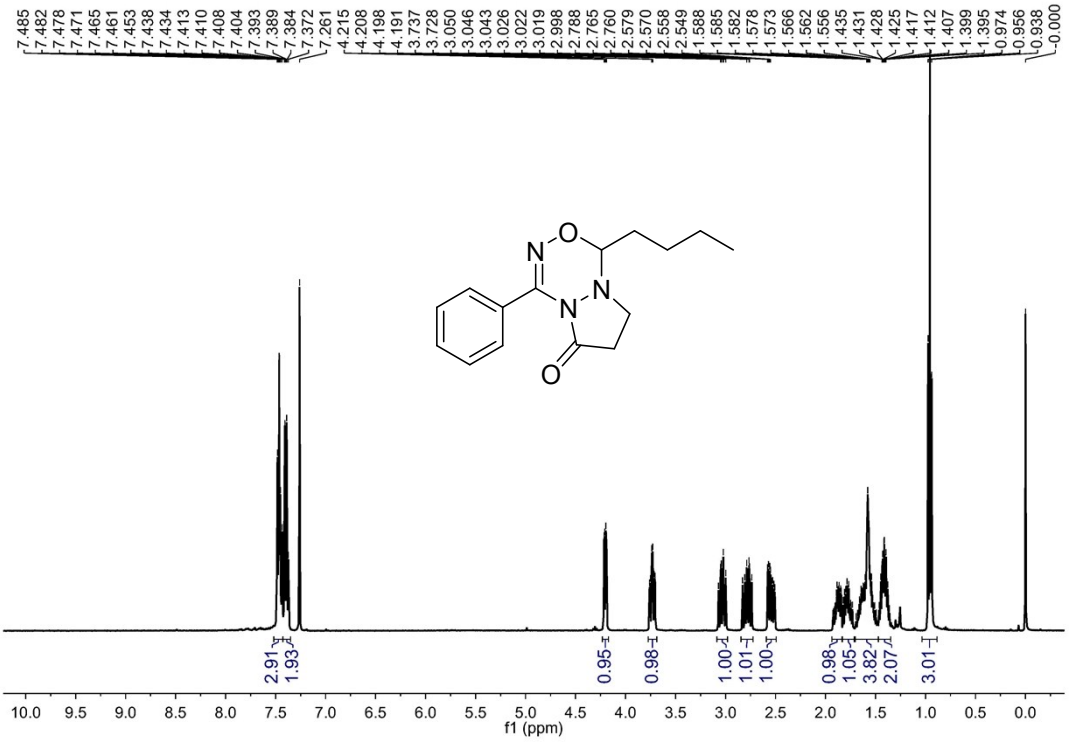
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3ja**



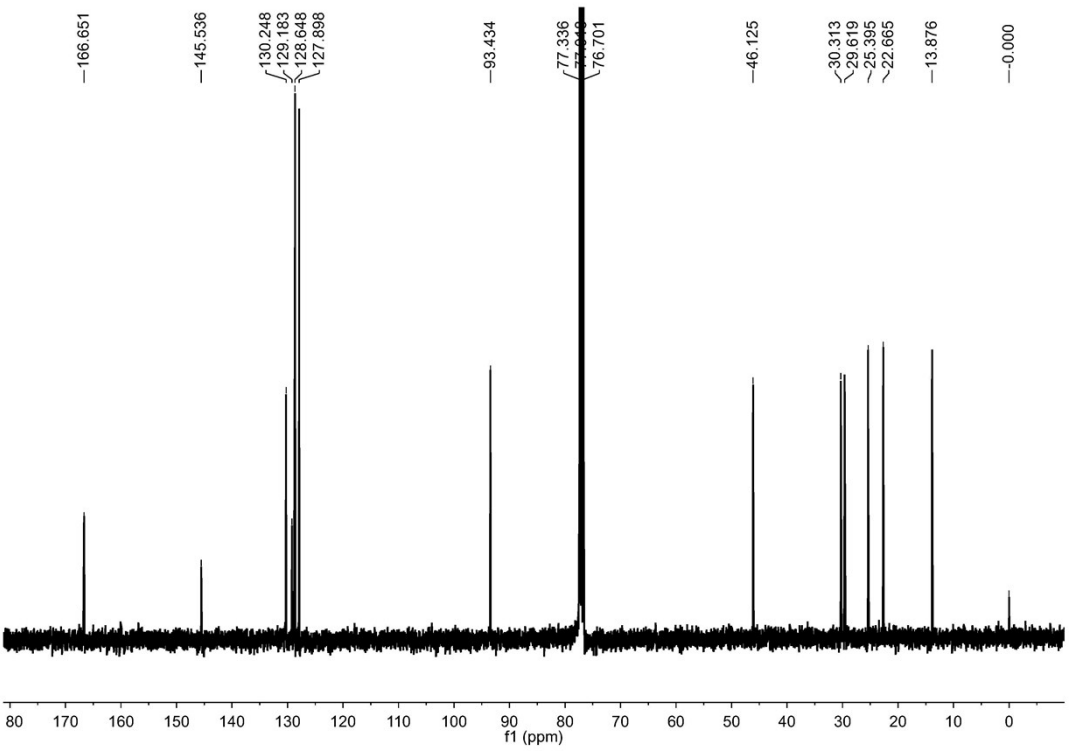
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3ka**



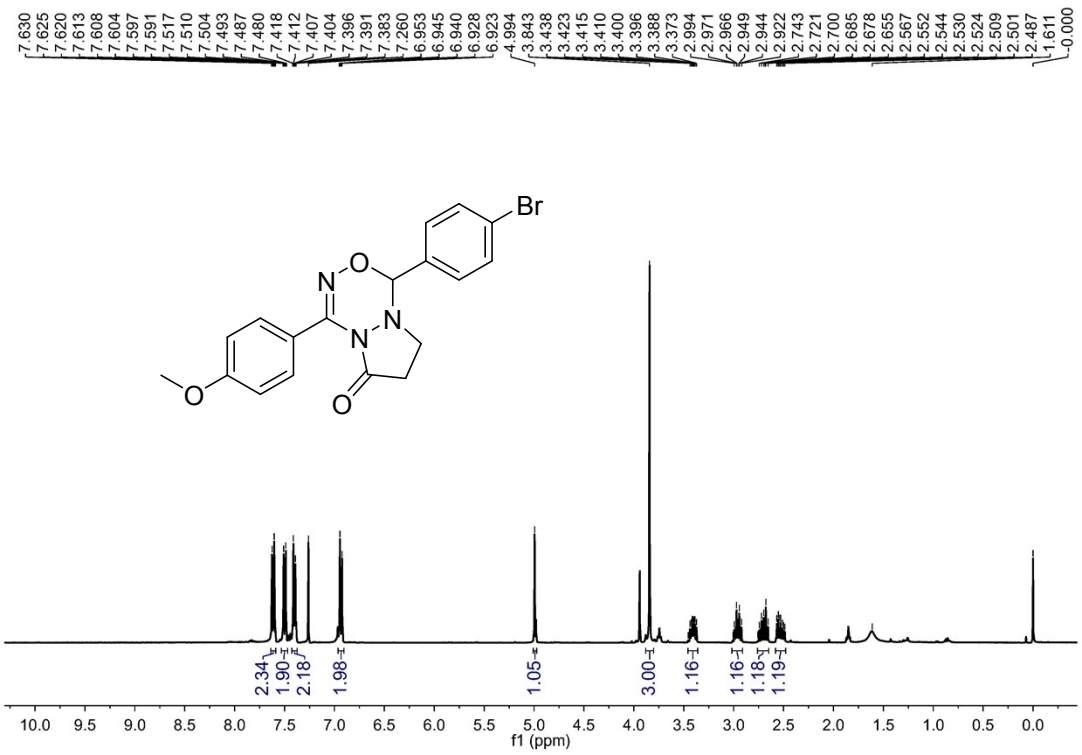
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3ka**



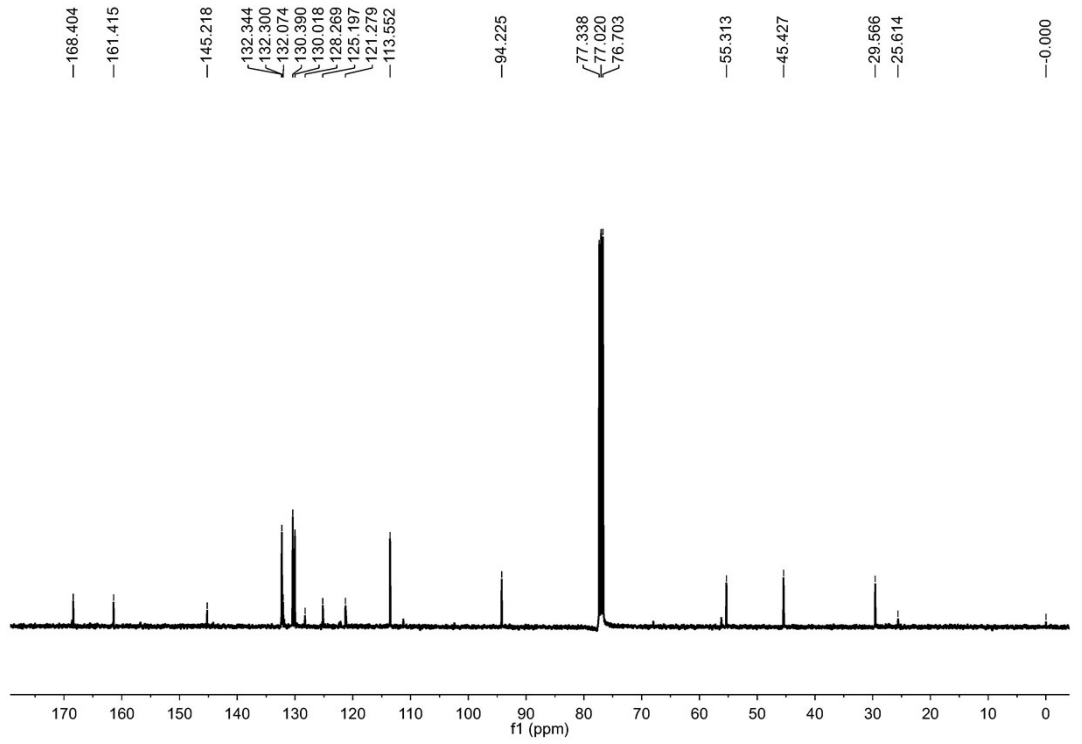
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3la**



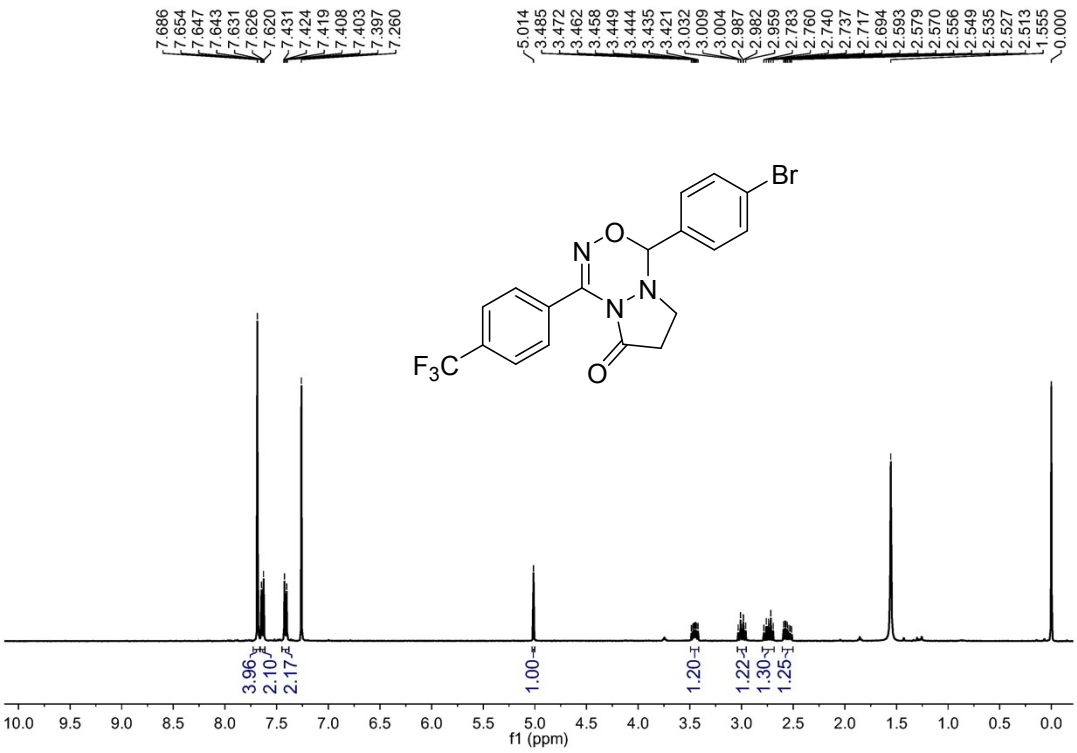
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3la**



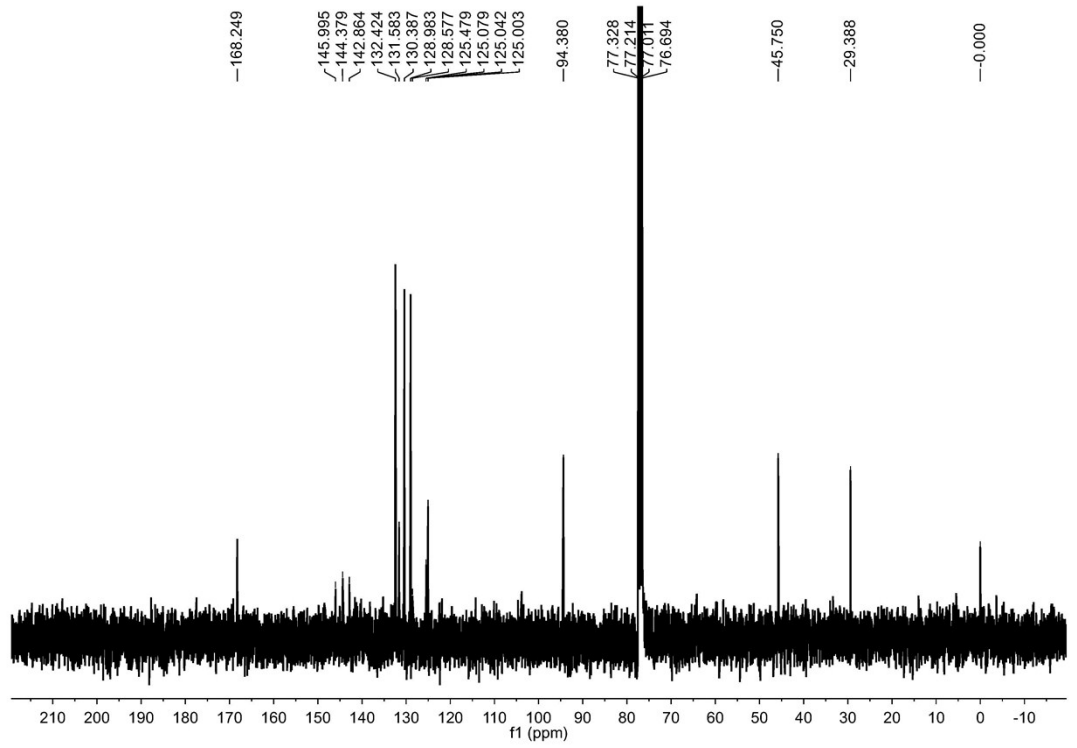
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3fe**



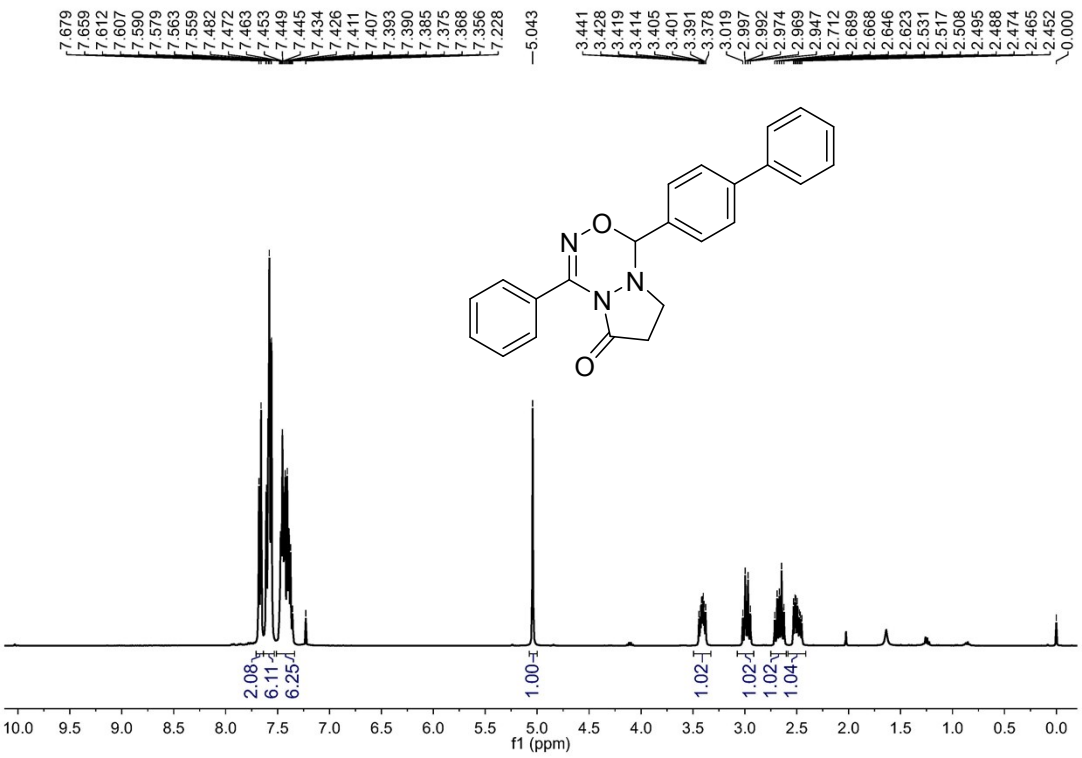
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3fe**



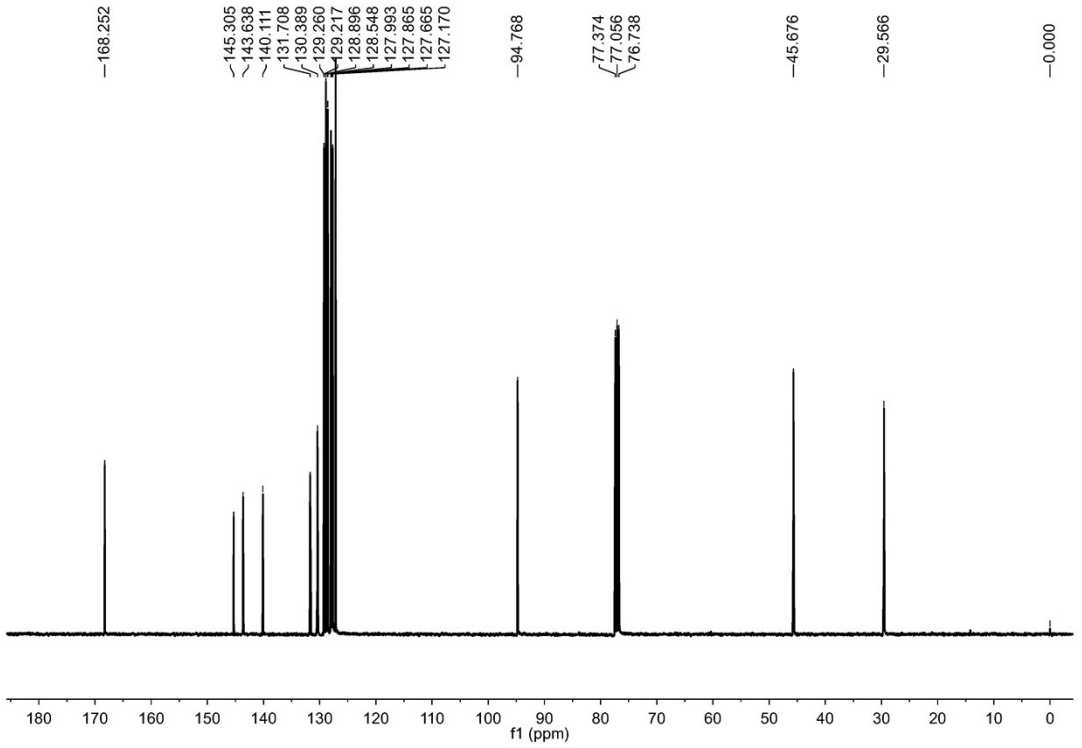
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3fk**



^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3fk**



^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **4**



^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **4**

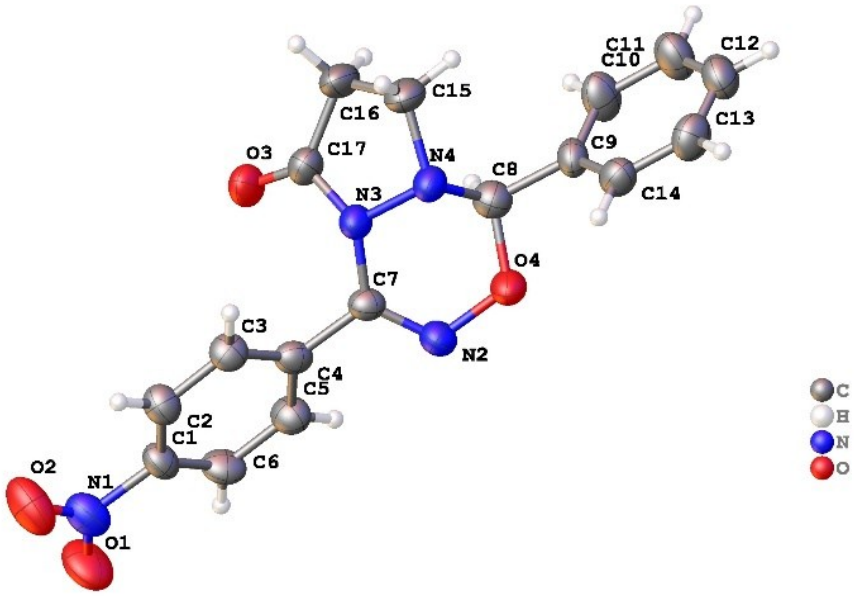


Figure S1. Crystal Structure of **3l** (50% probability level for the thermal ellipsoids).

Table S1. Crystal Data for Compound **3l**

Formula	$C_{17}H_{14}N_4O_4$
Formula weight	338.32
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	*P b c a*
Unit cell dimensions	a = 12.2898 (13) Å, α = 90 deg.
	b = 11.4074 (13) Å, β = 90 deg.
	c = 22.636 (3) Å, γ = 90 deg.
Volume	3173.5 (6) $Å^3$
Z	8
Density (calculated)	1.416 Mg / m^3
Absorption coefficient	0.104 mm^{-1}
F(000)	1408
Crystal	0.25 x 0.21 x 0.12 mm
Theta range for data collection	3.572 to 26.997 deg
Limiting indices	-15<=h<=9, -14<=k<=8, -17<=l<=28
Reflections collected	9906
Independent reflections	3429 [R(int) = 0.0849]
Data / restraints / parameters	3429 / 12 / 226
Goodness-of-fit on F^2	0.924
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0578, wR_2 = 0.0742
R indices (all data)	R_1 = 0.1541, wR_2 = 0.0984
Largest diff. peak and hole	0.160 and -0.210 e. $Å^{-3}$