Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Catalyst-free synthesis of oxazol-2(3*H*)-ones from sulfilimines and diazo compounds through a tandem rearrangement/aziridination/ring-expansion reaction

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Content

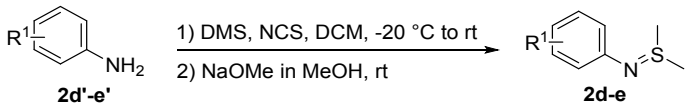
1. General Methods

Chemicals were purchased from commercial suppliers and used as delivered. The reagents **1** were prepared have been prepared according to the literature.[1] The reagents **2** were prepared in our previous reports[2] and were used directly. Dry solvents were dispensed from the solvent purification system MB SPS-800. Deuterated solvents were bought from Euriso-Top. NMR spectra were, if not mentioned otherwise, recorded at room temperature on the following spectrometers: Bruker Avance-III-300, Bruker Avance III 400, and Bruker Avance-III-500. Chemical shifts are given in ppm and coupling constants in Hz. The following abbreviations were used for ^{1}H NMR spectra to indicate the signal multiplicity: s (singlet), brs (broad singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet), sept (septet) and m (multiplet) as well as combinations of them. When combinations of multiplicities are given the first character noted refers to the biggest coupling constant. All ^{13}C NMR spectra were measured with ^{1}H-decoupling. The multiplicities mentioned in these spectra [s (singlet, quaternary carbon), d (doublet, CH-group), t (triplet, CH_2-group), q (quartet, CH_3-group)] were determined by DEPT135 spectra. Mass spectra (MS and HRMS) were determined at the chemistry department of the University of Heidelberg under the direction of Dr. J. Gross. EI^+-spectra were measured on a JOEL JMS-700 spectrometer. For ESI^+-spectra a Bruker ApexQu FT-ICR-MS spectrometer was applied. Infrared Spectroscopy (IR) was processed on an FT-IR Bruker (IF528), IR Perkin Elmer (283) or FT-IR Bruker Vector 22. The solvent or matrix is denoted in brackets. For the most significant bands the wave number ν (cm^{-1}) is given. X-ray crystal structure analyses were measured at the chemistry department of the University of Heidelberg under the direction of Dr. F. Rominger on a Bruker Smart CCD or Bruker APEX-II CCD instrument using Mo-Kα-radiation. Diffraction intensities were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using SADABS based on the Laue symmetry of reciprocal space. Heavy atom diffractions were solved by direct methods and refined against F2 with full matrix least square algorithm. Hydrogen atoms were either isotropically refined or calculated. The structures were solved and refined by Dr. F. Rominger using the SHELXTL software package. Gas Chromatography / Mass Spectrometry (GC/MS) spectra were measured on two different hardware systems: 1. HP 5972 Mass Selective Detector, coupled with a HP 5890 SERIES II plus gas chromatograph. 2. Agilent 5975C Mass Selective Detector, coupled with an Agilent 7890A gas chromatograph. In both cases, as a capillary column, an OPTIMA 5 cross-linked Methyl Silicone column (30 m x 0.32 mm, 0.25 μm) was employed and helium was used as the carrier gas. Gas Chromatography (GC) was carried out on a HP 5890 SERIES II plus gas chromatograph. As a capillary column, an OPTIMA 5 cross-linked Methyl Silicone column was employed and nitrogen was used as the carrier gas. Melting Points were measured in open glass capillaries in a Büchi melting point apparatus (according to Dr. Tottoli) and were not calibrated. Flash Column Chromatography was accomplished using Silica gel 60 (0.04 - 0.063 mm / 230 - 400 mesh ASTM) purchased from Macherey-Nagel or Aluminium oxide (neutral or basic) purchased from Macherey-Nagel. As eluents, mixtures of petroleum ether (PE), ethyl acetate (EA) were used. Analytical Thin Layer Chromatography (TLC) was carried out on precoated Macherey-Nagel POLYGRAM® SIL G/UV254 or POLYGRAM® ALOX N/UV254 plastic sheets. Detection was accomplished using UV-light (254 nm), $KMnO_4$ (in 1.5 M Na_2CO_3 (aq.)), molybdatophosphoric acid (5 % in ethanol), vanillin/H_2SO_4 (in ethanol) or anisaldehyde/HOAc (in ethanol). IUPAC names of the compounds described in the experimental section were determined with the program ACDLabs 12.0®.

2. Experimental Procedures

Substrates **2a-c**, **2f-q** were prepared and characterized in our previous work.[2] Substrates **2d-e** were prepared following the know literatures.[3]

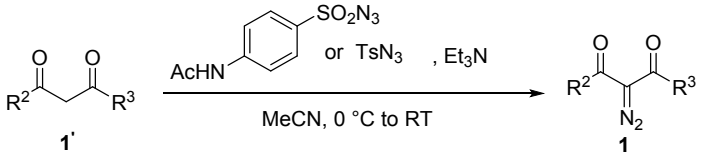
Procedure A: Synthesis of *S*,*S*-dimethyl-*N*-arylsulfilimines **2d-e**[3]



2d'-e' **2d-e**

NCS (1.33 g, 11.0 mmol) was slowly added to a solution of substituted anilines **2d'-e'** (10.0 mmol) and DMS (0.8 mL, 11.0 mmol) in 50 mL DCM at -20 °C. The resulting mixture was stirred at this temperature for 1 h and then for an additional hour at room temperature. NaOMe (25% w/w in MeOH, 4.5 mL) was added, and the resulting mixture was stirred for 10 min. After an addition of 40 mL H_2O, stirring continued for 1 h. The organic layer was separated, and the aqueous layer was extracted with DCM (3 × 40 mL). The combined organic layer was dried over anhydrous $MgSO_4$, and evaporated to give crude products. Recrystallization from Et_2O can give pure sulfilimines **2d-e**.

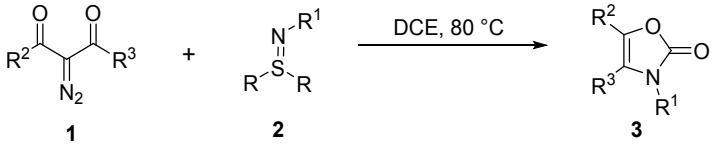
Procedure B: Synthesis of diazo compounds **1**[1]



1' **1**

At 0 °C, to a solution of 1,3-diketones **1'** (5.5 mmol, 1.1 eq.) and Et_3N (6 mmol, 1.2 eq.) in 30 mL acetonitrile was added 4-acetamidobenzenesulfonyl azide (5 mmol, 1.0 eq) or tosyl azide (5 mmol, 1.0 eq). The resulting reaction mixture was stirred for 1 h at 0 °C and another 4 h at room temperature. The solvent was removed under vacuum, and to the residue was added 50 mL EtOAc and 50 mL H_2O. The organic layer was separated, washed with brine, dried over anhydrous $MgSO_4$ and evaporated under vacuum. The residue was purified through column chromatography using EtOAc and petroleum ether as eluent to give the corresponding diazo compounds **1**.

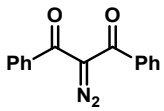
Procedure C: Synthesis of oxazol-2(3*H*)-ones **3** from diazo compounds **1** and sulfilimines **2**



1 **2** **3**

A reaction vial (3 mL in volume) was charged with sulfilimine **2** (0.2 mmol), diazo compound **1** (0.3 mmol) and a stirring bar. 2 mL Anhydrous DCE was added and the resulting mixture was stirred at 80 °C. After the full conversion of starting material **2** was observed by TLC, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using EtOAc and petroleum as eluent to provide the corresponding product **3**.

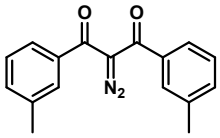
3. Characterization Data



2-diazo-1,3-diphenylpropane-1,3-dione (1a)

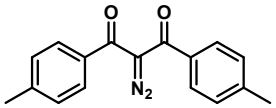
Yield: 566 mg, 90%; yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56-7.46 (m, 4H), 7.40-7.33 (m, 2H), 7.28-7.20 (m, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.4 (s, 2C), 136.9 (s, 2C), 132.5 (d, 2C), 128.3 (d, 4C), 128.2 (d, 4C), 84.3 (s) ppm.

The data is consistent with the previous literature.[4]



2-diazo-1,3-di-*m*-tolylpropane-1,3-dione (1b)

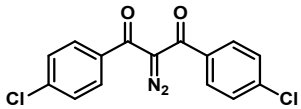
Yield: 461 mg, 83%; yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.22 (m, 4H), 7.17-7.07 (m, 4H), 2.20 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.8 (s, 2C), 138.1 (s, 2C), 137.0 (s, 2C), 133.2 (d, 2C), 128.9 (d, 2C), 128.2 (d, 2C), 125.5 (d, 2C), 84.9 (s), 21.1 (q, 2C) ppm; HRMS $C_{17}H_{15}N_2O_2$ calcd for 279.1128, found 279.1128.



2-diazo-1,3-di-*p*-tolylpropane-1,3-dione (1c)

Yield: 478 mg, 86%; yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, J = 8.1 Hz, 4H), 7.05 (d, J = 8.1 Hz, 4H), 2.26 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.2 (s, 2C), 143.5 (s, 2C), 134.4 (s, 2C), 129.0 (d, 4C), 128.6 (d, 4C), 83.2 (s), 21.6 (q, 2C) ppm.

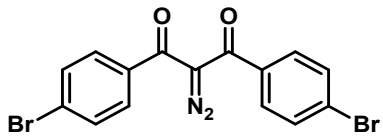
The data is consistent with the previous literature.[5]



1,3-bis(4-chlorophenyl)-2-diazopropane-1,3-dione (1d)

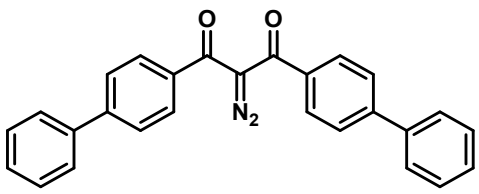
Yield: 530 mg, 83%; yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50-7.41 (m, 4H), 7.30-7.22 (m, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.8 (s, 2C), 139.3 (s, 2C), 135.1 (s, 2C), 129.8 (d, 4C), 128.8 (d, 4C), 84.3 (s) ppm.

The data is consistent with the previous literature.[5]



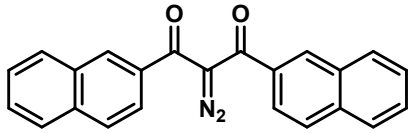
1,3-bis(4-bromophenyl)-2-diazopropane-1,3-dione (1e)

Yield: 620 mg, 76%; yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48-7.40 (m, 4H), 7.40-7.33 (m, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.0 (s, 2C), 135.5 (s, 2C), 131.8 (d, 4C), 129.8 (d, 4C), 127.8 (s, 2C), 84.3 (s) ppm; HRMS $C_{15}H_9{}^{79}Br_2N_2O_2$ calcd for 406.9025, found 406.9023.



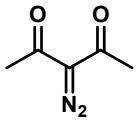
1,3-di([1,1'-biphenyl]-4-yl)-2-diazopropane-1,3-dione (1g)

Yield: 602 mg, 75%; yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63-7.55 (m, 4H), 7.50-7.40 (m, 8H), 7.37-7.25 (m, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.9 (s, 2C), 145.5 (s, 2C), 139.7 (s, 2C), 135.6 (s, 2C), 129.0 (d, 4C), 128.8 (d, 4C), 128.1 (d, 2C), 127.2 (d, 4C), 126.9 (d, 4C), 84.4 (s) ppm; HRMS $C_{27}H_{19}N_2O_2$ calcd for 403.1441, found 403.1429.



2-diazo-1,3-di(naphthalen-2-yl)propane-1,3-dione (1h)

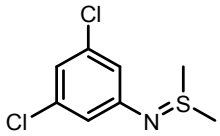
Yield: 630 mg, 90%; yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (s, 2H), 7.85-7.55 (m, 8H), 7.50-7.32 (m, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.3 (s, 2C), 135.1 (s, 2C), 134.2 (s, 2C), 132.1 (s, 2C), 129.7 (d, 2C), 129.1 (d, 2C), 128.3 (d, 4C), 127.6 (d, 2C), 126.8 (d, 2C), 124.2 (d, 2C), 84.3 (s) ppm; HRMS $C_{23}H_{15}N_2O_2$ calcd for 351.1128, found 351.1124.



3-diazopentane-2,4-dione (1i)

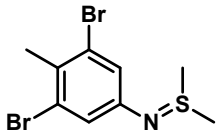
Yield: 90%; yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.37 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 188.2 (s, 2C), 84.6 (s), 28.4 (q, 2C) ppm.

The data is consistent with the previous literature.[4]



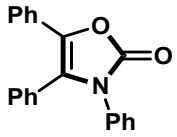
***N*-(3,5-dichlorophenyl)-1,1-dimethyl-λ^4-sulfanimine (2d)**

Yield: 677 mg, 61%; gray solid, 119-120 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.61 (d, J = 2.0 Hz, 2H), 6.54 (t, J = 2.0 Hz, 1H), 2.56 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.4 (s), 135.1 (s, 2C), 116.5 (d), 116.0 (d, 2C), 36.2 (q, 2C) ppm; HRMS (EI) (*m/z*) $C_8H_9{}^{35}Cl_2NS$ calcd for 220.9833, found 220.9833.



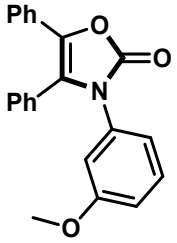
***N*-(3,5-dibromo-4-methylphenyl)-1,1-dimethyl-λ^4-sulfanimine (2e)**

Yield: 845 mg, 52%; light yellow crystal, 149-150 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.93 (s, 2H), 2.57 (s, 6H), 2.35 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.5 (s), 125.3 (s, 2C), 124.6 (s), 121.1 (d, 2C), 36.4 (q, 2C), 22.3 (q) ppm. IR (reflection) $\tilde{\nu}$ = 3414, 2917, 1606, 1555, 1494, 1381, 1289, 1245, 1115, 1031, 997, 885, 833, 739, 680 cm^{-1}; HRMS (EI) (*m/z*) $C_9H_{12}{}^{81}Br_2NS$ calcd for 325.9031, found 325.9031.



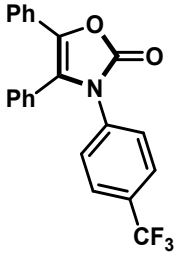
3,4,5-triphenyloxazol-2(3*H*)-one (3aa)[6]

Yield: 95%; white solid, mp: 231-233 ºC; R_f = 0.50 (EA/PE = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.13 (m, 13H), 7.09-7.03 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6 (s), 135.2 (s), 133.7 (s), 130.3 (d, 2C), 129.6 (d), 129.0 (d, 4C), 128.6 (d, 2C), 128.1 (d), 127.9 (d), 127.7 (s), 127.1 (s), 127.0 (d, 2C), 125.1 (d, 2C), 123.6 (s) ppm; IR (reflection) $\tilde{\nu}$ = 3488, 3054, 1963, 1747, 1673, 1595, 1490, 1445, 1376, 1315, 1292, 1268, 1183, 1146, 1076, 1060, 1028, 1003, 988, 954, 919, 841, 774, 763, 744, 704, 694, 666, 616 cm^{-1}; HRMS (DART) (*m/z*) [M+H] $C_{21}H_{16}NO_2$ calcd for 314.1176, found 314.1174.



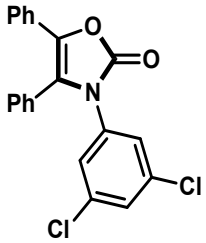
3-(3-methoxyphenyl)-4,5-diphenyloxazol-2(3*H*)-one (3ab)

Yield: 67%; white solid, mp: 199-200 ºC; R_f = 0.41 (EA/PE = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.23 (m, 5H), 7.21-7.15 (m, 5H), 7.13-7.08 (m, 1H), 6.75-6.69 (m, 1H), 6.68-6.63 (m, 1H), 6.61-6.58 (m, 1H), 3.58 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9 (s), 153.5 (s), 135.2 (s), 134.6 (s), 130.3 (d, 2C), 129.7 (d), 129.6 (d), 129.1 (d, 2C), 128.5 (d, 2C), 128.1 (d), 127.7 (s), 127.2 (s), 125.1 (d, 2C), 123.6 (s), 119.2 (d), 114.1 (d), 112.5 (d), 55.3 (q) ppm; IR (reflection) $\tilde{\nu}$ = 3070, 2965, 2833, 1954, 1748, 1669, 1601, 1592, 1494, 1464, 1446, 1373, 1321, 1288, 1265, 1253, 1154, 1074, 1059, 1042, 1029, 1009, 960, 919, 881, 846, 800, 790, 768, 745, 706, 693, 678, 666, 653, 616 cm^{-1}; HRMS (DART) (*m/z*) [M+H] $C_{22}H_{18}NO_3$ calcd for 344.1281, found 344.1282.



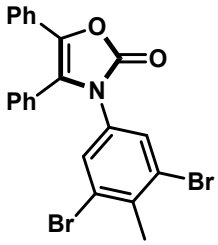
4,5-diphenyl-3-(4-(trifluoromethyl)phenyl)oxazol-2(3*H*)-one (3ac)

Yield: 99%; colourless solid, mp: 156-158 ºC; R_f = 0.70 (EA/PE = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.4 Hz, 2H), 7.37-7.26 (m, 5H), 7.23-7.13 (m, 7H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2 (s), 136.9 (s), 135.8 (s), 130.2 (d, 2C), 129.9 (d), 129.6 (q, $J_{C\text{-}F}$ = 32.7 Hz), 129.4 (d, 2C), 128.6 (d, 2C), 128.5 (d), 127.3 (s), 126.74 (s), 126.71 (d, 2C), 126.1 (q, $J_{C\text{-}F}$ = 3.7 Hz, 2C), 125.2 (d, 2C), 123.6 (q, $J_{C\text{-}F}$ = 270.5 Hz), 122.8 (s) ppm; IR (reflection) $\tilde{\nu}$ = 3515, 3066, 3030, 1762, 1661, 1618, 1602, 1577, 1523, 1501, 1446, 1417, 1386, 1356, 1324, 1254, 1167, 1124, 1107, 1066, 1056, 1027, 993, 954, 853, 830, 768, 746, 707, 691, 666, 635, 618 cm^{-1}; HRMS (DART) (*m/z*) [M+H] $C_{22}H_{15}F_3NO_2$ calcd for 382.1049, found 382.1048.



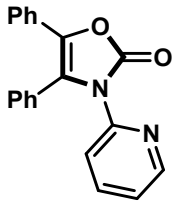
3-(3,5-dichlorophenyl)-4,5-diphenyloxazol-2(3*H*)-one (3ad)

Yield: 86%; colourless solid, mp: 216-217 ºC; R_f = 0.75 (EA/PE = 1/5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.25 (m, 5H), 7.22-7.13 (m, 6H), 6.98 (d, *J* = 1.8 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.8 (s), 135.7 (s), 135.4 (s), 135.1 (s, 2C), 130.1 (d, 2C), 130.0 (d), 129.4 (d, 2C), 128.6 (d, 2C), 128.5 (d), 127.9 (d), 127.1 (s), 126.4 (s), 125.13 (d, 2C), 125.12 (d, 2C), 122.6 (s) ppm; IR (reflection) $\tilde{\nu}$ = 3088, 1760, 1671, 1585, 1572, 1498, 1452, 1430, 1395, 1368, 1318, 1290, 1267, 1240, 1199, 1180, 1146, 1114, 1095, 1060, 1026, 996, 923, 898, 859, 806, 776, 759, 745, 705, 695, 665, 616 cm^{-1}; HRMS (DART) (*m/z*) [M+H] $C_{21}H_{14}{}^{35}Cl_2NO_2$ calcd for 382.0396, found 382.0398.8



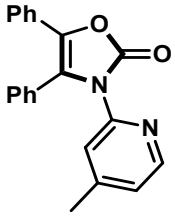
3-(3,5-dibromo-4-methylphenyl)-4,5-diphenyloxazol-2(3*H*)-one (3ae)

Yield: 76%; colourless solid, mp: 187-189 ºC; R_f = 0.77 (EA/PE = 1/5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.25 (m, 5H), 7.24 (s, 2H), 7.22-7.16 (m, 5H), 2.42 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.1 (s), 137.4 (s, 2C), 135.6 (s), 132.6 (s), 130.3 (d, 2C), 130.0 (d), 129.8 (d, 2C), 129.4 (d, 2C), 128.6 (d, 2C), 128.4 (d), 127.3 (s), 126.5 (s), 125.1 (d, 2C), 124.8 (s), 122.9 (s), 23.4 (q) ppm; IR (reflection) $\tilde{\nu}$ = 3079, 3051, 1769, 1597, 1548, 1503, 1467, 1449, 1392, 1370, 1318, 1293, 1258, 1216, 1183, 1146, 1077, 1061, 1028, 998, 955, 932, 915, 873, 861, 802, 767, 747, 737, 711, 695, 674, 664, 643, 616 cm^{-1}; HRMS (DART) (*m/z*) [M+H] $C_{22}H_{16}{}^{81}Br_2NO_2$ calcd for 485.9522, found 485.9527.



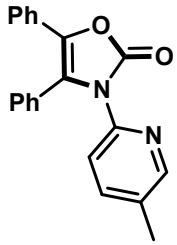
4,5-diphenyl-3-(pyridin-2-yl)oxazol-2(3*H*)-one (3af)

Yield: 82%; colourless solid, mp: 198-199 ºC; R_f = 0.22 (EA/PE = 1/5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25-8.18 (m, 1H), 7.67 (dt, *J* = 1.5, 7.8 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.34-7.15 (m, 10H), 7.12-7.05 (m, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.3 (s), 148.9 (d), 147.6 (s), 138.2 (d), 135.5 (s), 130.2 (d, 2C), 129.2 (d), 128.8 (d, 2C), 128.5 (d, 2C), 128.3 (d), 127.6 (s), 127.5 (s), 125.3 (d, 2C), 123.1 (s), 122.7 (d), 121.2 (d) ppm; IR (reflection) $\tilde{\nu}$ = 2925, 1753, 1671, 1589, 1574, 1503, 1471, 1438, 1371, 1290, 1263, 1211, 1148, 1062, 787, 769, 751, 741, 720, 705, 695, 667, 619 cm^{-1}; HRMS (DART) (*m/z*) [M+H] $C_{20}H_{15}N_2O_2$ calcd for 315.1128, found 315.1125.



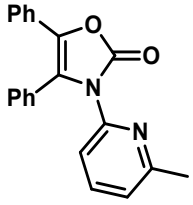
3-(4-methylpyridin-2-yl)-4,5-diphenyloxazol-2(3*H*)-one (3ag)

Yield: 82%; colourless solid, mp: 169-170 ºC; R_f = 0.27 (EA/PE = 1/5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, *J* = 6.5 Hz, 1H), 7.35-7.21 (m, 8H), 7.20-7.17 (m, 3H), 6.91 (d, *J* = 4.8 Hz, 1H), 2.30 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.4 (s), 149.9 (s), 148.4 (d), 147.6 (s), 135.5 (s), 130.2 (d, 2C), 129.1 (d), 128.7 (d, 2C), 128.5 (d, 2C), 128.2 (d), 127.7 (s), 127.6 (s), 125.3 (d, 2C), 123.9 (d), 123.3 (s), 121.9 (d), 21.0 (q) ppm; IR (reflection) $\tilde{\nu}$ = 3035, 2962, 2923, 1754, 1605, 1562, 1502, 1481, 1447, 1420, 1357, 1298, 1261, 1243, 1146, 1061, 1043, 994, 978, 957, 918, 878, 836, 808, 768, 756, 742, 719, 706, 691, 666, 617 cm^{-1}; HRMS (DART) (*m/z*) [M+H] $C_{21}H_{17}N_2O_2$ calcd for 329.1285, found 329.1283.



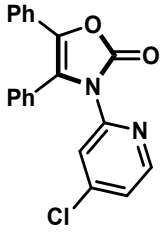
3-(5-methylpyridin-2-yl)-4,5-diphenyloxazol-2(3*H*)-one (3ah)

Yield: 80%; colourless solid, mp: 184-185 ºC; R_f = 0.28 (EA/PE = 1/5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.46 (dd, *J* = 8.1, 2.4 Hz, 1H), 7.34-7.20 (m, 8H), 7.20-7.13 (m, 3H), 2.21 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.4 (s), 149.3 (d), 145.2 (s), 138.8 (d), 135.4 (s), 132.8 (s), 130.2 (d, 2C), 129.2 (d), 128.8 (d, 2C), 128.5 (d, 2C), 128.2 (d), 127.63 (s), 127.59 (s), 125.2 (d, 2C), 123.3 (s), 120.8 (d), 18.0 (q) ppm; IR (reflection) $\tilde{\nu}$ = 3500, 3060, 2960, 1752, 1673, 1595, 1579, 1479, 1444, 1387, 1365, 1314, 1289, 1262, 1200, 1147, 1057, 1027, 1008, 953, 921, 822, 802, 772, 754, 744, 698, 664, 644, 610 cm^{-1}; HRMS (DART) (*m/z*) [M+H] $C_{21}H_{17}N_2O_2$ calcd for 329.1285, found 329.1283.



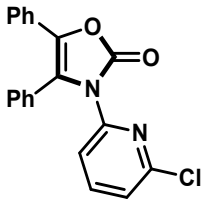
3-(6-methylpyridin-2-yl)-4,5-diphenyloxazol-2(3*H*)-one (3ai)

Yield: 88%; colourless solid, mp: 195-196 ºC; R_f = 0.39 (EA/PE = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.50 (m, 1H), 7.33-7.21 (m, 8H), 7.20-7.15 (m, 3H), 6.92 (d, *J* = 8.0 Hz, 1H), 2.19 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1 (s), 153.2 (s), 146.8 (s), 138.4 (d), 135.5 (s), 130.4 (d, 2C), 129.1 (d), 128.6 (d, 2C), 128.5 (d, 2C), 128.1 (d), 128.0 (s), 127.7 (s), 125.2 (d, 2C), 123.3 (s), 122.1 (d), 117.7 (d), 23.8 (q) ppm; IR (reflection) $\tilde{\nu}$ = 3514, 3064, 3029, 2960, 2919, 1763, 1672, 1598, 1570, 1500, 1458, 1370, 1293, 1268, 1214, 1156, 1144, 1090, 1068, 1046, 1025, 1000, 980, 956, 911, 877, 818, 797, 768, 748, 738, 697, 687, 666, 658, 616 cm^{-1}; HRMS (DART) (*m/z*) [M+H] $C_{21}H_{17}N_2O_2$ calcd for 329.1285, found 329.1281.



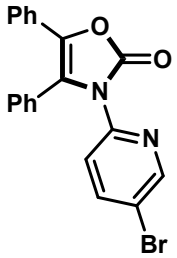
3-(4-chloropyridin-2-yl)-4,5-diphenyloxazol-2(3*H*)-one (3aj)

Yield: 99%; colourless solid, mp: 187-188 ºC; R_f = 0.47 (EA/PE = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 5.2 Hz, 1H), 7.54 (d, *J* = 1.6 Hz, 1H), 7.33-7.20 (m, 7H), 7.20-7.16 (m, 3H), 7.07 (dd, *J* = 5.6, 2.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9 (s), 149.1 (d), 148.6 (s), 145.6 (s), 135.9 (s), 130.2 (d, 2C), 129.4 (d), 128.8 (d, 2C), 128.6 (d, 2C), 128.5 (d), 127.6 (s), 127.3 (s), 125.3 (d, 2C), 123.0 (d), 122.8 (s), 121.0 (d) ppm; HRMS (DART) (*m/z*) [M+H] $C_{20}H_{14}{}^{35}ClN_2O_2$ calcd for 349.0738, found 349.0738.



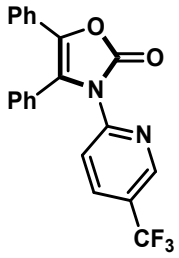
3-(6-chloropyridin-2-yl)-4,5-diphenyloxazol-2(3*H*)-one (3ak)

Yield: 99%; colourless solid, mp: 200-202 ºC; R_f = 0.50 (EA/PE = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (t, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.35-7.24 (m, 7H), 7.20-7.15 (m, 3H), 7.08 (d, *J* = 7.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8 (s), 149.7 (s), 147.2 (s), 140.5 (d), 135.9 (s), 130.5 (d, 2C), 129.5 (d), 128.8 (d, 2C), 128.6 (d, 2C), 128.4 (d), 127.5 (s), 127.3 (s), 125.2 (d, 2C), 122.9 (d), 122.8 (s), 118.5 (d) ppm; IR (reflection) $\tilde{\nu}$ = 3519, 3089, 3065, 3032, 1764, 1671, 1567, 1501, 1435, 1373, 1318, 1294, 1265, 1214, 1167, 1136, 1061, 1029, 988, 955, 911, 857, 809, 763, 746, 733, 697, 679, 666, 651, 617 cm^{-1}; HRMS (DART) (*m/z*) [M+H] $C_{20}H_{14}{}^{35}ClN_2O_2$ calcd for 349.0738, found 349.0738.



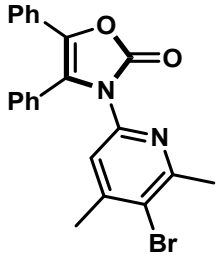
3-(5-bromopyridin-2-yl)-4,5-diphenyloxazol-2(3*H*)-one (3al)

Yield: 94%; colourless solid, mp: 193-194 ºC; R_f = 0.63 (EA/PE = 1/5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (d, *J* = 1.8 Hz, 1H), 7.78 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.32-7.15 (m, 10H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.9 (s), 149.7 (d), 146.3 (s), 140.8 (d), 135.8 (s), 130.2 (d, 2C), 129.4 (d), 128.9 (d, 2C), 128.6 (d, 2C), 128.4 (d), 127.5 (s), 127.3 (s), 125.3 (d, 2C), 122.8 (s), 121.9 (d), 119.1 (s) ppm; IR (reflection) $\tilde{\nu}$ = 3065, 1754, 1666, 1602, 1574, 1502, 1460, 1448, 1382, 1360, 1296, 1261, 1207, 1149, 1126, 1093, 1077, 1057, 1024, 1007, 953, 925, 846, 824, 770, 759, 746, 708, 692, 666, 630, 616 cm^{-1}; HRMS (DART) (*m/z*) [M+H] $C_{20}H_{14}{}^{81}BrN_2O_2$ calcd for 395.0213, found 395.0211.



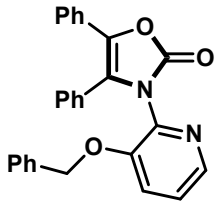
4,5-diphenyl-3-(5-(trifluoromethyl)pyridin-2-yl)oxazol-2(3*H*)-one (3am)

Yield: 89%; colourless solid, mp: 140-142 ºC; R_f = 0.72 (EA/PE = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.91 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.36-7.22 (m, 7H), 7.20-7.16 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8 (s), 150.6 (s), 145.6 (q, J_{C-F} = 4.1 Hz), 136.3 (s), 135.5 (q, J_{C-F} = 3.3 Hz), 130.3 (d, 2C), 129.5 (d), 128.9 (d, 2C), 128.6 (d, 3C), 127.7 (s), 127.2 (s), 125.4 (d, 2C), 124.9 (q, J_{C-F} = 33.3 Hz), 123.1 (q, J_{C-F} = 270.6 Hz), 122.5 (s), 119.6 (d) ppm; IR (reflection) $\tilde{\nu}$ = 1765, 1674, 1603, 1581, 1487, 1448, 1402, 1368, 1327, 1291, 1261, 1205, 1168, 1159, 1123, 1082, 1059, 1026, 1010, 978, 943, 852, 837, 775, 765, 747, 704, 694, 664, 636, 609 cm^{-1}; HRMS (DART) (*m/z*) [M+H] $C_{21}H_{14}F_3N_2O_2$ calcd for 383.1002, found 383.1001.



3-(5-bromo-4,6-dimethylpyridin-2-yl)-4,5-diphenyloxazol-2(3*H*)-one (3an)

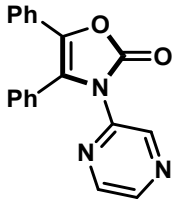
Yield: 61%; colourless solid, mp: 168-170 ºC; R_f = 0.72 (EA/PE = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.22 (m, 8H), 7.19-7.14 (m, 3H), 2.33 (s, 3H), 2.24 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6 (s), 153.0 (s), 149.8 (s), 145.0 (s), 135.6 (s), 130.5 (d, 2C), 129.2 (d), 128.6 (d, 2C), 128.5 (d, 2C), 128.2 (d), 128.0 (s), 127.5 (s), 125.2 (d, 2C), 123.1 (s), 122.5 (s), 119.6 (d), 24.8 (q), 23.5 (q) ppm; IR (reflection) $\tilde{\nu}$ = 3056, 2995, 2958, 2920, 1764, 1660, 1583, 1551, 1499, 1488, 1444, 1385, 1361, 1350, 1275, 1256, 1184, 1137, 1089, 1062, 1025, 986, 959, 931, 913, 861, 797, 766, 749, 736, 706, 690, 662, 617 cm^{-1}; HRMS (DART) (*m/z*) [M+H] $C_{22}H_{18}{}^{79}BrN_2O_2$ calcd for 421.0546, found 421.0547.



3-(3-(benzyloxy)pyridin-2-yl)-4,5-diphenyloxazol-2(3*H*)-one (3ao)

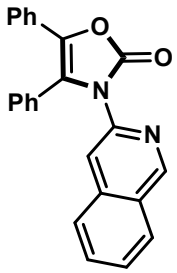
Yield: 58%; colourless solid, mp: 188-190 ºC; R_f = 0.11 (EA/PE = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 4.0, 2.0 Hz, 1H), 7.35-7.29 (m, 2H), 7.27-7.13 (m, 13H), 7.13-7.10 (m, 2H), 5.02 (d, *J* = 12.4 Hz, 1H), 4.99 (d, *J* = 12.4 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1 (s), 151.2 (s), 140.9 (d), 137.2 (s), 135.5 (s), 135.2 (s), 129.9 (d, 2C), 129.2 (d), 128.7 (d, 2C), 128.6 (d, 2C), 128.5 (d, 2C), 128.3 (d), 128.0 (d), 127.9 (s), 127.2 (s), 127.0 (d, 2C), 125.5 (d), 125.1 (d, 2C), 124.2 (s), 121.8 (d), 70.6 (t) ppm; IR (reflection) $\tilde{\nu}$ = 3064, 2929, 1763, 1573,

1500, 1452, 1372, 1284, 1266, 1225, 1179, 1153, 1124, 1061, 1027, 1008, 954, 914, 852, 799, 749, 696, 667, 617 cm^{-1}; HRMS (DART) (*m/z*) [M+H] $C_{27}H_{21}N_2O_3$ calcd for 421.1547, found 421.1547.



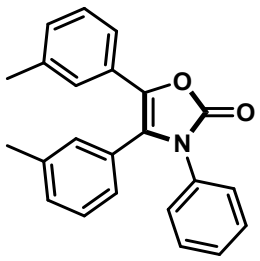
4,5-diphenyl-3-(pyrazin-2-yl)oxazol-2(3*H*)-one (3ap)

Yield: 79%; colourless solid, mp: 190-191 ºC; R_f = 0.22 (EA/PE = 1/5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.36 (d, *J* = 1.8 Hz, 1H), 8.18 (s, 1H), 7.36-7.17 (m, 10H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.7 (s), 143.6 (s), 141.9 (d), 141.8 (d), 141.4 (d), 135.3 (s), 129.2 (d, 2C), 128.6 (d), 128.0 (d, 2C), 127.6 (d, 3C), 126.09 (s), 126.06 (s), 124.3 (d, 2C), 121.5 (s) ppm; IR (reflection) $\tilde{\nu}$ = 3509, 3084, 3060, 3037, 1762, 1665, 1600, 1569, 1524, 1501, 1473, 1448, 1416, 1359, 1315, 1303, 1290, 1260, 1215, 1188, 1166, 1126, 1060, 1029, 1013, 975, 952, 920, 854, 841, 773, 764, 745, 700, 690, 664 cm^{-1}; HRMS (DART) (*m/z*) [M+H] $C_{19}H_{14}N_3O_2$ calcd for 316.1081, found 361.1081.



3-(isoquinolin-3-yl)-4,5-diphenyloxazol-2(3*H*)-one (3aq)

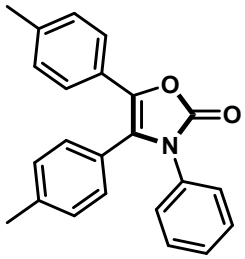
Yield: 86%; colourless solid, mp: 238-239 ºC; R_f = 0.27 (EA/PE = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (s, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.78 (s, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.66-7.59 (m, 1H), 7.56-7.49 (m, 1H), 7.36-7.31 (m, 2H), 7.28-7.24 (m, 2H), 7.24-7.16 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7 (s), 152.0 (d), 142.2 (s), 137.0 (s, 2C), 135.4 (s), 131.0 (d), 130.2 (d, 2C), 129.2 (d), 128.8 (d, 2C), 128.5 (d, 2C), 128.2 (d), 128.0 (d), 127.74 (s), 127.72 (d), 127.6 (d), 126.9 (d), 125.3 (d, 2C), 123.6 (s), 118.0 (d) ppm; IR (reflection) $\tilde{\nu}$ = 3059, 1754, 1628, 1583, 1489, 1448, 1373, 1334, 1314, 1278, 1255, 1209, 1172, 1141, 1075, 1064, 1028, 957, 944, 918, 882, 849, 807, 771, 746, 718,, 694, 677, 665 cm^{-1}; HRMS (DART) (*m/z*) [M+H] $C_{24}H_{17}N_2O_2$ calcd for 365.1285, found 365.1285.



3-phenyl-4,5-di-*m*-tolyloxazol-2(3*H*)-one (3ba)

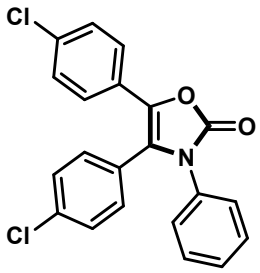
Yield: 99%; colourless solid, mp: 195-196 ºC; R_f = 0.59 (EA/PE = 1/5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26-7.17 (m, 4H), 7.15-7.02 (m, 6H), 7.02-6.90 (m, 3H), 2.20 (s, 3H), 2.19 (s, 3H)

ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.7 (s), 138.7 (s), 138.2 (s), 135.2 (s), 133.8 (s), 130.8 (d), 130.3 (d), 129.0 (d, 2C), 128.84 (d), 128.80 (d), 128.3 (d), 127.8 (d), 127.6 (s), 127.4 (d), 127.1 (s), 126.9 (d, 2C), 125.7 (d), 123.6 (s), 122.2 (d), 21.4 (q), 21.3 (q) ppm; IR (reflection) $\tilde{\nu}$ = 1756, 1671, 1597, 1504, 1493, 1458, 1364, 1290, 1269, 1208, 1169, 1136, 1076, 1063, 1004, 976, 912, 881, 826, 809, 789, 763, 750, 718, 698, 681, 664 cm^{-1}; HRMS (DART) (*m/z*) [M+H] $C_{23}H_{20}NO_2$ calcd for 342.1489, found 342.1487.



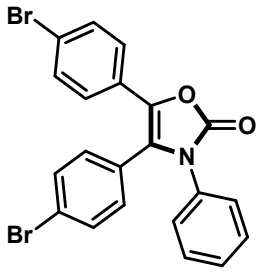
3-phenyl-4,5-di-*p*-tolyloxazol-2(3*H*)-one (3ca)

Yield: 98%; colourless solid, mp: 195-196 ºC; R_f = 0.53 (EA/PE = 1/5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27-7.13 (m, 5H), 7.07-6.96 (m, 8H), 2.26 (s, 3H), 2.24 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.8 (s), 139.5 (s), 138.0 (s), 135.3 (s), 133.8 (s), 130.1 (d, 2C), 129.7 (d, 2C), 129.2 (d, 2C), 129.0 (d, 2C), 127.8 (d), 127.0 (d, 2C), 125.03 (d, 2C), 124.98 (s), 124.2 (s), 123.0 (s), 21.4 (q), 21.3 (q) ppm; IR (reflection) $\tilde{\nu}$ = 3031, 1756, 1668, 1598, 1522, 1501, 1449, 1410, 1371, 1315, 1292, 1261, 1212, 1184, 1172, 1146, 1115, 1064, 1018, 1005, 992, 954, 911, 856, 819, 785, 761, 750, 728, 695, 617 cm^{-1}; HRMS (DART) (*m/z*) [M+H] $C_{23}H_{20}NO_2$ calcd for 342.1489, found 342.1491.



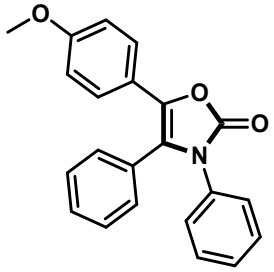
4,5-bis(4-chlorophenyl)-3-phenyloxazol-2(3*H*)-one (3da)

Yield: 95%; colourless solid, mp: 169-170 ºC; R_f = 0.52 (EA/PE = 1/5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31-7.17 (m, 9H), 7.12-7.00 (m, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.3 (s), 134.9 (s), 133.5 (s), 133.2 (s), 132.2 (s), 130.4 (d, 2C), 128.6 (d, 2C), 128.3 (d, 2C), 128.0 (d, 2C), 127.3 (d), 125.9 (d, 2C), 125.4 (d, 2C), 124.8 (s), 124.2 (s), 121.8 (s) ppm; IR (reflection) $\tilde{\nu}$ = 3087, 1755, 1596, 1494, 1456, 1406, 1370, 1256, 1175, 1145, 1092, 1060, 1013, 1005, 991, 971, 951, 914, 836, 819, 769, 751, 730, 712, 696, 682, 625 cm^{-1}; HRMS (DART) (*m/z*) [M+H] $C_{21}H_{14}{}^{35}Cl_2NO_2$ calcd for 382.0396, found 382.0398.

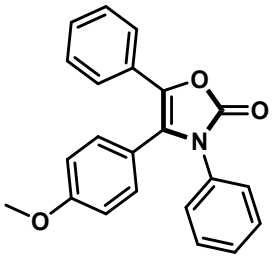


4,5-bis(4-bromophenyl)-3-phenyloxazol-2(3*H*)-one (3ea)

Yield: 99%; colourless solid, mp: 167-168 ºC; R_f = 0.54 (EA/PE = 1/5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.7 Hz, 2H), 7.30-7.20 (m, 3H), 7.15 (d, *J* = 8.7 Hz, 2H), 7.09-7.02 (m, 2H), 7.00 (d, *J* = 8.4 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.3 (s), 134.6 (s), 133.2 (s), 132.5 (d, 2C), 131.9 (d, 2C), 131.6 (d, 2C), 129.3 (d, 2C), 128.3 (d), 127.0 (d, 2C), 126.6 (d, 2C), 126.3 (s), 125.7 (s), 124.2 (s), 123.0 (s), 122.5 (s) ppm; IR (reflection) $\tilde{\nu}$ = 1756, 1671, 1597, 1504, 1493, 1458, 1364, 1290, 1269, 1208, 1169, 1136, 1076, 1063, 1004, 976, 912, 881, 826, 809, 789, 763, 750, 718, 698, 681, 664 cm^{-1}; HRMS (DART) (*m/z*) [M+H] $C_{21}H_{14}{}^{81}Br_2NO_2$ calcd for 471.9365, found 471.9378.



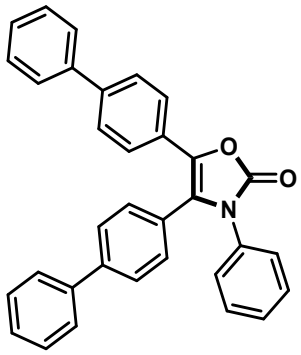
3fa, 43%



3fa', 35%

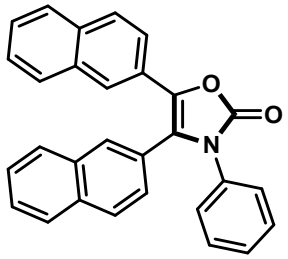
5-(4-methoxyphenyl)-3,4-diphenyloxazol-2(3H)-one (3fa); 4-(4-methoxyphenyl)-3,5-diphenyloxazol-2(3*H*)-one (3fa')

Combined yield: 78%; colourless solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.28 (m, 1H), 7.27-7.16 (m, 7H), 7.15-7.03 (m, 4H), 6.80-6.67 (m, 2H), 3.73 (q, 1.39 H, OMe in **3fa**), 3.71 (q, 1.61 H, OMe in **3fa'**) ppm; HRMS (DART) (*m/z*) [M+H] $C_{22}H_{18}NO_3$ calcd for 344.1281, found 344.1281.



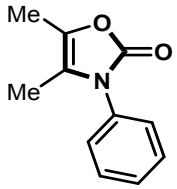
4,5-bis(4-bromophenyl)-3-phenyloxazol-2(3*H*)-one (3ga)

Yield: 95%; colourless solid, mp: 167-168 ºC; R_f = 0.33 (EA/PE = 1/5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55-7.42 (m, 10H), 7.40-7.17 (m, 11H), 7.14-7.06 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.6 (s), 142.0 (s), 140.7 (s), 140.1 (s), 139.6 (s), 135.1 (s), 133.6 (s), 130.6 (d, 2C), 129.1 (d, 2C), 128.9 (d, 2C), 128.8 (d, 2C), 127.9 (d, 2C), 127.53 (d), 127.49 (d, 2C), 127.1 (d, 2C), 126.93 (d, 2C), 126.92 (d, 2C), 126.8 (d, 2C), 126.5 (s), 125.8 (s), 125.5 (d, 2C), 123.4 (s) ppm; IR (reflection) $\tilde{\nu}$ = 3031, 1760, 1596, 1524, 1486, 1460, 1407, 1367, 1273, 1257, 1187, 1174, 1144, 1068, 1039, 1003, 987, 952, 914, 840, 830, 764, 748, 738, 696, 639 cm^{-1}; HRMS (DART) (*m/z*) [M+H] $C_{33}H_{24}NO_2$ calcd for 466.1802, found 466.1798.



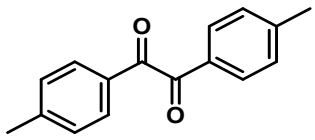
4,5-di(naphthalen-2-yl)-3-phenyloxazol-2(3*H*)-one (3ha)

Yield: 95%; colourless solid, mp: 231-232 ºC; R_f = 0.35 (EA/PE = 1/5); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.73-7.68 (m, 2H), 7.68-7.59 (m, 3H), 7.54-7.40 (m, 3H), 7.39-7.33 (m, 2H), 7.25-7.09 (m, 7H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.6 (s), 135.6 (s), 133.6 (s), 133.3 (s), 133.1 (s), 133.0 (s), 132.7 (d), 130.3 (d), 129.1 (d, 2C), 128.8 (d), 128.3 (d), 128.2 (d), 128.1 (d), 127.9 (d), 127.8 (d), 127.6 (d), 127.3 (d), 126.9 (d, 2C), 126.8 (d), 126.7 (d), 126.6 (d), 126.5 (s), 124.9 (s), 124.5 (d), 124.4 (s), 123.9 (s), 122.5 (d) ppm; IR (reflection) $\tilde{\nu}$ = 3058, 1750, 1628, 1595, 1499, 1456, 1435, 1383, 1365, 1342, 1276, 1235, 1201, 1170, 1140, 1129, 1061, 1020, 1005, 983, 962, 905, 888, 861, 830, 815, 790, 754, 740, 711, 683, 636 cm^{-1}; HRMS (DART) (*m/z*) [M+H] $C_{29}H_{20}NO_2$ calcd for 414.1489, found 414.1487.



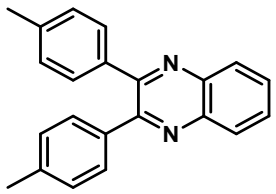
4,5-dimethyl-3-phenyloxazol-2(3*H*)-one (3ia)[6]

Yield: 7 mg, 19%; light yellow oil; R_f = 0.15 (EA/PE = 1/3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.39 (m, 2H), 7.35-7.31 (m, 1H), 7.28-7.23 (m, 2H), 2.07 (q, *J* = 1.2 Hz, 3H), 1.81 (q, *J* = 1.2 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.7 (s), 134.0 (s), 132.3 (s), 129.4 (d, 2C), 128.2 (d), 126.9 (d, 2C), 117.8 (s), 10.0 (q), 8.8 (q) ppm; HRMS (DART) (*m/z*) [M+H] $C_{11}H_{12}NO_2$ calcd for 190.0863, found 190.0861.



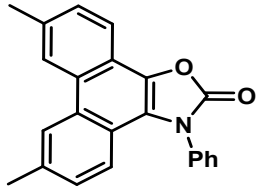
1,2-di-*p*-tolylethane-1,2-dione (5)[7]

Yield: 95%; light yellow solid, mp 107-109 °C; R_f = 0.45 (EA/PE = 1/20); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.5 Hz, 4H), 7.23 (d, *J* = 8.0 Hz, 4H), 2.37 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.55 (s, 2C), 146.12 (s, 2C), 130.69 (s, 2C), 130.05 (d, 4C), 129.73 (d, 4C), 21.97 (q, 2C) ppm; IR (ATR) $\tilde{\nu}$ = 2920, 1659, 1604, 1573, 1447, 1410, 1330, 1305, 1221, 1171, 1122, 1040, 884, 851, 829, 781, 741, 694 cm^{-1}; HRMS (EI) [M] $C_{16}H_{14}O_2$ calcd for 238.0988, found 238.0978.



2,3-di-*p*-tolylquinoxaline (6)[8]

Yield: 59 mg, 95%; colourless solid, mp 153-155 °C; R_f = 0.47 (EA/PE = 1/20); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11-8.04 (m, 2H), 7.70-7.64 (m, 2H), 7.36 (d, J = 8.1 Hz, 4H), 7.08 (d, J = 7.8 Hz, 4H), 2.30 (s, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.4 (s, 2C), 141.0 (s, 2C), 138.7 (s, 2C), 136.2 (s, 2C), 129.7 (d, 6C), 129.0 (d, 2C), 128.9 (d, 4C), 21.3 (q, 2C) ppm; IR (ATR) $\tilde{\nu}$ = 3032, 2969, 2915, 1910, 1613, 1515, 1476, 1394, 1344, 1308, 1213, 1185, 1111, 1057, 1021, 977, 952, 819, 761, 723, 631, 608 cm^{-1}; HRMS (ESI) $[M+H]^+$ $C_{22}H_{19}N_2$ calcd for 311.1543, found 311.1543.

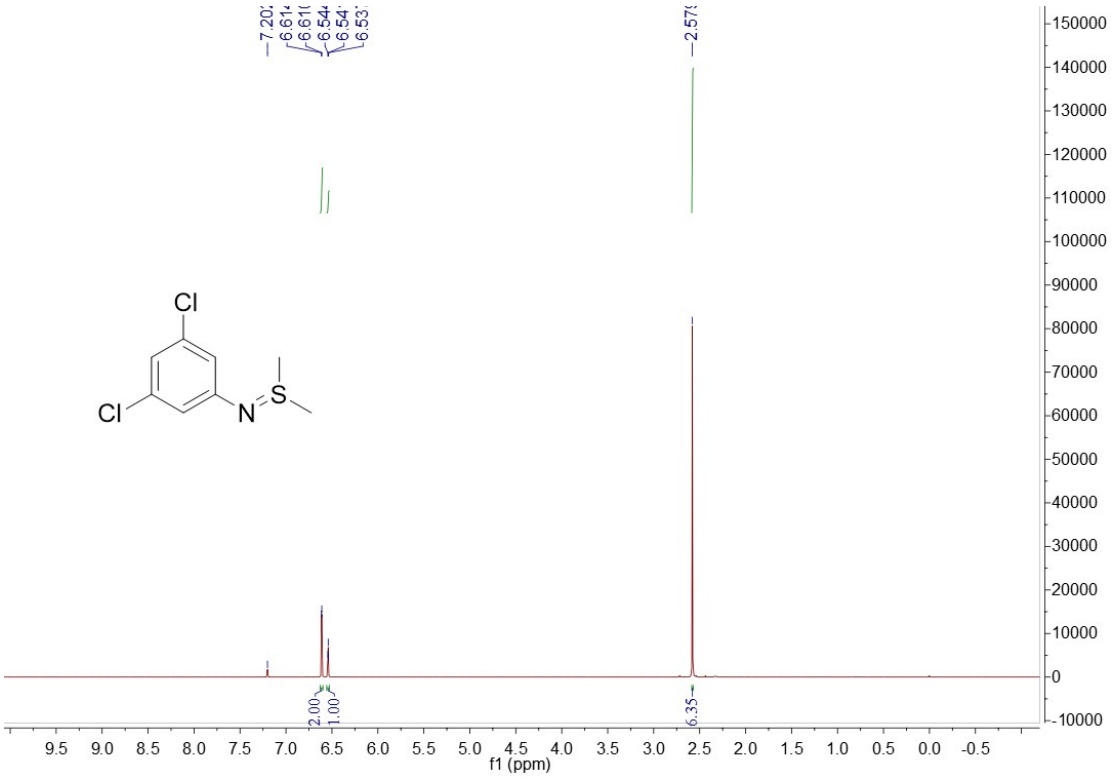


6,9-dimethyl-3-phenylphenanthro[9,10-*d*]oxazol-2(3*H*)-one (7)

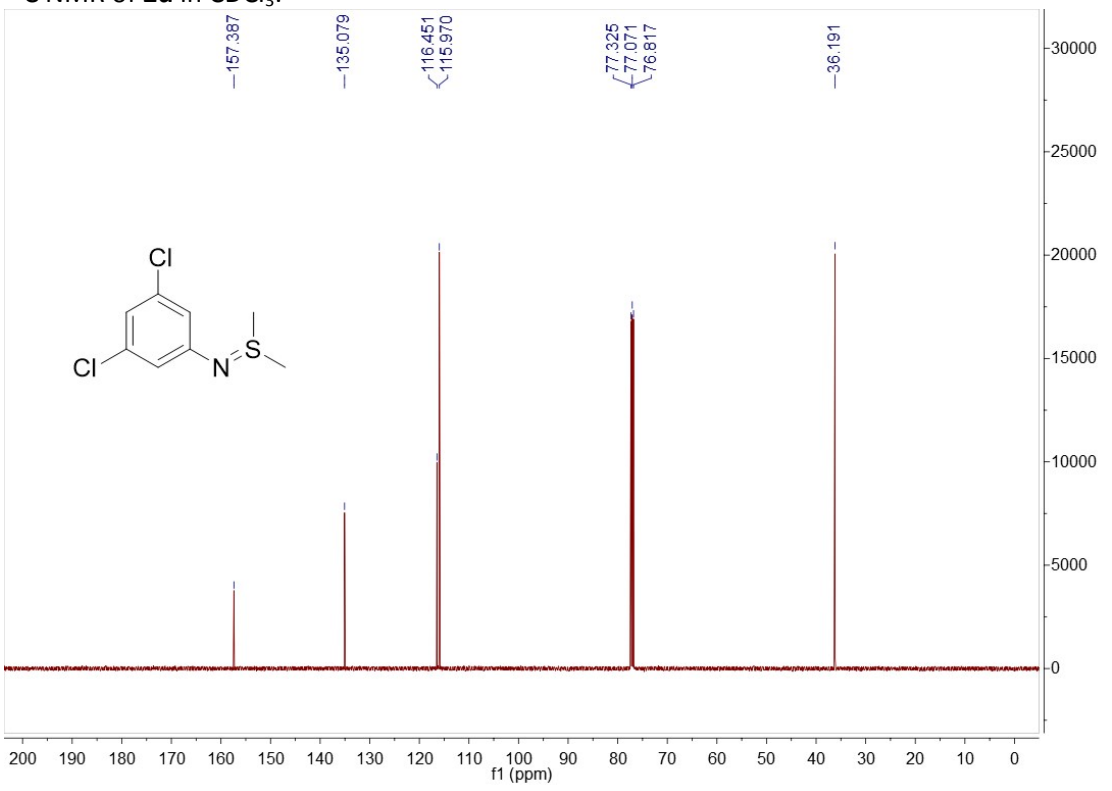
Yield: 35 mg, 52%; colourless solid, mp 235-236 °C; R_f = 0.26 (DCM/PE = 1/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.44 (d, J = 11.4 Hz, 2H), 8.00 (d, J = 8.4 Hz, 1H), 7.59-7.45 (m, 6H), 7.13-7.08 (m, 1H), 7.05-7.00 (m, 1H), 2.58 (s, 3H), 2.49 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.9 (s), 135.5 (s), 135.17 (s), 135.14 (s), 135.08 (s), 129.8 (d, 2C), 129.5 (d), 129.3 (d), 128.4 (d), 128.3 (s), 128.1 (d, 2C), 127.4 (s), 123.7 (d), 123.0 (d), 121.0 (s), 120.9 (d), 119.9 (d), 118.5 (s), 118.0 (s), 22.2 (q), 21.9 (q) ppm; IR (ATR) $\tilde{\nu}$ = 3056, 2918, 1760, 1594, 1538, 1498, 1432, 1387, 1332, 1282, 1163, 1143, 1062, 1040, 978, 950, 868, 823, 814, 768, 748, 712, 693, 637 cm^{-1}; HRMS (ESI) (*m/z*) $[M+Na]^+$ $C_{23}H_{17}NNaO_2$ calcd for 362.1151, found 362.1151.

4. NMR spectra

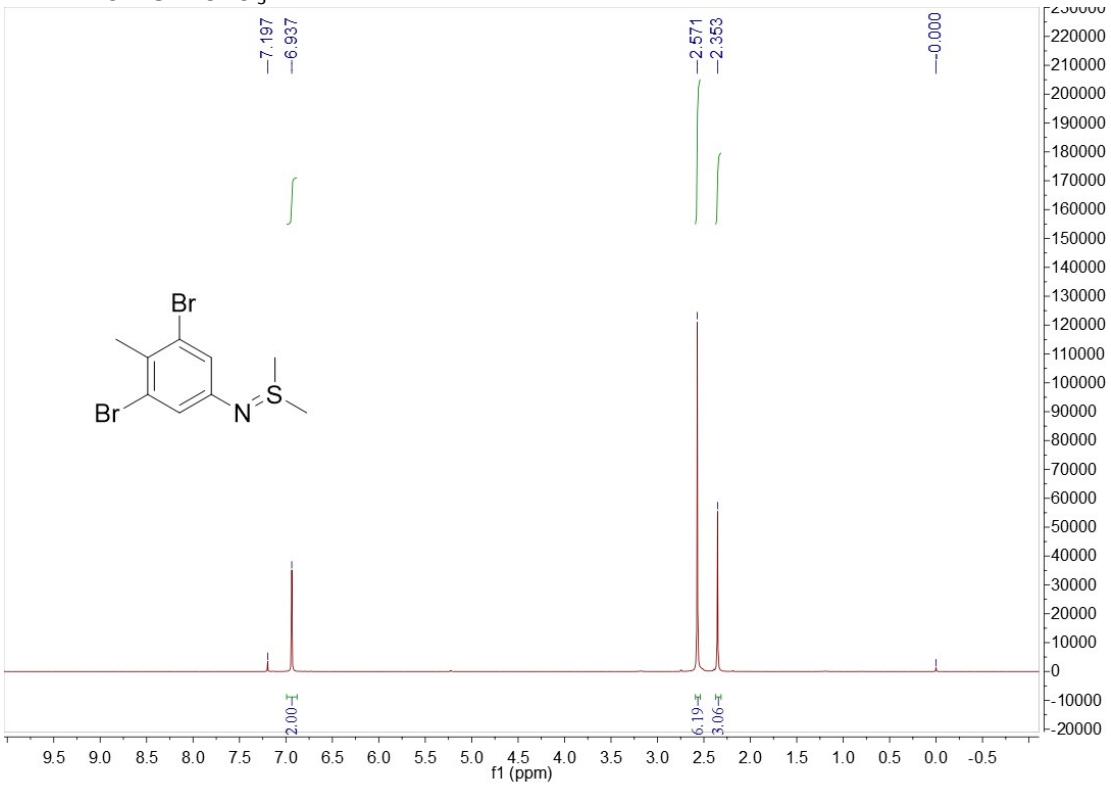
^{1}H NMR of **2d** in $CDCl_3$:



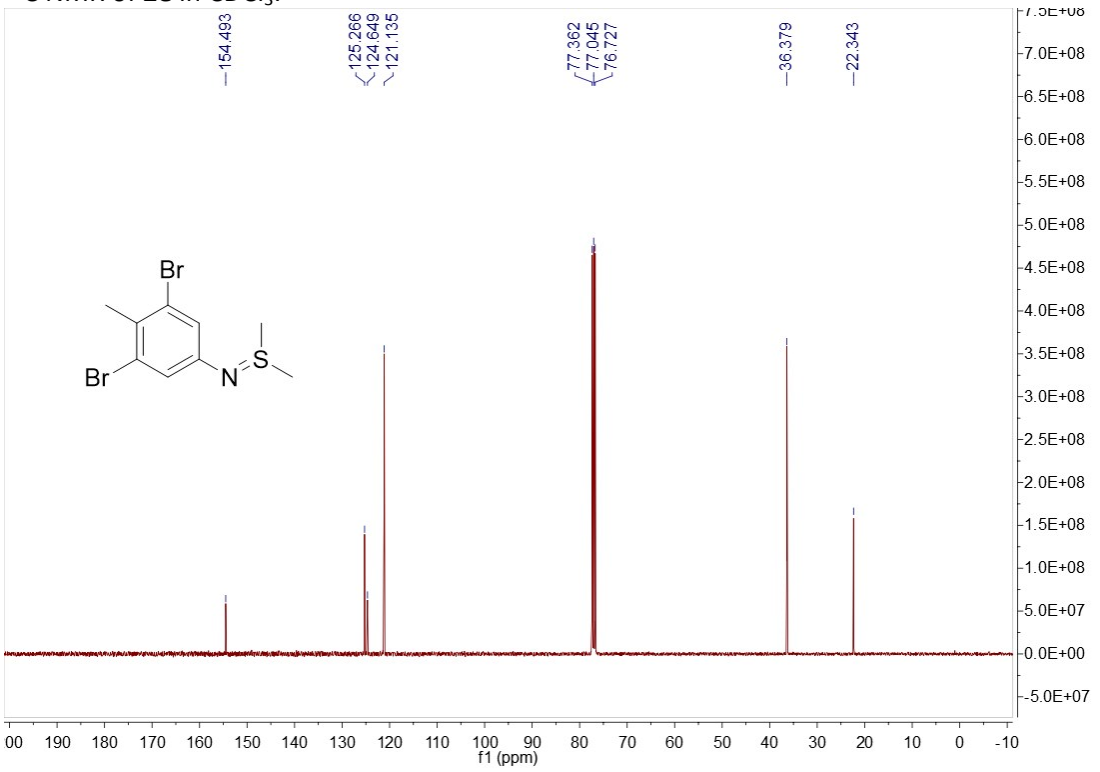
^{13}C NMR of **2d** in $CDCl_3$:



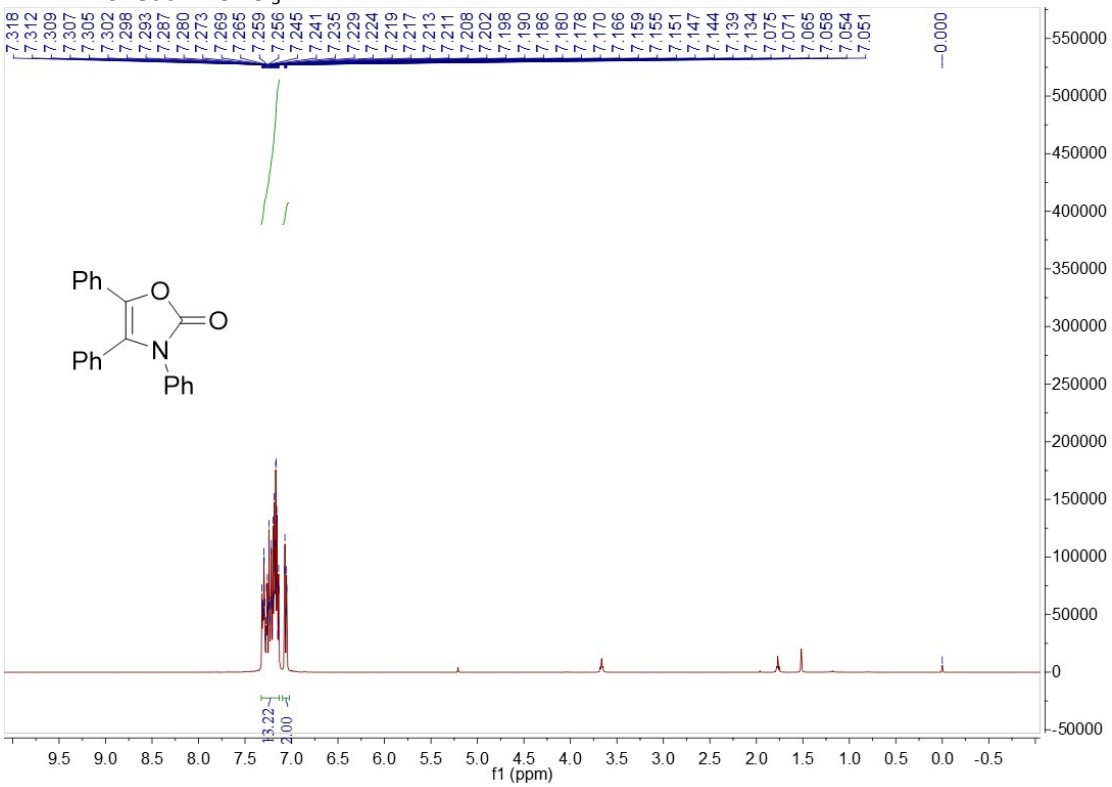
^{1}H NMR of **2e** in $CDCl_3$:



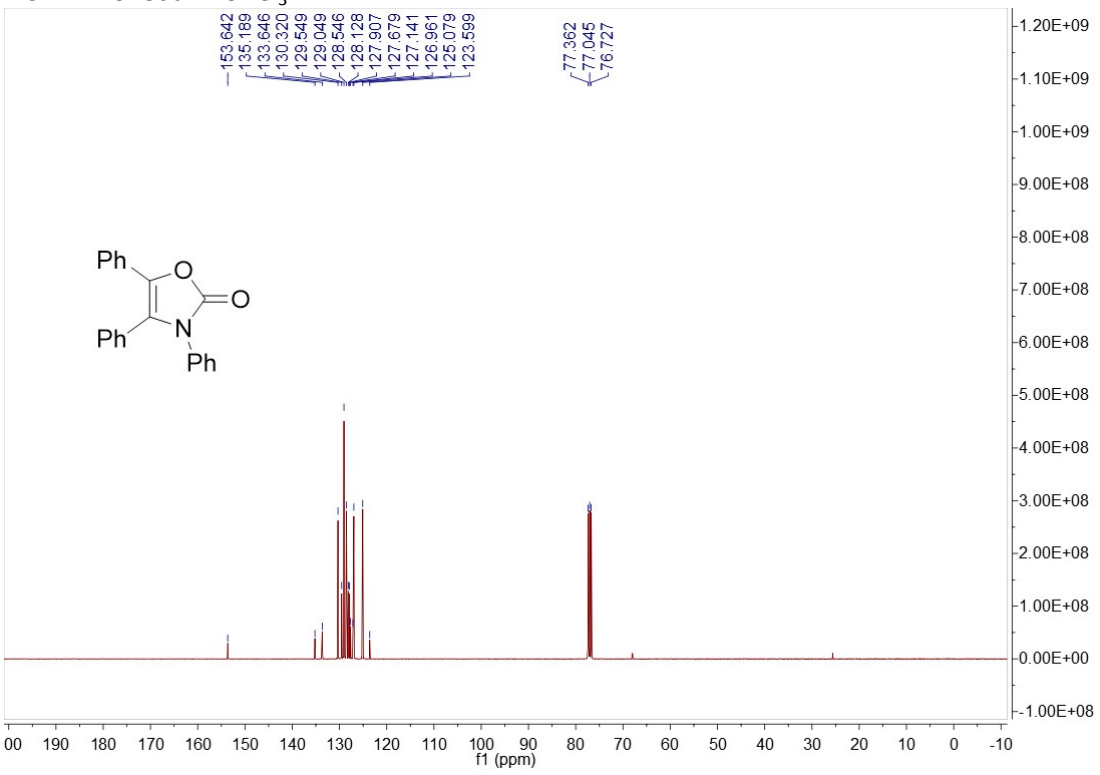
^{13}C NMR of **2e** in $CDCl_3$:



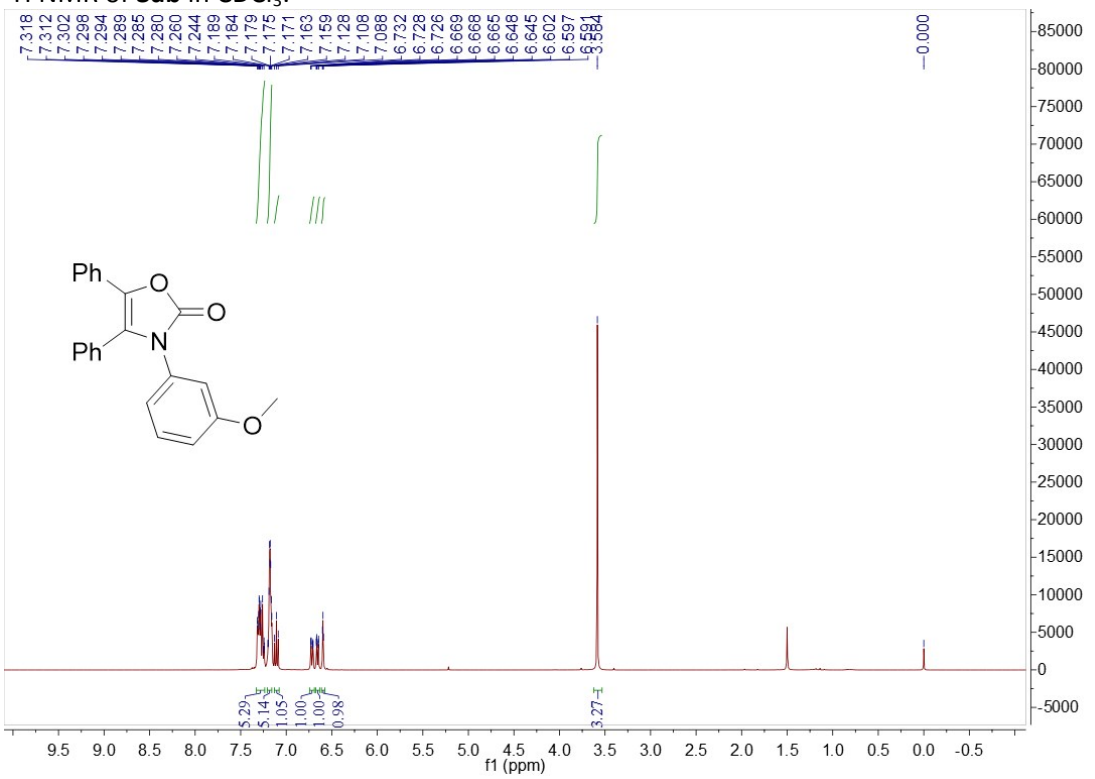
^{1}H NMR of **3aa** in $CDCl_3$:



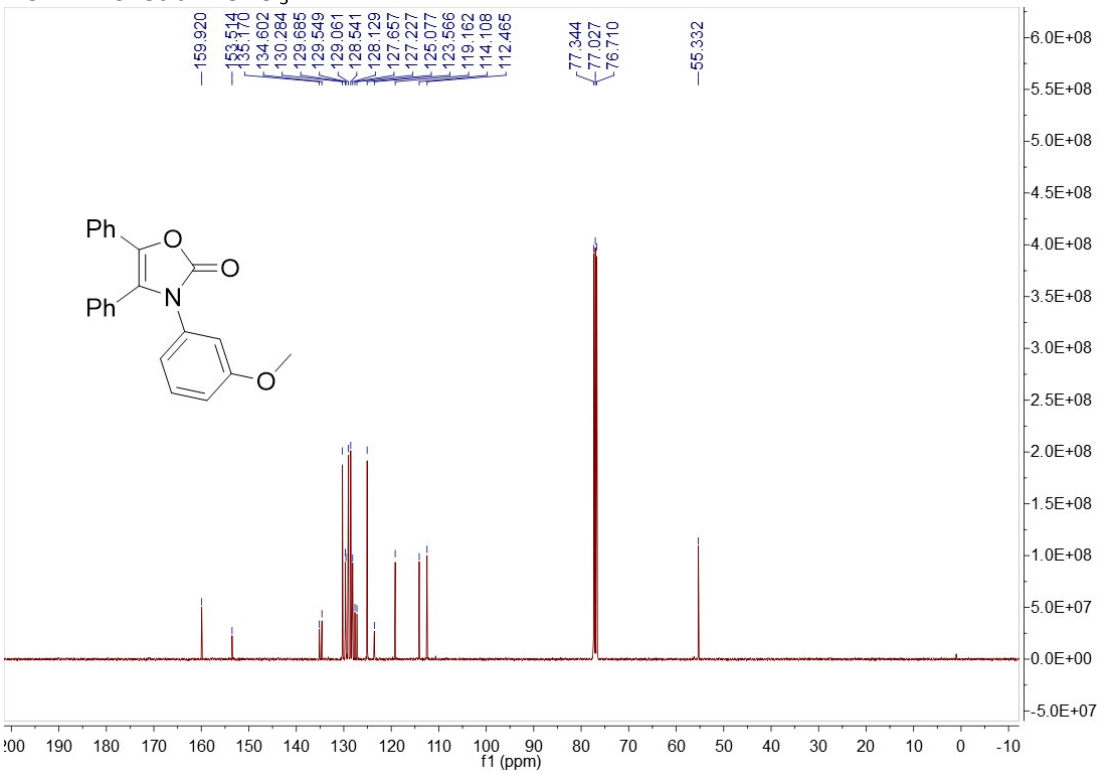
^{13}C NMR of **3aa** in $CDCl_3$:



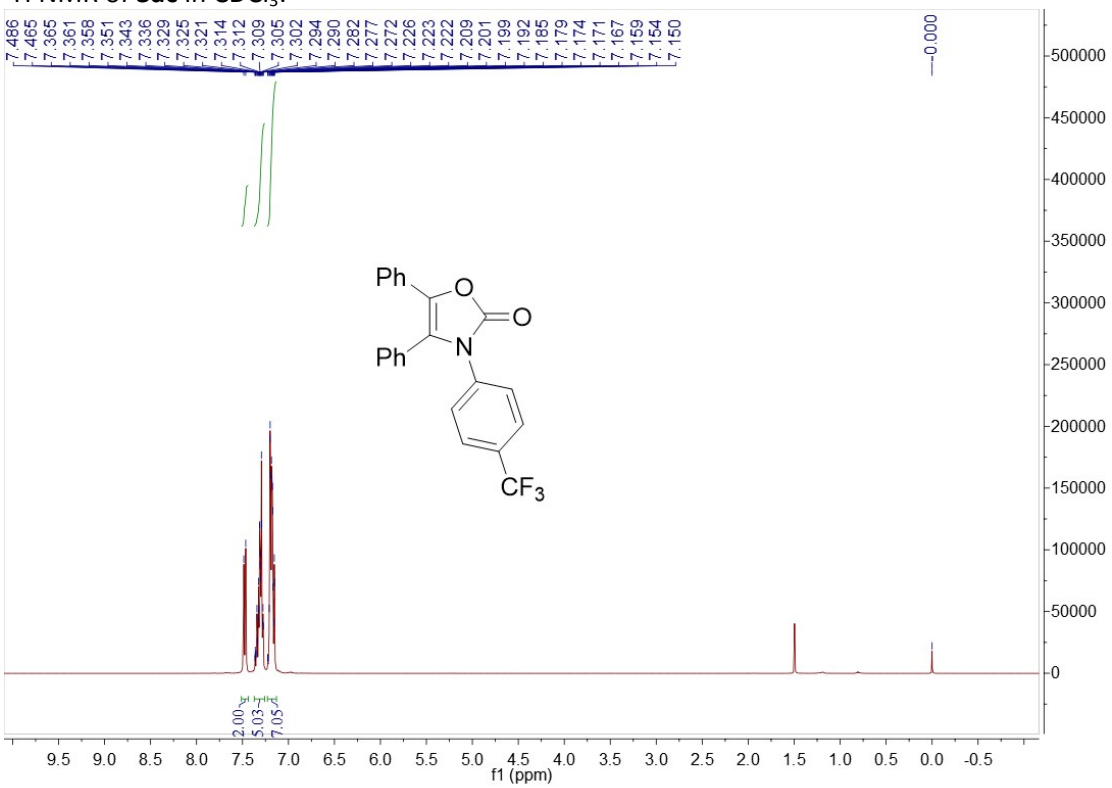
^{1}H NMR of **3ab** in $CDCl_3$:



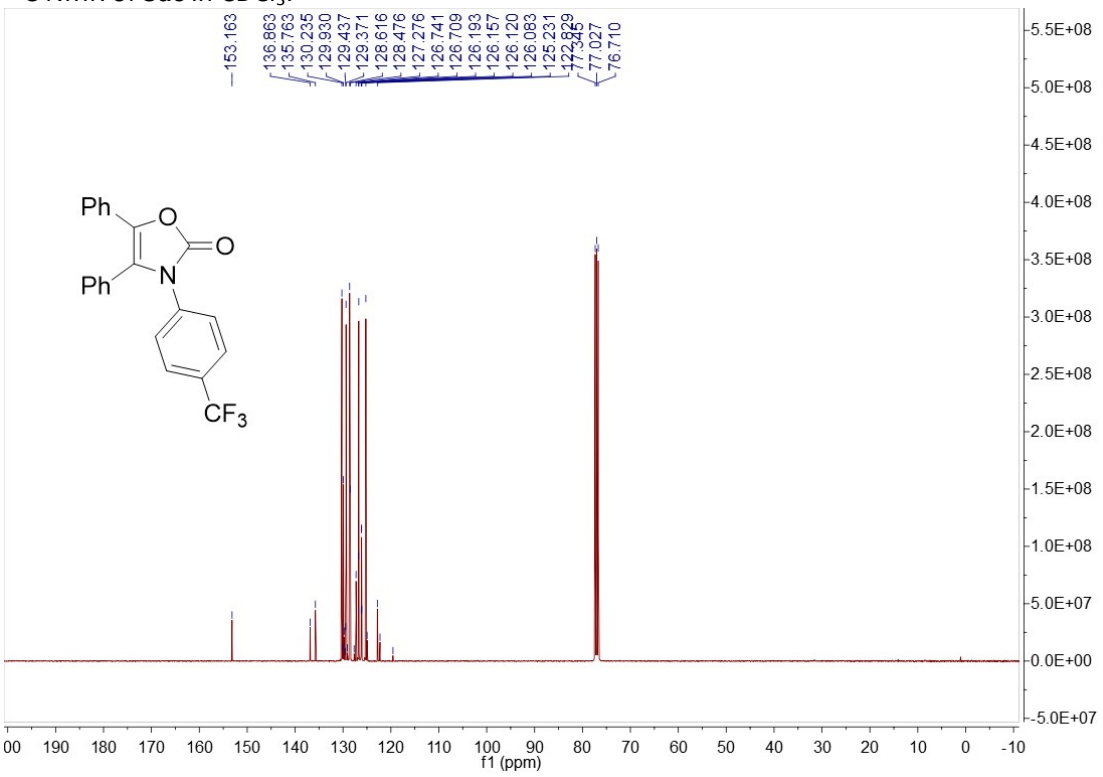
^{13}C NMR of **3ab** in $CDCl_3$:



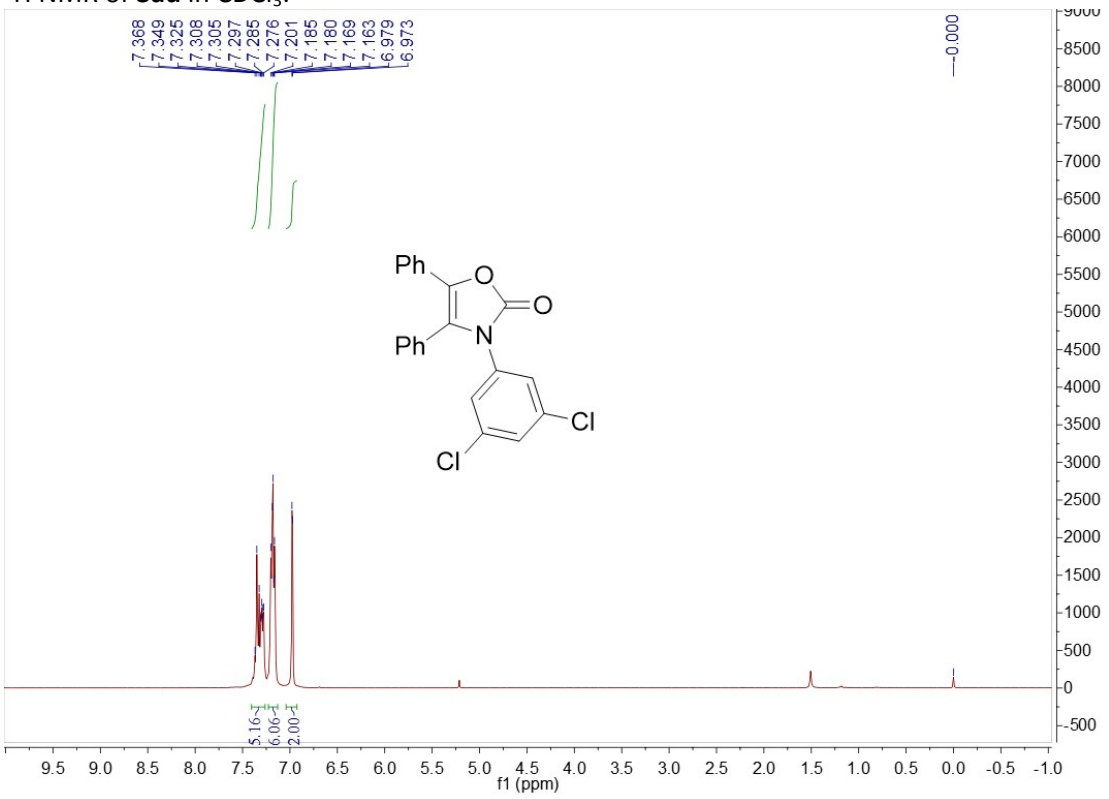
^{1}H NMR of **3ac** in $CDCl_3$:



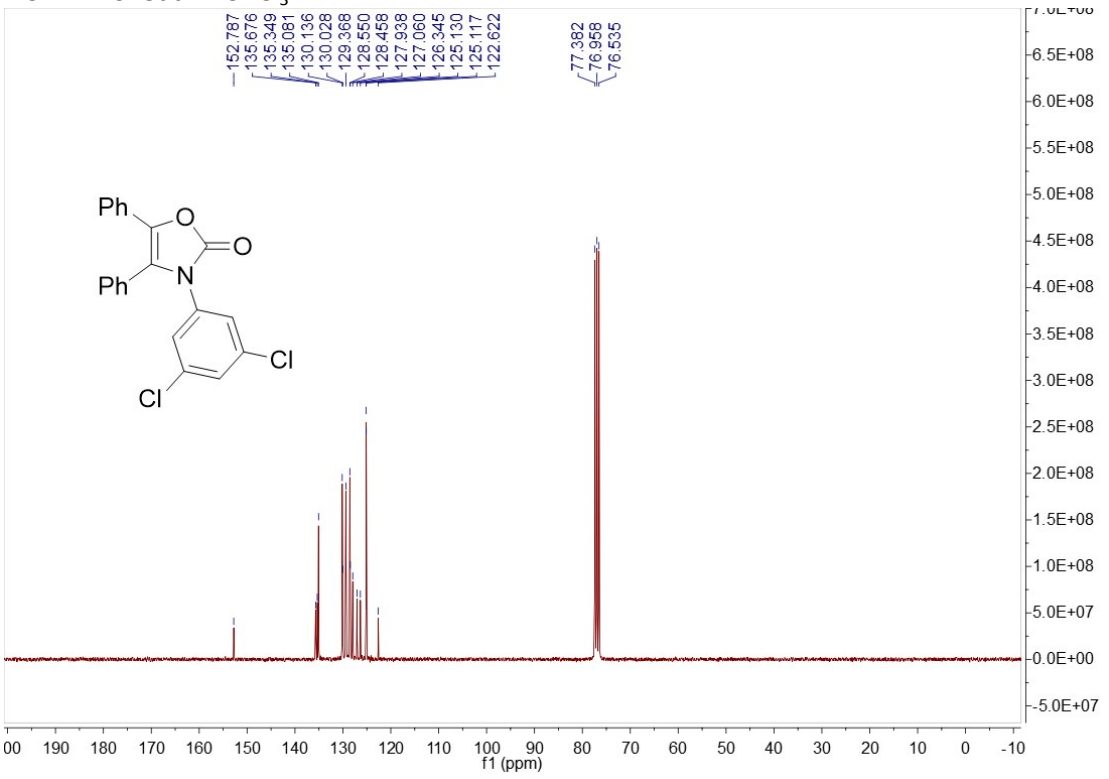
^{13}C NMR of **3ac** in $CDCl_3$:



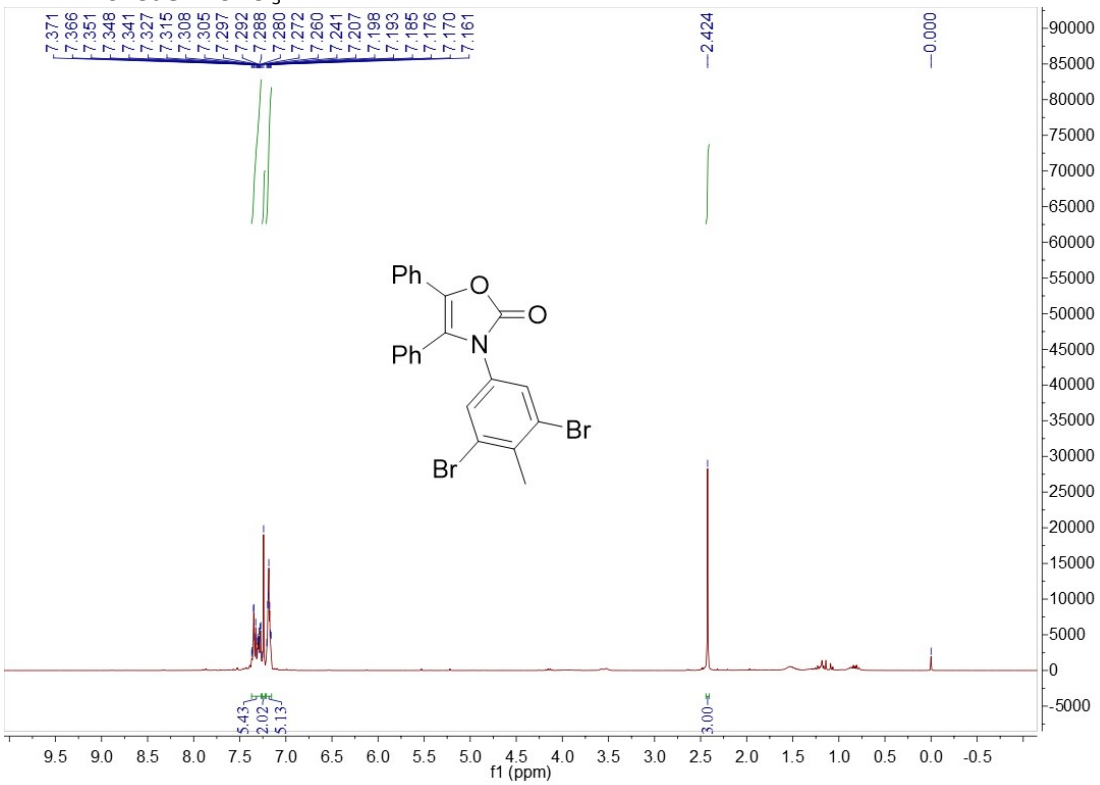
^{1}H NMR of **3ad** in $CDCl_3$:



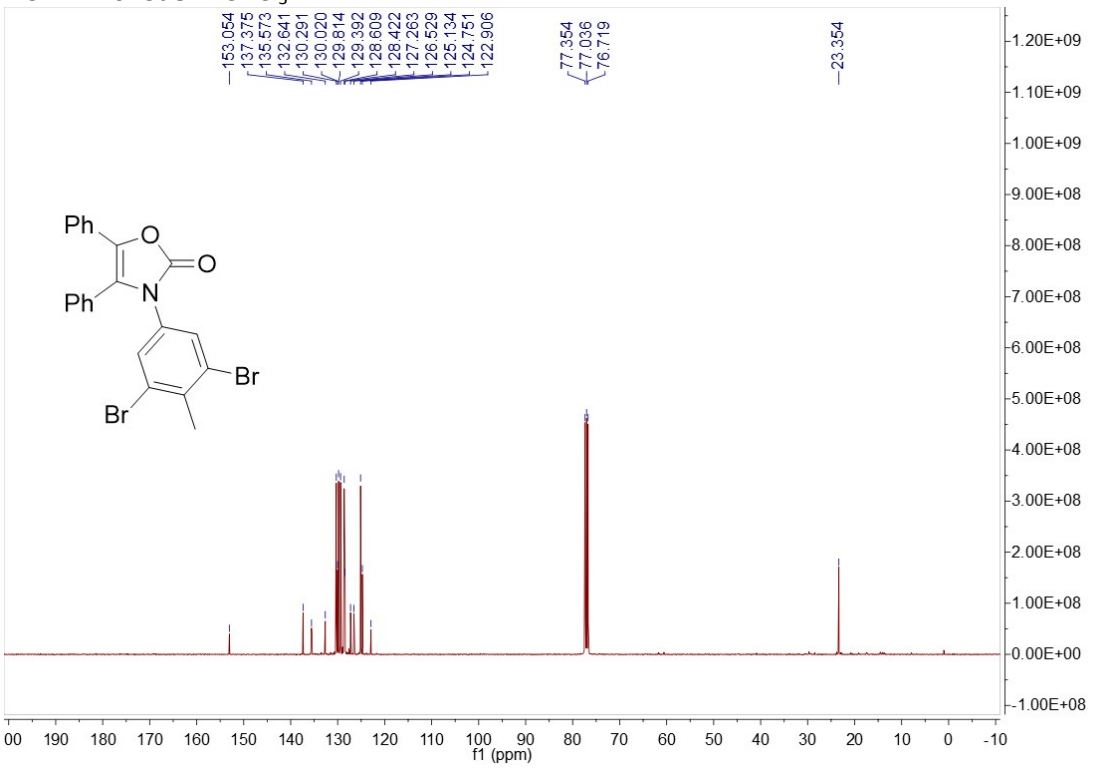
^{13}C NMR of **3ad** in $CDCl_3$:



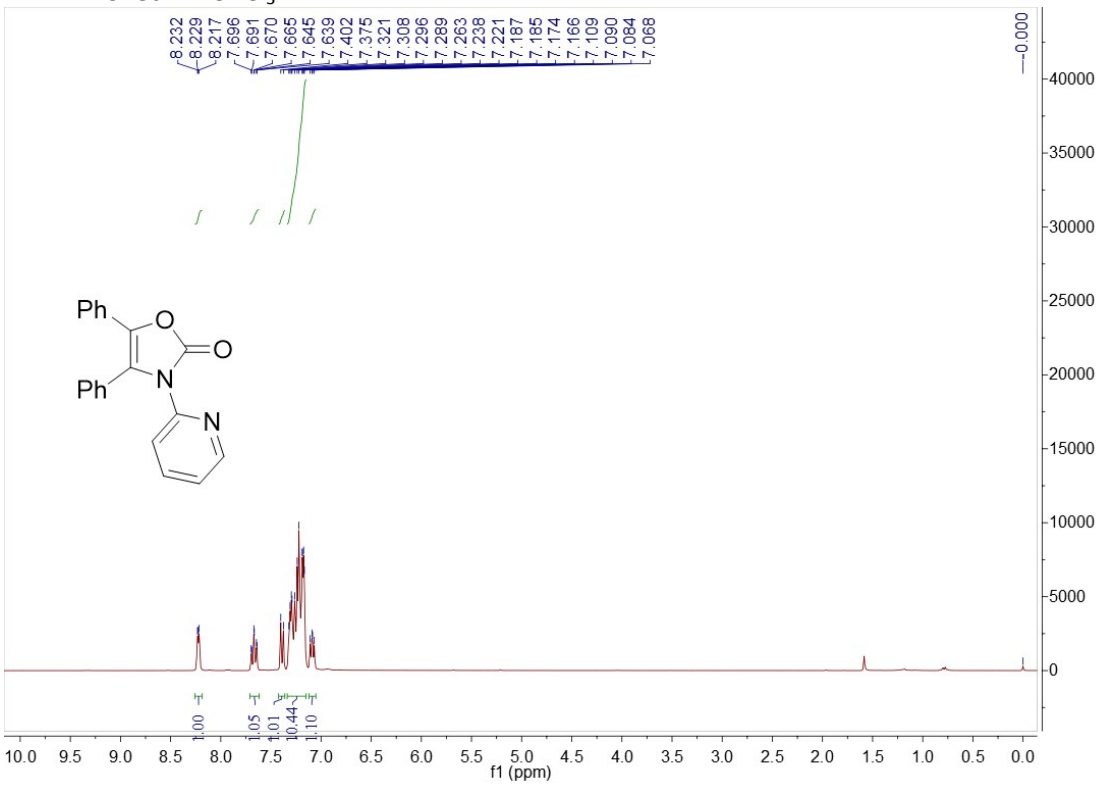
^{1}H NMR of **3ae** in $CDCl_3$:



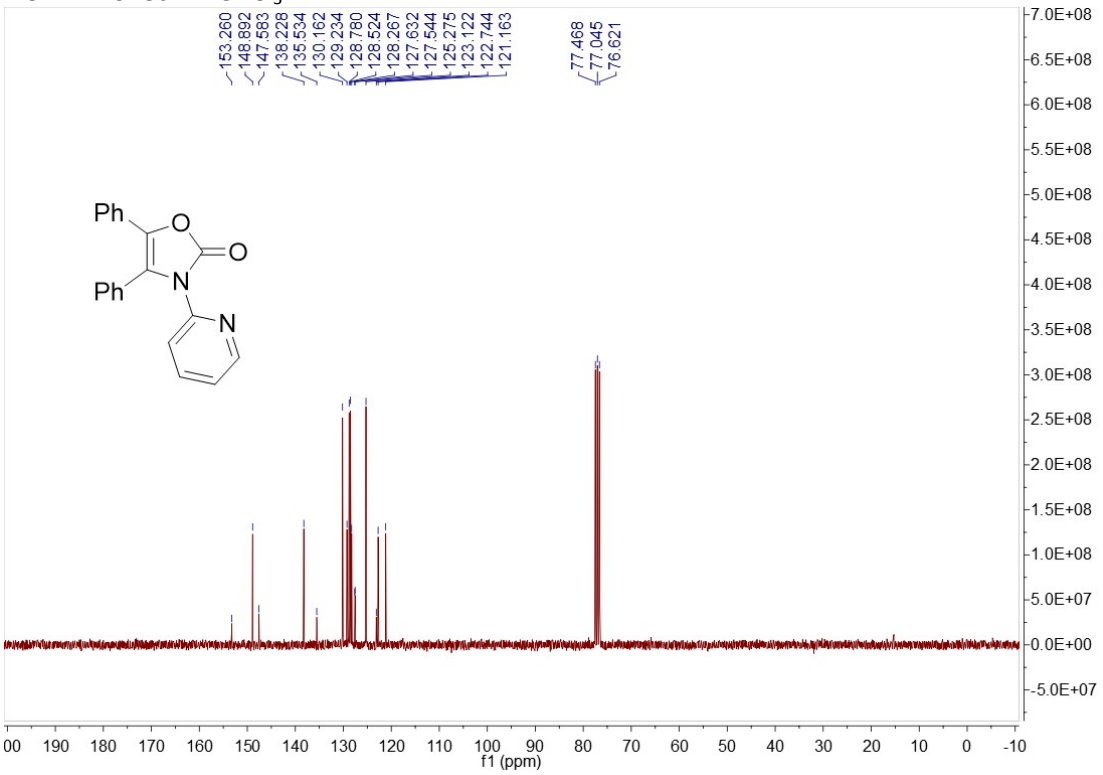
^{13}C NMR of **3ae** in $CDCl_3$:



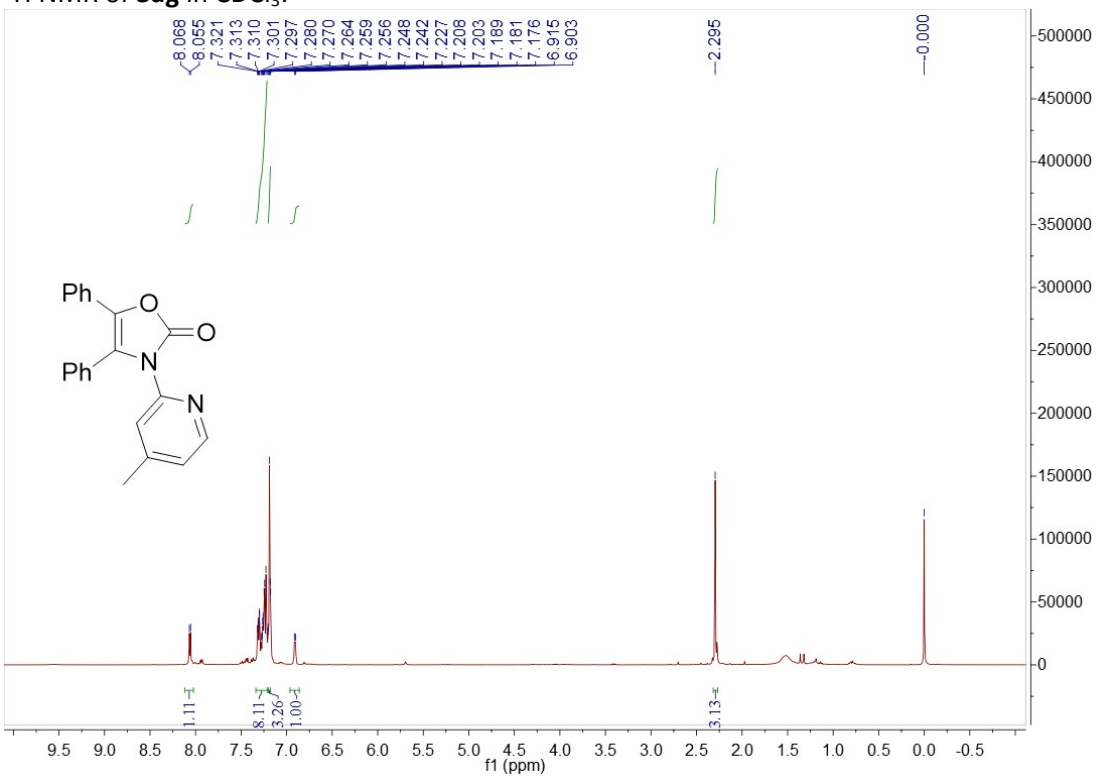
^{1}H NMR of **3af** in $CDCl_3$:



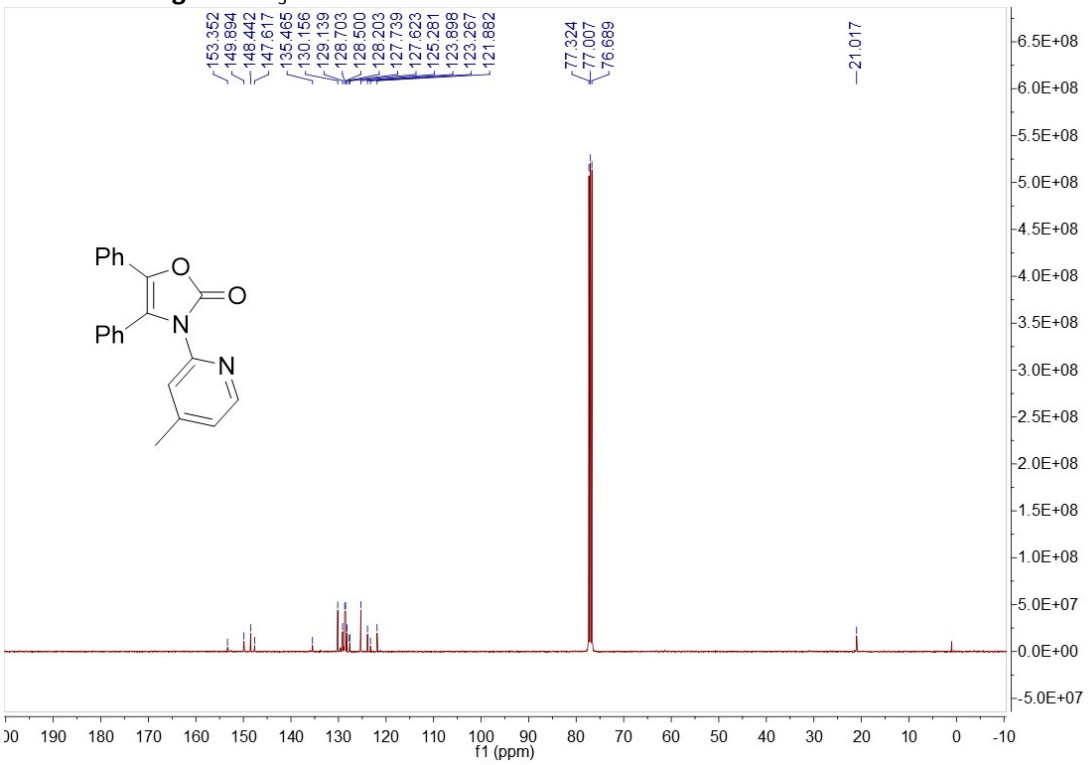
^{13}C NMR of **3af** in $CDCl_3$:



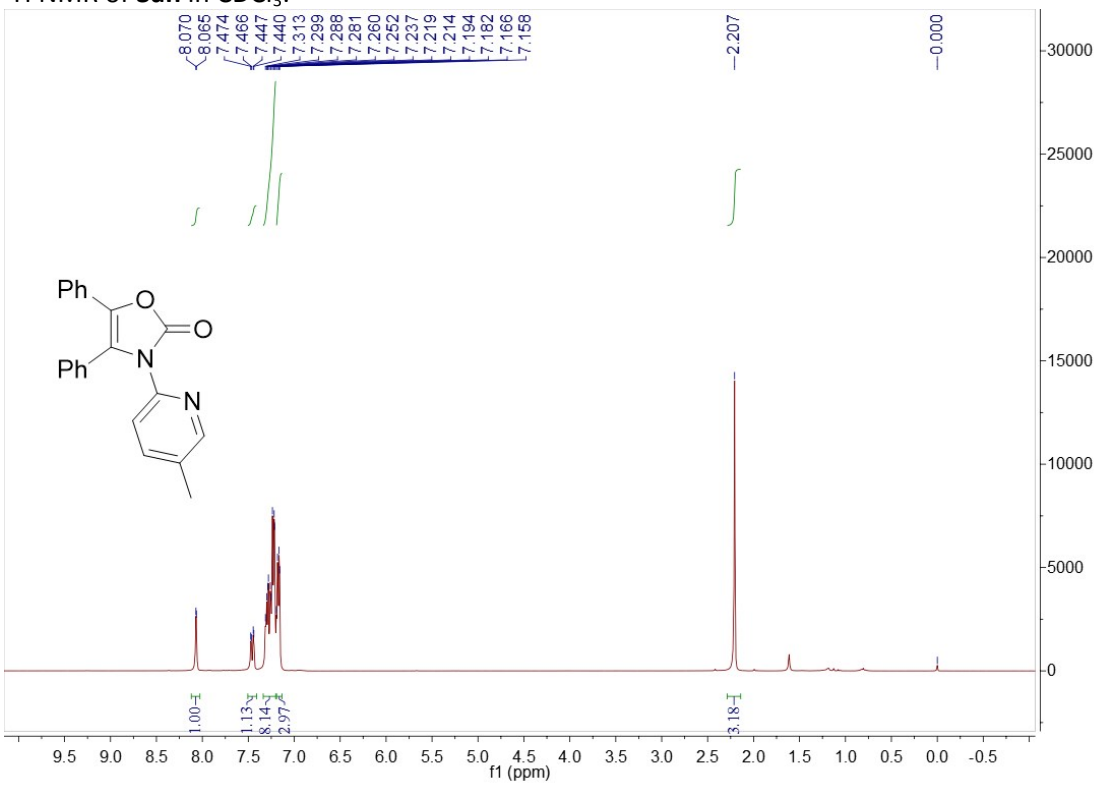
^{1}H NMR of **3ag** in $CDCl_3$:



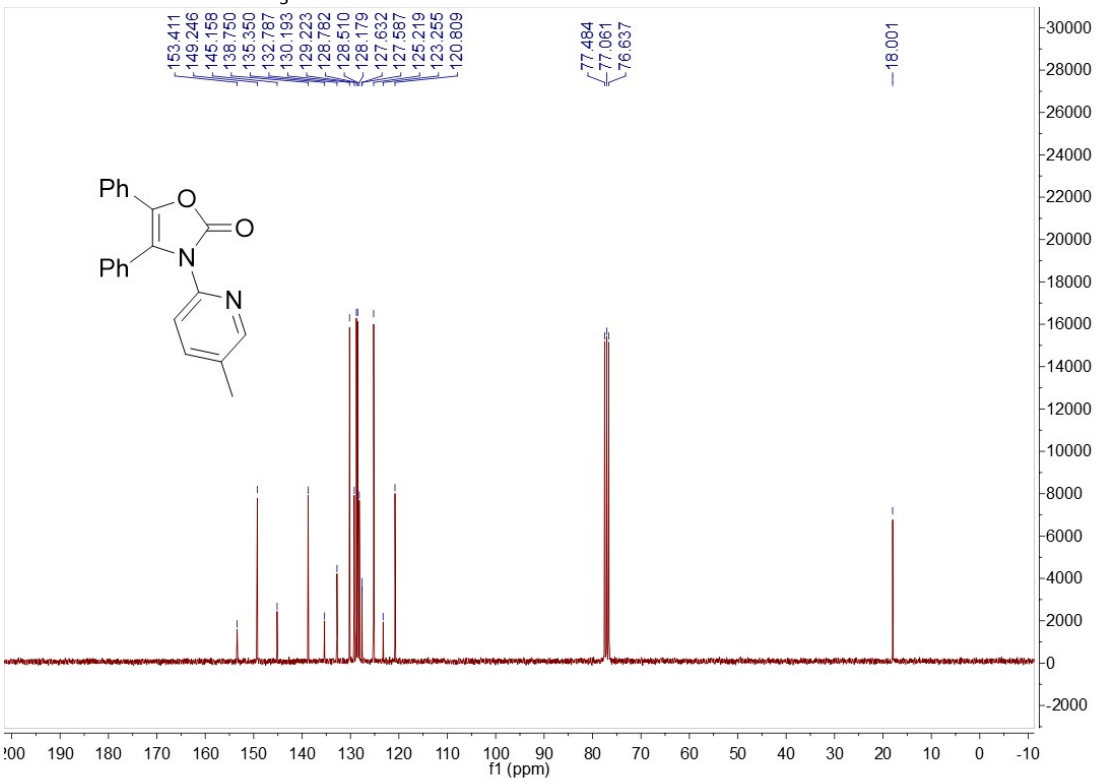
^{13}C NMR of **3ag** in $CDCl_3$:



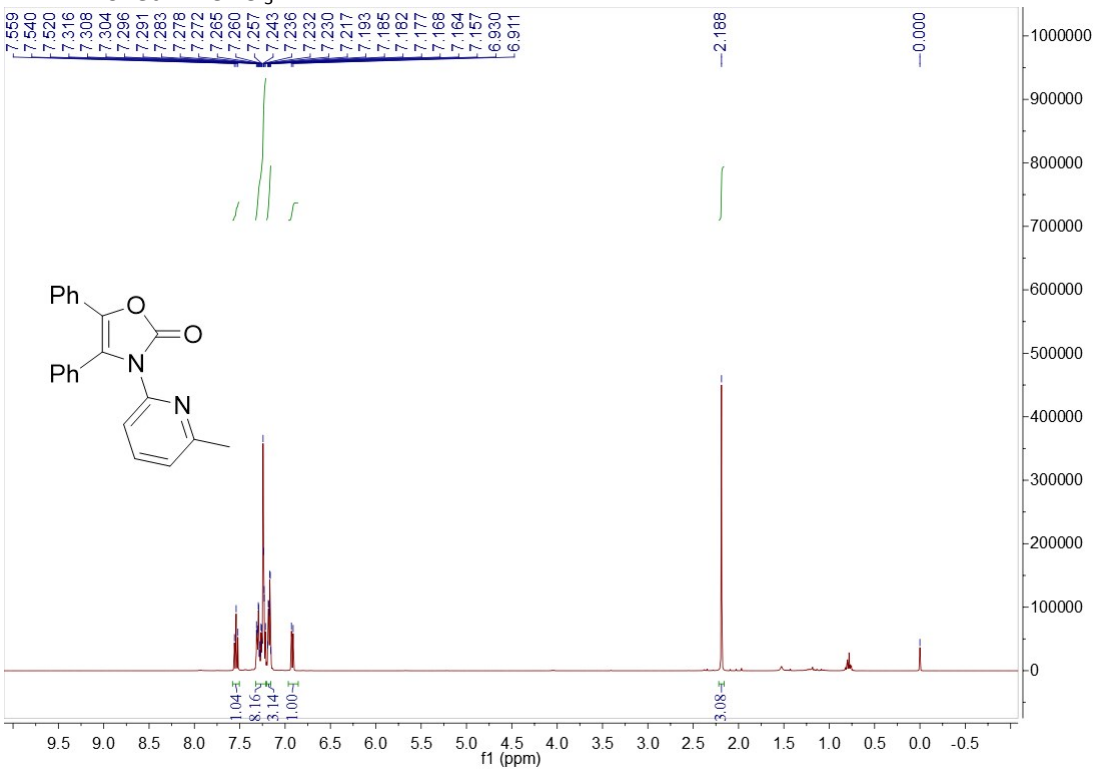
^{1}H NMR of **3ah** in $CDCl_3$:



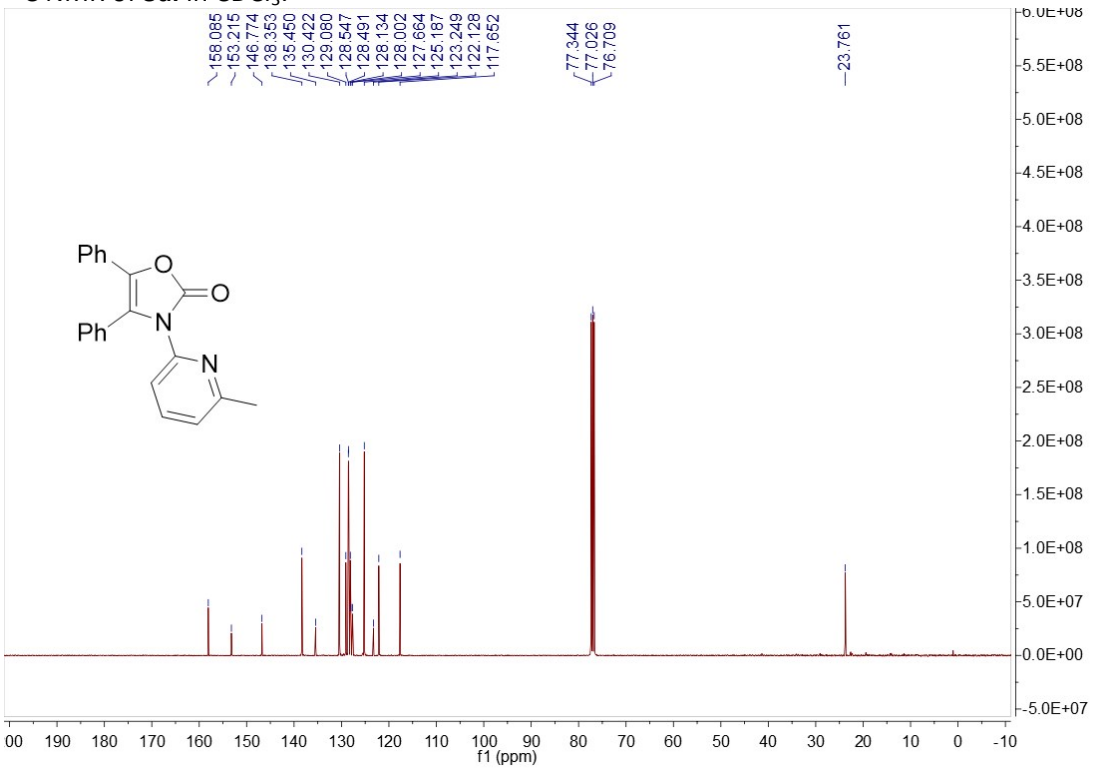
^{13}C NMR of **3ah** in $CDCl_3$:



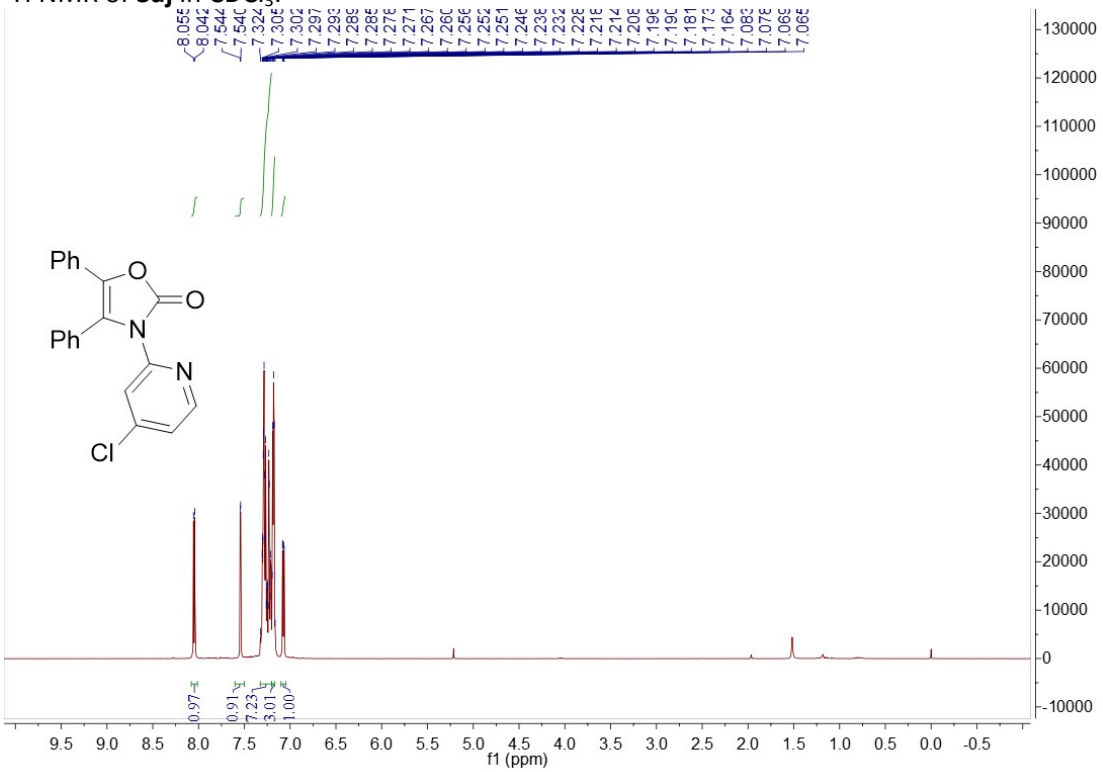
^{1}H NMR of **3ai** in $CDCl_3$:



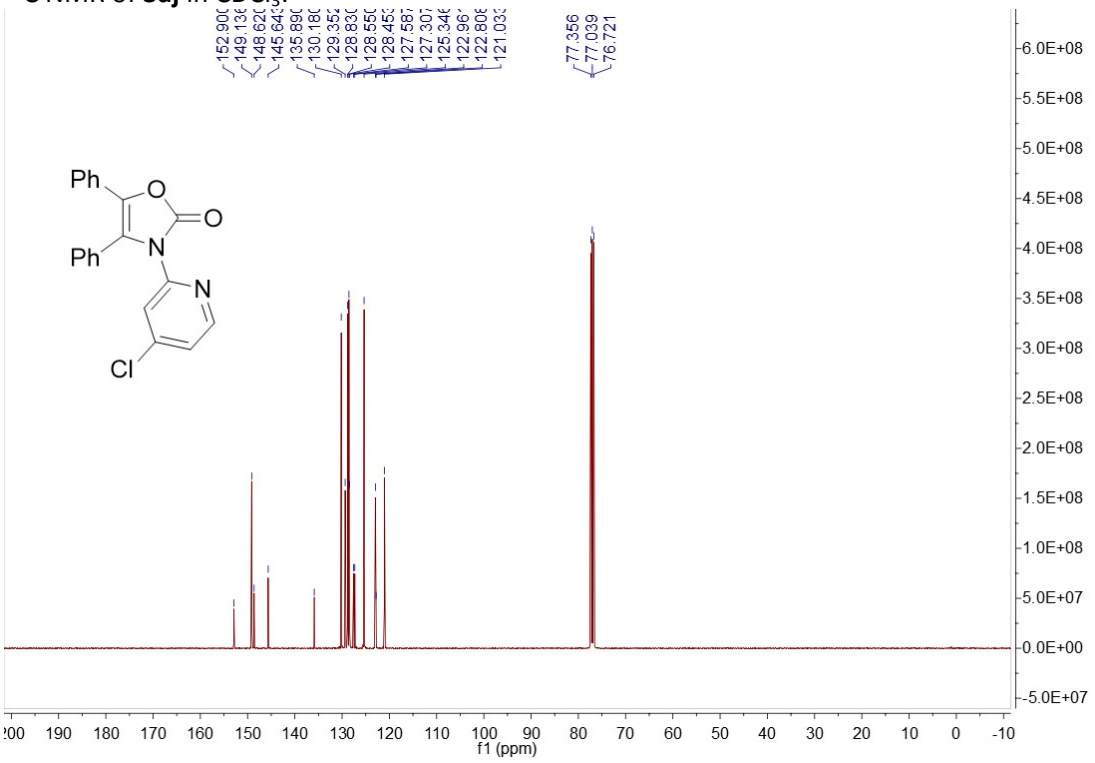
^{13}C NMR of **3ai** in $CDCl_3$:



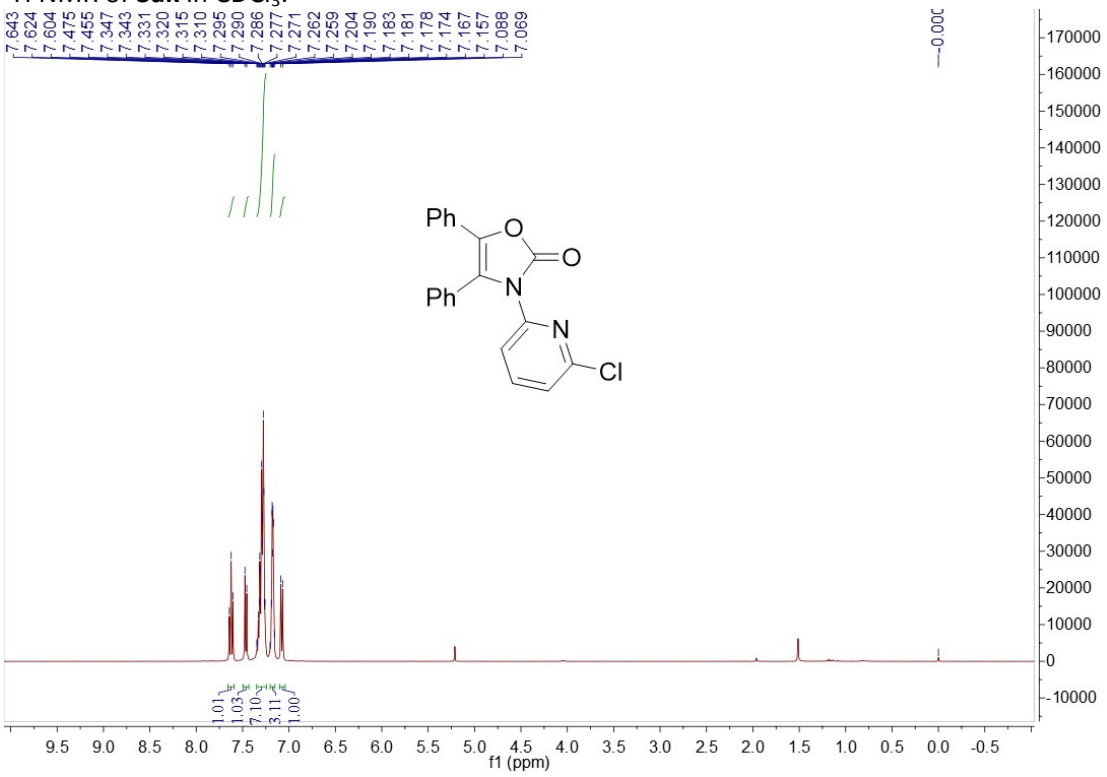
^{1}H NMR of **3aj** in $CDCl_3$:



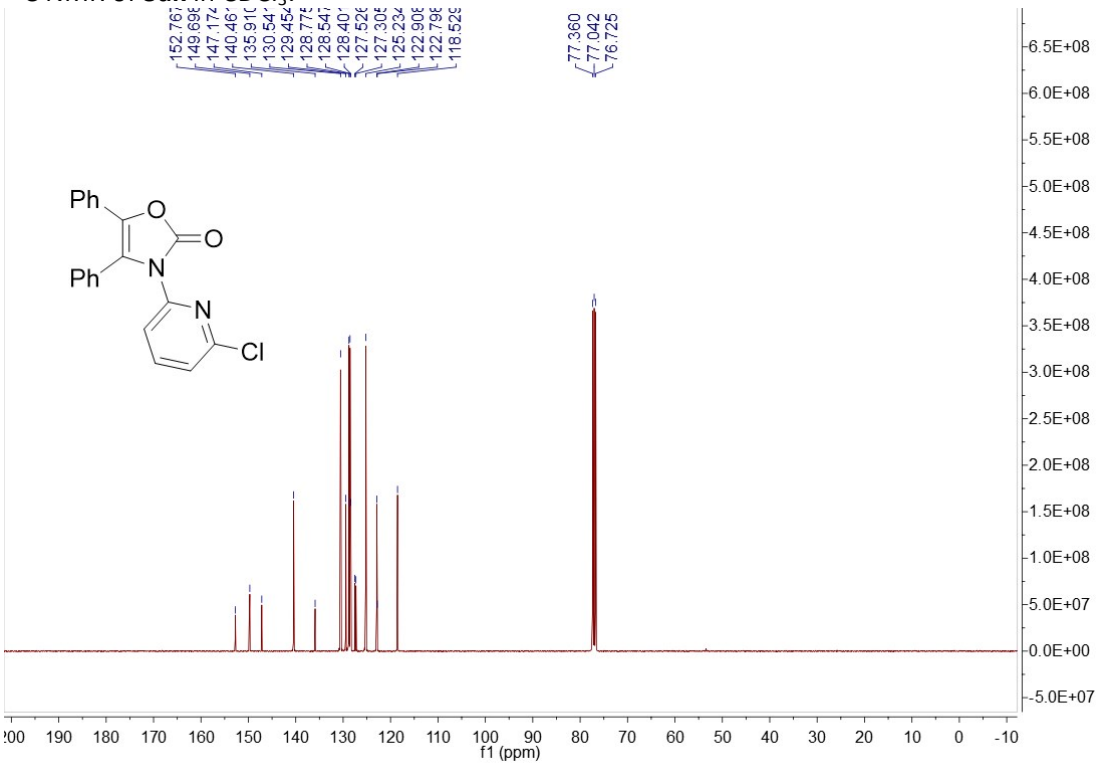
^{13}C NMR of **3aj** in $CDCl_3$:



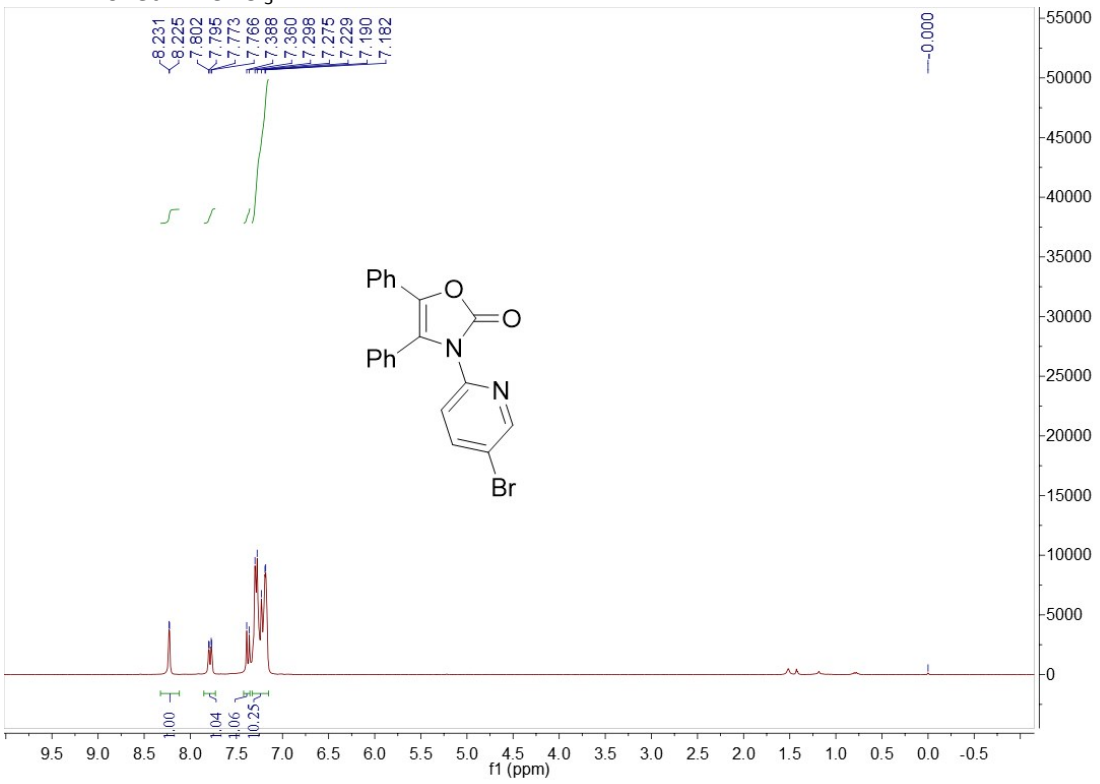
^{1}H NMR of **3ak** in $CDCl_3$:



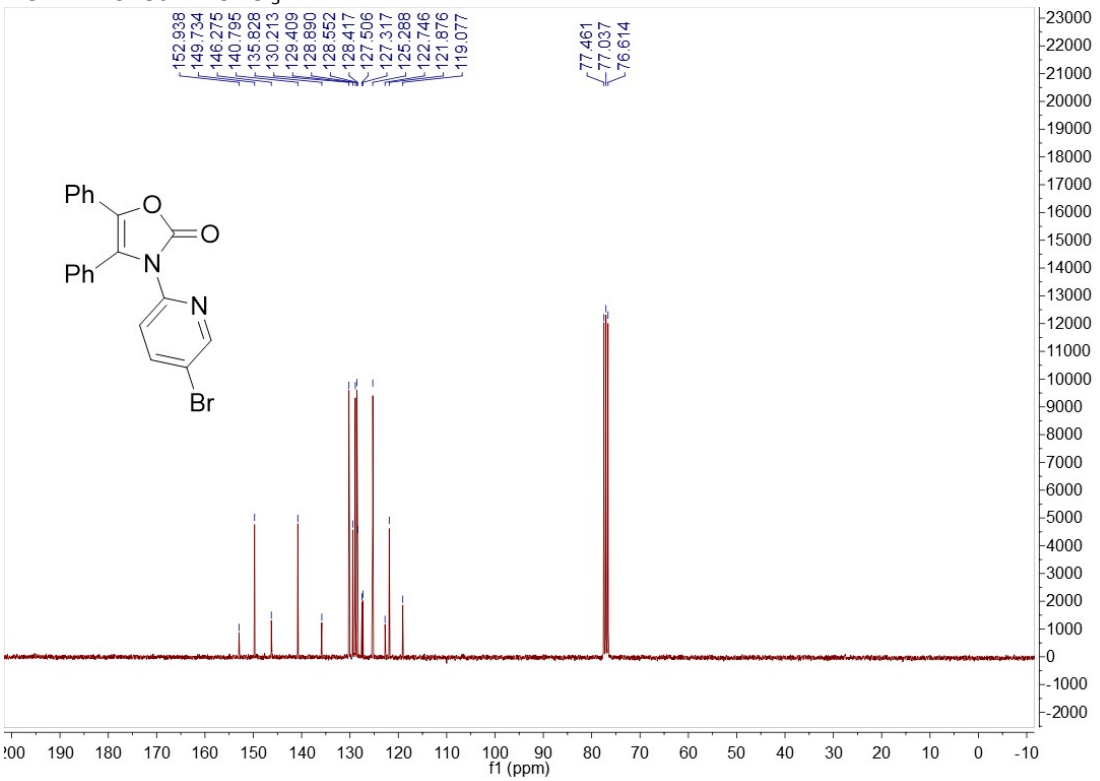
^{13}C NMR of **3ak** in $CDCl_3$:



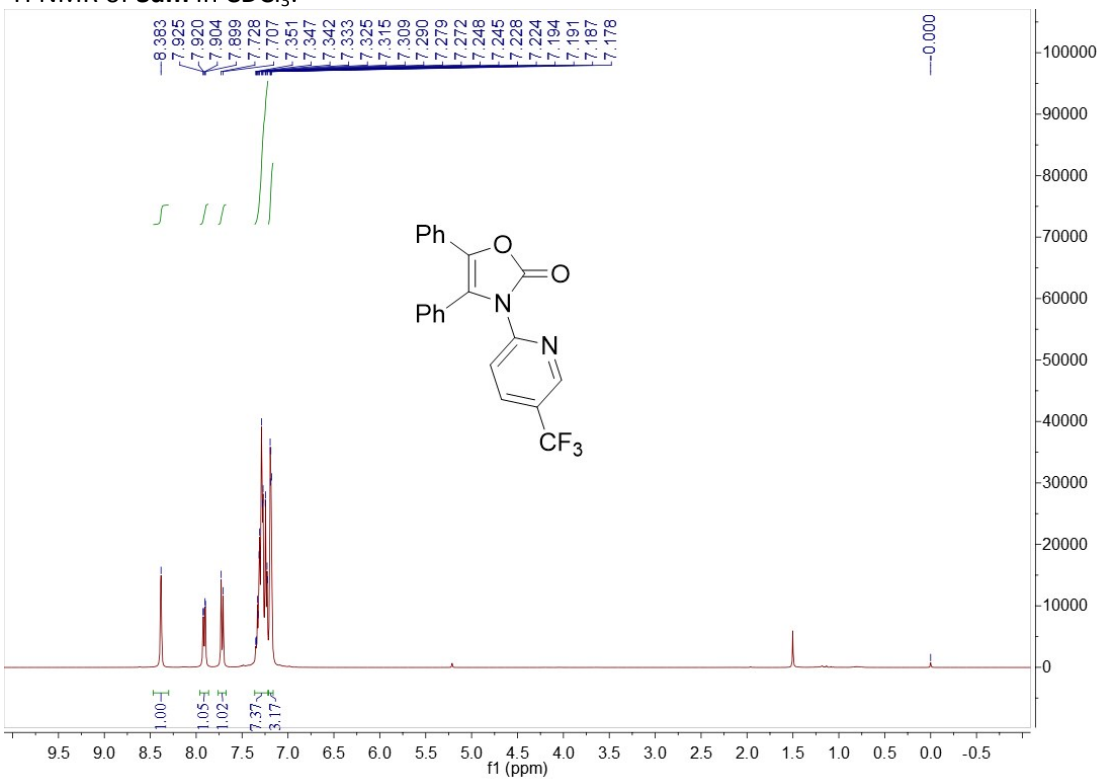
^{1}H NMR of **3al** in $CDCl_3$:



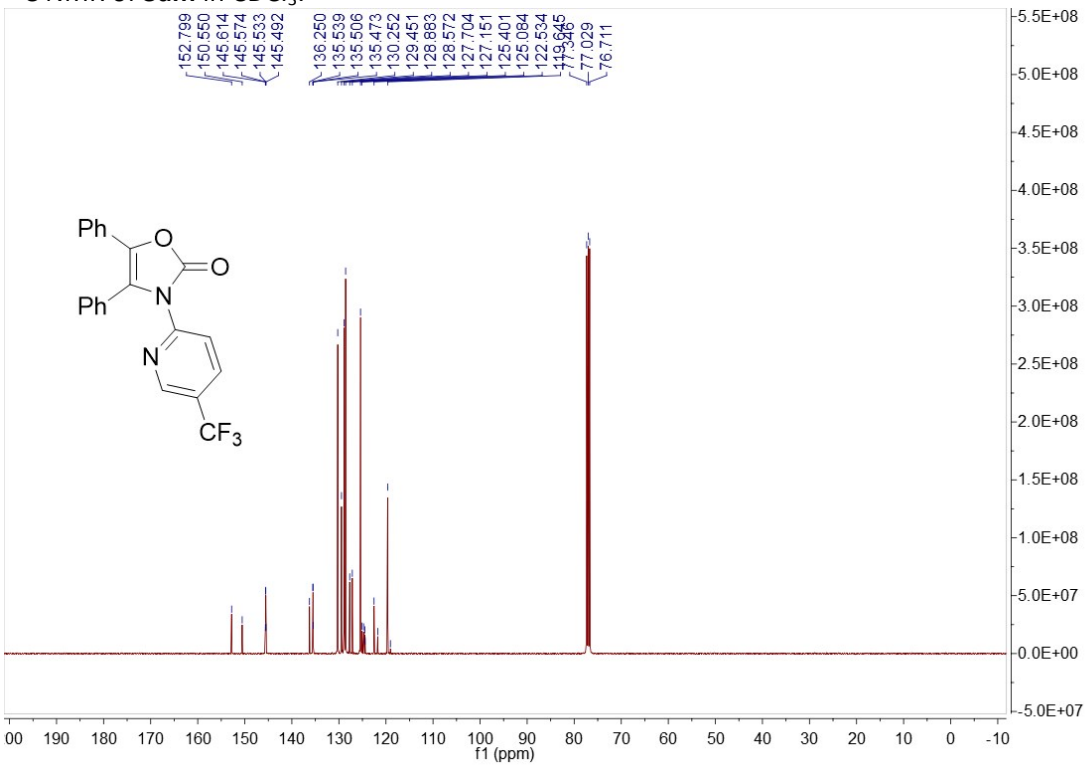
^{13}C NMR of **3al** in $CDCl_3$:



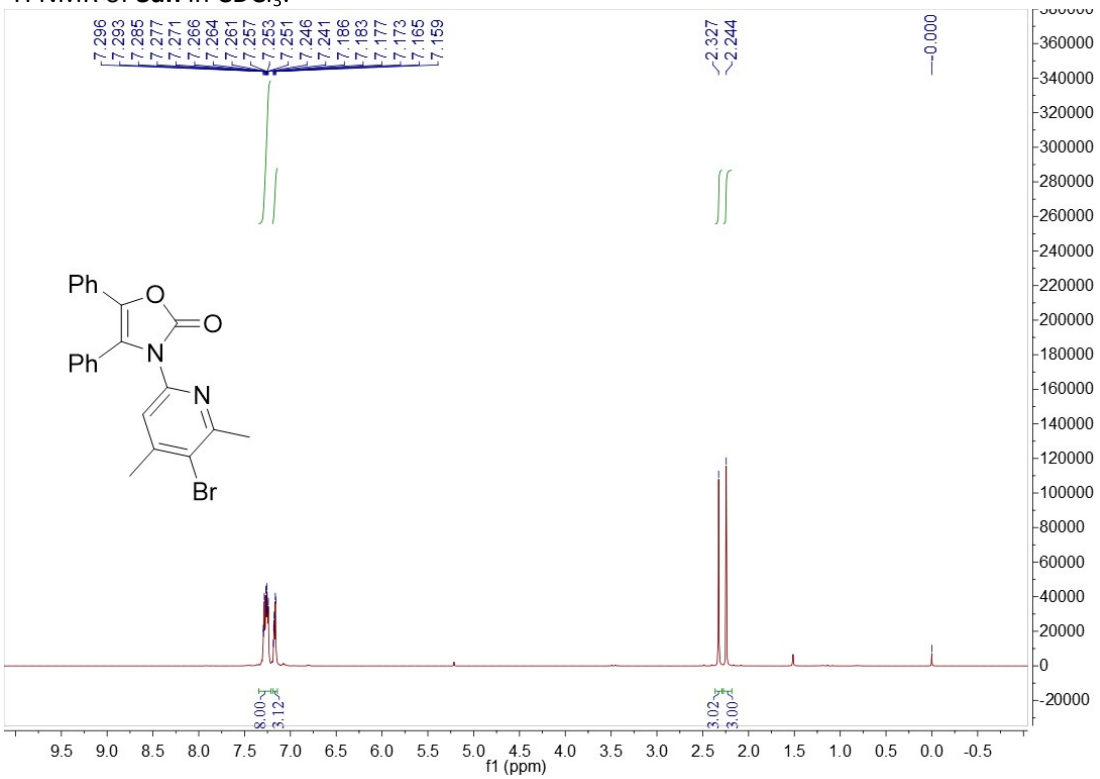
^{1}H NMR of **3am** in $CDCl_3$:



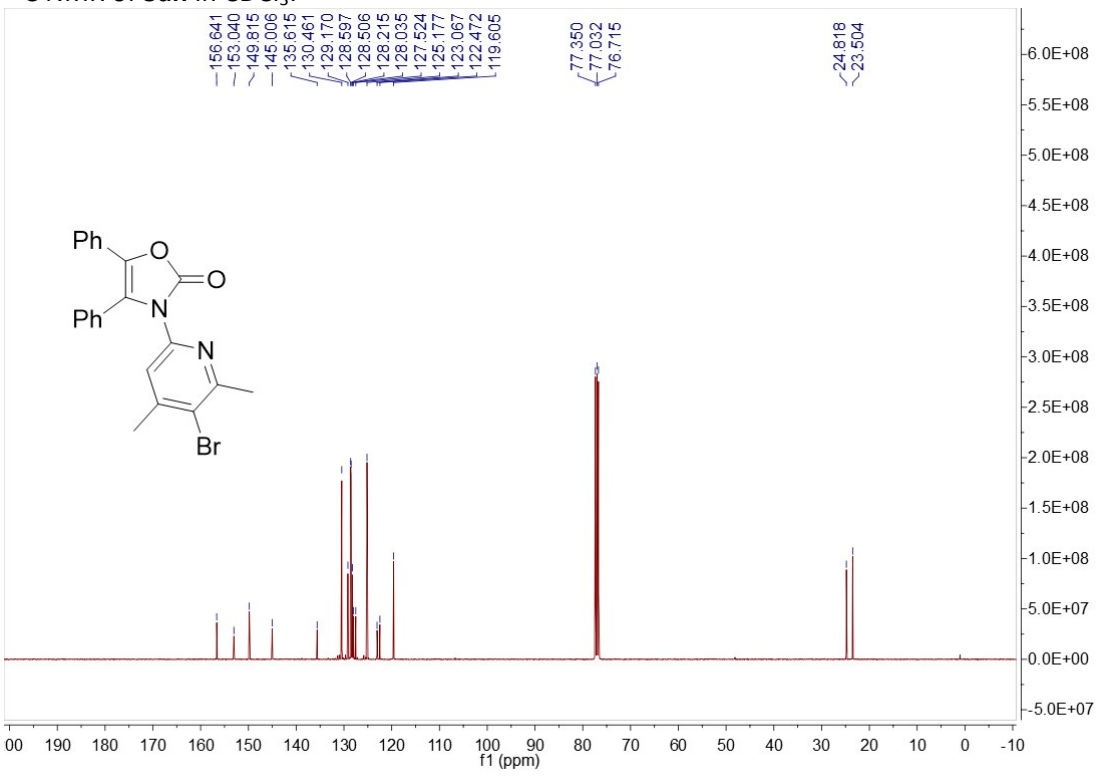
^{13}C NMR of **3am** in $CDCl_3$:



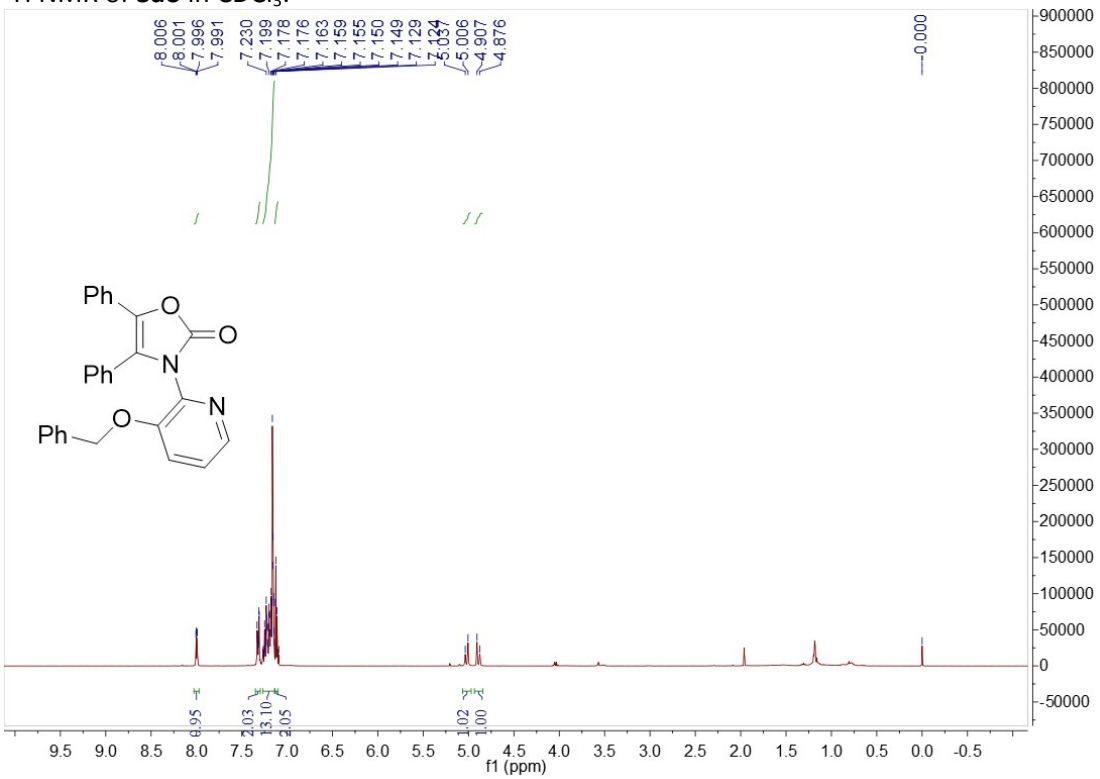
^{1}H NMR of **3an** in $CDCl_3$:



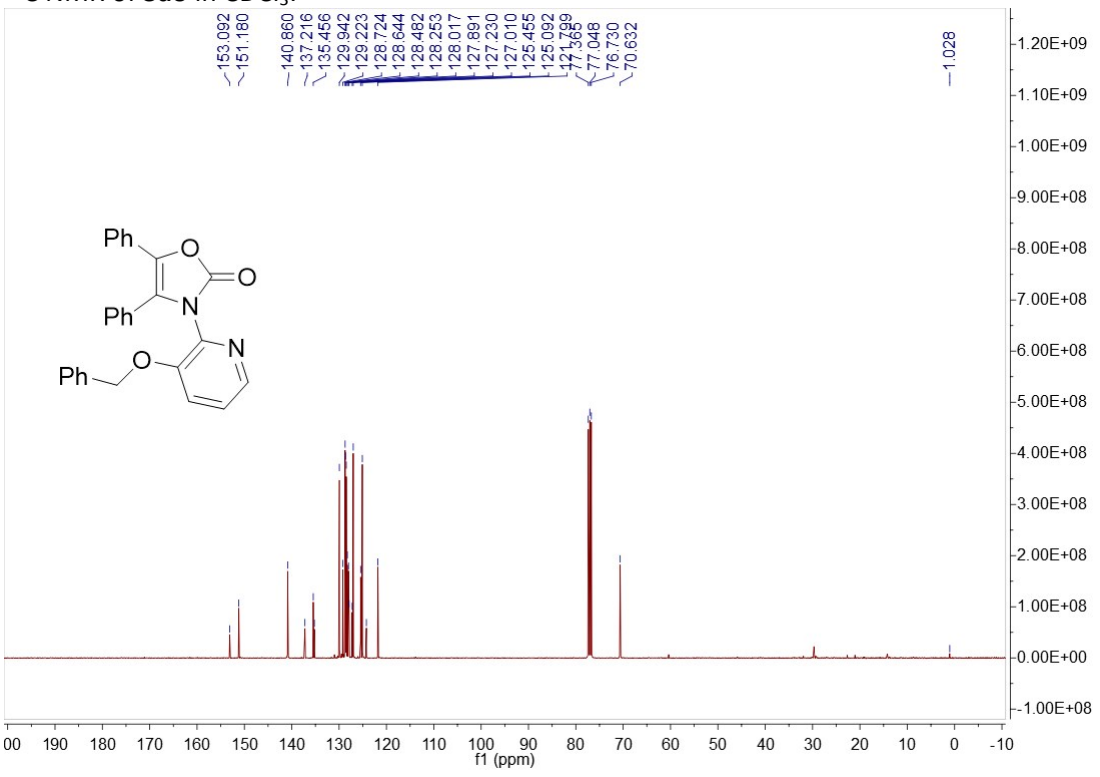
^{13}C NMR of **3an** in $CDCl_3$:



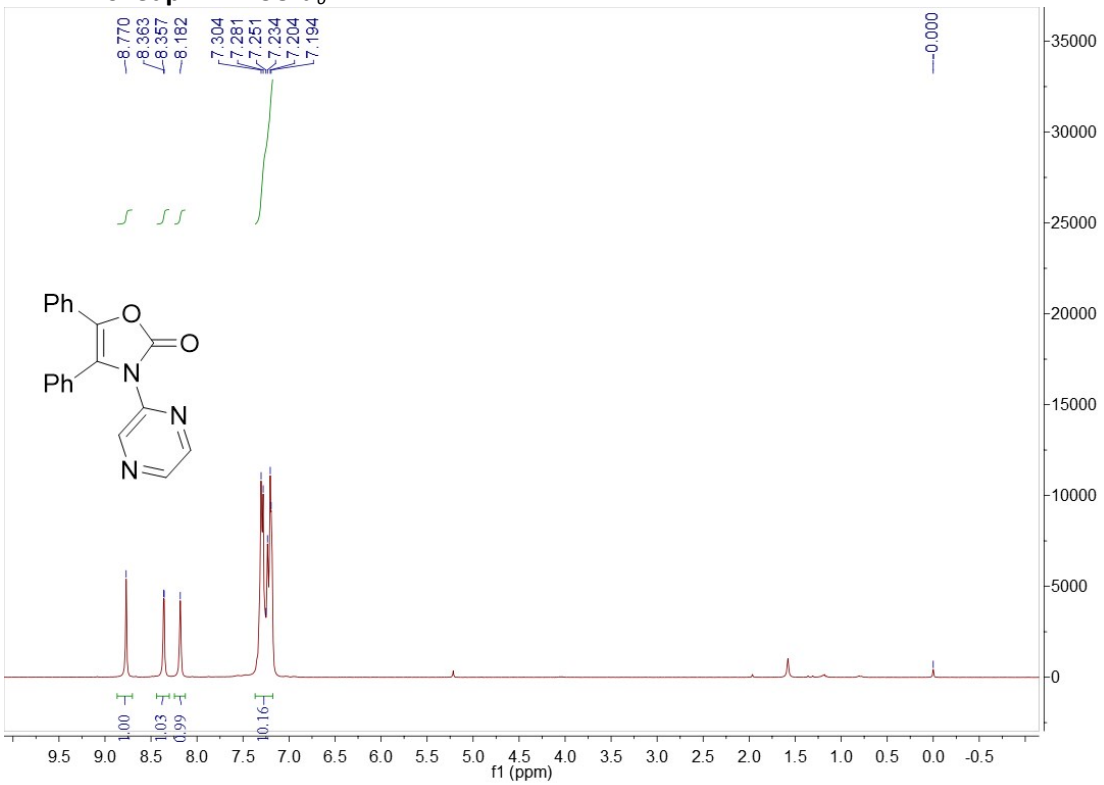
^{1}H NMR of **3ao** in $CDCl_3$:



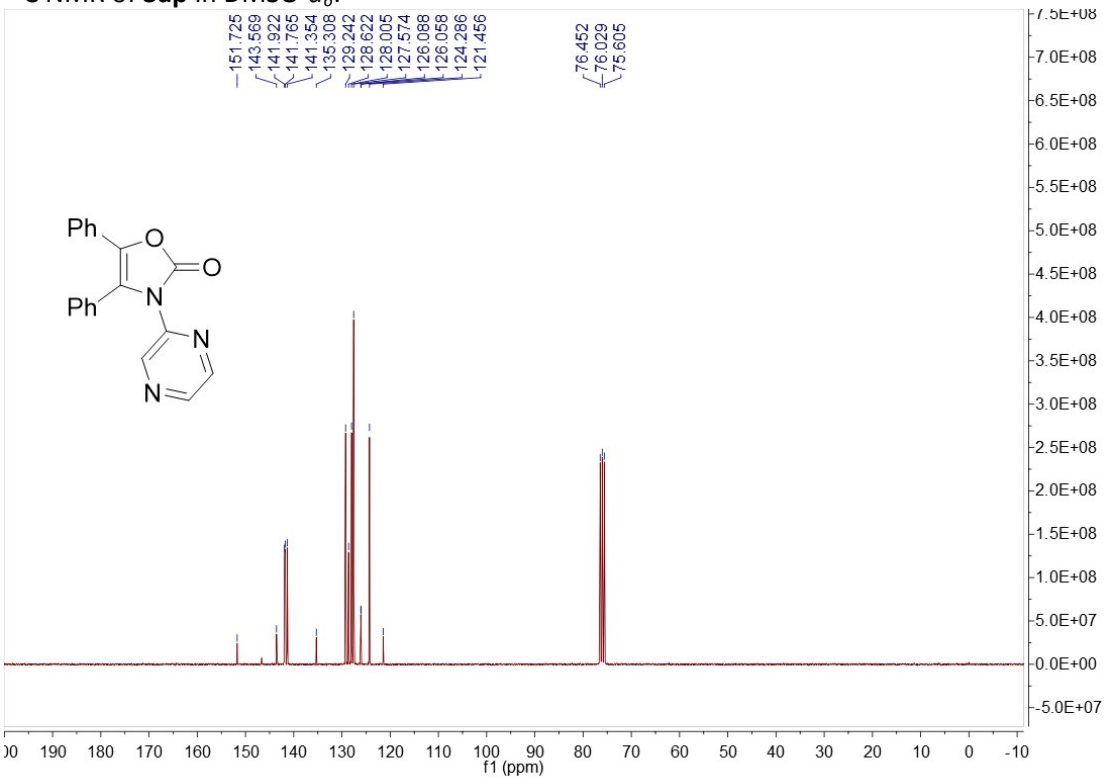
^{13}C NMR of **3ao** in $CDCl_3$:



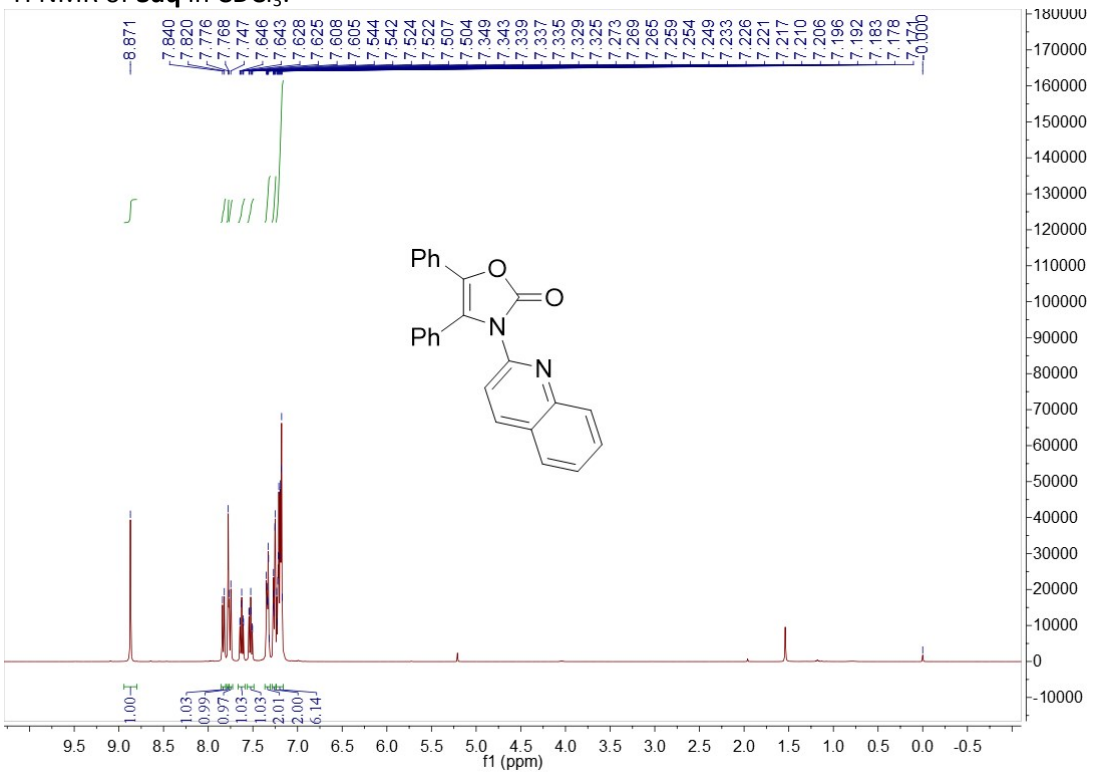
^{1}H NMR of **3ap** in DMSO-d_6:



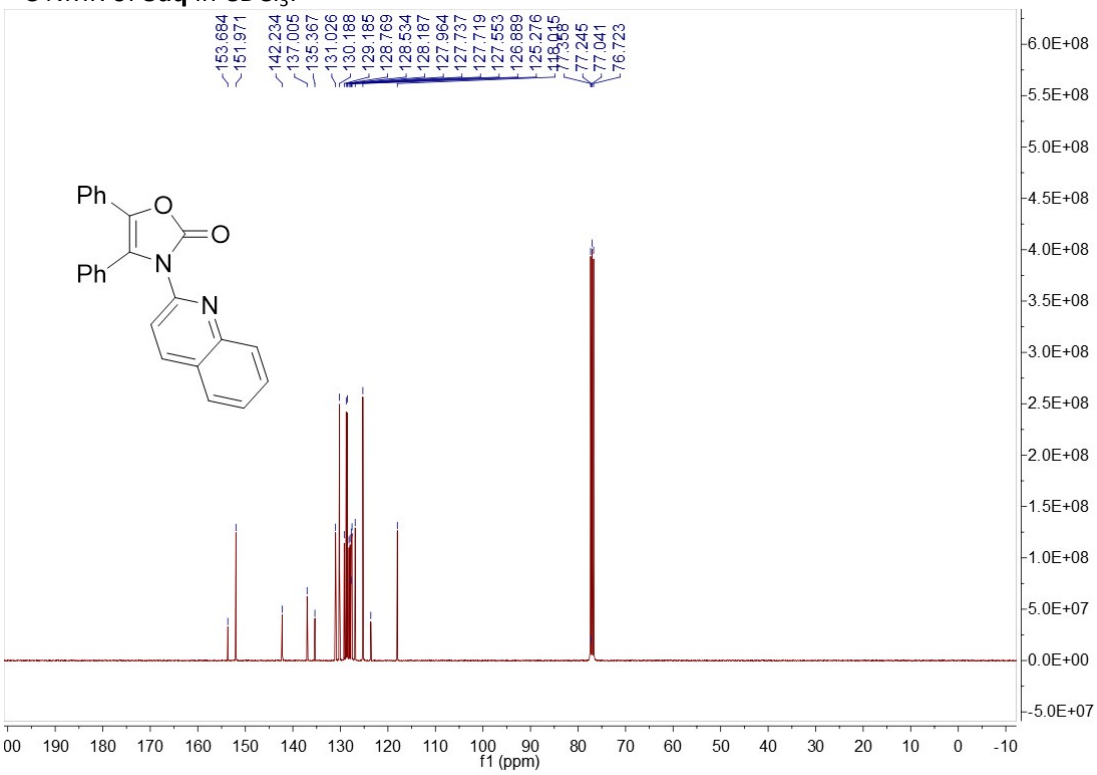
^{13}C NMR of **3ap** in DMSO-d_6:



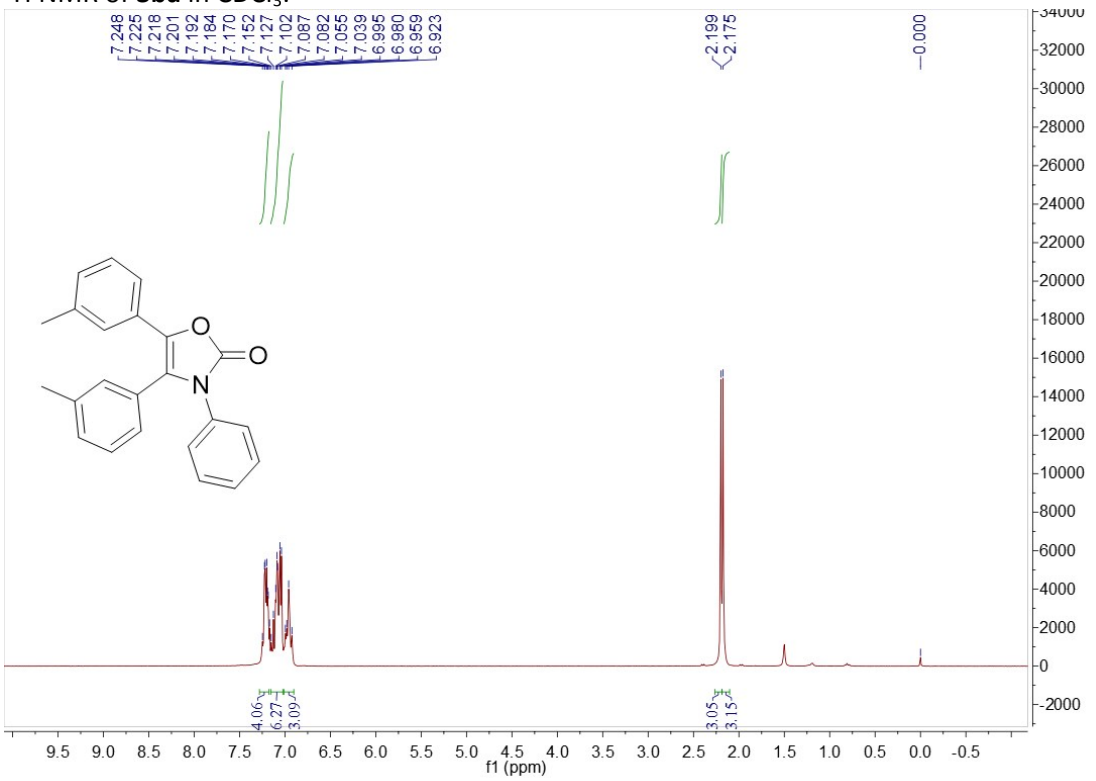
^{1}H NMR of **3aq** in $CDCl_3$:



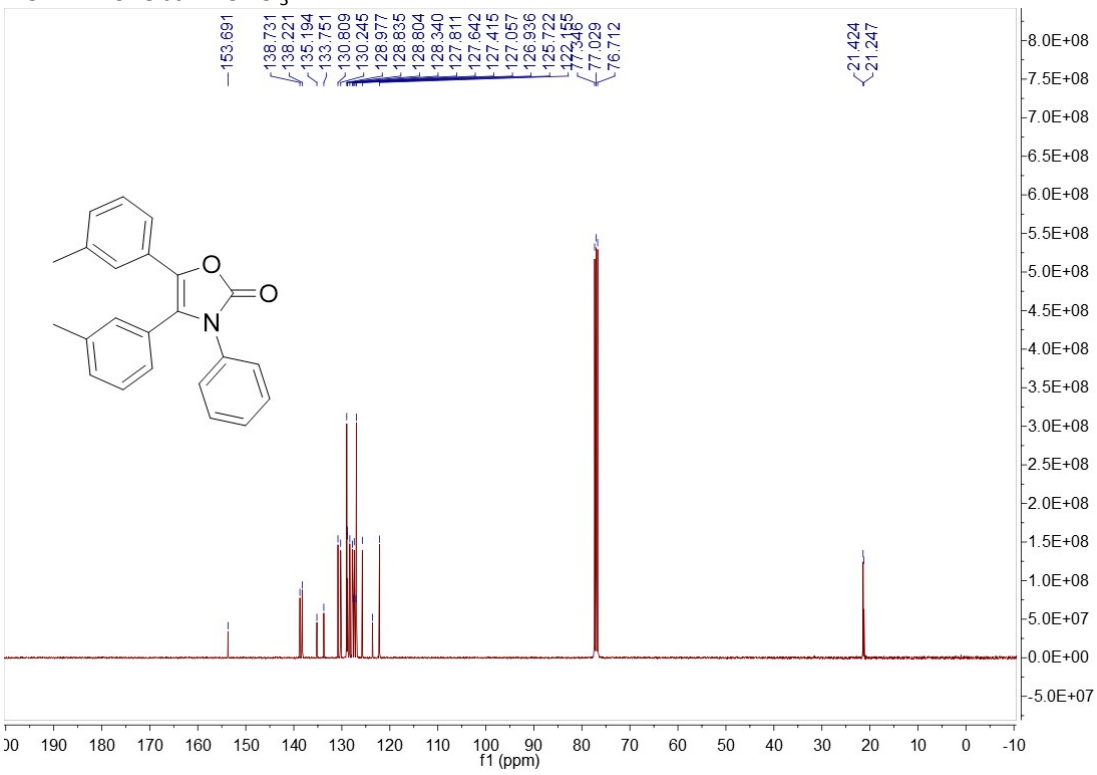
^{13}C NMR of **3aq** in $CDCl_3$:



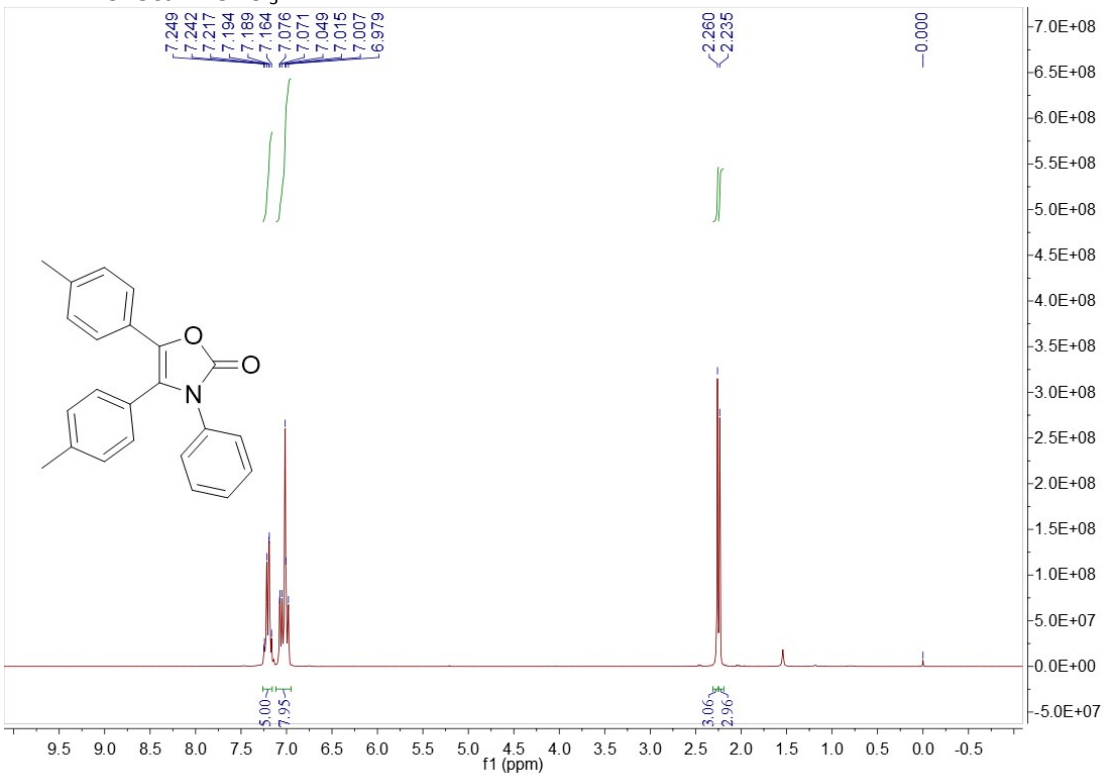
^{1}H NMR of **3ba** in $CDCl_3$:



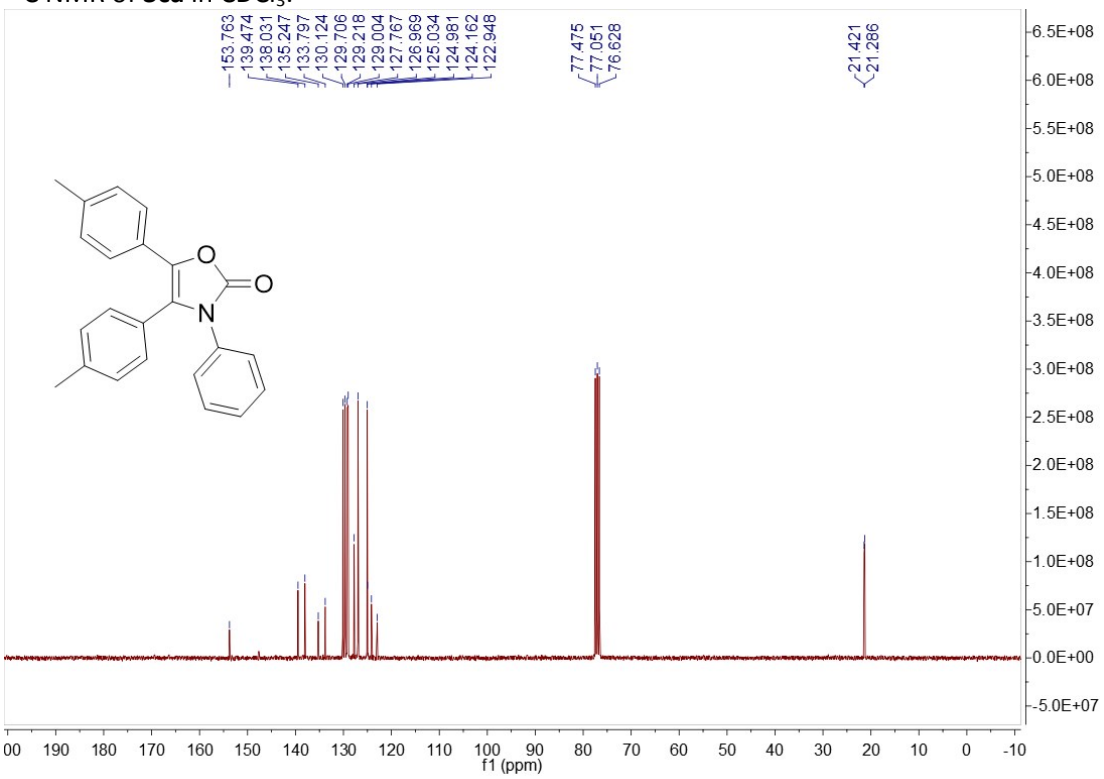
^{13}C NMR of **3ba** in $CDCl_3$:



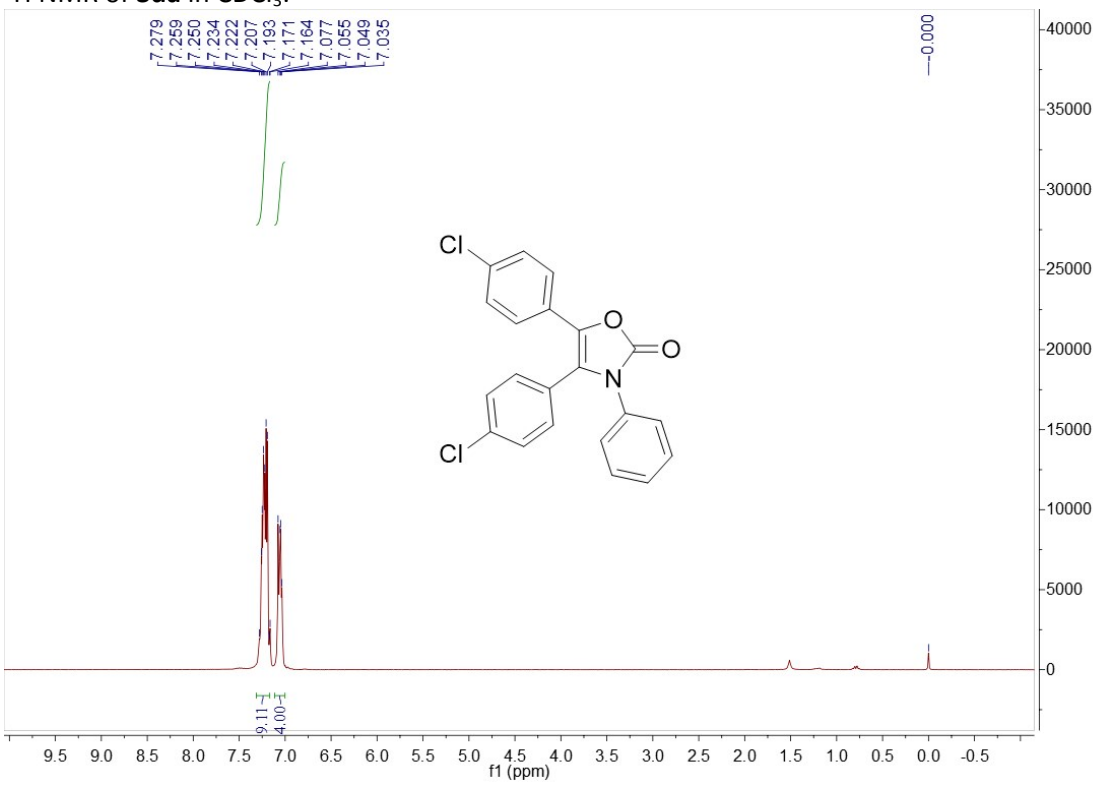
^{1}H NMR of **3ca** in $CDCl_3$:



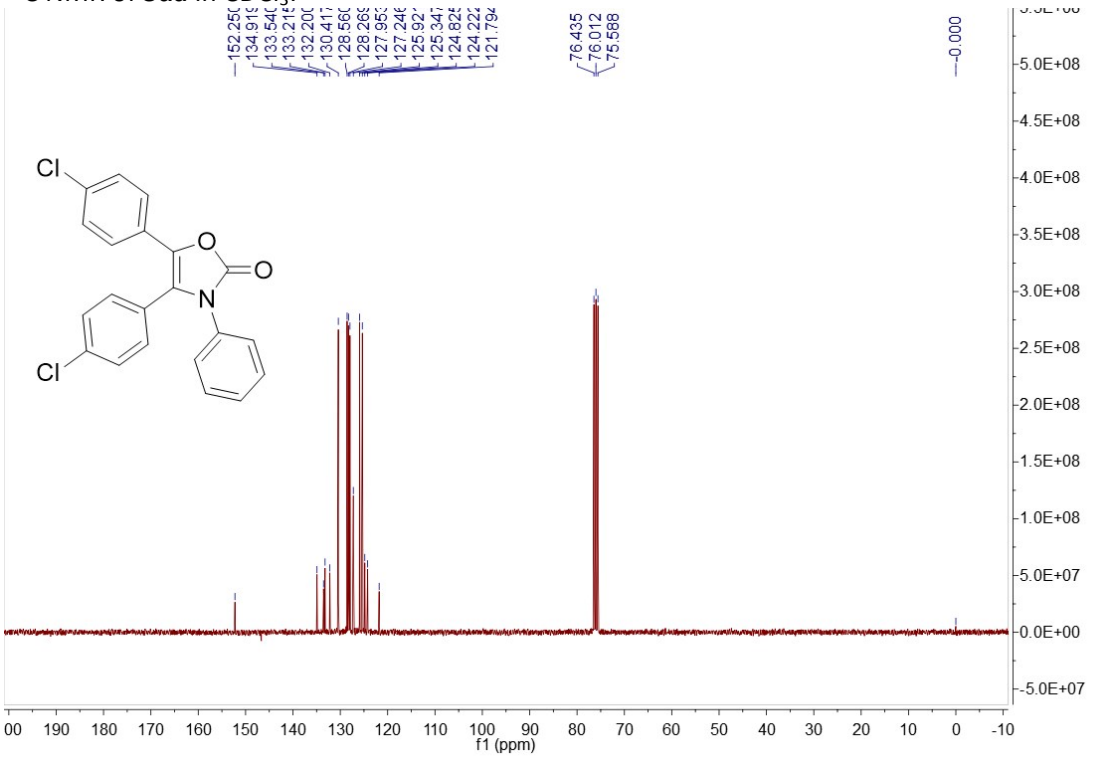
^{13}C NMR of **3ca** in $CDCl_3$:



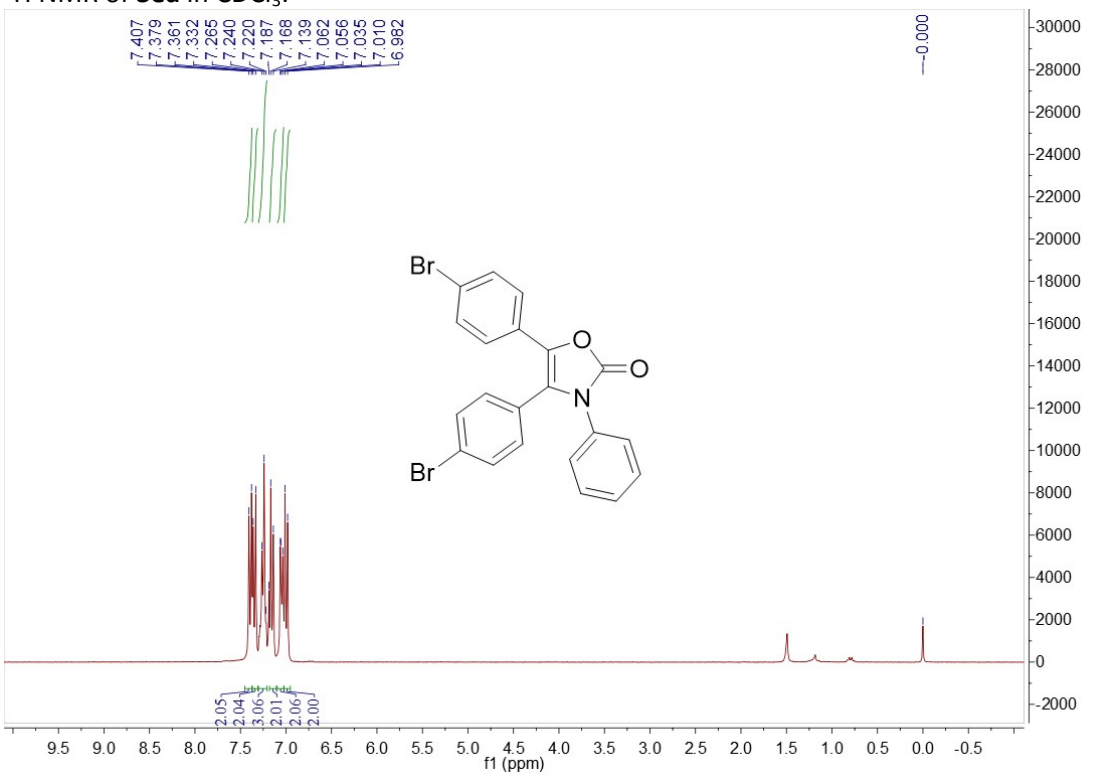
^{1}H NMR of **3da** in $CDCl_3$:



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



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



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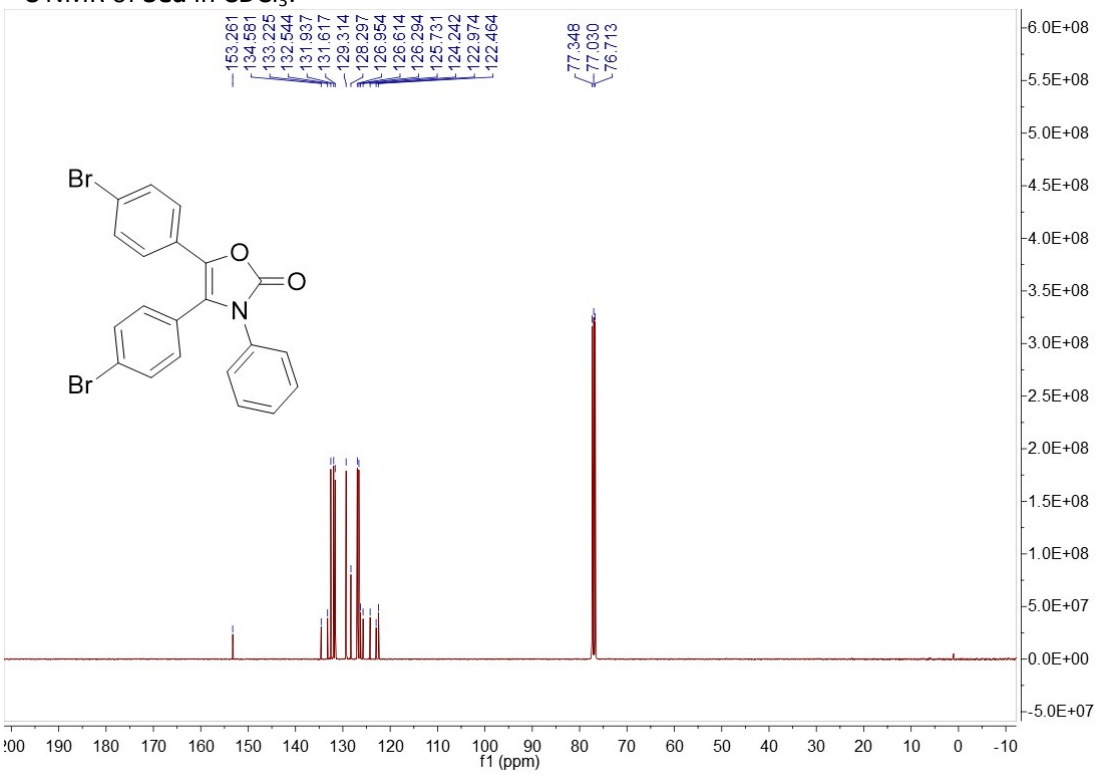
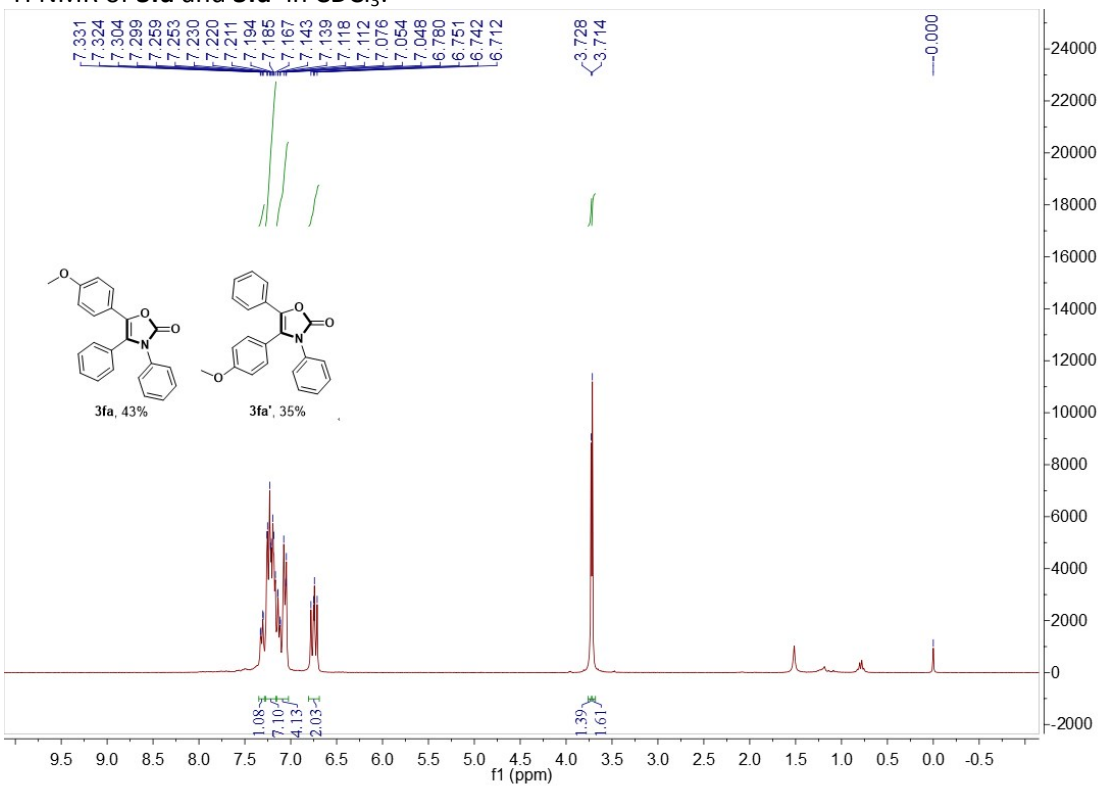
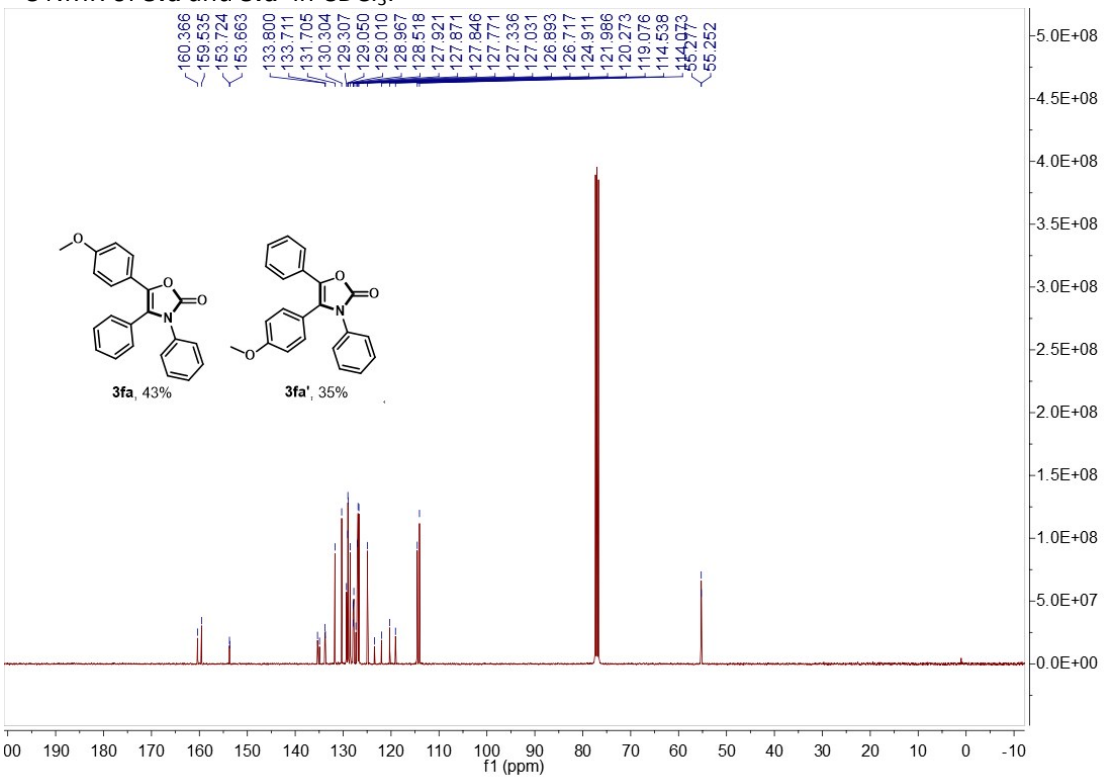


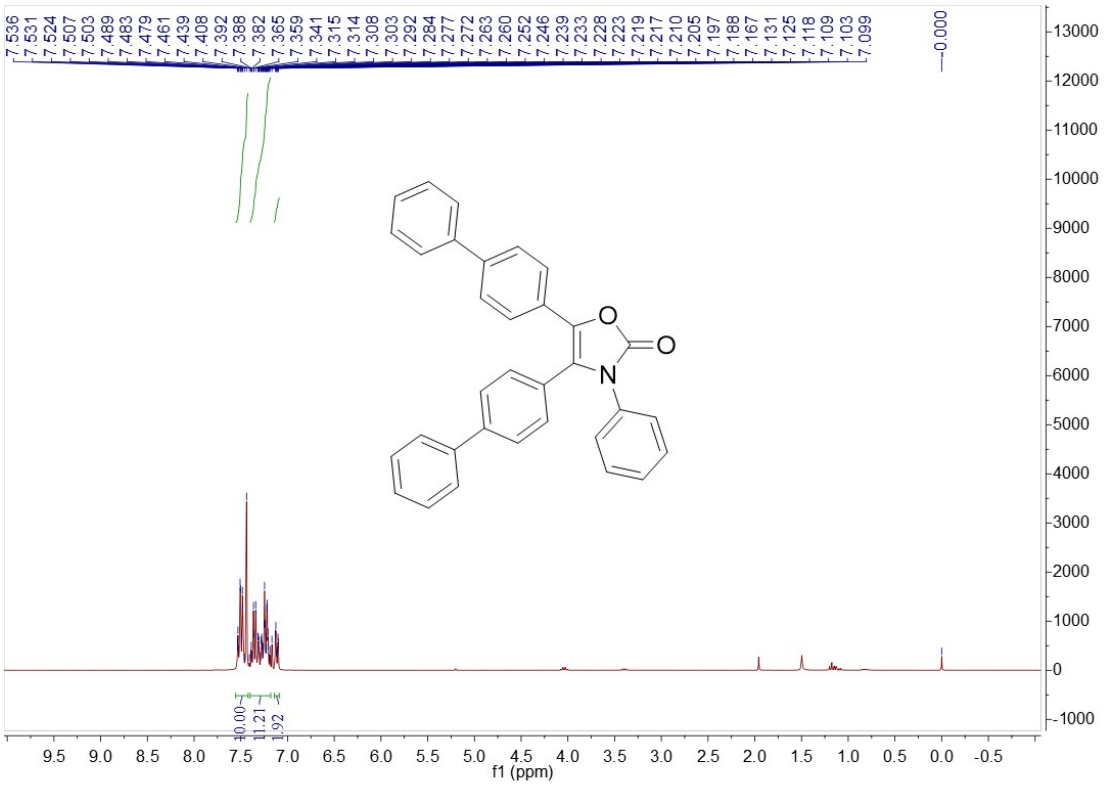
^{1}H NMR of **3fa** and **3fa'** in $CDCl_3$:



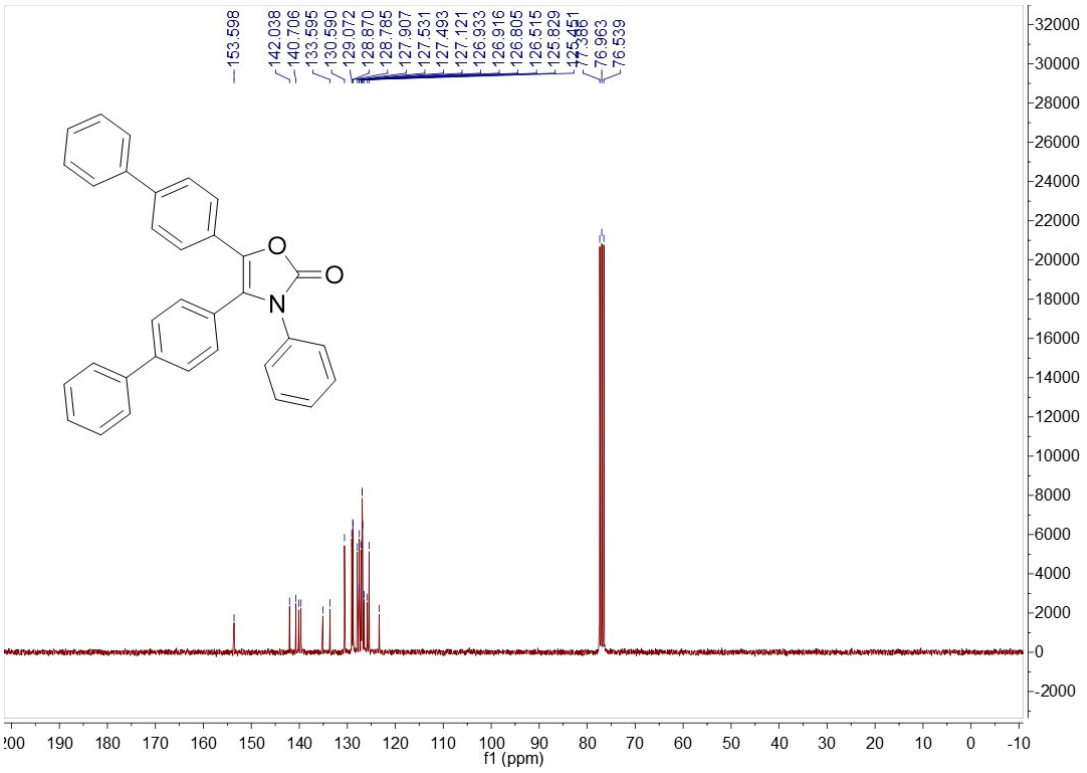
^{13}C NMR of **3fa** and **3fa'** in $CDCl_3$:



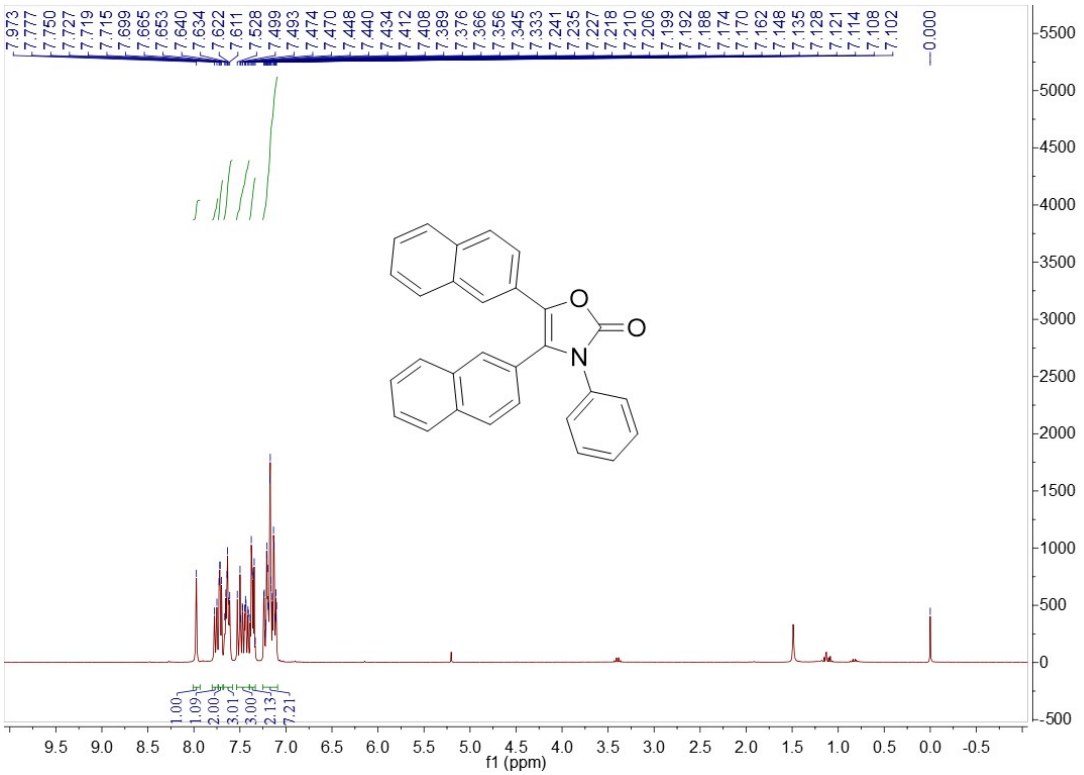
^{1}H NMR of **3ga** in $CDCl_3$:



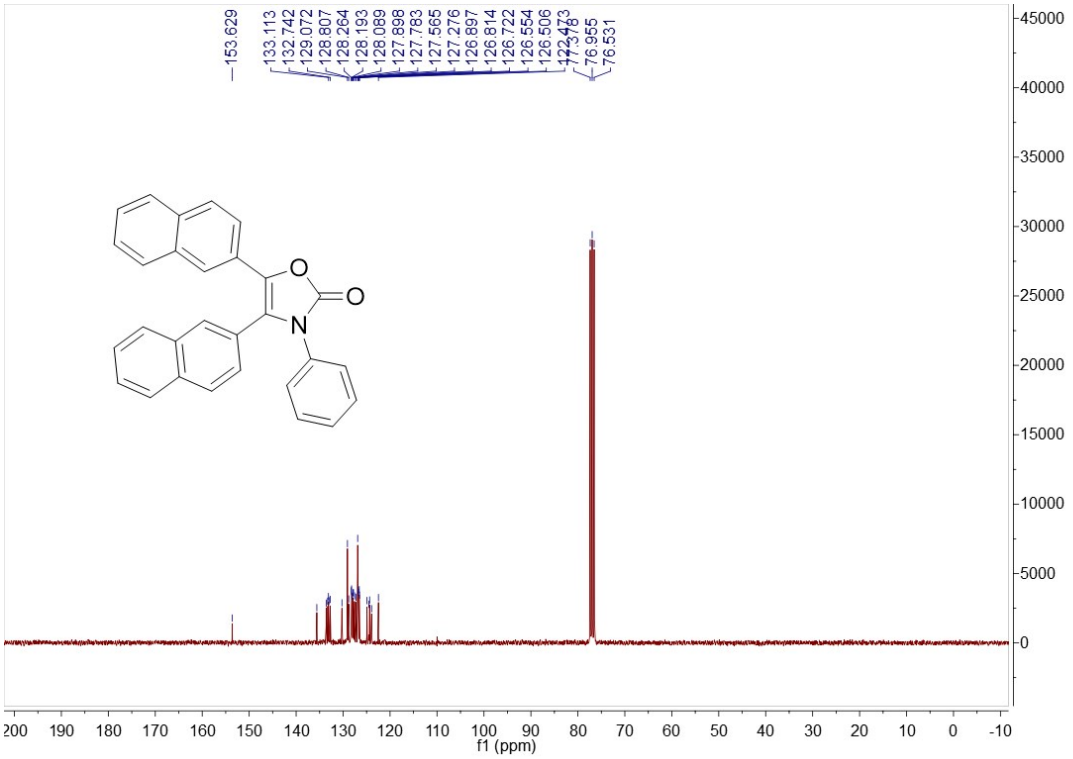
^{13}C NMR of **3ga** in $CDCl_3$:



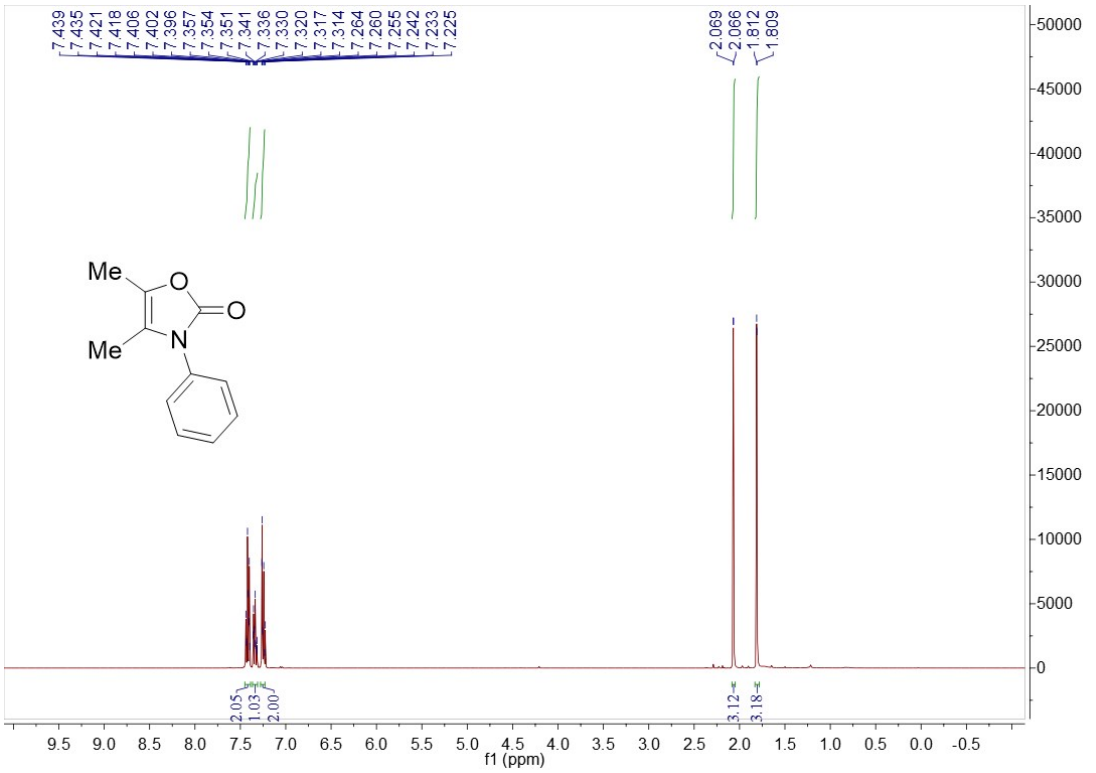
^{1}H NMR of **3ha** in $CDCl_3$:



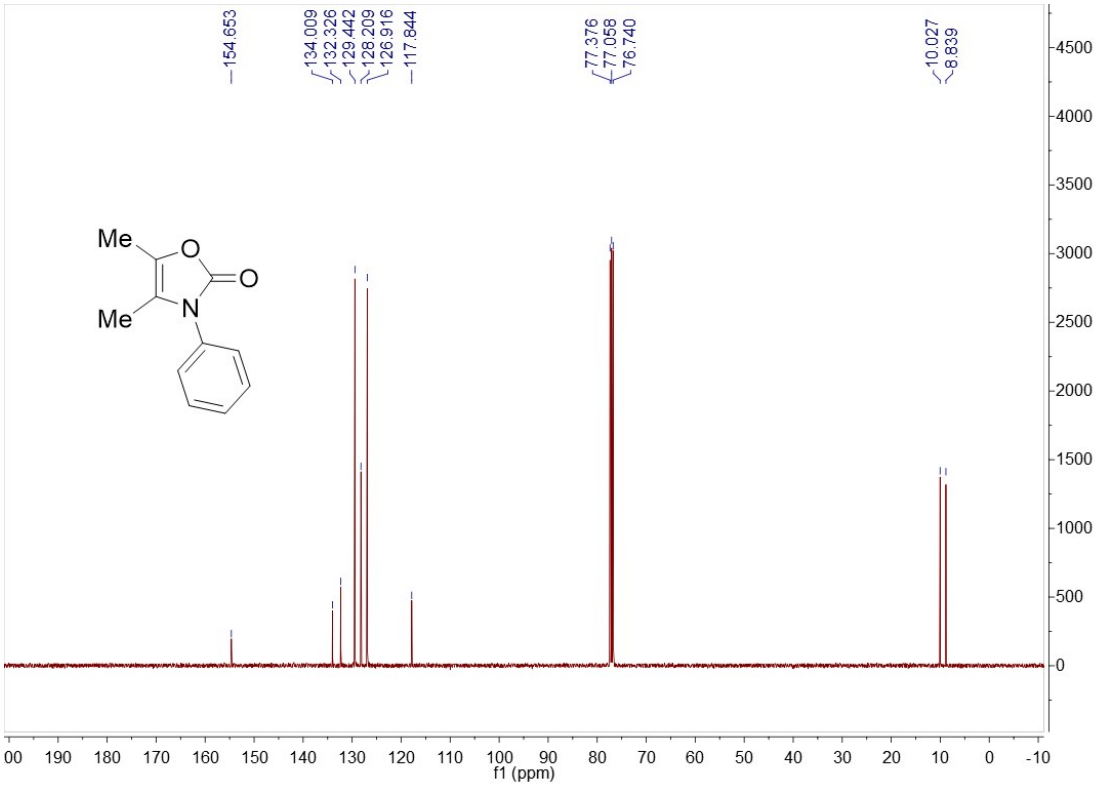
^{13}C NMR of **3ha** in $CDCl_3$:



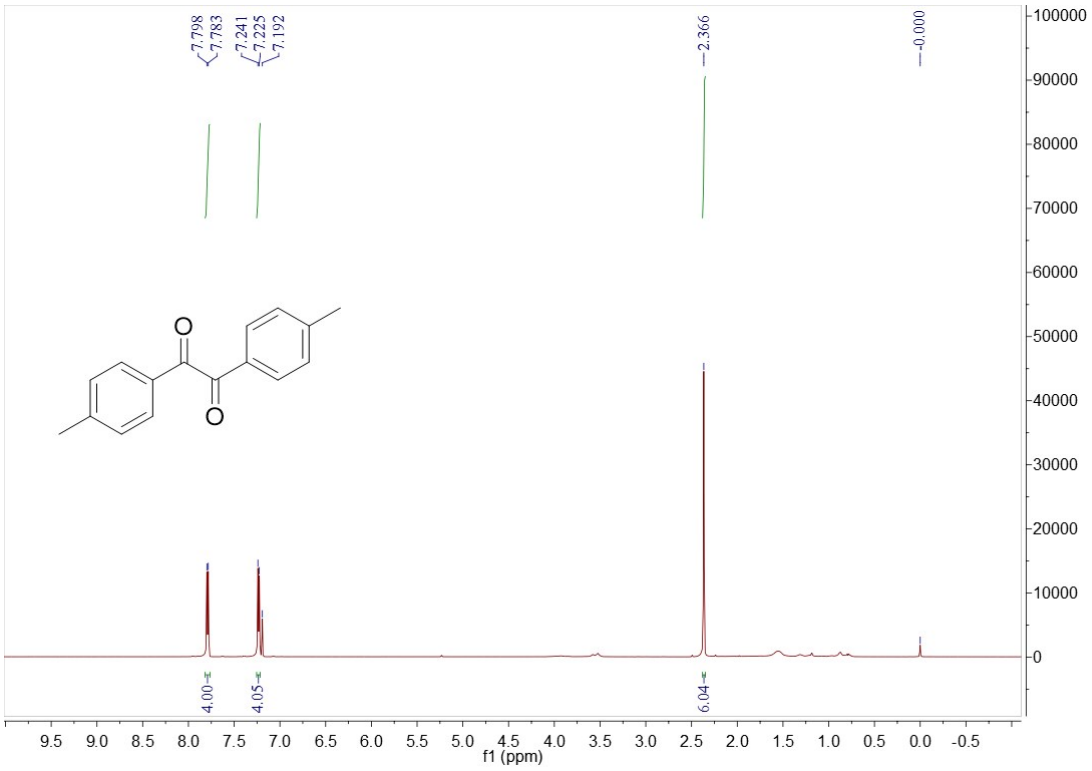
^{1}H NMR of **3ia** in $CDCl_3$:



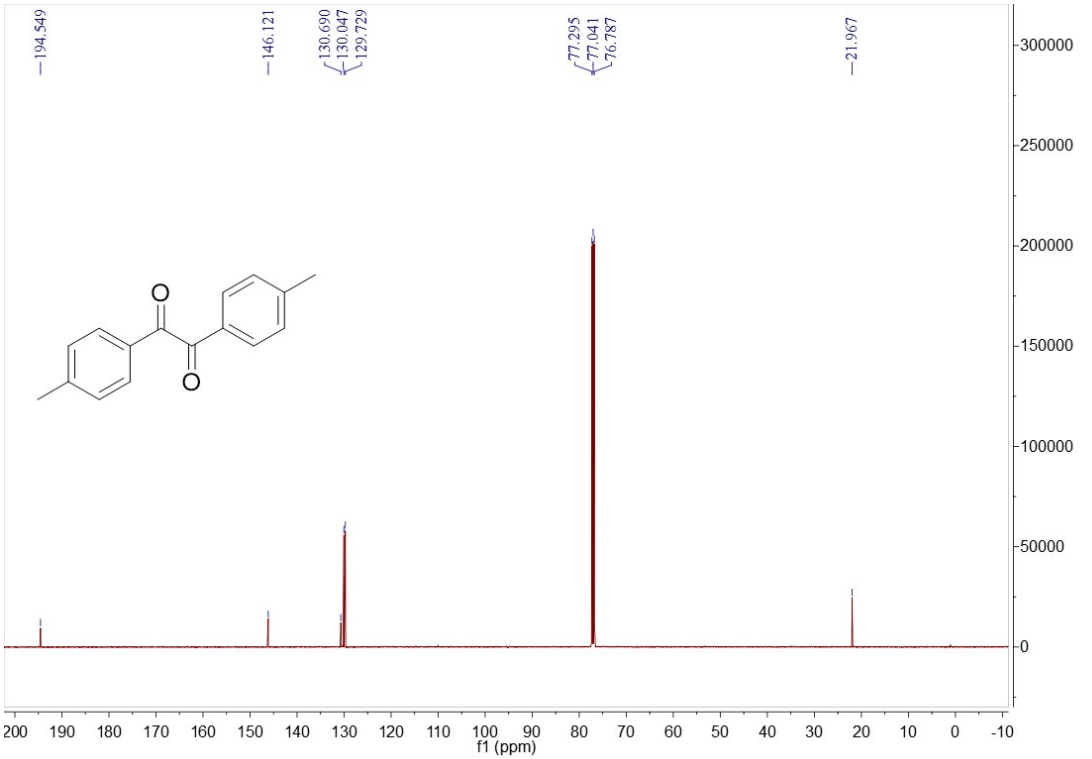
^{13}C NMR of **3ia** in $CDCl_3$:



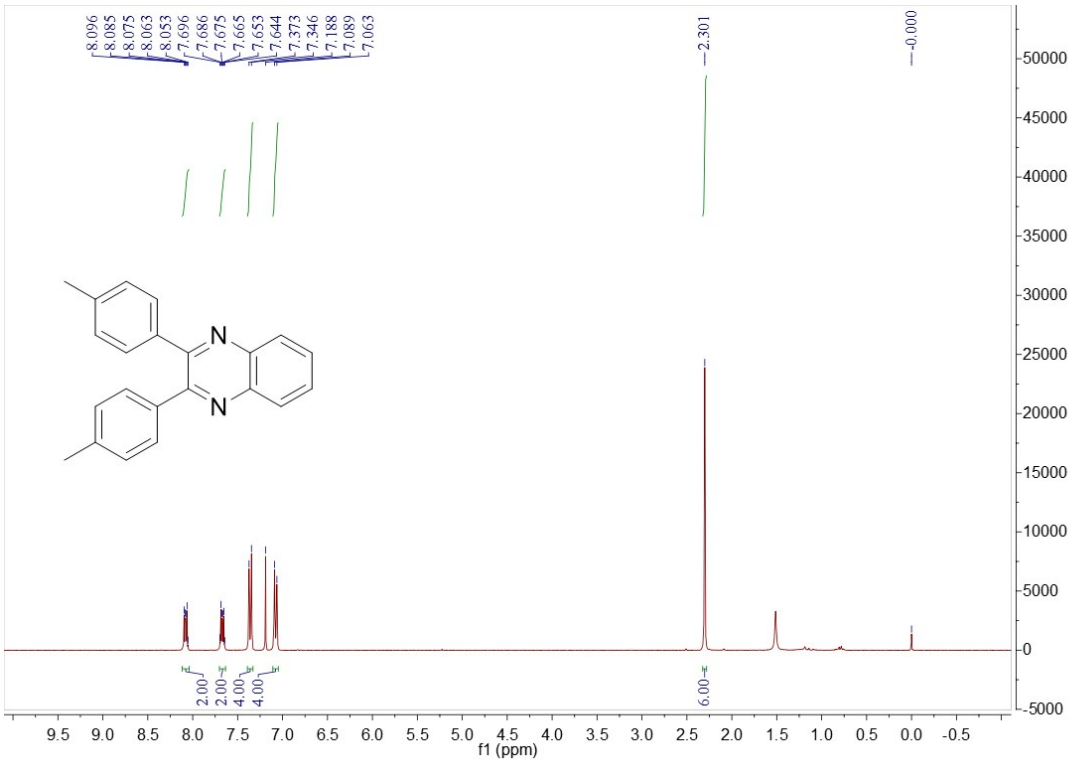
^{1}H NMR of **5** in $CDCl_3$:



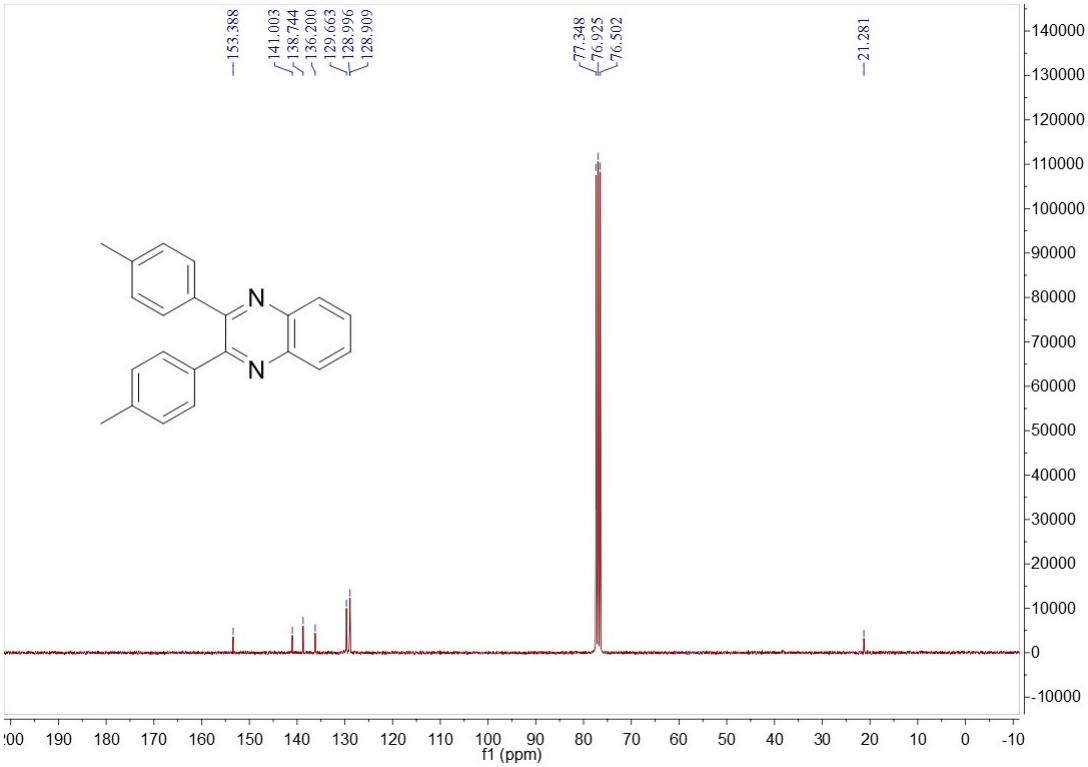
^{13}C NMR of **5** in $CDCl_3$:



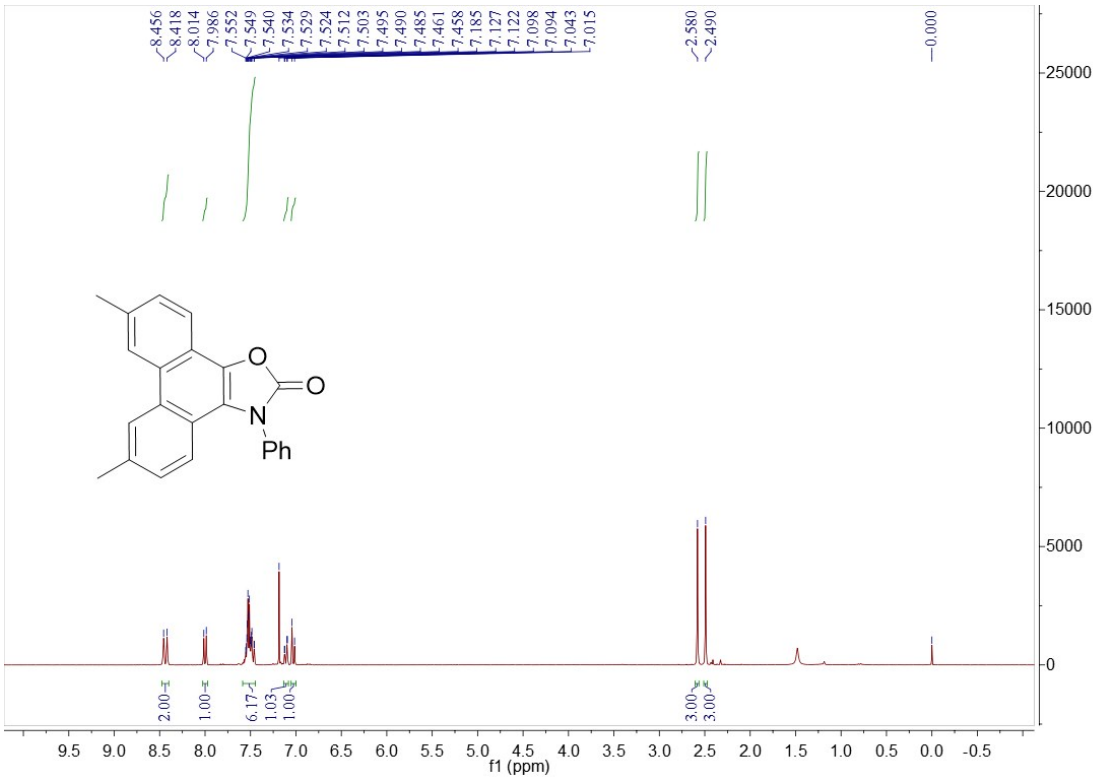
^{1}H NMR of **6** in $CDCl_3$:



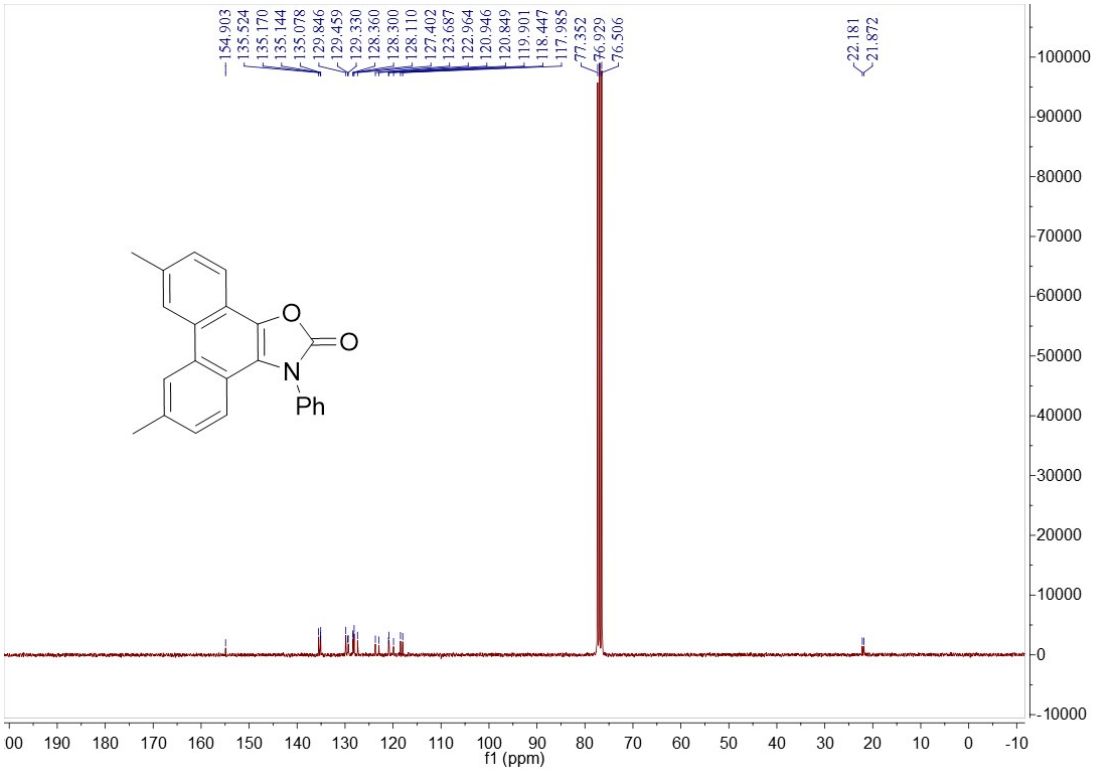
^{13}C NMR of **6** in $CDCl_3$:



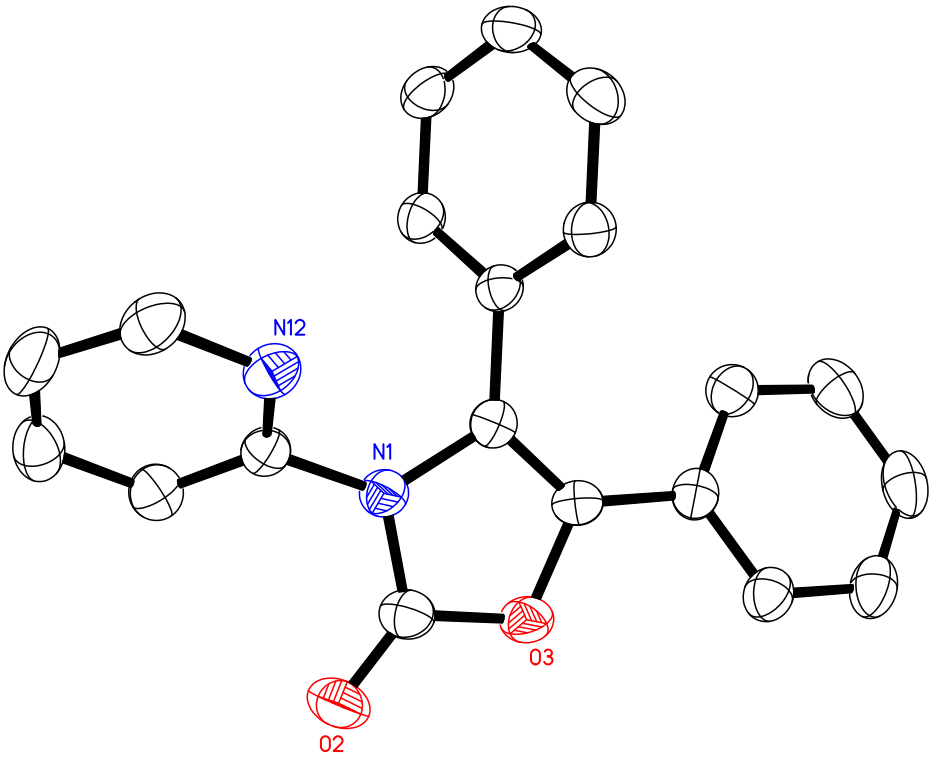
^{1}H NMR of **7** in $CDCl_3$:

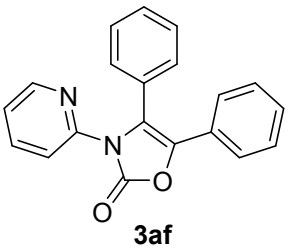


^{13}C NMR of **7** in $CDCl_3$:



5. Solid state molecular structure of 3af





3af

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[2] (a) X. Tian, L. Song, M. Rudolph, F. Rominger, T. Oeser and A. S. K. Hashmi, *Angew. Chem. Int. Ed.*, 2019, **58**, 3589; (b) X. Tian, L. Song, M. Rudolph, Q. Wang, X. Song, F. Rominger and A. S. K. Hashmi, *Org. Lett.*, 2019, **21**, 1598.

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