

Supporting Information

Synthesis of 2,5-Diaryloxazoles through Rhodium-Catalyzed Annulation of Triazoles and Aldehydes

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General Information

All reactions were carried out under an air atmosphere condition. Solvents and reagents were purchased from commercial source and used without further purification. Flash column chromatography was performed using silica gel (200-300 mesh). Analytical thin-layer chromatography was performed using glass plates pre-coated with 200-300 mesh silica gel impregnated with a fluorescent indicator (254 nm). NMR spectra were recorded in CDCl₃ on Bruker NMR-300 (400 MHz) and NMR-400 (500 MHz) with TMS as an internal reference. HRMS were performed on Agilent 6540 Q-TOF mass spectrometer (ESI). X-ray crystallographic data were collected using a SMART APEX II X-ray diffractometer.

ORTEP diagram of compound **3x**

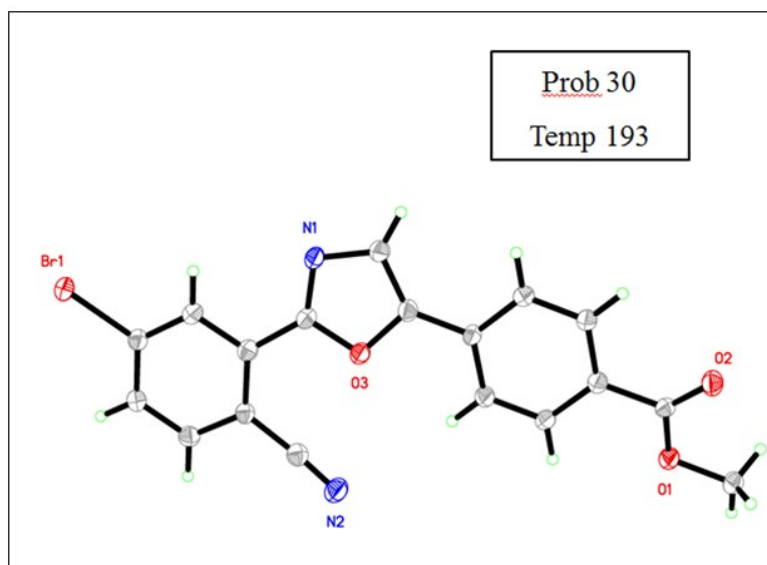


Figure S1. ORTEP drawing (30%) of the crystal structure **3x**

Crystallographic data **3x** (CCDC 1960749) has been deposited at the Cambridge Crystallographic Database Centre and is available on request from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (<http://www.ccdc.cam.ac.uk>).

Table S1. Crystal data parameter for compound 3x	
Formula unit	C ₂₄ H ₁₇ BrINO ₂
Formula wt.	558.20
Crystal system	monoclinic
T [K]	293
<i>a</i> [Å]	7.600
<i>b</i> [Å]	17.754
<i>c</i> [Å]	11.242
α [°]	90
β [°]	91.42
γ [°]	90
Volume [Å ³]	1516.5
Space group	P 21/n
<i>Z</i>	4
Reflns. Collected	3642
<i>R</i> 1 [<i>I</i> >2 σ (<i>I</i>)], <i>wR</i> 2	0.0596, 0.1622
GOF	1.084
CCDC Reference NO.	1960749

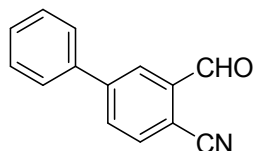
Experimental Information and Characterization Data

Synthesis of *N*-Sulfonyl-1,2,3-triazoles **1**.^[1]

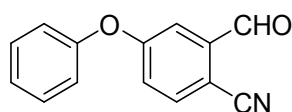
A flask was charged with copper(I) thiophene-2-carboxylate (CuTC, 0.1 equiv with respect to alkyne) and water and cooled in an ice-water bath. Subsequently, phenylacetylene (1 equiv) then tosyl azide (1 equiv) were added and the reaction mixture allowed to warm to room temperature for 2 h. The reaction mixture was diluted with saturated aq NH₄Cl and extracted into EtOAc. The combined organics were dried and filtered through celite. The eluent was concentrated in vacuo. Pulverizing the crude material in cold cyclohexane and collection by filtration afforded **1**.

Synthesis of target Compound **3** and **4**.

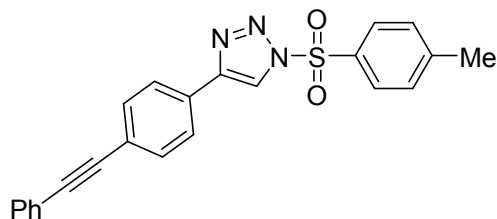
To a stirred solution of *N*-sulfonyl 1,2,3-triazoles **1** (0.6 mmol) was added aldehyde **2** (0.3 mmol) and catalyst (1 mol%) in solvent (2 mL). The mixture was heated at 120°C in a sealed tube for 12 h. After cooling to room temperature, the organic phase was washed with brine, dried over Na₂SO₄. The solvent was evaporated under reduced pressure and purification of the crude product by column chromatography, the product **3** (**4**) were obtained in 55%-91% yields.



Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 10.3 (s, 1H), 8.16 (d, *J* = 1.8 Hz, 1H), 7.88-7.85 (m, 1H), 7.81-7.79 (m, 1H), 7.56-7.54 (m, 2H), 7.46-7.38 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 188.7, 146.3, 137.8, 137.2, 134.6, 132.4, 129.4, 127.9, 127.3, 116.2, 112.1.

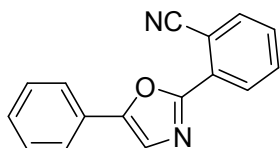


Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 10.2 (s, 1H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.42 (d, *J* = 2.6 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.23-7.19 (m, 2H), 7.02 (d, *J* = 8.2 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 188.1, 162.2, 154.1, 138.9, 135.8, 130.5, 125.8, 122.6, 120.6, 116.9, 116.0, 107.1.

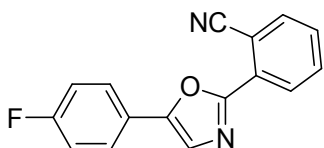


¹H NMR (400 MHz, CDCl₃) δ 8.26 (s, 1H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 8.2 Hz,

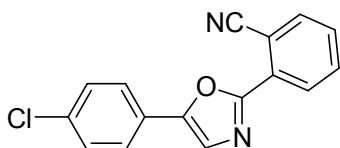
2H), 7.45-7.44 (m, 2H), 7.31-7.26 (m, 5H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.5, 146.7, 132.9, 132.2, 131.7, 130.5, 130.2, 128.7, 128.6, 128.5, 127.1, 125.9, 124.0, 122.9, 119.2, 90.8, 88.9, 21.8.



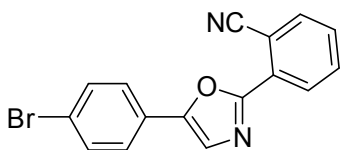
Compound 3a, White solid. ^1H NMR (400 MHz, CDCl_3) δ 8.23 (d, $J = 8.0$ Hz, 1H), 7.75 (t, $J = 8.4$ Hz, 3H), 7.64 (t, $J = 7.5$ Hz, 1H), 7.49-7.46 (m, 2H), 7.40 (t, $J = 7.5$ Hz, 2H), 7.31 (t, $J = 7.4$ Hz, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ 157.8, 152.7, 134.8, 132.9, 130.1, 129.1, 128.5, 127.3, 124.6, 123.6, 118.1, 109.4. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{11}\text{N}_2\text{O}^+$ ($[\text{M}+\text{H}]^+$): 247.0866 found. 247.0863.



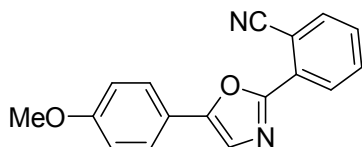
Compound 3b, White solid. ^1H NMR (400 MHz, CDCl_3) δ 8.21 (d, $J = 8.0$ Hz, 1H), 7.77-7.70 (m, 3H), 7.64 (dt, $J = 8.0, 1.1$ Hz, 1H), 7.47 (t, $J = 7.6$ Hz, 1H), 7.42 (s, 1H), 7.08 (t, $J = 8.7$ Hz, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 163.5 (d, $J = 233.2$ Hz), 157.7, 151.8, 134.8, 132.9, 130.2, 129.1, 128.5, 126.5 (d, $J = 8.3$ Hz), 123.6 (d, $J = 3.4$ Hz), 123.2, 118.2, 116.2 (d, $J = 22.1$ Hz), 109.3. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{10}\text{FN}_2\text{O}^+$ ($[\text{M}+\text{H}]^+$): 265.0772 found 265.0775.



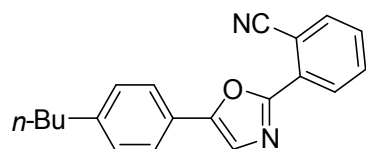
Compound 3c, White solid. ^1H NMR (400 MHz, CDCl_3) δ 8.24 (d, $J = 8.0$ Hz, 1H), 7.77 (d, $J = 7.7$ Hz, 1H), 7.68-7.63 (m, 3H), 7.51-7.48 (m, 2H), 7.37 (d, $J = 8.5$ Hz, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 158.0, 151.7, 134.9, 134.8, 132.9, 130.3, 129.4, 129.1, 128.6, 125.8, 124.1, 118.1, 109.4. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{10}\text{ClN}_2\text{O}^+$ ($[\text{M}+\text{H}]^+$): 281.0476 found 281.0470.



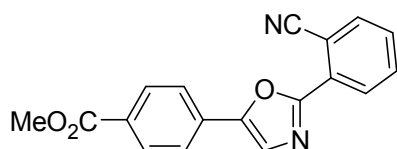
Compound 3d, White solid. ^1H NMR (400 MHz, CDCl_3) δ 8.22 (d, $J = 8.0$ Hz, 1H), 7.77 (d, $J = 7.8$ Hz, 1H), 7.67-7.60 (m, 3H), 7.51-7.48 (m, 4H). ^{13}C NMR (75 MHz, CDCl_3) δ 151.7, 134.8, 132.9, 132.4, 130.3, 129.1, 128.6, 126.3, 126.1, 124.1, 123.1, 118.1, 109.4. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{10}\text{BrN}_2\text{O}^+$ ($[\text{M}+\text{H}]^+$): 324.9971 found 324.9976.



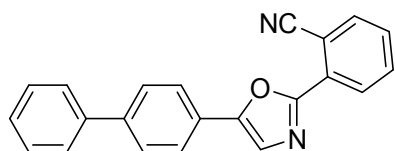
Compound 3e, White solid. ^1H NMR (400 MHz, CDCl_3) δ 8.20 (d, $J = 8.0$ Hz, 1H), 7.74 (d, $J = 7.7$ Hz, 1H), 7.66 (d, $J = 8.7$ Hz, 2H), 7.62 (t, $J = 8.0$ Hz, 1H), 7.44 (t, $J = 7.6$ Hz, 1H), 7.36 (s, 1H), 6.91 (d, $J = 8.7$ Hz, 2H), 3.77 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 160.3, 157.2, 152.7, 134.8, 132.8, 129.8, 129.4, 128.3, 126.2, 122.2, 120.1, 118.2, 114.6, 109.1, 55.4. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{13}\text{N}_2\text{O}^+$ ($[\text{M}+\text{H}]^+$): 277.0972 found 277.0973.



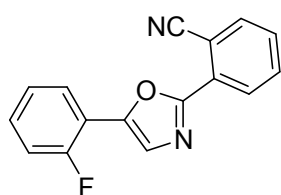
Compound **4f**, white solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.22 (d, $J = 8.0$ Hz, 1H), 7.75 (d, $J = 7.7$ Hz, 1H), 7.65-7.61 (m, 3H), 7.48-7.43 (m, 2H), 7.20 (d, $J = 8.1$ Hz, 2H), 2.57 (t, $J = 7.6$ Hz, 2H), 1.58-1.50 (m, 2H), 1.33-1.26 (m, 2H), 0.86 (t, $J = 7.3$ Hz, 3H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 157.5, 152.9, 144.3, 134.8, 132.8, 129.9, 129.4, 129.2, 128.4, 124.8, 124.6, 123.1, 118.2, 109.3, 35.6, 33.5, 22.3, 13.9. HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{19}\text{N}_2\text{O}^+$ ($[\text{M}+\text{H}]^+$): 303.1492 found 303.1491.



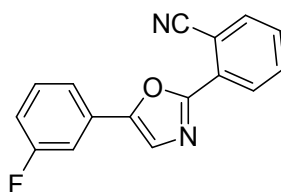
Compound **3g**, White solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.25 (d, $J = 8.0$ Hz, 1H), 8.06 (d, $J = 8.4$ Hz, 2H), 7.81-7.77 (m, 3H), 7.66 (t, $J = 7.4$ Hz, 1H), 7.60 (s, 1H), 7.51 (t, $J = 7.4$ Hz, 1H), 3.87 (s, 3H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 166.5, 151.6, 134.9, 132.9, 131.3, 130.5, 130.2, 129.0, 128.7, 125.5, 124.4, 118.1, 109.6, 52.3. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{13}\text{N}_2\text{O}_3^+$ ($[\text{M}+\text{H}]^+$): 305.0921 found 305.0920.



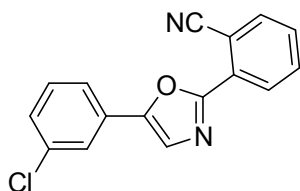
Compound **3h**, White solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.25 (d, $J = 8.0$ Hz, 1H), 7.81 (d, $J = 8.0$ Hz, 2H), 7.77 (d, $J = 7.8$ Hz, 1H), 7.67-7.62 (m, 3H), 7.56 (d, $J = 7.4$ Hz, 2H), 7.52 (s, 1H), 7.48 (t, $J = 7.6$ Hz, 1H), 7.39 (t, $J = 7.4$ Hz, 2H), 7.30 (t, $J = 7.3$ Hz, 1H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 152.6, 141.8, 140.2, 134.9, 132.9, 130.2, 129.1, 128.9, 128.6, 127.8, 127.0, 126.1, 125.1, 123.6, 118.1, 109.4. HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{15}\text{N}_2\text{O}^+$ ($[\text{M}+\text{H}]^+$): 323.1179 found 323.1184.



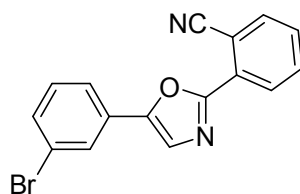
Compound **3i**, White solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.27 (d, $J = 8.0$ Hz, 1H), 7.98-7.94 (m, 1H), 7.77 (d, $J = 7.8$ Hz, 1H), 7.67-7.62 (m, 2H), 7.49 (t, $J = 7.6$ Hz, 1H), 7.29-7.21 (m, 2H), 7.14-7.09 (m, 1H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 158.4 (d, $J = 250.2$ Hz), 134.8, 132.9, 130.3, 130.2 (d, $J = 8.3$ Hz), 129.1, 128.7, 127.8 (d, $J = 13.2$ Hz), 126.8, 125.0 (d, $J = 3.5$ Hz), 118.2, 115.9 (d, $J = 16.2$ Hz), 109.4. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{10}\text{FN}_2\text{O}^+$ ($[\text{M}+\text{H}]^+$): 265.0772 found 265.0774.



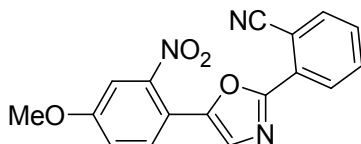
Compound 3j, White solid (mg, 83%), mp 108-110 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.23 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.66 (t, *J* = 7.8 Hz, 1H), 7.54-7.48 (m, 3H), 7.43-7.34 (m, 2H), 7.00 (td, *J* = 8.5, 2.4 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 162.5 (d, *J* = 245.2 Hz), 158.2, 151.5, 134.8, 132.9, 130.9 (d, *J* = 8.4 Hz), 130.3, 129.3, 129.0, 128.6, 124.6, 120.4, 118.0, 116.0 (d, *J* = 21.2 Hz), 111.6 (d, *J* = 23.7 Hz), 109.6. HRMS (ESI) calcd for C₁₆H₁₀FN₂O⁺ ([M+H]⁺): 265.0772 found 265.0768.



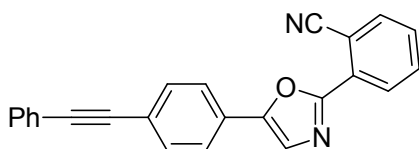
Compound 3k, White solid. ¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.68-7.62 (m, 3H), 7.50-7.47 (m, 2H), 7.33 (t, *J* = 7.9 Hz, 1H), 7.27-7.25 (m, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 158.2, 151.2, 135.1, 134.8, 132.9, 130.5, 130.4, 129.0, 128.6, 124.6, 124.5, 122.7, 118.1, 109.6. HRMS (ESI) calcd for C₁₆H₁₀ClN₂O⁺ ([M+H]⁺): 281.0476 found 281.0473.



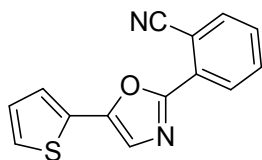
Compound 3l, Green solid. ¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, *J* = 8.0 Hz, 1H), 7.84 (t, *J* = 1.6 Hz, 1H), 7.78-7.76 (m, 1H), 7.69-7.63 (m, 2H), 7.52-7.47 (m, 2H), 7.43-7.41 (m, 1H), 7.27 (t, *J* = 7.9 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 158.2, 151.0, 134.9, 132.9, 131.9, 130.7, 130.4, 129.2, 129.0, 128.6, 127.4, 124.6, 123.2, 118.1, 109.6. HRMS (ESI) calcd for C₁₆H₁₀BrN₂O⁺ ([M+H]⁺): 324.9971 found 324.9973.



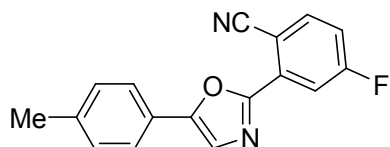
Compound 3m, Yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 8.34 (d, *J* = 7.8 Hz, 1H), 8.23-8.20 (m, 2H), 7.81 (d, *J* = 7.3 Hz, 1H), 7.71 (t, *J* = 6.9 Hz, 1H), 7.60 (t, *J* = 6.8 Hz, 1H), 7.01 (d, *J* = 9.0 Hz, 2H), 3.85 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 162.8, 150.7, 134.8, 133.2, 131.7, 131.4, 129.7, 127.5, 117.5, 116.8, 114.5, 110.0, 55.6.



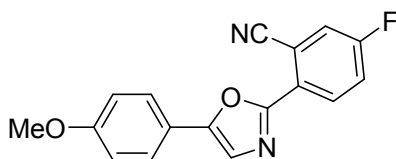
Compound 3n, White solid. ¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 7.7 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.65 (t, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.52-7.47 (m, 4H), 7.31-7.28 (m, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 158.1, 152.1, 134.9, 132.9, 132.3, 131.7, 130.2, 129.1, 128.6, 128.4, 126.8, 124.4, 123.9, 122.9, 118.1, 109.5. HRMS (ESI) calcd for C₂₄H₁₅N₂O⁺ ([M+H]⁺): 347.1179 found 347.1173.



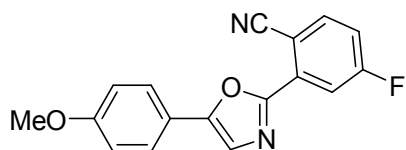
Compound **3o**, purple solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.18 (d, $J = 8.0$ Hz, 1H), 7.76 (d, $J = 8.4$ Hz, 1H), 7.63 (dt, $J = 7.6, 1.2$ Hz, 1H), 7.47 (dt, $J = 7.7, 1.1$ Hz, 1H), 7.42 (d, $J = 8.0$ Hz, 1H), 7.33 (s, 1H), 7.30 (dd, $J = 5.1, 1.0$ Hz, 1H), 7.06-7.04 (m, 1H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 157.2, 148.0, 134.9, 132.8, 130.1, 129.1, 128.9, 128.4, 128.1, 126.5, 125.5, 123.3, 118.0, 109.5. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_9\text{N}_2\text{OS}^+$ ($[\text{M}+\text{H}]^+$): 253.0430 found 253.0431.



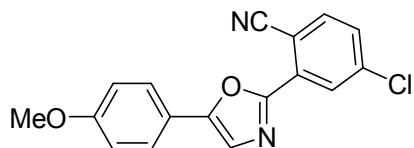
Compound **3p**, White solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.90 (dd, $J = 9.2, 2.6$ Hz, 1H), 7.75 (dd, $J = 8.6, 5.3$ Hz, 1H), 7.62 (d, $J = 8.0$ Hz, 1H), 7.44 (s, 1H), 7.22 (s, 1H), 7.18-7.14 (m, 2H), 2.33 (s, 3H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 164.4 (d, $J = 254.9$ Hz), 156.3, 153.4, 139.5, 137.2 (d, $J = 9.4$ Hz), 132.1 (d, $J = 9.7$ Hz), 129.8, 124.7, 124.4, 123.3, 117.6 (d, $J = 20.4$ Hz), 115.4 (d, $J = 25.2$ Hz), 105.4, 21.5. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{12}\text{FN}_2\text{O}^+$ ($[\text{M}+\text{H}]^+$): 279.0928 found 279.0933.



Compound **3q**, White solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.22 (dd, $J = 8.9, 5.4$ Hz, 1H), 7.65 (d, $J = 8.8$ Hz, 2H), 7.44 (dd, $J = 8.0, 2.6$ Hz, 1H), 7.38-7.31 (m, 2H), 6.92 (d, $J = 8.8$ Hz, 2H), 3.78 (s, 3H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 162.6 (d, $J = 253.1$ Hz), 160.4, 156.4, 152.9, 130.7 (d, $J = 8.6$ Hz), 126.2, 121.8, 121.9, 121.6, 121.3, 120.9 (d, $J = 21.6$ Hz), 120.7, 119.9, 116.8 (d, $J = 8.2$ Hz), 114.6, 110.7 (d, $J = 9.2$ Hz), 55.4. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{12}\text{FN}_2\text{O}^+$ ($[\text{M}+\text{H}]^+$): 295.0877 found 295.0871.

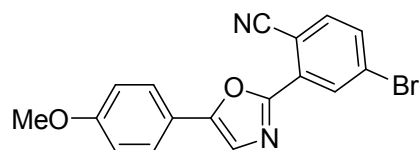


Compound **3r**, White solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.87 (dd, $J = 9.2, 2.6$ Hz, 1H), 7.74 (dd, $J = 8.6, 5.3$ Hz, 1H), 7.64 (d, $J = 8.8$ Hz, 2H), 7.35 (s, 1H), 7.18-7.11 (m, 1H), 6.90 (t, $J = 8.8$ Hz, 2H), 3.77 (s, 3H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 162.6 (d, $J = 253.1$ Hz), 160.4, 156.4, 152.9, 130.7 (d, $J = 8.6$ Hz), 126.2, 121.9, 121.6, 121.3, 120.9, 120.7, 119.9, 116.9 (d, $J = 2.5$ Hz), 114.6, 110.7 (d, $J = 9.2$ Hz), 55.4. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{12}\text{FN}_2\text{O}_2^+$ ($[\text{M}+\text{H}]^+$): 295.0877 found 295.0874.

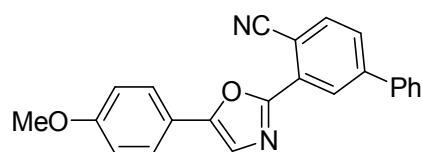


Compound **3s**, White solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.21 (d, $J = 2.0$ Hz, 1H), 7.67 (dd, $J = 8.4, 2.2$ Hz, 3H),

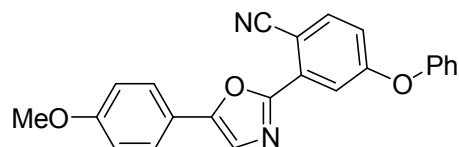
7.41 (dd, $J = 8.3, 2.0$ Hz, 1H), 7.37 (s, 1H), 6.93 (d, $J = 8.8$ Hz, 2H), 3.79 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 160.5, 153.3, 139.7, 135.8, 130.8, 130.0, 128.3, 126.4, 122.5, 119.8, 117.5, 114.6, 107.3, 55.4. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{12}\text{ClN}_2\text{O}_2^+$ ($[\text{M}+\text{H}]^+$): 311.0582 found 311.0586.



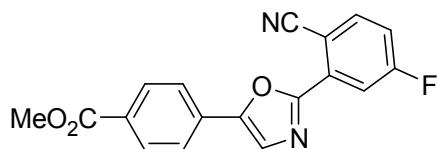
Compound 3t, Green solid. ^1H NMR (400 MHz, CDCl_3) δ 8.37 (s, 1H), 7.67 (d, $J = 8.8$ Hz, 2H), 7.60-7.57 (m, 2H), 7.37 (s, 1H), 6.92 (d, $J = 8.7$ Hz, 2H), 3.79 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 160.5, 155.8, 153.3, 135.8, 133.6, 132.9, 131.2, 130.7, 127.9, 127.2, 126.4, 122.5, 119.8, 117.6, 114.6, 107.7, 55.4. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{12}\text{BrN}_2\text{O}_2$ ($[\text{M}+\text{H}]^+$): 355.0077 found 355.0081.



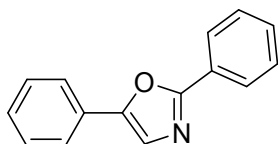
Compound 3u, White solid. ^1H NMR (400 MHz, CDCl_3) δ 8.45 (s, 1H), 7.81 (d, $J = 8.0$ Hz, 1H), 7.71-7.66 (m, 3H), 7.62 (d, $J = 7.2$ Hz, 2H), 7.45 (t, $J = 7.5$ Hz, 2H), 7.40-7.36 (m, 2H), 6.93 (d, $J = 8.7$ Hz, 2H), 3.79 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 160.3, 152.9, 145.8, 138.4, 135.3, 129.7, 129.2, 129.1, 128.4, 127.4, 127.1, 126.9, 126.4, 122.5, 120.1, 118.4, 114.6, 107.6, 55.4. HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{17}\text{N}_2\text{O}_2$ ($[\text{M}+\text{H}]^+$): 353.1285 found 353.1289.



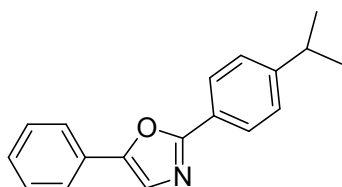
Compound 3v, White solid. ^1H NMR (400 MHz, CDCl_3) δ 7.75 (d, $J = 2.5$ Hz, 1H), 7.66 (t, $J = 8.4$ Hz, 3H), 7.37 (t, $J = 7.6$ Hz, 2H), 7.33 (s, 1H), 7.19-7.16 (m, 1H), 7.04 (d, $J = 7.7$ Hz, 2H), 6.98 (dd, $J = 8.6, 2.5$ Hz, 1H), 6.91 (d, $J = 8.8$ Hz, 2H), 3.78 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 164.5, 160.3, 156.8, 154.6, 152.9, 136.7, 131.4, 130.4, 126.3, 125.4, 122.1, 120.4, 120.0, 118.7, 118.3, 116.7, 114.5, 102.7, 55.4. HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{17}\text{N}_2\text{O}_3$ ($[\text{M}+\text{H}]^+$): 369.1234 found 369.1231.



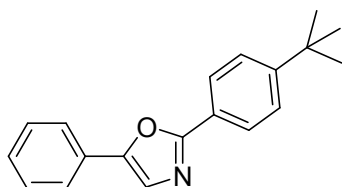
Compound 3w, White solid. ^1H NMR (400 MHz, CDCl_3) δ 8.06 (d, $J = 8.4$ Hz, 2H), 7.93 (dd, $J = 9.1, 2.3$ Hz, 1H), 7.80-7.68 (m, 3H), 7.61 (s, 1H), 7.22-7.20 (m, 1H), 3.87 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 166.5, 164.0 (d, $J = 255.4$ Hz), 157.4, 152.0, 137.3 (d, $J = 9.4$ Hz), 161.8, 131.6, 130.9, 130.5, 125.7, 124.5, 117.8 (d, $J = 22.7$ Hz), 117.4, 116.3 (d, $J = 25.3$ Hz), 105.6, 52.3. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{11}\text{FN}_2\text{O}_3$ ($[\text{M}+\text{H}]^+$): 322.0754 found 322.0750.



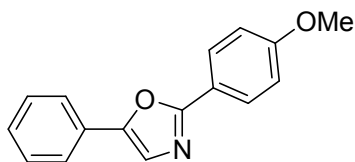
Compound **4a**, white solid, Spectral data for this compound was consistent with those previously reported^[2] ¹H NMR (400 MHz, DMSO-*d*₆) δ 6.92-6.90 (m, 2H), 6.66 (br, 3H), 6.37-6.31 (m, 5H), 6.23 (t, *J* = 6.6 Hz, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 160.7, 151.2, 131.1, 129.6, 129.1, 127.8, 127.3, 126.4, 124.6, 124.5.



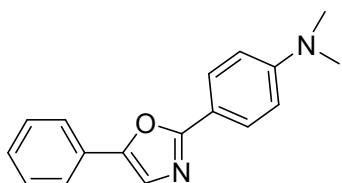
Compound **4b**, Pale yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 7.4 Hz, 2H), 7.46 (t, *J* = 8.9 Hz, 3H), 7.38-7.33 (m, 3H), 3.03-2.96 (m, 1H), 1.33 (s, 3H), 1.31 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 161.4, 151.7, 150.0, 128.9, 128.4, 128.0, 126.9, 126.5, 124.9, 124.2, 123.1, 34.2, 23.8. HRMS (ESI) calcd for C₁₈H₁₈NO⁺ ([M+H]⁺): 264.1383 found 264.1388.



Compound **4c**, Pale yellow solid, Spectral data for this compound was consistent with those previously reported.^[2] ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.02 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.41-7.37 (m, 1H), 7.85-7.82 (m, 3H), 7.51 (t, *J* = 7.6 Hz, 2H), 1.33 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 161.4, 154.1, 151.1, 133.8, 130.8, 128.9, 128.5, 127.9, 126.3, 126.8, 124.6, 122.8, 34.9, 31.2.

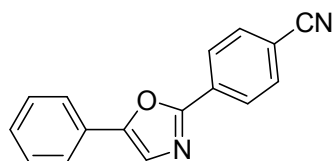


Compound **4d**, Pale yellow solid, Spectral data for this compound was consistent with those previously reported.^[2] ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 8.8 Hz, 2H), 7.69 (d, *J* = 7.5 Hz, 2H), 7.44-7.39 (m, 3H), 7.31 (t, *J* = 7.4 Hz, 1H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 161.4, 150.7, 128.9, 128.3, 128.2, 127.9, 124.1, 123.3, 120.3, 114.3, 56.4.

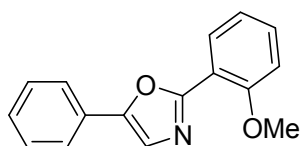


Compound **4e**, Pale yellow solid, Spectral data for this compound was consistent with those previously reported. ¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, *J* = 8.7 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.38 (s, 1H), 7.30 (t, *J* = 7.2 Hz, 1H), 6.75 (d, *J* = 8.7 Hz, 2H), 3.04 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 162.3, 151.7, 150.1, 128.9, 128.6, 127.9, 127.7, 123.9, 123.2, 115.3, 111.8, 40.3. HRMS (ESI) calcd for C₁₇H₁₇N₂O⁺

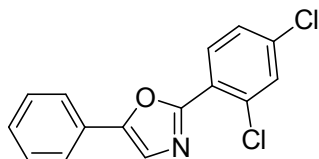
([M+H]⁺): 265.1335 found 265.1338.



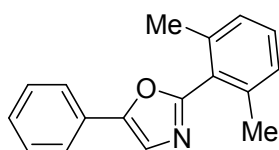
Compound **4f**, Pale yellow solid, Spectral data for this compound was consistent with those previously reported.^[3] ¹H NMR (400 MHz, CDCl₃) δ 8.21 (d, J = 8.0 Hz, 2H), 7.79-7.73 (m, 4H), 7.52 (s, 1H), 7.48 (t, J = 7.5Hz, 2H), 7.40 (t, J = 7.2 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 159.2, 56, 132.7, 131.1, 129.2, 126.7, 124.5, 118.5, 113.6.



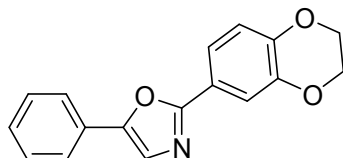
Compound **4g**, Pale yellow solid, Spectral data for this compound was consistent with those previously reported.^[2] ¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, J = 7.6 Hz, 1H), 7.66 (d, J = 8.0 Hz, 2H), 7.47 (s, 1H), 7.39-7.36 (m, 3H), 7.27 (t, J = 7.3 Hz, 1H), 7.01 (t, J = 8.2 Hz, 2H), 3.96 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 158.3, 151.1, 129.8, 129.3, 129.1, 128.8, 125.0, 124.5, 120.9, 112.1, 56.4.



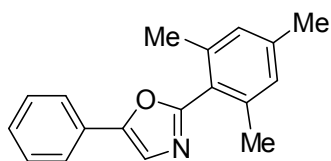
Compound **4h**, Pale yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, J = 8.5 Hz, 1H), 7.64 (d, J = 7.4 Hz, 2H), 7.46 (d, J = 1.8 Hz, 1H), 7.43 (s, 1H), 7.37 (t, J = 7.5 Hz, 2H), 7.29-7.27 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 158.2, 151.9, 136.4, 133.0, 131.4, 131.2, 129.0, 128.8, 127.6, 127.4, 124.7, 124.4, 123.3. HRMS (ESI) calcd for C₁₅H₁₀Cl₂NO⁺ ([M+H]⁺): 290.0134 found 290.0136.



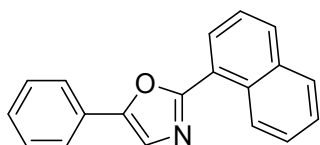
Compound **4i**, Pale yellow solid, Spectral data for this compound was consistent with those previously reported.^[3] ¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, J = 8.0 Hz, 2H), 7.54 (s, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.36 (t, J = 7.6 Hz, 1H), 7.30-7.28 (m, 1H), 7.17-7.15 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 160.7, 151.5, 138.7, 130.2, 129.0, 128.7, 127.9, 127.8, 124.2, 121.6.



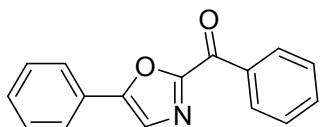
Compound **4j**, Pale yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, J = 8.0 Hz, 2H), 7.62-7.60 (m, 2H), 7.44-7.39 (m, 3H), 7.31 (t, J = 7.9 Hz, 1H), 6.95 (d, J = 8.0 Hz, 1H), 4.30 (s, 4H). ¹³C NMR (125 MHz, CDCl₃) δ 161.0, 150.9, 145.7, 143.8, 128.9, 128.3, 128.2, 124.1, 123.4, 121.1, 120.0, 117.8, 115.6, 64.6, 64.3. HRMS (ESI) calcd for C₁₇H₁₄NO₃⁺ ([M+H]⁺): 280.0968 found 280.0965.



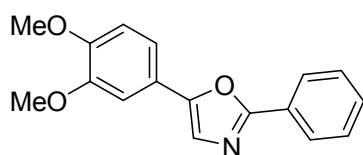
Compound **4k**, Pale yellow solid, Spectral data for this compound was consistent with those previously reported.^[2] ¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, *J* = 7.8 Hz, 2H), 7.53(s, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 1H), 6.99 (s, 2H), 2.37 (s, 3H), 2.34 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 161.0, 151.3, 140.2, 138.6, 129.1, 128.8, 128.6, 128.0, 124.7, 124.2, 121.9, 21.4, 20.6.



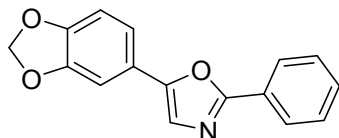
Compound **4l**, Pale yellow solid, Spectral data for this compound was consistent with those previously reported.^[3] ¹H NMR (400 MHz, CDCl₃) δ 9.35 (d, *J* = 8.6 Hz, 1H), 8.37 (d, *J* = 7.3 Hz, 1H), 8.12 (d, *J* = 8.2 Hz, 1H), 7.98 (s, 1H), 7.89 (d, *J* = 7.7 Hz, 2H), 7.73-7.63 (m, 3H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.41 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 161.1, 151.0, 134.0, 131.3, 130.2, 129.0, 128.6, 128.5, 128.1, 127.8, 127.7, 126.4, 126.2, 124.4, 123.9, 123.4.



Compound **4n**, Pale yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 8.40 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 7.8 Hz, 2H), 7.59-7.54 (m, 2H), 7.47 (t, *J* = 7.3 Hz, 2H), 7.41-7.36 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 178.8, 157.1, 154.3, 135.4, 133.8, 130.8, 130.0, 129.2, 128.5, 126.7, 125.4, 123.9. HRMS (ESI) calcd for C₁₆H₁₂NO₂⁺ ([M+H]⁺): 250.0863 found. 250.0858.



Compound **Balsoxin**, Pale yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 8.0 Hz, 2H), 7.42-7.38 (m, 3H), 7.27 (s, 1H), 7.23 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.11 (br, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 3.91 (s, 3H), 3.85 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.6, 151.5, 149.7, 149.4, 130.6, 128.9, 126.9, 126.4, 121.4, 120.7, 117.4, 111.5, 107.5, 56.1, 56.0.



Compound **Texamine**, Pale yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 8.04-8.02 (m, 2H), 7.42-7.40 (m, 3H), 7.25 (s, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.10 (s, 1H), 6.81 (d, *J* = 8.1 Hz, 1H), 5.95 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 160.7, 151.4, 148.4, 130.7, 129.0, 126.9, 118.6, 109.0, 104.9, 101.6.

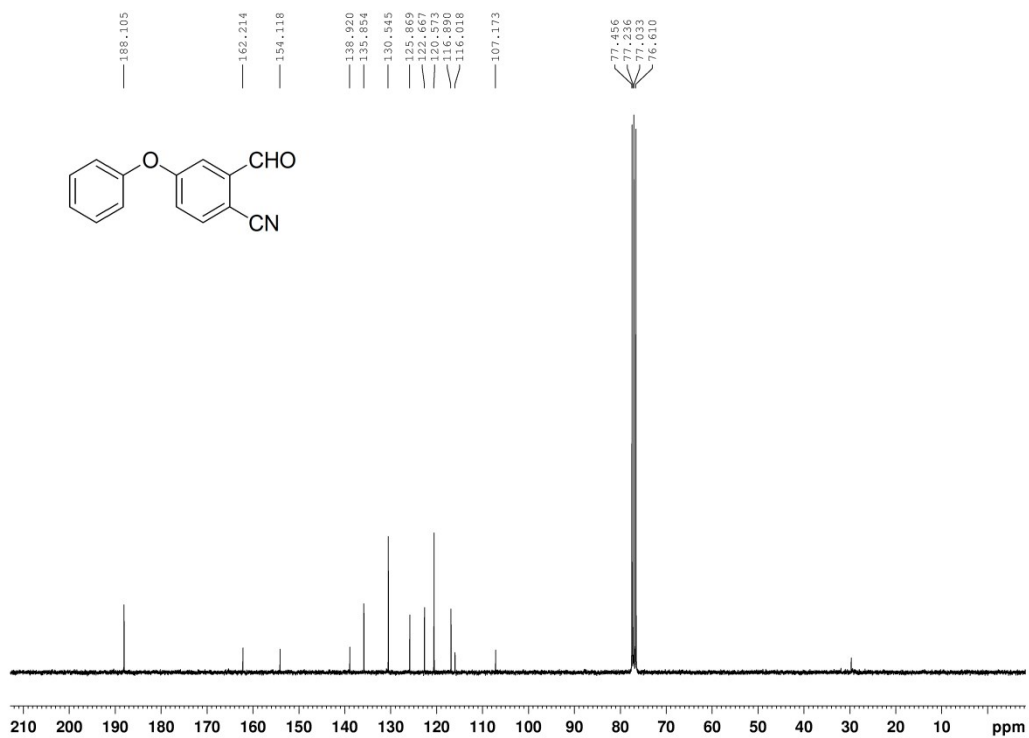
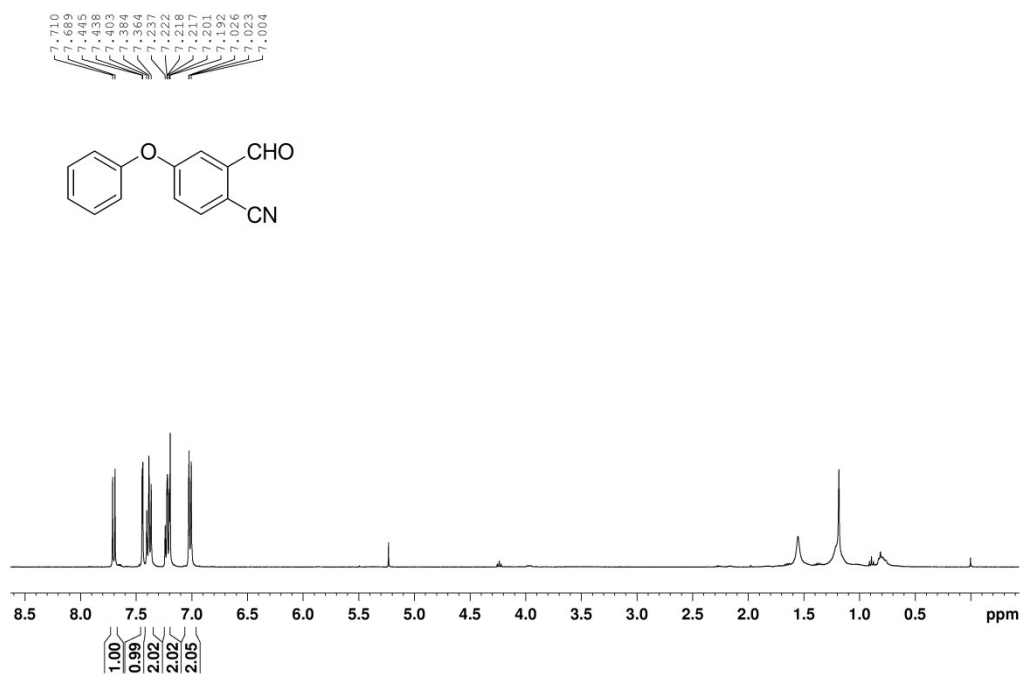
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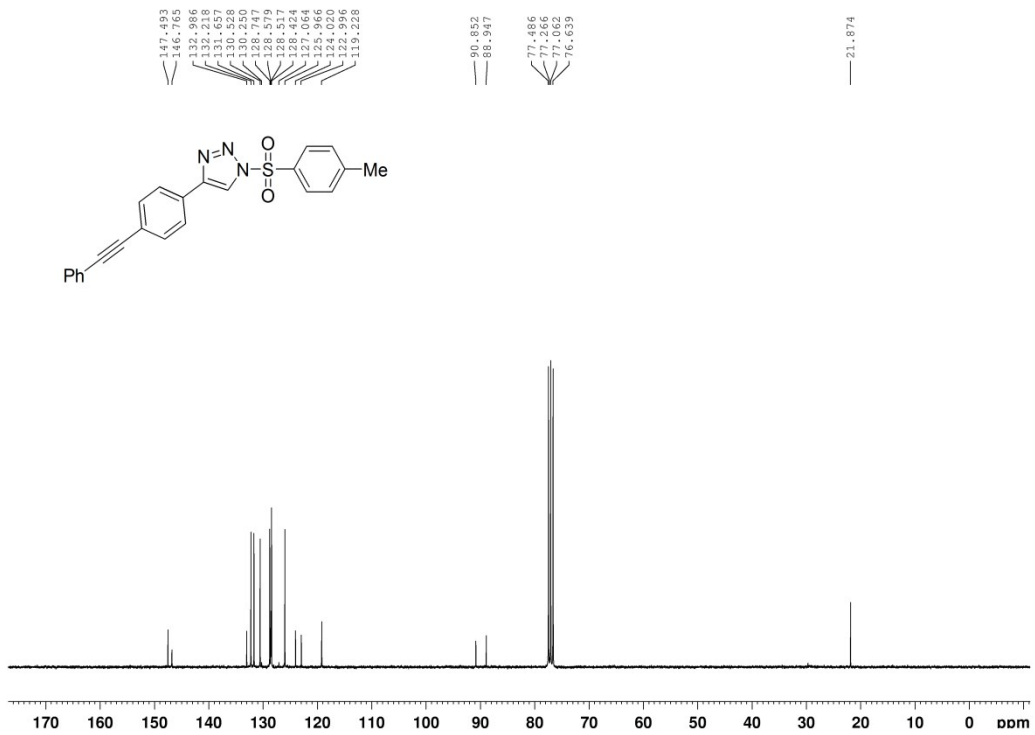
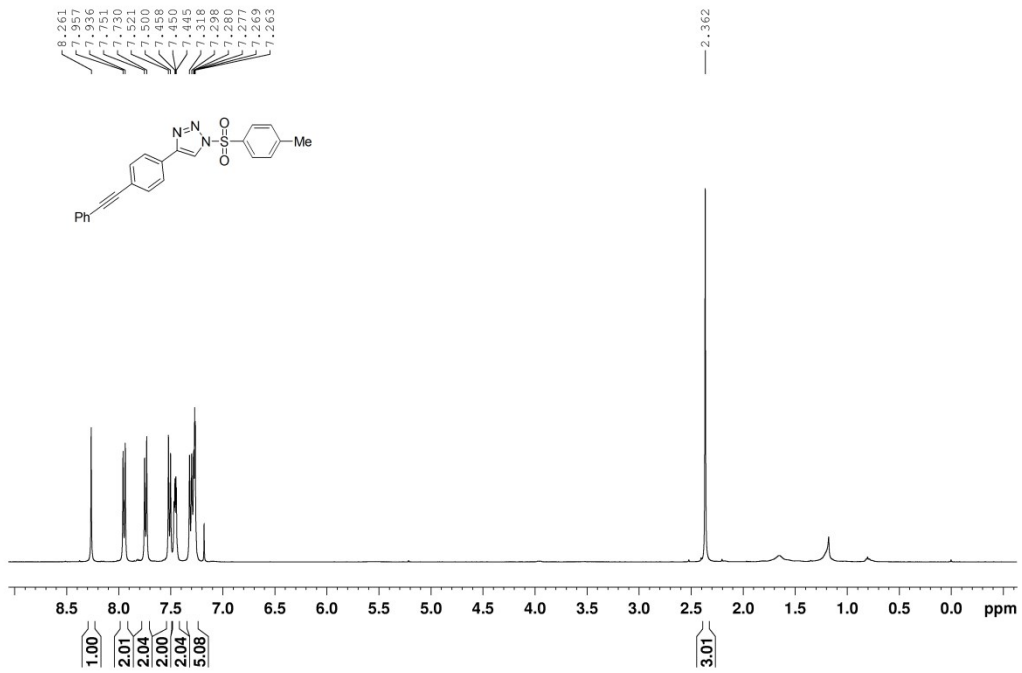
[1] Raushel, J.; Fokin, V. V. *Org. Lett.* **2010**, *12*, 4952-4955.

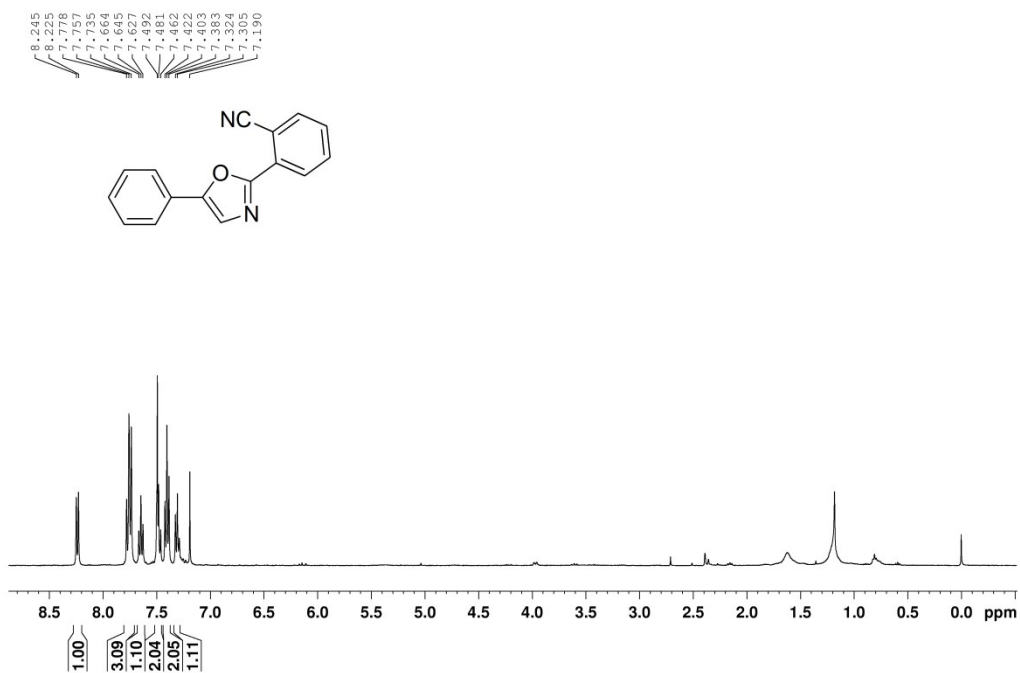
[2]. Mei, M.; Anand, D.; Zhou, L. *Org. Lett.* **2019**, *21*, 3548-3553.

[3]. Besselièvre, F.; Mahuteau-Betzer, F.; Grierson, D. S.; S. Piguel. *J. Org. Chem.* **2008**, *73*, 3278-3280.

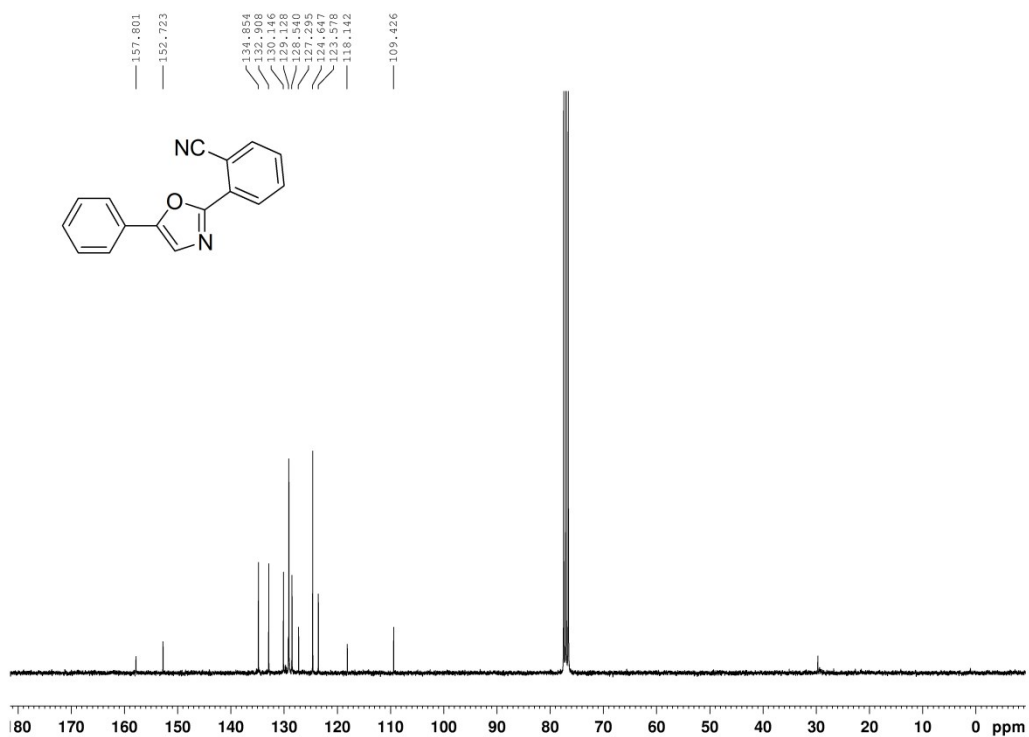
^1H and ^{13}C NMR of all the synthesized compounds



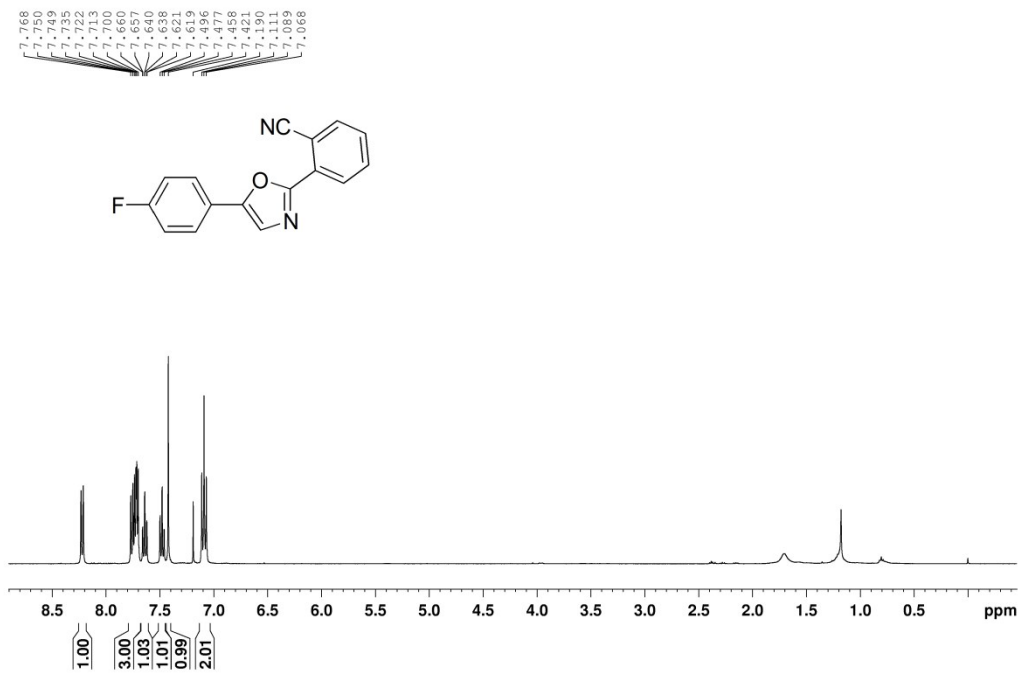




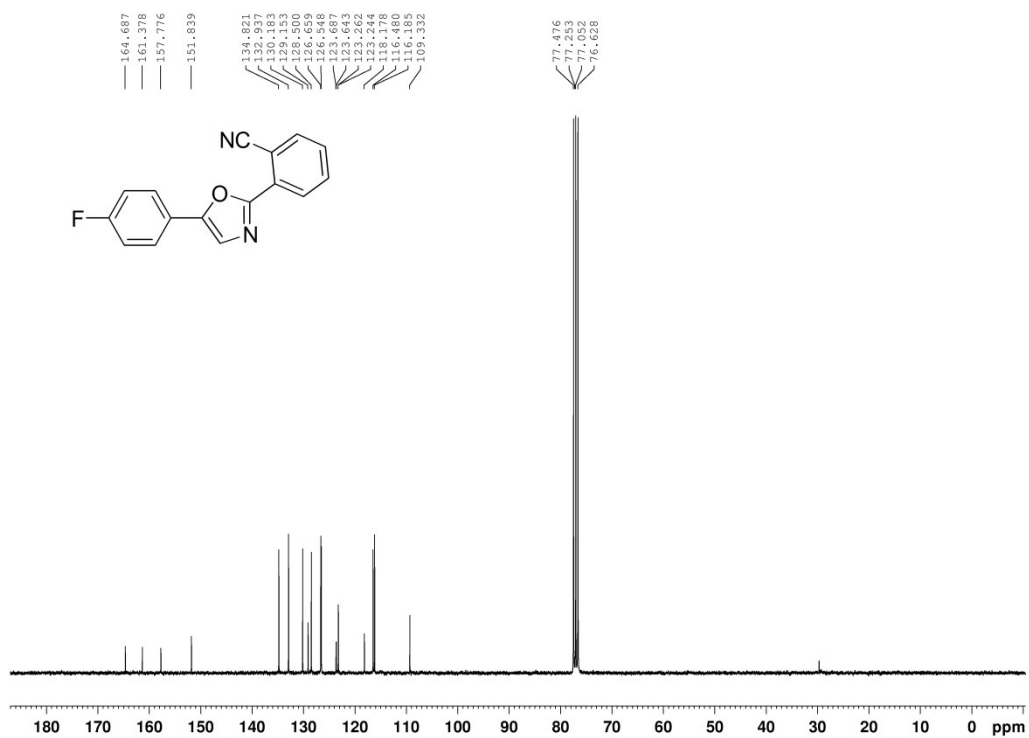
¹H NMR of **3a** in CDCl₃



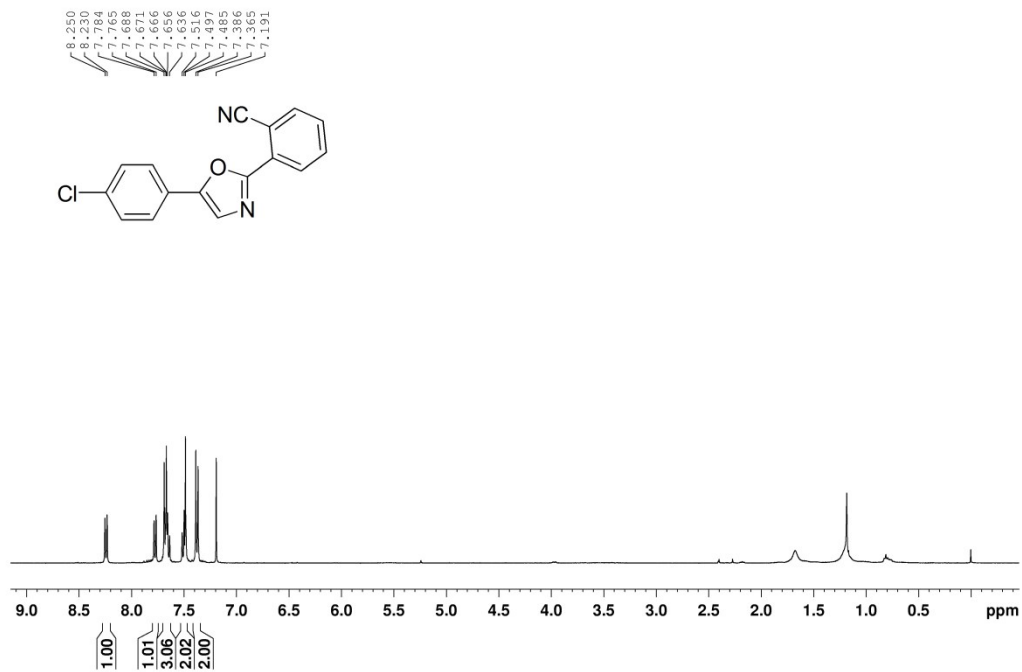
¹³C NMR of **3a** in CDCl₃



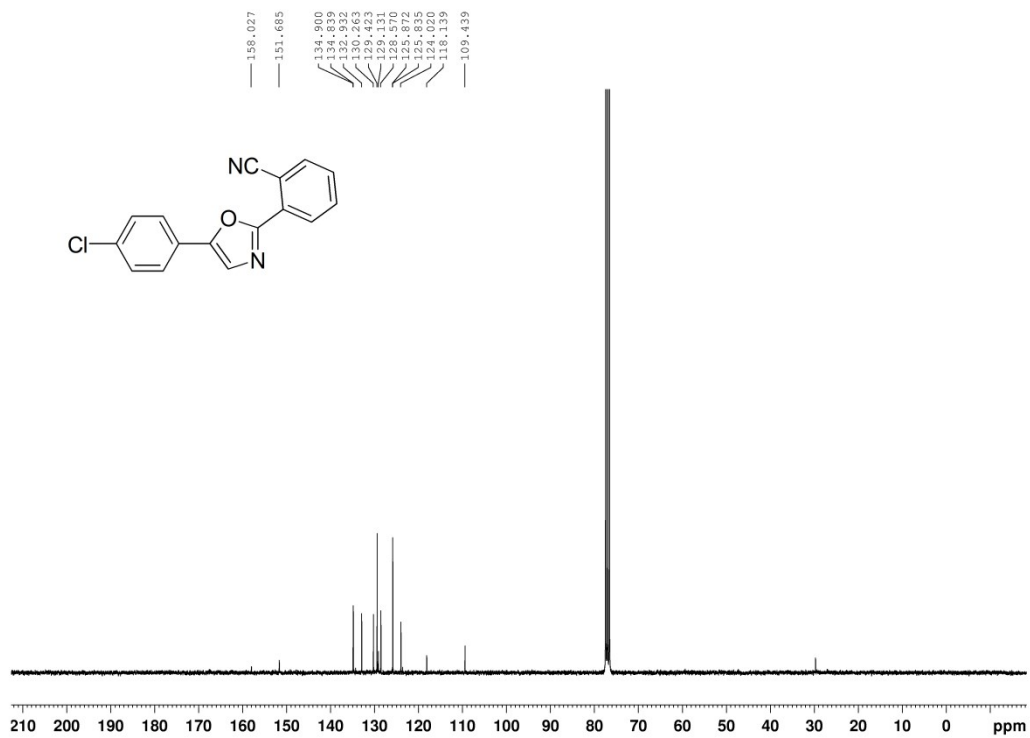
¹H NMR of **3b** in CDCl₃



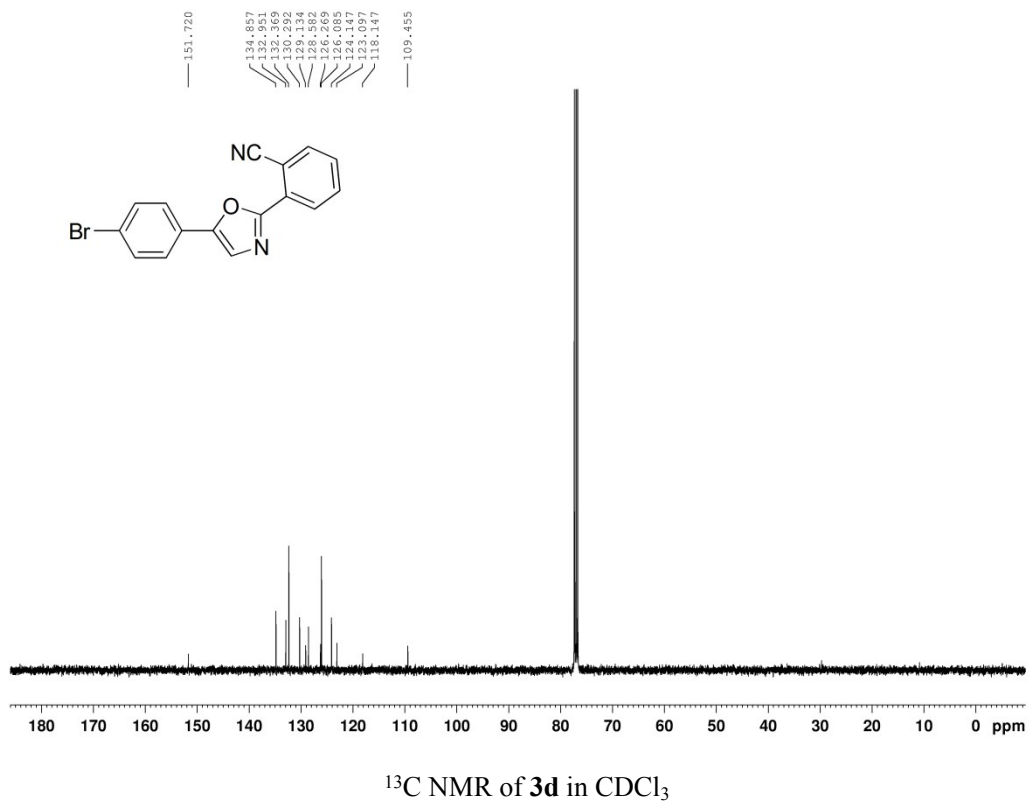
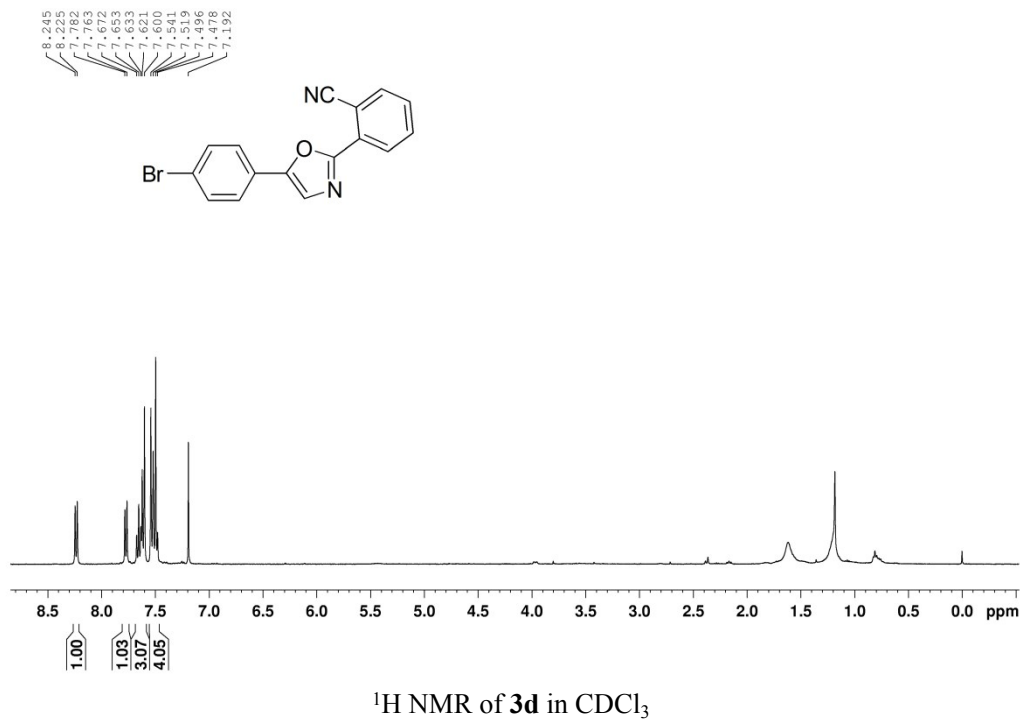
¹³C NMR of **3b** in CDCl₃

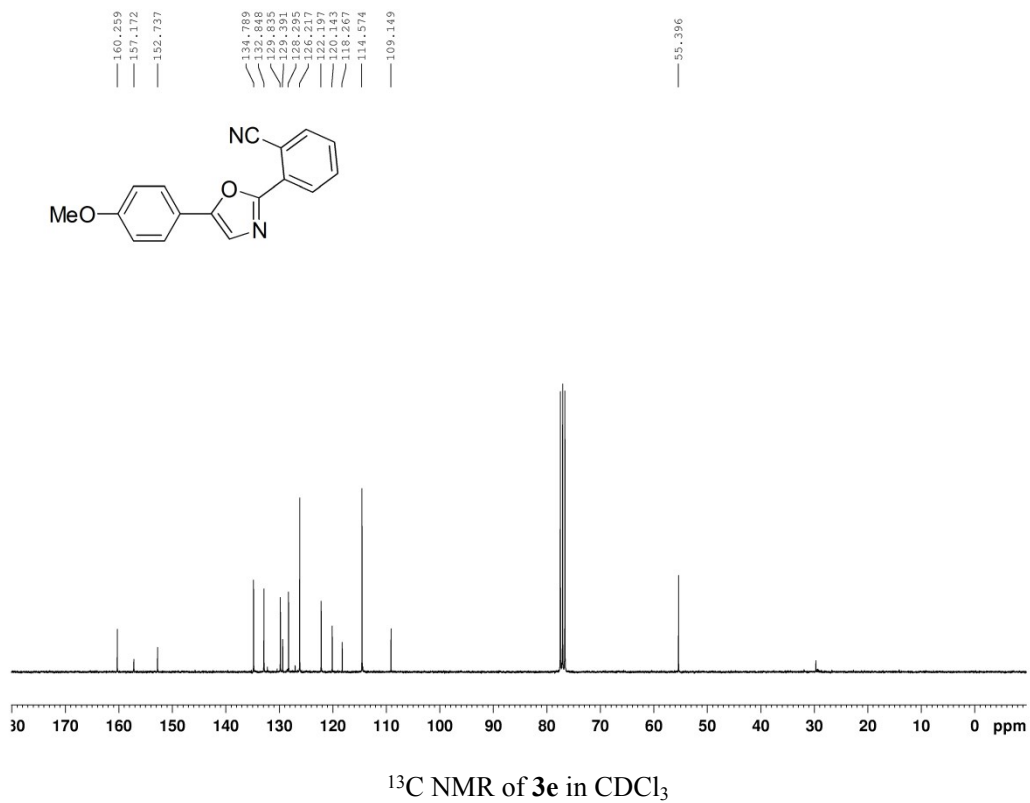
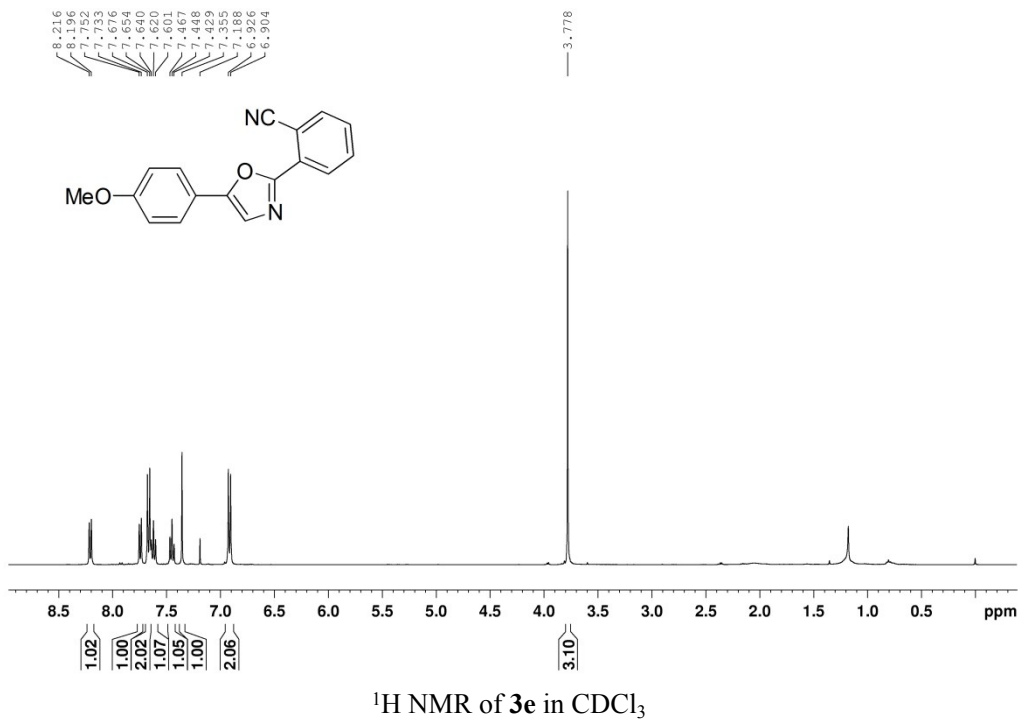


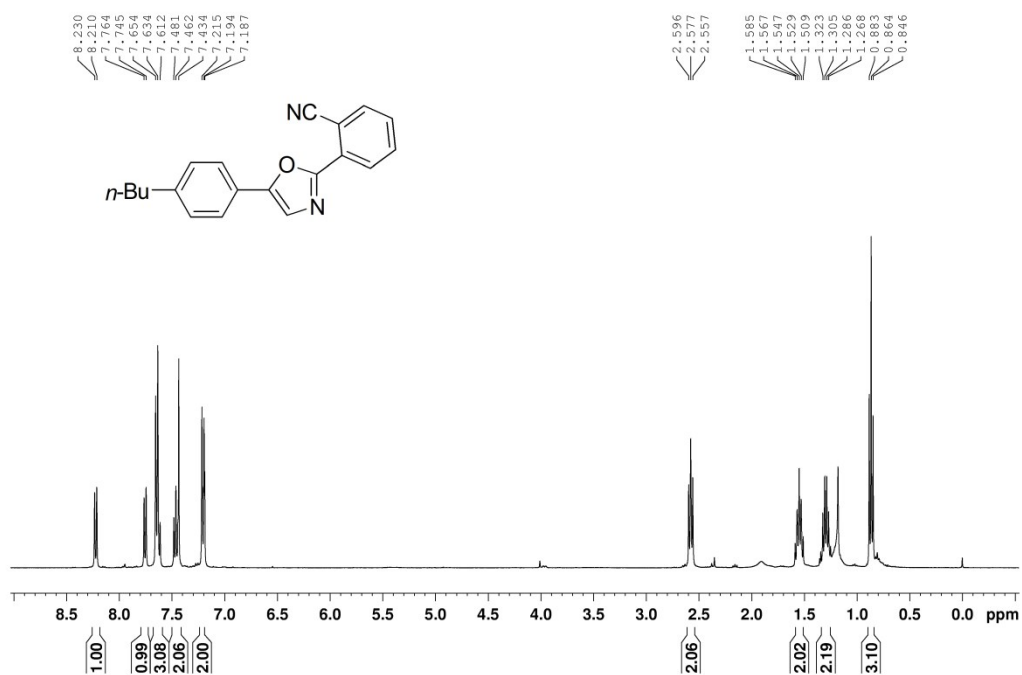
¹H NMR of **3c** in CDCl₃



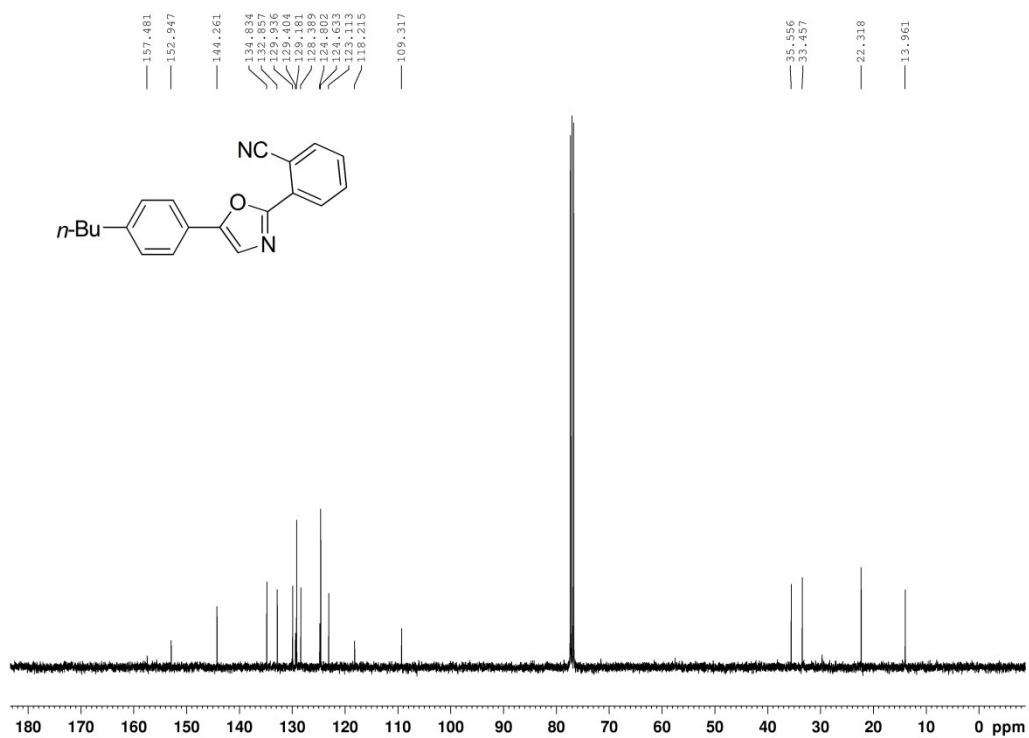
¹³C NMR of **3c** in CDCl₃



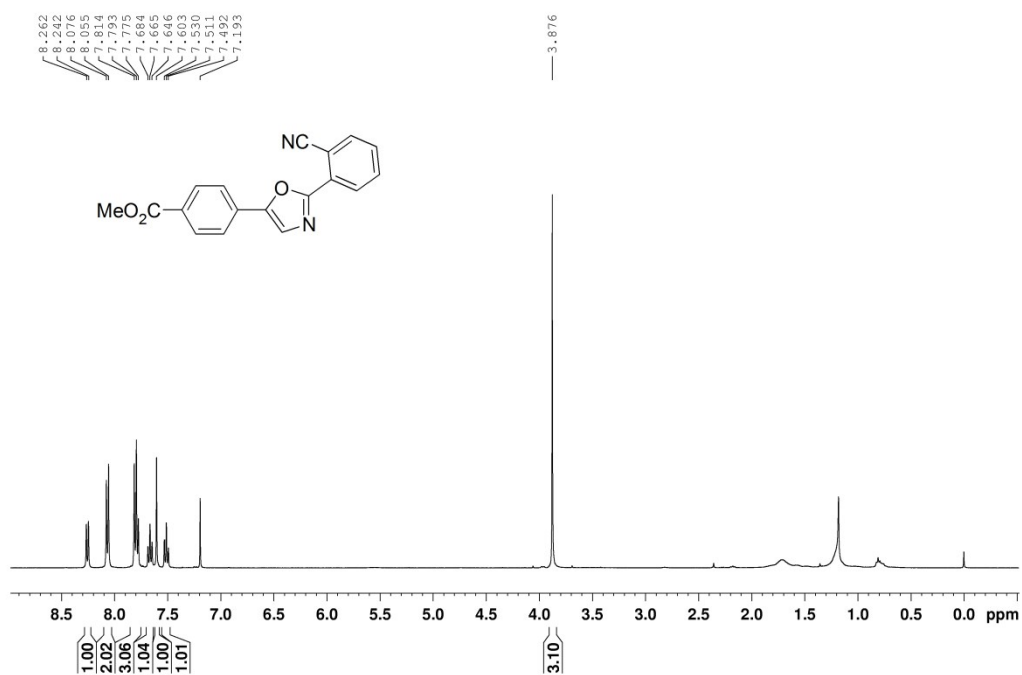




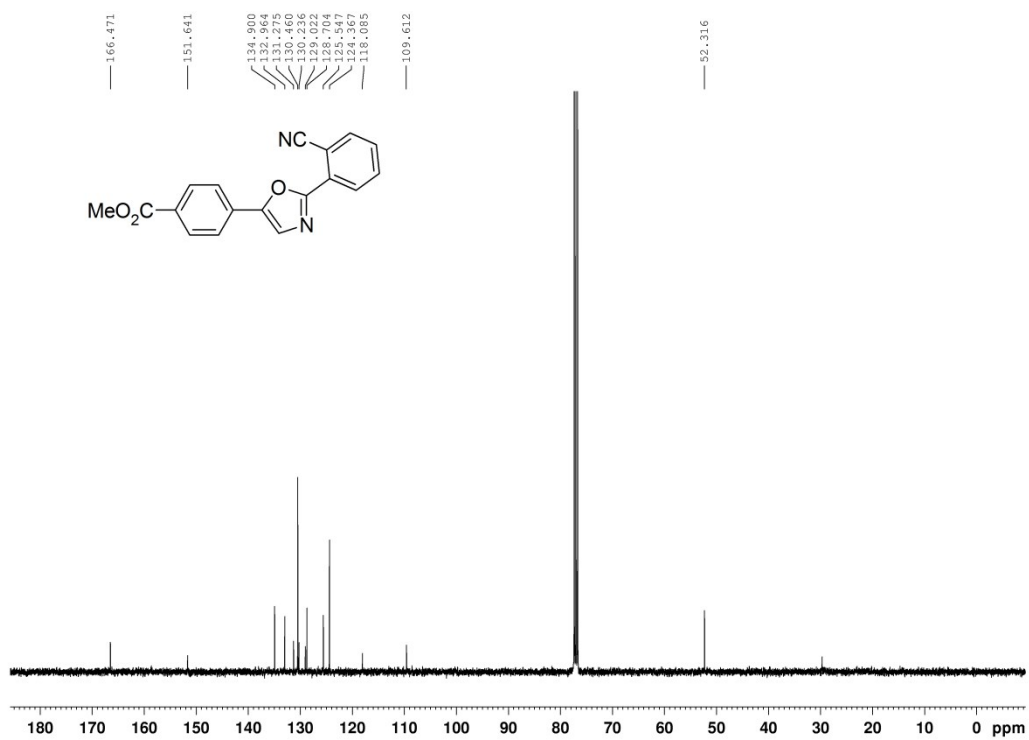
¹H NMR of **3f** in CDCl₃



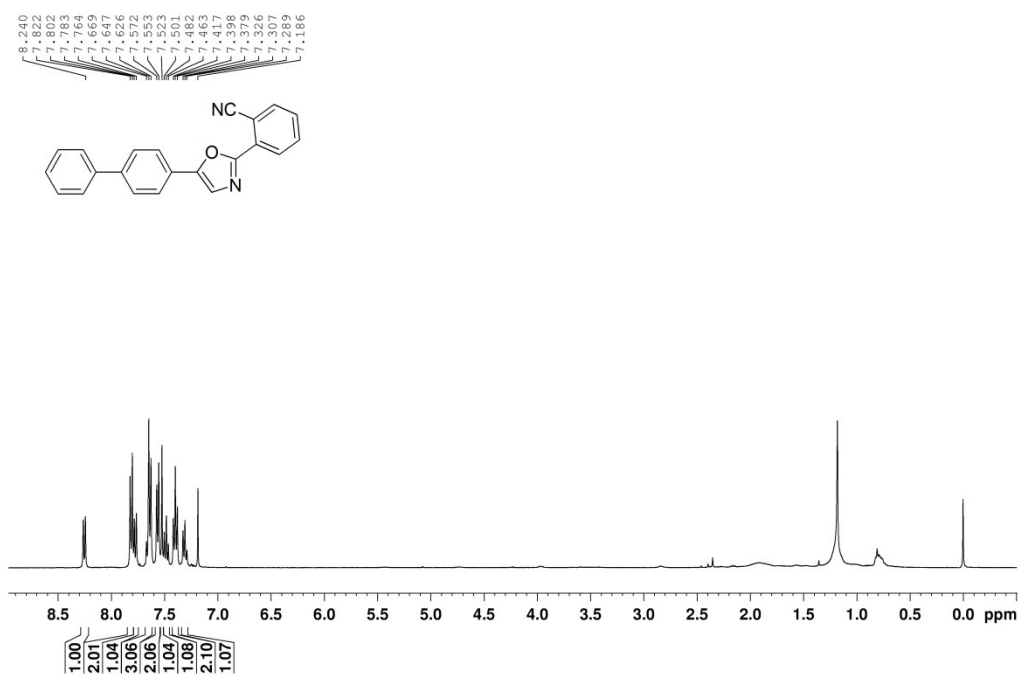
¹³C NMR of **3f** in CDCl₃



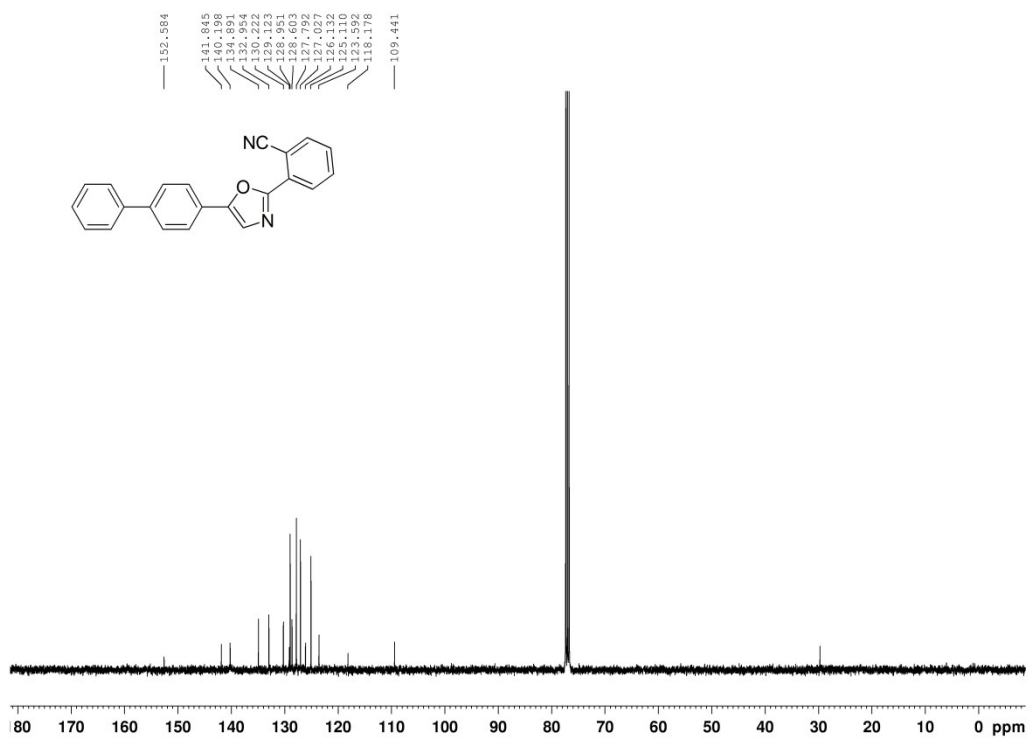
¹H NMR of 3g in CDCl₃



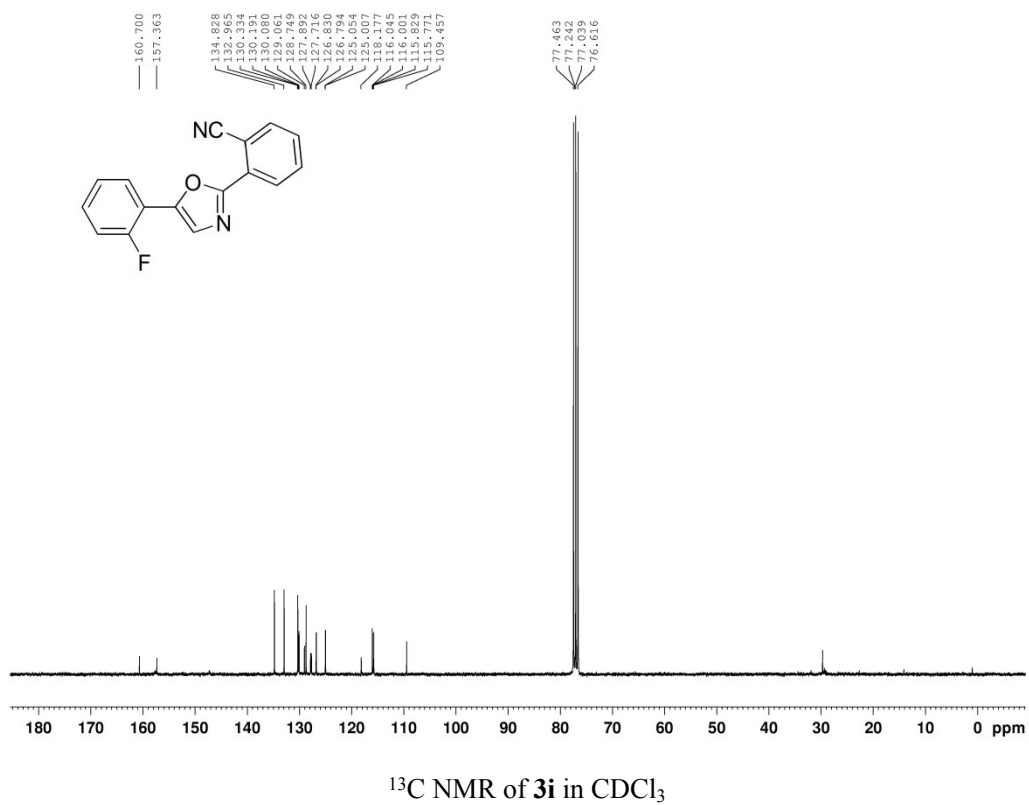
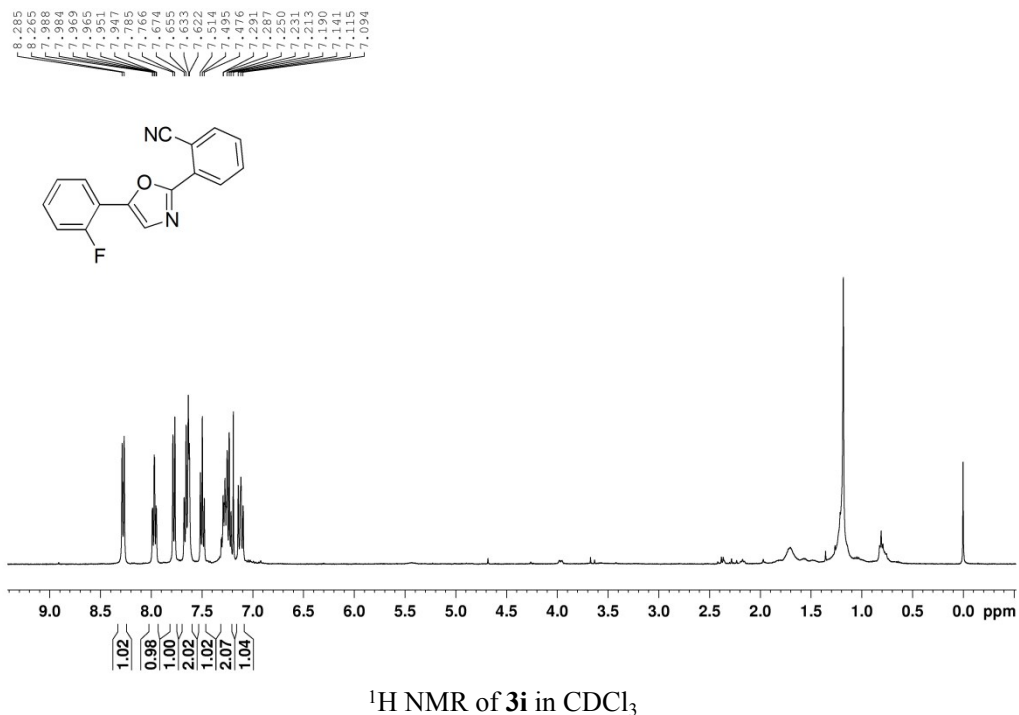
¹³C NMR of 3g in CDCl₃

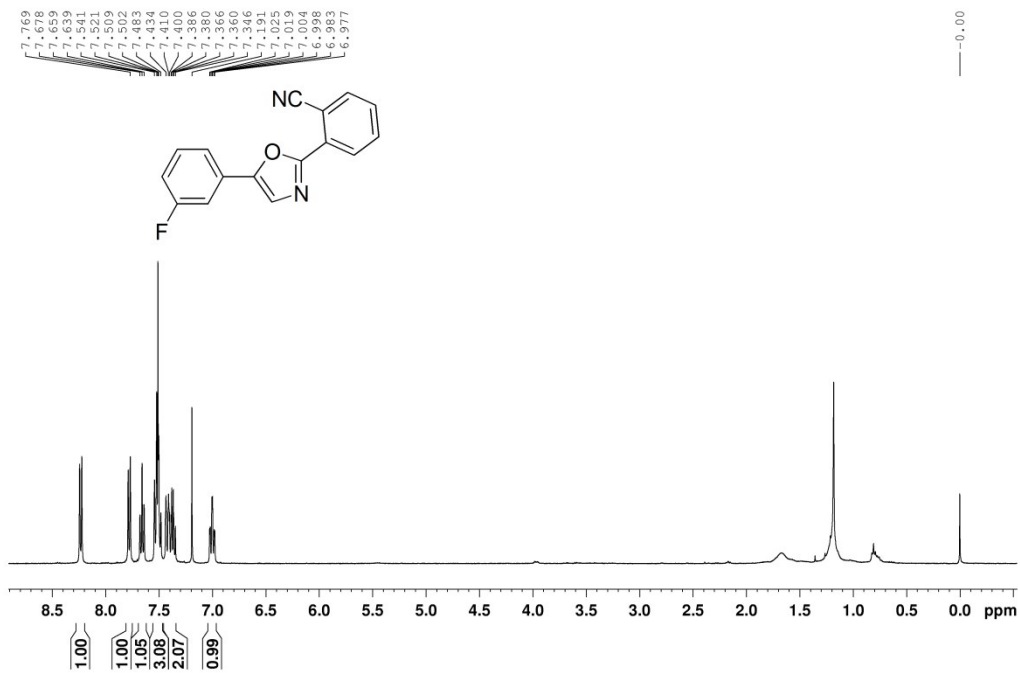


¹H NMR of **3h** in CDCl₃

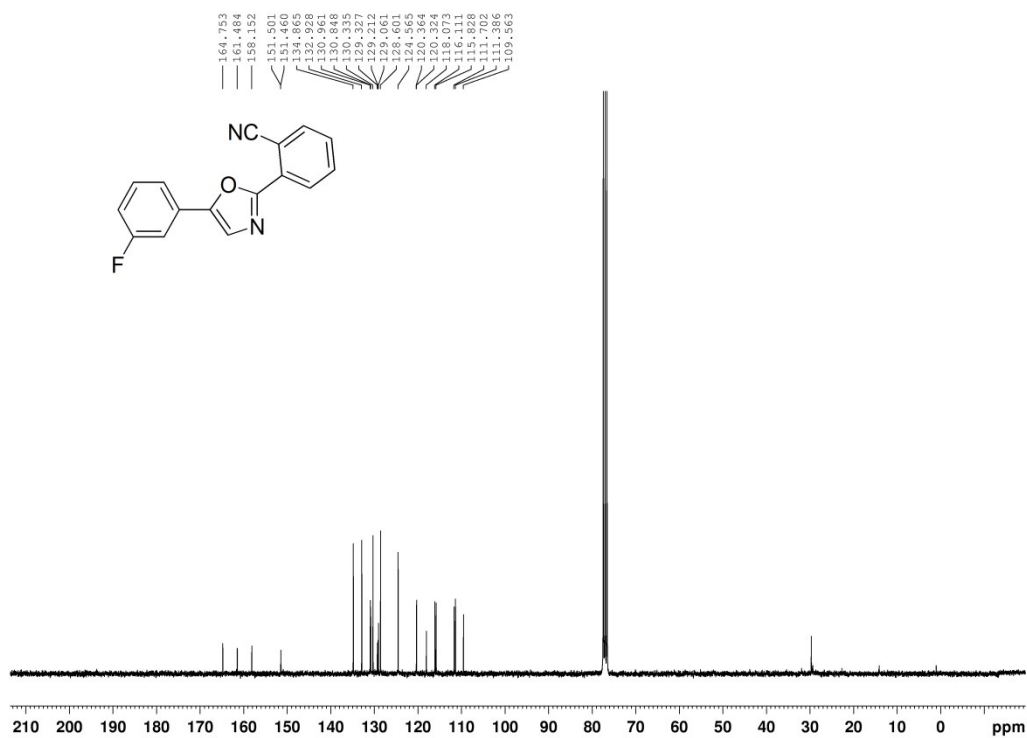


¹³C NMR of **3h** in CDCl₃

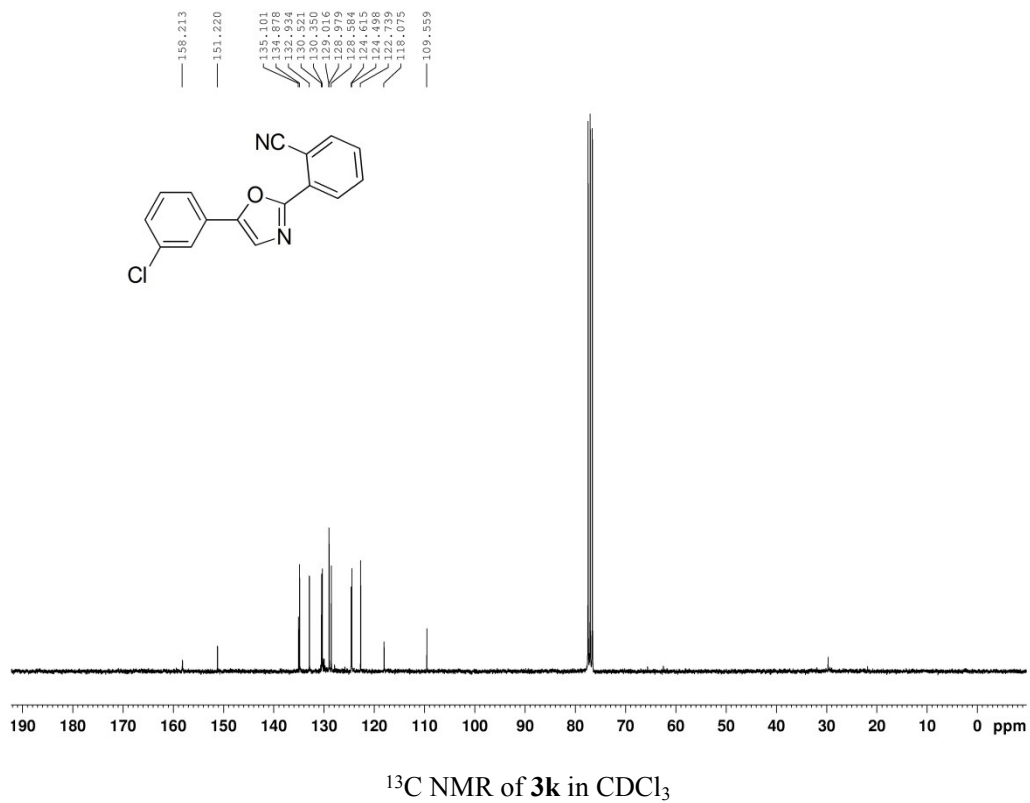
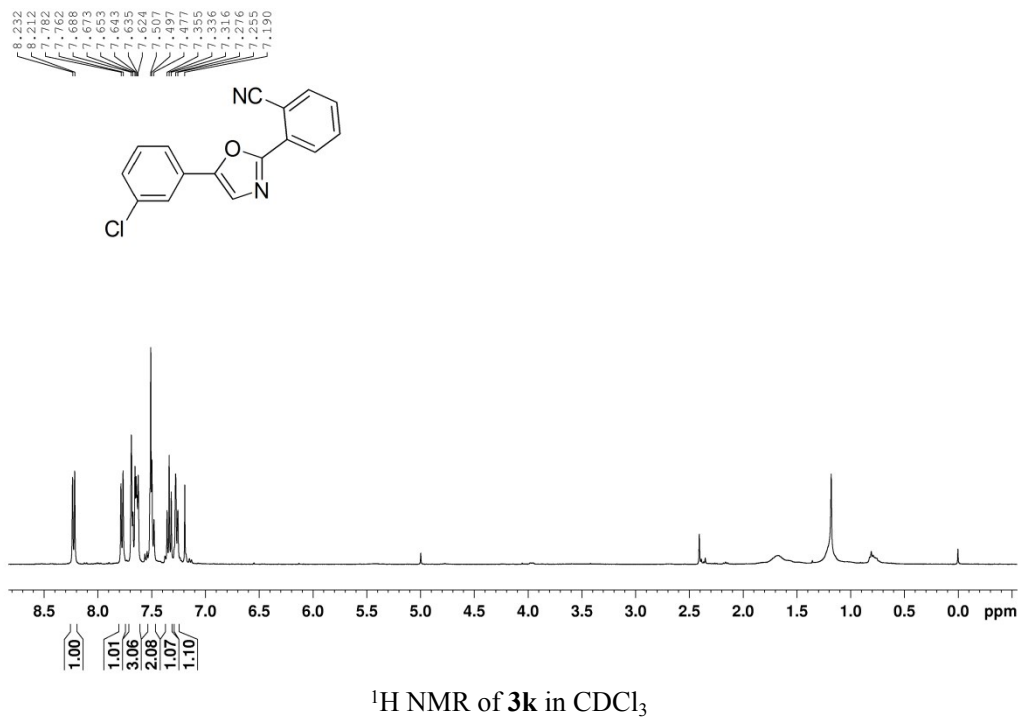


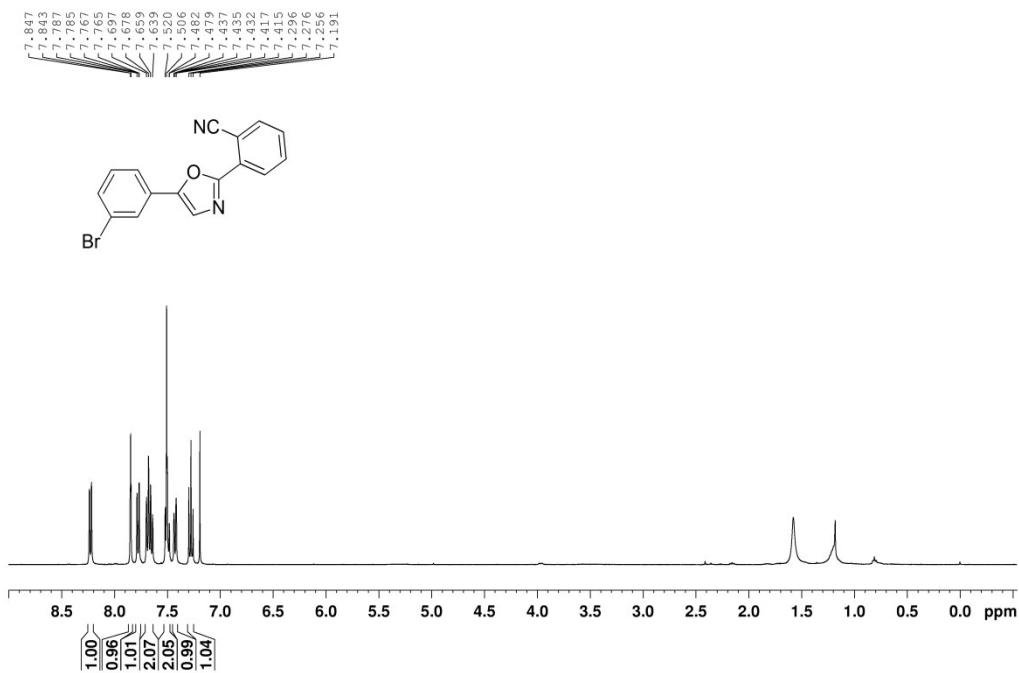


¹H NMR of **3j** in CDCl₃

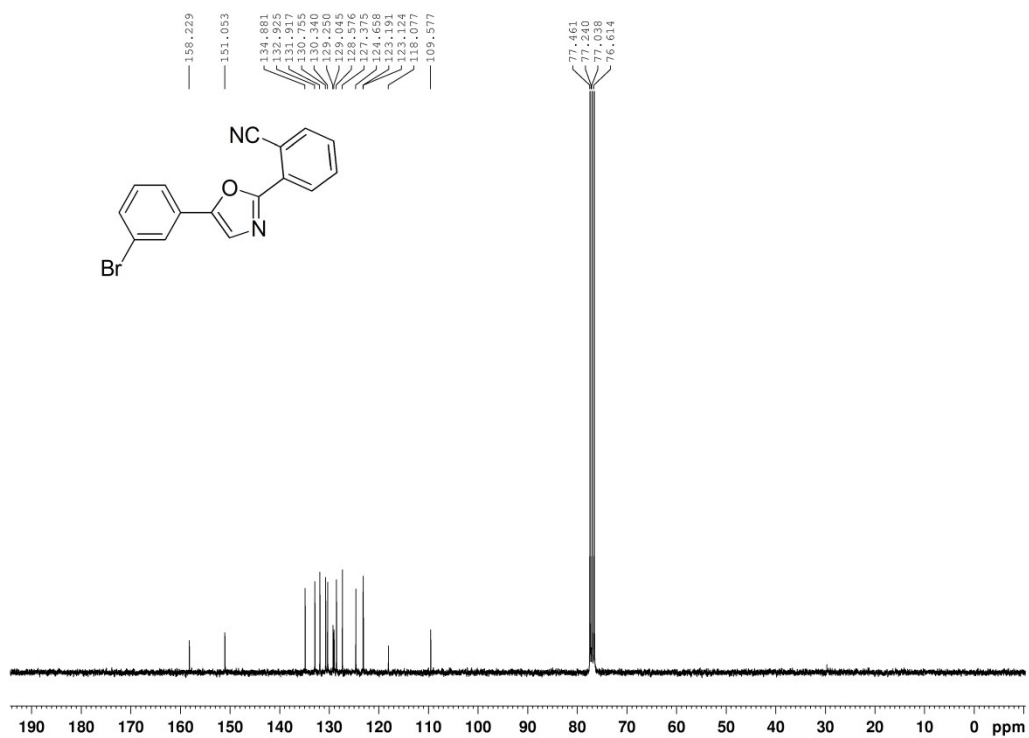


¹³C NMR of **3j** in CDCl₃

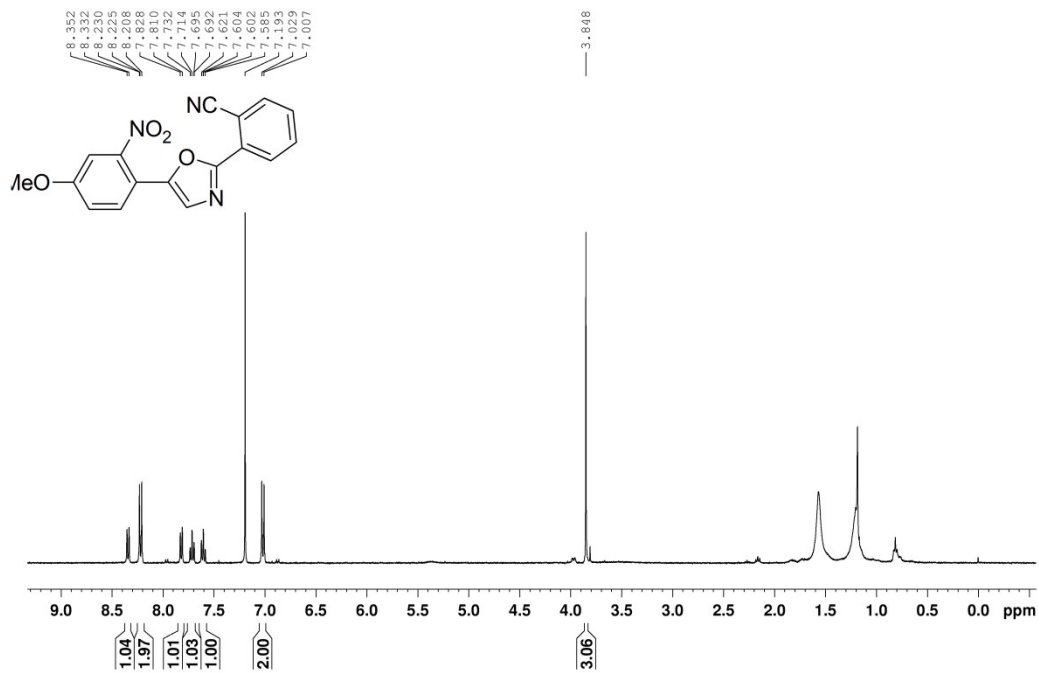




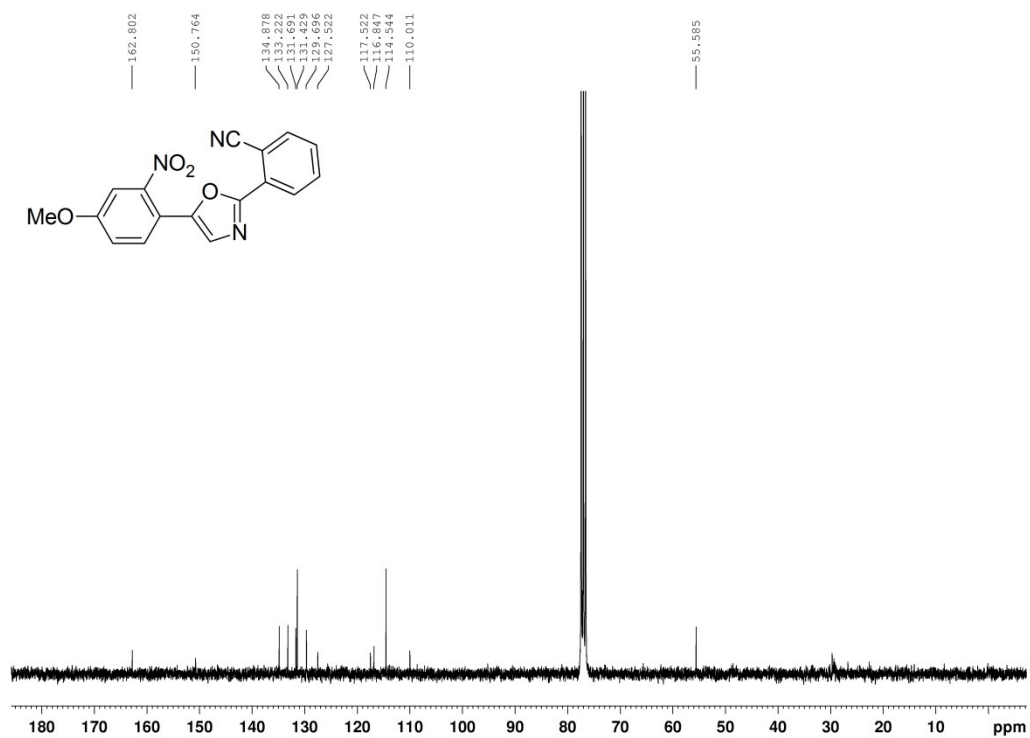
^1H NMR of **31** in CDCl_3



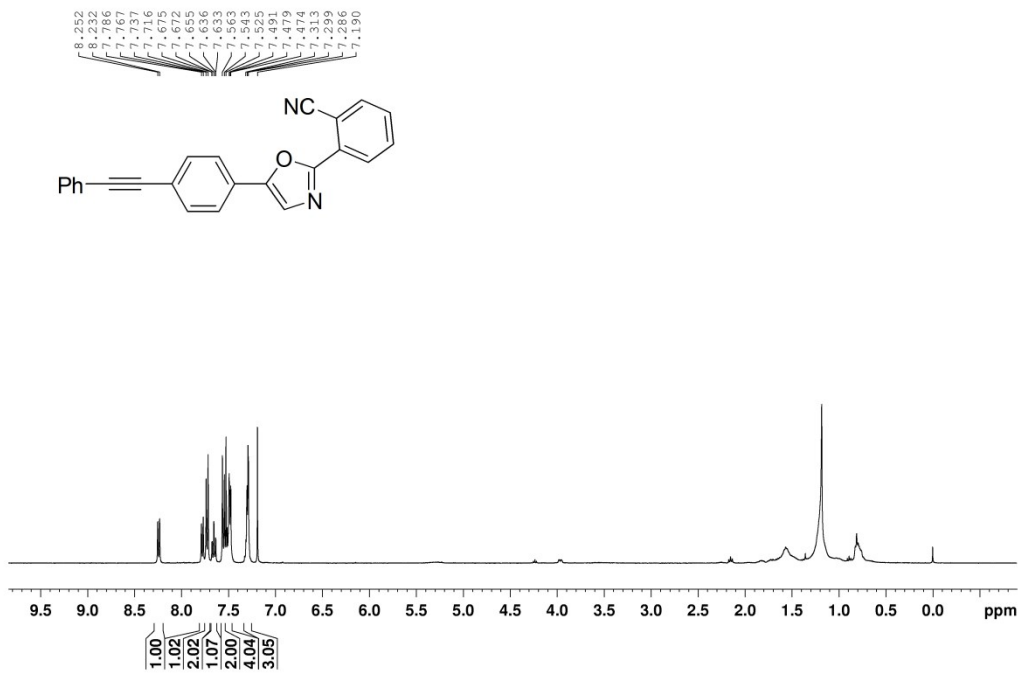
^{13}C NMR of **31** in CDCl_3



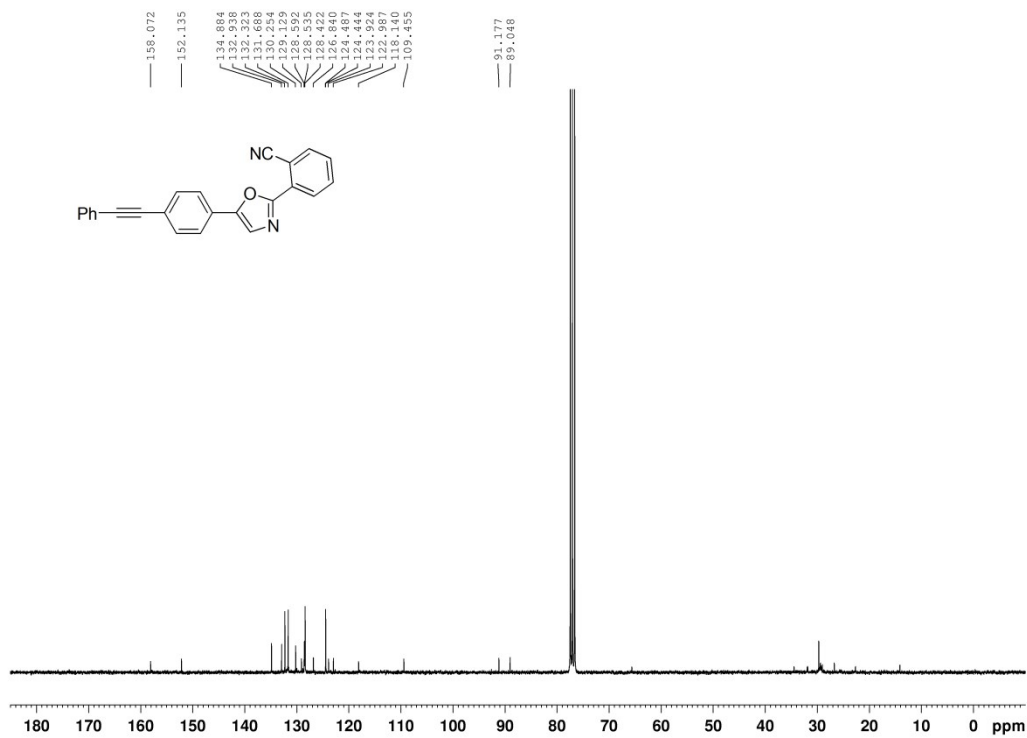
¹H NMR of **3m** in CDCl₃



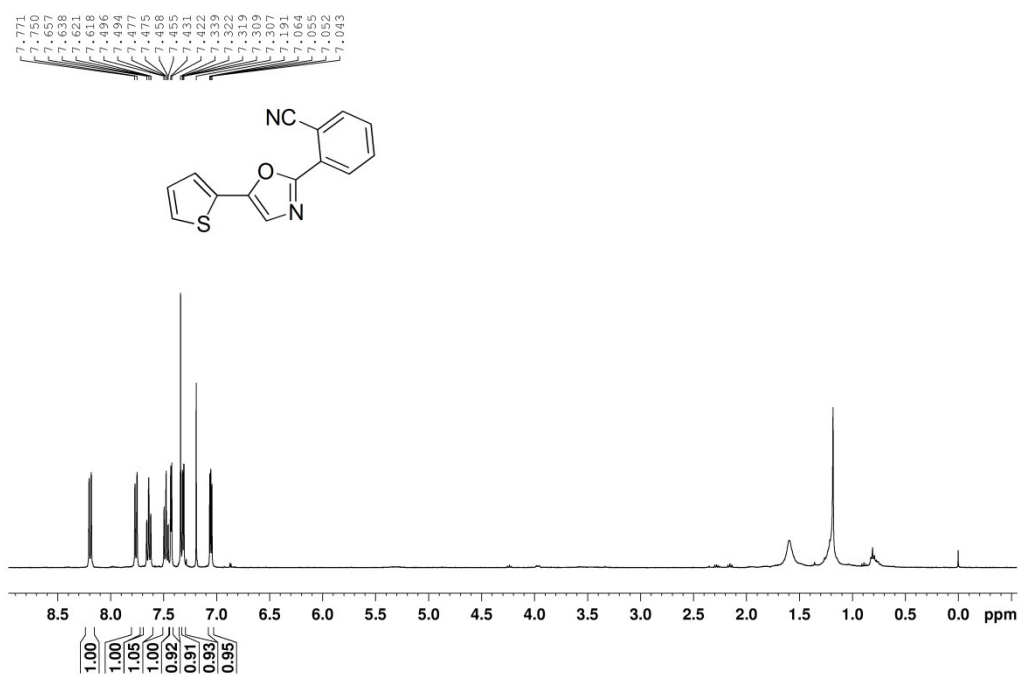
¹³C NMR of **3m** in CDCl₃



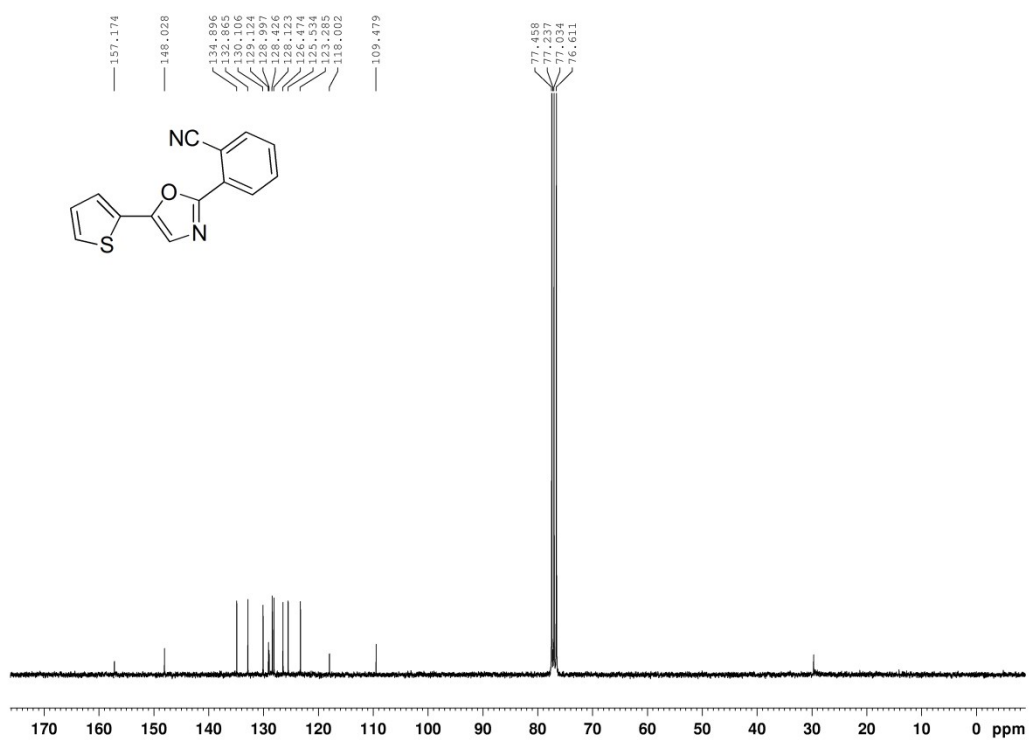
¹H NMR of **3n** in CDCl₃



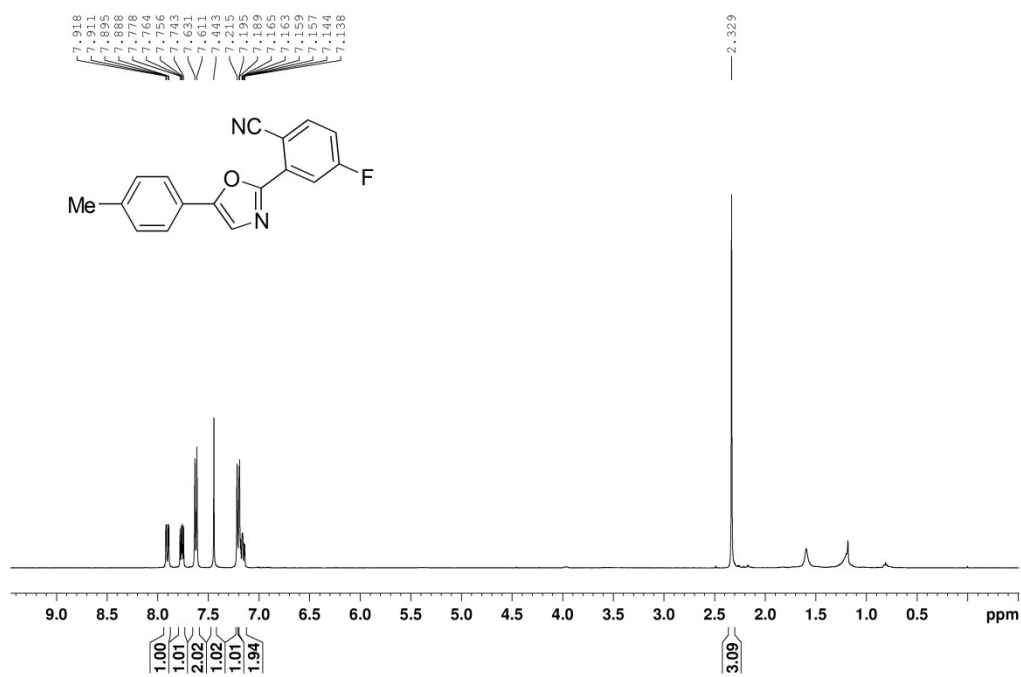
¹³C NMR of **3n** in CDCl₃



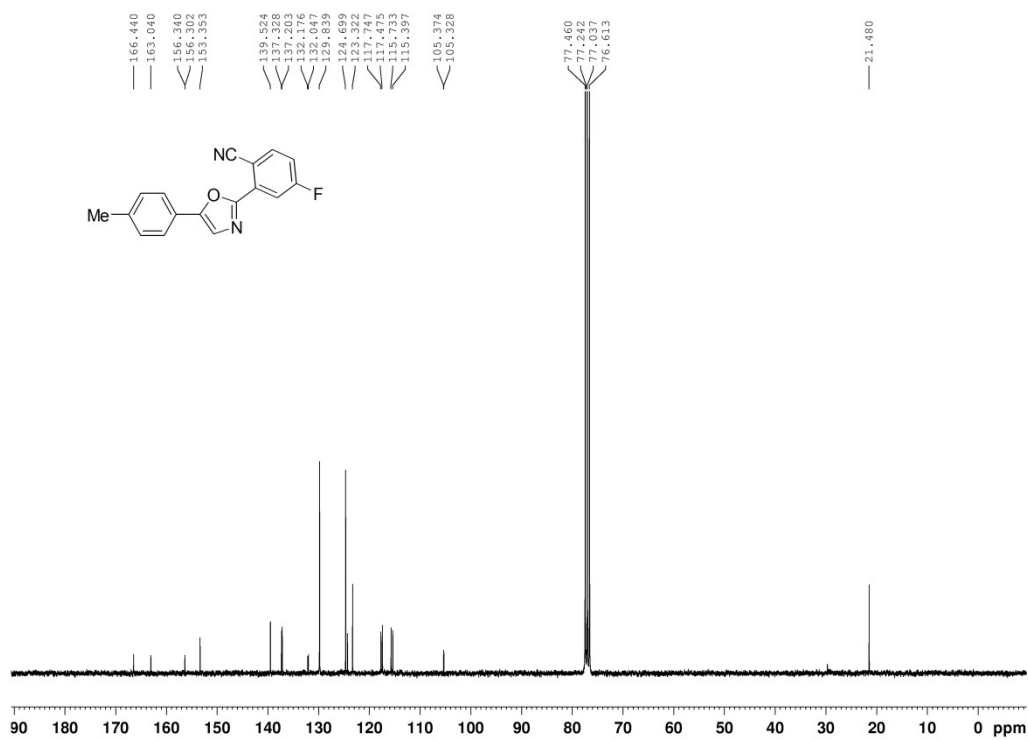
¹H NMR of **30** in CDCl₃



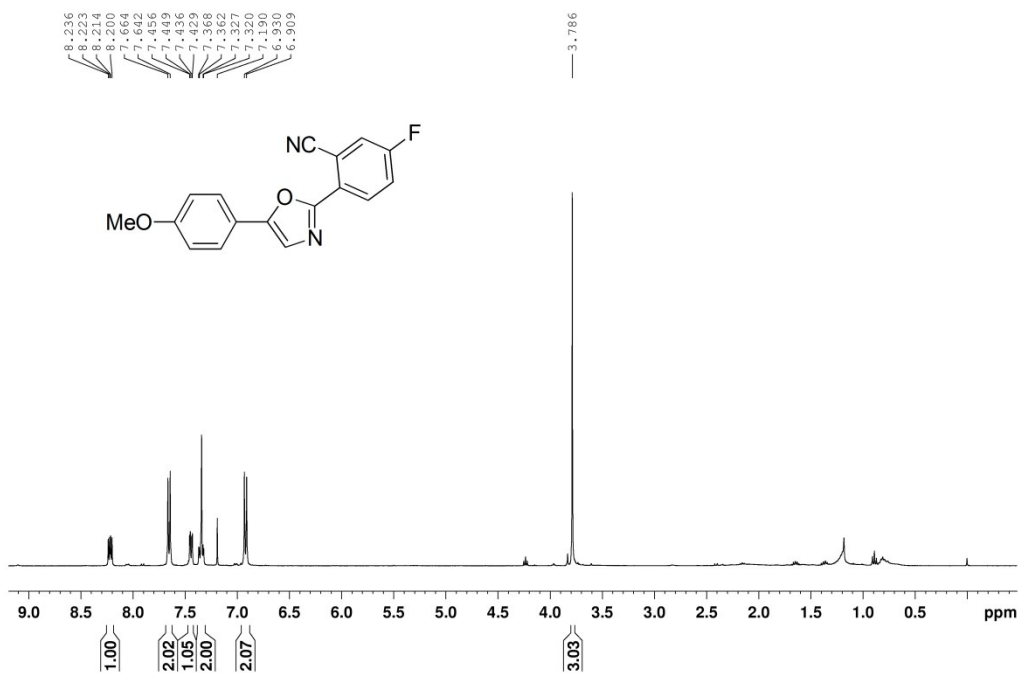
¹³C NMR of **30** in CDCl₃



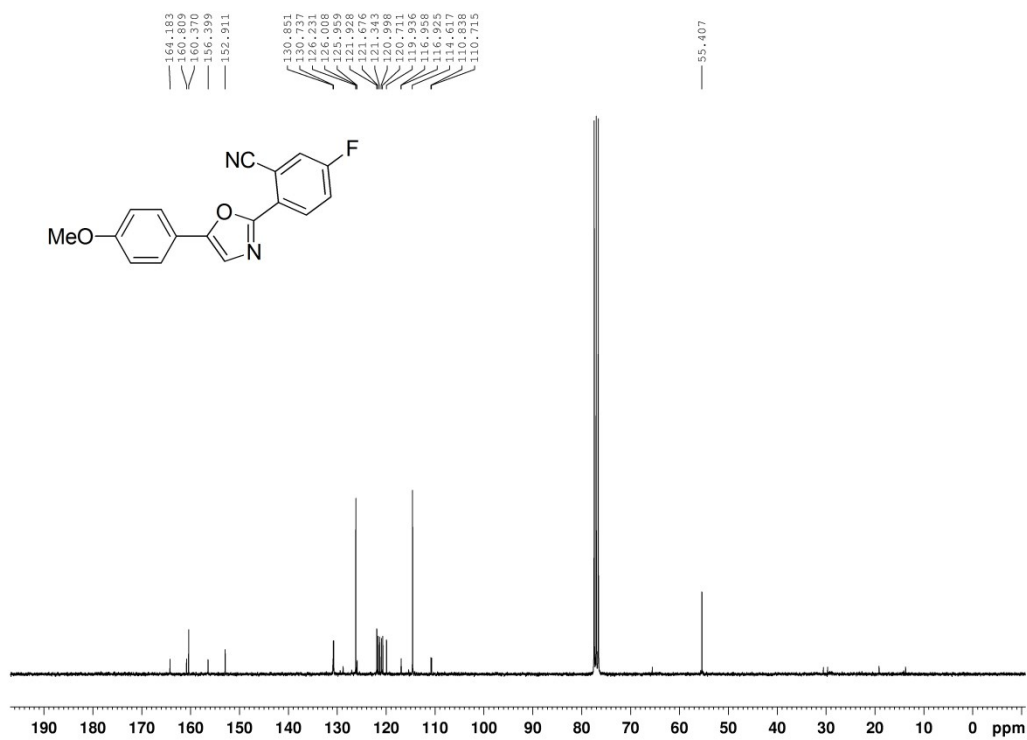
¹H NMR of **3p** in CDCl₃



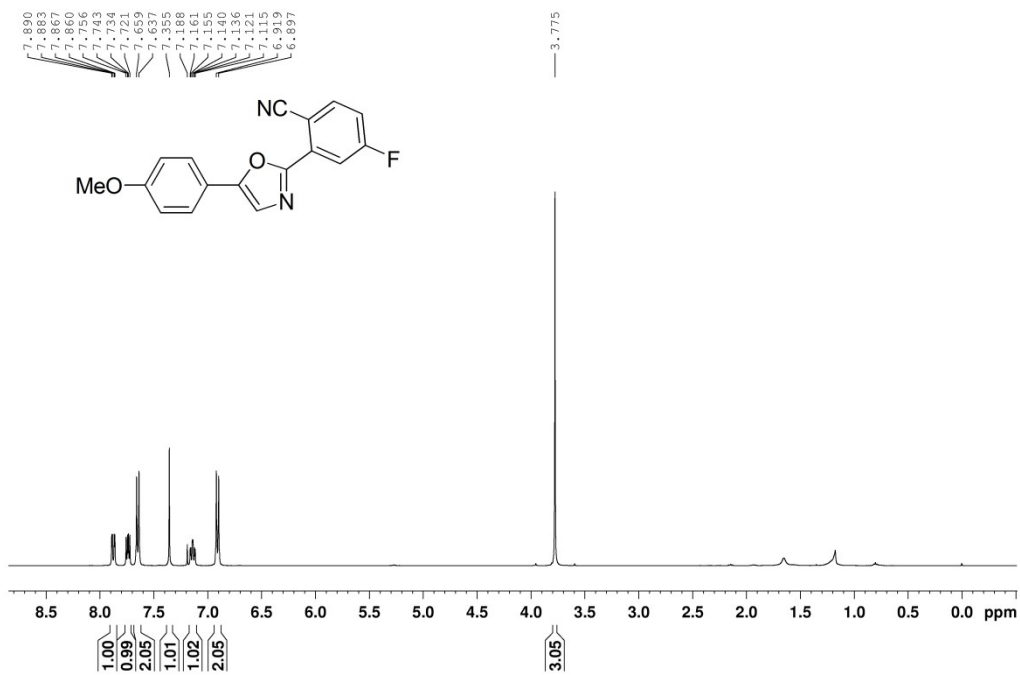
¹³C NMR of **3p** in CDCl₃



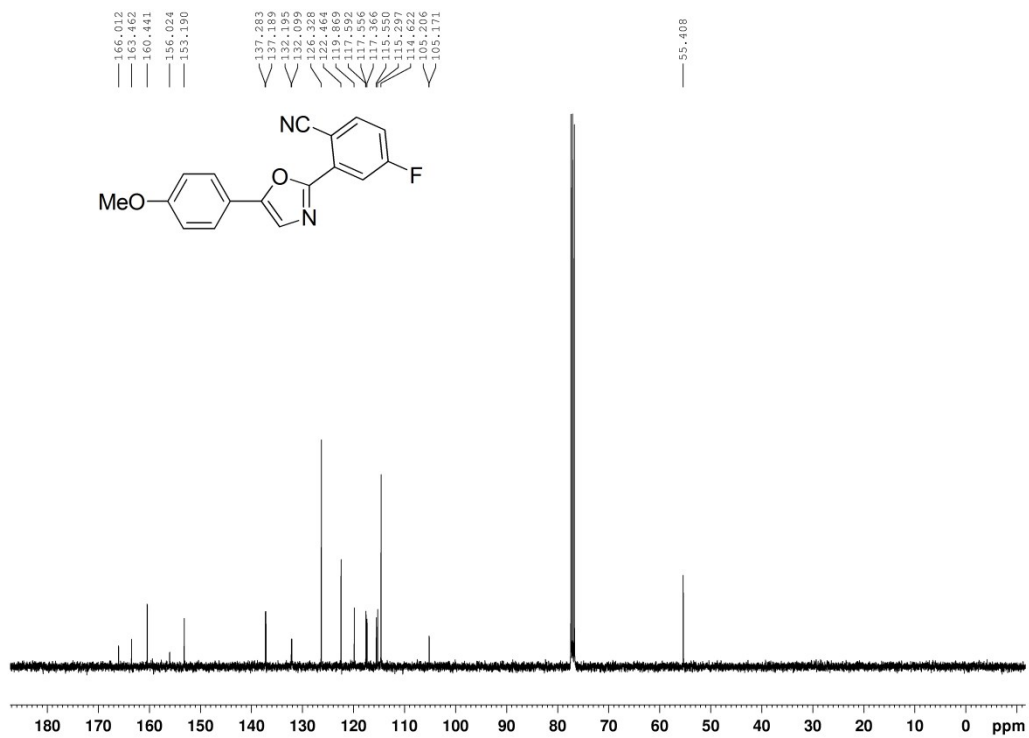
¹H NMR of 3q in CDCl₃



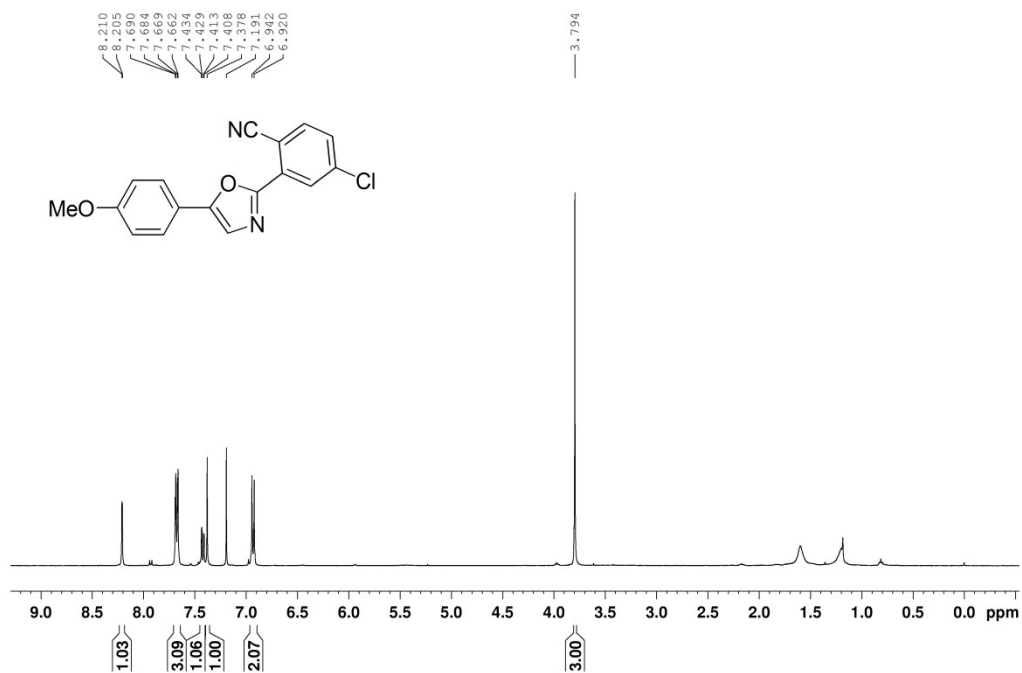
¹³C NMR of 3q in CDCl₃



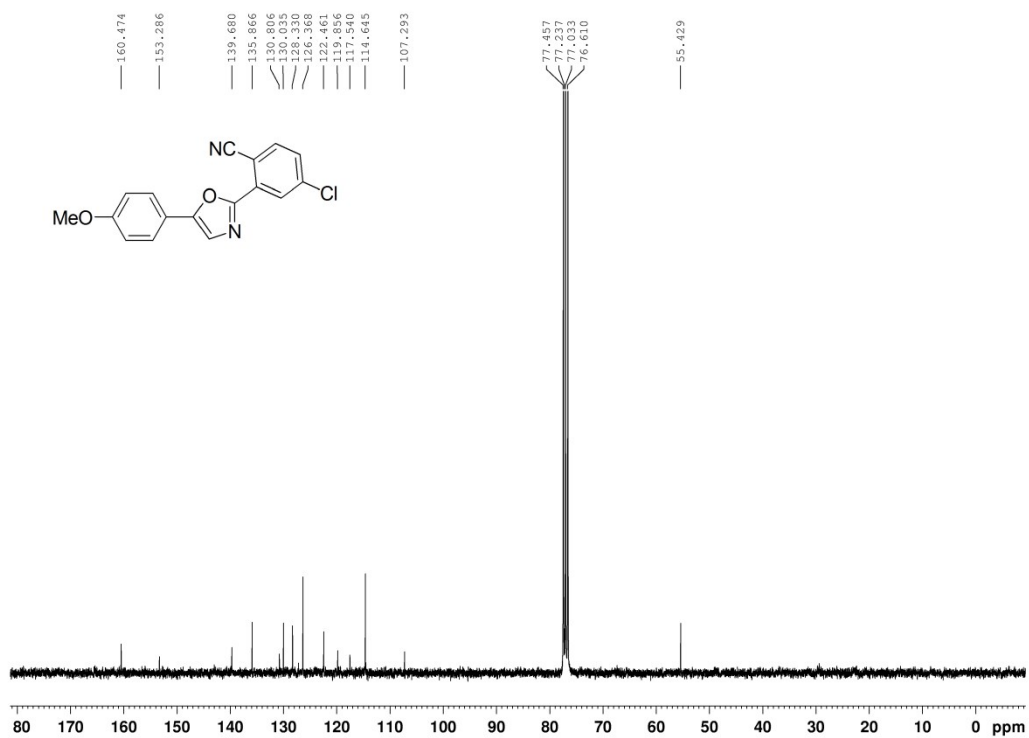
¹H NMR of 3r in CDCl₃



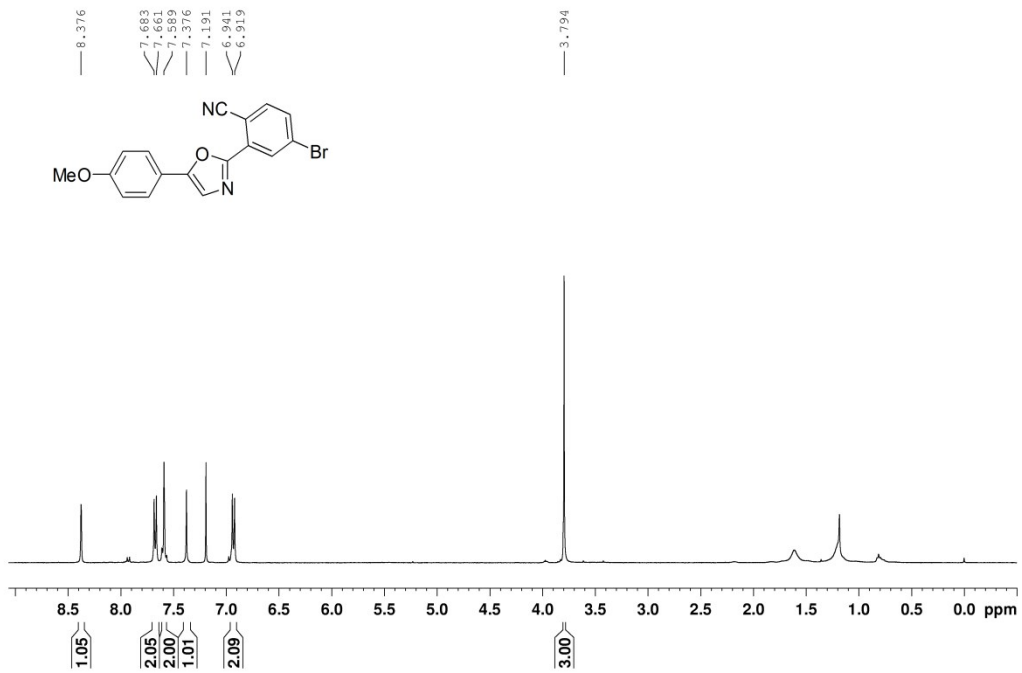
¹³C NMR of 3r in CDCl₃



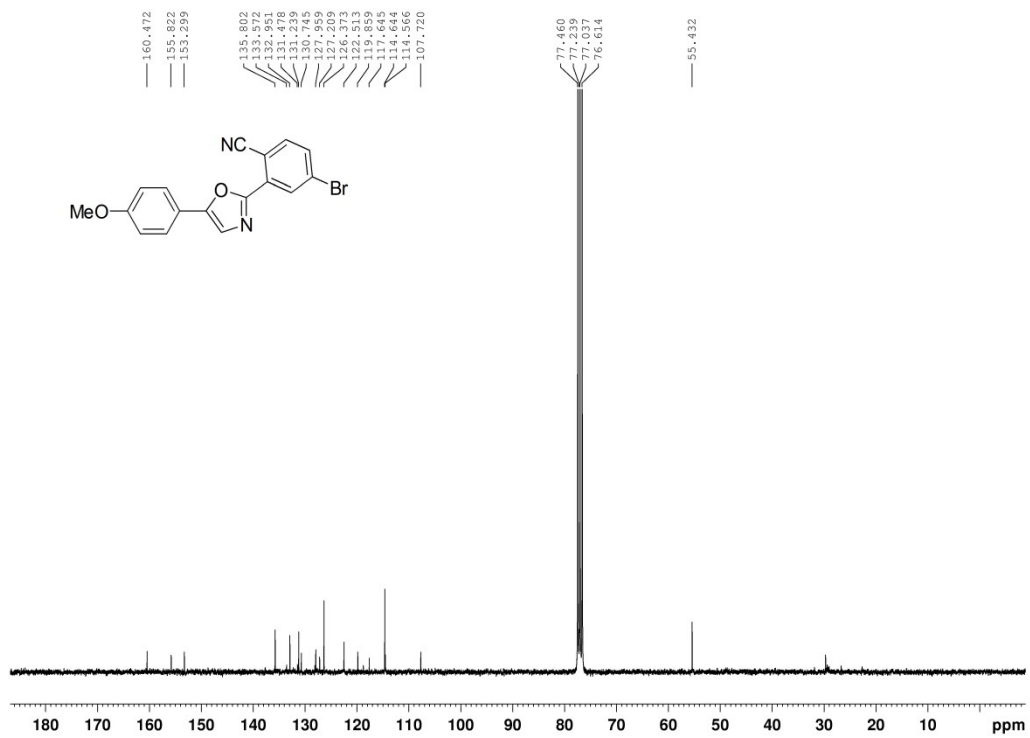
¹H NMR of **3s** in CDCl₃



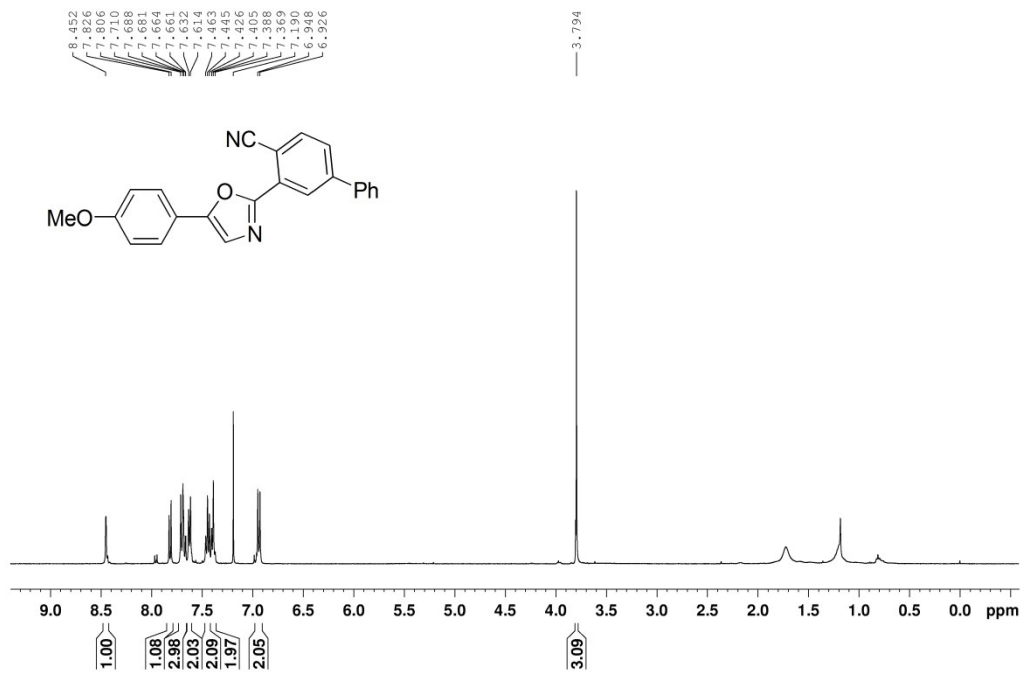
¹³C NMR of **3s** in CDCl₃



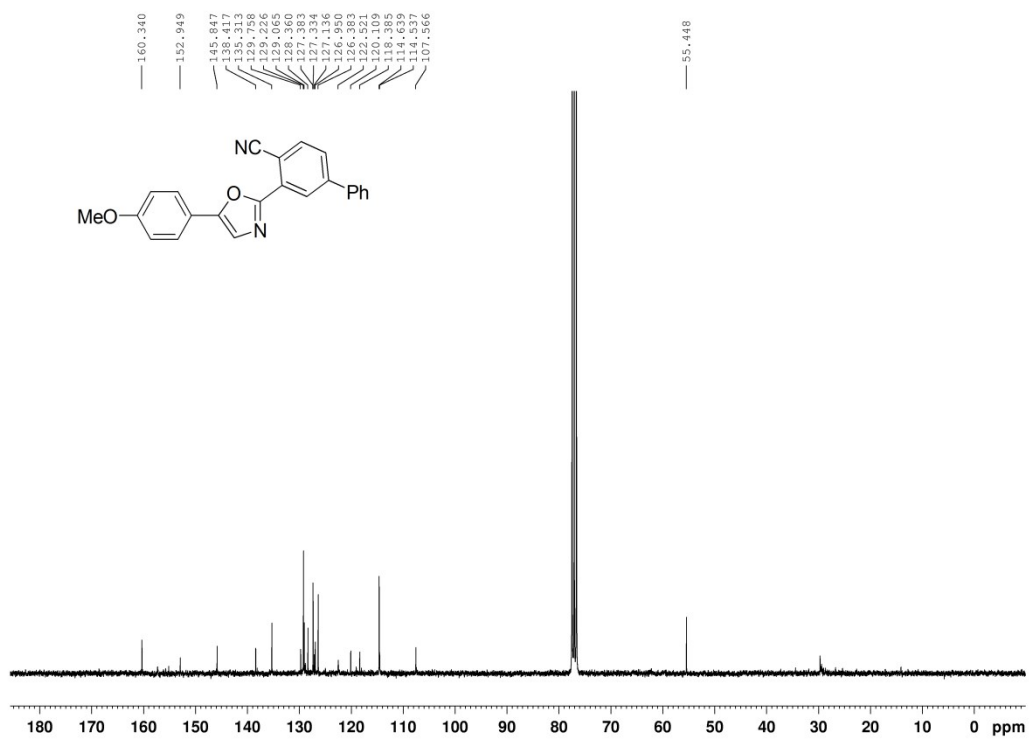
^1H NMR of **3t** in CDCl_3



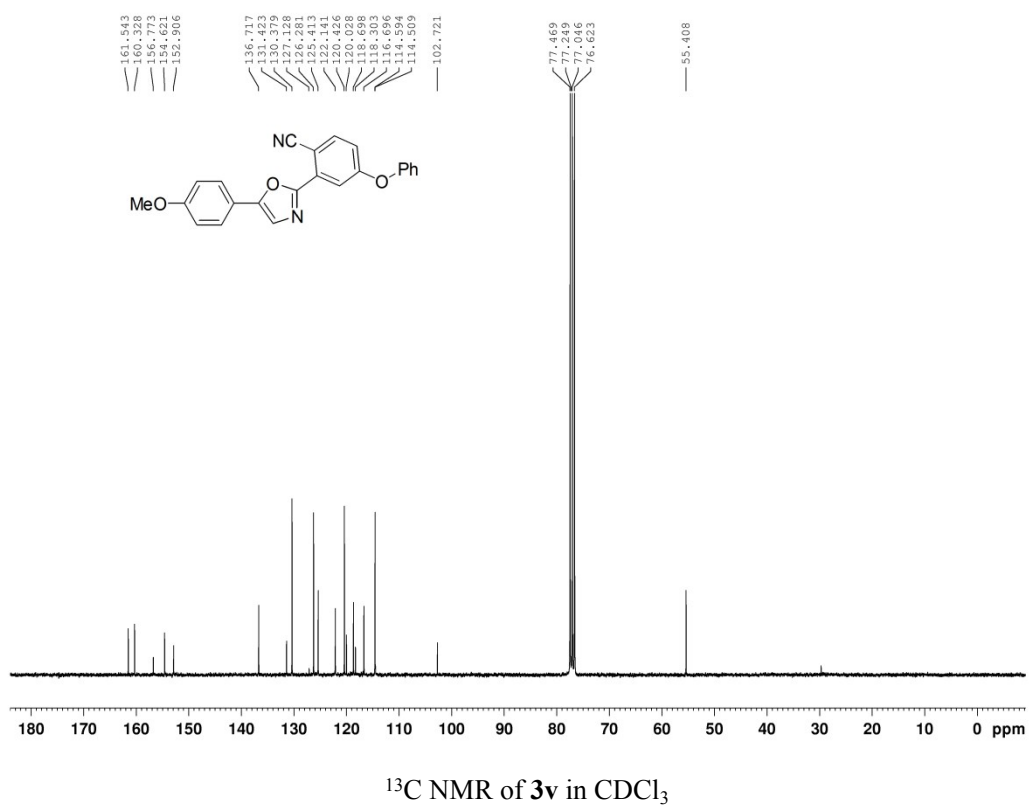
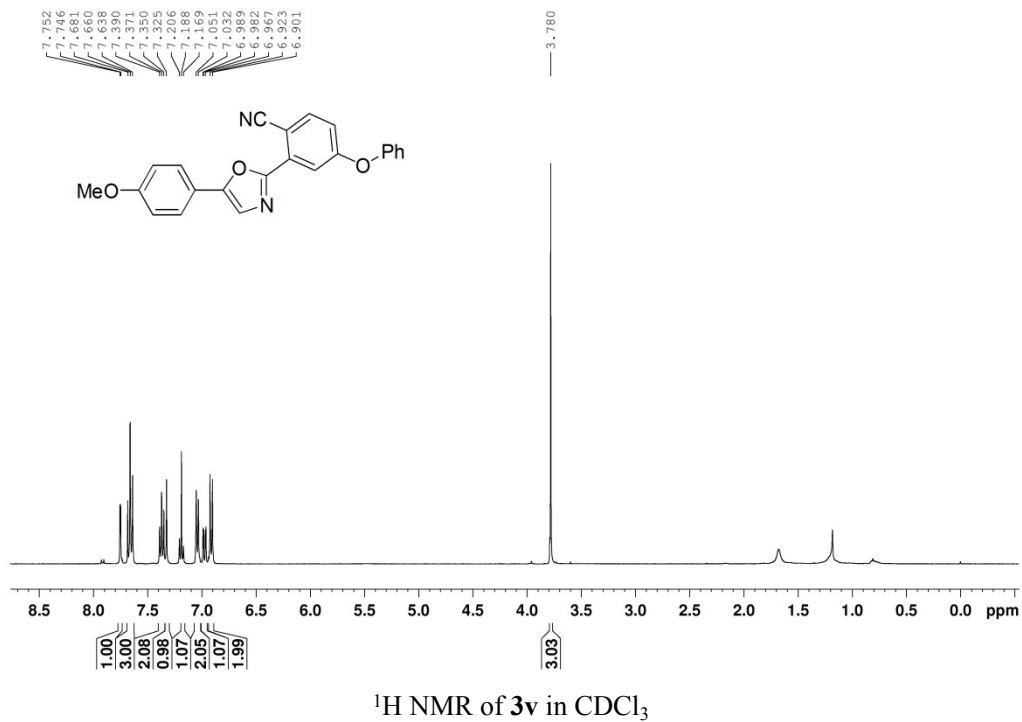
^{13}C NMR of **3t** in CDCl_3

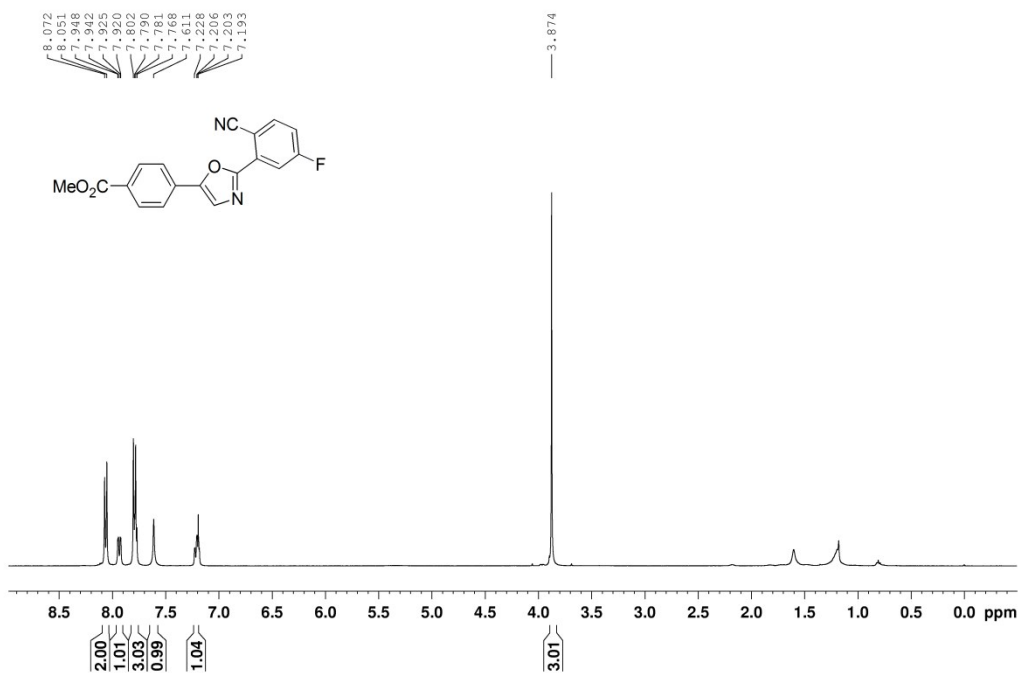


¹H NMR of **3u** in CDCl₃

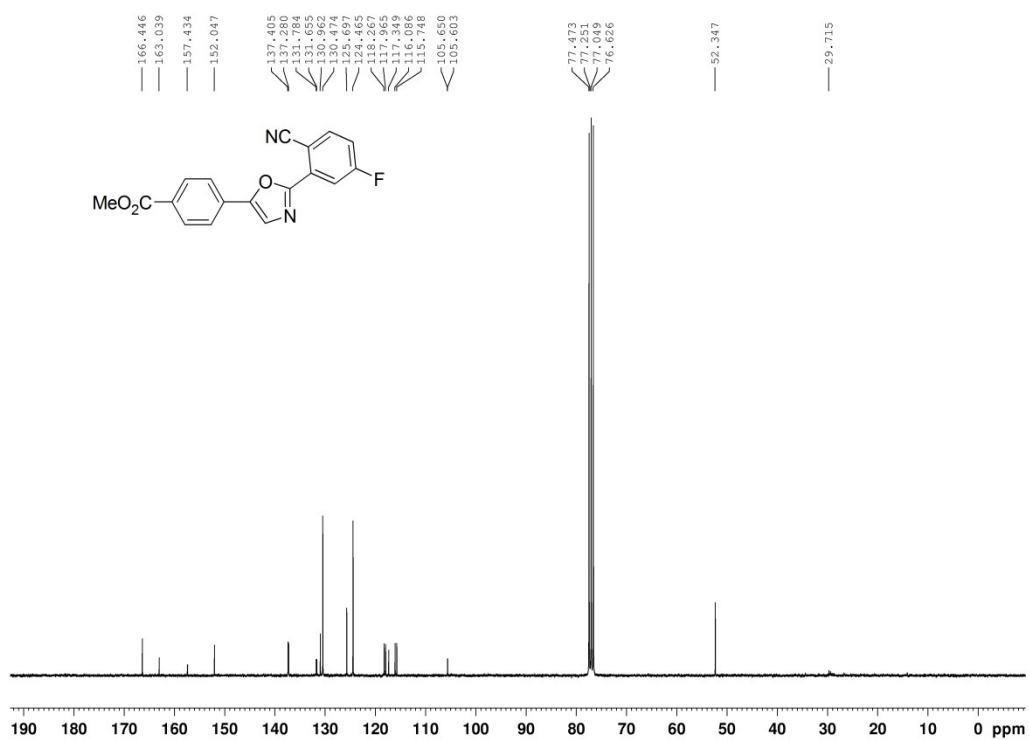


¹³C NMR of **3u** in CDCl₃

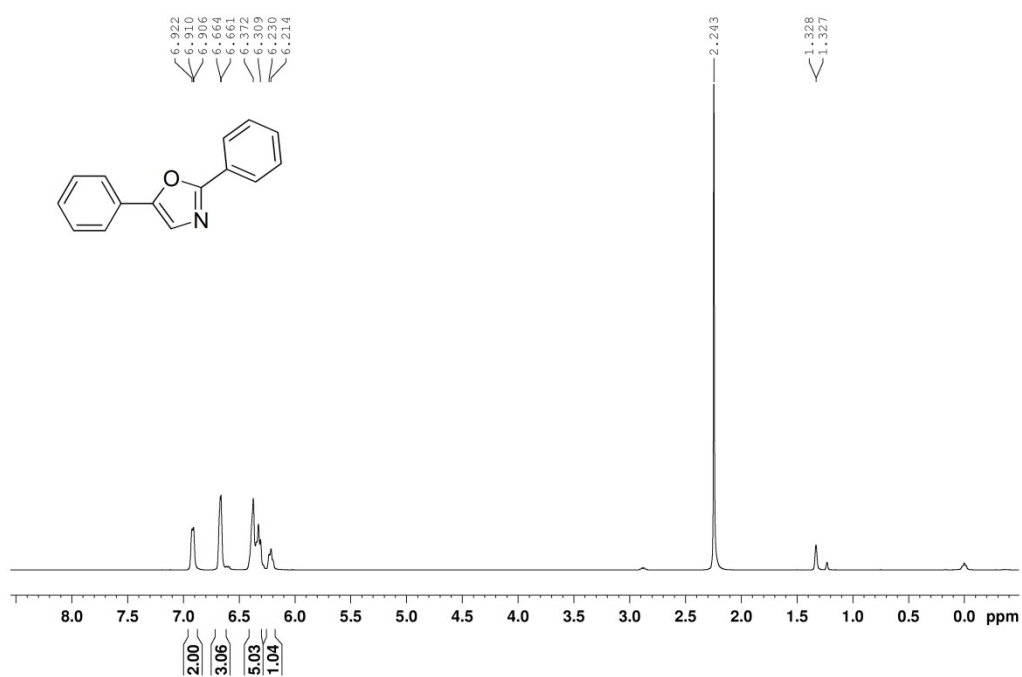




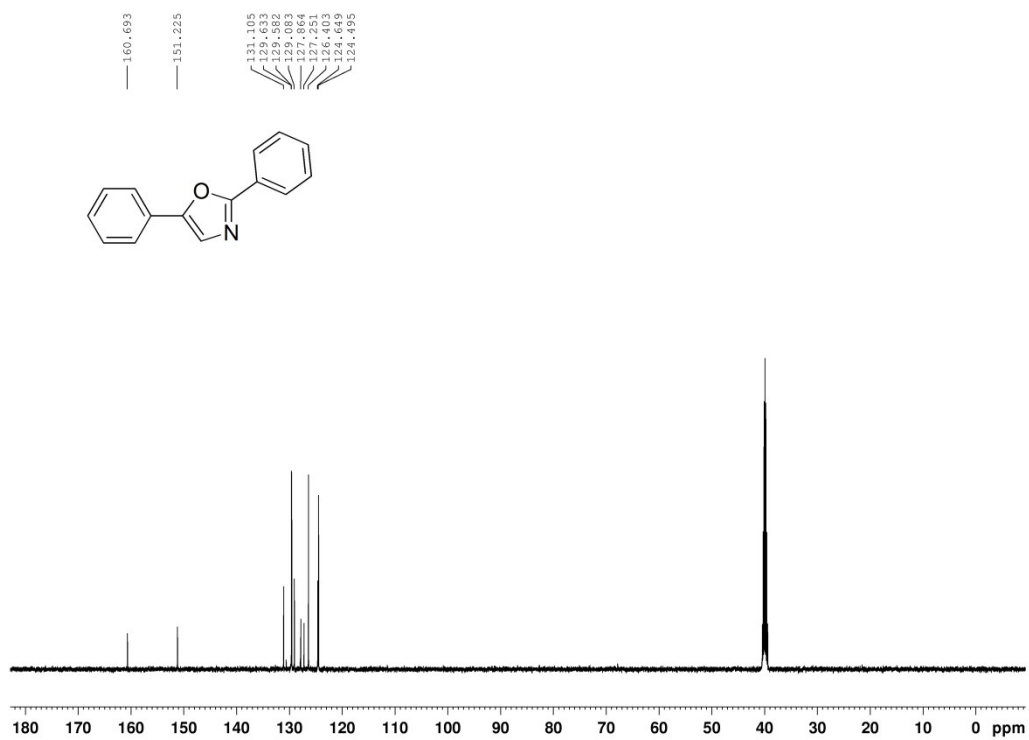
¹H NMR of **3w** in CDCl₃



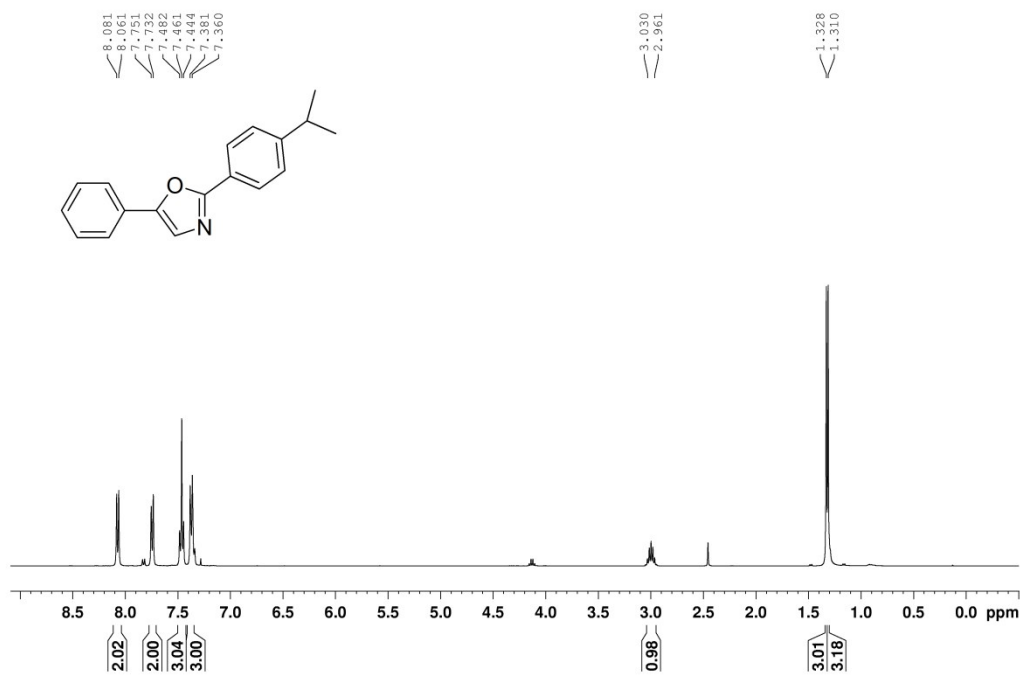
¹³C NMR of **3w** in CDCl₃



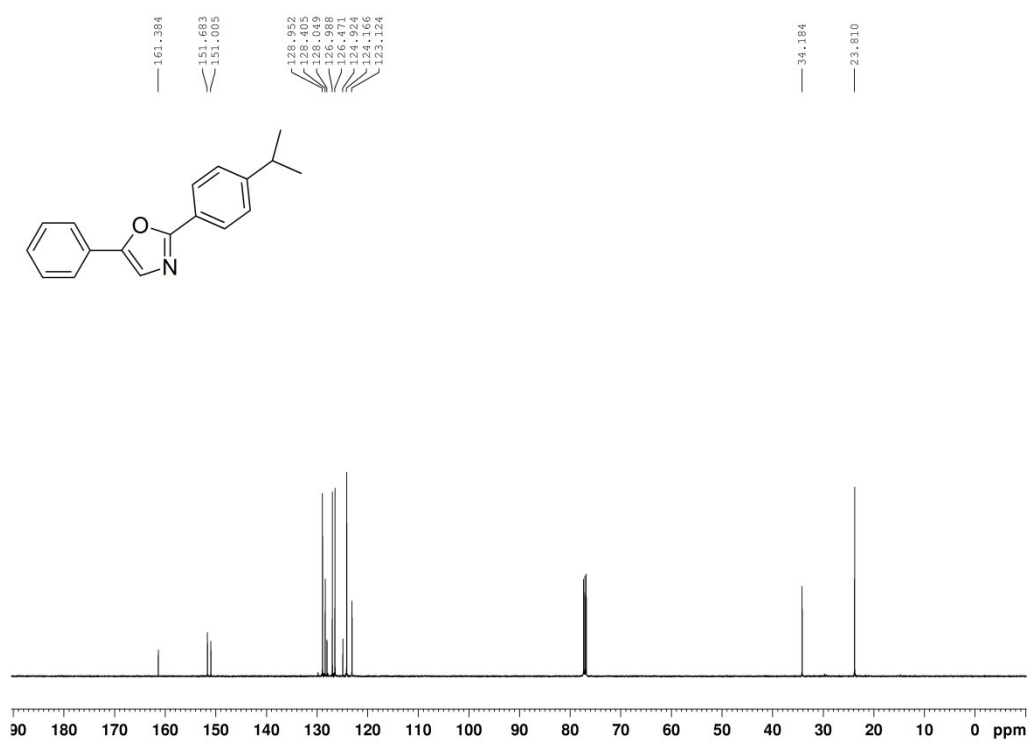
¹H NMR of **4a** in DMSO-*d*₆



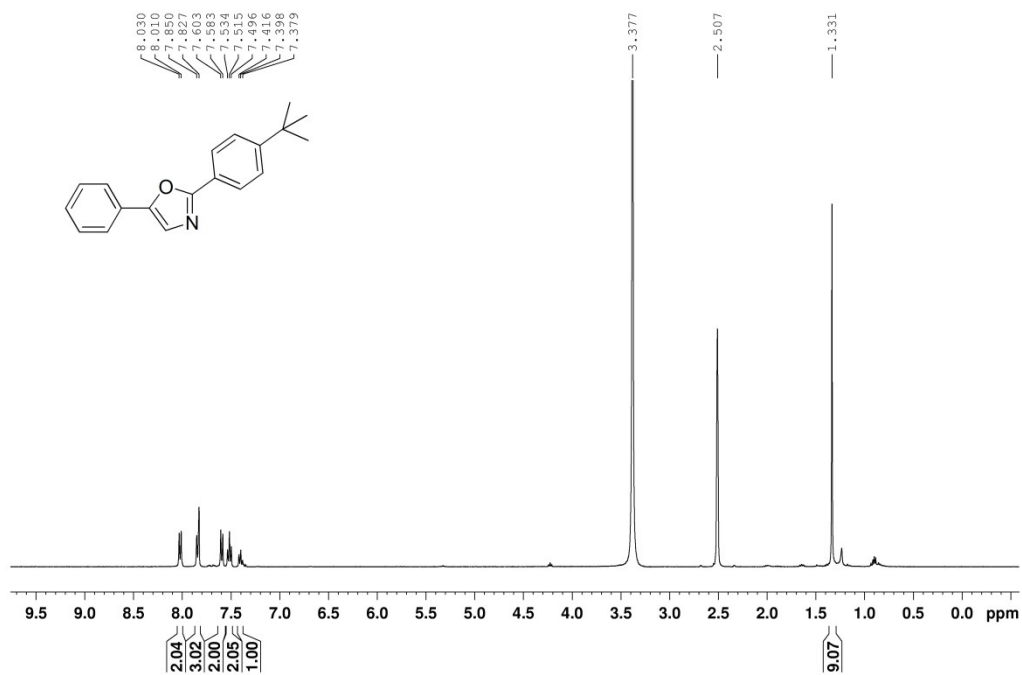
¹³C NMR of **4a** in DMSO-*d*₆



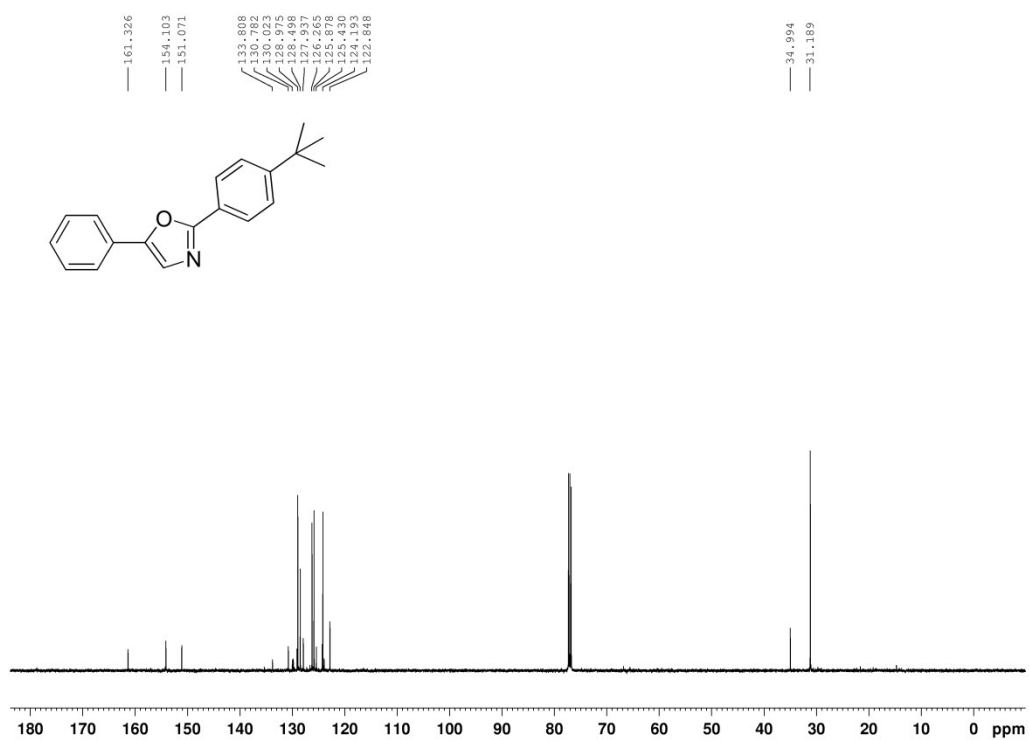
¹H NMR of **4b** in CDCl₃



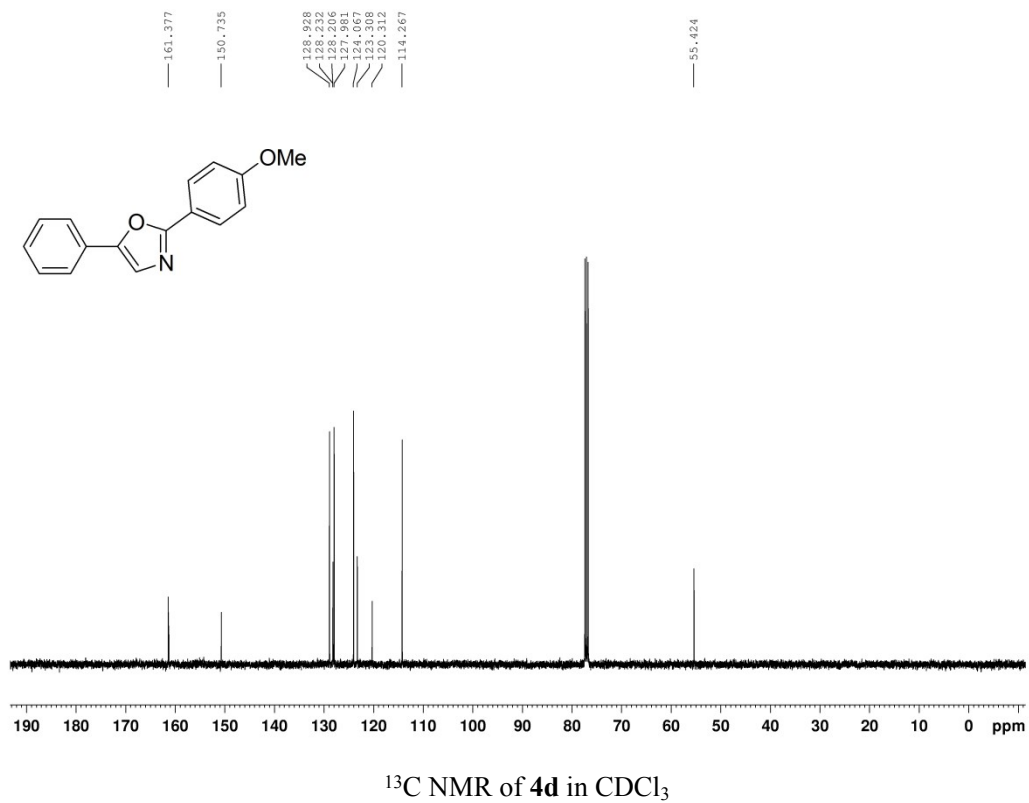
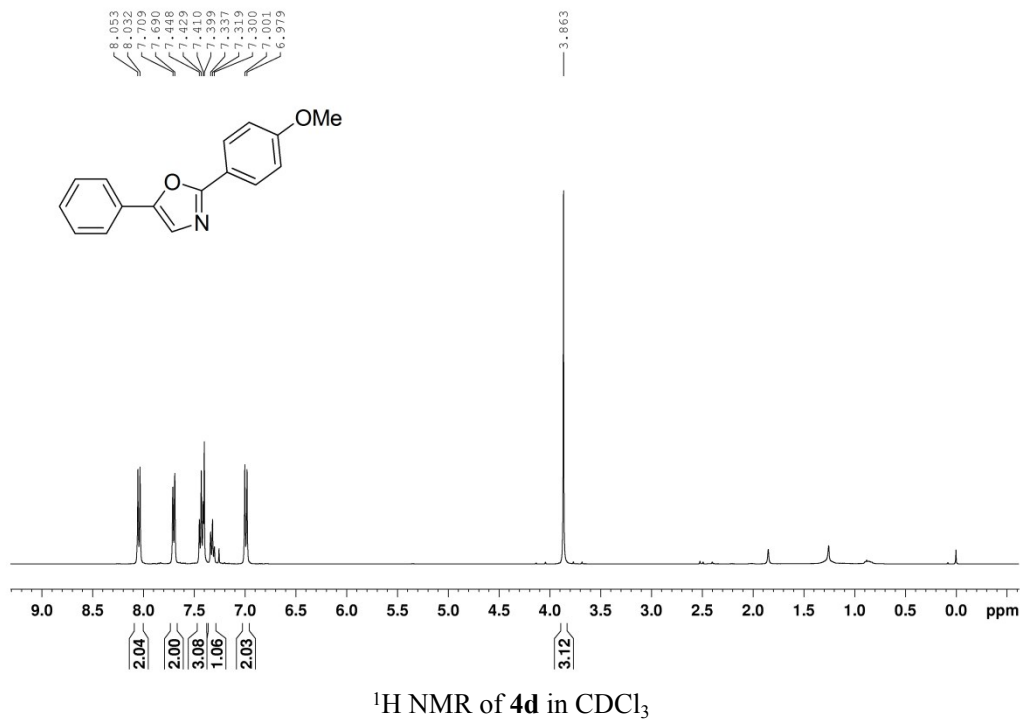
¹³C NMR of **4b** in CDCl₃

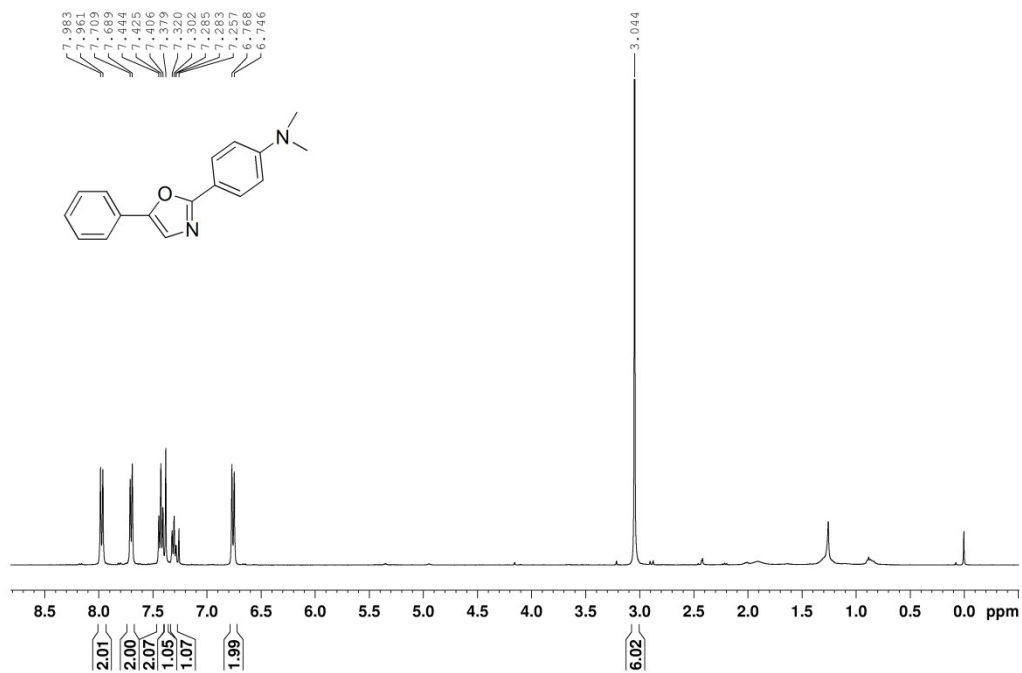


¹H NMR of 4c in DMSO-*d*₆

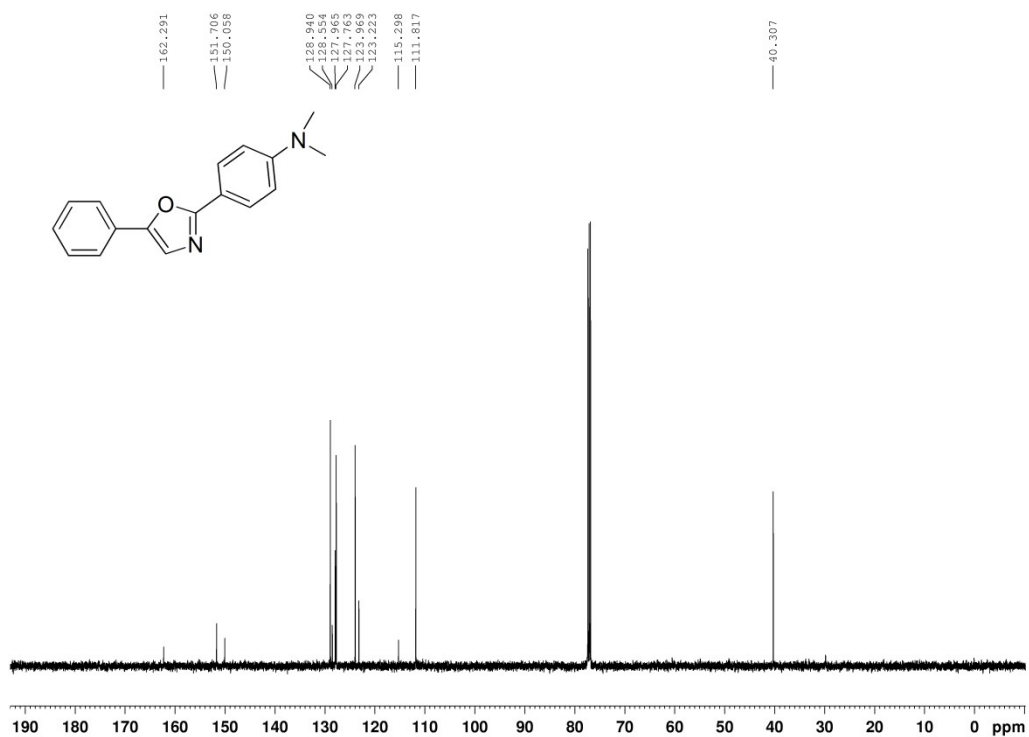


¹³C NMR of 4c in CDCl₃

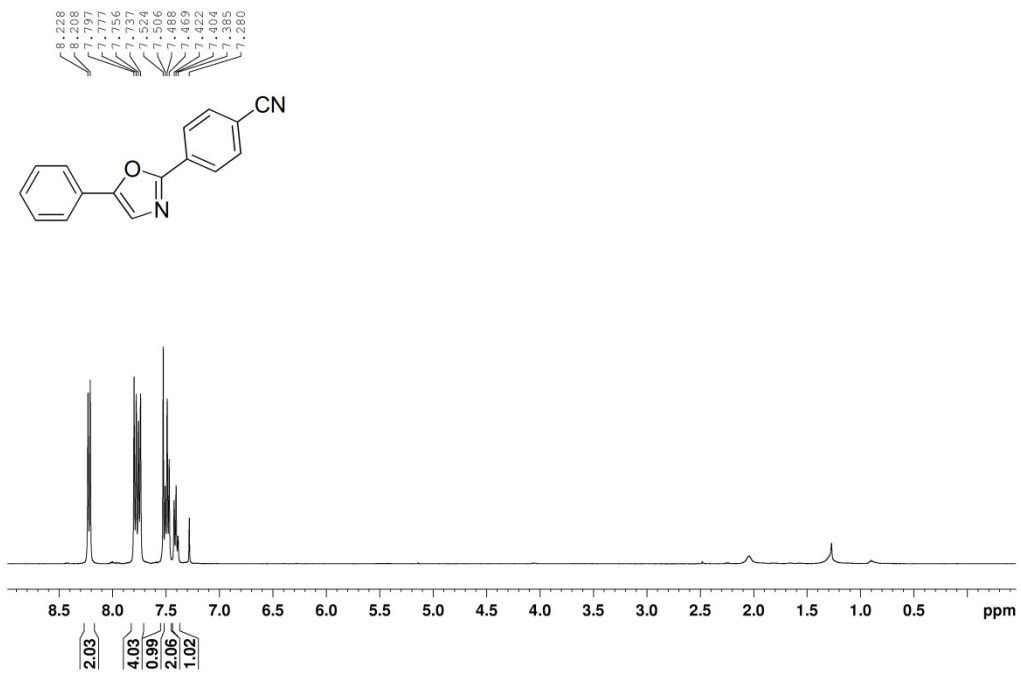




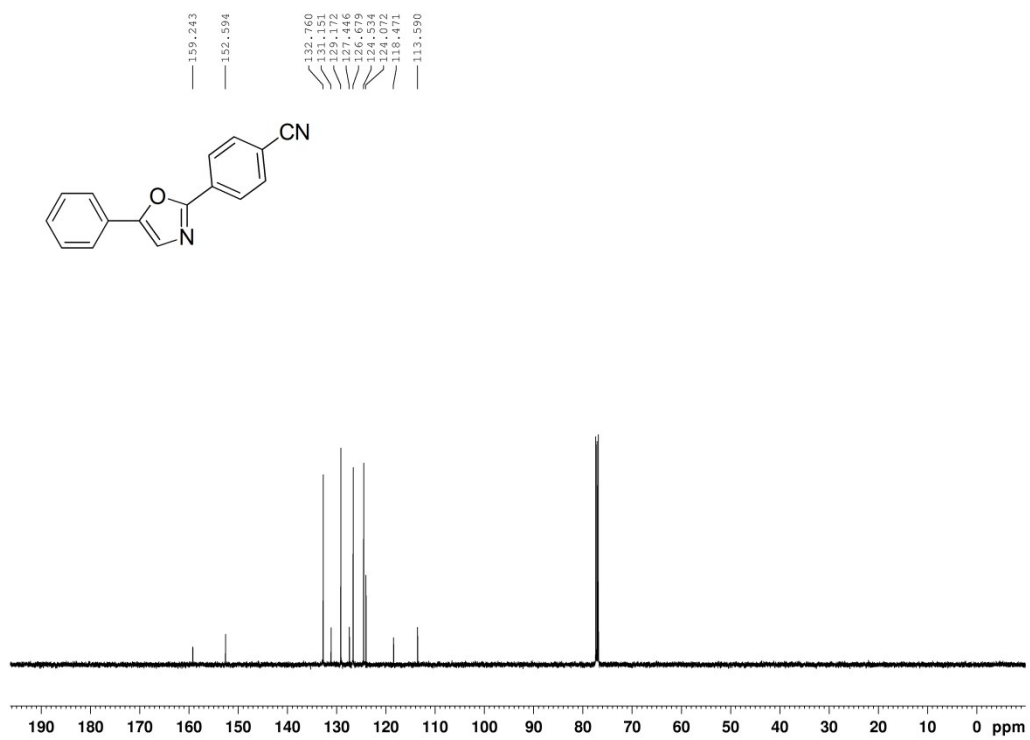
¹H NMR of **4e** in CDCl₃



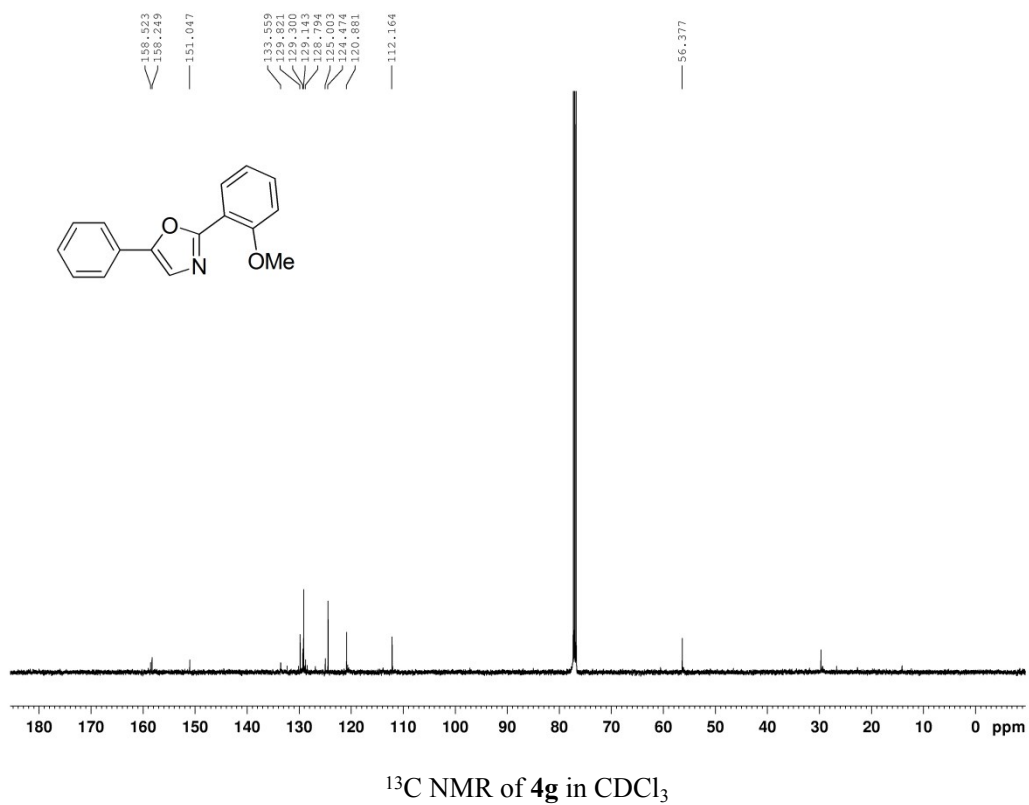
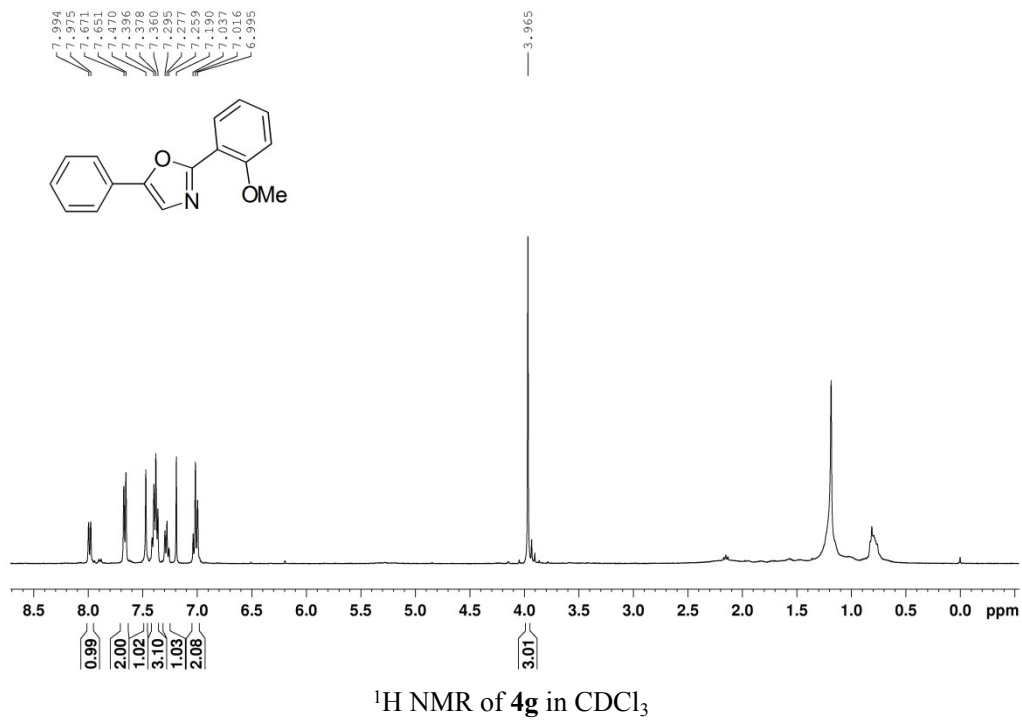
¹³C NMR of **4e** in CDCl₃

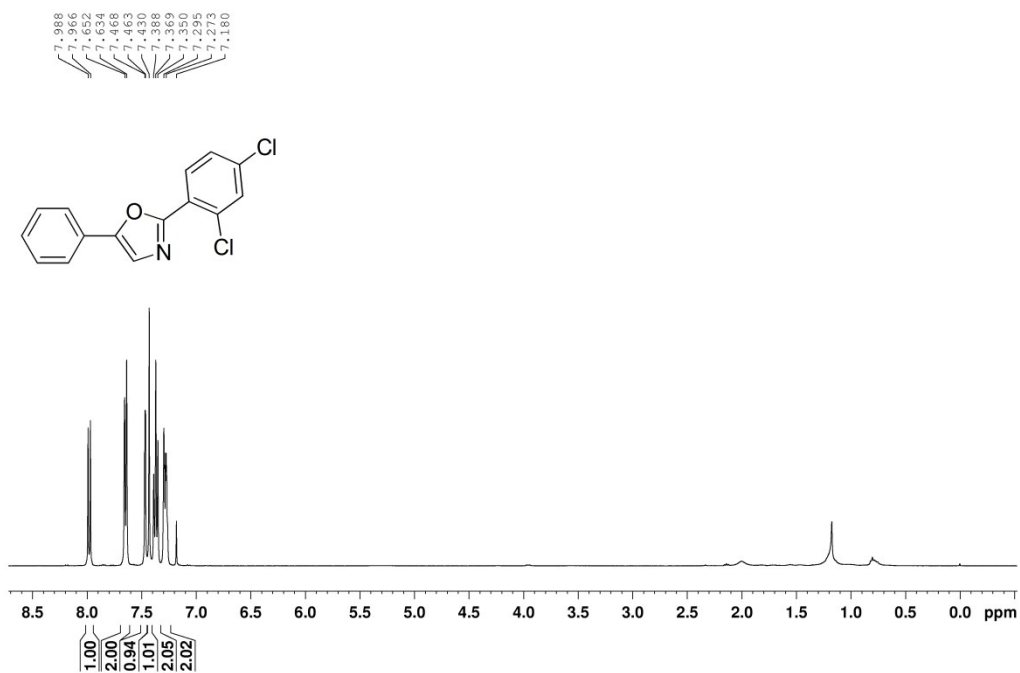


¹H NMR of **4f** in CDCl₃

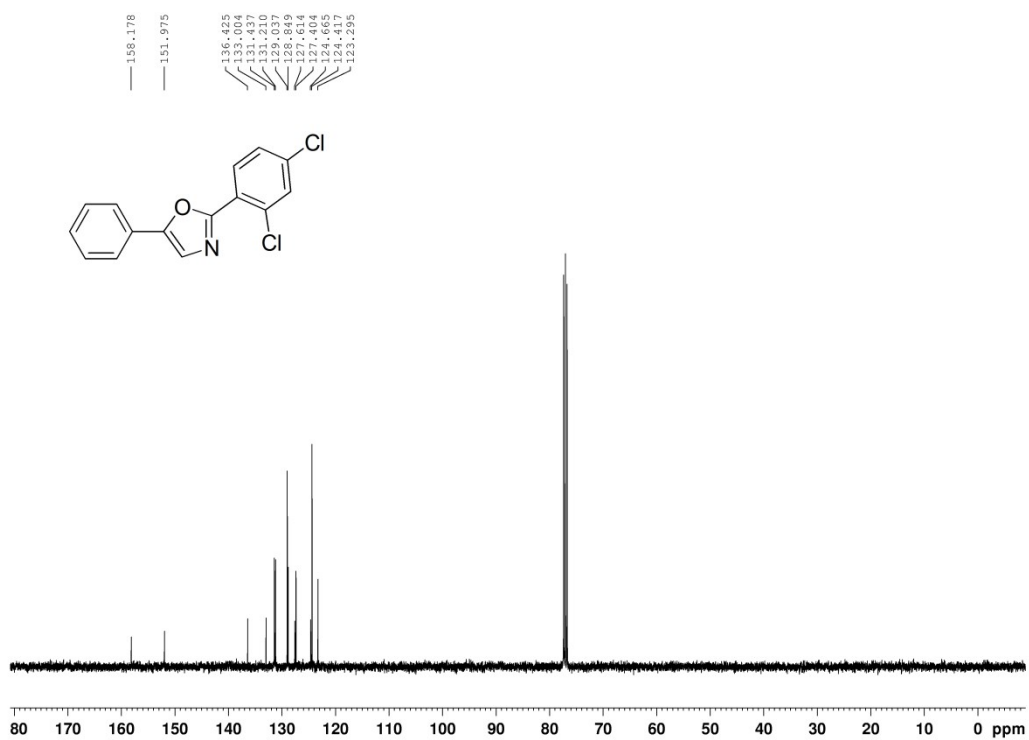


¹³C NMR of **4f** in CDCl₃

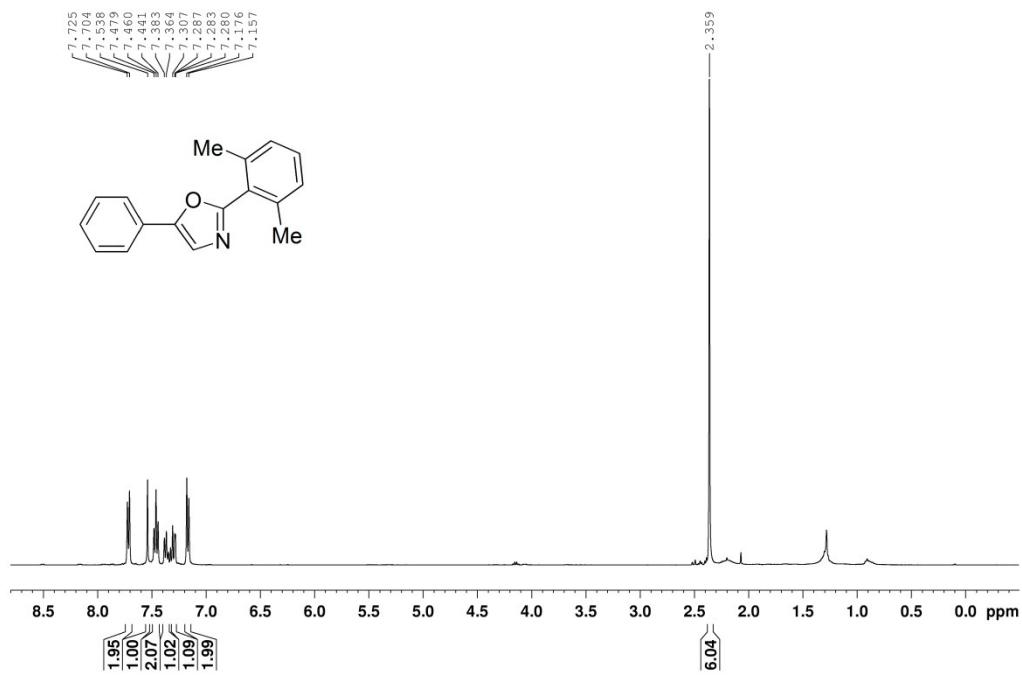




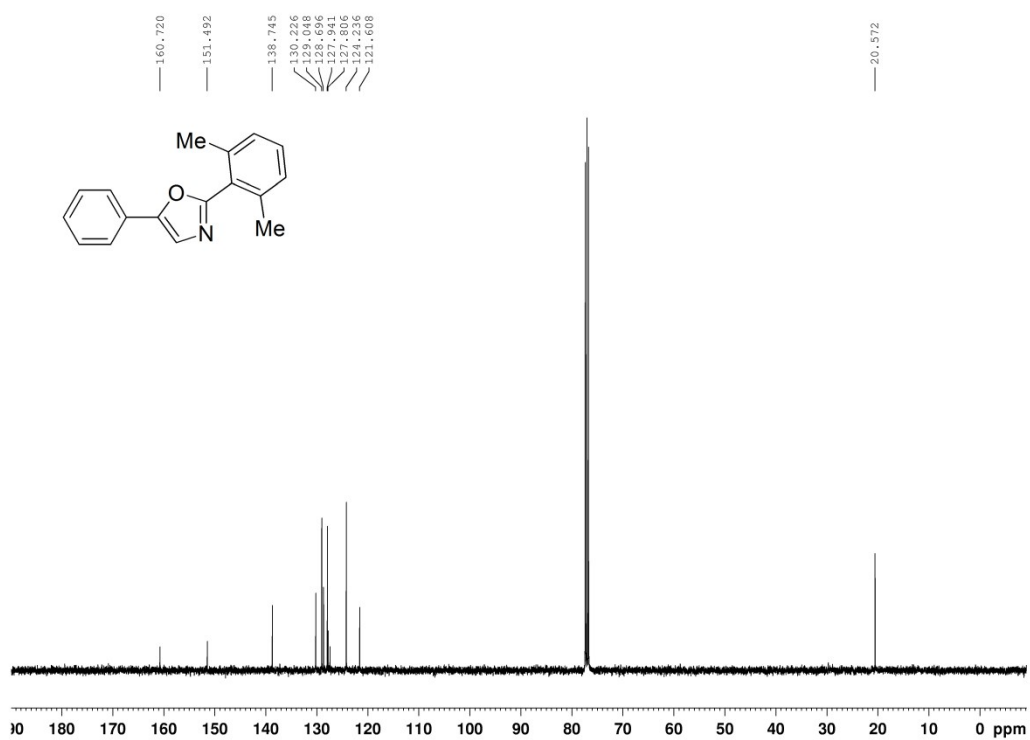
¹H NMR of **4h** in CDCl₃



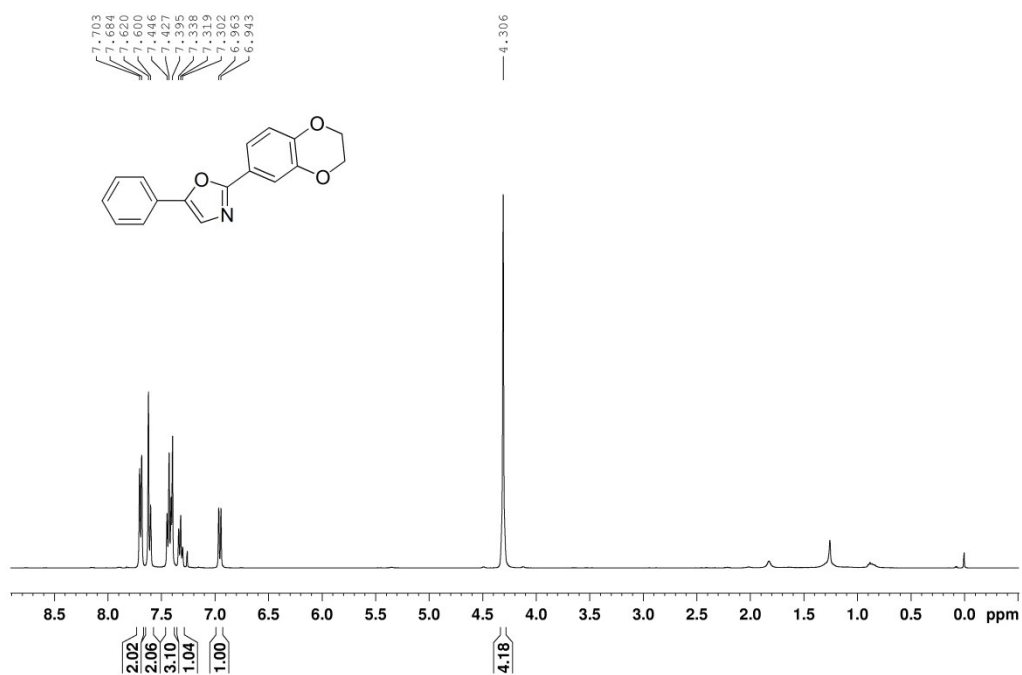
¹³C NMR of **4h** in CDCl₃



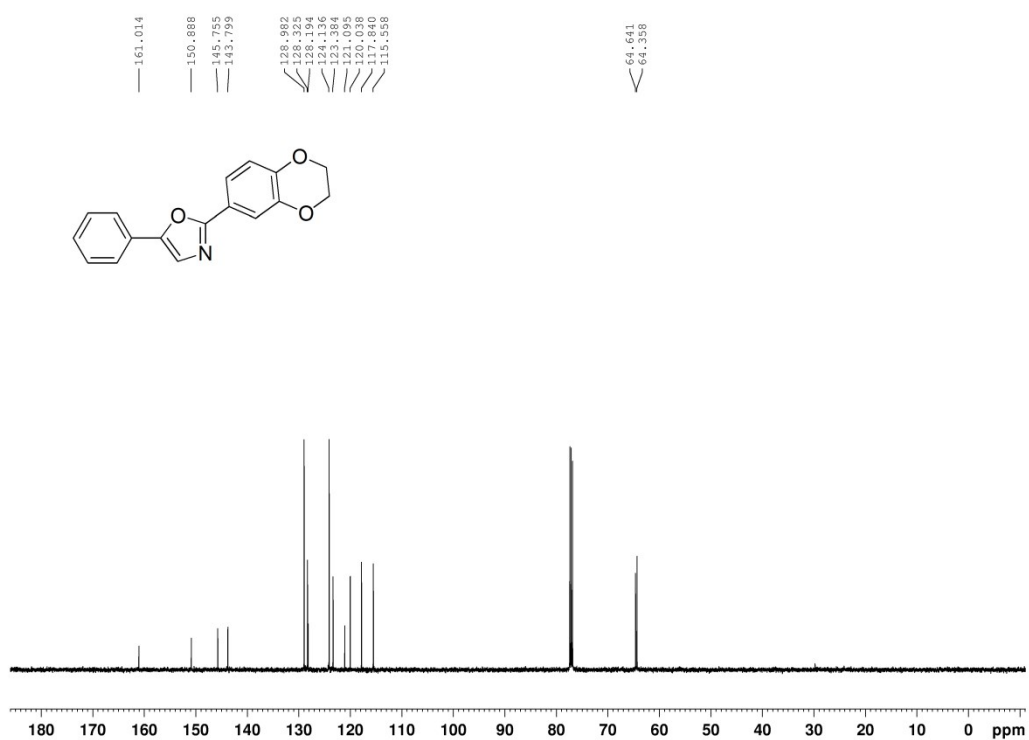
¹H NMR of **4i** in CDCl₃



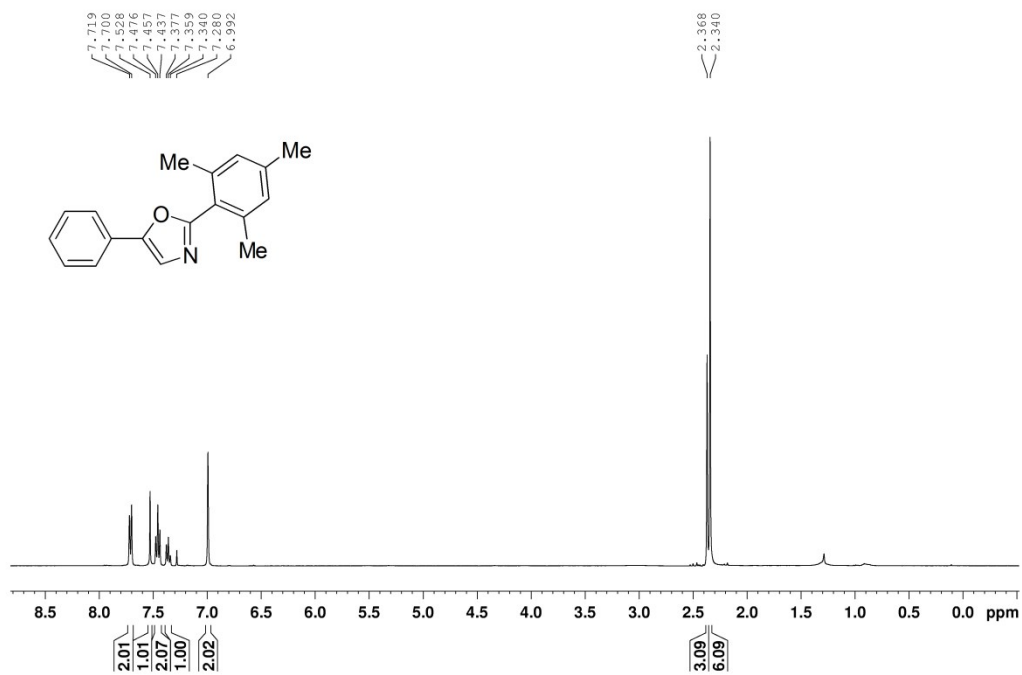
¹³C NMR of **4i** in CDCl₃



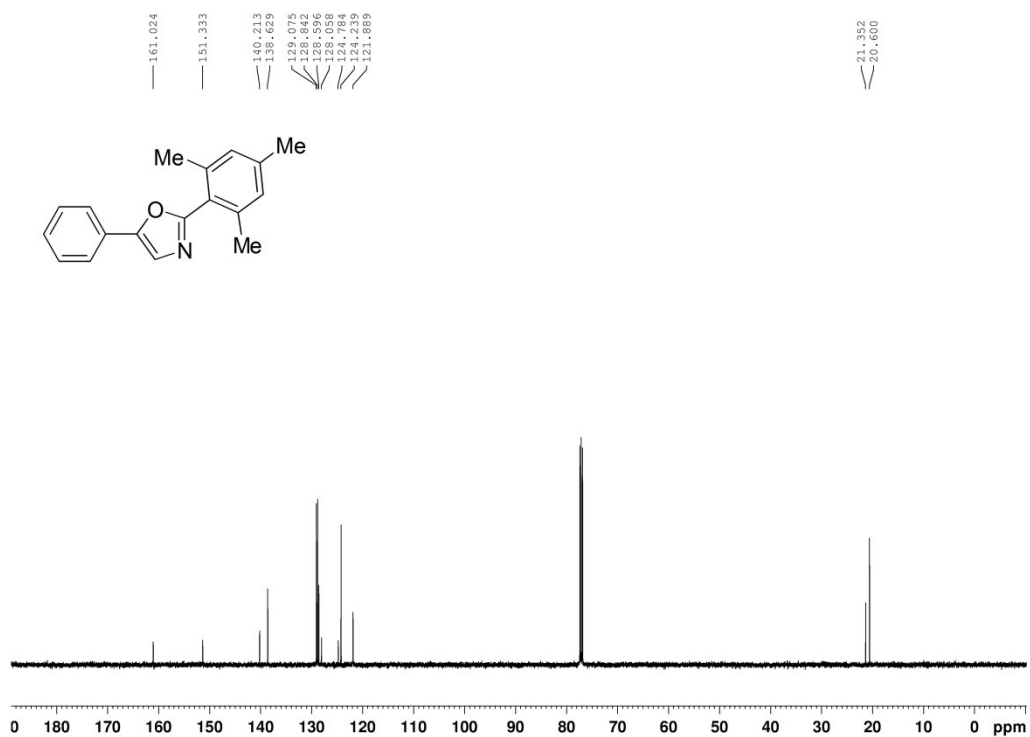
$^1\text{H NMR}$ of **4j** in CDCl_3



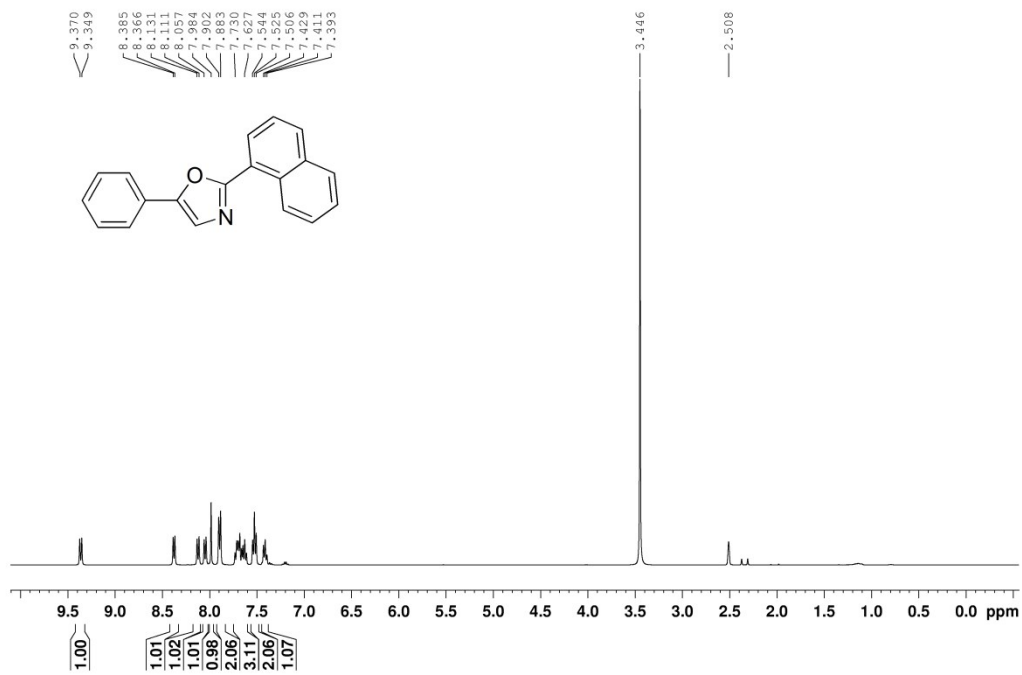
$^{13}\text{C NMR}$ of **4j** in CDCl_3



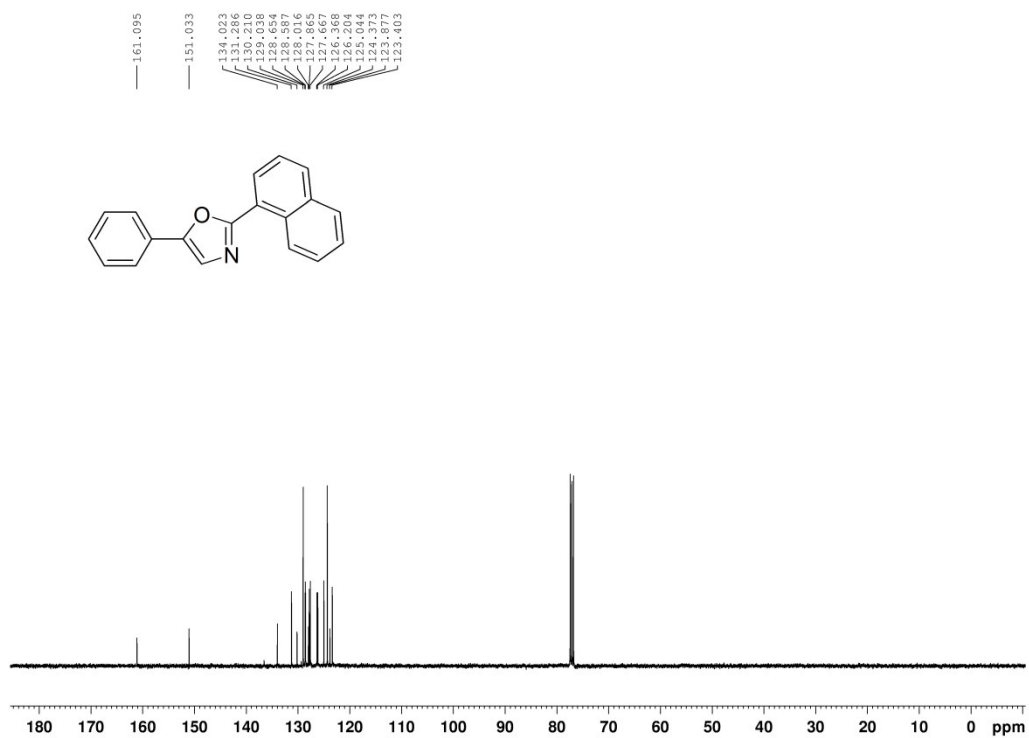
¹H NMR of **4k** in CDCl₃



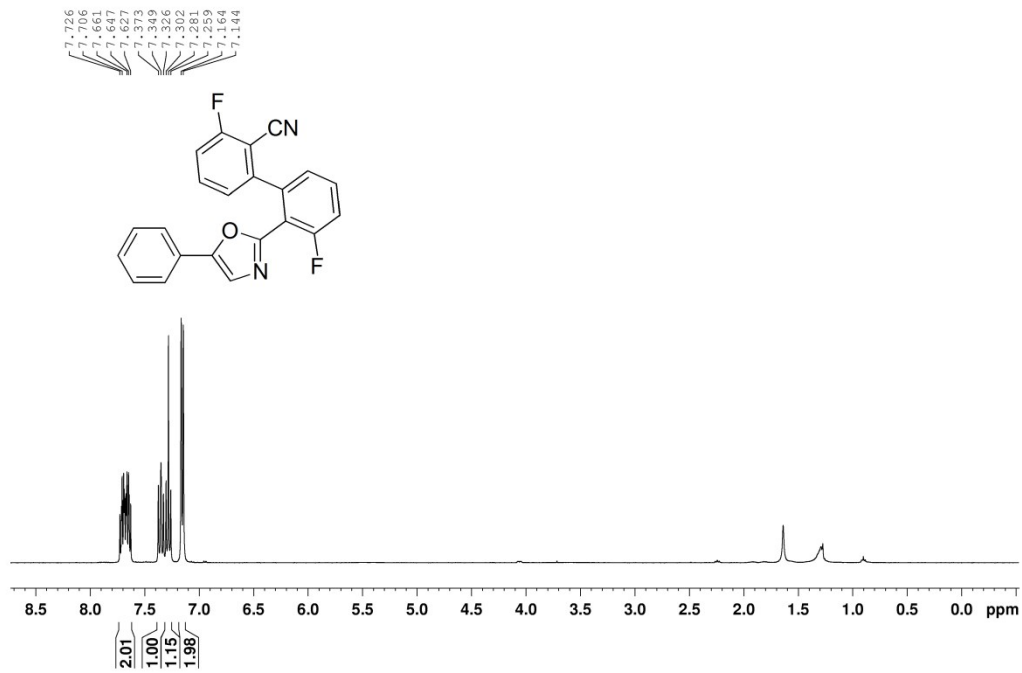
¹³C NMR of **4k** in CDCl₃



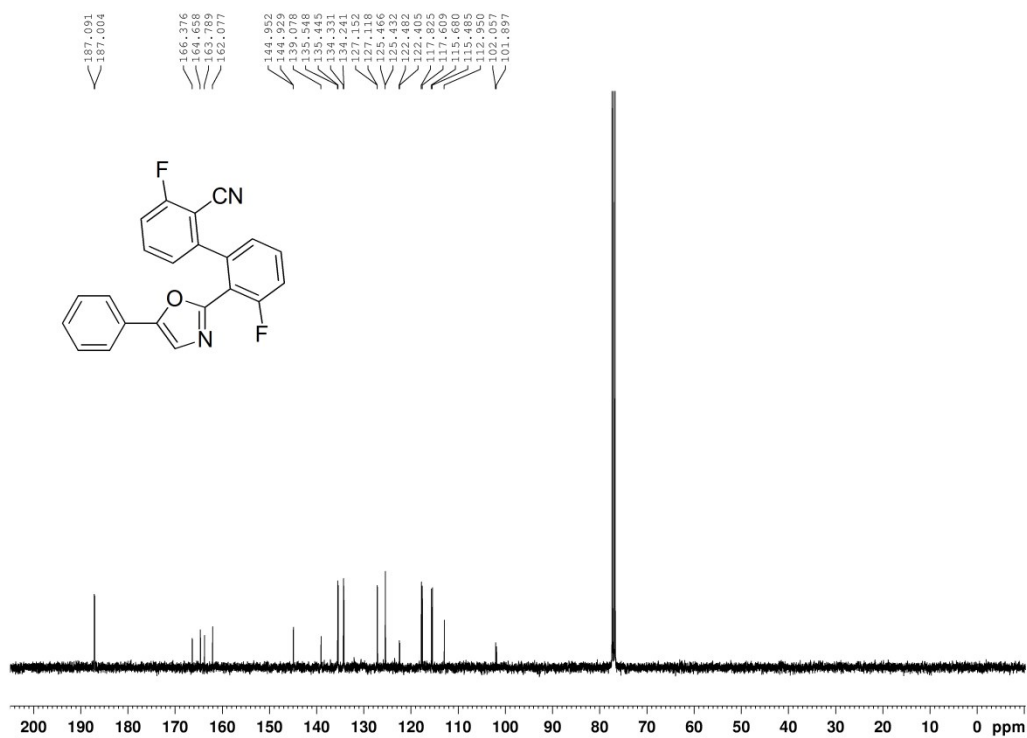
¹H NMR of **4I** in CDCl₃



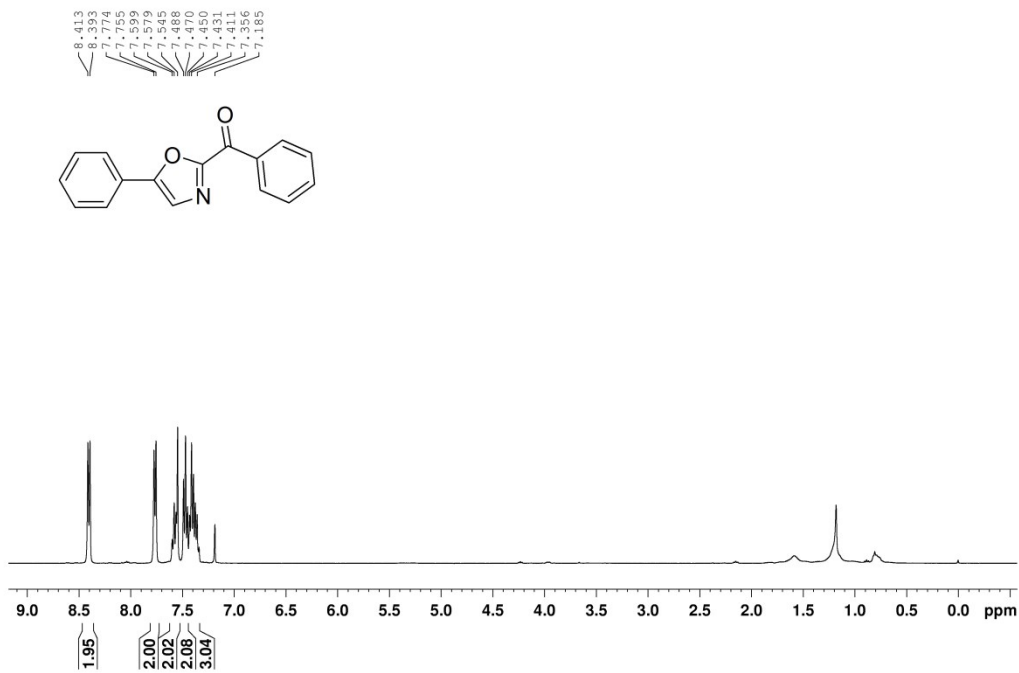
¹³C NMR of **4I** in CDCl₃



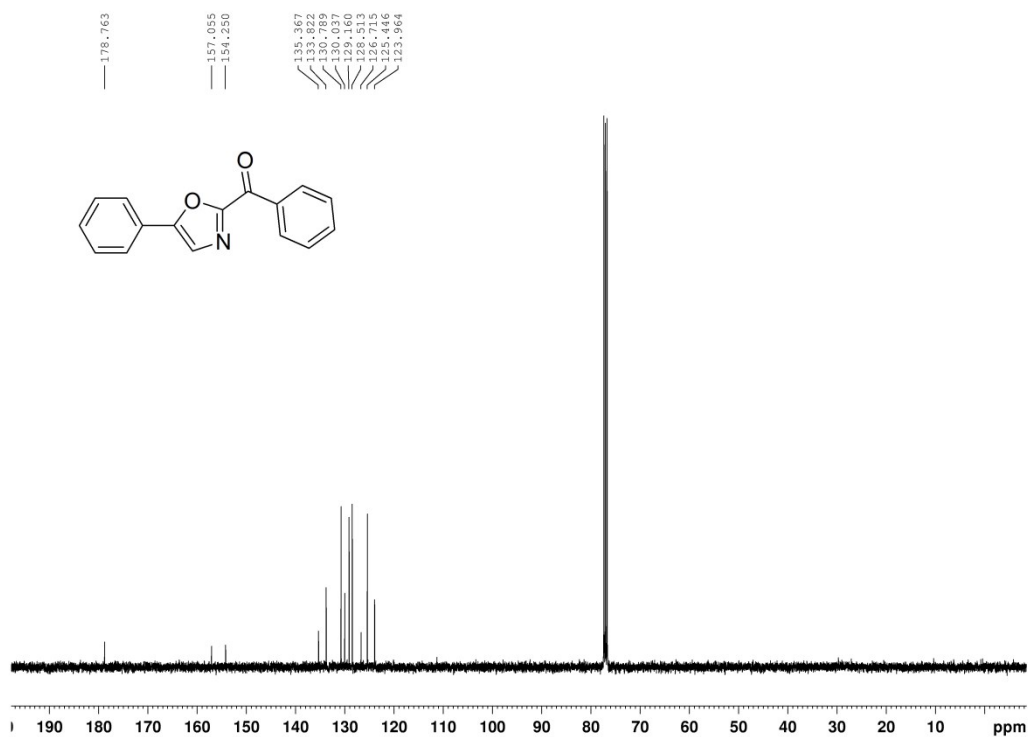
¹H NMR of **4m** in CDCl₃



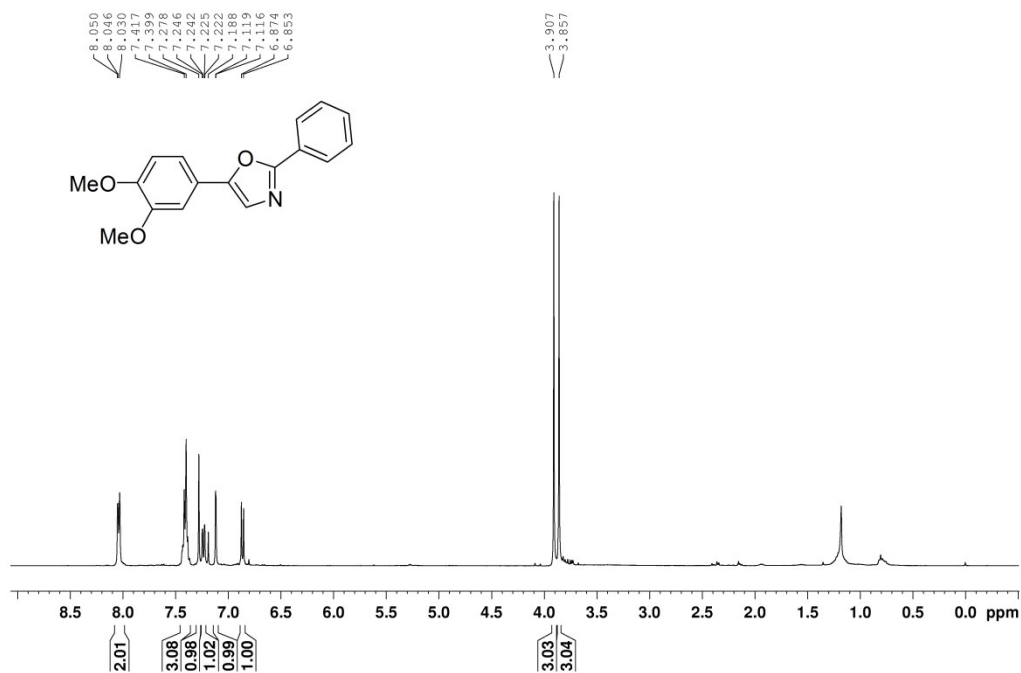
¹³C NMR of **4m** in CDCl₃



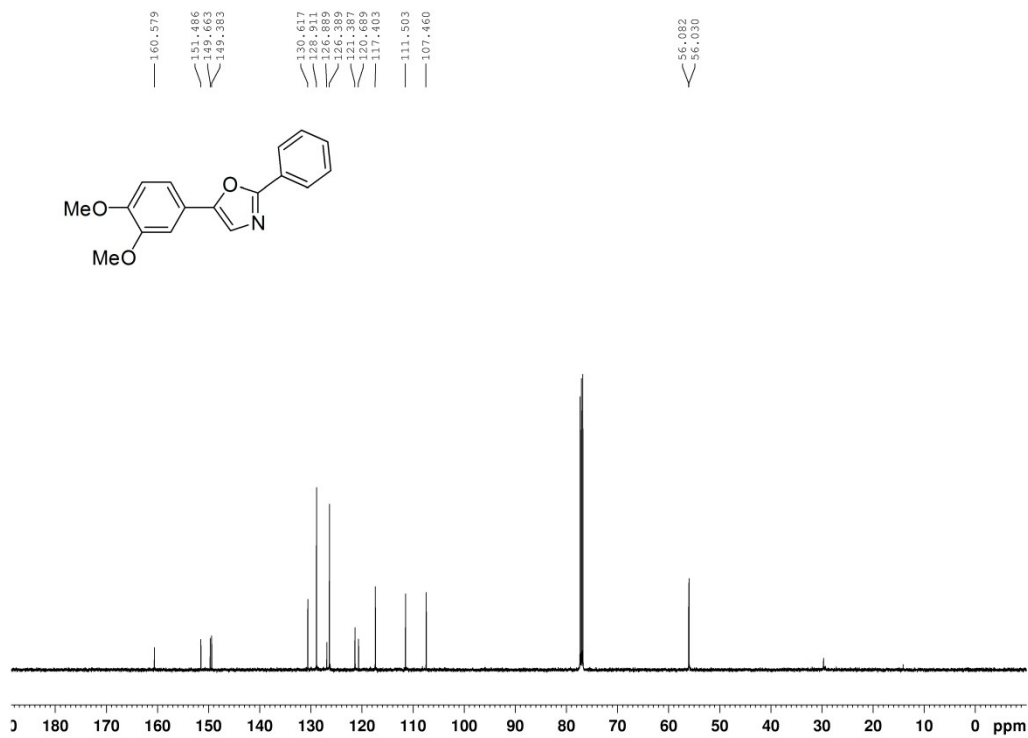
¹H NMR of **4n** in CDCl₃



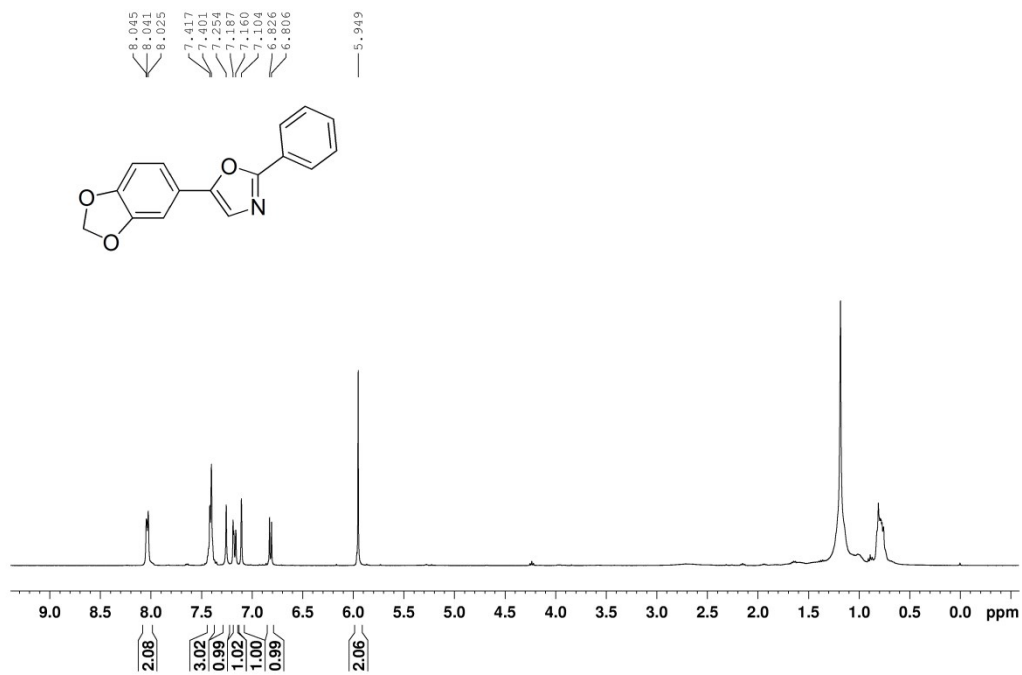
¹³C NMR of **4n** in CDCl₃



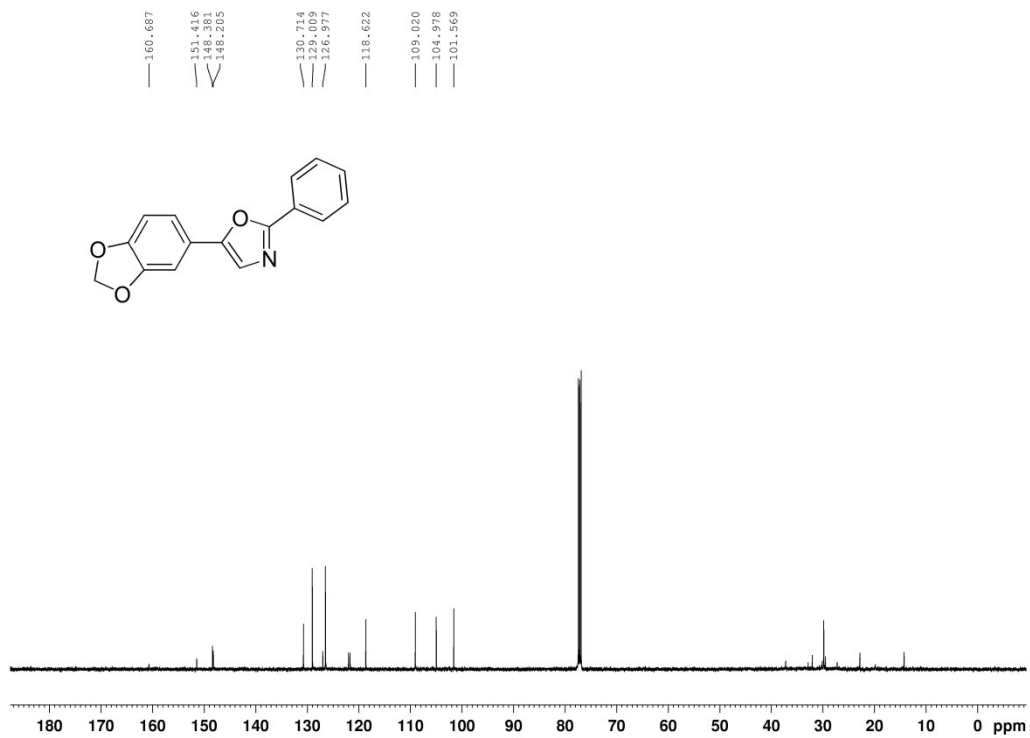
¹H NMR of Balsoxin in CDCl₃



¹³C NMR of Balsoxin in CDCl₃



¹H NMR of **Texamine** in CDCl₃



¹³C NMR of **Texamine** in CDCl₃