

Supporting information

For

PIDA-mediated oxidative annulation of aryl methyl ketone;

A Facile Approach for the chemoselective synthesis of 5-substituted Oxazoles

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1. General Discussion:

All the materials used were purchased from commercial supplier i.e Sigma Aldrich and they were used in the reaction without further purification. The reaction completion was confirmed by using TLC (Thin layer Chromatography) plate precoated with silica gel. All the synthesized compounds were purified by column chromatography using silica gel (60-120 mesh size). The characterization of synthesized compounds was done by ^1H NMR, ^{13}C NMR, and HRMS (ESI) characterization techniques. The NMR spectra were recorded by the JEOL-NMR Spectrometer instrument (JNM-ECZ400S/L1, 400 MHz) using DMSO- d_6 as a solvent with residual peaks at δ 3.3 and 2.5 ppm and at 7.25 (CDCl_3). Chemical shift (δ) values of compounds were recorded relative to internal standard TMS (tetramethylsilane). The multiplicity of NMR signals was expressed with abbreviations like s-singlet, d-doublet, t-triplet, q-quartet, dd-doublet of the doublet, m-multiplet, etc and Coupling constants (J -values) expressed in terms of Hz.

2. Crystallographic data and molecular structure

2.1 Crystal structure of 5-(3,4-dimethoxyphenyl)oxazole (2e)

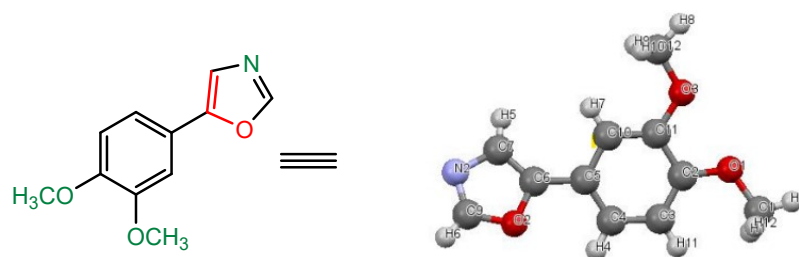


Figure 1. X-ray crystal structure of compound (2e)

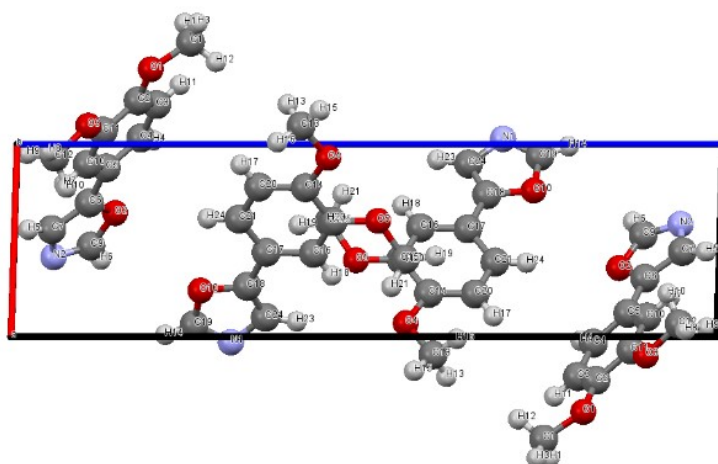


Figure 2. Crystal packing of compound 2e along b-axis

Table 1 Crystal data and structure refinement for (2e).

CCDC No	2291745
Identification code	AG16-R
Empirical formula	C ₁₁ H ₁₁ NO ₃
Formula weight	406.44
Temperature/K	298.15
Crystal system	monoclinic
Space group	P2 ₁
a/Å	5.6243(2)
b/Å	8.6813(4)
c/Å	20.6205(9)
α/°	90
β/°	91.817(2)
γ/°	90
Volume/Å ³	1006.32(7)
Z	2
ρ _{calc} /g/cm ³	1.341
μ/mm ⁻¹	0.094
F(000)	430.0
Crystal size/mm ³	0.342 × 0.179 × 0.097
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	5.092 to 59.268
Index ranges	-7 ≤ h ≤ 6, -12 ≤ k ≤ 12, -28 ≤ l ≤ 28
Reflections collected	26669
Independent reflections	5642 [R _{int} = 0.0227, R _{sigma} = 0.0184]
Data/restraints/parameters	5642/1/275
Goodness-of-fit on F ²	1.151
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0414, wR ₂ = 0.1193
Final R indexes [all data]	R ₁ = 0.0485, wR ₂ = 0.1343
Largest diff. peak/hole / e Å ⁻³	0.29/-0.42
Flack parameter	-0.04(17)

2.1 Crystal structure of 5-(4-(methylsulfonyl)phenyl)oxazole (2p)

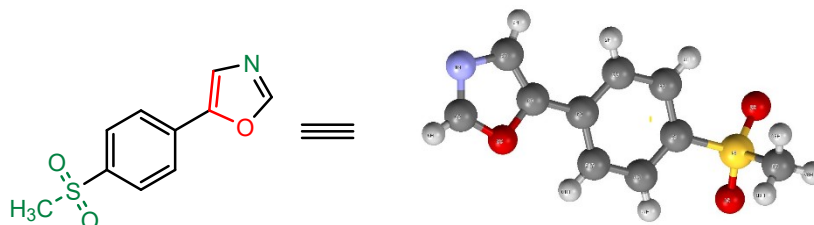


Figure 3. X-ray crystal structure of compound (2p)

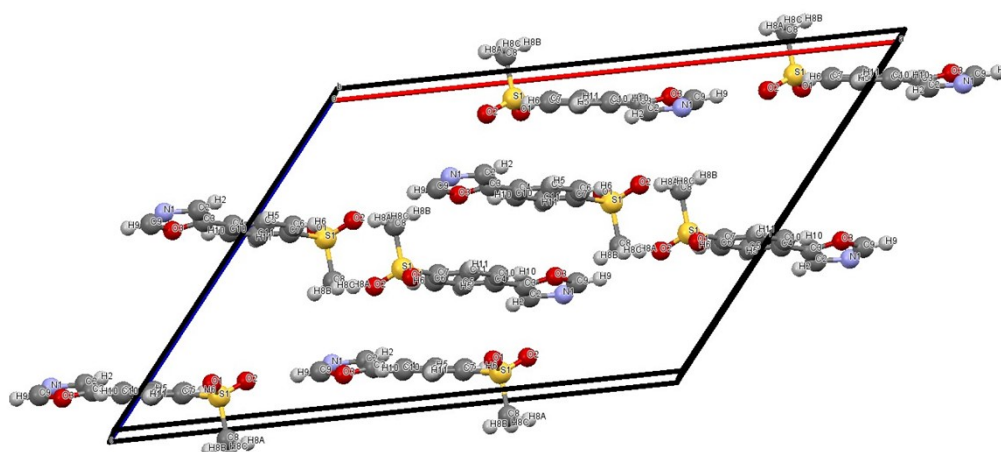


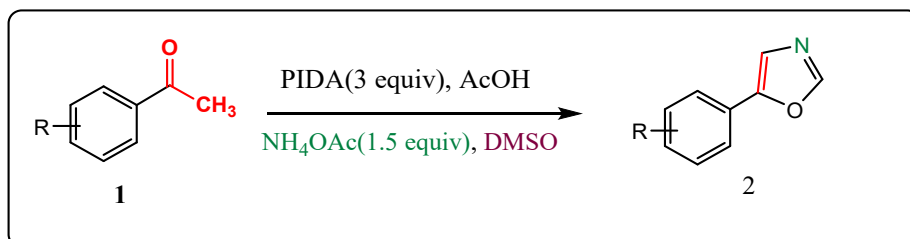
Figure 4. Crystal packing of compound **2p** along b-axis

Table.2 Crystal Data and structure refinement for compound **2p**

CCDC No	2354099
Identification code	AG11
Empirical formula	C ₁₀ H ₉ NO ₃ S
Formula weight	223.65
Temperature/K	298.15
Crystal system	monoclinic
Space group	C2/c
a/Å	22.6755(9)
b/Å	7.0600(3)
c/Å	16.2241(7)
α/°	90
β/°	129.1550(10)
γ/°	90
Volume/Å ³	2014.05(15)
Z	8
ρ _{calc} /cm ³	1.475
μ/mm ⁻¹	0.356
F(000)	928.0
Crystal size/mm ³	0.32 × 0.193 × 0.112
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	5.05 to 61.12
Index ranges	-32 ≤ h ≤ 32, -10 ≤ k ≤ 10, -23 ≤ l ≤ 23
Reflections collected	32079

Independent reflections	3075 [$R_{\text{int}} = 0.0288$, $R_{\text{sigma}} = 0.0150$]
Data/restraints/parameters	3075/0/137
Goodness-of-fit on F^2	1.209
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0550$, $wR_2 = 0.1476$
Final R indexes [all data]	$R_1 = 0.0659$, $wR_2 = 0.1648$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.40/-0.29

3. Experimental procedure for the synthesis of 5-substituted Oxazole derivatives:



A well-dried round bottom flask was charged with substituted acetophenone (**1**, 1.0 mmol), PIDA (3.0 mmol), acetic acid (10 equiv, 0.6 mL), and DMSO (10 mL) and heated at 120 °C for 2h. After the confirmation of the formation of α -acylated acetophenone, NH₄OAc (1.5 equiv) was added to the mixture and heated at 120 °C for 6h. The reaction completion was confirmed by TLC followed by the reaction mixture quenched with saturated brine solution and extracted twice by using ethyl acetate. After the solvent evaporation by using a rotary evaporator, the obtained crude product was purified by column chromatography by using silica gel (60-120 mesh size) (eluting solvent hexane: ethyl acetate; 10:2).

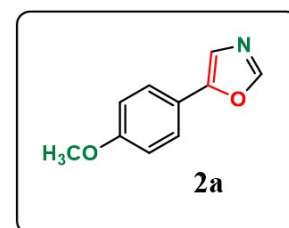
4. Spectral data of 5-disubstituted oxazole derivatives:

i) 5-(4-methoxyphenyl)oxazole (**2a**)^{1,2}

Yield: 161mg, 92%; Colourless solid; m.p. 58-60 °C;

¹H-NMR (400 MHz, DMSO-d₆) δ 8.39 (s, 1H), 7.68 (d, $J = 8.7$ Hz, 2H), 7.55 (s, 1H), 7.06 (d, $J = 8.9$ Hz, 2H), 3.82 (s, 3H); ¹³C-NMR (101 MHz, DMSO-d₆) δ 159.5, 151.1, 150.7, 125.7, 120.3, 120.2, 114.6, 55.3;

LCMS (ESI) Calcd for C₁₀H₉NO₂ [M+H]⁺, 176.0706; found, 176.8379.

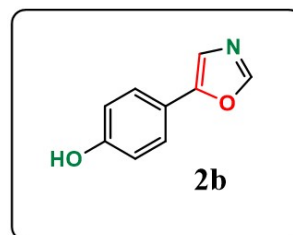


ii) **4-(oxazol-5-yl)phenol (2b)**

Yield: 136mg, 85%; Colourless solid; m.p. 140-142 °C;

¹H NMR (400 MHz, DMSO-d₆) δ 9.83 (s, 1H), 8.30 (s, 1H), 7.52 (d, *J* = 8.7 Hz, 2H), 7.42 (s, 1H), 6.84 (d, *J* = 8.7 Hz, 2H); ¹³C NMR (101 MHz, DMSO-d₆) δ 158.0, 151.0, 150.9, 125.9, 119.6, 118.7, 115.9;

LCMS (ESI) Calcd for C₉H₇NO₂ [M+H]⁺, 162.055; found, 162.131.

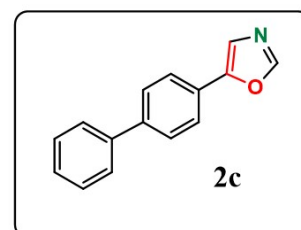


iii) **5-([1,1'-biphenyl]-4-yl)oxazole (2c)**

Yield: 98 mg, 88%; Colourless solid; m.p. 90-94 °C;

¹H NMR (400 MHz, CDCl₃) δ 7.84 (s, 1H), 7.63 (d, *J* = 8.6 Hz, 2H), 7.58-7.52 (m, 4H), 7.39-7.35 (m, 2H), 7.28 (t, *J* = 7.2 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 151.3, 150.5, 141.3, 140.2, 128.8, 127.6, 127.5, 126.9, 126.6, 124.8, 121.5,

LCMS (ESI) Calcd for C₁₅H₁₁NO [M+H]⁺, 222.0914; found, 222.050.

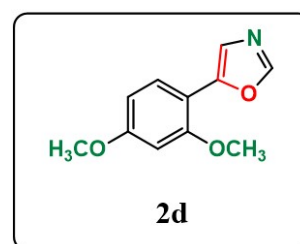


v) **5-(2,4-dimethoxyphenyl)oxazole(2d)¹**

Yield: 157 mg, 77%; Colourless liquid;

¹H NMR (400 MHz, CDCl₃) δ 7.73 (s, 1H), 7.53 (d, *J* = 8.6 Hz, 1H), 6.43 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.38 (d, *J* = 2.4 Hz, 1H), 3.76 (s, 3H), 3.69 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 160.7, 156.7, 148.7, 147.8, 126.6, 123.3, 110.1, 104.7, 98.3, 55.1;

LCMS (ESI) Calcd for C₁₁H₁₁NO₃ [M+H]⁺, 206.0812; found, 206.0500.

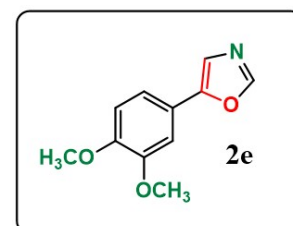


iv) **5-(3,4-dimethoxyphenyl)oxazole (2e)**

Yield: 196 mg, 96%; Colourless solid; m.p. 98-100 °C;

¹H NMR (400 MHz, DMSO-d₆) δ 8.32 (s, 1H), 7.54 (s, 1H), 7.24-7.21 (m, 2H), 7.00 (d, *J* = 8.3 Hz, 1H), 3.80 (s, 3H), 3.76 (s, 3H); ¹³C NMR (101 MHz, DMSO-d₆) δ 151.2, 150.9, 149.4, 149.3, 120.7, 120.4, 117.0, 112.2, 107.9, 55.7, 55.7;

LCMS(ESI) Calcd for C₁₁H₁₁NO₃ [M+H]⁺, 206.0812; found, 206.95.

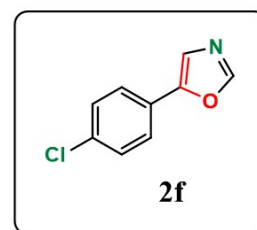


vi) **5-(4-chlorophenyl)oxazole (2f)**^{1,2}

Yield: 103 mg, 58%; Colourless solid; m.p. 80-82 °C;

¹H NMR (400 MHz, DMSO-d₆) δ 8.49 (s, 1H), 7.76 (t, *J* = 4.2 Hz, 3H), 7.55 (d, *J* = 8.6 Hz, 2H); ¹³C NMR (101 MHz, DMSO-d₆) δ 152.0, 149.6, 133.1, 129.1, 126.3, 125.8, 122.6;

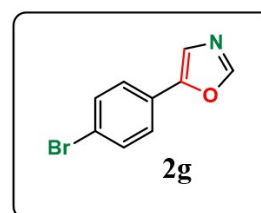
LCMS (ESI) Calcd for C₉H₆ClNO [M+H]⁺, 180.0211; found, 180.050.



vii) **5-(4-bromophenyl)oxazole (2g)**^{1,2}

Yield: 182 mg, 82%; Colourless solid; m.p. 76-78 °C;

¹H-NMR (400 MHz, DMSO-d₆) δ 8.48 (s, 1H), 7.75 (s, 1H), 7.68 (s, 4H); ¹³C-NMR (101 MHz, DMSO-d₆) δ 152.2, 149.7, 132.2, 126.7, 126.2, 122.7, 121.8; LCMS(ESI) Calcd for C₉H₆BrNO [M+H]⁺, 223.9706; found, 223.60, 225.3 (M+H+2)⁺, 227.2(M+H+4)⁺.

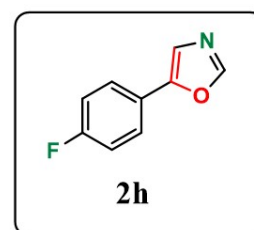


viii) **5-(4-fluorophenyl)oxazole (2h)**^{1,2}

Yield: 147 mg, 91%; Colourless liquid;

¹H NMR (400 MHz, DMSO-d₆) δ 8.43 (s, 1H), 7.81-7.77 (m, 2H), 7.67 (s, 1H), 7.34 (t, *J* = 8.9 Hz, 2H); ¹³C NMR (101 MHz, DMSO-d₆) δ 163.4, 161.0, 151.9, 149.9, 126.6, 126.5, 124.2, 121.9, 116.5, 116.2;

LCMS (ESI) Calcd for C₉H₁₀O₃ [M]⁺, 163.0433; found, 163.0857.

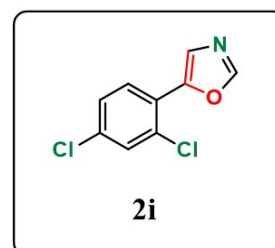


ix) **5-(2,4-dichlorophenyl)oxazole (2i)**

Yield: 122 mg, 58%; Colourless solid; m.p. 68-70 °C;

¹H NMR (400 MHz, DMSO-d₆) δ 8.60 (s, 1H), 7.83-7.74 (m, 3H), 7.56 (dd, *J* = 8.5, 2.2 Hz, 1H); ¹³C NMR (101 MHz, DMSO-d₆) δ 152.2, 146.3, 133.6, 130.5, 130.0, 129.1, 128.0, 126.3, 124.9;

LCMS (ESI) Calcd for C₉H₅Cl₂NO [M+H]⁺, 213.9821; found, 213.800.



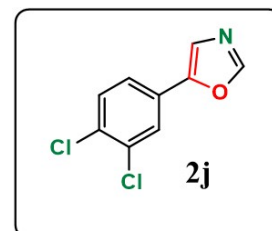
x) **5-(3,4-dichlorophenyl)oxazole (2j)**

Yield: 97 mg, 46%; Yellow liquid;

$^1\text{H NMR}$ (400 MHz, DMSO- d_6) δ 8.44 (s, 1H), 7.87 (d, $J = 1.7$ Hz, 1H), 7.77 (s, 1H), 7.61 (t, $J = 2.0$ Hz, 2H);

$^{13}\text{C NMR}$ (101 MHz, DMSO- d_6) δ 152.4, 148.3, 132.0, 131.2, 130.9, 127.9, 125.6, 124.0, 123.7;

LCMS(ESI) Calcd for $\text{C}_9\text{H}_5\text{Cl}_2\text{NO}$ $[\text{M}+\text{H}]^+$, 213.9821; found, 213.8.

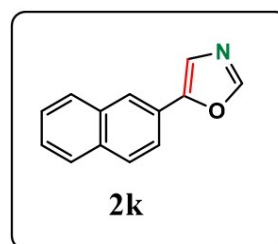


xi) **5-(naphthalen-2-yl)oxazole (2k)**

Yield: 163 mg, 84%; Colourless solid; m.p. 122-124 °C;

$^1\text{H NMR}$ (400 MHz, DMSO- d_6) δ 8.52 (s, 1H), 8.28 (s, 1H), 8.04-7.83 (m, 5H), 7.61-7.55 (m, 2H); $^{13}\text{C NMR}$ (101 MHz, DMSO- d_6) δ 151.6, 150.9, 138.5, 129.8, 124.8, 124.2, 121.3;

LCMS (ESI) Calcd for $\text{C}_{13}\text{H}_9\text{NO}$ $[\text{M}+\text{H}]^+$, 196.0757; found, 196.000.



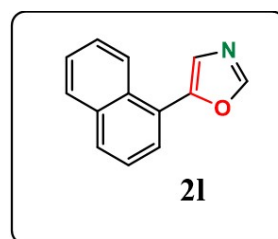
xii) **5-(naphthalen-1-yl)oxazole (2l)²**

Yield: 198 mg, 78%; Colourless liquid; m.p. 122-126 °C;

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.25 (d, $J = 7.6$ Hz, 1H), 8.07 (s, 1H), 7.90-7.88 (m, 2H), 7.73 (d, $J = 7.2$ Hz, 1H), 7.59-7.46 (m, 4H);

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 150.8, 150.6, 133.7, 130.0, 129.7, 128.6, 127.0, 126.6, 126.2, 125.1, 125.0, 124.8, 124.7.

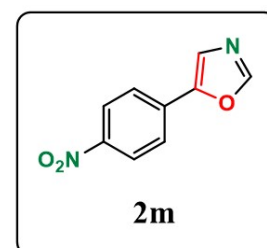
LCMS(ESI) Calcd for $\text{C}_{13}\text{H}_9\text{NO}$ $[\text{M}+\text{H}]^+$, 196.0757; found, 197.50



xiii) **5-(4-nitrophenyl)oxazole (2m)^{1,2}**

Yield: 98 mg, 52%; Colourless solid; m.p. 134-136 °C;

$^1\text{H NMR}$ (400 MHz, DMSO- d_6) δ 8.60 (s, 1H), 8.32 (d, $J = 9.0$ Hz, 2H), 8.00 (d, $J = 2.3$ Hz, 2H), 7.97 (s, 1H); $^{13}\text{C NMR}$ (101 MHz, DMSO- d_6) δ 153.5, 148.8, 146.8, 133.3, 125.7, 125.0, 124.6; LCMS (ESI) Calcd for $\text{C}_9\text{H}_6\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$, 191.0451; found, 190.90.

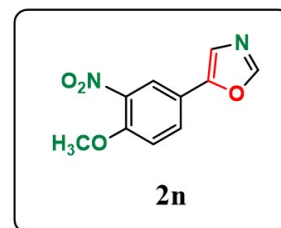


xiv) **5-(4-methoxy-3-nitrophenyl)oxazole (2n)**

Yield: 114 mg, 52%; Colourless solid; m.p. 138-140 °C;

$^1\text{H NMR}$ (400 MHz, DMSO- d_6) δ 8.47 (s, 1H), 8.22 (d, $J = 2.3$ Hz, 1H), 8.00 (dd, $J = 8.8, 2.2$ Hz, 1H), 7.75 (s, 1H), 7.49 (d, $J = 8.9$ Hz, 1H), 3.98 (s, 3H); $^{13}\text{C NMR}$ (101 MHz, DMSO- d_6) δ 152.0, 151.8, 148.6, 139.6, 129.8, 122.4, 120.5, 120.1, 115.3, 57.0;

LCMS (ESI) Calcd for $\text{C}_{10}\text{H}_8\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$, 221.0557; found, 222.000.

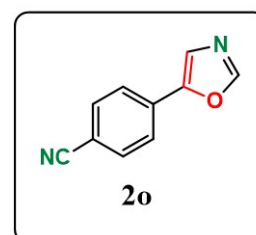


xv) **4-(oxazol-5-yl)benzonitrile (2o)**

Yield: 198 mg, 75%; Colourless solid; m.p. 70-72 °C;

$^1\text{H NMR}$ (400 MHz, DMSO- d_6) δ 8.57 (s, 1H), 7.96-7.91 (m, 5H); $^{13}\text{C NMR}$ (101 MHz, DMSO- d_6) δ 153.1, 149.1, 133.2, 131.5, 125.0, 124.7, 118.7, 110.7;

LCMS (ESI) Calcd for $\text{C}_{10}\text{H}_6\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$, 171.0553; found, 171.90.

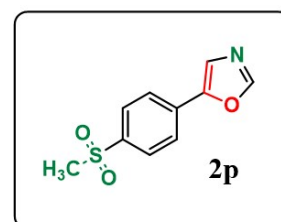


xvi) **5-(4-(methylsulfonyl)phenyl)oxazole (2p)¹**

Yield: 136 mg, 61%; Colourless solid; m.p. 120-122 °C;

$^1\text{H NMR}$ (400 MHz, DMSO- d_6) δ 8.59 (s, 1H), 8.06 (d, $J = 8.7$ Hz, 2H), 8.00 (d, $J = 8.7$ Hz, 2H), 7.96 (s, 1H), 3.43 (s, 3H); $^{13}\text{C NMR}$ (101 MHz, DMSO- d_6) δ 152.9, 149.1, 140.2, 131.9, 127.9, 124.7, 124.6, 43.5;

LCMS (ESI) Calcd for $\text{C}_{10}\text{H}_9\text{NO}_3\text{S}$ $[\text{M}+\text{H}]^+$, 224.0376; found, 224.1209 .



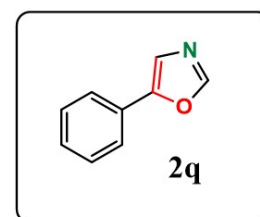
xvii) **5-phenyloxazole (2q)^{1,2}**

Yield: 137mg, 95%; Colourless liquid; m.p. 82-84 °C;

$^1\text{H NMR}$ (400 MHz, DMSO- d_6) δ 8.40 (s, 1H), 7.63 (d, $J = 8.3$ Hz, 4H), 7.30 (d, $J = 7.9$ Hz, 2H);

$^{13}\text{C NMR}$ (101 MHz, DMSO- d_6) δ 151.6, 150.9, 138.5, 129.8, 124.8, 124.2, 121.3;

LCMS(ESI) Calcd for $\text{C}_9\text{H}_7\text{NO}$ $[\text{M}+\text{H}]^+$, 146.0601; found, 146.1329.



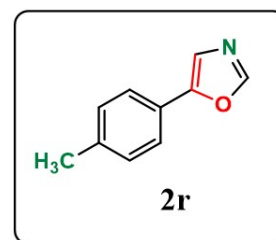
xviii) **5-(p-tolyl)oxazole (2r)**^{1,2}

Yield: 128 mg, 81%; Colourless solid; m.p. 64-66 °C;

¹H NMR (400 MHz, DMSO-d₆) δ 8.40 (s, 1H), 7.63 (d, *J* = 8.3 Hz, 3H), 7.30 (d, *J* = 7.9 Hz, 2H), 2.35 (s, 3H);

¹³C NMR (101 MHz, DMSO-d₆) δ 151.6, 150.9, 138.5, 129.8, 124.8, 124.2, 121.3, 21.0;

LCMS (ESI) Calcd for C₁₀H₉NO [M+H]⁺, 160.0757; found, 160.1541.

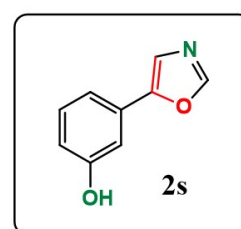


xix) **3-(oxazol-5-yl)phenol (2s)**¹

Yield: 120 mg, 75%; Colourless solid; m.p. 102-104 °C;

¹H NMR (400 MHz, DMSO-d₆) δ 9.73 (s, 1H), 8.42 (s, 1H), 7.63 (s, 1H), 7.29 (t, *J* = 7.9 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.13 (t, *J* = 2.0 Hz, 1H), 6.81 (m, 1H); ¹³C NMR (101 MHz, DMSO-d₆) δ 157.9, 151.7, 150.6, 130.3, 128.6, 121.9, 115.8, 115.0, 110.7;

LCMS (ESI) Calcd for C₉H₇NO₂ [M+H]⁺, 162.055; found, 161.90.

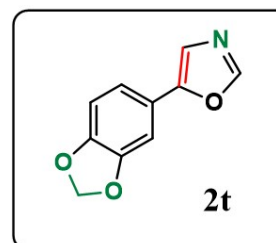


xx) **5-(benzo[d][1,3]dioxol-5-yl)oxazole (2t)**

Yield: 128 mg, 68%; Colourless solid; m.p. 88-90 °C;

¹H NMR (400 MHz, CDCl₃) δ 7.85 (s, 1H), 7.20 (s, 1H), 7.15 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.09 (d, *J* = 1.7 Hz, 1H), 6.85 (d, *J* = 8.1 Hz, 1H), 5.99 (s, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 151.3, 149.9, 148.1, 147.9, 121.9, 120.3, 118.5, 108.7, 104.9, 101.3;

LCMS (ESI) Calcd for C₁₀H₇NO₃ [M+H]⁺, 190.0499; found, 190.900.

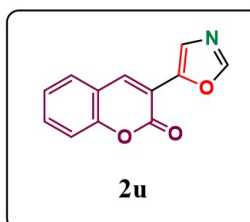


xxi) **3-(oxazol-5-yl)-2H-chromen-2-one (2u)**

Yield: 132 mg, 62%; Colourless solid; m.p. 98-100 °C;

¹H NMR (400 MHz, DMSO-d₆) δ 8.55 (s, 1H), 8.39 (s, 1H), 7.88-7.84 (m, 1H), 7.71-7.59 (m, 2H), 7.44-7.36 (m, 2H); ¹³C NMR (101 MHz, DMSO-d₆) δ 157.2, 152.6, 152.4, 145.2, 136.7, 132.5, 129.2, 126.8, 125.1, 118.7, 116.2, 115.1;

LCMS (ESI) Calcd for C₁₂H₇NO₃ [M+H]⁺, 214.0499; found, 214.0497.

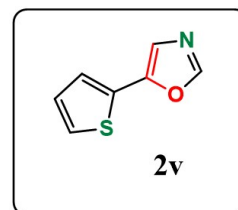


xxii) **5-(thiophen-2-yl)oxazole (2v)**

Yield: 124 mg, 82%; Colourless solid; m.p. 78-82 °C;

$^1\text{H NMR}$ (400 MHz, DMSO- d_6) δ 8.55 (s, 1H), 7.95 (s, 1H), 7.73-7.72 (d, $J=2.8$ Hz, 1H), 7.37-7.35 (m, 1H), 7.28-7.26 (m, 1H); $^{13}\text{C NMR}$ (101 MHz, DMSO- d_6) δ 149.4, 137.5, 133.2, 129.3, 129.0, 127.4, 124.0;

LCMS (ESI) Calcd for $\text{C}_7\text{H}_5\text{NOS}$ $[\text{M}+\text{H}]^+$, 152.0922; found, 152.0898

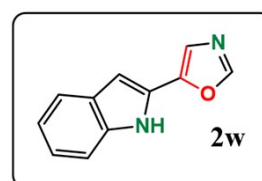


xxiii) **5-(1H-indol-2-yl)oxazole (2w)**

Yield: 143 mg, 78%; Colourless solid; m.p. 110-112 °C;

$^1\text{H NMR}$ (400 MHz, DMSO- d_6) δ 12.03(s, 1H), 8.09 (s, 1H), 7.78 (d, 2H), 7.55(s, 1H), 7.46-7.42(t, $J=6.8$ Hz, 1H), 6.98-6.95(m, 2H); $^{13}\text{C NMR}$ (101 MHz, DMSO- d_6) δ 167.1, 137.5, 129.3, 128.7, 124.0, 122.5, 121.5, 120.1, 118.8, 112.6, 101.1;

LCMS (ESI) Calcd for $\text{C}_{11}\text{H}_8\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$, 185.0637; found, 185.0629

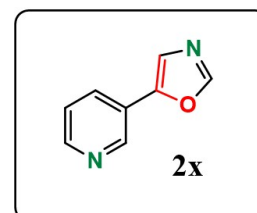


xxiv) **5-(pyridin-3-yl)oxazole (2x)**

Yield: 103 mg, 71%; Colourless solid; m.p. 148-150 °C;

$^1\text{H NMR}$ (400 MHz, DMSO- d_6) δ 9.06 (s, 1H), 8.78-8.77 (t, $J=3.2$ Hz, 1H), 8.25(s, 1H), 7.59-7.57(t, $J=2.4$ Hz, 1H), 7.13-7.09 (m, 2H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 151.3, 150.4, 148.2, 147.0, 134.0, 133.1, 124.7, 121.0;

LCMS (ESI) Calcd for $\text{C}_8\text{H}_6\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$, 147.0480; found, 147.0472.



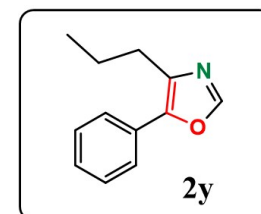
xxv) **5-phenyl-4-propyloxazole (2y)**

Yield: 140 mg, 75%; Colourless solid; m.p. 124-126 °C;

$^1\text{H NMR}$ (400 MHz, DMSO- d_6): δ 8.35 (s, 1H), 7.93 (d, $J=8.0$ Hz, 2H), 7.60 (t, $J=2.0$ Hz, 2H), 7.49 (t, $J=7.6$ Hz, 2H), 2.48 (t, $J=7.2$ Hz, 1H), 1.63-1.57 (m, 2H), 0.82 (t, $J=7.6$ Hz, 3H);

$^{13}\text{C NMR}$ (101 MHz, DMSO- d_6) δ 148.4, 138.4, 129.8, 124.8, 124.2, 121.3, 36.2, 18.2, 13.6;

LCMS (ESI) Calcd for $\text{C}_{12}\text{H}_{13}\text{NO}$ $[\text{M}+\text{H}]^+$, 188.0997; found, 188.0990.



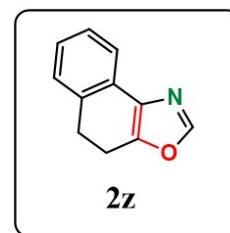
xxv) **4,5-dihydronaphtho[1,2-d]oxazole (2z)**

Yield: 138 mg, 81%; Colourless solid; m.p. 180-182 °C;

¹H-NMR (400 MHz, DMSO-*d*₆) δ 8.60 (s, 1H), 8.32 (dd, *J* = 7.1, 1.9 Hz, 2H), 8.00-7.97 (m, 2H), 2.99 (t, *J* = 7.9 Hz, 2H), 2.84 (t, *J* = 7.8 Hz, 2H);

¹³C-NMR (101 MHz, DMSO-*d*₆) δ 151.1, 138.0, 134.0, 130.1, 128.9, 127.9, 126.4, 124.9, 122.3, 35.0, 27.6;

LCMS (ESI) Calcd for C₁₁H₉NO [M+H]⁺, 171.0684; found, 171.05.



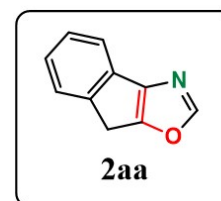
xxv) **8H-indeno[1,2-d]oxazole (2aa)**

Yield: 119 mg, 76%; Colourless solid; m.p. 164-166 °C;

¹H-NMR (400 MHz, DMSO-*d*₆) δ 8.60 (s, 1H), 7.83-7.74 (m, 3H), 7.56 (dd, *J* = 8.5, 2.2 Hz, 1H), 3.83 (s, 2H);

¹³C NMR (101 MHz, DMSO-*d*₆) δ 150.4, 138.4, 137.0, 128.1, 125.9, 125.3, 125.1, 121.9, 36.1;

LCMS (ESI) Calcd for C₁₀H₇NO [M+H]⁺, 158.0528; found, 158.01.



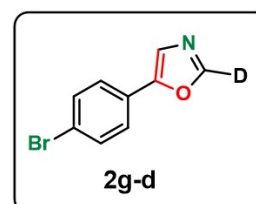
xxvi) **5-(4-bromophenyl)oxazole (2g-d)**

Yield: 70 mg, 63%; Colourless solid; m.p. 98-102 °C;

¹H NMR (400 MHz, DMSO-*d*₆): δ 7.72 (s, 1H), 7.30-7.28 (m, 4H);

¹³C NMR (101 MHz, DMSO-*d*₆): δ 153.1, 149.1, 133.2, 124.7, 122.0, 121.0;

LCMS (ESI) Calcd for C₉H₅DBrNO [M+H]⁺, 224.9696; found, 224.9560



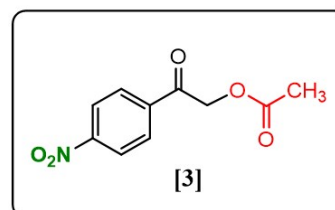
xxii) **2-(4-nitrophenyl)-2-oxoethyl acetate (3)⁴**

Yield: 207 mg, 92%; Colourless solid; m.p. 120-122 °C;

¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 9.0 Hz, 2H), 5.36 (s, 2H), 3.85 (s, 3H), 2.29 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 165.7, 163.4, 131.6, 122.0, 113.5, 68.3, 55.3, 15.3;

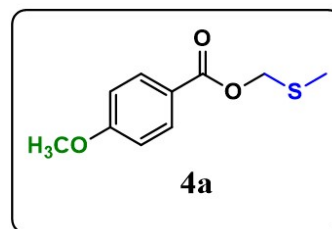
LCMS(ESI) Calcd for C₁₀H₉NO₅ [M+H]⁺, 224.0481; found, 224.1209.



xxiii) (methylthio)methyl 4-methoxybenzoate (4a)

Yield: 157 mg, 74%; Colourless liquid;

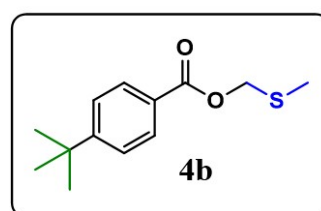
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.01 (d, $J = 8.9$ Hz, 2H), 6.92 (d, $J = 9.0$ Hz, 2H), 5.36 (s, 2H), 3.85 (s, 3H), 2.29 (s, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 165.7, 163.4, 131.6, 122.0, 113.5, 68.3, 55.3, 15.3; LCMS (ESI) Calcd for $\text{C}_{10}\text{H}_{12}\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$, 213.0580; found, 213.1457.



xxiii) (methylthio)methyl 4-(tert-butyl)benzoate (4b)

Yield: 191 mg, 80%; Colourless liquid;

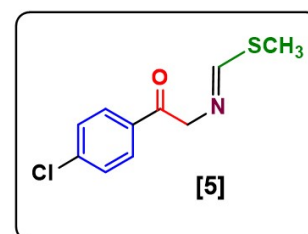
$^1\text{H NMR}$ (400 MHz, DMSO-d_6) δ 7.90 (d, $J = 8.6$ Hz, 2H), 7.54 (d, $J = 8.6$ Hz, 2H), 5.40 (s, 2H), 2.25 (s, 3H), 1.28 (s, 9H); $^{13}\text{C NMR}$ (101 MHz, DMSO-d_6) δ 165.3, 156.7, 129.2, 126.7, 125.7, 68.3, 34.9, 30.8, 14.7; LCMS (ESI) Calcd for $\text{C}_{13}\text{H}_{18}\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$, 239.1101; found, 239.10.



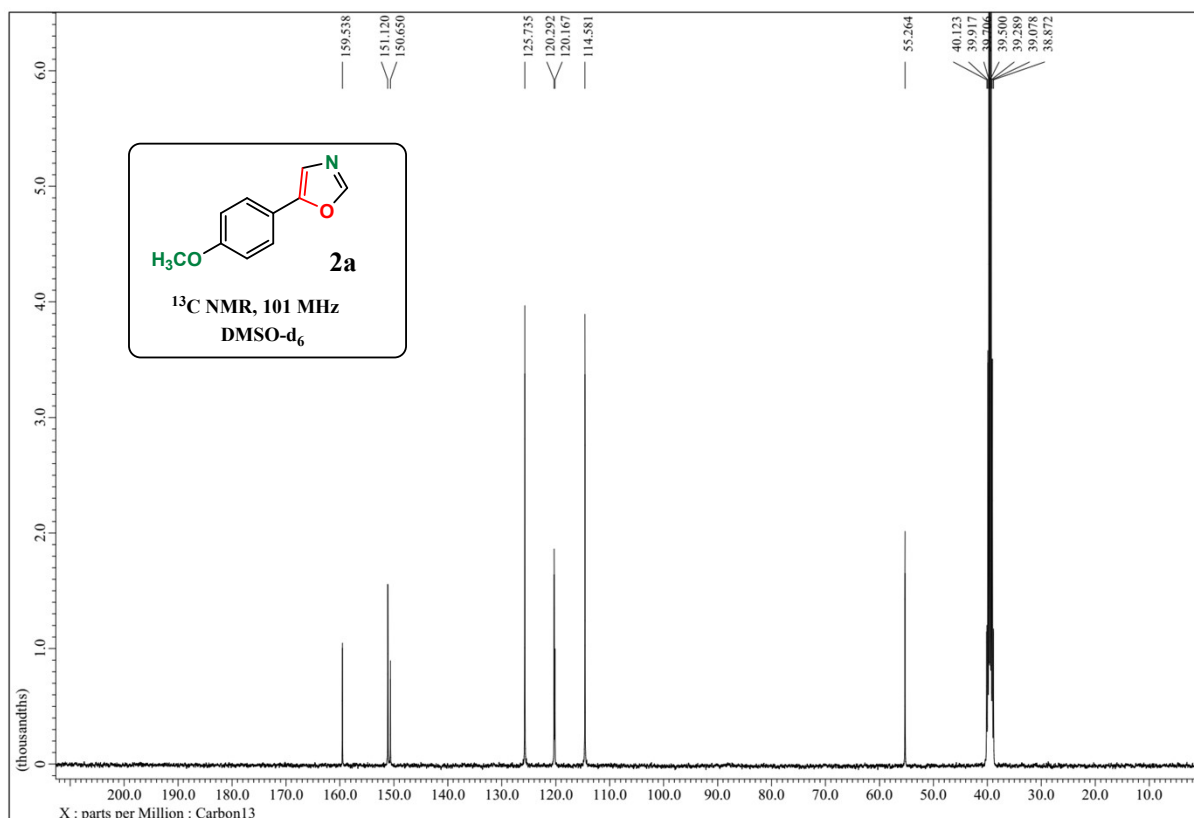
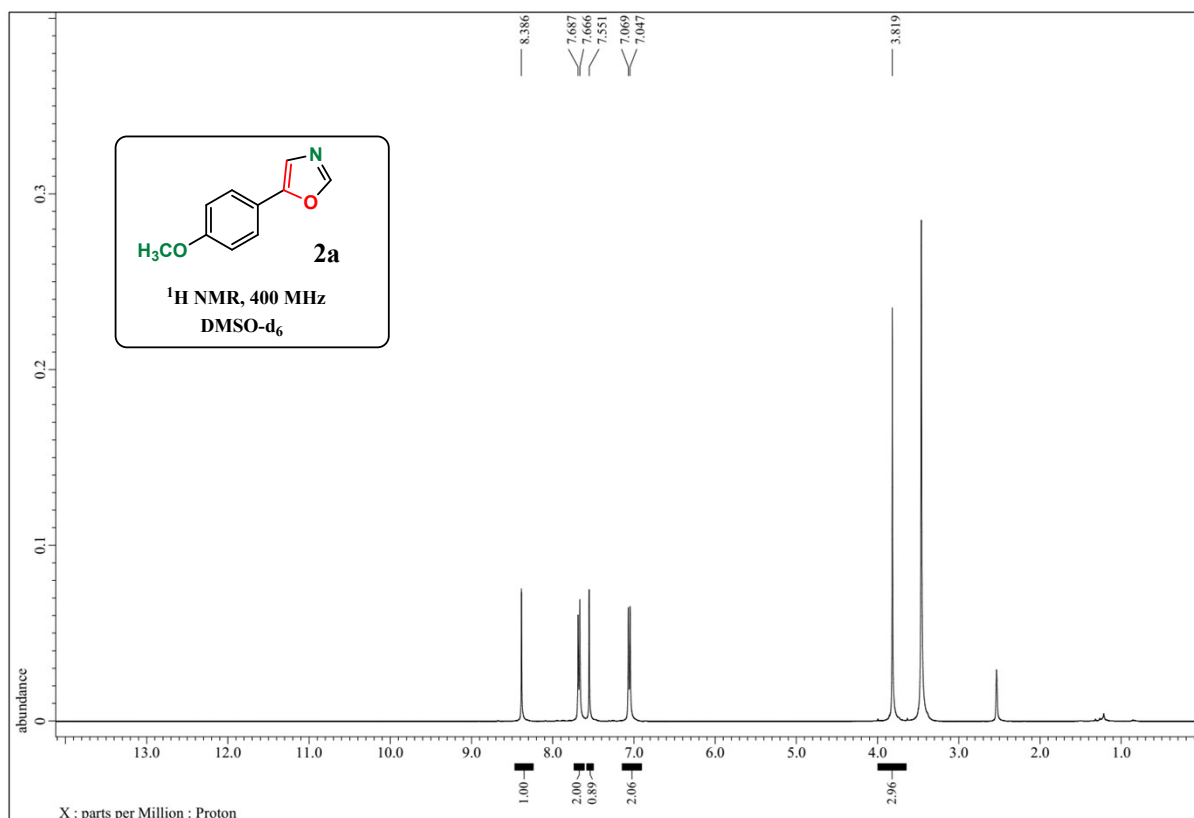
xxiii) methyl (E)-N-(2-(4-chlorophenyl)-2-oxoethyl)methanimidothioate (5)

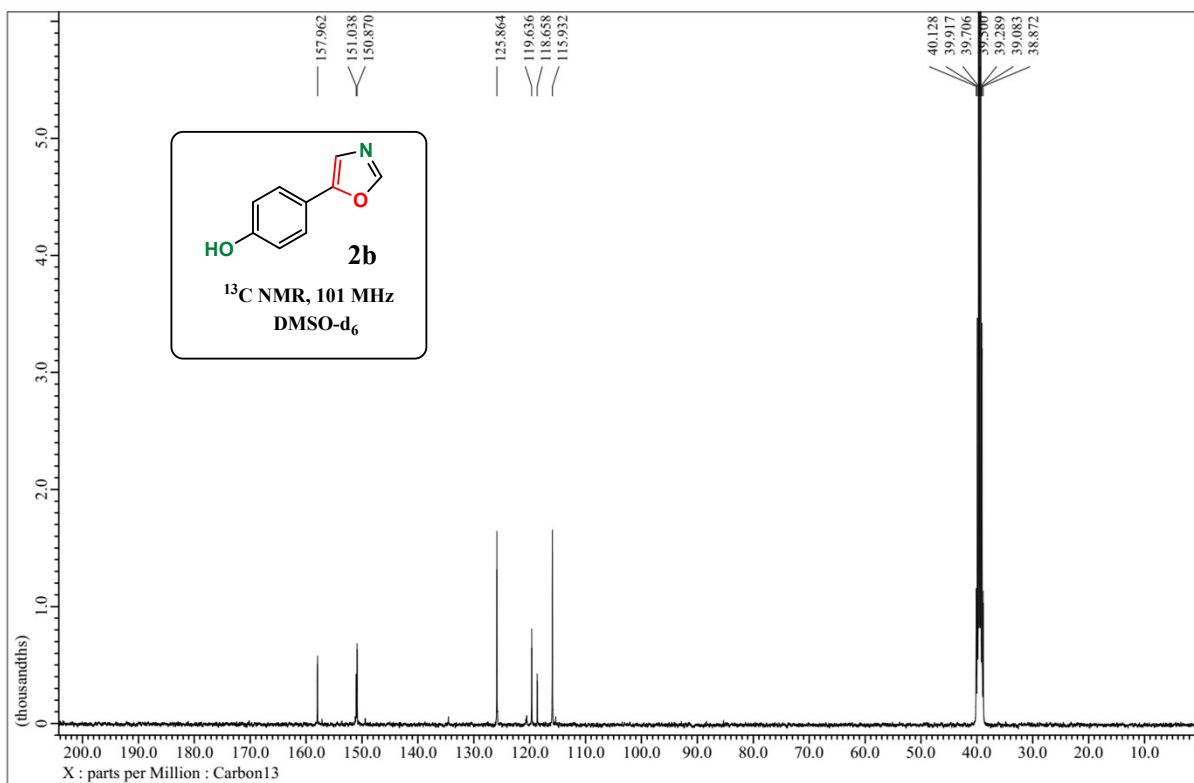
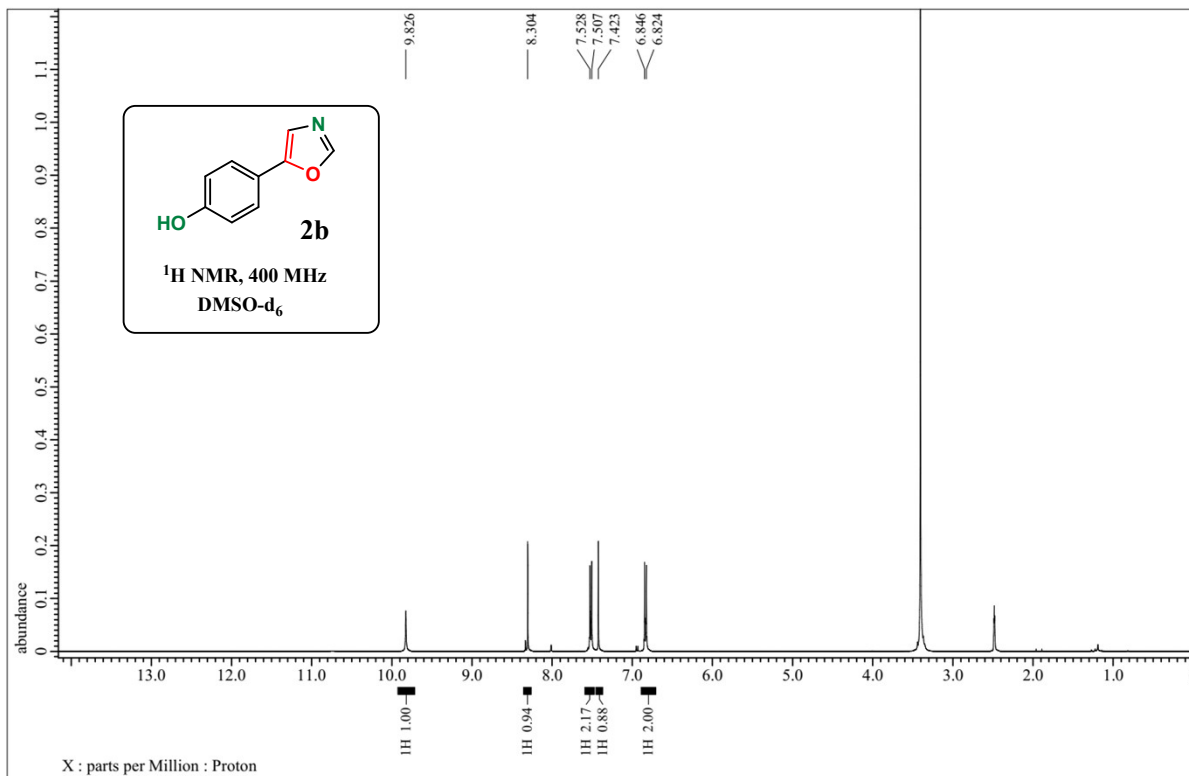
Yield: 102 mg, 45%; Colourless solid;

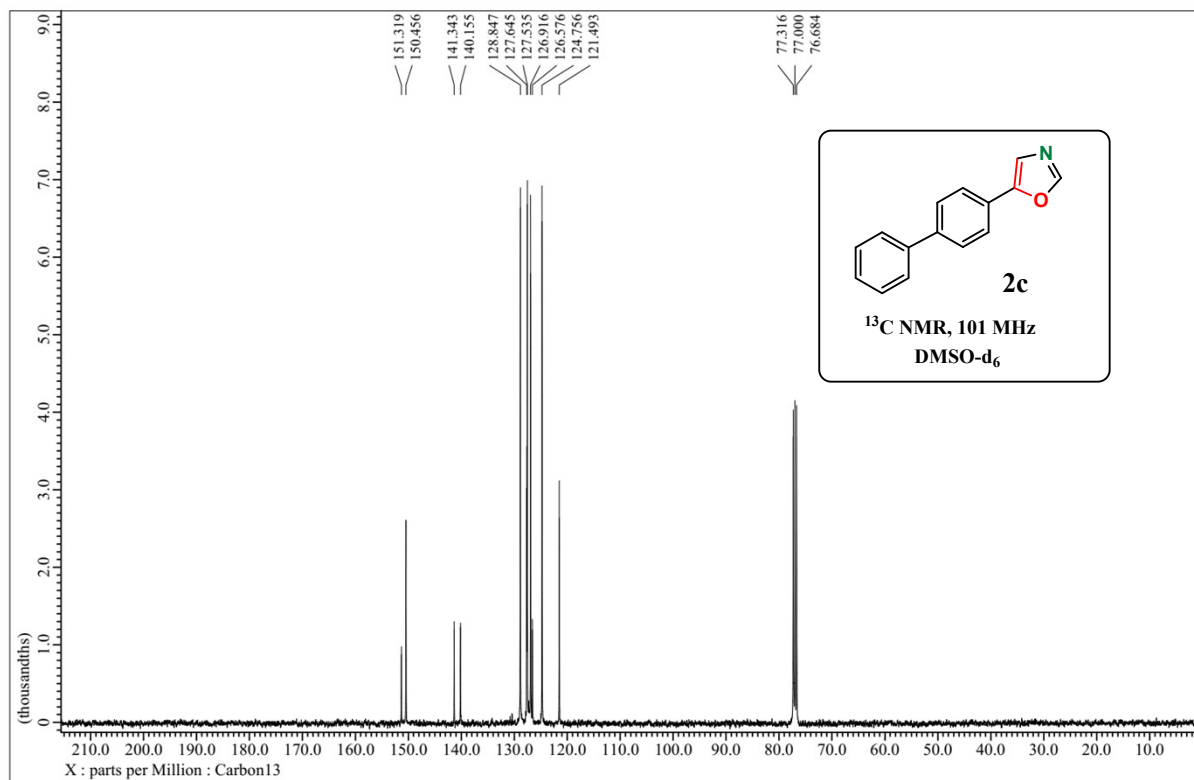
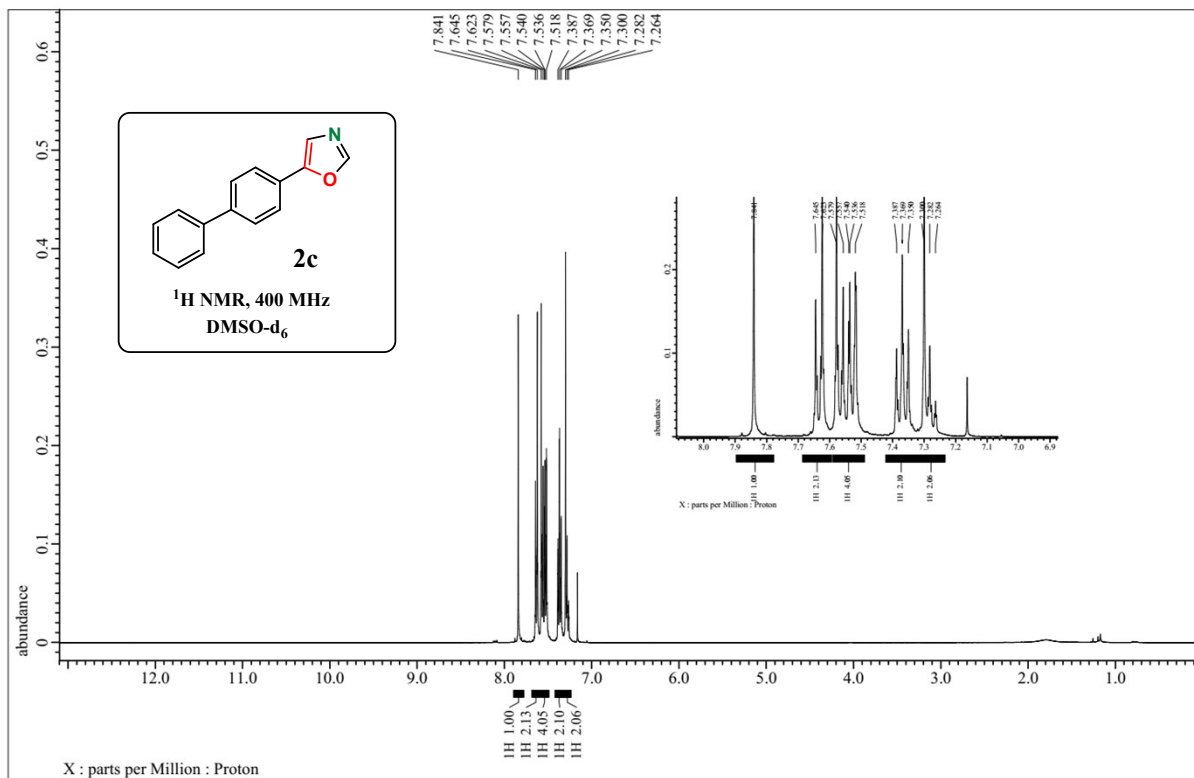
$^1\text{H NMR}$ (400 MHz, DMSO-d_6) δ 7.95 (d, $J = 8.6$ Hz, 2H), 7.60 (d, $J = 8.6$ Hz, 2H), 7.01 (s, 1H), 2.80 (s, 3H), 2.68 (s, 2H); $^{13}\text{C NMR}$ (101 MHz, DMSO-d_6) δ 199.3, 163.1, 134.7, 133.6, 129.0, 127.7, 65.4, 18.2; LCMS (ESI) Calcd for $\text{C}_{10}\text{H}_{10}\text{ClNOS}$ $[\text{M}+\text{H}]^+$, 227.0172; found, 227.10.

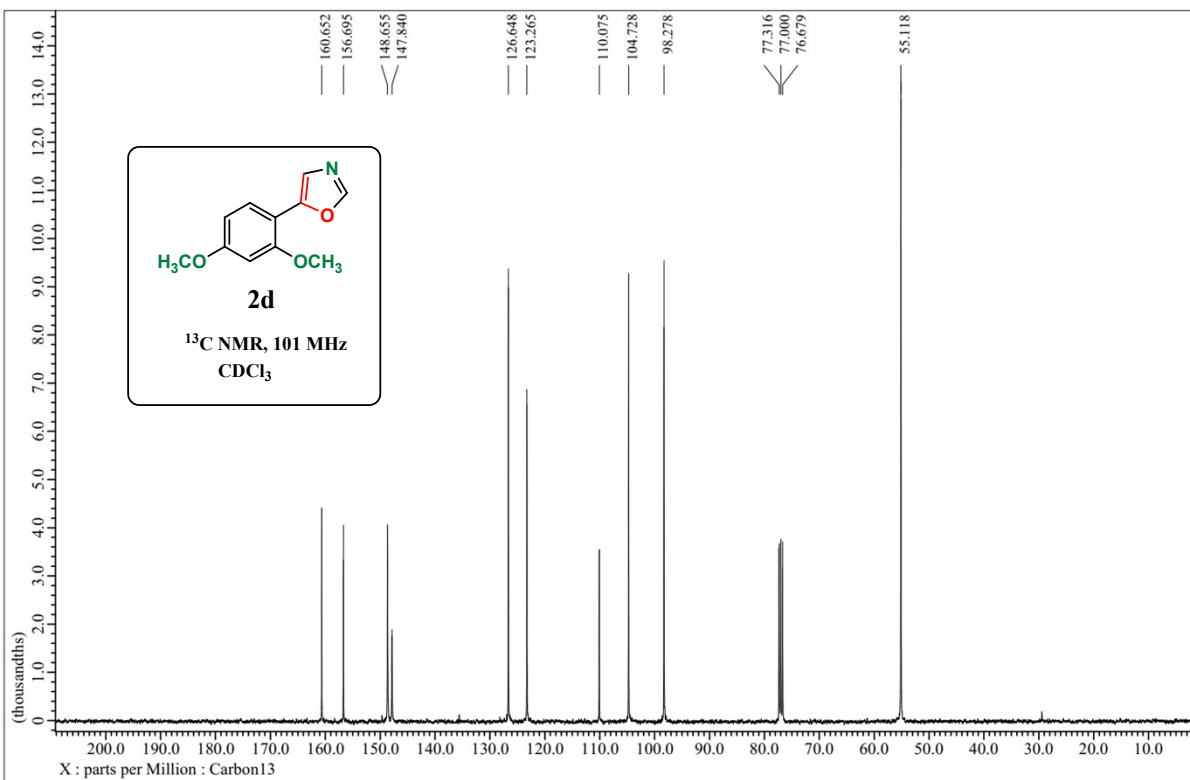
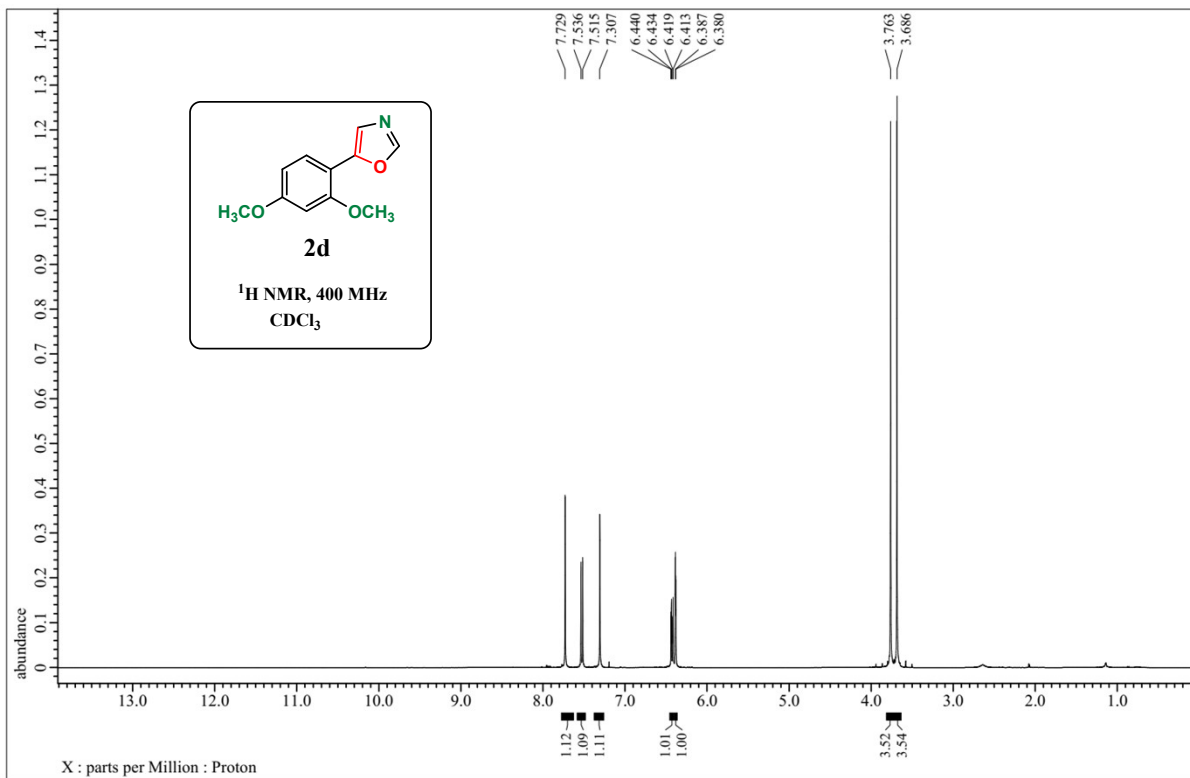


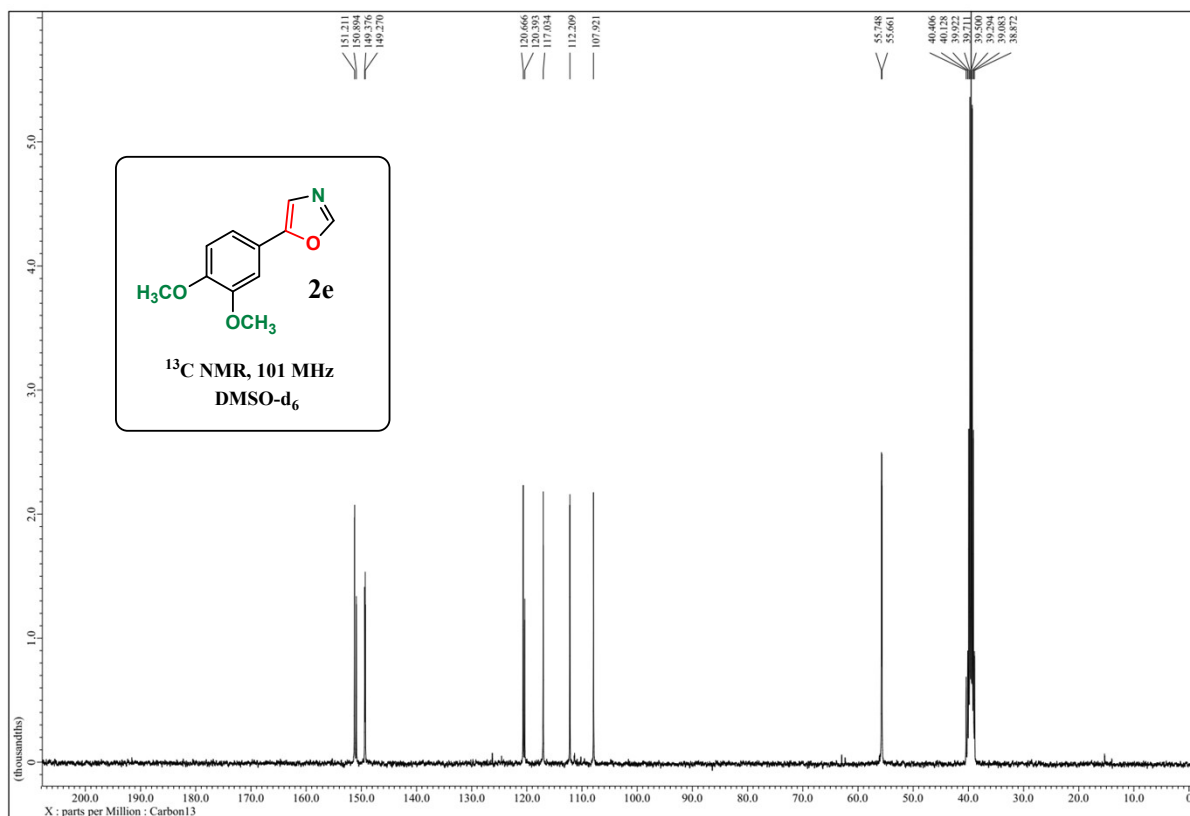
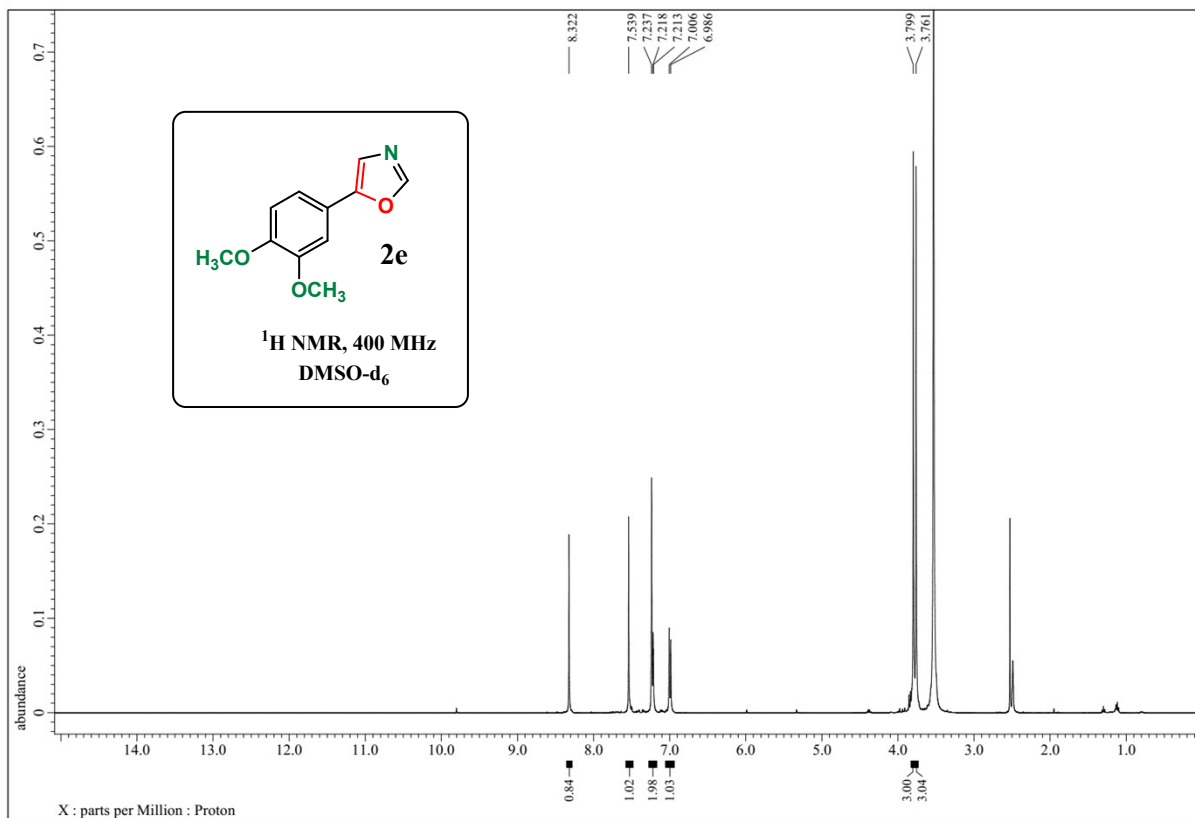
5. Copies of ^1H -NMR, ^{13}C -NMR and LCMS spectra of 5-substituted oxazole derivatives.

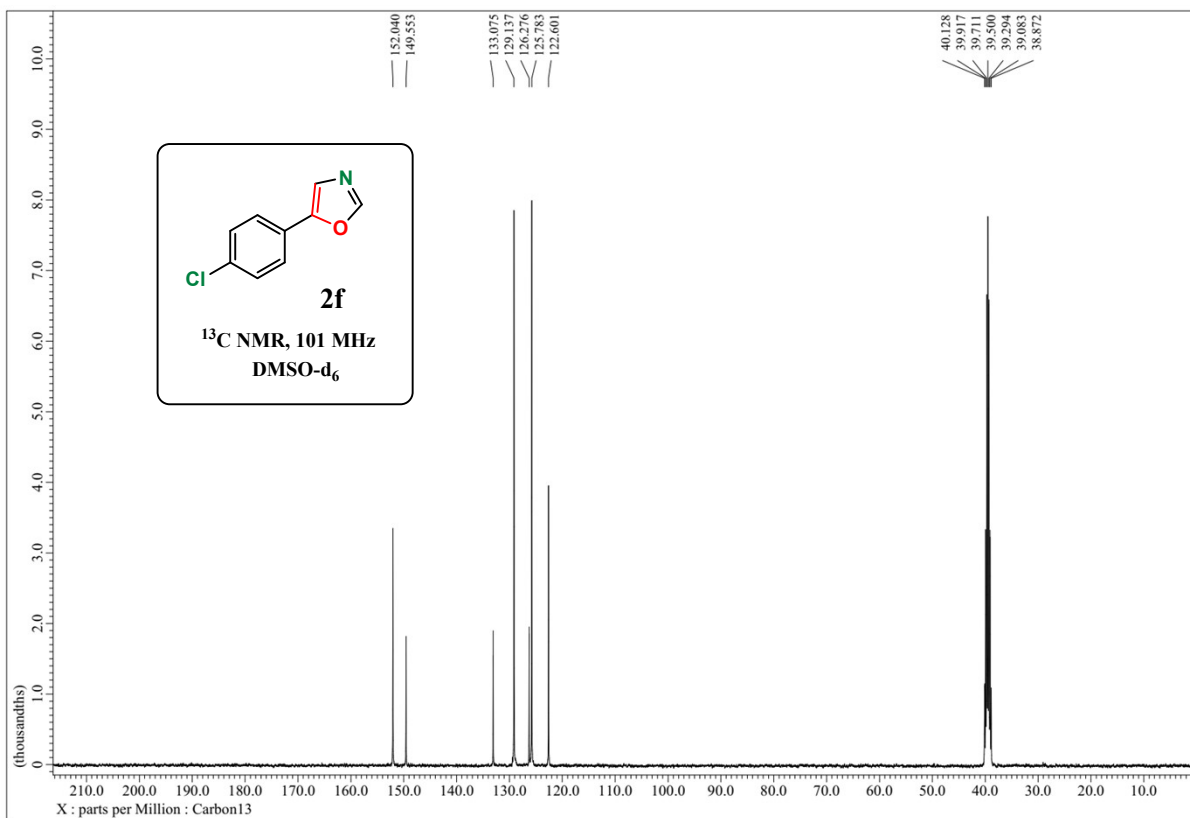
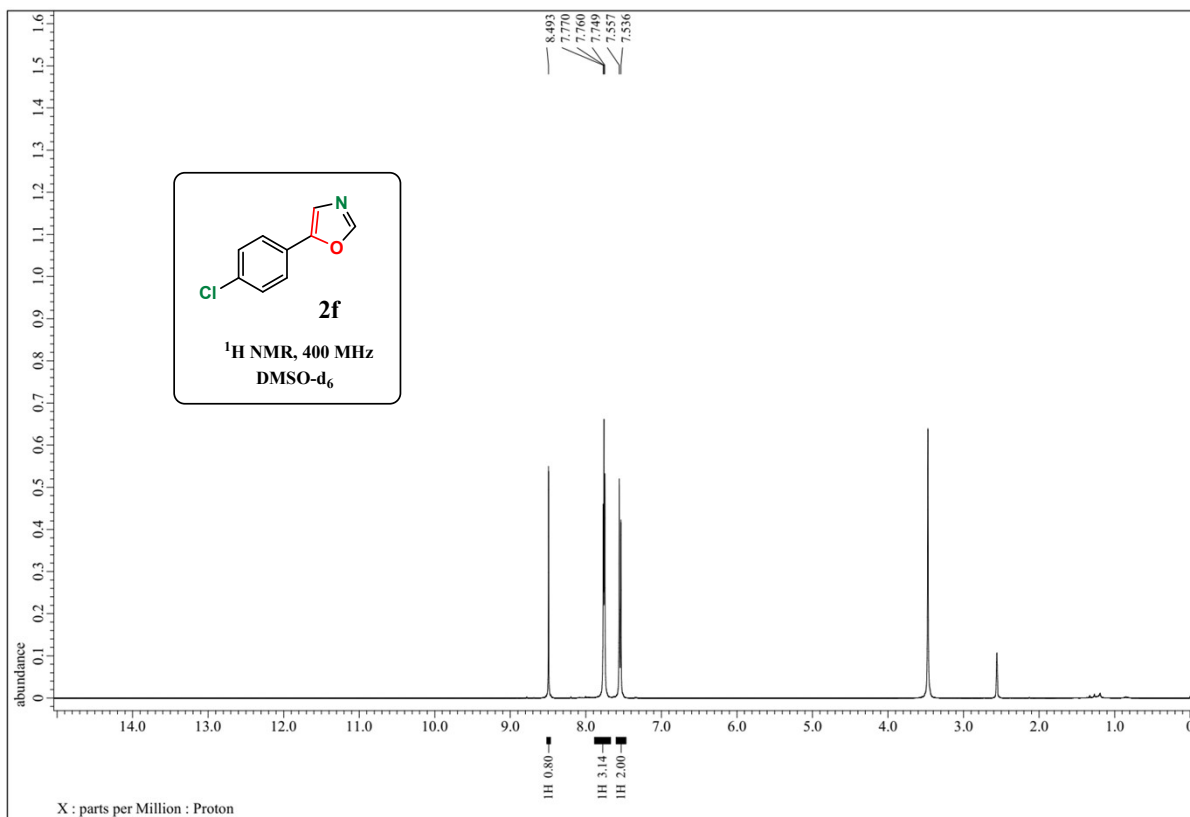


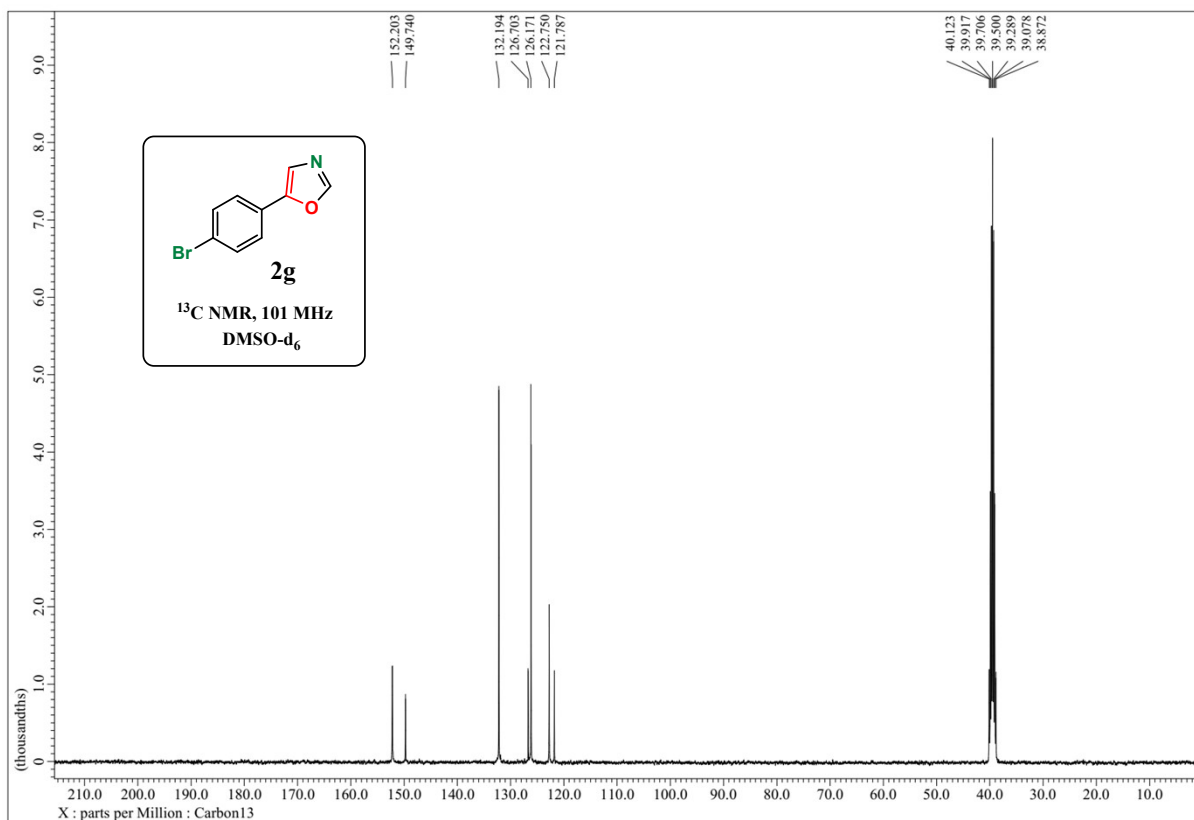
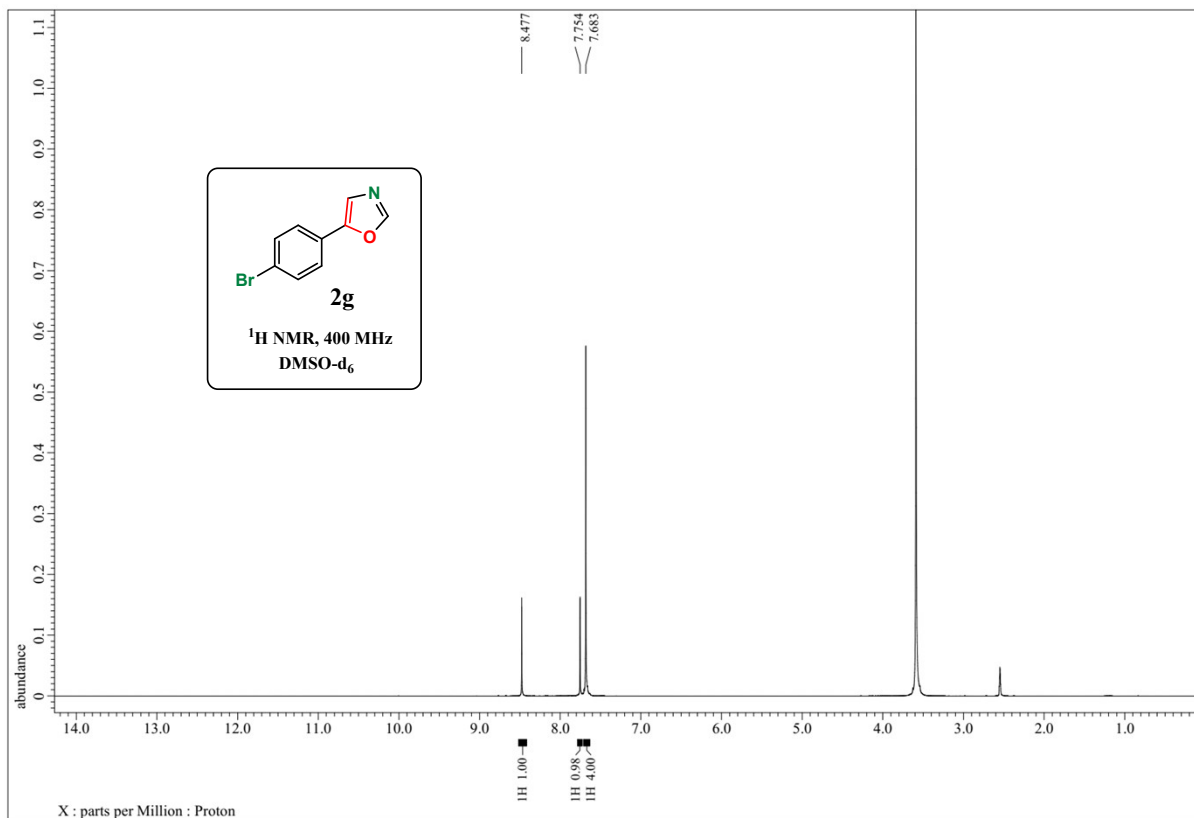


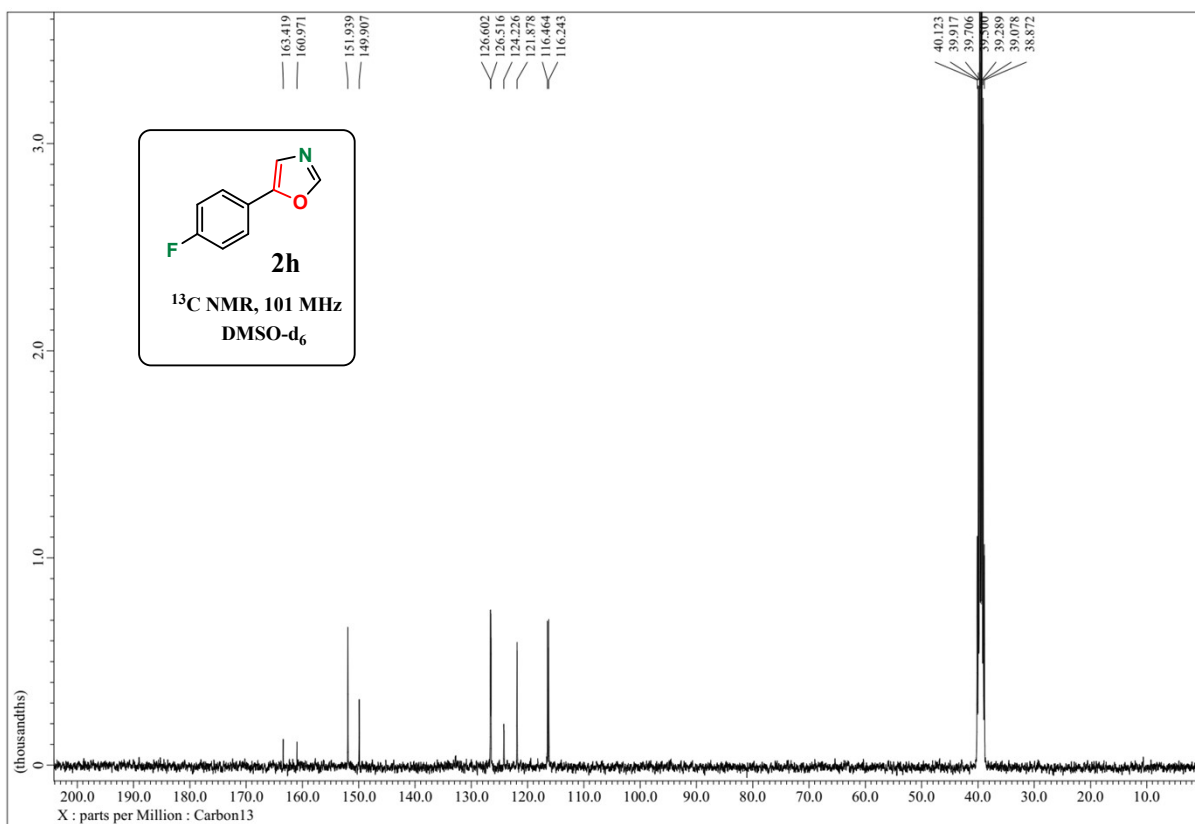
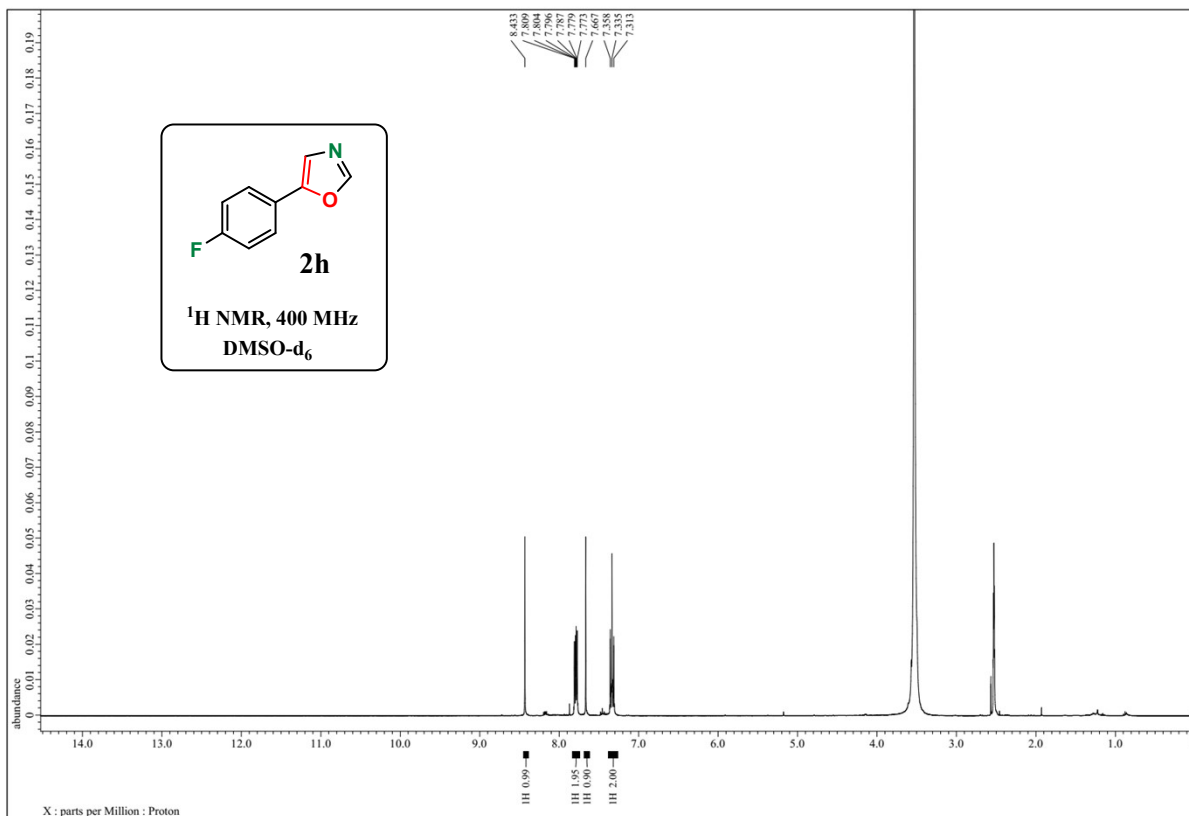


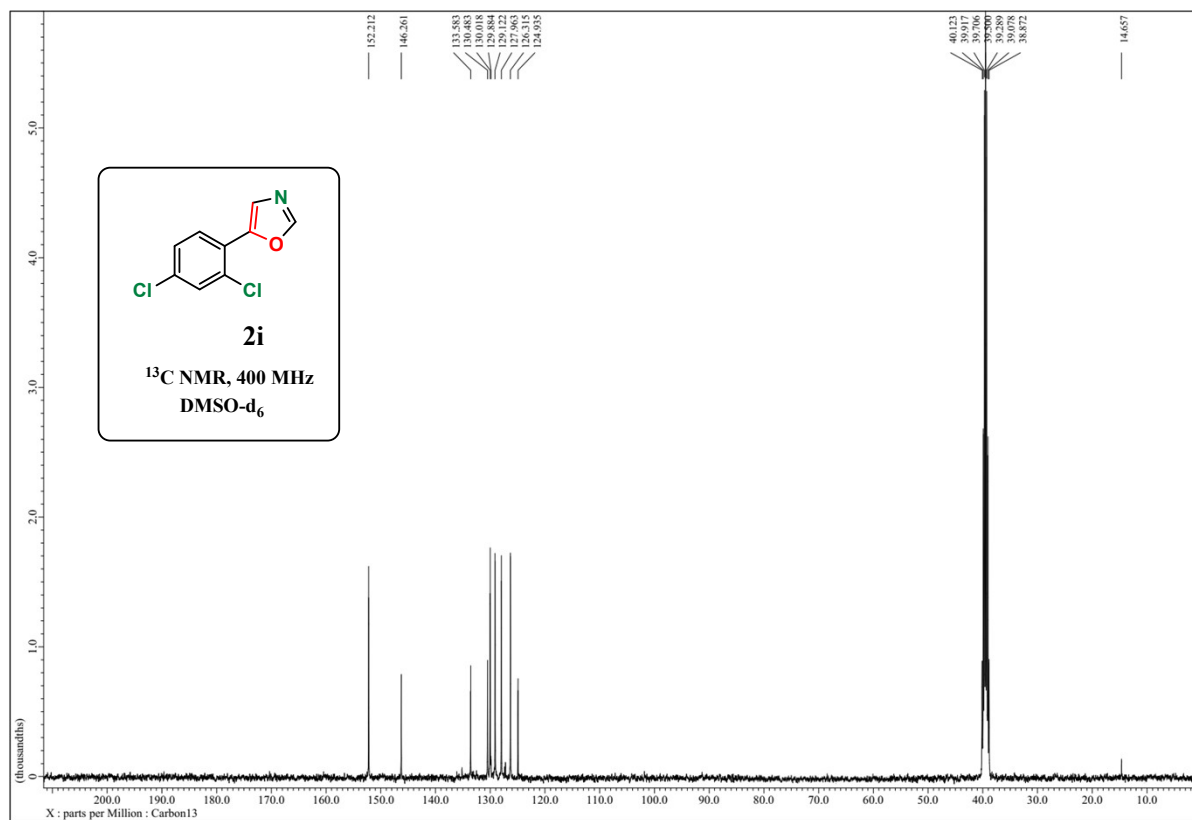
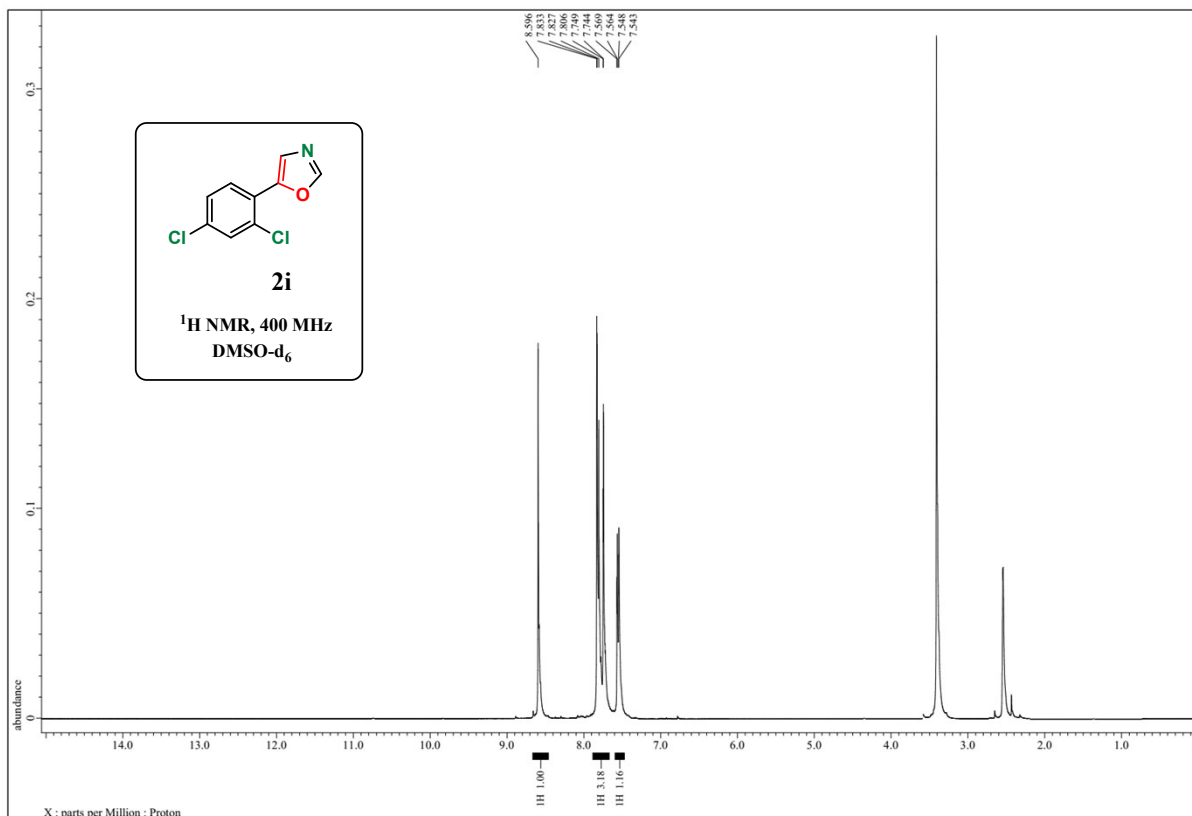


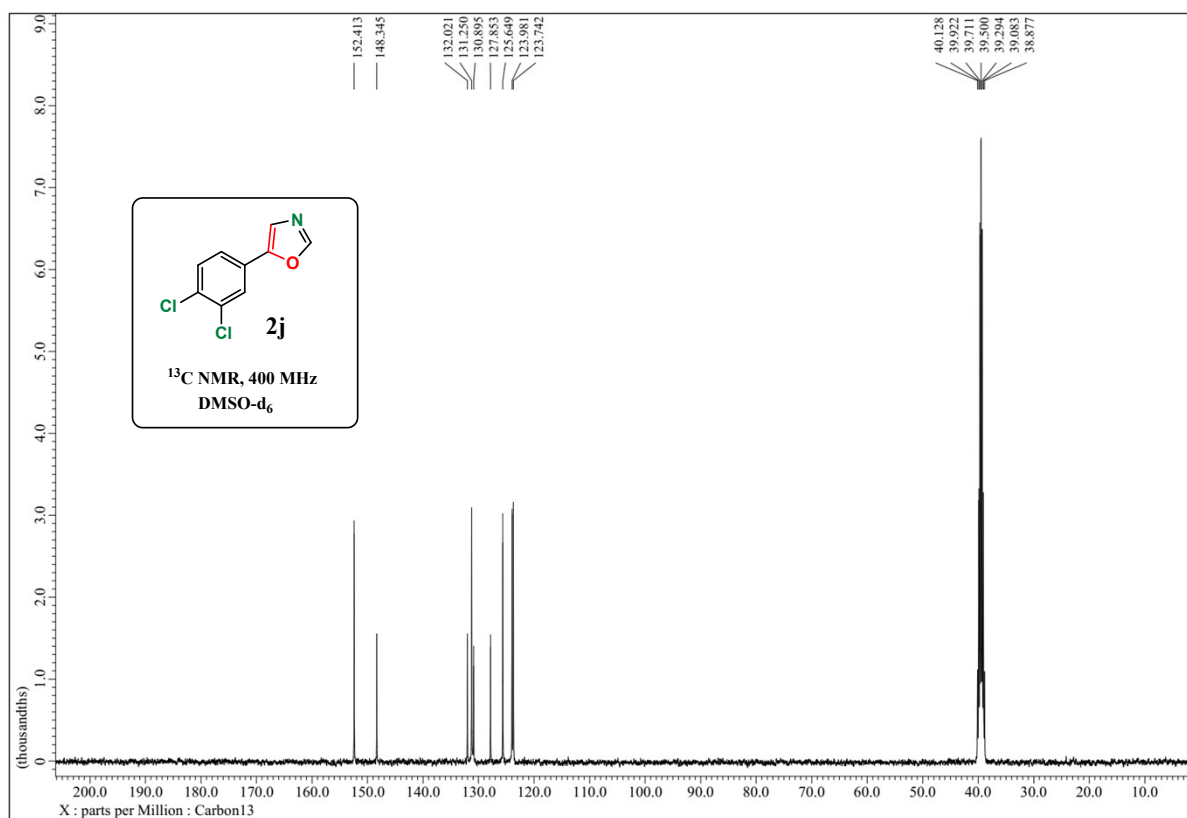
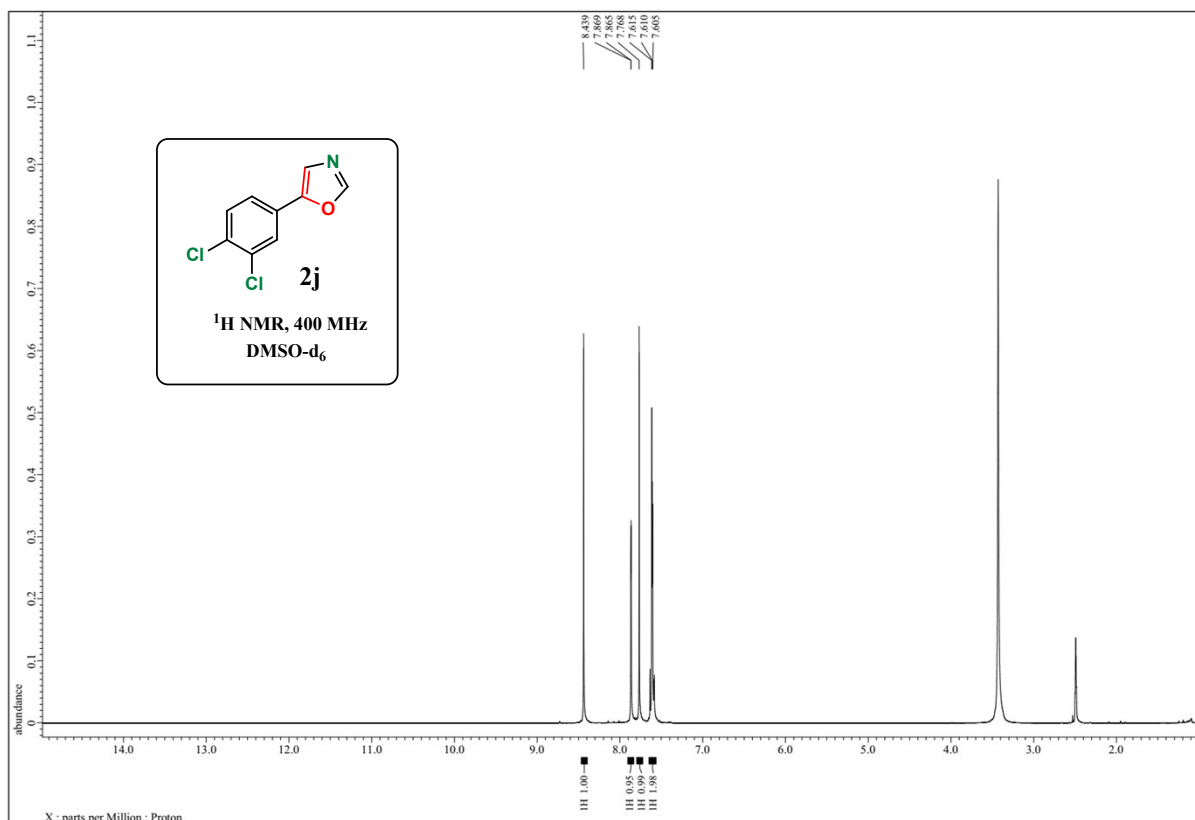


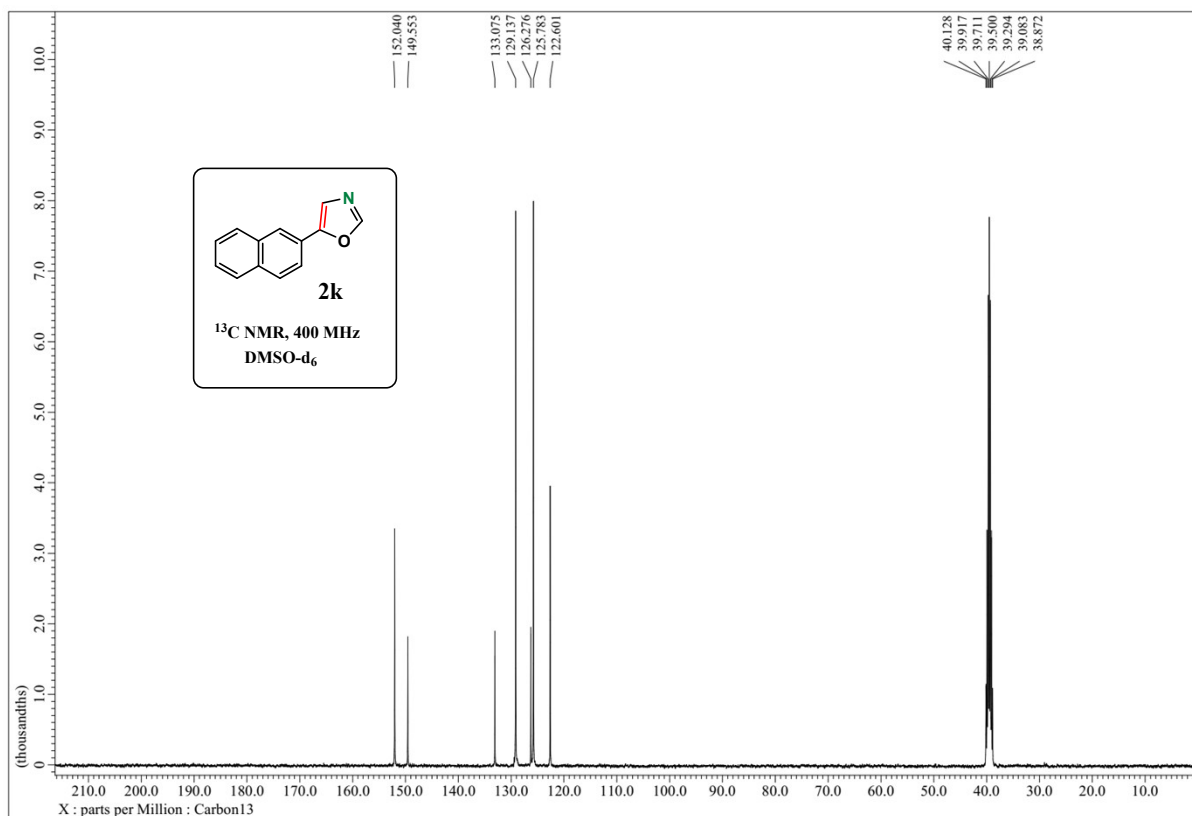
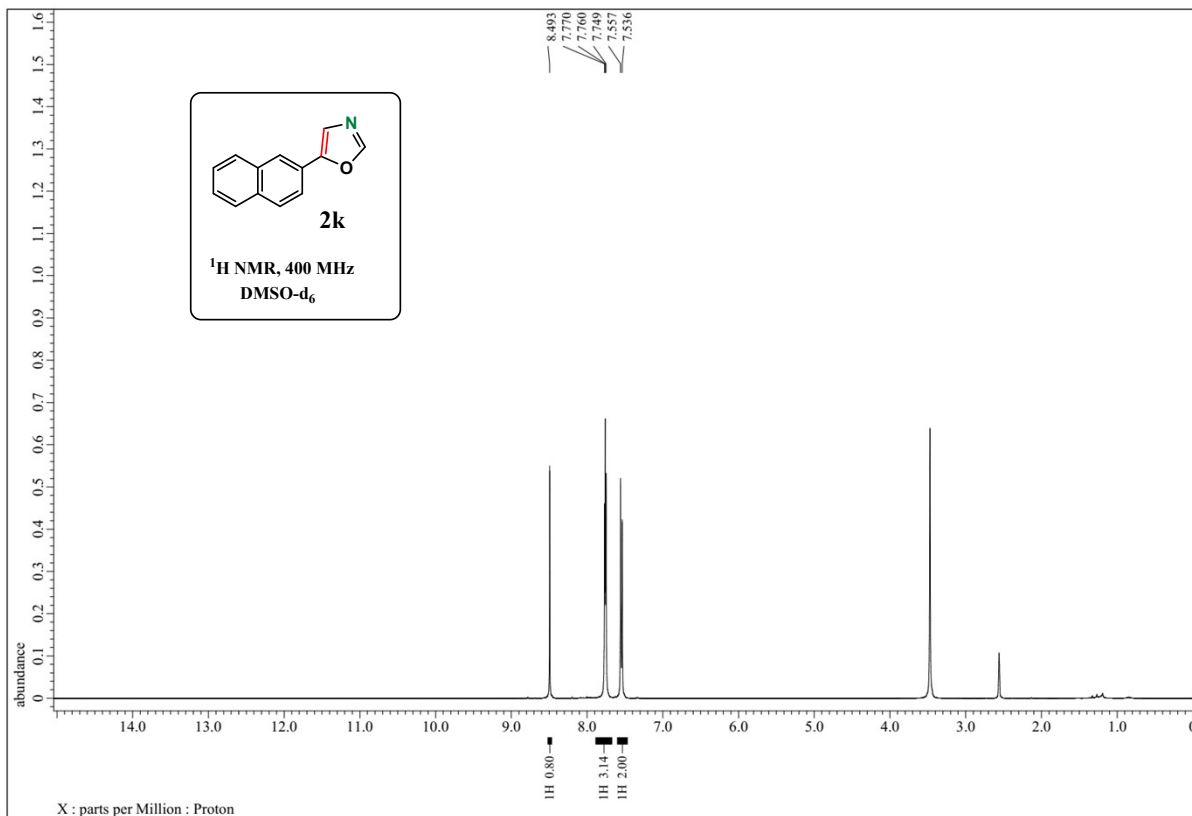


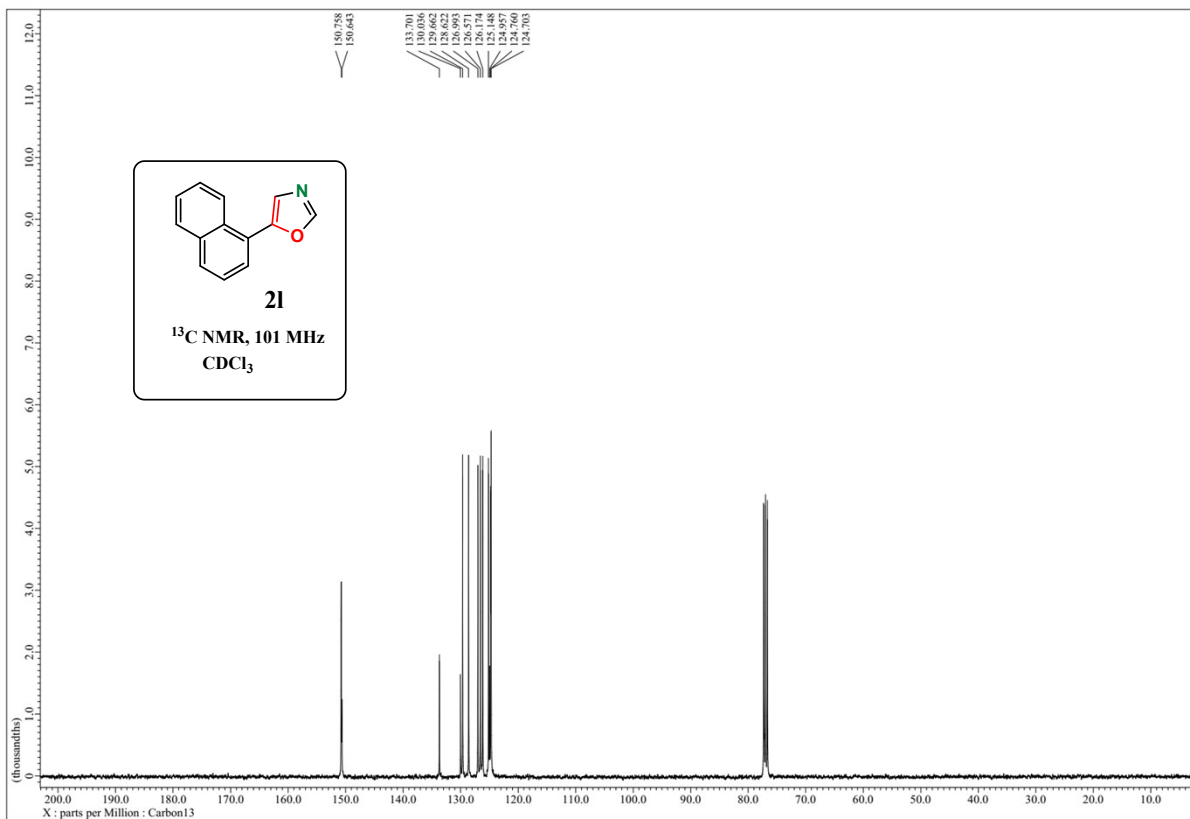
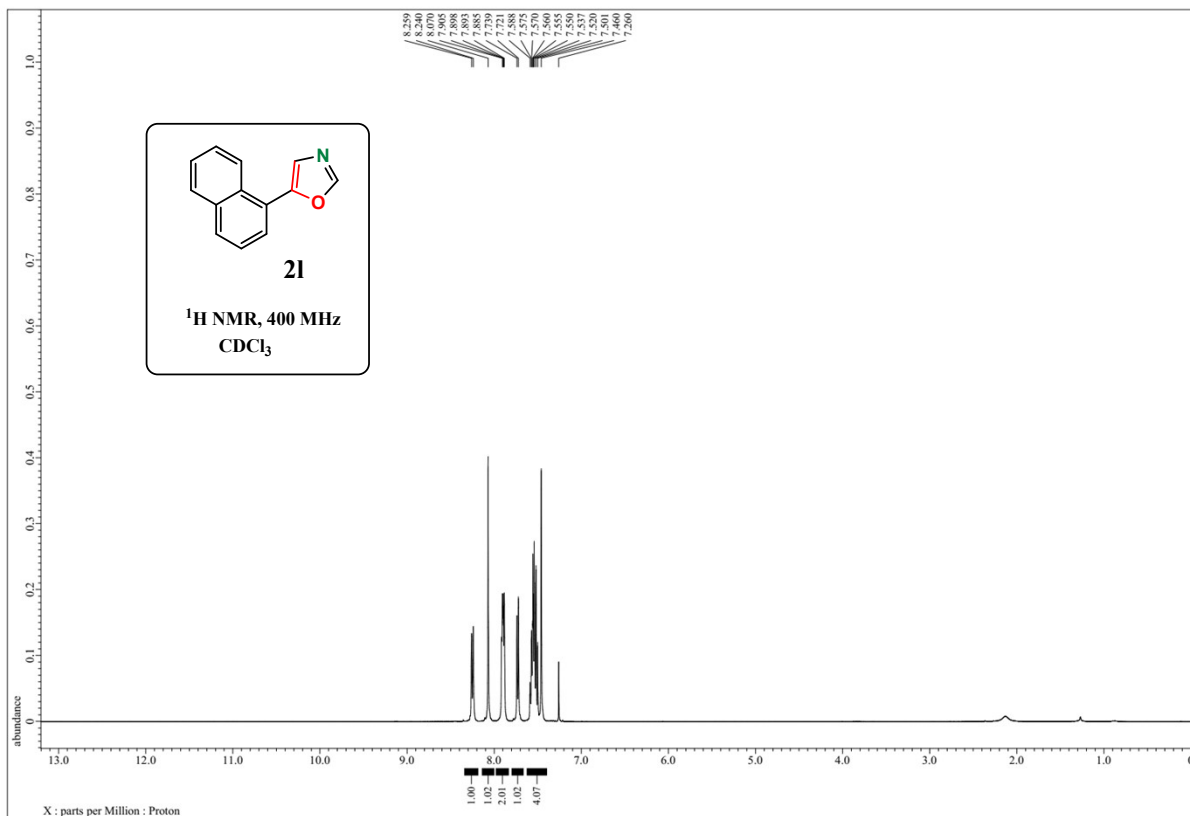


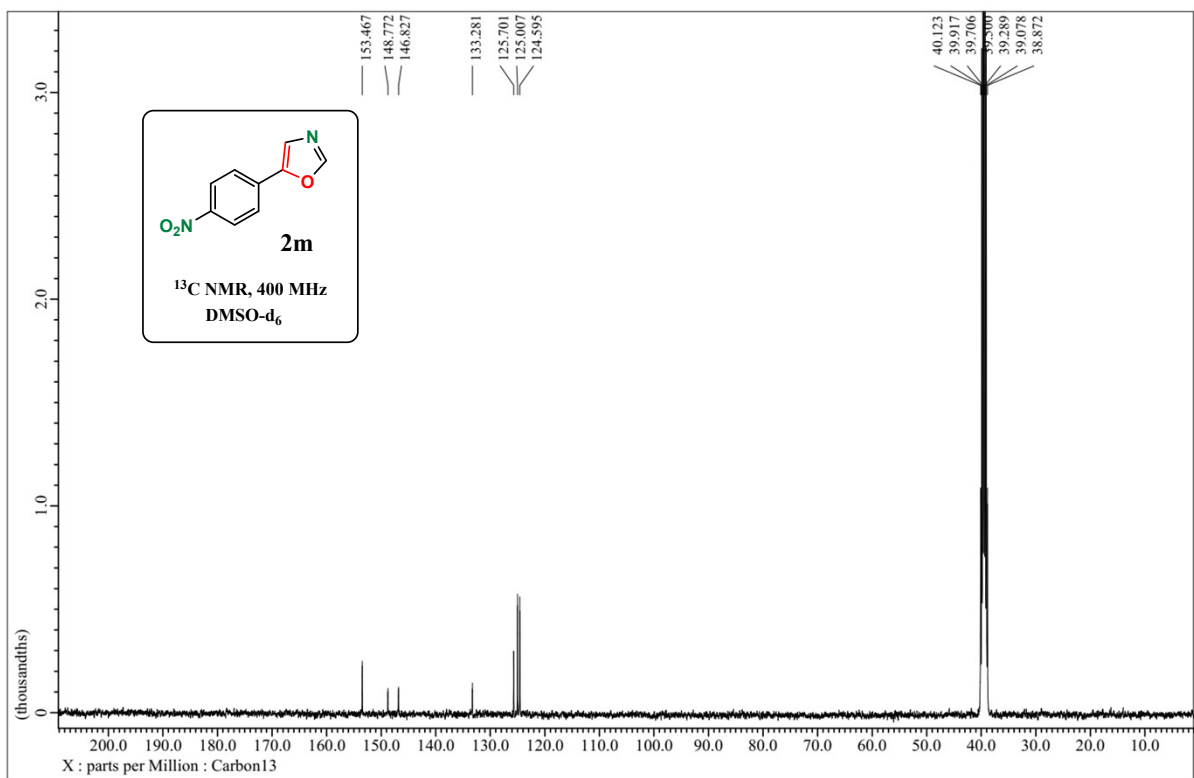
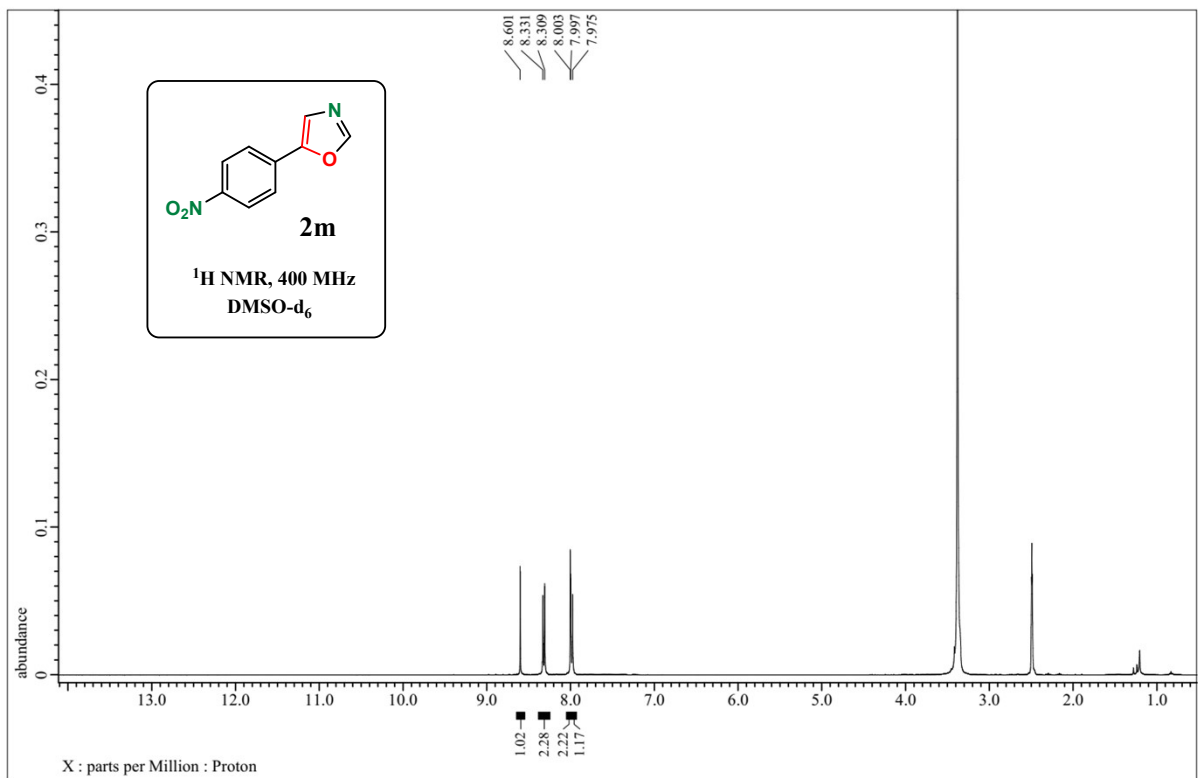


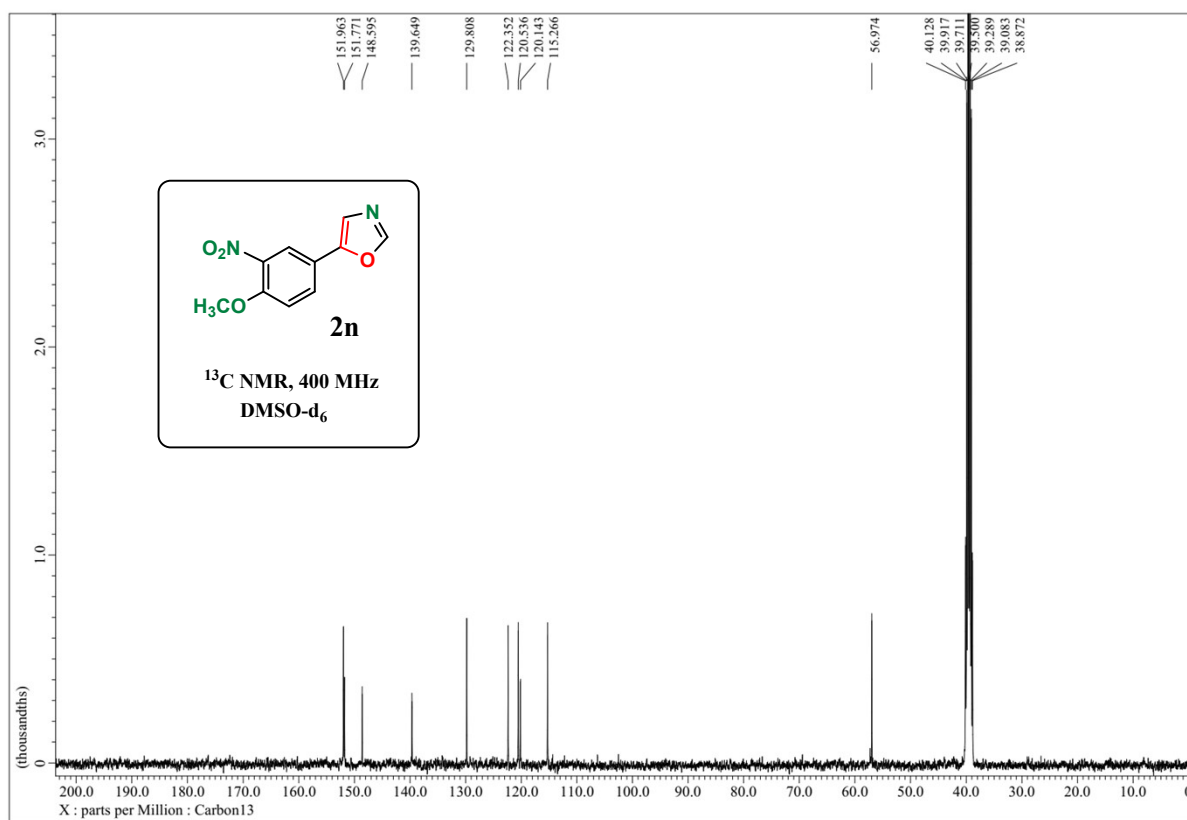
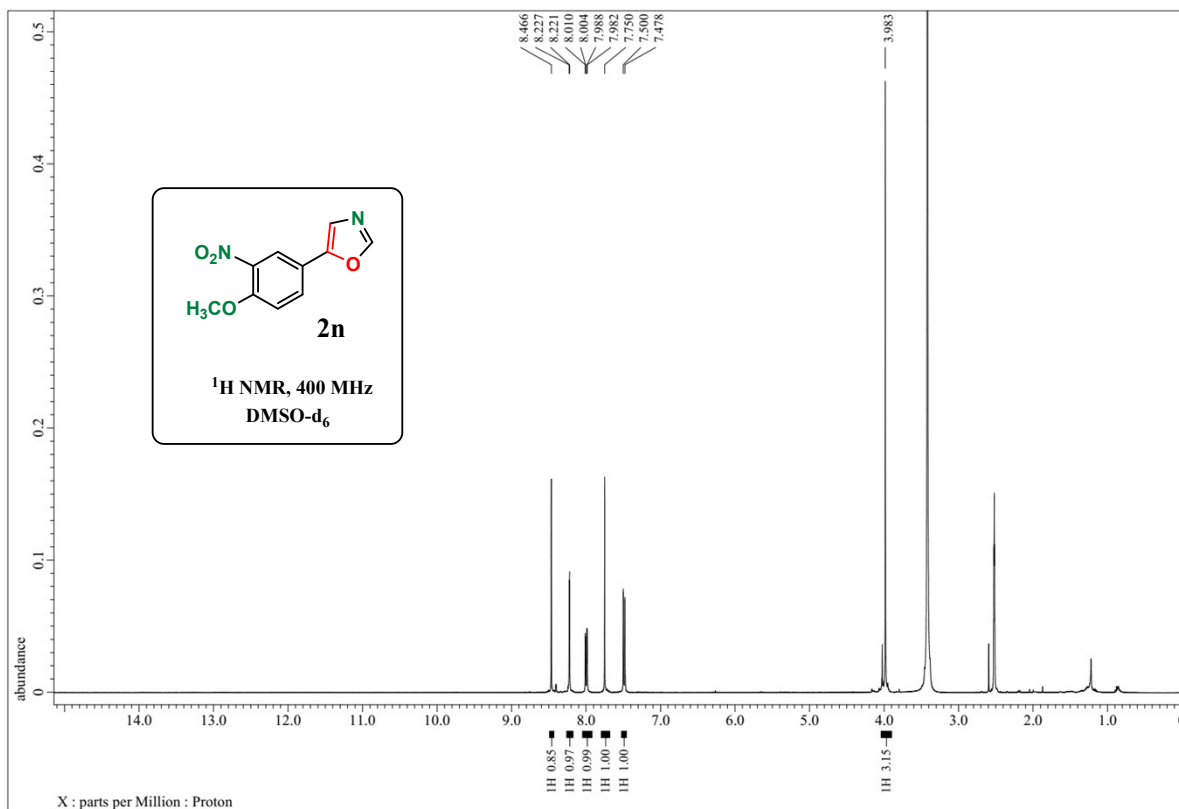


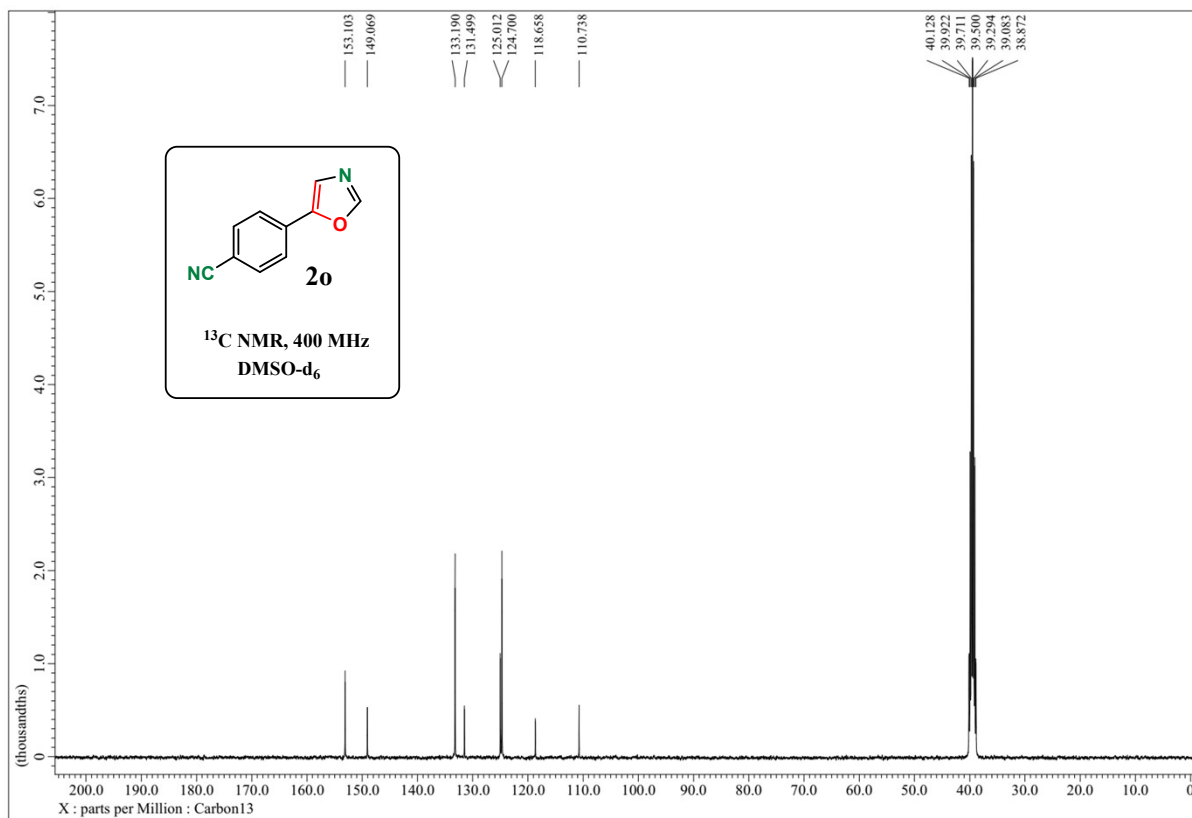
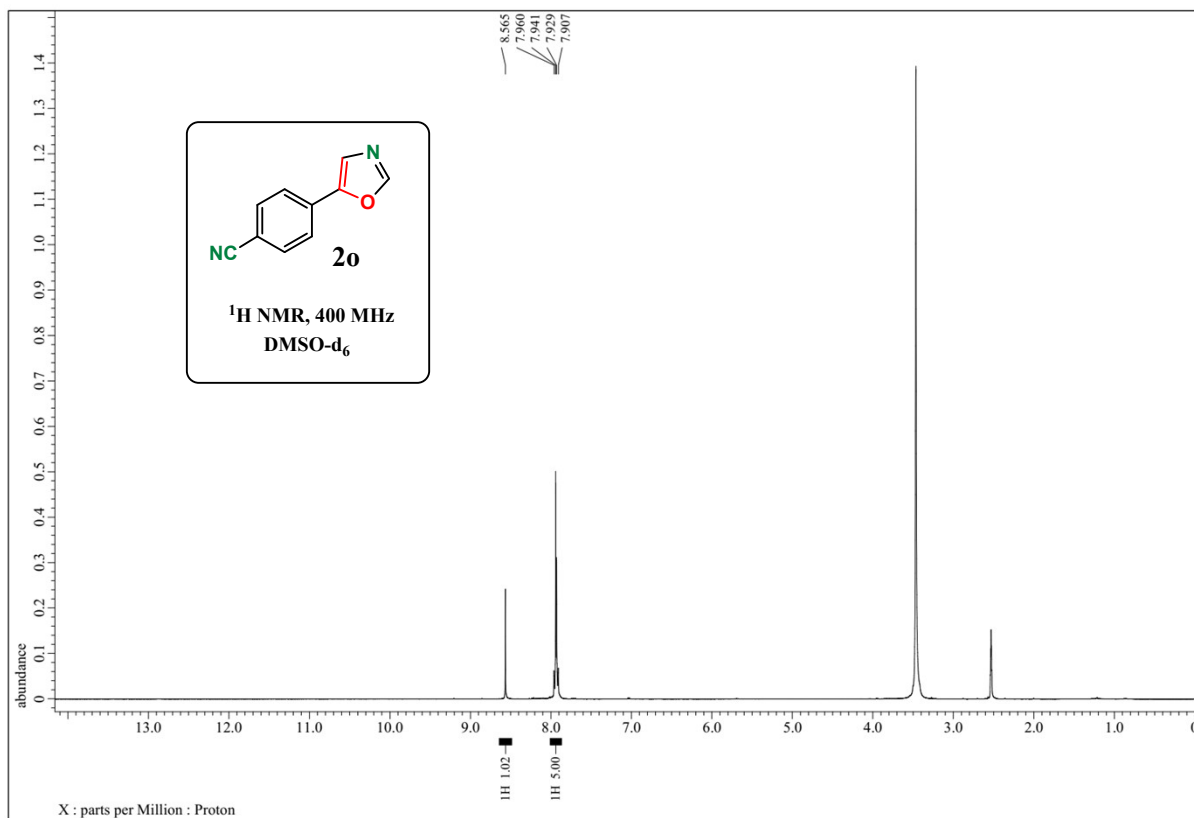


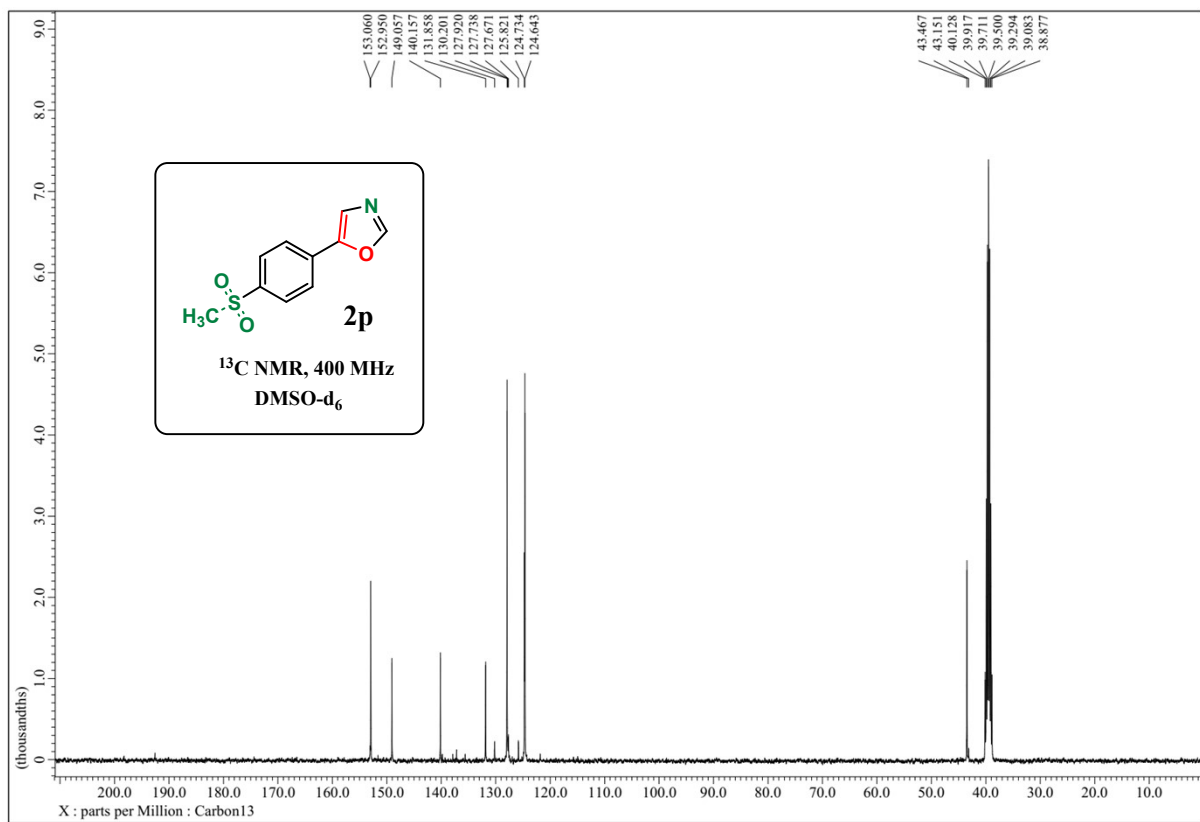
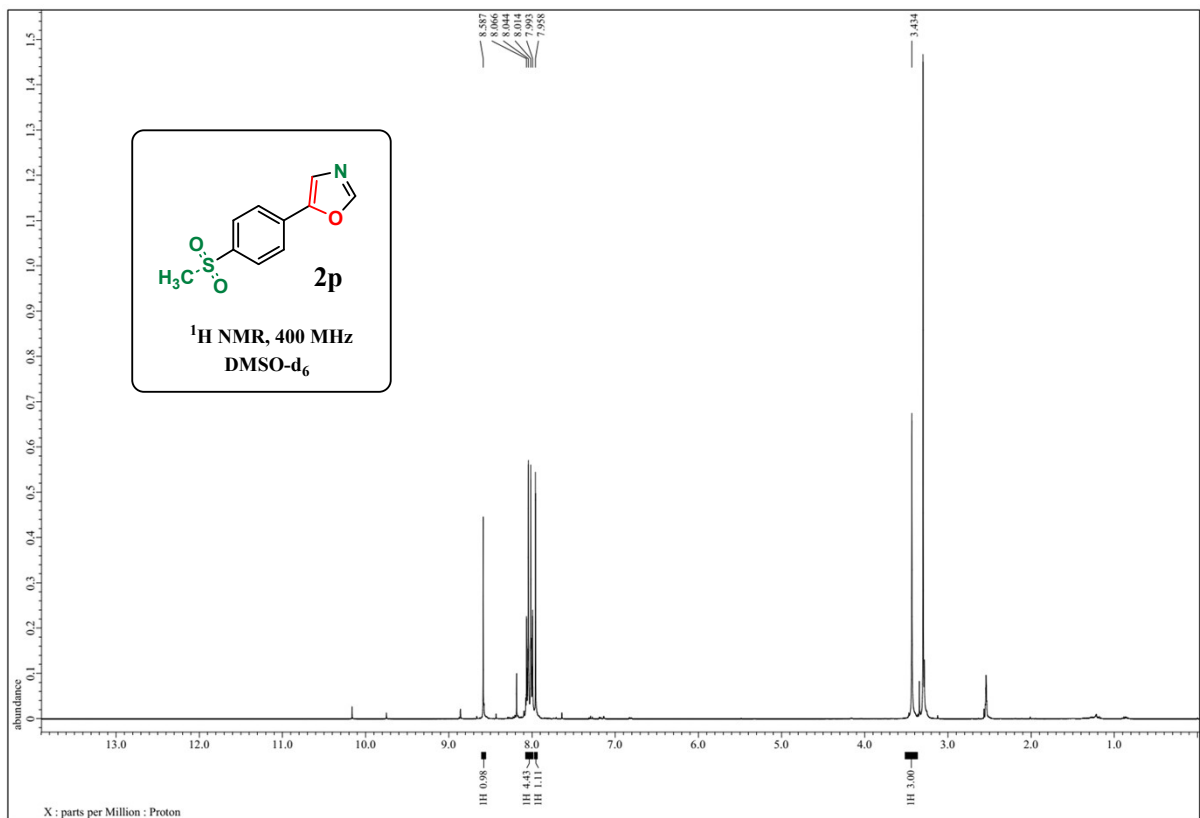


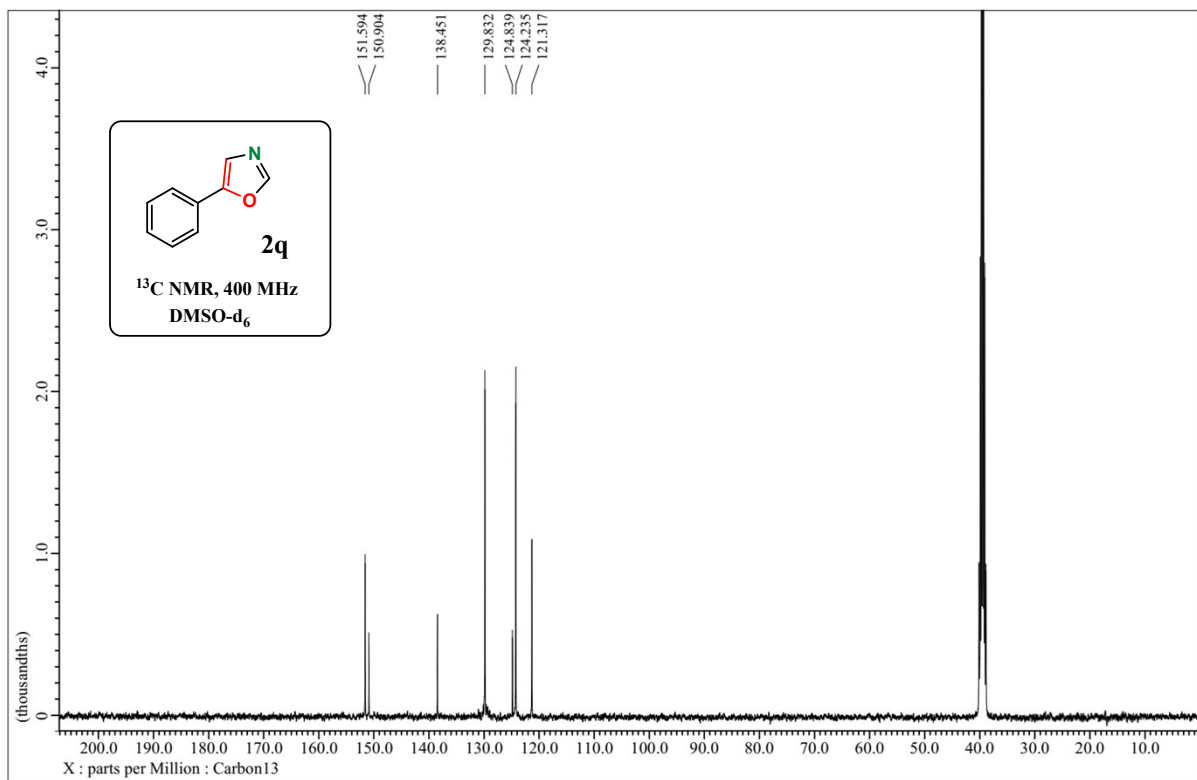
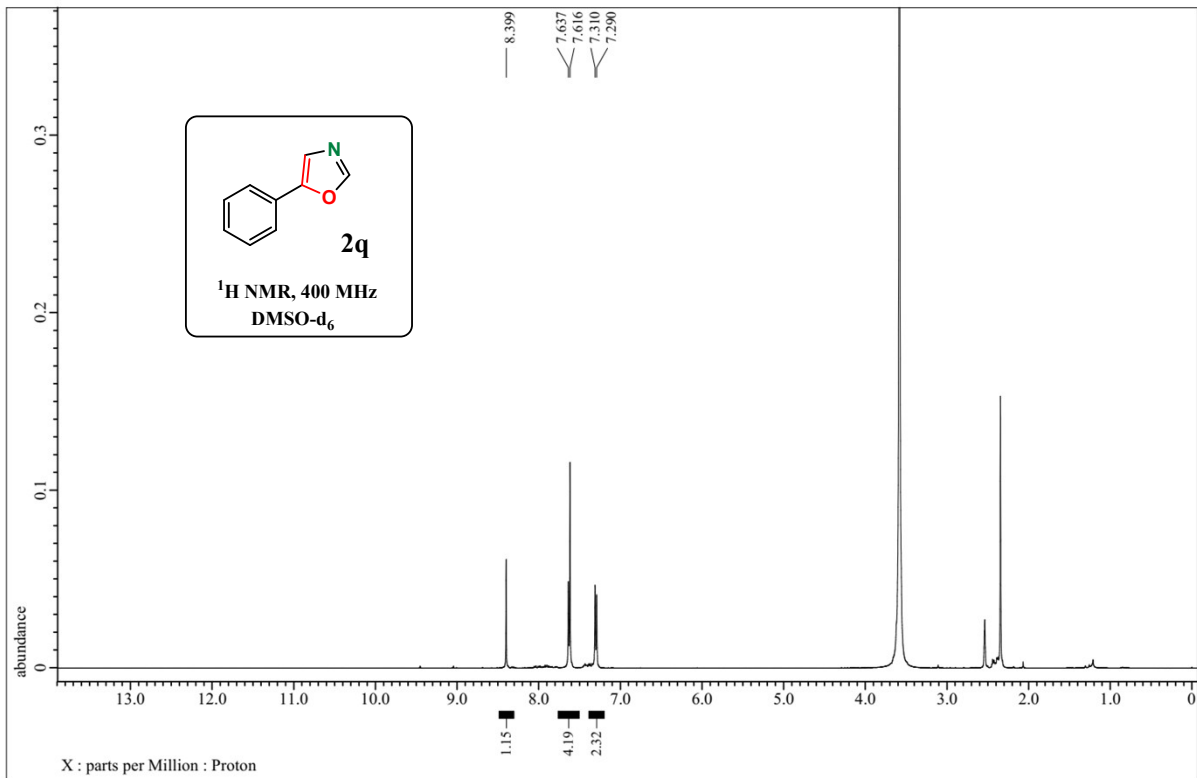


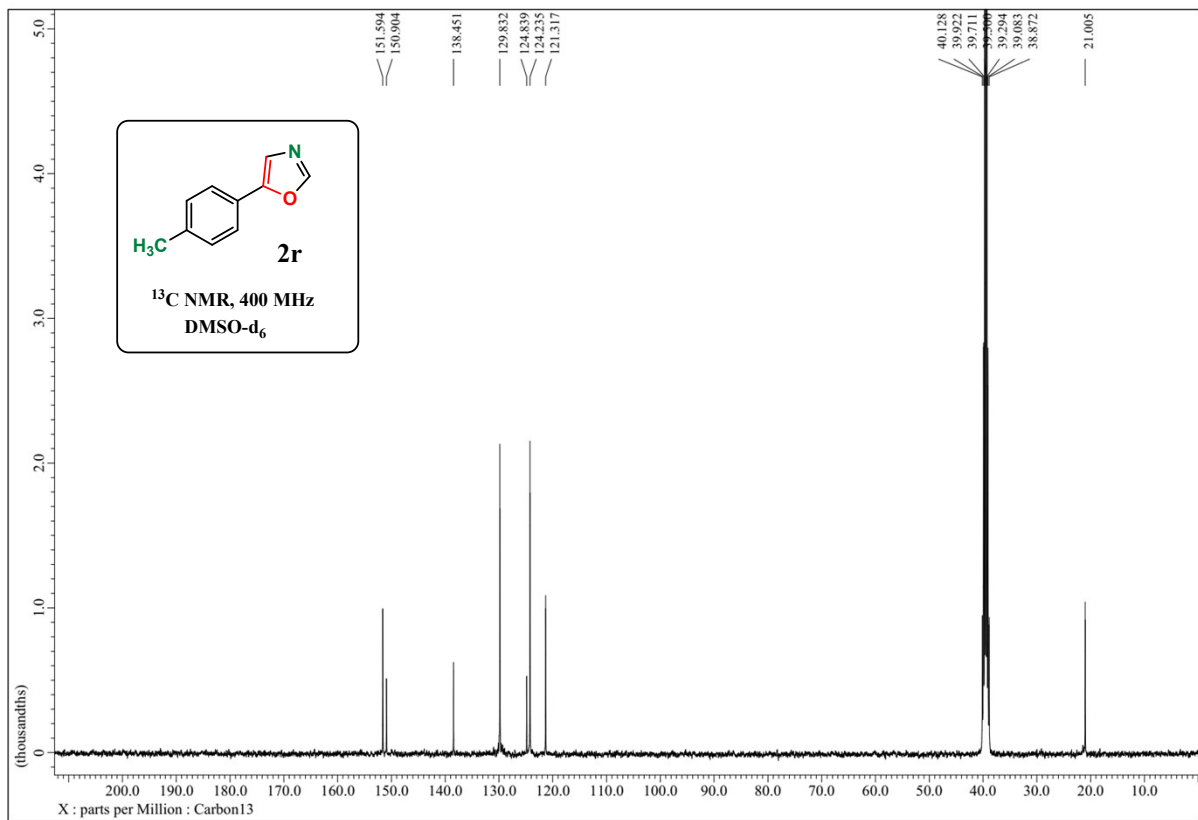
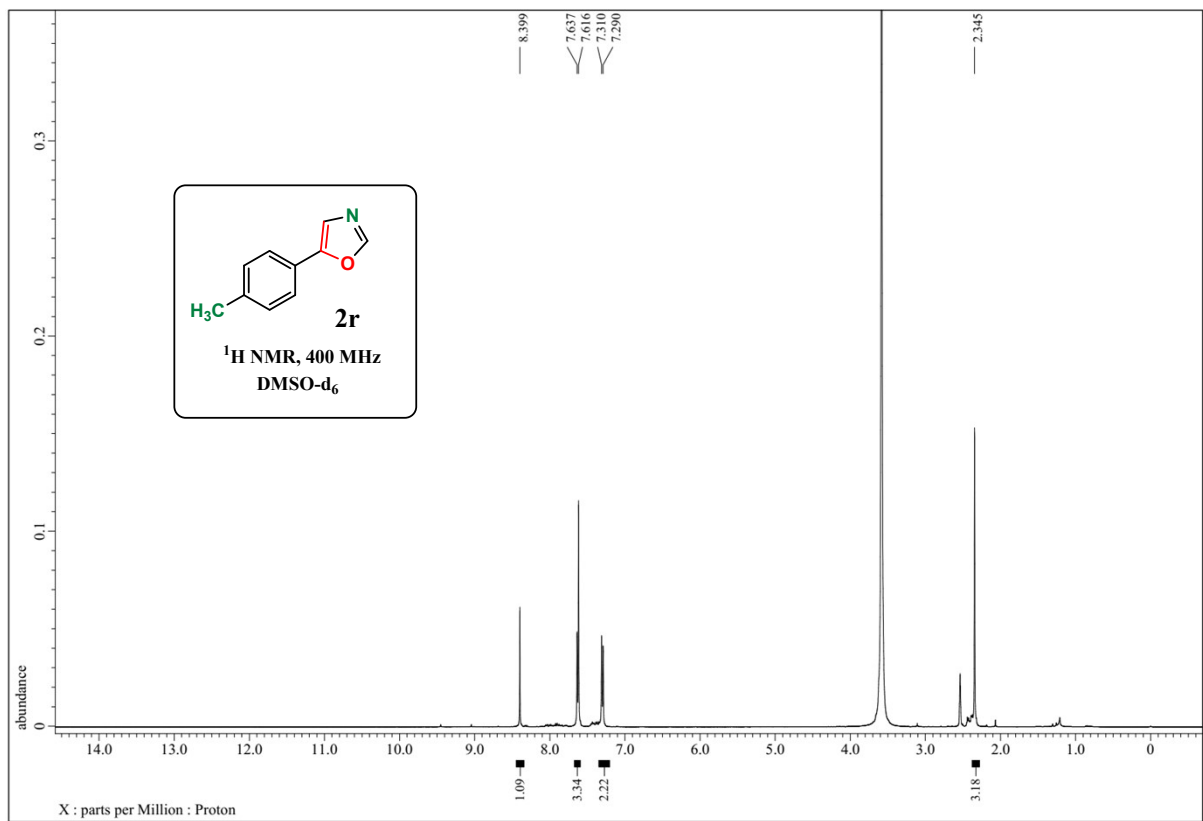


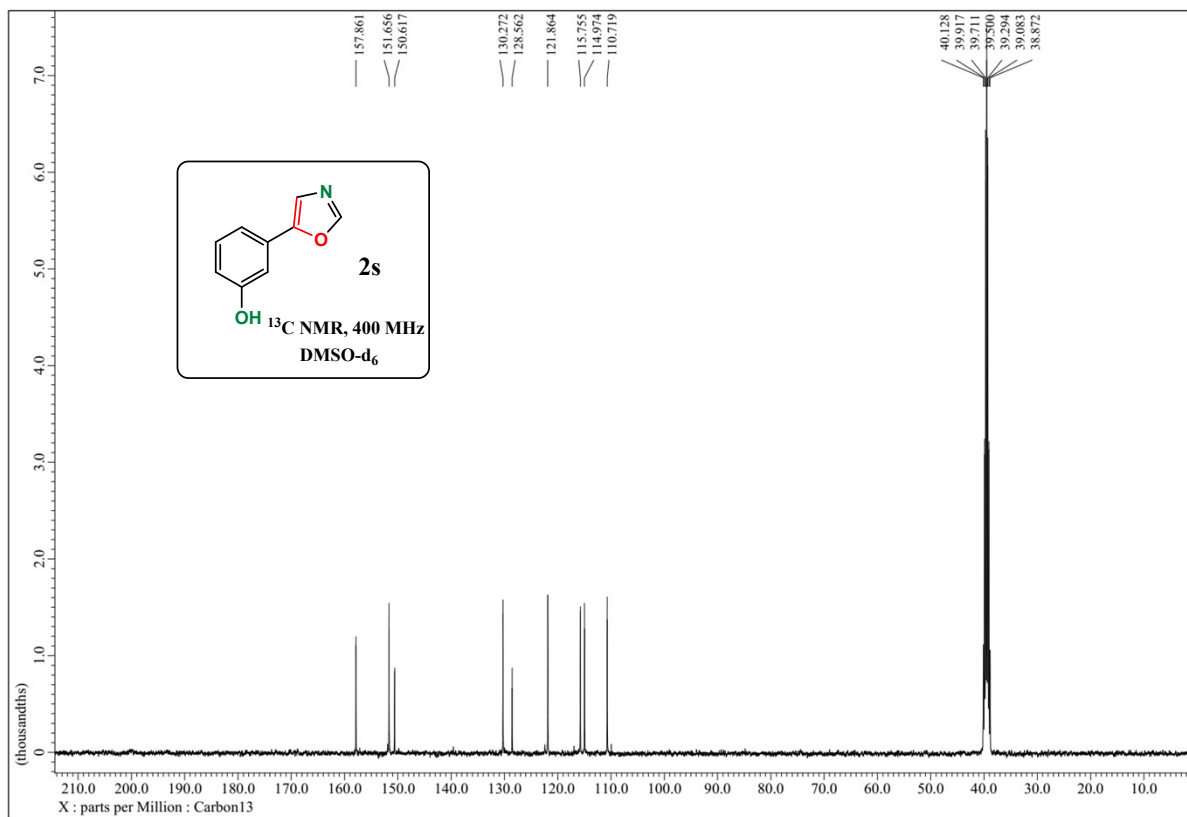
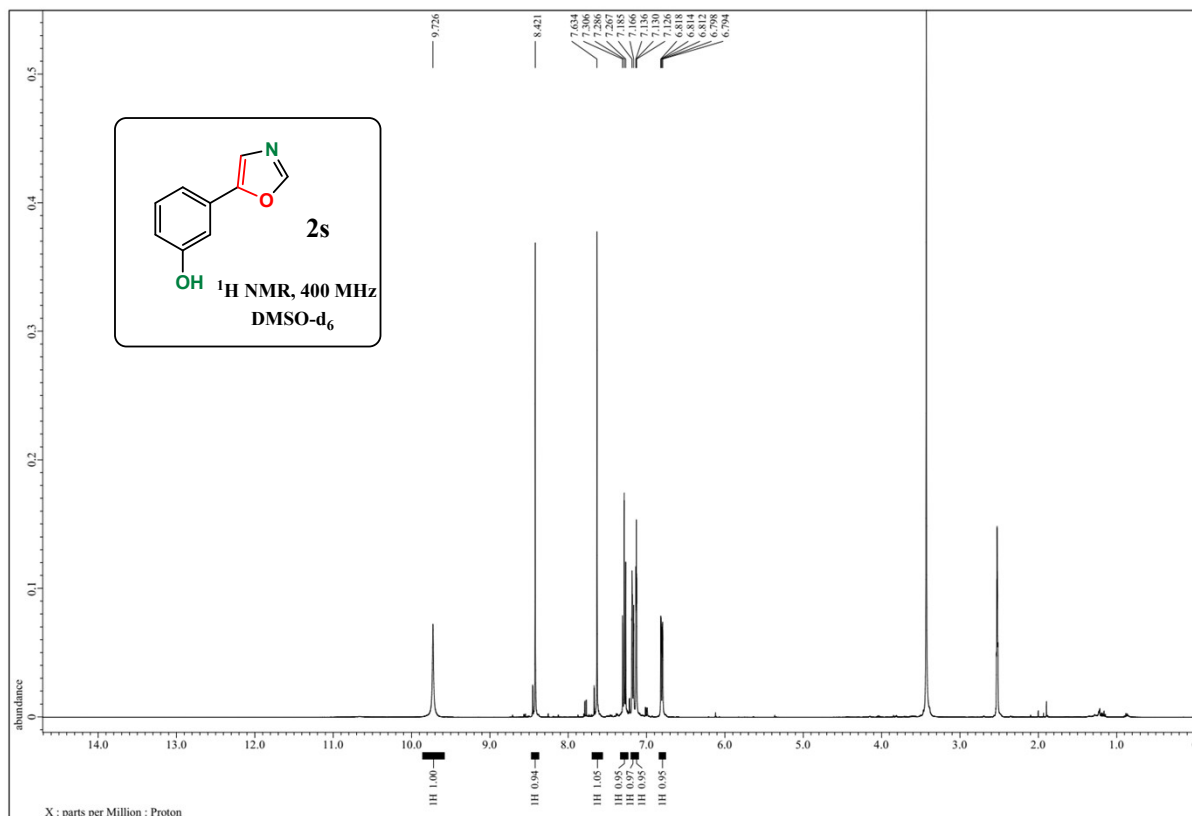


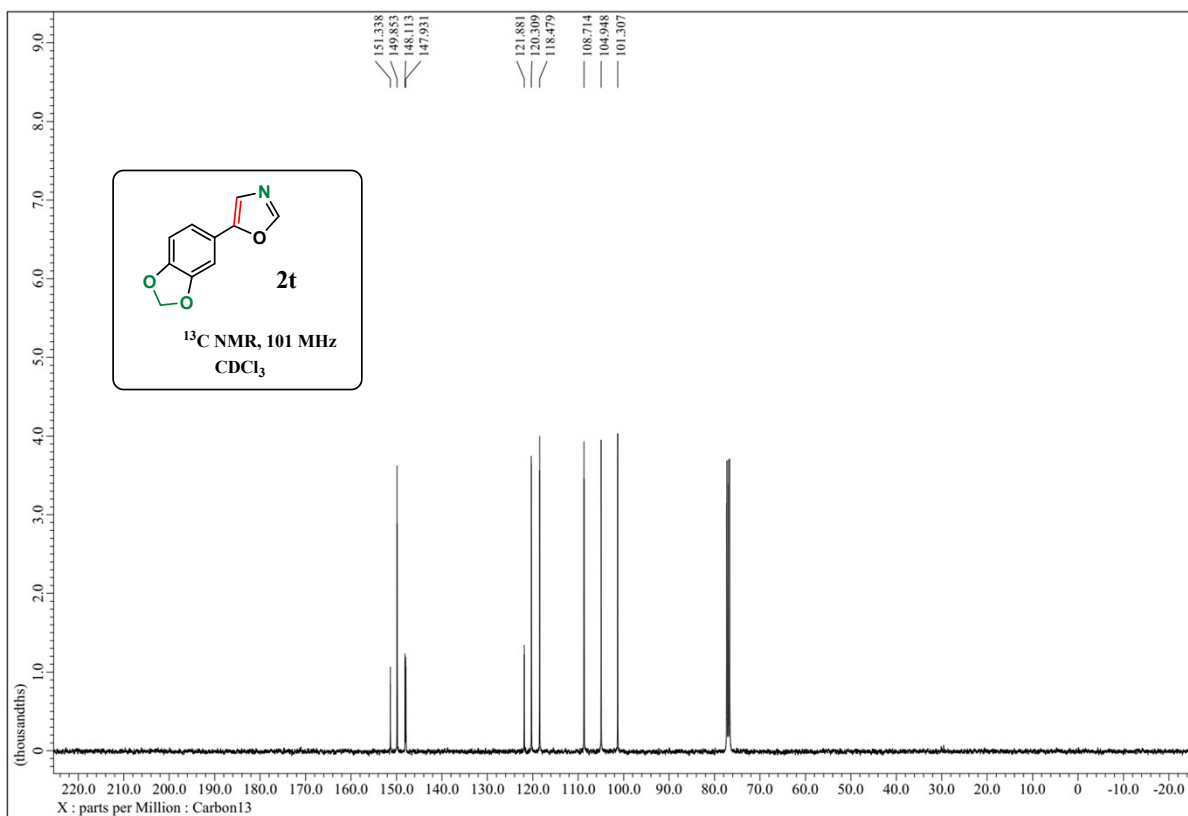
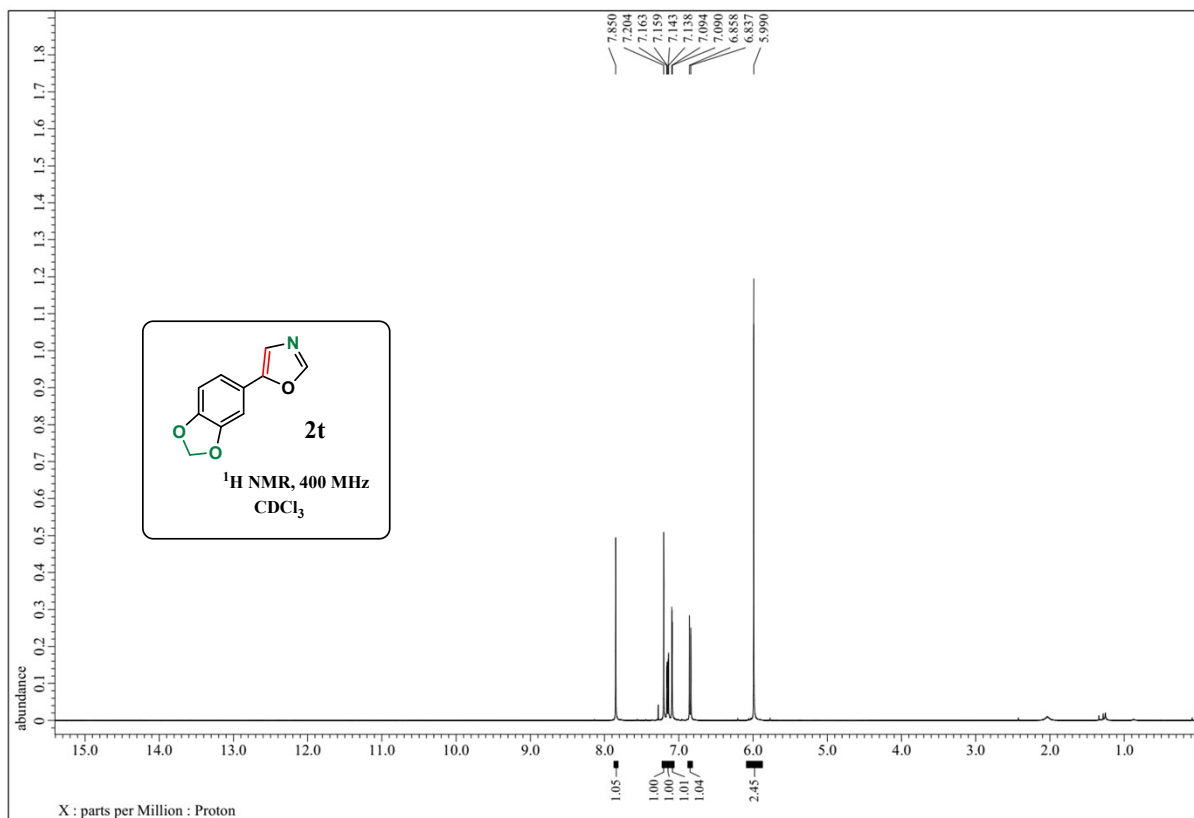


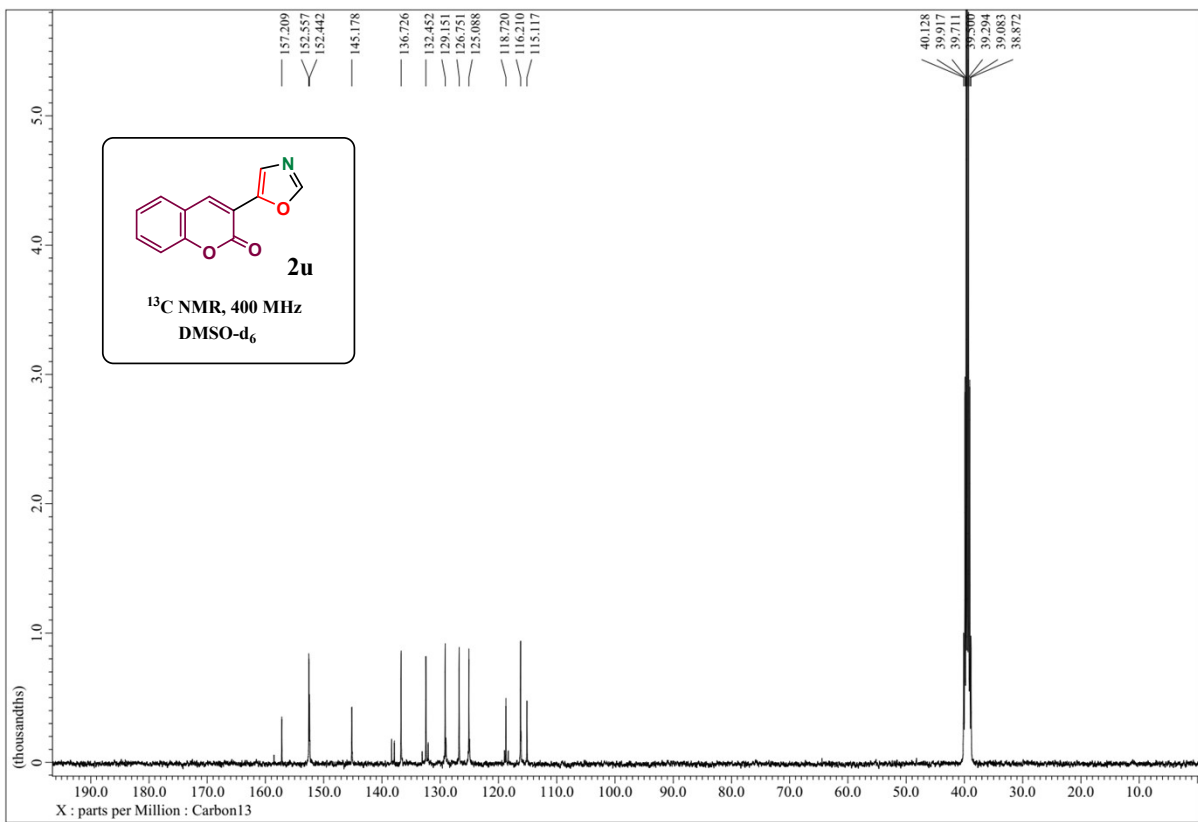
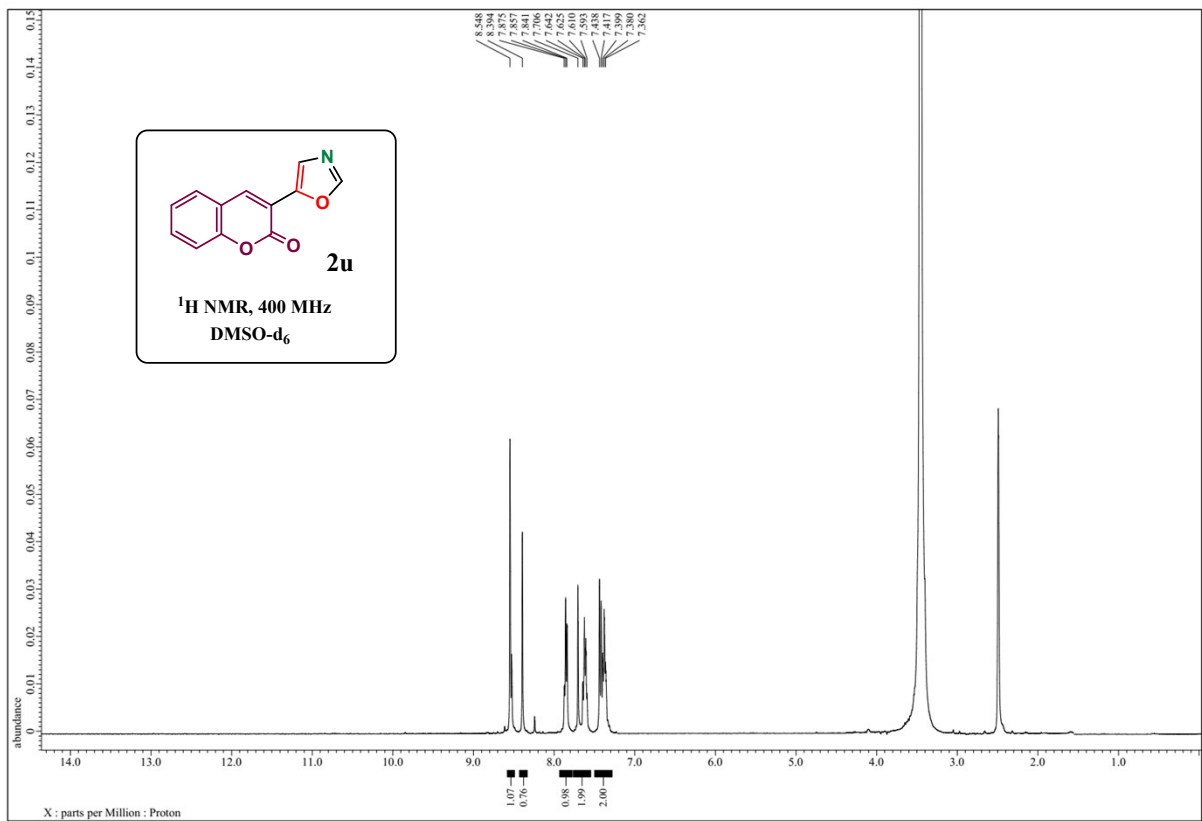


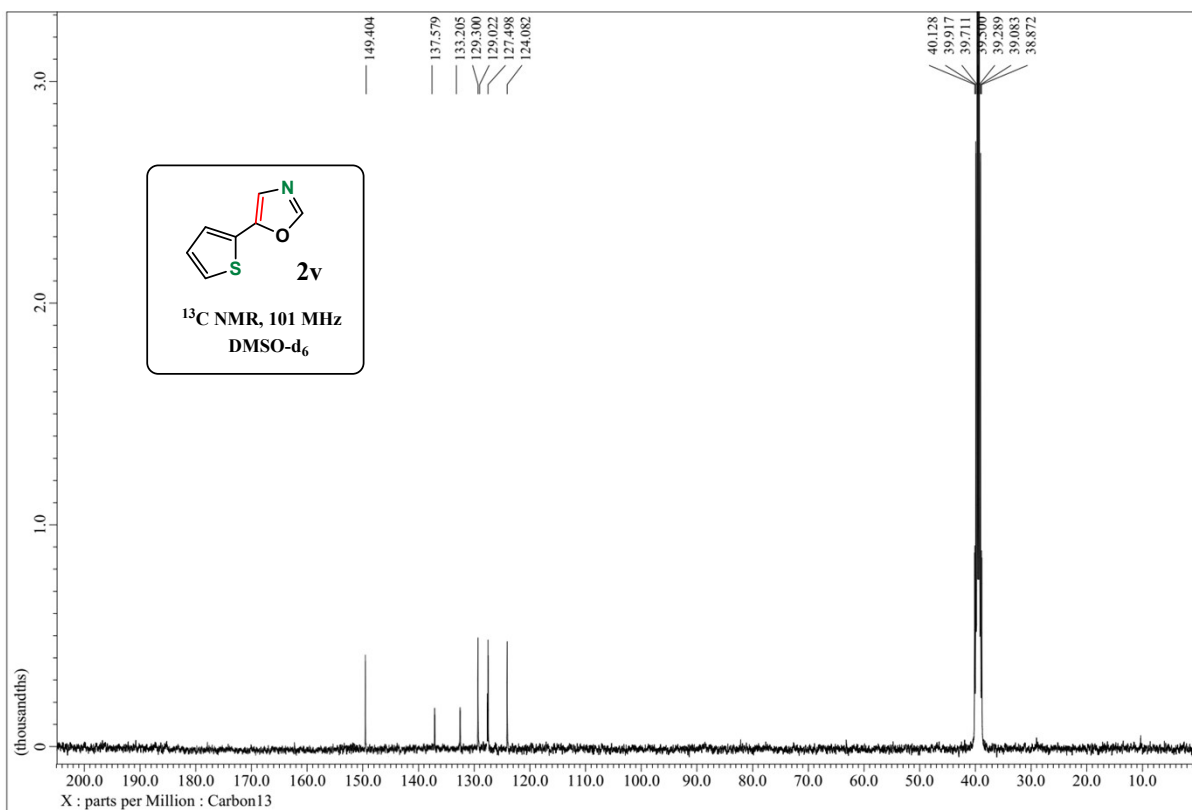
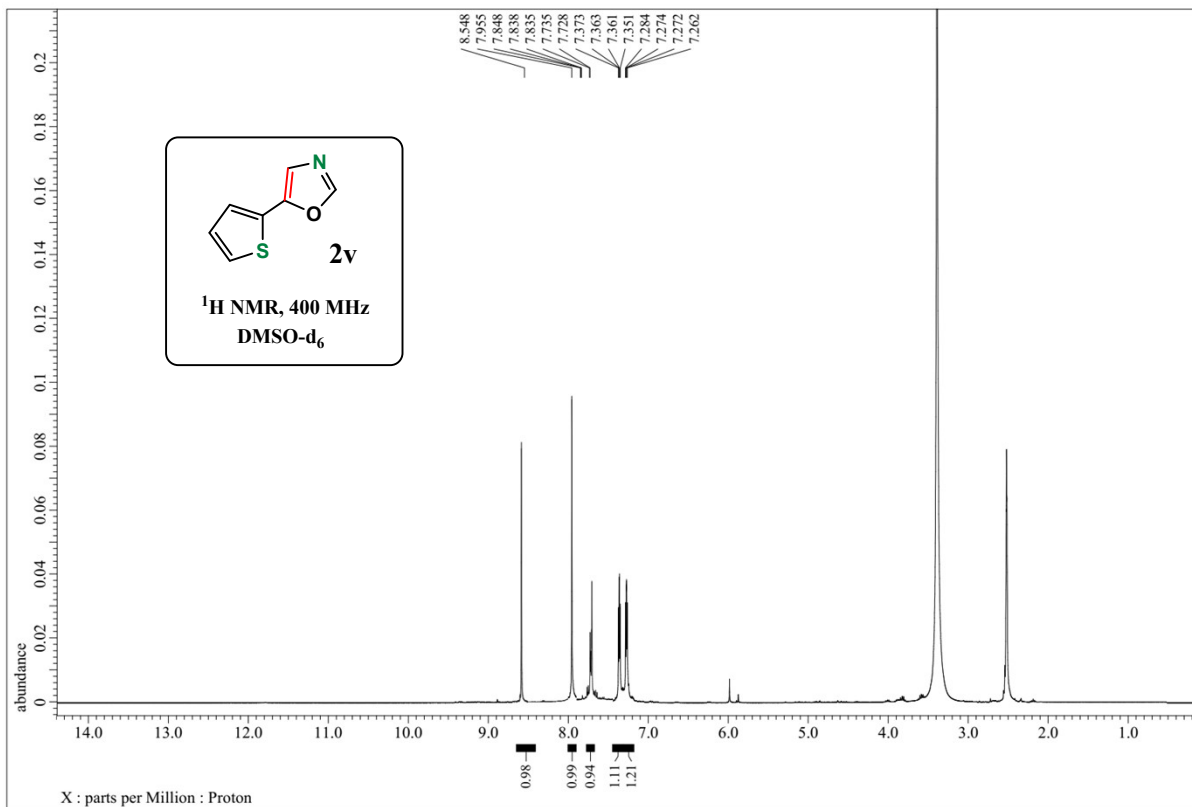


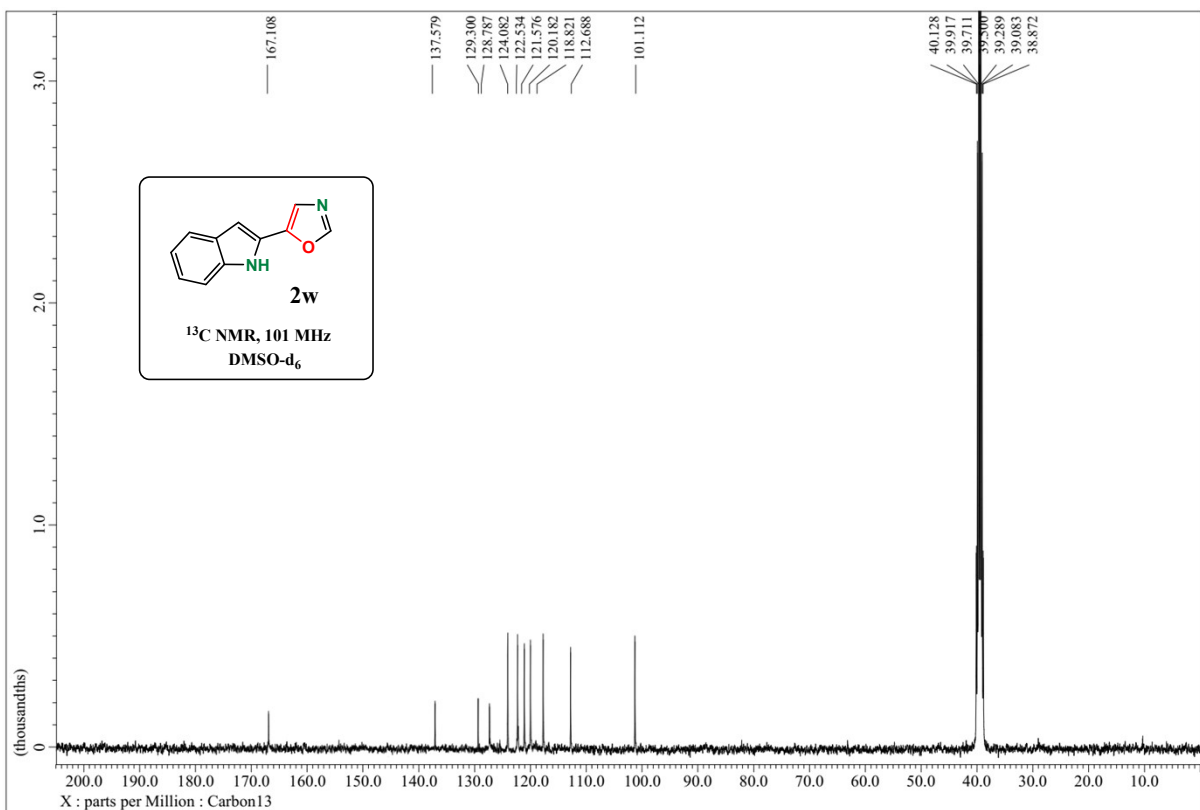
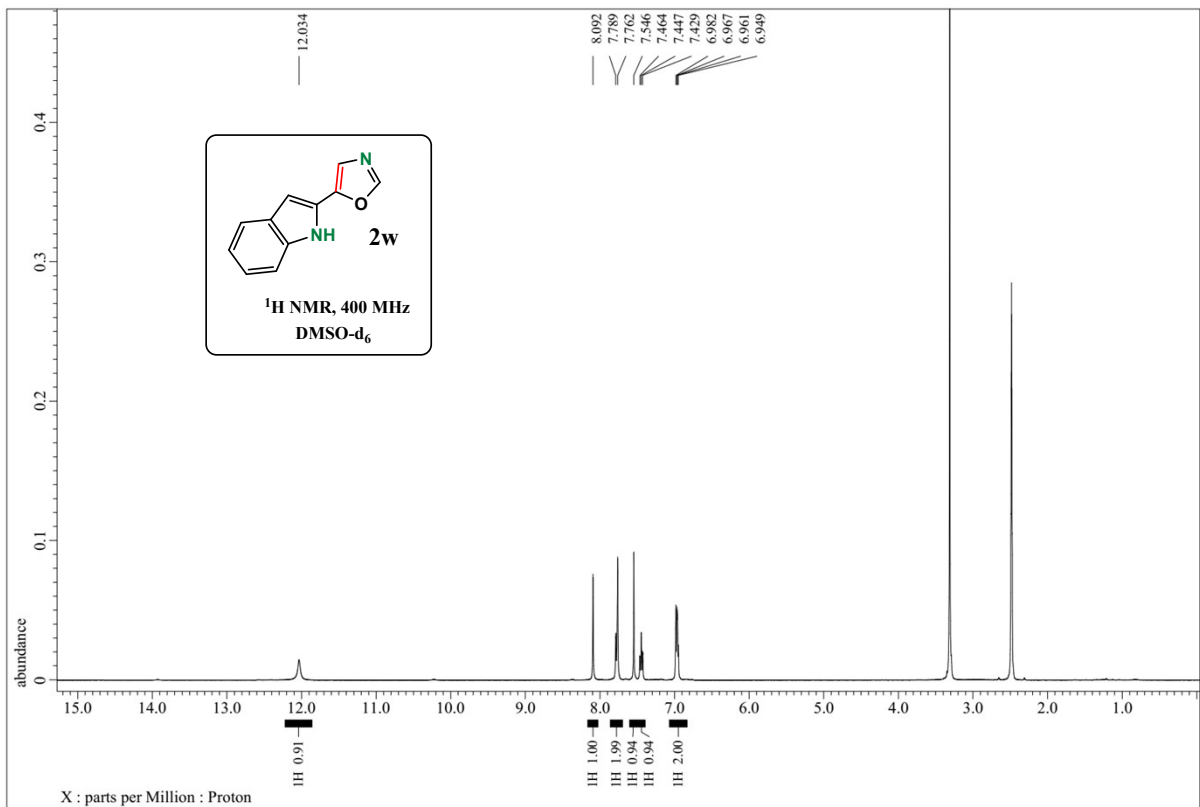


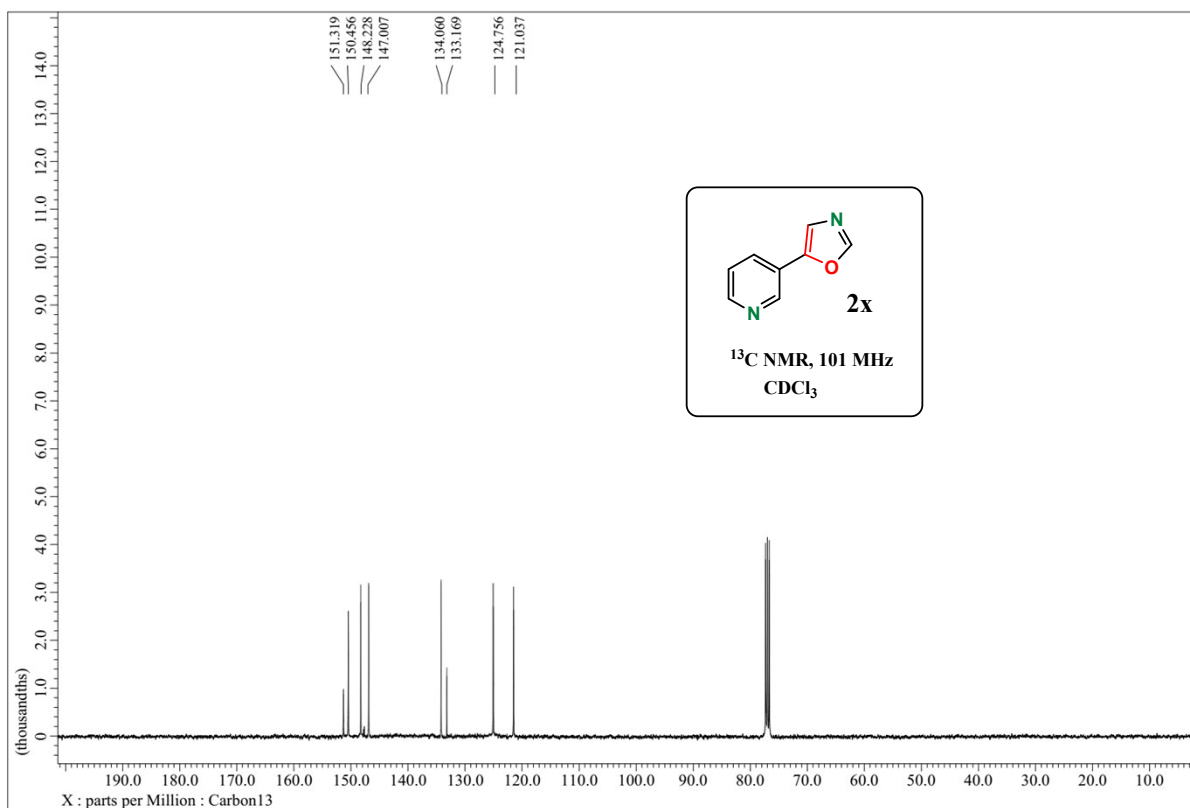
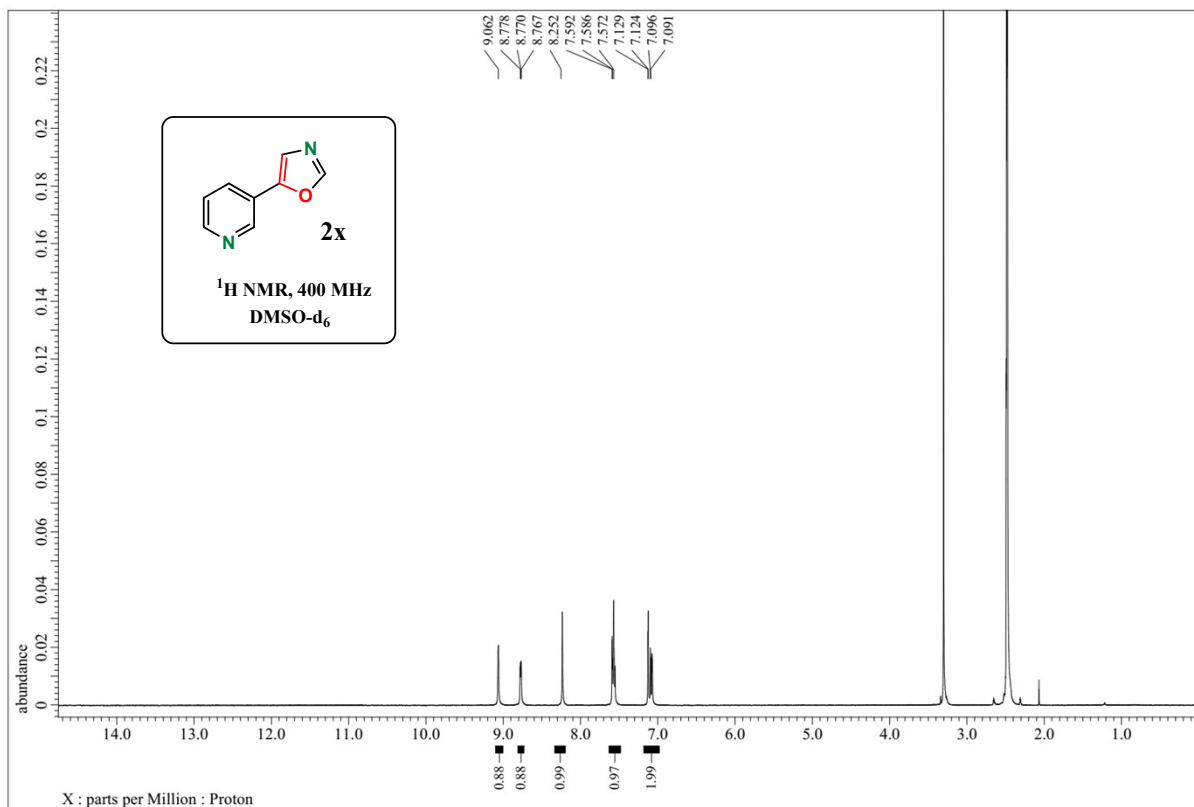


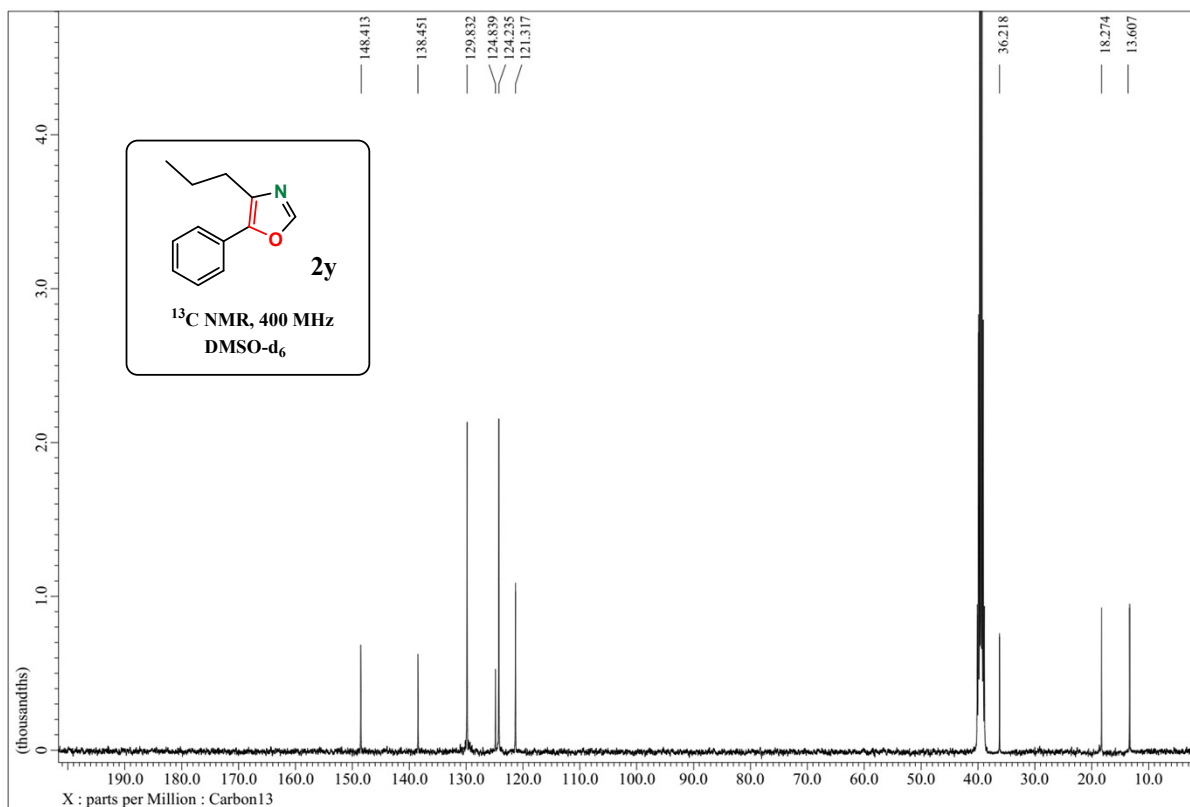
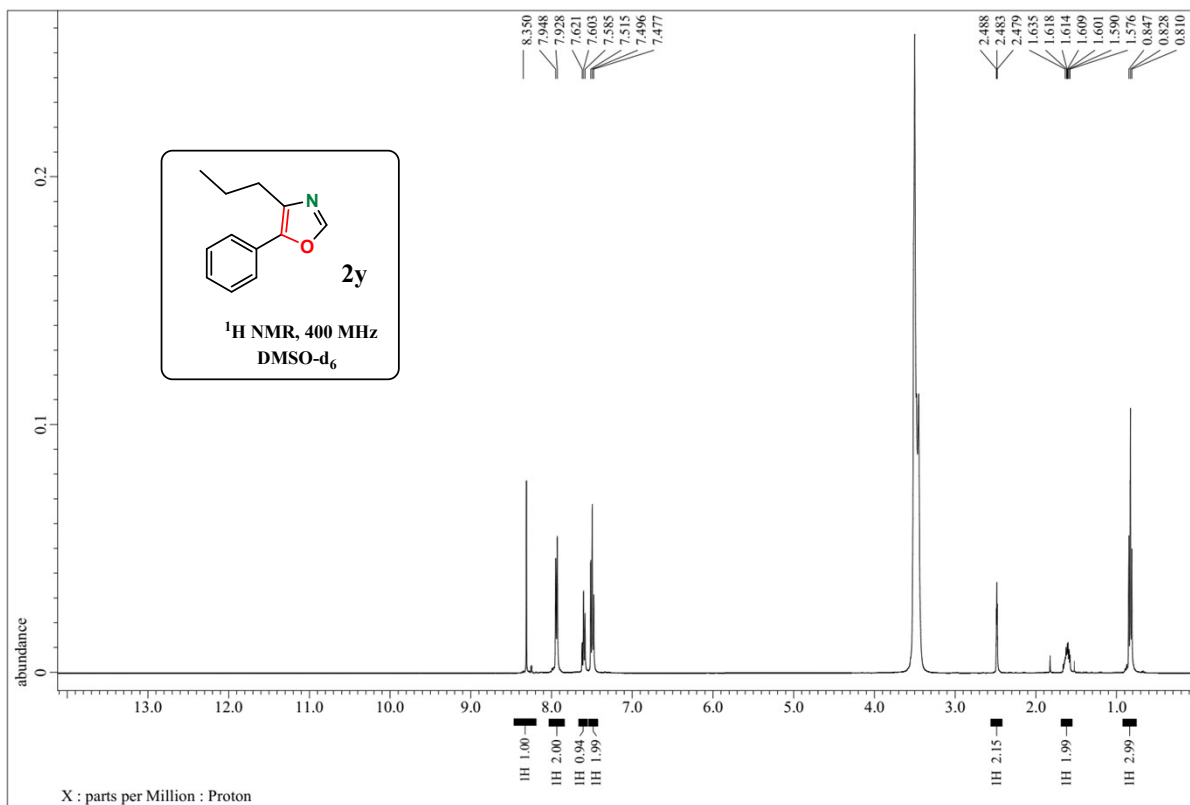


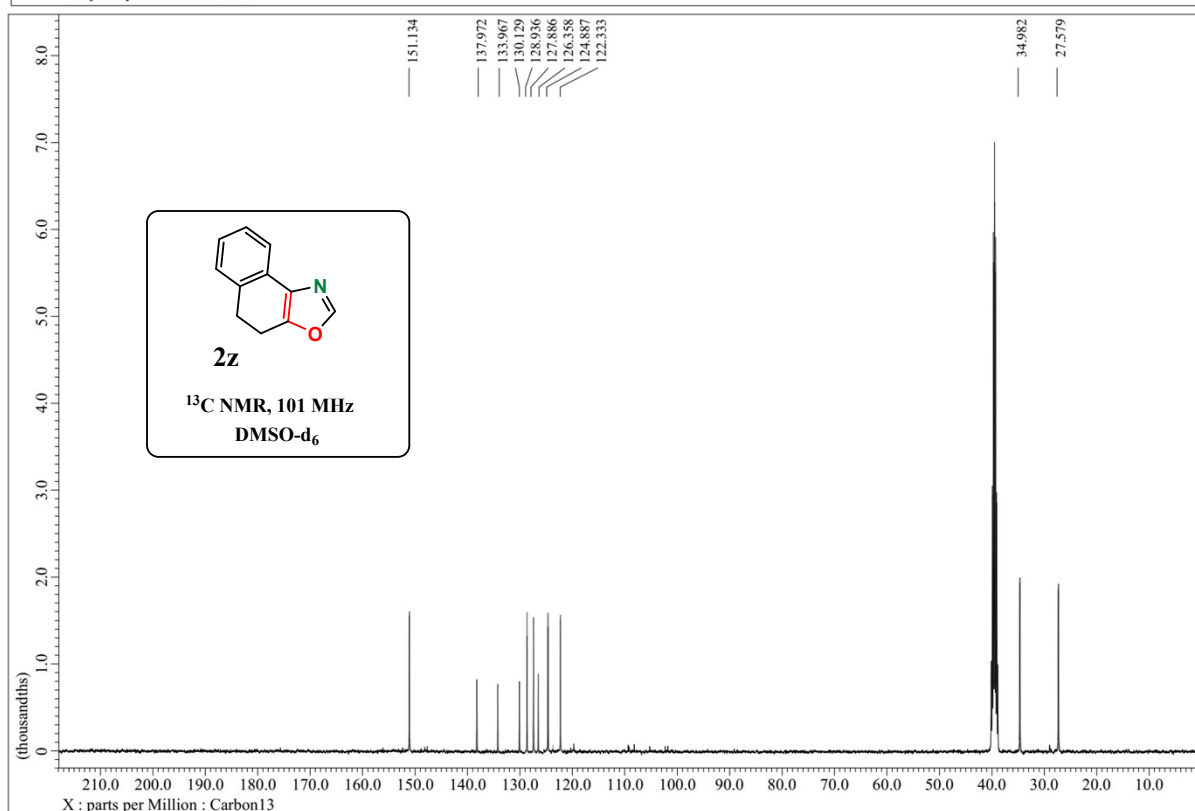
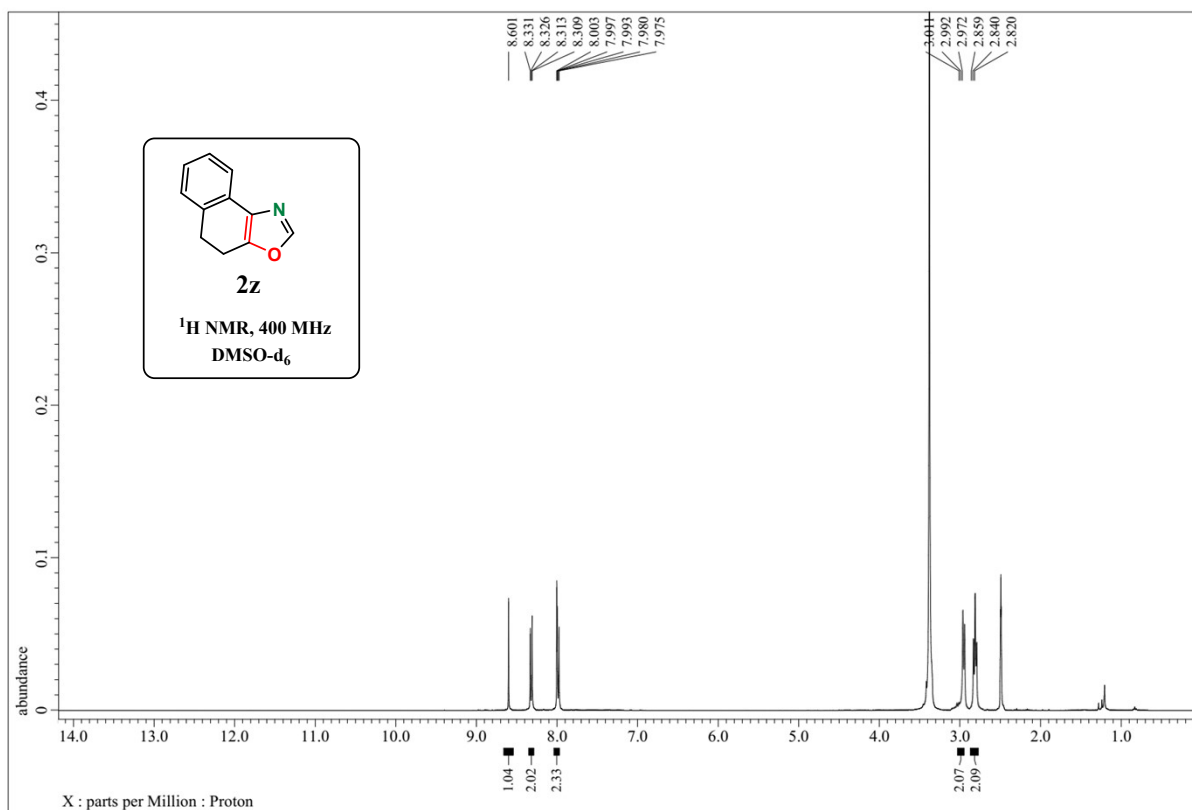


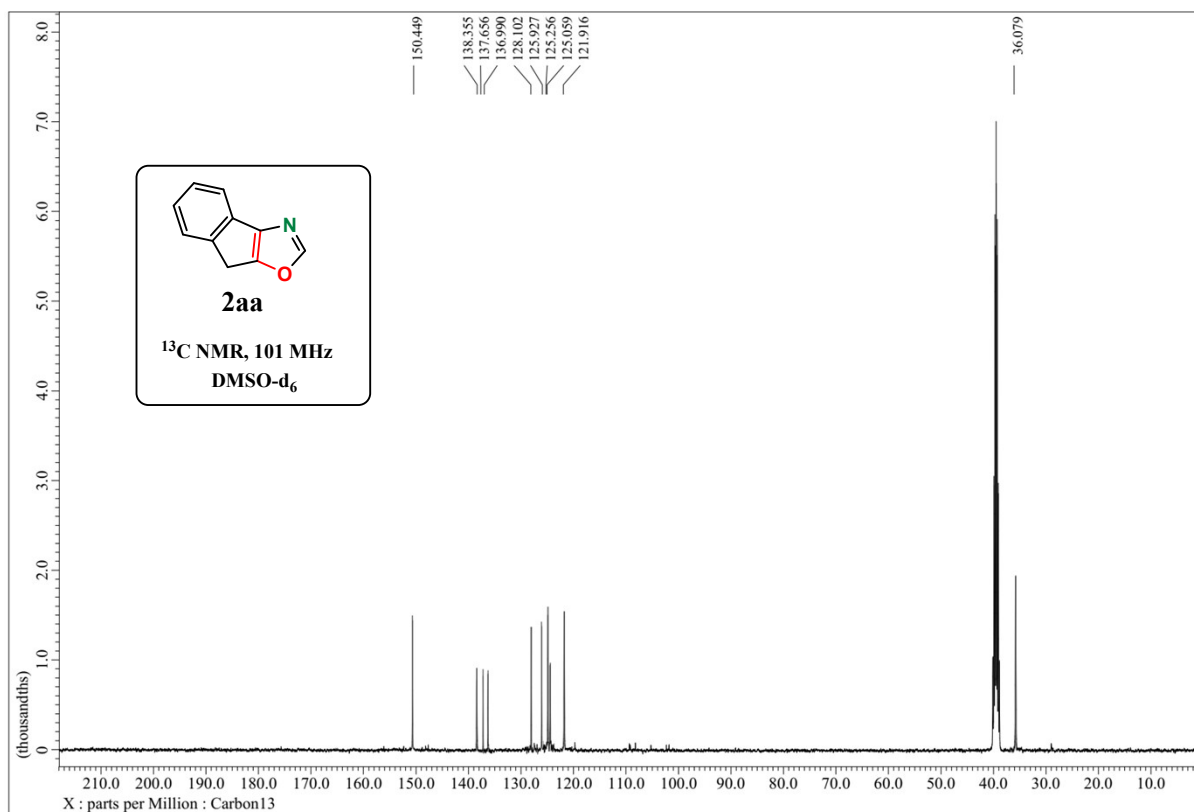
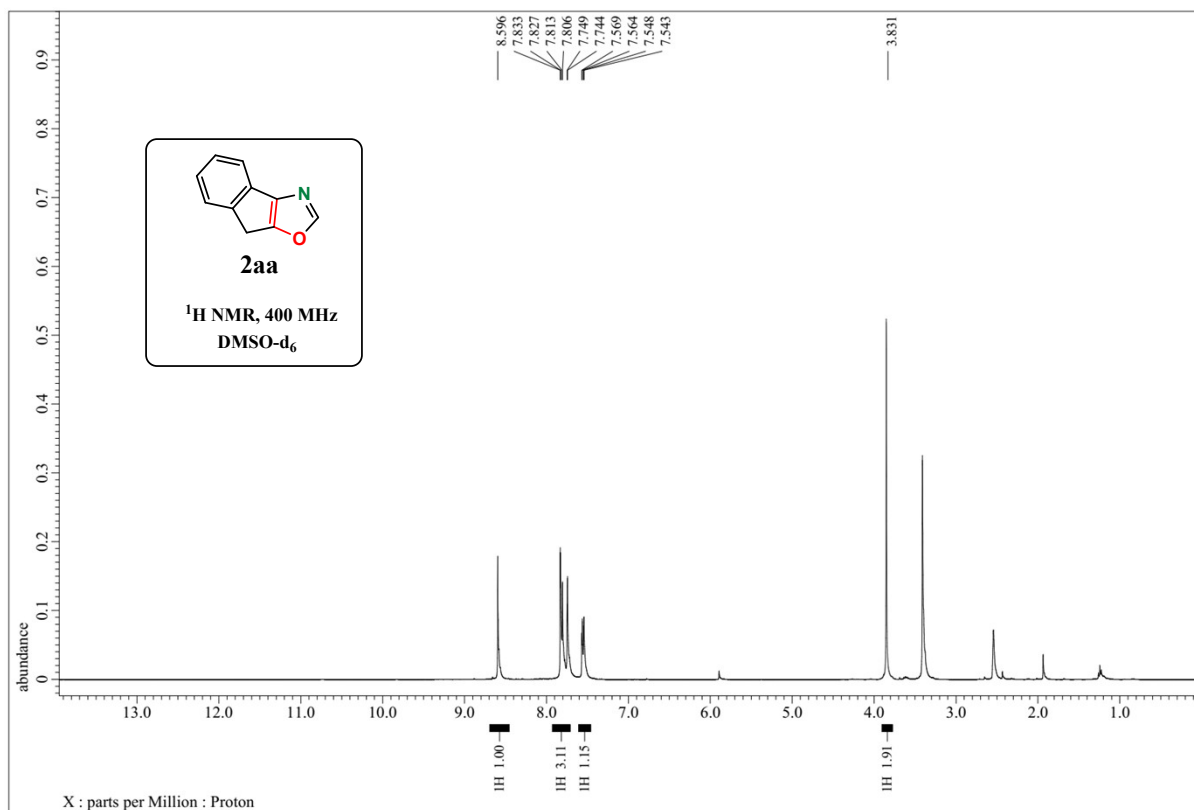


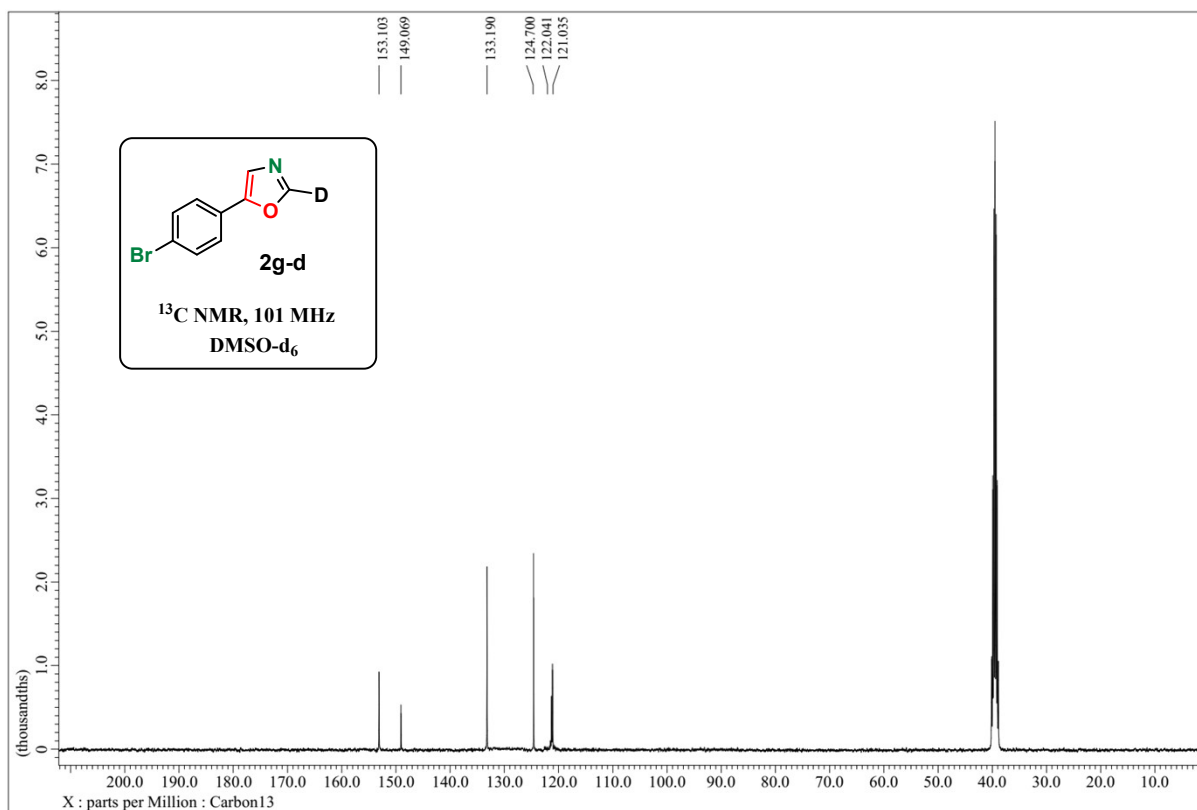
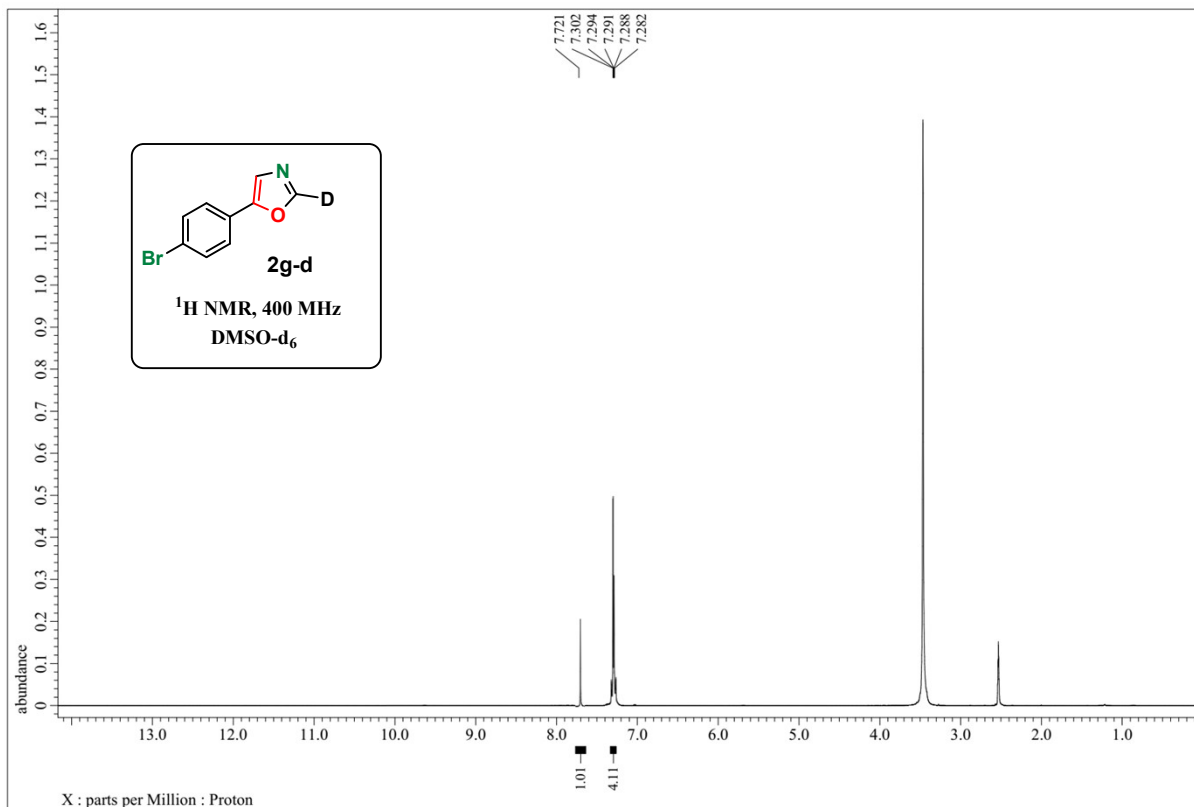


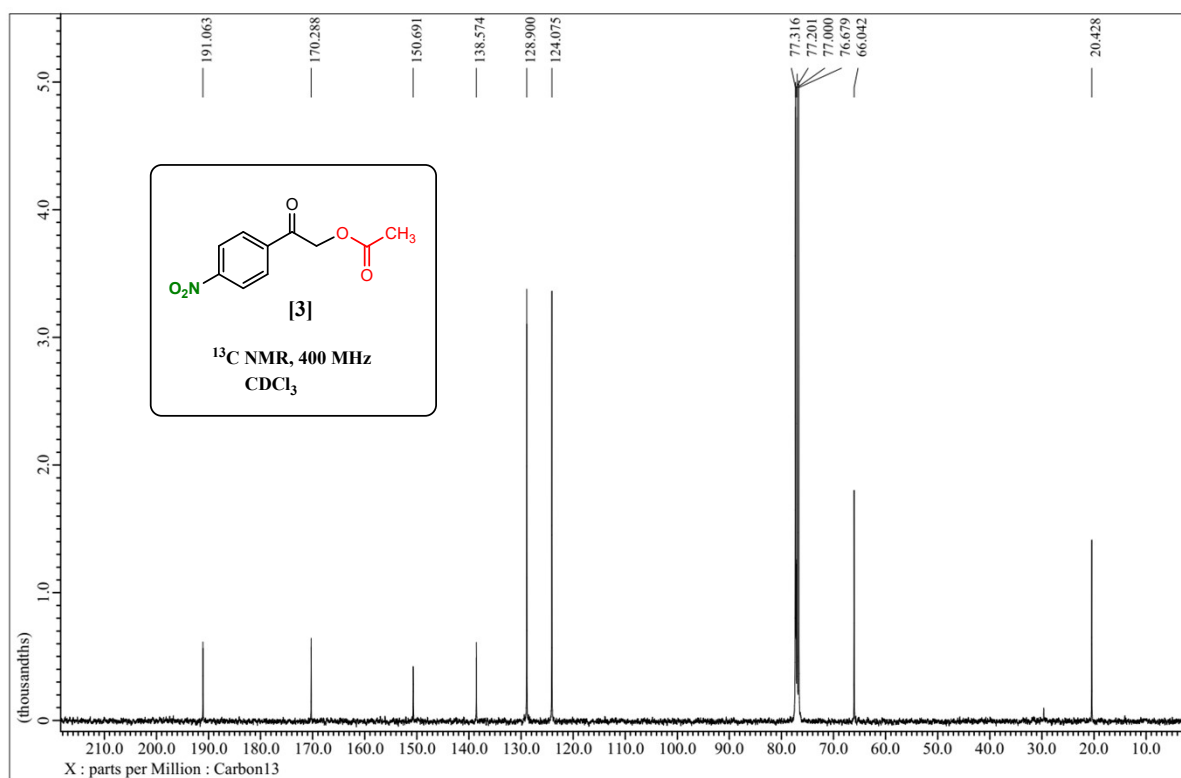
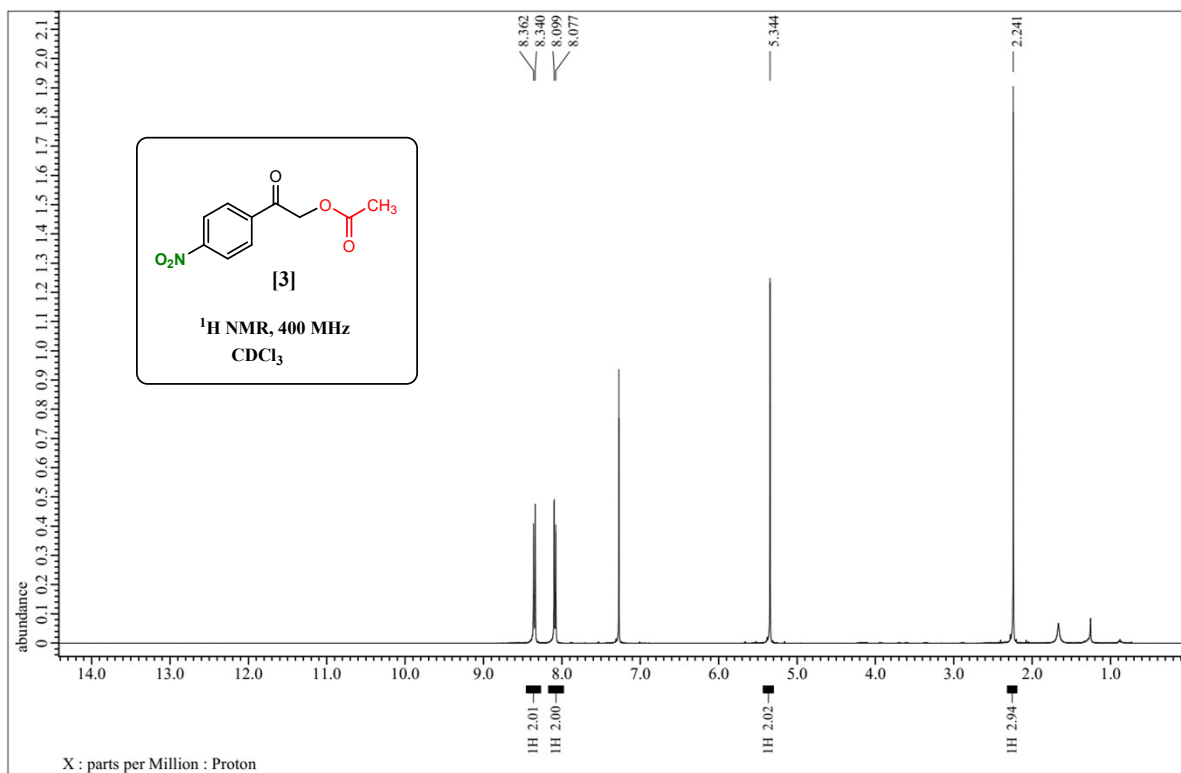


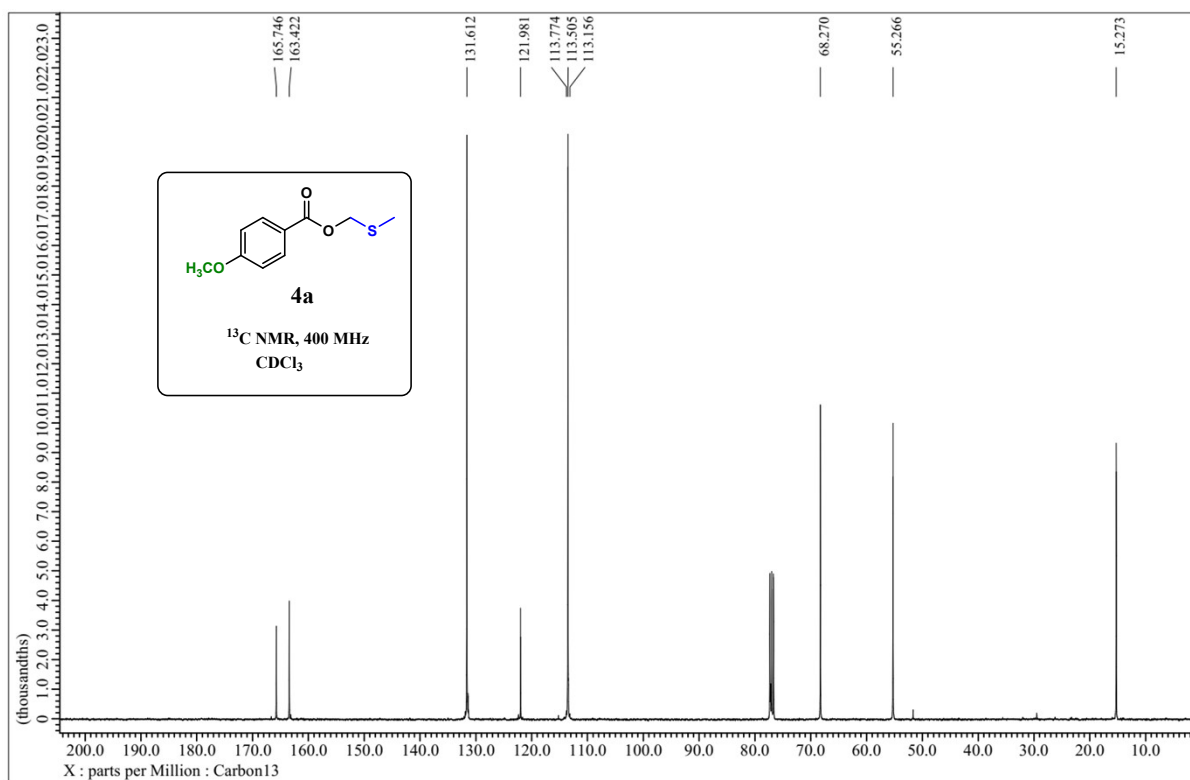
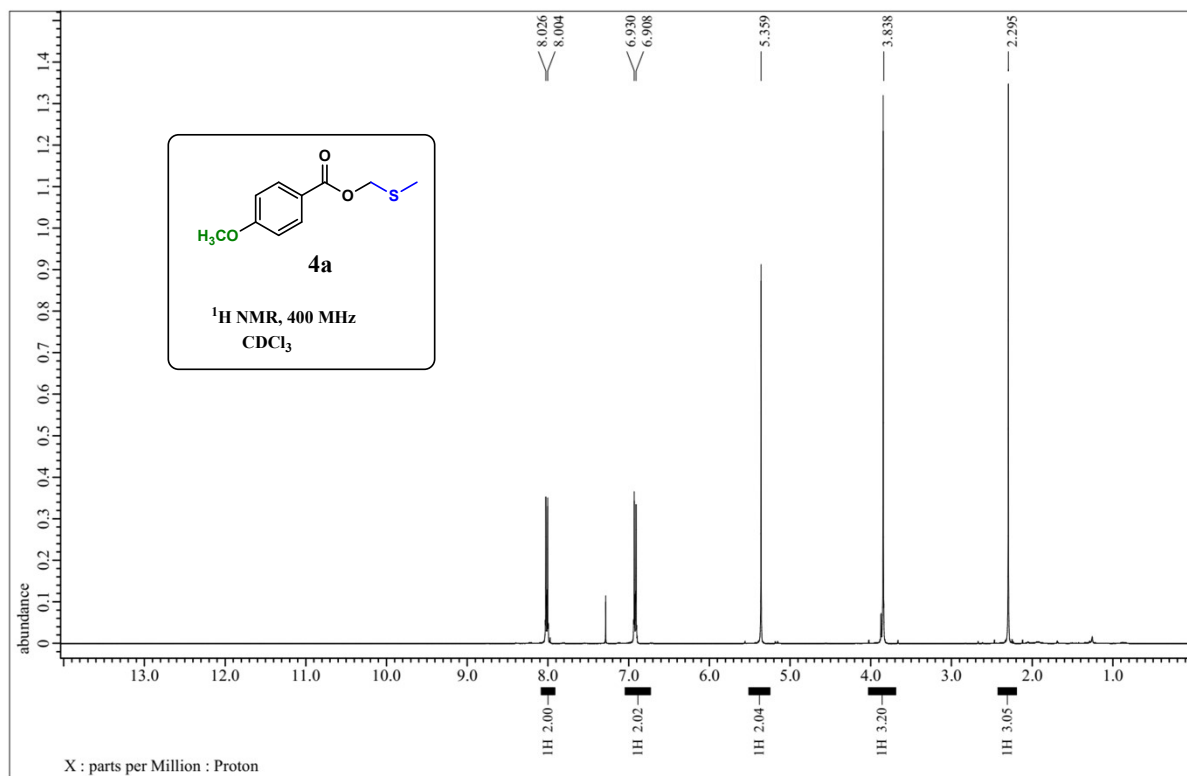


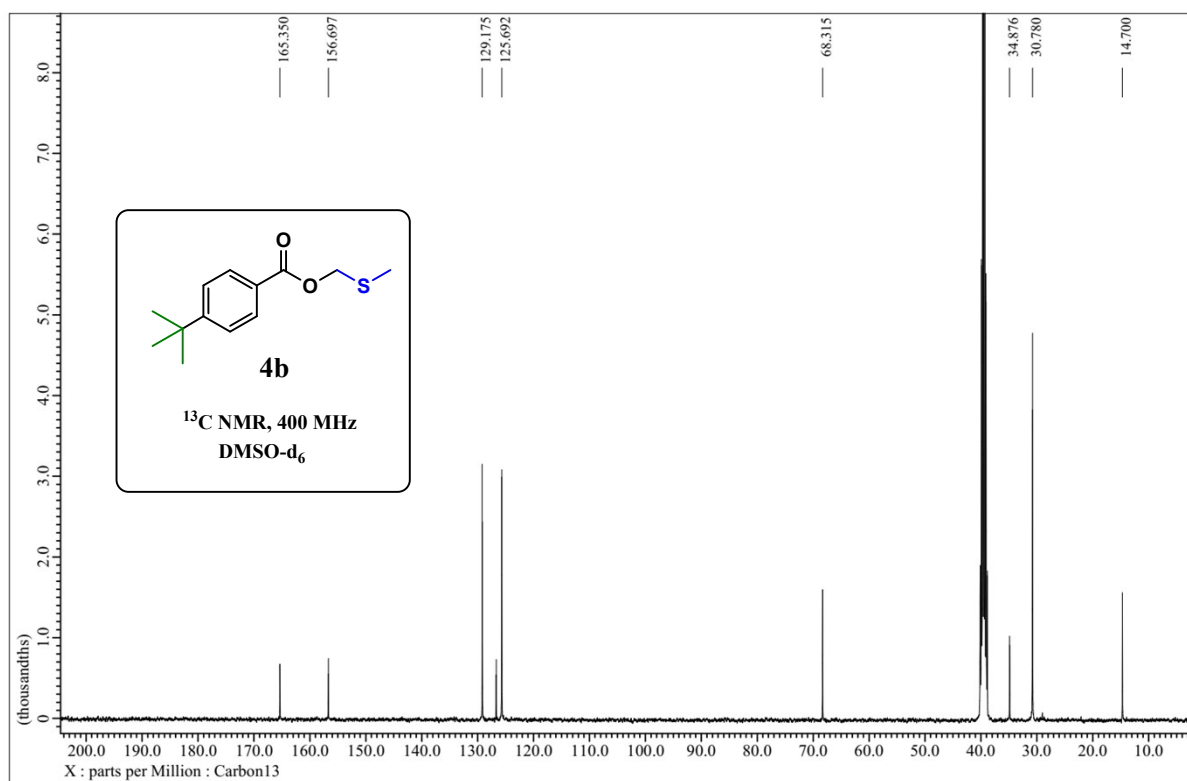
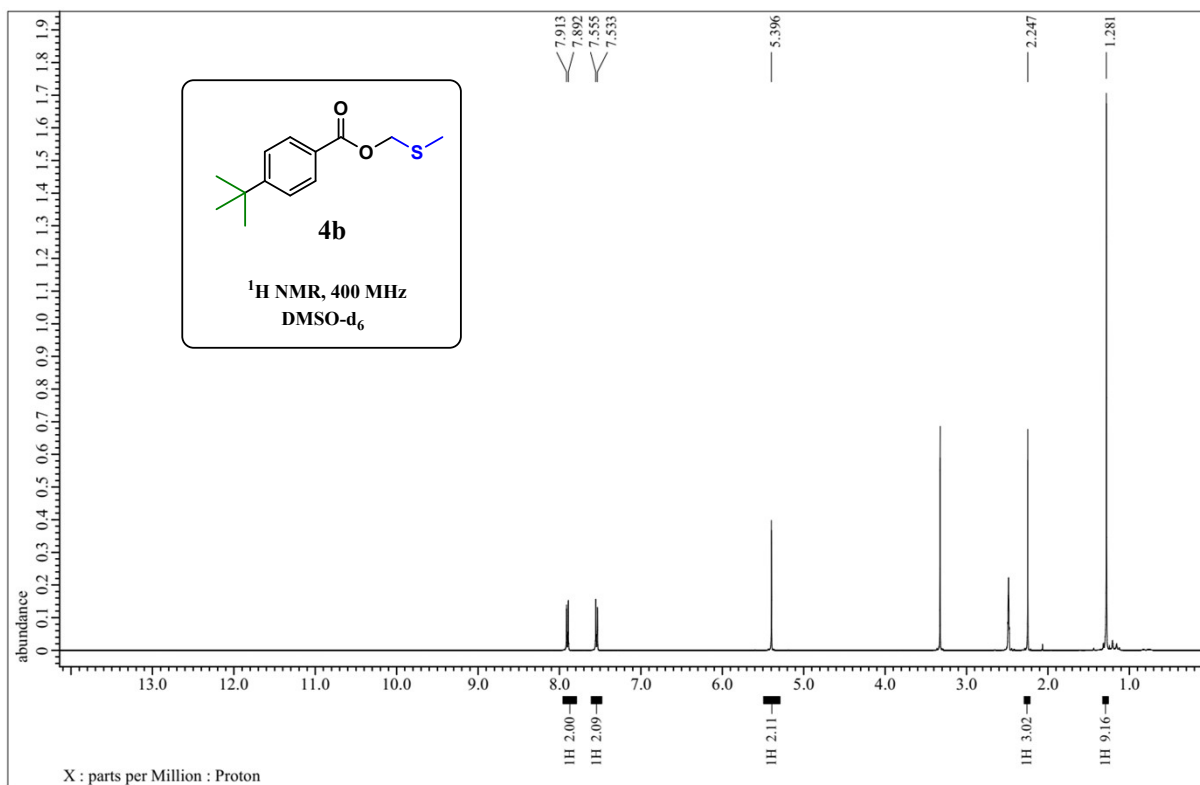


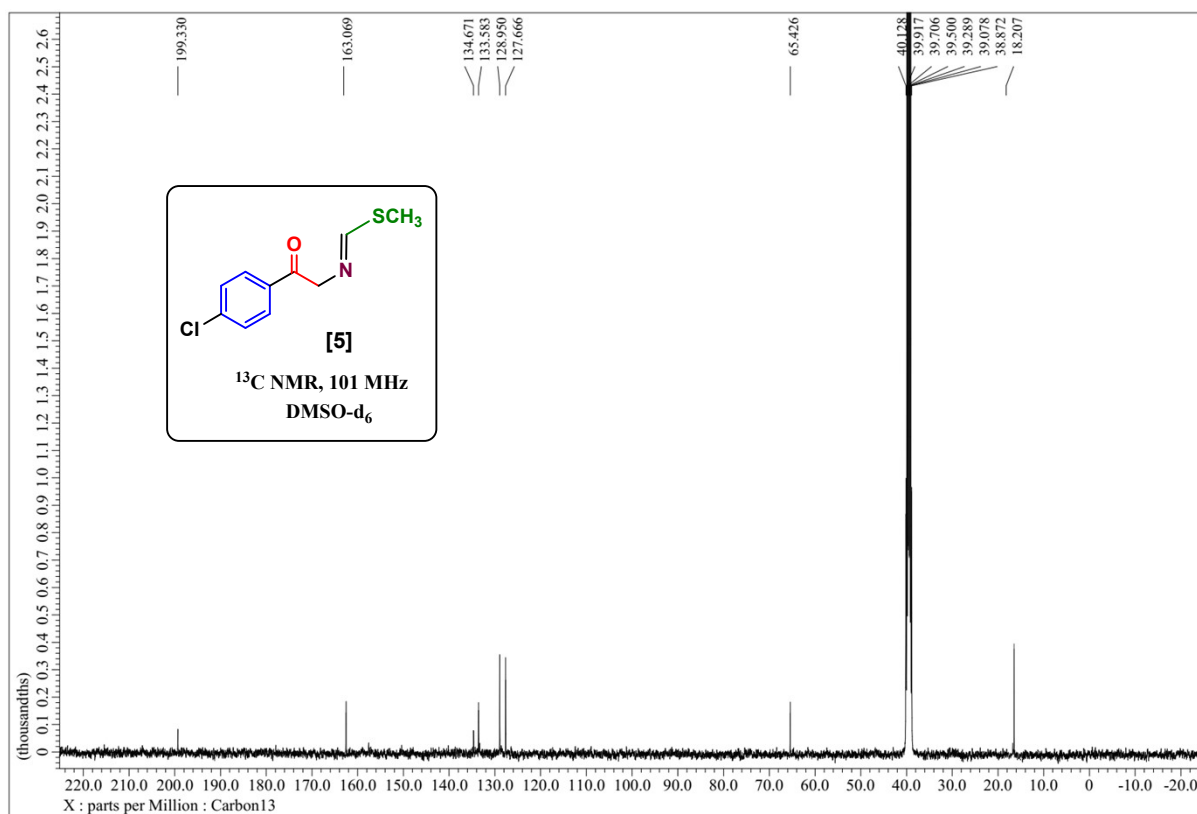
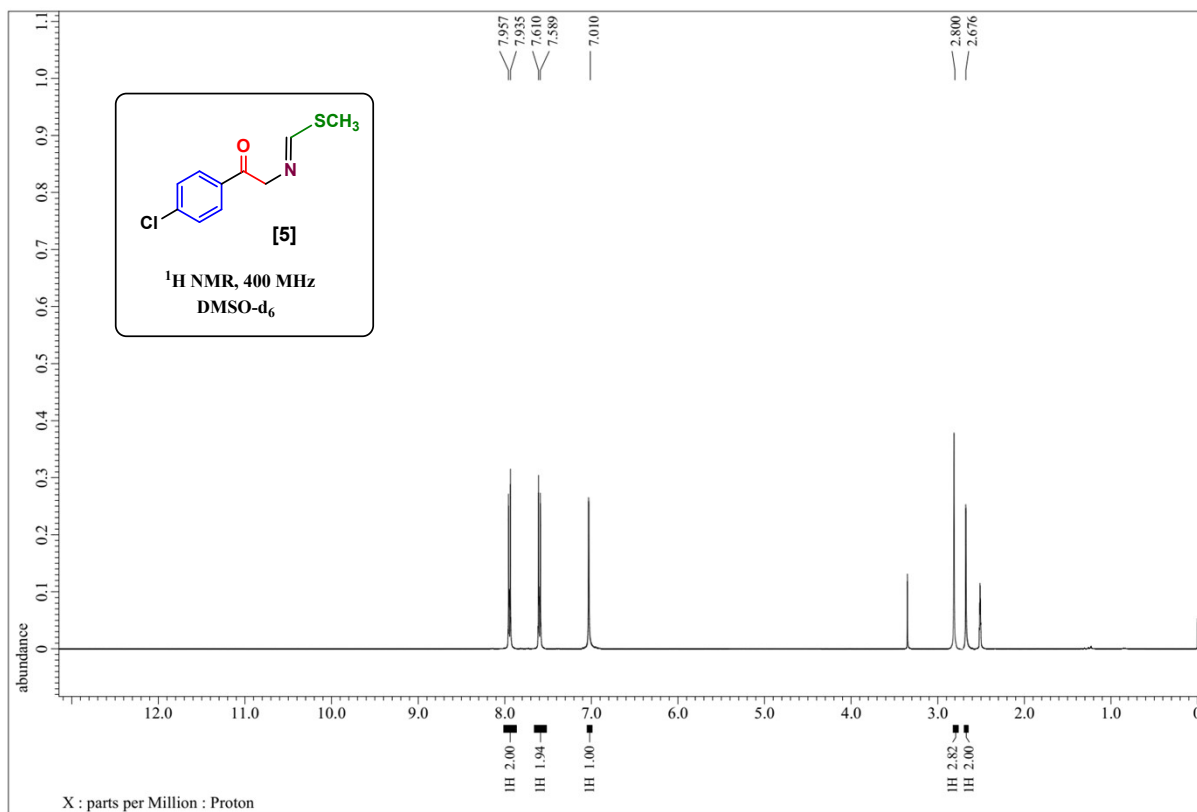












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