Ruthenium-Catalyzed *meta*-Selective C – H Nitration of various azole ring-substituted arenes

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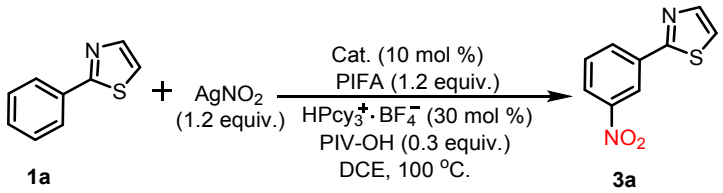
1. General Information

All reactions were carried out with magnetic stirring and in dried glassware. Standard syringe techniques were applied for transfer of dry solvents. All reagents and solvents were commercially available and used without any further purification unless specified. Proton (^{1}H NMR) and carbon (^{13}C NMR) nuclear magnetic resonance spectra were recorded at 400 MHz and 100 MHz respectively. The chemical shifts are given in parts per million (ppm) on the delta (δ) scale. ^{1}H NMR chemical shifts were determined relative to internal TMS at δ 0.0 ppm. ^{13}C NMR chemical shifts were determined relative to $CDCl_3$ at δ 77.00 ppm. The following abbreviations were used to explain multiplicities: s =singlet, d =doublet, dd = doublet of doublet, t = triplet, td = triplet of doublet, q = quartet, m = multiplet, and br = broad. Analytical TLC was performed on precoated silica gel plates. High-resolution mass spectra (HRMS) were obtained on an Agilent mass spectrometer using ESI-TOF (electrospray ionization-time of flight).

2. Optimization of Reaction Conditions

Table S1. Screening the catalysts in standard conditions

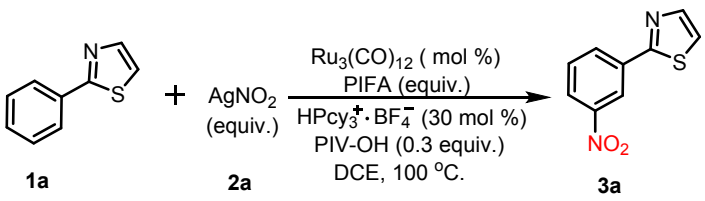


Entry	Catalysts (10 mol %)	Yield[b] (%, **3a**)
1	$RuCl_3$	0%
2	$[RuCl_2(p\text{-cymene})]_2$	0%
3	$Ru(acac)_3$	0%
4	$[Ru(O_2CMes)_2(p\text{-cymene})]$	0%

[a] Reaction conditions: **1a** (0.2 mmol), $AgNO_2$ (1.2 equiv.), Catalysts (10 mol %), $HPcy_3^+ \cdot BF_4^-$ (30 mol %), PIFA (1.2 equiv.) and PIV-OH (0.3 equiv.) in DCE (2 mL) for 24 h at 100 °C in a sealed tube.

[b] Yield was determined by ^{1}H NMR analysis using CH_2Br_2 as an internal standard.

Table S2. Screening loadings of $Ru_3(CO)_{12}$, $AgNO_2$ and PIFA

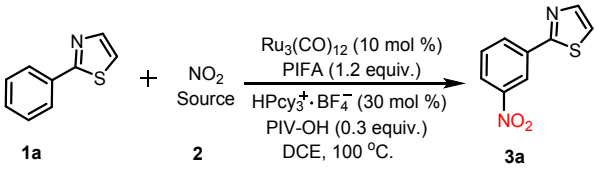


Entry	Catalysts (mol %)	PIFA (equiv.)	$AgNO_2$ (equiv.)	Yield[b] (%, **3a**)
1	$Ru_3(CO)_{12}$ (5)	1.2	1.2	61%
2	$Ru_3(CO)_{12}$ (20)	1.2	1.2	85%
3	$Ru_3(CO)_{12}$ (10)	1.0	1.2	77%
4	$Ru_3(CO)_{12}$ (10)	1.5	1.2	86%
5	$Ru_3(CO)_{12}$ (10)	1.2	1.0	73%
6	$Ru_3(CO)_{12}$ (10)	1.2	1.5	85%

[a] Reaction conditions: **1a** (0.2 mmol), $AgNO_2$ (equiv.), $Ru_3(CO)_{12}$ (10 mol %), $HPcy_3^+ \cdot BF_4^-$ (30 mol %), PIFA (equiv.) and PIV-OH (0.3 equiv.) in DCE (2 mL) for 24 h at 100 °C in a sealed tube.

[b] Yield was determined by ^1H NMR analysis using CH_2Br_2 as an internal standard.

Table S3. Screening the nitrating source



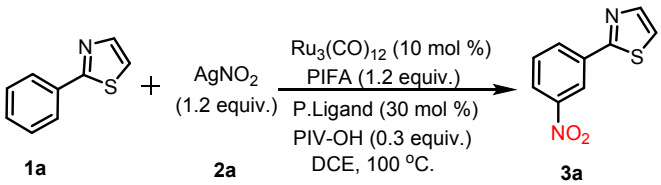
Entry	NO_2 Source	Yield[b] (%, **3a**)
1	TBN [c]	6%
2	$NaNO_2$	10%
3	$AgNO_3$	78%
4	$AgNO_2$	85%
5	$Fe(NO_3)_3 \cdot 9H_2O$	13%
6	$Cu(NO_3)_2 \cdot 3H_2O$	28%

[a] Reaction conditions: **1a** (0.2 mmol), NO_2 Source (1.2 equiv.), $Ru_3(CO)_{12}$ (10 mol %), $HPcy_3^+ \cdot BF_4^-$ (30 mol %), PIFA (1.2 equiv) and PIV-OH (0.3 equiv.) in DCE (2 mL) for 24 h at 100 °C in a sealed tube.

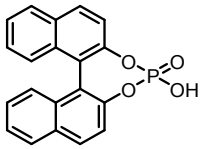
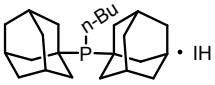
[b] Yield was determined by ^1H NMR analysis using CH_2Br_2 as an internal standard.

[c] TBN= *tert*-Butyl nitrite.

Table S4. Screening of P.Ligands



Entry	P.Ligand (30 mmol %)	Yield[b] (%, **3a**)
1	PPh_3	31%
2	PCy_2	46%
3	PCy_3	64%
4	$P(4\text{-}CH_3C_6H_4)_3$	41%

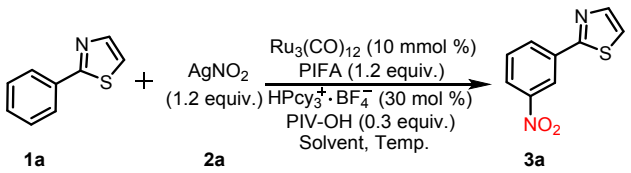
5	$P(4\text{-}CF_3C_6H_4)_3$	48%
6		35%
7		37%

[a] Reaction conditions: **1a** (0.2 mmol), $AgNO_2$ (1.2 equiv.), $Ru_3(CO)_{12}$ (10 mol %), P.Ligand (30 mol %), PIFA (1.2 equiv) and PIV-OH (0.3 equiv.) in DCE (2 mL) for 24 h at 100 °C in a sealed tube.

[b] Yield was determined by ^1H NMR analysis using CH_2Br_2 as an internal standard.

[c] PCy_2= dicyclohexylphosphane, PCy_3= tricyclohexylphosphane.

Table S5. Screening of solvents and tempertures

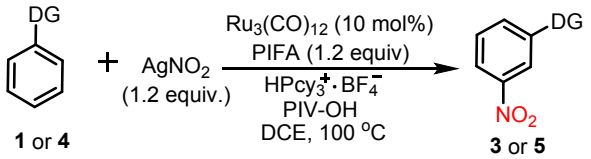


Entry	Solvent	Temp.	Yield[b] (%, **3a**)
1	CH_3CN	100 °C	0%
2	PhMe	100 °C	20%
3	PhCl	100 °C	35%
4	dioxane	100 °C	0%
5	DMF	100 °C	0%
6	DMSO	100 °C	0%
7	EtOAc	100 °C	0%
8	DCM	100 °C	58%
9 [c]	DCE	80 °C	65%
10 [d]	DCE	120 °C	73%

[a] Reaction conditions: **1a** (0.2 mmol), $AgNO_2$ (1.2 equiv.), $Ru_3(CO)_{12}$ (10 mol %), $HPcy_3^+ \cdot BF_4^-$ (30 mol %), PIFA (1.2 equiv) and PIV-OH (0.3 equiv.) in Solvent (2 mL) for 24 h at 100 °C in a sealed tube.

[b] Yield was determined by ^1H NMR analysis using CH_2Br_2 as an internal standard.

3. General procedures for the *meta*-nitration of various Arenes



In a 15 mL sealed tube the corresponding arenes **1** or **4** (0.2 mmol, 1.0 equiv.), $AgNO_2$ (0.24mmol, 1.2 equiv.), $Ru_3(CO)_{12}$ (12.8 mg, 10 mol %), PIFA (103.2 mg, 0.24 mmol, 1.2 equiv.),

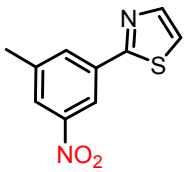
$HPcy_3^+ \cdot BF_4^-$ (22.1 mg 30 mol %), PIV-OH (6.12 mg, 0.3 equiv.) and 2 mL DCE were added under air. The tube was capped and submerged into a pre-heated 100 °C oil bath. The reaction was stirred for 24h and cooled down to room temperature. Then the reaction mixture was diluted with EtOAc (5 mL) and filtered through a pad of silica gel. The sealed tube and silica gel were washed with an additional of EtOAc (20 mL). The filtrate was concentrated *in vacuo*, and the resulting residue was purified by flash column chromatography using EtOAc/*n*-hexane (1:10) as the eluent to afford the product.

2-(3-Nitrophenyl) thiazole (**3a**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (t, *J* = 1.9 Hz, 1H), 8.28 (m, 2H), 7.94 (d, *J* = 3.2 Hz, 1H), 7.64 (t, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 3.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.43 , 148.73 , 144.24 , 135.09 , 132.13 , 130.08 , 124.34 , 121.41 , 120.32. HRMS (ESI-TOF) m/z Calcd for $C_9H_6N_2O_2S$ $[M+H]^+$: 207.0223, found: 207.0221.

2-(2-Methyl-3-nitrophenyl) thiazole (**3b**)

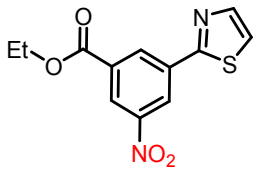
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 3.3 Hz, 1H), 7.83 (dd, *J* = 12.1, 8.4 Hz, 2H), 7.51 (d, *J* = 3.3 Hz, 1H), 7.42 (t, *J* = 7.9 Hz, 1H), 2.60 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.28 , 151.76 , 143.39 , 135.83 , 134.12 , 131.22 , 126.47 , 124.79 , 120.78 , 16.61 . HRMS (ESI-TOF) m/z Calcd for $C_{10}H_8N_2O_2S$ $[M+H]^+$: 221.0739, found: 221.0733.



2-(3-Methyl-5-nitrophenyl) thiazole (**3c**)

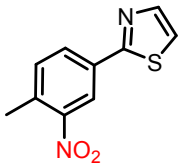
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.10 (d, *J* = 19.1 Hz, 2H), 7.92 (d, *J* = 3.2 Hz, 1H), 7.44 (d, *J* = 3.2 Hz, 1H), 2.54 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.66 , 148.65 , 144.06 , 140.72 ,

134.72 , 132.67 , 124.80 , 120.10 , 118.73 , 21.27 . HRMS (ESI-TOF) m/z Calcd for $C_{10}H_8N_2O_2S$ $[M+H]^+$: 221.0739, found: 221.0737.



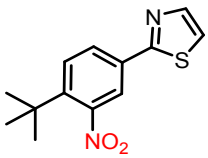
Ethyl 3-nitro-5-(thiazol-2-yl) benzoate (**3d**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 8.36 (s, 1H), 8.25 (d, *J* = 7.8 Hz, 1H), 8.20 (d, *J* = 6.7 Hz, 1H), 7.60 (t, *J* = 7.8 Hz, 1H), 4.45 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.33 , 165.48 , 157.07 , 132.53 , 131.98 , 131.74 , 130.72 , 129.48 , 127.69 , 121.14 , 61.58 , 14.32 . HRMS (ESI-TOF) m/z Calcd for $C_{12}H_{10}N_2O_4S$ $[M+H]^+$: 279.0434, found: 279.0432.



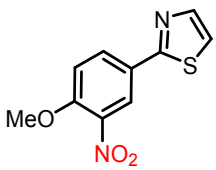
2-(4-Methyl-3-nitrophenyl) thiazole (**3e**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.09 (d, *J* = 9.8 Hz, 1H), 7.90 (d, *J* = 3.2 Hz, 1H), 7.46 – 7.38 (m, 2H), 2.64 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.45 , 149.47 , 143.97 , 134.97 , 133.46 , 132.69 , 130.33 , 122.46 , 119.79 , 20.41. HRMS (ESI-TOF) m/z Calcd for $C_{10}H_8N_2O_2S$ $[M+H]^+$: 221.0739, found: 221.0736.



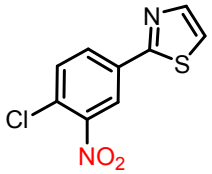
2-(4-(*tert*-butyl)-3-nitrophenyl) thiazole (**3f**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.93 (d, *J* = 2.0 Hz, 1H), 7.88 (d, *J* = 3.2 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.39 (d, *J* = 3.2 Hz, 1H), 1.43 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.14 , 151.49 , 144.02 , 142.66 , 132.44 , 129.39 , 128.16 , 121.62 , 119.73 , 35.76 , 30.50. HRMS (ESI-TOF) m/z Calcd for $C_{13}H_{14}N_2O_2S$ $[M+H]^+$: 263.0849, found: 263.0847.



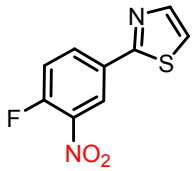
2-(4-Methoxy-3-nitrophenyl) thiazole (**3g**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.16 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.87 (d, *J* = 3.3 Hz, 1H), 7.37 (d, *J* = 3.3 Hz, 1H), 7.18 (d, *J* = 8.8 Hz, 1H), 4.03 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.39 , 153.85 , 143.88 , 139.71, 131.81 , 126.47 , 123.82 , 119.28 , 113.89 , 56.77. HRMS (ESI-TOF) m/z Calcd for $C_{10}H_8N_2O_3S$ $[M+H]^+$:237.0328, found: 237.0327.



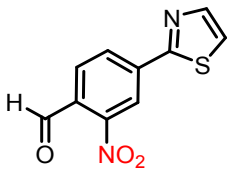
2-(4-Chloro-3-nitrophenyl) thiazole (**3h**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 3.0 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.38 (d, *J* = 3.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.19 , 144.44 , 133.50 , 132.52 , 130.43 , 129.60 , 127.99 , 123.24 , 120.60 . HRMS (ESI-TOF) m/z Calcd for $C_9H_5N_2O_2SCl$ $[M+H]^+$:240.9833, found: 240.9834.



2-(4-Fluoro-3-nitrophenyl) thiazole (**3i**)

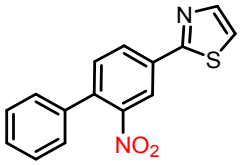
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (dd, *J* = 7.0, 2.3 Hz, 1H), 8.25 (m, 1H), 7.92 (d, *J* = 3.2 Hz, 1H), 7.45 (d, *J* = 3.2 Hz, 1H), 7.40 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.47. ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.23, 156.03 (d, *J* = 268.6 Hz), 144.26, 133.02 (d, *J* = 8.8 Hz), 130.70 (d, *J* = 4.3 Hz), 124.02 (d, *J* = 2.6 Hz), 120.34, 119.34, 119.12. HRMS (ESI-TOF) m/z Calcd for $C_9H_5N_2O_2SF$ $[M+H]^+$:225.0129, found: 225.0126.



2-Nitro-4-(thiazol-2-yl) benzaldehyde (**3j**)

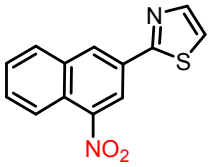
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.36 (s, 1H), 8.63 (s, 1H), 8.26 (d, *J* = 8.9 Hz, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.93 (d, *J* = 3.2 Hz, 1H), 7.48 (d, *J* = 3.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.36 ,

163.87 , 150.21 , 144.88 , 138.69 , 131.01 , 130.97 , 130.53 , 122.12 , 121.59. HRMS (ESI-TOF) m/z Calcd for $C_{10}H_6N_2O_3S$ [M+H]$^+$:235.0172, found: 235.0174.



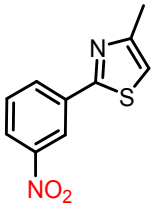
2-(2-Nitro-[1,1'-biphenyl]-4-yl) thiazole (**3k**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 1.8 Hz, 1H), 8.09 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.85 (d, *J* = 3.2 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.39 – 7.32 (m, 4H), 7.29 – 7.24 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.07 , 149.60 , 144.23 , 137.12 , 136.59 , 133.73 , 132.58 , 129.61 , 128.77 , 128.55 , 127.74 , 121.88 , 120.16. HRMS (ESI-TOF) m/z Calcd for $C_{15}H_{10}N_2O_2S$ [M+H]$^+$:283.0536, found: 283.0539.



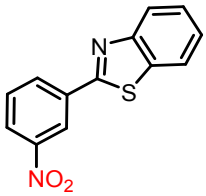
2-(4-Nitronaphthalen-2-yl) thiazole (**3l**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, *J* = 1.7 Hz, 1H), 8.64 (s, 1H), 8.52 (d, *J* = 8.7 Hz, 1H), 8.01 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 3.2 Hz, 1H), 7.77 – 7.70 (m, 1H), 7.65 (t, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 3.2 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.49 , 147.08 , 144.24 , 134.38 , 131.29 , 130.22 , 129.81 , 129.24 , 128.16 , 125.28 , 123.26 , 121.95 , 120.07 . HRMS (ESI-TOF) m/z Calcd for $C_{13}H_8N_2O_2S$ [M+H]$^+$:257.0379, found: 257.0374.



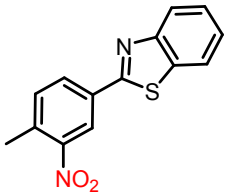
4-Methyl-2-(3-nitrophenyl) thiazole (**3m**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (t, *J* = 1.9 Hz, 1H), 8.30 (d, *J* = 7.8 Hz, 1H), 8.26 (d, *J* = 8.2 Hz, 1H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.01 (s, 1H), 2.55 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.55 , 154.42 , 148.66 , 135.05 , 132.04 , 129.99 , 124.20 , 121.26 , 114.95 , 17.11 . HRMS (ESI-TOF) m/z Calcd for $C_{10}H_8N_2O_2S$ [M+H]$^+$:221.0379, found: 221.0373.



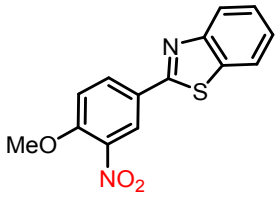
2-(3-Nitrophenyl) benzo [*d*] thiazole (**3n**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (t, *J* = 1.9 Hz, 1H), 8.43 (d, *J* = 7.8 Hz, 1H), 8.34 (d, *J* = 9.5 Hz, 1H), 8.12 (d, *J* = 8.1 Hz, 1H), 7.96 (d, *J* = 7.9 Hz, 1H), 7.70 (t, *J* = 8.0 Hz, 1H), 7.59 – 7.51 (m, 1H), 7.46 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.82 , 153.82 , 148.61 , 135.14 , 135.07 , 132.93 , 130.05 , 126.78 , 125.98 , 125.12 , 123.65 , 122.22 , 121.78 . HRMS (ESI-TOF) m/z Calcd for $C_{13}H_8N_2O_2S$ $[M+H]^+$:257.0379, found: 257.0377.



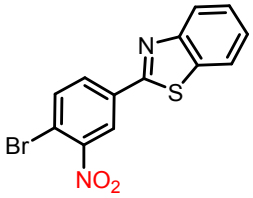
2-(4-Methyl-3-nitrophenyl) benzo[*d*] thiazole (**3o**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 1.7 Hz, 1H), 8.12 (dd, *J* = 8.0, 1.8 Hz, 1H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.41 – 7.31 (m, 2H), 2.60 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.97 , 153.84 , 149.50 , 136.03 , 134.98 , 133.53 , 132.81 , 131.18 , 126.69 , 125.78 , 123.48 , 123.41 , 121.75 , 20.57 . HRMS (ESI-TOF) m/z Calcd for $C_{14}H_{10}N_2O_2S$ $[M+H]^+$:271.0536, found: 271.0536.



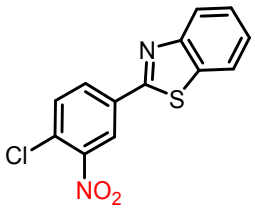
2-(4-Methoxy-3-nitrophenyl) benzo [*d*] thiazole (**3p**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 2.2 Hz, 1H), 8.20 (d, *J* = 8.8 Hz, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.44 (t, *J* = 8.2 Hz, 1H), 7.34 (t, *J* = 8.1 Hz, 1H), 7.12 (d, *J* = 8.8 Hz, 1H), 3.97 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.89 , 154.56 , 153.75 , 139.75 , 134.83 , 132.74 , 126.66 , 126.24 , 125.58 , 124.71 , 123.20 , 121.69 , 113.88 , 56.83 . HRMS (ESI-TOF) m/z Calcd for $C_{14}H_{10}N_2O_3S$ $[M+H]^+$:287.0485, found: 287.0487.



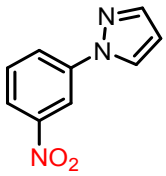
2-(4-Bromo-3-nitrophenyl) benzo[*d*] thiazole (**3q**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 2.1 Hz, 1H), 8.08 – 8.00 (m, 2H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.39 (t, *J* = 8.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.72 , 153.75 , 150.23 , 135.74 , 135.07 , 134.11 , 131.18 , 126.97 , 126.22 , 124.02 , 123.73 , 121.85 , 116.61 . HRMS (ESI-TOF) m/z Calcd for $C_{13}H_7N_2O_2SBr$ $[M+H]^+$:334.9484, found: 334.9487.



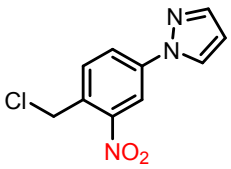
2-(4-Chloro-3-nitrophenyl) benzo [*d*] thiazole (**3r**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 2.1 Hz, 1H), 8.14 (d, *J* = 10.6 Hz, 1H), 8.03 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.48 (t, *J* = 8.3 Hz, 1H), 7.39 (t, *J* = 8.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.63 , 153.82 , 135.13 , 133.53 , 132.56 , 131.24 , 129.56 , 129.01 , 126.96 , 126.19 , 124.11 , 123.74 , 121.85 . HRMS (ESI-TOF) m/z Calcd for $C_{13}H_7N_2O_2SCl$ $[M+H]^+$:290.9990, found: 290.9993.



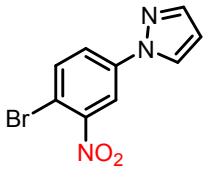
1-(3-Nitrophenyl)-1*H*-pyrazole (**5a**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (t, *J* = 2.1 Hz, 1H), 8.13 (dd, *J* = 8.2, 1.3 Hz, 1H), 8.09 (dd, *J* = 8.6, 1.7 Hz, 1H), 8.03 (d, *J* = 2.5 Hz, 1H), 7.78 (d, *J* = 1.5 Hz, 1H), 7.64 (t, *J* = 8.2 Hz, 1H), 6.57 – 6.51 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.87 , 142.11 , 140.85 , 130.39 , 126.81 , 124.36 , 120.68 , 113.64 , 108.81 . HRMS (ESI-TOF) m/z Calcd for $C_9H_7N_3O_2$ $[M+H]^+$:190.0611, found: 190.0613.



1-(4-(Chloromethyl)-3-nitrophenyl)-1*H*-pyrazole (**5b**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 2.3 Hz, 1H), 7.99 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.96 (d, *J* = 2.6 Hz, 1H), 7.72 (d, *J* = 1.6 Hz, 1H), 7.62 (d, *J* = 8.5 Hz, 1H), 6.55 – 6.40 (m, 1H), 5.83 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.01 , 142.53 , 140.97 , 130.46 , 126.79 , 126.11 , 123.34 , 115.35 , 109.24 , 70.08 . HRMS (ESI-TOF) m/z Calcd for $C_{10}H_8N_3O_2Cl$ $[M+H]^+$:238.0378, found: 238.0373.

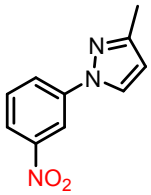


1-(4-Bromo-3-nitrophenyl)-1*H*-pyrazole (**5c**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.88 (d, *J* = 2.5 Hz, 1H), 7.71 (d, *J* = 1.3 Hz, 2H), 7.67 (d, *J* = 1.4 Hz, 1H), 6.48 – 6.40 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.10 , 142.39 , 139.73 , 135.91 , 126.69 , 122.63 , 115.66 , 110.85 , 109.17 . HRMS (ESI-TOF) m/z Calcd for $C_9H_6N_3O_2Br$ $[M+H]^+$:267.9716, found: 267.9719.

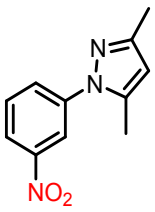
1-(4-Iodo-3-nitrophenyl)-1*H*-pyrazole (**5d**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 2.5 Hz, 1H), 8.00 (d, *J* = 8.6 Hz, 1H), 7.90 (d, *J* = 2.6 Hz, 1H), 7.68 (d, *J* = 1.4 Hz, 1H), 7.58 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.48 – 6.44 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.34 , 142.64 , 142.36 , 140.60 , 126.64 , 122.85 , 115.47 , 109.15 , 81.67 . HRMS (ESI-TOF) m/z Calcd for $C_9H_6N_3O_2I$ $[M+H]^+$:315.9577, found: 315.9577.



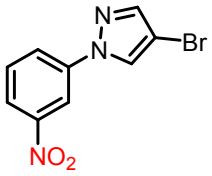
3-Methyl-1-(3-nitrophenyl)-1*H*-pyrazole (**5e**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (t, *J* = 2.1 Hz, 1H), 7.98 (dd, *J* = 17.2, 9.2 Hz, 2H), 7.83 (d, *J* = 2.4 Hz, 1H), 7.53 (t, *J* = 8.2 Hz, 1H), 6.25 (d, *J* = 2.4 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.77 , 148.87 , 140.82 , 130.29 , 127.40 , 123.90 , 120.11 , 113.12 , 108.89 , 13.67 . HRMS (ESI-TOF) m/z Calcd for $C_{10}H_9N_3O_2$ $[M+H]^+$:207.0768, found: 207.0765.



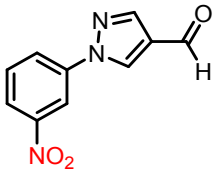
3,5-Dimethyl-1-(3-nitrophenyl)-1*H*-pyrazole (**5f**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (t, *J* = 2.1 Hz, 1H), 8.11 (d, *J* = 8.2 Hz, 1H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.56 (t, *J* = 8.1 Hz, 1H), 5.99 (s, 1H), 2.33 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.24 , 148.40 , 140.84 , 139.59 , 129.91 , 129.71 , 121.39 , 118.78 , 108.41 , 13.43 , 12.66 . HRMS (ESI-TOF) m/z Calcd for $C_{11}H_{11}N_3O_2$ $[M+H]^+$:218.0924, found: 218.0927.



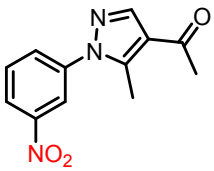
4-Bromo-1-(3-nitrophenyl)-1*H*-pyrazole (**5g**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (t, *J* = 2.1 Hz, 1H), 8.07 (d, *J* = 9.7 Hz, 1H), 7.97 (s, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.63 (s, 1H), 7.57 (t, *J* = 8.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.81 , 142.54 , 140.12 , 130.55 , 126.96 , 124.01 , 121.24 , 113.46 , 97.04 . HRMS (ESI-TOF) m/z Calcd for $C_9H_6N_3O_2$ Br$[M+H]^+$:267.9716, found: 267.9717.



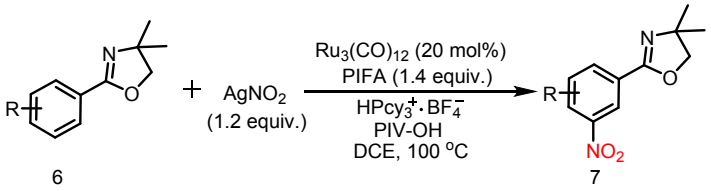
1-(3-Nitrophenyl)-1*H*-pyrazole-4-carbaldehyde (**5h**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 1H), 8.57 (t, *J* = 2.1 Hz, 1H), 8.50 (s, 1H), 8.19 (d, *J* = 8.2 Hz, 1H), 8.16 (s, 1H), 8.06 (d, *J* = 8.1 Hz, 1H), 7.66 (t, *J* = 8.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.78 , 148.95 , 142.24 , 139.85 , 130.84 , 130.13 , 126.33 , 125.00 , 122.34 , 114.58 . HRMS (ESI-TOF) m/z Calcd for $C_{10}H_7N_3O_3$ $[M+H]^+$:218.0560, found: 218.0563.



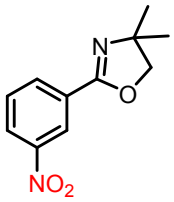
1-(5-Methyl-1-(3-nitrophenyl)-1*H*-pyrazol-4-yl) ethan-1-one (**5i**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (t, *J* = 2.0 Hz, 1H), 8.26 (d, *J* = 8.2 Hz, 1H), 7.99 (s, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.67 (t, *J* = 8.1 Hz, 1H), 2.59 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.32 , 148.46 , 143.10 , 142.59 , 139.41 , 130.90 , 130.26 , 123.25 , 121.62 , 120.39 , 28.79 , 12.40 . HRMS (ESI-TOF) m/z Calcd for $C_{12}H_{11}N_3O_3$ $[M+H]^+$:246.0873, found: 246.0871.



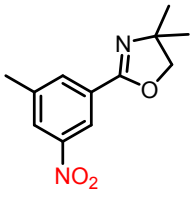
6 7

In a 15 mL sealed tube the corresponding arenes **6** (0.2 mmol, 1.0 equiv.), $AgNO_2$ (0.24 mmol, 1.2 equiv.), $Ru_3(CO)_{12}$ (25.6 mg, 20 mol %), PIFA (120.4 mg, 0.28 mmol, 1.4 equiv.), $HPcy_3^+ \cdot BF_4^-$ (22.1 mg 30 mol %), PIV-OH (6.12 mg, 0.3 equiv.) and 2 mL DCE were added under air. The tube was capped and submerged into a pre-heated 110 °C oil bath. The reaction was stirred for 24h and cooled down to room temperature. Then the reaction mixture was diluted with EtOAc (5 mL) and filtered through a pad of silica gel. The sealed tube and silica gel were washed with an additional of EtOAc (20 mL). The filtrate was concentrated *in vacuo*, and the resulting residue was purified by flash column chromatography using EtOAc/*n*-hexane (1:8) as the eluent to afford the product.



4,4-Dimethyl-2-(3-nitrophenyl)-4,5-dihydrooxazole (**7a**)

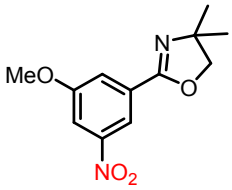
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 8.24 (dd, *J* = 14.3, 9.1 Hz, 2H), 7.53 (t, *J* = 8.0 Hz, 2H), 4.11 (s, 2H), 1.34 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.17 , 148.16 , 134.00 , 129.77 , 129.41 , 125.73 , 123.30 , 79.59 , 68.07 , 28.31 . HRMS (ESI-TOF) m/z Calcd for $C_{11}H_{12}N_2O_3$ $[M+H]^+$:221.0921, found: 221.0923.



4,4-Dimethyl-2-(3-methyl-5-nitrophenyl)-4,5-dihydrooxazole (**7b**)

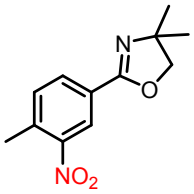
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.16 (d, *J* = 3.6 Hz, 2H), 4.19 (s, 2H), 2.50 (s, 3H), 1.42 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.30 , 148.16 , 140.06 , 134.61 , 129.46 , 126.13 , 120.46 ,

79.46 , 67.97 , 28.30 , 21.08 . HRMS (ESI-TOF) m/z Calcd for $C_{12}H_{14}N_2O_3$ $[M+H]^+$:235.1077, found: 235.1071.



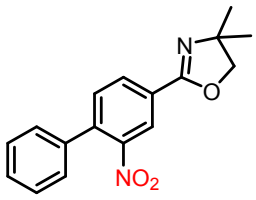
2-(3-Methoxy-5-nitrophenyl)-4,4-dimethyl-4,5-dihydrooxazole (**7c**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.76 (t, *J* = 2.3 Hz, 1H), 7.73 (s, 1H), 4.10 (s, 2H), 3.86 (s, 3H), 1.34 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.15 , 160.01 , 149.05 , 130.54 , 119.54 , 115.49 , 111.47 , 79.51 , 68.08 , 56.19 , 28.32 . HRMS (ESI-TOF) m/z Calcd for $C_{12}H_{14}N_2O_4$ $[M+H]^+$:251.1026, found: 251.1025.



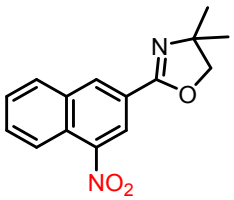
4,4-Dimethyl-2-(4-methyl-3-nitrophenyl)-4,5-dihydrooxazole (**7d**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 4.17 (s, 2H), 2.64 (s, 3H), 1.41 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.11 , 149.08 , 136.36 , 132.81 , 132.15 , 127.35 , 124.36 , 79.41 , 67.93 , 28.30 , 20.46 . HRMS (ESI-TOF) m/z Calcd for $C_{12}H_{14}N_2O_3$ $[M+H]^+$:235.1077, found: 235.1071.



4,4-Dimethyl-2-(2-nitro-[1,1'-biphenyl]-4-yl)-4,5-dihydrooxazole (**7e**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.36 – 7.31 (m, 3H), 7.23 (dd, *J* = 7.1, 2.2 Hz, 2H), 4.09 (s, 2H), 1.32 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.02 , 149.10 , 138.55 , 136.57 , 131.99 , 131.54 , 128.93 , 128.77 , 128.63 , 127.73 , 123.85 , 79.53 , 68.01 , 28.31 . HRMS (ESI-TOF) m/z Calcd for $C_{17}H_{16}N_2O_3$ $[M+H]^+$:297.1234, found: 297.1232.

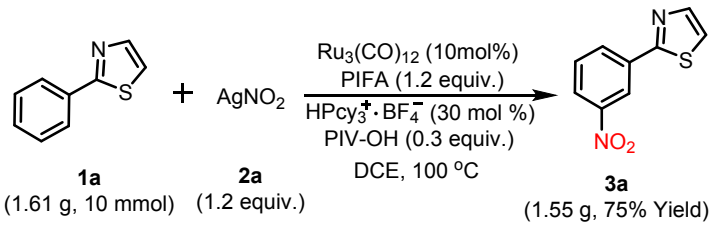


4,4-Dimethyl-2-(4-nitronaphthalen-2-yl)-4,5-dihydrooxazole (**7f**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.59 (s, 1H), 8.44 (d, *J* = 8.7 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.68 (t, *J* = 8.2 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 4.12 (s, 2H), 1.35 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.24 , 146.58 , 134.20 , 133.81 , 130.74 , 129.52 , 127.97 , 125.93 , 124.30 , 123.17 , 122.97 , 79.58 , 68.08 , 28.37 . HRMS (ESI-TOF) m/z Calcd for $C_{15}H_{14}N_2O_3$ $[M+H]^+$:271.1077, found: 271.1073.

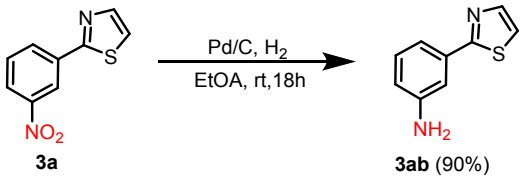
4. Gram scale synthesis and further Functional Transformations of Nitroarenes

4.1 Gram scale synthesis of 3a



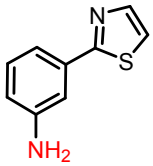
In a 100 mL sealed flask substrate **1a** (10 mmol, 1.0 equiv.), $AgNO_2$ (12 mmol, 1.2 equiv.), $Ru_3(CO)_{12}$ (10 mol %), PIFA (12 mmol, 1.2 equiv.), $HPcy_3^+ \cdot BF_4^-$ (30 mol %), PIV-OH (0.3 equiv.) and 20 mL DCE were added under air. The tube was capped and submerged into a pre-heated 100 °C oil bath. The reaction was stirred for 24h and cooled down to room temperature quenched with 20 mL water. Then the reaction mixture was extracted with EtOAc (3×20 mL). Combined organic phase dried over anhydrous Na_2SO_4 and concentrated *in vacuo*, and the resulting residue was purified by flash column chromatography using EtOAc/*n*-hexane (1:10) as the eluent to afford the product **3a** in 75% yield.

4.2 further Functional Transformations of 3a



3a **3ab** (90%)

In a 35mL tube, the compound **3a** (0.5 mmol, 1.0 eq), Pd/C (20% wt%) and 4 mL ethyl acetate were added under H2 atmosphere. The tube was sealed, the resulting solution was then placed under an atmosphere of hydrogen (1 atm, balloon) and stirred for 18 h at room temperature. When the reaction was complete, the reaction mixture was filtered through celite with ethyl acetate. The solvent was evaporated under vacuum to afford the product without further purification.

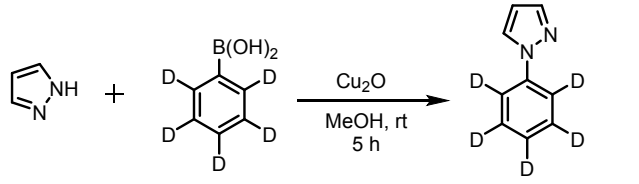


3-(Thiazol-2-yl) aniline (**3ab**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 3.3 Hz, 1H), 7.33 – 7.29 (m, 2H), 7.28 (d, J = 3.3 Hz, 1H), 7.20 (t, J = 7.7 Hz, 1H), 6.74 – 6.68 (m, 1H), 3.73 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.74 , 147.04 , 143.48 , 134.47 , 129.95 , 118.74 , 117.05 , 116.75 , 112.69 . HRMS (ESI-TOF) m/z Calcd for $C_9H_8N_2S$ $[M+H]^+$:177.0481, found: 177.0495.

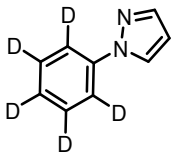
5. Kinetic isotope effect studies

5.1 Synthesis of 4a-D_5



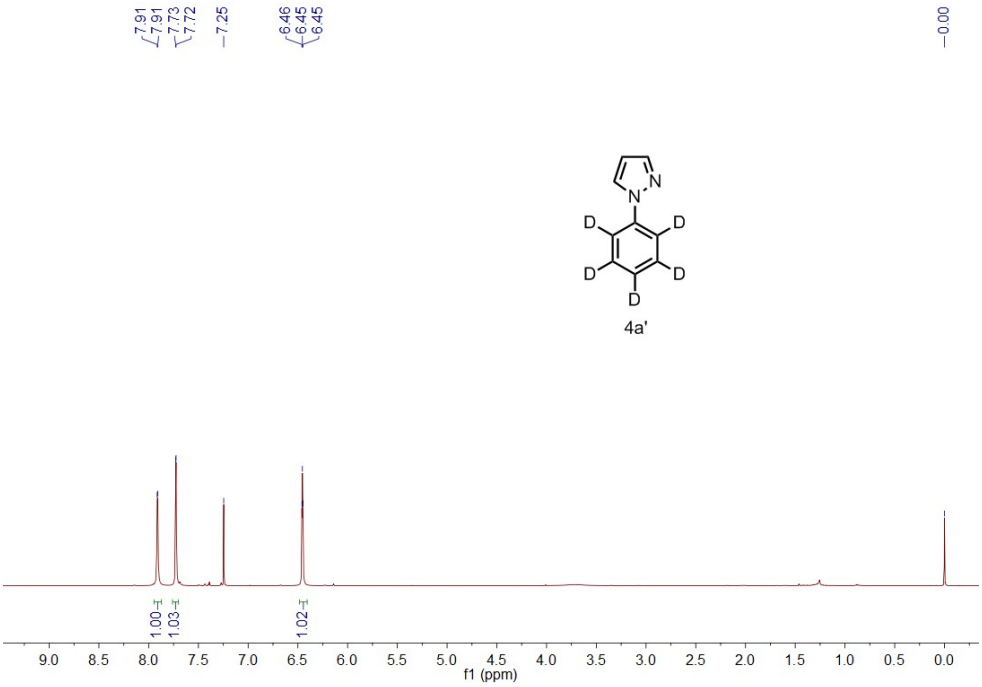
4a-D_5 85%, yield

In an oven dried round bottom flask (15 mL), pyrazole (1.2 mmol, 82 mg), D_5-phylboronic acid (1 mmol, 127 mg) and Cu_2O (0.06 mmol, 8.6 mg) were taken and then MeOH (5 mL) was added and stirred at room temperature for 12 h. The solvent was removed under reduced pressure and the crude was purified by silica gel column chromatography using PE and EA (7:3) as eluent.

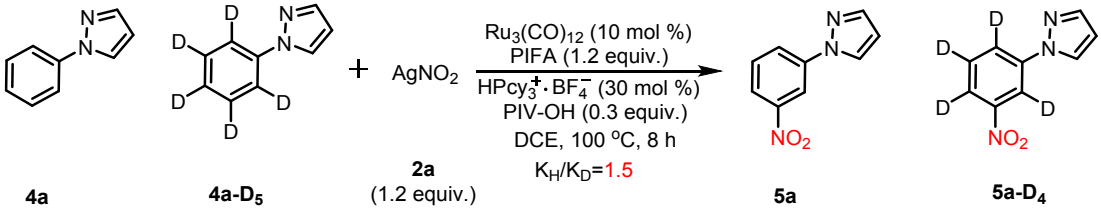


1-(Phenyl-d5)-1*H*-pyrazole (**4a-D$_5$**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 2.1 Hz, 1H), 7.73 (d, J = 1.4 Hz, 1H), 6.49 – 6.42 (m, 1H). HRMS (ESI-TOF) m/z Calcd for $C_9H_3D_5N_2$ $[M+H]^+$: 150.1074, found: 150.1056.

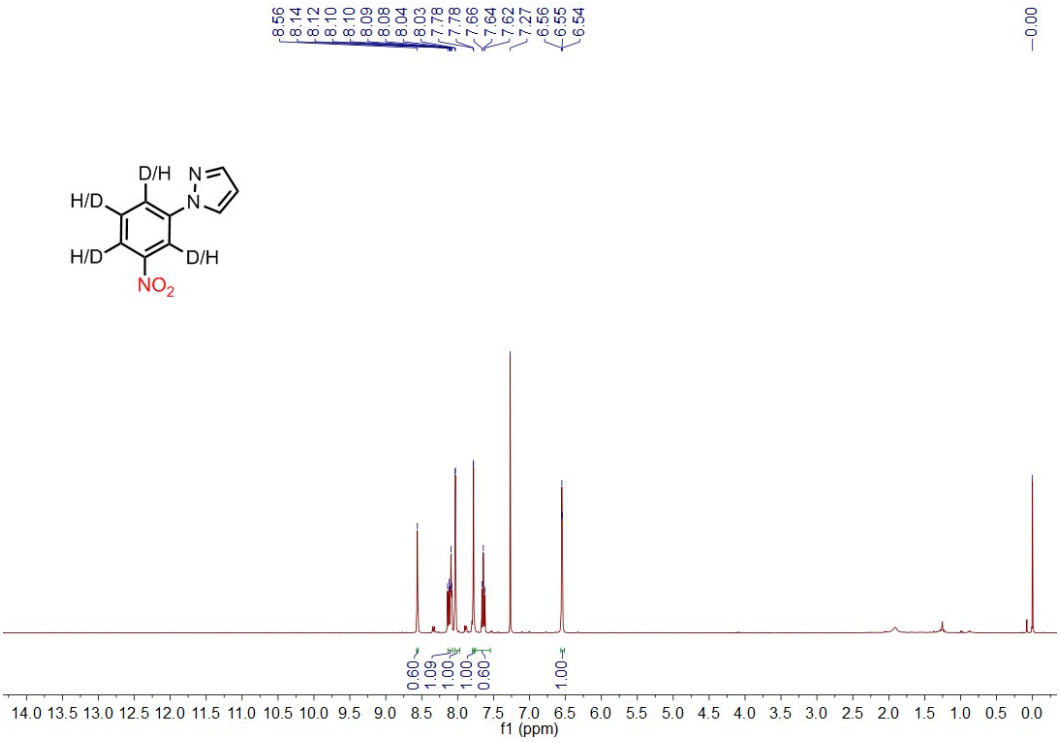


5.2 Intermolecular Competition Reactions

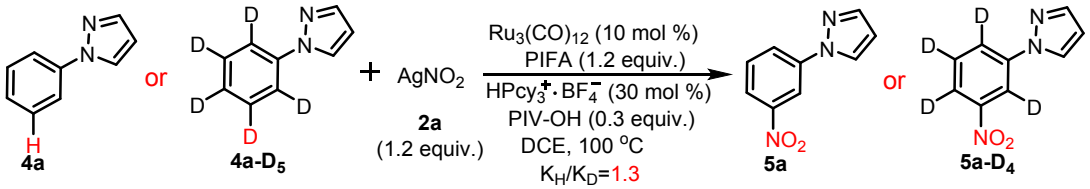


In a 15 mL sealed tube substrate **4a** (0.2 mmol) and **4a-D$_5$** (0.2 mmol), $AgNO_2$ (0.24 mmol, 1.2 equiv.), $Ru_3(CO)_{12}$ (12.8 mg, 10 mol %), PIFA (103.2 mg, 0.24 mmol, 1.2 equiv.), $HPcy_3^+ \cdot BF_4^-$ (22.1 mg , 30 mol %), PIV-OH (6.12 mg, 0.3 equiv.) and 2 mL DCE were added under air. The tube was capped and submerged into a pre-heated 100 °C oil bath. The reaction was stirred for 8h and cooled down to room temperature. Then the reaction mixture was diluted with EtOAc (5 mL) and filtered through a pad of silica gel. The sealed tube and silica gel were washed with an additional of EtOAc (20 mL). The filtrate was concentrated *in vacuo*, and the resulting residue was purified by flash column chromatography using EtOAc/*n*-hexane (1:10) as the eluent to afford the product. The

ratio of H/D was determined by ^{1}H NMR spectra. The KIE value was calculated as k_H/k_D = 1.5.

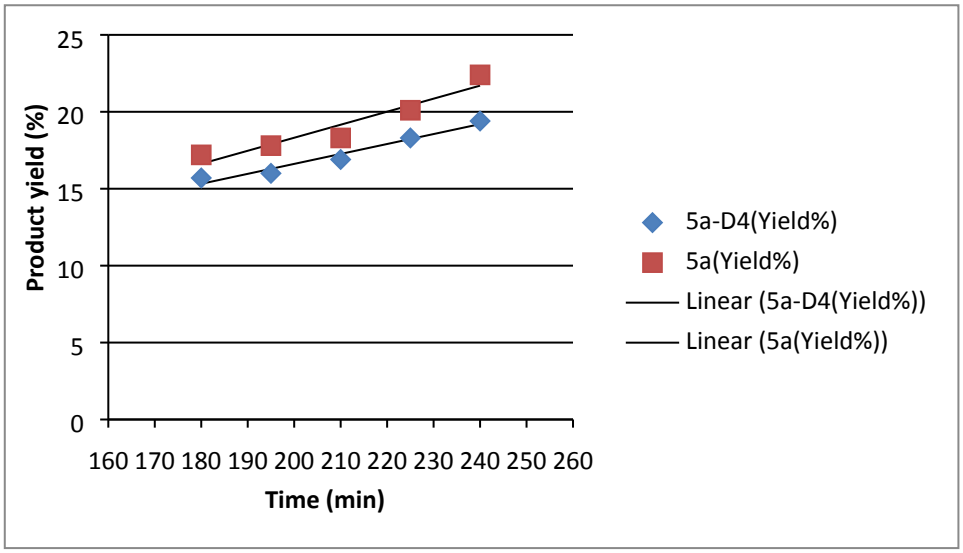


5.3 Parallel Reactions



In a 15 mL sealed tube substrate **4a** (0.2 mmol) or **4a-D$_5$** (0.2 mmol), $AgNO_2$ (0.24 mmol, 1.2 equiv.), $Ru_3(CO)_{12}$ (12.8 mg, 10 mol %), PIFA (103.2 mg, 0.24 mmol, 1.2 equiv.), $HPcy_3^+ \cdot BF_4^-$ (22.1 mg , 30 mol %), PIV-OH (6.12 mg, 0.3 equiv.) and 2 mL DCE were added under air. The tubes were capped with rubber plugs and submerged into a pre-heated 100 °C oil bath. A periodic aliquot (100 μl) was removed by a syringe and concentrated, ^{1}H NMR analysis using dibromomethane as an internal standard to provide the following conversions:

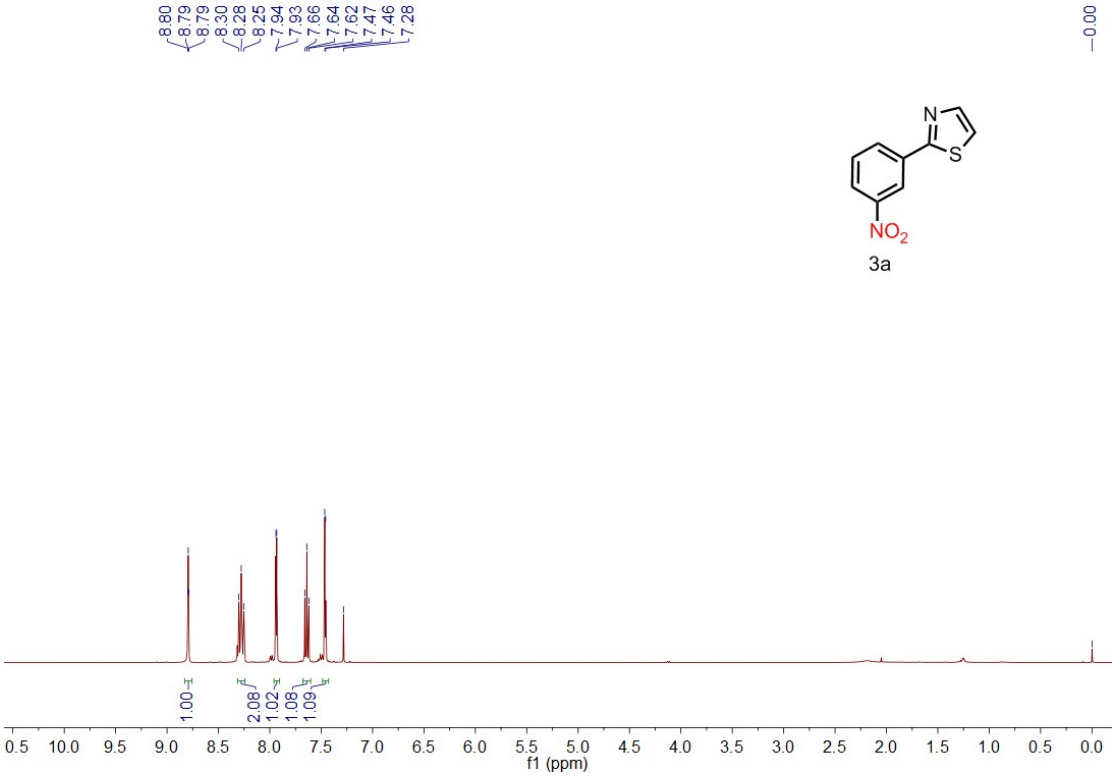
Time /(min)	180	195	210	225	240
Yield of 5a/(%)	17.2	17.8	18.3	20.1	22.4
Yield of 5a-D_4/(%)	15.7	16.0	16.9	18.3	19.4

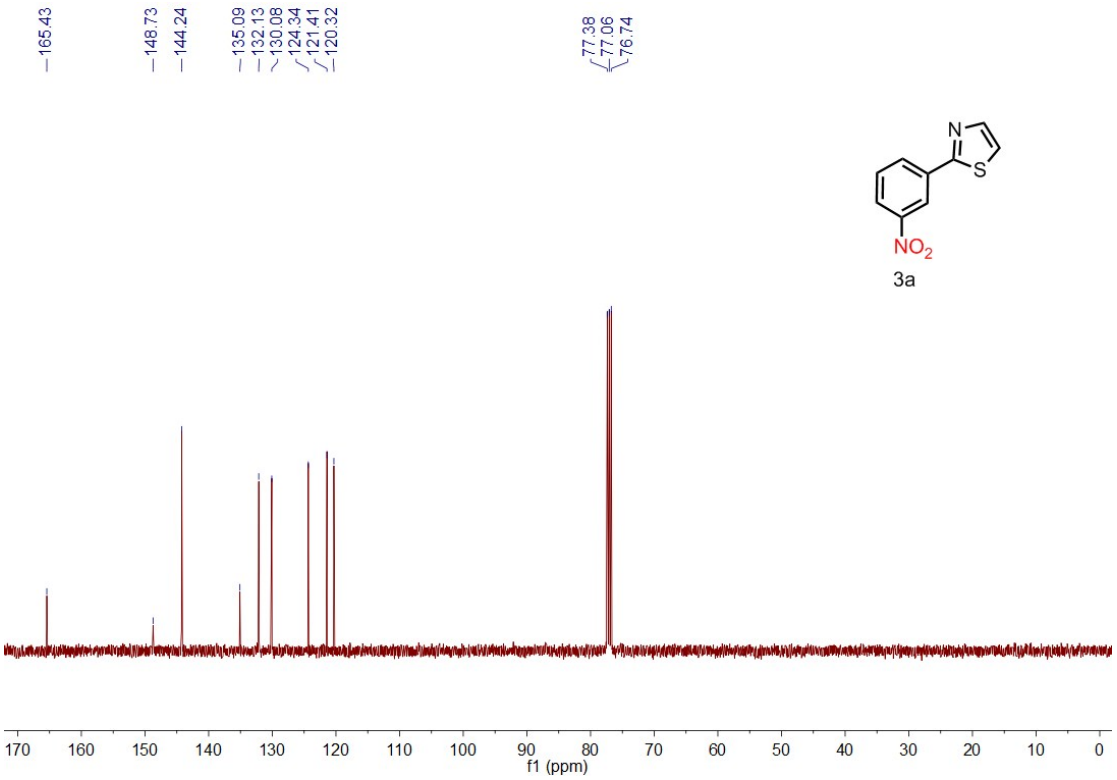


The KIE value was calculated as $k_H/k_D = 1.3$.

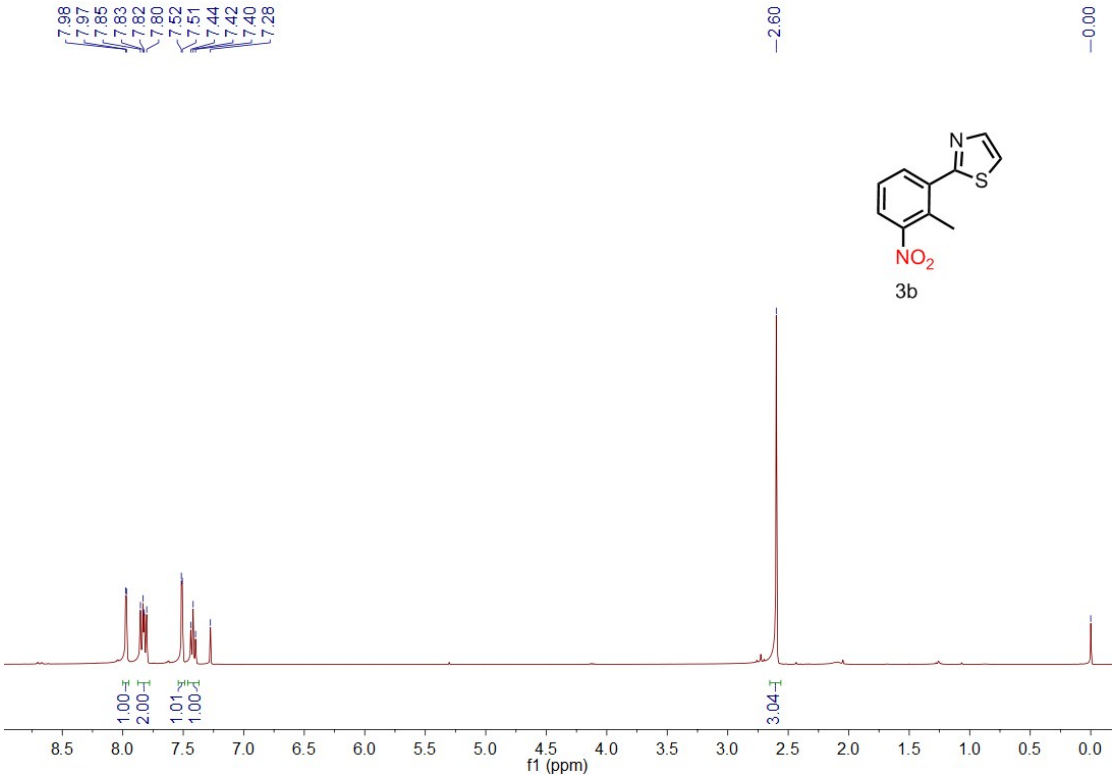
6. ^{1}H NMR and ^{13}C NMR spectra

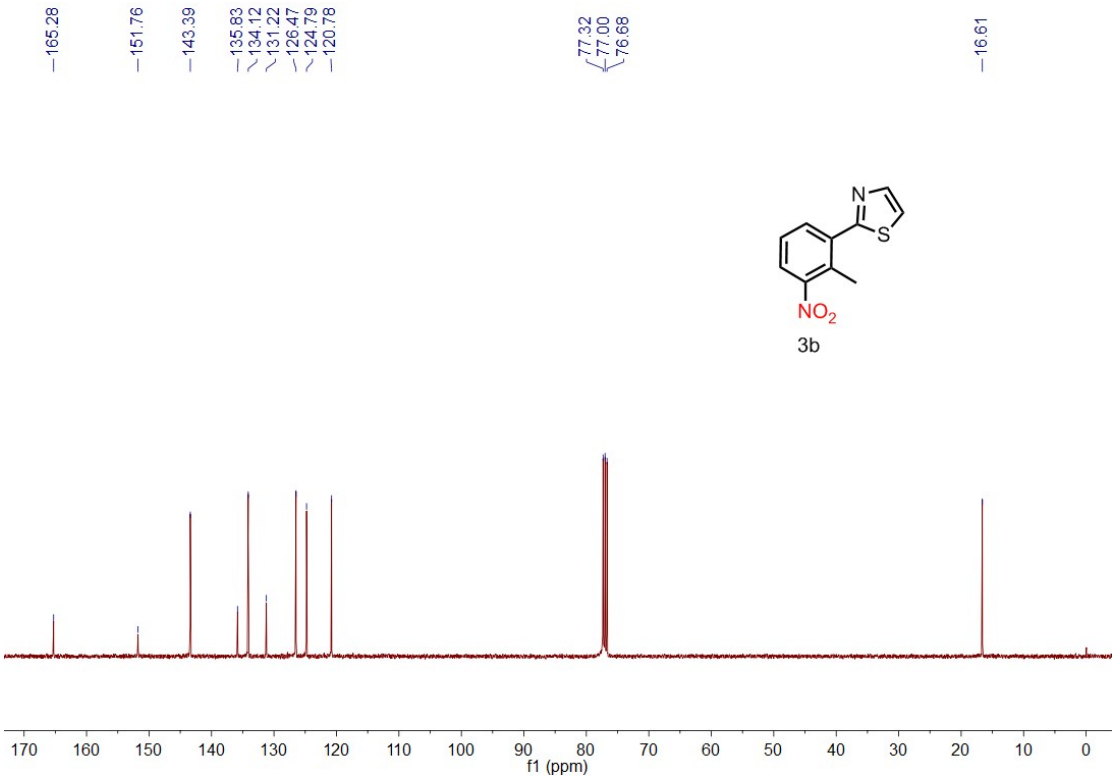
2-(3-Nitrophenyl) thiazole (**3a**)



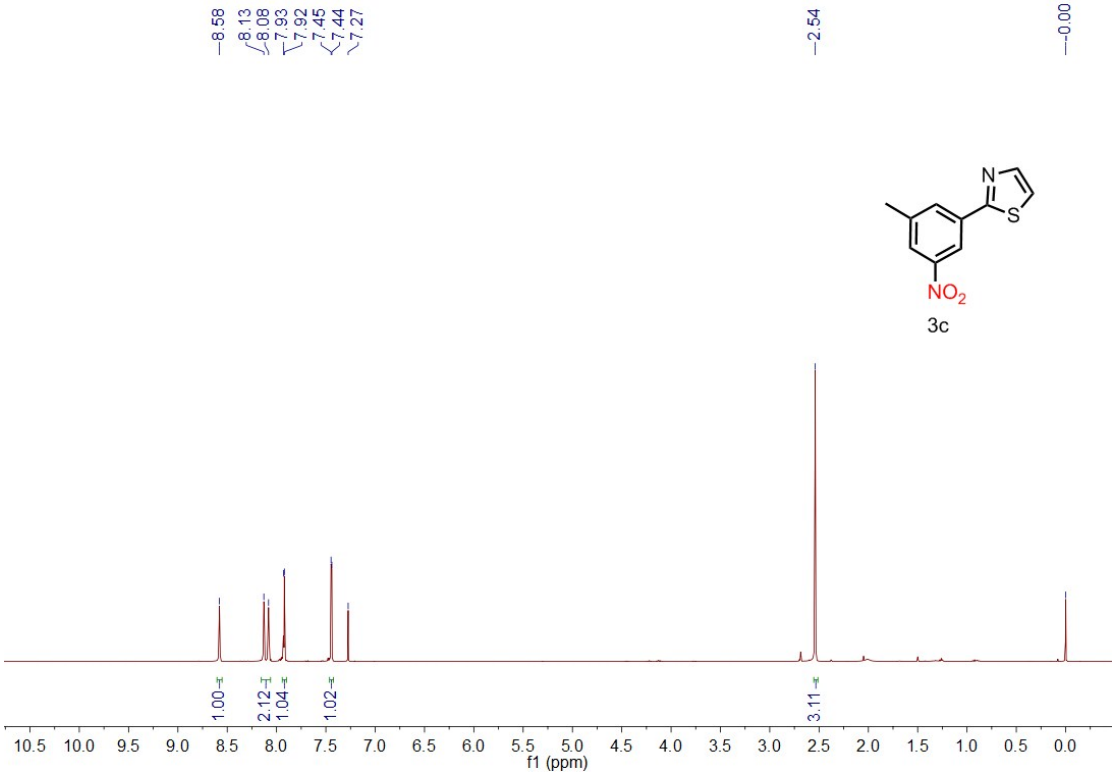


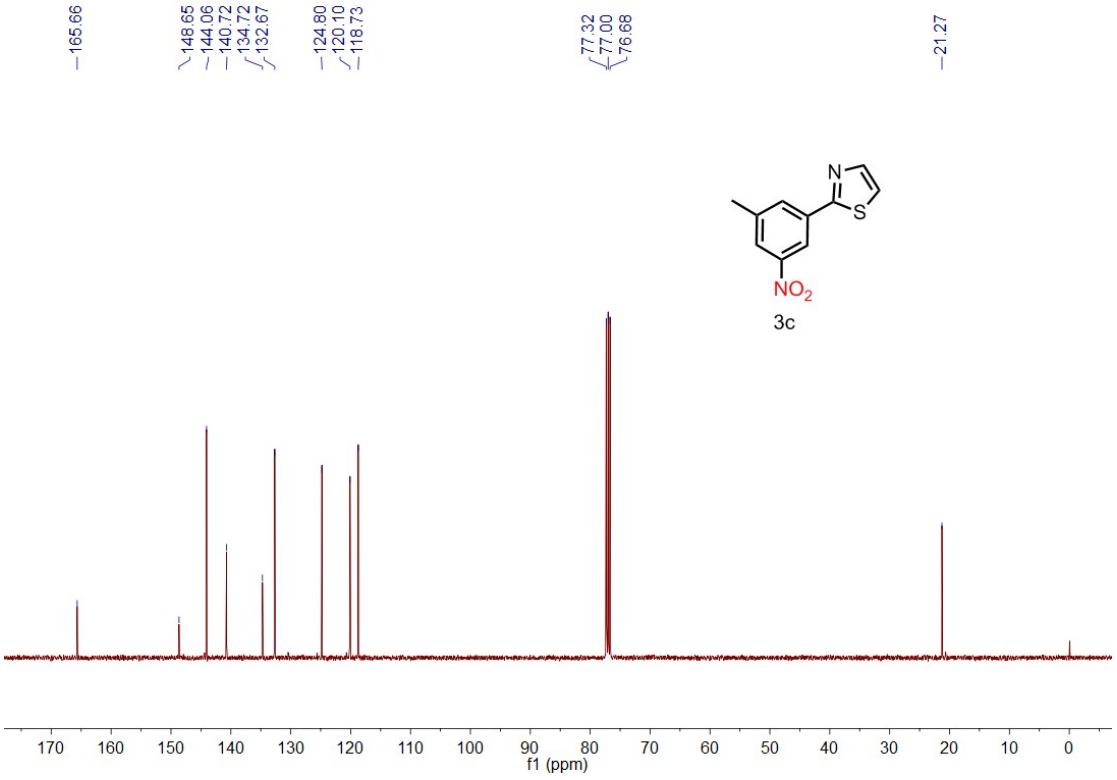
2-(2-Methyl-3-nitrophenyl) thiazole (**3b**)



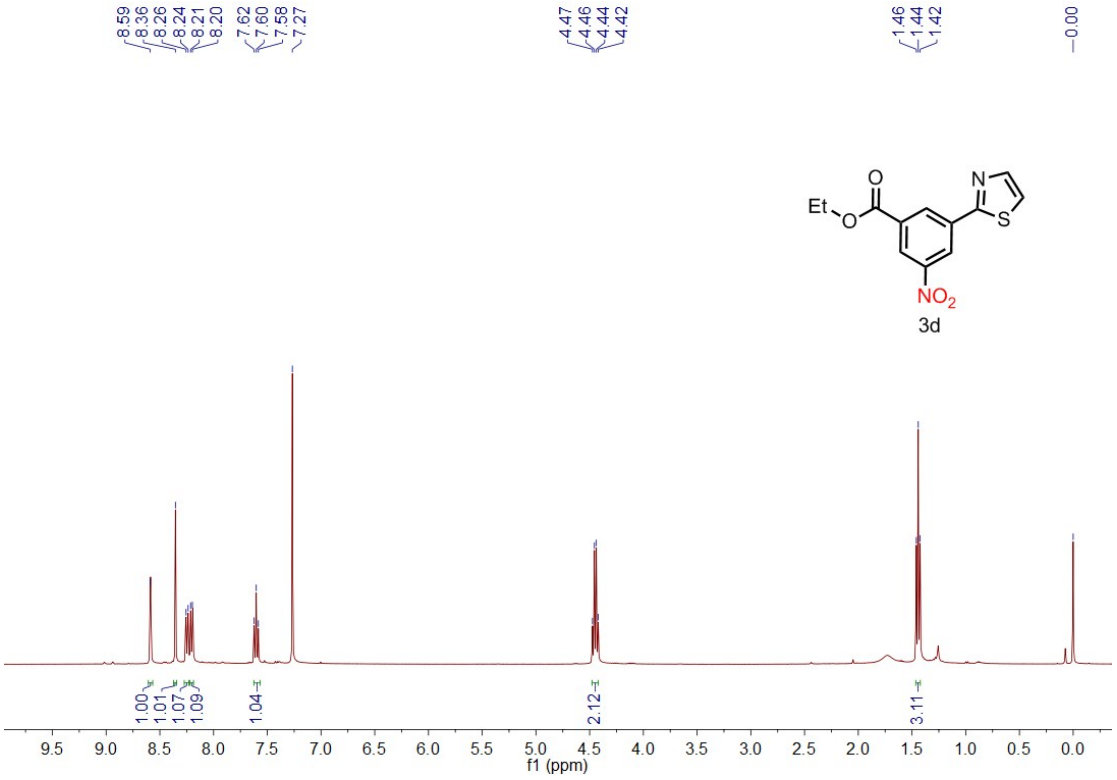


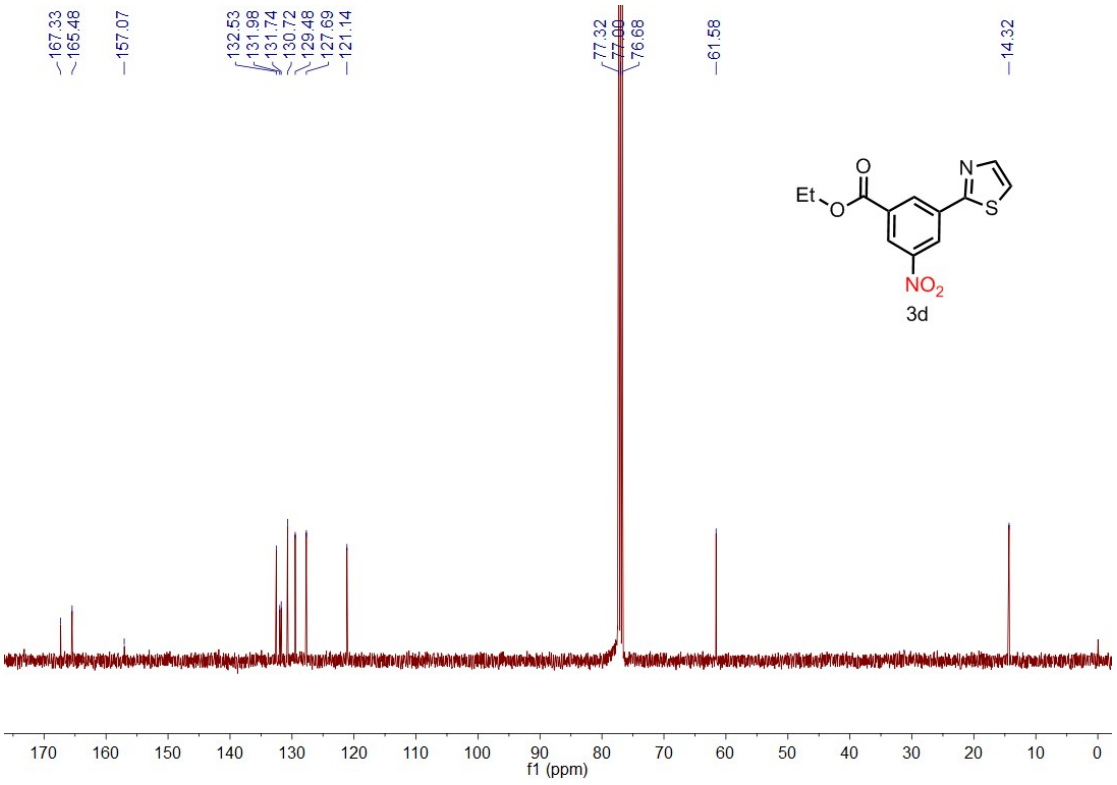
2-(3-Methyl-5-nitrophenyl) thiazole (**3c**)



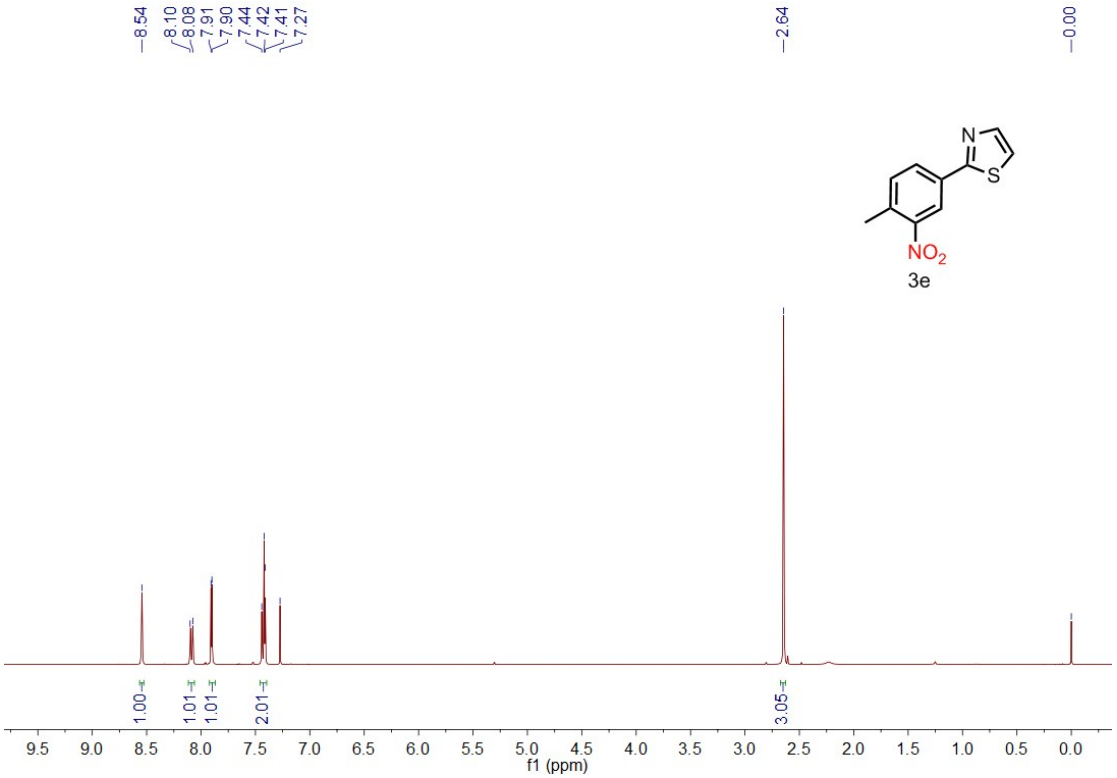


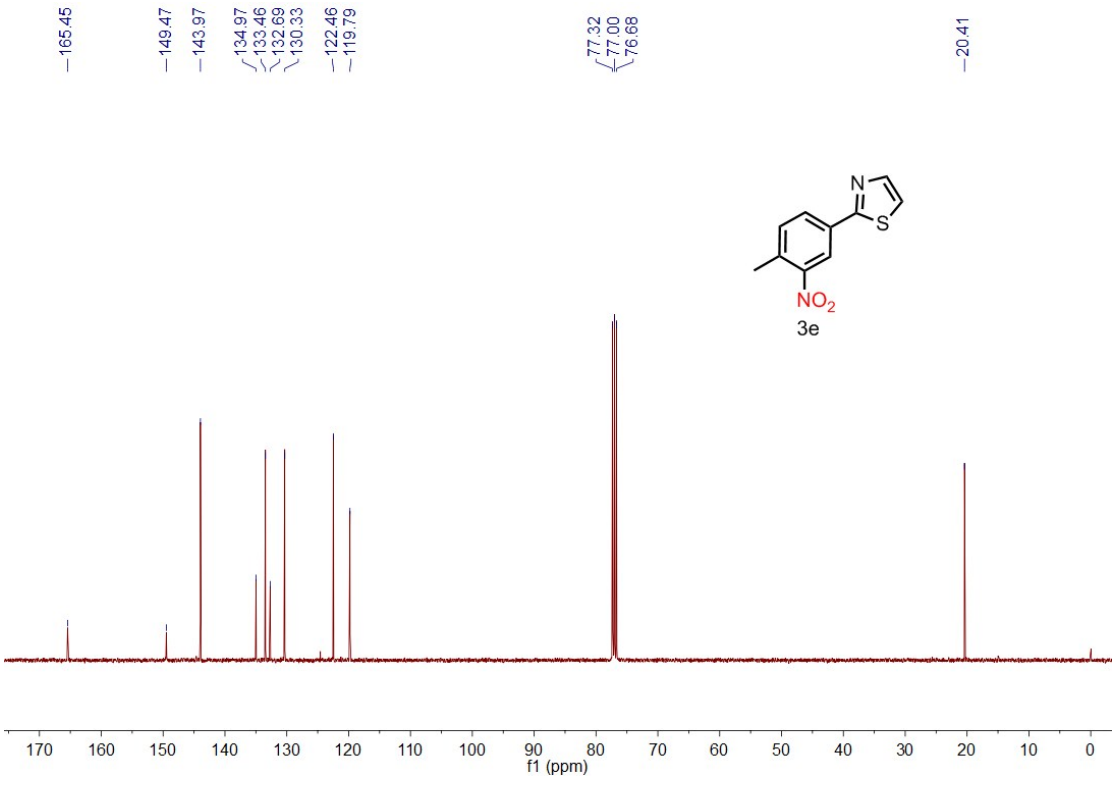
Ethyl 3-nitro-5-(thiazol-2-yl) benzoate (**3d**)



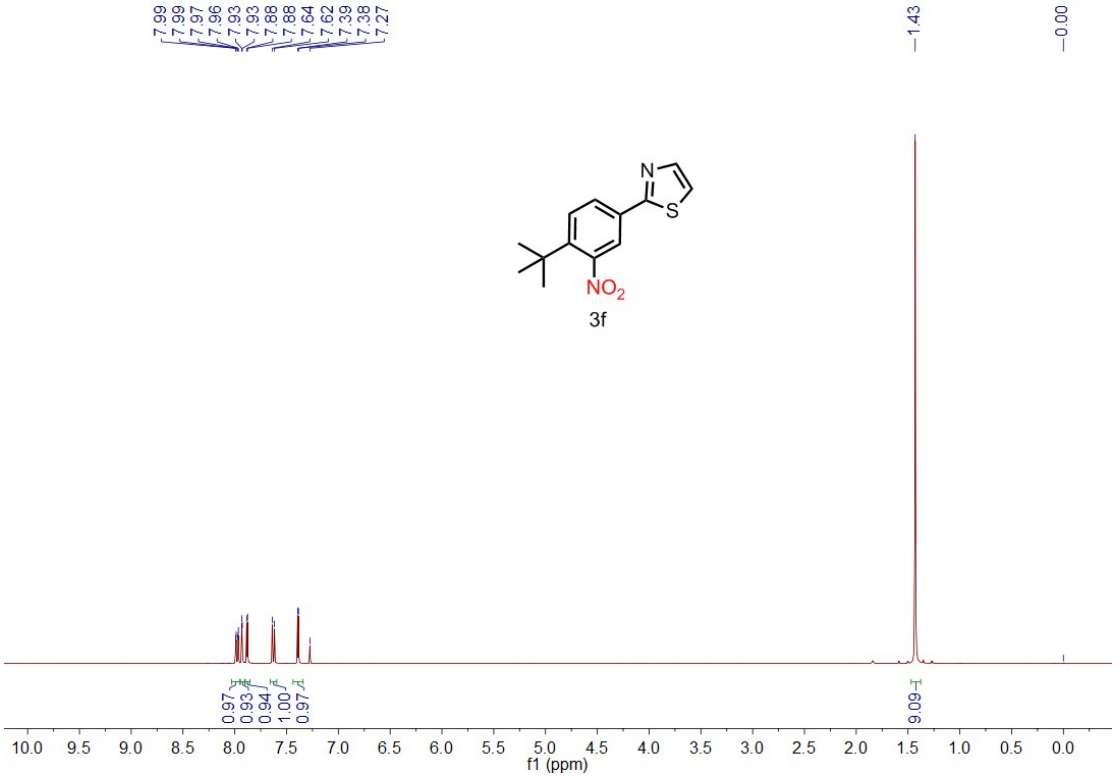


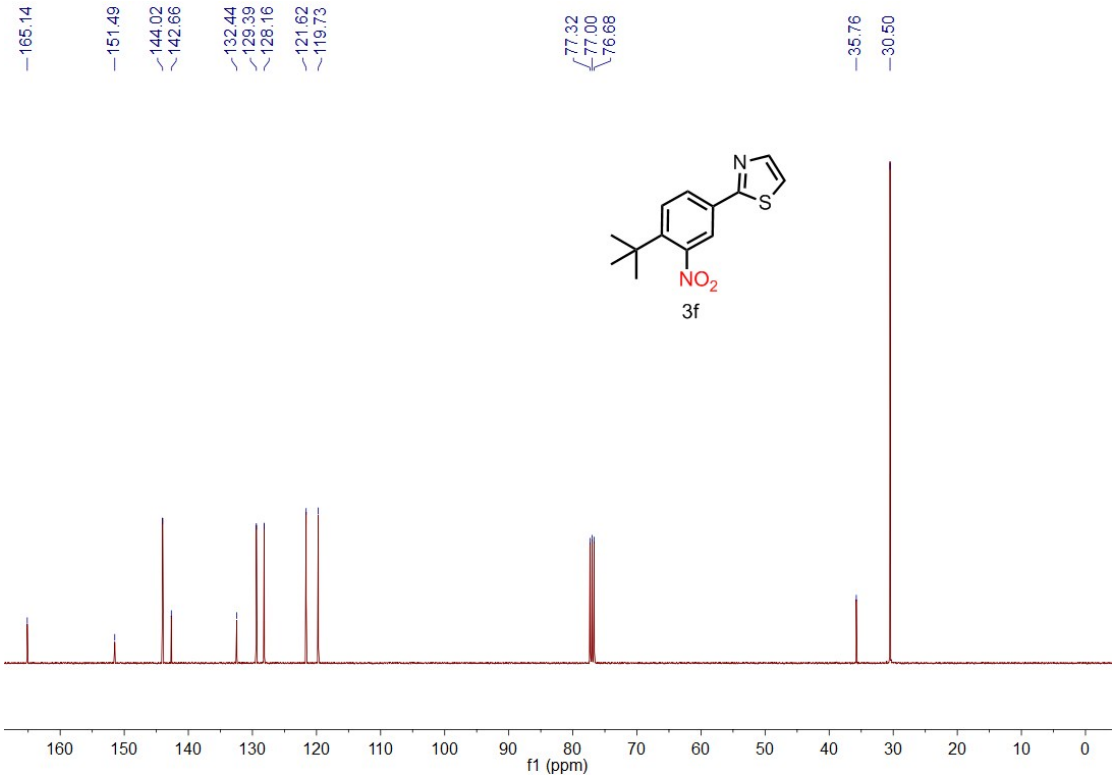
2-(4-Methyl-3-nitrophenyl) thiazole (**3e**)



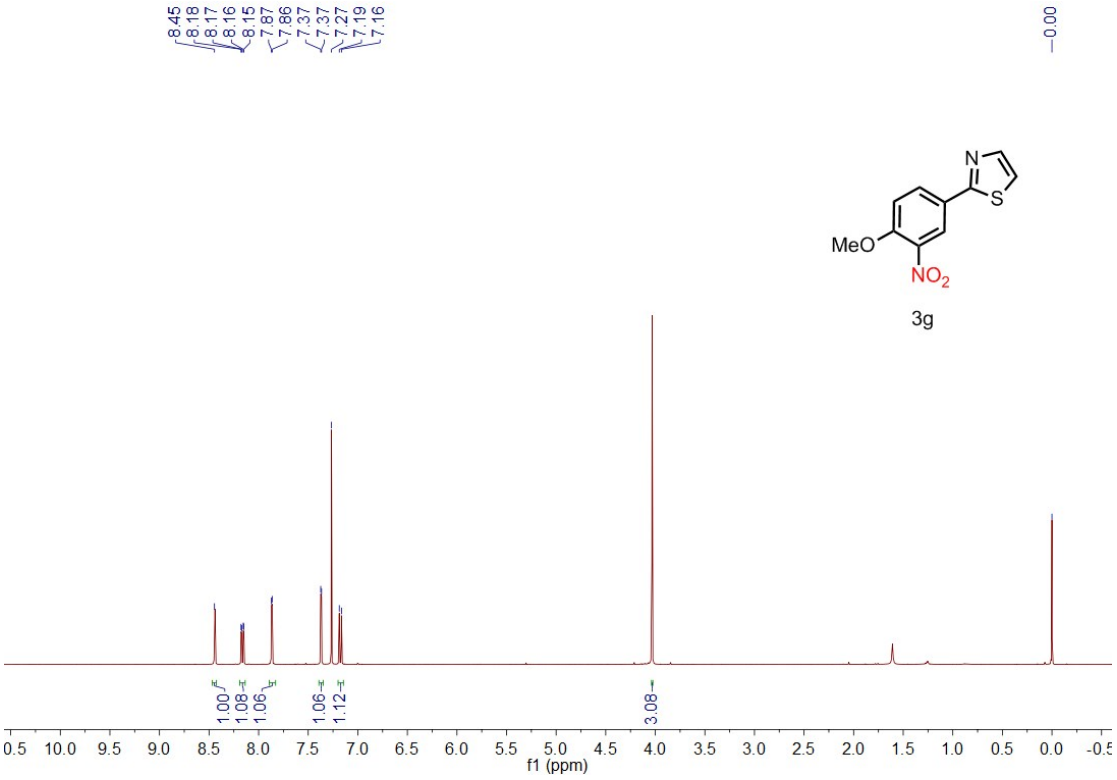


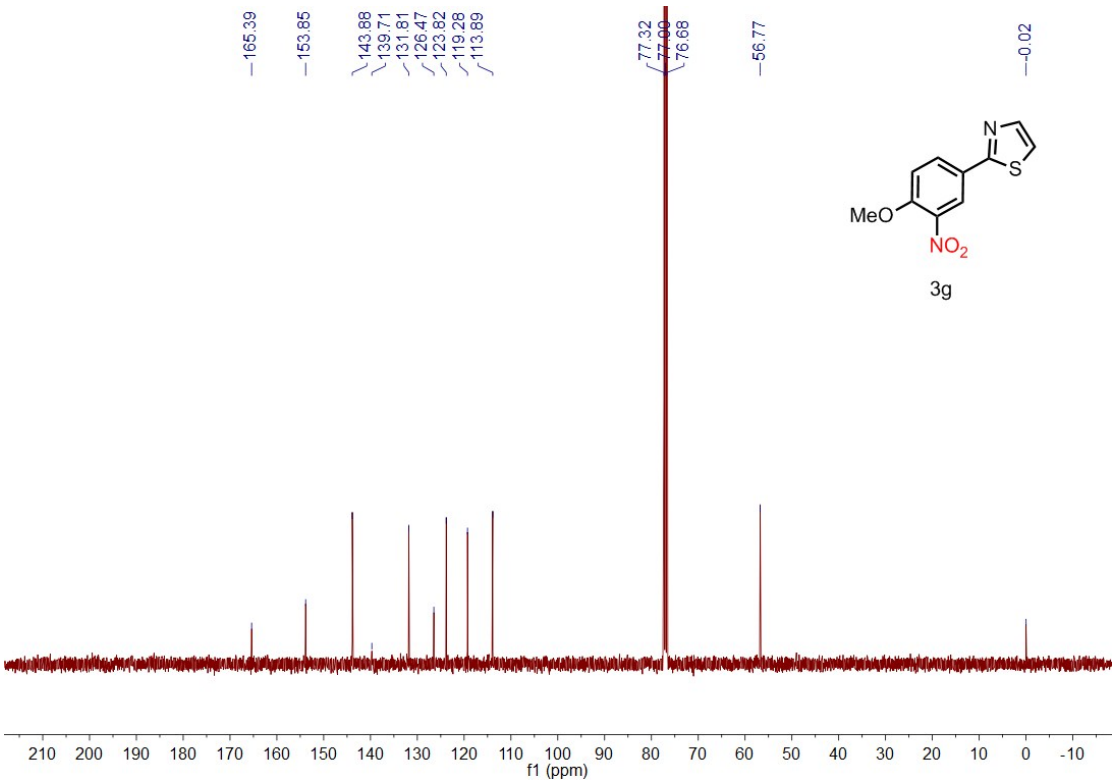
2-(4-(*tert*-butyl)-3-nitrophenyl) thiazole (**3f**)



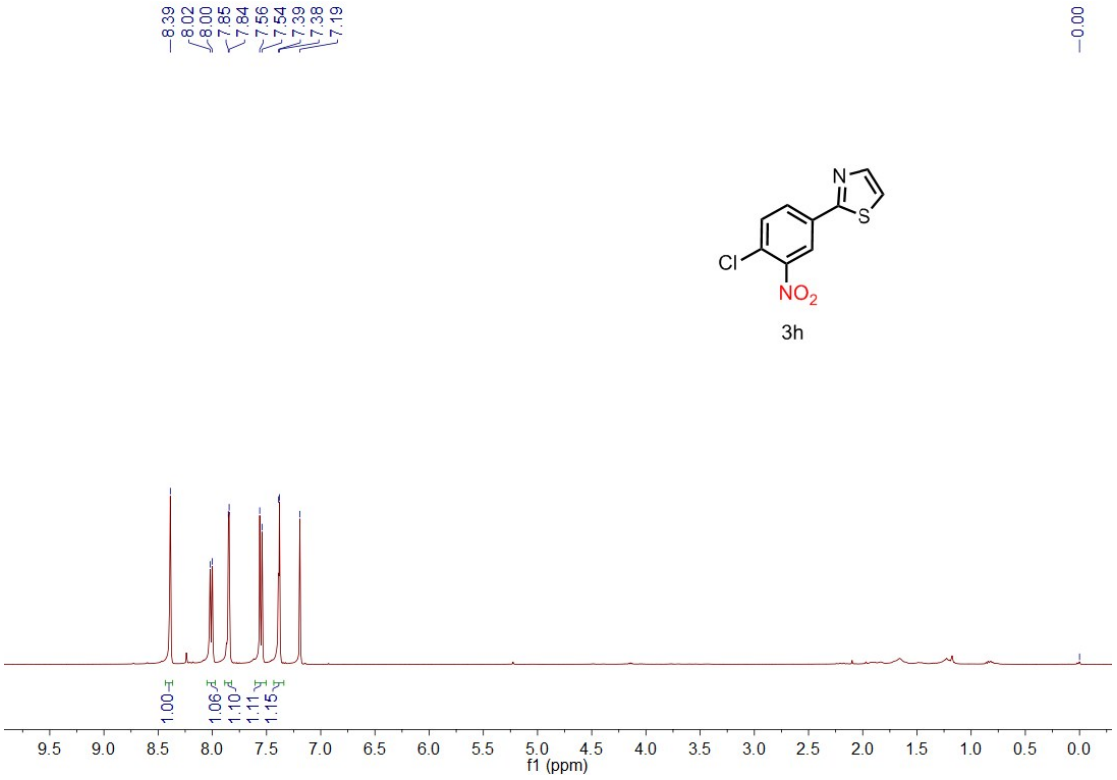


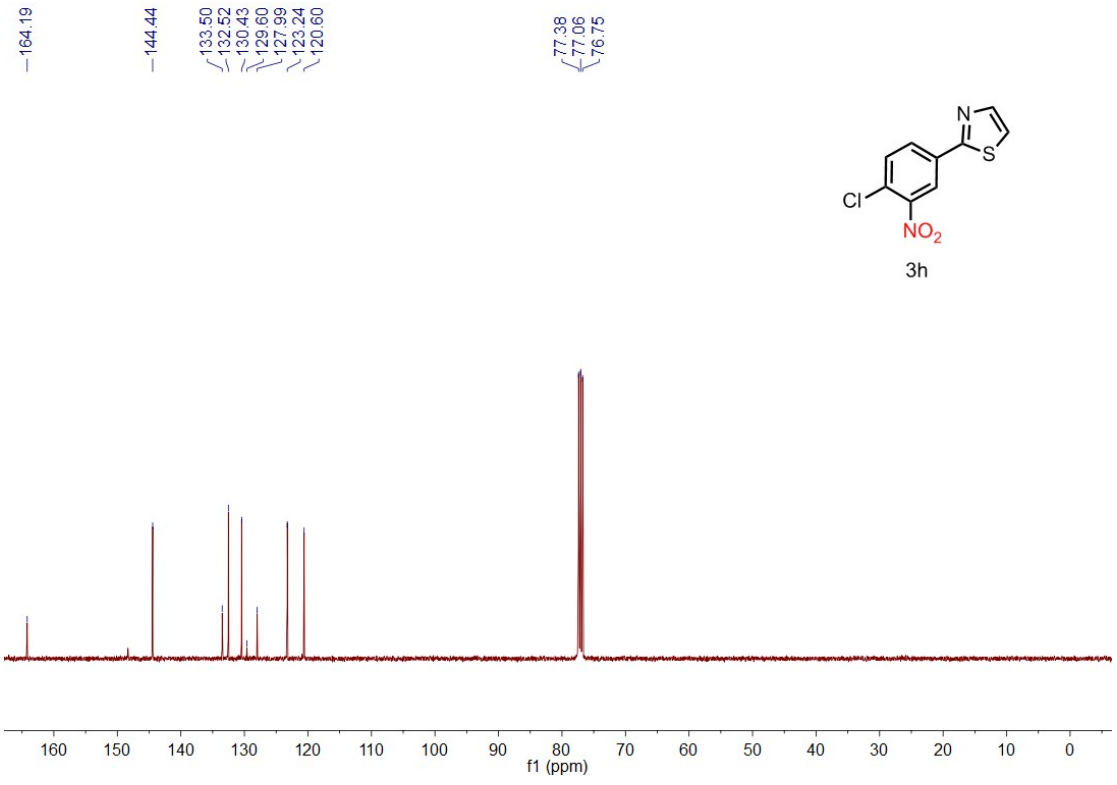
2-(4-Methoxy-3-nitrophenyl) thiazole (**3g**)



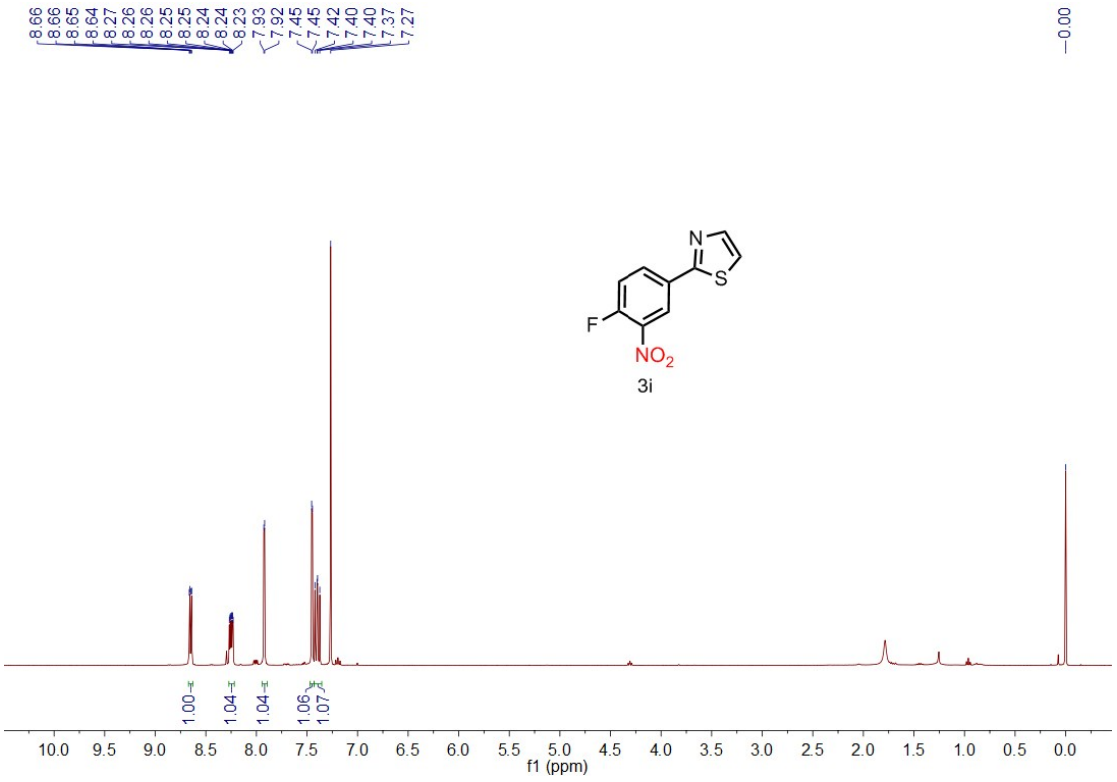


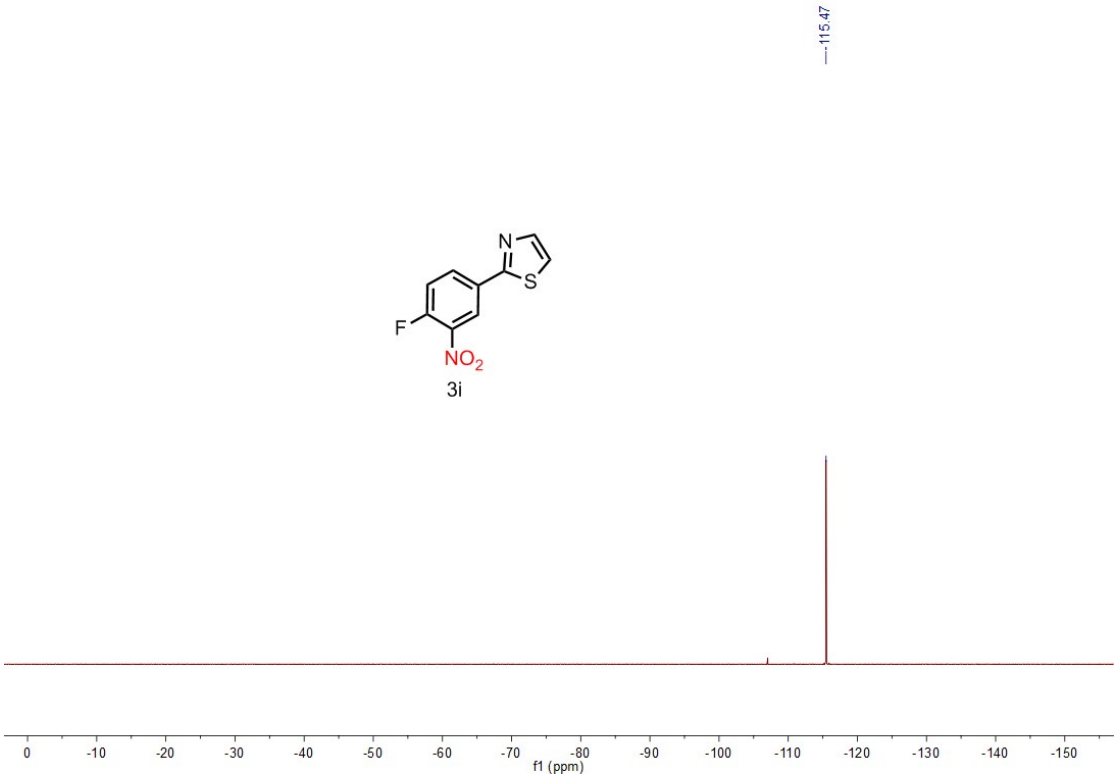
2-(4-Chloro-3-nitrophenyl) thiazole (**3h**)

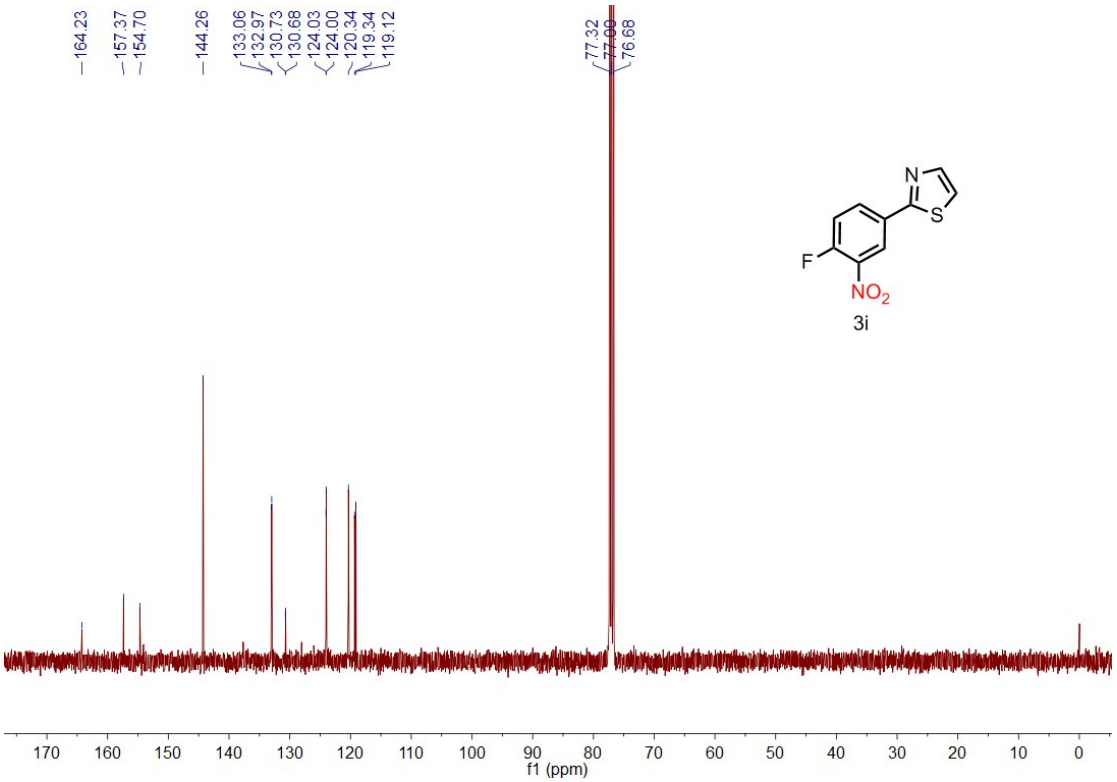




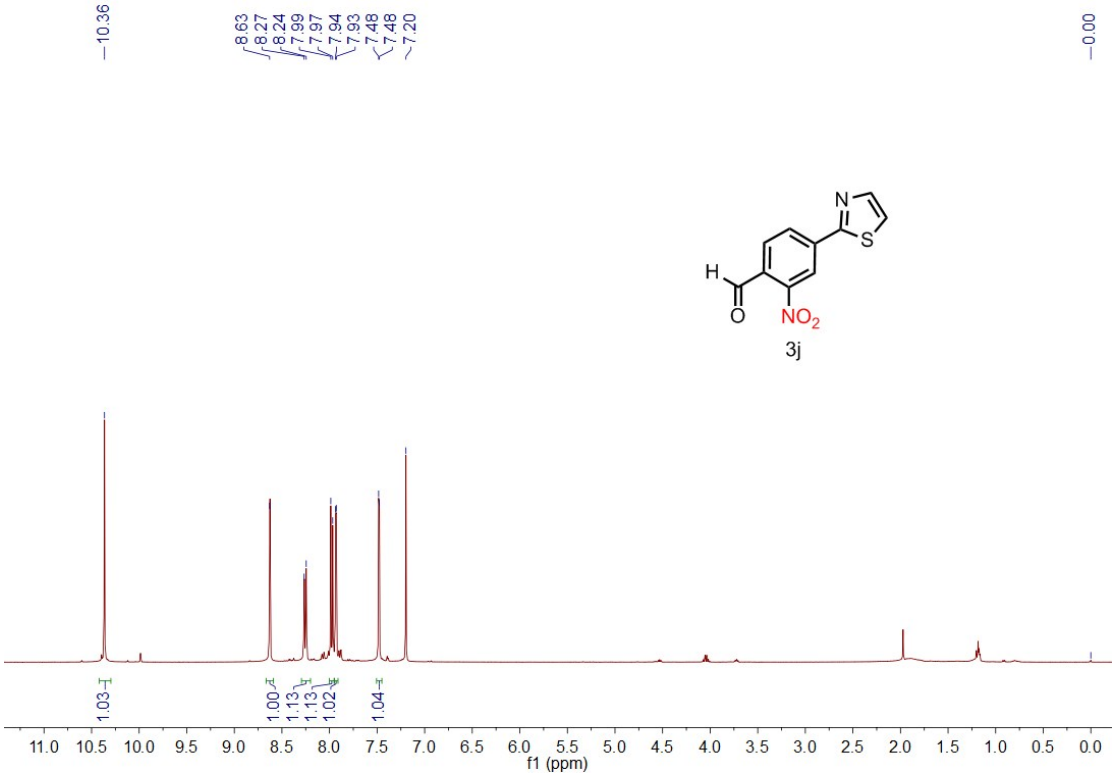
2-(4-Fluoro-3-nitrophenyl) thiazole (**3i**)

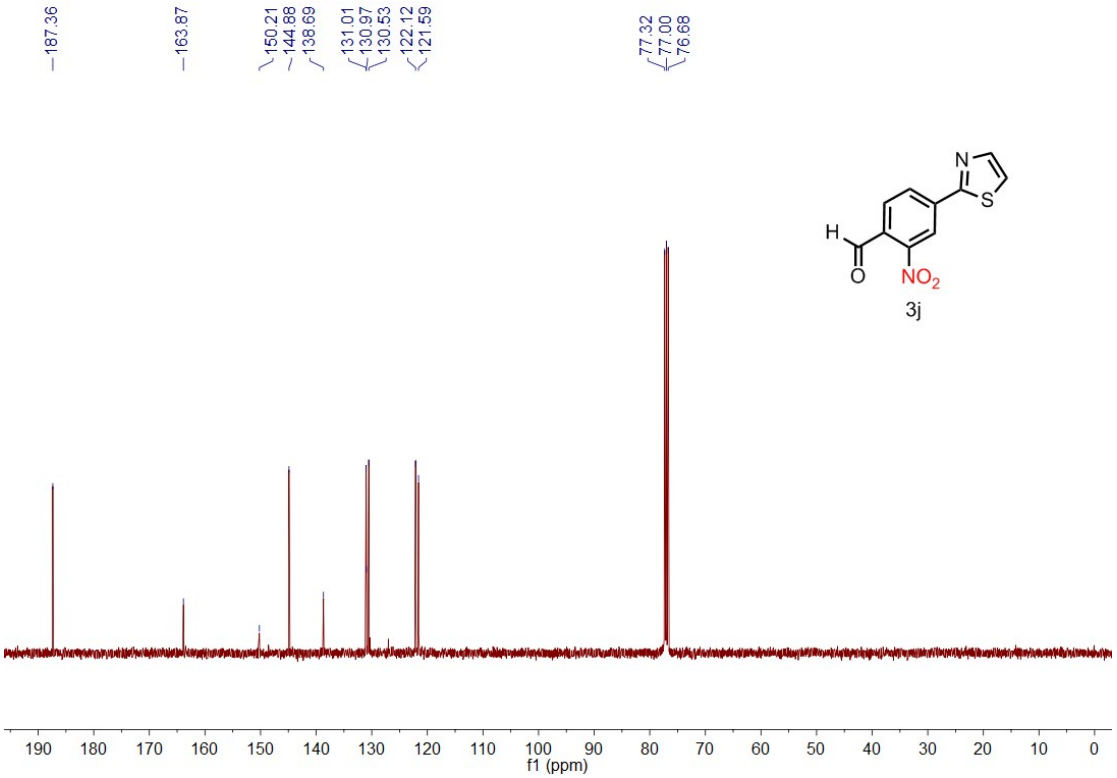




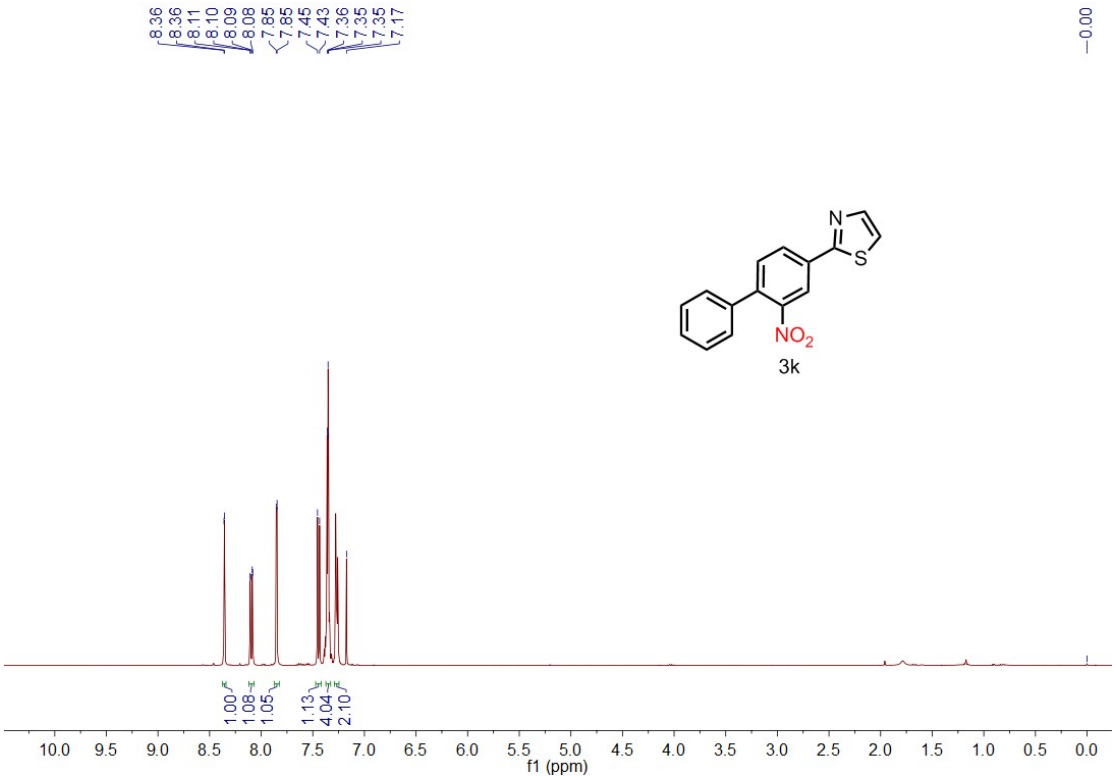


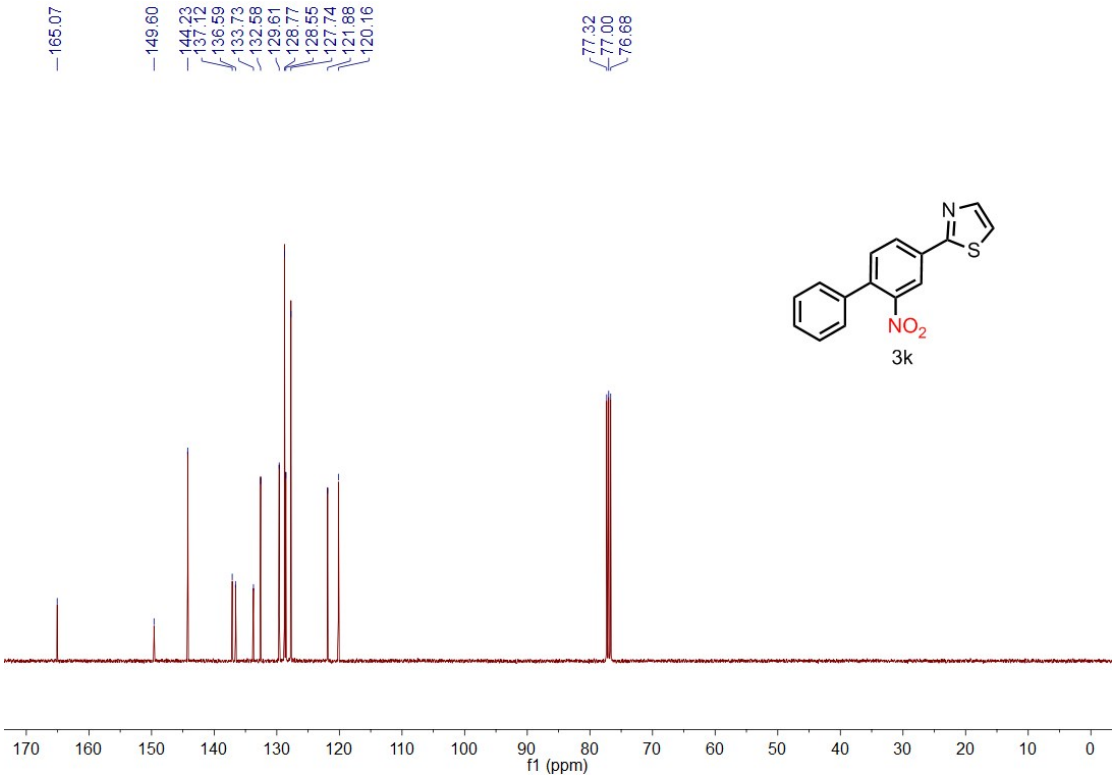
2-Nitro-4-(thiazol-2-yl) benzaldehyde (**3j**)



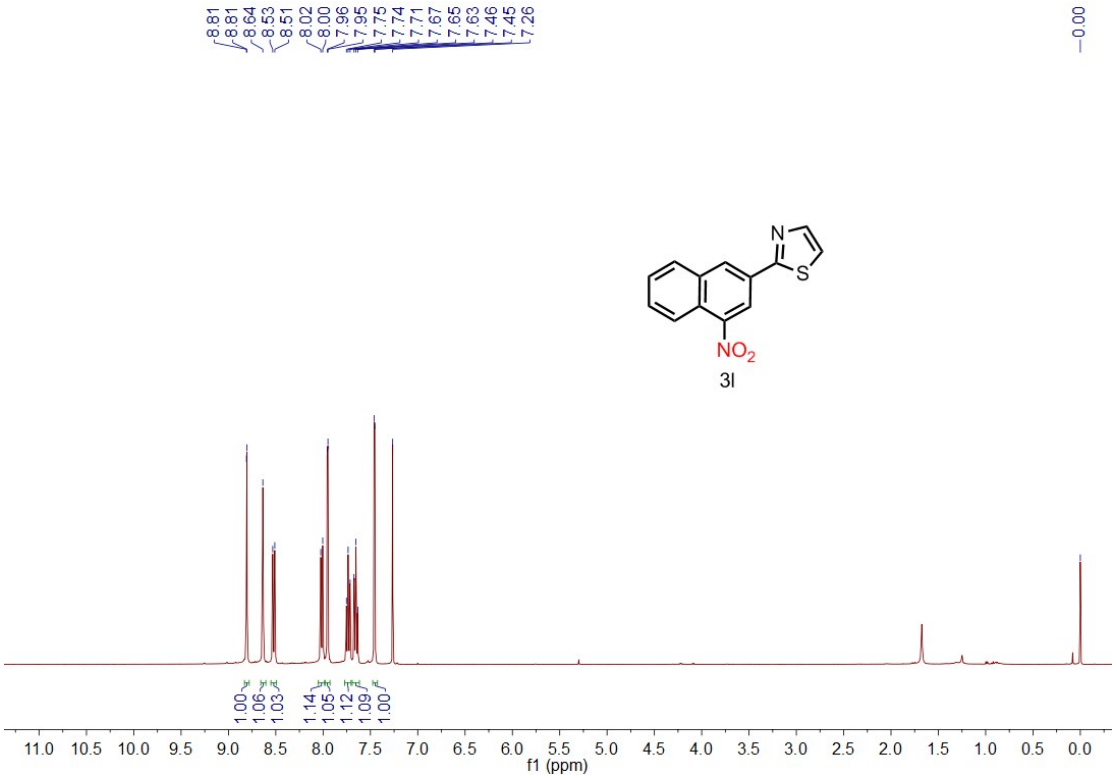


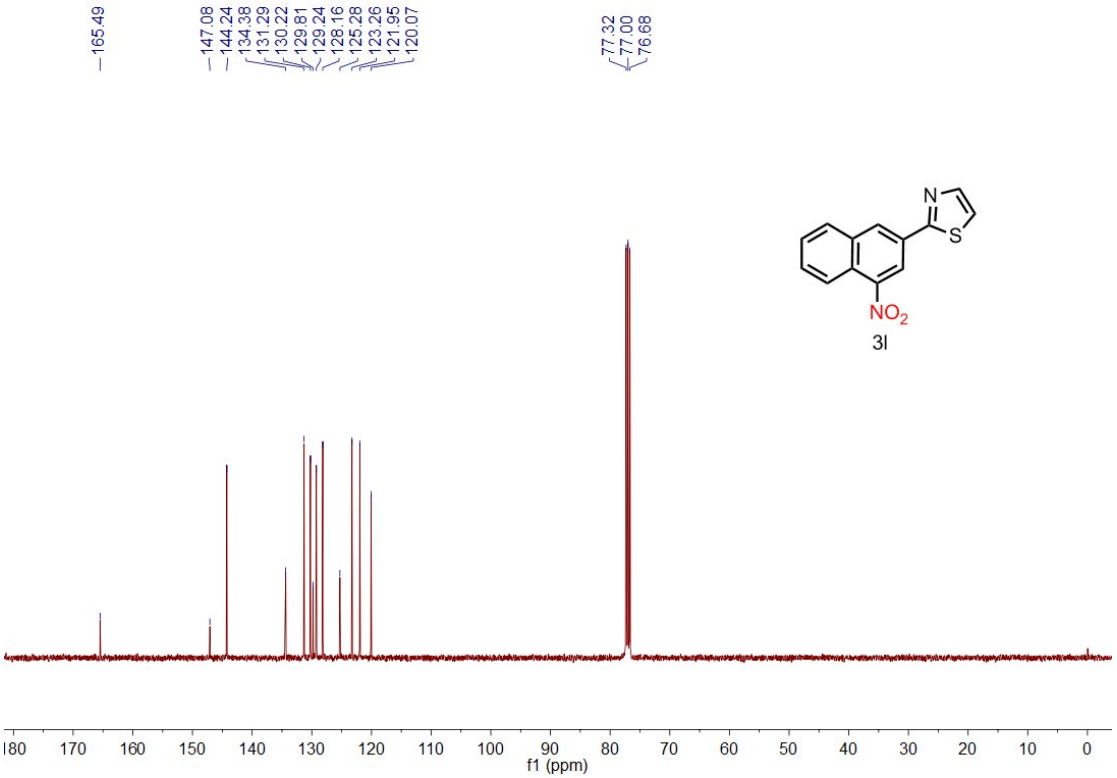
2-(2-Nitro-[1,1'-biphenyl]-4-yl) thiazole (**3k**)



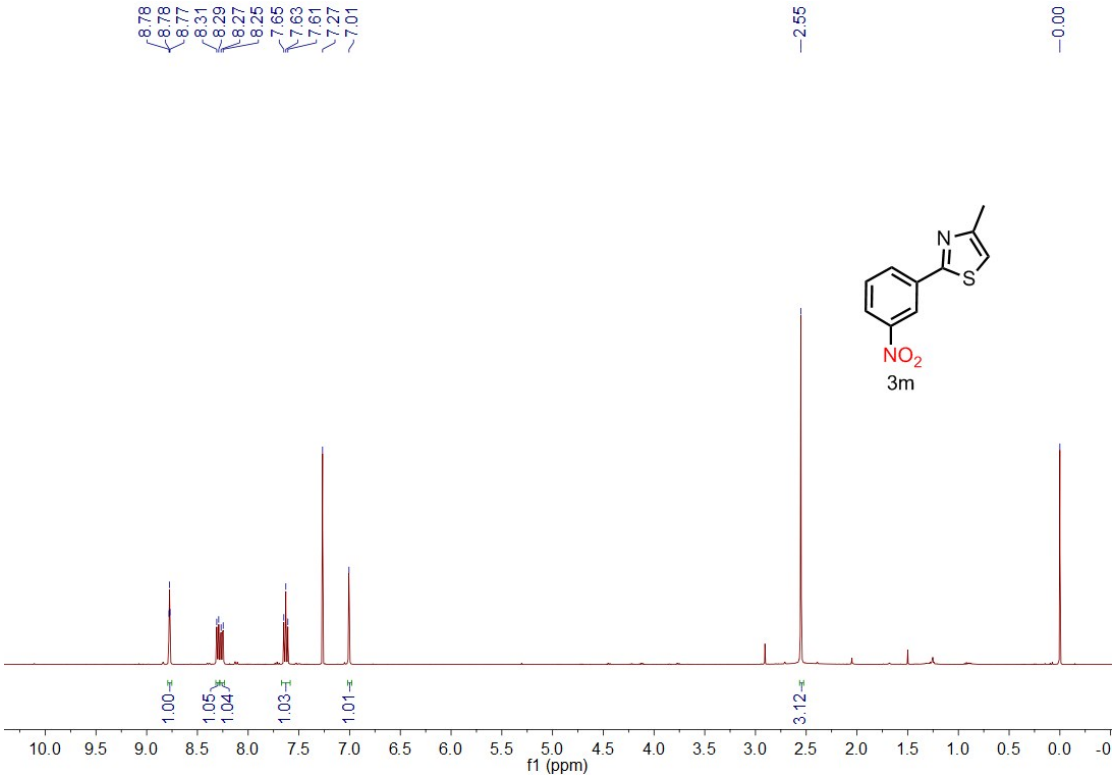


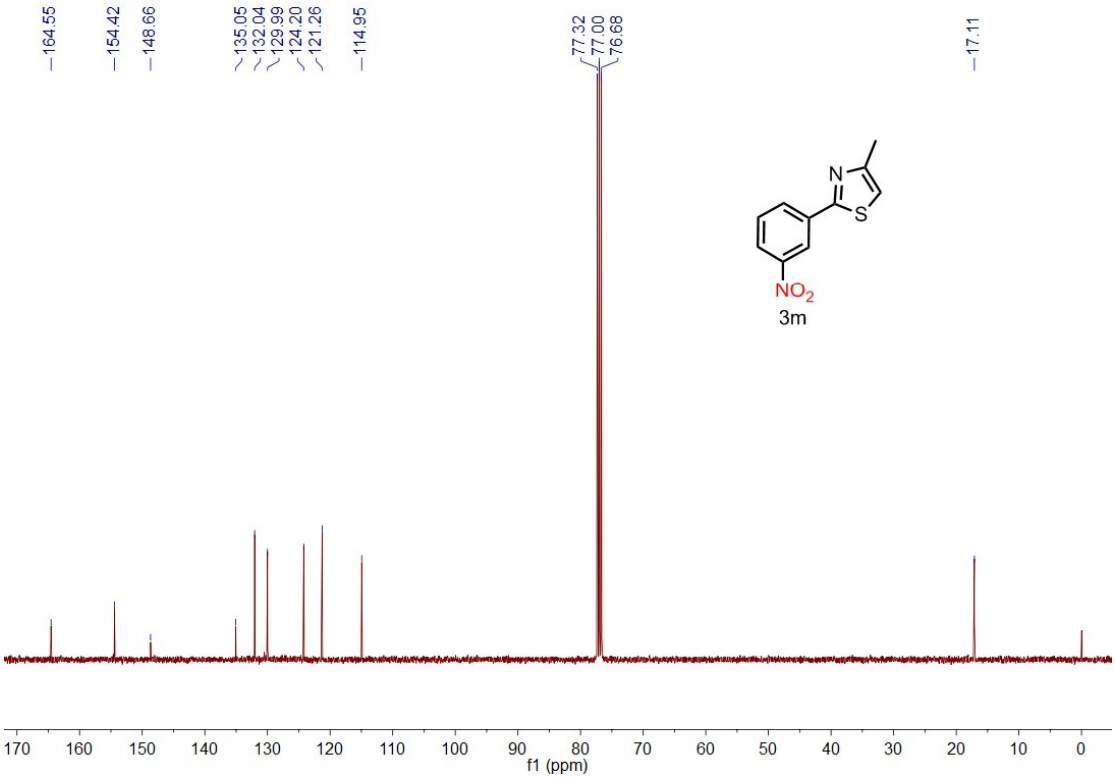
2-(4-Nitronaphthalen-2-yl) thiazole (**3l**)



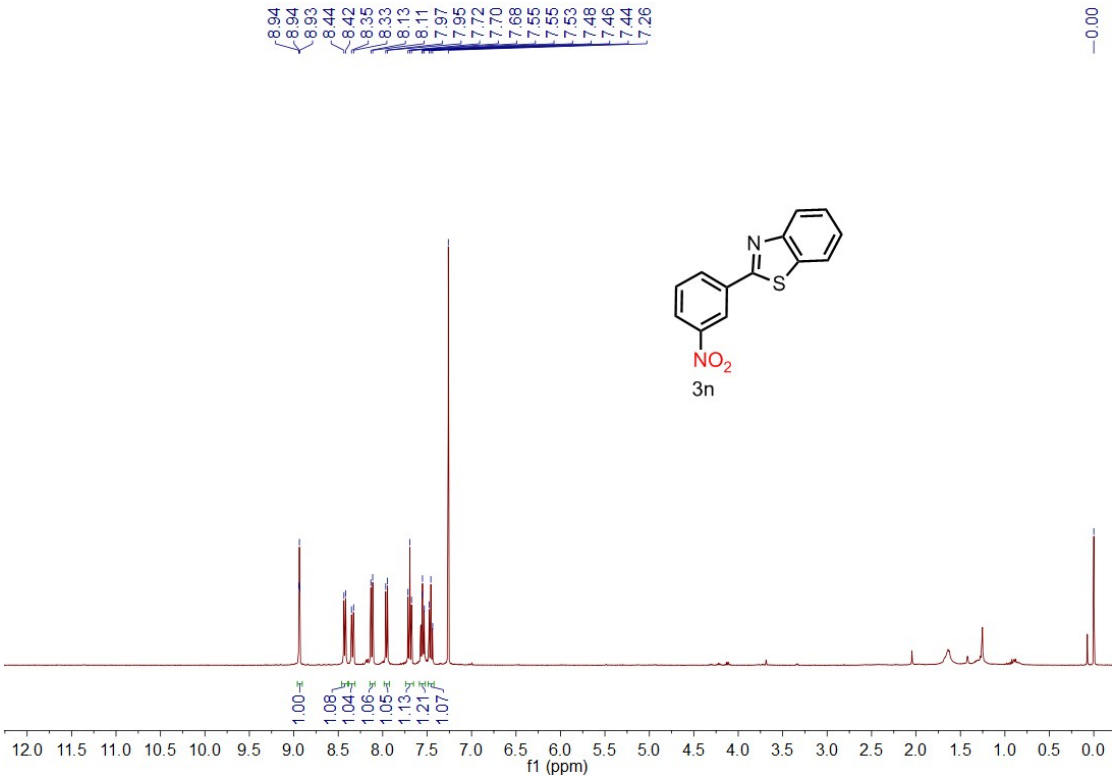


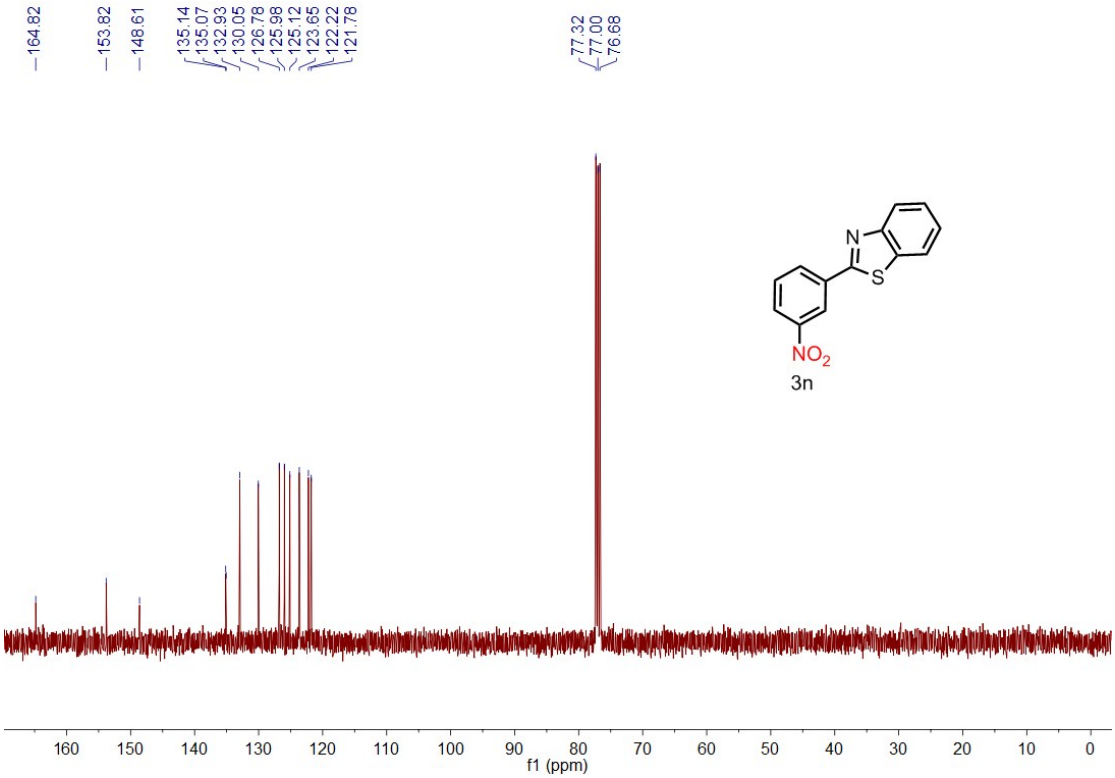
4-Methyl-2-(3-nitrophenyl) thiazole (**3m**)



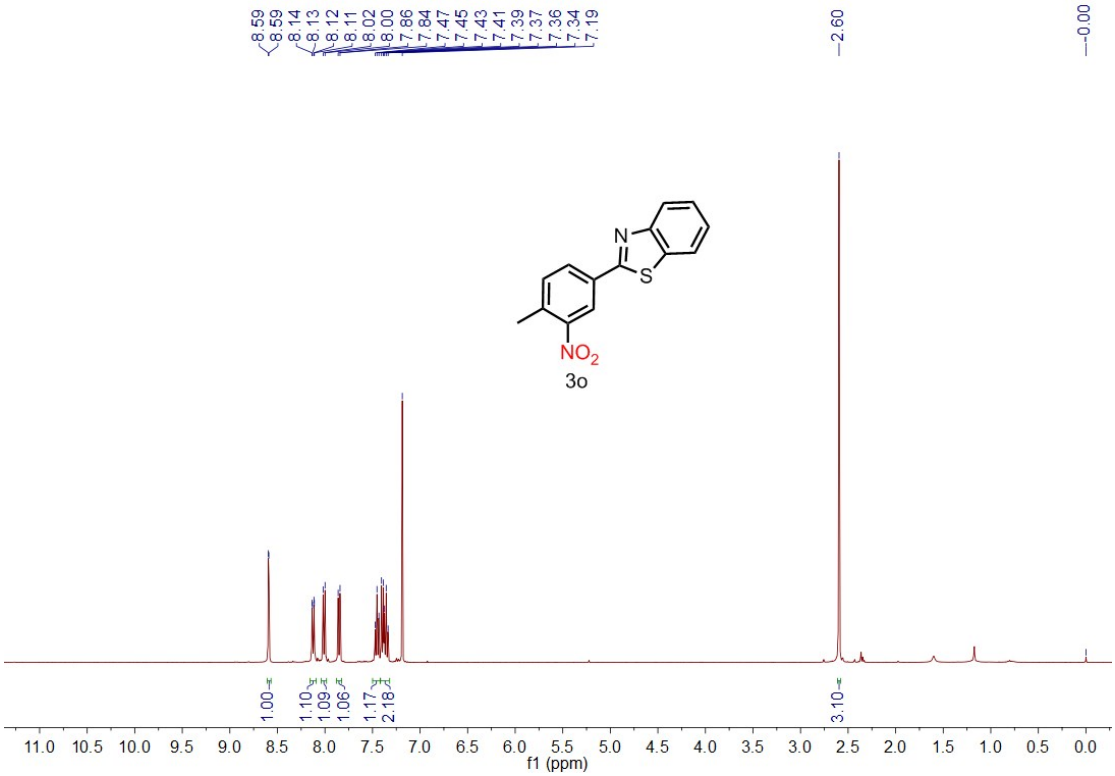


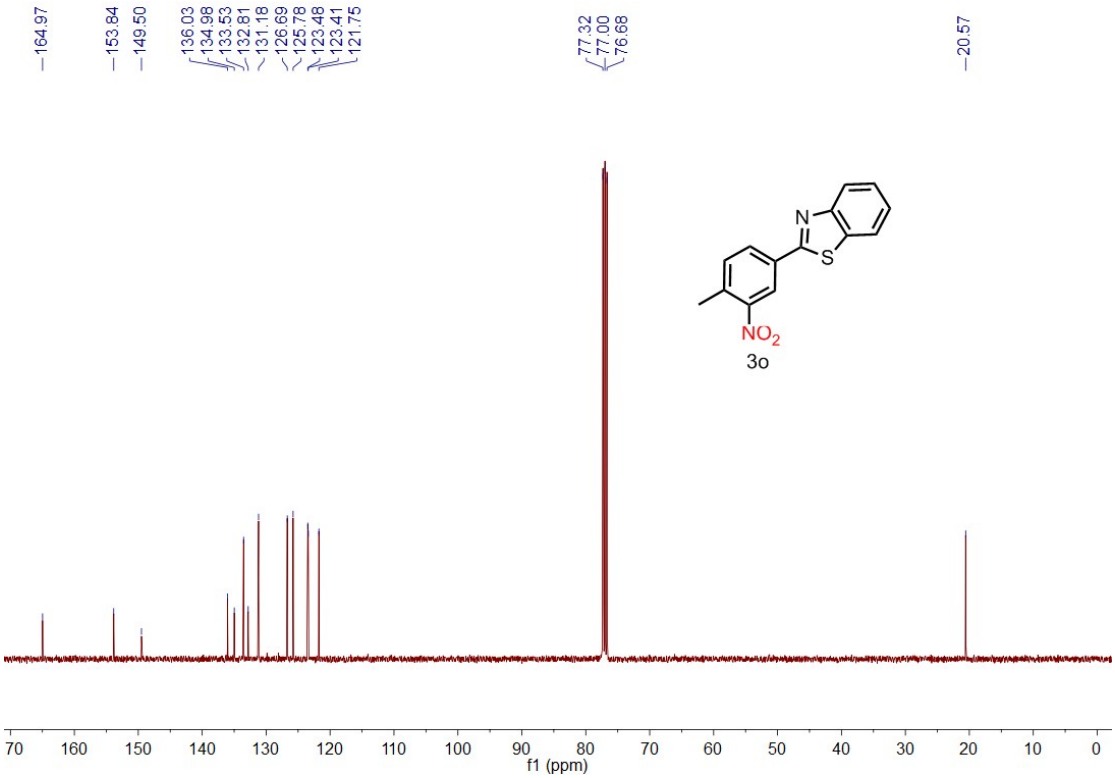
2-(3-Nitrophenyl)benzo[*d*] thiazole (**3n**)



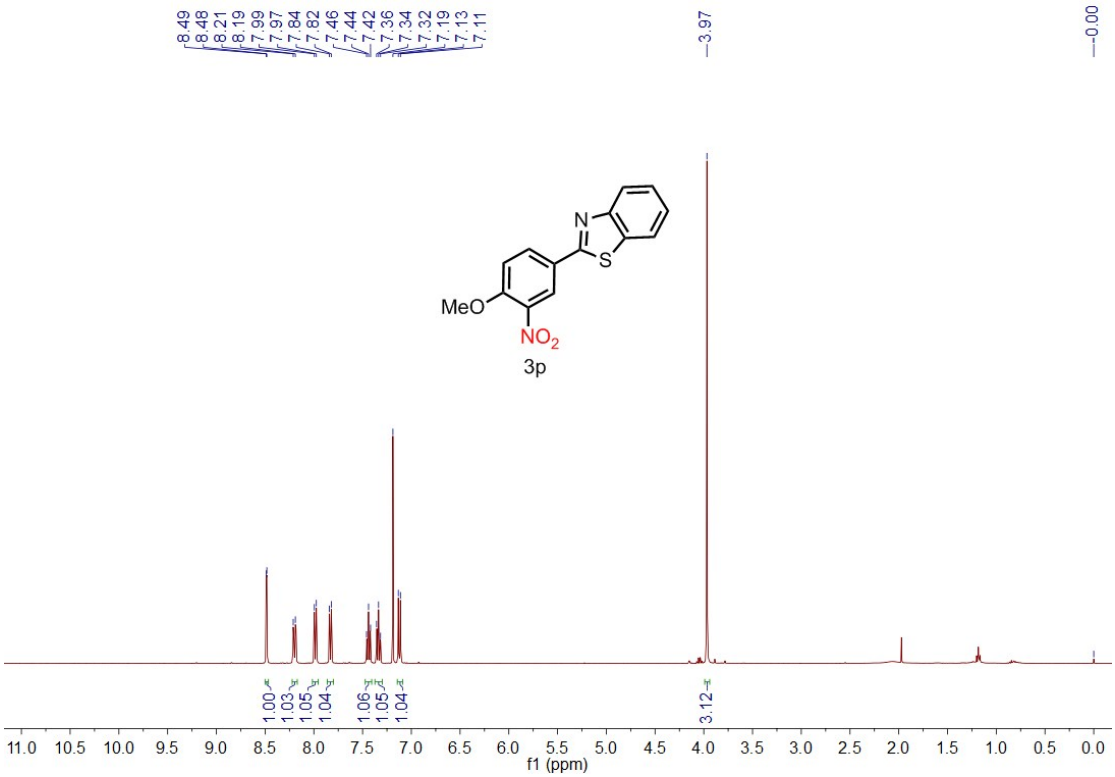


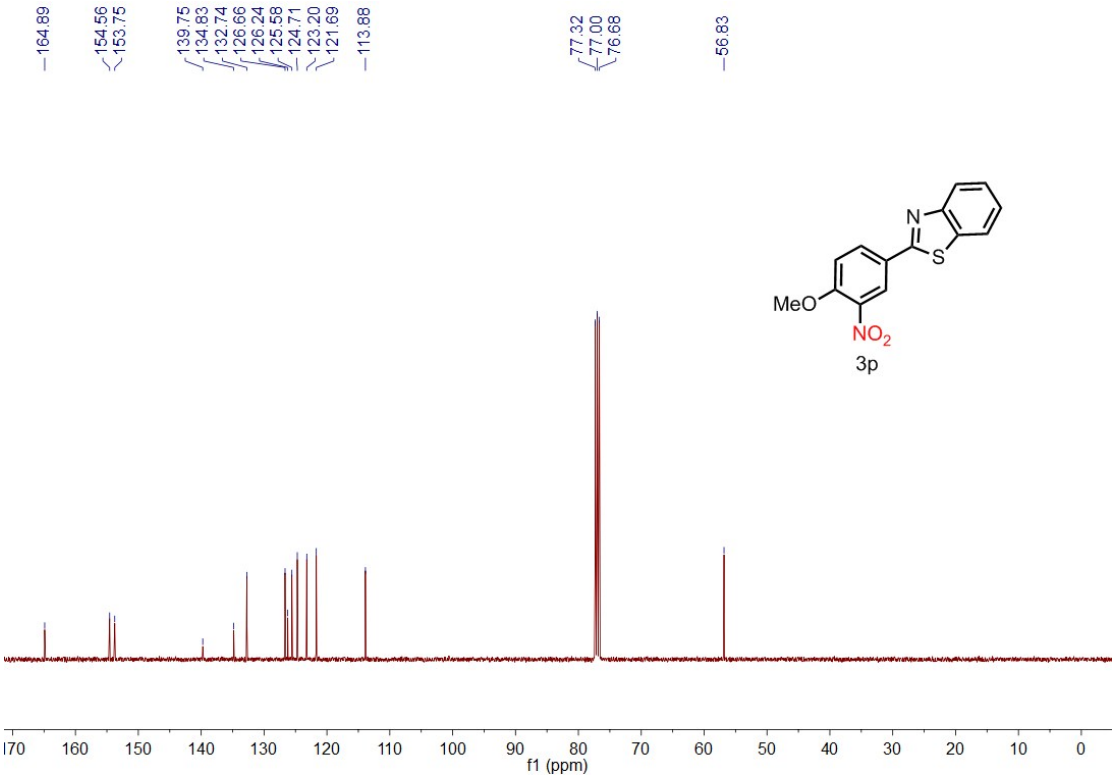
2-(4-Methyl-3-nitrophenyl) benzo[*d*] thiazole (**3o**)



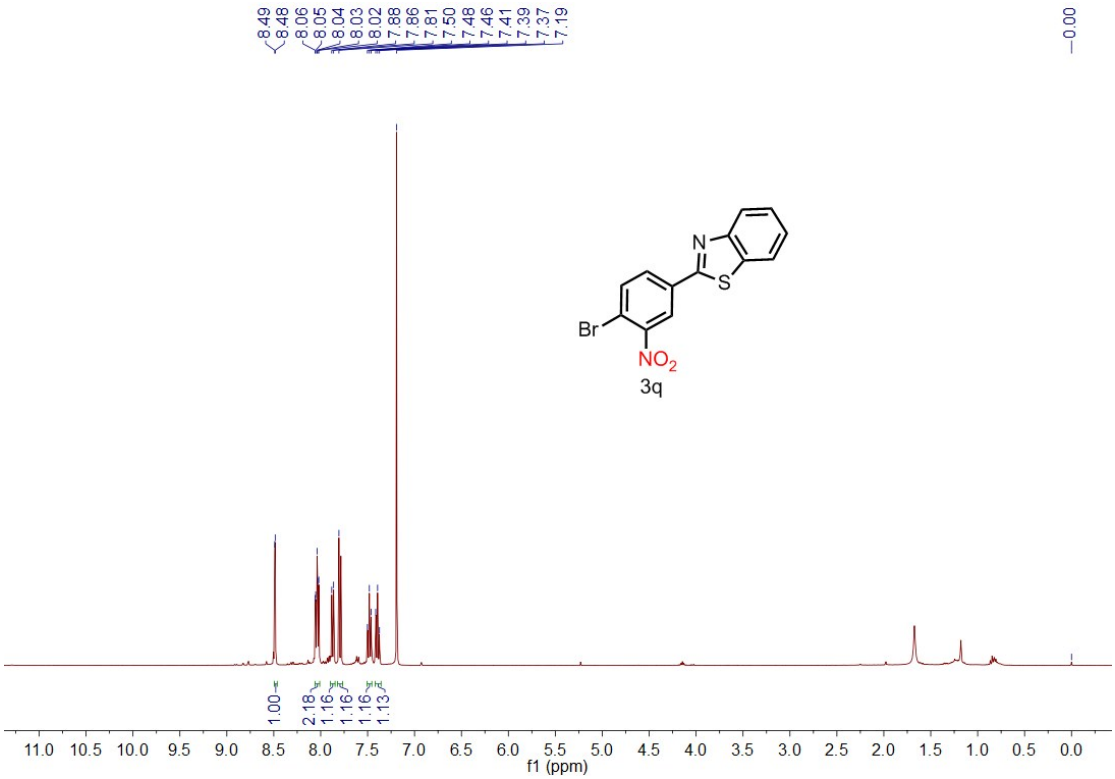


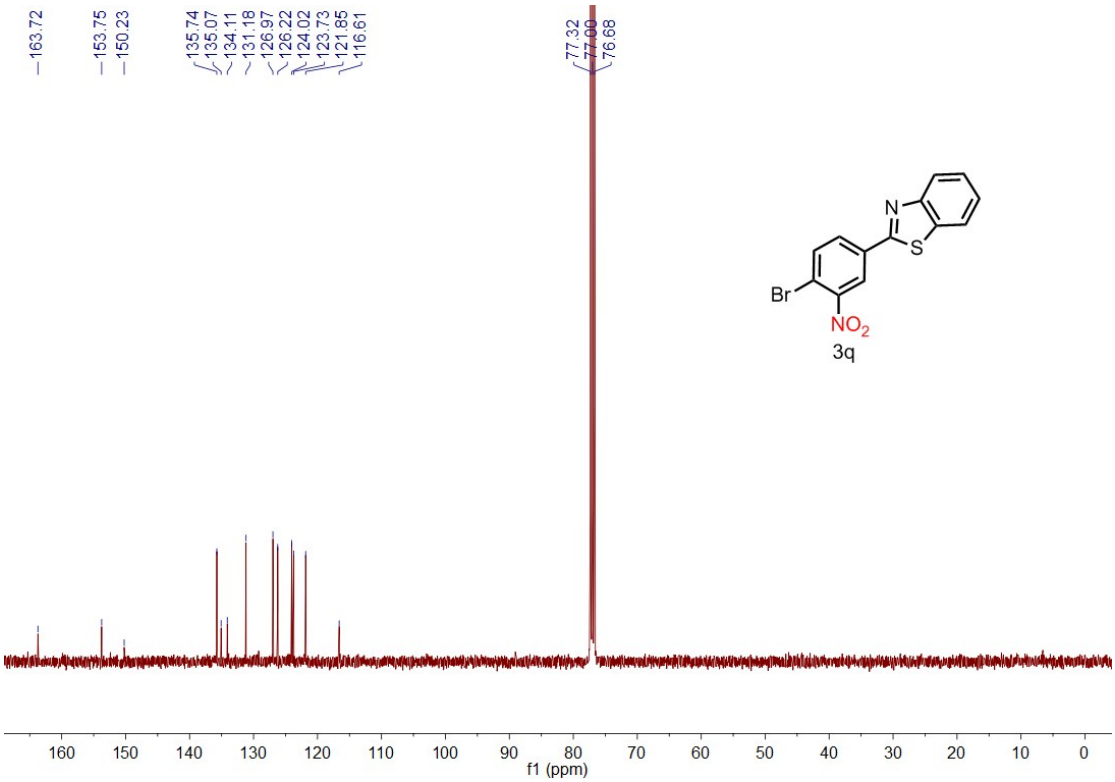
2-(4-Methoxy-3-nitrophenyl) benzo [*d*] thiazole (**3p**)



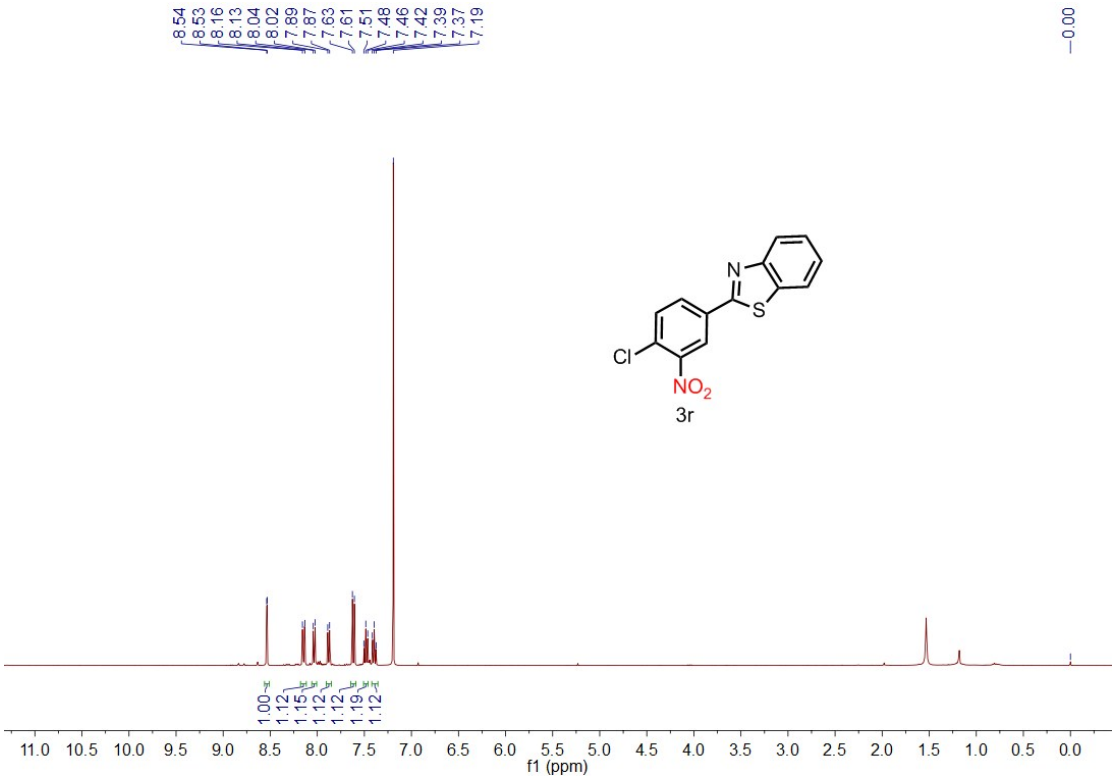


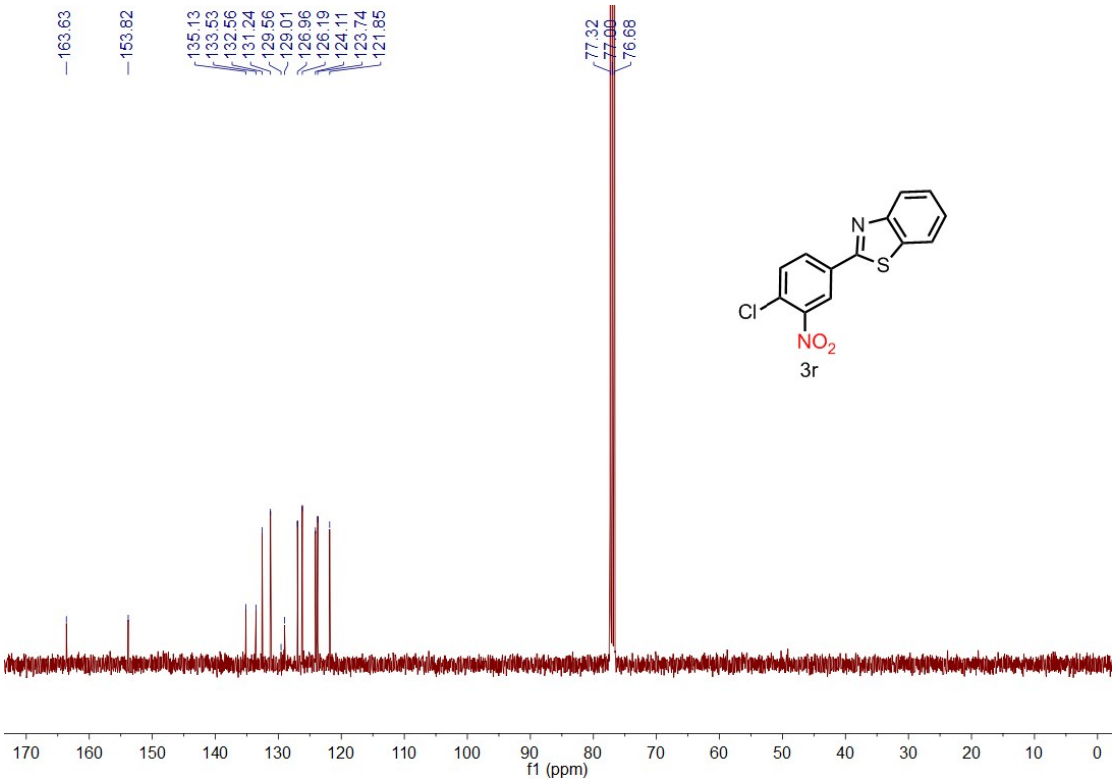
2-(4-Bromo-3-nitrophenyl) benzo[*d*] thiazole (**3q**)



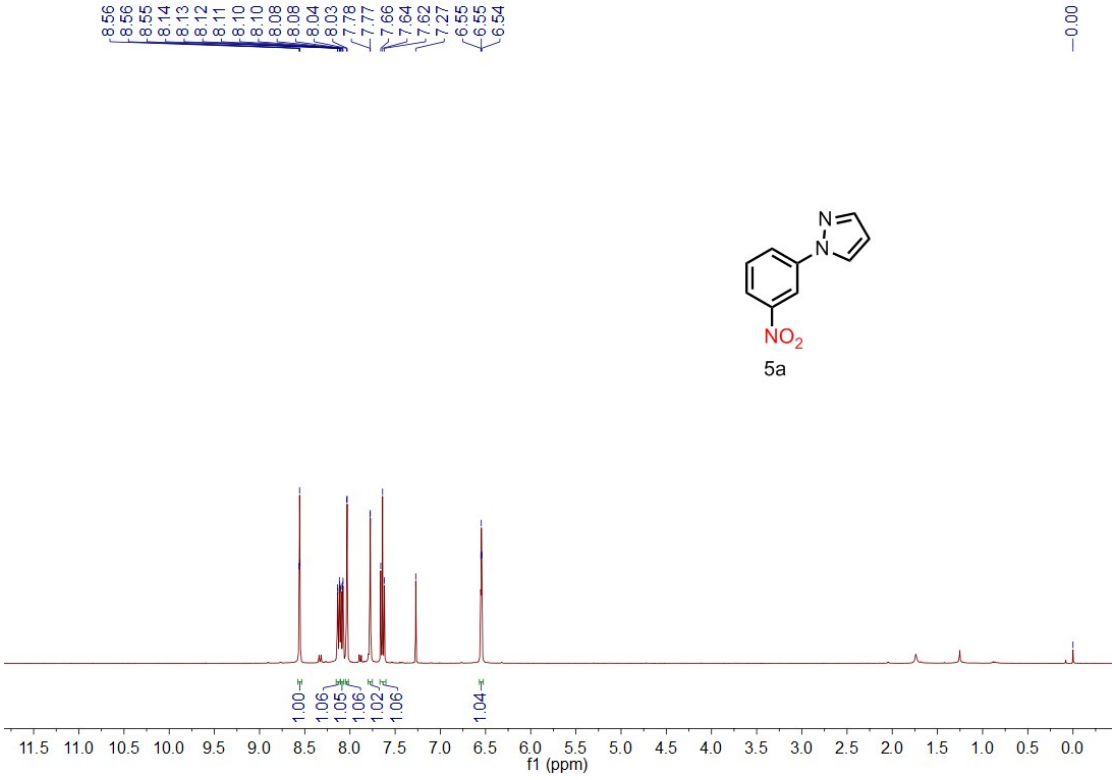


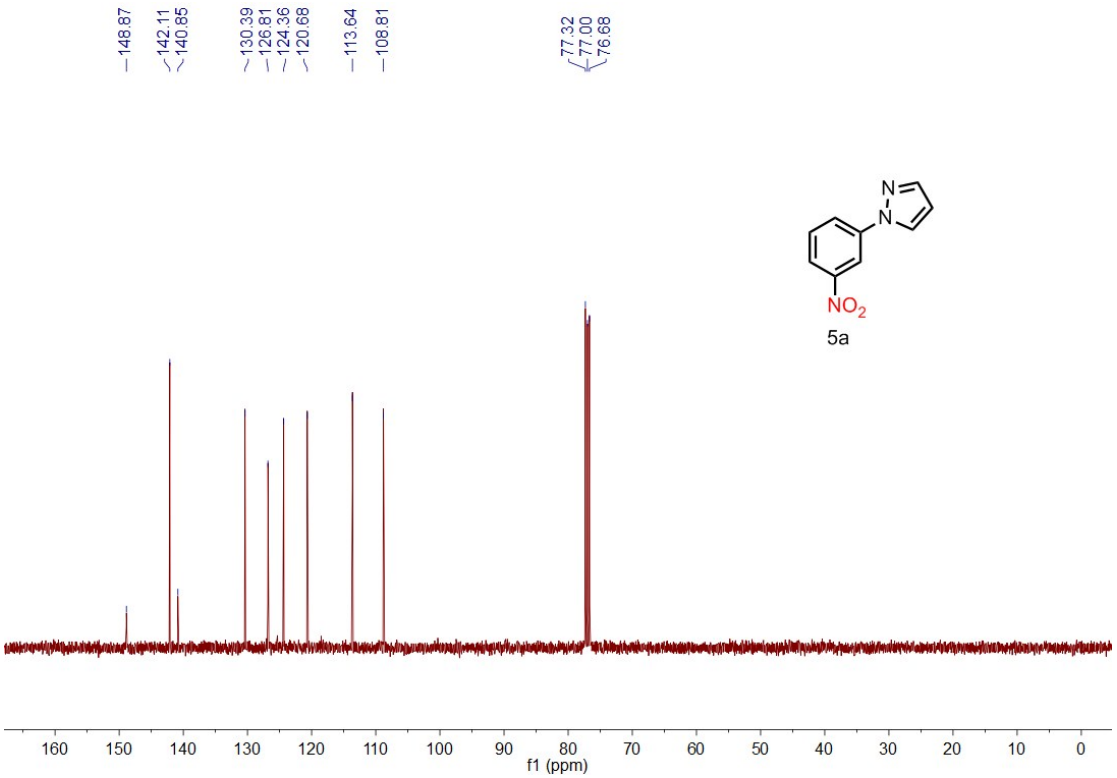
2-(4-Chloro-3-nitrophenyl) benzo [*d*] thiazole (**3r**)



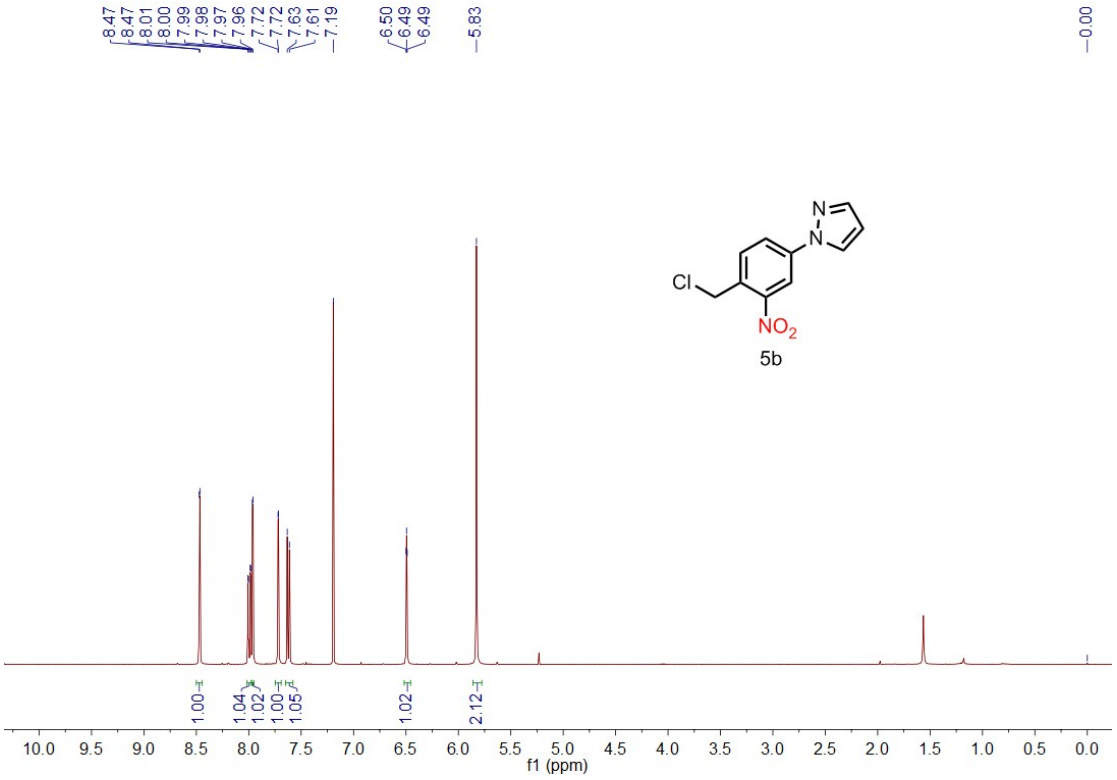


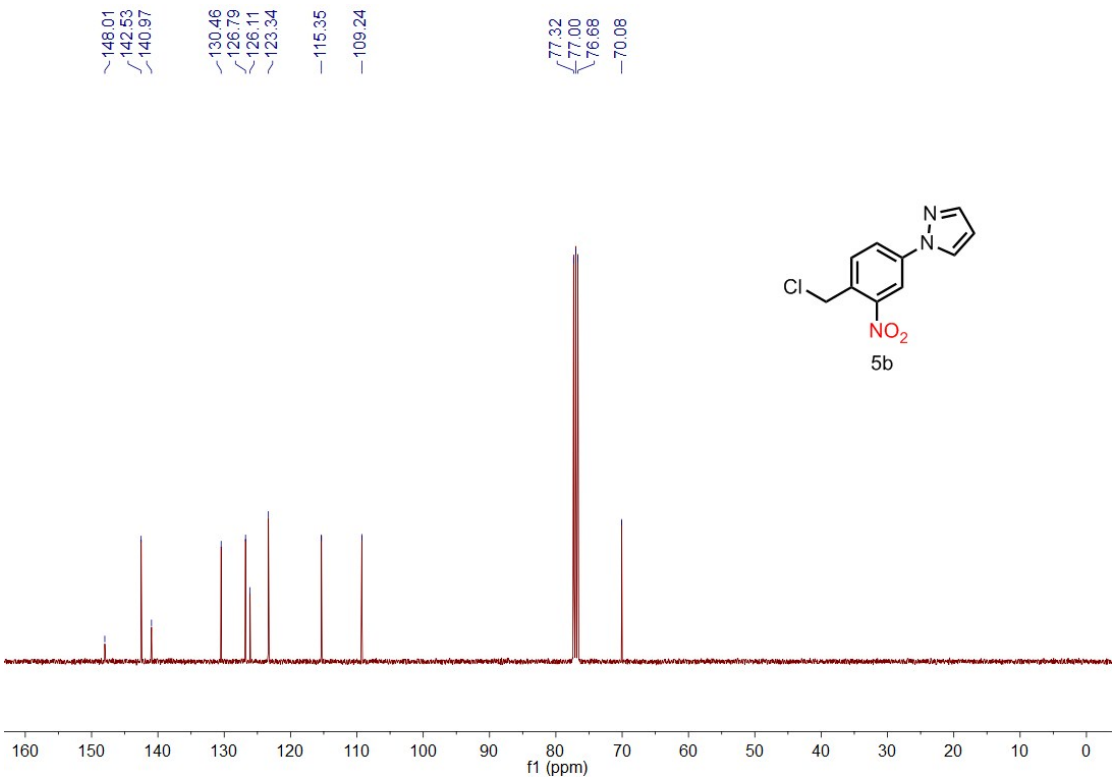
1-(3-Nitrophenyl)-1*H*-pyrazole (**5a**)



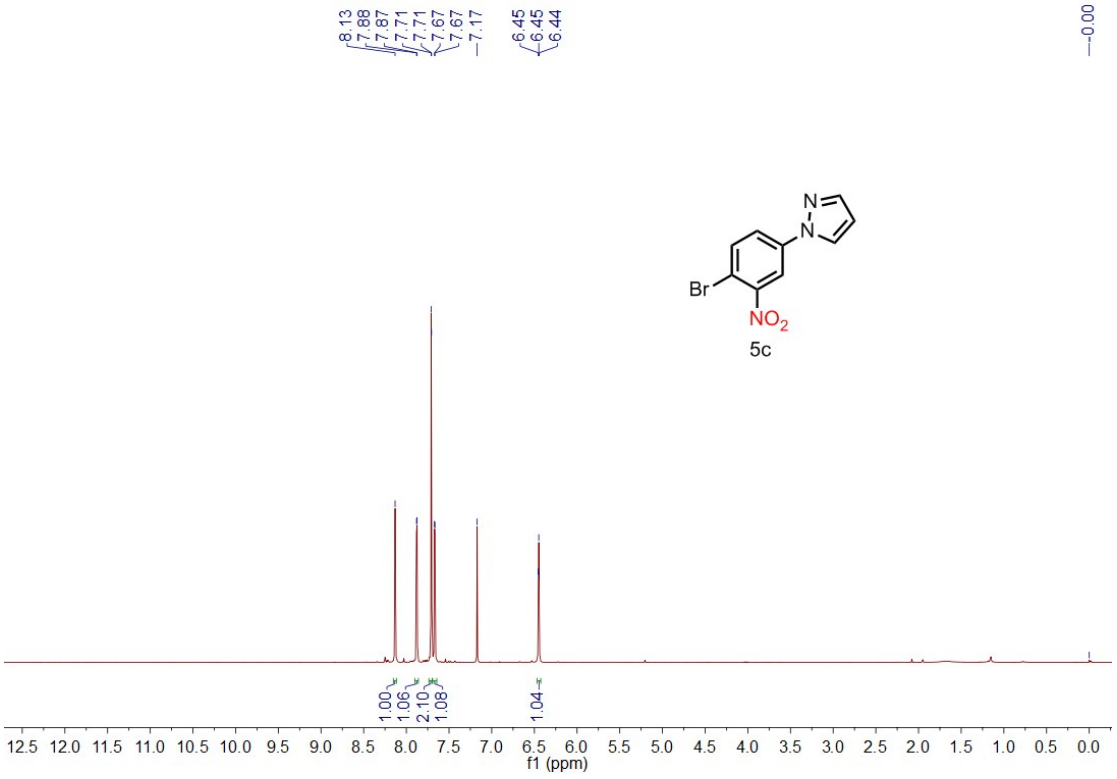


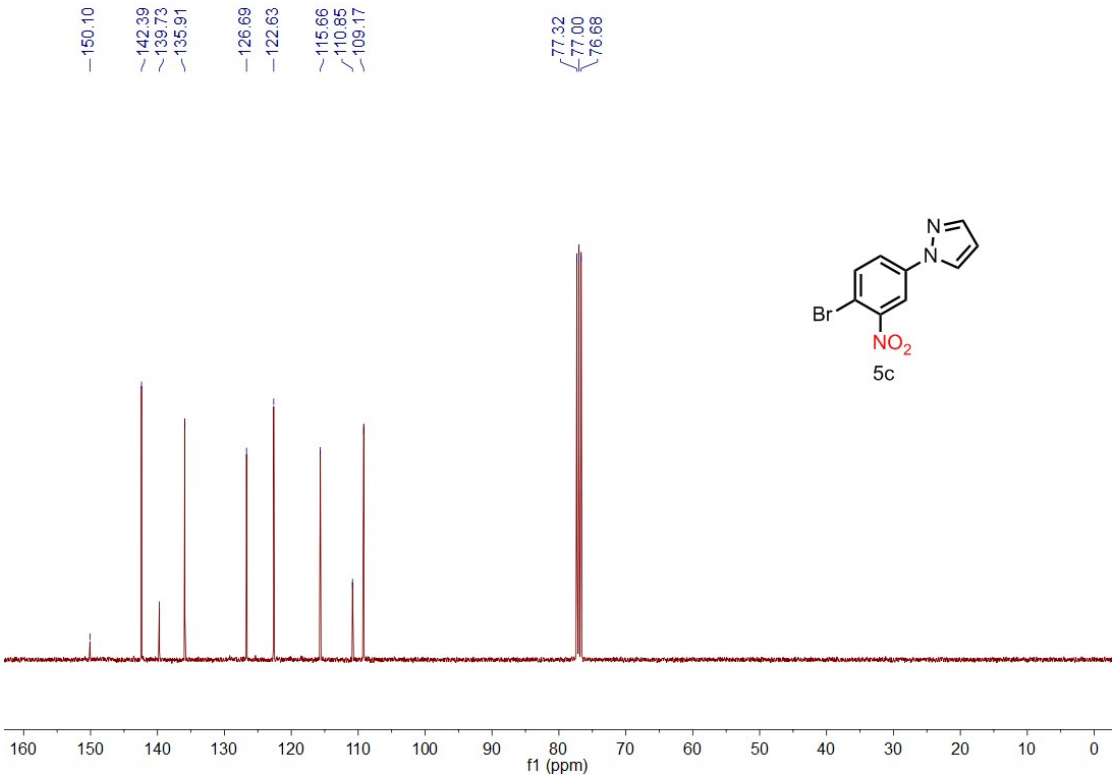
1-(4-(Chloromethyl)-3-nitrophenyl)-1*H*-pyrazole (**5b**)



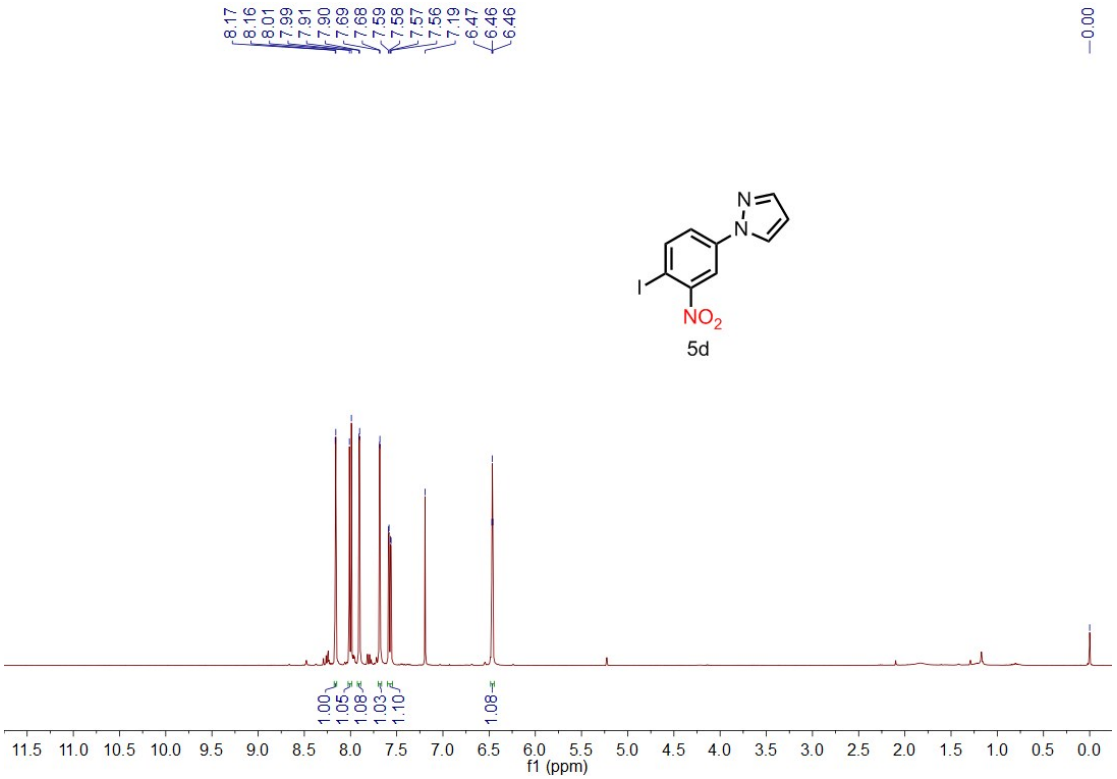


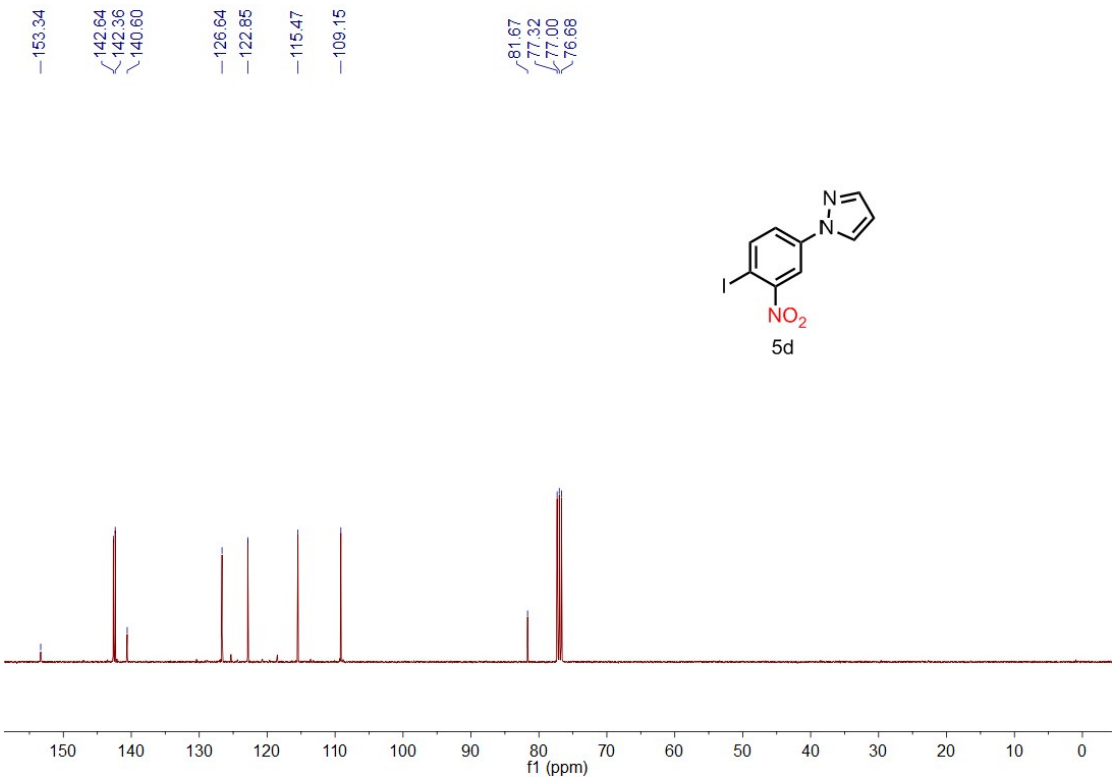
1-(4-Bromo-3-nitrophenyl)-1*H*-pyrazole (**5c**)



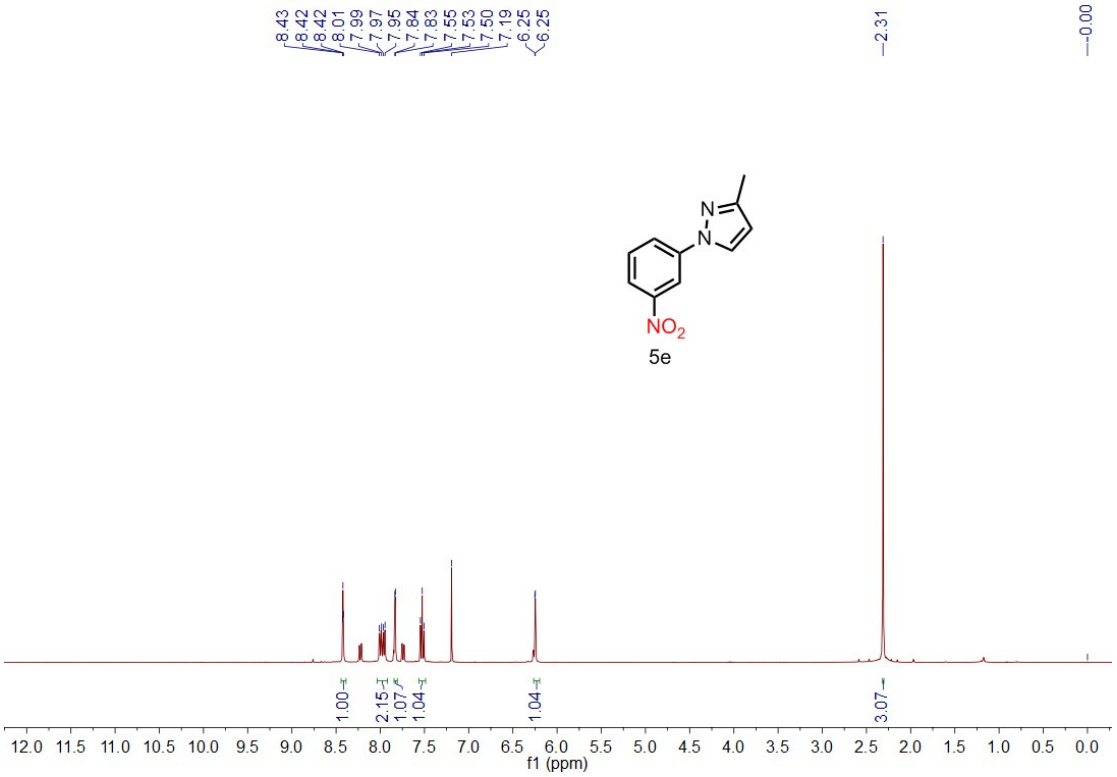


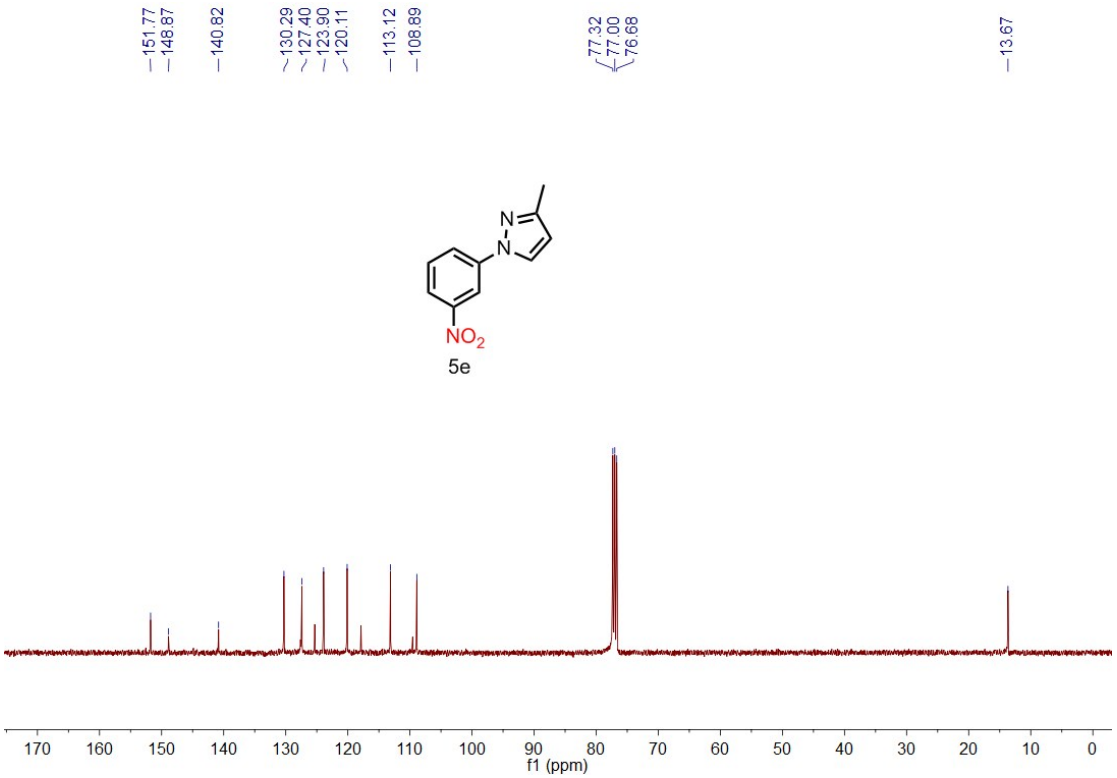
1-(4-Iodo-3-nitrophenyl)-1*H*-pyrazole (**5d**)



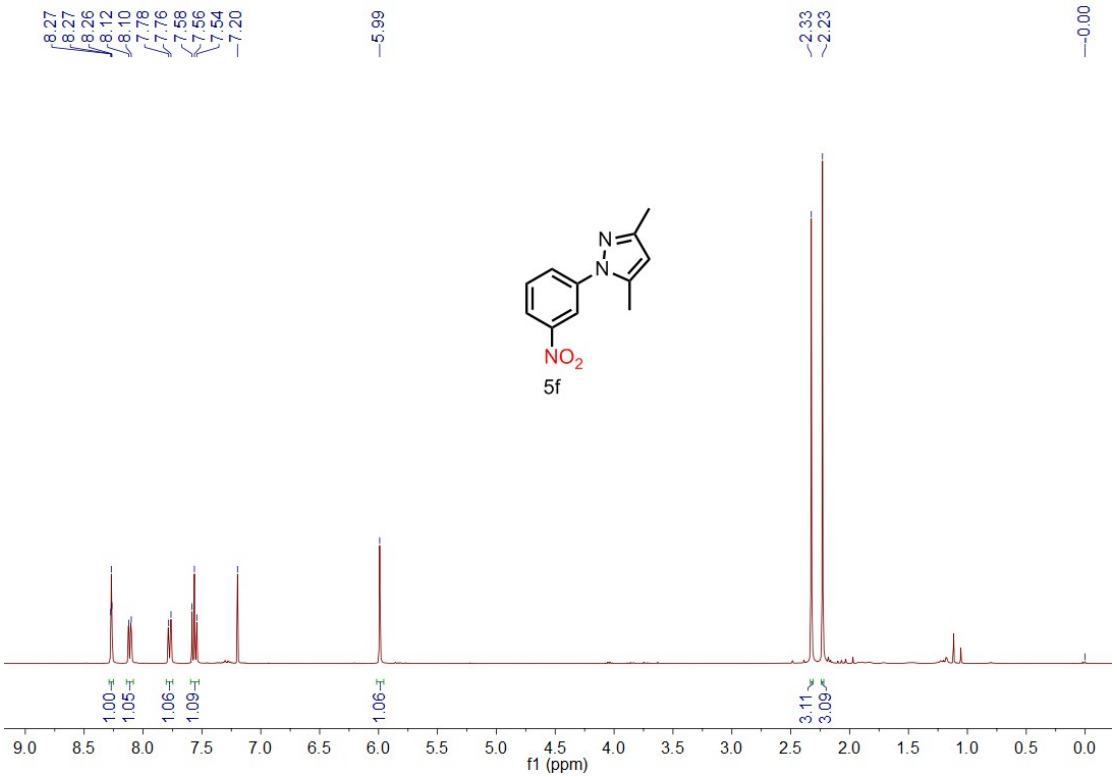


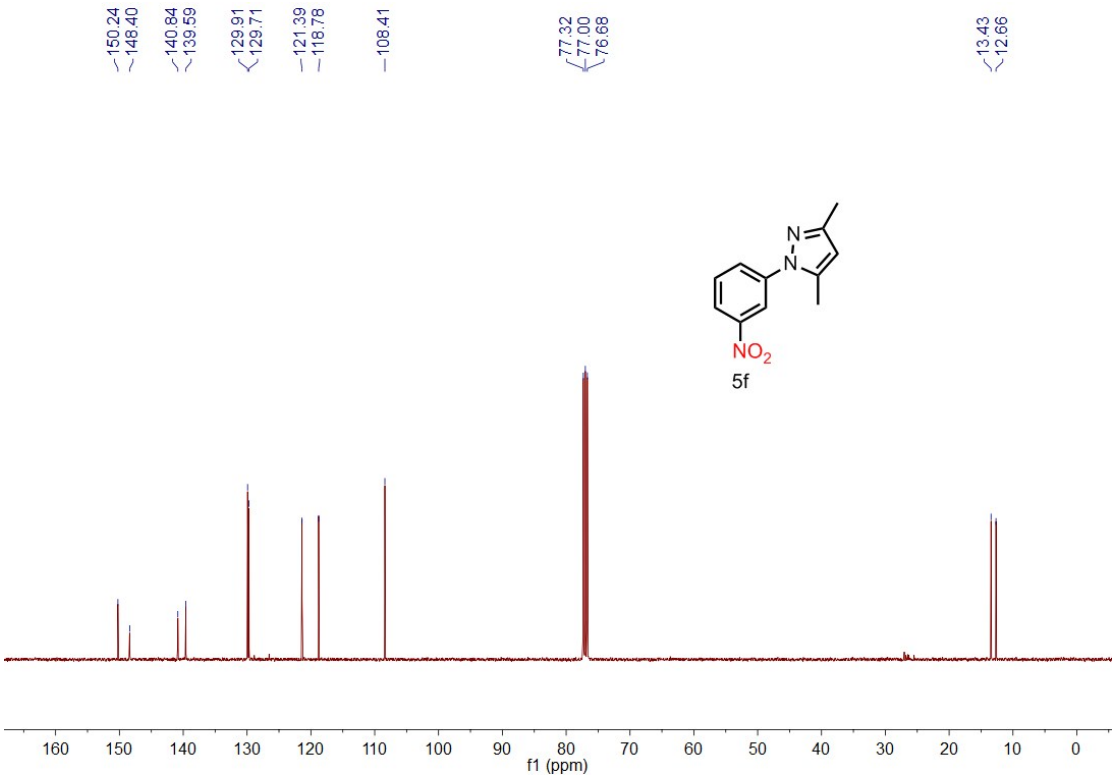
3-Methyl-1-(3-nitrophenyl)-1*H*-pyrazole (**5e**)



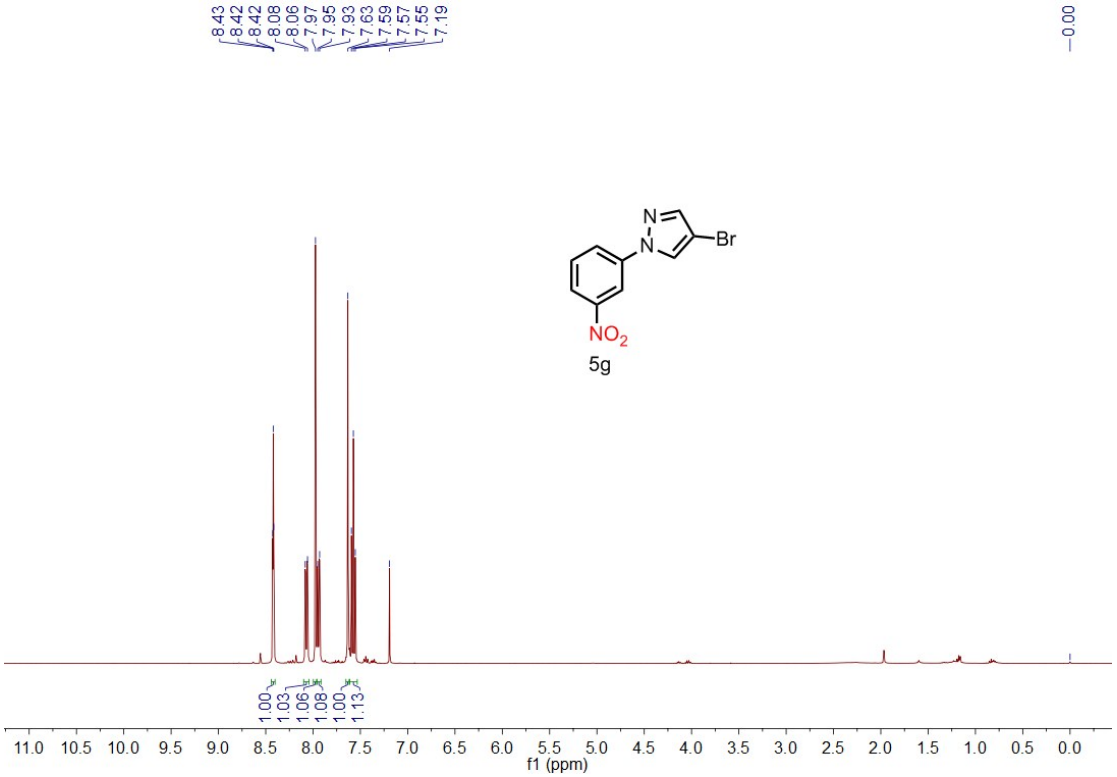


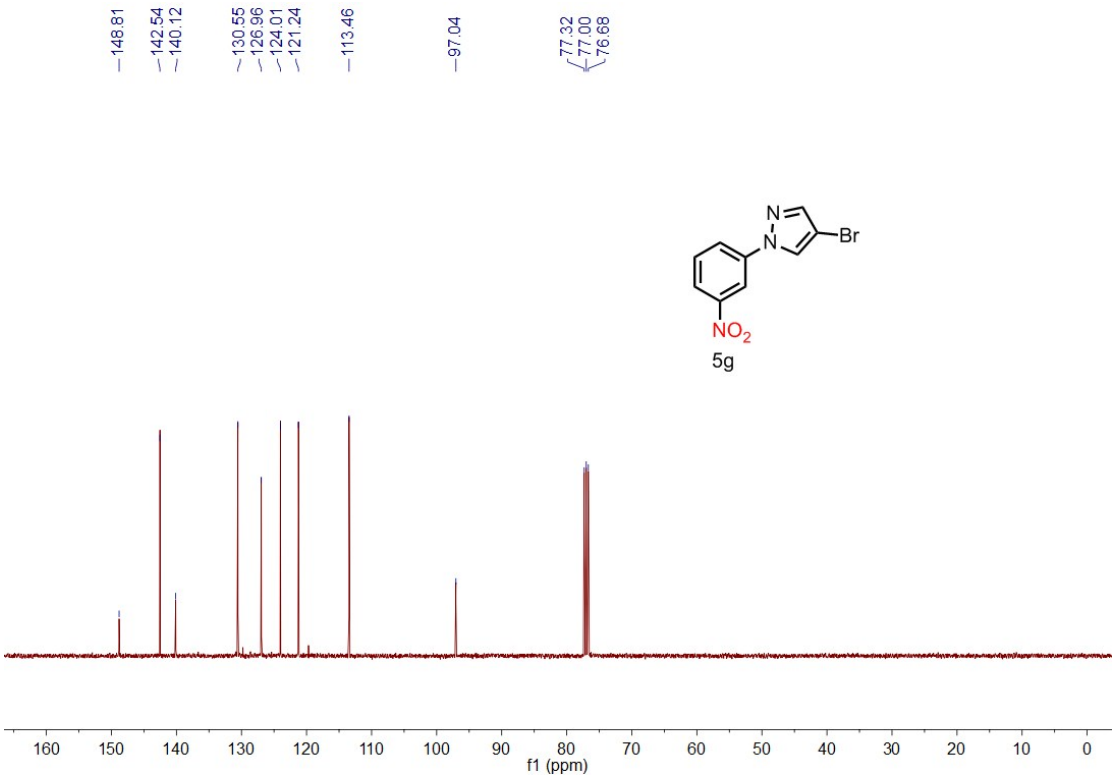
3,5-Dimethyl-1-(3-nitrophenyl)-1*H*-pyrazole (**5f**)



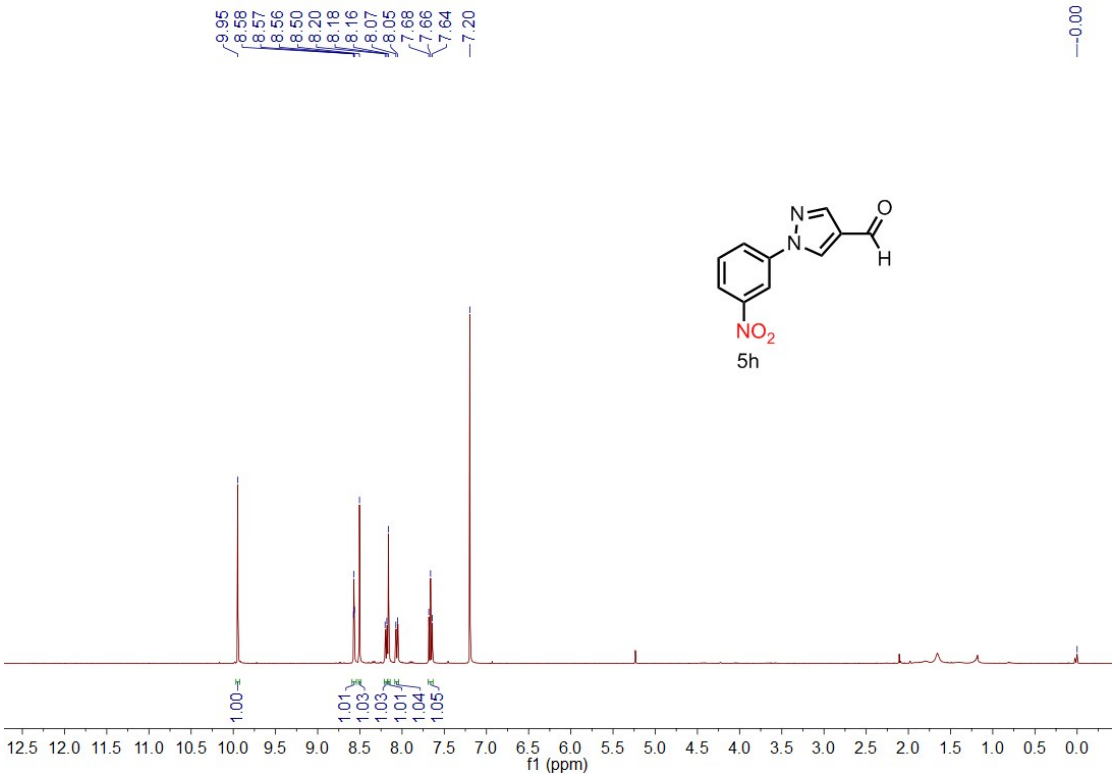


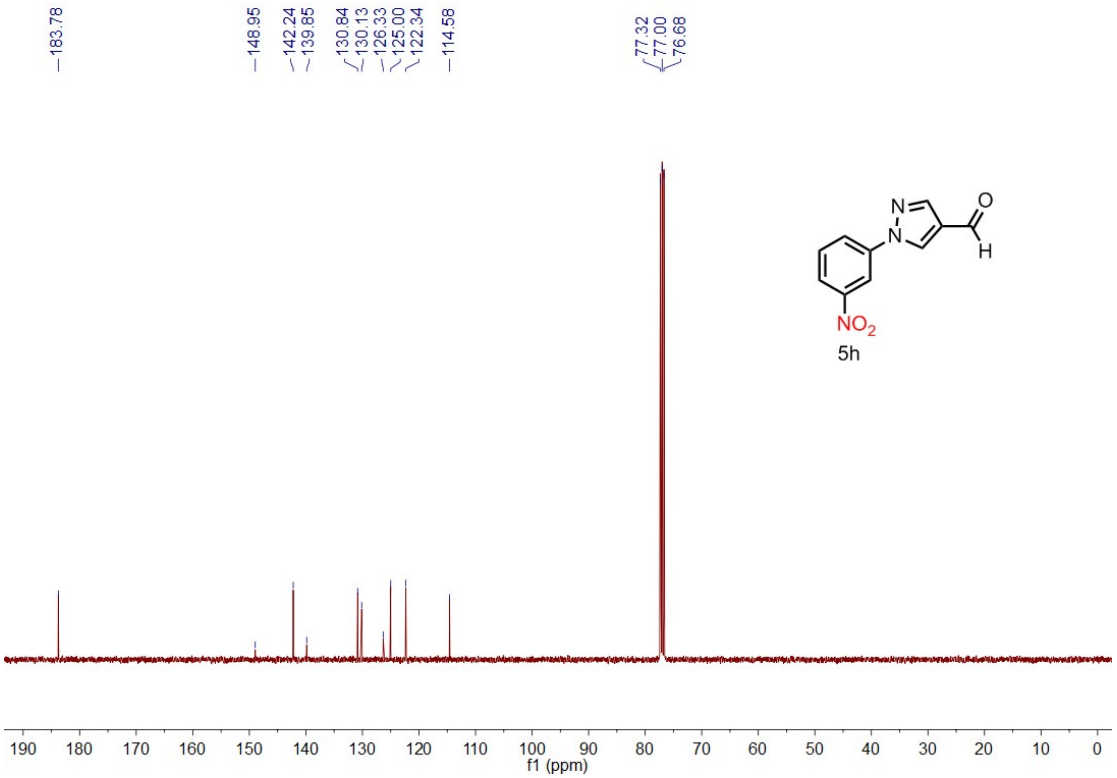
4-Bromo-1-(3-nitrophenyl)-1*H*-pyrazole (**5g**)



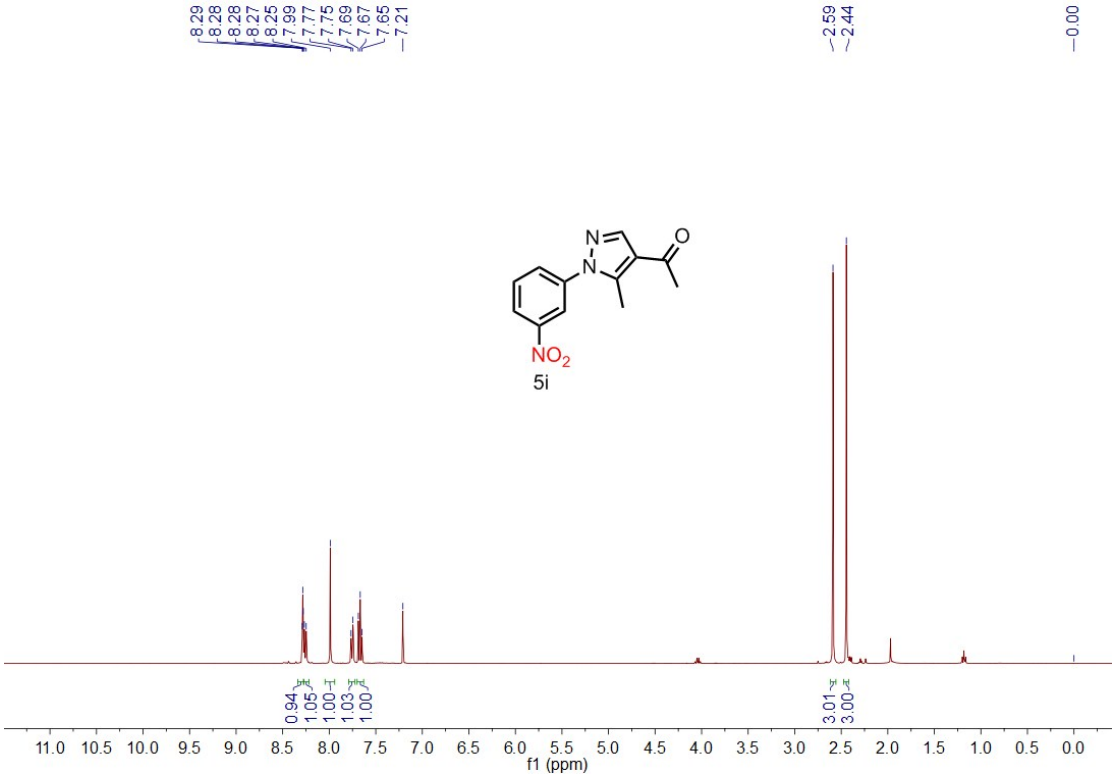


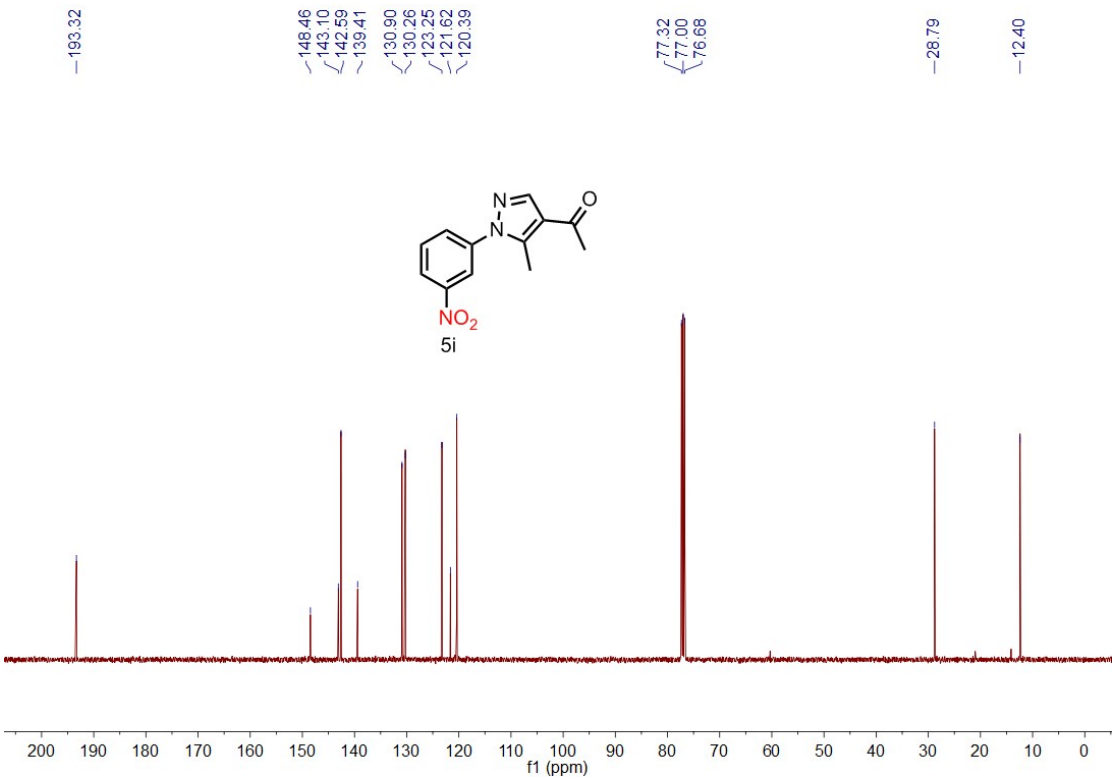
1-(3-Nitrophenyl)-1*H*-pyrazole-4-carbaldehyde (**5h**)



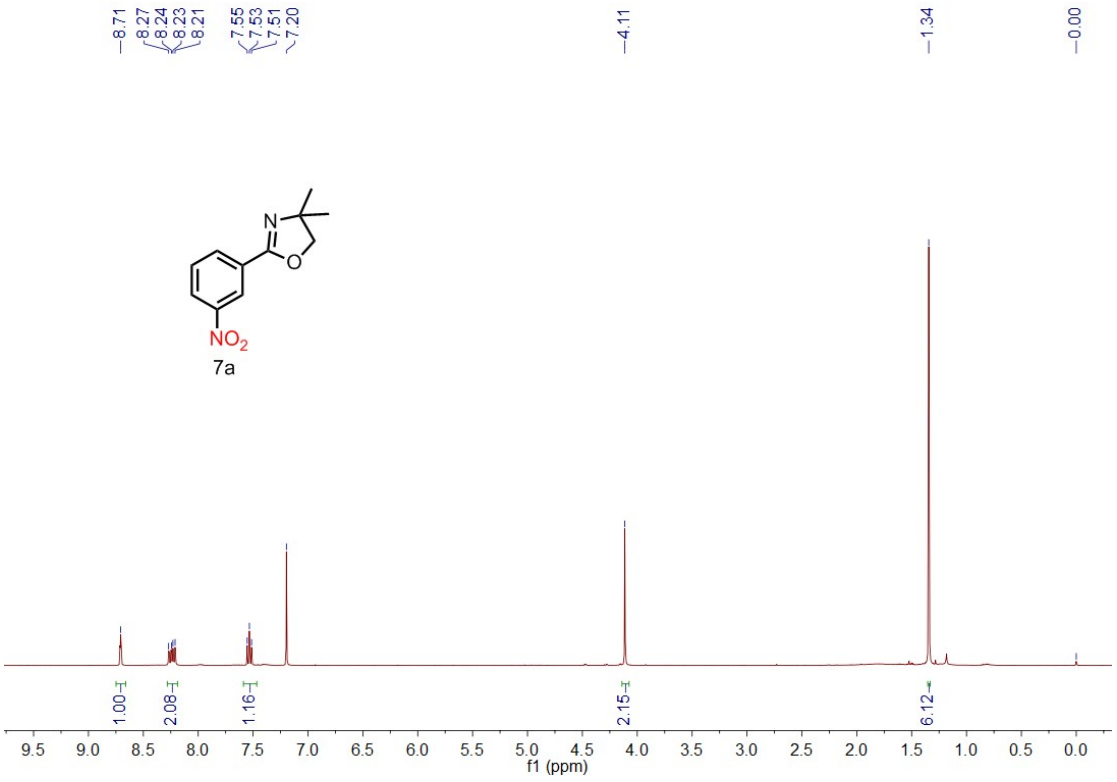


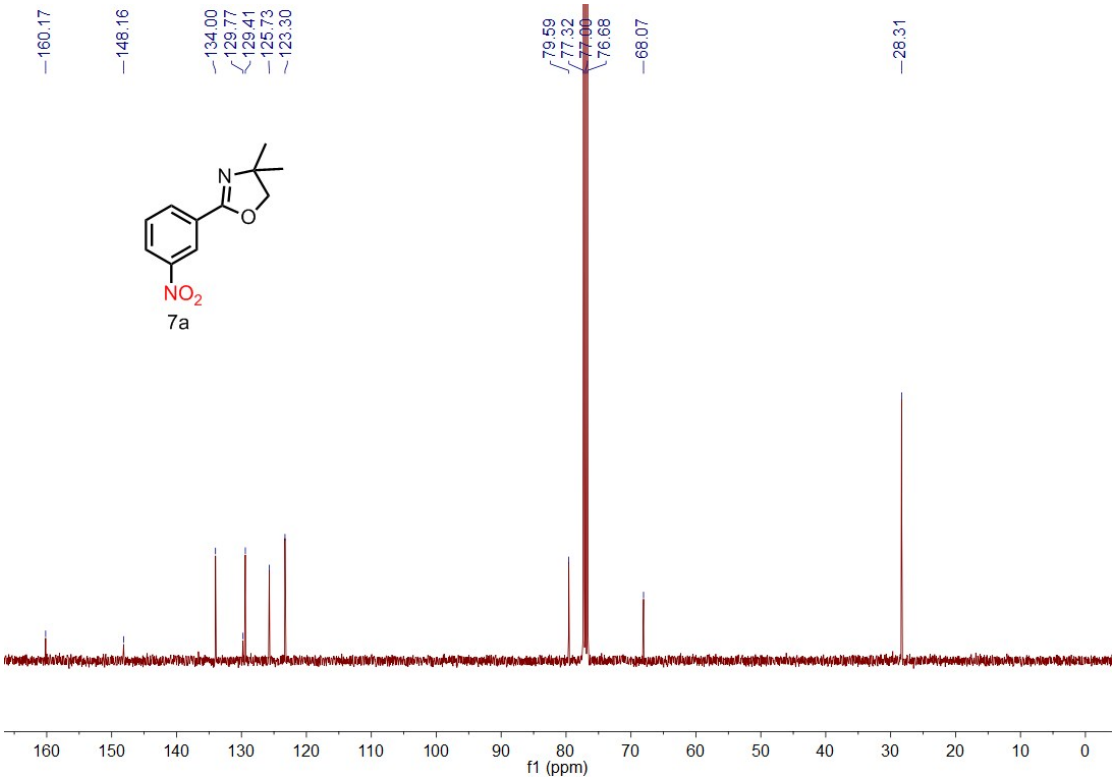
1-(5-Methyl-1-(3-nitrophenyl)-1*H*-pyrazol-4-yl) ethan-1-one (**5i**)



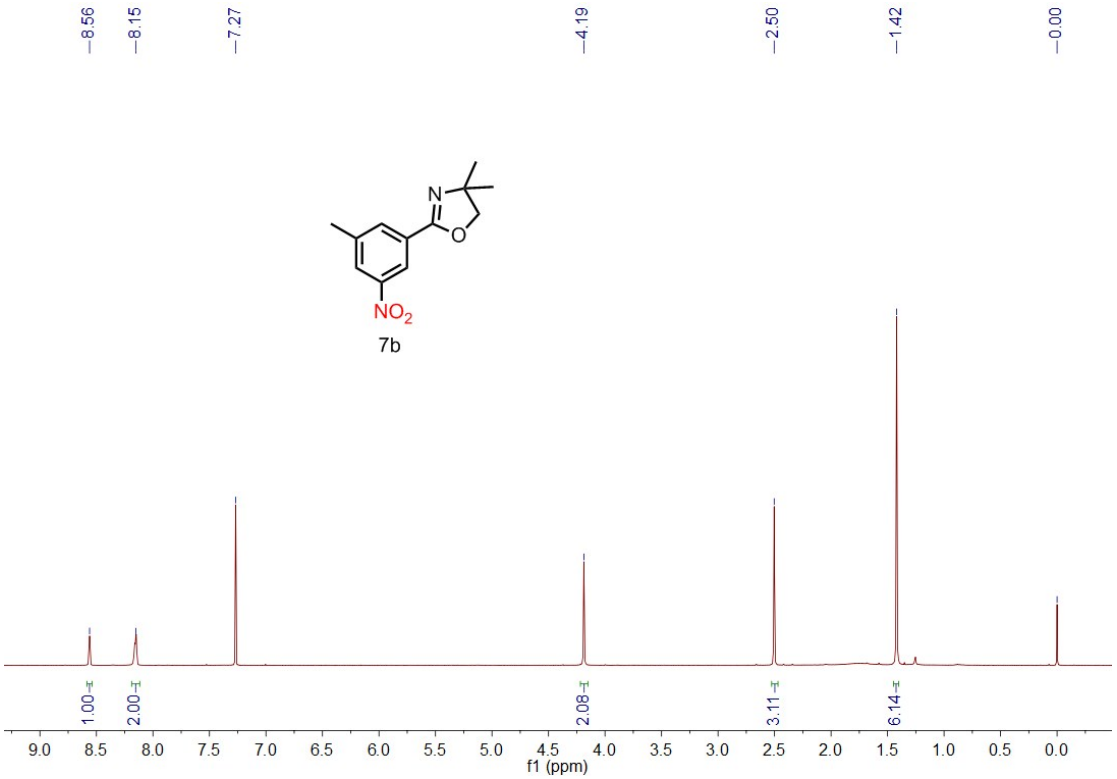


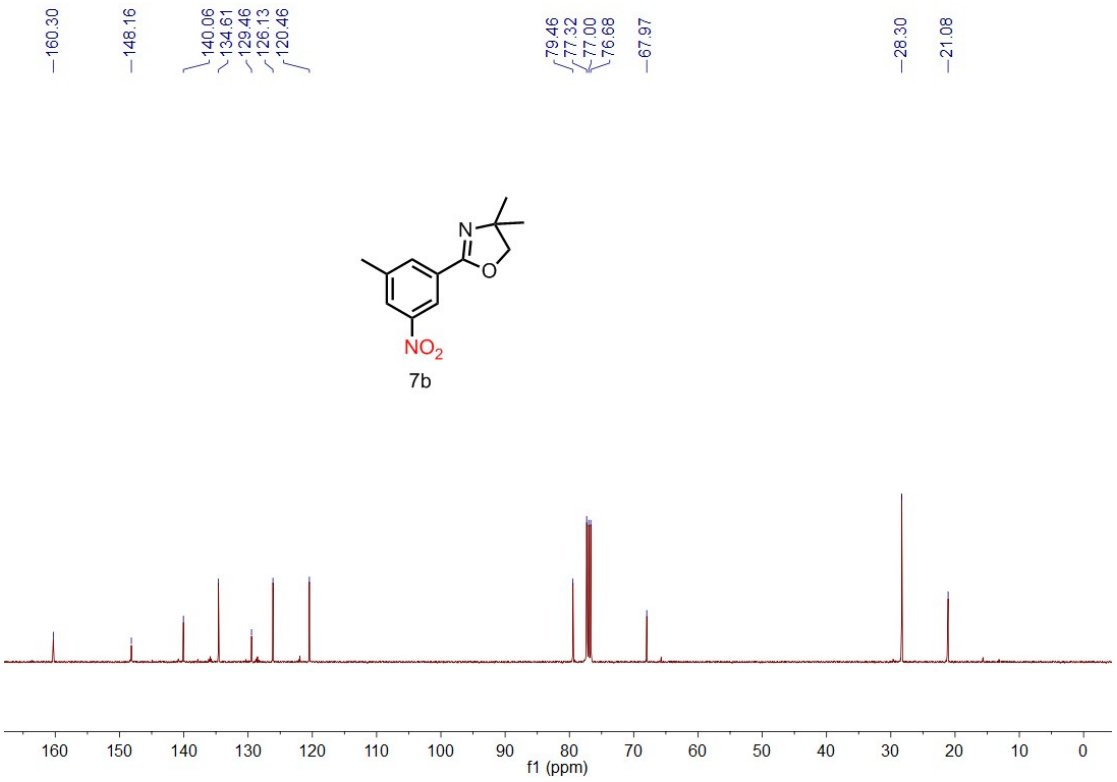
4,4-Dimethyl-2-(3-nitrophenyl)-4,5-dihydrooxazole (**7a**)



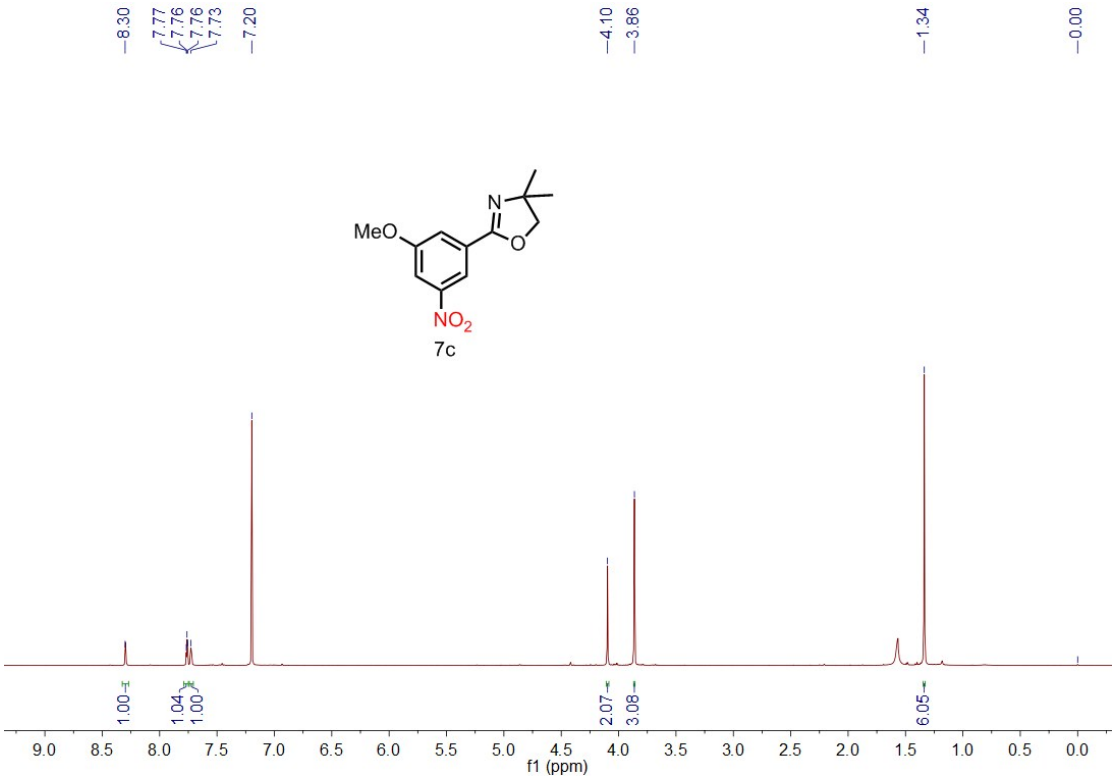


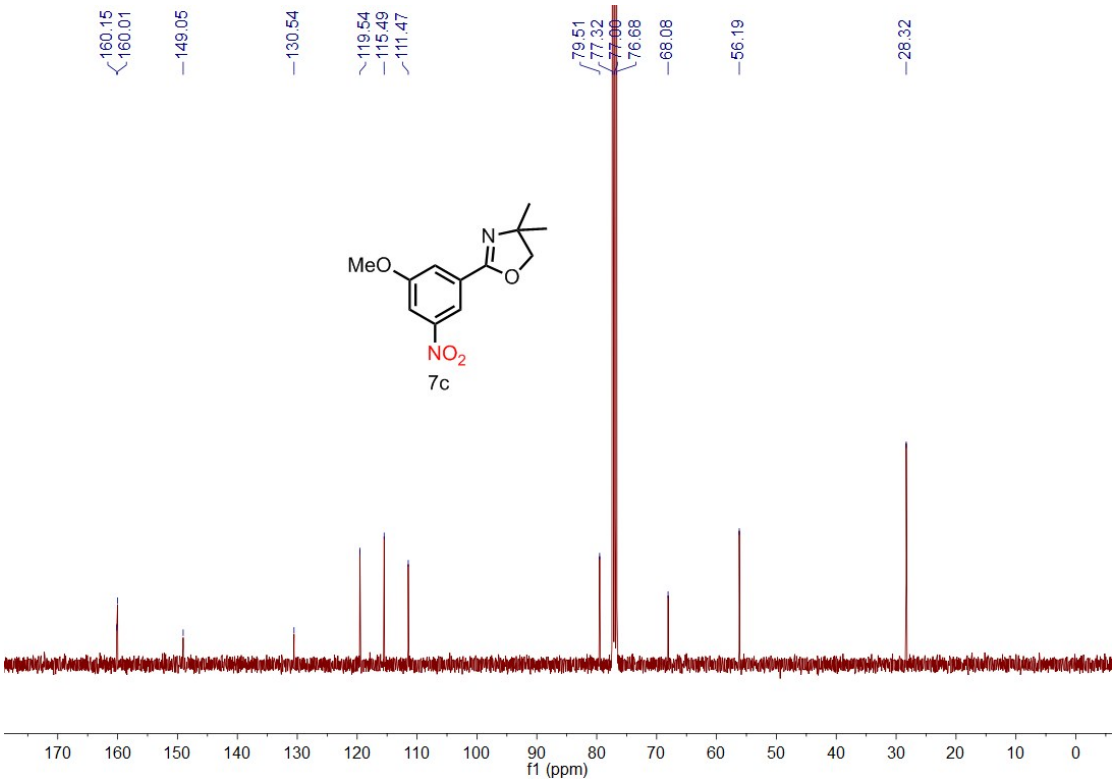
4,4-Dimethyl-2-(3-methyl-5-nitrophenyl)-4,5-dihydrooxazole (**7b**)



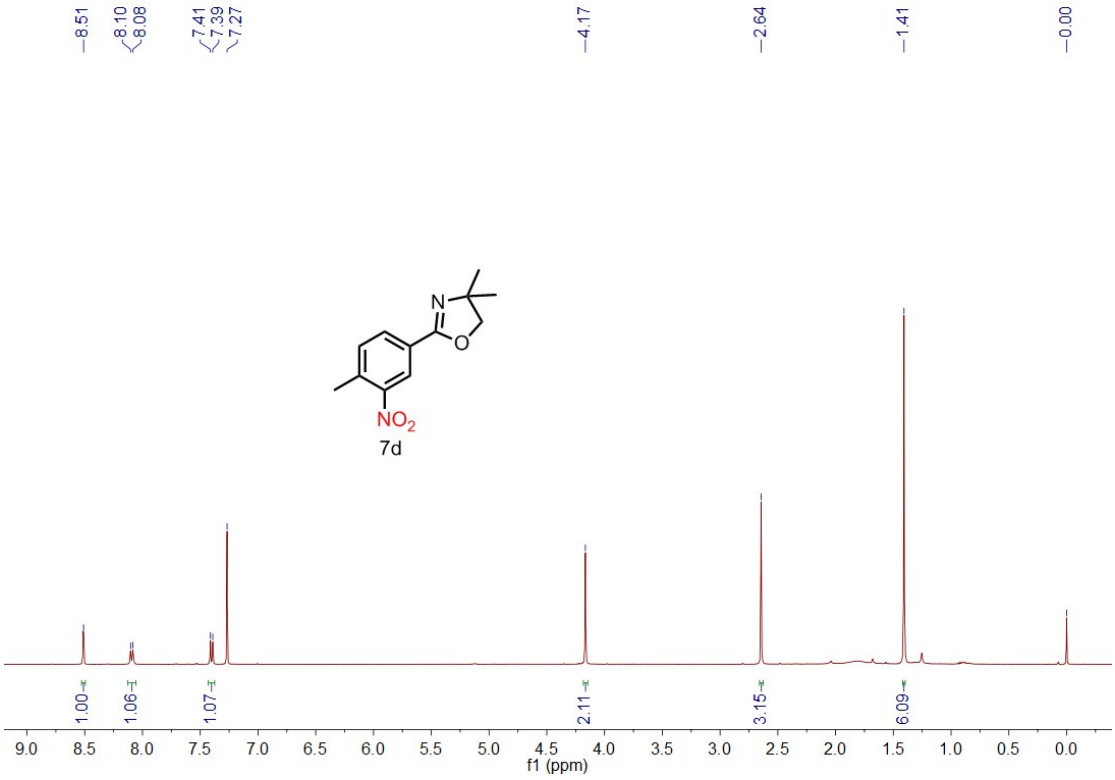


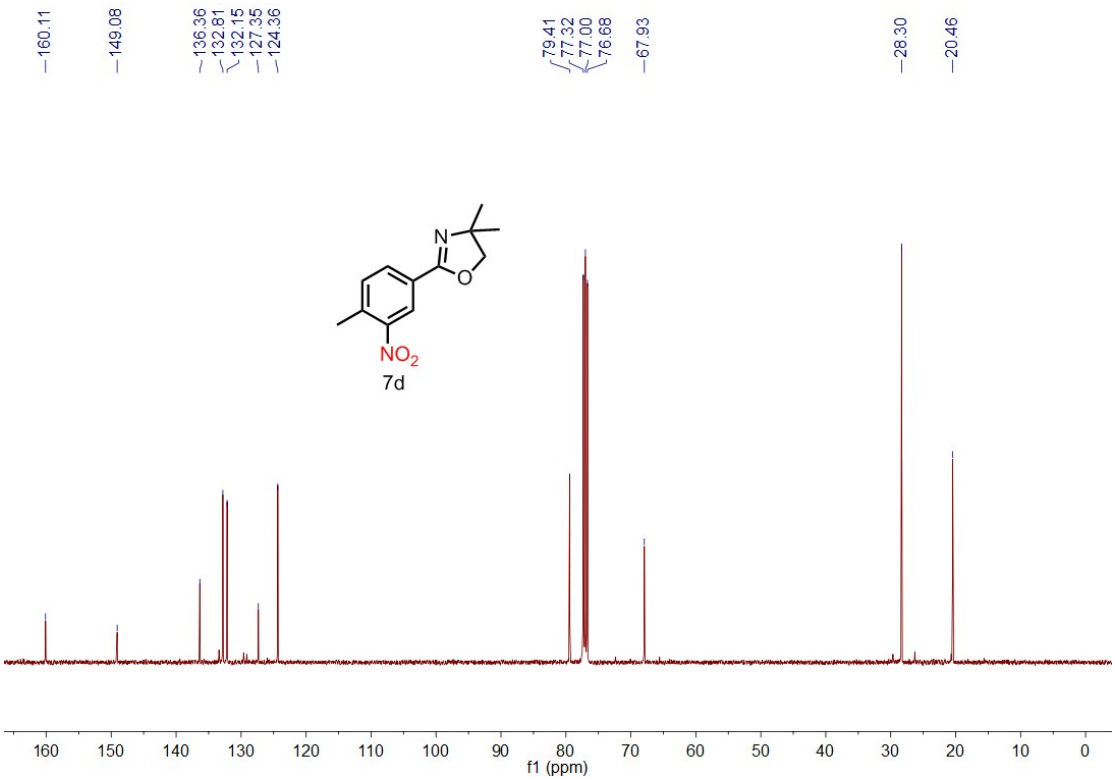
2-(3-Methoxy-5-nitrophenyl)-4,4-dimethyl-4,5-dihydrooxazole (**7c**)



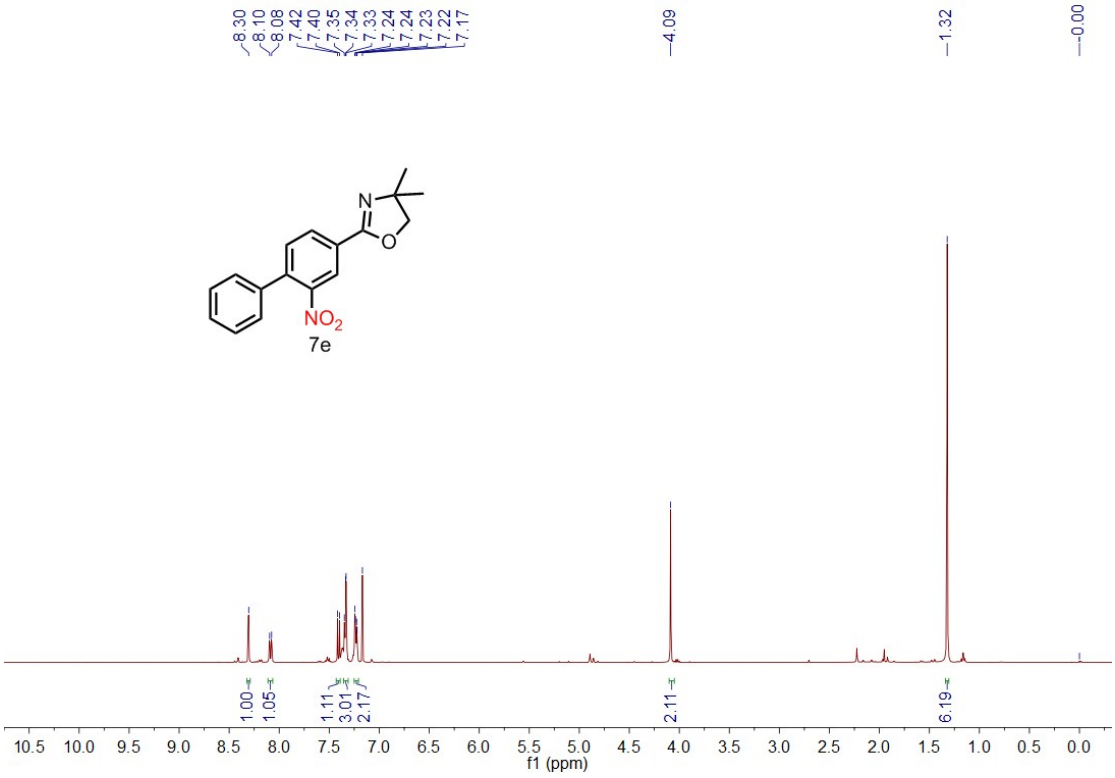


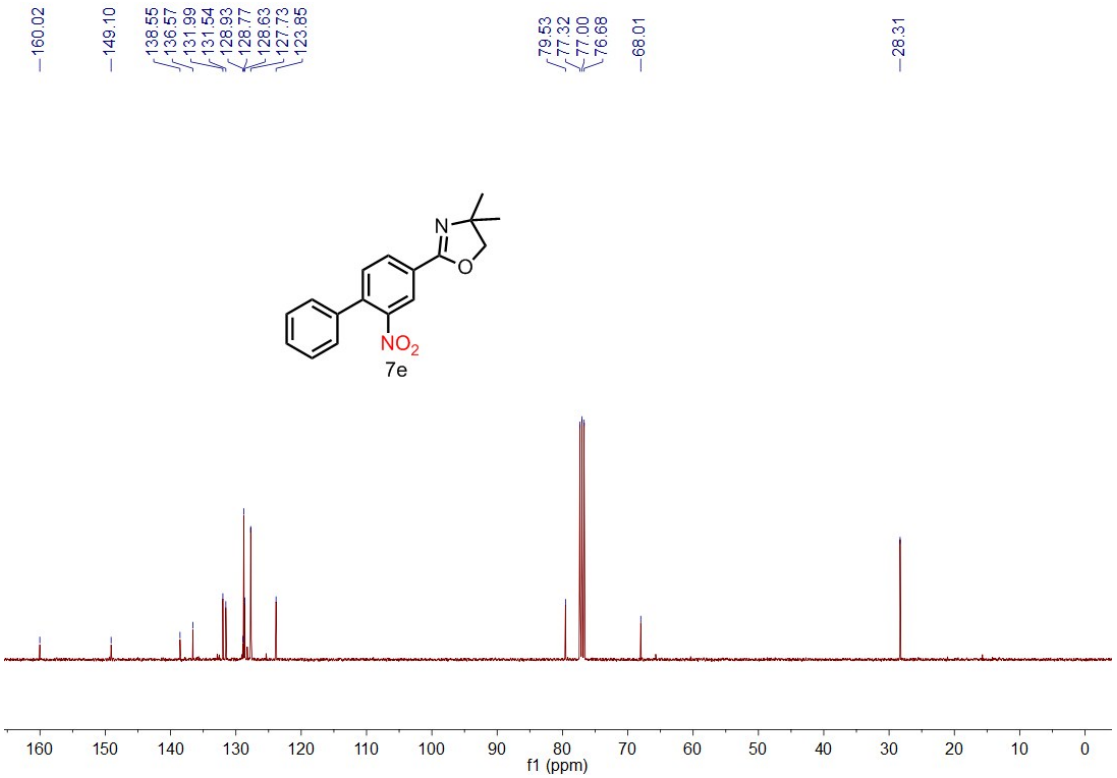
4,4-Dimethyl-2-(4-methyl-3-nitrophenyl)-4,5-dihydrooxazole (**7d**)



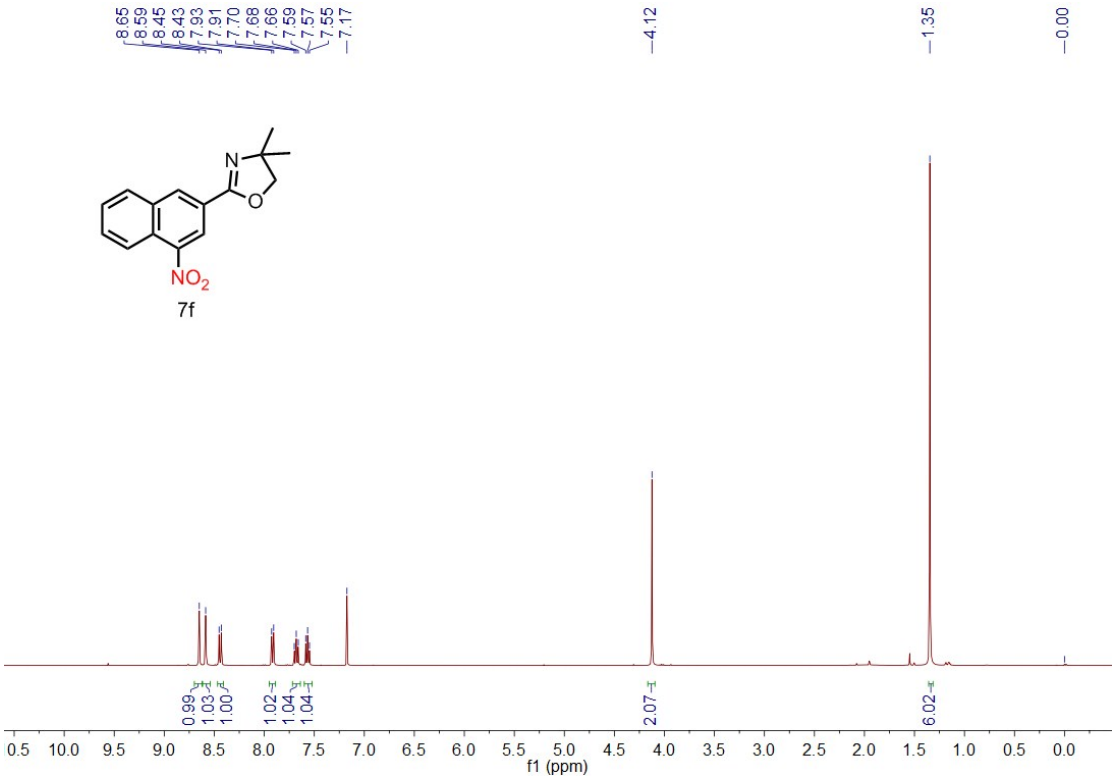


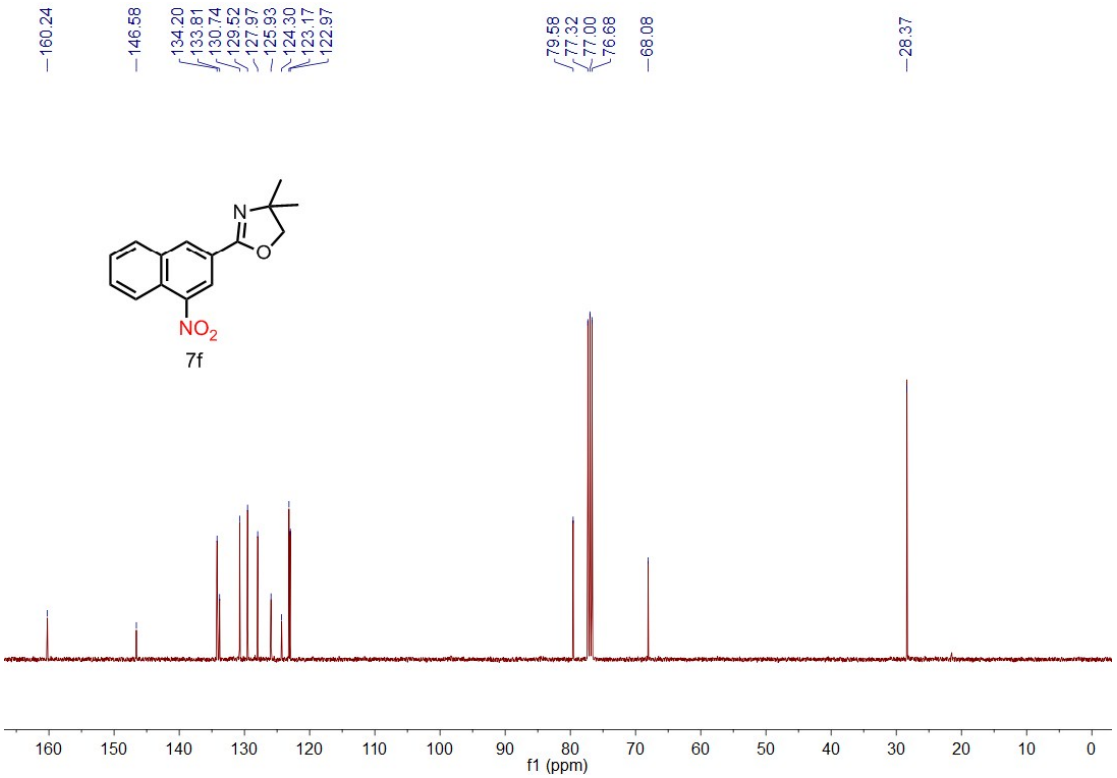
4,4-Dimethyl-2-(2-nitro-[1,1'-biphenyl]-4-yl)-4,5-dihydrooxazole (**7e**)





4,4-Dimethyl-2-(4-nitronaphthalen-2-yl)-4,5-dihydrooxazole (**7f**)

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