Formation of C=N bonds by the release of H_2: a new strategy for synthesis of imines and benzazoles

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Supporting Information

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General Experimental Information

Pd/C(10%) was washed by dry DMA which was distilled over CaH_2 . All the other chemical reagents were obtained from commercial sources and used without further purification. ^{1}H NMR (400MHz) and ^{13}C NMR (100 MHz) spectra were obtained on a Bruker DRX-400 NMR as solutions in $CDCl_3$. Chemical shifts are reported in parts per million and coupling constants are in hertz. The reaction mixture was filtered through 300-400 mesh silica gel and then injected into the GC equipped with FID detector (Agilent Technologies, GC7890A) for analysis. The detection of H_2 was carried out with GC with TCD detector (Shimadzu GC-2014C, stationary phase: AE 5A MS 3m*3mm（OD）). The chemical structures of products were confirmed by GC-MS (Agilent Technologies, GC7683B, MS5973).

General procedure for Synthesis of Imines and Benzazoles:

General procedure for the Pd/C catalytic cross-coupling of various benzylamine .

Benzylamine (107mg, 1mmol), Pd/C(53mg, 0.05mmol), *n*-dodecane(17mg, 0.1mmol, internal standard) and DMA(2mL) were added to a two-necks flask which was deoxidized and then heated at 120℃and stirred under an atmosphere of high-purity nitrogen (N2 balloon). The reaction was detected by GC.

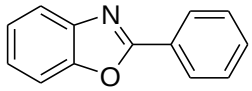
General procedure for the Pd/C catalytic dehydrogenation of cross-coupling of benzylamine and other amines.

Benzylamine (107mg, 1mmol), amine(465mg, 5mmol), Pd/C(53mg, 0.05mmol), *n*-dodecane(17mg, 0.1mmol, internal standard) and DMA(2mL) were added to a two-necks flask which was deoxidized and then heated at 120℃and stirred under an atmosphere of high-purity nitrogen (N_2 balloon). The reaction was detected by GC.

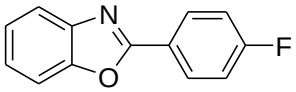
General procedure for the synthesis of benzazoles catalyzed by Pd/C.

Benzylamine (2mmol) , o-phenylenediamine (2-aminophenol or 2-aminothiophenol) (1mmol), Pd/C(53mg, 0.05mmol) and DMA(2mL) were added to a two-necks flask which was deoxidized and then heated at 120℃and stirred under an atmosphere of high-purity nitrogen(N_2 balloon). After the reaction was completed, Pd/C was filtrated .5ml water was added to the filtrate and extracted with 5ml EtOAc . The water layer was washed with EtOAc(2×5ml). The combined organic layer was dried over anhydrous Na_2SO_4 and the solvent evaporated under reduced pressure. The crude product was purified by silica gel column to afford the product.

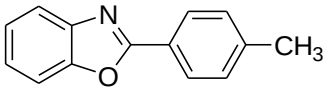
Characterization data for Benzazoles (benzoxazoles, benzimidazoles, and benzothiazoles)



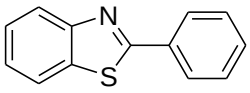
Prepared from Benzylamine (214 mg, 2 mmol) and 2-aminophenol (109mg, 1mmol), white solid, yield 150mg ,77%; ^{1}H NMR (400MHz, $CDCl_3$): δ 8.31-8.28 (m, 2 H), 7.82-7.80 (m, 1 H), 7.63-7.61 (m, 1 H), 7.57-7.55 (m, 3 H), 7.40-7.38 (m, 2 H); ^{13}C NMR (100MHz, $CDCl_3$): δ 109.6, 119.0, 123.5, 124.1, 126.2, 126.6, 127.9, 130.5, 141.1, 149.7, 162.0; HRMS-ESI Calcd for $C_{13}H_9NO$ $[M]^+$ 195.0684, found 195.0681. This compound was known.[1]



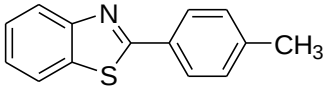
Prepared from 4- fluorobenzylamine (250 mg, 2 mmol) and 2-aminophenol (109mg, 1mmol), pale yellow solid, yield 149mg , 70%; ^{1}H NMR (400MHz, $CDCl_3$): δ 8.31-8.27 (m, 2 H), 7.80-7.78 (m, 1 H), 7.62-7.60 (m, 1 H), 7.40-7.38 (m, 2 H), 7.27-7.22 (m, 2 H); ^{13}C NMR (100MHz, $CDCl_3$): δ 110.6, 116.1, 116.3, 120.0, 124.7, 125.2, 129.8, 129.9, 142.1, 150.8, 162.2, 163.6, 166.1; HRMS-ESI Calcd for $C_{13}H_8FNO$ $[M]^+$ 213.059, found 213.0588. This compound was known.[2]



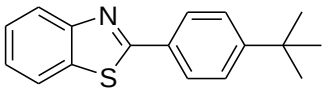
Prepared from 4-methylbenzylamine (242 mg, 2 mmol) and 2-aminophenol (109mg, 1mmol), pale yellow solid, yield 180mg , 86% ; ^{1}H NMR (400MHz, $CDCl_3$): δ 8.18 (d, 2 H, J = 8.4 Hz), 7.80-7.78 (m, 1 H), 7.61-7.60 (m, 1 H), 7.38-7.35 (m, 4 H), 2.47 (s, 3 H); ^{13}C NMR (100MHz, $CDCl_3$): δ 20.6, 109.5, 118.8, 123.4, 123.5, 123.8. 126.6, 128.6, 141.0, 141.2, 149.7, 162.3; HRMS-ESI Calcd for $C_{14}H_{11}NO$ $[M]^+$ 209.0841, found 209.0839. This compound was known.[3]



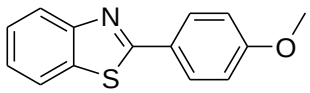
Prepared from benzylamine (214 mg, 2 mmol) and 2-aminothiophenol (125mg, 1mmol), white solid, yield 181mg , 85% ; ^{1}H NMR (400MHz, $CDCl_3$): δ 8.13-8.10 (m, 3 H), 7.94 (d, 1 H, J = 8.0 Hz), 7.54-7.51 (m, 4 H), 7.44-7.40 (m, 1 H); ^{13}C NMR (100MHz, $CDCl_3$): δ 121.6, 123.2, 125.2, 126.3, 127.6, 129.0, 131.0, 133.6, 135.1, 154.2, 168.1; HRMS-ESI Calcd for $C_{13}H_9NS$ $[M]^+$ 211.0456, found 211.0454. This compound was known.[4]



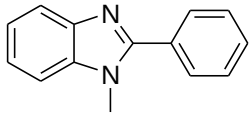
Prepared from 4-methylbenzylamine (242 mg, 2 mmol) and 2-aminothiophenol (125mg, 1mmol), white solid, yield 209mg , 93% ; ^{1}H NMR (400MHz, $CDCl_3$): δ 8.09 (d, 1 H, J = 8 Hz), 8.02-8.00 (m, 2 H), 7.92 (d, 1 H, J = 8 Hz), 7.53-7.49 (m, 1 H), 7.42-7.38 (m, 1 H), 7.33 (d, 2 H, J = 8 Hz), 2.46 (s, 3 H); ^{13}C NMR (100MHz, $CDCl_3$): δ 21.5, 121.6, 123.1, 125.0, 126.3, 127.5, 129.7, 131.0, 135.0, 141.4, 154.2, 168.3; HRMS-ESI Calcd for $C_{14}H_{11}NS$ $[M]^+$ 225.0612, found 225.0611. This compound was known.[5]



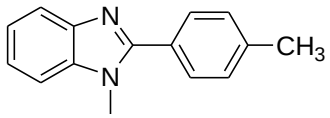
Prepared from 4-tert-butylbenzylamine (326 mg, 2 mmol) and 2-aminothiophenol (125mg, 1mmol), white solid, yield 254mg , 95% ; ^{1}H NMR (400MHz, $CDCl_3$): δ 8.10-8.04 (m, 3 H), 7.93 (d, 1 H, J = 8 Hz), 7.55-7.49 (m, 3 H), 7.42-7.38 (m, 1 H), 1.40 (s, 9 H); ^{13}C NMR (100MHz, $CDCl_3$): δ 31.2, 35.0, 121.6, 123.1, 125.0, 126.0, 126.2, 127.4, 130.9, 135.0, 154.2, 154.6, 168.2; HRMS-ESI Calcd for $C_{17}H_{17}NS$ $[M]^+$ 267.1082, found 267.1087. This compound was known.[6]



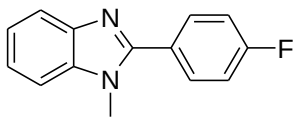
Prepared from 4-methoxybenzylamine (274 mg, 2 mmol) and 2-aminothiophenol (125mg, 1mmol), white solid, yield 169mg , 70% ; ^{1}H NMR (400MHz, CDCl3): δ 8.07-8.05 (m, 3 H), 7.91 (d, 1 H, J = 7.6 Hz), 7.52-7.48 (m, 1 H), 7.40-7.36 (m, 1 H), 7.03 (d, 2 H, J=8.8 Hz), 3.91 (s, 3 H); ^{13}C NMR (100MHz, CDCl3): δ 54.4, 113.3, 120.5, 121.8, 123.8, 125.2, 125.4, 128.1, 133.8, 153.2, 160.9, 166.8; HRMS-ESI Calcd for $C_{14}H_{11}NOS$ [M]+ 241.0561, found 241.0556. This compound was known.[7]



Prepared from benzylamine (214 mg, 2 mmol) and o-phenylenediamine (122mg, 1mmol), pale yellow solid, yield 156mg , 75% ; ^{1}H NMR (400MHz, $CDCl_3$): δ 7.87-7.85 (m, 1 H), 7.81-7.79 (m, 2 H), 7.59-7.55 (m, 3 H), 7.44-7.42 (m, 1 H), 7.38-7.32 (m, 2 H), 3.90 (s, 3 H); ^{13}C NMR (100MHz, $CDCl_3$): δ 31.7, 109.6, 119.9, 122.5, 122.8, 128.7, 129.5, 129.7, 130.3, 136.6, 143.0, 153.8; HRMS-ESI Calcd for $C_{14}H_{12}N_2$ $[M]^+$ 208.1, found 208.0996. This compound was known.[8]

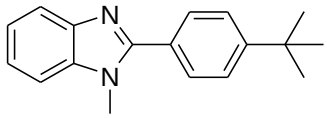


Prepared from 4-methylbenzylamine (242 mg, 2 mmol) and o-phenylenediamine (122mg, 1mmol), white solid, yield 191mg , 86% ; ^{1}H NMR (400MHz, $CDCl_3$): δ 7.86-7.83 (m, 1 H), 7.69 (d, 2 H, J = 8 Hz), 7.43-7.41 (m, 1 H), 7.37-7.33 (m, 4 H), 3.89 (s,3 H), 2.47 (s, 3 H); ^{13}C NMR (100MHz, $CDCl_3$): δ 21.5, 31.7, 109.6, 119.7, 122.4, 122.6, 127.3, 129.3, 129.4, 136.6, 139.8, 143.0, 154.0; HRMS-ESI Calcd for $C_{15}H_{14}N_2$ $[M]^+$ 222.1157, found 222.1156. This compound was known.[9]

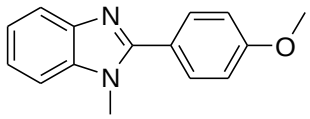


Prepared from 4- fluorobenzylamine (250 mg, 2 mmol) and o-phenylenediamine

(122mg, 1mmol), white solid, yield 207mg , 92%; ^{1}H NMR (400MHz, $CDCl_3$): δ 7.85-7.83 (m, 1 H), 7.80-7.77 (m, 2 H), 7.44-7.42 (m, 1 H), 7.37-7.35 (m, 2 H), 7.28-7.24 (m, 2 H), 3.89 (s, 3 H); ^{13}C NMR (100MHz, $CDCl_3$): δ 31.7, 109.7, 115.8, 116.0, 119.8, 122.6, 122.9, 131.4, 131.5, 136.5, 142.9, 152.8, 162.4, 164.9; HRMS-ESI Calcd for $C_{14}H_{11}FN_2$ $[M]^+$ 226.0906, found 226.0903.



Prepared from 4-tert-butylbenzylamine (326 mg, 2 mmol) and o-phenylenediamine (122mg, 1mmol), white solid, yield 237mg , 90% ; ^{1}H NMR (400MHz, $CDCl_3$): δ 7.86-7.83 (m, 1 H), 7.74 (d, 2 H, J = 8.8 Hz), 7.58-7.56 (m, 2 H), 7.43-7.41 (m, 1 H), 7.36-7.33 (m, 2 H), 3.91 (s, 3 H), 1.41 (s, 9 H); ^{13}C NMR (100MHz, $CDCl_3$): δ 31.3, 31.7, 34.9, 109.5, 119.8, 122.3, 122.6, 125.6, 127.2, 129.2, 136.6, 143.0, 153.0, 153.9; HRMS-ESI Calcd for $C_{18}H_{20}N_2$ $[M]^+$ 264.1626, found 264.1627.



Prepared from 4-methoxybenzylamine (274 mg, 2 mmol) and o-phenylenediamine (122mg, 1mmol), white solid, yield 202mg ,85% ; ^{1}H NMR (400MHz, CDCl3): δ 7.84-7.82 (m, 1 H), 7.74 (d, 2 H, J = 8.8 Hz), 7.42-7.39 (m, 1 H), 7.34-7.32 (m, 2 H), 7.07 (d, 2 H, J = 8.8 Hz), 3.91 (s, 3 H), 3.88 (s, 3 H); ^{13}C NMR (100MHz, CDCl3): δ 31.7, 55.4, 109.5, 114.2, 119.6, 122.3, 122.5, 122.6, 130.9, 136.6, 143.0, 153.8, 160.8; HRMS-ESI Calcd for $C_{15}H_{14}N_2O$ [M]+ 238.1106, found 238.1107. This compound was known.[10]

References

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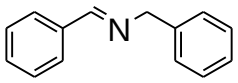
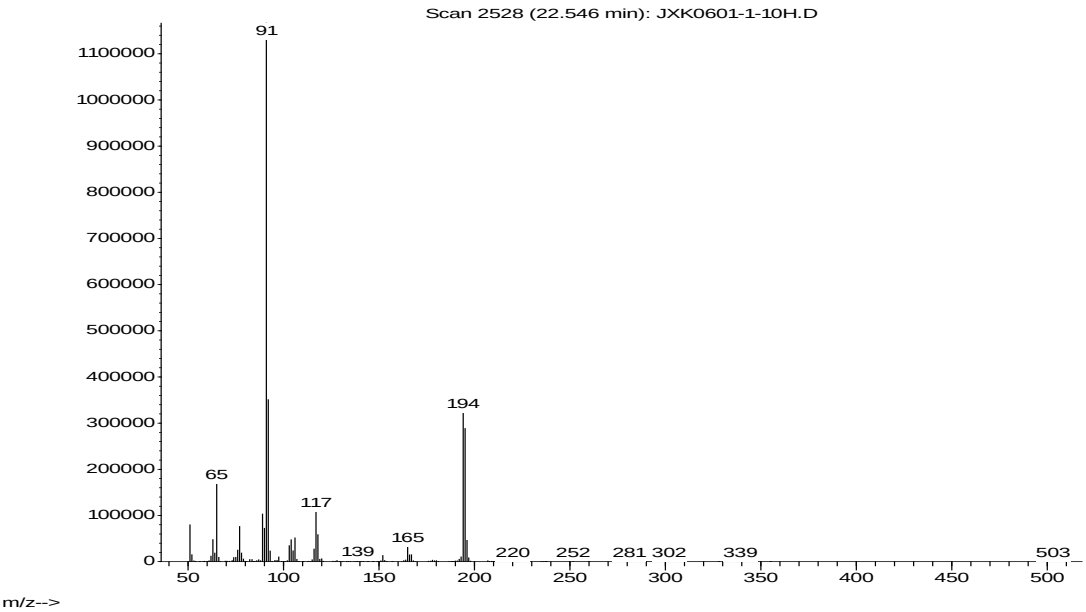
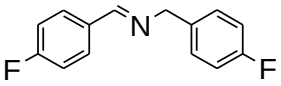
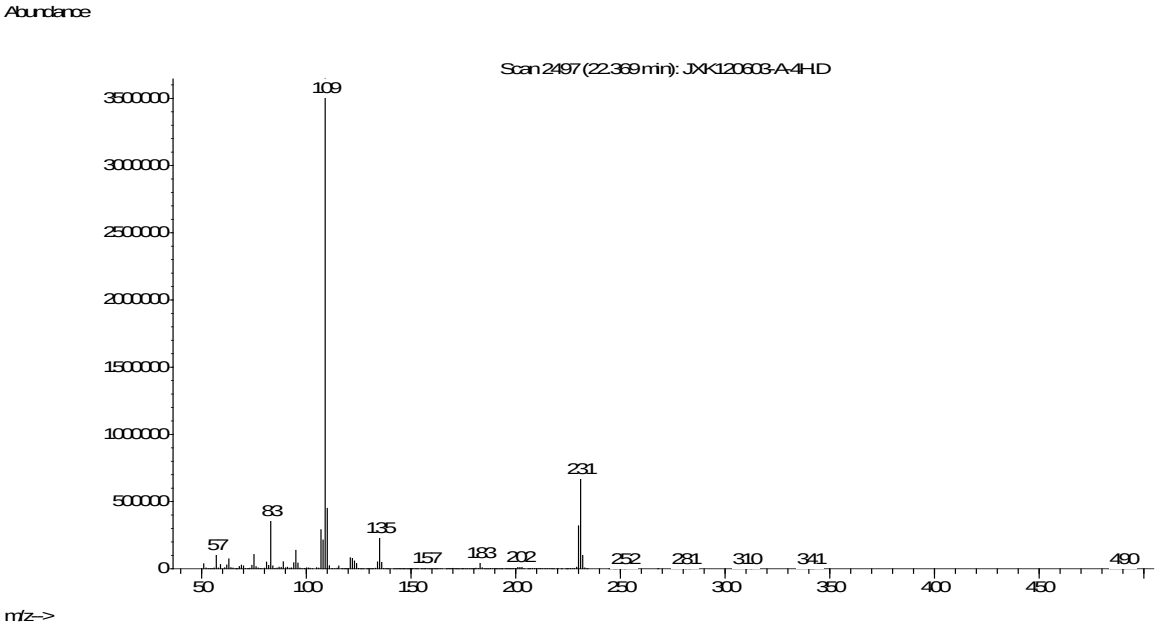
10. Fekner, T.; Gullucci, J.; Chan, M. K. *Org. Lett.*, **2003**, *5*, 4795.

Mass Spectra for Imines





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341
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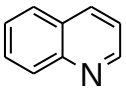
m/z-->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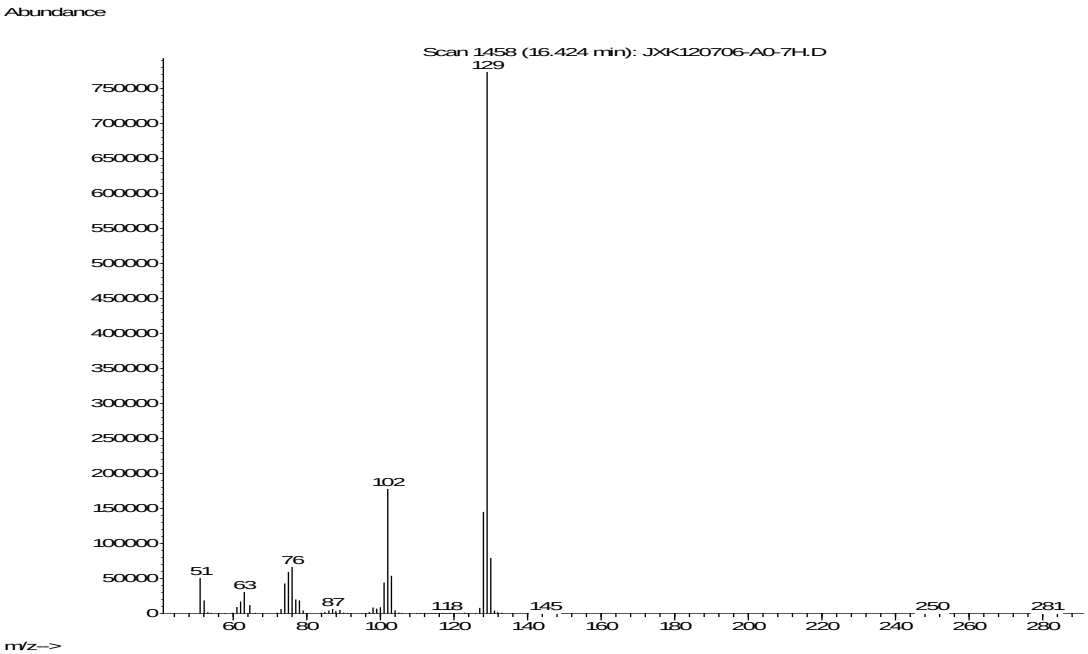
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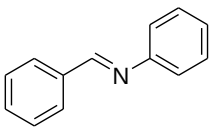
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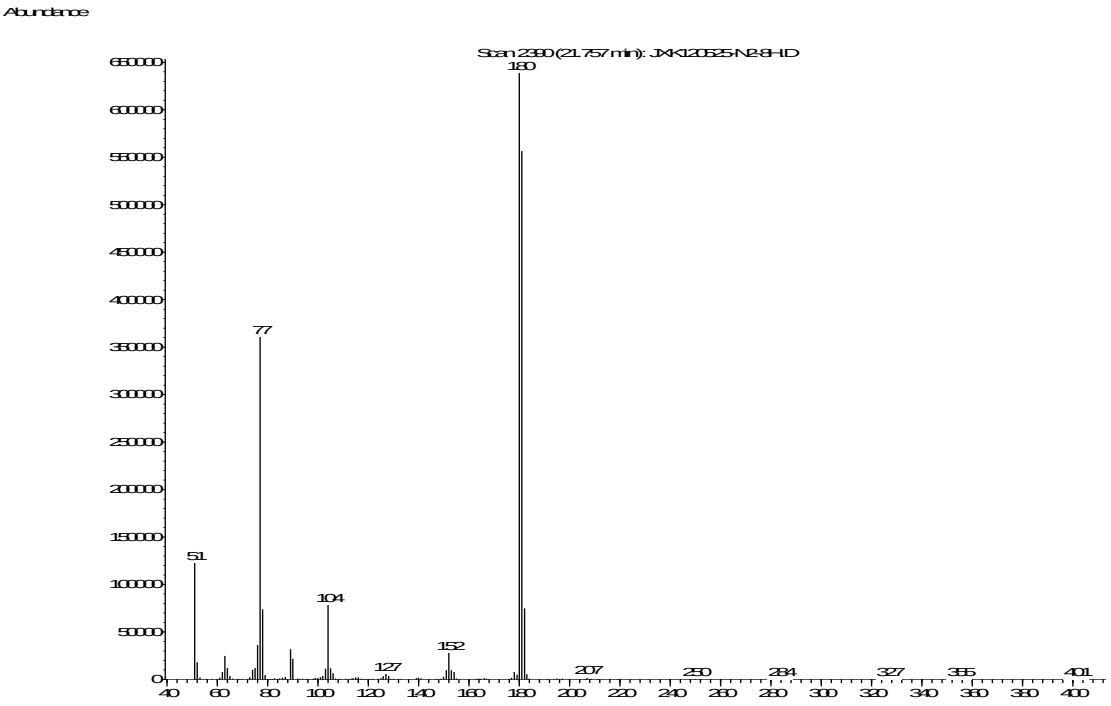
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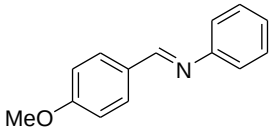
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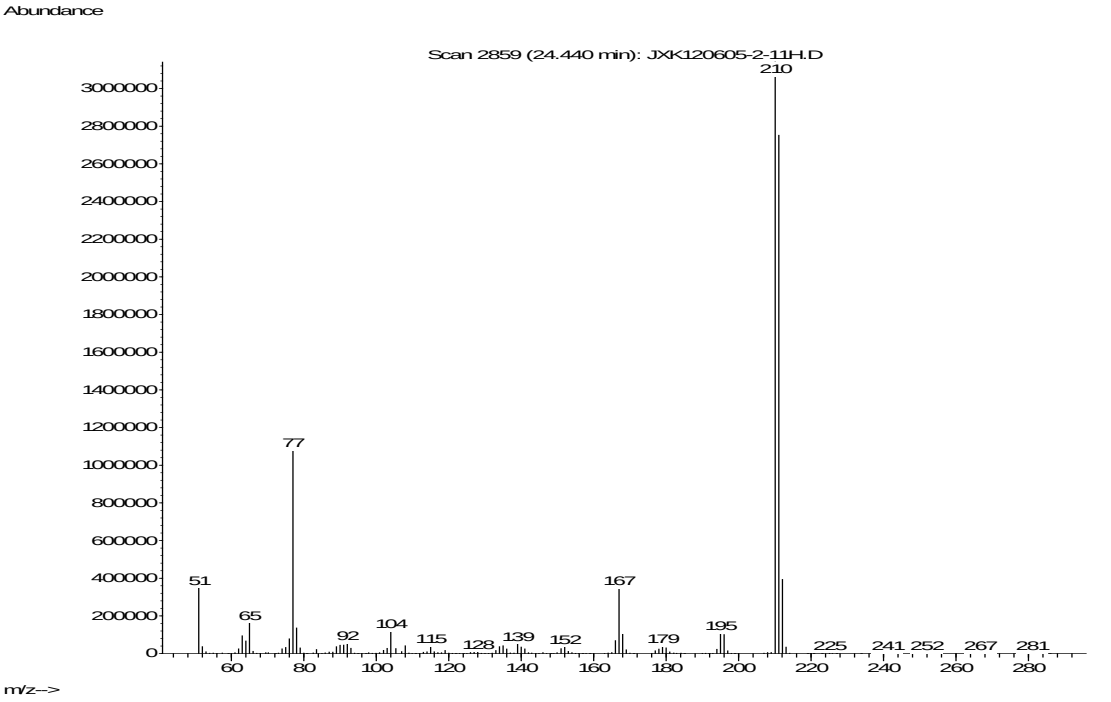
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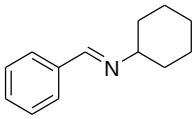
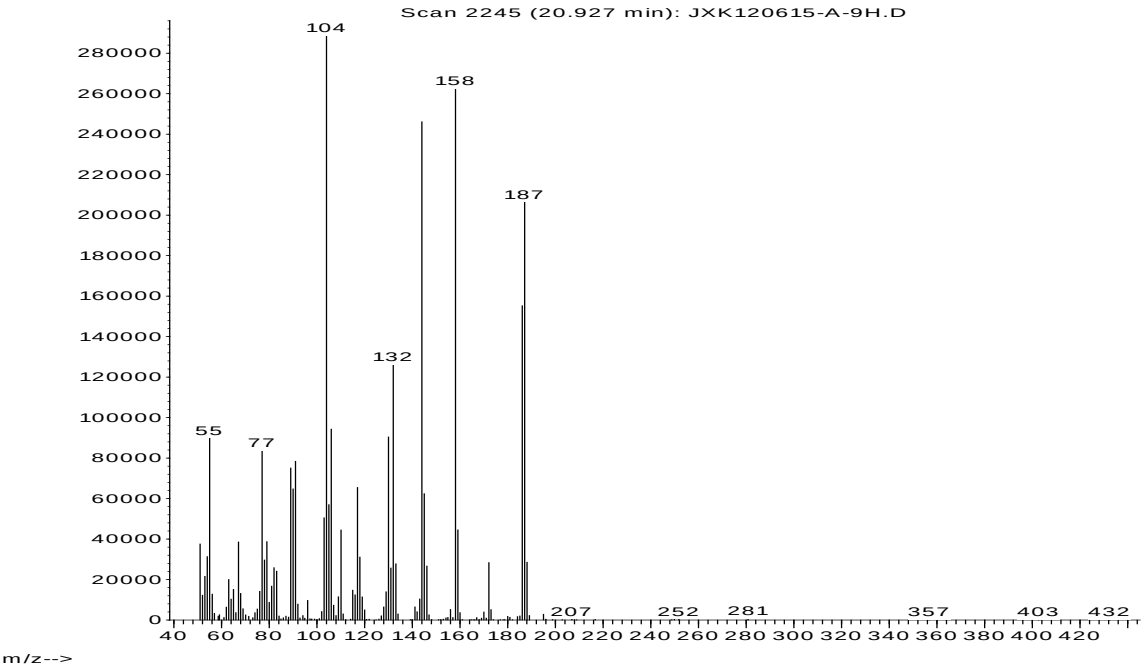
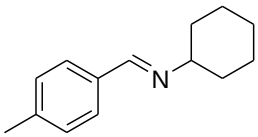
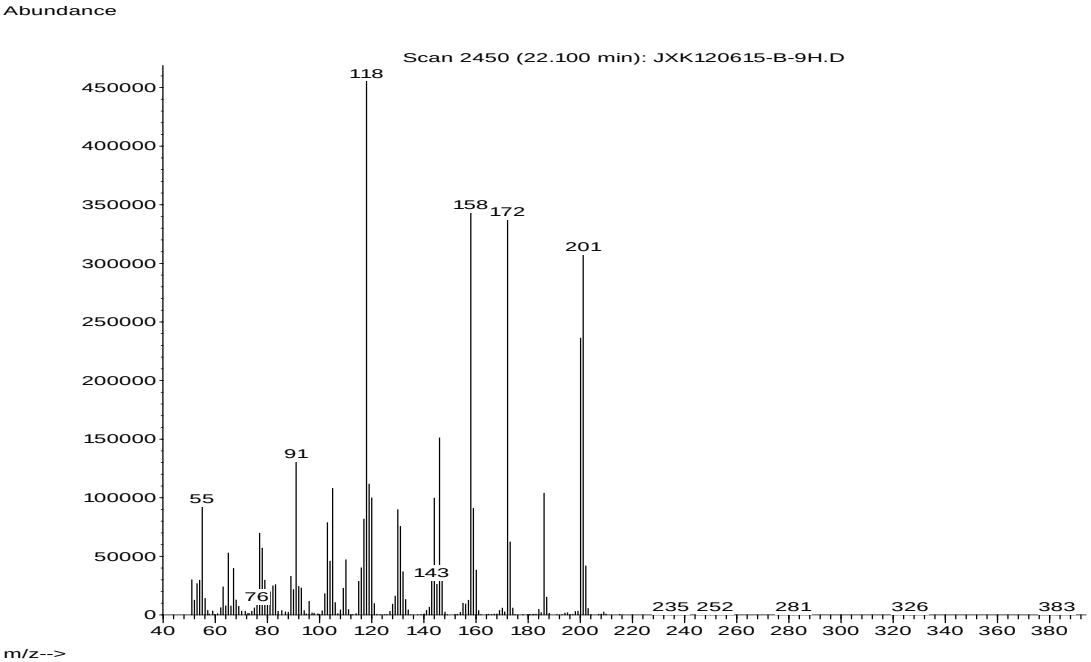
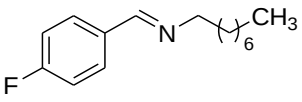
m/z-->







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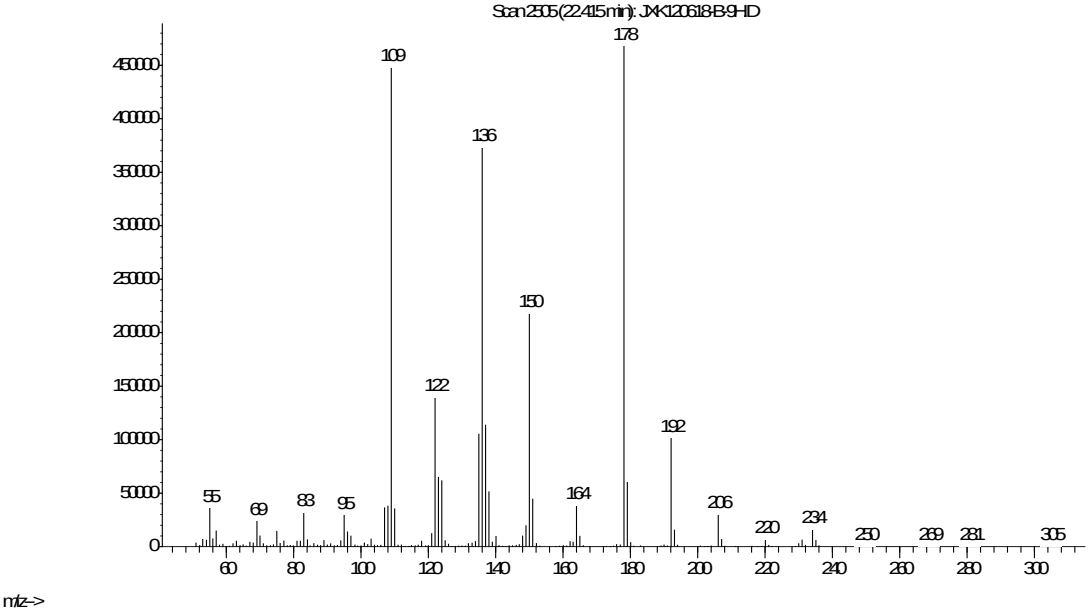
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69
83
95
164
206
220
234
250
269
281
305
m/z->
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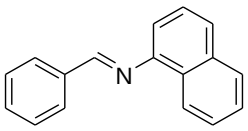
80
100
120
140
160
180
200
220
240
260
280
300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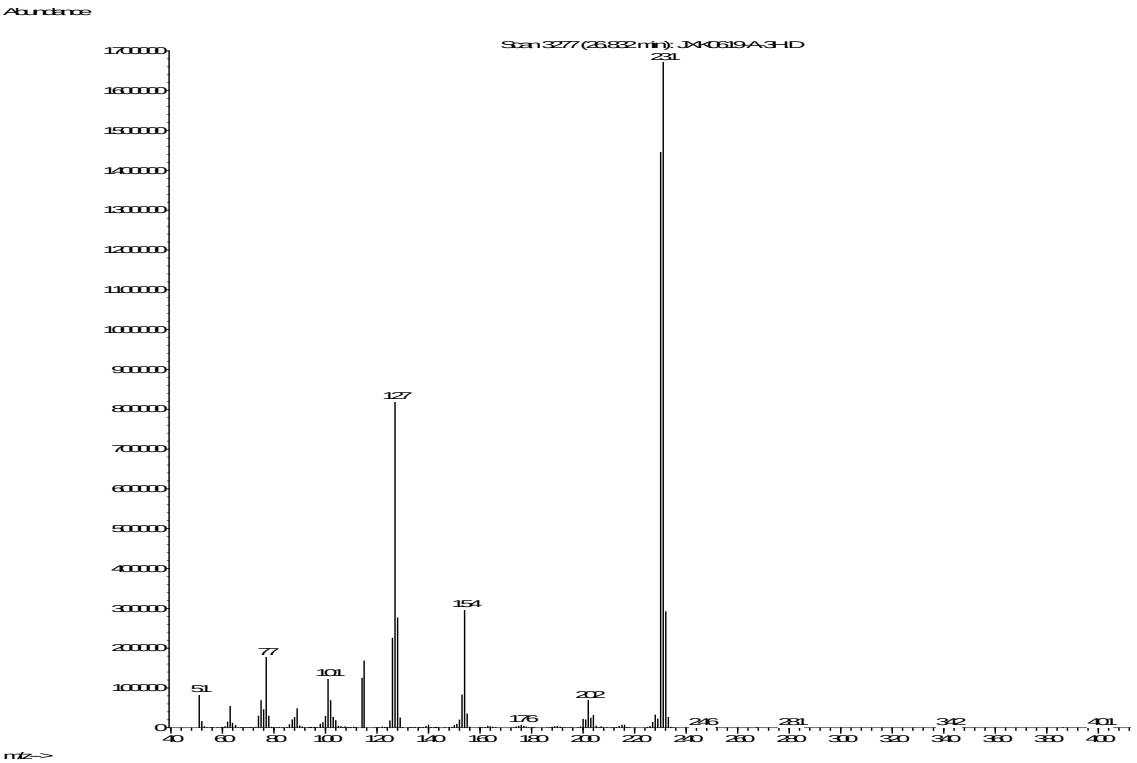
Abundance
Scan 3277 (26.832 min): JAK0619-A-3-HD
231
127
154
77
101
51
202
176
246
281
342
401
m/z->
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
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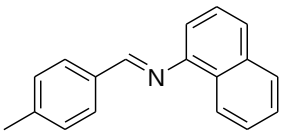
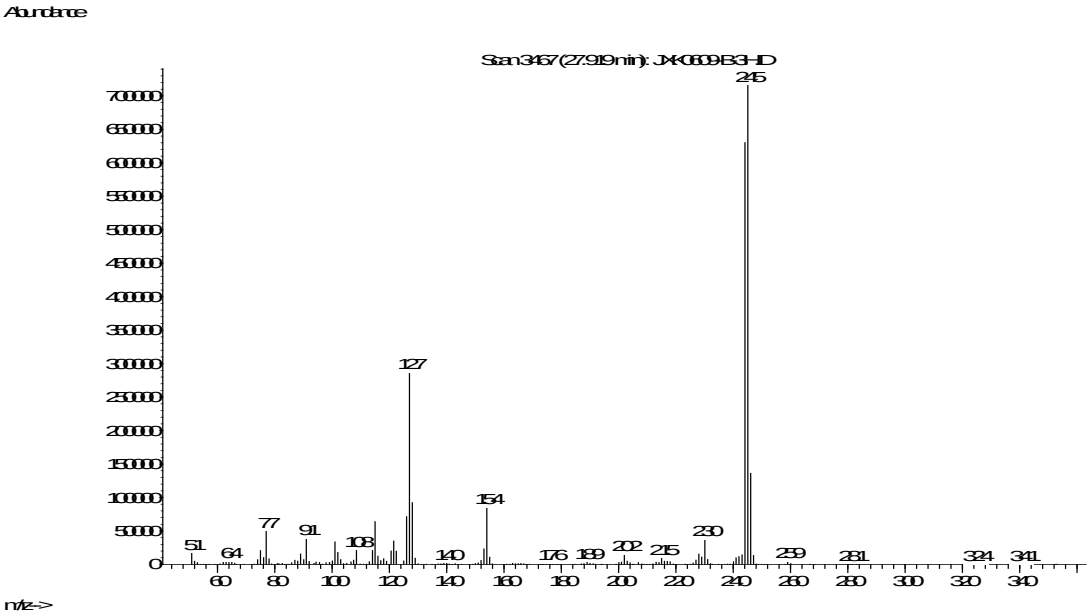
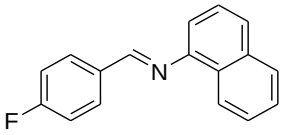
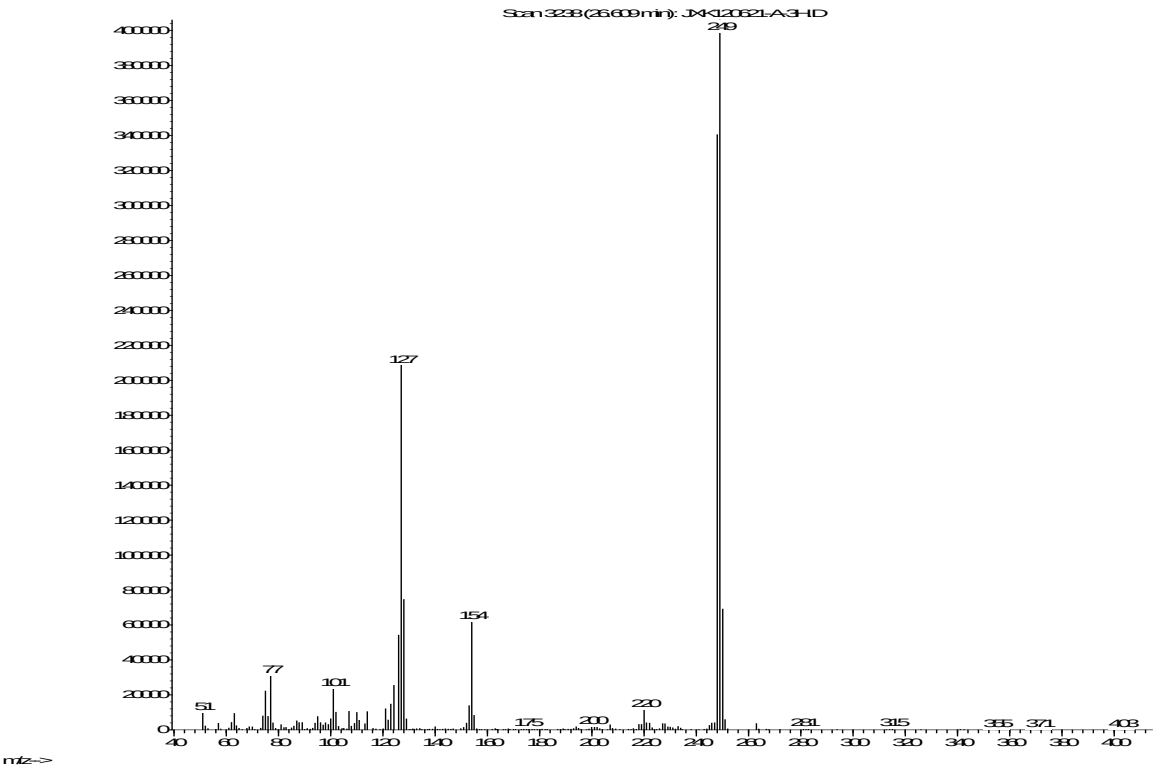
360
380
400



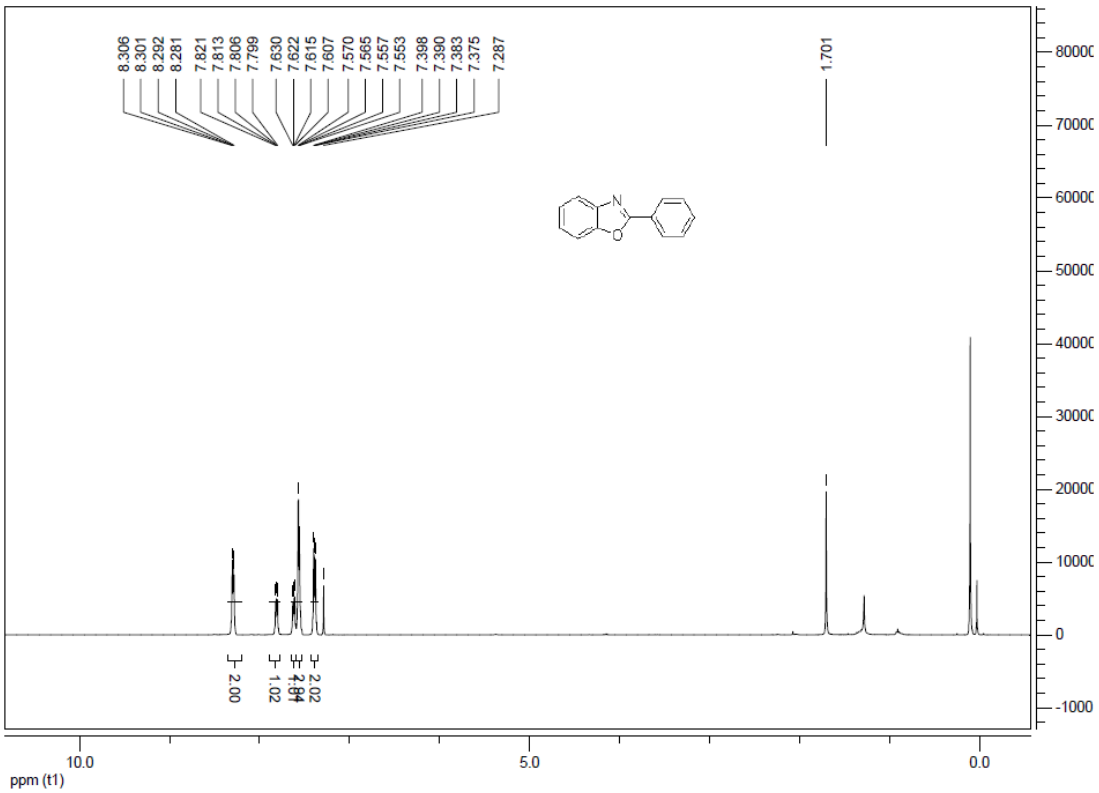


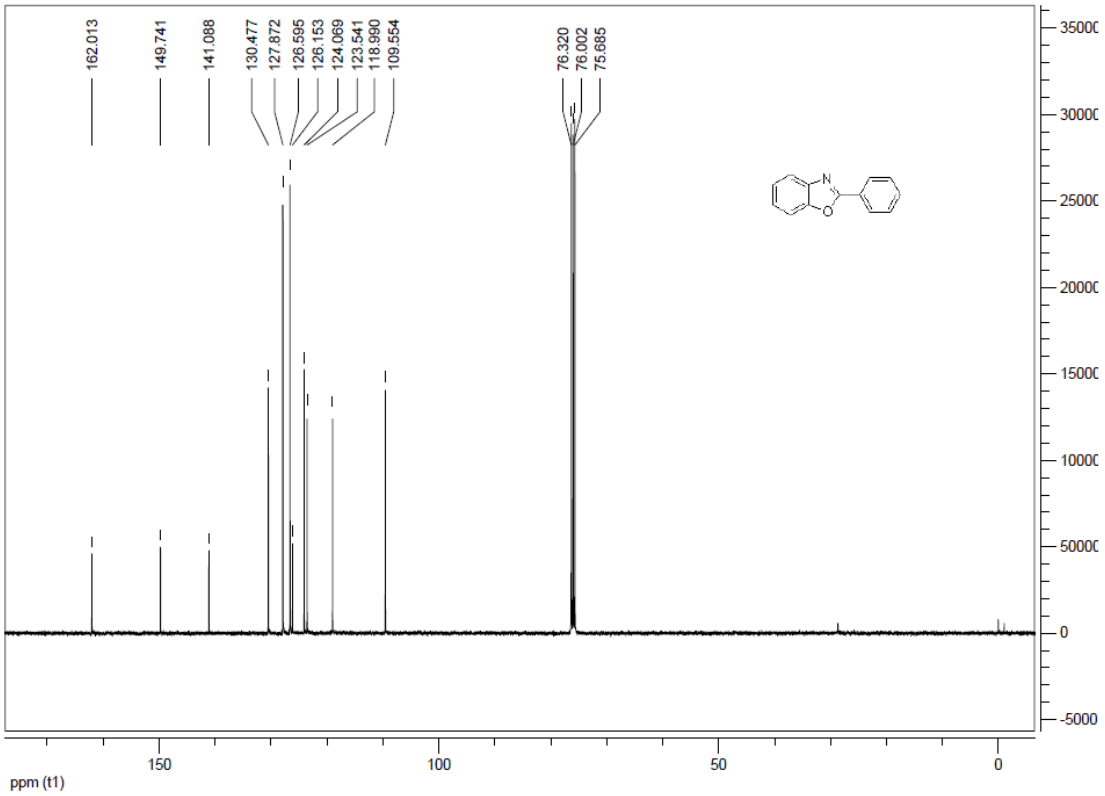




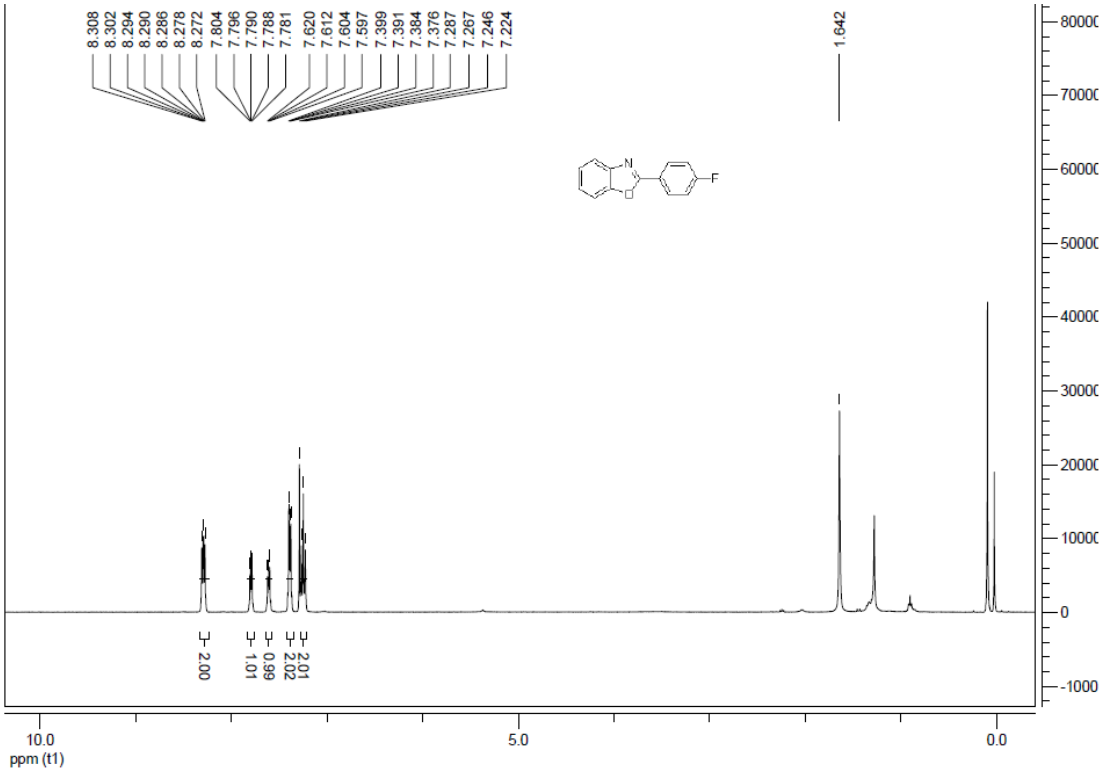
^{1}H and ^{13}C NMR Spectra for Benzazoles Compounds

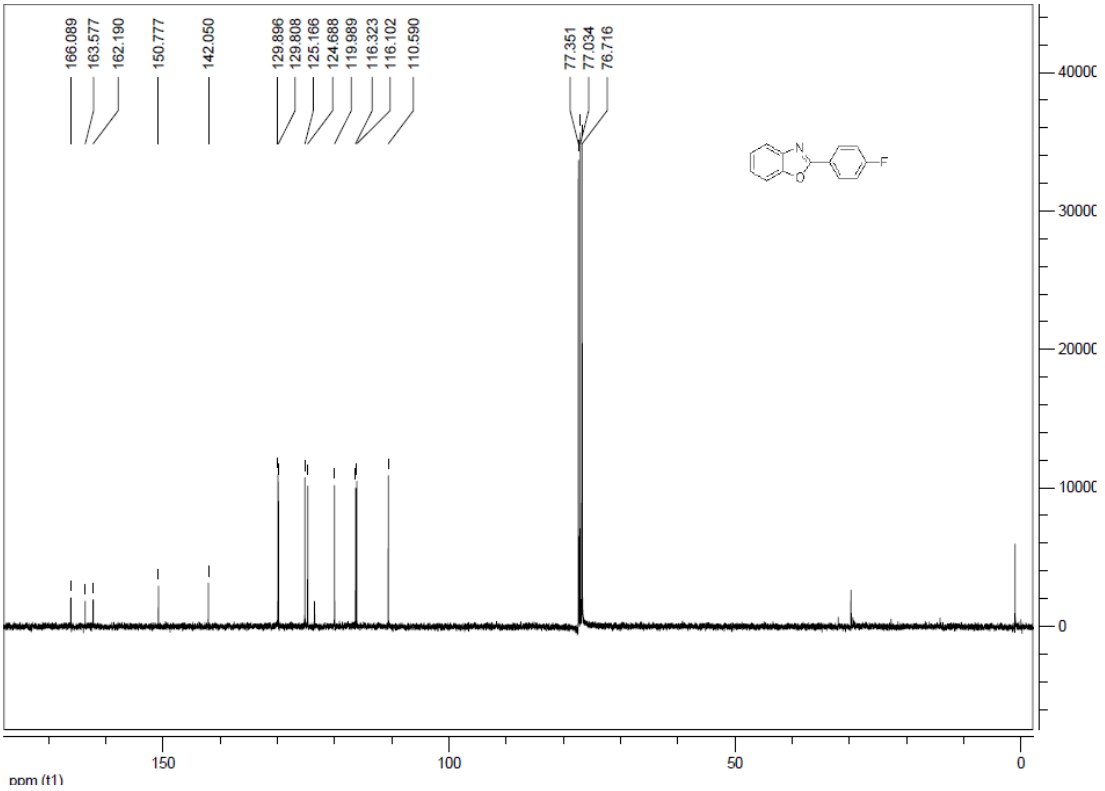
2-phenylbenzo[d]oxazole



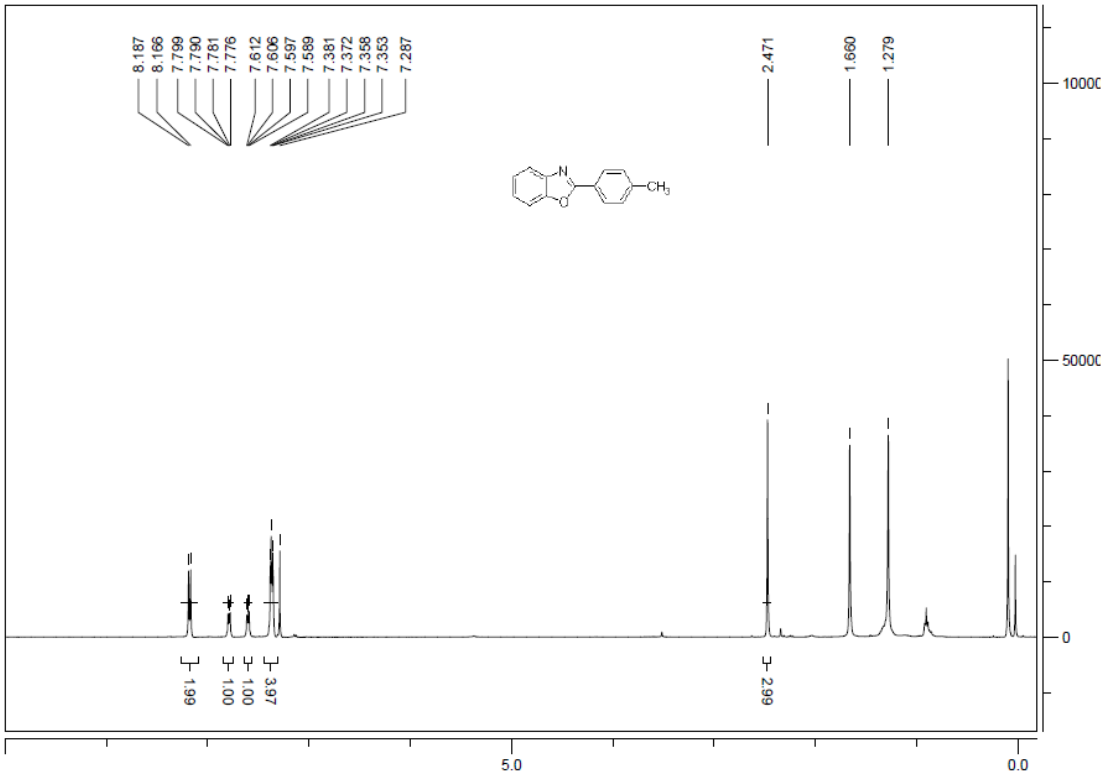


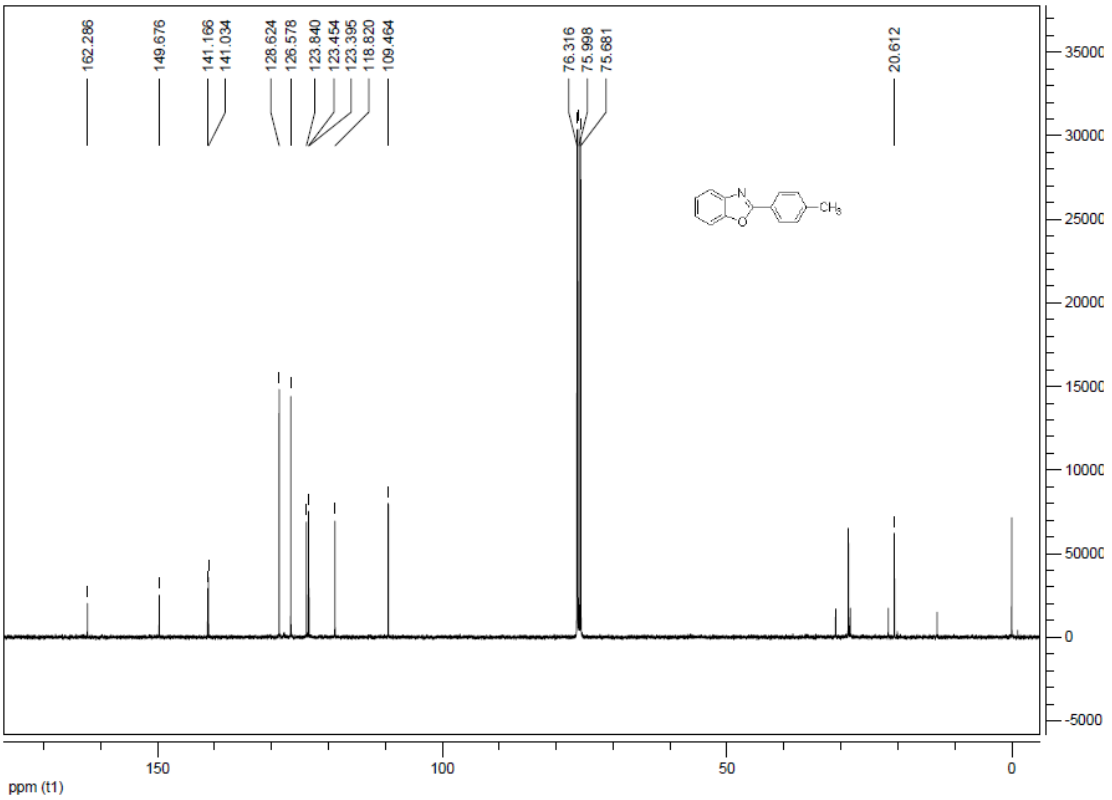
2-(4-fluorophenyl)benzo[d]oxazole



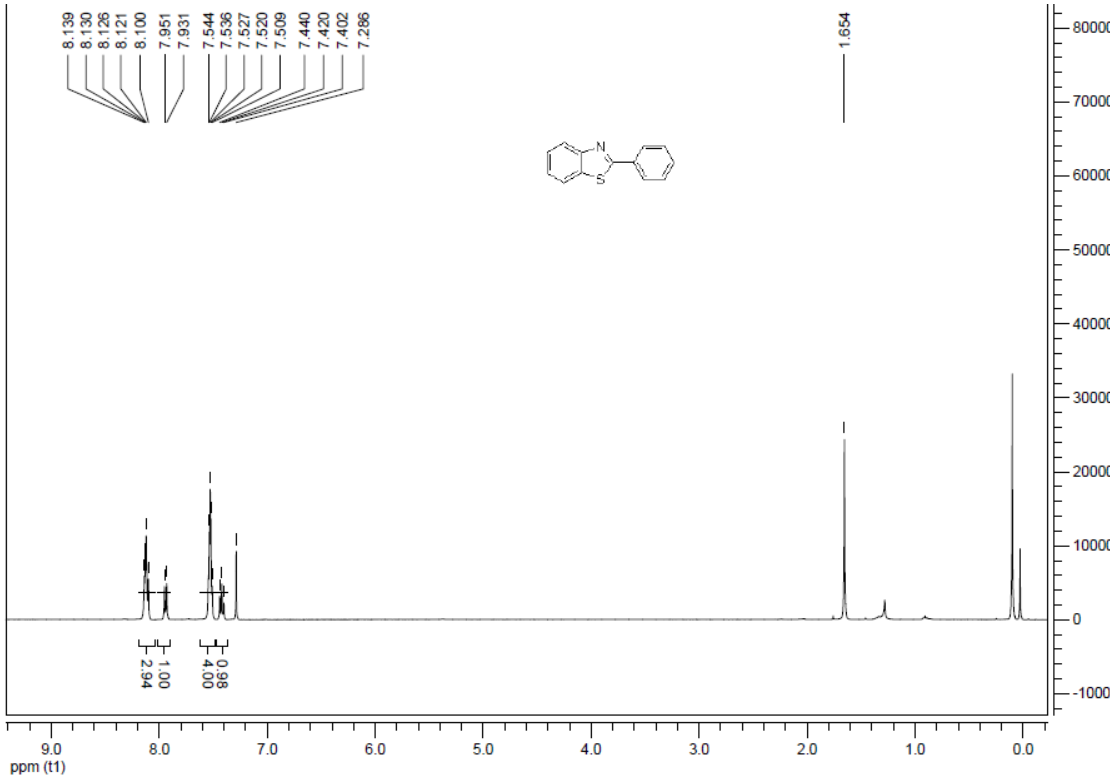


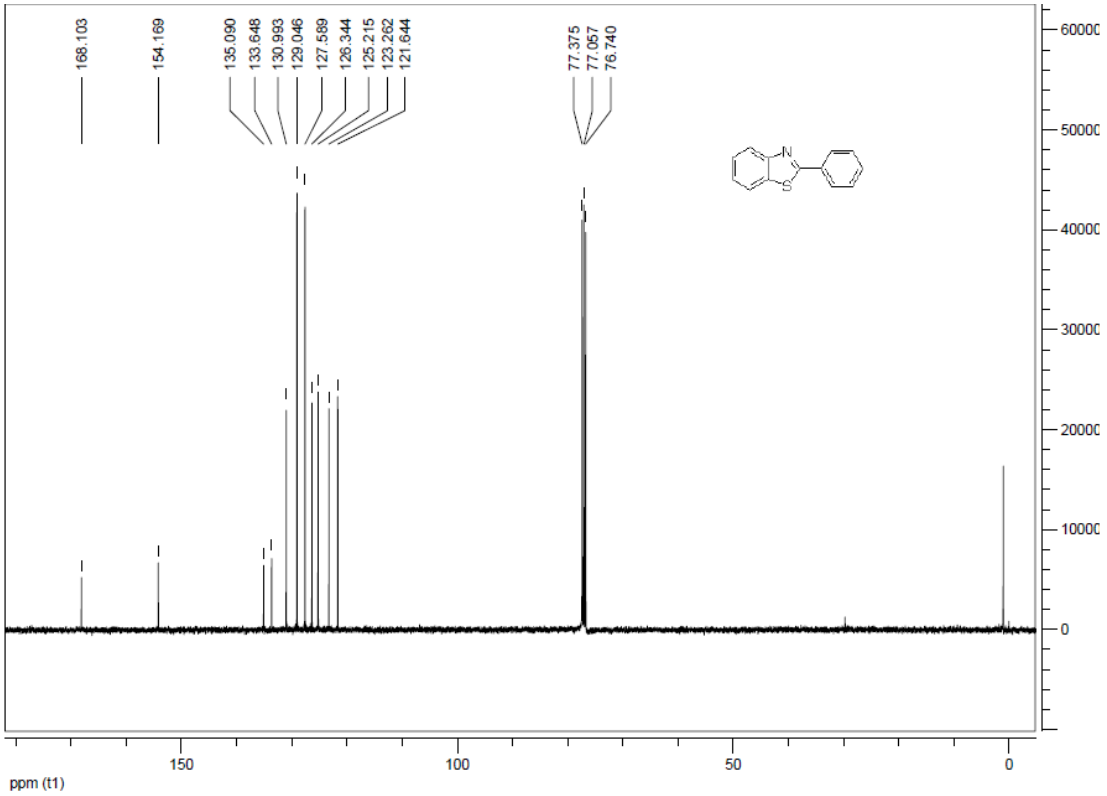
2-p-tolylbenzo[d]oxazole



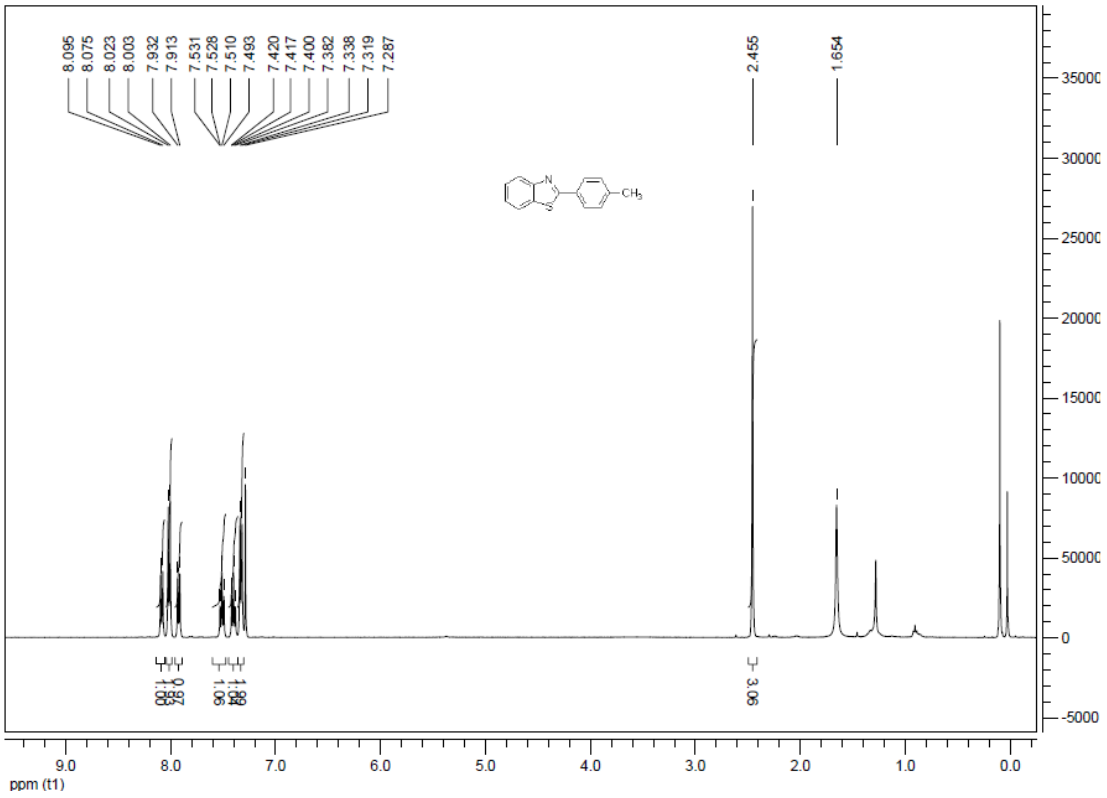


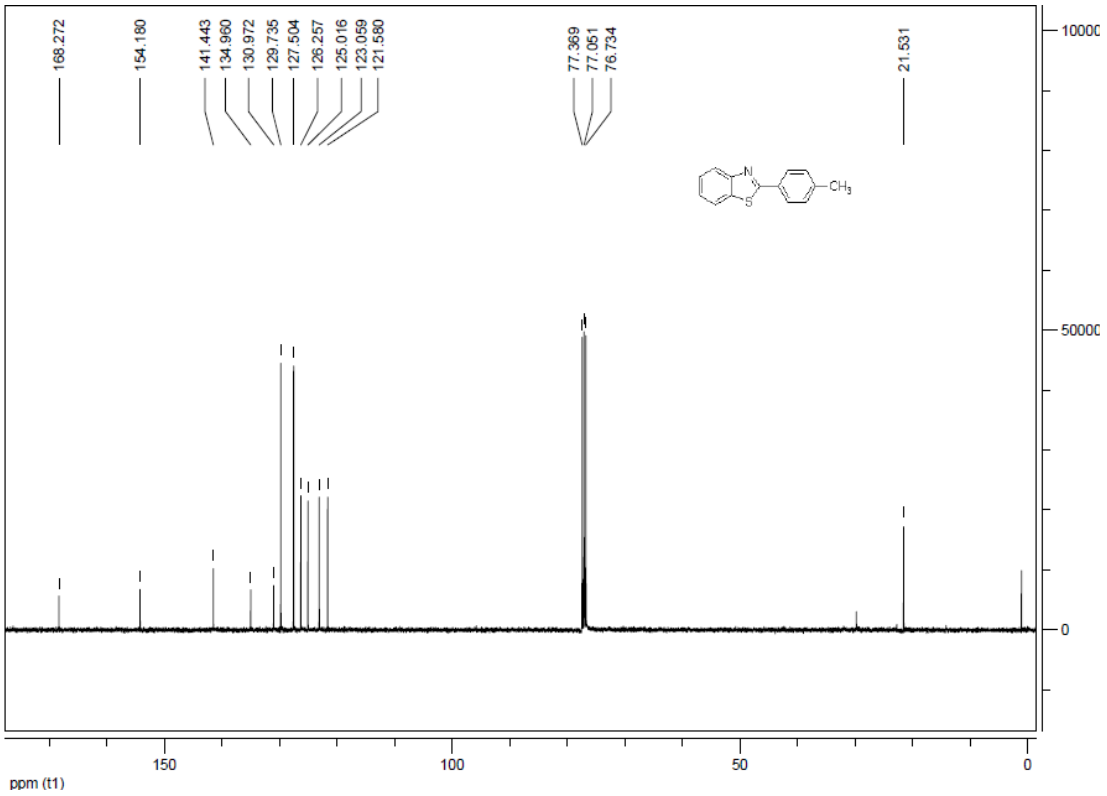
2-phenylbenzo[d]thiazole



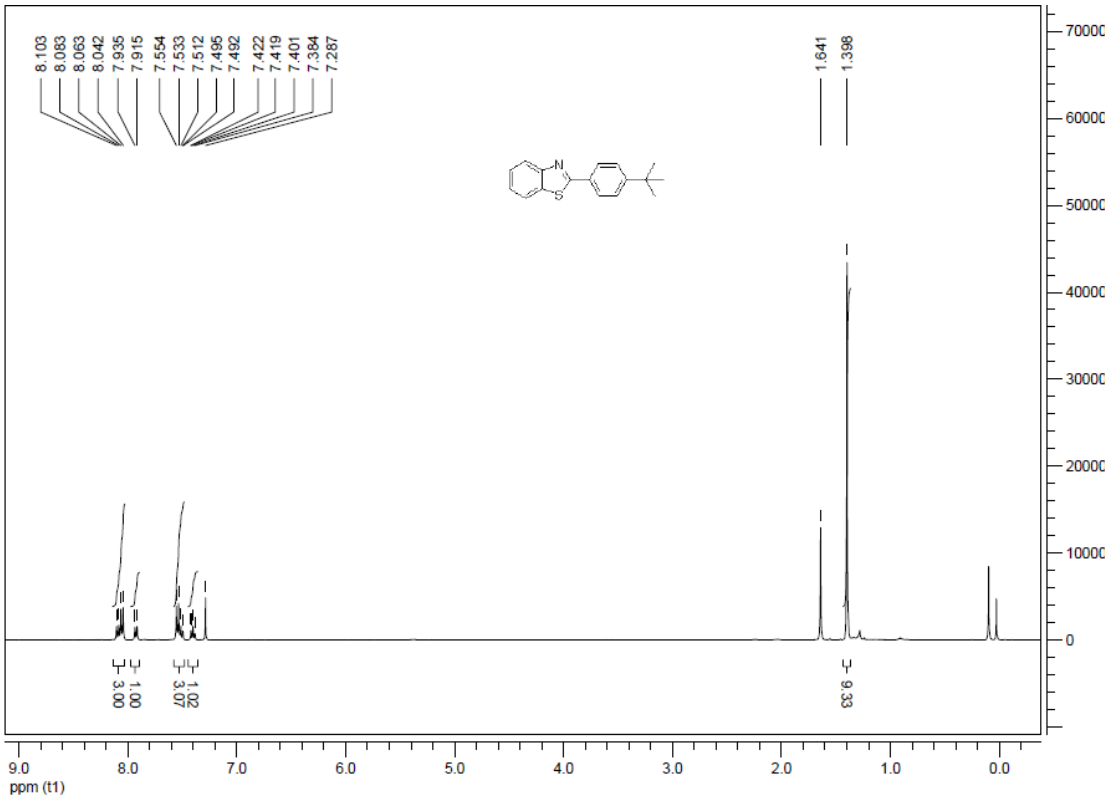


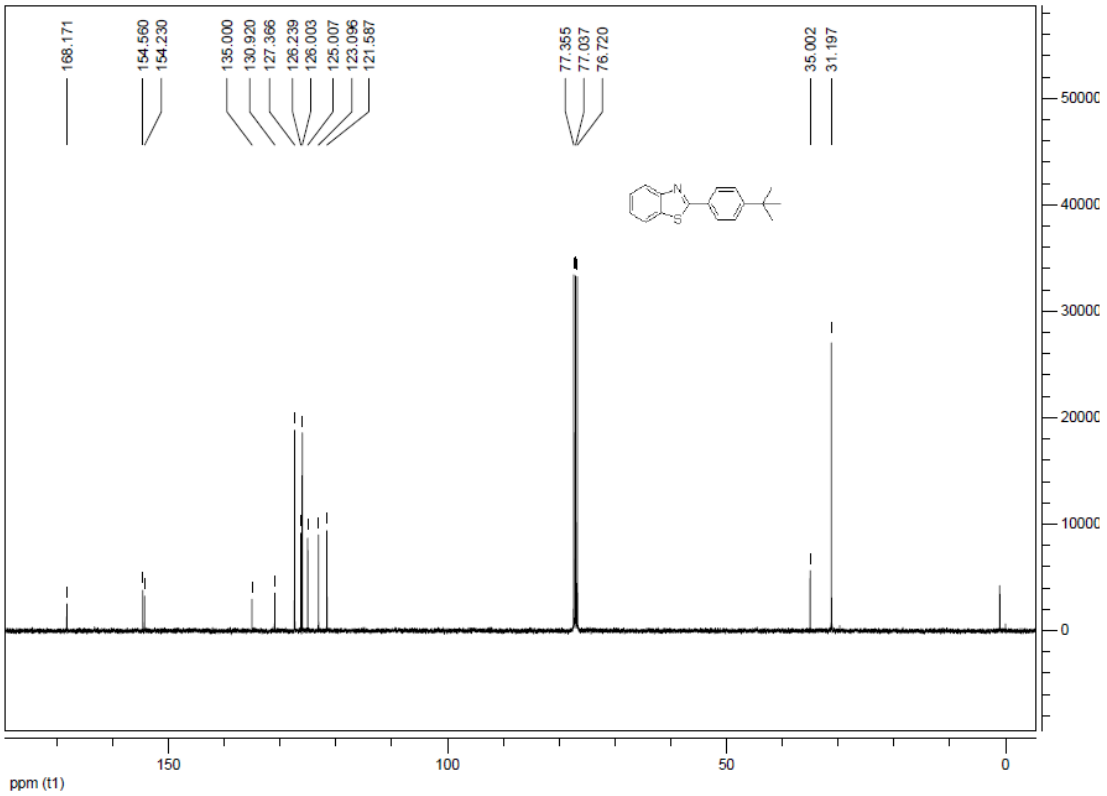
2-p-tolylbenzo[d]thiazole



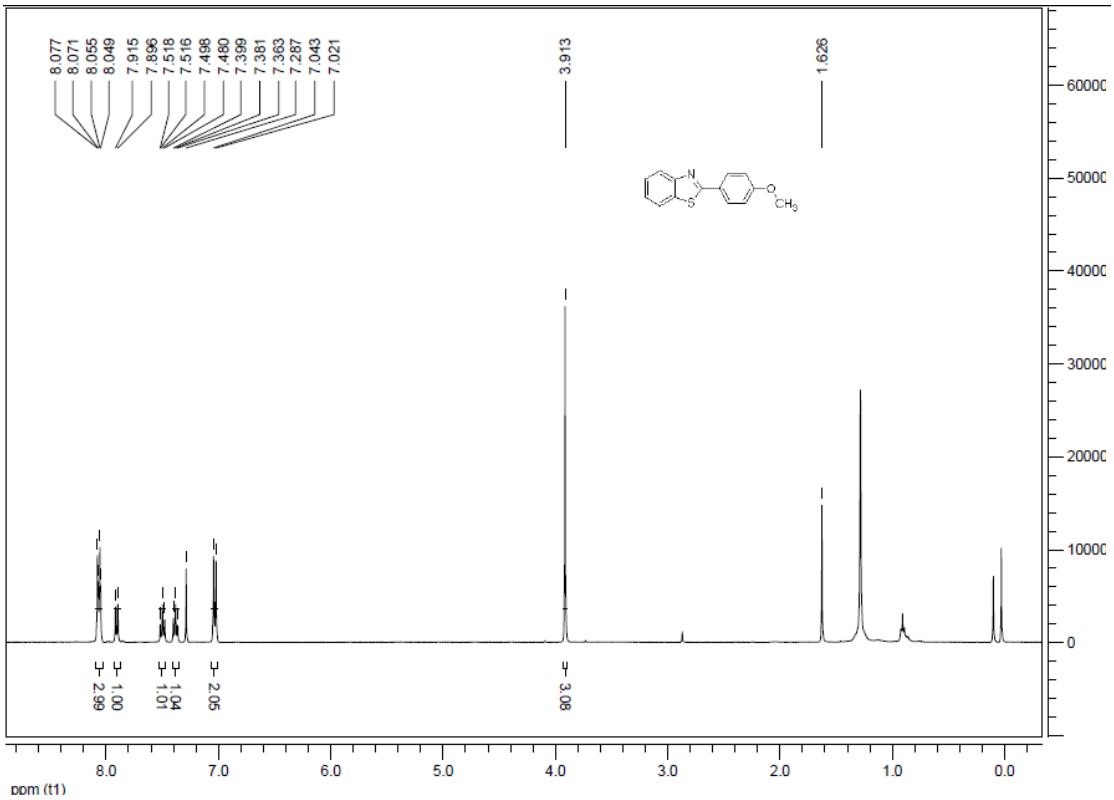


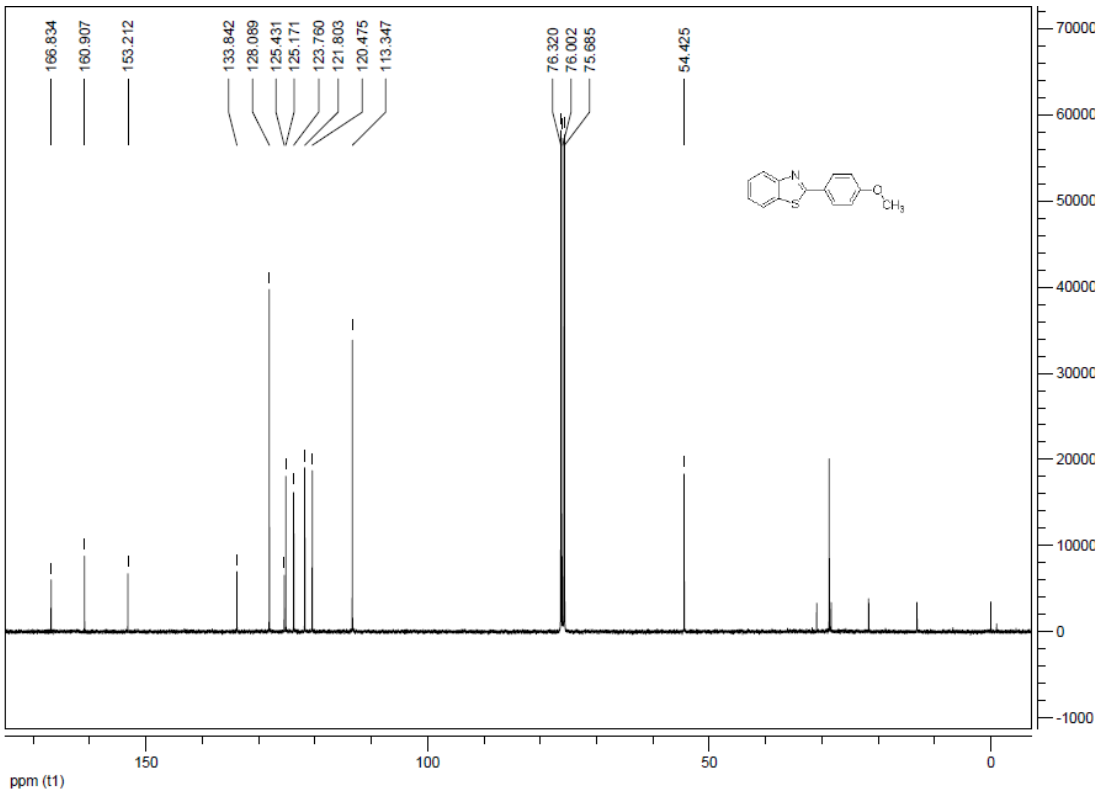
2-(4-tert-butylphenyl)benzo[d]thiazole



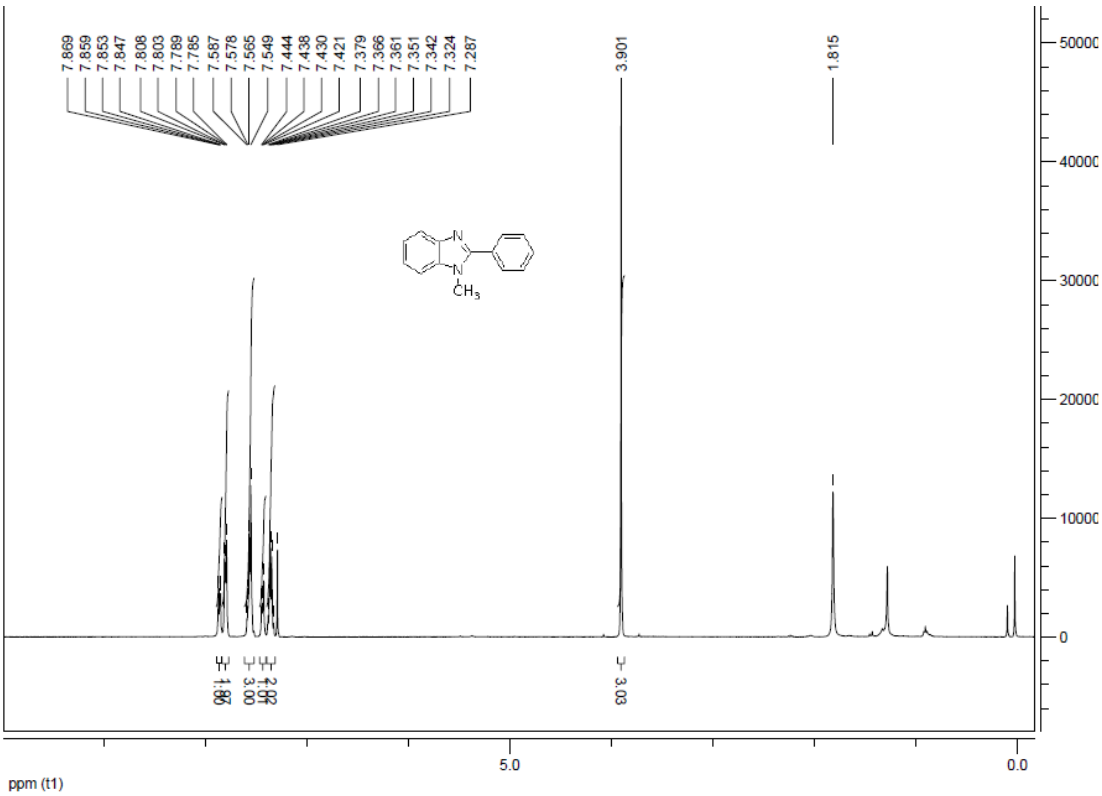


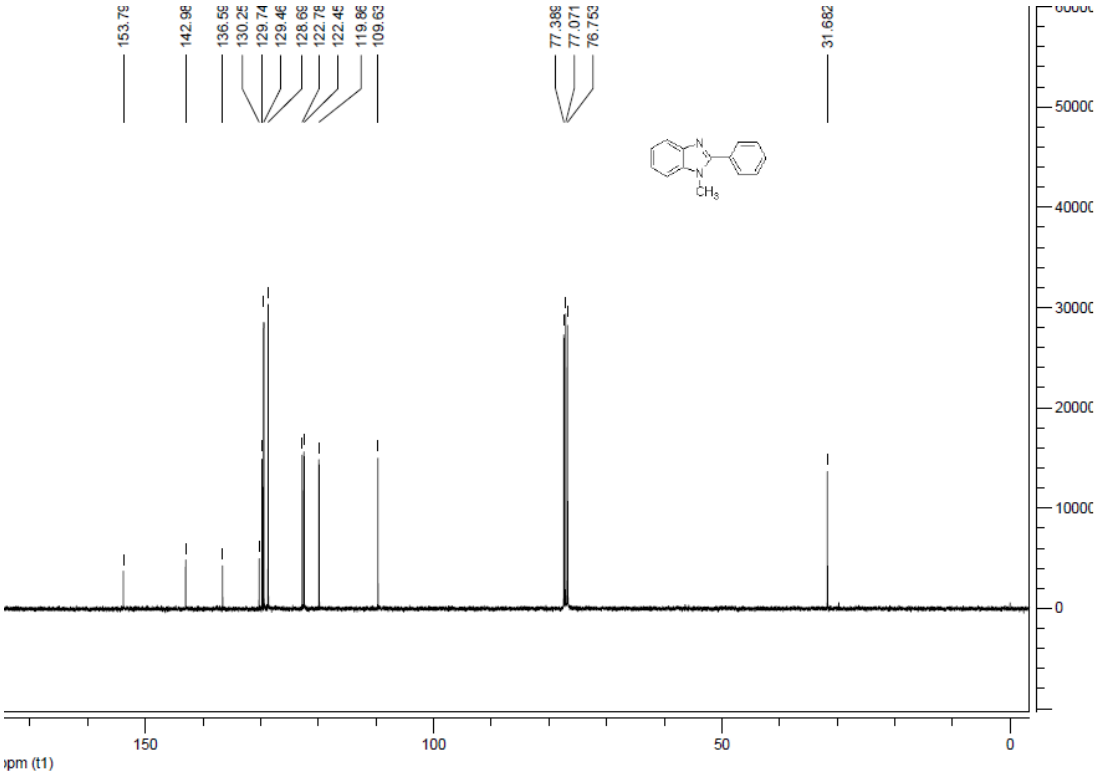
2-(4-methoxyphenyl)benzo[d]thiazole



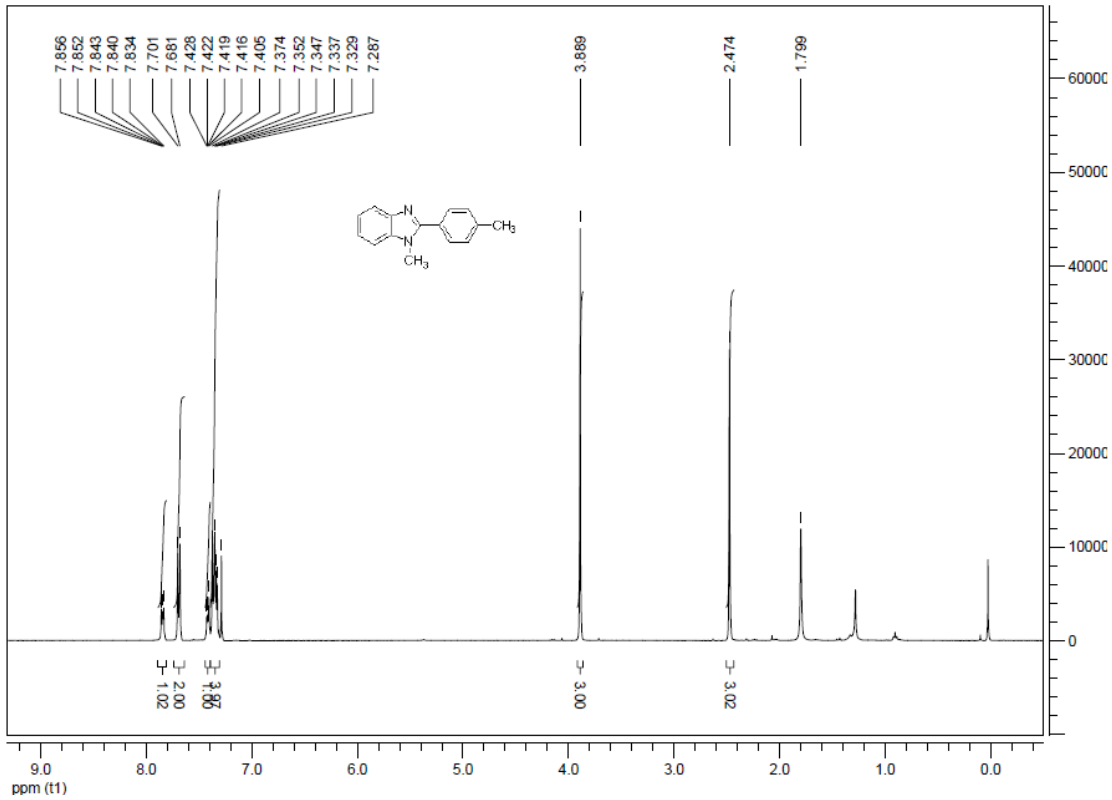


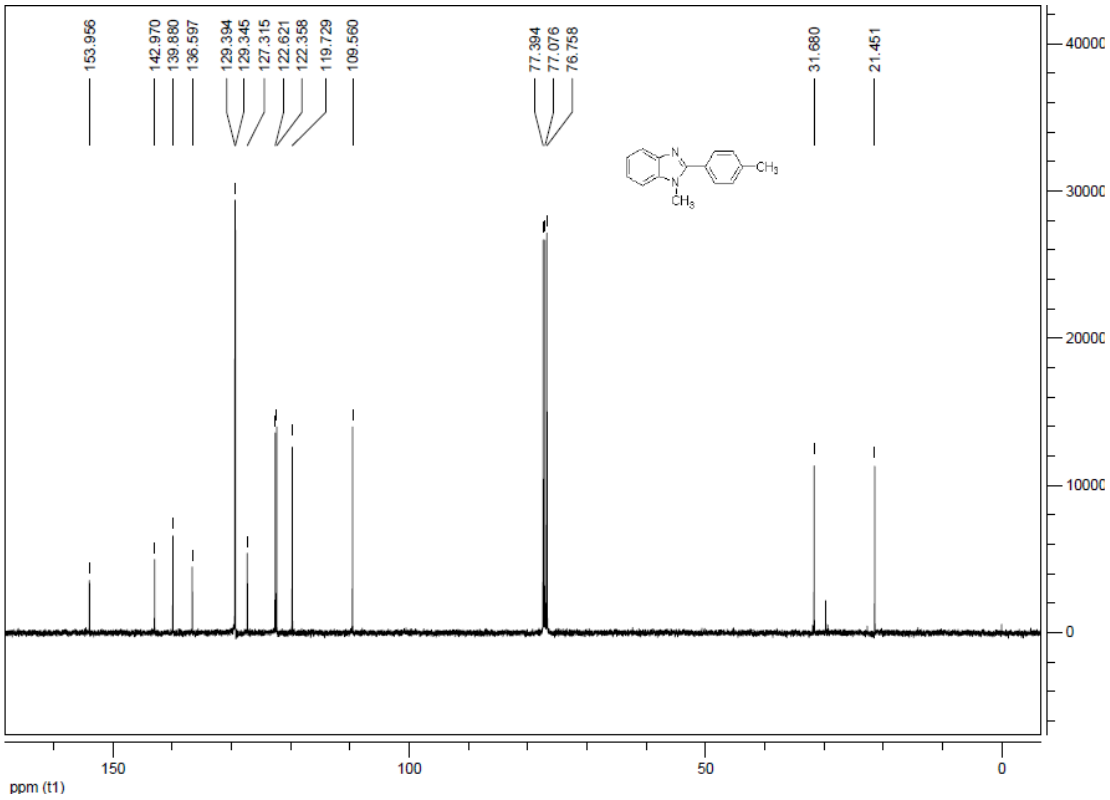
1-methyl-2-phenyl-1H-benzo[d]imidazole



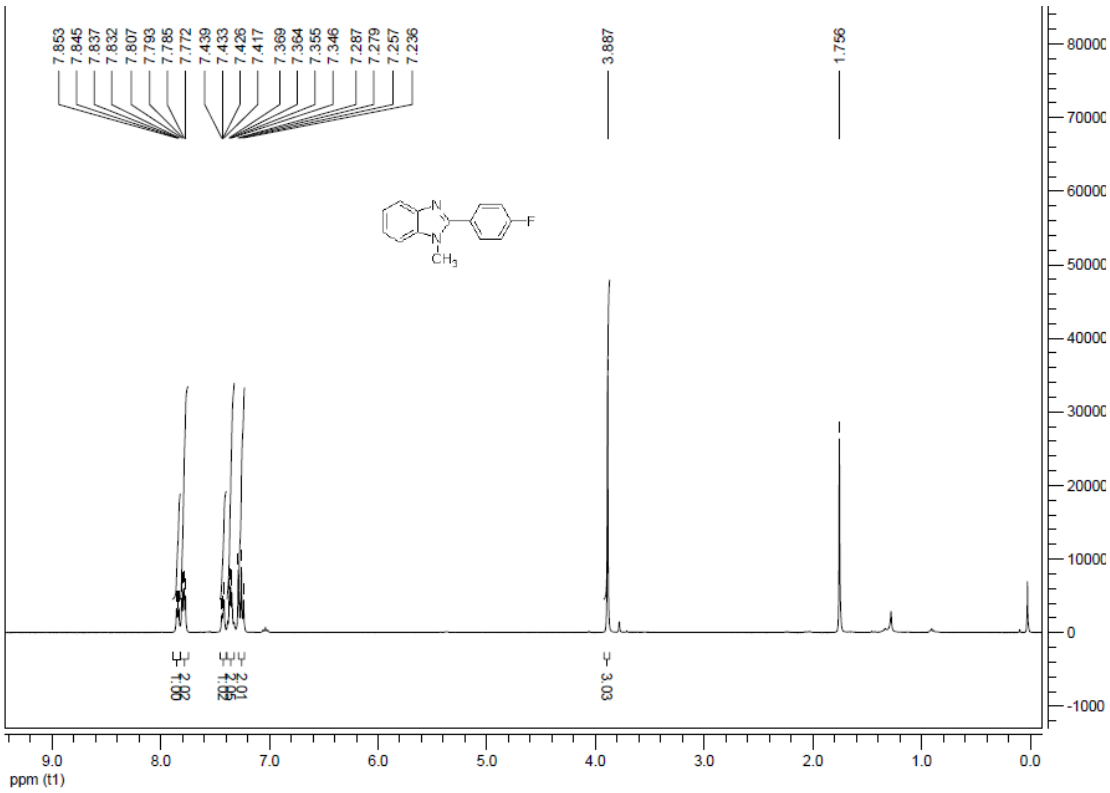


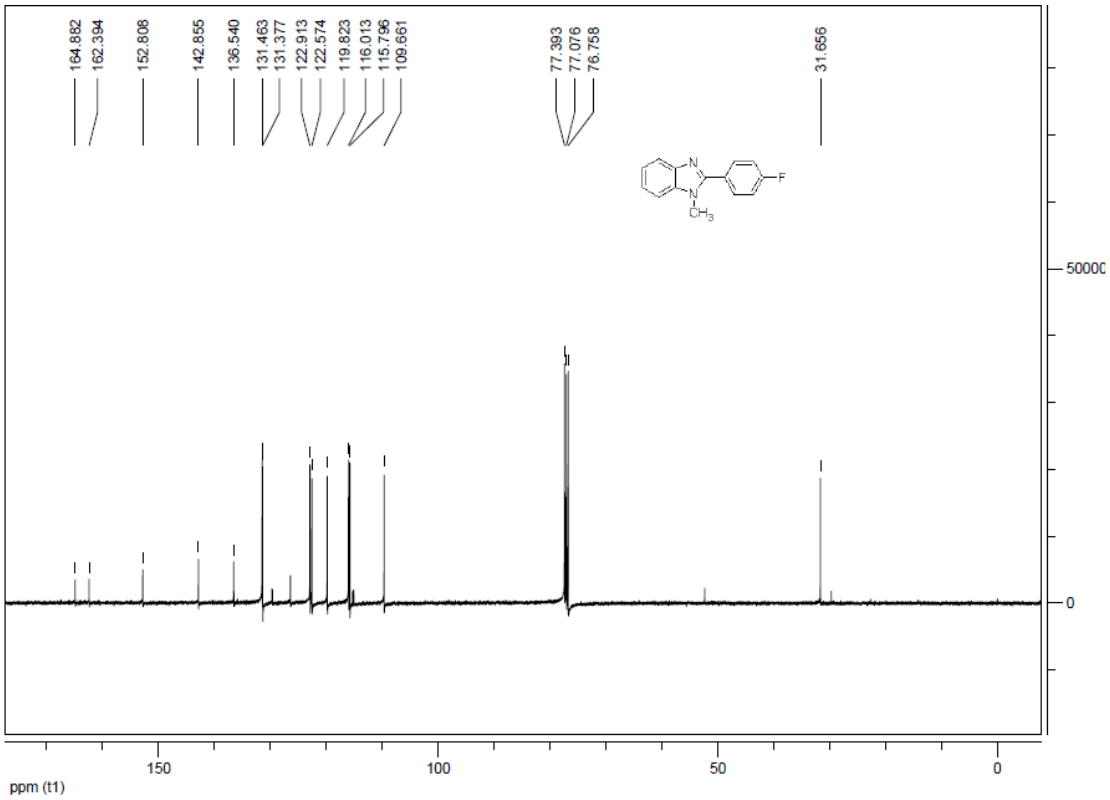
N-methyl-2-p-tolyl-1H-benzo[d]imidazole



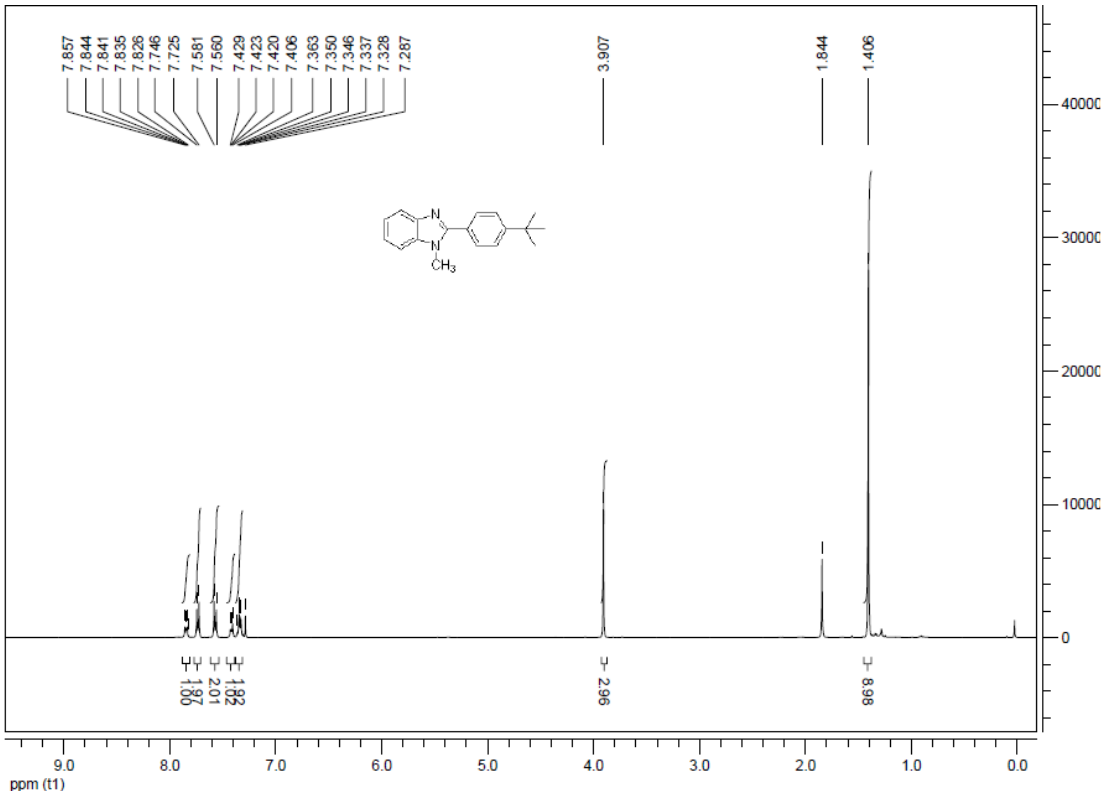


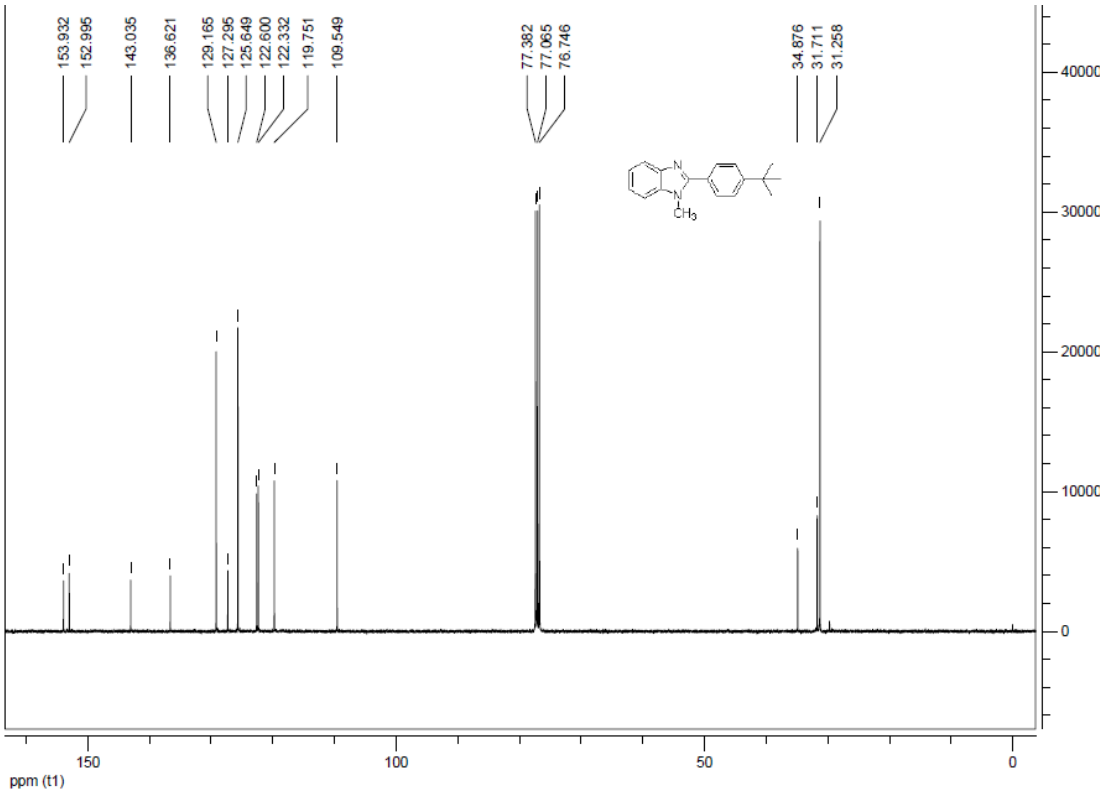
2-(4-fluorophenyl)-1-methyl-1H-benzo[d]imidazole



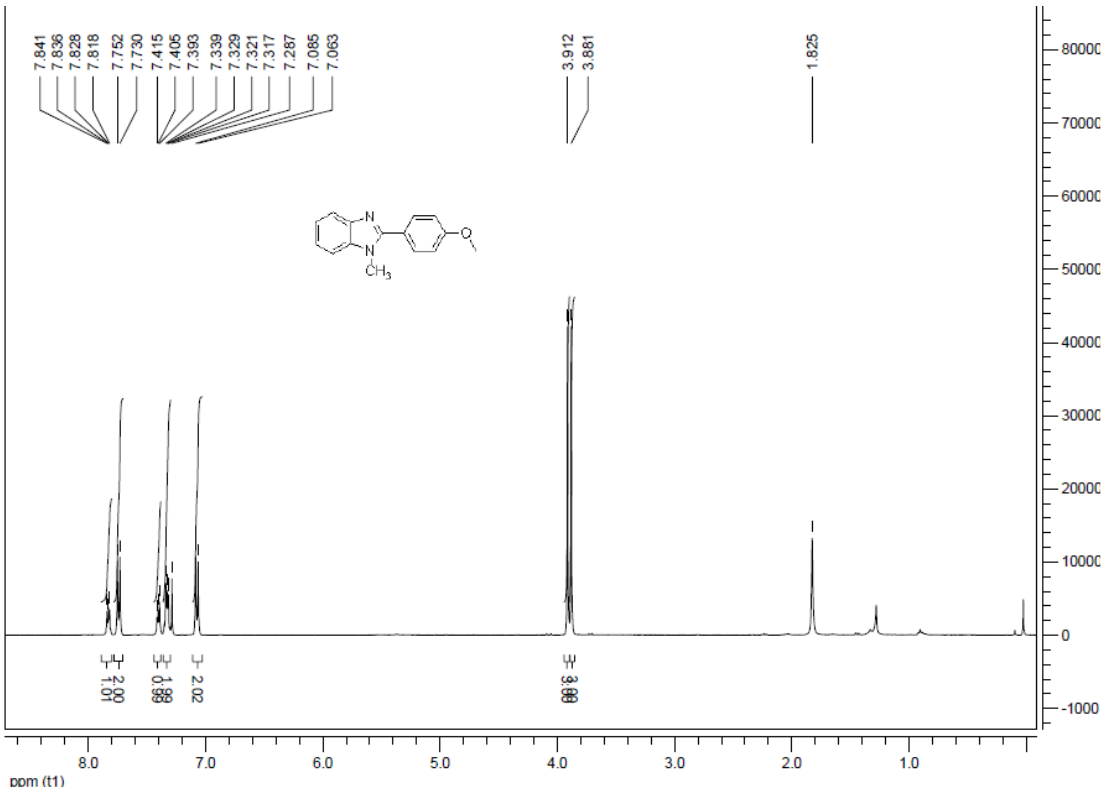


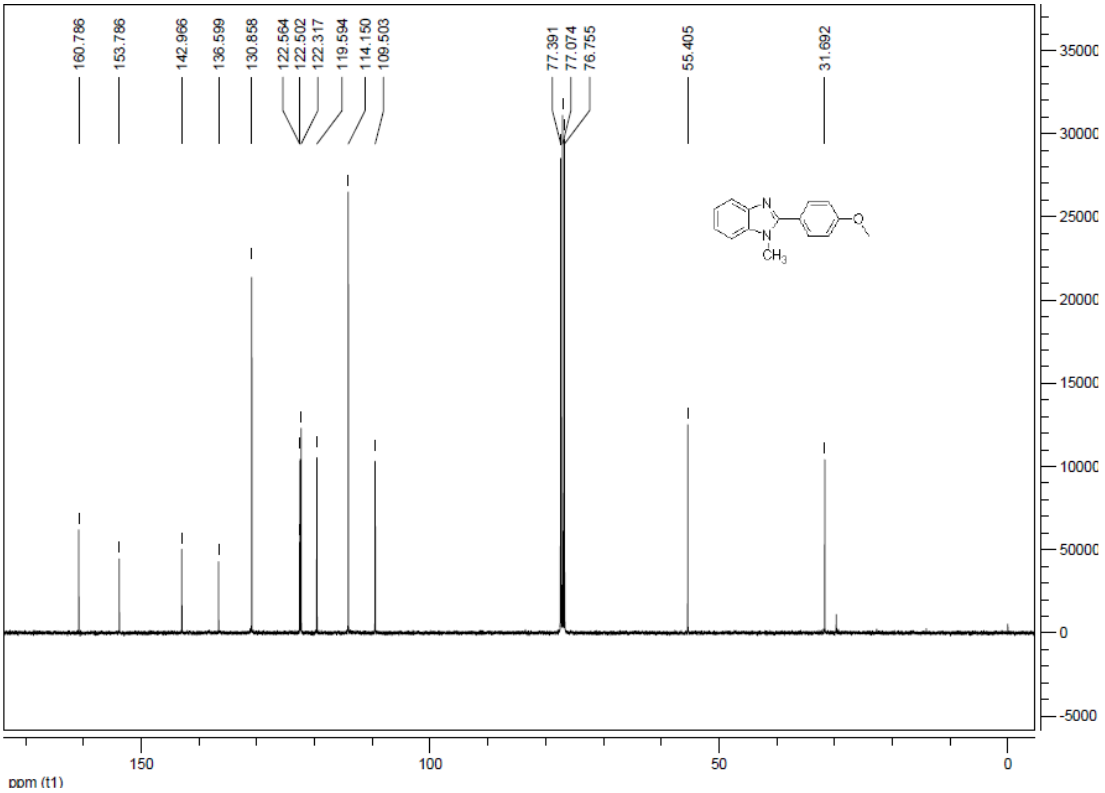
2-(4-tert-butylphenyl)-1-methyl-1H-benzo[d]imidazole





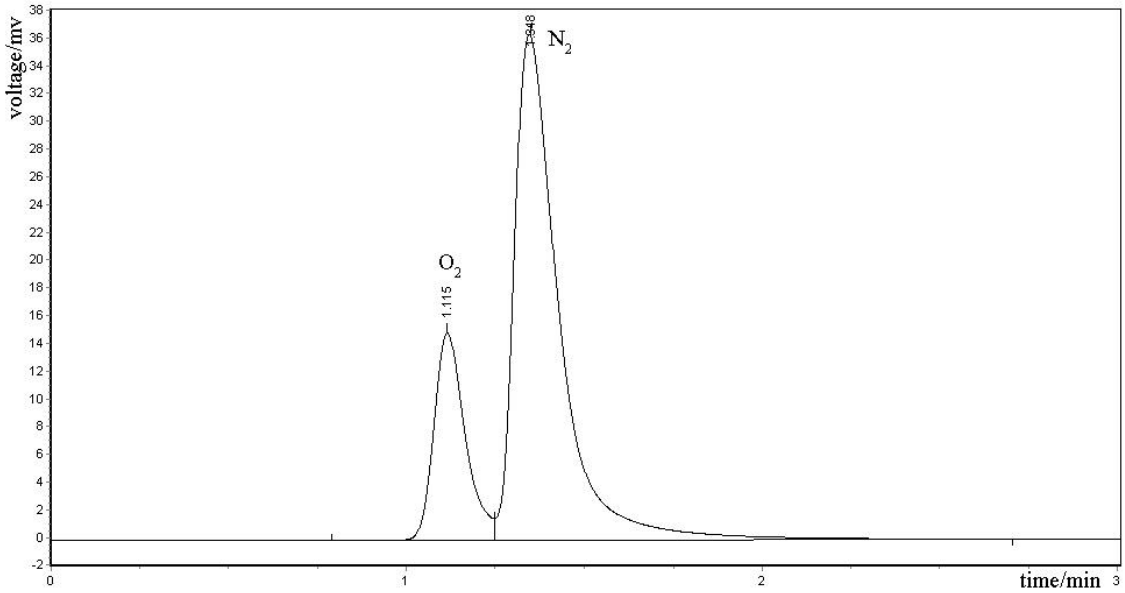
2-(4-methoxyphenyl)-1-methyl-1H-benzo[d]imidazole



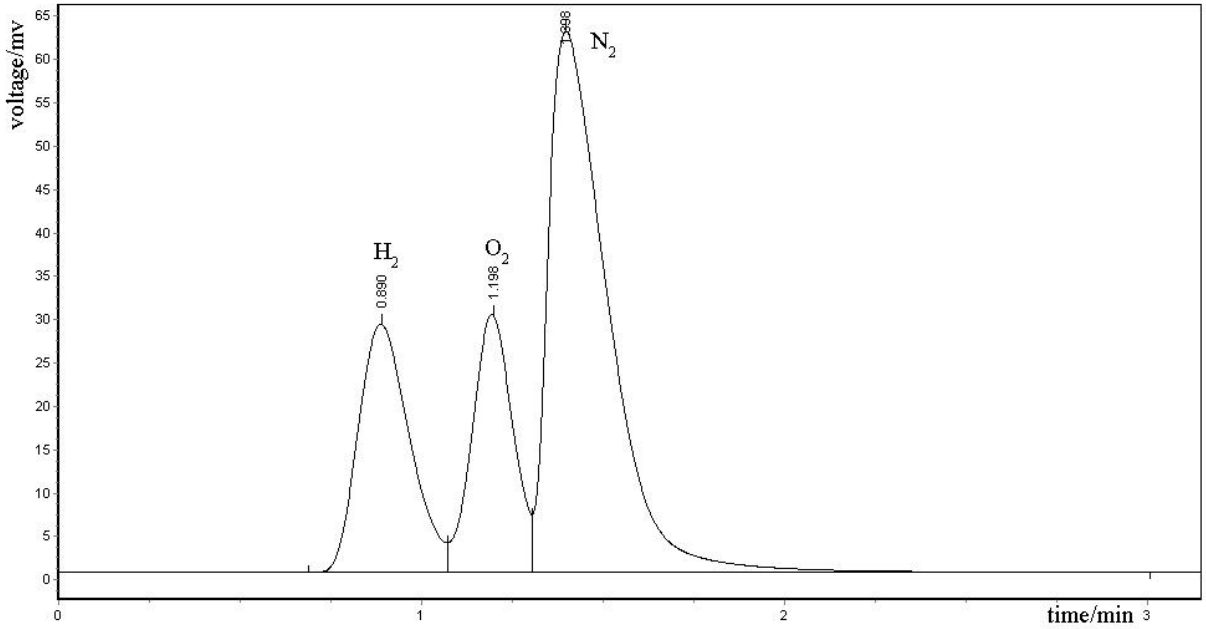


GC H_2 detection for the dehydrogenation of benzylamine.

GC for air.



GC for the mixture of hydrogen gas and air.



GC for the gas from reaction system (some air infiltrated into the gas sample during sampling).