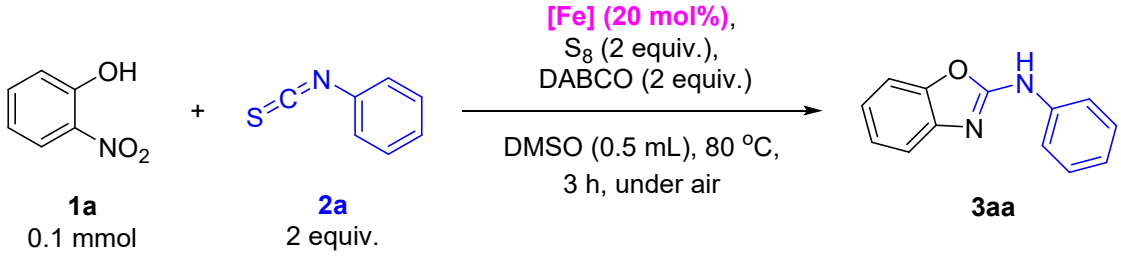
Electronic Supplementary Material (ESI) for RSC Advances.

1. General information

All reagents and starting materials were commercially obtained and were used without further purification unless otherwise noted. Gas chromatography (GC) analyses were performed using Shimadzu Nexis GC-2030 equipped with a flame ionization detector (FID) and an SPB-5 column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μm). The GC yield was calculated using diphenyl ether as the internal standard. Gas chromatography – mass spectrometry (GC-MS) analyses were performed using Shimadzu GCMS-QP2010 Ultra with a ZB-5MS column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μm). MS spectra were compared with the spectra gathered in the NIST library. Proton, carbon-13, and fluorine-19 nuclear magnetic resonance (^{1}H NMR, ^{13}C NMR, ^{19}F NMR) spectra were recorded on Bruker AV 500 or 600 spectrometers using residual solvent, TMS, or $CFCl_3$ as reference. Splitting is reported with the following symbols: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, dt = doublet of triplets, tt = triplet of triplets, ddd = doublet of doublets of doublets, tdd = triplet of doublets of doublets, and m = multiplet. Coupling constants (*J*) are reported in Hertz. HR-MS spectra were recorded by Agilent 6545 with 6200 Series TOF and 6500 Series Q-TOF LC/MS System and on Shimadzu LCMS-IT-TOF Mass Spectrometer. The mass spectrometry was performed in the positive electrospray ionization (ESI+) mode. Melting points were recorded on Stuart SMP30 melting point instrument. Analytical thin-layer chromatography (TLC) was performed on silica gel 60 F254 (Merck), visualized by irradiation with UV light. Column chromatography was performed on silica gel (230−400 mesh or 37−63 μm). Molecular weight of elemental sulfur is 32 g/mol.

2. Optimization of reaction condition

2.1. Effect of various Fe-based catalysts



1a
0.1 mmol

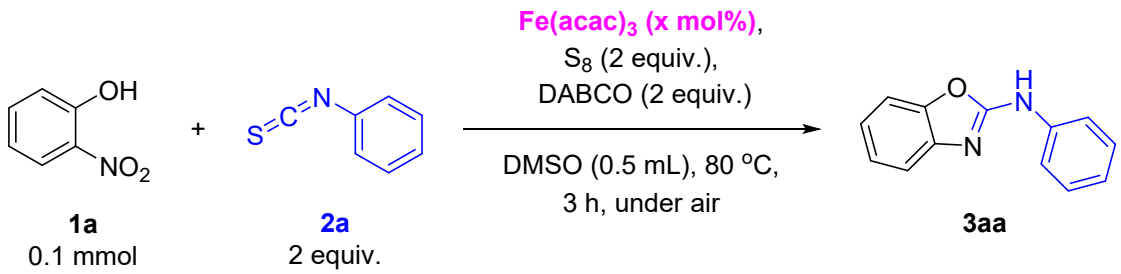
2a
2 equiv.

3aa

Entry	[Fe] (20 mol%)	GC yield (%)[a]
1	Fe^0	0
2	$FeSO_4$	38
3	$FeSO_4.7H_2O$	40
4	$FeCl_3$	30
5	$FeCl_3.6H_2O$	28
6	$Fe_2(SO_4)_3$	39
7	$Fe(NO_3)_3.9H_2O$	31
8	$K_3[Fe(CN)_6]$	0
9	**$Fe(acac)_3$**	**73**

[a]Reaction conditions: 2-nitrophenol (0.1 mmol), PhNCS (0.2 mmol), [Fe] (0.02 mmol), elemental sulfur (0.2 mmol), DABCO (0.2 mmol), DMSO (0.5 mL), 3 h, 80 °C.

2.2. Effect of catalyst amount



1a
0.1 mmol

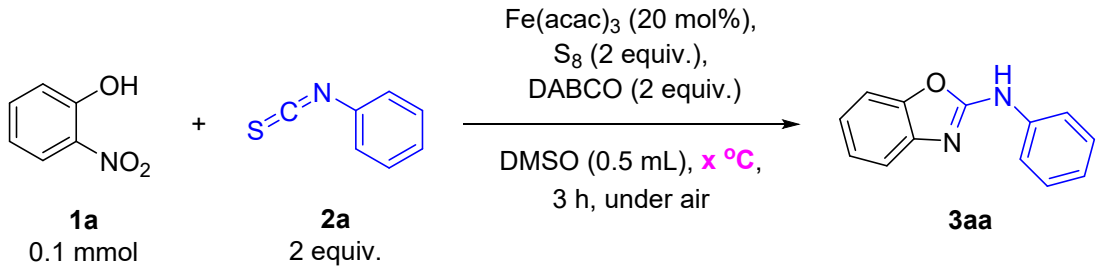
2a
2 equiv.

3aa

Entry	[Fe] amount (x mol%)	GC yield (%)[a]
1	0	0
2	10	57
3	**20**	**73**
4	30	71

[a]Reaction condition: 2-nitrophenol (0.1 mmol), PhNCS (0.2 mmol), $Fe(acac)_3$ (**x** mol%), elemental sulfur (0.2 mmol), DABCO (0.2 mmol), DMSO (0.5 mL), 3 h, 80 °C.

2.3. Effect of reaction temperature



1a
0.1 mmol

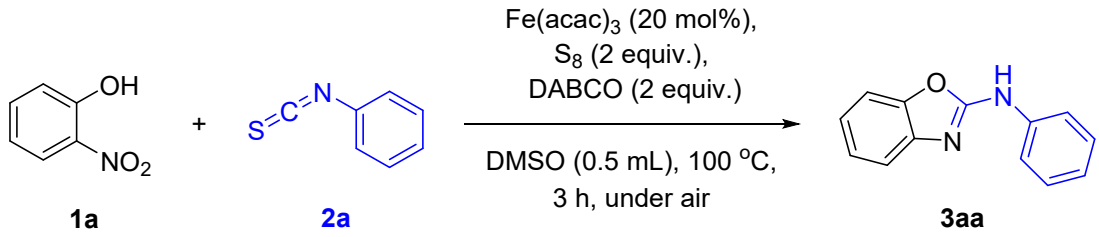
2a
2 equiv.

3aa

Entry	Temperature (°C)	GC yield (%)[a]
1	r.t.	n.d.
2	60	44
3	80	73
4	**100**	**81**
5	120	80
6	140	78

[a]Reaction condition: 2-nitrophenol (0.1 mmol), PhNCS (0.2 mmol), $Fe(acac)_3$ (0.02 mmol), elemental sulfur (0.2 mmol), DABCO (0.2 mmol), DMSO (0.5 mL), 3 h.

2.4. Effect of reactants molar ratio

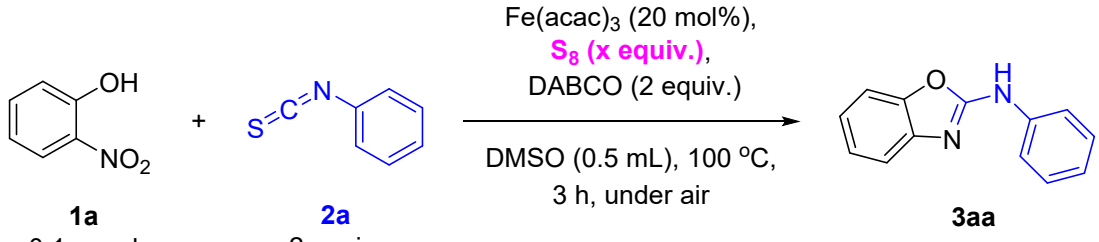


Entry	Molar ratio **1a**:**2a**	GC yield (%)
1[a]	2:1	62
2[a]	1.5:1	63
3[b]	1:1	54
4[b]	1:1.5	74
5[b]	**1:2**	**81**
6[b]	1:2.5	82
7[b]	1:3	78

[a]Reaction condition: 2-nitrophenol (**x** equiv.), PhNCS (0.1 mmol), $Fe(acac)_3$ (0.02 mmol), elemental sulfur (0.2 mmol), DABCO (0.2 mmol), DMSO (0.5 mL), 3 h, 100 °C.

[b]Reaction condition: 2-nitrophenol (0.1 mmol), PhNCS (**x** equiv.), $Fe(acac)_3$ (0.02 mmol), elemental sulfur (0.2 mmol), DABCO (0.2 mmol), DMSO (0.5 mL), 3 h, 100 °C.

2.5. Effect of sulfur amount

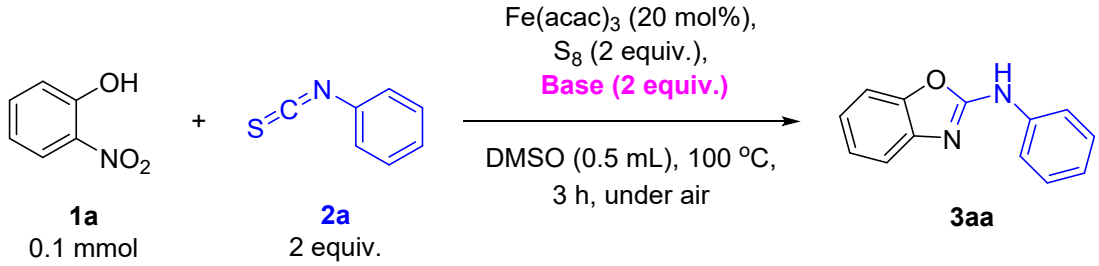


Entry	Sulfur amount (equiv.)	GC yield (%)[a]
1	0.2	67

2	1	67
3	**2**	**81**
4	3	78

[a]Reaction condition: 2-nitrophenol (0.1 mmol), PhNCS (0.2 mmol), $Fe(acac)_3$ (0.02 mmol), elemental sulfur (**x** equiv.), DABCO (0.2 mmol), DMSO (0.5 mL), 3 h, 100 °C.

2.6. Effect of various bases



1a
0.1 mmol

2a
2 equiv.

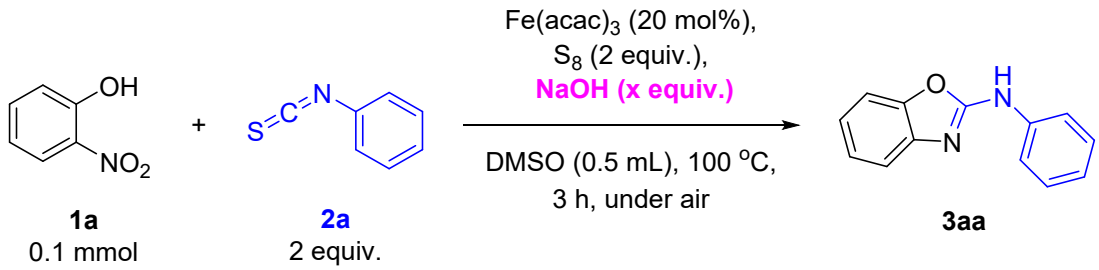
3aa

Entry	base	GC yield (%)[a]
1	DABCO	81
2	DMAP	85
3	$(i\text{Pr})_2\text{NEt}$	85
4	*N*-methylmorpholine	72
5	3-picoline	42
6	CH_3COONa	75
7	K_2CO_3	84
8	**NaOH**	**92**
9	KOH	87
10	Li_2CO_3	79
11	Cs_2CO_3	34
12	*t*BuOK	78

[a]Reaction condition: 2-nitrophenol (0.1 mmol), PhNCS (0.2 mmol), $Fe(acac)_3$ (0.02

mmol), elemental sulfur (0.2 mmol), base (0.2 mmol), DMSO (0.5 mL), 3 h, 100 °C.

2.7. Effect of base amount



1a
0.1 mmol

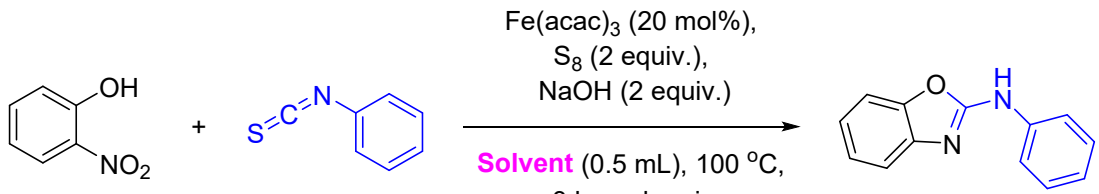
2a
2 equiv.

3aa

Entry	Base amount (equiv.)	GC yield (%)[a]
1	0	55
2	1	81
3	**2**	**92**
4	3	83

[a]Reaction condition: 2-nitrophenol (0.1 mmol), PhNCS (0.2 mmol), $Fe(acac)_3$ (0.02 mmol), elemental sulfur (0.2 mmol), NaOH (**x** equiv.), DMSO (0.5 mL), 3 h, 100 °C.

2.8. Effect of solvents



1a
0.1 mmol

2a
2 equiv.

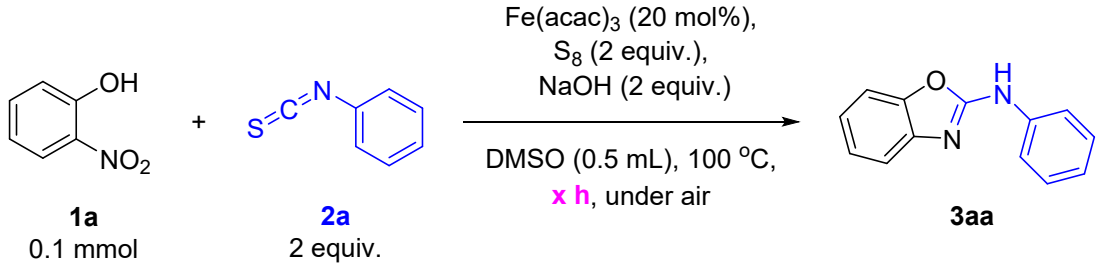
3aa

Entry	Solvent (0.5 mL)	GC yield (%)[a]
1	*n*-Butanol	54
2	DMF	79
3	Toluene	7
4	Chlorobenzene	12
5	**DMSO**	**92**

6	DMSO/H_2O 9:1 (v/v)	72
7	H_2O	58
8	*t*-Amyl alcohol	37

[a]Reaction condition: 2-nitrophenol (0.1 mmol), PhNCS (0.2 mmol), $Fe(acac)_3$ (0.02 mmol), elemental sulfur (0.2 mmol), NaOH (0.2 mmol), solvent (0.5 mL), 3 h, 100 °C.

2.9 Effect of reaction time



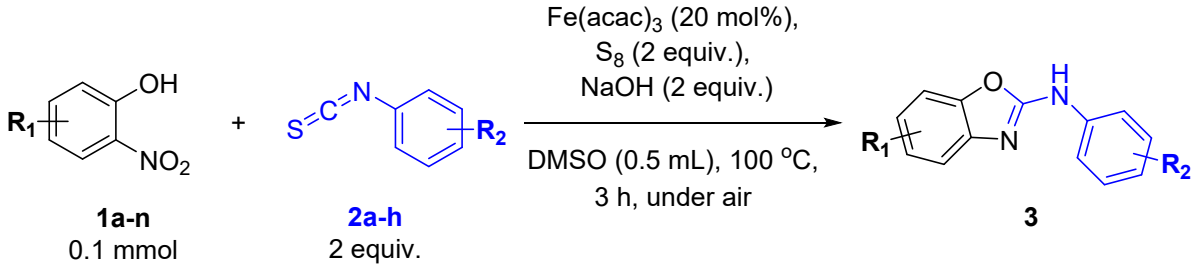
1a 0.1 mmol | **2a** 2 equiv. | **3aa**

Entry	time (h)	GC Yield (%)[a]
1	1	84
2	2	88
3	**3**	**92**
4	4	87

[a]Reaction condition: 2-nitrophenol (0.1 mmol), PhNCS (0.2 mmol), $Fe(acac)_3$ (0.02 mmol), elemental sulfur (0.2 mmol), NaOH (0.2 mmol), DMSO (0.5 mL), **x** h, 100 °C.

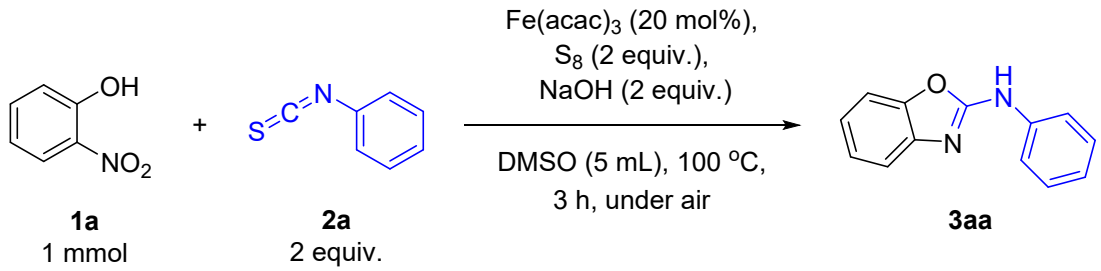
3. General procedures

3.1. General procedure for synthesis of 2-aminobenzoxazoles



To a 4-mL screw-cap vial equipped with a magnetic stirrer was added a derivative of 2-nitrophenol (0.1 mmol), an aryl isothiocyanate (0.2 mmol), iron(III) acetylacetonate (0.02 mmol, 7.1 mg), elemental sulfur (0.2 mmol, 6.4 mg), sodium hydroxide (0.2 mmol, 8.0 mg), and DMSO (0.5 mL). The reaction mixture was heated on a magnetic hot plate at 100 °C for 3 h. Upon completion, the mixture was cooled to ambient temperature and diluted with distilled water (5 mL). Organic components then were extracted to ethyl acetate (3 x 5 mL), washed with brine, dried with anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude mixture was purified by column chromatography on silica gel to obtain the desired products.

3.2. Scale-up experiment for the synthesis of *N*-phenylbenzo[*d*]oxazol-2-amine (3aa)

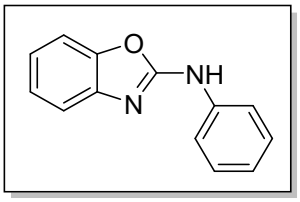


To a 100-mL round-bottom flask equipped with a magnetic stirrer was added 2-nitrophenol (1 mmol, 139 mg), phenyl isothiocyanate (2 mmol, 270 mg), iron(III) acetylacetonate (0.2 mmol, 70.6 mg), elemental sulfur (2 mmol, 64 mg), sodium hydroxide (2 mmol, 80 mg), and DMSO (5 mL). The reaction mixture was heated on a magnetic hot plate at 100 °C for 3 h. Upon completion, the mixture was cooled to ambient temperature and diluted with distilled water (15 mL). Organic components were extracted to ethyl acetate (3 x 15 mL), washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude mixture was purified by column

chromatography on silica gel (eluent hexanes/ethyl acetate 5:1) to obtain 187 mg (89%) of **3aa**.

4. Spectral data of products

N-phenylbenzo[*d*]oxazol-2-amine (3aa)



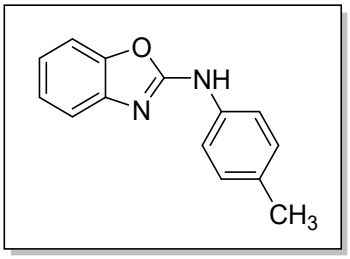
Prepared from 2-nitrophenol (0.1 mmol) and phenyl isothiocyanate (0.2 mmol) under air as described in the general procedure and purified by column chromatography on silica gel (230 – 400 mesh or 37 – 63 μm, hexanes/ethyl acetate 5:1, R_f = 0.44) as a pale-yellow solid (20.0 mg, 95% yield).

^{1}H NMR (600 MHz, DMSO-d_6) δ 10.59 (s, 1H), 7.77 (dd, J = 8.7, 1.1 Hz, 2H), 7.49 (dd, J = 7.9, 1.7 Hz, 1H), 7.46 (dd, J = 7.9, 1.2 Hz, 1H), 7.41 – 7.32 (m, 2H), 7.23 (td, J = 7.6, 1.2 Hz, 1H), 7.13 (td, J = 7.7, 1.3 Hz, 1H), 7.04 (tt, J = 7.3, 1.2 Hz, 1H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 157.96, 146.98, 142.40, 138.70, 128.95, 123.97, 122.10, 121.64, 117.56, 116.58, 108.91.

Data obtained are in agreement with published data.[1]

N-(*p*-tolyl)benzo[*d*]oxazol-2-amine (3ab)



Prepared from 2-nitrophenol (0.1 mmol) and 4-methylphenyl isothiocyanate (0.2 mmol) under air as described in the general procedure and purified by column chromatography on silica gel (230 – 400 mesh or 37 – 63 μm, hexanes/ethyl acetate 5:1, R_f = 0.50) as a pale-orange solid (18.1 mg, 81%).

^{1}H NMR (600 MHz, DMSO-d_6) δ 10.47 (s, 1H), 7.65 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 7.8 Hz, 1H), 7.44 (d, J = 7.2 Hz, 1H), 7.21 (td, J = 7.6, 1.1 Hz, 1H), 7.18 (d, J = 8.3 Hz, 2H), 7.12 (td, J = 7.7, 1.2 Hz, 1H), 2.28 (s, 3H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 158.10, 147.00, 142.52, 136.20, 130.99, 129.34, 123.92, 121.47, 117.60, 116.45, 108.83, 20.34.

Data obtained are in agreement with published data.[2]

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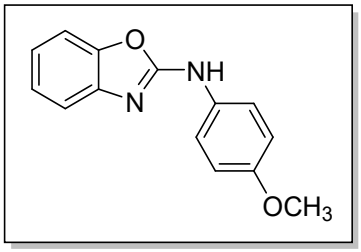
[1] V. K. Yadav, V. P. Srivastava, L. D. S. Yadav, Tetrahedron Lett. 59 (2018) 252.
[2] J. Zhang, L. Chen, Y. Dong, J. Yang, Y. Wu, Org. Biomol. Chem. 2020 (18) 7425.

_N_-(4-methoxyphenyl)benzo[_d_]oxazol-2-amine (3ac)



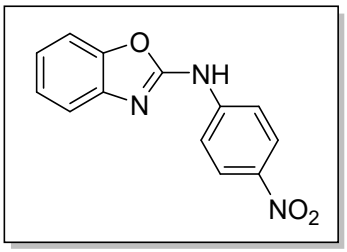
Prepared from 2-nitrophenol (0.1 mmol) and 4-methoxyphenyl isothiocyanate (0.2 mmol) under air as described in the general procedure and purified by column chromatography on silica gel (230 – 400 mesh or 37 – 63 μm, hexanes/ethyl acetate 5:1, R_f = 0.33) as a pale-yellow solid (17.5 mg, 73%).

^{1}H NMR (600 MHz, DMSO-d_6) δ 10.37 (s, 1H), 7.66 (d, J = 9.0 Hz, 2H), 7.45 (d, J = 7.8 Hz, 1H), 7.41 (d, J = 7.3 Hz, 1H), 7.20 (td, J = 7.6, 1.1 Hz, 1H), 7.10 (td, J = 7.7, 1.2 Hz, 1H), 6.97 (d, J = 9.0 Hz, 2H), 3.75 (s, 3H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 158.35, 154.65, 147.07, 142.61, 131.90, 123.87, 121.29, 119.18, 116.30, 114.21, 108.76, 55.23.

Data obtained are in agreement with published data.[2]

_N_-(4-nitrophenyl)benzo[_d_]oxazol-2-amine (3ad)



Prepared from 2-nitrophenol (0.1 mmol) and 4-nitrophenyl isothiocyanate (0.2 mmol) under air as described in the general procedure and purified by column chromatography on silica gel (230 – 400 mesh or 37 – 63 μm, hexanes/ethyl acetate 3:1, R_f = 0.46) as a yellow solid (8.7 mg, 34%).

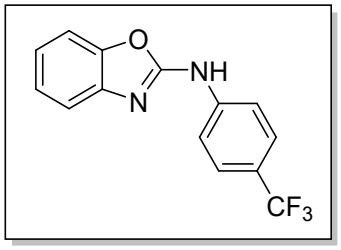
^{1}H NMR (600 MHz, DMSO-d_6) δ 11.42 (s, 1H), 8.30 (d, J = 9.2 Hz, 2H), 7.99 (d, J = 9.2 Hz, 2H), 7.59 – 7.54 (m, 2H), 7.29 (td, J = 7.6, 1.1 Hz, 1H), 7.22 (td, J = 7.7, 1.2 Hz, 1H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 156.83, 146.97, 144.88, 141.62, 141.25, 125.29, 124.32, 122.61, 117.25, 117.11, 109.34.

Data obtained are in agreement with published data.[3]

[3] C. Duangkamol, W. Phakhodee, M. Pattarawarapan, Synthesis 52 (2020) 1981.

***N*-(4-(trifluoromethyl)phenyl)benzo[*d*]oxazol-2-amine (3ae)**



Prepared from 2-nitrophenol (0.1 mmol) and 4-(trifluoromethyl)phenyl isothiocyanate (0.2 mmol) under air as described in the general procedure and purified by column chromatography on silica gel (230 – 400 mesh or 37 – 63 μm, hexanes/ethyl acetate 5:1, R_f = 0.50) as a pale-orange solid (19.7 mg, 71%).

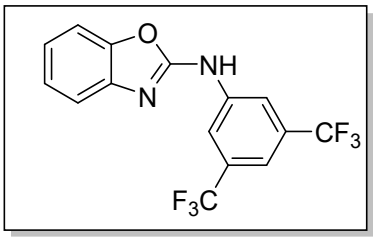
^{1}H NMR (600 MHz, DMSO-d_6) δ 11.06 (s, 1H), 7.97 (d, J = 8.5 Hz, 2H), 7.75 (d, J = 8.6 Hz, 2H), 7.56 – 7.49 (m, 2H), 7.27 (td, J = 7.6, 1.1 Hz, 1H), 7.19 (td, J = 7.7, 1.3 Hz, 1H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 157.36, 146.96, 142.28, 141.96, 126.32 (q, J = 3.8 Hz), 124.53 (q, J = 271 Hz), 124.20, 122.23, 122.07 (q, J = 32.1 Hz), 117.38, 116.99, 109.20.

^{19}F NMR (565 MHz, DMSO-d_6) δ -60.04.

Data obtained are in agreement with published data.[2]

***N*-(3,5-bis(trifluoromethyl)phenyl)benzo[*d*]oxazol-2-amine (3af)**



Prepared from 2-nitrophenol (0.1 mmol) and 3,5-bis(trifluoromethyl)phenyl isothiocyanate (0.2 mmol) under air as described in the general procedure and purified by column chromatography on silica gel (230 – 400 mesh or 37 – 63 μm, hexanes/ethyl acetate 5:1, R_f = 0.44) as a pale-orange solid (13.8 mg, 40%).

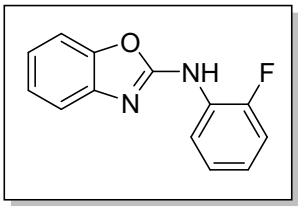
^{1}H NMR (600 MHz, DMSO-d_6) δ 11.35 (s, 1H), 8.42 (s, 2H), 7.70 (s, 1H), 7.59 – 7.53 (m, 2H), 7.28 (td, J = 7.6, 1.2 Hz, 1H), 7.21 (td, J = 7.7, 1.3 Hz, 1H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 156.96, 146.89, 141.56, 140.69, 131.00 (q, J = 32.9 Hz), 124.32, 123.26 (q, J = 273 Hz), 122.56, 122.18, 117.31, 117.10, 114.53, 109.33. Due to complexity, some coupling signals could not be assigned.

^{19}F NMR (565 MHz, DMSO-d_6) δ -61.65.

Data obtained are in agreement with published data.[4]

_N_-(2-fluorophenyl)benzo[_d_]oxazol-2-amine (3ag)



Prepared from 2-nitrophenol (0.1 mmol) and 2-fluorophenyl isothiocyanate (0.2 mmol) under air as described in the general procedure and purified by column chromatography on silica gel (230 – 400 mesh or 37 – 63 μm, hexanes/dichloromethane 1:1, R_f = 0.30) as a pale-yellow solid (17.0 mg, 75%).

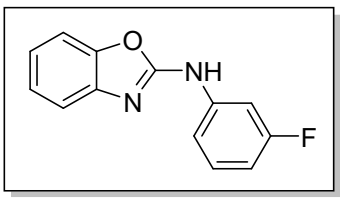
^{1}H NMR (600 MHz, DMSO-d_6) δ 10.36 (s, 1H), 8.23 (dd, J = 9.0, 7.2 Hz, 1H), 7.49 (d, J = 7.9 Hz, 1H), 7.44 (d, J = 7.7 Hz, 1H), 7.30 (ddd, J = 11.4, 8.1, 1.4 Hz, 1H), 7.26 (td, J = 7.6, 1.5 Hz, 1H), 7.23 (td, J = 7.6, 1.2 Hz, 1H), 7.18 – 7.11 (m, 2H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 158.42, 153.02 (d, J = 245.3 Hz), 147.35, 142.09, 126.45, 124.62 (d, J = 3.6 Hz), 124.19 (d, J = 7.2 Hz), 124.06, 122.02, 121.78, 116.67, 115.54 (d, J = 19.0 Hz), 109.07. Some coupling signals could not be located.

^{19}F NMR (565 MHz, DMSO-d_6) δ -125.91 – -125.99 (m).

Data obtained are in agreement with published data.[5]

_N_-(3-fluorophenyl)benzo[_d_]oxazol-2-amine (3ah)



Prepared from 2-nitrophenol (0.1 mmol) and 3-fluorophenyl isothiocyanate (0.2 mmol) under air as described in the general procedure and purified by column chromatography on silica gel (230 – 400 mesh or 37 – 63 μm, hexanes/ethyl acetate 5:1, R_f = 0.54) as a pale-yellow solid (17.2 mg, 75%).

^{1}H NMR (600 MHz, DMSO-d_6) δ 10.86 (s, 1H), 7.78 (dt, J = 11.8, 2.3 Hz, 1H), 7.53 – 7.50 (m, 2H), 7.48 (ddd, J = 8.2, 2.1, 0.9 Hz, 1H), 7.41 (td, J = 8.2, 6.8 Hz, 1H), 7.25 (td, J = 7.6, 1.1 Hz, 1H), 7.17 (td, J = 7.6, 1.2 Hz, 1H), 6.86 (tdd, J = 8.5, 2.6, 0.9 Hz, 1H).

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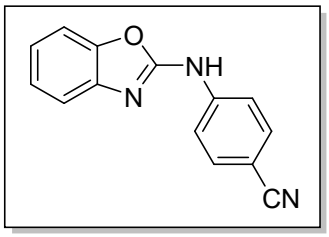
[4] D. T. Tran, T. N. Huynh, P. C. Nguyen, N. T. S. Phan, T. T. Nguyen, Tetrahedron Lett. 122 (2023) 154510.
[5] T. N. T. Huynh, T. Tankam, S. Koguchi, T. Rerkrachaneekorn, M. Sukwattanasinitt, S. Wacharasindhu, Green Chem. 23 (2021) 5189.

^{13}C NMR (126 MHz, DMSO-d_6) δ 162.50 (d, J = 241.2 Hz), 157.54, 146.91, 142.07, 140.49 (d, J = 11.5 Hz), 130.59 (d, J = 9.7 Hz), 124.10, 122.00, 116.87, 113.52 (d, J = 2.6 Hz), 109.08, 108.44 (d, J = 21.1 Hz), 104.31 (d, J = 26.9 Hz).

^{19}F NMR (565 MHz, DMSO-d_6) δ -111.83 – -111.91 (m).

Data obtained are in agreement with published data.[4]

4-(Benzo[*d*]oxazol-2-ylamino)benzonitrile (3ai)



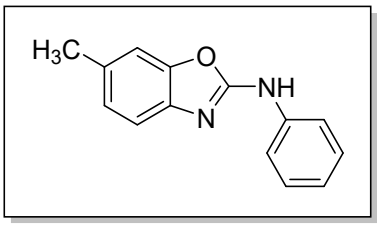
Prepared from 2-nitrophenol (0.1 mmol) and 4-cyanophenyl isothiocyanate (0.2 mmol) under air as described in the general procedure and purified by column chromatography on silica gel (230 – 400 mesh or 37 – 63 μm, hexanes/ethyl acetate = 3:1, R_f = 0.40) as a white solid (14.4 mg, 61%). m.p. 221 – 223 °C.

^{1}H NMR (600 MHz, DMSO-d_6) δ 11.24 (s, 1H), 7.99 (d, J = 8.8 Hz, 2H), 7.89 (d, J = 8.8 Hz, 2H), 7.62 – 7.54 (m, 2H), 7.32 (td, J = 7.6, 1.2 Hz, 1H), 7.25 (td, J = 7.7, 1.3 Hz, 1H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 157.03, 146.95, 142.88, 141.79, 133.46, 124.27, 122.44, 119.23, 117.61, 117.13, 109.28, 103.57.

HRMS (ESI) *m/z* [M+H$^+$] calcd for $C_{14}H_{10}N_3O^+$ 236.0818, found 236.0814.

6-Methyl-*N*-phenylbenzo[*d*]oxazol-2-amine (3ba)



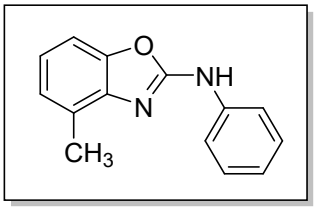
Prepared from 5-methyl-2-nitrophenol (0.1 mmol) and phenyl isothiocyanate (0.2 mmol) under air as described in the general procedure and purified by column chromatography on silica gel (230 – 400 mesh or 37 – 63 μm, hexanes/ethyl acetate 5:1, R_f = 0.50) as an orange solid (18.5 mg, 82%).

^{1}H NMR (600 MHz, DMSO-d_6) δ 10.50 (s, 1H), 7.76 (d, J = 7.5 Hz, 2H), 7.37 (t, J = 7.9 Hz, 2H), 7.33 (d, J = 7.9 Hz, 1H), 7.31 (s, 1H), 7.06 – 6.99 (m, 2H), 2.39 (s, 3H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 157.57, 147.15, 140.04, 138.81, 131.23, 128.93, 124.64, 121.93, 117.40, 116.06, 109.27, 21.02.

Data obtained are in agreement with published data.[2]

4-Methyl-*N*-phenylbenzo[*d*]oxazol-2-amine (3ca)



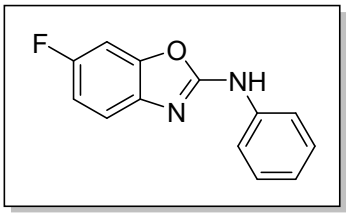
Prepared from 3-methyl-2-nitrophenol (0.1 mmol) and phenyl isothiocyanate (0.2 mmol) under air as described in the general procedure and purified by column chromatography on silica gel (230 – 400 mesh or 37 – 63 μm, hexanes/ethyl acetate 7:1, R_f = 0.50) as an orange solid (16.7 mg, 74%).

^{1}H NMR (600 MHz, DMSO-d_6) δ 10.52 (s, 1H), 7.79 (dd, J = 9.0, 1.2 Hz, 2H), 7.42 – 7.34 (m, 2H), 7.29 (dd, J = 7.8, 1.2 Hz, 1H), 7.08 – 6.97 (m, 3H), 2.48 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 158.90, 146.23, 144.46, 138.27, 128.96, 124.03, 122.47, 119.07, 117.82, 115.86, 110.58.

Data obtained are in agreement with published data.[2]

6-Fluoro-*N*-phenylbenzo[*d*]oxazol-2-amine (3da)



Prepared from 5-fluoro-2-nitrophenol (0.1 mmol) and phenyl isothiocyanate (0.2 mmol) under air as described in the general procedure and purified by column chromatography on silica gel (230 – 400 mesh or 37 – 63 μm, hexanes/ethyl acetate 5:1, R_f = 0.49) as a pale-yellow solid (6.3 mg, 27%).

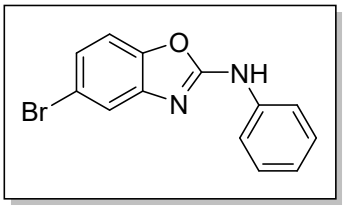
^{1}H NMR (600 MHz, DMSO-d_6) δ 10.62 (s, 1H), 7.74 (dd, J = 8.6, 1.2 Hz, 2H), 7.51 (dd, J = 8.4, 2.5 Hz, 1H), 7.44 (dd, J = 8.6, 4.9 Hz, 1H), 7.39 – 7.36 (m, 2H), 7.08 (ddd, J = 10.1, 8.6, 2.5 Hz, 1H), 7.04 (tt, J = 7.4, 1.2 Hz, 1H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 158.42, 157.77 (d, J = 237 Hz), 146.82 (d, J = 15.0 Hz), 138.77, 138.52, 128.93, 122.16, 117.52, 116.49 (d, J = 9.6 Hz), 110.72 (d, J = 24.0 Hz), 97.85 (d, J = 29.2 Hz).

^{19}F NMR (565 MHz, DMSO-d_6) δ -120.14 (td, J = 9.4, 5.0 Hz).

Data obtained are in agreement with published data.[2]

5-Bromo-*N*-phenylbenzo[*d*]oxazol-2-amine (3ea)



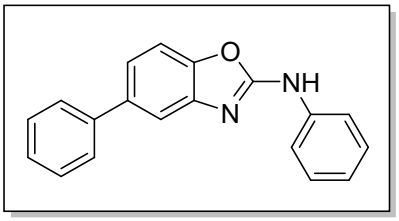
Prepared from 4-bromo-2-nitrophenol (0.1 mmol) and phenyl isothiocyanate (0.2 mmol) under air as described in the general procedure and purified by column chromatography on silica gel (230 – 400 mesh or 37 – 63 µm, hexanes/ethyl acetate 7:1, R_f = 0.40) as a pale-orange solid (21.7 mg, 75%).

^{1}H NMR (600 MHz, DMSO-d_6) δ 10.76 (s, 1H), 7.74 (dd, *J* = 8.7, 1.1 Hz, 2H), 7.64 (d, *J* = 2.0 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.43 – 7.36 (m, 2H), 7.28 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.06 (tt, *J* = 7.3, 1.2 Hz, 1H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 158.90, 146.23, 144.46, 138.27, 128.96, 124.03, 122.47, 119.07, 117.82, 115.86, 110.58.

Data obtained are in agreement with published data.[6]

***N*,5-diphenylbenzo[*d*]oxazol-2-amine (3fa)**



Prepared from 4-phenyl-2-nitrophenol (0.1 mmol) and phenyl isothiocyanate (0.2 mmol) under air as described in the general procedure and purified by column chromatography on silica gel (230 – 400 mesh or 37 – 63 µm, hexanes/ethyl acetate 5:1, R_f = 0.51) as a pale-orange solid (17.5 mg, 61%).

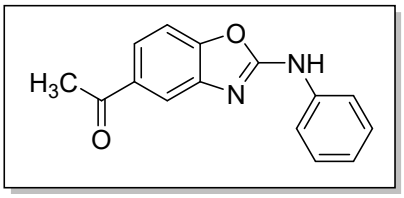
^{1}H NMR (600 MHz, DMSO-d_6) δ 10.66 (s, 1H), 7.79 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.72 (d, *J* = 1.8 Hz, 1H), 7.69 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.56 (d, *J* = 8.3 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.44 – 7.36 (m, 3H), 7.39 – 7.33 (m, 1H), 7.06 (tt, *J* = 7.3, 1.2 Hz, 1H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 158.44, 146.68, 143.22, 140.51, 138.61, 136.77, 128.96, 128.85, 127.02, 126.89, 122.19, 120.61, 117.62, 114.76, 109.07.

Data obtained are in agreement with published data.[4]

[6] Y. Murata, N. Matsumoto, M. Miyata, Y. Kitamura, N. Kakusawa, M. Matsumura, S. Yasuike, J. Organometallic Chem. 859 (2018) 18.

1-(2-(Phenylamino)benzo[*d*]oxazol-5-yl)ethan-1-one (3ga)



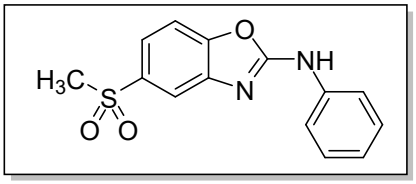
Prepared from 4'-hydroxy-3'-nitroacetophenone (0.1 mmol) and phenyl isothiocyanate (0.2 mmol) under air as described in the general procedure and purified by column chromatography on silica gel (230 – 400 mesh or 37 – 63 μm, hexanes/ethyl acetate 2:1, R_f = 0.55) as a pale-orange solid (14.6 mg, 58%). m.p. 207 – 208 °C.

^{1}H NMR (600 MHz, DMSO-d_6) δ 10.79 (s, 1H), 8.04 (d, J = 1.3 Hz, 1H), 7.80 (dd, J = 8.4, 1.7 Hz, 1H), 7.77 (dd, J = 8.7, 1.1 Hz, 2H), 7.60 (d, J = 8.3 Hz, 1H), 7.43 – 7.37 (m, 2H), 7.07 (tt, J = 7.4, 1.1 Hz, 1H), 2.63 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 197.10, 158.86, 150.23, 142.80, 138.33, 133.58, 128.97, 122.78, 122.45, 117.77, 116.60, 108.82, 26.81.

HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{15}H_{13}N_2O_2^+$ 253.0972, found: 253.0973.

5-(Methylsulfonyl)-*N*-phenylbenzo[*d*]oxazol-2-amine (3ha)



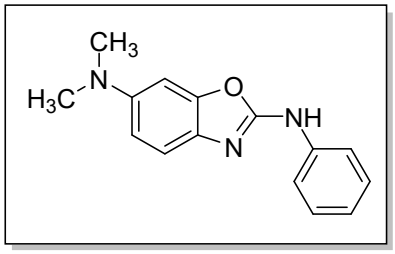
Prepared from 4-methylsulfonyl-2-nitrophenol (0.1 mmol) and phenyl isothiocyanate (0.2 mmol) under air as described in the general procedure and purified by column chromatography on silica gel (230 – 400 mesh or 37 – 63 μm, hexanes/ethyl acetate 2:1, R_f = 0.20) as a brown solid (19.0 mg, 66%). m.p. 241 – 242 °C.

^{1}H NMR (600 MHz, DMSO-d_6) δ 10.92 (s, 1H), 7.96 (d, J = 1.8 Hz, 1H), 7.79 – 7.73 (m, 3H), 7.72 (dd, J = 8.3, 1.8 Hz, 1H), 7.45 – 7.38 (m, 2H), 7.09 (tt, J = 7.4, 1.1 Hz, 1H), 3.25 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 159.55, 150.13, 143.18, 138.09, 136.92, 129.03, 122.74, 121.05, 117.97, 115.12, 109.48, 43.88.

HRMS (ESI) *m/z* $[M+H^+]$ calcd for $C_{14}H_{13}N_2O_3S^+$ 289.0641, found 289.0627.

N^6,N^6-dimethyl-N^2-phenylbenzo[*d*]oxazole-2,6-diamine (3ia)



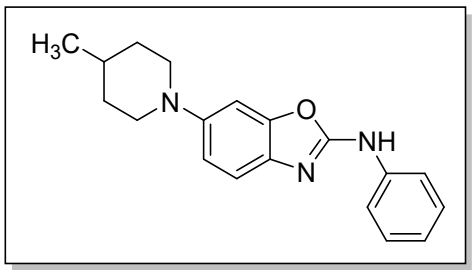
Prepared from 5-(dimethylamino)-2-nitrophenol (0.1 mmol) and phenyl isothiocyanate (0.2 mmol) under air as described in the general procedure and purified by column chromatography on silica gel (230 – 400 mesh or 37 – 63 μm, hexanes/ethyl acetate 3:1, R_f = 0.38) as an orange solid (12.2 mg, 48%). m.p. 143 – 145 °C.

^{1}H NMR (600 MHz, DMSO-d_6) δ 10.32 (s, 1H), 7.73 (dd, *J* = 7.8, 1.0 Hz, 2H), 7.38 – 7.31 (m, 2H), 7.26 (d, *J* = 8.6 Hz, 1H), 6.99 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.90 (d, *J* = 2.3 Hz, 1H), 6.65 (dd, *J* = 8.6, 2.4 Hz, 1H), 2.90 (s, 6H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 156.24, 148.32, 147.31, 139.07, 132.86, 128.84, 121.48, 117.06, 116.34, 109.36, 94.33, 41.13.

HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{15}H_{16}N_3O^+$ 254.1288, found: 254.1294.

6-(4-Methylpiperidin-1-yl)-*N*-phenylbenzo[*d*]oxazol-2-amine (3ja)



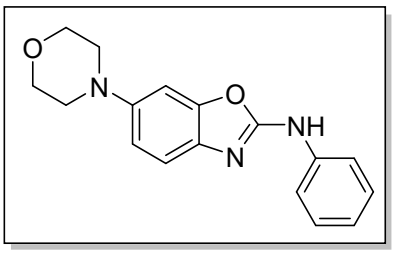
Prepared from 5-(4-methylpiperidin-1-yl)-2-nitrophenol (0.1 mmol) and phenyl isothiocyanate (0.2 mmol) under air as described in the general procedure and purified by column chromatography on silica gel (230 – 400 mesh or 37 – 63 μm, hexanes/ethyl acetate 4:1, R_f = 0.40) as a brown solid (20.0 mg, 65%). m.p. 153 – 155 °C.

^{1}H NMR (600 MHz, DMSO-d_6) δ 10.38 (s, 1H), 7.73 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.35 (dd, *J* = 8.6, 7.3 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 1H), 7.09 (d, *J* = 2.3 Hz, 1H), 7.00 (tt, *J* = 7.3, 1.2 Hz, 1H), 6.83 (dd, *J* = 8.6, 2.3 Hz, 1H), 3.61 – 3.54 (m, 2H), 2.67 – 2.59 (m, 2H), 1.73 – 1.66 (m, 2H), 1.53 – 1.42 (m, 1H), 1.32 – 1.22 (m, 2H), 0.94 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 156.85, 148.08, 147.96, 138.99, 134.77, 128.88, 121.62, 117.16, 116.20, 113.21, 98.06, 50.44, 33.76, 30.09, 21.74.

HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{19}H_{22}N_3O^+$ 308.1758, found: 308.1762.

6-Morpholino-*N*-phenylbenzo[*d*]oxazol-2-amine (3ka)



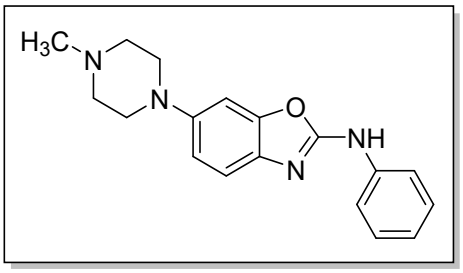
Prepared from 5-morpholino-2-nitrophenol (0.1 mmol) and phenyl isothiocyanate (0.2 mmol) under air as described in the general procedure and purified by column chromatography on silica gel (230 – 400 mesh or 37 – 63 μm, hexanes/ethyl acetate 3:1, R_f = 0.17) as a white solid (16.5 mg, 56%). m.p. 181 – 183 °C.

^{1}H NMR (600 MHz, DMSO-d_6) δ 10.41 (s, 1H), 7.74 (dd, *J* = 8.7, 1.1 Hz, 2H), 7.37 – 7.33 (m, 2H), 7.30 (d, *J* = 8.5 Hz, 1H), 7.14 (d, *J* = 2.3 Hz, 1H), 7.00 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.85 (dd, *J* = 8.6, 2.3 Hz, 1H), 3.78 – 3.73 (m, 4H), 3.11 – 3.07 (m, 4H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 156.99, 147.98, 147.51, 138.92, 135.26, 128.87, 121.68, 117.20, 116.27, 112.24, 97.42, 66.14, 49.84.

HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{18}N_3O_2^+$ 296.1394, found: 296.1396.

6-(4-Methylpiperazin-1-yl)-*N*-phenylbenzo[*d*]oxazol-2-amine (3la)



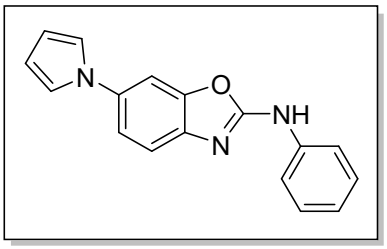
Prepared from 5-(4-methylpiperazin-1-yl)-2-nitrophenol (0.1 mmol) and phenyl isothiocyanate (0.2 mmol) under air as described in the general procedure and purified by column chromatography on silica gel (230 – 400 mesh or 37 – 63 μm, ethyl acetate/methanol 4:1, R_f = 0.23) as a dark-brown solid (18.6 mg, 60%). m.p. 173 – 175 °C.

^{1}H NMR (600 MHz, DMSO-d_6) δ 10.40 (s, 1H), 7.76 – 7.71 (m, 2H), 7.38 – 7.32 (m, 2H), 7.28 (d, *J* = 8.6 Hz, 1H), 7.12 (d, *J* = 2.3 Hz, 1H), 7.00 (tt, *J* = 7.3, 1.2 Hz, 1H), 6.84 (dd, *J* = 8.6, 2.4 Hz, 1H), 3.14 – 3.10 (m, 4H), 2.52 – 2.49 (m, 4H, overlapped), 2.25 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 156.90, 147.95, 147.43, 138.94, 134.99, 128.85, 121.63, 117.16, 116.21, 112.52, 97.60, 54.60, 49.36, 45.55.

HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{18}H_{21}N_4O^+$ 309.1710, found: 309.1716.

_N_-phenyl-6-(1_H_-pyrrol-1-yl)benzo[_d_]oxazol-2-amine (3ma)



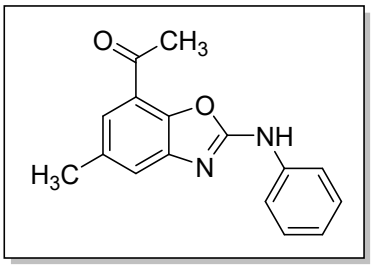
Prepared from 2-nitro-5-(1*H*-pyrrol-1-yl)phenol (0.1 mmol) and phenyl isothiocyanate (0.2 mmol) under air as described in the general procedure and purified by column chromatography on silica gel (230 – 400 mesh or 37 – 63 μm, hexanes/ethyl acetate 5:1, R_f = 0.42) as a pale-yellow solid (14.0 mg, 51%). m.p. 201 – 203 °C.

^{1}H NMR (600 MHz, DMSO-d_6) δ 10.67 (s, 1H), 7.79 (d, J = 2.2 Hz, 1H), 7.77 (dd, J = 8.4, 1.2 Hz, 2H), 7.49 (d, J = 8.4 Hz, 1H), 7.43 (dd, J = 8.4, 2.2 Hz, 1H), 7.42 – 7.36 (m, 2H), 7.36 (t, J = 2.2 Hz, 2H), 7.05 (tt, J = 7.4, 1.2 Hz, 1H), 6.26 (t, J = 2.2 Hz, 2H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 158.31, 147.53, 139.99, 138.56, 135.01, 128.97, 122.19, 119.51, 117.57, 116.67, 115.86, 110.11, 101.56.

HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{17}H_{14}N_3O^+$ 276.1132, found: 276.1134.

1-(5-Methyl-2-(phenylamino)benzo[_d_]oxazol-7-yl)ethan-1-one (3na)



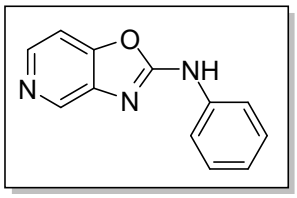
Prepared from 2'-hydroxy-5'-methyl-3'-nitroacetophenone (0.1 mmol) and phenyl isothiocyanate (0.2 mmol) under air as described in the general procedure and purified by column chromatography on silica gel (230 – 400 mesh or 37 – 63 μm, hexanes/ethyl acetate 3:1, R_f = 0.38) as a pale-yellow solid (5.6 mg, 21%). m.p. 212 – 214 °C.

^{1}H NMR (600 MHz, DMSO-d_6) δ 10.81 (s, 1H), 7.78 (dd, J = 8.7, 1.1 Hz, 2H), 7.51 (d, J = 2.5 Hz, 1H), 7.43 (d, J = 2.6 Hz, 1H), 7.40 – 7.37 (m, 2H), 7.05 (tt, J = 7.3, 1.1 Hz, 1H), 2.72 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 194.90, 158.54, 144.12, 144.04, 138.49, 133.22, 128.94, 122.27, 121.92, 121.62, 119.59, 117.65, 29.46, 20.82.

HRMS (ESI) *m/z* $[M+H]^+$ calcd for $C_{16}H_{15}N_2O_2^+$ 267.1128, found: 267.1130.

***N*-phenyloxazolo[4,5-*c*]pyridin-2-amine (3oa)**



Prepared from 3-nitropyridin-4-ol (0.1 mmol) and phenyl isothiocyanate (0.2 mmol) under air as described in the general procedure and purified by column chromatography on silica gel (230 – 400 mesh or 37 – 63 μm, hexane/ethyl acetate = 1:2, R_f = 0.46) as a pale-orange solid (13.9 mg, 66%). A 10 mol% unknown impurity was also obtained.

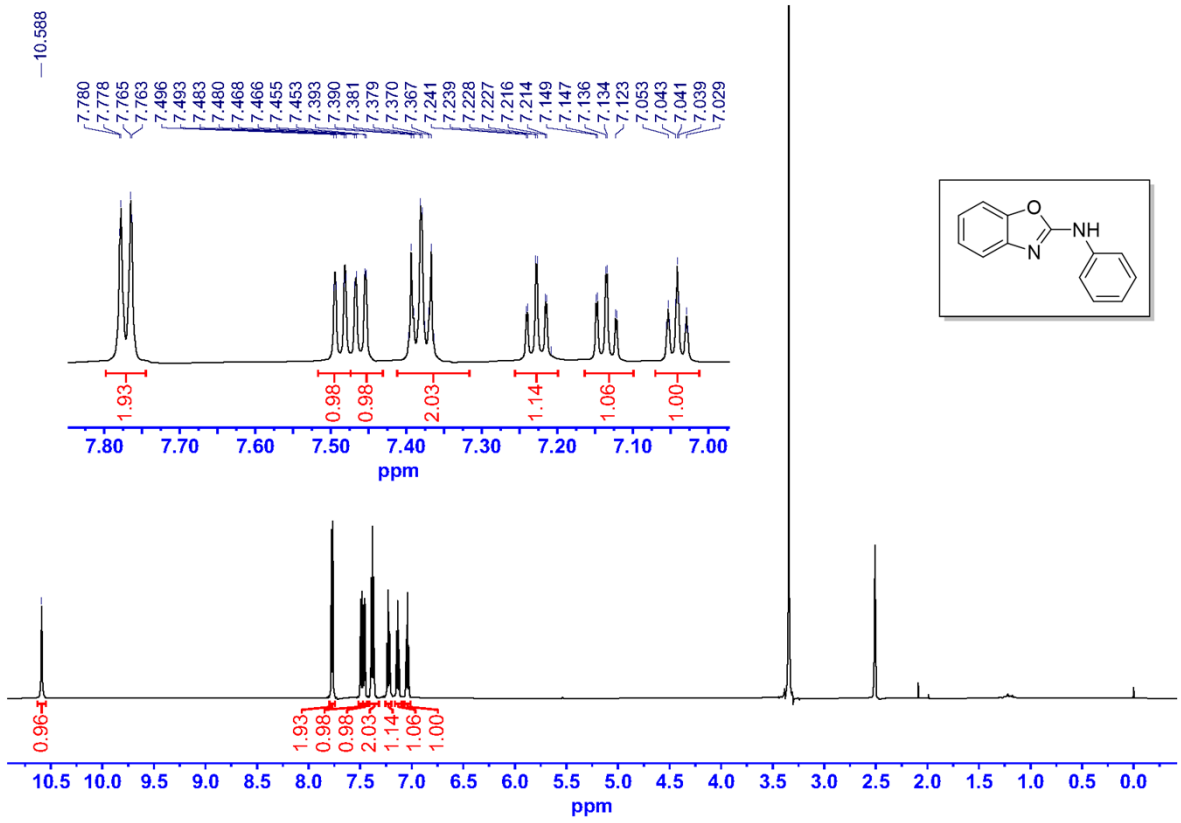
^{1}H NMR (600 MHz, DMSO-d_6) δ 10.90 (s, 1H), 8.72 (s, 1H), 8.35 (d, J = 5.3 Hz, 1H), 7.77 (d, J = 7.4 Hz, 2H), 7.60 (d, J = 5.3 Hz, 1H), 7.48 – 7.36 (m, 2H), 7.08 (tt, J = 7.2, 1.2 Hz, 1H).

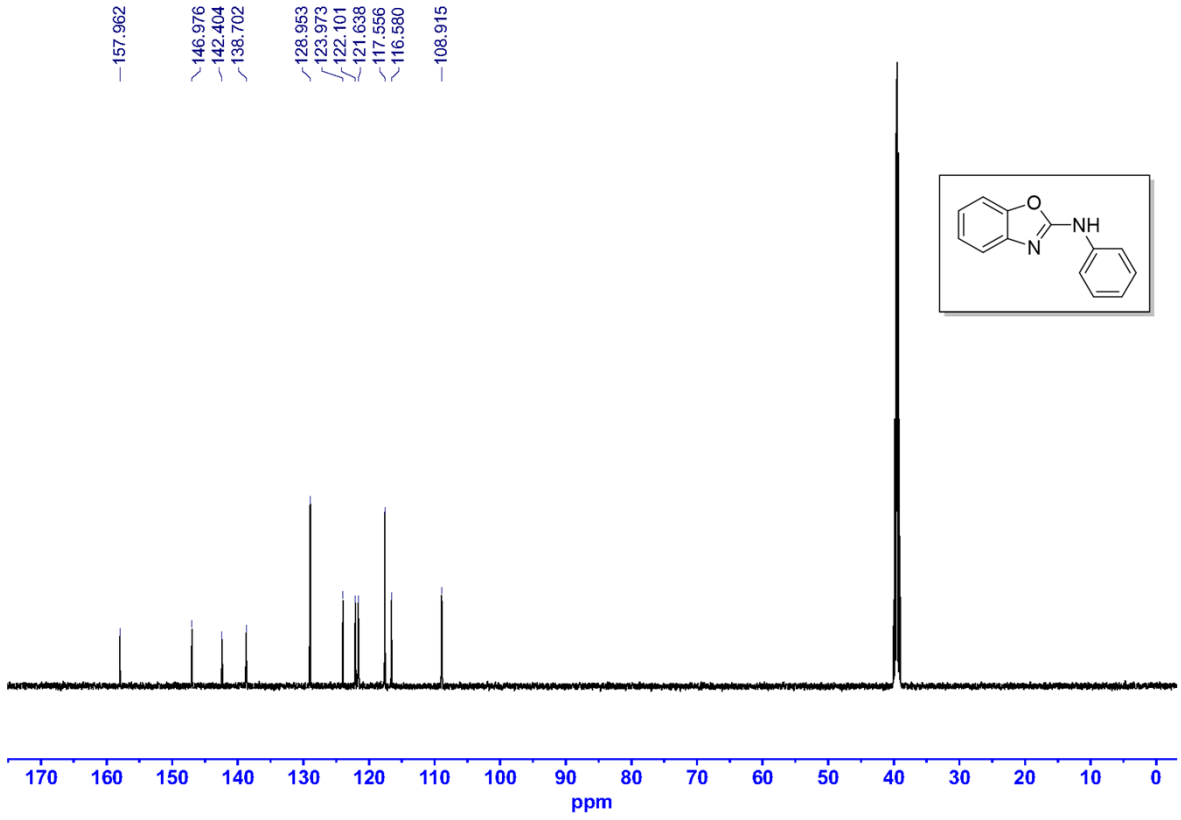
^{13}C NMR (151 MHz, DMSO-d_6) δ 158.17, 152.45, 142.89, 140.17, 138.19, 138.01, 129.04, 122.70, 117.93, 105.22.

Data obtained are in agreement with published data.[4]

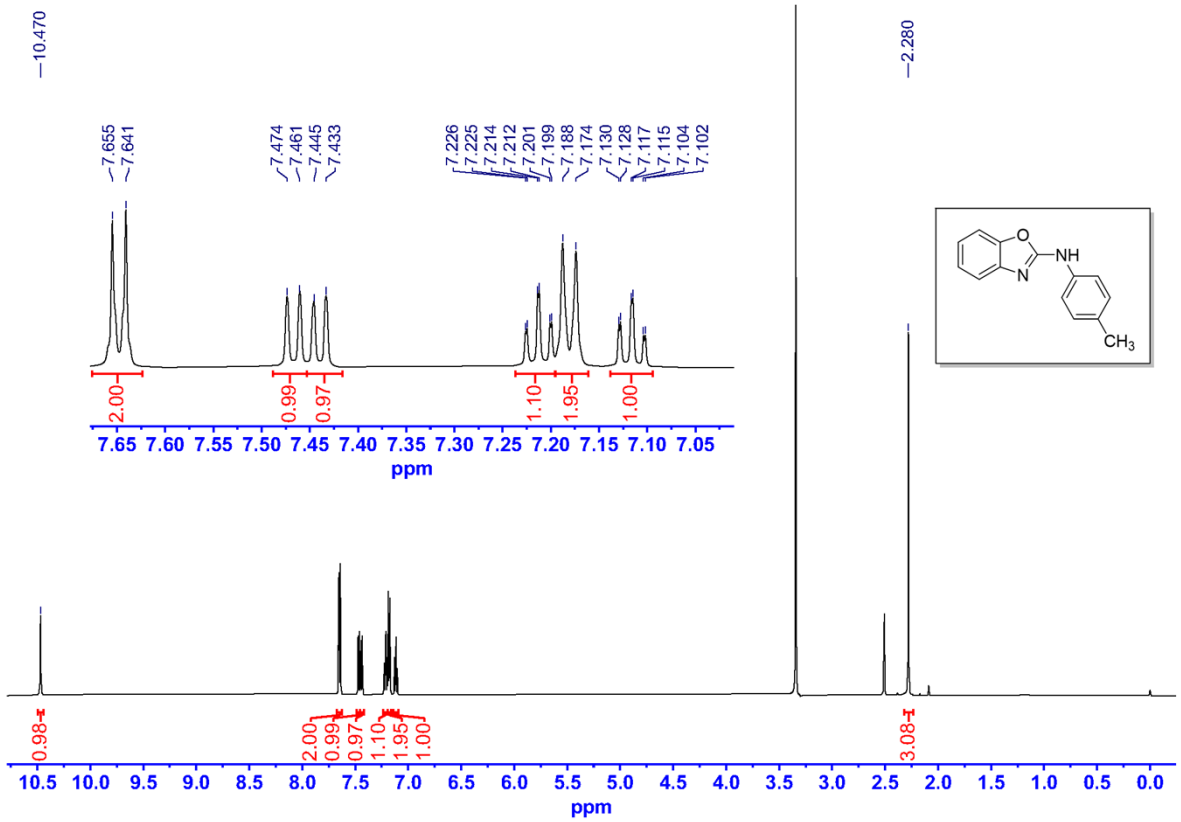
4. NMR Spectra

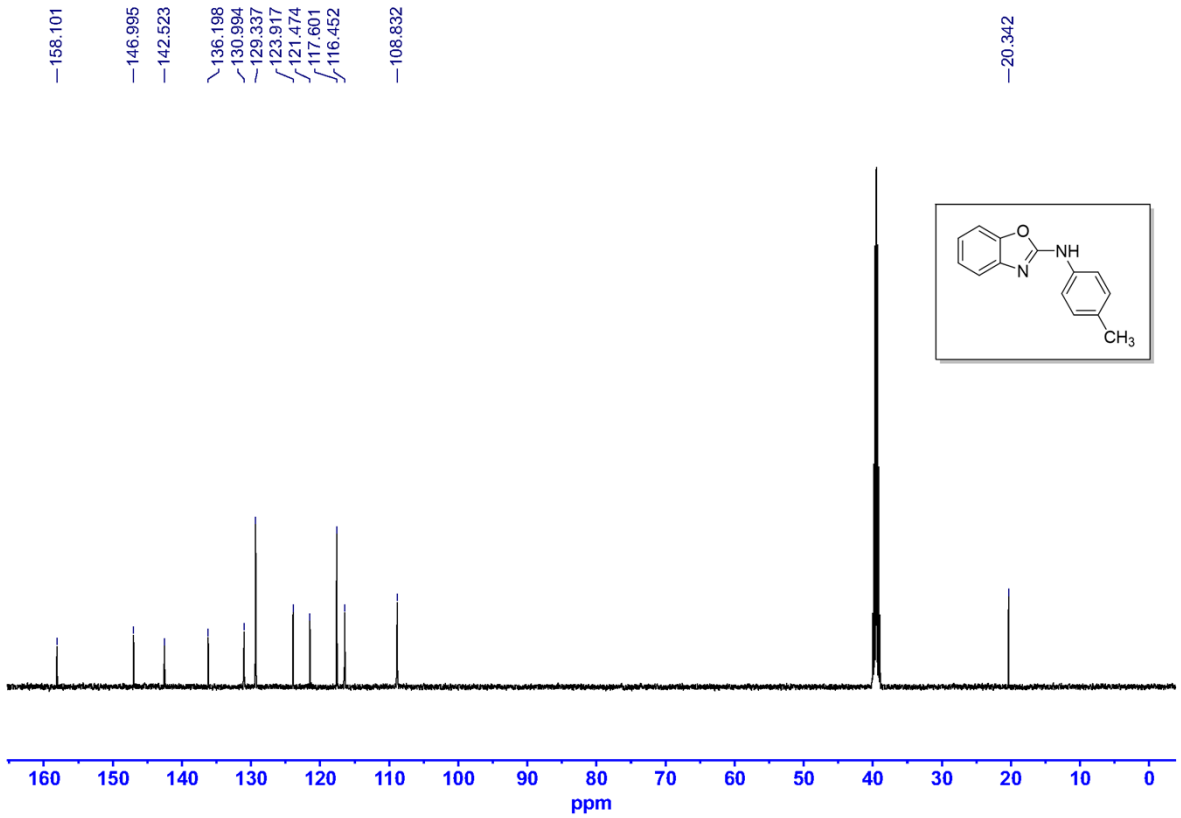
N-phenylbenzo[*d*]oxazol-2-amine (3aa)



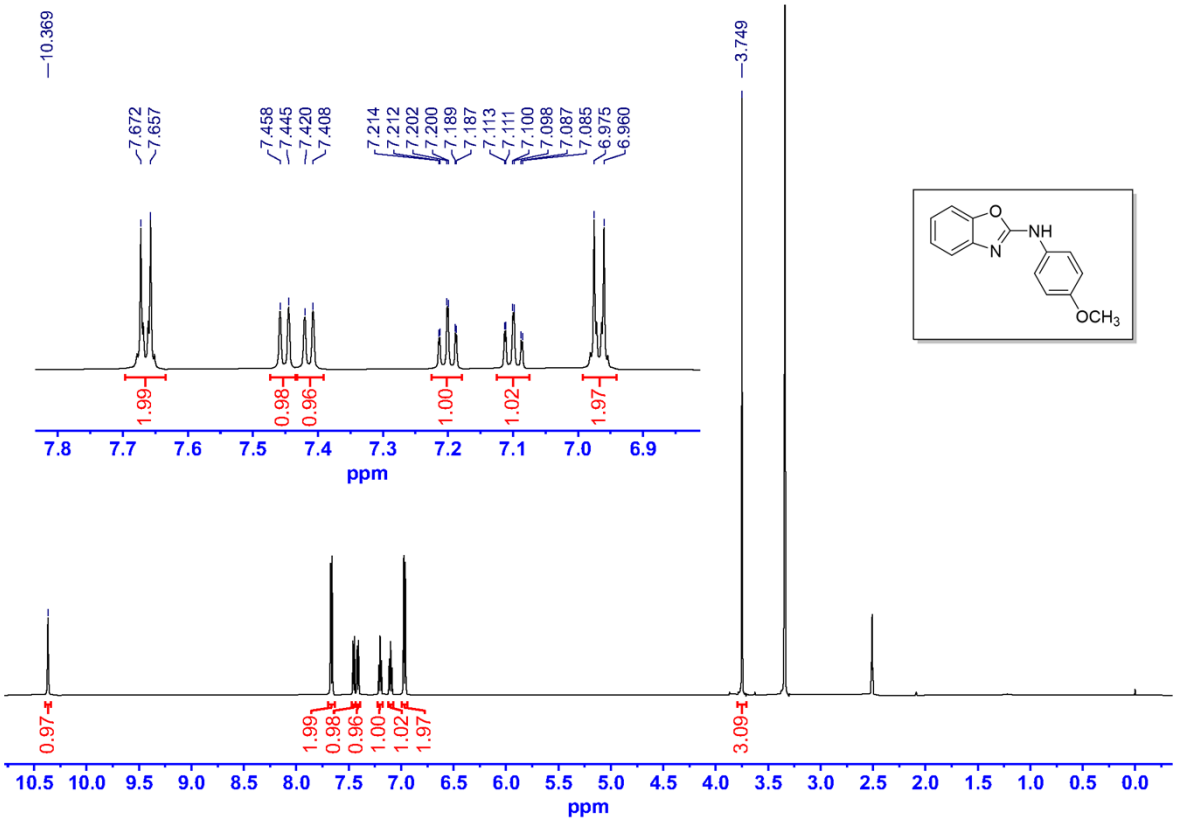


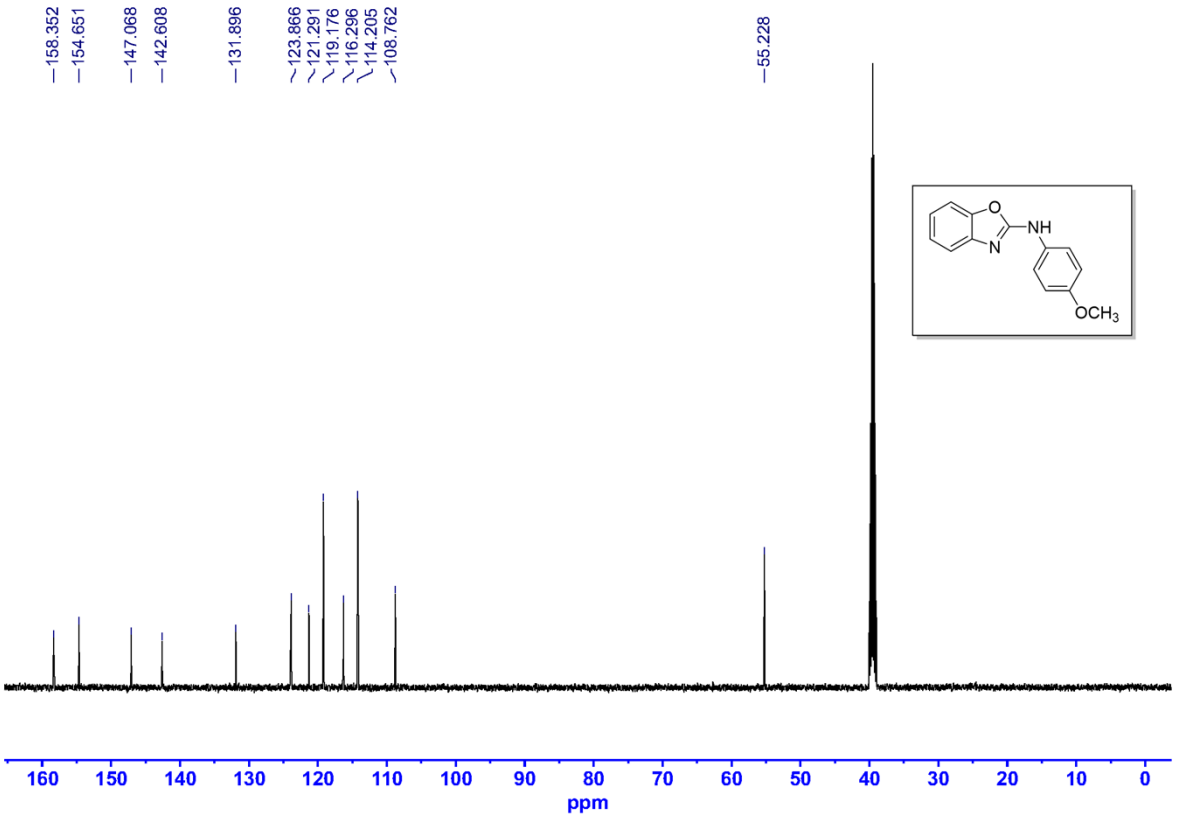
N-(*p*-tolyl)benzo[*d*]oxazol-2-amine (3ab)



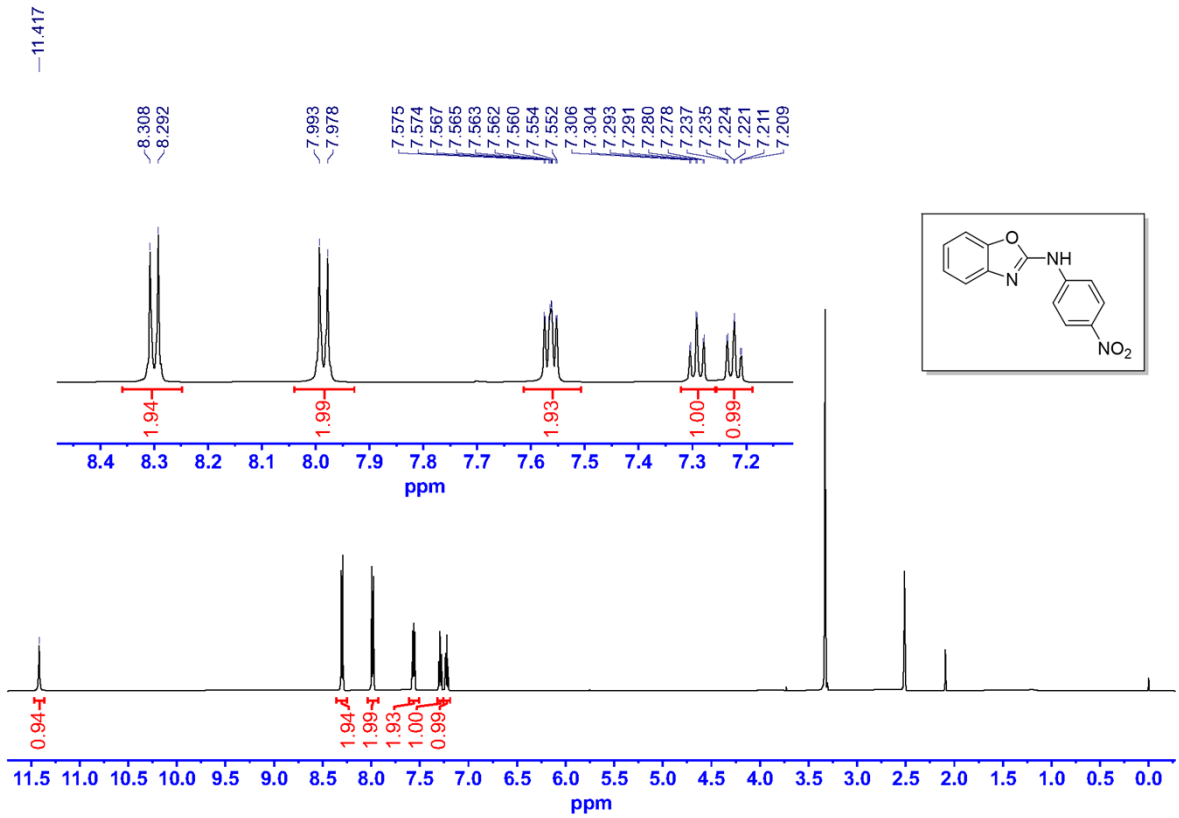


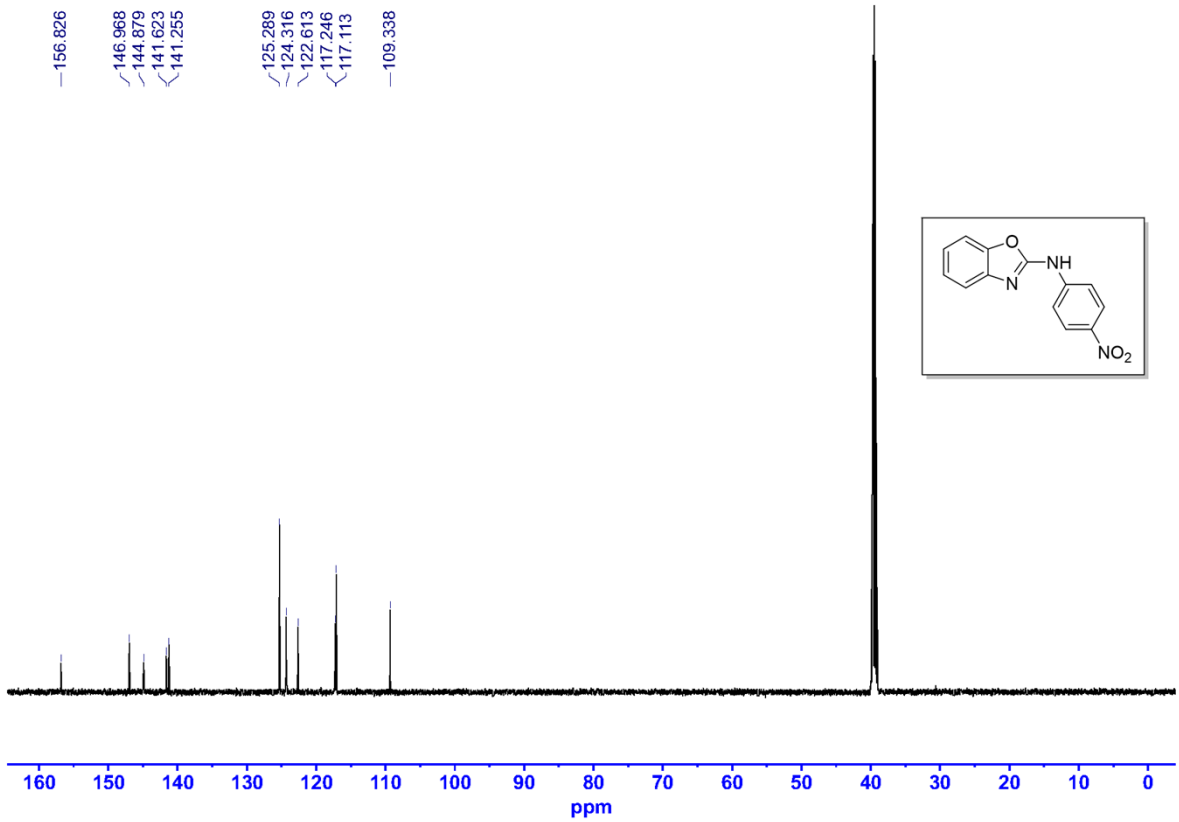
N-(4-methoxyphenyl)benzo[*d*]oxazol-2-amine (3ac)



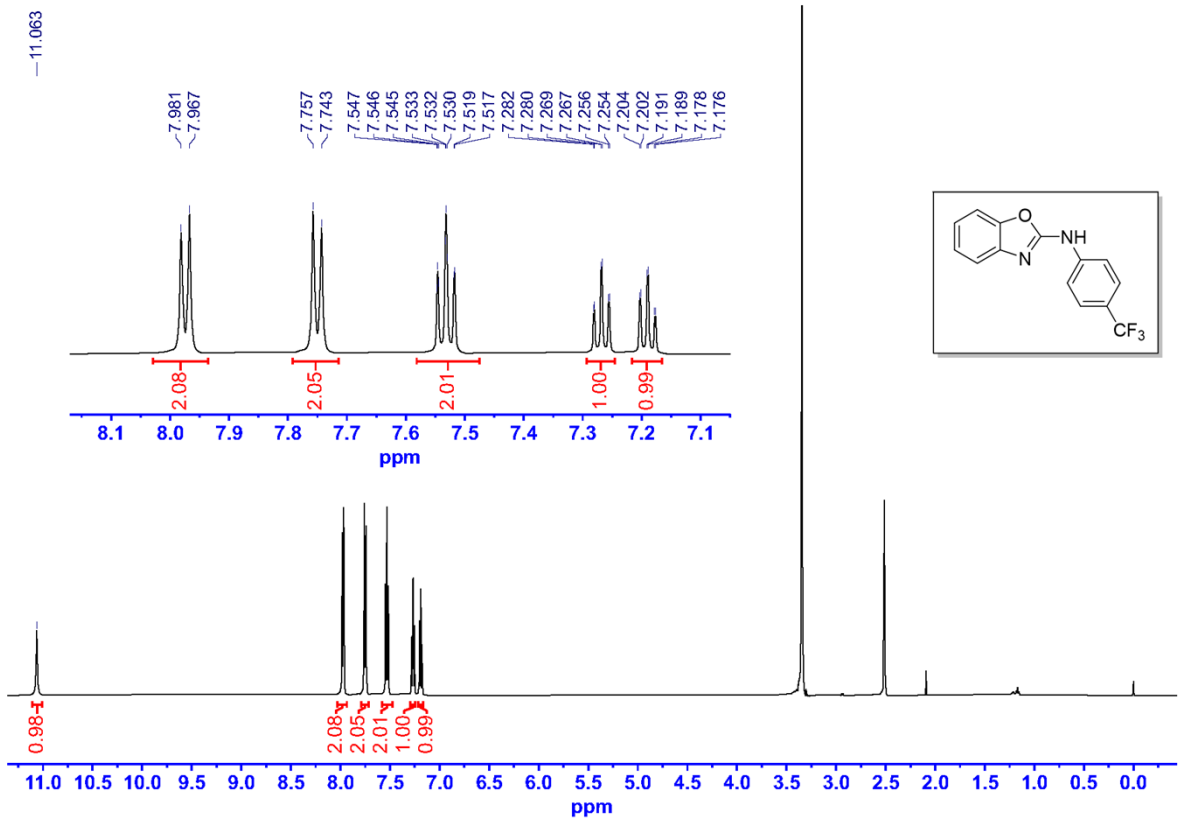


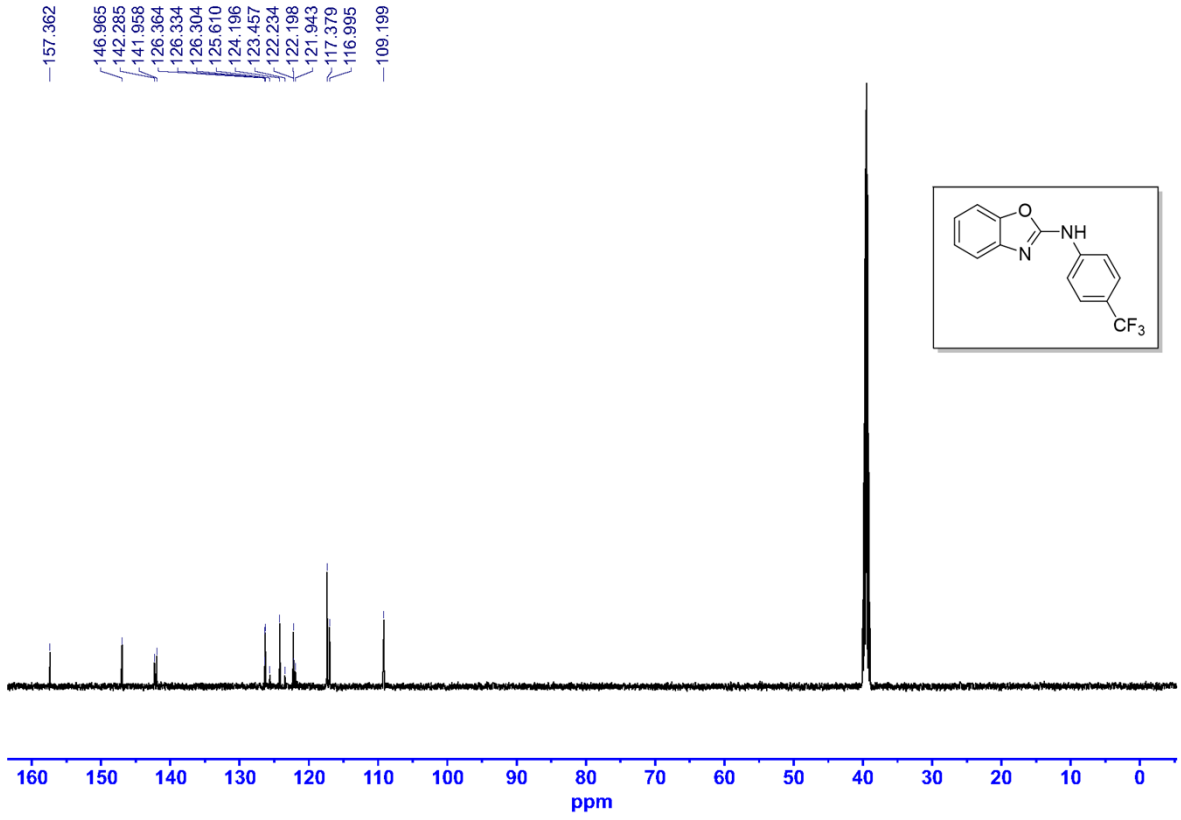
N-(4-nitrophenyl)benzo[*d*]oxazol-2-amine (3ad)

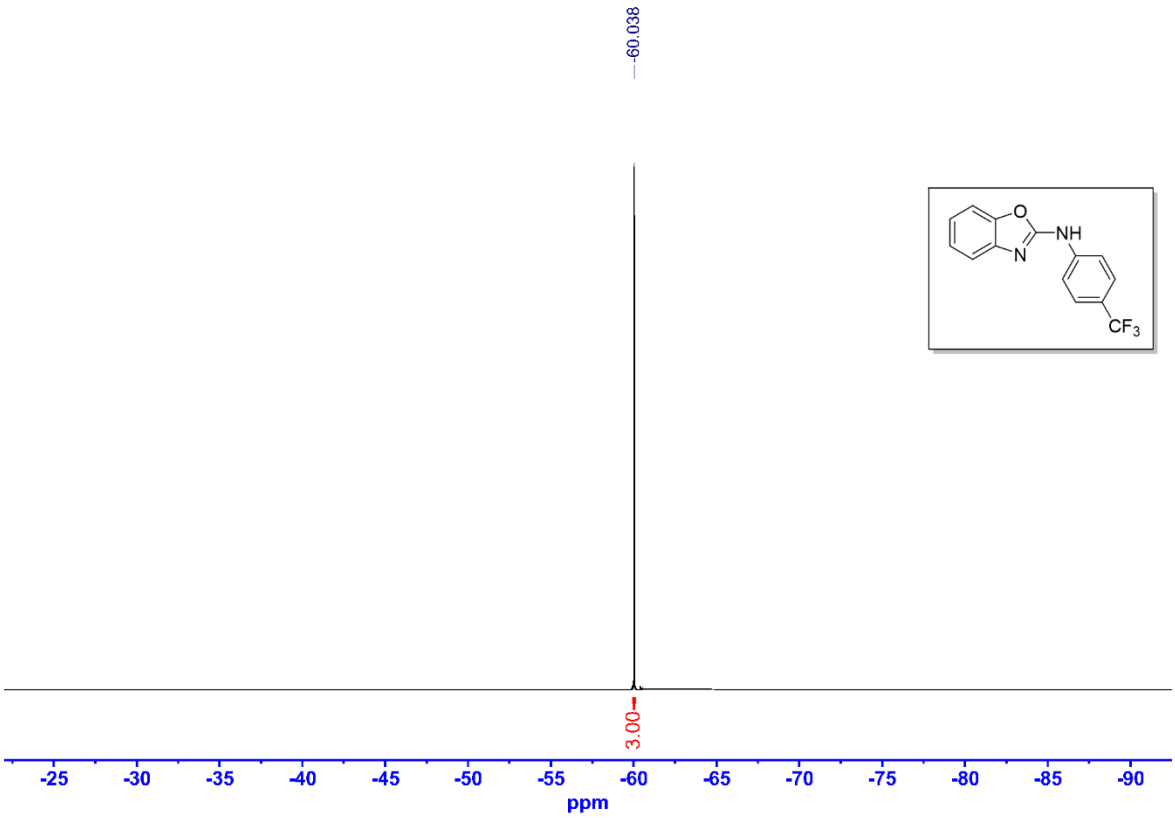




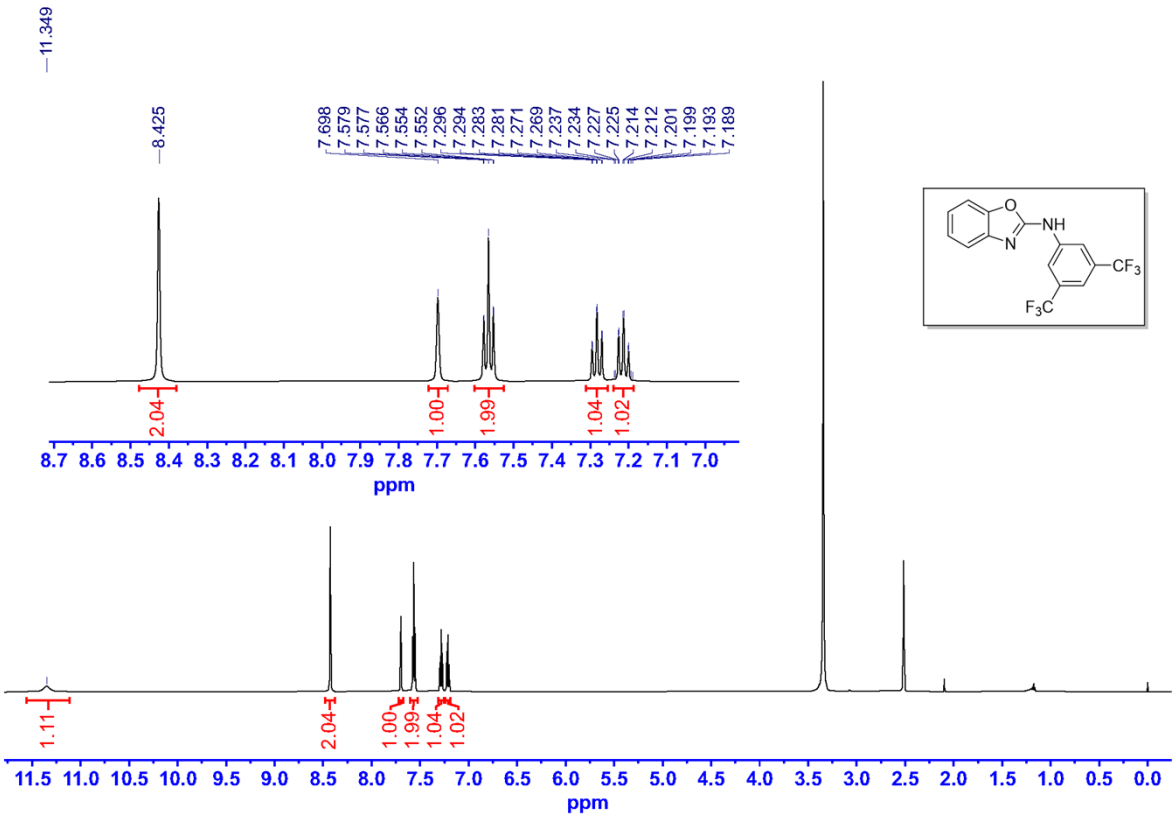
N-(4-(trifluoromethyl)phenyl)benzo[*d*]oxazol-2-amine (3ae)

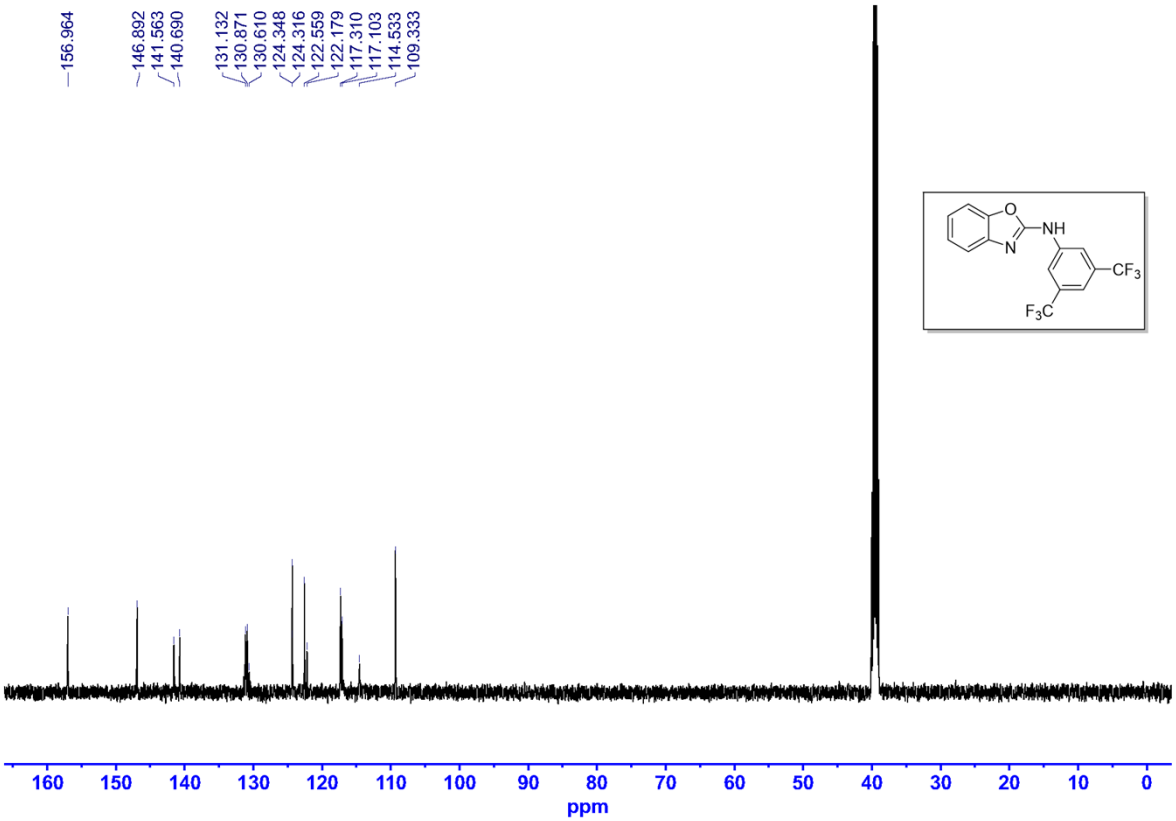


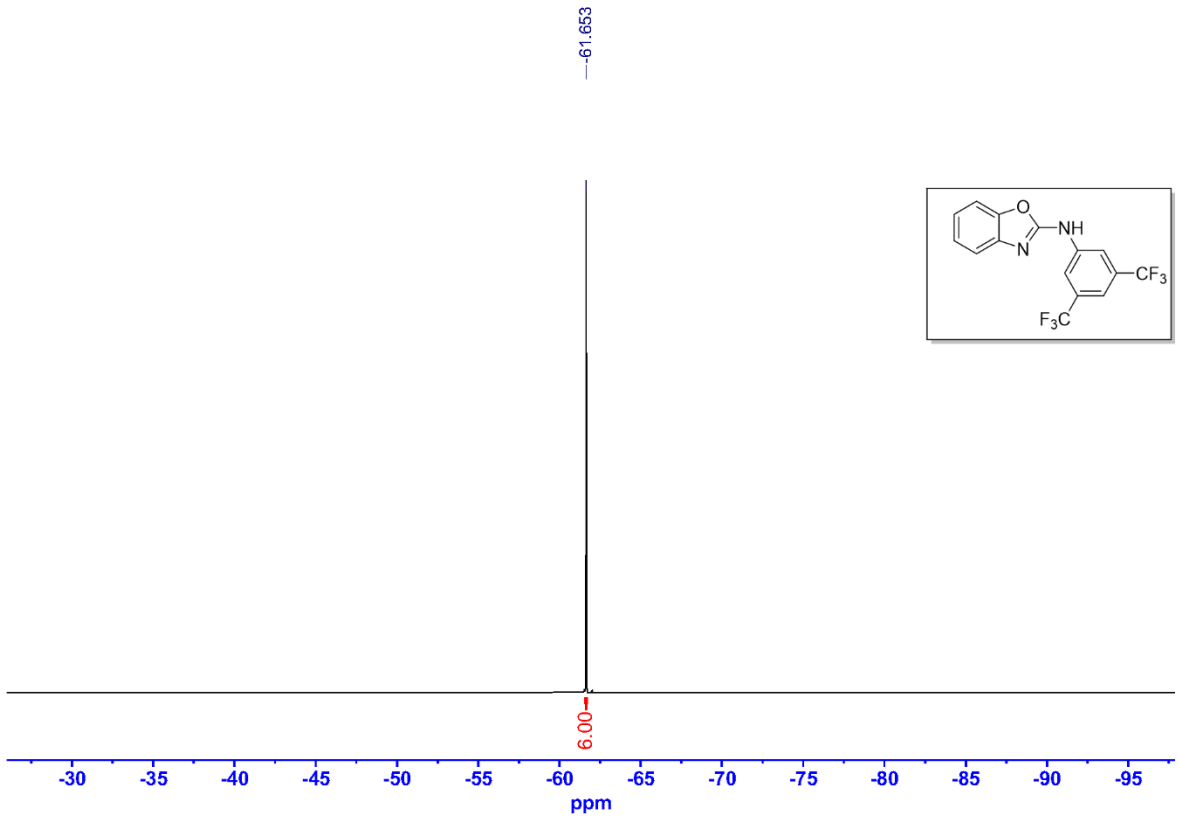



-60.038
O
NH
N
CF3
3.00
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
ppm

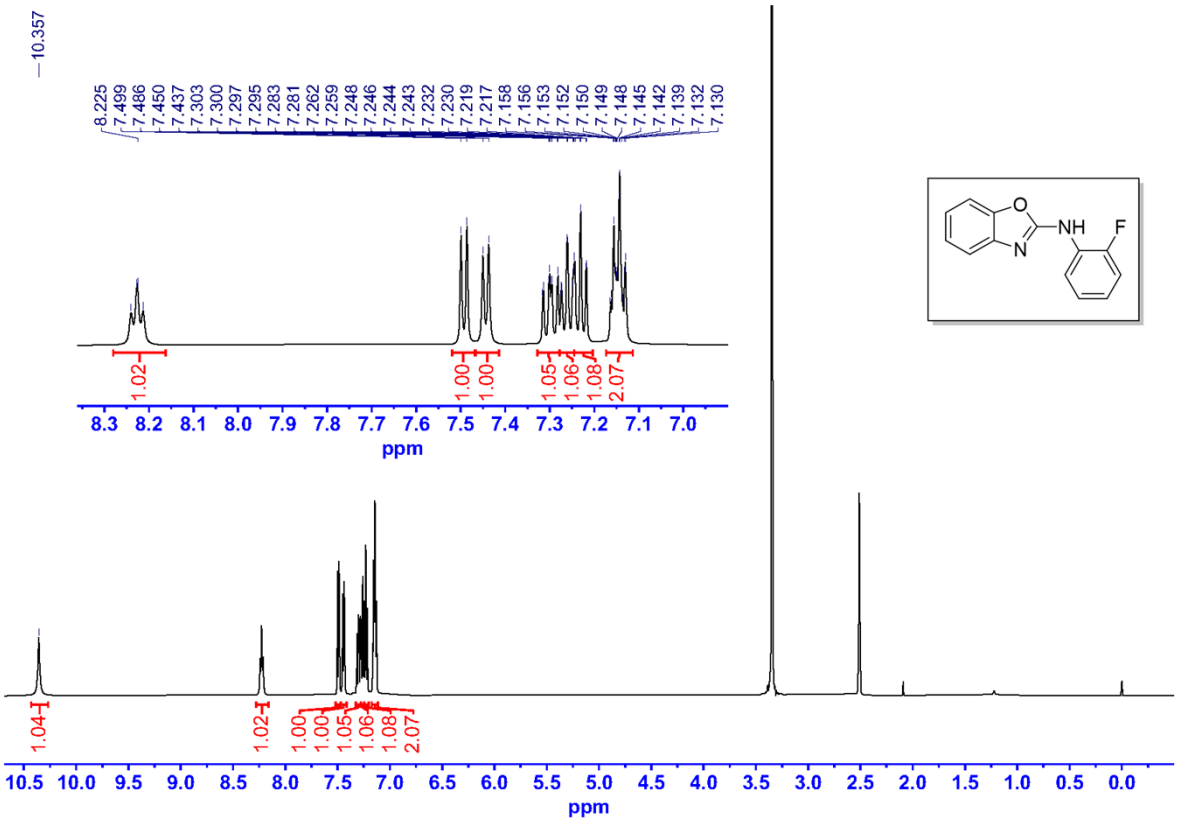
N-(3,5-bis(trifluoromethyl)phenyl)benzo[*d*]oxazol-2-amine (3af)

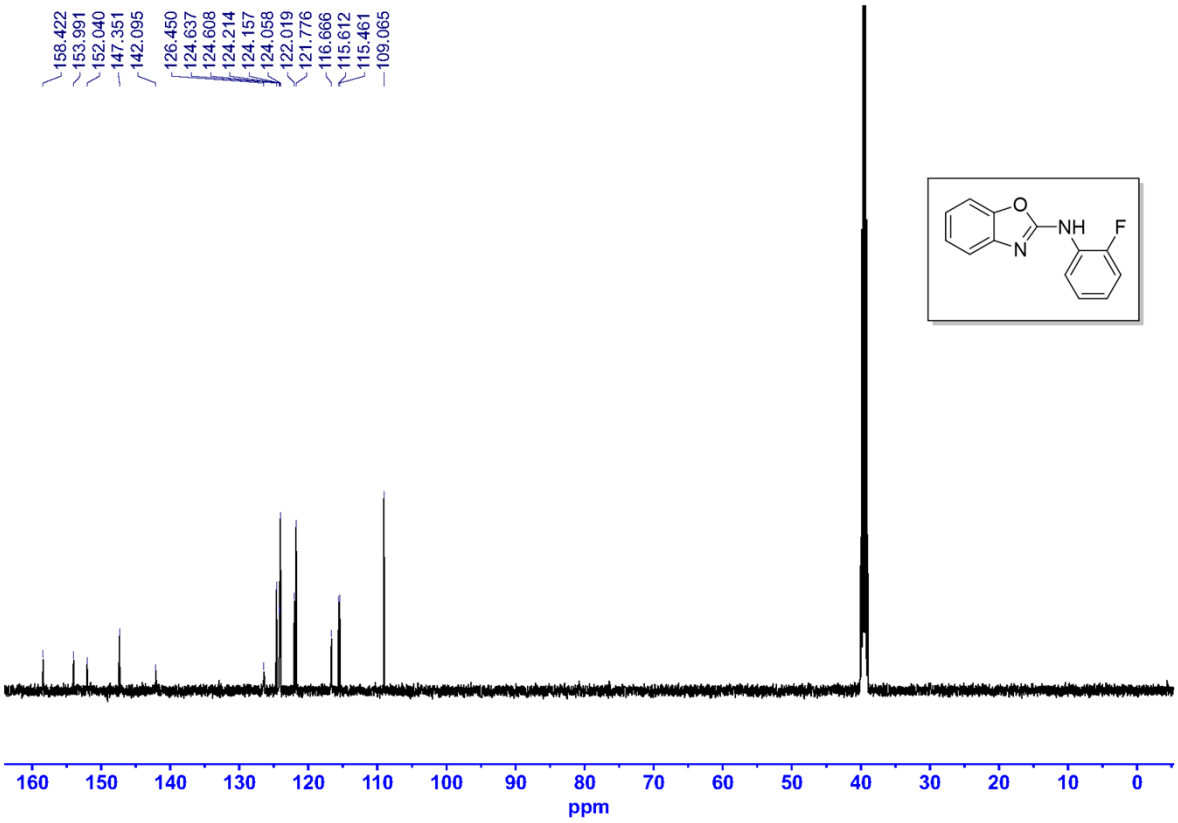


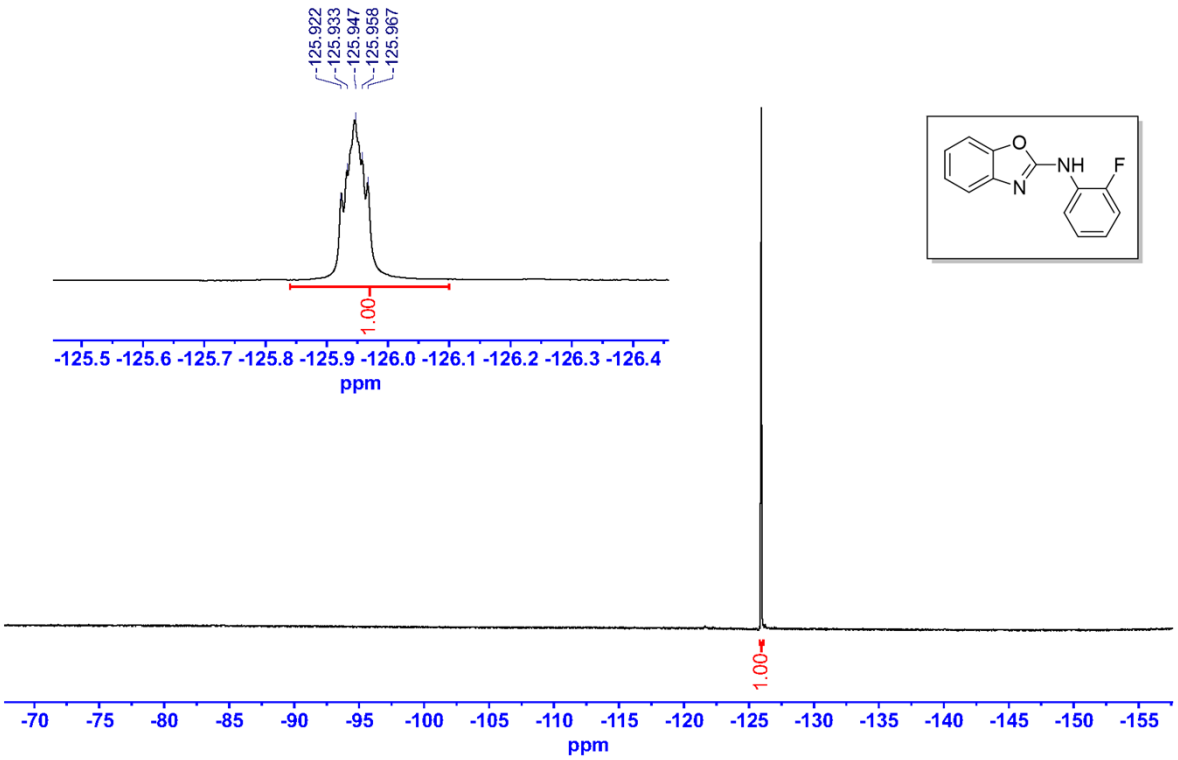



-61.653
O
N
NH
CF3
F3C
6.00
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
ppm

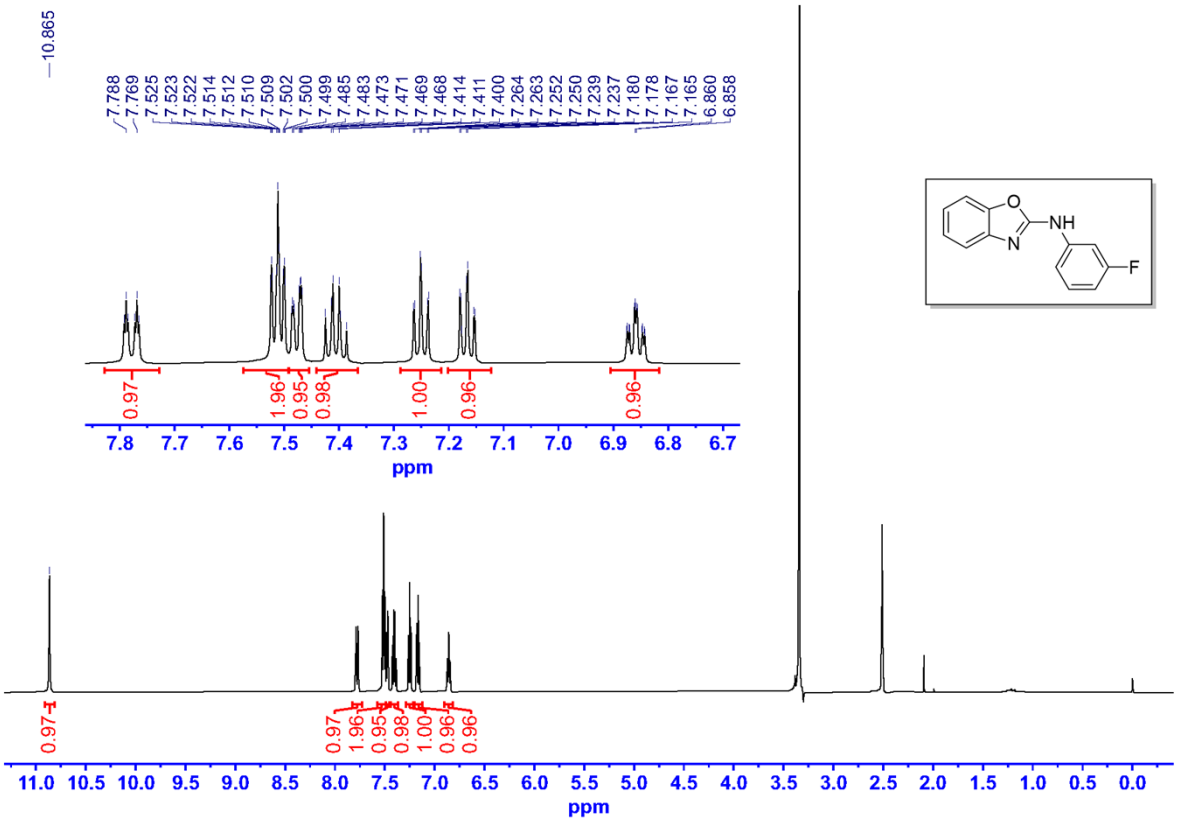
N-(2-fluorophenyl)benzo[*d*]oxazol-2-amine (3ag)

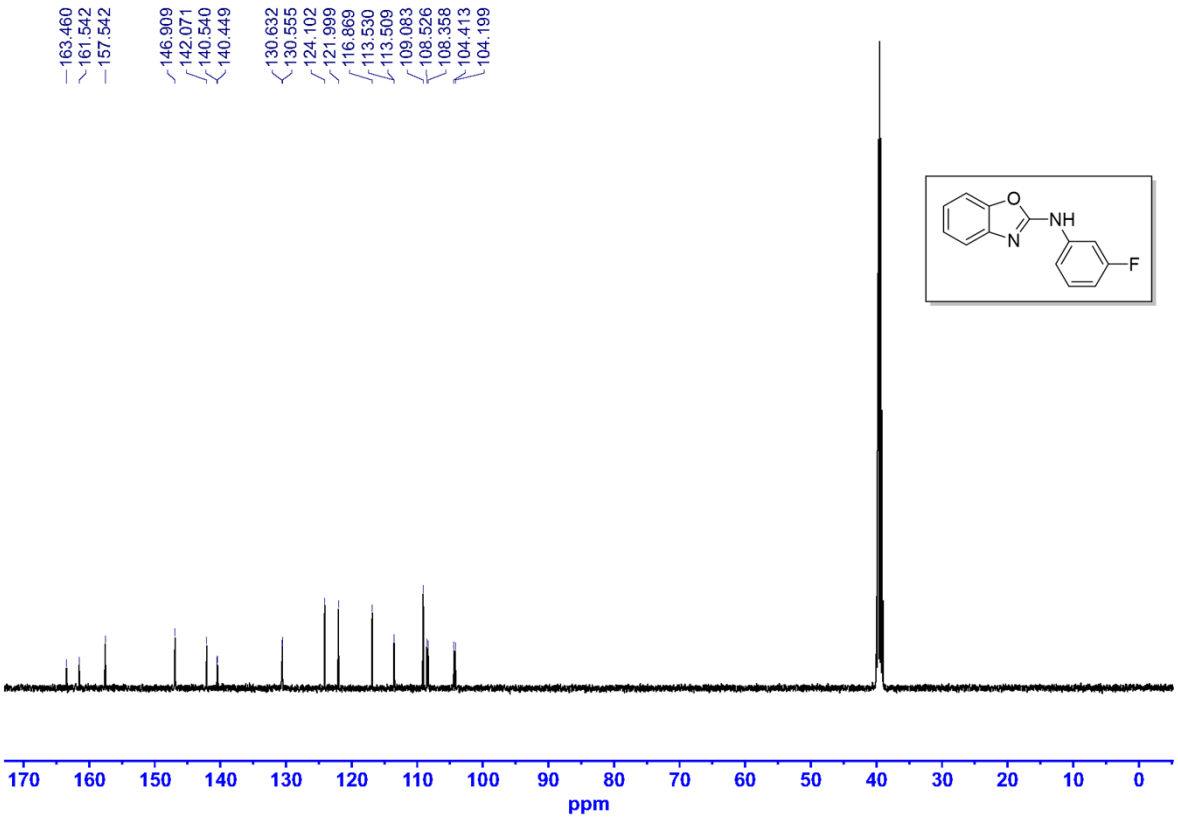


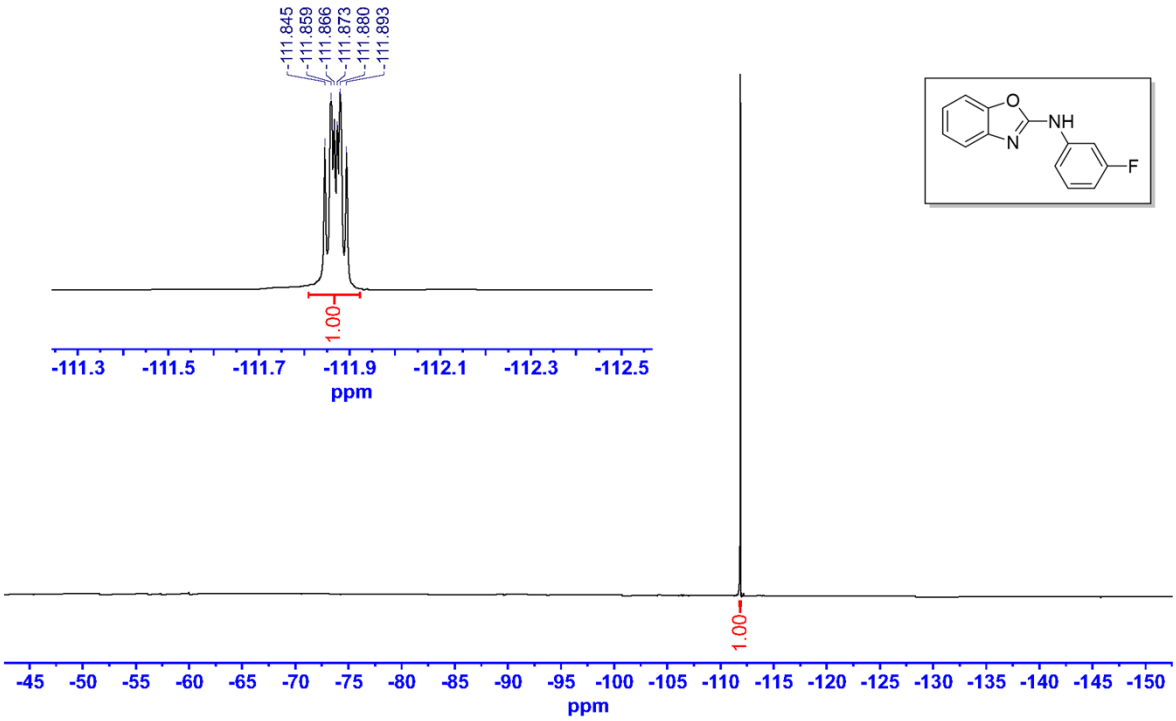



-125.922
-125.933
-125.947
-125.958
-125.967
1.00
-125.5 -125.6 -125.7 -125.8 -125.9 -126.0 -126.1 -126.2 -126.3 -126.4
ppm
O
N
NH
F
1.00
-70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155
ppm

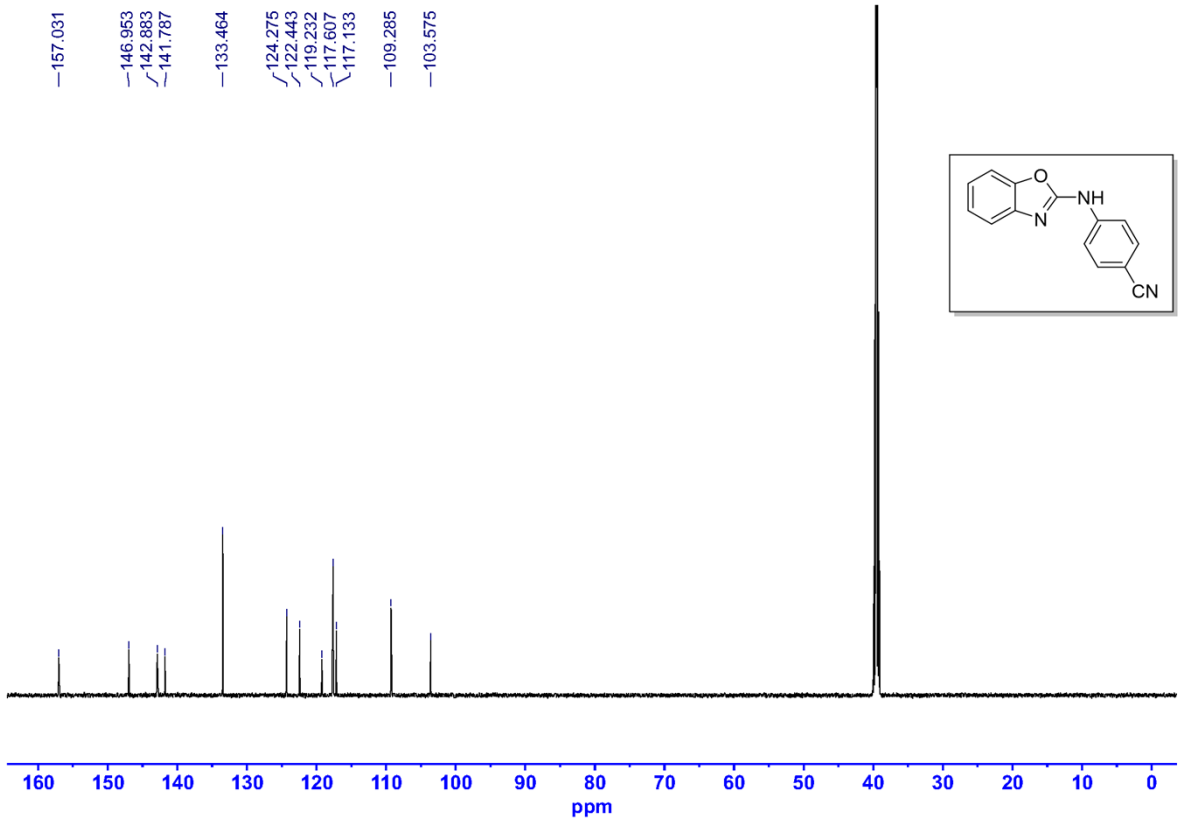
N-(3-fluorophenyl)benzo[*d*]oxazol-2-amine (3ah)

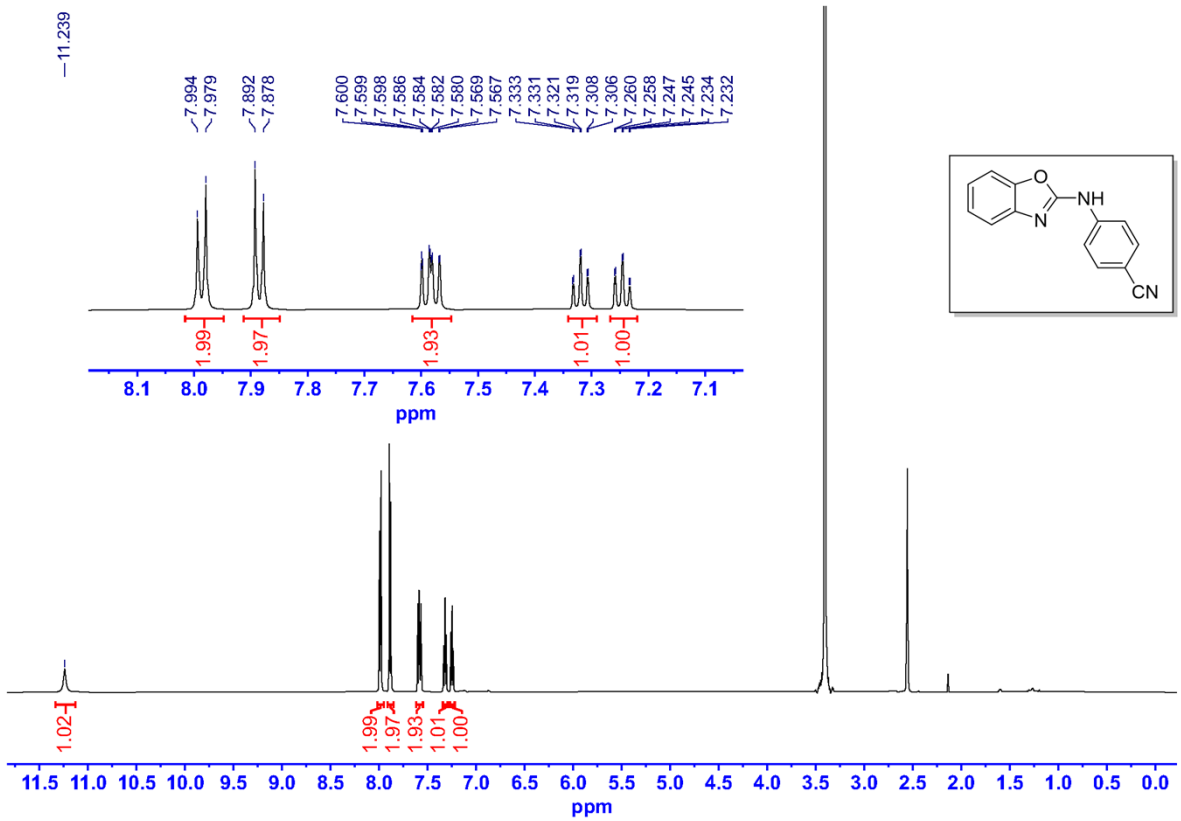




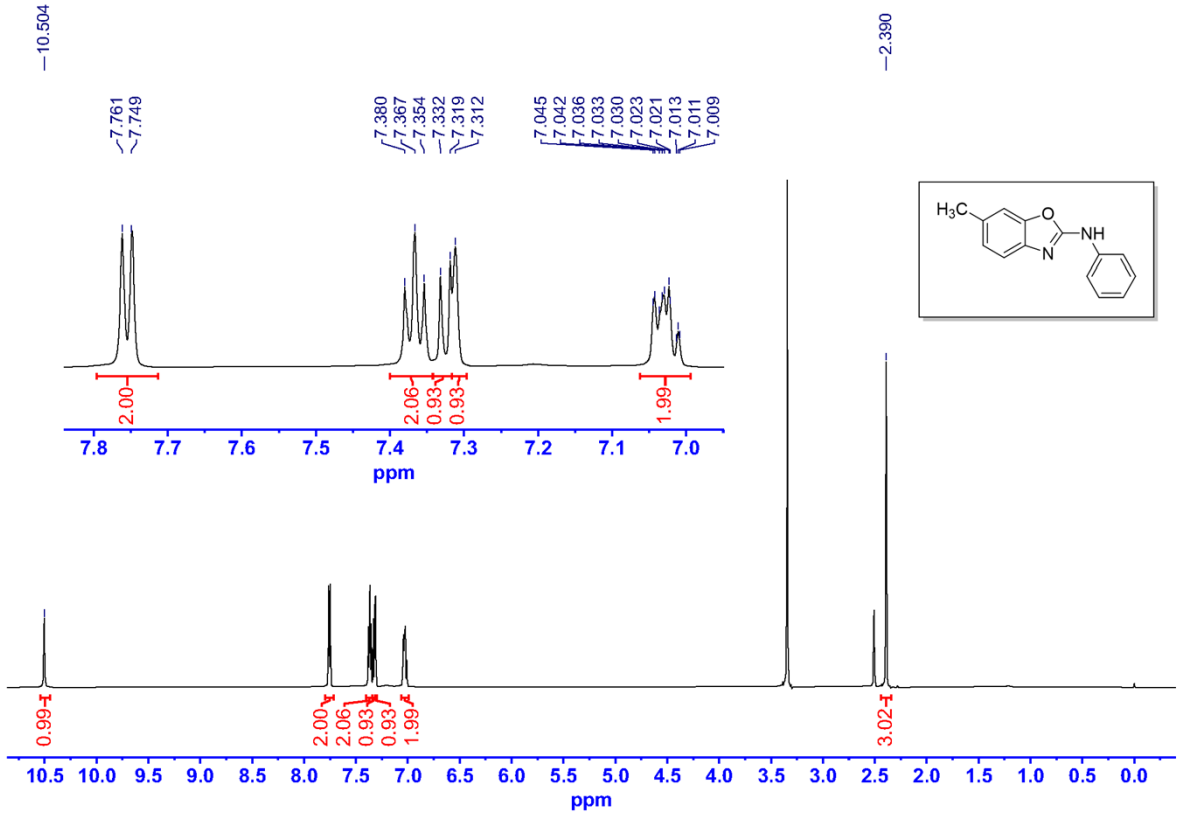

111.845
111.859
111.866
111.873
111.880
111.893
1.00
-111.3
-111.5
-111.7
-111.9
-112.1
-112.3
-112.5
ppm
O
NH
N
F
1.00
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
ppm

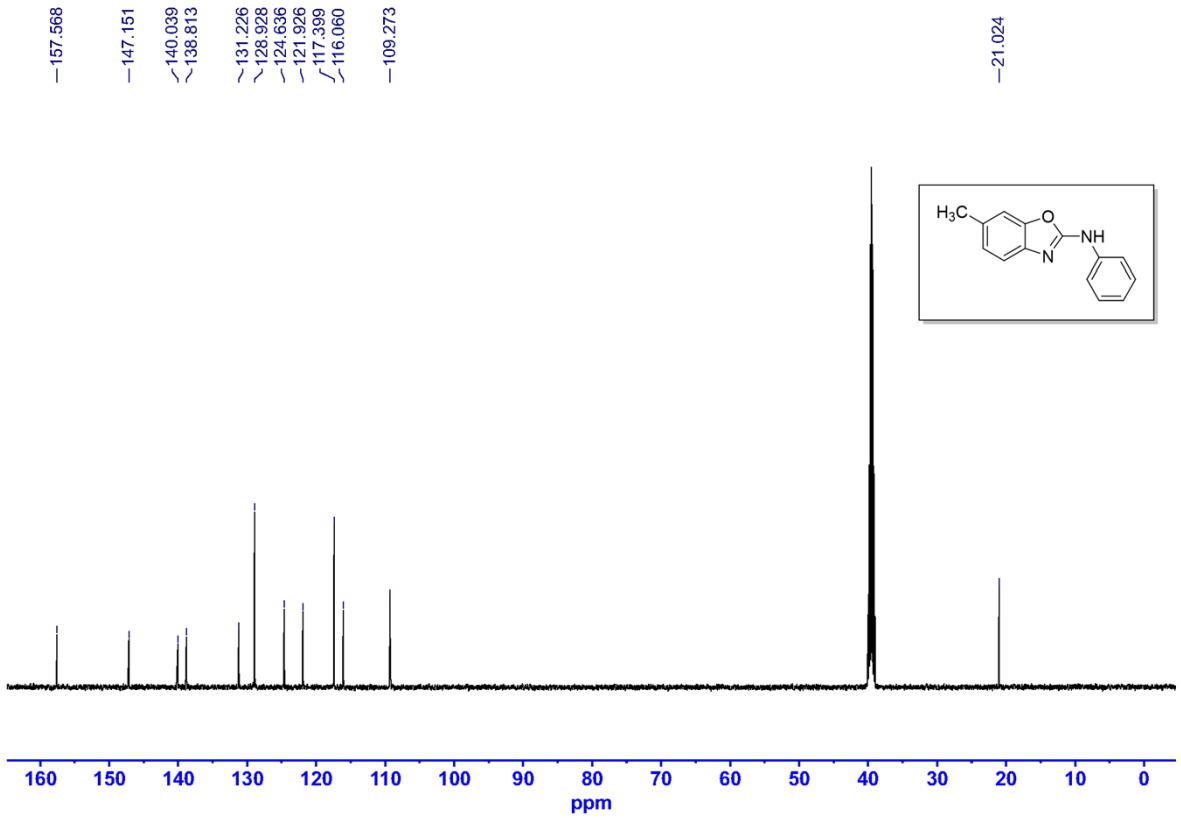
4-(Benzo[*d*]oxazol-2-ylamino)benzonitrile (3ai)



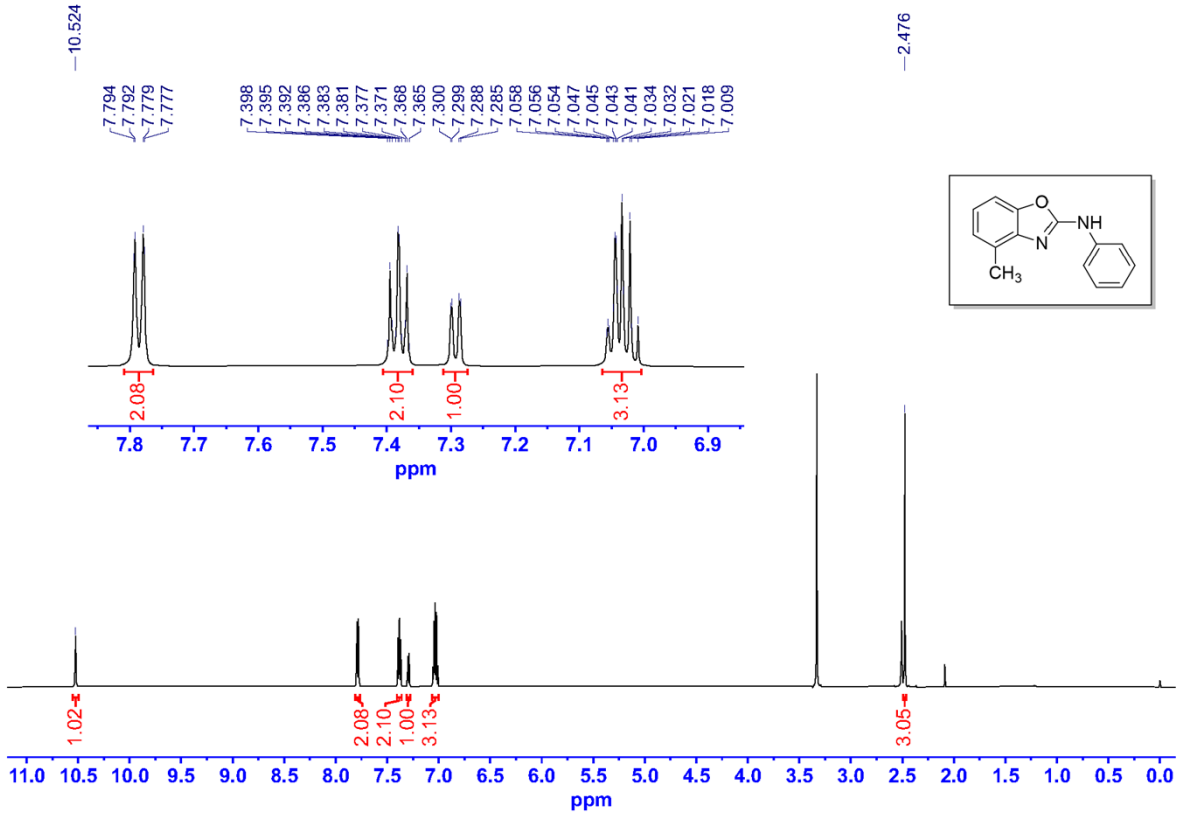


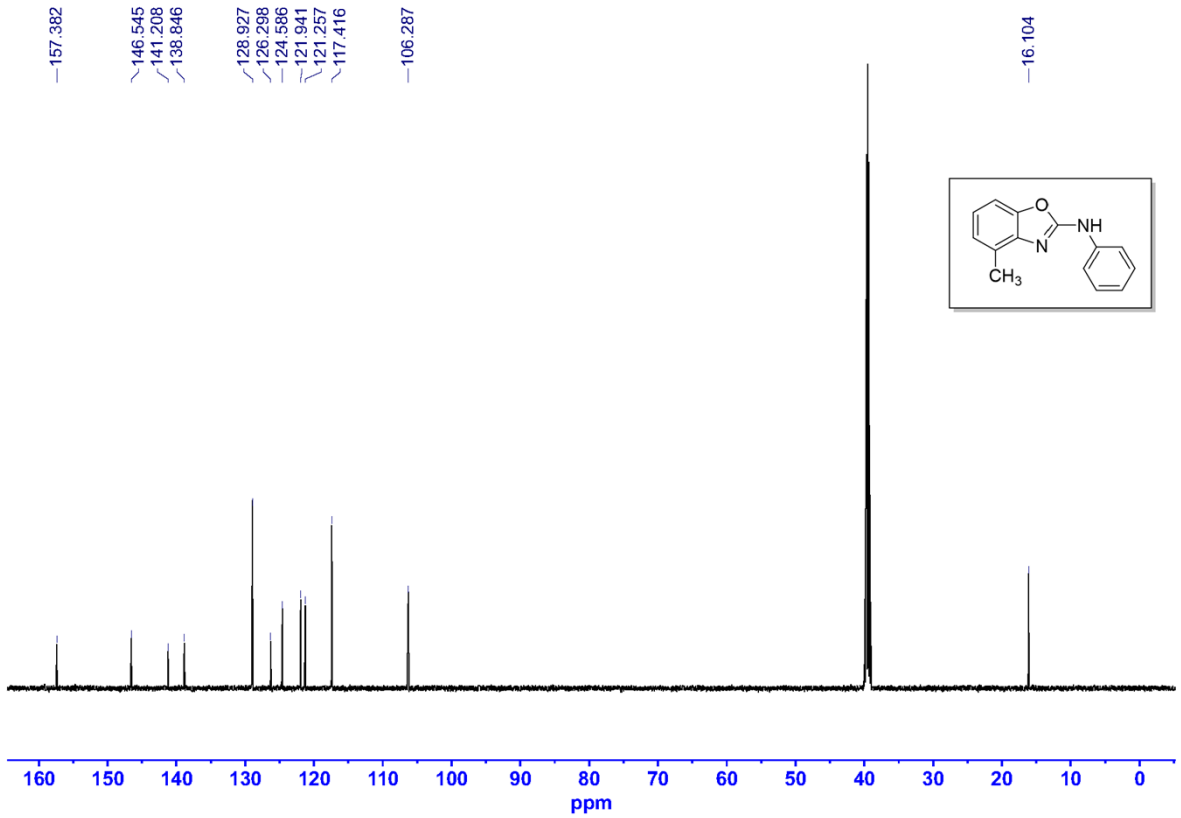
6-Methyl-*N*-phenylbenzo[*d*]oxazol-2-amine (3ba)



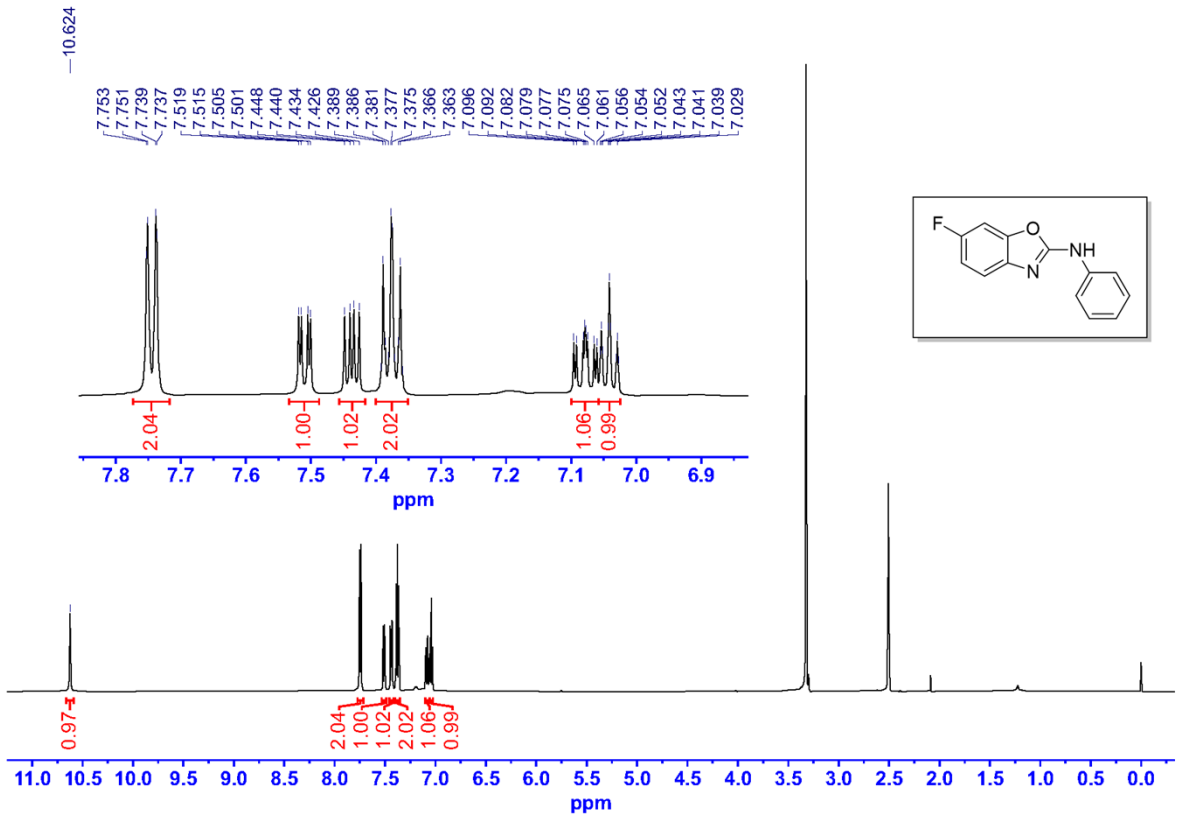


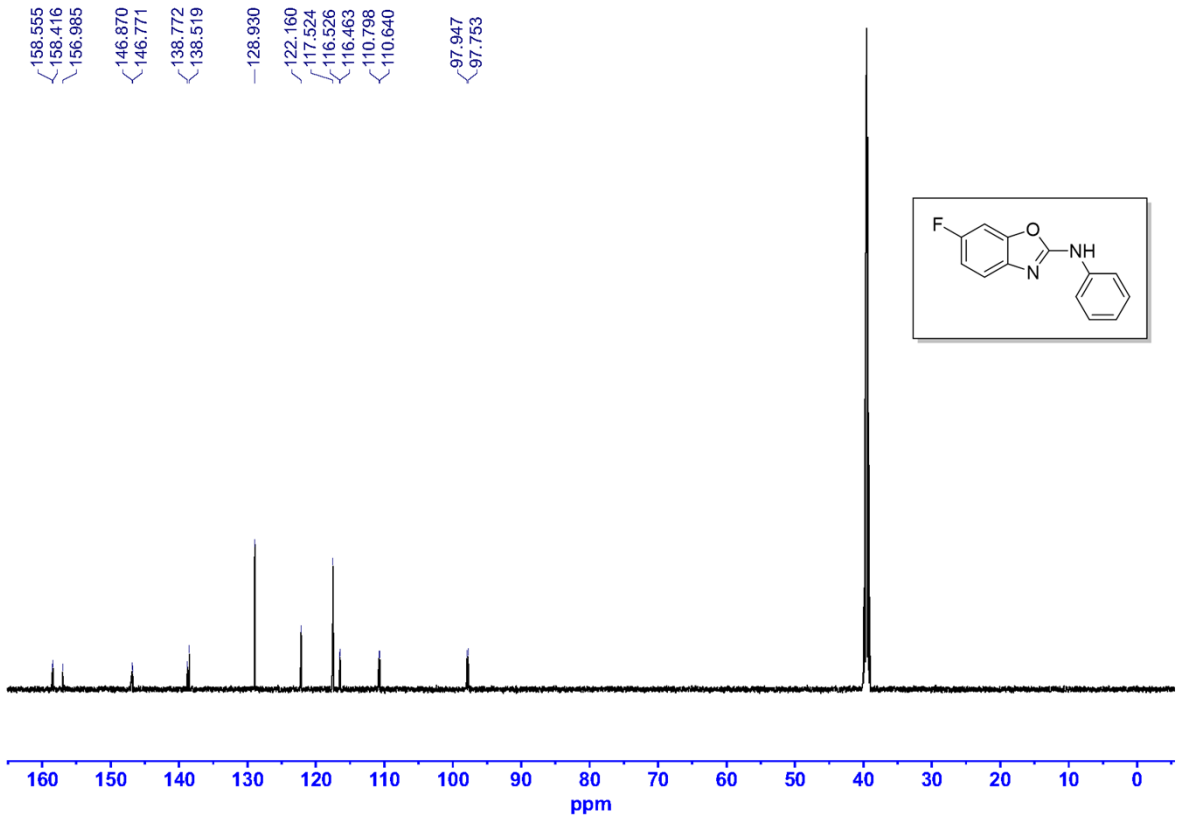
4-Methyl-*N*-phenylbenzo[*d*]oxazol-2-amine (3ca)

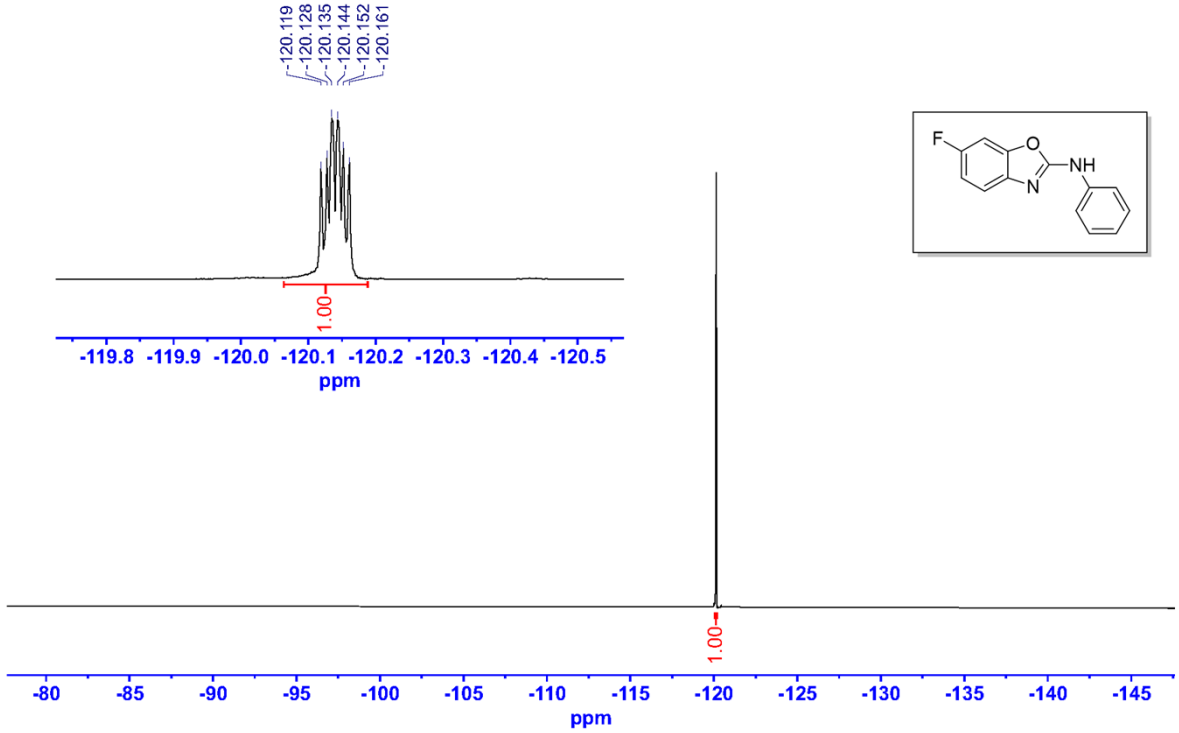




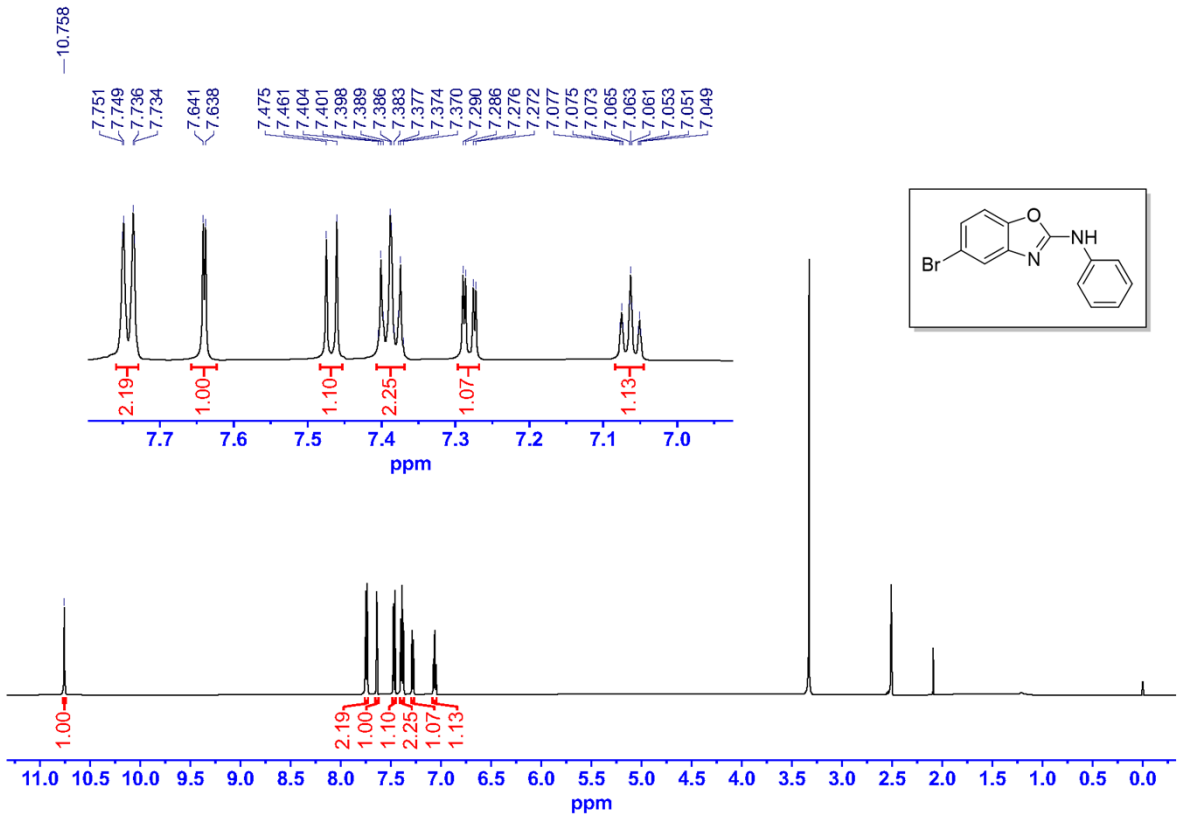
6-Fluoro-*N*-phenylbenzo[*d*]oxazol-2-amine (3da)

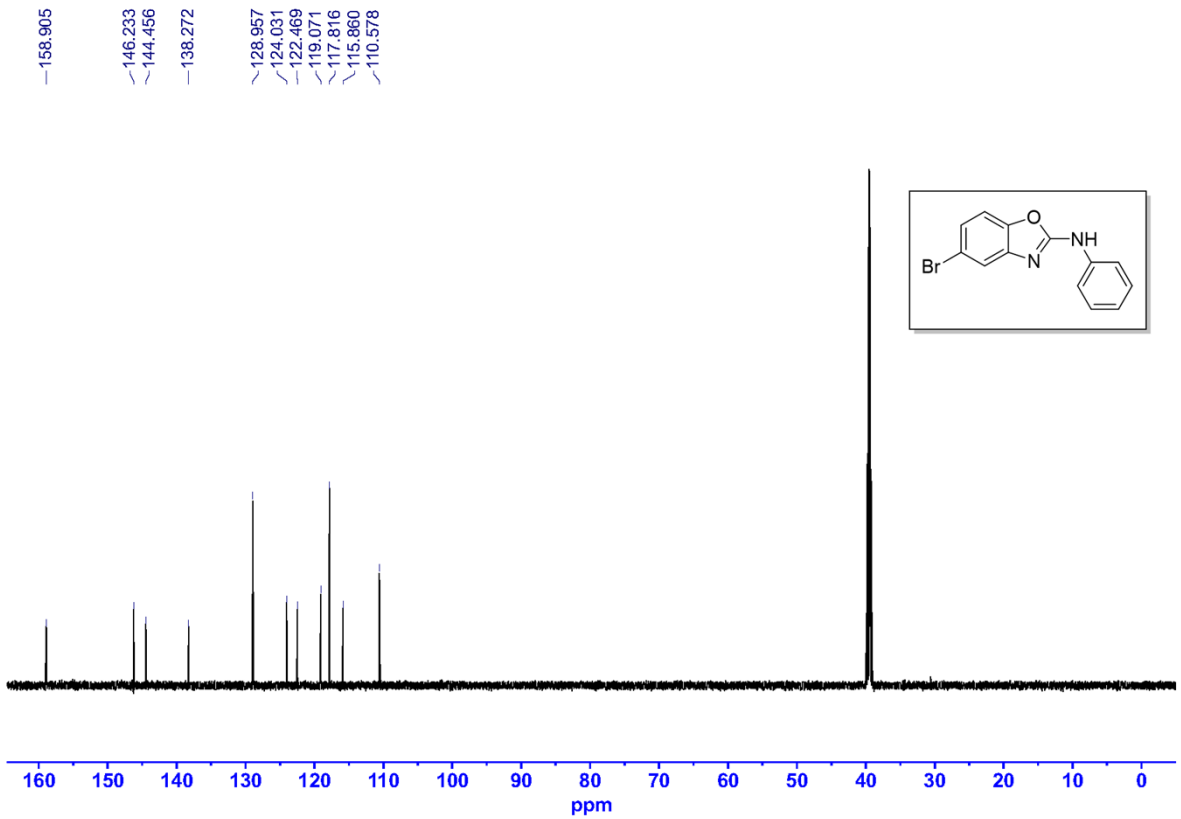




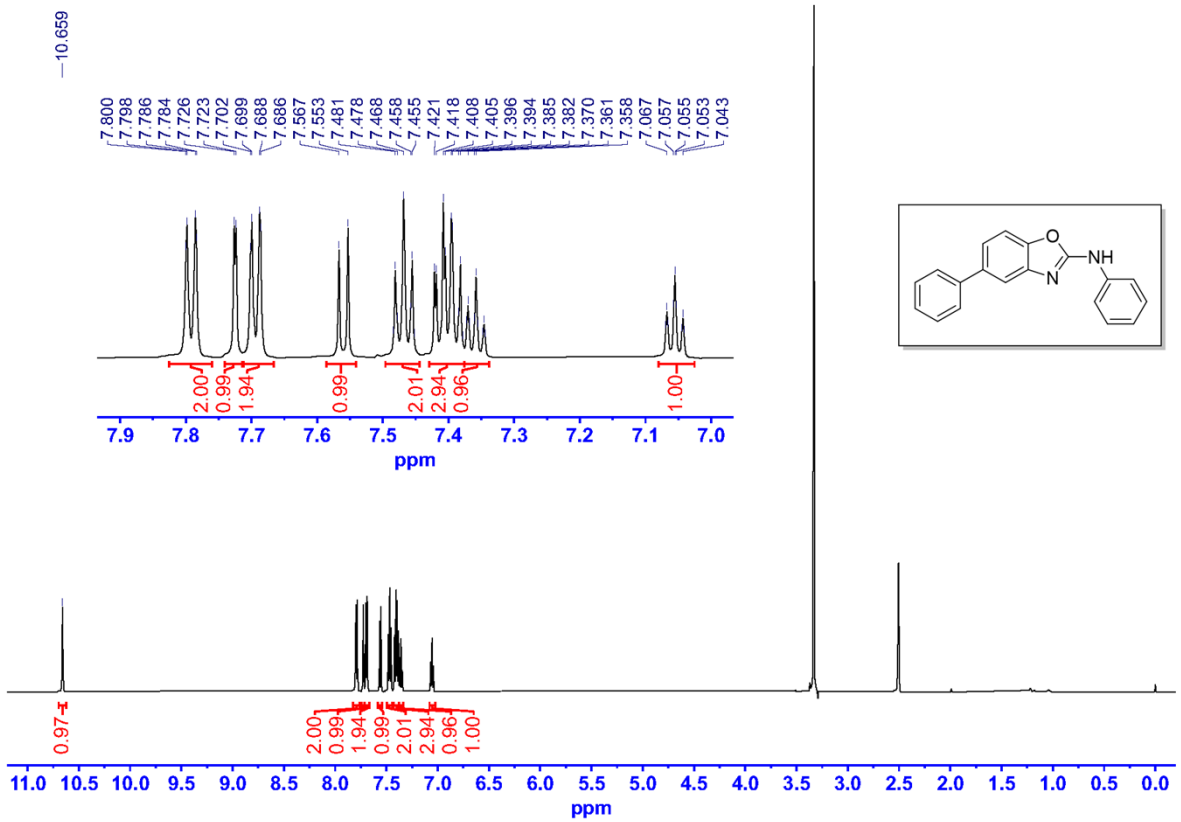

-120.119
-120.128
-120.135
-120.144
-120.152
-120.161
1.00
-119.8 -119.9 -120.0 -120.1 -120.2 -120.3 -120.4 -120.5
ppm
F
O
N
NH
1.00
-80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145
ppm

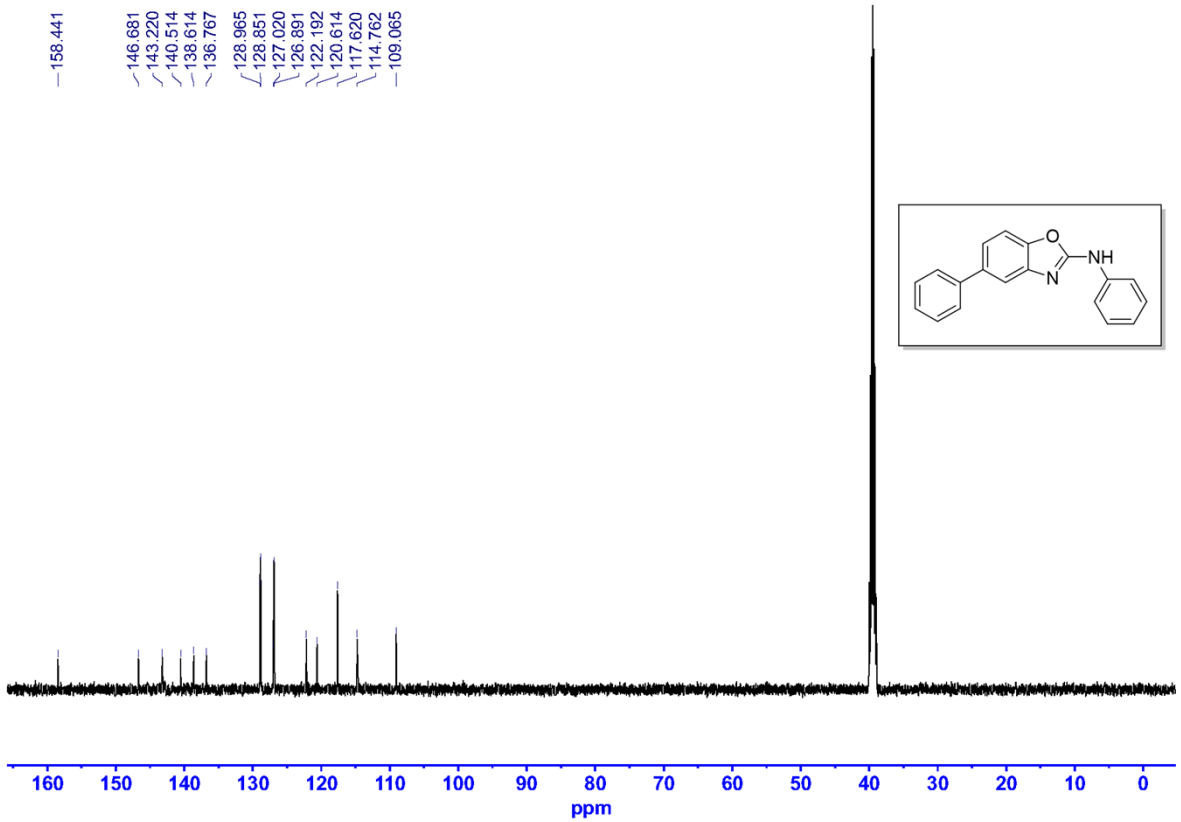
5-Bromo-*N*-phenylbenzo[*d*]oxazol-2-amine (3ea)



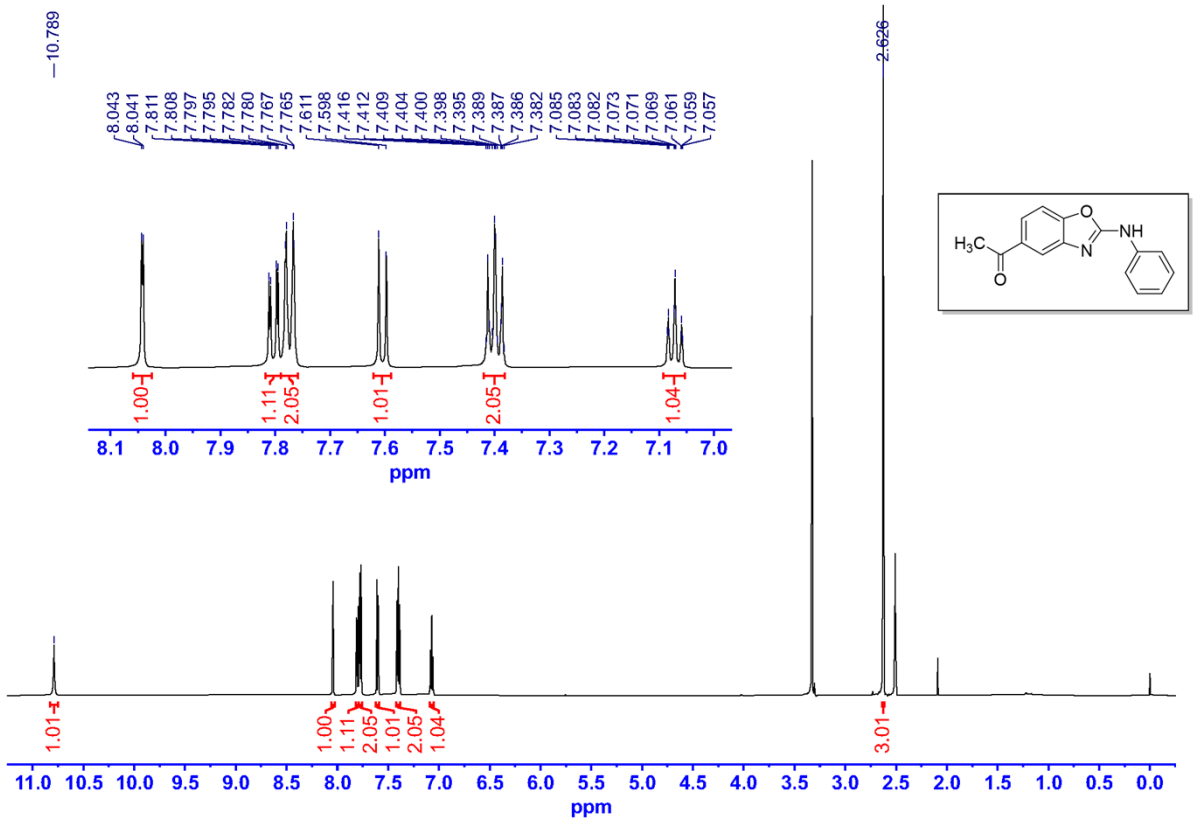


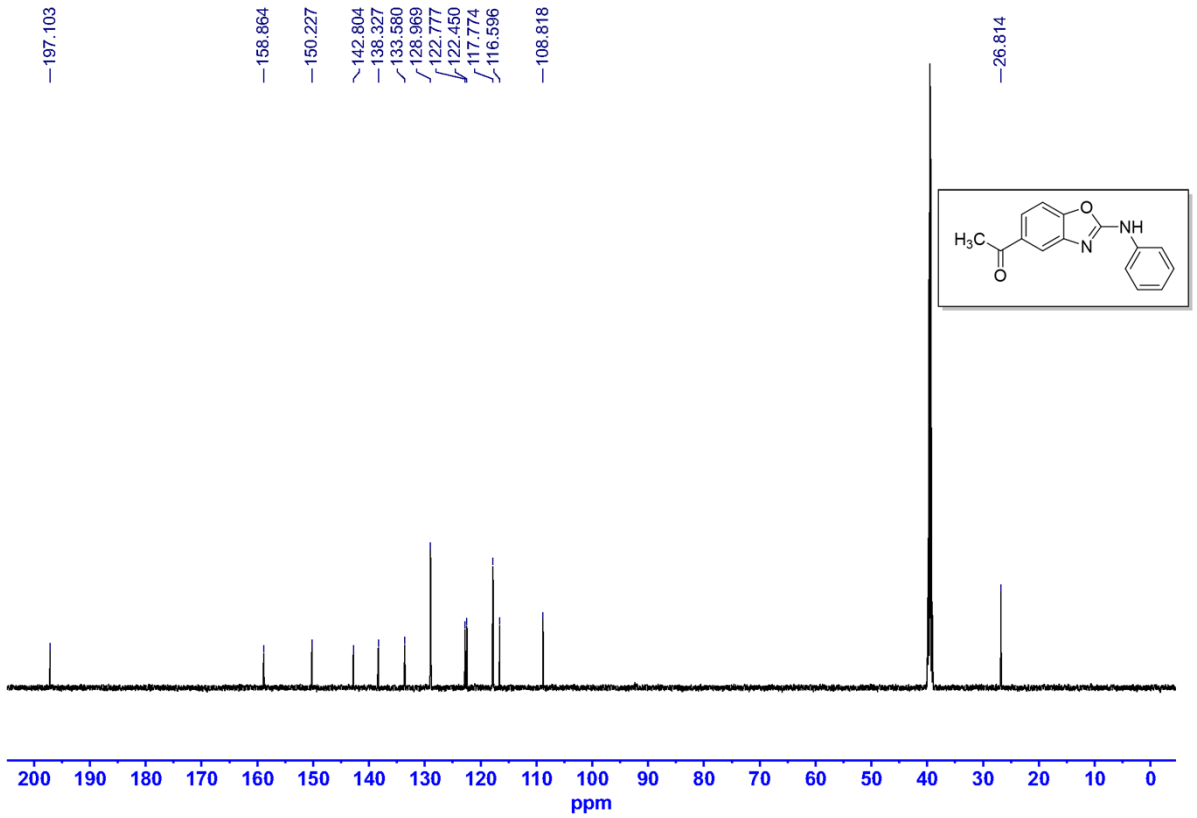
N,5-diphenylbenzo[*d*]oxazol-2-amine (3fa)



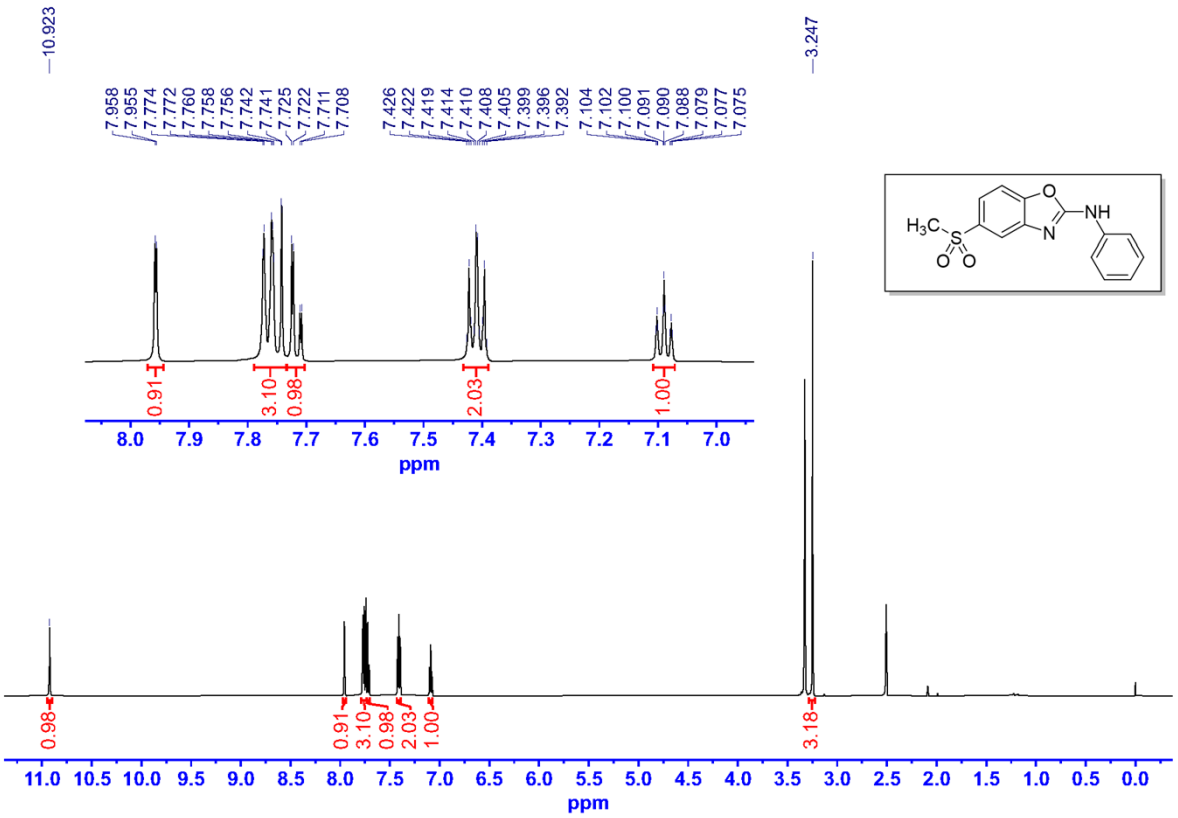


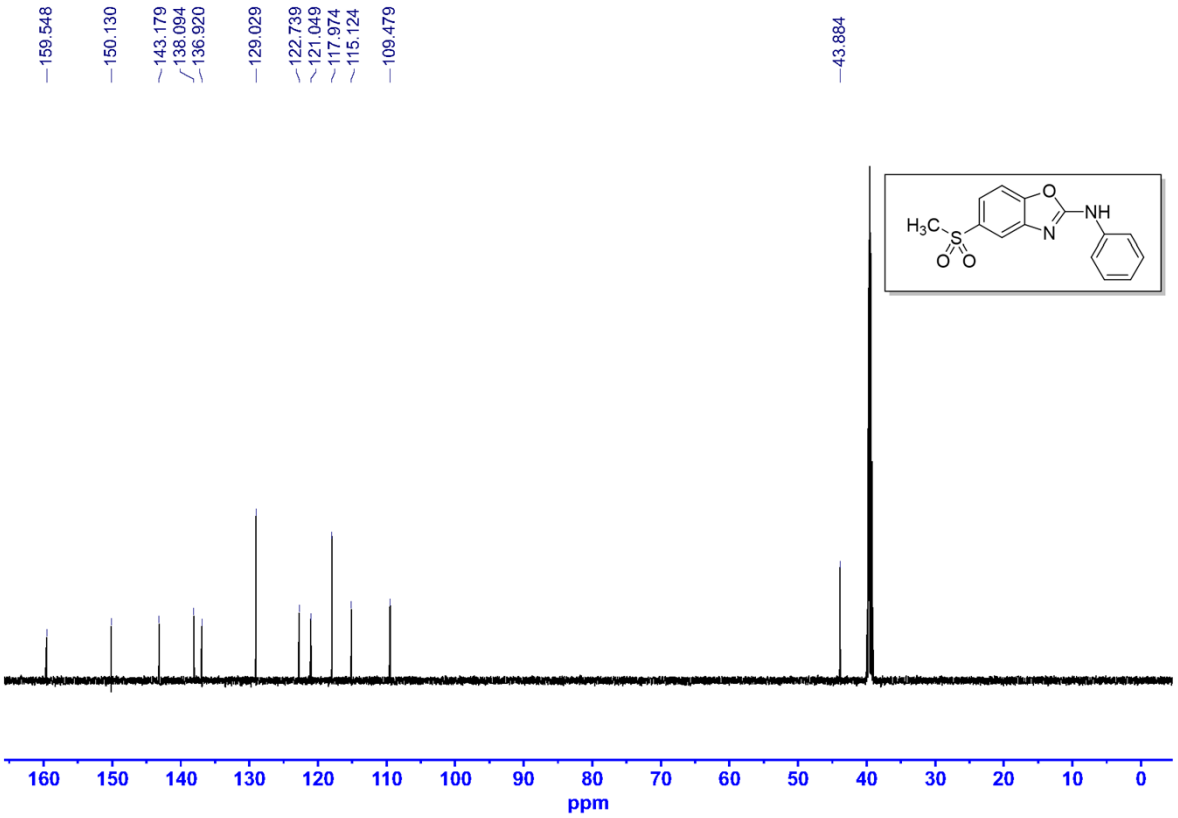
1-(2-(Phenylamino)benzo[*d*]oxazol-5-yl)ethan-1-one (3ga)



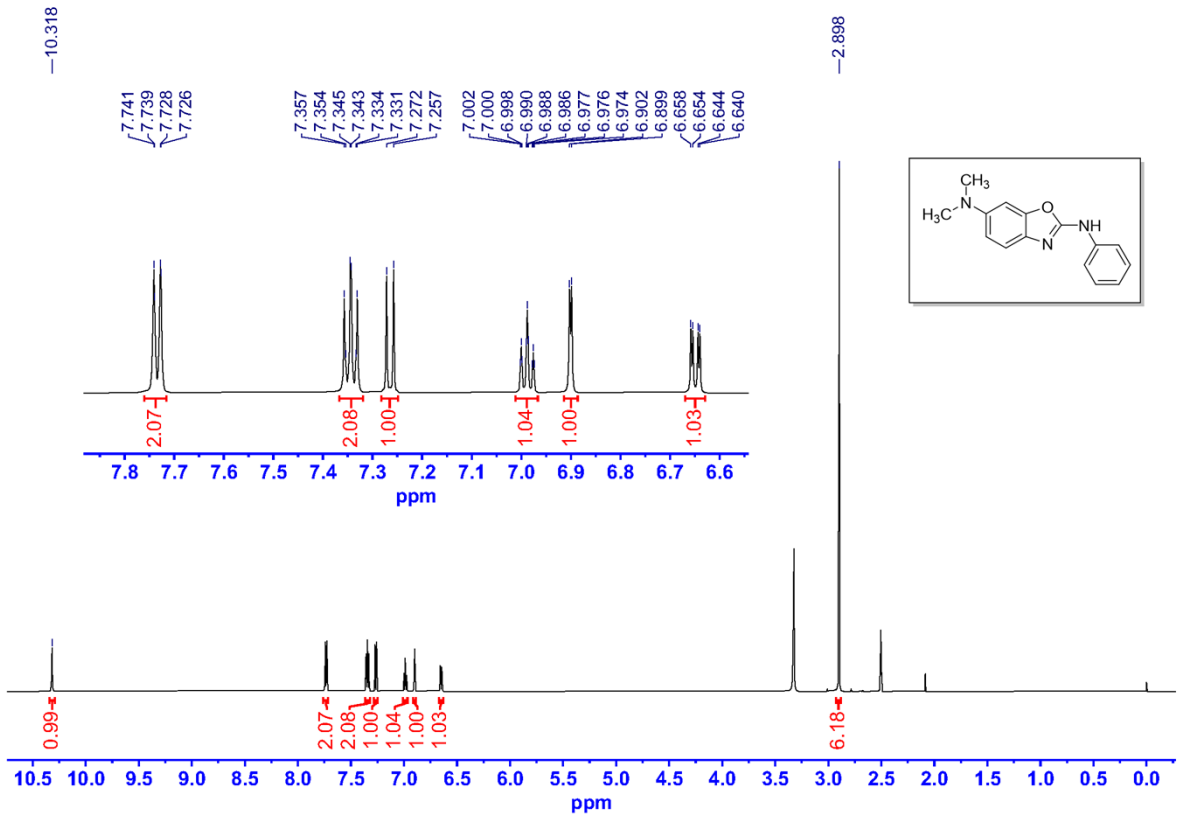


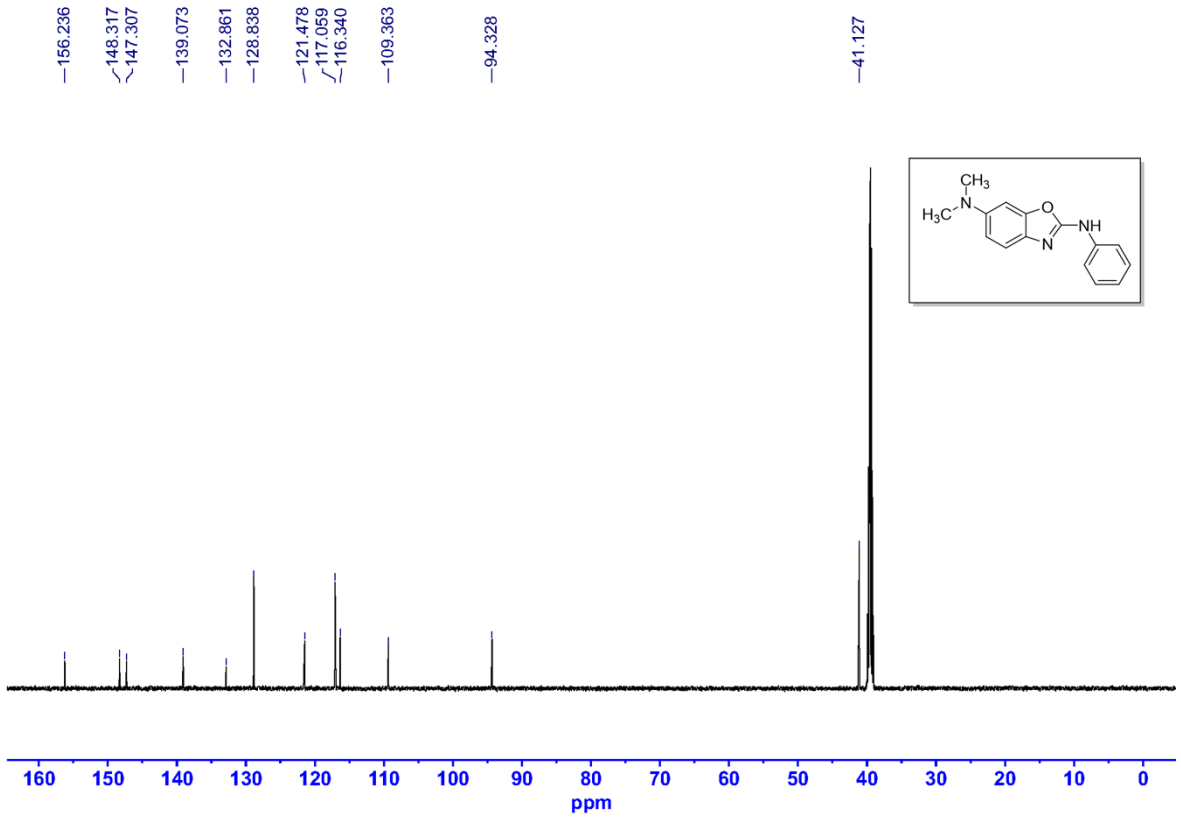
5-(Methylsulfonyl)-*N*-phenylbenzo[*d*]oxazol-2-amine (3ha)



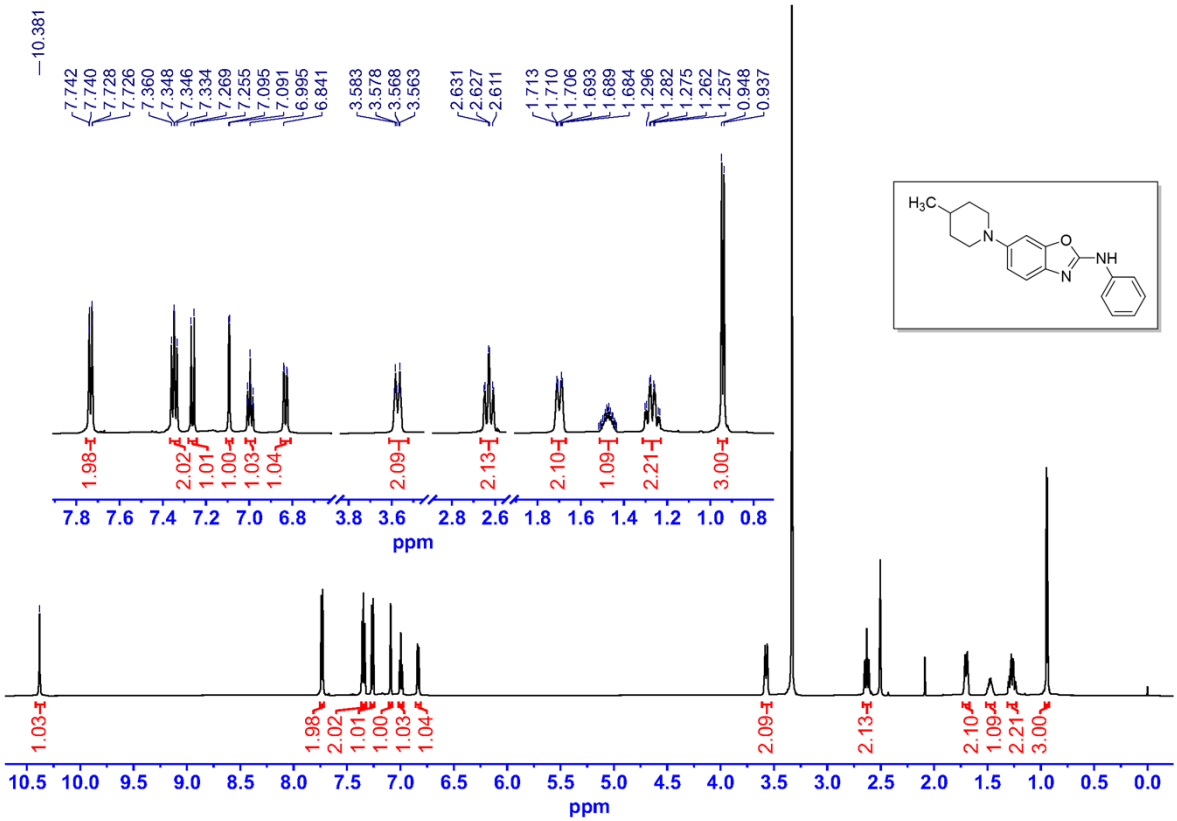


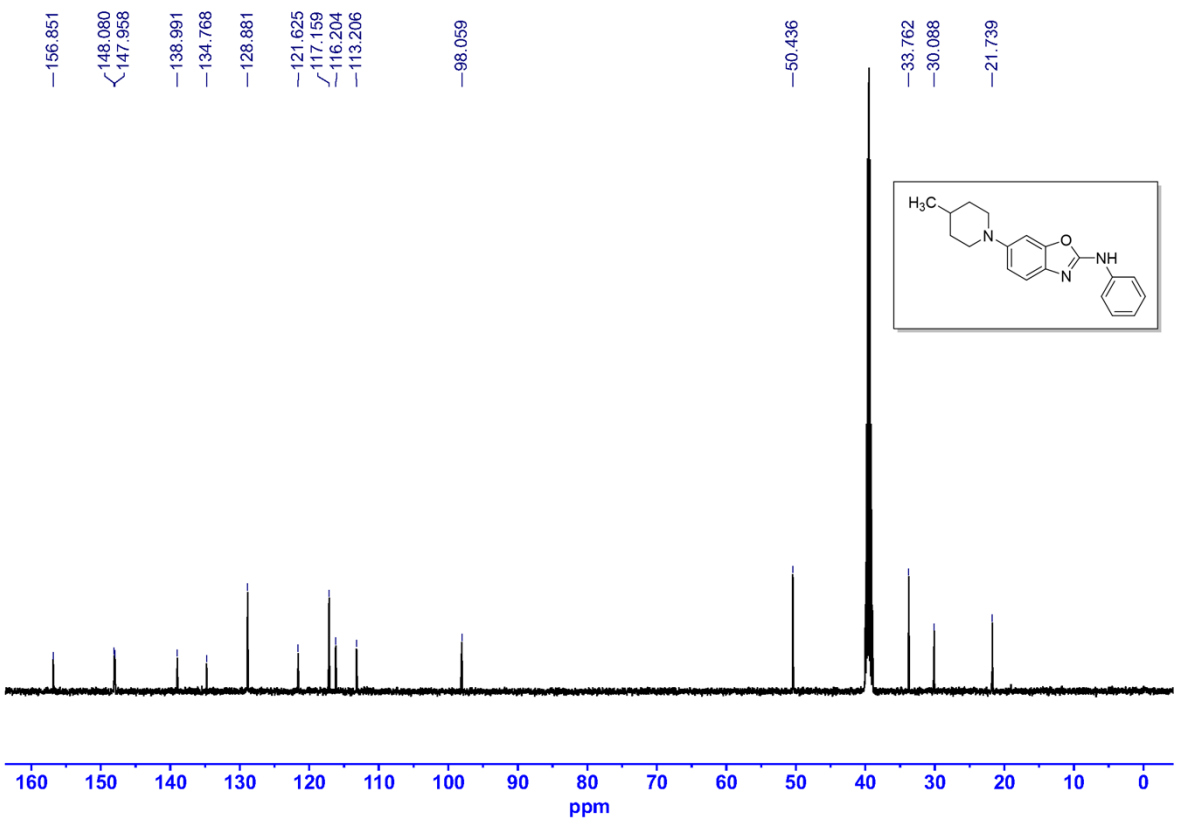
N^6,N^6-dimethyl-N^2-phenylbenzo[*d*]oxazole-2,6-diamine (3ia)



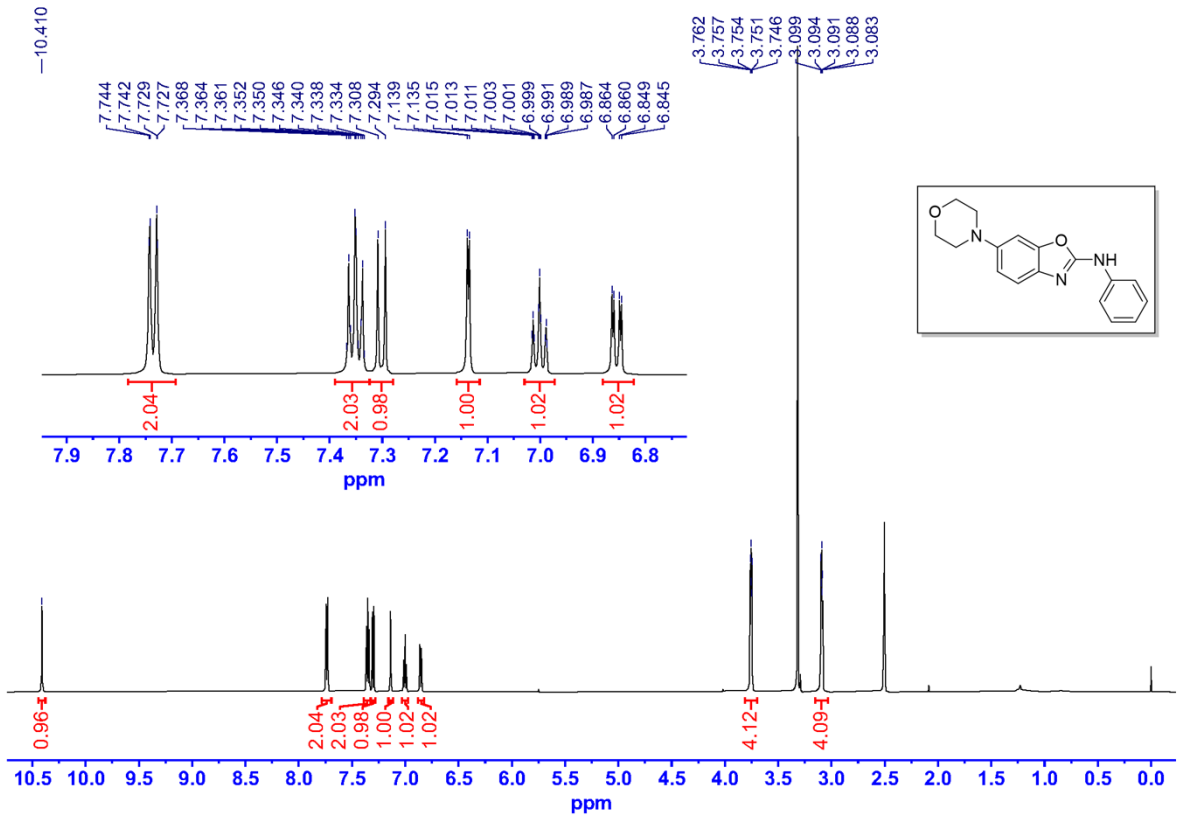


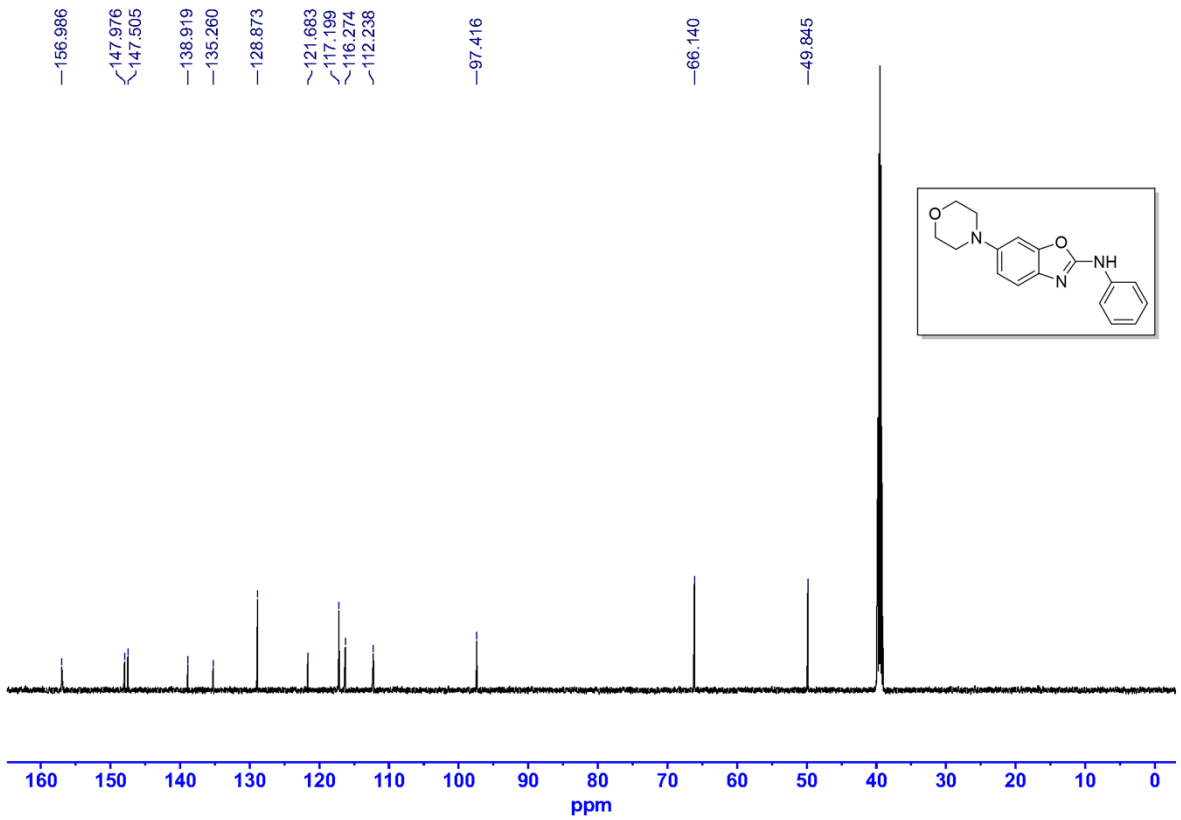
6-(4-Methylpiperidin-1-yl)-*N*-phenylbenzo[*d*]oxazol-2-amine (3ja)



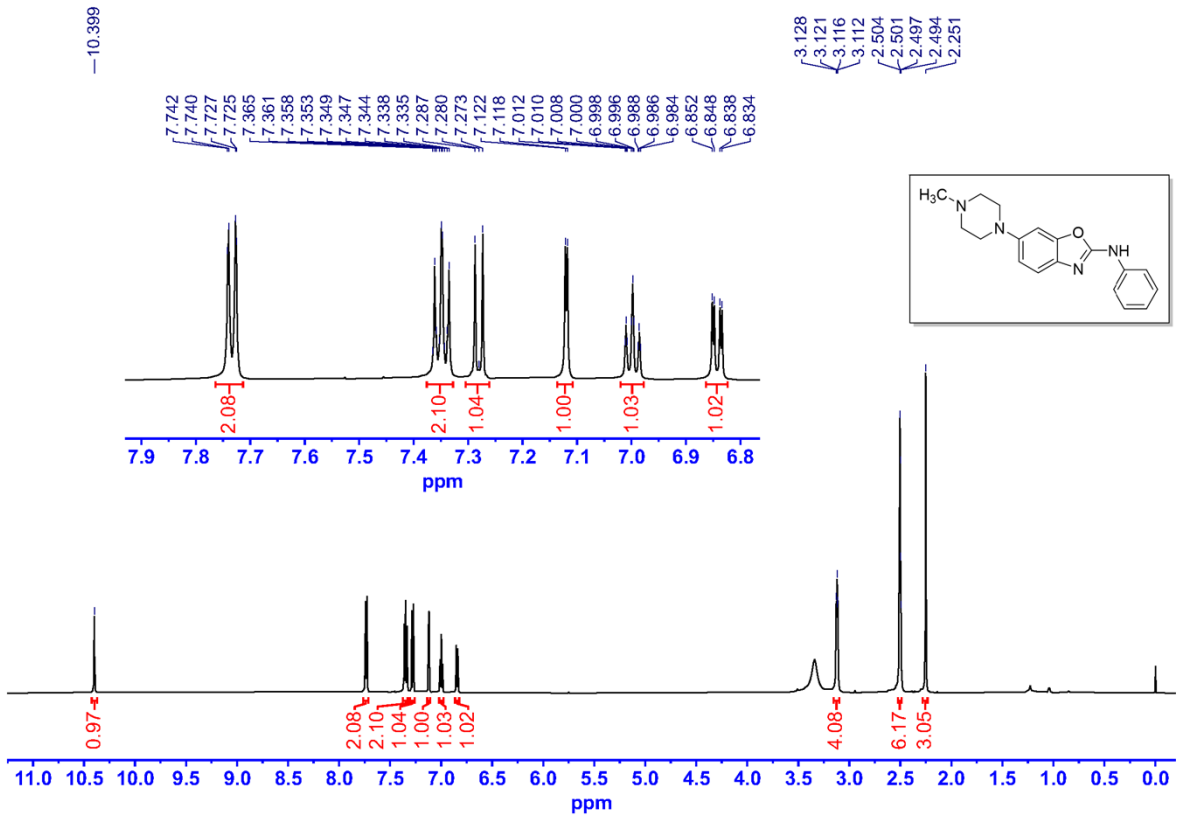


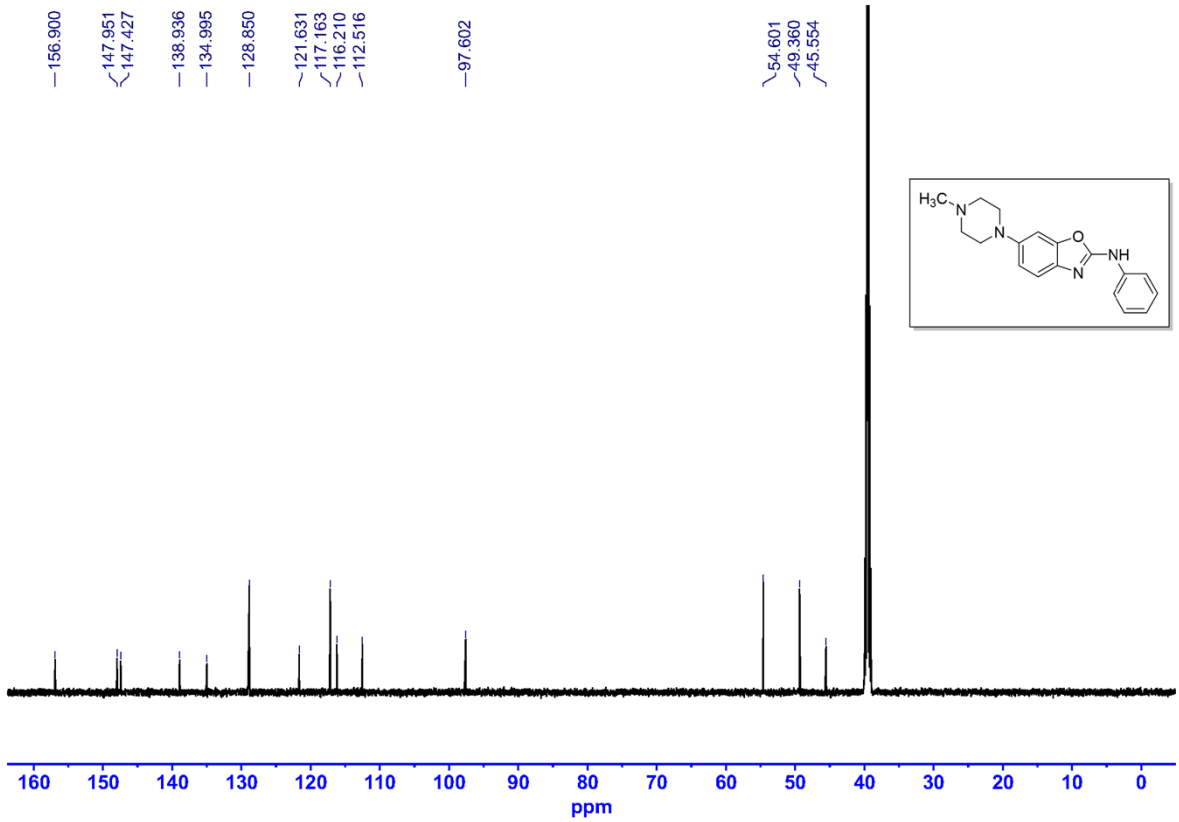
6-Morpholino-*N*-phenylbenzo[*d*]oxazol-2-amine (3ka)



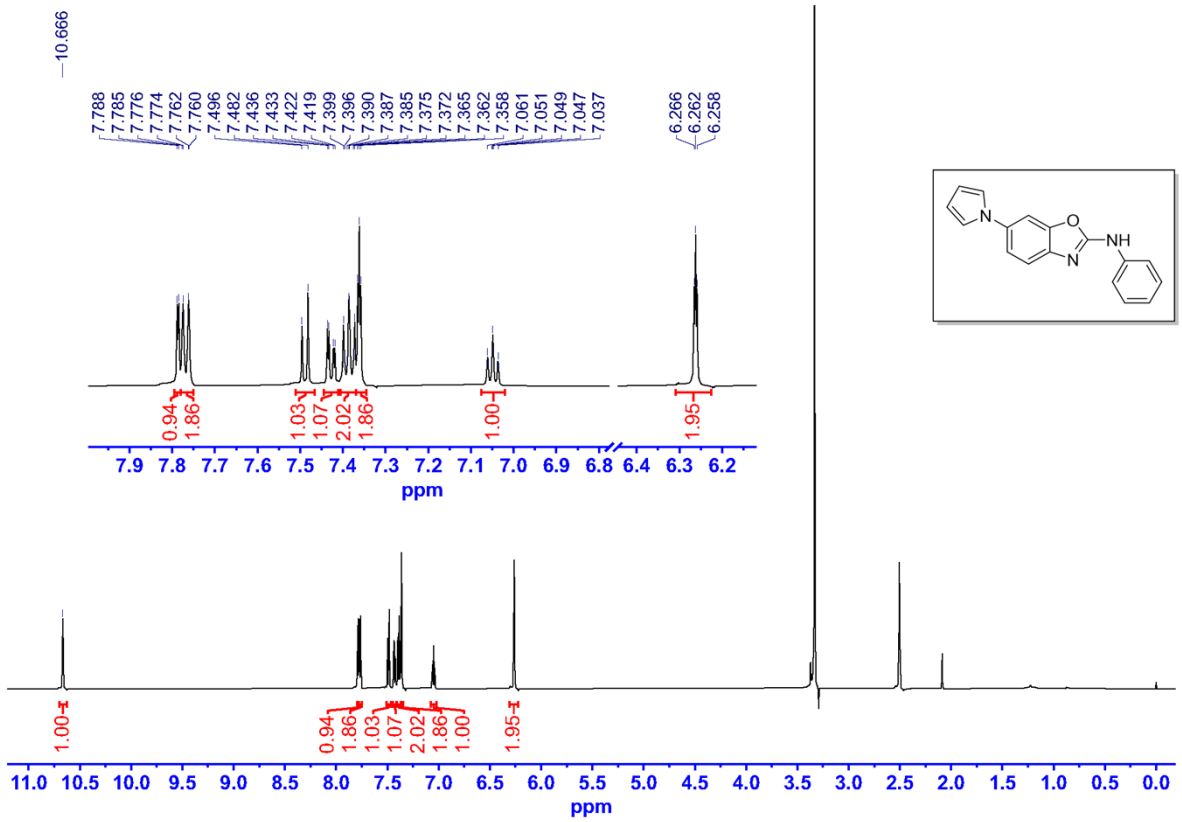


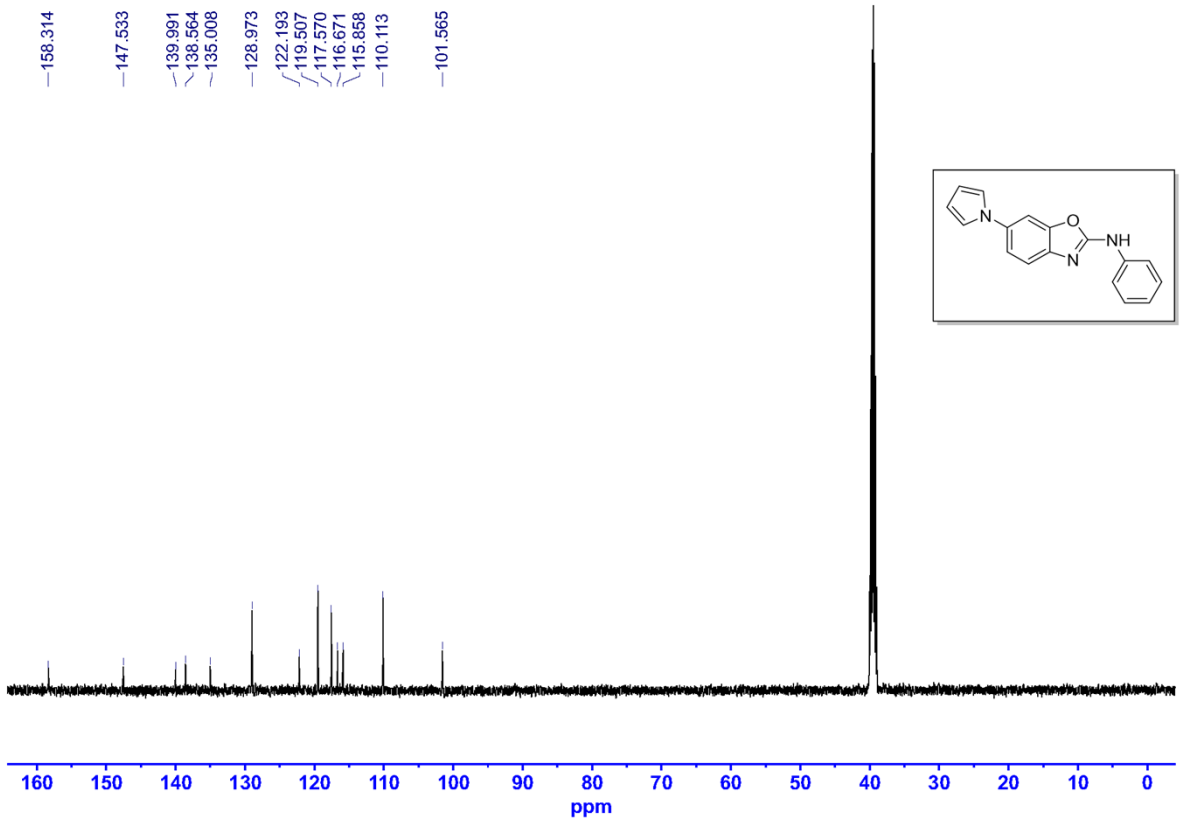
6-(4-Methylpiperazin-1-yl)-*N*-phenylbenzo[*d*]oxazol-2-amine (3la)



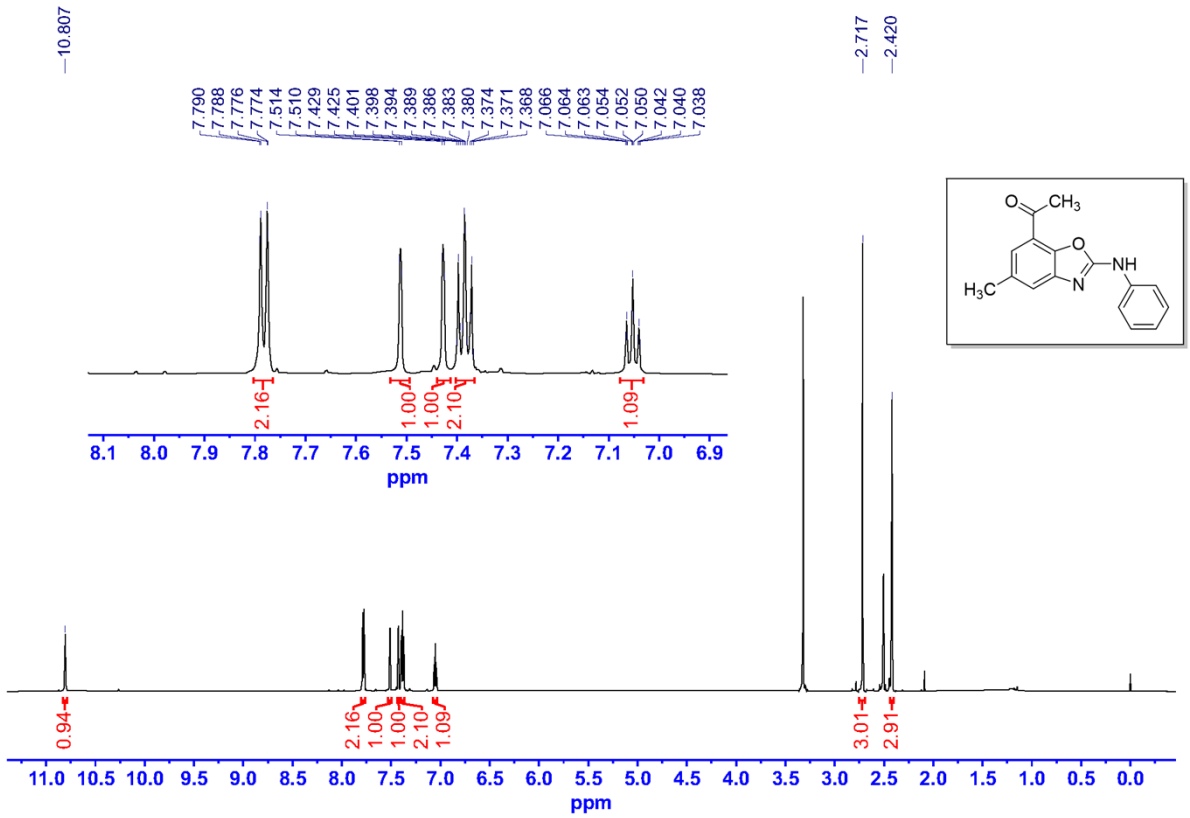


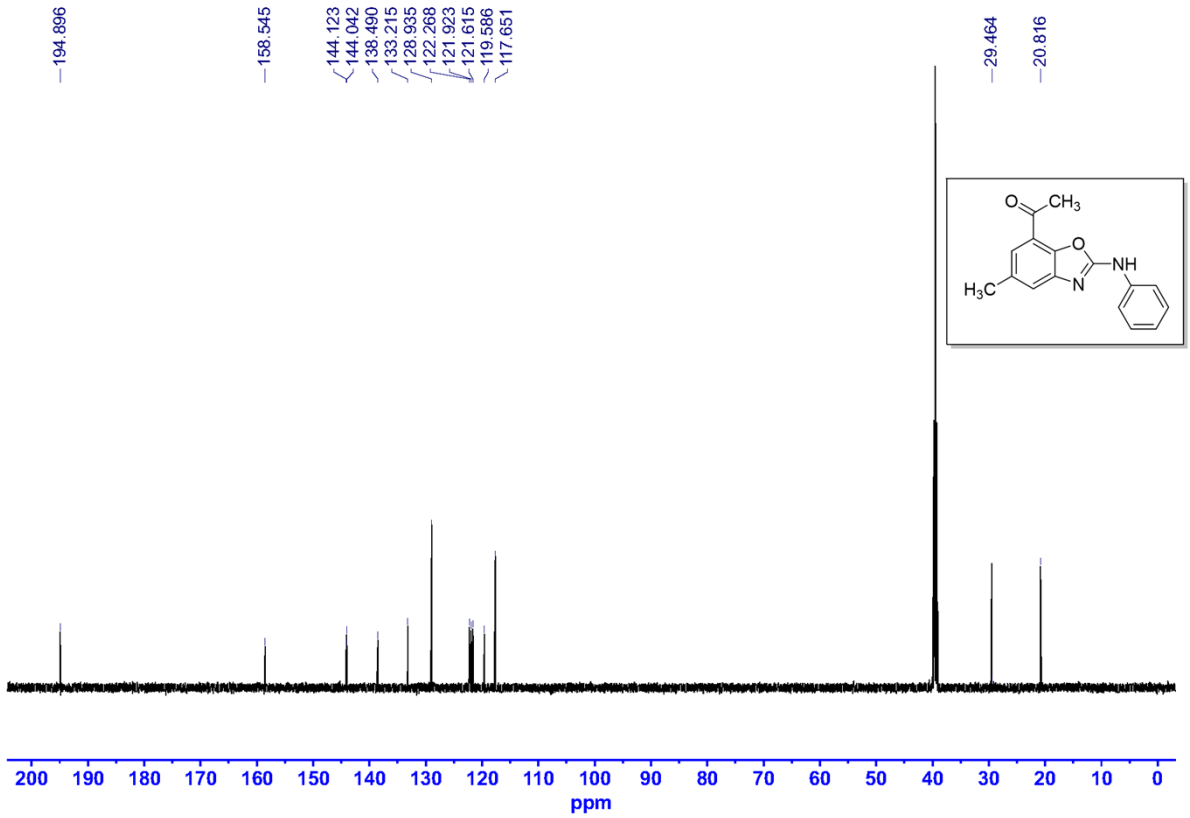
***N*-phenyl-6-(1*H*-pyrrol-1-yl)benzo[*d*]oxazol-2-amine (3ma)**





1-(5-Methyl-2-(phenylamino)benzo[*d*]oxazol-7-yl)ethan-1-one (3na)





N-phenyloxazolo[4,5-*c*]pyridin-2-amine (3oa)