Electronic Supplementary Material (ESI) for RSC Advances.

An optimized procedure for direct access to 1*H*-Indazole-3-carboxaldehyde derivatives by nitrosation of indoles.

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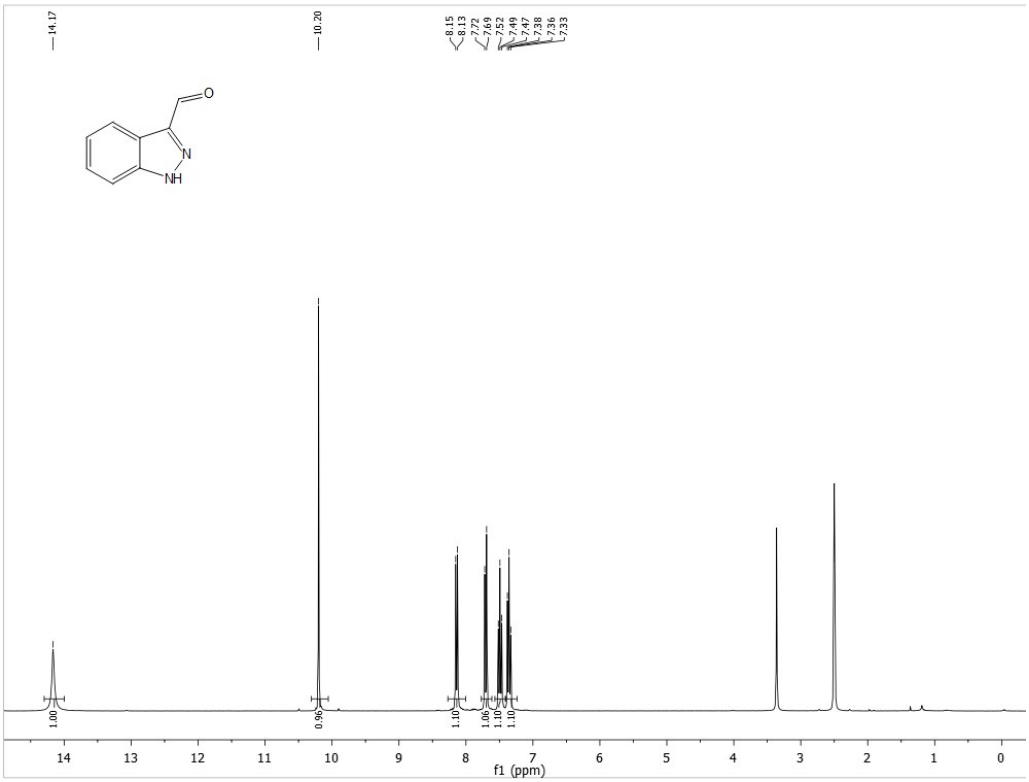
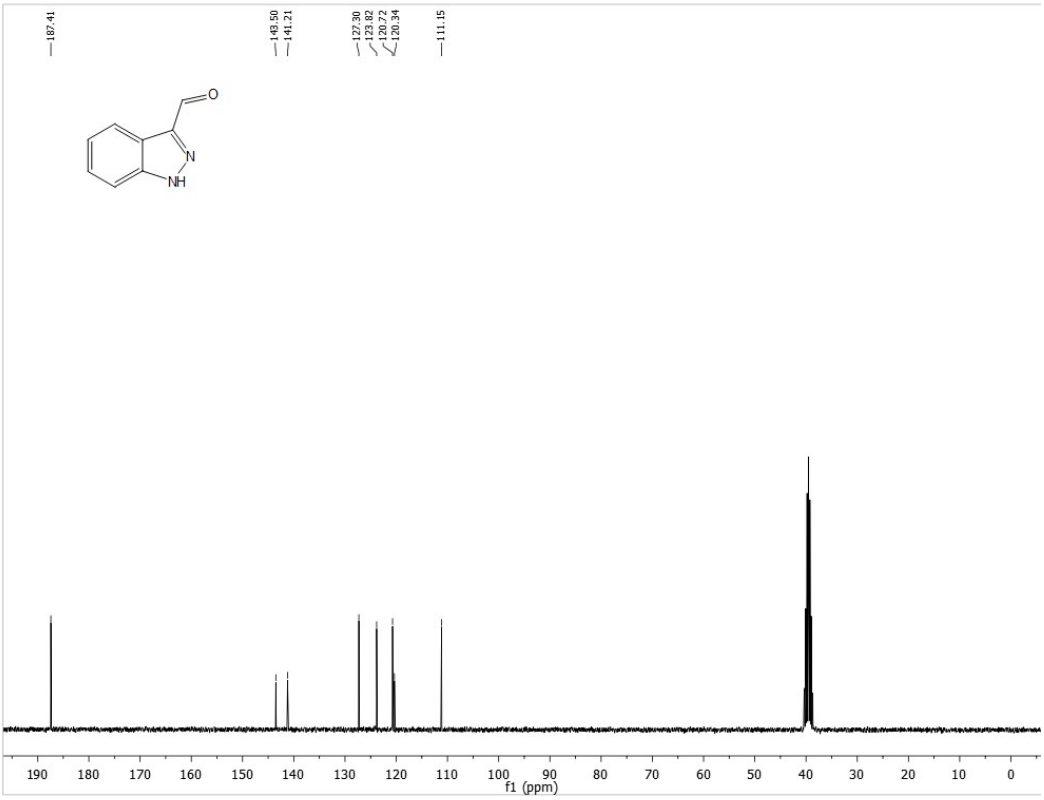
I. Materials and Methods

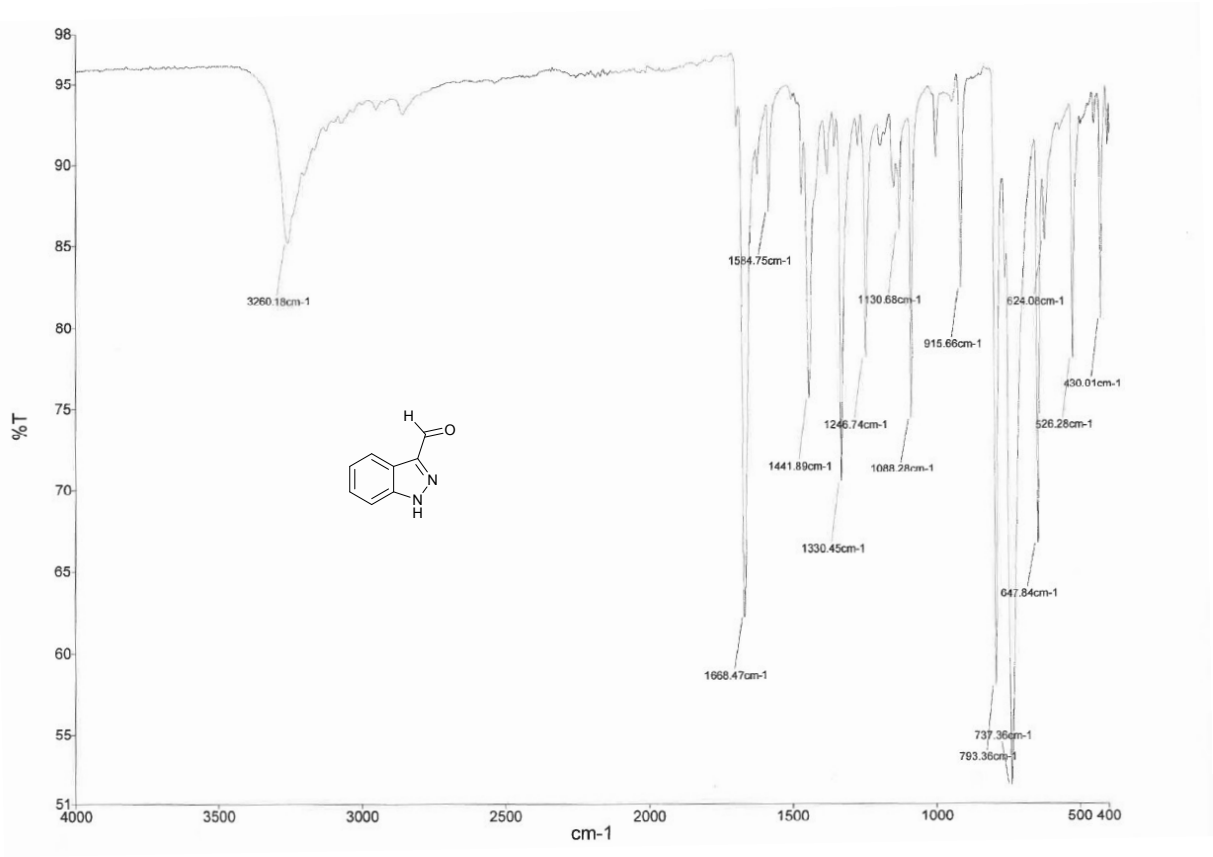
Commercially available reagents were used without further purification. Column chromatography purifications were performed on silica gel (40-63 µm). Thin-layer chromatography (TLC) analyses were carried out on Merck DC Kieselgel 60 F-254 aluminum sheets. The spots were visualized through illumination with UV lamp (λ = 254 nm and 360 nm) and/or staining with 4-hydrazinobenzenesulfonic acid. IR spectra were recorded with an ATR diamant Perkin Elmer. 1H and 13C NMR spectra (C13APT or C13CPD experiments) were recorded on a Bruker AVIII 300 MHz spectrometer (BBFO). Chemical shifts are expressed in parts per million (ppm) from the residual non-deuterated solvent signal contained in $CDCl_3$ (δH = 7.26, δC = 77.16), in Acetone-d_6 (δH = 2.05, δC = 29.84) and in DMSO-d_6 (δH = 2.50, δC = 39.52). Multiplicities are described as s (singlet), d (doublet), t (triplet), brs (broad peak) etc. Coupling constants, *J* values, are reported in Hz. High-resolution mass spectra (HRMS) were obtained using an orthogonal acceleration time-of-flight (oa-TOF) mass spectrometer equipped with an electrospray source and in the positive and negative modes (ESI+/-).

II. Copies of 1H and 13C NMR

1*H*-Indazole-3-carboxaldehyde (1b)



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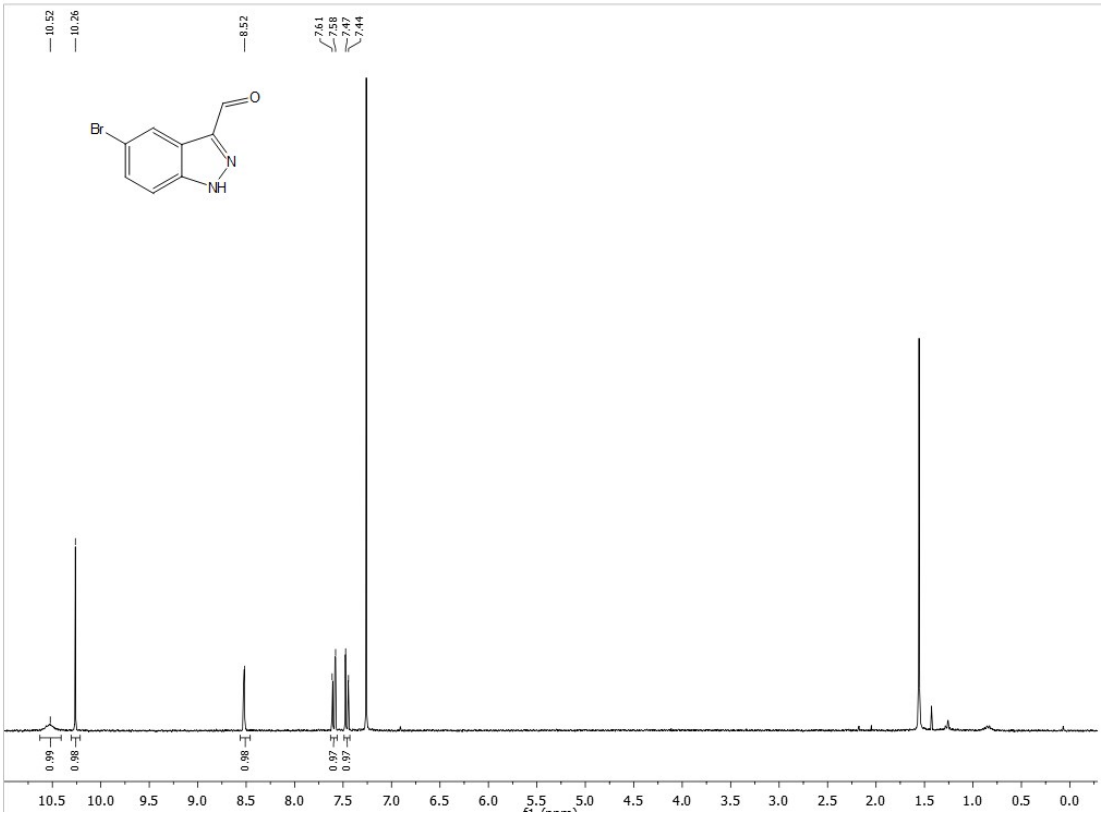
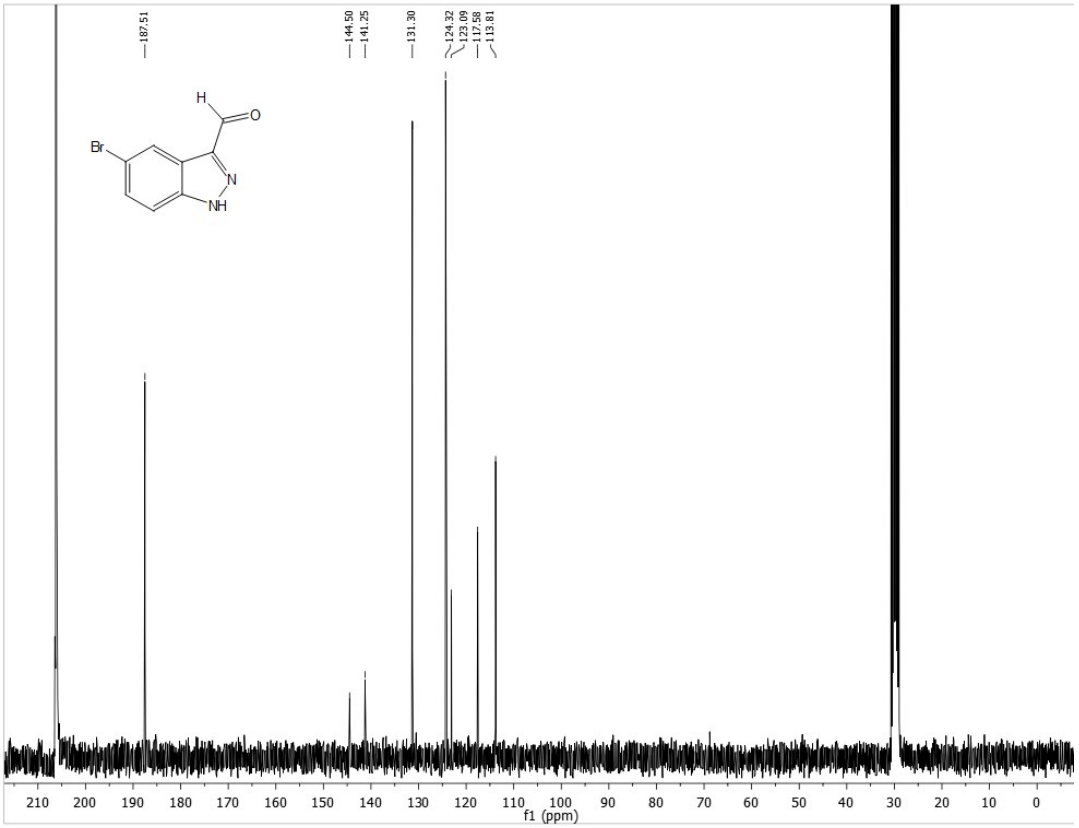
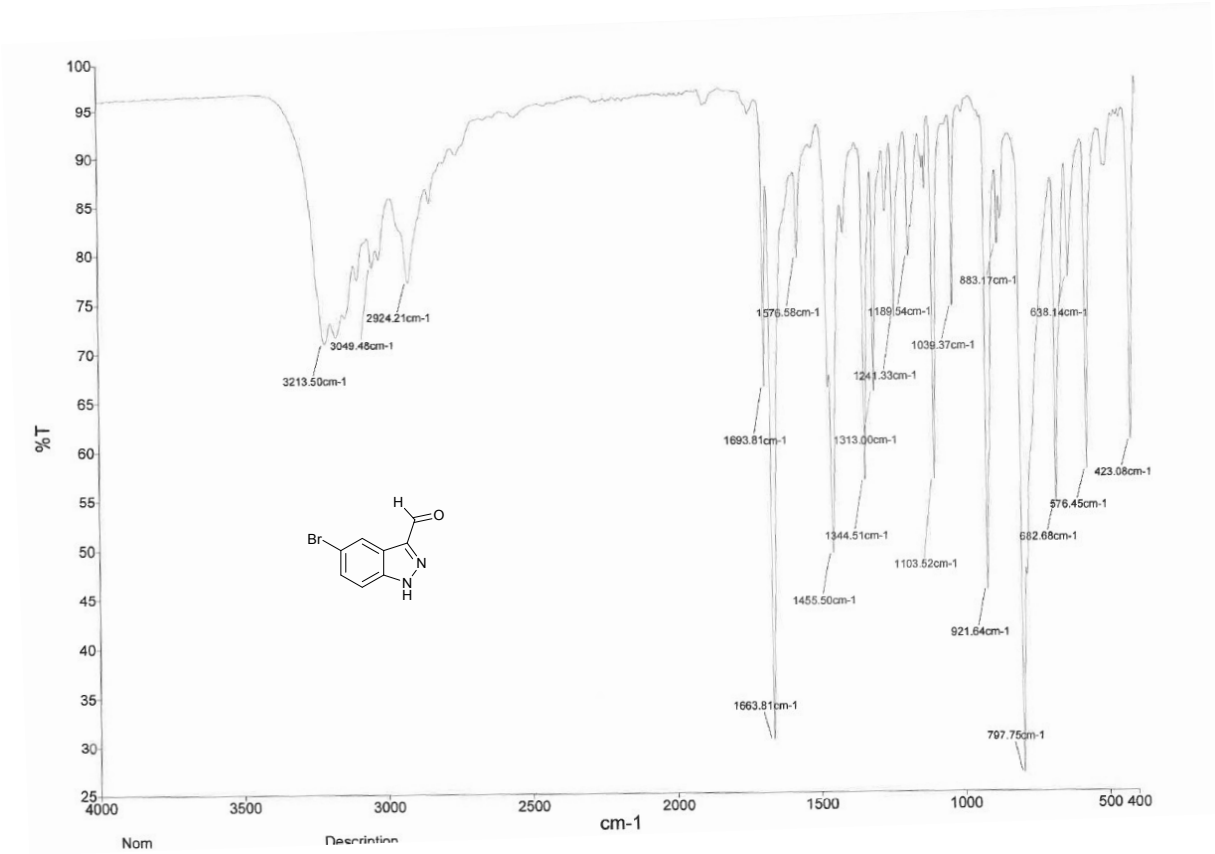
5-Bromo-1*H*-Indazole-3-carboxaldehyde (11b)



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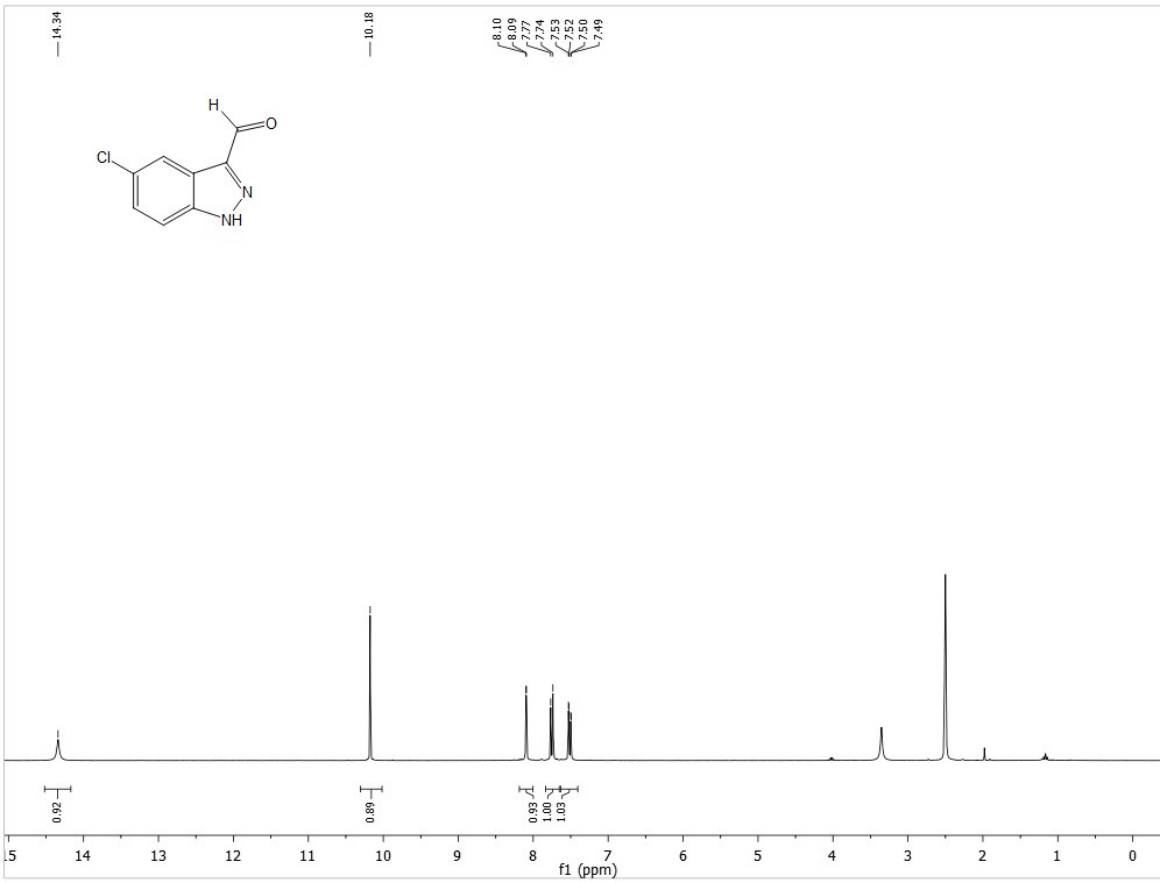
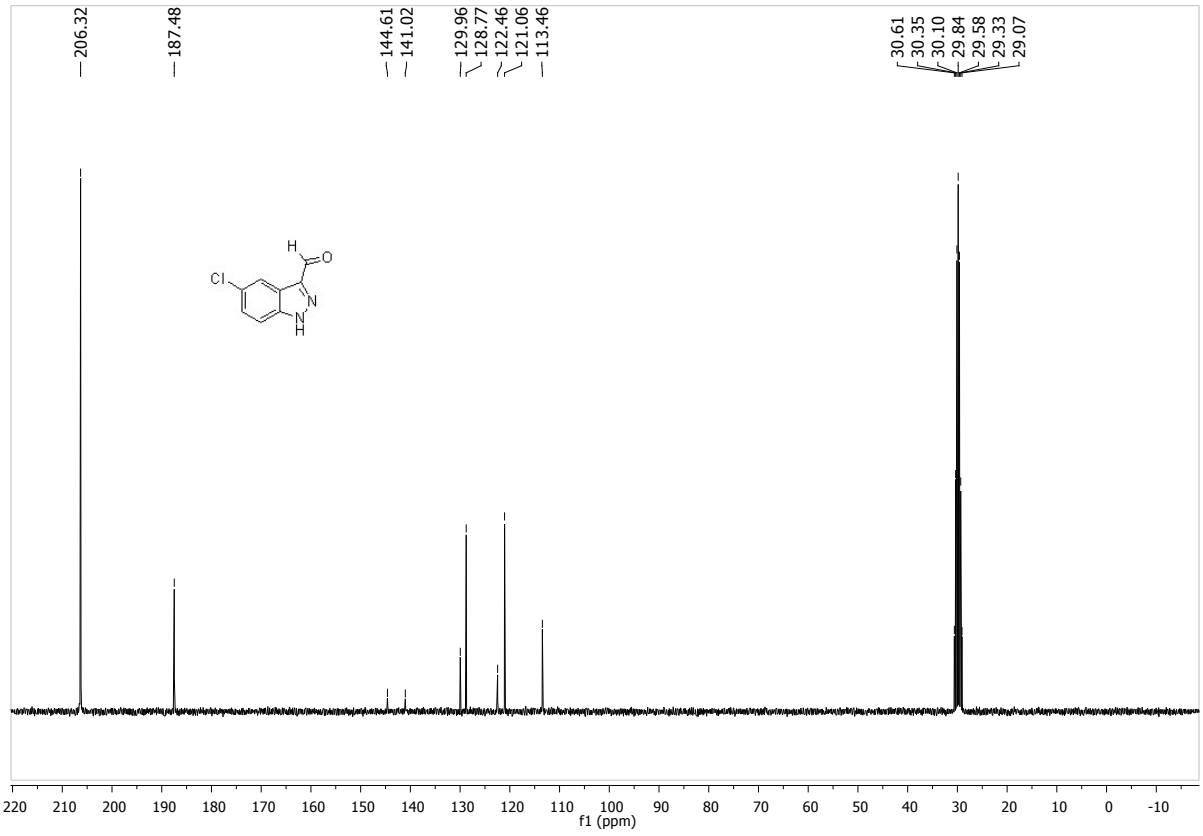
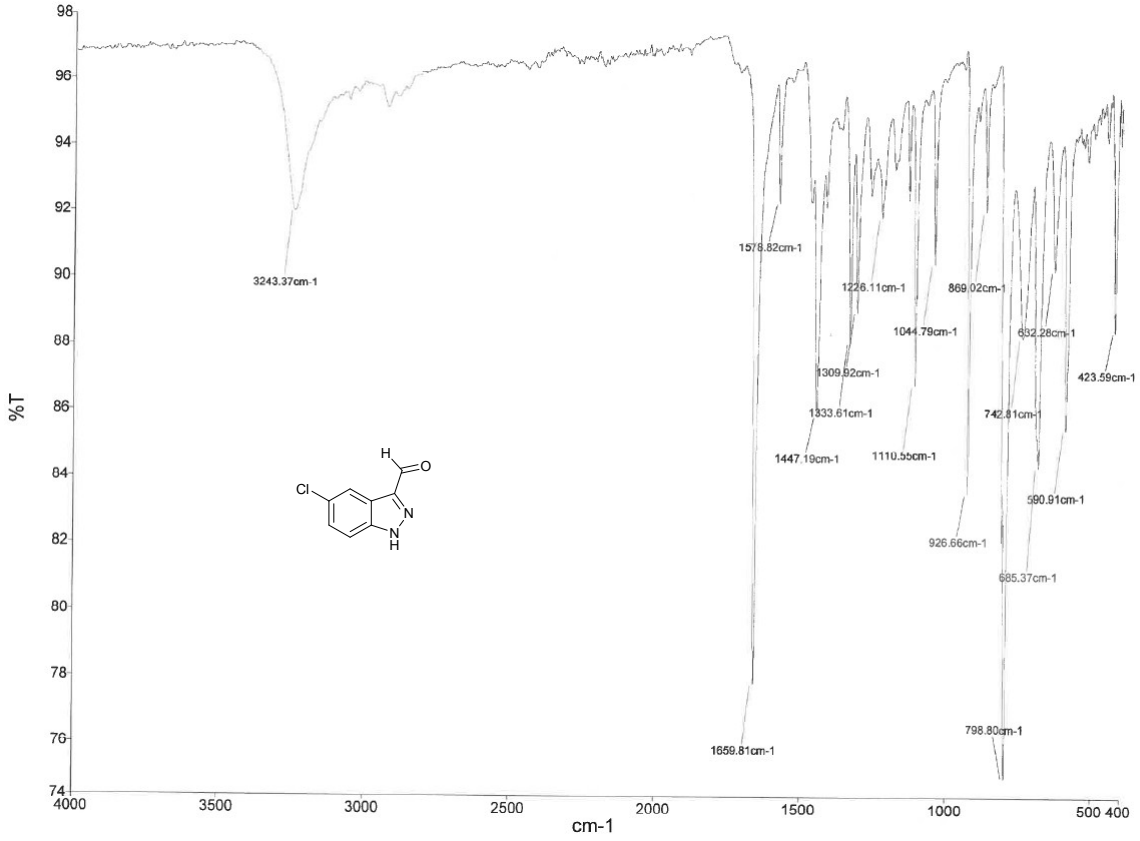
H

5-chloro-1*H*-indazole-3-carboxaldehyde (12b)



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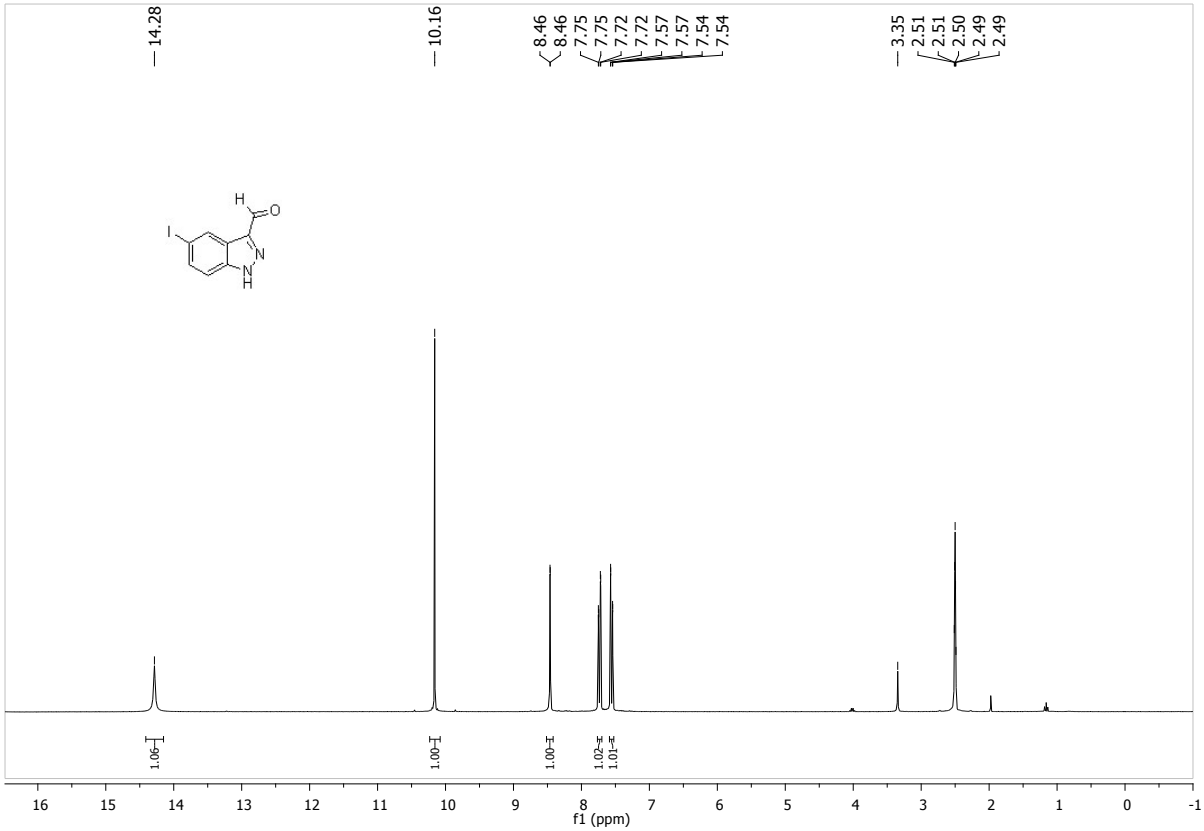
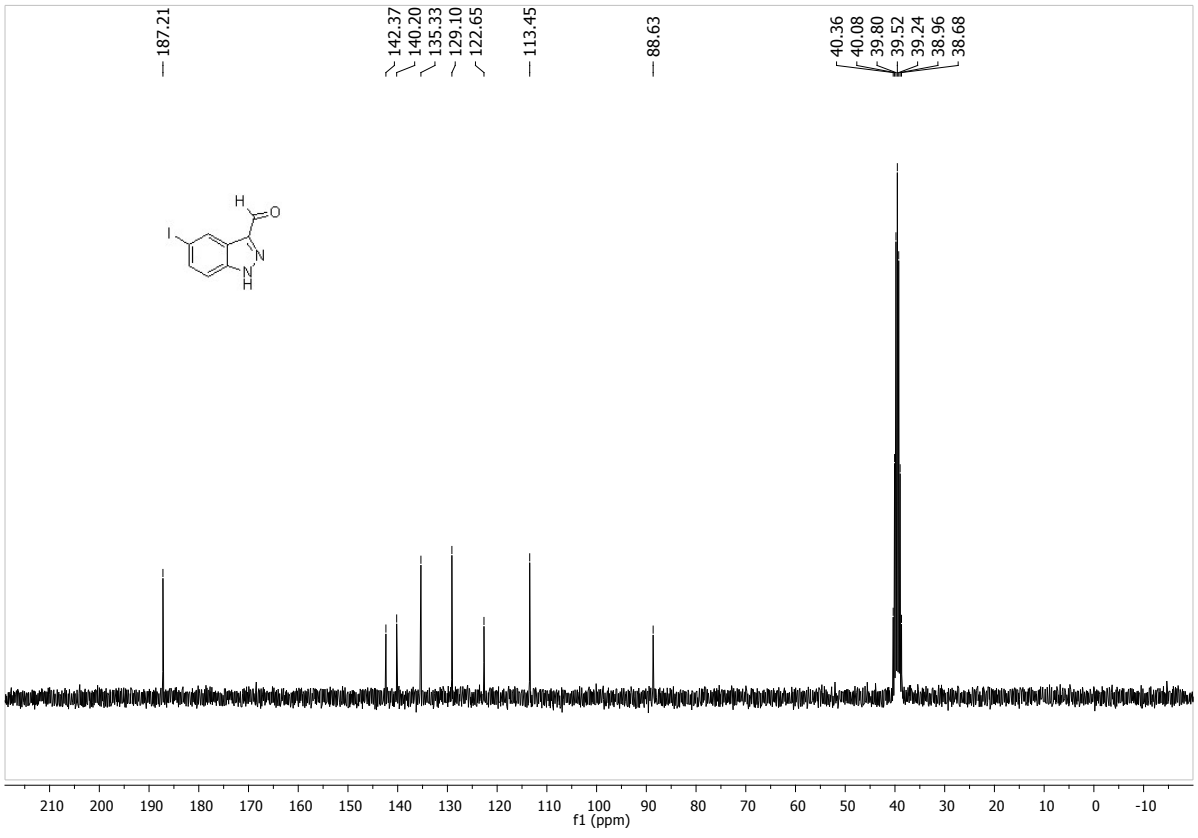
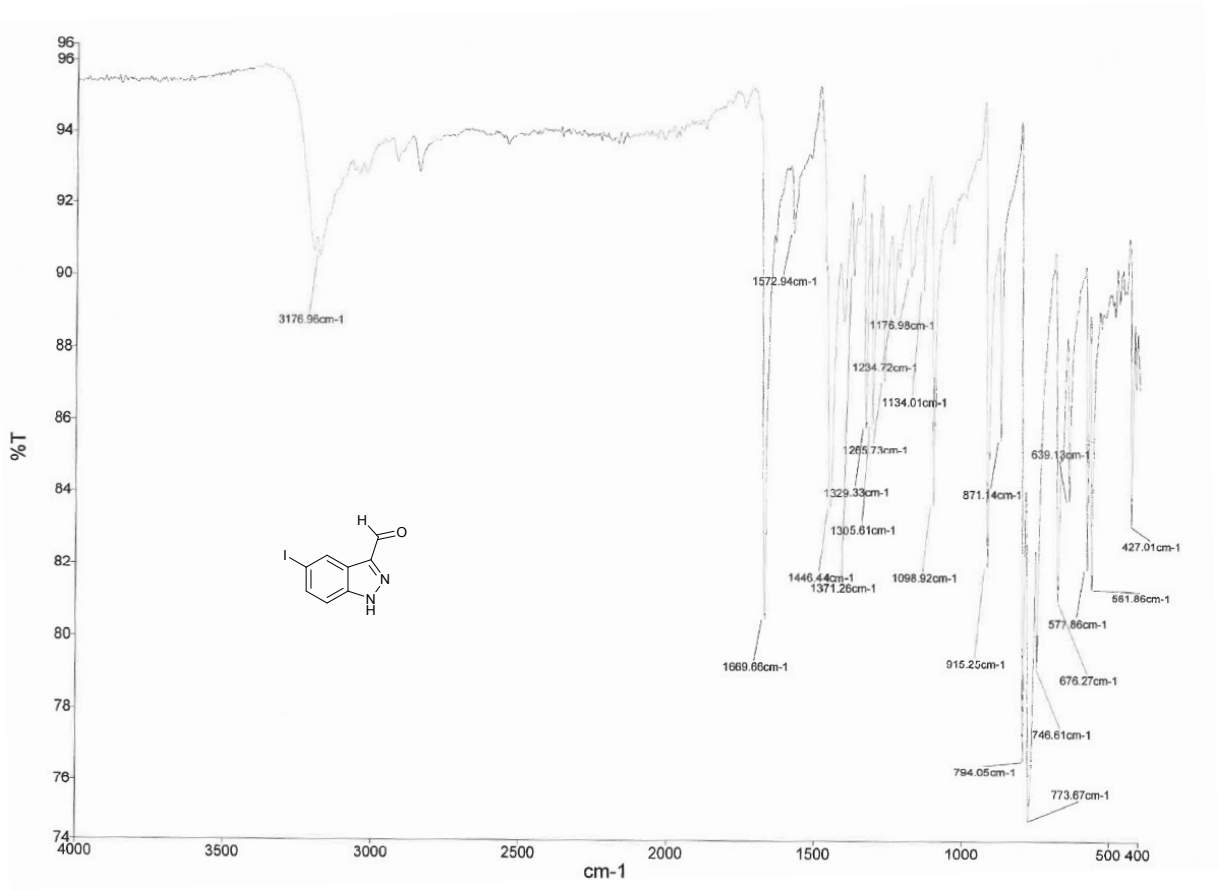
H
O

5-iodo-1*H*-indazole-3-carboxaldehyde (13b)



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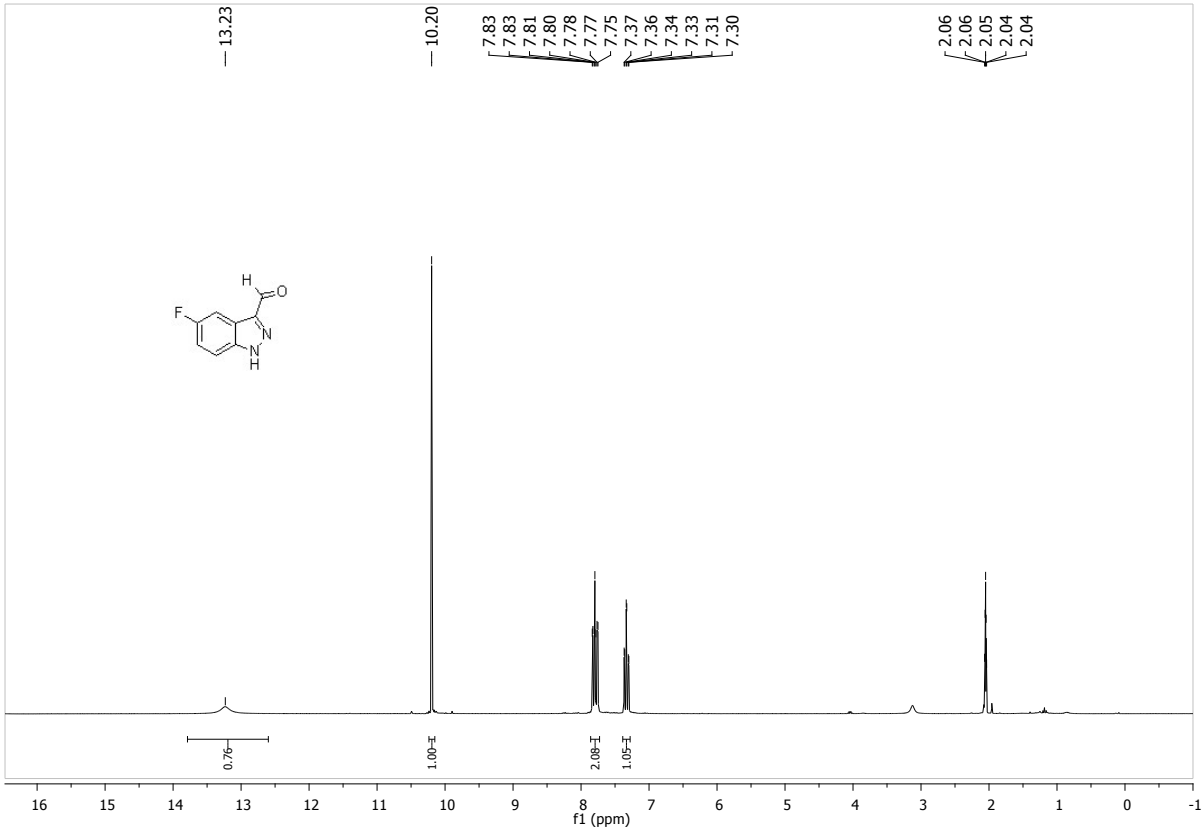
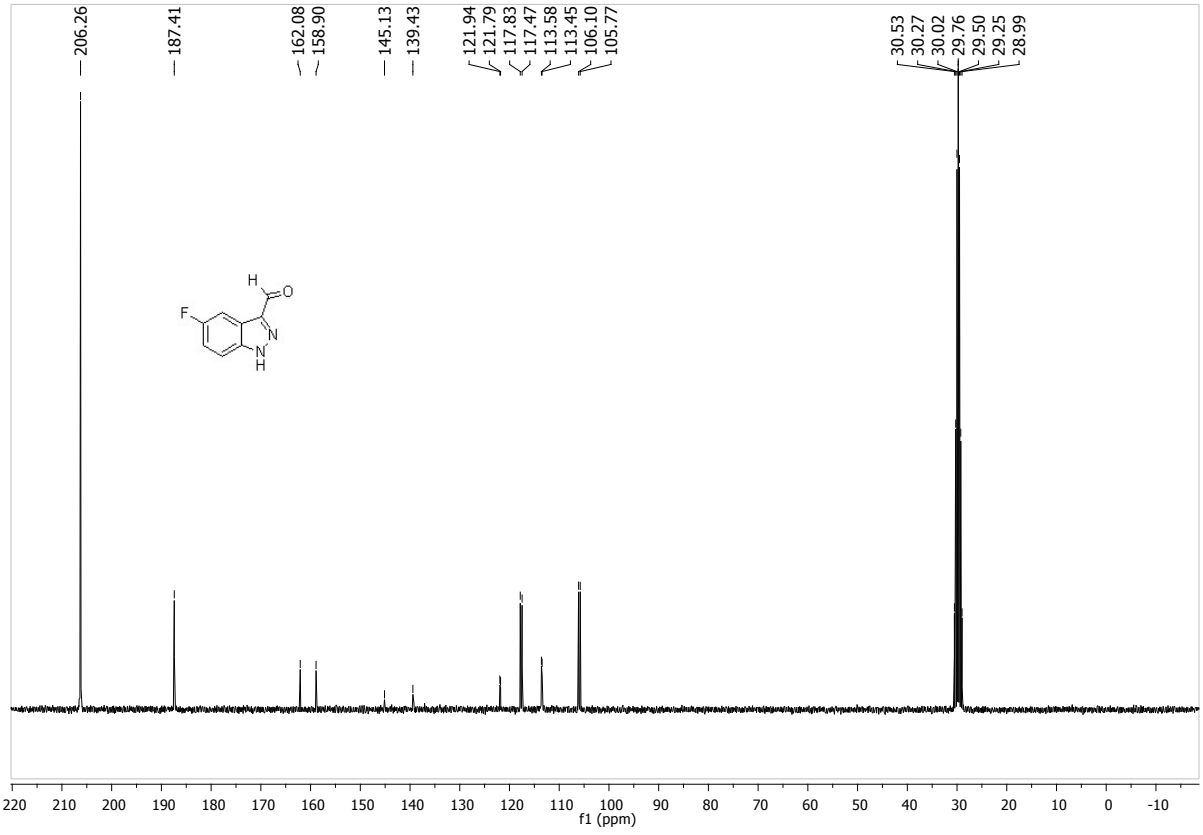
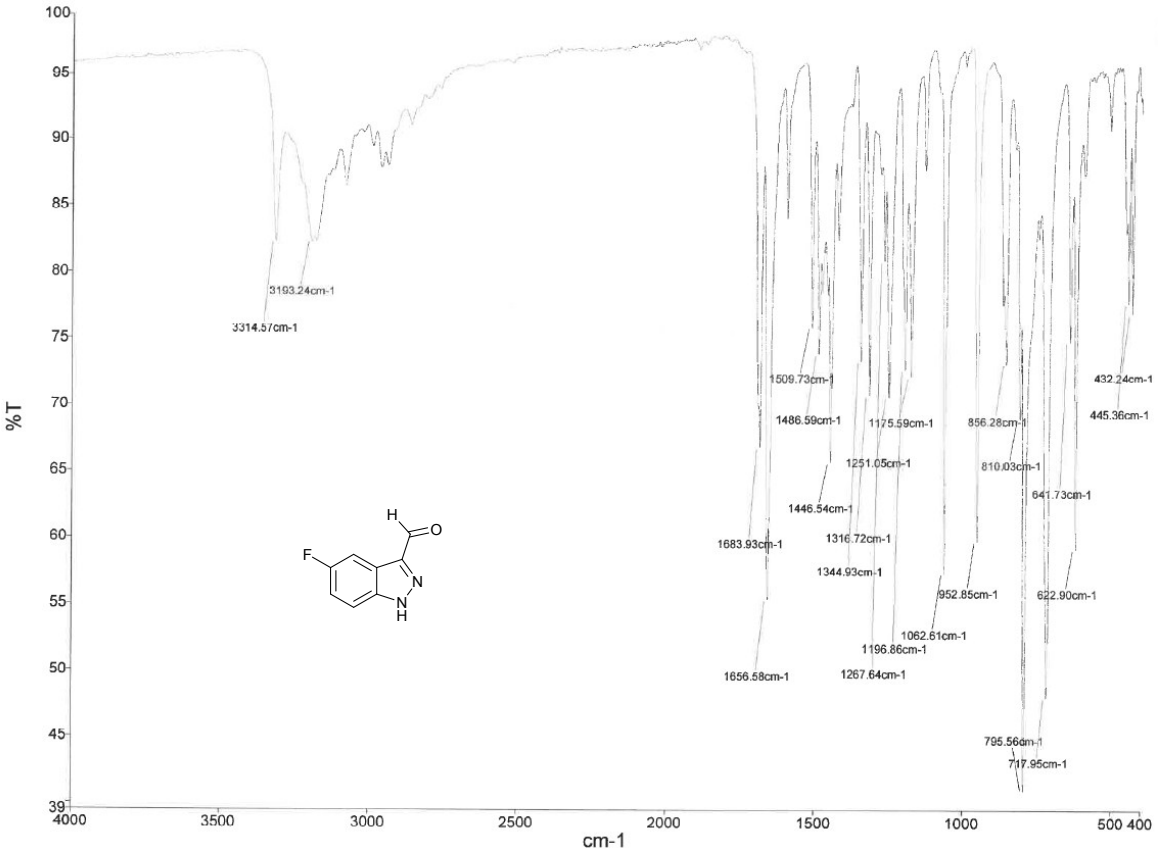
H

5-fluoro-1*H*-indazole-3-carboxaldehyde (14b)



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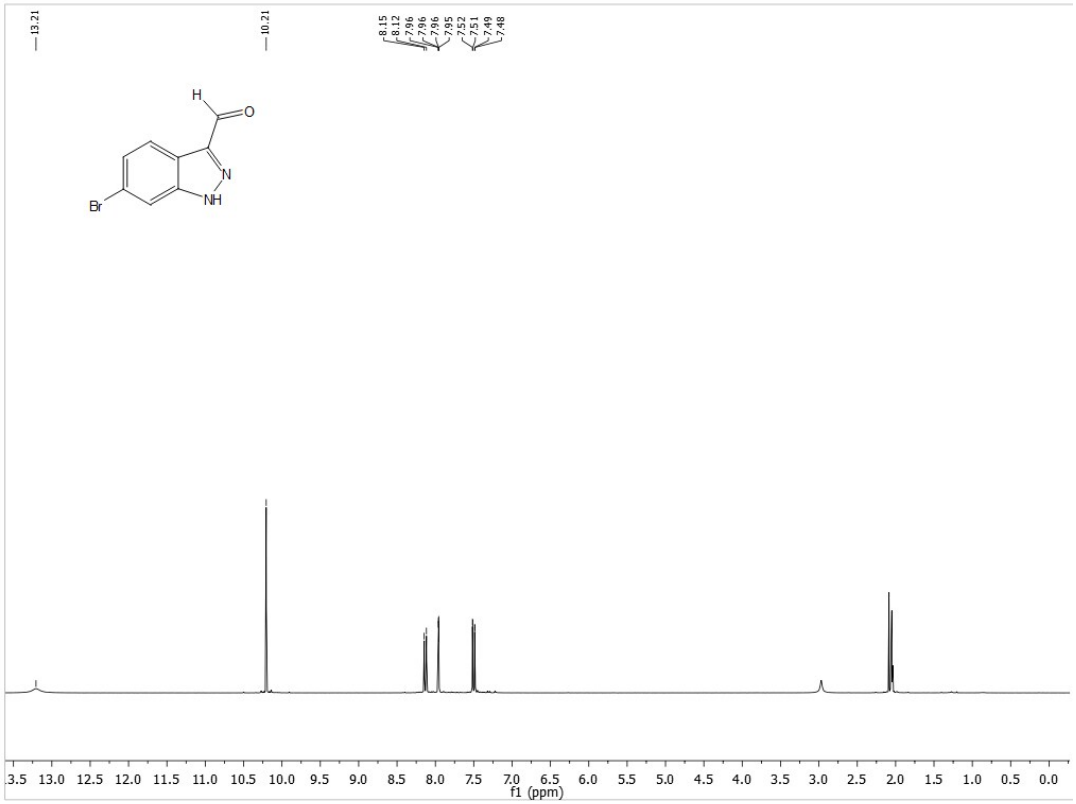
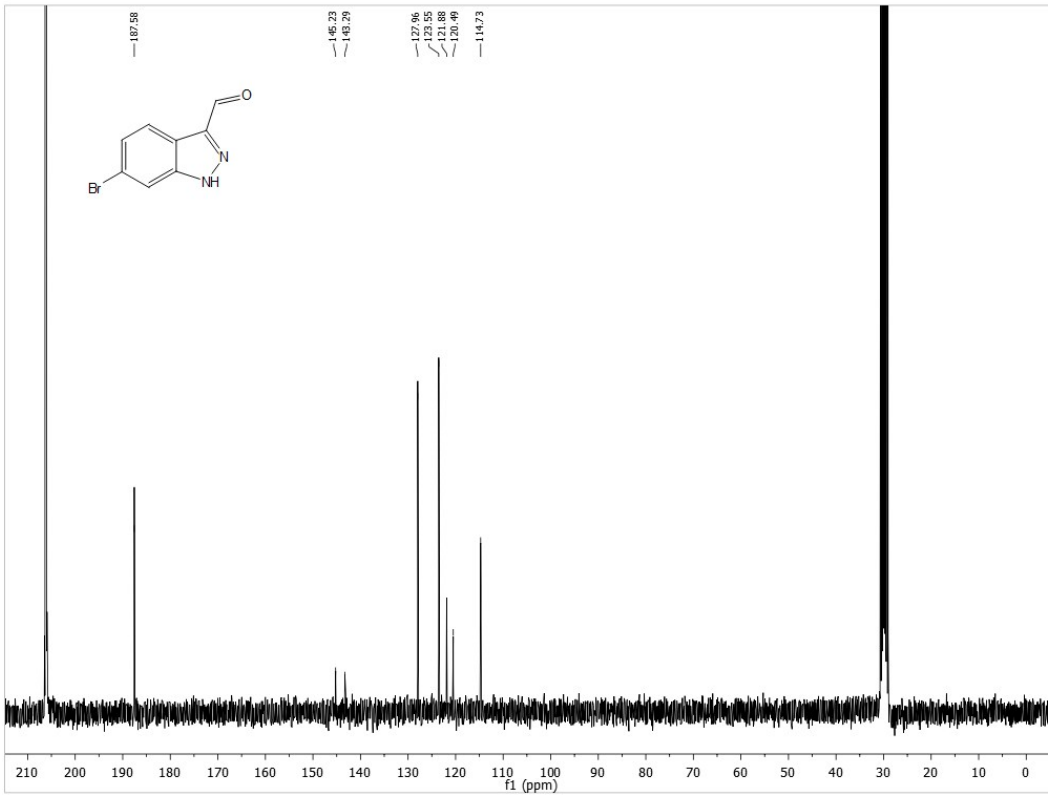
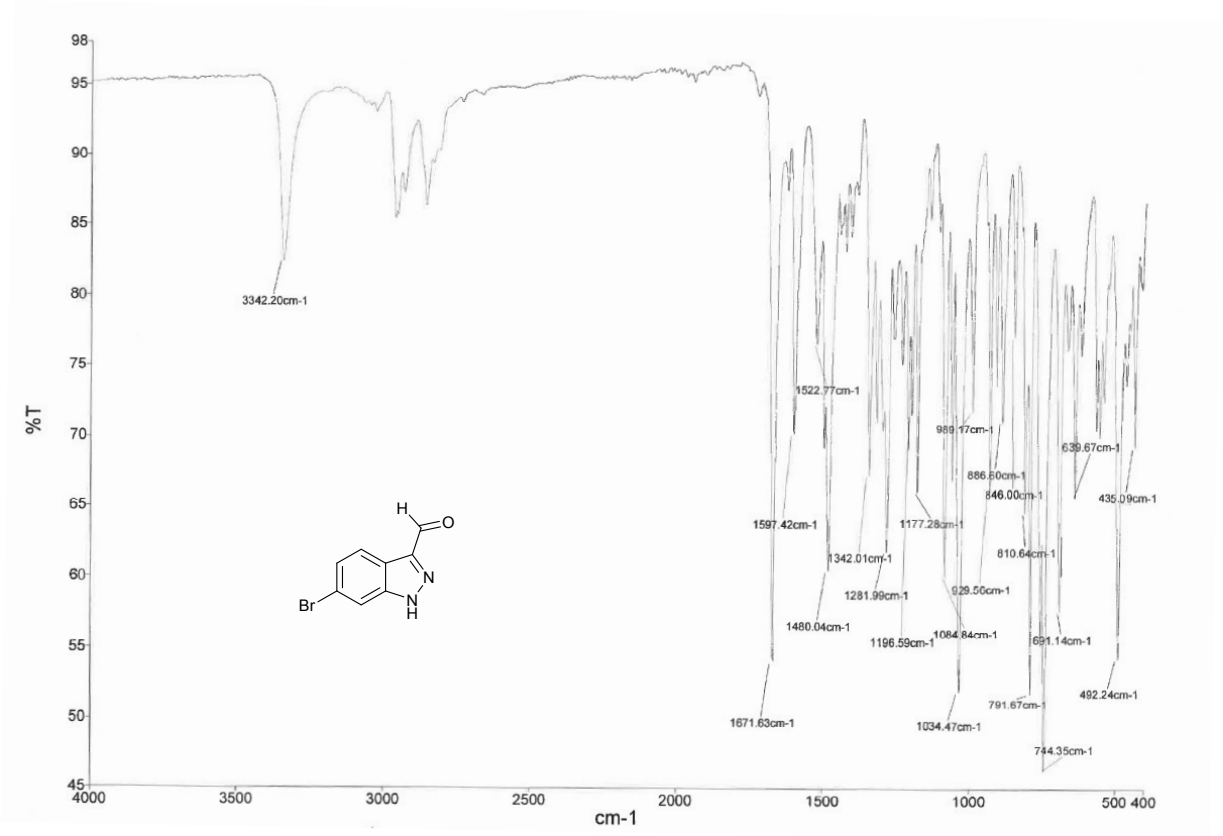
H

6-bromo-1*H*-Indazole-3-carboxaldehyde (15b)



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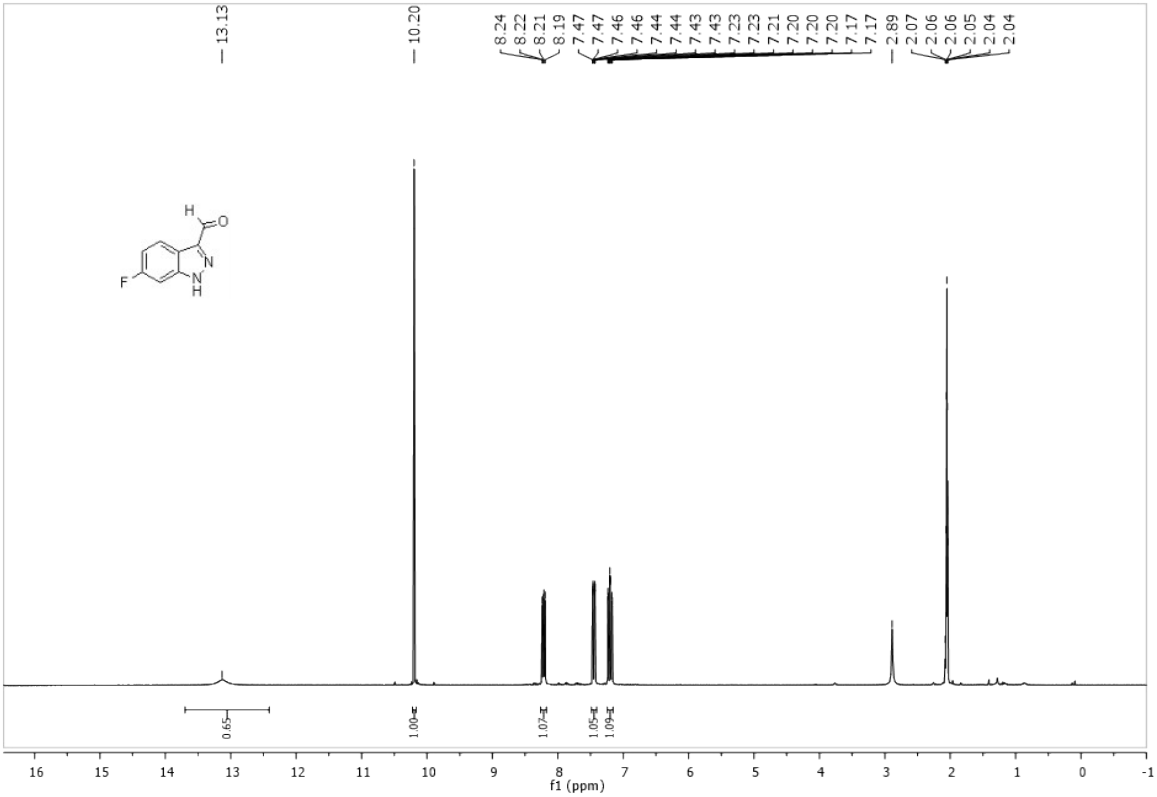
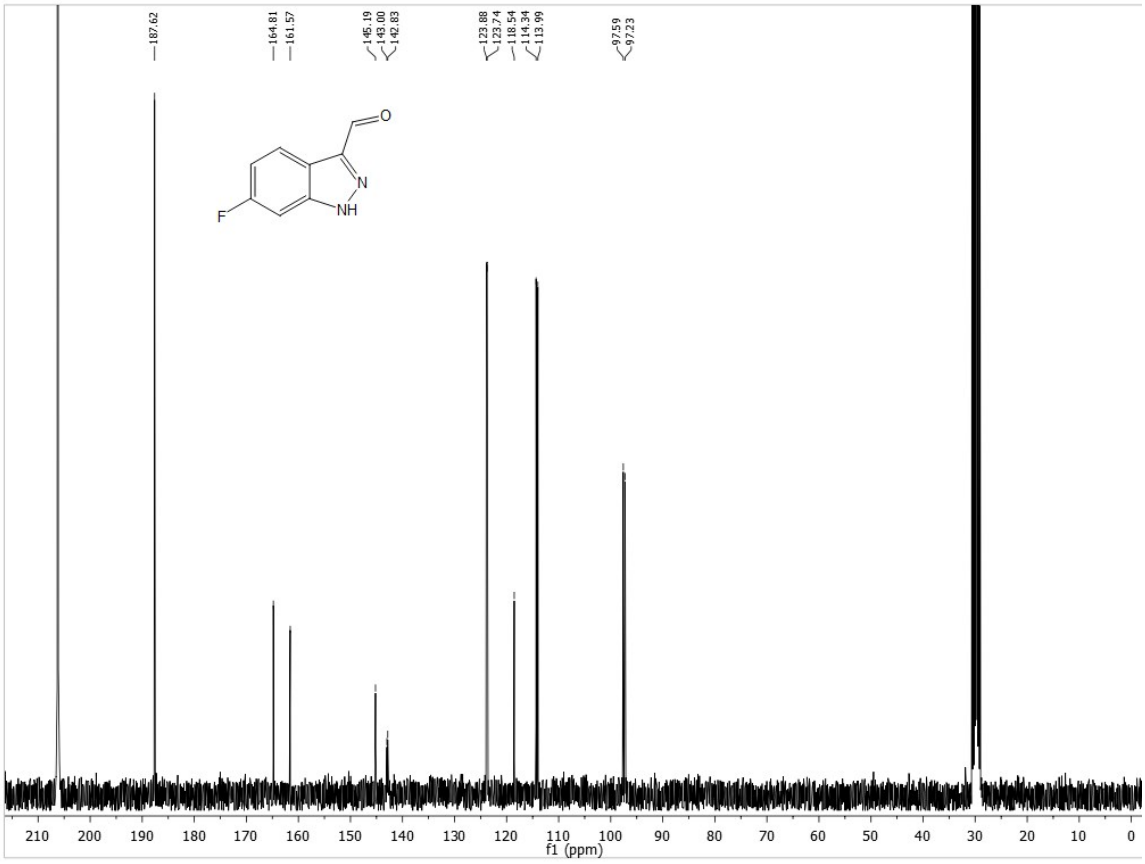
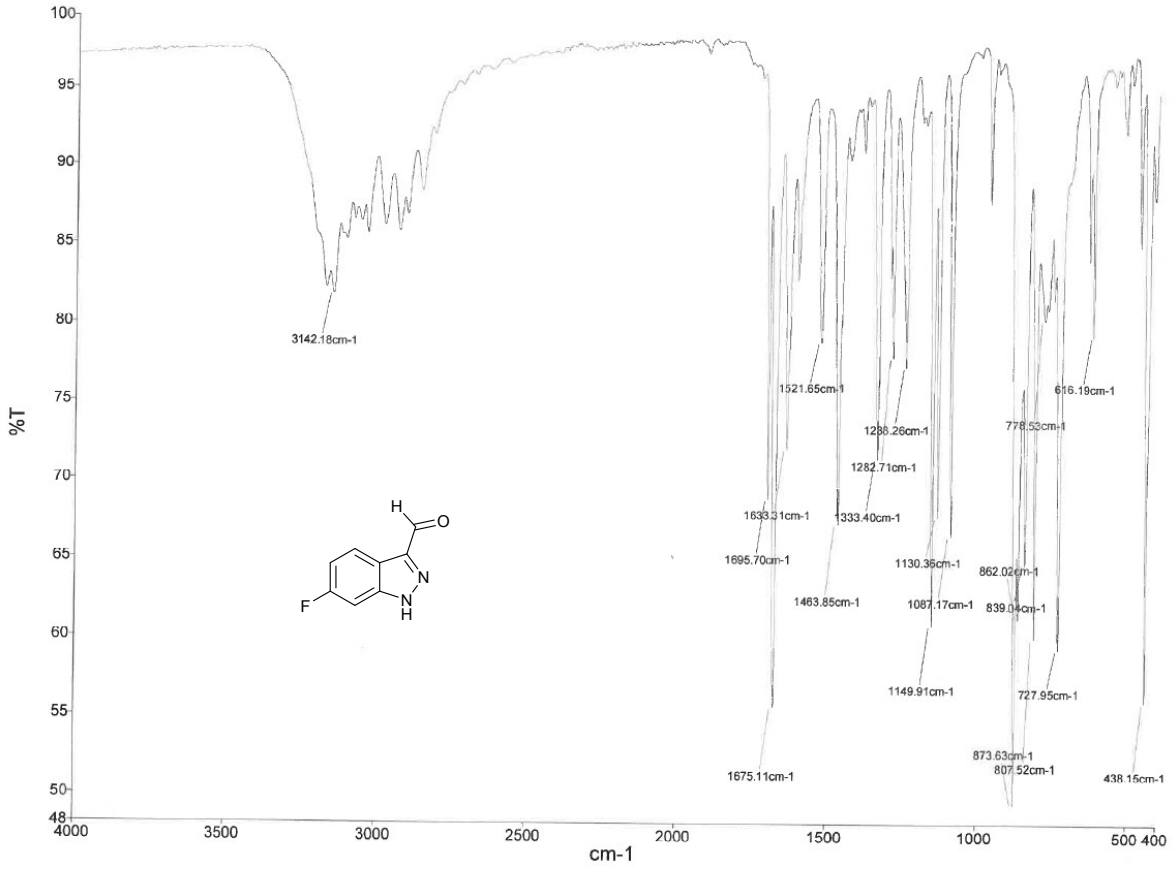
6-fluoro-1*H*-indazole-3-carboxaldehyde (16b).



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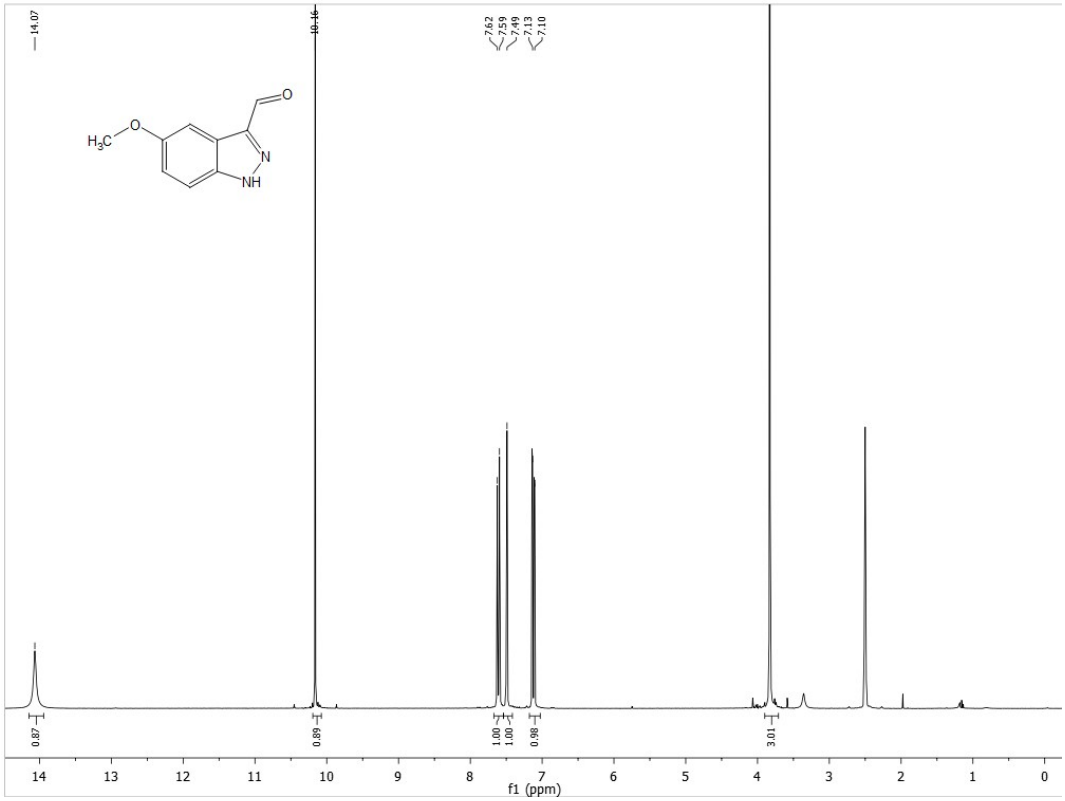
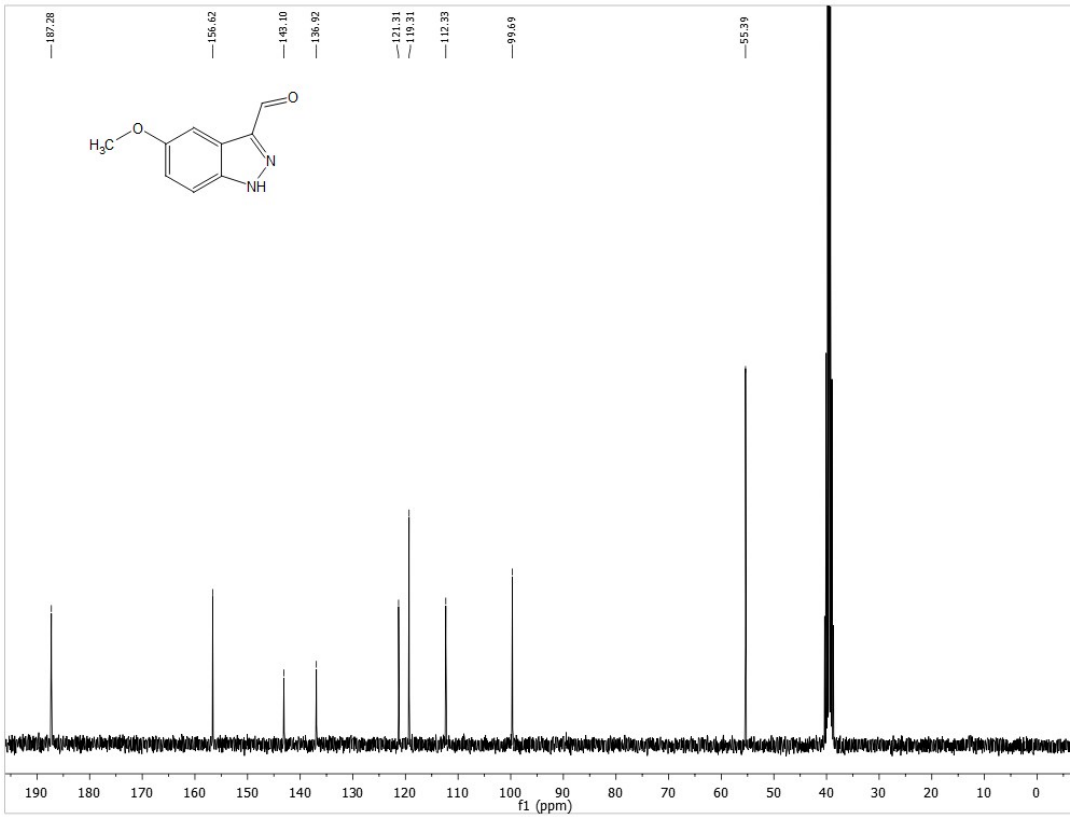
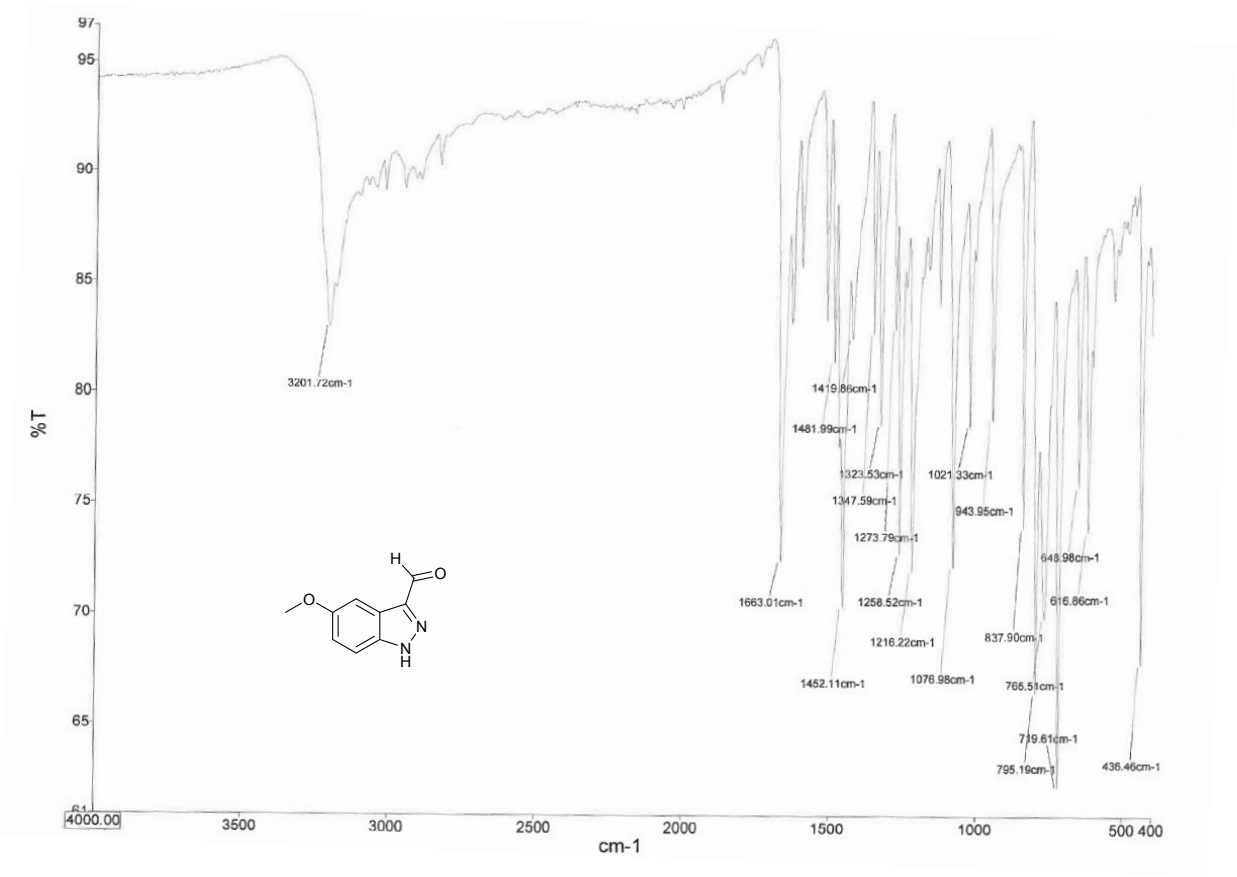
N
H
F

5-Methoxy-1*H*-Indazole-3-carboxaldehyde (17b)



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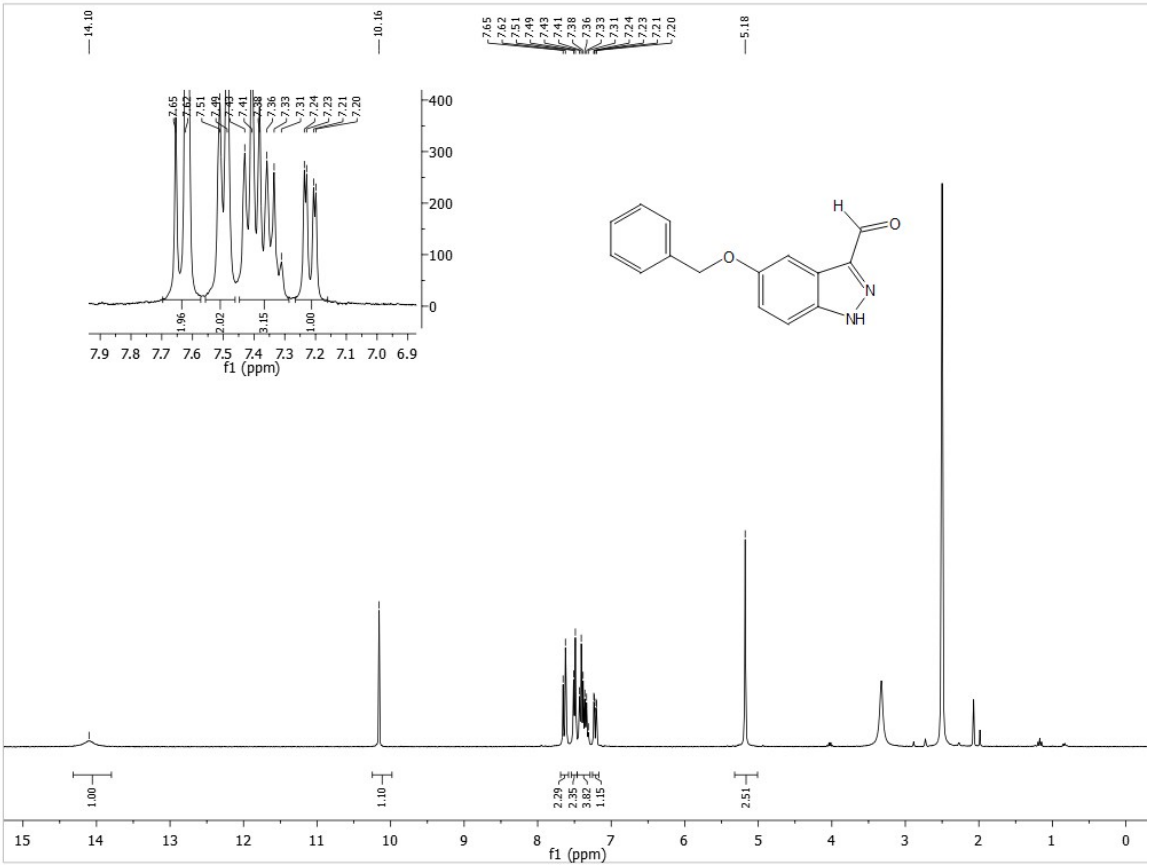
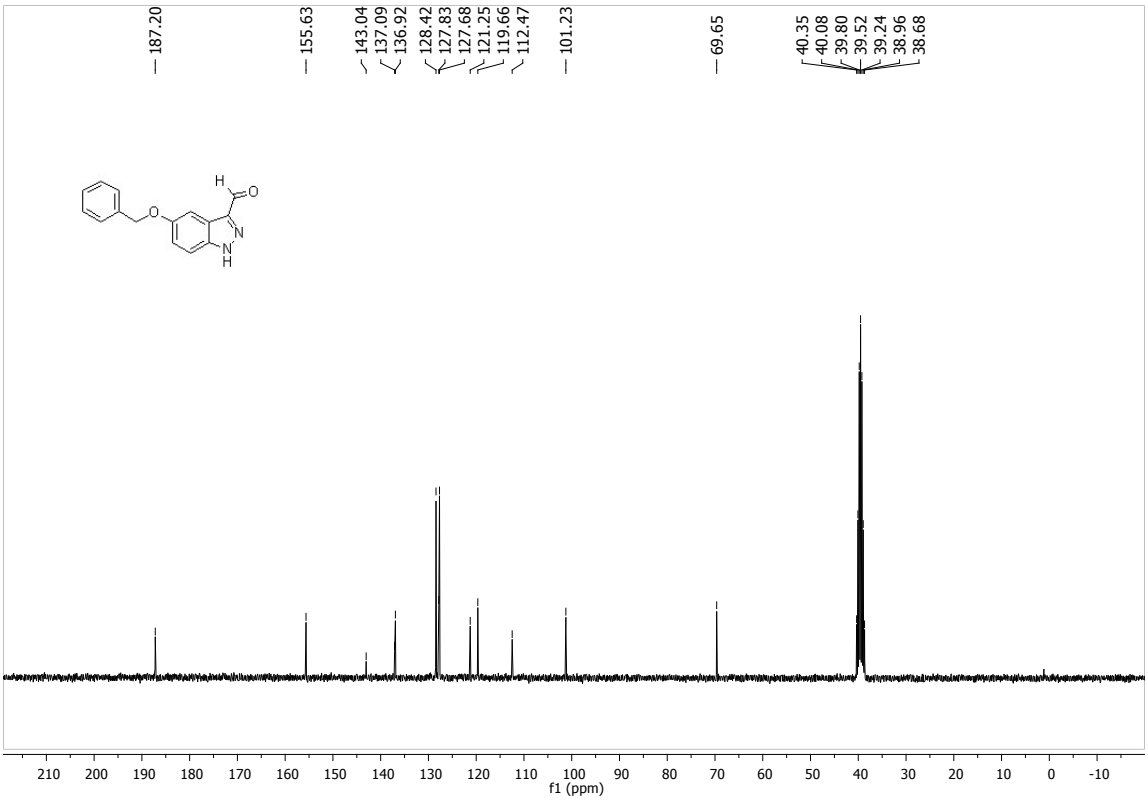
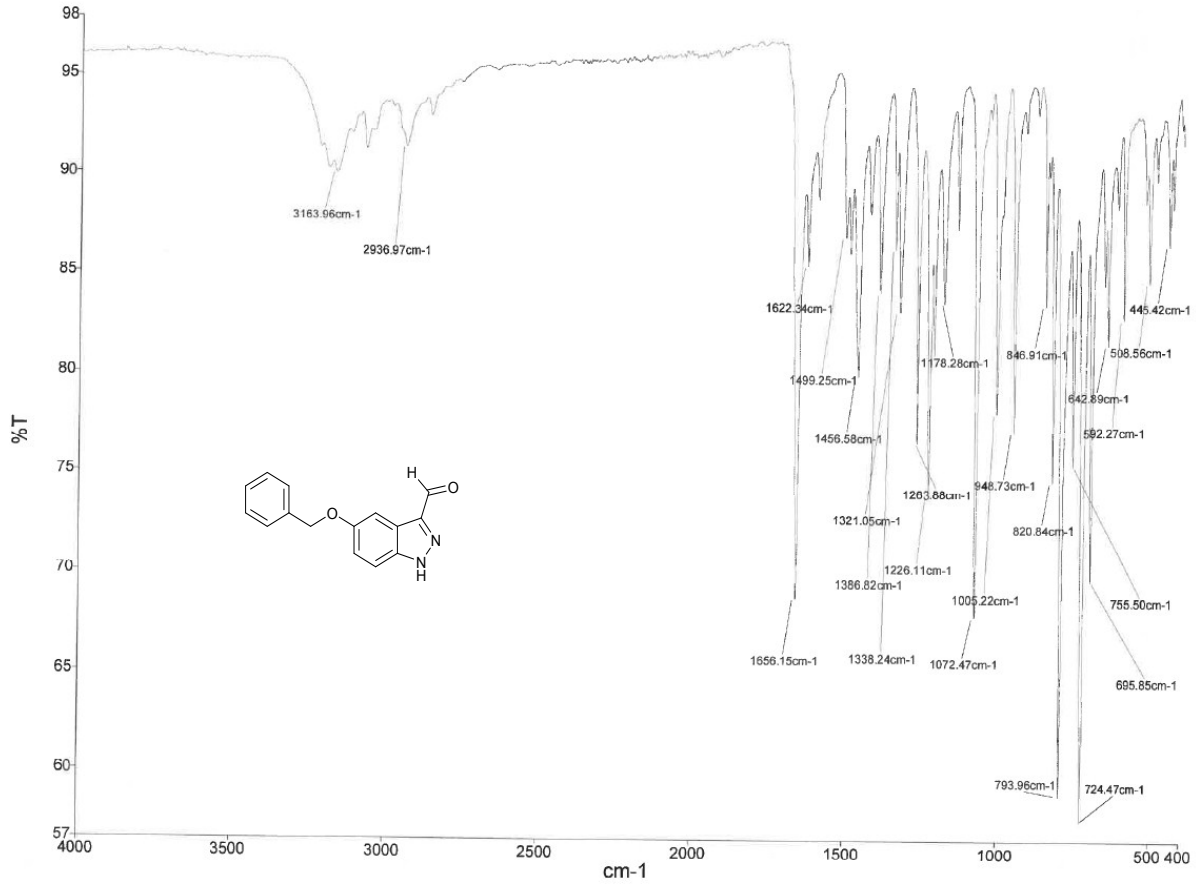
5-Benzyloxy-1*H*-indazole-3-carboxaldehyde (18b)



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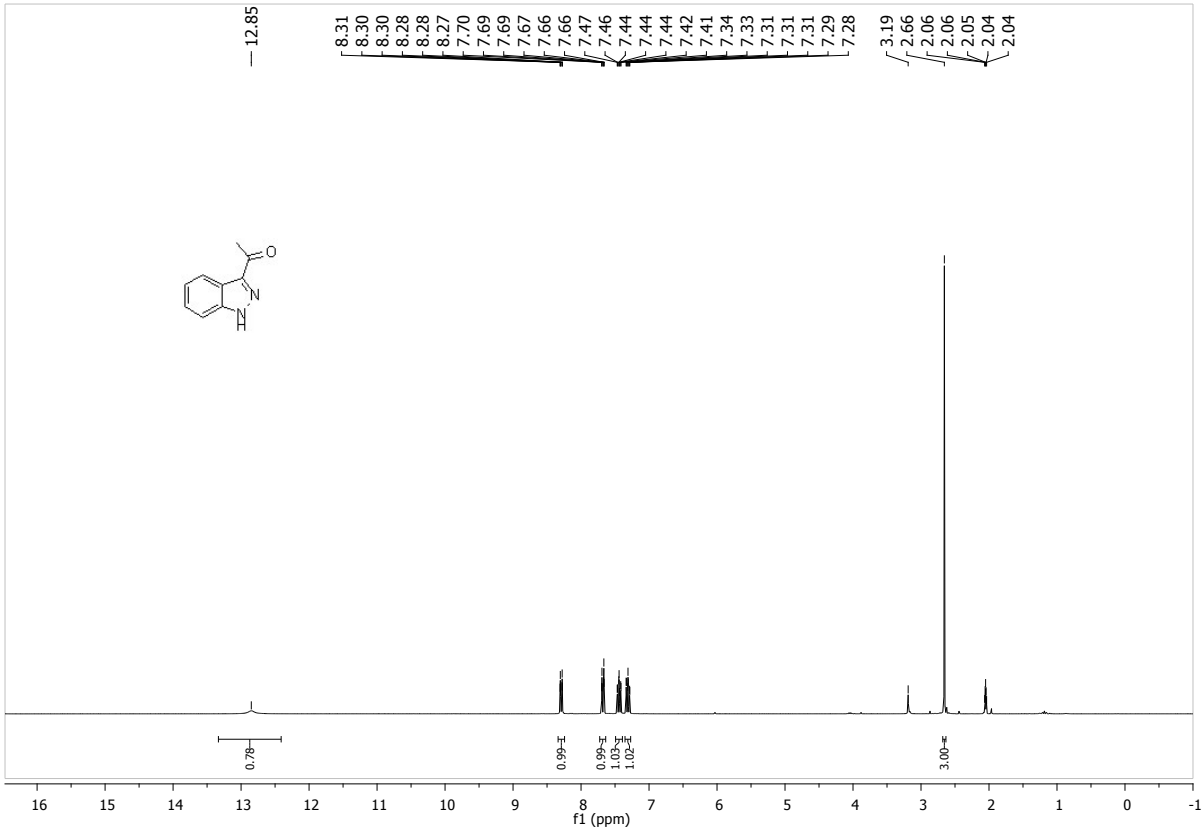
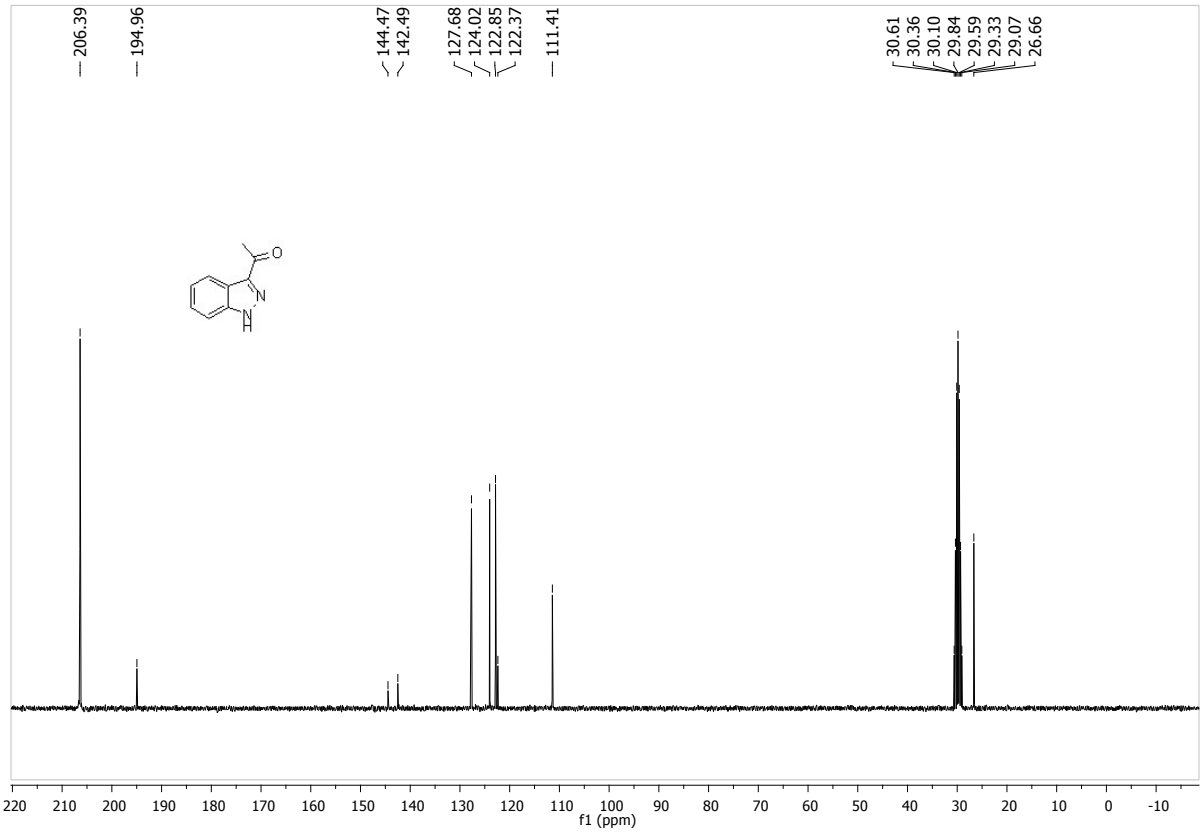
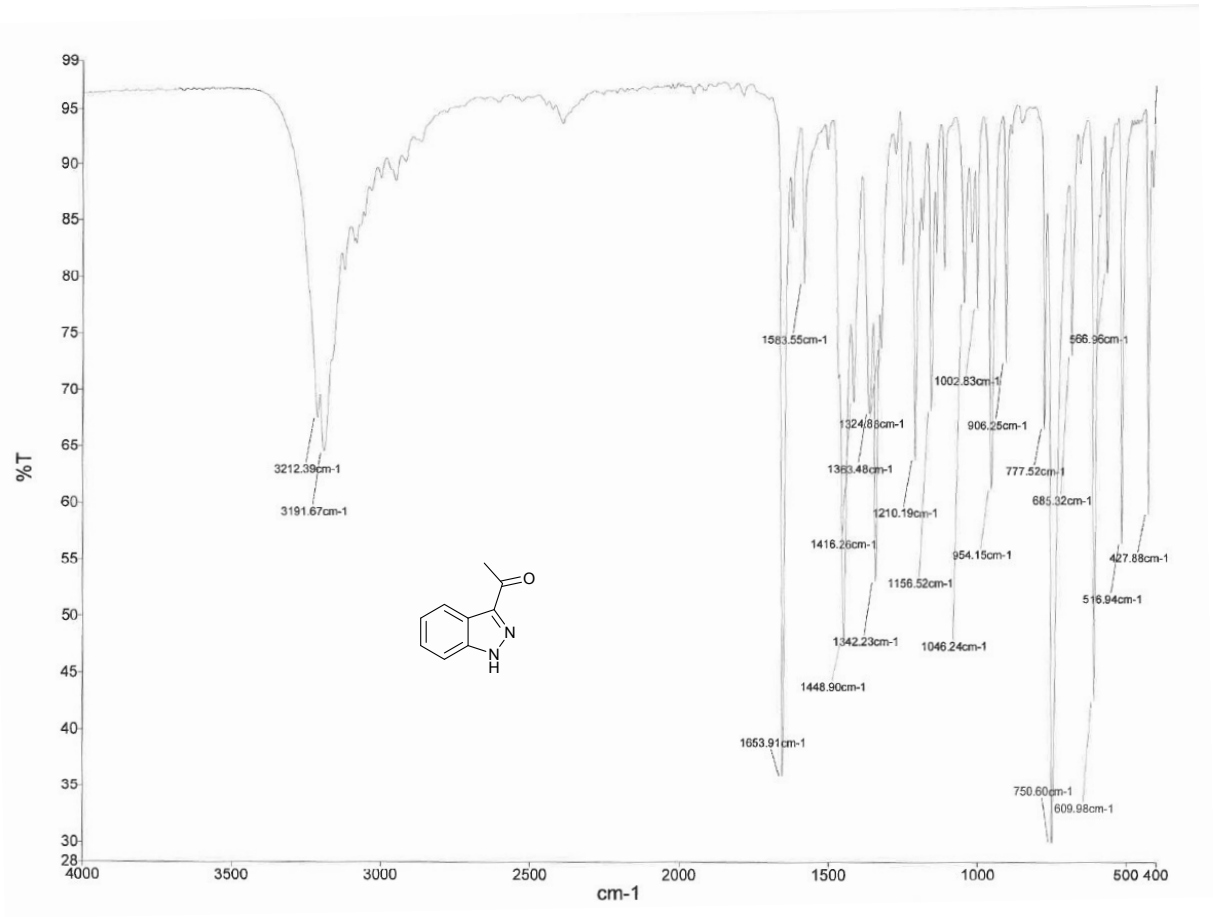
1-(1*H*-indazol-3-yl)ethanone (19b)



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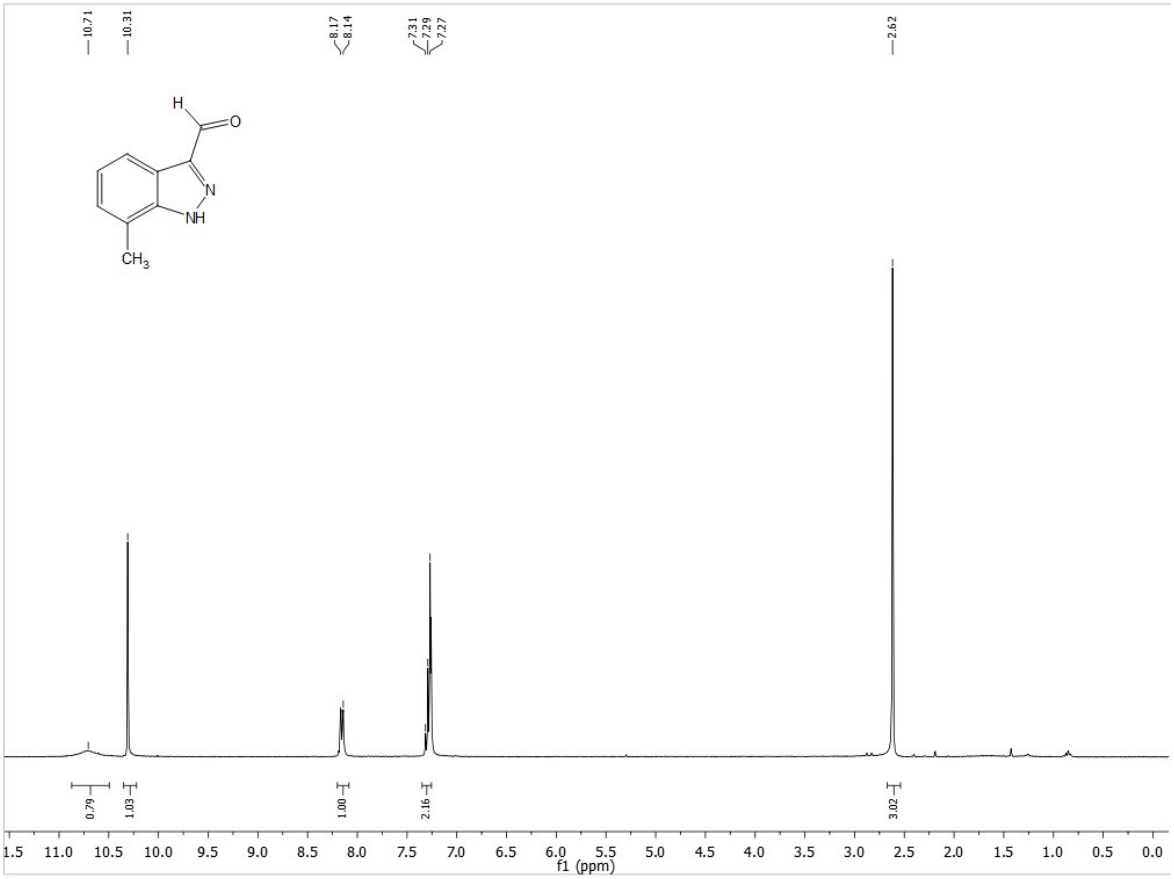
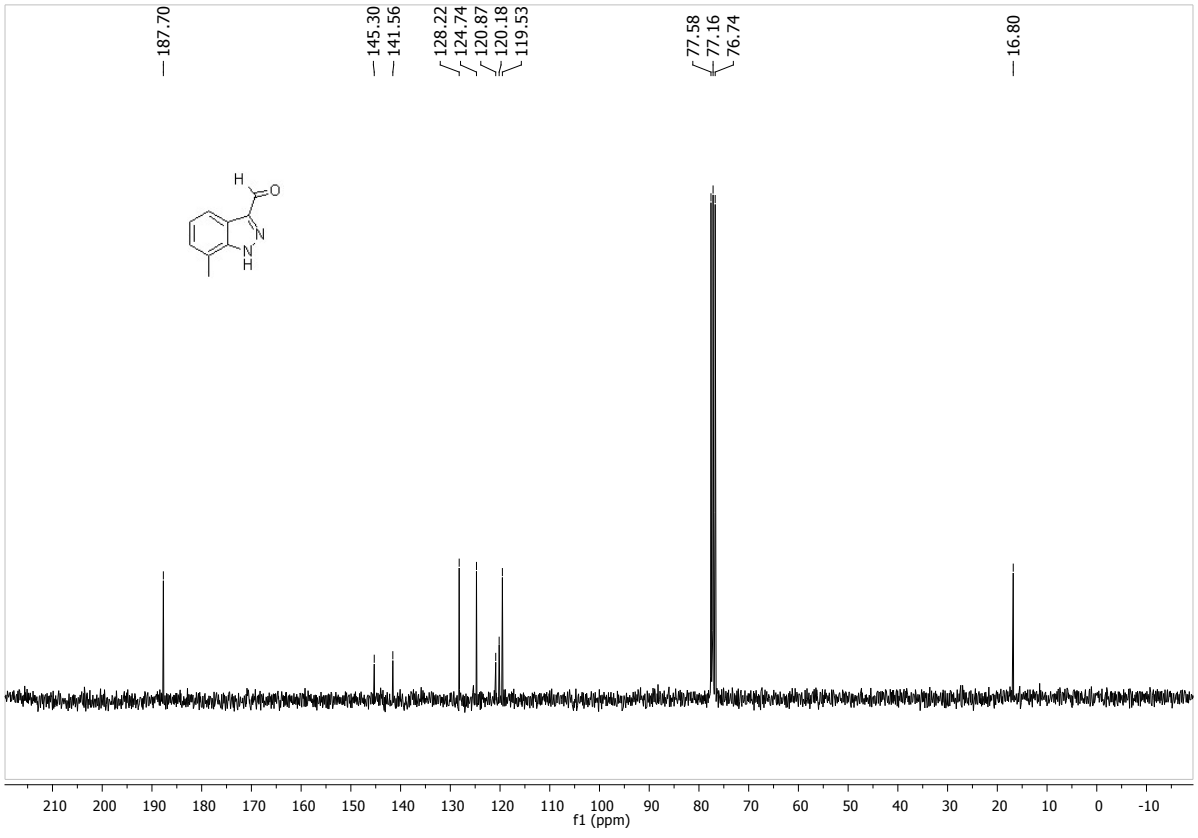
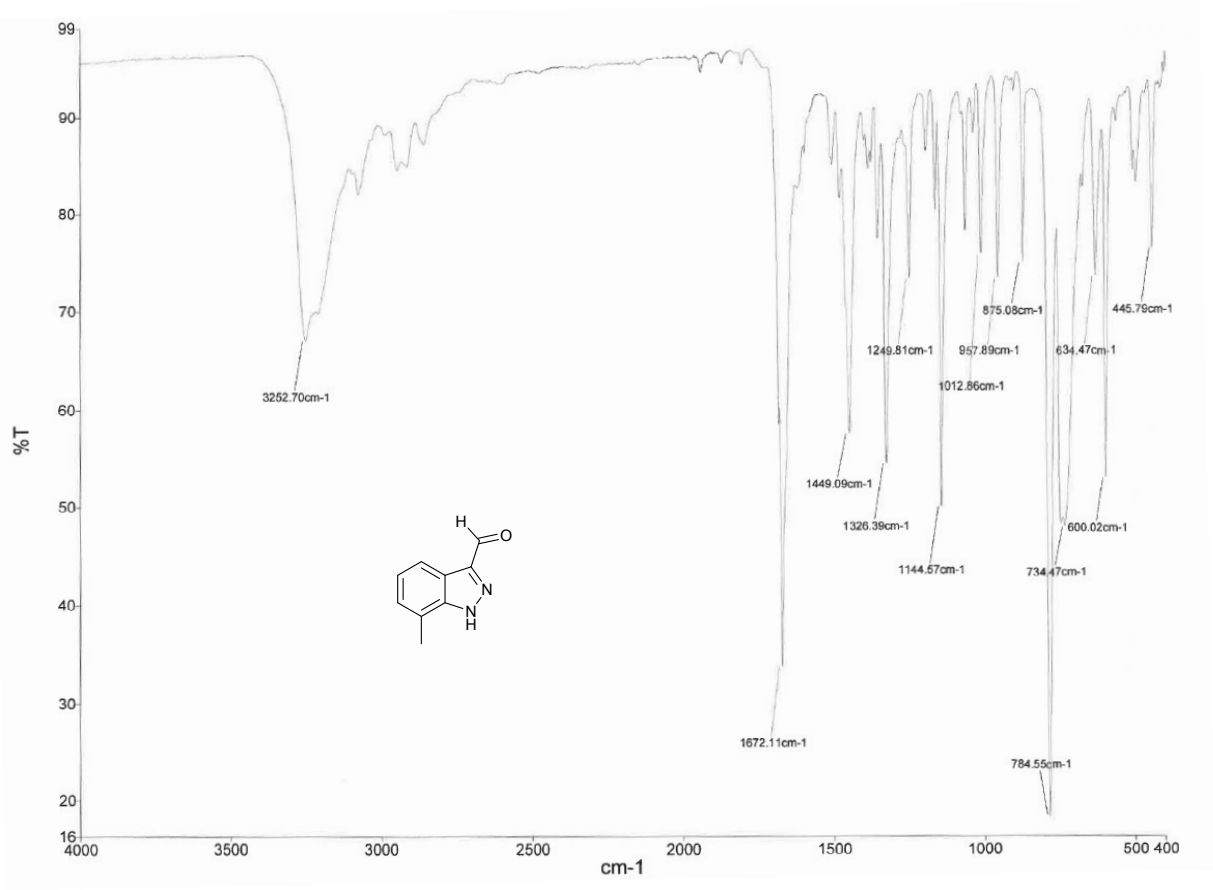
7-methyl-1*H*-indazole-3-carboxaldehyde (20b)



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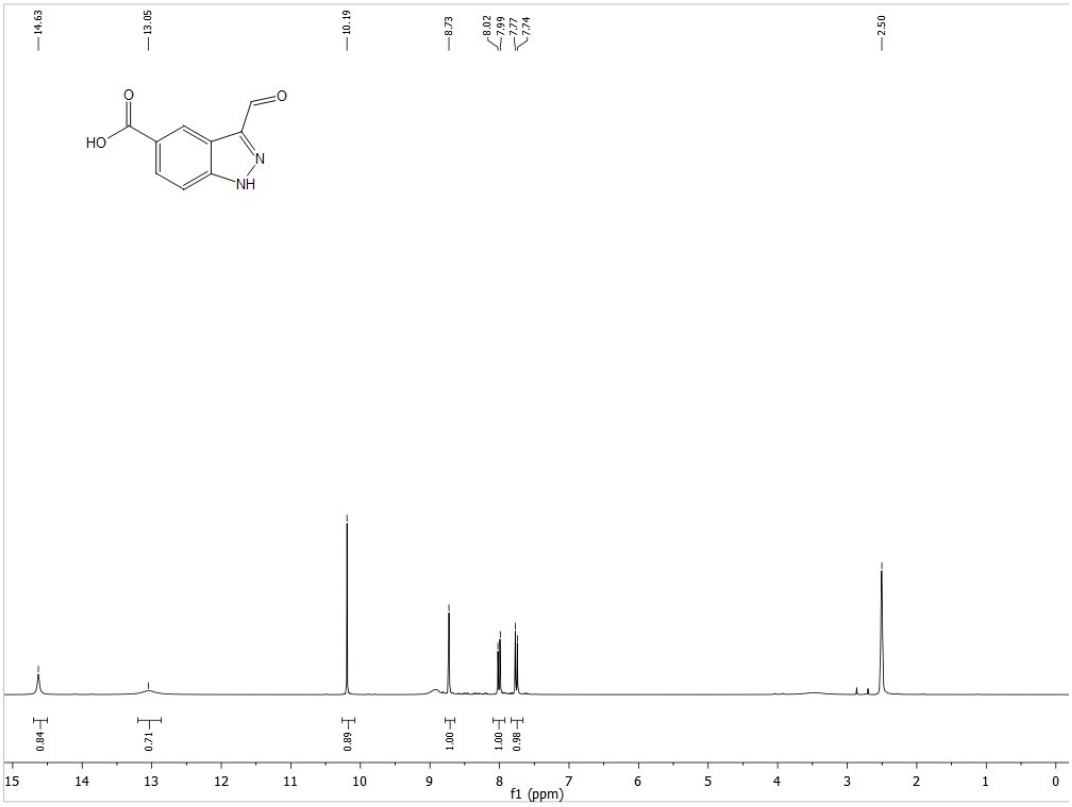
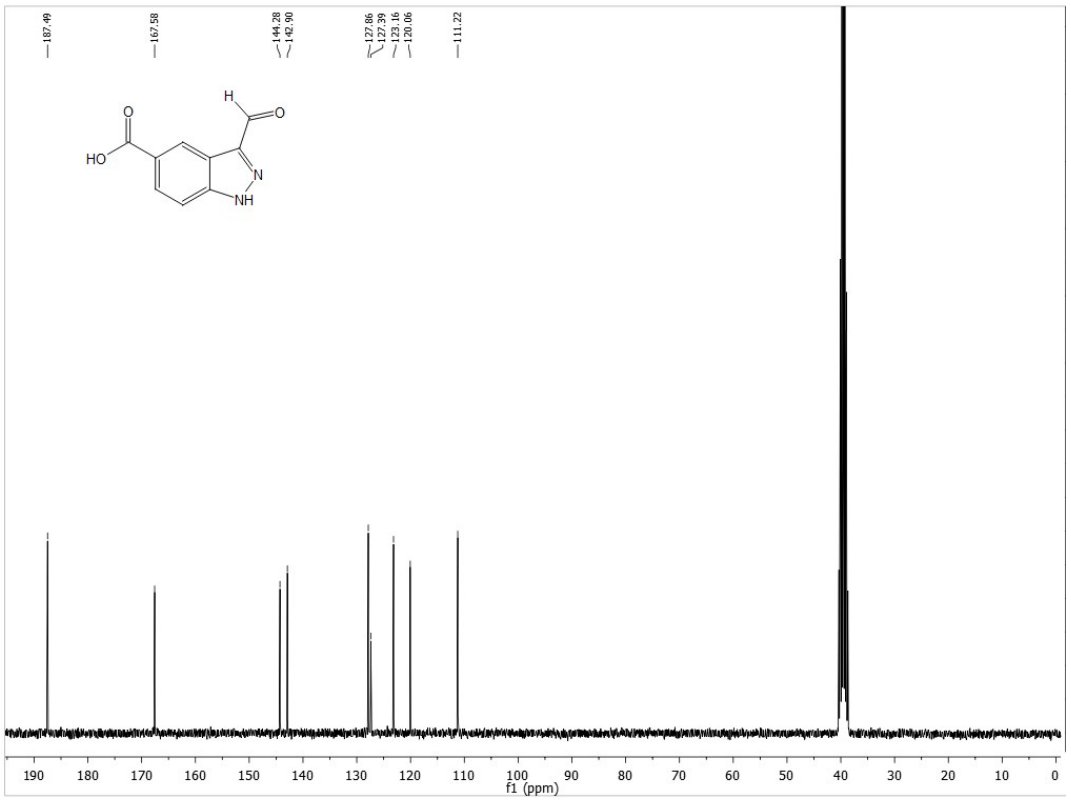
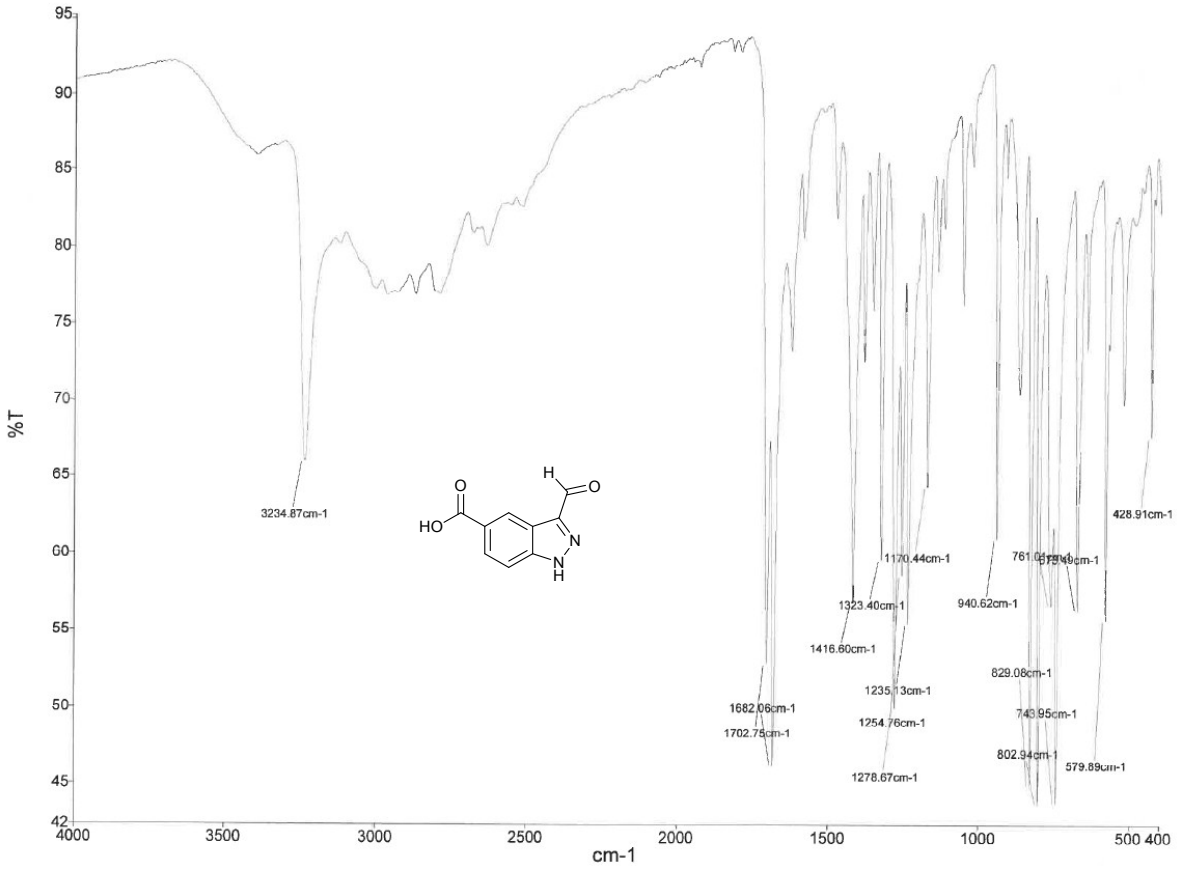
O
N
N
H

5-carboxy-1*H*-Indazole-3-carboxaldehyde (21b)



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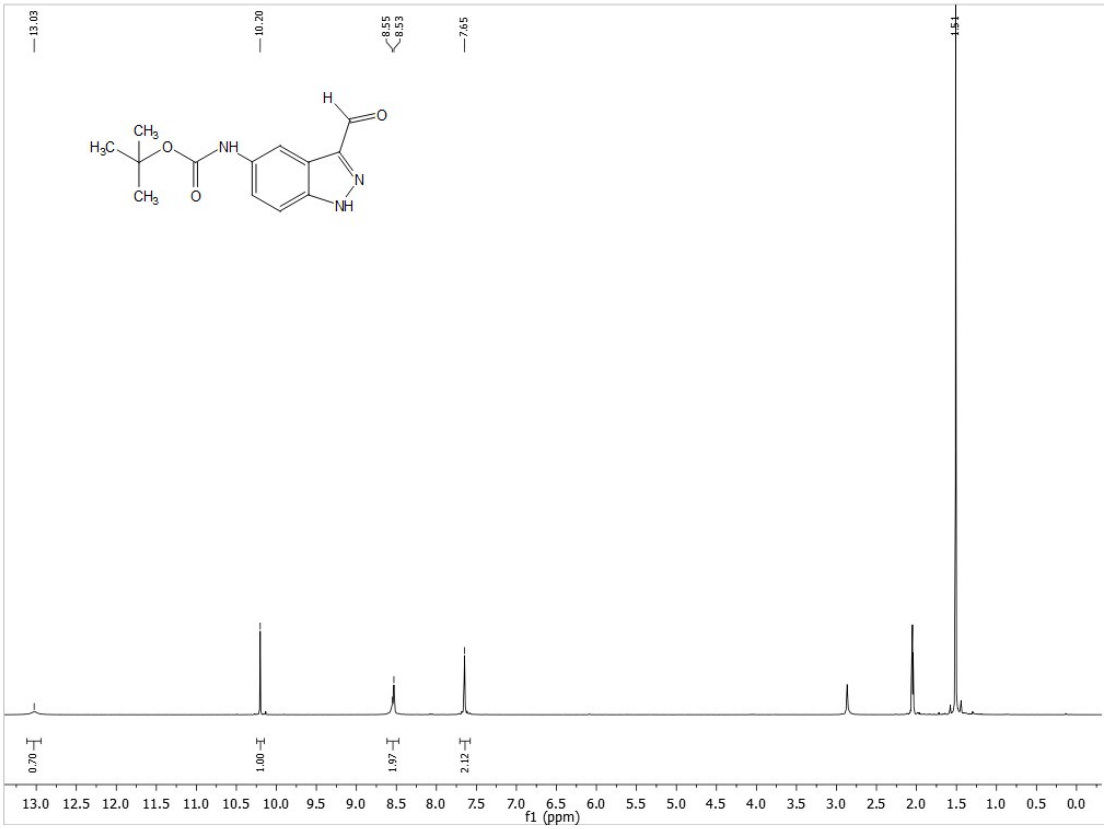
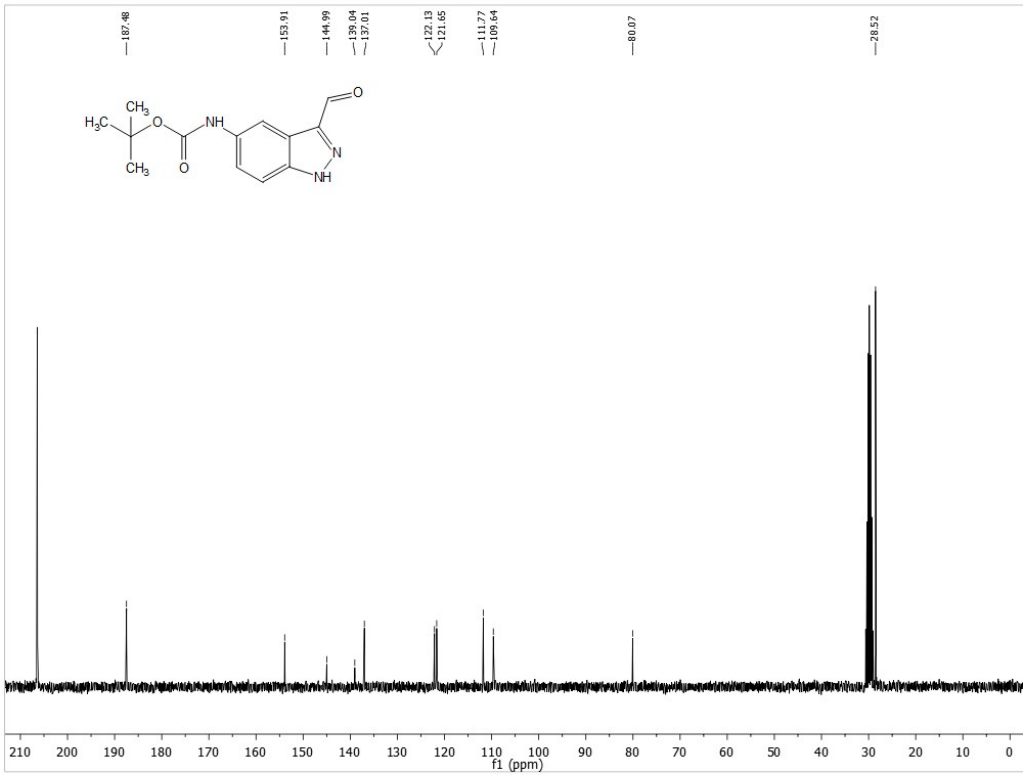
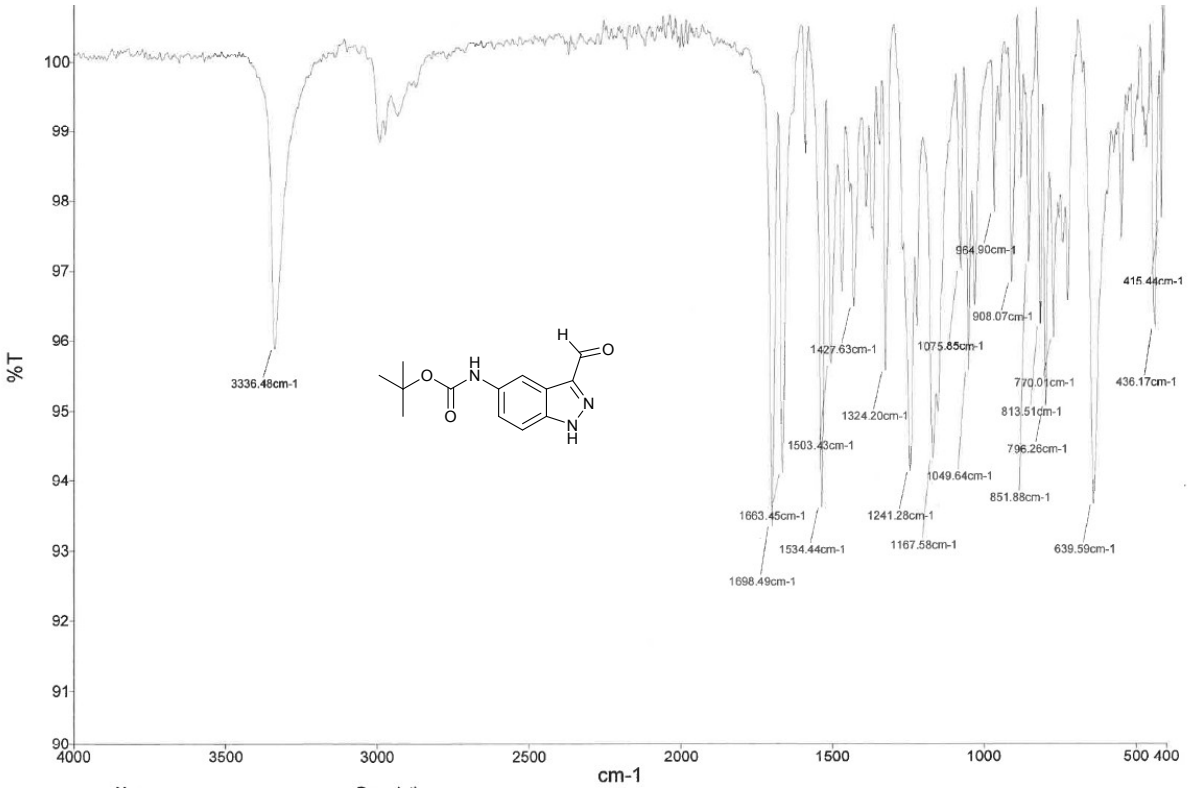
428.91cm-1

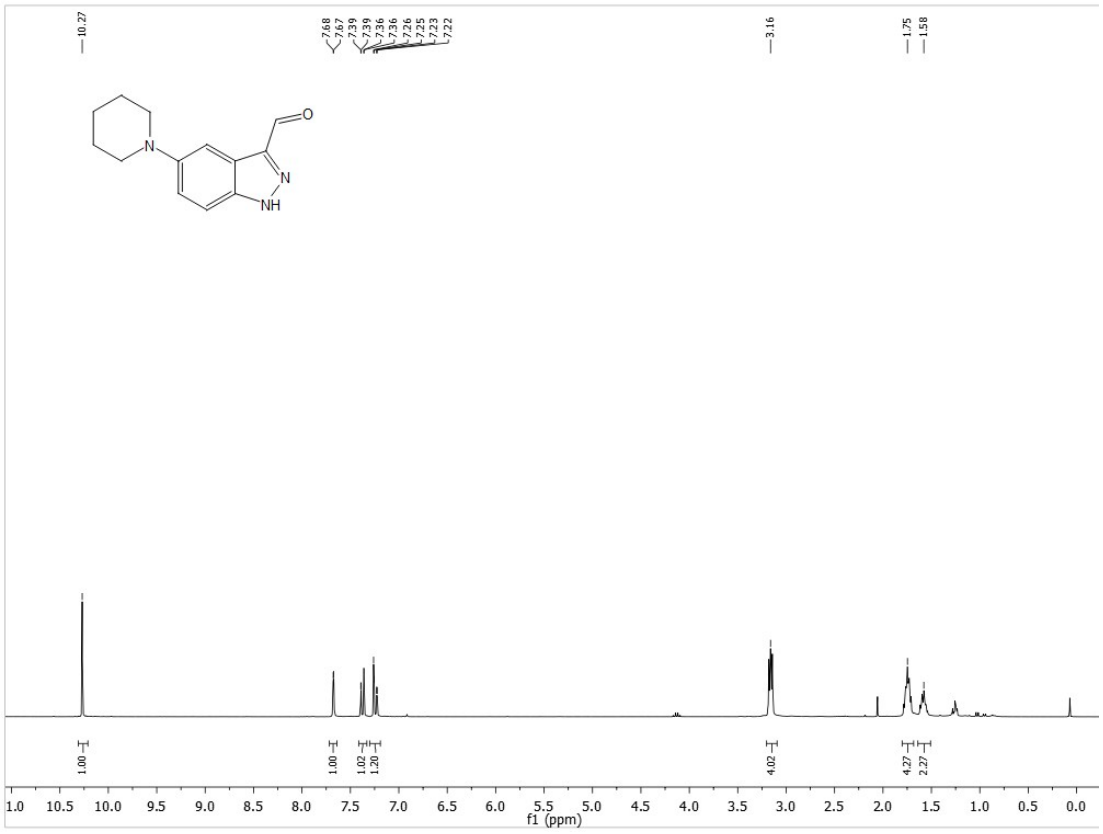
5-NHBoc -1*H*-indazole-3-carboxaldehyde (22b)

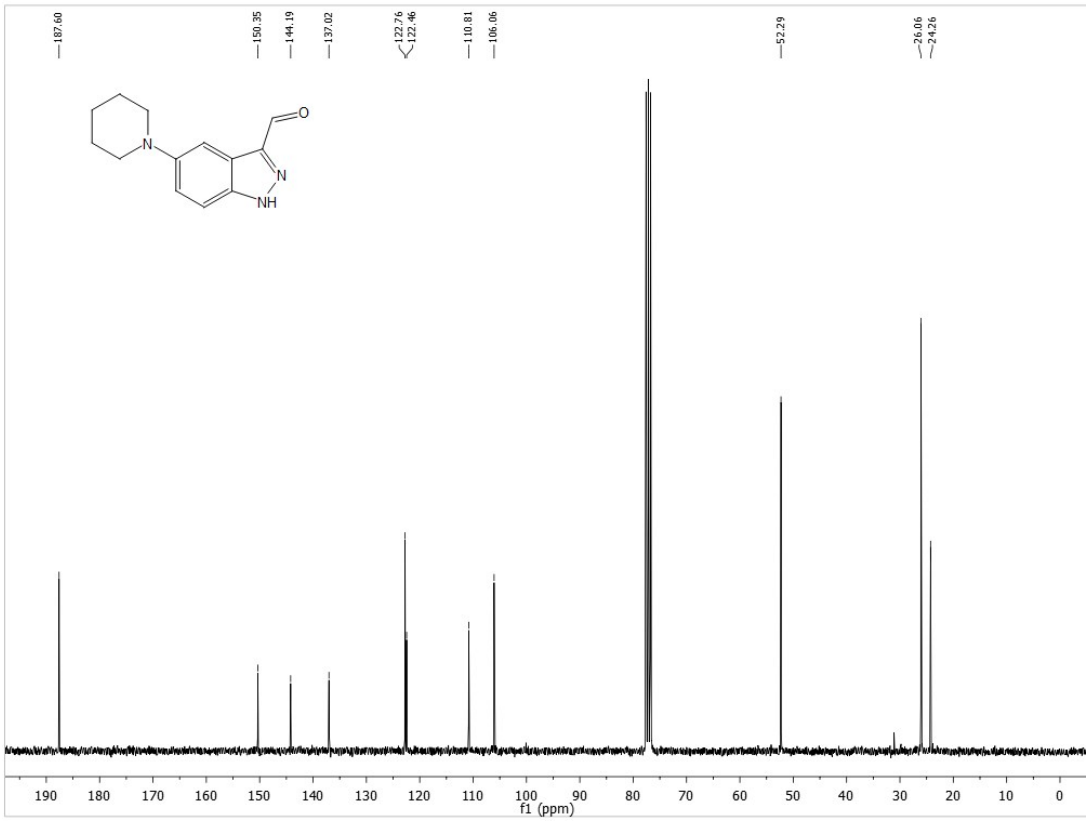


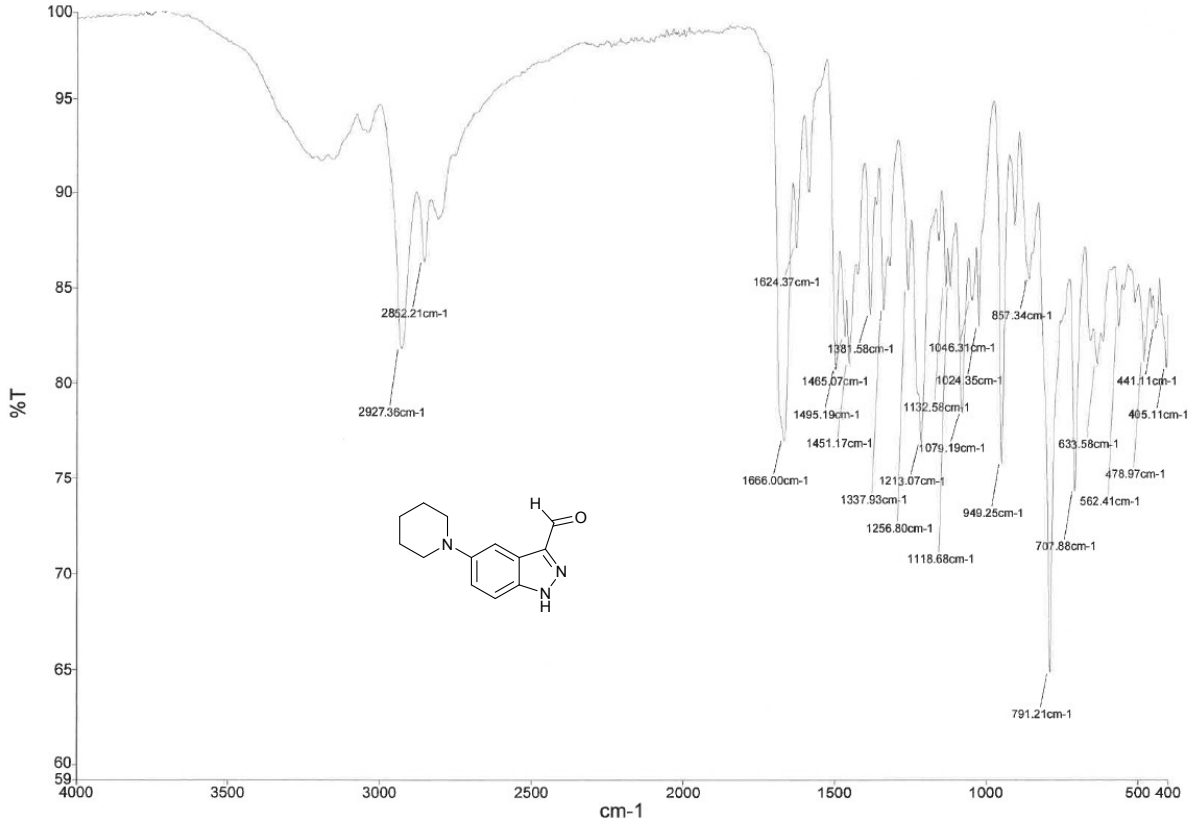



%T
cm-1
3336.48cm-1
1698.49cm-1
1663.45cm-1
1534.44cm-1
1503.43cm-1
1427.63cm-1
1324.20cm-1
1241.28cm-1
1167.58cm-1
1075.85cm-1
1049.64cm-1
964.90cm-1
908.07cm-1
851.88cm-1
813.51cm-1
796.26cm-1
770.01cm-1
639.59cm-1
436.17cm-1
415.44cm-1

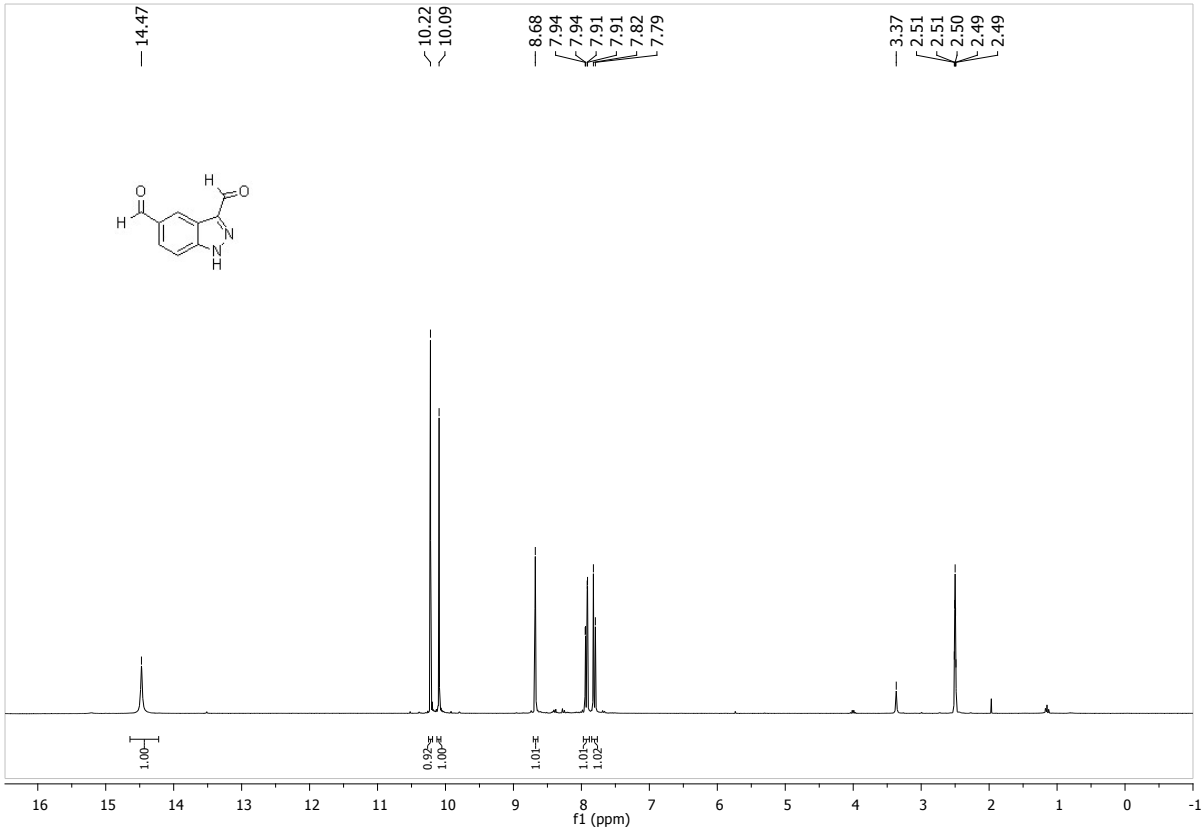
5-piperidyl-1*H*-indazole-3-carboxaldehyde (23b)

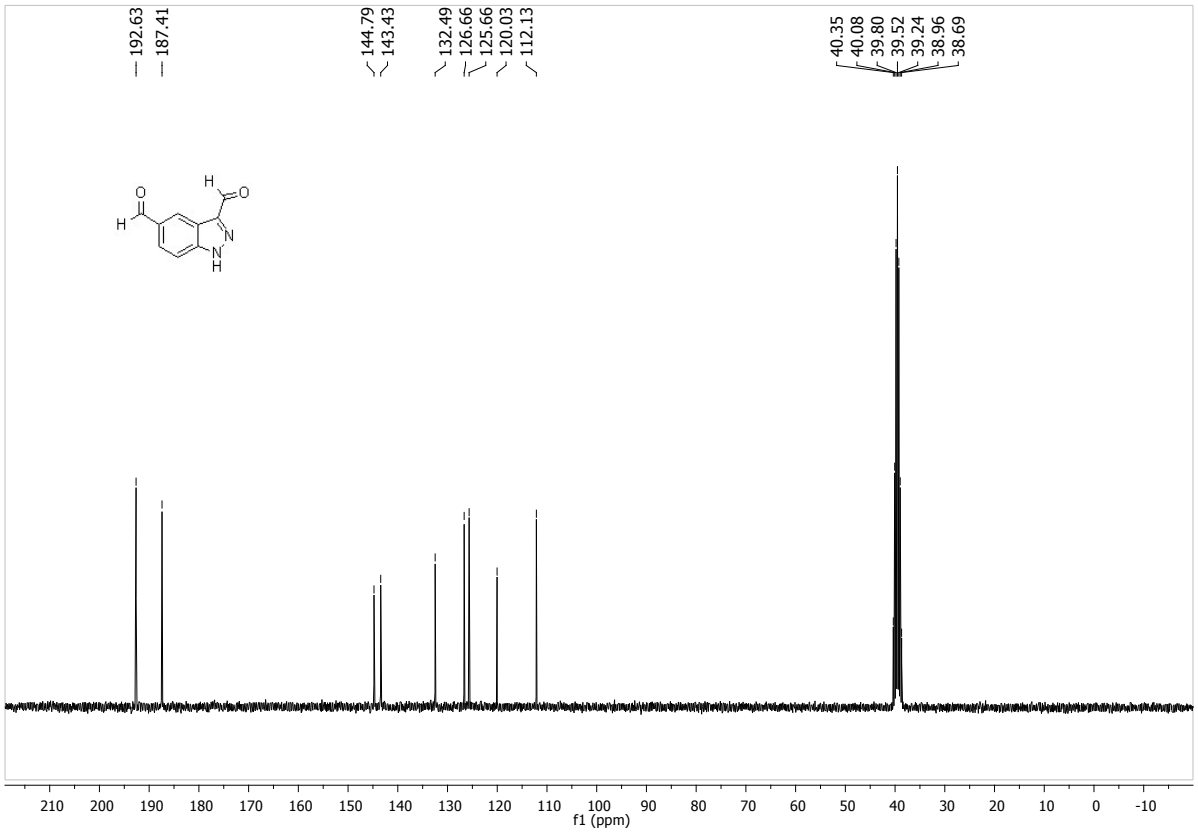


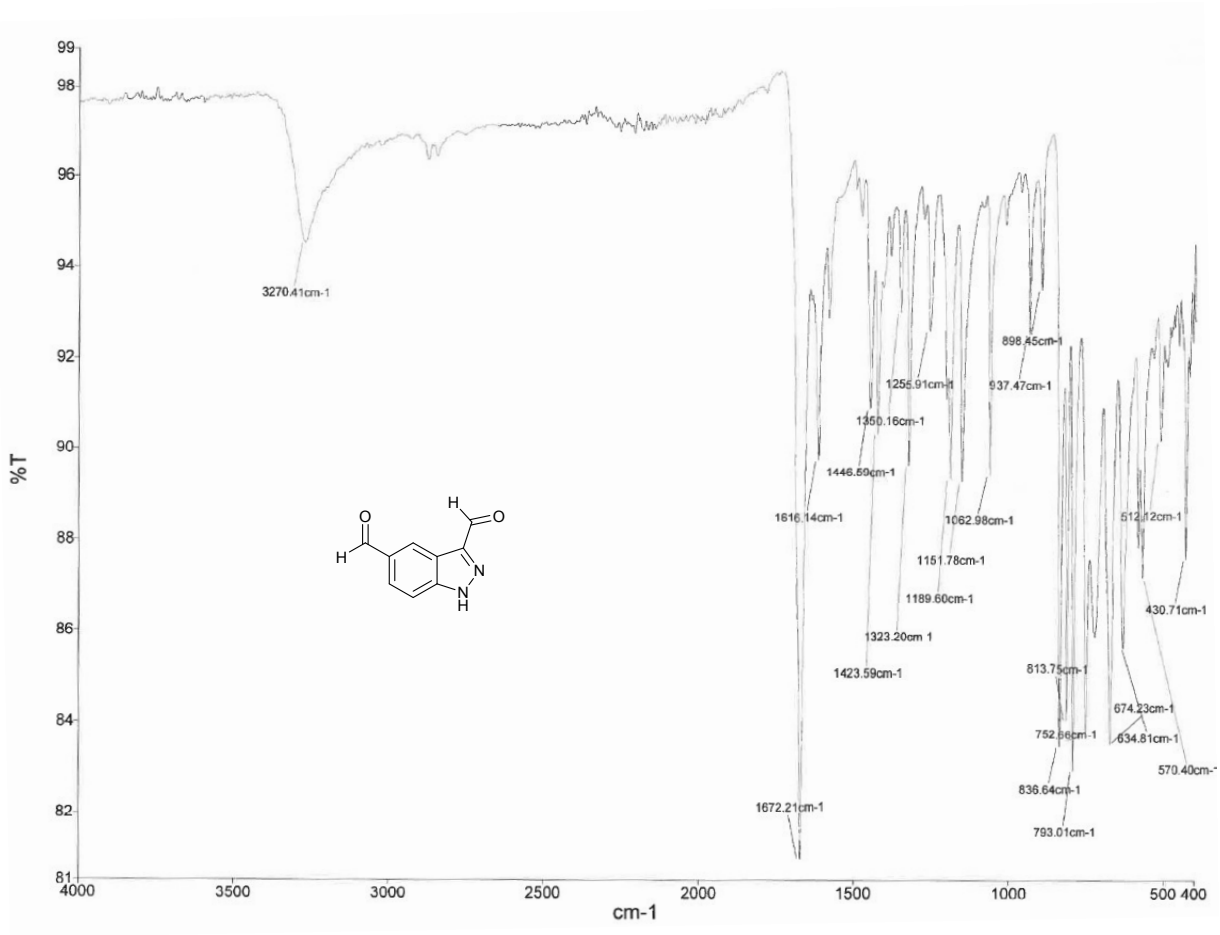



100
95
90
85
80
75
70
65
60
59
%T
4000
3500
3000
2500
2000
1500
1000
500 400
cm-1
2927.36cm-1
2852.21cm-1
1624.37cm-1
1666.00cm-1
1465.07cm-1
1495.19cm-1
1451.17cm-1
1381.58cm-1
1337.93cm-1
1256.80cm-1
1213.07cm-1
1132.58cm-1
1118.68cm-1
1079.19cm-1
1046.31cm-1
1024.35cm-1
949.25cm-1
857.34cm-1
791.21cm-1
707.88cm-1
633.58cm-1
562.41cm-1
478.97cm-1
441.11cm-1
405.11cm-1
H
O
N
N
N
H

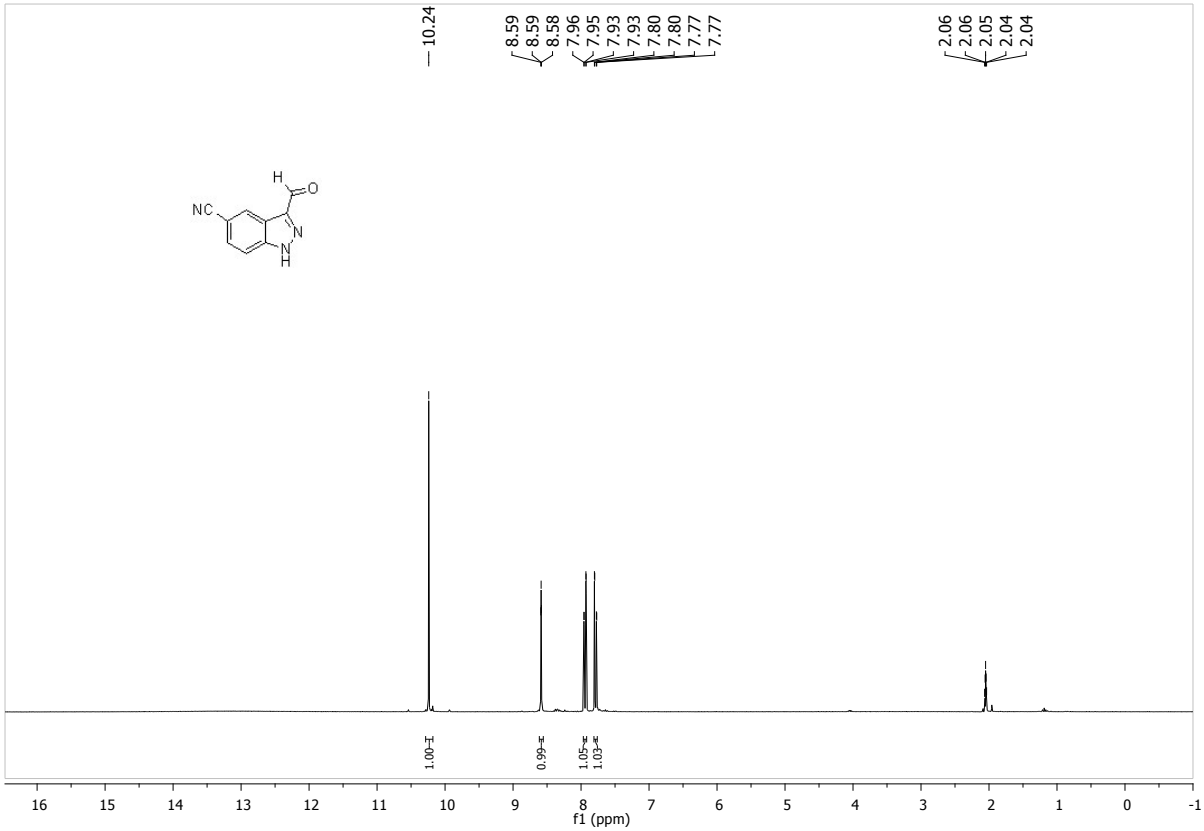
1*H*-indazole-3,5-dicarboxaldehyde (24b)

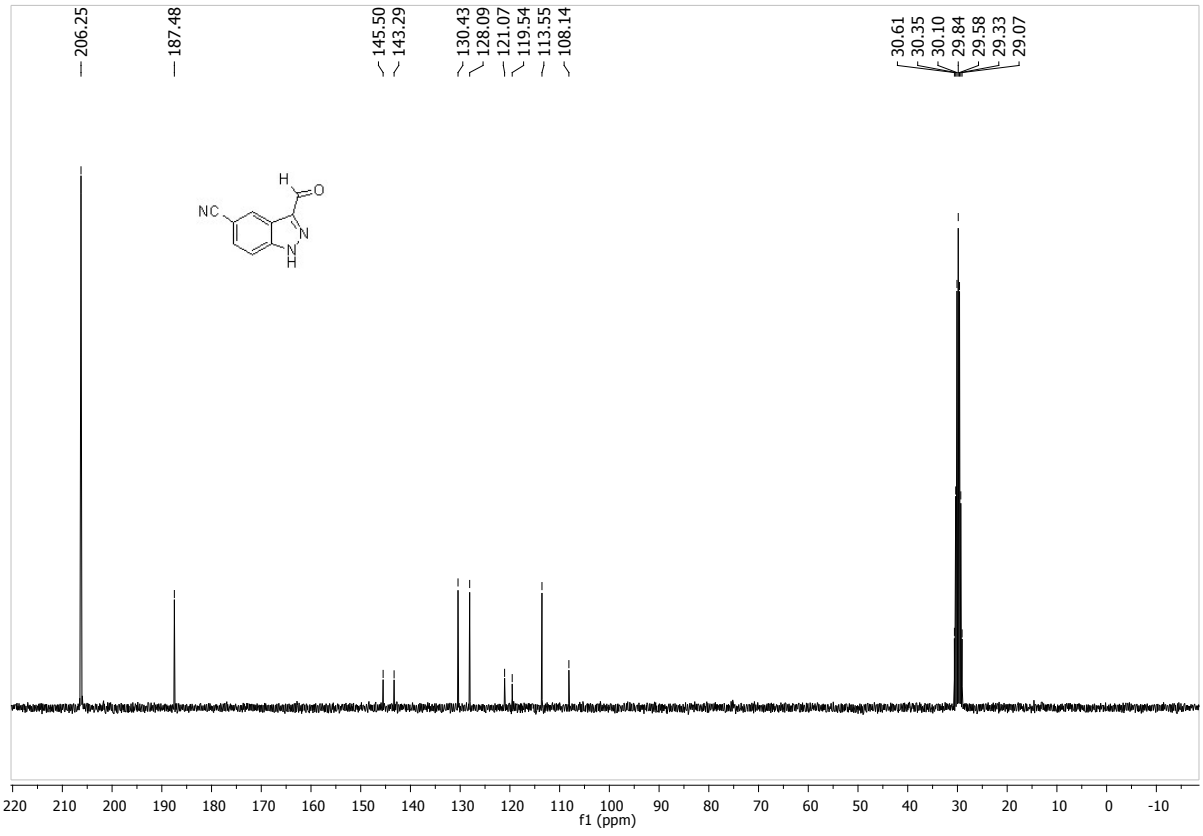


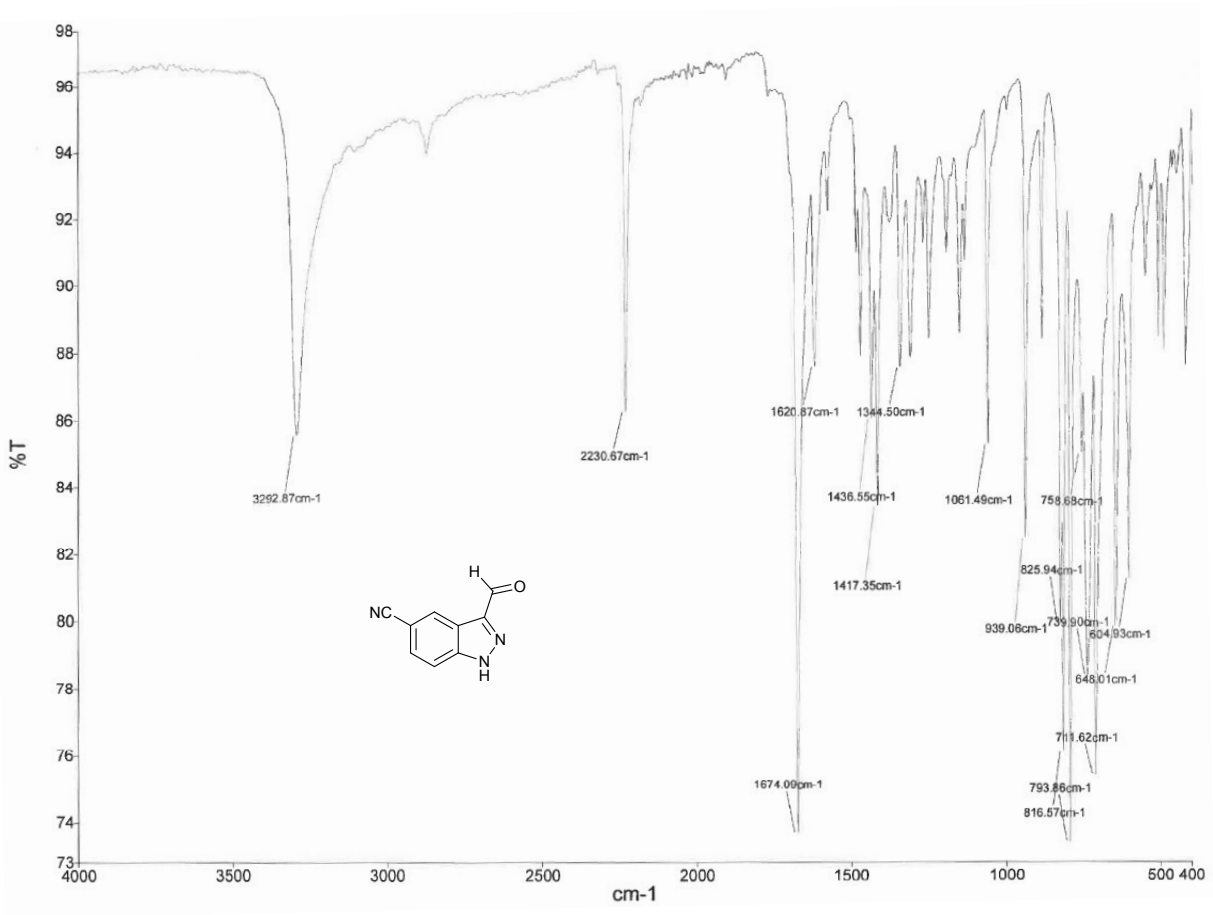



%T
cm-1
3270.41cm-1
1672.21cm-1
1616.14cm-1
1446.59cm-1
1350.16cm-1
1255.91cm-1
1151.78cm-1
1189.60cm-1
1323.20cm 1
1423.59cm-1
1062.98cm-1
937.47cm-1
898.45cm-1
813.75cm-1
752.66cm-1
836.64cm-1
793.01cm-1
674.23cm-1
634.81cm-1
512.12cm-1
430.71cm-1
570.40cm-1

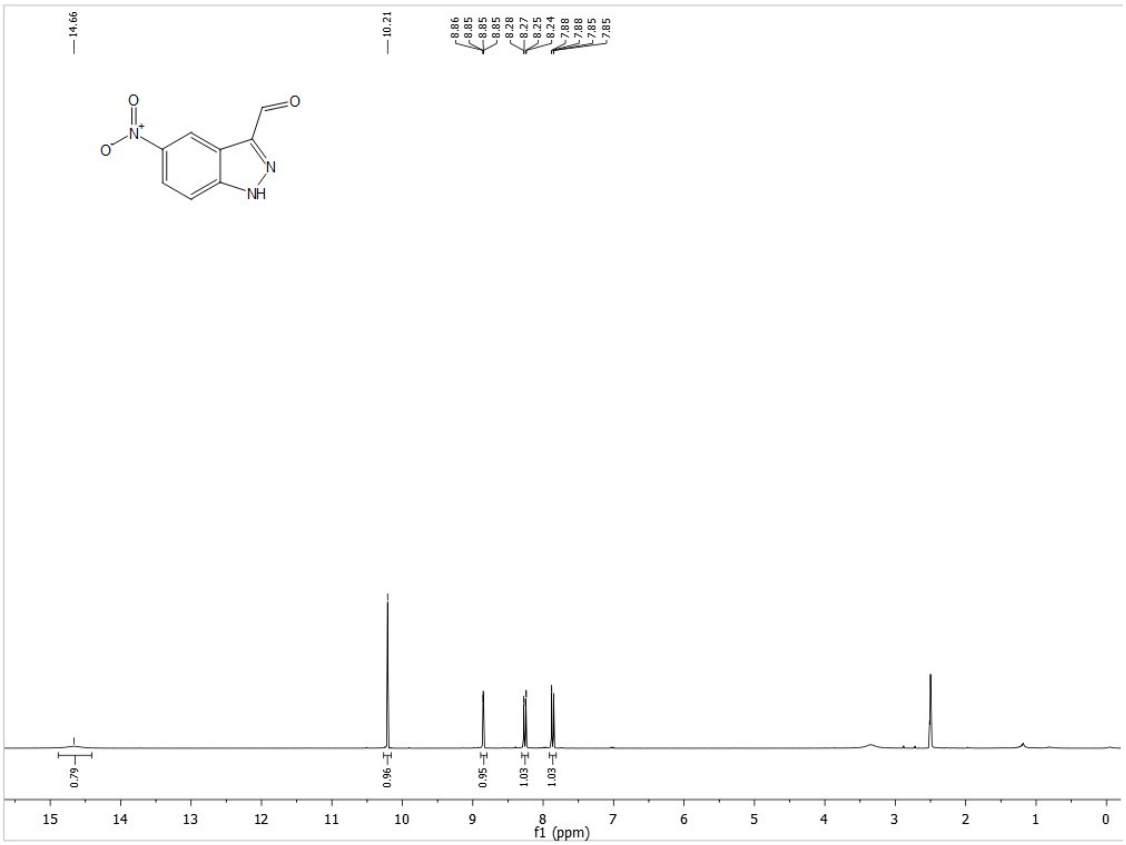
5-cyano-1*H*-indazole-3-carboxaldehyde (25b)

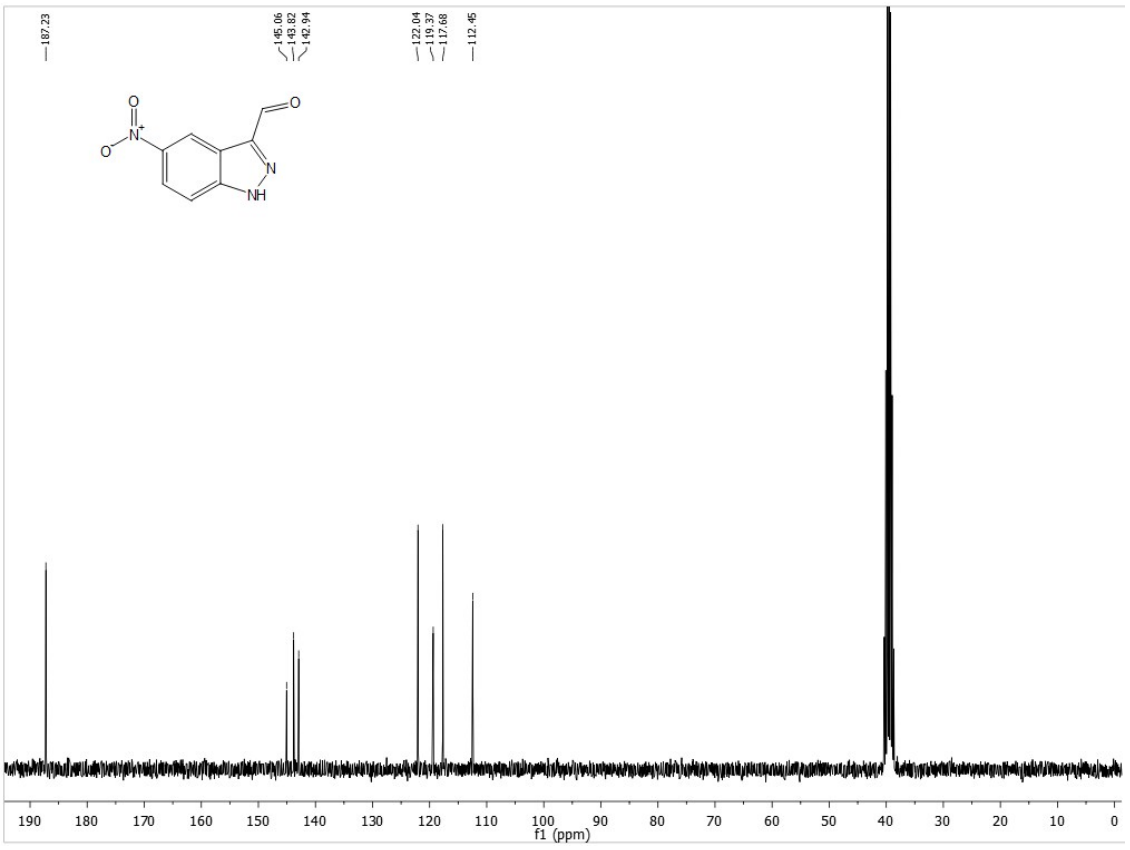


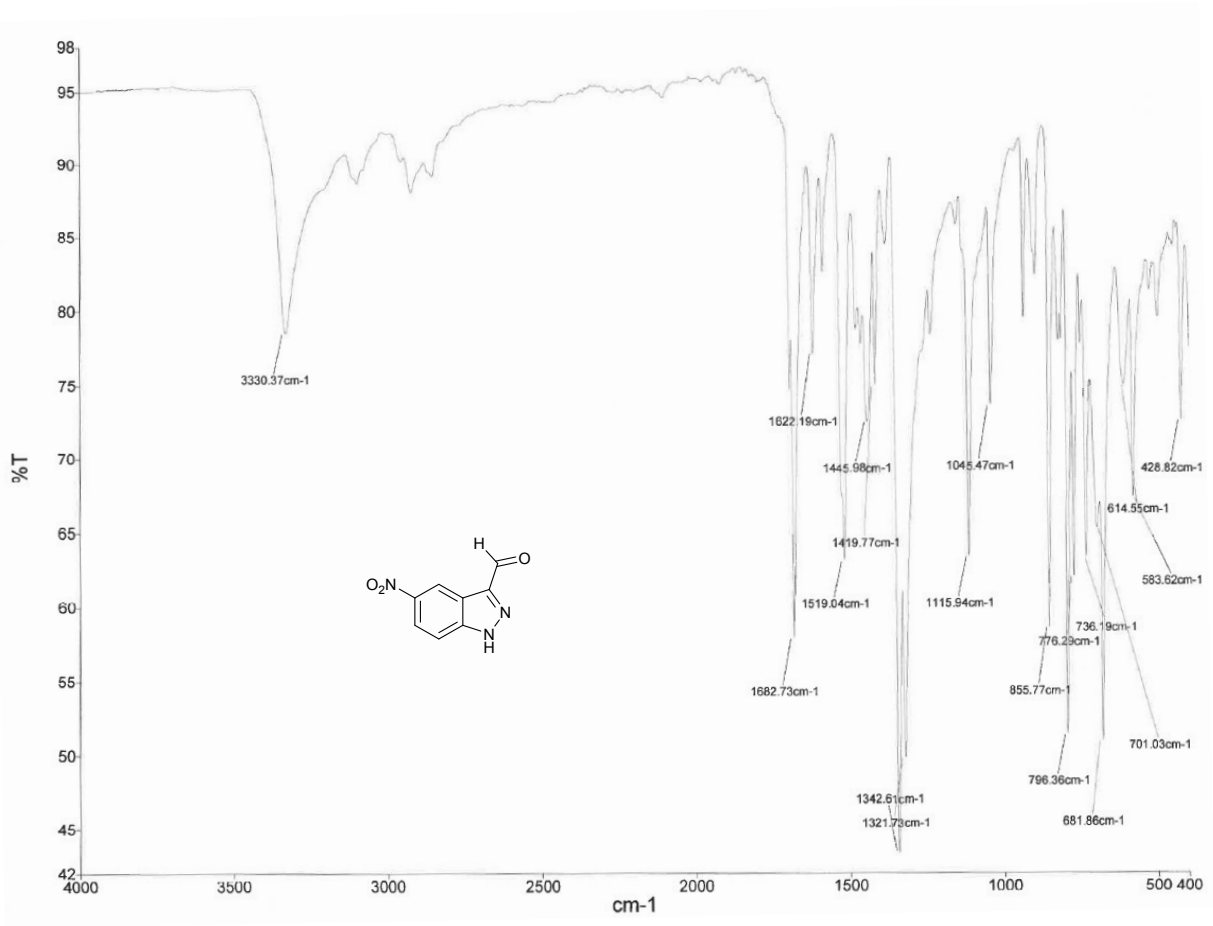



%T
cm-1
3292.87cm-1
2230.67cm-1
1620.87cm-1
1344.50cm-1
1436.55cm-1
1417.35cm-1
1061.49cm-1
758.68cm-1
825.94cm-1
939.06cm-1
739.90cm-1
604.93cm-1
648.01cm-1
711.62cm-1
1674.09cm-1
793.86cm-1
816.57cm-1
NC
H
O
N
N
H

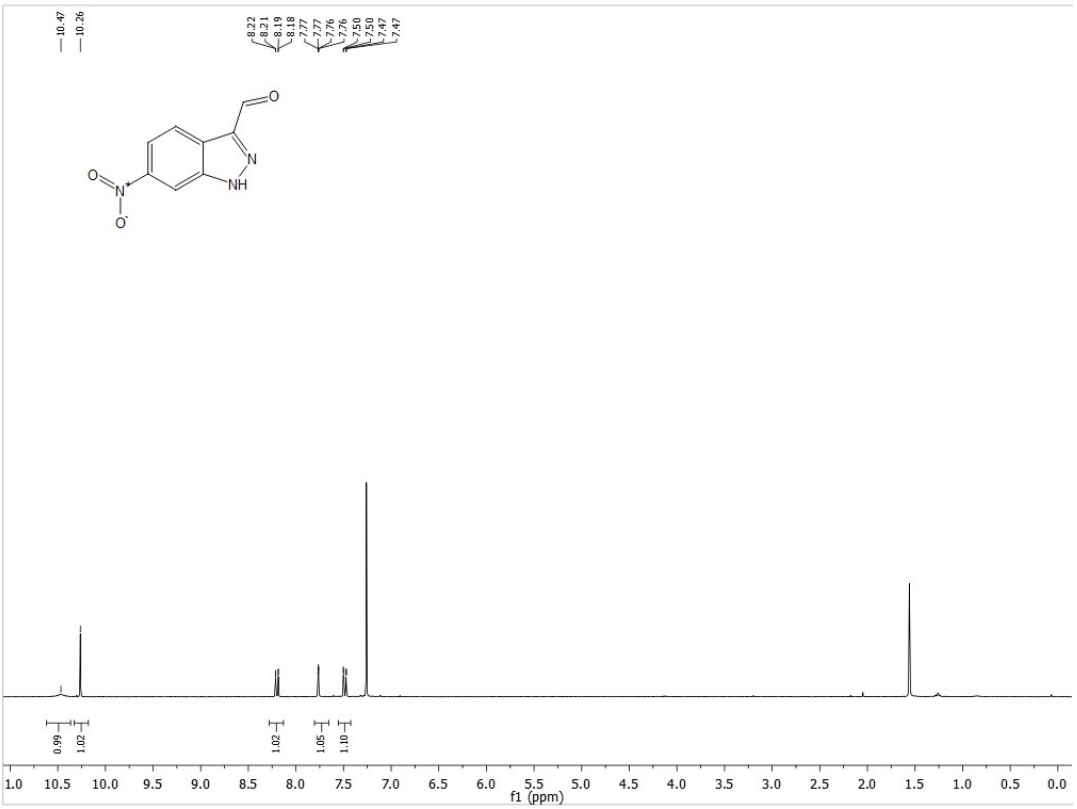
5-nitro-1*H*-indazole-3-carboxaldehyde (26b).

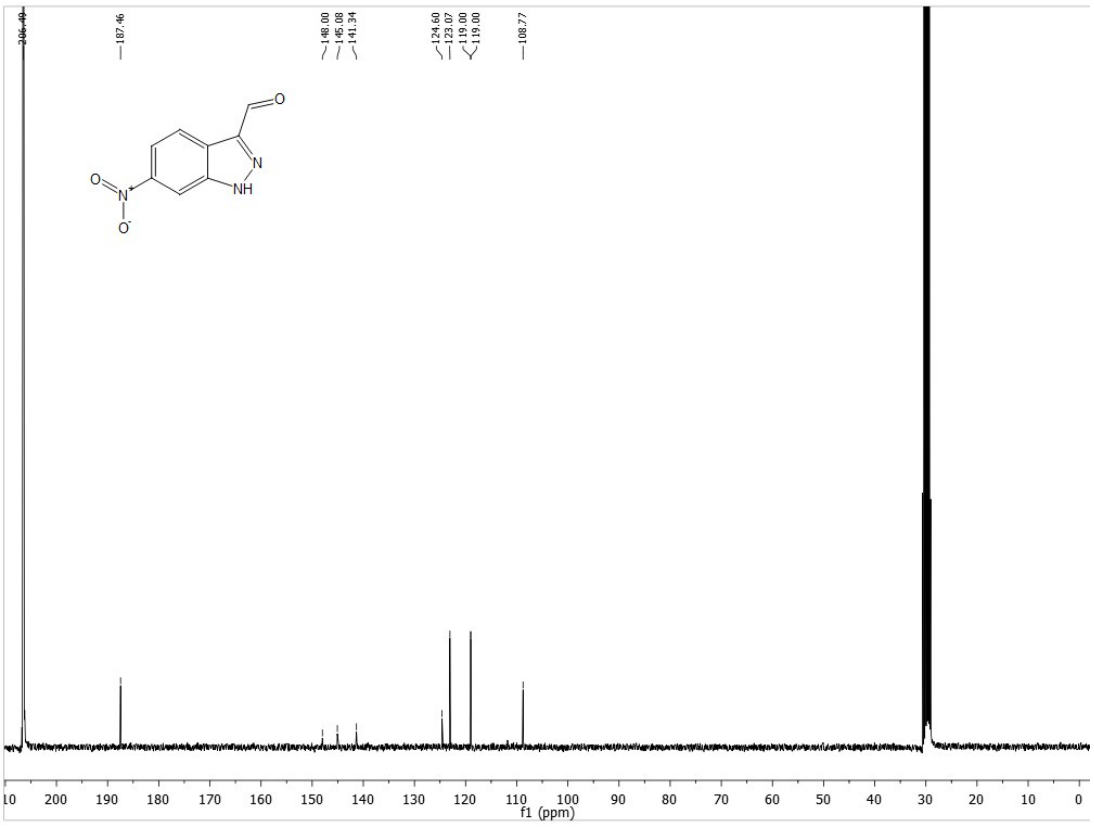


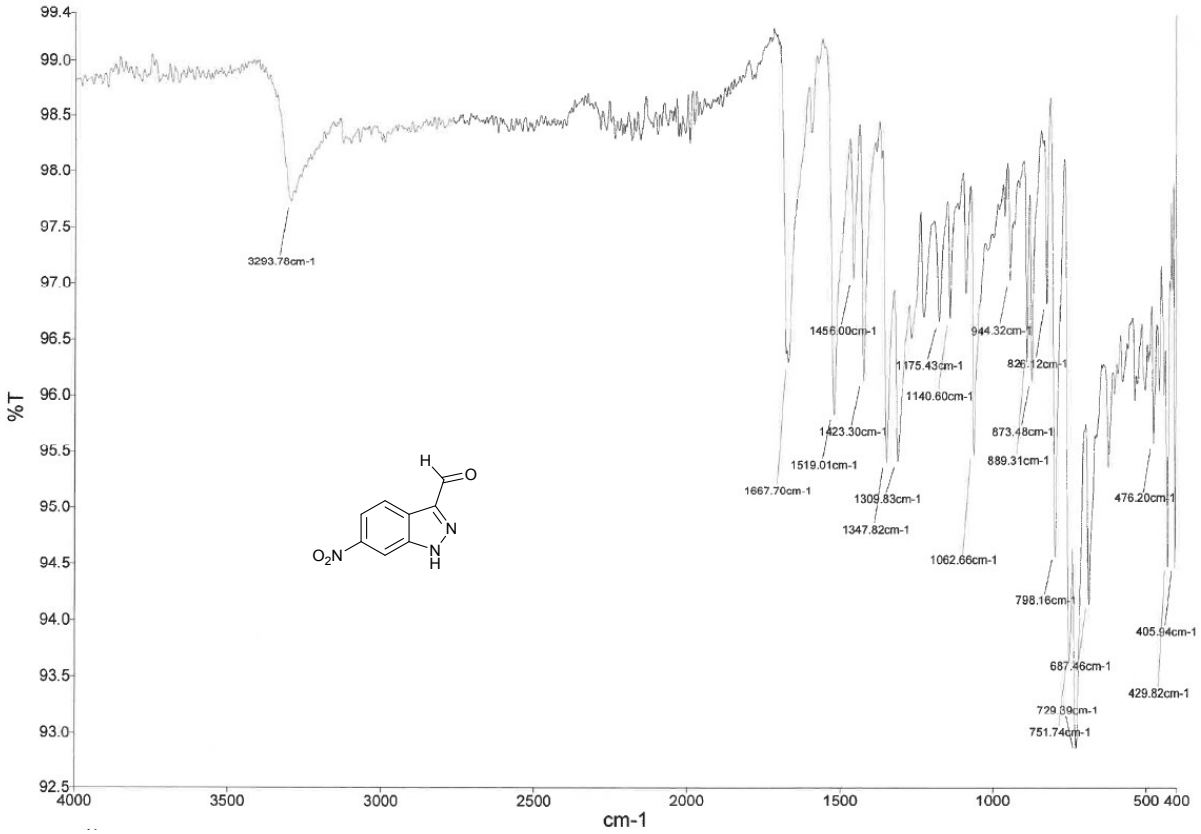



%T
cm-1
3330.37cm-1
1622.19cm-1
1445.98cm-1
1419.77cm-1
1519.04cm-1
1682.73cm-1
1342.61cm-1
1321.73cm-1
1045.47cm-1
1115.94cm-1
855.77cm-1
776.29cm-1
736.19cm-1
796.36cm-1
681.86cm-1
701.03cm-1
428.82cm-1
614.55cm-1
583.62cm-1
O2N
H
O
N
N
H

6-nitro-1*H*-indazole-3-carboxaldehyde (27b)






%T
cm-1
3293.78cm-1
1667.70cm-1
1519.01cm-1
1423.30cm-1
1309.83cm-1
1347.82cm-1
1062.66cm-1
1140.60cm-1
1175.43cm-1
944.32cm-1
889.31cm-1
873.48cm-1
798.16cm-1
751.74cm-1
729.89cm-1
687.46cm-1
476.20cm-1
429.82cm-1
405.94cm-1
O2N
H
O
N
N
H