SUPPORTING INFORMATION

Preparation of Polyfunctional Acyl Azides

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Table of Contents

I. General: S2

II. Typical procedure for preparation of acyl azides 1a-n S2

III. Characterization data for compounds 1a-k S2

IV. References S4

V. Copies of ^{1}H, ^{13}C NMR of 1l-n ……...……...S5

I. General

Melting points were determined on a capillary point apparatus equipped with a digital thermometer. NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 with TMS for ^{1}H (300 MHz) and ^{13}C (75 MHz) as the internal reference. Column chromatography was performed on 200–425 mesh silica gel.

II. Typical procedure for preparation of acyl azides 1a-n

Sodium azide (1.5 mmol, 97 mg) was added to a solution of appropriate *N*-acylbenzotriazoles (1 mmol) in acetonitrile (10 mL). One drop of water was added and the mixture was stirred at room temperature for 16 h. The solvent was evaporated and the residue was dissolved in diethyl ether, washed with dilute aqueous sodium carbonate and water. The organic layer was dried over $MgSO_4$ and filtered. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography using hexane-diethyl ether (2:1) to give the acyl azides **1a-n**.

III. Characterization data for compounds 1a-k

Benzoyl azide (1a):[1] yield 82%; white microcrystals (Et_2O/hexane); mp 32-34 ºC (lit.[49] mp 32 ºC); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44-7.48 (m, 2H), 7.60-7.64 (m, 1H), 8.03 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 128.6, 129.4, 130.6, 134.3, 172.5.

***p*-Toluoyl azide (1b):**[2] yield 82%; white microcrystals (Et_2O/hexane); mp 32-34 ºC (lit.[31] mp 32-33 ºC); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.42 (s, 3H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.92 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.8, 128.0, 129.4, 129.5, 145.4, 172.4.

Thiophene-2-carbonyl azide (1c):[3] yield 80%; white microcrystals (Et_2O/hexane); mp 34-36 ºC (lit.[16] mp 35-36 ºC); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.10-7.18 (m, 1H), 7.63-7.70 (m, 1H), 7.81-7.88 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 128.4, 134.4, 134.7, 134.8, 166.6.

Furan-2-carbonyl azide (1d):[4] yield 75%; white microcrystals (Et_2O/hexane); mp 60-62 ºC (lit.[34] mp 62-63 ºC); ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.56 (dd, *J* = 3.6, 1.6 Hz, 1H), 7.27 (d, *J* = 2.9 Hz, 1H), 7.66 (d, *J* = 0.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 112.5, 120.0, 145.5, 148.0, 162.5.

1*H*-Indole-2-carbonyl azide (1e):[5] yield 81%; white microcrystals (Et_2O/hexane); mp 142-143 ºC (lit.[50] mp 141-142 ºC); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.17 (ddd, *J* = 15.0, 6.9, 1.1 Hz, 1H), 7.28 (d, *J* = 1.2 Hz, 1H), 7.34-7.44 (m, 2H), 7.70 (dd, *J* = 8.1, 0.7 Hz, 1H), 9.05 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 110.9, 112.1, 121.3, 123.1, 126.7, 127.3, 128.2, 138.0, 166.2.

Pyridine-2-carbonyl azide (1f):[5] yield 72%, white microcrystals (Et_2O/hexane); mp 51-52 ºC (lit.[50] mp 49-50 ºC); ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.64 (m, 1H), 7.97-8.07 (m, 2H), 8.72 (d, *J* = 4.6 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 124.7, 127.1, 137.5, 148.4, 149.5, 166.2.

Pyridine-3-carbonyl azide (1g):[6] yield 78%; white microcrystals (Et_2O/hexane); mp 48-50 ºC (lit.[39] mp 47-49 ºC); ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.57 (dd, *J* = 8.0, 4.8 Hz, 1H), 8.29 (dt, *J* = 8.0, 1.9 Hz, 1H), 8.81 (dd, *J* = 4.8, 1.6 Hz, 1H), 9.10 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 123.9, 126.6, 137.0, 150.3, 153.4, 166.4.

Pyridine-4-carbonyl azide (1h):[5] yield 72%; white microcrystals (Et_2O/hexane); mp 49-51 ºC (lit.[50] mp 50-51 ºC); ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.83 (d, *J* = 5.9 Hz, 2H), 8.79 (d, *J* = 5.9 Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 122.8, 138.1, 150.7, 166.2.

***E*-3-Phenyl-2-propenoyl azide (1i):**[7] yield 72%; white microcrystals (Et_2O/hexane); mp 82-83 ºC (lit.[29] mp 82-84 ºC); ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.43 (d, *J* = 15.8 Hz, 1H), 7.40-7.43 (m, 3H), 7.53-7.56 (m, 2H), 7.76 (d, *J* = 15.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 119.0, 128.5, 129.0, 131.1, 133.7, 146.7, 172.0.

***E*-3-(2-Furanyl)-2-propenoyl azide (1j):**[8] yield 75%; white microcrystals (Et_2O/hexane); mp 70-72 ºC (lit.[25] mp 71-73 ºC); ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.30 (d, *J* = 15.5 Hz, 1H), 6.51 (dd, *J* = 3.4, 1.8 Hz, 1H), 6.71 (d, *J* = 3.4 Hz, 1H), 7.49 (d, *J* = 15.5 Hz, 1H), 7.53 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 112.7, 116.5, 116.8, 132.4, 145.7, 150.5, 171.9.

3-Hydroxy-2-naphthoyl azide (1k):[9] yield 81%; white microcrystals (Et_2O/hexane); mp 109-111 ºC (lit.[51] mp 108 ºC); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31-7.36 (m, 2H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 8.45 (s, 1H), 10.27 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 112.1, 115.2, 124.3, 126.4, 127.0, 129.5, 130.0, 133.0, 138.7, 156.2, 176.6.

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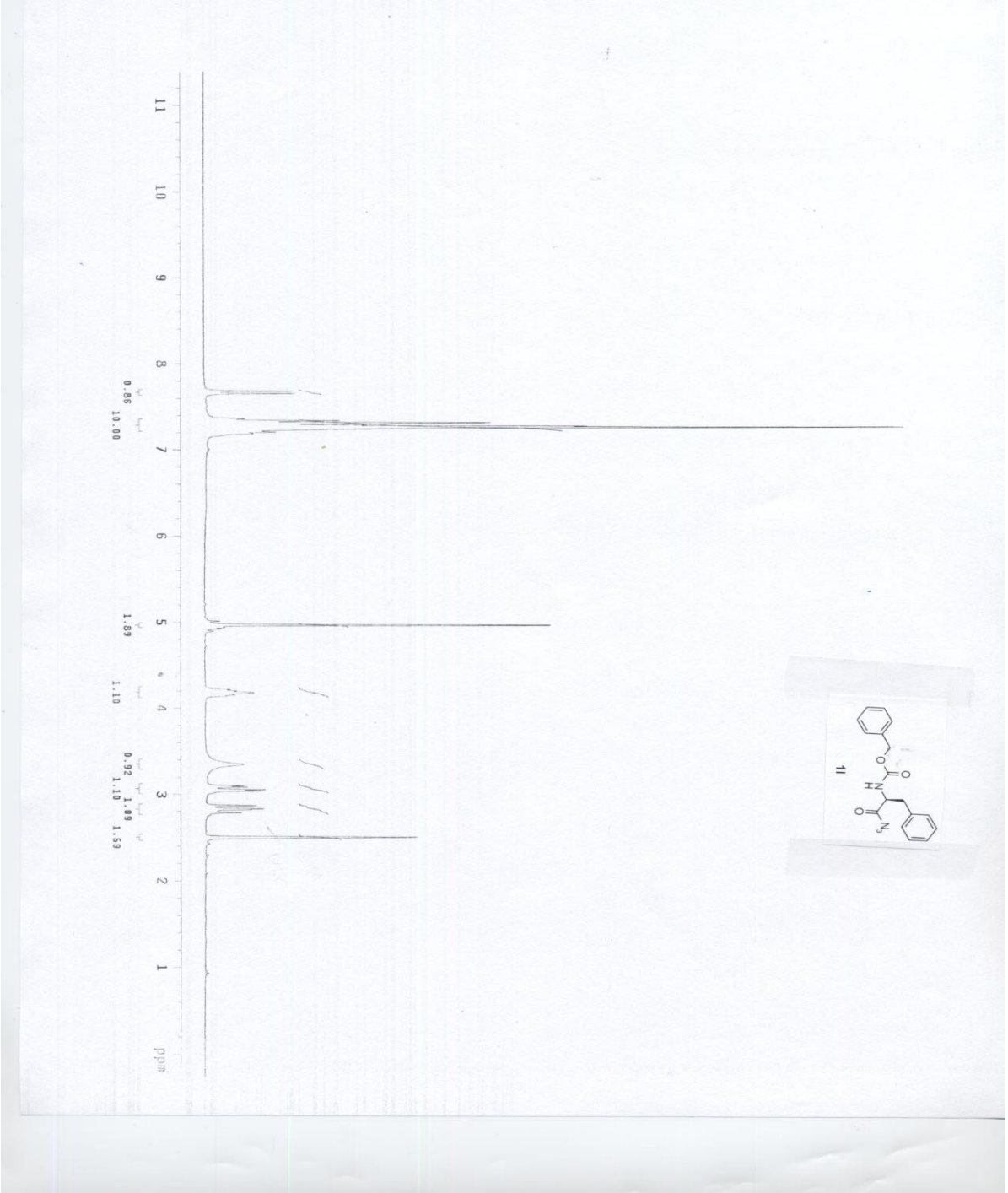
^{1}H NMR (300 MHz) spectra of compound **1l** in DMSO-d_6



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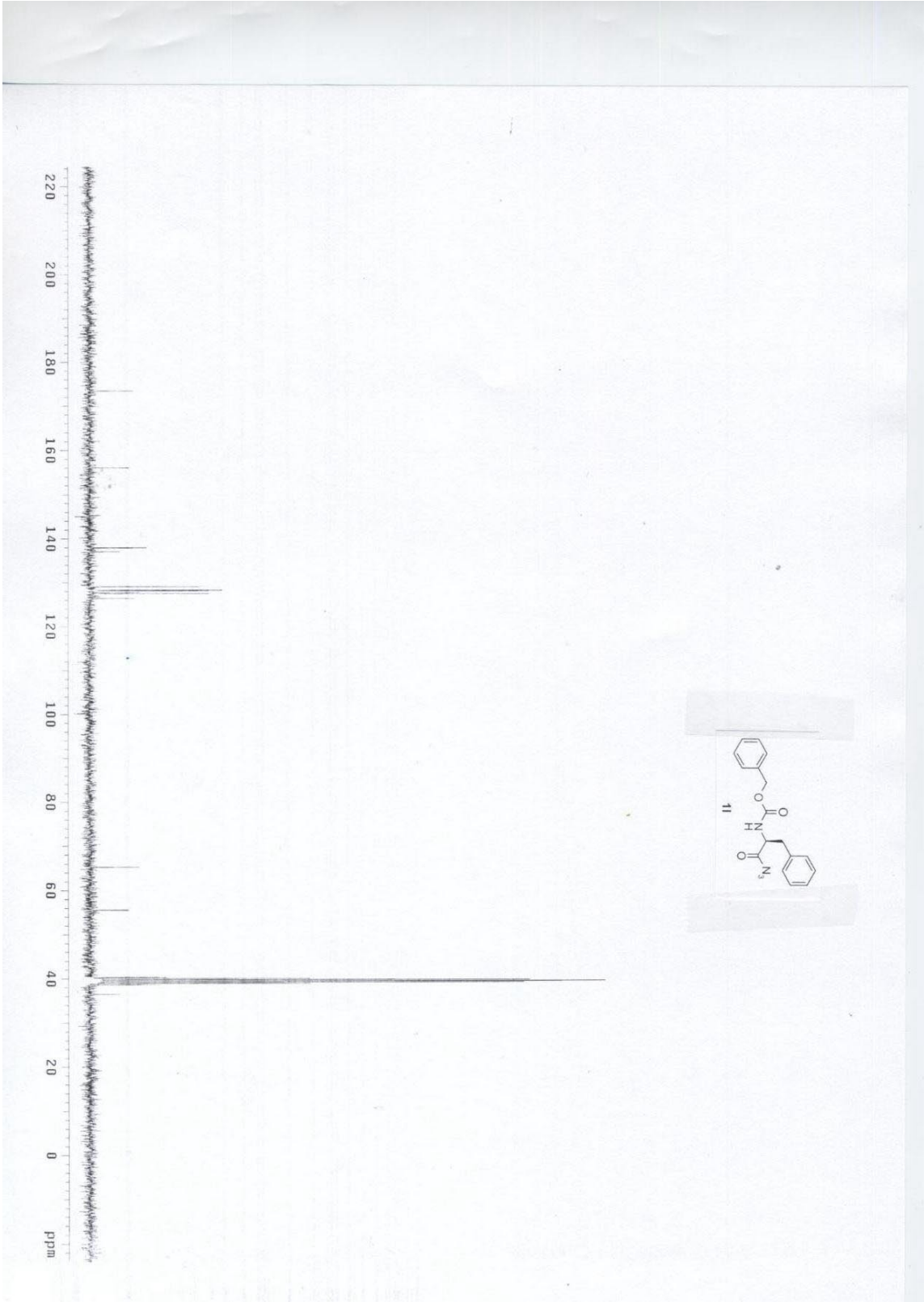

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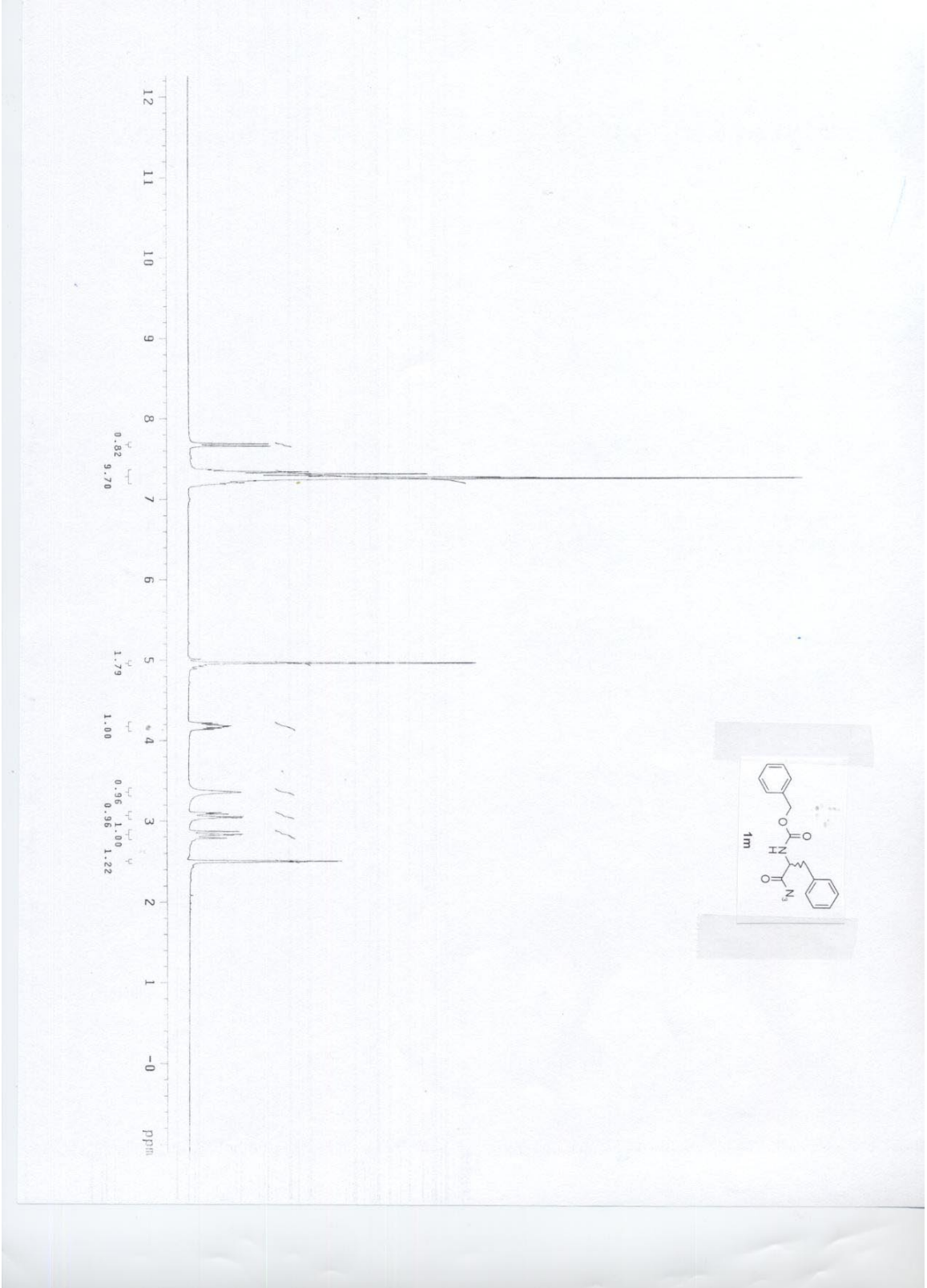
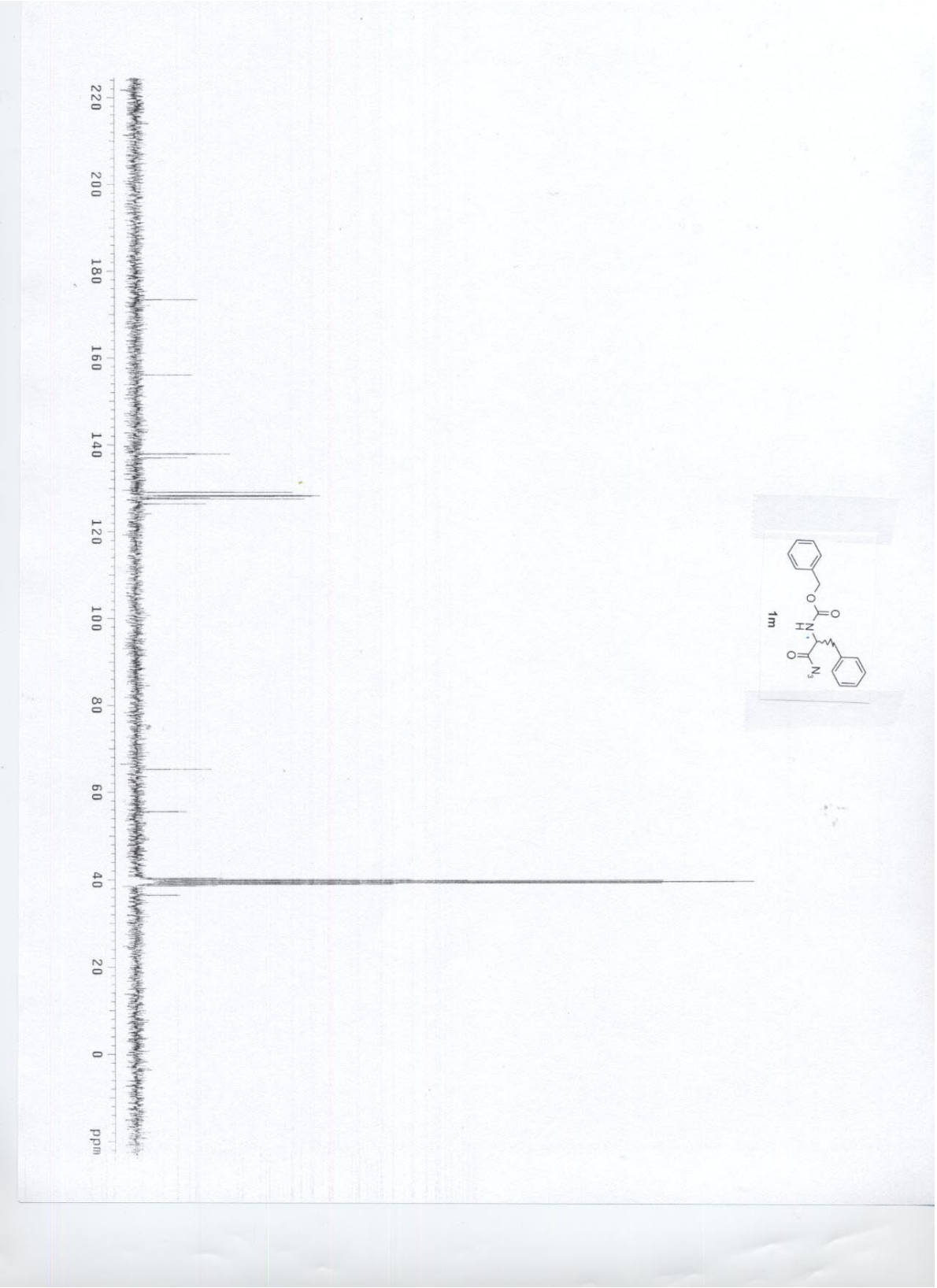
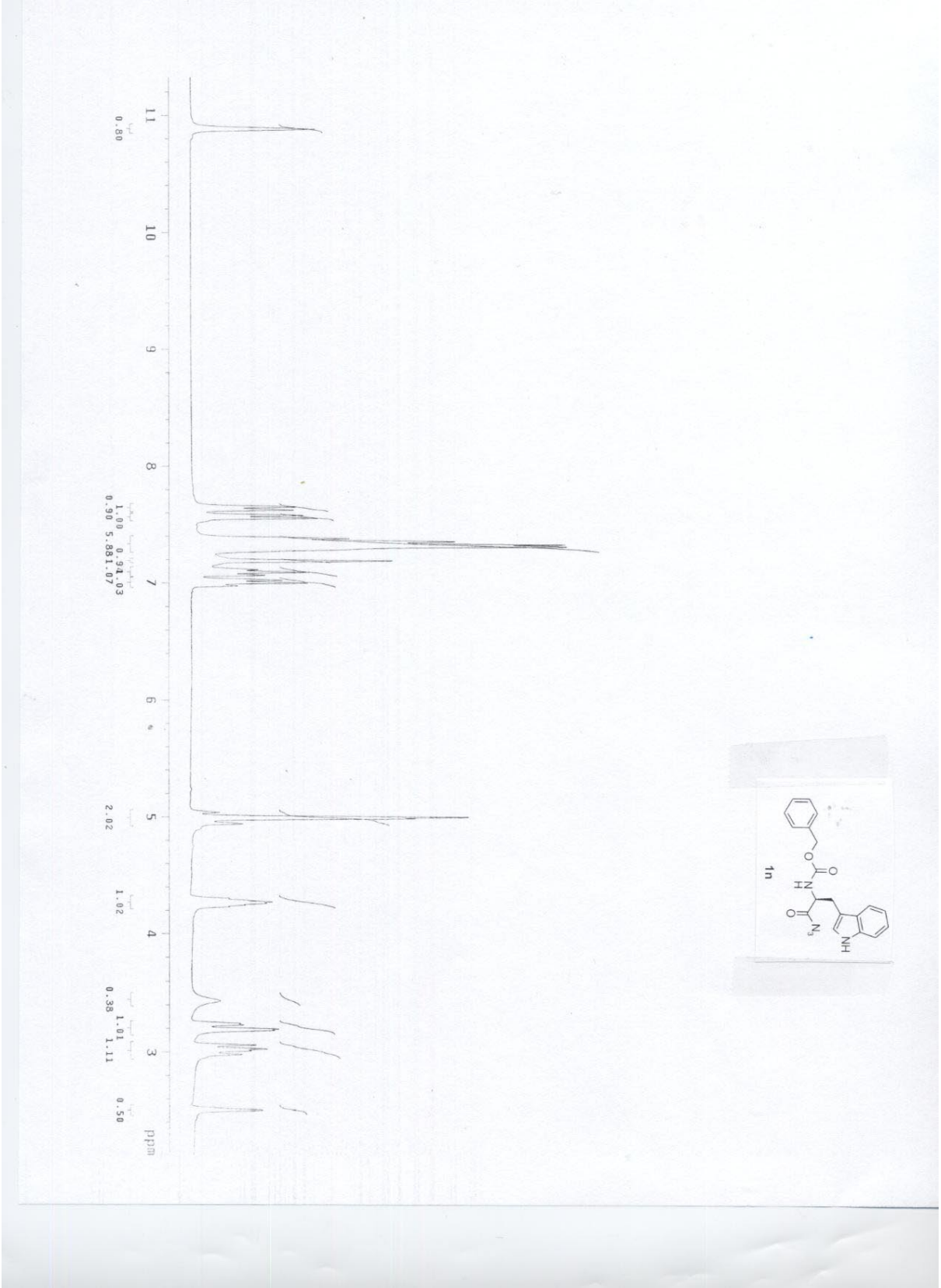
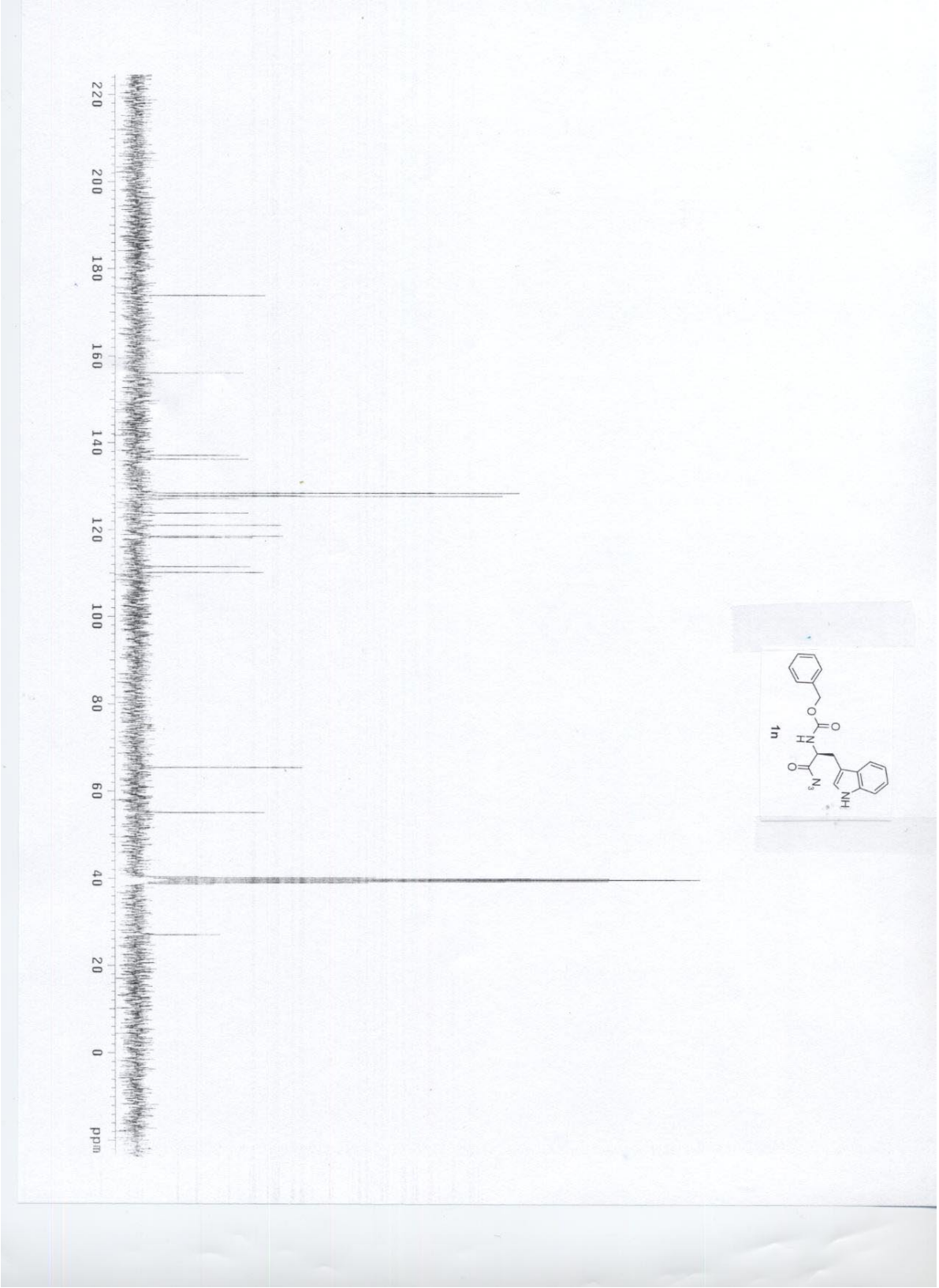


^{13}C NMR (75 MHz) spectra of compound **1m** in DMSO-d_6



^{1}H NMR (300 MHz) spectra of compound **1n** in DMSO-d_6



^{13}C NMR (75 MHz) spectra of compound **1n** in DMSO-d_6