Novel inorganic-organic hybrid silica based tin complex as a novel, highly efficient and recyclable heterogeneous catalyst and its application for the one-pot preparation of spirooxindoles in water

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SUPPORTING INFORMATION

Experimental Part

General. The chemicals used in this work were obtained from Fluka, Merck, and Aldrich was used without purification. Melting points were measured on an Electrothermal 9200 apparatus. IR spectra were recorded as KBr pellets on a Perkin-Elmer 781 spectrophotometer and an Impact 400 Nicolet FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a BRUKER DRX-300 AVANCE spectrometer at 300.13 and 75.47 MHz. ^{1}H and ^{13}C NMR spectra were obtained on solutions in DMSO-d_6 solvent using tetramethylsilane as internal reference. The elemental analyses (C.H.N) were obtained from a Carlo ERBA Model EA 1108analyzer. The content of tin in the heterogenized catalyst was determined by VISTA-PRO, CCD simultaneous ICP analyser. Thermogravimetric/differential thermal analyses (TG/DTA) was performed on a Thermal Analyzer with a heating rate of 20 °C min^{-1} over a temperature range of 25–1100 °C under flowing compressed N_2. The purity determination of the substrates and reaction monitoring were accomplished by TLC on silica-gel polygram SILG/UV 254 plates (from Merck Company).

Catalyst preparation

Typical experimental procedure for the preparation of catalyst

a) Activation of silica gel (SG):

Silica gel (Aldrich 70–270 mesh, 60 Å, Surface area > 500 m^2/G) was activated by treatment with HCl (5 M) and dried in vacuum at 120 ºC.

b) Preparation of the amino-functionalized silica gel (SG-NH_2):

Activated silica gel (1g) was added to a solution of APTES (1.8 g, 1.9 ml) in dry toluene (50 ml) and refluxed for 24h under N_2 atmosphere. The white solid was filtered and washed repeatedly with ethanol and finally dried at 50 ºC under vacuum.

c) Grafting of 2-amino benzamide through isatoic anhydride on functionalized silica gel (SG-NH_2-2AB):

The amino-functionalized silica gel (1 g) was added to the solution of isatoic anhydride (8 mmol, 1.3 g) in ethanol (25 ml) and refluxed for 24h. The resulting

solid was collected by filtration, repeatedly washed with ethanol to remove unreacted isatoic anhydride. It was dried under vacuum at 50 ºC.

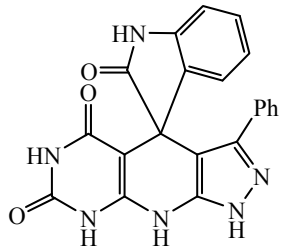
d) Synthesis of tin catalyst immobilized on silica gel (SG-NH2-2AB-Sn):

The catalyst was prepared by stirring a mixture of 2-amino benzamide on functionalized silica gel (SG-NH_2-2AB) (1 g) and tin chloride (8 mmol) in ethanol (50 ml) at reflux for 24h. After that, the catalyst was filtered, washed several times with ethanol, and dried under vacuum at 50 ºC

Typical Procedure for Preparation of 3'-phenyl-spiro[indoline-3,4'-pyrazolo [4′,3′:5,6] pyrido[2,3 d]pyrimidine]- 2,5',7'(6'H,8'H,9'H)-trione (4e):

A mixture of 1,3-diphenyl-1*H*-pyrazol-5-amine (0.24 g, 1 mmol), barbituric acid (0.13 g, 1 mmol), isatine (0.15 g, 1 mmol), and SG-NH_2-2AB-Sn as a catalyst (10 mol%) under refluxing water (5 mL) was stirred (the progress of the reaction was monitored by TLC). After completion of the reaction (TLC), the solution was cooled to room temperature, then the precipitated product was filtered and washed with water (10 mL) and ethanol (5 mL), dried to afford the crude product. The crude precipitate dissolved in DMF and again filtered for catalyst separation, and finally water was added into solution and the product was extracted and recrystallized by EtOH to afford the pure product.

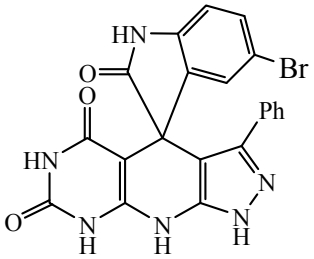
3'-Phenyl-spiro[indoline-3,4'-pyrazolo[4′,3′:5,6]pyrido[2,3 d]pyrimidine]- 2,5',7'(6'H,8'H,9'H)-trione (4a):



White powder (83%); MP >300 ˚C. IR (KBr) (ν_{max} /cm^{-1}): 3399, 1729, 1683, 1626. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 6.48-7.27 (9H, m, H-Ar), 9.10 (1H, s, NH), 9.99 (1H, s, NH), 11.67 (1H, s, NH), 12.00 (1H, s, NH), 12.55 (1H, s, NH). ^{13}C NMR

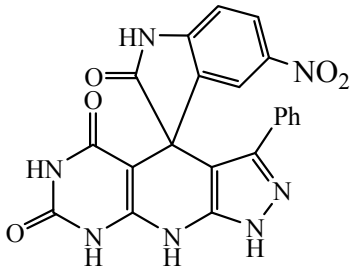
(75 MHz, DMSO-d_6): δ_C (ppm) 47.9, 90.1, 100.6, 109.4, 121.8, 123.8, 128.1, 128.2, 128.7, 129.1, 137.5, 139.9, 142.8, 145.3, 147.1, 159.6, 173.9, 178.9. Anal. Calcd for $C_{23}H_{18}N_6O_3$: C, 64.78; H, 4.25; N, 19.71. Found: C, 64.75; H, 4.28; N, 19.69.

5-Bromo-3'-phenyl-spiro[indoline-3,4'pyrazolo[4′,3′:5,6]pyrido[2,3-d]pyrimidine]-2,5',7'(6'H,8'H,9'H)-trione (**4b**):



White powder (89%); MP >300 ˚C. IR (KBr) (ν_{max} /cm^{-1}): 3460, 3203, 1727, 1606. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 6.41-7.32 (8H, m, H-Ar), 9.37 (1H, s, NH), 10.07 (1H, s, NH), 10.22 (1H, s, NH), 10.57 (1H, s, NH), 12.54 (1H, brs, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 48.2, 85.3, 100.4, 111.2, 113.3, 126.4, 128.3, 128.8, 129.2, 130.5, 140.4, 142.1, 148.0, 150.2, 162.4, 179.2. Anal. Calcd for $C_{21}H_{13}BrN_6O_3$: C, 52.85; H, 2.75; N, 17.61. Found: C, 52.82; H, 2.79; N, 17.64.

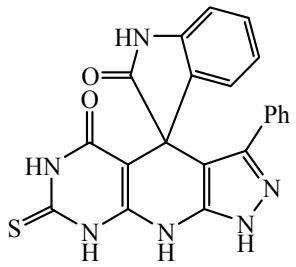
5-Nitro-3'-phenyl-spiro[indoline-3,4'pyrazolo[4′,3′:5,6]pyrido[2,3-d]pyrimidine]-2,5',7'(6'H,8'H,9'H)-trione (**4c**):



White powder (93%); MP >300 ˚C. IR (KBr) (ν_{max} /cm^{-1}): 3313, 1723, 1623. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 6.60-8.02 (8H, m, H-Ar), 9.21 (1H, s, NH), 10.74 (1H, s, NH), 11.72 (1H, s, NH), 12.08 (1H, s, NH), 12.68 (1H, s, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 47.9, 89.0, 99.7, 109.2, 119.5, 125.6, 128.4, 128.8, 128.9,

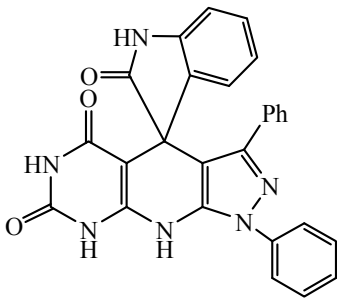
129.4, 138.0, 142.0, 142.5, 145.2, 147.7, 149.2, 159.9, 174.1, 179.7. Anal. Calcd for $C_{21}H_{13}N_7O_5$: C, 56.89; H, 2.96; N, 22.11. Found: C, 56.86; H, 2.93; N, 22.14.

3'-Phenyl-7'-thioxo-spiro[indoline-3,4' pyrazolo[4′,3′:5,6]pyrido[2,3 d]pyrimidine]- 2,5'(6'H,8'H,9'H)-dione (4d):



White powder (88%); MP >300 ˚C. IR (KBr) (ν_{max} /cm^{-1}): 3409, 3274, 3049, 1687, 1626. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 6.49-7.27 (9H, m, H-Ar), 9.10 (1H, s, NH), 9.99 (1H, s, NH), 11.68 (1H, s, NH), 12.00 (1H, s, NH), 12.55 (1H, s, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 47.9, 91.0, 100.6, 109.4, 121.8, 123.8, 128.1, 128.2, 128.8, 129.1, 137.5, 139.9, 142.8, 145.3, 147.1, 169.6, 173.9, 178.9. Anal. Calcd for $C_{21}H_{14}N_6O_2S$: C, 60.86; H, 3.40; N, 20.28. Found: C, 60.89; H, 3.43; N, 20.26.

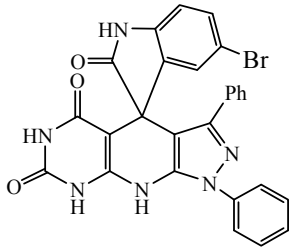
1',3'-diphenyl-spiro[indoline-3,4'- pyrazolo[4′,3′:5,6]pyrido[2,3-d]pyrimidine]- 2,5',7'(6'H,8'H,9'H)-trione (4e)



White powder (94%); MP >300 ˚C. IR (KBr) (ν_{max} /cm^{-1}): 3219, 1741, 1622. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 6.50-7.69 (14H, m, H-Ar), 9.36 (1H, s, NH), 9.93 (1H, s, NH), 10.18 (1H, s, NH), 10.67 (1H, s, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 48.3, 88.1, 100.7, 109.4, 121.7, 123.4, 124.1, 127.8, 128.2, 128.3, 128.9, 130.3, 132.9, 136.7, 137.4, 137.9, 142.9, 146.5, 149.8, 149.9, 162.2, 179.1. Anal.

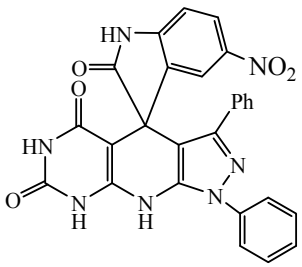
Calcd for $C_{27}H_{18}N_6O_3$: C, 68.35; H, 3.82; N, 17.71. Found: C, 68.31; H, 3.85; N, 17.74.

5-Bromo-1',3'-diphenyl-spiro[indoline-3,4'-pyrazolo[4′,3′:5,6]pyrido[2,3-*d*]pyrimidine]-2,5', 7'(6'*H*,8'*H*,9'*H*)-trione (4f):



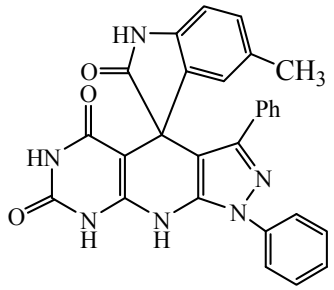
White powder (92%); mp >300 ˚C. IR (KBr) (ν_{max} /cm^{-1}): 3209, 1737, 1714, 1621. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 6.43-7.70 (13H, m, H-Ar), 9.43 (1H, s, NH), 10.12 (1H, s, NH), 10.19 (1H, s, NH), 10.77 (1H, s, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 48.5, 87.5, 100.12, 111.2, 113.3 , 123.5, 126.9, 127.9, 128.3, 128.5, 128.8, 130.3, 130.8, 132.8, 136.8, 137.8, 139.6, 142.2, 146.7, 149.7, 149.8, 162.3, 178.8. Anal. Calcd for $C_{27}H_{17}BrN_6O_3$: C, 58.60; H, 3.10; N, 15.19. Found: C, 58.57; H, 3.07; N, 15.22.

5-Nitro-1',3'-diphenyl-spiro[indoline-3,4'-pyrazolo[4′,3′:5,6]pyrido[2,3-*d*]pyrimidine]-2,5', 7'(6'*H*,8'*H*,9'*H*)-trione (4g):



White powder (95%); mp >300 ˚C. IR (KBr) (ν_{max} /cm^{-1}): 3404, 3101, 1632, 1580. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 6.63-8.06 (13H, m, H-Ar), 9.54 (1H, s, NH), 10.28 (1H, s, NH), 10.73 (1H, s, NH), 10.82 (1H, s, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 48.3, 87.0, 99.6 ,109.3, 119.7, 123.6, 125.7, 128.0, 128.4, 128.6, 128.9, 130.3, 132.5, 136.9, 137.8, 138.0, 142.5, 147.1, 149.3, 149.7, 149.8, 162.4,

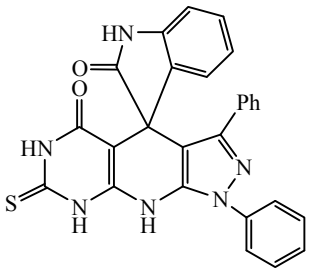
179.9. Anal. Calcd for $C_{27}H_{17}N_7O_5$: C, 62.43; H, 3.30; N, 18.87. Found: C, 62.45; H, 3.34; N, 18.84.



5-Methyl-1',3'-diphenyl-spiro[indoline-3,4'-pyrazolo[4′,3′:5,6]pyrido[2,3-*d*]pyrimidine]-2,5', 7'(6'*H*,8'*H*,9'*H*)-trione (4h):

White powder (88%); mp >300 ˚C. IR (KBr) (ν_{max} /cm^{-1}): 3209, 1738, 1713, 1611. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 2.21 (3H, s, CH_3), 6.42-7.70 (13H, m, H-Ar), 9.38 (1H, s, NH), 9.86 (1H, s, NH), 10.20 (1H, s, NH), 10.70 (1H, s, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 21.1, 48.4, 88.2, 100.8, 109.2, 23.5, 124.8, 127.8, 128.2, 128.4, 128.9, 130.3, 130.5, 133, 136.8, 137.6, 137.9, 140.5, 146.5, 149.8, 149.9, 162.2, 179. Anal. Calcd for $C_{28}H_{20}N_6O_3$: C, 68.84; H, 4.13; N, 17.20. Found: C, 68.80; H, 4.16; N, 17.17.

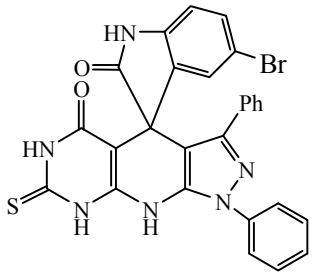
1',3'-Diphenyl-7'-thioxo-spiro[indoline-3,4'-pyrazolo[4′,3′:5,6]pyrido[2,3-*d*]pyrimidine]-2,5'(6'*H*,8'*H*,9'*H*)-dione (4i):



White powder (92%); mp >300 ˚C. IR (KBr) (ν_{max} /cm^{-1}): 3301, 3049, 1736, 1668. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 6.52-7.71 (14H, m, H-Ar), 9.41 (1H, s, NH), 10.04 (1H, s, NH), 11.75 (1H, s, NH), 12.17 (1H, s, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 48.4, 92.2, 100.4, 109.5, 121.9, 123.4, 124.5, 127.9, 128.3, 128.5, 128.9, 130.3, 132.8, 136.2, 136.9, 137.8, 142.9, 145.9, 149.8, 159.7, 173.8,

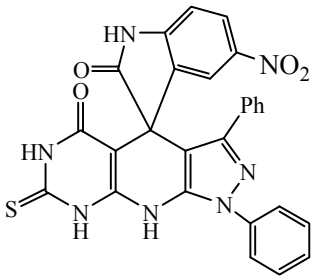
178.6. Anal. Calcd for $C_{27}H_{18}N_6O_2S$: C, 66.11; H, 3.70; N, 17.13. Found: C, 66.14; H, 3.74; N, 17.10.

5-Bromo-1',3'-diphenyl-7'-thioxo-spiro[indoline-3,4'-pyrazolo[4′,3′:5,6]pyrido[2,3-*d*]pyrimidine]-2,5'(6'*H*,8'*H*,9'*H*)-dione (4j):



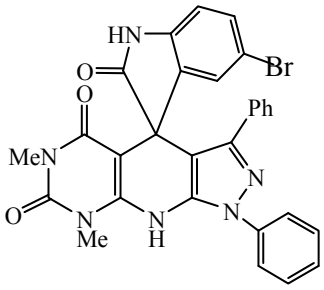
White powder (89%); mp >300 ˚C. IR (KBr) (ν_{max} /cm^{-1}): 3337, 1741, 1663. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 6.45-7.68 (13H, m, H-Ar), 9.44 (1H, s, NH), 10.21 (1H, s, NH), 11.73 (1H, s, NH), 12.24 (1H, s, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 48.6, 91.5, 99.8, 111.3, 113.5, 123.4, 127.2, 127.9, 128.4, 128.6, 128.8, 130.3, 131.1, 132.6, 136.3, 137.7, 139.1, 142.2, 146.2, 149.8, 159.7, 173.8, 178.4. Anal. Calcd for $C_{27}H_{17}BrN_6O_2S$: C, 56.95; H, 3.01; N, 14.76. Found: C, 56.92; H, 3.04; N, 14.73.

5-Nitro-1',3'-diphenyl-7'-thioxo-spiro[indoline-3,4'-pyrazolo[4′,3′:5,6]pyrido[2,3-*d*]pyrimidine]-2,5'(6'*H*,8'*H*,9'*H*)-dione (4k):



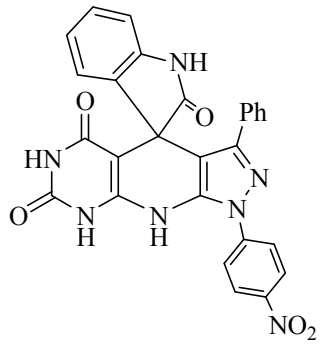
White powder (94%); mp >300 ˚C. IR (KBr) (ν_{max} /cm^{-1}): 3378, 1700, 1642. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 6.65-8.01 (13H, m, H-Ar), 9.54 (1H, s, NH), 10.82 (1H, s, NH), 11.79 (1H, s, NH), 12.28 (1H, s, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 48.3, 91.0, 99.3, 109.3, 120.1, 123.4, 125.9, 128.1, 128.4, 128.8, 128.9, 130.3, 132.4, 136.4, 137.4, 137.6, 142.6, 146.5, 149.3, 149.8, 159.9, 173.9, 179.4. Anal. Calcd for $C_{27}H_{17}N_7O_4S$: C, 60.55; H, 3.20; N, 18.31. Found: C, 60.52; H, 3.17; N, 18.28.

5-Bromo-6',8'-dimethyl-1',3'-diphenyl-spiro[indoline-3,4' pyrazolo[4′,3′:5,6]pyrido[2,3- d]pyrimidine]2,5',7'(6'H,8'H,9'H)-trione (4l)



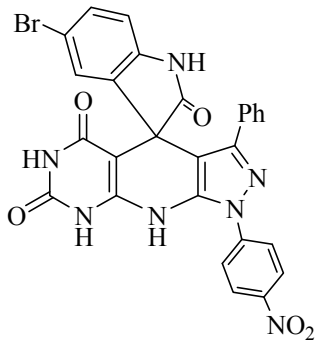
White powder (90%); MP >300 ˚C. IR (KBr) (ν_{max} /cm^{-1}): 3373, 3203, 1733, 1640, 1624. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 3.03 (3H, s, CH_3), 3.54 (3H, s, CH_3), 6.41-7.80 (13H, m, H-Ar), 9.73 (1H, s, NH), 10.14 (1H, s, NH). Anal. Calcd for $C_{29}H_{21}BrN_6O_3$: C, 59.91; H, 3.64; N, 14.45. Found: C, 59.94; H, 3.68; N, 14.42.

1'-Phenyl-3'-(4-nitrophenyl)-spiro[indoline-3,4'-pyrazolo[4′,3′:5,6]pyrido[2,3-*d*]pyrimidine]2,5',7'(6'*H*,8'*H*,9'*H*)-trione (4n):



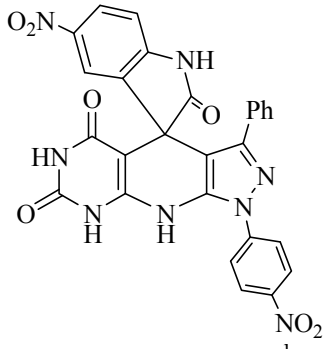
White powder (89%); mp >300 ˚C. IR (KBr) (ν_{max} /cm^{-1}): 3419, 3337, 1716, 1689. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 6.49-7.96 (9H, m, H-Ar), 7.97 (2H, d, J= 9.0 Hz, H-Ar), 8.45 (2H, d, J= 9.0 Hz, H-Ar), 9.64 (1H, s, NH), 9.99 (1H, s, NH), 10.52 (1H, s, NH), 10.77 (1H, s, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 48.2, 88.6, 102.1, 109.5, 121.8, 123.1, 124.1, 125.7, 127.9, 128.4, 128.7, 128.8, 132.4, 137.1, 137.7, 142.9, 143.2, 145.9, 146.8, 150.0, 151.4, 162.2, 178.9. Anal. Calcd for $C_{27}H_{17}N_7O_5$: C, 62.43; H, 3.30; N, 18.87. Found: C, 62.46; H, 3.26; N, 18.90.

5-Bromo-1'-phenyl-3'-(4-nitrophenyl)-spiro[indoline-3,4'-pyrazolo[4′,3′:5,6]pyrido[2,3-*d*]pyrimidine]2,5',7'(6'*H*,8'*H*,9'*H*)-trione (4o):



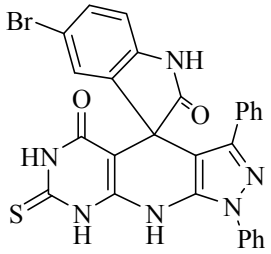
White powder (86%); mp >300 ˚C. IR (KBr) (ν_{max} /cm^{-1}): 3368, 3008, 1749, 1683, 1650. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 6.63-7.99 (8H, m, H-Ar), 7.98 (2H, d, J= 8.8 Hz, H-Ar), 8.46 (2H, d, J= 8.7 Hz, H-Ar), 9.68 (1H, s, NH), 10.14 (1H, s, NH), 10.48 (1H, s, NH), 10.83 (1H, s, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 48.4, 87,9, 101.4, 111.3, 113.3, 123.2, 125.7, 127.0, 128.0, 128.8, 131.0, 132.2, 137.8, 139.3, 142.2, 143.2, 146.0, 146.9, 149.9, 151.3, 162.3, 178.6. Anal. Calcd for $C_{27}H_{16}BrN_7O_5$: C, 54.20; H, 2.70; N, 16.39. Found: C, 54.23; H, 2.73; N, 16. 42.

5-Nitro-1'-phenyl-3'-(4-nitrophenyl)-spiro[indoline-3,4'-pyrazolo[4′,3′:5,6]pyrido[2,3-*d*]pyrimidine]2,5',7'(6'*H*,8'*H*,9'*H*)-trione (4p):



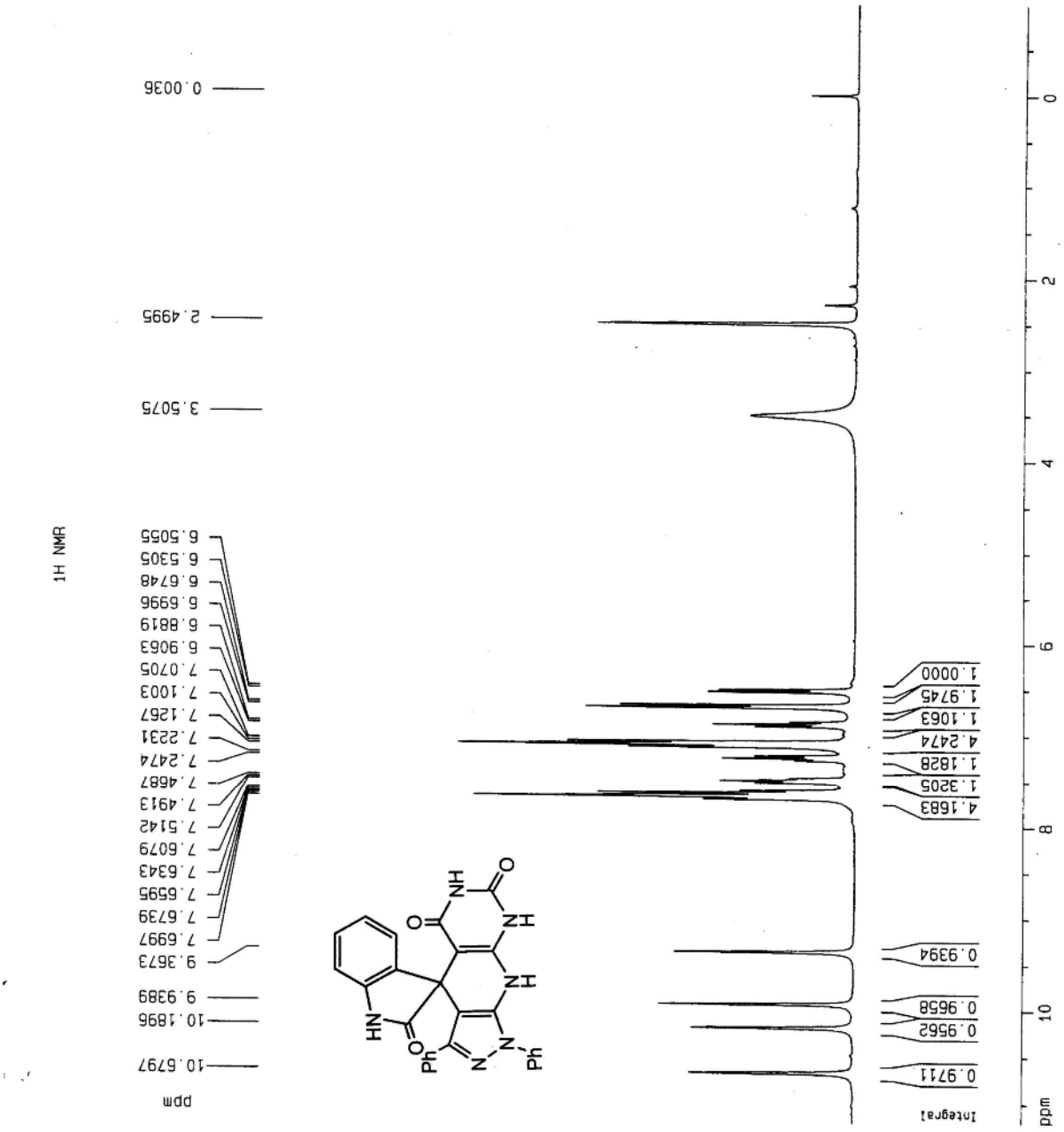
White powder (91%); mp >300 ˚C. IR (KBr) (ν_{max} /cm^{-1}): 3368, 3111, 1732, 1647. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 6.60-8.46 (12H, m, H-Ar), 9.77 (1H, s, NH), 10.55 (1H, s, NH), 10.74 (1H, s, NH), 10.87 (1H, s, NH). Anal. Calcd for $C_{27}H_{16}N_8O_7$: C, 57.45; H, 2.86; N, 19.85. Found: C, 57.42; H, 2.83; N, 19.82.

5-Bromo-1',3'-diphenyl-7'-thioxo-spiro[indoline-3,4'-pyrazolo[4′,3′:5,6]pyrido[2,3-*d*]pyrimidine]-2,5'(6'*H*,8'*H*,9'*H*)-dione (4q):

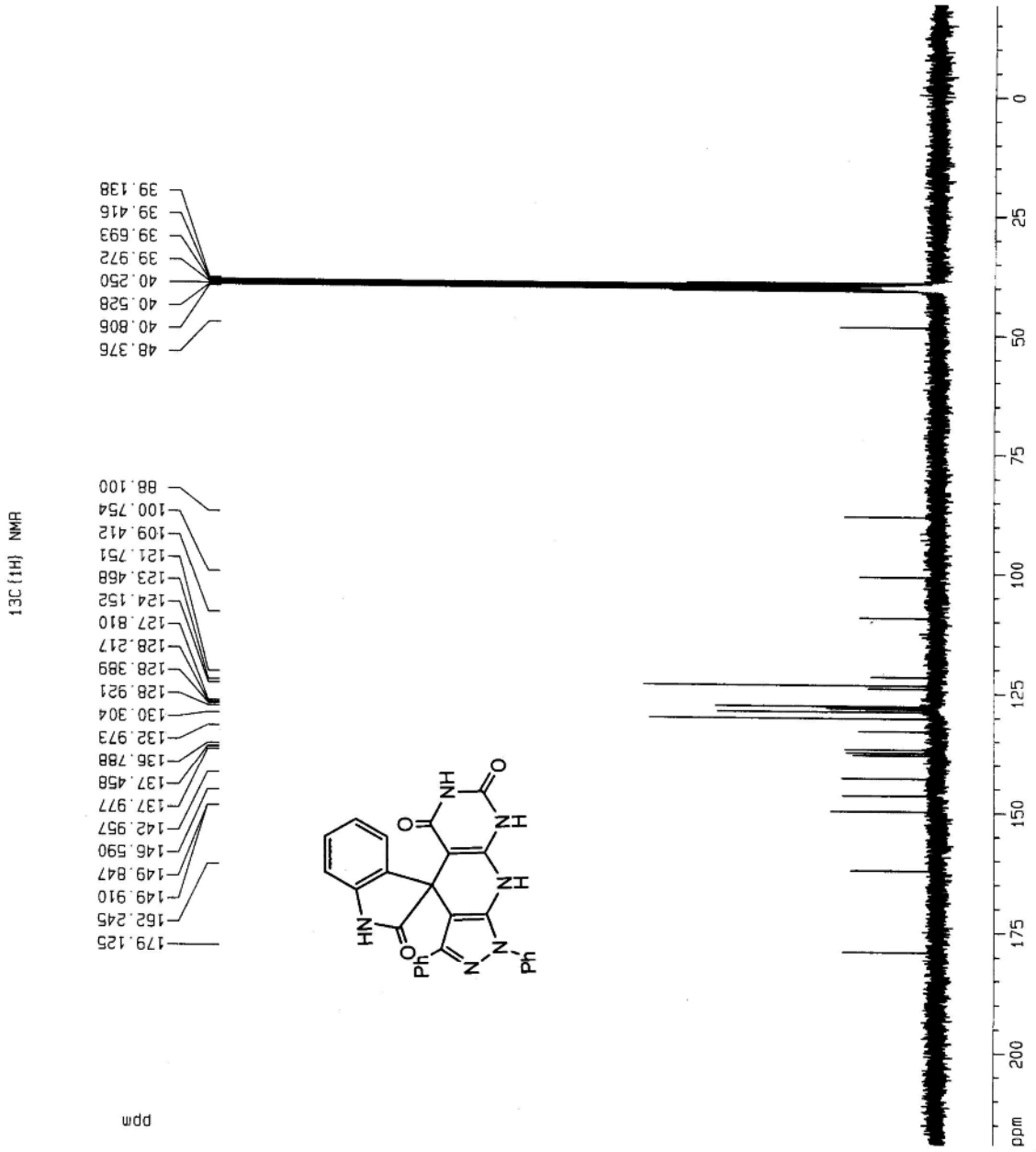


White powder (87%); mp >300 ˚C. IR (KBr) (ν_{max} /cm^{-1}): 3337, 1741, 1663. ^{1}H NMR (300 MHz, DMSO-d_6): δ_H (ppm) 6.45-7.68 (13H, m, H-Ar), 9.44 (1H, s, NH), 10.21 (1H, s, NH), 11.73 (1H, s, NH), 12.24 (1H, s, NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C (ppm) 48.6, 91.5, 99.8, 111.3, 113.5, 123.4, 127.2, 127.9, 128.4, 128.6, 128.8, 130.3, 131.1, 132.6, 136.3, 137.7, 139.1, 142.2, 146.2, 149.8, 159.7, 173.8, 178.4. Anal. Calcd for $C_{27}H_{17}BrN_6O_2S$: C, 56.95; H, 3.01; N, 14.76. Found: C, 56.92; H, 3.04; N, 14.71.

Selected ^{1}H and ^{13}C NMR spectrums



4e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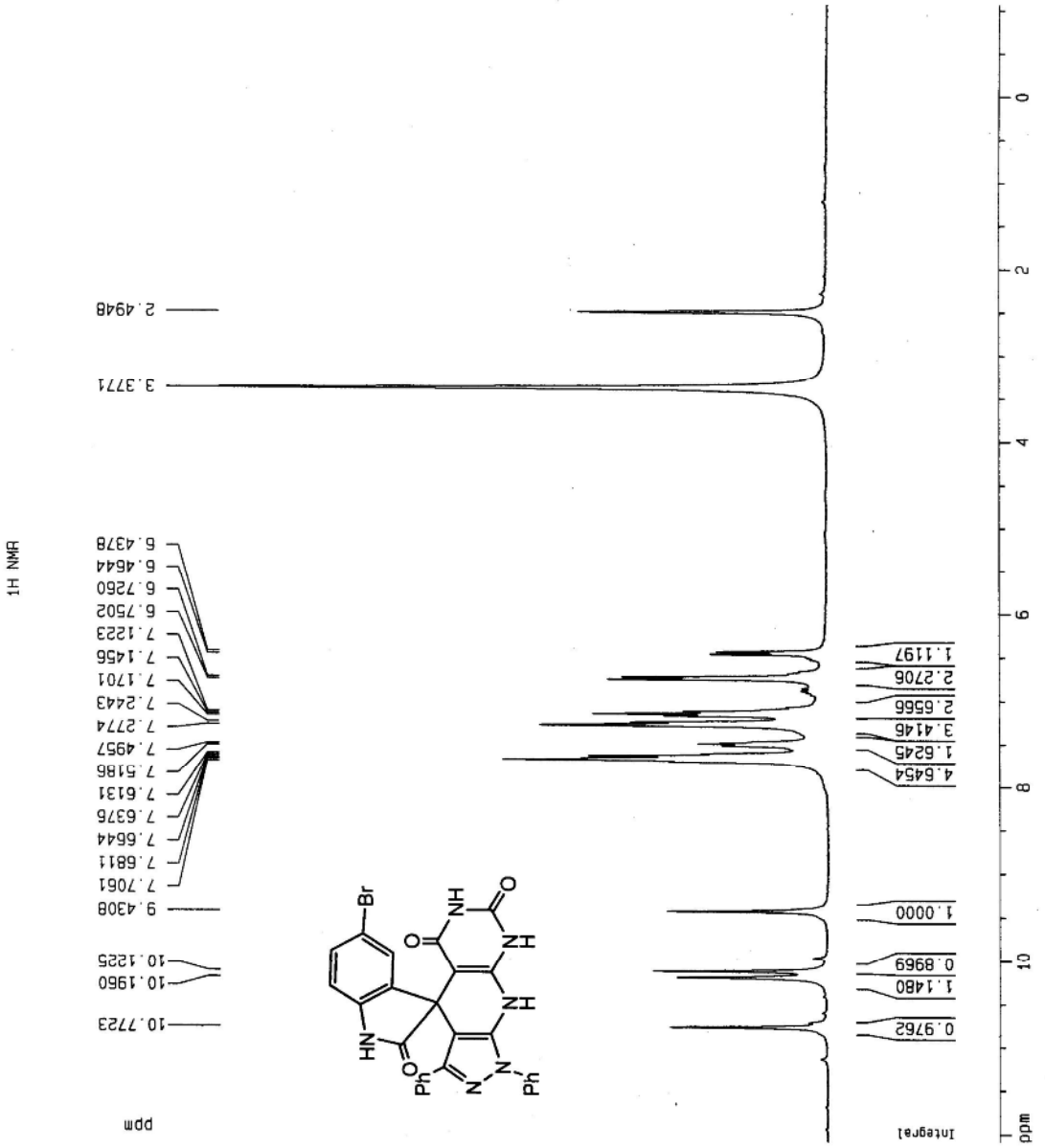
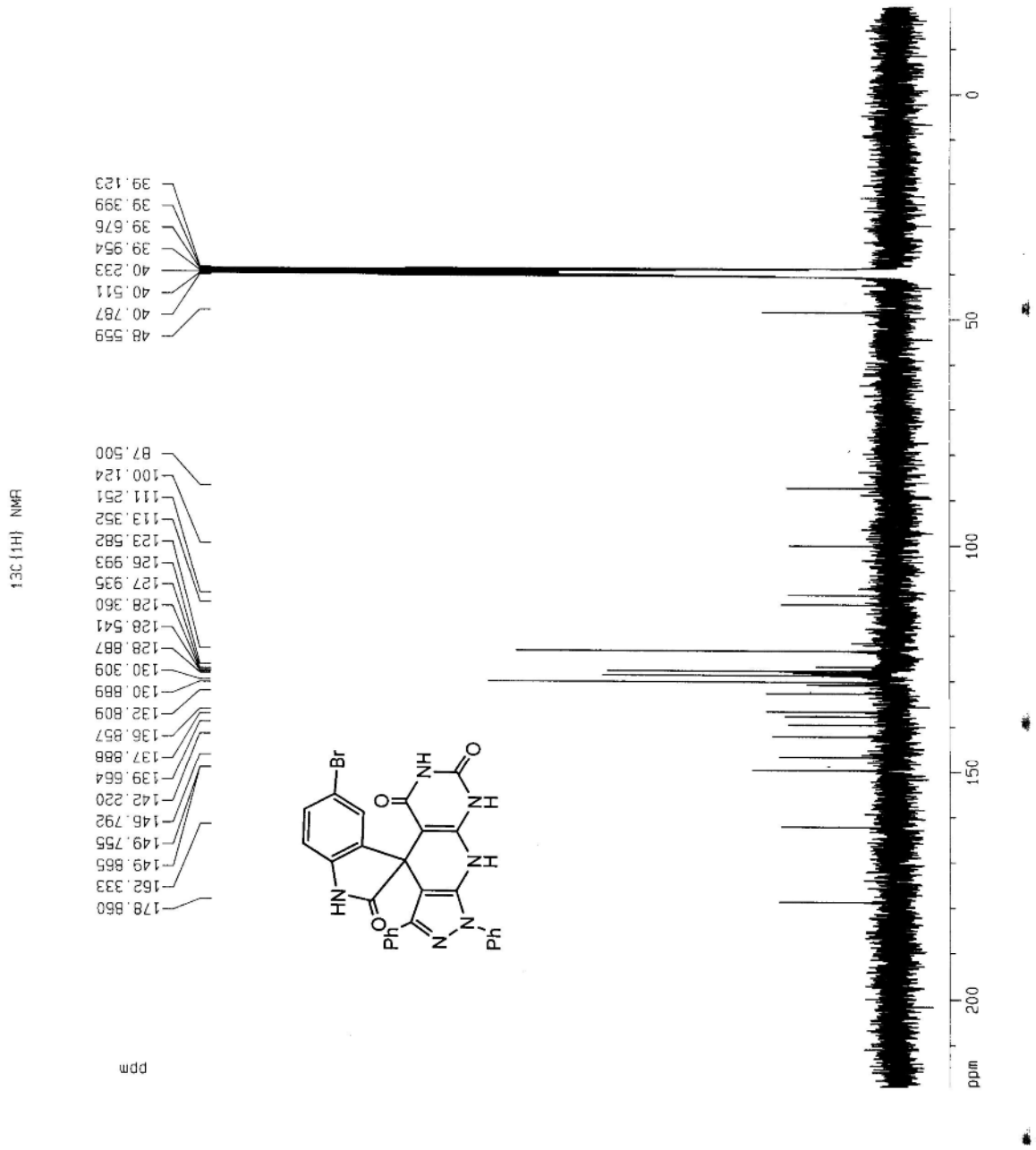
39.972
40.250
40.528
40.806
48.376
88.100
100.754
109.412
121.751
123.468
124.152
127.810
128.217
128.389
128.921
130.304
132.973
136.788
137.458
137.977
142.957
146.590
149.847
149.910
162.245
179.125
ppm
0
25
50
75
100
125
150
175
200
NH
O
HN
O
NH
N
N
Ph
Ph

4e



4f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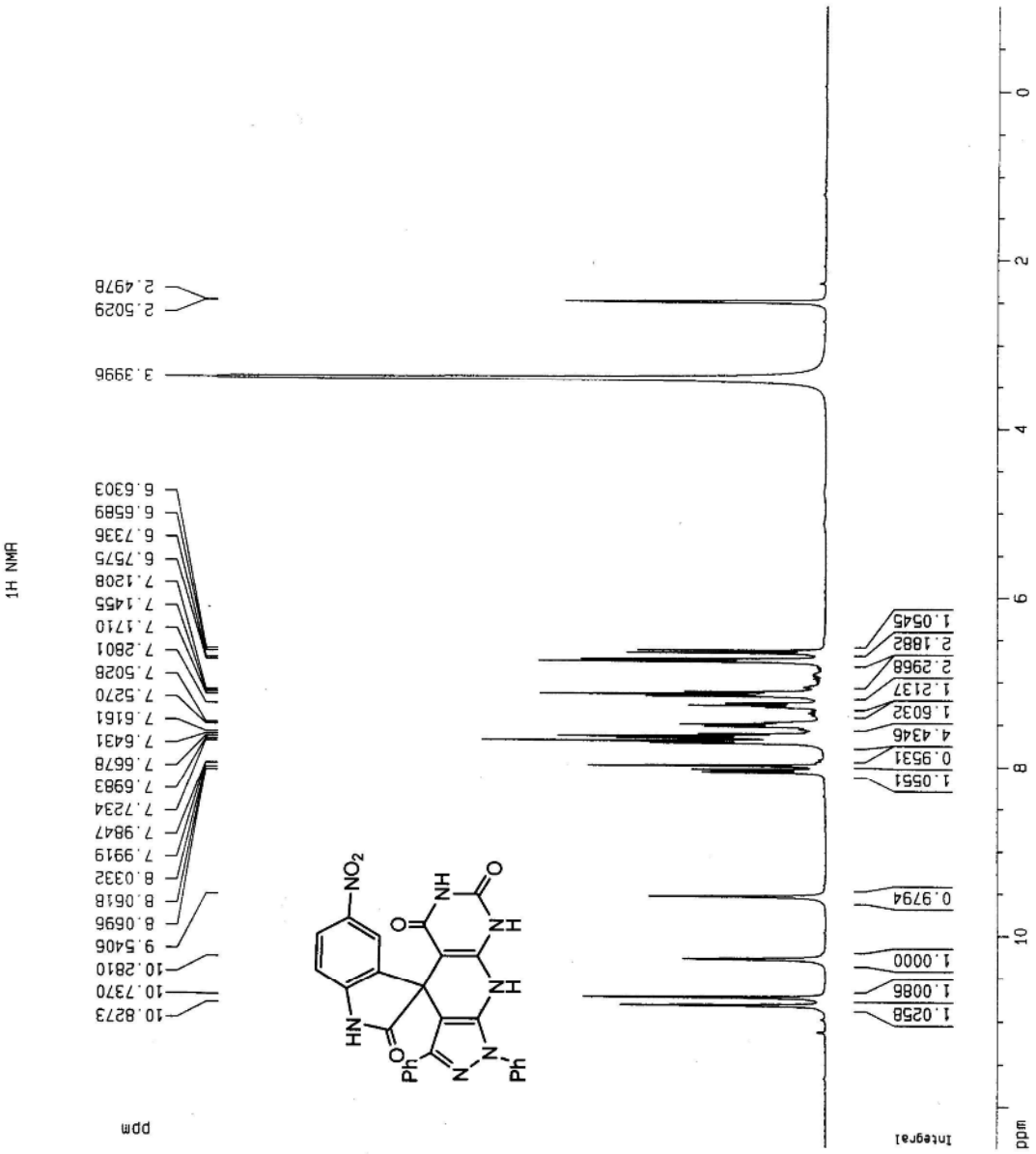
39.676
39.954
40.233
40.511
40.787
48.559
87.500
100.124
111.251
113.352
123.582
126.993
127.935
128.360
128.541
128.887
130.309
130.889
132.809
136.857
137.886
139.664
142.220
146.792
149.755
149.865
162.333
178.860
Br
HN
O
NH
O
NH
NH
N
N
Ph
Ph
0
50
100
150
200
ppm

4f


1H NMR
ppm
Integral
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10.2810
9.5406
8.0696
8.0618
8.0332
7.9919
7.9847
7.7234
7.6983
7.6678
7.6431
7.6161
7.5270
7.5028
7.2801
7.1710
7.1455
7.1208
6.7575
6.7336
6.5589
6.5303
3.3996
2.5029
2.4978
1.0545
2.1882
2.2968
1.2137
1.6032
4.4346
0.9531
1.0551
0.9794
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1.0258
NO2
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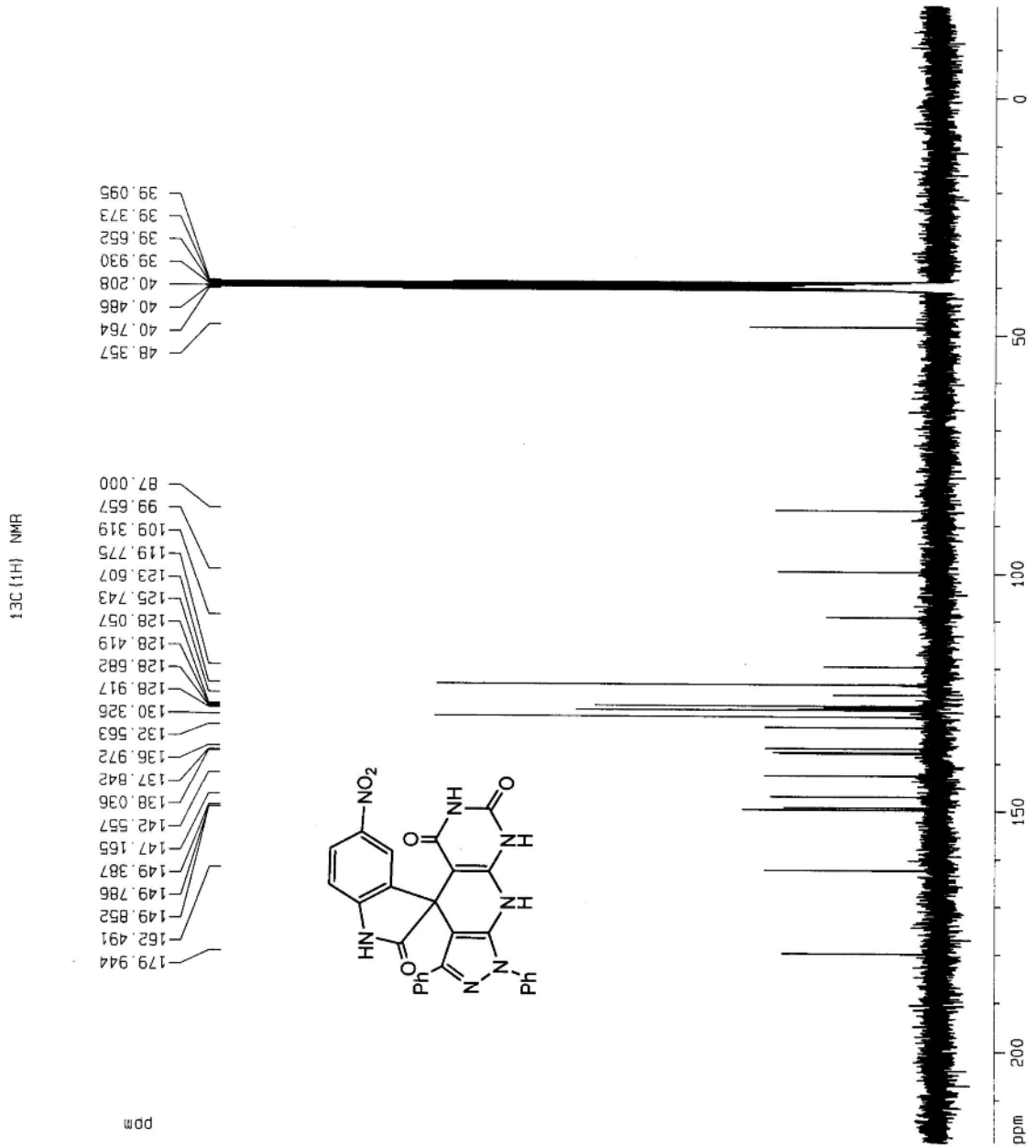
HN
Ph
N
0
2
4
6
8
10

4g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39.930
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40.486
40.764
48.357
87.000
99.657
109.319
119.775
123.607
125.743
128.057
128.419
128.682
128.917
130.325
132.563
136.972
137.842
138.036
142.557
147.165
149.387
149.786
149.852
162.491
179.944
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NH
O
NH
HN
O
Ph
N
N
Ph
ppm
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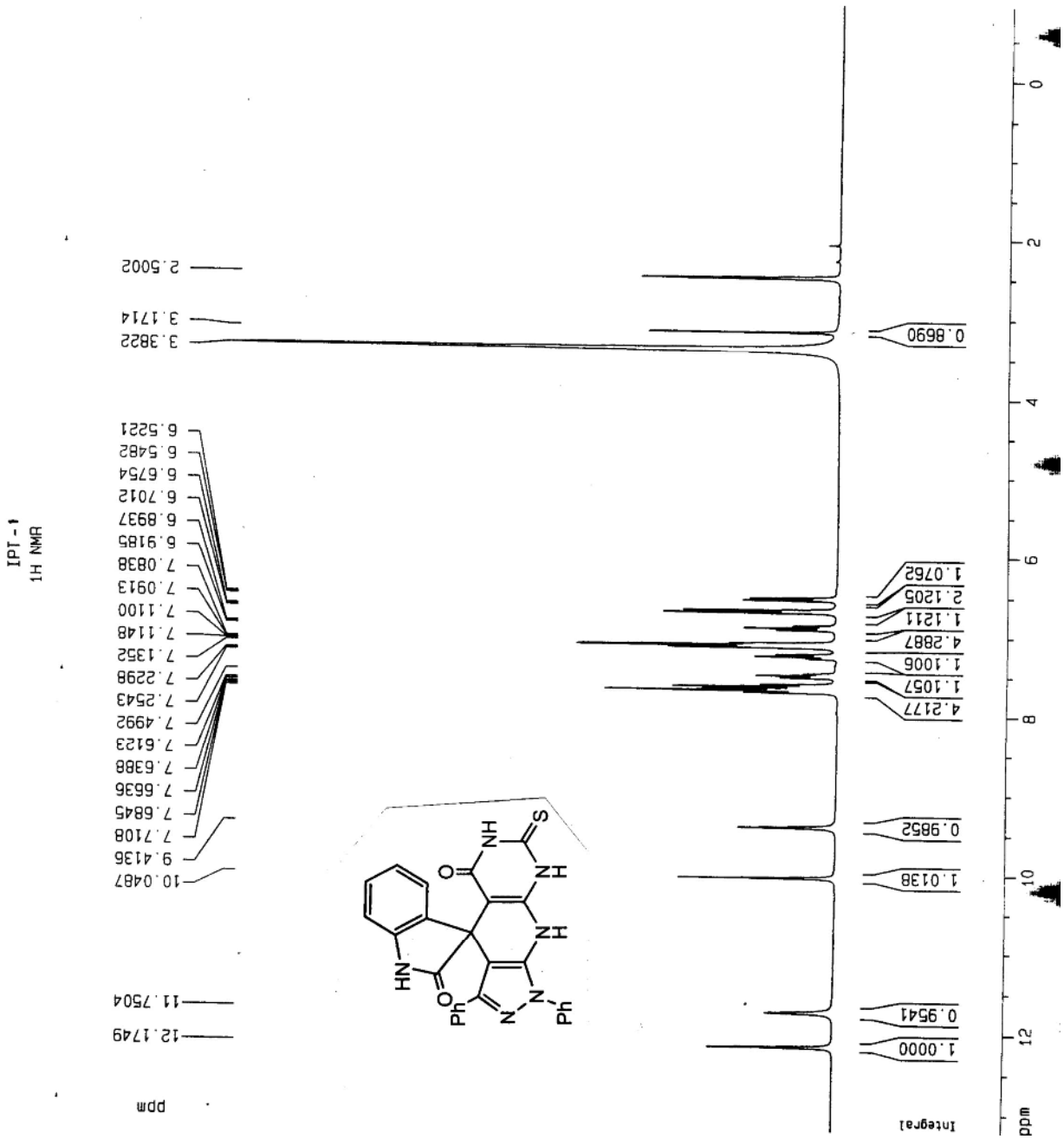
50
100
150
200
ppm

4g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3.1714
3.3822
6.5221
6.5482
6.6754
6.7012
6.8937
6.9185
7.0838
7.0913
7.1100
7.1148
7.1352
7.2298
7.2543
7.4992
7.6123
7.6388
7.6636
7.6845
7.7108
9.4136
10.0487
11.7504
12.1749
ppm
0.8690
1.0752
2.1205
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1.1057
4.2177
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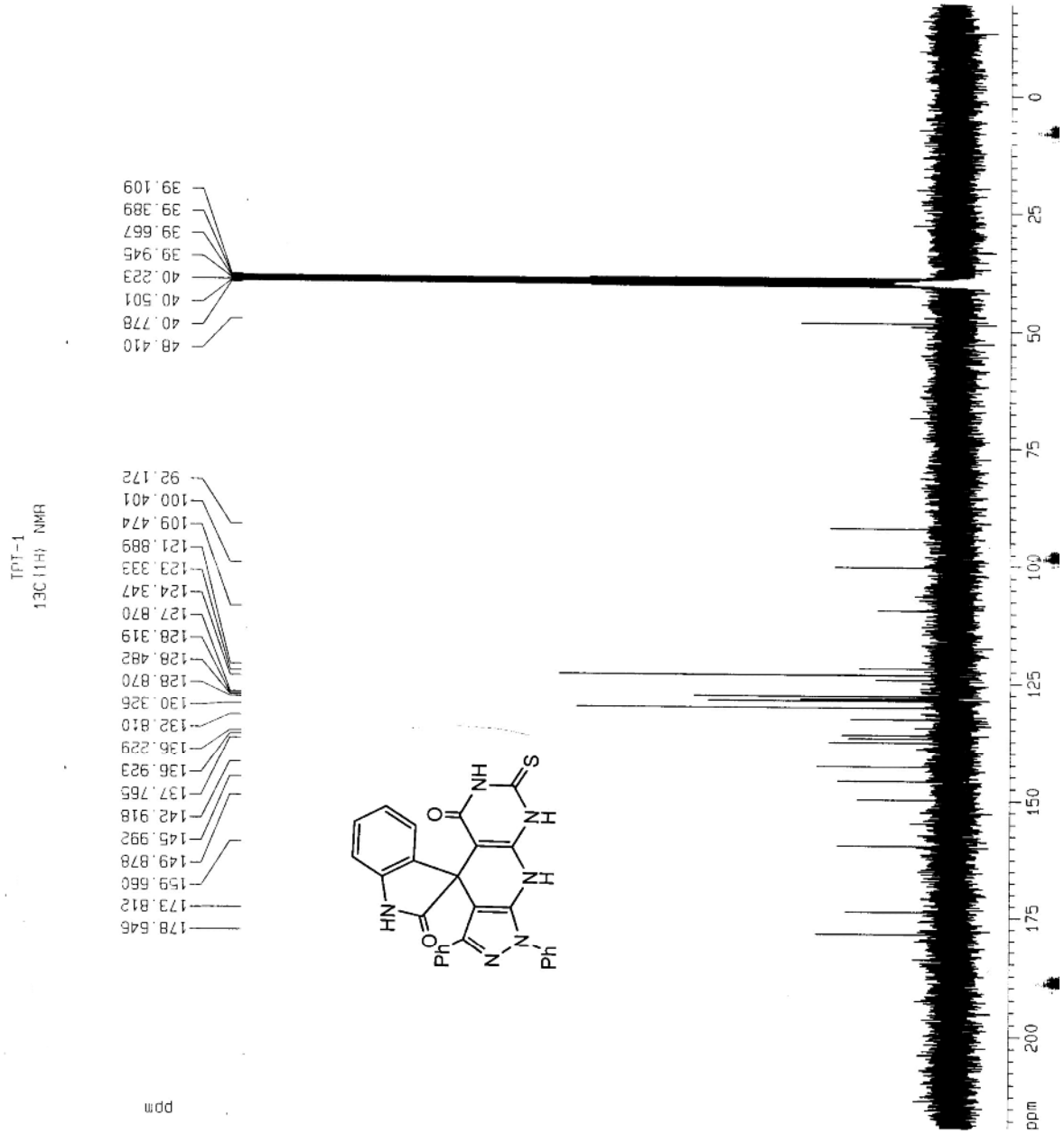
0.9541
1.0000
Integral
ppm

4i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ppm
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149.878
145.992
142.918
137.765
136.923
136.229
132.810
130.326
128.870
128.482
128.319
127.870
124.347
123.333
121.889
109.474
100.401
92.172
48.410
40.778
40.501
40.223
39.945
39.667
39.389
39.109
0
25
50
75
100
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175
200
NH
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O
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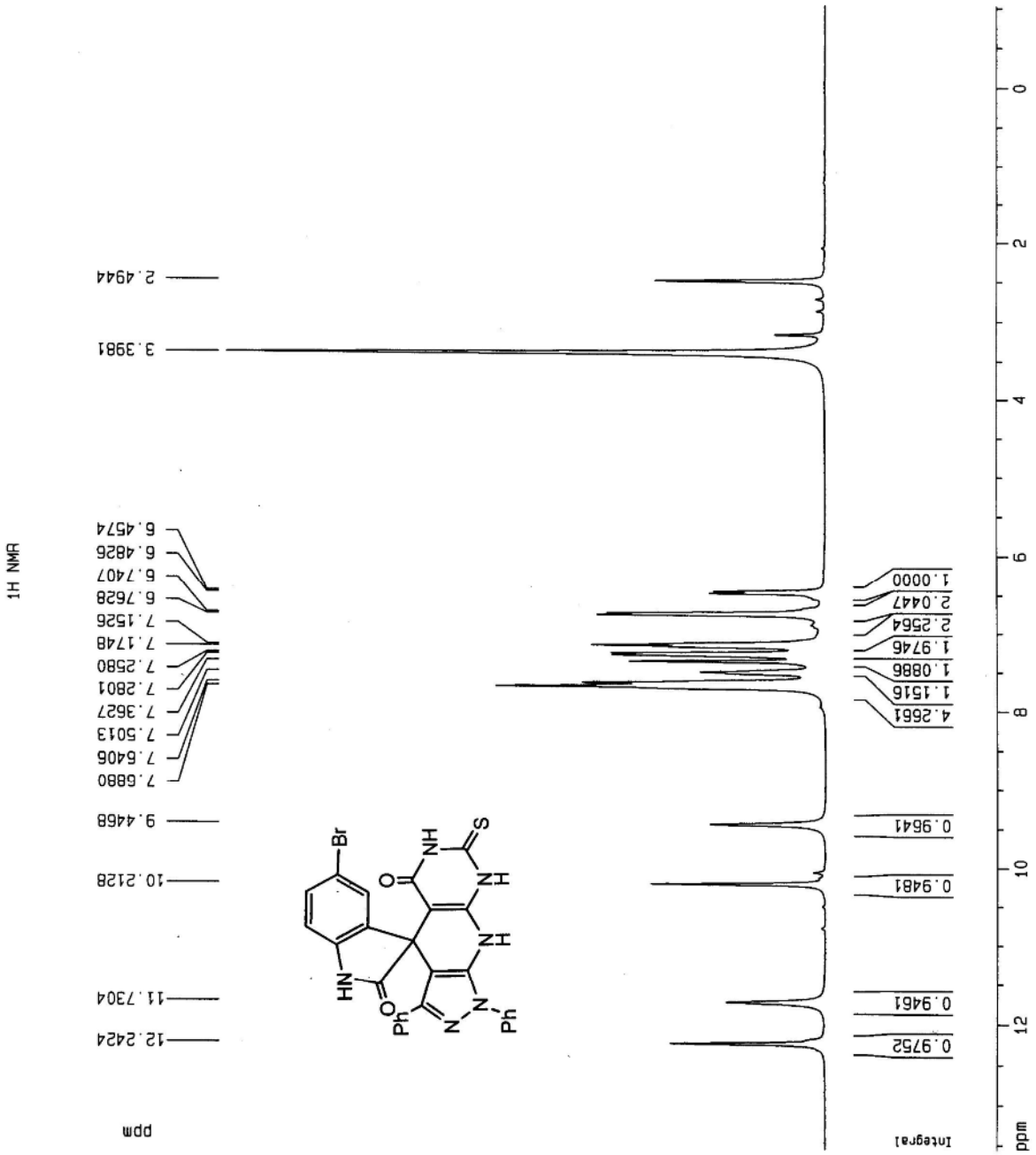
H
N
H
HN
O
Ph
N
N
Ph

4i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Integral
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7.1526
7.1748
7.2580
7.2801
7.3627
7.5013
7.6406
7.6880
9.4468
10.2128
11.7304
12.2424
1.0000
2.0447
2.2564
1.9746
1.0886
1.5156
4.2661
0.9641
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NH
HN
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Ph
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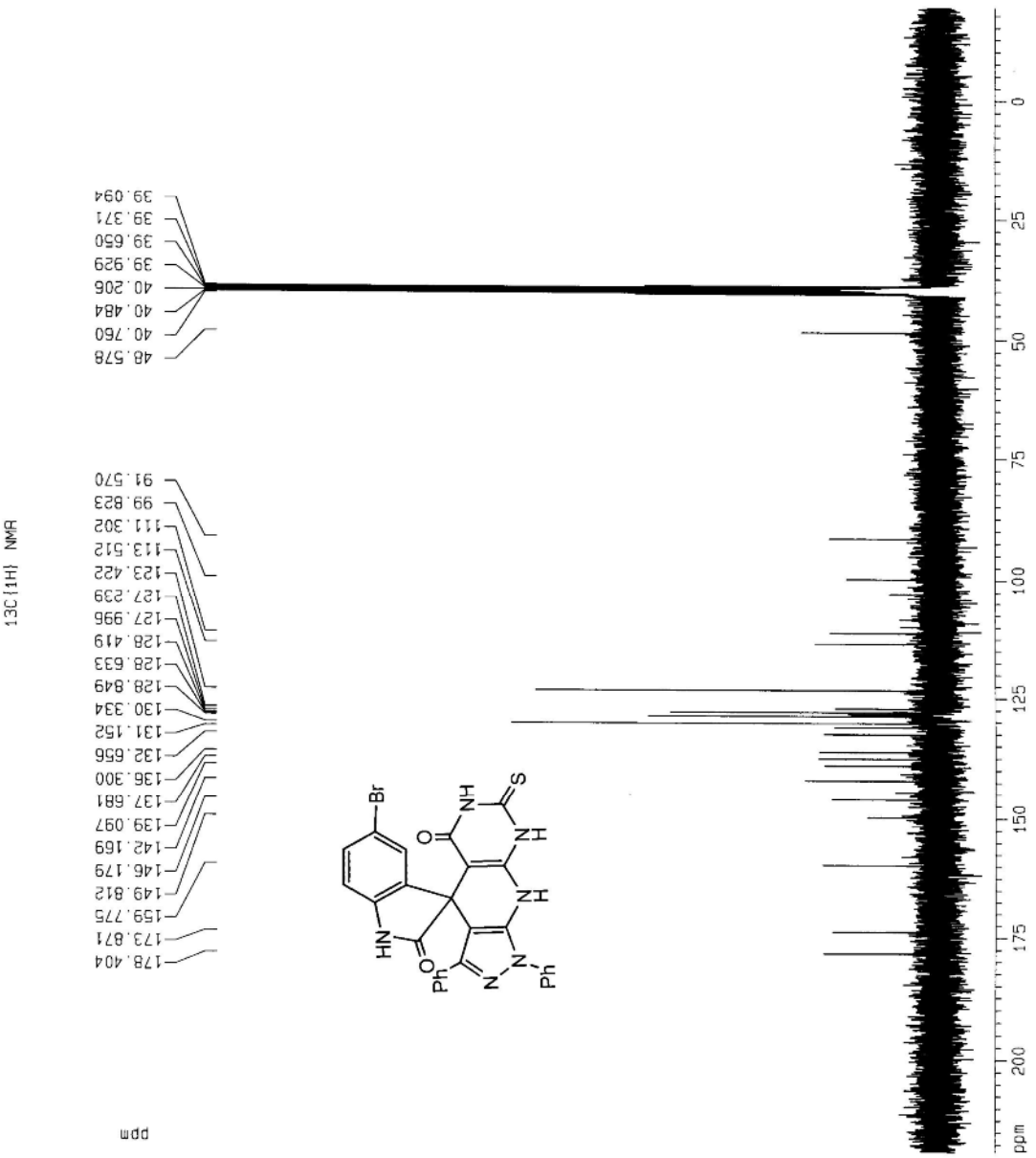
Ph

4j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50
75
100
125
150
175
200
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39.650
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40.206
40.484
40.760
48.578
91.570
99.823
111.302
113.512
123.422
127.239
127.996
128.419
128.633
128.849
130.334
131.152
132.656
136.300
137.681
139.097
142.169
146.179
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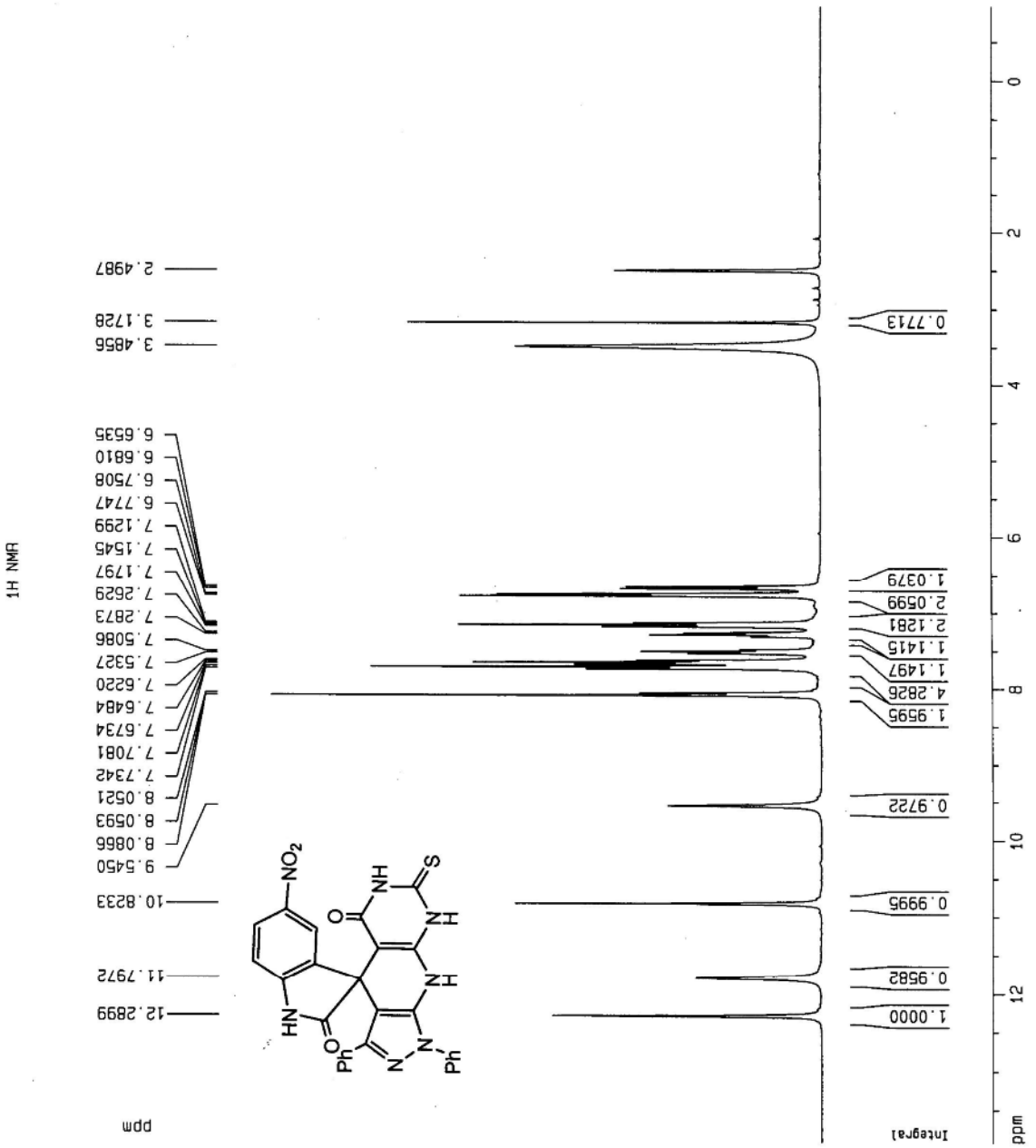
Ph

4j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6.6810
6.7508
6.7747
7.1299
7.1545
7.1797
7.2629
7.2873
7.5086
7.5327
7.6220
7.6484
7.6734
7.7081
7.7342
8.0521
8.0593
8.0866
9.5450
10.8233
11.7972
12.2899
ppm
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2.0599
2.1281
1.1415
1.1497
4.2826
1.9595
0.9722
0.9995
0.9582
1.0000
Integral
ppm
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NH
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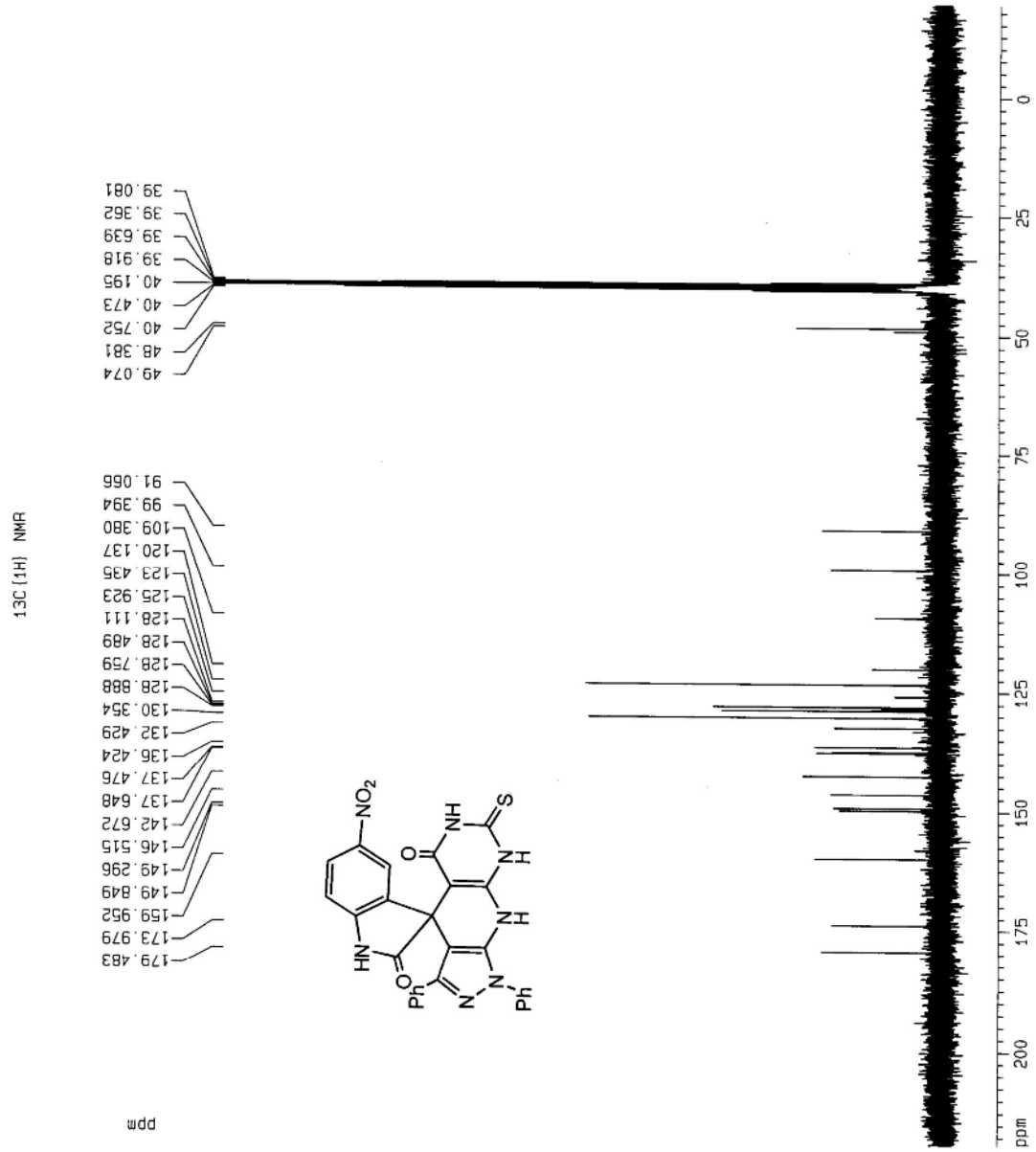
N
N
Ph

4k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123.435
125.923
128.111
128.489
128.759
128.888
130.354
132.429
136.424
137.476
137.648
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173.979
179.483
ppm
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150
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ppm
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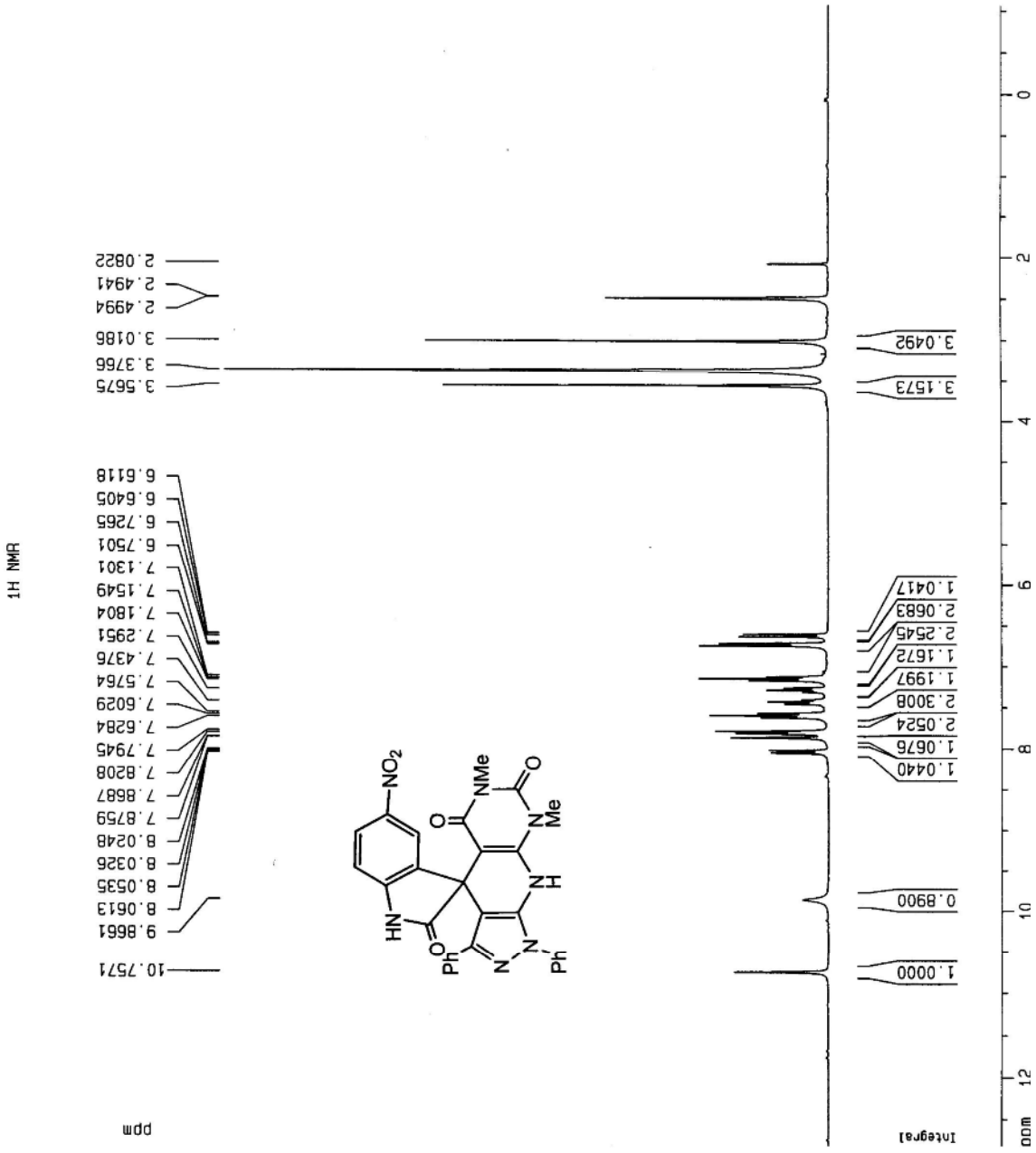
N
H
O
HN
Ph
Ph

4k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7.8208
7.7945
7.6284
7.6029
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7.4376
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7.1804
7.1549
7.1301
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6.7265
6.6405
6.6118
3.5675
3.3766
3.0186
2.4994
2.4941
2.0822
3.1573
3.0492
1.0417
2.0683
2.2545
1.1672
1.1997
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1.0440
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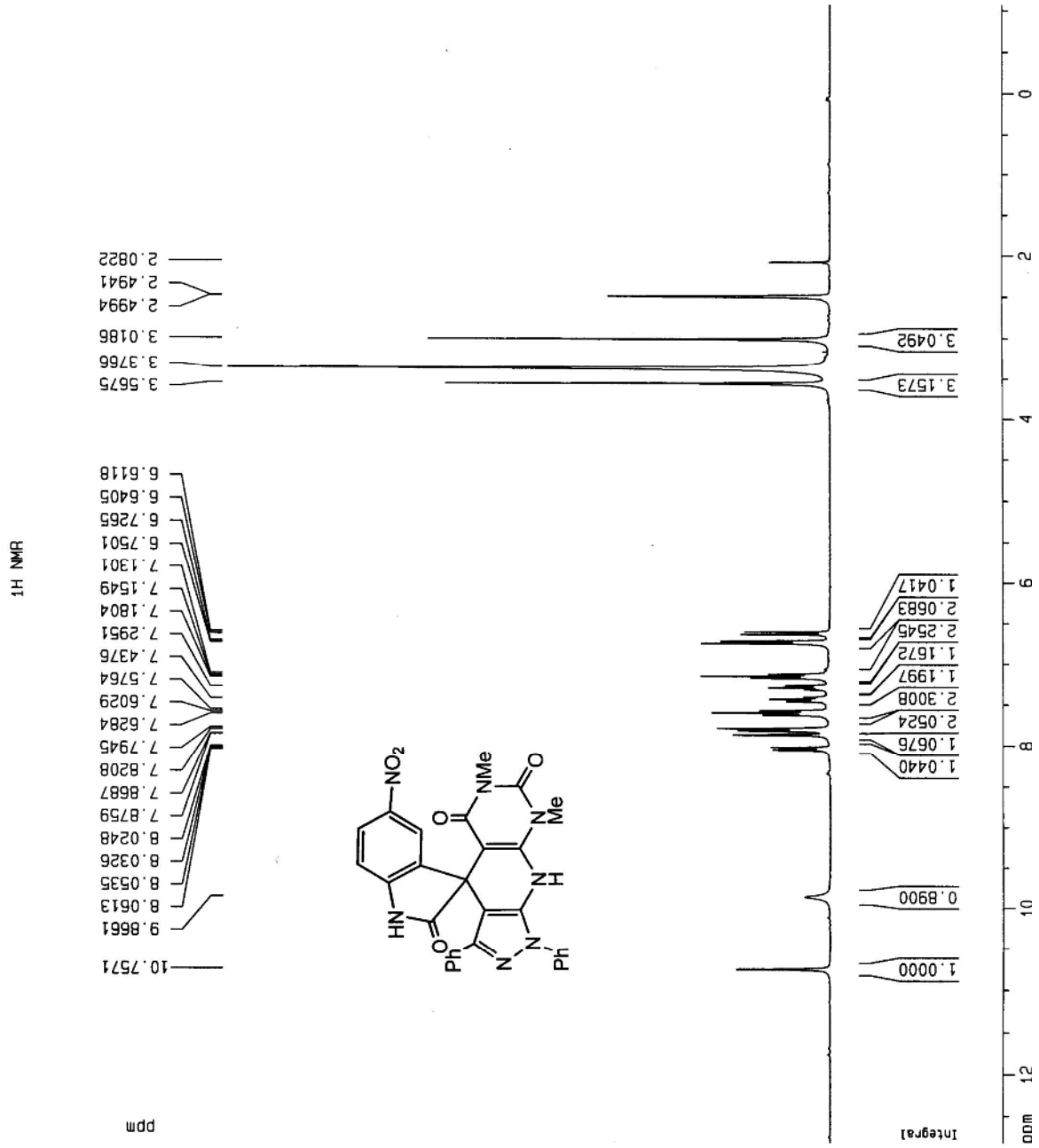
Ph
Ph

4l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7.7945
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7.6029
7.5764
7.4376
7.2951
7.1804
7.1549
7.1301
6.7501
6.7265
6.6405
6.6118
3.5675
3.3766
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2.4941
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3.1573
1.0440
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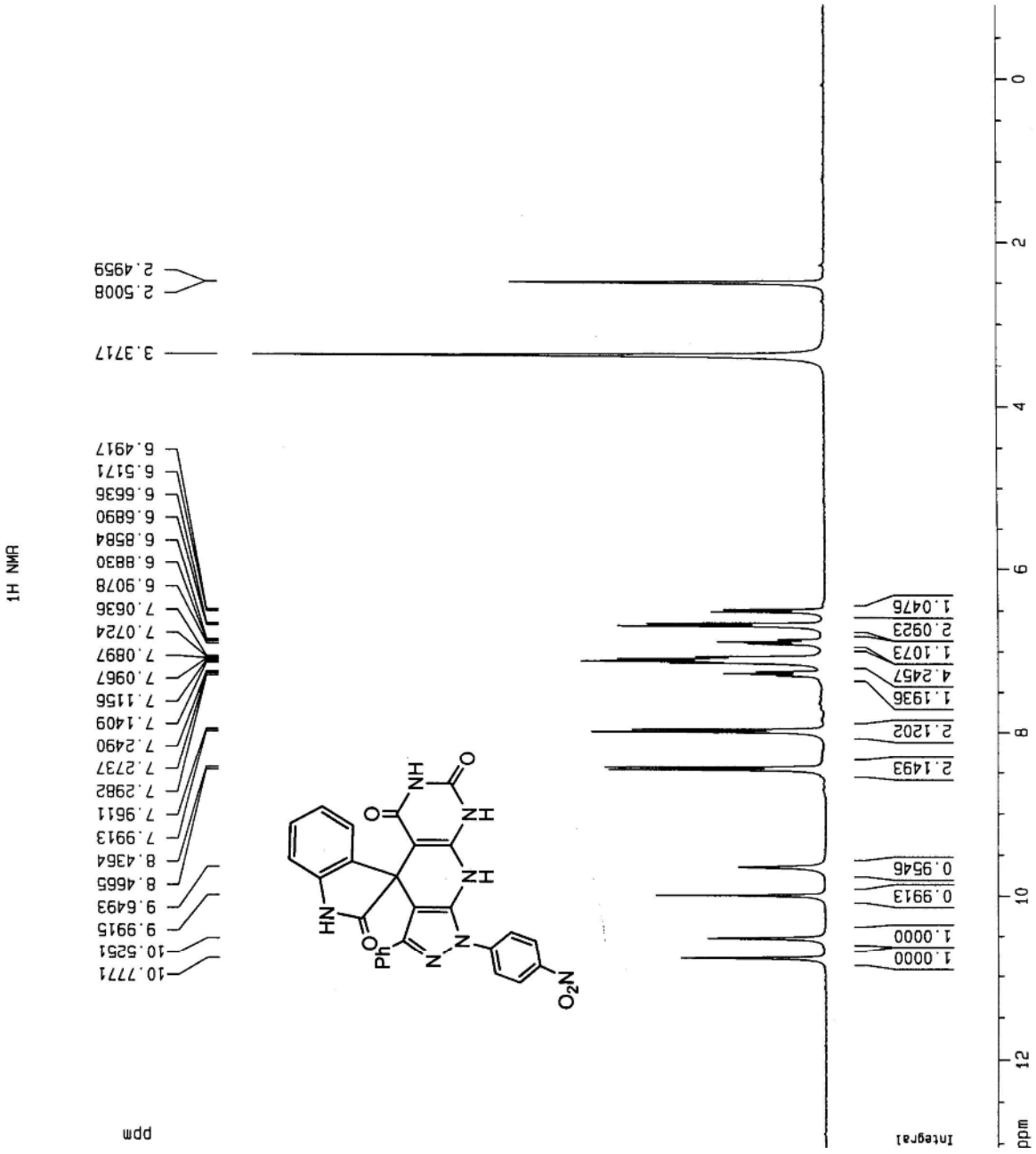
Ph

41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Integral
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6.9078
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7.0967
7.1156
7.1409
7.2490
7.2737
7.2982
7.9611
7.9913
8.4364
8.4665
9.6493
9.9915
10.5251
10.7771
1.0476
2.0923
1.1073
4.2457
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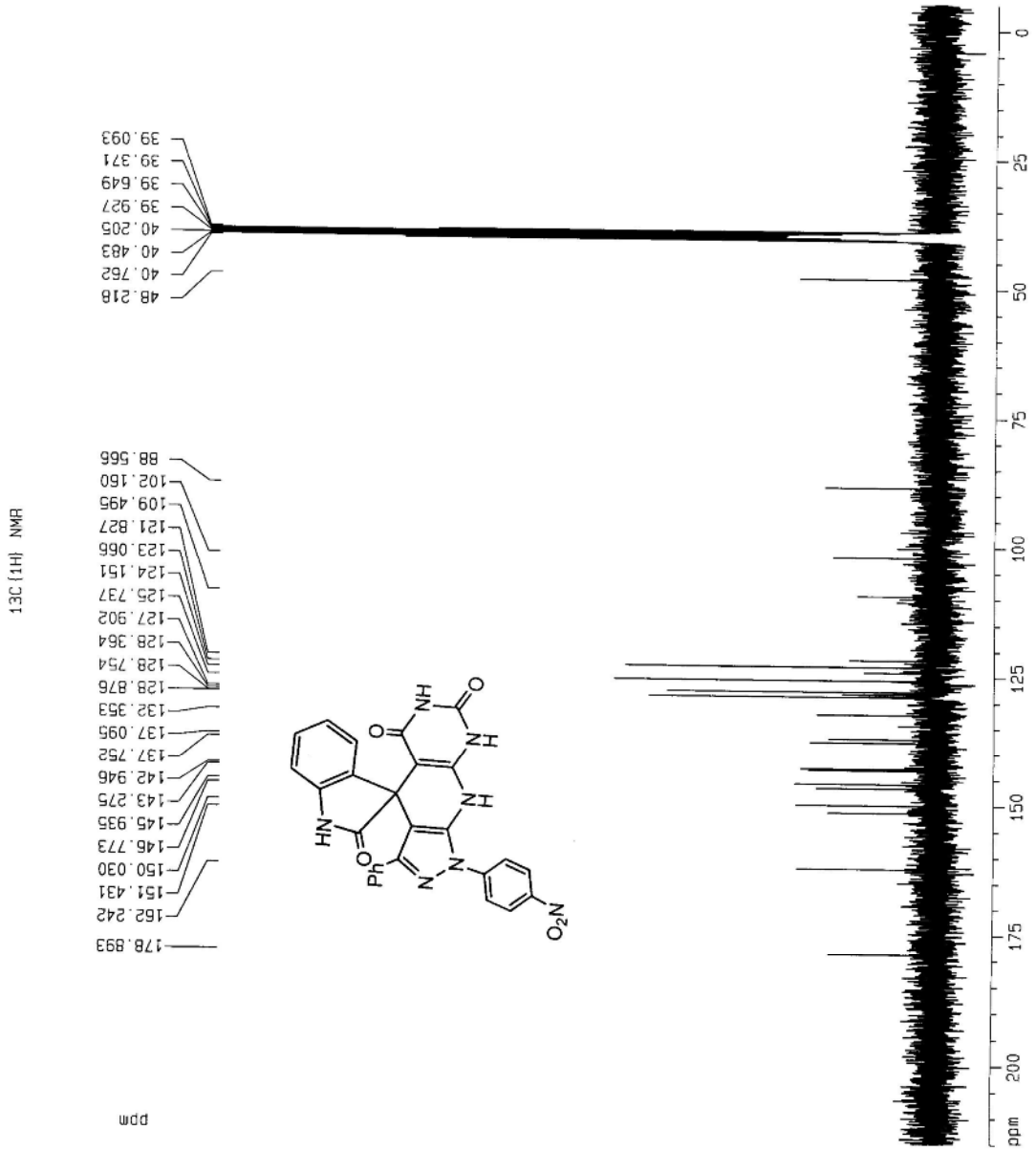
12

4n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39.927
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40.483
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48.218
88.566
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109.495
121.827
123.066
124.151
125.737
127.902
128.364
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128.876
132.353
137.095
137.752
142.946
143.275
145.935
146.773
150.030
151.431
162.242
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ppm
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ppm
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O
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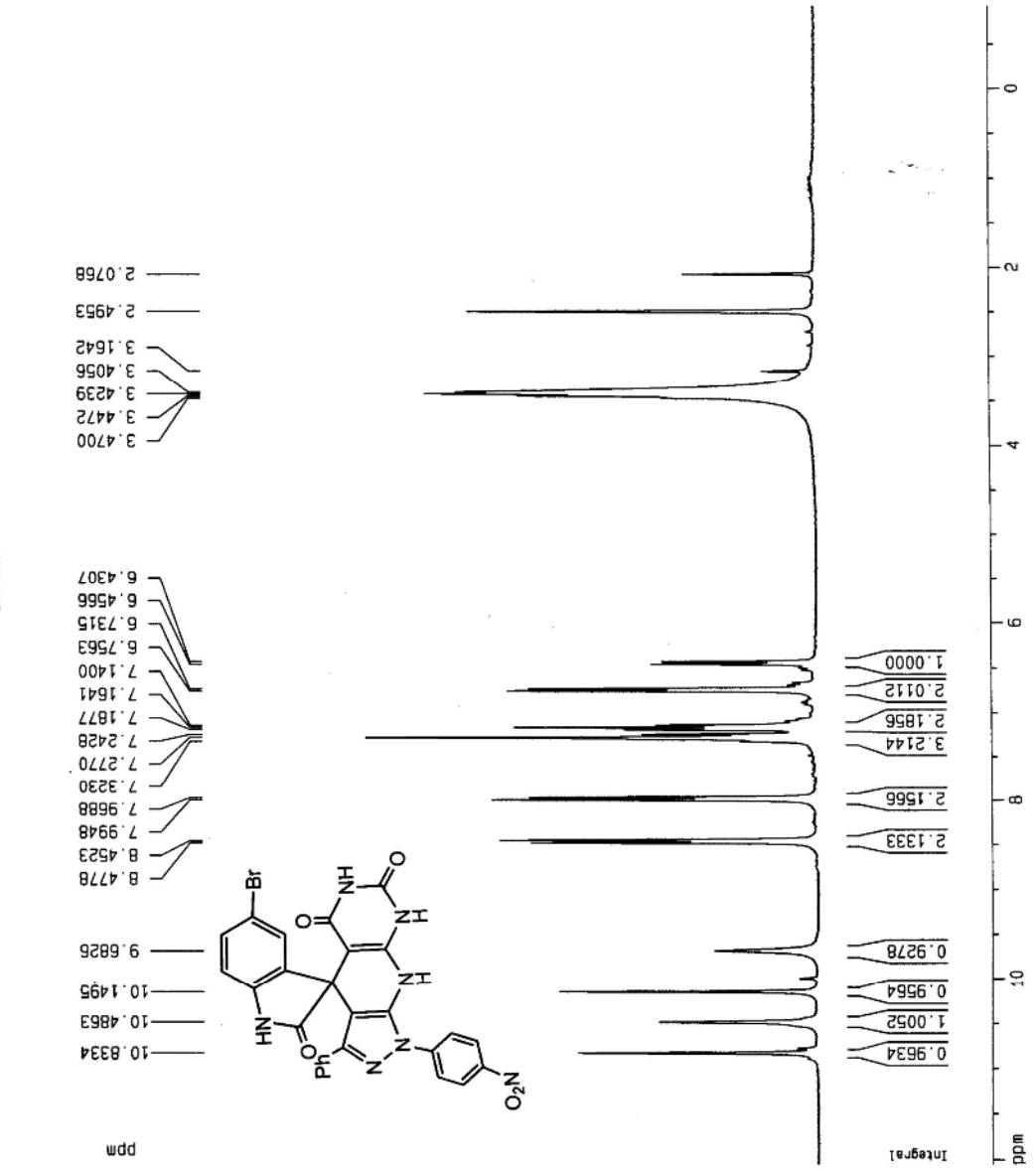
4n


1H NMR
ppm
Integral
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7.9330
7.2770
7.2428
7.1877
7.1641
7.1400
6.7563
6.7315
6.4566
6.4307
3.4700
3.4472
3.4239
3.4056
3.1642
2.4953
2.0768
0.9634
1.0052
0.9564
0.9278
2.1333
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O
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Ph
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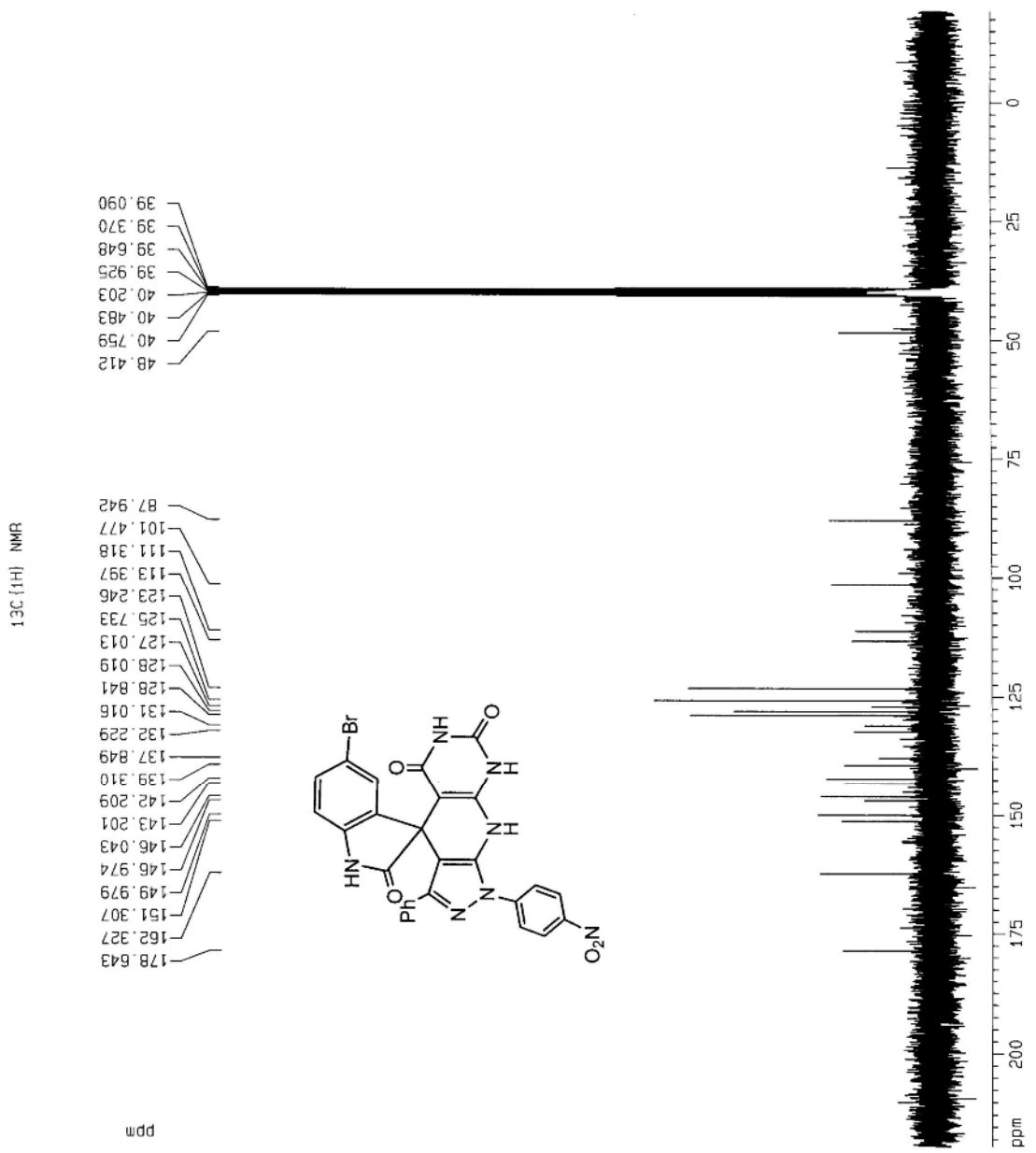
N
O2N

4o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48.412
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113.397
123.246
125.733
127.013
128.019
128.841
131.016
132.229
137.849
139.310
142.209
143.201
146.043
146.974
149.979
151.307
162.327
178.643
ppm
0
25
50
75
100
125
150
175
200
Br
NH
O
NH
NH
HN
O
Ph
N
N
O2N

4o