

Supporting information

Multicomponent synthesis of dispiroheterocycles using magnetically separable and reusable nanostructured heterogeneous catalyst

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Spectroscopy data of all synthesized compounds	Page 2-6
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Compounds name and spectral details

- 3'-(*p*-tolyl)-1'H,3'H-dispiro[indoline-3,2'-pyrimido[4,5-*d*]pyrimidine-4',3''-indoline]-2,2'',5',7'(6'H,8'H)-tetraone (4a).** m.p. >300 °C; ¹H NMR (DMSO-*d*₆, 400 MHz) δ (ppm): 2.35(s, 3H, CH₃), 6.64 (s, 1H, NH), 6.90-7.48 (m, 12H, ArH); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ (ppm): 22.7, 81.5, 89.7, 98.6, 118.7, 121.2, 122.5, 123.7, 124.8, 126.4, 128.4, 129.2, 129.8, 131.4, 132.3, 133.5, 138.2, 143.2, 143.8, 150.7, 156.7, 164.8, 165.6, 168.7, 169.2. Anal. calcd. For C₂₇H₂₀N₆O₄: C 65.85, H 4.09, N 17.06%; found: C 65.22, H 3.77, N 16.98 %.
- 5,5''-dibromo-3'-(*p*-tolyl)-1'H,3'H-dispiro[indoline-3,2'-pyrimido[4,5-*d*]pyrimidine-4',3''-indoline]-2,2'',5',7'(6'H,8'H)-tetraone(4b).** m.p. >300 °C; ¹H NMR (DMSO-*d*₆, 400 MHz) δ (ppm): 2.34(s, 3H, CH₃), 6.66 (s, 1H, NH), 6.93-7.51 (m, 10H, ArH); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ (ppm): 22.7, 80.6, 89.6, 98.4, 118.5, 121.2, 121.6, 123.6, 124.6, 125.3, 131.3, 131.9, 132.5, 133.2, 133.7, 135.7, 136.3, 142.8, 143.5, 150.5, 156.8, 164.2, 166.2, 168.6, 169.3; Anal. calcd. For C₂₇H₁₈Br₂N₆O₄: C 49.87, H 2.79, N 12.92%; found: C 49.02, H 2.48 N 12.68 %.
- 5,5''-difluoro-3'-(*p*-tolyl)-1'H,3'H-dispiro[indoline-3,2'-pyrimido[4,5-*d*]pyrimidine-4',3''-indoline]-2,2'',5',7'(6'H,8'H)-tetraone (4c).** m.p. >300 °C; ¹H NMR (DMSO-*d*₆, 400 MHz) δ (ppm): 2.36 (s, 3H, CH₃), 6.62 (s, 1H, NH), 6.88-7.70 (m, 10H, ArH); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ (ppm): 22.8, 81.4, 89.7, 98.4, 113.2, 113.9, 116.6, 116.8, 119.1, 119.3, 123.6, 130.6, 131.2, 132.5, 133.6, 138.3, 138.8, 150.4, 156.6, 160.3, 160.8, 164.8, 165.5, 168.7, 169.1; Anal. calcd. For C₂₇H₁₈F₂N₆O₄: C 61.36, H 3.43, N 15.90%; found: C 60.66, H 3.10, N 15.78 %.
- 5,5''-dinitro-3'-(*p*-tolyl)-phenyl-1'H,3'H-dispiro[indoline-3,2'-pyrimido[4,5-*d*]pyrimidine-4',3''-indoline]-2,2'',5',7'(6'H,8'H)-tetraone (4d).** m.p. >300 °C; ¹H NMR (DMSO-*d*₆, 400 MHz) δ (ppm): 2.34(s, 3H,

- CH₃), 6.68 (s, 1H, NH), 6.92-8.40 (m, 10H, ArH); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ (ppm): 22.8, 80.8, 89.8, 98.7, 110.0, 112.5, 118.2, 123.6, 124.4, 125.5, 127.3, 128.4, 131.7, 130.3, 133.9, 144.6, 146.7, 148.1, 148.7, 150.3, 156.9, 164.3, 165.3, 168.5, 169.3. Anal. calcd. For C₂₇H₁₈N₈O₈: C 55.67, H 3.11, N 19.24%; found: C 55.45, H 2.89, N 19.17 %.
5. **5,5'-dimethyl-3'-(*p*-tolyl)-1'H,3'H-dispiro[indoline-3,2'-pyrimido[4,5-d]pyrimidine-4',3''-indoline]-2,2'',5',7'(6'H,8'H)-tetraone (4e).** m.p. >300 °C; ¹H NMR (DMSO-*d*₆, 400 MHz) δ (ppm): 2.30(s, 6H, CH₃), 2.33 (s, 3H, CH₃), 6.65 (s, 1H, NH), 6.89-7.38 (m, 10H, ArH); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ (ppm): 21.9, 22.7, 81.8, 89.5, 98.5, 116.2, 116.7, 118.9, 123.7, 129.3, 129.8, 130.3, 131.1, 131.7, 133.2, 133.9, 135.6, 136.8, 139.9, 140.3, 150.8, 156.8, 164.7, 165.6, 168.8, 169.1; Anal. calcd. For C₂₉H₂₄N₆O₄: C 66.91, H 4.65, N 16.14%; found: C 66.37, H 4.35, N 16.02 %.
6. **3'-(*p*-tolyl)-7'-thioxo-7',8'-dihydro-1'H,3'H-dispiro[indoline-3,2'-pyrimido[4,5-d]pyrimidine-4',3''-indoline]-2,2'',5'(6'H)-trione (5a).** m.p. >300 °C; ¹H NMR (DMSO-*d*₆, 400 MHz) δ (ppm): 2.32 (s, 3H, CH₃), 6.65 (s, 1H, NH), 6.91-7.43 (m, 12H, ArH), 9.92(s, 1H, NH); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ (ppm): 22.7, 81.2, 88.6, 95.3, 118.2, 121.5, 122.8, 123.7, 124.7, 126.6, 128.2, 129.5, 129.7, 131.9, 132.5, 133.5, 138.3, 143.1, 143.6, 150.7, 158.8, 164.8, 168.3, 168.7, 169.2; Anal. calcd. For C₂₇H₂₀N₆O₃S: C 63.77, H 3.96, N 16.53%; found: C 63.12, H 3.63, N 16.34 %.
7. **5,5'-dibromo-3'-(*p*-tolyl)-7'-thioxo-7',8'-dihydro-1'H,3'H-dispiro[indoline-3,2'-pyrimido[4,5-d]pyrimidine-4',3''-indoline]-2,2'',5'(6'H)-trione (5b).** m.p. >300 °C; ¹H NMR (DMSO-*d*₆, 400 MHz) δ (ppm): 2.35 (s, 3H, CH₃), 6.67 (s, 1H, NH), 6.93-7.45 (m, 10H, ArH), 9.75(s, 1H, NH); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ (ppm): 22.7, 80.7, 89.6, 95.5, 118.3, 121.4, 121.6, 123.7, 124.9, 125.4, 131.2, 131.6, 132.6, 133.5, 133.5, 135.6, 136.4, 142.6, 143.7, 150.4, 158.8, 164.2, 168.5, 168.8, 169.5. Anal.

calcd. For C₂₇H₁₈Br₂N₆O₃S: C 48.67, H 2.72, N 12.61%; found: C 48.47, H 2.45, N 12.32%.

8. **5,5''-difluoro-3'-(*p*-tolyl)-7'-thioxo-7',8'-dihydro-1'H,3'H-dispiro[indoline-3,2'-pyrimido[4,5-d]pyrimidine-4',3''-indoline]-2,2'',5'(6'H)-trione (5c).** m.p. >300 °C; ¹H NMR (DMSO-*d*₆, 400 MHz) δ (ppm): 2.36 (s, 3H, CH₃), 6.66 (s, 1H, NH), 6.90-7.72 (m, 10H, ArH), 9.83 (s, 1H, NH); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ (ppm): 22.7, 81.5, 89.1, 95.4, 113.0, 113.6, 117.4, 117.9, 119.1, 119.5, 123.8, 130.5, 131.5, 132.6, 133.5, 138.2, 138.9, 150.3, 158.6, 160.1, 160.8, 164.8, 168.3, 168.5, 169.3. Anal. calcd. For C₂₇H₁₈F₂N₆O₃S: C 59.55, H 3.33, N 15.43%; found: C 59.15, H 3.02, N 15.22 %.
9. **5,5''-dinitro-3'-(*p*-tolyl)-7'-thioxo-7',8'-dihydro-1'H,3'H-dispiro[indoline-3,2'-pyrimido[4,5-d]pyrimidine-4',3''-indoline]-2,2'',5'(6'H)-trione (5d).** m.p. >300 °C; ¹H NMR (DMSO-*d*₆, 400 MHz) δ (ppm): 2.35 (s, 3H, CH₃), 6.69 (s, 1H, NH), 6.95-8.42 (m, 10H, ArH), 9.89 (s, 1H, NH); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ (ppm): 22.7, 80.5, 89.8, 95.6, 110.5, 112.5, 118.3, 123.7, 124.6, 125.3, 127.4, 128.7, 131.7, 130.6, 133.5, 144.6, 146.5, 148.4, 149.0, 150.6, 159.2, 165.1, 168.5, 168.9, 169.7. Anal. calcd. For C₂₇H₁₈N₈O₇S: C 54.18, H 3.03, N 18.72%; found: C 53.91, H 2.94, N 18.15 %.
10. **5,5''-dimethyl-3'-(*p*-tolyl)-7'-thioxo-7',8'-dihydro-1'H,3'H-dispiro[indoline-3,2'-pyrimido[4,5-d]pyrimidine-4',3''-indoline]-2,2'',5'(6'H)-trione (5e).** m.p. >200 °C; ¹H NMR (DMSO-*d*₆, 400 MHz) δ (ppm): 2.32 (s, 6H, CH₃), 2.35 (s, 3H, CH₃), 6.64 (s, 1H, NH), 6.88-7.41 (m, 10H, ArH), 9.95 (s, 1H, NH); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ (ppm): 21.8, 22.7, 81.6, 89.7, 95.5, 116.4, 116.9, 118.7, 123.5, 129.3, 129.9, 130.1, 131.3, 131.7, 133.5, 133.8, 135.6, 136.6, 139.8, 140.1, 150.6, 156.9, 164.5,

168.6,168.8,169.4. Anal. calcd. For C₂₉H₂₄N₆O₃S: C 64.91, H 4.54, N 15.66%; found: C 64.33, H 4.20, N 15.04 %.

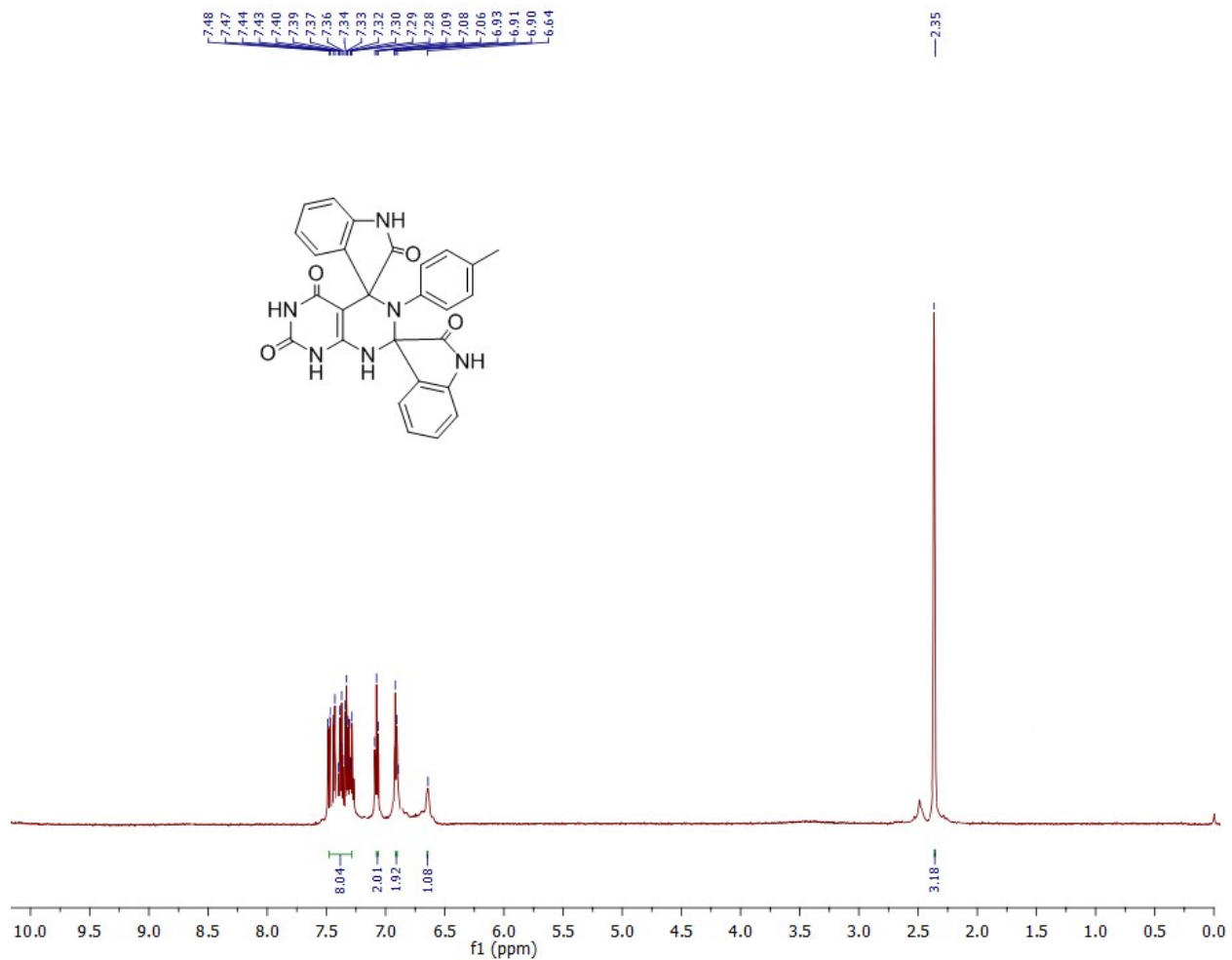
11. **6'-(*p*-tolyl)-6'H-dispiro[indoline-3,5'-[1,3,4]thiadiazolo[3,2-a][1,3,5]triazine-7',3''-indoline]-2,2''-dione (6a).** m.p. >200 °C; ¹H NMR (DMSO-*d*₆, 400 MHz) δ (ppm): 2.34 (s, 3H, CH₃), 6.90-7.50 (m, 12H, ArH), 7.96 (s, 1H, ArH); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ (ppm): 22.4, 89.8, 93.7, 116.8, 118.4, 118.9, 124.6, 126.7, 128.2, 129.2, 129.5, 130.1, 131.4, 131.8, 132.6, 140.1, 142.5, 144.2, 144.6, 151.6, 156.8, 168.8, 169.5. Anal. calcd. For C₂₅H₁₈N₆O₂S: C 64.37, H 3.89, N 18.01%; found: C 63.68, H 3.52, N 17.95 %.
12. **5,5''-dibromo-6'-(*p*-tolyl)-6'H-dispiro[indoline-3,5'-[1,3,4]thiadiazolo[3,2-a][1,3,5]triazine-7',3''-indoline]-2,2''-dione (6b).** m.p. >200 °C; ¹H NMR (DMSO-*d*₆, 400 MHz) δ (ppm): 2.32 (s, 3H, CH₃), 6.92-7.60 (m, 10H, ArH), 7.98 (s, 1H, ArH); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ (ppm): 22.4, 89.9, 93.5, 116.4, 121.5, 121.9, 123.8, 124.3, 124.6, 131.8, 132.2, 132.7, 133.4, 134.6, 137.3, 137.5, 142.3, 142.8, 143.3, 151.9, 156.5, 168.7, 169.3. Anal. calcd. For C₂₅H₁₆Br₂N₆O₂S: C 48.10, H 2.58, N 13.46%; found: C 47.90, H 2.29, N 13.25 %.
13. **5,5''-difluoro-6'-(*p*-tolyl)-6'H-dispiro[indoline-3,5'-[1,3,4]thiadiazolo[3,2-a][1,3,5]triazine-7',3''-indoline]-2,2''-dione (6c).** m.p. >200 °C; ¹H NMR (DMSO-*d*₆, 400 MHz) δ (ppm): 2.36 (s, 3H, CH₃), 6.90-7.70 (m, 10H, ArH), 7.94 (s, 1H, ArH); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ (ppm): 89.6, 93.4, 115.3, 115.7, 116.4, 116.9, 117.2, 120.5, 121.2, 124.6, 130.8, 131.5, 132.4, 134.7, 138.2, 138.6, 151.4, 156.2, 158.3, 158.7, 168.8, 169.4. Anal. calcd. For C₂₅H₁₆F₂N₆O₂S: C 59.76, H 3.21, N 16.72%; found: C 59.40, H 3.07, N 16.49%.
14. **5,5''-dinitro-6'-(*p*-tolyl)-6'H-dispiro[indoline-3,5'-[1,3,4]thiadiazolo[3,2-a][1,3,5]triazine-7',3''-indoline]-2,2''-dione (6d).** m.p. >200 °C; ¹H NMR

(DMSO-*d*₆, 400 MHz) δ (ppm): 2.37 (s, 3H, CH₃), 6.91-8.40 (m, 10H, ArH), 7.99 (s, 1H, ArH); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ (ppm): 22.4, 89.6, 93.7, 112.3, 112.7, 116.3, 124.6, 125.1, 126.2, 127.3, 127.7, 130.4, 131.5, 132.2, 132.7, 148.3, 148.6, 149.3, 149.8, 151.7, 156.8, 168.8, 169.5. Anal. calcd. For C₂₅H₁₆N₈O₆S: C 53.96, H 2.90, N 20.14%; found: C 53.12, H 2.57, N 19.95%.

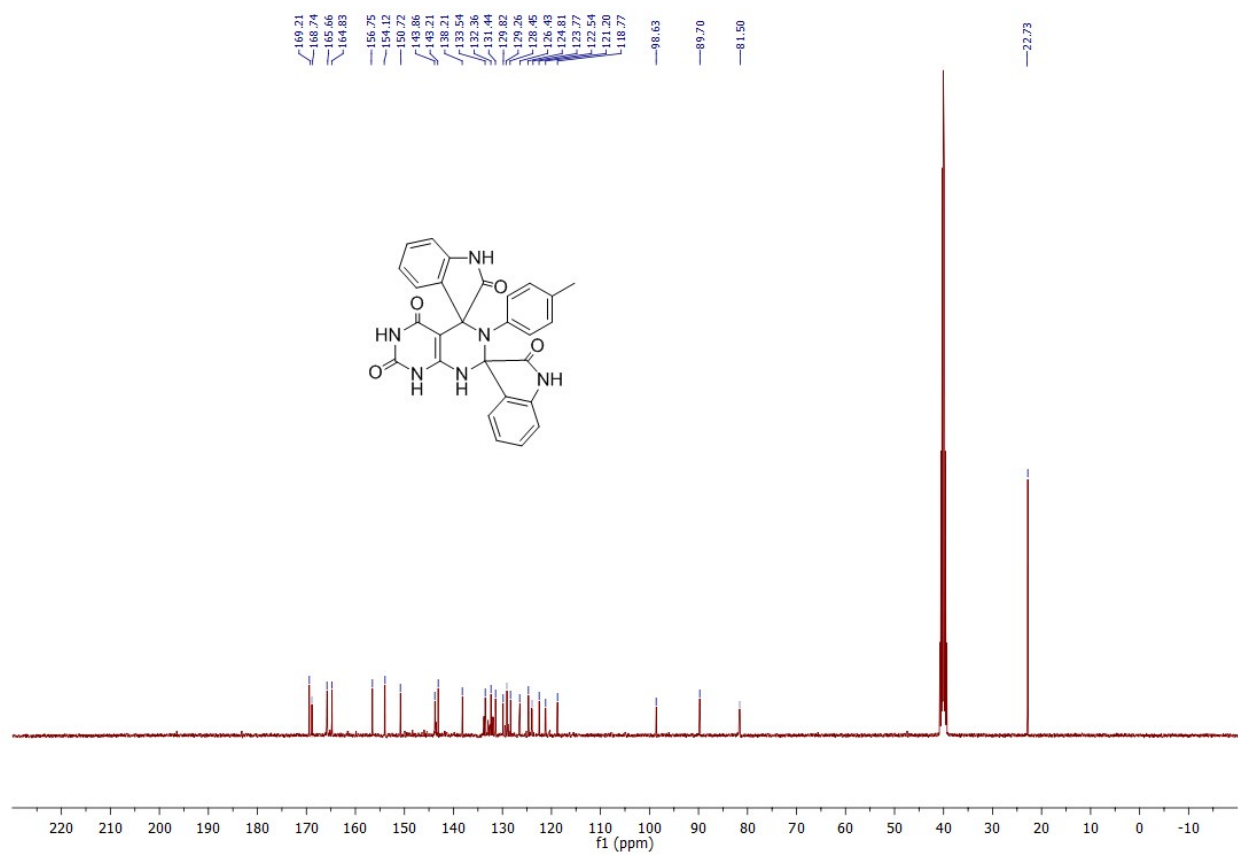
15. 5,5'-dimethyl-6'-(*p*-tolyl)-6'H-dispiro[indoline-3,5'-

[1,3,4]thiadiazolo[3,2-*a*][1,3,5]triazine-7',3''-indoline]-2,2''-dione (6e).

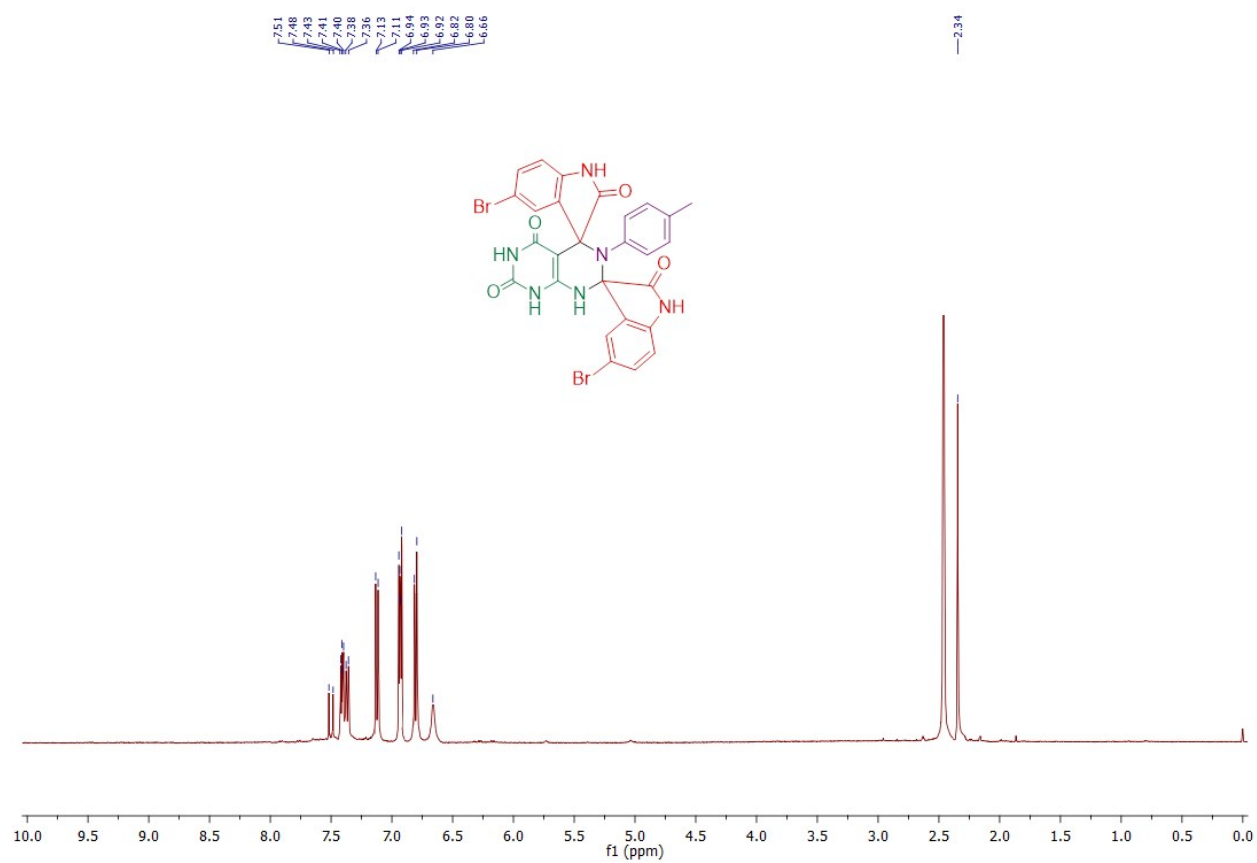
m.p. >200 °C; ¹H NMR (DMSO-*d*₆, 400 MHz) δ (ppm): 2.31(s, 3H, CH₃), 2.35 (s, 3H, CH₃), 6.89-7.48 (m, 10H, ArH), 7.96 (s, 1H, NH); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ (ppm): 21.8, 22.4, 89.5, 93.8, 116.6, 117.5, 118.2, 124.1, 129.3, 129.9, 130.4, 130.9, 131.5, 132.6, 133.7, 134.1, 136.8, 137.2, 141.6, 142.4, 151.6, 156.4, 168.9, 169.7 Anal. calcd. For C₂₇H₂₂N₆O₂S: C 65.57, H 4.48, N 16.99%; found: C 65.17, H 4.18, N 16.57%.



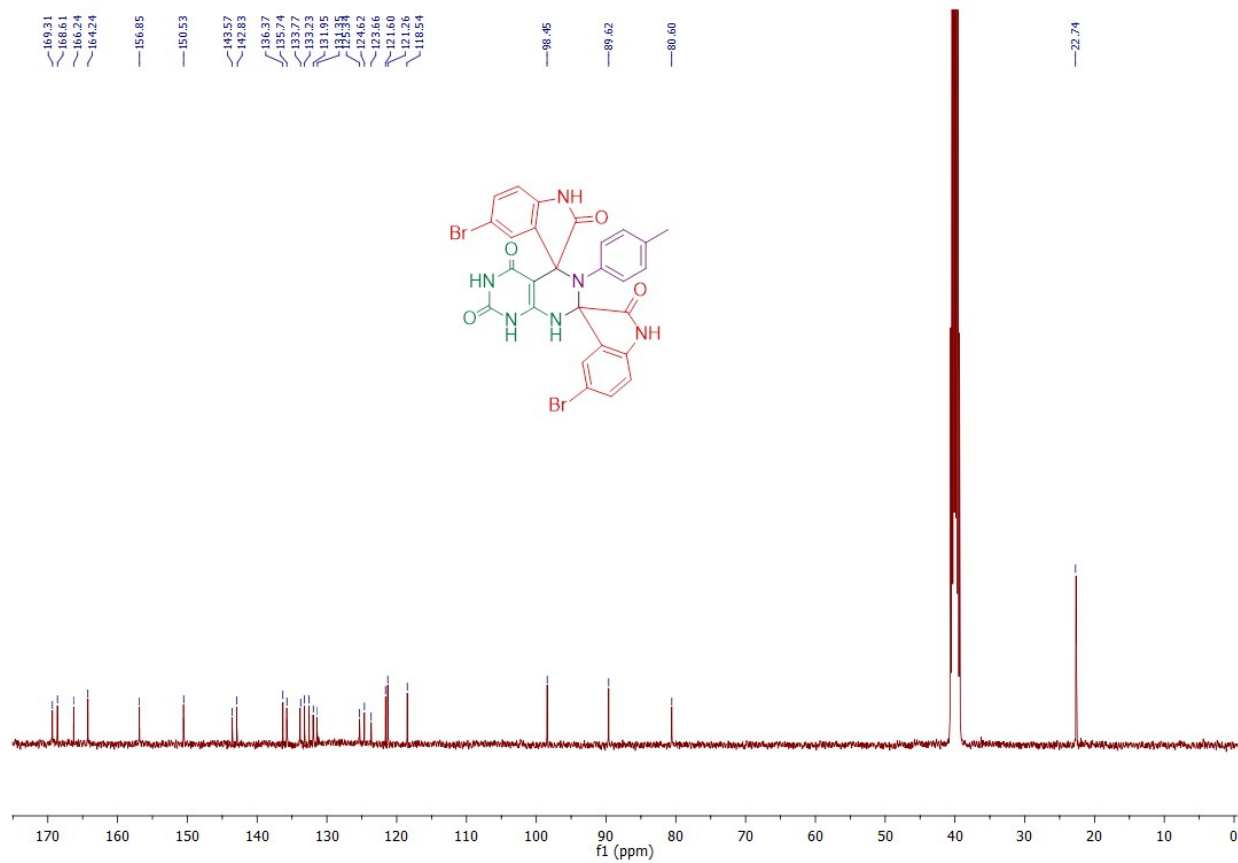
^1H spectra of 4a



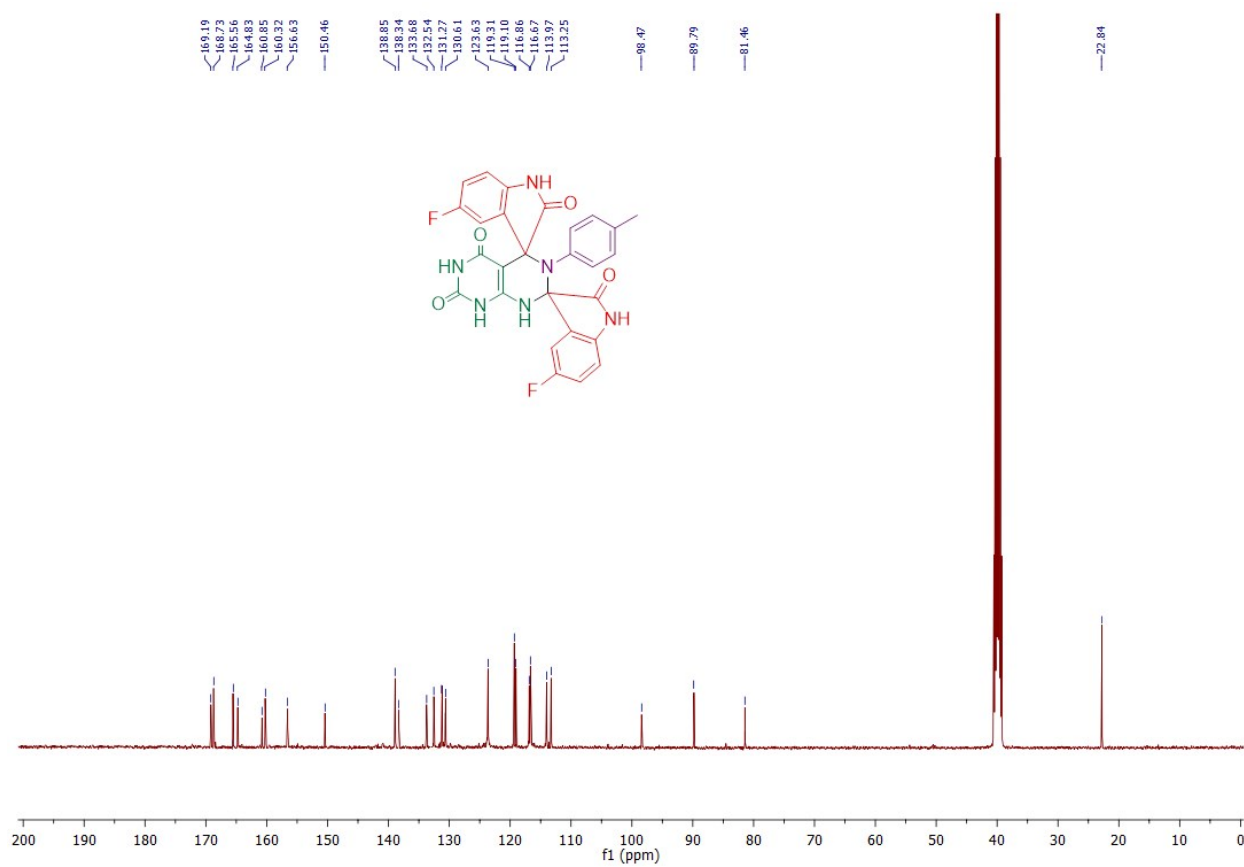
¹³C spectra of 4a



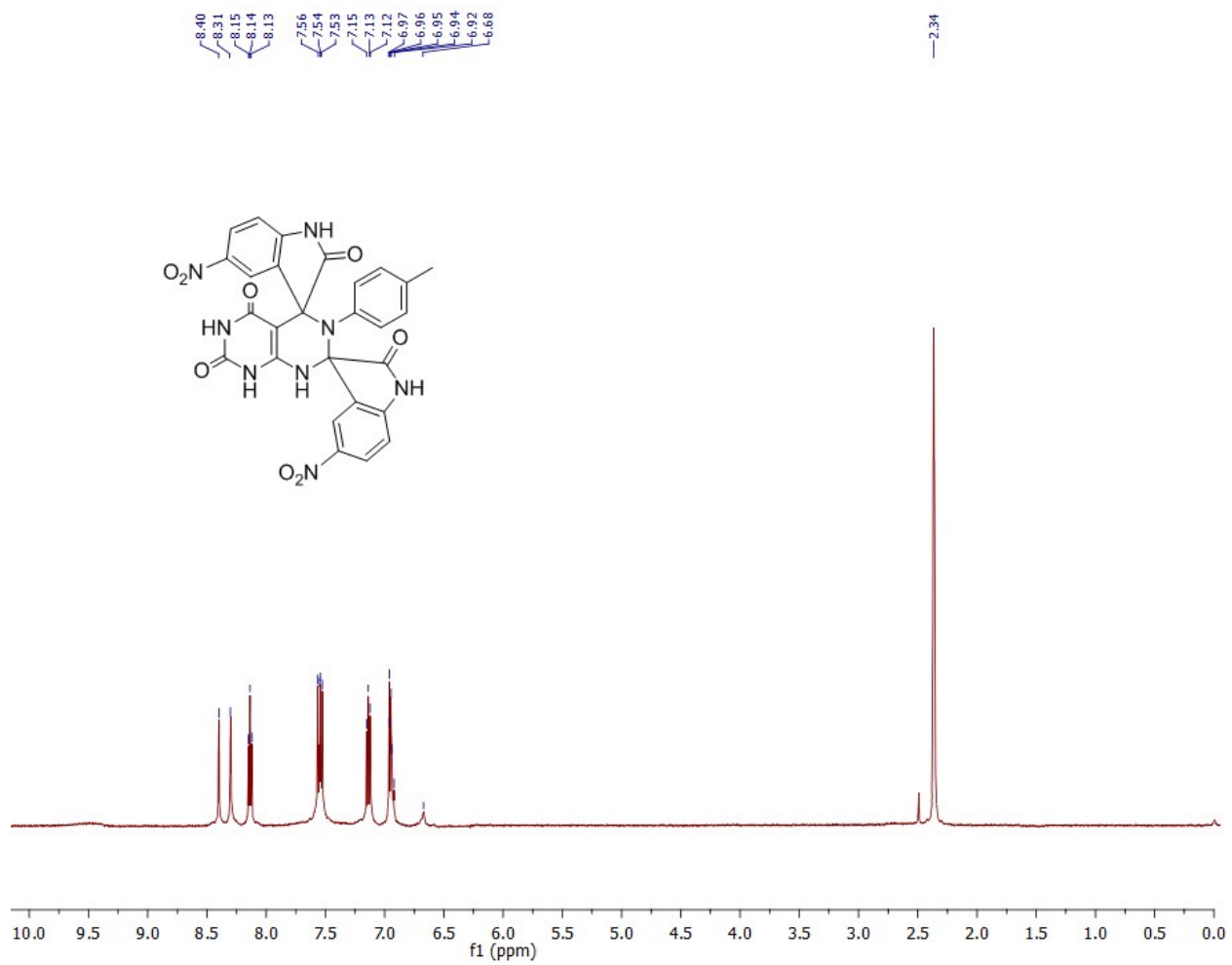
¹H spectra of 4b



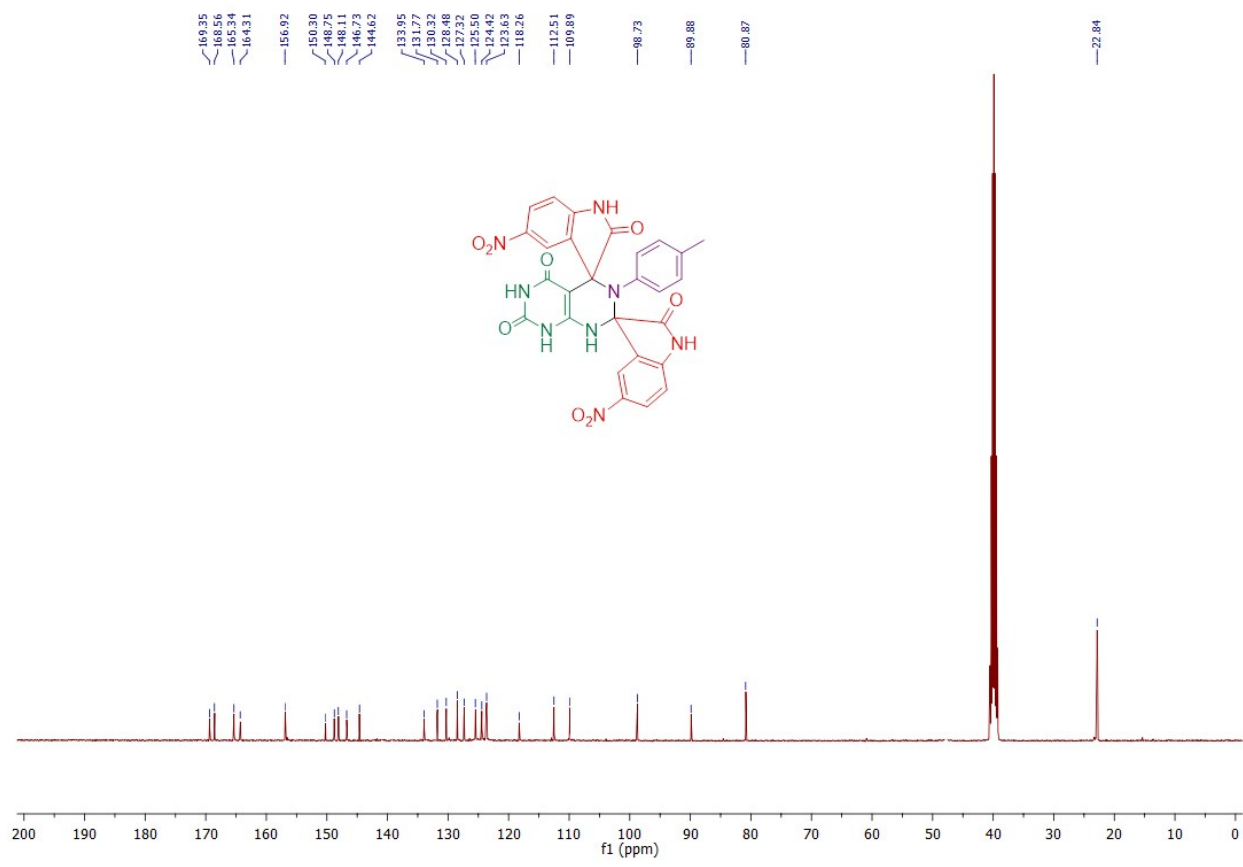
^{13}C spectra of 4b



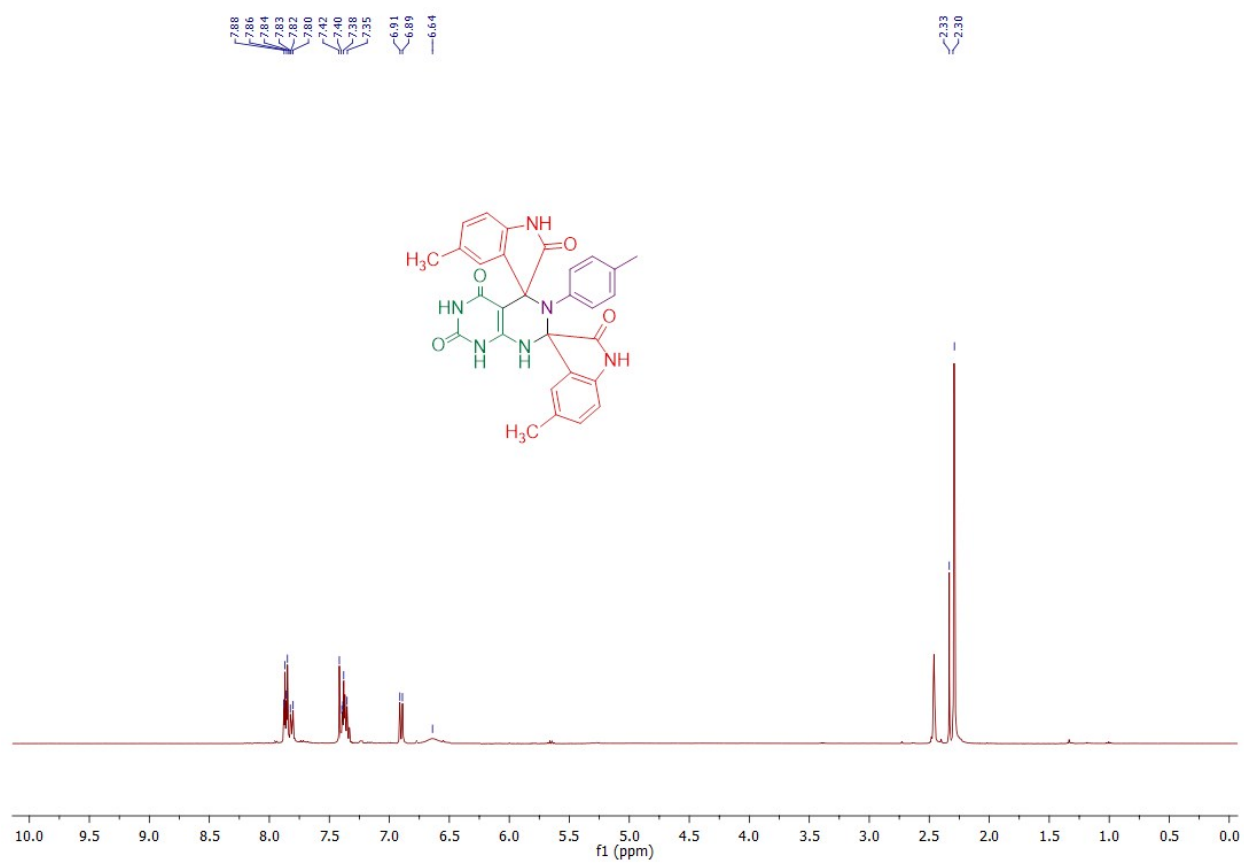
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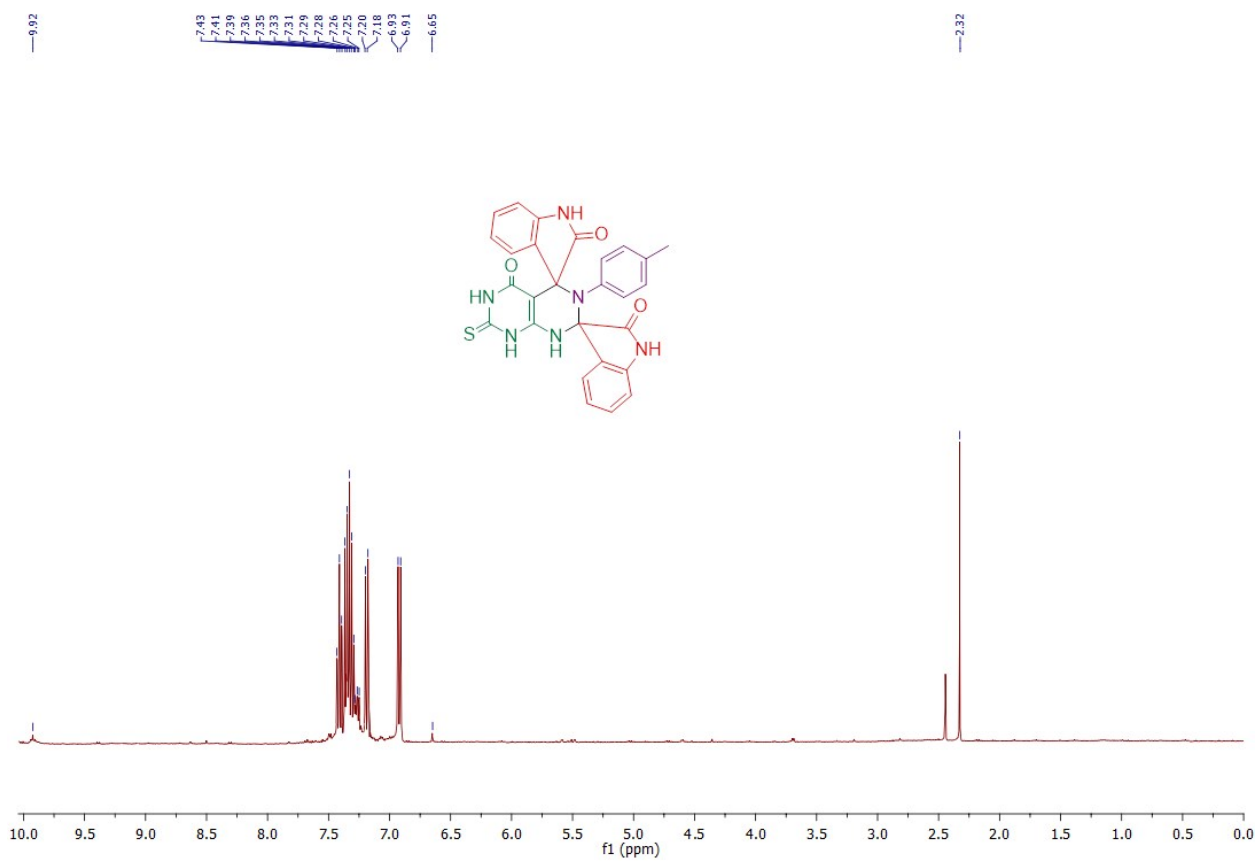
¹H spectra of 4d



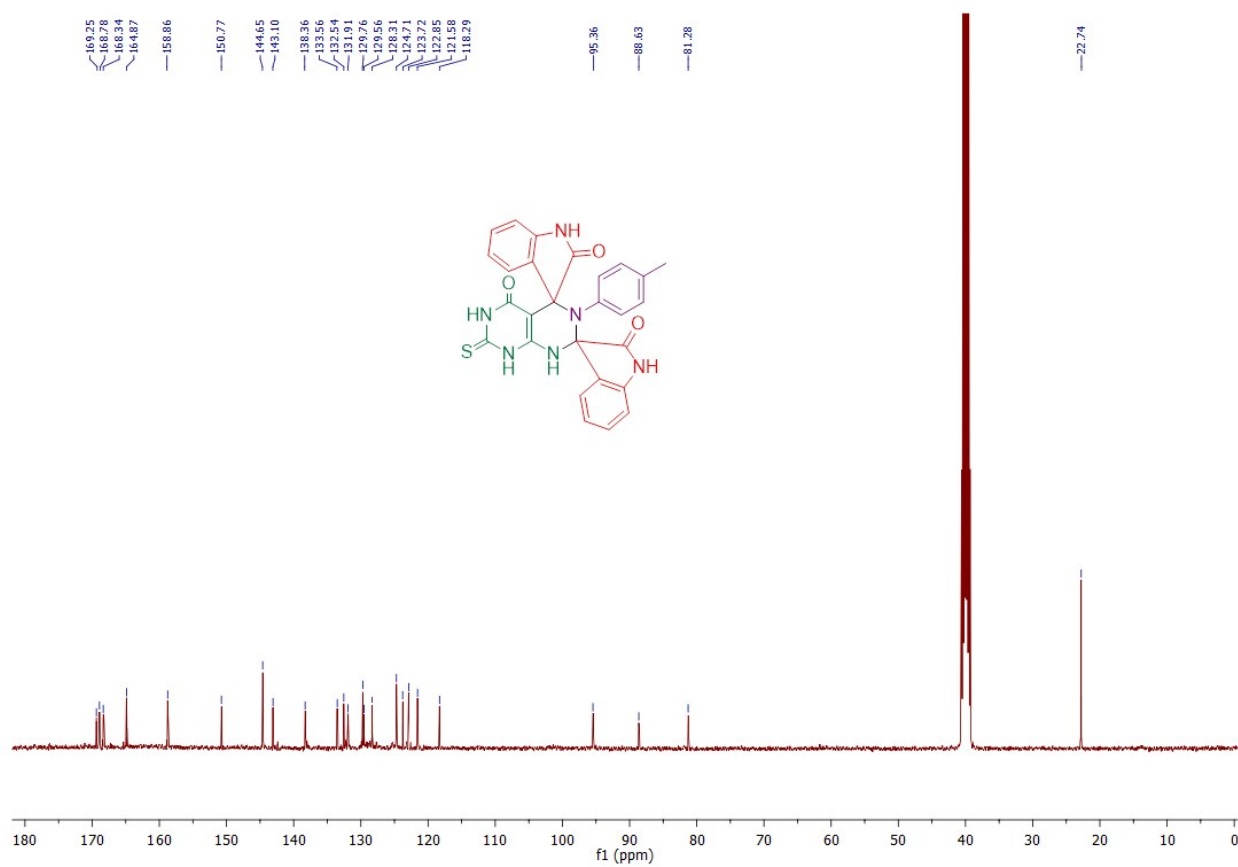
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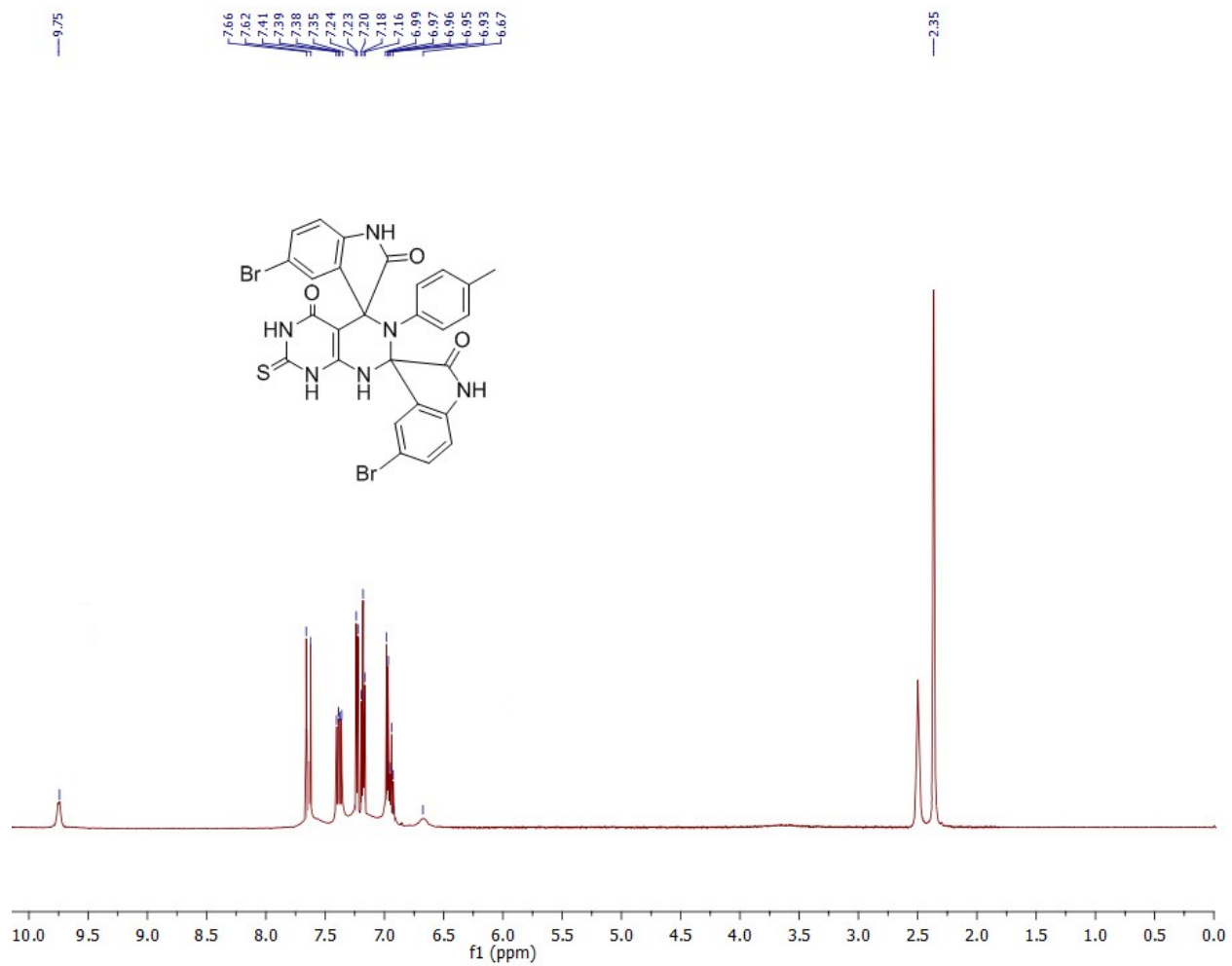
^1H spectra of 4e



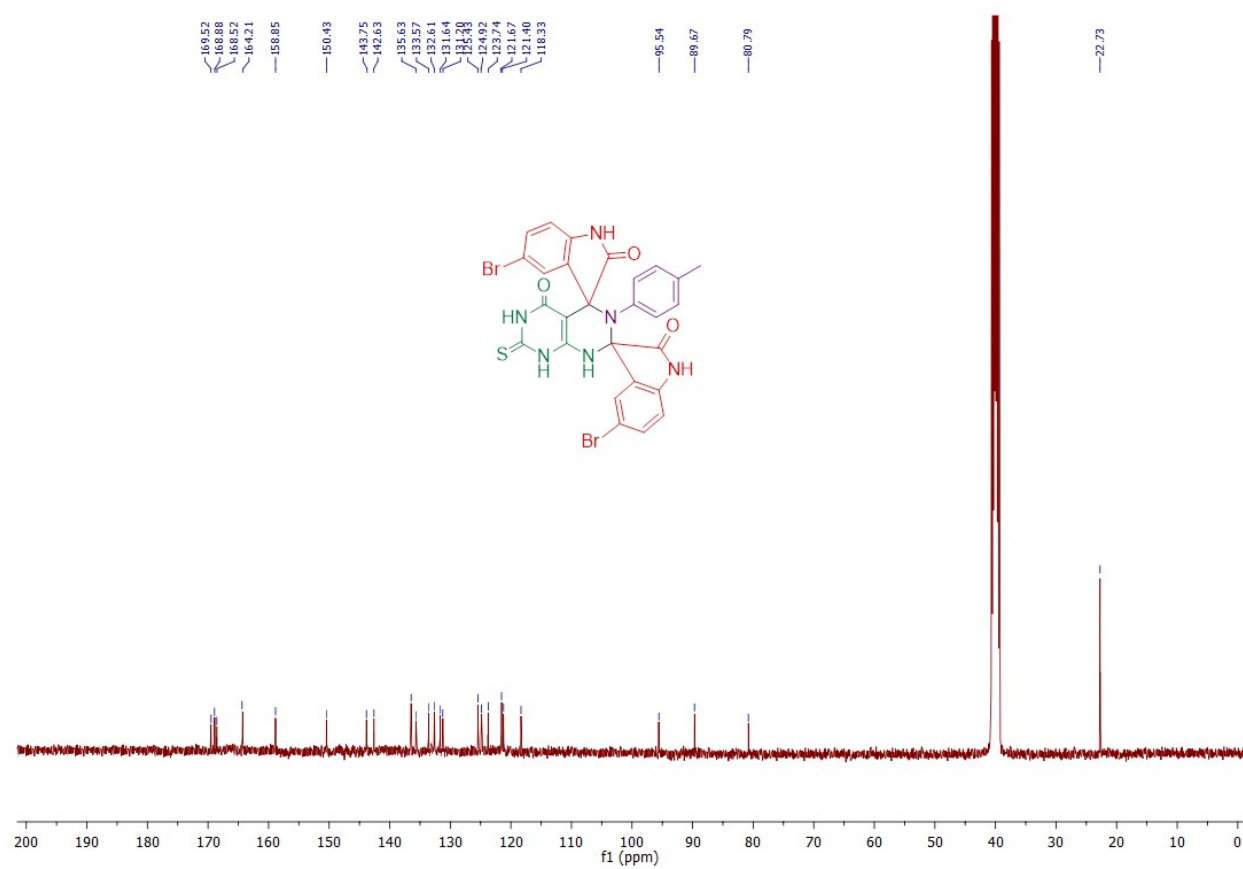
^1H spectra of 5a



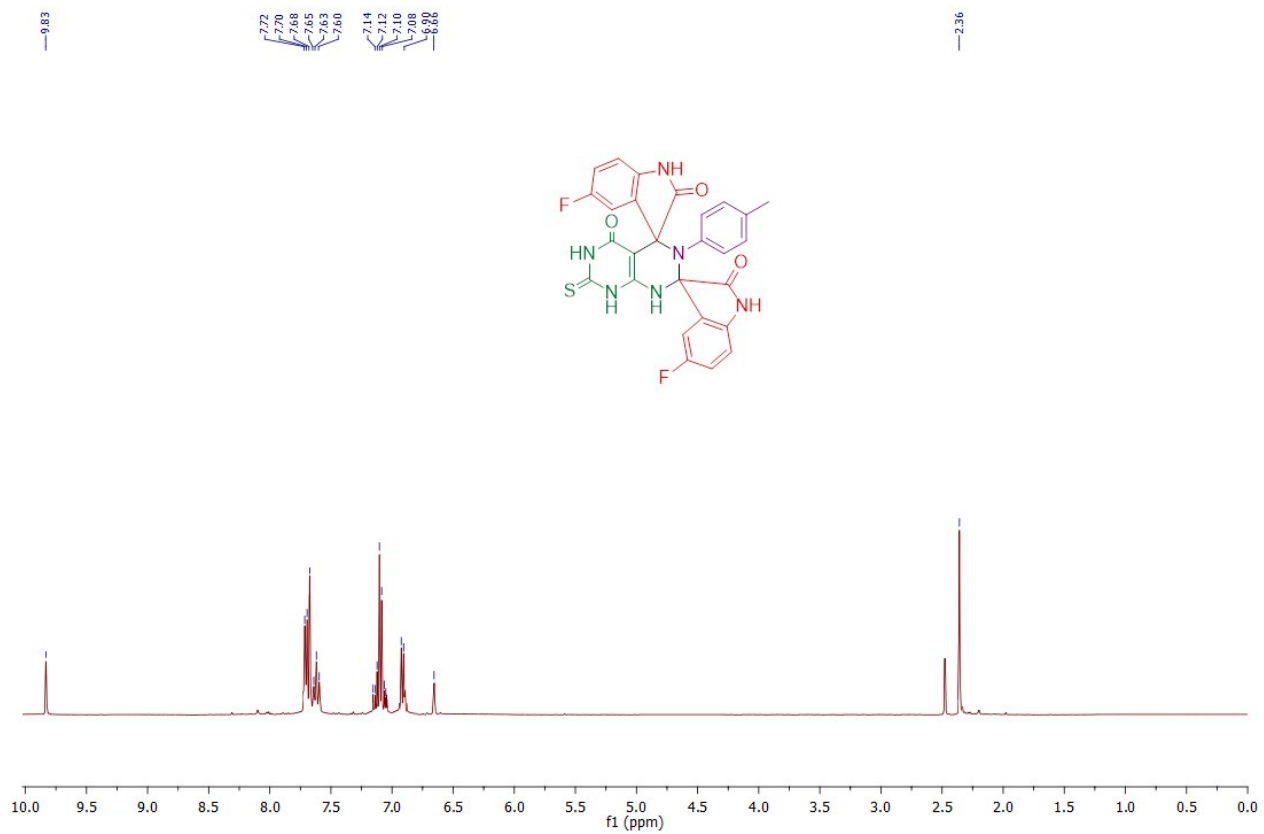
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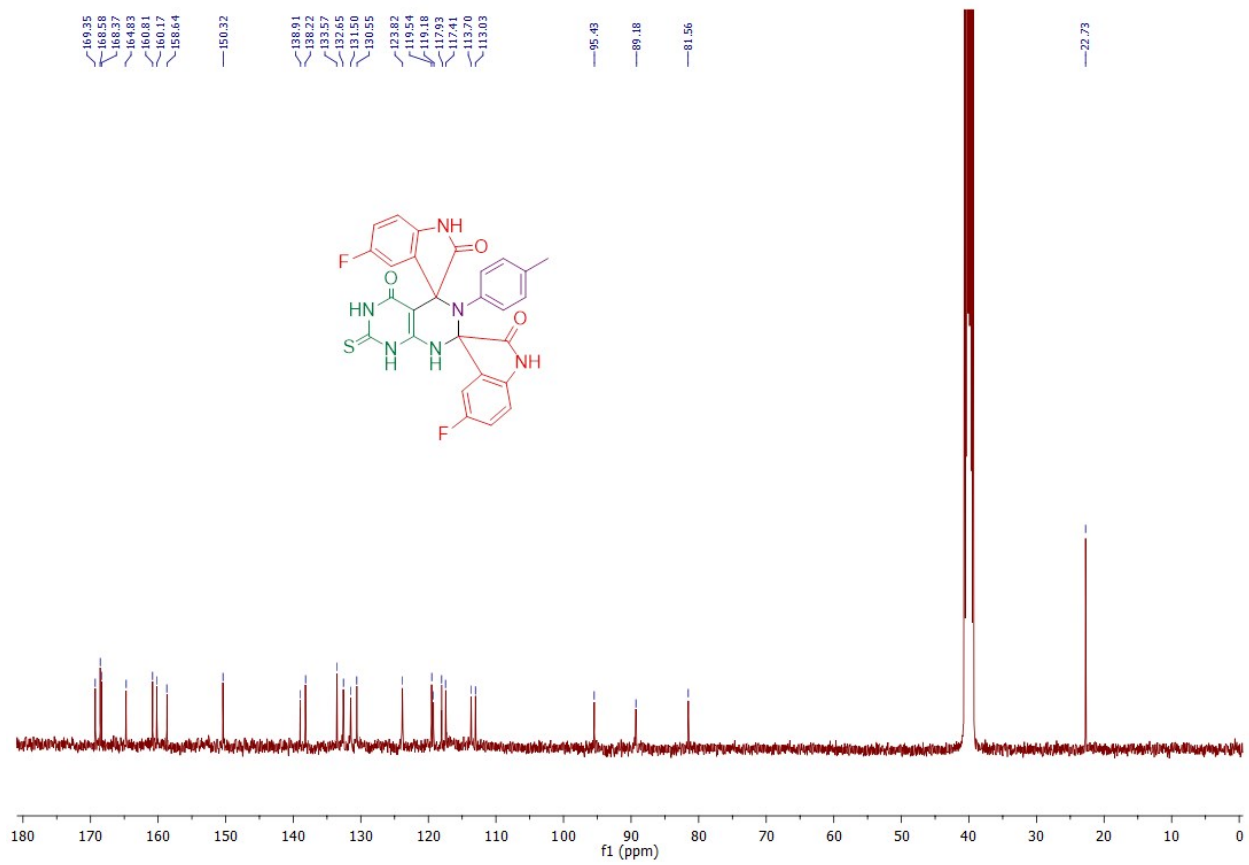
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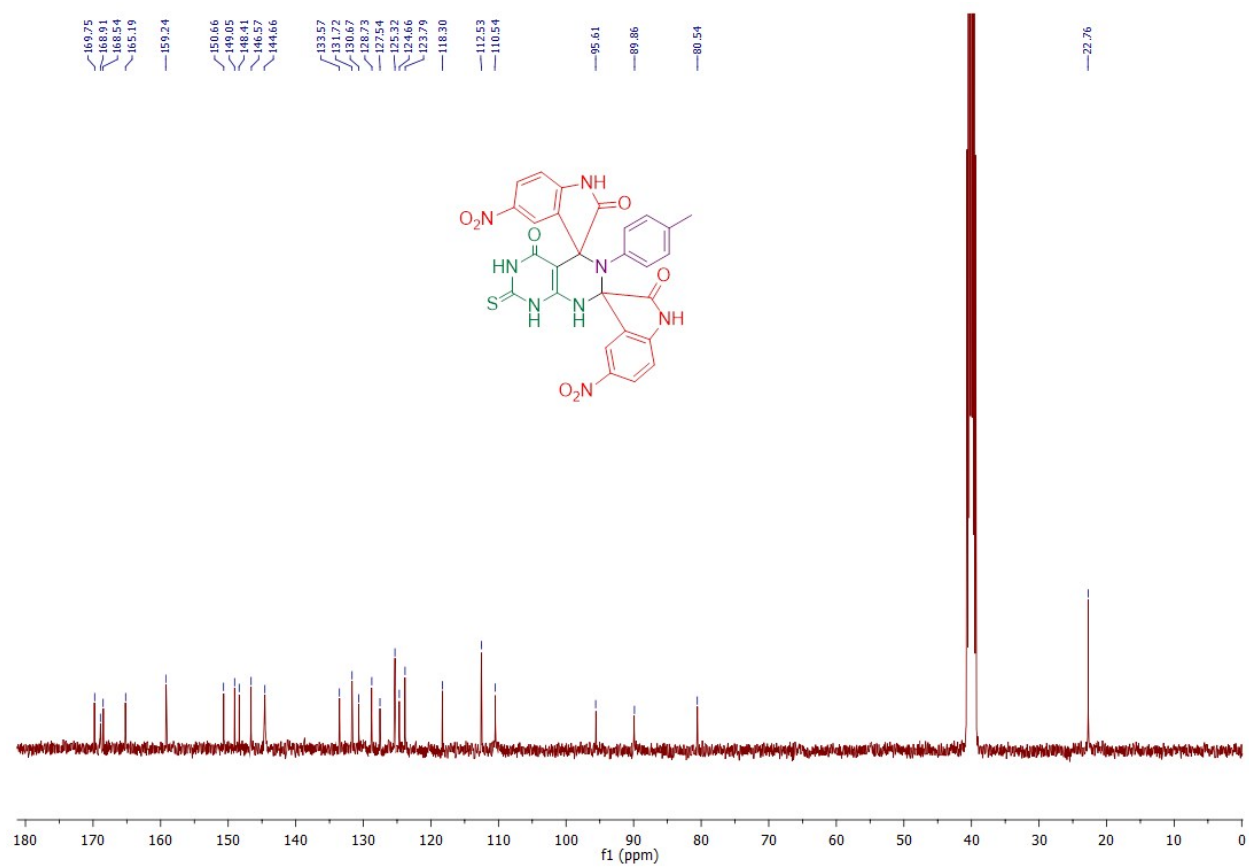
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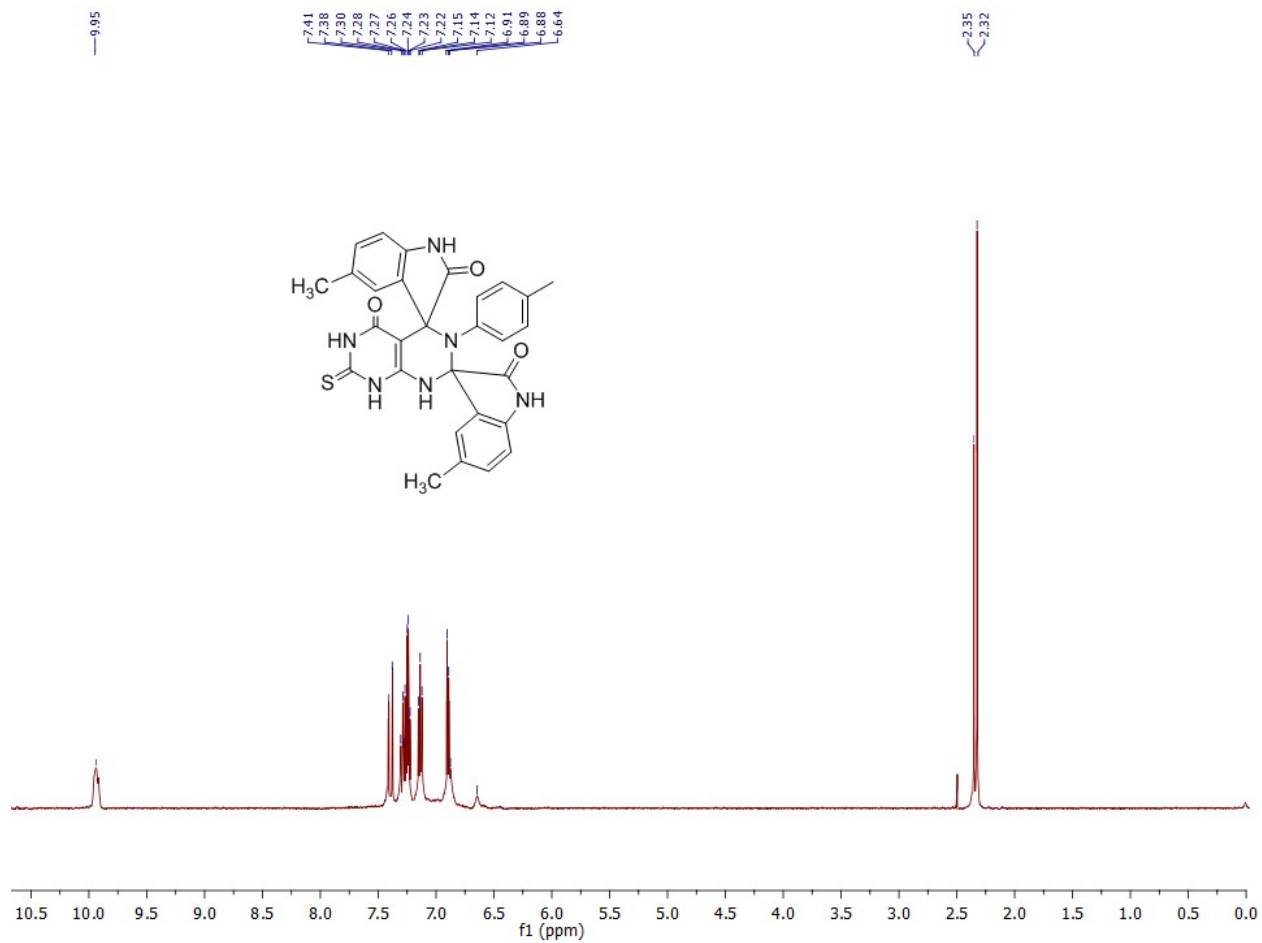
¹H spectra of 5c



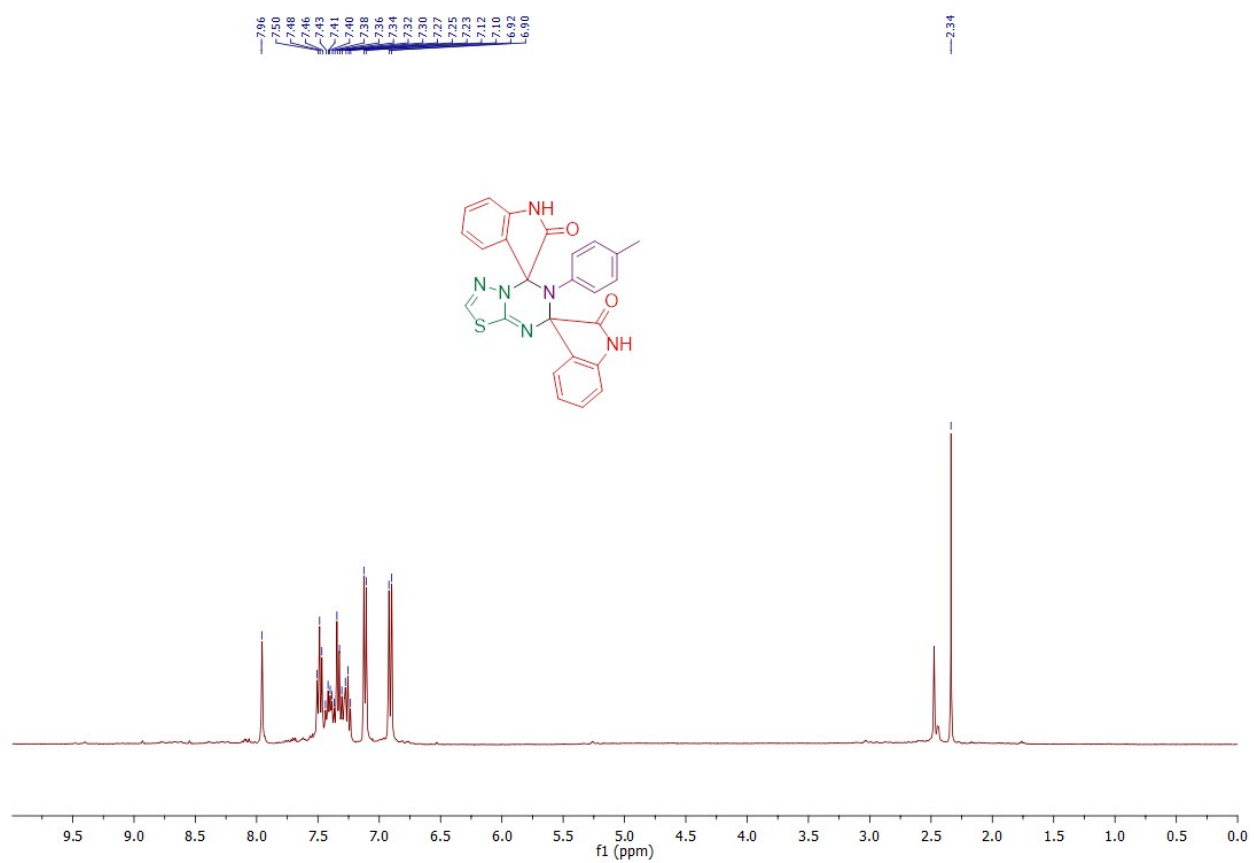
^{13}C spectra of 5c



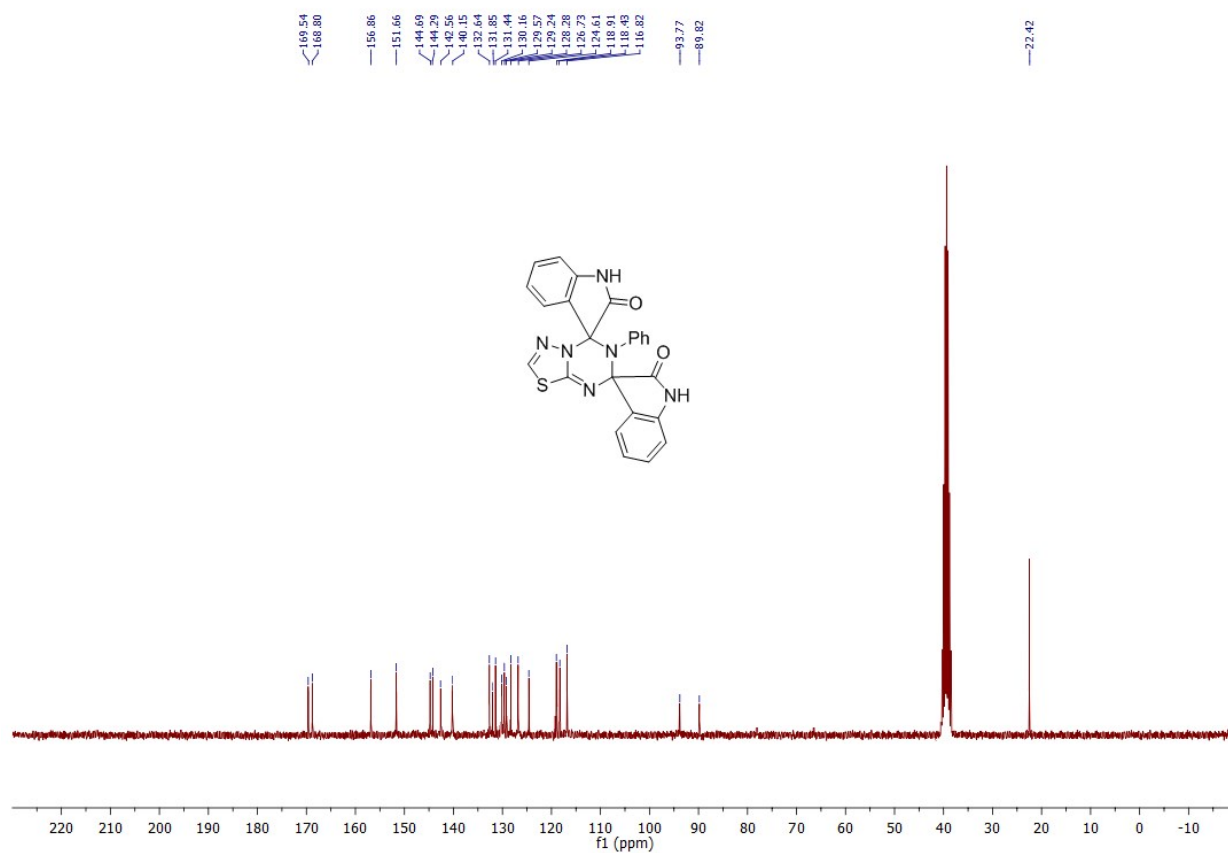
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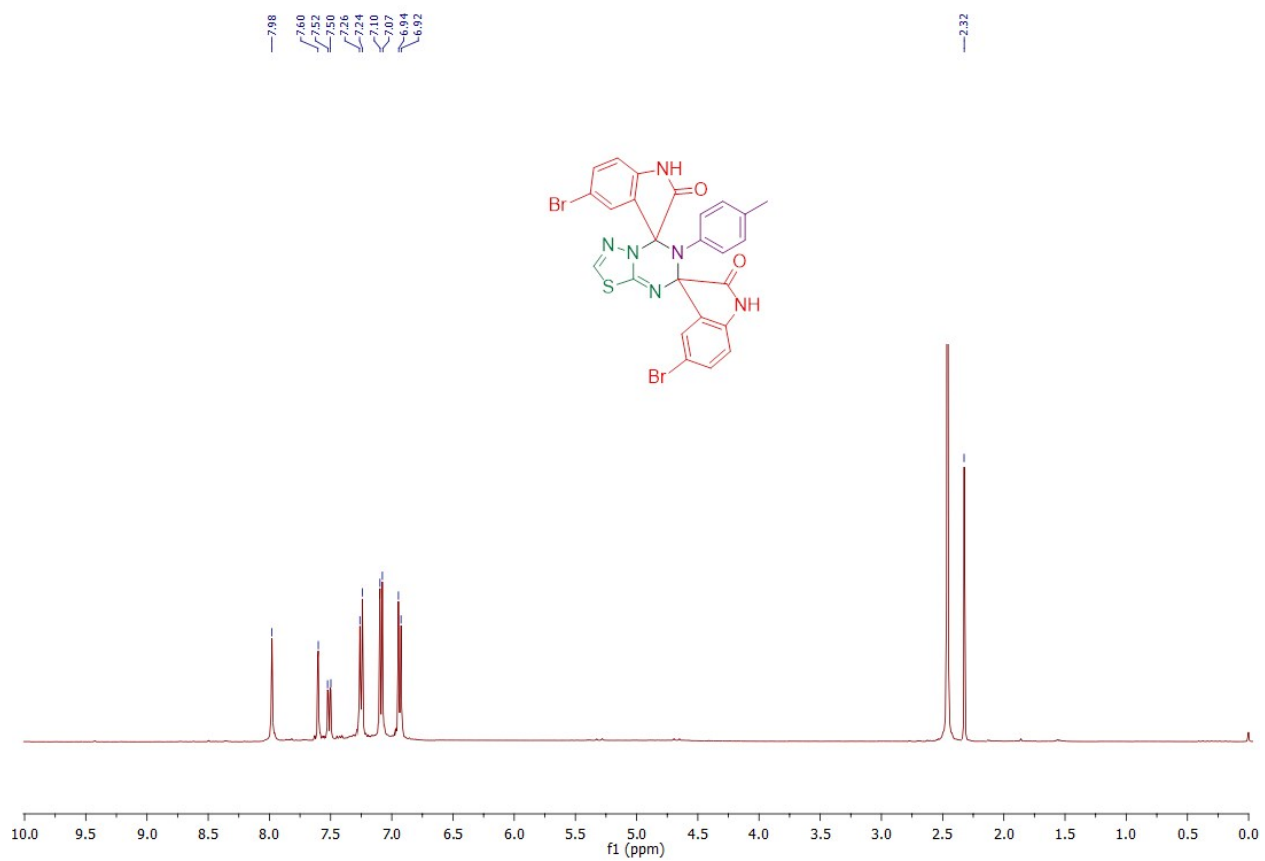
^1H spectra of 5e



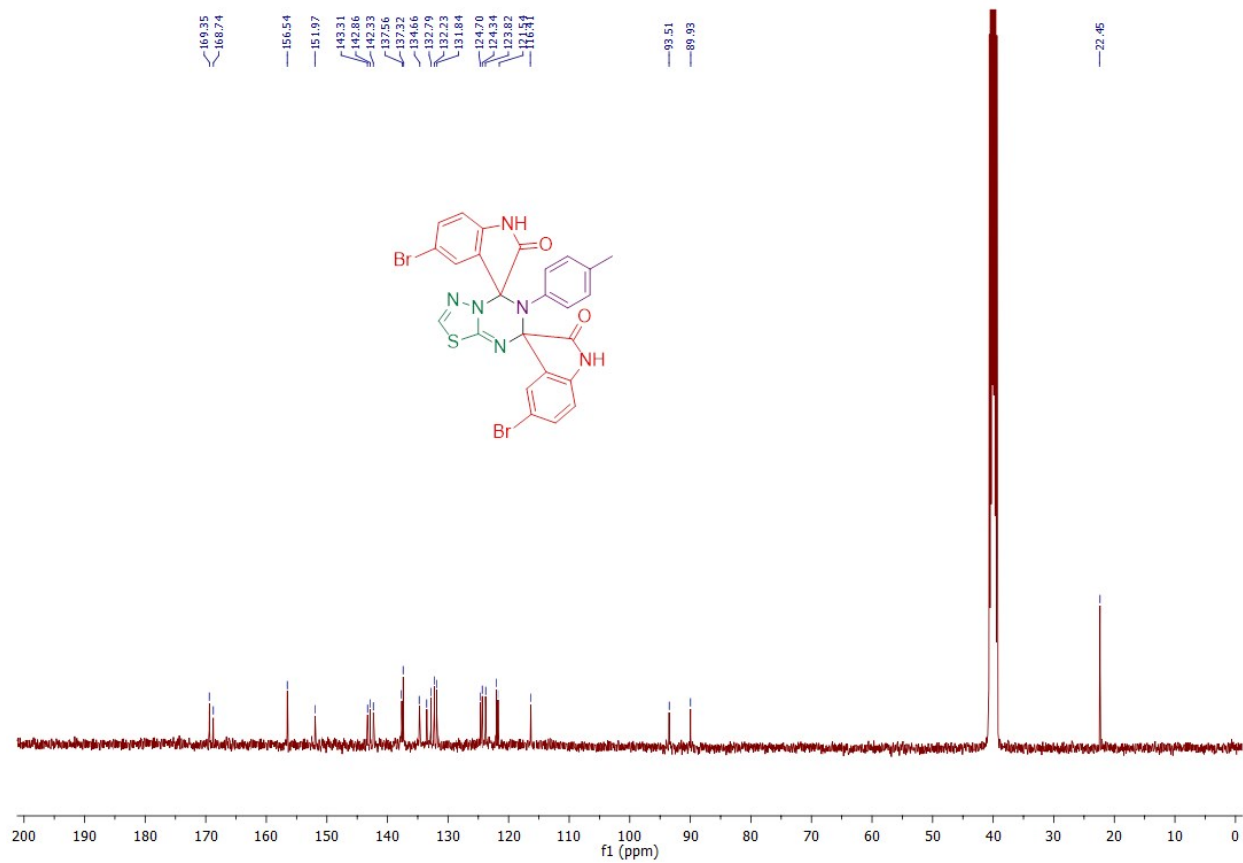
^1H spectra of **6a**



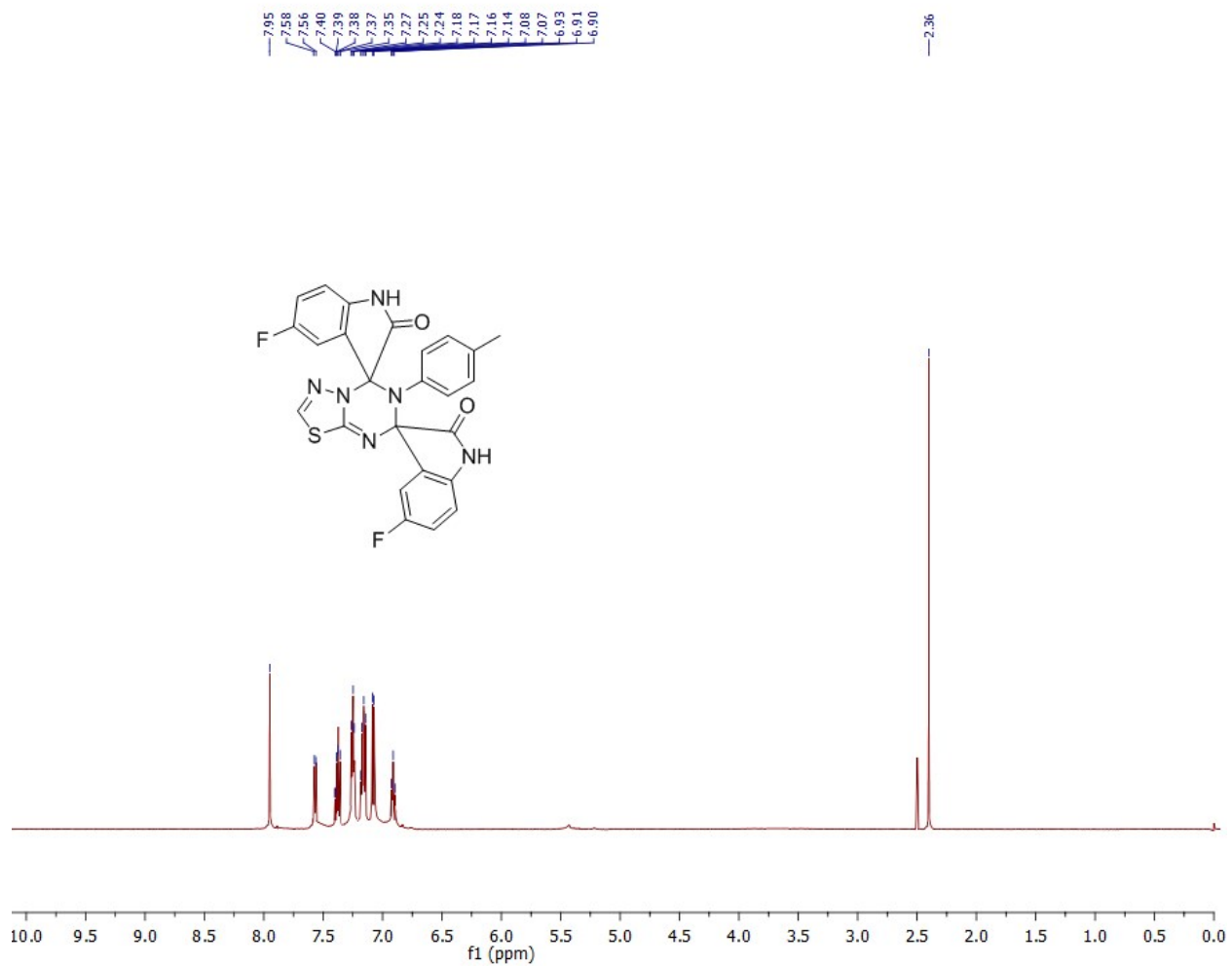
^{13}C spectra of 6a



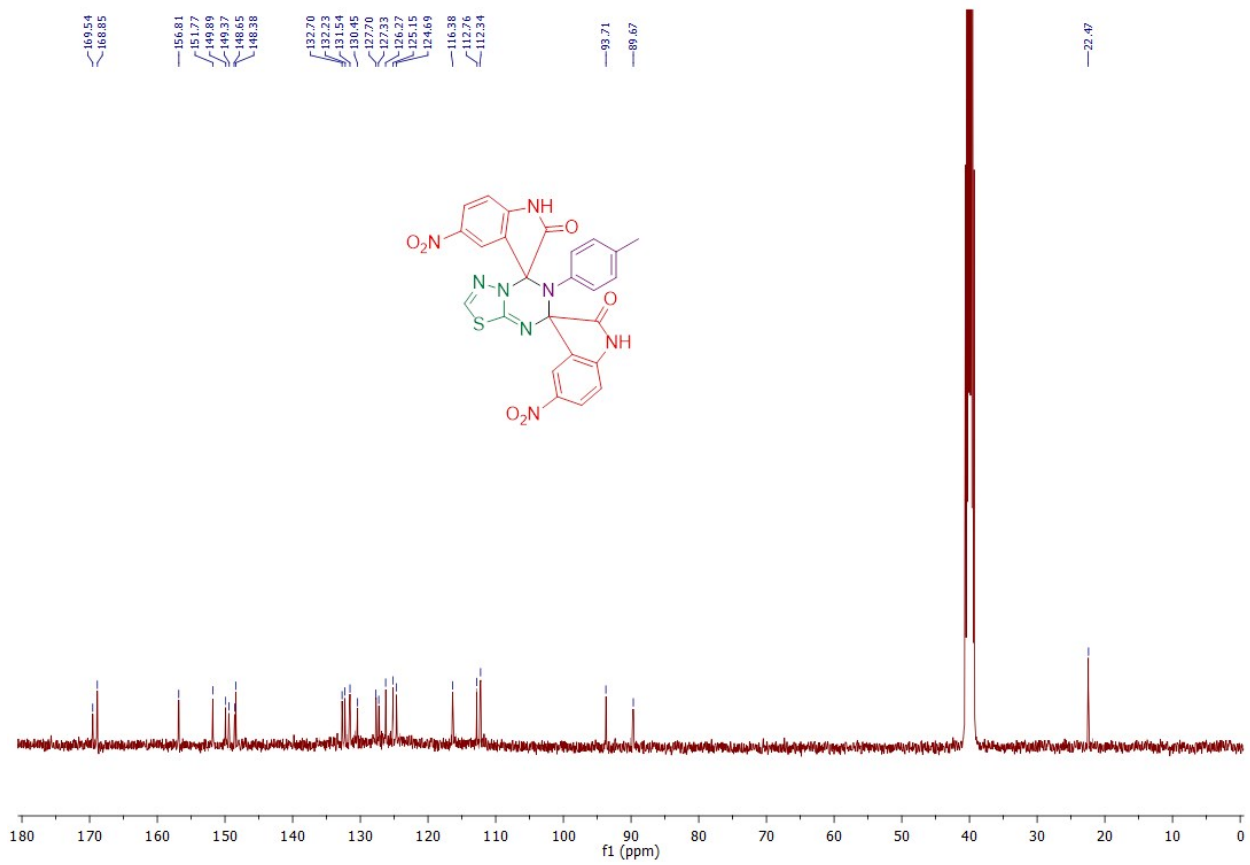
¹H spectra of 6b



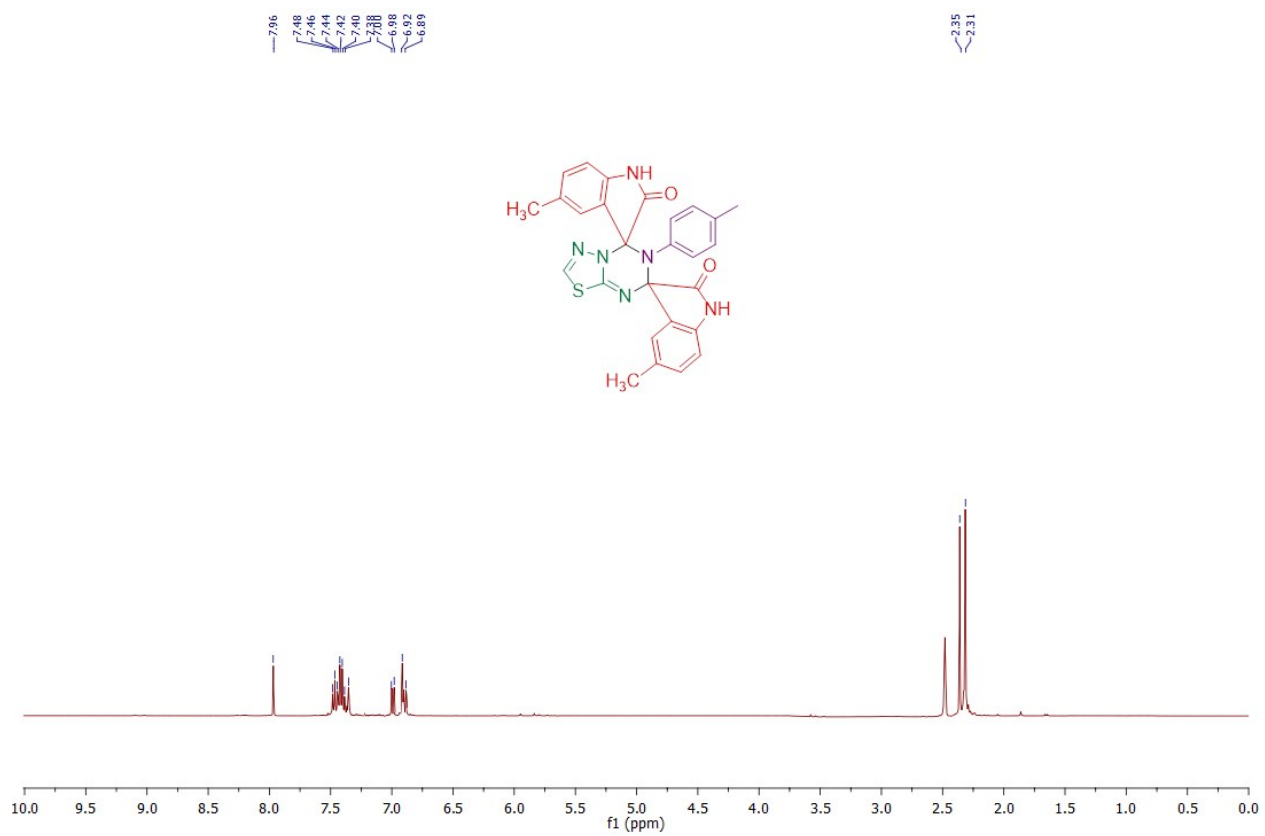
^{13}C spectra of 6b



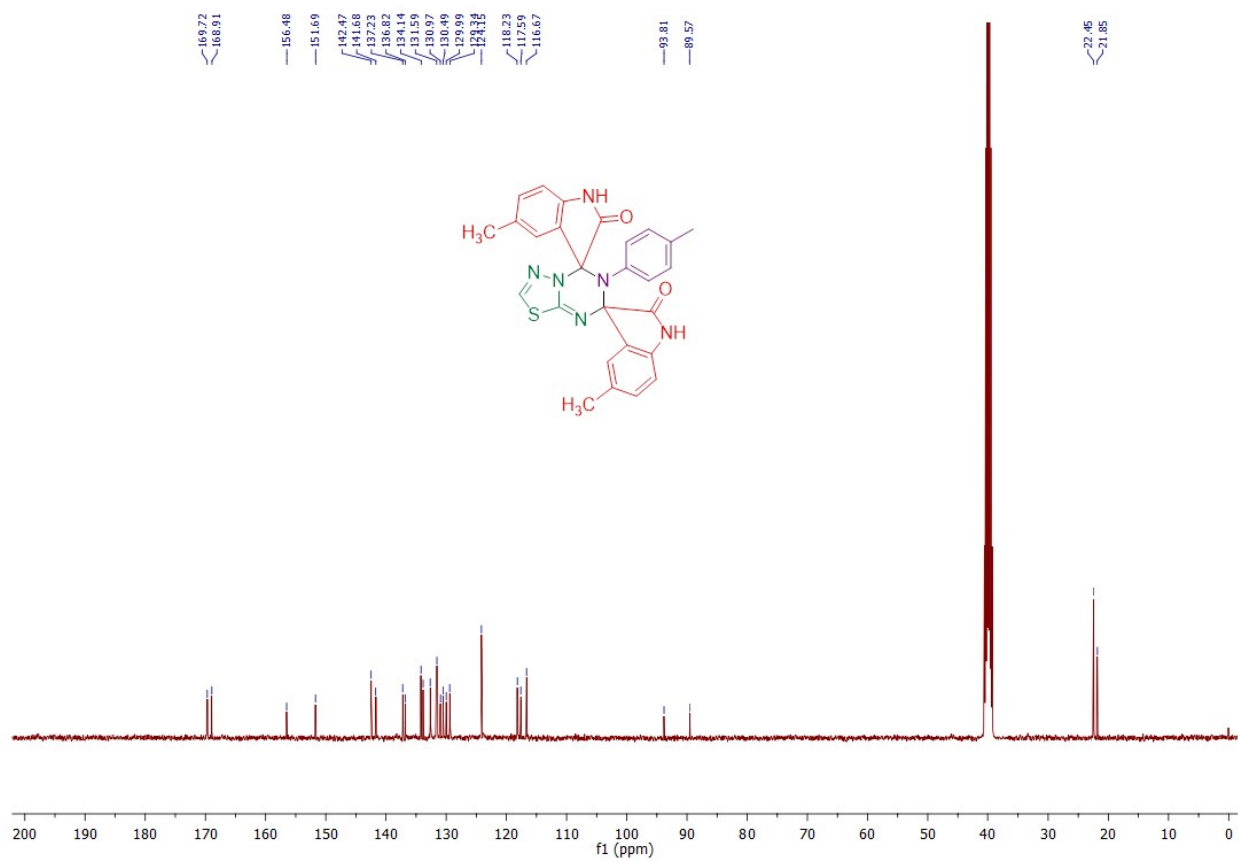
^1H spectra of **6c**



^{13}C spectra of 6d



¹H spectra of 6e



^{13}C spectra of 6e