

# **[3+2]-Cycloaddition of Nitrile Imines to Parabanic Acid Derivatives – an Approach to Novel Spiroimidazolidinediones**

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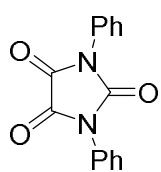
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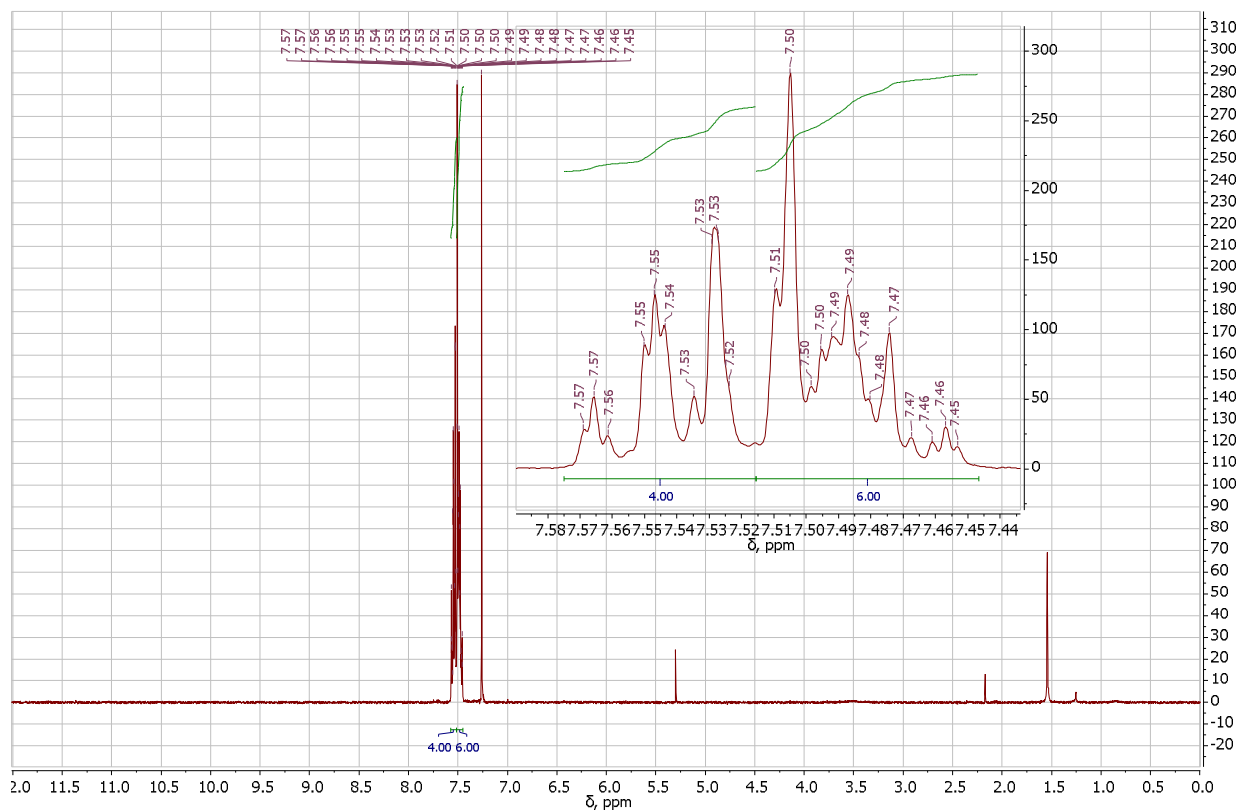
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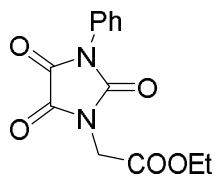
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**$^1\text{H}$ ,  $^{13}\text{C}$  NMR and HRMS spectral data of imidazolidine-4,5-diones 1a-f****1,3-Diphenylimidazolidine-2,4,5-trione (1a)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 – 7.52 (m, 4H, Ar), 7.51 – 7.45 (m, 6H, Ar).



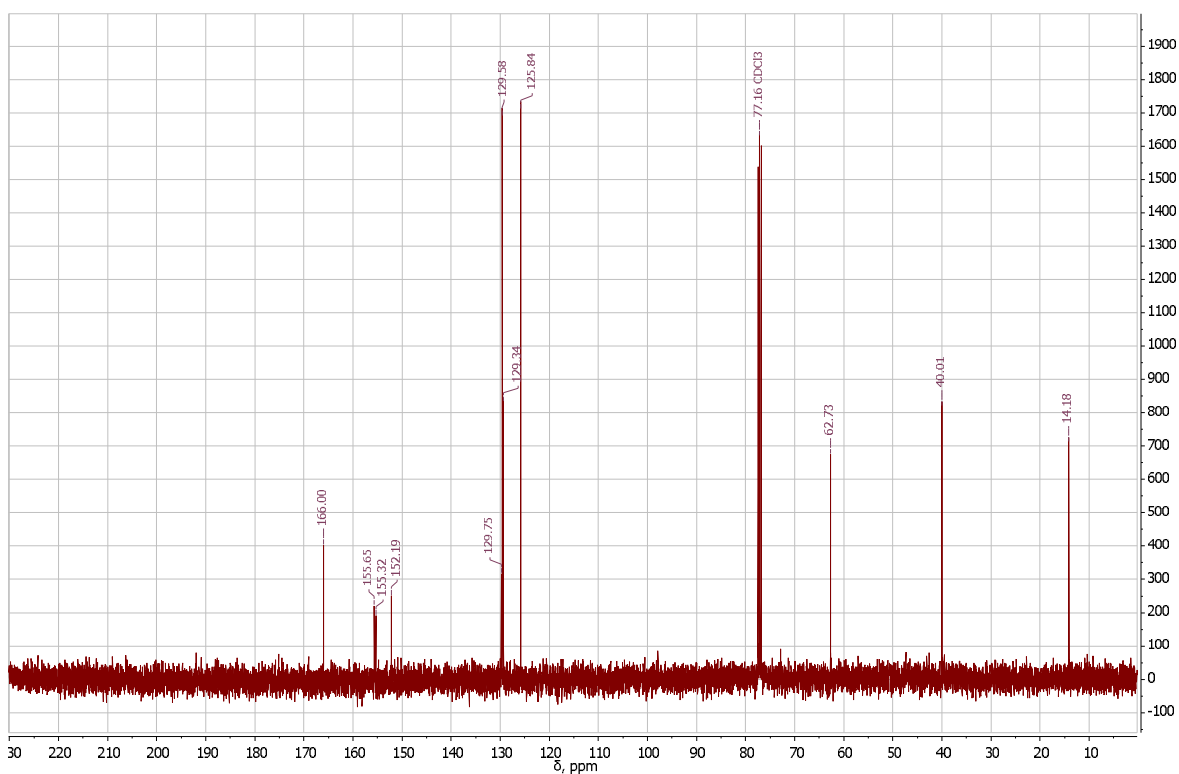
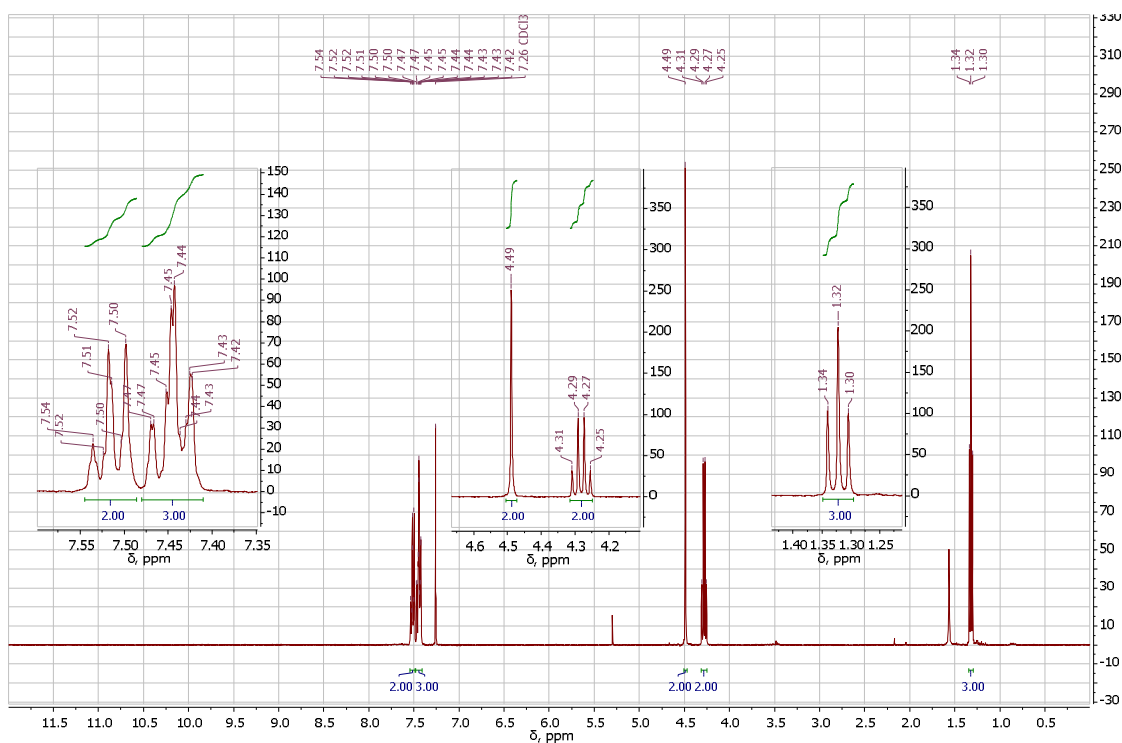
### Ethyl 2-(2,4,5-trioxo-3-phenylimidazolidin-1-yl)acetate (1b)



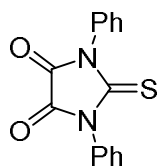
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 – 7.49 (m, 2H, Ar), 7.48 – 7.41 (m, 3H, Ar), 4.49 (s, 2H,  $\text{NCH}_2$ ), 4.28 (q,  $J = 7.1$  Hz, 2H,  $\text{COOCH}_2$ ), 1.32 (t,  $J = 7.1$  Hz, 3H,  $\text{CH}_3$ ).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.0, 155.7, 155.3, 152.2, 129.8, 129.6, 129.3, 125.8, 62.7, 40.0, 14.2.

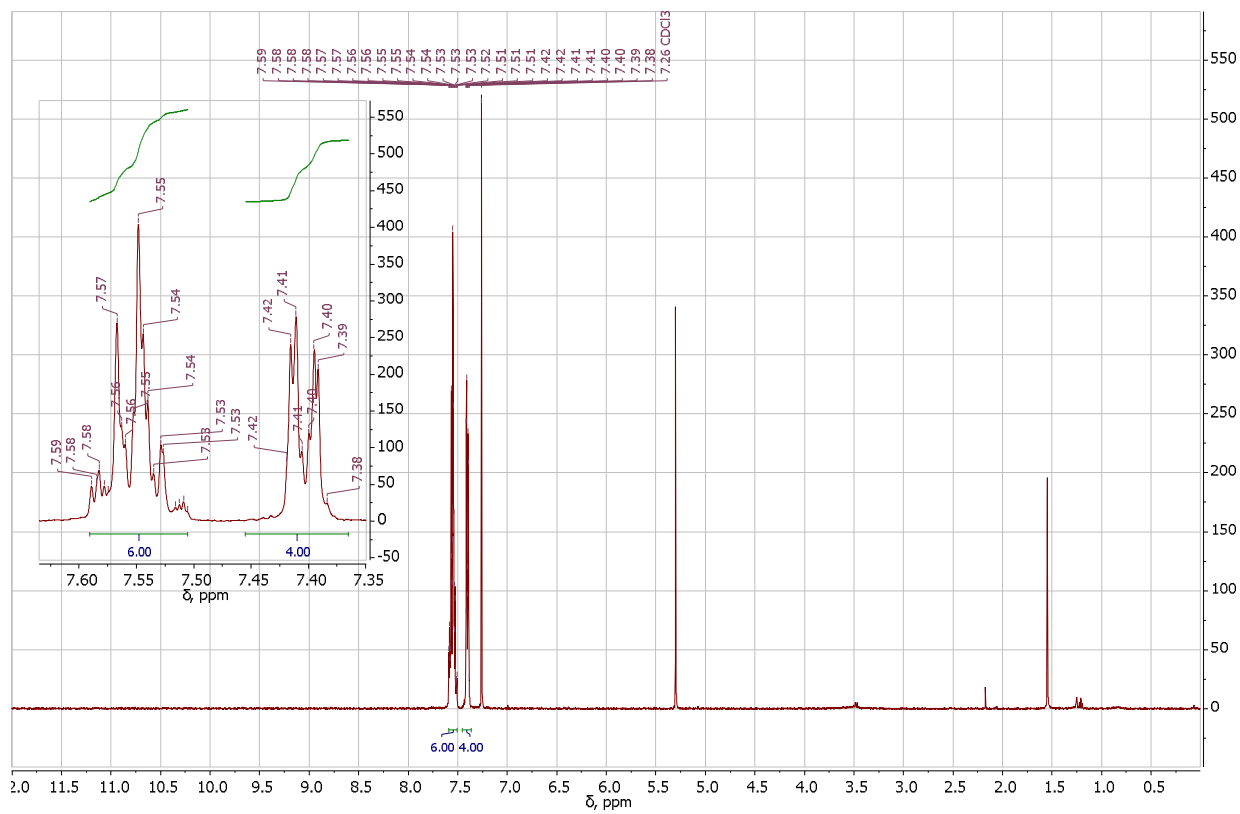
HRMS (ESI): calcd for  $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_5$  ( $\text{M}+\text{Na}$ ) $^+$  299.0638, found 299.0637.



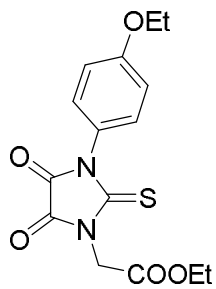
### 1,3-Diphenyl-2-thioxoimidazolidine-4,5-dione (1c)



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 – 7.50 (m, 6H, Ar), 7.42 – 7.37 (m, 4H, Ar).



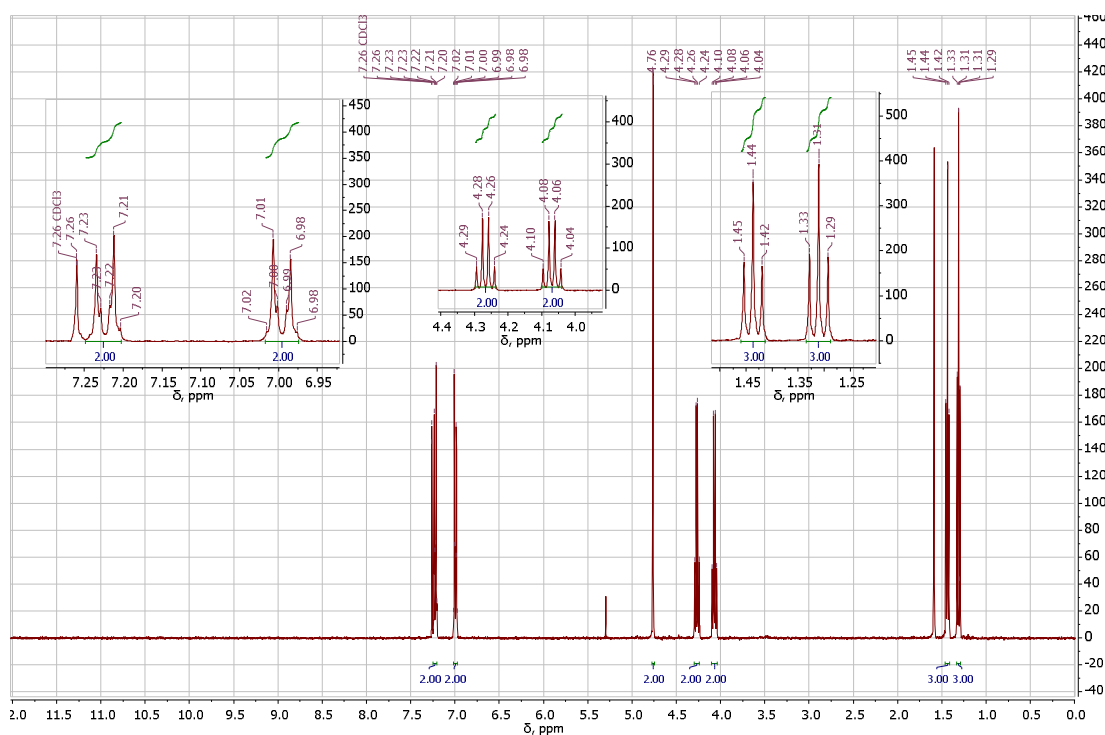
**Ethyl 2-(3-(4-ethoxyphenyl)-4,5-dioxo-2-thioxoimidazolidin-1-yl)acetate (1d)**



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25 – 7.20 (m, 2H, Ar), 7.02 – 6.97 (m, 2H, Ar), 4.76 (s, 2H,  $\text{NCH}_2$ ), 4.27 (q,  $J = 7.1$  Hz, 2H,  $\text{COOCH}_2\text{CH}_3$ ), 4.07 (q,  $J = 7.0$  Hz, 2H,  $\text{OCH}_2\text{CH}_3$ ), 1.44 (t,  $J = 7.0$  Hz, 3H,  $\text{OCH}_2\text{CH}_3$ ), 1.31 (t,  $J = 7.2$  Hz, 3H,  $\text{COOCH}_2\text{CH}_3$ ).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  180.0, 165.9, 160.0, 154.8, 154.4, 129.2, 123.7, 115.3, 63.9, 62.5, 42.7, 14.9, 14.2.

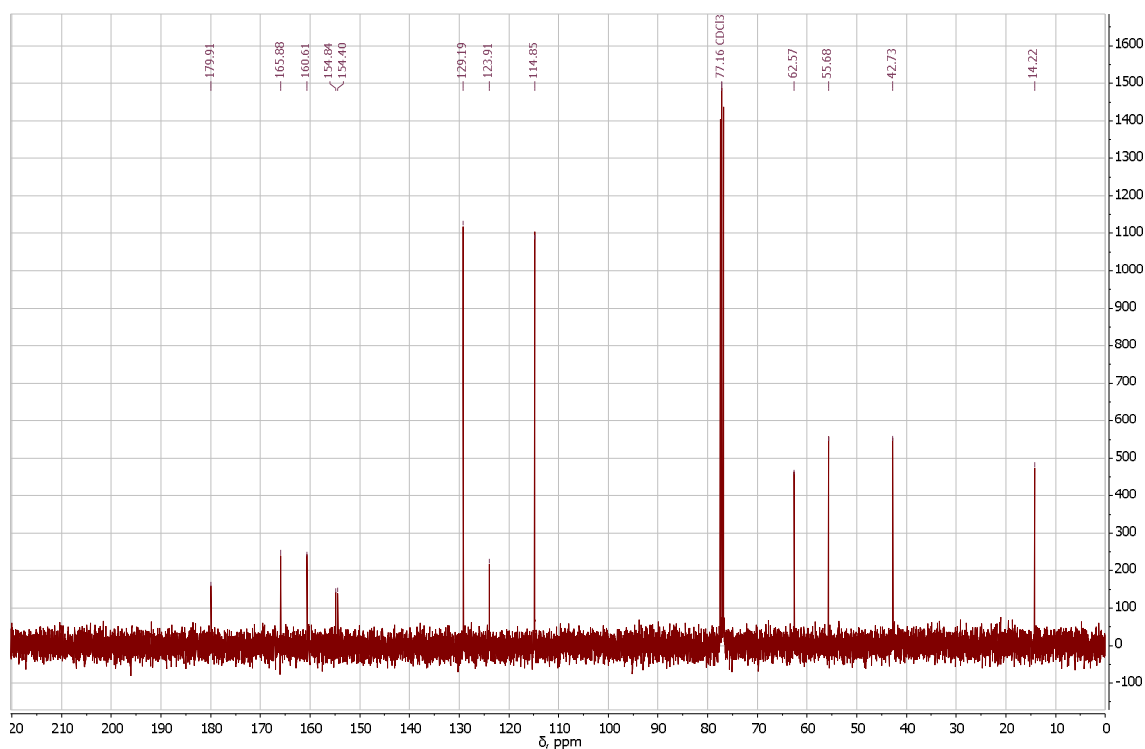
HRMS (ESI): calcd for  $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_5\text{S}$  ( $\text{M}+\text{Na}$ ) $^+$  359.0672, found 359.0675.



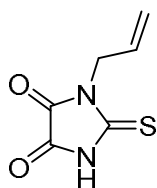
COc1ccc(cc1)N2C(=O)C(=O)N(C2C(=S)NCC(=O)OCC)C(=O)OCC

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 179.9, 165.9, 160.6, 154.8, 154.4, 129.2, 123.9, 114.9, 62.6, 55.7, 42.7, 14.2.





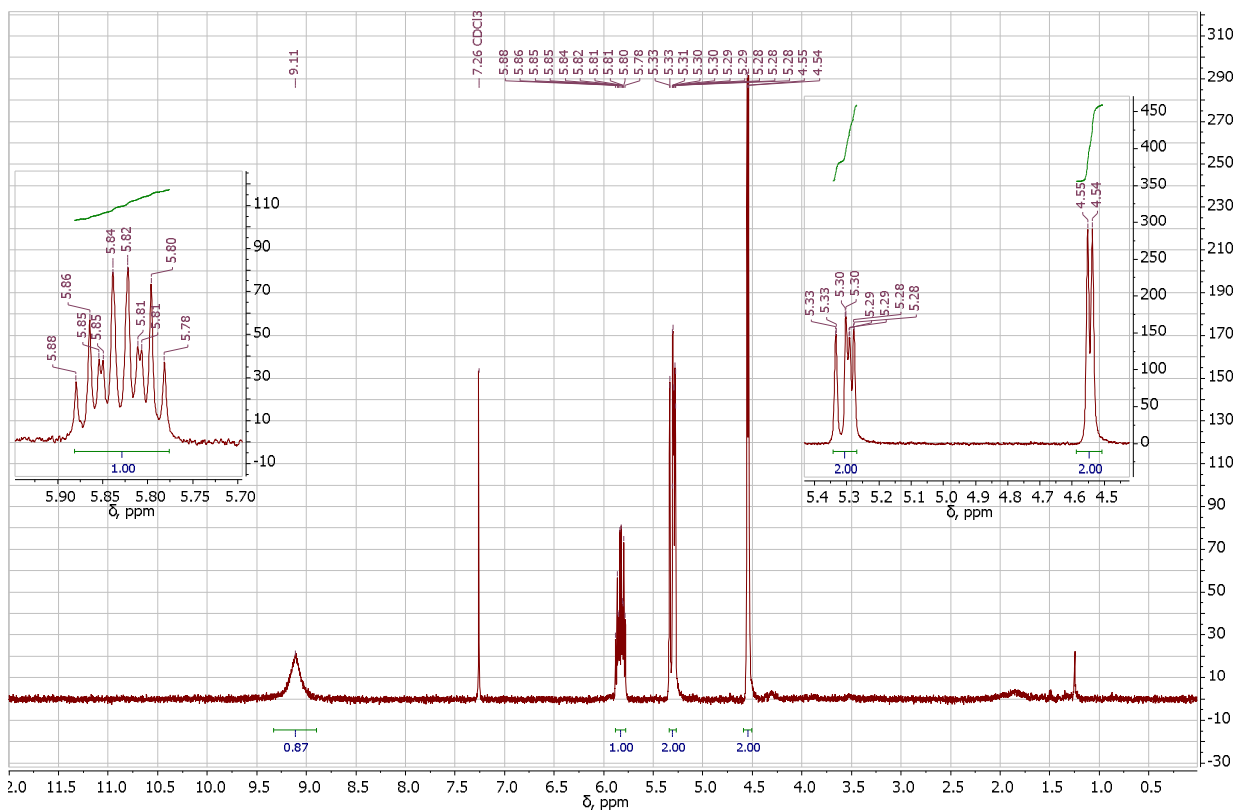
### 1-Allyl-2-thioxoimidazolidine-4,5-dione (1f)

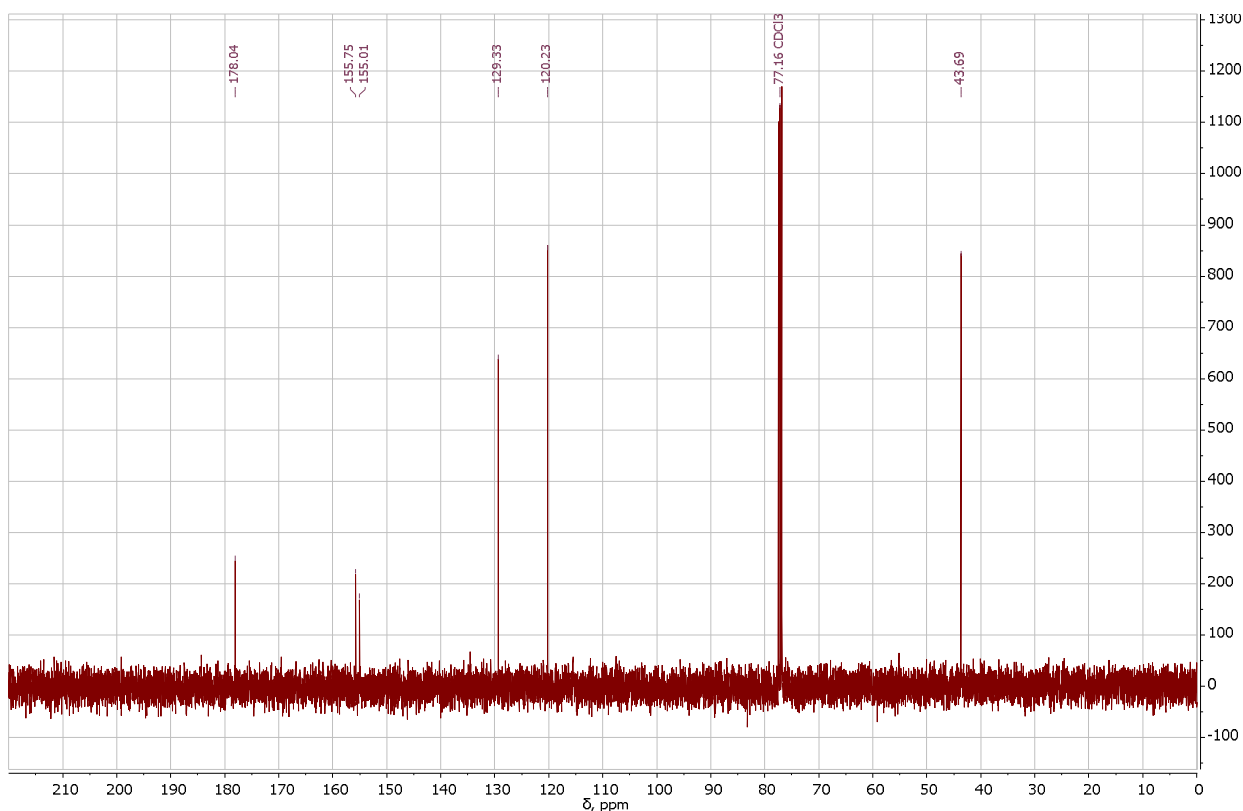


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.11 (br.s, 1H, NH), 5.83 (ddt,  $J$  = 16.4, 10.1, 6.0 Hz, 1H, CH), 5.34 – 5.27 (m, 2H,  $=\text{CH}_2$ ), 4.54 (d,  $J$  = 6.0 Hz, 2H,  $\text{NCH}_2$ ).

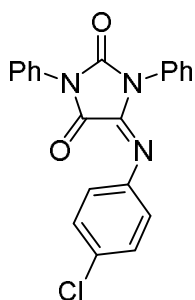
$^{13}\text{C}$  NMR (101 MHz, DMSO)  $\delta$  178.0, 155.7, 155.0, 129.3, 120.2, 43.7.

HRMS (ESI): calcd for  $\text{C}_6\text{H}_6\text{N}_2\text{O}_2\text{S}$  ( $\text{M}+\text{Na}$ ) $^+$  193.0042, found 193.0042.





**$^1\text{H}$ ,  $^{13}\text{C}$  NMR and HRMS spectral data of 5-aryliminoimidazolidine-4,5-diones 2a-m**

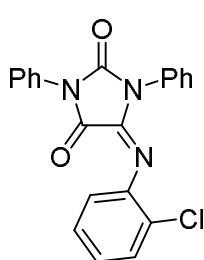
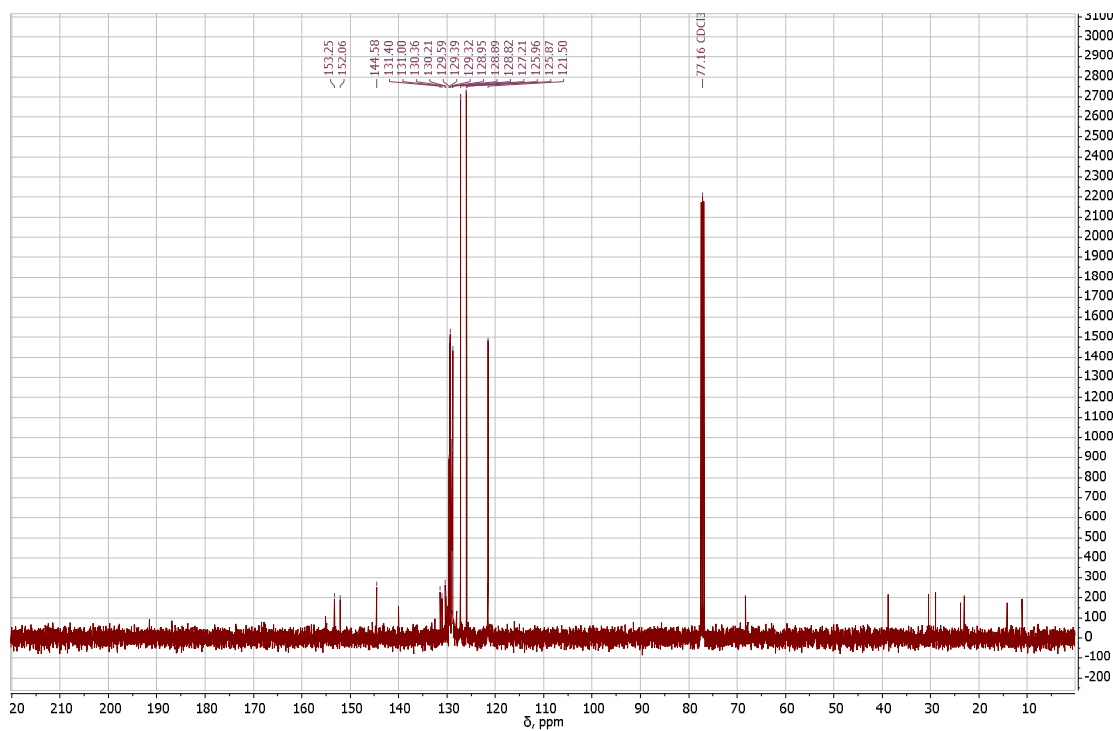
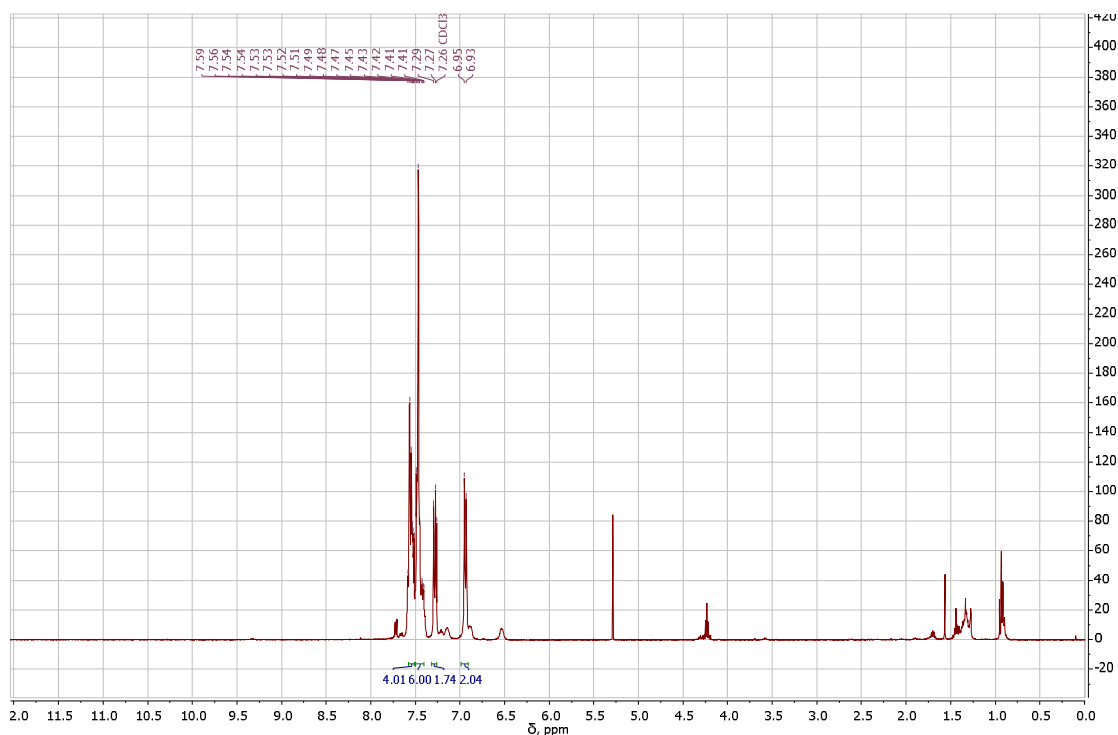


**(*E*)-5-((4-Chlorophenyl)imino)-1,3-diphenylimidazolidine-2,4-dione (2a)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 – 7.51 (m, 4H, Ar), 7.50 – 7.40 (m, 6H, Ar), 7.28 (d,  $J$  = 8.5 Hz, 2H, Ar), 6.94 (d,  $J$  = 8.5 Hz, 2H, Ar).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.3, 152.1, 144.6, 131.4, 131.0, 130.4, 130.2, 129.6, 129.4, 129.3, 128.9, 128.9, 128.8, 127.2, 126.0, 125.9, 121.5.

HRMS (ESI): calcd for  $\text{C}_{21}\text{H}_{14}\text{ClN}_3\text{O}_2$  ( $\text{M}+\text{H}$ ) $^+$  376.0847, found 376.0852.

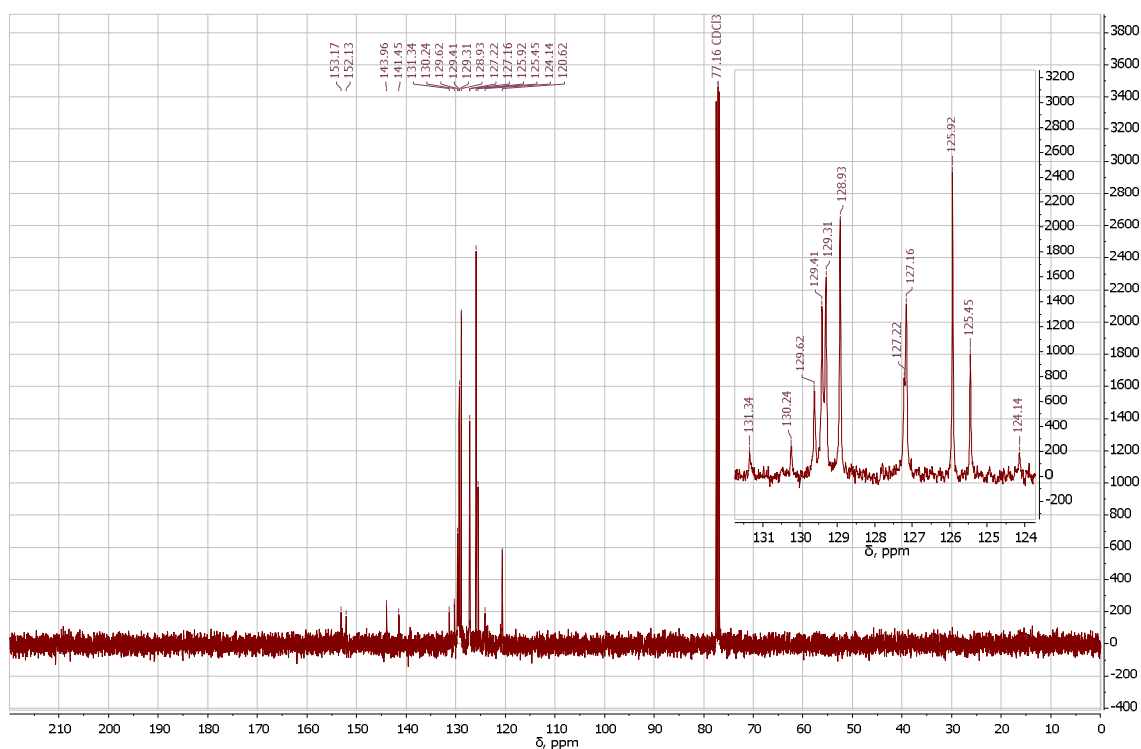
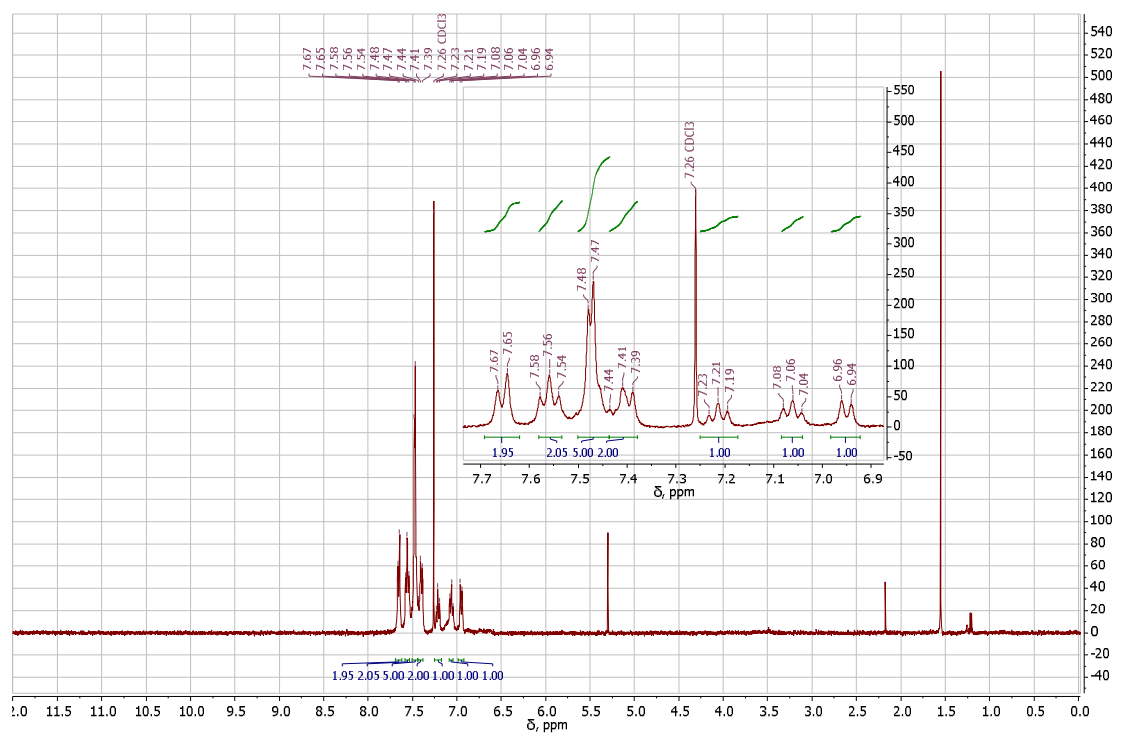


**(E)-5-((2-Chlorophenyl)imino)-1,3-diphenylimidazolidine-2,4-dione (2b)**

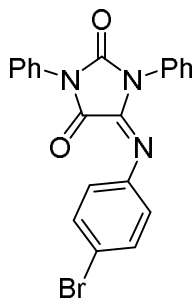
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 (d,  $J$  = 7.9 Hz, 2H, Ar), 7.56 (t,  $J$  = 7.7 Hz, 2H, Ar), 7.47 (d,  $J$  = 4.2 Hz, 5H, Ar), 7.40 (d,  $J$  = 8.2 Hz, 2H, Ar), 7.21 (t,  $J$  = 7.6 Hz, 1H, Ar), 7.06 (t,  $J$  = 7.6 Hz, 1H, Ar), 6.95 (d,  $J$  = 8.0 Hz, 1H, Ar).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.2, 152.1, 144.0, 141.5, 131.3, 130.2, 129.6, 129.4, 129.3, 128.9, 127.2, 127.2, 125.9, 125.4, 120.6.

HRMS (ESI): calcd for  $\text{C}_{21}\text{H}_{14}\text{ClN}_3\text{O}_2$  ( $2\text{M}+\text{Na}$ ) $^+$  773.1441, found 773.1443.



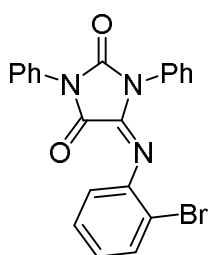
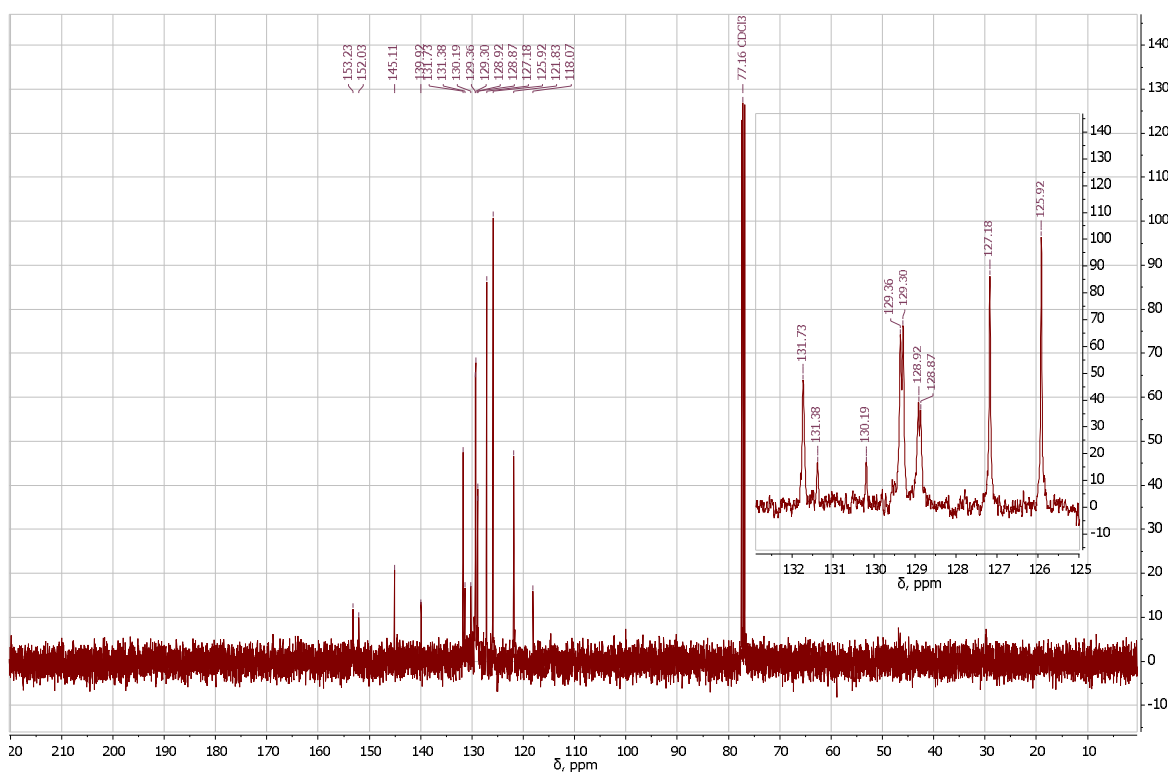
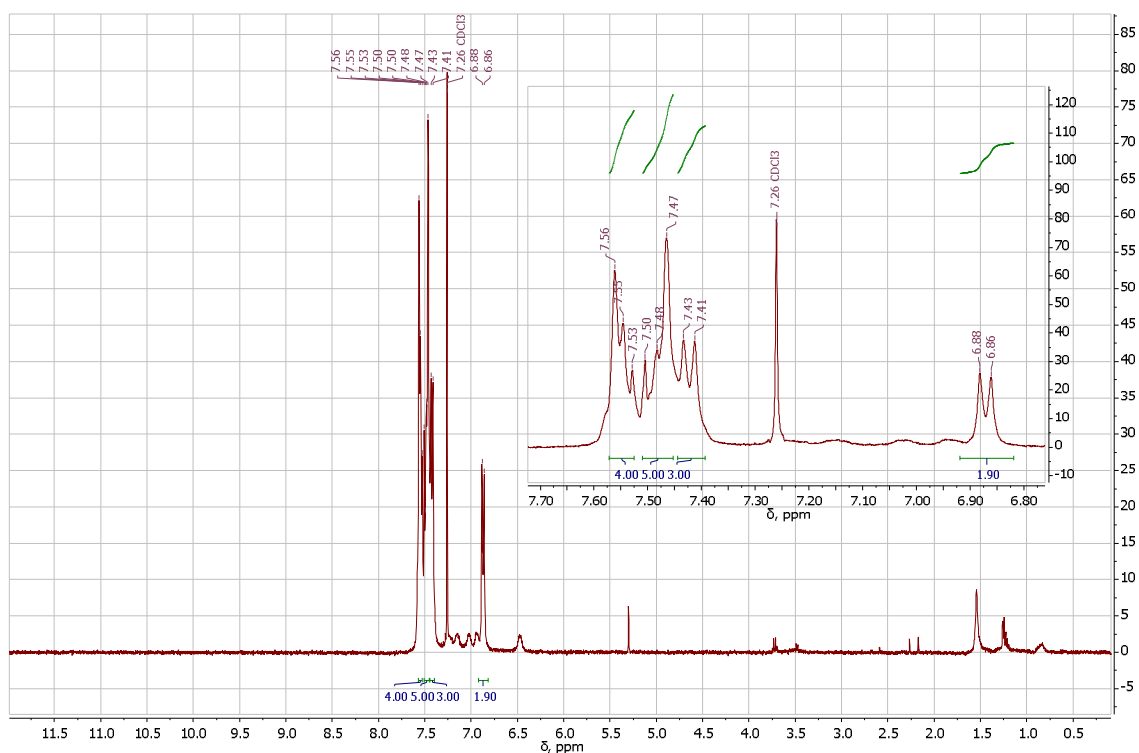
**(E)-5-((4-Bromophenyl)imino)-1,3-diphenylimidazolidine-2,4-dione (2c)**



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.57 – 7.53 (m, 4H, Ar), 7.51 – 7.45 (m, 5H, Ar), 7.42 (d, *J* = 8.3 Hz, 3H, Ar), 6.87 (d, *J* = 8.2 Hz, 2H, Ar).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 153.2, 152.0, 145.1, 139.9, 131.7, 131.4, 130.2, 129.4, 129.3, 128.9, 128.9, 127.2, 125.9, 121.8, 118.1.

HRMS (ESI): calcd for C<sub>21</sub>H<sub>14</sub>BrN<sub>3</sub>O<sub>2</sub> (M+H)<sup>+</sup> 420.0342, found 420.0344.

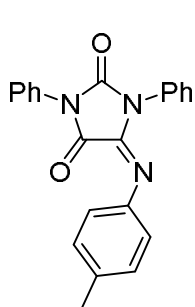
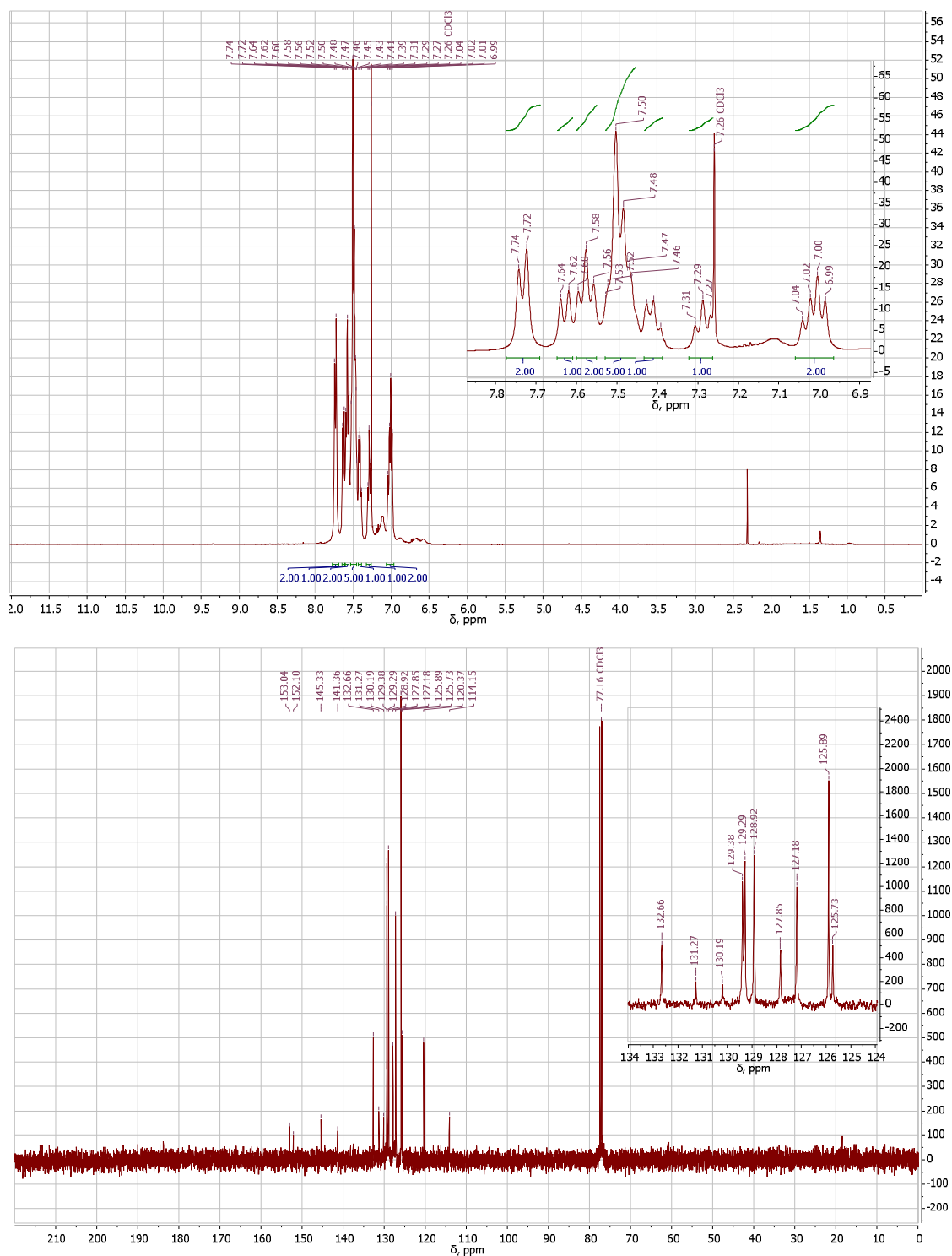


**(E)-5-((2-Bromophenyl)imino)-1,3-diphenylimidazolidine-2,4-dione (2d)**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.73 (d, *J* = 7.9 Hz, 2H, Ar), 7.63 (d, *J* = 8.0 Hz, 1H, Ar), 7.58 (t, *J* = 7.8 Hz, 2H, Ar), 7.53 – 7.45 (m, 5H, Ar), 7.43 – 7.39 (m, 1H, Ar), 7.29 (t, *J* = 7.6 Hz, 1H, Ar), 7.06 – 6.97 (m, 2H, Ar).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 153.0, 145.3, 132.7, 131.3, 130.2, 129.4, 129.3, 128.9, 127.8, 127.2, 125.9, 125.7, 120.4, 114.1.

HRMS (ESI): calcd for  $C_{21}H_{14}BrN_3O_2$  ( $M+Na$ )<sup>+</sup> 442.0162, found 442.0167.

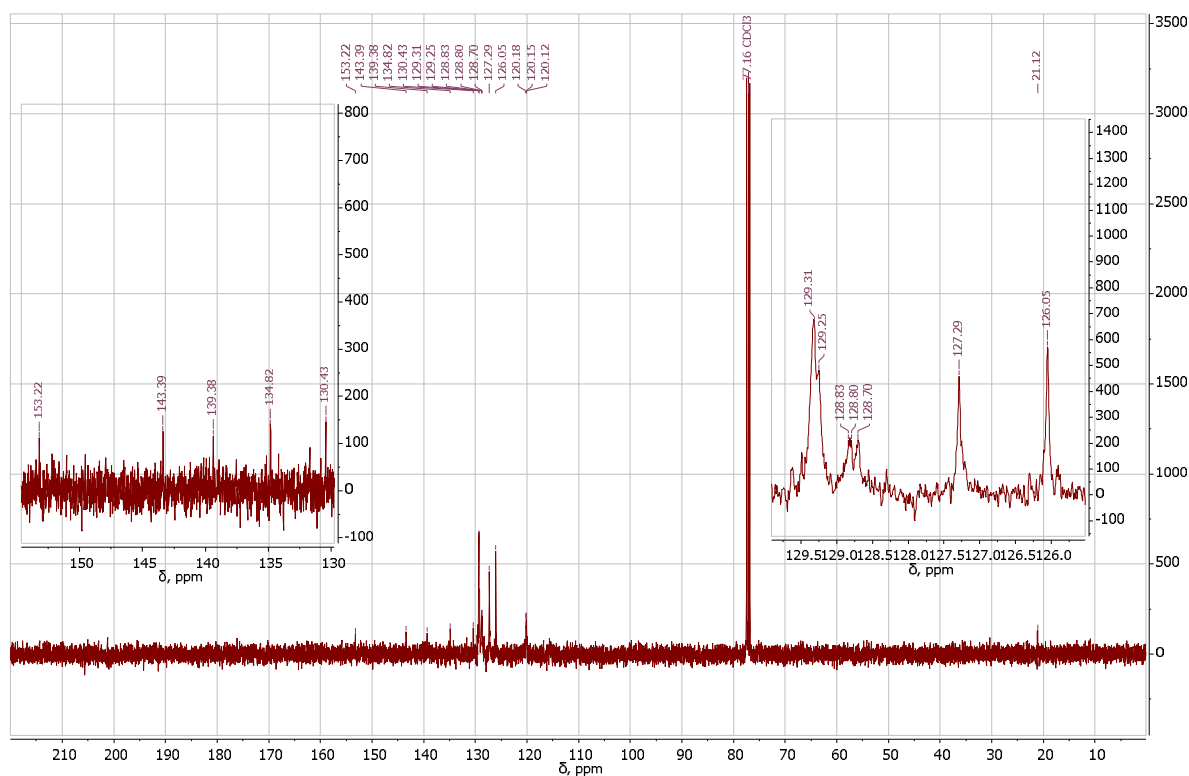
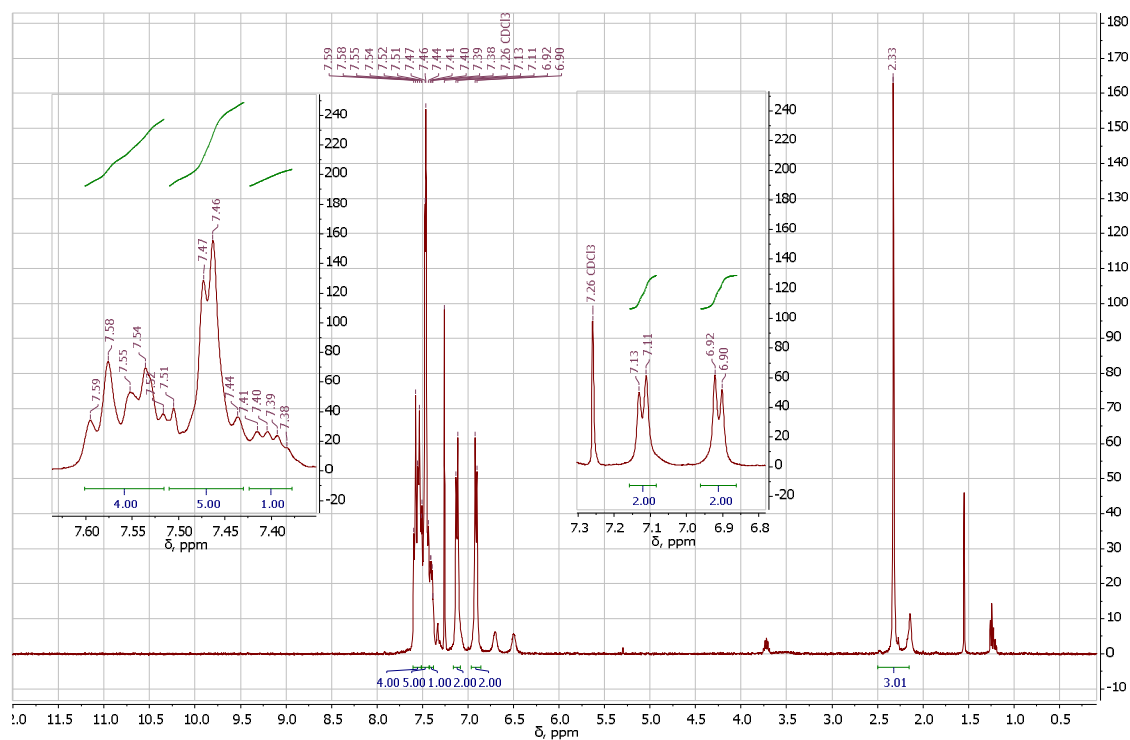


**(E)-1,3-Diphenyl-5-(p-tolylimino)imidazolidine-2,4-dione (2e)**

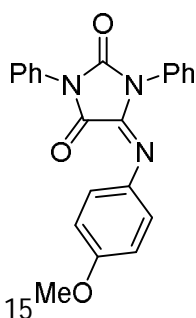
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.61 – 7.52 (m, 4H, Ar), 7.52 – 7.44 (m, 5H, Ar), 7.43 – 7.38 (m, 1H, Ar), 7.13 (d, *J* = 7.9 Hz, 2H, Ar), 6.92 (d, *J* = 7.9 Hz, 2H, Ar), 2.33 (s, 3H, CH<sub>3</sub>).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 153.2, 143.4, 139.4, 134.8, 130.4, 129.3, 129.2, 128.8, 128.8, 128.7, 127.3, 126.1, 120.2, 120.1, 120.1, 21.1.

HRMS (ESI): calcd for  $C_{22}H_{17}N_3O_2$  ( $M+H$ )<sup>+</sup> 356.1394, found 356.1396.



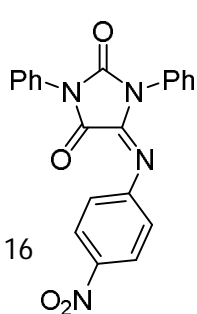
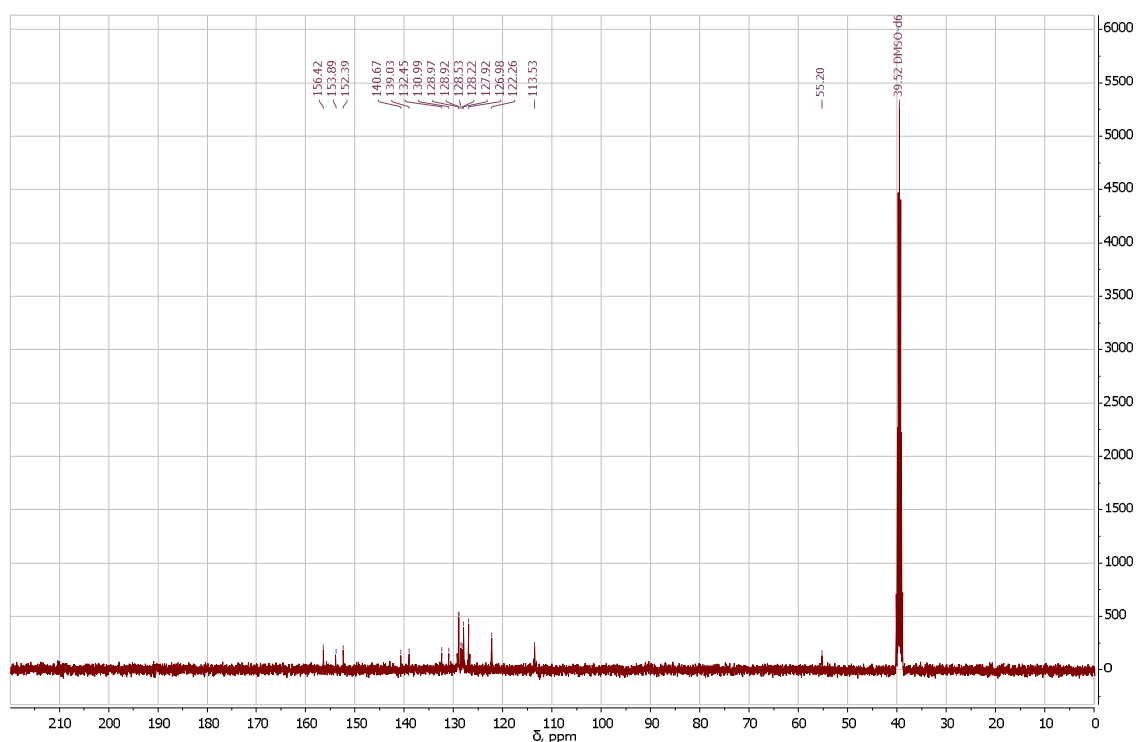
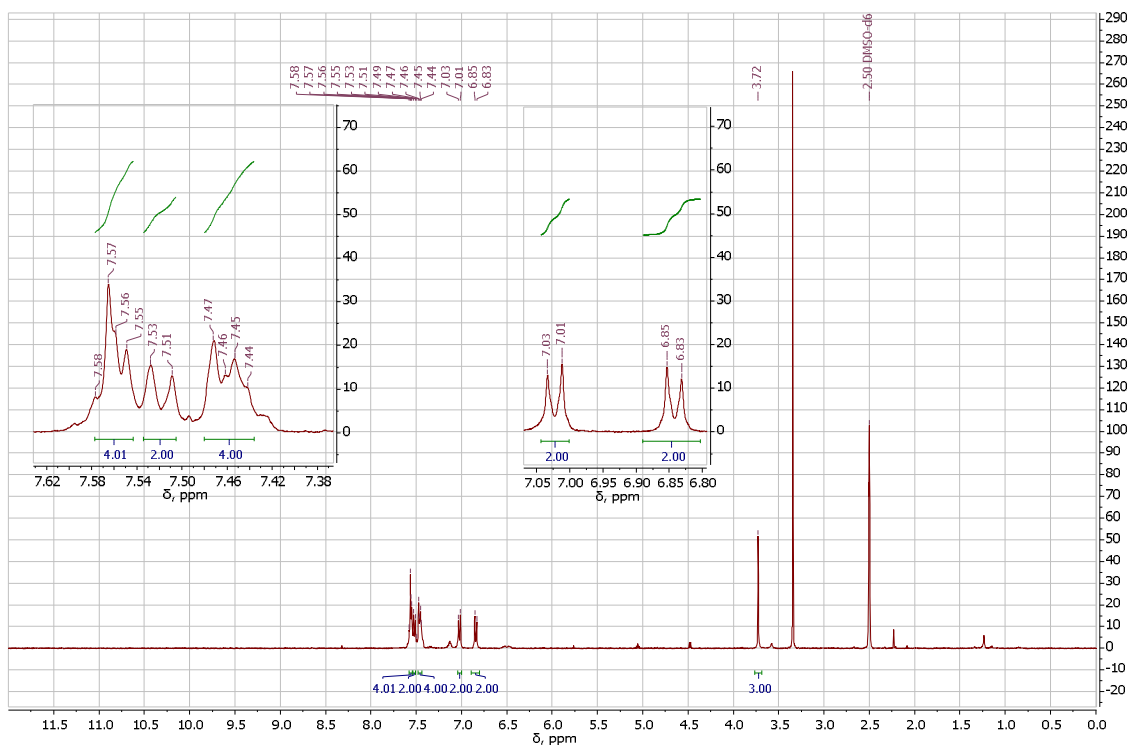
**(E)-5-((4-Methoxyphenyl)imino)-1,3-diphenylimidazolidine-2,4-dione (2f)**



<sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  7.58 – 7.54 (m, 4H, Ar), 7.52 (d,  $J = 7.6$  Hz, 2H, Ar), 7.48 – 7.44 (m, 4H, Ar), 7.02 (d,  $J = 8.7$  Hz, 2H, Ar), 6.84 (d,  $J = 8.8$  Hz, 2H, Ar), 3.72 (s, 3H, OCH<sub>3</sub>).

$^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$  156.4, 153.9, 152.4, 140.7, 139.0, 132.5, 131.0, 129.0, 128.9, 128.5, 128.2, 127.9, 127.0, 122.3, 113.5, 55.2.

HRMS (ESI): calcd for  $\text{C}_{22}\text{H}_{17}\text{N}_3\text{O}_3$  ( $\text{M}+\text{H}$ ) $^+$  372.1343, found 372.1347.



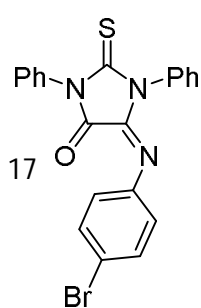
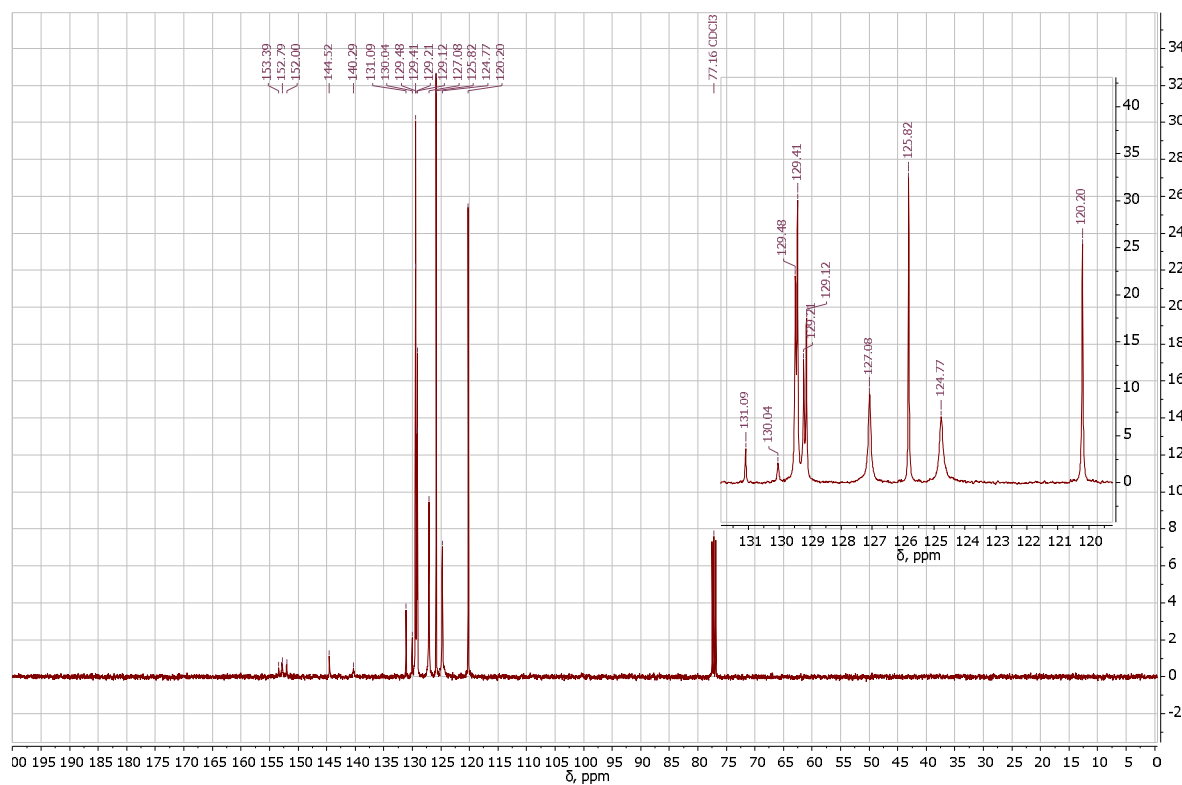
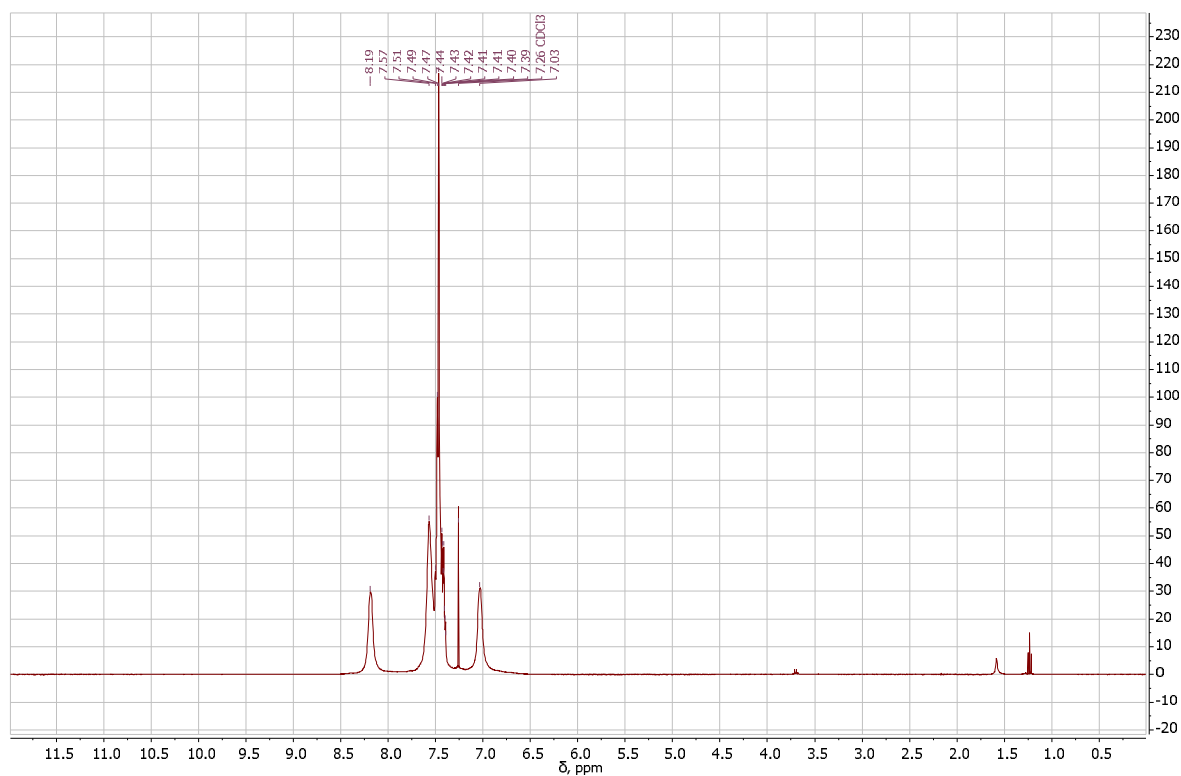
**(E)-5-((4-Nitrophenyl)imino)-1,3-diphenylimidazolidine-2,4-dione (2g)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.19 (s, 2H, Ar), 7.57 (m, 3H, Ar), 7.52 – 7.38 (m, 7H, Ar), 7.03 (s, 2H, Ar).



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.4, 152.8, 152.0, 144.5, 140.3, 131.1, 130.0, 129.5, 129.4, 129.2, 129.1, 127.1, 125.8, 124.8, 120.2.

HRMS (ESI): calcd for  $\text{C}_{21}\text{H}_{14}\text{N}_4\text{O}_4$  ( $\text{M}+\text{H}$ ) $^+$  409.0907, found 409.0911.

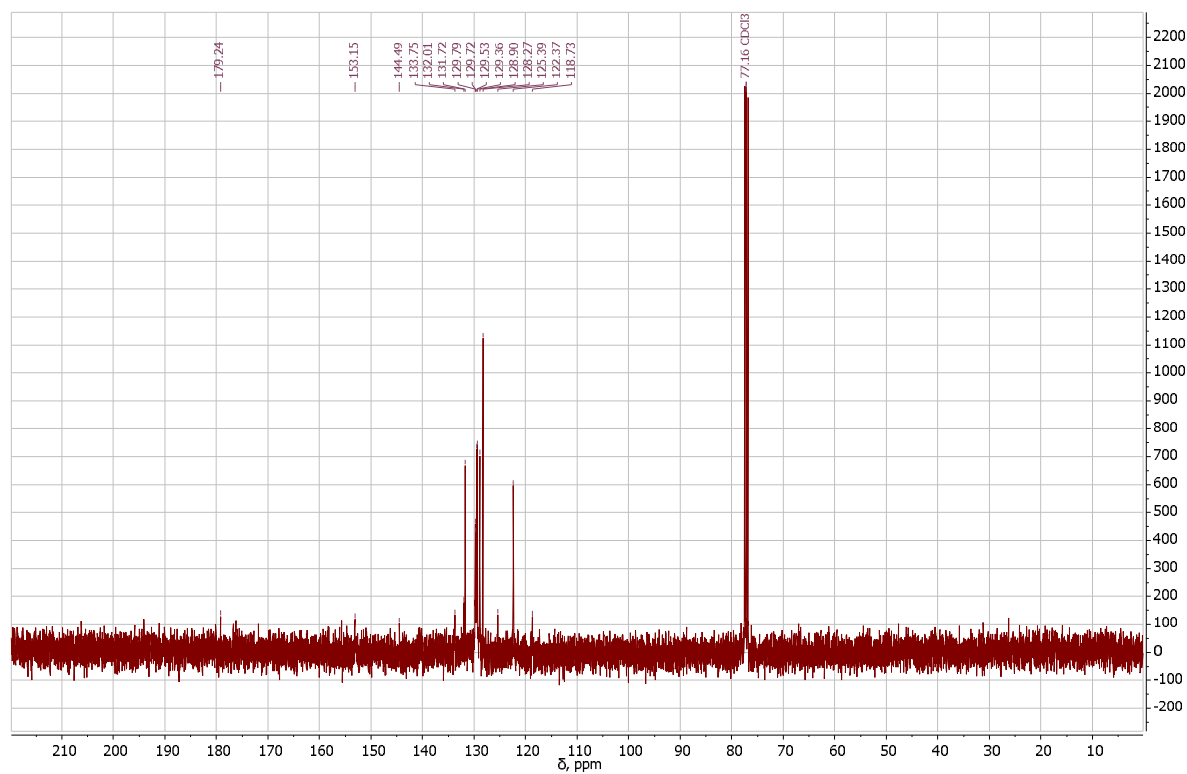
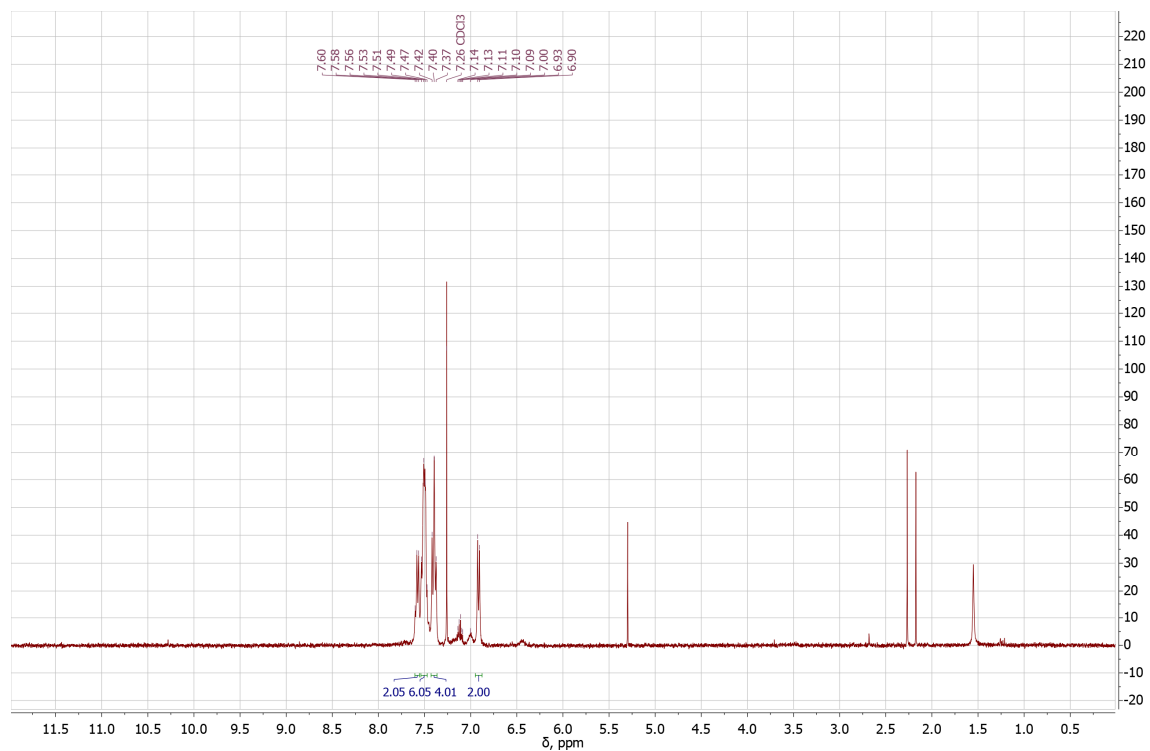


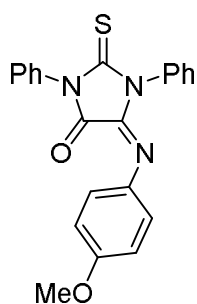
**(E)-5-((4-bromophenyl)imino)-1,3-diphenyl-2-thioxoimidazolidin-4-one (2h)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 – 7.55 (m, 2H, Ar), 7.50 (q,  $J$  = 9.2, 8.3 Hz, 6H, Ar), 7.43 – 7.36 (m, 4H, Ar), 6.91 (d,  $J$  = 8.3 Hz, 2H, Ar).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  179.2, 153.1, 144.5, 133.8, 132.0, 131.7, 129.8, 129.7, 129.5, 129.4, 128.9, 128.3, 125.4, 122.4, 118.7.

HRMS (ESI): calcd for  $\text{C}_{22}\text{H}_{17}\text{N}_3\text{O}_2\text{S}$  ( $2\text{M}+\text{Na}$ ) $^+$  797.1975, found 797.1986.



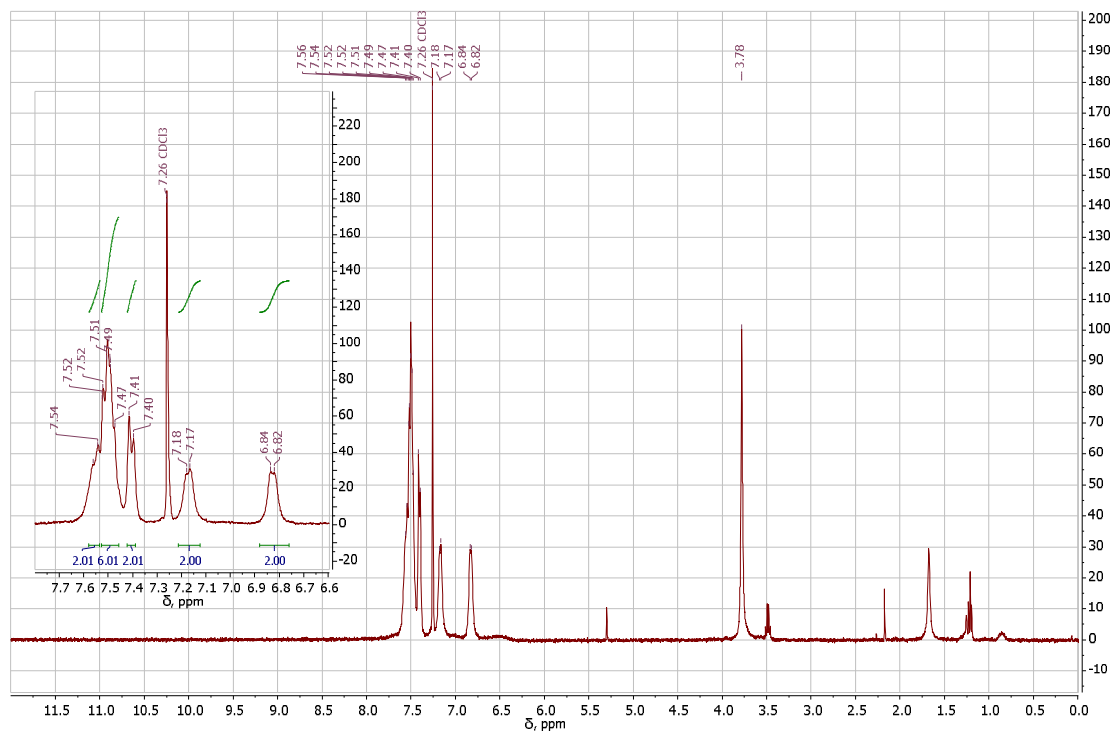


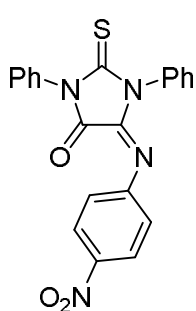
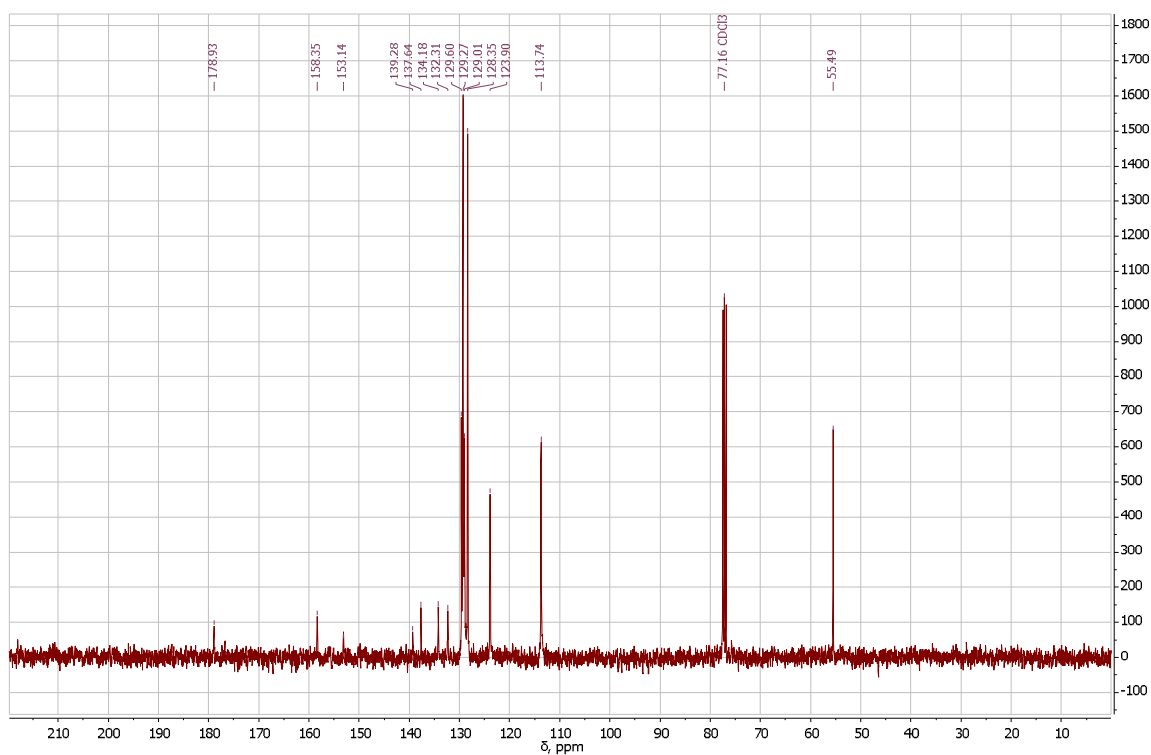
**(E)-5-((4-Methoxyphenyl)imino)-1,3-diphenyl-2-thioxoimidazolidin-4-one (2i)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 – 7.53 (m, 2H, Ar), 7.53 – 7.46 (m, 6H, Ar), 7.40 (d,  $J$  = 7.4 Hz, 2H, Ar), 7.17 (d,  $J$  = 6.5 Hz, 2H, Ar), 6.83 (d,  $J$  = 6.6 Hz, 2H, Ar), 3.78 (s, 3H,  $\text{OCH}_3$ ).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  178.9, 158.3, 153.1, 139.3, 137.6, 134.2, 132.3, 129.6, 129.3, 129.0, 128.4, 123.9, 113.7, 55.5.

HRMS (ESI): calcd for  $(\text{M}+\text{H})^+$  388.1114, found 388.1122.



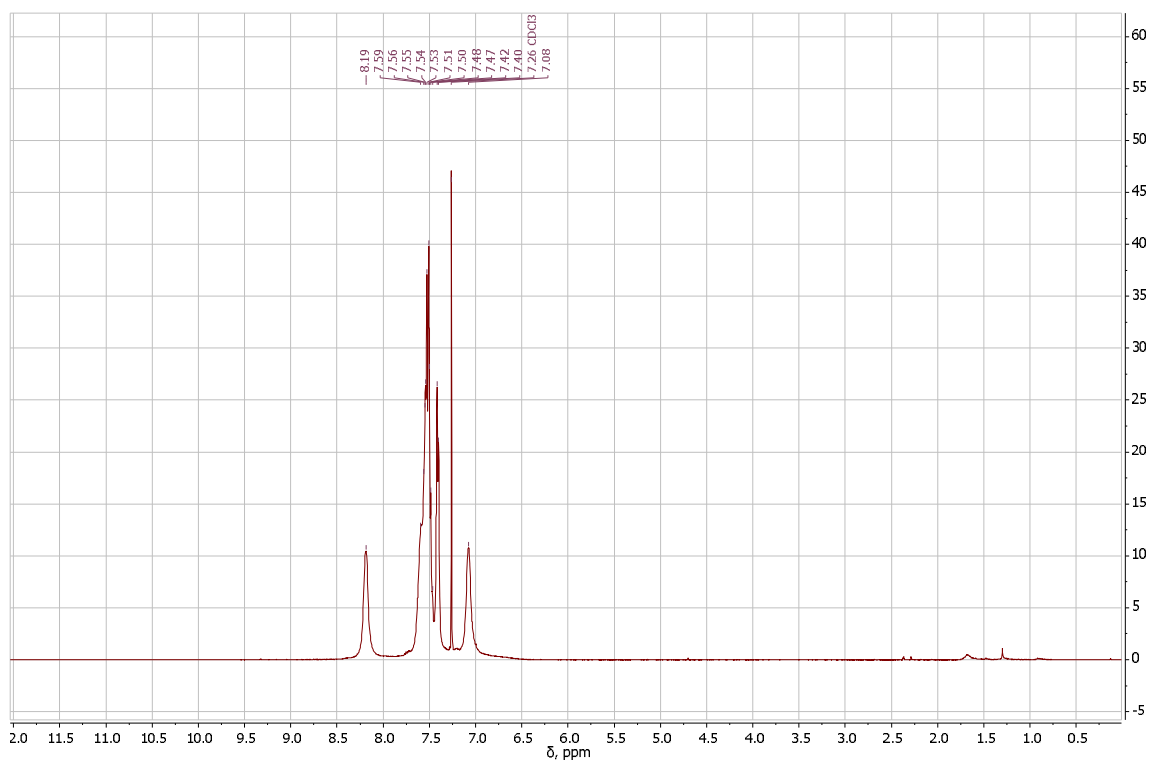


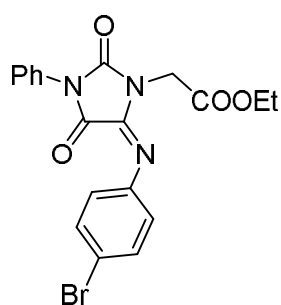
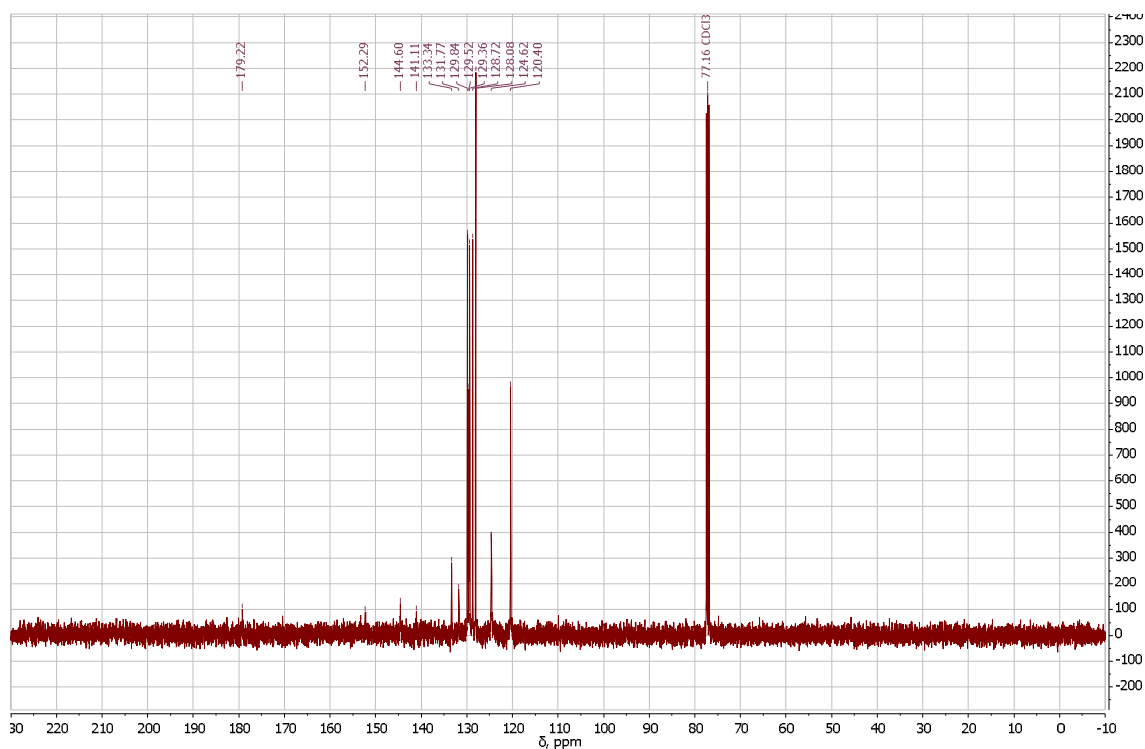
**(E)-5-((4-Nitrophenyl)imino)-1,3-diphenyl-2-thioxoimidazolidin-4-one (2j)**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.19 (s, 2H, Ar), 7.64 – 7.46 (m, 8H, Ar), 7.41 (d, *J* = 7.4 Hz, 2H, Ar), 7.08 (s, 2H, Ar).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 179.2, 152.3, 144.6, 141.1, 133.3, 131.8, 129.8, 129.5, 129.4, 128.7, 128.1, 124.6, 120.4.

HRMS (ESI): calcd for C<sub>21</sub>H<sub>14</sub>N<sub>4</sub>O<sub>3</sub>S (M+H)<sup>+</sup> 403.0859, found 403.0864.



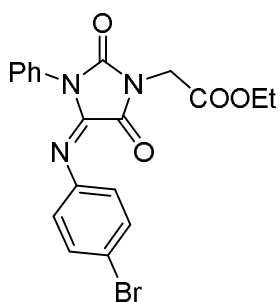
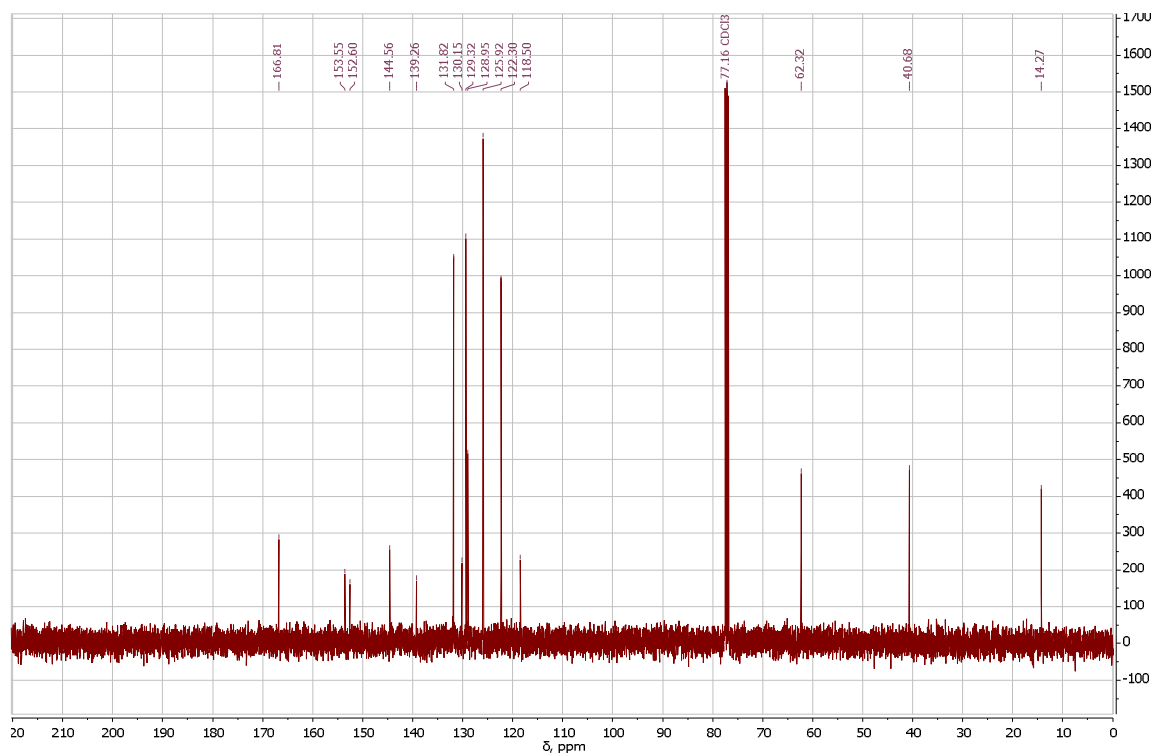
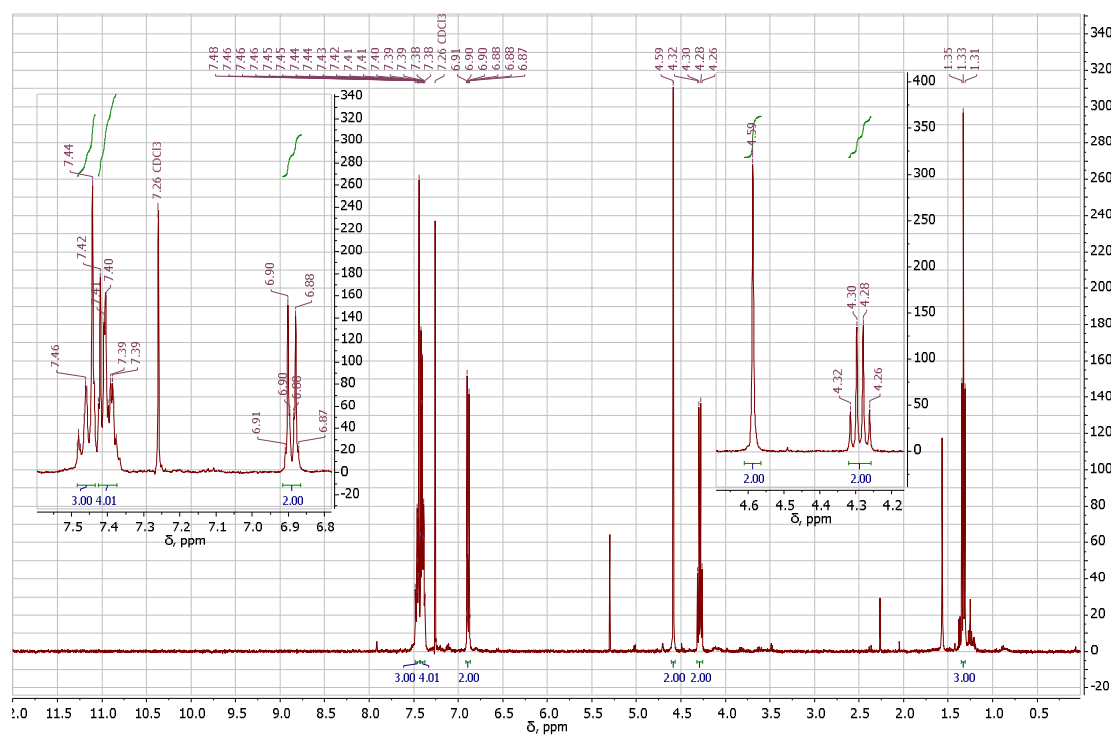


**Ethyl (E)-2-(5-((4-bromophenyl)imino)-2,4-dioxo-3-phenylimidazolidin-1-yl)acetate (2k)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 – 7.43 (m, 3H, Ar), 7.43 – 7.37 (m, 4H, Ar), 6.92 – 6.87 (m, 2H, Ar), 4.59 (s, 2H,  $\text{NCH}_2$ ), 4.29 (q,  $J = 7.2$  Hz, 2H,  $\text{COOCH}_2$ ), 1.33 (t,  $J = 7.1$  Hz, 3H,  $\text{CH}_3$ ).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.8, 153.5, 152.6, 144.6, 139.3, 131.8, 130.2, 129.3, 128.9, 125.9, 122.3, 118.5, 62.3, 40.7, 14.3.

HRMS (ESI): calcd for  $\text{C}_{19}\text{H}_{16}\text{BrN}_3\text{O}_4$  ( $\text{M}+\text{Na}$ ) $^+$  452.0216, found 452.0222.

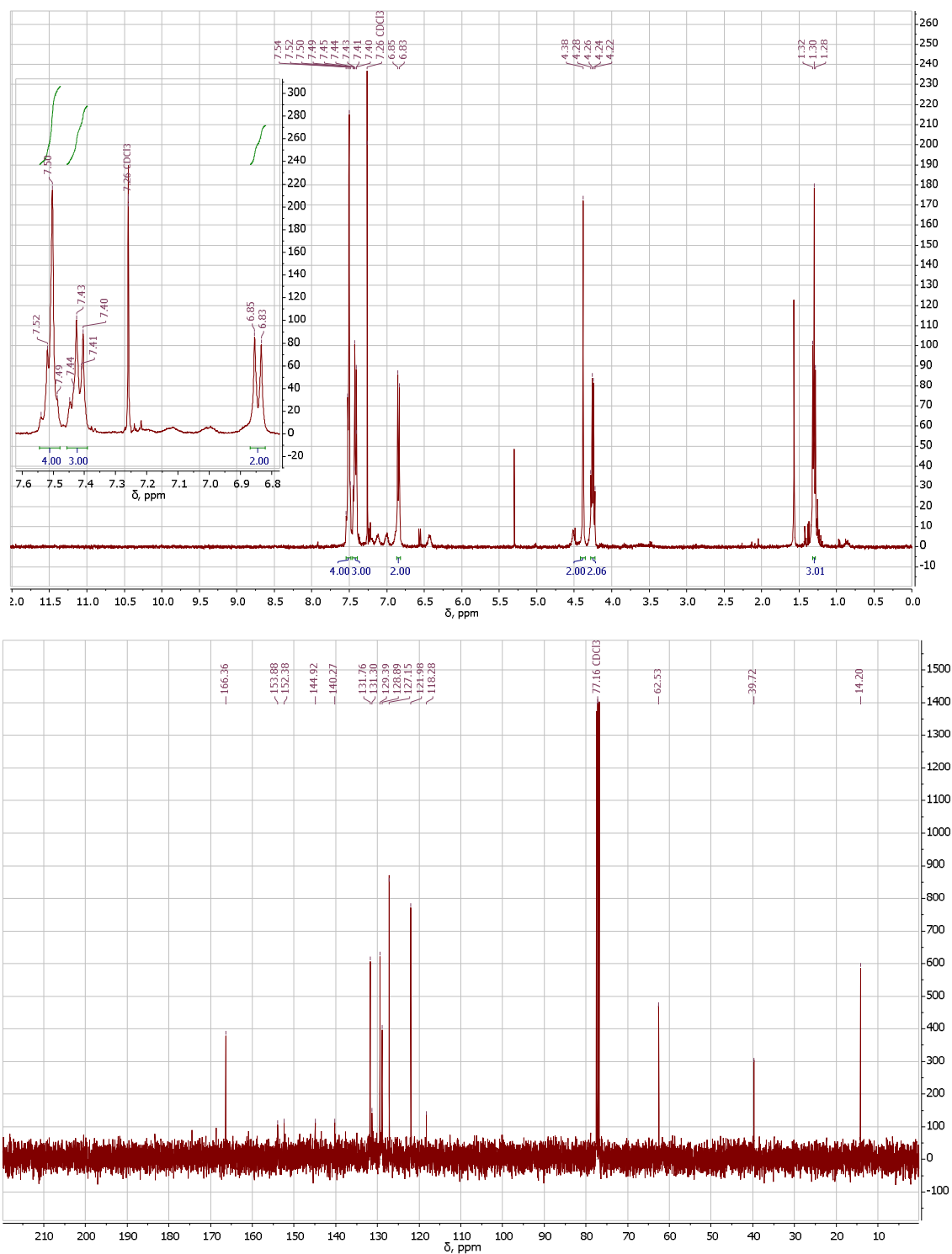


**Ethyl (E)-2-(4-((4-bromophenyl)imino)-2,5-dioxo-3-phenylimidazolidin-1-yl)acetate (2I)**

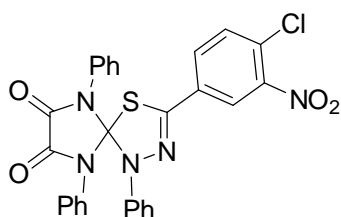
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.54 – 7.48 (m, 4H, Ar), 7.46 – 7.39 (m, 3H, Ar), 6.84 (d, *J* = 8.5 Hz, 2H, Ar), 4.38 (s, 2H, NCH<sub>2</sub>), 4.25 (q, *J* = 7.1 Hz, 2H, COOCH<sub>2</sub>), 1.30 (t, *J* = 7.1 Hz, 3H, CH<sub>3</sub>).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.4, 153.9, 152.4, 144.9, 140.3, 131.8, 131.3, 129.4, 128.9, 127.2, 122.0, 118.3, 62.5, 39.7, 14.2.

HRMS (ESI): calcd for  $C_{19}H_{16}BrN_3O_4$  ( $M+Na$ )<sup>+</sup> 452.0216, found 452.0220.



**<sup>1</sup>H, <sup>13</sup>C NMR and HRMS spectral data of 4-thia-1,2,6,9-tetraazaspiro[4.4]non-2-ene-7,8-diones 4a-g**



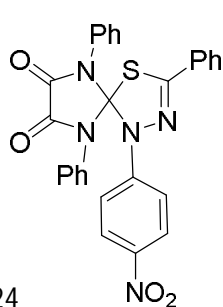
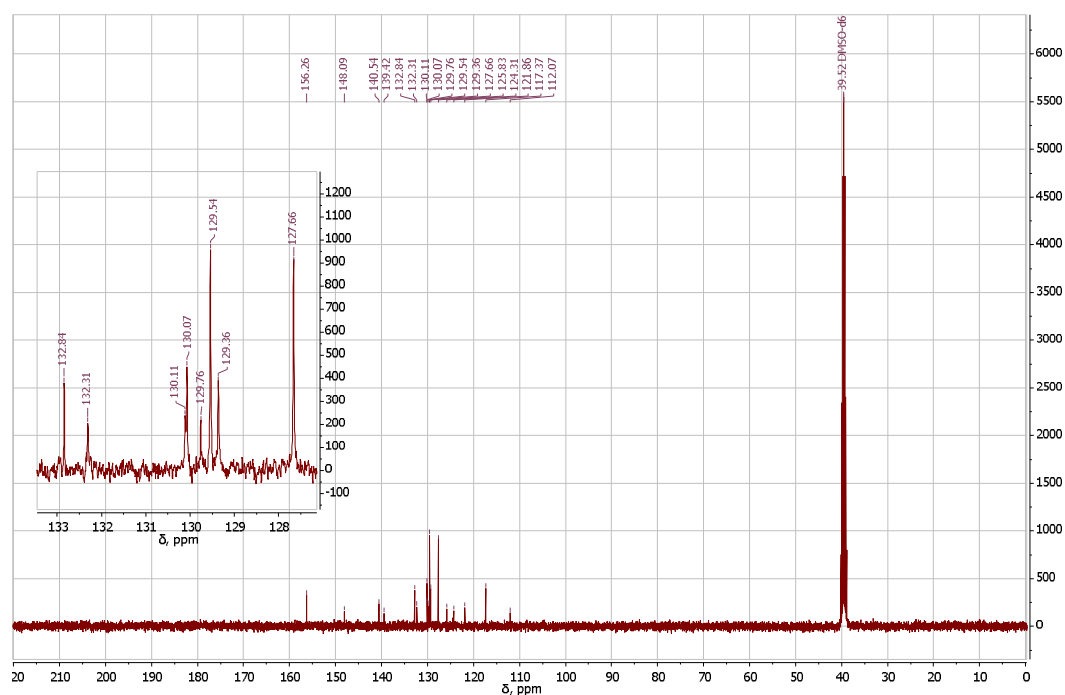
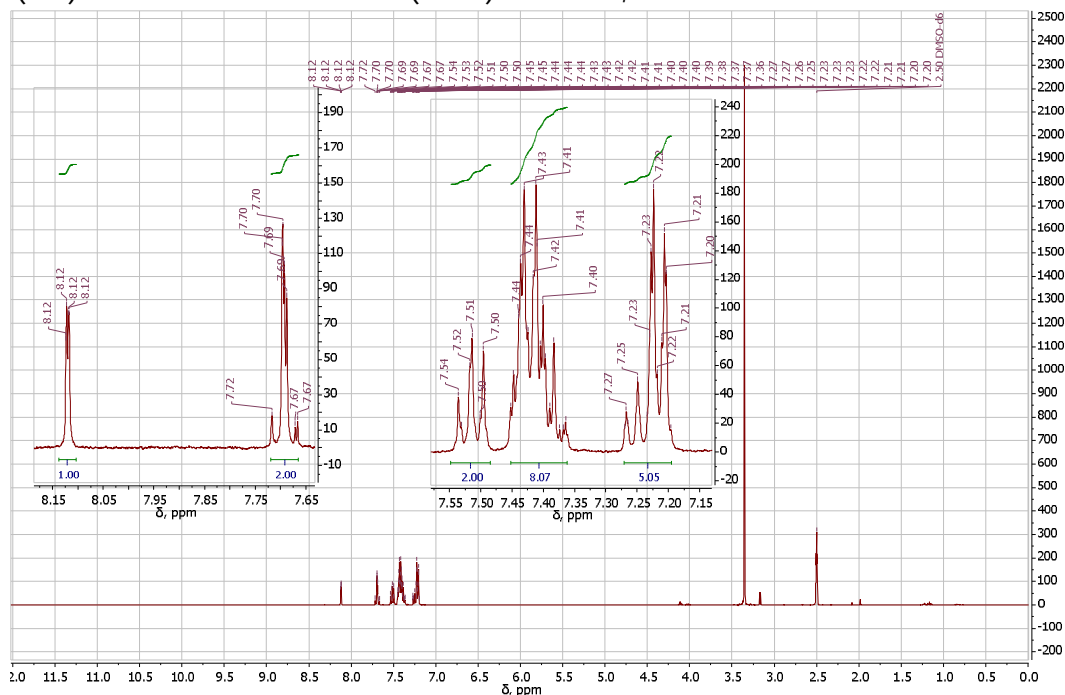
**3-(4-Chloro-3-nitrophenyl)-1,6,9-triphenyl-4-thia-1,2,6,9-tetraazaspiro[4.4]non-2-ene-7,8-dione (4a)**

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 8.12 (dd, *J* = 1.9, 0.7 Hz, 1H, Ar), 7.72 – 7.66 (m, 2H, Ar), 7.52 (dd, *J* = 8.8, 7.3 Hz, 2H, Ar), 7.42 (m, 8H,

Ar), 7.27 – 7.20 (m, 5H, Ar).

<sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ 156.3, 148.1, 140.5, 139.4, 132.8, 132.3, 130.1, 130.1, 129.8, 129.5, 129.4, 127.7, 125.8, 124.3, 121.9, 117.4, 112.1.

HRMS (ESI): calcd for C<sub>28</sub>H<sub>18</sub>ClN<sub>5</sub>O<sub>4</sub>S (M+H)<sup>+</sup> 578.0660, found 578.0665.



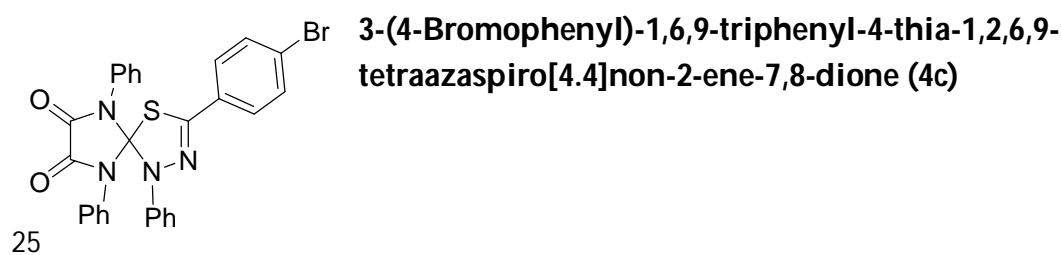
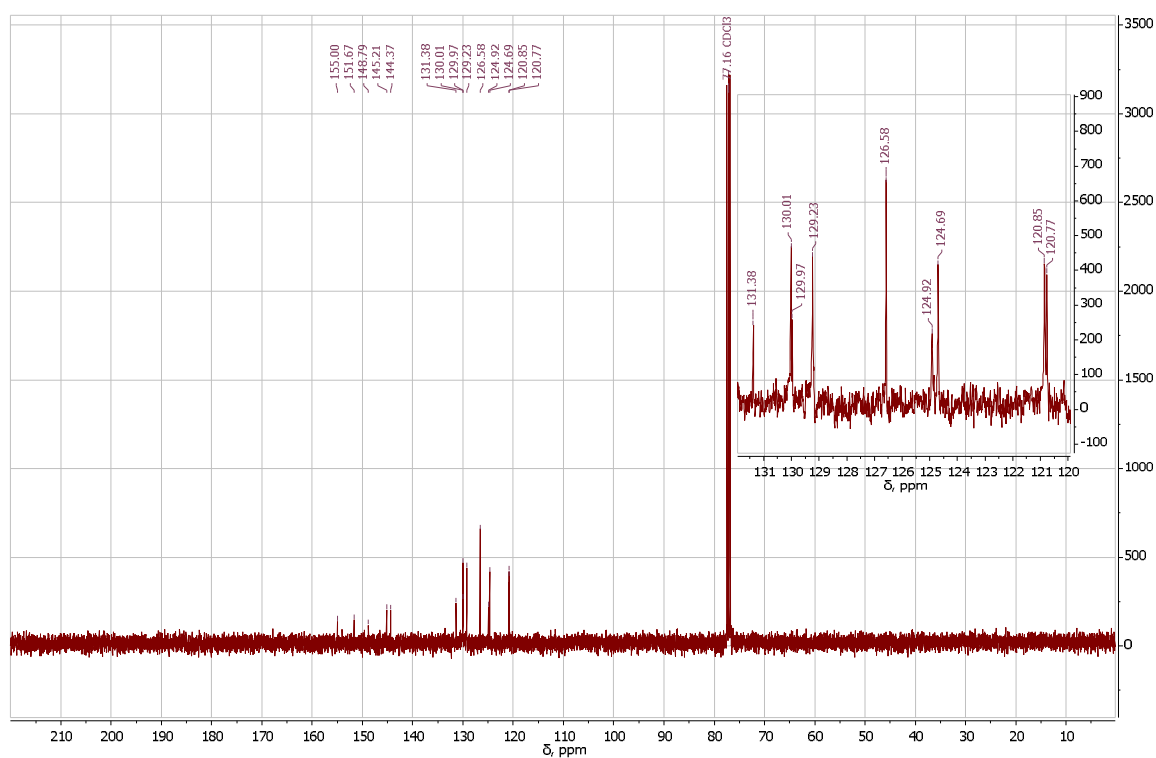
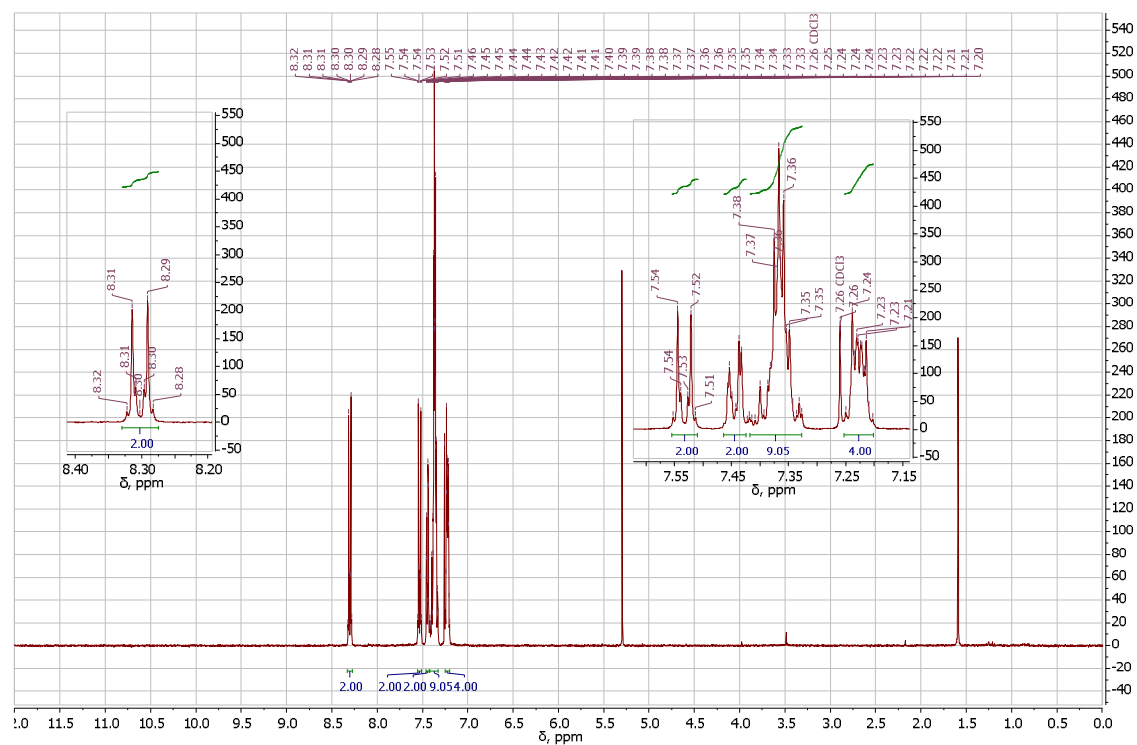
**1-(4-Nitrophenyl)-3,6,9-triphenyl-4-thia-1,2,6,9-tetraazaspiro[4.4]non-2-ene-7,8-dione (4b)**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.33 – 8.27 (m, 2H, Ar), 7.55 – 7.51 (m, 2H, Ar), 7.46 – 7.42 (m, 2H, Ar), 7.42 – 7.33 (m, 9H, Ar), 7.25 – 7.20 (m, 4H, Ar).



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  155.0, 151.7, 148.8, 145.2, 144.4, 131.4, 130.0, 130.0, 129.2, 126.6, 124.9, 124.7, 120.8, 120.8.

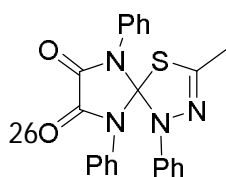
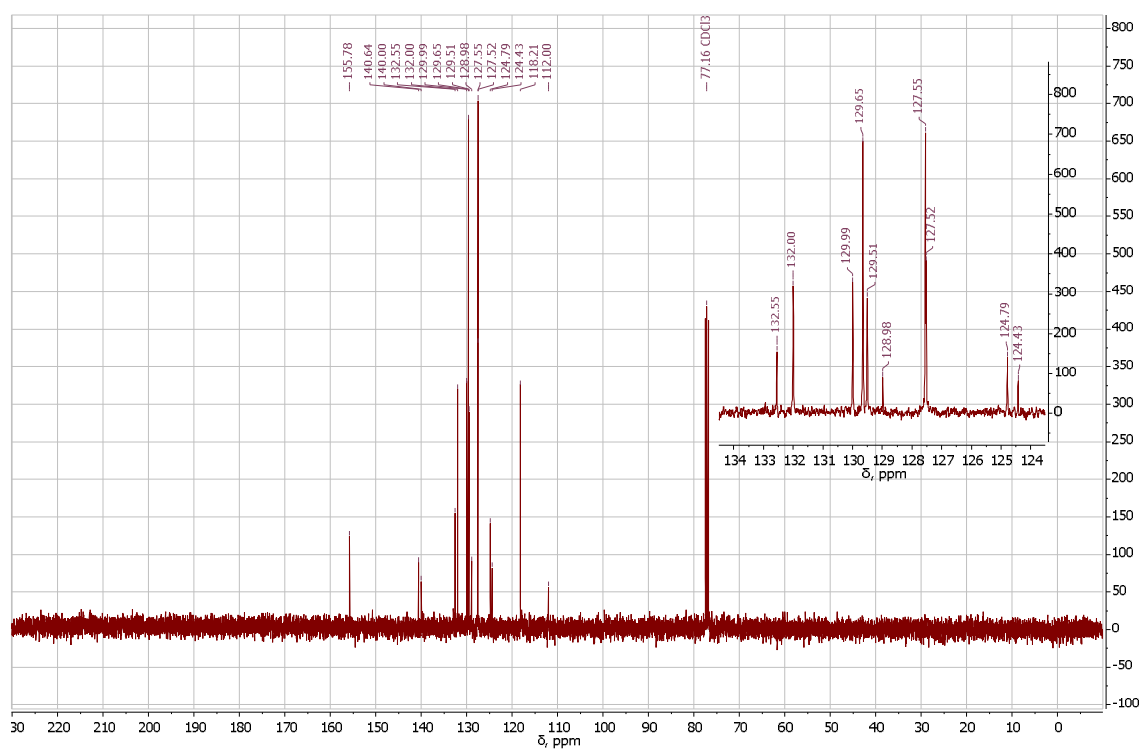
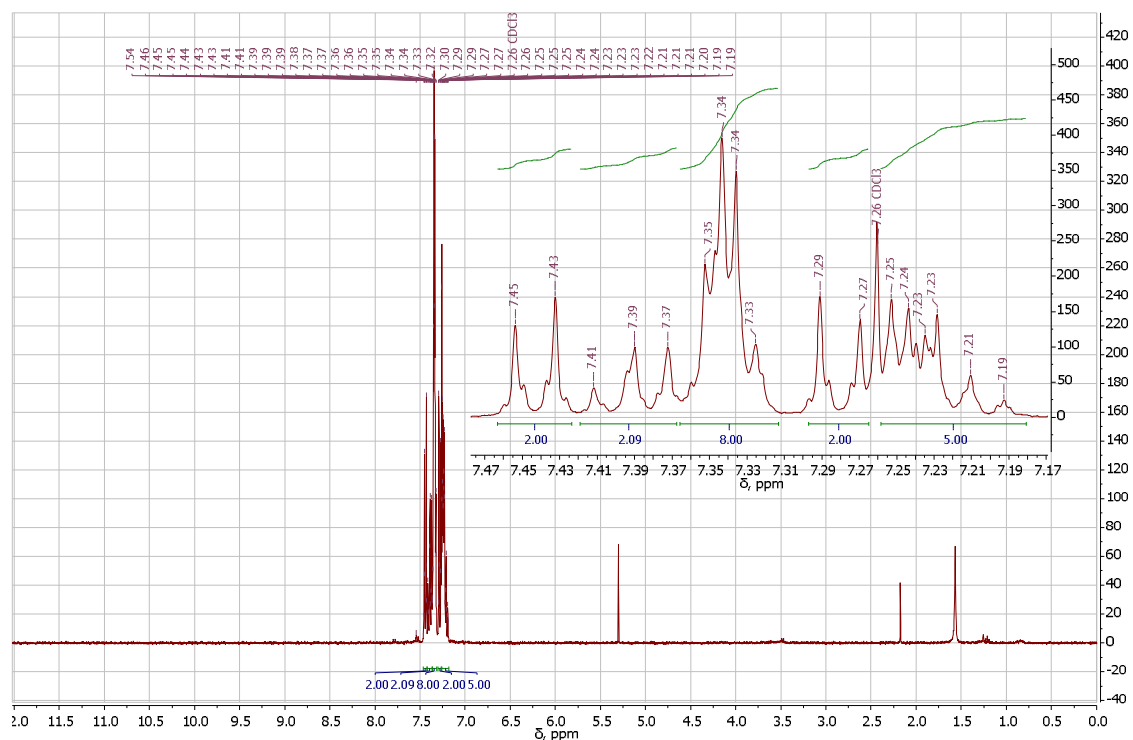
HRMS (ESI): calcd for  $\text{C}_{28}\text{H}_{19}\text{N}_5\text{O}_4\text{S}$  ( $\text{M}+\text{H}$ ) $^+$  522.1231, found 522.1226.



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 – 7.42 (m, 2H, Ar), 7.42 – 7.37 (m, 2H, Ar), 7.36 – 7.31 (m, 8H, Ar), 7.30 – 7.27 (m, 2H, Ar), 7.26 – 7.19 (m, 5H, Ar).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  155.78, 140.64, 140.00, 132.55, 132.00, 129.99, 129.65, 129.51, 128.98, 127.55, 127.52, 124.79, 124.43, 118.21, 112.00.

HRMS (ESI): calcd for  $\text{C}_{28}\text{H}_{19}\text{BrN}_4\text{O}_2\text{S}$  ( $\text{M}+\text{H}$ ) $^+$  555.0485, found 555.0487.

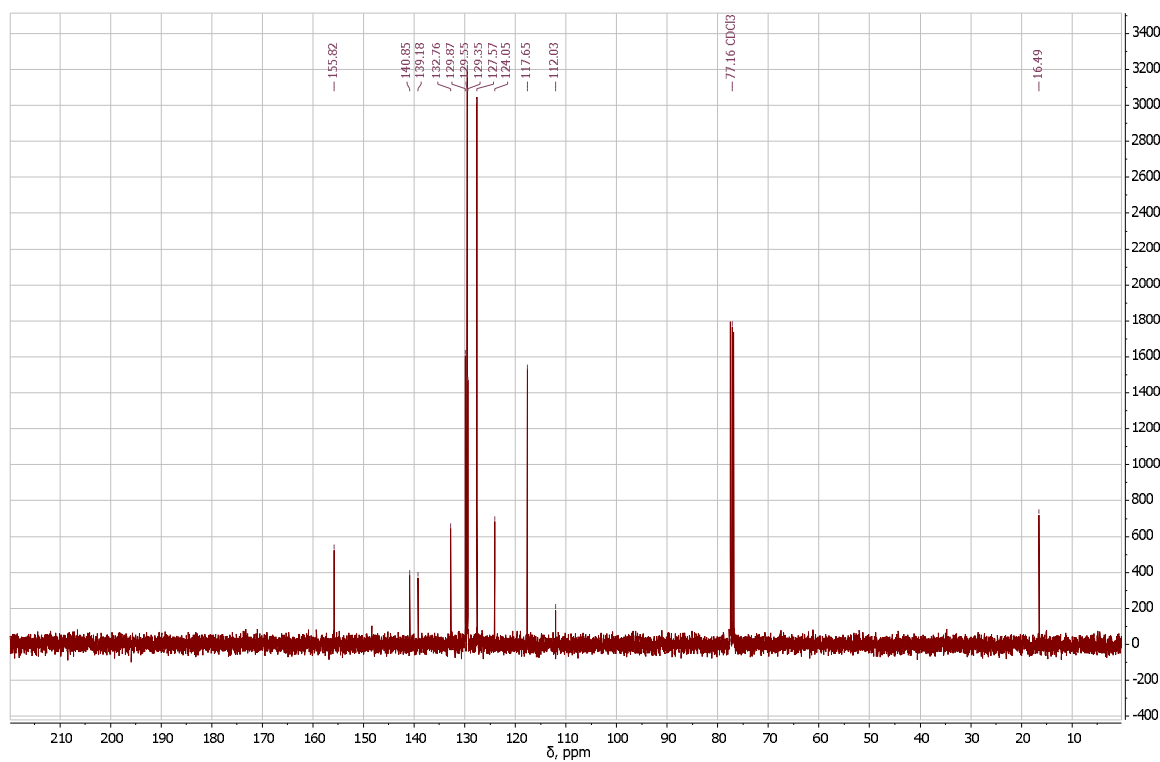
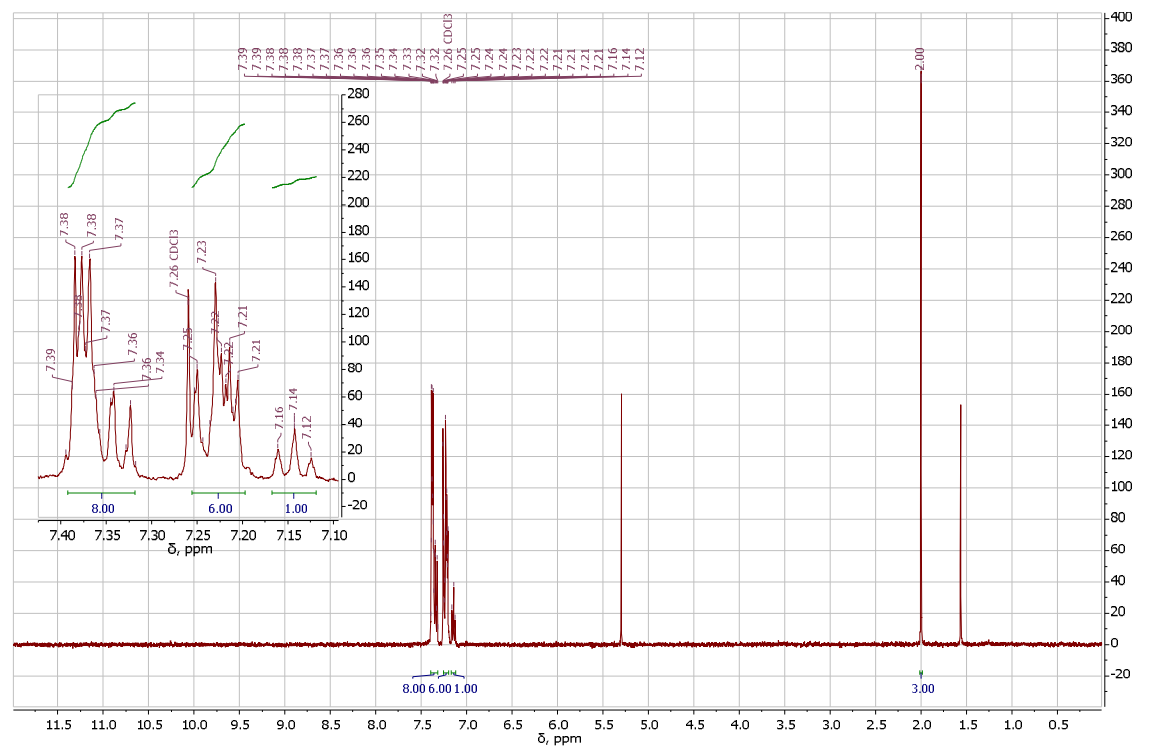


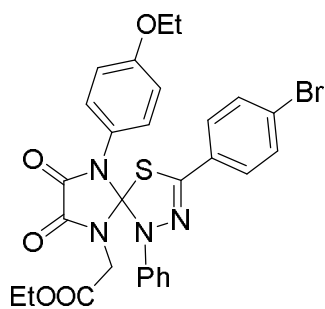
**3-Methyl-1,6,9-triphenyl-4-thia-1,2,6,9-tetraazaspiro[4.4]non-2-ene-7,8-dione (4d)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 – 7.32 (m, 8H, Ar), 7.26 – 7.20 (m, 6H, Ar), 7.14 (t,  $J = 7.3$  Hz, 1H, Ar), 2.00 (s, 3H,  $\text{CH}_3$ ).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  155.8, 140.9, 139.2, 132.8, 129.9, 129.6, 129.4, 127.6, 124.1, 117.7, 112.0, 16.5.

HRMS (ESI): calcd for  $\text{C}_{23}\text{H}_{18}\text{N}_4\text{O}_2\text{S}$  ( $2\text{M}+\text{Na}$ ) $^+$  851.2193, found 851.2186.



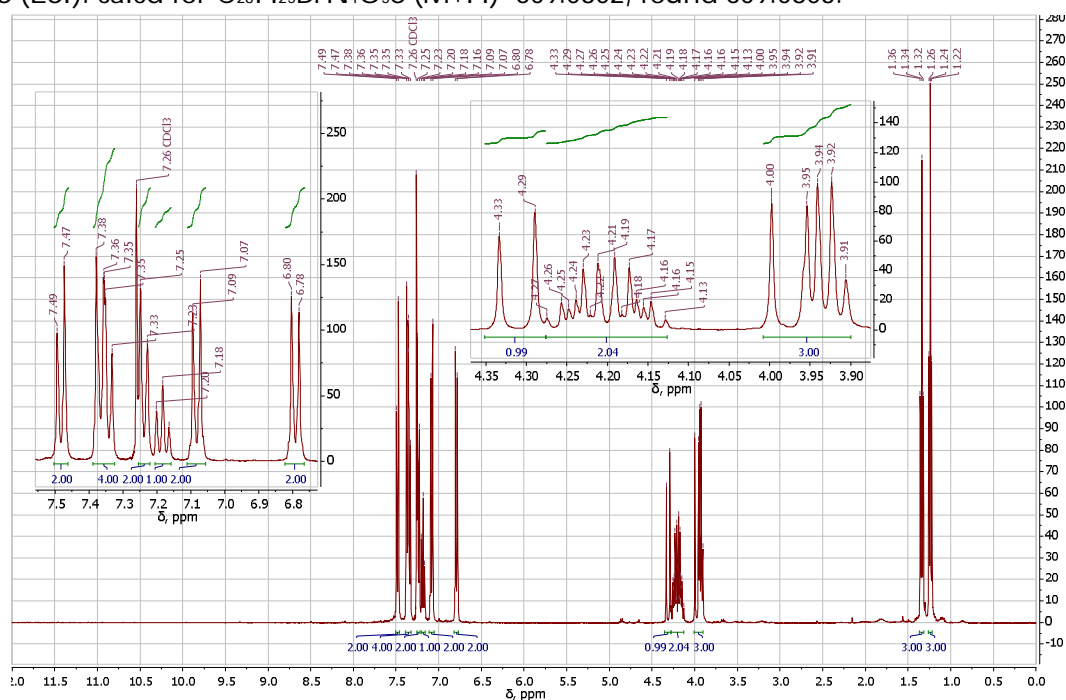


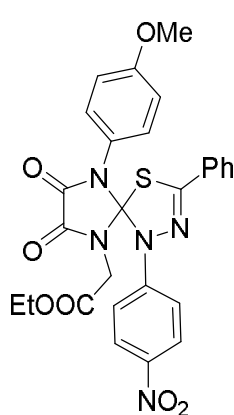
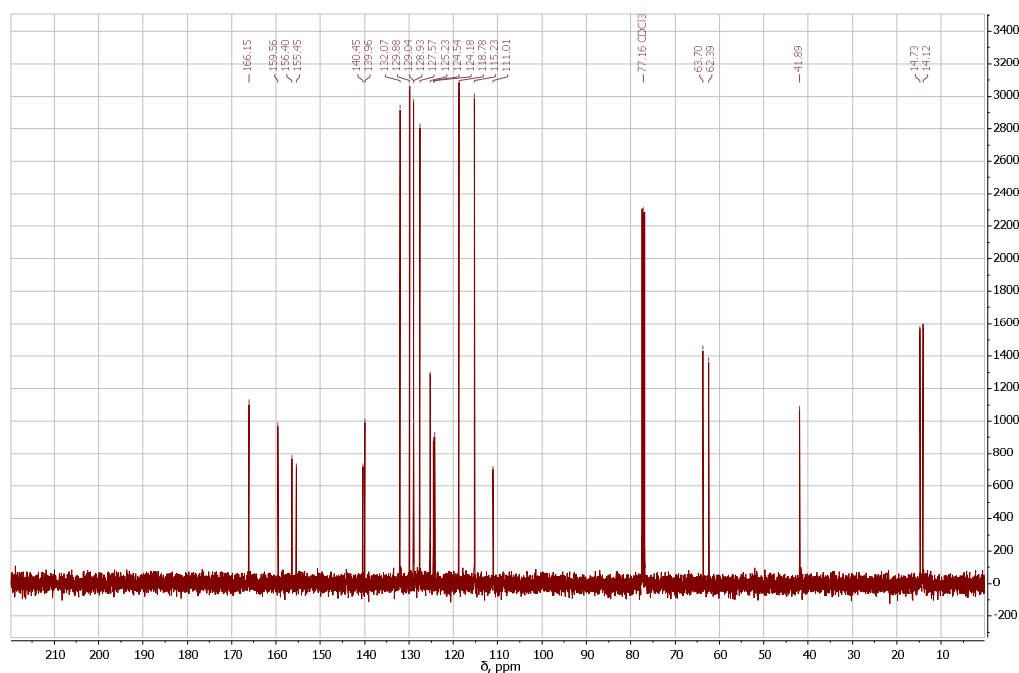
**Ethyl 2-(3-(4-bromophenyl)-9-(4-ethoxyphenyl)-7,8-dioxo-1-phenyl-4-thia-1,2,6,9-tetraazaspiro[4.4]non-2-en-6-yl)acetate (4e)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 (d,  $J = 8.5$  Hz, 2H, Ar), 7.39 – 7.32 (m, 4H, Ar), 7.24 (d,  $J = 8.4$  Hz, 2H, Ar), 7.18 (t,  $J = 7.3$  Hz, 1H, Ar), 7.08 (d,  $J = 9.0$  Hz, 2H, Ar), 6.79 (d,  $J = 9.0$  Hz, 2H, Ar), 4.31 (d,  $J = 17.6$  Hz, 1H,  $\text{NCH}_2$ ), 4.28 – 4.13 (m, 2H,  $\text{COOCH}_2\text{CH}_3$ ), 4.01 – 3.90 (m, 3H,  $\text{NCH}_2 + \text{OCH}_2\text{CH}_3$ ), 1.34 (t,  $J = 7.0$  Hz, 3H,  $\text{OCH}_2\text{CH}_3$ ), 1.24 (t,  $J = 7.1$  Hz, 3H,  $\text{COOCH}_2\text{CH}_3$ ).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.1, 159.6, 156.4, 155.4, 140.4, 140.0, 132.1, 129.9, 129.0, 128.9, 127.6, 125.2, 124.5, 124.2, 118.8, 115.2, 111.0, 63.7, 62.4, 41.9, 14.7, 14.1.

HRMS (ESI): calcd for  $\text{C}_{28}\text{H}_{25}\text{BrN}_4\text{O}_5\text{S}$  ( $\text{M} + \text{H}$ ) $^+$  609.0802, found 609.0803.



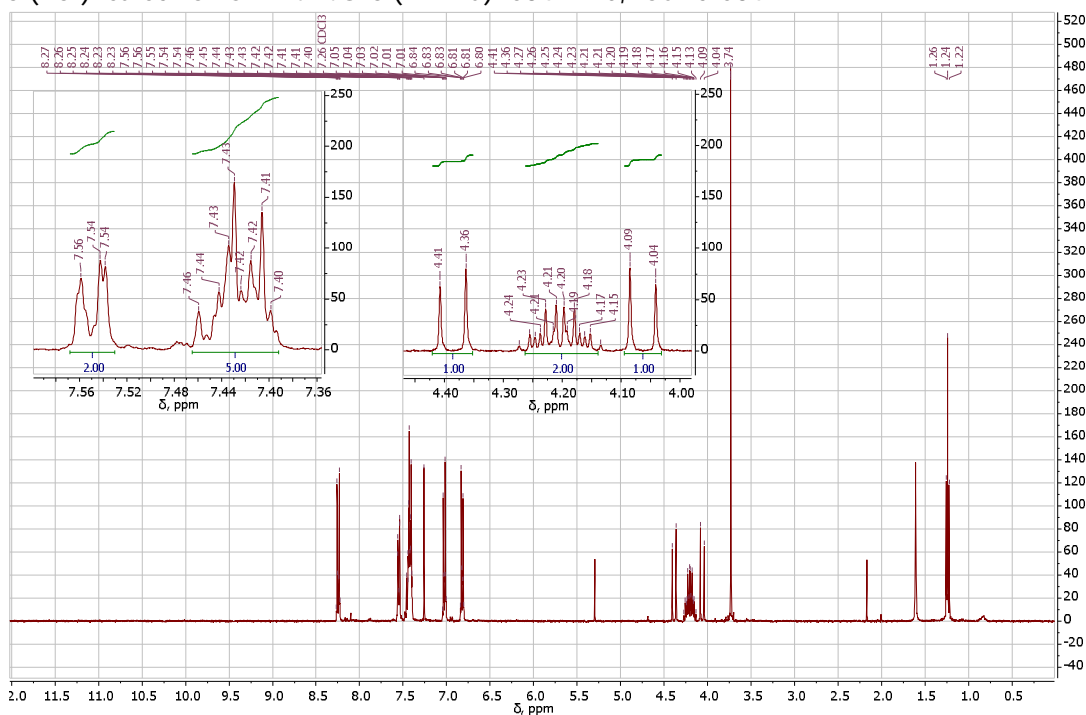


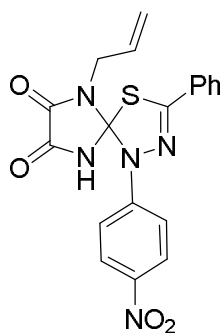
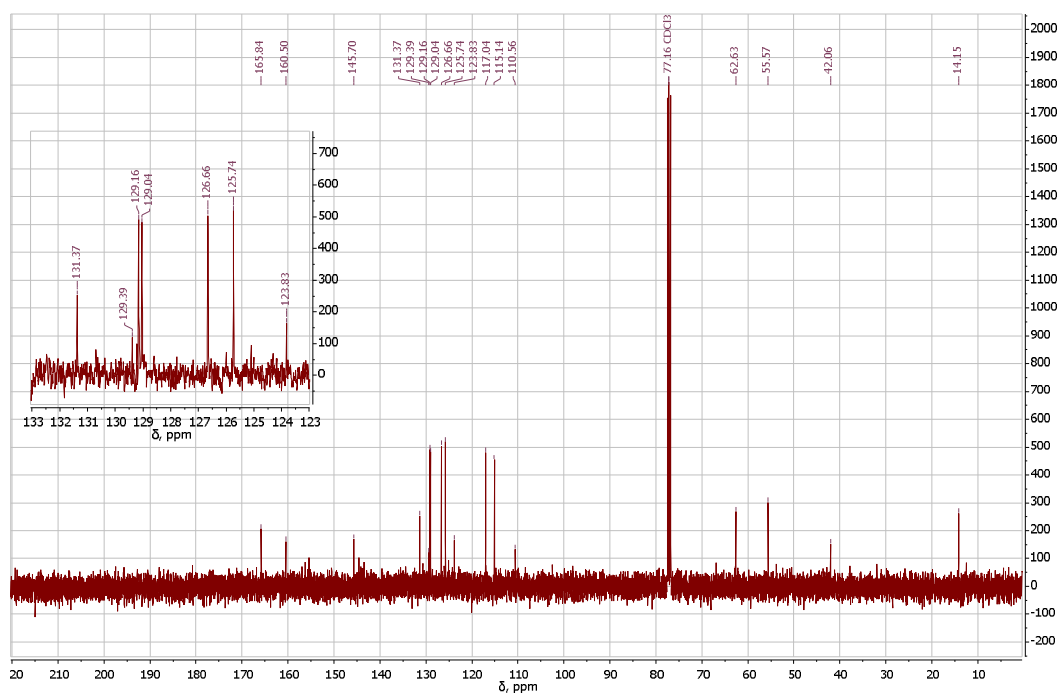
**Ethyl 2-(9-(4-methoxyphenyl)-1-(4-nitrophenyl)-7,8-dioxo-3-phenyl-4-thia-1,2,6,9-tetraazaspiro[4.4]non-2-en-6-yl)acetate (4f)**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.25 (d, *J* = 9.3 Hz, 2H, Ar), 7.58 – 7.52 (m, 2H, Ar), 7.47 – 7.39 (m, 5H, Ar), 7.03 (d, *J* = 9.0 Hz, 2H, Ar), 6.82 (d, *J* = 9.0 Hz, 2H, Ar), 4.39 (d, *J* = 17.5 Hz, 1H, NCH<sub>2</sub>), 4.20 (qq, *J* = 10.8, 7.1 Hz, 2H, COOCH<sub>2</sub>CH<sub>3</sub>), 4.06 (d, *J* = 17.5 Hz, 1H, NCH<sub>2</sub>), 3.74 (s, 3H, OCH<sub>3</sub>), 1.24 (t, *J* = 7.1 Hz, 3H, COOCH<sub>2</sub>CH<sub>3</sub>).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.8, 160.5, 145.7, 131.4, 129.4, 129.2, 129.0, 126.7, 125.7, 123.8, 117.0, 115.1, 110.6, 62.6, 55.6, 42.1, 14.2.

HRMS (ESI): calcd for C<sub>27</sub>H<sub>23</sub>N<sub>5</sub>O<sub>7</sub>S (M+Na)<sup>+</sup> 584.1210, found 584.1217.



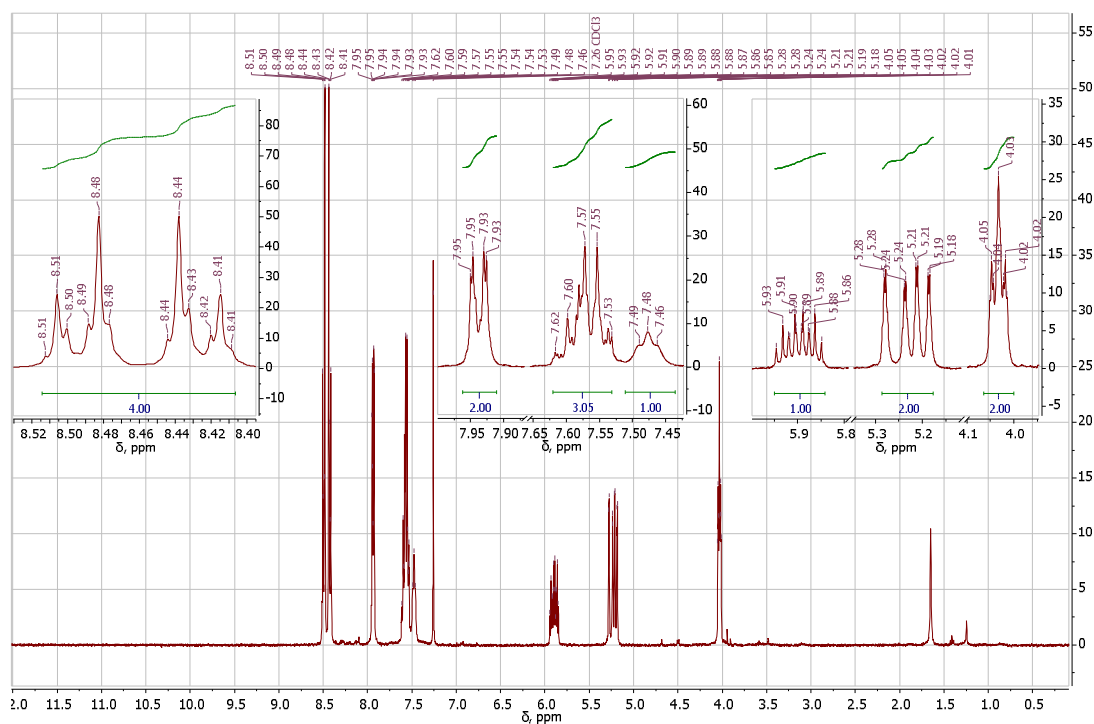


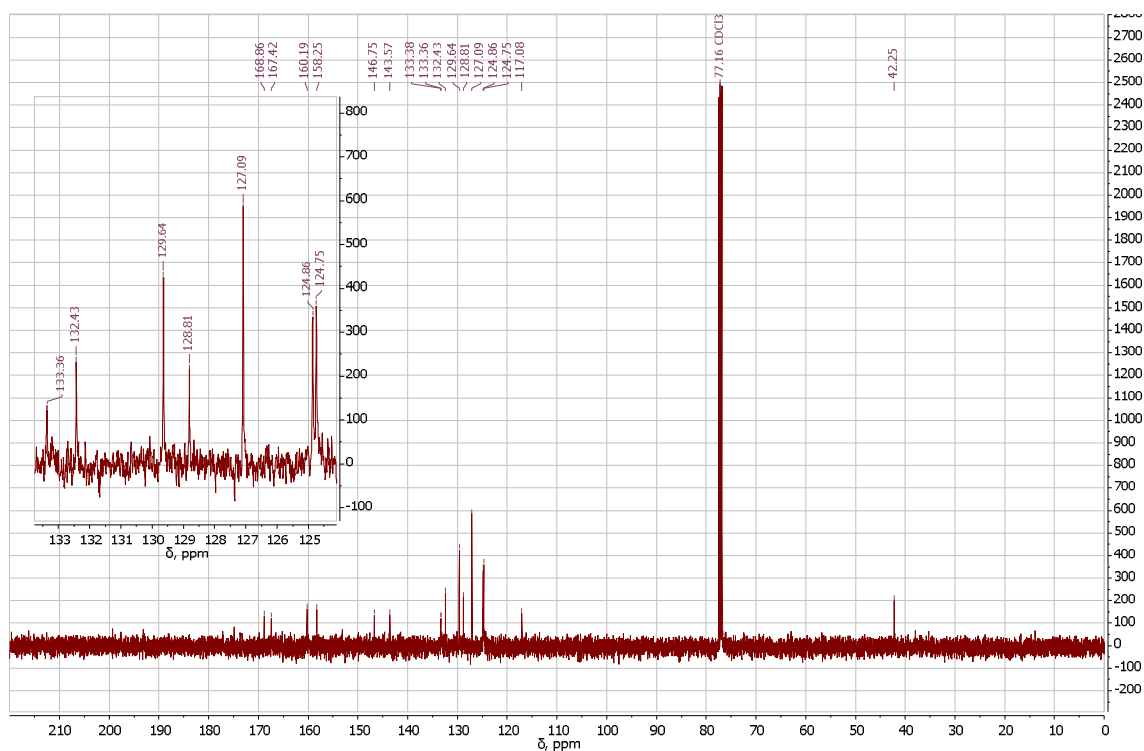
**6-Allyl-1-(4-nitrophenyl)-3-phenyl-4-thia-1,2,6,9-tetraazaspiro[4.4]non-2-ene-7,8-dione (4g)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.53 – 8.39 (m, 4H, Ar), 7.96 – 7.91 (m, 2H, Ar), 7.62 – 7.53 (m, 3H, Ar), 7.51 – 7.44 (m, 1H, NH), 5.90 (ddt,  $J$  = 17.2, 10.2, 5.6 Hz, 1H, CH), 5.29 – 5.18 (m, 2H,  $=\text{CH}_2$ ), 4.06 – 4.00 (m, 2H,  $\text{NCH}_2$ ).

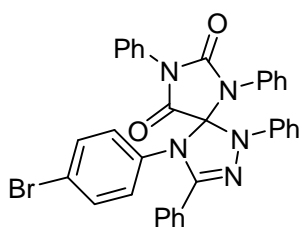
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  168.9, 167.4, 160.2, 158.2, 146.7, 143.6, 133.4, 133.4, 132.4, 129.6, 128.8, 127.1, 124.9, 124.7, 117.1, 42.2.

HRMS (ESI): calcd for  $\text{C}_{19}\text{H}_{15}\text{N}_5\text{O}_4\text{S}$  ( $2\text{M}+\text{Na}$ ) $^+$  841.1582, found 841.1582.





**$^1\text{H}$ ,  $^{13}\text{C}$  NMR and HRMS spectral data of 1,2,4,6,8-pentaazaspiro[4.4]non-2-ene-7,9-diones 5a-n**

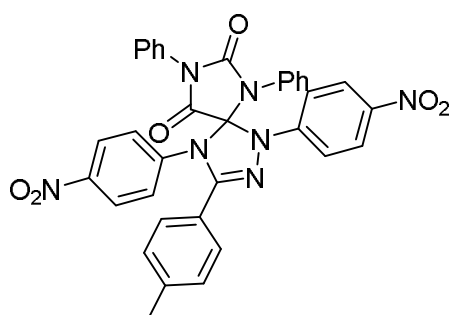
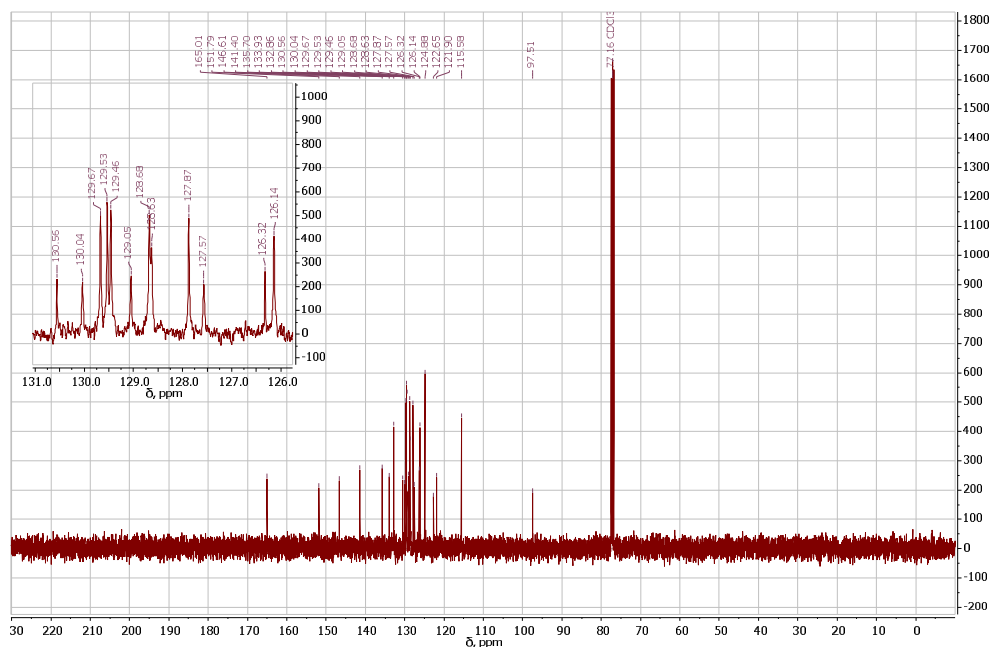
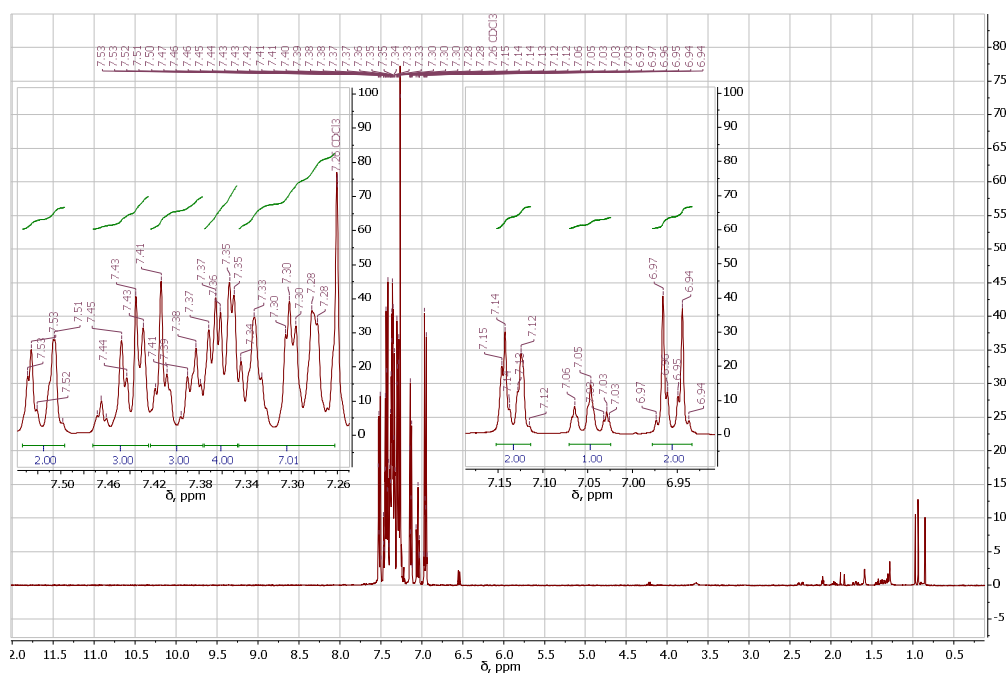


**4-(4-Bromophenyl)-1,3,6,8-tetraphenyl-1,2,4,6,8-pentaazaspiro[4.4]non-2-ene-7,9-dione (5a)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53 – 7.50 (m, 2H, Ar), 7.47 – 7.42 (m, 3H, Ar), 7.42 – 7.38 (m, 3H, Ar), 7.38 – 7.35 (m, 4H, Ar), 7.35 – 7.26 (m, 7H, Ar), 7.15 – 7.11 (m, 2H, Ar), 7.07 – 7.02 (m, 1H, Ar), 6.98 – 6.93 (m, 2H, Ar).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.0, 151.8, 146.6, 141.4, 135.7, 133.9, 132.9, 130.6, 130.0, 129.7, 129.5, 129.5, 129.0, 128.7, 128.6, 127.9, 127.6, 126.3, 126.1, 124.9, 122.7, 121.9, 115.6, 97.5.

HRMS (ESI): calcd for  $\text{C}_{34}\text{H}_{24}\text{BrN}_5\text{O}_2$  ( $\text{M}+\text{H}$ ) $^+$  614.1186, found 614.1193.



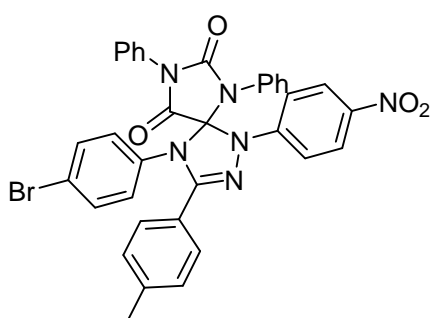
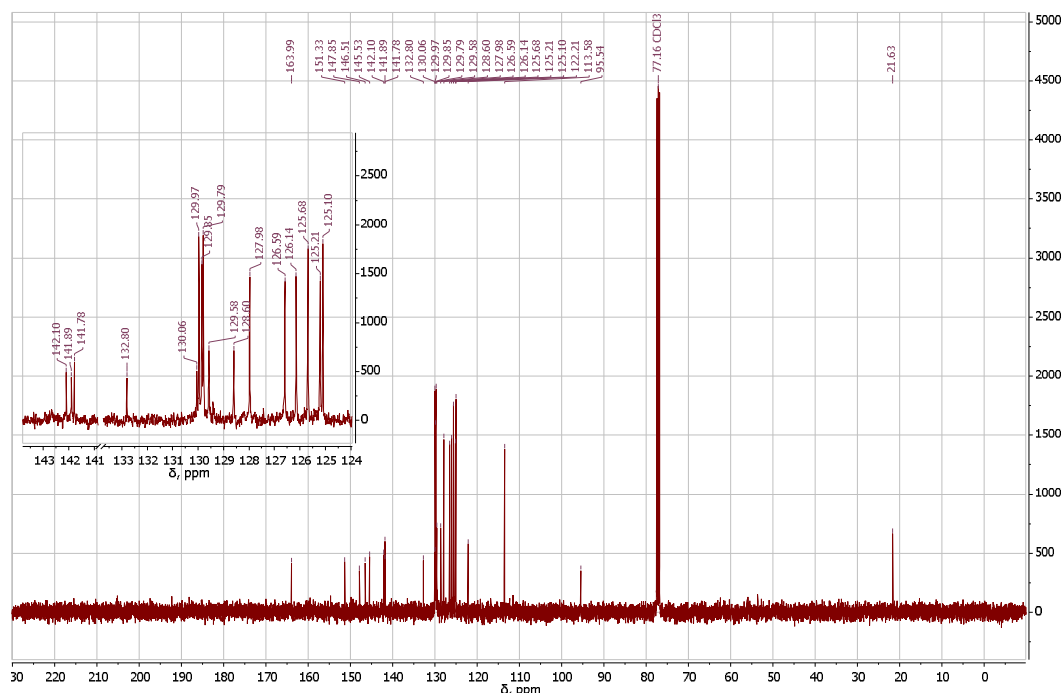
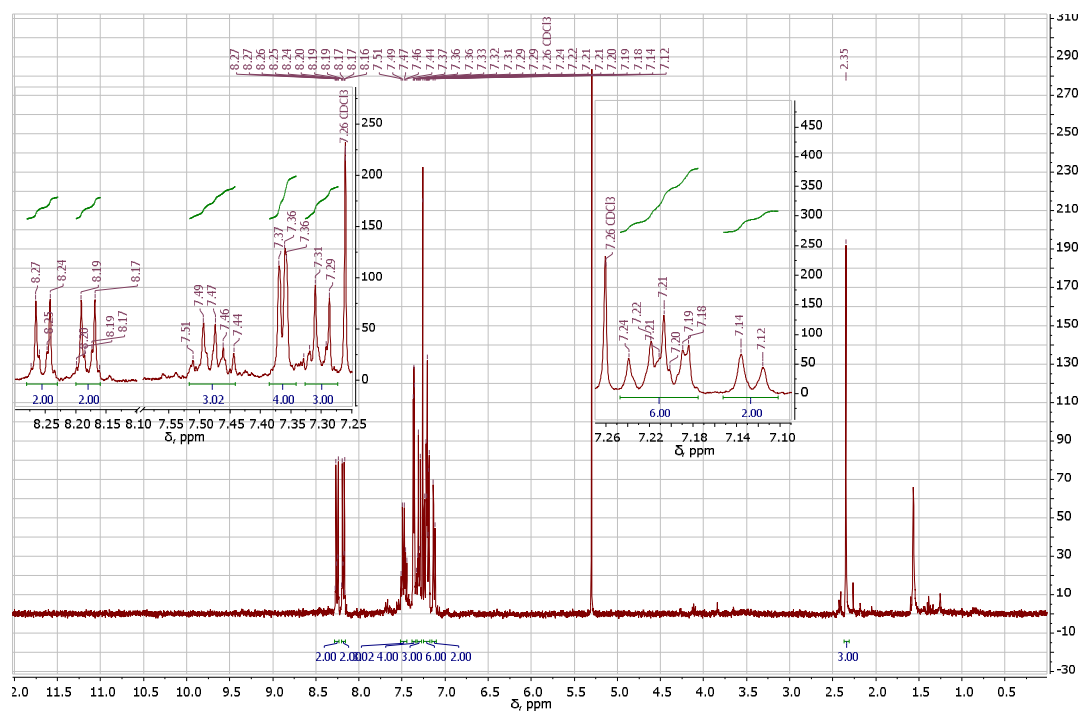
**1,4-Bis(4-nitrophenyl)-6,8-diphenyl-3-(p-tolyl)-  
1,2,4,6,8-pentaazaspiro[4.4]non-2-ene-7,9-dione (5b)**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.28 – 8.23 (m, 2H, Ar), 8.20 – 8.16 (m, 2H, Ar), 7.52 – 7.44 (m, 3H, Ar), 7.39 – 7.34 (m, 4H, Ar), 7.33 – 7.27 (m, 3H, Ar), 7.25 – 7.18 (m, 6H, Ar), 7.13 (d, *J* = 8.1 Hz, 2H, Ar), 2.35 (s, 3H, CH<sub>3</sub>).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 164.0, 151.3, 147.8, 146.5, 145.5, 142.1, 141.9, 141.8, 132.8, 130.1, 130.0, 129.9, 129.8, 129.6, 128.6, 128.0, 126.6, 126.1, 125.7, 125.2, 125.1, 122.2, 113.6, 95.5, 21.6.

HRMS (ESI): calcd for C<sub>35</sub>H<sub>25</sub>N<sub>7</sub>O<sub>6</sub> (M+Na)<sup>+</sup> 662.1759, found 662.1765.





**4-(4-Bromophenyl)-1-(4-nitrophenyl)-6,8-diphenyl-3-(p-tolyl)-1,2,4,6,8-pentaazaspiro[4.4]non-2-ene-7,9-dione (5c)**

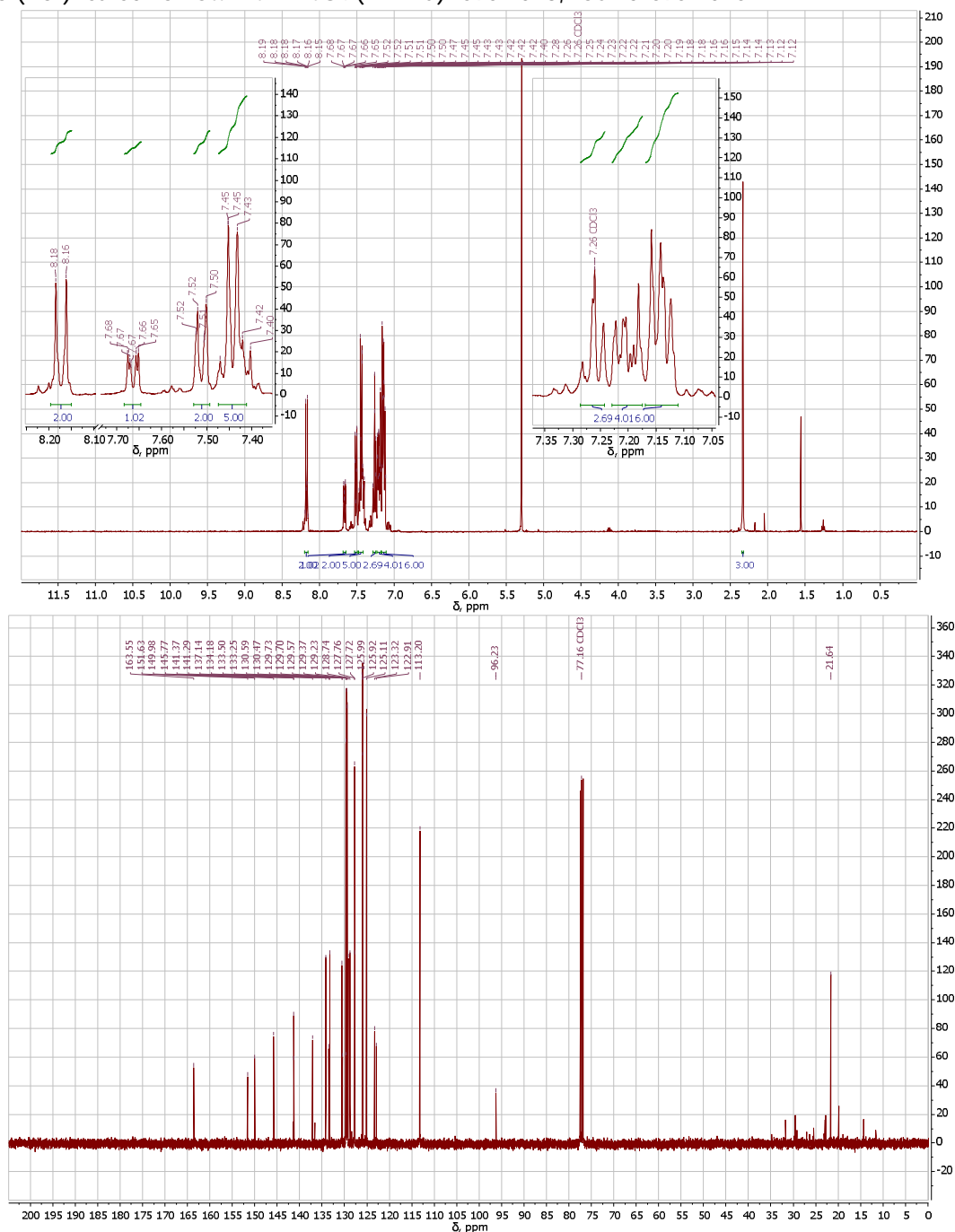
$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  8.34 (d,  $J$  = 9.4 Hz, 2H, Ar), 7.69 (d,  $J$  = 8.7 Hz, 2H, Ar), 7.55 – 7.50 (m, 3H, Ar), 7.49 – 7.43 (m, 4H, Ar), 7.39 – 7.35 (m, 3H, Ar), 7.33 (d,  $J$  = 8.2 Hz, 2H, Ar), 7.23 – 7.17 (m, 4H, Ar), 7.15 (d,  $J$  = 8.6 Hz, 2H, Ar), 2.29 (s, 3H, CH $_3$ ).

$^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$  163.5, 148.2, 145.2, 140.7, 135.0, 133.1, 132.5, 129.9, 129.9, 129.8, 129.6, 129.5, 128.9, 128.8, 128.6, 127.9, 126.8, 126.5, 126.1, 122.1, 121.5, 113.1, 95.3, 21.0.



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.6, 151.6, 150.0, 145.8, 141.4, 141.3, 137.1, 134.2, 133.5, 133.2, 130.6, 130.5, 129.7, 129.6, 129.4, 129.2, 128.7, 127.8, 127.7, 126.0, 125.9, 125.1, 123.3, 122.9, 113.2, 96.2, 21.6.

HRMS (ESI): calcd for  $\text{C}_{35}\text{H}_{25}\text{BrN}_6\text{O}_4$  ( $\text{M}+\text{Na}$ ) $^+$  695.1013, found 695.1016.

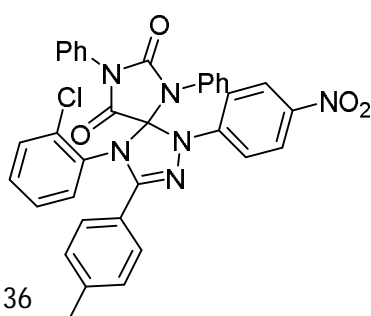
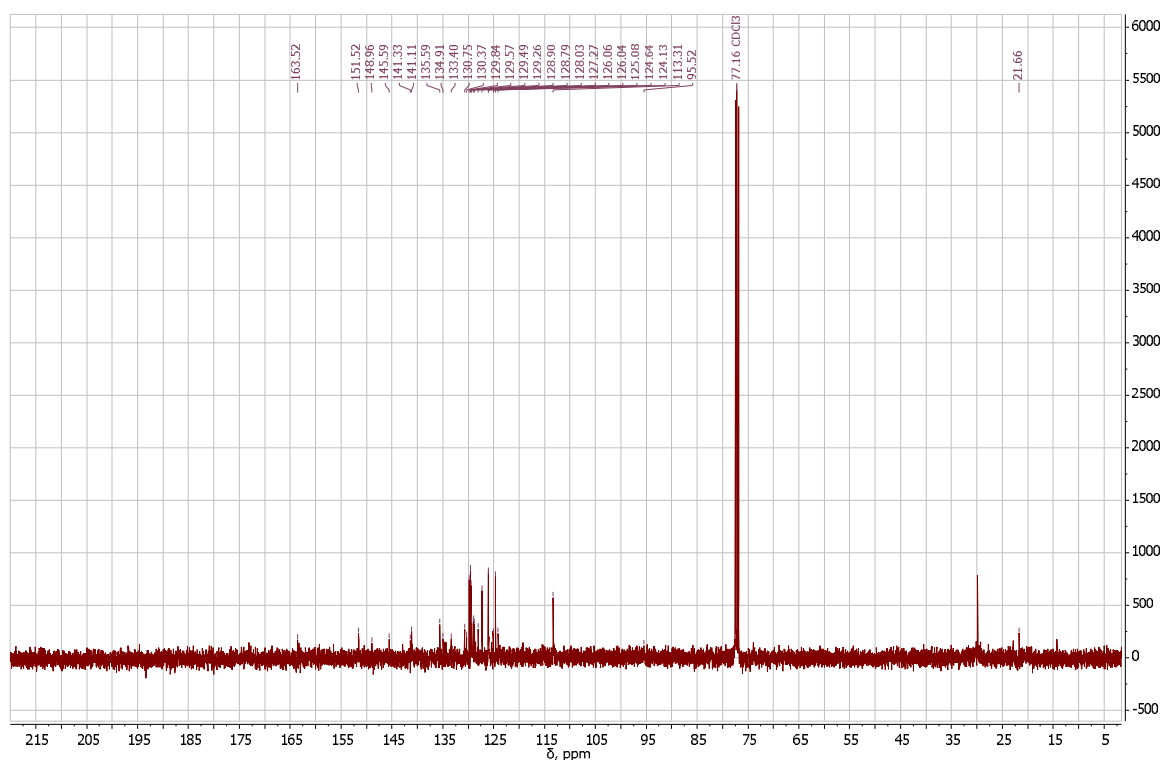
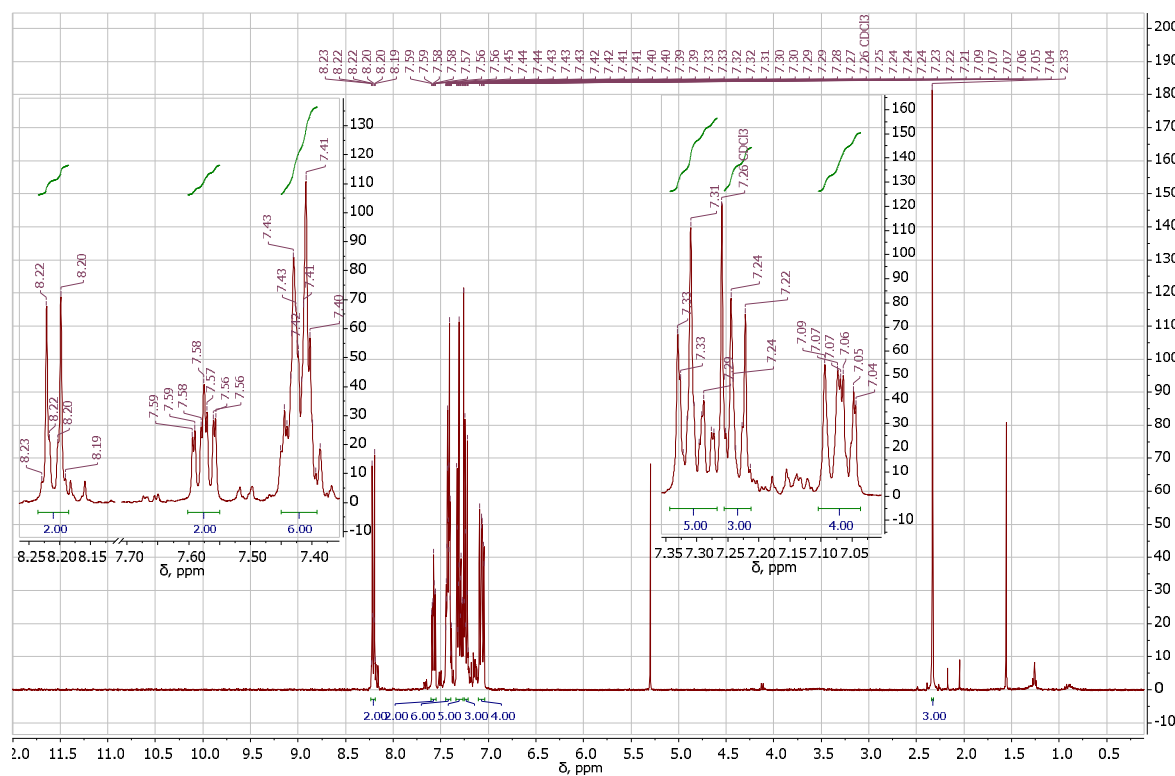


Isomer II:

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.24 – 8.19 (m, 2H, Ar), 7.60 – 7.55 (m, 2H, Ar), 7.45 – 7.39 (m, 6H, Ar), 7.34 – 7.27 (m, 5H, Ar), 7.26 – 7.21 (m, 3H, Ar), 7.10 – 7.04 (m, 4H, Ar), 2.33 (s, 3H,  $\text{CH}_3$ ).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.5, 151.5, 149.0, 145.6, 141.3, 141.1, 135.6, 134.9, 133.4, 130.8, 130.4, 129.8, 129.6, 129.5, 129.3, 128.9, 128.8, 128.0, 127.3, 126.1, 126.0, 125.1, 124.6, 124.1, 113.3, 95.5, 21.7.

HRMS (ESI): calcd for C<sub>35</sub>H<sub>25</sub>BrN<sub>6</sub>O<sub>4</sub> (M+Na)<sup>+</sup> 695.1013, found 695.1022.



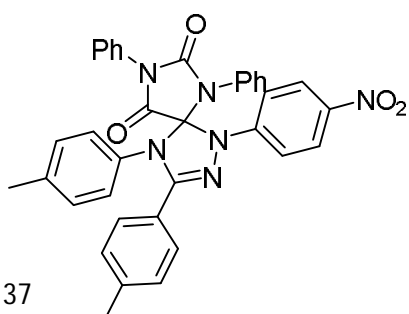
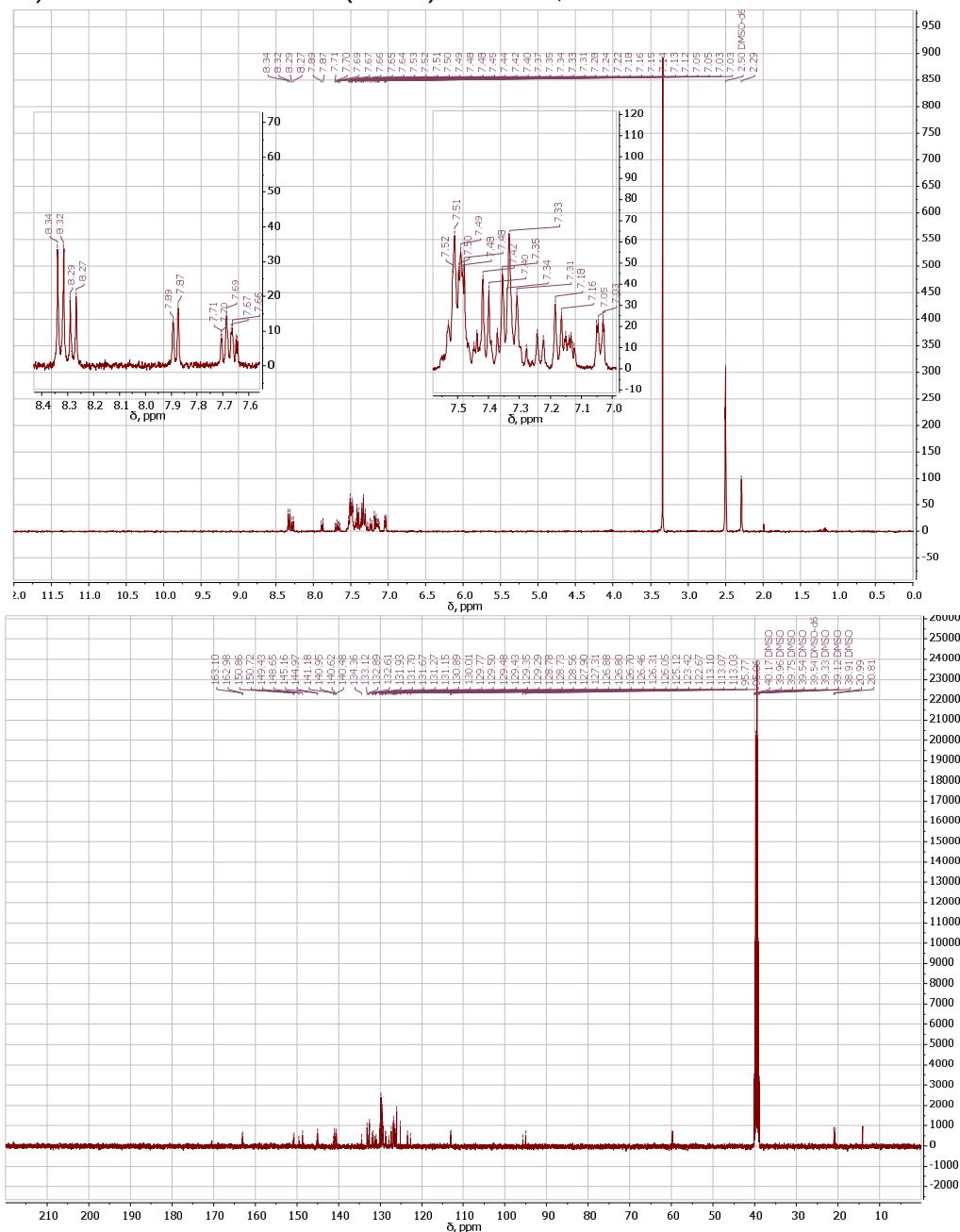
**4-(2-Chlorophenyl)-1-(4-nitrophenyl)-6,8-diphenyl-3-(p-tolyl)-1,2,4,6,8-pentaazaspiro[4.4]non-2-ene-7,9-dione (5e)**

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 8.33 (d, *J* = 9.3 Hz, 2H<sup>II</sup>, Ar), 8.28 (d, *J* = 9.2 Hz, 2H<sup>I</sup>, Ar), 7.88 (d, *J* = 7.8 Hz, 1H<sup>II</sup>, Ar), 7.71 – 7.64 (m, 1H<sup>I</sup>+1H<sup>II</sup>, Ar), 7.56 – 7.45 (m, 5H<sup>I</sup>+7H<sup>II</sup>, Ar), 7.44-7.35 (m, 3H<sup>I</sup>+3H<sup>II</sup>, Ar), 7.35-7.30 (m, 5H<sup>I</sup>+4H<sup>II</sup>, Ar), 7.29-7.26 (m, 1H<sup>I</sup>, Ar), 7.23 (d, *J* =

8.0 Hz, 2H<sup>I</sup>, Ar), 7.19-7.12 (m, 3H<sup>I</sup>+2H<sup>II</sup>, Ar), 7.06 – 7.02 (m, 2H<sup>II</sup>, Ar), 2.29 (s, 3H<sup>I</sup>+3H<sup>II</sup>, CH<sub>3</sub>).

<sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ 163.1, 163.0, 150.9, 150.7, 149.4, 148.7, 145.2, 145.0, 141.2, 141.0, 140.6, 140.5, 134.4, 133.1, 132.9, 132.6, 131.9, 131.7, 131.7, 131.3, 131.1, 130.9, 130.0, 129.8, 129.5, 129.5, 129.4, 129.3, 129.3, 128.8, 128.7, 128.6, 127.9, 127.3, 126.9, 126.8, 126.7, 126.5, 126.3, 126.0, 125.1, 123.4, 122.7, 113.1, 113.1, 113.0, 95.8, 95.1, 40.2, 40.0, 39.7, 39.5, 39.3, 39.1, 38.9, 21.0, 20.8.

HRMS (ESI): calcd for C<sub>35</sub>H<sub>25</sub>ClN<sub>6</sub>O<sub>4</sub> (M+Na)<sup>+</sup> 651.1518, found 651.1527.



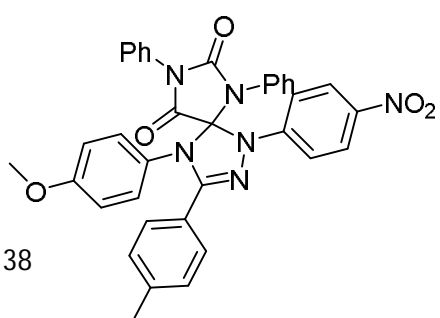
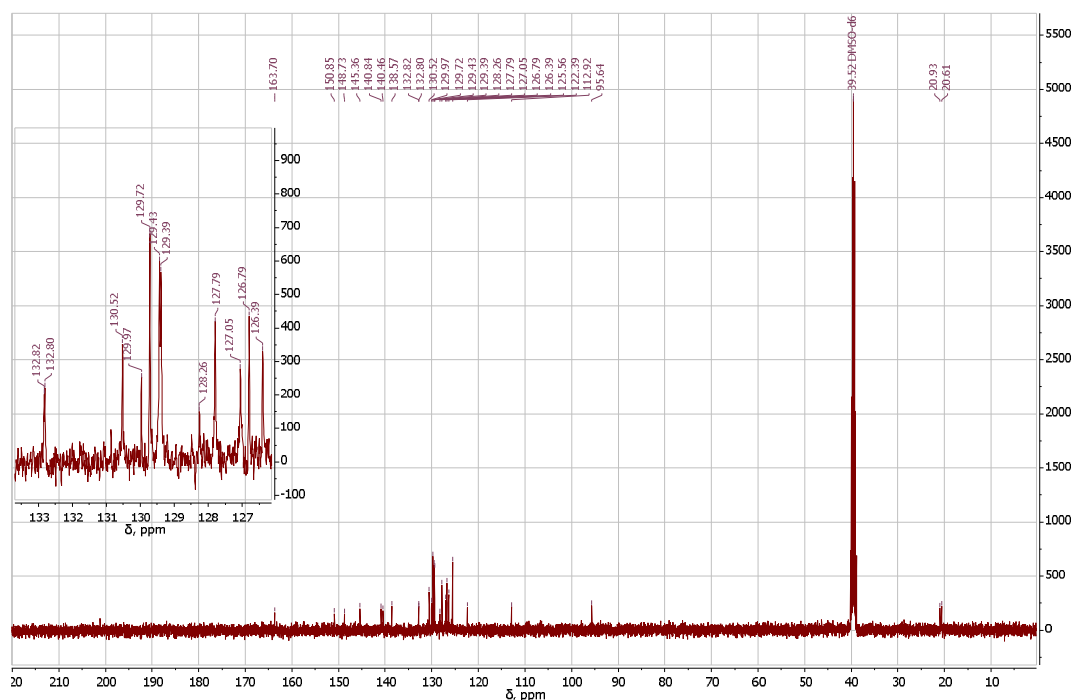
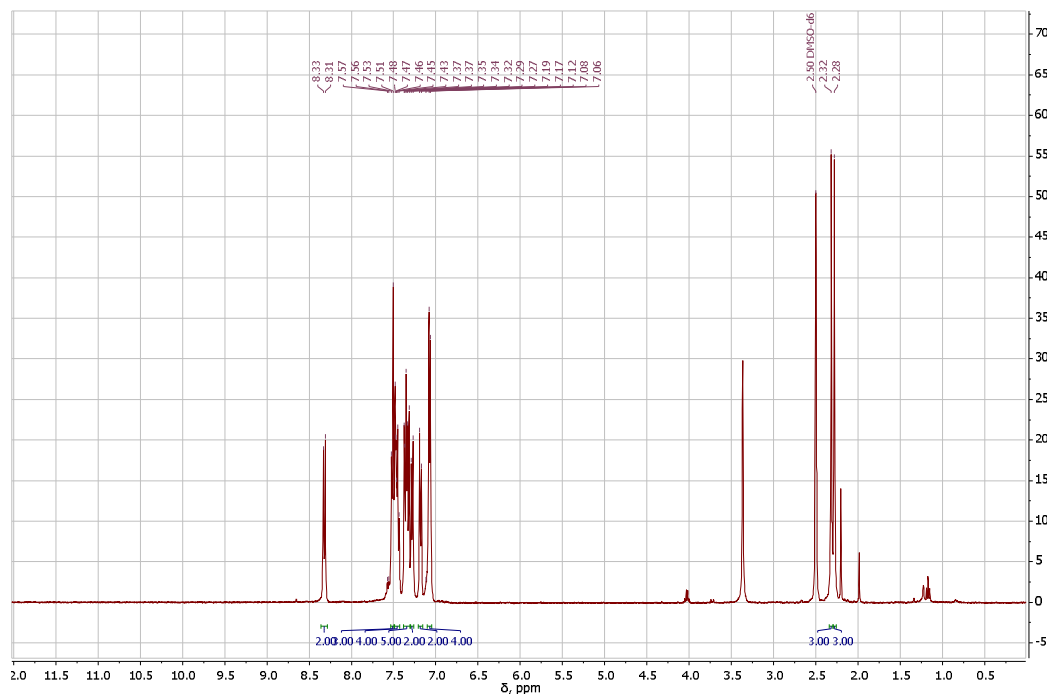
### 1-(4-Nitrophenyl)-6,8-diphenyl-3,4-di-p-tolyl-1,2,4,6,8-pentaazaspiro[4.4]non-2-ene-7,9-dione (5f)

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 8.32 (d, *J* = 9.0 Hz, 2H, Ar), 7.52 (d, *J* = 8.0 Hz, 3H, Ar), 7.46 (dd, *J* = 14.1, 6.4 Hz, 4H, Ar), 7.39 – 7.31 (m, 5H, Ar), 7.28 (d, *J* = 7.9 Hz, 2H, Ar), 7.18 (d, *J* =

7.9 Hz, 2H, Ar), 7.07 (d,  $J$  = 7.6 Hz, 4H, Ar), 2.32 (s, 3H, CH<sub>3</sub>), 2.28 (s, 3H, CH<sub>3</sub>).

<sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>)  $\delta$  163.7, 150.8, 148.7, 145.4, 140.8, 140.5, 138.6, 132.8, 132.8, 130.5, 130.0, 129.7, 129.4, 129.4, 128.3, 127.8, 127.1, 126.8, 126.4, 125.6, 122.4, 112.9, 95.6, 20.9, 20.6.

HRMS (ESI): calcd for C<sub>36</sub>H<sub>28</sub>N<sub>6</sub>O<sub>4</sub> (M+Na)<sup>+</sup> 631.2064, found 631.2072.



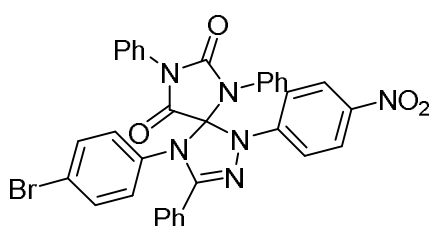
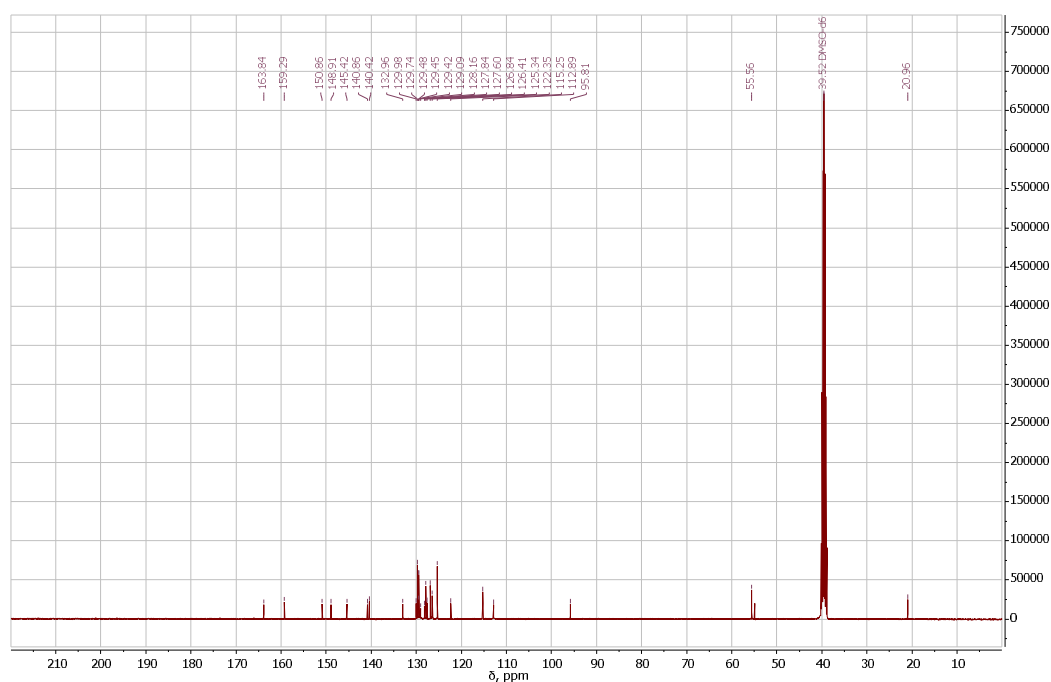
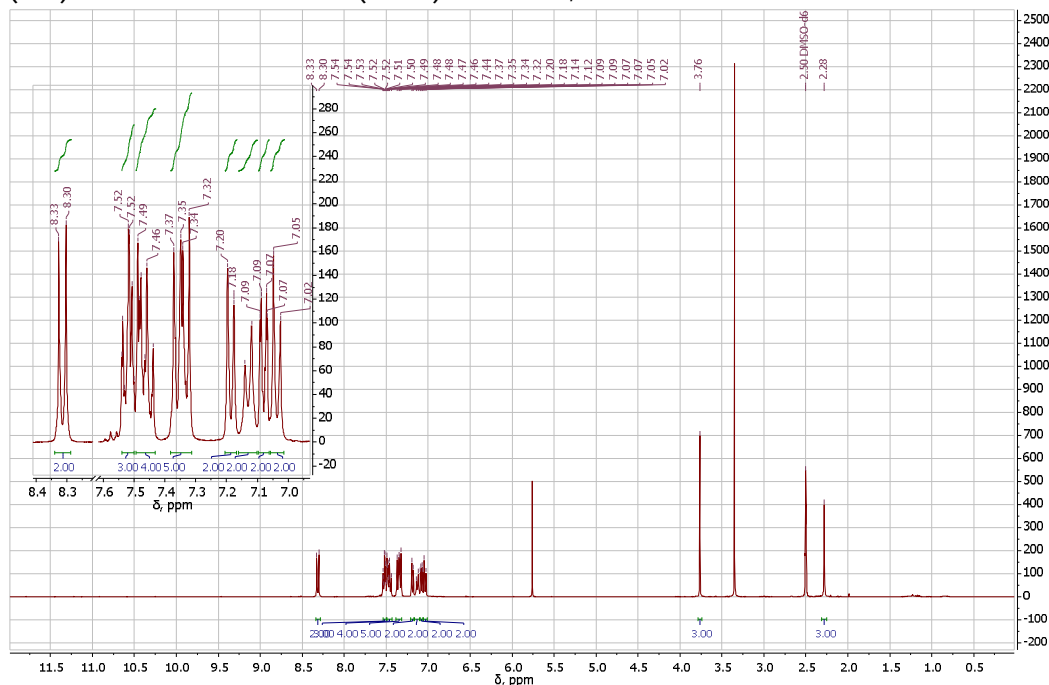
**4-(4-Methoxyphenyl)-1-(4-nitrophenyl)-6,8-diphenyl-3-(p-tolyl)-1,2,4,6,8-pentaazaspiro[4.4]non-2-ene-7,9-dione (5g)**

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  8.31 (d,  $J$  = 9.5 Hz, 2H, Ar), 7.55 – 7.50 (m, 3H, Ar), 7.50 – 7.43 (m, 4H, Ar), 7.39 – 7.31

(m, 5H, Ar), 7.19 (d,  $J = 7.5$  Hz, 2H, Ar), 7.13 (d,  $J = 8.4$  Hz, 2H, Ar), 7.10 – 7.06 (m, 2H, Ar), 7.04 (d,  $J = 9.3$  Hz, 2H, Ar), 3.76 (s, 3H, OCH<sub>3</sub>), 2.28 (s, 3H, CH<sub>3</sub>).

<sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>)  $\delta$  163.8, 159.3, 150.9, 148.9, 145.4, 140.9, 140.4, 133.0, 130.0, 129.7, 129.5, 129.4, 129.4, 129.1, 128.2, 127.8, 127.6, 126.8, 126.4, 125.3, 122.3, 115.2, 112.9, 95.8, 55.6, 21.0.

HRMS (ESI): calcd for C<sub>36</sub>H<sub>28</sub>N<sub>6</sub>O<sub>5</sub> (M+H)<sup>+</sup> 625.2194, found 625.2199.



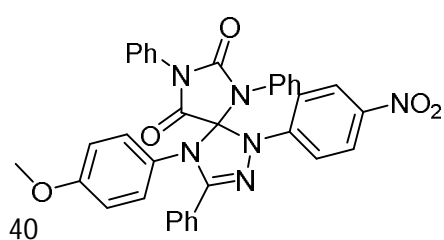
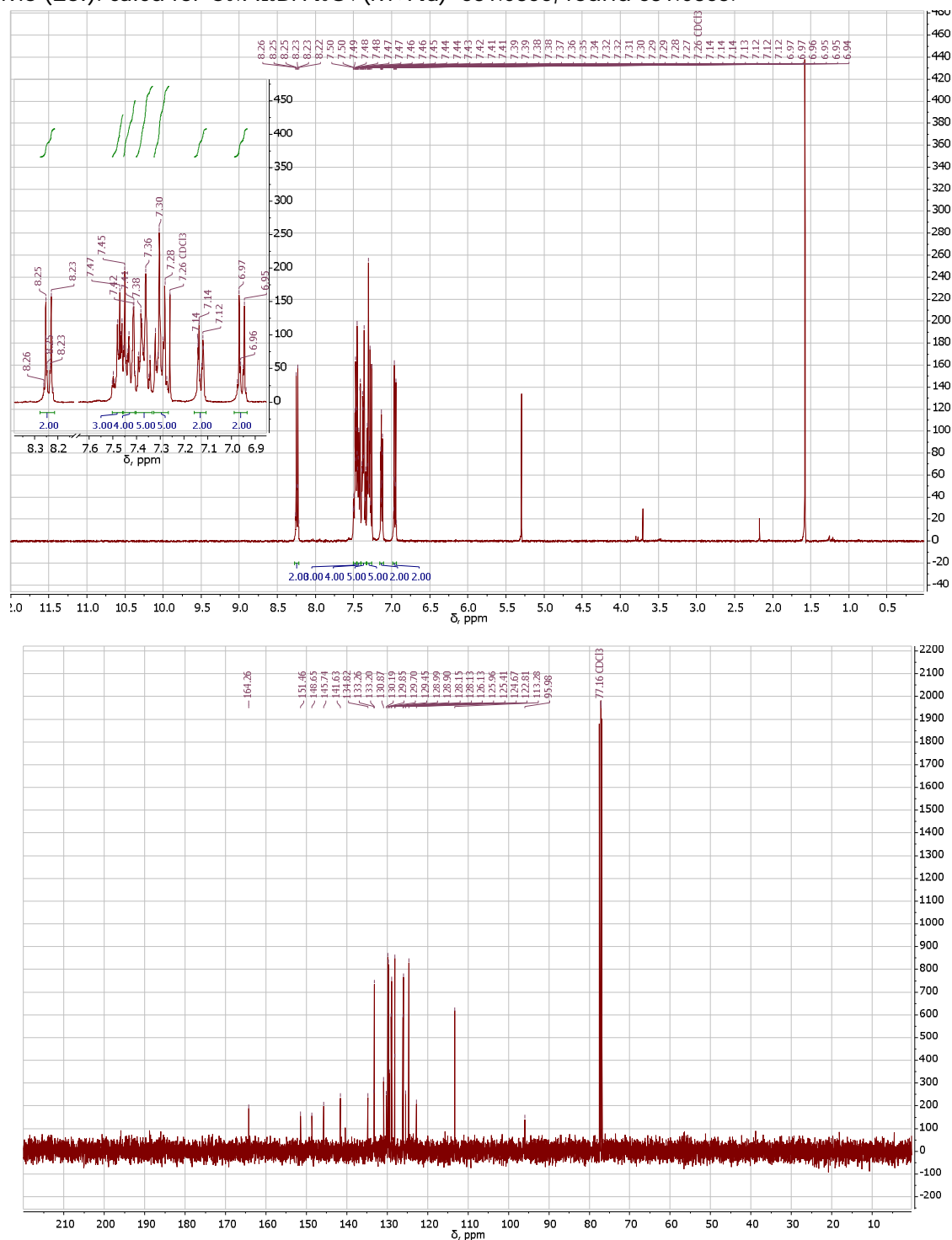
**4-(4-Bromophenyl)-1-(4-nitrophenyl)-3,6,8-triphenyl-1,2,4,6,8-pentaazaspiro[4.4]non-2-ene-7,9-dione (5h)**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.28 – 8.22 (m, 2H, Ar), 7.50 – 7.46 (m, 3H, Ar), 7.46 – 7.41 (m, 4H, Ar), 7.40 – 7.33 (m, 5H, Ar), 7.30 (m, 5H, Ar), 7.16 – 7.11 (m, 2H, Ar), 6.99 – 6.93 (m,

2H, Ar).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.3, 151.5, 148.7, 145.7, 141.6, 134.8, 133.3, 133.2, 130.9, 130.2, 129.9, 129.7, 129.5, 129.0, 128.9, 128.2, 128.1, 126.1, 126.0, 125.4, 124.7, 122.8, 113.3, 96.0.

HRMS (ESI): calcd for  $\text{C}_{34}\text{H}_{23}\text{BrN}_6\text{O}_4$  ( $\text{M}+\text{Na}$ ) $^+$  681.0856, found 681.0853.



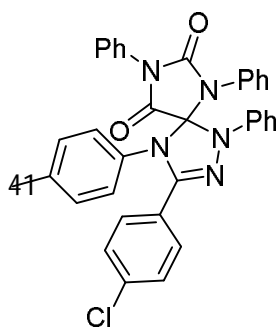
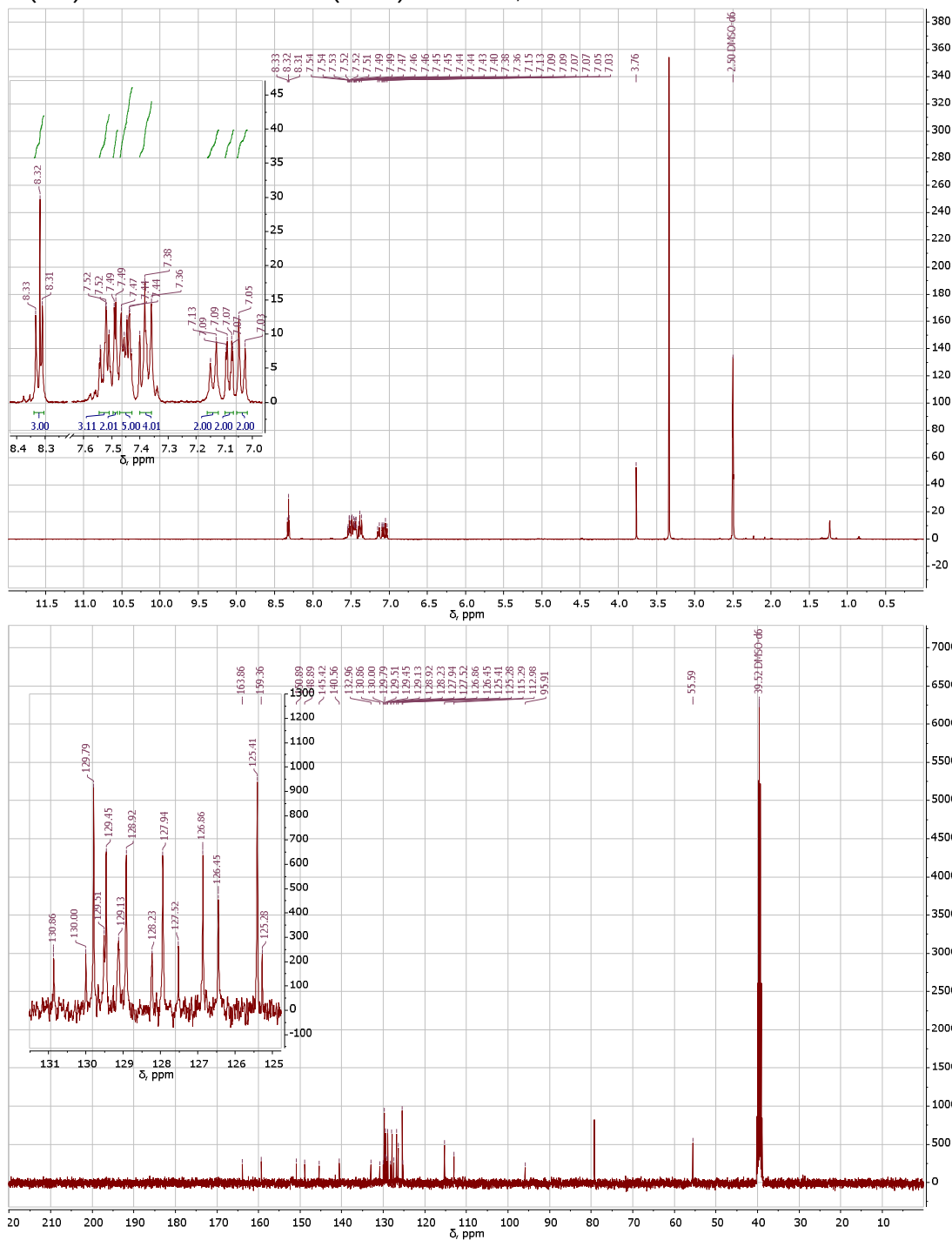
**4-(4-Methoxyphenyl)-1-(4-nitrophenyl)-3,6,8-triphenyl-1,2,4,6,8-pentaazaspiro[4.4]non-2-ene-7,9-dione (5i)**



$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  8.34 – 8.30 (m, 3H, Ar), 7.54 – 7.51 (m, 3H, Ar), 7.50 – 7.48 (m, 2H, Ar), 7.47 – 7.43 (m, 5H, Ar), 7.40 – 7.36 (m, 4H, Ar), 7.14 (d,  $J$  = 8.6 Hz, 2H, Ar), 7.10 – 7.07 (m, 2H, Ar), 7.04 (d,  $J$  = 9.1 Hz, 2H, Ar), 3.76 (s, 3H,  $\text{OCH}_3$ ).

$^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$  163.9, 159.4, 150.9, 148.9, 145.4, 140.6, 133.0, 130.9, 130.0, 129.8, 129.5, 129.5, 129.1, 128.9, 128.2, 127.9, 127.5, 126.9, 126.4, 125.4, 125.3, 115.3, 113.0, 95.9, 55.6.

HRMS (ESI): calcd for  $\text{C}_{35}\text{H}_{26}\text{N}_6\text{O}_5$  ( $\text{M}+\text{H}$ ) $^+$  611.2037, found 611.2041.

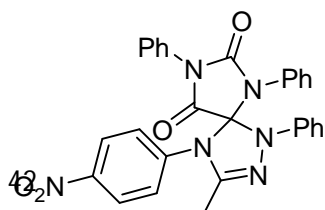
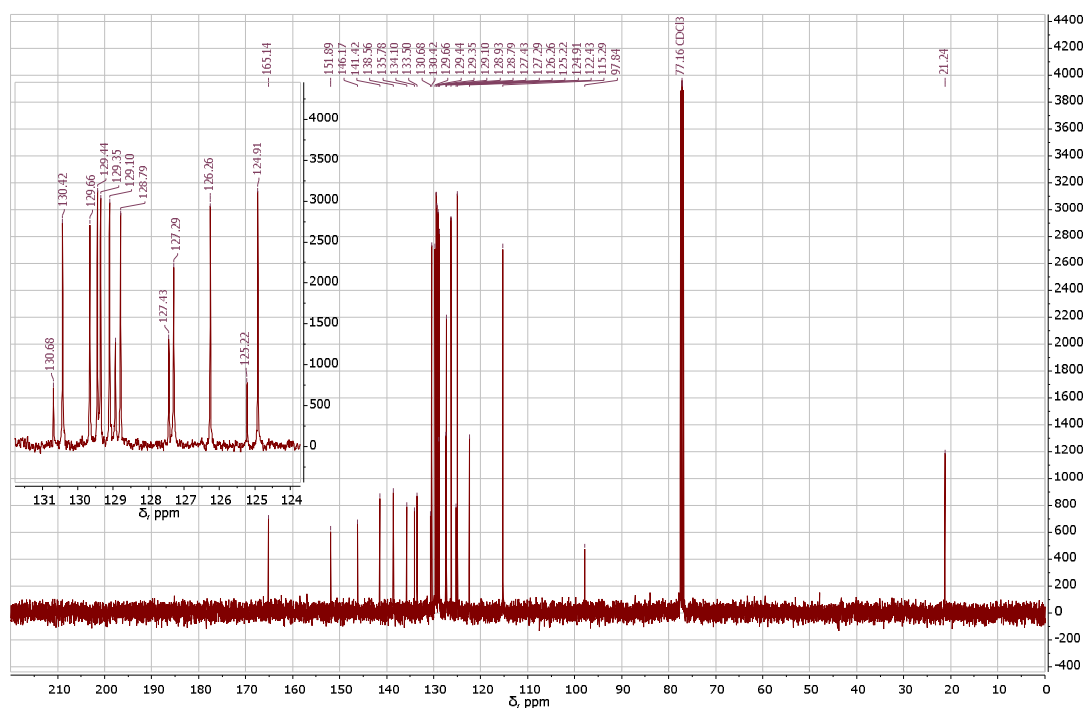
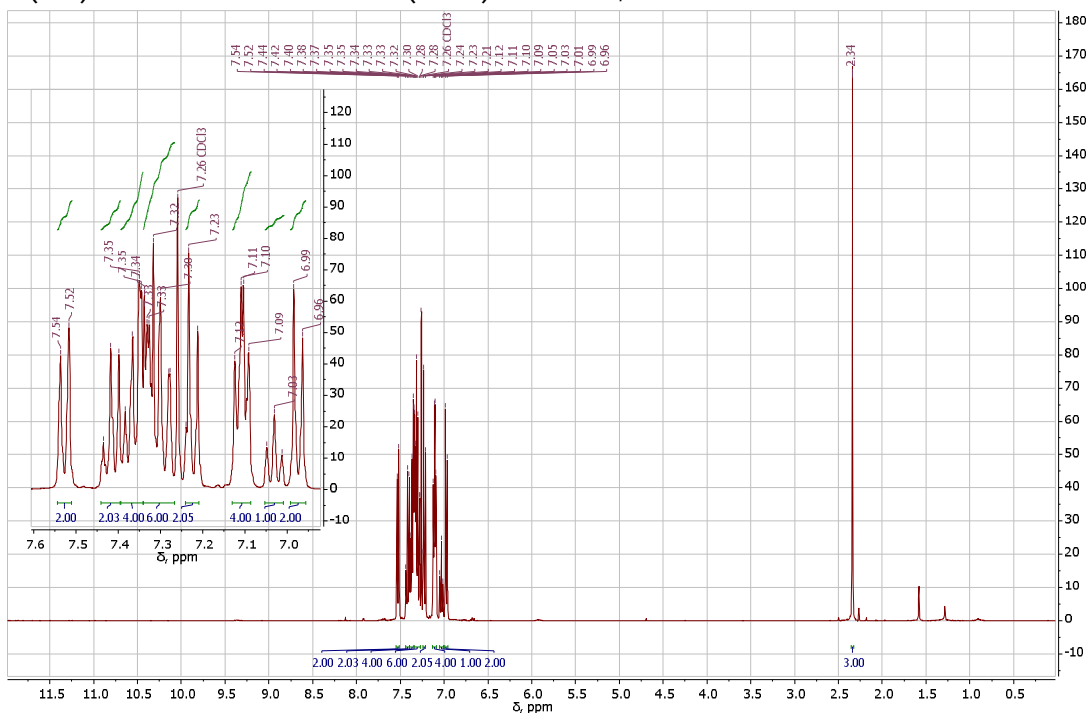


**3-(4-Chlorophenyl)-1,6,8-triphenyl-4-(p-tolyl)-1,2,4,6,8-pentaazaspiro[4.4]non-2-ene-7,9-dione (5j)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53 (d,  $J = 7.7$  Hz, 2H, Ar), 7.44 – 7.40 (m, 2H, Ar), 7.40 – 7.34 (m, 4H, Ar), 7.34 – 7.27 (m, 6H, Ar), 7.24 – 7.21 (m, 2H, Ar), 7.13 – 7.09 (m, 4H, Ar), 7.05 – 7.01 (m, 1H, Ar), 6.97 (d,  $J = 8.3$  Hz, 2H, Ar), 2.34 (s, 3H,  $\text{CH}_3$ ).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.1, 151.9, 146.2, 141.4, 138.6, 135.8, 134.1, 133.5, 130.7, 130.4, 129.7, 129.4, 129.4, 129.1, 128.9, 128.8, 127.4, 127.3, 126.3, 125.2, 124.9, 122.4, 115.3, 97.8, 21.2.

HRMS (ESI): calcd for  $\text{C}_{35}\text{H}_{26}\text{N}_5\text{O}_2$  ( $\text{M}+\text{H}$ ) $^+$  584.1848, found 584.1849.

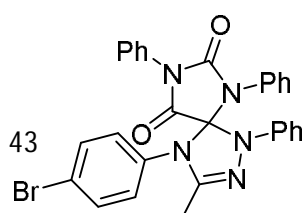
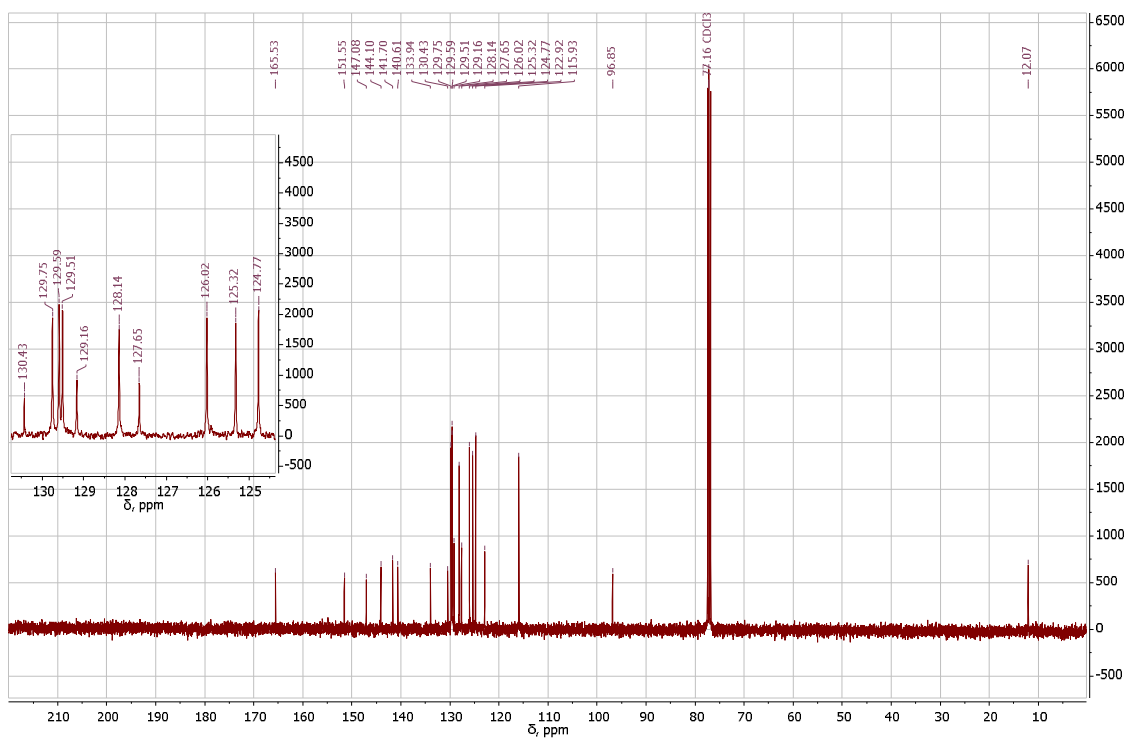
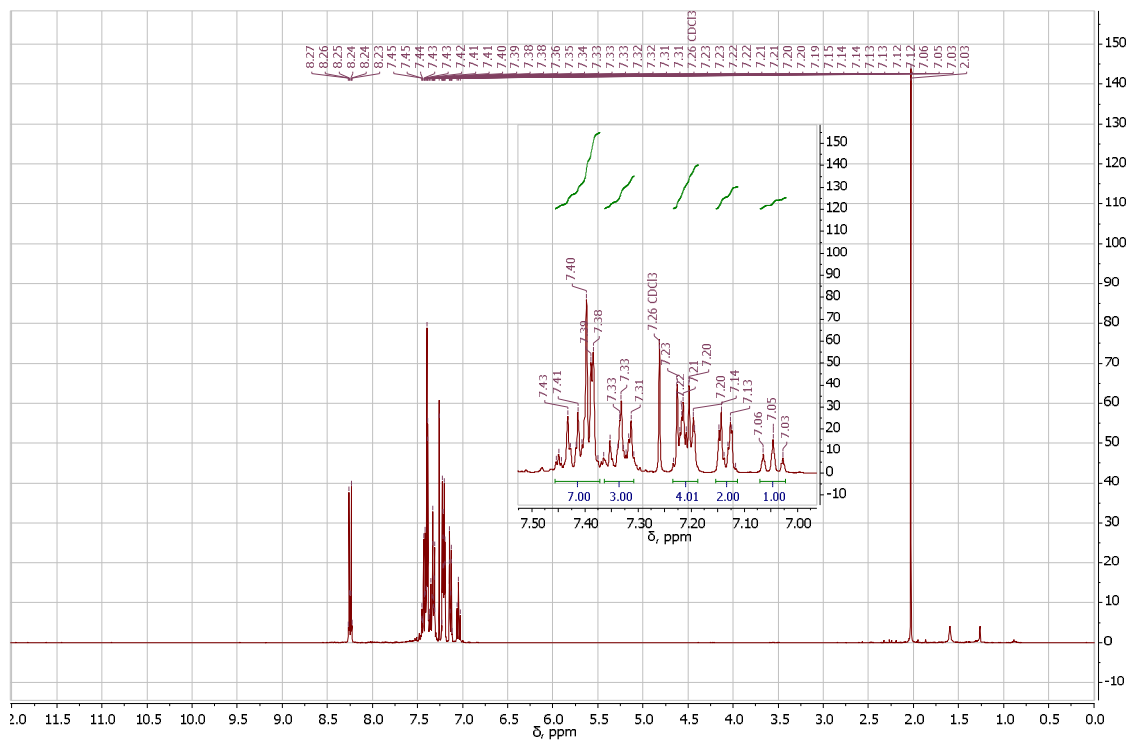


**3-Methyl-4-(4-nitrophenyl)-1,6,8-triphenyl-1,2,4,6,8-pentaazaspiro[4.4]non-2-ene-7,9-dione (5k)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.27 – 8.22 (m, 2H, Ar), 7.46 – 7.37 (m, 7H, Ar), 7.36 – 7.31 (m, 3H, Ar), 7.23 – 7.19 (m, 4H, Ar), 7.15 – 7.11 (m, 2H, Ar), 7.05 (m, 1H, Ar), 2.03 (s, 3H,  $\text{CH}_3$ ).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.5, 151.5, 147.1, 144.1, 141.7, 140.6, 133.9, 130.4, 129.8, 129.6, 129.5, 129.2, 128.1, 127.7, 126.0, 125.3, 124.8, 122.9, 115.9, 96.9, 12.1.

HRMS (ESI): calcd for  $\text{C}_{29}\text{H}_{22}\text{N}_6\text{O}_4$  ( $\text{M}+\text{H}$ ) $^+$  519.1775, found 519.1772.

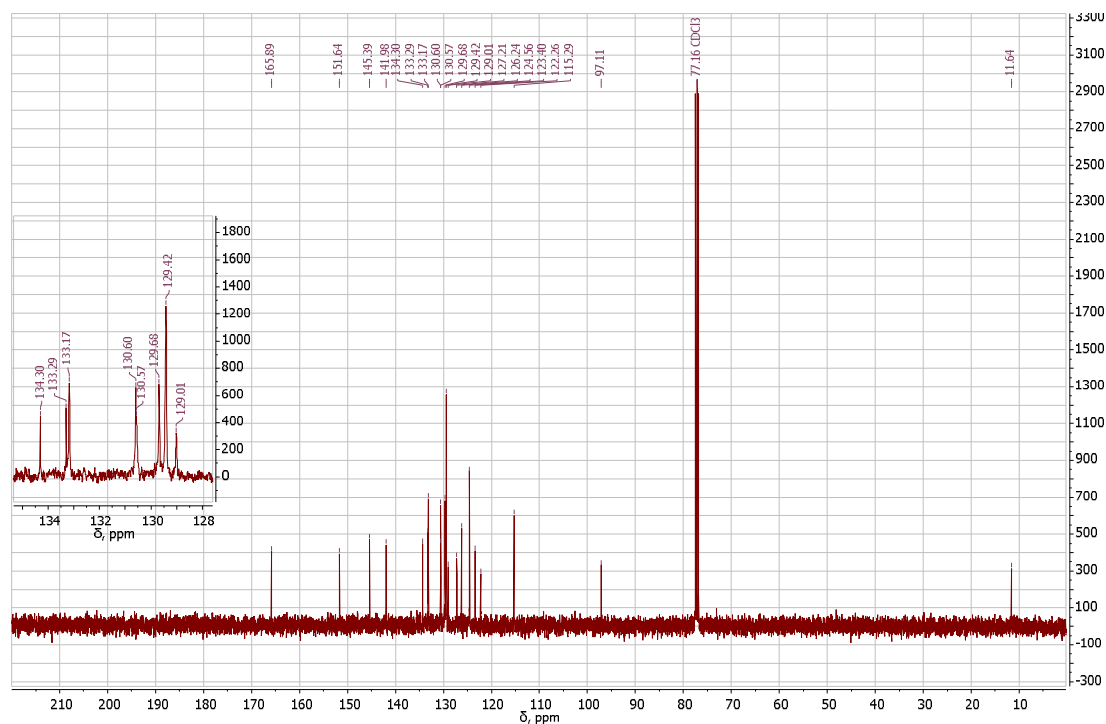
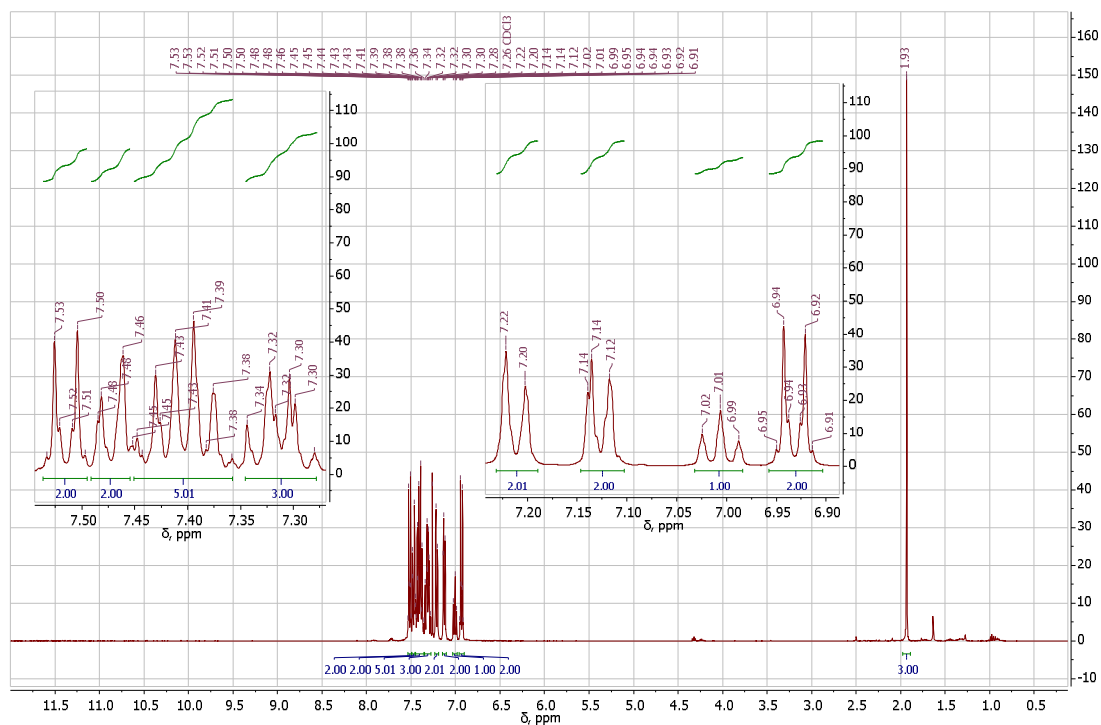


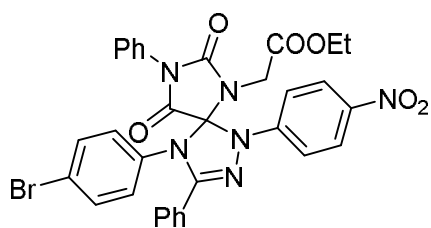
**4-(4-Bromophenyl)-3-methyl-1,6,8-triphenyl-1,2,4,6,8-pentaazaspiro[4.4]non-2-ene-7,9-dione (51)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 – 7.50 (m, 2H, Ar), 7.49 – 7.45 (m, 2H, Ar), 7.45 – 7.36 (m, 5H, Ar), 7.35 – 7.28 (m, 3H, Ar), 7.23 – 7.19 (m, 2H, Ar), 7.15 – 7.10 (m, 2H, Ar), 7.03 – 6.98 (m, 1H, Ar), 6.96 – 6.90 (m, 2H, Ar), 1.93 (s, 3H,  $\text{CH}_3$ ).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.9, 151.6, 145.4, 142.0, 134.3, 133.3, 133.2, 130.6, 130.6, 129.7, 129.4, 129.0, 127.2, 126.2, 124.6, 123.4, 122.3, 115.3, 97.1, 11.6.

HRMS (ESI): calcd for  $\text{C}_{29}\text{H}_{22}\text{BrN}_5\text{O}_2$  ( $\text{M}+\text{H}$ ) $^+$  552.1030, found 552.1023.



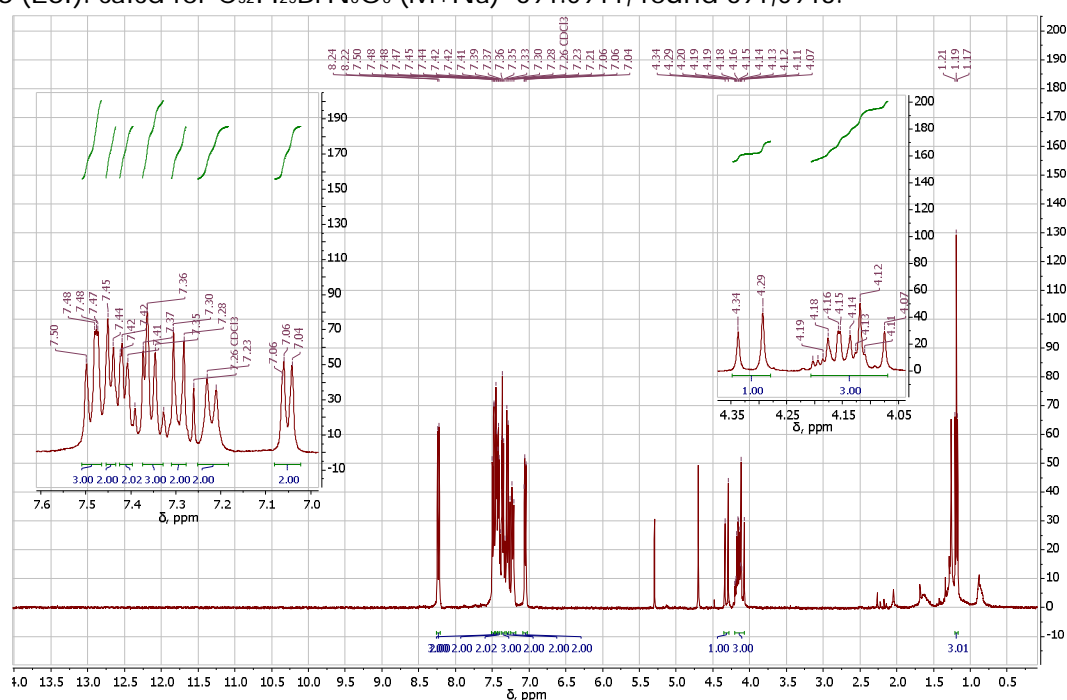


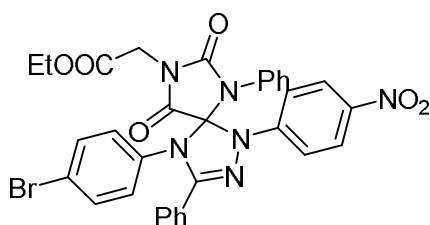
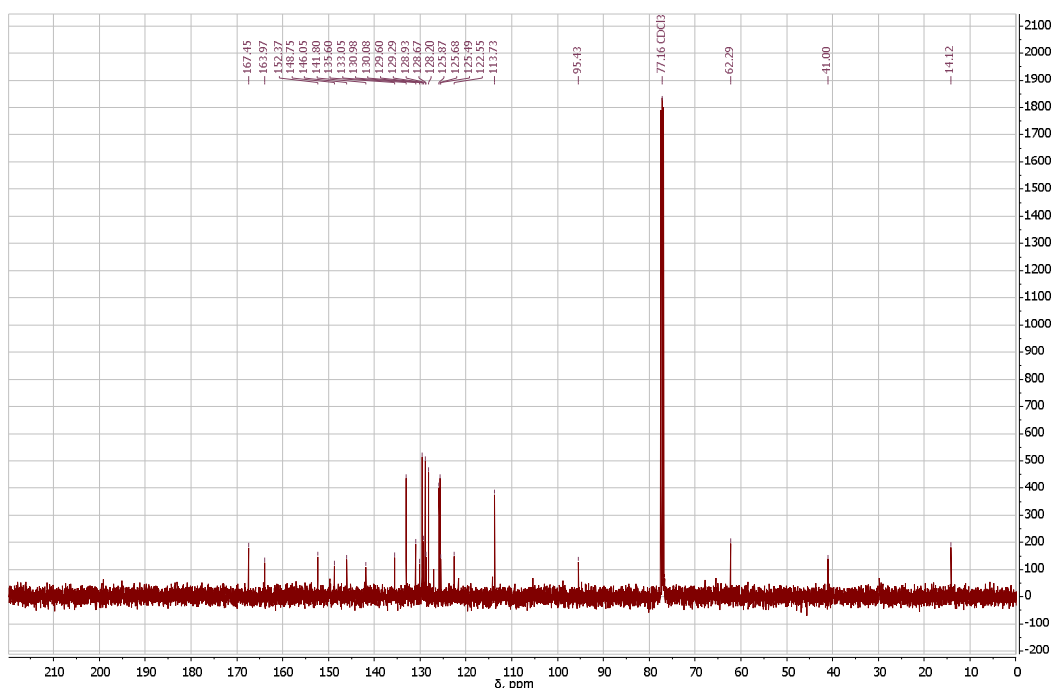
**Ethyl 2-(4-(4-bromophenyl)-1-(4-nitrophenyl)-7,9-dioxo-3,8-diphenyl-1,2,4,6,8-pentaazaspiro[4.4]non-2-en-6-yl)acetate (5m)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.23 (d,  $J = 9.2$  Hz, 2H, Ar), 7.51 – 7.47 (m, 3H, Ar), 7.46 – 7.43 (m, 2H, Ar), 7.42 – 7.40 (m, 2H, Ar), 7.37 – 7.33 (m, 3H, Ar), 7.29 (d,  $J = 9.2$  Hz, 2H, Ar), 7.22 (d,  $J = 8.1$  Hz, 2H, Ar), 7.09 – 7.02 (m, 2H, Ar), 4.32 (d,  $J = 17.6$  Hz, 1H,  $\text{NCH}_2$ ), 4.21 – 4.07 (m, 3H,  $\text{NCH}_2 + \text{COOCH}_2\text{CH}_3$ ), 1.19 (t,  $J = 7.1$  Hz, 3H,  $\text{COOCH}_2\text{CH}_3$ ).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.4, 164.0, 152.4, 148.8, 146.0, 141.8, 135.6, 133.1, 131.0, 130.1, 129.6, 129.3, 128.9, 128.7, 128.2, 125.9, 125.7, 125.5, 122.5, 113.7, 95.4, 62.3, 41.0, 14.1.

HRMS (ESI): calcd for  $\text{C}_{32}\text{H}_{25}\text{BrN}_6\text{O}_6$  ( $\text{M} + \text{Na}$ ) $^+$  691.0911, found 691.0913.



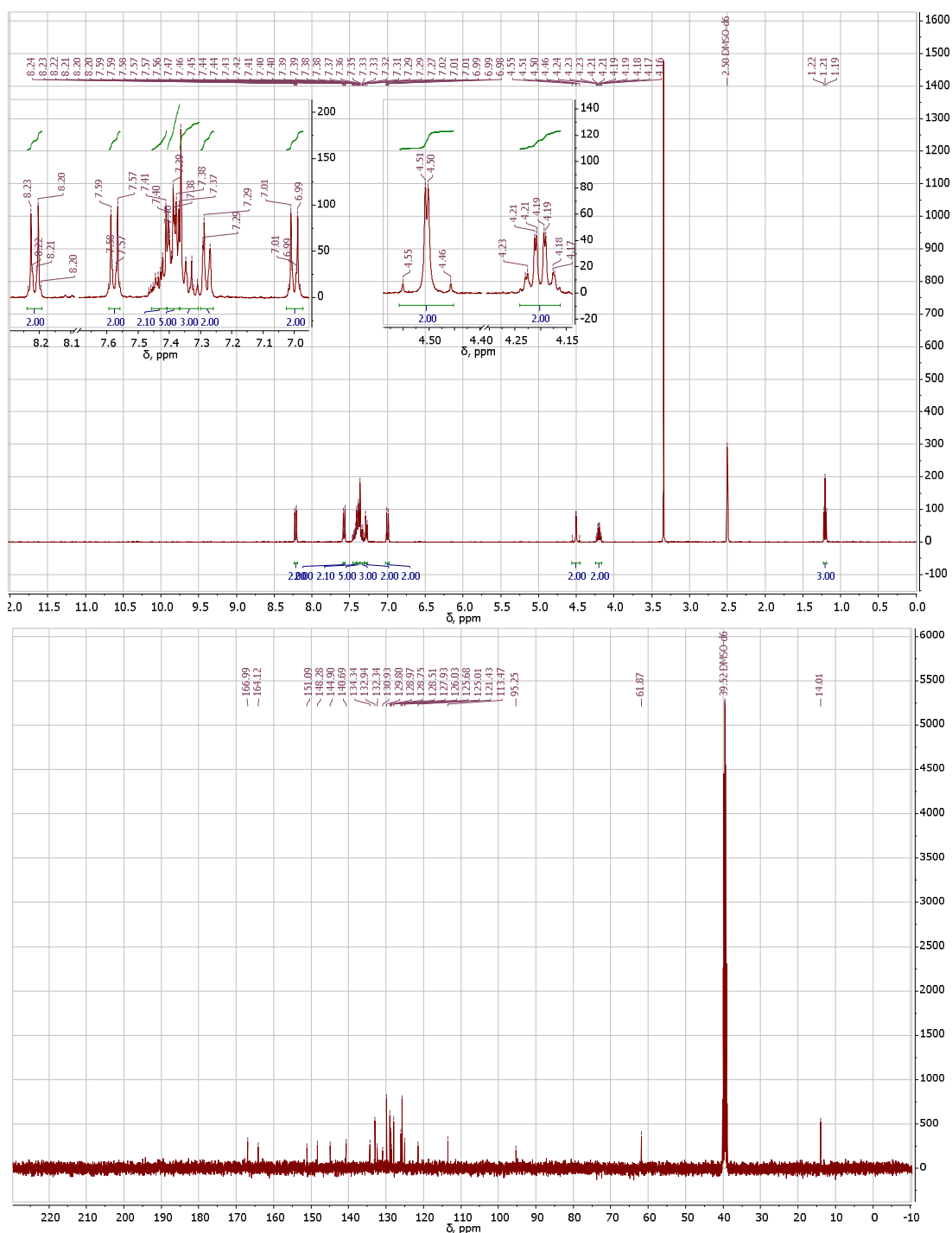


**Ethyl 2-(4-(4-bromophenyl)-1-(4-nitrophenyl)-7,9-dioxo-3,6-diphenyl-1,2,4,6,8-pentaazaspiro[4.4]non-2-en-8-yl)acetate (5n)**

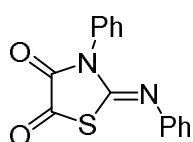
$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  8.24 – 8.19 (m, 2H, Ar), 7.60 – 7.56 (m, 2H, Ar), 7.46 – 7.41 (m, 2H, Ar), 7.41 – 7.37 (m, 5H, Ar), 7.37 – 7.31 (m, 3H, Ar), 7.30 – 7.26 (m, 2H, Ar), 7.03 – 6.97 (m, 2H, Ar), 4.56 – 4.45 (m, 2H, NCH<sub>2</sub>), 4.20 (qd,  $J$  = 7.0, 1.4 Hz, 2H, COOCH<sub>2</sub>CH<sub>3</sub>), 1.21 (t,  $J$  = 7.1 Hz, 3H, COOCH<sub>2</sub>CH<sub>3</sub>).

$^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$  167.0, 164.1, 151.1, 148.3, 144.9, 140.7, 134.3, 132.9, 132.3, 130.9, 129.8, 129.0, 128.8, 128.5, 127.9, 126.0, 125.7, 125.0, 121.4, 113.5, 95.3, 61.9, 14.0.

HRMS (ESI): calcd for C<sub>32</sub>H<sub>25</sub>BrN<sub>6</sub>O<sub>6</sub> (M+Na)<sup>+</sup> 691.0911, found 691.0913.

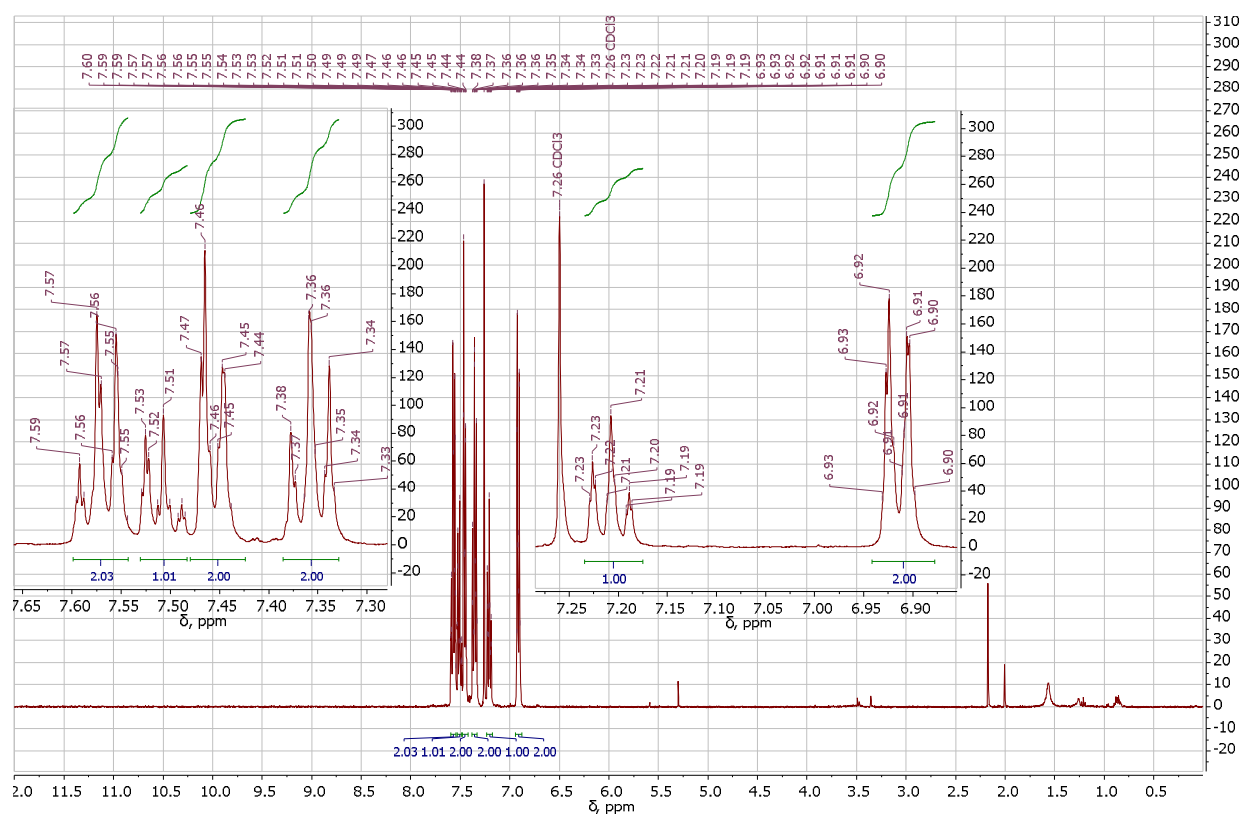


### <sup>1</sup>H NMR spectral data of compounds 5 and 6

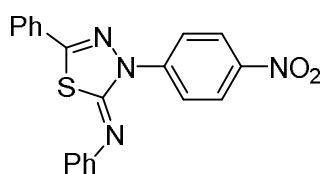


#### (Z)-3-Phenyl-2-(phenylimino)thiazolidine-4,5-dione (5)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.60 – 7.53 (m, 2H, Ar), 7.53 – 7.48 (m, 1H, Ar), 7.48 – 7.42 (m, 2H, Ar), 7.39 – 7.32 (m, 2H, Ar), 7.23 – 7.18 (m, 1H, Ar), 6.94 – 6.89 (m, 2H, Ar).

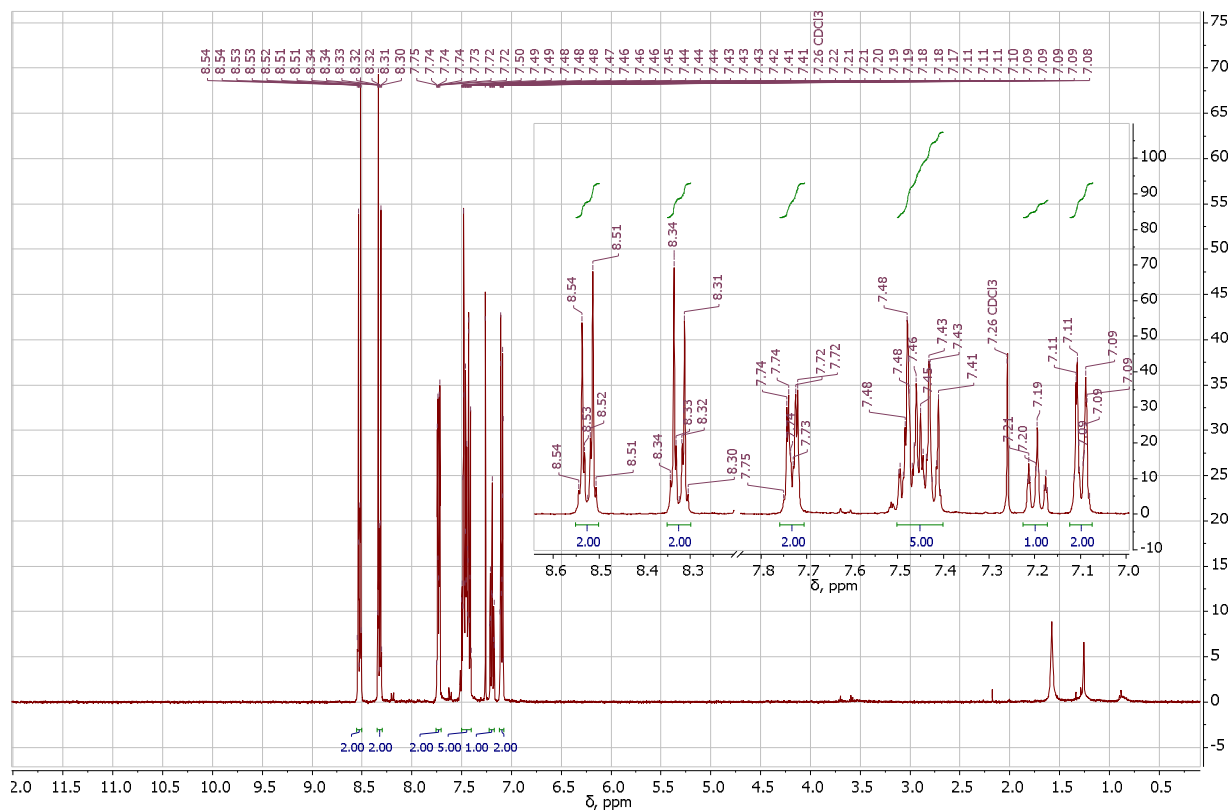






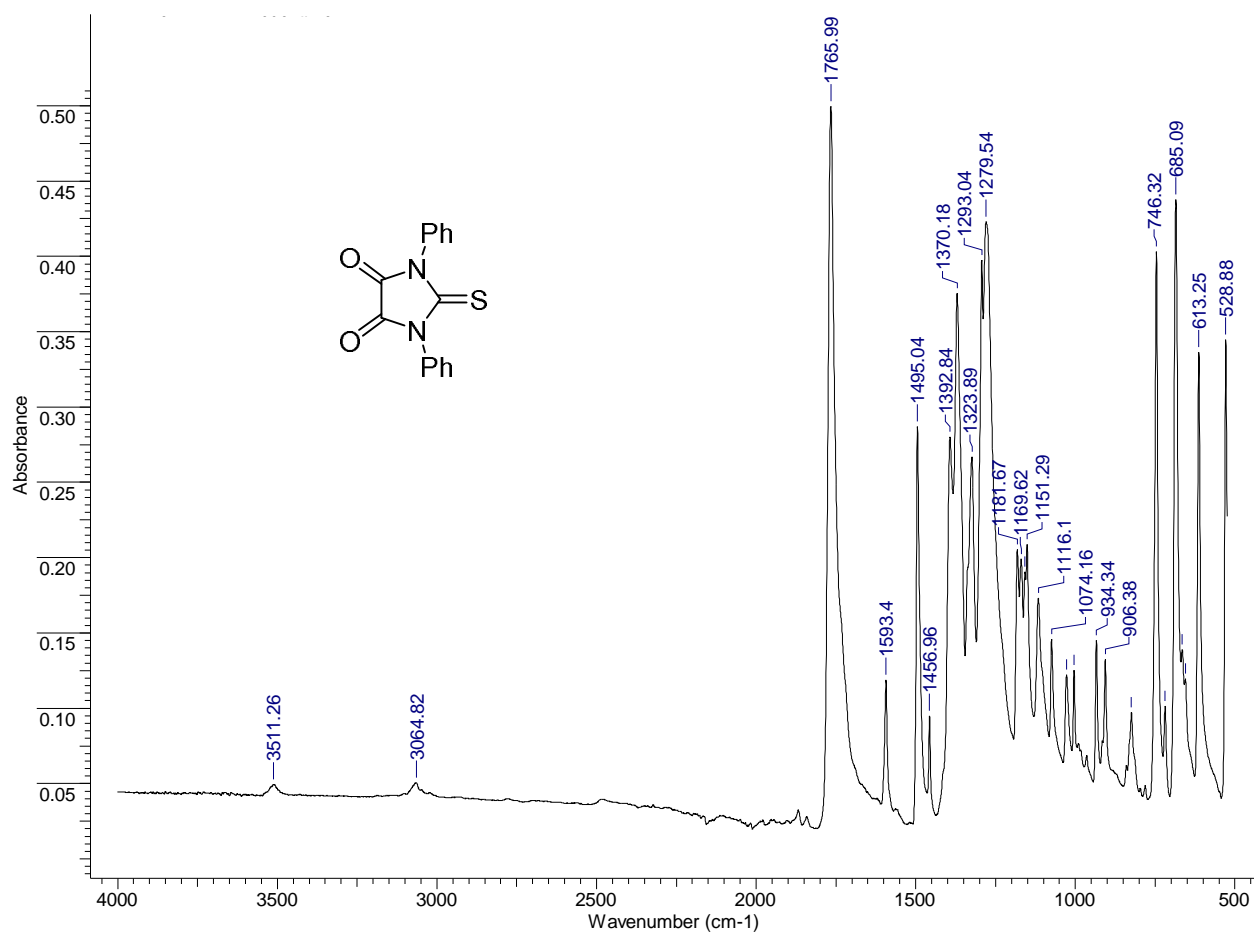
**(Z)-3-(4-nitrophenyl)-N,5-diphenyl-1,3,4-thiadiazol-2(3H)-imine (6)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.55 – 8.50 (m, 2H, Ar), 8.35 – 8.30 (m, 2H, Ar), 7.76 – 7.70 (m, 2H, Ar), 7.50 – 7.40 (m, 5H, Ar), 7.23 – 7.17 (m, 1H, Ar), 7.12 – 7.07 (m, 2H, Ar).

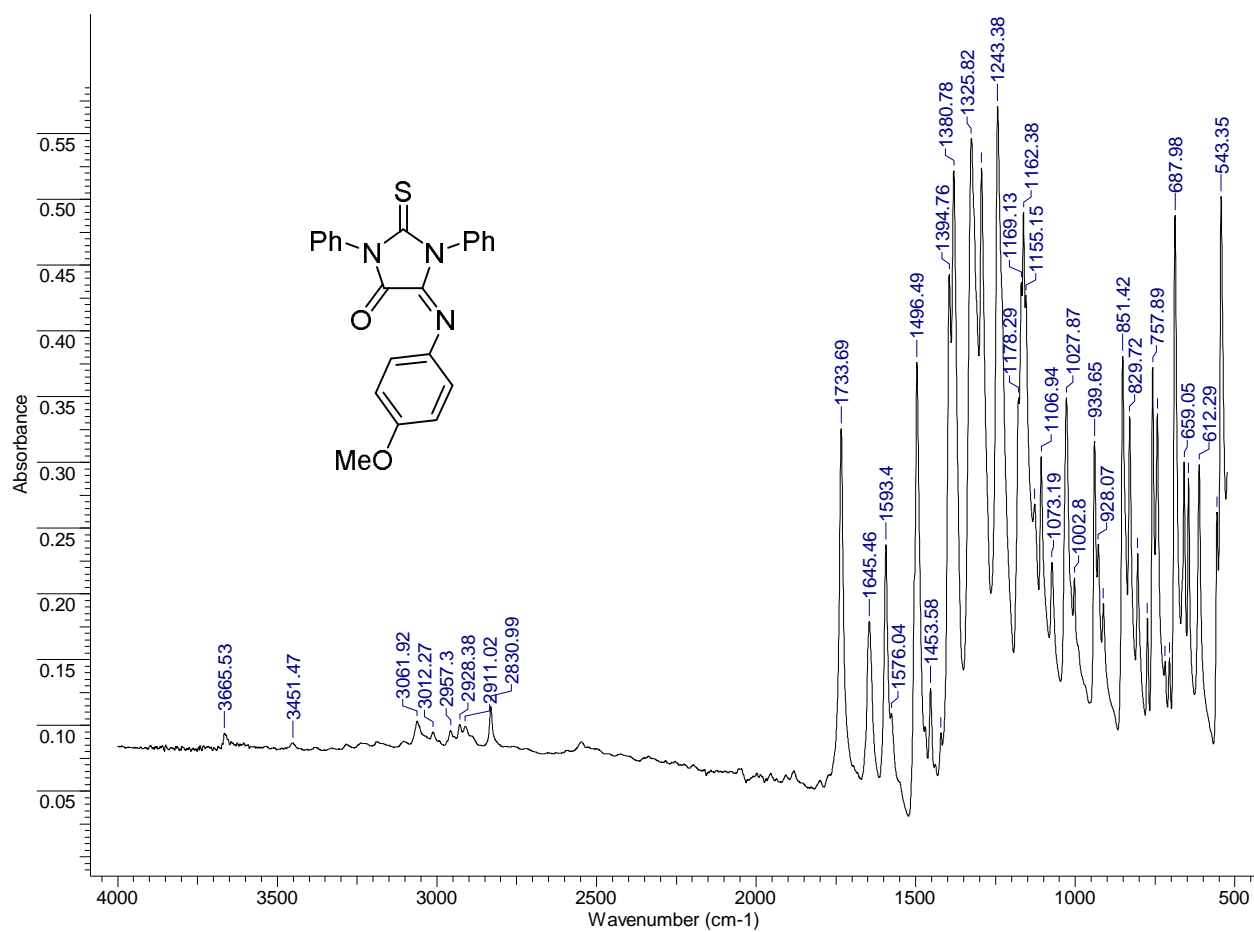


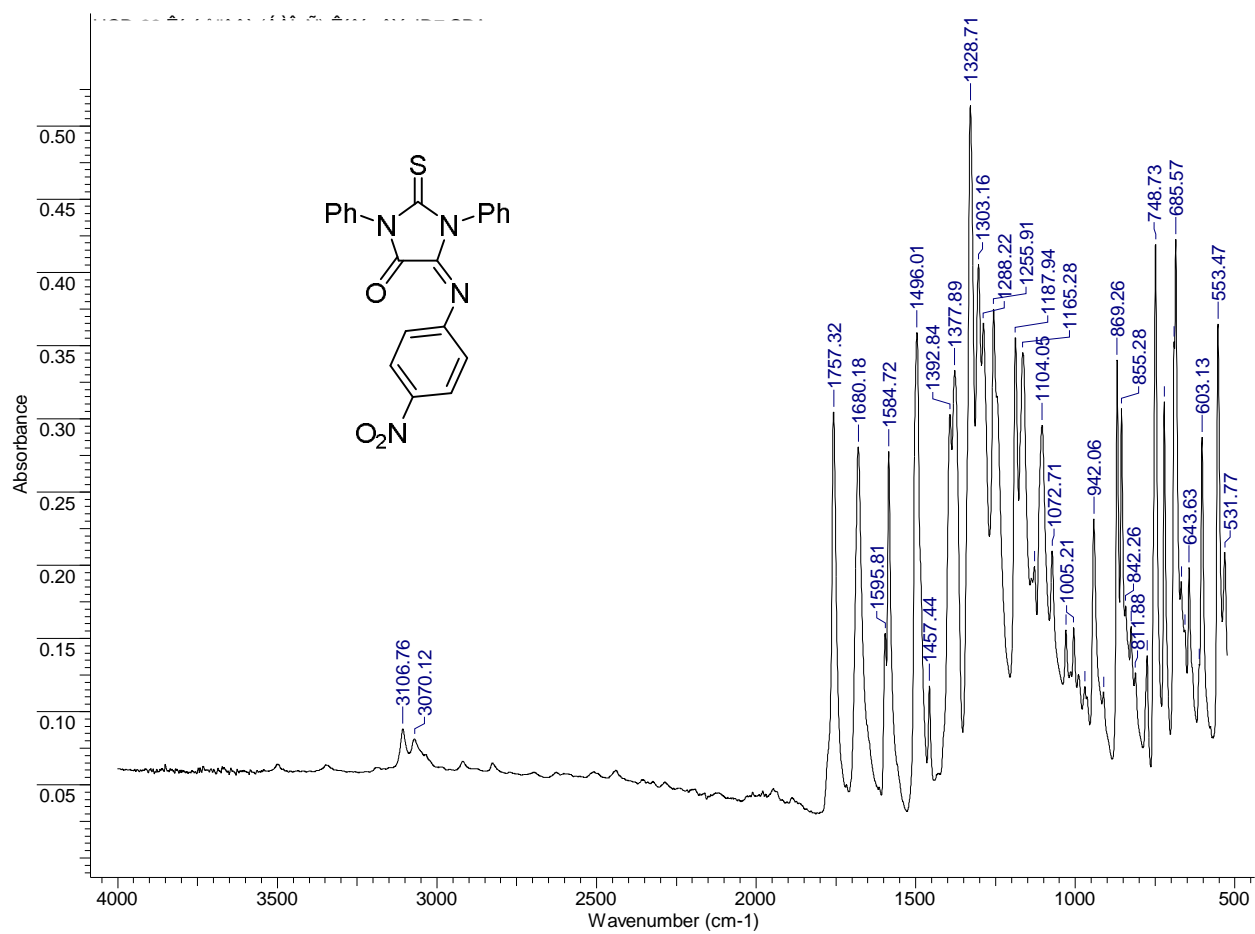
## IR spectral data of 1c, 2i, 2j and 5

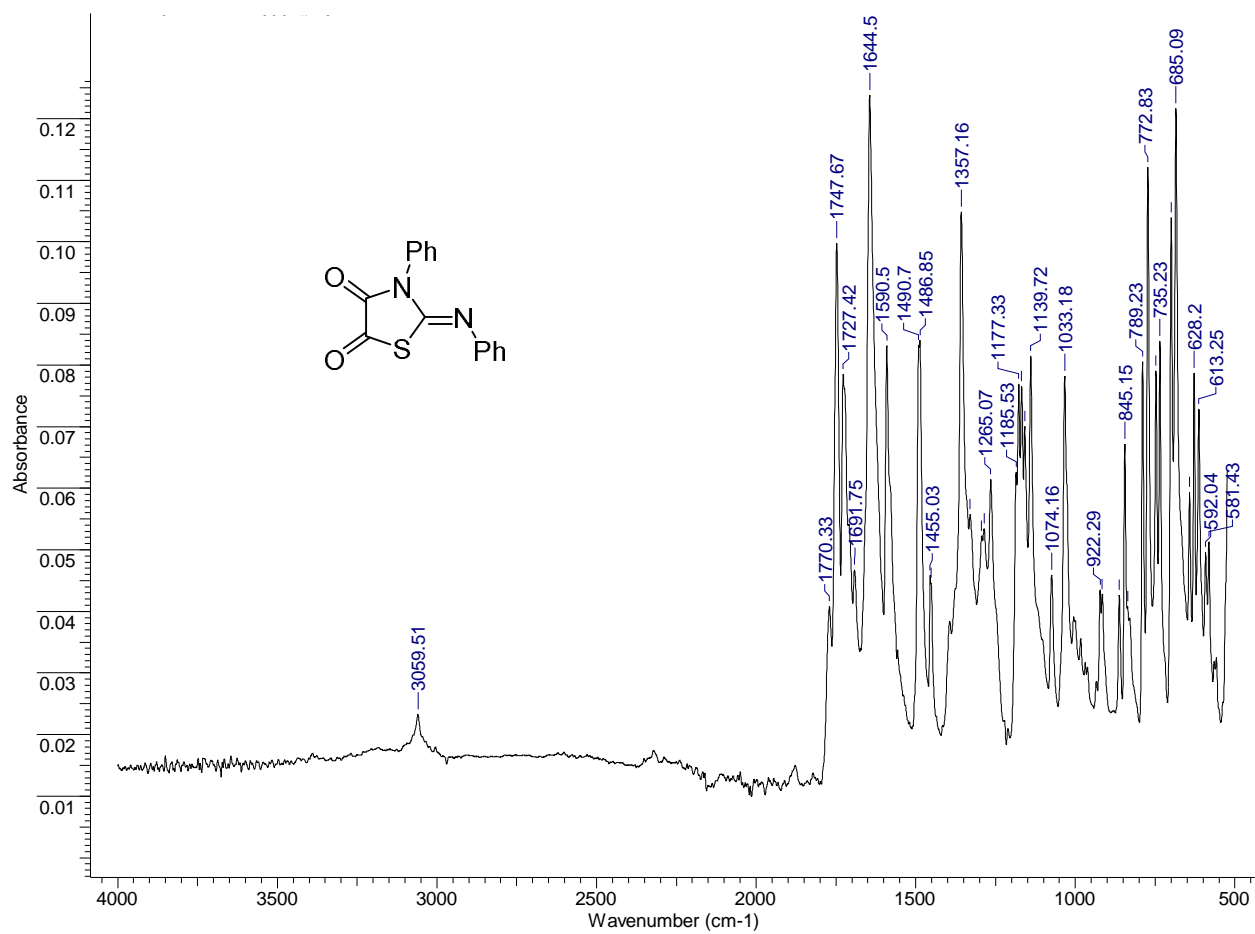
## 1,3-Diphenyl-2-thioxoimidazolidine-4,5-dione (1c)



## 5-((4-Methoxyphenyl)imino)-1,3-diphenyl-2-thioxoimidazolidin-4-one (2i)



**5-((4-Nitrophenyl)imino)-1,3-diphenyl-2-thioxoimidazolidin-4-one (2j)**

**3-Phenyl-2-(phenylimino)thiazolidine-4,5-dione (5)**

### Crystallographic data of 5c, 5g and 5i

Temperature: 295(2) K

Wavelength: 1.54186 Å

Refinement method: Full-matrix least-squares on  $F^2$

#	5c	5g	5i
Empirical formula	C <sub>35</sub> H <sub>25</sub> BrN <sub>6</sub> O <sub>4</sub>	C <sub>36</sub> H <sub>28</sub> N <sub>6</sub> O <sub>5</sub>	C <sub>36</sub> H <sub>27</sub> Cl <sub>3</sub> N <sub>6</sub> O <sub>5</sub>
Formula weight	673.52	624.64	729.98
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P -1	P 21/n	P 21/n
a, Å	10.7603(3)	16.2888(6)	11.3803(5)
b, Å	11.0967(3)	12.3447(3)	20.6633(8)
c, Å	15.1828(4)	16.4893(6)	15.5580(8)
$\alpha$ , °	93.286(3)	90	90
$\beta$ , °	94.472(3)	104.864(3)	108.201(3)
$\gamma$ , °	98.835(3)	90	90
V, Å <sup>3</sup>	1781.50(9)	3204.72(19)	3475.5(3)
Z	2	4	4
$d_{calc}$ , Mg/m <sup>3</sup>	1.256	1.295	1.395
Absorption coefficient, mm <sup>-1</sup>	1.933	0.726	2.823
F(000)	688	1304	1504
Theta range for data collection, °	2.927 to 67.410	4.425 to 67.584	4.246 to 67.625
Index ranges	-12 ≤ h ≤ 3 -13 ≤ k ≤ 13 -17 ≤ l ≤ 18	-19 ≤ h ≤ 19 -10 ≤ k ≤ 14 -15 ≤ l ≤ 19	-8 ≤ h ≤ 13 -24 ≤ k ≤ 23 -18 ≤ l ≤ 18
Reflections collected	7618	23681	25638
Independent reflections [R <sub>int</sub> ]	5047 [0.0689]	5748 [0.0915]	6196 [0.0802]
Completeness to $\theta = 66.511^\circ$ , %	78.8	99.2	98.6
Data / restraints / parameters	5047 / 0 / 417	5748 / 0 / 427	6196 / 0 / 452
Goodness-of-fit on $F^2$	0.907	0.716	0.894
Final R indices [I > 2 $\sigma$ (I)]	R1 = 0.0444 wR2 = 0.1144	R1 = 0.0403 wR2 = 0.0729	R1 = 0.0799 wR2 = 0.2182
R indices (all data)	R1 = 0.0646 wR2 = 0.1212	R1 = 0.1220 wR2 = 0.0872	R1 = 0.1639 wR2 = 0.2552
Extinction coefficient	0.0019(3)	0.00097(6)	0.0013(3)
Largest diff. peak and hole, e. Å <sup>-3</sup>	0.514 and -0.619	0.147 and -0.174	0.708 and -0.599