

**Direct Synthesis of Highly Functionalized Furans from Donor-Acceptor  
Cyclopropanes via DBU-mediated Ring Expansion Reactions**

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## Procedure for preparation of D-A cyclopropanes **1a-u**

D-A cyclopropanes **1a-t** were synthesized following a literature procedure method as described.<sup>29</sup> D-A cyclopropanes **1a-d**, **1j-k**, **1m**, **1o**, **1q** and **1u** were known compounds.<sup>25g, 26, 29</sup>

### Methyl-4-(2,2-dicyano-3-(3-methoxybenzoyl)cyclopropyl)- benzoate (**1a**)

White solid, 1.952 g, yield: 90%; mp 145.6–145.7 °C (EA/PE); IR (KBr, cm<sup>-1</sup>): 3360, 2930, 2912, 2760, 2670, 2421, 2210, 1762, 1680, 1536, 1435, 1320, 1265, 1102, 980; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ (ppm): 8.03 (d, J = 7.8 Hz, 2H), 7.62 (d, J = 7.8 Hz, 1H), 7.51 (s, 1H), 7.43 (dd, J = 7.8 Hz and 7.2 Hz, 1H), 7.39 (d, J = 7.8 Hz, 2H), 7.19 (d, J = 7.2 Hz, 1H), 4.02 (d, J = 7.8 Hz, 1H), 3.86 (d, J = 7.8 Hz, 1H), 3.85 (s, 3H), 3.81 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ (ppm): 188.4, 166.0, 160.3, 136.5, 134.3, 131.5, 130.4, 130.3, 128.5, 121.8, 121.3, 112.9, 111.9, 111.3, 55.6, 52.4, 38.1, 35.6, 15.3; HR-MS (ESI) calcd. for C<sub>21</sub>H<sub>16</sub>N<sub>2</sub>NaO<sub>4</sub> [(M+Na)<sup>+</sup>]: 383.1008; Found: 383.1002.

### 2-(4-Bromobenzoyl)-3-(m-tolyl)cyclopropane-1,1-dicarbonitrile (**1b**)

White solid, 1.994 g, yield: 91%; mp 178.0–178.4 °C (EA/PE); IR (KBr, cm<sup>-1</sup>): 3420, 2962, 2930, 2730, 2672, 2431, 2210, 1686, 1530, 1431, 1320, 1260, 1107, 982; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ (ppm): 7.88 (d, J = 6.6 Hz, 2H), 7.66 (d, J = 6.6 Hz, 2H), 7.26 (bs, 1H), 7.18 (s, 1H), 7.10 (bs, 2H), 3.90 (d, J = 6.6 Hz, 1H), 3.78 (d, J = 6.6 Hz, 1H), 2.32 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ (ppm): 188.1, 139.3, 134.1, 132.7, 130.7, 130.1, 129.2, 129.1, 129.0, 125.2, 112.1, 111.5, 38.8, 35.4, 21.4, 15.3; HR-MS (ESI) calcd. for C<sub>19</sub>H<sub>13</sub>BrN<sub>2</sub>NaO [(M+Na)<sup>+</sup>]: 387.0109; Found: 387.0101.

### 2-Benzoyl-3-(2-bromophenyl)cyclopropane-1,1-dicarbonitrile (**1e**)

White solid, 1.797 g, yield: 85%; mp 152.1–152.4 °C (EA/PE); IR (KBr, cm<sup>-1</sup>): 3330, 2950, 2676, 2435, 2212, 1678, 1530, 1432, 1316, 1260, 1107, 952, 860; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 8.11 (d, J = 6.8 Hz, 2H), 7.73 (d, J = 7.2 Hz, 1H), 7.70 (d, J = 7.2 Hz, 1H), 7.60 (dd, J = 6.6 Hz and 6.6 Hz, 2H), 7.38 (dd, J = 6.6 Hz and 6.6 Hz, 1H), 7.31 (dd, J = 7.2 Hz and 7.2 Hz, 1H), 7.25 (d, J = 6.6 Hz, 1H), 4.07 (d, J = 7.2 Hz, 1H), 3.89 (d, J = 7.2 Hz, 1H); <sup>13</sup>C NMR (150

MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 188.6, 135.3, 135.2, 133.6, 131.3, 130.2, 129.6, 129.4, 128.8, 128.0, 126.3, 112.1, 111.4, 39.4, 36.5, 15.4; HR-MS (ESI) calcd. for C<sub>18</sub>H<sub>11</sub>BrN<sub>2</sub>NaO [(M+Na)<sup>+</sup>]: 372.9952; Found: 372.9946.

2-(3-Chlorophenyl)-3-(3-methoxybenzoyl)cyclopropane-1,1-dicarbonitrile (**1g**)  
White solid, 1.752 g, yield: 87%; mp 138.3–138.5 °C (EA/PE); IR (KBr, cm<sup>-1</sup>): 3340, 2956, 2702, 2403, 2202, 1672, 1550, 1430, 1326, 1266, 1100, 918, 890; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.62 (d, J = 7.5 Hz, 1H), 7.51 (s, 1H), 7.47 (dd, J = 7.8 Hz and 7.8 Hz, 1H), 7.37-7.32 (m, 2H), 7.30 (s, 1H), 7.23-7.18 (m, 2H), 3.94 (d, J = 7.8 Hz, 1H), 3.83 (s, 3H), 3.81 (d, J = 7.8 Hz, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 187.2, 159.3, 135.5, 134.3, 130.4, 129.6, 129.3, 129.1, 127.6, 125.5, 120.9, 120.3, 111.8, 110.8, 110.2, 54.6, 36.7, 34.5, 14.2; HR-MS (ESI) calcd. for C<sub>19</sub>H<sub>13</sub>ClN<sub>2</sub>NaO<sub>2</sub> [(M+Na)<sup>+</sup>]: 359.0563; Found: 359.0560.

2-Benzoyl-3-(3-phenoxyphenyl)cyclopropane-1,1-dicarbonitrile (**1h**)  
Yellow crystal, 1.723 g, yield: 79%; mp 160.8–161.1 °C (EA/PE); IR (KBr, cm<sup>-1</sup>): 3332, 2950, 2709, 2679, 2418, 2208, 1679, 1550, 1546, 1430, 1326, 1266, 1106, 910, 898; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 8.00 (d, J = 7.8 Hz, 2H), 7.64 (dd, J = 7.4 Hz and 7.4 Hz, 1H), 7.51 (dd, J = 7.4 Hz and 7.4 Hz, 2H), 7.34-7.28 (m, 3H), 7.08 (dd, J = 7.2 Hz and 7.2 Hz, 1H), 7.07 (d, J = 7.2 Hz, 1H), 6.98-6.93 (m, 4H), 3.92 (d, J = 7.8 Hz, 1H), 3.89 (s, 3H), 3.79 (d, J = 7.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 188.7, 158.1, 156.3, 135.3, 135.1, 131.3, 130.7, 130.0, 129.3, 128.7, 124.0, 122.8, 119.8, 119.3, 118.4, 112.0, 111.4, 38.3, 35.5, 15.2; HR-MS (ESI) calcd. for C<sub>24</sub>H<sub>16</sub>N<sub>2</sub>NaO<sub>2</sub> [(M+Na)<sup>+</sup>]: 387.1109; Found: 387.1102.

2-(2-Chlorophenyl)-3-(3-methylbenzoyl)cyclopropane-1,1-dicarbonitrile (**1i**)  
White solid, 1.776 g, yield: 92%; mp 146.8-147.0 °C (EA/PE); IR (KBr, cm<sup>-1</sup>): 3303, 2958, 2701, 2604, 2420, 2216, 1670, 1555, 1432, 1320, 1260, 1102, 990, 875; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.82 (s, 2H), 7.46 (d, J = 6.9 Hz, 1H), 7.44 (d, J = 7.8 Hz, 1H), 7.41 (dd, J = 7.5 Hz and 7.5 Hz, 1H), 7.31 (dd, J = 6.9 Hz and 6.9 Hz, 1H), 7.25 (dd, J = 6.9 Hz and 6.9 Hz, 1H), 7.19 (d, J = 6.9

Hz, 1H), 3.97 (d,  $J = 7.8$  Hz, 1H), 3.84 (d,  $J = 7.8$  Hz, 1H), 2.39 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 188.7, 139.4, 136.2, 136.0, 135.3, 131.1, 130.3, 129.3, 129.2, 129.2, 128.5, 127.4, 126.1, 112.1, 111.4, 37.0, 36.1, 21.4, 15.0; HR-MS (ESI) calcd. for  $\text{C}_{19}\text{H}_{13}\text{ClN}_2\text{NaO}$   $[(\text{M}+\text{Na})^+]$ : 343.0614; Found: 343.0609.

**2-(4-Chlorobenzoyl)-3-(2-chlorophenyl)cyclopropane-1,1-dicarbonitrile (**1l**)**

White solid, 1.838 g, yield: 90%; mp 162.3–162.8 °C (EA/PE); IR (KBr,  $\text{cm}^{-1}$ ): 3326, 2950, 2768, 2624, 2426, 2210, 1668, 1550, 1438, 1320, 1266, 1102, 980, 896;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.99 (d,  $J = 7.8$  Hz, 2H), 7.51 (d,  $J = 7.8$  Hz, 2H), 7.47 (d,  $J = 7.8$  Hz, 1H), 7.34 (dd,  $J = 7.5$  Hz and 7.8 Hz, 1H), 7.28 (dd,  $J = 7.5$  Hz and 7.5 Hz, 1H), 7.19 (d,  $J = 7.5$  Hz, 1H), 3.91 (d,  $J = 7.8$  Hz, 1H), 3.86 (d,  $J = 7.8$  Hz, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 186.4, 141.0, 135.1, 132.6, 130.1, 129.3, 129.1, 128.7, 128.2, 127.2, 126.4, 110.9, 110.1, 36.0, 35.0, 14.0; HR-MS (ESI) calcd. for  $\text{C}_{18}\text{H}_{10}\text{Cl}_2\text{N}_2\text{NaO}$   $[(\text{M}+\text{Na})^+]$ : 363.0068; Found: 363.0075.

**2-Benzoyl-3-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)cyclopropane-1,1-dicarbonitrile (**1n**)**

White crystal, 1.762 g, yield: 89%; mp 177.5–177.6 °C (EA/PE); IR (KBr,  $\text{cm}^{-1}$ ): 3420, 3030, 2780, 2624, 2460, 2224, 1660, 1550, 1430, 1324, 1260, 1108, 976, 896;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 8.00 (d,  $J = 7.5$  Hz, 2H), 7.63 (dd,  $J = 7.5$  Hz and 7.5 Hz, 1H), 7.49 (dd,  $J = 7.5$  Hz and 7.5 Hz, 2H), 6.83 (d,  $J = 8.4$  Hz, 1H), 6.80 (s, 1H), 6.77 (d,  $J = 8.4$  Hz, 1H), 4.16 (s, 4H), 3.92 (d,  $J = 7.8$  Hz, 1H), 3.71 (d,  $J = 7.8$  Hz, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 189.0, 144.8, 144.0, 135.4, 135.0, 129.3, 128.7, 122.2, 121.4, 118.1, 117.2, 112.4, 111.7, 64.3, 64.3, 38.6, 35.6, 15.4; HR-MS (ESI) calcd. for  $\text{C}_{20}\text{H}_{14}\text{N}_2\text{NaO}_3$   $[(\text{M}+\text{Na})^+]$ : 353.0902; Found: 353.0914.

**2-(3-Methoxybenzoyl)-3-(*m*-tolyl)cyclopropane-1,1-dicarbonitrile (**1p**)**

White solid, 1.735 g, yield: 92%; mp 144.2–144.6 °C (EA/PE); IR (KBr,  $\text{cm}^{-1}$ ): 3408, 3030, 2760, 2650, 2462, 2226, 1665, 1556, 1436, 1325, 1260, 1112, 968, 906;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 7.62 (d,  $J = 7.5$  Hz, 1H), 7.51 (s,



1H), 7.43 (dd,  $J = 7.8$  Hz and  $7.8$  Hz, 1H), 7.26 (dd,  $J = 7.5$  Hz and  $7.5$  Hz, 1H), 7.18 (dd,  $J = 7.8$  Hz and  $7.8$  Hz, 2H), 7.10 (s, 1H), 7.09 (d,  $J = 7.8$  Hz, 1H), 3.94 (d,  $J = 7.8$  Hz, 1H), 3.82 (s, 3H), 3.78 (d,  $J = 7.8$  Hz, 1H), 2.32 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 187.7, 159.3, 138.2, 135.7, 129.6, 129.2, 128.3, 128.1, 128.0, 124.2, 120.7, 120.3, 111.7, 111.2, 110.6, 54.6, 37.7, 34.6, 20.3, 14.2; HR-MS (ESI) calcd. for  $\text{C}_{20}\text{H}_{16}\text{N}_2\text{NaO}_2$   $[(\text{M}+\text{Na})^+]$ : 339.1109; Found: 339.1102.

2-(4-Bromobenzoyl)-3-(2,4-dichlorophenyl)cyclopropane-1,1-dicarbonitrile  
(1r)

White solid, 2.001 g, yield: 79%; mp 186.1–186.4 °C (EA/PE); IR (KBr,  $\text{cm}^{-1}$ ): 3330, 2952, 2770, 2660, 2410, 2218, 1665, 1555, 1430, 1320, 1266, 1102, 988, 890;  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO}-d_6$ )  $\delta$  (ppm): 8.25 (d,  $J = 8.1$  Hz, 2H), 7.88 (d,  $J = 8.1$  Hz, 2H), 7.86 (s, 1H), 7.72 (d,  $J = 8.4$  Hz, 1H), 7.57 (d,  $J = 8.4$  Hz, 1H), 5.07 (d,  $J = 7.8$  Hz, 1H), 3.90 (d,  $J = 7.8$  Hz, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO}-d_6$ )  $\delta$  (ppm): 189.3, 136.1, 134.9, 134.4, 132.3, 132.0, 131.2, 129.0, 129.0, 128.2, 127.5, 112.5, 37.0, 34.7, 15.1; HR-MS (ESI) calcd. for  $\text{C}_{18}\text{H}_9\text{BrCl}_2\text{N}_2\text{NaO}$   $[(\text{M}+\text{Na})^+]$ : 440.9173; Found: 440.9160.

2-(4-Bromobenzoyl)-3-(3,5-dibromophenyl)cyclopropane-1,1-dicarbonitrile  
(1s)

Yellow solid, 2.591 g, yield: 85%; mp 220.6–220.9 °C (EA/PE); IR (KBr,  $\text{cm}^{-1}$ ): 3338, 2950, 2765, 2668, 2420, 2220, 1662, 1550, 1432, 1326, 1260, 1102, 985, 896;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  (ppm): 8.23 (d,  $J = 7.8$  Hz, 2H), 8.04 (s, 2H), 7.90 (s, 1H), 7.87 (d,  $J = 7.8$  Hz, 2H), 5.15 (d,  $J = 8.0$  Hz, 1H), 4.10 (d,  $J = 8.0$  Hz, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO}-d_6$ )  $\delta$  (ppm): 189.2, 135.3, 134.4, 134.0, 132.0, 131.2, 131.1, 129.0, 122.4, 112.4, 112.3, 36.7, 34.1, 15.9; HR-MS (ESI) calcd. for  $\text{C}_{18}\text{H}_9\text{Br}_3\text{N}_2\text{NaO}$   $[(\text{M}+\text{Na})^+]$ : 528.8163; Found: 528.8150.

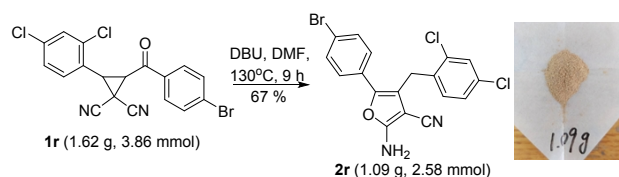
2-Benzoyl-3-(o-tolyl)cyclopropane-1,1-dicarbonitrile (1t)

White crystal, 1.327 g, yield: 77%; mp 167.3–167.6 °C (EA/PE); IR (KBr,  $\text{cm}^{-1}$ ): 3332, 2956, 2718, 2624, 2422, 2220, 1676, 1558, 1408, 1322, 1266, 1106, 996, 879;

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 8.13 (d,  $J = 7.6$  Hz, 2H), 7.75 (dd,  $J = 7.2$  Hz and 7.2 Hz, 1H), 7.62 (dd,  $J = 7.2$  Hz and 7.6 Hz, 2H), 7.37-7.33 (m, 2H), 7.25 (dd,  $J = 7.0$  Hz and 7.0 Hz, 1H), 7.14 (d,  $J = 7.6$  Hz, 1H), 4.07 (d,  $J = 8.0$  Hz, 1H), 3.86 (d,  $J = 8.0$  Hz, 1H), 2.51 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 187.9, 137.8, 134.4, 134.1, 130.1, 128.8, 128.3, 127.7, 127.3, 126.2, 125.5, 111.1, 110.6, 36.8, 34.7, 18.6, 13.7; HR-MS (ESI) calcd. for  $\text{C}_{19}\text{H}_{14}\text{N}_2\text{NaO}$   $[(\text{M}+\text{Na})^+]$ : 309.1004; Found: 309.1002.

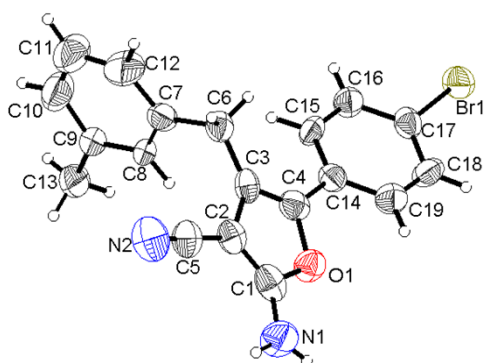
### Synthesis of **2r** in a Preparative Scale

Furthermore, this DBU-mediated cycloisomerization protocol was also evaluated in gram scale employing cyclopropane-1,1-dicarbonitrile **1r**, thus affording the corresponding 2-amino-5-aryl-4-benzylfuran-3-carbonitrile **2r** in similar yield as previously established (Scheme S1).

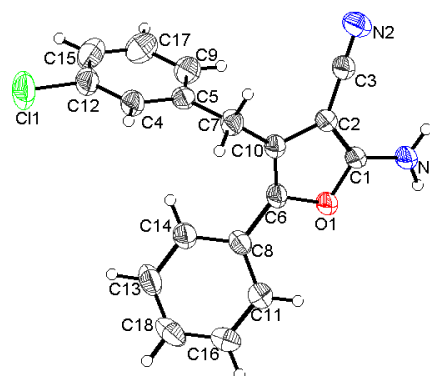


Scheme S1. Synthesis of **2r** in a Preparative Scale

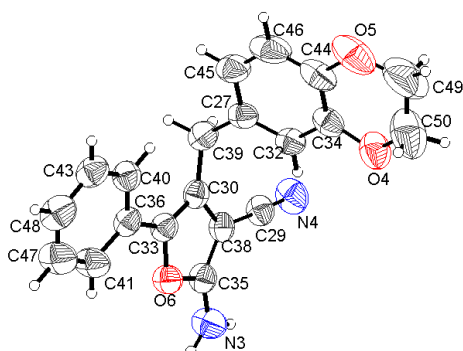
All single crystals were obtained using EtOAc/hexanes as a mixture solvent. X-ray crystallographic analysis was performed with a Smart-1000 CCD diffractometer using monochromatic Mo KR radiation ( $\lambda$  0.71073 Å) and integrated with the SAINT-Plus program. All calculations were performed with programs from the SHELXTL crystallographic software package.



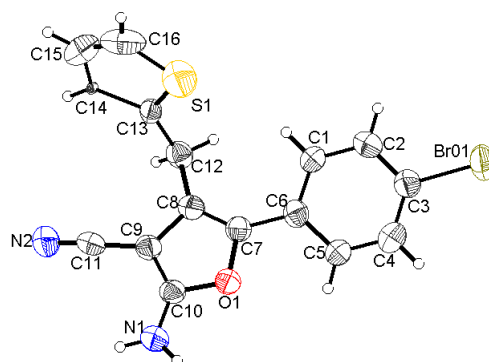
**2b** (CCDC 1891524)



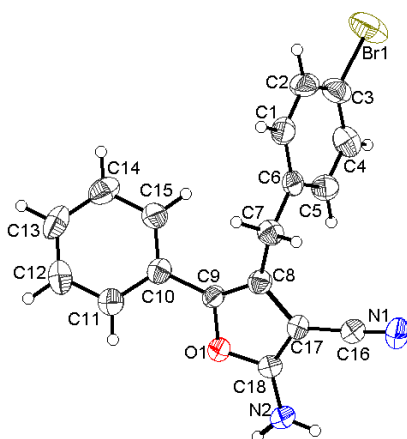
**2d** (CCDC 1858658)



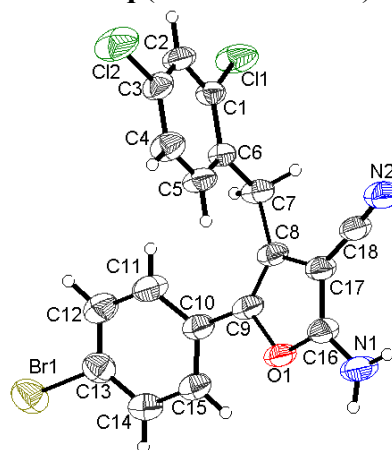
**2n** (CCDC 1875320)



**2q** (CCDC 1880678)



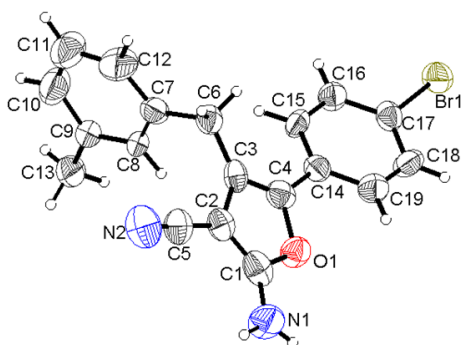
**2k** (CCDC 1908517)



**2r** (CCDC 1908517)

The X-ray crystal structure of compound **2b**, **2d**, **2k**, **2n**, **2q** and **2r**, non-hydrogen atoms are shown at the 30% probability level.





**2b** (CCDC 1891524)

Fig. S1 Molecular structure of 2-amino-5-aryl-4-benzylfuran-3-carbonitrile **2b**, non-hydrogen atoms are shown at the 30% probability level.

Table S1. Crystal data and structure refinement for **2b**.

|                             |                                                                                                                        |
|-----------------------------|------------------------------------------------------------------------------------------------------------------------|
| Identification code         | <b>2b</b>                                                                                                              |
| Empirical formula           | C <sub>20</sub> H <sub>15</sub> BrN <sub>2</sub> O                                                                     |
| Formula weight              | 379.24                                                                                                                 |
| Temperature                 | 296 K                                                                                                                  |
| Wavelength                  | 0.71073 Å                                                                                                              |
| Crystal system, space group | Monoclinic, P2(1)/c                                                                                                    |
| Unit cell dimensions        | a = 11.5956(17) Å    alpha = 90 deg.<br>b = 5.0269(7) Å    beta = 92.159(4) deg.<br>c = 33.000(5) Å    gamma = 90 deg. |
| Volume                      | 1922.2(5) Å <sup>3</sup>                                                                                               |
| Z, Calculated density       | 4, 1.311 Mg/m <sup>3</sup>                                                                                             |
| Absorption coefficient      | 2.146 mm <sup>-1</sup>                                                                                                 |
| F(000)                      | 768                                                                                                                    |
| Crystal size                | 0.35 x 0.33 x 0.3 mm                                                                                                   |

Theta range for data collection 1.23 to 24.99 deg.

Limiting indices  $-13 \leq h \leq 11$ ,  $-5 \leq k \leq 5$ ,  $-35 \leq l \leq 39$

Reflections collected / unique 7664 / 3352 [R(int) = 0.0786]

Completeness to theta = 24.99 97.0 %

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

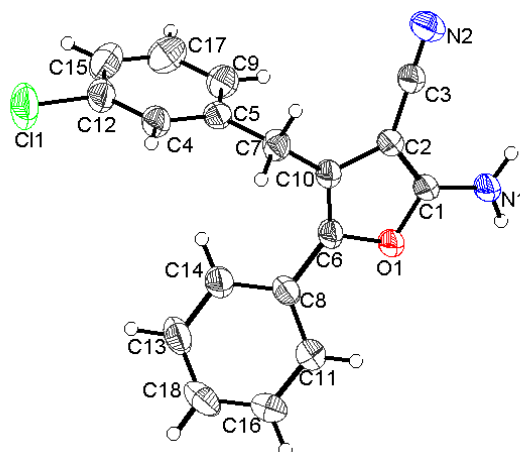
Data / restraints / parameters 3256 / 0 / 218

Goodness-of-fit on  $F^2$  1.072

Final R indices [ $I > 2\sigma(I)$ ] R1 = 0.0718, wR2 = 0.1954

R indices (all data) R1 = 0.1590, wR2 = 0.2375

Largest diff. peak and hole 0.805 and -0.509 e.Å<sup>-3</sup>



**2d** (CCDC 1858658)

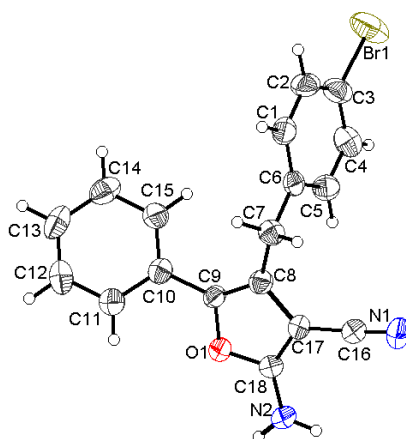
Fig. S2 Molecular structure of 2-amino-5-aryl-4-benzylfuran-3-carbonitrile **2d**, non-hydrogen atoms are shown at the 30% probability level.

Table S2. Crystal data and structure refinement for **2d**.

|                             |                                                                                                                                           |  |
|-----------------------------|-------------------------------------------------------------------------------------------------------------------------------------------|--|
| Identification code         | <b>2d</b>                                                                                                                                 |  |
| Empirical formula           | $C_{18}H_{13}ClN_2O$                                                                                                                      |  |
| Formula weight              | 308.75                                                                                                                                    |  |
| Temperature                 | 298 K                                                                                                                                     |  |
| Wavelength                  | 0.71073 Å                                                                                                                                 |  |
| Crystal system, space group | Triclinic, P-1                                                                                                                            |  |
| Unit cell dimensions        | $a = 6.3411(18)$ Å $\alpha = 93.165(9)$ deg.<br>$b = 7.109(2)$ Å $\beta = 92.574(9)$ deg.<br>$c = 16.557(5)$ Å $\gamma = 92.317(10)$ deg. |  |
| Volume                      | $743.8(4)$ Å <sup>3</sup>                                                                                                                 |  |
| Z, Calculated density       | 2, 1.379 Mg/m <sup>3</sup>                                                                                                                |  |
| Absorption coefficient      | 0.259 mm <sup>-1</sup>                                                                                                                    |  |

|                                      |                                                                |
|--------------------------------------|----------------------------------------------------------------|
| F(000)                               | 320                                                            |
| Crystal size                         | 0.35 x 0.33 x 0.3 mm                                           |
| Theta range for data collection      | 1.23 to 27.49 deg.                                             |
| Limiting indices                     | $-8 \leq h \leq 8$ , $-9 \leq k \leq 9$ , $-21 \leq l \leq 21$ |
| Reflections collected / unique       | 11288 / 3420 [R(int) = 0.0310]                                 |
| Completeness to theta = 27.49        | 98.1 %                                                         |
| Absorption correction                | None                                                           |
| Refinement method                    | Full-matrix least-squares on $F^2$                             |
| Data / restraints / parameters       | 3353 / 0 / 199                                                 |
| Goodness-of-fit on $F^2$             | 1.061                                                          |
| Final R indices [ $I > 2\sigma(I)$ ] | R1 = 0.0463, wR2 = 0.1120                                      |
| R indices (all data)                 | R1 = 0.0709, wR2 = 0.1297                                      |
| Largest diff. peak and hole          | 0.305 and -0.352 e. $\text{\AA}^{-3}$                          |





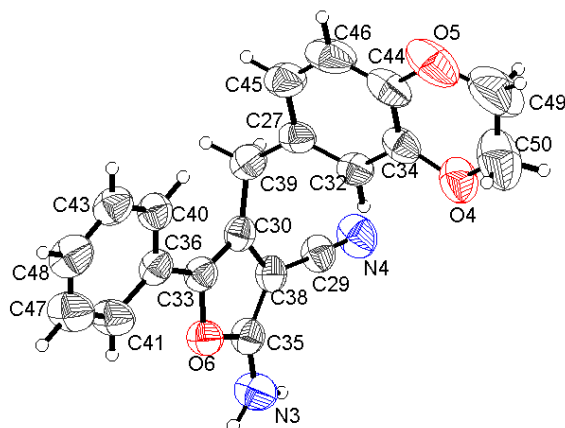
**2k** (CCDC 1908517)

Fig. S3 Molecular structure of 2-amino-5-aryl-4-benzylfuran-3-carbonitrile **2k**, non-hydrogen atoms are shown at the 30% probability level.

Table S3. Crystal data and structure refinement for **2k**.

|                             |                                                     |                                                                        |
|-----------------------------|-----------------------------------------------------|------------------------------------------------------------------------|
| Identification code         | <b>2k</b>                                           |                                                                        |
| Empirical formula           | C <sub>18</sub> H <sub>13</sub> Br N <sub>2</sub> O |                                                                        |
| Formula weight              | 353.20                                              |                                                                        |
| Temperature                 | 298 K                                               |                                                                        |
| Wavelength                  | 0.71073 Å                                           |                                                                        |
| Crystal system, space group | Triclinic, P-1                                      |                                                                        |
| Unit cell dimensions        | a = 6.192(5) Å<br>b = 7.311(2) Å<br>c = 16.718(3) Å | alpha = 87.67(2) deg.<br>beta = 85.16(3) deg.<br>gamma = 86.34(2) deg. |
| Volume                      | 752.1(7) Å <sup>3</sup>                             |                                                                        |
| Z, Calculated density       | 2, 1.560 Mg/m <sup>3</sup>                          |                                                                        |
| Absorption coefficient      | 2.736 mm <sup>-1</sup>                              |                                                                        |

|                                      |                                                                |
|--------------------------------------|----------------------------------------------------------------|
| F(000)                               | 356                                                            |
| Crystal size                         | 0.5 x 0.35 x 0.33 mm                                           |
| Theta range for data collection      | 1.22 to 24.99 deg.                                             |
| Limiting indices                     | $-7 \leq h \leq 7$ , $-8 \leq k \leq 8$ , $-19 \leq l \leq 19$ |
| Reflections collected / unique       | 9835 / 2646 [R(int) = 0.0376]                                  |
| Completeness to theta = 24.99        | 99.5 %                                                         |
| Absorption correction                | Semi-empirical from equivalents                                |
| Max. and min. transmission           | 0.788 and 0.729                                                |
| Refinement method                    | Full-matrix least-squares on $F^2$                             |
| Data / restraints / parameters       | 2632 / 0 / 199                                                 |
| Goodness-of-fit on $F^2$             | 1.042                                                          |
| Final R indices [ $I > 2\sigma(I)$ ] | R1 = 0.0623, wR2 = 0.1719                                      |
| R indices (all data)                 | R1 = 0.0770, wR2 = 0.1831                                      |
| Largest diff. peak and hole          | 0.707 and -0.595 e.Å <sup>-3</sup>                             |



**2n** (CCDC 1875320)

Fig. S4 Molecular structure of 2-amino-5-aryl-4-benzylfuran-3-carbonitrile **2n**, non-hydrogen atoms are shown at the 30% probability level.

Table S4. Crystal data and structure refinement for **2n**.

|                             |                                                                                                                                            |
|-----------------------------|--------------------------------------------------------------------------------------------------------------------------------------------|
| Identification code         | <b>2n</b>                                                                                                                                  |
| Empirical formula           | C <sub>20</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub>                                                                              |
| Formula weight              | 332.35                                                                                                                                     |
| Temperature                 | 298 K                                                                                                                                      |
| Wavelength                  | 0.71073 Å                                                                                                                                  |
| Crystal system, space group | Triclinic, P-1                                                                                                                             |
| Unit cell dimensions        | a = 9.8735(10) Å    alpha = 104.559(3) deg.<br>b = 11.1925(13) Å    beta = 102.943(3) deg.<br>c = 16.3751(18) Å    gamma = 102.875(3) deg. |
| Volume                      | 1630.6(3) Å <sup>3</sup>                                                                                                                   |
| Z, Calculated density       | 4, 1.354 Mg/m <sup>3</sup>                                                                                                                 |
| Absorption coefficient      | 0.092 mm <sup>-1</sup>                                                                                                                     |
| F(000)                      | 696                                                                                                                                        |
| Crystal size                | 0.35 x 0.33 x 0.3 mm                                                                                                                       |

Theta range for data collection 1.35 to 27.55 deg.

Limiting indices -12 $\leq$ h $\leq$ 12, -14 $\leq$ k $\leq$ 14, -21 $\leq$ l $\leq$ 21

Reflections collected / unique 25810 / 7544 [R(int) = 0.0370]

Completeness to theta = 27.55 99.1 %

Absorption correction None

Refinement method Full-matrix least-squares on F<sup>2</sup>

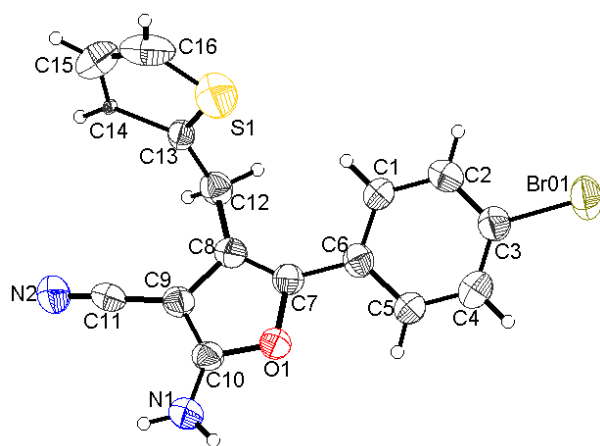
Data / restraints / parameters 7477 / 1 / 451

Goodness-of-fit on F<sup>2</sup> 1.033

Final R indices [I $>$ 2 $\sigma$ (I)] R1 = 0.0658, wR2 = 0.1675

R indices (all data) R1 = 0.1062, wR2 = 0.1904

Largest diff. peak and hole 0.509 and -0.458 e. $\text{\AA}^{-3}$



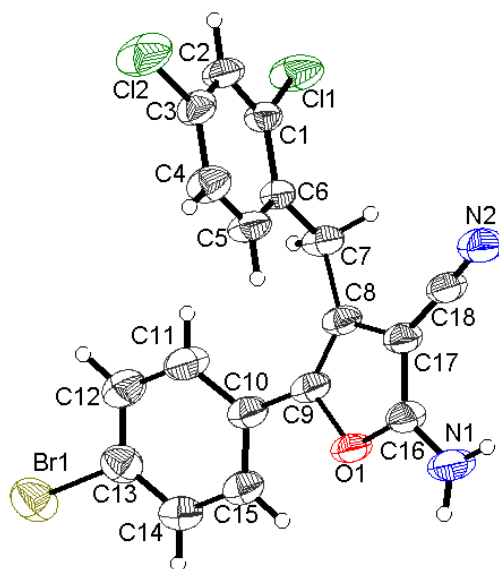
**2q** (CCDC 1880678)

Fig. S5 Molecular structure of 2-amino-5-aryl-4-benzylfuran-3-carbonitrile **2q**, non-hydrogen atoms are shown at the 30% probability level.

Table S5. Crystal data and structure refinement for **2q**.

|                             |                                                                                                                          |
|-----------------------------|--------------------------------------------------------------------------------------------------------------------------|
| Identification code         | <b>2q</b>                                                                                                                |
| Empirical formula           | C <sub>16</sub> H <sub>11</sub> BrN <sub>2</sub> OS                                                                      |
| Formula weight              | 359.23                                                                                                                   |
| Temperature                 | 298 K                                                                                                                    |
| Wavelength                  | 0.71073 Å                                                                                                                |
| Crystal system, space group | Triclinic, P-1                                                                                                           |
| Unit cell dimensions        | a = 4.73(1) Å    alpha = 77.0(1) deg.<br>b = 10.20(2) Å    beta = 86.0(1) deg.<br>c = 16.80(2) Å    gamma = 77.3(1) deg. |
| Volume                      | 770(2) Å <sup>3</sup>                                                                                                    |
| Z, Calculated density       | 2, 1.550 Mg/m <sup>3</sup>                                                                                               |
| Absorption coefficient      | 2.804 mm <sup>-1</sup>                                                                                                   |
| F(000)                      | 360                                                                                                                      |

|                                      |                                                                  |
|--------------------------------------|------------------------------------------------------------------|
| Crystal size                         | 0.35 x 0.33 x 0.3 mm                                             |
| Theta range for data collection      | 1.24 to 27.43 deg.                                               |
| Limiting indices                     | $-6 \leq h \leq 6$ , $-13 \leq k \leq 13$ , $-21 \leq l \leq 21$ |
| Reflections collected / unique       | 11664 / 3502 [R(int) = 0.0622]                                   |
| Completeness to theta = 27.43        | 97.9 %                                                           |
| Absorption correction                | Semi-empirical from equivalents                                  |
| Max. and min. transmission           | 1.0000 and 0.7961                                                |
| Refinement method                    | Full-matrix least-squares on $F^2$                               |
| Data / restraints / parameters       | 3436 / 3 / 190                                                   |
| Goodness-of-fit on $F^2$             | 1.048                                                            |
| Final R indices [ $I > 2\sigma(I)$ ] | R1 = 0.0803, wR2 = 0.2162                                        |
| R indices (all data)                 | R1 = 0.1723, wR2 = 0.2648                                        |
| Largest diff. peak and hole          | 1.353 and -0.896 e. $\text{\AA}^{-3}$                            |



**2r** (CCDC 1908518)

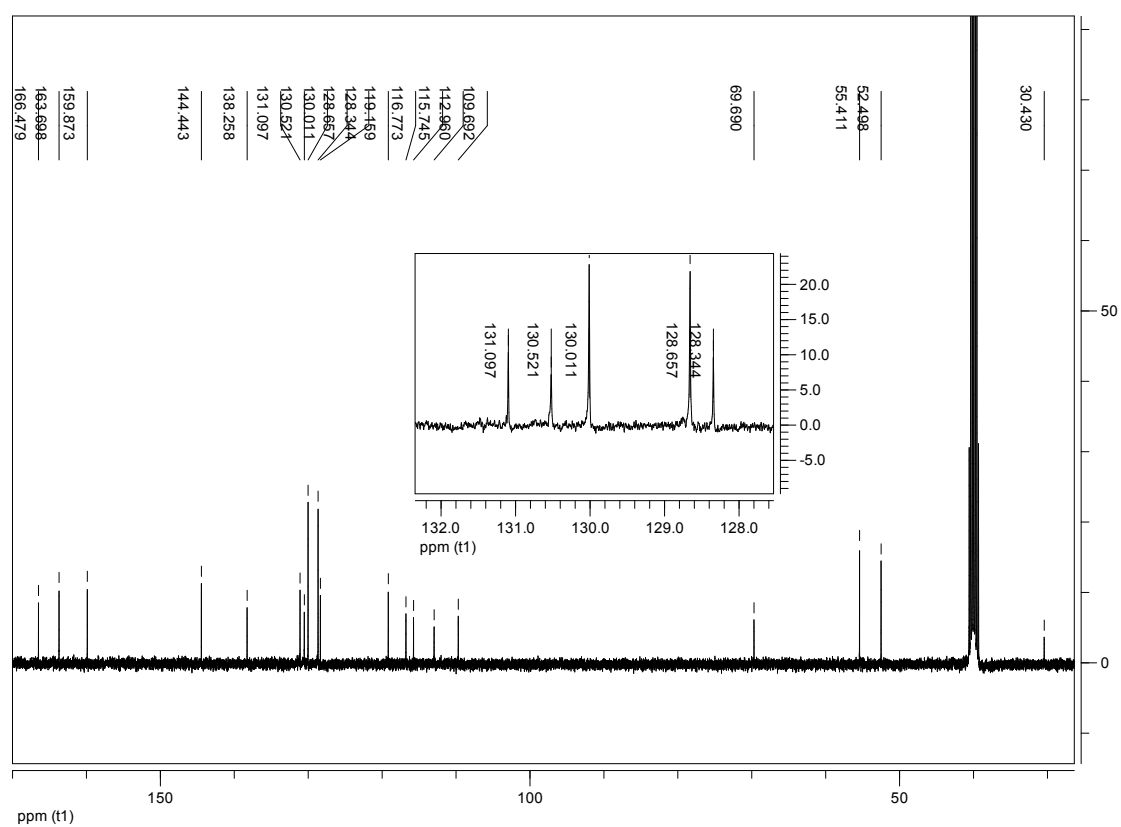
Fig. S6 Molecular structure of 2-amino-5-aryl-4-benzylfuran-3-carbonitrile **2r**, non-hydrogen atoms are shown at the 30% probability level.

Table S6. Crystal data and structure refinement for **2r**.

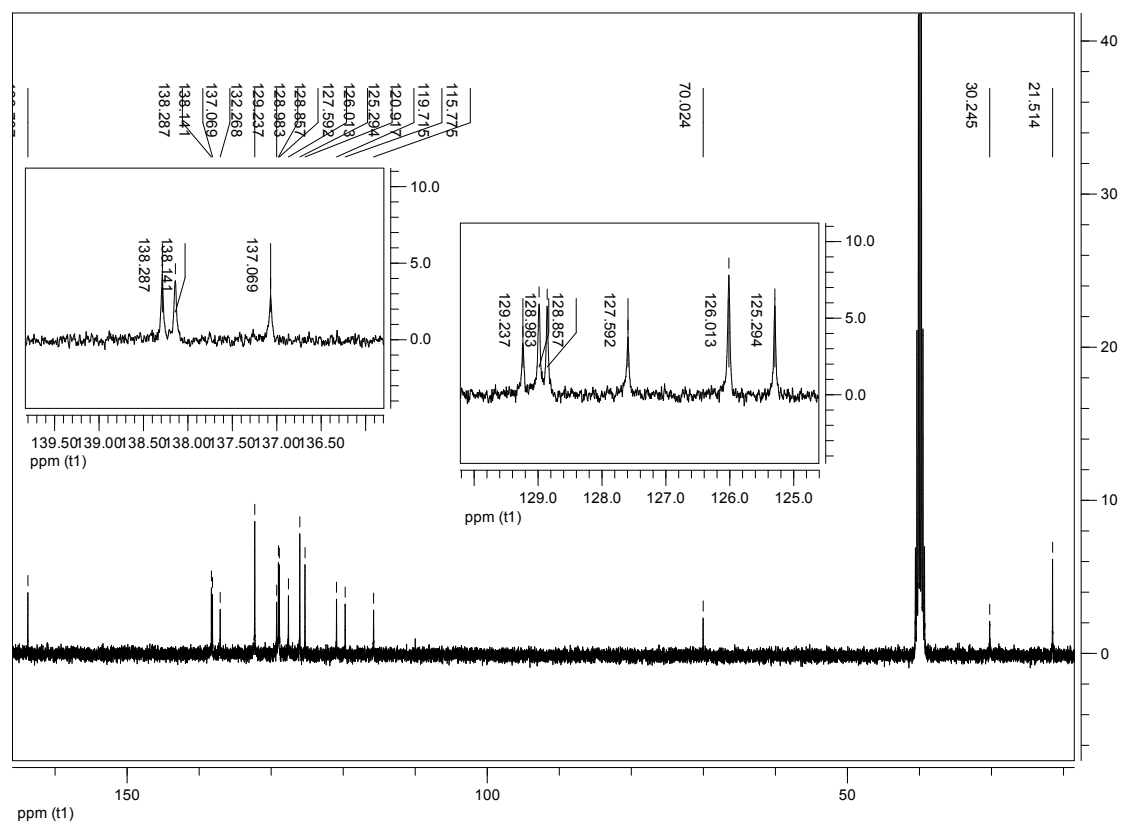
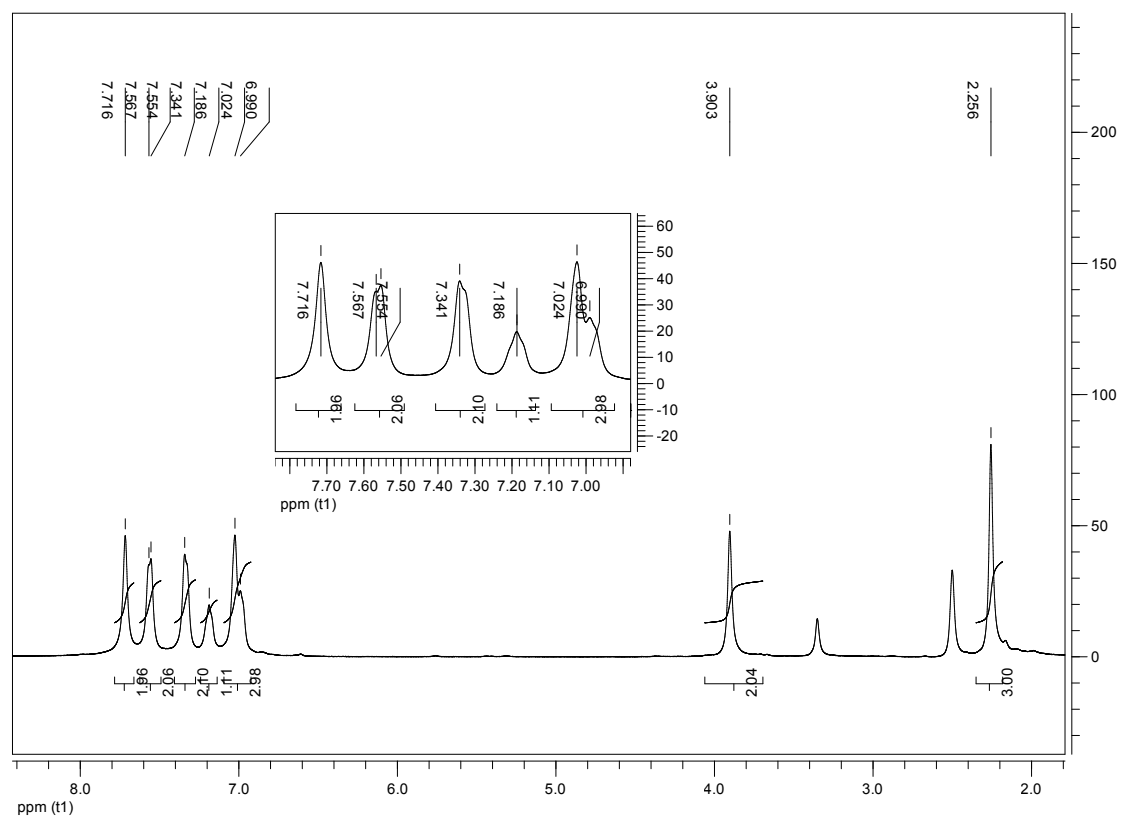
|                             |                                                                     |                                                                                 |
|-----------------------------|---------------------------------------------------------------------|---------------------------------------------------------------------------------|
| Identification code         | <b>2r</b>                                                           |                                                                                 |
| Empirical formula           | C <sub>18</sub> H <sub>11</sub> Br Cl <sub>2</sub> N <sub>2</sub> O |                                                                                 |
| Formula weight              | 422.09                                                              |                                                                                 |
| Temperature                 | 298 K                                                               |                                                                                 |
| Wavelength                  | 0.71073 Å                                                           |                                                                                 |
| Crystal system, space group | Triclinic, P-1                                                      |                                                                                 |
| Unit cell dimensions        | a = 8.722(5) Å<br>b = 9.677(6) Å<br>c = 11.637(8) Å                 | alpha = 101.028(14) deg.<br>beta = 103.348(17) deg.<br>gamma = 112.332(11) deg. |
| Volume                      | 840.4(9) Å <sup>3</sup>                                             |                                                                                 |
| Z, Calculated density       | 2, 1.668 Mg/m <sup>3</sup>                                          |                                                                                 |
| Absorption coefficient      | 2.770 mm <sup>-1</sup>                                              |                                                                                 |

|                                   |                                             |
|-----------------------------------|---------------------------------------------|
| F(000)                            | 420                                         |
| Crystal size                      | 0.5 x 0.35 x 0.3 mm                         |
| Theta range for data collection   | 1.89 to 27.63 deg.                          |
| Limiting indices                  | -11<=h<=9, -12<=k<=12, -15<=l<=15           |
| Reflections collected / unique    | 13120 / 3910 [R(int) = 0.0247]              |
| Completeness to theta = 27.63     | 99.0 %                                      |
| Absorption correction             | Semi-empirical from equivalents             |
| Max. and min. transmission        | 0.788 and 0.729                             |
| Refinement method                 | Full-matrix least-squares on F <sup>2</sup> |
| Data / restraints / parameters    | 3873 / 0 / 217                              |
| Goodness-of-fit on F <sup>2</sup> | 1.042                                       |
| Final R indices [I>2sigma(I)]     | R1 = 0.0346, wR2 = 0.0814                   |
| R indices (all data)              | R1 = 0.0484, wR2 = 0.0869                   |
| Largest diff. peak and hole       | 0.426 and -0.638 e.A <sup>-3</sup>          |

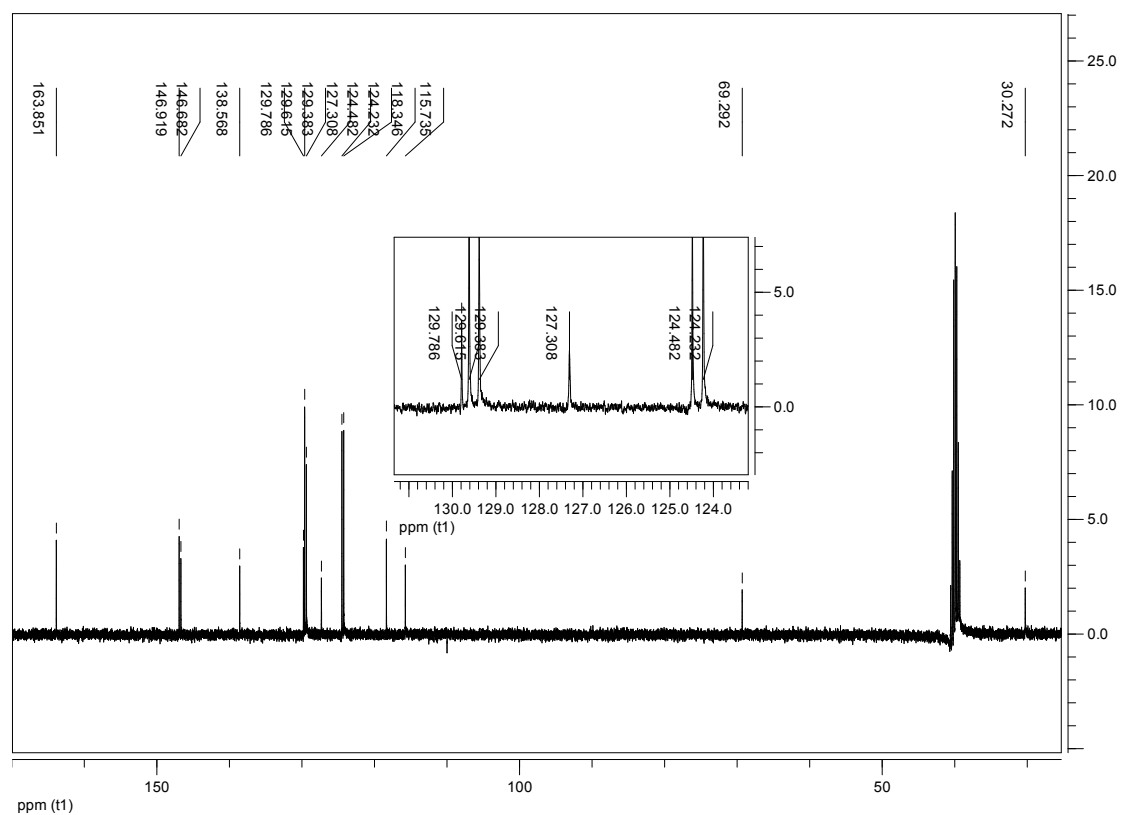
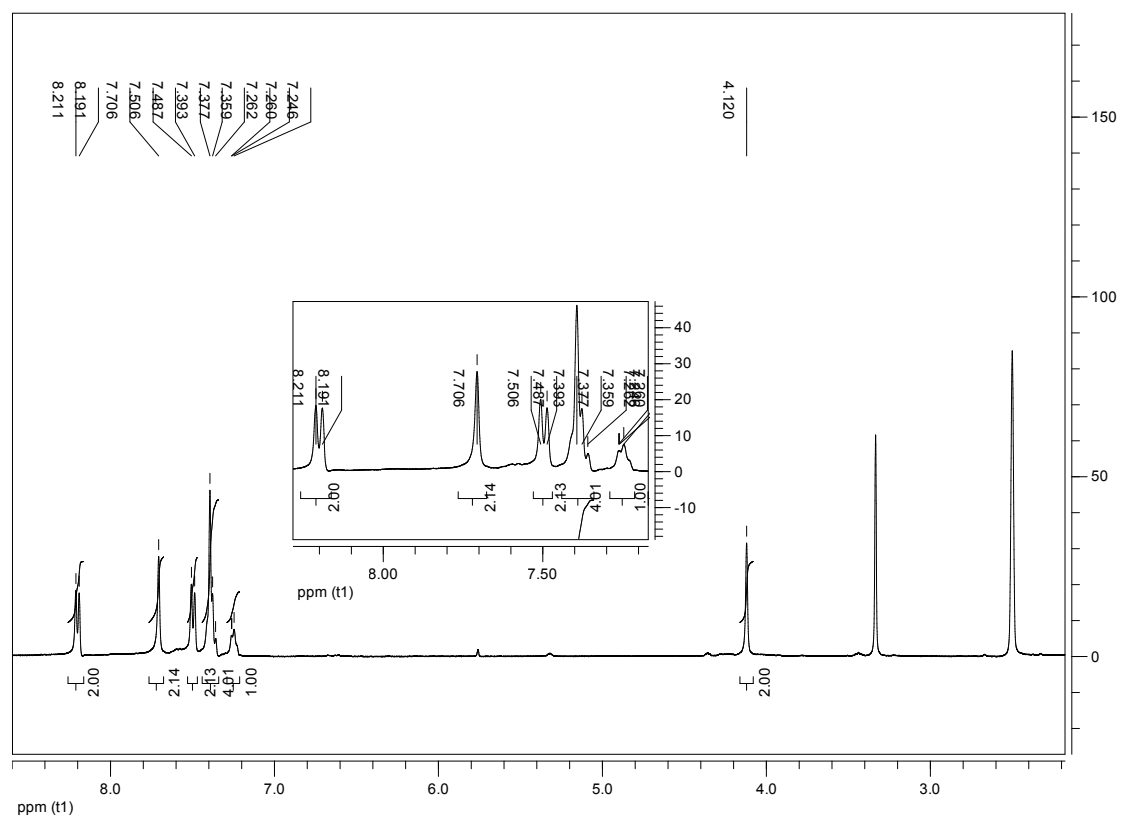




2-Amino-5-(4-bromophenyl)-4-(3-methylbenzyl)furan-3-carbonitrile (**2b**).



2-Amino-4-(4-nitrobenzyl)-5-phenylfuran-3-carbonitrile (**2c**).

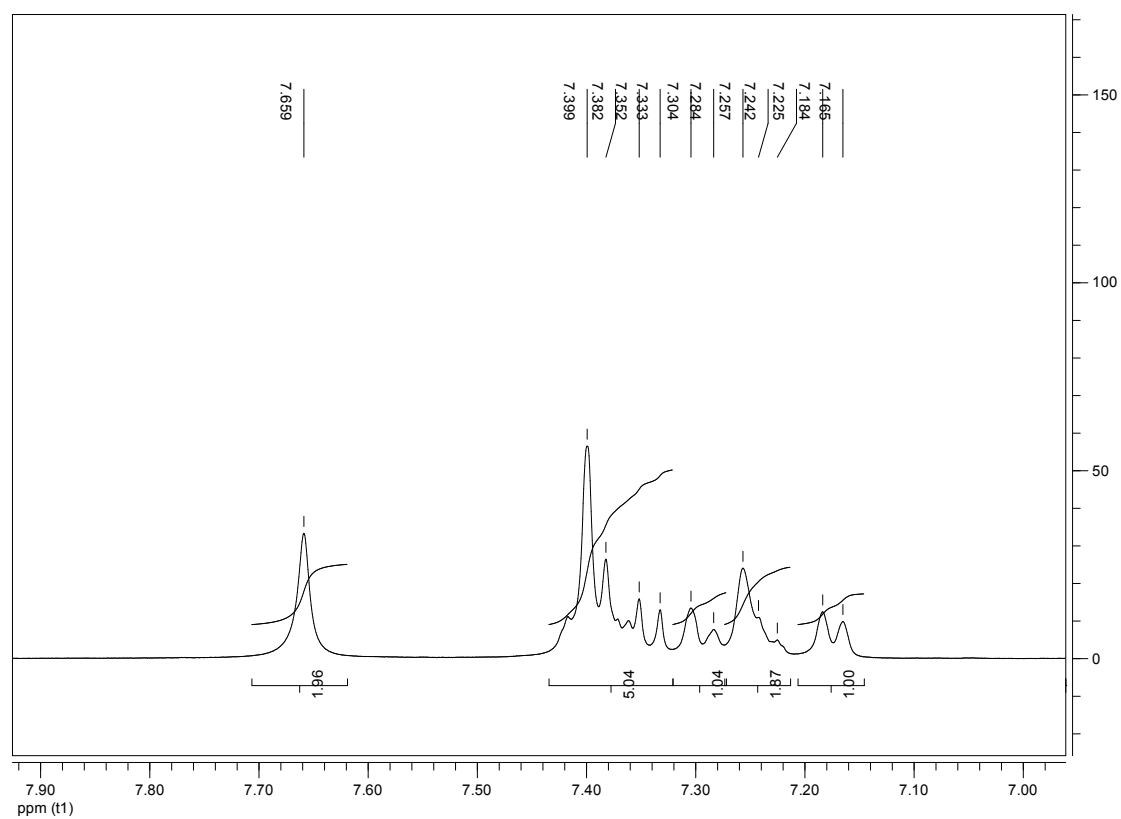


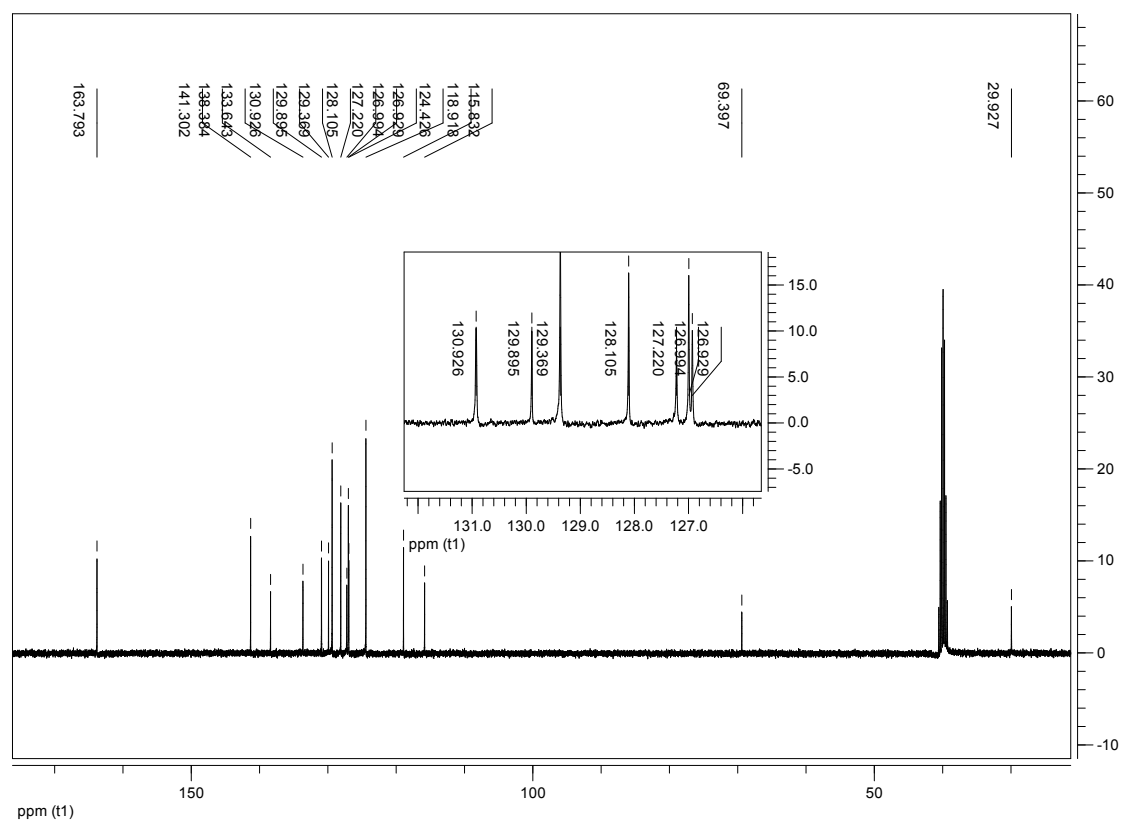
<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of compound 10a. The x-axis represents the chemical shift in ppm (t1), ranging from 8.0 to 3.0. The y-axis represents the intensity. The spectrum shows several peaks, with an inset providing a detailed view of the aromatic region (7.15-7.45 ppm). The inset shows peaks at 7.166, 7.184, 7.225, 7.242, 7.257, 7.304, 7.333, 7.352, 7.382, and 7.399 ppm, with corresponding integration values (0.00, 0.01, 0.04, 0.04, 0.04, 0.04, 0.04, 0.04, 0.04, 0.04).

Chemical shift values (ppm) labeled in the spectrum:

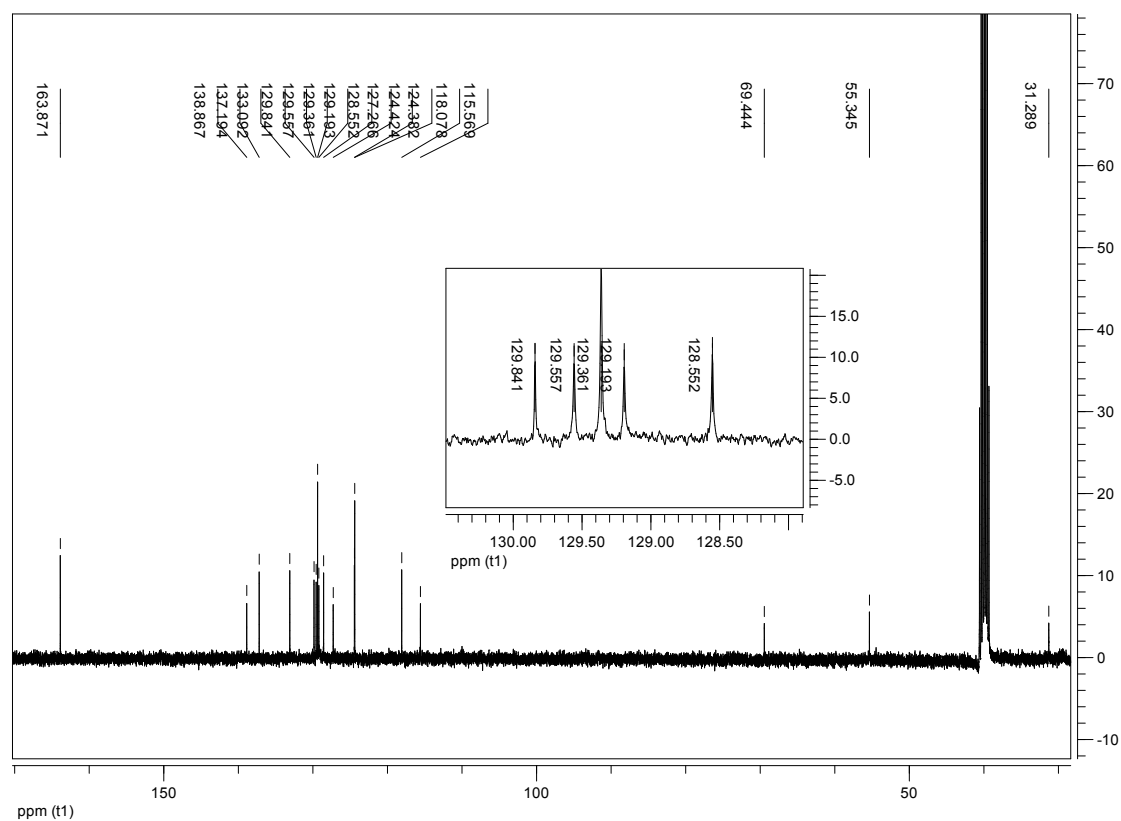
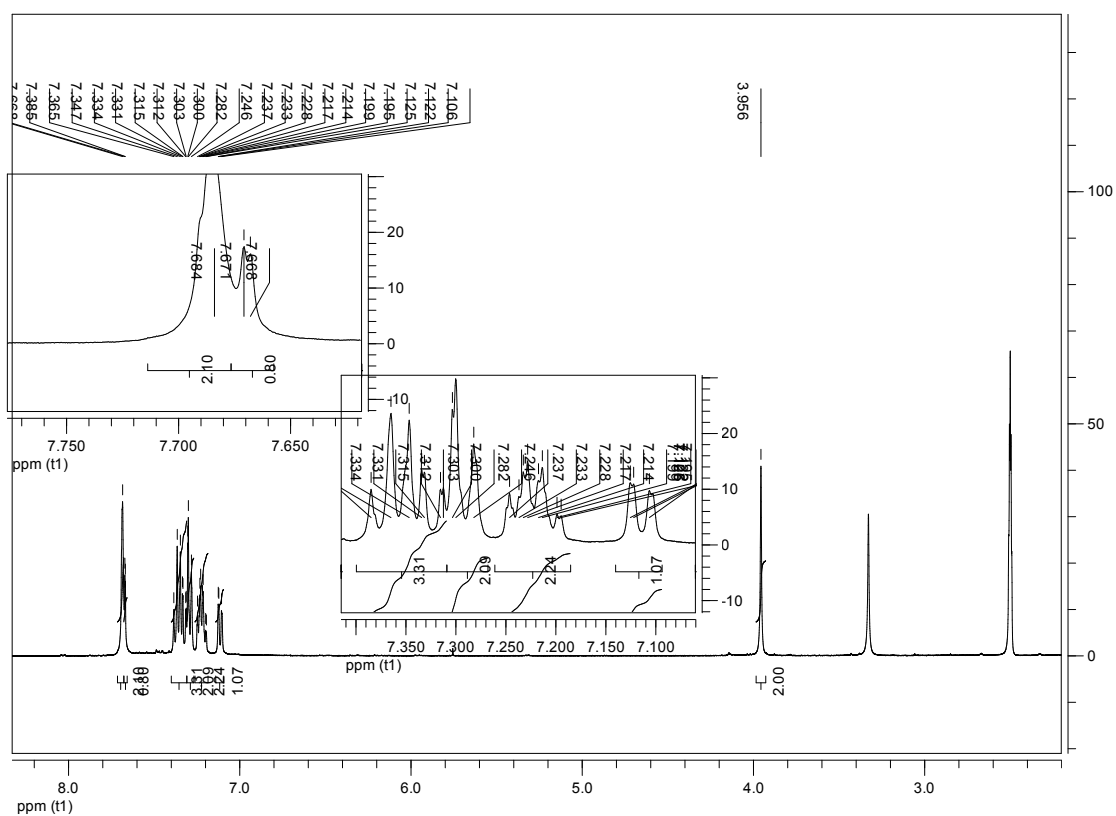
- 7.659
- 7.399
- 7.382
- 7.352
- 7.333
- 7.304
- 7.284
- 7.257
- 7.242
- 7.225
- 7.184
- 7.166
- 3.982

Integration values (from left to right): 0.96, 1.00, 0.04, 0.04, 0.04, 0.04, 0.04, 0.04, 0.04, 0.04, 0.04, 0.04, 0.96.

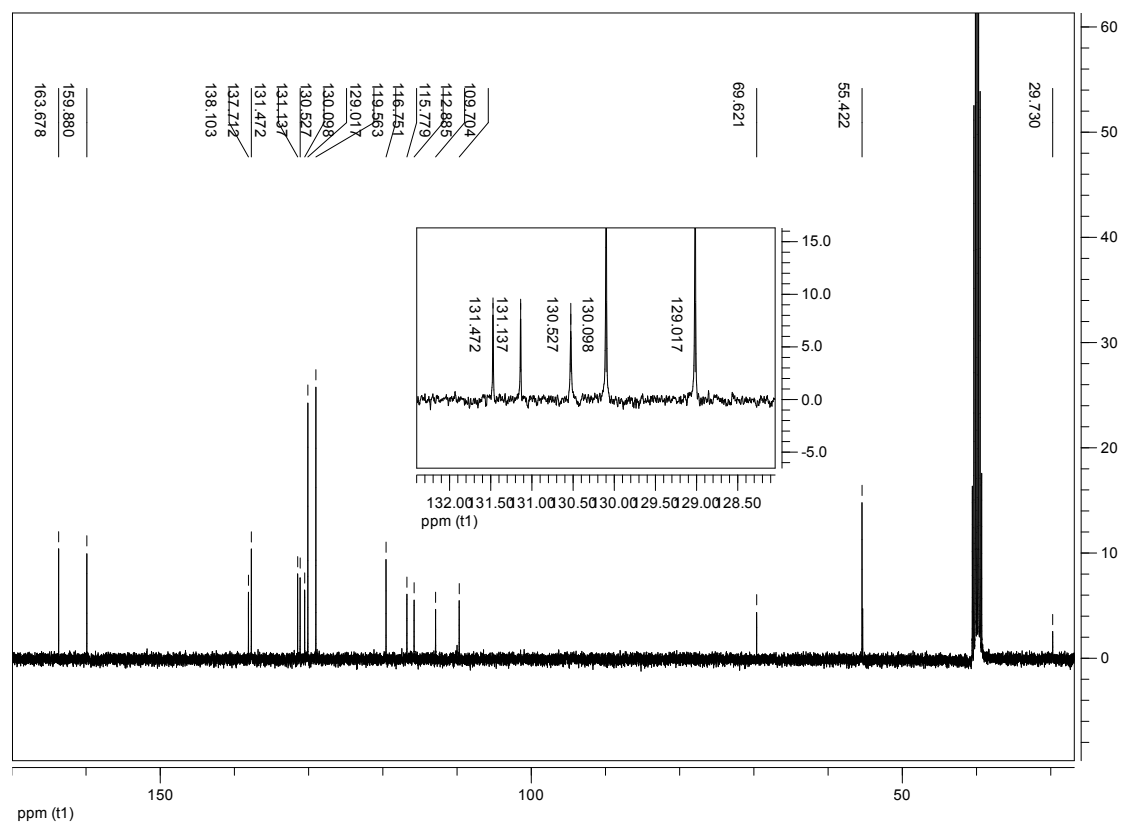
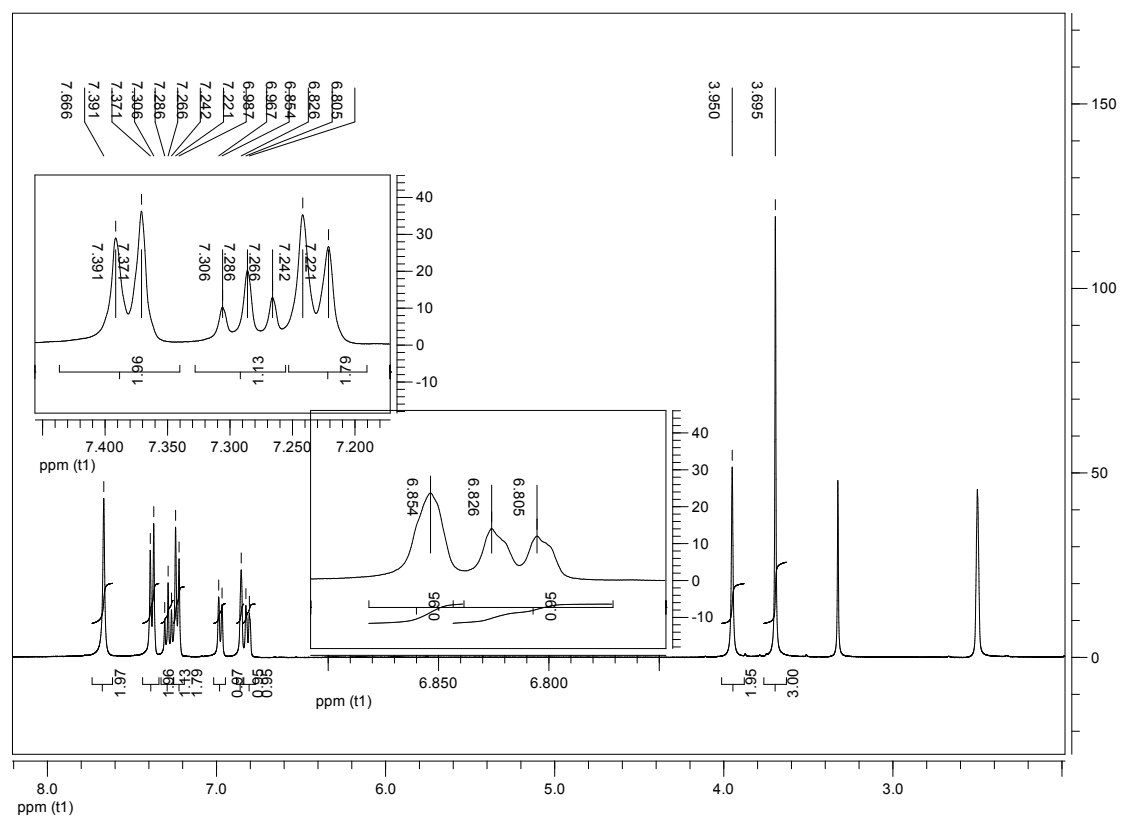




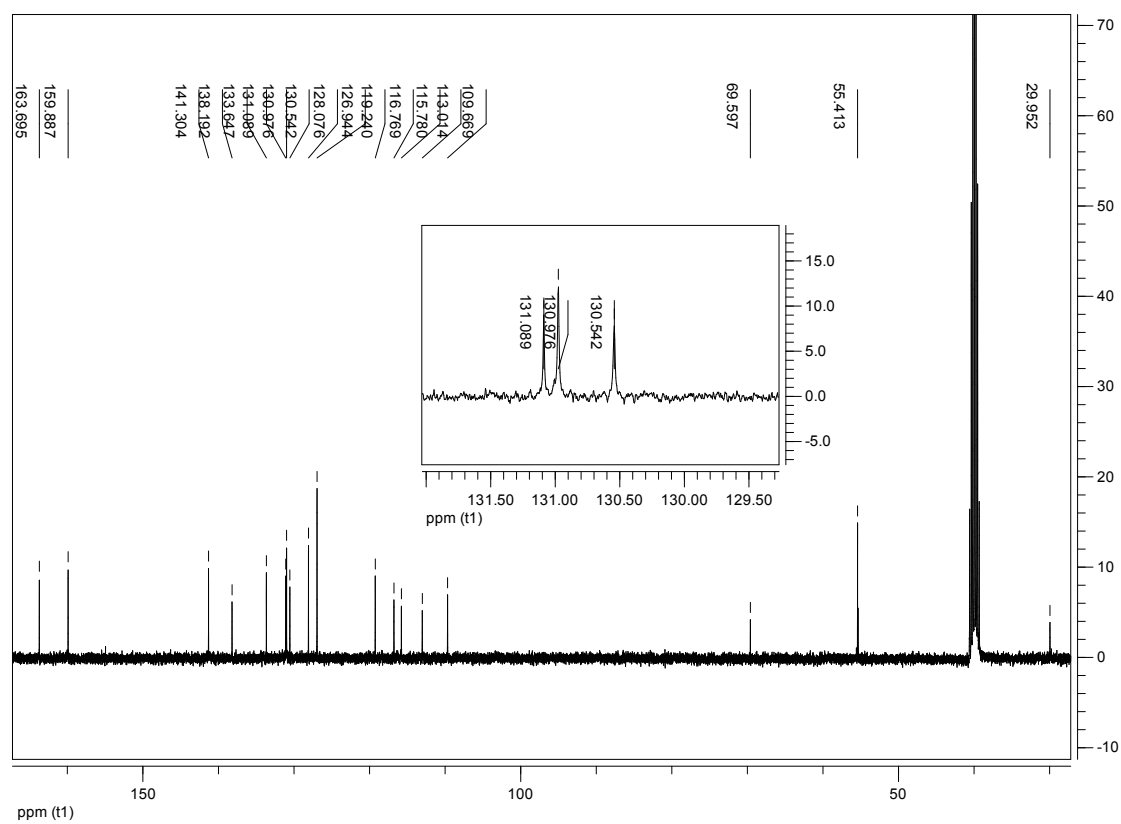
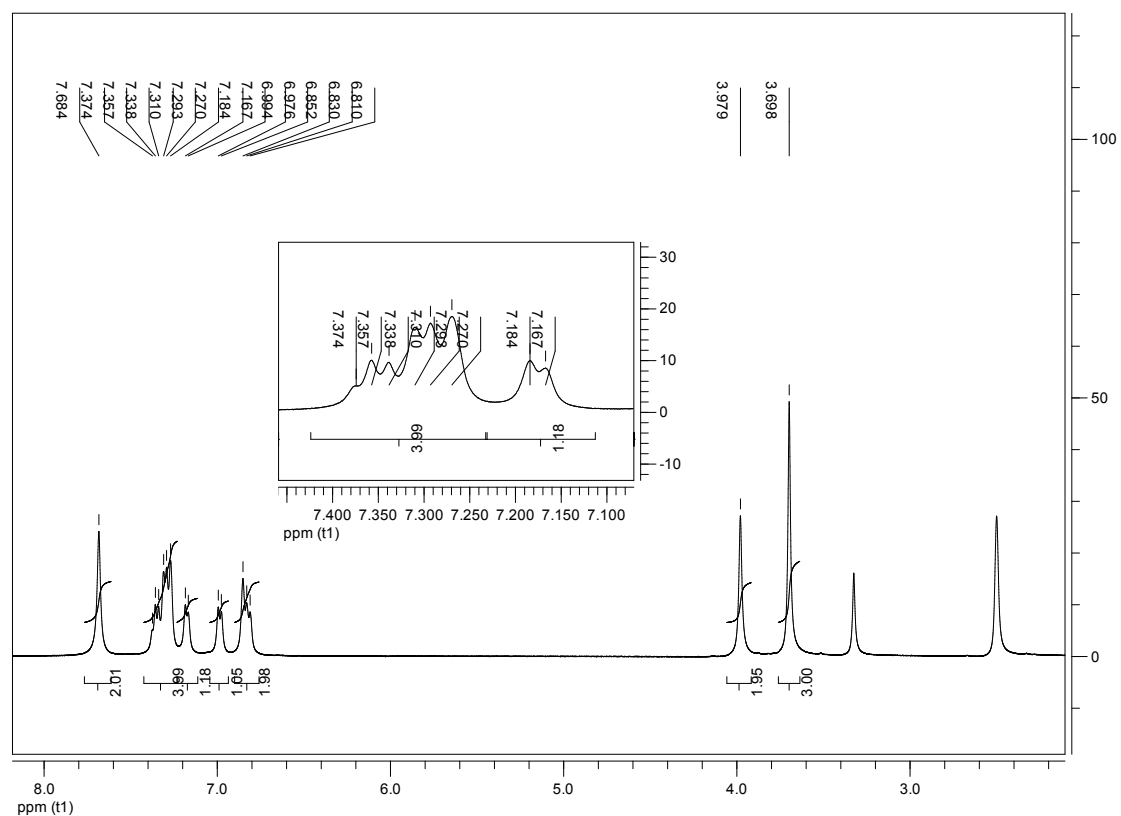
2-Amino-4-(2-bromobenzyl)-5-phenylfuran-3-carbonitrile (**2e**).



2-Amino-4-(4-chlorobenzyl)-5-(3-methoxyphenyl)furan-3-carbonitrile (**2f**).

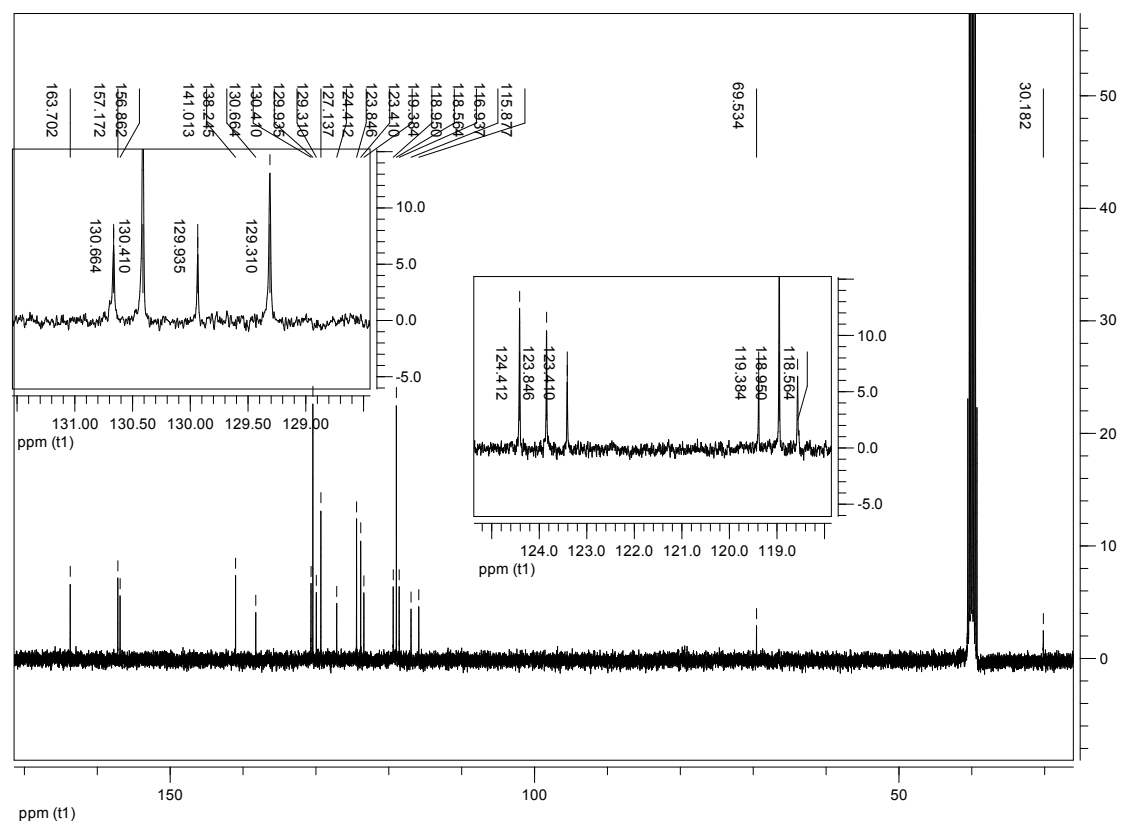
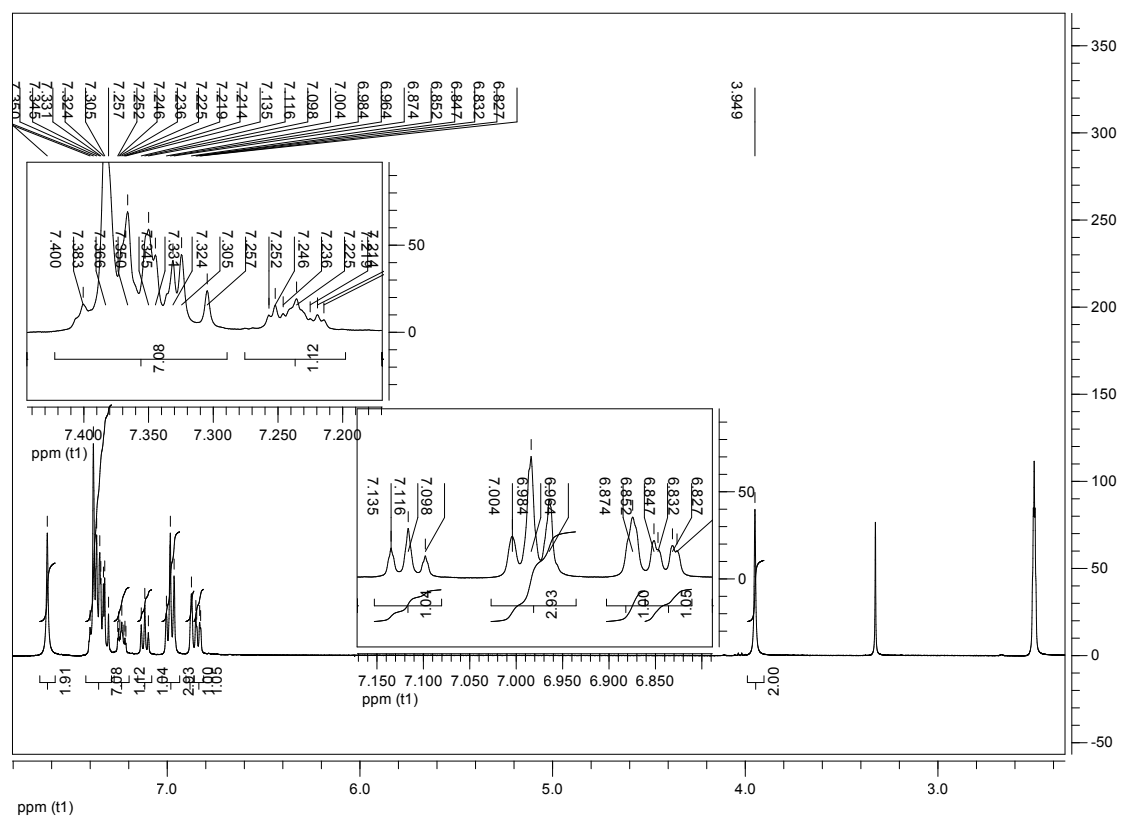


2-Amino-4-(3-chlorobenzyl)-5-(3-methoxyphenyl)furan-3-carbonitrile (**2g**).

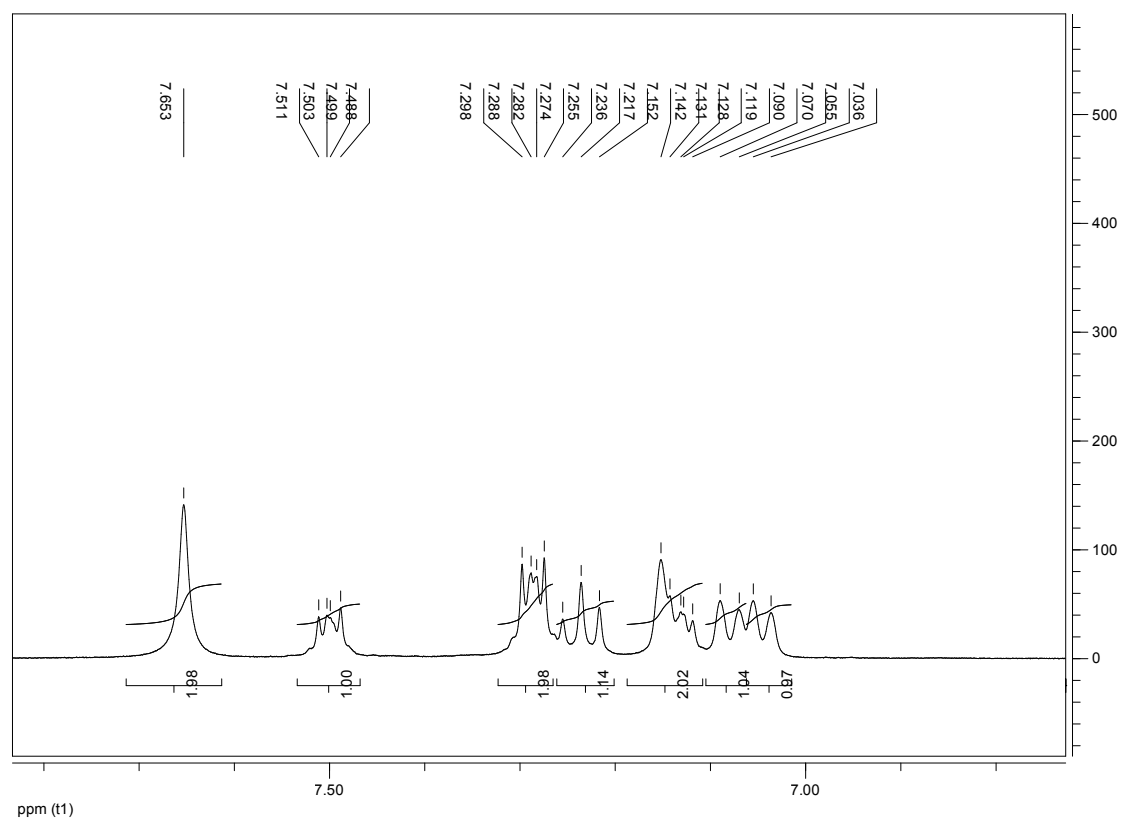
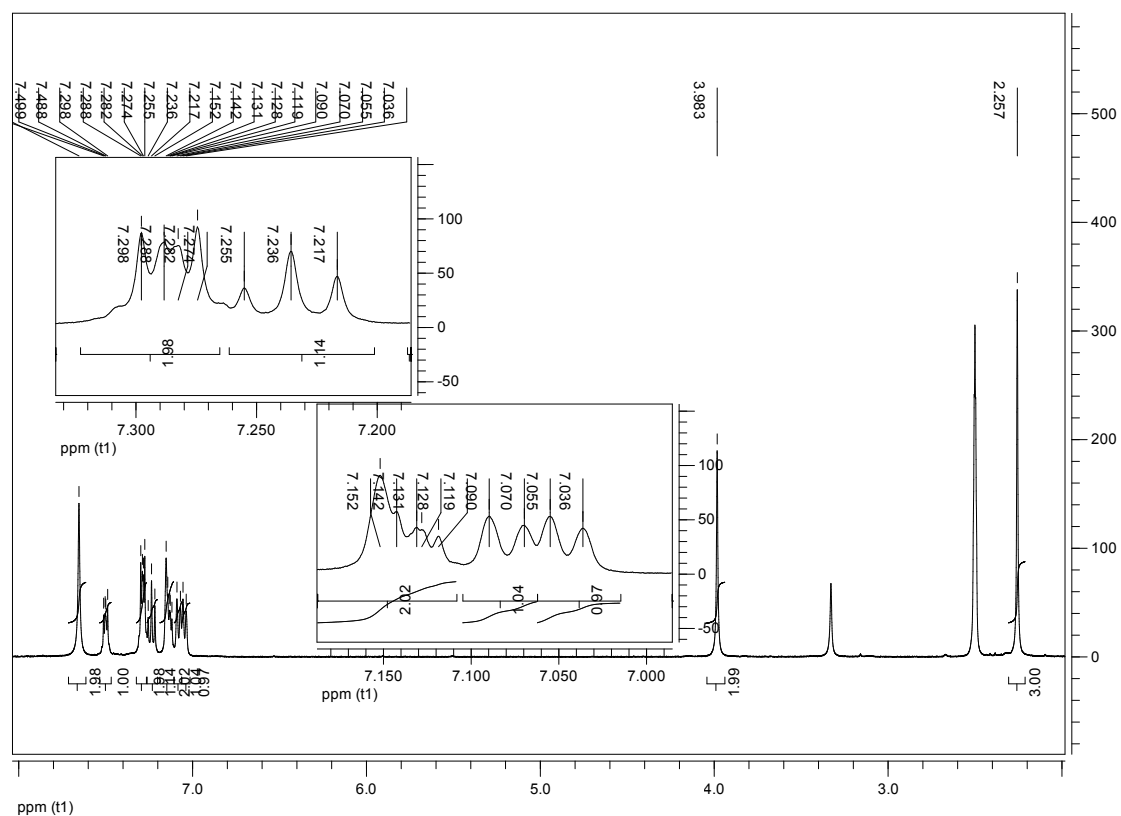


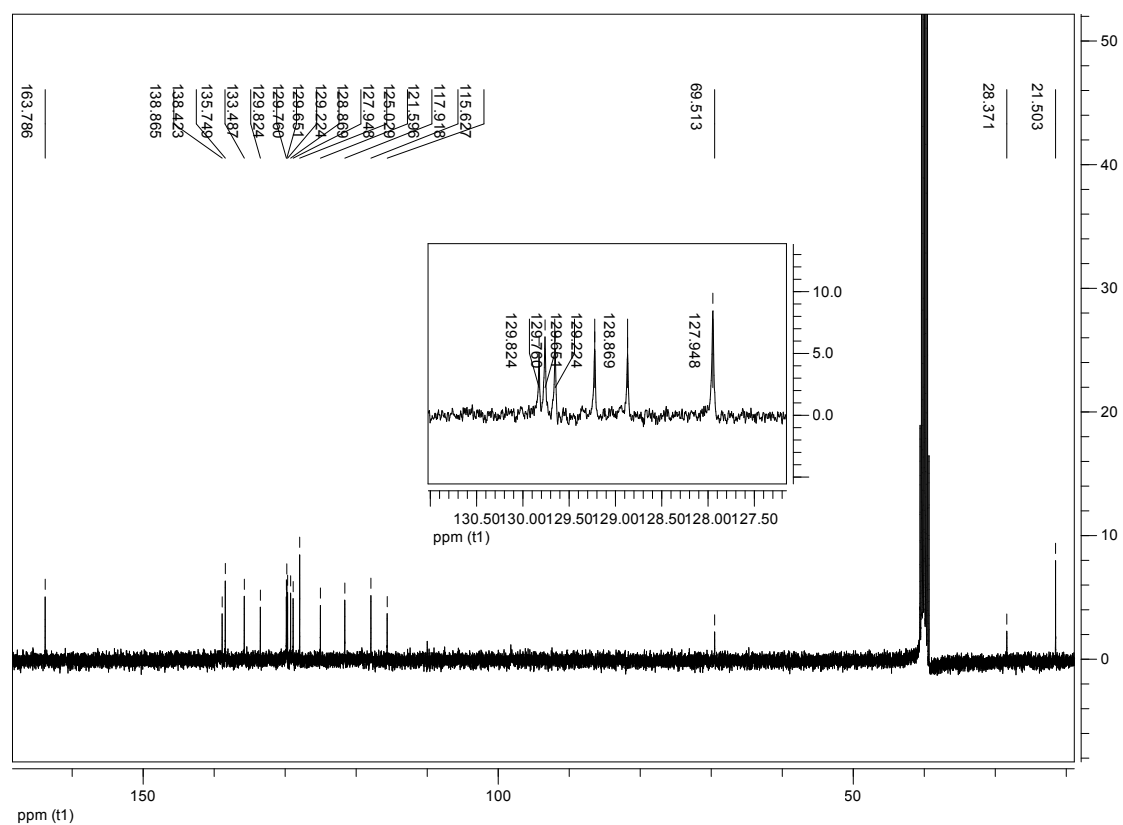


2-Amino-4-(3-phenoxybenzyl)-5-phenylfuran-3-carbonitrile (**2h**).

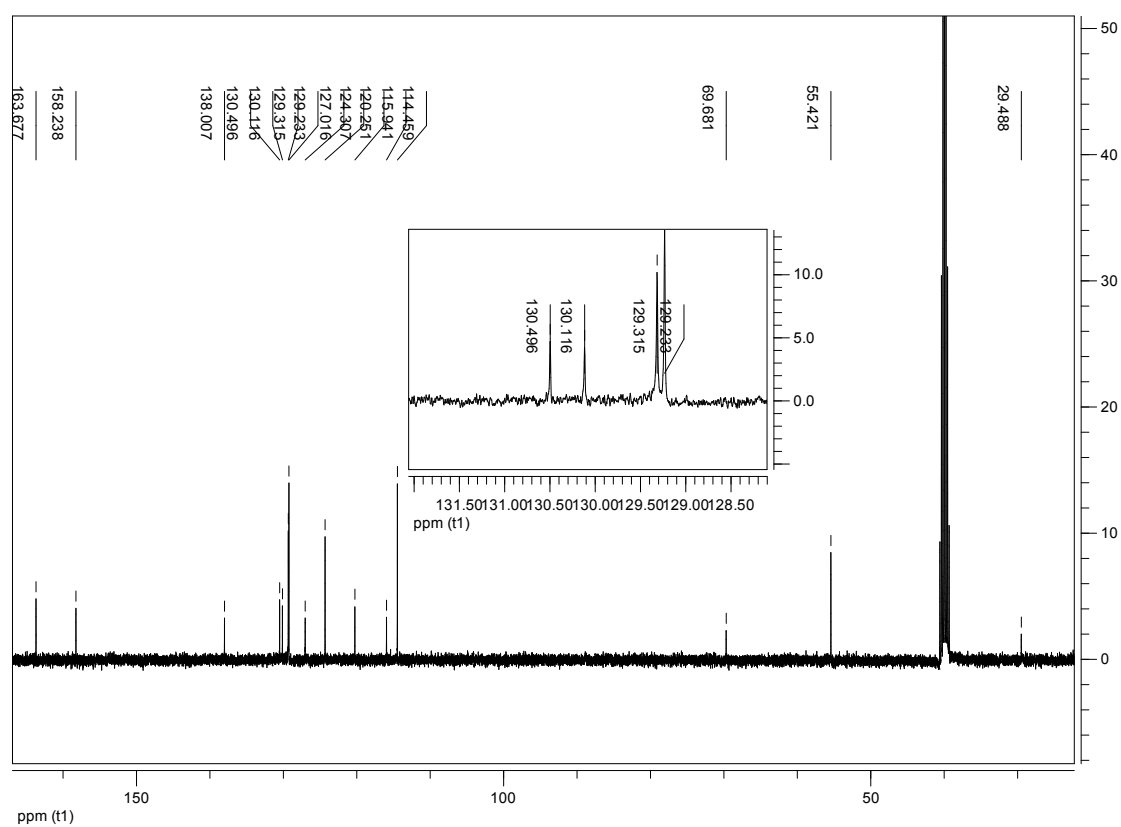
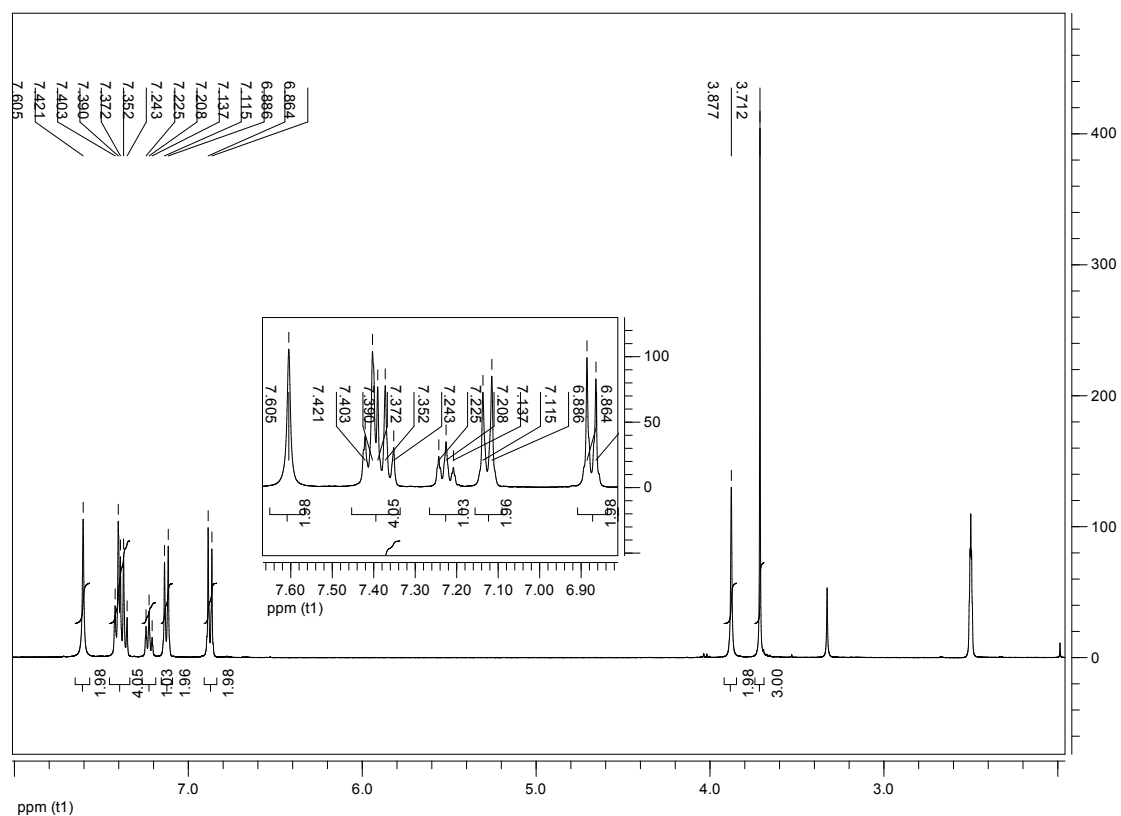


2-Amino-4-(2-chlorobenzyl)-5-(m-tolyl)furan-3-carbonitrile (**2i**).

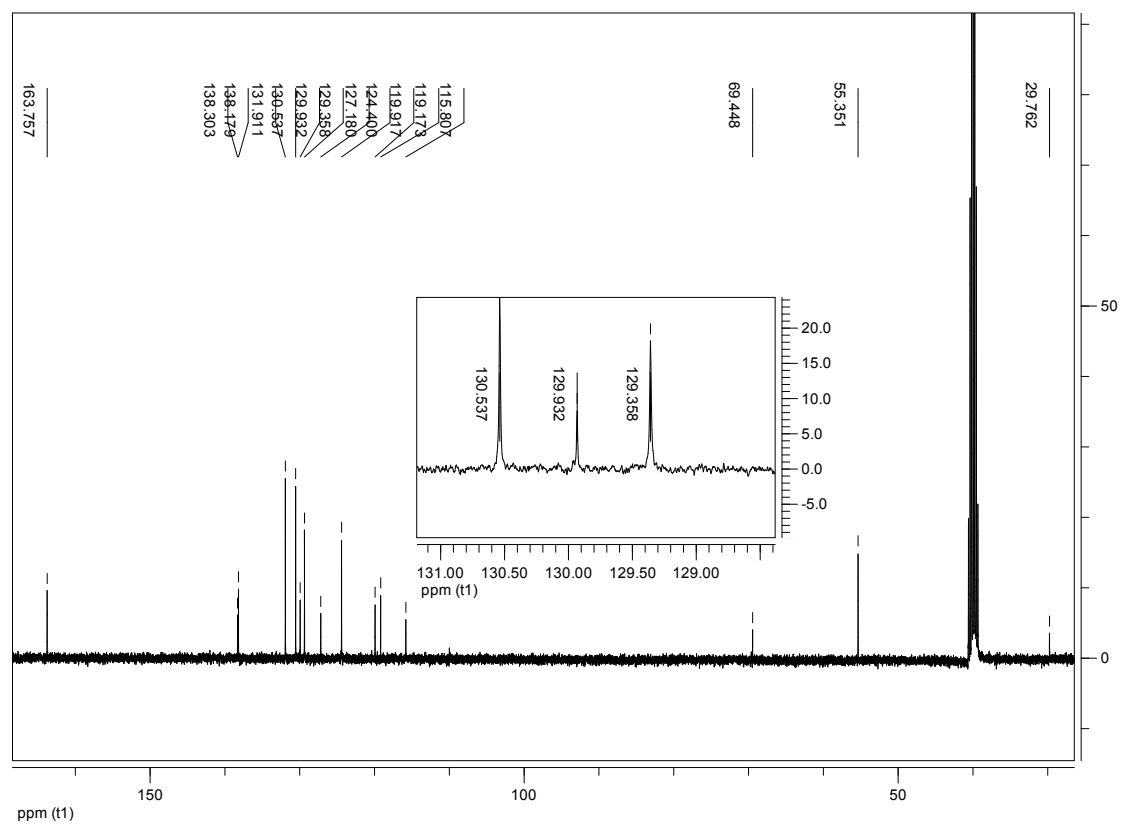
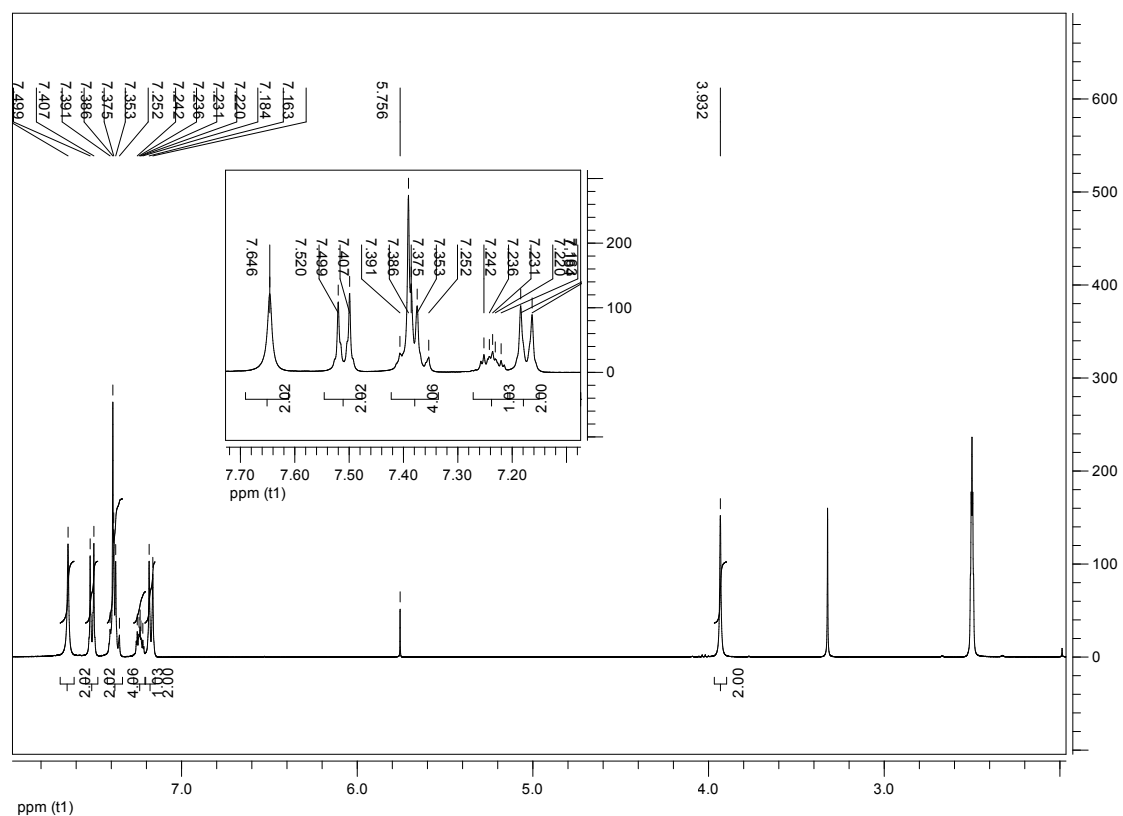


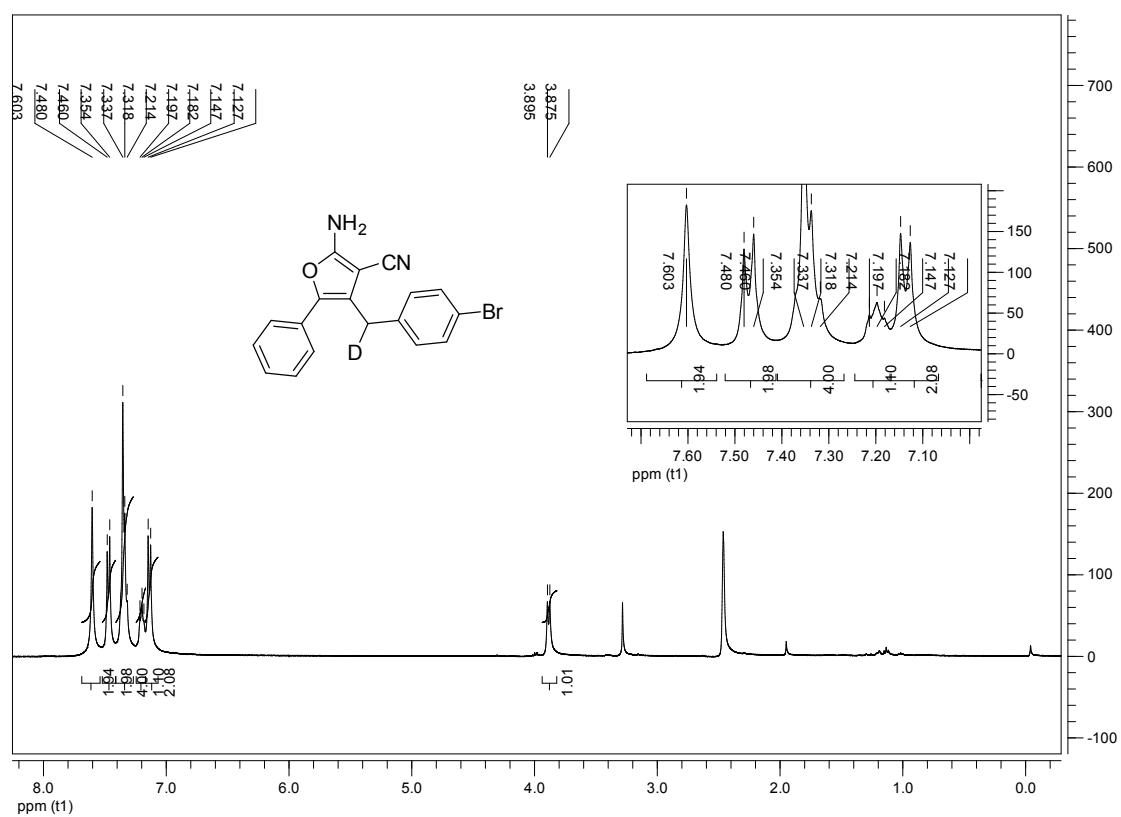


2-Amino-4-(4-methoxybenzyl)-5-phenylfuran-3-carbonitrile (**2j**).



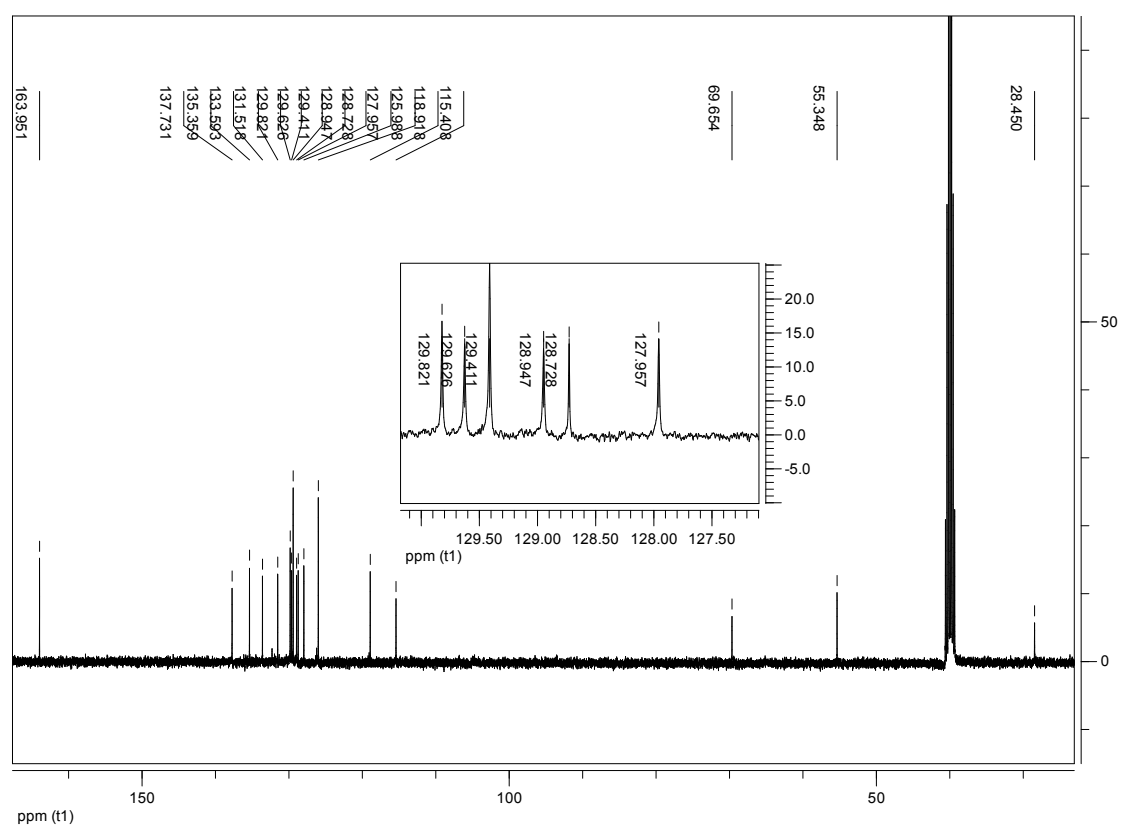
2-Amino-4-(4-bromobenzyl)-5-phenylfuran-3-carbonitrile (**2k**).



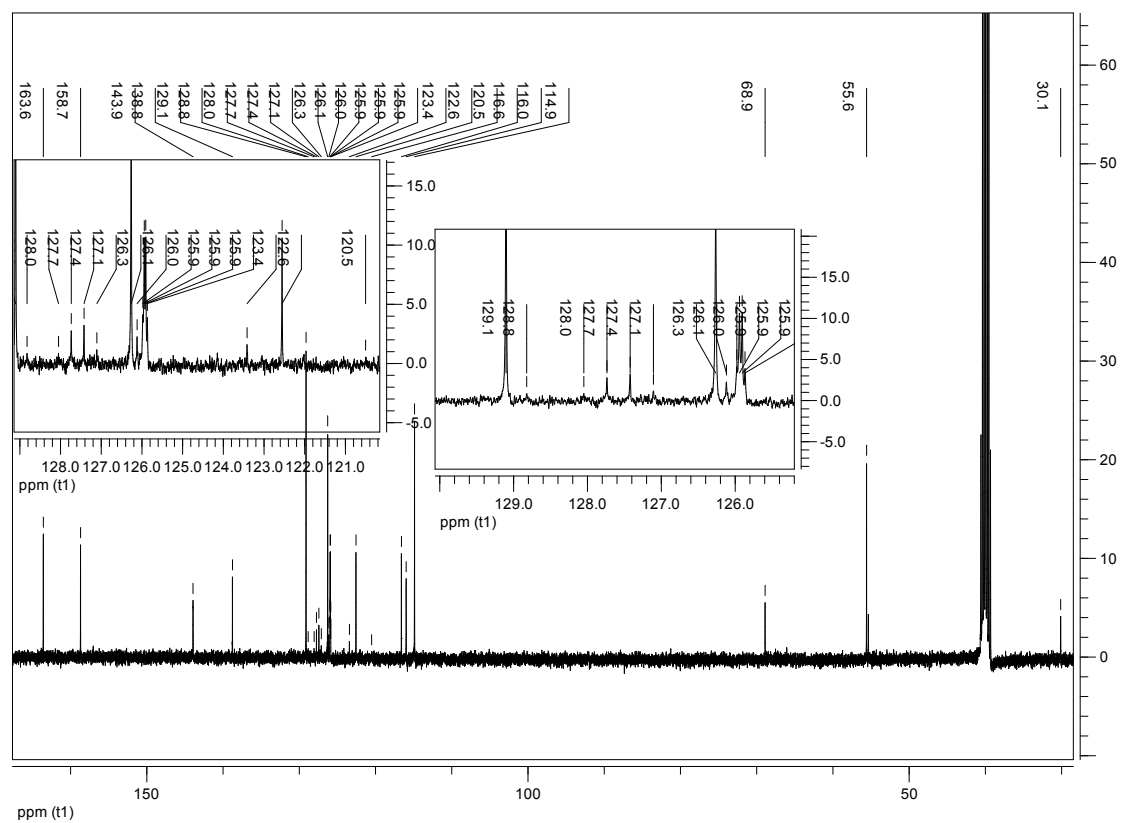
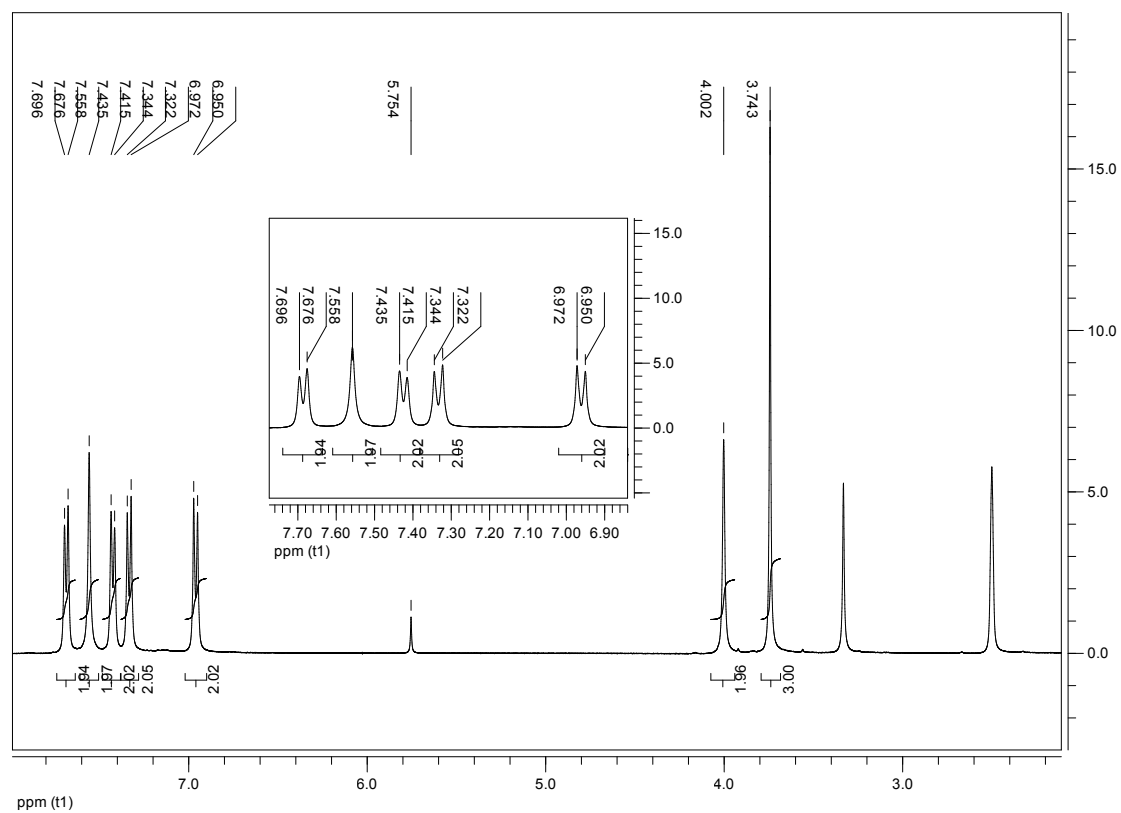


<sup>1</sup>H NMR spectrum of compound **1** in CDCl<sub>3</sub>. The x-axis represents the chemical shift in ppm (t1), ranging from 0 to 8. The y-axis represents the intensity. The spectrum shows several peaks, with an inset providing a detailed view of the aromatic region (7.1–7.7 ppm). Integration values are shown below the peaks.

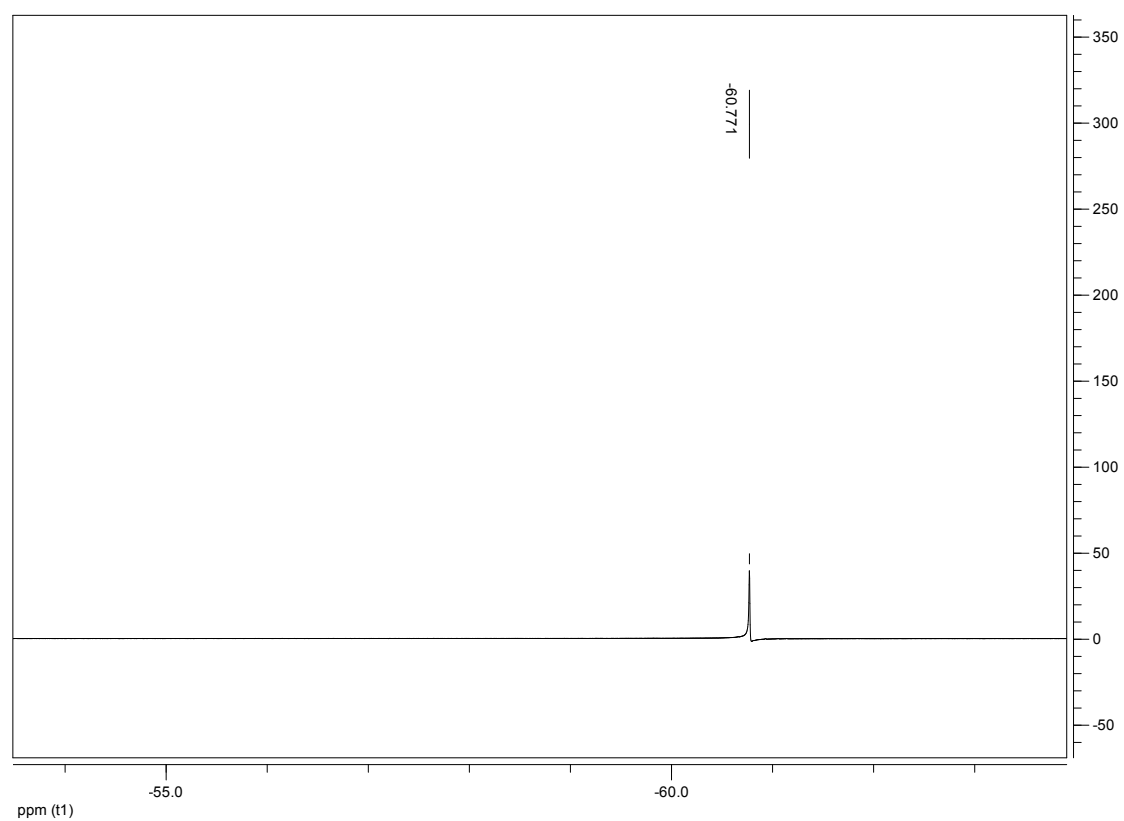
| Chemical Shift (ppm) | Integration |
|----------------------|-------------|
| 7.497                | 0.07        |
| 7.494                | 0.07        |
| 7.488                | 0.07        |
| 7.483                | 0.07        |
| 7.443                | 0.07        |
| 7.422                | 0.07        |
| 7.327                | 0.07        |
| 7.305                | 0.07        |
| 7.299                | 0.07        |
| 7.294                | 0.07        |
| 7.276                | 0.07        |
| 7.266                | 0.07        |
| 7.250                | 0.07        |
| 7.234                | 0.07        |
| 7.228                | 0.07        |
| 7.226                | 0.07        |
| 7.224                | 0.07        |
| 7.222                | 0.07        |
| 7.220                | 0.07        |
| 7.218                | 0.07        |
| 7.216                | 0.07        |
| 7.214                | 0.07        |
| 7.212                | 0.07        |
| 7.210                | 0.07        |
| 7.208                | 0.07        |
| 7.206                | 0.07        |
| 7.204                | 0.07        |
| 7.202                | 0.07        |
| 7.200                | 0.07        |
| 7.198                | 0.07        |
| 7.196                | 0.07        |
| 7.194                | 0.07        |
| 7.192                | 0.07        |
| 7.190                | 0.07        |
| 7.188                | 0.07        |
| 7.186                | 0.07        |
| 7.184                | 0.07        |
| 7.182                | 0.07        |
| 7.180                | 0.07        |
| 7.178                | 0.07        |
| 7.176                | 0.07        |
| 7.174                | 0.07        |
| 7.172                | 0.07        |
| 7.170                | 0.07        |
| 7.168                | 0.07        |
| 7.166                | 0.07        |
| 7.164                | 0.07        |
| 7.162                | 0.07        |
| 7.160                | 0.07        |
| 7.158                | 0.07        |
| 7.156                | 0.07        |
| 7.154                | 0.07        |
| 7.152                | 0.07        |
| 7.150                | 0.07        |
| 7.148                | 0.07        |
| 7.146                | 0.07        |
| 7.144                | 0.07        |
| 7.142                | 0.07        |
| 7.140                | 0.07        |
| 7.138                | 0.07        |
| 7.136                | 0.07        |
| 7.134                | 0.07        |
| 7.132                | 0.07        |
| 7.130                | 0.07        |
| 7.128                | 0.07        |
| 7.126                | 0.07        |
| 7.124                | 0.07        |
| 7.122                | 0.07        |
| 7.120                | 0.07        |
| 7.118                | 0.07        |
| 7.116                | 0.07        |
| 7.114                | 0.07        |
| 7.112                | 0.07        |
| 7.110                | 0.07        |
| 7.108                | 0.07        |
| 7.106                | 0.07        |
| 7.104                | 0.07        |
| 7.102                | 0.07        |
| 7.100                | 0.07        |
| 7.098                | 0.07        |
| 7.096                | 0.07        |
| 7.094                | 0.07        |
| 7.092                | 0.07        |
| 7.090                | 0.07        |
| 7.088                | 0.07        |
| 7.086                | 0.07        |
| 7.084                | 0.07        |
| 7.082                | 0.07        |
| 7.080                | 0.07        |
| 7.078                | 0.07        |
| 7.076                | 0.07        |
| 7.074                | 0.07        |
| 7.072                | 0.07        |
| 7.070                | 0.07        |
| 7.068                | 0.07        |
| 7.066                | 0.07        |
| 7.064                | 0.07        |
| 7.062                | 0.07        |
| 7.060                | 0.07        |
| 7.058                | 0.07        |
| 7.056                | 0.07        |
| 7.054                | 0.07        |
| 7.052                | 0.07        |
| 7.050                | 0.07        |
| 7.048                | 0.07        |
| 7.046                | 0.07        |
| 7.044                | 0.07        |
| 7.042                | 0.07        |
| 7.040                | 0.07        |
| 7.038                | 0.07        |
| 7.036                | 0.07        |
| 7.034                | 0.07        |
| 7.032                | 0.07        |
| 7.030                | 0.07        |
| 7.028                | 0.07        |
| 7.026                | 0.07        |
| 7.024                | 0.07        |
| 7.022                | 0.07        |
| 7.020                | 0.07        |
| 7.018                | 0.07        |
| 7.016                | 0.07        |
| 7.014                | 0.07        |
| 7.012                | 0.07        |
| 7.010                | 0.07        |
| 7.008                | 0.07        |
| 7.006                | 0.07        |
| 7.004                | 0.07        |
| 7.002                | 0.07        |
| 7.000                | 0.07        |
| 6.998                | 0.07        |
| 6.996                | 0.07        |
| 6.994                | 0.07        |
| 6.992                | 0.07        |
| 6.990                | 0.07        |
| 6.988                | 0.07        |
| 6.986                | 0.07        |
| 6.984                | 0.07        |
| 6.982                | 0.07        |
| 6.980                | 0.07        |
| 6.978                | 0.07        |
| 6.976                | 0.07        |
| 6.974                | 0.07        |
| 6.972                | 0.07        |
| 6.970                | 0.07        |
| 6.968                | 0.07        |
| 6.966                | 0.07        |
| 6.964                | 0.07        |
| 6.962                | 0.07        |
| 6.960                | 0.07        |
| 6.958                | 0.07        |
| 6.956                | 0.07        |
| 6.954                | 0.07        |
| 6.952                | 0.07        |
| 6.950                | 0.07        |
| 6.948                | 0.07        |
| 6.946                | 0.07        |
| 6.944                | 0.07        |
| 6.942                | 0.07        |
| 6.940                | 0.07        |
| 6.938                | 0.07        |
| 6.936                | 0.07        |
| 6.934                | 0.07        |
| 6.932                | 0.07        |
| 6.930                | 0.07        |
| 6.928                | 0.07        |
| 6.926                | 0.07        |
| 6.924                | 0.07        |
| 6.922                | 0.07        |
| 6.920                | 0.07        |
| 6.918                | 0.07        |
|                      |             |



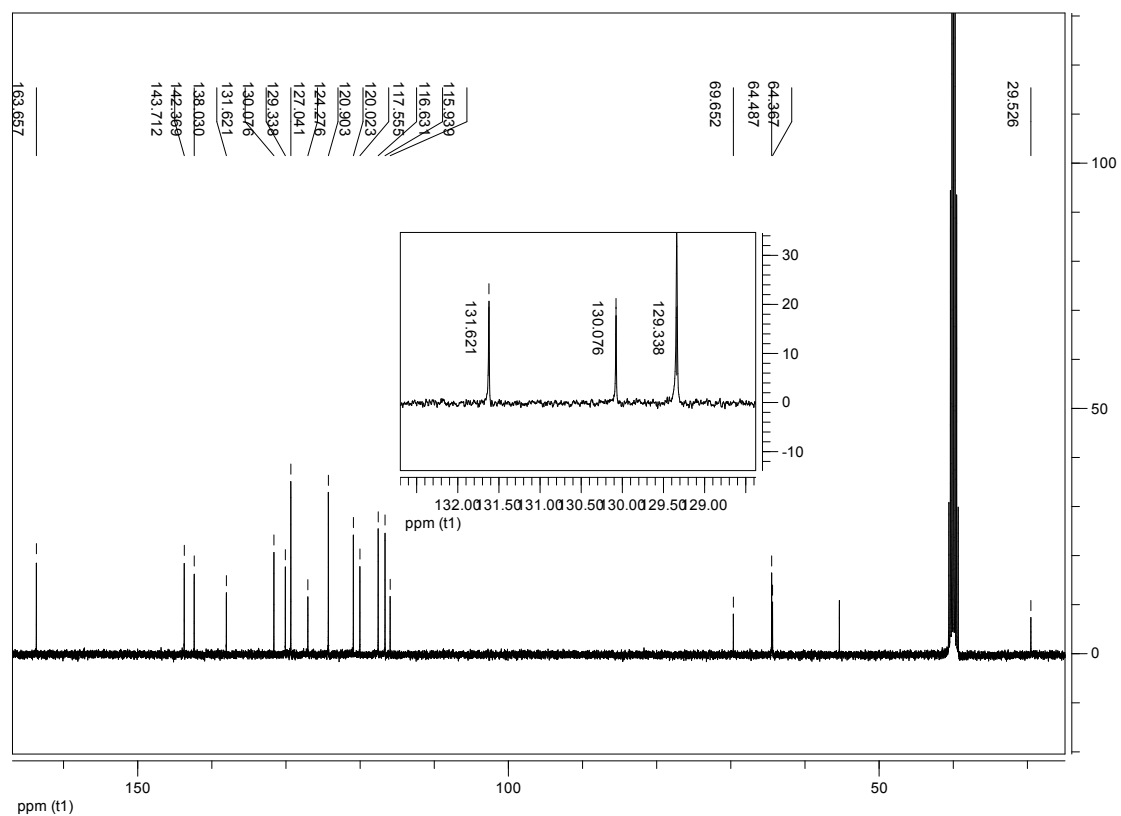
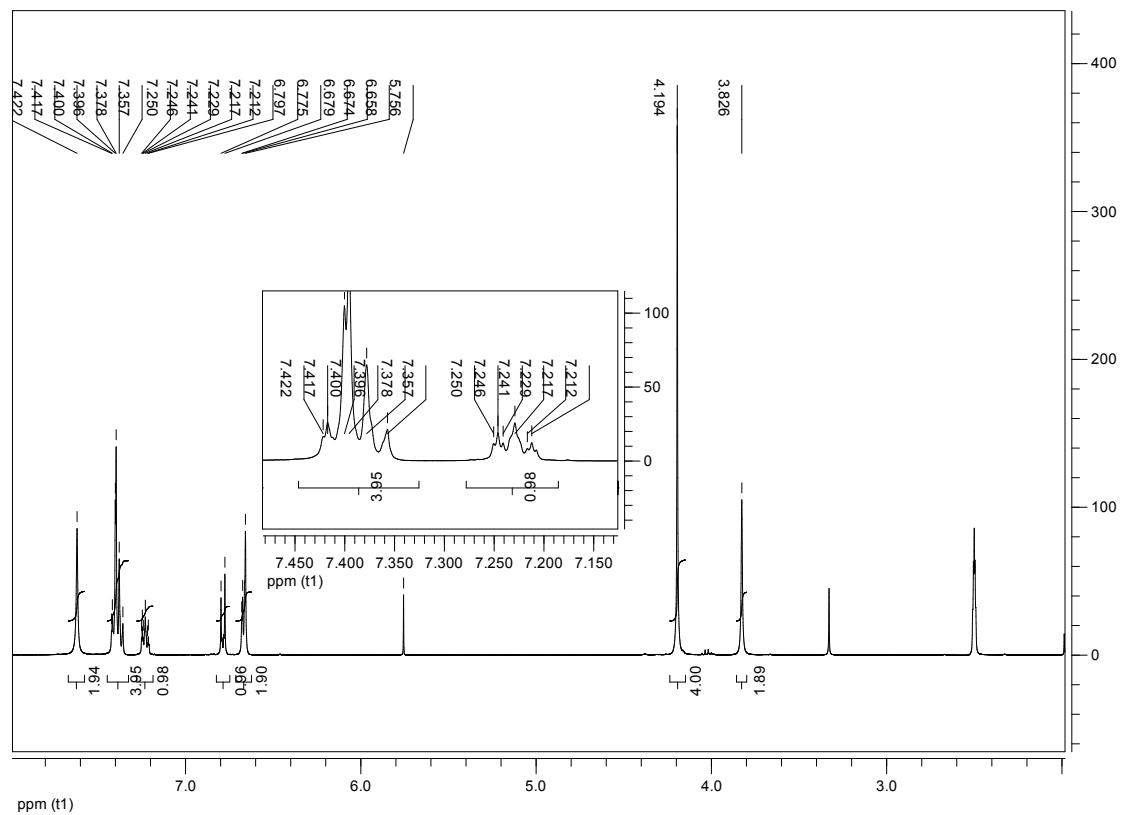
2-Amino-5-(4-methoxyphenyl)-4-(4-(trifluoromethyl)benzyl)furan-3-carbonitrile  
(2m).



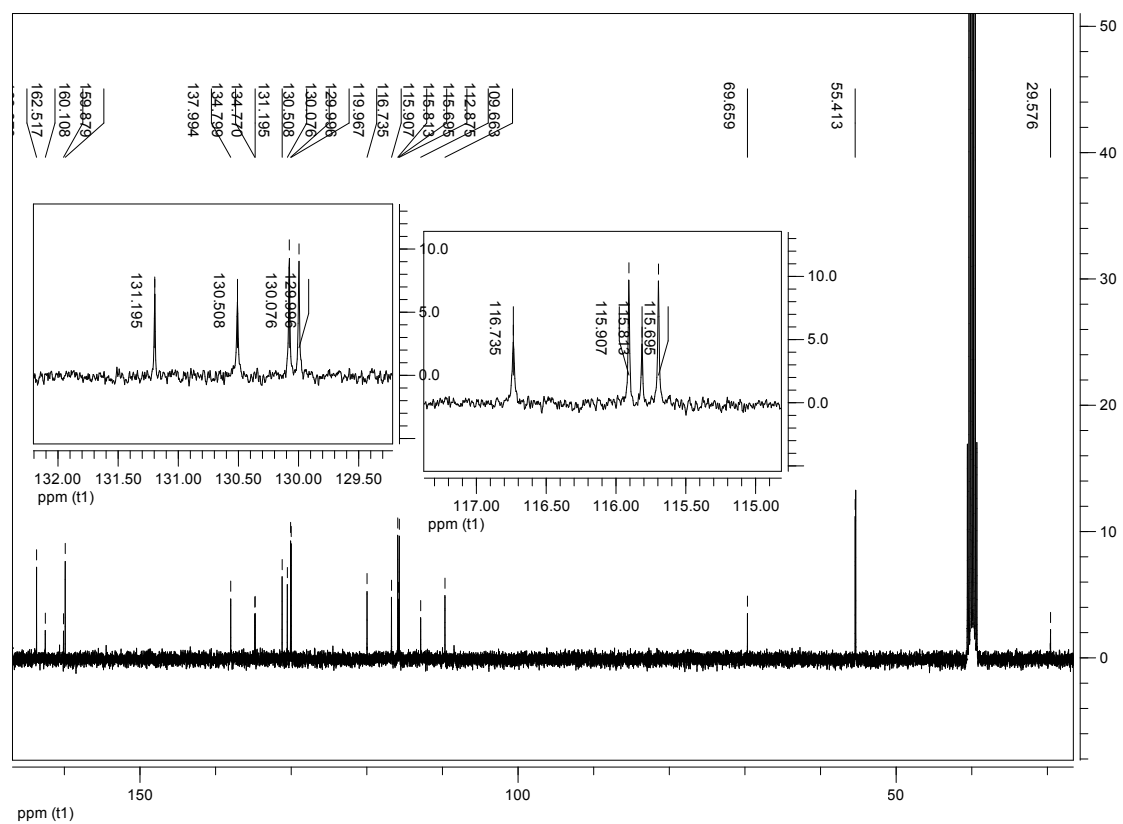
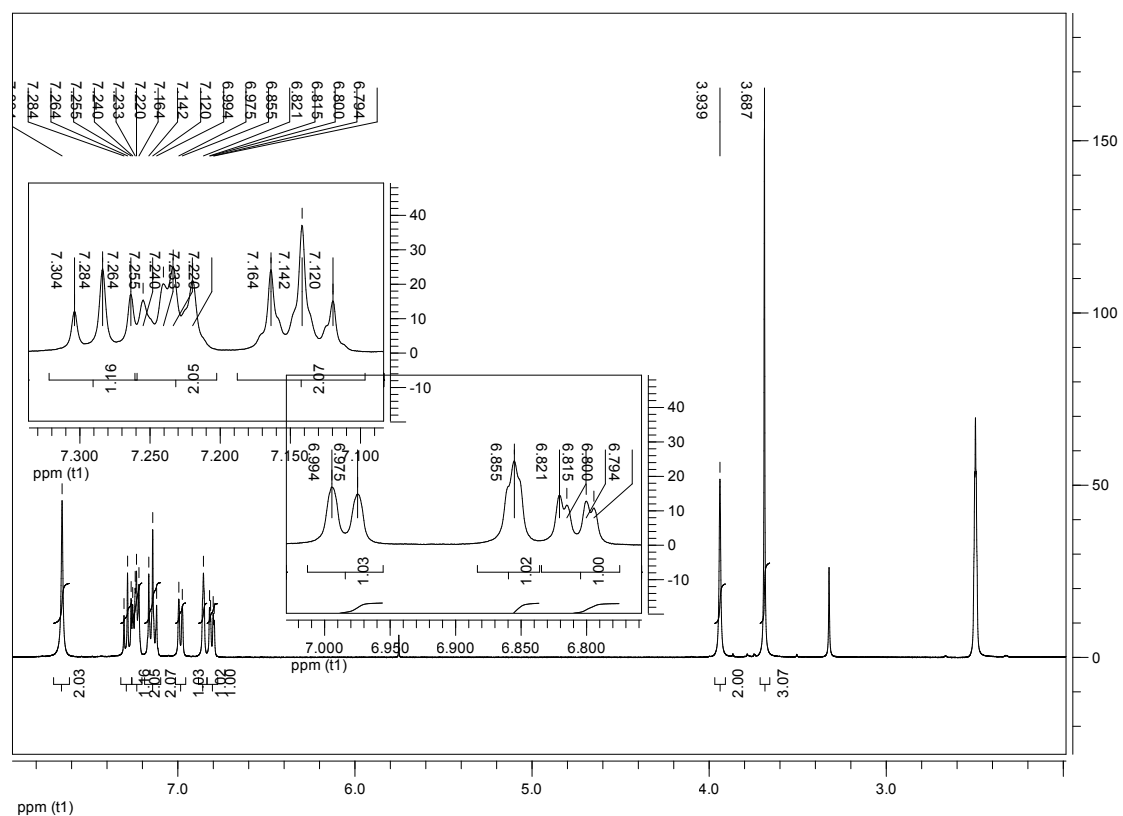


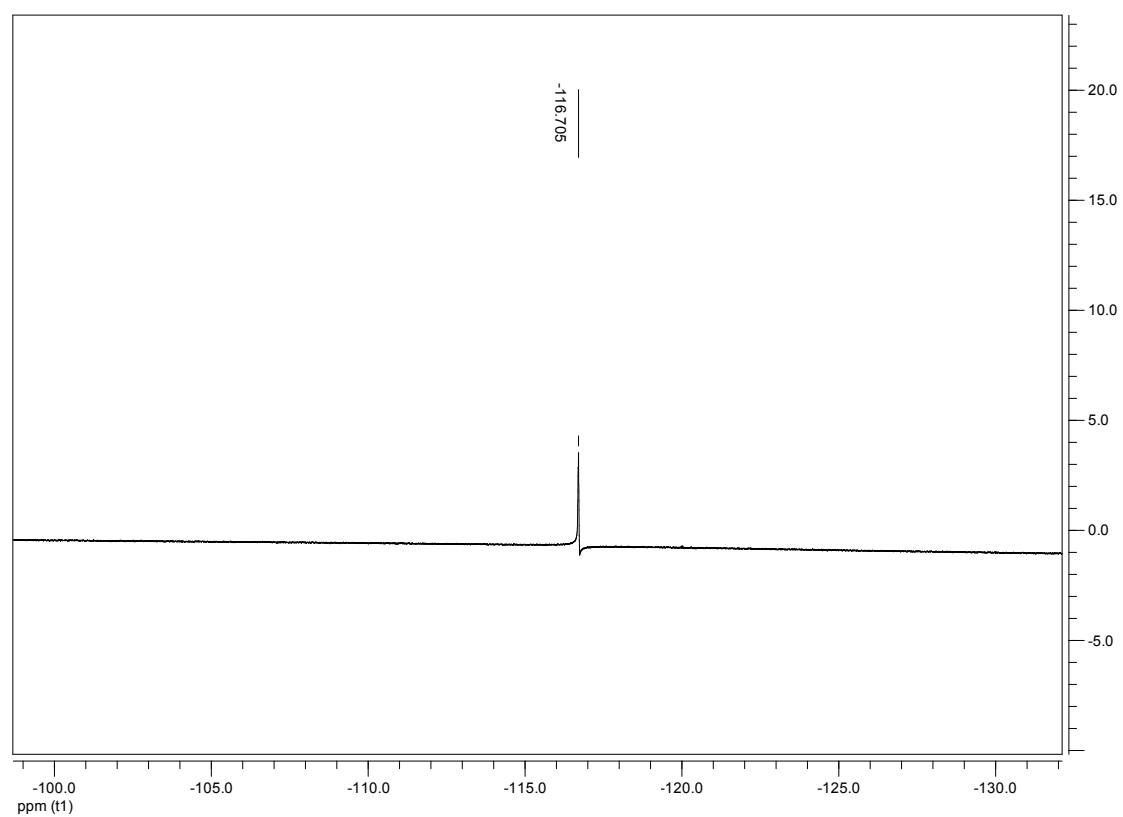


2-Amino-4-((2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)methyl)-5-phenylfuran-3-carbonitrile (**2n**).

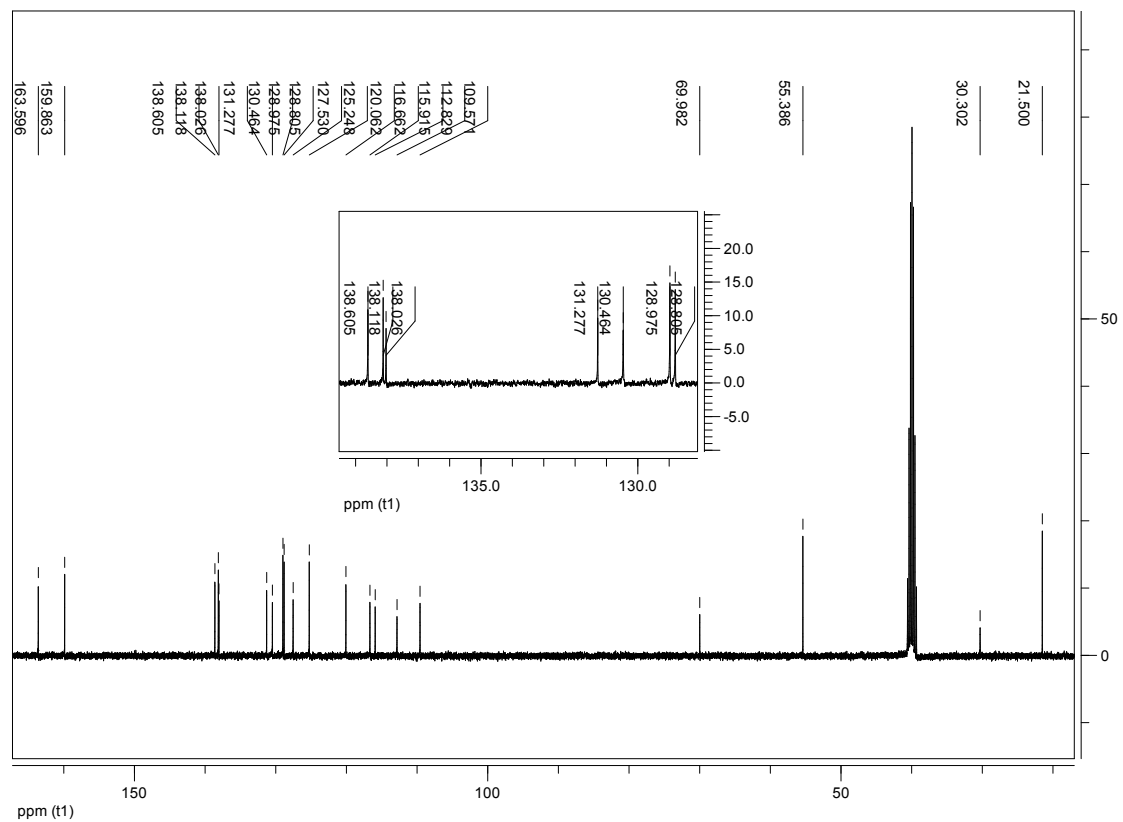


2-Amino-4-(4-fluorobenzyl)-5-(3-methoxyphenyl)furan-3-carbonitrile (**2o**).

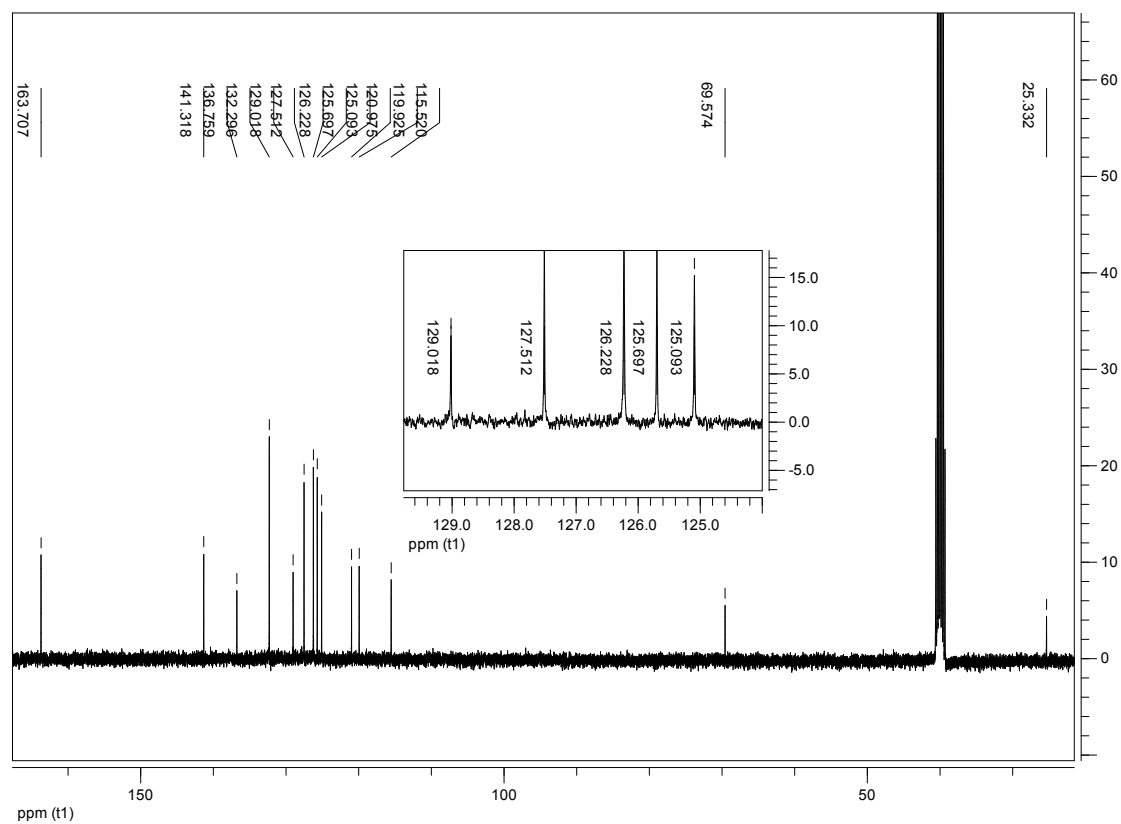
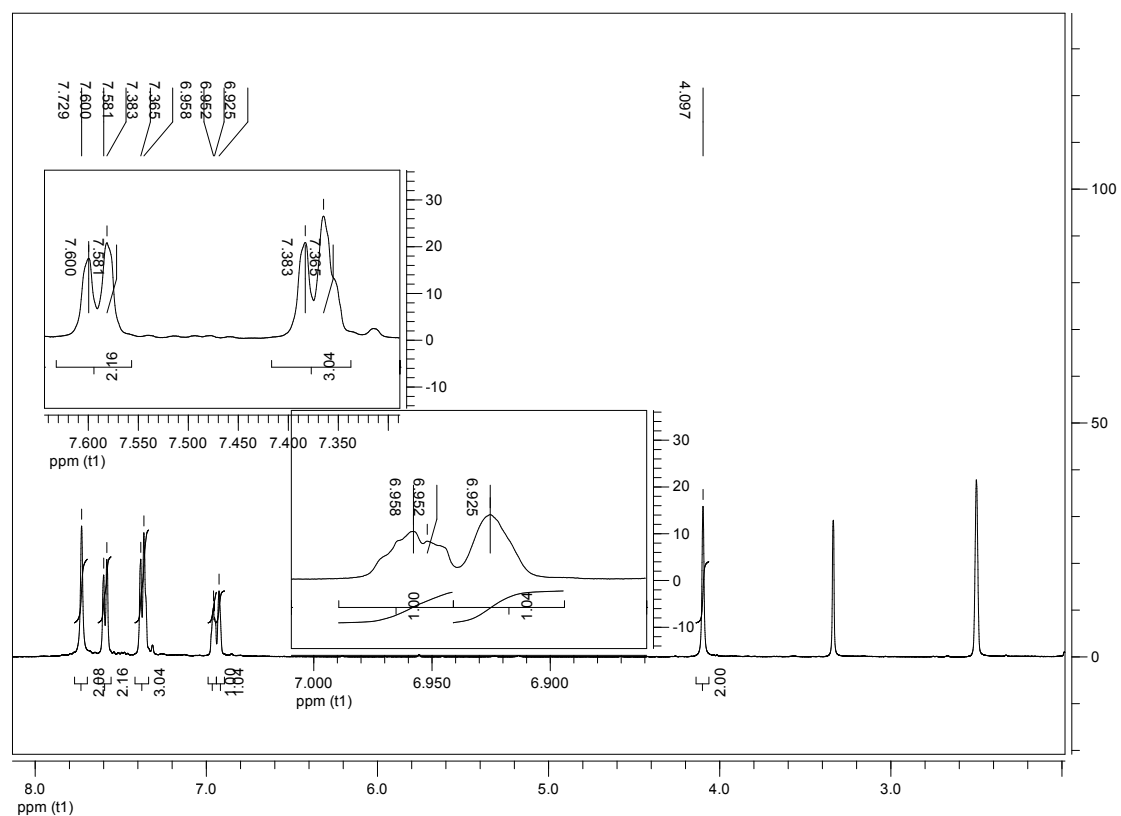




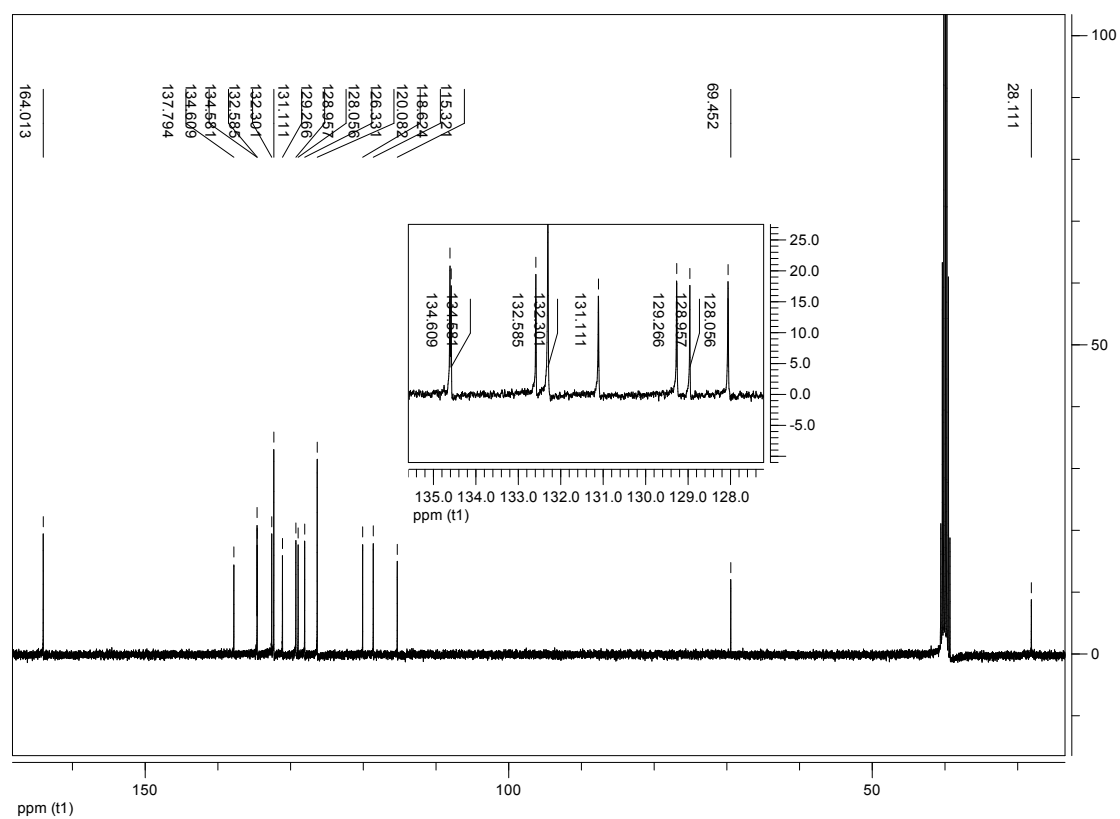
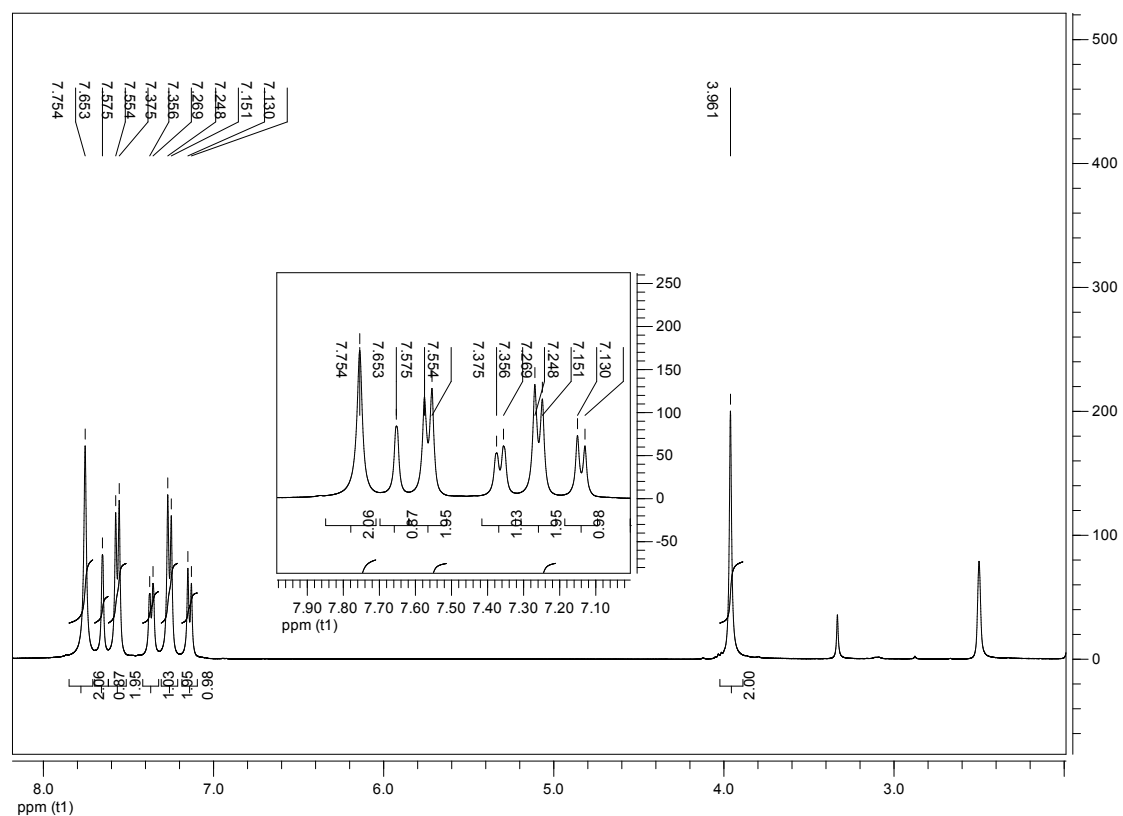
## S41



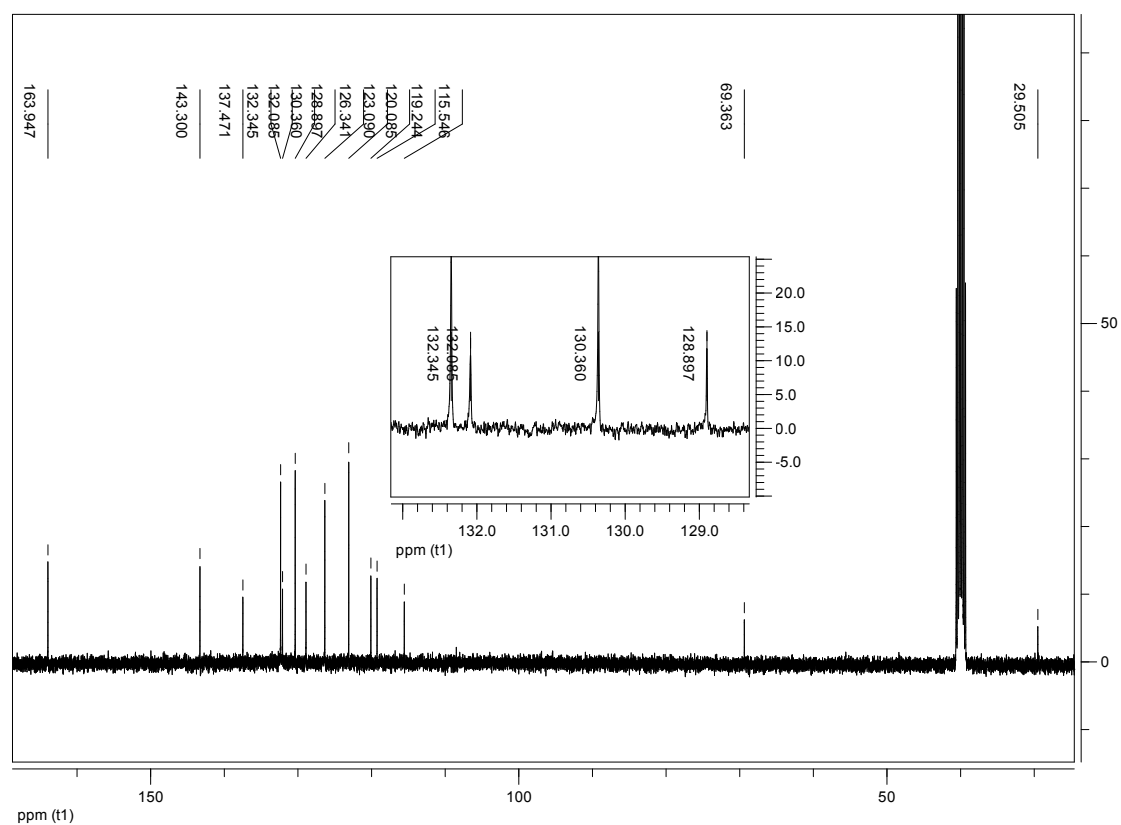
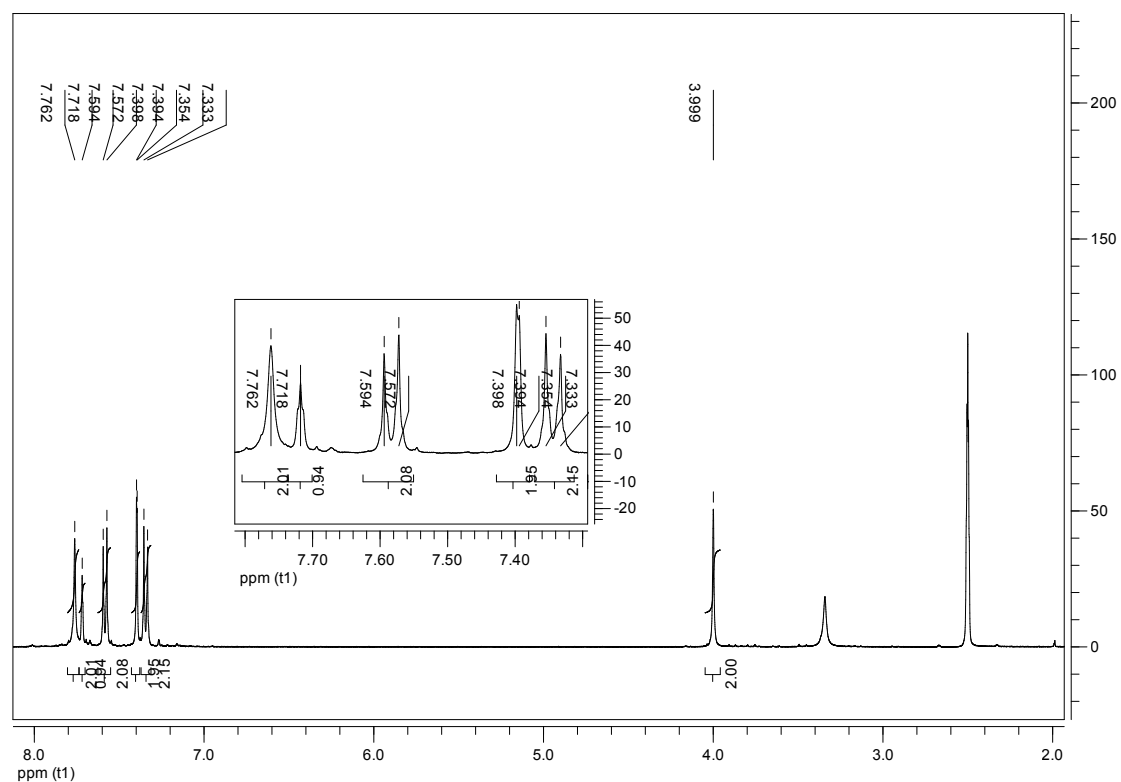
2-Amino-5-(4-bromophenyl)-4-(thiophen-2-ylmethyl)furan-3-carbonitrile (**2q**).



2-Amino-5-(4-bromophenyl)-4-(2,4-dichlorobenzyl)furan-3-carbonitrile (**2r**).

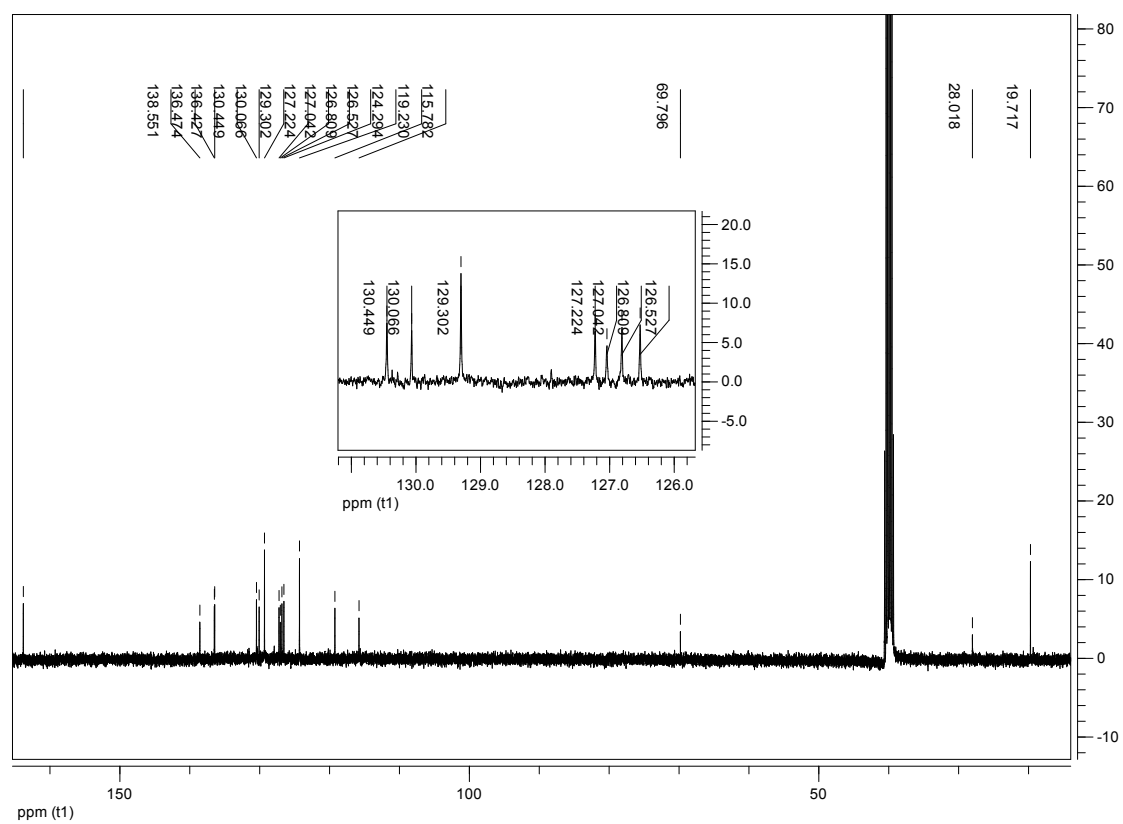
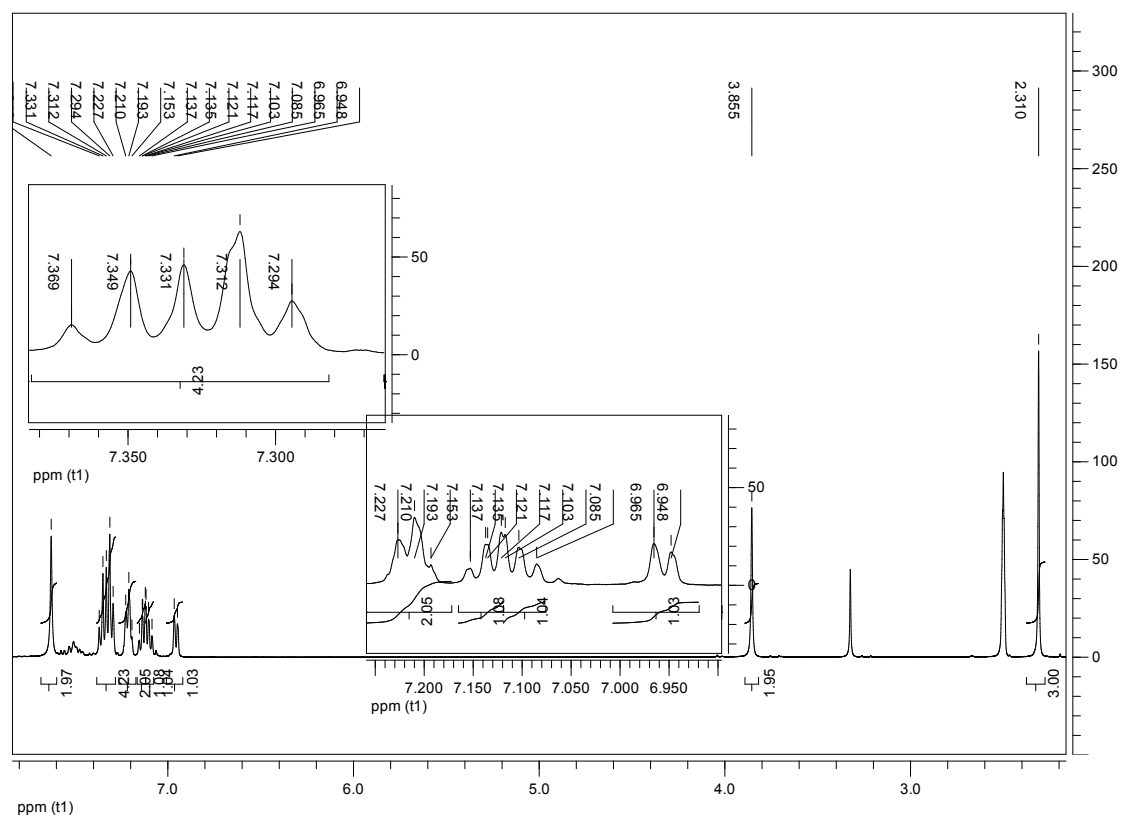


2-Amino-5-(4-bromophenyl)-4-(3,5-dibromobenzyl)furan-3-carbonitrile (**2s**).



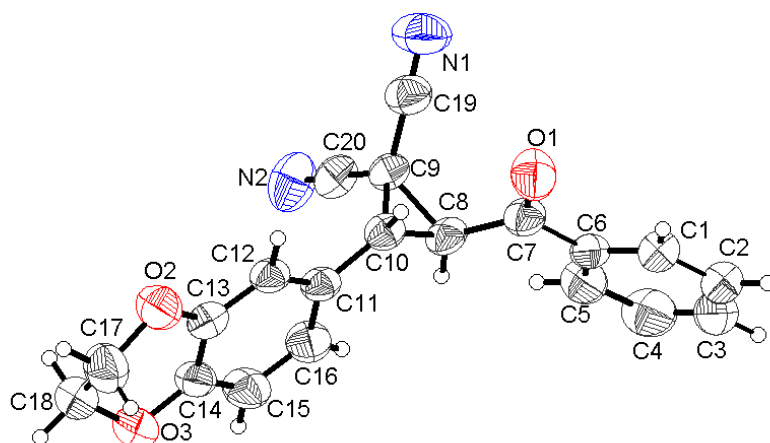


2-Amino-4-(2-methylbenzyl)-5-phenylfuran-3-carbonitrile (**2t**).



2-Amino-4-benzyl-5-phenylfuran-3-carbonitrile (**2u**)





**1n** (CCDC 1893325)

Fig. S7 Molecular structure of 2-benzoyl-3-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl) cyclopropane-1,1-dicarbonitrile (**1n**), non-hydrogen atoms are shown at the 30% probability level.

Table S7. Crystal data and structure refinement for **1n**.

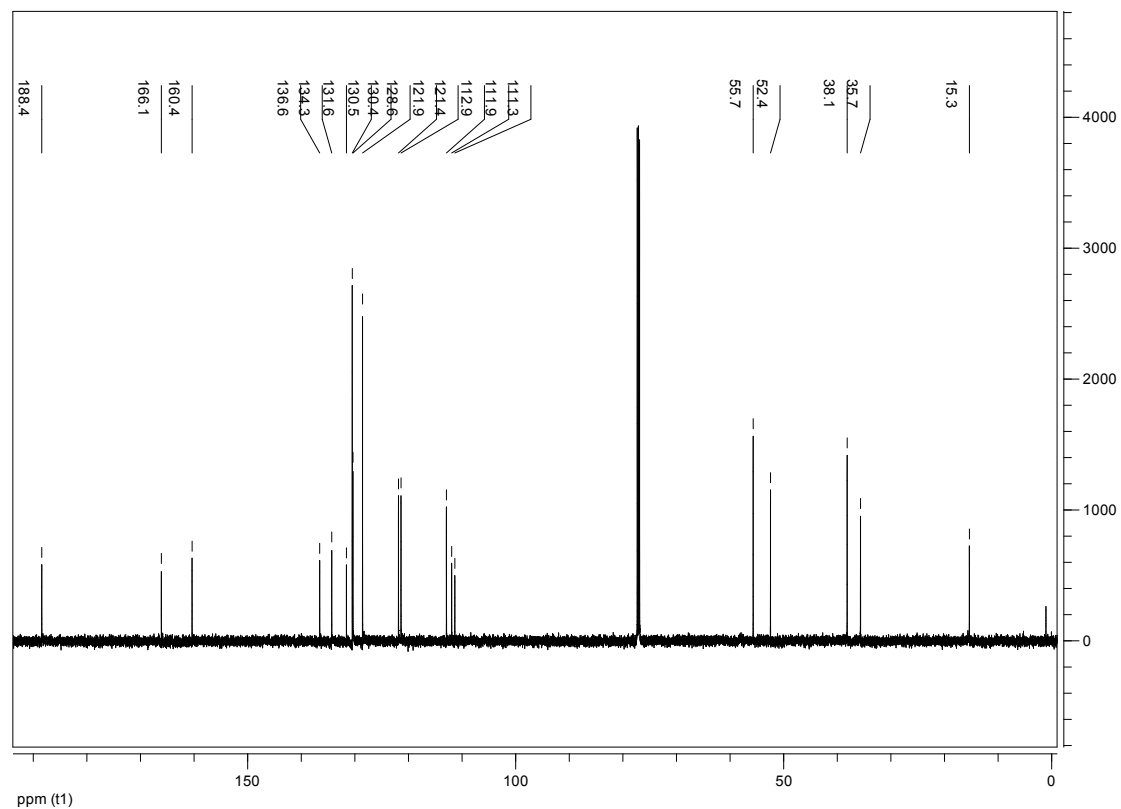
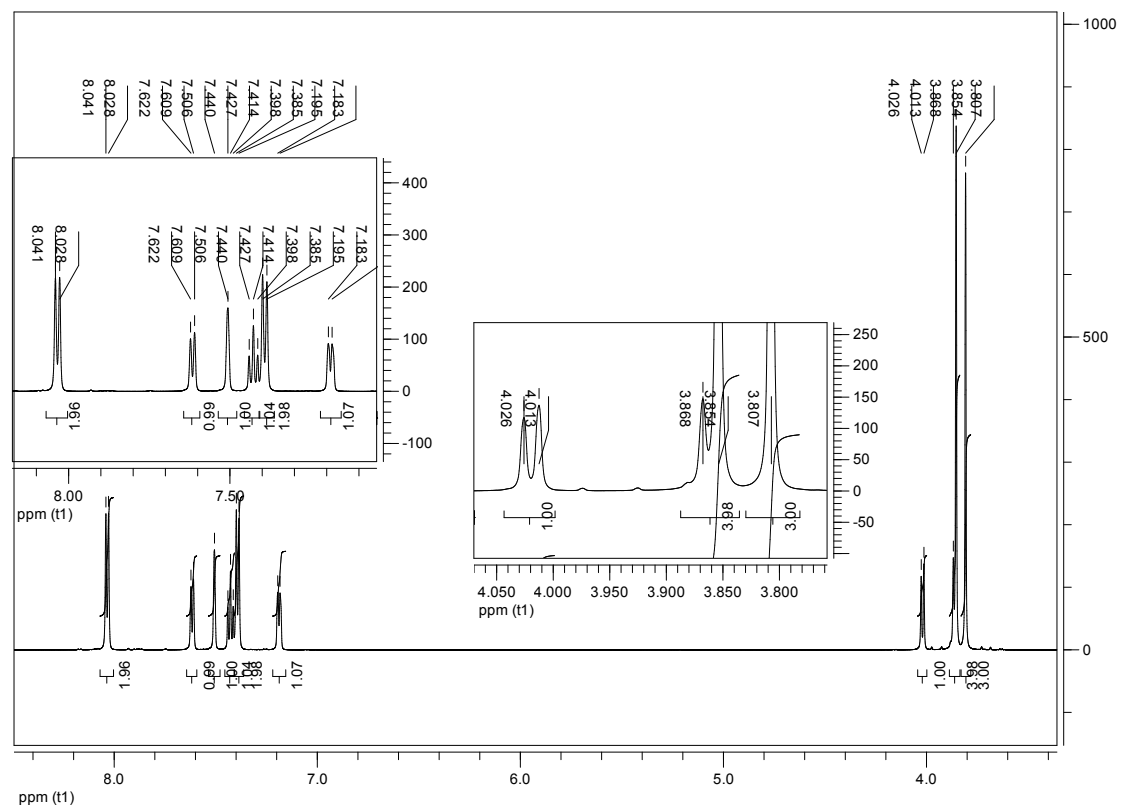
|                                   |                                                                                                                                          |
|-----------------------------------|------------------------------------------------------------------------------------------------------------------------------------------|
| Identification code               | <b>1n</b>                                                                                                                                |
| Empirical formula                 | C <sub>20</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub>                                                                            |
| Formula weight                    | 330.33                                                                                                                                   |
| Temperature                       | 293(2) K                                                                                                                                 |
| Wavelength                        | 0.71073 Å                                                                                                                                |
| Crystal system, space group       | Triclinic, P-1                                                                                                                           |
| Unit cell dimensions              | a = 11.542(4) Å    alpha = 100.009(11) deg.<br>b = 12.009(4) Å    beta = 105.015(10) deg.<br>c = 14.738(5) Å    gamma = 117.020(10) deg. |
| Volume                            | 1653.9(10) Å <sup>3</sup>                                                                                                                |
| Z, Calculated density             | 4, 1.327 Mg/m <sup>3</sup>                                                                                                               |
| Absorption coefficient            | 0.091 mm <sup>-1</sup>                                                                                                                   |
| F(000)                            | 688                                                                                                                                      |
| Crystal size                      | 0.50 x 0.45 x 0.40 mm                                                                                                                    |
| Theta range for data collection   | 1.52 to 27.66 deg.                                                                                                                       |
| Limiting indices                  | -13 ≤ h ≤ 14, -15 ≤ k ≤ 15, -19 ≤ l ≤ 18                                                                                                 |
| Reflections collected / unique    | 20658 / 7716 [R(int) = 0.0727]                                                                                                           |
| Completeness to theta = 27.66     | 96.3 %                                                                                                                                   |
| Absorption correction             | None                                                                                                                                     |
| Refinement method                 | Full-matrix least-squares on F <sup>2</sup>                                                                                              |
| Data / restraints / parameters    | 7426 / 0 / 451                                                                                                                           |
| Goodness-of-fit on F <sup>2</sup> | 1.054                                                                                                                                    |

Final R indices [ $I > 2\sigma(I)$ ]  $R_1 = 0.1032$ ,  $wR_2 = 0.2930$

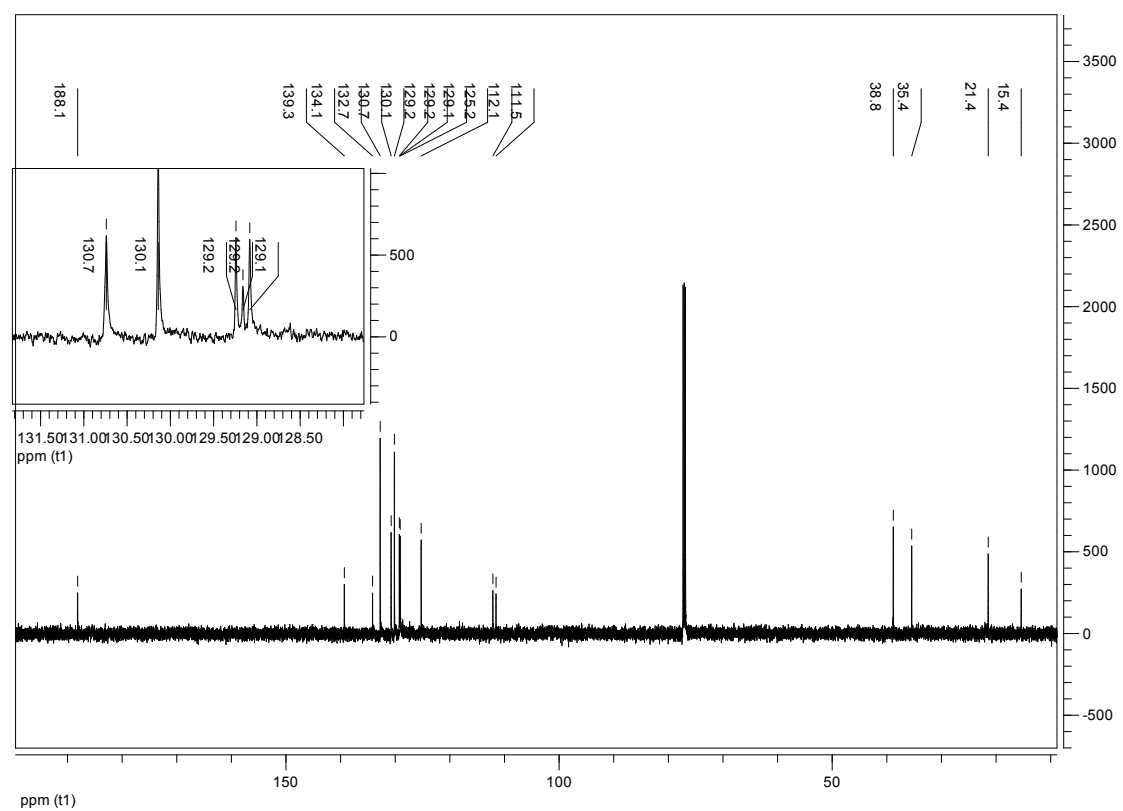
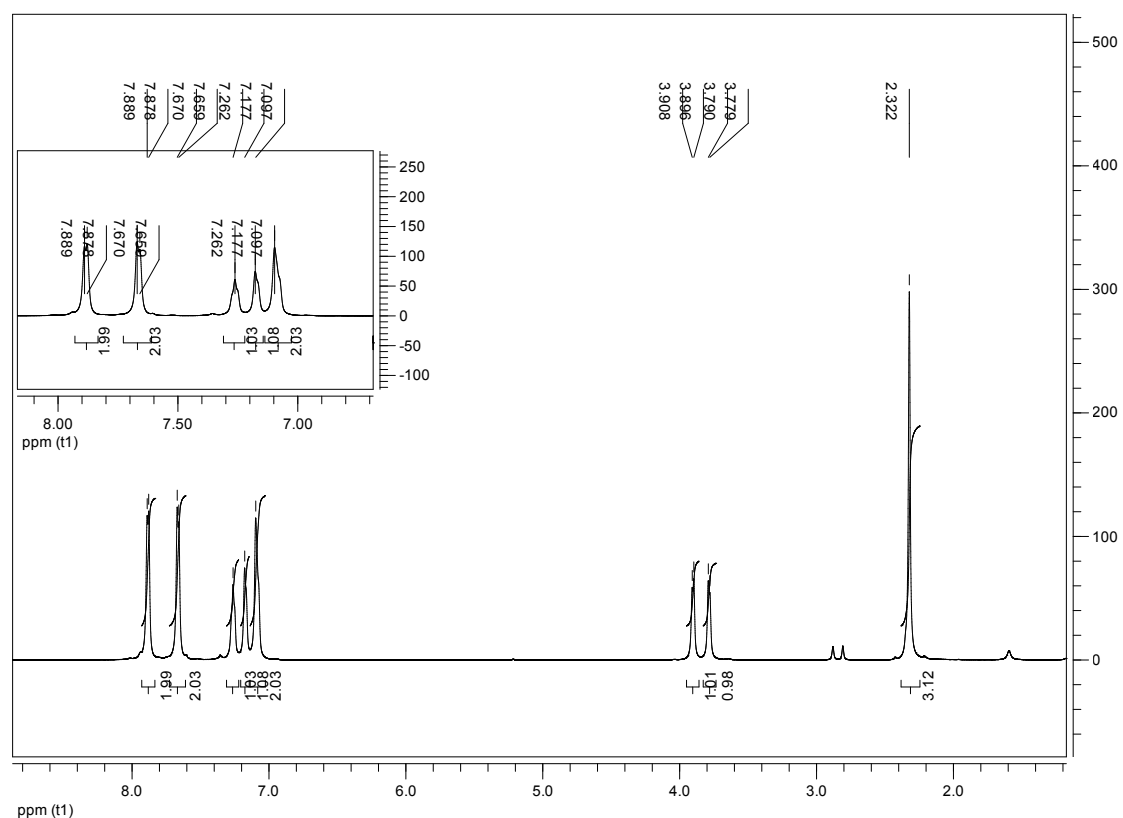
R indices (all data)  $R_1 = 0.1601$ ,  $wR_2 = 0.3322$

Largest diff. peak and hole 0.381 and -0.315 e.Å<sup>-3</sup>

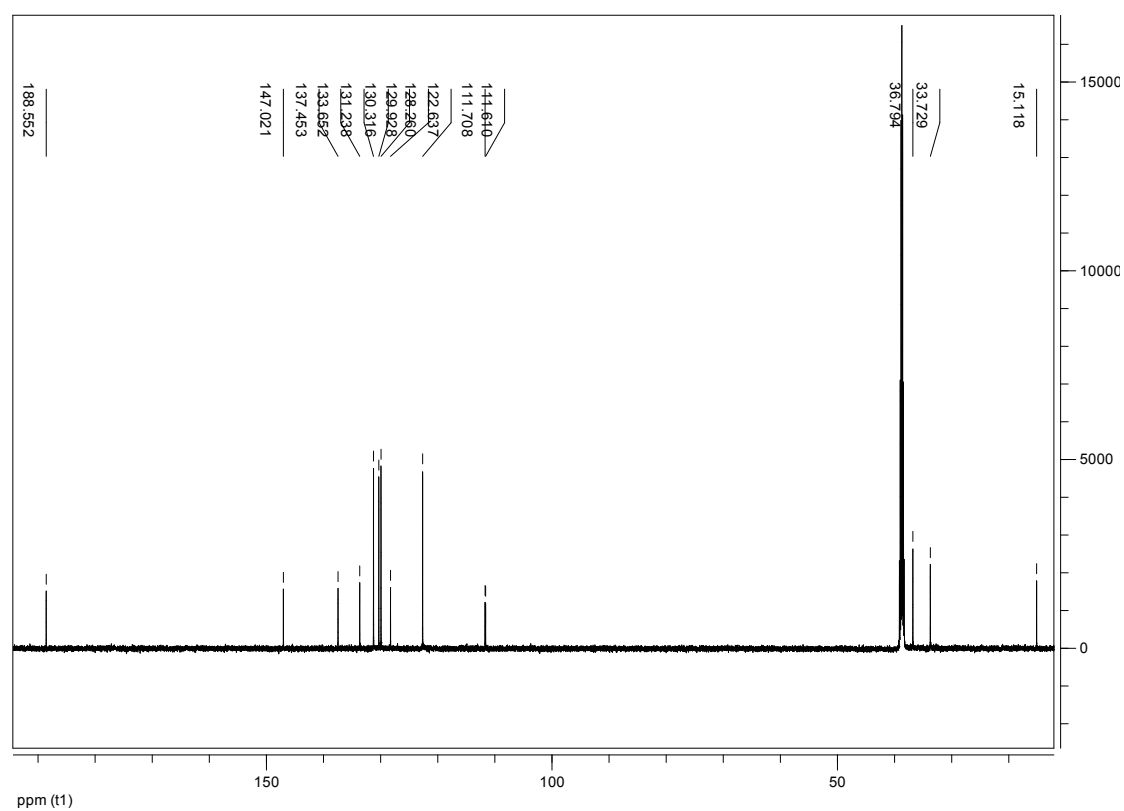
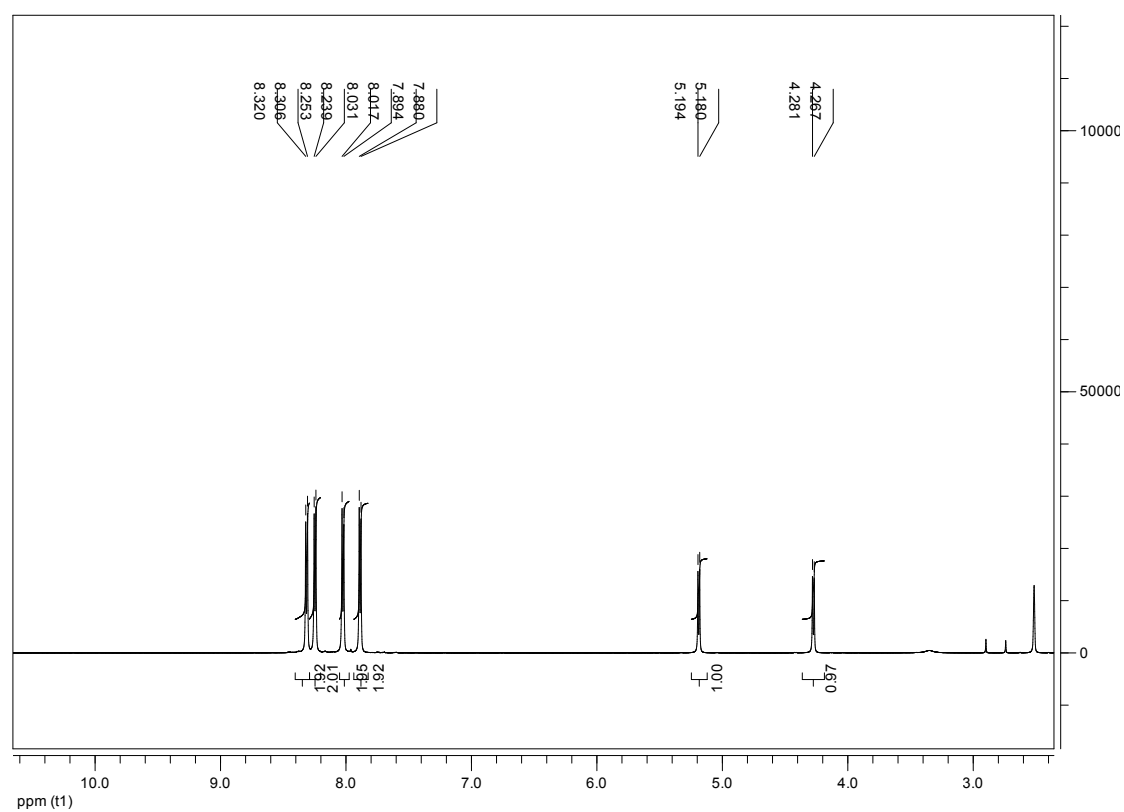
Methyl-4-(2,2-dicyano-3-(3-methoxybenzoyl)cyclopropyl)benzoate (**1a**)



2-(4-Bromobenzoyl)-3-(m-tolyl)cyclopropane-1,1-dicarbonitrile (**1b**).

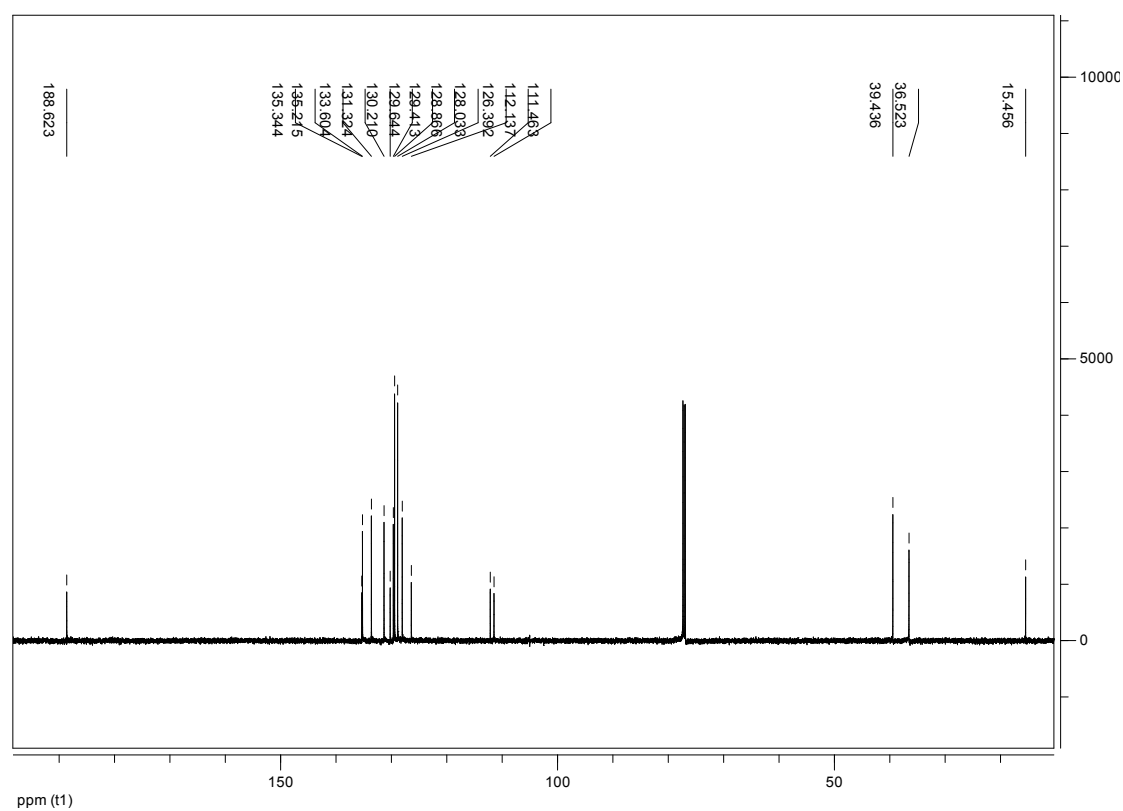


2-Benzoyl-3-(4-nitrophenyl)cyclopropane-1,1-dicarbonitrile (**1c**)

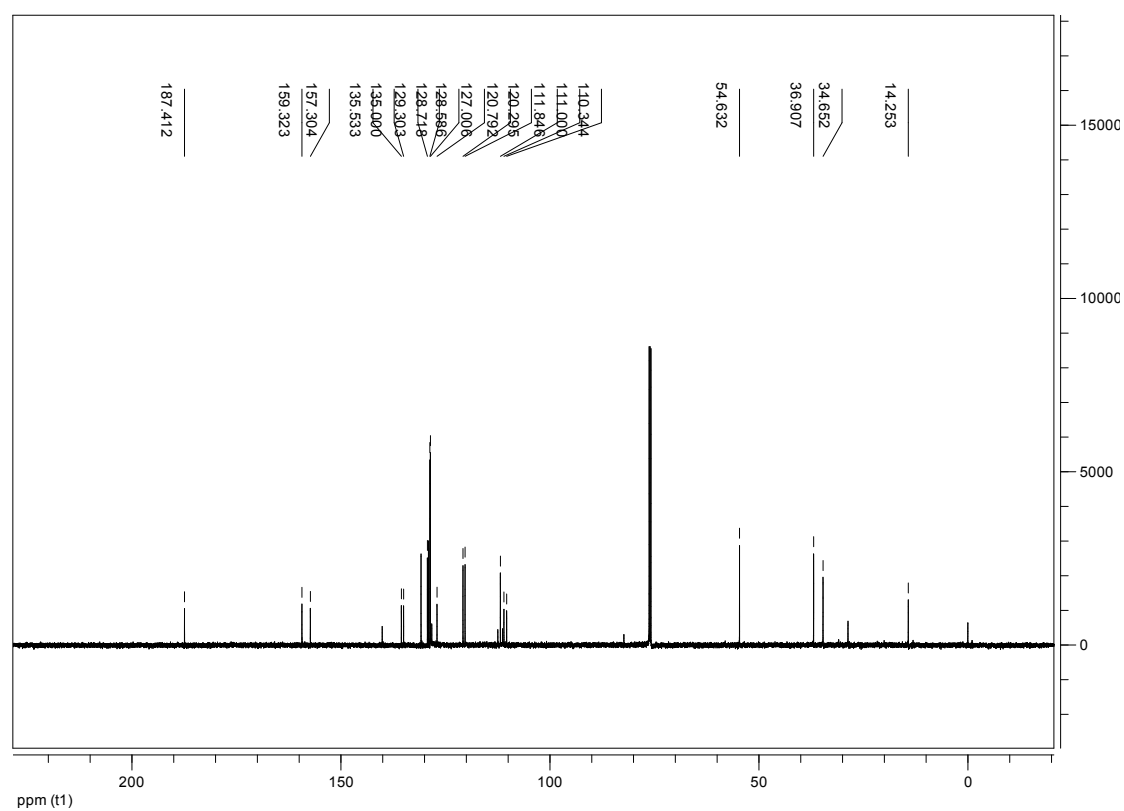
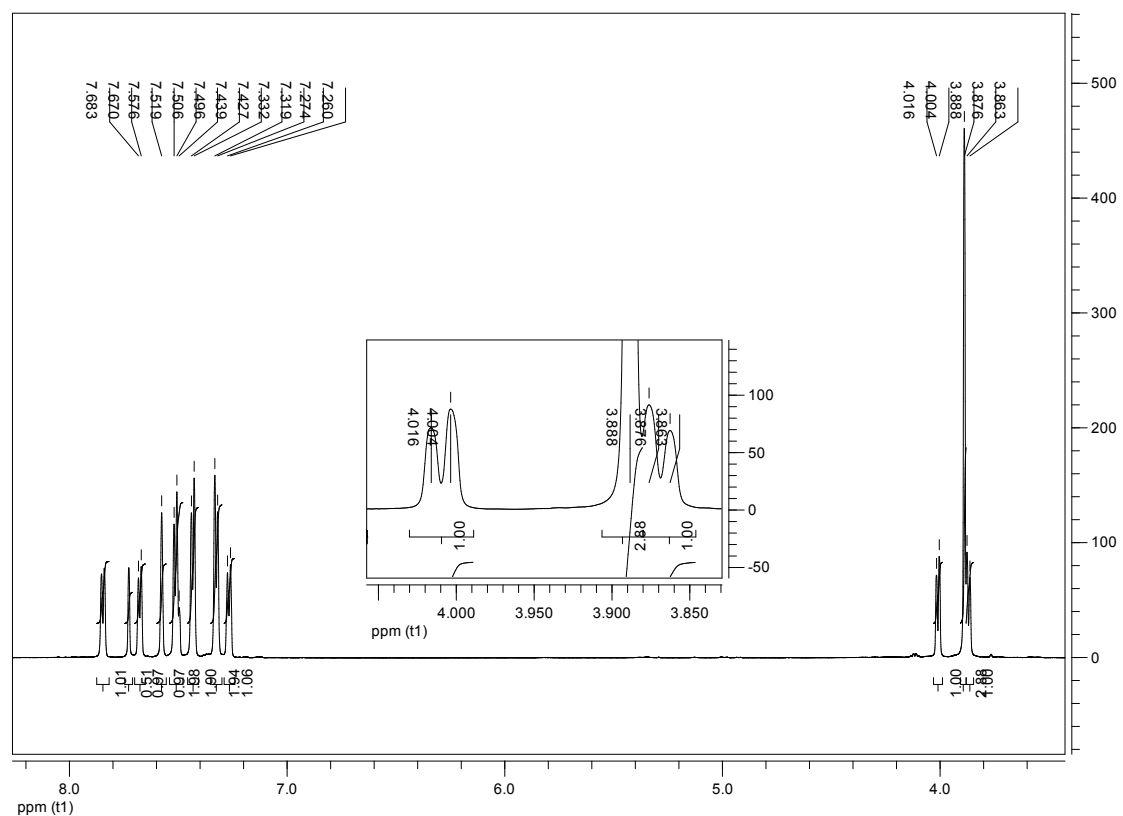




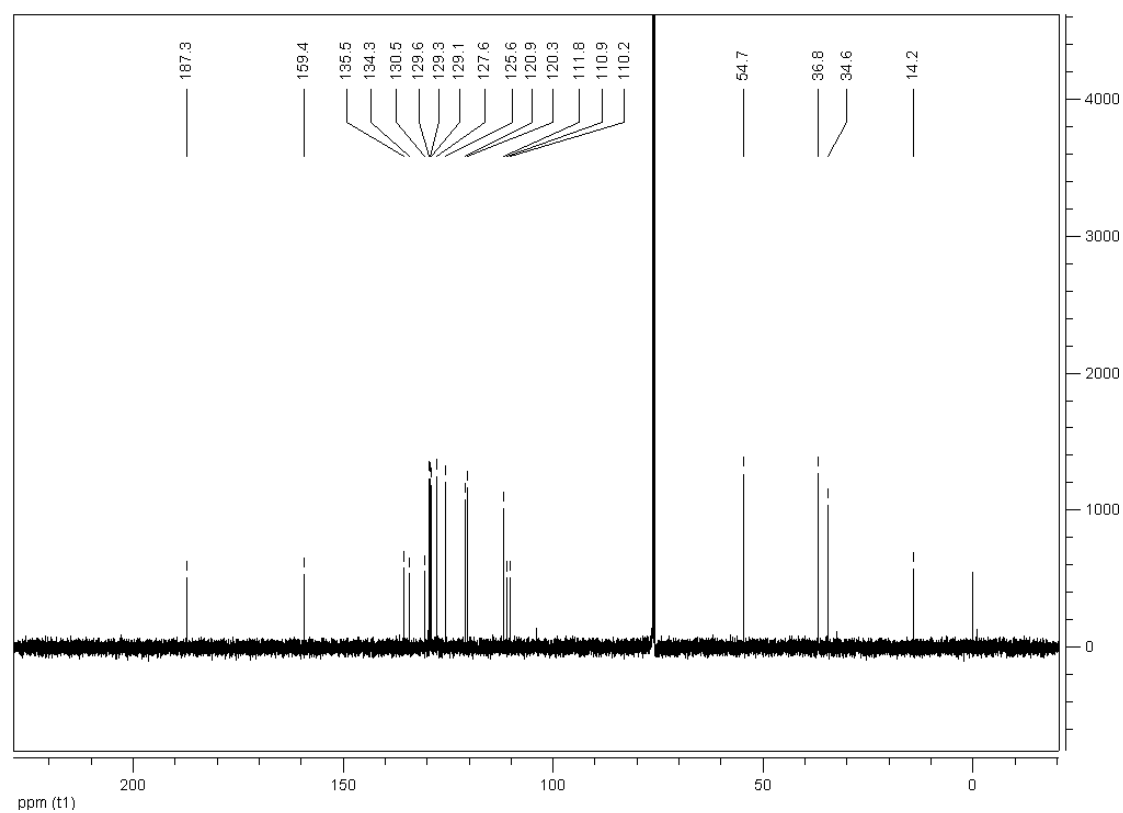
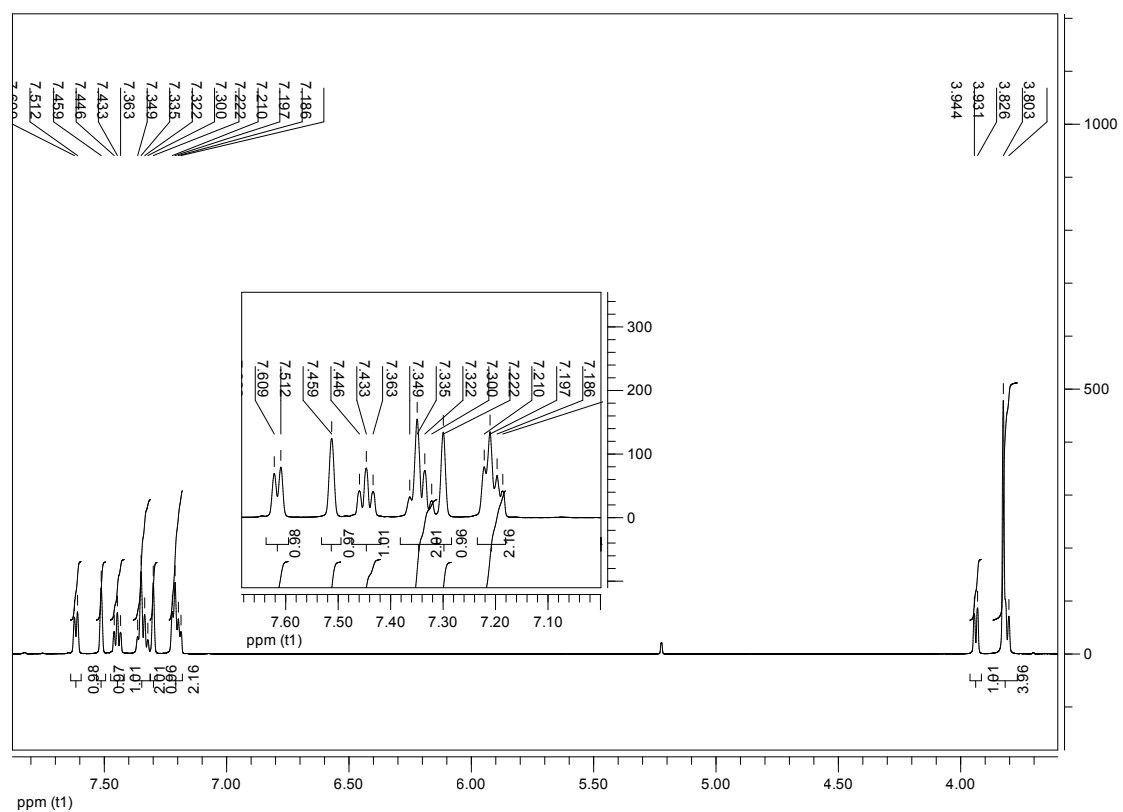
<sup>1</sup>H NMR spectrum of compound **1** in CDCl<sub>3</sub>. The spectrum shows peaks in the aromatic region (6.5–8.5 ppm) and a methoxy singlet (~3.8 ppm). An inset zooms in on the aromatic region from 7.0 to 8.5 ppm. Peak labels include chemical shifts (e.g., 8.121, 7.244, 3.880) and integration values (e.g., 1.02, 0.91, 2.01).



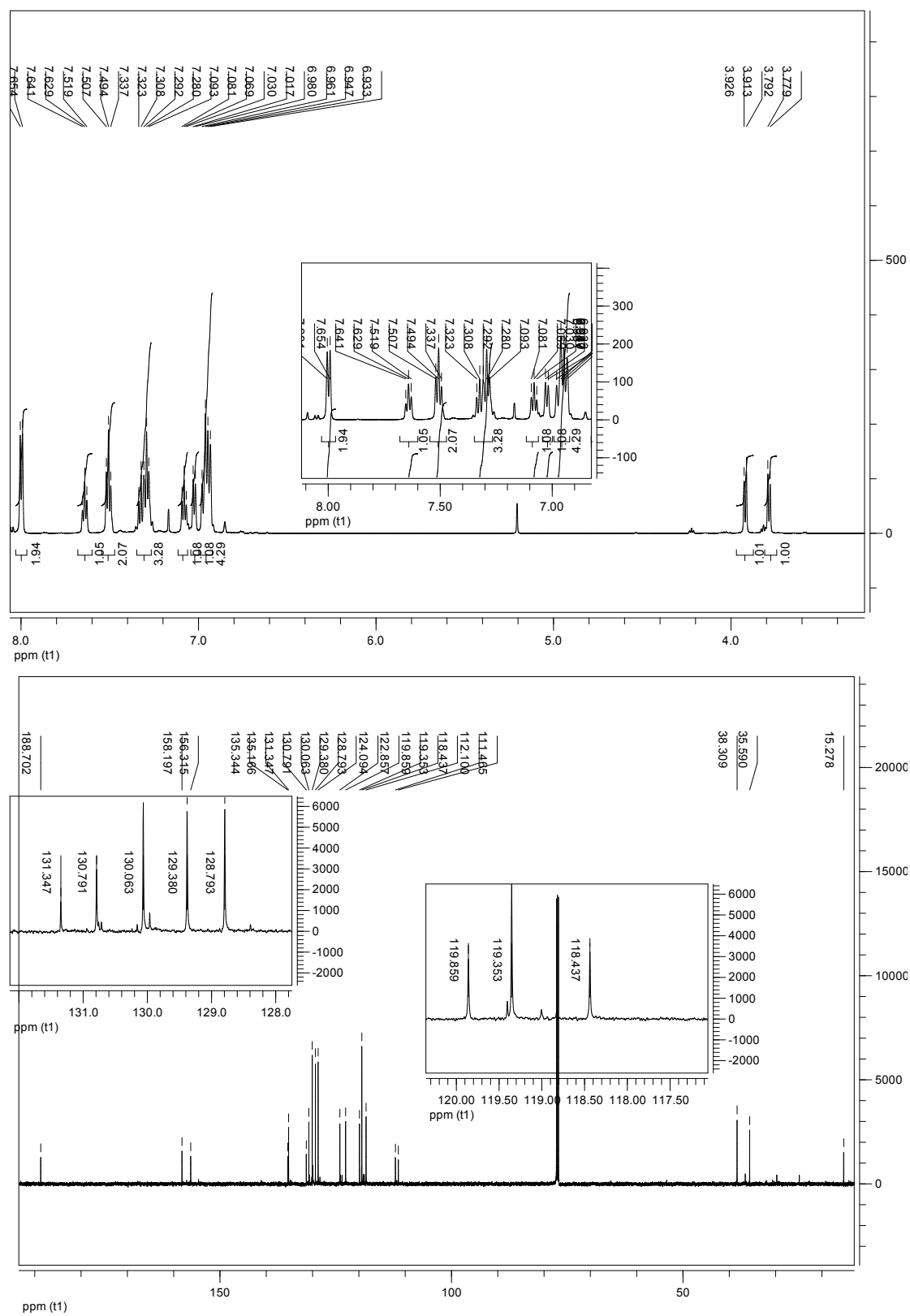
2-(4-Chlorophenyl)-3-(3-methoxybenzoyl)cyclopropane-1,1-dicarbonitrile (**1f**)



2-(3-Chlorophenyl)-3-(3-methoxybenzoyl)cyclopropane-1,1-dicarbonitrile (**1g**).

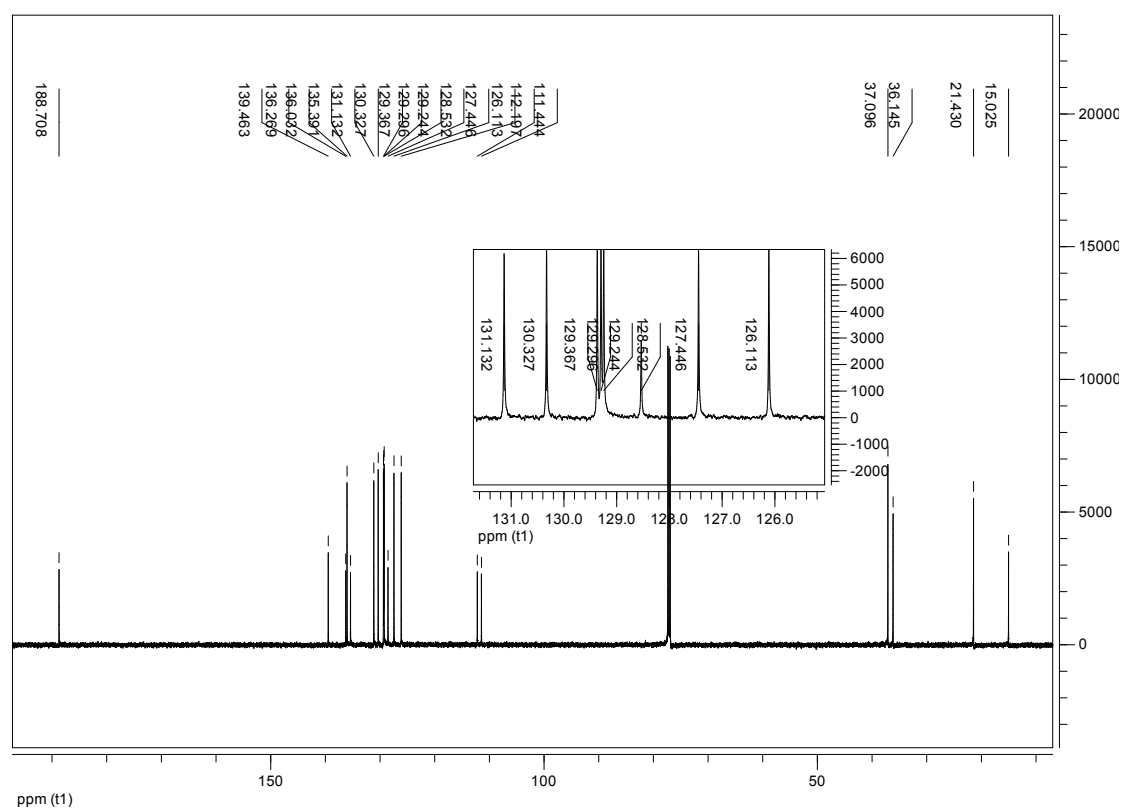


2-Benzoyl-3-(3-phenoxyphenyl)cyclopropane-1,1-dicarbonitrile (**1h**)

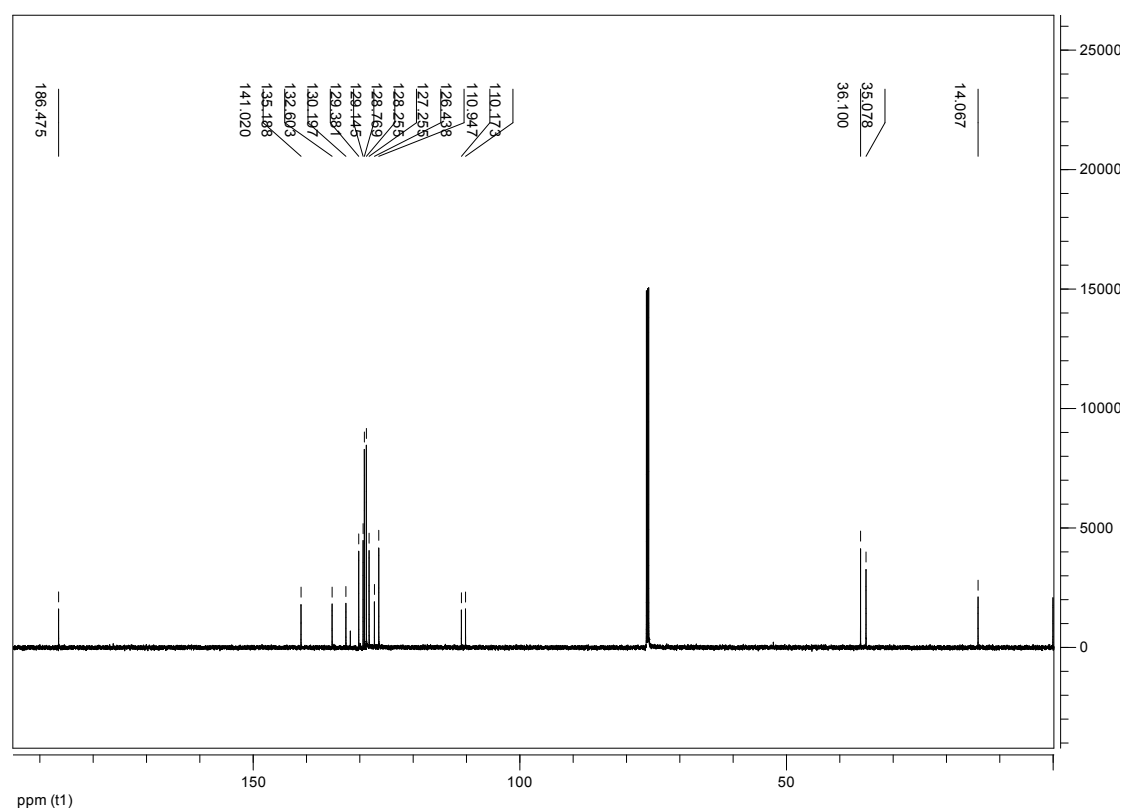
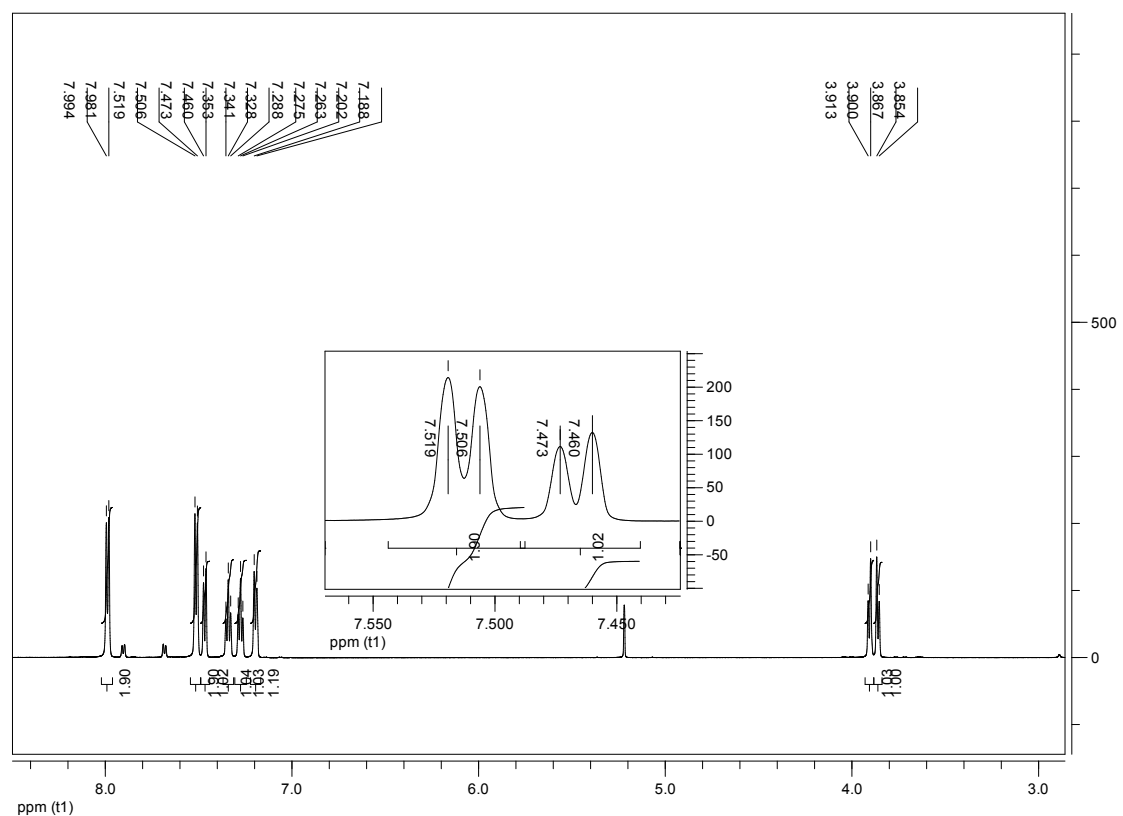


<sup>1</sup>H NMR spectrum of compound 10 in CDCl<sub>3</sub>. The spectrum shows peaks from 7.4 to 3.9 ppm. An inset shows the aromatic region from 7.2 to 7.5 ppm. Integration values are provided below the peaks.

| Chemical Shift (ppm)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | Integration |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------|
| 7.484, 7.482, 7.480, 7.478, 7.476, 7.474, 7.472, 7.470, 7.468, 7.466, 7.464, 7.462, 7.460, 7.458, 7.456, 7.454, 7.452, 7.450, 7.448, 7.446, 7.444, 7.442, 7.440, 7.438, 7.436, 7.434, 7.432, 7.430, 7.428, 7.426, 7.424, 7.422, 7.420, 7.418, 7.416, 7.414, 7.412, 7.410, 7.408, 7.406, 7.404, 7.402, 7.400, 7.398, 7.396, 7.394, 7.392, 7.390, 7.388, 7.386, 7.384, 7.382, 7.380, 7.378, 7.376, 7.374, 7.372, 7.370, 7.368, 7.366, 7.364, 7.362, 7.360, 7.358, 7.356, 7.354, 7.352, 7.350, 7.348, 7.346, 7.344, 7.342, 7.340, 7.338, 7.336, 7.334, 7.332, 7.330, 7.328, 7.326, 7.324, 7.322, 7.320, 7.318, 7.316, 7.314, 7.312, 7.310, 7.308, 7.306, 7.304, 7.302, 7.300, 7.298, 7.296, 7.294, 7.292, 7.290, 7.288, 7.286, 7.284, 7.282, 7.280, 7.278, 7.276, 7.274, 7.272, 7.270, 7.268, 7.266, 7.264, 7.262, 7.260, 7.258, 7.256, 7.254, 7.252, 7.250, 7.248, 7.246, 7.244, 7.242, 7.240, 7.238, 7.236, 7.234, 7.232, 7.230, 7.228, 7.226, 7.224, 7.222, 7.220, 7.218, 7.216, 7.214, 7.212, 7.210, 7.208, 7.206, 7.204, 7.202, 7.200, 7.198, 7.196, 7.194, 7.192, 7.190, 7.188, 7.186, 7.184, 7.182, 7.180, 7.178, 7.176, 7.174, 7.172, 7.170, 7.168, 7.166, 7.164, 7.162, 7.160, 7.158, 7.156, 7.154, 7.152, 7.150, 7.148, 7.146, 7.144, 7.142, 7.140, 7.138, 7.136, 7.134, 7.132, 7.130, 7.128, 7.126, 7.124, 7.122, 7.120, 7.118, 7.116, 7.114, 7.112, 7.110, 7.108, 7.106, 7.104, 7.102, 7.100, 7.098, 7.096, 7.094, 7.092, 7.090, 7.088, 7.086, 7.084, 7.082, 7.080, 7.078, 7.076, 7.074, 7.072, 7.070, 7.068, 7.066, 7.064, 7.062, 7.060, 7.058, 7.056, 7.054, 7.052, 7.050, 7.048, 7.046, 7.044, 7.042, 7.040, 7.038, 7.036, 7.034, 7.032, 7.030, 7.028, 7.026, 7.024, 7.022, 7.020, 7.018, 7.016, 7.014, 7.012, 7.010, 7.008, 7.006, 7.004, 7.002, 7.000, 6.998, 6.996, 6.994, 6.992, 6.990, 6.988, 6.986, 6.984, 6.982, 6.980, 6.978, 6.976, 6.974, 6.972, 6.970, 6.968, 6.966, 6.964, 6.962, 6.960, 6.958, 6.956, 6.954, 6.952, 6.950, 6.948, 6.946, 6.944, 6.942, 6.940, 6.938, 6.936, 6.934, 6.932, 6.930, 6.928, 6.926, 6.924, 6.922, 6.920, 6.918, 6.916, 6.914, 6.912, 6.910, 6.908, 6.906, 6.904, 6.902, 6.900, 6.898, 6.896, 6.894, 6.892, 6.890, 6.888, 6.886, 6.884, 6.882, 6.880, 6.878, 6.876, 6.874, 6.872, 6.870, 6.868, 6.866, 6.864, 6.862, 6.860, 6.858, 6.856, 6.854, 6.852, 6.850, 6.848, 6.846, 6.844, 6.842, 6.840, 6.838, 6.836, 6.834, 6.832, 6.830, 6.828, 6.826, 6.824, 6.822, 6.820, 6.818, 6.816, 6.814, 6.812, 6.810, 6.808, 6.806, 6.804, 6.802, 6.800, 6.798, 6.796, 6.794, 6.792, 6.790, 6.788, 6.786, 6.784, 6.782, 6.780, 6.778, 6.776, 6.774, 6.772, 6.770, 6.768, 6.766, 6.764, 6.762, 6.760, 6.758, 6.756, 6.754, 6.752, 6.750, 6.748, 6.746, 6.744, 6.742, 6.740, 6.738, 6.736, 6.734, 6.732, 6.730, 6.728, 6.726, 6.724, 6.722, 6.720, 6.718, 6.716, 6.714, 6.712, 6.710, 6.708, 6.706, 6.704, 6.702, 6.700, 6.698, 6.696, 6.694, 6.692, 6.690, 6.688, 6.686, 6.684, 6.682, 6.680, 6.678, 6.676, 6.674, 6.672, 6.670, 6.668, 6.666, 6.664, 6.662, 6.660, 6.658, 6.656, 6.654, 6.652, 6.650, 6.648, 6.646, 6.644, 6.642, 6.640, 6.638, 6.636, 6.634, 6.632, 6.630, 6.628, 6.626, 6.624, 6.622, 6.620, 6.618, 6.616, 6.614, 6.612, 6.610, 6.608, 6.606, 6.604, 6.602, 6.600, 6.598, 6.596, 6.594, 6.592, 6.590, 6.588, 6.586, 6.584, 6.582, 6.580, 6.578, 6.576, 6.574, 6.572, 6.570, 6.568, 6.566, 6.564, 6.562, 6.560, 6.558, 6.556, 6.554, 6.552, 6.550, 6.548, 6.546, 6.544, 6.542, 6.540, 6.538, 6.536, 6.534, 6.532, 6.530, 6.528, 6.526, 6.524, 6.522, 6.520, 6.518, 6.516, 6.514, 6.512, 6.510, 6.508, 6.506, 6.504, 6.502, 6.500, 6.498, 6.496, 6.494, 6.492, 6.490, 6.488, 6.486, 6.484, 6.482, 6.480, 6.478, 6.476, 6.474, 6.472, 6.470, 6.468, 6.466, 6.464, 6.462, 6.460, 6.458, 6.456, 6.454, 6.452, 6.450, 6.448, 6.446, 6.444, 6.442, 6.440, 6.438, 6.436, 6.434, 6.432, 6.430, 6.428, 6.426, 6.424, 6.422, 6.420, 6.418, 6.416, 6.414, 6.412, 6.410, 6.408, 6.406, 6.404, 6.402, 6.400, 6.398, 6.396, 6.394, 6.392, 6.390, 6.388, 6.386, 6.384, 6.382, 6.380, 6.378, 6.376, 6.374, 6.372, 6.370, 6.368, 6.366, 6.364, 6. |             |

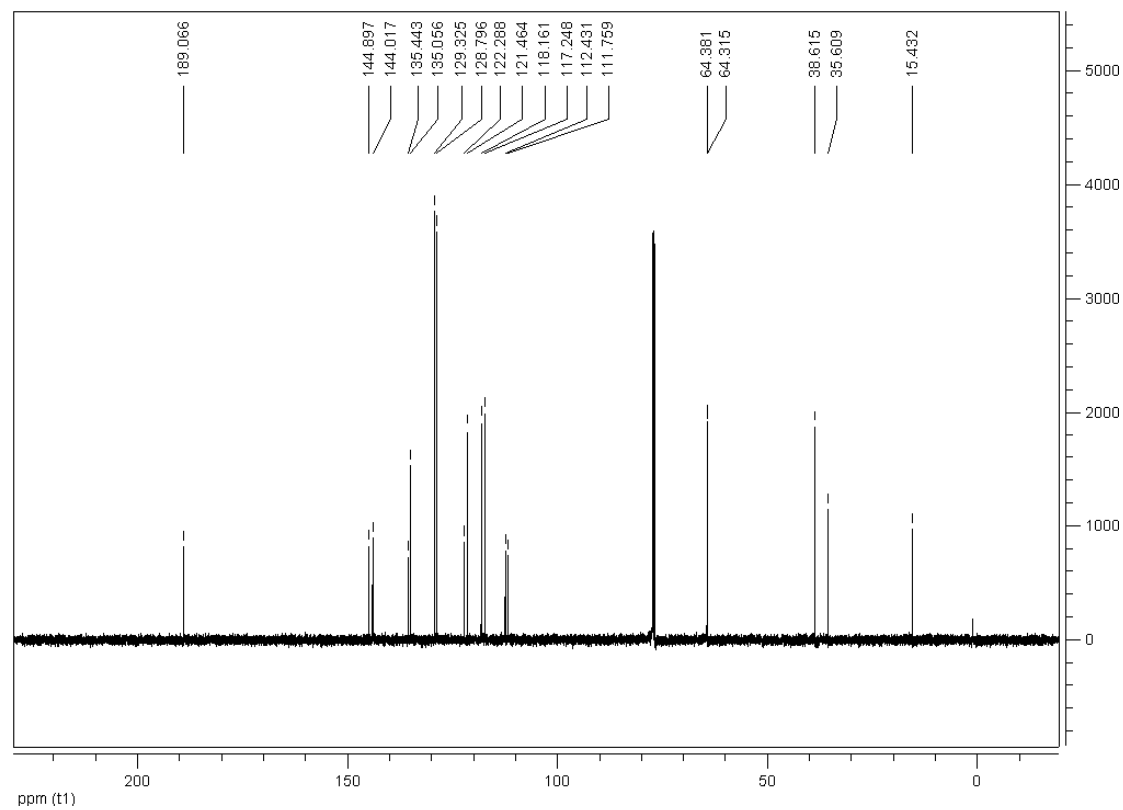
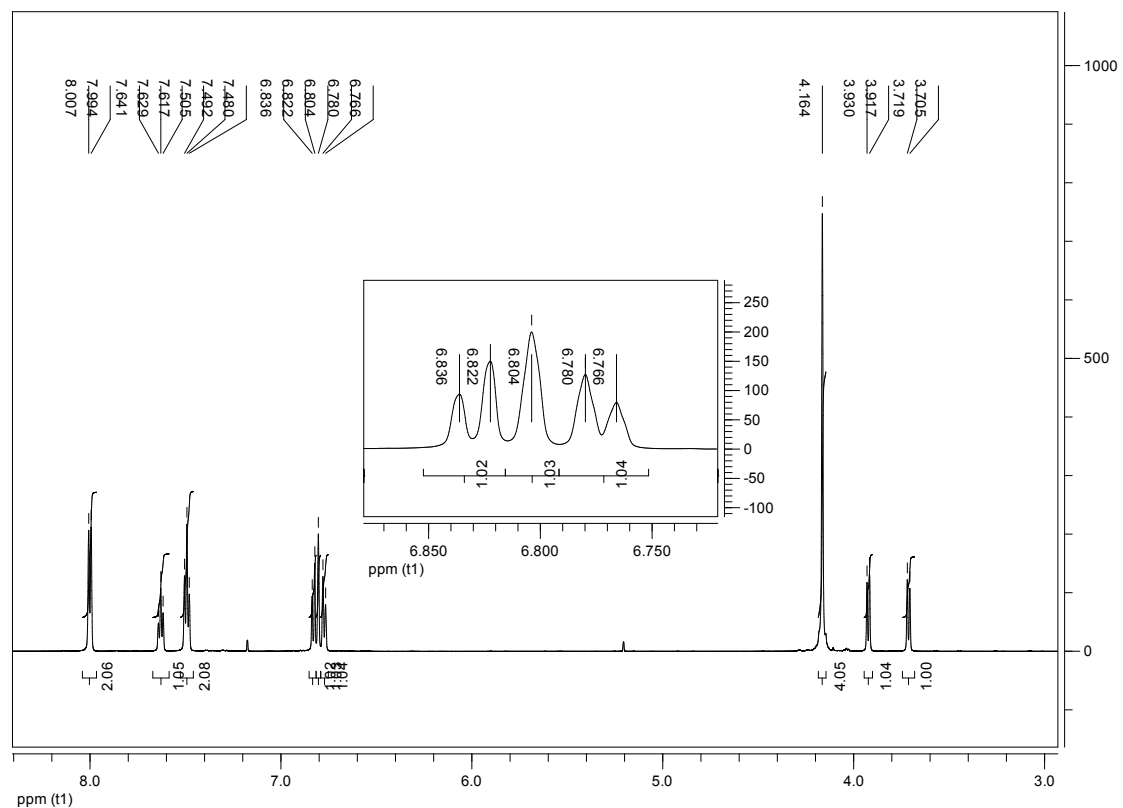


2-(4-Chlorobenzoyl)-3-(2-chlorophenyl)cyclopropane-1,1-dicarbonitrile (**II**).

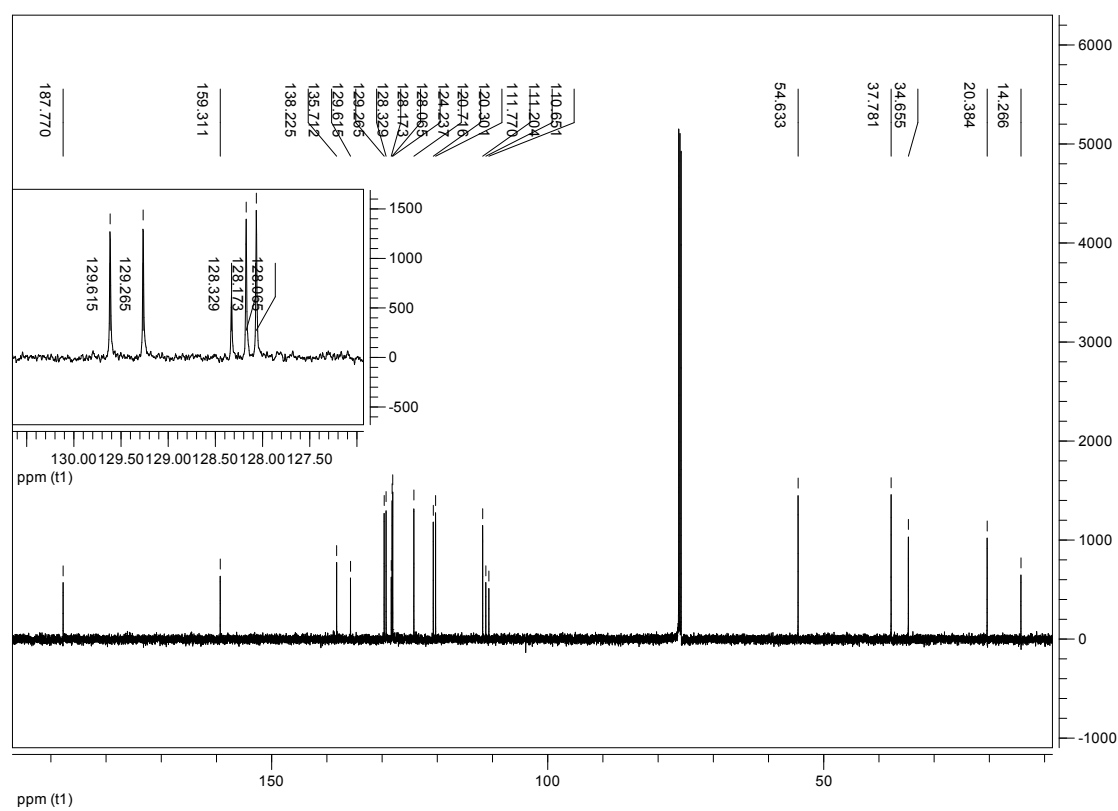
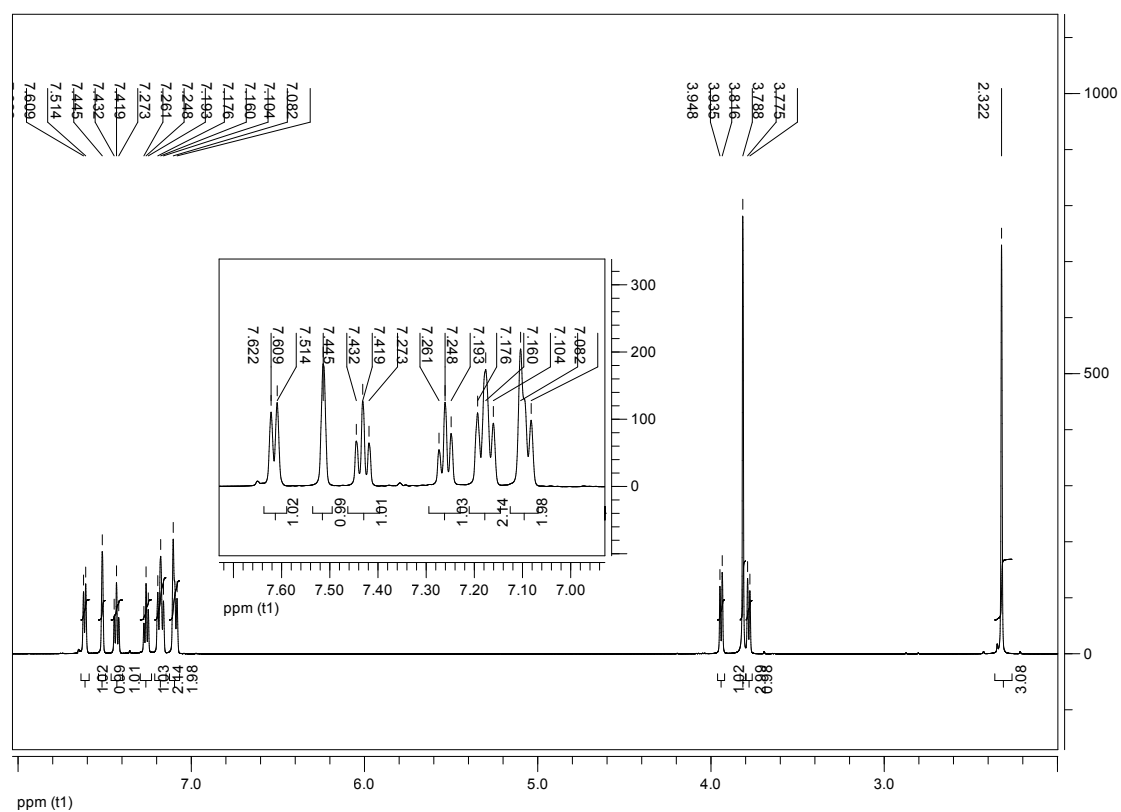


2-Benzoyl-3-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)cyclopropane-1,1-dicarbonitrile

(1n)

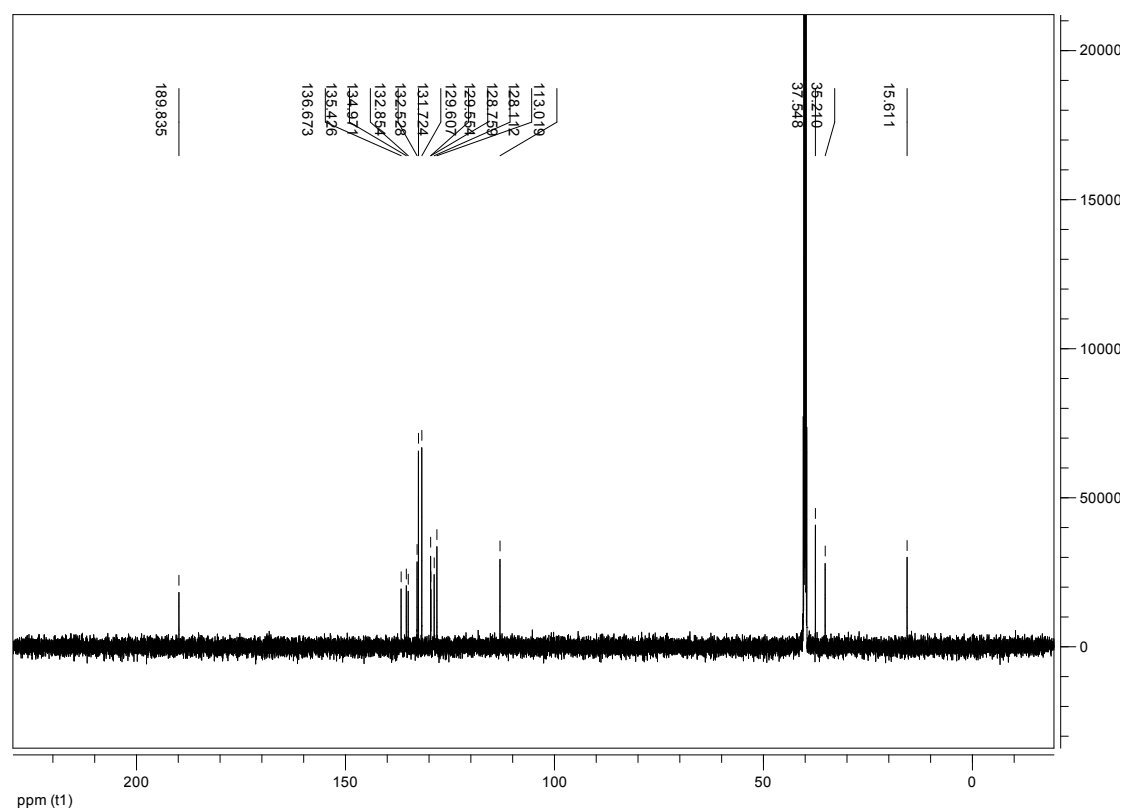
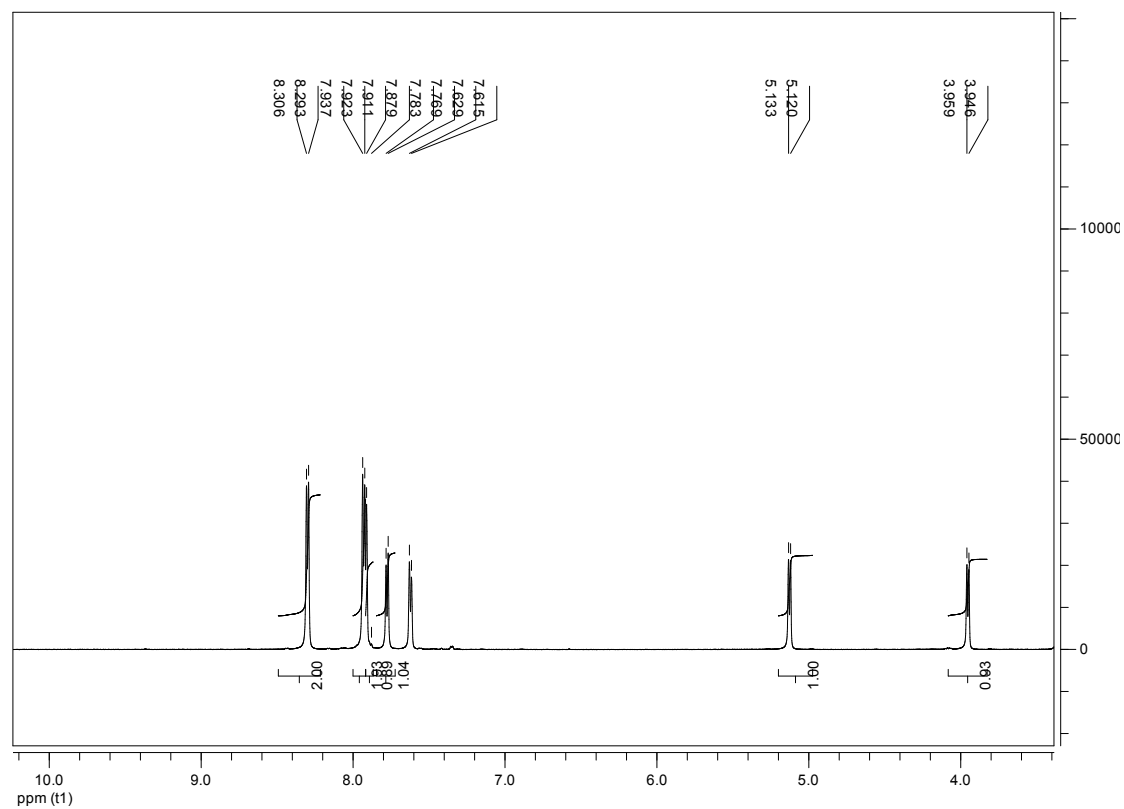


2-(3-Methoxybenzoyl)-3-(m-tolyl)cyclopropane-1,1-dicarbonitrile (**1p**)



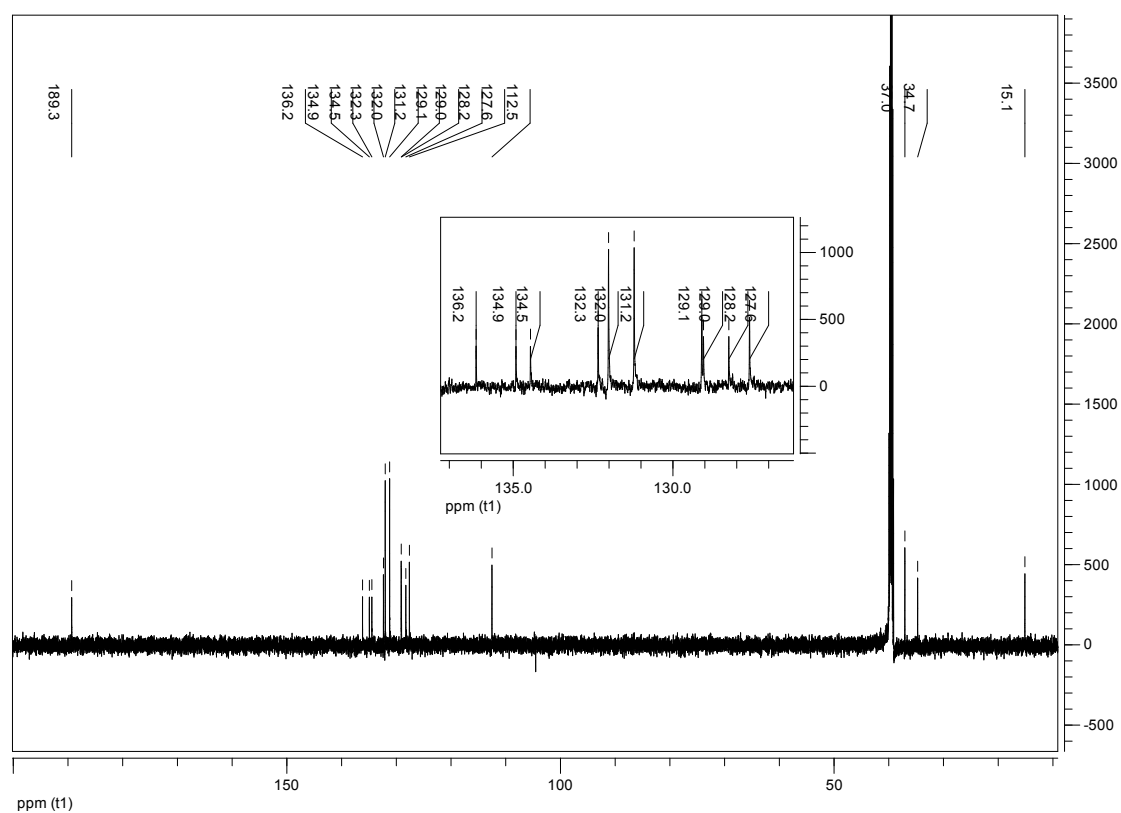


2-(4-Bromobenzoyl)-3-(thiophen-2-yl)cyclopropane-1,1-dicarbonitrile (**1q**)



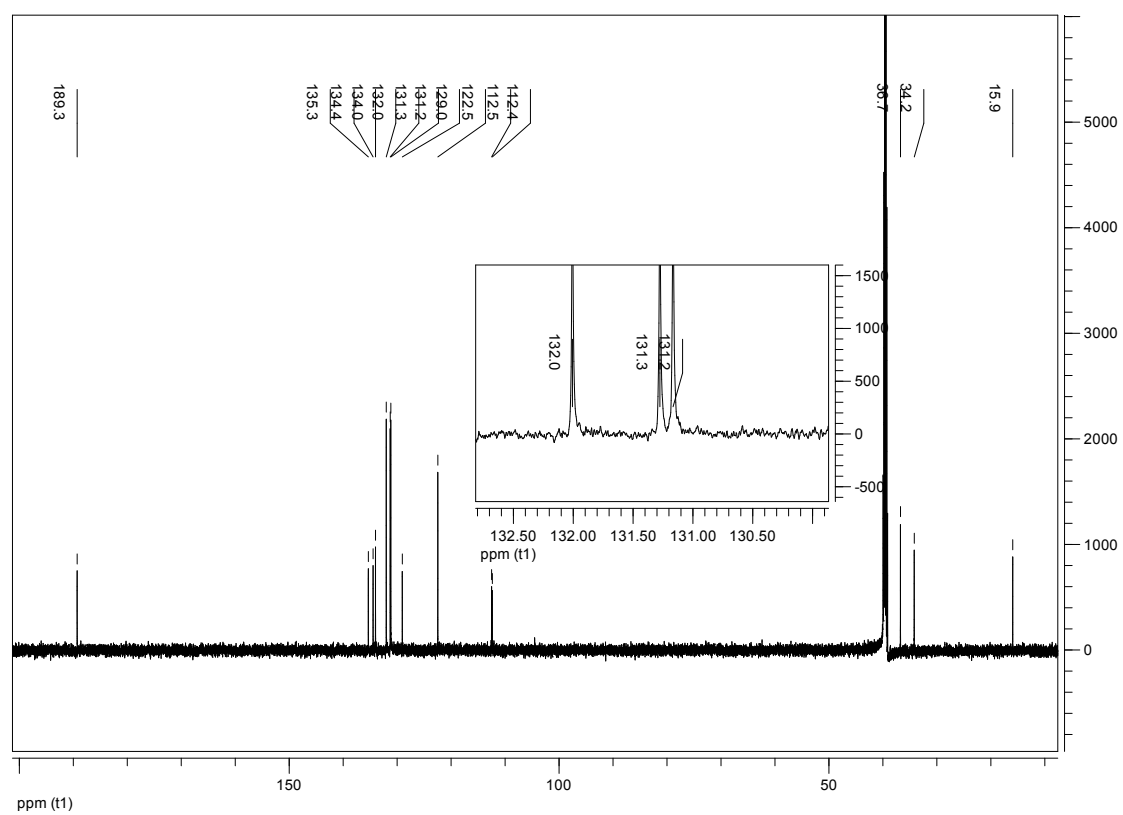
<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of compound 1. The x-axis represents the chemical shift in ppm (t1), ranging from 2.5 to 8.5. The y-axis represents the intensity, ranging from -100 to 700. The spectrum shows several peaks, with an inset providing a detailed view of the aromatic region (7.5–8.3 ppm). Integration values are indicated below the peaks.

| Chemical Shift (ppm) | Integration |
|----------------------|-------------|
| ~8.25                | 0.072       |
| ~8.23                | 0.072       |
| ~8.20                | 0.072       |
| ~8.18                | 0.072       |
| ~8.15                | 0.072       |
| ~8.12                | 0.072       |
| ~8.08                | 0.072       |
| ~8.05                | 0.072       |
| ~8.02                | 0.072       |
| ~7.88                | 0.072       |
| ~7.85                | 0.072       |
| ~7.82                | 0.072       |
| ~7.78                | 0.072       |
| ~7.75                | 0.072       |
| ~7.72                | 0.072       |
| ~7.68                | 0.072       |
| ~7.65                | 0.072       |
| ~7.62                | 0.072       |
| ~7.58                | 0.072       |
| ~7.55                | 0.072       |
| ~7.52                | 0.072       |
| ~7.48                | 0.072       |
| ~7.45                | 0.072       |
| ~7.42                | 0.072       |
| ~7.38                | 0.072       |
| ~7.35                | 0.072       |
| ~7.32                | 0.072       |
| ~7.28                | 0.072       |
| ~7.25                | 0.072       |
| ~7.22                | 0.072       |
| ~7.18                | 0.072       |
| ~7.15                | 0.072       |
| ~7.12                | 0.072       |
| ~7.08                | 0.072       |
| ~7.05                | 0.072       |
| ~7.02                | 0.072       |
| ~6.98                | 0.072       |
| ~6.95                | 0.072       |
| ~6.92                | 0.072       |
| ~6.88                | 0.072       |
| ~6.85                | 0.072       |
| ~6.82                | 0.072       |
| ~6.78                | 0.072       |
| ~6.75                | 0.072       |
| ~6.72                | 0.072       |
| ~6.68                | 0.072       |
| ~6.65                | 0.072       |
| ~6.62                | 0.072       |
| ~6.58                | 0.072       |
| ~6.55                | 0.072       |
| ~6.52                | 0.072       |
| ~6.48                | 0.072       |
| ~6.45                | 0.072       |
| ~6.42                | 0.072       |
| ~6.38                | 0.072       |
| ~6.35                | 0.072       |
| ~6.32                | 0.072       |
| ~6.28                | 0.072       |
| ~6.25                | 0.072       |
| ~6.22                | 0.072       |
| ~6.18                | 0.072       |
| ~6.15                | 0.072       |
| ~6.12                | 0.072       |
| ~6.08                | 0.072       |
| ~6.05                | 0.072       |
| ~6.02                | 0.072       |
| ~5.98                | 0.072       |
| ~5.95                | 0.072       |
| ~5.92                | 0.072       |
| ~5.88                | 0.072       |
| ~5.85                | 0.072       |
| ~5.82                | 0.072       |
| ~5.78                | 0.072       |
| ~5.75                | 0.072       |
| ~5.72                | 0.072       |
| ~5.68                | 0.072       |
| ~5.65                | 0.072       |
| ~5.62                | 0.072       |
| ~5.58                | 0.072       |
| ~5.55                | 0.072       |
| ~5.52                | 0.072       |
| ~5.48                | 0.072       |
| ~5.45                | 0.072       |
| ~5.42                | 0.072       |
| ~5.38                | 0.072       |
| ~5.35                | 0.072       |
| ~5.32                | 0.072       |
| ~5.28                | 0.072       |
| ~5.25                | 0.072       |
| ~5.22                | 0.072       |
| ~5.18                | 0.072       |
| ~5.15                | 0.072       |
| ~5.12                | 0.072       |
| ~5.08                | 0.072       |
| ~5.05                | 0.072       |
| ~5.02                | 0.072       |
| ~4.98                | 0.072       |
| ~4.95                | 0.072       |
| ~4.92                | 0.072       |
| ~4.88                | 0.072       |
| ~4.85                | 0.072       |
| ~4.82                | 0.072       |
| ~4.78                | 0.072       |
| ~4.75                | 0.072       |
| ~4.72                | 0.072       |
| ~4.68                | 0.072       |
| ~4.65                | 0.072       |
| ~4.62                | 0.072       |
| ~4.58                | 0.072       |
| ~4.55                | 0.072       |
| ~4.52                | 0.072       |
| ~4.48                | 0.072       |
| ~4.45                | 0.072       |
| ~4.42                | 0.072       |
| ~4.38                | 0.072       |
| ~4.35                | 0.072       |
| ~4.32                | 0.072       |
| ~4.28                | 0.072       |
| ~4.25                | 0.072       |
| ~4.22                | 0.072       |
| ~4.18                | 0.072       |
| ~4.15                | 0.072       |
| ~4.12                | 0.072       |
| ~4.08                | 0.072       |
| ~4.05                | 0.072       |
| ~4.02                | 0.072       |
| ~3.98                | 0.072       |
| ~3.95                | 0.072       |
| ~3.92                | 0.072       |
| ~3.88                | 0.072       |
| ~3.85                | 0.072       |
| ~3.82                | 0.072       |
| ~3.78                | 0.072       |
| ~3.75                | 0.072       |
| ~3.72                | 0.072       |
| ~3.68                | 0.072       |
| ~3.65                | 0.072       |
| ~3.62                | 0.072       |
| ~3.58                | 0.072       |
| ~3.55                | 0.072       |
| ~3.52                | 0.072       |
| ~3.48                | 0.072       |
| ~3.45                | 0.072       |
| ~3.42                | 0.072       |
| ~3.38                | 0.072       |
| ~3.35                | 0.072       |
| ~3.32                | 0.072       |
| ~3.28                | 0.072       |
| ~3.25                | 0.072       |
| ~3.22                | 0.072       |
| ~3.18                | 0.072       |
| ~3.15                | 0.072       |
| ~3.12                | 0.072       |
| ~3.08                | 0.072       |
| ~3.05                | 0.072       |
| ~3.02                | 0.072       |
| ~2.98                | 0.072       |
| ~2.95                | 0.072       |
| ~2.92                | 0.072       |
| ~2.88                | 0.072       |
| ~2.85                | 0.072       |
| ~2.82                | 0.072       |
| ~                    |             |

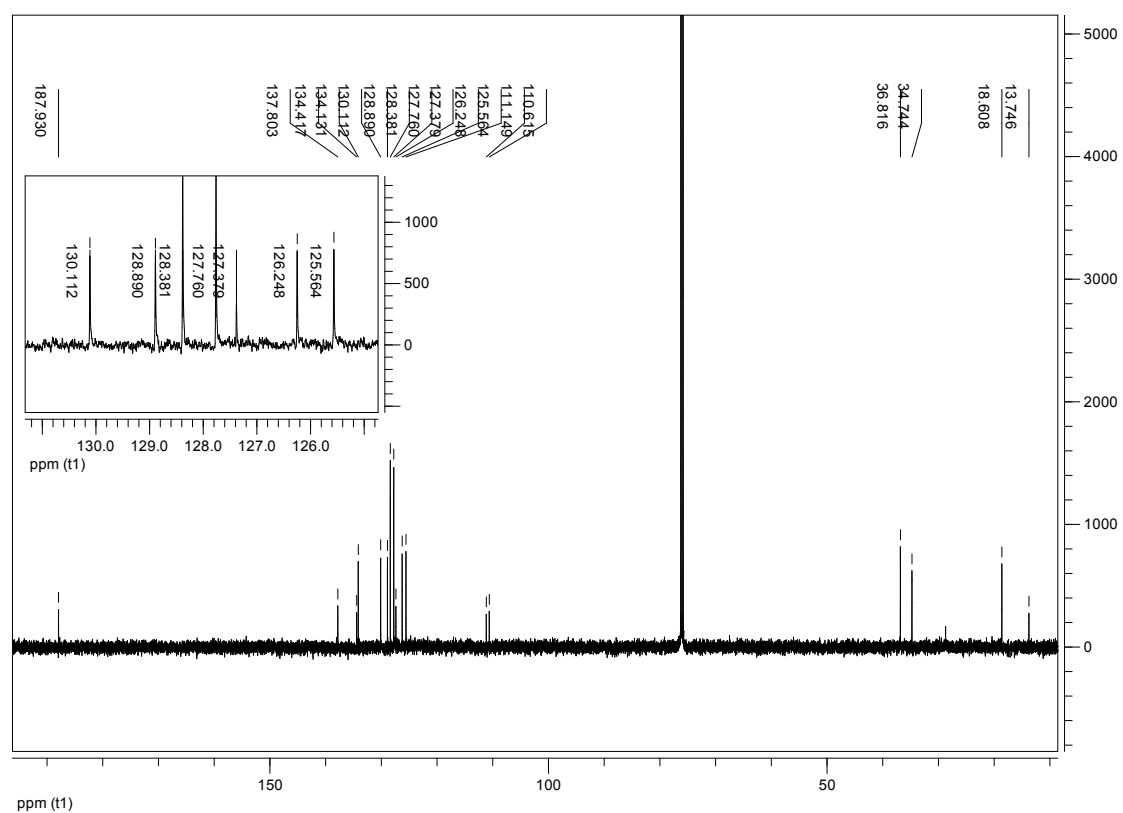
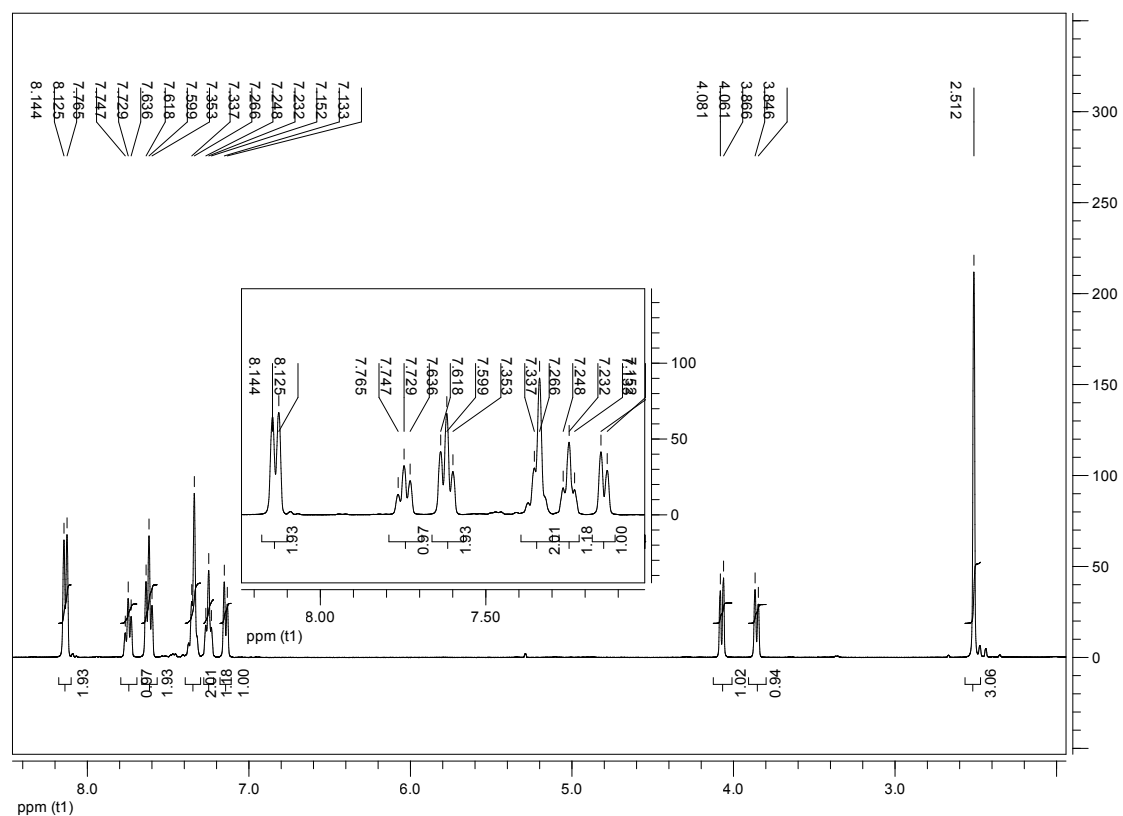


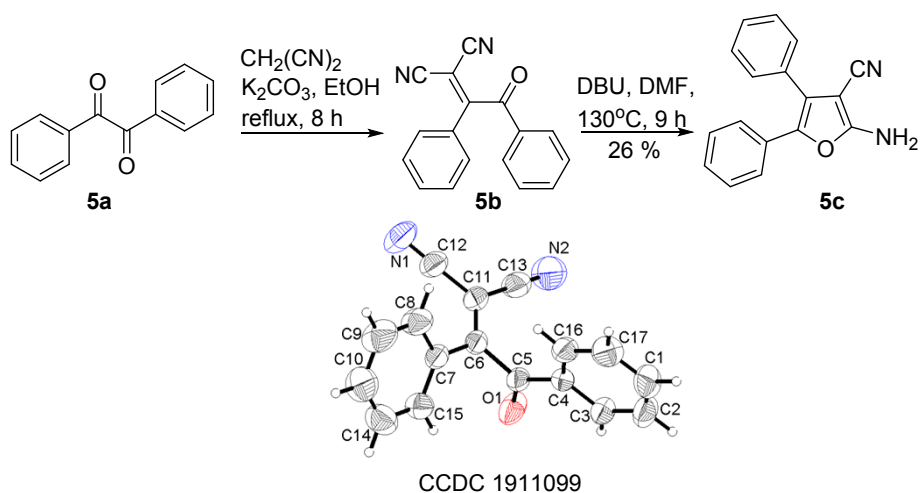
<sup>1</sup>H NMR spectrum of compound 10 in CDCl<sub>3</sub>. The spectrum shows peaks at 4.091, 4.111, 5.137, and 5.157 ppm. An inset shows the aromatic region from 7.80 to 8.30 ppm with peaks at 7.863, 7.882, 7.898, 8.037, 8.224, and 8.244 ppm. Integration values are provided for each peak.

| Chemical Shift (ppm) | Integration |
|----------------------|-------------|
| 4.091                | 0.01        |
| 4.111                | 0.01        |
| 5.137                | 0.01        |
| 5.157                | 0.01        |
| 7.863                | 0.02        |
| 7.882                | 0.02        |
| 7.898                | 0.02        |
| 8.037                | 0.02        |
| 8.224                | 0.02        |
| 8.244                | 0.02        |



2-Benzoyl-3-(o-tolyl)cyclopropane-1,1-dicarbonitrile (**1t**)





Scheme S1 Synthesis of 2-amino-4,5-diphenylfuran-3-carbonitrile under the title reaction conditions

Table S8. Crystal data and structure refinement for **5b**.

|                             |                                                                                                                       |
|-----------------------------|-----------------------------------------------------------------------------------------------------------------------|
| Identification code         | <b>5b</b>                                                                                                             |
| Empirical formula           | C <sub>17</sub> H <sub>10</sub> N <sub>2</sub> O                                                                      |
| Formula weight              | 258.27                                                                                                                |
| Temperature                 | 298 K                                                                                                                 |
| Wavelength                  | 0.71073 Å                                                                                                             |
| Crystal system, space group | Monoclinic, P2(1)/c                                                                                                   |
| Unit cell dimensions        | a = 7.761(4) Å    alpha = 90 deg.<br>b = 23.473(12) Å    beta = 111.679(12) deg.<br>c = 8.263(5) Å    gamma = 90 deg. |
| Volume                      | 1398.9(13) Å <sup>3</sup>                                                                                             |
| Z, Calculated density       | 4, 1.226 Mg/m <sup>3</sup>                                                                                            |
| Absorption coefficient      | 0.078 mm <sup>-1</sup>                                                                                                |
| F(000)                      | 536                                                                                                                   |
| Crystal size                | 0.35 x 0.33 x 0.3 mm                                                                                                  |

Theta range for data collection 1.74 to 25.00 deg.

Limiting indices  $-8 \leq h \leq 9$ ,  $-27 \leq k \leq 27$ ,  $-9 \leq l \leq 6$

Reflections collected / unique 5955 / 2464 [R(int) = 0.0213]

Completeness to theta = 25.00 96.6 %

Absorption correction None

Refinement method Full-matrix least-squares on F<sup>2</sup>

Data / restraints / parameters 2381 / 0 / 181

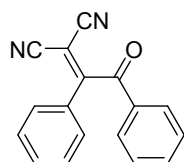
Goodness-of-fit on F<sup>2</sup> 1.081

Final R indices [ $I > 2\sigma(I)$ ] R1 = 0.0434, wR2 = 0.1237

R indices (all data) R1 = 0.0568, wR2 = 0.1429

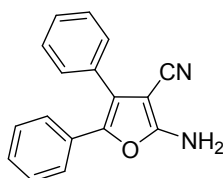
Largest diff. peak and hole 0.137 and -0.162 e.Å<sup>-3</sup>

2-(2-oxo-1,2-diphenylethylidene)malononitrile (**5b**)



<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ (ppm): 8.08 (d, *J* = 7.2 Hz, 2H), 7.82-7.72 (m, 1H), 7.79 (d, *J* = 7.2 Hz, 2H), 7.69-7.54 (m, 5H); <sup>13</sup>C{<sup>1</sup>H} NMR (150 MHz, DMSO-*d*<sub>6</sub>) δ (ppm): 191.6, 170.1, 136.6, 134.0, 133.0, 130.7, 130.5, 130.2, 130.1, 128.8, 112.6, 112.5, 85.9.

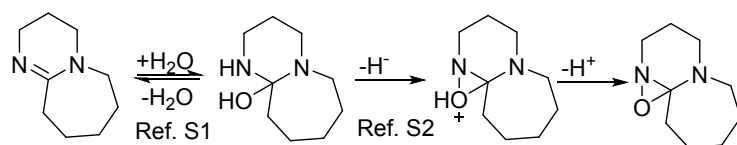
2-amino-4,5-diphenylfuran-3-carbonitrile (**5c**)



Yellow solid, 410 mg, yield: 26%; mp 205.1–205.5 °C (EA/PE); IR (KBr, cm<sup>-1</sup>): 3705, 3446, 3307, 3047, 2213, 1822, 1654, 1573, 1499, 1445, 1067, 763, 698; <sup>1</sup>H

NMR (400 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 7.70 (s, 2H), 7.46-7.44 (m, 3H), 7.40-7.38 (m, 2H), 7.26-7.23 (m, 5H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 163.5, 136.6, 131.2, 129.3, 128.9, 128.8, 128.5, 128.3, 126.9, 124.2, 121.8, 115.4, 69.2; HR-MS (ESI) calcd for  $\text{C}_{17}\text{H}_{12}\text{N}_2\text{NaO}$   $[(\text{M} + \text{Na})^+]$ : 283.0847; Found: 283.0850.

Scheme S2 Possible Mechanism of DBU as a Hydride Donor in Toluene or DCM



Reference S1 Okada, J. and Shimabayashi, M. N-Acetylation of 1,3-diazines, *J. Pharm. Soc. Jpn.*, 1977, 97, 962-967.

Reference S2 Ishikawa, T. and Iwami, M. Preparation of kakeromycin and its derivatives, WO 2016136963, 2016.