Organic & Biomolecular Chemistry *Supporting Information*

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

Zhenjie Su,[a,&] Zengyang Xie,[b,&] Shan Wang,[a] Naili Luo[a] and Cunde Wang*[a]

[a]*School of Chemistry and Chemical Engineering, Yangzhou University,180 Siwangting Street, Yangzhou 225002, P. R. China. Fax: +86-514-8797-5244; Tel: +86-514-8797-5568; E-mail: wangcd@yzu.edu.cn*

[b]*College of Basic Medicine, Jining Medical University, Jining 272067, P. R. China.*

[&]*These authors contributed equally to this work and should be considered co-first authors*

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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.[29] D-A cyclopropanes **1a-d**, **1j-k**, **1m**, **1o, 1q** and **1u** were known compounds.[25g, 26, 29]

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^{-1}): 3360, 2930, 2912, 2760, 2670, 2421, 2210, 1762, 1680, 1536, 1435, 1320, 1265, 1102, 980; ^{1}H NMR (600 MHz, $CDCl_3$) 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); ^{13}C NMR (150 MHz, $CDCl_3$) 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 $C_{21}H_{16}N_2NaO_4$ [$(M+Na)^+$]: 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^{-1}): 3420, 2962, 2930, 2730, 2672, 2431, 2210, 1686, 1530, 1431, 1320, 1260, 1107, 982; ^{1}H NMR (600 MHz, $CDCl_3$) 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); ^{13}C NMR (150 MHz, $CDCl_3$) 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 $C_{19}H_{13}BrN_2NaO$ [$(M+Na)^+$]: 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^{-1}): 3330, 2950, 2676, 2435, 2212, 1678, 1530, 1432, 1316, 1260, 1107, 952, 860; ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (150

MHz, $CDCl_3$) δ (*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 $C_{18}H_{11}BrN_2NaO$ [$(M+Na)^+$]: 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^{-1}): 3340, 2956, 2702, 2403, 2202, 1672, 1550, 1430, 1326, 1266, 1100, 918, 890; ^1H NMR (600 MHz, $CDCl_3$) δ (*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); ^{13}C NMR (150 MHz, $CDCl_3$) δ (*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 $C_{19}H_{13}ClN_2NaO_2$ [$(M+Na)^+$]: 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^{-1}): 3332, 2950, 2709, 2679, 2418, 2208, 1679, 1550, 1546, 1430, 1326, 1266, 1106, 910, 898; ^1H NMR (600 MHz, $CDCl_3$) δ (*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); ^{13}C NMR (100 MHz, $CDCl_3$) δ (*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 $C_{24}H_{16}N_2NaO_2$ [$(M+Na)^+$]: 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^{-1}): 3303, 2958, 2701, 2604, 2420, 2216, 1670, 1555, 1432, 1320, 1260, 1102, 990, 875; ^1H NMR (600 MHz, $CDCl_3$) δ (*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}C NMR (150 MHz, $CDCl_3$) δ (*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 $C_{19}H_{13}ClN_2NaO$ [$(M+Na)^+$]: 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, cm^{-1}): 3326, 2950, 2768, 2624, 2426, 2210, 1668, 1550, 1438, 1320, 1266, 1102, 980, 896; ^{1}H NMR (600 MHz, $CDCl_3$) δ (*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}C NMR (150 MHz, $CDCl_3$) δ (*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 $C_{18}H_{10}Cl_2N_2NaO$ [$(M+Na)^+$]: 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, cm^{-1}): 3420, 3030, 2780, 2624, 2460, 2224, 1660, 1550, 1430, 1324, 1260, 1108, 976, 896; ^{1}H NMR (600 MHz, $CDCl_3$) δ (*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}C NMR (150 MHz, $CDCl_3$) δ (*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 $C_{20}H_{14}N_2NaO_3$ [$(M+Na)^+$]: 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, cm^{-1}): 3408, 3030, 2760, 2650, 2462, 2226, 1665, 1556, 1436, 1325, 1260, 1112, 968, 906; ^{1}H NMR (400 MHz, $CDCl_3$) δ (*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}C NMR (100 MHz, $CDCl_3$) δ (*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 $C_{20}H_{16}N_2NaO_2$ [$(M+Na)^+$]: 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, cm^{-1}): 3330, 2952, 2770, 2660, 2410, 2218, 1665, 1555, 1430, 1320, 1266, 1102, 988, 890; ^{1}H NMR (600 MHz, DMSO-d_6) δ (*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}C NMR (150 MHz, DMSO-d_6) δ (*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 $C_{18}H_9BrCl_2N_2NaO$ [$(M+Na)^+$]: 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, cm^{-1}): 3338, 2950, 2765, 2668, 2420, 2220, 1662, 1550, 1432, 1326, 1260, 1102, 985, 896; ^{1}H NMR (400 MHz, DMSO-d_6) δ (*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}C NMR (150 MHz, DMSO-d_6) δ (*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 $C_{18}H_9Br_3N_2NaO$ [$(M+Na)^+$]: 528.8163; Found: 528.8150.

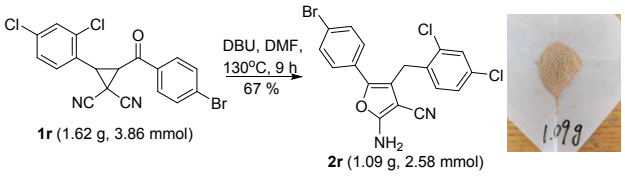
2-Benzoyl-3-(o-tolyl)cyclopropane-1,1-dicarbonitrile (**1t**)

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

^{1}H NMR (400 MHz, $CDCl_3$) δ (*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}C NMR (150 MHz, $CDCl_3$) δ (*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 $C_{19}H_{14}N_2NaO$ [$(M+Na)^+$]: 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).

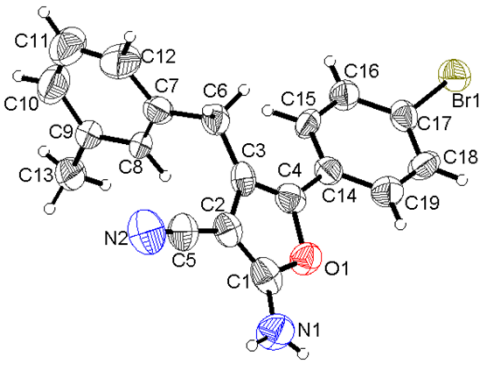


1r (1.62 g, 3.86 mmol)

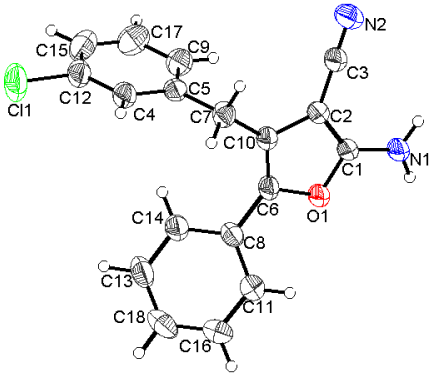
2r (1.09 g, 2.58 mmol)

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

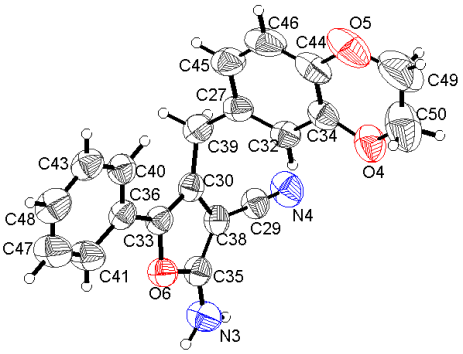
All single crystals were obtained using EtOAc/hexanes as a mixture solvent. X-ray crystallographic analysis was performed with a Smart-1000 CCD diffractometer using monochromatic Mo KR radiation (λ) 0.71073 Å) and integrated with the SAINT-Plus program. All calculations were performed with programs from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



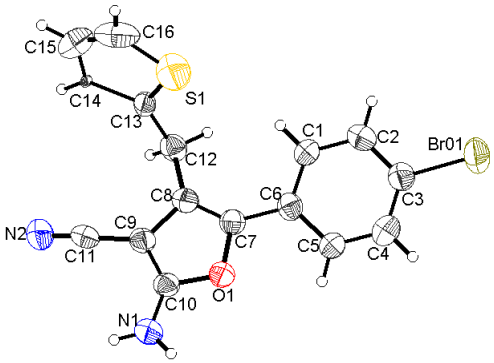
2b (CCDC 1891524)



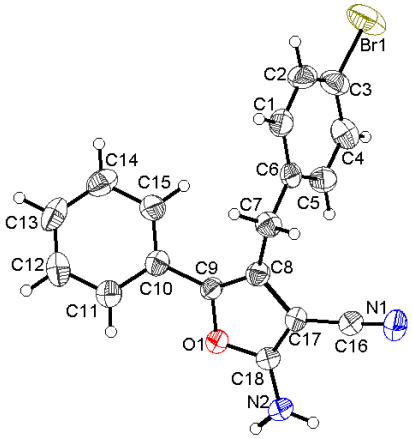
2d (CCDC 1858658)



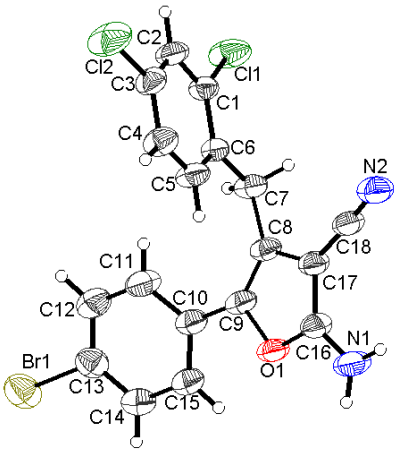
2n (CCDC 1875320)



2q (CCDC 1880678)

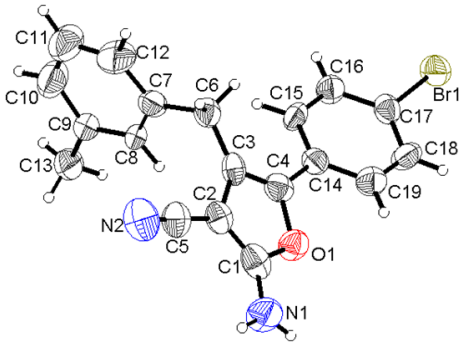


2k (CCDC 1908517)



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.



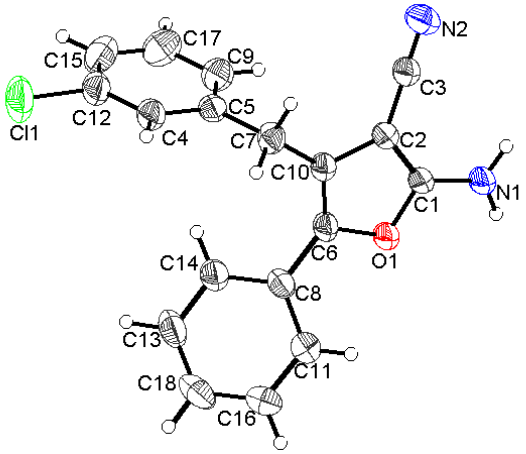
2b (CCDC 1891524)

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	**2b**
Empirical formula	$C_{20}H_{15}BrN_2O$
Formula weight	379.24
Temperature	296 K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 11.5956(17) A alpha = 90 deg. b = 5.0269(7) A beta = 92.159(4) deg. c = 33.000(5) A gamma = 90 deg.
Volume	1922.2(5) A^3
Z, Calculated density	4, 1.311 Mg/m^3
Absorption coefficient	2.146 mm^-1
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<=h<=11, -5<=k<=5, -35<=l<=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>2sigma(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.A^-3



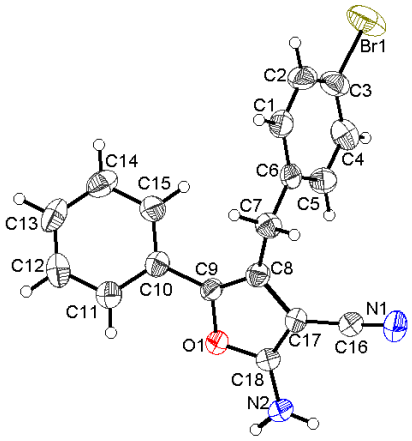
2d (CCDC 1858658)

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

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<=h<=8, -9<=k<=9, -21<=l<=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>2sigma(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.A^-3



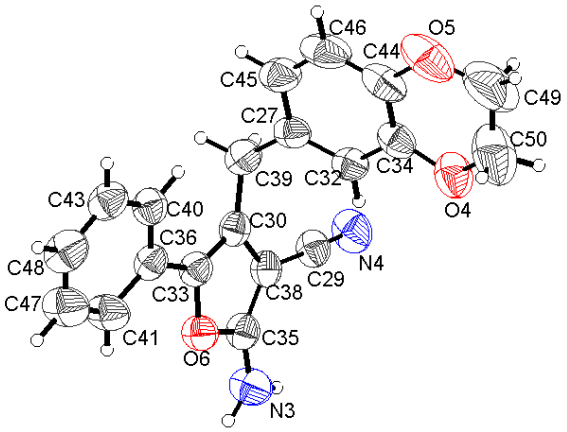
2k (CCDC 1908517)

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	**2k**
Empirical formula	C_{18} H_{13} Br N_2 O
Formula weight	353.20
Temperature	298 K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 6.192(5) A alpha = 87.67(2) deg. b = 7.311(2) A beta = 85.16(3) deg. c = 16.718(3) A gamma = 86.34(2) deg.
Volume	752.1(7) A^3
Z, Calculated density	2, 1.560 Mg/m^3
Absorption coefficient	2.736 mm^-1

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<=h<=7, -8<=k<=8, -19<=l<=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>2sigma(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.A^-3



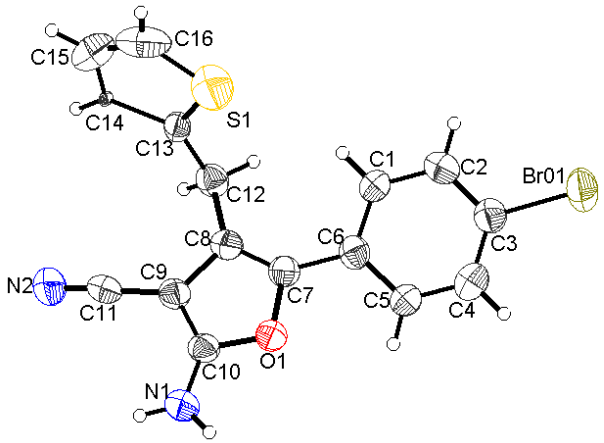
2n (CCDC 1875320)

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	**2n**
Empirical formula	$C_{20}H_{16}N_2O_3$
Formula weight	332.35
Temperature	298 K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 9.8735(10) A alpha = 104.559(3) deg. b = 11.1925(13) A beta = 102.943(3) deg. c = 16.3751(18) A gamma = 102.875(3) deg.
Volume	1630.6(3) A^3
Z, Calculated density	4, 1.354 Mg/m^3
Absorption coefficient	0.092 mm^-1
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<=h<=12, -14<=k<=14, -21<=l<=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^2
Data / restraints / parameters	7477 / 1 / 451
Goodness-of-fit on F^2	1.033
Final R indices [I>2sigma(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.A^-3



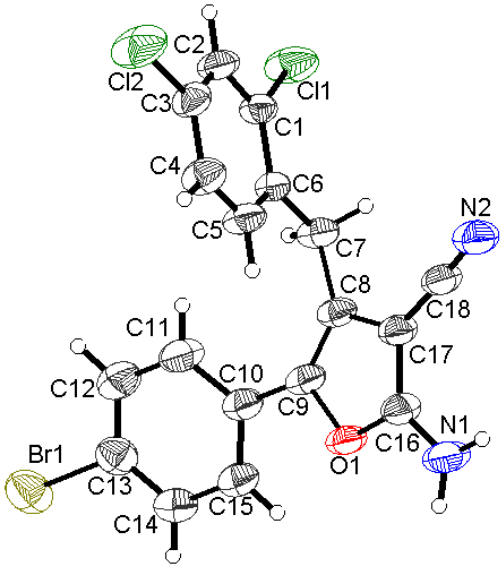
2q (CCDC 1880678)

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	**2q**
Empirical formula	$C_{16}H_{11}BrN_2OS$
Formula weight	359.23
Temperature	298 K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 4.73(1) A alpha = 77.0(1) deg. b = 10.20(2) A beta = 86.0(1) deg. c = 16.80(2) A gamma = 77.3(1) deg.
Volume	770(2) A^3
Z, Calculated density	2, 1.550 Mg/m^3
Absorption coefficient	2.804 mm^-1
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<=h<=6, -13<=k<=13, -21<=l<=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>2sigma(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.A^-3



2r (CCDC 1908518)

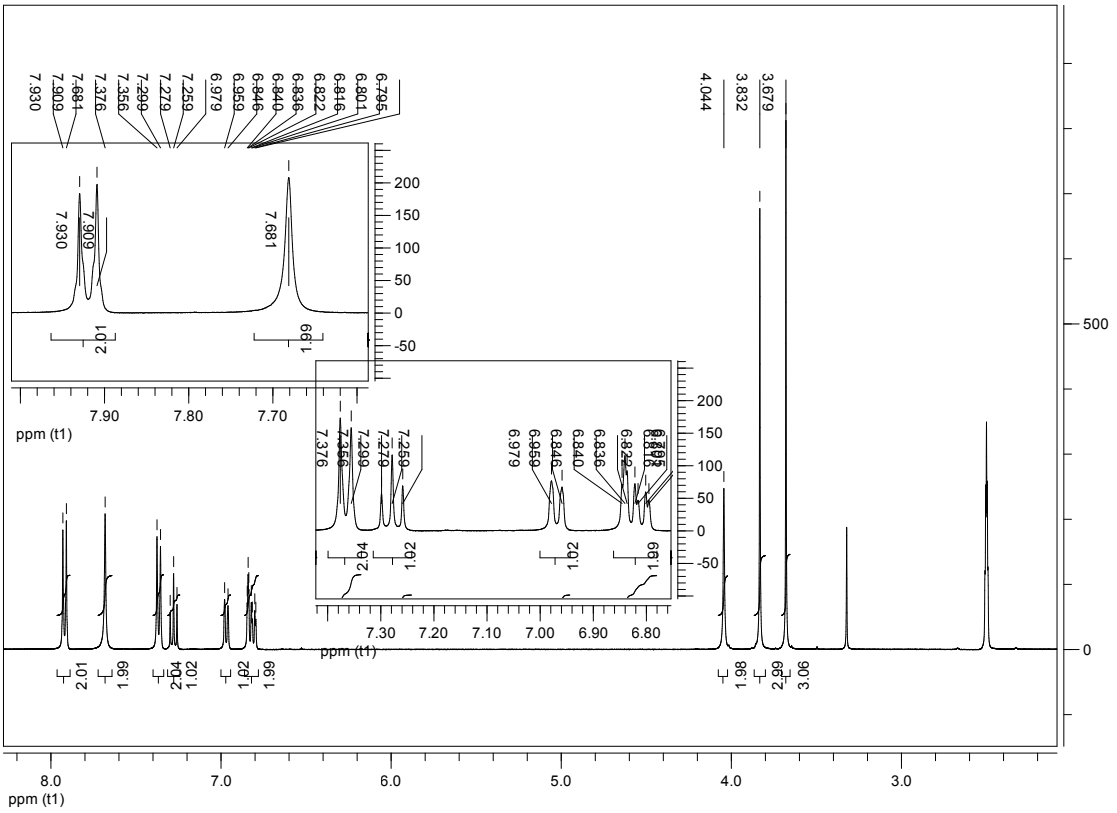
Fig. S6 Molecular structure of 2-amino-5-aryl-4-benzylfuran-3-carbonitrile **2r**, non-hydrogen atoms are shown at the 30% probability level.

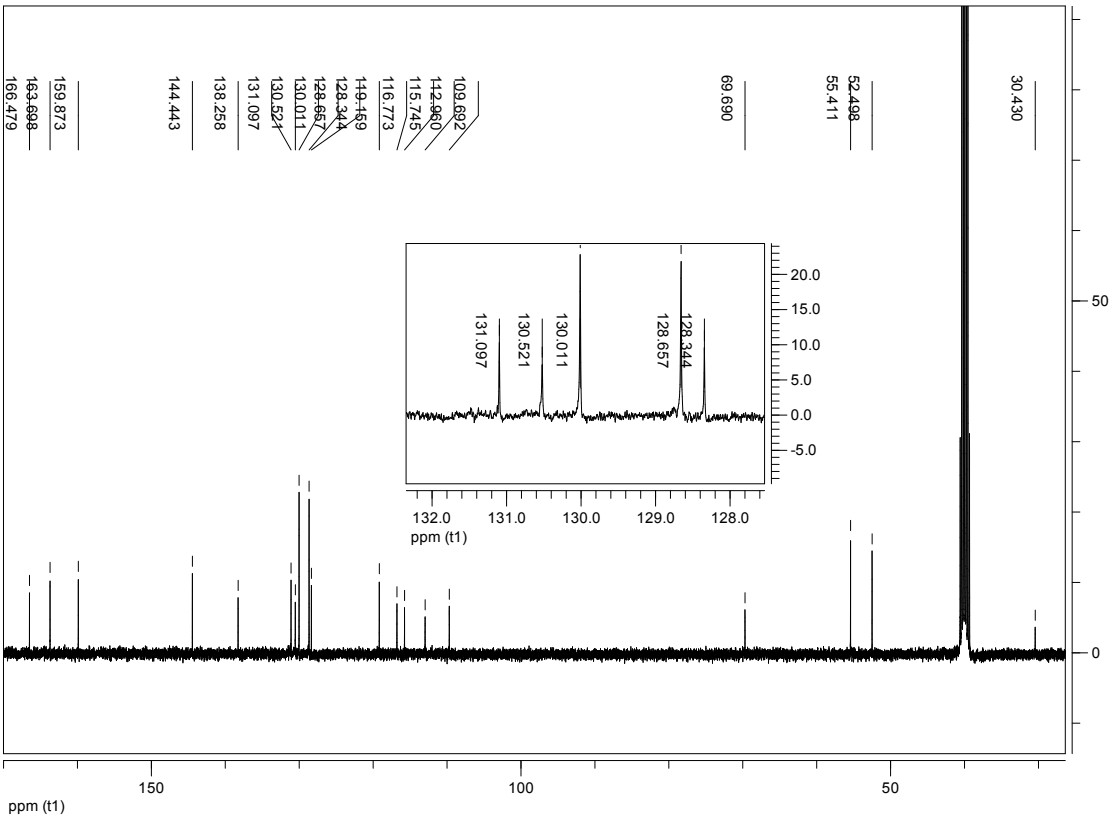
Table S6. Crystal data and structure refinement for **2r**.

Identification code	**2r**
Empirical formula	C_{18} H_{11} Br Cl_2 N_2 O
Formula weight	422.09
Temperature	298 K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 8.722(5) A alpha = 101.028(14) deg. b = 9.677(6) A beta = 103.348(17) deg. c = 11.637(8) A gamma = 112.332(11) deg.
Volume	840.4(9) A^3
Z, Calculated density	2, 1.668 Mg/m^3
Absorption coefficient	2.770 mm^-1

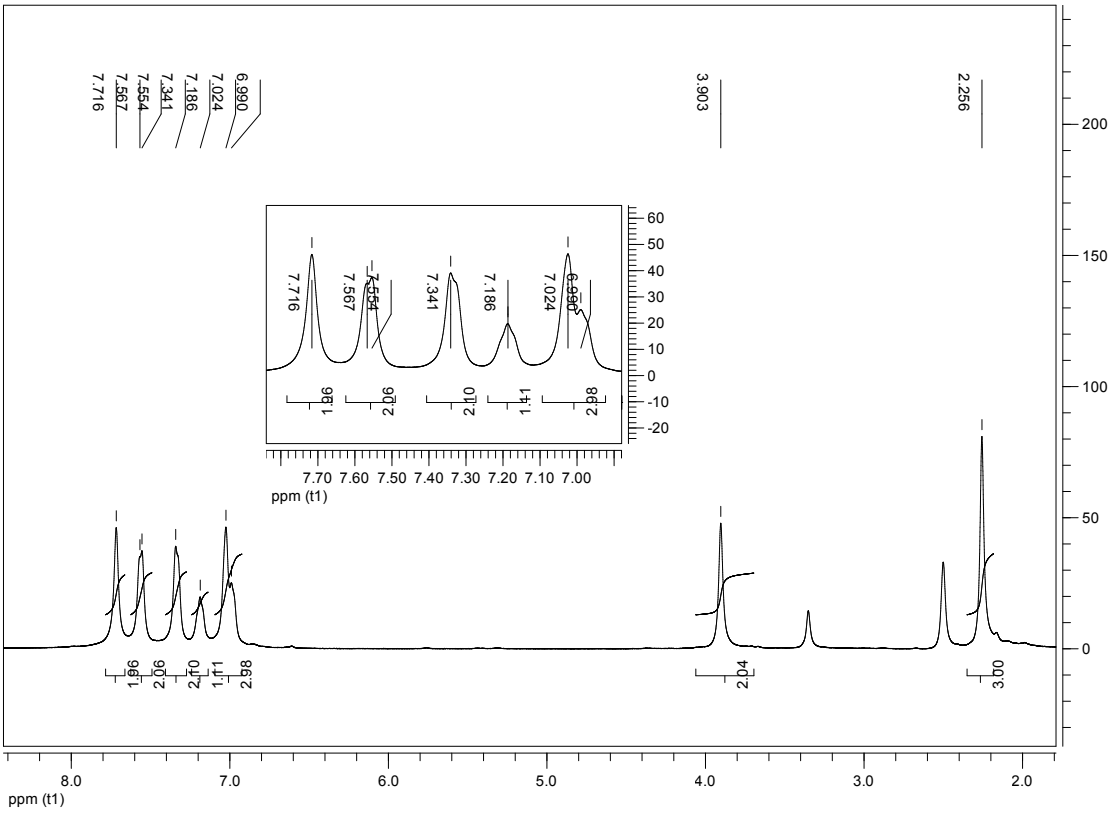
F(000)	420
Crystal size	0.5 x 0.35 x 0.3 mm
Theta range for data collection	1.89 to 27.63 deg.
Limiting indices	-11<=h<=9, -12<=k<=12, -15<=l<=15
Reflections collected / unique	13120 / 3910 [R(int) = 0.0247]
Completeness to theta = 27.63	99.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.788 and 0.729
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3873 / 0 / 217
Goodness-of-fit on F^2	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^-3

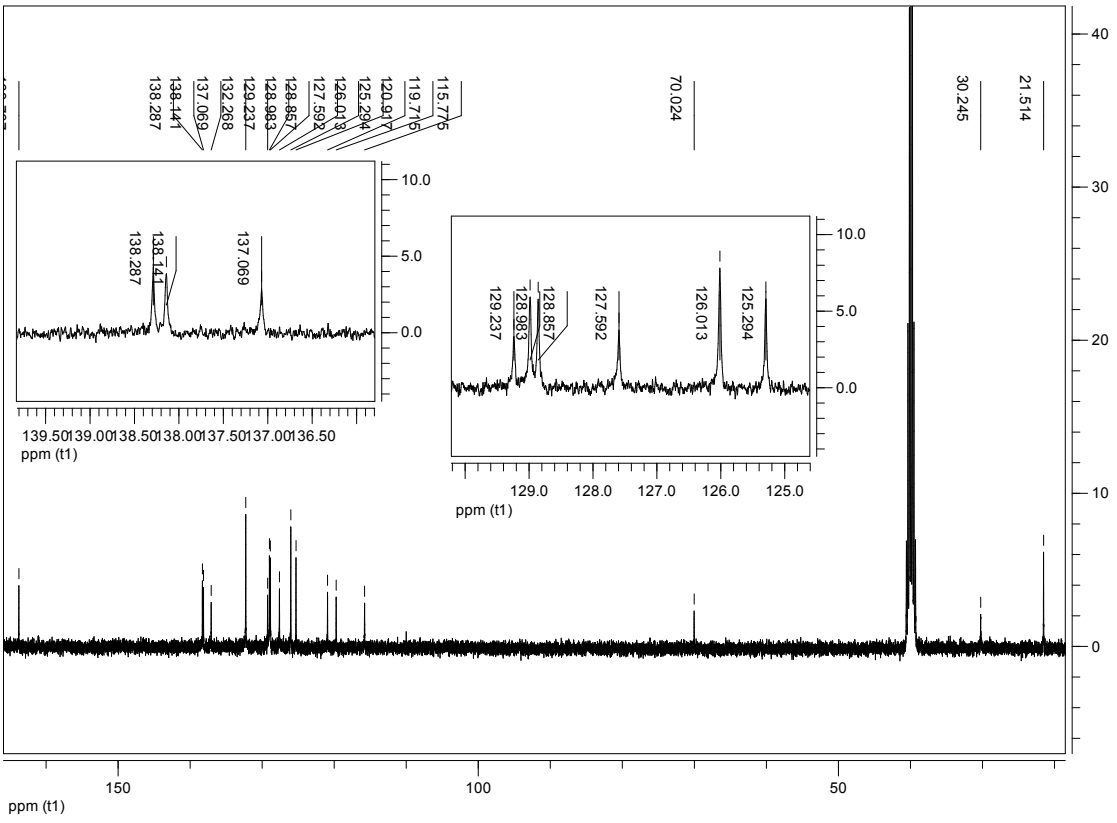
Methyl-4-((5-amino-4-cyano-2-(3-methoxyphenyl)furan-3-yl)methyl)benzoate (**2a**).



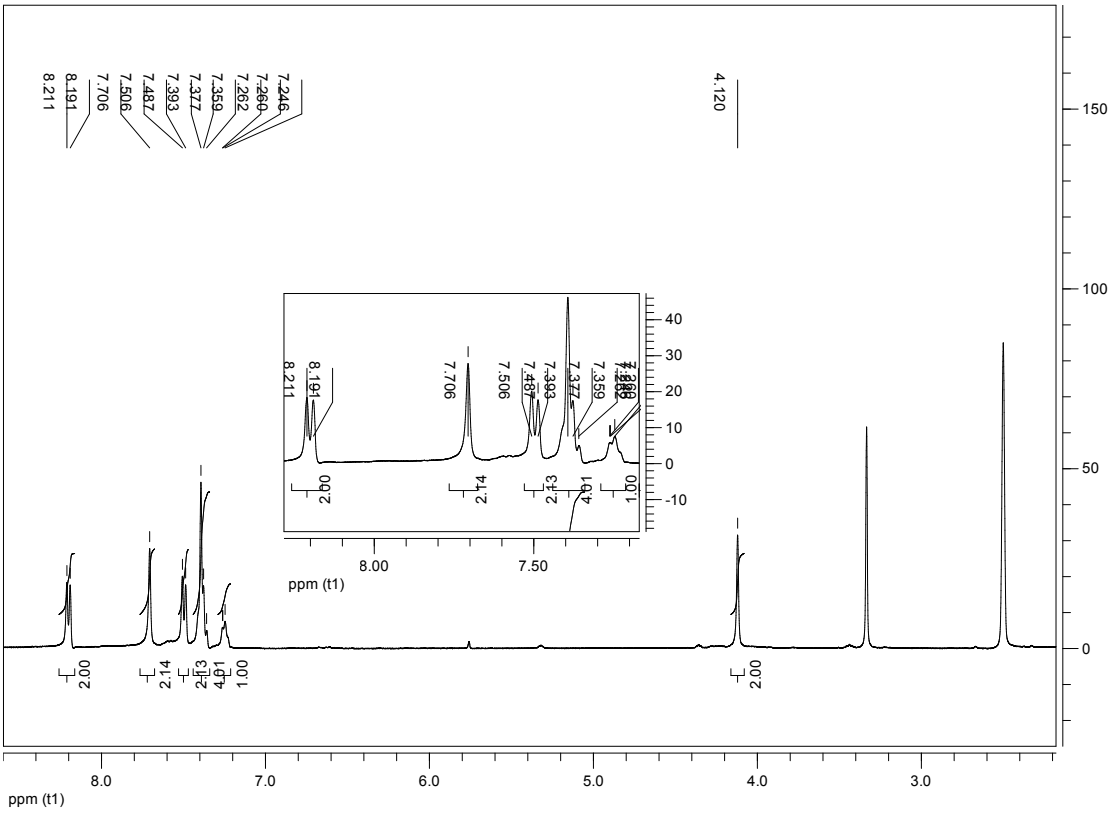


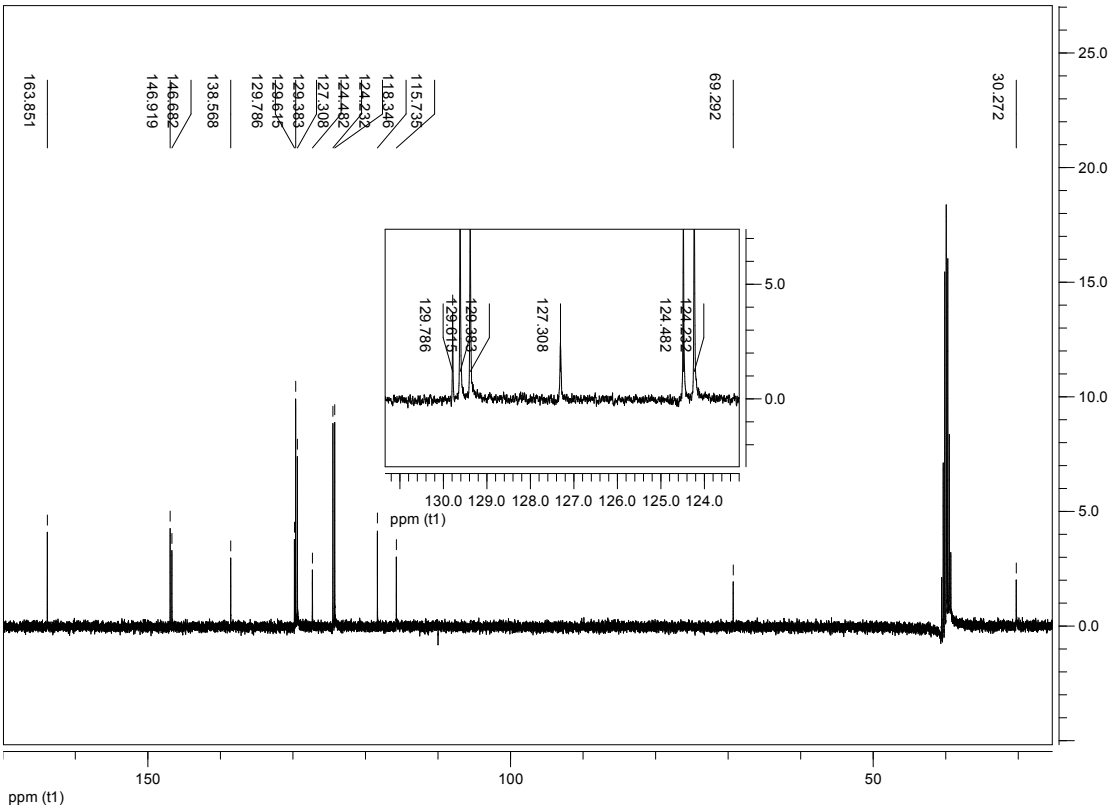
2-Amino-5-(4-bromophenyl)-4-(3-methylbenzyl)furan-3-carbonitrile (**2b**).



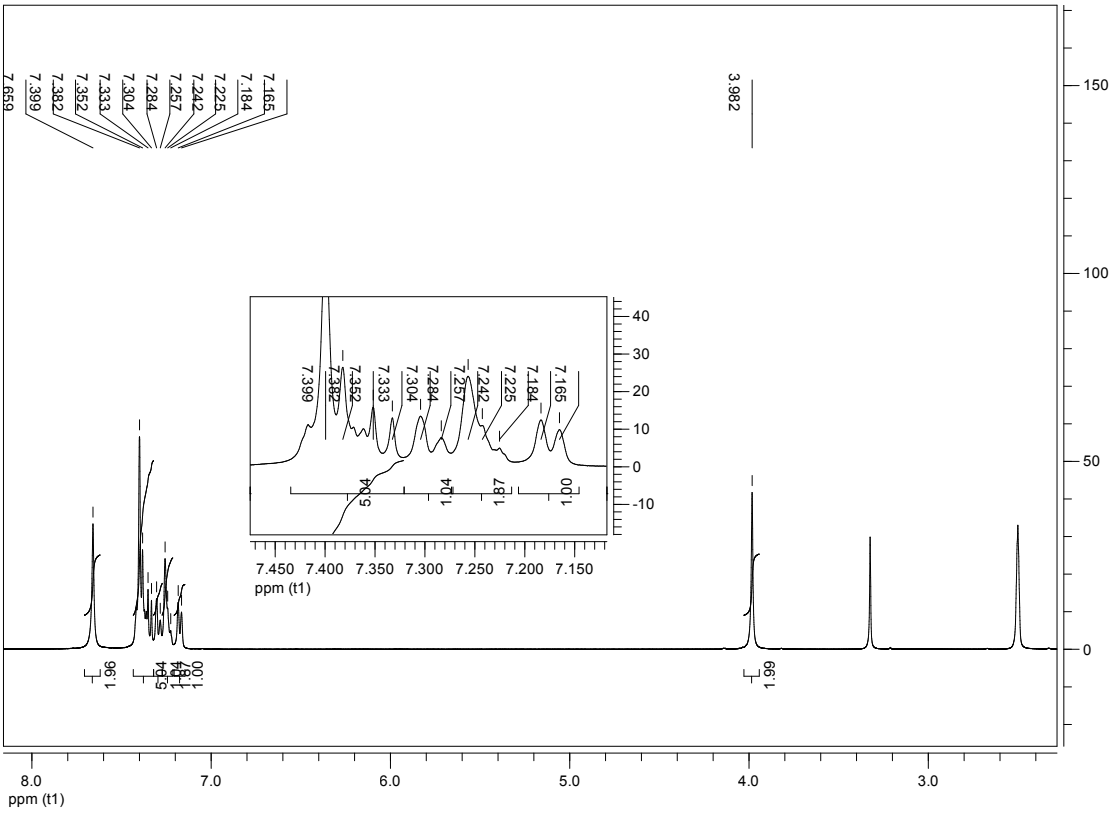


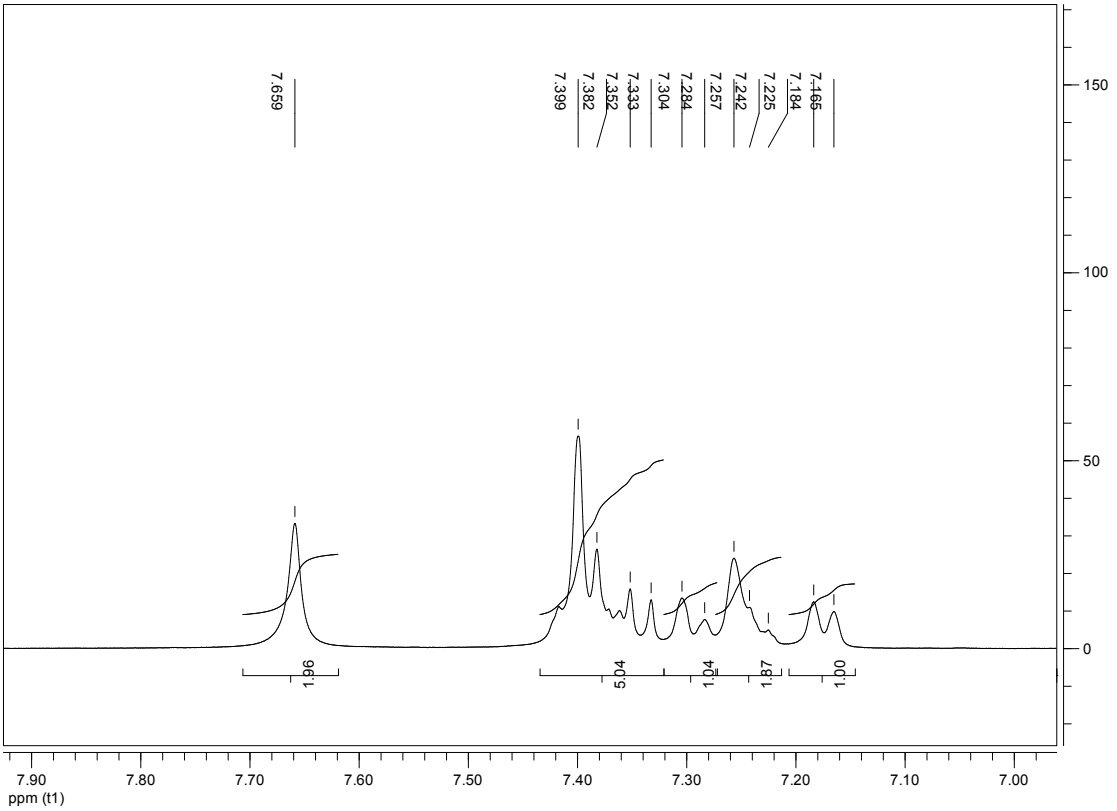
2-Amino-4-(4-nitrobenzyl)-5-phenylfuran-3-carbonitrile (**2c**).

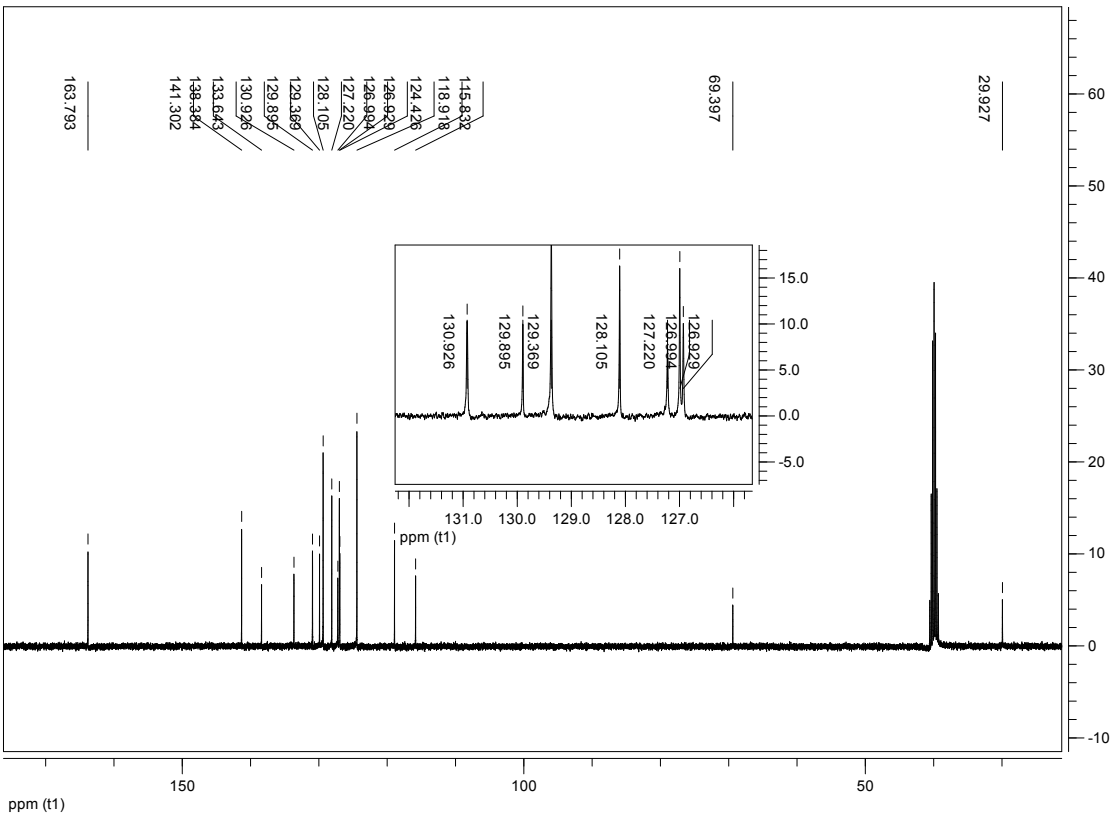




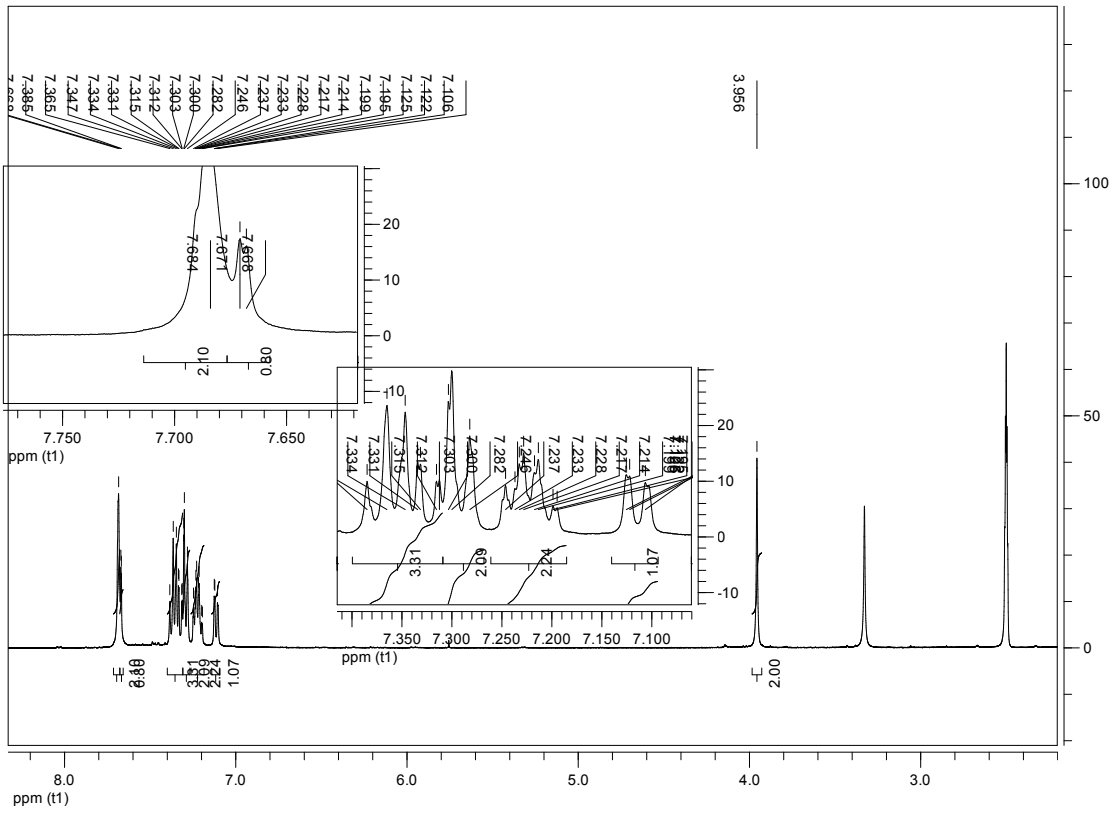
2-Amino-4-(3-chlorobenzyl)-5-phenylfuran-3-carbonitrile (**2d**).

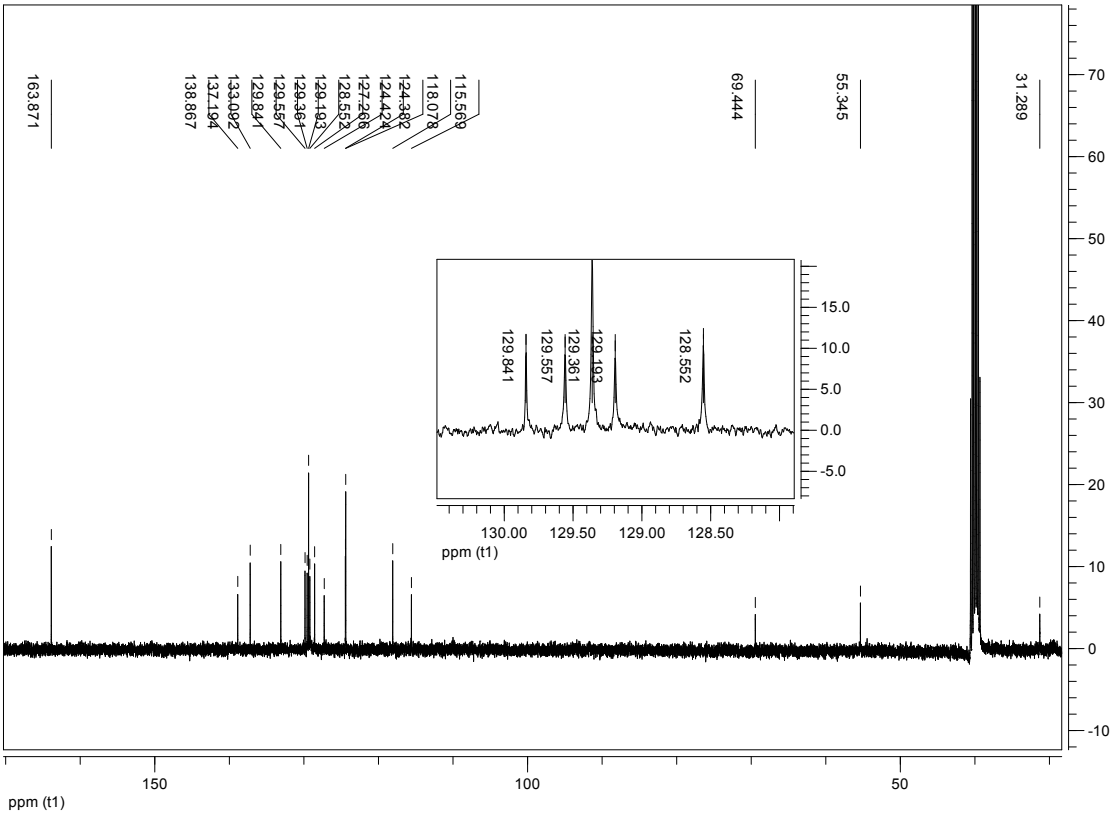




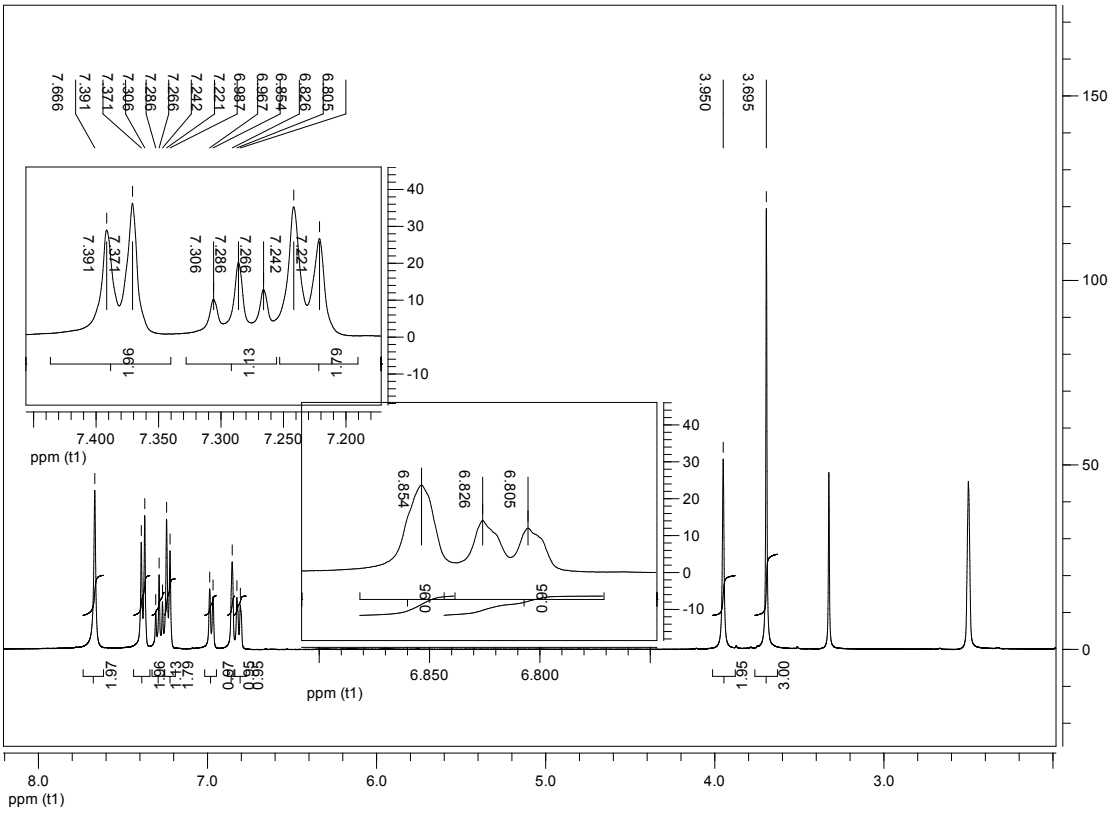

163.793
141.302
138.364
133.643
130.926
129.895
129.369
128.105
127.220
126.994
126.929
124.426
118.918
115.832
69.397
29.927
130.926
129.895
129.369
128.105
127.220
126.994
126.929
131.0 130.0 129.0 128.0 127.0
ppm (t1)
150
100
50
ppm (t1)

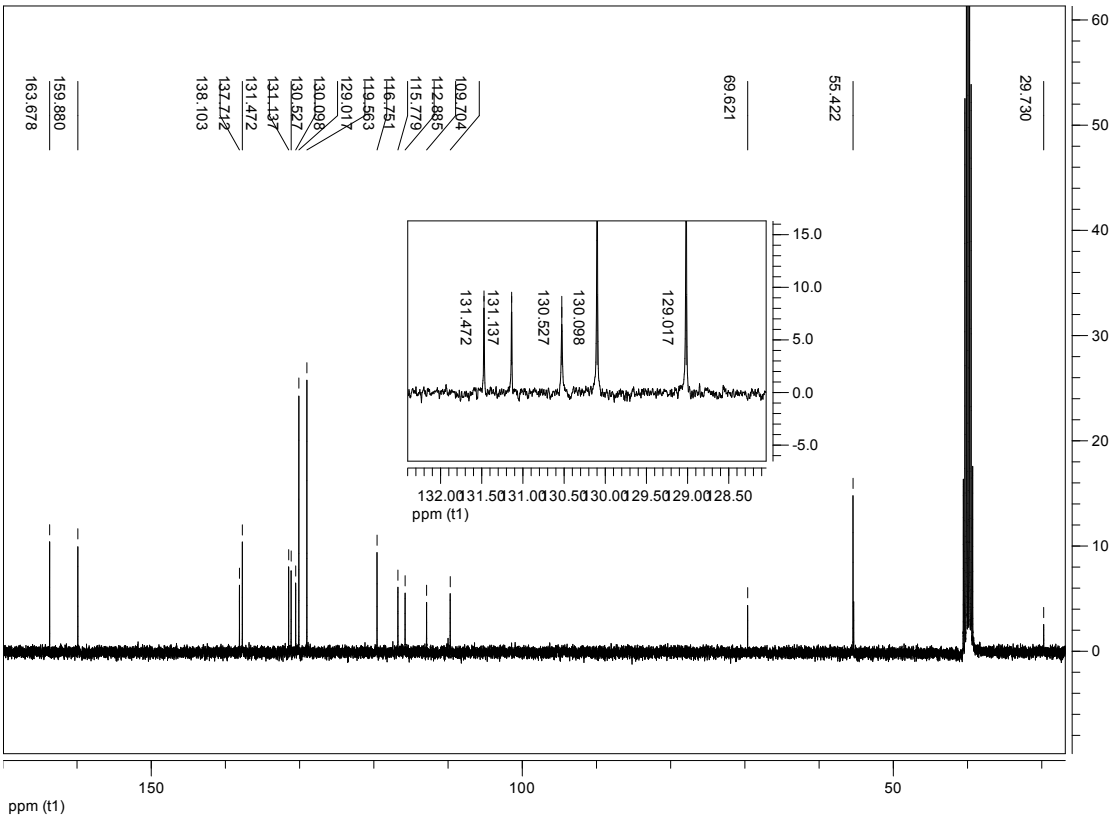
2-Amino-4-(2-bromobenzyl)-5-phenylfuran-3-carbonitrile (**2e**).



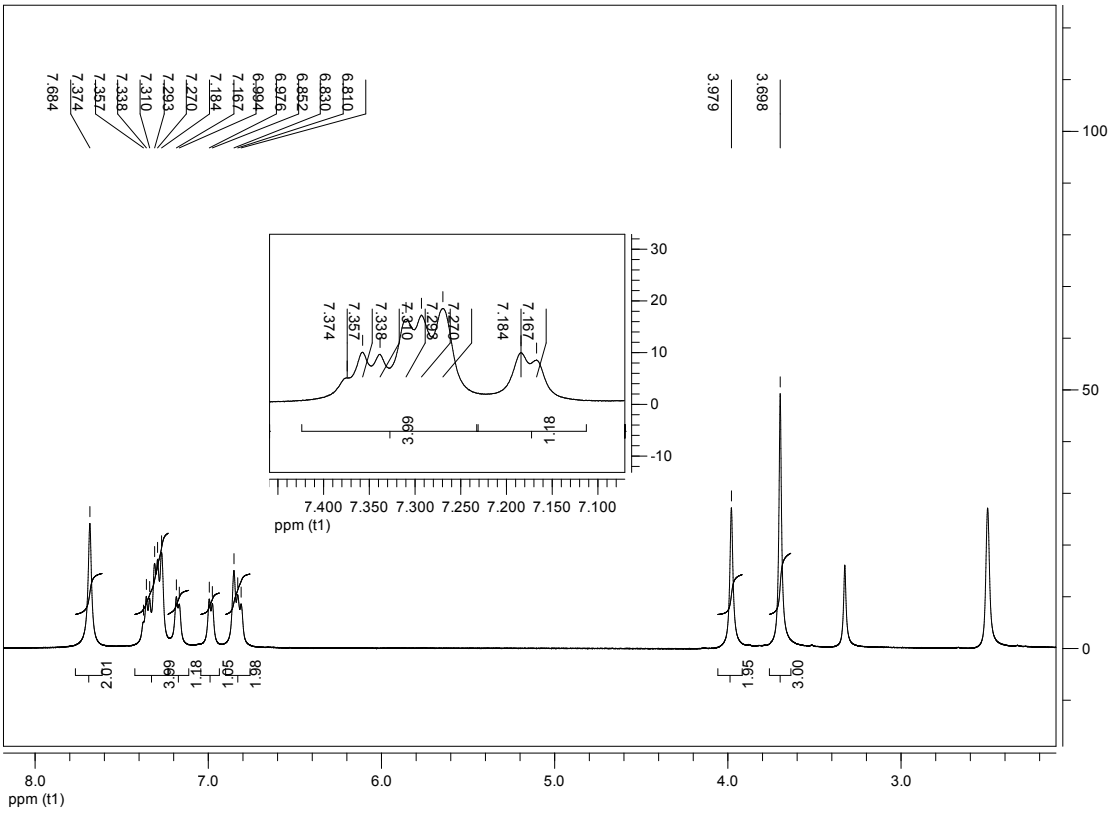


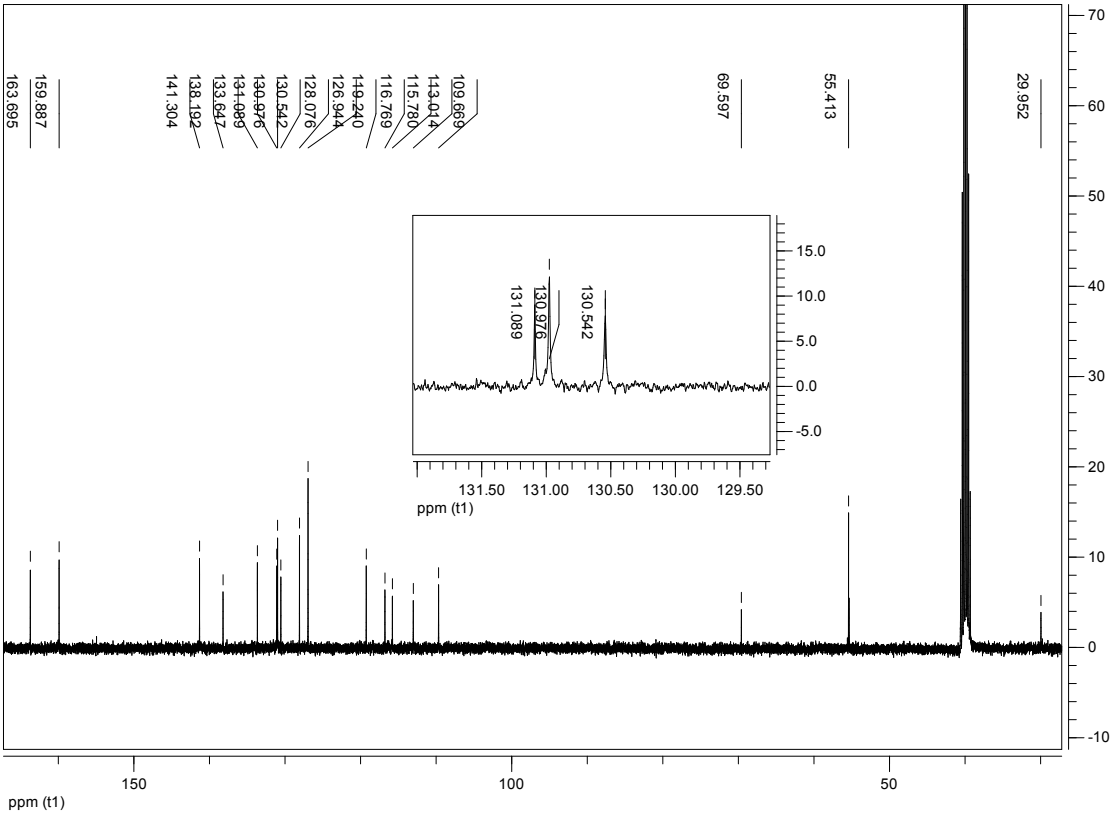
2-Amino-4-(4-chlorobenzyl)-5-(3-methoxyphenyl)furan-3-carbonitrile (**2f**).



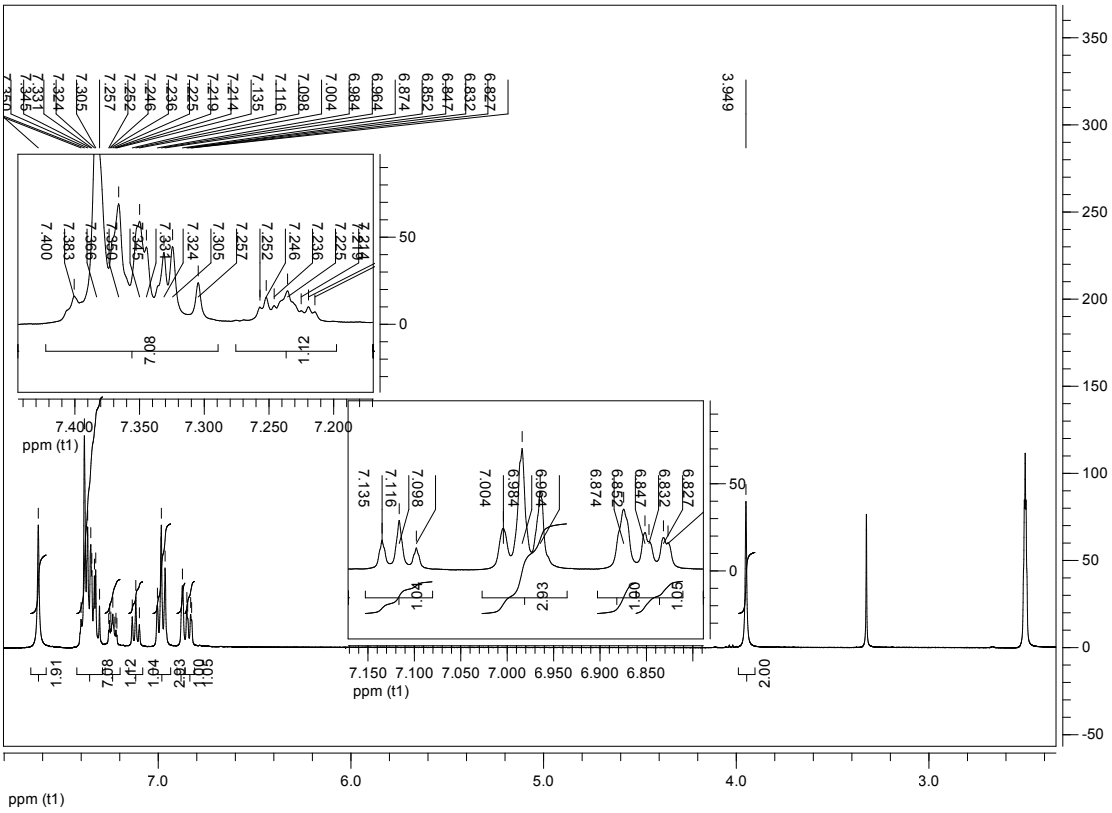


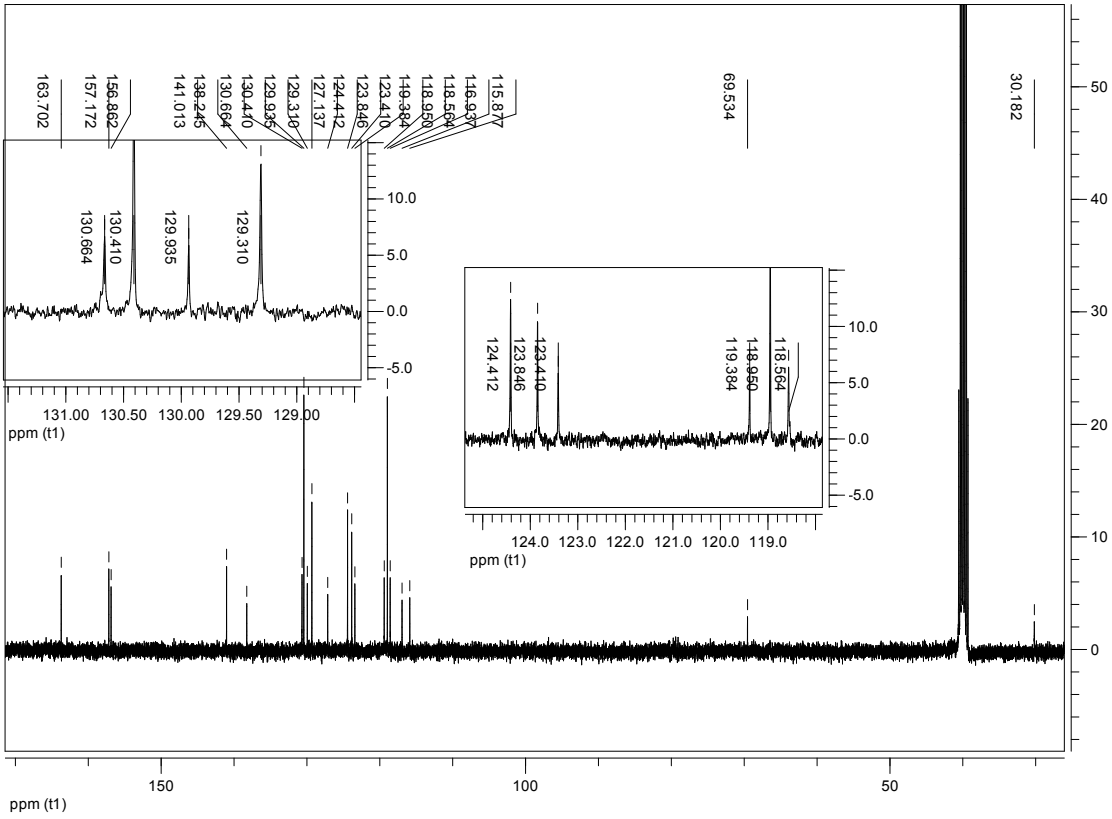
2-Amino-4-(3-chlorobenzyl)-5-(3-methoxyphenyl)furan-3-carbonitrile (**2g**).



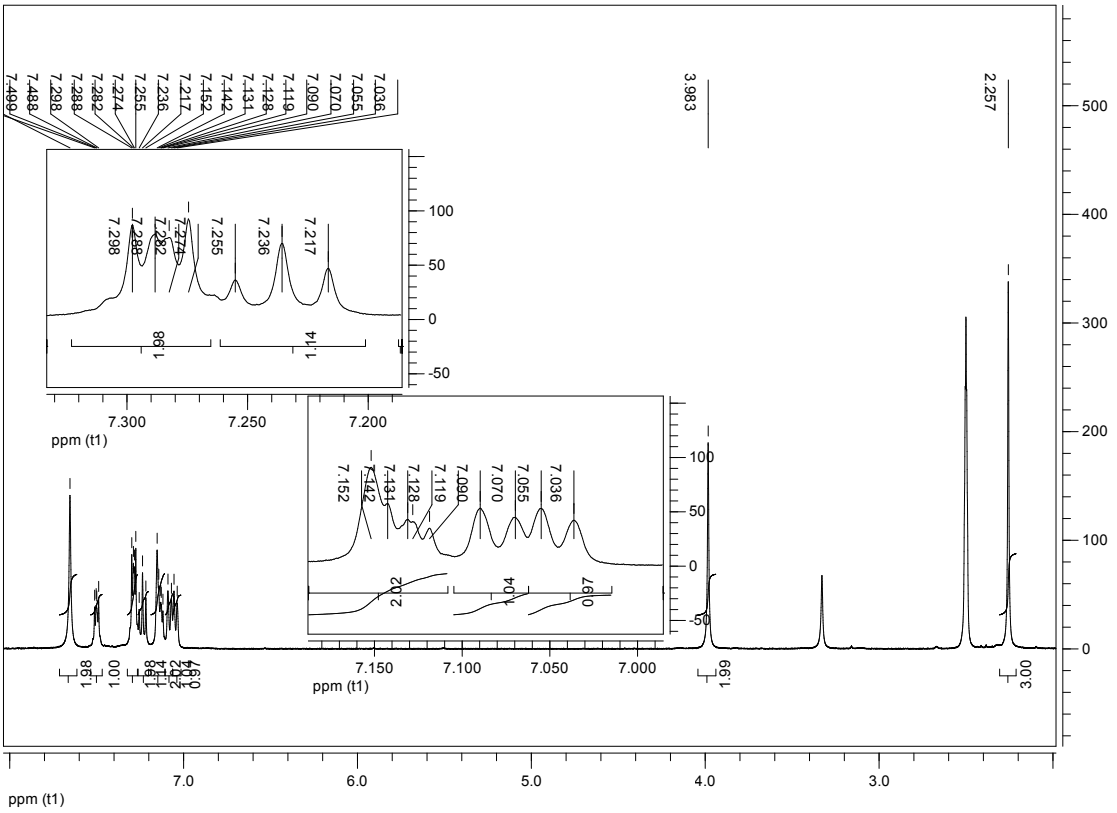


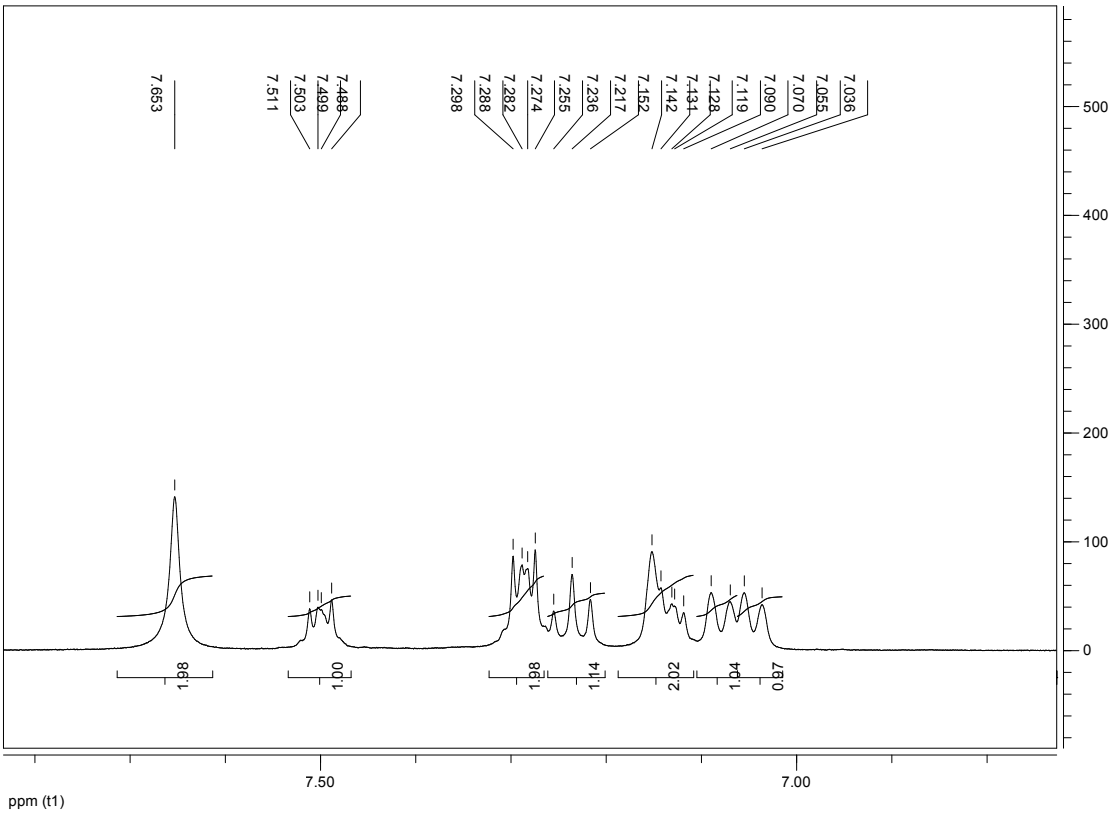
2-Amino-4-(3-phenoxybenzyl)-5-phenylfuran-3-carbonitrile (**2h**).

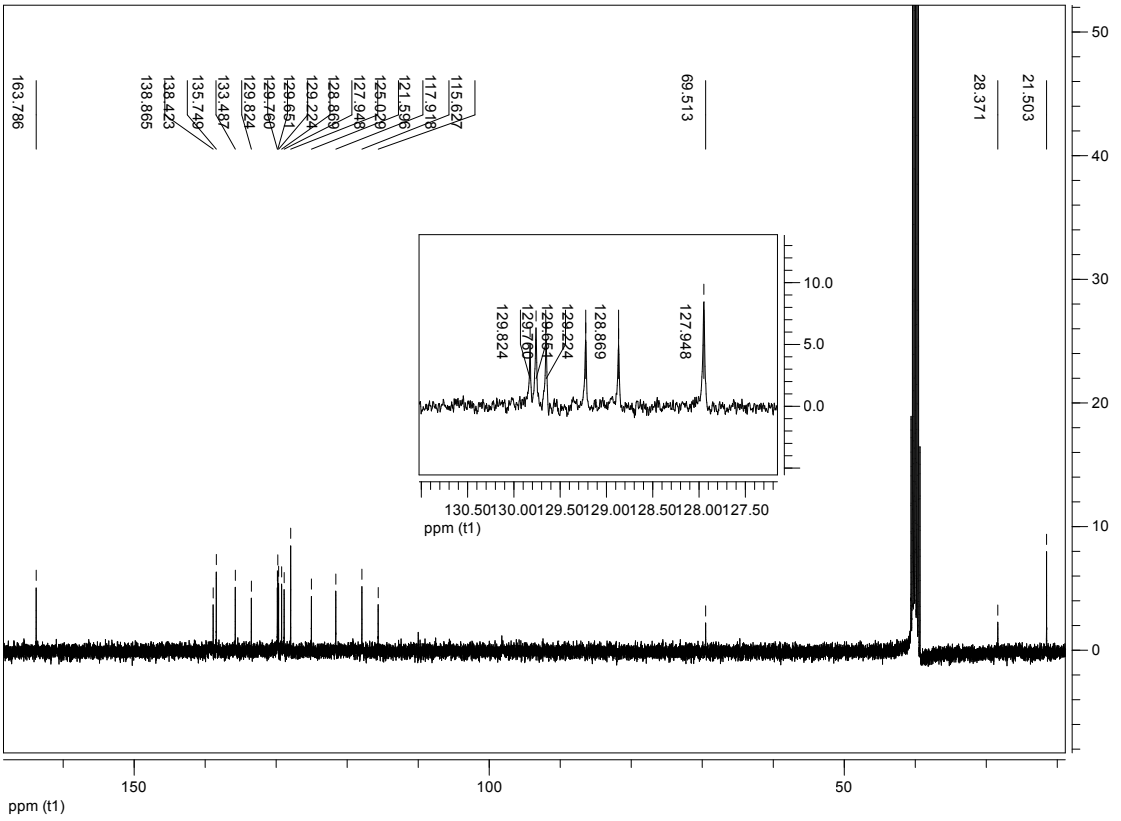




2-Amino-4-(2-chlorobenzyl)-5-(m-tolyl)furan-3-carbonitrile (**2i**).



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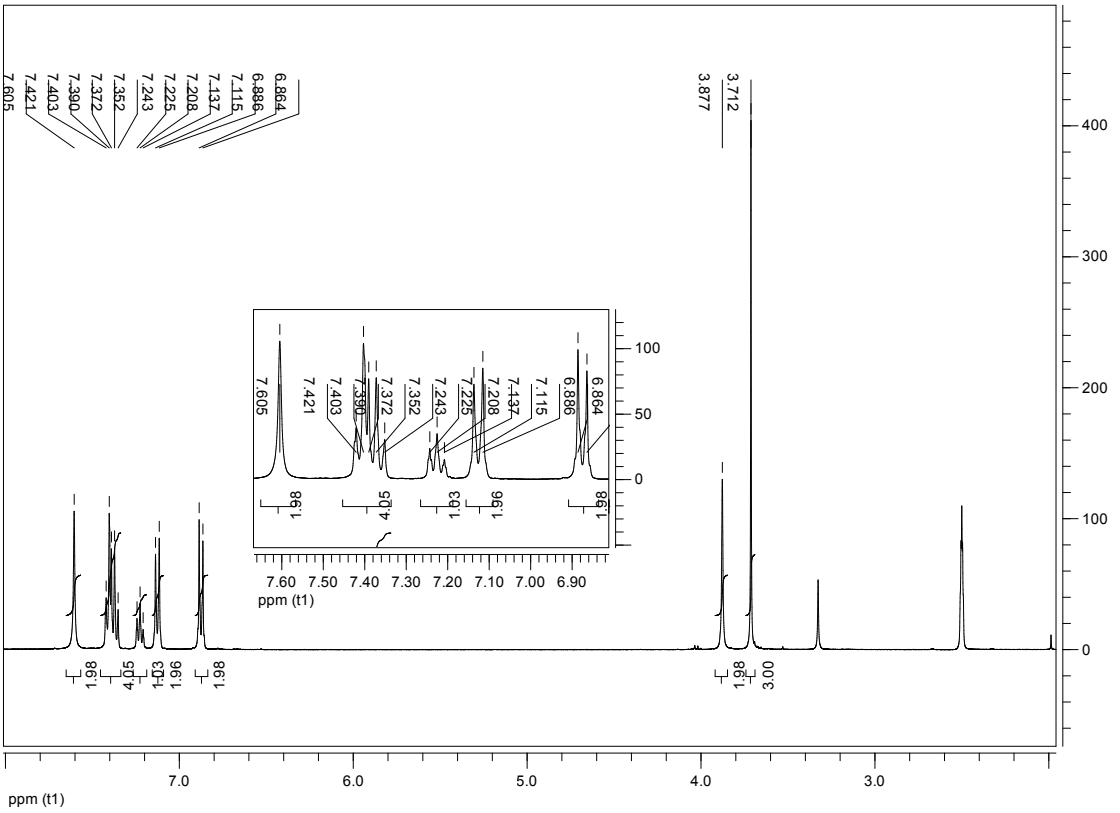
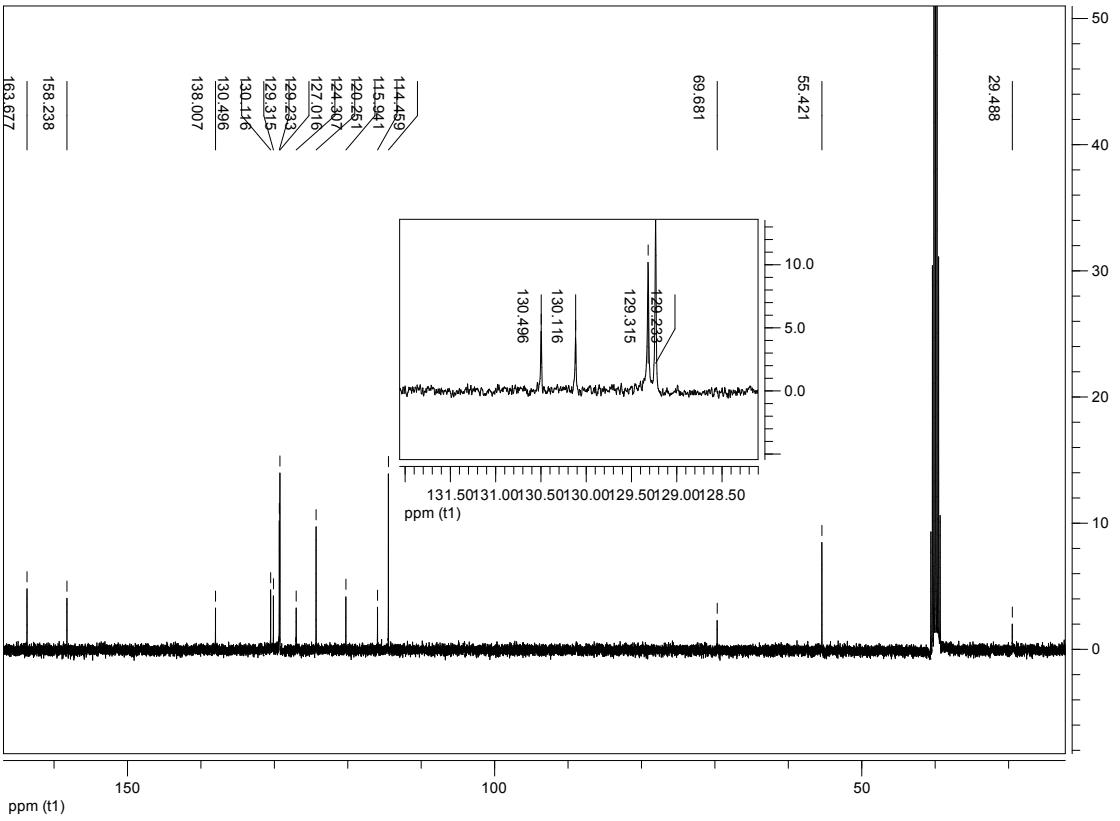
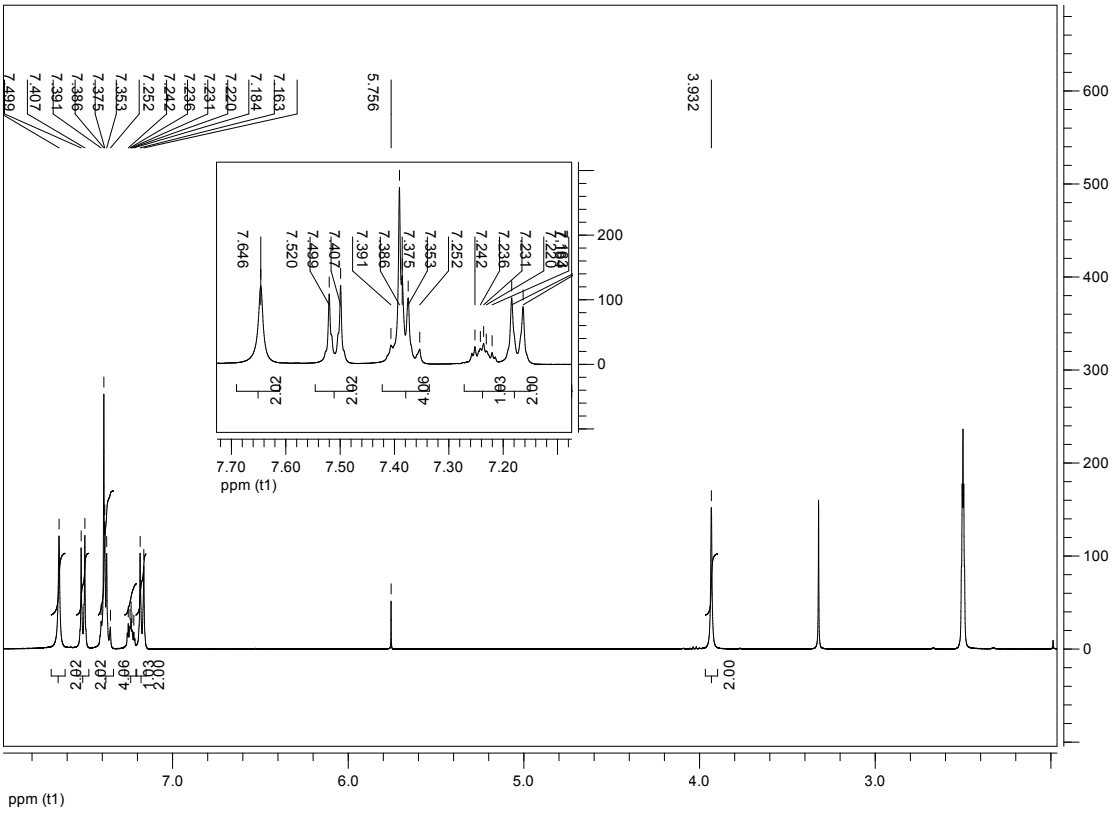
138.423
135.749
133.487
129.824
129.760
129.651
129.224
128.869
127.948
125.029
121.596
117.918
115.627
69.513
28.371
21.503
129.824
129.760
129.651
129.224
128.869
127.948
10.0
5.0
0.0
130.50130.00129.50129.00128.50128.00127.50
ppm (t1)
50
40
30
20
10
0
150
100
50
ppm (t1)

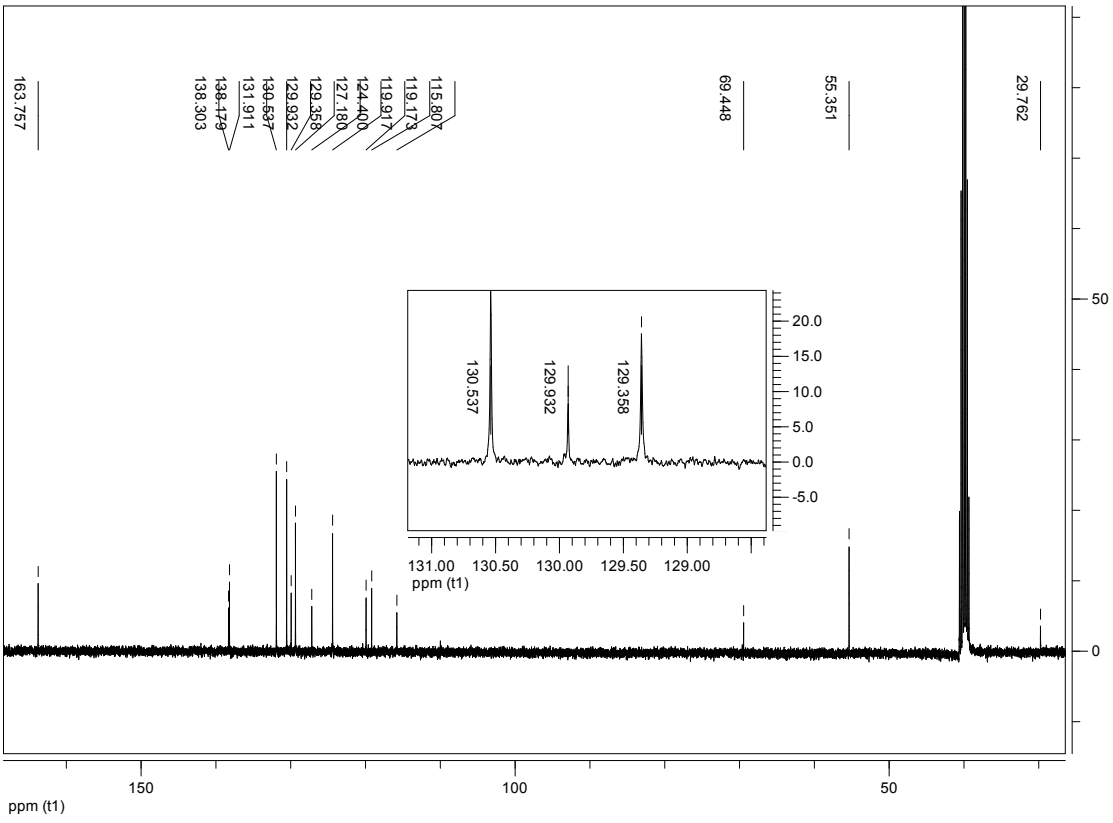
2-Amino-4-(4-methoxybenzyl)-5-phenylfuran-3-carbonitrile (**2j**).

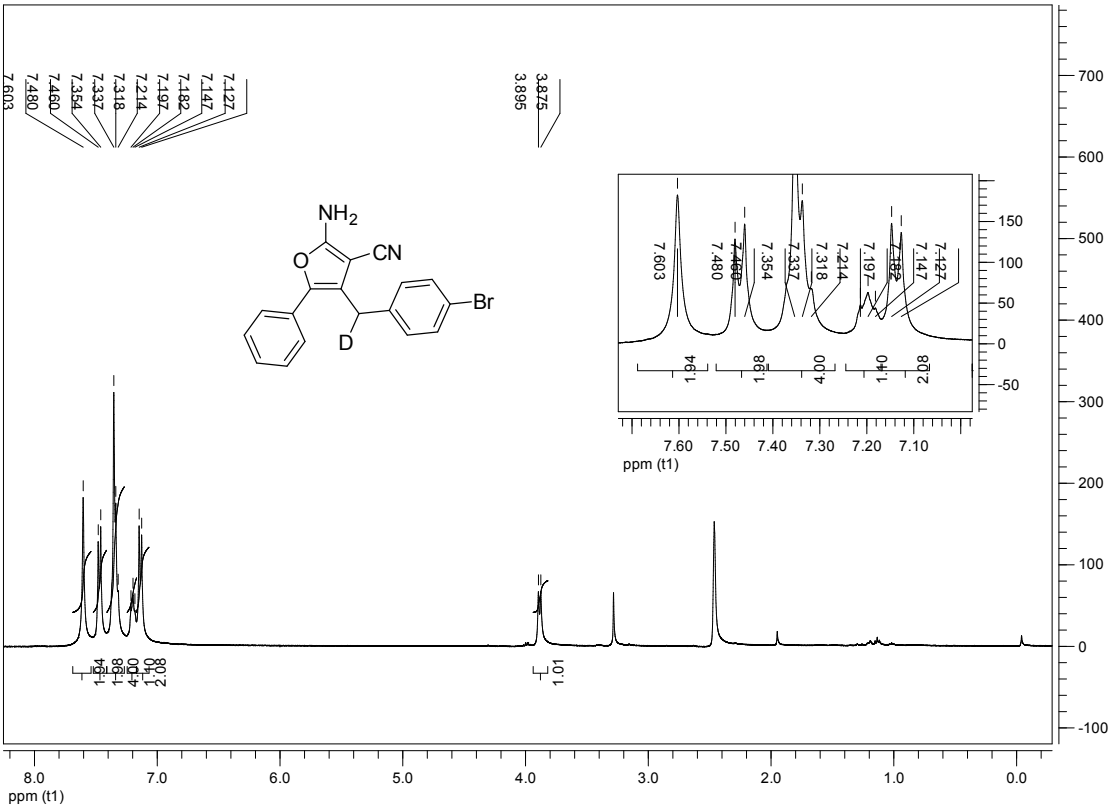




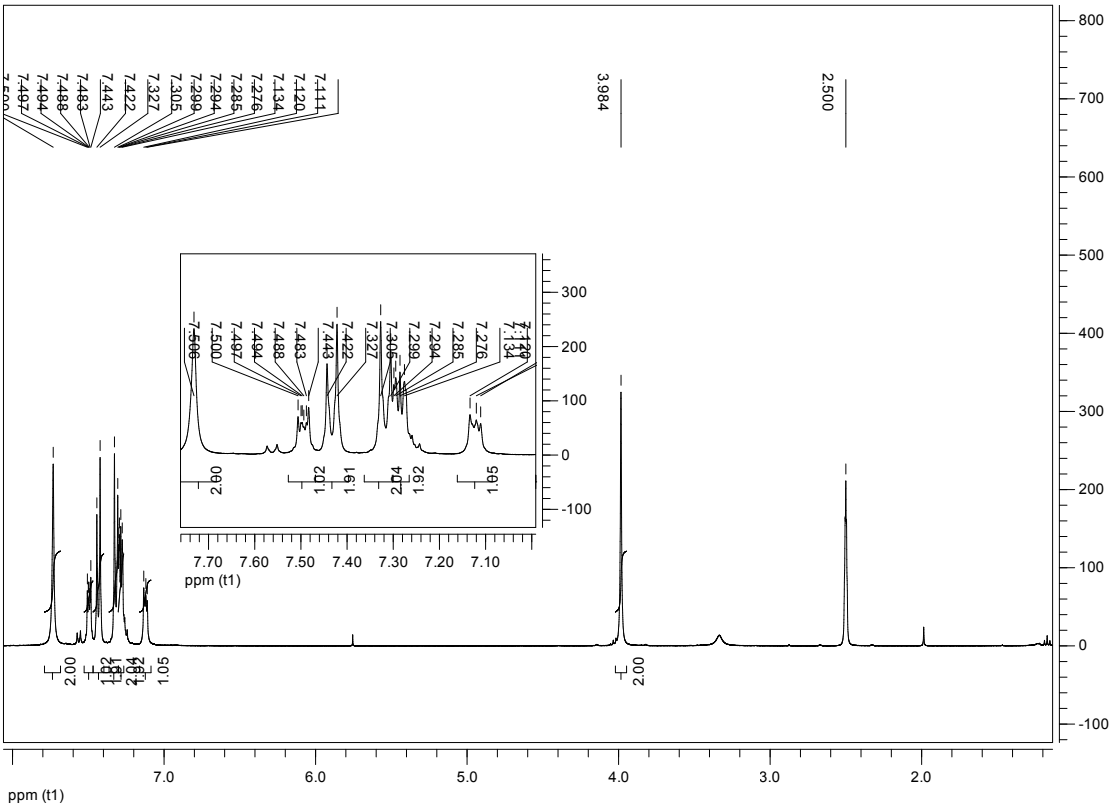
2-Amino-4-(4-bromobenzyl)-5-phenylfuran-3-carbonitrile (**2k**).

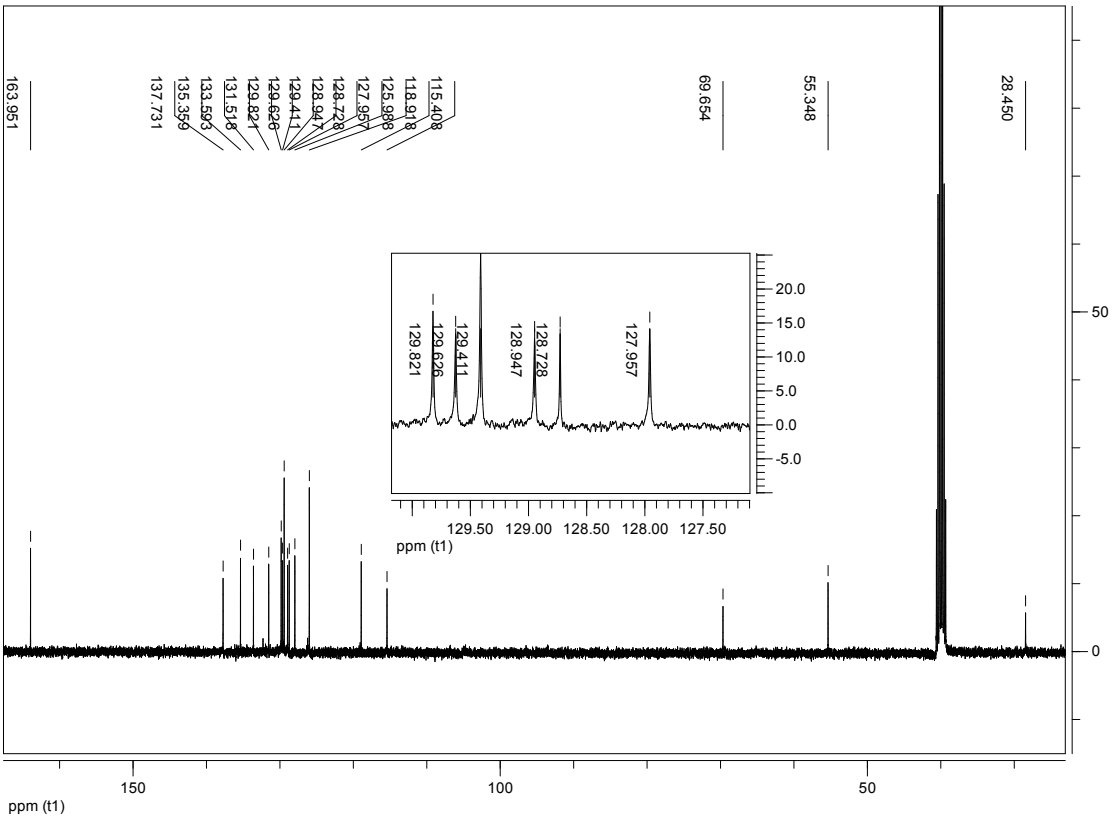




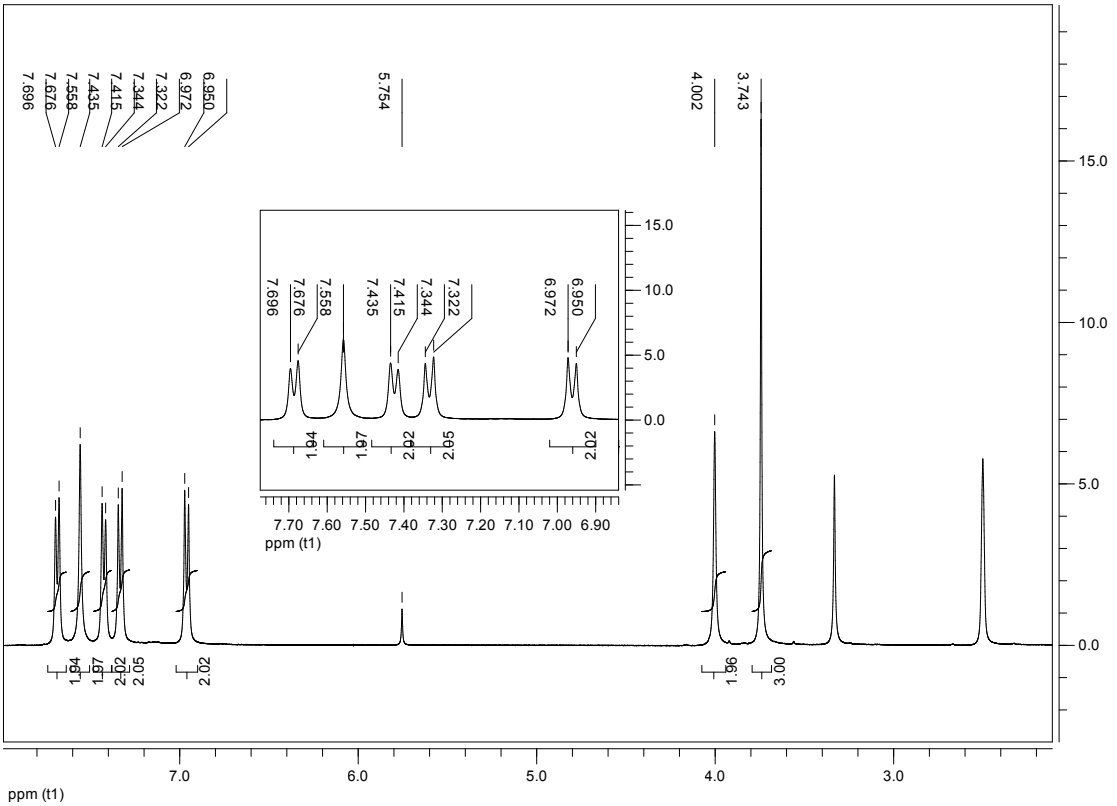

7.603
7.480
7.460
7.354
7.337
7.318
7.214
7.197
7.182
7.147
7.127
3.895
3.875
NH2
CN
O
Br
D
1.94
1.98
4.00
1.04
2.08
1.01
ppm (t1)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.60
7.50
7.40
7.30
7.20
7.10

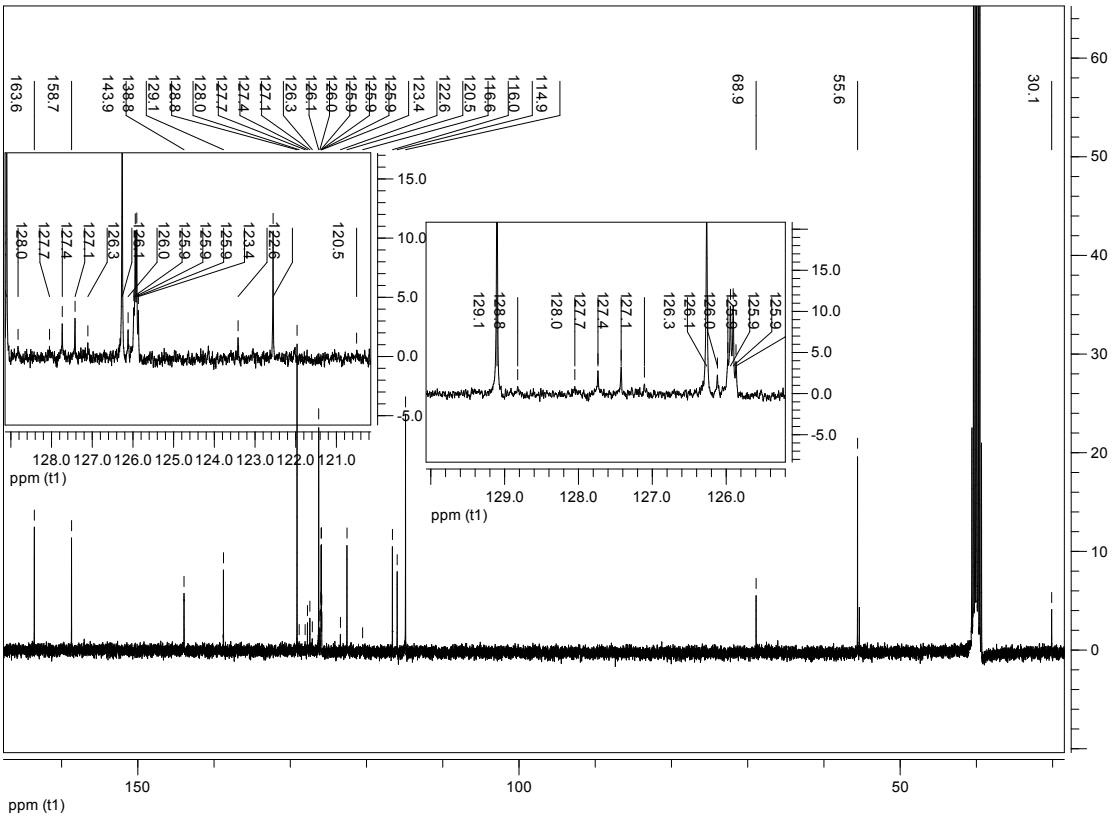
2-Amino-4-(2-chlorobenzyl)-5-(4-chlorophenyl)furan-3-carbonitrile (**2l**).

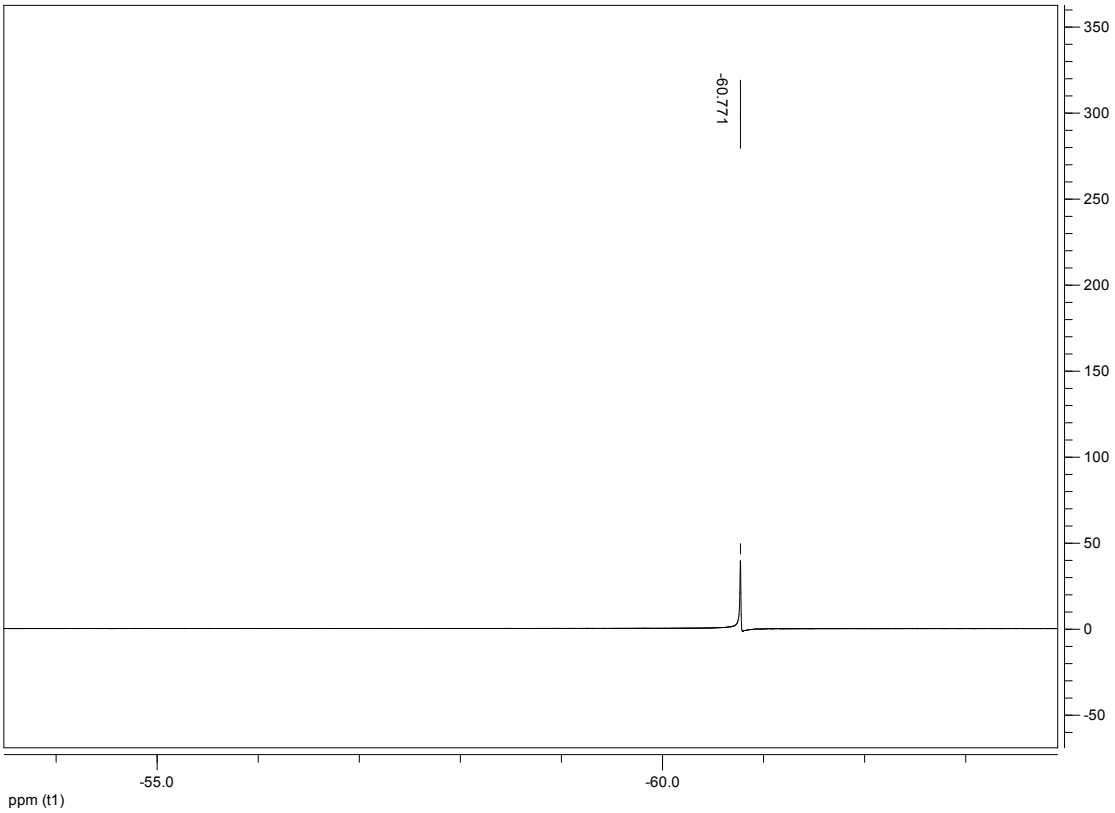




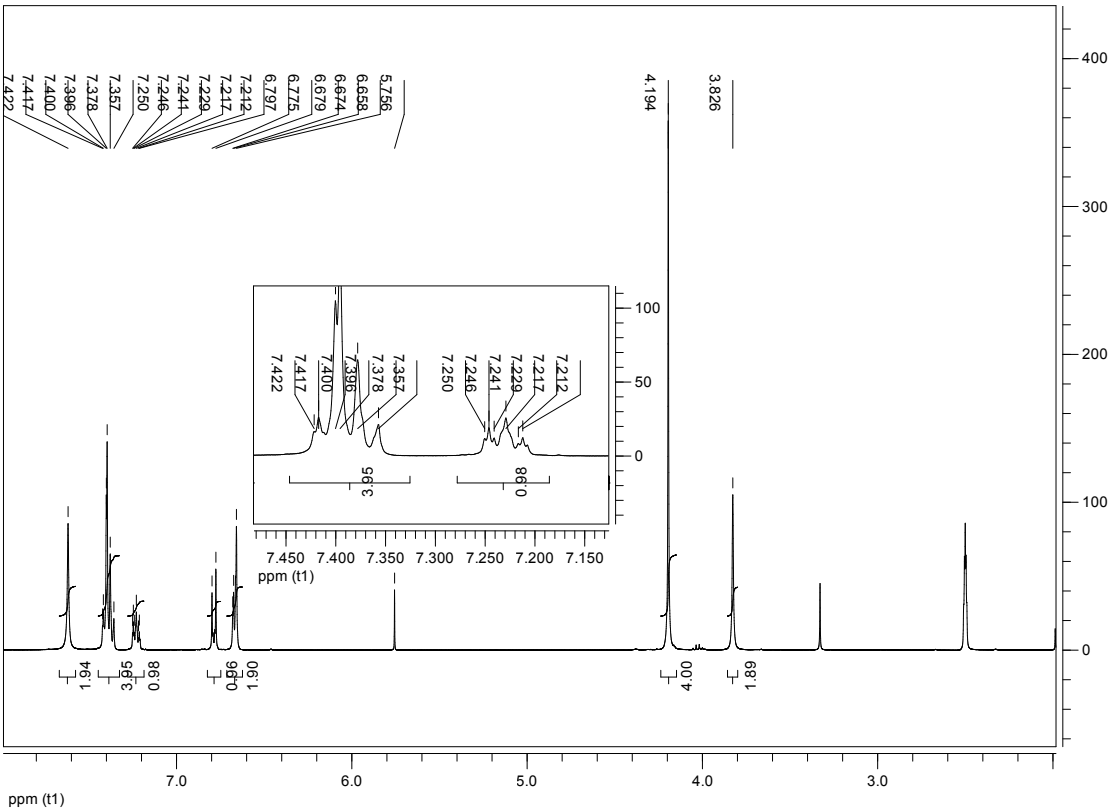
2-Amino-5-(4-methoxyphenyl)-4-(4-(trifluoromethyl)benzyl)furan-3-carbonitrile (**2m**).

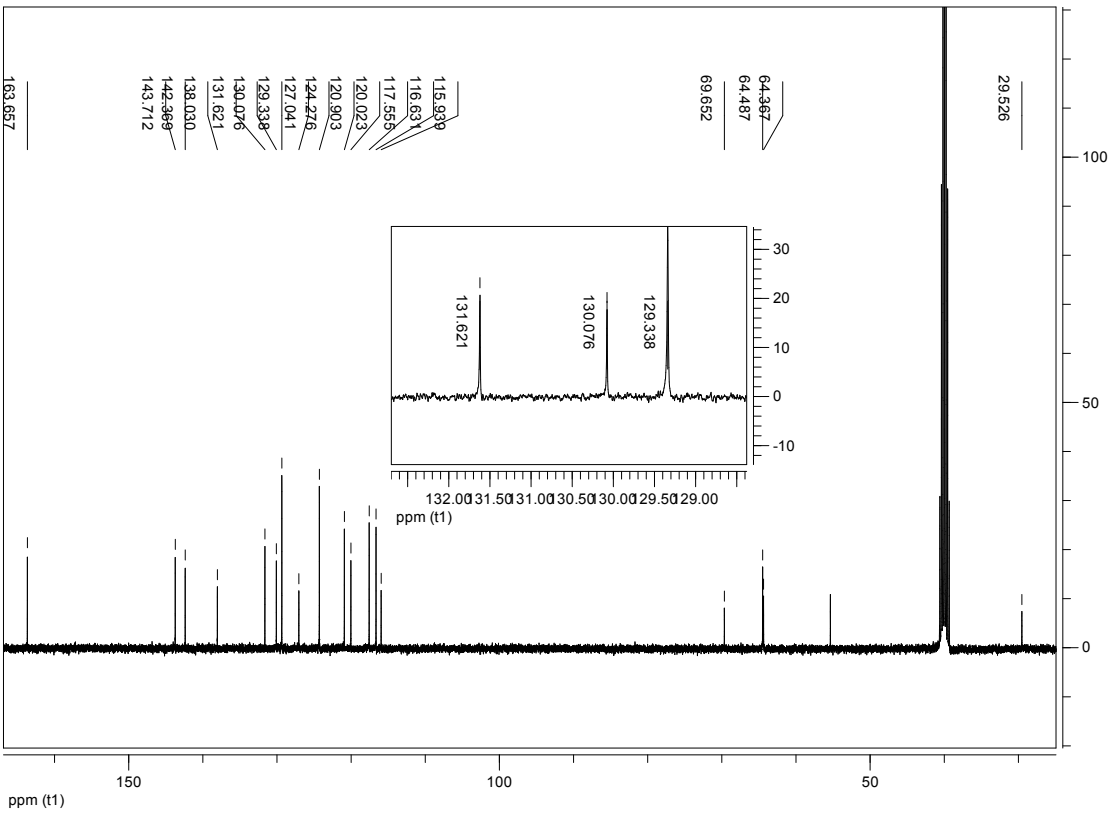




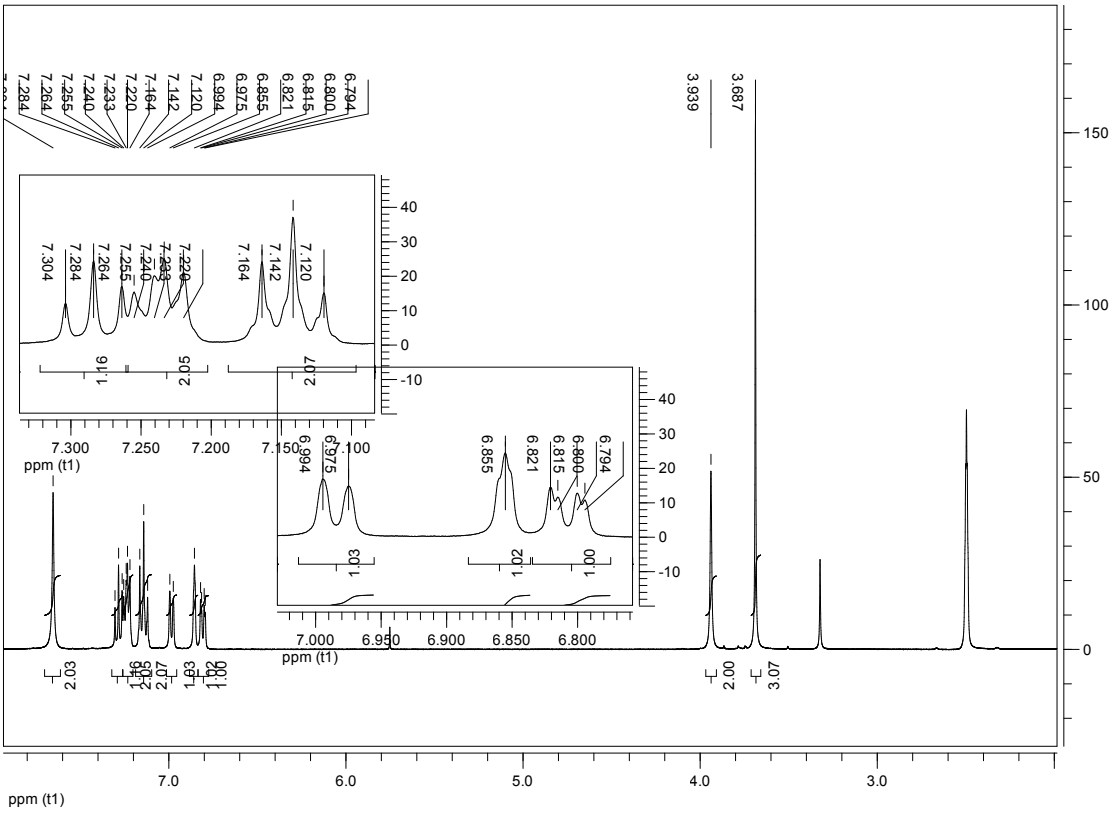

-59.771
350
300
250
200
150
100
50
0
-50
-55.0
-60.0
ppm (t1)

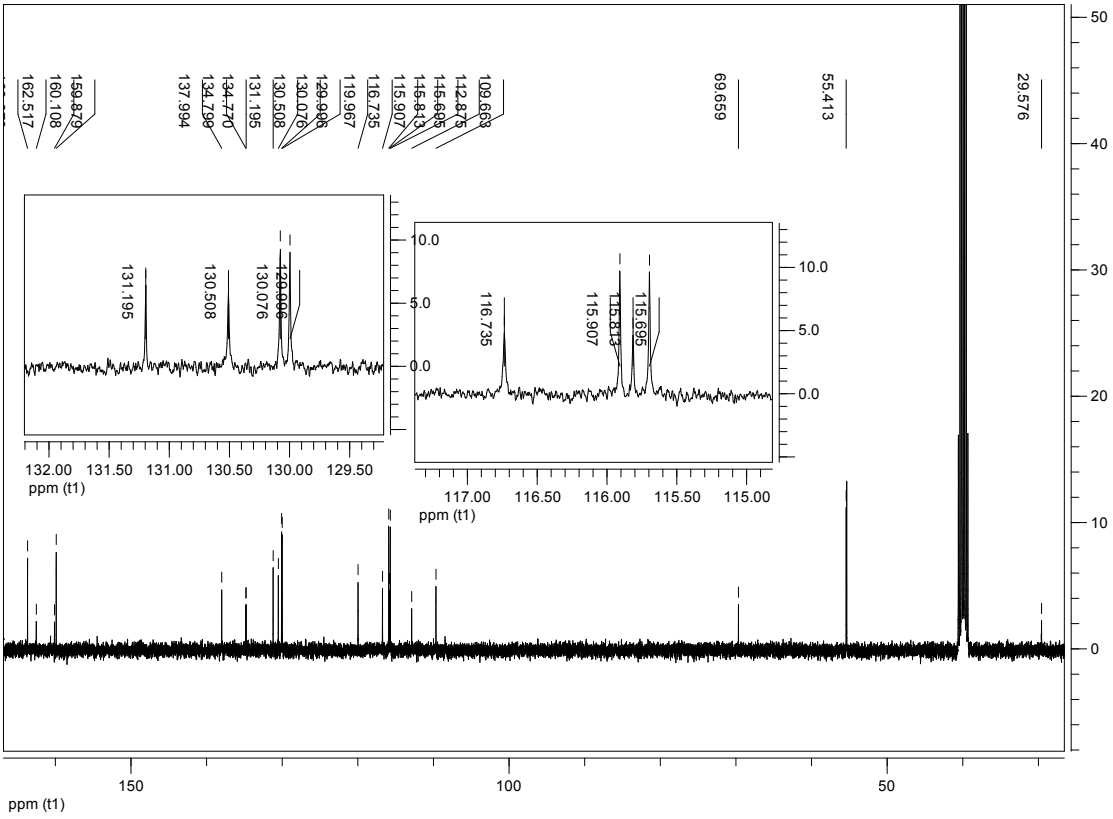
2-Amino-4-((2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)methyl)-5-phenylfuran-3-carbonitrile (**2n**).

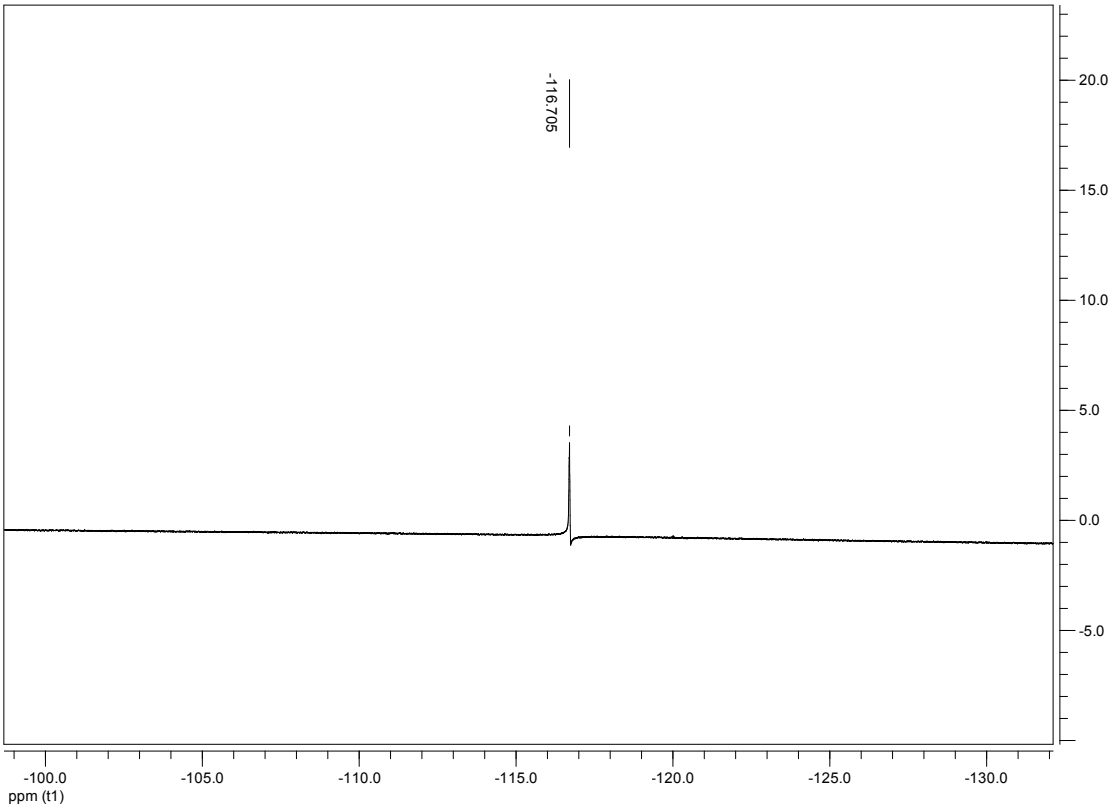




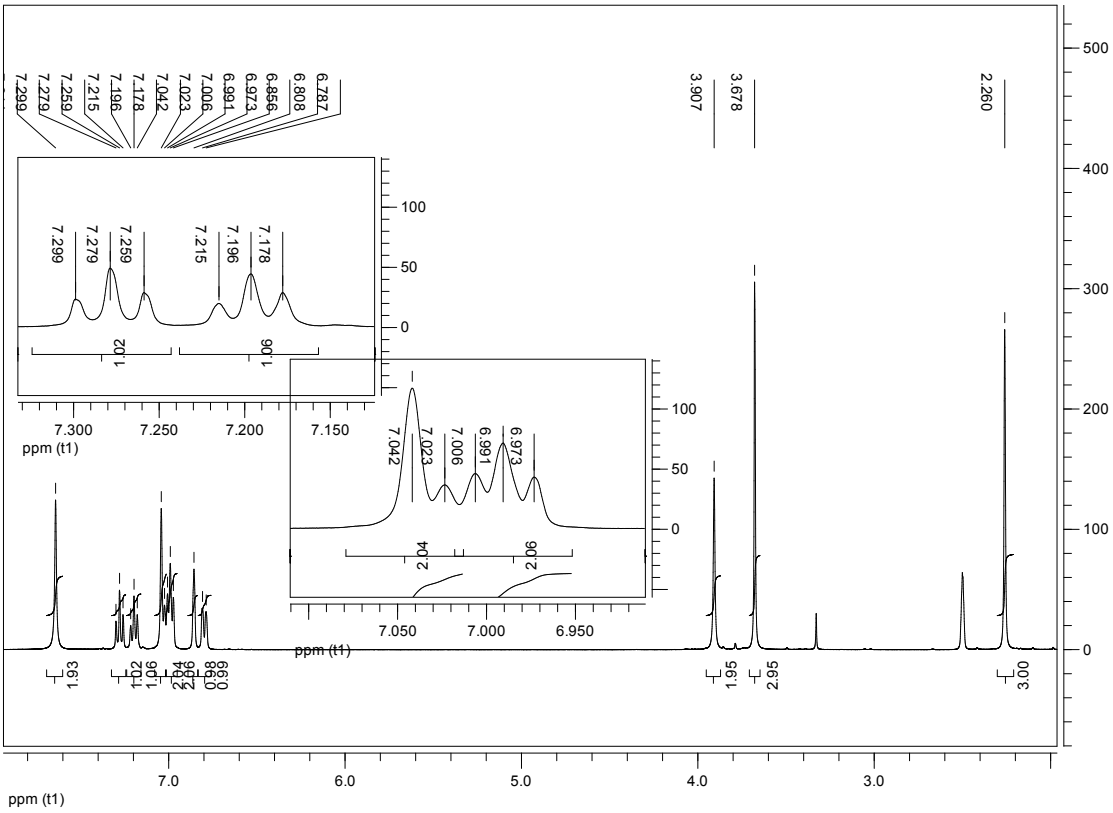
2-Amino-4-(4-fluorobenzyl)-5-(3-methoxyphenyl)furan-3-carbonitrile (**2o**).

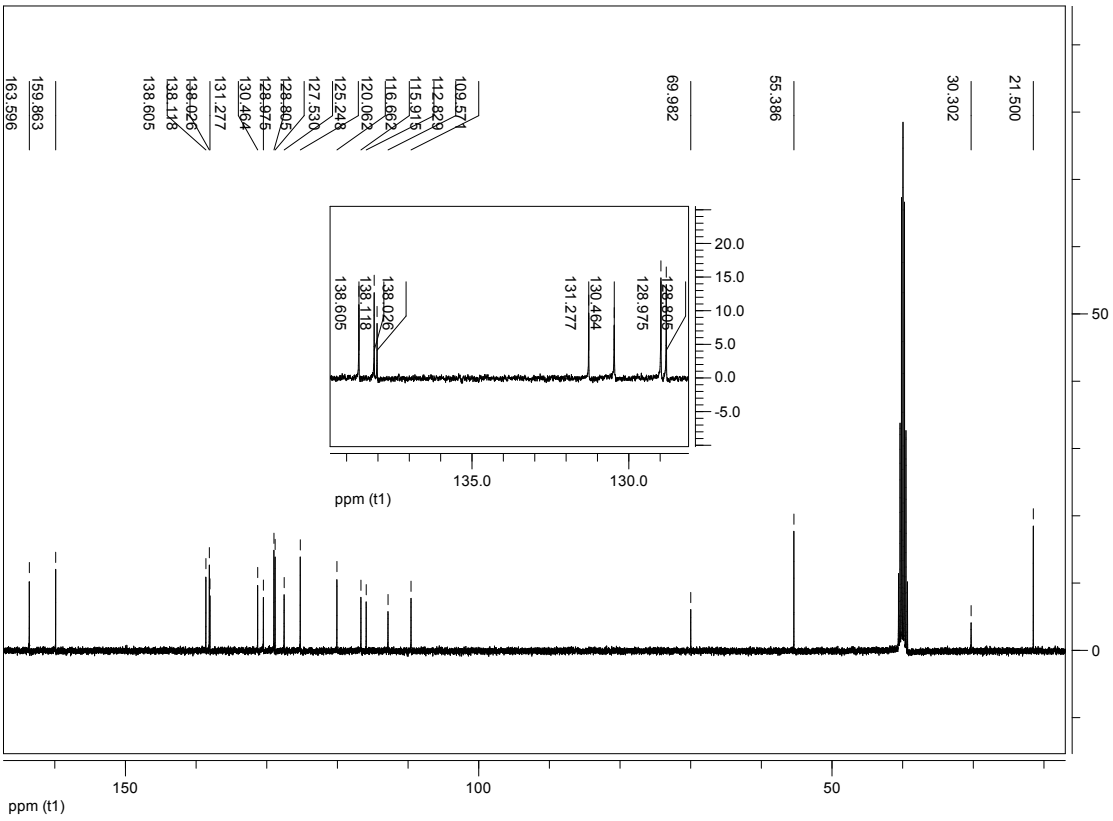




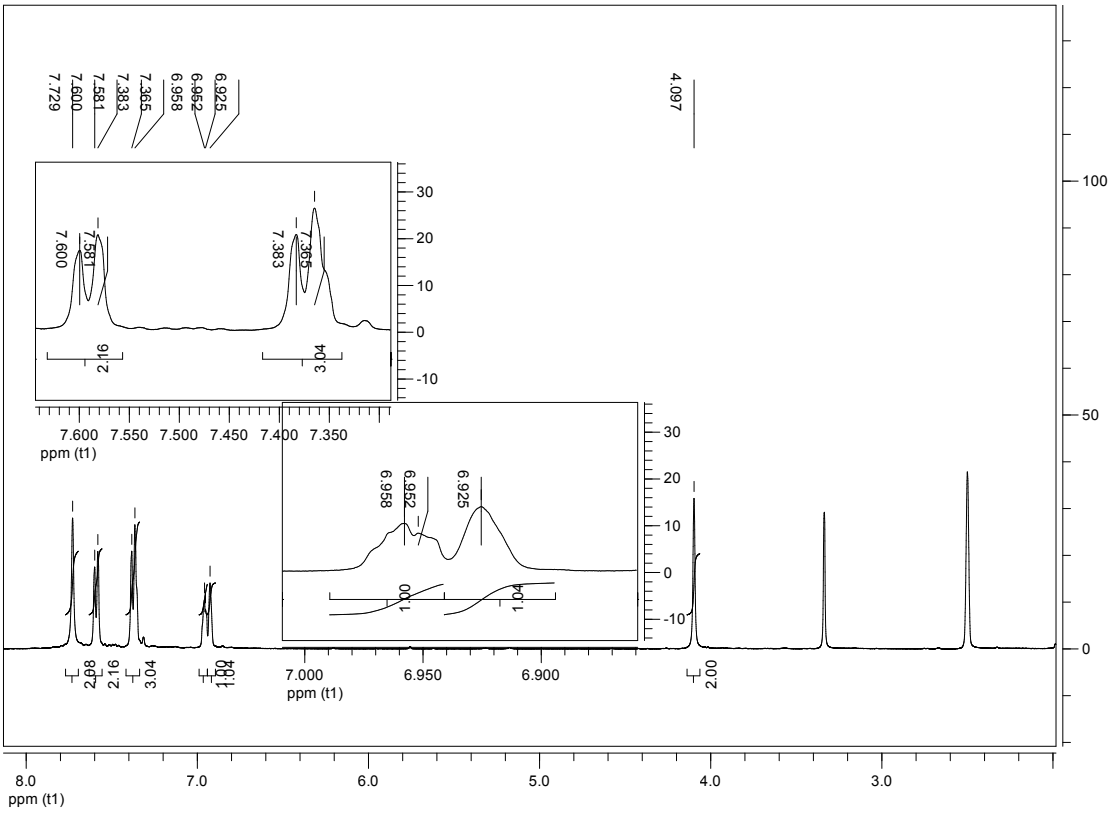

-116.705
20.0
15.0
10.0
5.0
0.0
-5.0
-100.0
-105.0
-110.0
-115.0
-120.0
-125.0
-130.0
ppm (t1)

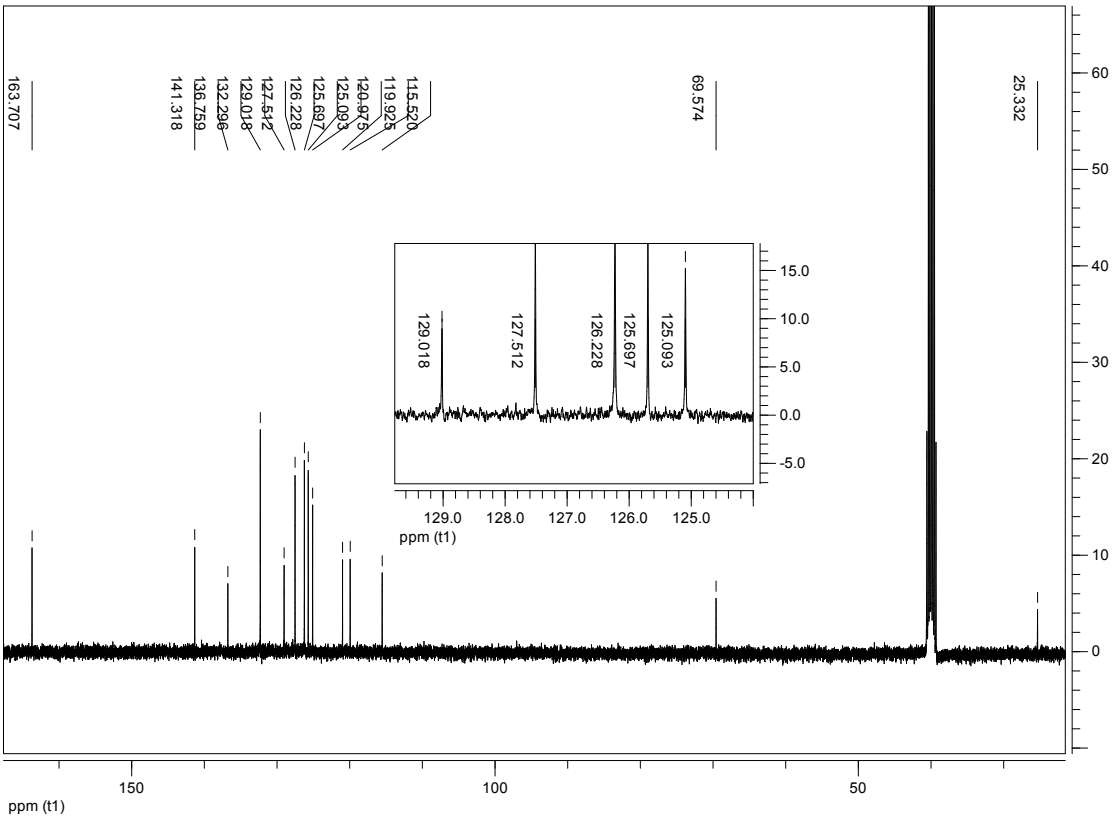
2-Amino-5-(3-methoxyphenyl)-4-(3-methylbenzyl)furan-3-carbonitrile (**2p**).



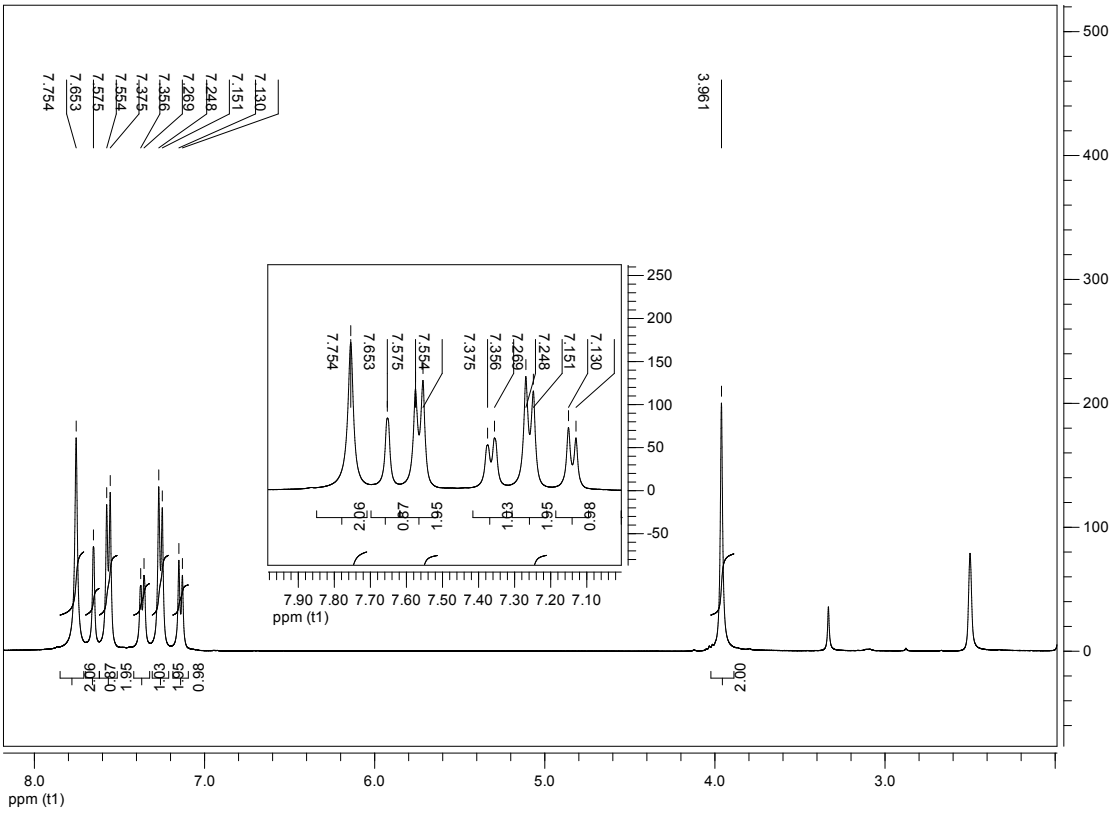


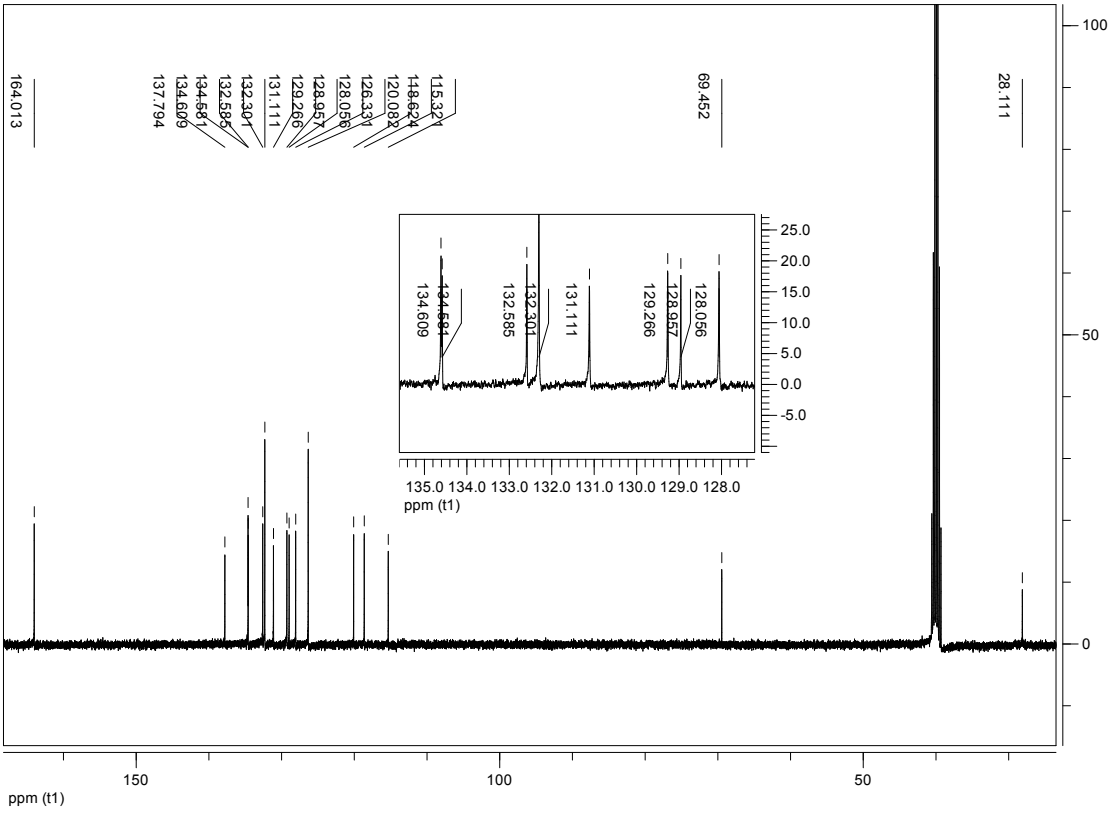
2-Amino-5-(4-bromophenyl)-4-(thiophen-2-ylmethyl)furan-3-carbonitrile (**2q**).



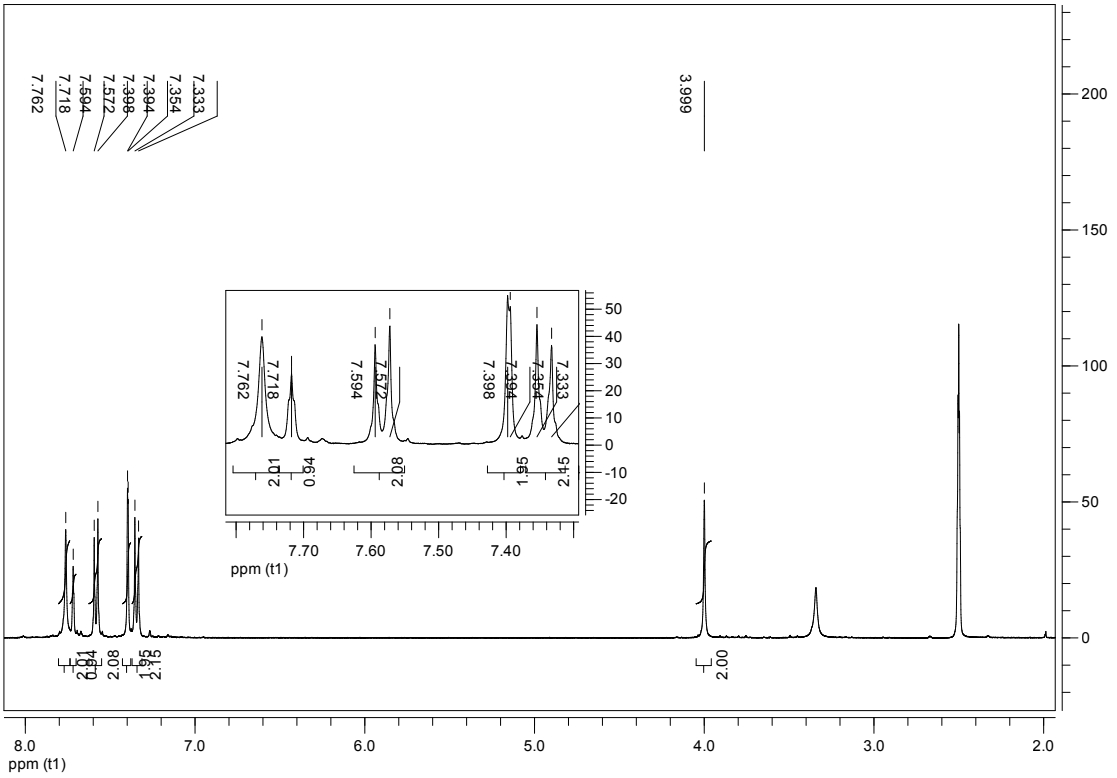


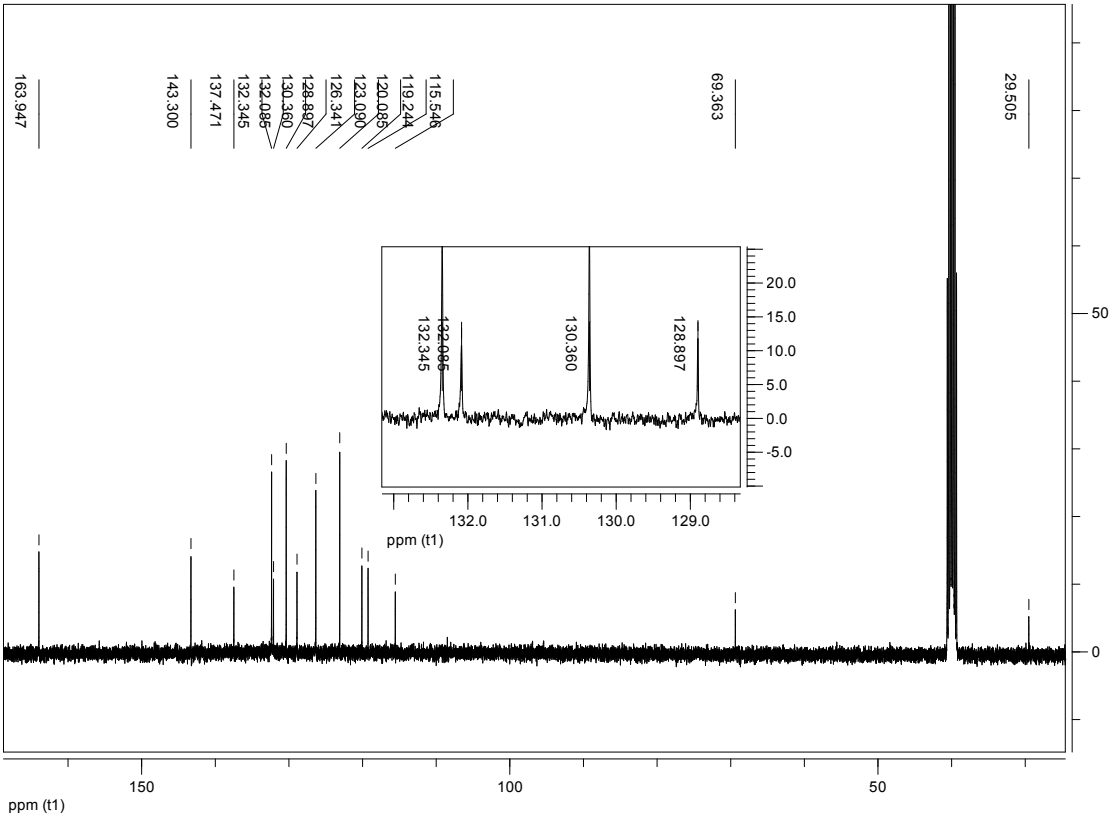
2-Amino-5-(4-bromophenyl)-4-(2,4-dichlorobenzyl)furan-3-carbonitrile (**2r**).



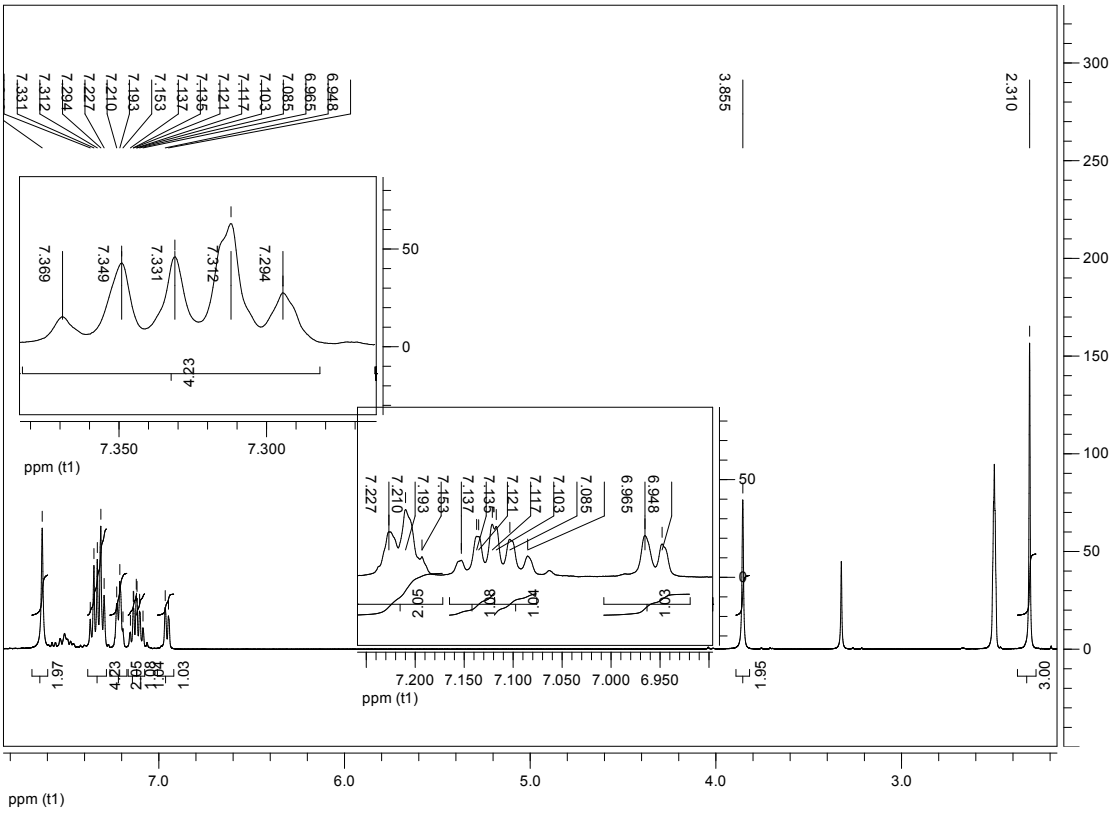


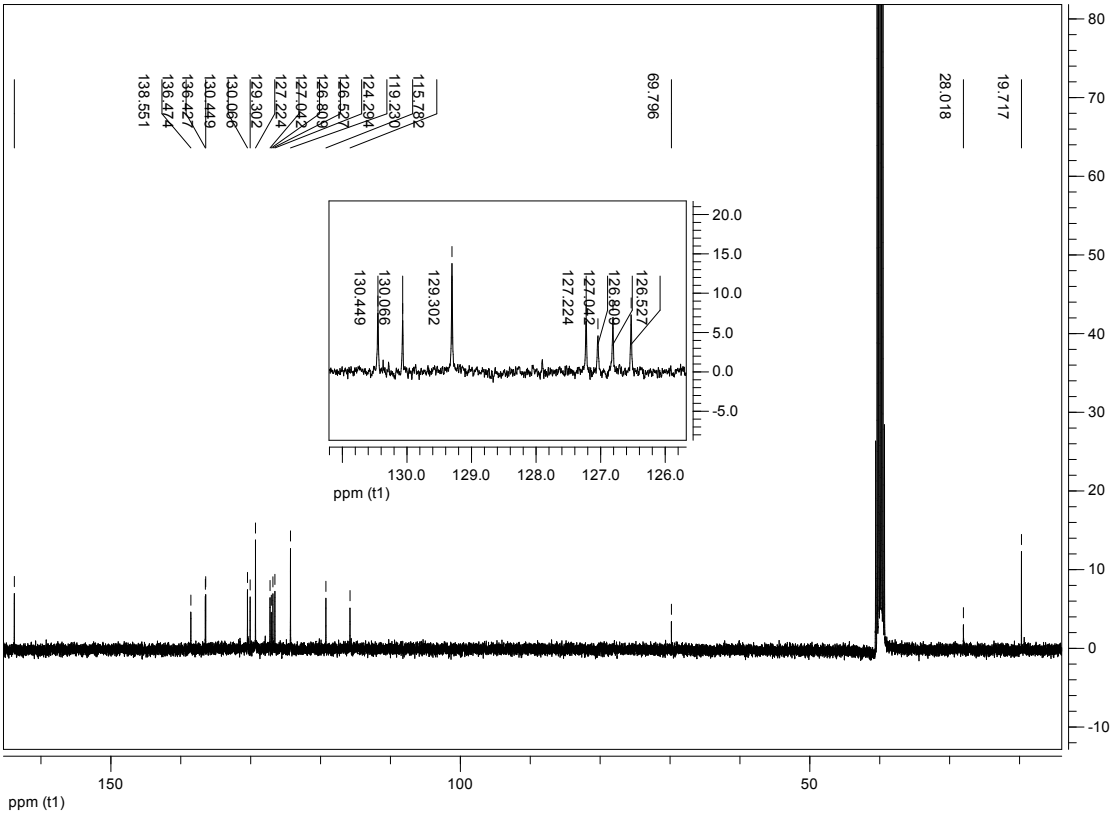
2-Amino-5-(4-bromophenyl)-4-(3,5-dibromobenzyl)furan-3-carbonitrile (**2s**).



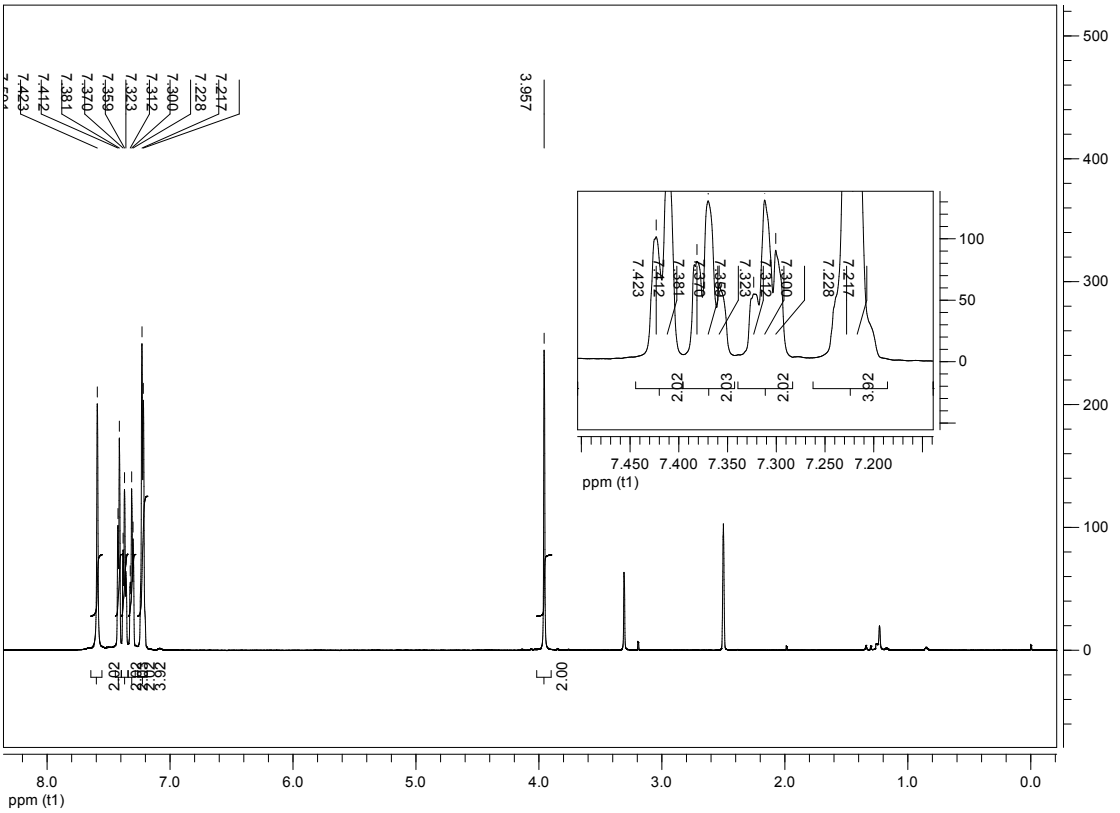


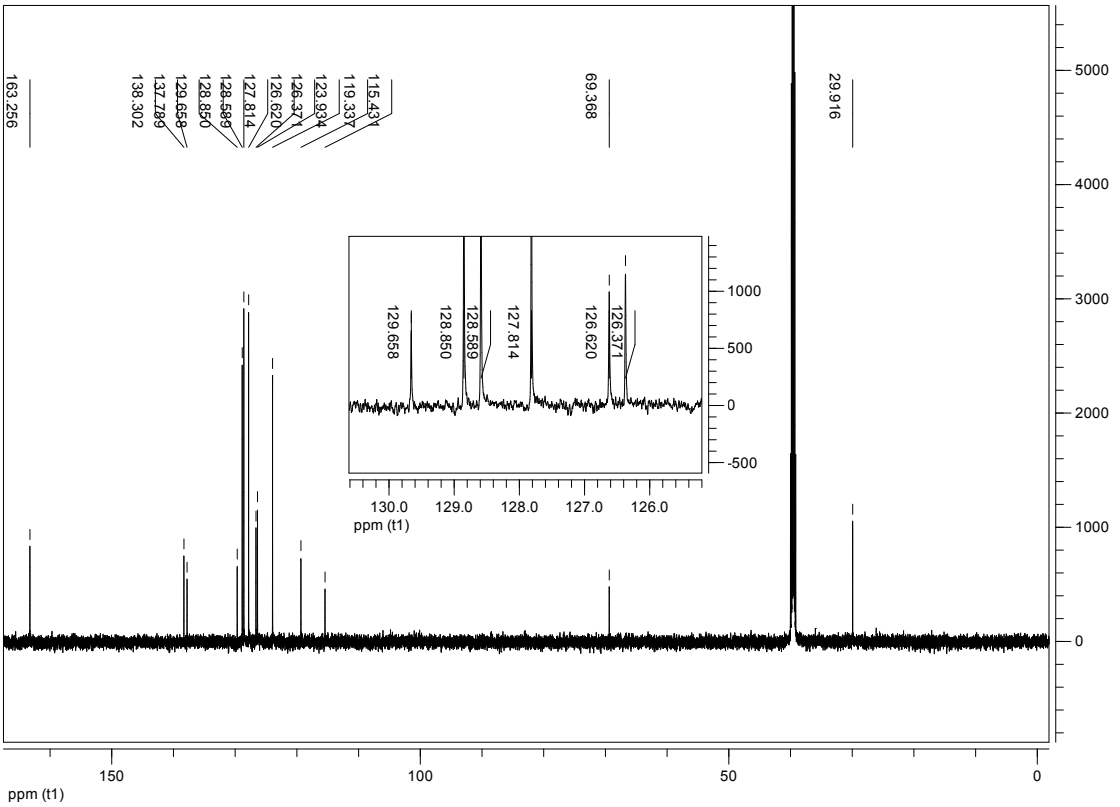
2-Amino-4-(2-methylbenzyl)-5-phenylfuran-3-carbonitrile (**2t**).

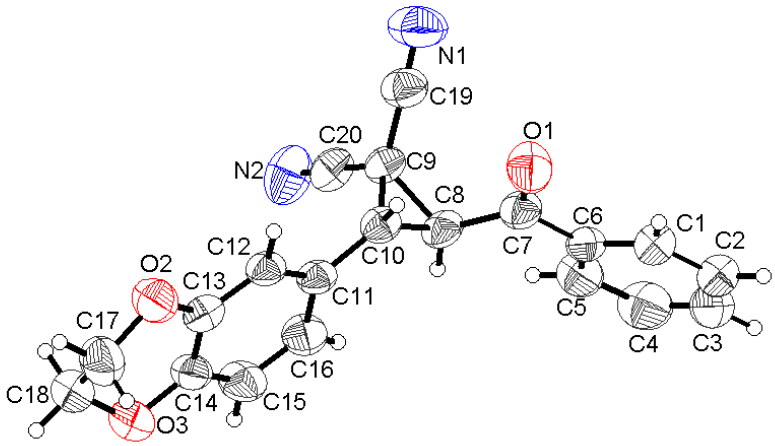




2-Amino-4-benzyl-5-phenylfuran-3-carbonitrile (**2u**)


7.423
7.412
7.381
7.370
7.359
7.323
7.312
7.300
7.228
7.217
3.957
2.02
2.03
2.02
3.98
2.00
ppm (t1)


163.256
138.302
137.789
129.658
128.850
128.589
127.814
126.620
126.371
123.934
119.337
115.431
69.368
29.916
ppm (t1)



1n (CCDC 1893325)

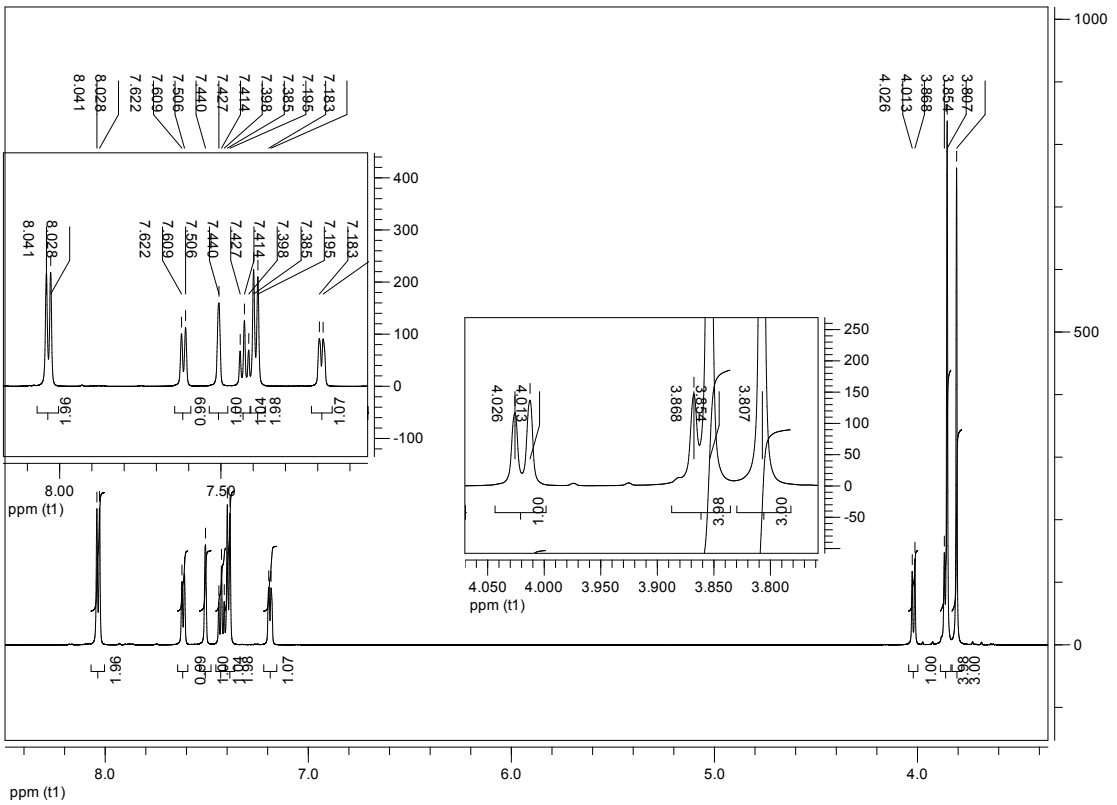
Fig. S7 Molecular structure of 2-benzoyl-3-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl) cyclopropane-1,1-dicarbonitrile (**1n**), non-hydrogen atoms are shown at the 30% probability level.

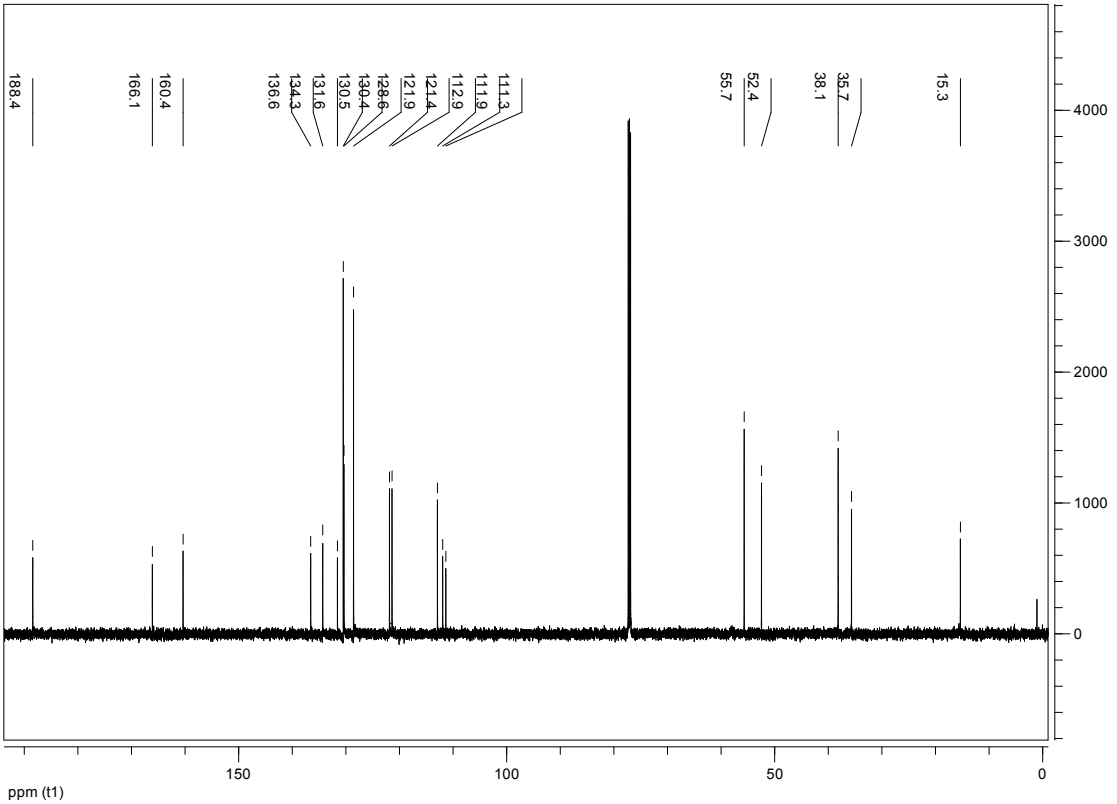
Table S7. Crystal data and structure refinement for **1n**.

Identification code	**1n**
Empirical formula	C_{20} H_{14} N_2 O_3
Formula weight	330.33
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 11.542(4) A alpha = 100.009(11) deg. b = 12.009(4) A beta = 105.015(10) deg. c = 14.738(5) A gamma = 117.020(10) deg.
Volume	1653.9(10) A^3
Z, Calculated density	4, 1.327 Mg/m^3
Absorption coefficient	0.091 mm^-1
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^2
Data / restraints / parameters	7426 / 0 / 451
Goodness-of-fit on F^2	1.054

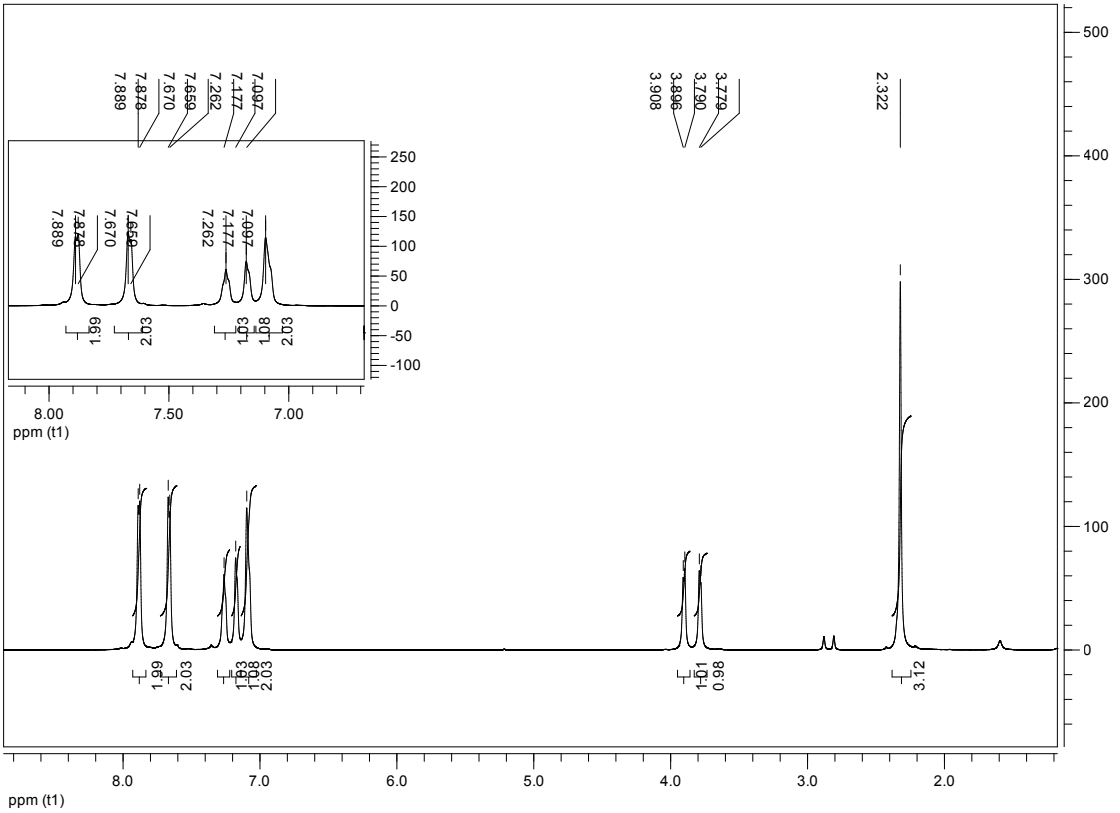
Final R indices [I>2sigma(I)]	R1 = 0.1032, wR2 = 0.2930
R indices (all data)	R1 = 0.1601, wR2 = 0.3322
Largest diff. peak and hole	0.381 and -0.315 e.A^-3

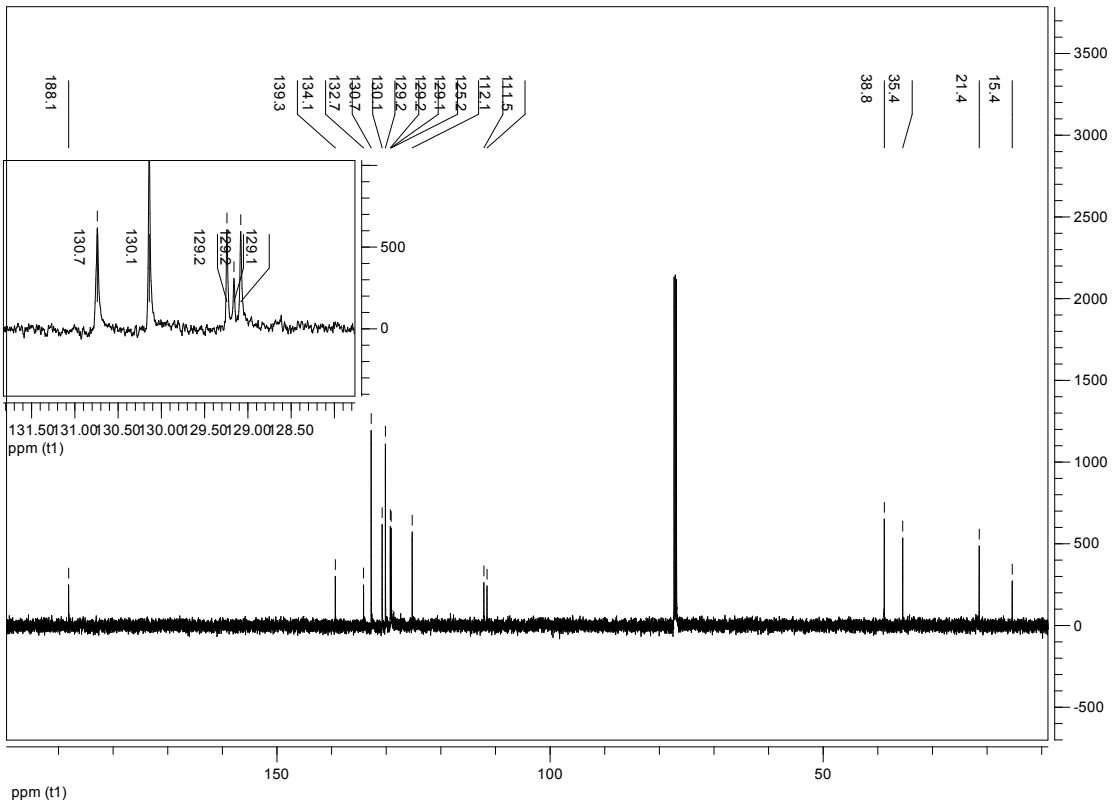
Methyl-4-(2,2-dicyano-3-(3-methoxybenzoyl)cyclopropyl)benzoate (**1a**)



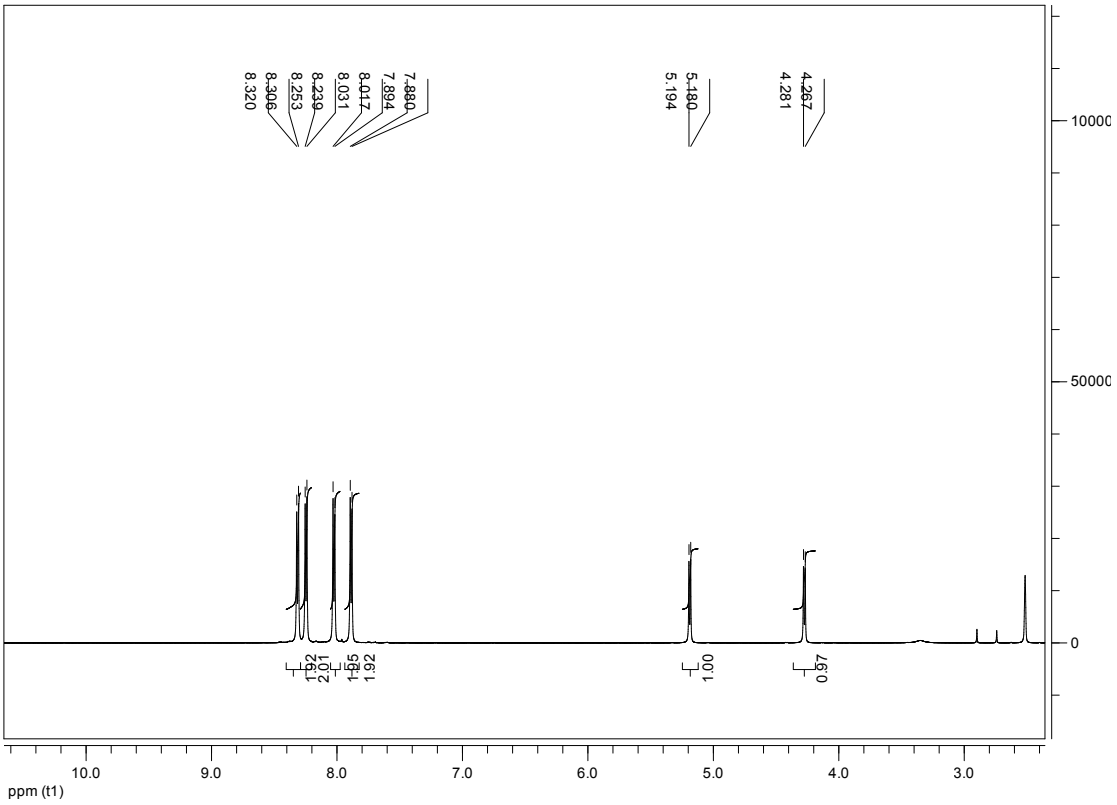


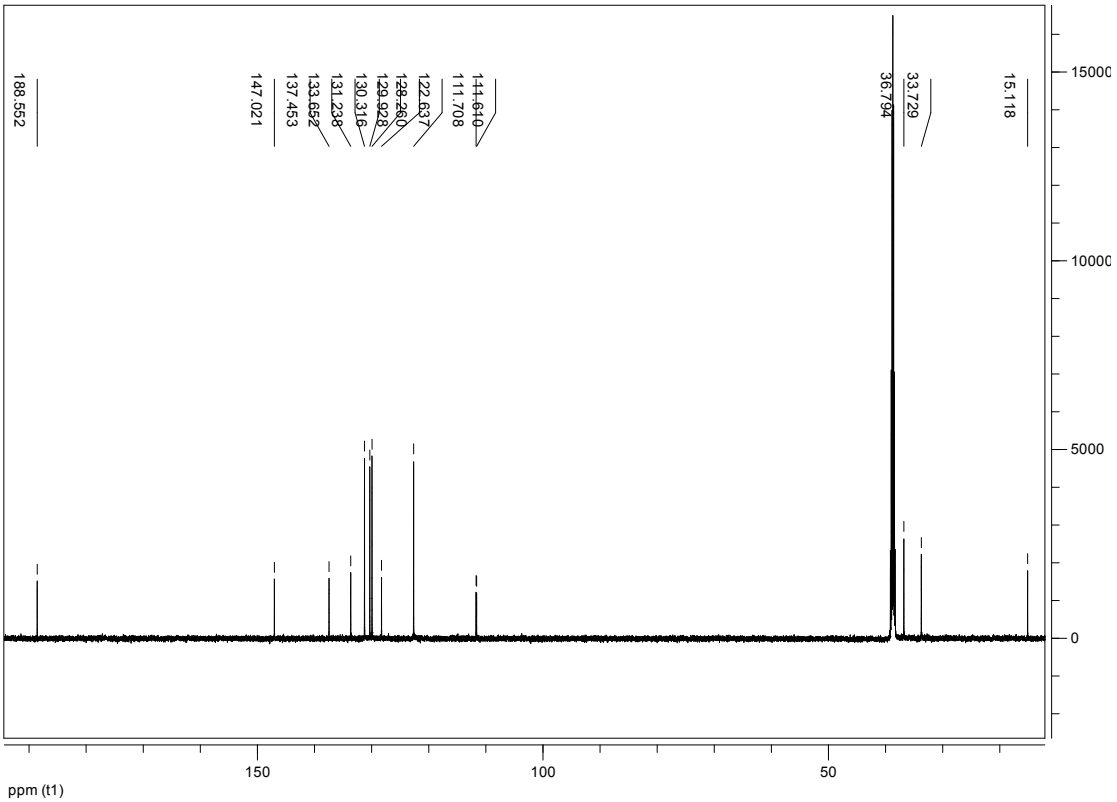
2-(4-Bromobenzoyl)-3-(m-tolyl)cyclopropane-1,1-dicarbonitrile (**1b**).



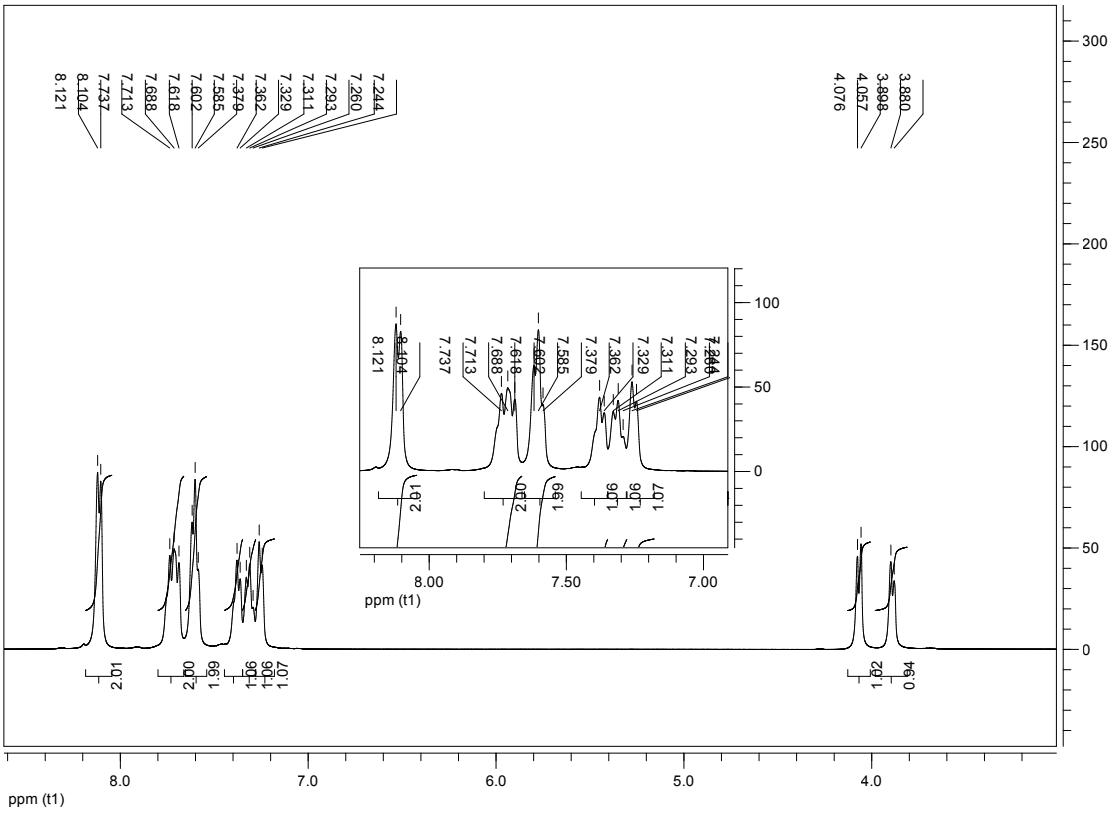


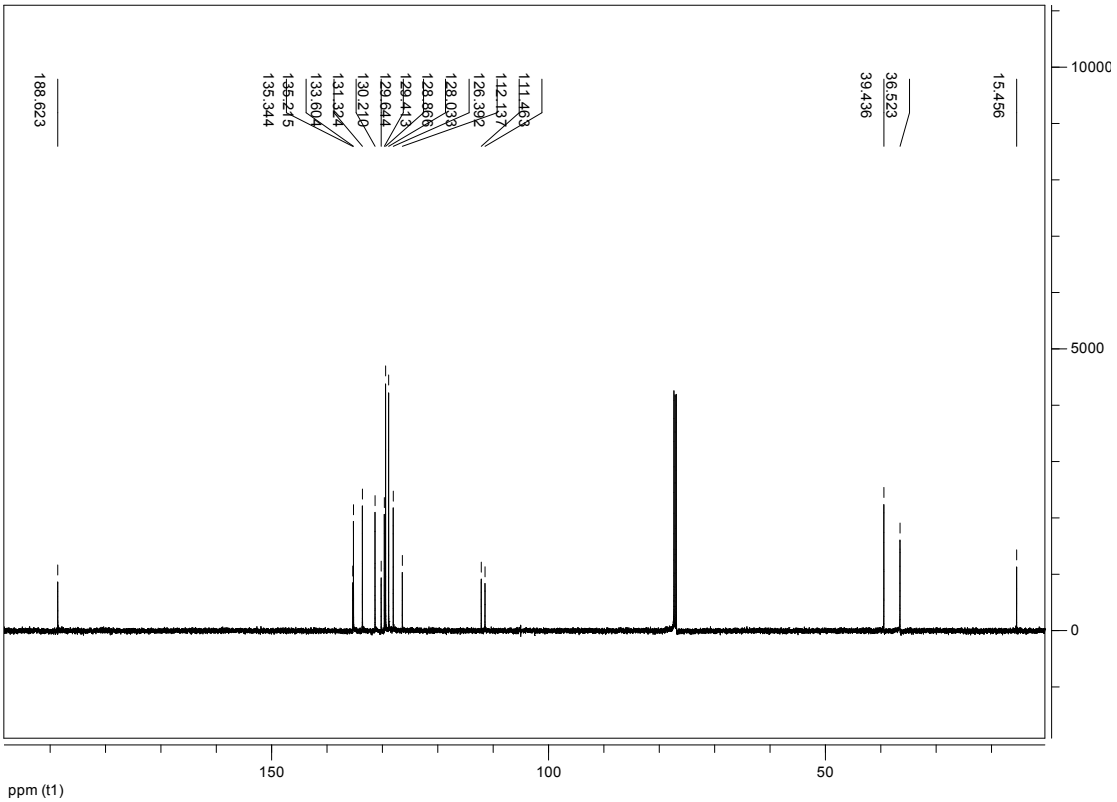
2-Benzoyl-3-(4-nitrophenyl)cyclopropane-1,1-dicarbonitrile (**1c**)



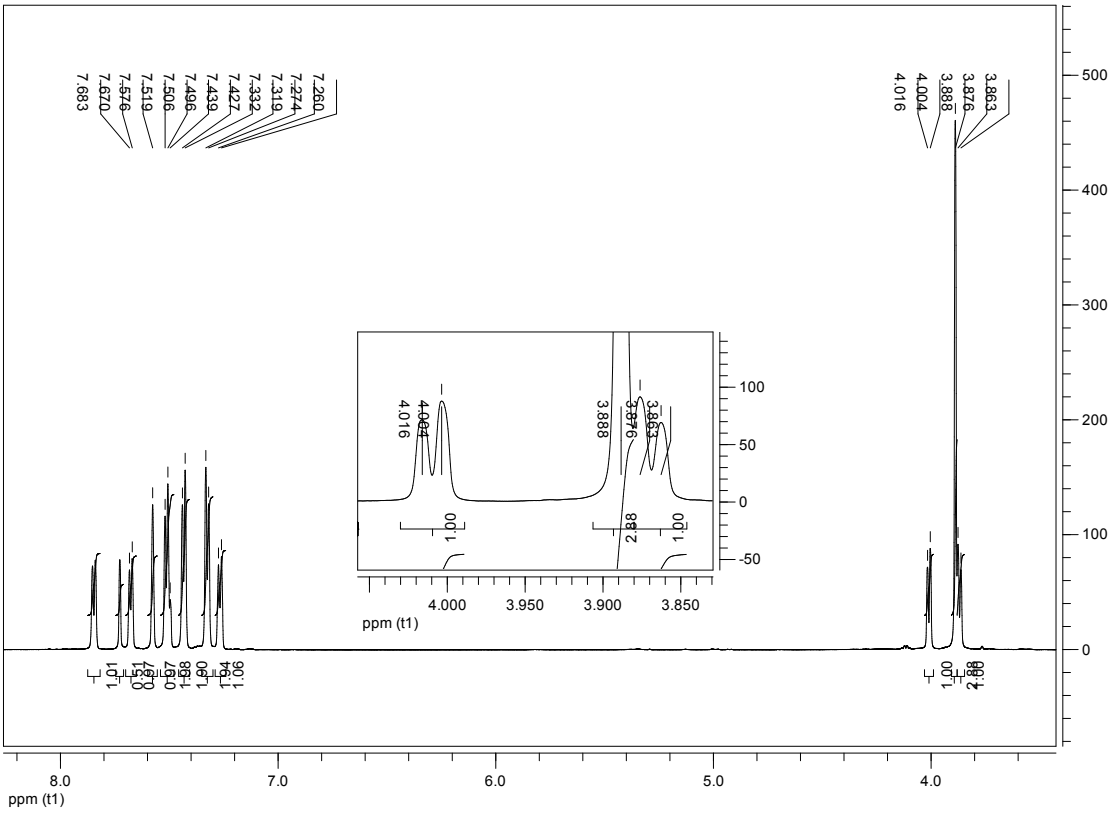


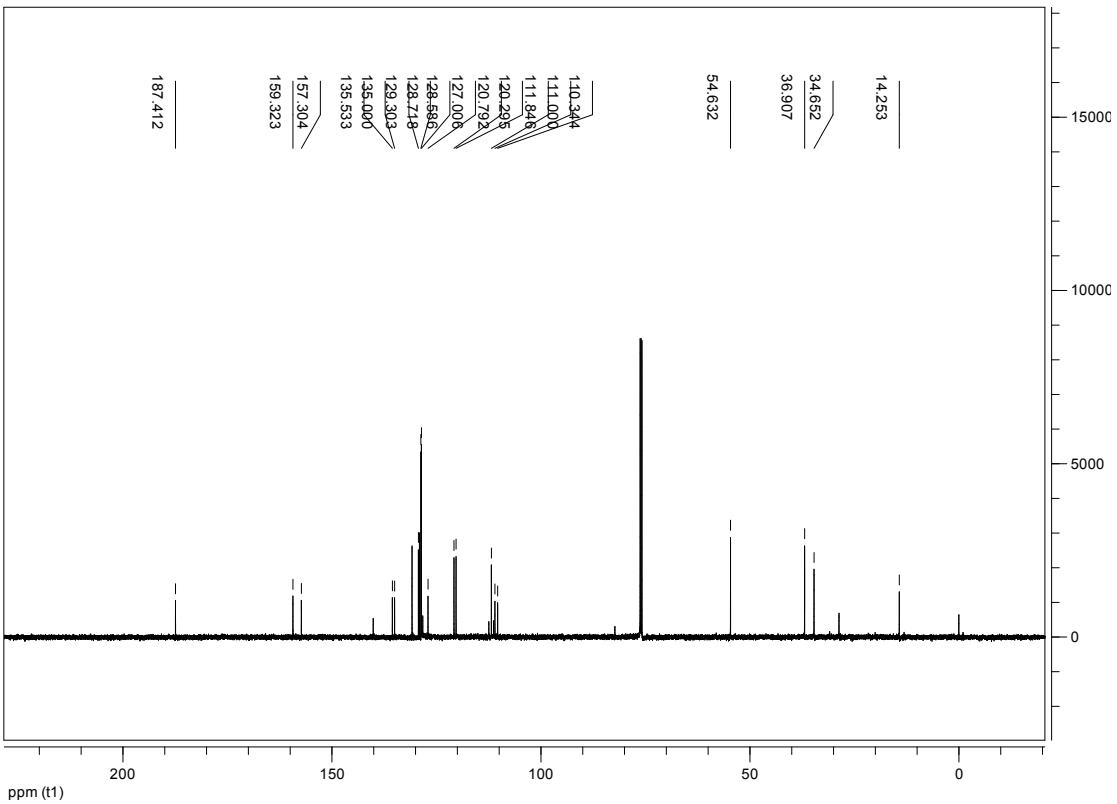
2-Benzoyl-3-(2-bromophenyl)cyclopropane-1,1-dicarbonitrile (**1e**).



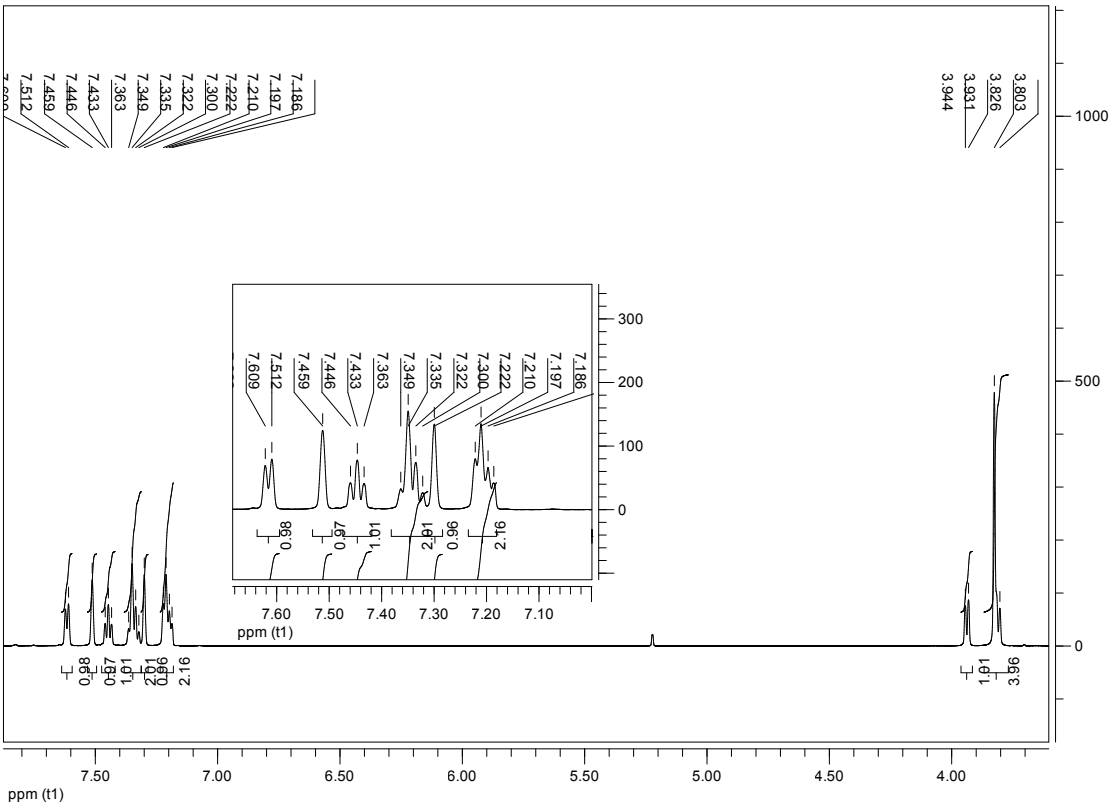


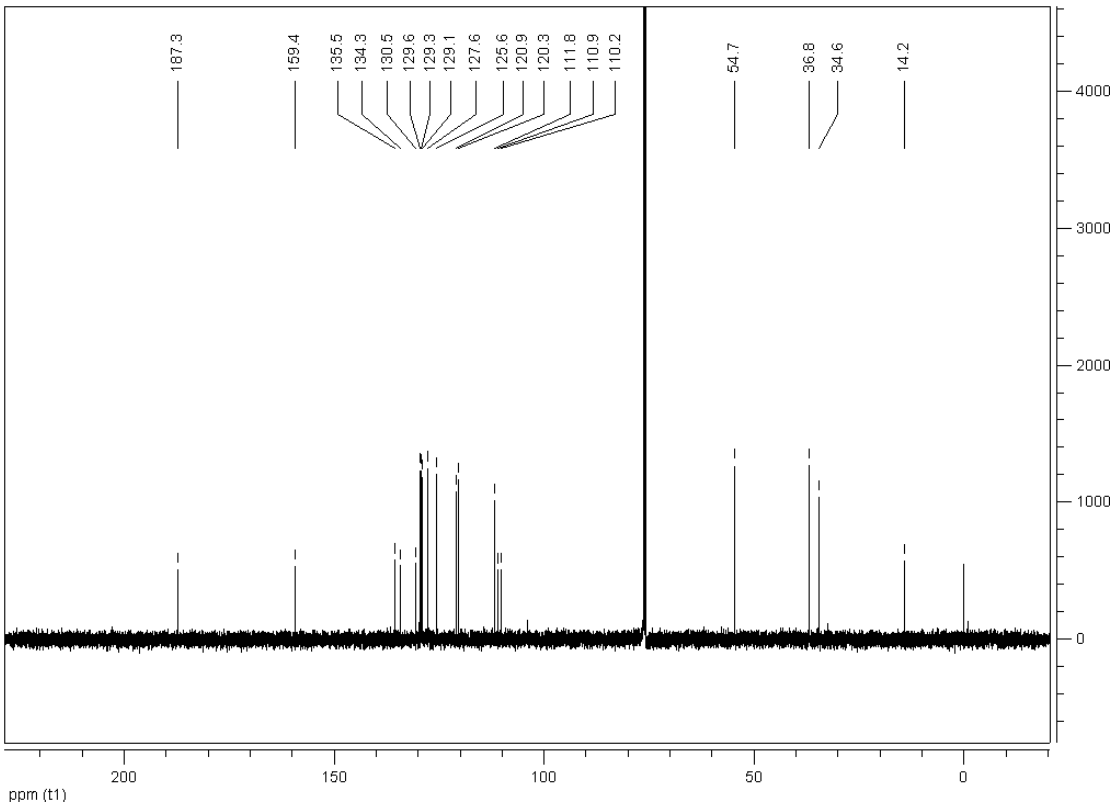
2-(4-Chlorophenyl)-3-(3-methoxybenzoyl)cyclopropane-1,1-dicarbonitrile (**1f**)



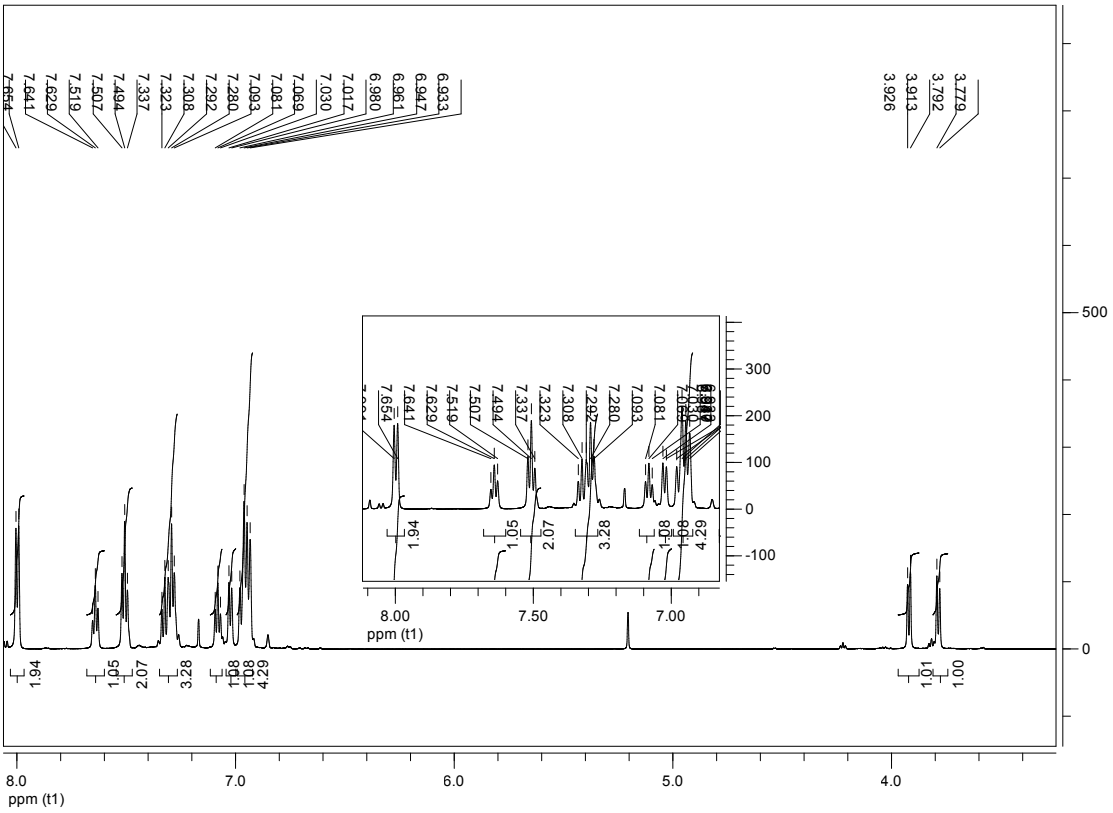


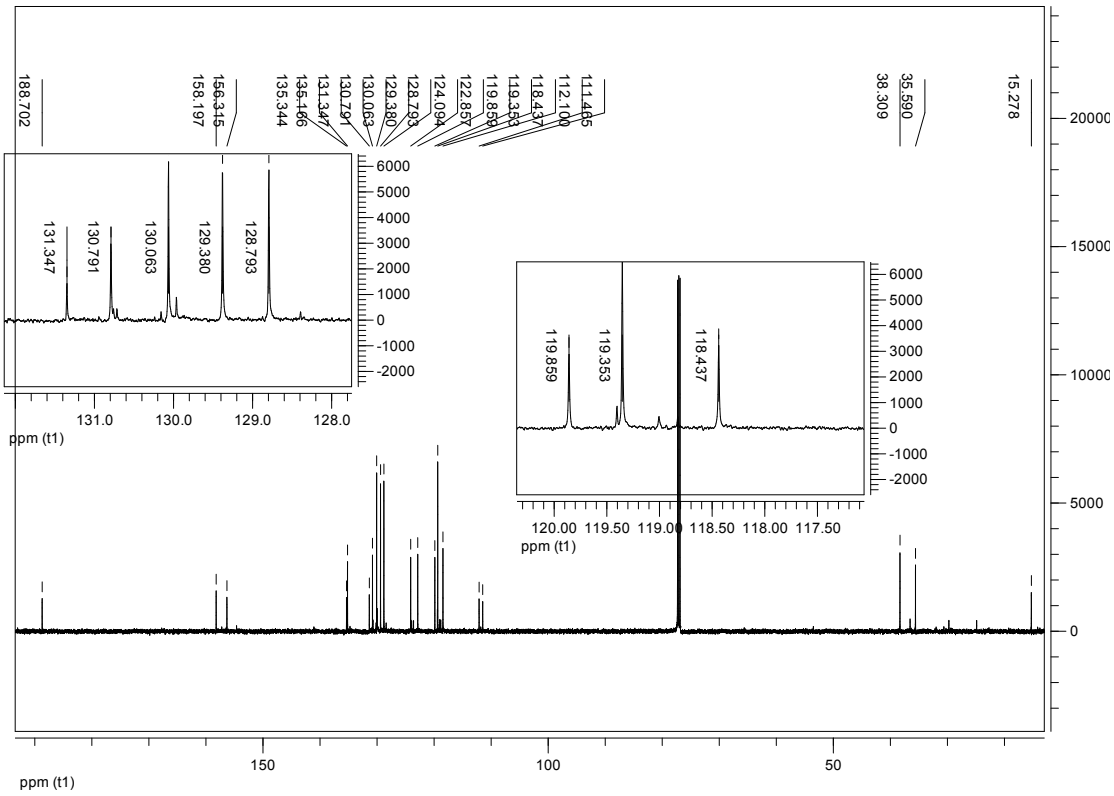
2-(3-Chlorophenyl)-3-(3-methoxybenzoyl)cyclopropane-1,1-dicarbonitrile (**1g**).



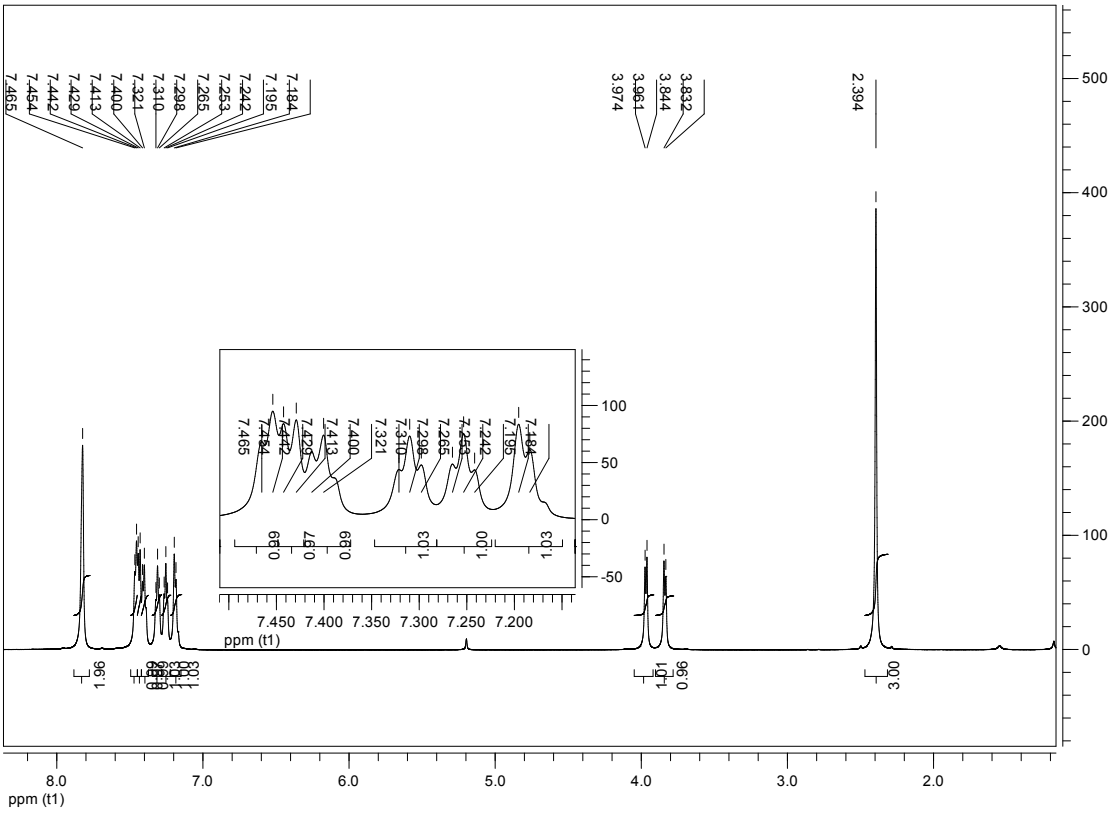


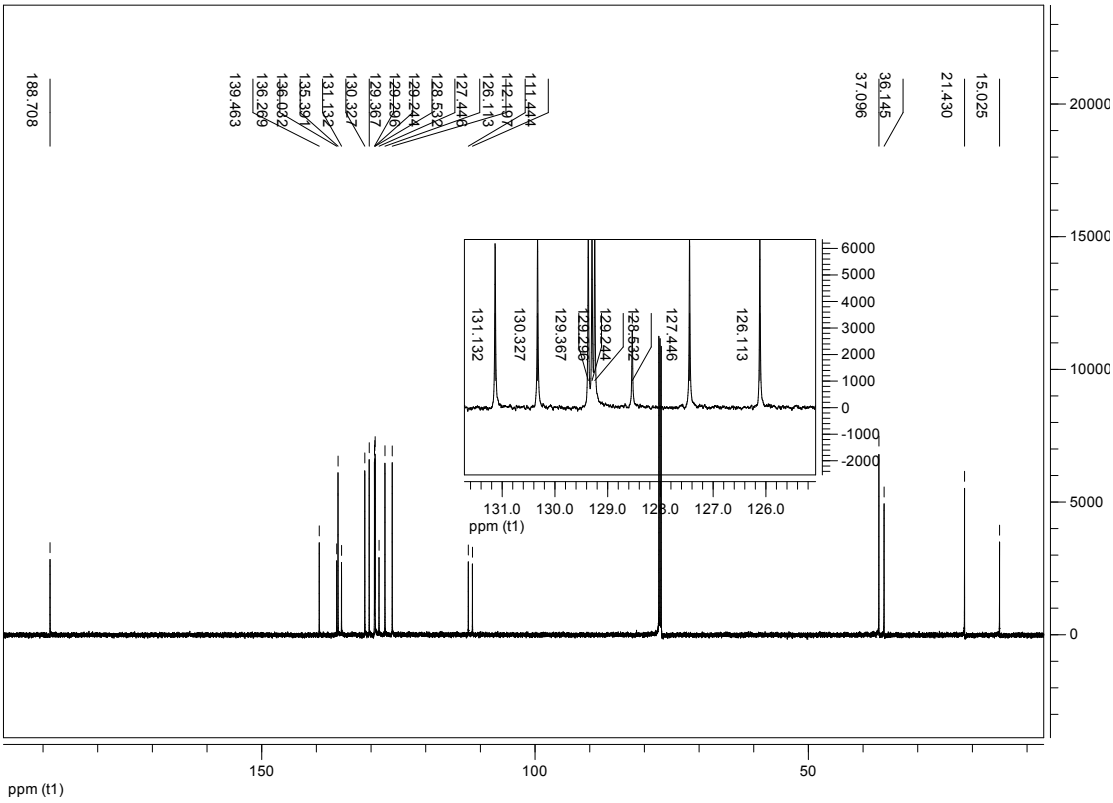
2-Benzoyl-3-(3-phenoxyphenyl)cyclopropane-1,1-dicarbonitrile (**1h**)



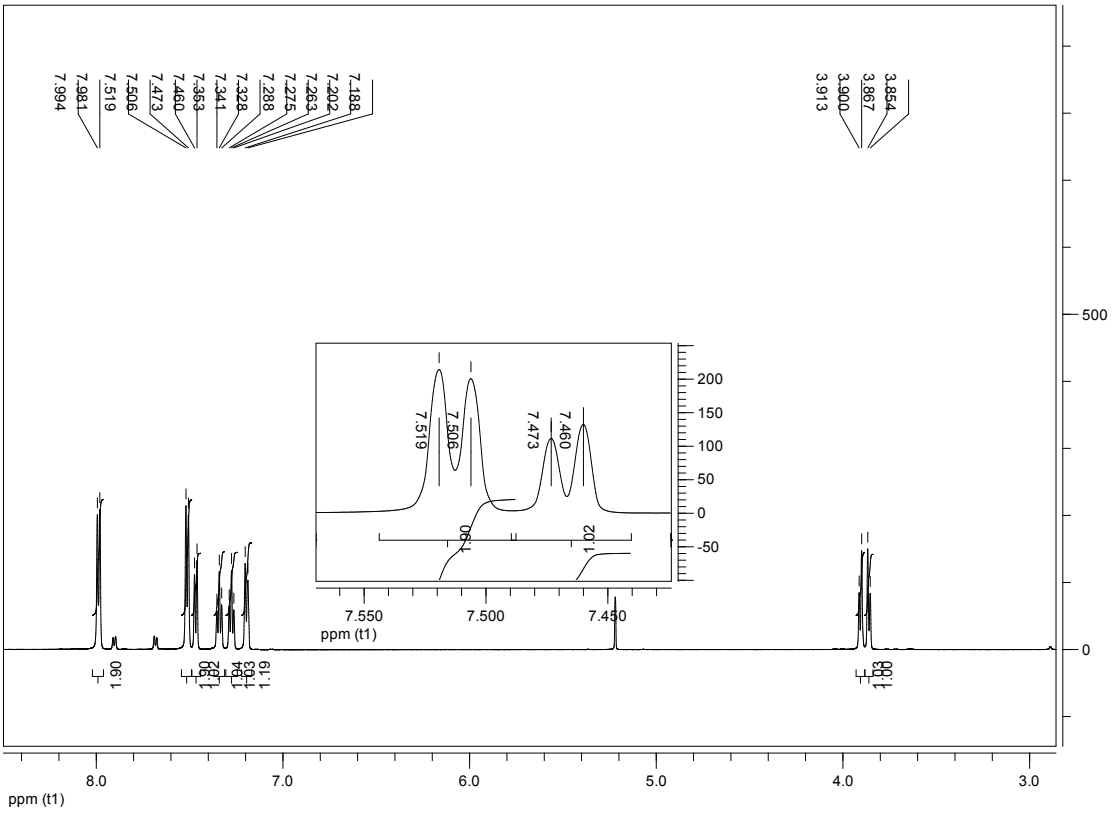


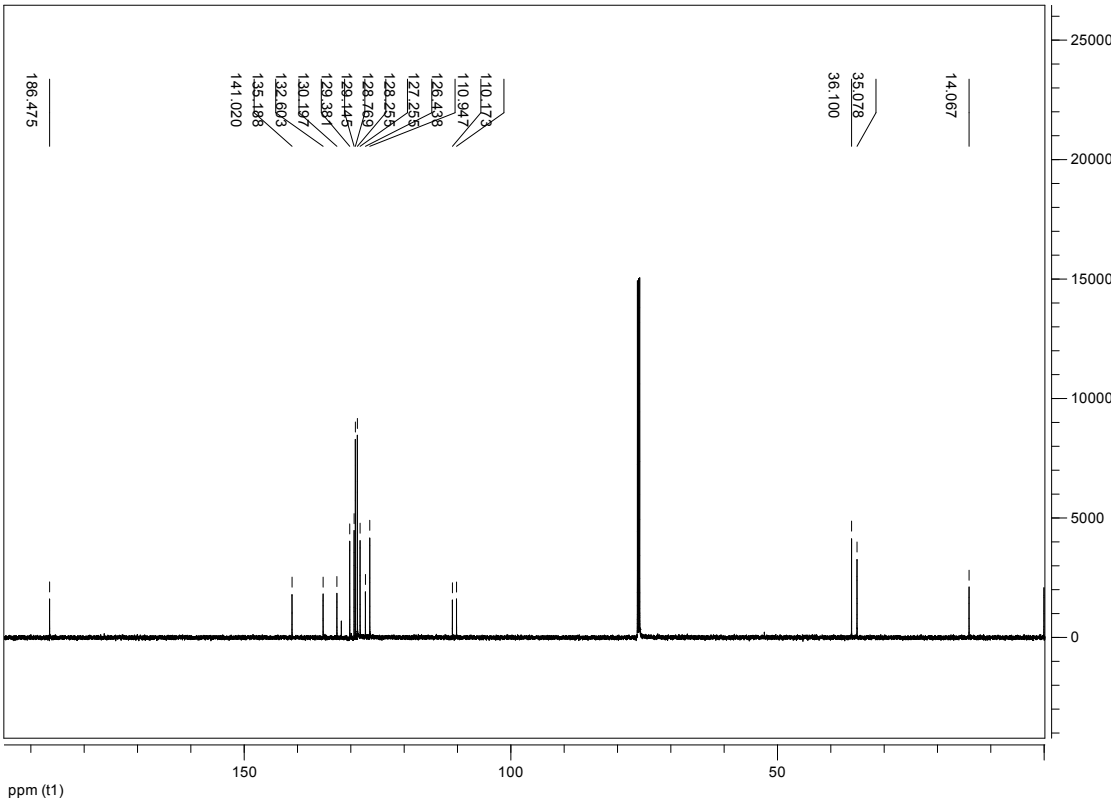
2-(2-Chlorophenyl)-3-(3-methylbenzoyl)cyclopropane-1,1-dicarbonitrile (**1i**)



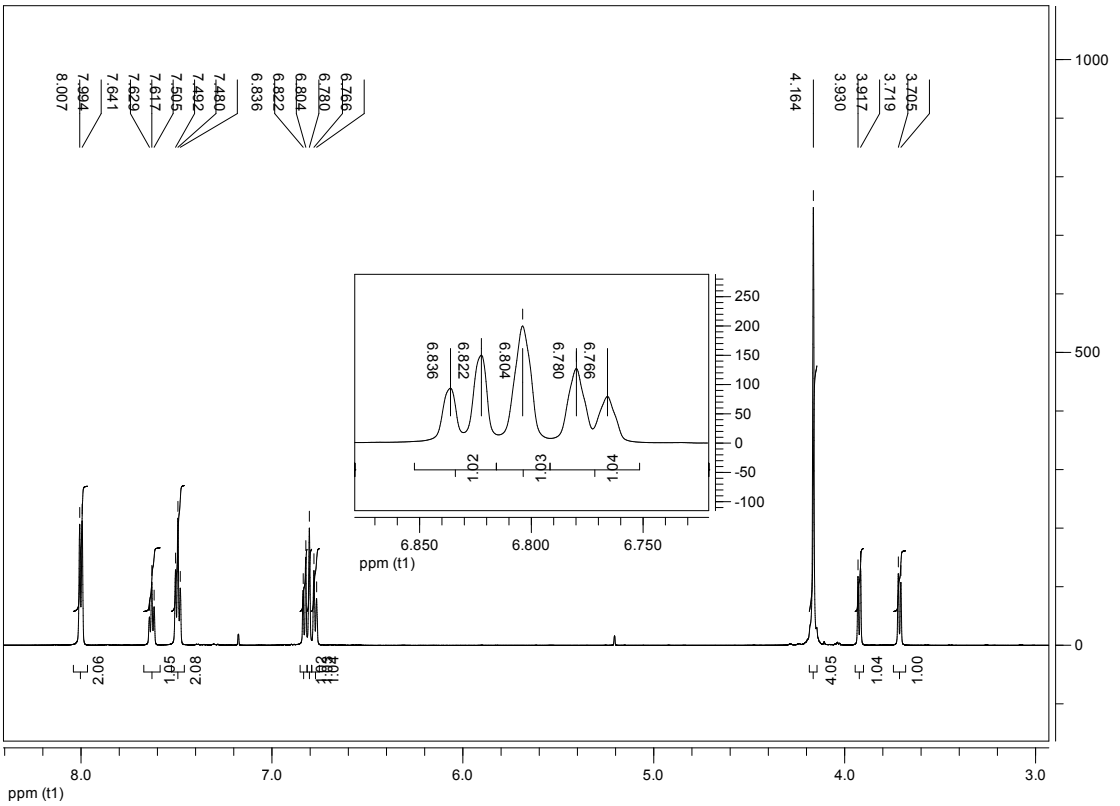


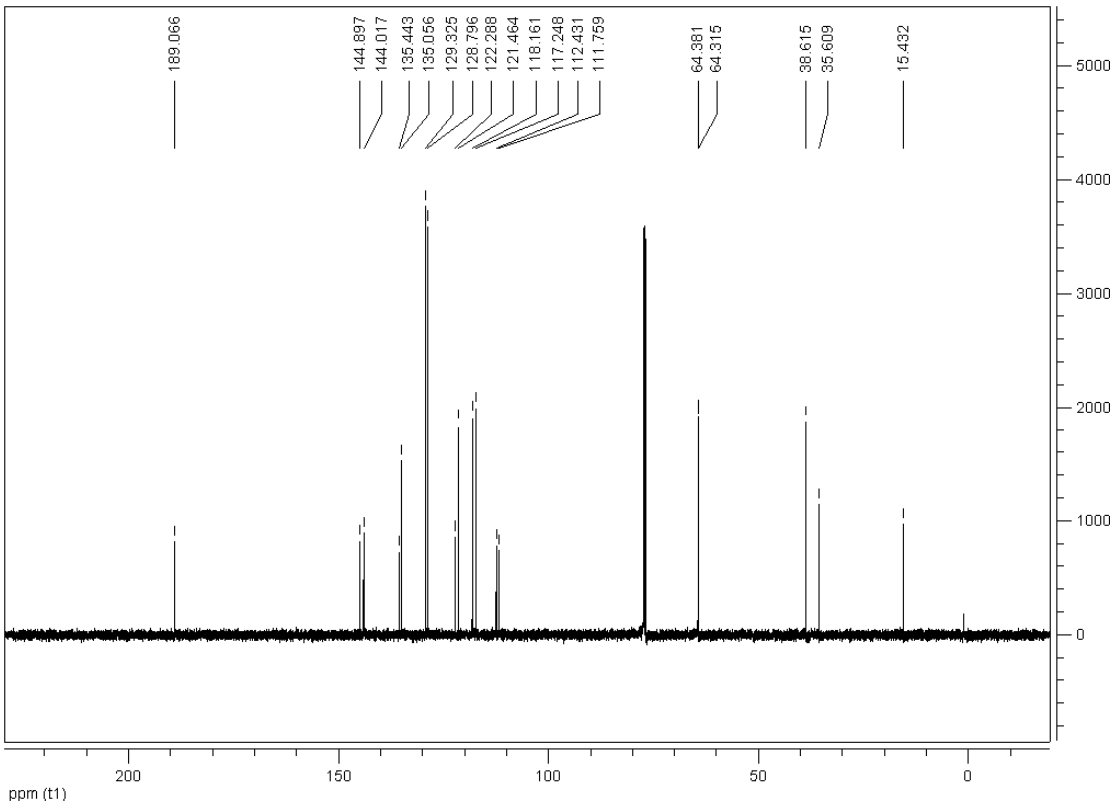
2-(4-Chlorobenzoyl)-3-(2-chlorophenyl)cyclopropane-1,1-dicarbonitrile (**1l**).



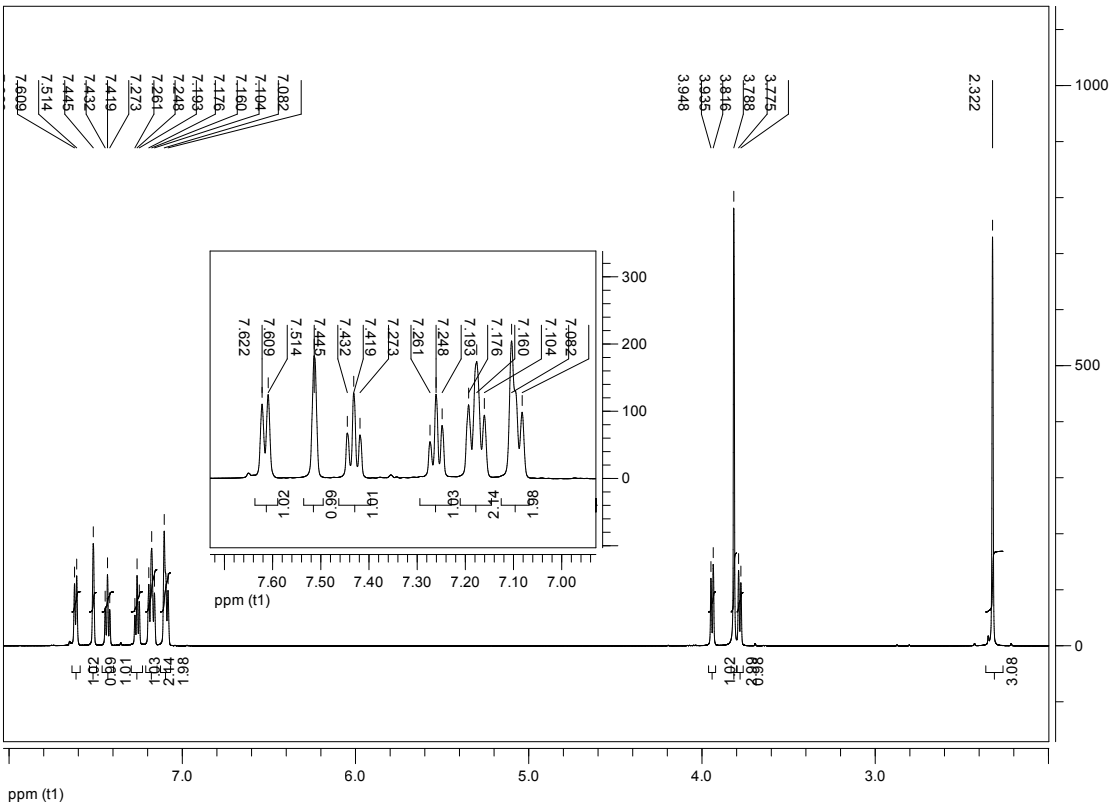


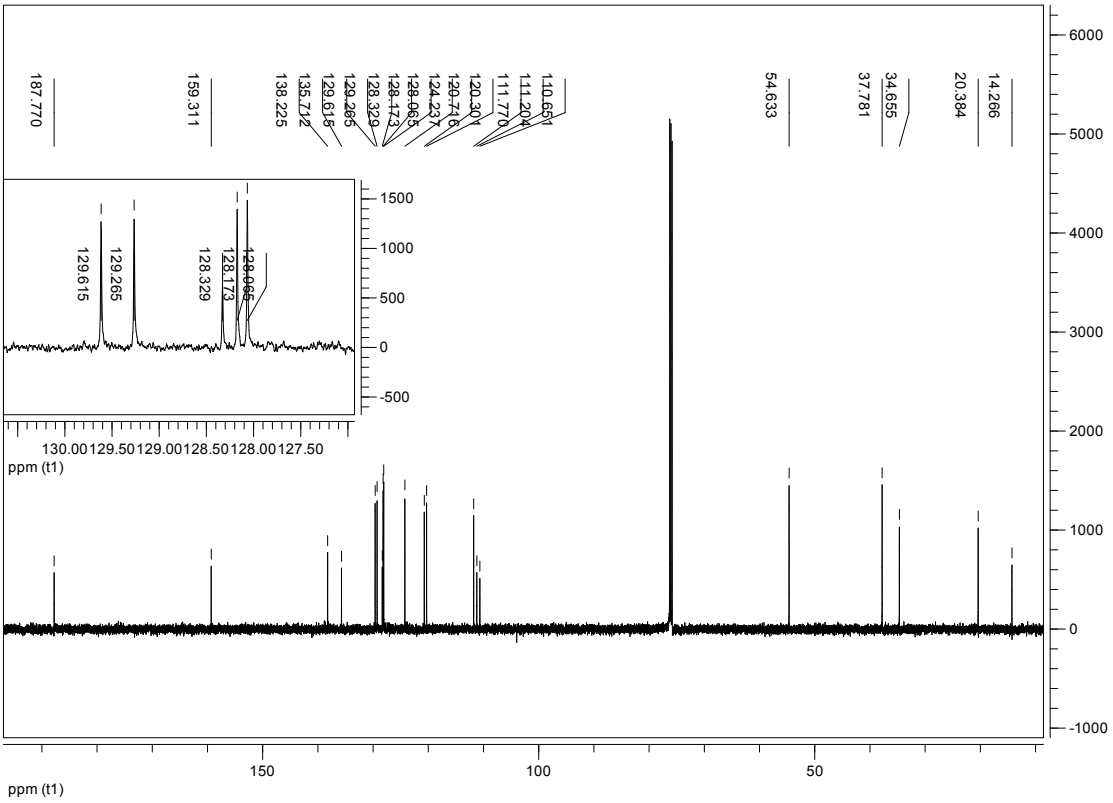
2-Benzoyl-3-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)cyclopropane-1,1-dicarbonitrile (**1n**)



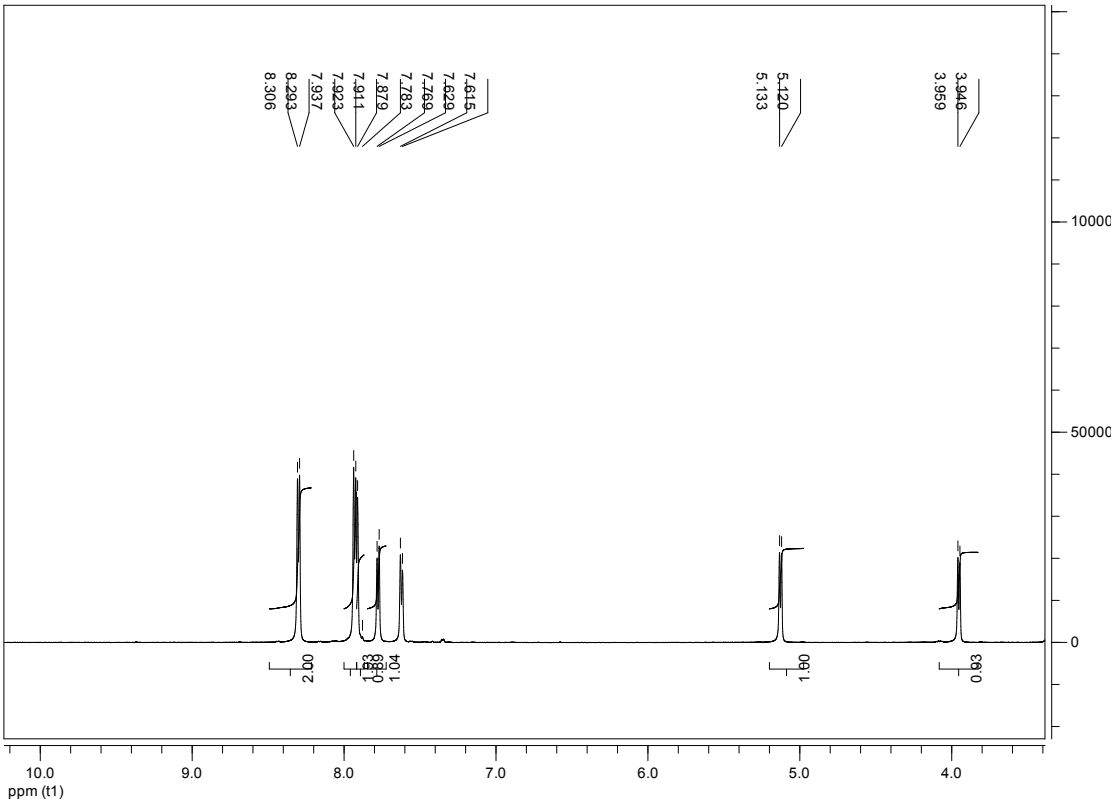


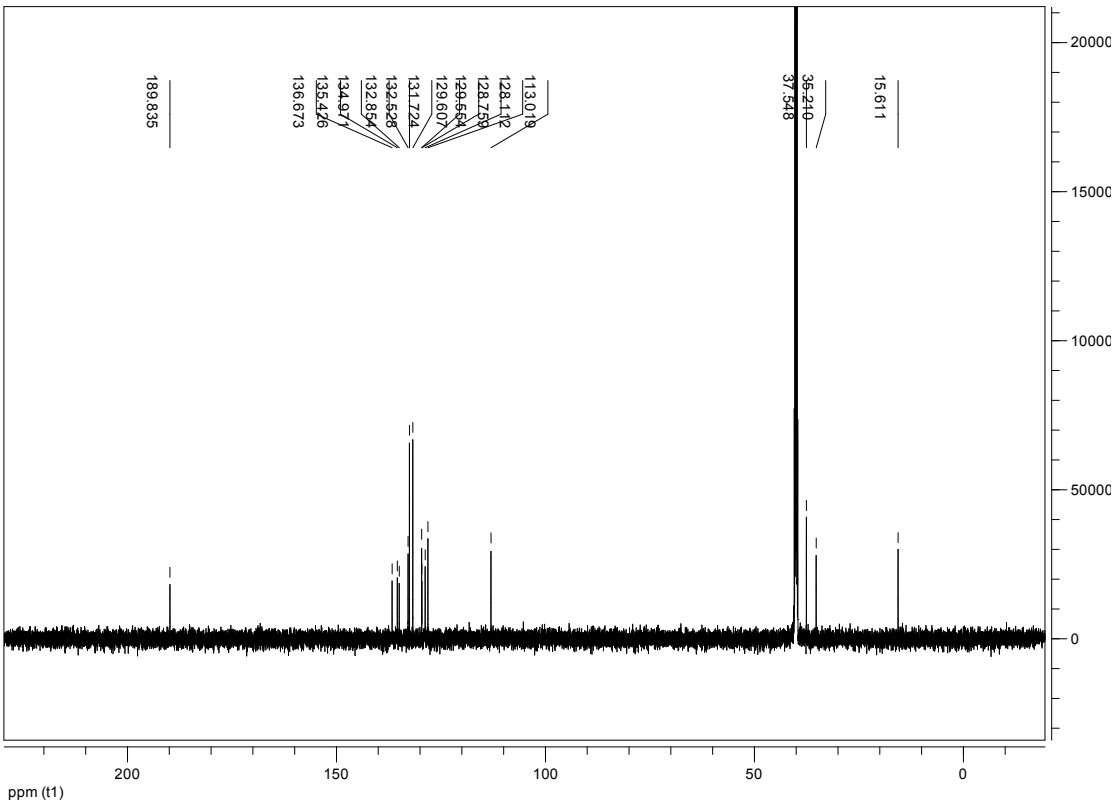
2-(3-Methoxybenzoyl)-3-(m-tolyl)cyclopropane-1,1-dicarbonitrile (**1p**)



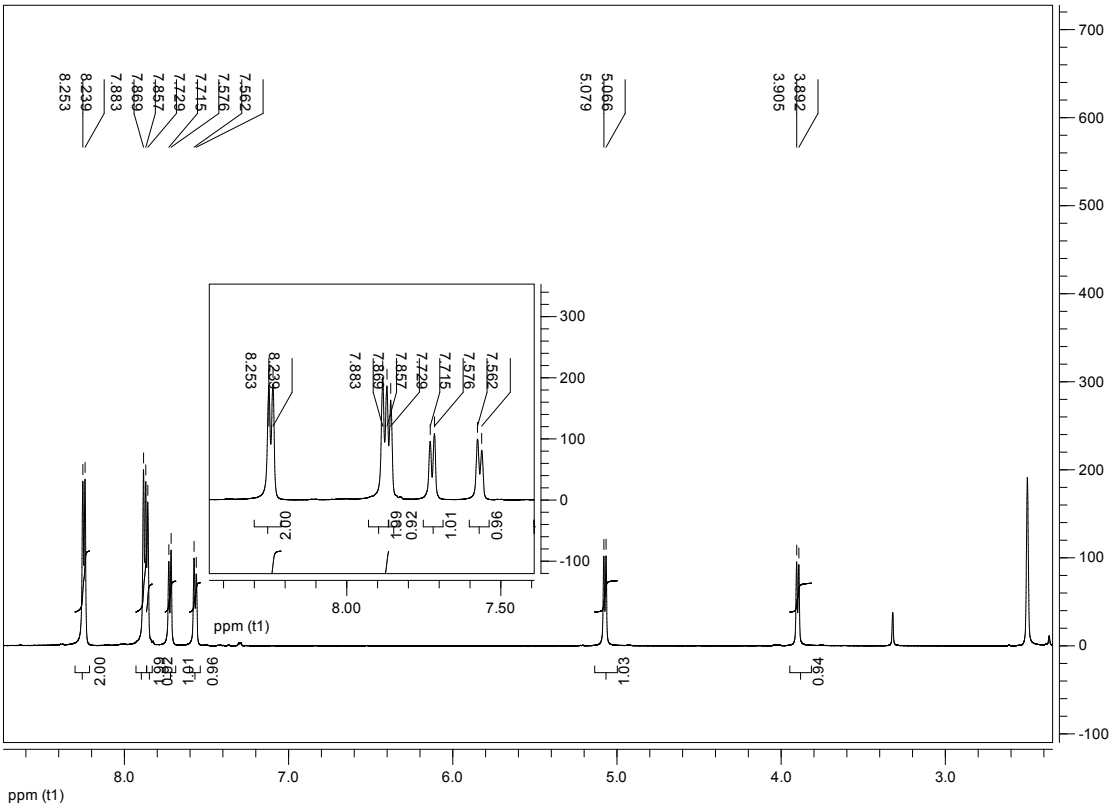


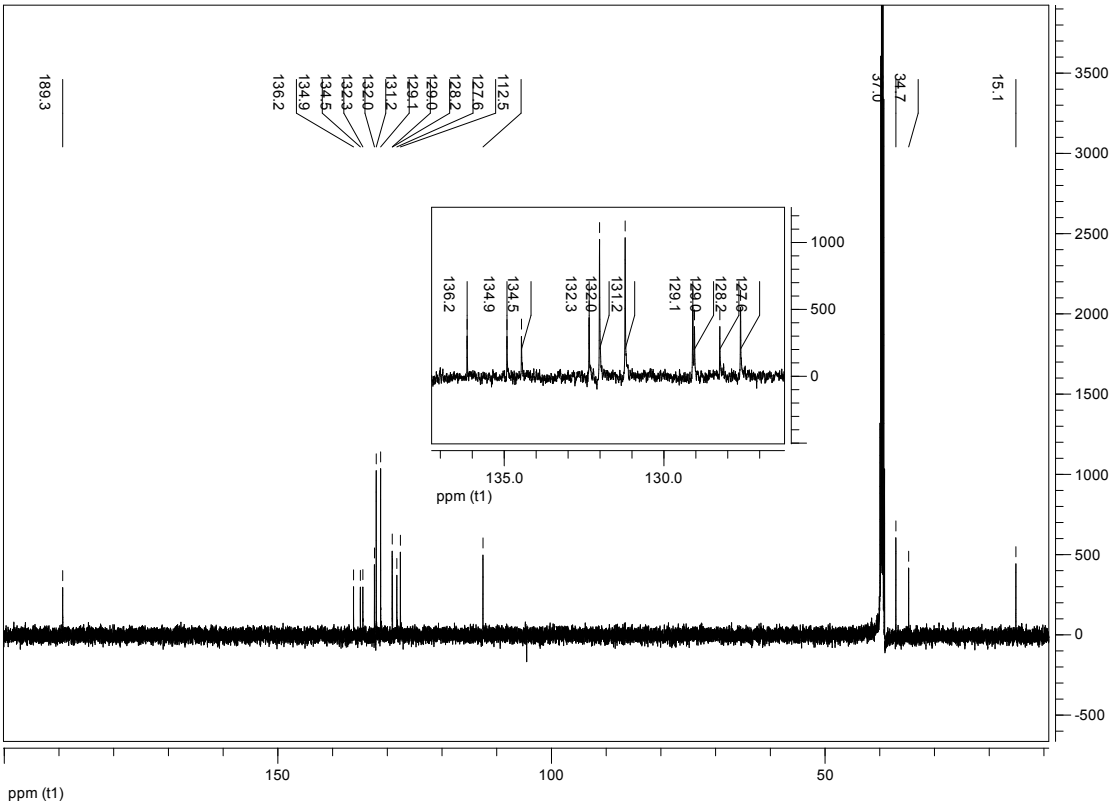
2-(4-Bromobenzoyl)-3-(thiophen-2-yl)cyclopropane-1,1-dicarbonitrile (**1q**)



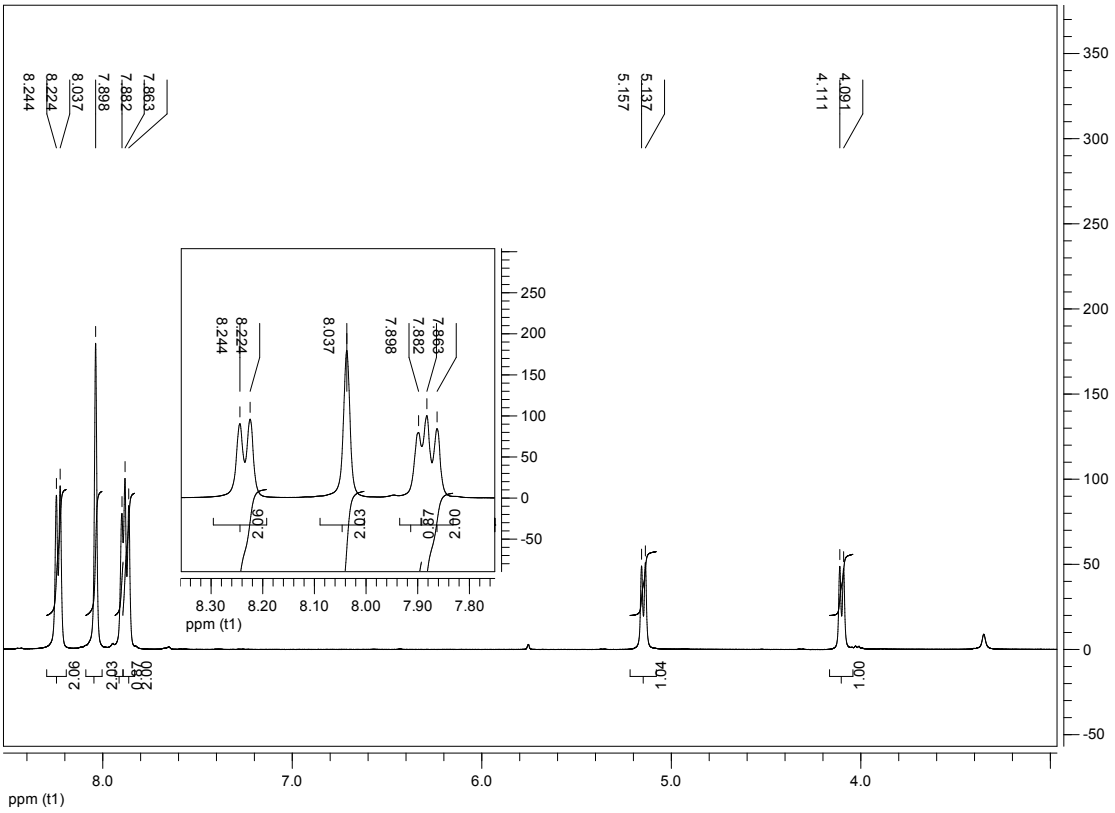


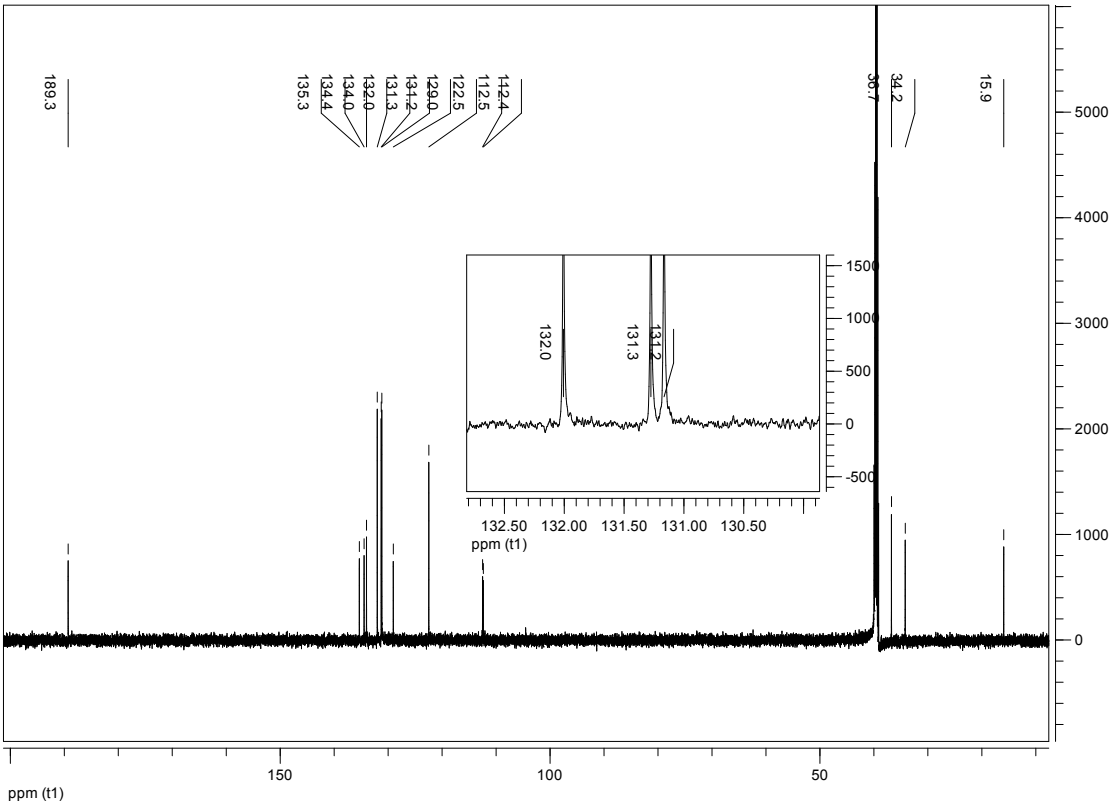
2-(4-Bromobenzoyl)-3-(2,4-dichlorophenyl)cyclopropane-1,1-dicarbonitrile (**1r**)



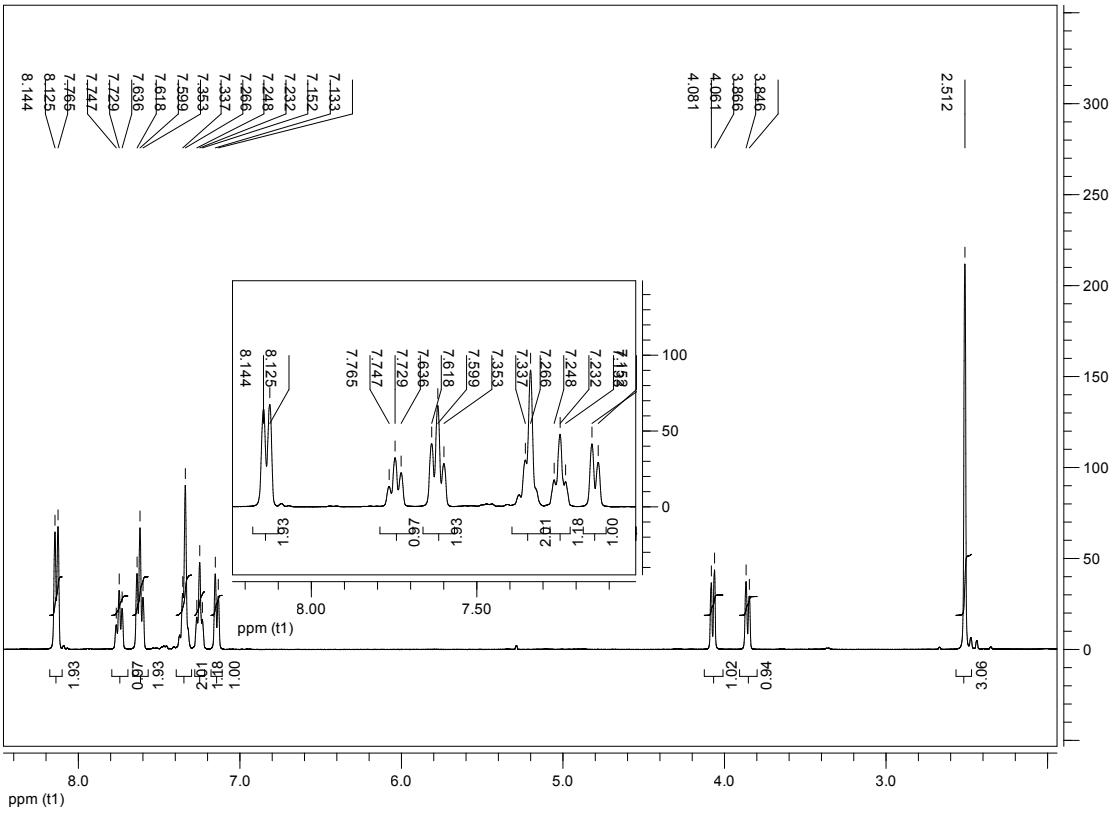


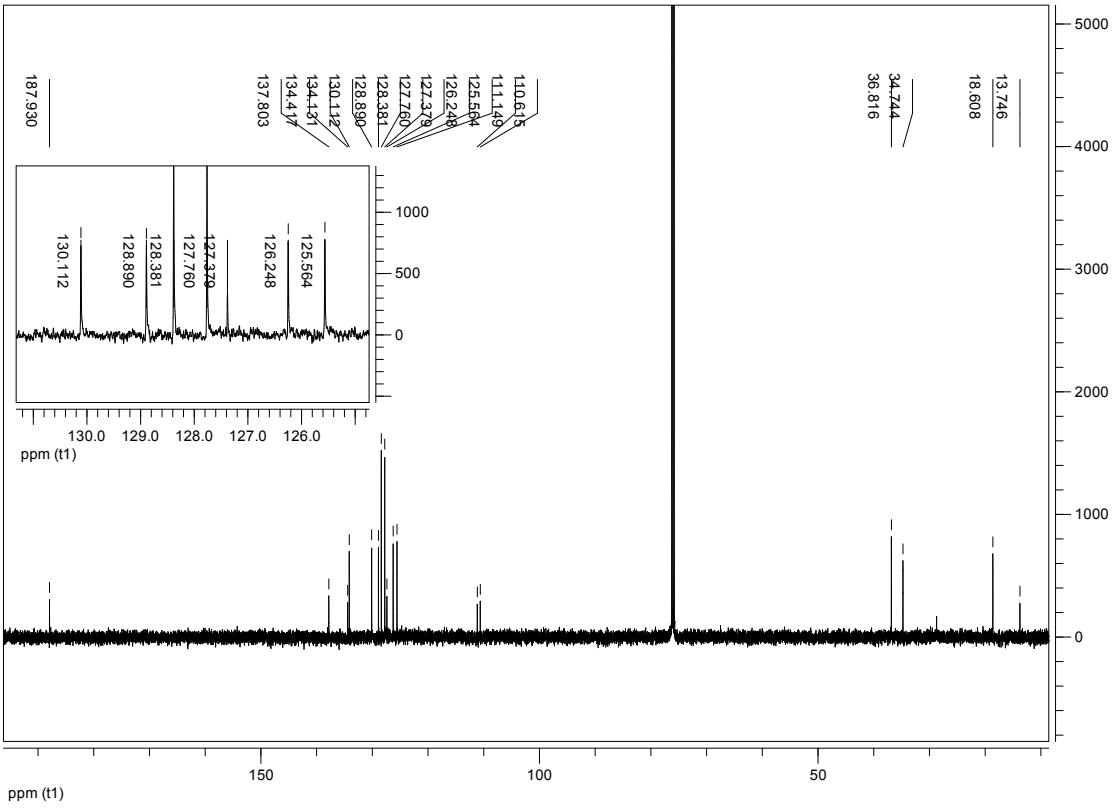
2-(4-Bromobenzoyl)-3-(3,5-dibromophenyl)cyclopropane-1,1-dicarbonitrile (**1s**)

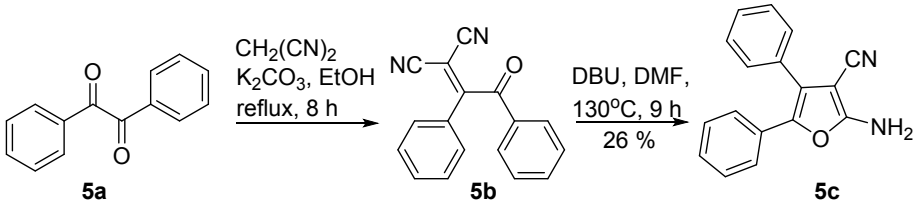


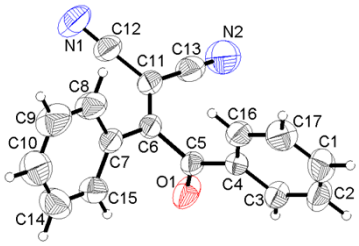


2-Benzoyl-3-(o-tolyl)cyclopropane-1,1-dicarbonitrile (**1t**)









CCDC 1911099

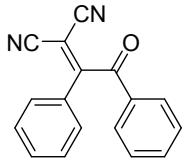
Scheme S1 Synthesis of 2-amino-4,5-diphenylfuran-3-carbonitrile under the title reaction conditions

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

Identification code	**5b**
Empirical formula	$C_{17}H_{10}N_2O$
Formula weight	258.27
Temperature	298 K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 7.761(4) A alpha = 90 deg. b = 23.473(12) A beta = 111.679(12) deg. c = 8.263(5) A gamma = 90 deg.
Volume	1398.9(13) A^3
Z, Calculated density	4, 1.226 Mg/m^3
Absorption coefficient	0.078 mm^-1
F(000)	536
Crystal size	0.35 x 0.33 x 0.3 mm

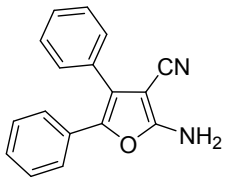
Theta range for data collection	1.74 to 25.00 deg.
Limiting indices	-8<=h<=9, -27<=k<=27, -9<=l<=6
Reflections collected / unique	5955 / 2464 [R(int) = 0.0213]
Completeness to theta = 25.00	96.6 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2381 / 0 / 181
Goodness-of-fit on F^2	1.081
Final R indices [I>2sigma(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.A^-3

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



^{1}H NMR (400 MHz, DMSO-d_6) 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); ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) 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.

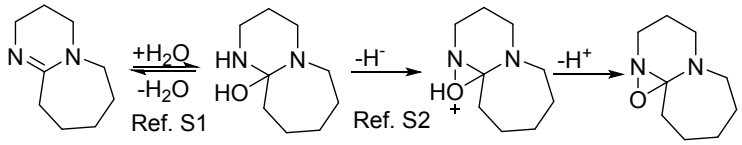
2-amino-4,5-diphenylfuran-3-carbonitrile (**5c**)



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

NMR (400 MHz, DMSO-d_6) δ (ppm): 7.70 (s, 2H), 7.46-7.44 (m, 3H), 7.40-7.38 (m, 2H), 7.26-7.23 (m, 5H); $^{13}C\{^1H\}$ NMR (150 MHz, DMSO-d_6) δ (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 $C_{17}H_{12}N_2NaO$ [$(M+Na)^+$]: 283.0847; Found: 283.0850.

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



Refence 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.