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A CONVENIENT METHOD FOR CYANATION OF AROMATIC IODO COMPOUNDS

Richard M Carr, Karl M Cable, Guy N Wells and Derek R Sutherland

Isotope Chemistry Group, Chemical Development Division,
Glaxo Research and Development Limited
Greenford, Middlesex UB6 OHE, UK.

Summary

A variety of [^{13}C]-labelled aromatic nitriles have been prepared in good yield from iodoaromatic substrates. Cyanation was achieved by reaction of aryl iodides with a mixture of potassium [^{13}C]cyanide and copper (I) iodide in an aprotic solvent at high temperature. The use of pre-prepared carbon-labelled copper (I) cyanide was therefore obviated.

Key words: cyanation, aryl iodides, carbon-13, carbon-14.

Introduction

Aromatic compounds with [^{13}C] or [^{14}C]-labelled cyano substituents are versatile synthetic intermediates which can be converted into labelled carboxylic acids (hydrolysis), primary amides (partial hydrolysis), benzylamines (catalytic reduction), methyl arenes (exhaustive catalytic transfer hydrogenation), imines (reduction) and aldehydes (reduction/hydrolysis). Aromatic nitriles are normally prepared from aryl bromides or iodides by reaction with copper (I) cyanide, or a mixture of copper (I) cyanide and potassium cyanide, either without solvent, or in pyridine or quinoline at 150-250°C (the Rosenmund-von Braun reaction) (1-6). Dipolar aprotic solvents such as N,N-dimethylformamide (DMF) (7) and N-methylpyrrolidinone (NMP) (8) have more recently been used as solvents. The cyanation mechanism is obscure, but is unlikely to involve simple aromatic nucleophilic displacement of halide anion by cyanide anion. Organocopper intermediates have been postulated (9 and 10). Cyanations have also been effected using alkali metal cyanides with a palladium (0) catalyst (11 and 12). Potassium [^{14}C]cyanide is a cheap, commercially available

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radiochemical, from which copper (I) [^{14}C]cyanide can be prepared by treatment with either copper (II) sulphate and sodium bisulphite (13), or copper sulphite (14). The investigation of methods for aromatic cyanation that avoid the use of pre-prepared [^{13}C] or [^{14}C]-labelled copper (I) cyanide is therefore of interest. A robust, very simple, and apparently general method has been developed whereby iodoaromatic compounds are cyanated with a mixture of potassium [^{13}C]cyanide and copper (I) iodide in NMP, DMF or N,N-dimethylacetamide (DMAC) (Scheme1).

$$\mathrm{ArI} \xrightarrow[\substack{\text{Aprotic Solvent} \\ >150^{o}\mathrm{C}}]{\mathrm{K^{13}CN,\ CuI}} \mathrm{Ar^{13}CN}$$

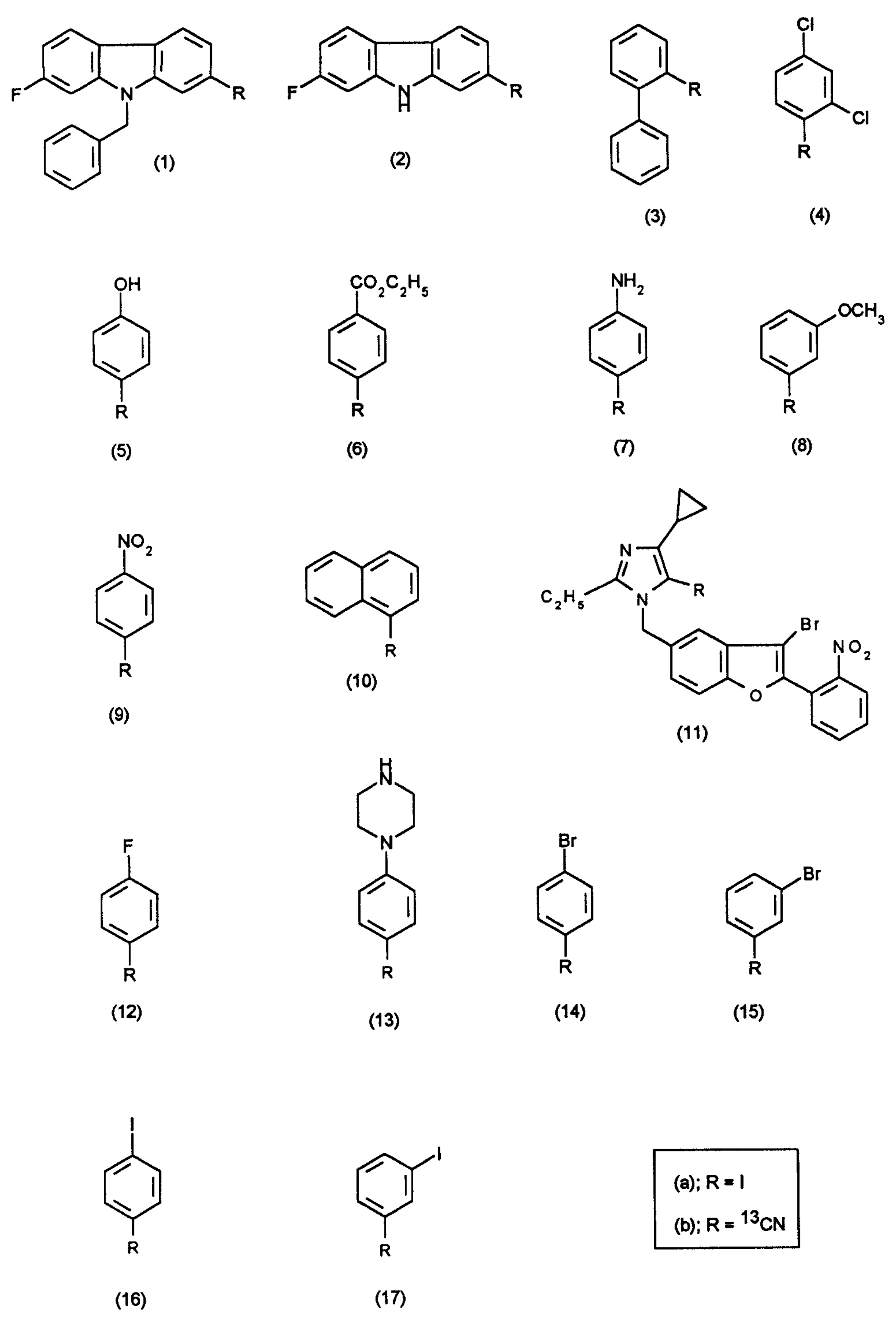
Scheme 1

Results And Discussion

A variety of iodoaromatic substrates (Scheme 2) with both activating (electron-withdrawing) and de-activating substituents have been cyanated in good yield using the methodology described. The iodoaromatic compounds used as substrates were available commercially, with the exception of (1a), (2a) and (11a). NMP was found to be the most useful solvent, allowing cyanations to be performed at temperatures up to 210°C (gentle reflux). In order to facilitate extraction of the aromatic nitriles into ethyl acetate during aqueous work-up, the reactions were carried out at high concentration. In general, one equivalent of potassium [^{13}C]cyanide and 0.5 equivalents of copper (I) iodide were included in the reaction mixture. The cyanation of carbazole (2a) also proceeded cleanly and in high yield, with only 0.05 equivalents of the copper (I) salt, although reaction time was considerably longer (Table). Aromatic nitriles are known to complex with copper (I) salts, and therefore, an aqueous iron (III) chloride wash was generally included in the work up to oxidise copper (I) to copper (II), which does not complex in this way. Molecular iodine, liberated during the oxidation, was removed by washing with aqueous sodium metabisulphite. The aromatic nitriles produced were all purified by flash chromatography on silica gel. Yields of nitriles obtained from substrates (1a) to

(11a) were in the range 73-97%, and have not been optimised. The cyanation of (12a) in DMF was shown by TLC to be complete after 6.5h at 150°C. However, the isolated yield of (12b) was only 40% owing to loss of the volatile product during work up. Subsequently, (12a) was cyanated and the resulting (12b) converted *in situ* to (13b) by reaction with piperazine and potassium carbonate. This procedure was carried out in DMAC, since in DMF (13b) underwent N-formylation at the secondary piperazinyl nitrogen atom. Involatile (13b) was isolated in 77% overall yield. In this case, the work up omitted the use of aqueous iron (III) chloride due to complexation of iron (III) with the piperazine moiety in (13b). Aryl iodo groups were selectively cyanated in the presence of fluoro and chloro substituents [eg (1a), (2a) and (4a)]. Additionally, the iodo group of (11a) was selectively cyanated in the presence of the bromo substituent, to give (11b). However, selective cyanation of bromo-iodobenzenes was not achieved. Thus, cyanation of 4-iodobromobenzene (14a) for 3h at 210°C in NMP, afforded a chromatographically inseparable mixture of 4-bromobenzo[^{13}C]nitrile (14b) and 4-iodobenzo[^{13}C]nitrile (16b) in the ratio 0.9:1 (by ^{1}H NMR and microanalysis). Another cyanation of (14a) in NMP at 150°C for 24h was more selective, giving (14b) and (16b) in a 2:1 ratio respectively. Cyanation of 3-iodobromobenzene (15a) in NMP at 210°C for 3h, gave an inseparable mixture of 3-bromobenzo[^{13}C]nitrile (15b) and 3-iodobenzo[^{13}C]nitrile (17b) in a ratio of 0.9:1 respectively. A second cyanation of (15a) at 150°C for 24h gave a 3:1 mixture (15b) and (17b). These results may simply indicate lack of selectivity for displacement of the iodo substituents in the presence of bromo substituents. Alternatively, selective cyanation of the iodo substituents may have occured initially, resulting in enhanced activation of the aromatic ring with respect to nucleophilic substitution. Displacement of the bromo substituent by iodide could then proceed *via* a copper (I)-catalysed process. The latter hypothesis is supported by the fact that dicyanobenzenes were not formed during any of the cyanations of (14a) and (15a).

Radiolabelled versions of nitriles (11b) and (13b) (^{14}C for ^{13}C) have been prepared by similar methods from potassium [^{14}C]cyanide.


F
N
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(1)
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$CO_2C_2H_5$
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C_2H_5
N
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Br
NO_2
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(11)
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(12)
H
N
N
R
(13)
Br
R
(14)
Br
R
(15)
I
R
(16)
I
R
(17)
(a); R = I
(b); R = ^{13}CN

Scheme 2

Table: Reaction Conditions for Cyanation of Aryl Iodides

Aryl Iodide	Equivs $K^{13}CN$	Equivs CuI	Reaction Temp °C	Reaction Time (h)	Reaction Solvent	Product Structure	Yield % from $K^{13}CN$[1]
1a	1	0.5	210	3	NMP	1b	96.6
2a	1	0.5	210	3	NMP	2b	96.2
2a	1	0.05	210	16	NMP	2b	96.7
3a	1	0.5	210	3	NMP	3b	91.7
4a	1	0.5	210	17	NMP	4b	83.8
5a	1	0.5	210	21	NMP	5b	72.7
6a	1	0.5	210	5	NMP	6b	89.2
7a	1	0.5	210	3	NMP	7b	75.0
8a	1	0.5	210	3	NMP	8b	74.3
9a	1	0.5	210	3	NMP	9b	85.7
10a	1	0.5	210	3	NMP	10b	89.2
11a	0.8	0.2	150	15	DMF	11b	86.1
12a	1	0.5	150	17	DMAC	13b	77.0[2]
14a	1	0.5	210	3	NMP	14b+16b (0.9:1)	66.4[3]
14a	1	0.5	150	24	NMP	14b+16b (2.0:1)	65.9[3]
15a	1	0.5	210	3	NMP	15b+17b (0.9:1)	72.3[3]
15a	1	0.5	150	24	NMP	15b+17b (3.0:1)	73.1[3]

[1] Yields before recrystallisation; [2] Overall yield over two steps; [3] Combined yields

Conclusion

A variety of [^{13}C]-labelled aromatic nitriles have been prepared in good yield by reacting the appropriate aryl iodide with a mixture of copper (I) iodide and potassium cyanide, in an aprotic solvent at >150°C. The preparation of copper (I) [^{13}C]cyanide was not required.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on Bruker AC250, Varian XL200, or Varian XR400 spectrometers. IR spectra were recorded on a Nicolet 20SXB FT-IR spectrometer. Low resolution and high resolution mass spectrometry were carried out using Finnigan 4600 quadrupole and VG Autospec spectrometers, respectively. Elemental analyses were performed using Carlo Erba 1106 and Perkin-Elmer 240C microanalysers. Merck silica gel Kieselgel 60 (9385) was used throughout for flash column chromatography.

General Method for the Cyanation of an Aryl Iodide.

9-Benzyl-7-fluoro-9H-carbazole[2-^{13}C]carbonitrile (1b).

A stirred mixture of 9-benzyl-2-fluoro-7-iodo-9H-carbazole (1a) (1.446g, 3.60mmol), potassium [^{13}C]cyanide (236mg, 3.57mmol) and finely-ground copper (I) iodide (340mg, 1.79mmol) in NMP (9ml) was heated at reflux under nitrogen for 3h. The dark mixture was allowed to cool to 20°C, and diluted with ethyl acetate (450ml). The solution was extracted sequentially with 2% w/v ferric chloride (450ml), water (450ml), sodium metabisulphite (1.8g) in water (450ml), water (450ml) and saturated brine (450ml), and then dried over magnesium sulphate. Solvent was removed by evaporation, and the residue purified by chromatography over silica gel (300g), eluted with dichloromethane-cyclohexane (2:1). The white, crystalline product was dried for 14h at 20°C *in vacuo* to give the *title compound* (1.039g, 96.6% from potassium [^{13}C]cyanide. A portion of this was recrystallised from boiling cyclohexane (10ml) (80% recovery); ν_{max} (nujol mull)/cm^{-1} 2174 (^{13}C≡N), 1634, 1602; δ_H (400MHz, DMSO-d$_6$) 8.36 (1H, d, 4-$\underline{H}$), 8.35 (1H, d, 5-$\underline{H}$), 8.23 (1H, d, 1-$\underline{H}$), 7.6-7.0 (8H, m, 3-$\underline{H}$, 6-$\underline{H}$, 8-$\underline{H}$ and $CH_2C_6\underline{H}_5$), 5.73 (2H, s, N-C$\underline{H}_2$); δ_C (100MHz, DMSO-d$_6$) 122.9 ($^{13}\underline{C}$N enhanced); m/z (CI ammonia +ve) 319

(MNH_4^+,100%), 301 (12%); (Found: C, 79.80; H, 4.25; N, 9.31; $C_{19}{}^{13}CH_{13}FN_2$ requires C, 79.78; H, 4.34; N, 9.27%).

The following compounds were prepared by similar methods:

7-Fluoro-9H-carbazole[2-^{13}C]carbonitrile (2b):

Iodocarbazole (2a) (1.736g, 5.58mmol), potassium [^{13}C]cyanide (314mg, 4.74mmol) and copper (I) iodide (452mg, 2.37mmol) gave the *title compound* as a white, crystalline solid (964mg, 96.2% from potassium [^{13}C]cyanide) after purification by chromatography over silica gel (280g), eluted with dichloromethane. A portion of product was recrystallised from boiling toluene (2ml) (67% recovery); ν_{max} (nujol)/cm^{-1} 2170 ($^{13}C{\equiv}N$), 1635, 1611; δ_H (200mHz, DMSO-d$_6$) 11.85 (1H, s, 9-H), 8.4-8.1 (2H, m, 4-H and 5-H), 7.95 (1H, d, 1-H), 7.52 (1H, m, 6-H), 7.34 (1H, dd, 3-H), 7.06 (1H, m, 8-H); δ_C (100MHz, DMSO-d$_6$) 122.6 (^{13}CN enhanced); (Found: m/z (electron impact) 211.062922 [M$^+$]. $C_{12}{}^{13}CH_7FN_2$ requires 211.062681).

Biphenyl-[2-^{13}C]carbonitrile (3b):

Iodobiphenyl (3a) (601mg, 2.15mmol,) gave the *title compound* (349mg, 91.7% from potassium [^{13}C]cyanide) after purification by chromatography over silica gel (80g), eluted with dichloromethane; ν_{max} (nujol)/cm^{-1} 2172 ($^{13}C{\equiv}N$), 1476, 1451, 1433, 757 and 699; δ_H (250MHz, DMSO-d$_6$) 7.77 (1H, m, 4-H), 7.63 (1H, d, 3-H), 7.6-7.4 (7H, m, 2-H, 5-H, 6-H, 7-H, 8-H, 9-H and 10-H); δ_C (63MHz, $CDCl_3$) 118.7 (^{13}CN enhanced); (Found: m/z (electron impact) 180.076965 [M$^+$]. $C_{12}{}^{13}CH_9N$ requires 180.076854)

2,4-Dichlorobenzo[^{13}C]nitrile (4b):

2,4-Dichloroiodobenzene (4a) (530mg, 1.94mmol), potassium [^{13}C]cyanide (128mg, 1.94mmol), and copper (I) iodide (185mg, 0.97mmol) in NMP (2ml) gave the *title compound* (281mg, 83.8%) after purification by chromatography over silica gel (80g), eluted with dichloromethane-cyclohexane (2:1); ν_{max} (nujol)/cm^{-1} 2182 (^{13}CN), 1581, 1102, 822; δ_H 8.1-7.8 (2H, m, 3-H and 6-H), 7.62 (1H, d, 5-H); δ_C (63MHz, $CDCl_3$) 116.0 (^{13}CN enhanced); (Found: m/z (electron impact) 171.967087 [M$^+$]. $C_6{}^{13}CH_3{}^{35}Cl_2N$ requires 171.967609).

4-Hydroxybenzo[^{13}C]nitrile (5b);

4-Iodophenol (5a) (653mg, 2.97mmol), potassium [^{13}C]cyanide (197mg, 2.87mmol), and copper (I) iodide (283mg, 1.49mmol) in NMP (2ml) gave the *title compound* (259mg, 72.7% from potassium [^{13}C]cyanide) after purification by chromatography over silica gel (80g), eluted with ethyl acetate-cyclohexane (1:1); ν_{max} (nujol)/cm^{-1} 2181 (^{13}C≡N), 1613, 1511, 1167, 839; δ_H (250MHz, DMSO-d_6) 7.64 (2H, m, 2-H), 6.92 (2H, d, 3-H); δ_C (63MHz, DMSO-d_6) 119.8 (^{13}CN enhanced); (Found: m/z (electron impact) 120.040794 [M$^+$]. $C_6{}^{13}CH_5NO$ requires 120.040469).

[4-^{13}C]Cyanobenzoic acid Ethyl Ester (6b):

4-Iodobenzoic acid ethyl ester (6a) (581mg, 2.10mmol), potassium [^{13}C]cyanide (139mg, 2.10mmol), and copper (I) iodide (200mg, 1.05mmol) in NMP (2ml) gave the *title compound* (330mg, 89.2% from potassium [^{13}C]cyanide) after purification by chromatography over silica gel (80g), eluted with dichloromethane-cyclohexane (1:1); ν_{max} (nujol)/cm^{-1} 2178 (^{13}C≡N), 1716; δ_H (250MHz, DMSO-d_6) 8.11 (2H, d, 3-H), 8.02 (2H, m, 2-H), 4.37 (2H, q, 5-H), 1.34 (3H, t, 6H); δ_C (62.5MHz, DMSO-d_6) 117.8 (^{13}CN enhanced); (Found: m/z (electron impact) 176.067505 [M$^+$]. $C_9{}^{13}CH_9NO_2$ requires 176.066683).

4-Aminobenzo[^{13}C]nitrile (7b):

4-Iodoaniline (7a) (482mg, 2.20mmol), potassium [^{13}C]cyanide (146mg, 2.20mmol), and copper (I) iodide (210mg, 1.10mmol) in NMP (3.5ml) gave the *title compound* (147mg, 75.0% from potassium [^{13}C]cyanide) after purification by chromatography over silica gel (80g), eluted with ethyl acetate-cyclohexane (1:1). The product was recrystallised from boiling toluene (2ml) (recovery 53.3%); ν_{max} (nujol)/cm^{-1} 3347,3371, 2165 (^{13}C≡N), 1514, 540; δ_H (250MHz, DMSO-d_6) 7.40 (2H, m, 2H and 6H), 6.62 (2H, d, 3H and 5H), 6.15 (2H, s, NH_2); δ_C (63MHz, DMSO-d_6) 120.2 (^{13}CN enhanced); (Found: m/z (electron impact) 119.056935 [M$^+$]. $C_6{}^{13}CH_6N_2$ requires 119.056453).

3-Methoxybenzo[^{13}C]nitrile (8b):

3-Methoxyiodobenzene (8a) (508mg, 2.17mmol), potassium [^{13}C]cyanide (144mg, 2.17mmol) and copper (I) iodide (207mg, 1.09mmol) in NMP (5ml) gave the *title* *compound* (216mg, 74.3% from potassium [^{13}C]cyanide) after purification by chromatography over silica gel (80g), eluted with dichloromethane-cyclohexane (1:1); ν_{max} (nujol)/cm^{-1} 2839, 2179 (^{13}C≡N), 682; δ_H (250MHz, CDCl$_3$) 7.37 (1H, m, 5-H), 7.24 (1H, m, 6$_T$H), 7.2-7.1 (2H, m, 2-H and 4-H), 3.83 (3H, s, OCH$_3$); δ_C (63MHz, CDCl$_3$) 118.7 (^{13}CN enhanced); (Found: m/z (electron impact) 136.061128 [M$^+$]; C$_7$^{13}CH$_7$NO requires 136.060901).

4-Nitrobenzo[^{13}C]nitrile (9b):

1-Iodo-4-nitrobenzene (9a) (524mg, 2.10mmol), potassium [^{13}C]cyanide (134mg, 2.10mmol), and copper (I) iodide (199mg, 1.04mmol) in NMP (2ml) gave the *title compound* (268mg, 85.7% from potassium [^{13}C]cyanide) after purification by chromatography over silica gel (80g), eluted with dichloromethane. The product was recrystallised from boiling ethanol (recovery 44.7%); ν_{max} (nujol)/cm^{-1} 2182 (^{13}C≡N), 1525, 1349; δ_H (250MHz, CDCl$_3$) 8.38 (2H, d, 3-H and 5-H), 7.92 (2H, m, 2-H and 6-H); δ_C (63MHz, CDCl$_3$) 116.8 (^{13}CN enhanced); (Found: m/z (electron impact) 149.030624 [M$^+$]. C$_6$^{13}CH$_4$N$_2$O$_2$ requires 149.030632).

Naphthalene[1-^{13}C]carbonitrile (10b):

1-Iodonaphthalene (10a) (550mg, 2.16mmol), potassium [^{13}C]cyanide (141mg, 2.13mmol), and copper (I) iodide (203mg, 1.06mmol) in NMP (2ml) gave the *title compound* (293mg, 89.2% from potassium [^{13}C]cyanide) after purification by chromatography over silica gel (80g), eluted with dichloromethane; ν_{max} (nujol)/cm^{-1} 2180 (^{13}C≡N), 800, 773; δ_H (250MHz, CDCl$_3$) 8.23 (1H, d, 4-H), 8.07 (1H, d, 2-H), 7.90 (2H, m, 6-H and 7-H), 7.75-7.55 (2H, m, 5-H and 8-H), 7.51 (1H, t, 3-H); δ_C (63MHz, CDCl$_3$) 117.8 (^{13}CN enhanced); (Found: m/z [electron impact] 154.060699 [M$^+$]. C$_7$^{13}CH$_7$NO requires 154.061204).

3-[3-Bromo-2-(2-nitrophenyl)-benzofuran-5-ylmethyl]-5-cyclopropyl-2-ethyl-3H-imidazole-[4-^{13}C]-carbonitrile (11b)

1-[3-Bromo-2-(nitrophenyl)-benzofuran-5-ylmethyl]-4-cyclopropyl-2-ethyl-5-iodo-1H-imidazole (11a) (570mg, 0.967mmol), potassium [^{13}C]cyanide (51mg, 0.771mmol) and copper (I) iodide (30mg, 0.152mmol) in DMF (4ml) gave the *title compound*

(326mg, 86.1% from potassium [^{13}C]cyanide) after purification by chromatography over silica gel (80g), eluted with cyclohexane-ethyl acetate (2:1); ν_{max} (nujol)/cm^{-1} 2161 (^{13}C≡N), 1532 (NO_2, asy), 1356 (NO_2, sym); δ_H (200MHz, DMSO-d_6) 8.22 (1H, d, nitrophenyl 3H), 8.05-7.95 (2H, m, nitrophenyl 5H and 6H), 7.84 (1H, m, nitrophenyl 4H), 7.74 (1H, d, benzofuran 7-H), 7.44 (1H, s, benzofuran 4-H), 7.24 (1H, dd, benzofuran 6-H), 5.43 (2H, s, NCH_2), 2.74 (2H, q, CH_2CH_3), 1.98 (1H, m, cyclopropyl CH), 1.16 (3H, t, CH_2CH_3), 1.05-0.83 (4H, m, cyclopropyl CH_2CH_2); δ_C (63MHz, DMSO-d_6) 113.3 (^{13}CN enhanced); (Found: *m/z* [LSIMS +ve] 494.072800 [MH^+]. $C_{23}{}^{13}CH_{19}BrN_4O_3$ requires 494.073186).

1-[4-^{13}C]Cyanophenyl)piperazine (13b)

A stirred mixture of 4-iodofluorobenzene (12a) (504mg, 2.29mmol), potassium [^{13}C]cyanide (151mg, 2.29mmol) and copper (I) iodide (218mg, 1.14mmol) in DMAC (4ml) was heated for 17h at 150°C under nitrogen. TLC indicated complete conversion of (12a) to (12b). The mixture was allowed to cool to 20°C before addition of piperazine (961mg, 11.2mmol) and potassium carbonate (308mg, 2.23mmol). The mixture was heated for 4h at 100°C under nitrogen then diluted with ethyl acetate (250ml). The resulting solution was extracted with water (250ml) and the aqueous phase re-extracted with ethyl acetate (2 x 100ml). The combined organic extracts were clarified with saturated brine (50ml) and dried over exsiccatedmagnesium sulphate. Solvent was removed by evaporation and the residue purified by chromatography over silica gel (50g) eluted with dichloromethane-methanol-aqueous ammonia (S.G. 0.880) 95:5:1 to give the *title compound* (331mg, 77.6%). This was triturated with diethyl ether (21% recovery); ν_{max} (nujol)/cm^{-1} 3335 (NH), 2162 (^{13}C≡N); δ_H (400MHz, $CDCl_3$) 7.26 (2H, m, phenyl 3H and 5H), 6.87 (2H, d, phenyl 2H and 6H), 3.32 (4H, m, piperazine 2H and 6H), 3.01 (4H, m, piperazine 3H and 5H); δ_C (100MHz, $CDCl_3$) 118.9 (^{13}CN enhanced); (Found: *m/z* [electron impact] 188.114630 [M^+]. $C_{10}{}^{13}CH_{13}N_3$ requires 188.114750).

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