Electronic Supplementary Material (ESI) for ChemComm.

Dual Copper- and Photoredox-Catalysed C(sp^2)-C(sp^3) Coupling

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SUPPORTING INFORMATION

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Supporting Information

General Considerations

^{1}H NMR spectra were recorded on a Bruker AV300 or AV400 spectrometer at 300 MHz or 400 MHz respectively and referenced to residual solvent. ^{13}C NMR spectra were recorded using the same spectrometers at 75 MHz or 101 MHz respectively. Chemical shifts (δ in ppm) were referenced to tetramethylsilane (TMS) or to residual solvent peaks ($CDCl_3$ at δ_H 7.26 ppm and δ_C at 77.0 ppm). ^{19}F NMR were recorded using the same spectrometers at 282 MHz or 376 MHz respectively. *J* values are given in Hz and s, d, t, q, dd, ddd and m are abbreviations corresponding to singlet, doublet, triplet, quartet, doublet of doublets, doublet of doublets of doublets and multiplet respectively. Mass spectra were obtained at the EPSRC UK National Mass Spectrometry Facility at Swansea University. Infrared spectra were obtained on Perkin-Elmer Spectrum 100 FT-IR Universal ATR Sampling Accessory, deposited neat or as a chloroform solution to a diamond/ZnSe plate.

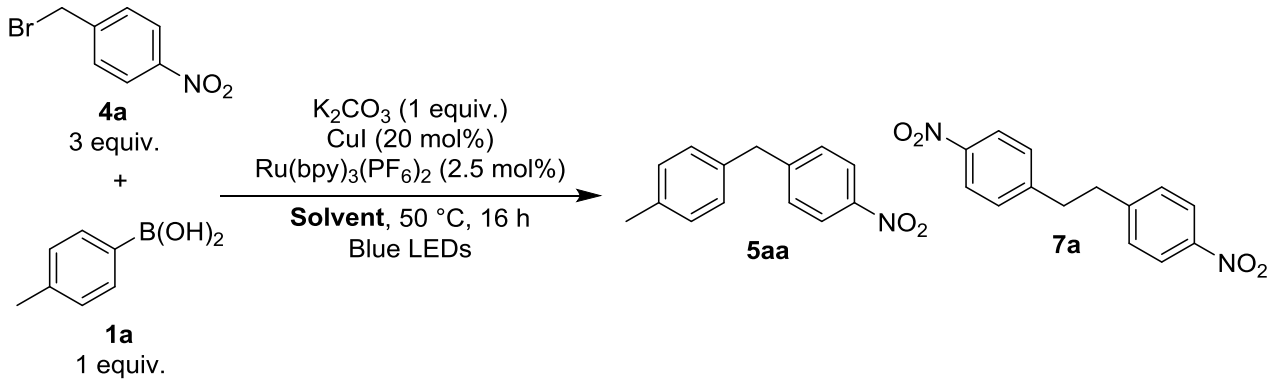
Column chromatography was carried out using Matrix silica gel 60 from Fluorochem and TLC performed using Merck silica gel 60 F_{254} pre-coated sheets and visualised by UV (254 nm) and/or aqueous acidic $KMnO_4$. Anhydrous solvents were obtained from a MBRAUN SPS-800 solvent purification system (SPS) and stored under an argon atmosphere until use. Arylboronic acids were bought from Sigma-Aldrich or Fluorochem and recrystallized from water prior to use unless otherwise stated. Arylboroxines were obtained by dehydrating boronic acids by heating the corresponding boronic acid under vacuum. Benzyl bromides other than those whose syntheses are detailed here were obtained from a number of commercial sources and were used without further purification. Unless otherwise stated, photoredox reactions were carried out under argon atmosphere. The reaction mixture was sparged with argon for 5 min before use. Light irradiation was performed using blue LEDs (1.5 Watt/foot). The light source was placed ca 10 cm away from the reaction vessel, to prevent excess heating. We found that the reactions are most reproducible when only one reaction vessel is irradiated per setup, to allow maximum light penetration.

Selected Optimisation Tables

Unless otherwise stated, the reaction mixture was sparged with argon for 5 min before the reaction commenced and reactions were carried out in oven dried 1 dram screw cap vials. *p*-tolylboronic acid was recrystallized from water unless otherwise stated.

Initial Screens

Solvent Optimisation

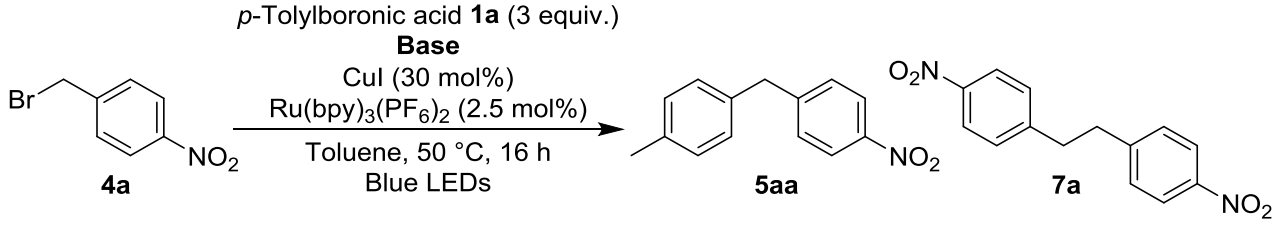


Entry	Solvent	**5aa** (%)[a]	**4a (%)**[a]	**7a (%)**[a,b]
1	DCM	Trace	N/A[f]	25
2	THF	8	N/A[f]	31
3	Toluene	23	N/A[f]	17
4	DMF	8	N/A[f]	41
5[c]	MeCN	10	N/A[f]	24
6[d,e]	NMP	Trace	Trace	23
7[d,e]	DMSO	8%	5%	26
8[e]	**Toluene**	**29**	**28**	**20**

Reaction carried out on a 0.1 mmol scale (0.1 M unless stated otherwise).[a]Yield determined by ^{1}H NMR analysis using mesitylene as an internal standard. [b]Yields with respect to theoretical maximum formation of **7a**. [c]Reaction carried out at r.t. [d]30 mol% CuI, 1 mol% $Ru(bpy)_3(PF_6)_2$, 4 equiv. KF. [e]Stoichiometry of benzyl bromide and boronic acid reversed. [f]Not applicable as **4a** is in excess.

Solvent screen showed toluene to be by far the best solvent.

Base Optimisation



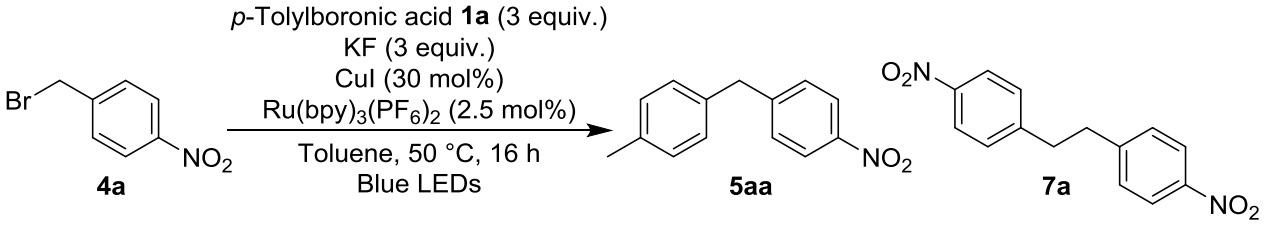
Entry	Base	Equiv.	**5aa** (%)[a]	**4a** (%)[a]	**7a** (%)[a,b]
1	-	-	0	100	0
2	K_2CO_3	3	29	28	20
3	KO*t*Bu	3	19	24	16
4	DMAP	3	0	0	0
5	LiF	3	0	100	0
6	NaF	3	0	95	0
7	NH_4F	3	0	45	26
8	CsF	3	35	30	18
9	KF	3	37	13	22
10	KF	1	17	54	14
11	**KF**	**6**	**45**	**0**	**28**

Reactions carried out on a 0.1 mmol scale (0.1 M unless stated otherwise). [a]Yield determined by ^{1}H NMR analysis using mesitylene as an internal standard. [b]Yields with respect to theoretical maximum formation of **7a**.

Base screen identified KF to be the best base.

The increase in yield of **5aa** when moving from LiF (0%) and NaF (0%) to CsF (35%) to KF (45%) indicates that ion pairing plays a role, with the tighter LiF/KF pairs showing no reactivity while the less tightly bound CsF and KF progressively show more reactivity.

Other parameters

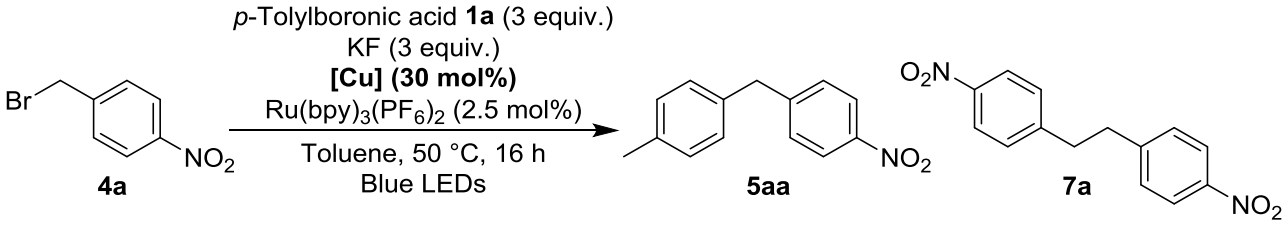


Entry	Parameter	**5aa** (%)[a]	**4a** (%)[a]	**7a** (%)[a,b]
1	Control	37	13	22
2	1 mol% Ru	40	7	26
3	5 mol% Ru	31	11	20
4	1 equiv. KF	17	54	14
5	6 equiv. KF	45	0	28
6	5 equiv. of **1**	44	3	30
7	Half concentration	36	24	20
8	Half concentration	33	0	24
9	Double concentration	35	0	30
10	100 °C instead of 50 °C	20	19	16
11	1 equiv. CuI	35	0	18

Reactions carried out on a 0.1 mmol scale (0.1 M unless stated otherwise). [a]Yield determined by ^{1}H NMR analysis using mesitylene as an internal standard. [b]Yields with respect to theoretical maximum formation of **7a**.

From these screens it was shown that the photocatalyst loading could be lowered to 1 mol% without any detriment to the reaction performance (entry 2).

Copper Catalyst Optimisation

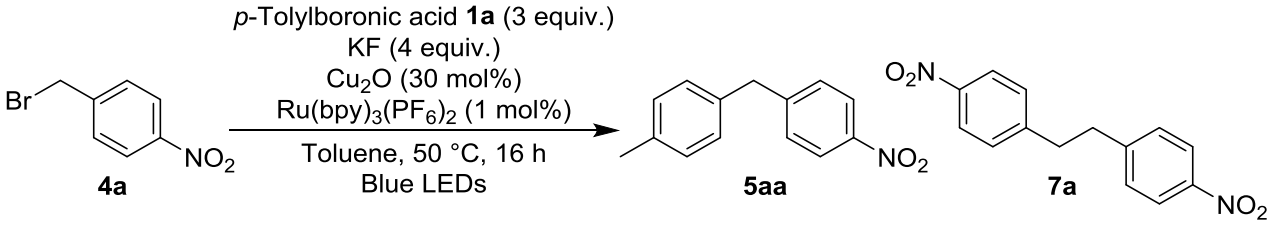


Entry	Catalyst	**5aa** (%)[a]	**4a** (%)[a]	**7a** (%)[a,b]
1	CuI	39	6	12
2	CuBr	41	12	18
3	PhenCu(PPh_3)Br	36	7	26
4	$Cu(OAc)_2$	29	30	20
5	$Cu(OTf)_2$	30	28	16
6	$CuBr_2$	36	23	16
7[c,d]	**Cu_2O**	**55**	**0**	**20**

Reactions carried out on a 0.1 mmol scale (0.1 M unless stated otherwise). [a]Yield determined by ^{1}H NMR analysis using mesitylene as an internal standard. [b]Yields with respect to theoretical maximum formation of **7a**. [c]4 equivalents of KF used. [d]$Ru(bpy)_3(PF_6)_2$ (1 mol%)

Cu_2O was identified as the best copper source.

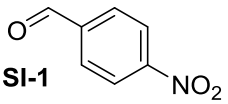
Miscellaneous tests



Entry	Parameter	**5aa**(%)[a]	**4a** (%)[a]	**7a** (%)[a,b]
1	Control	55	0	20
2	r.t. instead of 50 °C	16	64	8
3	CFL instead of LEDs	46	18	16
4	Schlenk Conditions	40	0	16
5	AgF instead of KF	31	0	0
6	Portion wise Cu	50	0	18
7*	O_2 Atmosphere	0	17	0
8	KF and AgF	0	0	0

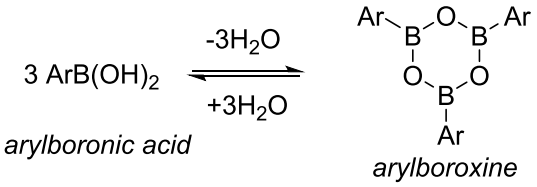
Reactions carried out on a 0.1 mmol scale (0.1 M unless stated otherwise). [a]Yield determined by ^{1}H NMR analysis using mesitylene as an internal standard. [b]Yields with respect to theoretical maximum formation of **7a**. CFL= compact fluorescent lamp.

*Oxygen atmosphere reaction results in a large amount of aldehyde product deriving from oxidation of benzylic radical:

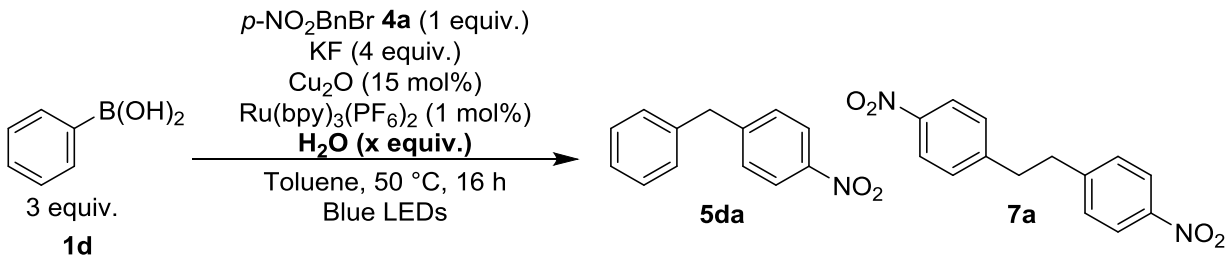


Main product under O_2 atm.

Up until this point, all optimisation had been carried out on recrystalised *p*-tolyboronic acid **1** as a model substrate. To our surprise, when the optimised reaction conditions for **1** (Entry 1, above) were applied to other arylboronic acids, either no coupling or low yields were obtained. We hypothesized that this difference in reactivity may be due to the different position of equilibrium between arylboronic acids and their corresponding arylboroxine for each arylboronic acid. This potentially leads to different reactivity as the arylboroxine is thought to be less efficient as a coupling partner. The reaction conditions would therefore need to be re-optimised in order to find a set of *general* conditions which would work for all arylboronic acids. We started by adding a known quantity of water to our reaction mixture in order to perturb the equilibrium towards the desired arylboronic acid.



Water Content Optimisation[a]

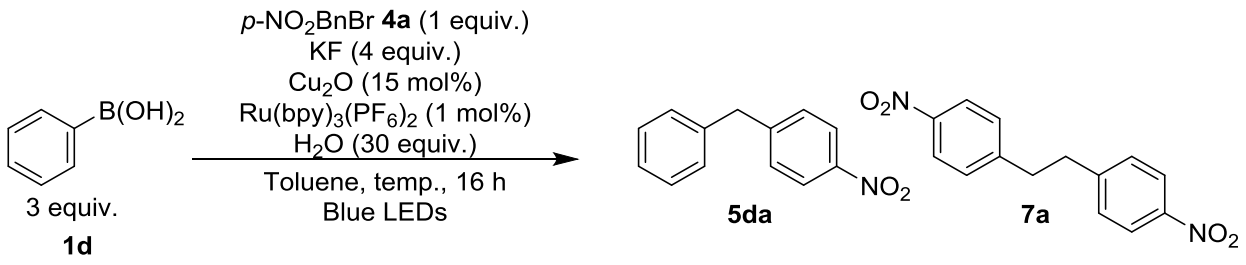


Entry	Equiv.	**5da**(%)[b]	**4a** (%)[b]	**7a** (%)[b,c]
1	0	8	89	4
2	3	3	92	0
3	6	11	77	6
4	9	15	69	6
5[d]	3	0	95	0
6[d]	6	3	68	1
7[d]	9	8	81	2
8	15	42	6	20
9	20	38	33	16
10	25	51	9	24
11	**30**	**53**	**3**	**28**
12	40	45	9	22
13	55	48	14	22
14	60	44	12	20
15	70	42	14	16

[a]Phenylboronic acid **1d** was used straight from the bottle without prior recrystallization unless otherwise stated. Reactions carried out on a 0.1 mmol scale (0.1 M unless stated otherwise). [b]Yield determined by ^{1}H NMR analysis using mesitylene as an internal standard. [c]Yields with respect to theoretical maximum formation of **7a**. [d]Arylboroxine (dehydrated from phenylboronic acid) used instead of arylboronic acid from bottle.

The addition of 30 equiv. of water was deemed to be optimal in order to gain consistent yields for a variety of arylboronic acids. The conditions in Entry 11 were therefore taken forward for further screening.

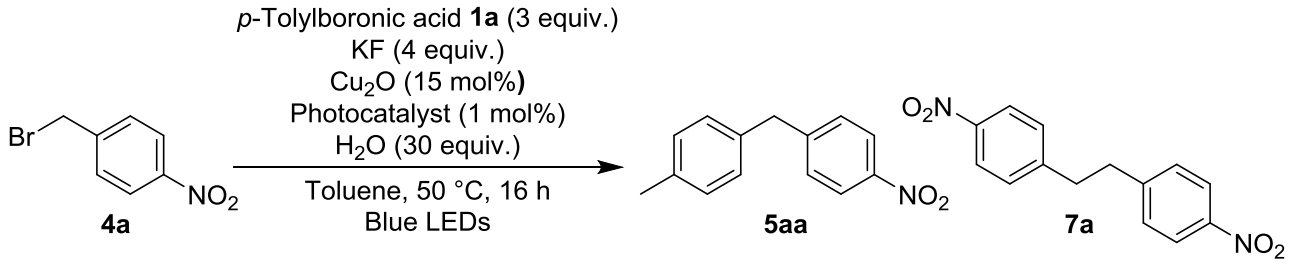
Temperature Screen



Entry	Temp (°C)	**5da** (%)[a]	**4a** (%)[a]	**7a** (%)[a,b]
1	40	45	17	24
2	**50**	**53**	**3**	**28**
3	60	51	0	32

Reactions carried out on a 0.1 mmol scale (0.1 M unless stated otherwise). [a]Yield determined by ^{1}H NMR analysis using mesitylene as an internal standard. [b]Yields with respect to theoretical maximum formation of **7a**.

Photocatalyst Screening



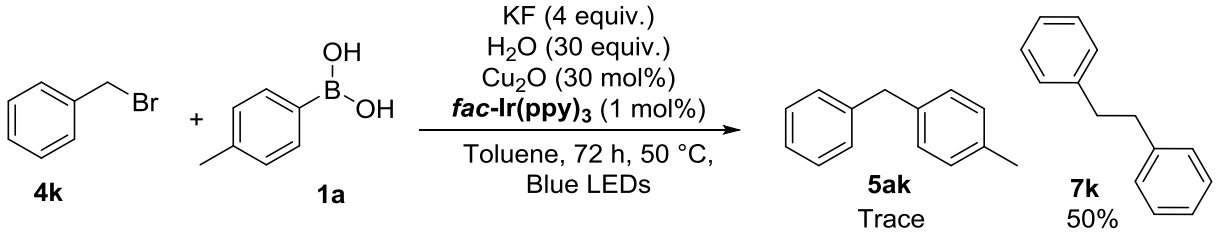
Entry	Photocatalyst	**5aa** (%)[a]	**4a** (%)[a]	**7a** (%)[a,b]
1	**$Ru(bpy)_3(PF_6)_2$**	**59**	**3**	**24**
2	$Ir(ppy)_2(dtbbpy)(PF_6)$	51	0	16
3	$Ir(ppy)_3$	14	8	22
4[c]	Eosin Y	21	35	10
5[c]	Fluorescein	20	62	10
6[c]	Fukuzumi's catalyst	3	78	4

Reactions carried out on a 0.1 mmol scale (0.1 M unless stated otherwise). [a]Yield determined by ^{1}H NMR analysis using mesitylene as an internal standard. [b]Yields with respect to theoretical maximum formation of **7a**. [c]Cu_2O (30 mol%) Fukuzumi's Catalyst: 9-mesitylene-10-methylacridinium perchlorate.

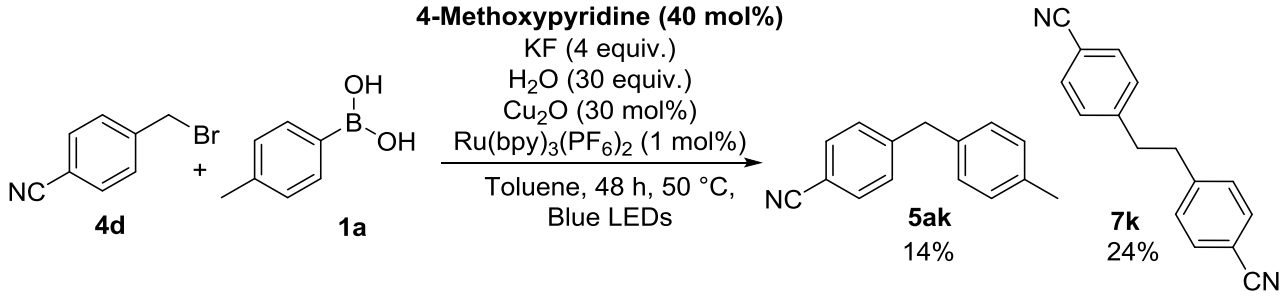
$Ru(bpy)_3(PF_6)_2$ is the best photocatalyst for the reaction of the examples screened. Organic dyes such as Eosin Y and Fluorescein can also catalyse the reaction, but are far less efficient.

Testing more reducing catalyst for more electron-rich benzyl bromides:

The reaction using more electron-rich benzyl bromides (**4k**) was also attempted using the more reducing *fac*-Ir(ppy)$_3$ photocatalyst. However this resulted in only trace amounts of the desired product being detected by ^{1}H NMR with large amounts of homocoupled benzyl bromide product **7k** being detected (50%) and 11% of the benzyl bromide **4k** starting material being recovered. Therefore, this result indicates that although the benzyl radical is forming from **4k** with the more reducing photocatalyst, homocoupling predominates over the cross-coupling reaction.



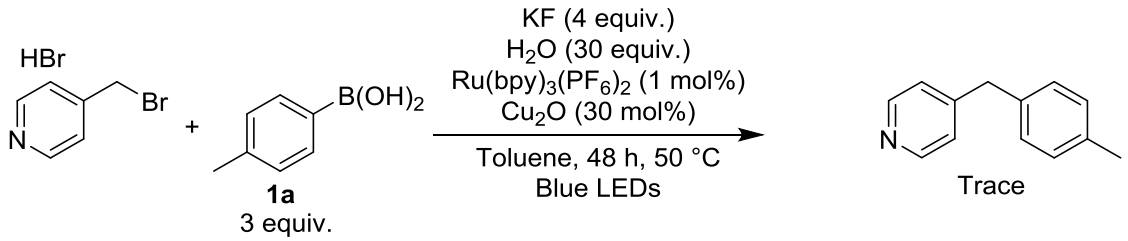
Reaction Using 4-Methoxypyridine as an Additive

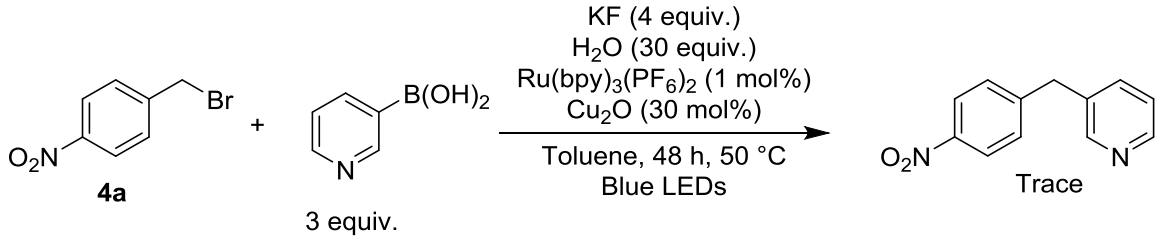


In an attempt to improve the yields of product **5** and reduce reaction times, the reaction was carried out in the presence of a substoichiometric amount of 4-methoxypyridine which has been previously shown in the literature to activate benzyl bromides towards single electron reduction.[1]

However, under our reaction conditions, the addition of 4-methoxypyridine resulted in a reduction in the yield of **5ak** (14% *vs*. 42%) but with comparable amounts of remaining starting material **4d** and homocoupling product **7k** being observed when compared with the reaction without additive. Therefore, we hypothesise that this is caused by the 4-methoxypyridine coordinating to the copper catalyst and inhibiting the cross-coupling reaction.

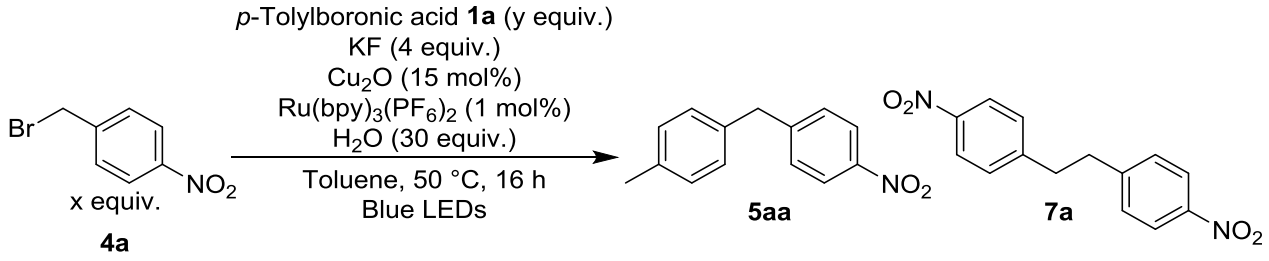
Similarly, we also observe that no appreciable amount of cross-coupling product **5** is detected when a pyridyl moiety is present in either substrate **1** or **4**, indicating that this type of motif is incompatible with our reaction conditions.





In both cases only traces of the desired products were observed and only traces of homocoupling product and left over starting material were detected.

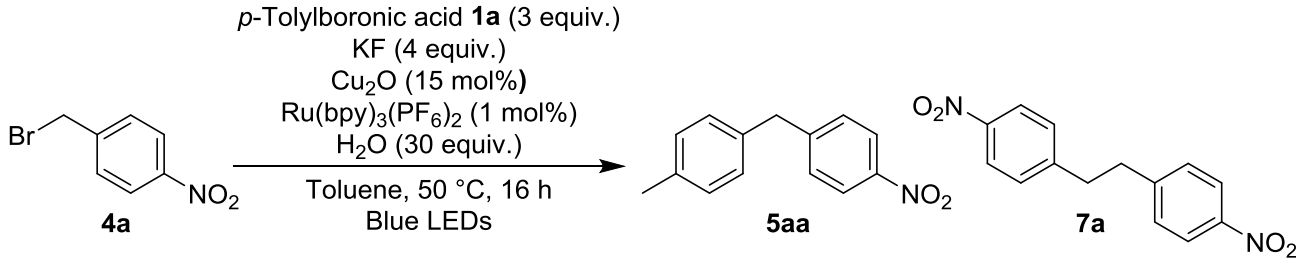
Stoichiometry Optimisation



Entry	x	y	**5aa** (%)[a]	**4a** (%)[a]	**7a** (%)[a,b]
1	**1**	**3**	**59**	**3**	**24**
2	1	2	54	24	22
3	1	1	27	69	12
4	2	1	32	N/A[c]	8

Reactions carried out on a 0.1 mmol scale (0.1 M unless stated otherwise). [a]Yield determined by ^{1}H NMR analysis using mesitylene as an internal standard. [b]Yields with respect to theoretical maximum formation of **7a**. [c]Not applicable as **4a** in excess.

Control Reactions



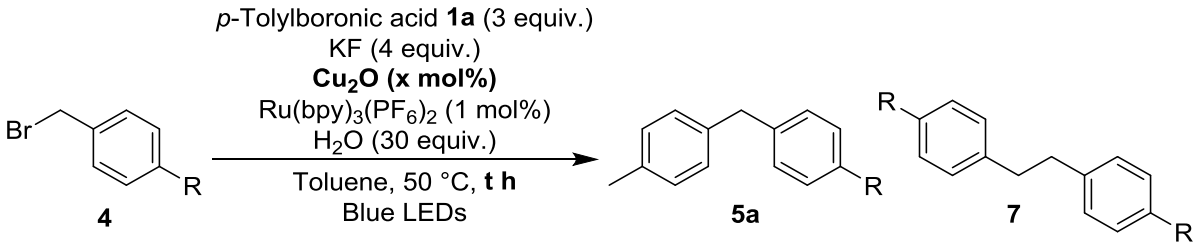
Entry	Change	**5aa** (%)[a,b]	**4a** (%)[a,b]	**7a** (%)[a,b]
1	Normal Conditions	59	3	24
2	No $Ru(bpy)_3(PF_6)_2$	0	100	0
3	No Cu_2O	21	56	14
4	No KF	0	100	0
5	In the dark	0	100	0
6*[c]	Under Air	17	17	10

Reactions carried out on a 0.1 mmol scale (0.1 M unless stated otherwise). [a]Yield determined by ^{1}H NMR analysis using mesitylene as an internal standard. [b]Yields with respect to theoretical maximum formation of **7a**. [c]No water, 20 mol% Cu_2O.

*Carrying out the reaction under air results 15% aldehyde **SI-1** formation.

These control reactions confirm that both the photoredox and copper catalysts are required for the coupling reaction to proceed efficiently (Entries 2-3). Base (KF, Entry 3) and light (Entry 4) are also necessary.

Miscellaneous Optimisation



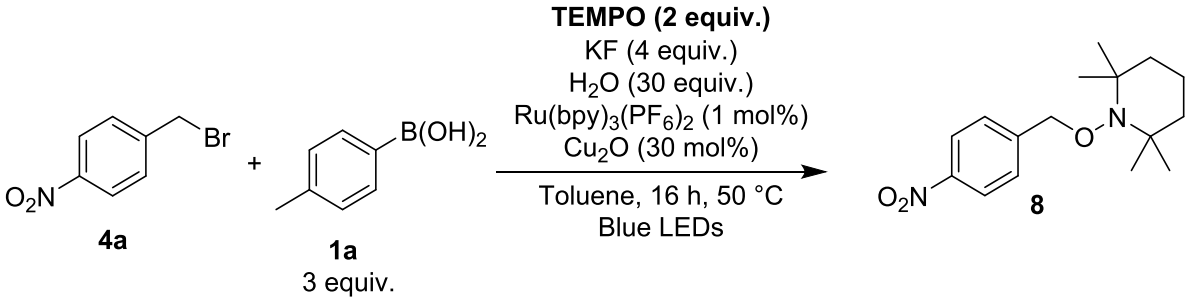
Entry	R	x	t	**5a** (%)[a]	**4** (%)[a]	**7** (%)[a,b]
1	CN	15	16	42	41	28
2	CN	15	72	60	6	30
3	CN	15	120	60	5	34
4	**CN**	**30**	**72**	**66(60)[c]**	**trace**	**34**
5	NO_2	15	16	59	3	24
6	**NO_2**	**30**	**16**	**65(62)[c]**	**0**	**28**

Reactions carried out on a 0.1 mmol scale (0.1 M unless stated otherwise). [a]Yield determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. [b]Yields with respect to theoretical maximum formation of **7a**. [c]Isolated yield.

It was found that when the relative strength of the electron withdrawing effect from the benzyl bromide substituents was decreased, the reaction required extended reaction times to reach completion. It was also observed that in addition to increasing the yields of the reaction, increasing the copper loading from 15 to 30 mol% made the results of each reaction much more reproducible.

Mechanistic Investigations

Radical Trap Experiment



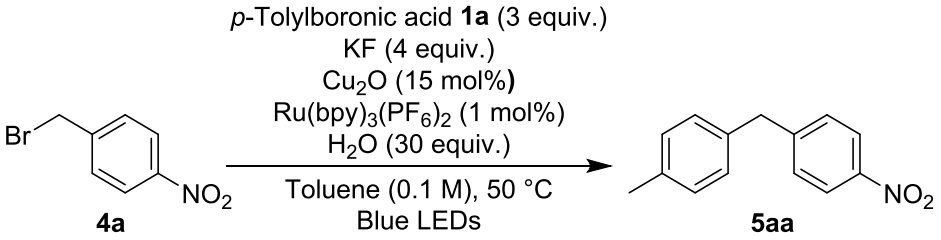
A oven-dried one dram vial was charged sequentially with 4-nitrobenzyl bromide (21.6 mg, 0.1 mmol), 4-tolylboronic acid (40.8 mg, 0.3 mmol), KF (23.2 mg, 0.4 mmol), TEMPO (31.3 mg, 0.2 mmol), $Ru(bpy)_3(PF_6)_2$ (0.9 mg, 0.001 mmol) and Cu_2O (4.3 mg, 0.03 mmol) under an argon atmosphere. H_2O (54 mg, 54 µL, 3 mmol) was then added before all reagents were dissolved in anhydrous toluene (1 mL). The resulting solution was then sparged with an argon balloon for 5 minutes, before the vial was sealed and the resulting solution stirred at 50 °C under blue LED irradiation for 16 h. The reaction was then diluted with EtOAc (10 mL) and H_2O (10 mL). The organic and aqueous layers were then separated before the aqueous layer was extracted with EtOAc (3x10 mL). The combined organic layers were washed with saturated $Na_2S_2O_3$ solution (10 mL) followed by brine (10 mL). They were then dried over $MgSO_4$ and concentrated *in vacuo* to yield the crude product. Purification of the crude product by silica gel flash chromatography (49:1 to 19:1 petrol 40-60 °C: EtOAc, R_f = 0.30) followed by Kugelrohr distillation provided TEMPO-trapped adduct **8**[2] as a yellow solid (18.7 mg, 0.064 mmol, 64%).

R_f ; **ν_{max}**/cm^{-1} 3006 (C-H Ar), 2975 (C-H), 2931 (C-H), 1605 (C-C Ar), 1521 (NO_2), 1470 (C-C Ar), 1451 (C-C Ar), 1345 (NO_2); **^{1}H NMR** (300 MHz, $CDCl_3$) δ_H 8.20 (d, *J* = 8.9 Hz, 2H, Ar-H), 7.50 (d, *J* = 8.9 Hz, 2H, Ar-H), 4.93 (s, 2H, OCH_2), 1.68 – 1.31 (m, 6H, 3xCH_2), 1.21 (s, 6H, 2xCH_3), 1.17 (s, 6H, 2xCH_3); **^{13}C NMR** ($CDCl_3$, 75 MHz) δ_C 147.2 (C), 146.1 (C), 127.5 (CH), 123.7 (CH), 77.7 (CH_2), 60.3 (C), 39.8 (CH_2), 33.1 (CH_3), 20.4 (CH_3) , 17.2 (CH_2); **m.p.** = 61-62 °C (lit.[2] 60-62 °C).

No formation of coupling product **5aa** was detected in the presence of TEMPO. Isolation of the TEMPO trapped adduct of the benzylic radical originating from reduction of the benzyl bromide would suggest that the mechanism of the reaction is radical based with benzylic radicals serving as intermediates.

Quantum Yield Determination

The following model reaction was used in order to determine the quantum yield of the reaction (following the method used by Nicewicz and co-workers.)[3]



In the dark, potasium ferrioxalate trihydrate ($K_2Fe(C_2O_4)_3$) was prepared by adapting a previously reported literature procedure and was purified by recrystallization from water prior to use.[4] A 0.15 M aqueous solution of $K_2Fe(C_2O_4)_3$ was made up before 1 mL of the solution was irradiated under our standard reaction set up (Figure S1) for 30 seconds (a second measurement was also carried out irradiating for 15 seconds). After irradiation, the samples were kept in the dark as much as possible. After being irradiated for the appropriate amount of time, 0.5 mL of each sample was transferred to a 25 mL volumetric flask. To this 5 mL of a buffered 1,10-phenanthroline solution, previously prepared in accordance with the literature,[5] was added and the flask made up to the mark with H_2O. The resulting solution was then stirred at room temperature for 30 minutes. 0.25 mL of the solution was then transferred to a cuvette and diluted to 2.75 mL with H_2O.

The moles of tris-phenanthroline-Fe^{2+} complex ($\varepsilon_{510\ nm}$= 11110 $M^{-1}cm^{-1}$)[6] was then determined using UV/vis spectroscopy. The photon flux on the system was determined using the absolute quantum yield of 0.85 at 457.9 nm for the photodecomposition of $K_2Fe(C_2O_4)_3$. The photon flux averaged over the two experiments was determined to be 1.69×10^{-7} mol photons s^{-1} (std. dev. 4.60×10^{-8} mol photons s^{-1}). The quantum yield of the reaction was then obtained by stopping the reaction at varying degrees of conversion, using the following relationship,

$$\Phi_R = \frac{moles\ of\ product}{moles\ of\ incident\ photons}$$

Three measurements were taken at 29%, 57% and 61% conversion. The average quantum yield of the reaction was φ = 0.012 (std. dev. 0.0023).

(Sample calculation from 61% converted experiment, reaction time 8 h)

NMR yield = 47%

$$\Phi_R = \frac{moles\ of\ product}{moles\ of\ incident\ photons}$$

$$\Phi_R = \frac{moles\ of\ product}{Photon\ flux\ \times reaction\ time}$$

$$\Phi_R = \frac{4.7 \times 10^{-5}\ mol}{1.69 \times 10^{-7}\ mols^{-1}\ \times 28800\ s}$$

$$\Phi_R = 0.0096$$

(Sample calculation from 57% converted experiment, reaction time 5 h)

NMR yield = 39%

$$\Phi_R = \frac{moles\ of\ product}{moles\ of\ incident\ photons}$$

$$\Phi_R = \frac{moles\ of\ product}{Photon\ flux\ \times reaction\ time}$$

$$\Phi_R = \frac{3.9 \times 10^{-5}\ mol}{1.69 \times 10^{-7}\ mols^{-1}\ \times 18000\ s}$$

$$\Phi_R = 0.013$$

(Sample calculation from 29% converted experiment, reaction time 3 h)

NMR yield = 26%

$$\Phi_R = \frac{moles\ of\ product}{moles\ of\ incident\ photons}$$

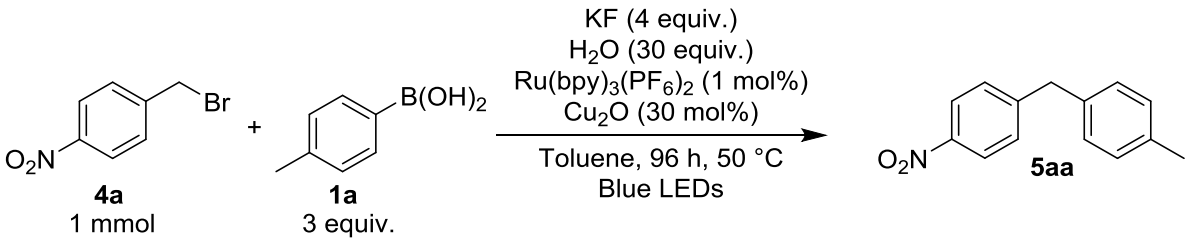
$$\Phi_R = \frac{moles\ of\ product}{Photon\ flux\ \times reaction\ time}$$

$$\Phi_R = \frac{2.6 \times 10^{-5}\ mol}{1.69 \times 10^{-7}\ mols^{-1}\ \times 10800\ s}$$

$$\Phi_R = 0.014$$

Taking the average of the three experiments gives the average quantum yield of the reaction as ***φ* = 0.012 (std. dev. 0.0023)**.

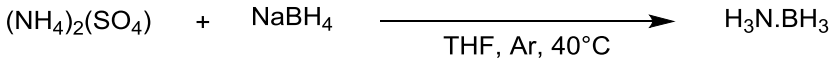
Procedure for the 1 mmol Scale Reaction



An oven-dried pyrex test tube was charged sequentially with the 4-nitrobenzyl bromide **4a** (1 mmol), the *p*-tolyllboronic acid **1a** (3 mmol), KF (232 mg, 4 mmol), $Ru(bpy)_3(PF_6)_2$ (8.6 mg, 0.01 mmol) and Cu_2O (42.9 mg, 0.3 mmol) under an argon atmosphere. H_2O (540 mg, 540 µL, 30 mmol) was then added before all reagents were dissolved in anhydrous toluene which had previously been rigorously degassed by 3 consecutive freeze-pump-thaw cycles (10 mL). The resulting solution was then sparged vigorously with argon balloons for 45 minutes in the dark, before the test tube was sealed using a fresh rubber seal and parafilm. The solution was then stirred at 50 °C under blue LED irradiation for 96 h. The reaction was then diluted with EtOAc (20 mL) and H_2O (20 mL). The organic and aqueous layers were then separated, before the aqueous layer was extracted with EtOAc (3x20 mL). The combined organic layers were washed with brine (20 mL), dried over $MgSO_4$ and concentrated *in vacuo* to yield the crude product. Purification of the crude product by silica gel flash chromatography (7:3 petrol 40-60°C /toluene) yielded coupled product **5aa** as a yellow crystalline solid (116.9 mg, 0.51 mmol, 51%).

Starting Material Synthesis

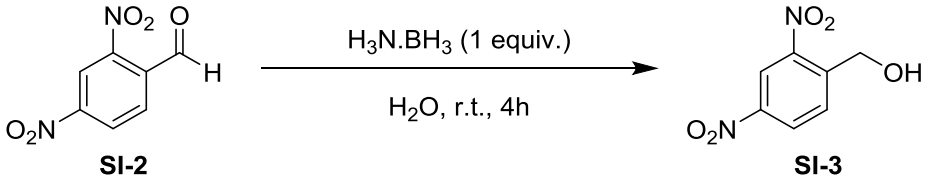
Ammonia-borane ($H_3N.BH_3$)[7]



Following a procedure by Zhang,[7] ammonium sulphate (3.30 g, 25 mmol) and sodium borohydride (0.95 g, 25 mmol) were dissolved in anhydrous THF (150 mL) under an argon atmosphere. The resulting solution was then vigorously stirred for 3 h at 40 °C. Upon completion of the reaction, the mixture was allowed to cool to room temperature before being filtered. Concentration of the solution under reduced pressure yielded the title compound (0.59 g, 19 mmol, 76%) as a white solid, with spectral data in accordance with the literature.

R_f ; **ν_{max}**/cm^{-1}; 3306 (N-H), 3248 (N-H), 2322, 2279, 1368, 1312 **^{1}H NMR** (300 MHz, DMSO) δ_H 4.40 (br s, 3H, NH_3), 2.08 – 0.40 (m, 3H, BH_3).; **^{11}B NMR** (96 MHz, DMSO) δ_B -22.96; **m.p.** = 110-112 °C (lit.[7] 108.9-110 °C).

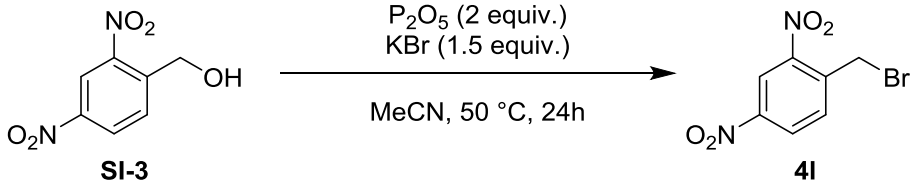
(2,4-Dinitrophenyl)methanol[7] (SI-3)



SI-2 **SI-3**

Following a procedure by Zhang,[7] 2,4-dinitrobenzaldehyde **SI-2** (1.00 g, 5.1 mmol) and ammonia-borane (0.16 g, 5.1 mmol) were dissolved in H_2O (20 mL), the resulting solution was then stirred at room temperature for 4 h. Upon completion, the reaction mixture was extracted with EtOAc (3 x 40 mL). The combined organic layers were then washed with brine, dried over $MgSO_4$, filtered and concentrated at reduced pressure to give the crude product. Purification by silica gel column chromatography (7:3 petrol 40-60 °C: EtOAc, R_f: 0.29) yielded **SI-3** (0.88 g, 4.4 mmol, 87%) as an orange solid with spectral data in accordance with the literature.[7] Some impurities remained in the product but it was deemed pure enough to be taken to the next step.

1-(Bromomethyl)-2,4-dinitrobenzene[8] (4l)



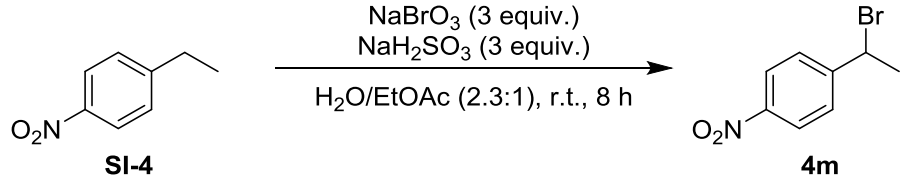
SI-3 **4l**

N.B.: Reaction carried out under an argon atmosphere.

Adapting a procedure by Gheisari[9] (2,4-dinitrophenyl)methanol **SI-3** (500 mg, 2.52 mmol), potassium bromide (451 mg, 3.78 mmol) and phosphorus pentoxide (715 mg, 5.04 mmol) were dissolved in anhydrous acetonitrile (12.5 mL). The resulting solution was then stirred at 50 °C for 24 h. Upon completion of the reaction, the mixture was allowed to cool to room temperature before being extracted with EtOAc (3 x 20 mL). The combined organic layers were then washed with brine, dried over $MgSO_4$ and filtered. Concentration of the solution under reduced pressure gave the crude product. Purification of the crude product by silica gel column chromatography (9:1 to 85:15 to 4:1 petrol 40-60 °C/EtOAc) yielded the title compound **4l** (470 mg, 1.81 mmol, 72%) as a yellow solid.

R_f 0.21 (9:1 petrol 40-60 °C/EtOAc); **ν_{max}**/cm^{-1} 3022 (C-H Ar), 2877 (C-H), 1606 (C-C Ar), 1537 (NO_2), 1440 (C-C Ar), 1346 (NO_2); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ_H 8.89 (d, *J* = 2.4 Hz, 1H, Ar-H), 8.46 (d, *J* = 8.5, 2.4 Hz, 1H, Ar-H), 7.84 (d, *J* = 8.5 Hz, 1H, Ar-H), 4.88 (s, 2H, CH_2); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ_C 148.2 (C), 147.9 (C), 139.3 (C), 134.1 (CH), 127.8 (CH), 121.1 (CH), 27.0 (CH_2); **m.p.** = 43-46 °C (lit.[8] 42-43 °C).

1-(1-Bromoethyl)-4-nitrobenzene[10] (4m)

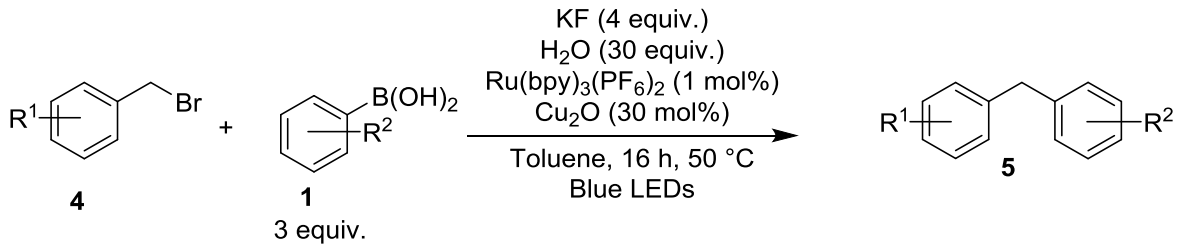


SI-4 **4m**

Following a procedure by Ishii,[10] to a solution of sodium bromate (600 mg, 3.96 mmol) in H_2O (2 mL) a solution of 4-ethylnitrobenzene (202 mg, 1.32 mmol) was added. A solution of sodium hydrogen sulphite (414 mg, 3.96 mmol) in H_2O (4 mL) was added dropwise over a period of 15 minutes. Once addition was complete, the resulting solution was then stirred at r.t. for 8 h. The crude mixture was then diluted with Et_2O (20 mL) before the organic and aqueous layers were separated. The aqueous layer was then washed with Et_2O (2×20 mL), the combined organic layers were then washed with saturated Na_2SO_3 solution (20 mL) dried over $MgSO_4$ filtered and concentrated at reduced pressure. Purification of the crude residue by silica gel flash column chromatography (19:1 petrol 40-60 °C/ EtOAc) afforded the product **4m** (246.9 mg, 1.07 mmol) as yellow oil which crystallised on standing.

R_f 0.36 (19:1 petrol 40-60 °C/EtOAc; **ν_{max}**/cm^{-1} 3076 (C-H Ar), 2920 (C-H), 1596 (C-C Ar), 1513 (NO_2) 1492 (C-C Ar), 1452 (C-C Ar), 1339 (NO_2); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ_H 8.20 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.60 (d, *J* = 8.6 Hz, 2H, Ar-H), 5.20 (q, *J* = 6.9 Hz, 1H, ArCH), 2.05 (d, *J* = 6.9 Hz, 3H, CH_3); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ_C 150.2 (C), 147.7 (C), 128.0 (CH), 124.1 (CH), 46.5 (CH), 26.6 (CH_3); **m.p.** = 36-38 °C.

General Procedure for the Dual Copper- and Photoredox-Catalysed C(sp^2)-C(sp^3) Cross-Coupling



An oven-dried one dram vial was charged sequentially with the benzyl bromide **4** (0.1 mmol), the arylboronic acid **1** (0.3 mmol), KF (23.2 mg, 0.4 mmol), $Ru(bpy)_3(PF_6)_2$ (0.9 mg, 0.001 mmol) and Cu_2O (4.3 mg, 0.03 mmol) under an argon atmosphere. H_2O (54 mg, 54 µL, 3 mmol) was then added before all reagents were dissolved in anhydrous toluene (1 mL). The resulting solution was then sparged with an argon balloon for 5 minutes, before the vial was sealed. The solution was then stirred at 50 °C under blue LED irradiation for 16-96 h. The reaction was then diluted with EtOAc (10 mL) and H_2O (10 mL). The organic and aqueous layers were then separated, before the aqueous layer was extracted with EtOAc (3x10 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$ and concentrated *in vacuo* to yield the crude product. Purification of the crude product by silica gel flash chromatography then yielded coupled products **5**.

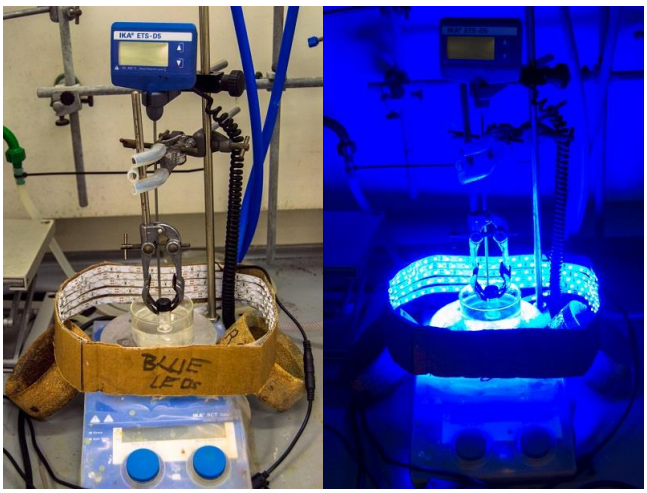
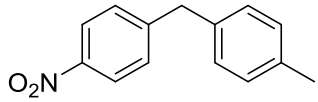


Figure S1

Product Characterisation

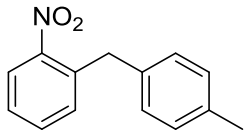
1-Methyl-4-(4-nitrobenzyl)benzene (5aa)[11]



Following the general procedure, 4-nitrobenzyl bromide (21.6 mg, 0.1 mmol) was reacted with 4-tolylboronic acid (40.8 mg, 0.3 mmol) for 16 h. The crude was purified by silica gel flash column chromatography (7:3 petrol 40-60 °C/toluene) to yield product **5aa** (14.1 mg, 0.062 mmol, 62%) as a yellow solid.

R_f 0.26 (7:3 petrol 40-60 °C/toluene) ; **ν_{max}**/cm^{-1} 3048 (C-H Ar), 2929 (C-H), 2860 (C-H), 1601 (C-C Ar), 1592 (C-C Ar), 1511 (NO_2), 1339 (NO_2); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ_H 8.14 (d, *J* = 8.9 Hz, 2H, Ar-H), 7.33 (d, *J* = 8.9 Hz, 2H, Ar-H), 7.13 (d, *J* = 7.9 Hz, 2H, Ar-H), 7.06 (d, *J* = 7.9 Hz, 2H, Ar-H), 4.04 (s, 2H, CH_2), 2.33 (s, 3H, CH_3); **^{13}C NMR** ($CDCl_3$, 100 MHz) 149.3 (C), 146.7 (C), 136.5 (C), 136.3 (C), 129.7 (CH), 129.6 (CH), 129.0 (CH), 123.9 (CH), 41.5 (CH_2), 21.1 (CH_3); **m.p.** = 74-75 °C.

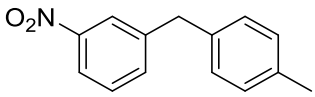
1-Methyl-4-(2-nitrobenzyl)benzene (5ab)



Following the general procedure, 2-nitrobenzyl bromide (21.6 mg, 0.1 mmol) was reacted with 4-tolylboronic acid (40.8 mg, 0.3 mmol) for 16 h. The crude was purified by silica gel flash column chromatography (17:3→4:1→1:1 petrol 40-60 °C/toluene) to yield product **5ab** (14.8 mg, 0.065 mmol, 65%) as a yellow oil.

R_f 0.37 (9:1 petrol 40-60 °C/toluene); **ν_{max}**/cm^{-1} 3010 (C-H Ar), 2923 (C-H), 1578 (C-C Ar), 1525 (NO_2), 1514 (C-C Ar), 1445 (C-C Ar), 1349 (NO_2); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ_H 7.91 (dd, *J* = 8.3, 1.3 Hz, 1H, Ar-H), 7.50 (ddd, *J* = 7.5, 7.5, 1.3 Hz, 1H, Ar-H), 7.39 – 7.34 (m, 1H, Ar-H), 7.29 – 7.27 (m, 1H, Ar-H), 7.10 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.04 (d, *J* = 8.0 Hz, 2H, Ar-H), 4.27 (s, 2H, CH_2), 2.32 (s, 3H, CH_3); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ_C 149.6 (C), 136.3 (C), 136.2 (C), 135.8 (C), 133.0 (CH), 132.5 (CH), 129.5 (CH), 129.1 (CH), 127.4 (CH), 124.8 (CH), 38.0 (CH_2), 21.2 (CH_3); **HRMS** Found (TOF MS ASAP+) $[M-H]^+$ 226.0870, $C_{14}H_{12}NO_2$ requires 226.0868.

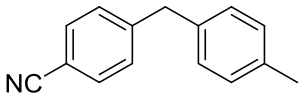
1-(4-Methylbenzyl)-3-nitrobenzene (5ac)[12]



Following the general procedure, 3-nitrobenzyl bromide (21.6 mg, 0.1 mmol) was reacted with 4-tolyboronic acid (40.8 mg, 0.3 mmol) for 96 h. giving an NMR yield of 44%. Analysis of the crude ^{1}H NMR spectra using 1,3,5 trimethoxybenzene as an internal standard gave an NMR yield of 44% with spectral data matching literature data.[12] Due to co-ellution with the benzyl bromide starting material, an accurate isolated yield for the reaction could not be determined. The co-elluted mixture was dissolved in acetonitrile (5 mL) before potassium acetate (49 mg, 0.5 mmol) was added and the mixture stirred overnight. Any remaining potassium acetate was removed by vacuum filtration before the solvent was removed *in vacuo*. The resulting residue was then subjected to silica gel flash column chromatography (7:3 petrol 40-60 °C/toluene) which yielded a pure sample of **5ac** as a white solid which was then used for characterisation.

R_f 0.33 (7:3 petrol 40-60 °C/toluene); **ν_{max}**/cm^{-1} 3010 (C-H Ar), 2922 (C-H), 1527 (NO_2), 1514 (C-C Ar), 1479 (C-C Ar), 1442 (C-C Ar), 1350 (NO_2); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ_H 8.08 – 8.03 (m, 2H, Ar-H), 7.53 – 7.49 (m, 1H, Ar-H), 7.47 – 7.41 (m, 1H, Ar-H), 7.13 (d, *J* = 7.9 Hz, 2H, Ar-H), 7.08 (d, *J* = 7.9 Hz, 2H, Ar-H), 4.04 (s, 2H, CH_2), 2.33 (s, 3H, CH_3); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ_C 148.7 (C), 143.7 (C), 136.5 (C), 136.5 (C), 135.1 (CH), 129.7 (CH), 129.4 (CH), 128.9 (CH), 123.8 (CH), 121.4 (CH), 41.3 (CH_2), 21.2 (CH_3); **m.p.** = 61-63 °C.

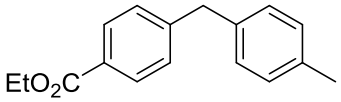
4-(4-Methylbenzyl)benzonitrile (5ad)[13]



Following the general procedure, 4-(bromomethyl)benzonitrile (19.6 mg, 0.1 mmol) was reacted with 4-tolylboronic acid (40.8 mg, 0.3 mmol) for 72 h. The crude was purified by silica gel flash column chromatography (1:1 petrol 40-60 °C/toluene) to yield product **5ad** (12.4 mg, 0.060 mmol, 60%) as a white solid.

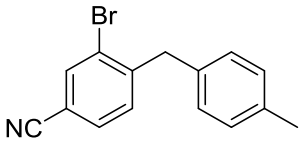
R_f = 0.19 (1:1 petrol 40-60 °C/toluene); **ν_{max}**/cm^{-1} 3020 (C-H Ar), 2924 (C-H), 2229 (C≡N), 1607 (C-C Ar), 1515 (C-C Ar), 1505 (C-C Ar); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ_H 7.56 (d, *J* = 8.3 Hz, 2H, Ar-H), 7.28 (d, *J* = 8.3 Hz, 2H, Ar-H), 7.12 (d, *J* = 7.9 Hz, 2H, Ar-H), 7.05 (d, *J* = 7.9 Hz, 2H, Ar-H), 3.99 (s, 2H, CH_2), 2.33 (s, 3H, CH_3); **^{13}C NMR** ($CDCl_3$, 101 MHz) 147.2 (C), 136.4 (C), 132.4 (CH), 129.7 (CH), 129.6 (CH), 129.0 (CH), 119.1 (C), 110.2 (C), 41.7 (CH_2), 21.1 (CH_3) + 1 overlapping C; **m.p.** = 63-66 °C (lit.[13] 65 °C).

Ethyl 4-(4-methylbenzyl)benzoate (5ae)[14]



Following the general procedure, ethyl 4-(bromomethyl)benzoate (24.3 mg, 0.1 mmol) was reacted with 4-tolyboronic acid (40.8 mg, 0.3 mmol) for 96 h. Analysis of the crude ^{1}H NMR spectra using 1,3,5 trimethoxybenzene as an internal standard gave an NMR yield of 44% with spectral data matching literature data.[14] Column chromatography was attempted but product **5ae** co-eluted with unreacted benzyl bromide starting material under a number of solvent systems and could not be separated.

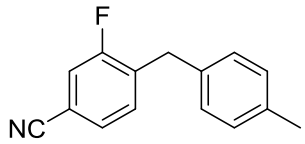
3-Bromo-4-(4-methylbenzyl)benzonitrile (5af)



Following the general procedure, 3-bromo-4-(bromomethyl)benzonitrile (27.5 mg, 0.1 mmol) was reacted with 4-tolylboronic acid (40.8 mg, 0.3 mmol) for 72 h. The crude was purified by silica gel flash column chromatography (1:1 petrol 40-60 °C/toluene) to yield product **5af** (15.8 mg, 0.055 mmol, 55%) as a colourless oil.

R_f 0.40 (1:1 petrol 40-60 °C/toluene); **ν_{max}**/cm^{-1} 3023 (C-H Ar), 2922 (C-H), 2231 (C≡N), 1597 (C-C Ar), 1514 (C-C Ar), 1479 (C-C Ar) ; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ_H 7.86 (d, *J* = 1.7 Hz, 1H, Ar-H), 7.50 (dd, *J* = 8.0, 1.7 Hz, 1H, Ar-H), 7.19 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.14 (d, *J* = 7.9 Hz, 2H, Ar-H), 7.06 (d, *J* = 7.9 Hz, 2H, Ar-H), 4.11 (s, 2H, CH_2), 2.34 (s, 3H, CH_3); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ_C 146.8 (C), 136.7 (C), 136.1 (CH), 134.9 (C), 131.5 (CH), 131.1 (CH), 129.6 (CH), 129.1 (CH), 125.3 (C), 117.5 (C), 111.9 (C), 41.7 (CH_2), 21.2 (CH_3); **HRMS** Found (FTMS + p APCI) $[M+H]^+$ 286.0225, $C_{15}H_{13}NBr$ requires 286.0226.

3-Fluoro-4-(4-methylbenzyl)benzonitrile (5ag)

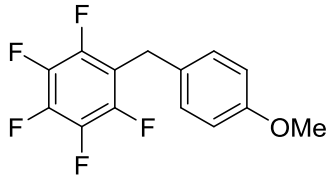


Following the general procedure, 4-(bromomethyl)-3-fluorobenzonitrile (21.4 mg, 0.1 mmol) was reacted with 4-tolylboronic acid (40.8 mg, 0.3 mmol) for 96 h. The crude was purified by silica gel flash column chromatography (9:11 petrol 40-60 °C/toluene) to yield product **5ag** (13.4 mg, 0.060 mmol, 60%) as a colourless oil.

R_f 0.43 (2:3 petrol 40-60 °C/toluene); **ν_{max}**/cm^{-1} 3023 (C-H Ar), 2922 (C-H), 2233 (C≡N), 1607 (C-C Ar), 1571 (C-C Ar), 1498 (C-C Ar); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ_H 7.39 – 7.31 (m, 2H, Ar-H), 7.26 – 7.21 (m, 1H, Ar-H), 7.21 – 7.18 (m, 1H, (*p*-tolyl)), 7.09 – 7.03 (m, 1H, (*p*-tolyl)), 7.01 – 6.97 (m, 2H, Ar-H (*p*-tolyl)), 4.00 (s, 2H, CH_2), 2.33 (s, 3H, CH_3).; **^{13}C NMR** ($CDCl_3$, 101 MHz) δ_C 160.5 (d, *J* = 249.3 Hz, C), 138.7 (C) , 138.1 (C) , 134.7 (d, *J* = 16.0 Hz, C), 132.1 (d, *J* = 5.1 Hz, CH), 129.8 (CH), 128.9 (CH), 128.3 (d, *J* = 3.8 Hz, CH), 127.7 (CH), 126.0 (CH), 119.2 (d, *J* = 25.9 Hz, CH), 117.8 (d, *J* = 2.7 Hz, C), 111.7 (d, *J* = 9.4 Hz, C), 34.9 (d, *J* = 2.8 Hz, CH_2), 21.5 (CH_3); **^{19}F NMR** ($CDCl_3$, 376 MHz) δ_F -114.37 (dd, *J* = 7.9 Hz, 7.9 Hz); **HRMS** Found (TOF MS ASAP+) $[M+H]^+$ 226.1035 $C_{15}H_{13}NF$ requires 226.1032.

Note: The seemingly "extra" CH signals in the ^{13}C NMR spectra are due to the 4 CHs on the *p*-tolyl ring being inequivalent. This is supported by HSQC NMR experiments. Spectra provided in Section 8.

1,2,3,4,5-Pentafluoro-6-(4-methoxybenzyl)benzene (5bh)[15]

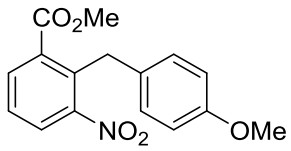


Following the general procedure, 1-(bromomethyl)-2,3,4,5,6-pentafluorobenzene (26.1 mg, 0.1 mmol) was reacted with (4-methoxyphenyl)boronic acid (45.6 mg, 0.3 mmol) for 48 h. The crude was purified by silica gel flash column chromatography (1:0→99:1→19:1 petrol 40-60 °C/toluene) to yield product **5bh** (14.8 mg, 0.051 mmol, 51%) as a colourless oil.

R_f 0.24 (99:1 petrol 40-60 °C/toluene); **ν_{max}**/cm^{-1} 3006 (C-H Ar), 2931 (C-H), 1504 (C-C Ar), 1465 (C-C Ar), 1422 (C-C Ar), 1247 (C-O-C); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ_H 7.16 (d, *J* = 8.8 Hz, 2H, Ar-H), 6.83 (d, *J* = 8.8 Hz, 2H, Ar-H), 3.96 (t, *J* = 1.9 Hz, 2H, CH_2), 3.78 (s, 3H, CH_3); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ_C 158.8 (C), 129.7 (C), 129.5 (CH), 114.4 (CH), 55.4 (CH_3), 27.5 (CH_2), 6 quaternary Cs (4 signals expected) on the pentafluorophenyl moiety are missing due to low intensity resulting from extensive coupling to fluorine but all other spectral and characterisation

data are consistent with literature data;[15] **^{19}F NMR** ($CDCl_3$, 376 MHz) δ_F -143.55 – -143.68 (m), -157.39 (t, *J* = 21.3 Hz), -162.32 – -162.51 (m).

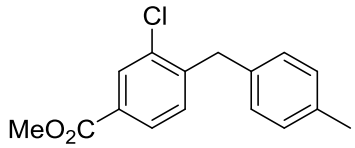
Methyl 2-(4-methoxybenzyl)-3-nitrobenzoate (5bi)



Following the general procedure, methyl 2-(bromomethyl)-3-nitrobenzoate (27.4 mg, 0.1 mmol) was reacted with (4-methoxyphenyl)boronic acid (45.6 mg, 0.3 mmol) for 16 h. The crude was purified by silica gel flash column chromatography (1:3→1:5→1:7→1:10 petrol 40-60 °C/toluene) to yield product **5bi** (16.2 mg, 0.054 mmol, 54%) as a yellow oil.

R_f 0.22 (1:7 petrol 40-60 °C/toluene); **ν_{max}**/cm^{-1} 3026 (C-H Ar), 2925 (C-H), 2852 (C-H), 1727 (C=O), 1606 (C-C Ar), 1532 (NO_2), 1480 (C-C Ar), 1435 (C-C Ar), 1347 (NO_2), 1249 (C-O-C); **^{1}H NMR** ($CDCl_3$, 300 MHz) δ_H 7.94 (dd, *J* = 7.9, 1.4 Hz, 1H, Ar-H), 7.82 (dd, *J* = 7.9, 1.4 Hz, 1H, Ar-H), 7.44 (dd, *J* = 7.9, 7.9 Hz, 1H, Ar-H), 7.00 – 6.91 (m, 2H, Ar-H), 6.81 – 6.72 (m, 2H, Ar-H), 4.45 (s, 2H, CH_2), 3.81 (s, 3H, CH_3), 3.75 (s, 3H, CH_3); **^{13}C NMR** ($CDCl_3$, 75 MHz) δ_C 167.2 (C), 158.2 (C), 152.1 (C), 135.1 (C), 134.2 (C), 133.6 (CH), 130.9 (C), 129.7 (CH), 127.4 (CH), 126.9 (CH), 113.9 (CH), 55.3 (CH_3), 52.8 (CH_3), 32.8 (CH_2); **HRMS** Found (TOF MS ASAP+) $[M\text{-}CH_3]^+$ 286.0714 $C_{15}H_{12}NO_5$ requires 286.0715.

Methyl 3-chloro-4-(4-methylbenzyl)benzoate (5aj)

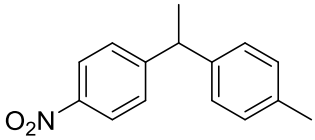


Following the general procedure, methyl 2-(bromomethyl)-5-chlorobenzoate (26.4 mg, 0.1 mmol) was reacted with 4-tolyboronic acid (40.8 mg, 0.3 mmol) for 96 h. Analysis of the crude ^{1}H NMR spectra using 1,3,5 trimethoxybenzene as an internal standard gave an NMR yield of 47%. Due to co-ellution with the benzyl bromide starting material an accurate isolated yield for the reaction could not be determined. **5aj** was previously unknown in the literature therefore, the co-elluted mixture was dissolved in acetonitrile (5 mL) before potassium acetate (49 mg, 0.5 mmol) was added and the mixture stirred overnight. Any remaining potassium acetate was removed by vacuum filtration before the solvent was removed *in vacuo*. The resulting residue was then subjected to silica gel flash column chromatography (7:3 petrol 40-60 °C/toluene) which yielded a pure sample of **5aj** as a colourless oil which was then used for characterisation.

R_f 0.28 (7:3 petrol 40-60 °C/toluene); **ν_{max}**/cm^{-1} 3023 (C-H Ar), 2952 (C-H), 2924 (C-H), 1721 (C=O), 1604 (C-C Ar), 1562 (C-C Ar), 1514 (C-C Ar), 1436 (C-C Ar); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ_H

8.04 (d, *J* = 1.7 Hz, 1H, Ar-H), 7.83 (dd, *J* = 8.0, 1.7 Hz, 1H, Ar-H), 7.20 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.12 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.07 (d, *J* = 8.0 Hz, 2H, Ar-H), 4.10 (s, 2H, CH_2), 3.91 (s, 3H, CH_3), 2.33 (s, 3H, CH_3); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ_C 166.1 (C), 144.3 (C), 136.3 (C), 135.7 (C), 134.6 (C), 131.0 (CH), 130.8 (CH), 129.9 (C), 129.5 (CH), 129.0 (CH), 128.0 (CH), 52.4 (CH_3), 39.1 (CH_2), 21.2 (CH_3); **HRMS** Found (TOF MS ASAP+) $[M+H]^+$ 275.0840 $C_{16}H_{16}O_2Cl$ requires 275.0839.

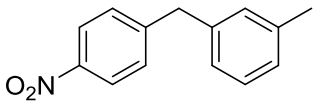
1-Methyl-4-(1-(4-nitrophenyl)ethyl)benzene (5am)[16]



Following the general procedure**,** 1-(1-bromoethyl)-4-nitrobenzene (23.0 mg, 0.1 mmol) was reacted with 4-tolylboronic acid (40.8 mg, 0.3 mmol) for 40 h. Analysis of the crude ^{1}H NMR spectra using 1,3,5 trimethoxybenzene as an internal standard gave an NMR yield of 45%. The crude was purified by silica gel flash column chromatography (4:1 petrol 40-60 °C/toluene) to yield product **5am** (6.4 mg, 0.027 mmol, 27%) as a yellow solid.

R_f 0.33 (4:1 petrol 40-60 °C/toluene); **ν_{max}**/cm^{-1} 2970 (C-H Ar), 2925 (C-H), 1597 (C-C Ar), 1514 (NO_2), 1492 (C-C Ar), 1453 (C-C Ar), 1345 (NO_2); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ_H 8.13 (d, *J* = 8.9 Hz, 2H, Ar-H), 7.36 (d, *J* = 8.9 Hz, 2H, Ar-H), 7.13 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.08 (d, *J* = 8.2 Hz, 2H, Ar-H), 4.22 (q, *J* = 7.2 Hz, 1H, CH), 2.32 (s, 3H, Ar-CH_3), 1.66 (d, *J* = 7.2 Hz, 3H, CH_3); **^{13}C** ($CDCl_3$, 101 MHz) δ_C 154.5 (C), 146.6 (C), 141.7 (C), 136.5 (C), 129.6 (CH), 128.5 (CH), 127.6 (CH), 123.8 (CH), 44.6 (CH), 21.7 (CH_3), 21.1 (CH_3); **m.p.** = 69-71 °C.

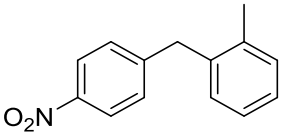
1-Methyl-3-(4-nitrobenzyl)benzene (5ba)[17]



Following the general procedure, 4-nitrobenzyl bromide (21.6 mg, 0.1 mmol) was reacted with 3-tolylboronic acid (40.8 mg, 0.3 mmol) for 16 h. The crude was purified by silica gel flash column chromatography (4:1 petrol 40-60 °C/toluene) to yield product **5ba** (13.0 mg, 0.057 mmol, 57%) as a yellow oil.

R_f 0.34 (4:1 petrol 40-60 °C/toluene); **ν_{max}**/cm^{-1} 3010 (C-H Ar), 2922 (C-H), 1605 (C-C Ar), 1515 (NO_2) 1492 (C-H Ar), 1345 (NO_2); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ_H 8.14 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.34 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.25 – 7.18 (m, 1H, Ar-H), 7.09 – 7.03 (m, 1H, Ar-H), 7.00 – 6.95 (m, 2H, Ar-H), 4.04 (s, 2H, CH_2), 2.33 (s, 3H, CH_3); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ_C 149.1 (C), 146.7 (C), 139.3 (C), 138.7 (C), 129.9 (CH), 129.8 (CH), 128.9 (CH), 127.7 (CH), 126.1(CH), 123.9 (CH), 41.9 (CH_2), 21.5 (CH_3).

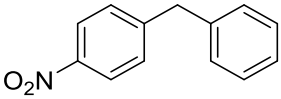
1-Methyl-2-(4-nitrobenzyl)benzene (5ca)[18]



Following the general procedure, 4-nitrobenzyl bromide (21.6 mg, 0.1 mmol) was reacted with 2-tolyboronic acid (40.8 mg, 0.3 mmol) for 96 h. Analysis of the crude ^{1}H NMR spectra using 1,3,5 trimethoxybenzene as an internal standard gave an NMR yield of 51%. Due to co-ellution with the benzyl bromide starting material an accurate isolated yield for the reaction could not be determined. **5ca** was previously known in the literature but as part of a mixture of isomers, therefore, the co-elluted mixture was dissolved in acetonitrile (5 mL) before potassium acetate (49 mg, 0.5 mmol) was added and the mixture stirred overnight. Any remaining potassium acetate was removed by vacuum filtration before the solvent was removed *in vacuo*. The resulting residue was then subjected to silica gel flash column chromatography (7:3 petrol 40-60 °C/toluene) which yielded a pure sample of **5ca** as a colourless oil which was then used for characterisation.

R_f 0.30 (7:3 petrol 40-60 °C/toluene); **ν_{max}**/cm^{-1} 3013 (C-H Ar), 2925 (C-H), 1597 (C-C Ar), 1516 (NO_2), 1492 (C-C Ar), 1462 (C-C Ar), 1345 (NO_2); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ_H 8.13 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.26 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.22 – 7.17 (m, 3H, Ar-H), 7.12 – 7.08 (m, 1H, Ar-H), 4.09 (s, 2H, CH_2), 2.21 (s, 3H, CH_3); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ_C 148.5 (C), 146.7 (C), 137.3 (C), 136.7 (C), 130.8 (CH), 130.2 (CH), 129.5 (CH), 127.3 (CH), 126.5 (CH), 123.8 (CH), 39.6 (CH_2), 19.8 (CH_3).

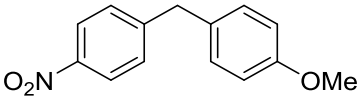
1-Benzyl-4-nitrobenzene (5da)[11]



Following the general procedure, 4-nitrobenzyl bromide (21.6 mg, 0.1 mmol) was reacted with 2-tolyboronic acid (36.6 mg, 0.3 mmol) for 16 h. The crude was purified by silica gel flash column chromatography (4:1 petrol 40-60 °C/toluene) to yield product **5da** (12.3 mg, 0.058 mmol, 58%) as a yellow oil

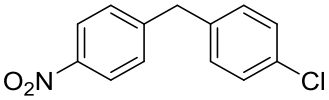
R_f 0.30 (4:1 petrol 40-60 °C/toluene); **ν_{max}**/cm^{-1} 3028 (C-H Ar), 2922 (C-H), 1605 (C-C Ar), 1595 (C-C Ar), 1516 (NO_2), 1495 (C-C Ar), 1453 (C-H), 1347 (NO_2); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ_H 8.15 (d, *J* = 8.7 Hz, 2H, Ar-H), 7.37 – 7.30 (m, 4H, Ar-H), 7.28 – 7.22 (m, 1H, Ar-H), 7.17 (d, *J* = 8.7 Hz, 2H,Ar-H), 4.08 (s, 2H, CH_2); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ_C 149.0 (C), 146.8 (C), 139.3 (C), 129.8 (CH), 129.1 (CH), 129.0 (CH), 126.9 (CH), 123.9 (CH), 41.9 (CH_2).

1-Methoxy-4-(4-nitrobenzyl)benzene (5ea)[19]



Following the general procedure, 4-nitrobenzyl bromide (21.6 mg, 0.1 mmol) was reacted with (4-methoxyphenyl)boronic acid (45.6 mg, 0.3 mmol) for 16 h. Analysis of the crude ^{1}H NMR spectra using 1,3,5 trimethoxybenzene as an internal standard gave an NMR yield of 57%, with spectral data matching literature data.[19] Column chromatography was attempted but product **5ea** co-elluted with homocoupling product under a number of solvent systems and could not be separated.

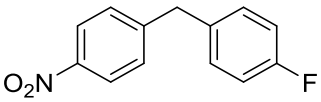
1-Chloro-4-(4-nitrobenzyl)benzene (5fa)[11]



Following the general procedure, 4-nitrobenzyl bromide (21.6 mg, 0.1 mmol) was reacted with (4-chlorophenyl)boronic acid (46.9mg, 0.3 mmol) for 72 h. The crude was purified by silica gel flash column chromatography (8:1:1 petrol 40-60 °C/toluene/ethyl acetate) to yield product **5fa** (10.8 mg, 0.044 mmol, 44%) as an orange solid.

R_f 0.51 (8:1:1 petrol 40-60 °C/toluene/ethyl acetate); **ν_{max}**/cm^{-1} 3028 (C-H Ar), 2926 (C-H), 1606 (C-C Ar), 1519 (NO_2), 1492 (C-C Ar), 1347 (NO_2); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ_H 8.15 (d, *J* = 8.9 Hz, 2H, Ar-H), 7.32 (d, *J* = 8.9 Hz, 2H, Ar-H), 7.29 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.10 (d, *J* = 8.6 Hz, 2H, Ar-H), 4.05 (s, 2H, CH_2).; **^{13}C NMR** ($CDCl_3$, 101 MHz) δ_C 148.3 (C), 146.9 (C), 137.8 (C), 132.9 (C), 130.4 (CH), 129.8 (CH), 129.1 (CH), 124.0 (CH), 41.2 (CH_2); **m.p.** = 63-66 °C.

1-Fluoro-4-(4-nitrobenzyl)benzene (5ga)[20]

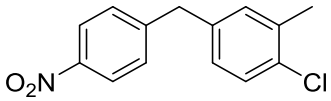


Following the general procedure, 4-nitrobenzyl bromide (21.6 mg, 0.1 mmol) was reacted with (4-fluorophenyl)boronic acid (42.0 mg, 0.3 mmol) for 72 h. The crude was purified by silica gel flash column chromatography (4:1 petrol 40-60 °C/toluene) to yield product **5ga** (12.1 mg, 0.052 mmol, 52%) as an off-white solid.

R_f 0.25 (4:1 petrol 40-60 °C/toluene); **ν_{max}**/cm^{-1} 3029 (C-H Ar), 2925 (C-H), 2853 (C-H), 1606 (C-C Ar), 1520 (NO_2), 1510 (C-C Ar), 1492 (C-C Ar) 1347 (NO_2); **^{1}H NMR** ($CDCl_3$, 300 MHz) δ_H 8.15 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.31 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.19 – 7.07 (m, 2H, Ar-H), 7.07 – 6.94 (m, 2H, Ar-H), 4.05 (s, 2H, CH_2); **^{13}C NMR** ($CDCl_3$, 75 MHz) δ_C 161.9 (d, *J* = 245.3 Hz, C), 148.7 (C), 146.8 (C), 135.0 (d, *J* = 3.2 Hz, C), 130.6 (d, *J* = 8.2 Hz, CH), 129.7 (CH), 124.0 (CH),

115.8 (d, *J* = 21.5 Hz, CH), 41.0 (CH_2); **^{19}F NMR** ($CDCl_3$, 282 MHz) δ_F -116.05 (tt, *J* = 9.3, 5.3 Hz); **m.p.** = 55-56 °C (lit.[20] 58-60 °C).

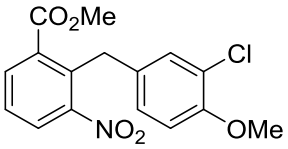
1-Chloro-2-methyl-4-(4-nitrobenzyl)benzene (5ha)



Following the general procedure, 4-nitrobenzyl bromide (21.6 mg, 0.1 mmol) was reacted with (4-chloro-3-methylphenyl)boronic acid (51.1 mg, 0.3 mmol) for 96 h. The crude was purified by silica gel flash column chromatography (4:1 petrol 40-60 °C/toluene) to yield product **5ha** (13.0 mg, 0.050 mmol, 50%) as a colorless solid.

R_f 0.30 (4:1 petrol 40-60 °C/toluene); **ν_{max}**/cm^{-1} 3027 (C-H Ar), 2925 (C-H), 2852 (C-H), 1606 (C-C Ar), 1597 (C-C Ar), 1517 (NO_2), 1480 (C-C Ar), 1346 (NO_2); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ_H 8.15 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.32 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.28 (d, *J* = 8.2 Hz, 1H, Ar-H), 7.02 (d, *J* = 1.7 Hz, 1H, Ar-H), 6.93 (dd, *J* = 8.2, 1.7 Hz, 1H, Ar-H), 4.01 (s, 2H, CH_2), 2.34 (s, 3H, CH_3); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ_C 148.5 (C), 146.9 (C), 137.8 (C), 136.6 (C), 133.0 (C), 131.7 (CH), 129.7 (CH), 129.6 (CH), 127.8 (CH), 124.0 (CH), 41.2 (CH_2), 20.2 (CH_3); **HRMS** Found (TOF MS ASAP+) $[M+H]^+$ 262.0640 $C_{14}H_{13}NO_2Cl$ requires 262.0635; **m.p.** = 78-79 °C.

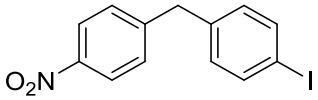
Methyl 2-(3-chloro-4-methoxybenzyl)-3-nitrobenzoate (5ib)



Following the general procedure, methyl 2-(bromomethyl)-3-nitrobenzoate (27.4 mg, 0.1 mmol) was reacted with (3-chloro-4-methoxyphenyl)boronic acid (55.9 mg, 0.3 mmol) for 72 h. The crude was purified by silica gel flash column chromatography (1:2→1:3→1:5 petrol 40-60 °C/toluene) to yield product **5ib** (16.8 mg, 0.050 mmol, 50%) as a yellow solid.

R_f 0.30 (petrol 40-60 °C/toluene 1:3) ; **ν_{max}**/cm^{-1} 3022 (C-H Ar), 2954 (C-H), 1727 (C=O), 1606 (C-C Ar), 1532 (NO_2), 1501 (C-H Ar), 1463 (C-C Ar), 1441 (C-C Ar), 1359 (NO_2), 1286 (ester C-O) 1259 (C-O-C); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ_H 7.99 (dd, *J* = 8.0, 1.4 Hz, 1H, Ar-H), 7.86 (dd, *J* = 8.0, 1.4 Hz, 1H, Ar-H), 7.48 (dd, *J* = 8.0 Hz, 1H, Ar-H), 7.07 (d, *J* = 2.2 Hz, 1H, Ar-H), 6.90 (dd, *J* = 8.4, 2.2 Hz, 1H, Ar-H), 6.79 (d, *J* = 8.4 Hz, 1H, Ar-H), 4.44 (s, 2H, CH_2), 3.84 (s, 3H, CH_3), 3.83 (s, 3H, CH_3); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ_C 166.9 (C), 153.7 (C), 152.1 (C), 134.4 (C), 134.1 (C), 133.9 (CH), 132.1 (C), 130.4 (CH), 127.9 (CH), 127.7 (CH), 127.1 (CH), 122.5 (C), 112.1 (CH), 56.3 (CH_3), 52.9 (CH_3), 32.6 (CH_2); **HRMS** Found (TOF MS ASAP+) $[M-CH_3]^+$ 304.0379 $C_{15}H_{11}NO_4Cl$ requires 304.0377; **m.p.** = 80-81 °C.

1-Iodo-4-(4-nitrobenzyl)benzene (5la)

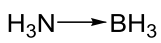


Adapting the general procedure, 4-nitrobenzyl bromide (21.6 mg, 0.1 mmol) was reacted with tris(4-iodophenyl)boroxine (110.4 mg, 0.16 mmol) added in two portions at the start and half-way through the reaction time of 72 h. After the second addition the vial was sparged with argon. Analysis of the crude ^{1}H NMR spectra using 1,3,5 trimethoxybenzene as an internal standard gave an NMR yield of 44%. Due to co-ellution with the benzyl bromide starting material an accurate isolated yield for the reaction could not be determined. **5la** was previously unknown in the literature therefore, the co-elluted mixture was dissolved in acetonitrile (5 mL) before potassium acetate (49 mg, 0.5 mmol) was added and the mixture stirred overnight. Any remaining potassium acetate was removed by vacuum filtration before the solvent was removed *in vacuo*. The resulting residue was then subjected to silica gel flash column chromatography (4:1 petrol 40-60 °C/toluene) which yielded a pure sample of **5la** as a white solid which was then used for characterisation.

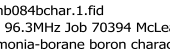
R_f 0.22 (4:1 petrol 40-60 °C/toluene); **ν_{max}**/cm^{-1} 3032 (C-H Ar), 2923 (C-H) 2855 (C-H), 1599 (C-C Ar), 1520 (NO_2), 1493 (C-C Ar), 1484 (C-C Ar), 1400 (C-C Ar), 1346 (NO_2); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ_H 8.15 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.64 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.31 (d, *J* = 8.8 Hz, 2H, Ar-H), 6.92 (d, *J* = 8.4 Hz, 2H, Ar-H), 4.02 (s, 2H, CH_2); **^{13}C NMR** ($CDCl_3$, 101 MHz) δ_C 148.1(C), 146.9 (C), 139.0 (C), 138.1 (CH), 131.1 (CH), 129.8 (CH), 124.0 (CH), 92.2 (C), 41.4 (CH_2); **HRMS** Found (TOF MS ASAP+) $[M+H]^+$ 339.9834 $C_{13}H_{11}NO_2I$ requires 339.9834; **m.p.** = 108-110 °C.

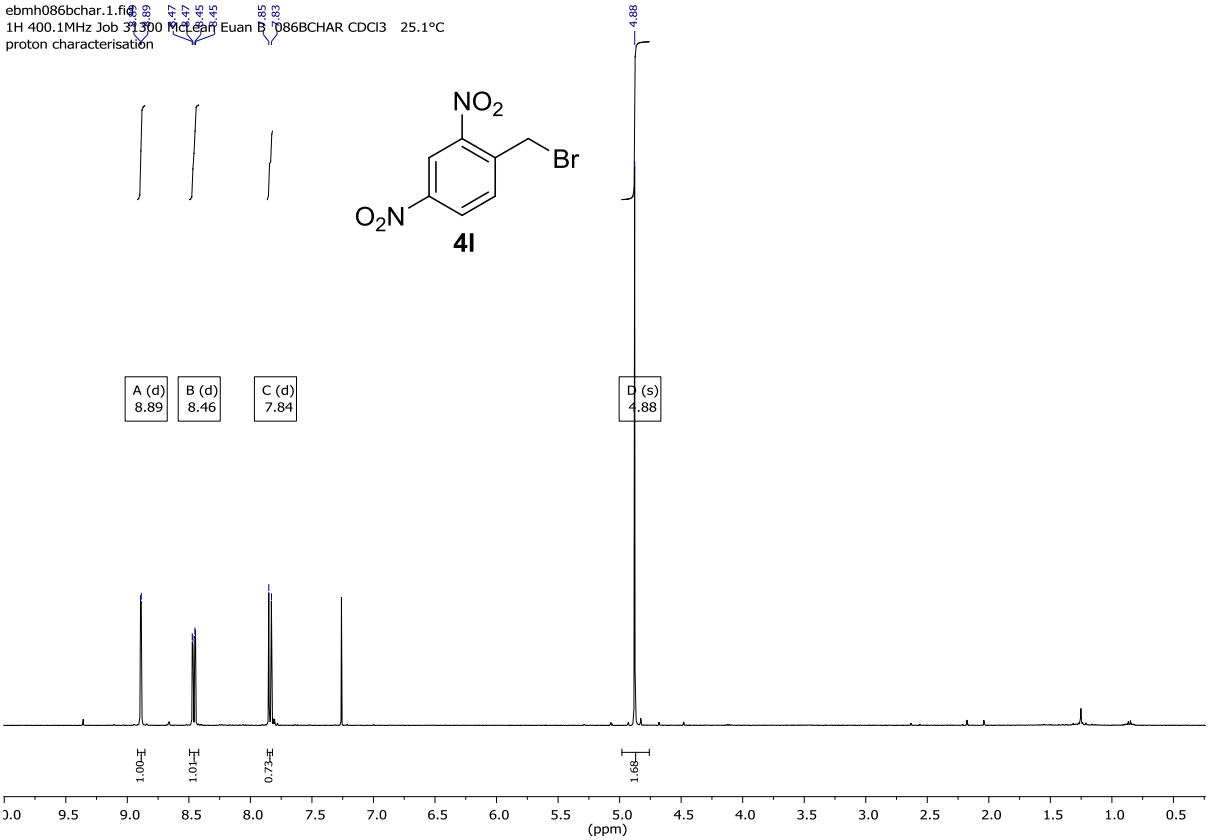
NMR Spectra

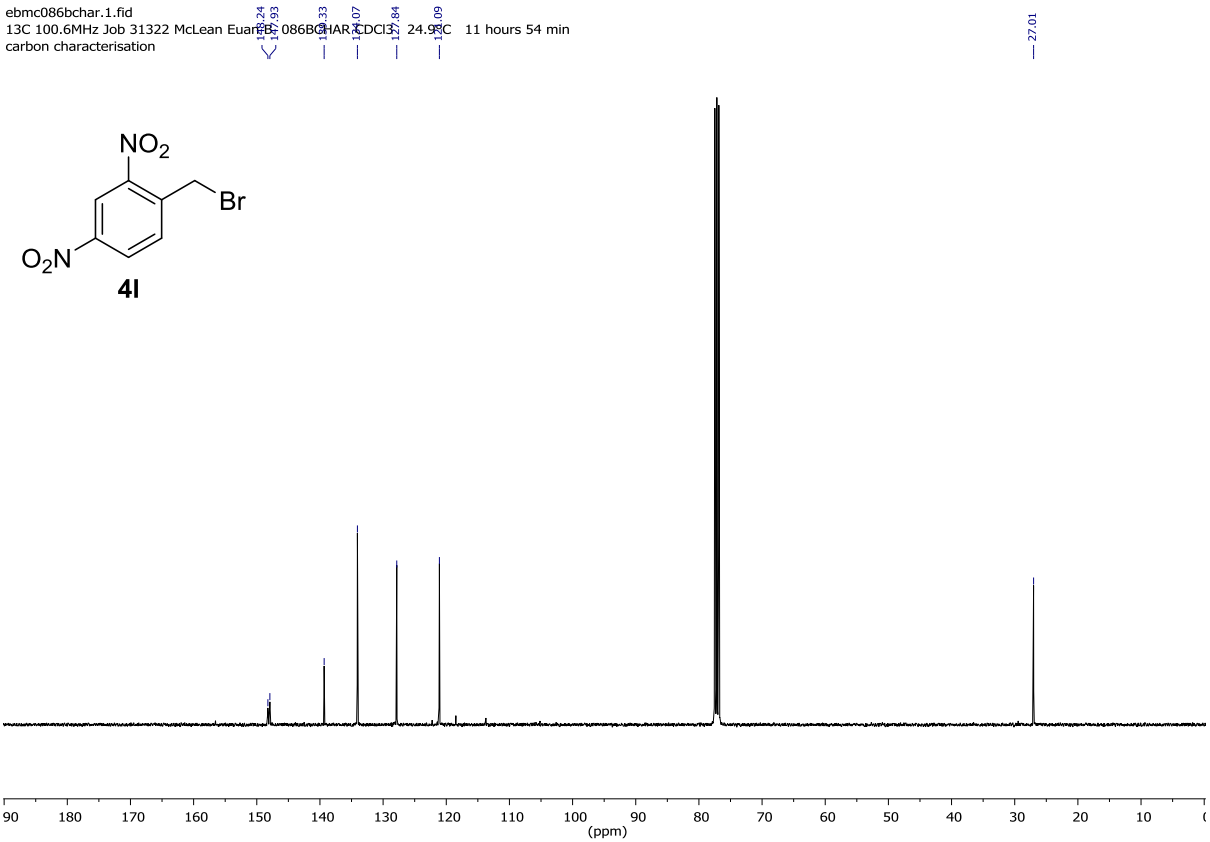
ebmh084bchar.1.fid
1H 300.1MHz Job 70393 McLean Euan B 084BCHAR DMSO 24.9°C
ammonia borane proton chracterisation

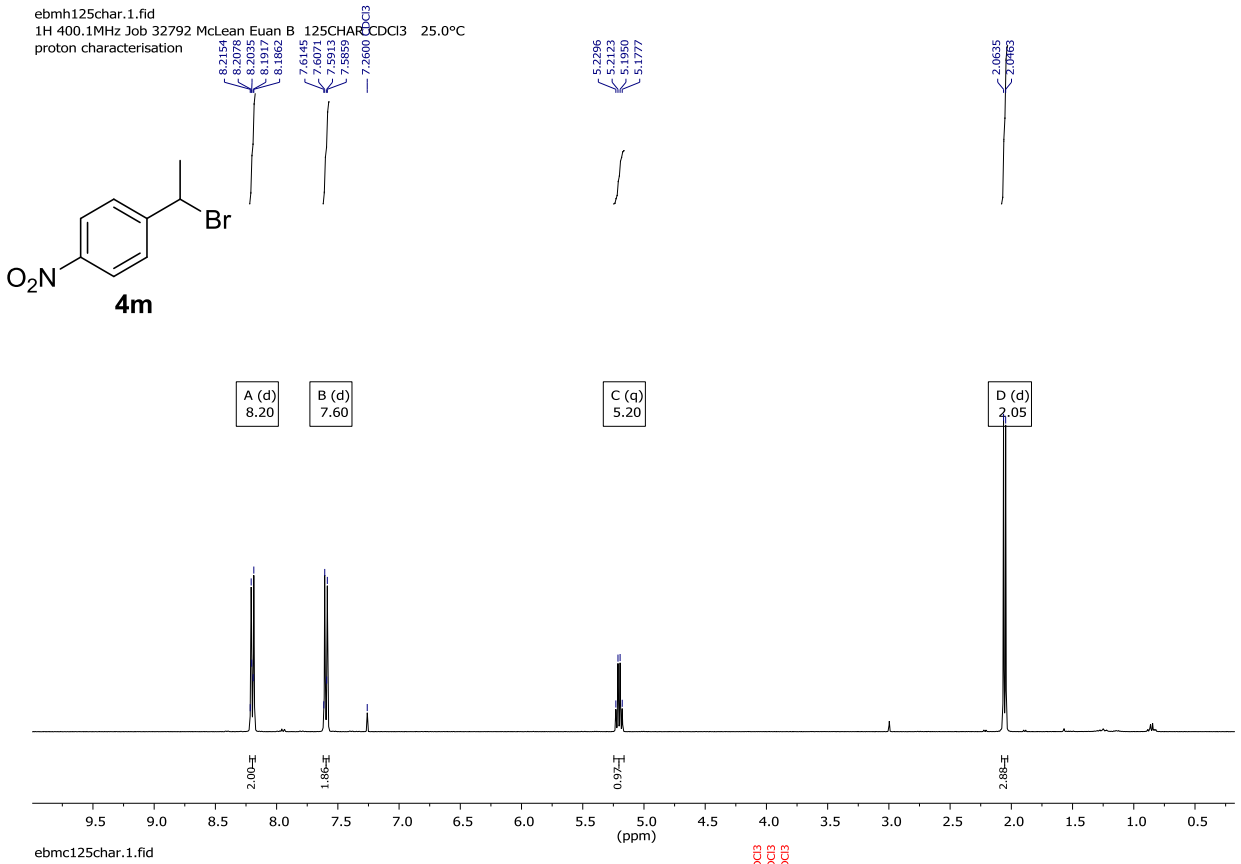


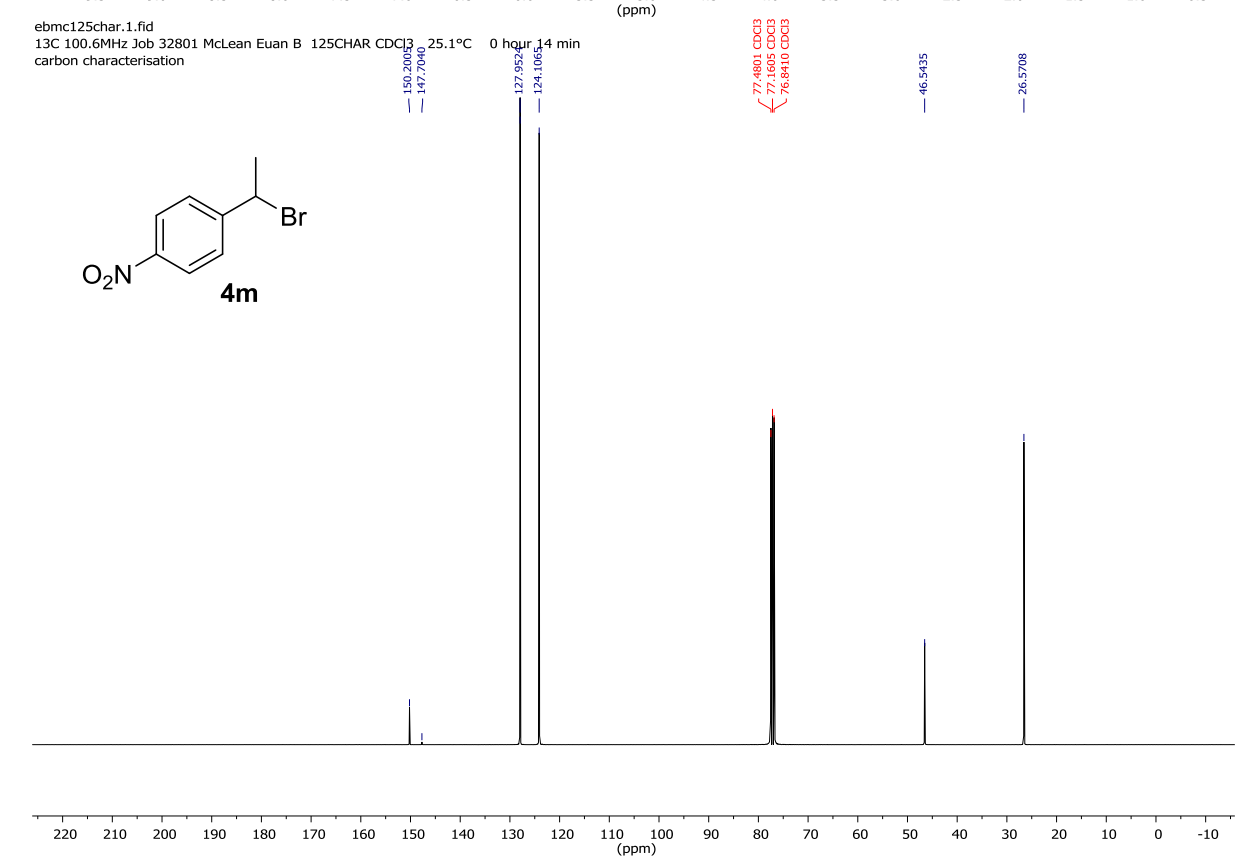
ebmb084bchar.1.fid
11B 96.3MHz Job 70394 McLean Euan B 084BCHAR DMSO 25.1°C
ammonia-borane boron characterisation

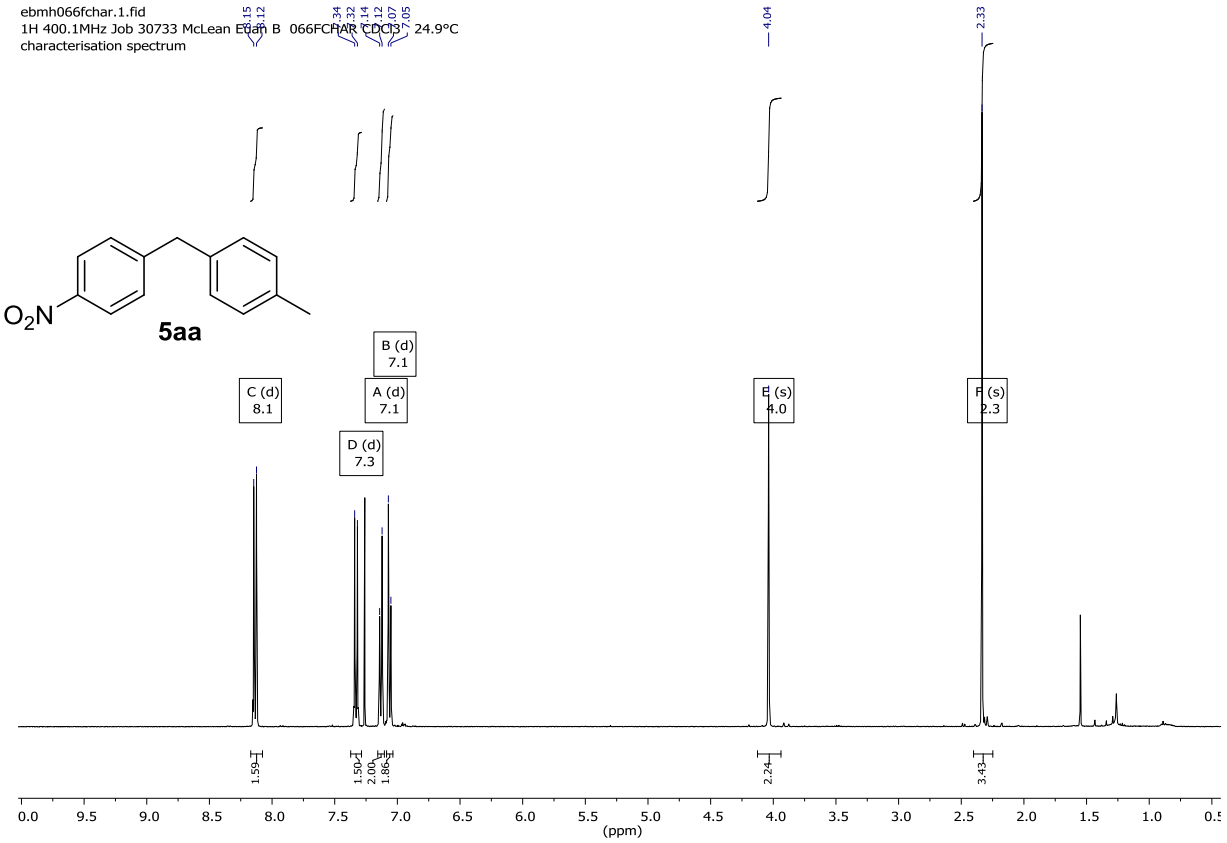


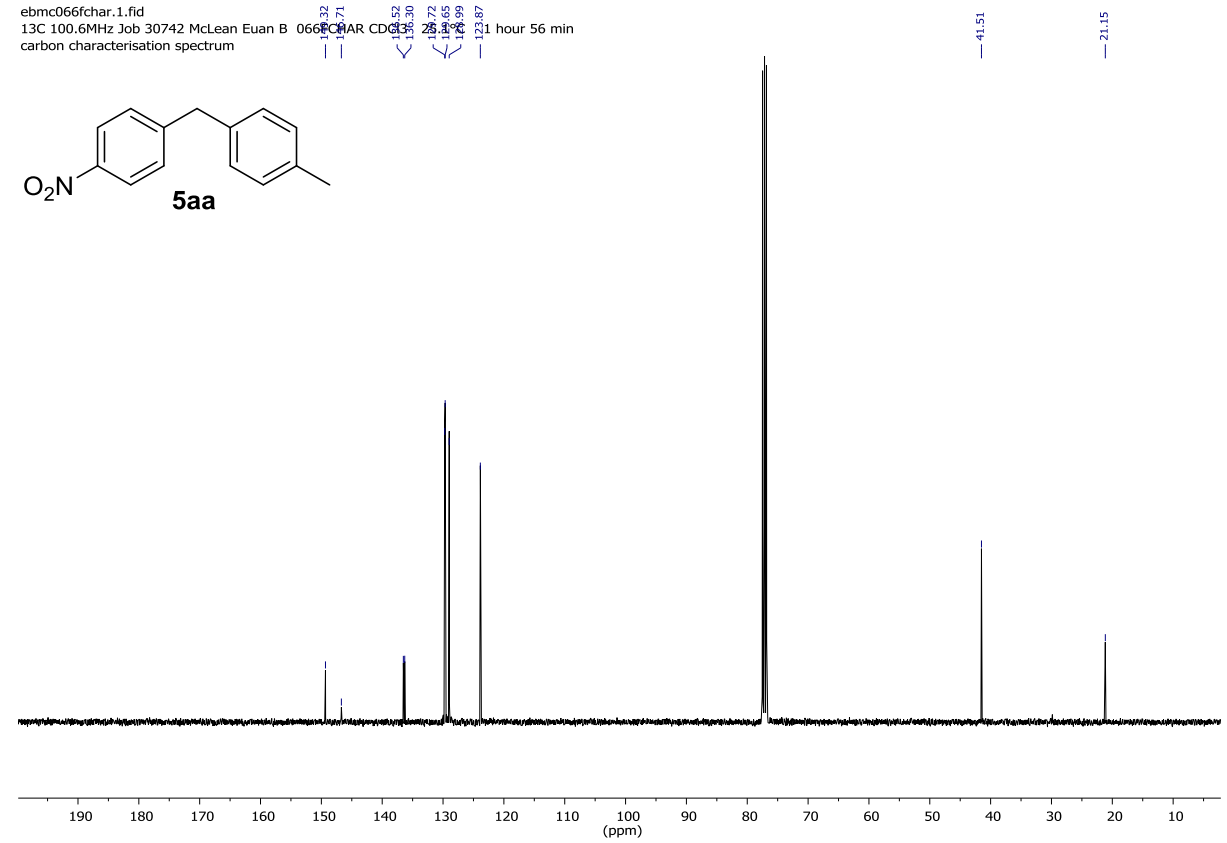

ebmh086bchar.1.fid
1H 400.1MHz Job 31300 McLean Euan B 086BCHAR CDCl3 25.1°C
proton characterisation
8.89
8.47
8.45
7.85
7.83
4.88
NO2
Br
O2N
4l
A (d) 8.89
B (d) 8.46
C (d) 7.84
D (s) 4.88
1.00
1.01
0.73
1.68
(ppm)

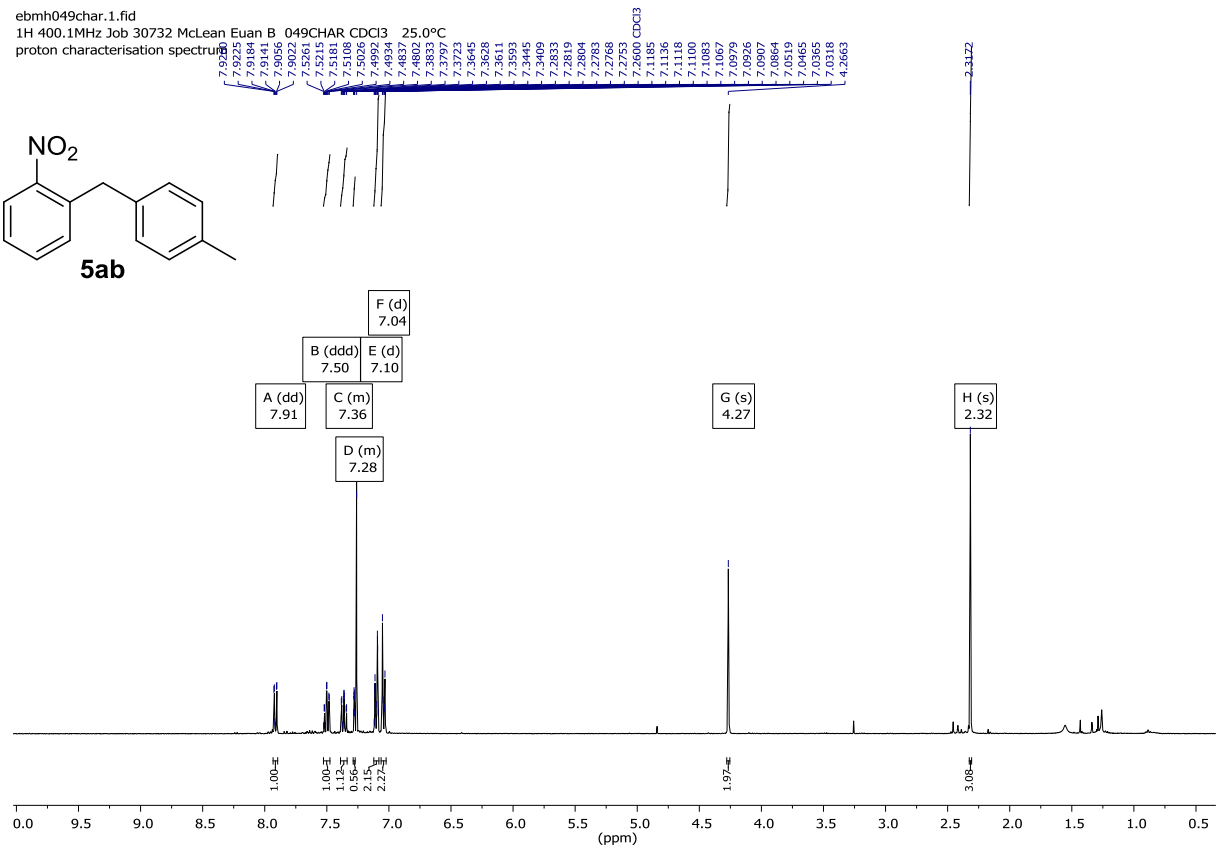

ebmc086bchar.1.fid
13C 100.6MHz Job 31322 McLean Euan B 086BCHAR CDCl3 24.9°C 11 hours 54 min
carbon characterisation
150.24
147.93
140.33
135.07
127.84
120.09
27.01
NO2
Br
O2N
4l
(ppm)

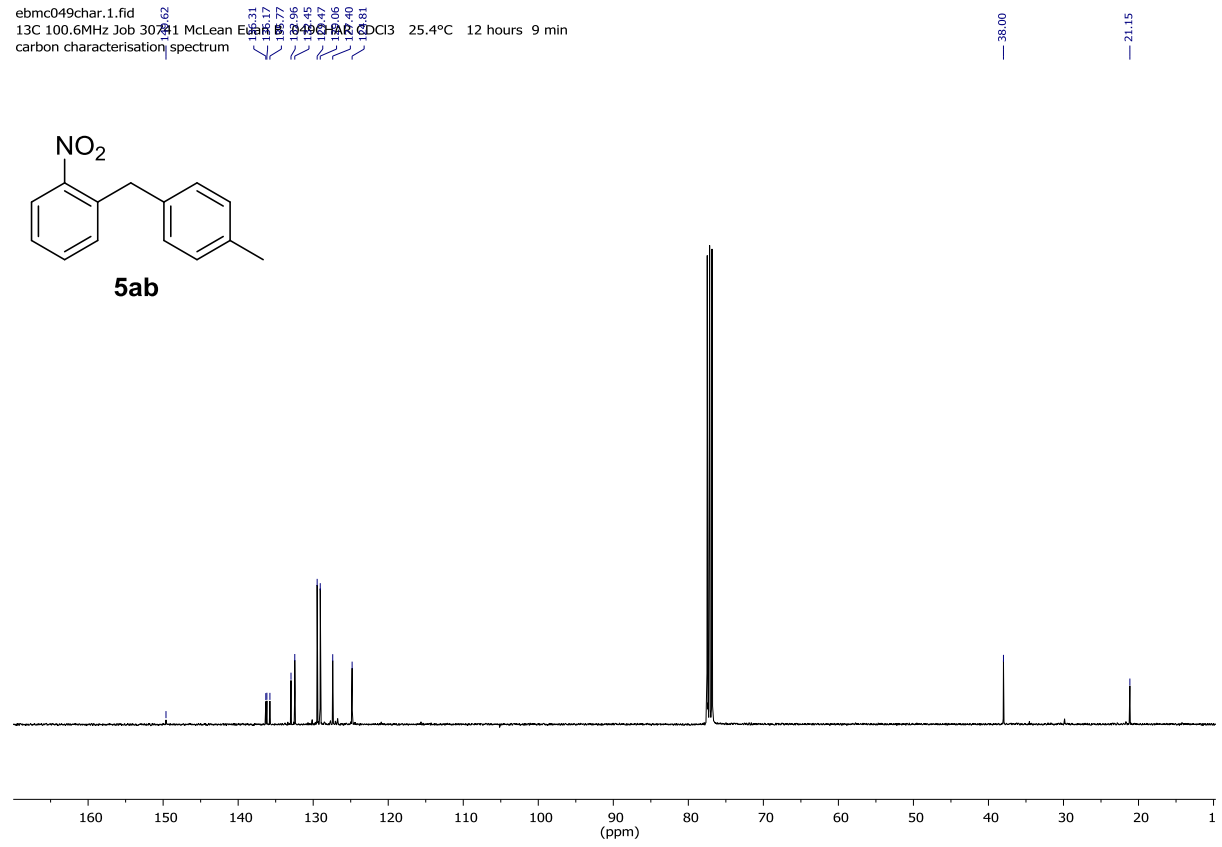

ebmh125char.1.fid
1H 400.1MHz Job 32792 McLean Euan B 125CHAR CDCl3 25.0°C
proton characterisation
8.2154
8.2078
8.2035
8.1917
8.1862
7.6145
7.6071
7.5913
7.5859
7.2600 CDCl3
5.2296
5.2123
5.1950
5.1777
2.0635
2.0463
Br
O2N
4m
A (d) 8.20
B (d) 7.60
C (q) 5.20
D (d) 2.05
2.00
1.86
0.97
2.88
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

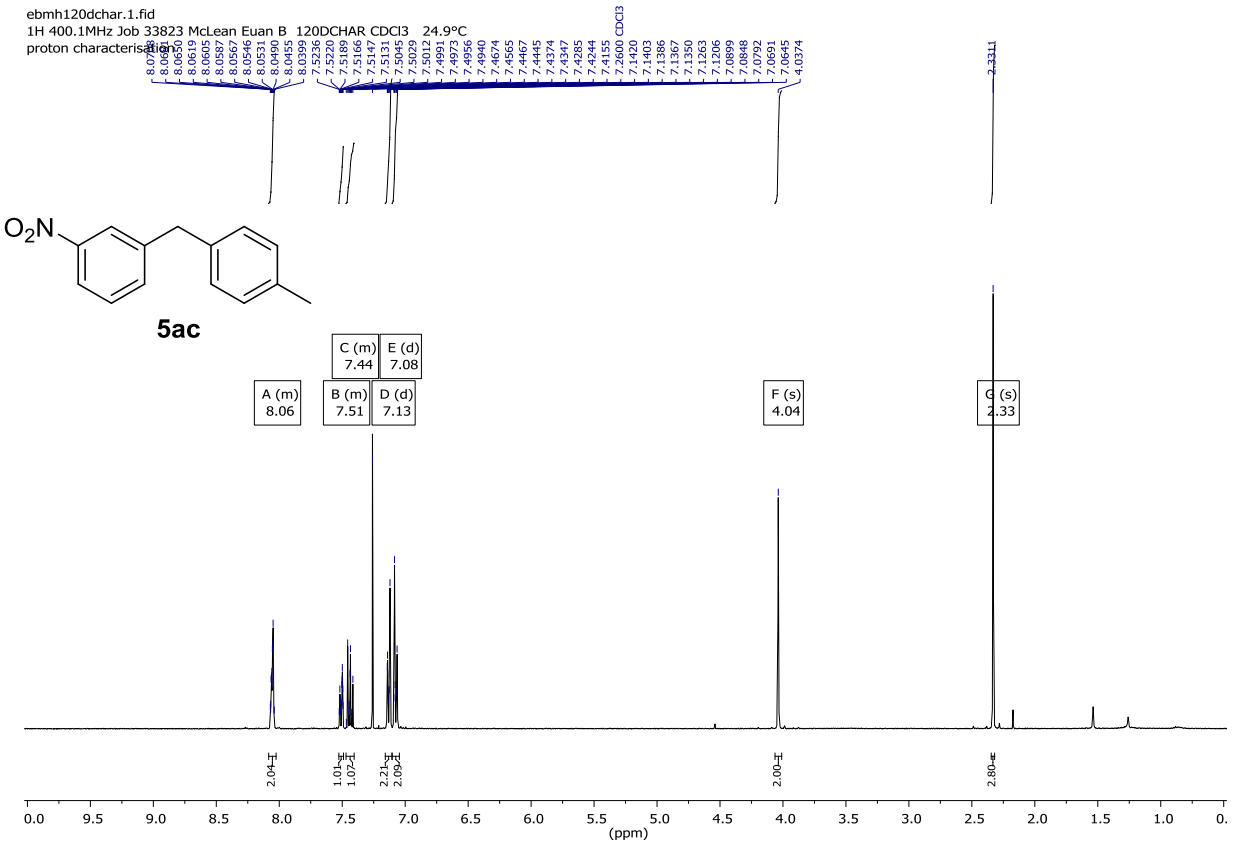

ebmc125char.1.fid
13C 100.6MHz Job 32801 McLean Euan B 125CHAR CDCl3 25.1°C 0 hour 14 min
carbon characterisation
150.2005
147.7040
127.9524
124.1065
77.4801 CDCl3
77.1605 CDCl3
76.8410 CDCl3
46.5435
26.5708
Br
O2N
4m
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
(ppm)

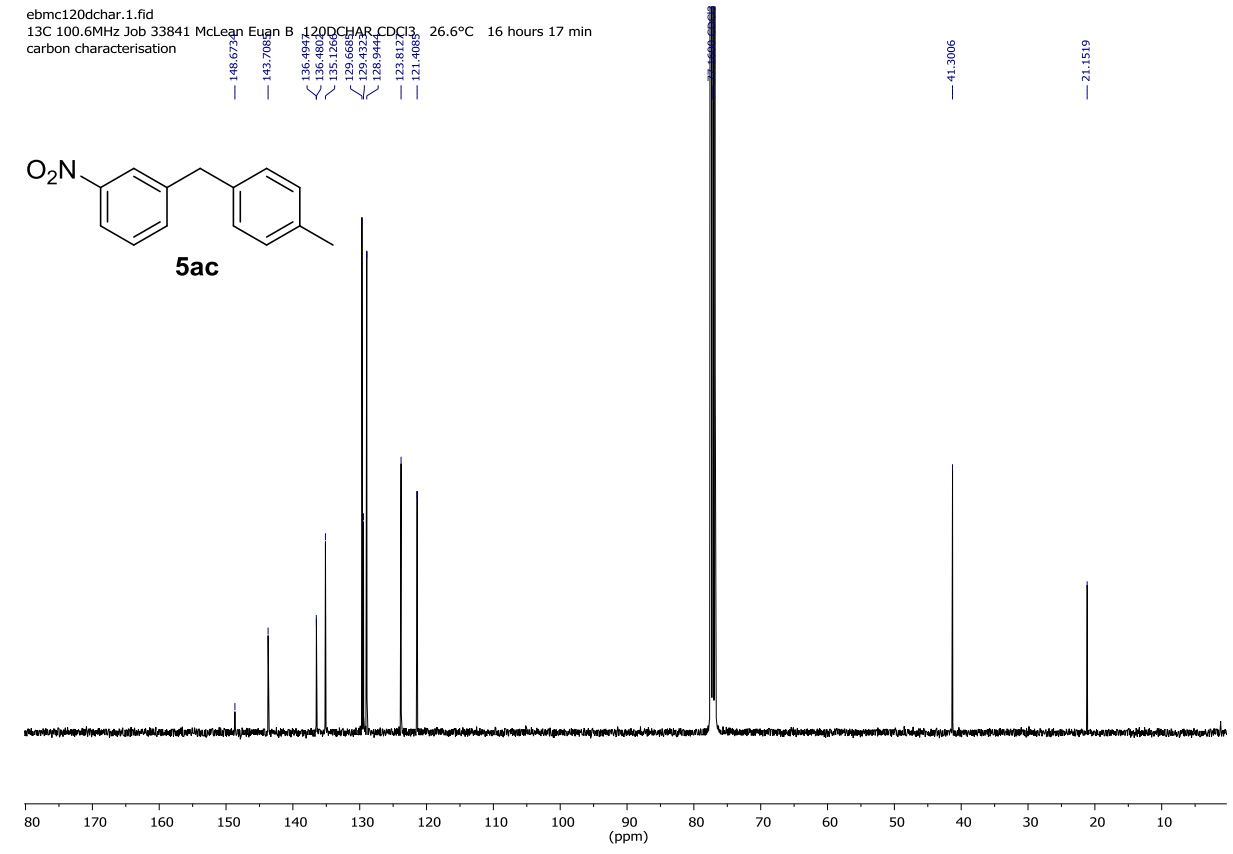

ebmh066fchar.1.fid
1H 400.1MHz Job 30733 McLean Euan B 066FCHAR CDCl3 24.9°C
characterisation spectrum
8.15
8.12
7.34
7.32
7.14
7.12
7.07
7.05
4.04
2.33
O2N
5aa
B (d)
7.1
C (d)
8.1
A (d)
7.1
E (s)
4.0
F (s)
2.3
D (d)
7.3
1.59
1.50
2.00
1.86
2.24
3.43
(ppm)

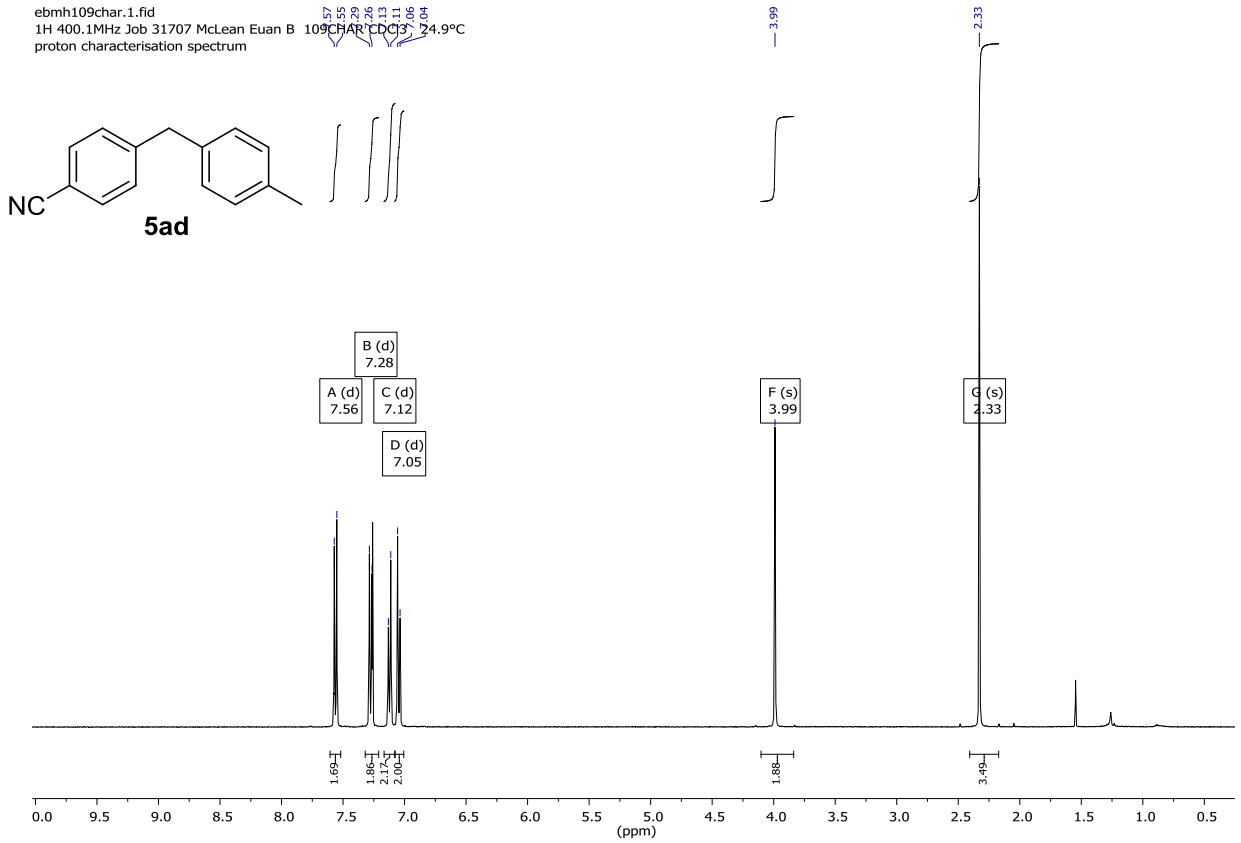

ebmc066fchar.1.fid
13C 100.6MHz Job 30742 McLean Euan B 066FCHAR CDCl3 21.1 hour 56 min
carbon characterisation spectrum
132.32
131.71
129.52
128.30
125.72
124.65
124.99
123.87
41.51
21.15
O2N
5aa
(ppm)

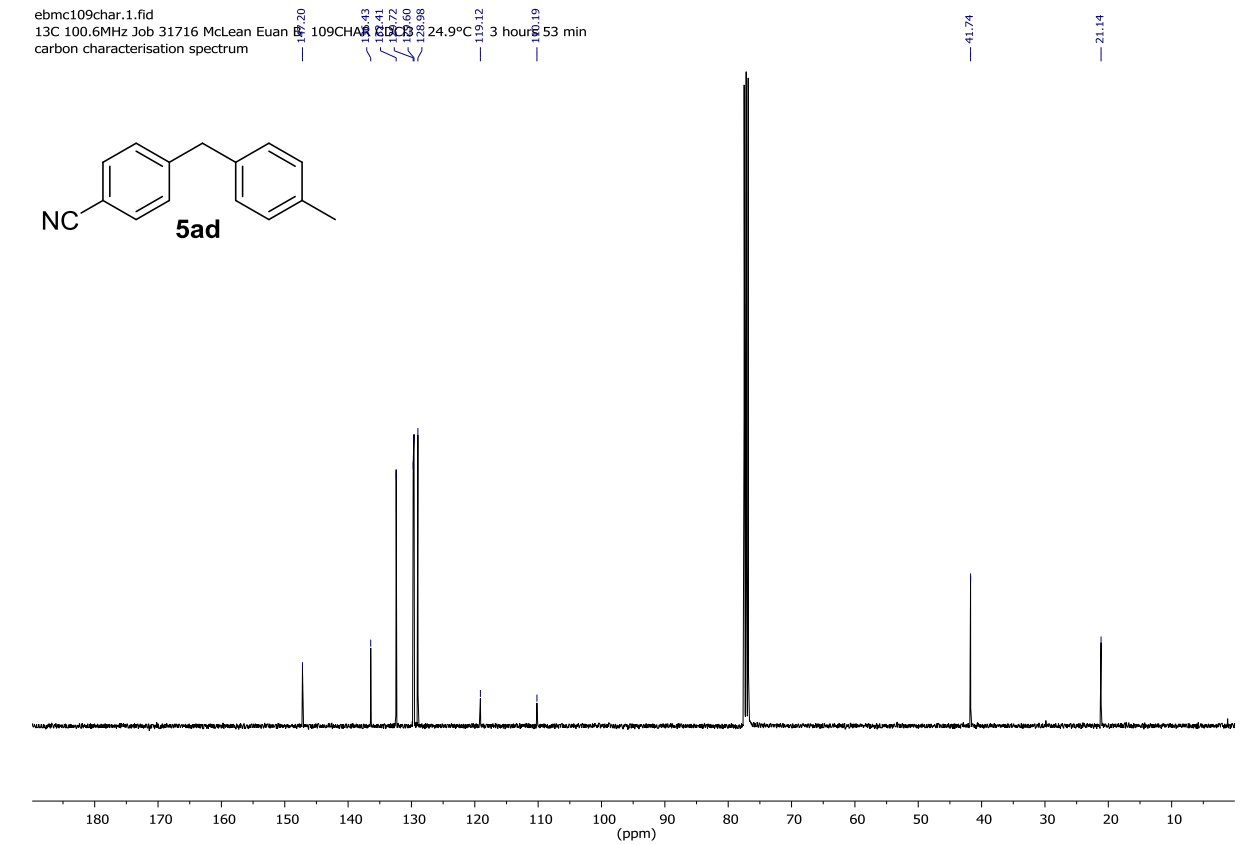

ebmh049char.1.fid
1H 400.1MHz Job 30732 McLean Euan B 049CHAR CDCl3 25.0°C
proton characterisation spectrum
NO2
5ab
F (d) 7.04
B (ddd) 7.50
E (d) 7.10
A (dd) 7.91
C (m) 7.36
D (m) 7.28
G (s) 4.27
H (s) 2.32
(ppm)

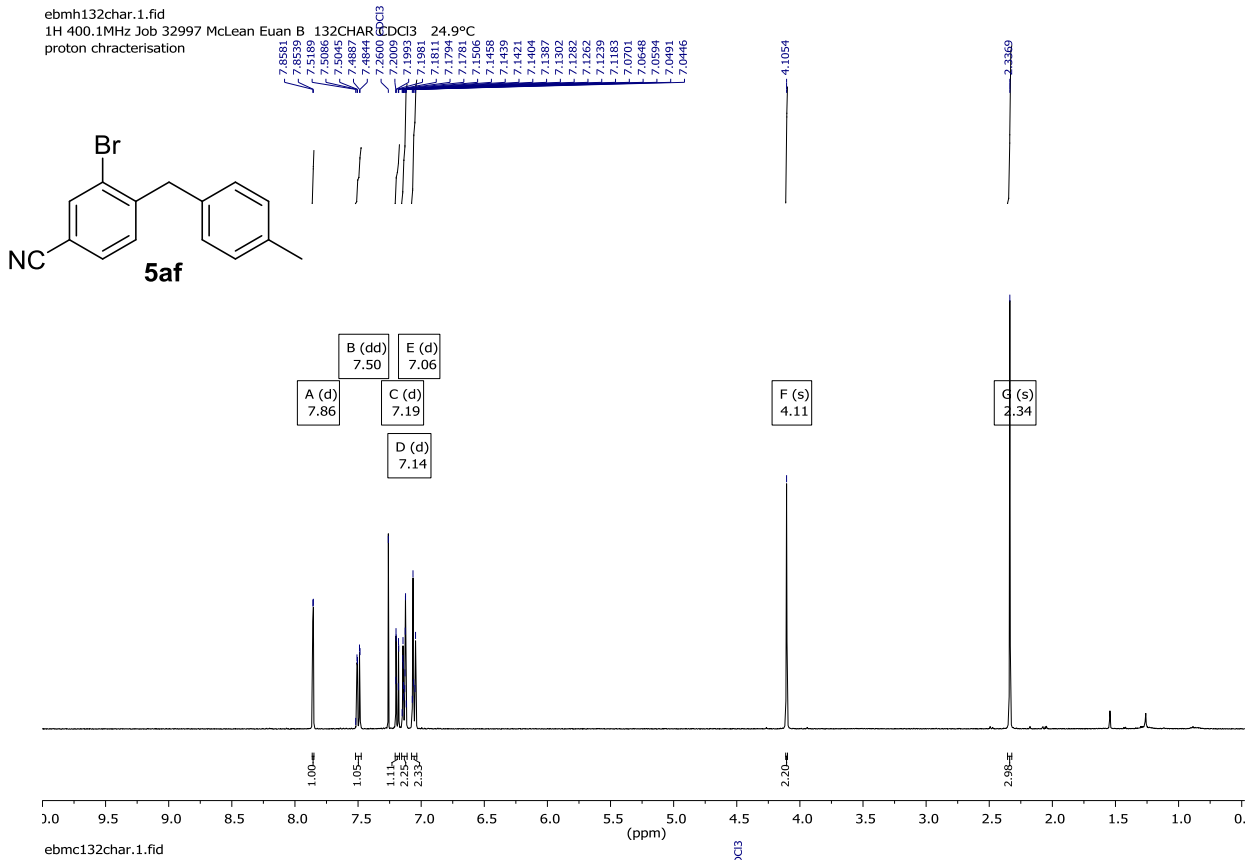

ebmc049char.1.fid
13C 100.6MHz Job 30741 McLean Euan B 049CHAR CDCl3 25.4°C 12 hours 9 min
carbon characterisation spectrum
NO2
5ab
38.00
21.15
(ppm)

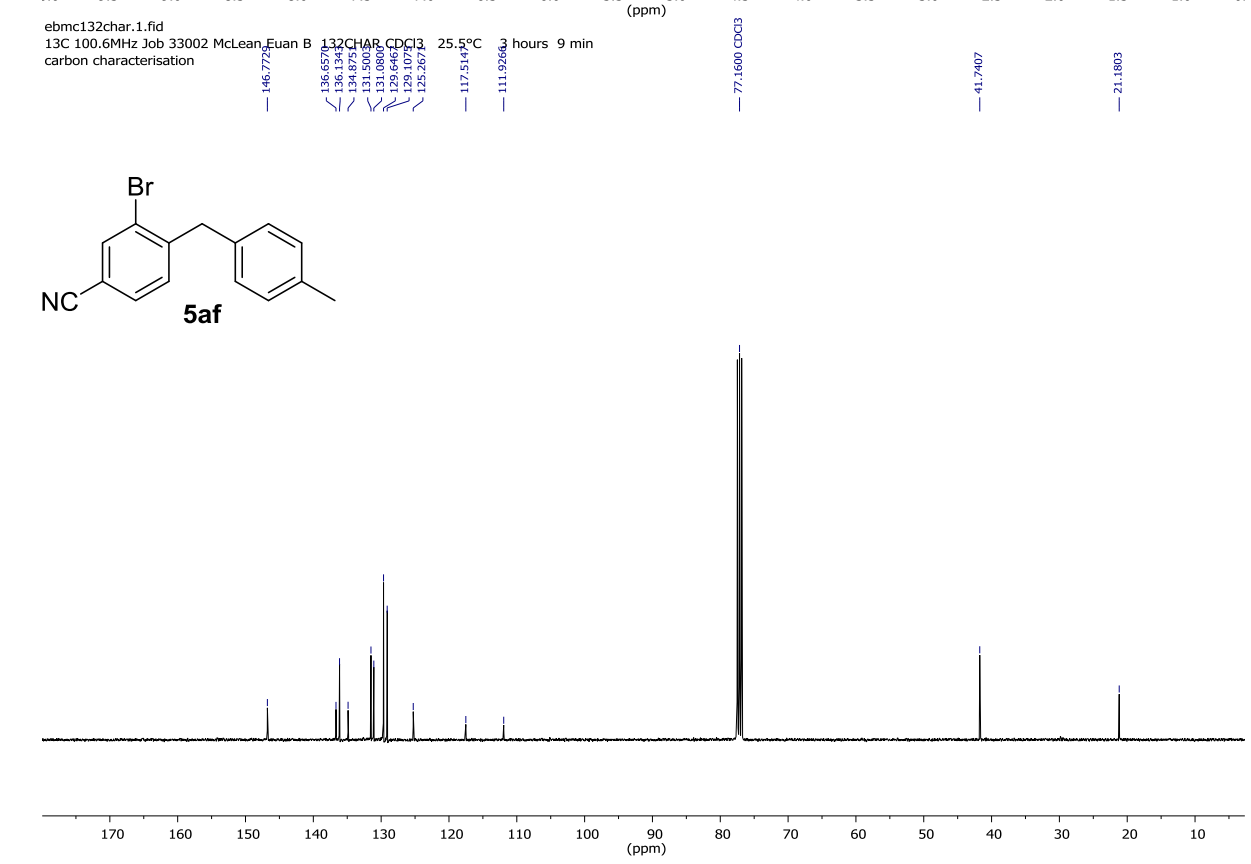

ebmh120dchar.1.fid
1H 400.1MHz Job 33823 McLean Euan B 120DCHAR CDCl3 24.9°C
proton characterisation
5ac
A (m) 8.06
B (m) 7.51
C (m) 7.44
D (d) 7.13
E (d) 7.08
F (s) 4.04
G (s) 2.33
(ppm)

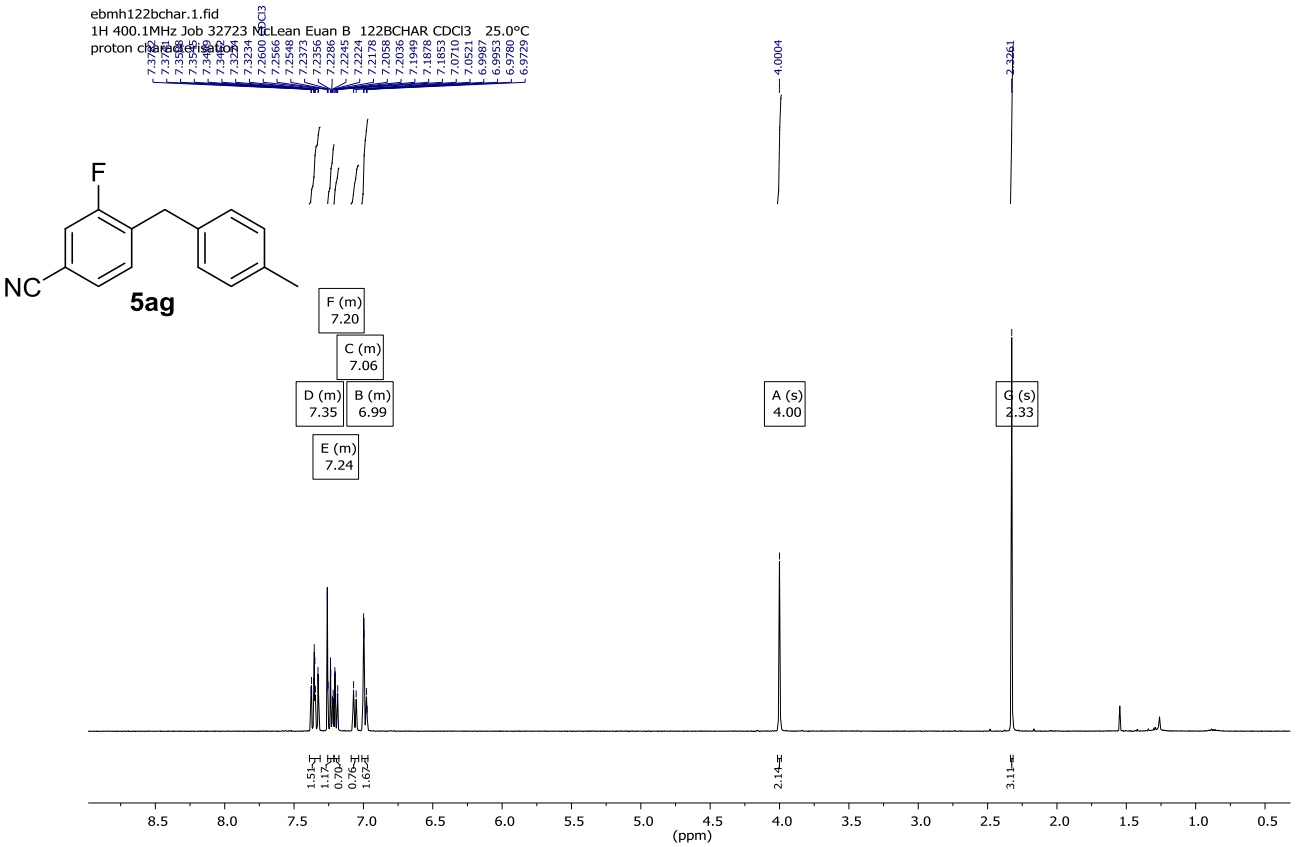

ebmc120dchar.1.fid
13C 100.6MHz Job 33841 McLean Euan B 120DCHAR CDCl3 26.6°C 16 hours 17 min
carbon characterisation
5ac
(ppm)

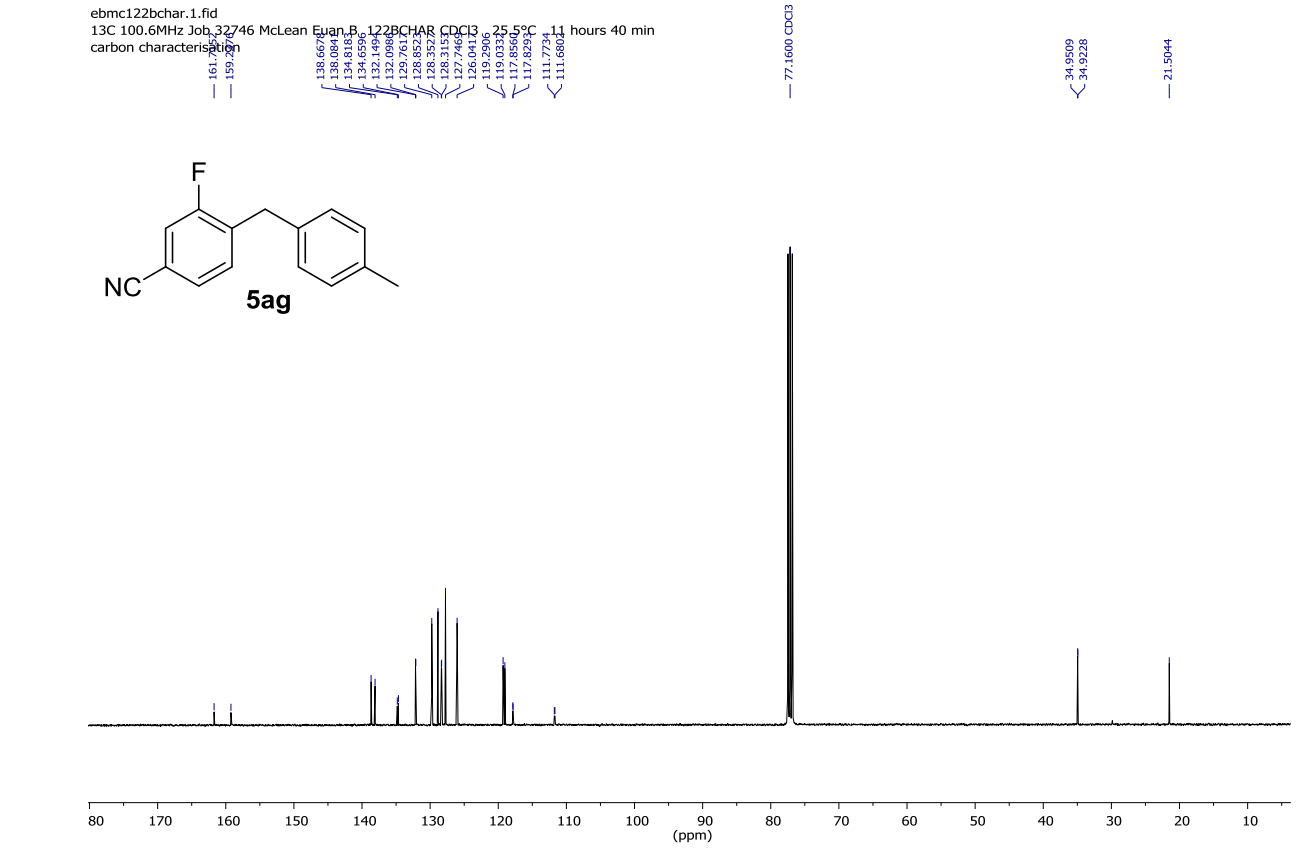

ebmh109char.1.fid
1H 400.1MHz Job 31707 McLean Euan B 109CHAR CDCl3 24.9°C
proton characterisation spectrum
NC
5ad
B (d) 7.28
A (d) 7.56
C (d) 7.12
D (d) 7.05
F (s) 3.99
G (s) 2.33
1.69
1.86
2.17
2.00
1.88
3.49
(ppm)


ebmc109char.1.fid
13C 100.6MHz Job 31716 McLean Euan B 109CHAR CDCl3 24.9°C 3 hours 53 min
carbon characterisation spectrum
NC
5ad
(ppm)

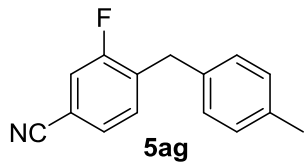

ebmh132char.1.fid
1H 400.1MHz Job 32997 McLean Euan B 132CHAR CDCl3 24.9°C
proton chracterisation
Br
NC
5af
B (dd) 7.50
E (d) 7.06
A (d) 7.86
C (d) 7.19
D (d) 7.14
F (s) 4.11
G (s) 2.34
(ppm)


ebmc132char.1.fid
13C 100.6MHz Job 33002 McLean Euan B 132CHAR CDCl3 25.5°C
carbon characterisation
Br
NC
5af
(ppm)


ebmh122bchar.1.fid
1H 400.1MHz Job 32723 McLean Euan B 122BCHAR CDCl3 25.0°C
proton characterisation
F
NC
5ag
F (m) 7.20
C (m) 7.06
D (m) 7.35
B (m) 6.99
E (m) 7.24
A (s) 4.00
G (s) 2.33
(ppm)

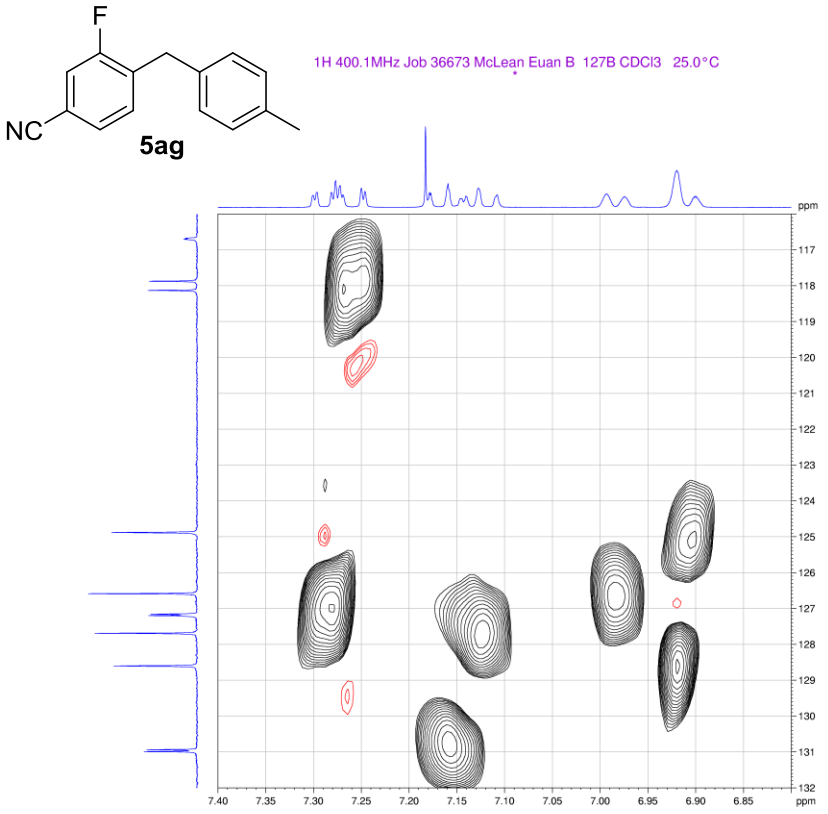

ebmc122bchar.1.fid
13C 100.6MHz Job 32746 McLean Euan B 122BCHAR CDCl3 25.5°C 11 hours 40 min
carbon characterisation
77.1600 CDCl3
34.9509
34.9228
21.5044
F
NC
5ag
(ppm)

ebmf122bchar.1.fid
19F 376.5MHz Job 32774 McLean Euan B 122BCHAR CDCl3 24.9°C 0hours 1min
fluorine characterisation

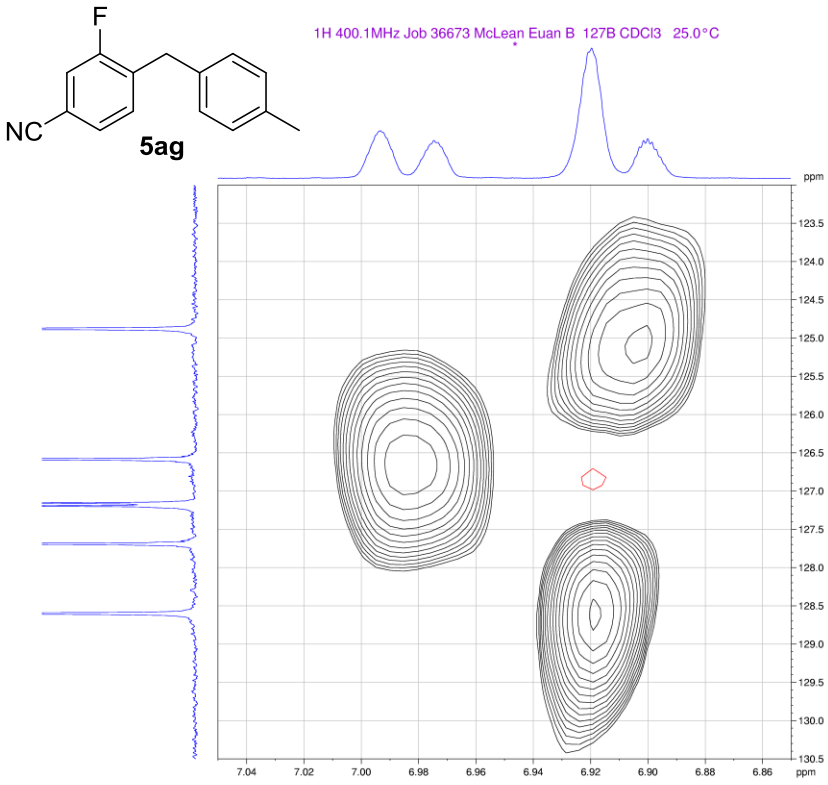


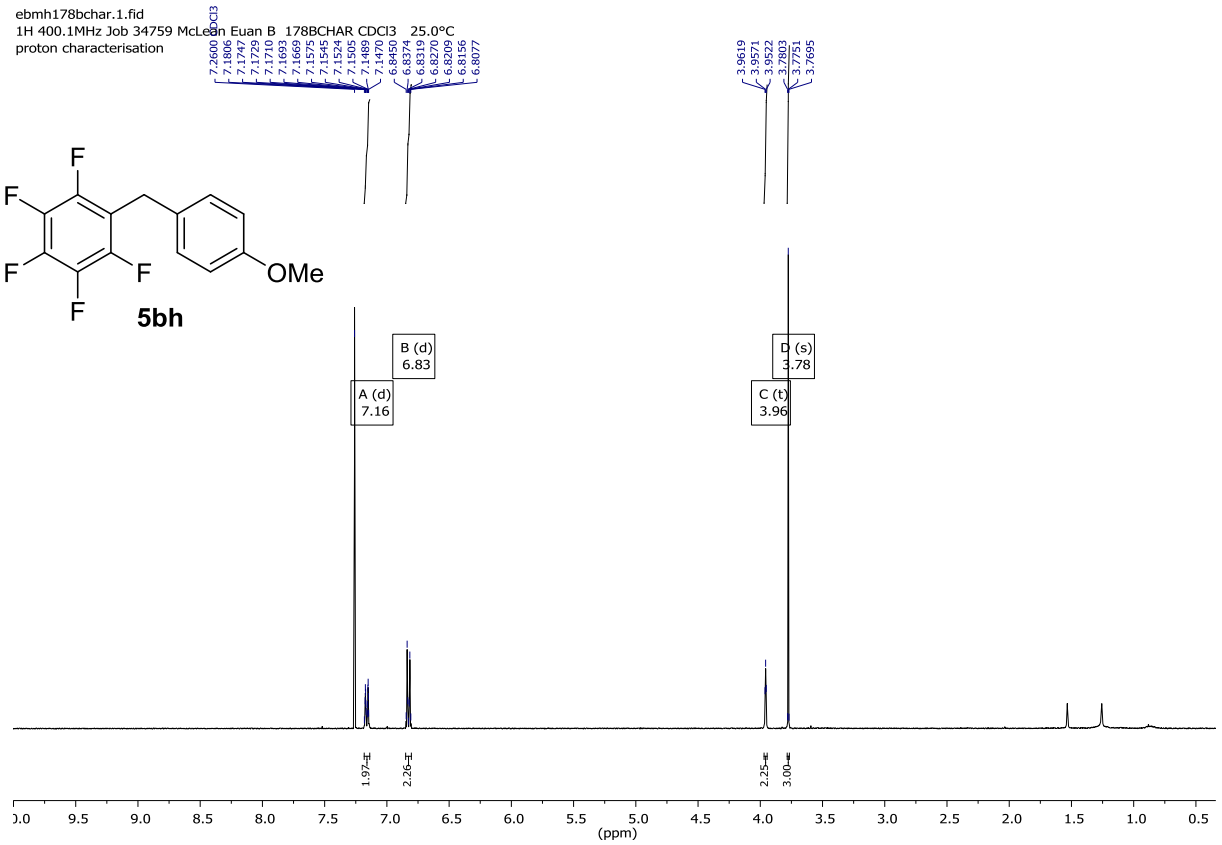
5ag

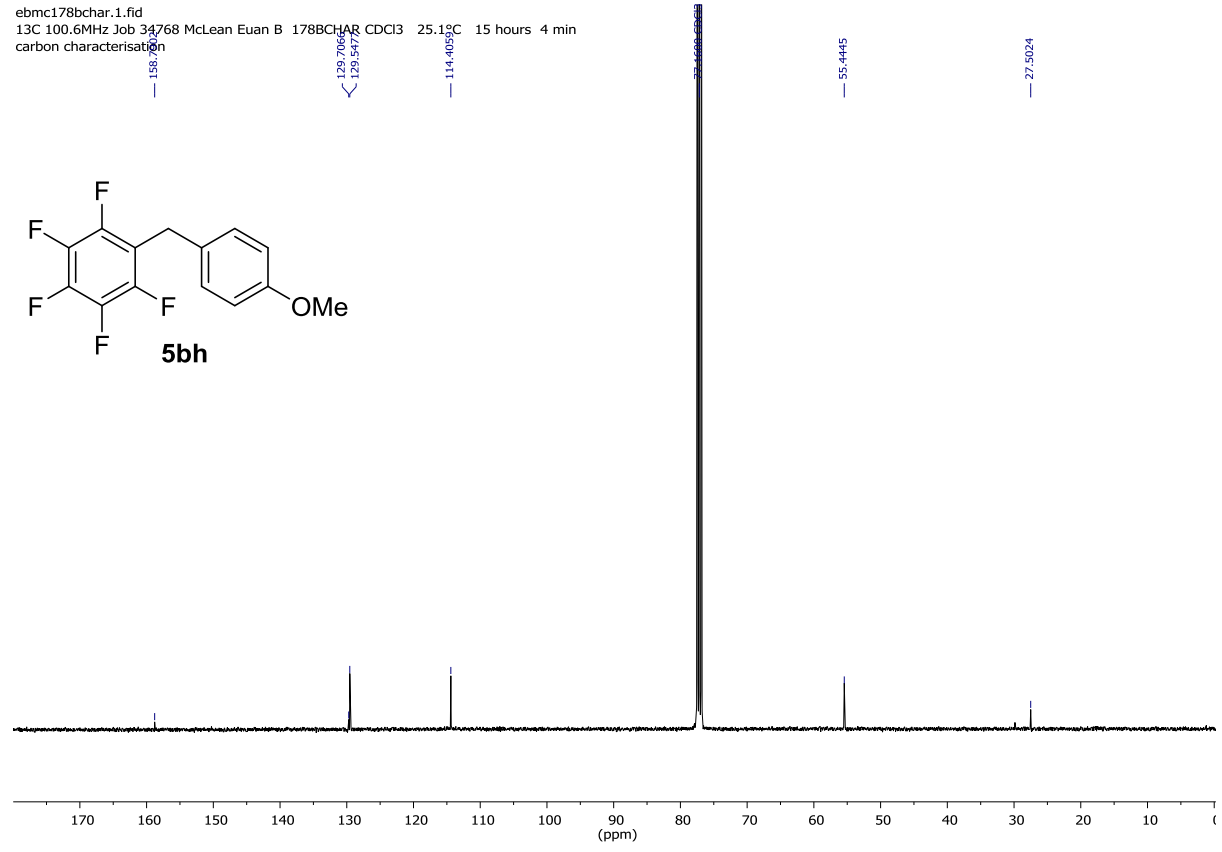
HSQC:



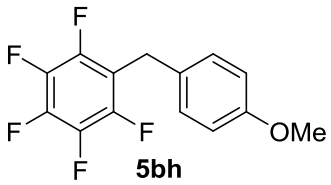
Expansion:



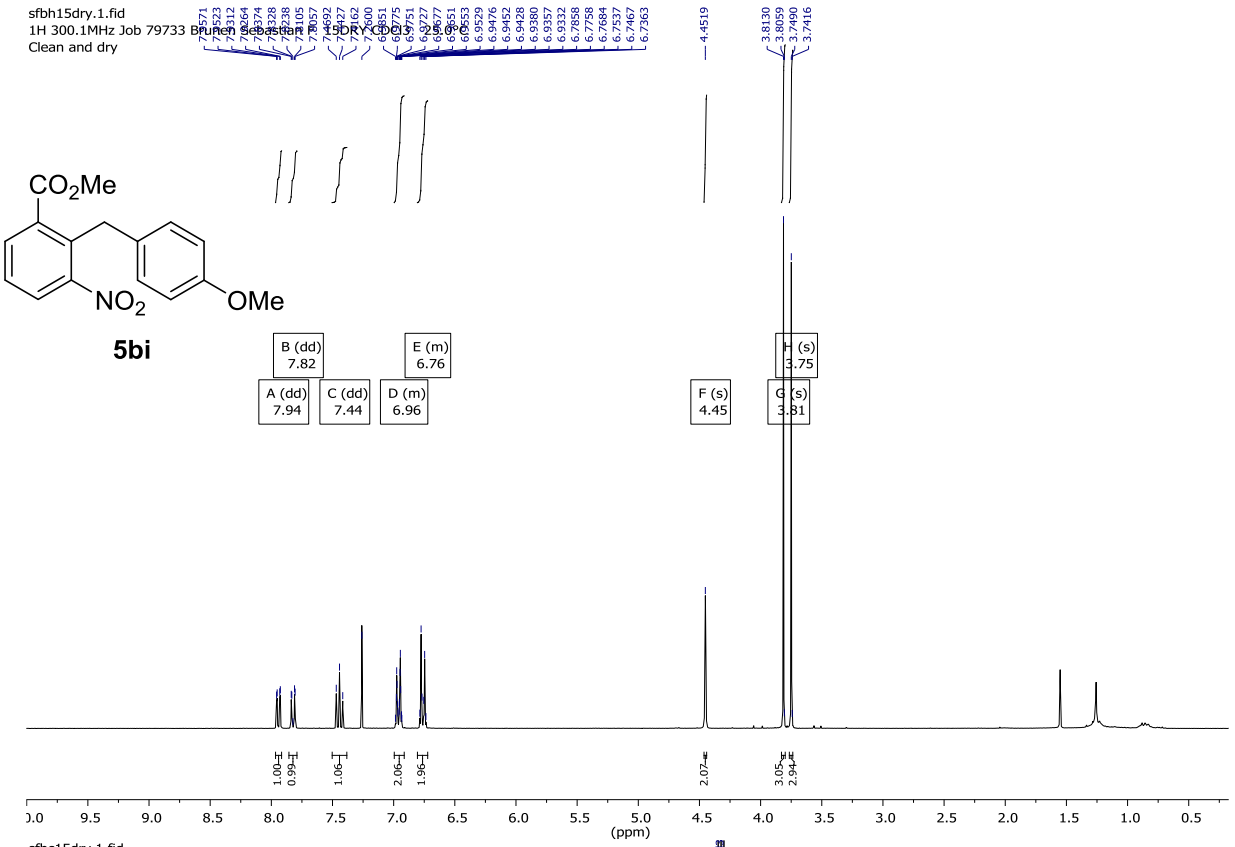

ebmh178bchar.1.fid
1H 400.1MHz Job 34759 McLean Euan B 178BCHAR CDCl3 25.0°C
proton characterisation
F
F
F
F
F
OMe
5bh
A (d)
7.16
B (d)
6.83
C (t)
3.96
D (s)
3.78
1.97
2.26
2.25
3.00
(ppm)

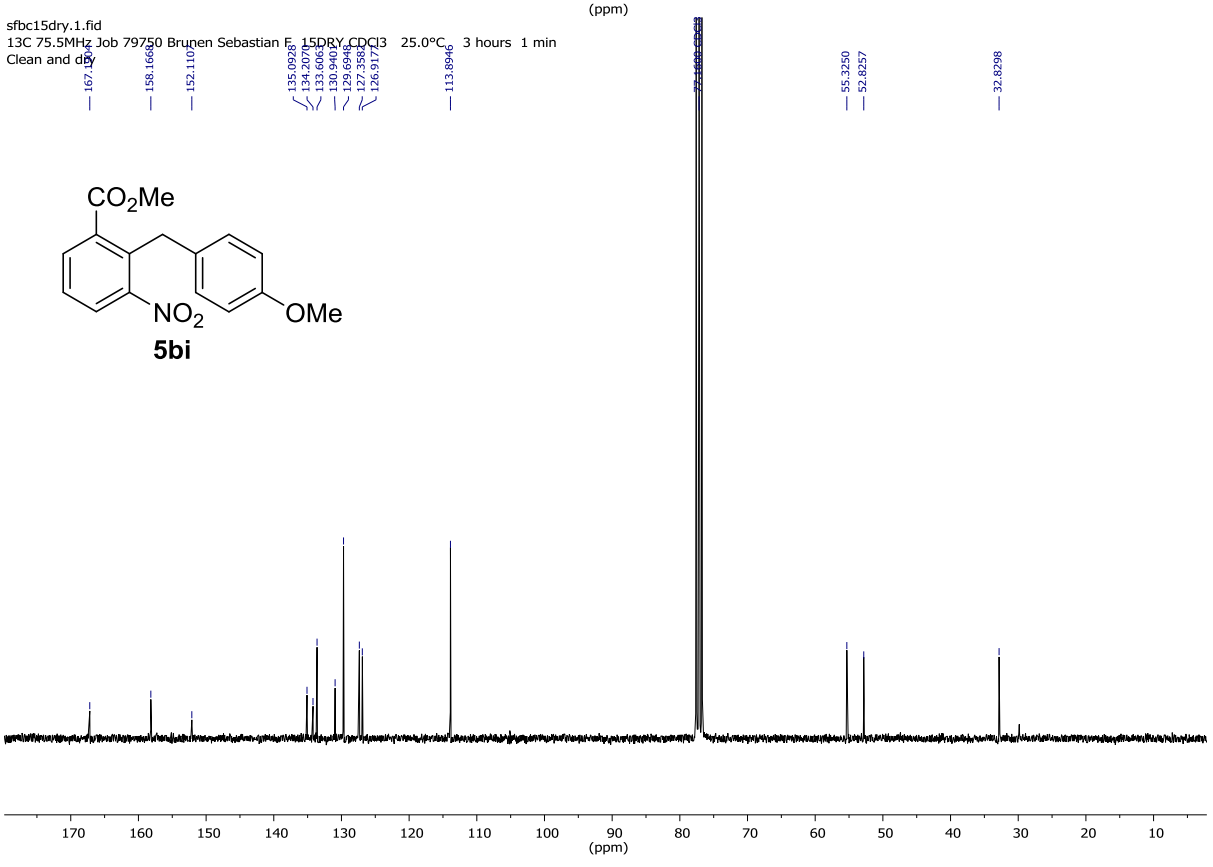

ebmc178bchar.1.fid
13C 100.6MHz Job 34768 McLean Euan B 178BCHAR CDCl3 25.1°C 15 hours 4 min
carbon characterisation
158.7020
129.7065
129.5477
114.4059
77.1600
55.4445
27.5024
F
F
F
F
F
OMe
5bh
(ppm)

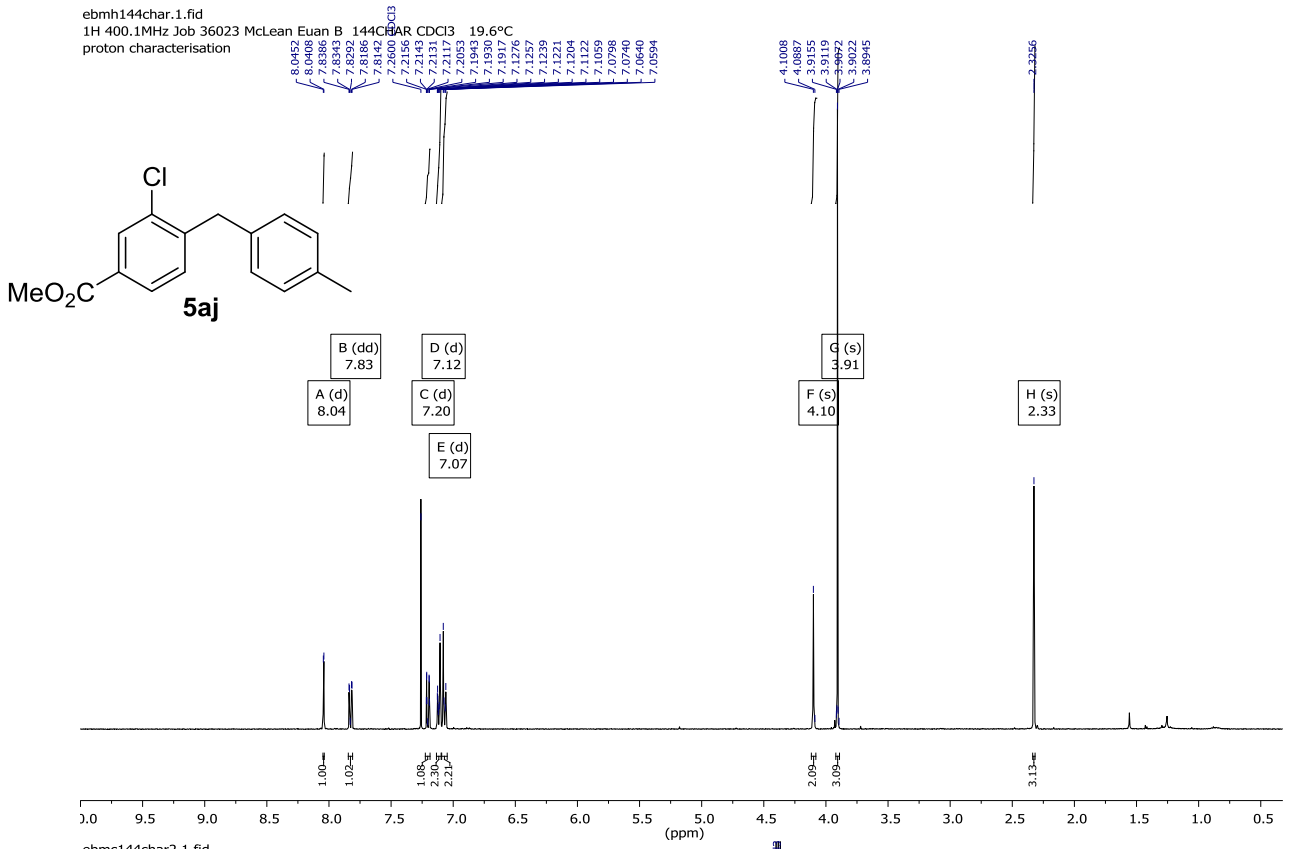
ebmf178bchar.1.fid
19F 376.5MHz Job 34760 McLean Euan B 178BCHAR CDCl3 25.0°C 0hours 5min
fluorine characterisation

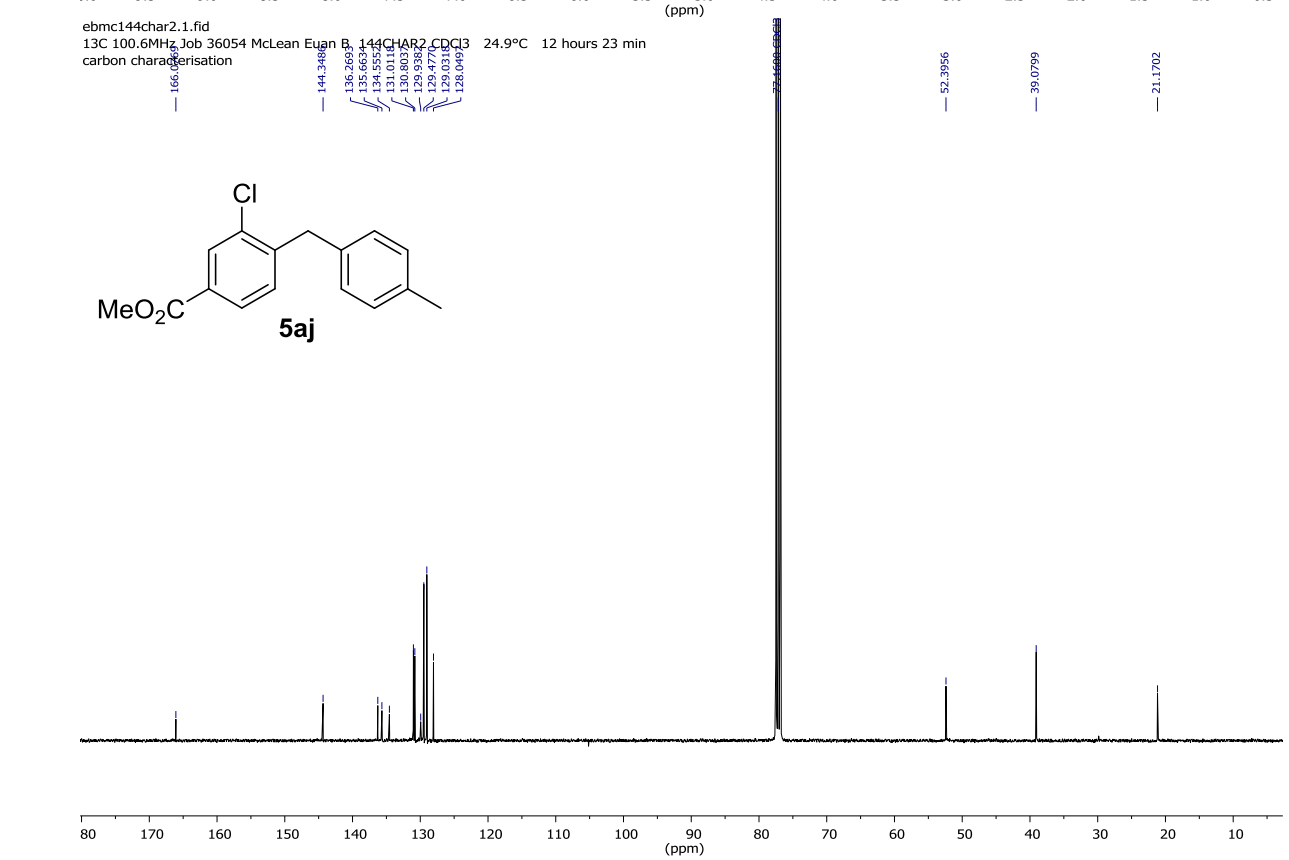


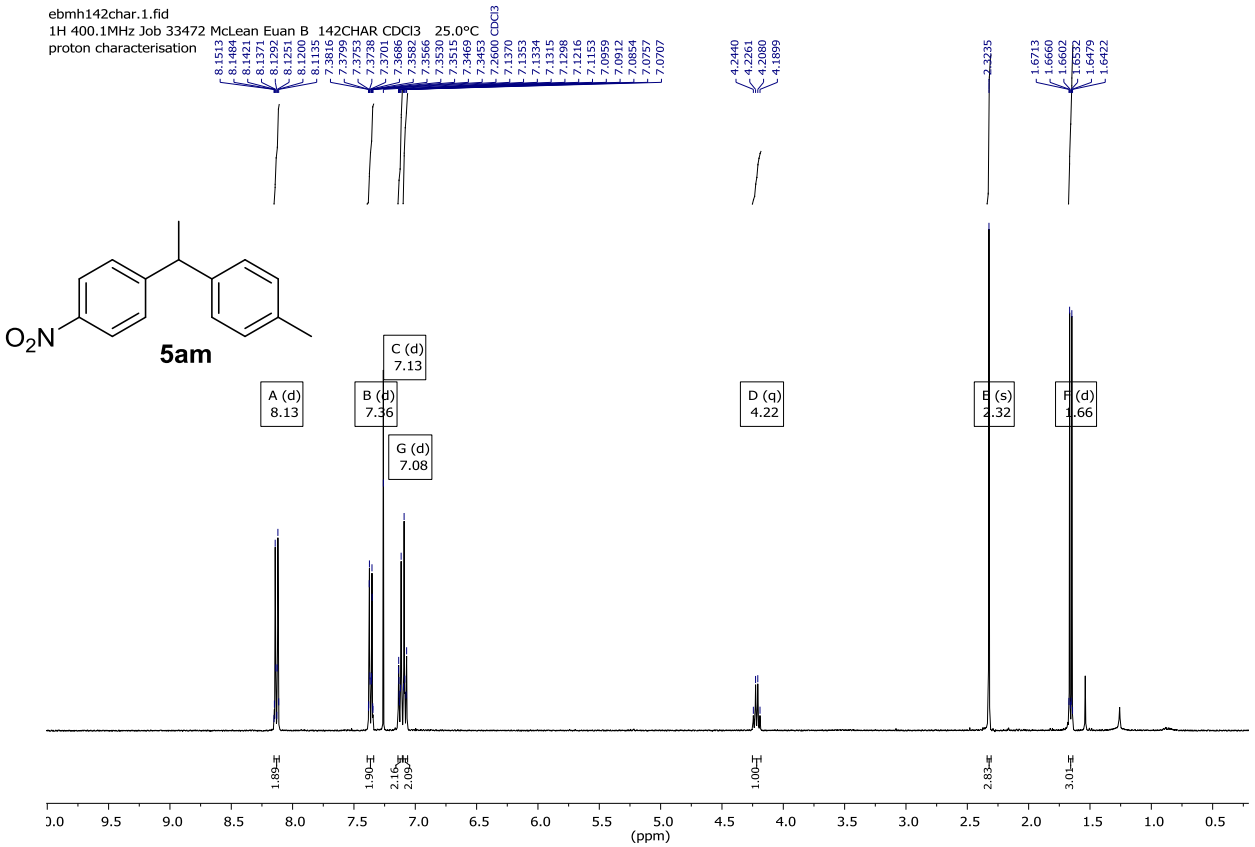
5bh

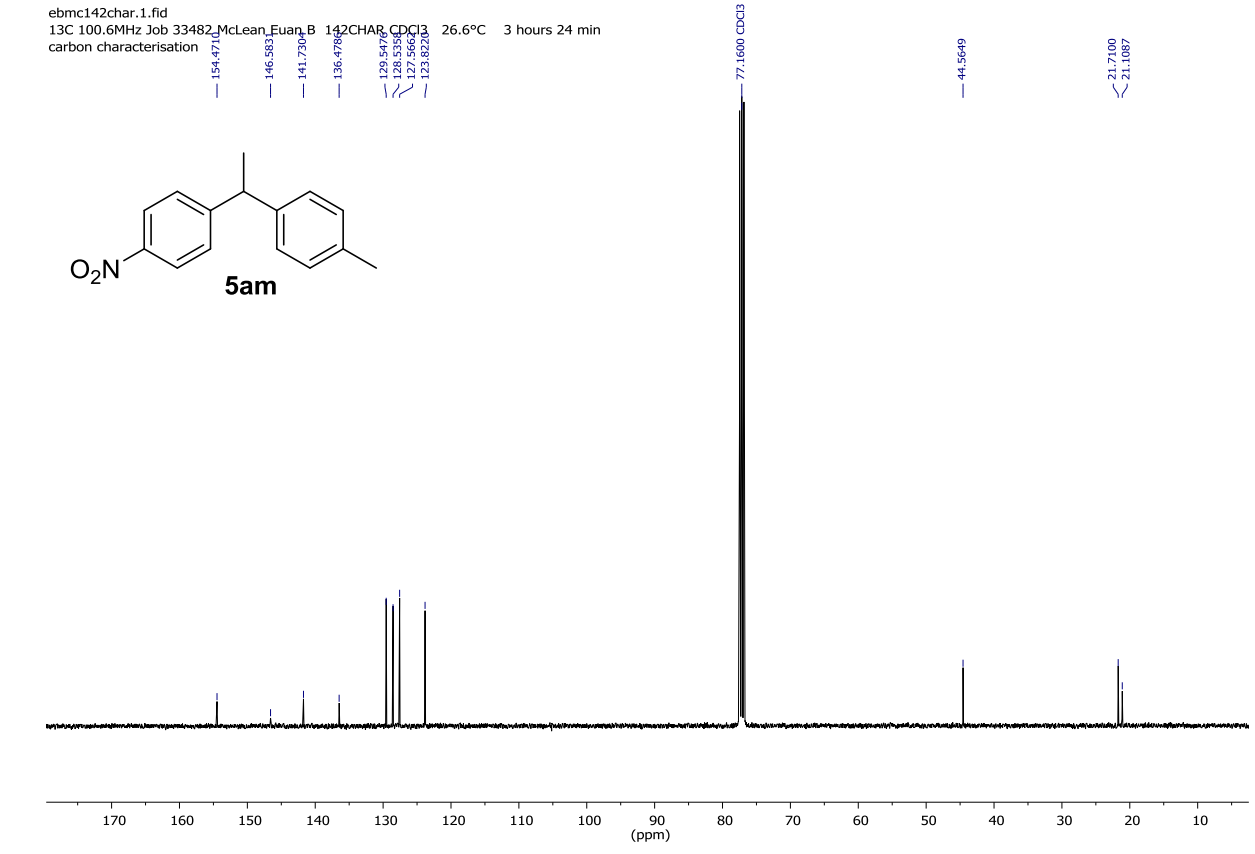

sfbh15dry.1.fid
1H 300.1MHz Job 79733 Brunen Sebastian F 15DRY CDCl3 25.0°C
Clean and dry
CO2Me
NO2
OMe
5bi
B (dd) 7.82
E (m) 6.76
H (s) 3.75
A (dd) 7.94
C (dd) 7.44
D (m) 6.96
F (s) 4.45
G (s) 3.81
(ppm)


sfbc15dry.1.fid
13C 75.5MHz Job 79750 Brunen Sebastian F 15DRY CDCl3 25.0°C 3 hours 1 min
Clean and dry
CO2Me
NO2
OMe
5bi
(ppm)

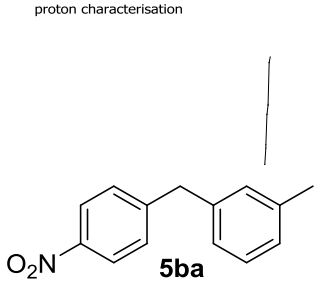

ebmh144char.1.fid
1H 400.1MHz Job 36023 McLean Euan B 144CHAR CDCl3 19.6°C
proton characterisation
Cl
MeO2C
5aj
A (d) 8.04
B (dd) 7.83
C (d) 7.20
D (d) 7.12
E (d) 7.07
F (s) 4.10
G (s) 3.91
H (s) 2.33
(ppm)


ebmc144char2.1.fid
13C 100.6MHz Job 36054 McLean Euan B 144CHAR2 CDCl3 24.9°C 12 hours 23 min
carbon characterisation
Cl
MeO2C
5aj
(ppm)


ebmh142char.1.fid
1H 400.1MHz Job 33472 McLean Euan B 142CHAR CDCl3 25.0°C
proton characterisation
5am
A (d) 8.13
B (d) 7.36
C (d) 7.13
D (q) 4.22
E (s) 2.32
F (d) 1.66
G (d) 7.08
(ppm)

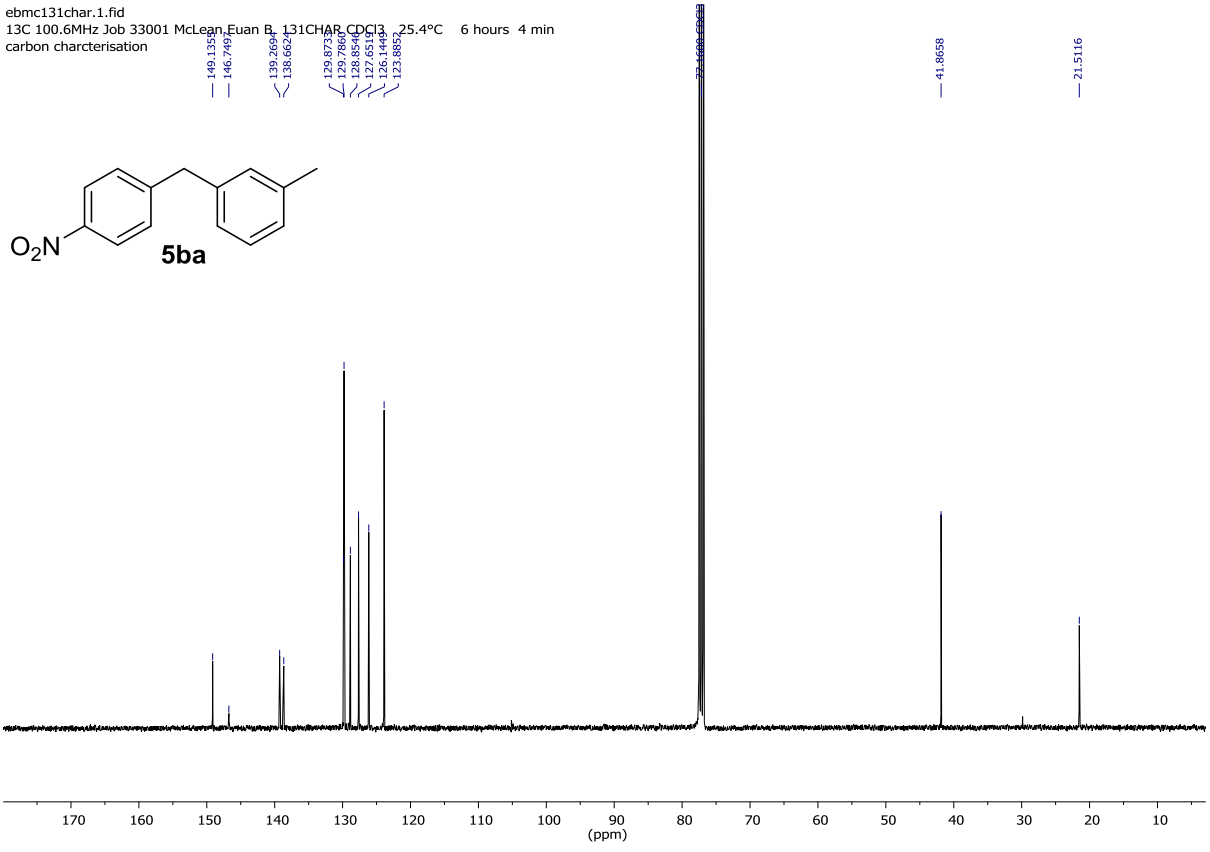

ebmc142char.1.fid
13C 100.6MHz Job 33482 McLean Euan B 142CHAR CDCl3 26.6°C 3 hours 24 min
carbon characterisation
5am
77.1600 CDCl3
(ppm)

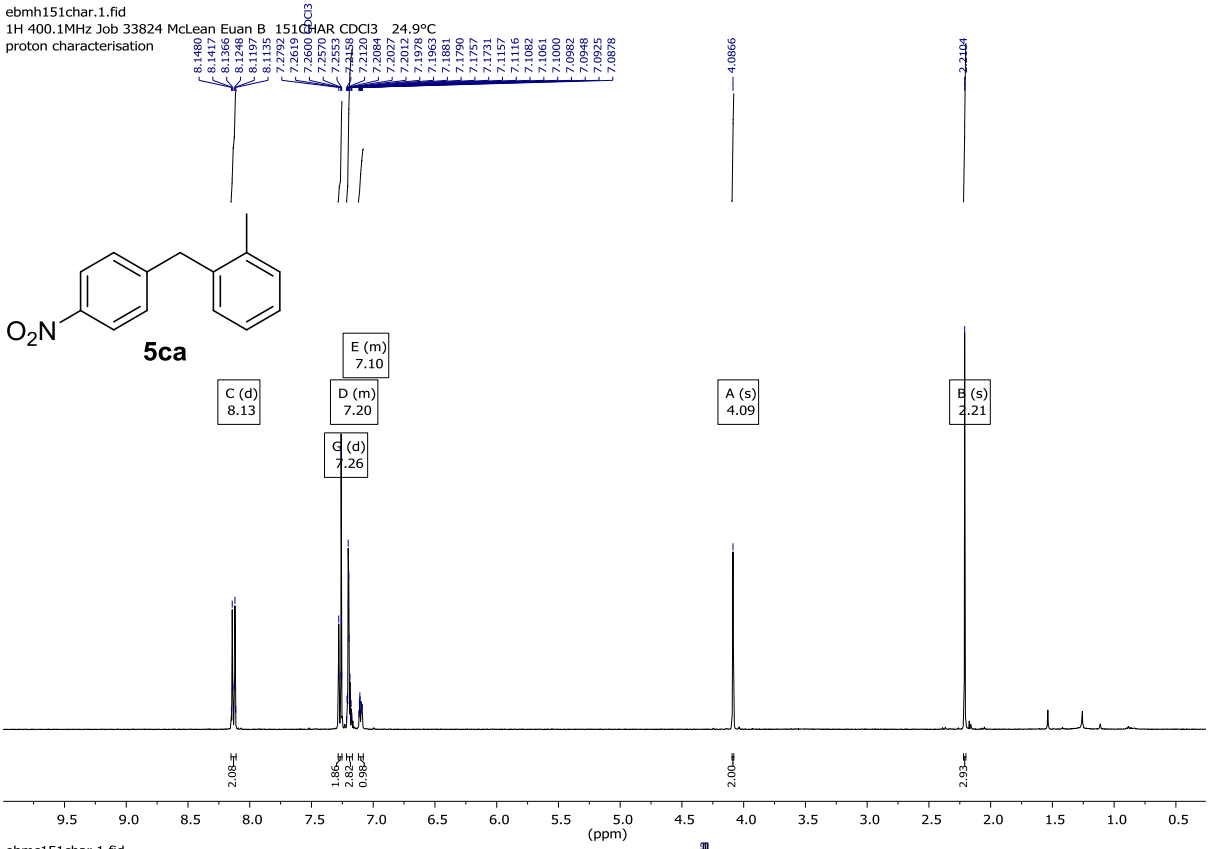
ebmh131char.1.fid
1H 400.1MHz Job 32996 McLean Euan B 131CHAR CDCl3 25.0°C
proton characterisation

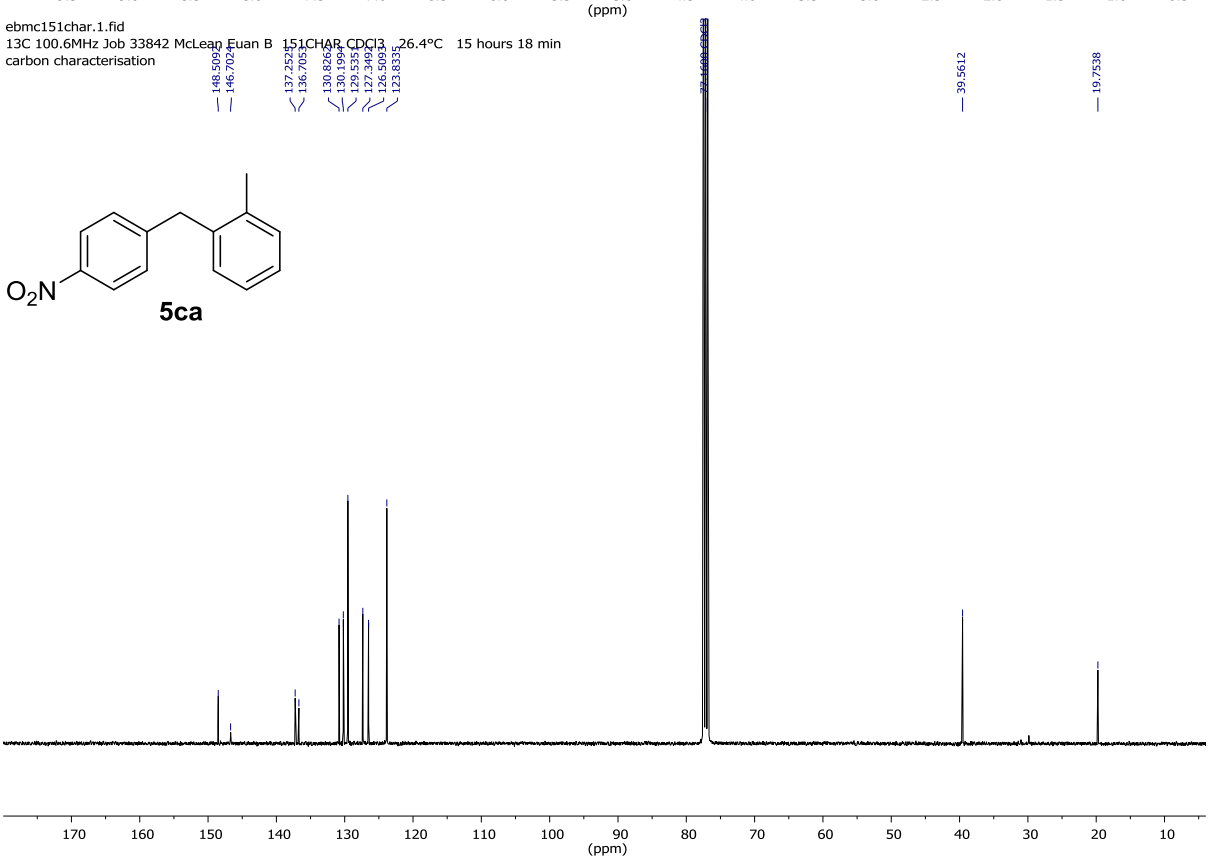


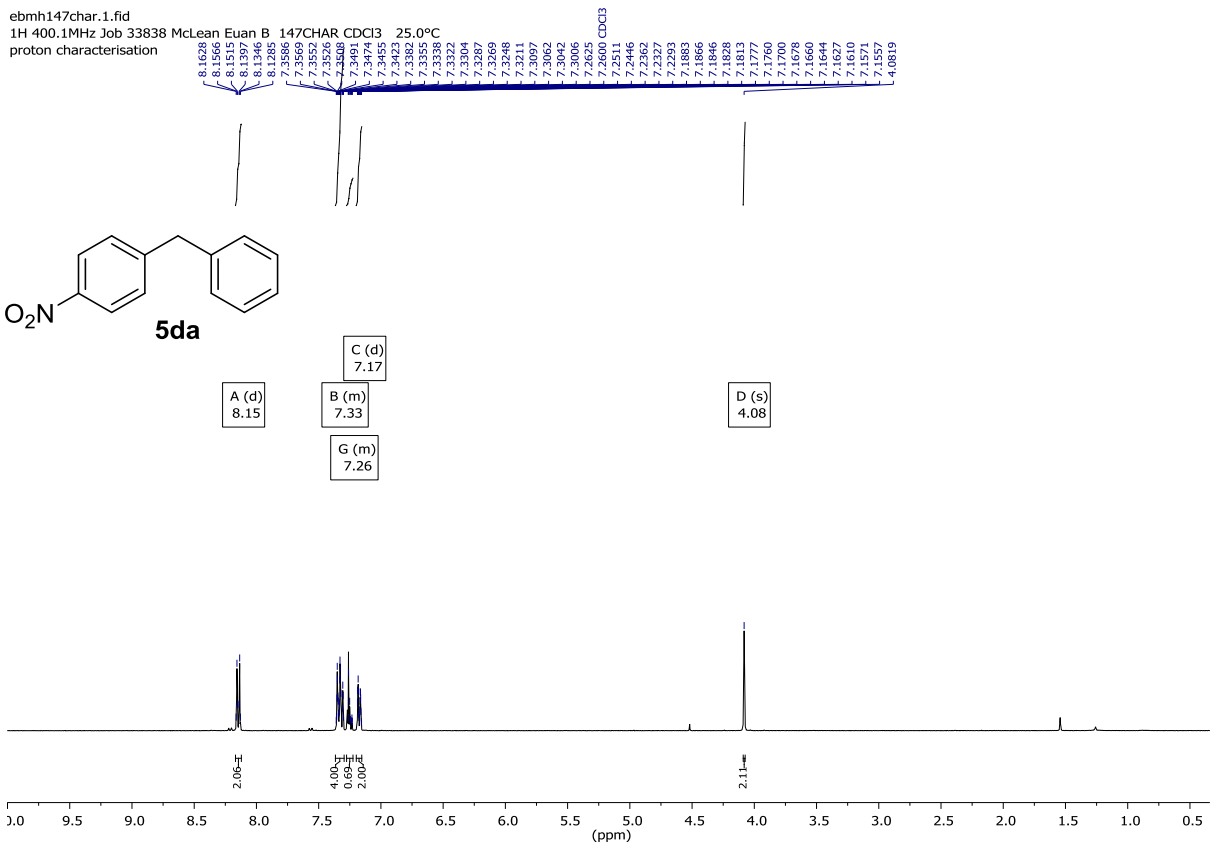
5ba

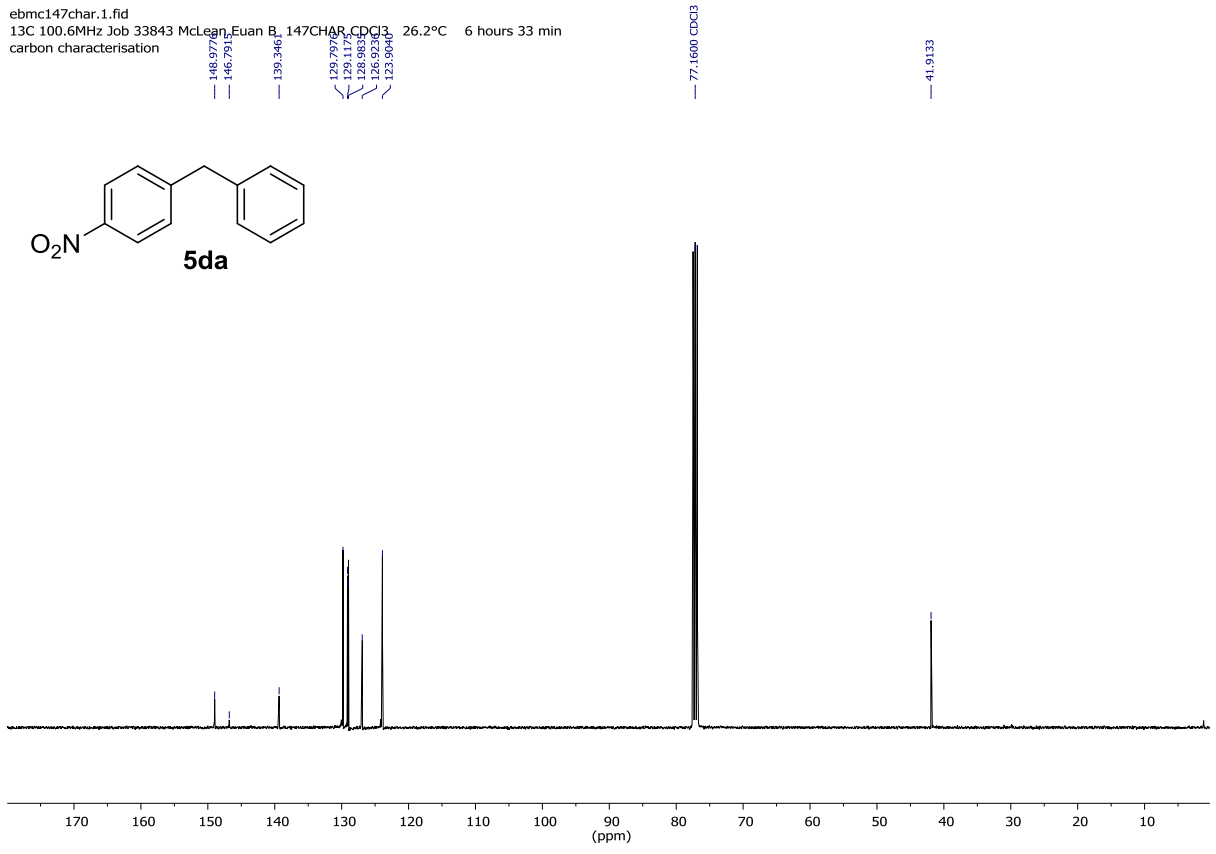
ebmc131char.1.fid
13C 100.6MHz Job 33001 McLean Euan B 131CHAR CDCl3 25.4°C 6 hours 4 min
carbon charcterisation

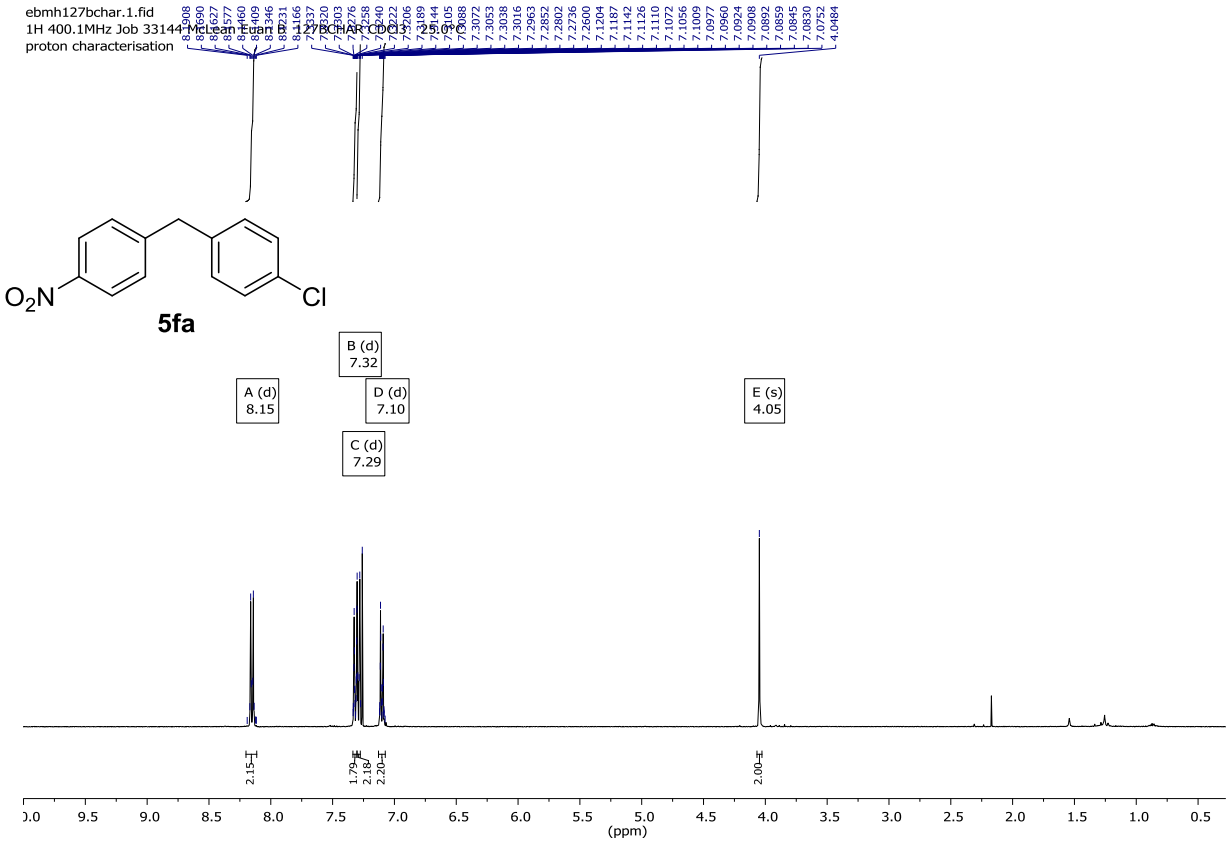


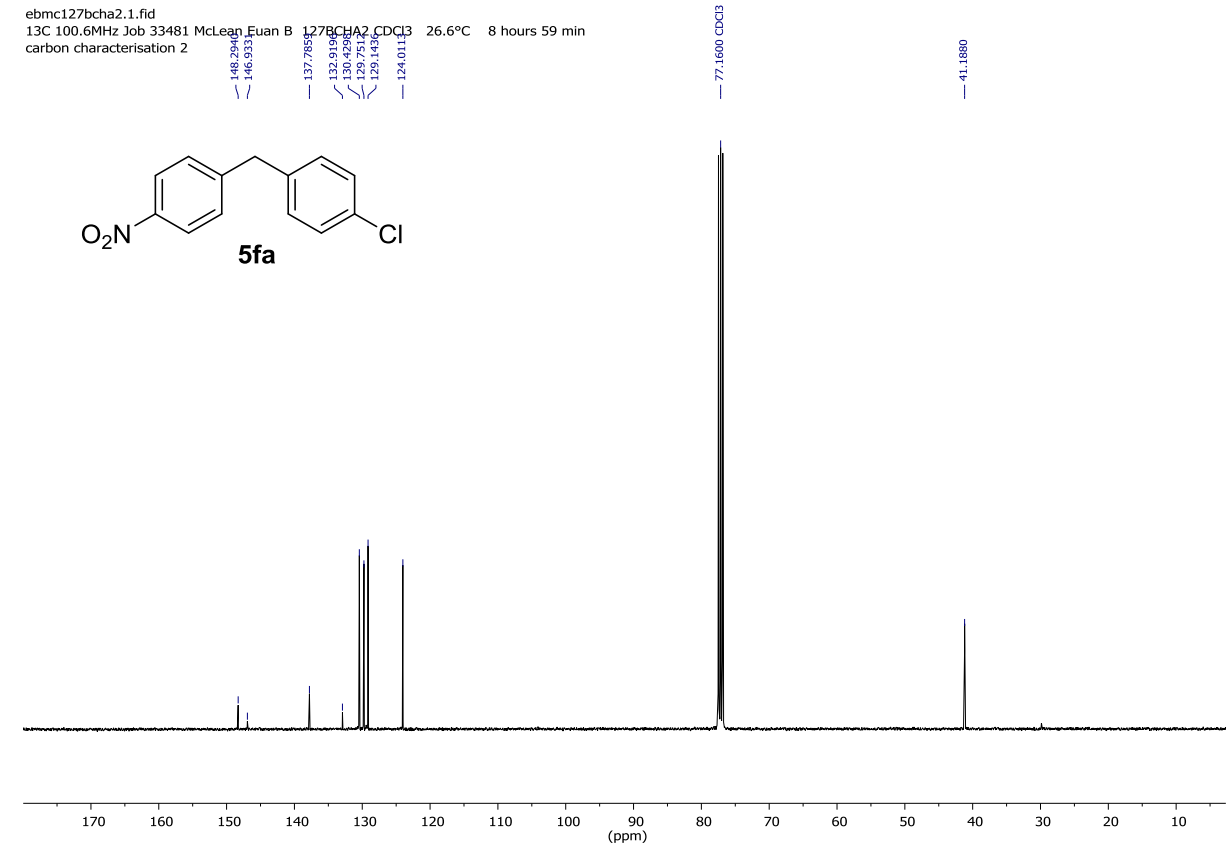

ebmh151char.1.fid
1H 400.1MHz Job 33824 McLean Euan B 151CHAR CDCl3 24.9°C
proton characterisation
O2N
5ca
C (d) 8.13
D (m) 7.20
E (m) 7.10
G (d) 7.26
A (s) 4.09
B (s) 2.21
(ppm)

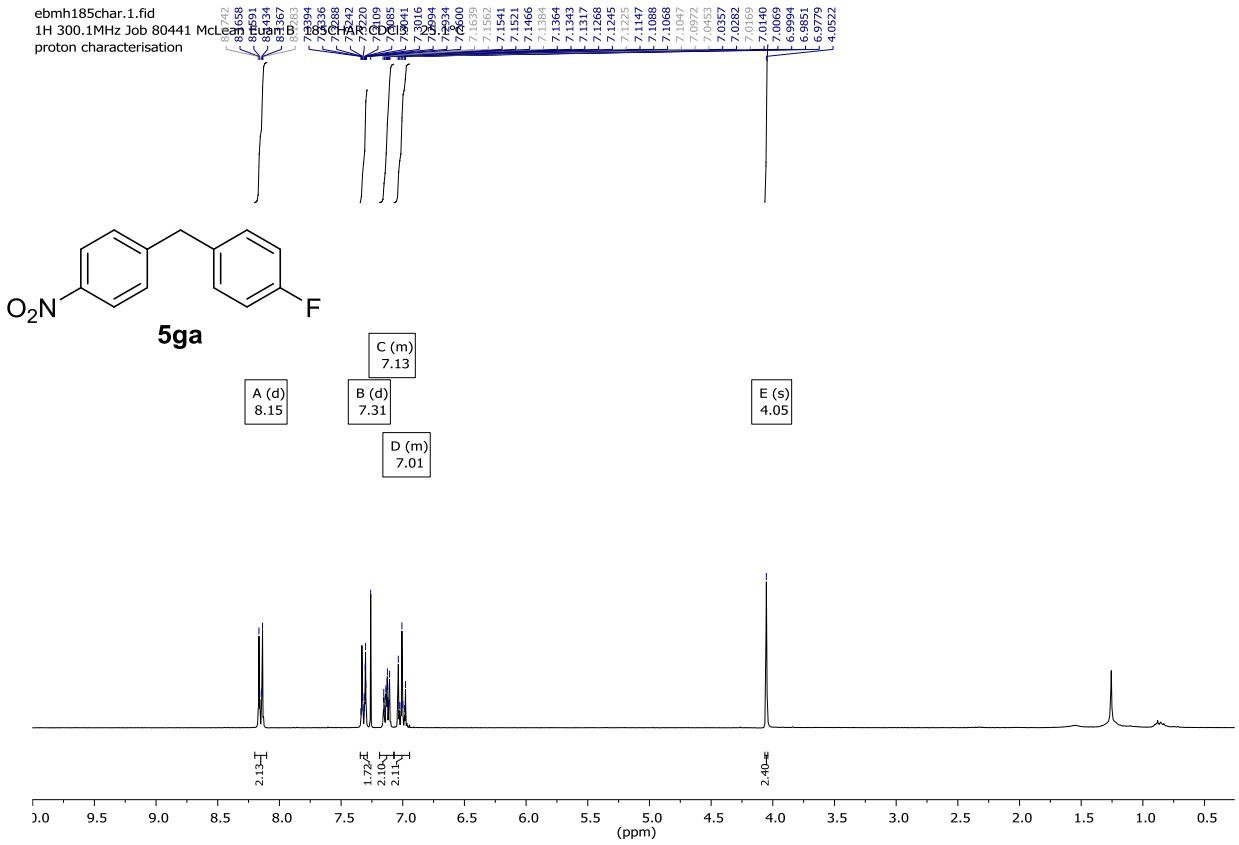

ebmc151char.1.fid
13C 100.6MHz Job 33842 McLean Euan B 151CHAR CDCl3 26.4°C 15 hours 18 min
carbon characterisation
O2N
5ca
(ppm)

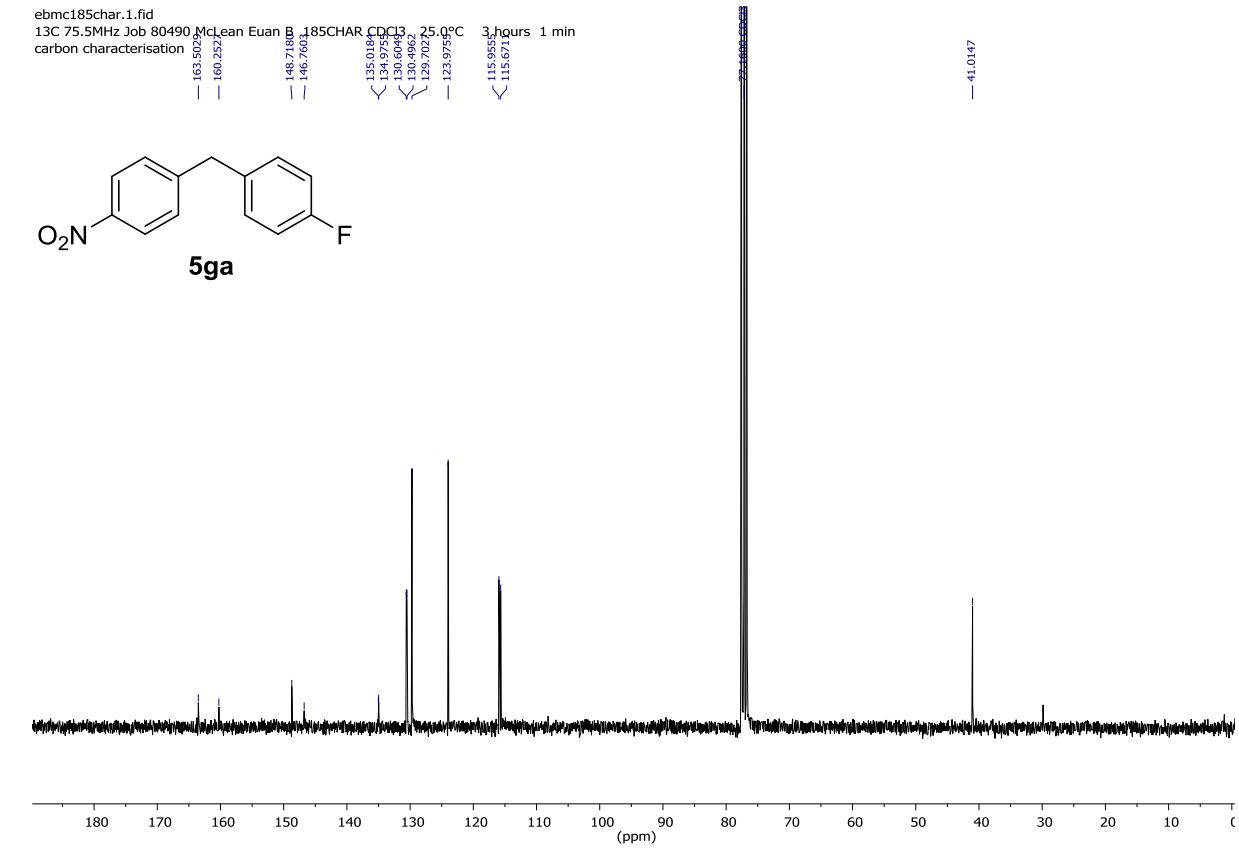

ebmh147char.1.fid
1H 400.1MHz Job 33838 McLean Euan B 147CHAR CDCl3 25.0°C
proton characterisation
8.1628 8.1566 8.1515 8.1397 8.1346 8.1285 7.3586 7.3569 7.3552 7.3526 7.3508 7.3491 7.3474 7.3455 7.3423 7.3382 7.3355 7.3338 7.3322 7.3304 7.3287 7.3269 7.3248 7.3211 7.3097 7.3062 7.3042 7.3006 7.2625 7.2600 CDCl3 7.2511 7.2446 7.2362 7.2327 7.2293 7.1883 7.1866 7.1846 7.1828 7.1813 7.1777 7.1760 7.1700 7.1678 7.1660 7.1644 7.1627 7.1610 7.1571 7.1557 4.0819
O2N
5da
A (d) 8.15
B (m) 7.33
C (d) 7.17
G (m) 7.26
D (s) 4.08
2.06
4.00
0.69
2.00
2.11
(ppm)


ebmc147char.1.fid
13C 100.6MHz Job 33843 McLean Euan B 147CHAR CDCl3 26.2°C 6 hours 33 min
carbon characterisation
148.9776 146.7915 139.3461 129.7976 129.1175 128.9833 126.9236 123.9040 77.1600 CDCl3 41.9133
O2N
5da
(ppm)

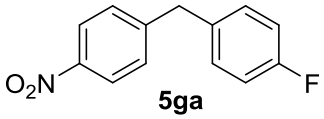

ebmh127bchar.1.fid
1H 400.1MHz Job 33144 McLean Euan B 127BCHAR CDCl3 25.0°C
proton characterisation
8.1908
8.1690
8.1627
8.1577
8.1460
8.1409
8.1346
8.1231
8.1166
7.3337
7.3320
7.3303
7.3276
7.3258
7.3240
7.3222
7.3206
7.3189
7.3144
7.3105
7.3088
7.3072
7.3053
7.3038
7.3016
7.2965
7.2852
7.2802
7.2736
7.2600
7.1204
7.1187
7.1142
7.1126
7.1110
7.1072
7.1056
7.1009
7.0977
7.0960
7.0924
7.0908
7.0892
7.0859
7.0845
7.0830
7.0752
4.0484
O2N
Cl
5fa
A (d)
8.15
B (d)
7.32
C (d)
7.29
D (d)
7.10
E (s)
4.05
2.15
1.79
2.18
2.20
2.00
(ppm)


ebmc127bcha2.1.fid
13C 100.6MHz Job 33481 McLean Euan B 127BCHA2 CDCl3 26.6°C 8 hours 59 min
carbon characterisation 2
148.2940
146.9331
137.7659
132.9196
130.4296
129.7512
129.1436
124.0111
77.1690 CDCl3
41.1880
O2N
Cl
5fa
(ppm)

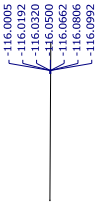

ebmh185char.1.fid
1H 300.1MHz Job 80441 McLean Euan B 185CHAR CDCl3 25.0°C
proton characterisation
5ga
A (d) 8.15
B (d) 7.31
C (m) 7.13
D (m) 7.01
E (s) 4.05
(ppm)

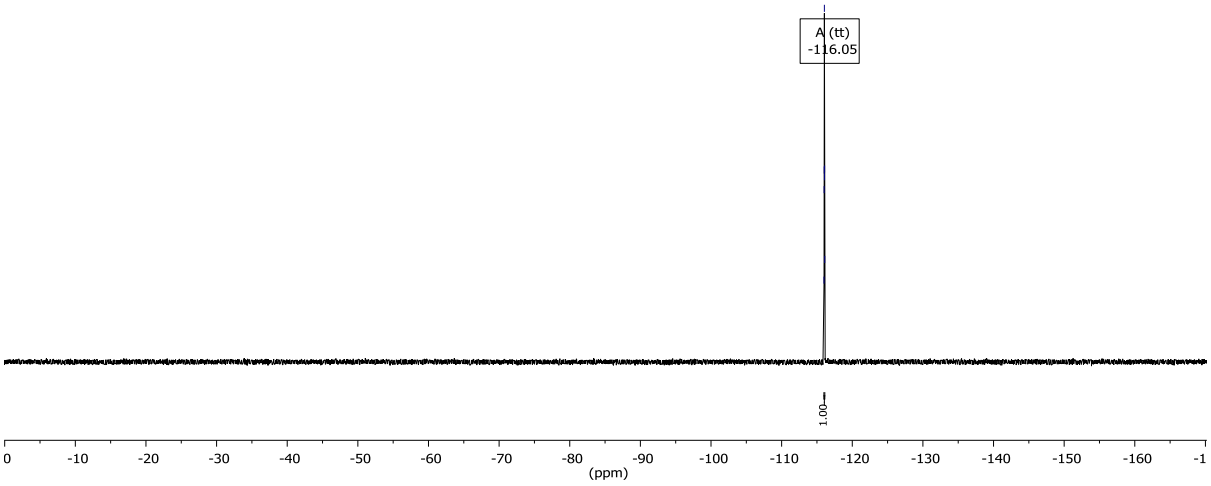

ebmc185char.1.fid
13C 75.5MHz Job 80490 McLean Euan B 185CHAR CDCl3 25.0°C 3 hours 1 min
carbon characterisation
5ga
(ppm)

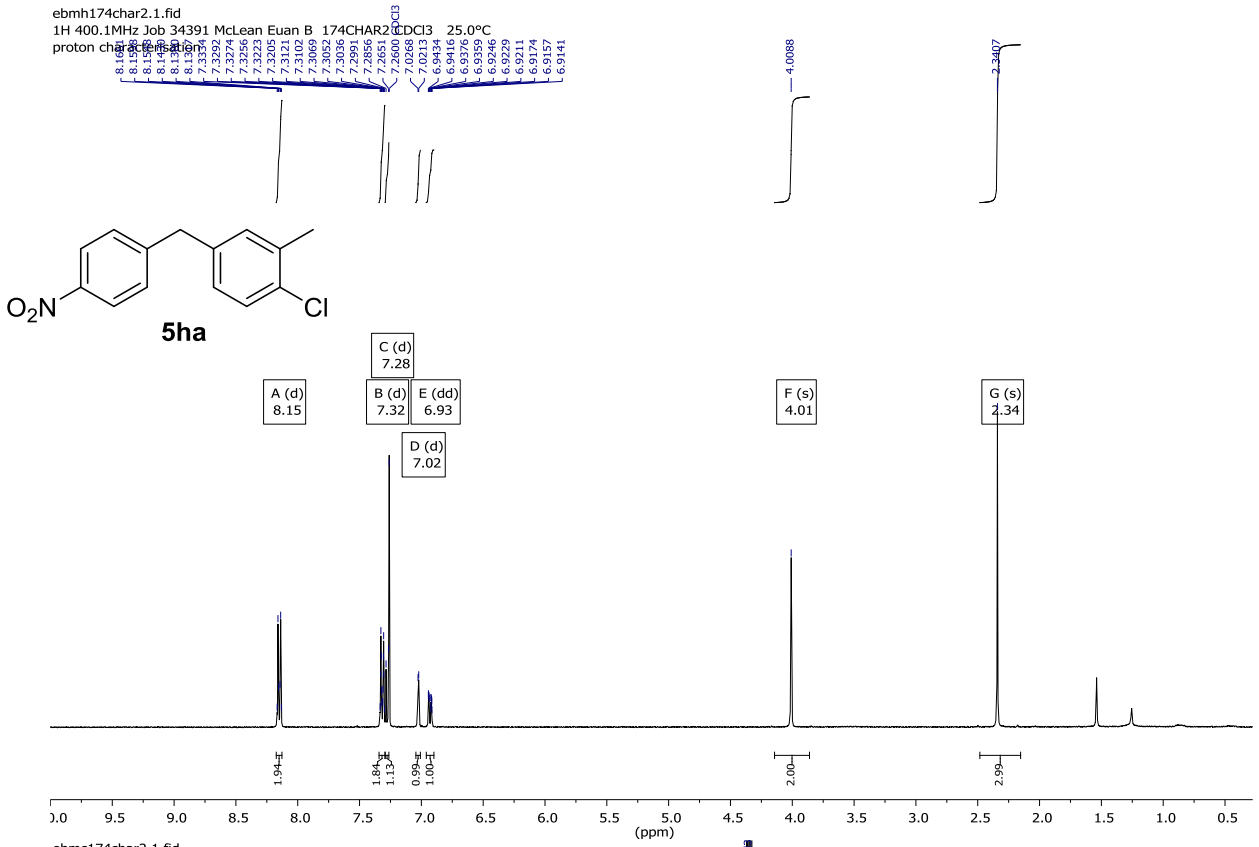
ebmf185char.1.fid
19F 282.4MHz Job 80442 McLean Euan B 185CHAR CDCl3 25.0°C 0hours 1min
fluorine characterisation

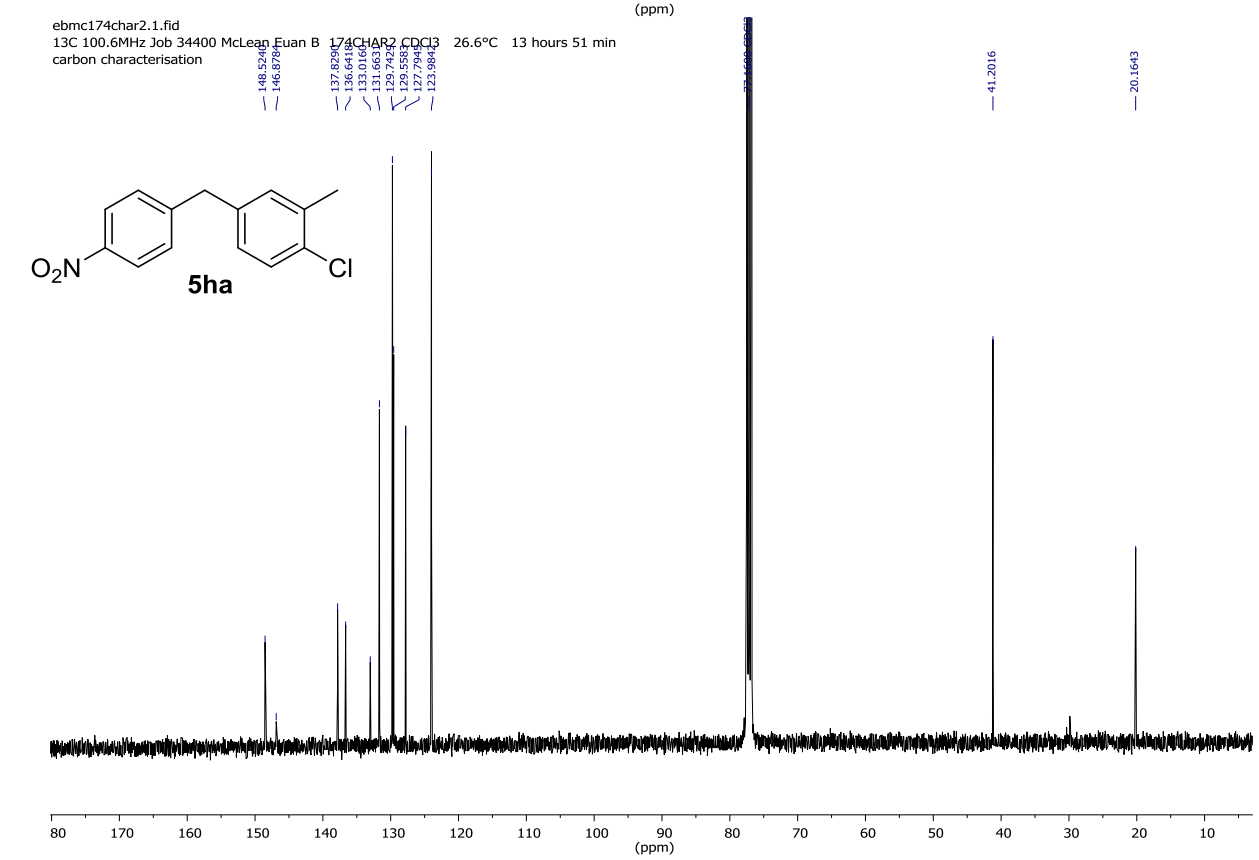


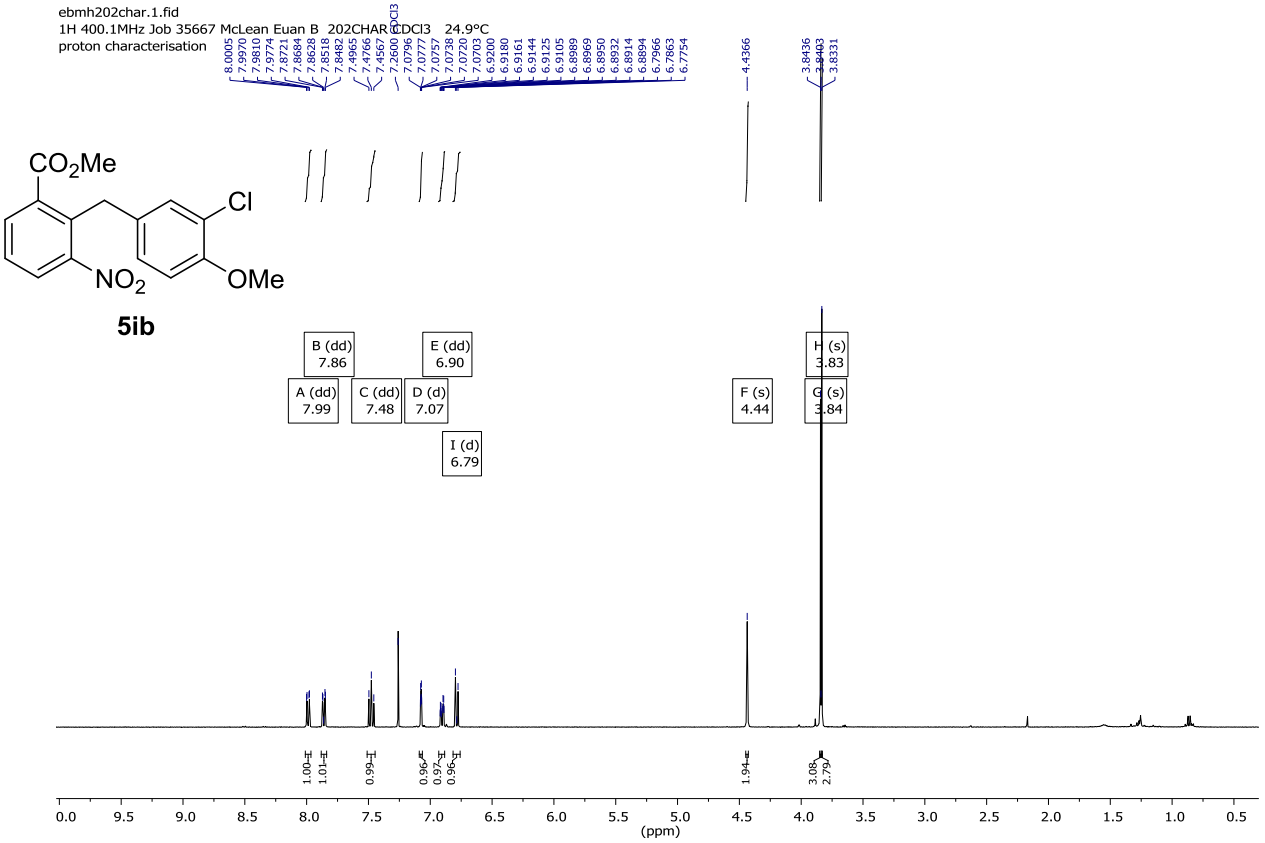
5ga

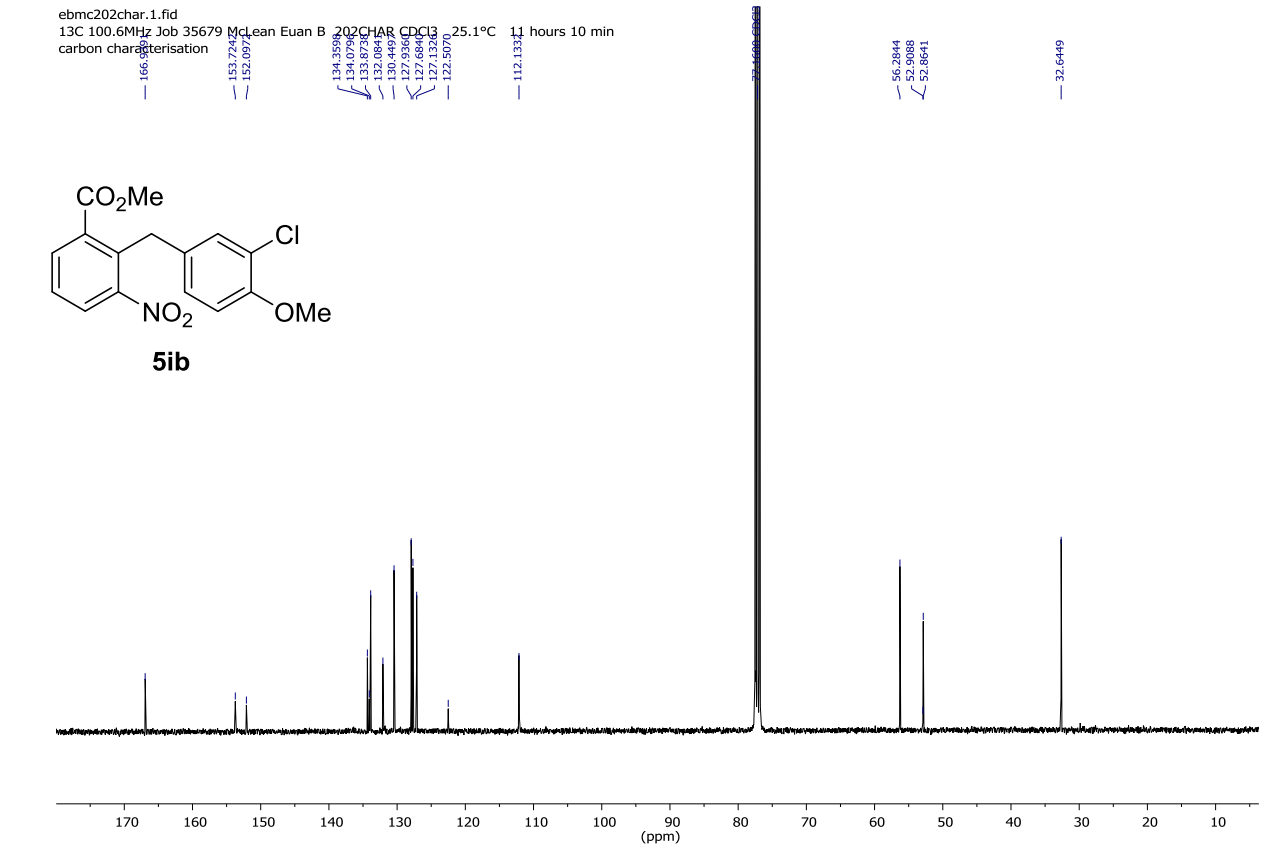


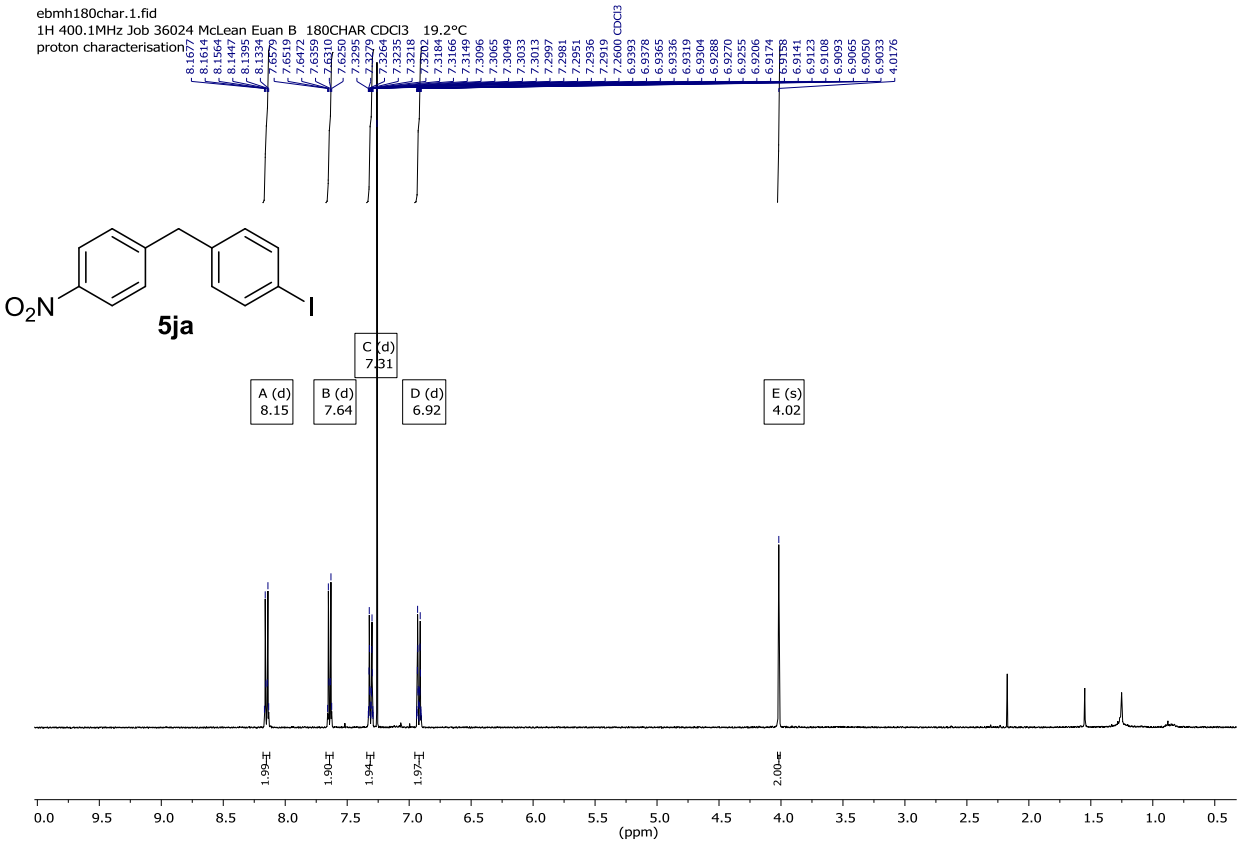


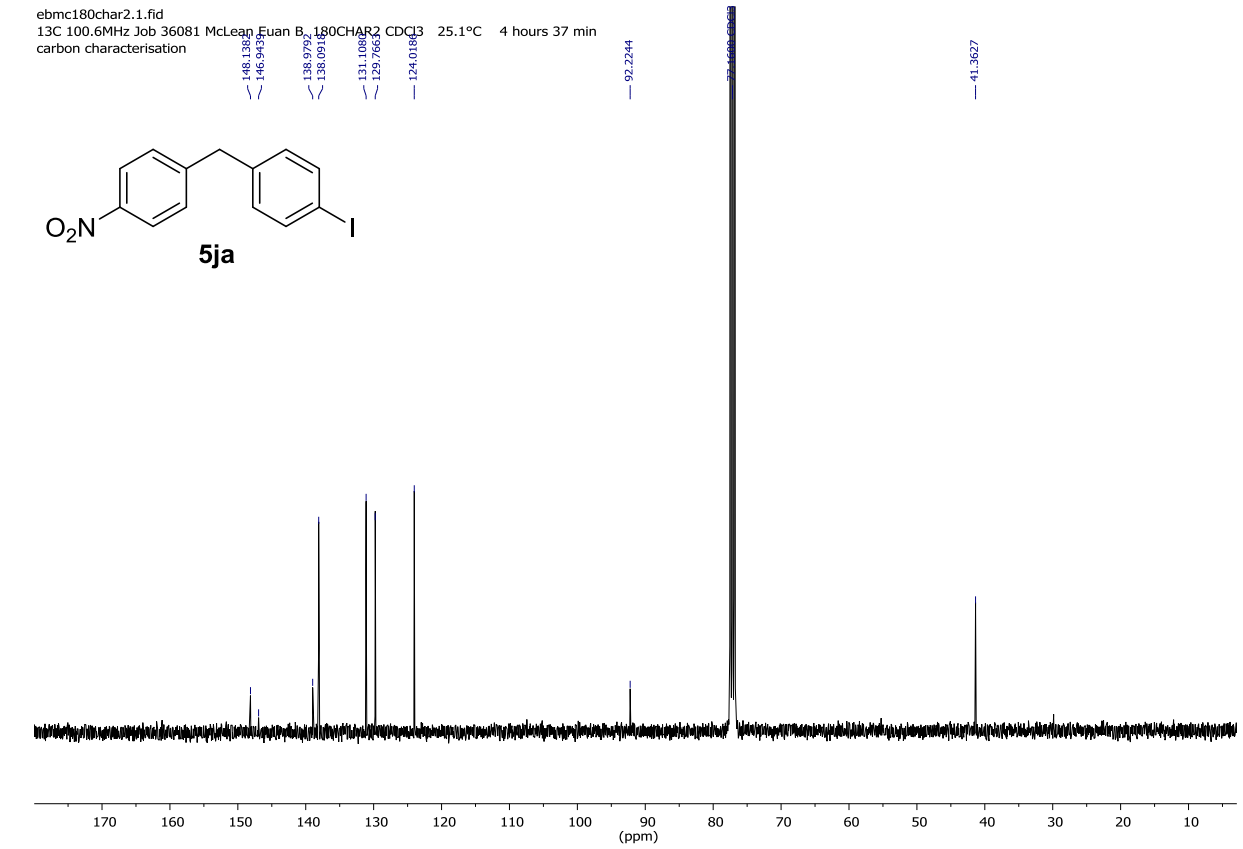

ebmh174char2.1.fid
1H 400.1MHz Job 34391 McLean Euan B 174CHAR2 CDCl3 25.0°C
proton characterisation
5ha
A (d) 8.15
B (d) 7.32
C (d) 7.28
D (d) 7.02
E (dd) 6.93
F (s) 4.01
G (s) 2.34
(ppm)


ebmc174char2.1.fid
13C 100.6MHz Job 34400 McLean Euan B 174CHAR2 CDCl3 26.6°C 13 hours 51 min
carbon characterisation
5ha
(ppm)

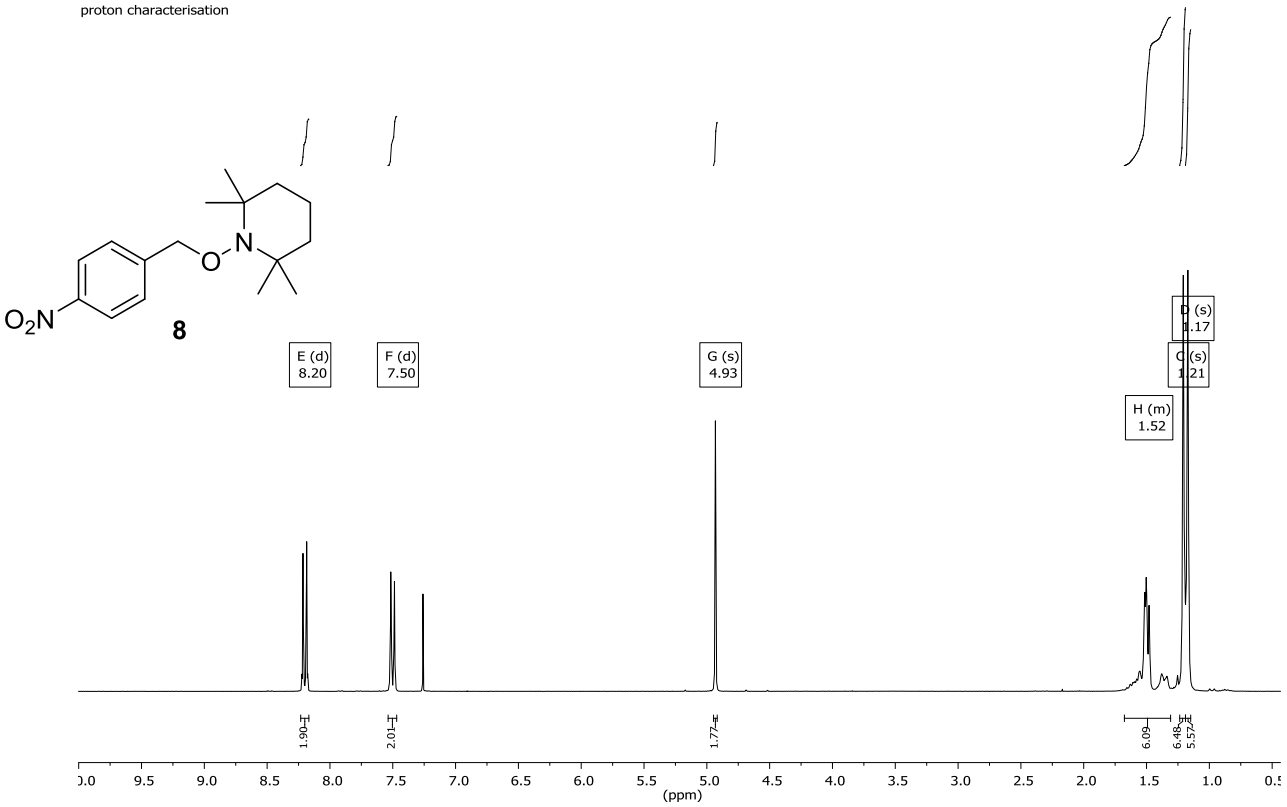

ebmh202char.1.fid
1H 400.1MHz Job 35667 McLean Euan B 202CHAR CDCl3 24.9°C
proton characterisation
CO2Me
Cl
NO2
OMe
5ib
B (dd) 7.86
E (dd) 6.90
H (s) 3.83
A (dd) 7.99
C (dd) 7.48
D (d) 7.07
F (s) 4.44
G (s) 3.84
I (d) 6.79
(ppm)


ebmc202char.1.fid
13C 100.6MHz Job 35679 McLean Euan B 202CHAR CDCl3 25.1°C 11 hours 10 min
carbon characterisation
CO2Me
Cl
NO2
OMe
5ib
(ppm)

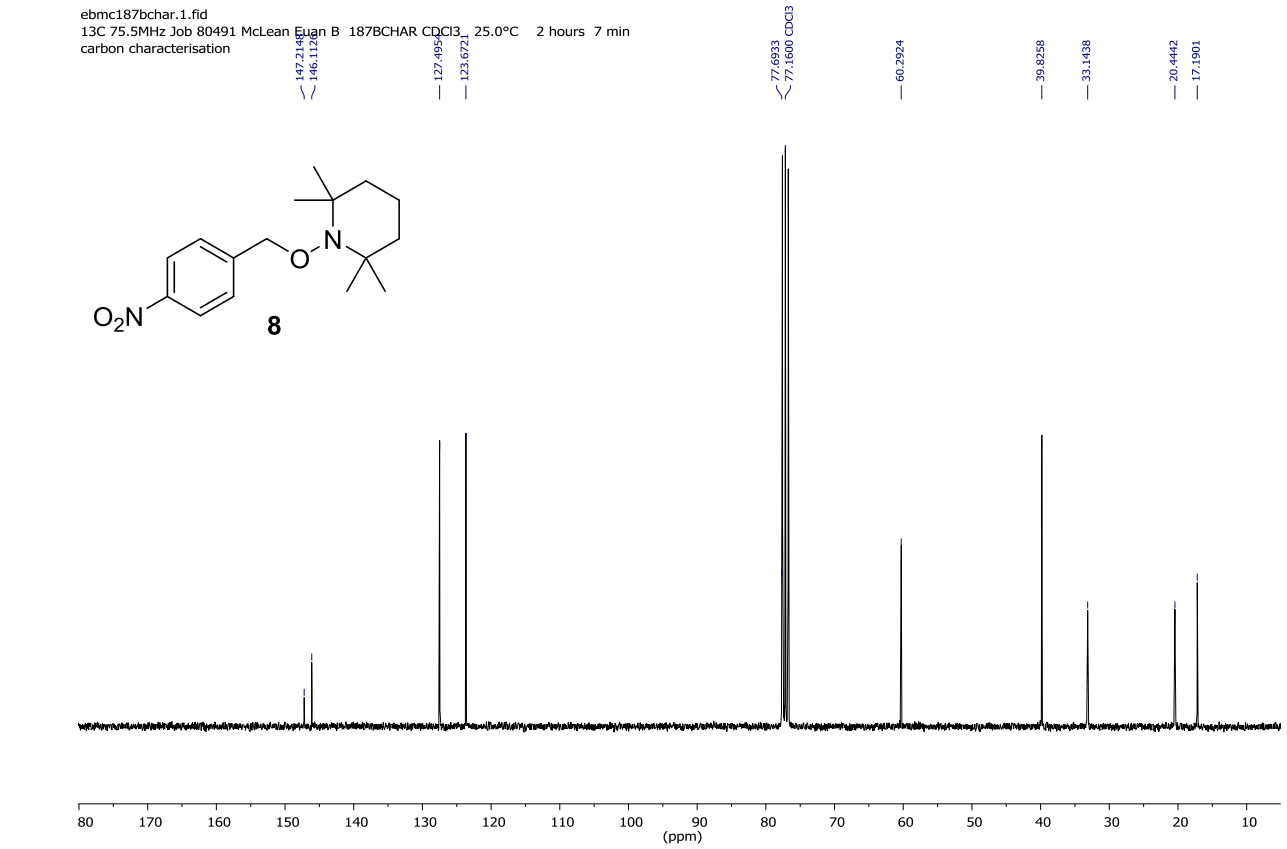

ebmh180char.1.fid
1H 400.1MHz Job 36024 McLean Euan B 180CHAR CDCl3 19.2°C
proton characterisation
5ja
A (d) 8.15
B (d) 7.64
C (d) 7.31
D (d) 6.92
E (s) 4.02
1.99
1.90
1.94
1.97
2.00
(ppm)


ebmc180char2.1.fid
13C 100.6MHz Job 36081 McLean Euan B 180CHAR2 CDCl3 25.1°C 4 hours 37 min
carbon characterisation
148.1385
146.9435
138.9792
138.0918
131.1080
129.7663
124.0184
92.2244
41.3627
5ja
(ppm)

ebmh187bchar.1.fid
1H 300.1MHz Job 80443 McLean Euan B 187BCHAR CDCl3 25.1°C
proton characterisation



ebmc187bchar.1.fid
13C 75.5MHz Job 80491 McLean Euan B 187BCHAR CDCl3 25.0°C 2 hours 7 min
carbon characterisation



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