# Electronic Supplementary Information

# EPR and ENDOR spectroscopic study of the reactions of aromatic azides with gallium trichloride

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**General Procedures.** $^{1}$H NMR spectra were recorded at 400 MHz using $CDCl_3$ solvent as reference and/or internal deuterium lock. $^{13}$C NMR spectra were recorded at 75.5 MHz using the PENDANT sequence and internal deuterium lock. The chemical shifts for all NMR spectra are expressed in parts per million to high frequency of TMS reference. Coupling constants (*J*) are quoted in Hz and are recorded to the nearest 0.1 Hz. The IR spectra were obtained with an FT-IR system. Solids were run as nujol mulls and liquids were run as thin films on NaCl plates. Mass Spectra were recorded at low resolution and high-resolution (HR) using a CI, Time-of-Flight, orthogonal acceleration spectrometer coupled to a GC system. Electrospray mass spectrometry (ESMS) was recorded on a high performance orthogonal acceleration reflecting TOF mass spectrometer, coupled to an HPLC instrument. Only major peaks are reported and intensities are quoted as percentages of the base peak. TLC was carried out using Polygram silica plates (0.2 mm with 254 nm fluorescent dye) and the components were observed under ultraviolet light (254 nm/365 nm). Column chromatography was performed using silica gel (40-63 μm, Fluorochem). Hexane, DCM, ethyl acetate and toluene were used as supplied. Pyridine was dried with KOH. Nitrogen gas was dried (NaOH, $CaCl_2$, 4 Å molecular sieves) prior to use.

**General procedure for EPR analysis of reactions of aryl azides with gallium trichloride.** A pentane solution of gallium trichloride (0.5 M, 1.1 equiv.) was added under nitrogen to a dichloromethane solution of the azide (1 equiv. in 4 mL) at rt. The resulting solution was then transferred in a capillary quartz glass tube and purged with nitrogen for 15 min. Then the capillary was sealed and the sample was transferred to the resonant cavity of the EPR spectrometer. Several spectra were recorded at different temperatures and over a period of several hours (sometimes days). Product analysis was performed by quenching the reaction with an aqueous solution of NaOH and extracting with dichloromethane. The extract was analyzed by GC-MS and, when possible, by $^{1}$H-NMR and $^{13}$C-NMR spectroscopy. Product identification was performed by comparison with literature data.

**Preparation of aromatic azides**. Phenyl azide (**1a**) and 4-methoxyphenyl azide (**8a**) were prepared by standard diazotisation of the corresponding anilines followed by treatment with sodium azide, and were identified by comparison with literature data.[1]

Deuteriated azides **1b-d** and **8b-e** were prepared by standard diazotisation techniques starting from the previously reported (or commercially available) deuteriated anilines (see below); azide **8f** was synthesised from the known 4-methoxyaniline-$^{15}$N by diazo-transfer with azido tris(diethylamino)phosphonium bromide.[2a]

**2,4,6-Trideuteriophenyl azide 1b**. To aniline (20 mmol) was added concentrated HCl (5 mL) and the resulting salt was washed with diethyl ether and dried over filter paper. The salt was dissolved in $D_2O$ (7 mL) and heated at 110 °C for 24 h in a sealed tube. Water was distilled off and the residual salt was dissolved in fresh $D_2O$ (7 mL) and heated again for further 48 h at 110 °C. The reaction mixture was then treated with aq. NaOH and extracted with diethyl ether to give 2,4,6-trideuterioaniline (18 mmol, 90%).[3] $^{1}$H-NMR (400 MHz) $\delta_H$ 3.67 (2H, bs, $NH_2$), 7.14 (2H, s); $^{13}$C-NMR (100 MHz) $\delta_C$ 114,5 (CD, t, $J$ = 23.7 Hz), 117.7 (CD, t, $J$ = 23.7 Hz), 128.7 (CH), 146.6 (C), MS TOF EI$^+$: 96.07 (M$^+$, 100%), 80.06 (2%). The 2,4,6-trideuterioaniline (18 mmol.) was reacted with DCl/$D_2O$ 35% to give the corresponding deuterio-chloride salt, which was diazotised in $D_2O$ to give the azide **1b** (14.4 mmol, 80%). IR ($\nu_{max}$, neat) 2098 ($N_3$) cm$^{-1}$; $^{1}$H-NMR (400 MHz) $\delta_H$ 7.35 (1H, s); $^{13}$C-NMR (100 MHz) $\delta_C$ 118.6 (CD, t, $J$ = 24.2 Hz), 124.5 (CD, t, $J$ = 24.2 Hz), 129.5 (CH), 139.8 (C); TOF MS CI$^+$: 123.03 (M$^+$ + 1, 100%).

**2,3,5,6-Tetradeuteriophenyl azide 1c**. 1,4-Phenylendiamine dihydrochloride (12 mmol) was deuteriated with boiling $D_2O$ (7 mL) in a sealed glass tube for 72 h. Then exhausted $D_2O$ was removed by distillation and the salt was dissolved in fresh $D_2O$ (7mL) and boiled again. The reaction mixture was then treated with aq. NaOH and extracted with diethyl ether to give 2,3,5,6-tetradeuterio-*p*-phenylendiamine (100%).[4] $^{1}$H-NMR (400 MHz; with toluene as internal standard) $\delta_H$ 3.37 (4H, bs, 2$NH_2$,); TOF MS EI$^+$: 112.04 (M$^+$, 100%).

2,3,5,6-Tetradeuterio-*p*-phenylendiamine (12 mmol.) was treated with DCl/$D_2O$ 35% to give the corresponding deuterio-chloride salt that was selectively diazotised with an excess of $H_3PO_2$ (50% aq. Solution), furnishing the corresponding 2,3,5,6-tetradeuterioaniline (7.2 mmol., 60%) after basic aqueous work up. $^{1}$H-NMR (400 MHz) $\delta_H$ 3.64 (2H, bs, $NH_2$), 6.77 (1H, s); $^{13}$C-NMR (100 MHz) $\delta_H$ 114.72 (CD, t, $J$ =

24.2 Hz), 118.3 (CH), 128.8 (CD, t, *J* = 24.2 Hz), 146.1 (C); TOF MS $CI^+$: 98.09 ($M^+$ + 1, 100%). Standard diazotisation of the 2,3,5,6-tetradeuterioaniline gave the corresponding azide **1c** (3.17 mmol., 44%). IR ($\nu_{max}$, neat) 2102 $cm^{-1}$($N_3$); $^1$H-NMR (400 MHz) $\delta_H$ 7.15 (1H, s); $^{13}$C-NMR (100 MHz) $\delta_C$ 118.6 (CD, t, *J* = 24.2 Hz), 126.6 (CH), 129.3 (CD, t, *J* = 24.2 Hz), 139.8 (C); TOF MS $CI^+$: 124.01 ($M^+$ + 1, 100%).

**2,3,4,5,6-Pentadeuteriophenyl azide 1d** was prepared in 81% yield by standard diazotisation of the commercially available $d_5$-aniline 98% atom d (7.7 mmol). IR ($\nu_{max}$, neat) 2097 $cm^{-1}$ ($N_3$); $^{13}$C-NMR (100 MHz) $\delta_C$ 118,6 (CD, t, *J* = 24,2 Hz), 124.3 (CD, t, *J* = 24,2 Hz), 129.2 (CD, t, J = 24,2 Hz), 139.8 (C); TOF MS $CI^+$: 125.06 ($M^+$ + 1, 100%).

**4-Methoxy-$d_3$-phenyl azide 8b**. To a carefully cooled solution (0 °C) of KOH (1.5 equiv) in $d_4$-methanol (20 mL) 1-fluoro-4-nitrobenzene (13.3 mmol) was slowly added under nitrogen. The dark yellow mixture was reacted for 24 h at rt and then refluxed for 12 h. The crude of reaction was poured into water and extracted with diethyl ether (3 x 20 mL). The solvent was removed and the yellow oil crystallised by adding few drops of petroleum ether. 4-Methoxy-$d_3$-1-nitrobenzene was obtained as yellow crystals (12.35 mmol, 93%). $^1$H-NMR (400 MHz) $\delta_H$ 6.95 (2 H, A part of AA’BB’, *J* = 9.3 Hz), 8.19 (2 H, B part of AA’BB’, *J* = 9.3 Hz); $^{13}$C-NMR (100 MHz) $\delta_C$ 55.12 ($CD_3$, quint., *J* = 22 Hz), 114.0 (CH), 125.9 (CH), 141.5 (C), 164.6 (C); TOF MS $EI^+$: 156.06 ($M^+$, 100%).

To a suspension of $Cu(acac)_2$ (0.2 equiv) in isopropanol (20 mL), an ethanol solution of $NaBH_4$ was added (1 equiv in 10 mL). Then a solution of 4-methoxy-$d_3$-1-nitrobenzene in isopropanol (12.4 mmol in 20 mL) was added. Subsequently a new ethanol solution of $NaBH_4$ (2 equiv in 10 mL) was added dropwise in 1h. The solution was stirred at rt for 18 h, diluted with water, and the solvent removed under reduced pressure. The aqueous phase was filtered from the black solid and extracted with dichloromethane. The organic phase was dried over $MgSO_4$ and the solvent removed under reduced pressure. After purification by chromatography, solid 4-methoxy-$d_3$-aniline was obtained (10.2 mmol, 83%). $^1$H-NMR (400 MHz) $\delta_H$ . 3.41 (2H, bs, $NH_2$), 6.65 (2 H, A part of AA’BB’, *J* = 9.0 Hz), 6.75 (2 H, B part of AA’BB’, *J*

= 9.0 Hz); $^{13}$C-NMR (100 MHz) $\delta_C$ 54.81 ($CD_3$, quint., $J$ = 22 Hz), 114.7 (CH), 116.4 (CH), 139.8 (C), 152.7 (C); TOF MS EI$^+$: 126.08 ($M^+$, 55%), 108.04 ($M^+$ − 18, 100%).
Standard diazotisation of the 4-methoxy-$d_3$-aniline gave the corresponding azide **8b** (9.2 mmol, 90%). IR ($\nu_{max}$, $CHCl_3$) 2097 cm$^{-1}$ ($N_3$); $^1$H-NMR (400 MHz) $\delta_H$ 6.88 (2 H, A part of AA’BB’, $J$ = 9.1 Hz), 6.96 (2 H, B part of AA’BB’, $J$ = 9.1 Hz); $^{13}$C-NMR (100 MHz) $\delta_C$ 54.6 ($CD_3$, quint., $J$ = 22 Hz), 115.0 (CH), 119.9 (CH), 132.2 (C), 156.9 (C); TOF MS CI$^+$: 153 ($M^+$ + 1, 48%), 135 (5%), 125 (100%).

**2,6-Dideuterio-4-methoxyphenyl azide 8c.** Gaseous HCl was bubbled into a solution of 4-methoxyaniline (10 mmol) in diethyl ether to give the corresponding hydrochloride salt which was filtered, transferred to a glass tube, and dissolved in $D_2O$ (6 mL). The glass was sealed and the mixture was boiled for 3 days, then exhausted $D_2O$ was removed by distillation and replaced with fresh $D_2O$ (6 mL). The new mixture was boiled for 3 days again. The reaction was neutralised with aq. NaOH and extracted with dichloromethane to give the 2,6-dideuterio-4-methoxyaniline (9.8 mmol, 98%).[3] $^1$H-NMR (400 MHz) $\delta_H$ 3.42 (2H, bs, $NH_2$), 3.75 (3H, s), 6.75 (2H, s); $^{13}$C-NMR (100 MHz) $\delta_C$ 55.7 ($CH_3$), 114.6 (CH), 116.1 (CD, t, $J$ = 24.2 Hz), 139.7 (C), 152.7 (C); TOF MS EI$^+$: 125.08 ($M^+$, 50%), 110.05 (100%).
2,6-Dideuterio-4-methoxyaniline (9.8 mmol) was diazotised following the classical methodology to give the corresponding azide **8c** (8.33 mmol, 85%). IR ($\nu_{max}$, $CHCl_3$) 2098 cm$^{-1}$ ($N_3$); $^1$H-NMR (400 MHz) $\delta_H$ 3.67 (3H, s), 6.72 (2H, s); $^{13}$C-NMR (100 MHz) $\delta_C$ 55.5 ($CH_3$), 115.0 (CH), 119.7 (CD, t, J = 24.2 Hz), 132.2 (C), 157.0 (C); MS TOF CI$^+$: 152 ($M^+$ + 1, 23%), 124(100%).

**3,5-Dideuterio-4-methoxyphenyl azide 8d.** Commercially available 4-nitrophenol (20 mmol) was added to a solution of $D_2SO_4$ (4 mL) in $D_2O$ (10 mL) at 0 °C in a glass tube. The tube was sealed and the yellow solution was heated at 120 °C for 48 h. The mixture was cooled and diluted with water and extracted with dichloromethane (4 x 10 mL). The solvent was removed under reduced pressure and solid 2,6-dideuterio-4-nitrophenol[5a] was obtained in quantitative yield. $^1$H-NMR (400 MHz) $\delta_H$ 6.02 (1H, s, OH), 8.09 (2H, s); $^{13}$C-NMR (100 MHz) $\delta_C$ 115.4 (CD, t, $J$ = 25 Hz), 126.2 (CH), 141.4 (C), 161.3 (C); TOF MS ES$^+$: 164.02 ($M^+$ + Na, 100%).

To 2,6-dideuterio-4-nitrophenol (20 mmol) in DMF (50 mL) was added $Cs_2CO_3$ (2 equiv) and MeI (2 equiv) under nitrogen and the resulting mixture was stirred for 18 h. The reaction mixture was poured into water and extracted with DCM (3 x 50 mL). The organic phase was washed several times with water to remove DMF. The solvent was removed under reduced pressure and the brown oil was crystallised by adding water and petroleum ether. After 12 h under reduced pressure, dried crystals of 2,6-dideuterio-1-methoxy-4-nitrobenzene[5b] were collected (18.4 mmol, 92%). $^1$H-NMR (400 MHz) $\delta_H$ 3.90 (3H, s), 8.20 (2H, s); $^{13}$C-NMR (100 MHz) $\delta_C$ 55.9 ($CH_3$), 113.7 (CD, t, J = 24.9 Hz), 125.8 (CH), 141.5 (C), 164,5 (C); TOF MS EI$^+$: 155.05 ($M^+$, 100%), 125.05 (25%), 109.06 (3%).

To a suspension of Cu(acac)$_2$ (0.2 equiv) in isopropanol (20 mL), was added an ethanol solution of $NaBH_4$ (1 equiv in 20 mL). Then 2,6-dideuterio-1-methoxy-4-nitrobenzene (18.4 mmol) was added followed by dropwise addition of a new ethanol solution of $NaBH_4$ (2 equiv. in 30 mL) over 1h. The solution was stirred at rt for 18 h, diluted with water, and the solvent removed under reduced pressure. The aqueous phase was filtered from the black solid and extracted with dichloromethane. The organic phase was dried over $MgSO_4$ and the solvent removed under reduced pressure. After purification by chromatography 3,5-dideuterio-4-methoxyaniline was obtained (15.46 mmol, 84%). $^1$H-NMR (400 MHz) $\delta_H$ 3.47 (2H, bs, $NH_2$), 3.72 (3H, s), 6.61 (2H, s); $^{13}$C-NMR (100 MHz) $\delta_C$ 55.2 ($CH_3$), 114.1 (CD, t, *J* = 24.2 Hz), 116.0 (CH), 139.7 (C), 152.2 (C); TOF MS EI$^+$: 125.08 ($M^+$, 50 %), 110.05 (100%).

Final diazotisation of 3,5-dideuterio-4-methoxyaniline gave the azide **8d** (14.7 mmol, 95%). IR ($\nu_{max}$, neat) 2098 cm$^{-1}$ ($N_3$); $^1$H-NMR (400 MHz) $\delta_H$ 3.79 (3H, s), 6.95 (2H, s); $^{13}$C-NMR (100 MHz) $\delta_C$ 55.4 ($CH_3$), 114.8 (CD, t, *J* = 24.2 Hz), 119.9 (CH), 132.2 (C), 156.8 (C). TOF MS CI$^+$: 152.09 ($M^+$ + 1, 35%), 137.08 (15%), 124.08 (100%).

**2,3,5,6-Tetradeuterio-4-methoxyphenyl azide 8e.** Gaseous HCl was bubbled into a solution of 3,5-dideuterio-4-methoxyaniline (8.5 mmol) in diethyl ether to give the corresponding hydrochloride salt which was filtered, transferred in a glass tube and dissolved in $D_2O$ (6 mL). The glass was sealed and the mixture was boiled for 2 days, then exhausted $D_2O$ was removed by distillation and replaced with fresh $D_2O$ (6 mL).[3] The new mixture was boiled for a further 2 days. The reaction was neutralised with aq. NaOH and extracted with dichloromethane to give the 2,3,5,6-

tetradeuterio-4-methoxyaniline (7.48 mmol., 88%). $^1$H-NMR (400 MHz) $\delta_H$ 3.36 (2H, bs), 3.74 (3H, s); $^{13}$C-NMR (100 MHz) $\delta_C$ 55.7 ($CH_3$), 114.4 (CD, t, *J* = 24.2 Hz), 116.0 (CD, t, *J* = 24.2 Hz), 139.7 (C), 152.7 (C). TOF MS EI$^+$: 127.07 (M$^+$, 62 %), 112.06 (100%).

2,3,5,6-Tetradeuterio-4-methoxyaniline was diazotised to give the corresponding azide **8e** (5.23 mmol, 70 %). IR ($\nu_{max}$, neat) 2099 cm$^{-1}$ ($N_3$); $^1$H-NMR (400 MHz) $\delta_H$ 3.79 (3H, s), $^{13}$C-NMR (100 MHz) $\delta_C$ 55.5 ($CH_3$), 114.7 (CD, t, *J* = 24.2 Hz), 119.5 (CD, t, *J* = 24.9 Hz), 123.1 (C), 156.8 (C); TOF MS CI$^+$: 154.1 (M$^+$ + 1, 25%), 139.09 (5%), 126.09 (100%).

**4-Methoxyphenyl azide-$^{15}$N 8f**. Ammonium chloride-$^{15}$N (1 equiv) was dissolved in a mixture of water (4 mL) and chloroform (30 mL) and the solution was cooled to 0 °C. Then anisoyl chloride (8.66 mmol) and an aqueous solution of NaOH (2.2 equiv) were added and the mixture was stirred all night at rt. A new solution of NaOH 1N in water was poured into the mixture and the chloroform layer was separated and washed with water. The solvent was distilled off and crystallisation of the white amorphous solid in water gave the 4-methoxybenzamide-$^{15}$N (6.66 mmol, 77% yield).[6a] $^1$H-NMR (400 MHz) $\delta_C$ 3.85 (3H, s), 5.88 (2H, bs, $NH_2$), 6.94 (2 H, A part of AA'BB', *J* = 9.0 Hz), 7.78 (2 H, B part of AA'BB', *J* = 9.0 Hz); $^{13}$C-NMR (100 MHz) $\delta_C$ 55.4 ($CH_3$), 113.0 (CH), 129.3 (CH), 162.6 (C), 169.0 (C).

A solution of sodium hypobromide was prepared by dropwise addition of $Br_2$ (1 equiv) to an ice cold stirring solution of NaOH (22 equiv) in water (18 mL). After 5 min 4-methoxybenzamide-$^{15}$N (6.35 mmol) was added and the resulting suspension was stirred at rt for 20 min then slowly heated to 95 °C for 4 days. The reaction mixture was cooled and extracted with dichloromethane to give 4-methoxyaniline-$^{15}$N (4 mmol, 63%).[6b] $^1$H-NMR (400 MHz) $\delta_H$ 3.27 (2H, bs, $NH_2$), 3.74 (3H, s), 6.65 (2 H, A part of AA'BB', *J* = 8.8 Hz), 6.75 (2 H, B part of AA'BB', *J* = 8.8 Hz); $^{13}$C-NMR (100 MHz) $\delta_C$ 55.7 ($CH_3$), 114.8 (CH), 116.4 (CH), 153.9 (C), 152.8 (C); TOF MS EI$^+$: 124.06 (M$^+$, 55%), 109 (100%).

A solution of $PCl_3$ (50 mmol) in diethyl ether (20 mL) was added to a solution of diethylamine (6 equiv) in diethyl ether (100 mL) at 0 °C under nitrogen. The resulting solution was stirred for 1 day at rt. The mixture was filtered to give the resulting tris(diethylamino)phosphine as a yellow oil (47 mmol, 94%). $^1$H-NMR (400 MHz) $\delta_H$ 1.0 (18H, t, *J* = 7.0 Hz), 2.86-2.93 (12H, m); $^{31}$P-NMR $\delta$ 116.6 (1P, s).

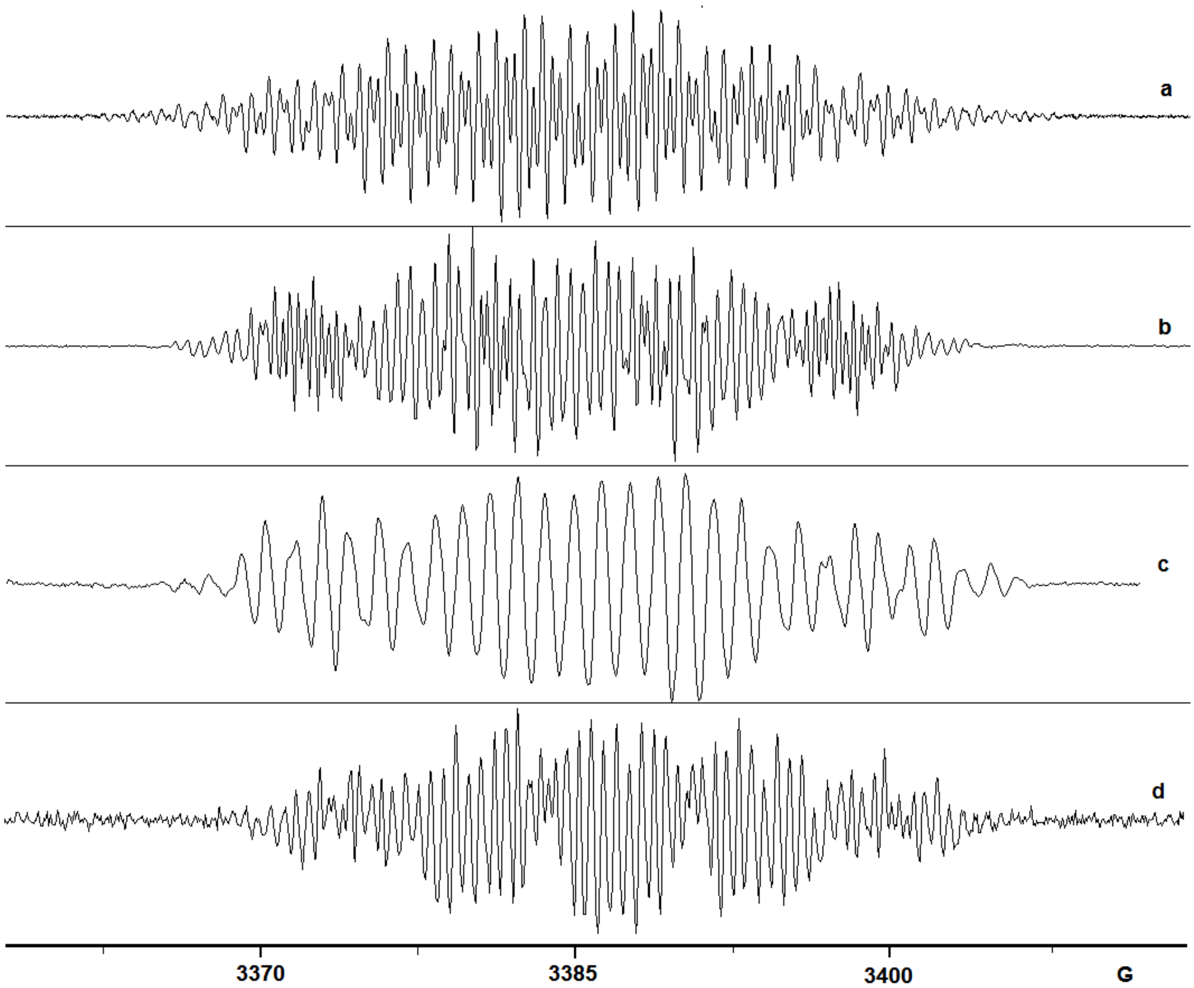
Tris(diethylamino)phosphine (47 mmol) was added dropwise to a stirred solution of $Br_2$ (44.8 mmol) in THF (20 mL) at 0 °C. After the addition was complete, sodium azide (2 equiv) and 18-crown-6 (0.2 equiv) were added. The mixture was stirred under nitrogen for two days. Then the solvent was removed and the oil was crystallised from THF to give azidotris(diethylamino)phosphonium bromide (36.2 mmol, 77%).[2] $^1$H-NMR (400 MHz) $\delta_H$ 1.1 (18H, t, *J* = 7.1 Hz), 3.1-3.2 (12H, m); $^{31}$P-NMR $\delta$ 36.97 (1P, s); TOF MS EI$^+$: 289.15 ($M^+$ + 1, 95%), 175.08 (100%).[2a]

4-Methoxyaniline-$^{15}$N (4 mmol) was deprotonated with *n*-BuLi (4.8 mmol of 2.5 M soln. in hexane) in dry THF at -78 °C. Azidotris(diethylamino)phosphonium bromide (4.8 mmol) was added as a THF solution (31 mL).[2b] The reaction was stirred for 45 min at -78 °C. At ambient temperature, aq. $NH_4Cl$ (0.25 M) was added and the mixture extracted with dichloromethane. Filtration over silica gel gave the azide **8f** (2.11 mmol, 53%). IR ($\nu_{max}$, neat) 2097 cm$^{-1}$ ($N_3$); $^1$H-NMR (400 MHz) $\delta_H$ 3.8 (3H, s), 6.88 (2 H, A part of AA'BB', *J* = 8.9 Hz), 6.95 (2 H, B part of AA'BB', *J* = 8.9 Hz) $^{13}$C-NMR (100 MHz) $\delta_C$ 55.5 ($CH_3$), 115.1 (CH), 119.9 (CH), 132.3 (C), 157 (C); TOF MS CI$^+$: 150.06 ($M^+$ + 1, 30%), 123.05 (100%), 107.03 (10%).

**Reactions of phenyl azide 1a with gallium trichloride.** The reactions were carried out according to the general procedure described above with different proportions of **1a** and $GaCl_3$. Reaction proceeded for 2 h at rt and then the mixture was quenched with an aqueous solution of NaOH and extracted with dichloromethane. The extract was analyzed by GC-MS which showed known amines **2a-7a** as the main products. The products were isolated by column chromatography using silica gel (40-63 µm, Fluorochem) and hexane/ethyl acetate (10/1) as eluant; comparison of the $^1$H-NMR and $^{13}$C-NMR spectra with literature data confirmed their identities. Product yields are in Table 1 of the main text.

**Reaction of 4-methoxyphenyl azide 8a with gallium trichloride.** The reaction was carried out for 2 h at rt according to the general procedure described above. The mixture was quenched with an aqueous solution of NaOH and extracted with dichloromethane. The extract was analyzed by GC-MS which showed known variamine blue **9a** as the main product along with minor amounts of *p*-anisidine **10a** and compounds **11a-13a**. Variamine blue **9a** was isolated by column chromatography using silica gel (40-63 μm, Fluorochem) and hexane/ethyl acetate (10/1) as eluant and its identity confirmed by comparison of its NMR spectra with those of a commercial sample. The identity of **10a** was also confirmed by comparison with a commercial sample. Compounds **11a** and **12a** were characterised by comparison of their $^{1}$H and $^{13}$C NMR spectra with literature data.[7] Compound **13a** is known,[8] but we were not able to isolate it in sufficient quantity for NMR analysis. It was identified on the basis of its MS and the other reaction products.

**9.5 GHz EPR spectra** obtained on treatment of deuteriated derivatives of 4-methoxyphenyl azide with $GaCl_3$ in DCM/pentane at 300 K. Broad central components of the spectra were digitally removed. Hfs obtained from the simulations are in Table 4 of the main text.




Top (a): 1st derivative spectrum of $CD_3O$-substituted 4-aminodiphenyl amine radical cation (dimer radical cation) **14** derived from azide **8b**.

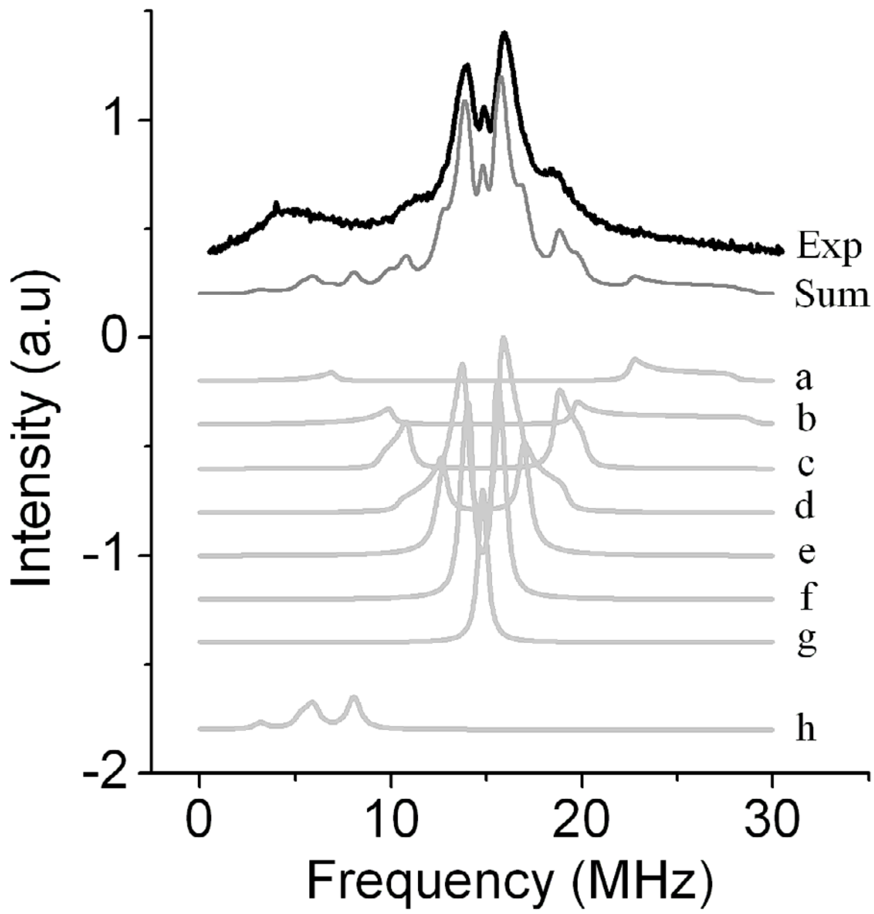
2nd Down (b): 1st derivative spectrum of dimer radical cation from 2,6-dideuterio-4-methoxyphenyl azide **8c.**

3rd Down (c): 1st derivative spectrum of dimer radical cation from 3,5-dideuterio-4-methoxyphenyl azide **8d.**

Bottom (d): 2nd derivative spectrum of dimer radical cation from 2,3,5,6-tetradeuterio-4-methoxyphenyl azide **8e.**

**Davies ENDOR spectrum of dimer species 14a from azide 1a at 50K**

Showing the breakdown of the simulation into individual components from each magnetic nucleus

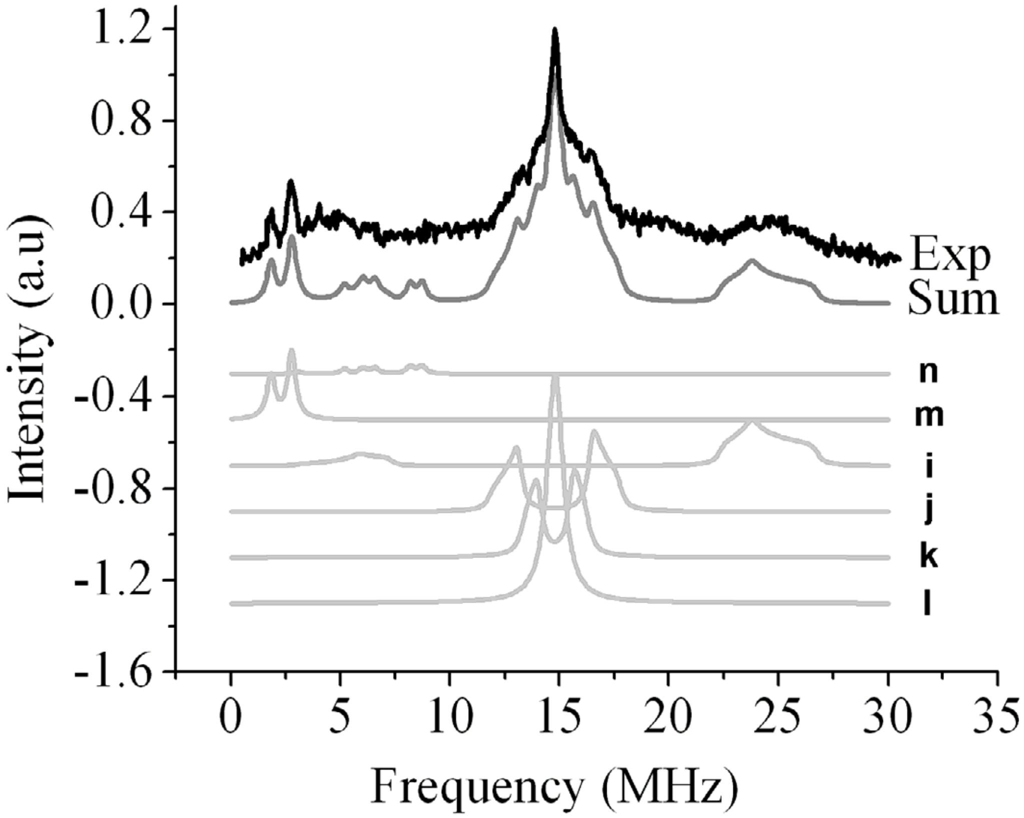


## Hyperfine constants (G) derived from simulations of the ENDOR spectra.

| Azide/ nucleus | $A_x$ | $A_y$ | $A_z$ | $A_{iso}$ | Key to Figs.[1] |
|---|---|---|---|---|---|
| **1a** | dimer **14a** | | | | |
| H | 5.5 | 5.5 | 9.3 | 6.8 | a |
| H | 3.4 | 3.4 | 10.0 | 5.6 | b |
| H | 2.7 | 2.7 | 3.8 | 3.1 | c |
| H | 1.4 | 1.4 | 3.1 | 2.0 | d |
| H | 0.6 | 0.6 | 1.7 | 1.0 | e |
| H | 0.4 | 0.4 | 0.9 | 0.6 | f |
| H | -0.1 | -0.1 | 0.2 | 0 | g |
| $^{14}N$ | - | - | - | 5.0 | h |
| $^{14}N$ | - | - | - | 4.9 | h |
| **1c** | trimer **15y** | | | | |
| H | 5.3 | 6.4 | 8.5 | 6.7 | i |
| H | 1.2 | 1.2 | 2.1 | 1.5 | j |
| H | 0.5 | 0.5 | 1.1 | 0.7 | k |
| H | -0.1 | -0.1 | 0.2 | 0.0 | l |
| D | - | - | - | 0.3 | m |
| $^{14}N$ | - | - | - | 5.4 | n |
| $^{14}N$ | - | - | - | 5.0 | n |
| $^{14}N$ | - | - | - | 2.9 | n |

[1] The letters a,b,c,d,e,f,g,h and I, j, k, l, m, n in the ENDOR spectra of the species from **1a** and **1c** respectively (shown in the figure above and figure below) indicate the hfs of the individual simulated powder patterns
Hfs of weakly coupled protons used in both simulations are labelled with g and l in the figures.

**Davies ENDOR spectrum of trimer species 15y from azide 1c at 50K**
Showing the breakdown of the simulation into individual components from each magnetic nucleus



## DFT Computed structures

Computed with the Gaussian 03 suite of programmes using the UB3LYP functional and a 6-31G(d) basis set.[9]

### Dimer Radical Cation **14**

| Centre No. | Atomic No. | x | y | z |
|---|---|---|---|---|
| 1 | 6 | 3.167114 | -1.448563 | 0.548867 |
| 2 | 6 | 1.906045 | -0.862782 | 0.603316 |
| 3 | 6 | 1.722927 | 0.426831 | 0.073314 |
| 4 | 6 | 2.812143 | 1.130898 | -0.470395 |
| 5 | 6 | 4.065553 | 0.532677 | -0.516030 |
| 6 | 6 | 4.246275 | -0.760770 | -0.014403 |
| 7 | 1 | 3.312644 | -2.438886 | 0.968906 |
| 8 | 1 | 1.087885 | -1.375039 | 1.097304 |
| 9 | 1 | 2.665283 | 2.129996 | -0.872828 |
| 10 | 1 | 4.902483 | 1.074225 | -0.945234 |
| 11 | 7 | 0.478576 | 1.086140 | 0.121235 |
| 12 | 1 | 0.539595 | 2.095971 | 0.211988 |
| 13 | 6 | -0.789002 | 0.585143 | 0.048075 |
| 14 | 6 | -1.874093 | 1.444522 | 0.389134 |
| 15 | 6 | -1.079671 | -0.735990 | -0.396676 |
| 16 | 6 | -3.170032 | 1.002573 | 0.331878 |
| 17 | 1 | -1.666650 | 2.458910 | 0.719609 |
| 18 | 6 | -2.377807 | -1.177480 | -0.460131 |
| 19 | 1 | -0.276736 | -1.383054 | -0.727138 |
| 20 | 6 | -3.459392 | -0.328712 | -0.086483 |
| 21 | 1 | -3.983960 | 1.666059 | 0.608662 |
| 22 | 1 | -2.588820 | -2.179672 | -0.821790 |
| 23 | 7 | -4.732184 | -0.770381 | -0.143334 |
| 24 | 1 | -5.510899 | -0.174091 | 0.102526 |
| 25 | 1 | -4.953144 | -1.710730 | -0.442132 |
| 26 | 1 | 5.227212 | -1.224083 | -0.047962 |

E = -573.7827308 Hartrees    $\langle S^2 \rangle$ = 0.750081.

### Trimer Radical Cation **15**

| Centre No. | Atomic No. | | x | y | z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -0.621299 | -1.351075 | -0.455575 |
| 2 | 6 | 0 | 0.657039 | -0.838692 | -0.469011 |
| 3 | 6 | 0 | 0.868057 | 0.556639 | -0.348943 |
| 4 | 6 | 0 | -0.264740 | 1.403390 | -0.267640 |
| 5 | 6 | 0 | -1.543320 | 0.892763 | -0.249470 |
| 6 | 6 | 0 | -1.756474 | -0.508743 | -0.320936 |
| 7 | 1 | 0 | -0.765537 | -2.423307 | -0.561135 |
| 8 | 1 | 0 | 1.496835 | -1.506910 | -0.615521 |
| 9 | 1 | 0 | -0.122788 | 2.480189 | -0.214523 |
| 10 | 1 | 0 | -2.389399 | 1.567194 | -0.206674 |
| 11 | 7 | 0 | 2.117907 | 1.140944 | -0.368980 |
| 12 | 1 | 0 | 2.118883 | 2.129508 | -0.598267 |
| 13 | 6 | 0 | 3.377239 | 0.599670 | -0.134057 |
| 14 | 6 | 0 | 4.500362 | 1.266048 | -0.675096 |
| 15 | 6 | 0 | 3.590721 | -0.543643 | 0.667628 |
| 16 | 6 | 0 | 5.777426 | 0.794518 | -0.460808 |

| | | | | | |
|---|---|---|---|---|---|
| 17 | 1 | 0 | 4.354946 | 2.153226 | -1.286530 |
| 18 | 6 | 0 | 4.868878 | -1.018366 | 0.884072 |
| 19 | 1 | 0 | 2.755984 | -1.028259 | 1.160243 |
| 20 | 6 | 0 | 5.994847 | -0.370376 | 0.317685 |
| 21 | 1 | 0 | 6.625470 | 1.315429 | -0.895812 |
| 22 | 1 | 0 | 5.016825 | -1.887559 | 1.518697 |
| 23 | 7 | 0 | 7.250247 | -0.849938 | 0.518426 |
| 24 | 1 | 0 | 8.060526 | -0.350189 | 0.183536 |
| 25 | 1 | 0 | 7.418383 | -1.637622 | 1.126424 |
| 26 | 7 | 0 | -3.000570 | -1.078922 | -0.321755 |
| 27 | 1 | 0 | -3.034437 | -2.051280 | -0.605025 |
| 28 | 6 | 0 | -4.256756 | -0.497517 | -0.027247 |
| 29 | 6 | 0 | -4.415806 | 0.438435 | 1.006121 |
| 30 | 6 | 0 | -5.373499 | -0.930429 | -0.757948 |
| 31 | 6 | 0 | -5.681117 | 0.955950 | 1.276489 |
| 32 | 1 | 0 | -3.566853 | 0.727973 | 1.616383 |
| 33 | 6 | 0 | -6.633896 | -0.414812 | -0.469938 |
| 34 | 1 | 0 | -5.247236 | -1.656691 | -1.556958 |
| 35 | 6 | 0 | -6.791964 | 0.536400 | 0.541396 |
| 36 | 1 | 0 | -5.800432 | 1.675757 | 2.080762 |
| 37 | 1 | 0 | -7.492953 | -0.752266 | -1.041757 |
| 38 | 1 | 0 | -7.775496 | 0.939261 | 0.761989 |

E = -860.2017216 Hartrees, $\langle S^2 \rangle$ = 0.750074

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