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Supplementary Material for

Photoinduced Ullmann C–N Coupling: Demonstrating the Viability of a Radical Pathway

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I. General

General considerations: All manipulations of air-sensitive materials were carried out using standard Schlenk or dry-glove box techniques under an N_2 atmosphere. Benzene and acetonitrile were deoxygenated and dried by sparging with inert gas followed by passage through an activated alumina column in a solvent purification system designed by SG Water, USA LLC, and stored over 4 Å molecular sieves. All reagents were purchased from commercial vendors and used without further purification unless otherwise stated. Lithium carbazolide (*21*), $(Ph_3P)_2Cu(cbz)$ (**2**) (*21*), 2-allyloxyiodobenzene (*34*), 2-propargyloxyiodobenzene (*35*), 2-propargyloxybromobenzene (*36*), Cp_2ZrHCl (*37*), and 4-(1-pentenyl)bromobenzene (*38, 39*) were synthesized according to published procedures. The syntheses of (*E)*-(3-deuterioallyl)oxy-2-iodobenzene and (*E*)-(3-deuterioallyl)oxy-2-bromobenzene were adapted from reference (*40*). Elemental analyses were performed by Midwest Microlab, LLC., Indianapolis, IN. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., degassed, and dried over activated 4 Å molecular sieves before use. Propionitrile, butyronitrile, and deuterated acetonitrile were dried over calcium hydride prior to use. The lamps used for irradiation were either a 13 W compact fluorescent lamp (Westpointe model #WP13MSLT2) or a 100 W mercury lamp (Blak-Ray Long-Wave Ultraviolet Lamp, Model B). ^1H, ^2H, and ^{13}C NMR chemical shifts are reported in ppm relative to tetramethylsilane, using residual solvent proton, deuterium, and ^{13}C resonances as internal standards. ^{31}P NMR chemical shifts are reported in ppm relative to 85% aqueous H_3PO_4. X-band EPR spectra were obtained on a Bruker EMX spectrometer and simulated using Easyspin (*41)*. Emission and excitation spectra were measured at room temperature with a Jobin Yvon Spex Fluorolog®-3 at the Beckman Institute Laser Resource Center. An excitation wavelength of 310 nm was employed for the emission spectra, and emission at 458 nm was monitored for the excitation spectra.

X-ray crystallography: XRD studies were carried out at the Beckman Institute Crystallography Facility on a Bruker Kappa Apex II diffractometer (Mo Kα radiation). Structures were solved using SHELXS (*42*) and refined against F^2 on all data by full-matrix least squares with SHELXL. The crystals were mounted on a glass fiber.

II. Experimental section

A. Synthesis and characterization of $[(m\text{-tol})_3P]_2Cu(carbazolide)$, 1

Synthesis of $[P(m\text{tol}_3)]_2Cu(cbz)$, 1: $CuBr(Me_2S)$ (393 mg, 1.91 mmol) was suspended in 3 mL of benzene. Tris(2-methylphenyl)phosphine (1.162 g, 3.82 mmol) was added as a solution in 20 mL of benzene, and the resulting clear and colorless solution was diluted to a total volume of 50 mL. Lithium carbazolide (340 mg, 1.96 mmol) was added as a solid in small portions over 40 minutes. The reaction mixture became cloudy and developed a green-yellow color over the course of the addition. After four hours, the reaction mixture was filtered through Celite to remove lithium bromide. The filtrate was concentrated to dryness to give a sticky green foam, which was then dissolved in minimal 5:1 diethyl ether:pentane and stored at -40° C for 30 minutes until a green-yellow precipitate formed. The yellow supernatant was decanted, and the solids were washed with cold diethyl ether and dried under vacuum, giving 1.048 g of **1** (65%), m.p. 140-141 °C. Single crystals suitable for X-ray diffraction were grown *via*

slow evaporation of a diethyl ether solution of **1** into methylcyclohexane. ^{1}H NMR (C_6D_6, 300 MHz, ppm): δ 8.51 (d, 2H, NAr-*H*), 7.74 (d, 2H, NAr-*H*), 7.51 (d, 6H, $P(CH_3C_6H_5)_3$), 7.39 (t, 2H, NAr-*H*), 7.29 (t, 2H, NAr-*H*), 7.22 (t, 6H, $P(CH_3C_6H_5)_3$), 6.88-6.78 (m, 12H, $P(CH_3C_6H_5)_3$), 1.75 (s, 18H, $P(CH_3C_6H_5)_3$). $^{13}C\{^{1}H\}$ NMR (C_6D_6, 100 MHz, ppm): δ 151.2 (s), 139.01 (d, J_{CP} = 8.6 Hz), 135.36 (d, J_{CP} = 18.5 Hz), 133.39 (d, J_{CP} = 39.3 Hz), 130.99 (s), 130.84 (d, J_{CP} = 9.6 Hz), 128.95 (d, J_{CP} = 6.5 Hz), 128.59 (s), 126.37 (s), 123.73 (s), 120.34 (s), 115.22 (d, J_{CP} = 9.4 Hz), 21.00 (s). ^{31}P NMR (C_6D_6, 121 MHz, ppm): δ -4 (s). Anal. Calcd. For $C_{54}H_{50}NP_2Cu$: C, 77.35; H, 6.01; N, 1.67; Found: C, 77.19; H, 6.39; N, 1.56.

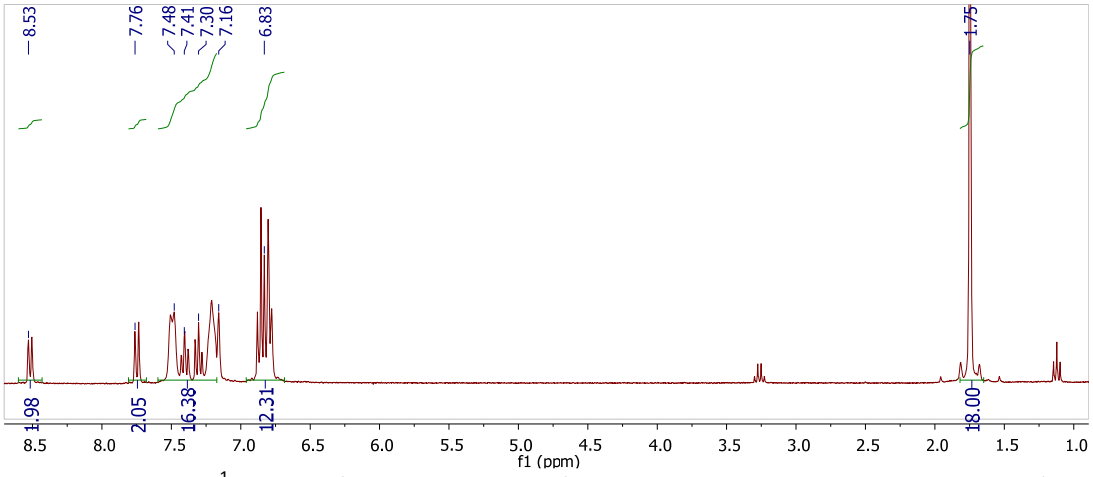


Figure S1. ^{1}H NMR of **1**, C_6D_6, 300 MHz (residual Et_2O is present in the spectrum)

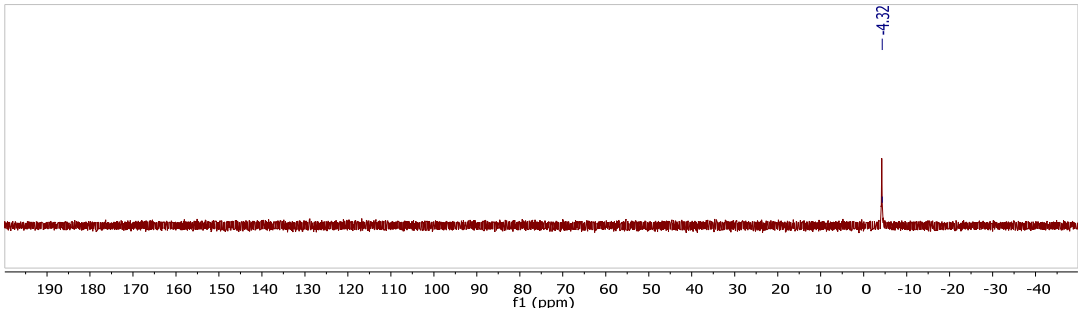


Figure S2. ^{31}P NMR of **1**, C_6D_6, 121 MHz

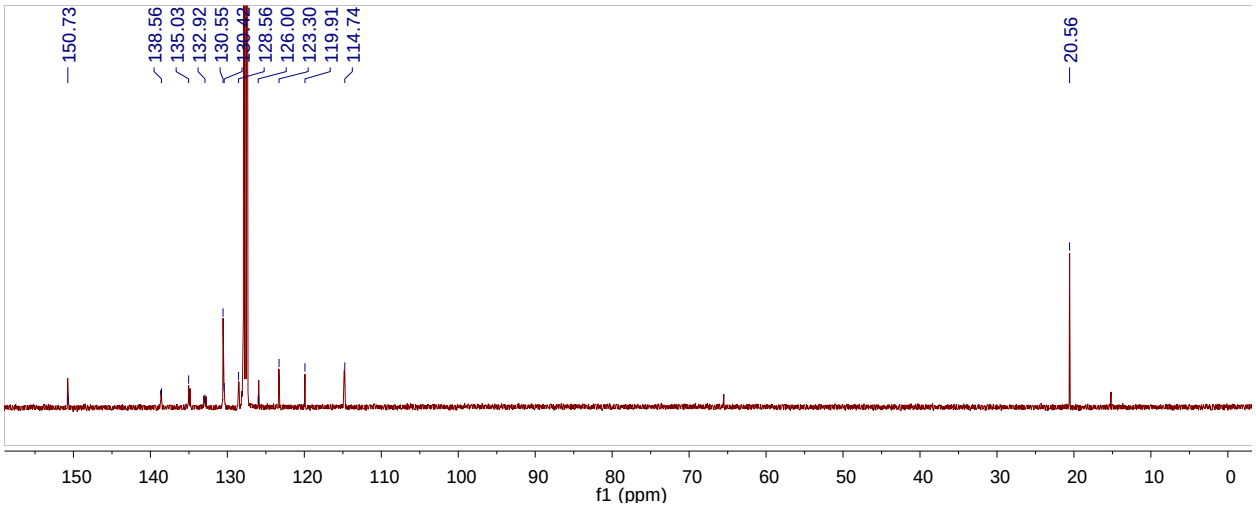


Figure S3. ^{13}C NMR of **1**, C_6D_6, 100 MHz

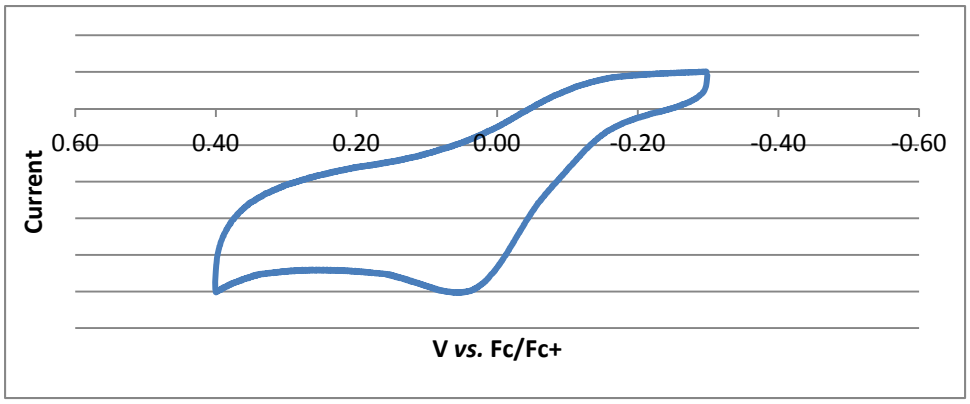


Figure S4. Cyclic voltammogram of **1** measured in acetonitrile, scan rate 0.1 V/s, internally referenced to the ferrocene/ferrocenium couple; electrolyte: 0.1 M [TBA][PF_6]; auxiliary electrode: platinum wire; working electrode: glassy carbon; reference electrode: Ag/$AgNO_3$. CV data collected in a dry-glove box using a CH Instruments Model 620C Electrochemical Analyzer.

B. Stoichiometric C-N coupling to give *N*-phenylcarbazole

Synthesis of *N*-phenylcarbazole from 1 and PhX (X = I, Br, Cl), general procedure: PhX (1.2 equiv or 5 equiv) was dissolved in CH_3CN (10 mL) and added to solid **1** (200 mg, 0.24 mmol) to give a clear solution after stirring for ca. 10 minutes in the dark. The solution was transferred to a 500 mL Erlenmeyer flask equipped with a ground glass joint. The Erlenmeyer flask was sealed with a well-greased stopper. The reaction mixture was irradiated from the bottom of the Erlenmeyer with either a 13 W compact fluorescent light bulb or a 100 W mercury lamp for 10 hours while the temperature was maintained at either 28 °C by the use of cooling airflow, or at -40 °C in a dry ice/acetonitrile bath. At the end of the reaction time the reaction mixture was a clear, pale yellow-orange. The reaction mixture was then opened to air, diluted with diethyl ether (15 mL), and washed with distilled water (3 x 5 mL). The aqueous fractions were re-extracted with 5 mL of diethyl ether, and the combined organic layers were stirred with 5 mL of an aqueous 30% hydrogen peroxide solution for 20 minutes (This workup is

designed to oxidize the residual P(*m*-tol)$_3$ to facilitate its removal and is adapted from Reference 43). The aqueous layer was then separated, and the organic layer was washed with water (2 x 5 mL); the aqueous layers were washed with 5 mL of diethyl ether, and then the combined organic layers were stirred with 10 mL of saturated aqueous ferrous sulfate for 30 minutes. Then the aqueous layer was removed, and the organic layer was washed with water (2 x 5 mL). The aqueous layers were washed with 5 mL of diethyl ether. The combined organic layers were then washed with 5 mL of saturated aqueous sodium chloride, dried over magnesium sulfate, filtered, and concentrated. The resulting orange residue was taken up in minimal toluene and filtered through a plug of silica, washing with hexanes. The filtrate was then concentrated to a light orange residue. This residue was purified by column chromatography on silica gel, eluting with hexanes, giving *N*-phenylcarbazole as a white solid. The identity of the product was confirmed by comparison of GC-MS and NMR data with those of a commercial sample.

General procedure for synthesis of *N*-phenylcarbazole from 1 and PhX (X = I, Br, Cl), GC scale: A solution of PhX in acetonitrile or deuterated acetonitrile was added to solid **1** (10 mg) in a glass vial with a Teflon stirbar. The resulting solution was clear and colorless. The vial was sealed with a PTFE-lined cap and electrical tape. The reaction mixture was allowed to stir in darkness for 10-20 minutes until all solids were dissolved. The reaction was then subjected to illumination using a 13 W CFL light bulb or a 100 W Hg lamp while stirring. Cooling airflow was maintained to keep the temperature at 27-30 ^{o}C. In the case of low-temperature (-40 ^{o}C) reactions, the reaction mixture was transferred to a small Schlenk tube, which was immersed in a dry ice/acetonitrile bath, taking care to avoid freezing the reaction mixture. After a few hours the reaction mixture was typically pale orange in color. When the desired reaction time was reached, the reaction mixture was opened to air, diluted with THF, filtered through a silica plug, and analyzed by GC against a calibrated internal standard (4, 4'-di-*tert*-butylbiphenyl).

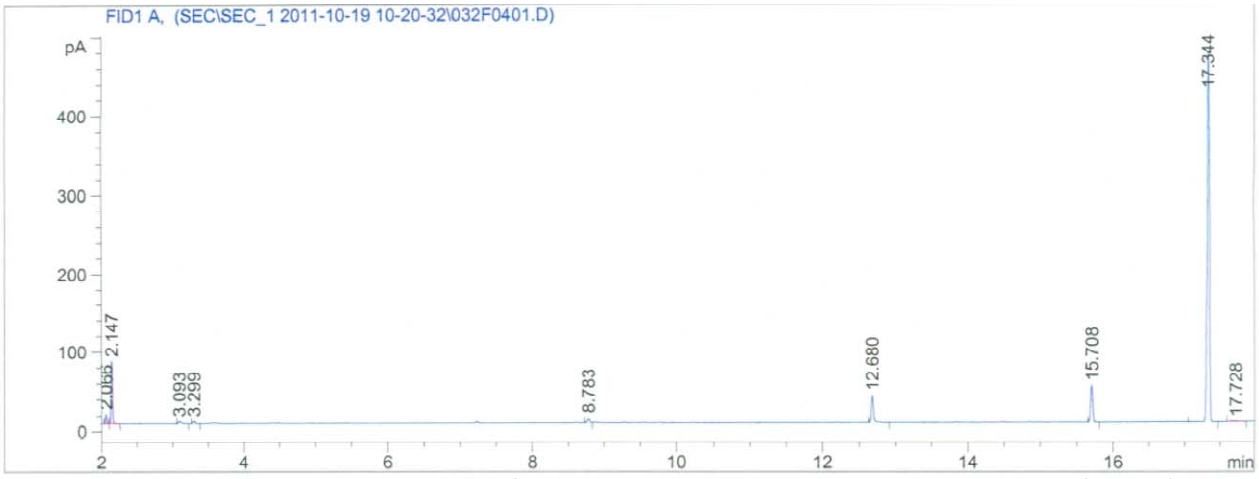


Figure S5. Representative GC trace. (0.3 M **1** with 1.2 equiv PhI in CD_3CN, irradiated for 9 hr)

Retention times, independently confirmed with authentic samples: 2.147 (PhI), 12.680 (carbazole), 15.708 (di-*tert*-butylbiphenyl), 17.344 (*N*-phenylcarbazole).

C. Oxidation of 1

Oxidation of 1 with $NOSbF_6$: a. An *acetonitrile* solution (1 mL) of $NOSbF_6$ (3.3 mg, 0.0124 mmol) was added drop-wise to a stirring 1 mL acetonitrile solution of **1** (9.7 mg, 0.0116). The solution color did not change. After 30 minutes the reaction mixture was concentrated to dryness and analyzed by ^{1}H NMR spectroscopy. **b.** A *THF* solution (1 mL) of $NOSbF_6$ (4.3 mg, 0.0162 mmol) was added drop-wise to a stirring 1 mL THF solution of **1** (11.2 mg, 0.0134 mmol). The solution color did not change. After 30 minutes the reaction mixture was concentrated to dryness and analyzed by ^{1}H NMR spectroscopy. In both cases (a) and (b), the only carbazole-containing product observable by ^{1}H NMR spectroscopy, and confirmed by GC, was unsubstituted carbazole.

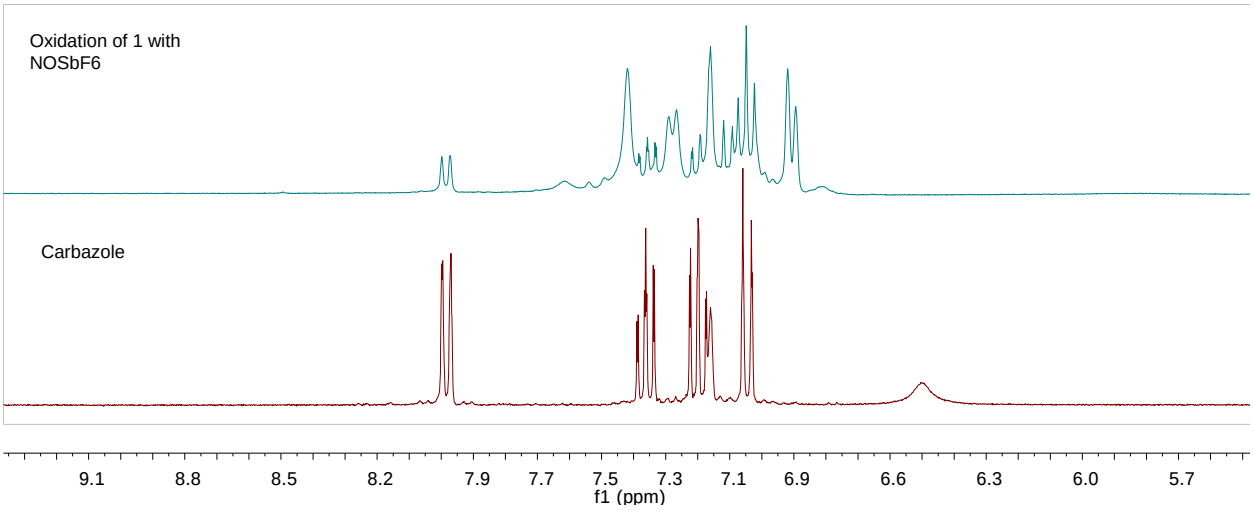


Figure S6. ^{1}H NMR, C_6D_6, 300 MHz

D. Catalytic C-N coupling to give *N*-phenylcarbazole

Synthesis of *N*-phenylcarbazole with catalyst 1: Lithium carbazolide (100 mg, 0.58 mmol, 1.0 equiv), iodobenzene (142 mg, 0.70 mmol, 1.2 equiv), and **1** (48.8 mg, 0.058 mmol, 0.10 equiv) were combined in 2 mL of acetonitrile to give a clear yellow solution in a 20 mL scintillation vial, which was sealed with a PTFE-lined cap and electrical tape. This reaction mixture was irradiated for 10 hours with a 100 W mercury lamp at 28 ^{o}C, resulting in a dark brown mixture. The reaction mixture was then opened to air, diluted with diethyl ether (15 mL), and washed with distilled water (3 x 5 mL). The aqueous fractions were back-extracted with 5 mL of diethyl ether, and the combined organic layers were stirred with 5 mL of an aqueous 30% hydrogen peroxide solution for 20 minutes. The aqueous layer was then separated, and the organic layer was washed with water (2 x 5 mL); the aqueous layers were washed with 5 mL of diethyl ether, and then the combined organic layers were stirred with 10 mL of saturated aqueous ferrous sulfate for 30 minutes. The aqueous layer was then removed, and the organic layer was washed with water (2 x 5 mL). The aqueous layers were washed with 5 mL of diethyl ether, and then the combined organic layers were washed with 5 mL of saturated aqueous sodium chloride and dried over

magnesium sulfate, filtered, and concentrated. The resulting orange residue was taken up in minimal toluene, filtered through a plug of silica, washing with hexanes, and the resulting filtrate concentrated to a light orange residue. This residue was purified by column chromatography on silica gel, eluting with hexanes, giving *N*-phenylcarbazole as a white solid (73 mg, 52%). The identity of the product was confirmed by comparison of its GC-MS and NMR data with those of an authentic sample.

Synthesis of *N*-phenylcarbazole with catalytic CuI: Lithium carbazolide (100 mg, 0.58 mmol, 1.0 equiv), iodobenzene (142 mg, 0.70 mmol, 1.2 equiv), and copper(I) iodide (10.6 mg, 0.058 mmol, 0.10 equiv) were combined in 2 mL of acetonitrile to give a clear yellow solution in a 20 mL scintillation vial, which was sealed with a PTFE-lined cap and electrical tape. This reaction mixture was irradiated for 10 hours with a 100 W mercury lamp at 28 ^{o}C, giving a dark brown mixture. The reaction mixture was then opened to air, diluted with diethyl ether (15 mL), and washed with distilled water (3 x 5 mL). The aqueous fractions were then extracted with 5 mL of diethyl ether, and the combined organic layers were washed with 5 mL of saturated aqueous sodium chloride and dried over magnesium sulfate, filtered, and concentrated. The resulting orange residue was taken up in minimal toluene, filtered through a plug of silica, washing with hexanes, and the resulting filtrate concentrated to a light orange residue. This residue was purified by column chromatography on silica gel, eluting with hexanes, giving *N*-phenylcarbazole as a white solid (82 mg, 58%). The identity of the product was confirmed by comparison of GC-MS and NMR data with those of a commercial sample.

Catalytic synthesis of *N*-phenylcarbazole, GC-scale, general procedure: Lithium carbazolide (25 mg, 0.144 mmol) and iodobenzene (35.4 mg, 0.174 mmol, 1.2 equiv) were combined with 0.014 mmol of the catalyst (**1** or CuI) in 0.5 mL of acetonitrile in a 20 mL scintillation vial or small Schlenk tube. The reaction mixture was irradiated for 10 hours with a 100 W mercury lamp, either at ambient temperature (28-30 ^{o}C) or at -40 ^{o}C in a dry ice/acetonitrile bath. The reaction mixture, which was typically brown in color, was diluted with THF, filtered through a plug of silica, and analyzed by GC against a calibrated internal standard (4,4'-di-*tert*-butylbiphenyl).

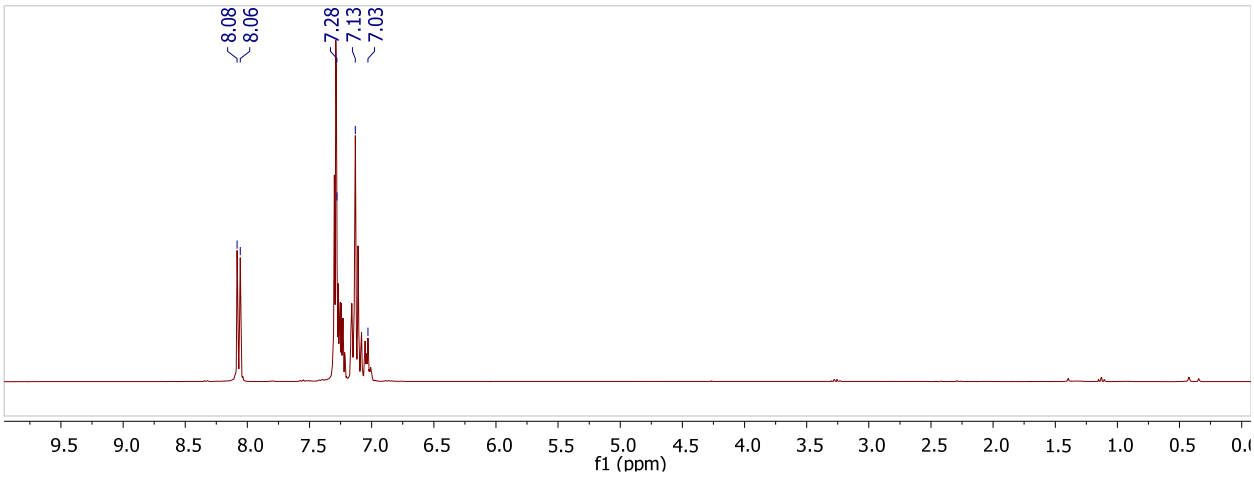


Figure S7. ^{1}H NMR (C_6D_6, 300 MHz, 298 K) of *N*-phenylcarbazole from catalytic reaction with CuI.

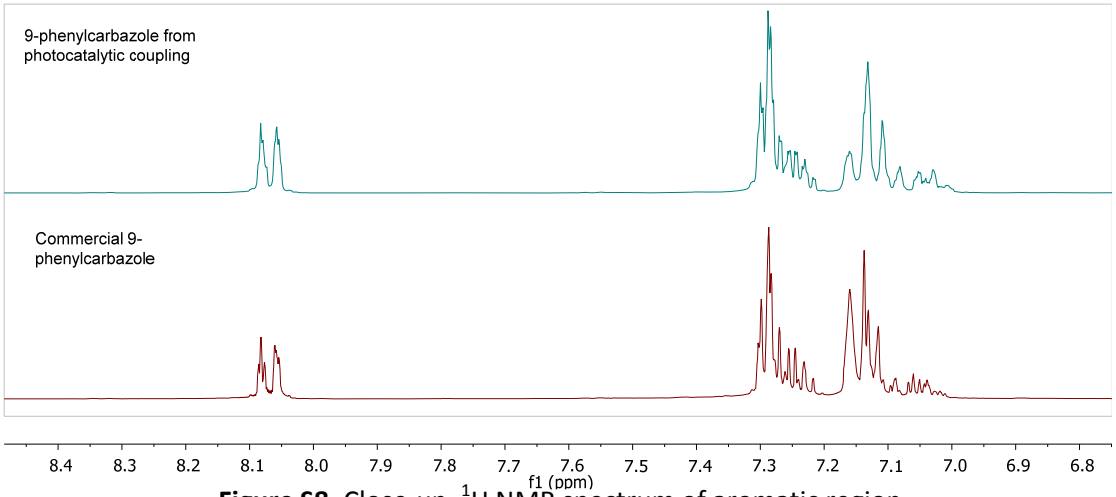


Figure S8. Close-up, ^{1}H NMR spectrum of aromatic region.

E. Synthesis and characterization of 6

Synthesis of 6: 2-allyloxyiodobenzene (74 mg, 0.29 mmol, 1.2 equiv) was added to an acetonitrile solution (0.5 mL) of **1** (200 mg, 0.24 mmol). The reaction mixture was stirred in darkness for 20 minutes and then subjected to irradiation using a 13 W CFL lightbulb at 28 ^{o}C for 10 hours. The reaction mixture was then opened to air, diluted with diethyl ether (15 mL), and washed with distilled water (3 x 5 mL). The aqueous fractions were then extracted with 5 mL of diethyl ether, and the combined organic layers were stirred with 5 mL of an aqueous 30% hydrogen peroxide solution for 20 minutes. The aqueous layer was then separated, and the organic layer was washed with water (2 x 5 mL); the aqueous layers were washed with 5 mL of diethyl ether, and then the combined organic layers were stirred with 10 mL of saturated aqueous ferrous sulfate for 30 minutes. Then the aqueous layer was removed, and the organic layer was washed with water (2 x 5 mL). The aqueous layers were washed with 5 mL of diethyl ether, and the combined organic layers were then washed with 5 mL of saturated aqueous sodium chloride and dried over magnesium sulfate, filtered, and concentrated. The yellow-orange residue was purified by silica gel chromatography (5% EtOAc:hexanes) to give **6** as a white solid (29.2 mg, 41%), m.p. 159-160 °C. ^{1}H NMR (C_6D_6, 300 MHz, 298 K, ppm): δ 8.04 (d, 2H, 4-*H*-cbz, *J* = 8 Hz), 7.34 (t, 2H, 2-*H*-cbz, *J* = 8 Hz), 7.23 (t, 2H, 2-*H*-cbz, *J* = 8 Hz), 7.01 (d, 2H, 1-*H*-cbz, *J* = 8 Hz), 6.98 (t, 1H, 6-*H*-dihydrobenzofuran, *J* = 8 Hz), 6.87 (d, 1H, 4-*H*-dihydrobenzofuran, *J* = 8 Hz, 6.59 (m, 2H, 7-*H*-dihydrobenzofuran and 5-*H*-dihydrobenzofuran), 4.03 (dd, 1H, 2-C*H*H-dihydrobenzofuran, *J* = 9 Hz, 4 Hz), 3.73-3.91 (m, 3H, 2-CH*H*-dihydrobenzofuran and N(cbz)-CH_2-dihydrobenzofuran), 3.55 (m, 1H, 3-C*H*-dihydrobenzofuran). ^{13}C{^{1}H} (C_6D_6, 75 MHz, 298 K, ppm) δ 160.8 (7a-*C*-dihydrobenzofuran), 140.8 (*C*(Ar)), 129.4 (*C*(Ar)), 128.2 (*C*(Ar)), 127.9 (*C*(Ar)), 126.1 (*C*(Ar)), 125.3 (*C*(Ar)), 123.5 (*C*(Ar)), 120.8 (*C*(Ar)), 119.7 (*C*(Ar)), 110.2 (*C*(Ar)), 109.1 (*C*(Ar)), 74.4 (2-*C*H_2-dihydrobenzofuran), 46.6 (N-*C*H_2), 42.1 (3-*C*H-dihydrobenzofuran).

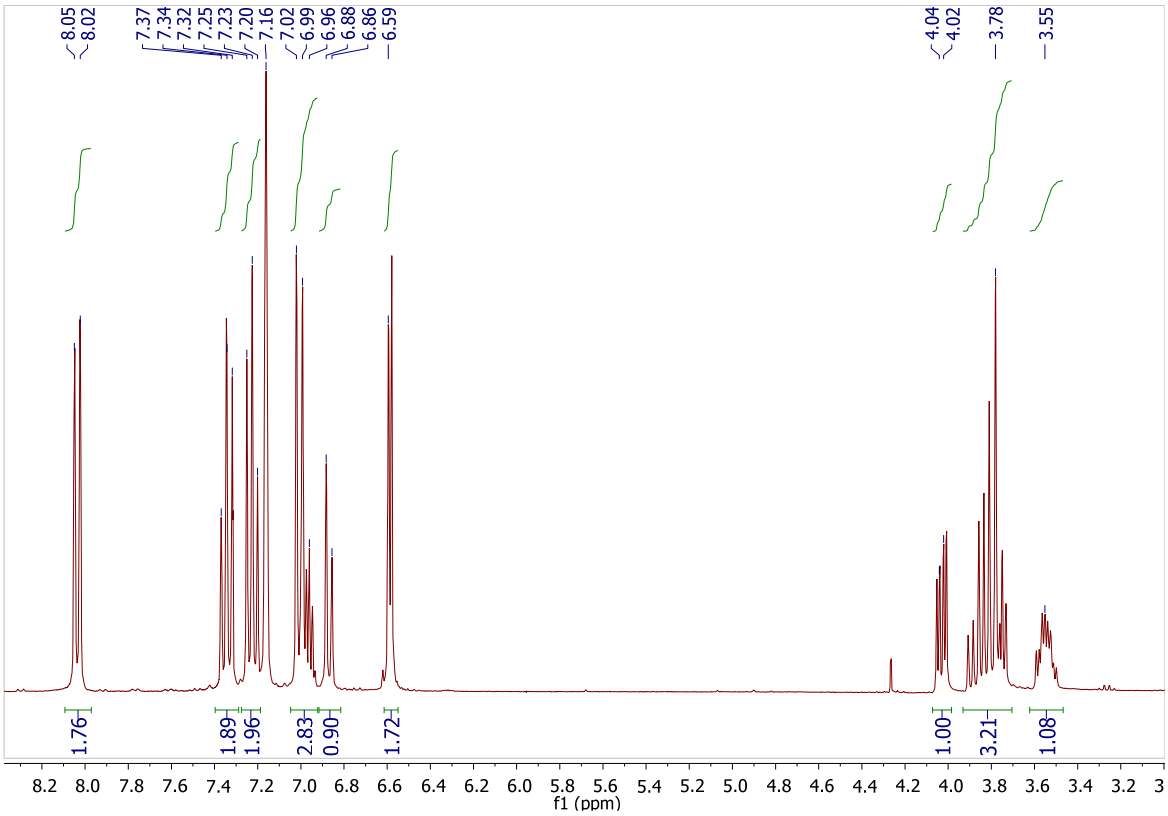


Figure S9. ^{1}H NMR spectrum of **6**.

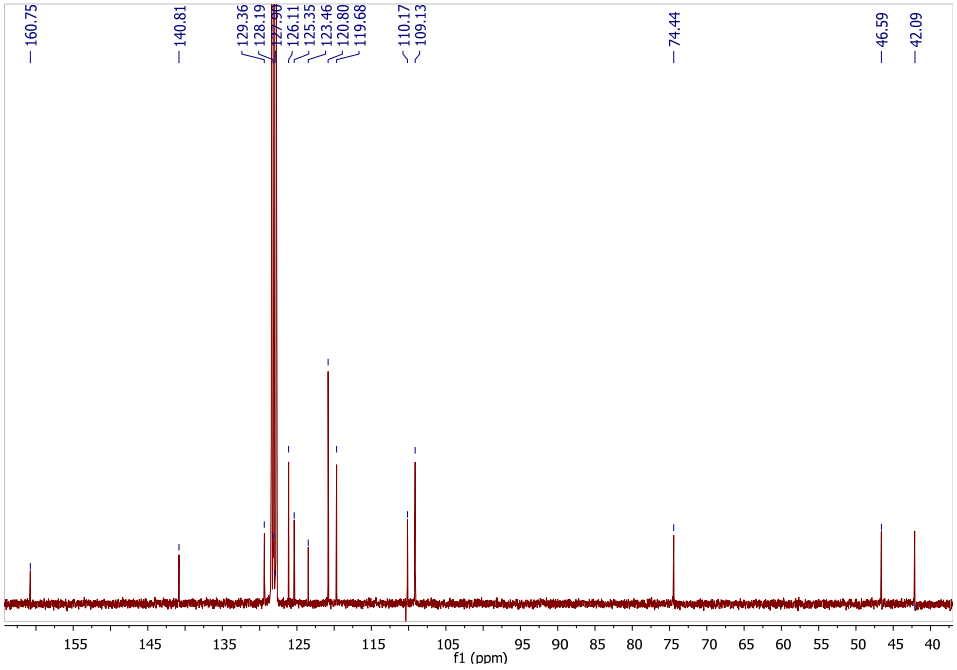


Figure S10. ^{13}C NMR of **6**

F. Synthesis and characterization of 4-d and its bromoarene analogue

Synthesis of (*E*)-(3-deuterioallyl)oxy-2-iodobenzene, 4-d: In the dry glove-box, 2-propargyloxyiodobenzene (1.019 g, 3.95 mmol) was dissolved in 5 mL THF and added dropwise to a white suspension of Cp_2ZrHCl (Schwartz's reagent, 1.2 g, 4.65 mmol, 1.18 equiv) in 20 mL THF. Within a few minutes the white suspension had turned clear dark orange-red. The reaction mixture was allowed to stir at room temperature for 4 hours, and then brought out of the glove box in a septum-covered round-bottomed flask. D_2O (1.5 mL) was added via syringe to the reaction, causing the red-orange color to immediately disappear, leaving a pale yellow solution. The solution was stirred at room temperature for 30 minutes. The reaction mixture was then diluted with ca. 100 mL of diethyl ether, causing white solids to precipitate. The solution was dried over magnesium sulfate, filtered, concentrated, filtered through a plug of silica, and concentrated. The remaining yellowish oil was distilled at reduced pressure to give (*E*)-(3-deuterioallyl)oxy-2-iodobenzene as a clear, colorless oil. The isolated material is approximately a 10:1 mixture of the desired isotopomer and (2-deuterioallyl)oxy-2-iodobenzene (370 mg, 36%). ^{1}H NMR (C_6D_6, 400 MHz, 298 K, ppm): δ 7.67 (d, 1H, 3-Ar-*H*, *J* = 8 Hz), 6.91 (t, 1H, Ar-*H*, *J* = 8 Hz), 6.38 (t, 1H, Ar-*H*, *J* = 8 Hz), 6.31 (d, 1H, Ar-*H*, *J* = 8 Hz), 5.70 (dt, 1H, -OCH$_2$C*H*CHD, *J* = 17 Hz, 5 Hz), 5.32 (d, 1H, -OCH$_2$CHC*H*D, *J* = 17 Hz), 4.01 (d, 2H, -OC*H*$_2$CHCHD, *J* = 5 Hz) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz, 298 K, ppm): δ 157.2, 139.5, 132.5, 129.0, 122.3, 116.4 (1:1:1 t, J_{CD} = 24 Hz), 112.2, 86.7, 69.0. ^{2}H{^{1}H} NMR (C_6H_6, 76 MHz, 298 K): δ 5.03 (s).

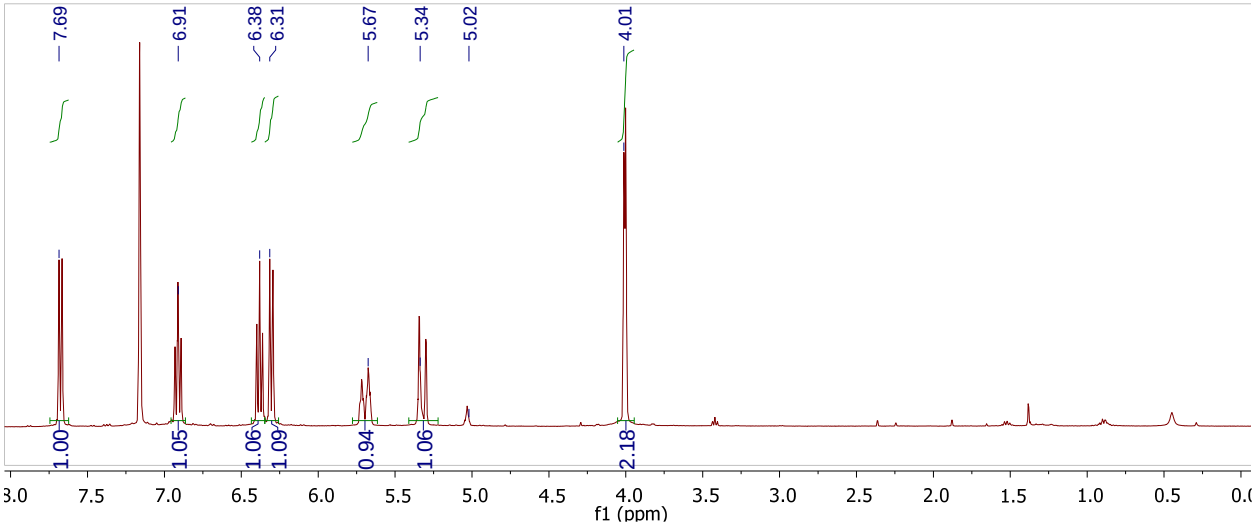


Figure S11. ^{1}H NMR spectrum of (*E*)-(3-deuterioallyl)oxy-2-iodobenzene, **4-d**

The assignment of *E* stereochemistry for **4-d** is corroborated by the coupling constants in the ^{1}H NMR spectra. The peak at 5.67 ppm, corresponding to the internal alkenyl proton, shows couplings of 5 Hz (triplet, coupling to methylene protons) and 17 Hz (doublet, coupling to terminal alkenyl proton). A coupling constant of 17 Hz is consistent with three-bond coupling to a *trans* proton and is outside the expected range for coupling to a *cis* proton.

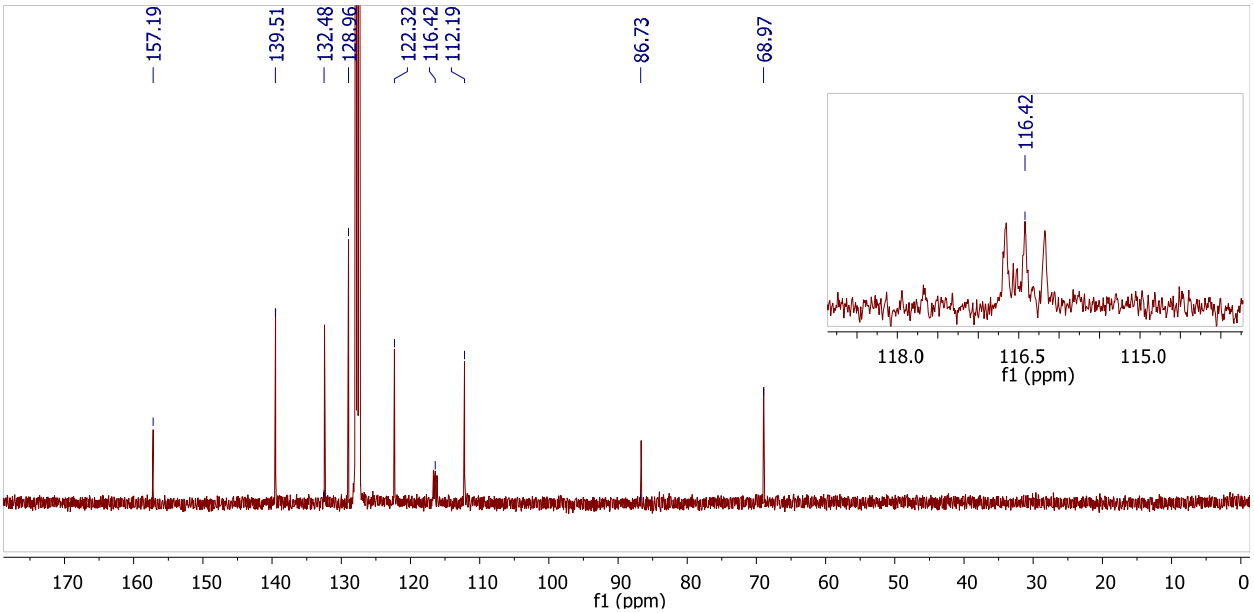


Figure S12. ^{13}C NMR spectrum of (*E*)-(3-deuterioallyl)oxy-2-iodobenzene, **4-d**

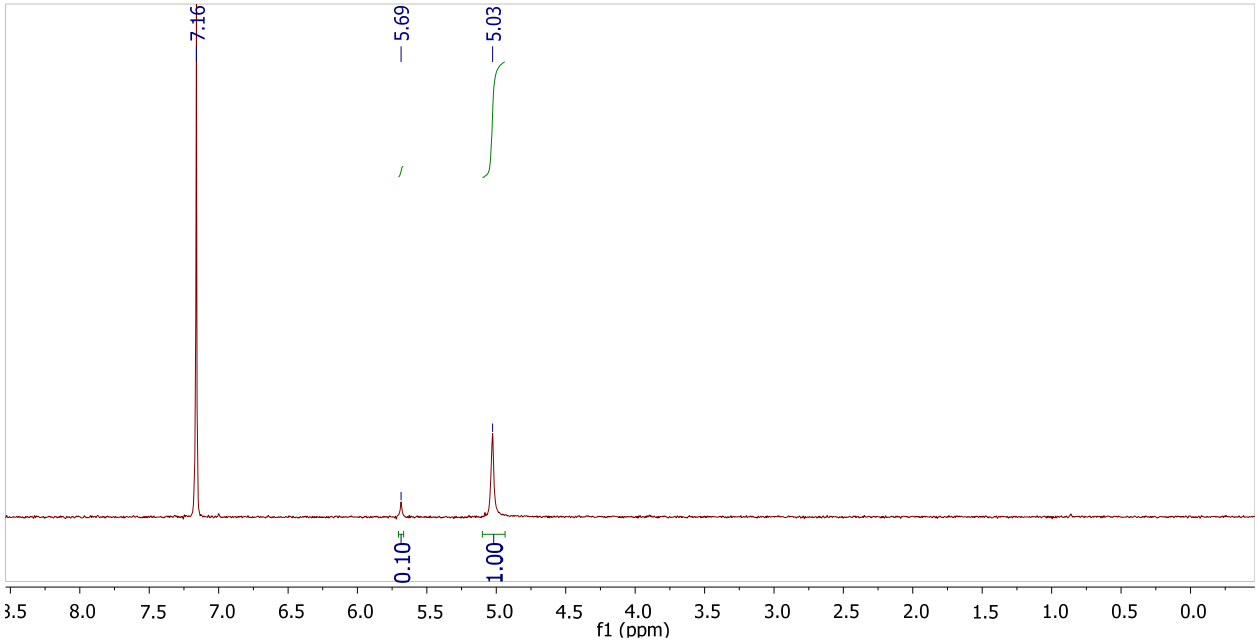


Figure S13. ^{2}H NMR spectrum of (*E*)-(3-deuterioallyl)oxy-2-iodobenzene, **4-d**

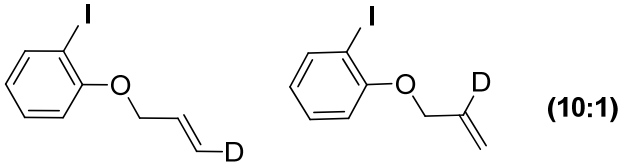


Figure S14. Isotopomers formed in synthesis of deuterated radical clock probe, **4-d**.

Synthesis of (*E*)-(3-deuterioallyl)oxy-2-bromobenzene: In a dry-glove box, 2-propargyloxybromobenzene (265 mg, 0.85 equiv) was dissolved in 1 mL of THF and added dropwise to a white suspension of Cp_2ZrHCl (Schwartz's reagent, 380 mg) in 2 mL of THF. Almost immediately, the white suspension turned clear yellow. The reaction mixture was allowed to stir at room temperature for 2 hours, and then brought out of the glove box in a septum-covered round-bottomed flask. D_2O (0.7 mL) was added via syringe to the reaction, causing the yellow color to immediately disappear. The solution was stirred at room temperature for 20 minutes. The reaction mixture was then diluted with ca. 40 mL of diethyl ether, causing white solids to precipitate. The solution was dried over magnesium sulfate, filtered through a plug of silica, and concentrated. The remaining yellowish oil was distilled at reduced pressure to give (*E*)-(3-deuterioallyl)oxy-2-bromobenzene as a clear, colorless oil. As with **4-d**, the product was contaminated with ca. 10% of the (2-deuterioallyl)oxy-2-bromobenzene isotopomer. The NMR properties are consistent with those reported for the non-deuterated analogue, *o*-allyloxybromobenzene (*44*). ^{1}H NMR (C_6D_6, 300 MHz, 298 K, ppm): δ 7.43 (dd, 1H, Ar-*H*, *J* = 8 Hz, 2 Hz), 6.88 (m, Ar-*H*, 1H), 6.49 (td, 1H, Ar-*H*, *J* = 8 Hz, 2 Hz), 6.39 (dd, 1H, Ar-*H*, *J* = 8 hz, 2 Hz), 5.68 (m, 1H, -OCH_2CHCHD), 5.27 (dt, 1H, -OCH_2CHCHD, *J* = 17 Hz, 2 Hz), 4.02 (dd, 2H, -OCH_2CHCHD, *J* = 5 Hz, 2 Hz). ^{2}H NMR (C_6H_6, 76 MHz, 298 K, ppm): δ 4.98 (s).

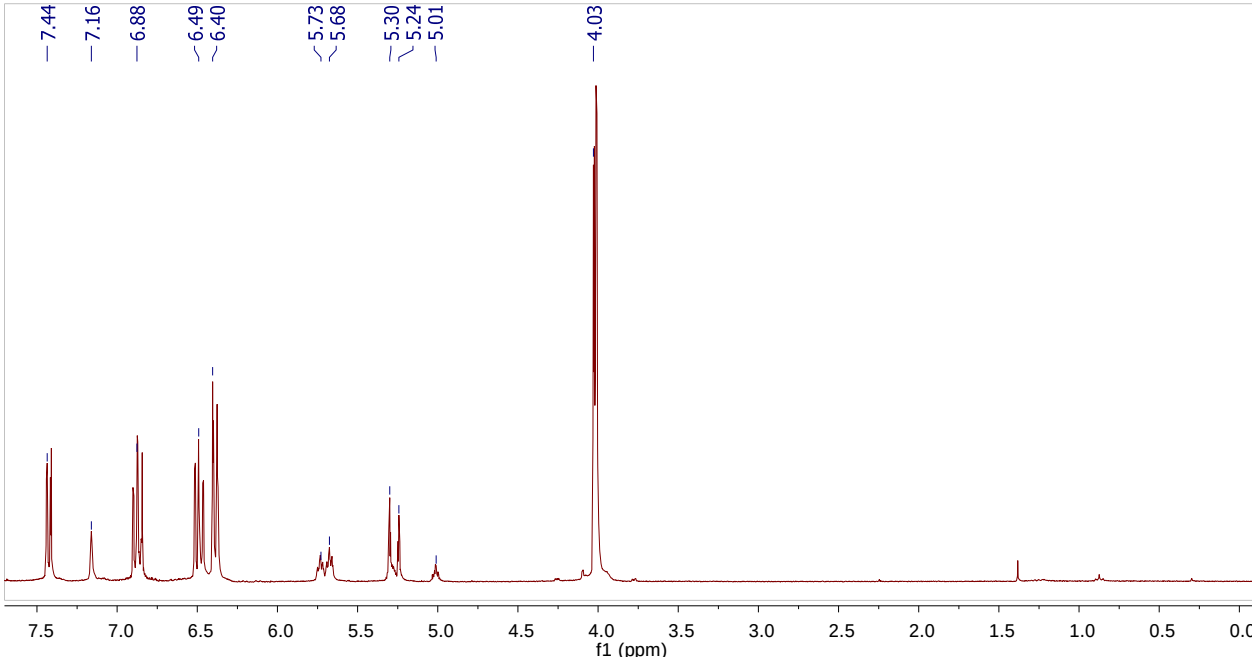


Figure S15. ^{1}H NMR spectrum of (*E*)-(3-deuterioallyl)oxy-2-bromobenzene, C_6D_6

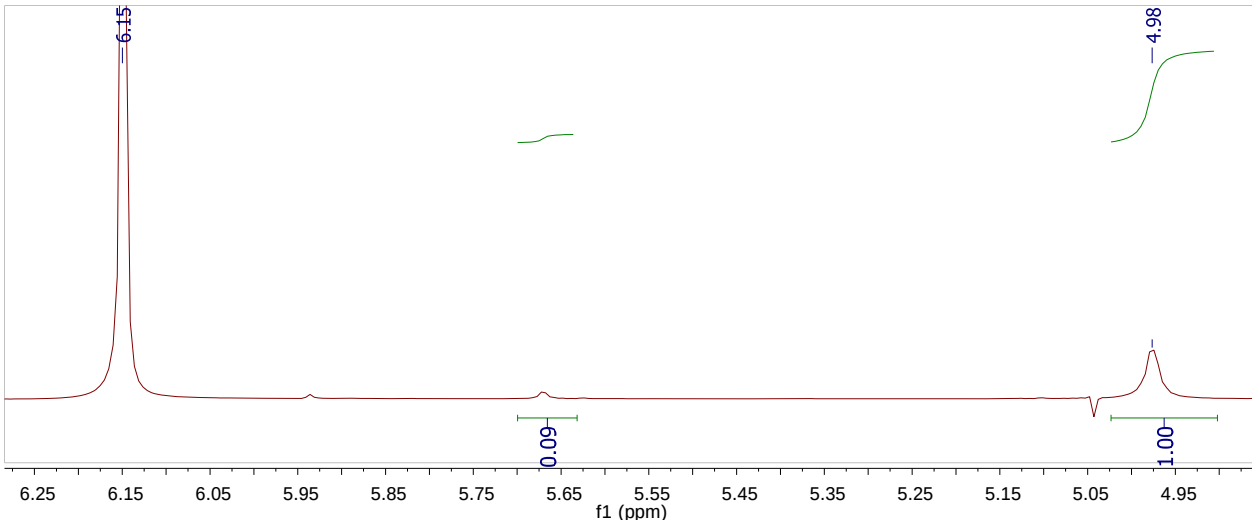


Figure S16. ^{2}H NMR spectrum of (*E*)-(3-deuterioallyl)oxy-2-bromobenzene, C_6H_6 with $CDCl_3$ standard

G. Synthesis and characterization of 6-d and 6'-d

Synthesis of 6-d and 6'-d: 4-d (41 mg, 0.16 mmol, 1.1 equiv), as a mixture of isotopomers, was added to **1** (119 mg, 0.14 mmol) in acetonitrile (5 mL) to give a clear, colorless solution. The reaction mixture was subjected to irradiation at room temperature under a 100 W mercury lamp for 8 hours, resulting in a color change to pale orange. GC-MS confirmed the presence of the cyclized, deuterodehalogenation product 3-deuteriomethyl-2,3-dihydrobenzofuran and the carbazole coupling products **6-d** and **6'-d** (m/z = 300.1, 181.2). None of the uncyclized coupling product N-(2-allyloxyphenyl)carbazole was observed by GC-MS or by NMR. The reaction mixture was diluted with diethyl ether, washed with water, stirred over 10 mL of 30% H_2O_2, washed with water, stirred over 10 mL of saturated aqueous ferrous sulfate, washed with water, washed with brine, dried over magnesium sulfate, filtered, and concentrated. The resulting orange residue was purified by column chromatography (5% EtOAc/hexanes) and then recrystallized from cold hexanes to give **6-d** and **6'-d** as off-white crystals (19.1 mg, 45%). The isolated product was a mixture of the desired pair of diastereomers and the isomer derived from the minor isotopomer of the starting material. ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K, ppm): δ 8.16 (d, 2H, 4-*H*-cbz, *J* = 8 Hz), 7.50 (t, 2H, 2-*H*-cbz, *J* = 8 Hz), 7.42 (d, 2H, 1-*H*-cbz, *J* = 8 Hz), 7.30 (t, 2H, 2-*H*-cbz, *J* = 8 Hz), 7.22 (t, 1H, 6-*H*-dihydrobenzofuran, *J* = 8 Hz), 7.02 (dd, 1H, 4-*H*-dihydrobenzofuran, *J* = 8 Hz, 3 Hz), 6.93 (d, 1H, 7-*H*-dihydrobenzofuran, *J* = 8 Hz), 6.83 (t, 1H, 5-*H*-dihydrobenzofuran, *J* = 8 Hz), 4.52-4.38 (m, 3H, N-C*H*D, 2-*H*$_2$-dihydrobenzofuran), 4.14 (m, 1H, 3-*H*-dihydrobenzofuran). ^{13}C{^{1}H} ($CDCl_3$, 126 MHz, 298 K, ppm) δ 160.1 (7a-*C*-dihydrobenzofuran), 140.4 (8a-*C*-cbz), 129.2 (6-*C*H-dihydrobenzofuran), 127.7 (3a-*C*-dihydrobenzofuran), 125.9 (2-*C*H-cbz), 125.1 (4-*C*H-dihydrobenzofuran), 123.0 (4a-*C*-cbz), 120.8 (5-*C*H-dihydrobenzofuran), 120.5 (4-*C*H-cbz), 119.4 (3-*C*H-cbz), 110.0 (7-*C*H-dihydrobenzofuran), 108.7 (1-*C*H-cbz), 74.6 (2-*C*H$_2$-dihydrobenzofuran), 46.47 (1:1:1 triplet, N-*C*HD, J_{CD} = 21 Hz), 42.2 (3-*C*H-dihydrobenzofuran). ^{2}H{^{1}H} (C_6H_6, 76 MHz, 298 K, ppm) δ 3.84 (0.5D, N-CH*D*), 3.75 (0.5D, N-C*D*H).

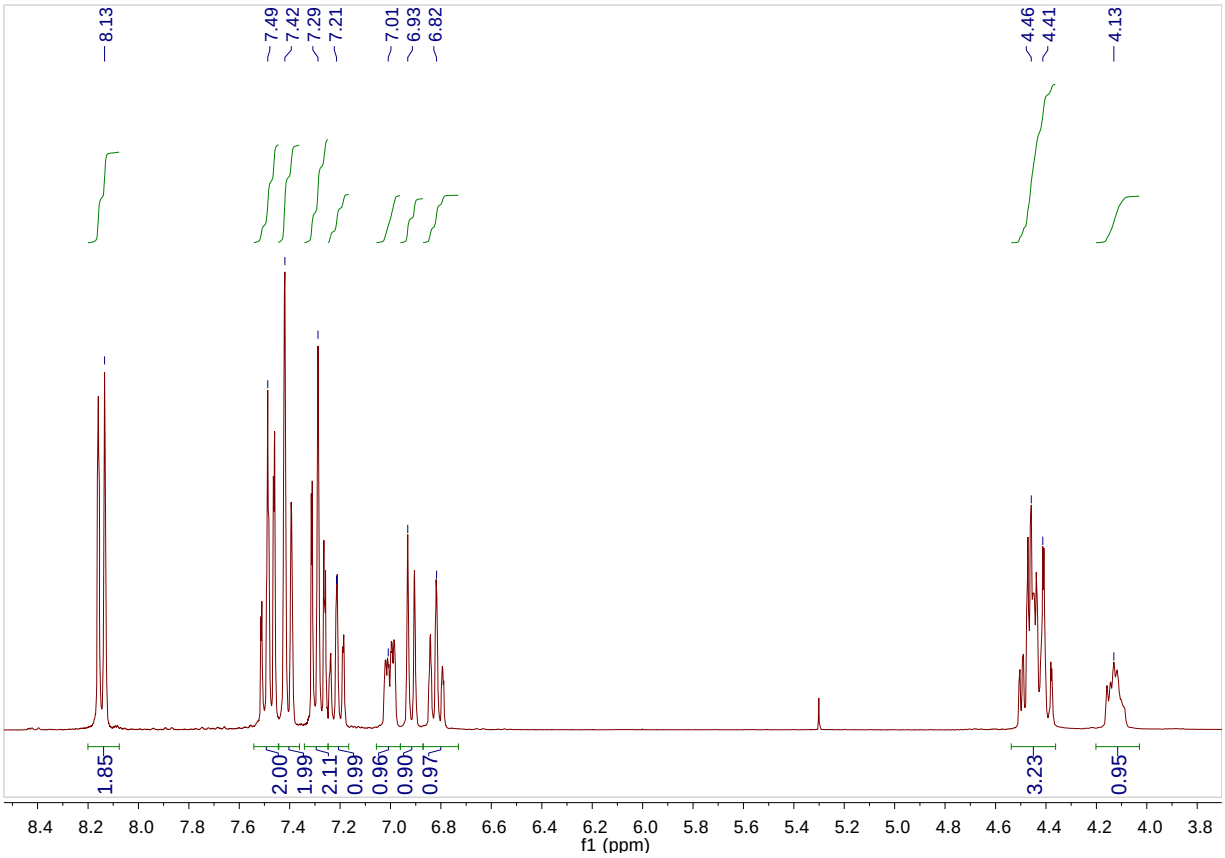


Figure S17. ^{1}H NMR spectrum, **6-d** and **6'-d**

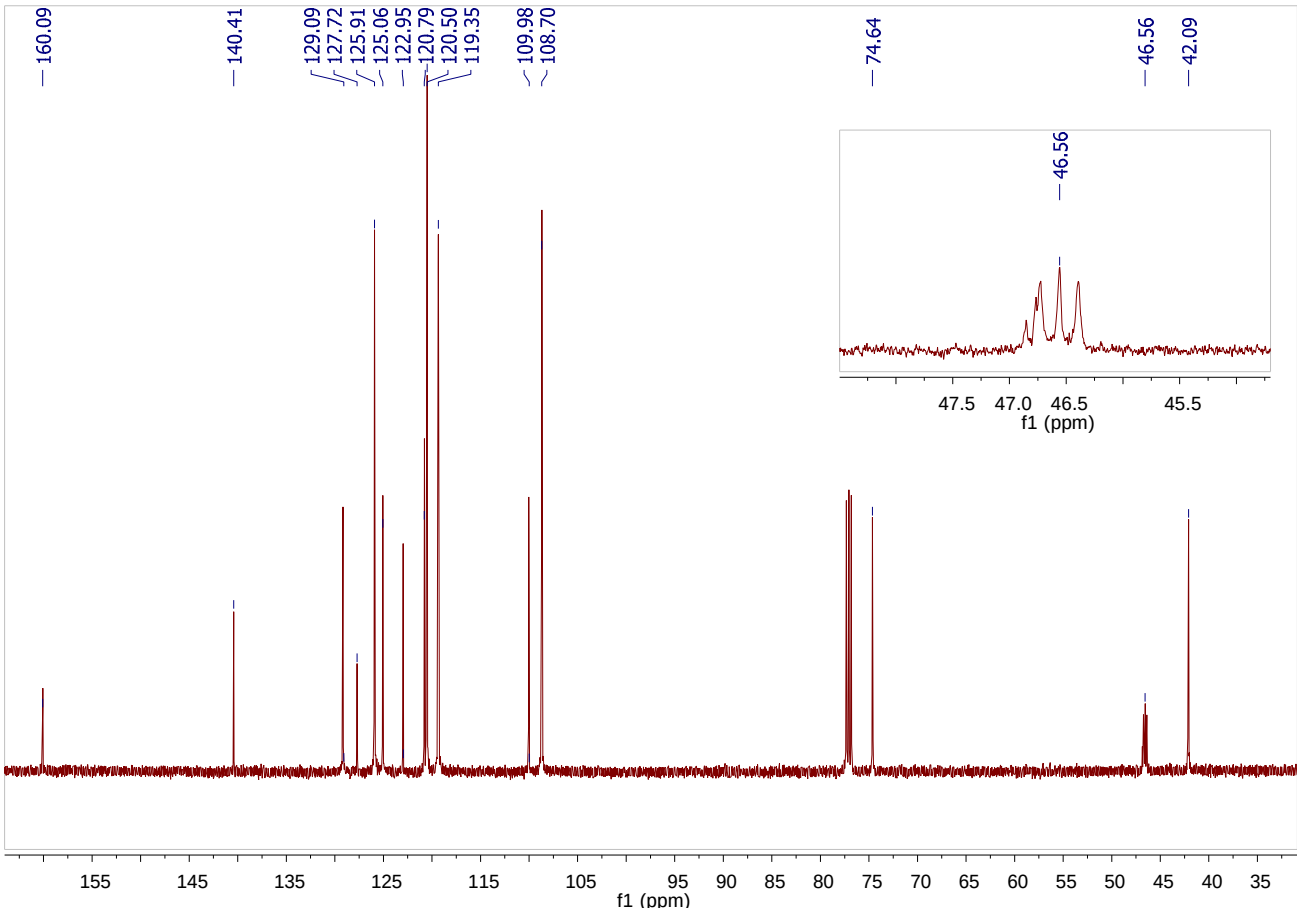


Figure S18. ^{13}C NMR spectrum of **6-d** and **6'-d** with inset showing C-D coupling

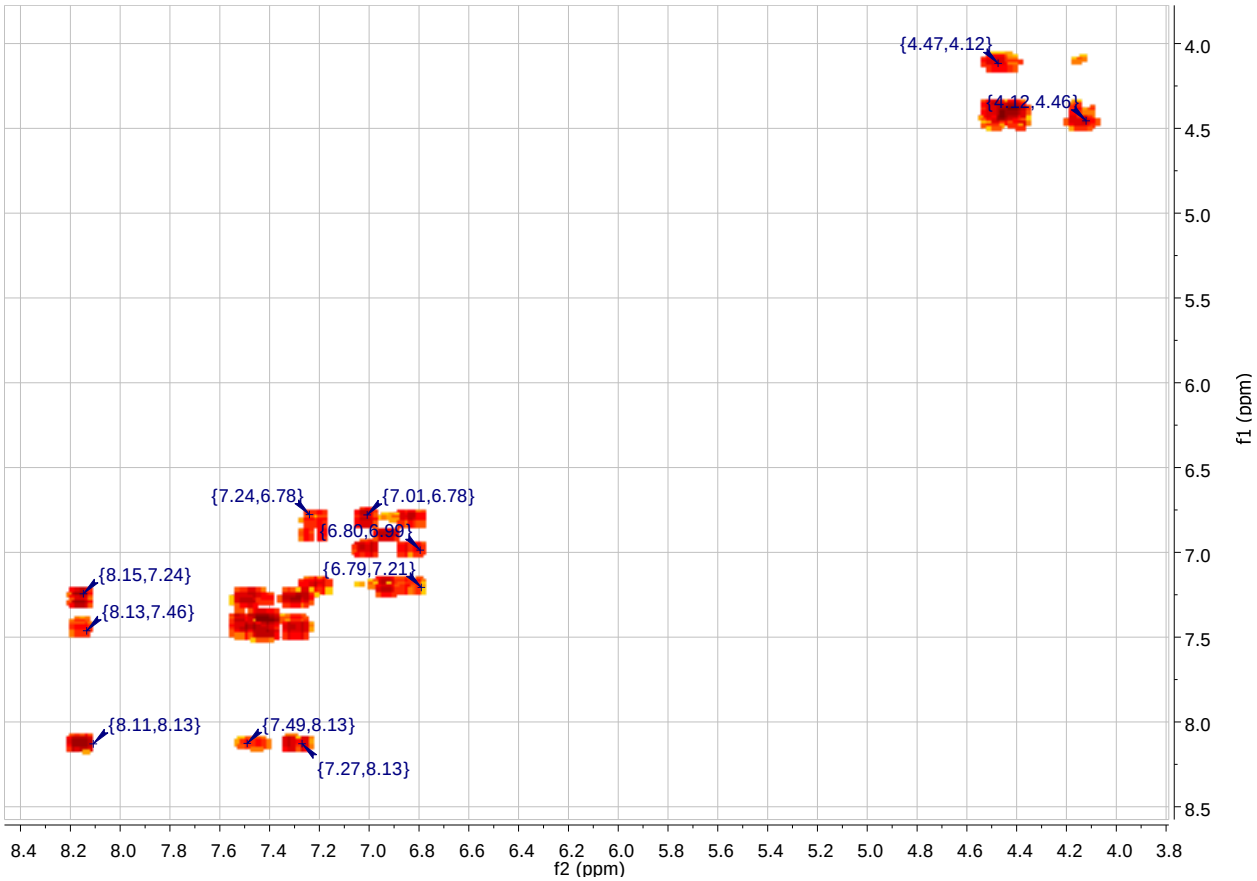


Figure S19. gCOSY spectrum of **6-d** and **6'-d**

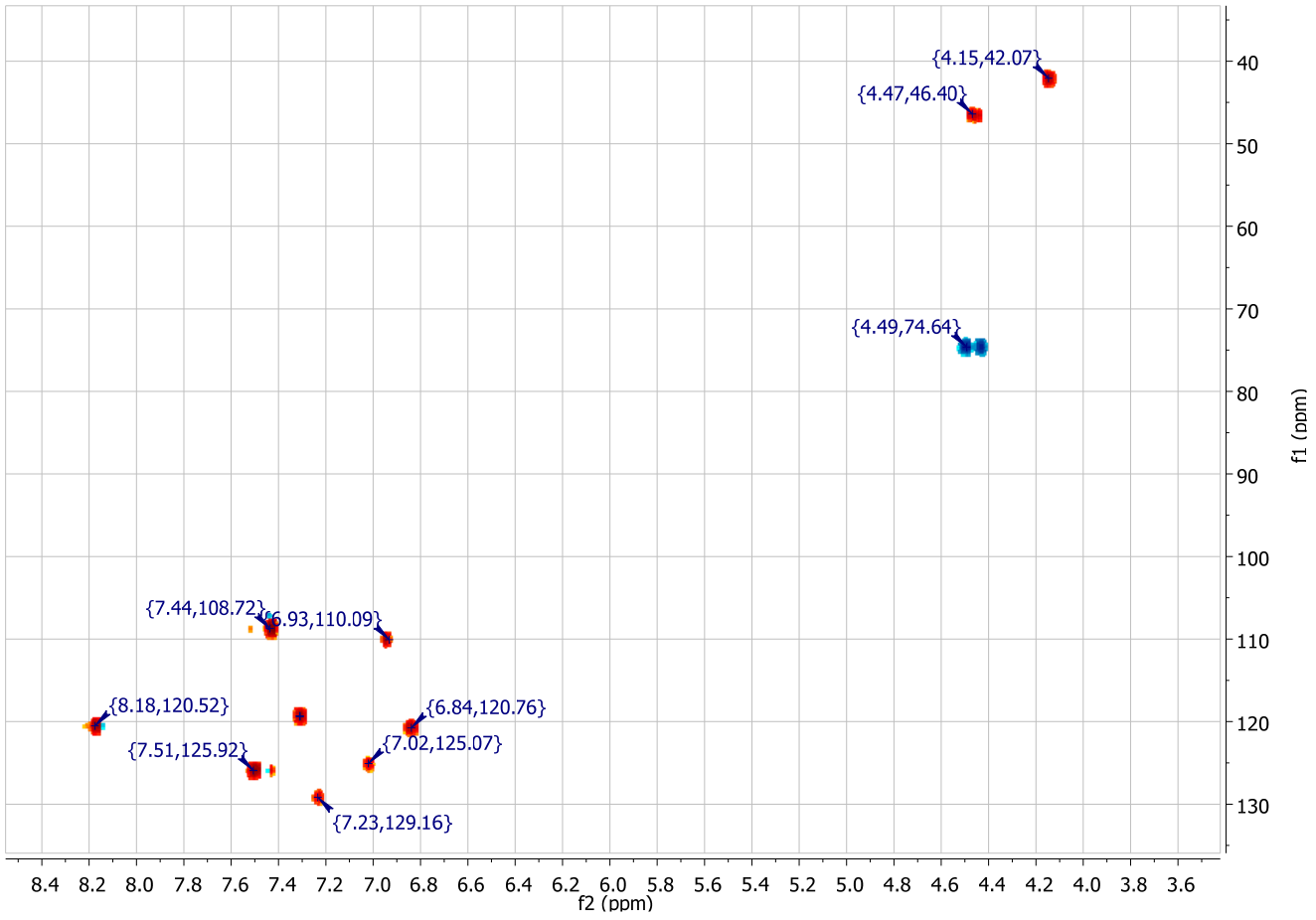


Figure S20. Phase-sensitive HSQC spectrum of **6-d** and **6'-d**

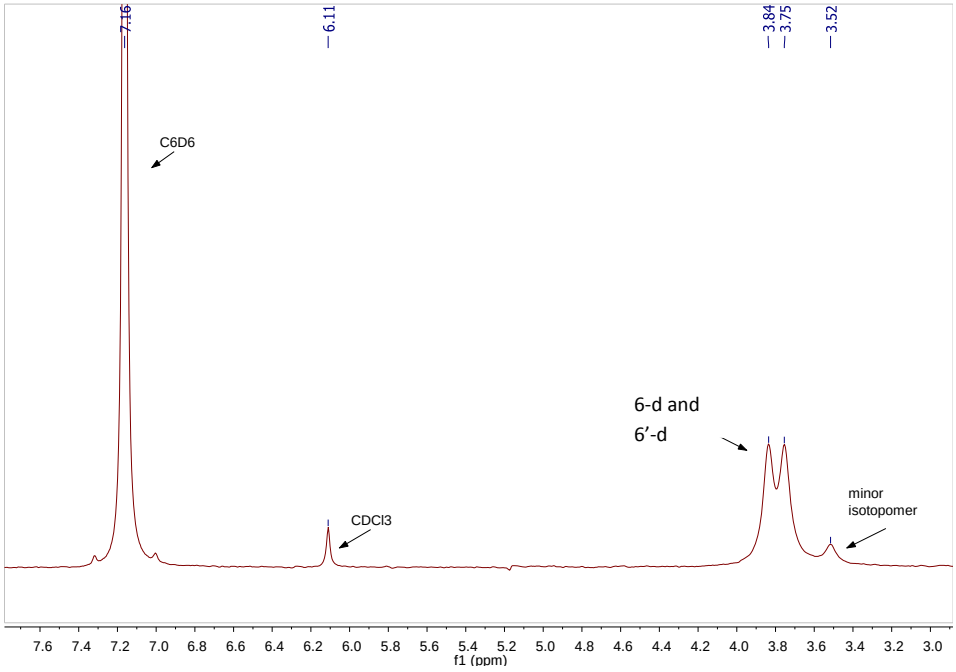


Figure S21. ^{2}H NMR spectrum of **6-d** and **6'-d** in C_6H_6

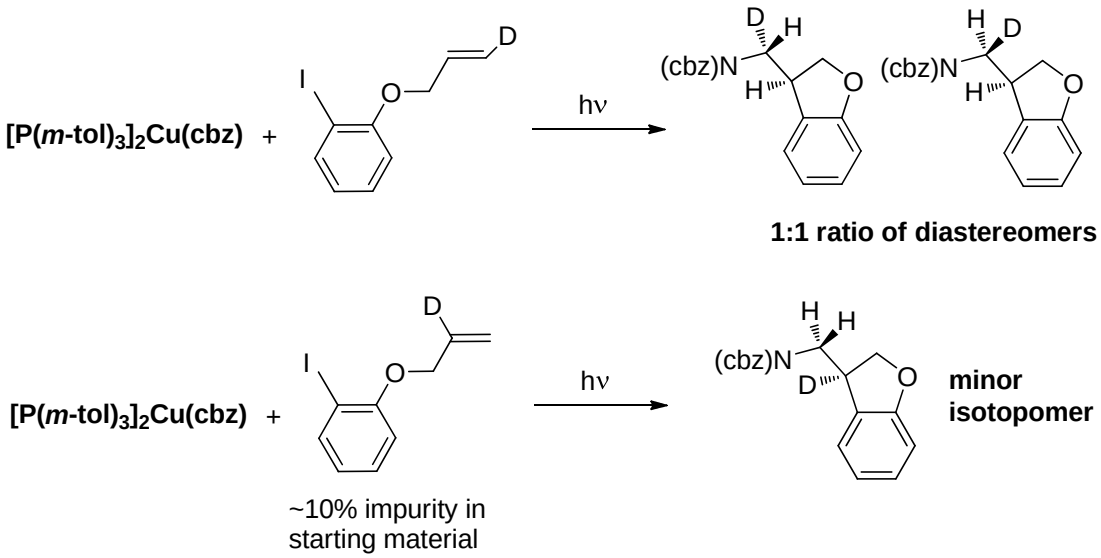


Figure S22. Formation of isotopomers of the coupling product from **4-d** and **1**

NMR spectroscopy of the crude reaction shows a lack of isomerized starting material ((*Z*)-(3-deuterioallyl)oxy-2-iodobenzene), indicating that the double bond of the radical trap probe **4-d** does not isomerize under the reaction conditions. The deuterium NMR resonance for the isomerized material would be expected at 5.34 ppm.

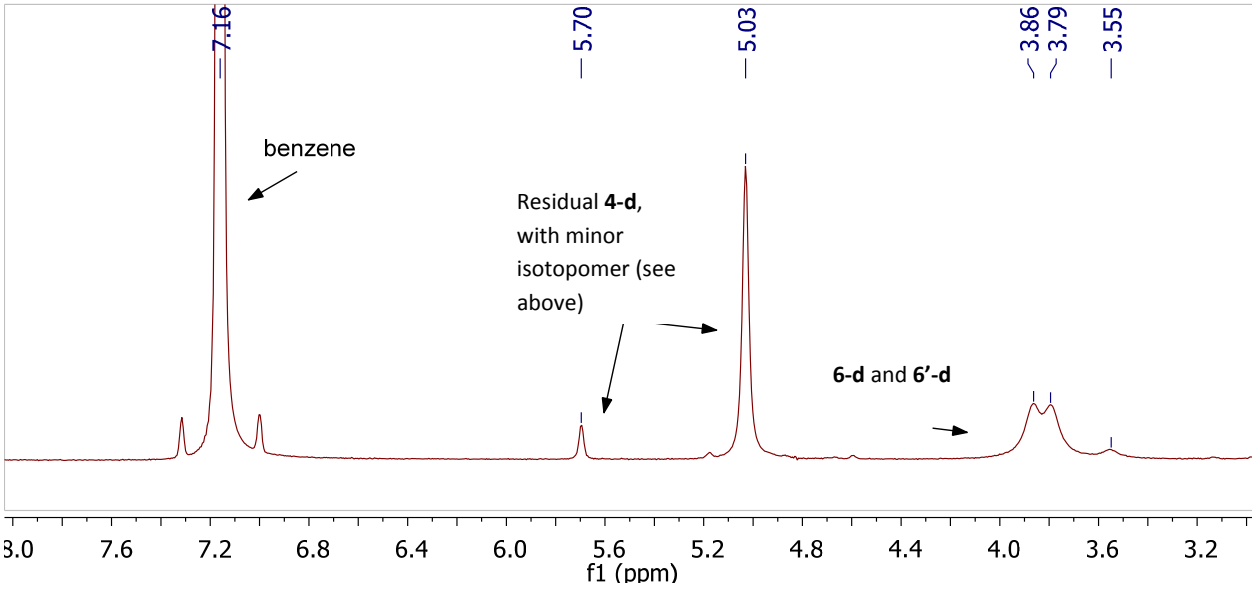


Figure S23. $^{2}H\{^{1}H\}$ NMR (76 MHz) spectrum of the crude reaction mixture from irradiation of **1** and **4-d**

Formation of 6-d and 6'-d in the reaction of 1 with (*E*)-(3-deuterioallyl)oxy-2-bromobenzene: **1** (65 mg, 0.078 mmol) was combined with (*E*)-(3-deuterioallyl)oxy-2-bromobenzene (25 mg, 0.117 mmol, 1.5 equiv) were combined in 3 mL of acetonitrile in a Schlenk tube and irradiated at room temperature with a 100 W mercury lamp for 12 hours. GC-MS of the reaction mixture showed exclusive formation of cyclized products (**6-d** and **6'-d** and 3-methyl-2,3-dihydrobenzofuran) and no uncyclized coupling or hydrodehalogenation products. The products of this reaction were analyzed by deuterium NMR spectroscopy and showed the formation of **6-d** and **6'-d** in a 1:1 ratio of diastereomers.

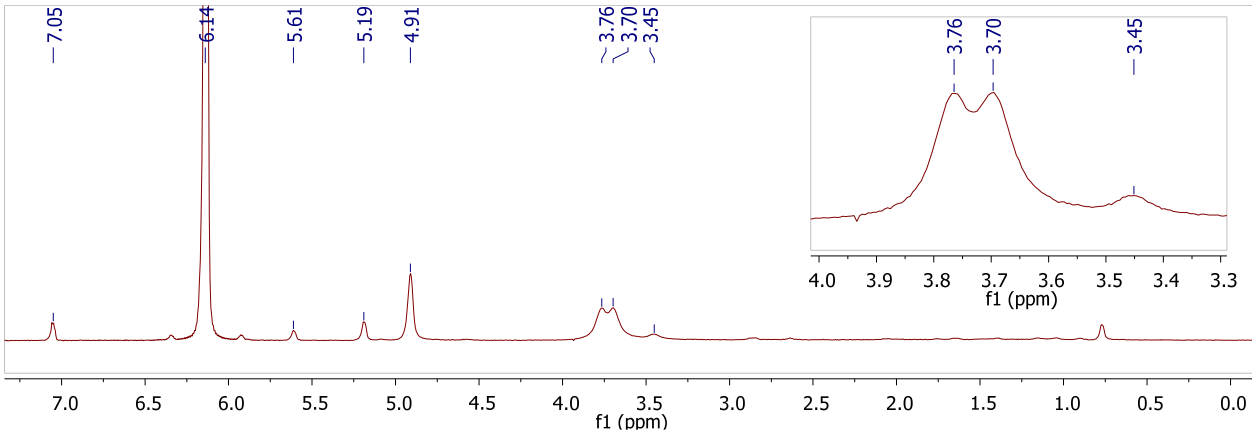


Figure S24: ^{2}H NMR spectrum of the crude reaction from irradiation of **1** with (*E*)-(3-deuterioallyl)oxy-2-bromobenzene (C_6H_6 with $CDCl_3$ internal standard, 76 MHz)

Formation of 8 and 9 in catalytic coupling reactions with 1 or CuI: Catalytic reactions with **4-d** were executed as for the general procedure described above, with either CuI or **1** as the catalyst. GC-MS and NMR analysis of the product profiles showed no formation of uncyclized coupling or hydrodehalogenation products, and formation of **6-d** and **6'-d** in a 1:1 ratio of diastereomers.

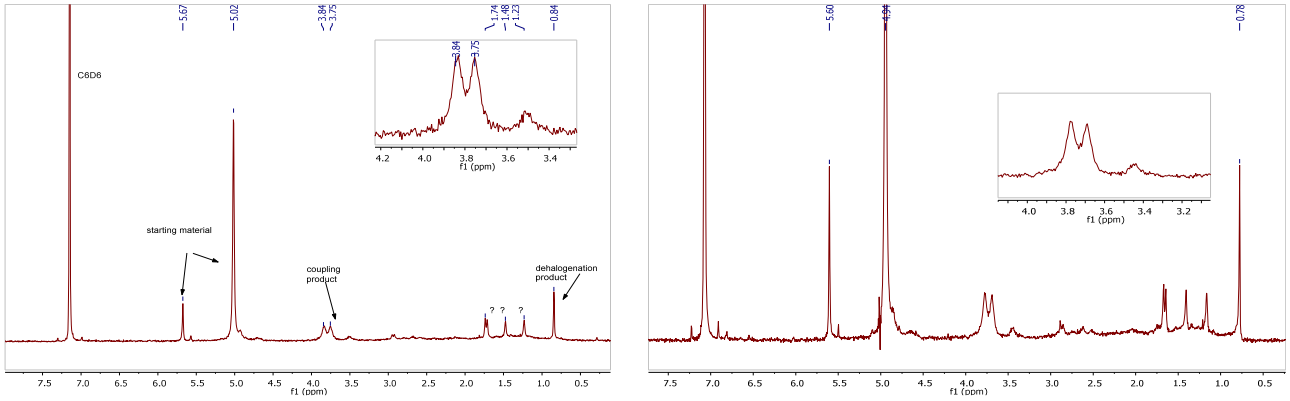


Figure S25: ^{2}H NMR of the crude reaction mixture from coupling of **4-d** with lithium carbazolide, catalyzed by **1** (left) or CuI (right)

H. Synthesis of 9 and 10, and competition experiment

Synthesis of *N*-(1-naphthyl)carbazole (9) from 1-bromonaphthalene and 1: 1-Bromonaphthalene (59.3 mg, 0.29 mmol, 1.2 equiv) was dissolved in CH_3CN (20 mL) and added to solid **1** (200 mg, 0.24 mmol) to give a clear solution after stirring for ca. 10 minutes in the dark. The solution was transferred to a 500 mL Erlenmeyer flask equipped with a ground glass joint. The Erlenmeyer flask was sealed with a well-greased stopper. The reaction mixture was irradiated from the bottom of the Erlenmeyer with a 100 W mercury lamp for 10 hours while the temperature was maintained at 28-30 °C. At the end of the reaction time the reaction mixture was a clear, pale yellow. The reaction mixture was then opened to air, diluted with diethyl ether (15 mL), and washed with distilled water (3 x 5 mL). The aqueous fractions were then extracted with 5 mL of diethyl ether, and the combined organic layers were stirred with 5 mL of an aqueous 30% hydrogen peroxide solution for 20 minutes. The aqueous layer was then separated, and the organic layer was washed with water (2 x 5 mL); the aqueous layers were washed with 5 mL of diethyl ether, and then the combined organic layers were stirred with 10 mL of saturated aqueous ferrous sulfate for 30 minutes. The aqueous layer was then removed, and the organic layer was washed with water (2 x 5 mL). The aqueous layers were washed with 5 mL of diethyl ether, and the combined organic layers were then washed with 5 mL of saturated aqueous sodium chloride and dried over magnesium sulfate, filtered, and concentrated. This residue was purified by column chromatography on silica gel, eluting with hexanes, affording *N*-(1-naphthyl)carbazole as a white solid. The NMR parameters for the isolated material match those previously reported (*45*). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 8.27 (d, 2H, *J* = 8 Hz), 8.07 (m, 2H), 7.69 (m, 2H), 7.58 (t, 1H, *J* = 8 Hz), 7.41-7.34 (m, 6H), 7.06 (d, 2H, *J* = 8 Hz) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz, ppm): δ 142.2, 134.9, 134.1, 131.0, 129.1, 127.0, 126.8, 125.9, 123.7, 123.3, 130.4, 119.8, 110.3.

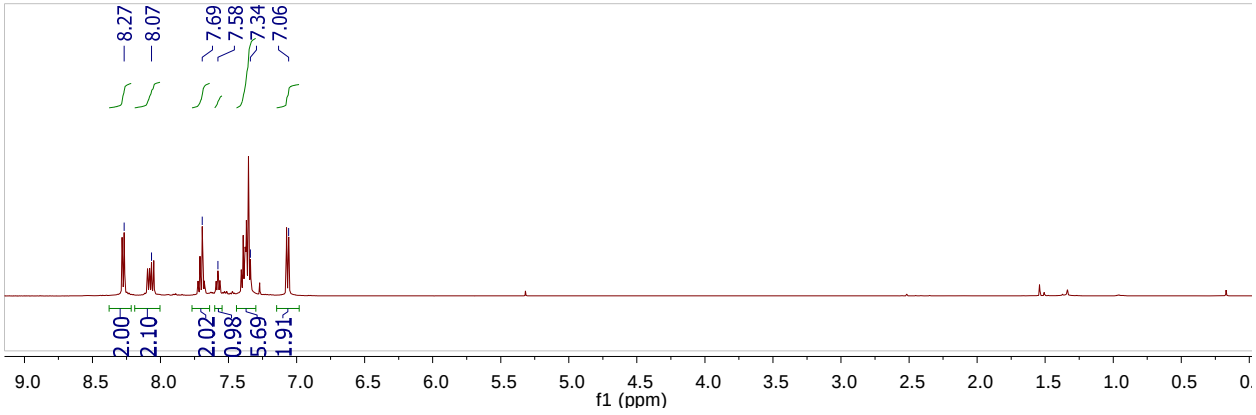


Figure S26: ^{1}H NMR spectrum of **9**

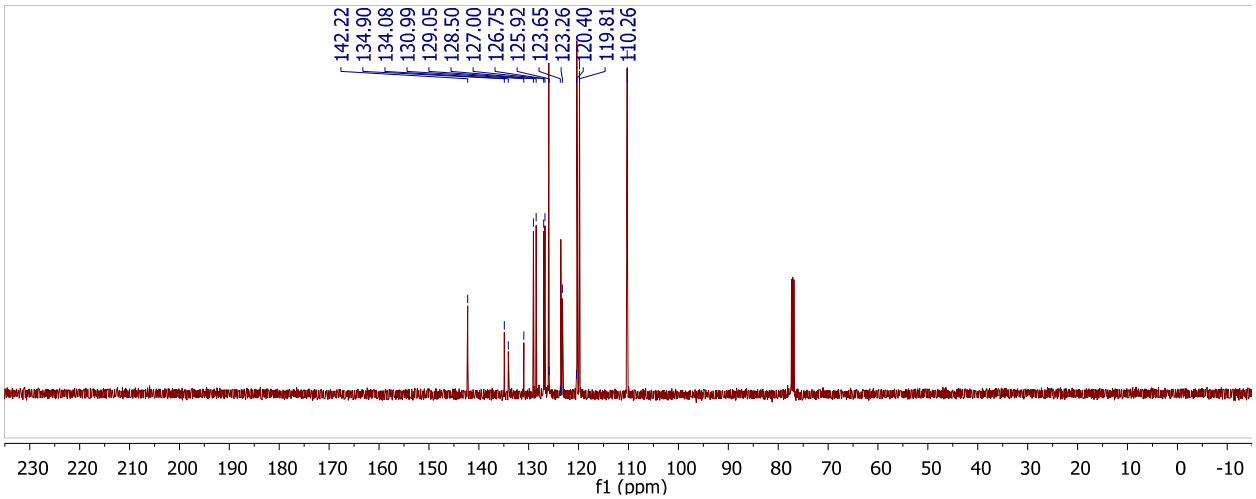


Figure S27: ^{13}C NMR spectrum of **9**

Synthesis of *N*-(4-cyanophenyl)carbazole (10) from 4-chlorobenzonitrile and 1: 4-chlorobenzonitrile (39.4 mg, 0.29 mmol, 1.2 equiv) was dissolved in CH_3CN (20 mL) and added to solid **1** (200 mg, 0.24 mmol) to give a clear solution after stirring for ca. 10 minutes in the dark. The solution was transferred to a 500 mL Erlenmeyer flask equipped with a ground glass joint. The Erlenmeyer flask was sealed with a well-greased stopper. The reaction mixture was irradiated from the bottom of the Erlenmeyer with a 100 W mercury lamp for 10 hours while the temperature was maintained at 28-30 °C. At the end of the reaction time the reaction mixture was a clear, pale pinkish-orange. The reaction mixture was then opened to air, diluted with diethyl ether (15 mL), and washed with distilled water (3 x 5 mL). The aqueous fractions were extracted with 5 mL of diethyl ether, and the combined organic layers were stirred with 5 mL of an aqueous 30% hydrogen peroxide solution for 5 minutes. The aqueous layer was then separated, and the organic layer was washed with water (2 x 5 mL); the aqueous layers were washed with 5 mL of diethyl ether, and then the combined organic layers were stirred with 10 mL of saturated aqueous ferrous sulfate for 30 minutes. Then the aqueous layer was removed, and the organic layer was washed with water (2 x 5 mL). The aqueous layers were washed with 5 mL of diethyl ether, and the combined organic layers were then washed with 5 mL of saturated aqueous sodium chloride and then dried over magnesium sulfate, filtered, and concentrated. This residue was purified by column chromatography on silica gel, eluting with 2% ethyl acetate in hexanes, giving *N*-(4-cyanophenyl)carbazole as a white solid. The NMR parameters for the isolated material match those previously reported (*46*). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.15 (d, 2H, *J* = 8 Hz), 7.9 (d, 2H, *J* = 8Hz), 7.7 (d, 2H, *J* = 8 Hz), 7.47 (m, 4H), 7.36 (t, 2H, *J* = 8 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz, ppm): δ 142.0, 139.9, 133.9, 127.1, 136.4, 123.9, 121.0, 120.6, 118.4, 110.4, 109.5.

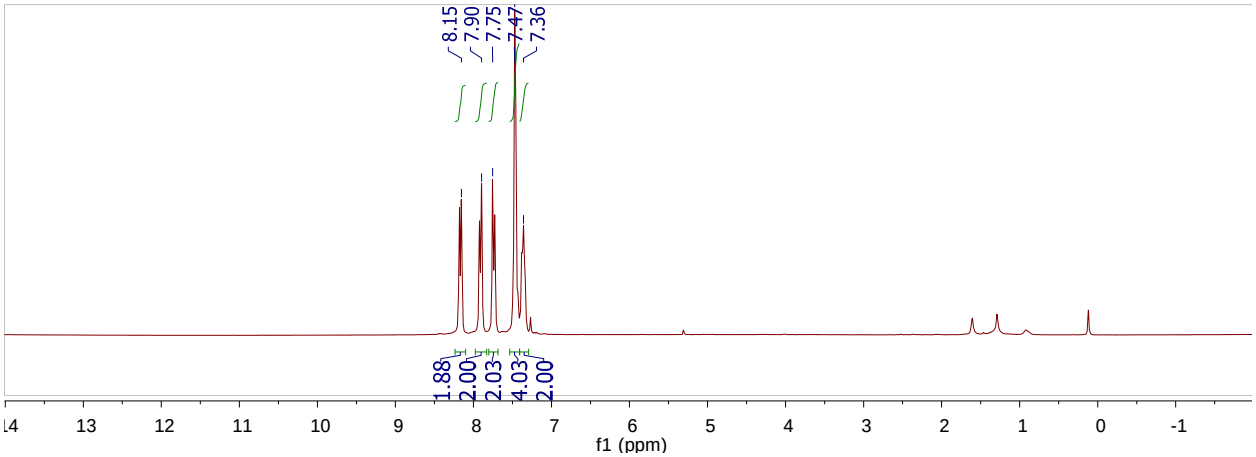


Figure S28: ^{1}H NMR spectrum of **10**

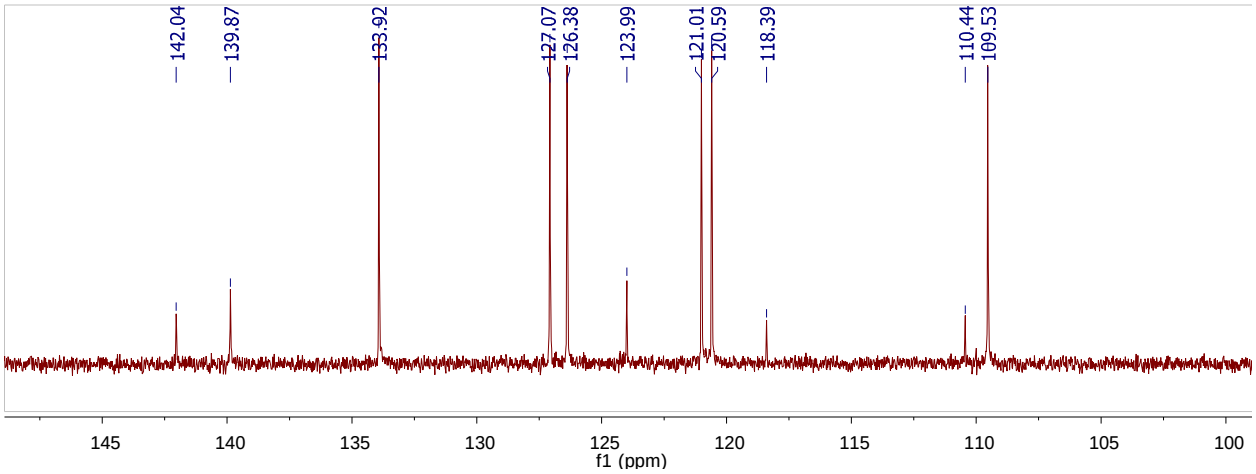


Figure S29: ^{13}C NMR spectrum of **10**

GC-scale coupling of 1-bromonaphthalene and 4-chlorocyanobenzene with 1: Separately, **1** (10 mg, 0.0119 mmol), and the aryl halide (10 equiv) were combined in 1.0 mL of acetonitrile in a 20 mL glass scintillation vial, and sealed with a PTFE-lined cap and electrical tape. The vials were illuminated from the bottom with a 100 W Hg lamp for 10 hours, then opened to the atmosphere, diluted with THF, and analyzed by GC against a calibrated internal standard (4,4'-di-*t*-butylbiphenyl), affording 58% and 70% yield of **9** and **10**, respectively.

Competition reaction between 1-bromonaphthalene and 4-chlorocyanobenzene: 10 mg of **1** (0.0119 mmol) was combined with 5 equiv each of 1-bromonaphthalene and 4-chlorocyanobenzene in 1.0 mL of acetonitrile in a 20 mL glass scintillation vial, and sealed with a PTFE-lined cap and electrical tape. The vial was illuminated from the bottom with a 100 W Hg lamp for 10 hours, then opened to the atmosphere, diluted with THF, and analyzed by GC against a calibrated internal standard (4,4'-di-*tert*-

butylbiphenyl). On average over two trials, **9** and **10** were formed in a 1:1.83 ratio (24% yield of **9**, 44% yield of **10**).

I. Identification of side products

Detection and quantification of benzene formed in coupling between 1 and PhI:

A coupling reaction was carried out between **1** (9.8 mg, 0.012 mmol) and PhI (0.014 mmol, 1.2 equiv) in CD_3CN (0.409 mL) as in the general procedure. The reaction mixture was irradiated for 10 hours, and then 0.370 mL of the reaction solution were transferred via syringe to a Schlenk tube; the volatile components of the reaction mixture were vac-transferred into a J-young tube. After the vacuum transfer was complete, 0.200 mL of a standard solution of 0.018 M trimethoxybenzene in CD_3CN was added to the tube. The resulting solution was analyzed by ^1H NMR spectroscopy, and integration of the benzene peak relative to the trimethoxybenzene standard indicated that approximately 0.8 µmols of benzene were formed in the reaction.

Detection of succinonitrile in coupling reaction mixtures:

A small peak in the GC traces of coupling reactions run in acetonitrile is consistently observed that matches the retention time of an authentic succinonitrile sample. In addition, NMR evidence for the formation of succinonitrile has been independently obtained:

Reaction in CD_3CN: The crude reaction mixture from the reaction between **1** and iodobenzene in CD_3CN was concentrated to dryness, redissolved in benzene, and analyzed by deuterium NMR spectroscopy. In addition to residual CD_3CN, a sharp singlet is observed at 1.39 ppm which is assigned to d_4-succinonitrile.

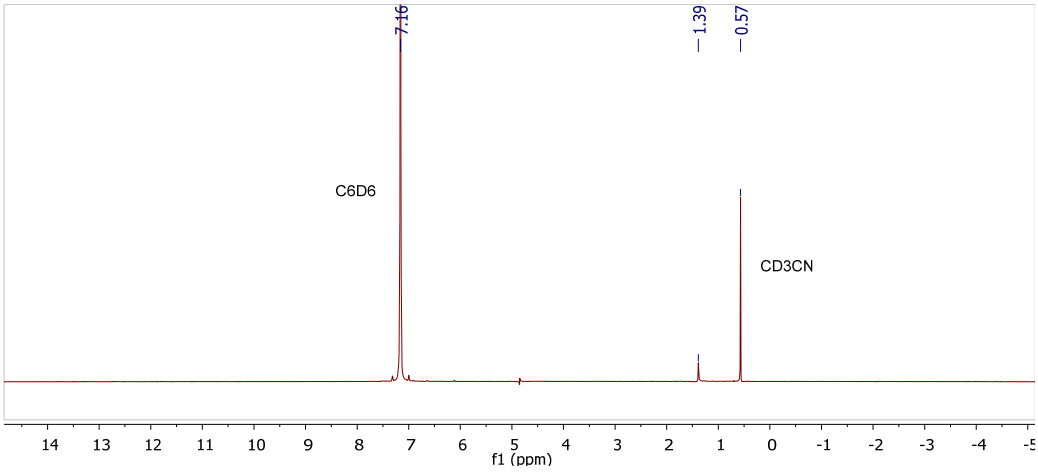


Figure S30. $^2H\{^1H\}$ NMR showing perdeuterated succinonitrile

Reaction in CH_3CN: Addition of authentic succinonitrile to the crude reaction from a coupling reaction between **1** and PhI run in CH_3CN corroborates the presence of succinonitrile:

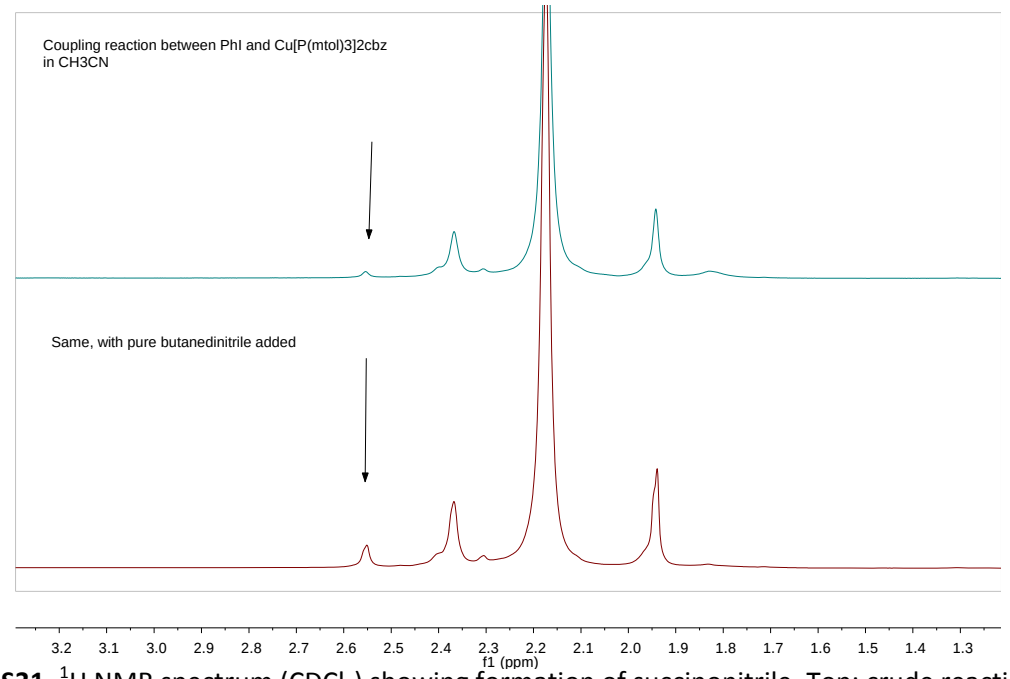


Figure S31. ^{1}H NMR spectrum ($CDCl_3$) showing formation of succinonitrile. Top: crude reaction mixture. Bottom: Spectrum with pure succinonitrile (butanedinitrile) added.

Detection of monodeuterated (N*D*) carbazole:

A coupling reaction between **1** and iodobenzene was carried out in the usual manner using CD_3CN as the solvent, but contrary to the typical procedure the GC sample was prepared using dry, aprotic solvents in an inert atmosphere. GC-MS analysis shows approximately 22% monodeuteration of the carbazole present at the end of the reaction. It should be noted that if the GC sample is prepared using wet solvents, no deuterium enrichment is detected, suggesting that the deuteron is readily exchanged in the presence of proton sources.

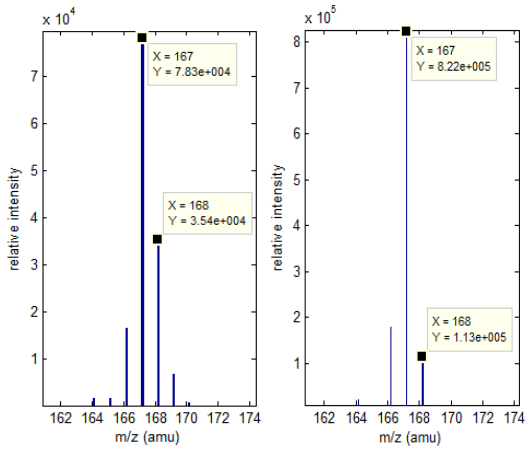


Figure S32. (Left) GC-MS peak for carbazole from a coupling reaction carried out in CD_3CN. (Right) GC-MS peak for carbazole from a coupling reaction carried out in CH_3CN.

Detection of iodobiphenyls:

When **1** is irradiated in the presence of a large excess of iodobenzene (e.g. 30 equiv or neat iodobenzene), in addition to *N*-phenylcarbazole and carbazole, significant amounts of three products assigned as *o*-, *m*-, and *p*-iodobiphenyl are detected by GC-MS.

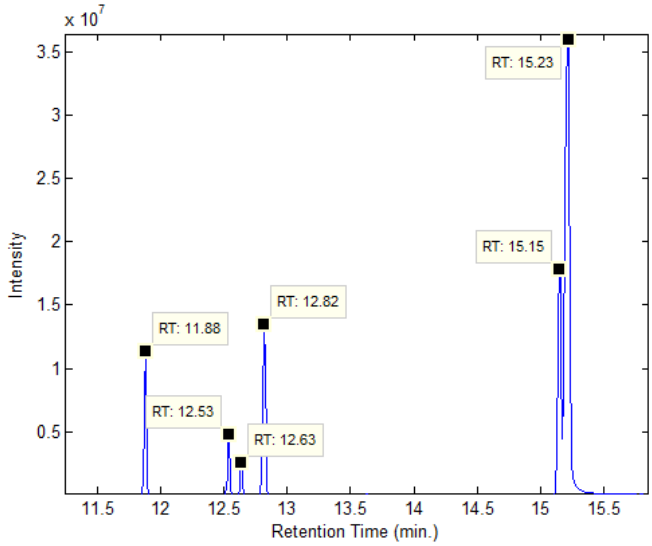


Figure S33: GC trace of coupling of **1** in neat iodobenzene.

In the GC trace shown, RT = 12.82 is carbazole, RT = 15.15 is *N*-phenylcarbazole, and RT = 15.23 is P(*m*-tol)$_3$; the mass spectra for RT = 11.88, 12.53, and 12.63 correspond to the three isomers of iodobiphenyl.

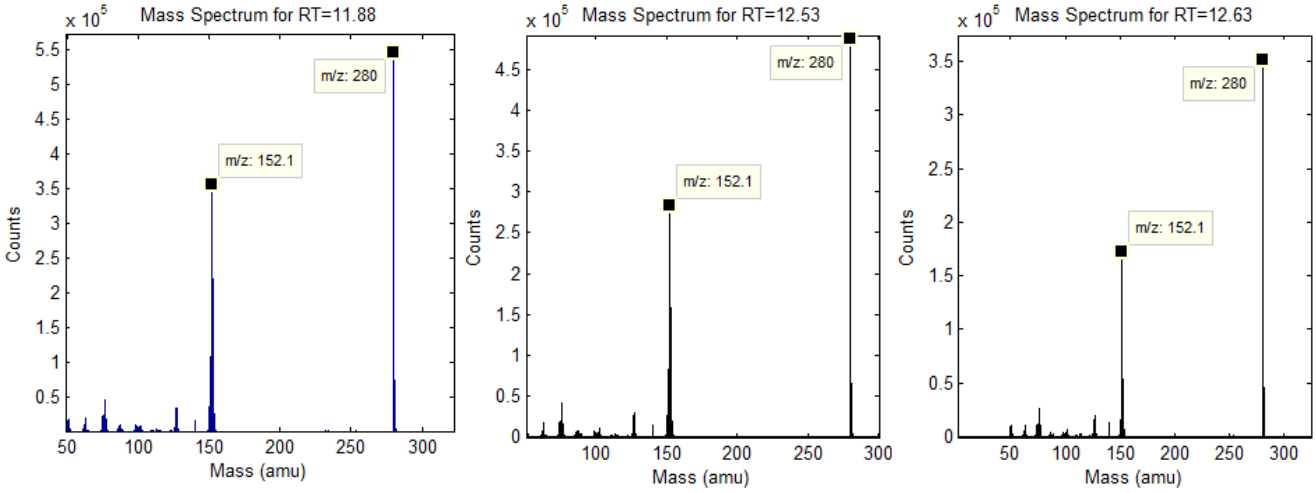
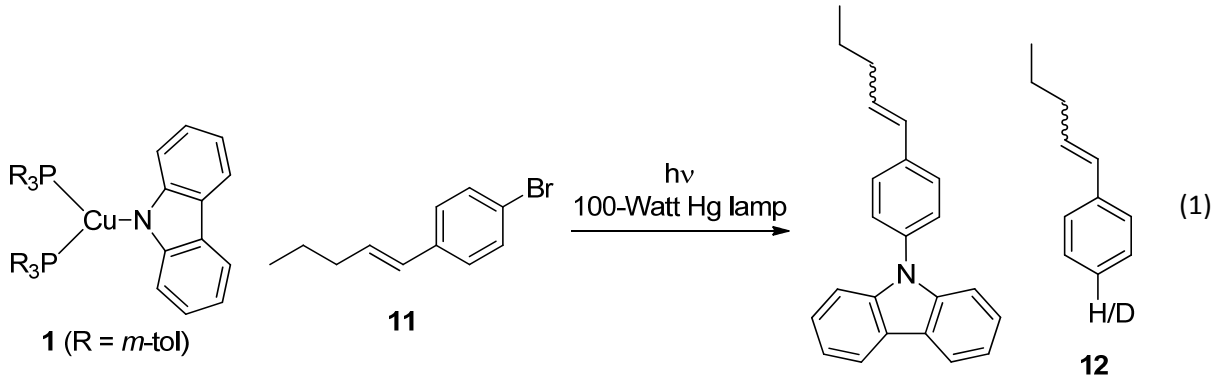


Figure S34: Mass spectra of three isomeric iodobiphenyl byproducts.

Detection of deuterodehalogenated arene side products:

4-(1-pentenyl)bromobenzene, **11**, was used as a heavier arene substrate to facilitate product analysis by GC-MS. A coupling reaction with **1** under irradiation with a 100W lamp was carried out in the usual manner in CD_3CN. GC-MS of the crude reaction mixture after irradiation showed formation of partially deuterated 1-pentenylbenzene (~30% monodeuteration). A deuterium NMR resonance was also detected that was consistent with monodeuteration of the arene ring. The alkene isomerizes under the reaction conditions.



(1)

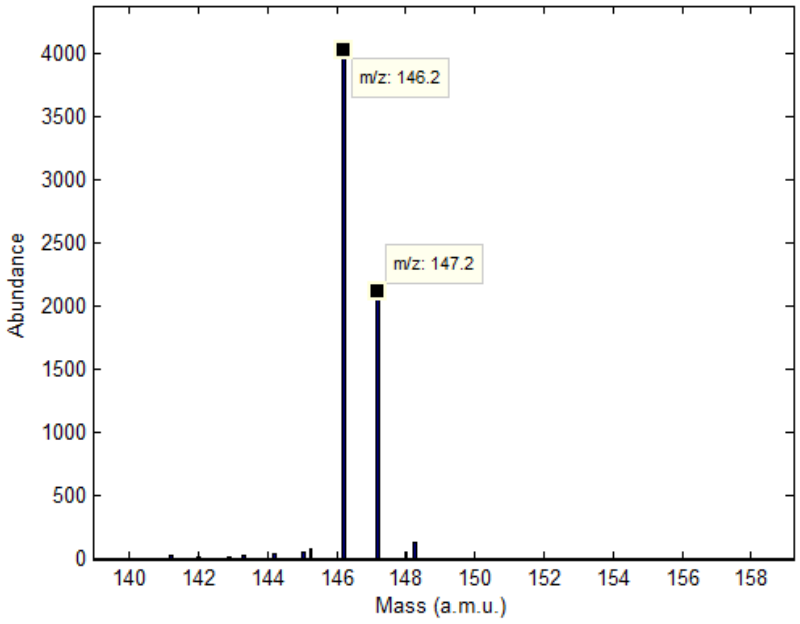


Figure S35. Mass spectrum, molecular ion peak for **12**

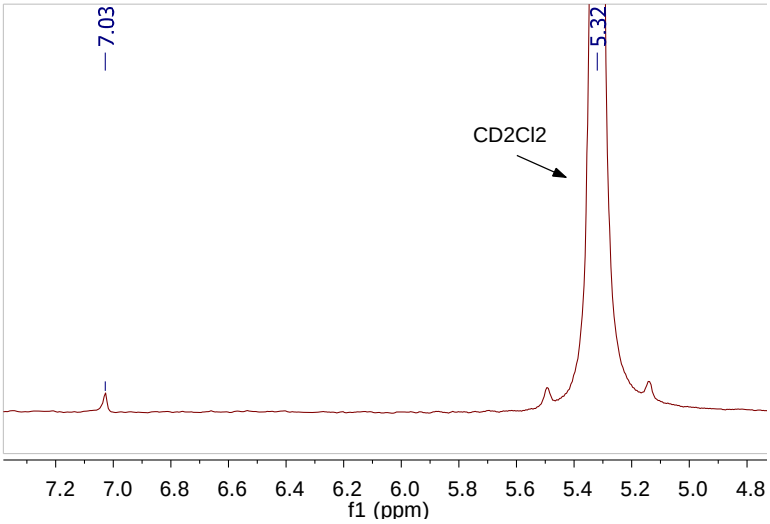


Figure S36. ^{2}H NMR, 76 MHz, in CH_2Cl_2 with added CD_2Cl_2

Identification of (*C*,*N*)-diphenylcarbazole side products in coupling reactions of 1 and halobenzenes:

In addition to *N*-phenylcarbazole and unsubstituted carbazole, three products are isolated from coupling reactions of **1** and PhX (X = I, Br, Cl) in small amounts (<2% each). Mass spectrometry shows that these species have m/z = 319 a.m.u., consistent with the formula $C_{24}H_{17}N$, *e.g.* carbazole with two phenyl substituents. This could plausibly be either (*C*,*N*)-diphenylcarbazole or *N*-biphenylcarbazole, both of which have several possible isomers. One of these products was isolated and characterized by NMR spectroscopy, and the NMR data are more consistent with (3,9)-diphenylcarbazole. The most upfield peaks are characteristic for the 4- and 5-*H* protons on carbazole (see spectrum of *N*-phenylcarbazole above, Figure S7), and the NMR pattern observed here is therefore most consistent with this assignment and inconsistent with an *N*-biphenylcarbazole product.

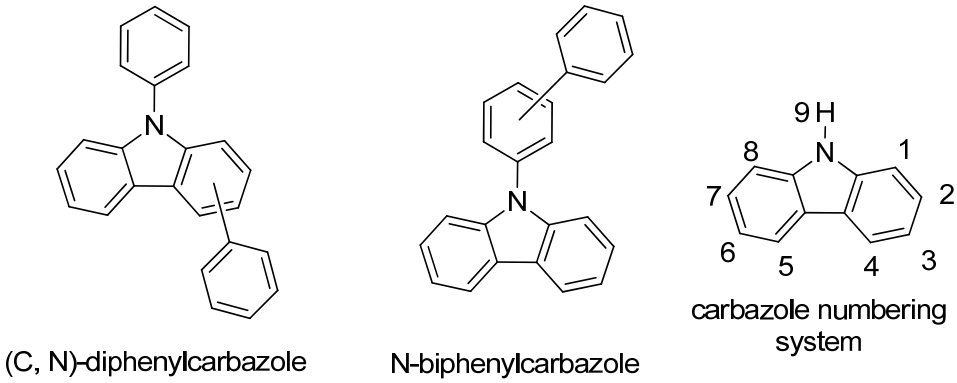


Figure S37. Possible side products consistent with the observed mass.

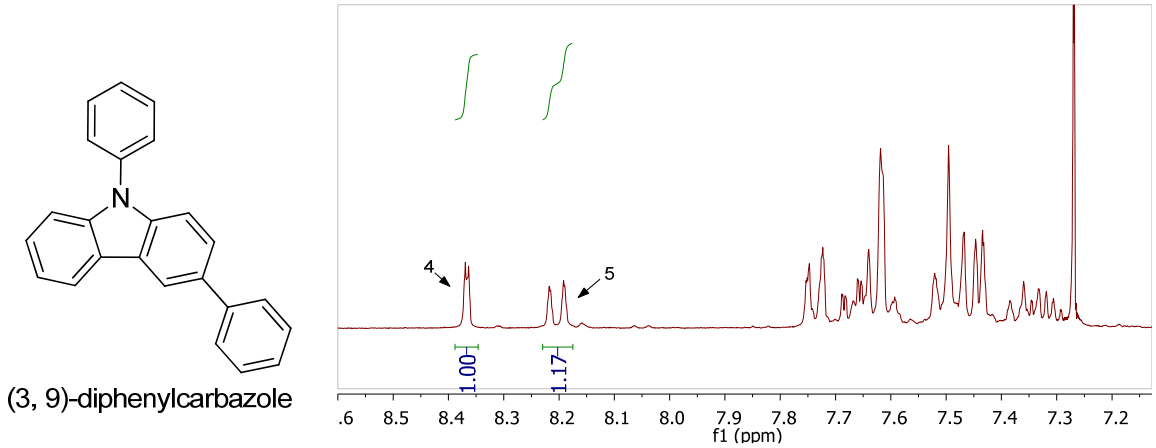
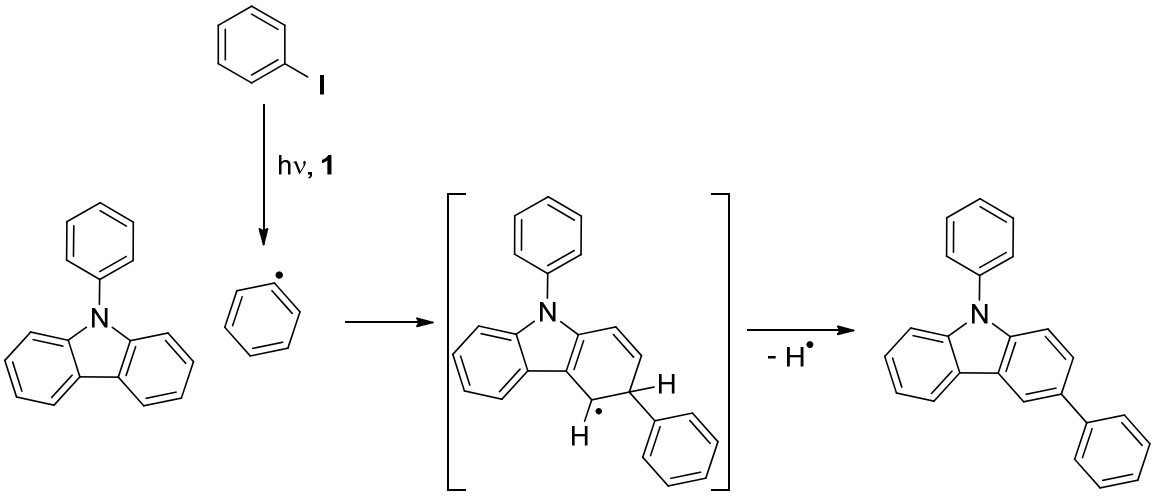


Figure S38. ^{1}H NMR spectrum of one of the side products of the coupling reaction between **1** and iodobenzene, and its proposed structure

One plausible pathway by which this product could form is *via* the $S_{RN}1$ reaction of photogenerated phenyl radicals with N-phenylcarbazole (equation 2); however, the mechanism of formation of these side products has not been investigated.



(2)

J. EPR studies

Low-temperature irradiation and EPR: The starting complex **1** is EPR-silent at 77K. Approximately 5 mg of **1** were dissolved in 4:5 proprionitrile:butyronitrile with a large excess of iodobenzene (40 mg) to give a clear solution; an aliquot of this solution was transferred to an EPR tube that was cooled to -40 °C in a dry ice/acetonitrile bath. This reaction mixture was irradiated with a 100 W mercury lamp at -40 °C for 15 minutes, at which point the solution is a deep blue color. At this point the tube was frozen in liquid nitrogen and EPR spectra were acquired at 15 K and 30 K at 9.375 GHz (X-band). After allowing the tube to thaw at -40 °C, the blue color disappears within <30 sec of removing the tube from the cold bath.

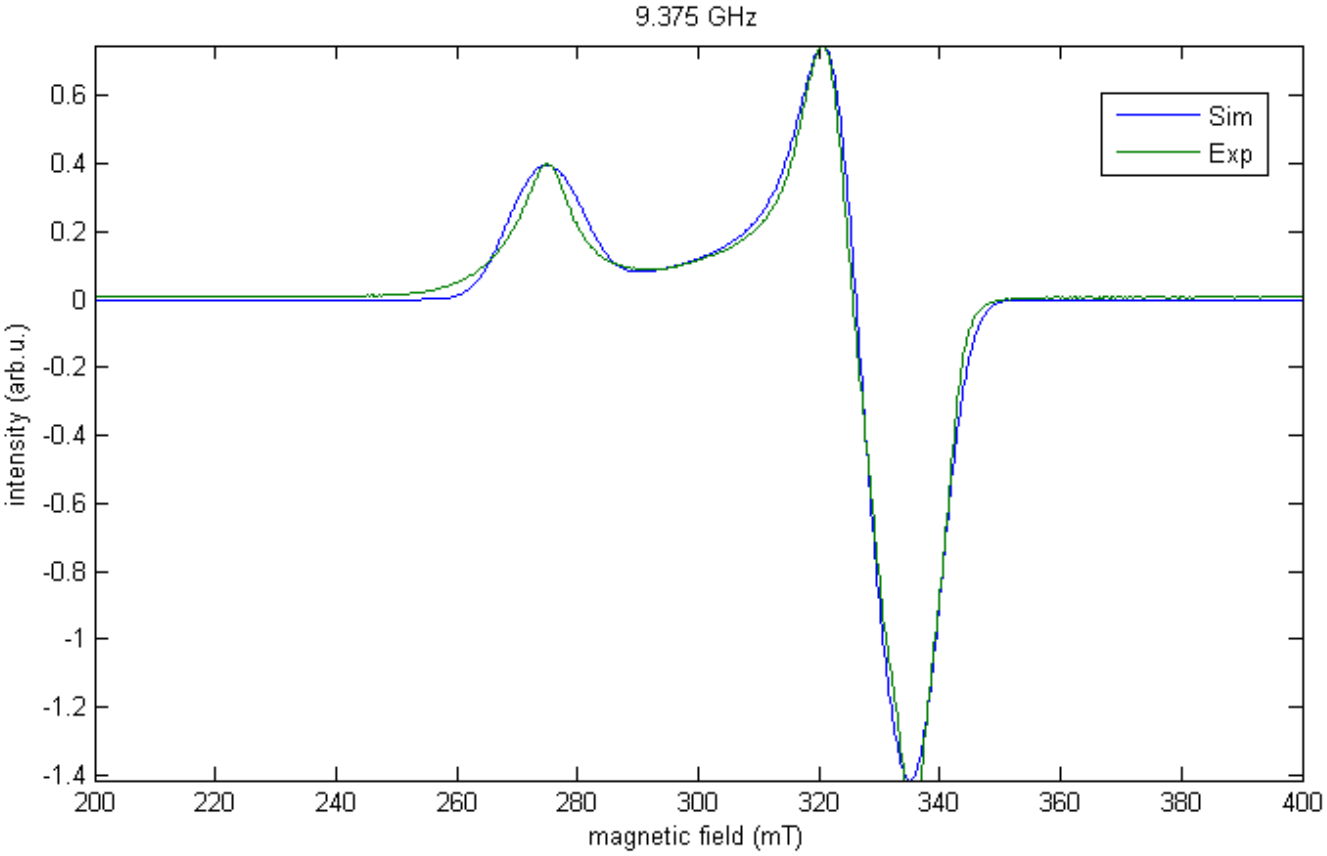


Figure S39. EPR spectrum (experimental and simulated). Simulation parameters: g = [2.440, 2.055, 1.990]; isotropic linewidth (Gaussian lineshape, FWHM = 10 mT). Coupling to one ^{63}Cu nucleus was included with A = [110, 15, 15].

Low-temperature oxidation studied by EPR spectroscopy: **1** (5.0 mg) was dissolved in 4:5 proprionitrile:butyronitrile and frozen. Separately, tris(4-bromophenyl)aminium hexachloroantimonate ("magic blue", 1.5 mg, 0.3 equiv) was dissolved in the same solvent and frozen. The magic blue-containing solution was thawed and added to the solution of **1**, which was then allowed to thaw briefly and mixed, giving a deep blue solution. This solution was quickly transferred to an EPR tube and frozen again. The X-band EPR spectrum of this reaction mixture was measured at 77 K. *Note that addition of a full equivalent of oxidant results in a color change to yellow, and the EPR signal is not seen*. Also, thawing of the sample to room temperature results in rapid disappearance of the blue color and the associated EPR signal.

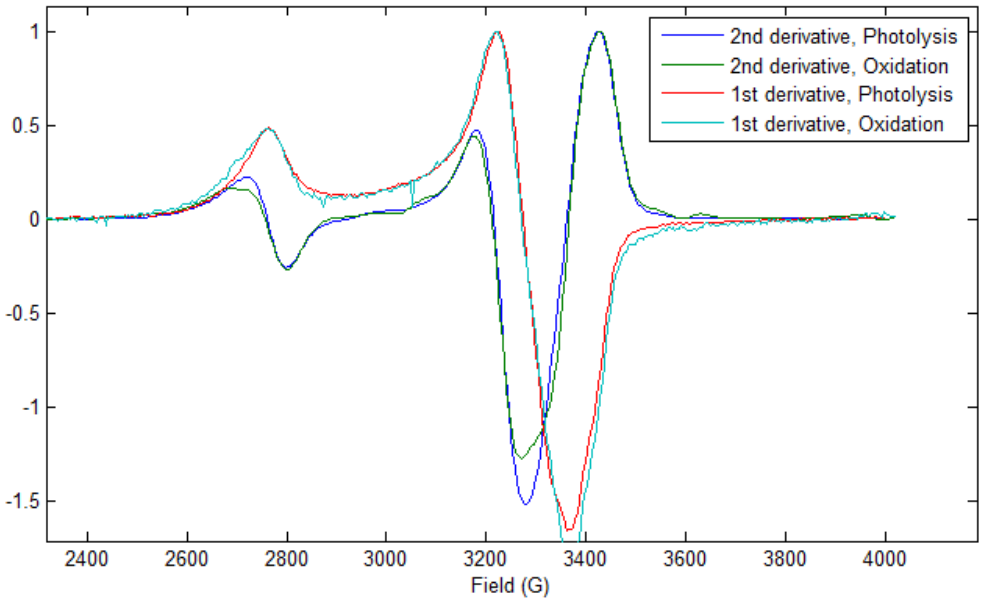


Figure S40: This graph shows overlays of the 77 K, X-band EPR spectra from the low-temperature oxidation of **1** with 0.3 equiv of "magic blue" with that from low temperature irradiation (see above). Both first and second derivative spectra are shown. A second-order baseline correction has been applied to all spectra, and the spectra have been normalized to show the same intensity. A smoothing algorithm was applied to the first derivative spectra before differentiating. The magnetic field axis of the low-temperature oxidation spectrum was multiplied by a factor of 9.416/9.364 to account for a shift of the spectrometer microwave frequency from 9.416 GHz to 9.364 GHz between the two measurements.

III. Crystallographic information

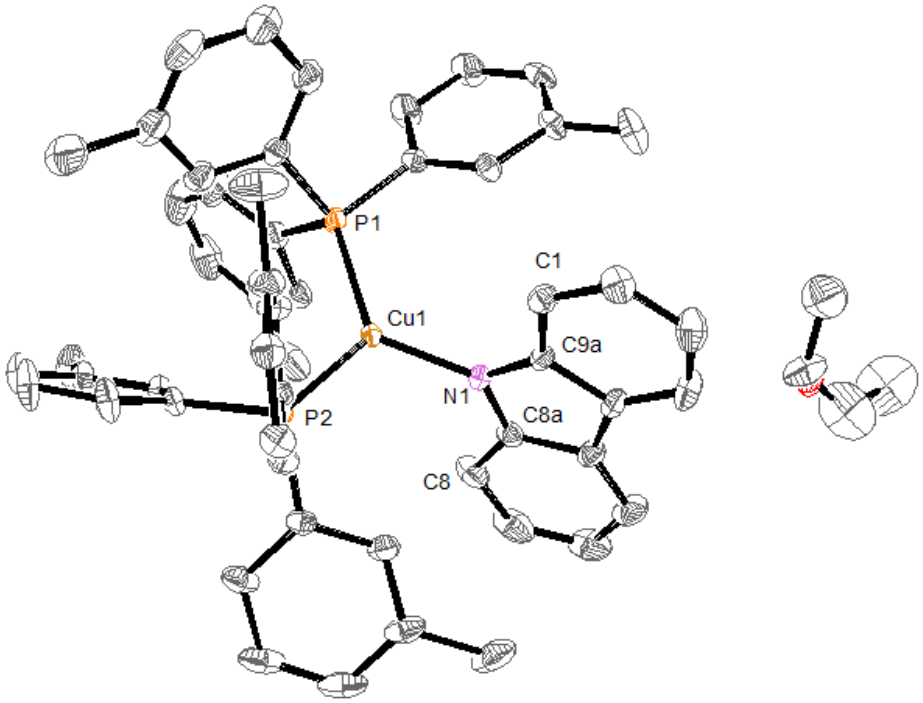


Figure S41. Displacement ellipsoid representation (50% probability) of **1**. Hydrogen atoms have been omitted for clarity. **1** crystallizes in the space group $P2_1/c$ with one molecule of **1** and half a molecule of diethyl ether in the asymmetric unit. The diethyl ether molecule is disordered over a special position.

Table S1. Selected bond lengths [Å] and angles [°] for **1.**

Cu(1)-N(1)	1.9451(9)
Cu(1)-P(1)	2.2354(3)
Cu(1)-P(2)	2.2461(3)
N(1)-C(9A)	1.3717(15)
N(1)-C(8A)	1.3761(15)
N(1)-Cu(1)-P(1)	123.70(3)
N(1)-Cu(1)-P(2)	114.92(3)
P(1)-Cu(1)-P(2)	121.314(12)
C(9A)-N(1)-C(8A)	105.63(9)
C(9A)-N(1)-Cu(1)	124.00(8)
C(8A)-N(1)-Cu(1)	130.05(8)

Table S2. Crystal data and structure refinement for **1.**

Identification code	1	
Empirical formula	C56 H55 Cu N O0.5 P2	
Formula weight	875.53	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/c	
Unit cell dimensions	a = 18.9529(7) Å	α= 90°.
	b = 13.0404(5) Å	β= 94.636(2)°.
	c = 18.8374(7) Å	γ = 90°.
Volume	4640.5(3) $Å^3$	
Z	4	
Density (calculated)	1.223 Mg/m^3	
Absorption coefficient	0.578 mm^{-1}	
F(000)	1792	
Crystal size	0.41 x 0.29 x 0.11 mm^3	
Theta range for data collection	1.90 to 39.39°.	
Index ranges	-33<=h<=33, -23<=k<=22, -33<=l<=33	
Reflections collected	166283	
Independent reflections	27658 [R(int) = 0.0411]	
Completeness to theta = 39.39°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9392 and 0.7975	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	27658 / 537 / 574	
Goodness-of-fit on F^2	1.022	
Final R indices [I>2sigma(I)]	R1 = 0.0477, wR2 = 0.1182	
R indices (all data)	R1 = 0.0799, wR2 = 0.1331	
Largest diff. peak and hole	1.351 and -0.452 $e.Å^{-3}$	

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu(1)	2462(1)	-678(1)	1068(1)	17(1)
P(2)	3514(1)	-1070(1)	1638(1)	16(1)
P(1)	1706(1)	-1902(1)	666(1)	19(1)
N(1)	2292(1)	780(1)	919(1)	19(1)
C(226)	4872(1)	-656(1)	1178(1)	22(1)
C(112)	1079(1)	-587(1)	-337(1)	21(1)
C(9A)	2453(1)	1303(1)	322(1)	18(1)
C(131)	2106(1)	-2933(1)	186(1)	22(1)
C(231)	3576(1)	-2293(1)	2108(1)	19(1)
C(212)	3727(1)	906(1)	2125(1)	25(1)
C(121)	1269(1)	-2531(1)	1373(1)	22(1)
C(221)	4222(1)	-1144(1)	1039(1)	18(1)
C(114)	-98(1)	-697(1)	-892(1)	28(1)
C(232)	2994(1)	-2620(1)	2457(1)	19(1)
C(233)	2988(1)	-3570(1)	2796(1)	22(1)
C(225)	5402(1)	-787(1)	714(1)	26(1)
C(222)	4106(1)	-1738(1)	422(1)	25(1)
C(211)	3819(1)	-126(1)	2305(1)	21(1)
C(113)	550(1)	-194(1)	-822(1)	24(1)
C(111)	973(1)	-1466(1)	57(1)	21(1)
C(8A)	2071(1)	1513(1)	1378(1)	21(1)
C(4A)	2328(1)	2377(1)	384(1)	23(1)
C(1)	2702(1)	910(1)	-304(1)	23(1)
C(4B)	2086(1)	2515(1)	1078(1)	24(1)
C(234)	3577(1)	-4205(1)	2766(1)	31(1)
C(133)	2996(1)	-4278(1)	184(1)	35(1)
C(236)	4164(1)	-2931(1)	2097(1)	31(1)
C(223)	4636(1)	-1886(1)	-38(1)	28(1)
C(216)	4104(1)	-390(1)	2988(1)	30(1)
C(224)	5287(1)	-1409(1)	120(1)	26(1)
C(122)	1040(1)	-1906(1)	1912(1)	28(1)

C(132)	2628(1)	-3541(1)	543(1)	28(1)
C(117)	690(1)	738(2)	-1254(1)	41(1)
C(134)	2834(1)	-4397(1)	-544(1)	37(1)
C(213)	3908(1)	1682(1)	2618(1)	31(1)
C(237)	2364(1)	-3912(1)	3177(1)	35(1)
C(215)	4279(1)	385(2)	3482(1)	38(1)
C(136)	1951(1)	-3072(1)	-547(1)	31(1)
C(4)	2440(1)	3032(1)	-185(1)	34(1)
C(2)	2802(1)	1574(1)	-860(1)	30(1)
C(8)	1853(1)	1377(1)	2067(1)	32(1)
C(214)	4177(1)	1400(1)	3302(1)	36(1)
C(5)	1895(1)	3371(1)	1469(1)	36(1)
C(126)	1120(1)	-3576(1)	1382(1)	34(1)
C(235)	4159(1)	-3890(1)	2419(1)	38(1)
C(3)	2672(1)	2628(1)	-806(1)	37(1)
C(135)	2317(1)	-3801(1)	-907(1)	38(1)
C(116)	322(1)	-1965(1)	-27(1)	37(1)
C(115)	-214(1)	-1570(1)	-502(1)	38(1)
C(123)	644(1)	-2299(2)	2442(1)	36(1)
C(6)	1685(1)	3225(2)	2146(1)	44(1)
C(7)	1659(1)	2243(2)	2438(1)	42(1)
C(227)	4503(1)	-2539(2)	-696(1)	49(1)
C(217)	3798(1)	2785(1)	2410(1)	48(1)
C(124)	497(1)	-3334(2)	2432(1)	47(1)
C(125)	737(1)	-3971(2)	1920(1)	48(1)
C(127)	381(1)	-1604(2)	3000(1)	54(1)
C(137)	3559(1)	-4920(2)	570(1)	58(1)
C(1S)	801(6)	4281(6)	-160(4)	44(1)
C(2S)	87(4)	4799(8)	-325(4)	89(2)
O(1S)	-175(2)	5464(2)	-144(2)	44(1)
C(3S)	-806(7)	5571(9)	291(6)	76(3)
C(4S)	-877(2)	6032(4)	967(3)	57(1)

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