Electronic Supplementary Material (ESI) for Organdic and Biomolecular Chemistry

Synthesis of 7-aryl/heteraryl-1,3-diphenyl-1,2,4-benzotriazinyls *via* palladium catalyzed Stille and Suzuki-Miyaura reactions

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Supporting Information

Section A: General Information

Solvents DCM, PhH and PhMe were freshly distilled from CaH_2 under argon. DMF was azeotropically distilled with PhH then distilled under vacuum from anhydrous $MgSO_4$ and stored over 4 Å molecular sieves. Reactions were protected by $CaCl_2$ drying tubes. Anhydrous $MgSO_4$ was used for drying organic extracts, and all volatiles were removed under reduced pressure. All reaction mixtures and column eluents were monitored by TLC using commercial aluminium backed thin layer chromatography (TLC) plates (Merck Kieselgel 60 F_{254}). The plates were observed under UV light at 254 and 365 nm. The technique of dry flash chromatography was used throughout for all non-TLC scale chromatographic separations using Merck Silica Gel 60 (less than 0.063 mm). Melting points were determined using a PolyTherm-A, Wagner & Munz, Koefler-Hotstage Microscope apparatus. Solvents used for recrystallization are indicated after the melting point. UV spectra were obtained using a Perkin-Elmer Lambda-25 UV/*vis* spectrophotometer and inflections are identified by the abbreviation "inf". IR spectra were recorded on a Shimidazu FTIR-NIR Prestige-21 spectrometer with Pike *Miracle* Ge ATR accessory and strong, medium and weak peaks are represented by s, m and w respectively. Low resolution (EI) mass spectra were recorded on a Shimadzu Q2010 GCMS with direct inlet probe. EPR spectra were recorded on a Bruker ESP-300E EPR spectrometer running at X-band (~ 9.77 GHz) at room temperature. 1,3-Diphenyl-1,2,4-benzotriazin-7(*H*)-one (**4**) isolated in trace or minor amounts from several of the reactions was identical to an authentic sample prepared in accordance with the literature (ref. 9 in main manuscript).

Section B: Experimental Procedures and Spectral Analysis

A. Stille reaction (general procedure): A stirred mixture of 7-iodo-1,3-diphenyl-1,4-dihydro-1,2,4-benzotriazinyl **2e** (50 mg, 0.122 mmol), organostannane (2 equiv.) and $Pd(OAc)_2$ (5 mol%) was heated to *ca.* 100 ^oC in dry DMF (2 ml) for 0.5-1 h under inert conditions until all the starting material was consumed (TLC). Dry flash chromatography

(Et_2O/hexane, 1:3) of the reaction mixture gave the following phenyl, fur-2-yl, thien-2-yl 7 substituted-benzotriazinyls **3a-c**, respectively.

B. Suzuki reaction (general procedure): A stirred mixture of 7-iodo-1,3-diphenyl-1,4-dihydro-1,2,4-benzotriazinyl, arylboronic acid (3 equiv.), K_2CO_3 (3 equiv.) and $Pd(OAc)_2$ (5 mol%) was heated to *ca.* 100 ^oC in dry toluene for 1-3 h under argon until all the starting material was consumed (TLC). Dry flash chromatography (Et_2O/hexane, 1:3) of the reaction mixture gave the following 4-$MeOC_6H_4$, 4-MeC_6H_4, 4-FC_6H_4, 4-PhC_6H_4, thien-3-yl 7 substituted benzotriazinyls **3d-h**, respectively.

1,3,7-Triphenyl-1,4-dihydro-1,2,4-benzotriazin-4-yl (3a): black needles, mp 152-154 ^oC (cyclohexane). (Found: C, 83.45; H, 5.12; N, 11.68. $C_{19}H_{13}IN_3$ requires C, 83.31; H, 5.03; N, 11.66%); g = 2.0071; λ_{max}(DCM)/nm 293 (log ε 3.50), 323 inf (2.88), 385 (2.78), 443 (2.46), 514 (2.20); ν_{max}/cm^{-1} 3062vw, 3032vw, 2953vw, 2924vw, 1595w, 1510w, 1481m, 1448w, 1415w, 1392m, 1317w, 1278w, 1247w, 1199w, 1168w, 1080w, 1066w, 1022w, 898w, 839w 776m; *m/z* (EI) 361 (M^+ + 1, 37%), 360 (M^+, 100), 255 (12), 180 (12), 152 (26), 126 (5), 102 (46), 77 ($C_6H_5^+$, 51), 57 (5), 51 (22).

7-Fur-2-yl-1,4-dihydro-1,2,4-benzotriazin-4-yl (3b): red needles, mp 163-165 ^oC (cyclohexane). (Found: C, 78.86; H, 4.67; N, 11.97. $C_{26}H_{16}N_3O$ requires C, 78.84; H, 4.60; N, 11.99%); g = 2.0071; λ_{max}(DCM) 309 (log ε 3.73), 401 (2.98), 433 (2.91), 459 (2.80), 507 (2.50), 541 (2.75); ν_{max}/cm^{-1} 3062vw, 1593w, 1508w, 1487w, 1454w, 1392m, 1317w, 1222w, 1172w, 1047w, 1016w, 817w, 783m; *m/z* (EI) 351 (M^+ + 1, 32%), 350 (M^+, 100), 142 (19), 92 (13), 77 ($C_6H_5^+$, 20), 51 (10).

7-Thien-2-yl-1,4-dihydro-1,2,4-benzotriazin-4-yl (3c): red needles, mp 145-146 ^oC (pentane/cyclohexane). (Found: C, 75.31; H, 4.47; N, 11.39. $C_{23}H_{16}N_3S$ requires C, 75.38; H, 4.40; N, 11.47%); g = 2.0071; λ_{max}(DCM) 310 (log ε 3.49), 394 (2.82), 468 (2.56), 542 (2.41); ν_{max}/cm^{-1} 3062vw, 3005vw, 1589w, 1533w, 1487m, 1456w, 1392m, 1317w, 1274w, 1259w, 1176w, 1028w, 854w, 808m, 779m, 784s, 750s; *m/z* (EI) 367 (M^+ + 1, 33%), 366 (M^+, 100), 183 (5), 158 (23), 108 (16), 77 ($C_6H_5^+$, 22), 51 (10).

7-*p*-Methoxyphenyl-1,4-dihydro-1,2,4-benzotriazin-4-yl (3d): black plates, mp 183-184 ^{o}C (pentane/cyclohexane). (Found: C, 80.06; H, 5.1; N, 10.63. $C_{26}H_{20}N_3O$ requires C, 79.98; H, 5.16; N, 10.76%); g = 2.0071; λ_{max}(DCM) 300 (log ε 3.54), 389 (2.88), 523 (2.31); ν_{max}/cm^{-1} 2951vw, 2833vw, 1604w, 1587w, 1485m, 1438w, 1390m, 1319w, 1282w, 1263w, 1242m, 1190m, 1168m, 1037w,1020w, 819m, 781w, 761w; *m/z* (EI) 391 (M^+ + 1, 36%), 390 (M^+, 100), 375 (10), 348 (6), 347 (20), 195 (11), 139 (10), 132 (13) 77 ($C_6H_5^+$, 20), 51 (8).

7-Tolyl-1,4-dihydro-1,2,4-benzotriazin-4-yl (3e): brown needles, mp 188-189 ^{o}C (pentane/cyclohexane). (Found: C, 83.25; H, 5.35; N, 11.19. $C_{26}H_{20}N_3$ requires C, 83.39; H, 5.38; N, 11.22%); g = 2.0071; λ_{max}(DCM) 296 (log ε 3.56), 385 (2.87), 516 (2.24); ν_{max}/cm^{-1} 3062vw, 3026vw, 1591w, 1487m, 1452w, 1425w, 1400m, 1328w, 1317w, 1247w, 1203w, 1168w, 1068w, 1024w, 900w, 864w, 846w, 815m, 779m, 759w; *m/z* (EI) 375 (M^+ + 1, 34%), 374 (M^+, 100), 187 (10), 180 (5), 166 (16), 116 (18), 115 (12), 77 ($C_6H_5^+$, 18), 51 (7).

7-*p*-Fluorophenyl-1,4-dihydro-1,2,4-benzotriazinyl (3f): black needles, mp 194-195 ^{o}C (pentane/cyclohexane). (Found: C, 79.41; H, 4.57; N, 11.05. $C_{25}H_{17}FN3$ requires C, 79.35; H, 4.53; N, 5.02%); g = 2.0069; λ_{max}(DCM) 293 (log ε 3.52), 382 (2.81), 513 (2.14); ν_{max}/cm^{-1} 3066vw, 3039vw, 1593w, 1487m, 1450w, 1431w, 1390m, 1328w, 1315w, 1219m, 1163w, 1066w, 1024w, 900w, 862w, 837w, 821s, 779m, 758m; *m/z* (EI) 379 (M^+ + 1, 32%), 378 (M^+, 100), 180 (6), 170 (25), 120 (44), 77 ($C_6H_5^+$, 45), 51 (21).

7-Biphenyl-1,4-dihydro-1,2,4-benzotriazin-4-yl (3g): red plates, mp 188-189 ^{o}C (pentane/cyclohexane). (Found: C, 85.22; H, 5.06; N, 9.68. $C_{31}H_{22}N_3$ requires C, 85.29; H, 5.08; N, 9.63%); g = 2.0071; λ_{max}(DCM) 303 (log ε 3.77), 388 (3.13), 521 (2.51); ν_{max}/cm^{-1} 3064vw, 3035vw, 1502w, 1481w, 1450w, 1396m, 1319w, 1247w, 1172w, 1070w, 1026w, 1002w, 898w, 821m, 763m; *m/z* (EI) 437 (M^+ + 1, 42%), 436 (M^+, 100), 228 (12), 218 (14), 178 (18), 77 ($C_6H_5^+$, 14).

7-Thien-3-yl-1,4-dihydro-1,2,4-benzotriazin-4-yl (3h): black prisms, mp 185-187 ^{o}C (pentane/cyclohexane). (Found: C, 75.43; H, 4.49; N, 11.42. $C_{23}H_{16}N_3S$ requires C, 75.38; H, 4.40; N, 11.47%); g = 2.0069; λ_{max}(DCM) 298 (log ε 3.52), 388 (2.79), 520 (2.23); ν_{max}/cm^{-1} 3101vw, 3062vw, 1587w, 1525w, 1485w, 1450w, 1433w, 1390m, 1317w, 1274w, 1246w, 1170w, 1066w, 1024w, 864w, 856w, 825w, 779s; *m/z* (EI) 367 (M^+ + 1, 31%), 366 (M^+, 100), 183 (9), 180 (5), 158 (18), 108 (18), 77 ($C_6H_5^+$, 18), 51 (9).

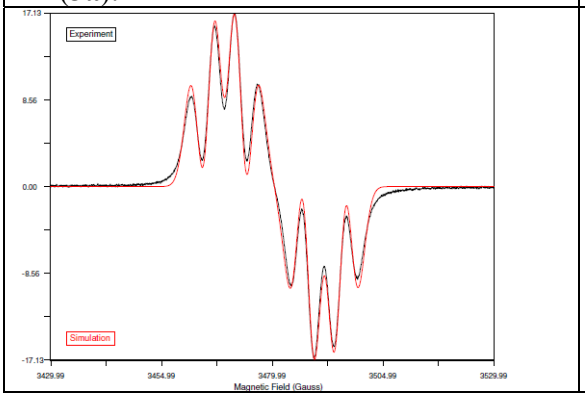
Section C: EPR Spectra

EPR spectra were recorded on a Bruker ESP-300E EPR spectrometer running at X-band (~ 9.77 GHz) at room temperature. Accurate microwave frequencies were measured using a microwave counter. All spectra were recorded in both first and second derivative modes on solutions in DCM and simulations undertaken with Winsim[1] using a pure Gaussian lineshape with linewidths of *ca*. 2 G. Generally better resolution and estimates of hyperfine couplings were afforded by the second derivative spectra (see Table 1).

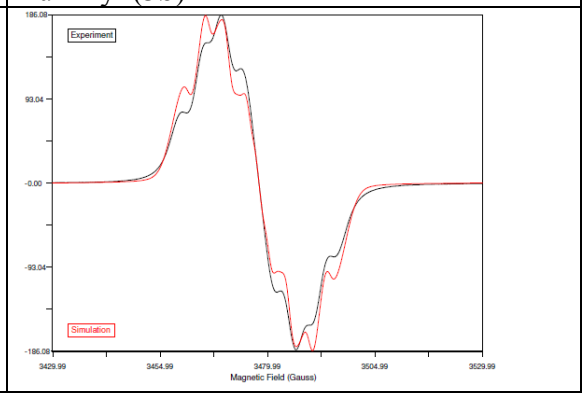
Derivative	g	a_N(1)/G	a_N(2)/G	a_N(3)/G
Ph (**3a**)	2.0071	7.49	4.89	4.65
Fur-2-yl (**3b**)	2.0071	7.06	4.75	4.53
Thien-2-yl (**3c**)	2.0071	7.38	4.92	4.59
4-MeOC_6H_4 (**3d**)	2.0071	7.24	4.84	4.57
Tolyl (**3e**)	2.0071	7.47	4.90	4.66
4-FC_6H_4 (**3f**)	2.0069	7.47	4.84	4.70
Biphenyl (**3g**)	2.0071	7.45	4.84	467
Thien-3-yl (**3h**)	2.0069	7.31	4.84	4.60

[1] Winsim 2002 (v.0.98), Public EPR Software Tools, D.A. O'Brien, D.R. Duling and Y.C. Fann, NIEHS, National Institutes of Health, USA.

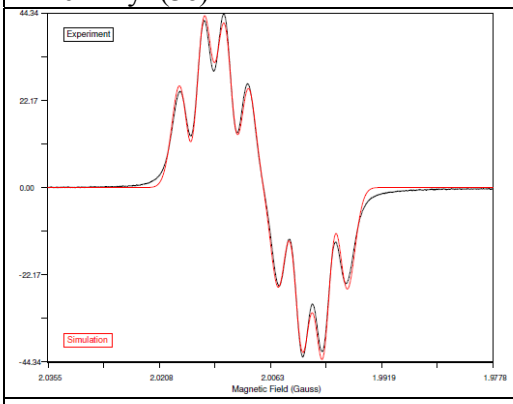
Ph (**3a**):



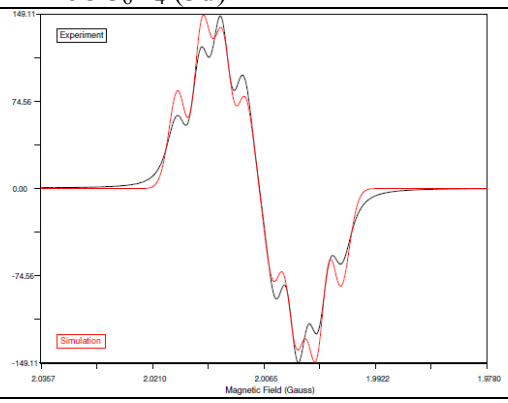
Fur-2-yl (**3b**)



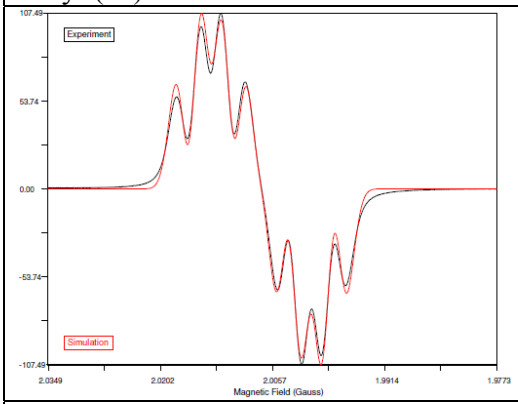
Thien-2-yl (**3c**)



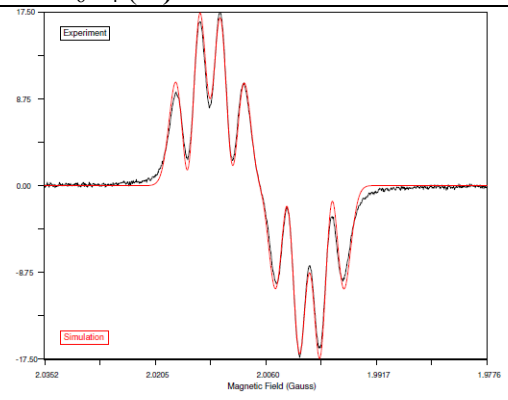
4-$MeOC_6H_4$ (**3d**)



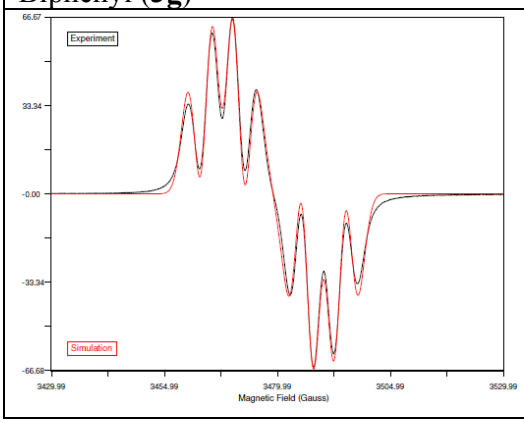
Tolyl (**3e**)



4-FC_6H_4 (**3f**)



Biphenyl (**3g**)



Thien-3-yl (**3h**)