Electronic Supporting Information (ESI)

Cross-Coupling Reaction between Arylboronic Acids and Carboranyl Iodides Catalyzed by Graphene Oxide (GO)-Supported Pd (0) Recyclable Nanoparticles for the Synthesis of Carboranylaryl Ketones

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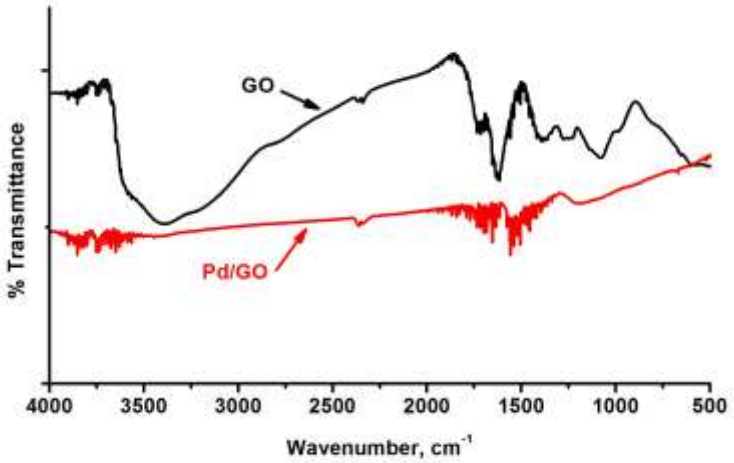
Figure S-1 FT-IR of GO and Pd@GO



Spectroscopic data for products:

1-Me-2-[C(=O)Ar]-1,2-$C_2B_{10}H_{10}$ (Ar=C_6H_5): Yield 62%. MS (ESI) for $C_{10}H_{18}B_{10}O$: m/z = 285.22 $[M+Na]^+$. ^1H NMR ($CDCl_3$, ppm), δ = 7.67-6.35 (m, 5H, $C_6\underline{H}_5$), 2.73-1.24 (m, br, 10H, $B_{10}\underline{H}_{10}$), 2.04 (s, 3H, $C\underline{H}_3$). ^{13}C NMR ($CDCl_3$, ppm), δ = 187.32 ($\underline{C}O$), 136.38, 132.93, 128.89, 128.27 ($\underline{C}_6H_4$), 78.33 and 77.70 ($\underline{C}_{cage}$), 23.76 (C_{cage}-$\underline{C}H_3$). ^{11}B NMR ($CDCl_3$, ppm), δ = -0.21 (1B, $^1J_{BH}$ = 148 Hz), -5.24 (1B, $^1J_{BH}$ = 152 Hz), -9.19 (6B, $^1J_{BH}$ = 172 Hz), -10.66 (2B, $^1J_{BH}$ = 183 Hz). IR (KBr pellet, cm^{-1}), 3744 (m, s), 3071 (m, s), 2965 (m, s), 2859 (m, s), 2580 (vs, s, ν_{BH}), 1788 (m, s), 1717 (m, s), 1600 (s, s), 1504 (s, s), 1384 (w, s), 1240 (s, s), 1155 (m, s), 1089 (m, s), 1034 (m, s), 940 (w, s), 846 (s, s), 816 (m, s), 764 (m, s), 726 (m, s), 683 (w, s), 592 (w, s), 498 (w, s).

1-Me-2-[C(=O)Ar]-1,2-$C_2B_{10}H_{10}$ (Ar=C_6H_4-4-OMe): Yield 83%. MS (ESI) for $C_{11}H_{20}B_{10}O_2$: m/z = 292.39 $[M+H]^+$. ^1H NMR ($CDCl_3$, ppm), δ = 7.87-6.84 (m, 4H, $C_6\underline{H}_4$), 3.81 (s, 3H, $OC\underline{H}_3$), 3.29-1.48 (m, br, 10H, $B_{10}\underline{H}_{10}$), 1.99 (s, 3H, $C\underline{H}_3$). ^{13}C NMR ($CDCl_3$, ppm), δ = 183.96 ($\underline{C}O$), 163.88, 132.67, 128.16, 113.59 ($\underline{C}_6H_4$), 78.86 and 77.55 ($\underline{C}_{cage}$), 55.60 (O-$\underline{C}H_3$), 24.55 (C_{cage}-$\underline{C}H_3$). ^{11}B NMR ($CDCl_3$, ppm), δ = -0.41 (1B, $^1J_{BH}$ = 149 Hz), -5.24 (1B, $^1J_{BH}$ = 153 Hz), -9.28 (6B, $^1J_{BH}$ = 136 Hz), -10.53 (2B, $^1J_{BH}$ = 150 Hz). IR (KBr pellet, cm^{-1}), 3745 (s, s), 2970 (m, s, br), 2934 (s, s), 2842 (m, s), 2577 (vs, s, ν_{BH}), 2045 (w, s), 1769 (s, s), 1734 (s, s), 1602 (s, s), 1507 (s, s), 1457 (s, s), 1437 (m, s), 1309 (m, s), 1258 (s, s), 1213 (m, s), 1168 (s, s), 1115 (m, s), 1026 (m, s), 933 (w, s), 875 (m, s), 841 (m, s), 772 (m, s), 728 (w, s), 650 (w, s), 502 (w, s).

1-Me-2-[C(=O)Ar]-1,2-$C_2B_{10}H_{10}$ (Ar=C_6H_4-4-F): Yield 70%. MS (ESI) for $C_{10}H_{17}B_{10}OF$: m/z = 303.12 $[M+Na]^+$. ^1H NMR ($CDCl_3$, ppm), δ = 7.79-7.04 (m, 4H, $C_6\underline{H}_4$), 2.39-1.12 (m, br, 10H, $B_{10}\underline{H}_{10}$), 2.03 (s, 3H, $C\underline{H}_3$). ^{13}C NMR ($CDCl_3$, ppm), δ = 185.50 ($\underline{C}O$), 164.26, 132.02, 116.41, 116.07 ($\underline{C}_6H_4$), 78.14 and 77.80 ($\underline{C}_{cage}$), 23.74 (C_{cage}-$\underline{C}H_3$). ^{11}B NMR ($CDCl_3$, ppm), δ = -0.08 (1B, $^1J_{BH}$ = 120 Hz), -5.21 (1B, $^1J_{BH}$ = 154 Hz), -9.16 (6B, $^1J_{BH}$ = 172 Hz), -10.75 (2B, $^1J_{BH}$ = 187 Hz). IR (KBr pellet, cm^{-1}), 3744 (s, s), 3071 (w, s), 2976 (m, s), 2922 (s, s), 2832 (m, s), 2580 (vs, s, ν_{BH}), 1788 (m, s), 1717 (s, s), 1600 (s, s), 1504 (s, s), 1446 (m, s), 1386 (m, s), 1240 (s, s), 1155 (s, s), 1089 (s, s), 1034 (m, s), 940 (m, s), 845 (s, s), 816 (s, s), 764 (m, s), 726 (s, s), 683 (w, s), 592 (m, s)., 498 (w, s).

1-[C(=O)-Ar]-1,2-$C_2B_{10}H_{11}$ (Ar=C_6H_5): Yield 51%. MS (ESI) for $C_9H_{16}B_{10}O$: m/z = 248.16 $[Ma]^+$. ^1H NMR ($CDCl_3$, ppm), δ = 7.93-7.33 (m, 5H, $C_6\underline{H}_5$), 3.45 (s, 1H, $\underline{H}C_{cage}$), 3.38-1.11(m, br, 10H, $B_{10}\underline{H}_{10}$). ^{13}C NMR ($CDCl_3$, ppm), δ = 184.35 ($\underline{C}O$), 132.08, 129.90, 128.35, 127.48 ($\underline{C}_6H_5$), 82.93 and 75.19 ($\underline{C}_{cage}$). ^{11}B NMR ($CDCl_3$, ppm), δ = -1.27 (1B, $^1J_{BH}$ = 147 Hz), -2.45 (1B, $^1J_{BH}$ = 155 Hz), -9.22 (2B, $^1J_{BH}$ = 152 Hz), -10.66 (1B, $^1J_{BH}$ = 142 Hz), -11.52 (1B, $^1J_{BH}$ = 172 Hz), -13.59 (3B, $^1J_{BH}$ = 159 Hz), -14.72 (2B, $^1J_{BH}$ = 168 Hz). IR (KBr pellet, cm^{-1}), 3745 (m, m), 3196 (w, s), 3075 (s, s), 2960 (m, s), 2929 (m, s), 2859 (w, s), 2584 (vs, s, ν_{BH}), 1682 (vs, s), 1595 (s, s), 1447 (s, s), 1252 (vs, s), 1115 (m, s), 1087 (m, s), 1018 (m, s), 949 (m, s), 853 (w, s), 764 (s, s), 725 (s, s), 688 (s, s), 613 (m, s), 570 (w, s).

1-[C(=O)-Ar]-1,2-$C_2B_{10}H_{11}$ (Ar=C_6H_4-4-OMe): Yield 72%. MS (ESI) for $C_{10}H_{18}B_{10}O_2$: m/z = 279.16 $[M+H]^+$. ^1H NMR ($CDCl_3$, ppm), δ = 7.93-6.84 (m, 4H, $C_6\underline{H}_4$), 3.83(s, 3H, $OC\underline{H}_3$), 3.48 (s, 1H, $\underline{H}C_{cage}$), 2.91-1.43 (m, br, 10H, $B_{10}\underline{H}_{10}$). ^{13}C NMR ($CDCl_3$, ppm), δ = 182.62 ($\underline{C}O$), 134.03, 133.75, 127.20, 113.85 ($\underline{C}_6H_4$), 84.78 and 77.20 ($\underline{C}_{cage}$), 55.59 (O-$\underline{C}H_3$). ^{11}B NMR ($CDCl_3$, ppm), δ = -1.56 (1B, $^1J_{BH}$ = 122 Hz), -2.33 (2B, $^1J_{BH}$ = 142 Hz), -8.14 (1B, $^1J_{BH}$ = 141 Hz), -9.20 (2B, $^1J_{BH}$ = 142 Hz), -13.67 (3B, $^1J_{BH}$ = 160 Hz), -14.78 (1B, $^1J_{BH}$ = 157 Hz). IR (KBr pellet, cm^{-1}), 3744 (m, s), 3675 (m, s), 3067 (m, s), 3014 (w, s), 2937 (w, s), 2842 (m, s), 2579 (vs, s), 3346 (vs, s), 3065 (m, s), 3040 (m, s), 2918 (w, s), 2849 (w, s), 2580 (vs, s, ν_{BH}), 2042 (w, s), 1661 (vs, s), 1593 (vs, s), 1508 (s, s), 1309 (m, s), 1250 (vs, s), 1171 (vs, s), 1103 (m, s), 1025 (s, s), 945 (s, s), 885 (w, s), 841 (m, s), 807 (m, s), 716 (m, s), 565 (w, s), 419 (m, s).

1-[C(=O)-Ar]-1,2-$C_2B_{10}H_{11}$ (Ar=C_6H_4-4-F): Yield 66%. MS (ESI) for $C_9H_{15}B_{10}OF$: m/z = 268.34 $[M+2H]^+$. ^1H NMR ($CDCl_3$, ppm), δ = 7.87-7.02 (m, 4H, $C_6\underline{H}_4$), 3.44 (s, 1H, $\underline{H}C_{cage}$), 2.88-1.20 (m, br, 10H, $B_{10}\underline{H}_{10}$). ^{13}C NMR ($CDCl_3$, ppm), δ = 182.90 ($\underline{C}O$), 137.01, 132.20, 115.06, 115.01 ($\underline{C}_6H_4$), 83.20 and 68.20 ($\underline{C}_{cage}$). ^{11}B NMR ($CDCl_3$, ppm), δ = -1.25 (1B, $^1J_{BH}$ = 165 Hz), -2.44 (1B, $^1J_{BH}$ = 153 Hz), -7.92 (1B, $^1J_{BH}$ = 166 Hz), -9.23 (2B, $^1J_{BH}$ = 158 Hz), -10.59 (2B, $^1J_{BH}$ = 156 Hz), -13.62 (2B, $^1J_{BH}$ = 165 Hz), -14.77 (1B, $^1J_{BH}$ = 154 Hz). IR (KBr pellet, cm^{-1}), 3744 (s, s), 3671 (s, s), 3213 (m, br), 3073 (m, s), 2961 (w, s), 2571 (vs, s, ν_{BH}), 1675 (s, s), 1661 (s, s), 1595 (s, s), 1504 (s, s), 1240 (s, s), 1159 (s, s), 1099 (m, s), 1013 (m, s), 947 (m, s), 887 (w, s), 849 (m, s), 813 (m, s), 718 (m, s), 635 (w, s), 564 (w, s), 501 (w, s).

1-Ph-2-[C(=O)Ar]-1,2-$C_2B_{10}H_{10}$ (Ar=C_6H_5): Yield 55%. MS (ESI) for $C_{15}H_{20}B_{10}O$: m/z = 325.26 $[M+H]^+$. ^1H NMR ($CDCl_3$, ppm), δ = 7.60-7.18 (m, 10H, 2x$C_6\underline{H}_5$), 2.89-1.24 (m, br, 10H, $B_{10}\underline{H}_{10}$). ^{13}C NMR ($CDCl_3$, ppm), δ = 185.55 ($\underline{C}O$), 136.41, 134.56, 132.57, 130.90, 130.71, 128.90, 128.54, 128.43 (2x$\underline{C}_6H_5$), 85.10 and 82.63 ($\underline{C}_{cage}$). ^{11}B NMR ($CDCl_3$, ppm), δ = 0.12 (1B, $^1J_{BH}$ = 151 Hz), -3.07 (1B, $^1J_{BH}$ = 150 Hz), -9.43 (5B, $^1J_{BH}$ = 148 Hz), -10.70 (3B, $^1J_{BH}$ = 148 Hz). IR (KBr pellet, cm^{-1}), 3744 (m, s), 3373 (w, s), 3065 (s, s), 2960 (s, s), 2930 (s, s), 2865 (m, s), 2583 (vs, s, ν_{BH}), 1962 (w, s), 1788 (s, s), 1725 (s, s), 1697 (s, s), 1653 (m, s), 1595 (m, s), 1447 (s, s), 1387 (w, s), 1258 (s, s), 1213 (vs, s), 1119 (m, s), 1071 (m, s), 1039 (s, s), 995 (s, s), 953 (m, s), 882 (w, s), 851 (w, s), 760 (s, s), 694 (s, s), 611 (m, s), 554 (m, s), 486 (w, s).

1-Ph-2-[C(=O)Ar]-1,2-$C_2B_{10}H_{10}$ (Ar=C_6H_4-4-OMe): Yield 64%. MS (ESI) for $C_{16}H_{22}B_{10}O_2$: m/z = 355.27 $[M+H]^+$. ^1H NMR ($CDCl_3$, ppm), δ = 7.55-6.71 (m, 9H, $C_6\underline{H}_4$ and $C_6\underline{H}_5$), 3.75 (s, 3H, $OC\underline{H}_3$), 2.85-1.30 (m, br, 10H, $B_{10}\underline{H}_{10}$). ^{13}C NMR ($CDCl_3$, ppm), δ = 182.54 ($\underline{C}O$), 163.57, 134.03, 132.84, 130.79, 130.48, 128.44, 128.32, 113.55 (2x$\underline{C}_6H_4$), 85.04 and 82.96 ($\underline{C}_{cage}$), 55.60 ($O\underline{C}H_3$). ^{11}B NMR ($CDCl_3$, ppm), δ = 0.03 (1B, $^1J_{BH}$ = 149 Hz), -3.01 (1B, $^1J_{BH}$ = 152 Hz), -9.68 (5B, $^1J_{BH}$ = 104 Hz), -10.51 (3B, $^1J_{BH}$ = 141 Hz). IR (KBr pellet, cm^{-1}), 3744 (m, s), 3063 (m, s), 3006 (w, s), 2968 (m, s), 2932 (m, s), 2839 (m, s), 2581 (vs, s, ν_{BH}), 2048 (w, s), 1769 (s, s), 1674 (s, s), 1601 (vs, s), 1507 (s, s), 1457 (s, s), 1312 (m, s), 1258 (s, s0, 1169 (s, s), 1108 (s, s), 1028 (s, s), 932 (m, s), 878 (m, s), 845 (s, s), 770 (m, s), 689 (s, s), 600 (s, s), 554 (m, s), 519 (w, s), 419 (w, s).

1-Ph-2-[C(=O)Ar]-1,2-$C_2B_{10}H_{10}$ (Ar=C_6H_4-4-F): Yield 78%. MS (ESI) for $C_{15}H_{19}B_{10}OF$: m/z = 345.45 $[M+3H]^+$. ^1H NMR ($CDCl_3$, ppm), δ = 7.48-6.89 (m, 9H, $C_6\underline{H}_4$ and $C_6\underline{H}_5$), 2.58-1.14 (m, br, 10H, $B_{10}\underline{H}_{10}$). ^{13}C NMR ($CDCl_3$, ppm), δ = 183.88 ($\underline{C}O$), 163.97, 131.61, 131.51, 130.84, 130.69, 128.56, 115.45, 115.23 (2x$\underline{C}_6H_4$), 85.16 and 82.40 ($\underline{C}_{cage}$). ^{11}B NMR ($CDCl_3$, ppm), δ = 0.23 (1B, $^1J_{BH}$ = 150 Hz), -3.02 (1B, $^1J_{BH}$ = 153 Hz), -9.46 (5B, $^1J_{BH}$ = 144 Hz), -10.81 (3B, $^1J_{BH}$ = 156 Hz). IR (KBr pellet, cm^{-1}), 3745 (m, s), 3013 (m, s), 2959 (m, s), 2930 (m, s), 2866 (w, s), 2590 (vs, s, ν_{BH}), 1787 (m, s), 1718 (s, s), 1685 (s, s), 1594 (s, s0, 1503 (s, s), 1236 (s, s), 1155 (s, s), 1103 (s, s), 1070 (s, s), 1006 (m, s), 934 (m, s), 853 (s, s), 813 (s, s), 758 (s, s), 731 (m, s), 685 (s, s), 592 (m, s), 556 (m, s), 509 (w, s), 419 (w, s).

Table S-1 Crystallographic data of compound 1-Me-2-[C(=O)Ar]-1,2-$C_2B_{10}H_{10}$ (Ar=C_6H_4-4-OMe).

Empirical formula	**$C_{11}H_{20}B_{10}O_2$**
Formula weight	**292.37**
Crystal system	**Monoclinic**
Space group	***$P2_1/c$***
T [K]	**110(2)**
***a* [Å]**	**10.050(2)**
***b* [Å]**	**7.5783(15)**
***c* [Å]**	**22.381**
α [°]	**90**
β [°]	**110.40(3)**
γ [°]	**90**
Z	**4**
***V* [Å^3]**	**1597.7(6)**
D_{calc} [g cm^{-3}]	**1.215**
μ [mm^{-1}]	**0.068**
Reflections used	**8868**
Unique reflections	**2765**
Observed reflections	**2626**
Parameters	**250**
R1[I > 2σ(I)]	**0.0541**
wR_2 [all]	**0.1487**
GOF	**1.1116**

Figure S-2 Structure of compound 1-Me-2-[C(=O)Ar]-1,2-$C_2B_{10}H_{10}$ (Ar=C_6H_4-4-OMe).

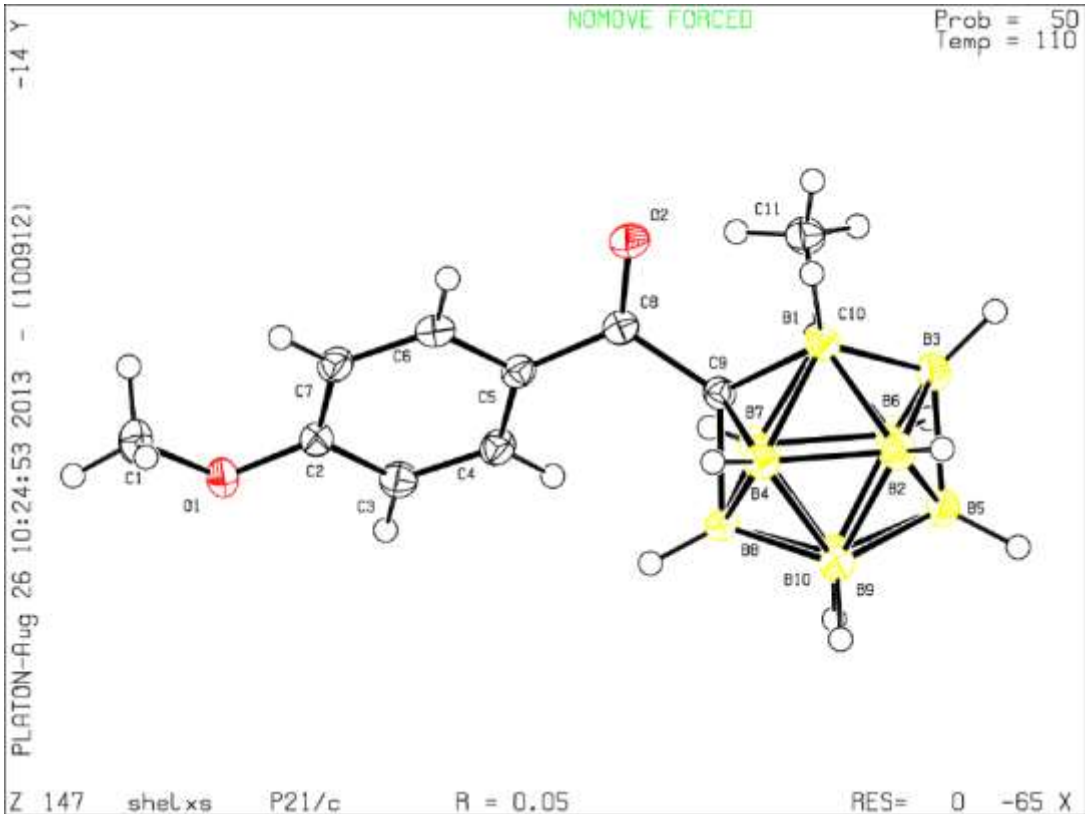
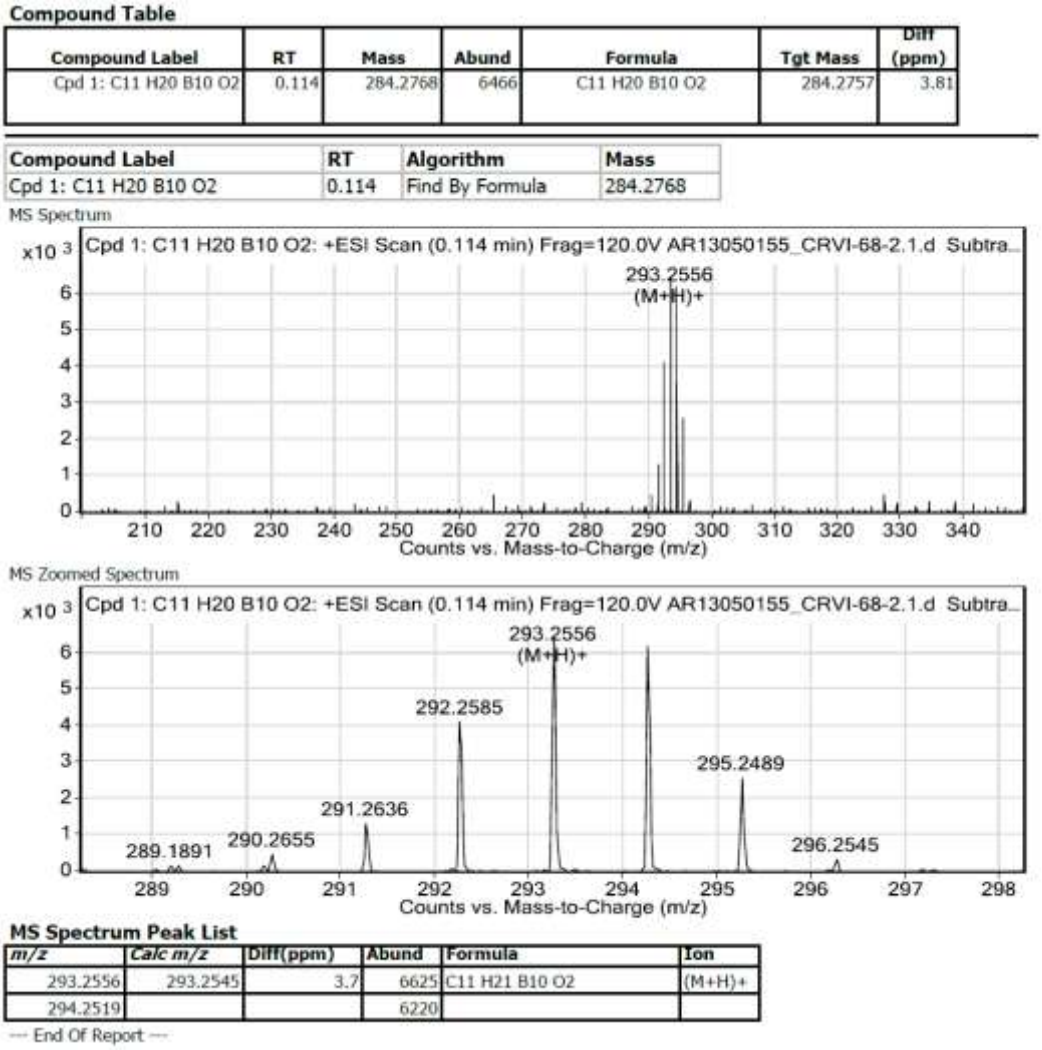


Figure S-3 Mass spectra of compound 1-Me-2-[C(=O)Ar]-1,2-$C_2B_{10}H_{10}$ (Ar=C_6H_4-4-OMe).



Compound Table

Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)
Cpd 1: C11 H20 B10 O2	0.114	284.2768	6466	C11 H20 B10 O2	284.2757	3.81

Compound Label	RT	Algorithm	Mass
Cpd 1: C11 H20 B10 O2	0.114	Find By Formula	284.2768

MS Spectrum

MS Zoomed Spectrum

MS Spectrum Peak List

m/z	Calc m/z	Diff(ppm)	Abund	Formula	Ion
293.2556	293.2545	3.7	6625	C11 H21 B10 O2	(M+H)+
294.2519			6220		

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Figure S-4 ^{1}H NMR of PhCOPh ($CDCl_3$)

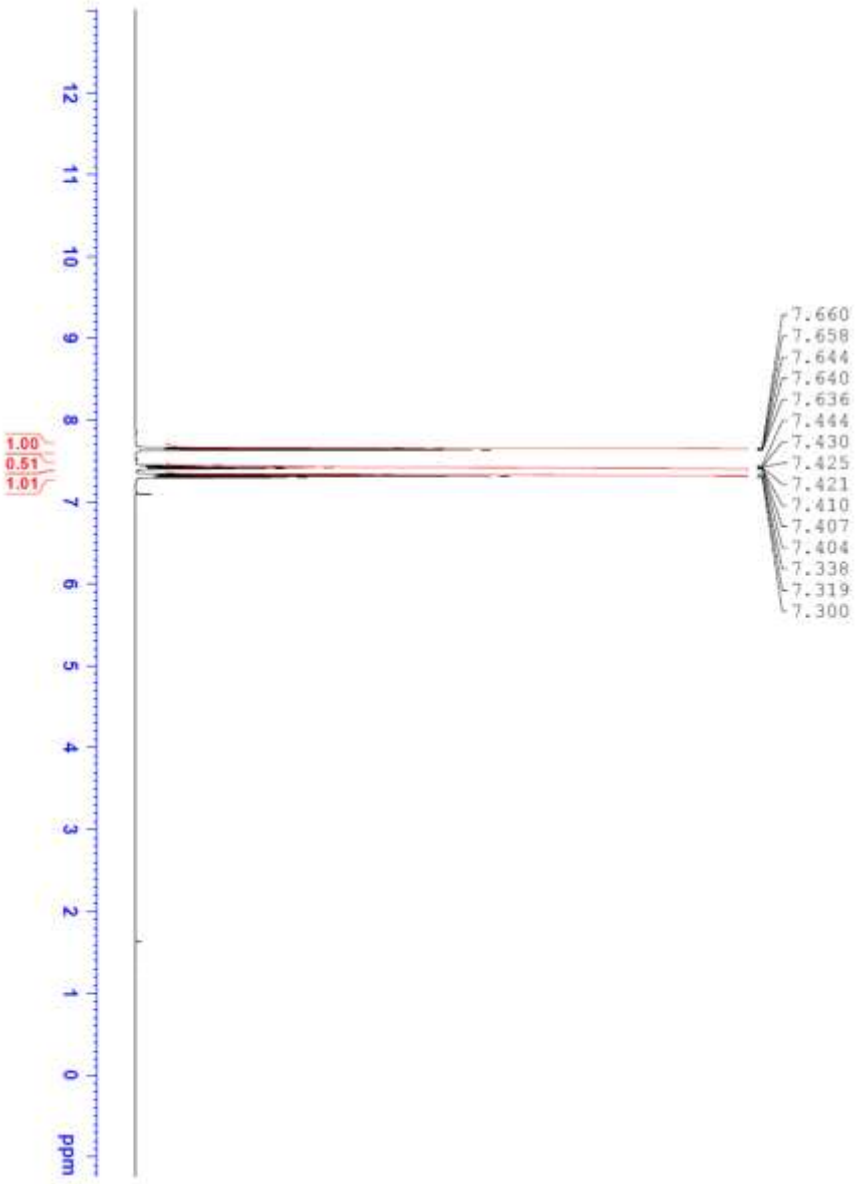

Figure S-5 ^{13}C NMR of PhCOPh ($CDCl_3$)

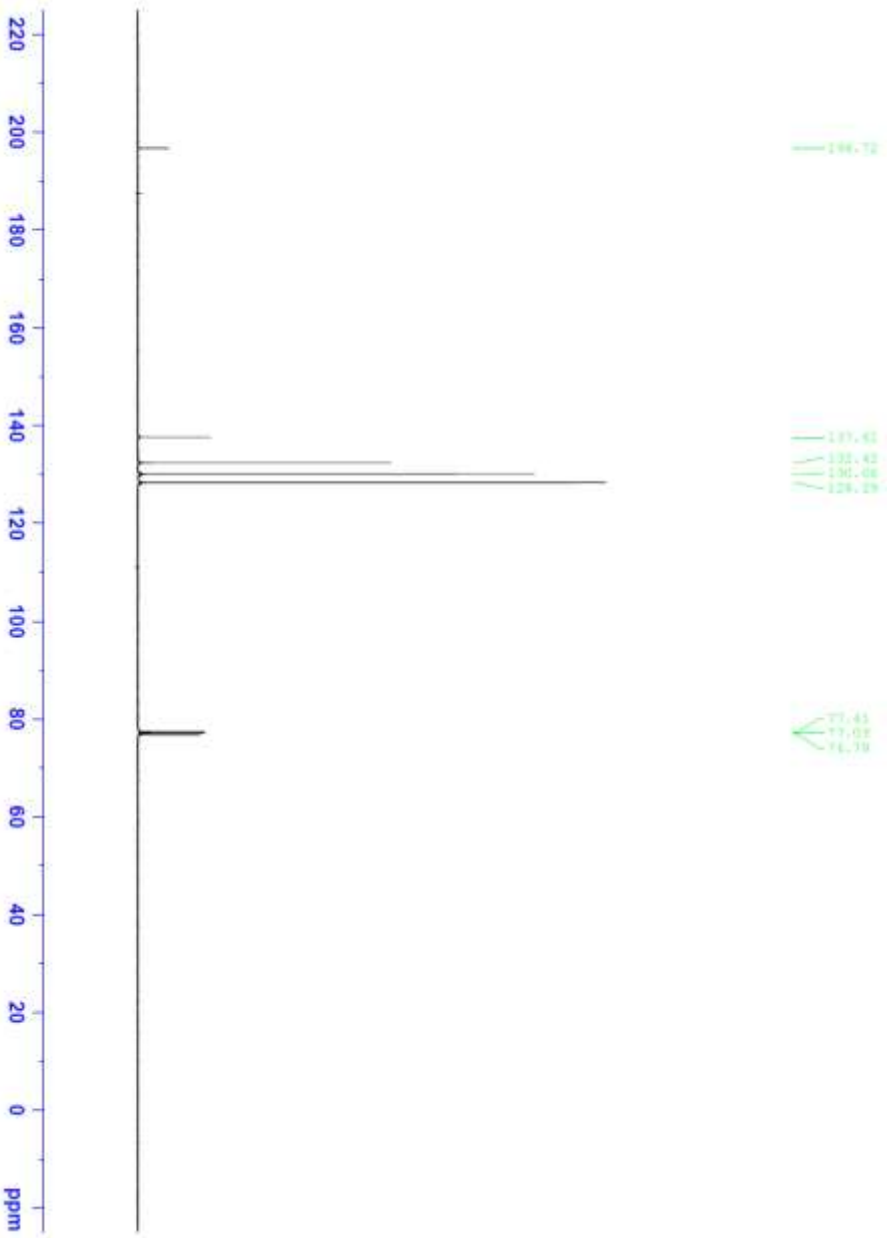

Figure S-6 ^{1}H NMR of 1-Me-2-[C(=O)Ar]-1,2-$C_2B_{10}H_{10}$ (Ar=C_6H_4-4-OMe) ($CDCl_3$)

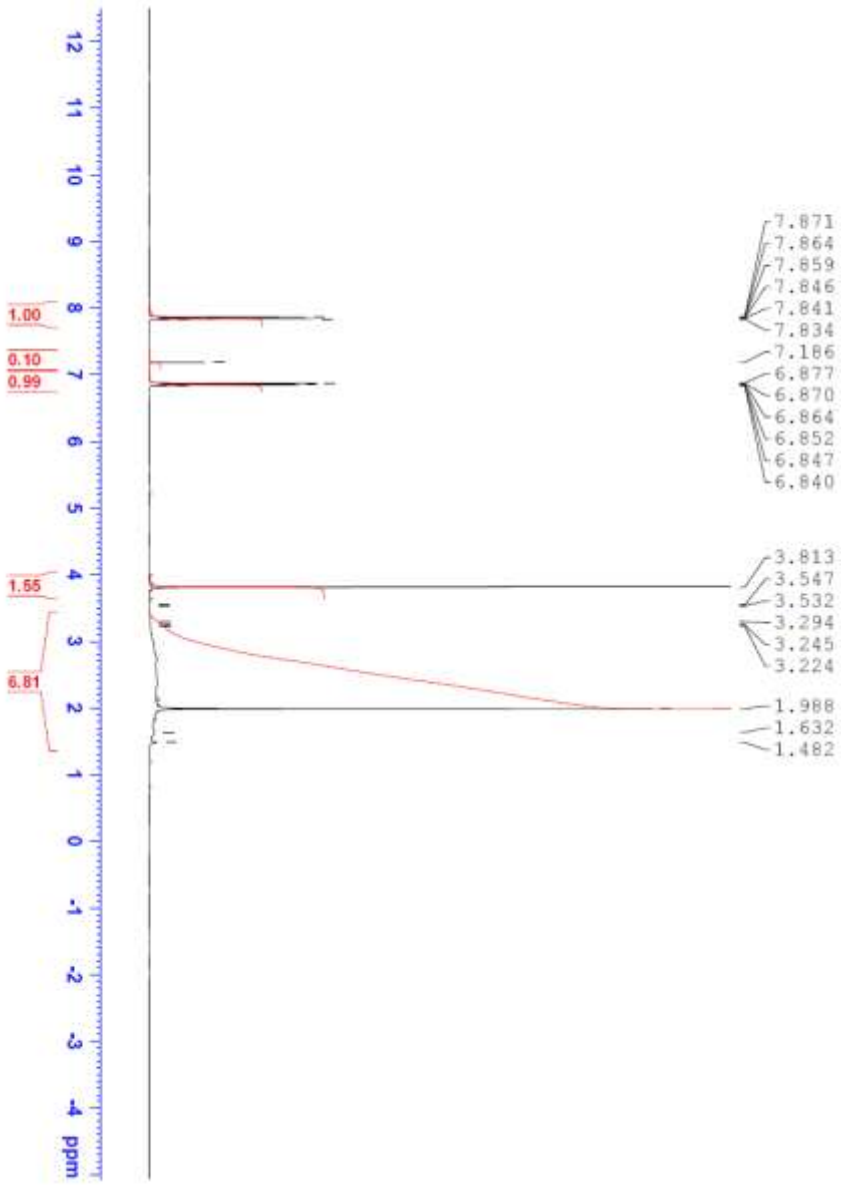

Figure S-7 ^{13}C NMR of 1-Me-2-[C(=O)Ar]-1,2-$C_2B_{10}H_{10}$ (Ar=C_6H_4-4-OMe) ($CDCl_3$)

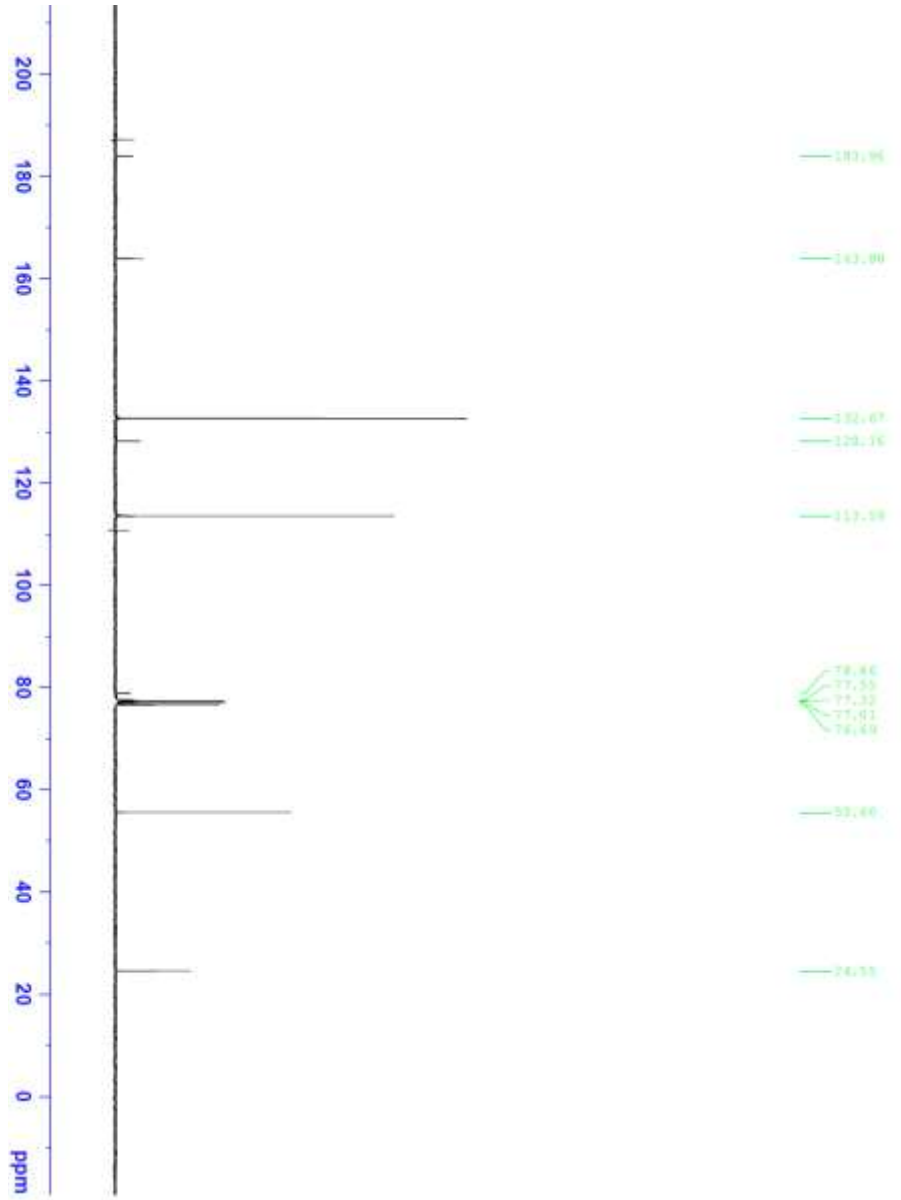

Figure S-8 ^{11}B (H-decoupled) NMR of 1-Me-2-[C(=O)Ar]-1,2-$C_2B_{10}H_{10}$ (Ar=C_6H_4-4-OMe) ($CDCl_3$)

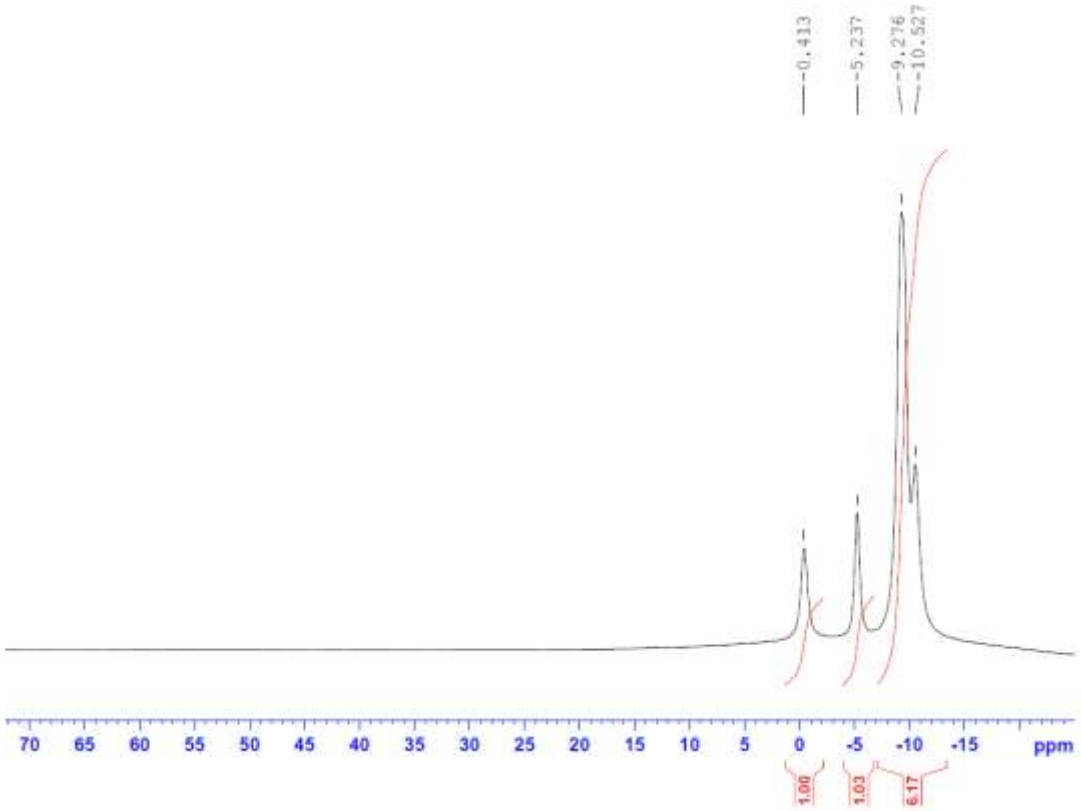

Figure S-9 ^{11}B (H-coupled) NMR of 1-Me-2-[C(=O)Ar]-1,2-$C_2B_{10}H_{10}$ (Ar=C_6H_4-4-OMe) ($CDCl_3$)