A $RuH_2(CO)(PPh_3)_3$-Catalyzed Regioselective Arylation of Aromatic Ketones with Arylboronates via Carbon-Hydrogen Bond Cleavage

Fumitoshi Kakiuchi,[*,†,‡], Yusuke Matsuura, [†] Shintaro Kan,[†] and Naoto Chatani[†]

[†]Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565-0971, Japan, and [‡]PRESTO, JST, 4-1-8 Honcho Kawaguchi, Saitama, Japan.

kakiuchi@chem.eng.osaka-u.ac.jp

Experimental Section

General Information. ^{1}H NMR and ^{13}C NMR were recorded on a JEOL JNM-EX270 spectrometer operating at 270 and 67.5 MHz, respectively. ^{11}B NMR was recorded on a JEOL ECP-400 spectrometer operating at 128 MHz. ^{1}H NMR and ^{13}C NMR signals are quoted relative to internal $CHCl_3$ (δ = 7.26 and 77.0) or tetramethylsilane. ^{11}B NMR signals are quoted relative to BF_3. ^{1}H NMR data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, hept = heptet, m = multiplet, br = broad), coupling constant (Hz), relative intensity. ^{13}C NMR data are reported as follows: chemical shift in ppm (δ). IR spectra were measured on a Hitachi 270-50 infrared spectrometer. GCMS analyses were performed on a Shimadzu GCMS QP-5000 gas chromatography mass spectrometer.

GC Analysis. Conditions for the GC analysis were as follows: Shimadzu GC-14A (equipped with CBP-20 25 m x 0.2 mm); initial temperature, 70 °C or 120 °C; final temperature, 250 °C; rate, 10 °C/min; injection temperature, 250 °C; detector temperature, 250 °C

Solvents and Materials. Toluene was distilled under nitrogen over CaH_2. Aliphatic and aromatic ketones were distilled under nitrogen over $CaSO_4$. $RuH_2(CO)(PPh_3)_3$ was prepared by previously described method.[3c]

General Procedure. The apparatus used in the reactions consisted of a 10-mL two-necked flask equipped with a reflux condenser connected to a nitrogen line, a rubber septum, and a magnetic stirring bar. The flask was flame dried under a stream of nitrogen. The ruthenium complex (0.02 mmol), 1 mL of pinacolone, aromatic ketone (1 mmol), and arylboronic acid ester (1-1.5 mmol) were then placed in the flask. The resulting mixture was refluxed under a nitrogen atmosphere. The progress of the reaction was monitored by GC analysis and the product was isolated and purified by alumina and/or silica gel column chromatography.

Intermolecular deuterium-labeling experiment using pivalophenone-d_0 (7) and pivalophenone-d_5 (7-d_5). The apparatus consisted of a 10-mL two-necked flask equipped with a reflux condenser connected to a nitrogen line, a rubber septum, and a magnetic stirring bar. The flask was flame dried under a stream of nitrogen. The ruthenium complex (0.02 mmol), 1 mL of toluene, pivalophenone (**7**) (0.5 mmol), pivalophenone-d_5 (**7**-d_5) (0.5 mmol), and p-methoxyphenylboronate **28** (0.5 mmol) were then placed in the flask. The resulting mixture was refluxed under a nitrogen atmosphere for 15 min. The reaction mixture was analyzed by GC and GC/MS, and the ratio of the **30**-d_0 and **30**-d_4 in the reaction mixture was determined by GC/MS spectrometry.[31] The products and the starting materials were isolated and purified by alumina and silica gel column chromatography.

Intramolecular deuterium-labeling experiment using pivalophenone-d_1 (7-d_1). The apparatus consisted of 10-mL two-necked flask equipped with a reflux condenser connected to a nitrogen line, a rubber septum, and a magnetic stirring bar. The flask was flame dried under a stream of nitrogen. The ruthenium complex (0.02 mmol), 1 mL of toluene, pivalophenone-d_1 (1 mmol), and p-

methoxyphenylboronate **28** (0.5 mmol) were then placed in the flask. The resulting mixture was refluxed under a nitrogen atmosphere for 15 min. The reaction mixture was analyzed by GC and GC/MS, and the ratio of the **30**-d_0 and **30**-d_1 in the reaction mixture was determined by GC/MS and ^{1}H NMR spectrometry.[31] The products and the starting materials were isolated and purified by alumina and silica gel column chromatography.

Confirmation of the direct reduction of pinacolone with HB-species. The apparatus consisted of 10-mL two-necked flask equipped with a reflux condenser connected to a nitrogen line, a rubber septum, and a magnetic stirring bar. The flask was flame dried under a stream of nitrogen. The ruthenium complex (0.02 mmol), 1 mL of toluene, 2'-methylacetophenone (**1**) (1 mmol), and phenylboronate **2** (1 mmol) were then placed in the flask. The resulting mixture was refluxed under a nitrogen atmosphere for 1.5 h. The reaction mixture was analyzed by GC. To the reaction mixture, pinacolone (2 mmol) was carefully added at the same temperature using a syringe. The resulting reaction mixture was refluxed for further 16 h, and the reaction mixture was analyzed by GC.

1-(3-Methylbiphenyl-2-yl)ethanone. ^{1}H NMR ($CDCl_3$) 1.94 (s, 3H, $CH_3C(O)$), 2.34 (s, 3H, CH_3), 7.2-7.4 (m, 8H, ArH); ^{13}C NMR ($CDCl_3$) 19.63, 32.12, 127.20, 127.58, 128.46, 128.71, 128.86, 129.45, 133.55, 138.42, 140.29, 141.24, 207.42; IR (neat) 3062 w, 3030 w, 2962 w, 2928 w, 1697 s, 1590 w, 1499 w, 1462 m, 1447 w, 1423 m, 1385 w, 1350 m, 1252 s, 1232 m, 1073 w, 1051 w, 1030 w, 962 w, 795 m, 760 s, 702 s cm^{-1}; MS *m/z* (% relative intensity) 210 (41, M^+), 195 (100), 168 (21), 165 (50), 152 (35), 83 (19), 76 (11), 63 (13), 51 (14). Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71%. Found: C, 85.46; H, 6.47%.

1-[1,1';3',1'']Terphenyl-2'-yl-ethanone. ^{1}H NMR ($CDCl_3$) 1.88 (s, 3H, CH_3), 7.3-7.5 (m, 13H, ArH); ^{13}C NMR ($CDCl_3$) 33.00, 127.49, 128.27, 128.55, 128.97, 129.11, 138.89, 140.20, 141.14, 206.04; IR (KBr) 3064 w, 1693 s, 1569 w, 1495 w, 1455 m, 1442 m, 1344 m, 1242 s, 1179 w, 1101 w, 1071 w, 1044 w, 1027 w, 804 w, 771 s, 759 s, 705 s, 669 m, 595 w, 508 w cm^{-1}; MS *m/z* (% relative

intensity) 272 (M^+, 28), 258 (22), 257 (100), 229 (22), 228 (30), 227 (14), 226 (18), 202 (10), 128 (11), 126 (16), 114 (12), 113 (19), 101 (15). Anal. Calcd for $C_{20}H_{16}O$: C, 88.20; H, 5.92%. Found: C, 88.01; H, 5.80%.

1-Biphenyl-2-yl-2-methylpropan-1-one. ^{1}H NMR ($CDCl_3$) 0.87 (d , *J* = 7.0 Hz, 6H, CH_3), 2.42 (hept, *J* = 7.0 Hz, 1H, CH), 7.3-7.5 (m, 9H); ^{13}C NMR ($CDCl_3$) 18.72, 40.27, 127.24, 127.67, 127.89, 128.57, 128.73, 129.88, 130.03, 139.54, 140.49, 140.61, 212.48, 216.48; MS *m/z* (% relative intensity) 224 (M^+, 4.7), 182 (15), 181 (100), 153 (23), 152 (34). HRMS Calcd for $C_{16}H_{16}O$: 224.1201. Found: 224.1193.

2-Methyl-1-[1,1';3',1'']terphenyl-2'-yl-propan-1-one. ^{1}H NMR ($CDCl_3$) 0.49 (d, *J* = 7.0 Hz, 6H, CH_3), 2.07 (hept, *J* = 7.0 Hz, 1H, CH), 7.3-7.5 (m, 13H, ArH); ^{13}C NMR ($CDCl_3$) 17.66, 42.19, 127.38, 127.93, 128.29, 129.02, 129.86, 139.06, 140.25, 140.40, 211.54; IR (neat) 3058 w, 3026 w, 2972 m, 2930 w, 2872 w, 1704 s, 1600 w, 1586 w,, 1571 w, 1497 m, 1468 m, 1456 m, 1418 w 1381 w, 1361 w, 1363 w, 1338 w, 1283 w, 1206 m, 1178 w, 1071 w, 1027 w, 973 s, 920 w, 815 m, 775 s, 759 s, 702 s, 669 w, 655 w cm^{-1}; MS *m/z* (% relative intensity) 258 [$(M-42)^+$, 21], 257[$(M-43)^+$, 100], 229 (14), 228 (24), 227 (11), 226 (12). Anal. Calcd for $C_{22}H_{20}O$: C, 87.96; H, 6.71%. Found: C, 87.68; H, 6.62%.

1-Biphenyl-2-yl-2,2-dimethylpropan-1-one. ^{1}H NMR ($CDCl_3$) 0.87 (s, 9H, CH_3), 7.14 (d, *J* = 7.6Hz, 1H, ArH), 7.3-7.5 (m, 8H, ArH); ^{13}C NMR ($CDCl_3$) 27.29, 45.00, 125.59, 126.65, 127.48, 128.33, 128.60, 129.48, 129.63, 137.92, 140.82, 140.95, 216.38; IR (neat) 3060 w, 2976 m, 2934 w, 2870 w, 1683 s, 1479 s, 1463 w, 1450 w, 1433 w, 1395 w, 1365 w, 1287 w, 1276 w, 1186 m, 967 m, 952 m, 918 m, 784 w, 773 m, 744 s, 703 s, 674 m, 612 w, 596 w, 572 w, 552 w, 518 m cm^{-1}; MS *m/z* (% relative intensity) 238 (M^+, 1.3), 182 (15), 181 (100), 153 (20), 152 (34). Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61%. Found: C, 85.37; H, 7.62%.

1-(3-Trifluoromethylbiphenyl-2-yl)ethanone. ^{1}H NMR ($CDCl_3$) 2.00 (s, 3H, CH_3), 7.28-7.35 (m, 2H, ArH), 7.38-7.44 (m, 3H, ArH), 7.52-7.58 (m, 2H, ArH), 7.67-7.74 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$) 31.760 (d, *J* = 1.7 Hz, CH_3), 123.65 (q, *J* =274.0 Hz, CF_3), 125.25 (q, 5.0 Hz), 126.68 (q, 31.9 Hz), 128.36, 128.72, 128.91, 129.19, 133.61 (broad), 138.56, 139.41, 139.97, 204.11; IR (KBr) 3064 w, 1705 s, 1582 w, 1498 w, 1455 m, 1439 m, 1417 w, 1354 m, 1329 s, 1287 m, 1266 m, 1242 s, 1194 m, 1171 s,

1118 s, 1075 m, 1044 m, 1023 w, 996 w, 965 w, 932 w, 923 w, 854 w, 817 m, 767 s, 759 m, 709 s, 703 s, 669 w, 654 w, 634 w, 596 w cm^{-1}; MS *m/z* (% relative intensity) 264 (M^+, 34), 250 (16), 249 (100), 229 (36), 201 (59), 152 (28), 151 (14), 101 (13), 98 (14), 76 (10), 75 (15), 63 (11), 51 (18), 50 (12). Anal. Calcd for $C_{15}H_{11}F_3O$: C, 68.18; H, 4.20%. Found: C, 67.89; H, 4.08%.

1-(5-Methoxybiphenyl-2-yl)-2,2-dimethylpropan-1-one. ^1H NMR ($CDCl_3$) 0.87 (s, 9H, CH_3), 3.83 (s, 3H, OCH_3), 6.86-6.92 (m, 2H, ArH), 7.09 (dd, *J* = 8.2, 0.66 Hz, 1H, ArH), 7.26-7.38 (m, 5H, ArH); ^{13}C NMR ($CDCl_3$) 27.34, 44.97, 55.25, 112.00, 114.88, 127.09, 127.49, 128.23, 129.15, 135.60, 139.76, 140.78, 159.33, 215.93; IR (neat) 2966 m, 2906 m, 2870 m, 1685 s, 1604 s, 1564 m, 1481 s, 1464 m, 1448 m, 1413 w, 1393 m, 1365 m, 1321 m, 1297 s, 1277 m, 1258 m, 1221 s, 1210 s, 1192 m, 1174 s, 1132 w, 1118 w, 1074 w, 1037 m, 1017 m, 963 s, 874 w, 824 m, 807 w, 774 m, 734 w, 701 s, 655 w, 622 w, 578 w cm^{-1}; MS *m/z* (% relative intensity) 268 (M^+, 0.65), 212 (15), 211 (100), 168 (16), 139 (15). Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51%. Found: C, 80.31; H, 7.56%.

1-(5-Fluorobiphenyl-2-yl)-2,2-dimethylpropan-1-one. ^1H NMR ($CDCl_3$) 0.86 (s, 9H, CH_3), 7.00-7.16 (m, 3H, ArH), 7.30-7.41 (m, 5H, ArH); ^{13}C NMR ($CDCl_3$) 27.22, 45.04, 113.59 (d, *J* = 21.8 Hz), 116.39 (d, *J* = 21.2 Hz), 127.51 (d, *J* = 8.4 Hz), 127.96, 128.43, 129.20, 136.96 (d, *J* = 3.3 Hz), 139.63 (d, *J* =2.2 Hz), 140.47 (d, *J* = 7.8 Hz), 162.17 (d, *J* = 247.6 Hz), 215.39; IR (neat) 3060 w, 2970 s, 2906 m, 2872 m, 1690 s, 1608 s, 1585 m, 1573 s, 1479 s, 1462 m, 1447 m, 1394 m, 1365 m, 1296 s, 1260 m, 1227 m, 1183 s, 1112 m, 1075 w, 1040 w, 1022 w, 1000 w, 965 s, 941 m, 875 m, 824 s, 809 m, 773 s, 734 m, 700 s, 649 m, 619 w, 604 w, 571 m cm^{-1}; MS *m/z* (% relative intensity) 256 (M^+, 0.82), 200 (14), 199 (100), 171 (14), 170 (33), 57 (16). Anal. Calcd for $C_{17}H_{17}FO$: C, 79.66; H, 6.69%. Found: C, 79.44; H, 6.69%.

1-(2-Phenylnaphthalen-1-yl)ethanone. ^1H NMR ($CDCl_3$) 2.12 (s, 3H, CH_3), 7.40-7.60 (m, 8H, ArH), 7.89-7.96 (m, 3H, ArH); ^{13}C NMR ($CDCl_3$) 32.60, 124.55, 126.06, 127.18, 127.75, 128.02, 128.49, 128.60, 129.10, 129.19, 132.31, 135.72, 138.05, 140.04, 206.98; IR (neat) 3056 w, 1693 s, 1595 m, 1495 m, 1448 m, 1423 m, 1375 w, 1350 m, 1280 w, 1214 s, 1127 w, 1084 w, 1070 w, 1028 w, 954 w, 865 w, 823 m, 763 s, 746 w, 701 s, 601 w cm^{-1}; MS *m/z* (% relative intensity) 246 (M^+, 36), 232 (17),

231 (100), 203 (29), 202 (60), 201 (15), 200 (13), 100 (42), 88 (13). Anal. Calcd for $C_{18}H_{14}O$: C, 87.78; H, 5.73%. Found: C, 87.49; H, 5.74%.

1-(3-Phenylnaphthalen-2-yl)ethanone. ^{1}H NMR ($CDCl_3$) 2.12 (s, 3H, CH_3), 7.38-7.51 (m, 5H, C_6H_5), 7.51-7.62 (m, 2H, naphtyl), 7.84 (s, 1H, naphtyl), 7.88 (d, *J* = 8.9 Hz, 1H, naphtyl), 7.94 (d, *J* = 8.9 Hz, 1H, naphtyl), 8.09 (s, 1H, naphtyl); ^{13}C NMR ($CDCl_3$) 30.43, 126.80, 127.68, 127.79, 127.99, 128.49, 128.69, 128.72, 128.92, 129.42, 131.76, 134.08, 137.42, 139.26, 140.92, 204.23; IR (KBr) 3054 w, 3022 w, 1688 s, 1628 w, 1590 w, 1490 m, 1456 w, 1447 w, 1355 m, 1270 m, 1206 m, 1193 m, 1133 m, 1074 w, 1017 w, 957 w, 893 m, 772 m, 764 m cm^{-1}; MS *m/z* (% relative intensity) 246 (M^+, 74), 231 (100), 202 (89), 123 (30), 101 (82), 100 (40), 88 (39), 75 (18), 51 (19). HRMS Calcd for $C_{18}H_{14}O$: 246.1044. Found: 246.1043.

1-(1,3-Diphenylnaphthalen-2-yl)ethanone. ^{1}H NMR ($CDCl_3$) 1.83 (s, 3H, CH_3), 7.35-7.57 (m, 13H, ArH), 7.86 (s, 1H, naphtyl), 7.91 (d, *J* = 7.8 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$) 32.85, 126.64, 126.81, 126.94, 127.57, 127.84, 128.01, 128.19, 128.46, 128.78, 129.26, 130.61, 131.44, 133.05, 135.87, 136.14, 137.53, 140.04, 140.42, 206.09; IR (KBr) 3054 w, 3027 w, 1697 s, 1488 w, 1444 w, 1413 w, 1376 w, 1346 m, 1255 w, 1224 w, 1180 w, 1128 w, 1089 w, 1027 w, 958 w, 889 w, 854 w, 794 w, 767 m, 750 m, 703 s cm^{-1}; MS *m/z* (% relative intensity) 322 (M^+, 68), 307 (62), 306 (100), 201 (40), 152 (34), 151 (23), 150 (23), 145 (35), 139 (22), 138 (49), 137 (23), 132 (26), 125 (27), 77 (10), 51 (13). Anal. Calcd for $C_{24}H_{18}O$: C, 89.41; H, 5.63%. Found: C, 89.14; H, 5.63%.

2,2-Dimethyl-1-(1-phenylnaphthalen-2-yl)propan-1-one. ^{1}H NMR ($CDCl_3$) 0.92 (s, 9H, CH_3), 7.28 (d, *J* = 8.3 Hz, 1H, naphtyl), 7.36-7.54 (m, 7H, ArH), 7.70 (d, *J* = 8.3 Hz, 1H, naphtyl), 7.85-7.91 (dd, *J* = 8.1, 7.3 Hz, 2H, naphtyl); ^{13}C NMR ($CDCl_3$) 27.47, 44.48, 122.21, 126.28, 126.58, 126.68, 127.39, 127.76, 127.97, 128.04, 131.70, 132.08, 133.19, 134.79, 137.55, 139.28, 215.94; IR (neat) 3054 m, 2967 s, 2902 m, 2867 m, 1689 s, 1477 s, 1392 m, 1363 m, 1330 w, 1288 m, 1195 m, 1159 w, 1116 w, 1074 w, 1047 s, 1002 m, 958 m, 863 m, 823 s, 790 m, 763 s, 750 s, 705 s cm^{-1}; MS *m/z* (% relative

intensity) 288 (M^+, 2.2), 232 (17), 231 (100), 203 (12), 202 (35). Anal. Calcd for $C_{21}H_{20}O$: C, 87.46; H, 6.99%. Found: C, 87.23; H, 6.89%.

2,2-Dimethyl-1-(3-phenylnaphthalen-2-yl)propan-1-one. ^{1}H NMR ($CDCl_3$) 0.92 (s, 9H, CH_3), 7.32-7.51 (m, 5H, C_6H_5), 7.51-7.58 (m, 2H, naphthyl), 7.62 (s, 1H, naphthyl), 7.85 (s, 1H, naphthyl), 7.85-7.90 (m, 2H, naphthyl); ^{13}C NMR ($CDCl_3$) 27.32, 45.01, 124.93, 126.65, 126.95, 127.58, 127.89, 128.49, 128.71, 129.78, 131.51, 133.09, 136.17, 139.80, 140.94, 216.54; IR (neat) 3056 m, 2967 m, 2904 m, 2867 m, 1685 s, 1594 w, 1481 m, 1446 m, 1392 w, 1363 w, 1278 m, 1230 w, 1164 m, 1124 w, 1037 w, 998 m, 944 m, 914 m, 894 m, 877 s, 775 m, 752 s, 705 s cm^{-1}; MS *m/z* (% relative intensity) 288 (M^+, 2.8), 232 (19), 231 (100), 203 (16), 202 (38). Anal. Calcd for $C_{21}H_{20}O$: C, 87.46; H, 6.99%. Found: C, 87.23; H, 6.89%.

8-Phenyl-3,4-dihydro-2*H*-naphthalen-1-one. ^{1}H NMR ($CDCl_3$) 2.13 (tt, J = 6.5, 5.9 Hz, 2H, CH_2), 2.61 (t, J = 6.5 Hz, 2H, $C(O)CH_2$), 3.00 (t, J = 5.9 Hz, 2H, $ArCH_2$), 7.08-7.46 (m, 8H, ArH); ^{13}C NMR ($CDCl_3$) 23.09, 30.74, 40.46, 126.43, 127.62, 127.98, 130.09, 131.03, 131.64, 142.71, 143.75, 145.40, 198.19; IR (neat) 3056 w, 3030 w, 2938 m, 2866 w, 1683 s, 1587 m, 1576 w, 1497 w, 1460 m, 1440 w, 1402 w, 1346 w, 1319 w, 1289 w, 1248 m, 1205 m, 1180 w, 1075 w, 1015 w, 934 w, 829 w, 804 w, 760 s, 697 s, 669 w, 655 m, 525 w, 508 w cm^{-1}; MS *m/z* (% relative intensity) 222 (M^+, 49), 221 (100), 194 (38), 166 (20), 165 (87), 164 (14), 110 (13), 97 (11), 95 (13), 89 (13), 82 (73), 76 (13), 70 (16), 63 (16), 51 (14). HRMS Calcd for $C_{16}H_{14}O$: 222.1044. Found: 222.1052.

4-Phenyl-6,7,8,9-tetrahydrobenzocyclohepten-5-one. ^{1}H NMR ($CDCl_3$) 1.80-1.95 (m, 4H, CH_2CH_2); 2.65 (t, J = 5.8 Hz, 2H, $C(O)CH_2$), 2.78 (t, J = 6.1 Hz, 2H, $ArCH_2$), 7.11 (d, J = 7.6 Hz, 1H, ArH), 7.18-7.38 (m, 7H, ArH); ^{13}C NMR ($CDCl_3$) 22.86, 25.60, 32.49, 42.86, 126.93, 127.57, 128.08, 128.45, 128.63, 129.62, 137.37, 139.97, 140.25, 140.67, 209.93; IR (KBr) 3058 w, 3022 w, 2932 m, 2858 m, 1684 s, 1587 m, 1574 m, 1498 w, 1457 m, 1405 w, 1343 w, 1328 w, 1312 w, 1277 w, 1239 s, 1214 m, 1176 w, 1165 w, 1076 w, 1031 w, 1022 w, 968 w, 953 w, 916 w, 898 w, 876 w, 832 w, 809 m, 774 m, 756 s, 699 s, 630 w, 586 w cm^{-1}; MS *m/z* (% relative intensity) 237 ($(M+1)^+$, 17), 236 (M^+, 100), 235 (94), 208 (31), 207 (96), 194 (12), 193 (13), 181 (12), 180 (31), 179 (39), 178 (54), 167 (20), 166

(16), 165 (70), 164 (13), 159 (12), 152 (37), 151 (15), 115 (14), 102 (10), 94 (19), 89 (32), 88 (16), 82 (55), 77 (17), 76 (34), 75 (13), 70 (12), 63 (25), 51 (27), 50 (11). Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.82%. Found: C, 86.18; H, 6.89%.

2,2-Dimethyl-8-phenyl-3,4-dihydro-2*H*-naphthalen-1-one. ^{1}H NMR ($CDCl_3$) 1.20 (s, 6H, CH_3), 1.99 (t, *J* = 6.8 Hz, 2H, CH_2), 3.03 (t, *J* = 6.8 Hz, 2H, $ArCH_2$), 7.11-7.43 (m, 8H, ArH); ^{13}C NMR ($CDCl_3$) 24.44, 26.66, 36.91, 42.81, 126.46, 127.71, 127.75, 1278.78, 129.95, 130.80, 131.23, 142.91, 144.21, 144.26, 203.43; IR (KBr) 965 m, 2859 w, 1685 s, 1581 m, 1492 w, 1454 m, 1384 w, 1301 w, 1224 m, 1201 m, 1162 w, 1078 w, 1025 w, 960 m, 836 w, 808 m, 759 s, 700 m cm^{-1}; MS *m/z* (% relative intensity) 250 (M^+, 29), 249 (10), 195 (18), 194 (100), 166 (17), 165 (70). Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25%. Found: C, 86.12; H, 7.23%.

4-(4-Methoxyphenyl)-6,7,8,9-tetrahydrobenzocyclohepten-5-one. ^{1}H NMR ($CDCl_3$) 1.82-1.99 (m, 4H, CH_2), 2.67 (dd, *J* = 6.8, 5.1 Hz, 2H, CH_2), 2.80 (t, *J* = 6.4 Hz, 2H, CH_2), 3.82 (s, 3H, OCH_3), 6.90 (dt, *J* = 8.9, 2.1 Hz, 2H, ArH), 7.10 (d, *J* = 7.6 Hz, 1H, ArH), 7.17 (dt, *J* = 8.9, 2.1 Hz, 2H, ArH), 7.15 (dd, *J* = 7.6, 1.1 Hz, 1H, ArH), 7.34 (t, *J* = 7.6 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$) 22.98, 25.68, 32.56, 42.97, 55.23, 113.69, 127.26, 128.68, 129.58, 129.63, 133.04, 137.34, 139.55, 140.22, 158.61, 210.38; IR (KBr) 3060 w, 2944 s, 2857 m, 2838 w, 1893 w, 1683 s, 1606 m, 1585 m, 1509 s, 1457 s, 1403 w, 1288 m, 1241 s, 1178 s, 1110 w, 1085 w, 1033 w, 958 w, 879 w, 836 m, 798 s, 761 m, 734 w cm^{-1}; MS *m/z* (% relative intensity) 267 (20), 266 (M^+, 100), 265 (48), 251 (11), 238 (22), 237 (41), 223 (13), 210 (11), 209 (10), 197 (10), 195 (17), 194 (11), 178 (12), 166 (10), 165 (33), 153 (16), 152 (33), 139 (13), 89 (10), 82 (18), 76 (16), 63 (12). Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81%. Found: C, 81.03; H, 6.84%.

4-(4-Dimethylaminophenyl)-6,7,8,9-tetrahydrobenzocyclohepten-5-one. ^{1}H NMR ($CDCl_3$) 1.81-2.00 (m, 4H, CH_2), 2.70 (dd, *J* = 6.6, 5.7 Hz, 2H, CH_2), 2.79 (t, *J* = 6.5 Hz, 2H, CH_2), 2.97 (s, 6H, NCH_3), 6.72 (dt, *J* = 8.9, 2.9 Hz, 2H, ArH), 7.16 (d, *J* = 7.3 Hz, 1H, ArH), 7.13 (dt, *J* = 8.9, 2.9 Hz, 2H, ArH), 7.15 (dd, *J* = 7.0, 1.4 Hz, 1H, ArH), 7.33 (t, *J* = 7.5 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$) 23.10, 25.75, 32.60, 40.51, 43.06, 112.24, 126.66, 128.45, 128.57, 129.22, 129.50, 137.13, 139.99, 149.45,

210.70; IR (KBr) 3048 w, 2938 m, 2854 m, 2802 w, 1685 s, 1610 s, 1583 w, 1525 s, 1481 w, 1455 m, 1402 w, 1359 m, 1282 w, 1236 m, 1199 m, 1170 m, 1132 w, 1064 w, 1029 w, 948 w, 823 w, 796 m, 752 w, 586 w, 534 w, cm^{-1}; MS *m/z* (% relative intensity) 280 (22), 279 (M^+, 100), 278 (33), 251 (11), 250 (25), 207 (11), 179 (11), 178 (16), 165 (20), 152 (18), 139 (13), 124 (14), 118 (23), 111 (10), 110 (15) , 104 (15), 103 (37), 96 (10), 89 (13), 82 (15), 76 (12). Anal. Calcd for $C_{19}H_{21}NO$: C, 81.68; H, 7.58; N, 5.01%. Found: C, 81.52; H, 7.49; N, 4.97%.

4-(4-Fluorophenyl)-6,7,8,9-tetrahydrobenzocyclohepten-5-one. ^1H NMR ($CDCl_3$) 1.80-1.96 (m, 4H, CH_2), 2.64 (dd, *J* = 7.5, 4.8 Hz, 2H, CH_2), 2.80 (t, *J* = 6.2 Hz, 2H, CH_2), 7.03 (tt, *J* = 8.6, 1.9 Hz, 2H, ArH), 7.13 (d, *J* = 7.3 Hz, 1H, ArH), 7.15-7.22 (m, 3H, ArH), 7.35 (t, *J* = 7.6 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$) 22.81, 25.56, 32.48, 42.83, 115.07 (d, *J* = 21.2 Hz), 127.77, 128.65, 129.73, 130.05 (d, *J* = 7.8 Hz), 136.58 (d, *J* = 3.3 Hz), 137.54, 138.92, 140.16, 161.90 (d, *J* = 245.4 Hz), 209.93; IR (KBr) 3058 w, 2950 m, 2894 w, 2863 m, 1683 s, 1598 m, 1509 s, 1459 s, 1398 m, 1240 s, 1220 s, 1160 m, 1097 w, 1027 w, 948 w, 912 w, 875 w, 836 s, 813 m, 794 m, 759 m, 736 w cm^{-1}; MS *m/z* (% relative intensity) 255 (17), 254 (M^+, 100), 253 (47), 226 (35), 225 (91), 212 (12), 199 (10), 198 (29), 197 (24), 196 (30), 185 (12), 184 (12), 183 (56), 177 (10), 98 (13) , 91 (19), 85 (11), 81 (13). Anal. Calcd for $C_{17}H_{15}FO$: C, 80.29; H, 5.95%. Found: C, 80.56; H, 6.03%.

4-(4-Trifluoromethylphenyl)-6,7,8,9-tetrahydrobenzocyclohepten-5-one. ^1H NMR ($CDCl_3$) 1.82-1.99 (m, 4H, CH_2), 2.66 (dd, *J* = 7.0, 4.9 Hz, 2H, CH_2), 2.82 (t, *J* = 6.2 Hz, 2H, CH_2), 7.17-7.23 (m, 2H, ArH), 7.31-7.42 (m, 3H, ArH), 7.61 (d, *J* = 8.1 Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) 22.57, 25.45, 32.42, 42.68, 124.19 (q, *J* = 271.6 Hz), 125.70 (q, *J* = 3.9 Hz), 128.55, 128.71, 128.97, 129.18 (q, *J* = 31.8 Hz), 130.108, 138.05, 138.93, 140.20, 144.64, 209.77; IR (KBr) 2962 w, 2944 w, 2865 w, 1685 s, 1616 w, 1589 w, 1459 w, 1402 w, 1324 s, 1240 w, 1159 s, 1126 s, 1108 m, 1083 w, 1064 m, 1016 m, 879 w, 838 w, 798 w, 781 w, 752 w, 680 w, 613 w, 566 w, 532 w, cm^{-1}; MS *m/z* (% relative intensity) 305 (19), 304 (M^+, 94), 303 (56), 285 (12), 276 (36), 275 (100), 262 (12), 249 (10), 247 (40), 235 (31), 233 (27), 227 (15), 207 (22), 201 (11), 179 (25) , 178 (54), 176 (11), 166 (13), 165 (49), 159 (22), 152 (14) , 151 (10) ,

107 (10), 76 (11), 75 (12), 69 (26), 63 (16), 55 (10) , 51 (17). Anal. Calcd for $C_{18}H_{15}F_3O$: C, 71.04; H, 4.97%. Found: C, 70.92; H, 4.96%.

4-o-Tolyl-6,7,8,9-tetrahydrobenzocyclohepten-5-one. ^{1}H NMR ($CDCl_3$) 1.80-1.91 (m, 4H, CH_2), 2.14 (s, 3H, CH_3), 2.50 (t, *J* = 4.3 Hz, 2H, CH_2), 2.83 (t, *J* = 6.2 Hz, 2H, CH_2), 7.01 (d, *J* = 7.3 Hz, 1H, ArH), 7.09-7.23 (m, 5H, ArH), 7.36 (t, *J* = 7.6 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$) 20.30, 22.42, 25.64, 32.43, 41.98, 125.00, 127.18, 127.47, 128.63, 128.82, 129.47, 129.57, 135.62, 137.62, 139.99, 139.72, 140.37, 208.70; IR (KBr) 3056 w, 3010 w, 2938 m, 2859 w, 1685 s, 1583 w, 1492 w, 1457 m, 1403 w, 1286 w, 1243 m, 1218 w, 1172 w, 1118 w, 1089 w, 1029 w, 950 w, 809 w, 794 w, 759 s, 728 w cm^{-1}; MS *m/z* (% relative intensity) 251 (17), 250 (M^+, 62), 249 (30), 236 (14), 235 (79), 233 (25), 232 (77), 222 (19), 221 (76), 218 (11), 217 (45), 208 (26), 207 (47), 206 (11), 205 (25), 204 (24), 194 (18), 192 (15), 191 (49), 189 (16), 180 (12), 179 (64), 178 (97), 176 (19), 166 (21), 165 (100), 164 (16), 152 (31), 139 (14), 128 (13), 124 (18), 115 (25), 110 (21), 109 (12), 102 (11), 101 (16), 94 (19), 91 (10), 89 (59), 88 (16), 82 (48), 77 (16), 76 (40), 75 (12), 65 (10), 63 (25), 55 (15), 51 (23), 50 (10). Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25%. Found: C, 86.29; H, 7.26%.

4-Naphthalen-1-yl-6,7,8,9-tetrahydrobenzocyclohepten-5-one. ^{1}H NMR ($CDCl_3$) 1.85-1.98 (m, 4H, CH_2), 2.42 (t, *J* = 6.2 Hz, 2H, CH_2), 2.86 (t, *J* = 6.2 Hz, 2H, CH_2), 7.22-7.58 (m, 8H, ArH), 7.80-7.88 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$) 22.50, 25.66, 32.41, 41.76, 124.96, 125.49, 125.55, 125.71, 126.70, 127.51, 127.90, 128.19, 129.59, 129.64, 132.05, 133.31, 137.60, 138.28, 138.37, 141.06, 208.81; IR (KBr) 3052 w, 2952 w, 2921 m, 2896 w, 2857 m, 1685 s, 1585 m, 1506 w, 1465 w, 1394 m, 1324 w, 1282 w, 1241 s, 1220 m, 1172 w, 1087 w, 1037 w, 1002 w, 950 m, 896 w, 833 w, 798 s, 777 s, 755 m, 728 w cm^{-1}; MS *m/z* (% relative intensity) 286 (M^+, 100), 285 (71), 258 (26), 257 (27), 243 (25), 242 (28), 241 (25), 216 (26), 215 (61), 203 (26), 202 (45), 189 (19), 114 (12), 108 (14), 106 (28), 101 (21), 100 (15), 95 (10), 94 (35). Anal. Calcd for $C_{21}H_{18}O$: C, 88.08; H, 6.34%. Found: C, 88.02; H, 6.40%.

5,5-Dimethyl-2-(1,2,2-trimethyl-propoxy)[1,3,2]dioxaborinane. ^{1}H NMR (benzene-d_6) 0.61 (s, 6H, CH_3), 0.97 (s, 9H, $C(CH_3)_3$), 1.19 (d, J = 6.5 Hz, 3H, CH_3), 3.35 (s, 4H, CH_2), 4.17 (q, J = 6.5 Hz, 1H, CH); ^{11}B NMR (benzene-d_8) 26.5; MS *m/z* 199 (M^+-Me), 157, 156, 115, 101, 87, 71, 69, 57, 56, 55.