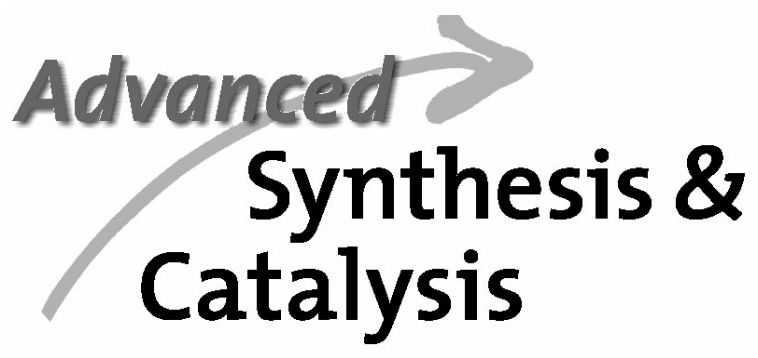

Supporting Information

Supporting Information

for

An Unprecedented Rhodium-Catalyzed Asymmetric Intermolecular Hydroacylation Reaction with Salicylaldehydes

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Contents

(–)-*exo*-Bicyclo[2.2.1]heptan-2-yl(2-hydroxyphenyl)methanone [(–)-*exo*-3a].[S1] Colorless oil; $[\alpha]_D^{21} = -19.6$ (c = 1.40, $CHCl_3$); ^{1}H NMR (300 MHz) δ = 1.16–1.39 (m, 2H), 1.42–1.68 (m, 5H), 2.04 (dddd, J = 12.2, 5.6, 4.3, 2.6 Hz, 1H), 2.37 (br s, 1H), 2.55 (br s, 1H), 3.25 (dd, J = 8.8, 5.6 Hz, 1H), 6.89 (ddd, J = 8.4, 7.2, 1.2 Hz, 1H), 6.98 (dd, J = 8.4, 1.2 Hz, 1H), 7.45 (ddd, J = 8.4, 7.2, 1.7 Hz, 1H), 7.78 (ddd, J = 8.1, 1.6, 0.4 Hz, 1H), 12.49 (s, 1H); ^{13}C NMR (75 MHz) δ = 27.9 (CH_2), 28.7 (CH_2), 32.8 (CH_2), 35.2 (CH), 35.3 (CH_2), 40.5 (CH), 48.2 (CH), 117.6 (CH), 117.7 (CH), 129.0 (CH), 134.8 (CH), 136.3 (C), 161.9 (C), 206.9 (C); IR (neat) ν = 3049, 2955, 2871, 1636, 1581, 1486, 1448, 1352, 1311, 1276, 1239, 1202, 1158, 1033, 993, 943, 805, 757, 653, 529; MS (EI) m/z (%) = 216 (M^+, 50), 187 (14), 149 [$(M+1-C_5H_8)^+$, 20], 121 [$(M-C_7H_{11})^+$, 100]. Anal. calcd. for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 78.15; H, 7.22. The enantiomer ratio was determined by HPLC using a chiral stationary phase: Daicel Chiralcel OD-H, heptane, 0.5 mL/min, 230 nm, 20 °C, 22.0 min (+), 25.9 min (–): 62% ee.

(–)-*exo*-Bicyclo[2.2.1]heptan-2-yl(3,5-dichloro-2-hydroxyphenyl)methanone [(–)-*exo*-3b]. Mp 87–89°C; $[\alpha]_D^{22} = -1.6$ (c = 0.21, $CHCl_3$); ^{1}H NMR (300 MHz) δ = 1.14–1.75 (m, 7H), 1.91–2.03 (m, 1H), 2.39 (s, 1H), 2.54 (s, 1H), 3.17 (dd, J = 8.9, 5.7 Hz, 1H), 7.55 (d, J = 2.4 Hz, 1H), 7.65 (d, J = 2.4 Hz, 1H), 12.99 (s, 1H); ^{13}C NMR (75 MHz) δ = 28.8 (CH_2), 29.6 (CH_2), 34.1 (CH_2), 36.2 (CH), 36.4 (CH_2), 41.3 (CH), 49.5 (CH), 119.7 (C), 123.1 (C), 124.1 (C), 127.8 (CH), 135.4 (CH), 157.4 (C), 207.0 (C); IR (KBr) ν = 3780, 3714, 3432, 3064, 2949, 2870, 2289, 1639, 1440, 1382, 1269, 1215, 1167, 1024, 945, 805, 735, 551; MS (EI) m/z (%) = 286 [$(M+1)^+$, 31], 284 [$(M-1)^+$, 48], 257 (18), 255 (28), 219 (20), 217 (35), 191 [$(M+1-C_7H_{11})^+$, 42], 189 [$(M-1-C_7H_{11})^+$, 42], 95 ($C_7H_{11}^+$, 100], 67 ($C_5H_7^+$, 28). Anal. calcd.

for $C_{14}H_{14}Cl_2O_2$: C, 58.97; H, 4.95. Found: C, 58.96; H, 4.72. The enantiomer ratio was determined by HPLC using a chiral stationary phase: Daicel Chiralcel AD, heptane, 1.0 mL/min, 230 nm, 20 °C, 22.2 min (+), 26.0 min (–): 7% ee.

(–)-*exo*-Bicyclo[2.2.1]heptan-2-yl(2-hydroxy-5-nitrophenyl)methanone [(–)-*exo*-3c]. Mp 87–90°C; $[\alpha]_D^{22}$ = –1.0 (*c* = 0.53, $CHCl_3$); ^{1}H NMR (300 MHz) δ = 1.25 (dtd, *J* = 9.9, 2.8, 1.4 Hz, 1H), 1.31–1.57 (m, 3H), 1.57–1.77 (m, 3H), 1.99 (dddd, *J* = 12.3, 5.8, 4.1, 2.6 Hz, 1H), 2.41 (s, 1H), 2.57 (s, 1H), 3.30 (dd, *J* = 9.1, 5.7 Hz, 1H), 7.08 (d, *J* = 9.2 Hz, 1H), 8.33 (dd, *J* = 9.2, 2.7 Hz, 1H), 8.73 (d, *J* = 2.7 Hz, 1H), 13.11 (s, 1H); ^{13}C NMR (75 MHz) δ = 28.7 (CH_2), 29.5 (CH_2), 34.3 (CH_2), 36.3 (CH), 36.5 (CH_2), 41.2 (CH), 49.4 (CH), 117.5 (C), 119.6 (CH), 126.5 (CH), 130.5 (CH), 139.4 (C), 167.8 (C), 207.5 (C); IR (KBr) ν = 2953, 2871, 1648, 1583, 1516, 1473, 1340, 1291, 1264, 1182, 1111, 1023, 947, 804, 747, 705, 639; MS (EI) *m*/*z* (%) = 261 (M^+, 51), 232 (16), 194 [$(M+1-C_5H_8)^+$, 66], 166 [$(M-C_7H_{11})^+$, 34], 120 (18), 95 ($C_7H_{11}^+$, 100), 67 (30). HRMS calcd. for $C_{14}H_{15}NO_4$ 261.1001, found 261.1001. The enantiomer ratio was determined by HPLC using a chiral stationary phase: Daicel Chiralcel OJ, heptane/2-PrOH 99:1, 0.7 mL/min, 230 nm, 20 °C, 18.8 min (–), 23.0 min (+): 6% ee.

(+)-*endo*-Bicyclo[2.2.1]hept-5-en-2-yl(2-hydroxyphenyl)methanone [(+)-*endo*-5a]. Mp 42–44 °C; $[\alpha]_D^{22}$ = +96.7 (*c* = 0.65, $CHCl_3$); ^{1}H NMR (400 MHz) δ = 1.45–1.57 (m, 2H), 1.63 (ddd, *J* = 11.6, 4.5, 2.3 Hz, 1H), 1.98 (ddd, *J* = 11.6, 9.1, 3.7 Hz, 1H), 2.99 (s, 1H), 3.29 (s, 1H), 3.90 (ddd, *J* = 9.0, 4.2, 3.7 Hz, 1H), 5.86 (dd, *J* = 5.6, 2.9 Hz, 1H), 6.22 (dd, *J* = 5.6, 3.1 Hz, 1H), 6.91 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1H), 6.97 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.45 (ddd, *J* =

8.5, 7.2, 1.7 Hz, 1H), 7.92 (dd, J = 8.1, 1.7 Hz, 1H), 12.39 (s, 1H); ^{13}C NMR (100 MHz) δ = 29.3 (CH_2), 43.0 (CH), 47.0 (CH), 48.1 (CH), 50.1 (CH_2), 118.4 (CH), 118.6 (CH), 119.2 (C), 129.9 (CH), 131.6 (CH), 135.7 (CH), 137.2 (CH), 162.4 (C), 206.7 (C); IR (KBr) ν = 3058, 2974, 2871, 1636, 1487, 1447, 1352, 1282, 1237, 1203, 1158, 1033, 757, 717; MS (EI) *m*/*z* (%) = 214 (M^+, 34), 149 [$(M+H-C_5H_6)^+$, 56], 148 (42), 147 (100), 121 [$(M-C_7H_9)^+$, 95), 66 (49). Anal. calcd. for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.40; H, 6.75. The enantiomer ratio was determined by HPLC using a chiral stationary phase: Daicel Chiralcel AD-H, heptane/2-PrOH 98:2, 0.5 mL/min, 254 nm, 20 °C, 10.8 min (+), 11.7 min (–): 41% ee.

(+)-*endo*-Bicyclo[2.2.1]hept-5-en-2-yl(3,5-dichloro-2-hydroxyphenyl)methanone [(+)-*endo*-5b]. Mp 54–56 °C; $[\alpha]_D^{22}$ = +54.4 (c = 0.40, $CHCl_3$); ^{1}H NMR (400 MHz) δ = 1.48–1.57 (m, 2H), 1.62 (ddd, J = 11.6, 4.4, 2.5 Hz, 1H), 2.00 (ddd, J = 11.7, 9.1, 3.7 Hz, 1H), 3.02 (s, 1H), 3.29 (s, 1H), 3.83 (ddd, J = 9.0, 4.1, 3.7 Hz, 1H), 5.83 (dd, J = 5.7, 2.9 Hz, 1H), 6.24 (dd, J = 5.6, 3.1 Hz, 1H), 7.56 (dd, J = 2.5, 0.4 Hz, 1H), 7.81 (d, J = 2.5 Hz, 1H), 12.88 (s, 1H); ^{13}C NMR (100 MHz) δ = 29.5 (CH_2), 43.0 (CH), 47.5 (CH), 48.3 (CH), 50.2 (CH_2), 120.3 (C), 123.1 (C), 124.0 (C), 127.8 (CH), 131.3 (CH), 135.3 (CH), 137.7 (CH), 156.9 (C), 205.9 (C); IR (KBr) ν = 2988, 2935, 2861, 1646, 1592, 1441, 1371, 1336, 1274, 1218, 1171, 1142, 1101, 811, 739, 709; MS (EI) *m*/*z* (%) = 284 [$(M+1)^+$, 26], 282 [$(M-1)^+$, 49], 219 (40), 218 (55), 217 [$(M-C_5H_6)^+$, 100], 216 (82), 215 (85), 191 (28), 189 [$(M-C_7H_9)^+$, 58], 66 ($C_5H_6^+$, 74). Anal. calcd. for $C_{14}H_{12}Cl_2O_2$: C, 59.39; H, 4.27. Found: C, 59.45; H, 4.17. The enantiomer ratio was determined by HPLC using a chiral stationary phase: Daicel Chiralcel OD-H, heptane, 0.5 mL/min, 230 nm, 20 °C, 27.6 min (–), 30.5 min (+): 42% ee.

(+)-*endo*-Bicyclo[2.2.1]hept-5-en-2-yl(2-hydroxy-5-nitrophenyl)methanone [(+)-*endo*-5c]. Mp 133–136 °C; $[\alpha]_D^{22}$ = +91.2 (*c* = 0.49, $CHCl_3$); ^{1}H NMR (300 MHz) δ = 1.57 (d, *J* = 1.3 Hz, 2H), 1.63 (dd, *J* = 11.8, 4.3 Hz, 1H), 2.08 (ddd, *J* = 11.4, 9.1, 3.6 Hz, 1H), 3.04 (s, 1H), 3.34 (s, 1H), 3.95 (dt, *J* = 8.8, 3.9 Hz, 1H), 5.85 (dd, *J* = 5.6, 2.8 Hz, 1H), 6.24 (dd, *J* = 5.6, 3.1 Hz, 1H), 7.07 (d, *J* = 9.2 Hz, 1H), 8.33 (dd, *J* = 9.2, 2.7 Hz, 1H), 8.88 (d, *J* = 2.7 Hz, 1H), 13.02 (s, 1H); ^{13}C NMR (75 MHz) δ = 29.4 (CH_2), 43.0 (CH), 47.4 (CH), 48.2 (CH), 50.2 (CH_2), 118.1 (C), 119.6 (CH), 126.5 (CH), 130.5 (CH), 131.4 CH), 137.9 (CH), 139.5 (C), 167.5 (C), 206.6 (C); IR (KBr) ν = 3462, 2968, 2946, 1638, 1583, 1516, 1476, 1369, 1338, 1288, 1245, 1190, 1112, 910, 840, 737, 700, 640; MS (EI) *m*/*z* (%) = 259 (M^+, 28), 194 [$(M+1-C_5H_6)^+$, 64], 166 [$(M-C_7H_9)^+$, 20], 148 (11), 120 (12), 93 [$(M-C_7H_4NO_4)^+$, 18], 66 ($C_5H_6^+$, 100]. Anal. calcd. for $C_{14}H_{13}NO_4$: C, 64.86; H, 5.05; N, 5.40. Found: C, 64.58; H, 5.17; N, 5.37. The enantiomer ratio was determined by HPLC using a chiral stationary phase: Daicel Chiralcel AD, heptane/2-PrOH 95:5, 1.0 mL/min, 220 nm, 20 °C, 10.9 min (+), 17.7 min (–): 40% ee.

(+)-*endo*-(2-Amino-3,5-dibromophenyl)(bicyclo[2.2.1]hept-5-en-2-yl)methanone [(+)-*endo*-5d]. Yellow oil; $[\alpha]_D^{22}$ = +51.9 (*c* = 0.34, $CHCl_3$); ^{1}H NMR (400 MHz) δ = 1.37–1.52 (m, 2H), 1.57 (ddd, *J* = 11.3, 4.3, 2.1 Hz, 1H), 1.96 (ddd, *J* = 11.7, 9.2, 3.7 Hz, 1H), 2.96 (s, 1H), 3.22 (s, 1H), 3.79 (dt, *J* = 8.8, 4.0 Hz, 1H), 5.84 (dd, *J* = 5.6, 2.9 Hz, 1H), 6.19 (dd, *J* = 5.6, 3.1 Hz, 1H), 6.80 (br s, 2H), 7.67 (d, *J* = 2.2 Hz, 1H), 7.96 (d, *J* = 2.1 Hz, 1H); ^{13}C NMR (100 MHz) δ = 29.8 (CH_2), 43.0 (CH), 47.8 (CH), 47.9 (CH), 50.0 (CH_2), 105.8 (C), 111.8 (C), 119.7 (C), 131.8 (CH), 132.7 (CH), 137.0 (CH), 138.6 (CH), 146.2 (C), 201.5 (C); IR ($CHCl_3$) ν = 3471, 3327, 3064, 2971, 2870, 1651, 1598, 1563, 1526, 1436, 1340, 1204, 1070, 874, 835, 755, 696, 542; MS (EI) *m*/*z* (%) = 373 [$(M+2)^+$, 24], 371 (M^+, 50), 369 [$(M-2)^+$,

25], 307 (45), 306 (62), 305 [$(M–C_5H_6)^+$, 97], 304 (100), 303 (50), 302 (48), 280 (14), 278 (30), 276 (16). Anal. calcd. for $C_{14}H_{13}Br_2NO$: C, 45.32; H, 3.53; N, 3.77. Found: C, 45.46; H, 3.54; N, 4.04. The enantiomer ratio was determined by HPLC using a chiral stationary phase: Daicel Chiralcel OD-H, heptane/2-PrOH 99:1, 0.5 mL/min, 254 nm, 20 °C, 15.5 min (–), 16.8 min (+): 41% ee.

(+)-*endo*-Bicyclo[2.2.1]hept-5-en-2-yl(2-hydroxynaphthalen-1-yl)methanone [(+)-*endo*-5e]. Colorless oil; $[\alpha]_D^{22}$ = +40.9 (c = 0.46, $CHCl_3$); ^{1}H NMR (300 MHz) δ = 1.32–1.46 (m, 2H), 1.52 (ddd, J = 11.6, 4.6, 2.5 Hz, 1H), 2.06 (ddd, J = 12.0, 9.2, 3.8 Hz, 1H), 2.92 (s, 1H), 3.14 (s, 1H), 4.11–4.21 (m, 1H), 5.81 (dd, J = 5.6, 2.8 Hz, 1H), 6.20 (dd, J = 5.7, 3.1 Hz, 1H), 7.13 (d, J = 9.0 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 9.0 Hz, 1H), 7.38 (dd, J = 8.0, 7.0 Hz, 1H), 7.54 (ddd, J = 8.5, 7.0, 1.5 Hz, 1H), 8.12 (d, J = 8.6 Hz, 1H), 11.26 (s, 1H); ^{13}C NMR (75 MHz) δ = 31.2 (CH_2), 43.0 (CH), 47.3 (CH), 49.8 (CH_2), 52.4 (CH), 116.9 (C), 119.4 (CH), 123.7 (CH), 124.5 (CH), 127.6 (CH), 128.6 (C), 129.1 (CH), 131.4 (C), 132.5 (CH), 135.4 (CH), 137.7 (CH), 159.7 (C), 209.6 (C); IR ($CHCl_3$) ν = 3360, 2972, 2872, 1744, 1673, 1625, 1578, 1512, 1463, 1435, 1349, 1272, 1241, 1183, 1100, 916, 819, 754, 716; MS (EI) m/z (%) = 264 (M^+, 44), 198 [$(M–C_5H_6)^+$, 36], 197 (37), 171 [$(M–C_7H_9)^+$, 100], 170 (41), 144 [$(M+H–C_8H_9O)^+$, 21], 115 (29). HRMS calcd. for $C_{18}H_{16}O_2$ 264.1150, found 264.1152. The enantiomer ratio was determined by HPLC using a chiral stationary phase: Daicel Chiralcel AD-H, heptane/2-PrOH 90:10, 0.5 mL/min, 254 nm, 20 °C, 20.1 min (+), 26.9 min (–): 32% ee.

(+)-*endo*-Bicyclo[2.2.1]hept-5-en-2-yl(2-hydroxy-5-methylphenyl)methanone [(+)-*endo*-5f]. Colorless oil; $[\alpha]_D^{23}$ = +74.5 (c = 0.37, $CHCl_3$); ^{1}H NMR (300 MHz) δ = 1.49–1.54 (m,

2H), 1.59–1.69 (m, 1H), 1.97 (ddd, J = 11.5, 9.1, 3.7 Hz, 1H), 2.34 (s, 3H), 3.00 (br s, 1H), 3.30 (br s, 1H), 3.89 (ddd, J = 9.1, 4.4, 3.5 Hz, 1H), 5.86 (dd, J = 5.6, 2.9 Hz, 1H), 6.22 (dd, J = 5.6, 3.1 Hz, 1H), 6.88 (d, J = 8.5 Hz, 1H), 7.24–7.31 (m, 1H), 7.69 (d, J = 1.5 Hz, 1H), 12.20 (s, 1H); ^{13}C NMR (75 MHz) δ = 20.7 (CH_3), 29.3 (CH_2), 43.0 (CH), 46.9 (CH), 48.1 (CH), 50.2 (CH_2), 118.3 (CH), 119.0 (C), 127.7 (C), 129.7 (CH), 131.7 (CH), 136.9 (CH), 137.3 (CH), 160.5 (C), 206.8 (C); IR ($CHCl_3$) ν = 2973, 2868, 1639, 1613, 1486, 1353, 1285, 1214, 1189, 825, 802, 775, 714, 670, 537; MS (EI) m/z (%) = 228 (M^+, 41), 161 [(M–1-$C_5H_6)^+$, 100], 135 [(M–$C_7H_9)^+$, 66], 77 (15). HRMS calcd. for $C_{15}H_{16}O_2$ 228.1150, found 228.1151. The enantiomer ratio was determined by HPLC using a chiral stationary phase: Daicel Chiralcel AD-H, heptane/2-PrOH 98:2, 0.5 mL/min, 254 nm, 20 °C, 11.3 min (+), 14.1 min (–): 11% ee.

(+)-*endo*-Bicyclo[2.2.1]hept-5-en-2-yl(3,5-di-*tert*-butyl-2-hydroxyphenyl)methanone [(+)-*endo*-5g]. Mp 68–70 °C; $[\alpha]_D^{23}$ = +66.7 (c = 0.27, $CHCl_3$); ^{1}H NMR (300 MHz) δ = 1.35 (s, 9H), 1.42 (s, 9H), 1.52 (m, 2H), 1.62 (dd, J = 11.5, 4.6 Hz, 1H), 2.02 (ddd, J = 11.4, 9.2, 3.7 Hz, 1H), 2.98 (br s, 1H), 3.29 (br s, 1H), 3.91 (ddd, J = 9.2, 4.4, 3.6 Hz, 1H), 5.93 (dd, J = 5.6, 3.0 Hz, 1H), 6.20 (dd, J = 5.6, 3.1 Hz, 1H), 7.53 (d, J = 2.4 Hz, 1H), 7.76 (d, J = 2.1 Hz, 1H), 13.06 (d, J = 0.5 Hz, 1H); ^{13}C NMR (75 MHz) δ = 29.4 (CH_3, 3C), 29.9 (CH_2), 31.4 (CH_3, 3C), 34.3 (C), 35.2 (C), 42.9 (CH), 47.4 (CH), 47.9 (CH), 50.0 (CH_2), 118.3 (C), 123.8 (CH), 130.7 (CH), 132.3 (CH), 137.0 (CH), 138.0 (C), 139.6 (C), 160.2 (C), 207.6 (C); IR (KBr) ν = 2959, 2909, 2870, 1624, 1437, 1390, 1270, 1246, 1201, 1173, 821, 684; MS (EI) m/z (%) = 326 (M^+, 32), 260 [(M–$C_5H_6)^+$, 69], 245 (100), 233 [(M–$C_7H_9)^+$, 71], 189 (19), 57 (19). HRMS calcd. for $C_{22}H_{30}O_2$ 326.2246, found 326.2245. The enantiomer ratio was

determined by HPLC using a chiral stationary phase: Daicel Chiralcel OG, heptane, 0.7 mL/min, 254 nm, 10 °C, 7.2 min (+), 8.1 min (–): 35% ee.

(+)-*endo*-Bicyclo[2.2.1]hept-5-en-2-yl(2,3-dihydroxyphenyl)methanone [(+)-*endo*-5h]. Mp 91–94 °C; $[\alpha]_D^{22}$ = +115 (c = 0.43, $CHCl_3$); ^{1}H NMR (400 MHz) δ = 1.45–1.56 (m, 2H), 1.63 (ddd, J = 11.6, 4.5, 2.4 Hz, 1H), 1.97 (ddd, J = 11.6, 9.1, 3.7 Hz, 1H), 3.00 (s, 1H), 3.31 (s, 1H), 3.90 (ddd, J = 9.0, 4.3, 3.6 Hz, 1H), 5.75 (br s, 1H), 5.85 (dd, J = 5.6, 2.9 Hz, 1H), 6.23 (dd, J = 5.6, 3.1 Hz, 1H), 6.89–6.79 (m, 1H), 7.11 (dd, J = 7.9, 1.4 Hz, 1H), 7.47 (dd, J = 8.2, 1.4 Hz, 1H), 12.63 (s, 1H); ^{13}C NMR (100 MHz) δ = 29.3 (CH_2), 43.1 (CH), 47.2 (CH), 48.3 (CH), 50.2 (CH_2), 118.6 (CH), 119.1 (C), 119.6 (CH), 120.7 (CH), 131.5 (CH), 137.4 (CH), 145.4 (C), 149.6 (C), 207.2 (C); IR (KBr) ν = 3488, 2967, 2864, 1631, 1449, 1366, 1327, 1269, 1197, 1064, 1044, 905, 846, 765, 708, 570, 529, 490; MS (EI) m/z (%) = 230 (M^+, 35), 212 (9), 164 [$(M–C_5H_6)^+$, 100], 146 (9), 137 [$(M–C_7H_9)^+$, 40]; Anal. calcd. for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 73.04; H, 6.21. The enantiomer ratio was determined by HPLC using a chiral stationary phase: Daicel Chiralcel AD-H, heptane/2-PrOH 99:1, 0.5 mL/min, 230 nm, 20 °C, 47.2 min (+), 48.8 min (–): 54% ee.

(–)-*exo*-Bicyclo[2.2.1]hept-5-en-2-yl(2-hydroxyphenyl)methanone [(–)-*exo*-5a]. Colorless oil; $[\alpha]_D^{21}$ = –43.4 (c = 0.15, $CHCl_3$); ^{1}H NMR (400 MHz) δ = 1.39–1.47 (m, 1H), 1.47–1.58 (m, 2H), 2.01 (ddd, J = 11.6, 4.9, 3.6 Hz, 1H), 2.99 (s, 1H), 3.11 (s, 1H), 3.16 (ddd, J = 9.1, 4.9, 1.0 Hz, 1H), 6.19–6.32 (m, 2H), 6.89 (ddd, J = 8.3, 7.2, 1.2 Hz, 1H), 6.98 (dd, J = 8.4, 1.1 Hz, 1H), 7.45 (ddd, J = 8.5, 7.2, 1.7 Hz, 1H), 7.77 (dd, J = 8.1, 1.7 Hz, 1H), 12.49 (s, 1H); ^{13}C NMR (100 MHz) δ = 31.2 (CH_2), 42.1 (CH), 46.3 (CH), 46.3 (CH), 46.5 (CH_2),

118.4 (CH), 118.7 (CH), 119.2 (C), 130.0 (CH), 135.7 (CH), 135.8 (CH), 138.6 (CH), 162.5 (C), 208.7 (C); IR ($CHCl_3$) ν = 3059, 2976, 2872, 2362, 2335, 1636, 1579, 1487, 1447, 1350, 1287, 1237, 1203, 1157, 756, 714, 662; MS (EI) *m*/*z* (%) = 214 (M^+, 35), 149 [$(M+H-C_5H_6)^+$, 70], 148 (47), 147 (100), 121 [$(M-C_7H_9)^+$, 79], 66 ($C_5H_6^+$, 31). HRMS calcd. for $C_{14}H_{14}O_2$ 214.0994, found 214.0994. The enantiomer ratio was determined after hydrogenation to *exo*-**3a**.

(+)-*exo*-Bicyclo[2.2.1]hept-5-en-2-yl(3,5-dichloro-2-hydroxyphenyl)methanone [(+)-*exo*-5b]. Mp 86–88°C; $[\alpha]_D^{22}$ = +65.3 (*c* = 0.35, $CHCl_3$); ^{1}H NMR (400 MHz) δ = 1.44–1.60 (m, 3H), 1.98 (ddd, *J* = 11.6, 4.9, 3.6 Hz, 1H), 3.02 (br s, 1H), 3.07 (ddd, *J* = 9.2, 5.0, 0.8 Hz, 1H), 3.11 (br s, 1H), 6.27 (dq, *J* = 5.6, 3.0 Hz, 1H), 7.56 (d, *J* = 2.5 Hz, 1H), 7.64 (d, *J* = 2.5 Hz, 1H), 12.99 (s, 1H); ^{13}C NMR (100 MHz) δ = 31.6 (CH_2), 42.2 (CH), 46.3 (CH), 46.6 (CH_2), 46.8 (CH), 120.3 (C), 123.2 (C), 127.9 (CH), 135.4 (CH), 138.9 (CH), 157.1 (C), 208.1 (C); IR (KBr) ν = 3063, 2977, 2948, 2875, 1644, 1594, 1563, 1439, 1367, 1334, 1283, 1213, 1171, 1017, 900, 856, 800, 742, 721, 574, 558; MS (EI) *m*/*z* (%) = 284 [$(M+2)^+$, 22], 283 [$(M+1)^+$, 11], 282 (M^+, 49), 219 (42), 218 [$(M+2-C_5H_6)^+$, 68], 217 [$(M+1-C_5H_6)^+$, 100], 216 [$(M-C_5H_6)^+$, 98], 215 [$(M-1-C_5H_6)^+$, 80], 191 [$(M+2-C_7H_9)^+$, 27], 189 [$(M-C_7H_9)^+$, 42], 66 ($C_5H_6^+$, 63). Anal. calcd. for $C_{14}H_{12}Cl_2O_2$: C, 59.39; H, 4.27. Found: C, 59.49; H, 4.18. The enantiomer ratio was determined by HPLC using a chiral stationary phase: Daicel Chiralcel OD-H, heptane, 0.5 mL/min, 254 nm, 20 °C, 25.9 min (–), 28.5 min (+): 80% ee.

(–)-*exo*-Bicyclo[2.2.1]hept-5-en-2-yl(2-hydroxy-5-nitrophenyl)methanone [(–)-*exo*-5c]. Mp 87–88°C; $[\alpha]_D^{22}$ = –95.6 (*c* = 0.11, $CHCl_3$); ^{1}H NMR (400 MHz) δ = 1.45–1.51 (m, 1H), 1.54 (br d, *J* = 9.4 Hz, 1H), 1.65 (ddd, *J* = 11.6, 9.3, 2.5 Hz, 1H), 1.99 (ddd, *J* = 11.6, 4.9, 3.5

Hz, 1H), 3.05 (br s, 1H), 3.14 (br s, 1H), 3.20 (ddd, J = 9.3, 4.9, 0.9 Hz, 1H), 6.23–6.36 (m, 2H), 7.09 (d, J = 9.2 Hz, 1H), 8.34 (dd, J = 9.2, 2.7 Hz, 1H), 8.73 (d, J = 2.7 Hz, 1H), 13.11 (s, 1H); ^{13}C NMR (100 MHz) δ = 31.6 (CH_2), 42.2 (CH), 46.2 (CH), 46.6 (CH_2), 46.7 (CH), 118.1 (C), 119.6 (CH), 126.5 (CH), 130.6 (CH), 135.6 (CH), 138.9 (CH), 139.4 (C), 167.4 (C), 208.5 (C); IR (KBr) ν = 2972, 1642, 1581, 1515, 1475, 1337, 1292, 1220, 1183, 1114, 824, 722; MS (EI) m/z (%) = 259 (M^+, 22), 194 [$(M+1-C_5H_6)^+$, 77], 166 (15), 148 (15), 120 (13), 93 (14), 66($C_5H_6^+$, 100). Anal. calcd. for $C_{14}H_{13}NO_4$: C, 64.86; H, 5.05; N, 5.40. Found: C, 65.23; H, 5.17; N, 5.26. The enantiomer ratio was determined by HPLC using a chiral stationary phase: Daicel Chiralcel AD-H, heptane/2-PrOH 90:10, 0.5 mL/min, 254 nm, 20 °C, 23.7 min (–), 38.5 min (+): 94% ee.

(+)-*exo*-Bicyclo[2.2.1]hept-5-en-2-yl(2,3-dihydroxyphenyl)methanone [(+)-*exo*-5h]. Mp 83–85°C; $[\alpha]_D^{22}$ = +43.1 (c = 0.12, $CHCl_3$); ^{1}H NMR (400 MHz) δ = 1.40–1.57 (m, 3H), 2.02 (ddd, J = 11.6, 4.6, 3.7 Hz, 1H), 3.00 (s, 1H), 3.11 (s, 1H), 3.15 (dd, J = 9.0, 5.0 Hz, 1H), 5.73 (br s, 1H), 6.21–6.30 (m, 2H), 6.81 (t, J = 8.0, 8.0 Hz, 1H), 7.15-7.08 (m, 1H), 7.28–7.35 (m, 1H), 12.72 (s, 1H); ^{13}C NMR (100 MHz) δ = 31.1 (CH_2), 42.1 (CH), 46.5 (CH), 46.6 (CH, 2C), 118.7 (CH), 119.1 (C), 119.7 (CH), 120.7 (CH), 135.7 (CH), 138.7 (CH), 145,4 (C), 149.7 (C), 209.2 (C); IR (KBr) ν = 3484, 2963, 2874, 1629, 1449, 1328, 1272, 1193, 1060, 908, 748, 714, 570, 528; MS (EI) m/z (%) = 230 (M^+, 20), 164[$(M-C_5H_6)^+$, 100], 146 (7), 137 [$(M-C_7H_9)^+$, 26]. Anal. calcd. for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 73.01; H, 6.16. The enantiomer ratio was determined by HPLC using a chiral stationary phase: Daicel Chiralcel OJ, heptane/2-PrOH, 0.7 mL/min, 230 nm, 20 °C, 22.1 min (+), 25.0 min (–): 55% ee.

(11b*R*)-*N*,*N*-Dimethyl-2,6-bis[4-(trifluoromethyl)phenyl]dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine [(*R*)-19]. Mp 156–159 °C; $[\alpha]_D^{22}$ = –397 (*c* = 0.16, $CHCl_3$); ^{1}H NMR (300 MHz) δ = 1.95 (s, 3H), 1.98 (s, 3H), 7.30-7.52 (m, 6H), 7.67–8.15 (m, 12H); ^{13}C NMR (75 MHz) δ = 34.4 (d, $^2J_{C,P}$ = 20.3 Hz, CH_3, 2C), 124.3 (q, $^1J_{C,F}$ = 266 Hz, C, 2C), 125.1 (q, $^3J_{C,F}$ = 3.7 Hz, CH, 4C), 125.5 (CH, 2C), 126.5 (CH, 2C), 126.7 (CH, 2C), 126.9 (CH, 2C), 128.6 (CH, 2C), 129.4 (q, $^2J_{C,F}$ = 32.4 Hz, C, 2C), 130.2 (CH, 4C), 130.9 (C, 2C), 131.0 (C, 2C), 132.7 (d, $J_{C,P}$ = 8.8 Hz, C, 2C), 133.5 (C, 2C), 141.7 (C, 2C), 146.8 (d, $J_{C,P}$ = 10.0 Hz, C, 2C); IR (KBr) ν = 3487, 3058, 2924, 1497, 1403, 1324, 1121, 1064, 1017, 956, 838, 746, 506; MS (EI) *m*/*z* (%) = 647 (M^+, 100), 601 (13), 583 (18), 556 [$(M-C_2H_6NOP)^+$, 28], 278 (17), 91 (22), 85 (35), 83 (42). HRMS calcd. for $C_{36}H_{24}F_6NO_2P$ 647.1449, found 647.1448.

***exo*-(2-Hydroxyphenyl)(1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)methanone (*exo*-29).** This compound was prepared in analogy to **RP4**, using 1,4-epoxy-1,4-dihydronaphthalene (**28**) and salicylaldehyde (**1a**, 3 h, 80 °C): 75% yield; mp 118–120 °C; ^{1}H NMR (300 MHz) δ = 1.93 (dd, *J* = 11.6, 9.0 Hz, 1H), 2.49 (dt, *J* = 11.5, 4.9 Hz, 1H), 3.48 (dd, *J* = 8.9, 4.7 Hz, 1H), 5.53 (d, *J* = 4.9 Hz, 1H), 5.70 (s, 1H), 6.89 (t, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 7.19–7.28 (m, 2H), 7.29–7.40 (m, 2H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.64 (dd, *J* = 8.0, 1.2 Hz, 1H), 12.29 (s, 1H); ^{13}C NMR (75 MHz) δ = 32.9 (CH_2), 47.8 (CH), 79.0 (CH), 80.6 (CH), 118.6 (C), 118.9 (CH, 2C), 118.9 (CH), 119.4 (CH), 127.0 (CH), 127.2 (CH), 129.6 (CH), 136.4 (CH), 144.4 (C), 146.0 (C), 162.9 (C), 205.1 (C); IR (KBr) ν = 3026, 3009, 1637, 1612, 1579, 1485, 1446, 1353, 1288, 1261, 1217, 1196, 1159, 1030, 990, 968, 915, 862, 840, 786, 758, 609; MS (EI) *m*/*z* (%) = 266 (M^+, 28), 145 [$(M-C_7H_5O_2)^+$, 25], 121 [$(M-C_{10}H_9O)^+$, 33], 118 [$(M-C_9H_8O_2)^+$, 100]. Anal. calcd. for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30.

Found: C, 77.09; H, 5.43. The enantiomer ratio was determined by HPLC using a chiral stationary phase: Daicel Chiralcel AD, heptane/2-PrOH 90:10, 1.0 mL/min, 254 nm, 20 °C, 14.4 min, 29.8 min: racemate.

Representative procedure for the synthesis of catalyst precursors 30-32. These compounds were prepared in analogy to the procedure for the preparation of [Rh(acac)(coe)$_2$] by Varshavsky.[S2] To a solution of {[Rh(cod)Cl]$_2$} (200 mg, 0.509 mmol, 0.5 equiv.) in benzene (30 mL) was added sodium 2,2,6,6-tetramethyl-3,5-heptanedionate (210 mg, 1.02 mmol, 1.0 equiv.) and the reaction mixture was heated to reflux for 80 min. After cooling to rt, the solution was filtered and the filtrate was concentrated in vacuo. The residue was taken up in Et_2O (5 mL) and concentrated again to give (2,2,6,6-tetramethyl-3,5-heptanedionato)-(1,5-cyclooctadiene)rhodium(I) (**30**) as a yellow crystalline powder (358 mg, 89%).

(2,2,6,6-Tetramethyl-3,5-heptanedionato)-(1,5-cyclooctadiene)rhodium(I) (30). Mp 168–171 °C (Lit.[S3] 185 °C); ^{1}H NMR (300 MHz) δ = 1.08 (s, 18H), 1.70–1.98 (m, 4H), 2.31-2.63 (m, 4H), 4.07 (br s, 4H), 5.68 (s, 1H); ^{13}C NMR (75 MHz) δ = 28.6 (CH_3, 6C), 30.2 (CH_2, 4C), 40.9 (C, 2C), 76.4 (d, $J_{C,Rh}$ = 14.1 Hz, CH, 4C), 89.8 (CH, 1C), 196.0 (C, 2C); IR (KBr) ν = 2962, 2873, 2833, 1544, 1499, 1457, 1386, 1357, 1225, 1139, 963, 874; MS (EI) *m*/*z* (%) = 394 (M^+, 100), 337 (24), 309 (19), 211 [(M-dpm)$^+$, 78], 207 (25), 181 (17). Anal. calcd. for $C_{19}H_{31}O_2Rh$: C, 57.87; H, 7.92. Found: C, 58.10; H, 8.14.

(1,3-Diphenyl-1,3-propanedionato)-(1,5-cyclooctadiene)rhodium(I) (31). The same procedure as described for the synthesis of **30** was applied using sodium 1,3-diphenyl-1,3-propanedionate (251 mg, 1.02 mmol, 1.0 equiv.). Rhodium complex **31** was obtained in 90%

yield (398 mg). Mp 176–178 °C (dec.); ^{1}H NMR (300 MHz) δ = 1.83–2.03 (m, 4H), 2.40–2.70 (m, 4H), 4.29 (br s, 4H), 6.66 (s, 1H), 7.32–7.50 (m, 6H), 7.78–7.89 (m, 4H); ^{13}C NMR (75 MHz) δ = 30.3 (CH_2, 4C), 77.0 (d, $J_{C,Rh}$ = 14.0 Hz, 4C), 94.1 (CH, 1C), 127.3 (CH, 4C), 128.2 (CH, 4C), 130.8 (CH, 2C), 139.6 (C, 2C), 181.5 (C, 2C); IR (KBr) ν = 2829, 1590, 1477, 1452, 1381, 1305, 1263, 1225, 1073, 1023, 755, 694, 652; MS (EI) *m/z* (%) = 434 (M^+, 100), 208 (22), 182 (16), 149 (20). Anal. calcd. for $C_{23}H_{23}O_2Rh$: C, 63.60; H, 5.38. Found: C, 63.48; H, 5.10.

(1,1,1,5,5,5-Hexafluoroacetylacetonato)-(1,5-cyclooctadiene)rhodium(I) (32). The same procedure as described for the synthesis of **30** was applied using sodium 1,1,1,5,5,5-hexafluoroacetylacetonate (187 mg, 0.811 mmol, 1.0 equiv.). Rhodium complex **32** was obtained in 98% yield (336 mg). Mp 122–124 °C; ^{1}H NMR (400 MHz) δ = 1.87–1.94 (m, 4H, CH_2), 2.37–2.63 (m, 4H, CH_2), 4.30 (br s, 4H, CH), 6.12 (s, 1H, CH); ^{13}C NMR (100 MHz) δ = 30.1 (s, CH_2, 4C), 78.2 (s, CH, 2C), 78.4 (s, CH, 2C), 90.1 (s, CH), 117.6 (q, $J_{C,F}$ = 284.0 Hz, CF_3, 2C), 174.6 (q, $J_{C,F}$ = 34.3 Hz, CO, 2C) ^{19}F NMR (376 MHz) δ = –74.91 (s); IR (KBr) ν = 2953, 2887, 2843, 1618, 1553, 1463, 1345, 1263, 1200, 1146, 802, 681, 590; MS (EI) *m/z* (%) = 418 (M^+, 100), 211 [$(M–hfac)^+$, 38]. Anal. calcd. for $C_{13}H_{13}F_6O_2Rh$: C, 37.34; H, 3.13. Found: C, 37.24; H, 3.35.

(*R*)-2,2'-Bis(methoxymethoxy)-3,3'-bis(4-(trifluoromethyl)phenyl)-1,1'-binaphthyl [(*R*)-40]. Mp 79–82 °C; $[\alpha]_D^{22}$ = –103 (*c* = 0.37, $CHCl_3$); ^{1}H NMR (300 MHz) δ = 2.38 (s, 6H), 4.36 (d, J_{gem} = 5.9 Hz, 2H), 4.41 (d, J_{gem} = 5.9 Hz, 2H), 7.28–7.39 (m, 4H), 7.47 (ddd, *J* = 8.1, 5.7, 2.3 Hz, 2H), 7.71–7.80 (m, 4H), 7.89–7.94 (m, 6H), 7.99 (s, 2H); ^{13}C NMR (75

MHz) δ = 55.9 (CH_3, 2C), 98.8 (CH_2, 2C), 124.3 (q, $^1J_{C,F}$ = 272 Hz, C, 2C), 125.2 (q, $^3J_{C,F}$ = 3.6 Hz, CH, 4C), 125.5 (CH, 2C), 126.3 (CH, 2C), 126.5 (C, 2C), 126.9 (CH, 2C), 128.1 (CH, 2C), 129.4 (q, $^2J_{C,F}$ = 32.4 Hz, C, 2C), 130.0 (CH, 4C), 130.8 (C, 2C), 130.8 (CH, 2C), 133.9 (C, 2C), 134.1 (C, 2C), 142.7 (C, 2C), 151.1 (C, 2C); ^{19}F NMR (282 MHz) δ = –62.38 (s); IR (KBr) ν = 3854, 3743, 3060, 2942, 2361, 2339, 1737, 1618, 1502, 1455, 1398, 1124, 1070, 969, 917, 842, 749, 666, 606; MS (EI) *m*/*z* (%) = 662 (M^+, 16), 586 [$(M–C_3H_8O_2)^+$, 100], 558 (58), 413 (10). Anal. calcd. for $C_{38}H_{28}O_4F_6$: C, 68.88; H, 4.26. Found: C, 68.61; H, 4.49.

(*R*)-3,3'-Bis[4-(trifluoromethyl)phenyl]-1,1'-binaphthyl-2,2'-diol [(*R*)-41]. Mp 102–105 °C; $[\alpha]_D^{22}$ = +50.2 (*c* = 0.21, $CHCl_3$); ^{1}H NMR (400 MHz) δ = 5.35 (s, 2H), 7.38 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 7.44 (ddd, *J* = 8.0, 6.9, 0.9 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 4H), 7.88 (d, *J* = 8.1 Hz, 4H), 7.97 (d, *J* = 8.0 Hz, 2H), 8.07 (s, 2H); ^{13}C NMR (100 MHz) δ = 111.9 (C, 2C), 124.0 (CH, 2C), 124.2 (q, $^1J_{C,F}$ = 272 Hz, C, 2C), 127.7 (CH, 2C), 125.2 (q, $^3J_{C,F}$ = 3.5 Hz, CH, 4C), 128.0 (CH, 2C), 128.6 (CH, 2C), 129.4 (C, 2C), 129.5 (C, 2C), 129.7 (q, $^2J_{C,F}$ = 32.9 Hz, C, 2C), 129.9 (CH, 4C), 132.0 (CH, 2C), 133.0 (C, 2C), 141.0 (C, 2C), 150.0 (C, 2C); IR (KBr) ν = 3854, 3742, 3513, 2361, 2341, 1714, 1619, 1510, 1325, 1122, 1068, 841; MS (EI) *m*/*z* (%) = 574 (M^+, 100), 555(7), 259 (23). Anal. calcd. for $C_{34}H_{20}O_2F_6$: C, 71.08; H, 3.51. Found: C, 71.02; H, 3.78.

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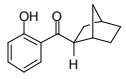
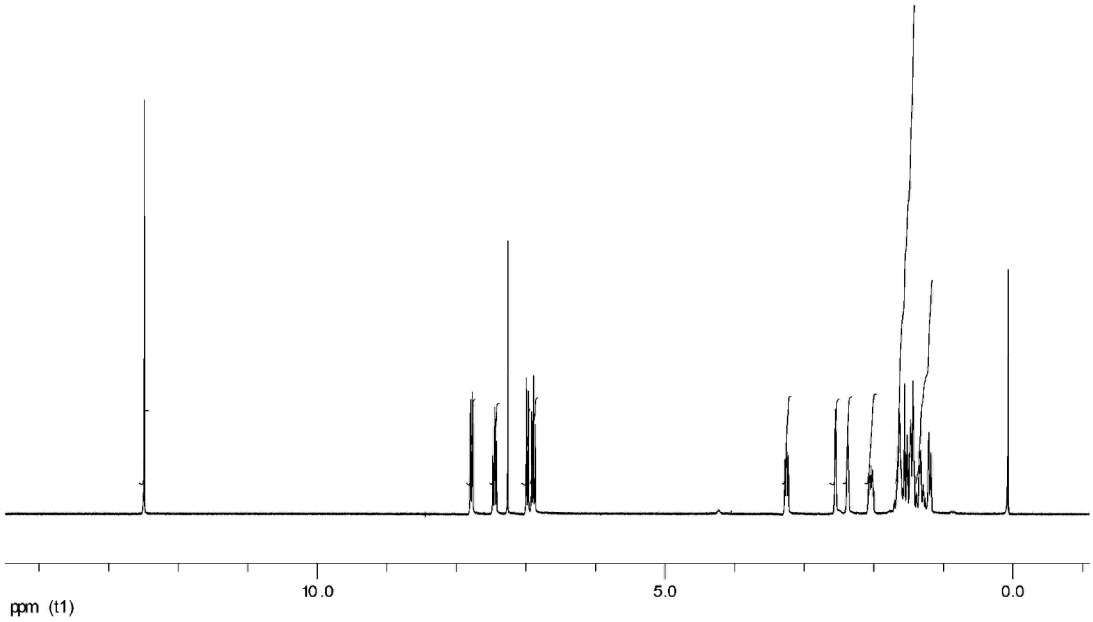
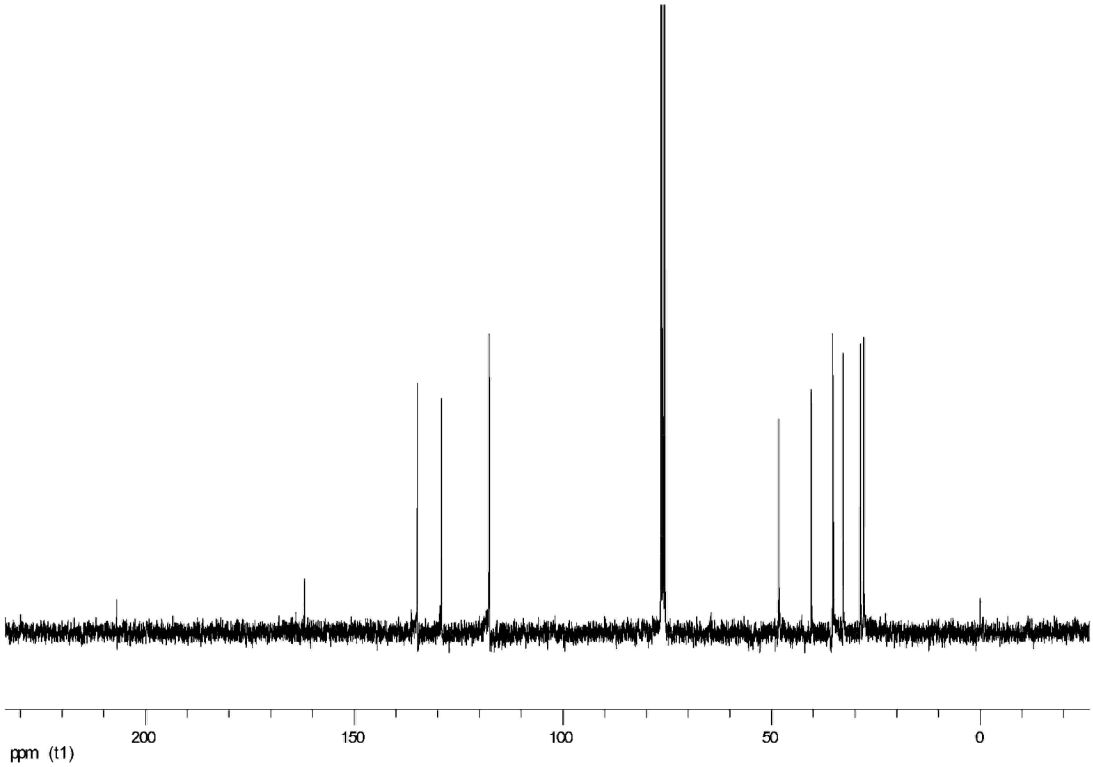
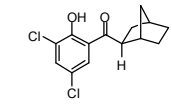
exo-Bicyclo[2.2.1]heptan-2-yl(2-hydroxyphenyl)methanone (*exo*-**3a**)

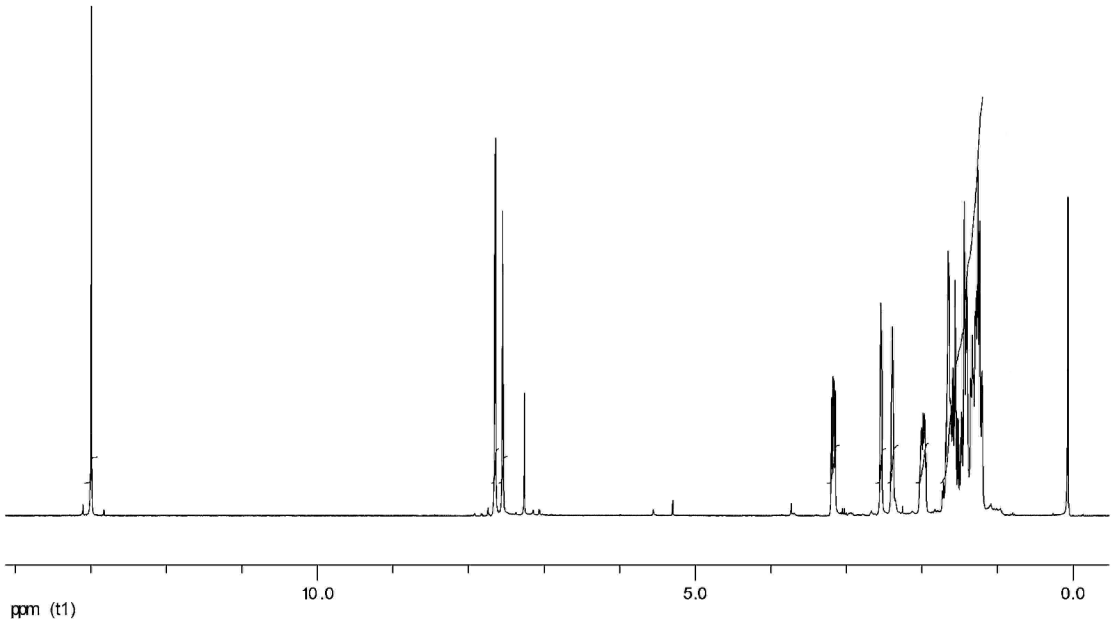


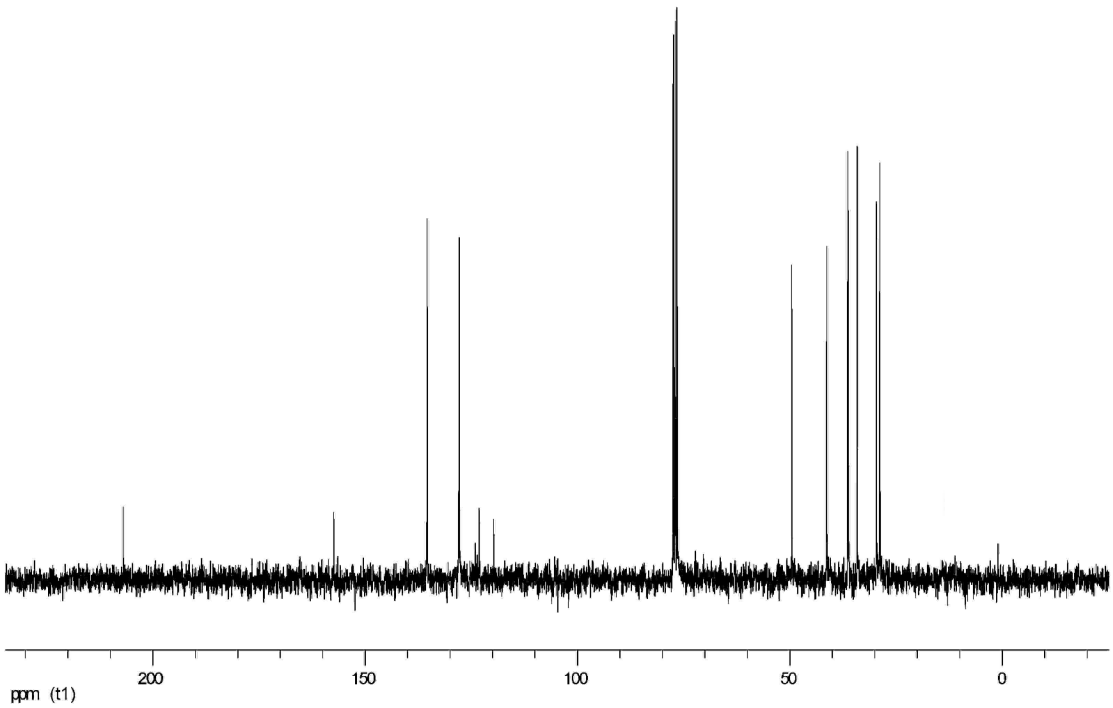




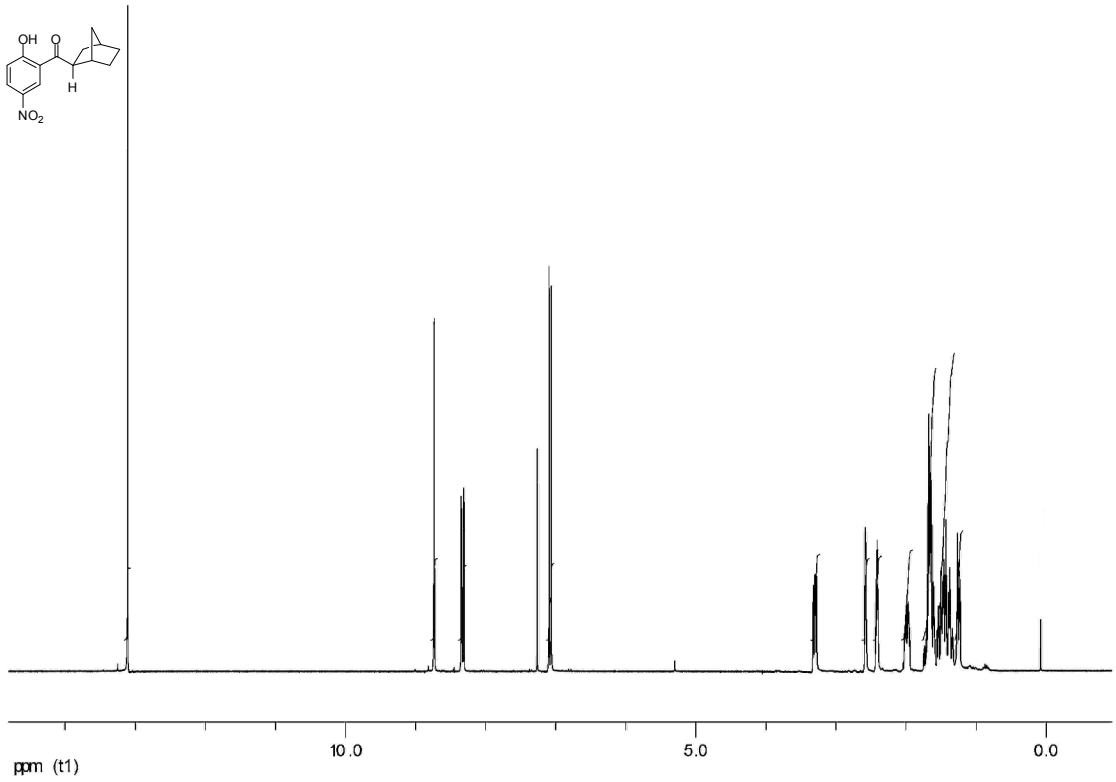
exo-Bicyclo[2.2.1]heptan-2-yl(3,5-dichloro-2-hydroxyphenyl)methanone [*exo*-**3b**]

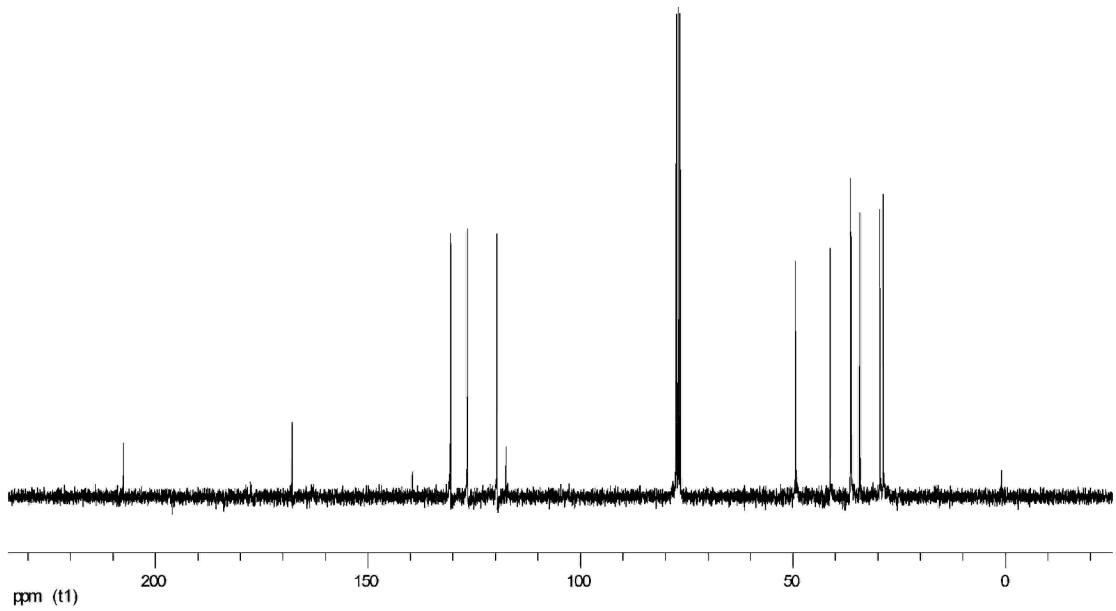




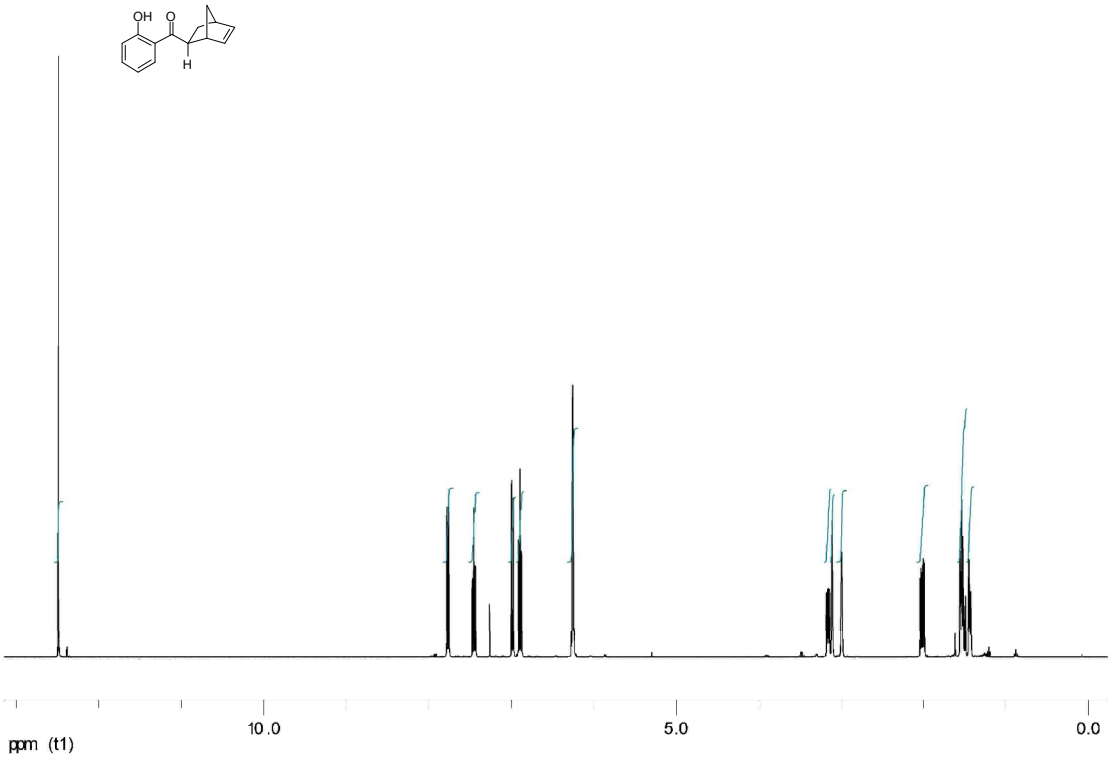


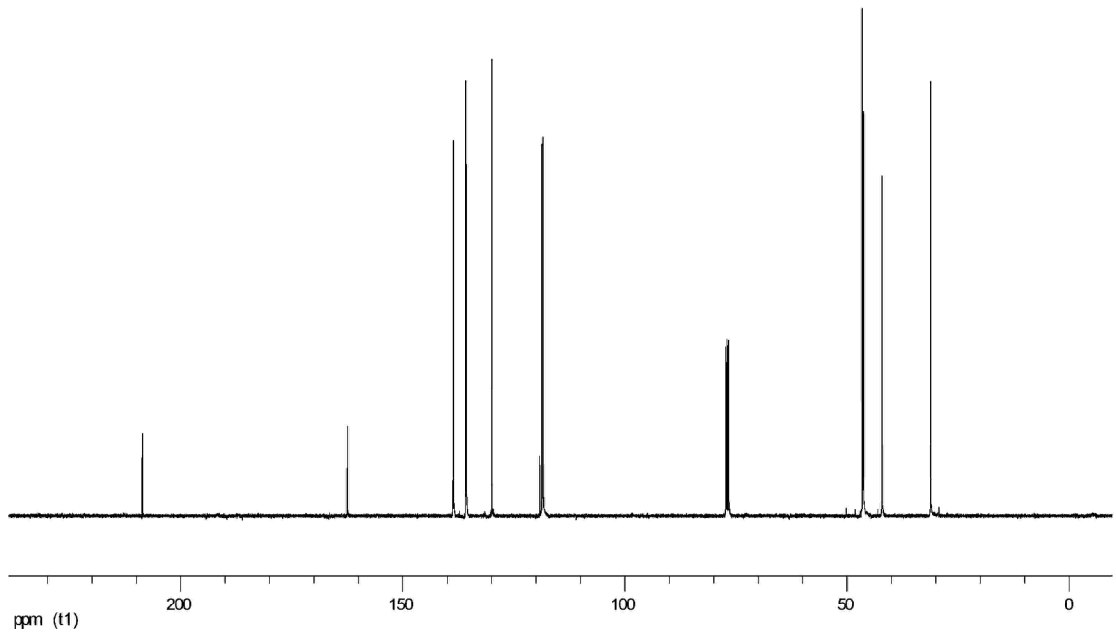
exo-Bicyclo[2.2.1]heptan-2-yl(2-hydroxy-5-nitrophenyl)methanone (*exo*-**3c**)



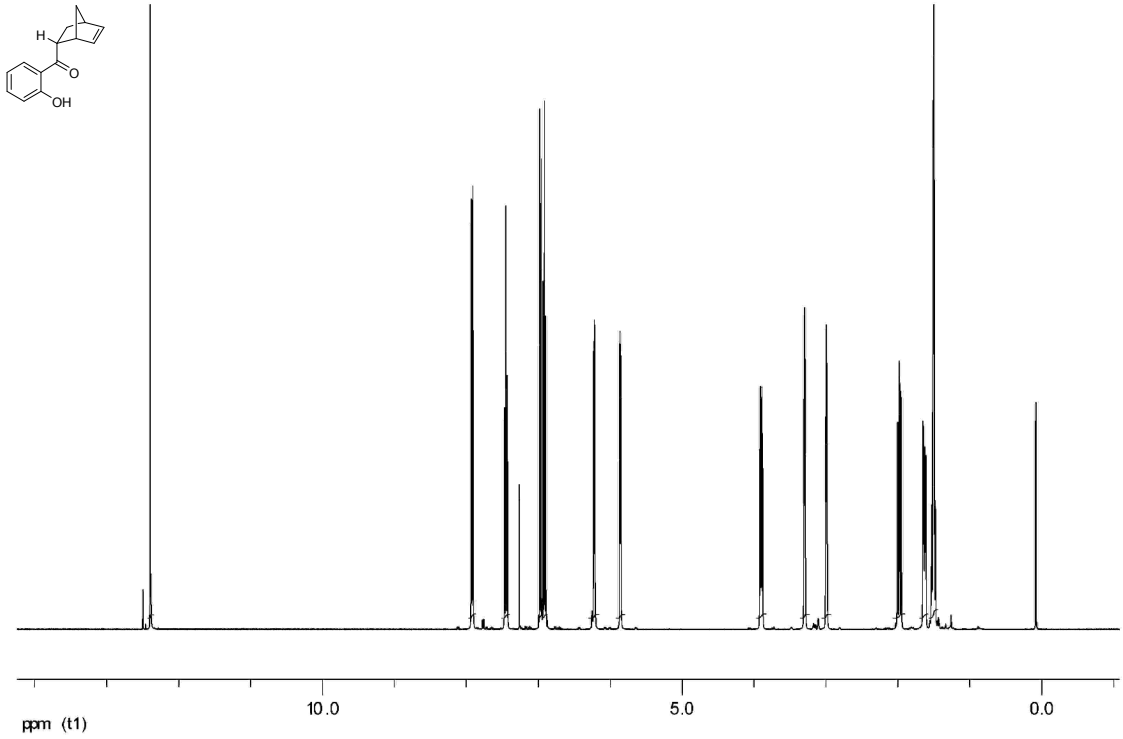


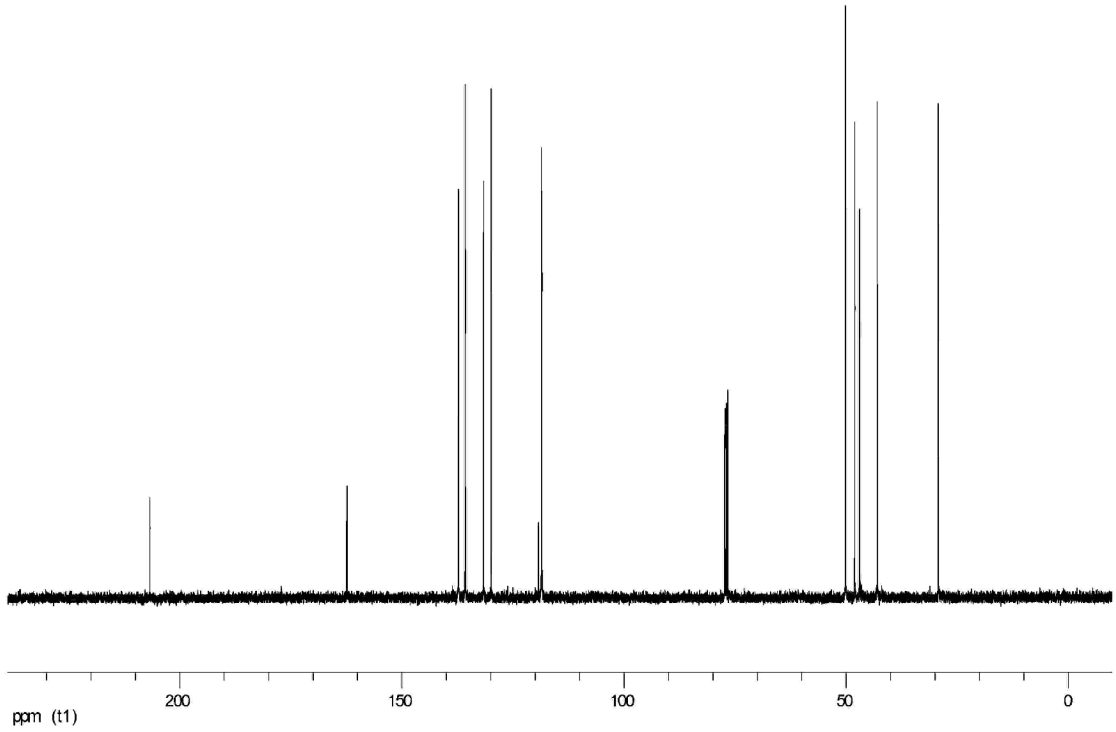
exo-Bicyclo[2.2.1]hept-5-en-2-yl(2-hydroxyphenyl)methanone (*exo*-**5a**)



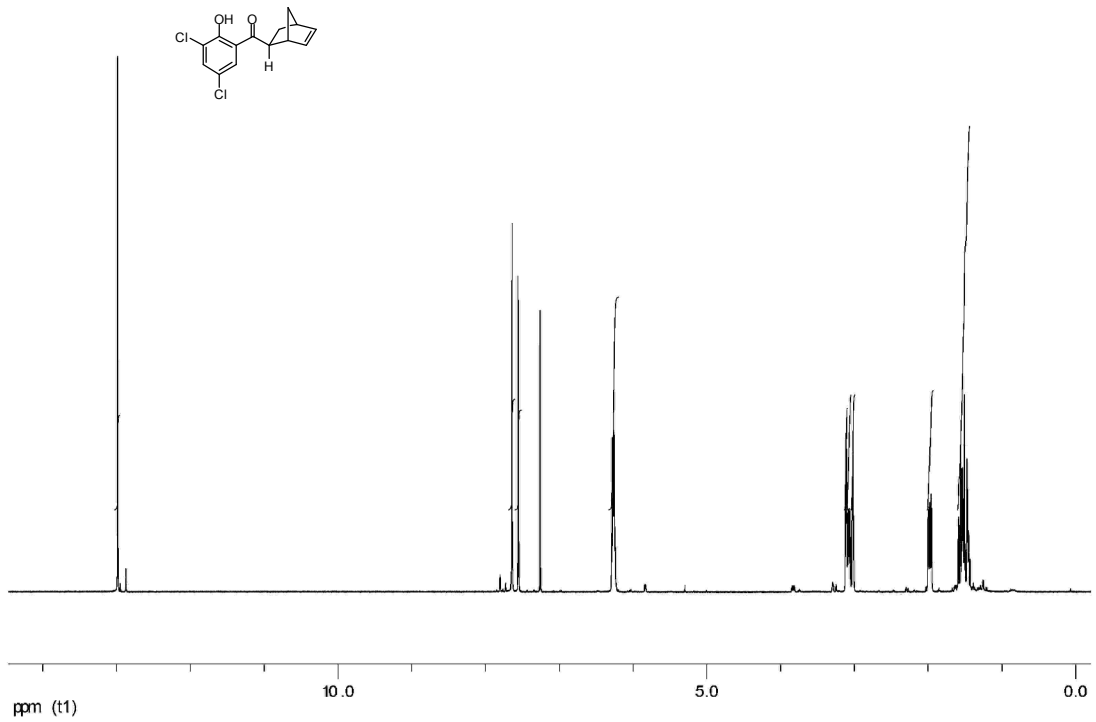


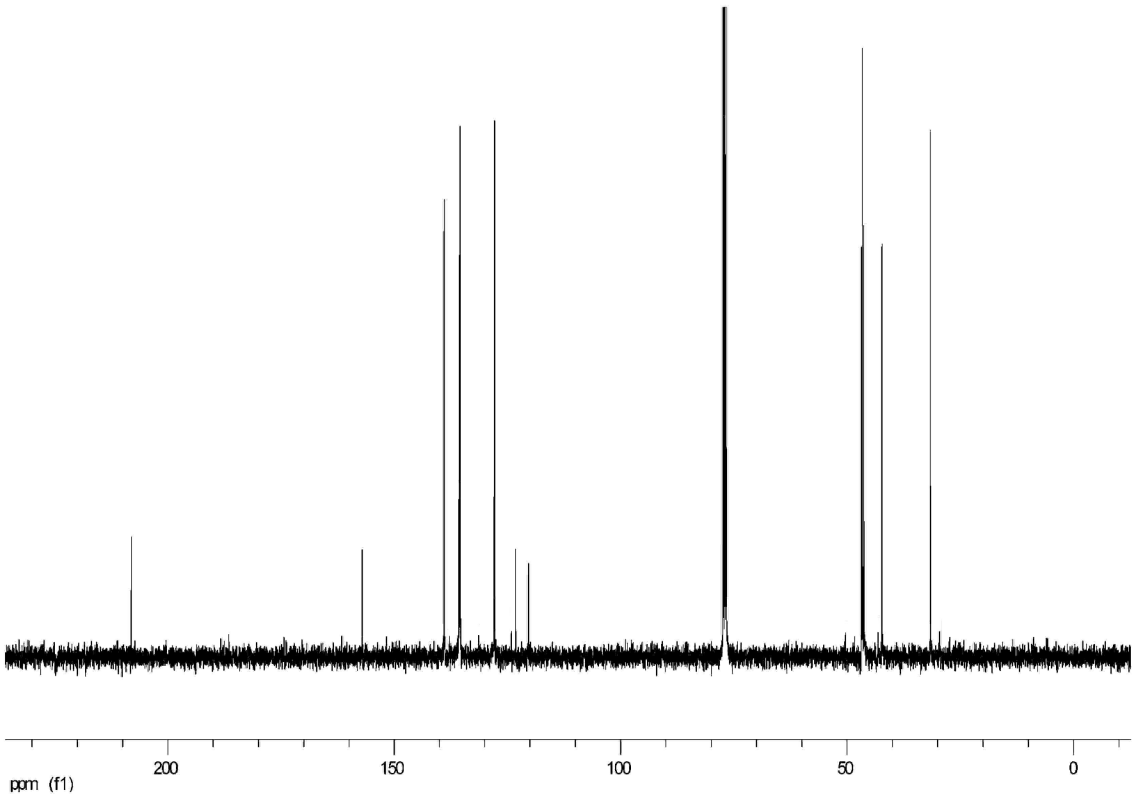
(+)-*endo*-Bicyclo[2.2.1]hept-5-en-2-yl(2-hydroxyphenyl)methanone (*endo*-**5a**)



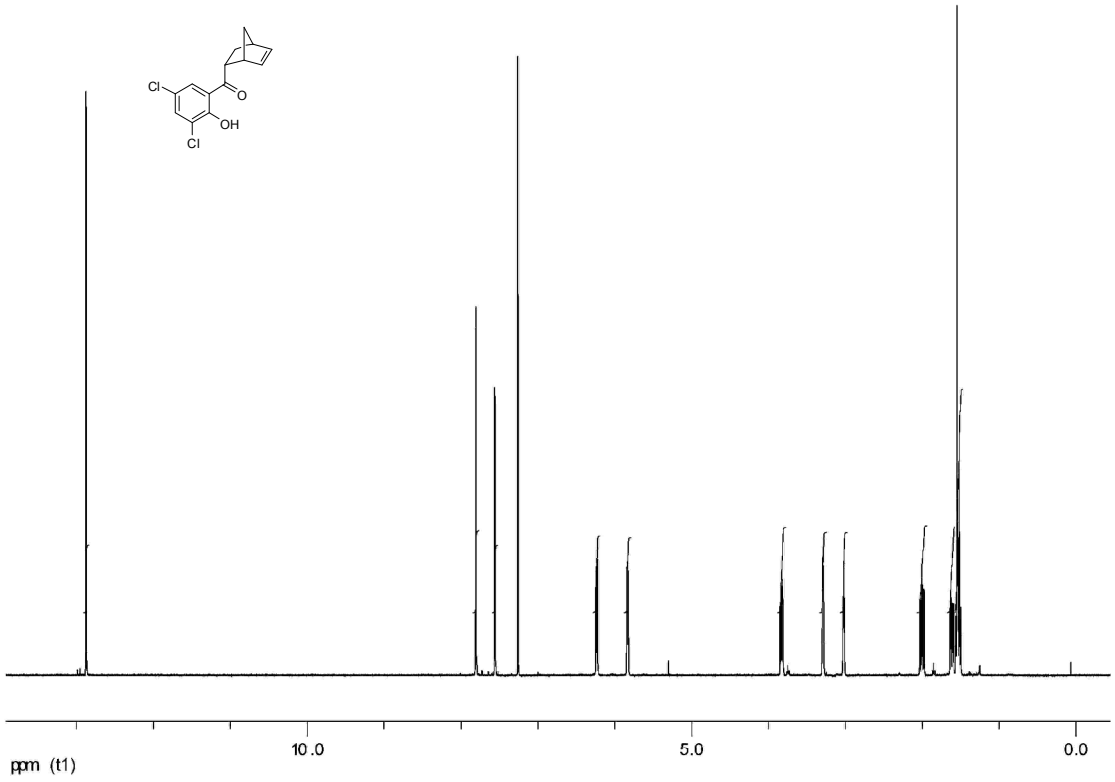


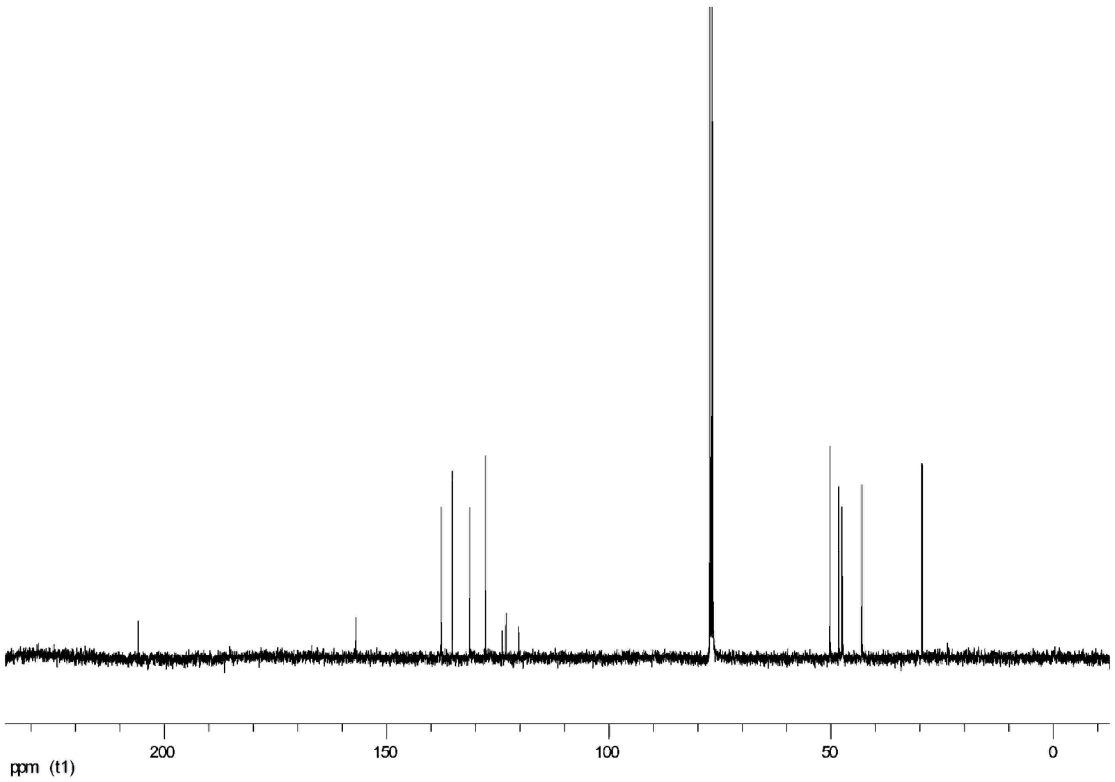
exo-Bicyclo[2.2.1]hept-5-en-2-yl(3,5-dichloro-2-hydroxyphenyl)methanone (*exo*-**5b**)



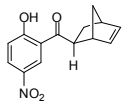


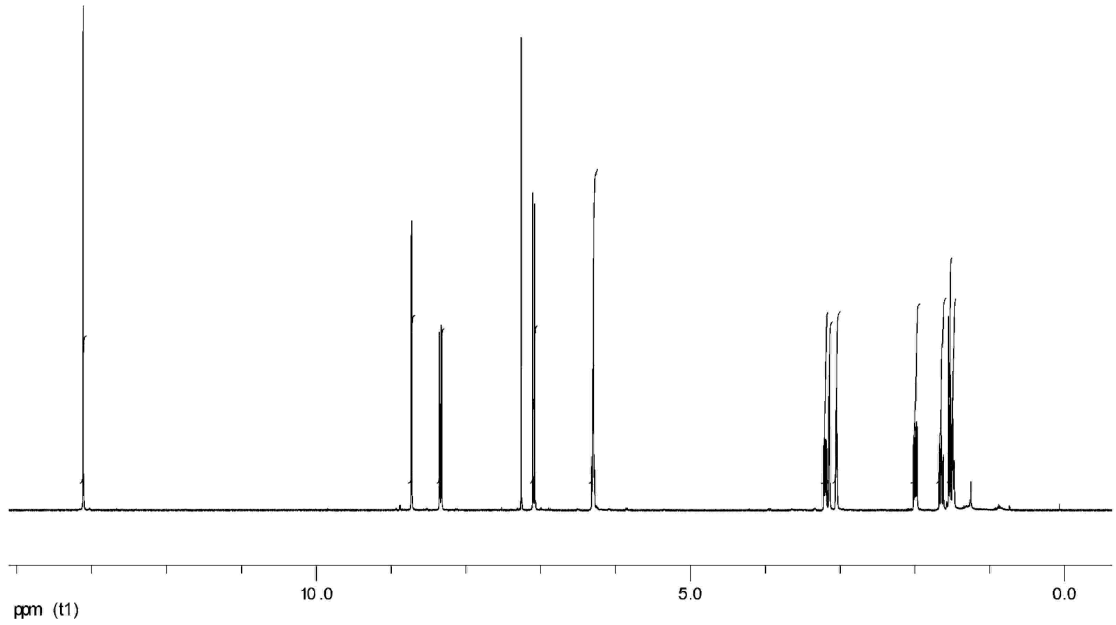
endo-Bicyclo[2.2.1]hept-5-en-2-yl(3,5-dichloro-2-hydroxyphenyl)methanone (*endo*-**5b**)

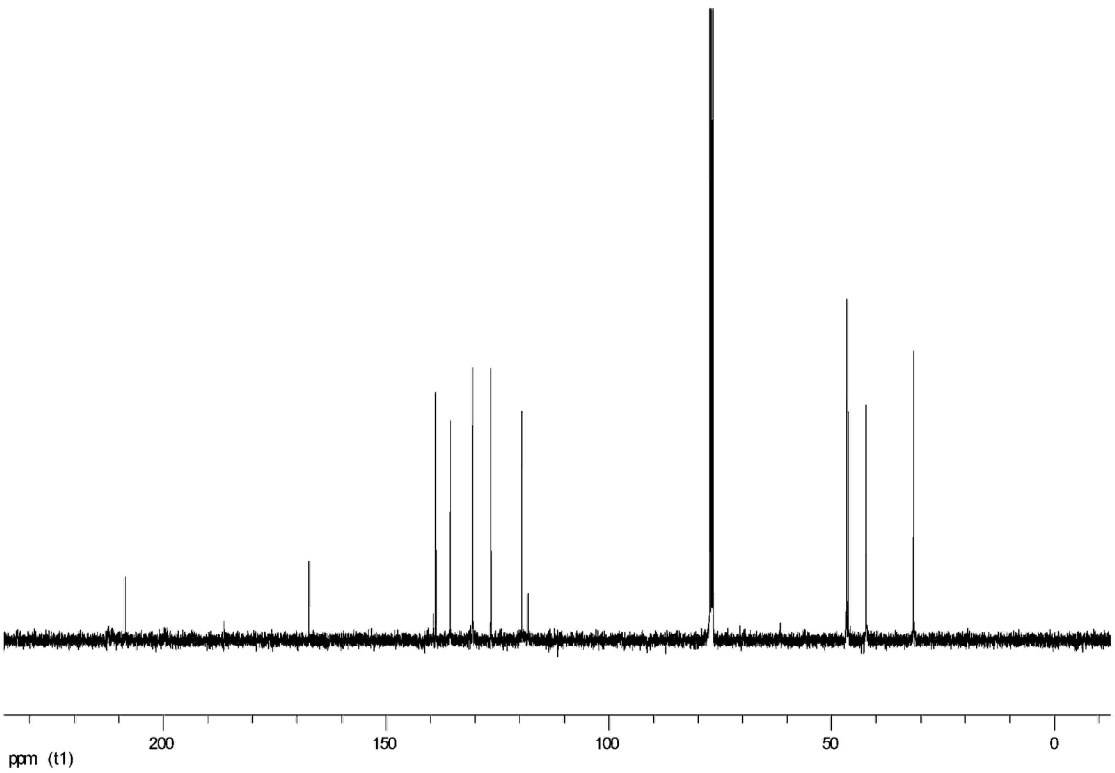




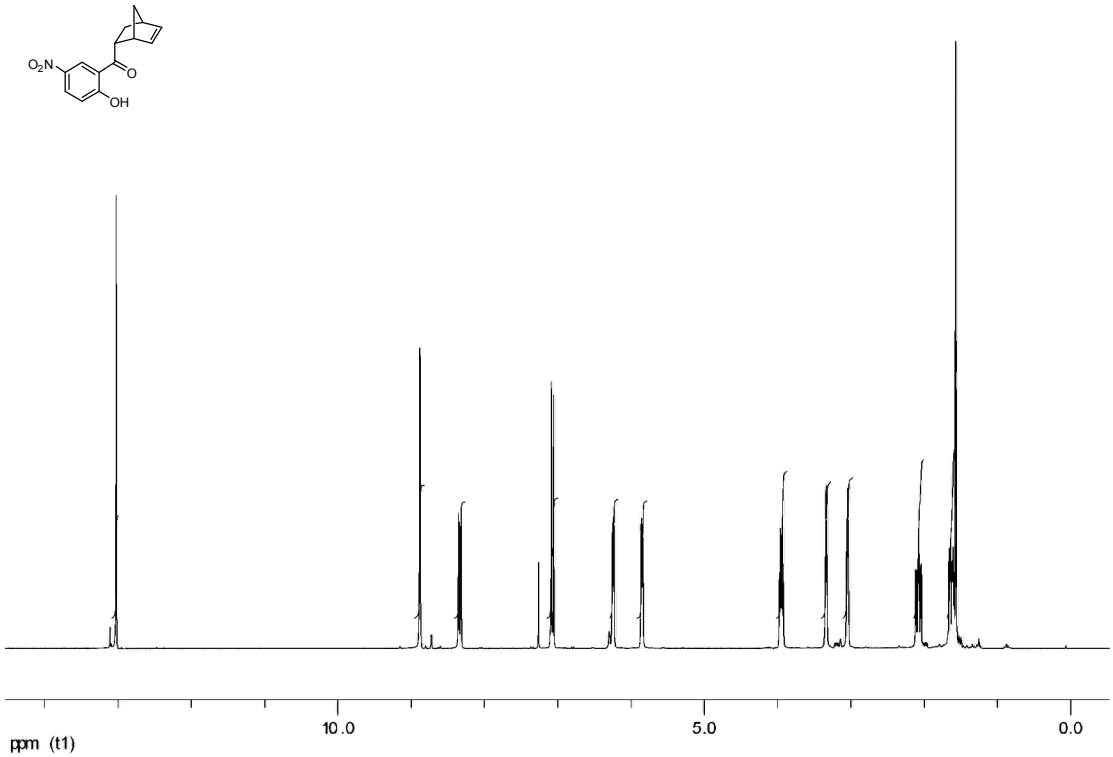
exo-Bicyclo[2.2.1]hept-5-en-2-yl(2-hydroxy-5-nitrophenyl)methanone (*exo*-**5c**)

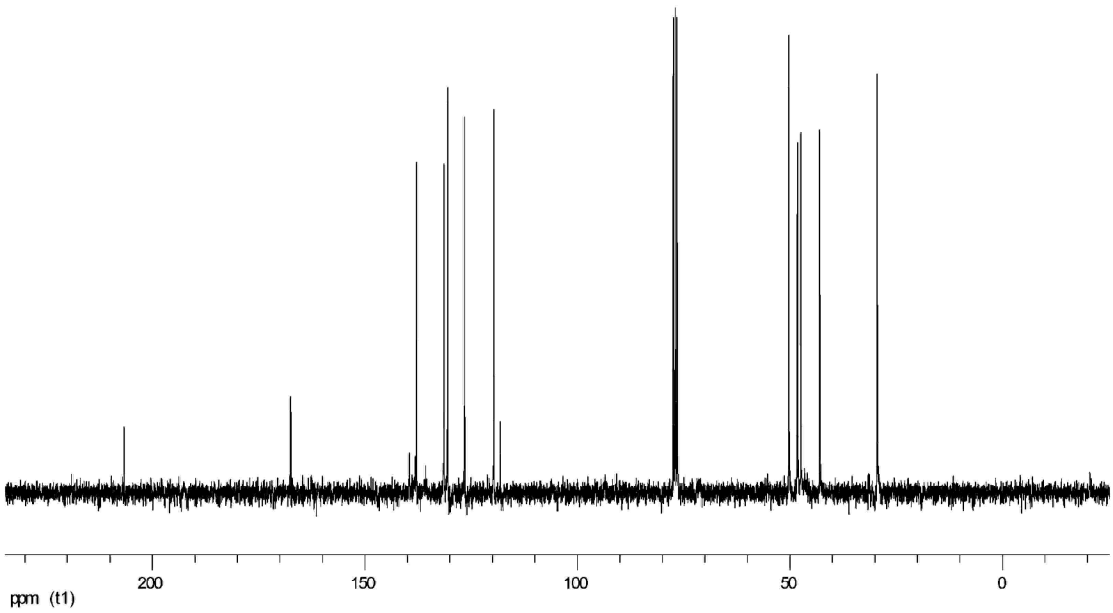




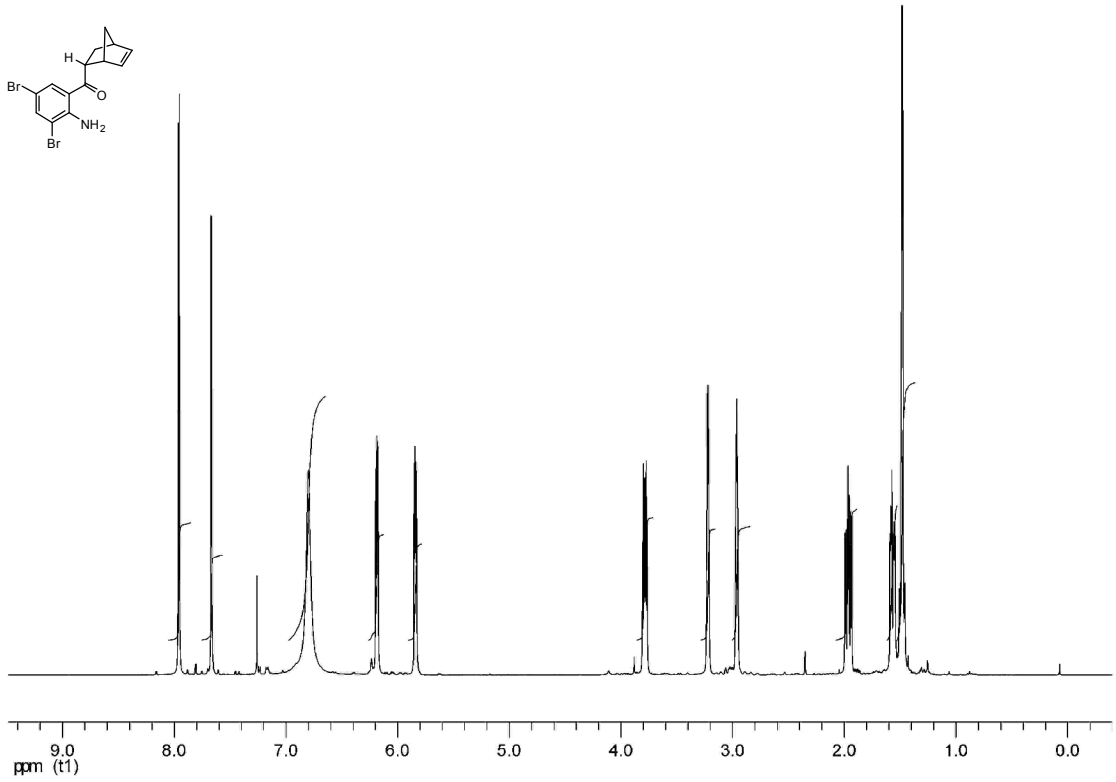


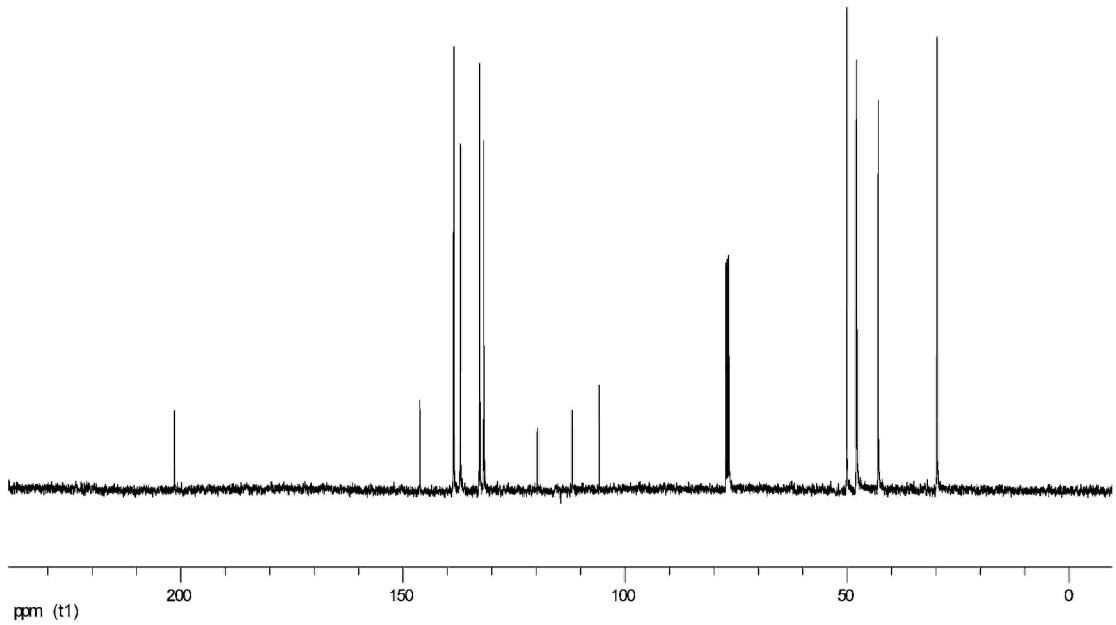
endo-Bicyclo[2.2.1]hept-5-en-2-yl(2-hydroxy-5-nitrophenyl)methanone (*endo*-**5c**)



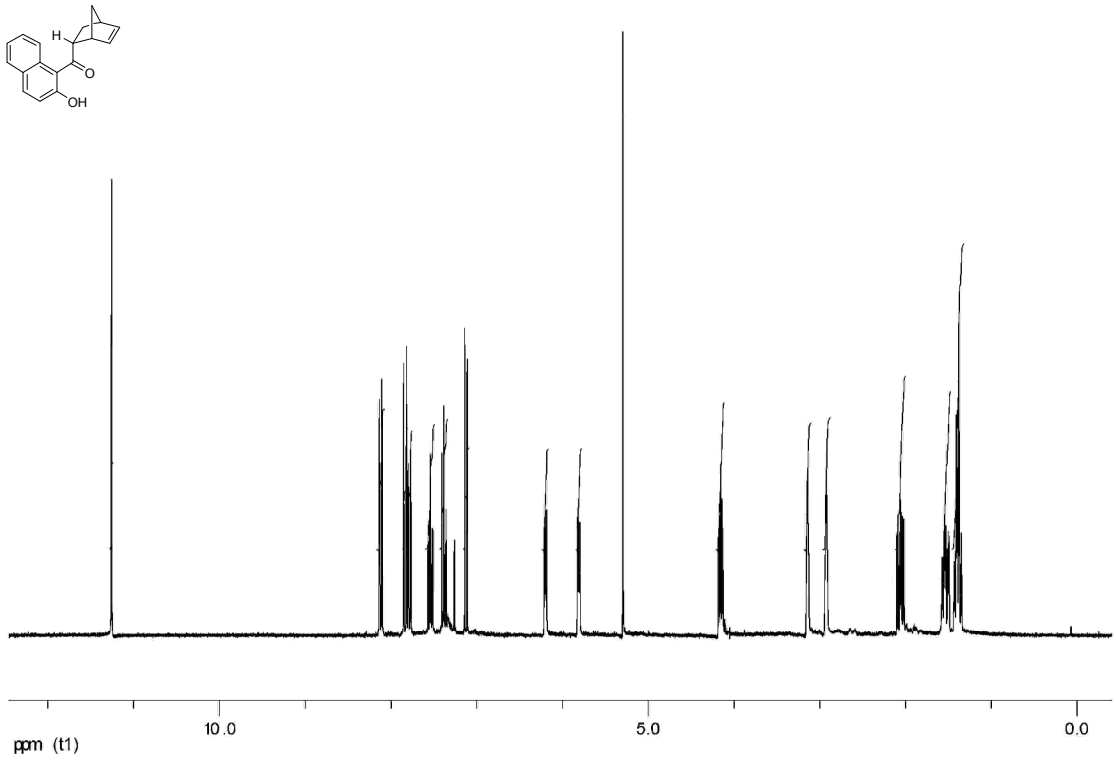


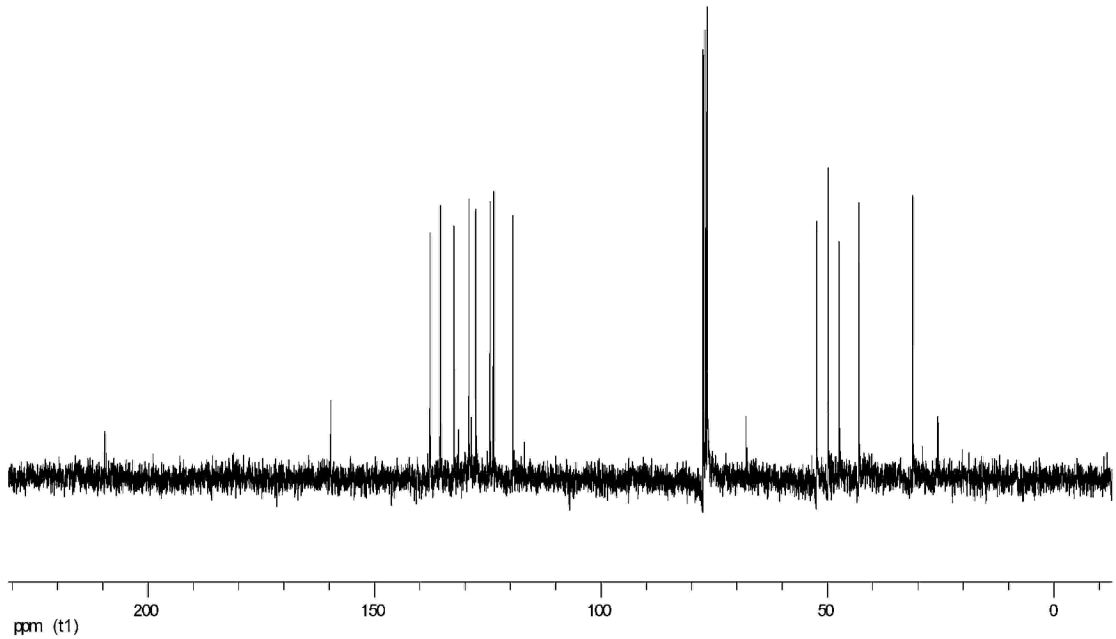
endo-(2-Amino-3,5-dibromophenyl)(bicyclo[2.2.1]hept-5-en-2-yl)methanone (*endo*-**5d**)



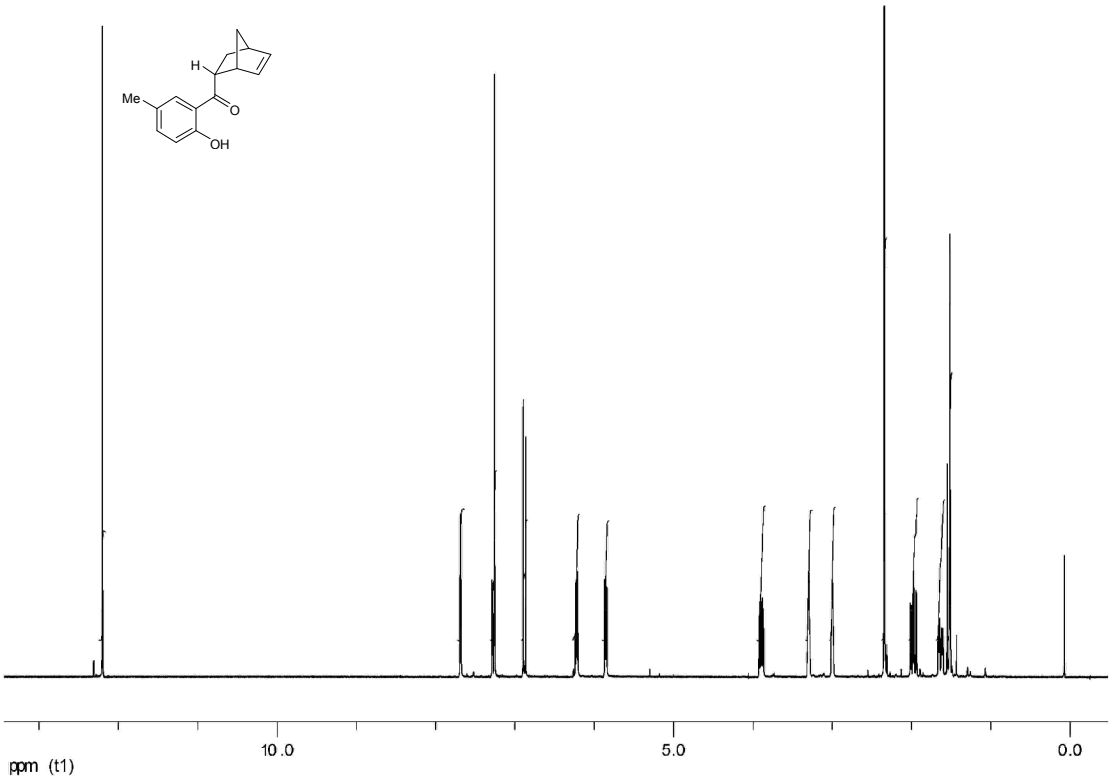


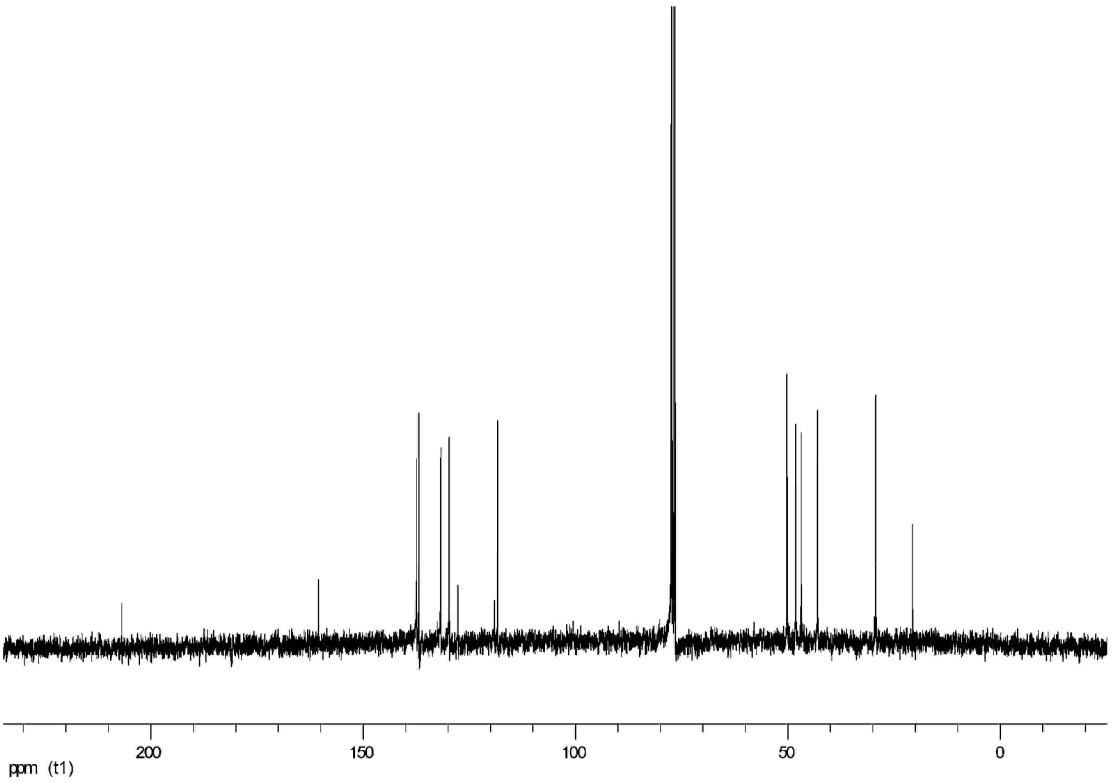
endo-Bicyclo[2.2.1]hept-5-en-2-yl(2-hydroxynaphthalen-1-yl)methanone (*endo*-**5e**)



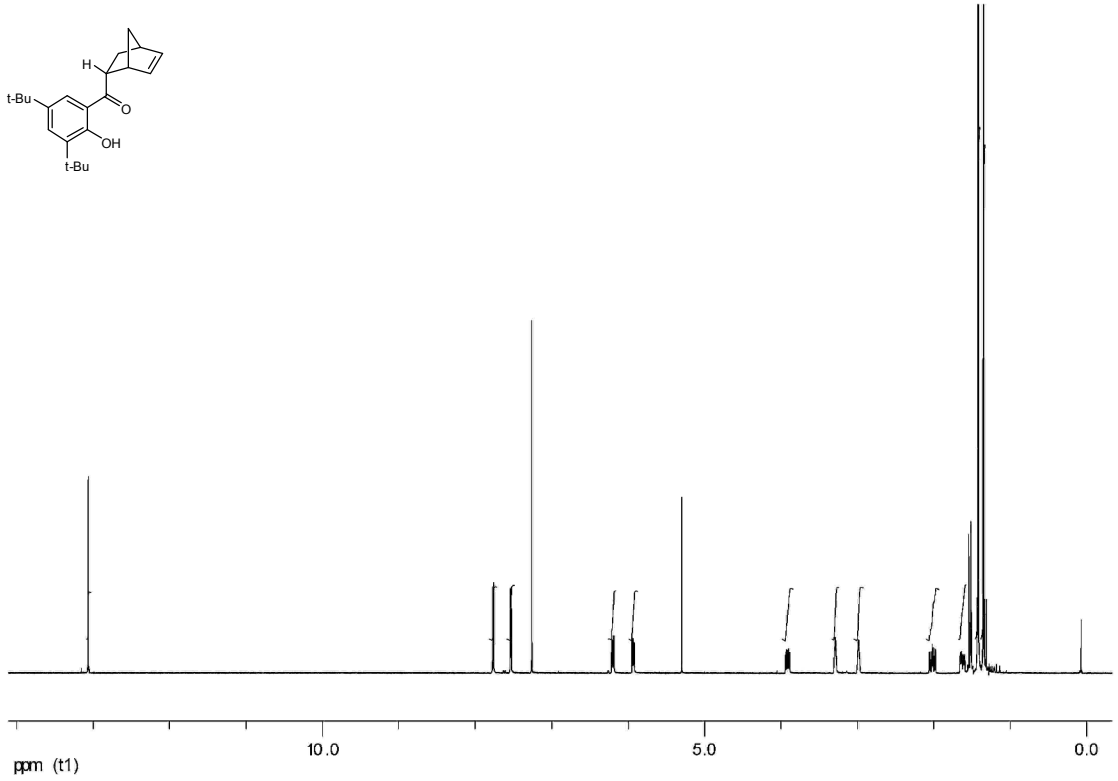


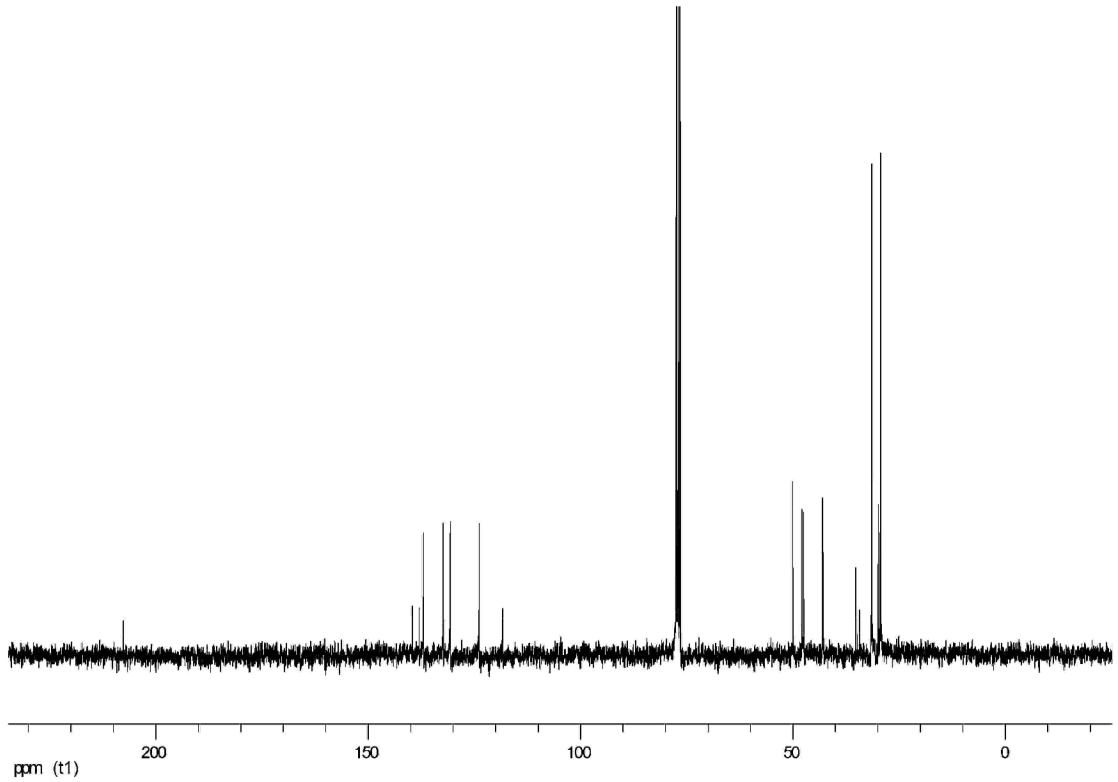
endo-Bicyclo[2.2.1]hept-5-en-2-yl(2-hydroxy-5-methylphenyl)methanone (*endo*-**5f**)



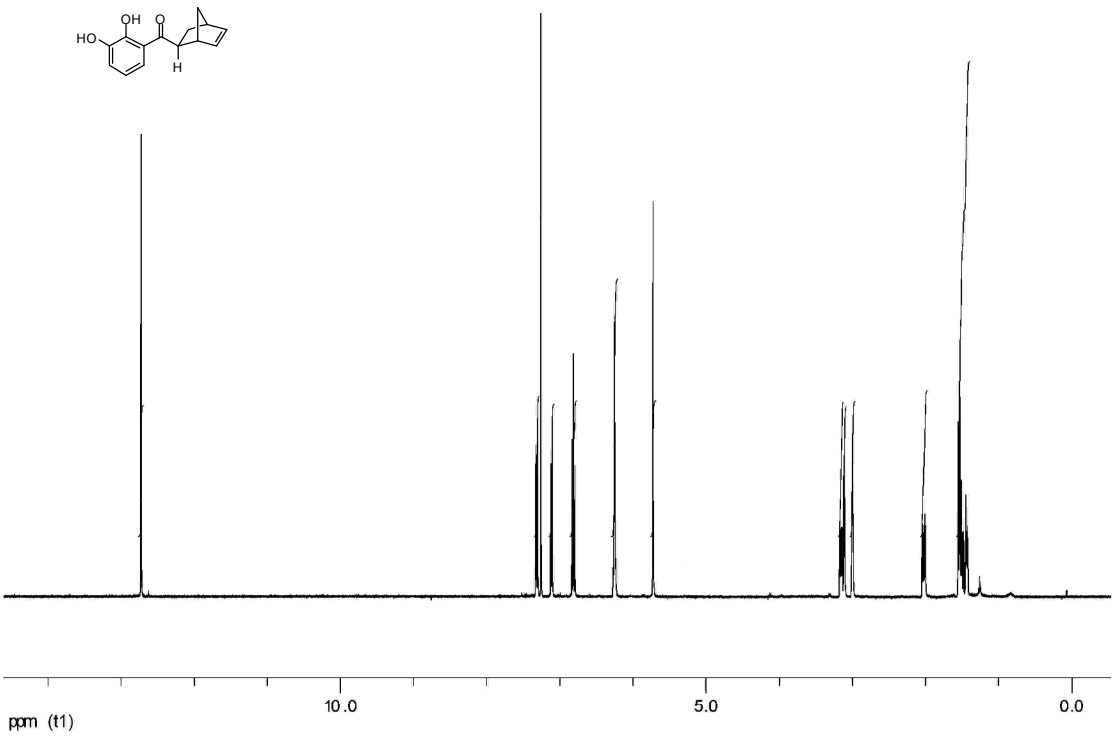


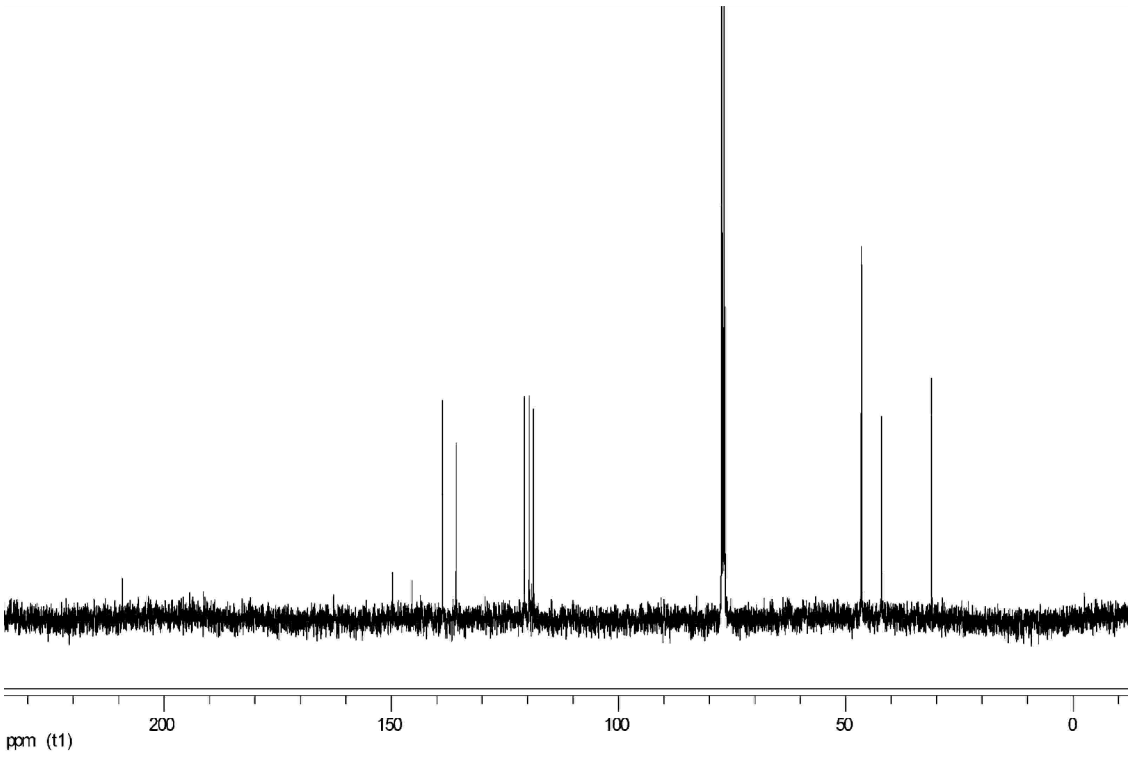
endo-Bicyclo[2.2.1]hept-5-en-2-yl(3,5-di-*tert*-butyl-2-hydroxyphenyl)methanone (*endo*-**5g**)



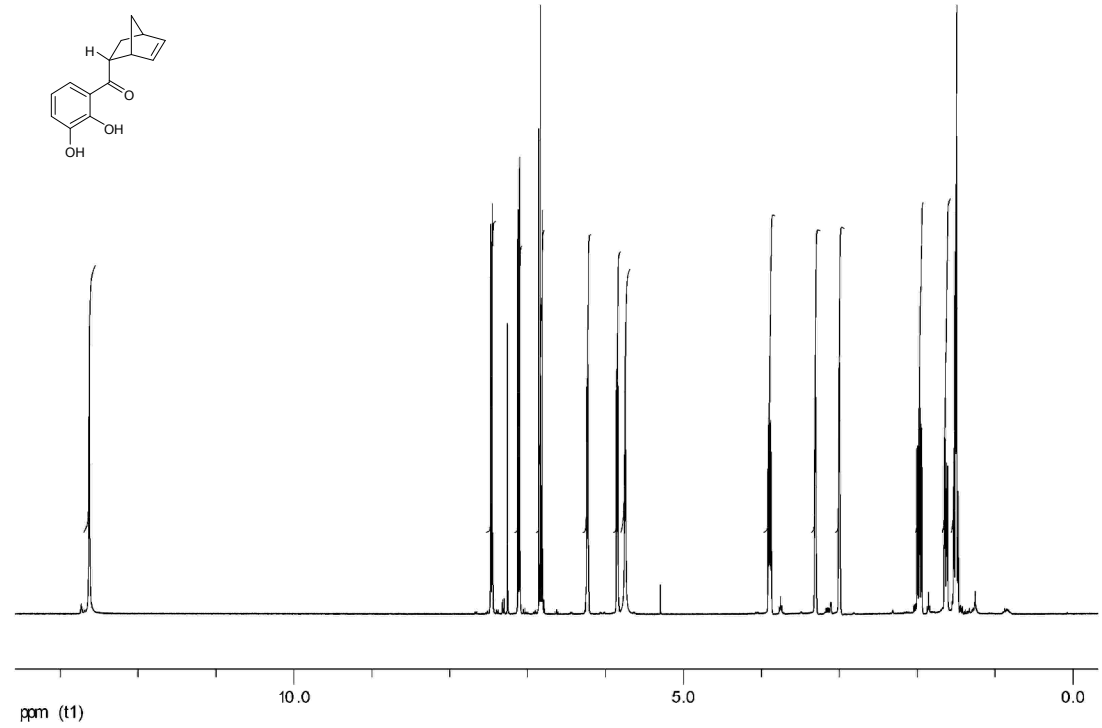


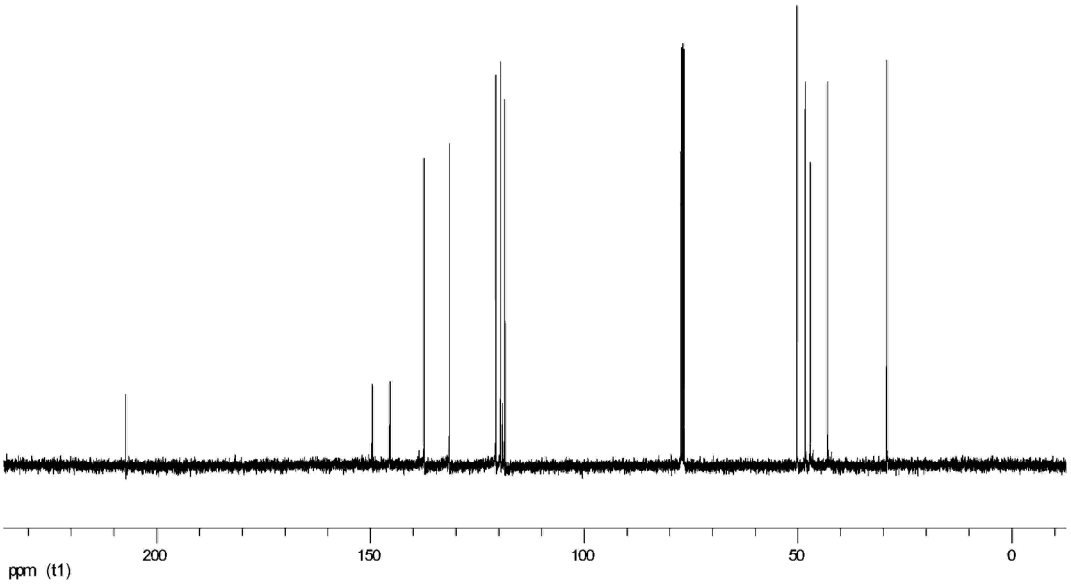
exo-Bicyclo[2.2.1]hept-5-en-2-yl(2,3-dihydroxyphenyl)methanone (*exo*-**5h**)



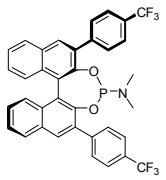


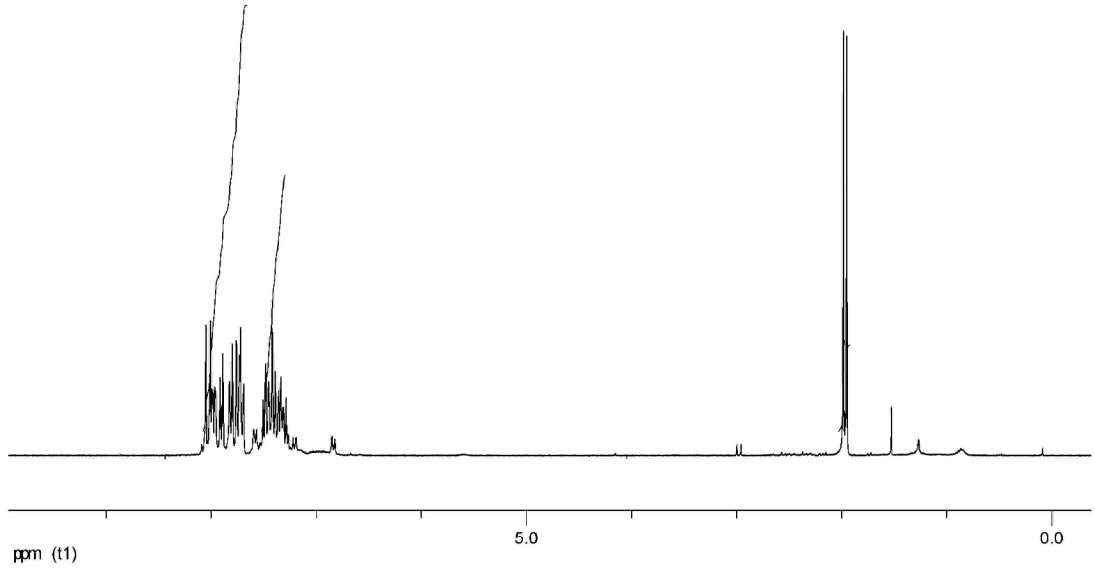
endo-Bicyclo[2.2.1]hept-5-en-2-yl(2,3-dihydroxyphenyl)methanone (*endo*-**5h**)

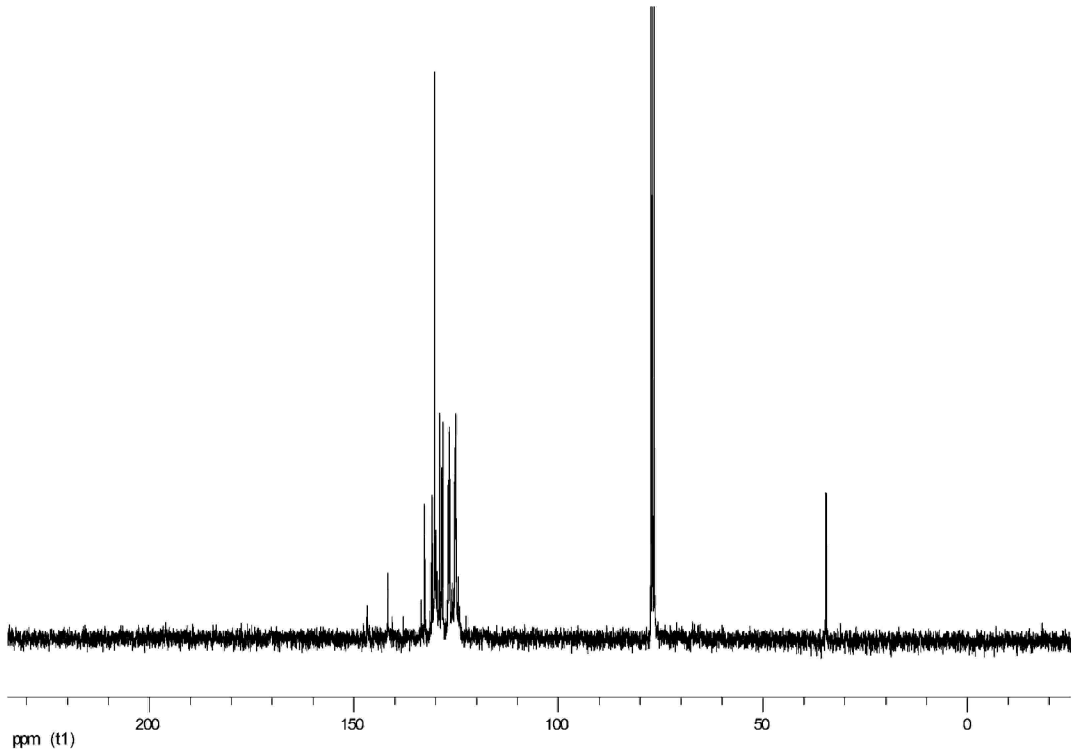




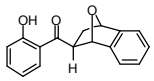
(11b*R*)-*N*,*N*-dimethyl-2,6-bis[4-(trifluoromethyl)phenyl]dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-amine **[**(*R*)-**19**]

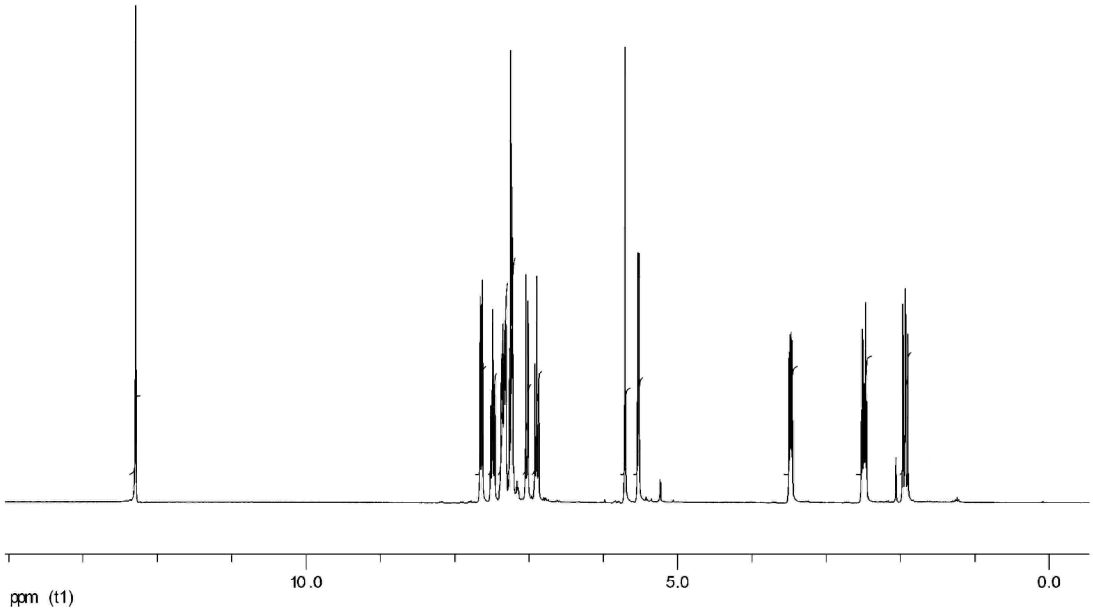


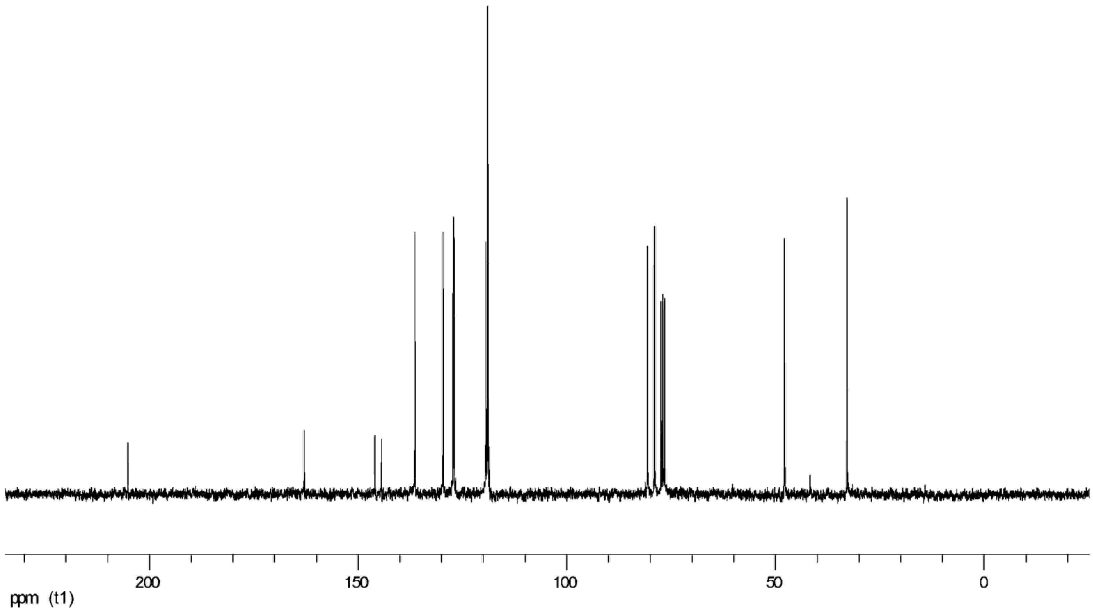




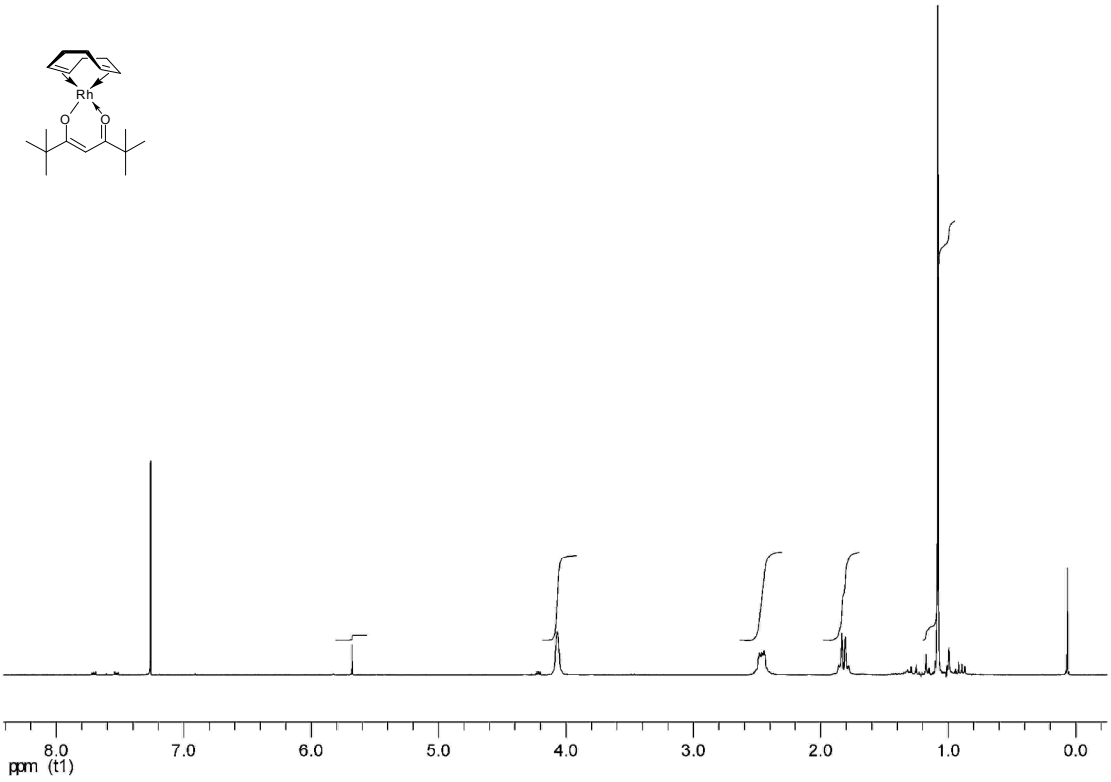
exo-(2-Hydroxyphenyl)(1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)methanone (*exo*-**29**)

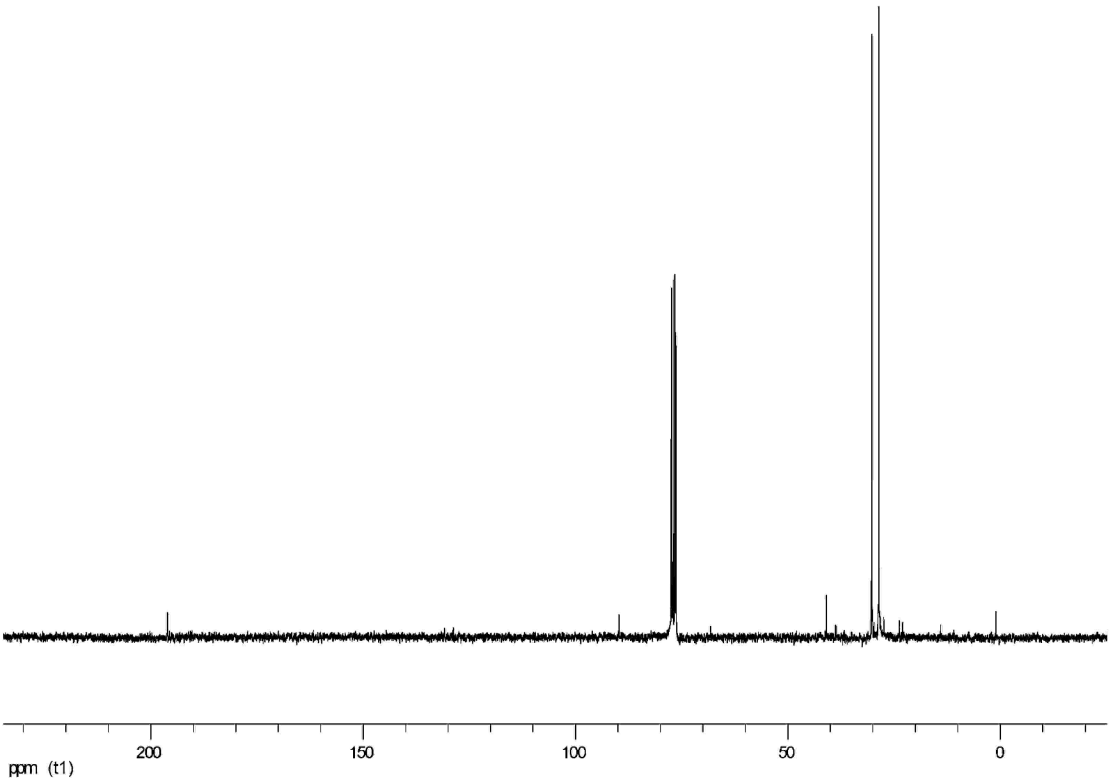




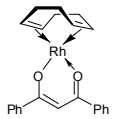


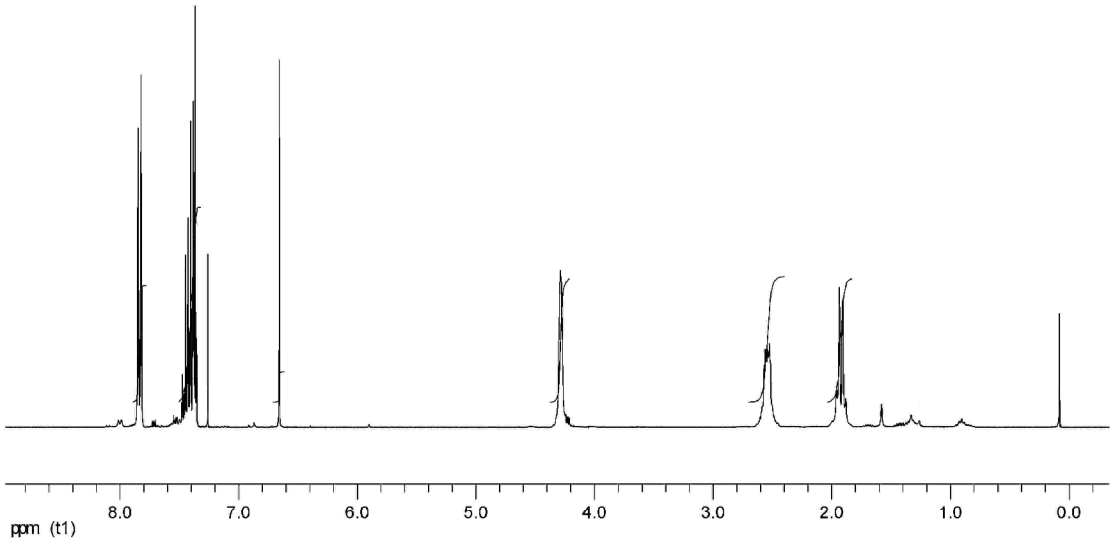
(2,2,6,6-Tetramethyl-3,5-heptanedionato)-(1,5-cyclooctadiene)rhodium(I) (**30**)

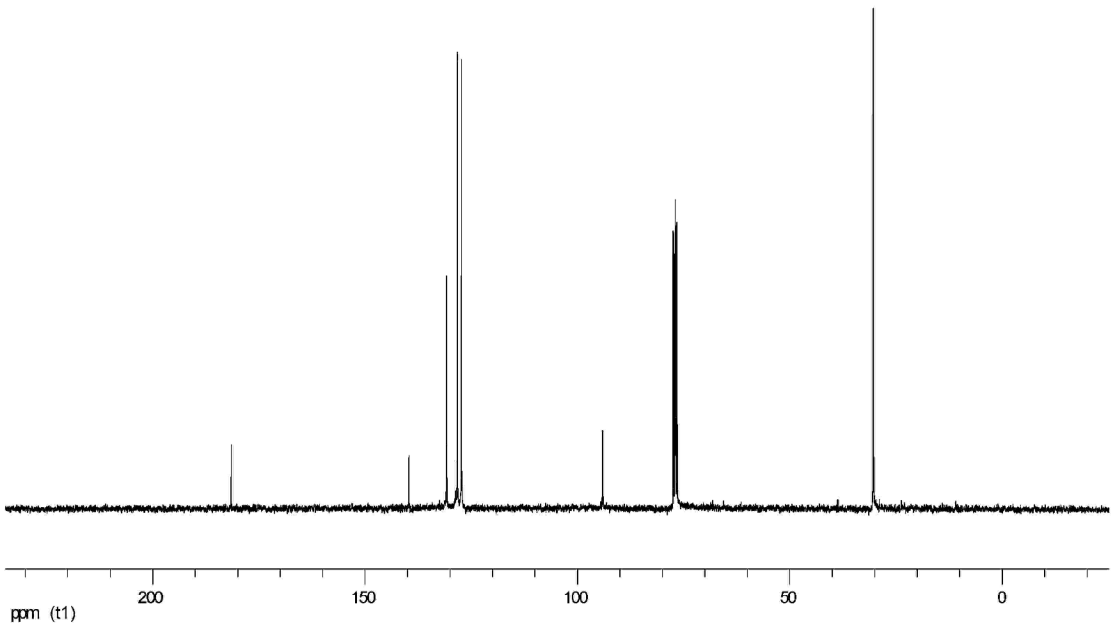




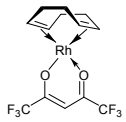
(1,3-Diphenyl-1,3-propanedionato)-(1,5-cyclooctadiene)rhodium(I) (**31**)

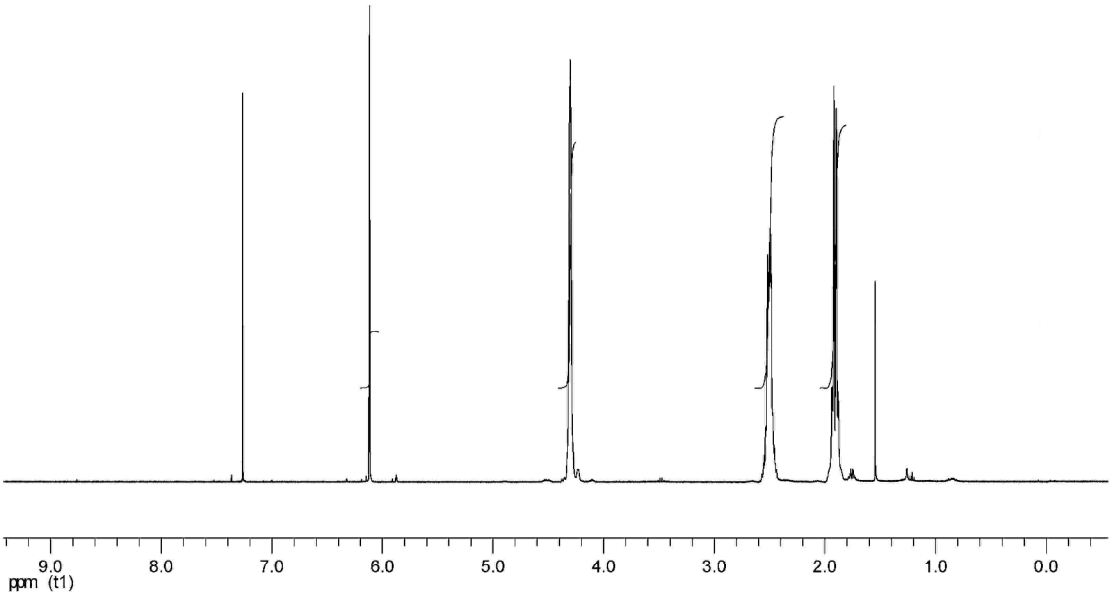


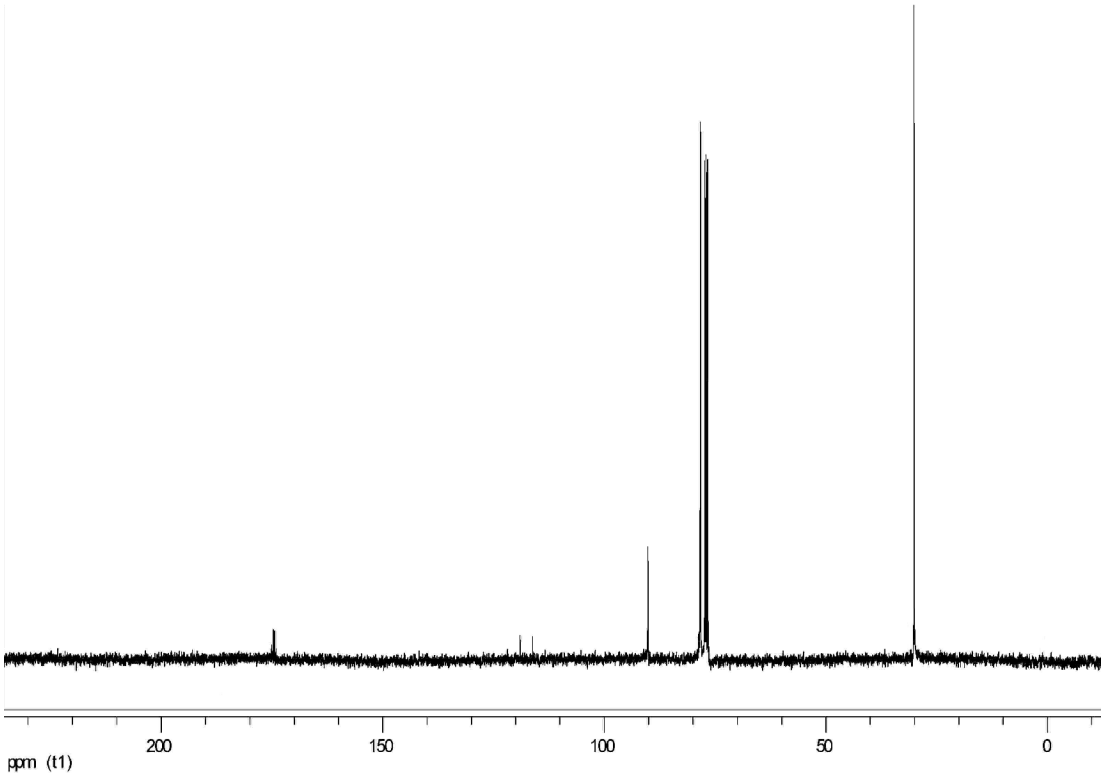




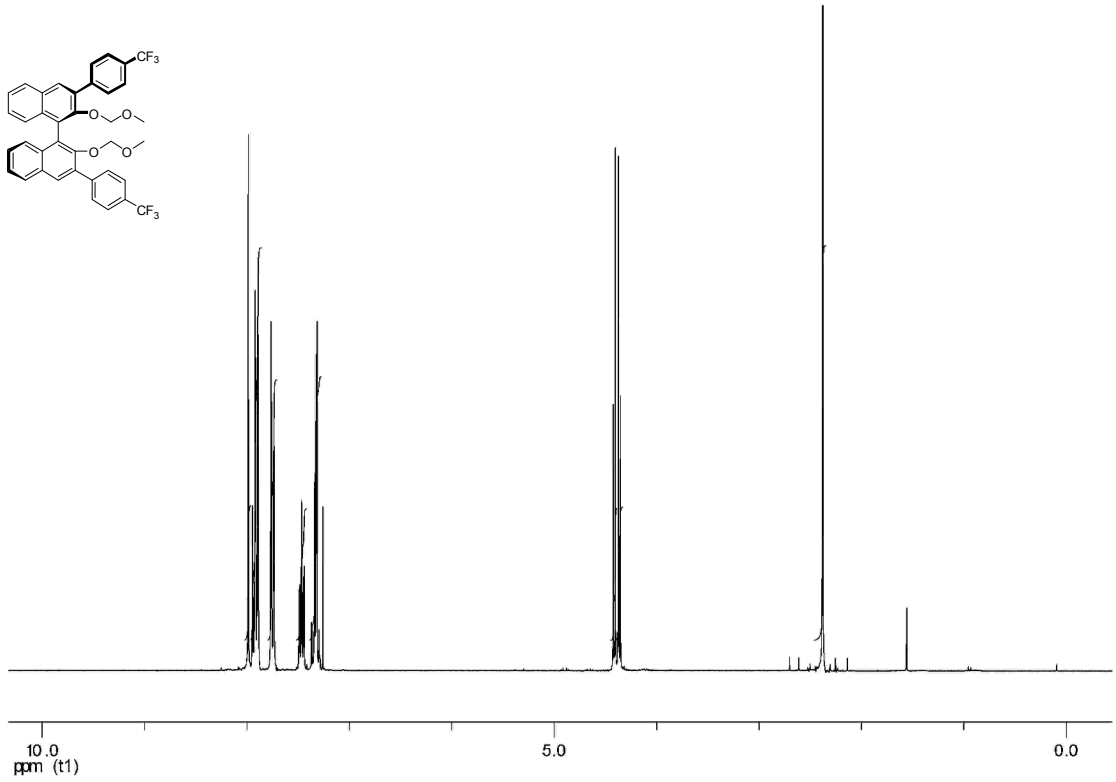
(1,1,1,5,5,5-Hexafluoroacetylacetonato)-(1,5-cyclooctadiene)rhodium(I) (**32**)

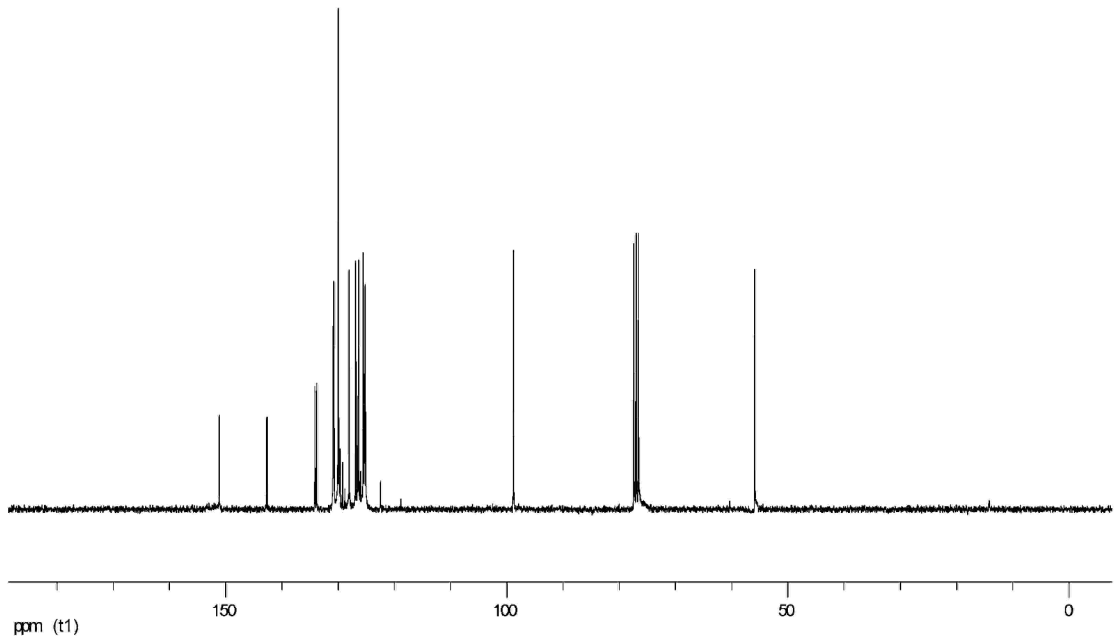






(*R*)-2,2'-Bis(methoxymethoxy)-3,3'-bis(4-(trifluoromethyl)phenyl)-1,1'-binaphthyl [(*R*)-**40**]





(*R*)-3,3'-Bis[4-(trifluoromethyl)phenyl]-1,1'-binaphthyl-2,2'-diol **[**(*R*)-**41**]