Supplementary Material (ESI) for Chemical Communications

Supporting Information

Rhodium-Catalyzed Cycloaddition of 1,6-Enynes with 2-Bromophenylboronic Acids: Synthesis of Multi-substituted Dihydronaphthalene Scaffold

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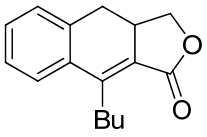
General Information:

1. Unless otherwise noted, all reagents were obtained commercially and used without further purification.
2. NMR spectra were recorded on a Bruker ARX 300 or Bruker AVANCE 400 spectrometer, operating at 300 MHz or 400 MHz for ^{1}H NMR, 75 MHz or 100 MHz for ^{13}C NMR were reported downfield from $CDCl_3$ (δ: 7.27 ppm) for ^{1}H NMR. For ^{13}C NMR, chemical shifts were reported in the scale relative to the solvent of $CDCl_3$ (δ: 77.0 ppm) used as an internal reference.
3. Mass spectra were in general recorded on an AMD 402/3 or a HP 5989A mass selective detector.
4. Column chromatographies were performed with silica gel (200-300 mesh ASTM).
5. Melting points. Melting points were measured on a SGW® X-4 melting point apparatus using open glass capillaries and are uncorrected.
6. IR spectra. IR spectra were recorded on a Nicolet 6700 spectrometer as thin film. Absorptions are given in wavenumbers (cm^{-1}).

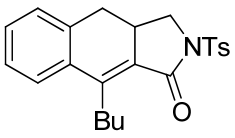
General procedure for the Rh(I)-catalyzed reaction of 2-Bromophenyl boronic Acids 1 with 1,6-Enynes 2: 1,6-Enynes **2** (0.3 mmol), 2-Bromophenyl boronic Acids **1** (90.4mg, 0.45 mmol), $Rh(CO)_2(acac)$ (7.8 mg, 10 mol%), PPh_3 (15.7 mg, 20 mol%) and K_2CO_3 (49.8 mg, 0.36 mmol) were added to 1,4-dioxane/H_2O (20/1, 3 mL) in Schlenk tube. The mixture was stirred at 100 °C and monitored by TLC. When the starting material was disappeared the reaction was cooled to room temperature. The contents were transferred to a round-bottom flask, and volatiles were removed in vacuo. The residue was subjected to column chromatography on silica-gel (hexane: ethyl acetate = 1:20 to 1:5) to give the product **3**.



3a

Light yellow liquid; 52.9 mg, 73% yield.

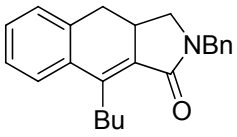
^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94 (t, *J* = 6.8 Hz, 3H), 1.40-1.52 (m, 4H), 2.68 (t, *J* = 15.2 Hz, 1H), 2.91-2.99 (m, 2H), 3.18-3.29 (m, 1H), 3.37-3.44 (m, 1H), 3.97 (t, *J* = 8.8 Hz, 1H), 4.67 (t, *J* = 8.8 Hz, 1H), 7.25-7.36 (m, 3H), 7.57 (d, *J* = 6.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 13.88, 22.76, 25.86, 31.76, 33.03, 35.05, 71.18, 121.43, 125.68, 127.30, 128.38, 129.48, 134.46, 135.70, 149.09, 169.80; **MS** (EI, m/z): 242 (M^+, 23), 228 (48), 200 (61), 174 (11), 160 (33), 103 (32); HRMS Calcd for $C_{16}H_{18}O_2$ 242.1307, Found 242.1308; **IR** (thin film): 3061, 2956, 2926, 2869, 2857, 1742, 1645, 1455, 1377, 1224, 1183, 1049, 1006, 766, 735, 702 cm^{-1}.



3b

White solid; Melting point: 139-141 ^oC; 75.8 mg, 64% yield.

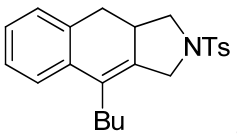
^{1}H NMR (300 MHz, $CDCl_3$): δ 0.80 (t, *J* = 7.2 Hz, 3H), 1.30-1.54 (m, 4H), 2.37 (s, 3H), 2.50 (t, *J* = 15.0 Hz, 1H), 2.83-2.94 (m, 3H), 3.09-3.17 (m, 1H), 3.31 (dd, *J* = 8.4 Hz, *J* = 9.3 Hz, 1H), 4.23 (dd, *J* = 8.4 Hz, *J* = 9.3 Hz, 1H), 7.12-7.29 (m, 5H), 7.41-7.44 (m, 1H), 7.90-7.94 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 13.89, 21.66, 22.84, 26.01, 31.65, 31.82, 33.59, 50.41, 125.24, 125.65, 127.32, 128.10, 128.26, 129.37, 129.63, 134.36, 135.44, 135.72, 144.87, 148.78, 165.72; **MS** (EI, m/z): 395 (M^+, 91), 338 (52), 171 (34), 143 (12), 103 (26); HRMS Calcd for $C_{23}H_{25}NO_3S$ 395.1555, Found 395.1553; **IR** (thin film): 3126, 2951, 2922, 2864, 1712, 1644, 1352, 1187, 1168, 1123, 1090, 772, 660, 594, 551, 542 cm^{-1}.



3c

Yellow liquid; 68.5 mg, 69% yield.

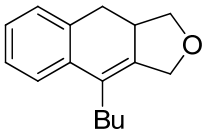
^{1}H NMR (400 MHz, $CDCl_3$): δ 0.98 (t, *J* = 7.2 Hz, 3H), 1.44-1.69 (m, 4H), 2.57 (t, *J* = 16.4 Hz, 1H), 2.85-3.05 (m, 4H), 3.51-3.60 (m, 2H), 4.53 (d, *J* = 14.8 Hz, 1H), 4.70 (d, *J* = 14.8 Hz, 1H), 7.20-7.38 (m, 8H), 7.55 (d, *J* = 7.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 14.05, 22.97, 25.46, 32.02, 32.11, 34.08, 46.91, 50.38, 125.11, 127.05, 127.54, 128.09, 128.11, 128.27, 128.32, 128.71, 135.37, 135.92, 136.78, 142.11, 168.25; **MS** (EI, m/z): 331 (M^+, 13), 184 (54), 129 (11), 91 (53); HRMS Calcd for $C_{23}H_{25}NO$ 331.1936, Found 331.1939; **IR** (thin film): 3086, 3067, 3029, 2955, 2927, 2868, 1673, 1648, 1493, 1484, 1453, 1418, 1356, 1266, 1244, 1195, 762, 731, 701, 521 cm^{-1}.



3d

White solid; Melting point: 135-137 ^oC; 70.8 mg, 62% yield.

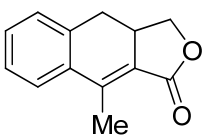
^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91 (t, *J* = 7.2 Hz, 3H), 1.31-1.42 (m, 4H), 2.20-2.28 (m, 1H), 2.39-2.47 (m, 5H), 2.76-2.81 (m, 2H), 2.85-2.99 (m, 1H), 3.92 (d, *J* = 15.6 Hz, 1H), 3.96 (t, *J* = 8.0 Hz, 1H), 4.25 (d, *J* = 15.6 Hz, 1H), 7.07-7.12 (m, 2H), 7.18-7.22 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 14.01, 21.59, 22.86, 29.10, 30.55, 32.81, 38.40, 50.15, 54.89, 122.83, 126.65, 126.85, 127.77, 127.93, 129.33, 129.78, 132.94, 134.51, 134.69, 135.17, 143.75; **MS** (EI, m/z): 381 (M^+, 28), 368 (63), 312 (45), 224 (9), 170 (34); HRMS Calcd for $C_{23}H_{27}NO_2S$ 381.1762, Found 381.1766; **IR** (thin film): 3059, 3021, 2950, 2849, 1922, 1599, 1481, 1451, 1339, 1169, 1096, 1060, 1028, 968, 935, 816, 767, 712 cm^{-1}.



3e

Light yellow liquid; 31.4 mg, 46% yield.

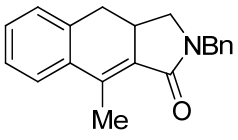
^{1}H NMR (400 MHz, $CDCl_3$): δ 0.93 (t, *J* = 7.2 Hz, 1H), 1.35-1.51 (m, 4H), 2.23-2.30 (m, 1H), 2.47-2.52 (m, 1H), 2.56 (t, *J* = 15.2 Hz, 1H), 2.85 (dd, *J* = 6.0 Hz, *J* = 15.2 Hz, 1H), 2.90-3.00 (m, 1H), 3.52 (t, *J* = 8.4 Hz, 1H), 4.38 (t, *J* = 8.4 Hz, 1H), 4.53 (d, *J* = 14.0 Hz, 1H), 4.64 (d, *J* = 14.0 Hz, 1H), 7.12-7.28 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 14.00, 22.82, 29.28, 30.66, 32.06, 39.71, 69.14, 75.20, 122.71, 126.33, 126.66, 126.87, 127.97, 135.16, 135.65, 139.83; **MS** (EI, m/z): 228 (M^+, 10), 171 (44), 159 (20), 147 (13), 131 (8), 103 (21); HRMS Calcd for $C_{16}H_{20}O$ 228.1514, Found 228.1516; **IR** (thin film): 3068, 3024, 2957, 2930, 2870, 1724, 1456, 1174, 1054, 919, 758 cm^{-1}.



3f

Light yellow solid; Melting point: 120-122 ^oC; 41.8 mg, 70% yield.

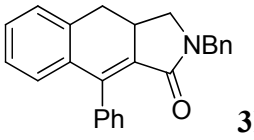
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.50 (s, 3H), 2.63 (t, *J* = 15.0 Hz, 1H), 2.90 (dd, *J* = 8.4 Hz, *J* = 15.0 Hz, 1H), 3.14-3.22 (m, 1H), 3.90 (t, *J* = 8.7 Hz, 1H), 4.60 (t, *J* = 8.7 Hz, 1H), 7.15-7.29 (m, 3H), 7.47-7.50 (m, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 13.01, 32.84, 35.14, 121.76, 125.72, 127.42, 128.16, 129.64, 135.17, 135.69, 144.19, 170.21; **MS** (EI, m/z): 200 (M^+, 21), 171 (18), 143 (9), 117 (18); HRMS Calcd for $C_{13}H_{12}O_2$ 200.0837, Found 200.0835; **IR** (thin film): 3102, 3059, 3021, 2986, 2935, 2899, 2833, 1739, 1649, 1451, 1432, 1376, 1319, 1227, 1184, 1113, 1019, 775, 733, 519 cm^{-1}.



3g

Orange liquid; 64.8 mg, 75% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.59 (t, *J* = 16.4 Hz, 1H), 2.65 (s, 3H), 2.87-2.93 (m, 2H), 2.98 (t, *J* = 8.4 Hz, 1H), 3.54 (t, *J* = 8.4 Hz, 1H), 4.52 (d, *J* = 14.8 Hz, 1H), 4.70 (d, *J* = 14.8 Hz, 1H), 7.20-7.38 (m, 8H), 7.53 (d, *J* = 7.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 12.46, 32.08, 33.83, 46.92, 50.50, 125.07, 127.14, 127.57, 127.85, 128.29, 128.50, 128.73, 135.37, 136.56, 136.70, 137.14, 168.57; **MS** (EI, m/z): 289 (M^+, 20), 198 (37), 185 (29), 91 (85); HRMS Calcd for $C_{20}H_{19}NO$ 289.1467, Found 289.1465; **IR** (thin film): 3086, 3062, 3029, 2920, 2873, 2828, 2242, 1679, 1651, 1493, 1484, 1452, 1420, 1356, 1269, 1244, 1198, 1072, 988, 926, 764, 729, 703, 519 cm^{-1}.

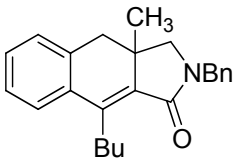


3h

White solid; Melting point: 134-136 ^oC; 57.7 mg, 55% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.79 (t, *J* =15.6 Hz, 1H), 2.98-3.05 (m, 2H), 3.09-3.19 (m, 1H), 3.63 (t, *J* = 8.8 Hz, 1H), 4.40 (d, *J* = 14.4 Hz, 1H), 4.68 (d, *J* = 14.4 Hz, 1H), 6.96 (d,

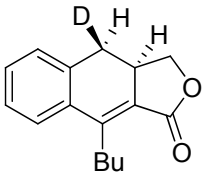
J = 7.6 Hz, 1H), 7.15-7.48 (m, 13H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 32.28, 33.94, 47.00, 50.34, 126.99, 127.57, 127.66, 127.79, 128.28, 128.46, 128.68, 129.26, 135.47, 135.60, 136.58, 141.03, 166,58; **MS** (EI, m/z): 351 (M^+,17), 260 (63), 183 (11), 91 (53); HRMS Calcd for $C_{25}H_{21}NO$ 351.1623, Found 351.1626; **IR** (thin film): 3050, 3025, 2905, 2864, 1674, 1480, 1414, 1269, 1247, 1192, 1080, 760, 701 cm^{-1}.



3i

White solid; Melting Point: 70-72 ^{o}C; 48.6 mg, 47% yield.

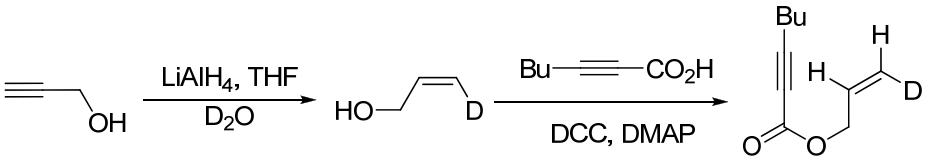
^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (s, 3H), 0.96 (t, *J* = 7.2 Hz, 3H), 1.42-1.64 (m, 4H), 2.71 (d, *J* = 14.8 Hz, 1H), 2.83 (d, *J* = 14.8 Hz, 1H), 2.96-3.04 (m, 1H), 3.10 (t, *J* = 10.4Hz, 2H), 3.49-3.56 (m, 1H), 4.45 (d, *J* = 14.8 Hz, 1H), 4.78 (d, *J* = 14.8 Hz, 1H), 7.18-7.38 (m, 8H), 7.54 (d, *J* = 7.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 14.05, 22.93, 25.47, 28.72, 32.14, 34.67, 40.80, 46.83, 58.25, 125.18, 126.94, 127.51, 128.22, 128.68, 128.78, 132.96, 134.18, 135.29, 136.82, 141.29, 167.82; **MS** (EI, m/z): 345 (M^+, 39), 254 (24), 227 (17), 187 (9), 129 (26), 91 (78); HRMS Calcd for $C_{24}H_{27}NO$ 345.2093, Found 345.2091; **IR** (thin film): 3112, 3061, 2955, 2909, 2855, 1672, 1640, 1491, 1420, 1271, 1188, 765, 707 cm^{-1}.



(*cis*)-3a-*d*

Light yellow liquid; 53.2 mg, 73% yield.

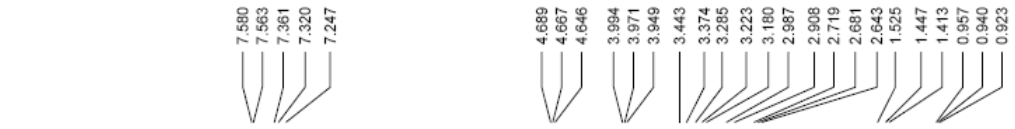
^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94 (t, *J* = 7.2 Hz, 3H), 1.41-1.49 (m, 4H), 2.91-2.97 (m, 2H), 3.23 (d, *J* = 7.6 Hz, 1H), 3.38-3.45 (m, 1H), 3.97 (t, *J* = 9.2 Hz, 1H), 4.67 (t, *J* = 8.8 Hz, 1H), 7.24-7.37 (m, 3H), 7.56-7.58 (m, 1H); **MS** (ESI, m/z): 244 ($M+H^+$).

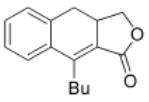


(*Z*)-2a-*d*

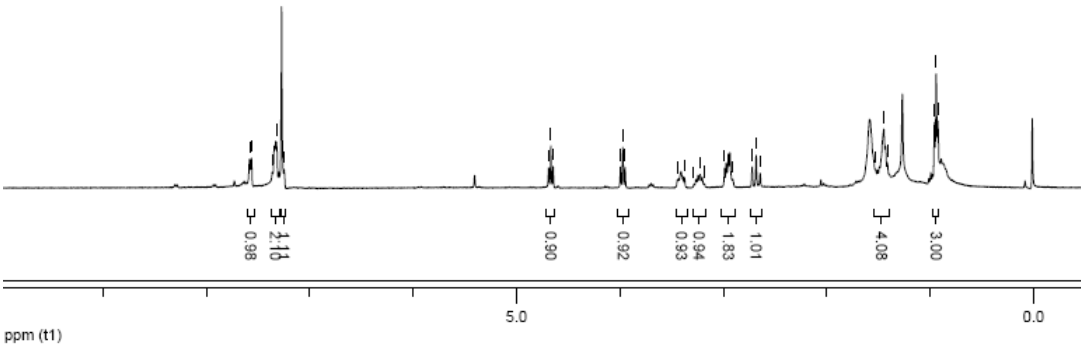
Synthesis the deuterium-labeled substrate (*Z*)-2a-*d*: Propargyl alcohol (1 g, 17.8 mmol) was added drop wise at 0°C to a stirred solution of lithium aluminium hydride (0.88 g, 23.2 mmol) in THF (30 ml). After 3 h a mixture of THF (2 ml) and deuterium oxide (1 mL) was added carefully until hydrogen gas ceased to evolve.[1] The mixture was filtered, the insoluble material washed with CH_2Cl_2 (30 mL) and the combined filtrate added to 2-heptynoic acid (2.24 g, 17.8 mmol). A solution of 1,3-dicyclohexylcarbodiimide (3.68 g, 17.8 mmol) and 4-(dimethylamino)pyridine (20 mg) in CH_2Cl_2 (10 mL) was then added slowly with vigorous strirring. The reaction mixture was stirred at room temperature for 10 h. After the reaction was complete, the white solid was filtered off and the solvent was removed in vacuo. The residue was then submitted to column chromatography on silica gel (petroleum ether:ethyl acetate 50:1) to afford an oil (1.5 g, 51% yield).

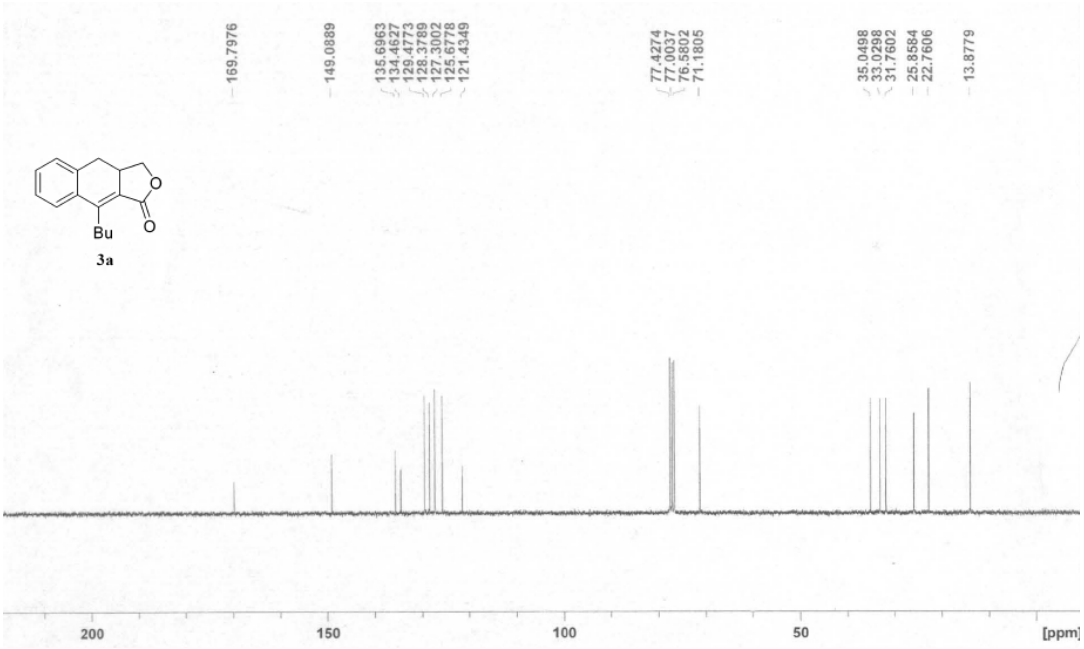
[1] Nieschalk, J.; O'Hagan, D. *Tetrahedron: Asymmetry,* **1997**, *8*, 2325-2330.





3a





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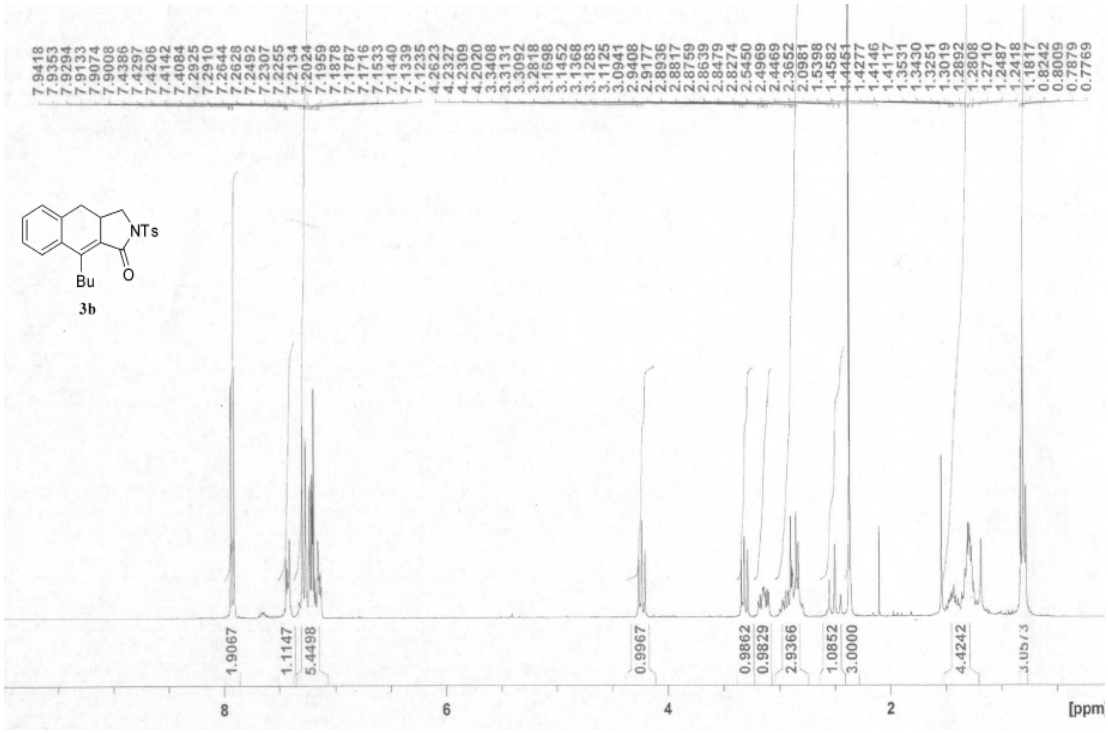
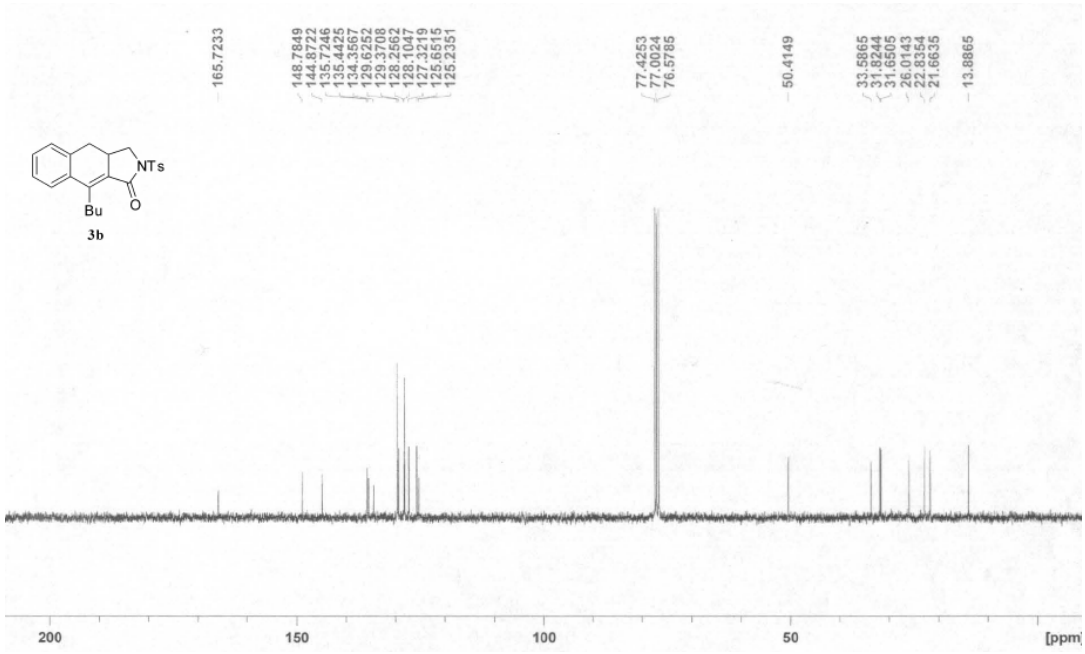
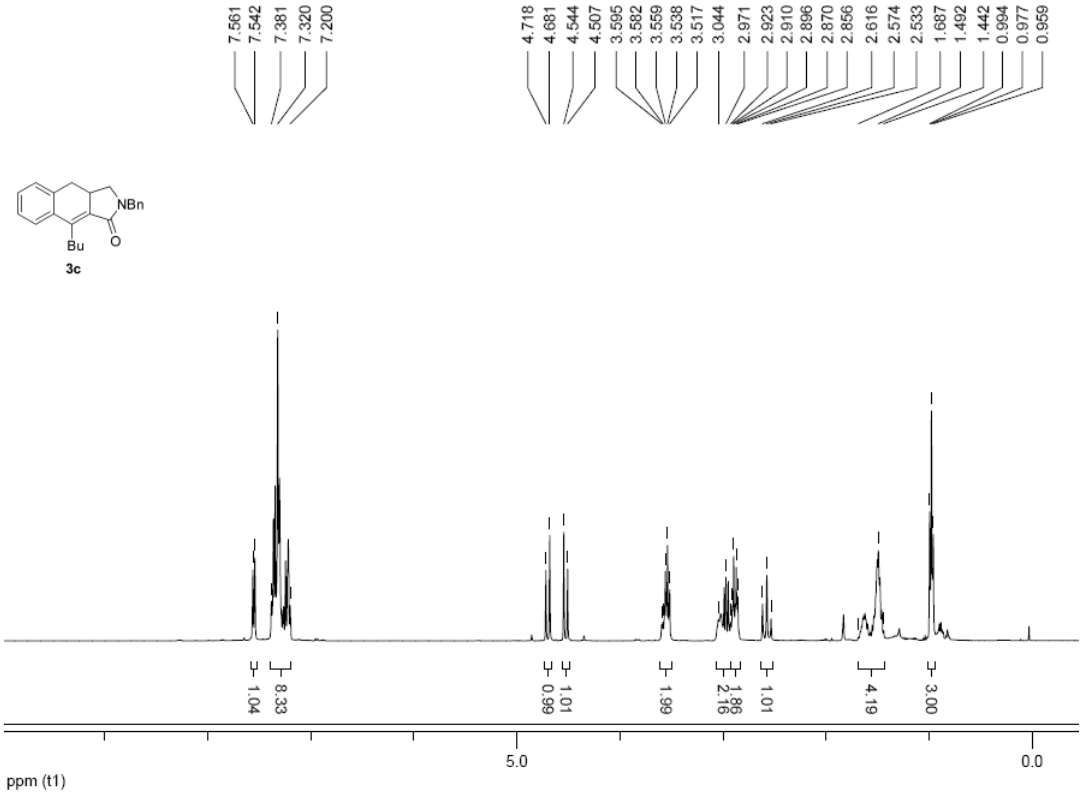
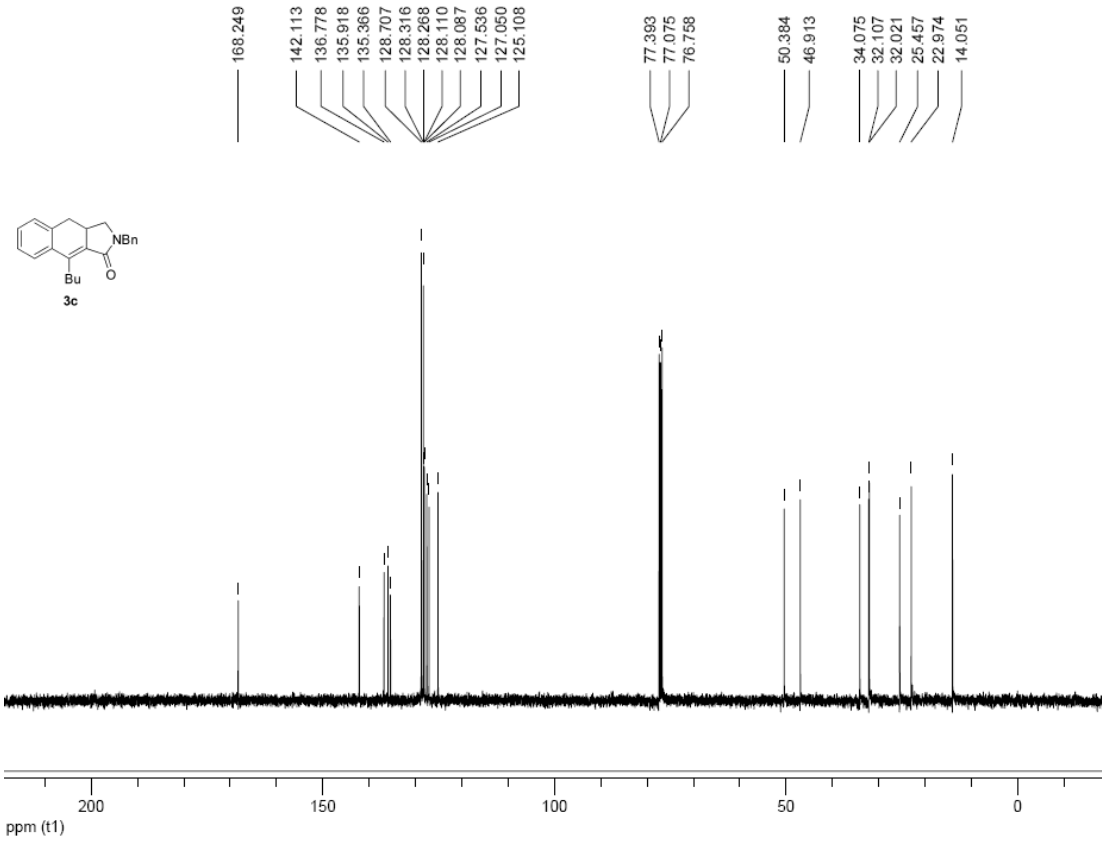
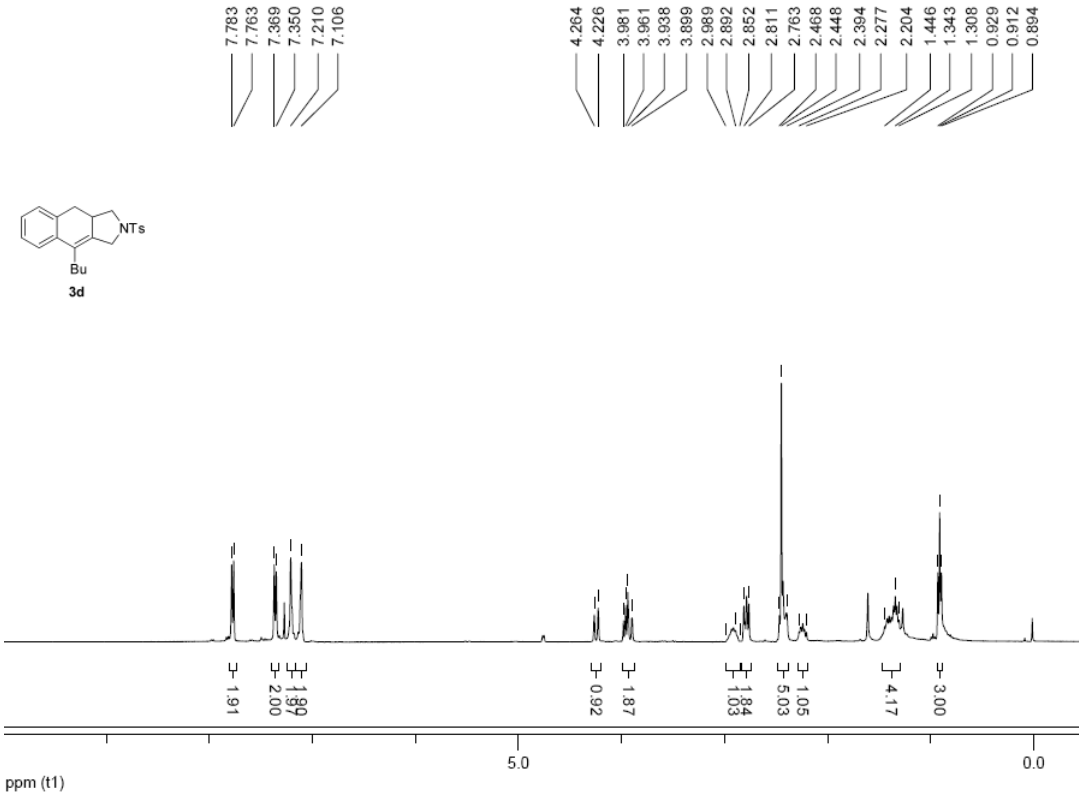
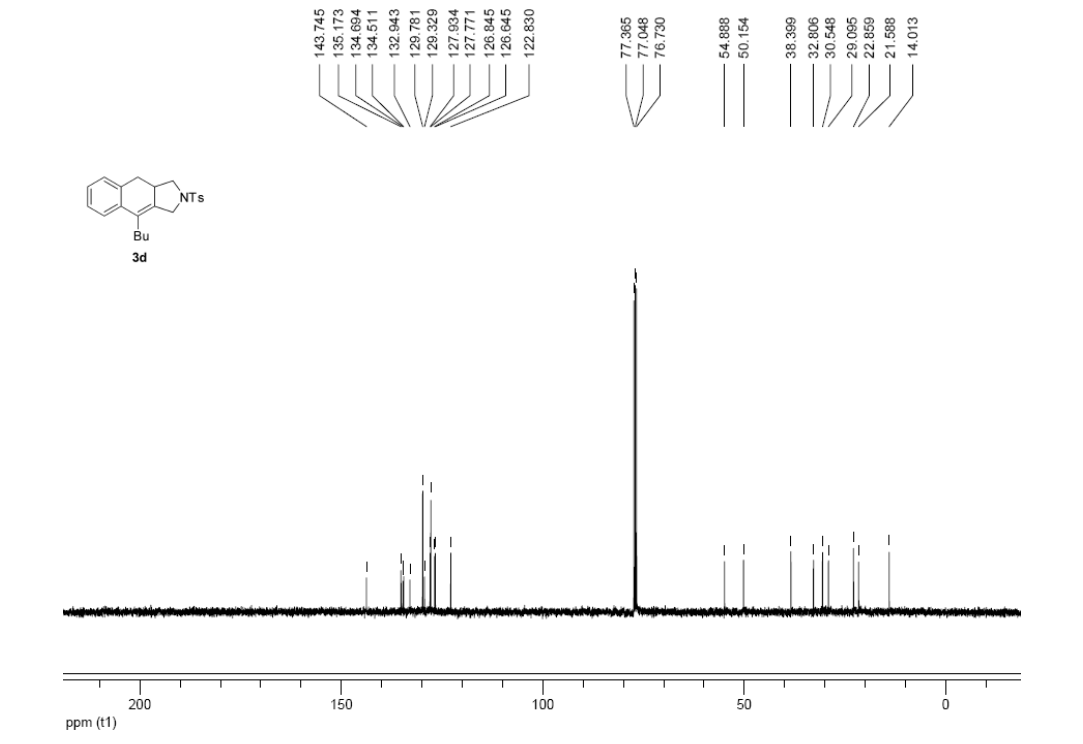


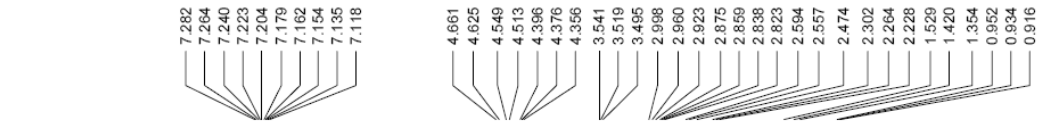


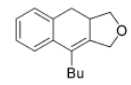




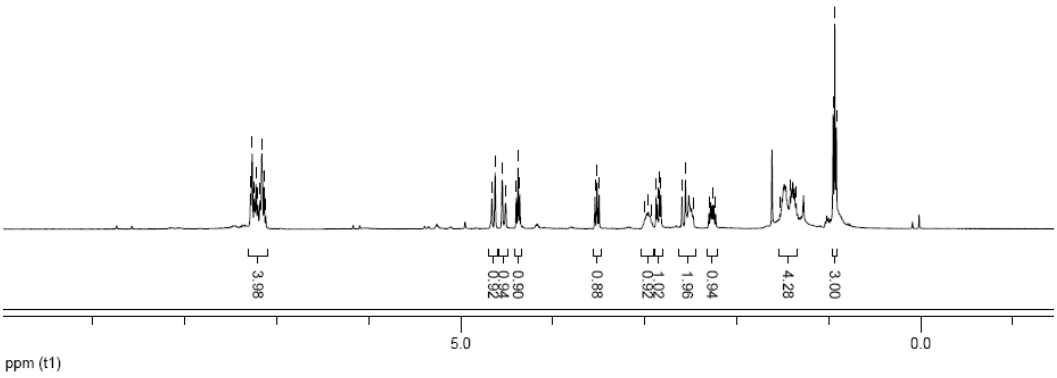


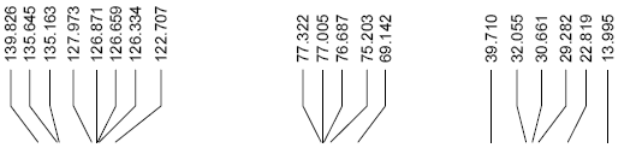


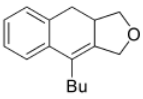




3e







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