

Rh-Catalyzed Decarbonylative Coupling with Alkynes via C–C Activation of Isatins

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Table of Contents

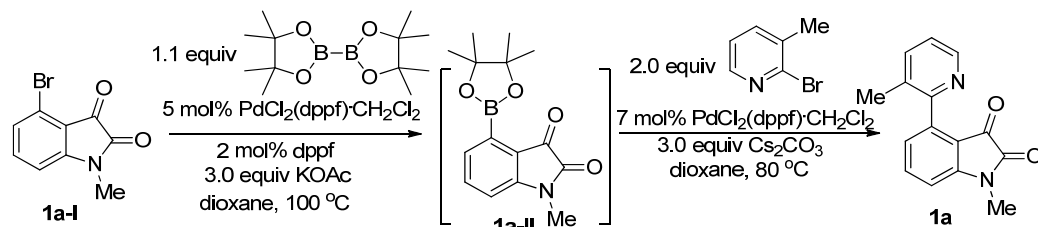
General information	S2
Preparation of starting materials	S3-S11
Decarbonylative ‘cut and sew’ reactions	S12-S24
Preparation of intermediates	S24-S25
X-Ray data	S26-S29
Spectra	S30-S60

Supporting Information

Materials: THF, dioxane and toluene were purchased from Fischer Scientific and distilled freshly over sodium. PhCl was purchased from Alfa Aesar and distilled freshly over P₂O₅ and freeze-pump-thawed. Other commercially available chemicals were purchased and used without additional purification unless noted otherwise. All reactions were carried out under nitrogen with stirring bar in a rubber septum sealed flask. Reaction temperatures were reported as the temperatures of the bath surrounding the flasks or vials. Sensitive reagents and solvents were transferred under nitrogen into a nitrogen-filled glove-box with standard techniques. Analytical thin-layer chromatography (TLC) was carried out using 0.2 mm commercial silica gel plates (silica gel 60, F254, EMD chemical). Vials (15 x 45 mm 1 dram (4 mL) / 27.75 x 95 mm 10 dram (40 mL) with PTFE lined cap attached) were purchased from Qorpak and flame-dried or put in an oven overnight and cooled in a dessicator. High-resolution mass spectra (HRSM) were obtained on a Karatos MS9 and are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion [M+Na]⁺, [M+H]⁺, [M-H]⁻ or [M]⁺. Infrared spectra were recorded on a Nicolet 380 FTIR using neat thin film technique. Nuclear magnetic resonance spectra (¹H NMR and ¹³C NMR) were recorded with a Varian Gemini (400 MHz, ¹H at 400 MHz, ¹³C at 100 MHz). Unless otherwise noted, all spectra were acquired in CDCl₃. Chemical shifts are reported in parts per million (ppm, δ), downfield from tetramethylsilane (TMS, δ = 0.00 ppm) and are referenced to residual solvent (CDCl₃, δ=7.26 ppm (¹H) and 77.00 ppm (¹³C)). Coupling constants were reported in Hertz (Hz). Data for ¹H NMR spectra were reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets, m = multiplet, coupling constant (Hz), and integration).

Preparation of starting materials 1.

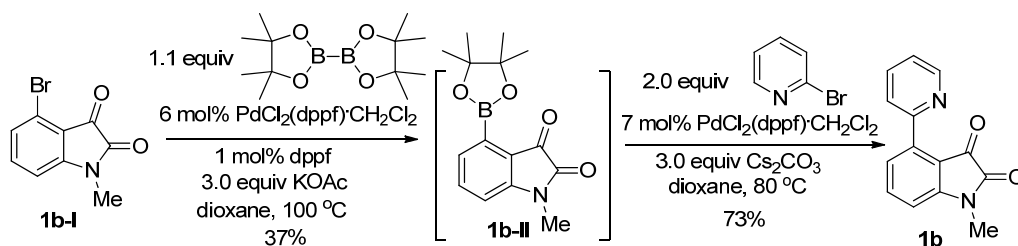
(1) Synthesis of 1-methyl-4-(3-methylpyridin-2-yl)-isatin **1a**. (zr-4-15, 17)



Typical Procedure 1 for Boronation and Suzuki Coupling: To a dried flask were added 4-bromo-1-methyl-isatin (3.60 g, 15 mmol), bis(pinacolato)diboron (4.07 g, 16 mmol), $\text{Pd}(\text{dppf})\text{Cl}_2 \cdot \text{CH}_2\text{Cl}_2$ (612.9 mg, 0.075 mmol, 5 mol%), KOAc (4.44 g, 45 mmol), dppf (166.0 mg, 0.3 mmol), and dioxane (150 mL) under a nitrogen atmosphere. The resulting mixture was stirred at 100 °C for 33 h, then filtered through celite, washed with ethyl acetate, and evaporated to afford the crude product. Flash chromatograph (eluent: hexane/ethyl acetate = 3/1 to 2/1) afforded compound **1a-II** (3.6606 g), which was used for next step directly.

To a dried flask were added compound **1a-II** (3.66 g, 12.8 mmol), 2-bromo-3-methylpyridine (2.8 mL, $d = 1.544$, 25.5 mmol), Cs_2CO_3 (5.70 g, 38.4 mmol), and $\text{Pd}(\text{dppf})\text{Cl}_2 \cdot \text{CH}_2\text{Cl}_2$ (612.9 mg, 0.075 mmol, 5 mol%) in dioxane (150 mL) under a nitrogen atmosphere. The resulting mixture was stirred at 80 °C for 39 h, then filtered through celite, washed with ethyl acetate, and evaporated to afford the crude product. Flash chromatograph (eluent: toluene/ethyl acetate = 1.5/1 to hexane/ethyl acetate = 1/2) afforded compound **1a** (1.49 g, 39% for 2 steps): Red solid; mp: 198-200 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.50 (d, $J = 4.5$ Hz, 1 H, Ar-H), 7.67 (t, $J = 7.9$ Hz, 1 H, Ar-H), 7.62 (d, $J = 7.7$ Hz, 1 H, Ar-H), 7.33-7.22 (m, 1 H, Ar-H), 7.09 (d, $J = 7.8$ Hz, 1 H, Ar-H), 6.94 (d, $J = 7.9$ Hz, 1 H, Ar-H), 3.29 (s, 3 H, CH_3), 2.15 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 182.0, 157.7, 154.1, 151.3, 146.8, 140.2, 138.0, 137.8, 131.8, 125.3, 123.3, 114.9, 109.4, 26.3, 18.6; IR ν (neat, cm^{-1}) 2930, 1727, 1596, 1442, 1354, 1303, 1088, 1038; HRMS (ESI) for $\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_2$ (MW = 253, $(\text{M}+\text{H})^+$): 253.0972. Found: 253.0974.

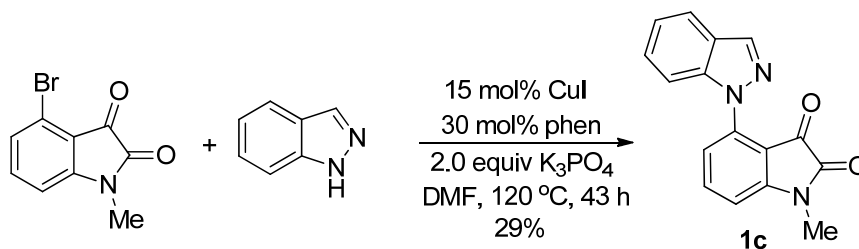
(2) Synthesis of 1-methyl-4-(pyridin-2-yl)-isatin **1b**. (zr-3-36, 44)



Following Typical Procedure 1, the reaction of 4-bromo-1-methyl-isatin (361.1 mg, 1.5 mmol), bis(pinacolato)diboron (407.8 mg, 1.6 mmol), Pd(dppf)Cl₂·CH₂Cl₂ (66.1 mg, 0.09 mmol, 6 mol%), dppf (7.2 mg, 1 mol%), and KOAc (444.1 mg, 4.5 mmol) in dioxane (10 mL) afforded **1b-II** (164.3 mg, 37%) (flash chromatograph eluent: hexane/ethyl acetate = 2/1 to 1/1), which was used for next step directly.

The reaction of **1b-II** (164.3 mg, 0.57 mmol), 2-bromopyridine (109 μ L, 180.6 mg, 1.14 mmol, $d = 1.657$), Cs₂CO₃ (254.9 mg, 1.7 mmol), and Pd(dppf)Cl₂·CH₂Cl₂ (33.1 mg, 0.4 mmol, 7 mol%) in dioxane (4 mL) afforded **1b** (99.4 mg, 73%) (flash chromatograph eluent: hexane/ethyl acetate = 1/1 to 1/2): Red solid; mp: 187-189 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.77 – 8.69 (m, 1H), 7.84-7.78 (m, 2 H, Ar-H), 7.68 (t, $J = 8.0$ Hz, 1 H, Ar-H), 7.52 (dd, $J_1 = 8.0$ Hz, $J_2 = 0.9$ Hz, 1 H, Ar-H), 7.39-7.31 (m, 1 H, Ar-H), 6.94 (dt, $J_1 = 8.0$ Hz, $J_2 = 0.9$ Hz, 1 H, Ar-H), 3.30 (s, 3 H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 182.0, 157.6, 153.2, 151.9, 149.7, 141.0, 137.9, 136.0, 125.8, 124.8, 123.6, 113.7, 109.7, 26.3; IR ν (neat, cm⁻¹) 3059, 1737, 1589, 1566, 1460, 1431, 1357, 1321, 1205, 1102, 1090; HRMS (CI) for C₁₄H₁₀N₂O₂ (MW = 238, M⁺): 238.0742. Found: 238.0744.

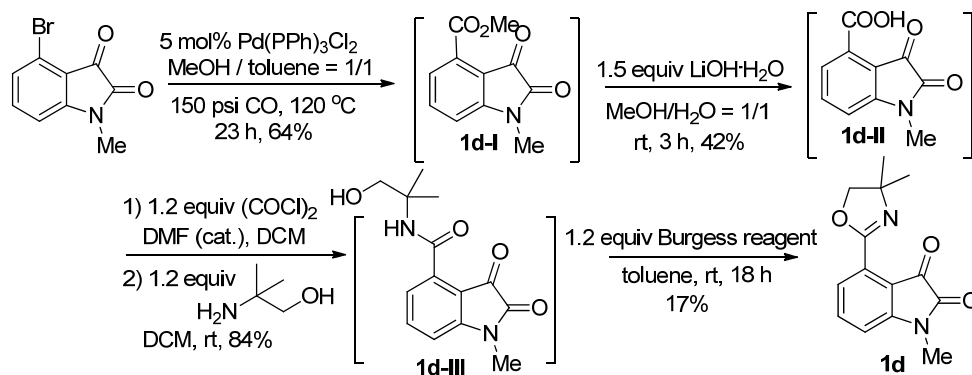
(3) Synthesis of 4-(1*H*-indazol-1-yl)-1-methyl-isatin **1c**. (zr-5-42)



To a 40 mL vial were added 4-bromo-1-methyl-isatin (360.2 mg, 1.5 mmol), CuI (47.7 mg, 0.25 mmol), phen (81.2 mg, 0.45 mmol), K₃PO₄ (633.8 mg, 3 mmol),

1*H*-indazole (265.5 mg, 2.25 mmol), and DMF (7.5 mL). The resulting mixture was stirred at 120 °C for 43 h, filtered through celite, evaporated to afford the crude product. Flash chromatograph (eluent: hexane/ethyl acetate/DCM = 3/1/1 to 2/1/1 to 1/1/0.5) afforded compound **1c** (122.1 mg, 29%): Red solid; mp: 248-251 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.29 (d, *J* = 0.9 Hz, 1 H, Ar-H), 7.86-7.81 (m, 1 H, Ar-H), 7.74 (t, *J* = 8.2 Hz, 1 H, Ar-H), 7.47-7.41 (m, 1 H, Ar-H), 7.39 (dd, *J*₁ = 8.3 Hz, *J*₂ = 0.7 Hz, 1 H, Ar-H), 7.32-7.26 (m, 1 H, Ar-H), 7.23-7.18 (m, 1 H, Ar-H), 6.91 (dd, *J*₁ = 8.3 Hz, *J*₂ = 0.7 Hz, 1 H, Ar-H), 3.35 (s, 3 H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 179.3, 157.7, 152.1, 139.2, 138.9, 137.7, 137.3, 127.4, 125.5, 122.4, 121.5, 120.8, 111.5, 110.0, 107.9, 26.6; IR ν (neat, cm⁻¹) 3102, 3063, 1734, 1609, 1578, 1501, 1467, 1349, 1319, 1194, 1151, 1089; HRMS (ESI) for C₁₆H₁₂N₃O₂ (MW = 278, (M+H)⁺): 278.0924. Found: 278.0924.

(4) Synthesis of 4-(4',4'-dimethyl-4',5'-dihydrooxazol-2'-yl)-1-methyl-isatin **1d**.
(zr-6-77, 79, 80, 89)



To Q-Tube pressure tube reactor were added 4-bromo-1-methyl-isatin (1.68 g, 7 mmol), Pd(PPh₃)₂Cl₂ (251.1 mg, 0.36 mmol, 5 mol%), Et₃N (3 mL), toluene (10 mL), and MeOH (16 mL). The resulting mixture was degassed with CO three times, stirred at 120 °C for 23 h, filtered through celite, and evaporated to afford the crude product. Flash chromatograph (eluent: hexane/ethyl acetate = 2/1 to 1/1) afforded compound **1d-I** (0.99 g, 64%), which was used for next step directly.

To a flask were added **1d-I** (986.9 mg, 4.5 mmol), LiOH·H₂O (289.4 mg, 6.8 mmol), MeOH (20 mL), and H₂O (25 mL). The resulting mixture was stirred at room

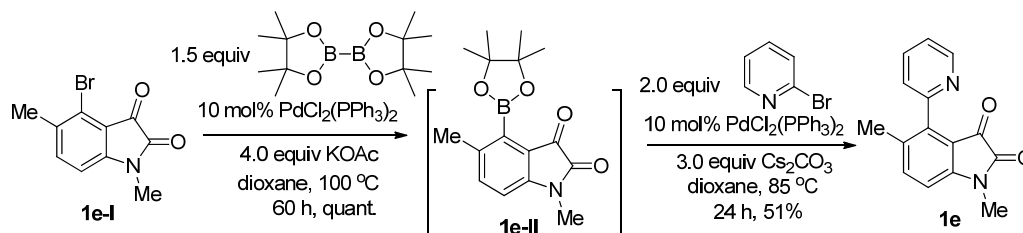
temperature for 3 h, quenched by adding HCl solution (1 N, 15 mL), extracted with ethyl acetate (30 mL $\times$ 3), and dried with MgSO₄. Evaporation and flash chromatograph (eluent: DCM/ethyl acetate = 2/1 to 1/4) afforded compound **1d-II** (383.9 mg, 42%), which was used for next step directly.

To a 40 mL vial were added **1d-II** (383.9 mg, 1.87 mmol), DCM (15 mL), DMF (2 drops), and oxalyl chloride (0.2 mL, $d = 1.488$, 2.3 mmol). The resulting mixture was stirred at room temperature and evaporated to afford the crude acyl chloride.

To a 40 mL vial were added 2-amino-2-methylpropan-1-ol (204.0 mg, 2.24 mmol), DCM (2 mL), Et₃N (0.5 mL, $d = 0.726$, 4 mmol), and the crude acyl chloride in DCM (5 mL). The resulting mixture was stirred at room temperature for 12.5 h and then evaporated to afford the crude product. Flash chromatograph (eluent: DCM/ethyl acetate = 1/1 to 1/2) afforded compound **1d-III** (435.5 mg, 84%), which was used for next step directly.

To a 40 mL vial were added **1d-III** (177.1 mg, 0.65 mmol), Burgess reagent (190.2 mg, 0.8 mmol, 1.2 equiv), and toluene (10 mL). The resulting mixture was stirred at room temperature for 18 h, filtered through celite, and evaporated to afford the crude mixture. Flash chromatograph (eluent: hexane/ethyl acetate = 1/1 to 1/1.5) afforded compound **1d** (28.8 mg, 17%) (rotamer ratio = 3/1): oil; ¹H NMR (500 MHz, CDCl₃) δ 7.60 and 7.38 (t, $J = 8.0$ Hz, 1 H, Ar-H), 7.44-7.40 (m, 1 H, Ar-H), 7.00-6.94 (m, 1 H, Ar-H), 4.20 and 4.19 (s, 2 H, CH₂), 3.25 and 3.20 (s, ratio = 3/1, 3 H, CH₃), 1.41 and 1.40 (s, 6 H, CH₃ $\times$ 2); ¹³C NMR (125 MHz, CDCl₃) δ 180.5, 172.4, 162.2, 159.9, 157.2, 151.7, 143.4, 137.5, 130.1, 128.4, 127.9, 124.6, 123.9, 122.7, 115.2, 111.70, 111.68, 91.8, 79.9, 79.5, 68.2, 67.5, 28.13, 28.09, 26.3, 26.1; IR ν (neat, cm⁻¹) 2969, 2931, 1743, 1735, 1729, 1720, 1647, 1641, 1604, 1466, 1366, 1312, 1206, 1110, 1080, 1026; HRMS (ESI) for C₁₄H₁₄N₂O₃Na (MW = 281, (M+Na)⁺): 281.0897. Found: 281.0900.

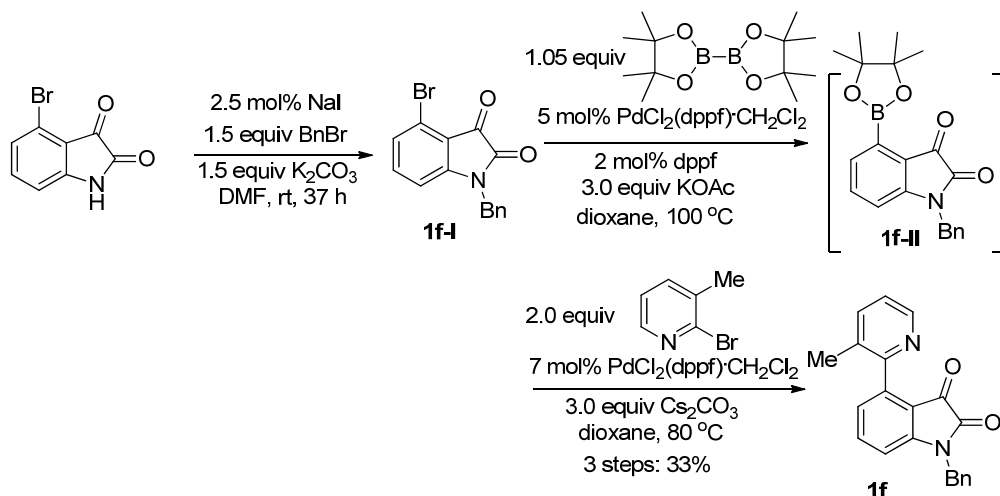
(5) Synthesis of 1,5-dimethyl-4-(pyridin-2-yl)-isatin **1e**. (zr-5-15, 22)



Following Typical Procedure 1, the reaction of 4-bromo-1,5-dimethyl-isatin (510.0 mg, 2 mmol), bis(pinacolato)diboron (762.2 mg, 3 mmol), Pd(PPh₃)₂Cl₂ (140.9 mg, 0.2 mmol, 10 mol%), and KOAc (789.9 mg, 8 mmol) in dioxane (20 mL) afforded **1e-II** (699.5 mg) (flash chromatograph eluent: hexane/ethyl acetate = 3/1 to 2/1), which was used for next step directly.

The reaction of **1e-II** (241.1 mg, 0.8 mmol), 2-bromo-pyridine (152.9 mg, 1.6 mmol), Cs₂CO₃ (789.4 mg, 2.4 mmol), and Pd(PPh₃)₂Cl₂ (56.1 mg, 0.08 mmol, 10 mol%) in dioxane (10 mL) afforded **1e** (102.0 mg, 51%) (flash chromatograph eluent: hexane/ethyl acetate = 1/1 to 1/2): Red solid; mp: 160-162 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.71 (d, *J* = 4.8 Hz, 1 H, Ar-H), 7.80 (t, *J* = 7.6 Hz, 1 H, Ar-H), 7.49 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.35 (dd, *J*₁ = 6.8 Hz, *J*₂ = 5.7 Hz, 1 H, Ar-H), 7.29 (t, *J* = 6.4 Hz, 1 H, Ar-H), 6.84 (d, *J* = 8.0 Hz, 1 H, Ar-H), 3.25 (s, 3 H, CH₃), 2.11 (s, 3 H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 182.2, 157.8, 154.3, 149.6, 149.5, 139.6, 139.4, 136.2, 132.5, 124.2, 122.9, 115.0, 109.5, 26.2, 18.7; IR ν(neat, cm⁻¹) 3057, 2931, 1736, 1640, 1598, 1474, 1348, 1312, 1113; HRMS (ESI) for C₁₅H₁₃N₂O₂ (MW = 253, (M+H)⁺): 253.0972. Found: 253.0971.

(6) Synthesis of 1-benzyl-4-(pyridin-2-yl)-isatin **1f**. (zr-4-41, 49, 73)



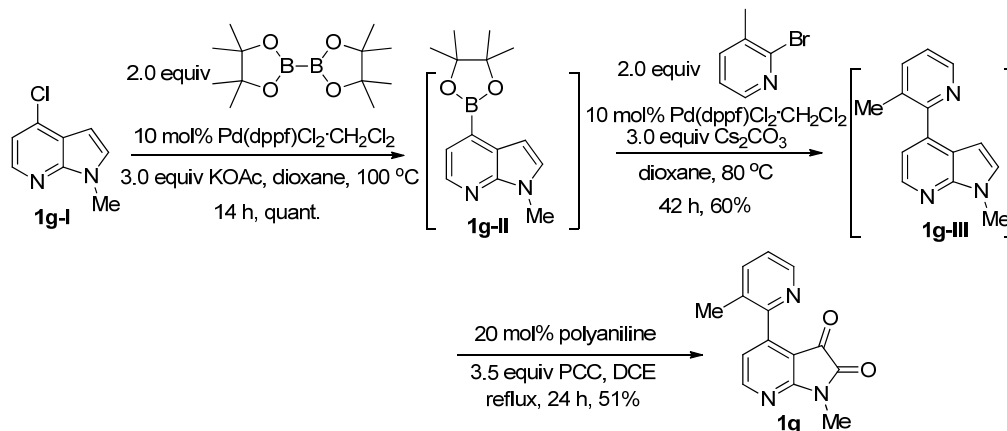
To a 40 mL vial were added 4-bromo-isatin (1.82 g, 8 mmol), K₂CO₃ (1.66 g, 12 mmol), NaI (30.3 mg, 0.2 mmol), DMF (20 mL), and BnBr (1.4 mL, *d* = 1.438, 12 mmol). The resulting mixture was stirred at room temperature for 33 h, then quenched with H₂O (40 mL), filtered through silica gel, extracted with DCM (40 mL × 4), dried with MgSO₄. Evaporation afforded the crude product **1f-I**, which was used for next step directly.

Following Typical Procedure 1, the reaction of **1f-I**, bis(pinacolato)diboron (2.16 g, 8.5 mmol), Pd(dppf)Cl₂·CH₂Cl₂ (326.8 mg, 0.4 mmol, 5 mol%), dppf (55.4 mg, 0.1 mmol), and KOAc (2.35 g, 24 mmol) in dioxane (80 mL) afforded **1f-II** (flash chromatograph eluent: hexane/ethyl acetate = 2/1 to 1/1 to 1/2), which was used for next step directly.

The reaction of **1f-II**, 2-bromo-3-methylpyridine (1.8 mL, *d* = 1.544, 16 mmol), Cs₂CO₃ (3.55 g, 24 mmol), and Pd(dppf)Cl₂·CH₂Cl₂ (408.5 mg, 0.5 mmol, 6 mol%) in dioxane (120 mL) afforded **1f** (866.6 mg, 33% for 3 steps) (flash chromatograph eluent: hexane/ethyl acetate = 3/1 to 2/1 to 1/1): Red solid; mp: 199-201 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.49 (dd, *J*₁ = 4.8 Hz, *J*₂ = 1.2 Hz, 1 H, Ar-H), 7.65-7.59 (m, 1 H, Ar-H), 7.53 (t, *J* = 7.8 Hz, 1 H, Ar-H), 7.40-7.24 (m, 6 H, Ar-H), 7.04 (dd, *J*₁ = 7.8 Hz, *J*₂ = 0.7 Hz, 1 H, Ar-H), 6.83-6.79 (m, 1 H, Ar-H), 4.97 (brs, 2 H, CH₂), 2.16 (s, 3 H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 181.9, 157.8, 154.1, 150.6, 146.8, 140.3, 137.90, 137.87, 134.4, 131.8, 129.0, 128.1, 127.3, 125.3, 123.4, 115.1, 110.5, 44.0, 18.6; IR *ν* (neat, cm⁻¹) 3058, 2923, 1737, 1595, 1496, 1445, 1333, 1235, 1082; HRMS (ESI) for

C₂₁H₁₇N₂O₂ (MW = 329, (M+H)⁺): 329.1285. Found: 329.1288.

(7) Synthesis of 1-methyl-4-(3-methylpyridin-2-yl)-7-aza-isatin **1g**. (zr-6-36, 44, 50)



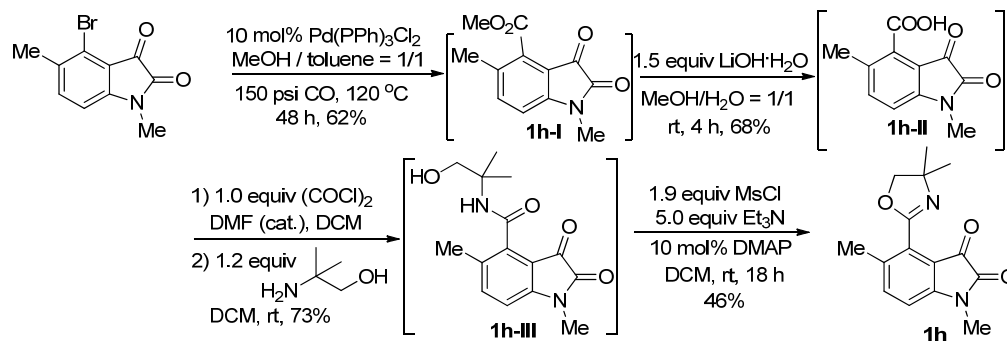
Following Typical Procedure 1, the reaction of 4-chloro-1-methyl-7-aza-indole (228.9 mg, 1.5 mmol), bis(pinacolato)diboron (762.1 mg, 3 mmol), Pd(dppf)Cl₂·CH₂Cl₂ (122.2 mg, 0.15 mmol, 10 mol%), and KOAc (441.3 mg, 4.5 mmol) in dioxane (12 mL) afforded **1g-II** (386.4 mg, quant.) (flash chromatograph eluent: hexane/ethyl acetate = 2/1), which was used for next step directly.

The reaction of **1g-II** (334.2 mg, 1.3 mmol), 2-bromo-3-methylpyridine (447.7 mg, 2.6 mmol), Cs₂CO₃ (1.27 g, 3.9 mmol), and Pd(dppf)Cl₂·CH₂Cl₂ (106.6 mg, 0.13 mmol, 10 mol%) in dioxane (10 mL) afforded **1g-III** (182.4 mg, 63%) (flash chromatograph eluent: hexane/ethyl acetate = 1/1 to 1/2 to 1/3), which was used for next step directly.

To a 40 mL vial were added **1g-III** (138.0 mg, 0.61 mmol), polyaniline (24.9 mg), PCC (466.6 mg, 2.16 mmol), and DCE (6 mL). The resulting mixture was stirred at 90 °C for 24 h, filtered through celite, evaporated to afford the crude product. Flash chromatograph (eluent: toluene/ethyl acetate = 1.5/1 to DCM/ ethyl acetate = 1/1) afforded compound **1e** (79.7 mg, 51%): Yellow solid; mp: 202-204 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.56-8.50 (m, 2 H, Ar-H), 7.70-7.62 (m, 1 H, Ar-H), 7.33 (dd, J₁ = 7.8 Hz, J₂ = 5.0 Hz, 1 H, Ar-H), 7.09 (d, J = 5.4 Hz, 1 H, Ar-H), 3.39 (s, 3 H, CH₃), 2.20 (s, 3 H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 180.8, 163.8, 158.1, 155.4, 151.8, 147.4, 147.2, 138.3, 132.1, 124.2, 121.0, 109.6, 25.3, 18.5; IR ν (neat, cm⁻¹) 2928, 1745,

1610, 1578, 1459, 1398, 1308, 1194, 1013; HRMS (ESI) for $C_{14}H_{11}N_3O_2Na$ (MW = 276, $(M+Na)^+$): 276.0743. Found: 276.0747.

(8) Synthesis of 4-(4',4'-dimethyl-4',5'-dihydrooxazol-2'-yl)-1,5-dimethyl-isatin **1h**.
(zr-6-47, 56, 58, 61)



To Q-Tube pressure tube reactor were added 4-bromo-1,5-dimethyl-isatin (508.8 mg, 2 mmol), $Pd(PPh_3)_2Cl_2$ (142.8 mg, 0.2 mmol, 10 mol%), Et_3N (1 mL), toluene (5 mL), and MeOH (5 mL). The resulting mixture was degassed with CO three times, stirred at 120 °C for 48 h, filtered through celite, and evaporated to afford the crude product. Flash chromatograph (eluent: hexane/ethyl acetate = 1/1) afforded compound **1h-I** (289.4 mg, 62%), which was used for next step directly.

To a 40 mL vial were added **1h-I** (234.9 mg, 1 mmol), $LiOH \cdot H_2O$ (64.1 mg, 1.5 mmol), MeOH (5 mL), and H_2O (5 mL). The resulting mixture was stirred at room temperature for 4 h, quenched by adding HCl solution (1 N, 2 mL), extracted with ethyl acetate (15 mL $\times$ 3), and dried with $MgSO_4$. Evaporation and flash chromatograph (eluent: DCM/ethyl acetate = 2/1 to 1/4) afforded compound **1h-II** (150.1 mg, 68%), which was used for next step directly.

To a 40 mL vial were added **1h-II** (150.1 mg, 0.685 mmol), DCM (5 mL), DMF (1 drop), and oxalyl chloride (58.4 μ L, $d = 1.488$, 0.685 mmol). The resulting mixture was stirred at room temperature and evaporated to afford the crude acyl chloride.

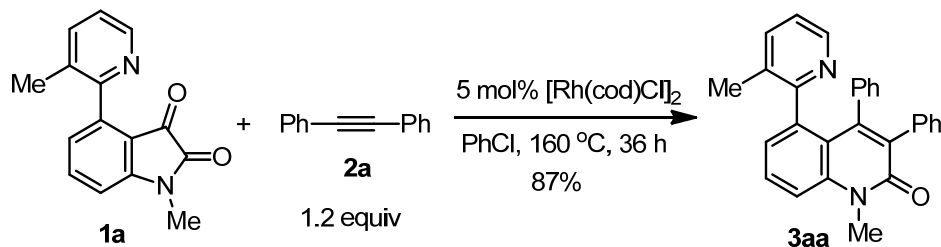
To a 40 mL vial were added 2-amino-2-methylpropan-1-ol (73.2 mg, 0.822 mmol), DCM (2 mL), Et_3N (208 μ L, $d = 0.726$, 1.5 mmol), and the crude acyl chloride in DCM (5 mL). The resulting mixture was stirred at room temperature for 16 h and then evaporated to afford the crude product. Flash chromatograph (eluent: hexane/ethyl

acetate = 1/1 to DCM/ethyl acetate = 1/1 to DCM/MeOH = 20/1) afforded compound **1h-III** (144.2 mg, 73%), which was used for next step directly.

To a 40 mL vial were added **1h-III** (100.1 mg, 0.34 mmol), DMAP (4.4 mg, 0.036 mmol), DCM (6 mL), Et₃N (0.24 mL, *d* = 0.726, 0.16 mmol), and MsCl (50 μ L, *d* = 1.48, 0.65 mmol). The resulting mixture was stirred at room temperature for 18 h, quenched with brine (15 mL), extracted with DCM (20 mL $\times$ 3), and dried with MgSO₄. Evaporation and flash chromatograph (eluent: hexane/ethyl acetate = 1/1 to 1/1.5 to 1/3) afforded compound **1h** (43.4 mg, 46%): Red solid; mp: 154-156 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.48-7.42 (m, 1 H, Ar-H), 6.86 (d, *J* = 8.1 Hz, 1 H, Ar-H), 4.23 (s, 2 H, CH₂), 3.22 (s, 3 H, CH₃), 2.34 (d, *J* = 0.5 Hz, 3 H, CH₃), 1.48 (s, 6 H, CH₃ $\times$ 3); ¹³C NMR (125 MHz, CDCl₃) δ 181.4, 158.7, 157.6, 149.4, 139.2, 132.6, 127.1, 115.7, 111.1, 79.9, 68.4, 28.0, 26.2, 17.9; IR ν (neat, cm⁻¹) 2968, 1736, 1671, 1600, 1477, 1349, 1314, 1113; HRMS (ESI) for C₁₅H₁₆N₂O₃Na (MW = 295, (M+Na)⁺): 295.1053. Found: 295.1057.

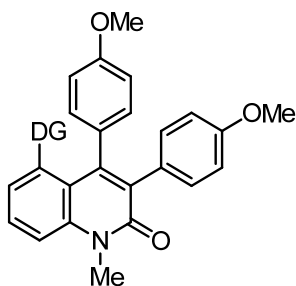
The decarbonylative ‘cut and sew’ reactions of isatin 1 with alkynes 2.

Synthesis of **3aa**: (zr-4-20, 22)



Typical Procedure 2: To an 40 mL vial were added **1a** (40.4 mg, 0.16 mmol), diphenylacetylene **2a** (34.5 mg, 0.192 mmol), and $[\text{Rh}(\text{cod})\text{Cl}]_2$ (3.9 mg, 0.008 mmol), then was transferred into nitrogen-filled glovebox via standard glovebox technique. After adding PhCl (4 mL), the vial was sealed and stirred at a pre-heated pie-block at 160 °C for 36 h. Upon reaction completion, the reaction mixture was concentrated under vacuum and directly purified via flash chromatography to give the desired 2-quinolinone product **3aa** (55.8 mg, 87%) (eluent: hexane/ethyl acetate = 1/1 to 1/2 to 1/3): solid; mp: 176-178 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.15 (dd, $J_1 = 4.8$ Hz, $J_2 = 1.3$ Hz, 1 H, Ar-H), 7.62 (dd, $J_1 = 8.5$ Hz, $J_2 = 7.2$ Hz, 1 H, Ar-H), 7.55 (dd, $J_1 = 8.6$ Hz, $J_2 = 1.3$ Hz, 1 H, Ar-H), 7.11-6.81 (m, 7 H, Ar-H), 6.80-6.65 (m, 4 H, Ar-H), 6.64-6.55 (m, 2 H, Ar-H), 3.90 (s, 3 H, CH_3), 1.94 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 161.4, 159.4, 147.4, 145.8, 141.0, 140.7, 137.5, 137.2, 136.0, 134.3, 131.1, 130.8, 130.2, 129.4, 128.0, 127.2, 126.7, 126.4, 126.3, 126.0, 125.6, 121.8, 119.8, 114.4, 30.7, 19.8; IR ν (neat, cm^{-1}) 3054, 2925, 1638, 1586, 1455, 1443, 1422, 1308, 1251, 1070; HRMS (ESI) for $\text{C}_{28}\text{H}_{23}\text{N}_2\text{O}$ (MW = 403, $(\text{M}+\text{H})^+$): 403.1805. Found: 403.1805.

The following compounds were prepared according to Typical Procedure 2.

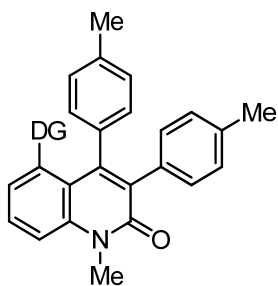


DG = 3-methyl-pyridine-2-yl

3ab

(Zr-4-27)

The reaction of **1a** (40.3 mg, 0.16 mmol), di(4-methoxyphenyl)acetylene **2b** (45.4 mg, 0.192 mmol), and $[\text{Rh}(\text{cod})\text{Cl}]_2$ (4.0 mg, 0.008 mmol) in PhCl (4 mL) at 160 °C for 36 h afforded **3ab** (70.9 mg, 96%) (eluent: hexane/ethyl acetate = 1/1 to 1/4 to ethyl acetate): Solid; 172-174 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.17 (dd, $J_1 = 4.8$ Hz, $J_2 = 1.1$ Hz, 1 H, Ar-H), 7.59 (dd, $J_1 = 8.5$ Hz, $J_2 = 7.2$ Hz, 1 H, Ar-H), 7.53 (dd, $J_1 = 8.6$ Hz, $J_2 = 1.3$ Hz, 1 H, Ar-H), 7.03-6.89 (m, 2 H, Ar-H), 6.89-6.81 (m, 2 H, Ar-H), 6.74 (dd, $J_1 = 7.7$ Hz, $J_2 = 4.8$ Hz, 1 H, Ar-H), 6.68-6.59 (m, 3 H, Ar-H), 6.55 (dd, $J_1 = 8.5$ Hz, $J_2 = 2.2$ Hz, 1 H, Ar-H), 6.30 (dd, $J = 8.4$, 2.7 Hz, 1H), 6.17 (dd, $J = 8.5$, 2.7 Hz, 1H), 3.88 (s, 3 H, CH_3), 3.68 (s, 3 H, CH_3), 3.60 (s, 3 H, CH_3), 1.91 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 161.7, 159.7, 157.9, 157.5, 147.0, 145.9, 140.9, 140.5, 137.1, 133.8, 132.6, 131.5, 130.8, 130.1, 129.3, 129.2, 128.4, 125.6, 121.5, 120.1, 114.3, 112.8, 112.3, 111.9, 55.0, 30.7, 19.9; IR ν (neat, cm^{-1}) 2926, 1634, 1610, 1585, 1509, 1455, 1290, 1245, 1176, 1032; HRMS (CI) for $\text{C}_{30}\text{H}_{26}\text{N}_2\text{O}_3$ (MW = 462, M^+): 462.1943. Found: 462.1940.



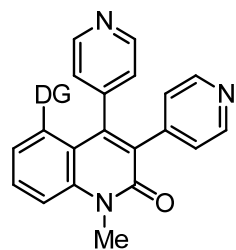
DG = 3-methyl-pyridine-2-yl

3ac

(Zr-4-45)

The reaction of **1a** (50.4 mg, 0.2 mmol), di(4-methylphenyl)acetylene **2c** (51.5 mg, 0.24 mmol), and $[\text{Rh}(\text{cod})\text{Cl}]_2$ (4.9 mg, 0.01 mmol) in PhCl (4 mL) at 160 °C for 36 h

afforded **3ac** (77.7 mg, 90%) (eluent: hexane/ethyl acetate = 1.5/1 to 1/3 to 1/5): Solid; 196-198 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.16-8.11 (m, 1 H, Ar-H), 7.59 (t, *J* = 8.0 Hz, 1 H, Ar-H), 7.52 (d, *J* = 7.8 Hz, 1 H, Ar-H), 7.00-6.95 (m, 1 H, Ar-H), 6.95-6.90 (m, 1 H, Ar-H), 6.88 (d, *J* = 8.1 Hz, 2 H, Ar-H), 6.80 (d, *J* = 8.0 Hz, 2 H, Ar-H), 6.74 (dd, *J*₁ = 7.7 Hz, *J*₂ = 4.8 Hz, 1 H, Ar-H), 6.62 (dd, *J*₁ = 7.7 Hz, *J*₂ = 1.8 Hz, 1 H, Ar-H), 6.53 (d, *J* = 7.8 Hz, 1 H, Ar-H), 6.49 (dd, *J*₁ = 7.8 Hz, *J*₂ = 1.7 Hz, 1 H, Ar-H), 6.39 (d, *J* = 7.9 Hz, 1 H, Ar-H), 3.88 (s, 3 H, CH₃), 2.19 (s, 3 H, CH₃), 2.01 (s, 3 H, CH₃), 1.90 (s, 3 H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 161.6, 159.6, 147.2, 145.7, 141.0, 140.6, 136.9, 135.8, 135.5, 134.5, 134.0, 133.1, 131.1, 130.8, 130.1, 129.2, 128.0, 127.4, 126.7, 125.6, 121.1, 120.1, 114.3, 30.7, 21.2, 20.9, 19.9; IR ν(neat, cm⁻¹) 3025, 2921, 1640, 1585, 1453, 1423, 1308, 1252, 1112, 1069; HRMS (ESI) for C₃₀H₂₇N₂O (MW = 431, (M+H)⁺): 431.2118. Found: 431.2120.

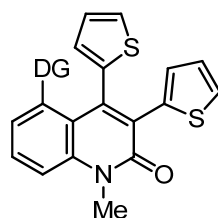


DG = 3-methyl-pyridine-2-yl

3ad

(Zr-5-2)

The reaction of **1a** (50.6 mg, 0.2 mmol), di(4-pyridinyl)acetylene **2d** (43.4 mg, 0.24 mmol), and [Rh(cod)Cl]₂ (4.9 mg, 0.01 mmol) in PhCl (4 mL) at 160 °C for 60 h afforded **3ad** (75.2 mg, 93%) (eluent: ethyl acetate to DCM/MeOH = 15/1 to 8/1): Solid; >250 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.35 (d, *J* = 5.4 Hz, 2 H, Ar-H), 8.22-8.15 (m, 1 H, Ar-H), 8.08 (d, *J* = 5.0 Hz, 1 H, Ar-H), 7.92 (d, *J* = 5.1 Hz, 1 H, Ar-H), 7.74-7.65 (m, 1 H, Ar-H), 7.60 (dd, *J*₁ = 8.7 Hz, *J*₂ = 1.1 Hz, 1 H, Ar-H), 7.10-7.01 (m, 2 H, Ar-H), 6.91-6.81 (m, 3 H, Ar-H), 6.76-6.70 (m, 1 H, Ar-H), 6.56-6.51 (m, 1 H, Ar-H), 3.90 (s, 3 H, CH₃), 1.99 (s, 3 H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 160.1, 158.4, 149.0, 148.3, 147.7, 146.0, 145.0, 144.8, 143.7, 141.0, 140.8, 137.6, 131.6, 131.1, 130.5, 125.8, 125.3, 125.0, 122.7, 122.6, 118.2, 114.7, 30.7, 19.6; IR ν(neat, cm⁻¹) 3042, 2923, 1637, 1588, 1458, 1408, 1310, 1237, 1067; HRMS (ESI) for C₂₆H₂₁N₄O (MW = 405, (M+H)⁺): 405.1710. Found: 405.1712.

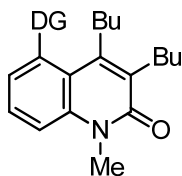


DG = 3-methyl-pyridine-2-yl

3ae

(Zr-4-66)

The reaction of **1a** (50.3 mg, 0.2 mmol), di-(thiophen-2-yl)acetylene **2e** (45.4 mg, 0.24 mmol), and [Rh(cod)Cl]₂ (4.9 mg, 0.01 mmol) in PhCl (4 mL) at 160 °C for 38.5 h afforded **3ae** (78.6 mg, 95%) (eluent: hexane/ethyl acetate = 1/1 to 1/2 to 1/4): oil; ¹H NMR (400 MHz, CDCl₃) δ 8.23 (dd, *J*₁ = 4.7 Hz, *J*₂ = 1.1 Hz, 1 H, Ar-H), 7.62 (dd, *J*₁ = 8.6 Hz, *J*₂ = 7.3 Hz, 1 H, Ar-H), 7.52 (dd, *J*₁ = 8.6 Hz, *J*₂ = 1.2 Hz, 1 H, Ar-H), 7.22 (dd, *J*₁ = 5.1 Hz, *J*₂ = 1.2 Hz, 1 H, Ar-H), 7.13 (dd, *J*₁ = 7.7 Hz, *J*₂ = 0.8 Hz, 1 H, Ar-H), 7.03 (dd, *J*₁ = 7.3 Hz, *J*₂ = 1.2 Hz, 1 H, Ar-H), 6.88-6.76 (m, 2 H, Ar-H), 6.79 (dd, *J*₁ = 5.1 Hz, *J*₂ = 3.6 Hz, 1 H, Ar-H), 6.69 (dd, *J*₁ = 3.6 Hz, *J*₂ = 1.2 Hz, 1 H, Ar-H), 6.44 (d, *J* = 2.7 Hz, 1 H, Ar-H), 6.40 (dd, *J*₁ = 5.0 Hz, *J*₂ = 3.6 Hz, 1 H, Ar-H), 3.88 (s, 3 H, CH₃), 2.00 (s, 3 H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 160.4, 159.3, 145.9, 141.0, 140.3, 137.3, 135.9, 130.7, 129.8, 129.3, 128.9, 126.7, 126.0, 125.9, 121.6, 120.3, 114.2, 30.9, 20.1; IR ν(neat, cm⁻¹) 3004, 2924, 2853, 1639, 1587, 1454, 1380, 1242, 1110; HRMS (ESI) for C₂₄H₁₉N₂OS₂ (MW = 415, (M+H)⁺): 415.0933. Found: 415.0944.



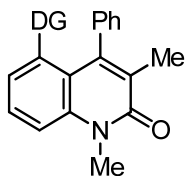
DG = 3-methyl-pyridine-2-yl

3af

(Zr-4-23)

The reaction of **1a** (40.5 mg, 0.16 mmol), dibutyl-acetylene **2f** (27.1 mg, 0.192 mmol), and [Rh(cod)Cl]₂ (4.0 mg, 0.008 mmol) in PhCl (4 mL) at 160 °C for 37 h afforded **3af** (52.9 mg, 91%) (eluent: hexane/ethyl acetate = 3/1 to 2/1 to 1/1): oil; ¹H NMR (400 MHz, CDCl₃) δ 8.52 (d, *J* = 4.7 Hz, 1 H, Ar-H), 7.58-7.46 (m, 2 H, Ar-H), 7.44 (d, *J* = 8.4 Hz, 1 H, Ar-H), 7.31-7.20 (m, 1 H, Ar-H), 7.03-6.93 (m, 1 H, Ar-H), 3.81 (s, 3 H, CH₃), 2.80-2.67 (m, 1 H, Bu-H), 2.67-2.53 (m, 1 H, CH), 2.23 (td, *J*₁ =

13.1 Hz, $J_2 = 4.7$ Hz, 1 H, CH), 2.09-1.86 (m, 4 H, CH₃ and CH), 1.63-1.30 (m, 5 H, Bu-H), 1.07-0.86 (m, 4 H), 0.86-0.60 (m, 5 H, Bu-H); ¹³C NMR (100 MHz, CDCl₃) δ 161.8, 161.0, 146.4, 146.3, 139.6, 138.7, 137.3, 132.8, 131.9, 128.2, 125.4, 122.4, 118.9, 114.6, 32.1, 31.6, 30.6, 30.0, 27.8, 23.2, 23.0, 19.3, 13.9, 13.6; IR ν (neat, cm⁻¹) 2956, 2927, 2858, 1634, 1586, 1461, 1421, 1378, 1308, 1117, 1075; HRMS (CI) for C₂₄H₂₉N₂O₁ (MW = 362, M⁺): 362.2358. Found: 362.2344.

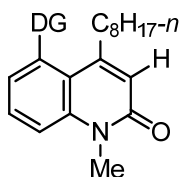


DG = 3-methyl-pyridine-2-yl

3ag

(Zr-4-28)

The reaction of **1a** (40.4 mg, 0.16 mmol), 1-phenyl-1-propyne **2g** (23.0 mg, 0.198 mmol), and [Rh(cod)Cl]₂ (4.0 mg, 0.008 mmol) in PhCl (4 mL) at 160 °C for 36 h afforded **3ag** (45.2 mg, 83%) (eluent: hexane/ethyl acetate = 1/1 to 1/2 to 1/4): Solid; <35 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.18 (dd, $J_1 = 4.8$ Hz, $J_2 = 1.1$ Hz, 1 H, Ar-H), 7.58-7.47 (m, 2 H, Ar-H), 7.07-6.96 (m, 2 H, Ar-H), 6.96-6.87 (m, 3 H, Ar-H), 6.87-6.74 (m, 3 H, Ar-H), 3.89 (s, 3 H, CH₃), 1.89 (s, 3 H, CH₃), 1.83 (s, 3 H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 162.1, 159.6, 146.2, 145.7, 140.1, 139.6, 138.3, 137.1, 130.8, 130.0, 129.8, 128.5, 127.4, 126.90, 126.87, 126.5, 125.1, 121.8, 119.6, 114.1, 30.5, 19.8, 15.3; IR ν (neat, cm⁻¹) 2924, 2854, 1634, 1587, 1462, 1423, 1378, 1354, 1311, 1081; HRMS (CI) for C₂₃H₂₀N₂O₁ (MW = 340, M⁺): 340.1576. Found: 340.1579.



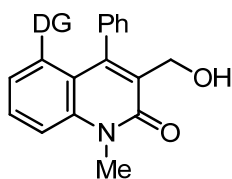
DG = 3-methyl-pyridine-2-yl

3ah

(Zr-4-58)

The reaction of **1a** (40.2 mg, 0.16 mmol), 1-decyne **2h** (34.4 mg, 0.25 mmol), and [Rh(cod)Cl]₂ (3.9 mg, 0.008 mmol) in PhCl (4 mL) at 160 °C for 36 h afforded **3ah** (29.0 mg, 50%) (eluent: hexane/ethyl acetate = 1/2 to 1/4): oil; ¹H NMR (400 MHz,

CDCl₃) δ 8.51 (dd, $J_1 = 4.8$ Hz, $J_2 = 1.1$ Hz, 1 H, Ar-H), 7.68-7.52 (m, 2 H, Ar-H), 7.48 (dd, $J_1 = 8.6$ Hz, $J_2 = 1.2$ Hz, 1 H, Ar-H), 7.32-7.22 (m, 1 H, Ar-H), 7.01 (dd, $J_1 = 7.3$ Hz, $J_2 = 1.2$ Hz, 1 H, Ar-H), 6.57 (s, 1 H, CH=), 3.78 (s, 3 H, CH₃), 2.05 (s, 3 H, CH₃), 1.95-1.77 (m, 2 H, CH₂), 1.44-1.00 (m, 10 H), 0.98-0.77 (m, 5 H); ¹³C NMR (100 MHz, CDCl₃) δ 161.8, 160.6, 151.4, 146.4, 141.1, 139.4, 137.5, 131.9, 129.4, 124.9, 122.7, 121.4, 119.1, 115.0, 34.5, 31.8, 30.0, 29.4, 29.1, 29.0, 28.8, 22.6, 19.4, 14.1; IR ν (neat, cm⁻¹) 2924, 2853, 1660, 1585, 1458, 1425, 1378, 1314, 1073; HRMS (ESI) for C₂₄H₃₁N₂O₁ (MW = 363, (M+H)⁺): 363.2431. Found: 363.2432.

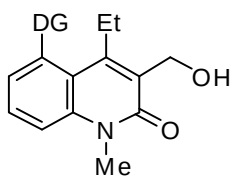


DG = 3-methyl-pyridine-2-yl

3ai

(Zr-4-26)

The reaction of **1a** (40.3 mg, 0.16 mmol), 3-phenyl-2-propyn-1-ol **2i** (26.7 mg, 0.2 mmol), and [Rh(cod)Cl]₂ (3.8 mg, 0.008 mmol) in PhCl (4 mL) at 160 °C for 36 h afforded **3ai** (51.3 mg, 90%) (eluent: ethyl acetate to DCM/MeOH = 15/1): Solid; 212-214 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.22-8.14 (m, 1 H, Ar-H), 7.61 (dd, $J_1 = 8.6$ Hz, $J_2 = 7.2$ Hz, 1 H, Ar-H), 7.54 (dd, $J_1 = 8.6$ Hz, $J_2 = 1.3$ Hz, 1 H, Ar-H), 7.06-6.87 (m, 6 H, Ar-H), 6.85-6.80 (m, 1 H, Ar-H), 6.78 (dd, $J_1 = 7.7$ Hz, $J_2 = 4.8$ Hz, 1 H, Ar-H), 4.32-3.96 (m, 3 H, CH₂OH), 3.89 (s, 3 H, CH₃), 1.88 (s, 3 H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 162.3, 159.2, 147.0, 145.8, 141.3, 140.0, 137.1, 136.2, 130.80, 130.79, 130.0, 129.6, 127.4, 127.1, 127.0, 126.9, 125.8, 121.9, 119.5, 114.5, 60.2, 30.1, 19.7; IR ν (neat, cm⁻¹) 3435, 3055, 2925, 1633, 1586, 1455, 1423, 1312, 1014; HRMS (CI) for C₂₃H₂₀N₂O₂ (MW = 356, M⁺): 356.1525. Found: 356.1521.

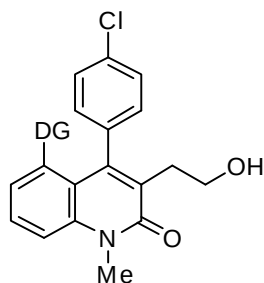


DG = 3-methyl-pyridine-2-yl

3aj

(Zr-4-26)

The reaction of **1a** (50.3 mg, 0.2 mmol), 2-pentyn-1-ol **2j** (20.1 mg, 0.24 mmol), and [Rh(cod)Cl]₂ (4.9 mg, 0.01 mmol) in PhCl (4 mL) at 160 °C for 36 h afforded **3aj** (49.2 mg, 80%) (eluent: DCM to ethyl acetate to DCM/MeOH = 20/1): oil; ¹H NMR (400 MHz, CDCl₃) δ 8.50 (dd, *J*₁ = 4.8 Hz, *J*₂ = 1.2 Hz, 1 H, Ar-H), 7.59 (dd, *J*₁ = 8.5 Hz, *J*₂ = 7.4 Hz, 2 H, Ar-H), 7.51 (dd, *J*₁ = 8.6 Hz, *J*₂ = 1.2 Hz, 1 H, Ar-H), 7.32-7.20 (m, 1 H, Ar-H), 7.04 (dd, *J*₁ = 7.3 Hz, *J*₂ = 1.2 Hz, 1 H, Ar-H), 4.81-4.60 (m, 2 H, CH₂), 4.24 (brs, 1 H, OH), 3.82 (s, 3 H, CH₃), 2.41-2.28 (m, 1 H, one proton of CH₂), 2.18-1.99 (m, 4 H, CH₃ and one proton of CH₂), 0.76 (t, *J* = 7.4 Hz, 3 H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 162.3, 160.6, 149.5, 146.5, 140.1, 139.7, 137.6, 131.5, 130.0, 129.3, 125.9, 122.7, 118.8, 115.0, 59.2, 30.2, 22.7, 19.4, 14.8; IR ν(neat, cm⁻¹) 3418, 2927, 1626, 1585, 1455, 1421, 1312, 1218, 1005; HRMS (ESI) for C₁₉H₂₁N₂O₂ (MW = 309, (M+H)⁺): 309.1598. Found: 309.1598.



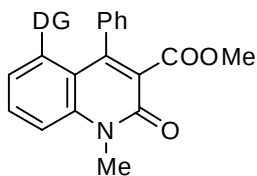
DG = 3-methyl-pyridine-2-yl

3ak

(Zr-4-26)

The reaction of **1a** (40.5 mg, 0.16 mmol), 4-(4'-chlorophenyl)-4-butyn-1-ol **2k** (34.9 mg, 0.192 mmol), and [Rh(cod)Cl]₂ (3.9 mg, 0.008 mmol) in PhCl (4 mL) at 160 °C for 50 h afforded **3ak** (60.1 mg, 93%) (eluent: ethyl acetate to DCM/MeOH = 30/1): Solid; 148-150 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.23-8.15 (m, 1 H, Ar-H), 7.59 (dd, *J*₁ = 8.6 Hz, *J*₂ = 7.1 Hz, 1 H, Ar-H), 7.53 (dd, *J*₁ = 8.6 Hz, *J*₂ = 1.4 Hz, 1 H, Ar-H), 7.12-7.06 (m, 1 H, Ar-H), 7.03-6.89 (m, 3 H, Ar-H), 6.85 (dd, *J*₁ = 8.2 Hz, *J*₂ = 2.1 Hz, 1 H, Ar-H), 6.80 (dd, *J*₁ = 8.1 Hz, *J*₂ = 2.0 Hz, 1 H, Ar-H), 6.74 (dd, *J*₁ = 8.2 Hz, *J*₂ = 2.1 Hz, 1 H, Ar-H), 3.89 (s, 3 H, CH₃), 3.79 (brs, 1 H, OH), 3.67-3.54 (m, 2 H, CH₂O), 2.58-2.44 (m, 2 H, CH₂), 1.88 (s, 3 H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 163.4, 159.4, 146.7, 145.9, 140.4, 139.7, 137.2, 135.8, 132.9, 131.6, 131.5, 130.9, 129.4, 128.3, 127.6, 127.0, 125.8, 121.8, 119.7, 114.5, 63.1, 32.3, 30.9, 19.8; IR ν

(neat, cm^{-1}) 3398, 3050, 2929, 1635, 1586, 1457, 1424, 1312, 1090, 1015; HRMS (ESI) for $\text{C}_{24}\text{H}_{22}\text{ClN}_2\text{O}_2$ (MW = 405, $(\text{M}+\text{H})^+$): 405.1364. Found: 405.1368.

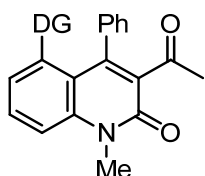


DG = 3-methyl-pyridine-2-yl

3al

(Zr-4-42)

The reaction of **1a** (50.5 mg, 0.2 mmol), methyl 3-phenylpropiolate **2l** (35.3 μL , $d = 1.086$, 38.6 mg, 0.24 mmol), and $[\text{Rh}(\text{cod})\text{Cl}]_2$ (4.9 mg, 0.01 mmol) in PhCl (4 mL) at 160°C for 36 h afforded **3al** (45.9 mg, 60%) (eluent: hexane/ethyl acetate = 1/2 to 1/5): Solid; $204\text{--}206^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.19 (d, $J = 4.0$ Hz, 1 H, Ar-H), 7.67 (dd, $J_1 = 8.5$ Hz, $J_2 = 7.5$ Hz, 1 H, Ar-H), 7.55 (dd, $J_1 = 8.6$ Hz, $J_2 = 0.8$ Hz, 1 H, Ar-H), 7.08–7.02 (m, 2 H, Ar-H), 7.01–6.80 (m, 5 H, Ar-H), 6.75 (dd, $J_1 = 7.7$ Hz, $J_2 = 4.8$ Hz, 1 H, Ar-H), 3.87 (s, 3 H, CH_3), 3.45 (s, 3 H, CH_3), 1.88 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 166.1, 158.53, 158.48, 147.5, 146.0, 141.5, 140.8, 137.1, 135.5, 131.1, 130.8, 130.1, 129.2, 127.6, 127.1, 126.7, 126.6, 126.0, 122.1, 118.2, 114.7, 52.0, 30.3, 19.6; IR ν (neat, cm^{-1}) 3054, 2950, 2924, 2853, 1739, 1644, 1588, 1456, 1433, 1364, 1312, 1263, 1207, 1156, 1078, 1009; HRMS (ESI) for $\text{C}_{24}\text{H}_{21}\text{N}_2\text{O}_3$ (MW = 385, $(\text{M}+\text{H})^+$): 385.1547. Found: 385.1548.



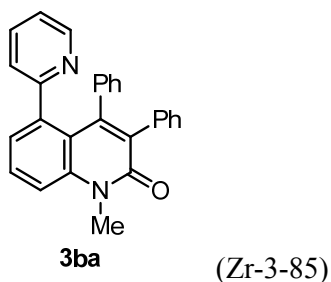
DG = 3-methyl-pyridine-2-yl

3am

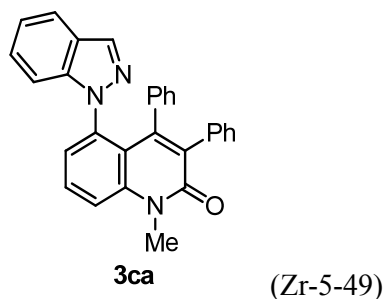
(Zr-4-59)

The reaction of **1a** (40.4 mg, 0.16 mmol), 4-phenyl-3-butyne-2-one **2m** (29.4 mg, 0.20 mmol), and $[\text{Rh}(\text{cod})\text{Cl}]_2$ (3.9 mg, 0.008 mmol) in PhCl (4 mL) at 160°C for 36 h afforded **3am** (48.8 mg, 83%) (eluent: toluene/ethyl acetate = 1/2 to 1/4 to ethyl acetate): oil; ^1H NMR (400 MHz, CDCl_3) δ 8.18 (dd, $J_1 = 4.8$ Hz, $J_2 = 1.1$ Hz, 1 H, Ar-H), 7.66 (dd, $J_1 = 8.6$ Hz, $J_2 = 7.3$ Hz, 1 H, Ar-H), 7.55 (dd, $J_1 = 8.6$ Hz, $J_2 = 1.2$ Hz, 1 H, Ar-H), 7.10–6.83 (m, 7 H, Ar-H), 6.76 (dd, $J_1 = 7.7$ Hz, $J_2 = 4.8$ Hz, 1 H,

Ar-H), 3.85 (s, 3 H, CH₃), 1.98 (s, 3 H, CH₃), 1.88 (s, 3 H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 201.8, 158.7, 158.6, 146.0, 145.3, 141.4, 140.6, 137.8, 137.1, 135.5, 135.1, 131.0, 130.5, 130.1, 128.9, 128.1, 127.7, 127.5, 127.3, 126.8, 125.9, 125.2, 122.1, 118.5, 114.6, 31.0, 30.0, 19.6; IR ν (neat, cm⁻¹) 3056, 2924, 2853, 1710, 1634, 1587, 1454, 1423, 1359, 1310, 1150, 1075, 1029; HRMS (ESI) for C₂₄H₂₁N₂O₂ (MW = 369, (M+H)⁺): 369.1598. Found: 369.1602.

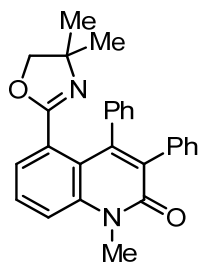


The reaction of **1b** (9.5 mg, 0.04 mmol), **2a** (8.4 mg, 0.048 mmol), and [Rh(cod)Cl]₂ (1.0 mg, 0.002 mmol) in PhCl (1 mL) at 160 °C for 36 h afforded **3ba** (9.3 mg, 60%) (eluent: hexane/ethyl acetate = 1/1 to 1/2 to 1/3): ¹H NMR (500 MHz, CDCl₃) δ 8.26-8.19 (m, 1 H, Ar-H), 7.63 (dd, *J*₁ = 8.5 Hz, *J*₂ = 7.3 Hz, 1 H, Ar-H), 7.57 (dd, *J*₁ = 8.6 Hz, *J*₂ = 1.3 Hz, 1 H, Ar-H), 7.22-7.14 (m, 2 H, Ar-H), 7.12-7.03 (m, 3 H, Ar-H), 6.97-6.88 (m, 2 H, Ar-H), 6.87-6.82 (m, 1 H, Ar-H), 6.80-6.60 (m, 6 H, Ar-H), 3.90 (s, 3 H, CH₃); ¹³C NMR (126 MHz, CDCl₃) δ 161.5, 160.0, 148.4, 147.1, 141.9, 141.0, 138.2, 136.1, 135.2, 134.1, 131.4, 130.5, 129.3, 127.2, 127.0, 126.54, 126.51, 126.4, 125.2, 120.8, 119.4, 114.6, 30.7; IR ν (neat, cm⁻¹) 3057, 1638, 1586, 1457, 1427, 1309, 1251, 1070; HRMS (ESI) for C₂₇H₂₁N₂O₁ (MW = 389, (M+H)⁺): 389.1648. Found: 389.1643.



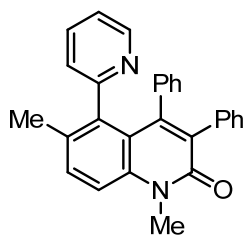
The reaction of **1c** (42.2 mg, 0.15 mmol), **2a** (32.4 mg, 0.18 mmol), and [Rh(cod)Cl]₂ (3.7 mg, 0.0075 mmol) in PhCl (4 mL) at 160 °C for 36 h afforded **3ca**

(63.4 mg, 98%) (eluent: hexane/ethyl acetate = 3/1 to 1/1): Solid; 194-196 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.70 (dd, $J_1 = 8.6$ Hz, $J_2 = 7.5$ Hz, 1 H, Ar-H), 7.66-7.55 (m, 2 H, Ar-H), 7.36-7.32 (m, 1 H, Ar-H), 7.27-7.20 (m, 2 H, Ar-H), 7.13-6.92 (m, 5 H, Ar-H), 6.89-6.82 (m, 2 H, Ar-H), 6.73 (d, $J = 7.8$ Hz, 1 H, Ar-H), 6.66 (t, $J = 7.6$ Hz, 1 H, Ar-H), 6.42 (tt, $J_1 = 7.4$ Hz, $J_2 = 1.3$ Hz, 1 H, Ar-H), 6.23 (d, $J = 7.7$ Hz, 1 H, Ar-H), 6.09 (td, $J_1 = 7.6$ Hz, $J_2 = 0.7$ Hz, 1 H, Ar-H), 3.91 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 161.3, 145.3, 141.4, 140.7, 137.6, 135.5, 135.3, 135.03, 135.00, 130.24, 129.98, 129.1, 127.5, 127.1, 126.5, 126.3, 125.8, 125.6, 124.6, 124.0, 123.7, 120.7, 120.5, 118.2, 115.0, 110.2, 30.8; IR ν (neat, cm^{-1}) 3059, 3024, 1644, 1596, 1499, 1474, 1461, 1354, 1303, 1254, 1221, 1201, 1149, 1074; HRMS (ESI) for $\text{C}_{29}\text{H}_{22}\text{N}_3\text{O}$ (MW = 428, $(\text{M}+\text{H})^+$): 428.1757. Found: 428.1761.



3da (Zr-7-6)

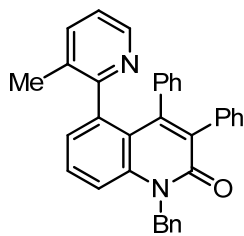
The reaction of **1d** (28.8 mg, 0.113 mmol), **2a** (24.5 mg, 0.136 mmol), and $[\text{Rh}(\text{cod})\text{Cl}]_2$ (2.8 mg, 0.0057 mmol) in PhCl (2.5 mL) at 160 °C for 48 h afforded **3da** (23.9 mg, 52%) (eluent: hexane/ethyl acetate = 1/2 to 1/3): solid; 212-214 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.65-7.57 (m, 2 H, Ar-H), 7.49 (dd, $J_1 = 5.9$ Hz, $J_2 = 2.8$ Hz, 1 H, Ar-H), 7.20-7.08 (m, 6 H, Ar-H), 7.08-7.00 (m, 2 H, Ar-H), 6.91 (brs, 2 H, Ar-H), 3.84 (s, 3 H, CH_3), 3.21 (brs, 2 H, CH_2), 0.96 (s, 6 H, $\text{CH}_3 \times 2$); ^{13}C NMR (100 MHz, CDCl_3) δ 163.5, 161.2, 146.0, 140.6, 137.3, 135.8, 134.4, 131.1, 130.4, 129.5, 129.2, 127.3, 127.2, 126.7, 126.5, 119.3, 116.8, 77.9, 66.9, 30.6, 27.5; IR ν (neat, cm^{-1}) 2965, 1641, 1586, 1460, 1356, 1314, 1198, 1073; HRMS (ESI) for $\text{C}_{27}\text{H}_{25}\text{N}_2\text{O}_2$ (MW = 409, $(\text{M}+\text{H})^+$): 409.1911. Found: 409.1913.



3ea

(Zr-5-31)

The reaction of **1e** (40.5 mg, 0.16 mmol), **2a** (35.1 mg, 0.19 mmol), and $[\text{Rh}(\text{cod})\text{Cl}]_2$ (4.0 mg, 0.008 mmol) in PhCl (4 mL) at 160 °C for 48 h afforded **3ea** (59.2 mg, 92%) (eluent: hexane/ethyl acetate = 1/1 to 1/3 to 1/4): Solid; 196-198 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.28-8.24 (m, 1 H, Ar-H), 7.52-7.45 (m, 1 H, Ar-H), 7.13 (td, $J_1 = 7.7$ Hz, $J_2 = 1.8$ Hz, 1 H, Ar-H), 7.08-6.96 (m, 3 H, Ar-H), 6.85 (d, $J = 6.4$ Hz, 2 H, Ar-H), 6.80-6.68 (m, 3 H, Ar-H), 6.68-6.54 (m, 3 H, Ar-H), 6.52-6.44 (m, 1 H, Ar-H), 3.87 (s, 3 H, CH_3), 1.88 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 161.2, 159.0, 148.6, 147.7, 140.1, 138.8, 138.7, 136.2, 134.8, 134.5, 132.2, 131.6, 130.7, 130.1, 129.7, 128.5, 127.1, 127.0, 126.41, 126.36, 126.3, 125.8, 120.8, 120.0, 114.3, 30.5, 20.0; IR ν (neat, cm^{-1}) 3054, 2925, 1638, 1586, 1455, 1443, 1422, 1308, 1251, 1070; HRMS (ESI) for $\text{C}_{28}\text{H}_{23}\text{N}_2\text{O}_1$ (MW = 403, $(\text{M}+\text{H})^+$): 403.1805. Found: 403.1807.

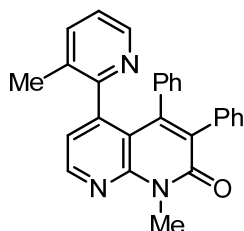


3fa

(Zr-5-3)

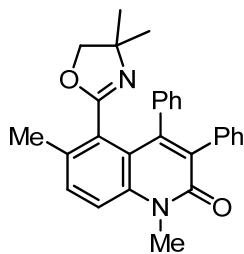
The reaction of **1f** (65.4 mg, 0.2 mmol), **2a** (43.0 mg, 0.24 mmol), and $[\text{Rh}(\text{cod})\text{Cl}]_2$ (4.9 mg, 0.01 mmol) in PhCl (4 mL) at 160 °C for 62 h afforded **3fa** (84%) (eluent: hexane/ethyl acetate = 1/1 to 1/3): solid; mp: 177-179 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.15 (d, $J = 4.7$ Hz, 1 H, Ar-H), 7.54-7.41 (m, 2 H, Ar-H), 7.41-7.32 (m, 4 H, Ar-H), 7.30-7.20 (m, 1 H), 7.13-6.85 (m, 7 H, Ar-H), 6.84-6.76 (m, 2 H, Ar-H), 6.73-6.66 (m, 2 H, Ar-H), 6.64-6.56 (m, 2 H, Ar-H), 5.95-5.45 (m, 2 H, CH_2), 5.90-5.50 (m, 2H), 1.95 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 161.6,

159.4, 147.9, 145.7, 141.1, 140.3, 137.6, 137.3, 136.5, 135.9, 134.1, 130.9, 130.7, 130.3, 129.2, 128.7, 127.9, 127.2, 127.1, 126.9, 126.7, 126.4, 126.2, 125.9, 125.6, 121.7, 120.0, 115.1, 47.4, 19.9; IR ν (neat, cm^{-1}) 3061, 1640, 1586, 1463, 1442, 1067; HRMS (ESI) for $\text{C}_{34}\text{H}_{27}\text{N}_2\text{O}_1$ (MW = 479, $(\text{M}+\text{H})^+$): 479.2118. Found: 479.2119.



3ga (Zr-6-53, 69)

The reaction of **1g** (10.1 mg, 0.04 mmol), **2a** (8.5 mg, 0.048 mmol), and $[\text{Rh}(\text{cod})\text{Cl}]_2$ (1.0 mg, 0.002 mmol) in PhCl (1 mL) at 160 °C for 72 h afforded **3ga** (10.9 mg, 68%) (17% of **1g** was observed by crude NMR using tetrachloroethane as internal standard) (Isolated by preparative TLC): solid; mp: 221-223 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.64 (d, J = 4.7 Hz, 1 H, Ar-H), 8.19-8.16 (m, 1 H, Ar-H), 7.10-7.01 (m, 3 H, Ar-H), 6.99-6.95 (m, 1 H, Ar-H), 6.94-6.89 (m, 3 H, Ar-H), 6.78-6.62 (m, 6 H, Ar-H), 4.01 (s, 3 H, CH_3), 1.91 (s, 3 H, CH_3); ^{13}C NMR (126 MHz, CDCl_3) δ 162.2, 157.2, 150.4, 149.0, 148.4, 146.1, 145.8, 137.3, 136.4, 135.4, 135.3, 131.2, 130.6, 130.3, 128.1, 127.3, 126.81, 126.75, 126.7, 126.3, 122.5, 120.7, 114.7, 29.6, 19.5; IR ν (neat, cm^{-1}) 3056, 1646, 1592, 1551, 1443, 1305, 1253, 1170; HRMS (ESI) for $\text{C}_{27}\text{H}_{21}\text{N}_3\text{ONa}$ (MW = 426, $(\text{M}+\text{Na})^+$): 426.1577. Found: 426.1580.

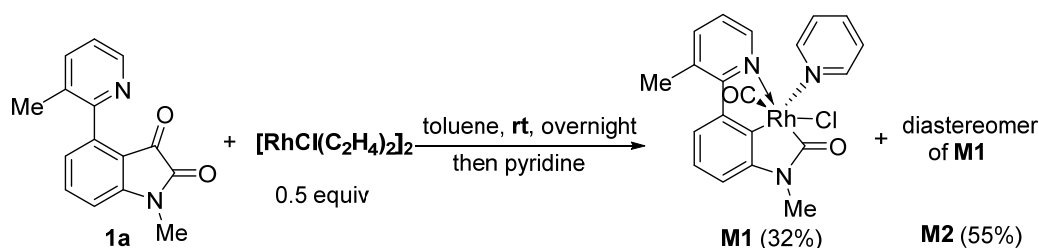


3ha (Zr-6-71)

The reaction of **1h** (30.2 mg, 0.11 mmol), **2a** (24.2 mg, 0.132 mmol), and $[\text{Rh}(\text{cod})\text{Cl}]_2$ (2.7 mg, 0.0055 mmol) in PhCl (2.5 mL) at 160 °C for 60 h afforded **3ha** (35.3 mg, 75%) (eluent: hexane/ethyl acetate = 1/1.5 to 1/2.5): solid; 187-189 °C;

^1H NMR (400 MHz, CDCl_3) δ 7.47 (s, 2 H, Ar-H), 7.19-6.94 (m, 8 H, Ar-H), 6.93-6.75 (m, 2 H, Ar-H), 3.82 (s, 3 H, CH_3), 3.72 (brs, 1 H, one proton of CH_2), 2.78 (brs, 1 H, one proton of CH_2), 2.40 (s, 3 H, CH_3), 1.12 (brs, 3 H, CH_3), 0.82 (brs, 3 H, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 161.00, 160.96, 146.3, 138.7, 137.1, 136.2, 134.7, 132.9, 132.4, 130.2, 128.0, 127.23, 127.21, 126.4, 119.6, 115.7, 77.1, 67.6, 30.5, 19.9; IR ν (neat, cm^{-1}) 2965, 1639, 1572, 1462, 1443, 1306, 1280, 1070; HRMS (ESI) for $\text{C}_{28}\text{H}_{26}\text{N}_2\text{O}_2\text{Na}$ (MW = 445, $(\text{M}+\text{Na})^+$): 445.1886. Found: 445.1890.

Preparation of intermediates **M1** and **M2**.



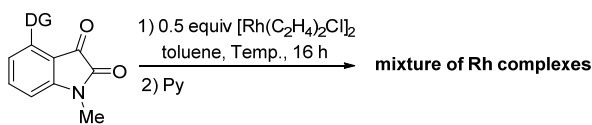
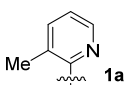
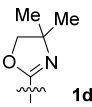
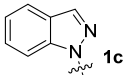
To an 40 mL vial were added **1a** (10.2 mg, 0.04 mmol) and $[\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]_2$ (7.8 mg, 0.02 mmol), then was transferred into nitrogen-filled glovebox via standard glovebox technique. After adding PhCl (3 mL), the vial was sealed and stirred at room temperature for 17.5 h. Upon reaction completion, pyridine (3 mL) was added and kept the afforded mixture stirring for additional 2 h. A clear homogeneous was afforded, which was evaporated and purified via flash chromatography to give the intermediates **M1** (more polar, 6.1 mg, 32%) and **M2** (less polar, 10.4 mg, 55%, slight decomposed during purification) (eluent: hexane/ethyl acetate = 1/2 to 1/4 to ethyl acetate).

M1: more polar; solid; ^1H NMR (400 MHz, CD_2Cl_2) δ 9.04-8.96 (m, 1 H, Ar-H), 8.34-8.23 (m, 2 H, Ar-H), 7.80-7.76 (m, 1 H, Ar-H), 7.74 (dd, $J_1 = 8.1$, $J_2 = 0.6$ Hz, 1 H, Ar-H), 7.69-7.62 (m, 1 H, Ar-H), 7.37-7.30 (m, 1 H, Ar-H), 7.28 (dd, $J_1 = 7.7$, $J_2 = 5.2$ Hz, 1 H, Ar-H), 7.18-7.09 (m, 2 H, Ar-H), 6.74 (d, $J = 7.4$ Hz, 1 H, Ar-H), 3.19 (s, 3 H), 2.89 (s, 3 H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 184.2 (d, $J = 35.5$ Hz), 183.0 (d, $J = 66.9$ Hz), 160.1 (d, $J = 2.1$ Hz), 159.23 (d, $J = 26.7$ Hz), 150.77, 149.49, 149.23, 143.48, 143.07, 138.87, 134.04, 126.82, 125.23, 125.22, 123.34, 121.21, 110.44,

28.72, 22.91; IR ν (neat, cm^{-1}) 3045, 2067, 1649, 1555, 1243; HRMS (ESI) for $\text{C}_{20}\text{H}_{17}\text{ClN}_3\text{O}_2\text{NaRh}$ (MW = 492, $(\text{M}+\text{Na})^+$): 491.9957. Found: 491.9956.

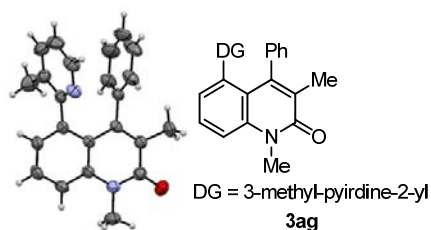
M2: less polar; solid; ^1H NMR (400 MHz, acetone) δ 9.32-9.19 (m, 2 H, Ar-H), 8.39 (dd, $J_1 = 5.2$, $J_2 = 1.6$ Hz, 1 H, Ar-H), 8.18-8.11 (m, 1 H, Ar-H), 7.92 (ddd, $J_1 = 7.7$, $J_2 = 1.6$, $J_3 = 0.7$ Hz, 1 H, Ar-H), 7.78-7.69 (m, 3 H, Ar-H), 7.36 (dd, $J_1 = 7.7$, $J_2 = 5.2$ Hz, 1 H, Ar-H), 7.27 (d, $J_1 = 8.0$ Hz, 1 H, Ar-H), 6.85 (d, $J_1 = 7.2$ Hz, 1 H, Ar-H), 3.30 (s, 3 H), 2.88 (s, 3 H); IR ν (neat, cm^{-1}) 3074, 2044, 1651, 1557, 1447, 1242; HRMS (ESI) for $\text{C}_{20}\text{H}_{17}\text{N}_3\text{O}_2\text{Rh}$ (MW = 434, $(\text{M}-\text{Cl})^+$): 434.0370. Found: 434.0369. Clean ^{13}C NMR of **M2** cannot be obtained due to the stability issue of this complex.

Qualitative results for C–C cleavage using different directing groups: the Rh-mediated C–C cleavage using other DGs has also been examined by following the same procedure as above for isatin **1a**. For isatins **1b** (pyridyl) and **1d** (oxazolinyl), the C–C activation also proceeded at room temperature within 16h; however, the reaction with substrate **1c** (1H-indazol-1-yl) did not occur until 50 °C. Isolation of pure Rh-CO complexes for all these cases proved nontrivial, but their characteristic Rh-CO IR stretching frequencies can be observed.

		
DG	Temp. for C–C cleavage	Rh-CO frequency in IR / cm^{-1}
 1a	rt	2067 & 2044
 1b	rt	2054
 1d	rt	2077
 1c	50 °C (rt, no reaction)	2056 & 2078

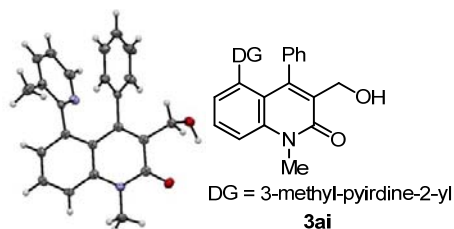
X-Ray data:

X-Ray data for **3ag**:



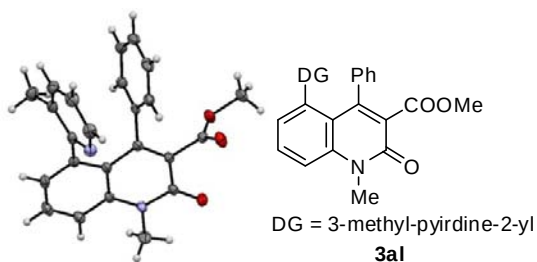
Empirical formula	C ₂₃ H ₂₀ N ₂ O
Formula weight	340.41
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	P b c a
Unit cell dimensions	a = 13.9808(5) Å α = 90°. b = 14.9970(5) Å β = 90°. c = 17.3046(6) Å γ = 90°.
Volume	3628.3(2) Å ³
Z	8
Density (calculated)	1.246 Mg/m ³
Absorption coefficient	0.077 mm ⁻¹
F(000)	1440
Crystal size	0.230 x 0.210 x 0.080 mm
Theta range for data collection	3.424 to 30.640°.
Index ranges	-19 ≤ h ≤ 19, -21 ≤ k ≤ 21, -22 ≤ l ≤ 24
Reflections collected	37834
Independent reflections	5206 [R(int) = 0.0477]
Completeness to theta = 25.242°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00 and 0.859
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5206 / 0 / 238
Goodness-of-fit on F ²	1.178
Final R indices [I > 2σ(I)]	R1 = 0.0641, wR2 = 0.1501
R indices (all data)	R1 = 0.0974, wR2 = 0.1628
Extinction coefficient	n/a
Largest diff. peak and hole	0.216 and -0.185 e.Å ⁻³

X-Ray data for **3ai**:



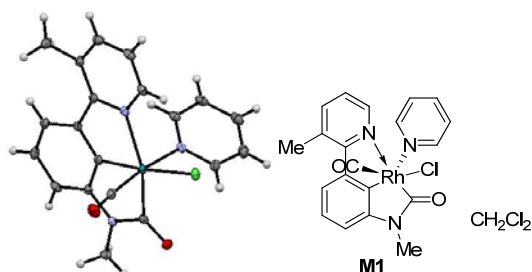
Empirical formula	C ₂₃ H ₂₀ N ₂ O ₂	
Formula weight	356.41	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 14.428(9) Å	α = 90°.
	b = 14.478(9) Å	β = 90°.
	c = 17.101(11) Å	γ = 90°.
Volume	3572(4) Å ³	
Z	8	
Density (calculated)	1.325 Mg/m ³	
Absorption coefficient	0.085 mm ⁻¹	
F(000)	1504	
Crystal size	0.450 x 0.440 x 0.350 mm	
Theta range for data collection	3.056 to 27.498°.	
Index ranges	-18 ≤ h ≤ 18, -18 ≤ k ≤ 18, -22 ≤ l ≤ 22	
Reflections collected	40079	
Independent reflections	4106 [R(int) = 0.0802]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.785	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4106 / 0 / 250	
Goodness-of-fit on F ²	1.068	
Final R indices [I > 2σ(I)]	R1 = 0.0554, wR2 = 0.1101	
R indices (all data)	R1 = 0.0755, wR2 = 0.1189	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.278 and -0.227 e.Å ⁻³	

X-Ray data for **3al**:

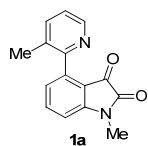


Empirical formula	C ₂₄ H ₂₀ N ₂ O ₃	
Formula weight	384.42	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 2 ₁ /n	
Unit cell dimensions	a = 8.7932(19) Å	α = 90°.
	b = 14.204(3) Å	β = 94.193(5)°.
	c = 15.309(3) Å	γ = 90°.
Volume	1907.0(7) Å ³	
Z	4	
Density (calculated)	1.339 Mg/m ³	
Absorption coefficient	0.089 mm ⁻¹	
F(000)	808	
Crystal size	0.160 x 0.090 x 0.050 mm	
Theta range for data collection	3.029 to 27.485°.	
Index ranges	-11 ≤ h ≤ 11, -18 ≤ k ≤ 18, -19 ≤ l ≤ 19	
Reflections collected	23716	
Independent reflections	4365 [R(int) = 0.0548]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.750	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4365 / 0 / 265	
Goodness-of-fit on F ²	1.064	
Final R indices [I > 2σ(I)]	R1 = 0.0531, wR2 = 0.1120	
R indices (all data)	R1 = 0.0800, wR2 = 0.1246	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.231 and -0.215 e.Å ⁻³	

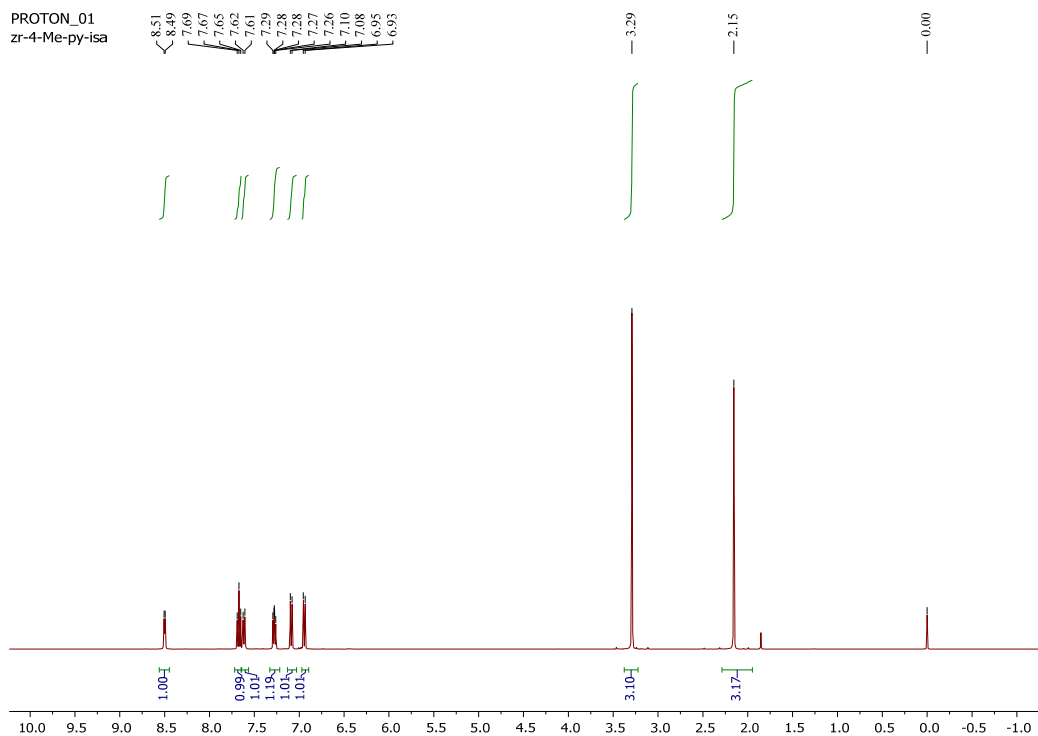
X-Ray data for **M1**:



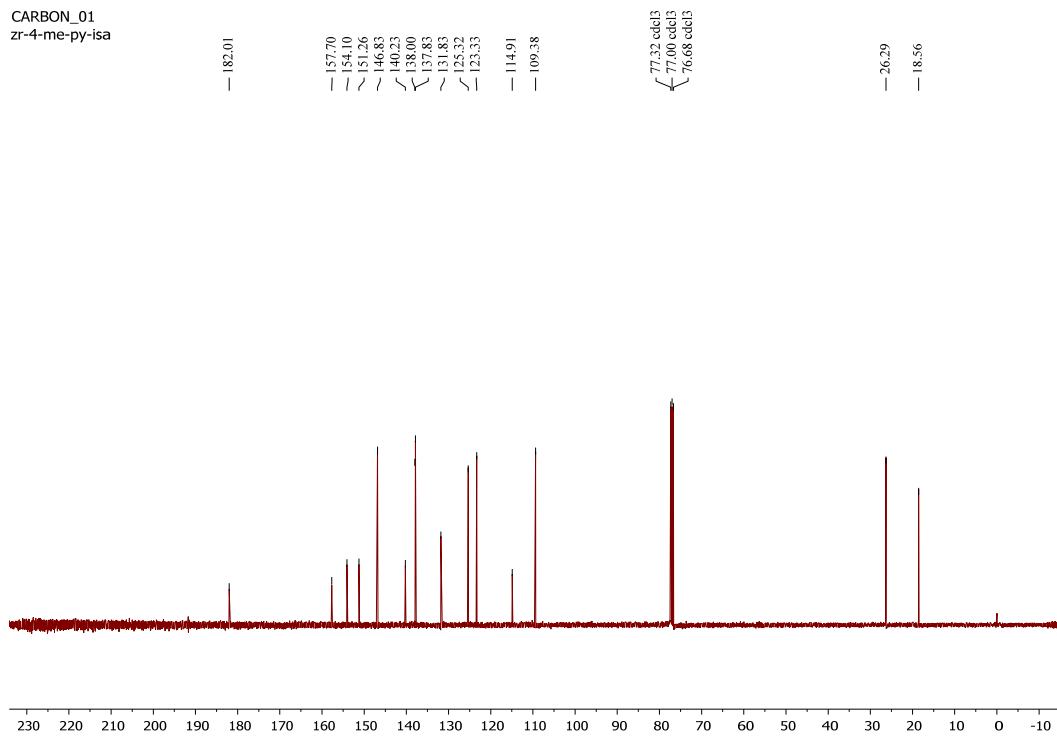
Empirical formula	C ₂₁ H ₁₉ Cl ₃ N ₃ O ₂ Rh	
Formula weight	554.65	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.115(2) Å	α = 93.432(3)°.
	b = 10.156(3) Å	β = 98.034(4)°.
	c = 13.490(4) Å	γ = 102.618(5)°.
Volume	1069.6(5) Å ³	
Z	2	
Density (calculated)	1.722 Mg/m ³	
Absorption coefficient	1.197 mm ⁻¹	
F(000)	556	
Crystal size	0.11 x 0.08 x 0.03 mm ³	
Theta range for data collection	2.064 to 25.242°.	
Index ranges	-10 ≤ h ≤ 10, -13 ≤ k ≤ 11, -17 ≤ l ≤ 17	
Reflections collected	4891	
Independent reflections	4891 [R(int) = 0.0360]	
Completeness to theta = 27.482°	99.7 %	
Absorption correction	DTABSCOR	
Max. and min. transmission	0.965 and 0.880	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4891 / 180/ 273	
Goodness-of-fit on F ²	1.041	
Final R indices [I > 2sigma(I)]	R1 = 0.0297, wR2 = 0.0683	
R indices (all data)	R1 = 0.0353, wR2 = 0.0709	
Largest diff. peak and hole	1.331 and -0.881 e.Å ⁻³	

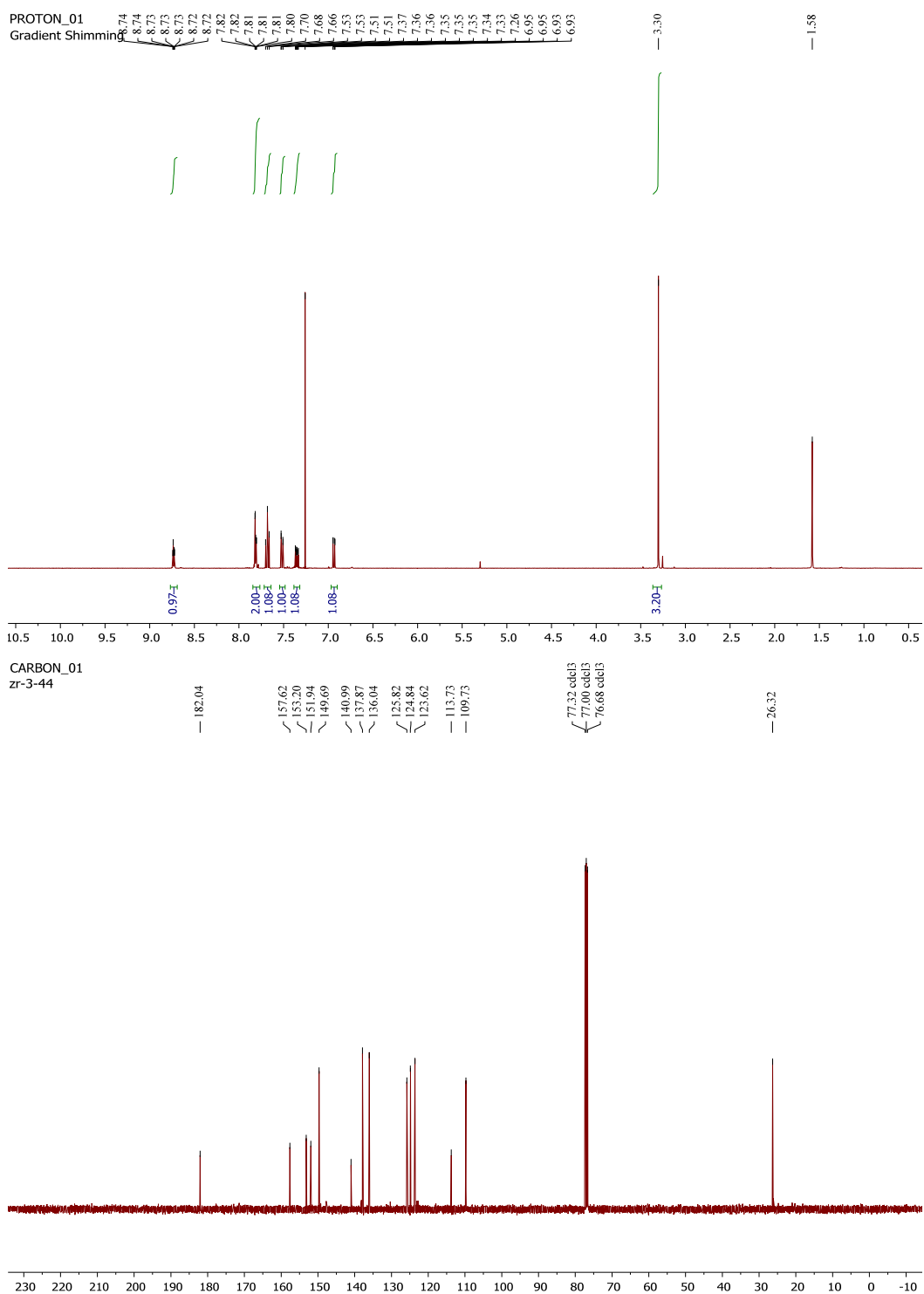
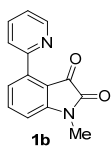


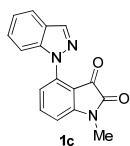
PROTON_01
zr-4-Me-py-isa



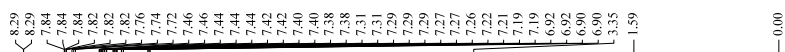
CARBON_01
zr-4-me-py-isa



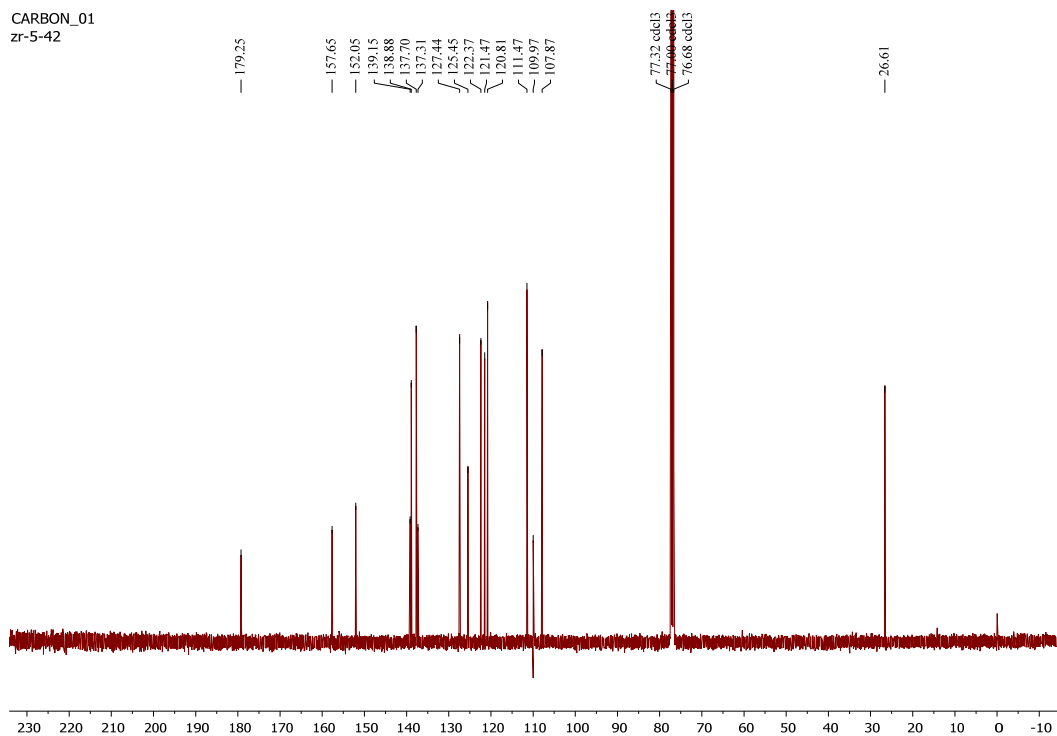


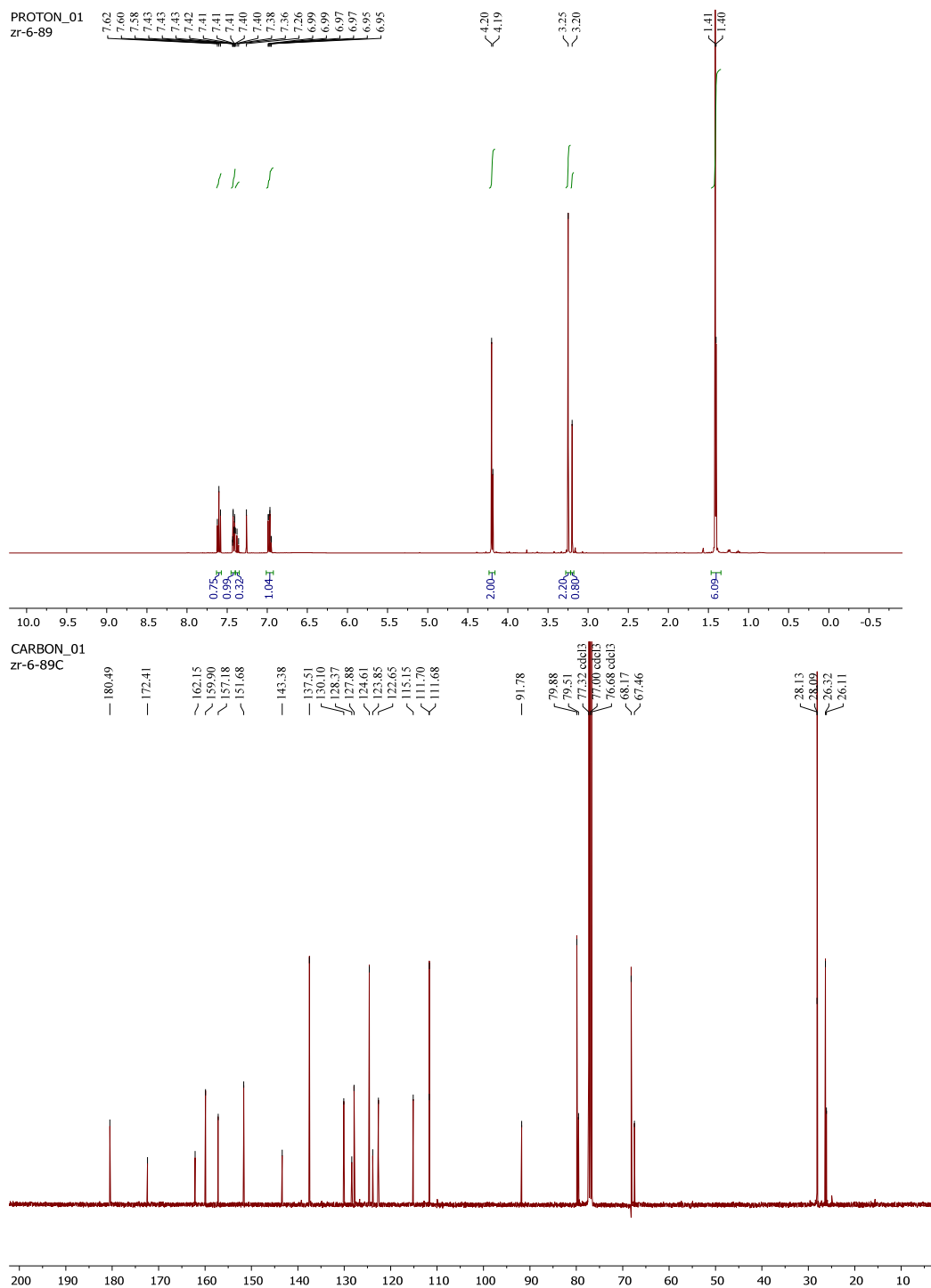
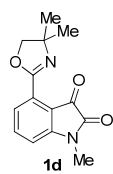


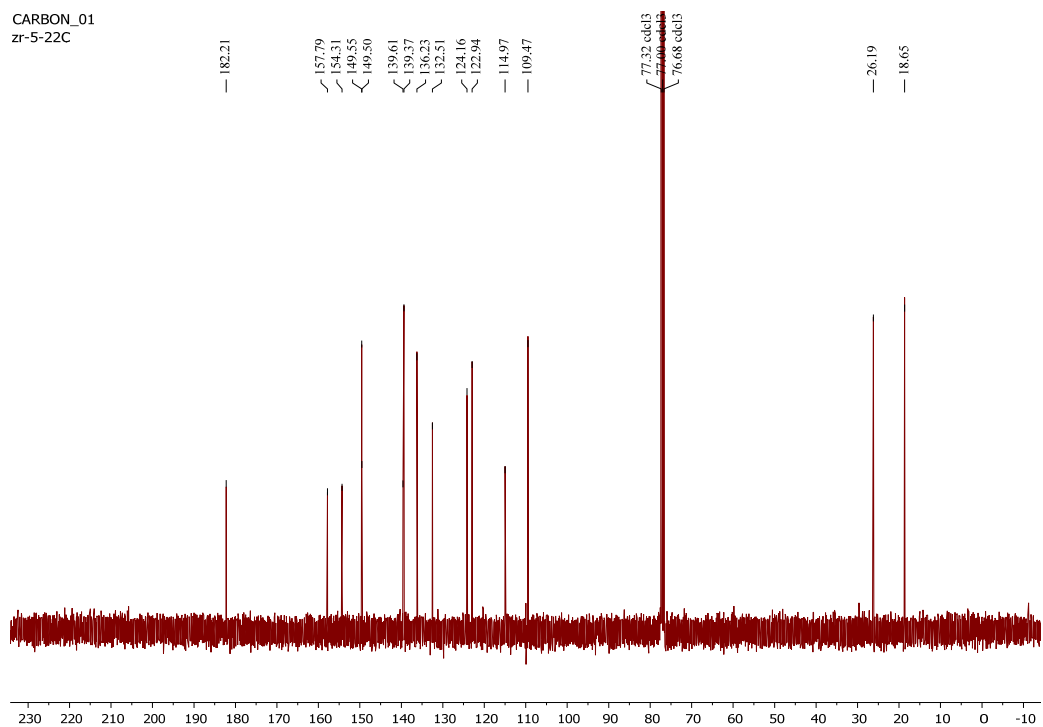
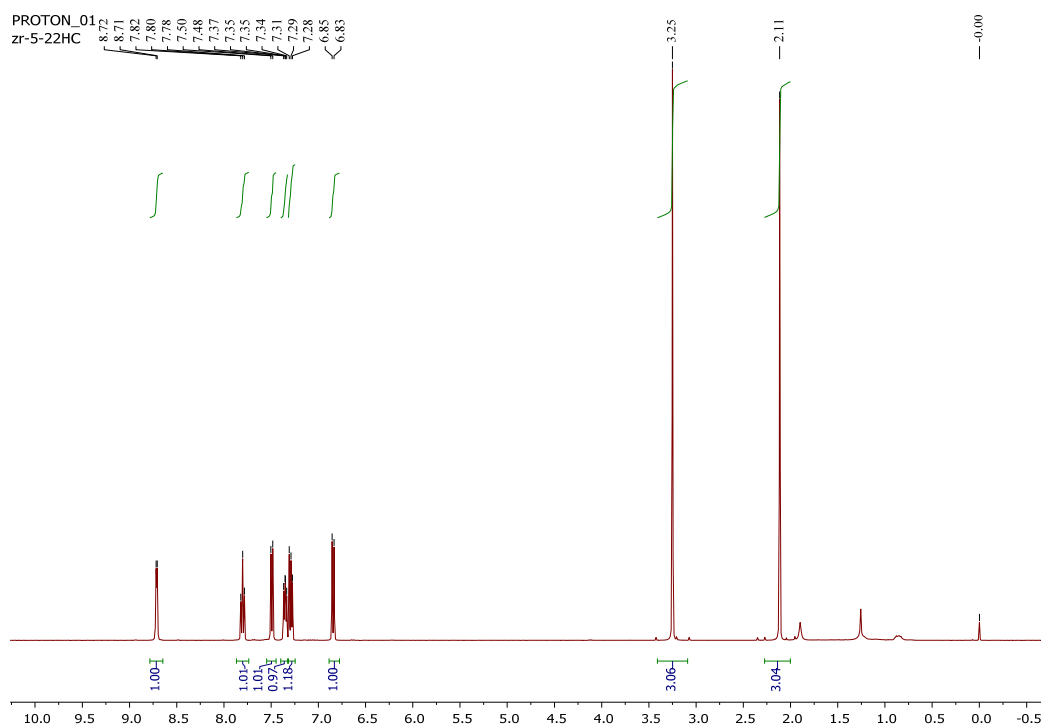
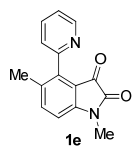
PROTON_01
zr-5-42

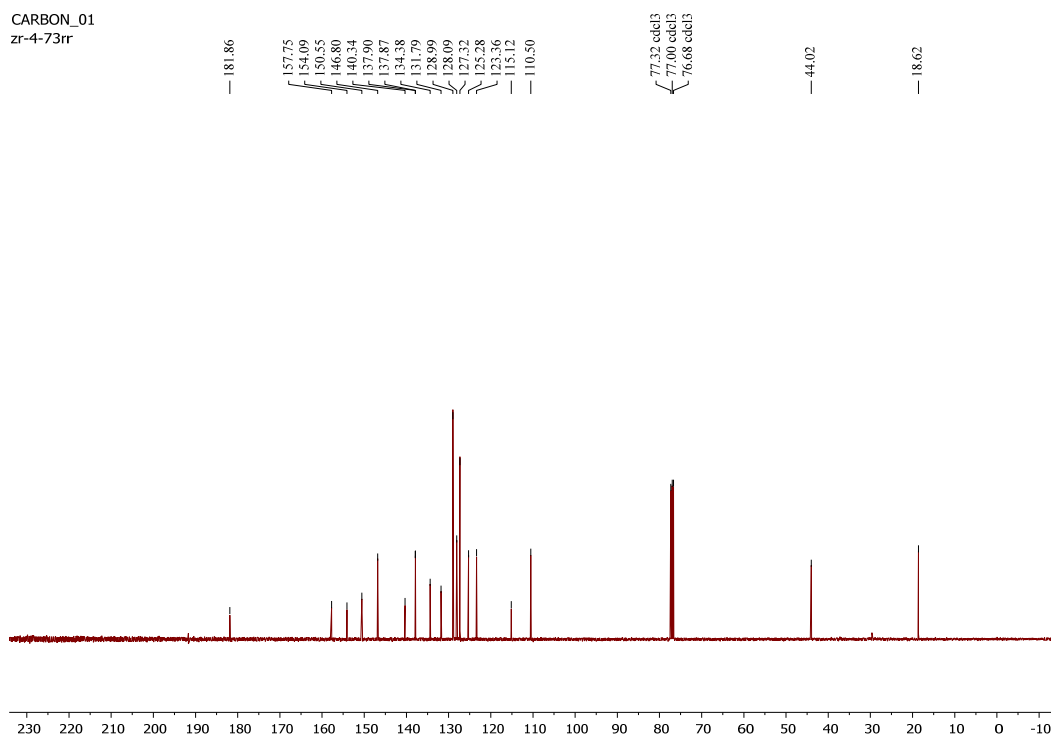
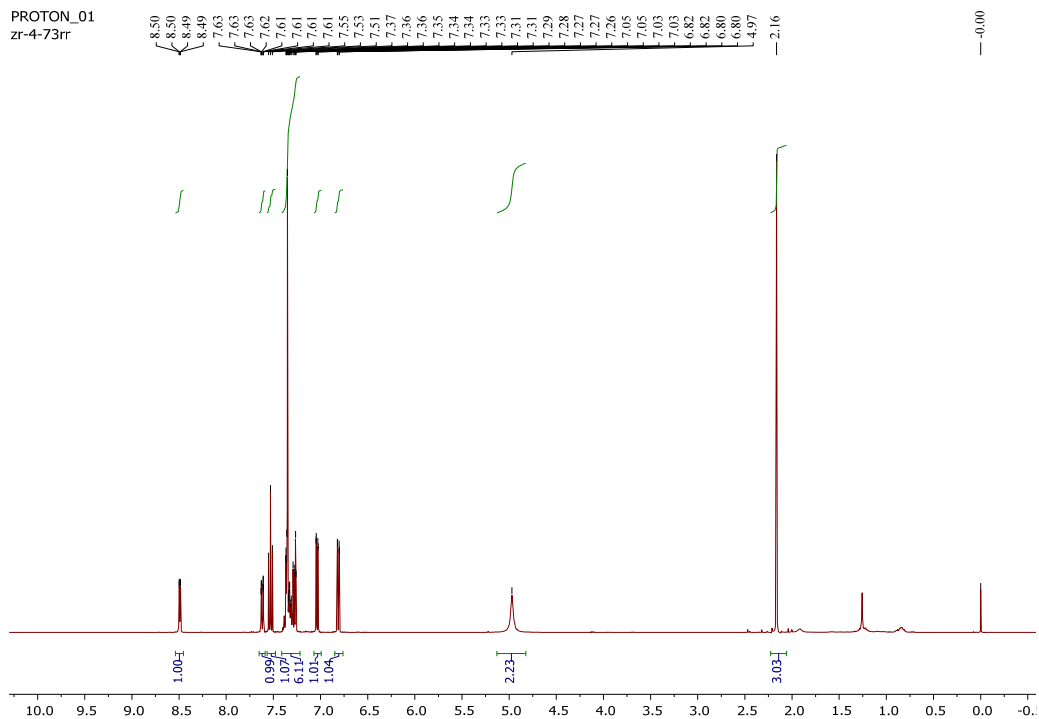
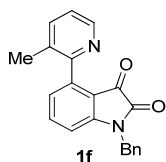


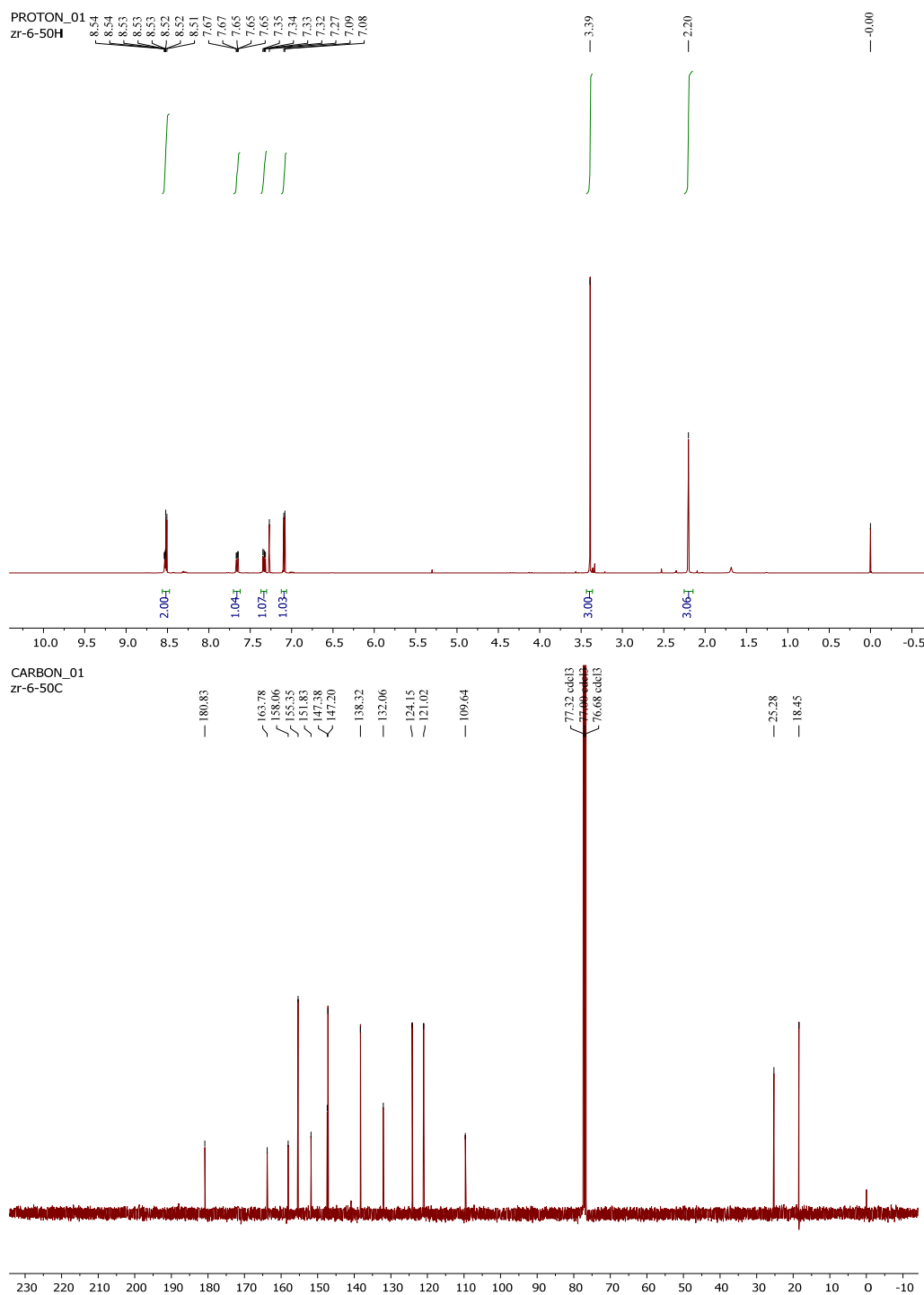
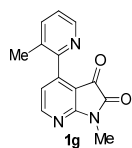
CARBON_01
zr-5-42

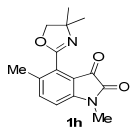




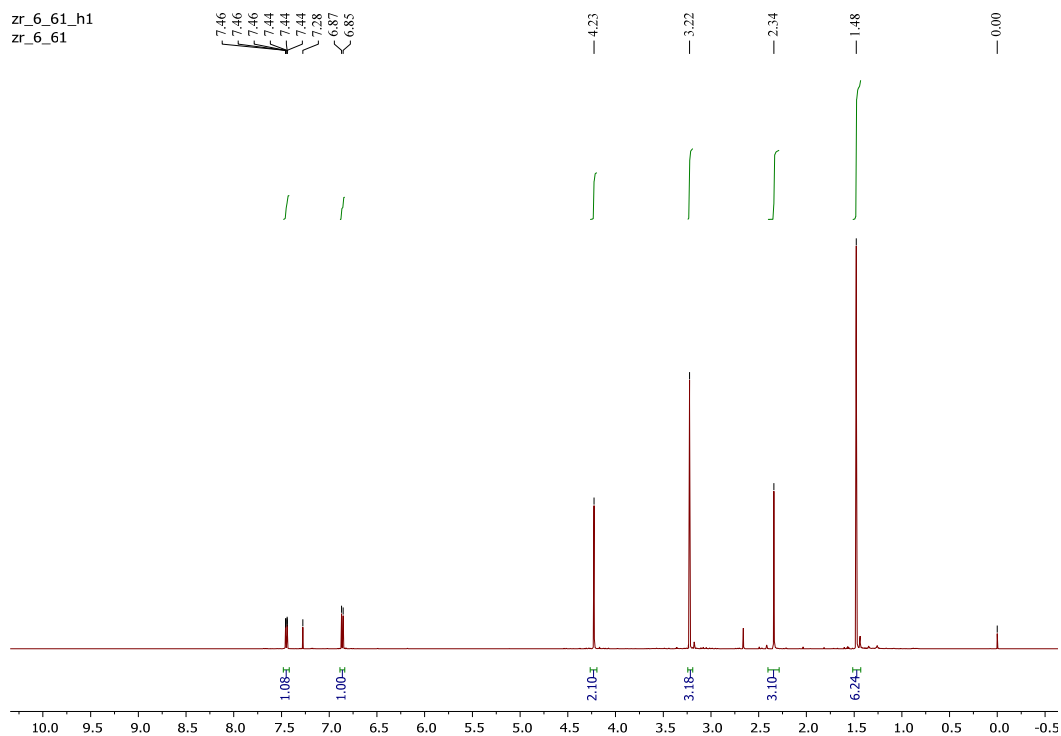




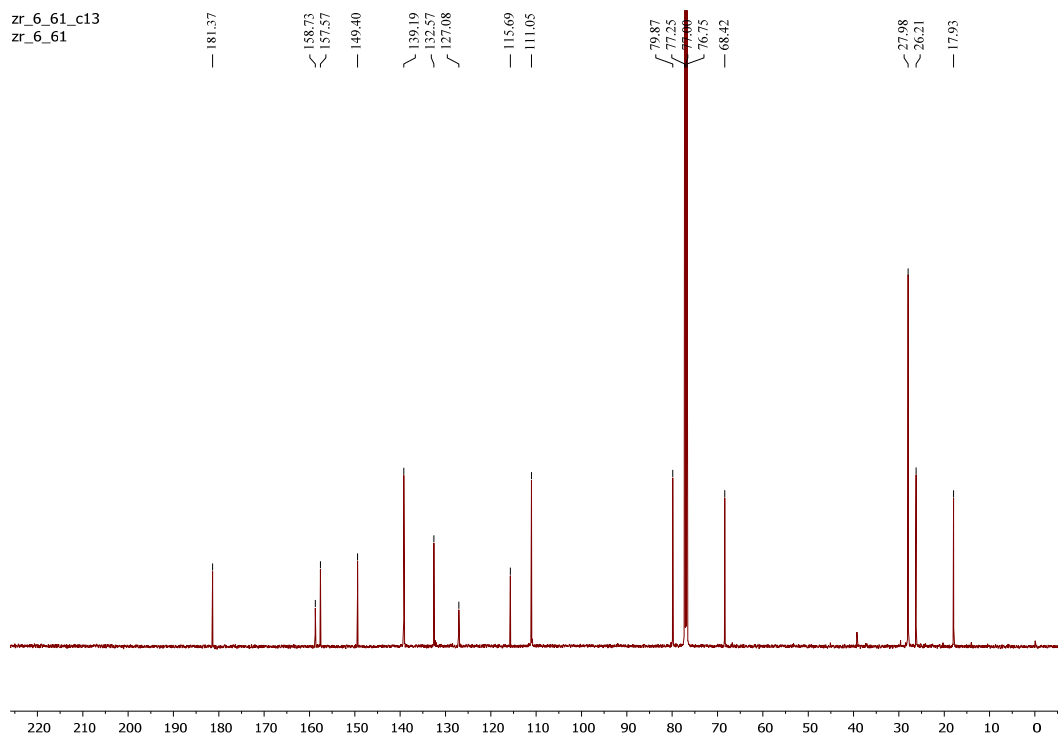


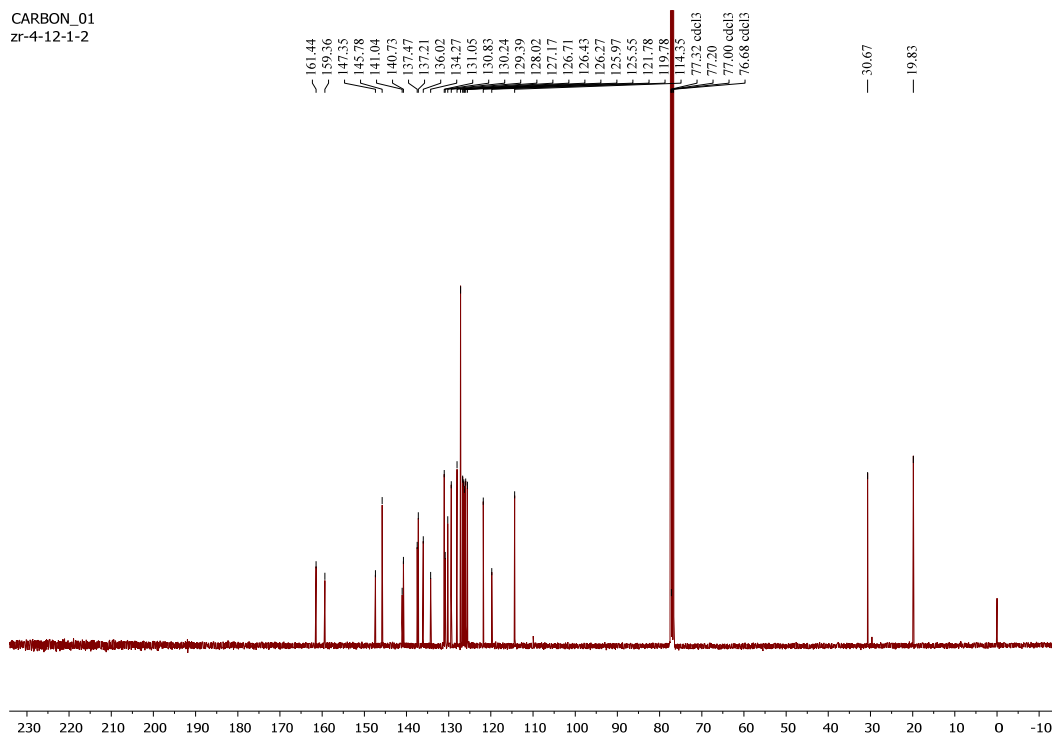
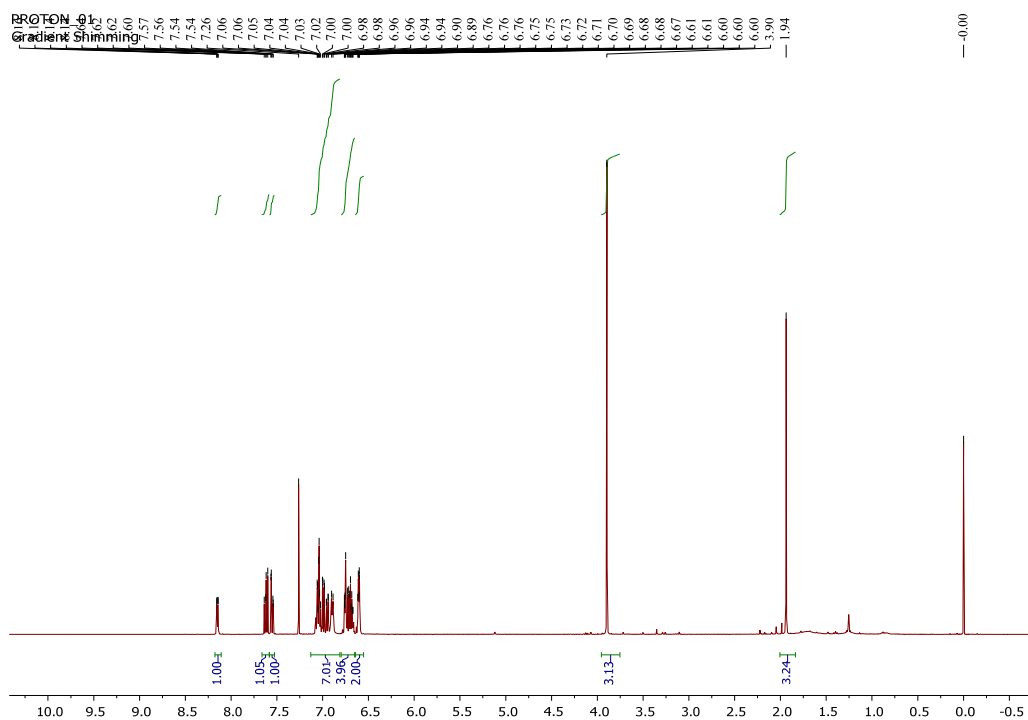
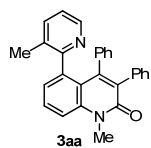


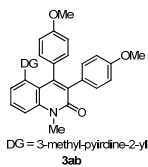
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zr_6_61



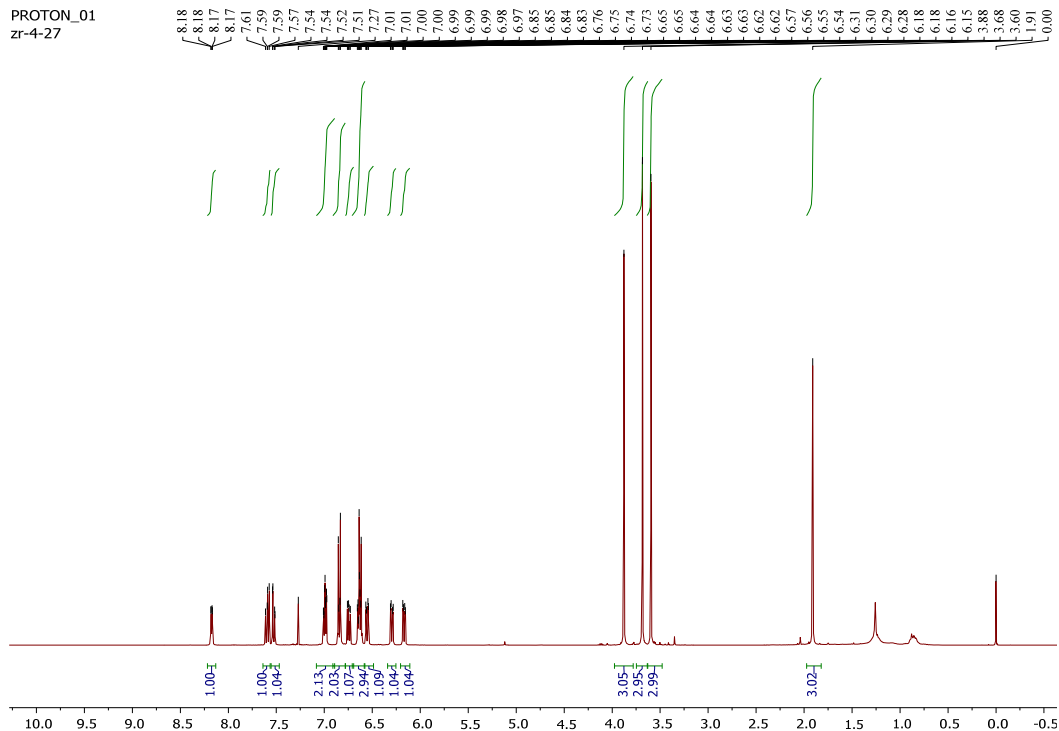
zr_6_61_c13
zr_6_61



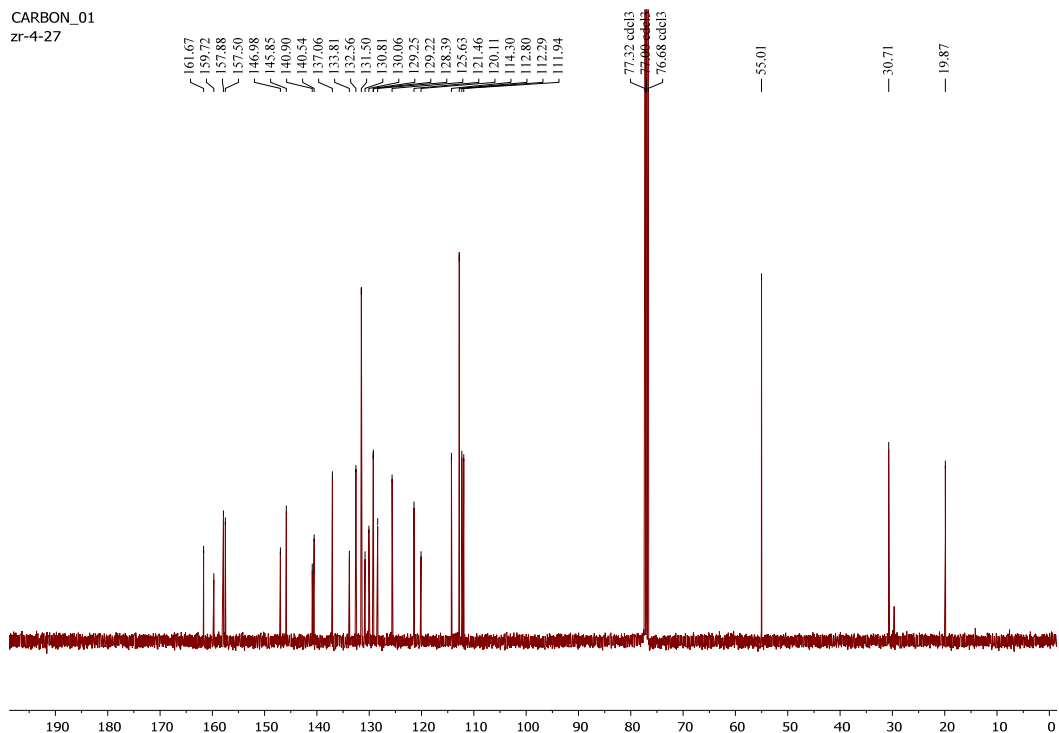


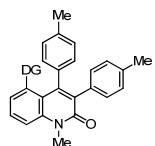


PROTON_01
zr-4-27

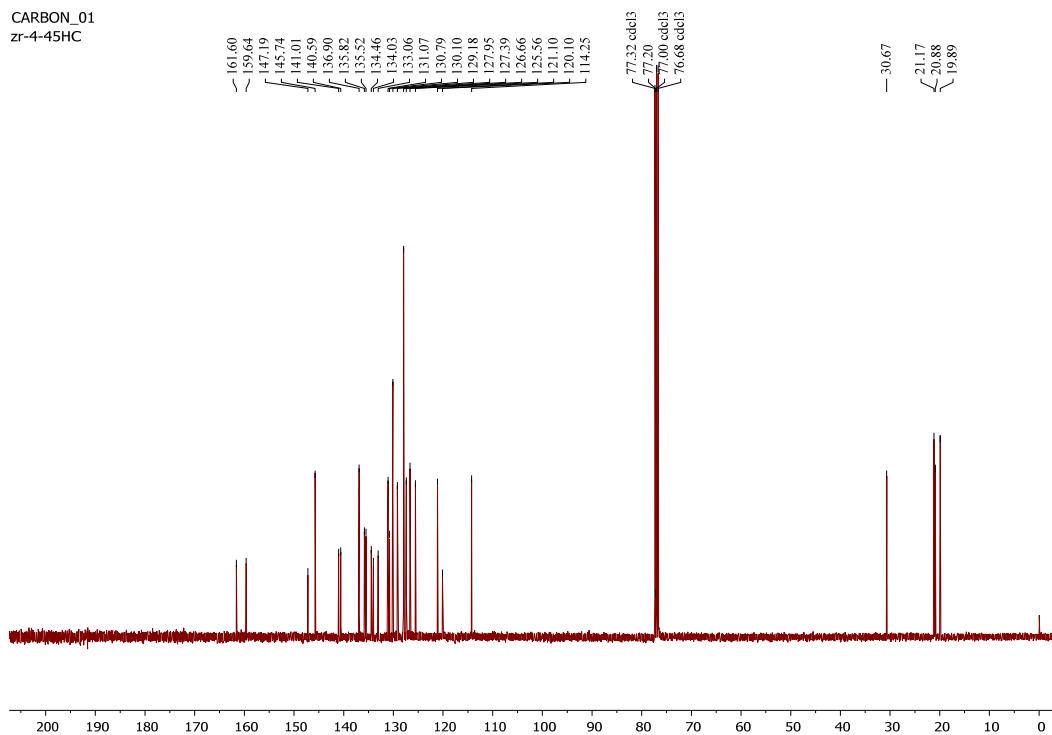
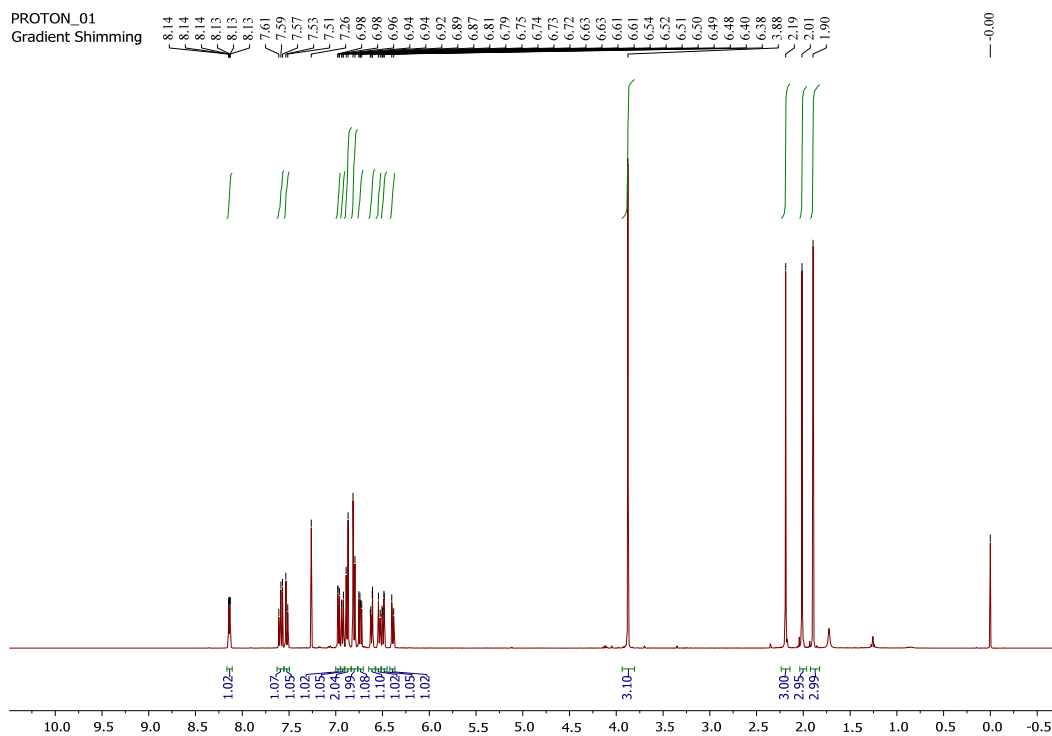


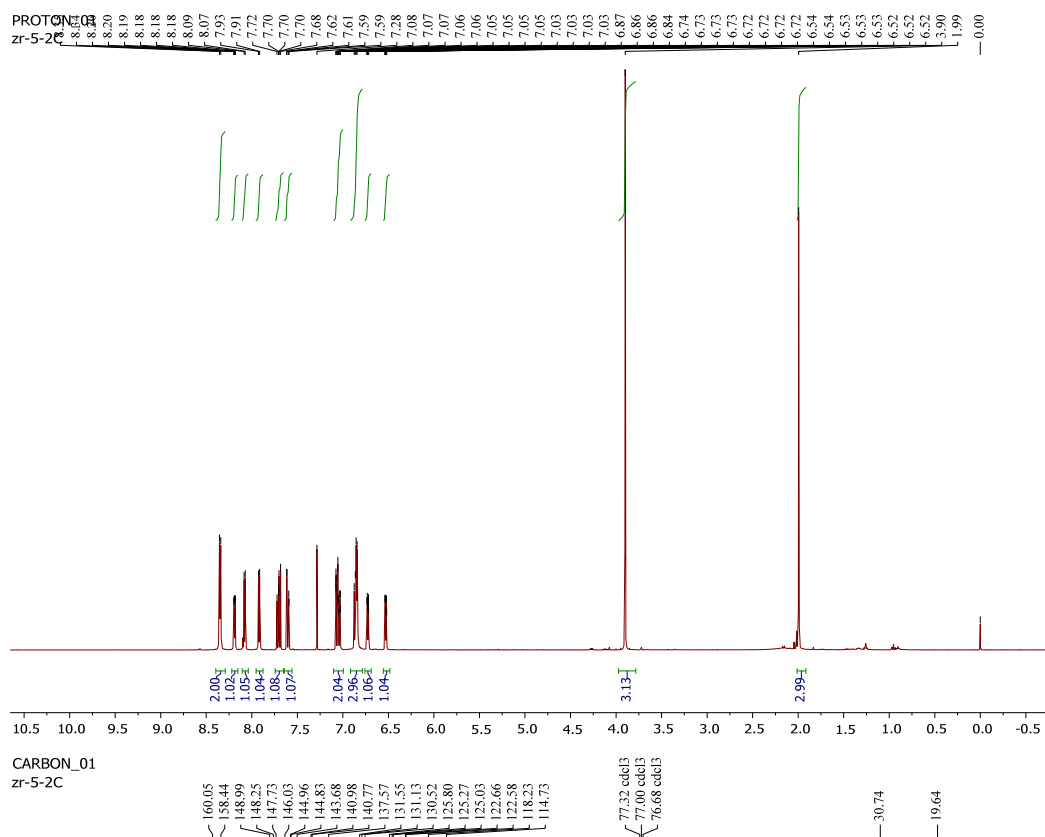
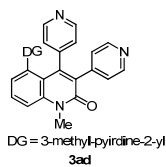
CARBON_01
zr-4-27

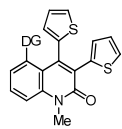




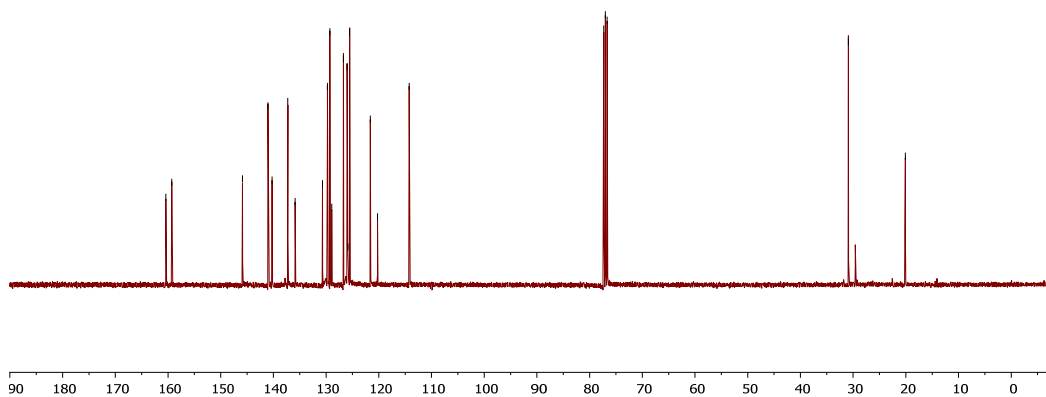
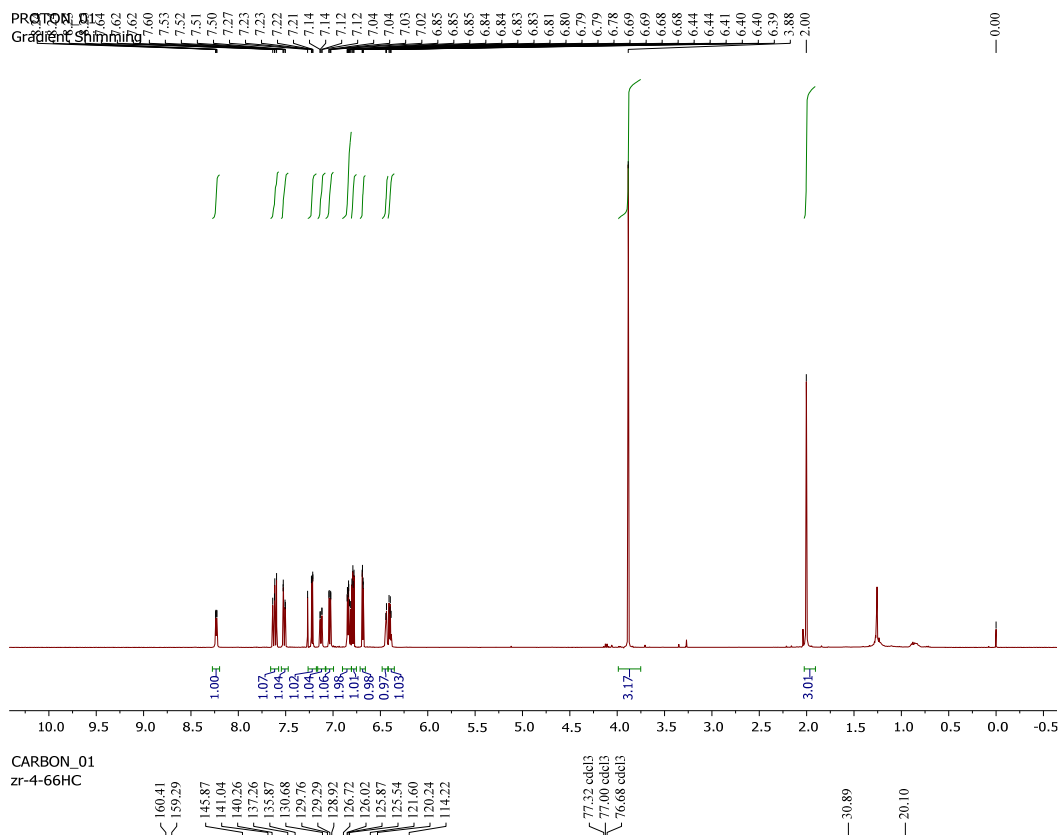
DG=3-methylpyridine-2-yl
3ac

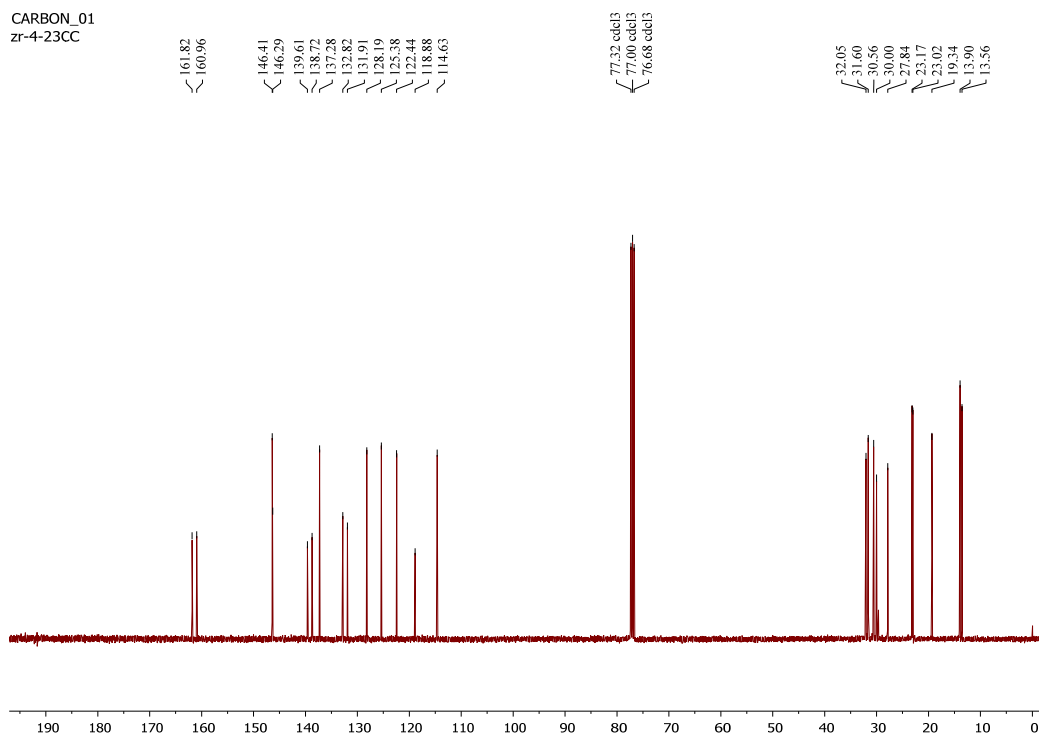
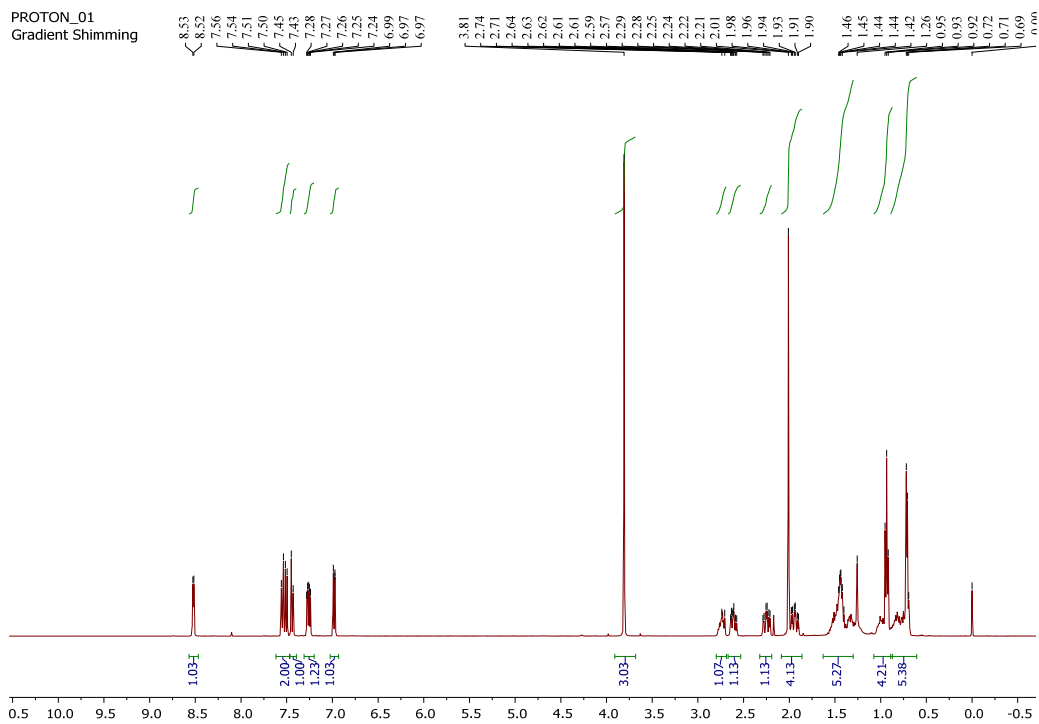
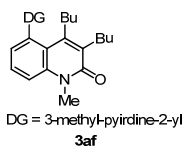


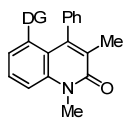




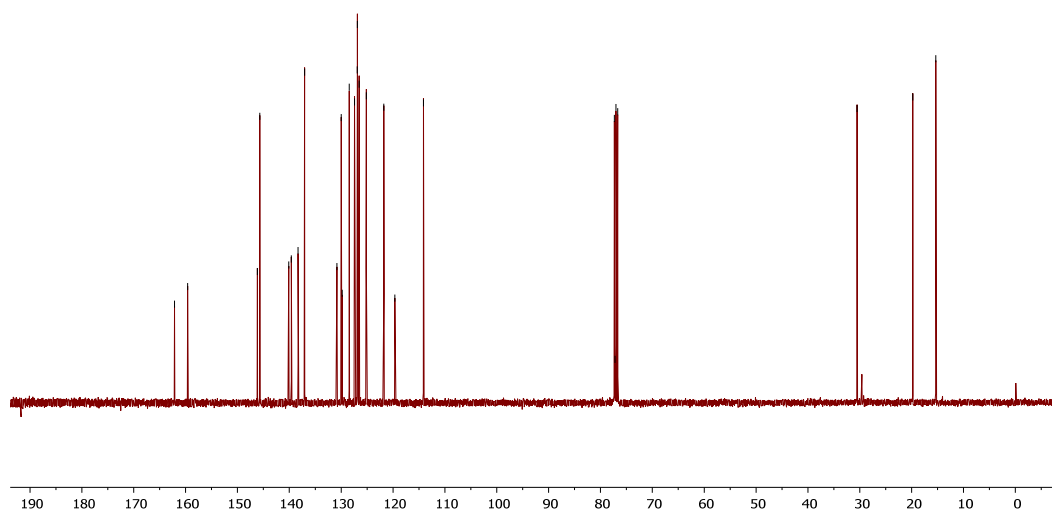
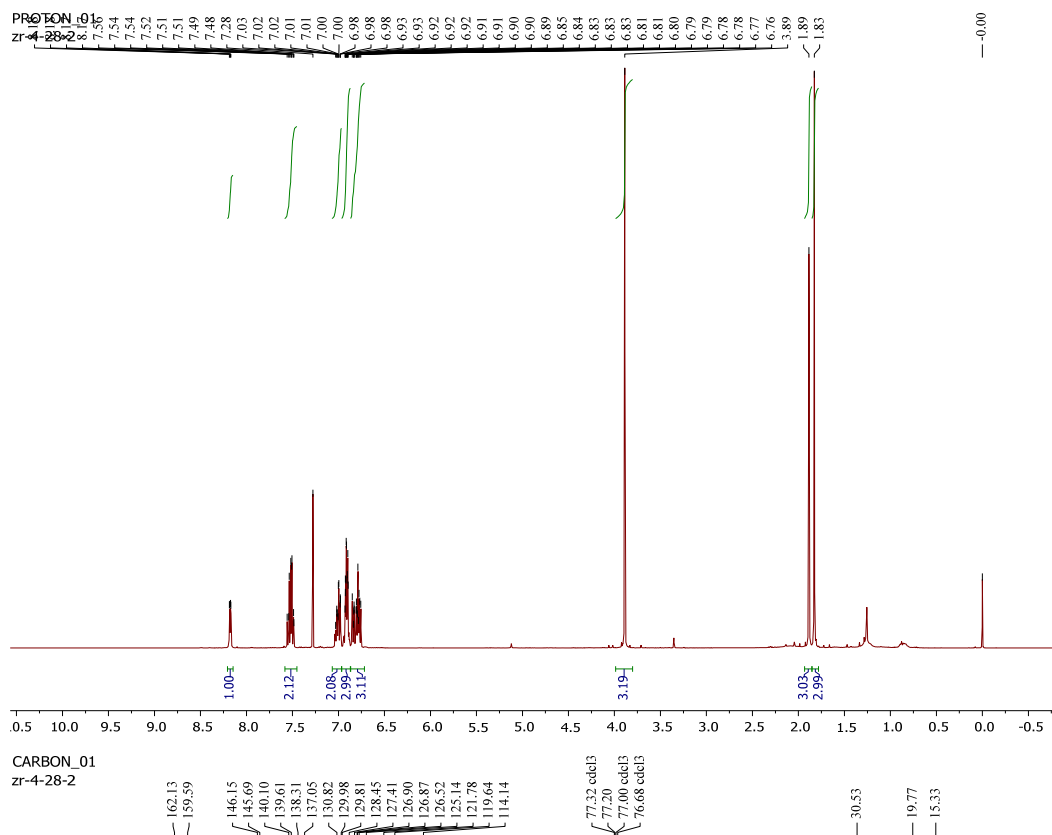
DG = 3-methylpyridine-2-yl
3ae

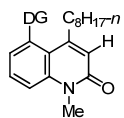






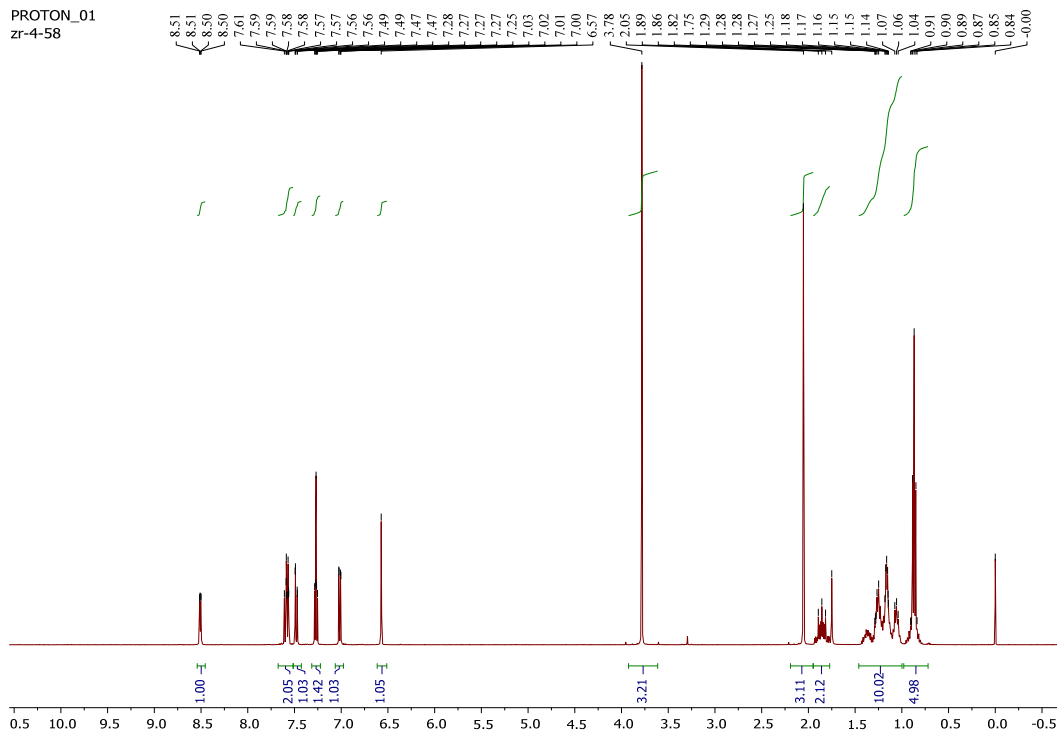
DG = 3-methyl-pyridine-2-yl
3ag



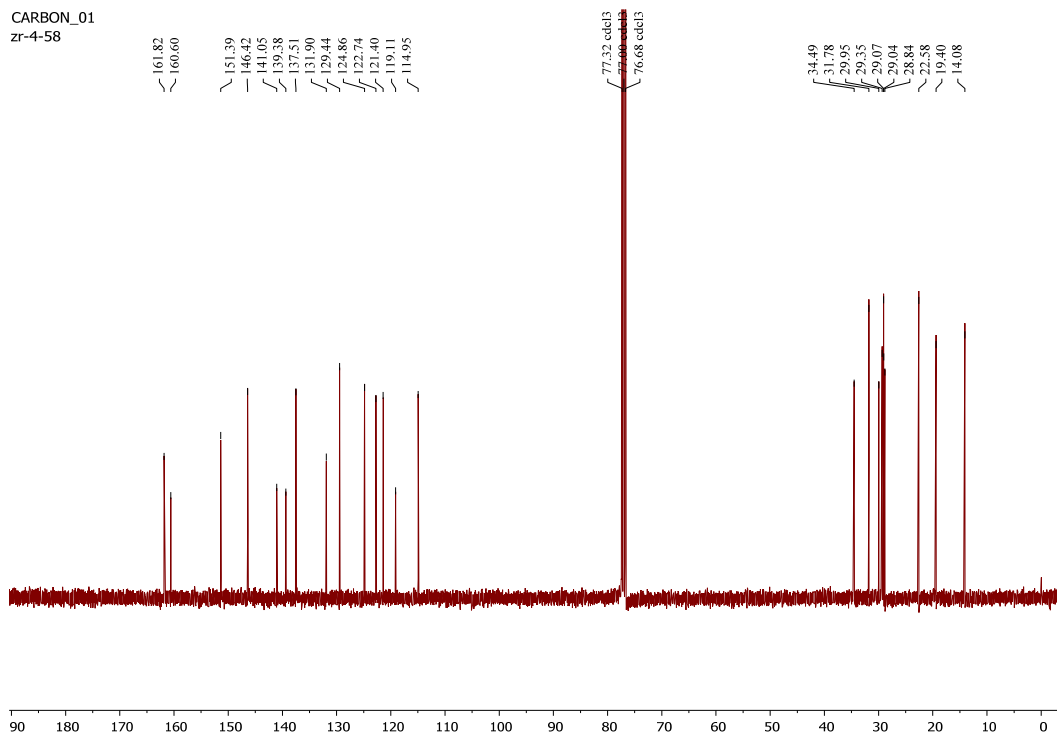


3ah

PROTON_01
zr-4-58

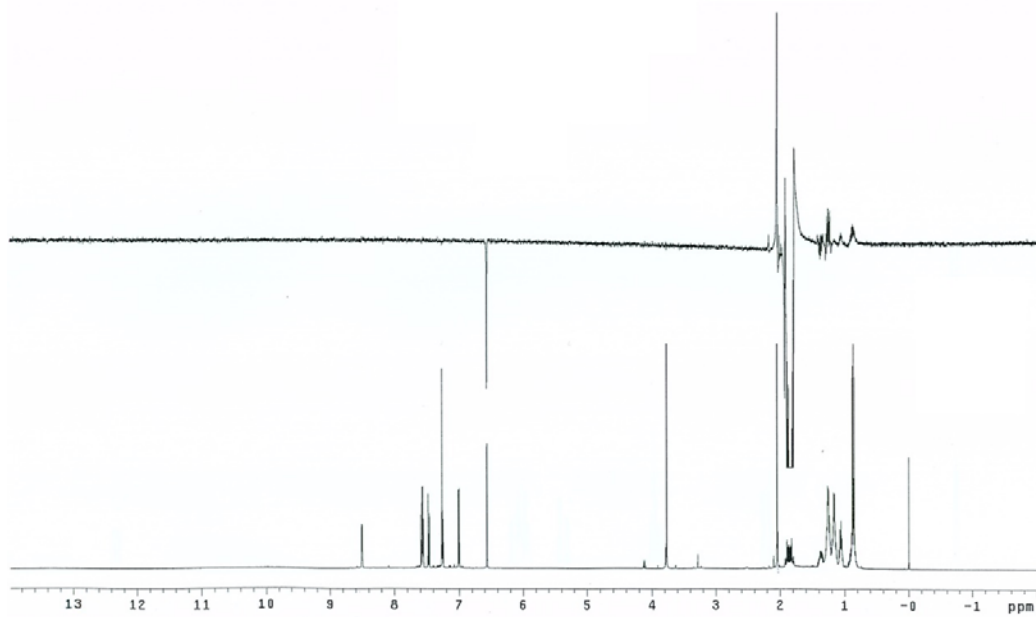


CARBON_01
zr-4-58

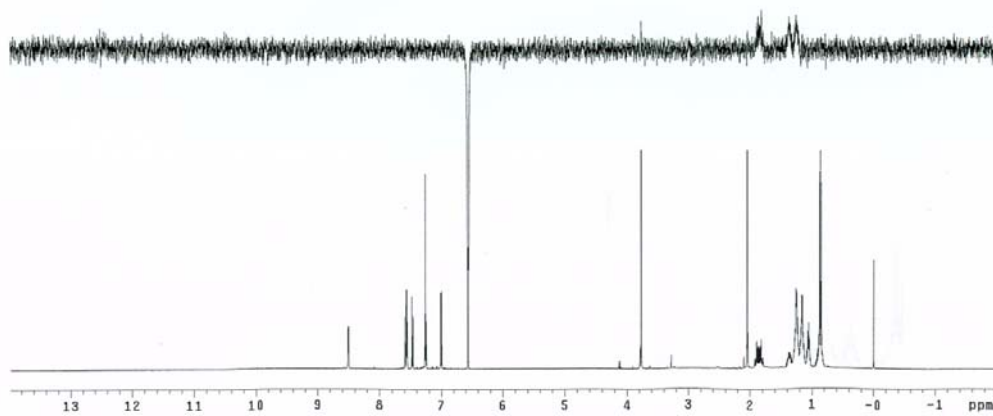


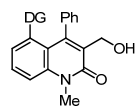
1D NOESY of **3ah**

zr_4_58_1_89p_1dnoe
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Pulse Sequence: NOESY1D



zr_4_58_6_58p_1dnoe
File: Noesy1d
Pulse Sequence: NOESY1D

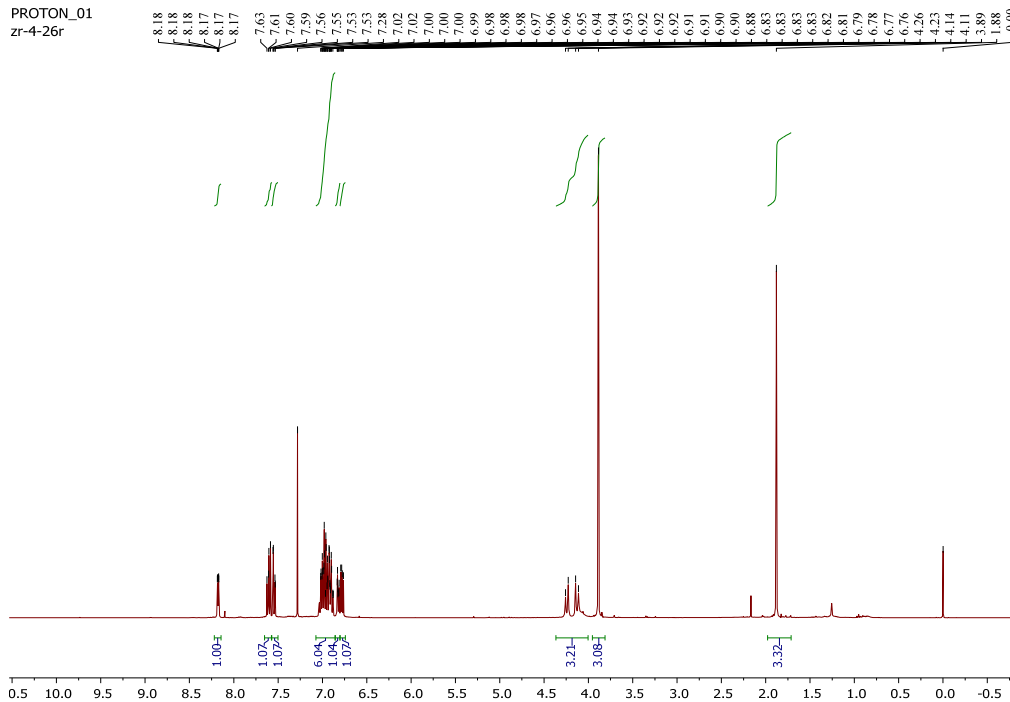




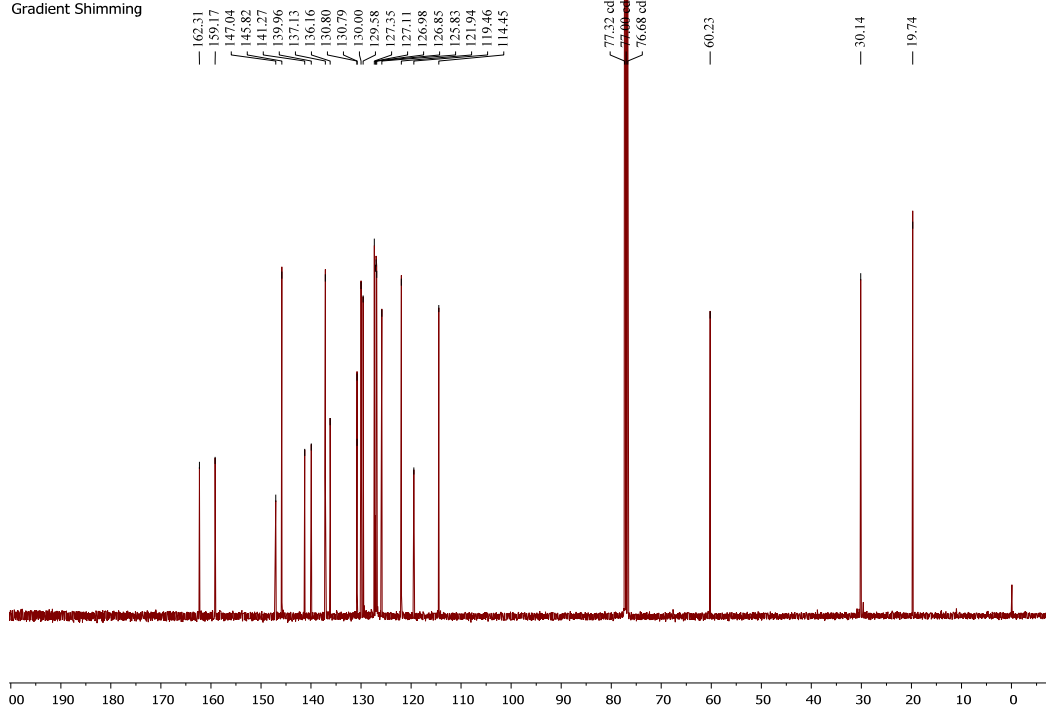
DG = 3-methyl-pyridine-2-yl

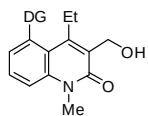
3ai

PROTON_01
zr-4-26r



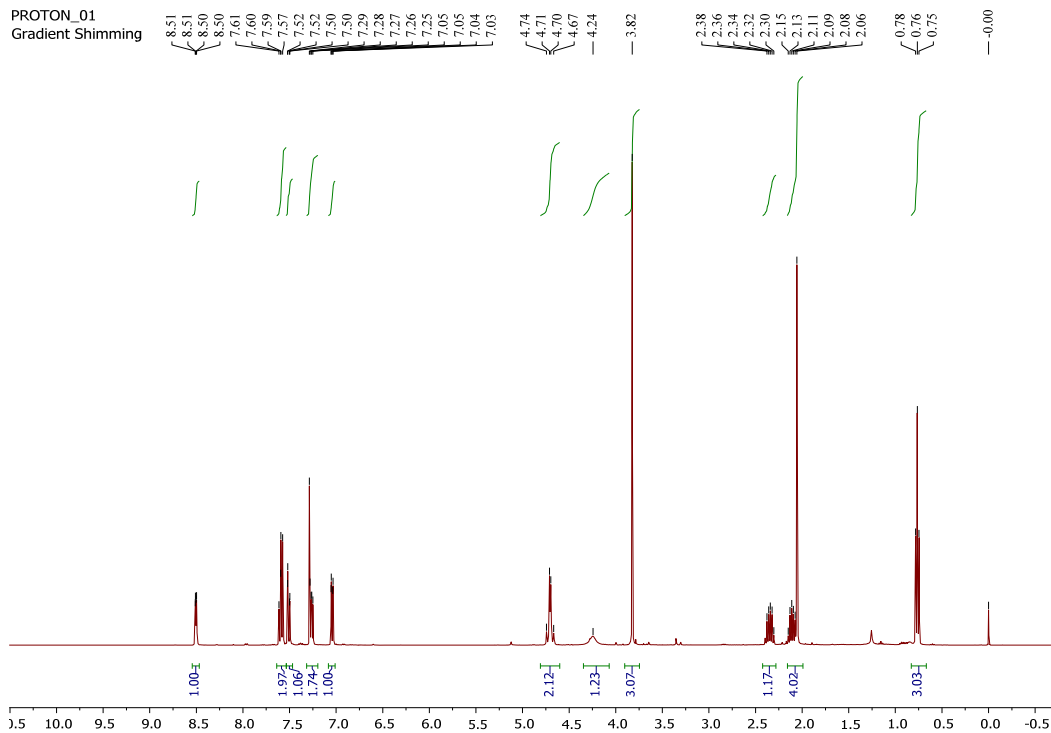
CARBON_01
Gradient Shimming



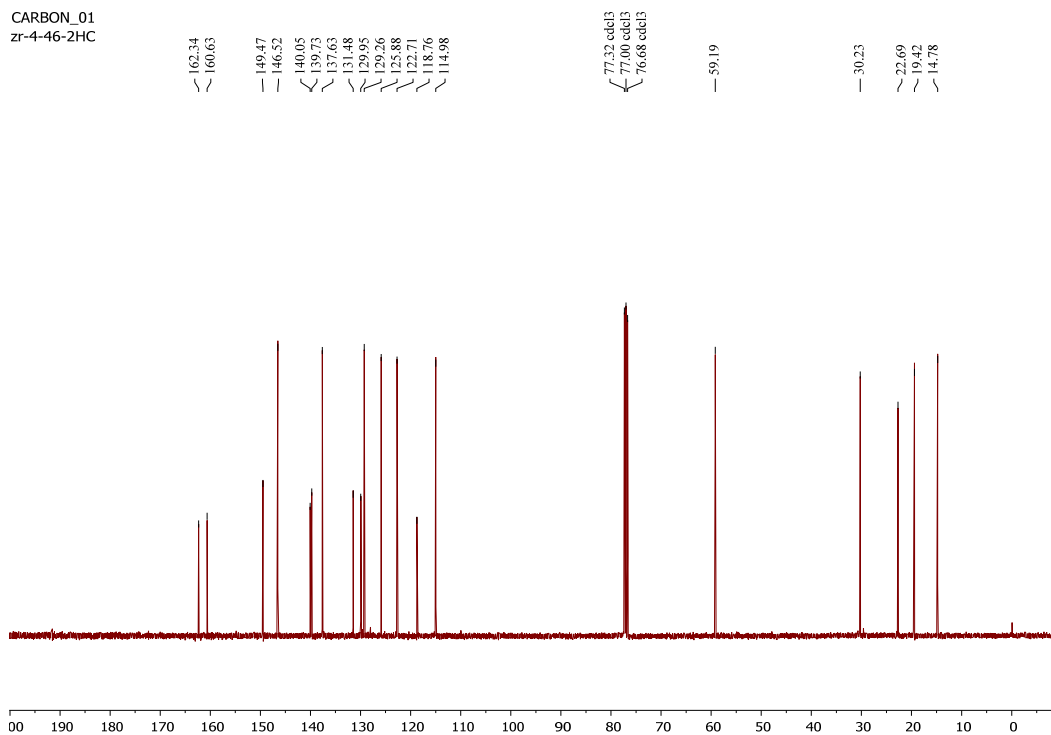


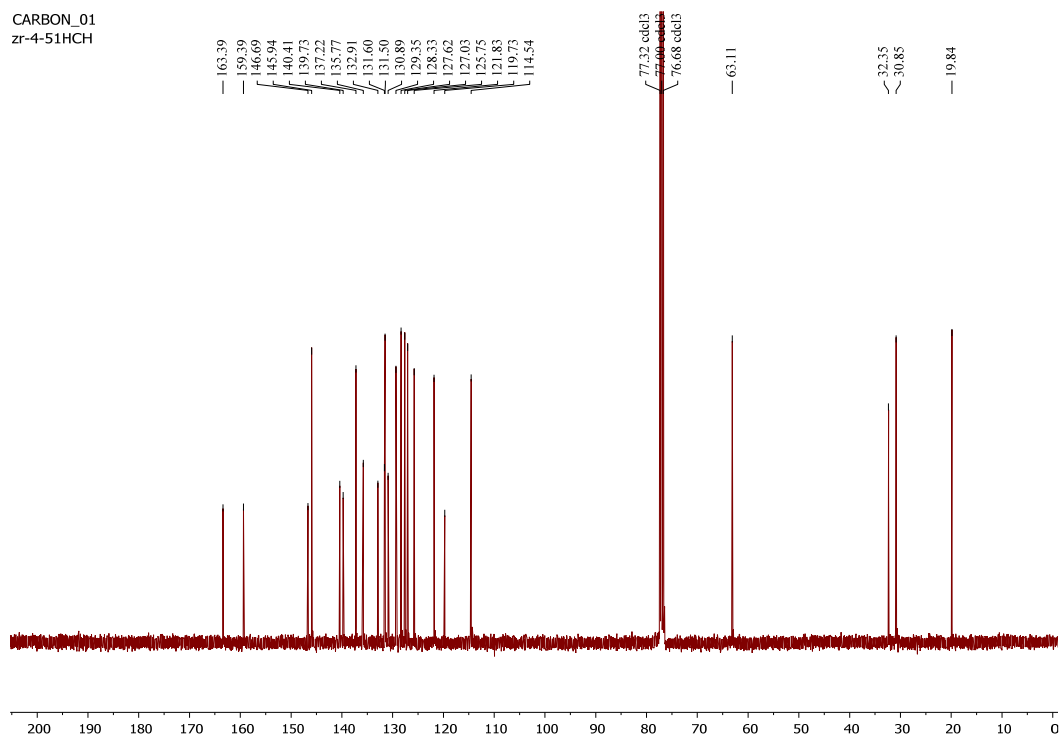
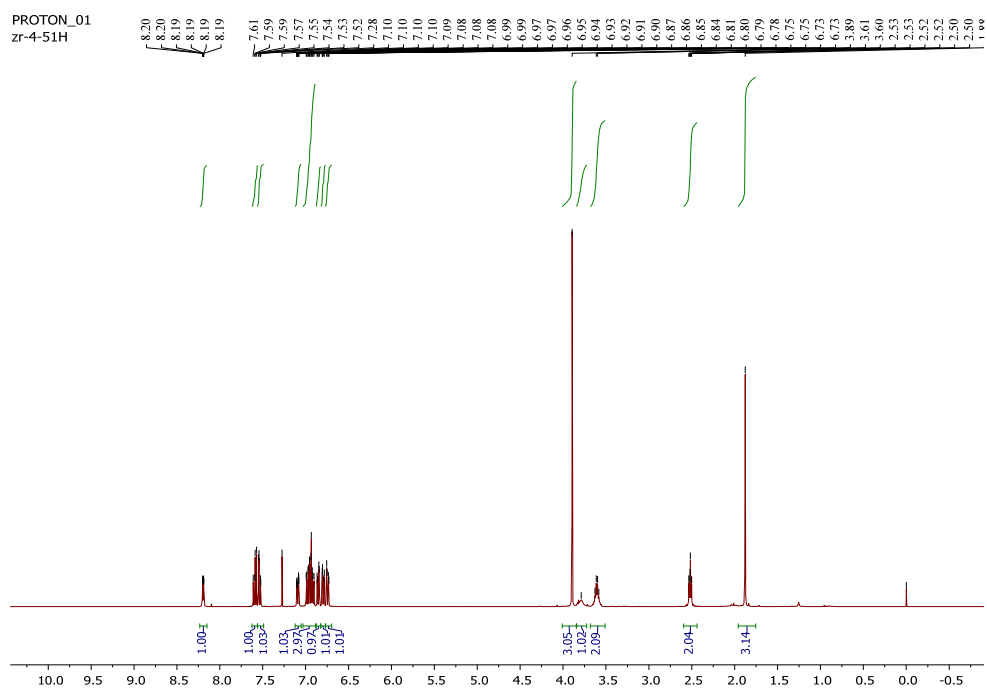
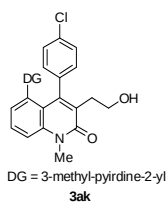
DG = 3-methyl-pyridine-2-yl
3aj

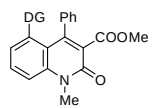
PROTON_01
 Gradient Shimming



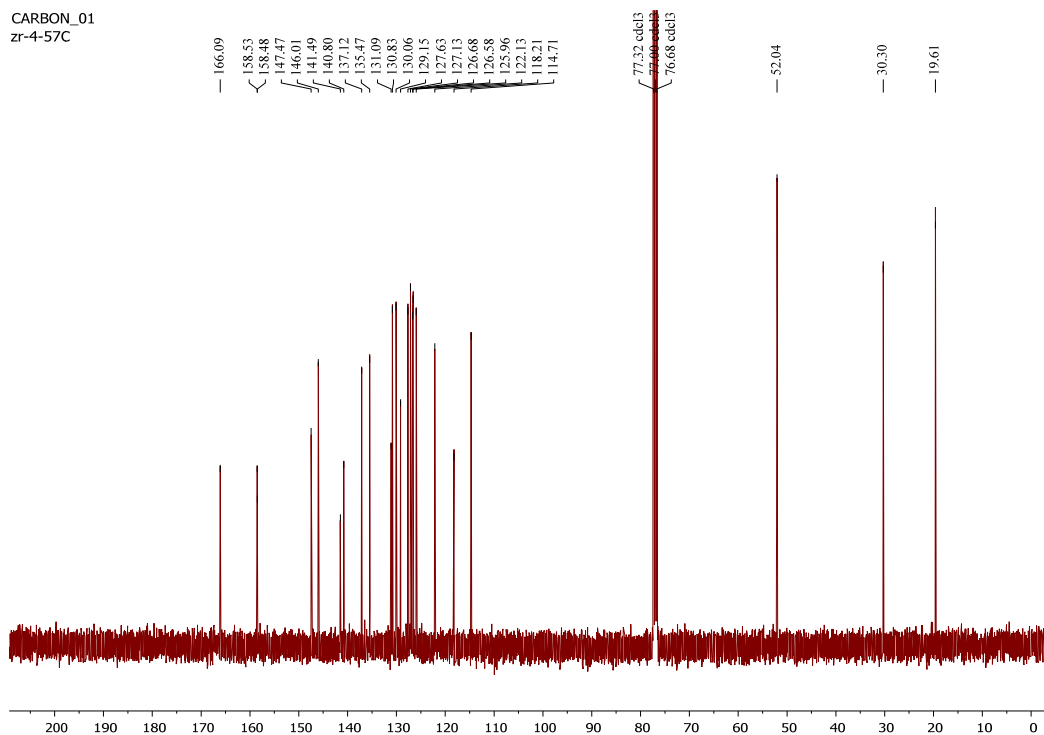
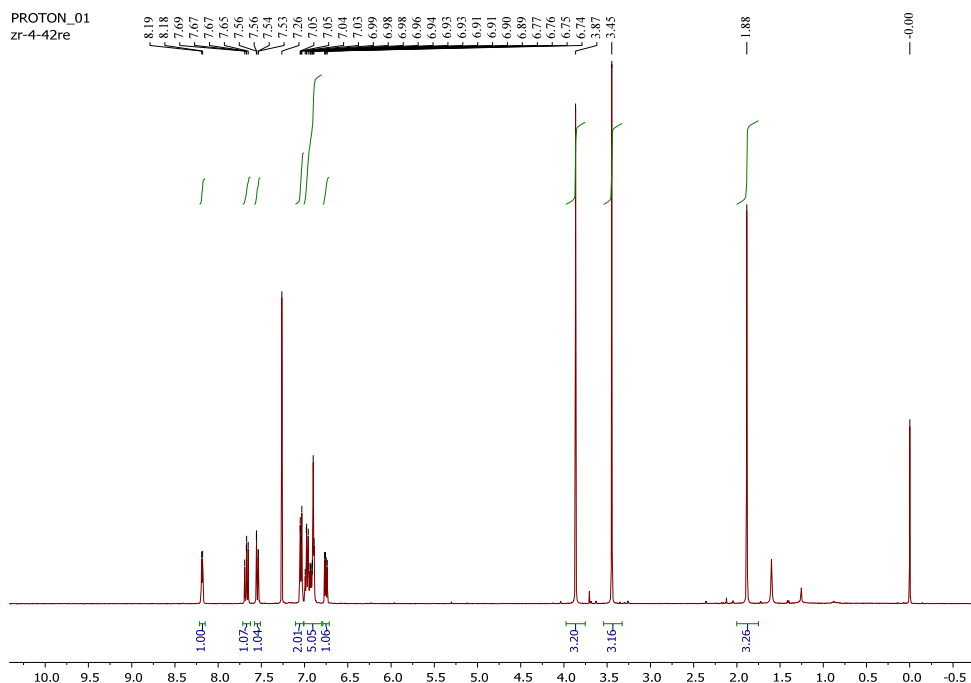
CARBON_01
 Zr-4-46-2HC

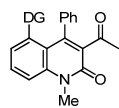






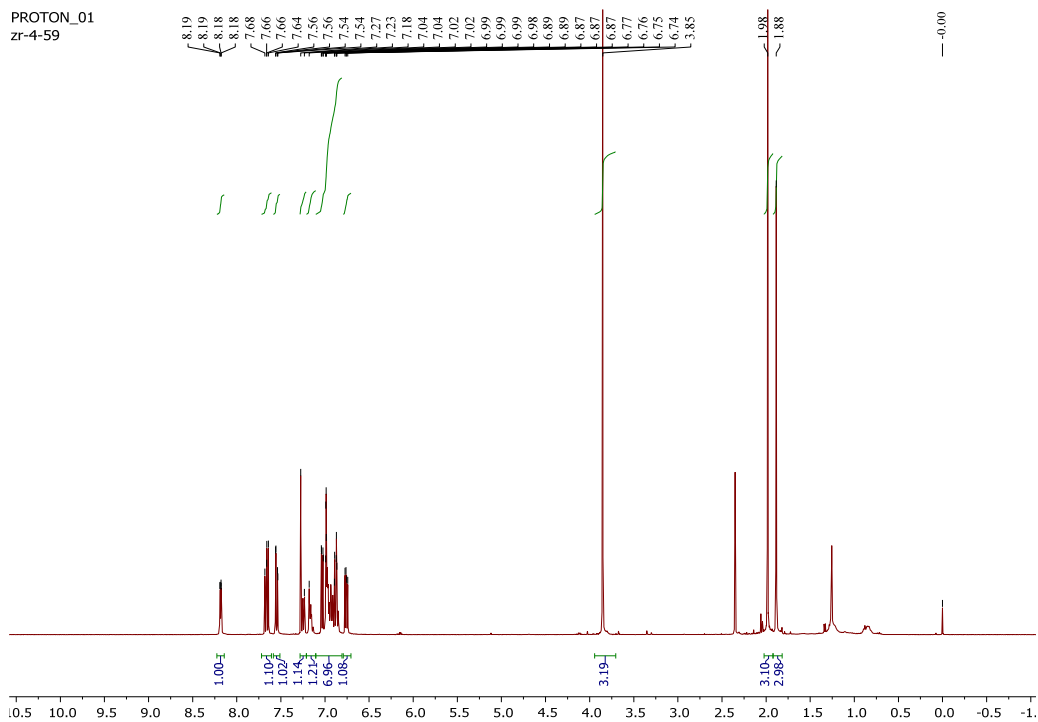
DG = 3-methyl-pyridine-2-yl
3al



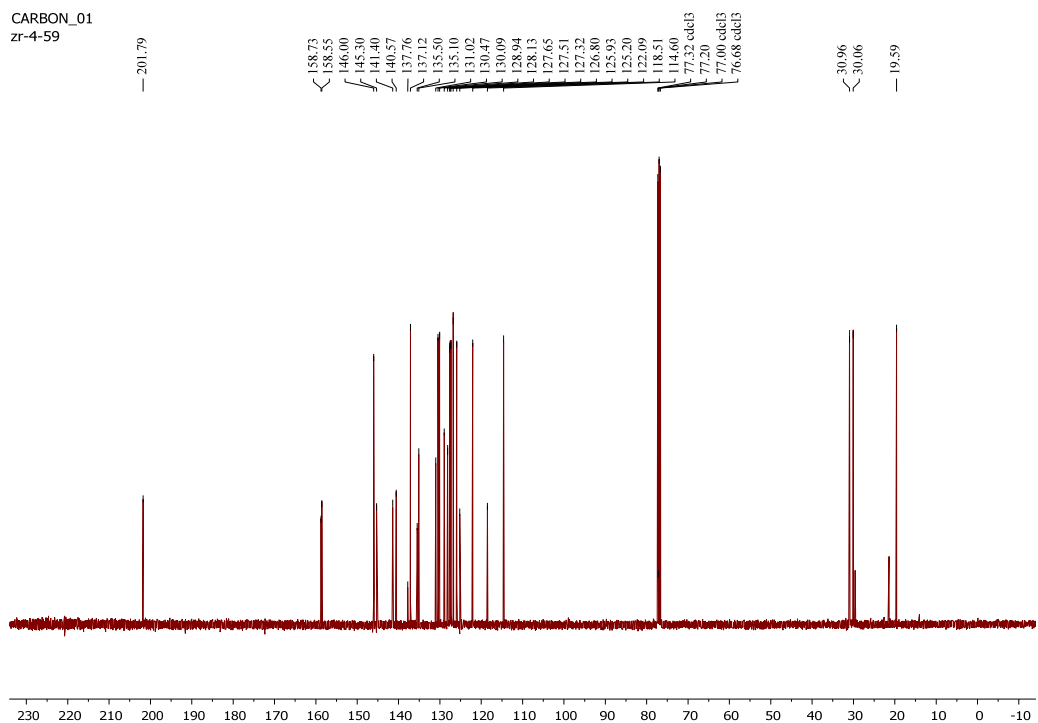


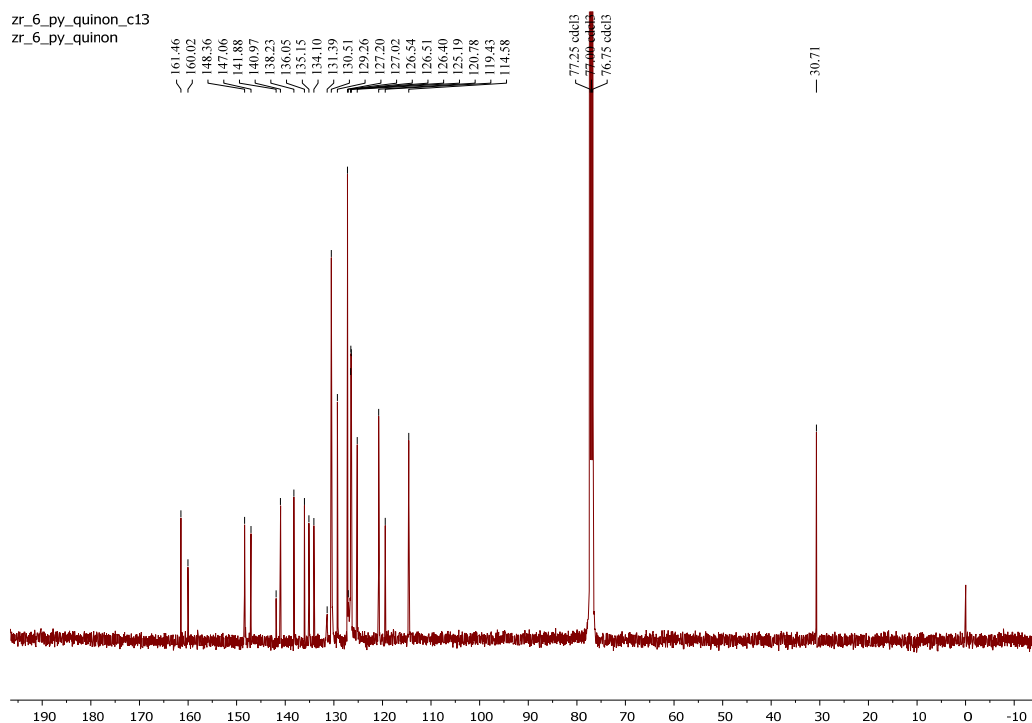
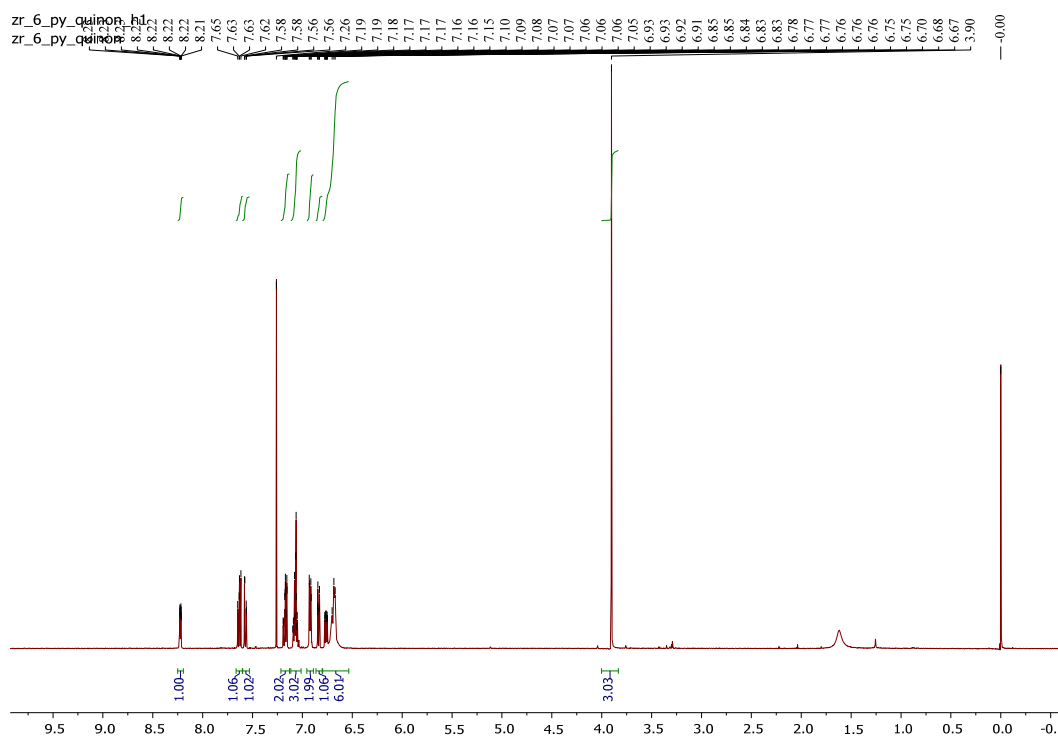
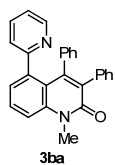
DG = 3-methyl-pyridine-2-yl
3am

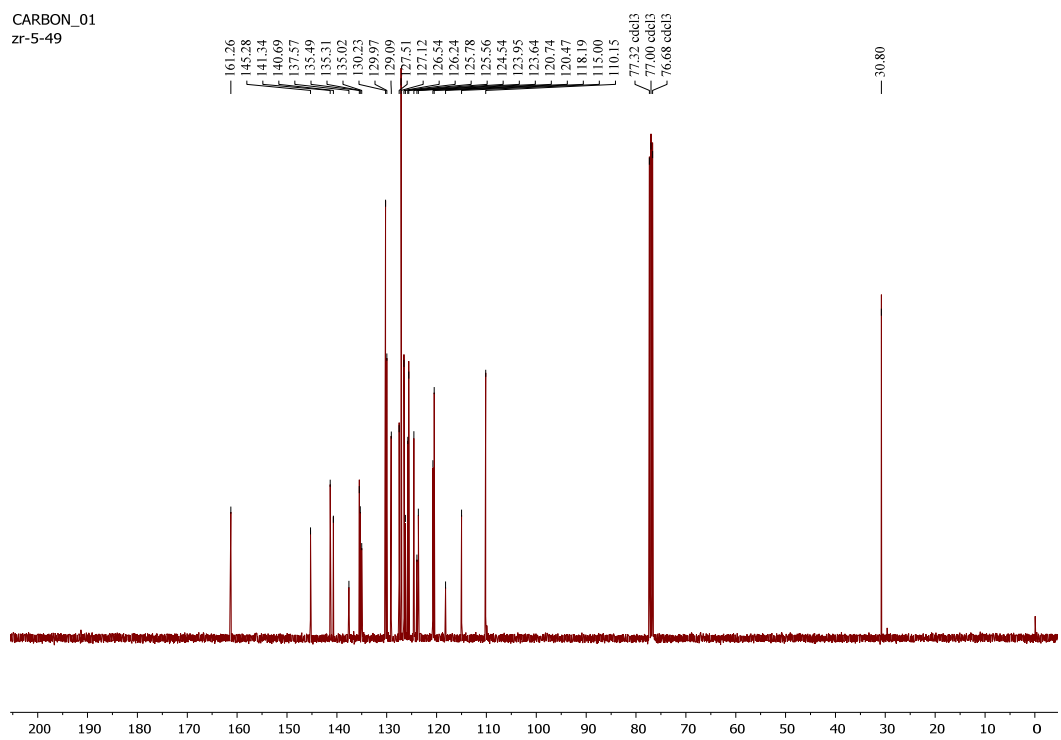
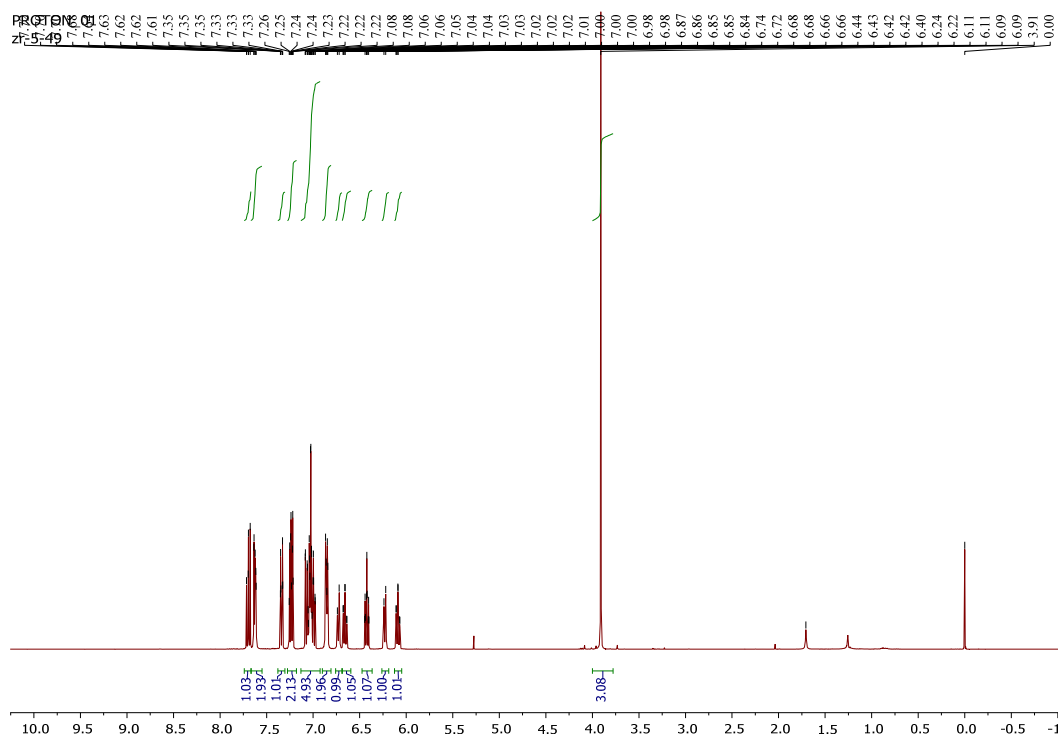
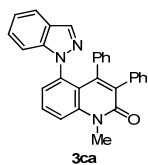
PROTON_01
zr-4-59

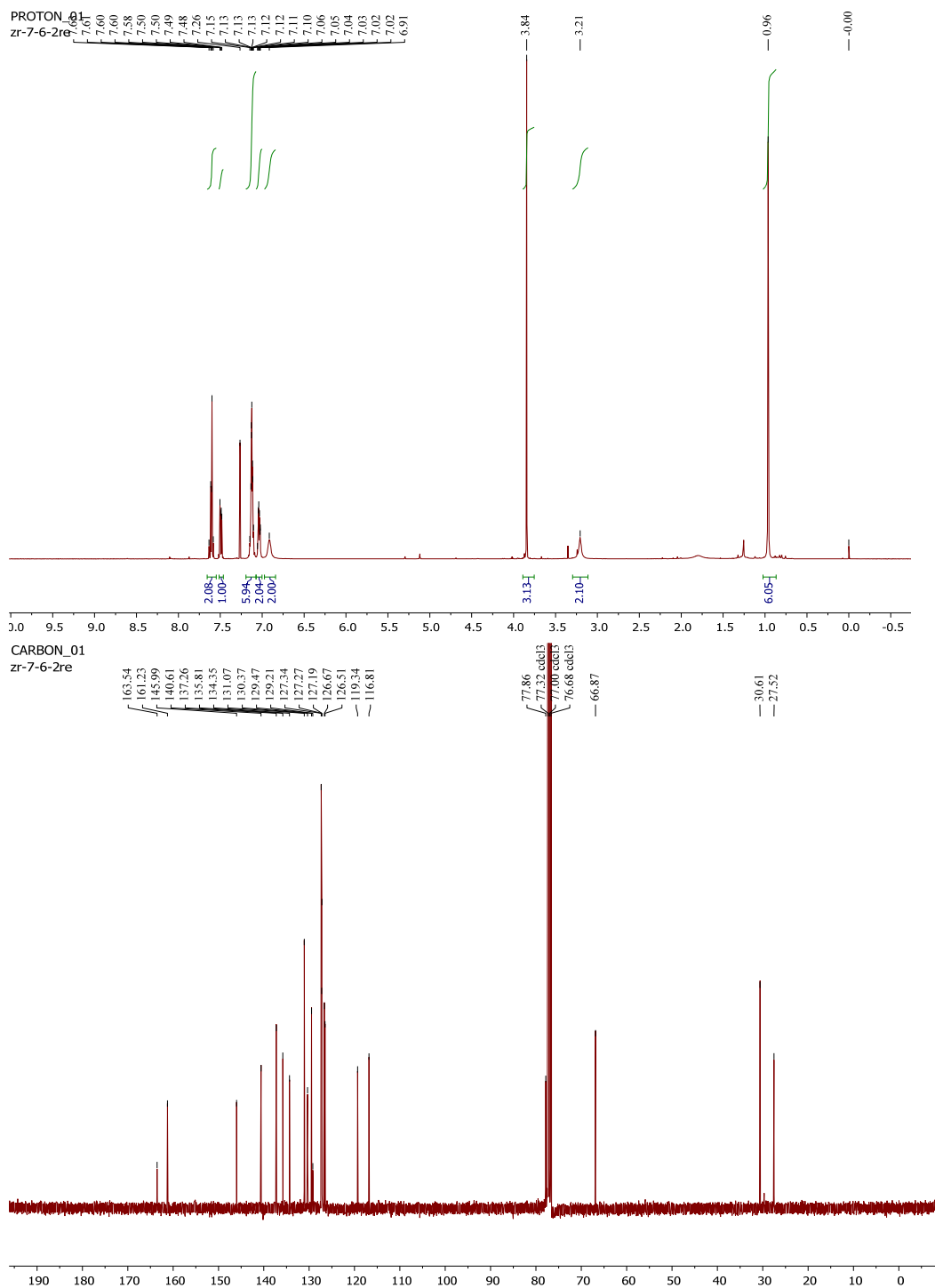
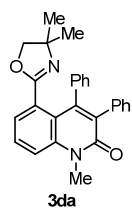


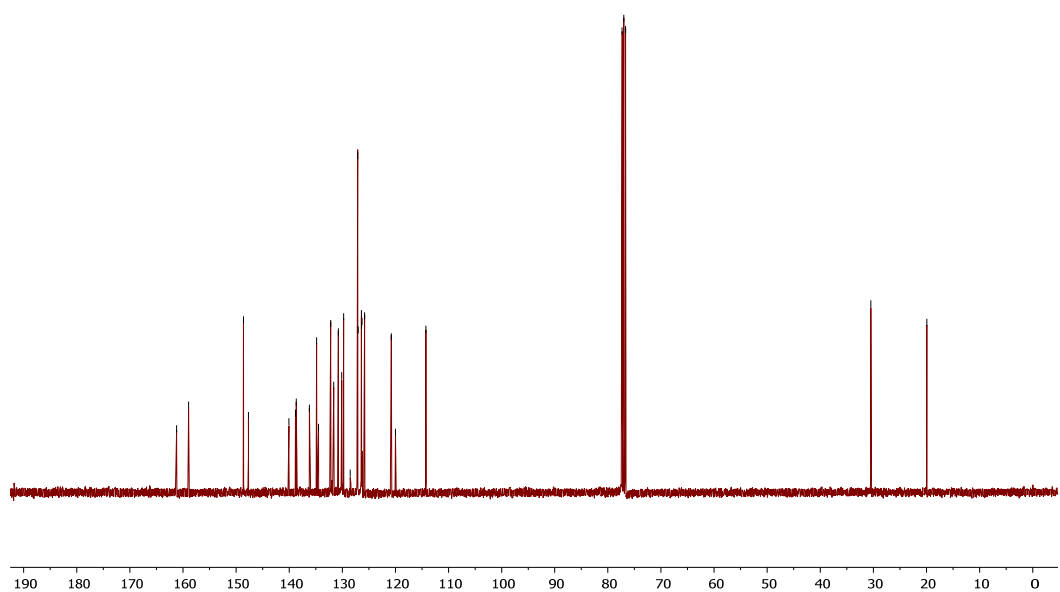
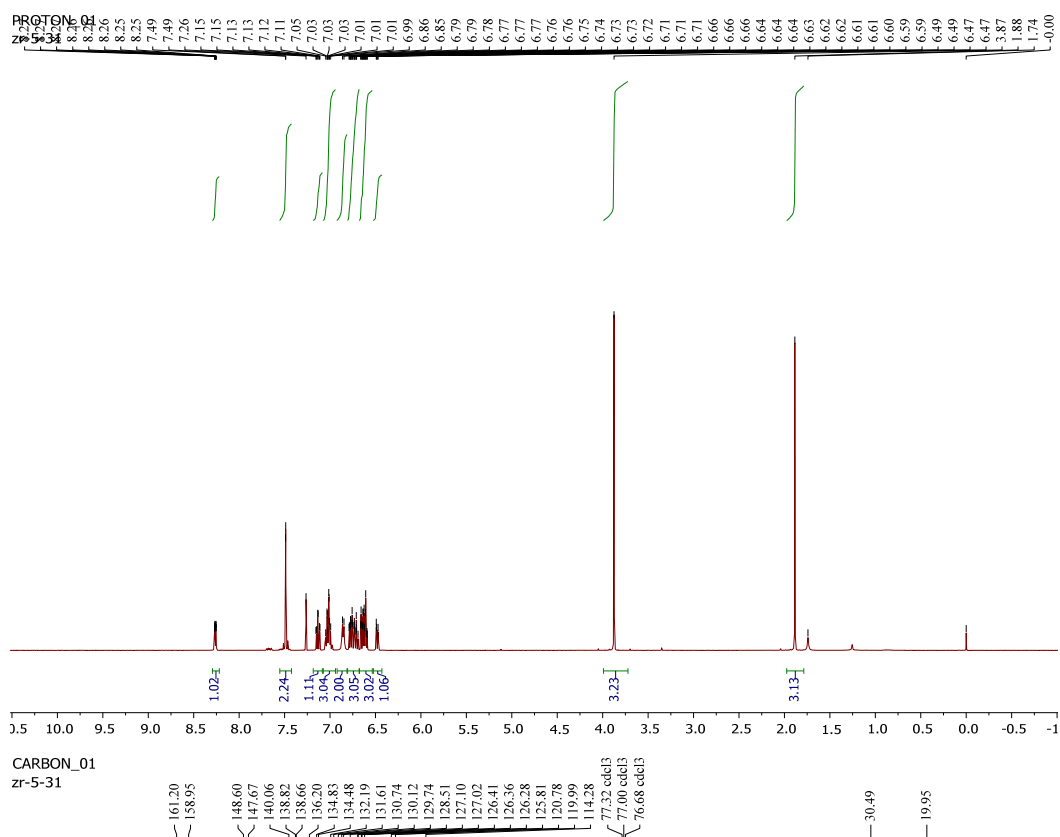
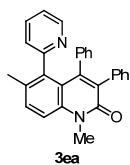
CARBON_01
zr-4-59

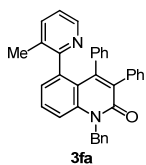




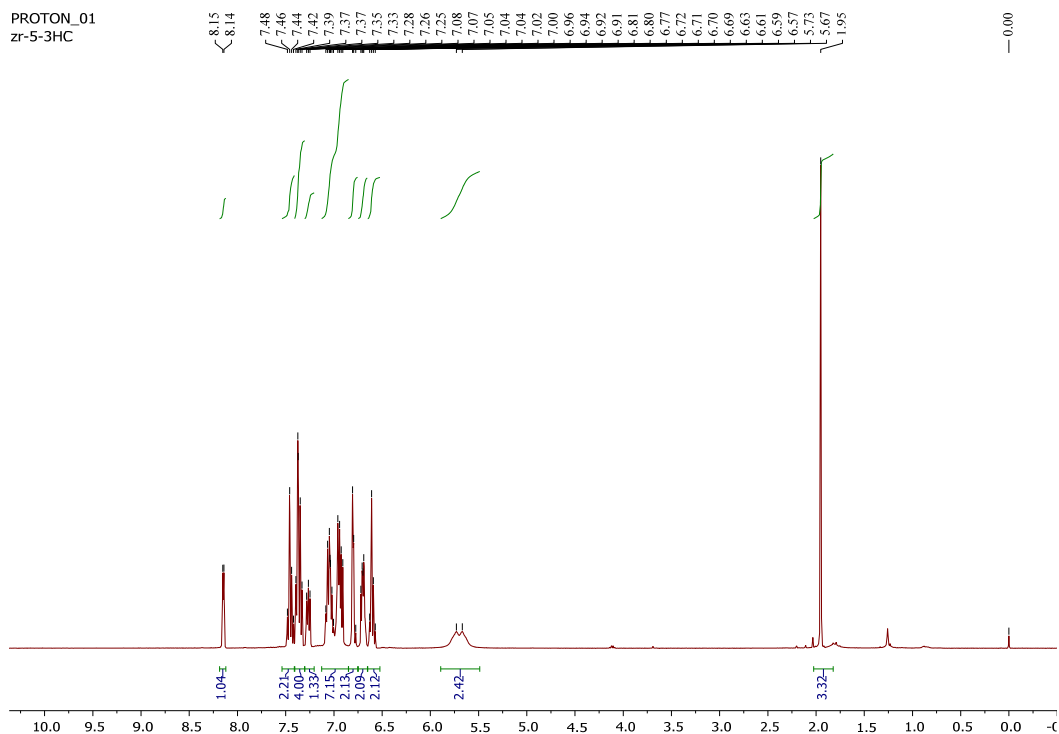




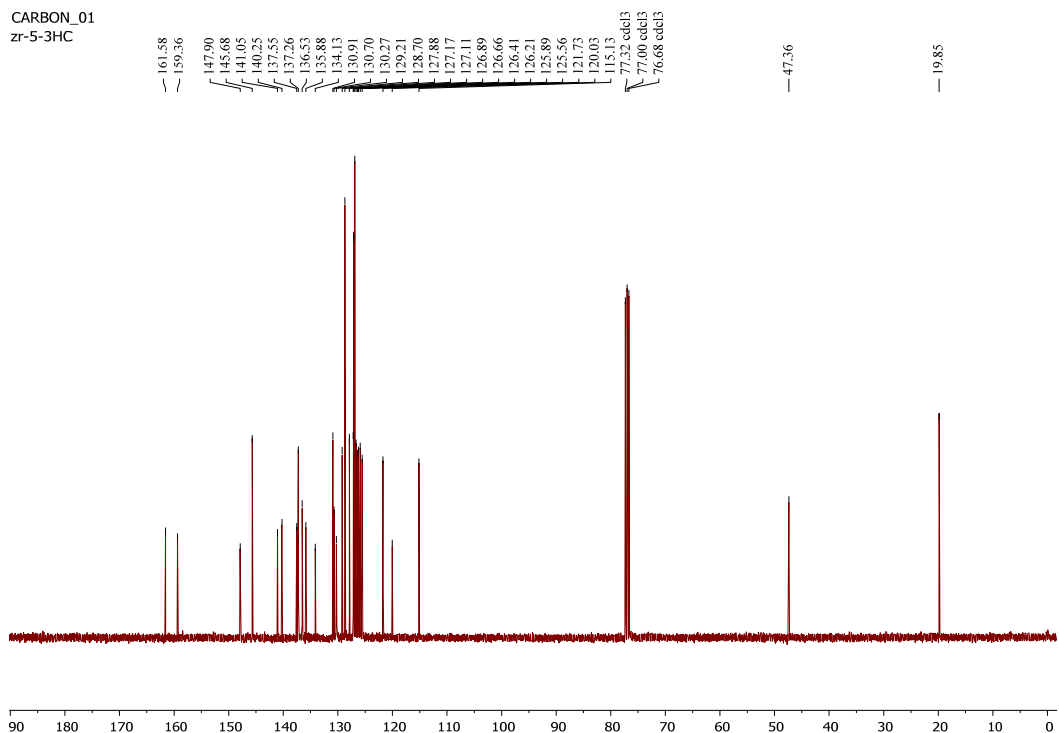


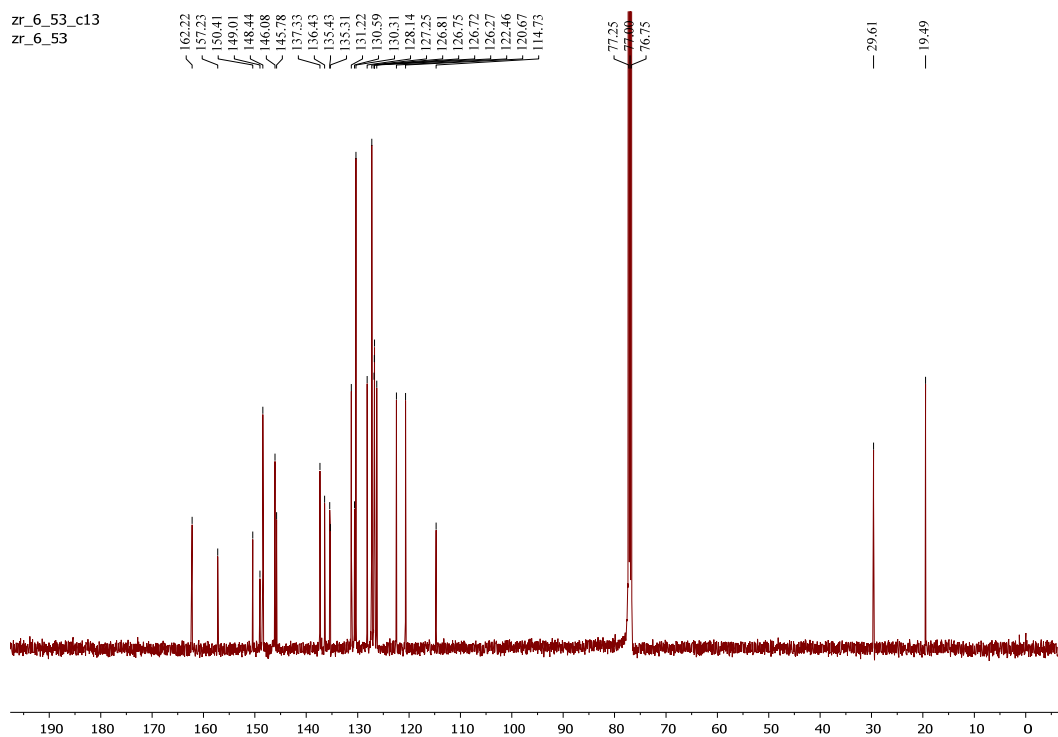
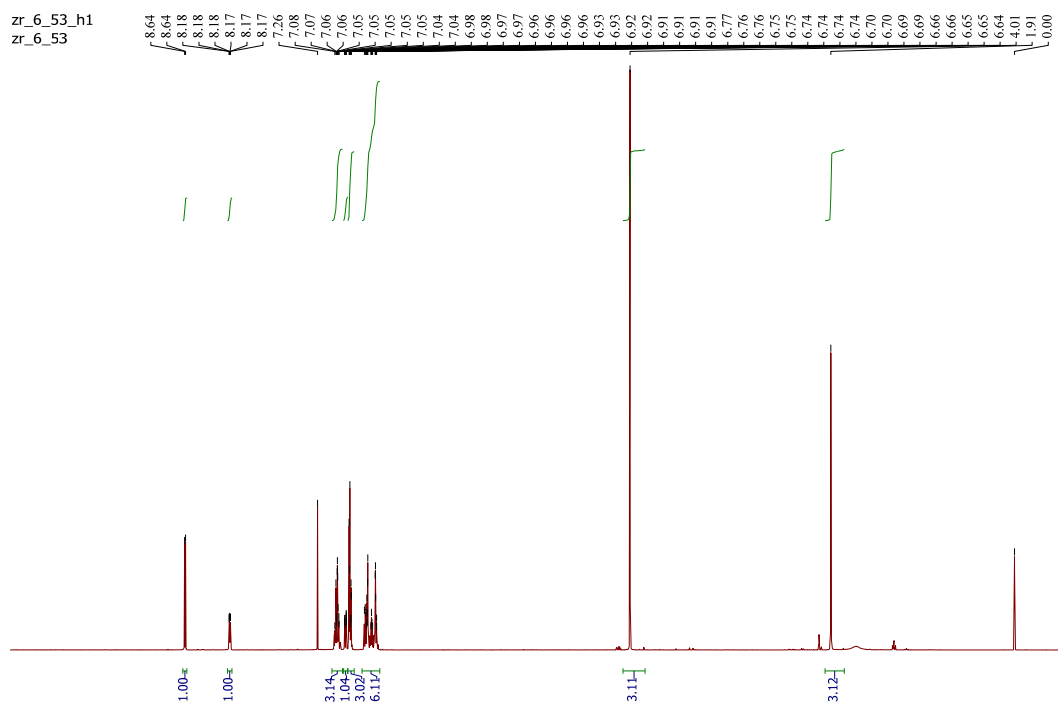
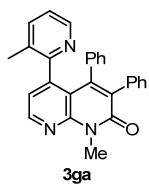


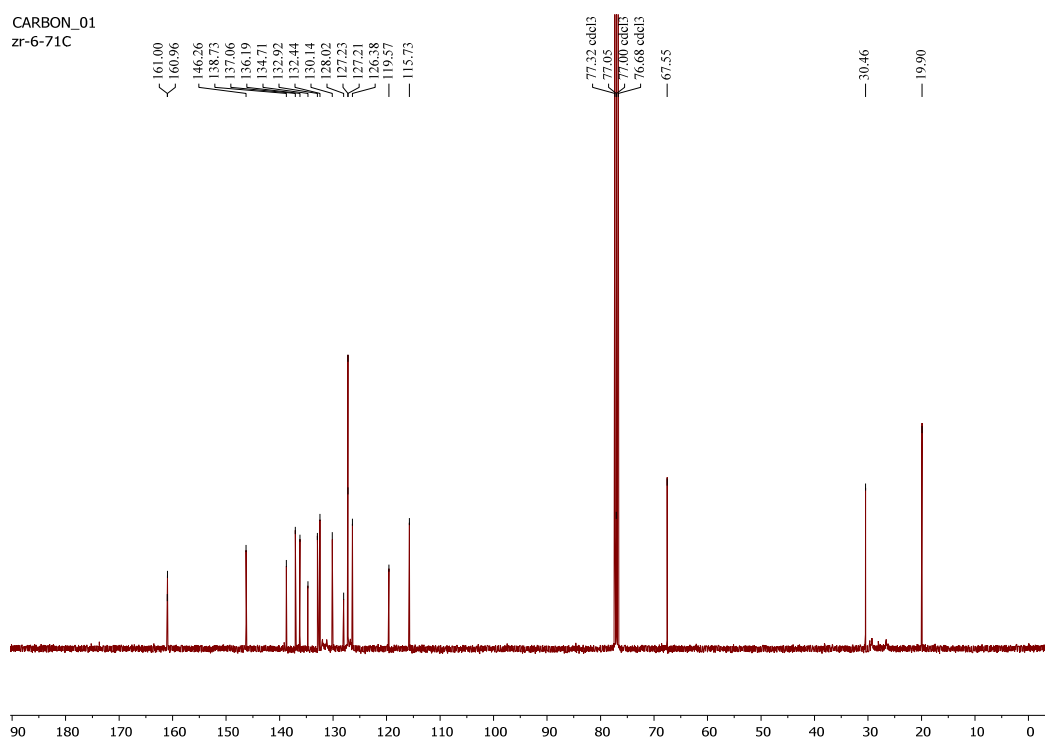
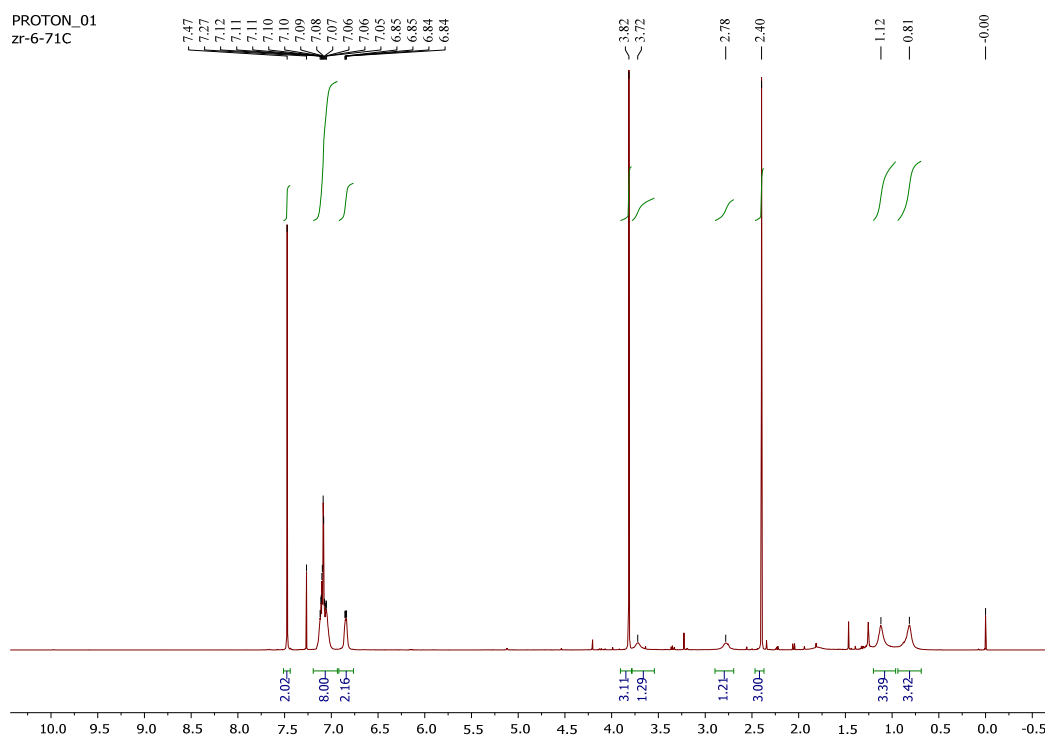
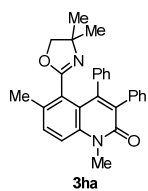
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zr-5-3HC

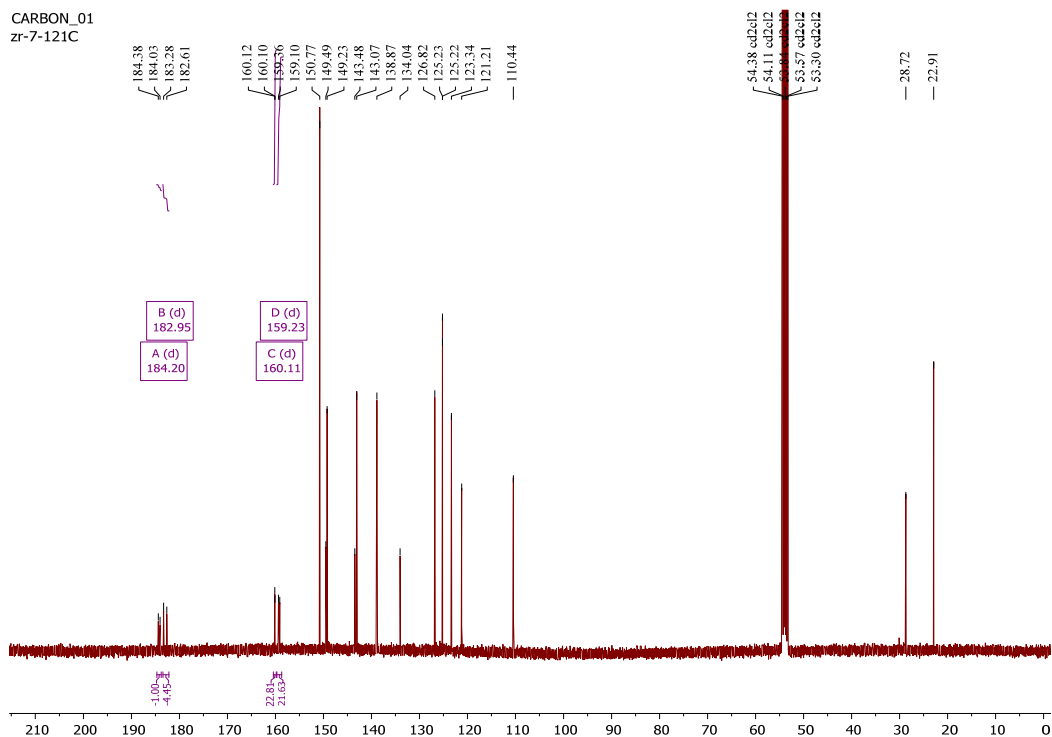
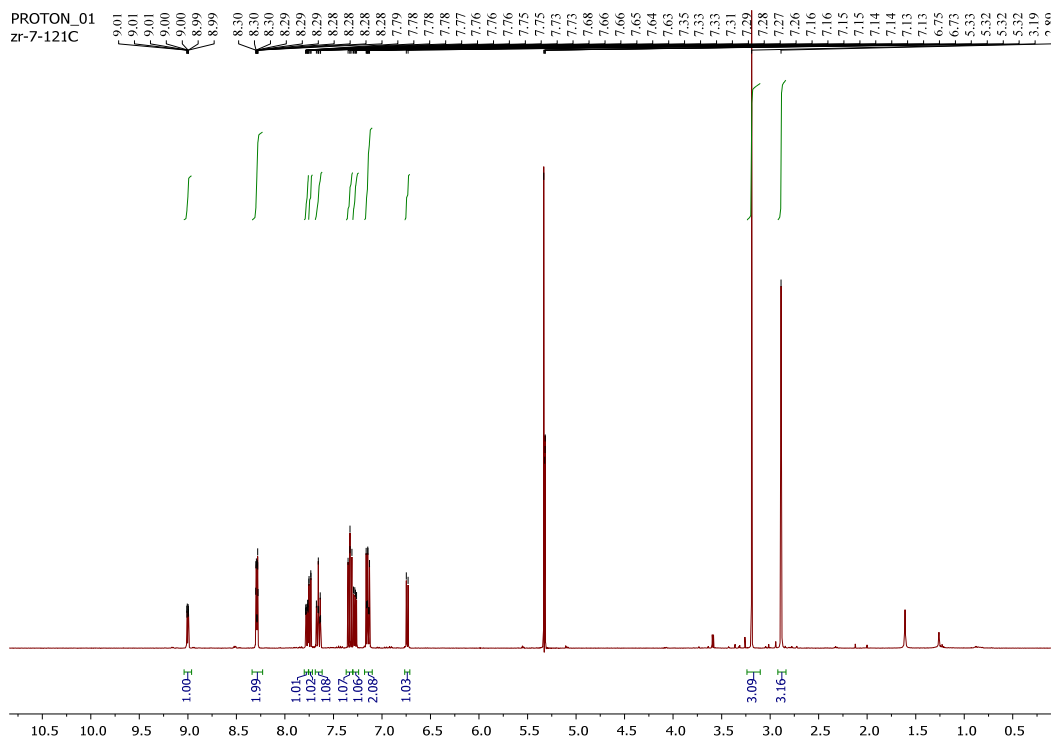
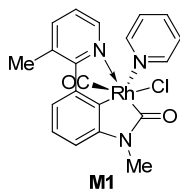


CARBON_01
zr-5-3HC









M2

(The ^{13}C NMR cannot be obtained due to the stability issue with this complex)

