Supporting Information

Synthesis of Naturally Occurring Acetylenes via an Alkylidene Carbenoid Rearrangement

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1. Experimental details for compounds **5, 6, 8, 9, 11-16, 18-20**.
2. ^1H and ^{13}C NMR spectra for all unpublished alcohols, ketones, dibromoolefins, diynes, and triynes.
3. UV-Vis spectra for compounds **1-3**.

Experimental

General. Reagents were purchased reagent grade from commercial suppliers and used without further purification. Et₂O and THF were distilled from sodium/benzophenone ketyl, and hexanes and dichloromethane were distilled from CaH₂ immediately prior to use. Anhydrous MgSO₄ was used as the drying agent after aqueous work-up. Evaporation and concentration *in vacuo* was done at H₂O-aspirator pressure. All reactions were performed in standard, dry glassware under an inert atmosphere of N₂. Column chromatography: *silica gel-60* (230-400 mesh). Thin Layer Chromatography (TLC): plastic sheets covered with *silica gel-60 F₂₅₄*; visualization by UV light or KMnO₄ stain. Mp: uncorrected. UV-Vis spectra: at rt; λ_{max} in nm (ϵ in L M⁻¹ cm⁻¹). ¹H- and ¹³C-NMR: at rt in CDCl₃; solvent peaks (7.24 ppm for ¹H and 77.0 ppm for ¹³C) as reference. For mass spectral analyses, low-resolution data are provided in cases when M⁺ is not the base peak; otherwise, only high-resolution data are provided.

General Procedure for Acid Chloride Formation. To the appropriate carboxylic acid (1 equiv) was added thionyl chloride (6 equiv). After stirring for 24 hours, the excess thionyl chloride was evaporated, and the acid chloride was used directly in the next step without further purification.

General Procedure for Ketone Formation via Friedel-Crafts Acylation. The formation of **5**, **8**, **11**, **13** and **15** was accomplished as reported for similar derivatives.ⁱ

General Procedure for Dibromoolefin Formation. Literature procedures were followed.ⁱⁱ

General Procedure for Diyne/Triyne formation. Unless otherwise noted, the following procedure was followed. To the appropriate dibromoolefin (0.368 mmol) in dry hexanes (10 mL) at -78 °C was added dropwise over ten minutes 1.1–1.2 equivalent of *n*-BuLi (0.15 mL, 2.5 M in hexanes, 0.38 mmol). The mixture was warmed to approximately -40 °C for 30 min, re-cooled to -78 °C, and quenched with a saturated aqueous solution of NH₄Cl. Et₂O was added (~50 mL), the organic layer separated, washed with brine, and dried over magnesium sulfate. Solvent removal *in vacuo* and passing the residue through a short plug of silica gel with the solvent system detailed for

each product afforded the desired diyne/triyn. If necessary, additional purification could be achieved via flash column chromatography.

1-(2-Furyl)-7-trimethylsilylhept-1-en-4,6-diyn-3-one (5). To a solution of 3-(2-furyl)acryloyl chloride (0.585 g, 3.73 mmol) in dry CH₂Cl₂ at 0 °C, 1,4-bis(trimethylsilyl)-1,3-butadiyne (0.726 g, 3.73 mmol) was added, followed by slow addition of AlCl₃ (0.498 g, 3.73 mmol). The reaction mixture was stirred for 3 h. Aqueous work-up and purification by column chromatography (hexanes/CH₂Cl₂, 2:1) gave the ketone **5** (0.535 g, 59%) as a reddish brown oil: *R_f* = 0.62 (CH₂Cl₂); IR (CH₂Cl₂ cast) 3127, 2962, 2209, 2098, 1621, 1593, 1550, 1469, 1266 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.53 (m, 2H), 6.79 (d, *J* = 3.5 Hz, 1H), 6.66 (d, *J* = 15.8 Hz, 1H), 6.52 (ddd, *J* = 3.5, 1.8, 0.7 Hz, 1H), 0.24 (s, 9H); ¹³C NMR (100 MHz, APT, CDCl₃) δ 176.1, 150.5, 146.1, 134.6, 125.8, 117.6, 113.0, 96.3, 86.0, 75.2, 72.2, -0.8; MS (EI, 70 eV) *m/z* 242.1 (M⁺, 72), 227.1 ([M - CH₃]⁺, 100); EI HRMS *m/z* calcd for C₁₄H₁₄O₂Si (M⁺) 242.0763, found 242.0766. Anal. Calcd for C₁₄H₁₄O₂Si: C, 69.38; H, 5.82. Found C, 69.01; H, 5.68.

[5-Dibromomethylene-7-(2-furyl)-hept-6-en-1,3-diynyl]trimethylsilane (6). Ketone **5** (0.374 g, 1.54 mmol) was reacted with CBr₄ (1.03 g, 3.08 mmol) and PPh₃ (1.63 g, 6.17 mmol) as per the general procedure to give **6** (0.412 g, 67%) as an unstable yellow oil which should be kept refrigerated: *R_f* = 0.33 (hexanes); IR (CH₂Cl₂ cast) 2958, 2103, 1623, 1472, 1360, 1251 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.43 (d, *J* = 1.8 Hz, 1H), 6.90 (s, 2H), 6.48 (dd, *J* = 3.4, 0.7 Hz, 1H), 6.42 (d, *J* = 3.4, 1.8 Hz, 1H), 0.24 (s, 9H); ¹³C NMR (100 MHz, APT, CDCl₃) δ 152.1, 143.4, 127.5, 123.2, 122.7, 112.1, 111.8, 102.1, 94.2, 87.1, 82.4, 71.5, -0.5; MS (EI, 70 eV) *m/z* 395.9/397.9/399.9 (M⁺, 22/43/21); HRMS *m/z* calcd for C₁₅H₁₄OSi⁷⁹Br₂/C₁₅H₁₄OSi⁷⁹Br⁸¹Br/C₁₅H₁₄OSi⁸¹Br₂ (M⁺) 395.9181/397.9160/399.9140, found 395.9175/397.9157/399.9137.

1-(2-Furyl)-5-trimethylsilylpent-1-en-4-yn-3-one (8). To a solution of 3-(2-furyl)acryloyl chloride (2.98 g, 0.0190 mol) in dry CH₂Cl₂ at 0 °C, bis(trimethylsilyl)acetylene (3.24 g, 0.0190 mol) was added, followed by slow addition of AlCl₃ (2.54 g, 0.0190 mol). The reaction mixture was stirred for 3 h. Aqueous work-up and purification by column chromatography (hexanes/CH₂Cl₂, 2:1) gave the ketone **8** (2.82 g, 68%) as a yellow oil which solidifies upon refrigeration to a yellow crystalline

solid: mp 21-23 °C; R_f = 0.52 (CH₂Cl₂); IR (CH₂Cl₂ cast) 3126, 2961, 2925, 2854, 2155, 1652, 1623, 1552, 1470, 1251 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.53 (m, 1H), 7.526 (d, J = 15.8 Hz, 1H), 6.75 (d, J = 3.4 Hz, 1H), 6.64 (d, J = 15.8 Hz, 1H), 6.51 (m, 1H), 0.27 (s, 9H); ¹³C NMR (100 MHz, APT, CDCl₃) δ 177.3, 150.6, 145.8, 134.1, 125.7, 117.0, 112.9, 100.6, 98.2, -0.7; MS (EI, 70 eV) m/z 218.1 (M⁺, 57), 203.1 ([M - CH₃]⁺, 100); EI HRMS m/z calcd for C₁₂H₁₄O₂Si (M⁺) 218.0763, found 218.0764. Anal. Calcd for C₁₂H₁₄O₂Si: C, 66.01; H, 6.46. Found: C, 65.61; H, 6.54.

[3-Dibromomethylene-5-(2-furyl)-pent-4-en-1-ynyl]trimethylsilane (9). Ketone **8** (0.159 g, 0.728 mmol) was reacted with CBr₄ (0.488 g, 1.46 mmol) and PPh₃ (0.772 g, 2.91 mmol) as per the general procedure to give **9** (0.157 g, 58%) as a pale yellow oil which should be kept refrigerated (rapid decomposition occurs at rt): R_f = 0.33 (hexanes); IR (CH₂Cl₂ cast) 2959, 2145, 1621, 1476, 1251 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.43 (d, J = 1.7 Hz, 1H), 6.93 and 6.91 (AB quartet, J = 15.5 Hz, 2H), 6.46 (d, J = 3.3 Hz, 1H), 6.42 (dd, J = 3.3, 1.7 Hz, 1H), 0.27 (s, 9H); ¹³C NMR (100 MHz, APT, CDCl₃) δ 152.4, 143.2, 128.6, 123.2, 123.0, 112.0, 111.3, 104.7, 100.3, 99.5, -0.3; MS (EI, 70 eV) m/z 371.9/373.9/375.9 (M⁺, 25/58/29); HRMS m/z calcd for C₁₃H₁₄OSi⁷⁹Br₂/C₁₃H₁₄OSi⁷⁹Br⁸¹Br/C₁₃H₁₄OSi⁸¹Br₂ (M⁺) 371.9181/373.9160/375.9140, found 371.9172/373.9157/375.9154.

1-(2-Furyl)-oct-1-en-4,6-diyn-3-one (11). To a solution of 3-(2-furyl)acryloyl chloride (1.05 g, 6.71 mmol) in dry CH₂Cl₂ (25 mL) at 0 °C, trimethylsilylpenta-1,3-diyne (1.02 g, 7.46 mmol) was added, followed by slow addition of AlCl₃ (0.895 g, 6.71 mmol). The reaction mixture was stirred for 3 h. Aqueous work-up and purification by column chromatography gave the ketone **11** (0.694 g, 56%) as a bright yellow solid: mp 103–105 °C; R_f = 0.52 (CH₂Cl₂); IR (CH₂Cl₂ cast) 3119, 2234, 2189, 1607, 1561, 1462, 1310, 1279 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.53 (m, 1H), 7.51 (d, J = 15.8 Hz, 1H), 6.77 (d, J = 3.5 Hz, 1H), 6.65 (d, J = 15.8 Hz, 1H), 6.51 (dd, J = 3.5, 1.8 Hz, 1H), 2.05 (s, 3H); ¹³C NMR (100 MHz, APT, CDCl₃) δ 176.6, 150.5, 146.0, 134.3, 126.0, 117.3, 112.9, 85.4, 76.4, 70.5, 63.3, 4.8; EI HRMS m/z calcd for C₁₂H₈O₂ (M⁺) 184.0524, found 184.0523. Anal. Calcd for C₁₂H₈O₂: C, 78.25; H, 4.38. Found: C, 78.17; H, 4.31.

2-(3-Dibromomethylene-oct-1-en-4,6-diynyl)furan (12). Ketone **11** (0.211 g, 1.14 mmol) was reacted with CBr₄ (0.759 g, 2.29 mmol) and PPh₃ (1.20 g, 4.58 mmol) as

per the general procedure. Another equivalent of the brominating agent (0.759 g of CBr₄ and 1.20 g of PPh₃) was required for the reaction to reach completion, affording **12** (0.171 g, 44%) as an unstable white solid which turned rapidly yellow: mp 89-90 °C; R_f = 0.23 (hexanes); IR (CHCl₃ cast) 3057, 2911, 2851, 2239, 1621, 1511, 1474, 1384, 1269 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, J = 1.8 Hz, 1H), 6.91 and 6.88 (AB quartet, J = 15.5 Hz, 2H), 6.45 (dd, J = 3.4, 0.6 Hz, 1H), 6.40 (dd, J = 3.4, 1.8 Hz, 1H), 2.01 (s, 3H); ¹³C NMR (100 MHz, APT, CDCl₃) δ 152.2, 143.3, 127.8, 123.1, 122.9, 112.1, 111.7, 101.2, 83.7, 82.9, 69.1, 64.1, 4.8; MS (EI, 70 eV) m/z 337.9/339.9/341.9 (M⁺, 24/47/24); HRMS m/z calcd for C₁₃H₈O⁷⁹Br₂/C₁₃H₈O⁷⁹Br⁸¹Br/C₁₃H₈OSi⁸¹Br₂ (M⁺) 337.8942/339.8922/341.8901, found 337.8941/339.8922/341.8899.

1-(2-Furyl)-hex-1-en-4-yn-3-one (13). To a solution of 3-(2-furyl)acryloyl chloride (0.842 g, 5.38 mmol) in dry CH₂Cl₂ at 0 °C, trimethylsilylpropyne (0.604 g, 5.38 mmol) was added, followed by slow addition of AlCl₃ (0.717 g, 5.38 mmol). The reaction mixture was stirred for 3 h. Aqueous work-up and purification by column chromatography (hexanes/CH₂Cl₂, 4:1) gave the ketone **13** (0.596 g, 69%) as an orange oil: R_f = 0.46 (CH₂Cl₂); IR (CH₂Cl₂ cast) 3125, 2223, 1617, 1551, 1470, 1263 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, J = 15.8 Hz, 1H), 7.517 (m, 1H), 6.73 (d, J = 3.5 Hz, 1H), 6.61 (d, J = 15.8 Hz, 1H), 6.50 (dd, J = 3.5, 1.8 Hz, 1H), 2.07 (s, 3H); ¹³C NMR (100 MHz, APT, CDCl₃) δ 177.9, 150.6, 145.6, 133.7, 126.1, 116.6, 112.8, 90.3, 78.5, 4.1; EI HRMS m/z calcd for C₁₀H₈O₂ (M⁺) 160.0524, found 160.0523.

2-(3-Dibromomethylene-hex-1-en-4-ynyl)furan (14). Ketone **13** (0.463 g, 2.89 mmol) was reacted with CBr₄ (1.92 g, 5.78 mmol) and PPh₃ (3.30 g, 11.6 mmol) as per the general procedure to give **14** (0.281 g, 31%) as an unstable orange oil which should be kept refrigerated: R_f = 0.30 (hexanes); IR (CH₂Cl₂ cast) 3114, 2915, 2850, 2230, 1621, 1475, 1268 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, J = 1.8 Hz, 1H), 6.95 and 6.90 (AB quartet, J = 15.4 Hz, 2H), 6.44 (d, J = 3.3 Hz, 1H), 6.41 (dd, J = 3.3, 1.8 Hz, 1H), 2.08 (s, 3H); ¹³C NMR (100 MHz, APT, CDCl₃) δ 152.5, 143.1, 128.8, 123.5, 122.9, 112.0, 111.0, 98.2, 95.6, 75.4, 4.7; MS (EI, 70 eV) m/z 313.9/315.9/317.9 (M⁺, 12/23/12); HRMS m/z calcd for C₁₁H₈O⁷⁹Br₂/C₁₁H₈O⁷⁹Br⁸¹Br/C₁₁H₈OSi⁸¹Br₂ (M⁺) 313.8942/315.8922/317.8901, found 313.8939/315.8920/317.8907.

1-Phenyl-hexa-1,4-diyn-3-one (15). To a solution of phenylpropiolyl chloride (0.885 g, 5.38 mmol) in dry CH₂Cl₂ at 0 °C, trimethylsilylpropyne (0.604 g, 5.38 mmol) was added, followed by slow addition of AlCl₃ (0.717 g, 5.38 mmol). The reaction mixture was stirred for 3 h. Aqueous work-up and purification by column chromatography (hexanes/CH₂Cl₂, 5:1) gave the ketone **15** (0.504 g, 56%) as a yellow solid: mp 66-68 °C; *R_f* = 0.82 (CH₂Cl₂); ¹³C NMR (100 MHz, APT, CDCl₃) δ 161.0, 133.2, 131.0, 128.6, 119.5, 91.5, 90.5, 89.2, 81.5, 4.4; EI HRMS *m/z* calcd for C₁₂H₈O (M⁺) 168.0575, found 168.0578. ¹H NMR data consistent with published results: Rule, G. N.; Detty, M. R.; Kaeding, J. E.; Sinicropi, J. A. *J. Org. Chem.* **1995**, 60, 1665-1673.

(3-Dibromomethylene-hexa-1,4-diynyl)benzene (16). Ketone **15** (0.102 g, 0.608 mmol) was reacted with CBr₄ (0.403 g, 1.22 mmol) and PPh₃ (0.638 g, 2.43 mmol) as per the general procedure to give **16** (0.131 g, 67%) as a pale yellow oil: *R_f* = 0.35 (hexanes); IR (CH₂Cl₂ cast) 3054, 2915, 2849, 2242, 2215, 1597, 1571, 1487, 1442 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.44 (m, 2H), 7.33 (m, 3H), 2.01 (s, 3H); ¹³C NMR (100 MHz, APT, CDCl₃) δ 131.6, 129.1, 128.4, 122.2, 114.4, 106.4, 95.1, 93.8, 86.4, 76.7, 4.8; MS (EI, 70 eV) *m/z* 321.9/323.9/325.9 (M⁺, 51/100/50); HRMS *m/z* calcd for C₁₃H₈⁷⁹Br₂/C₁₃H₈⁷⁹Br⁸¹Br/C₁₃H₈⁸¹Br₂ (M⁺) 321.8993/323.8972/325.8952, found 321.8999/323.8975/325.8956. Anal. Calcd for C₁₃H₈Br₂: C, 48.19; H, 2.49. Found: C, 48.00; H, 2.35.

1-(2-Furyl)-octa-1,6-dien-4-yn-3-ol (18). Crotonaldehyde (0.505 g, 7.13 mmol) was reacted with CBr₄ (4.73 g, 14.3 mmol) and PPh₃ (7.48 g, 28.5 mmol) as per the general procedure to give 1,1-dibromo(1*E*,3*E*)-1,3-pentadiene (1.401 g, 87%).ⁱⁱⁱ To a solution of this dibromoolefin (1.401 g, 6.20 mmol) in THF at -78 °C was added *n*-BuLi (5.21 mL, 2.5 M in hexanes, 13.0 mmol). After the reaction mixture was stirred for 1 h at -78 °C and for a further hour at rt, furanacrolein (0.682 g, 5.58 mmol) in THF (5 mL) was added at -78 °C. The reaction mixture was slowly warmed to rt until the reaction was judged complete by TLC analysis. The reaction was quenched with satd. aq. NH₄Cl at -78 °C, and the solution mixture was extracted with ether. Evaporation of the solvent, and purification by column chromatography (CH₂Cl₂/hexanes, 3:4) yielded alcohol **18** (0.568 g, 54%) as an orange oil; *R_f* = 0.30 (CH₂Cl₂); IR (CH₂Cl₂ cast) 3351, 3027, 2914, 2101, 1629, 1488, 1443, 1384, 1296, 1258 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.34 (d, *J*

= 1.8 Hz, 1H), 6.57 (dd, J = 15.7, 1.4 Hz, 1H), 6.35 (dd, J = 3.3, 1.8 Hz, 1H), 6.28 (d, J = 3.3 Hz, 1H), 6.23 (dd, J = 15.7, 5.8 Hz, 1H), 6.19 (ddq, J = 15.8, 6.8, 0.5 Hz, 1H), 5.53 (app. quint, J = 15.8, 1.8 Hz, 1H), 5.10 (bs, 1H), 2.01 (bs, 1H), 1.77 (ddd, J = 6.8, 1.8, 0.5 Hz, 3H); ^{13}C NMR (100 MHz, APT, CDCl_3) δ 151.8, 142.4, 140.7, 126.7, 119.8, 111.3, 109.9, 109.1, 85.8, 85.2, 63.0, 18.6; EI HRMS m/z calcd for $\text{C}_{12}\text{H}_{12}\text{O}_2$ (M^+) 188.0837, found 188.0836.

1-(2-Furyl)-octa-1,6-dien-4-yn-3-one (19). To the alcohol **18** (0.181 g, 0.961 mmol) in CH_2Cl_2 was added manganese dioxide (1.00 g, 11.53 mmol, 12 equiv). After the reaction mixture was stirred at rt until the reaction was judged complete by TLC analysis, the solution mixture was filtered through a pad of Celite. After removal of the solvent under reduced pressure, the resulting crude product was recrystallized from methanol–water to give ketone **19** (0.105 g, 59%) as colorless needle-like crystals: mp 53–55 °C; R_f = 0.31 (CH_2Cl_2); IR (CHCl_3 cast) 3124, 3031, 2914, 2191, 1616, 1551 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.53 (d, J = 1.8 Hz, 1H), 7.50 (d, J = 15.7 Hz, 1H), 6.73 (d, J = 3.4 Hz, 1H), 6.66 (d, J = 15.7 Hz, 1H), 6.54 (dq, J = 15.8, 6.9 Hz, 1H), 6.50 (dd, J = 3.4, 1.8 Hz, 1H), 5.69 (dq, J = 15.8, 1.8 Hz, 1H), 1.89 (dd, J = 6.9, 1.8 Hz, 3H); ^{13}C NMR (100 MHz, APT, CDCl_3) δ 177.8, 150.7, 147.0, 145.7, 133.4, 126.2, 116.6, 112.8, 109.0, 90.6, 85.6, 19.2; MS (EI, 70 eV) m/z 186.1 (M^+ , 76), 171.0 ($[\text{M}-\text{CH}_3]^+$, 100); HRMS m/z calcd for $\text{C}_{12}\text{H}_{10}\text{O}_2$ (M^+) 186.0681, found 186.0675. Anal. Calcd for $\text{C}_{12}\text{H}_{10}\text{O}_2$: C, 77.40; H, 5.41. Found C, 77.59; H, 5.32.

2-(3-Dibromomethylene-octa-1,6-dien-4-ynyl)furan (20). Ketone **19** (0.057 g, 0.31 mmol) was reacted with CBr_4 (0.203 g, 0.611 mmol) and PPh_3 (0.321 g, 1.22 mmol) as per the general procedure to give **20** (60.9 mg, 58%) as a relatively unstable pale yellow oil; R_f = 0.24 (hexanes); IR (CHCl_3 cast) 3027, 2923, 2851, 2201, 1624, 1510, 1474, 1441 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.42 (d, J = 1.8 Hz, 1H), 6.95 and 6.88 (AB quartet, J = 15.4 Hz, 2H), 6.43 (d, J = 3.4 Hz, 1H), 6.40 (dd, J = 3.4, 1.8 Hz, 1H), 6.34 (dq, J = 15.8, 6.9 Hz, 1H), 5.71 (dq, J = 15.8, 1.8 Hz, 1H), 1.84 (dd, J = 6.9, 1.8 Hz, 3H); ^{13}C NMR (100 MHz, APT, CDCl_3) δ 152.4, 143.2, 141.7, 128.7, 123.2, 123.0, 112.0, 111.2, 110.3, 98.6, 97.2, 83.1, 18.9; MS (EI, 70 eV) m/z 339.9/341.9/343.9 (M^+ , 9/17/8), 182.1 ($[\text{M}-\text{Br}_2]^+$, 100); HRMS m/z calcd for

$\text{C}_{13}\text{H}_{10}\text{O}^{79}\text{Br}_2/\text{C}_{13}\text{H}_{10}\text{O}^{79}\text{Br}^{81}\text{Br}/\text{C}_{13}\text{H}_{10}\text{O}^{81}\text{Br}_2$ (M^+) 339.9099/341.9078/343.9057, found
339.9094/341.9076/343.9057.

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Figure S1. ¹H and ¹³C NMR spectra of compound **1**.

Figure S2. ¹H and ¹³C NMR spectra of compound **2**.

Figure S3. ¹H and ¹³C NMR spectra of compound **3**.

Figure S4. ¹H and ¹³C NMR spectra of compound 4.

Figure S5. ^1H and ^{13}C NMR spectra of compound 5.

Figure S7. ^1H and ^{13}C NMR spectra of compound **7**.

Figure S8. ^1H and ^{13}C NMR spectra of compound **8**.

Figure S9. ^1H and ^{13}C NMR spectra of compound **9**.

Figure S10. ¹H and ¹³C NMR spectra of compound **10**.

Figure S11. ^1H and ^{13}C NMR spectra of compound **11**.

Figure S12. ^1H and ^{13}C NMR spectra of compound **12**.

Figure S13. ¹H and ¹³C NMR spectra of compound **13**.

Figure S14. ¹H and ¹³C NMR spectra of compound **14**.

Figure S15. ^1H and ^{13}C NMR spectra of compound **16**.

Figure S16. ^1H and ^{13}C NMR spectra of compound **18**.

Figure S17. ¹H and ¹³C NMR spectra of compound **19**.

Figure S18. ¹H and ¹³C NMR spectra of compound **20**.

Figure S19. UV-Vis spectra of compounds **1** and **3**.

Figure S20. UV-Vis spectrum of compound **2**.