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SYNTHESIS OF ALLENIC NAPHTHALENE DERIVATIVES

Ramazan Erenler

Department of Chemistry, Faculty of Art and Science, Gaziosmanpasa University, 60240 Tokat, Turkey

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ABSTRACT. Propargylic alcohol of naphthalene derivatives were synthesized and converted to the corresponding propargylic acetate using acetic anhydride. Reduction of the propargylic acetates by SmI_2 afforded allenes and acetylenes. Base-promoted isomerisation of acetylene formed allene in high yield.

KEY WORDS: Isomerisation, Allenic derivatives of naphthalene

INTRODUCTION

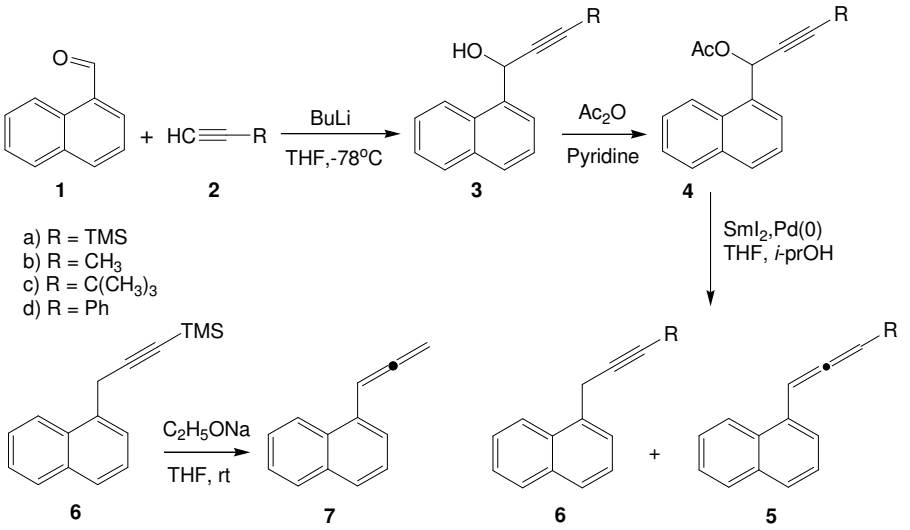
The functionalized allenes have been of intense interest as the versatile building blocks for organic synthesis [1]. A large number of natural products containing an allene moiety have been isolated [2]. Propargylic alcohols have been used as intermediate in the synthesis of some optically active natural product [3] and also they are useful building blocks for the enantioselective synthesis of complex molecules [4]. Numerous methods have been known for the synthesis of allenes, reduction of propargylic halides, ethers, or esters with the conventional reducing agents, usually affords a mixture of allenes and acetylenes in varying ratio [5]. The Pd (0)-SmI_2-alcohol system is effective in reduction of the propargylic acetates, therefore providing a mild and convenient method for the preparation of allenes [6].

In previous work, we described hydroxyl, epoxyl, methoxyl and nitroxyl derivatives of naphthalene [7]. The present work reports the synthesis of allenic derivatives of naphthalene.

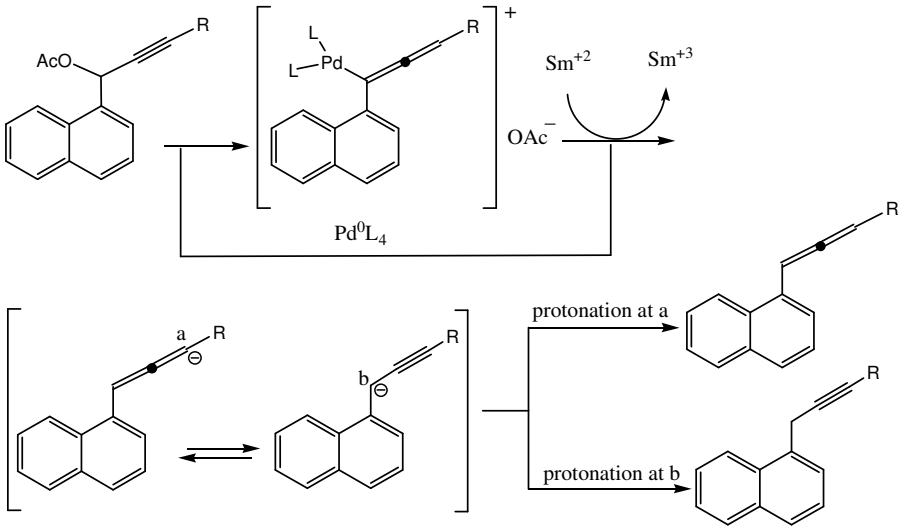
RESULTS AND DISCUSSION

Trimethylsilyl derivative of **3a** [8] was synthesized by treating 1-naphthaldehyde with (trimethylsilyl)acetylene and n-BuLi at -78 ^{o}C in THF in 94 % yield as a liquid. This compound **3a** was converted to acetoxyl **4a** by treating with acetyl anhydride at rt for 5 h 74 % yield. Treatment of acetoxyl **4a** with SmI_2-THF solution, 2-propanol as a proton source and Pd $(PPh_3)_4$ yielded allene **5a** and acetylene **6a** [9] isolated by column chromatography in 24 % and 57 % yields, respectively. The acetylene **6a** is the appropriate starting material for 1-allenylnaphthalene **7** [10]. The reaction of acetylene **6a** with sodium ethoxide at rt in THF gave rise to 1-allenylnaphthalene **7** in 74 % yield (Scheme 1). Using the same procedure methyl, t-butyl and phenyl substituent have also been prepared. For methyl derivative of propargylic alcohol **3b**, the propynyl was reacted with BuLi and 1-naphthaldehyde at -78 ^{o}C for 2 h generated the compound **3b** in a yield of 85 % as a liquid. Then by using Ac_2O, compound **3b** was converted to acethoxyl **4b** in a yield of 76 %. The treatment of acethoxyl **4b** with SmI_2-THF solution, 2-propanol and Pd $(PPh_3)_4$ yielded the methyl allene **5b** and acetylene **6b** which were purified by column chromatography but methyl allene **5b** couldn't be isolated purely.

*Corresponding author. E-mail: rerenler@gop.edu.tr



Scheme 1



Scheme 2

^{1}H NMR and ^{13}C NMR spectrum indicated the formation of compound **5b**. To obtain the propargylic t-butyl alcohol **3c**, the reaction of 1-naphthaldehyde, t-butylacetylene and BuLi were carried out at -78 ^{o}C for 2 h under argon in a high yield (88 %). Then acetate **4c** was generated by the treatment of alcohol **3c** with Ac_2O. After the reaction of SmI_2 with acetate **4c** two

products purified by column chromatography were obtained, t-butylallene **5c** and acetylene **6c**. Although this compound **6c** was detected by NMR spectroscopy, it could not be isolated in a pure form. For phenyl propargyl alcohol **3d** [11], phenylacetylene was treated with 1-napthaldehyde and butyllithium at -78 ^{o}C for 2 h in 75 % yield. After the reaction of proparglic alcohol **3d** with acetyl anhydride**,** acetate formed **4d** [12] as a yield of 77 %. Reduction of acetate **4d** with SmI_2 in the presence of 2-propanol and catalytic amount of Pd(0), allene **5d** and acetylene **6d** were generated in yields of 24 % and 55 %, respectively. Reaction mechanism is given in Scheme 2.

EXPERIMENTAL

General procedures

Melting points were determined with a Büchi B-540 apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AMX400 and 500 MHz instruments. Chemical shifts are in ppm from Me_4Si, generated from the $CDCl_3$. IR spectra were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrometer. Elemental analyses were measured with a Perkin-Elmer 2400 CHN instrument. Mass spectra were obtained on a FAB JMS-700 double focusing mass spectrometer (JEOL, Tokyo, Japan).

*Preparation of compound **3***. To a solution of substituted acetylene (1.2 equiv) in THF (5.0 mL) was added n-BuLi (1.2 equiv, 1.6 M in hexane) at -78 ^{o}C under argon. The reaction mixture was allowed to warm to -50 ^{o}C then 1-naphthaldehyde (1 equiv) in THF (2.0 mL) was added. After being stirred for further 1 h, the mixture was washed with saturated NH_4Cl and extracted with CH_2Cl_2 (2 x 10 mL), dried over $MgSO_4$, concentrated under vacuum to yield the product.

*Preparation of compound **4***. To a solution of compound **3** in Ac_2O was added 3 drops of pyridine. After the reaction mixture was stirred for 5 h at rt, water was added, then extracted with CH_2Cl_2 (3 x 10 mL). The organic layer was dried ($MgSO_4$) and the solvent was removed. The residue was purified by chromatography (silica, n-hexane) affording the product.

*Reduction of propargylic acetate by samarium(II)iodide, preparation of compound **5** and **6***. To a solution of compound **4** (1 equiv), 2-propanol (1 equiv) and Pd $(PPh_3)_4$ (0.05 equiv) in THF (1.0 mL) was added SmI_2-THF solution (3 equiv) under argon. After the reaction mixture was stirred for 3 h at rt, the solvent was removed. The mixture was extracted with CH_2Cl_2, washed with brine (2 x 10 mL), dried over $MgSO_4$, concentrated under reduced pressure. The residue was purified by chromatography (silica, n-hexane) to afford the products.

*3-(Trimethylsilyl)-1-(naphthalene-5-yl)prop-2-yn-1-ol (**3a**).* (Trimethylsilyl)acetylene **2a** (1.13 g, 1.60 mL, 11.5 mmol) in THF (5.0 mL), n-BuLi (7.2 mL, 11.5 mmol, 1.6 M in hexane), 1-naphthaldehyde (1.50 g, 1.30 mL, 9.6 mmol) in THF (2.0 mL). Yield 2.3 g, (94 %), liquid. ^{1}H NMR (500 MHz, $CDCl_3$), δ: 0.23 (s, 9H), 2.41 (d, J = 5.2 Hz, 1H), 6.13 (d, J = 5.9 Hz, 1H), 7.47-7.60 (m, 3H), 7.85-7.90 (m, 3H), 8.31 (d, J = 8.4 Hz, 1H), ^{13}C NMR (125 MHz, $CDCl_3$), δ: -0.054, 63.4, 92.5, 104.9, 124.1, 124.9, 125.3, 125.9, 126.5, 128.8, 129.5, 130.8, 134.1, 135.5. IR (CH_2Cl_2), ν_{max}: 1503, 1695, 2163, 2296, 2894, 2959, 3041 cm^{-1}; UV/Vis (CH_2Cl_2), λ_{max} (ε) = 233 (11100), 273 (9330), 282 (7750). MS (FAB^{+}) *m/z*: 254 $[M]^{+}$ (40), 237 (100), 197 (10), 165 (12), 129 (10); elemental analysis calcd (%) for $C_{16}H_{18}OSi$, C 75.54, H 7.13; found, C 75.51, H 7.9.

*3-(Trimethylsilyl)-1-(naphthalene-5-yl)prop-2-ynyl acetate (**4a**).* 3-(Trimethylsilyl)-1-(naphthalene-5-yl)prop-2-yn-1-ol **3a** (1.88 g) in Ac_2O (4.0 mL), pyridine(3 drops). Yield 1.63 g, (74 %), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 0.24 (s, 9H), 2.13 (s, 3H), 7.16 (s, 1H), 7.50-7.60 (m, 3H), 7.88-7.92 (m, 3H), 8.24 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$), δ: -0.124, 21.2, 64.4, 93.2, 101.5, 123.9, 125.3, 126.1, 126.7, 126.9, 128.9, 130.0, 130.7, 132.4, 134.1, 169.9, IR (CH_2Cl_2), ν_{max}: 842, 1008, 1365, 1505, 1738, 2170, 2959 cm^{-1}; UV/Vis (CH_2Cl_2), λ_{max} (ε) = 232 (14640), 274 (6410), 283 (7630); MS (FAB$^+$), *m/z*: 296 $[M+H]^+$ (10), 237 (100), 221(20), 165 (25), 119 (50); elemental analysis calcd (%) for $C_{18}H_{20}O_2Si$, C 72.93, H 6.80; found C 72.88, H 6.96.

Reduction of propargylic acetate (4a) to compounds 5a and 6a by samarium(II)iodide: 3-(trimethylsilyl)-1-(naphthalene-5-yl)prop-2-ynyl acetate **4a** (0.85 g, 2.87 mmol), 2-propanol (0.172 g, 0.22 mL, 2.87 mmol), Pd $(PPh_3)_4$ (0.166 g, 0.144 mmol) in THF (1.0 mL), SmI_2-THF solution (0.1 M, 86.1 mL, 8.61 mmol).

*Trimethyl(3-(naphthalen-5-yl)propa-1,2-dienyl)silane (**5a**).* Yield 0.160 g, (24 %), ^{1}H NMR (500 MHz, $CDCl_3$), δ: 0.25 (s, 9H), 5.51 (d, J = 6.9 Hz, 1H), 6.61 (d, J = 6.9 Hz, 1H), 7.45-7.54 (m, 3H), 7.58 (d, J = 7.2 Hz, 1H), 7.72 (d, J = 8.1 Hz, 1H), 7.86 (dd, J = 1.1 Hz, J = 6.8 Hz, 1H), 8.23 (d, J = 1.1 Hz, J = 8.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$), δ: -0.74, 84.1, 85.8, 123.6, 124.2, 125.5, 125.6, 125.7, 126.5, 128.6, 130.6, 131.2, 134.0, 211.3; IR (CH_2Cl_2), ν_{max}: 846, 1247, 1922, 2944, 3018 cm^{-1}; UV/Vis ($CHCl_3$), λ_{max} (ε) = 243 (23300), 296 (9540), 312 (10450); MS (FAB$^+$), *m/z*: 238 $[M]^+$ (100), 223 (70), 165 (60), 141 (10); HRMS (FAB$^+$) calcd for $C_{16}H_{18}Si$: *m/z* 238.1178, found *m/z* 238.1175.

*Trimethyl(3-(naphthalen-5-yl)prop-1-ynyl)silane (**6a**).* Yield 0.34 g, (57 %). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 0.26 (s, 9H), 4.1 (s, 2H), 7.47-7.58 (m, 3H), 7.70 (d, J = 7.0 Hz, 1H), 7.80 (d, J = 8.2 Hz, 1H), 7.90 (d, J = 7.8 Hz, 1H), 8.03 (d, J = 8.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$), δ: 0.15, 24.1, 88.0, 104.0, 123.3, 125.6 (2C), 125.7, 126.1, 127.6, 128.7, 131.4, 132.1, 133.7; IR ($CHCl_3$), ν_{max}: 838, 993, 1251, 2162, 2959, 3055 cm^{-1}; UV/Vis ($CHCl_3$), λ_{max} (ε) = 273 (4790), 283 (5550), 293 (4090); HRMS (FAB$^+$) calcd for $C_{16}H_{18}Si$: *m/z* 238.1178, found *m/z* 238.1171.

*1-(Naphthalene-5-yl)but-2-yn-1-ol (**3b**).* Propynyl **2b** (0.60 g, 15.4 mmol) in THF (2.0 mL), n-BuLi (9.6 mL, 15.4 mmol, 1.6 M in hexane), 1-naphthaldehyde (2.0 g, 1.74 mL, 12.8 mmol) in THF (2.0 mL). Yield 2.13 g (85 %), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 1.92 (d, J = 2.2 Hz, 3H), 3.17 (brs, 1H), 6.08 (s, 1H), 7.47-7.59 (m, 3H), 7.84-7.92 (m, 3H), 8.32 (d, J = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$), δ: 3.9, 62.9, 79.4, 83.7, 124.3, 124.5, 125.4, 125.9, 126.4, 128.9, 129.2, 130.7, 134.2, 136.6; IR ($CHCl_3$), ν_{max}: 978, 1138, 1375, 1510, 1599, 1730, 1946, 2219, 2276, 2914, 3007, 3068, 3404, 3588 cm^{-1}; UV/Vis ($CHCl_3$), λ_{max} (ε) = 283 (10300), 293 (8000), MS (FAB$^+$), *m/z*: 196 $[M]^+$ (40), 179 (100), 129 (10); HRMS (FAB$^+$) calcd for $C_{14}H_{12}O$: *m/z* 196.0888, found 196.0884.

*1-(Naphthalene-5-yl)but-2-ynylacetate (**4b**).* 1-(Naphthalene-5-yl)but-2-yn-1-ol (1.24 g, 6.32 mmol), acetyl anhydride (3.0 mL), pyridine (3 drops). Yield 1.14 g, (76 %) colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$), δ: 1.91 (d, J = 2.2 Hz, 3H), 2.11 (s, 3H), 7.12 (d, J = 2.2 Hz, 1H), 7.46-7.53 (m, 2H), 7.57 (m, 1H), 7.87 (m, 3H), 8.24 (d, J = 8.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$), δ: 3.8, 21.1, 64.4, 76.0, 84.4, 123.8, 125.2, 125.9, 126.3, 126.6, 128.8, 129.7, 130.5, 132.9, 134.0, 169.9; IR ($CHCl_3$), ν_{max}: 953, 1017, 1230, 1372, 1507, 1599, 1730, 2241, 2229, 3021 cm^{-1}; UV/Vis ($CHCl_3$), λ_{max} (ε) = 274 (6350), 283 (7580); Ms (FAB$^+$), *m/z*: 238 $[M]^+$ (10), 179 (100), 178 (45); HRMS (FAB$^+$) calcd for $C_{16}H_{14}O_2$: *m/z* 238.0994, found 238.0988.

*The reaction of 1-(naphthalene-5-yl)but-2-ynylacetate (**4b**) with samarium(II) iodide*. 1-(Naphthalene-5-yl)but-2-ynylacetate **4b** (0.78 g, 3.27 mmol) in THF (1.0 mL), 2-propanol (0.25 mL, 3.27 mmol), $Pd(PPh_3)_4$ (0.189 g, 0.164 mmol), SmI_2 (82 mL, 8.2 mmol, 0.1 M in THF).

*1-(But-2-ynyl)naphthalene (**6b**)*. Yield 50 mg, (8 %); NMR (500 MHz, $CDCl_3$), δ: 1.87 (t, J = 2.5 Hz, J = 5.1 Hz, 3H), 3.96 (d, J = 2.4 Hz, 2H), 7.43-7.55 (m, 3H), 7.64 (d, J = 7.0 Hz, 1H), 7.76 (d, J = 8.2 Hz, 1H), 7.87 (d, J = 7.8 Hz, 1H), 8.04 (d, J = 8.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$), δ: 3.7, 23.0, 76.4, 78.7, 123.4, 125.5 (2C), 125.6, 126.0, 127.4, 128.7, 131.4, 133.3, 133.7; IR ($CHCl_3$), ν_{max}: 1391, 1509, 1598, 2922, 3011, 3062 cm^{-1}; UV/Vis ($CHCl_3$), λ_{max} (ε) = 273 (5460), 283 (6310); MS (FAB^+), *m/z* 180 $[M]^+$ (82), 105 (50); HRMS (FAB^+) calcd for $C_{14}H_{21}$: *m/z* 180.0939, found 180.0935.

*4,4-Dimethyl-1-(naphthalene-5-yl)pent-2-yn-1-ol (**3c**)*. t-Butylacetylene **2c** (0.379 g, 0.562 mL, 4.61 mmol) in THF (5.0 mL), n-BuLi (2.88 mL, 4.61 mmol, 1.6 M in hexane), 1-naphthaldehyde (0.60 g, 0.52 mL, 3.84 mmol) in THF (2.0 mL). Yield 0.81 g (88 %), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 1.30 (s, 9H), 2.51 (brs, 1H), 6.10 (d, J = 5.8 Hz, 1H), 7.46-7.57 (m, 3H), 7.82-7.89 (m, 3H), 8.33 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$), δ: 27.6, 30.9, 62.9, 78.3, 96.3, 124.1, 124.5, 125.2, 125.7, 126.2, 128.6, 129.1, 130.7, 134.0, 136.3; IR ($CHCl_3$), ν_{max}: 506, 798, 964, 1262, 1365, 1454, 1502, 1594, 2236, 2966, 3018, 3062, 3594 cm^{-1}; UV/Vis ($CHCl_3$), λ_{max} (ε) = 273 (6600), 283 (8730), 293 (5470); MS (FAB^+), *m/z*: 238 $[M]^+$ (40), 221 (100), 179 (10), 165 (12); HRMS (FAB^+) calcd for $C_{17}H_{18}O$: *m/z* 238.1358, found *m/z* 238.1354.

*4,4-Dimethyl-1-(naphthalene-5-yl)pent-2-ynyl acetate (**4c**)*. 4,4-Dimethyl-1-(naphthalene-5-yl)pent-2-yn-1-ol **3c** (0.64 g, 2.69 mmol), Ac_2O (3.0 mL), pyridine (3.0 drops). Yield 0.57 g, (76 %). ^{1}H NMR (500 MHz, $CDCl_3$), δ: 1.24 (s, 9H), 2.08 (s, 3H), 7.09 (s, 1H), 7.45-7.54 (m, 3H), 7.81-7.88 (m, 3H), 8.19 (d, J = 8.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$), δ: 21.1, 27.6, 30.7, 64.3, 75.3, 96.8, 123.9, 125.1, 125.8, 126.3, 126.5, 128.7, 129.6, 130.6, 133.1, 133.9, 169.9; IR ($CHCl_3$), ν_{max}: 669, 798, 945, 1011, 1229, 1369, 1454, 1513, 1598, 1730, 2243, 2974, 3018 cm^{-1}; UV/Vis ($CHCl_3$), λ_{max} (ε) = 274 (5900), 283 (7060); HRMS (FAB^+) calcd for $C_{19}H_{20}O_2$: *m/z* 280.1463, found *m/z* 280.1459.

*The reaction of 4,4-dimethyl-1-(naphthalene-5-yl)pent-2-ynyl acetate (**4c**) with samarium(II) iodide, 1-(4,4-dimethylpenta-1,2-dienyl)naphthalene (**5c**)*. 4,4-Dimetyl-1-(naphthalene-5-yl)pent-2ynylacetate **4c** (0.40 g, 1.43 mmol) in THF (1.0 mL), 2-propanol (86 µg, 0.11 mL, 1.43 mmol), $Pd(PPh_3)_4$ (82 mg, 72 µmol), SmI_2 (42.9 mL, 0.1 M in THF). Yield 43 mg, (14 %), ^{1}H NMR (400 MHz, $CDCl_3$), δ: 1.22 (s, 9H), 5.67 (d, J 6.5 Hz, 1H), 6.95 (d, J = 6.5 Hz, 1H), 7.45-7.55 (m, 3H), 7.63 (d, J = 7.2 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.87 (t, J = 1.8 Hz, J = 7.2 Hz, 1H), 8.29 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$), δ: 30.4, 32.8, 92.8, 106.0, 123.7, 124.8, 125.7, 125.8, 125.9, 127.3, 128.8, 130.9, 131.5, 134.1, 204; IR ($CHCl_3$), ν_{max}: 879, 1188, 1247, 1362, 1465, 1601, 1944, 2966, 3011, 3055, 3690 cm^{-1}; UV/Vis ($CHCl_3$), λ_{max} (ε) = 246 (9620), 309 (6310); MS (FAB^+), *m/z*: 222 $[M]^+$ (83), 207 (85), 165 (100), 119 (50); HRMS (FAB^+) calcd for $C_{17}H_{18}$: *m/z* 222.1408, found 222.14.04.

*1-(Naphthlen-5-yl)-3-phenylprop-2-yn-1-ol (**3d**)*. Phenylacetylene **2d** (1.1 g, 1.2 mL, 10.6 mmol) in THF (10 mL), n-BuLi (1.6 M, 7.2 mL, 11.5 mmol), 1-napthaldehyde (1.50 g, 1.3 mL, 9.6 mmol). Yield 1.86 g, (75 %), liquid; ^{1}H NMR (400 MHz, $CDCl_3$), δ: 3.06 (brs, 1H), 6.34 (s, 1H), 7.32 (m, 3H), 7.48-7.61 (m, 5H), 7.87 (d, J = 8.2 Hz, 1H), 7.93 (m, 2H), 8.38 (d, J = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$), δ: 63.3, 87.2, 88.8, 122.5, 124.1, 124.7, 125.3, 125.9, 126.5, 128.3, 128.6, 128.8, 129.4, 130.6, 131.8, 134.0, 153.7.

*1-(Naphthlen-5-yl)-3-phenylprop-2-ynyl acetate (**4d**).* 1-(Naphthlen-5-yl)-3-phenylprop-2-yn-1-ol **3d** (0.90 g, 3.48 mmol), Ac_2O (2 mL), pyridine (3 drops). Yield 0.81 g, (77), colorless crystals, m.p. 84-85 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 2.15 (s, 3H), 7.28-7.46 (m, 4H), 7.46-7.59 (m, 5H), 7.89 (m, 3 H), 8.30 (d, J = 8.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$), δ: 21.1, 64.5, 85.6, 87.5, 122.1, 123.8, 125.2, 125.9, 126.5, 126.6, 128.2, 128.7, 128.8, 129.9, 130.6, 131.9, 132.4, 134.0, 169.9; IR (CH_2Cl_2), ν_{max}: 1512, 1600, 1742, 2227, 2342, 2359 cm^{-1}; UV/Vis (CH_2Cl_2), λ_{max} (ε) = 231 (38000), 244 (22900), 284 (11000); MS (FAB), *m/z*: 300 [M$^+$] (8), 241 (100); elemental analysis calcd (%) for $C_{21}H_{16}O_2$, C 83.98, H 5.37; found, C 83.94, H 5.42.

*The reaction of 1-(naphthlen-5-yl)-3-phenylprop-2-ynyl acetate (**4d**) with samarium(II) iodide.* Acetate **4d** (0.20 g, 0.67 mmol) in THF (2.0 mL), 2-propanol (40 mg, 51 µL, 0.67 mmol), $Pd(PPh_3)_4$ (38.7 mg, 34 µmol), SmI_2-THF (16.7 mL, 1.67 mmol, 0.1 M solution).

*1-(3-Phenylpropa-1,2-dienyl)naphthalene (**5d**).* Yield 39 mg (24 %). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 6.67 (d, J = 6.6 Hz, 1H), 7.26 (d, J = 6.6 Hz, 1H), 7.30-7.37 (m, 3H), 7.42-7.46 (m, 3H), 7.51-7.56 (m, 2H), 7.63 (d, J = 7.1 Hz, 1H), 7.78 (d, J = 8.2 Hz, 1H), 7.88 (dd, J = 2.0 Hz, J = 9.5 Hz, 1H), 8.32 (d, J = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$), δ: 95.3, 97.6, 123.7, 125.8, 125.9, 126.4, 127.1, 127.4, 128.1, 128.8, 128.9, 129.9, 131.0, 133.9, 134.1, 209.2, (2 carbons are overlapped); UV/Vis (CH_2Cl_2), λ_{max} (ε) = 242 (34600), 307 (14800); MS (FAB$^+$), *m/z*, 242 [M+H]$^+$ (40), 241 (35), 219 (5); HRMS (FAB$^+$) calcd for $C_{19}H_{14}$: *m/z* 242.1096, found *m/z* 242.1093.

*1-(3-Phenylprop-2-ynyl)naphthalene (**6d**).* 89 mg, 55 %, ^{1}H NMR (400 MHz, $CDCl_3$), δ: 4.25 (s, 2H), 7.29-7.31 (m, 3H), 7.45-7.59 (m, 5H), 7.71 (dd, J = 0.9 Hz, J = 7.0 Hz, 1H), 7.80 (d, J = 8.3 Hz, 1H), 7.89 (d, J = 7.4 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$), δ: 23.8, 83.7, 87.3, 123.5, 123.8, 125.7, 125.8, 126.3, 127.7, 127.9, 128.3 (2C), 128.8, 131.6, 131.8, 132.6, 133.9, UV/Vis (CH_2Cl_2), λ_{max} (ε) = 233 (23500), 252 (18400), 282 (7700); MS (FAB$^+$), *m/z*: 242 [M]$^+$ (15), 241 (16), 235 (10), 178 (7); HRMS (FAB$^+$) calcd for $C_{19}H_{14}$: *m/z* 242.1096, found *m/z* 242.1091.

*1-(Propa-1,2-dienyl)naphthalene (**7**).* To a solution of trimethyl(3-(naphthalene-5-yl)prop-1-ynyl)silane (0.178 g, 0.75 mmol) in THF (5.0 mL) was added C_2H_5ONa (61.2 mg, 0.9 mmol) in THF (3.0 mL) under argon at rt. After stirring for 6 h the reaction was quenched with water (5.0 mL) followed by extraction with diethyl ether (3 x 10 mL) provided crude, which was purified by column flash chromatography over silica gel (hexane) affording pure compound (92 mg, 74 %) as a liquid. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 5.23 (d, J = 6.8 Hz, 2H), 6.90 (t, J = 6.8 Hz, J = 13.8 Hz, 1H), 7.45-7.56 (m, 3H), 7.62 (d, J = 2.1 Hz, J = 6.8 Hz, 1H), 7.76 (d, J = 8.2 Hz, 1H), 7.87 (dd, J = 2.0 Hz, J = 8.2 Hz, 1H), 8.24 (d, J = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$), δ: 77.8, 90.4, 123.5, 125.3, 125.6, 125.7, 126.0, 127.5, 128.6, 130.1, 130.8, 133.9, 211.0; IR ($CHCl_3$), ν_{max}: 1391, 1508, 1685, 1942 cm^{-1}; UV/Vis ($CHCl_3$), λ_{max} (ε) = 248 (7310), 296 (4950); MS (FAB$^+$), *m/z*: 166 [M]$^+$ (100); HRMS (FAB$^+$) calcd for $C_{13}H_{10}$: *m/z* 166.0783, found 166.0779.

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