A Convenient Preparation of 3-Substituted Furans: Synthesis of Perillene and Dendrolasin

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Supporting Information

1-(2,2,2-Trichloro-ethoxy)-dec-2-yne (1)

R_f = 0.25 (hexane)

¹H NMR (CDCl₃, 300 MHz): δ 0.88 (t, 3H, J = 6.9 Hz), 1.20-1.60 (m, 10H), 2.20-2.27 (m, 2H), 4.17 (s, 3H), 4.45 (t, 2H, J = 1.8 Hz). ¹³C NMR (CDCl₃, 75 MHz): δ 14.29, 18.94, 22.82, 28.67, 28.98, 29.01, 31.93, 60.22, 74.60, 81.26, 89.12, 96.99. MS: m/z 284 (M⁺), 286 (M⁺+2), 288 (M⁺+4), 290 (M⁺+6).

2-Methyl-7-(2,2,2-trichloro-ethoxy)-hept-2-en-5-yne (3)

R_f = 0.30 (10% dichloromethane in hexane).

¹H NMR (CDCl₃, 300 MHz): δ 1.64 (s, 3H), 1.72 (s, 3H), 2.94 (d, 2H, J = 7.0 Hz), 4.16 (s, 2H), 4.44 (t, 2H, J = 2.1 Hz), 5.15-5.21 (m, 1H). ¹³C NMR (CDCl₃, 75 MHz): δ 17.93, 18.11, 25.70, 60.28, 74.18, 81.35, 87.64, 96.98, 118.45, 134.57. MS: m/z 272 (M⁺), 274 (M⁺+2).

6,10-Dimethyl-1-(2,2,2-trichloro-ethoxy)-undeca-5,9-dien-2-yne (5)

R_f = 0.28 (hexane)

¹H NMR (CDCl₃, 300 MHz): δ 1.60 (s, 3H), 1.64 (s, 3H), 1.69 (s, 3H), 1.98-2.12 (m, 4H), 2.95 (d, 2H, J = 5.4 Hz), 4.16 (s, 2H), 4.45 (t, 2H, J = 1.5 Hz), 5.05-5.13 (m, 1H), 5.16-5.22 (m, 1H). ¹³C NMR (CDCl₃, 75 MHz): δ 16.33, 17.90, 18.02, 25.90, 26.64, 39.57, 60.26, 74.14, 81.31,

87.72, 96.97, 118.33, 124.13, 131.86, 138.10. MS: m/z 322 (M^+), 324 (M^++2), 326 (M^++4), 328 (M^++6).

[6-(2,2,2-Trichloro-ethoxy)-hex-1-en-4-ynyl]-benzene (7)

R_f = 0.28 (hexane)

^1H NMR (CDCl_3 , 400 MHz): δ 3.18-3.22 (m, 2H), 4.21 (s, 2H), 4.52 (t, 2H, J = 1.8 Hz), 6.12-6.20 (m, 1H), 6.64 (d, 1H, J = 15.6 Hz), 7.20-7.40 (m, 5H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 22.53, 60.19, 77.12, 81.44, 85.51, 96.91, 123.76, 126.44, 127.67, 128.77, 131.79, 137.05. MS: m/z 302 (M^+), 304 (M^++2), 306 (M^++4), 308 (M^++6).

3-(4-Phenylbut-3-enyl)-furan (8)

R_f = 0.53 (hexane)

^1H NMR (CDCl_3 , 300 MHz): δ 2.42-2.52 (m, 2H), 2.60 (t, 2H, J = 7.8 Hz), 6.18-6.32 (m, 2H), 6.42 (d, 1H, J = 15.9 Hz), 7.16-7.36 (m, 7H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 25.0, 33.65, 111.24, 124.66, 126.19, 127.19, 128.71, 130.10, 130.70, 137.86, 139.16, 142.94. MS: m/z 198 (M^+).

[3-(2,2,2-Trichloro-ethoxy)-prop-1-ynyl]-benzene (9)

R_f = 0.15 (hexane)

^1H NMR (CDCl_3 , 300 MHz): δ 4.26 (s, 2H), 4.70 (s, 2H), 7.30-7.37 (m, 3H), 7.44-7.49 (m, 2H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 60.43, 81.55, 83.57, 87.91, 96.87, 122.31, 128.59, 129.05, 132.05. MS: m/z 262 (M^+), 264 (M^++2), 266 (M^++4), 268 (M^++6).

***tert*-Butyldimethyl-[4-(2,2,2-trichloro-ethoxy)-but-2-ynyloxy]-silane (11)**

R_f = 0.45 (30% dichloromethane in hexane)

^1H NMR (CDCl_3 , 300 MHz): δ 0.12 (s, 6H), 0.91 (s, 9H), 4.16 (s, 2H), 4.37 (t, 2H, J = 1.5 Hz), 4.88 (t, 2H, J = 1.9 Hz). ^{13}C NMR (CDCl_3 , 75 MHz): δ -4.95, 18.52, 26.01, 51.87, 59.89, 76.81, 77.23, 77.65, 79.35, 81.42, 86.87, 96.77. MS: m/z 330 (M^+), 332 (M^++2), 334 (M^++4), 336 (M^++6).

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***tert*-Butyl-(2-furan-3-yl-ethoxy)-dimethylsilane (12)**

R_f = 0.4 (2% ethyl acetate in hexane)

^1H NMR (CDCl_3 , 300 MHz): δ 0.05 (s, 6H), 0.90 (s, 9H), 2.65 (t, 2H, J = 4.8 Hz), 3.76 (t, 2H, J = 5.4 Hz), 6.31 (s, 1H), 7.27 (s, 1H), 7.35 (s, 1H). ^{13}C NMR (CDCl_3 , 75 MHz): δ -5.13, 18.54, 26.12, 28.80, 63.66, 77.44, 111.67, 122.08, 139.78, 142.67. MS: m/z 226 (M^+).

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2,2-Dimethyl-4-phenyl-5-[4-(2,2,2-trichloro-ethoxy)-but-2-ynyl]-[1,3]dioxane (13)

R_f = 0.27 (5% EtOAc in hexane)

^1H NMR (CDCl_3 , 300 MHz): δ 1.54 (s, 3H), 1.58 (s, 3H), 2.50-2.75 (m, 2H), 3.87-3.94 (m, 1H), 4.10 (s, 2H), 4.37-4.41 (m, 1H), 4.88 (d, 1H, J = 8.7 Hz), 7.30-7.42 (m, 5H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 21.56, 27.34, 27.39, 60.01, 77.27, 80.82, 81.34, 82.45, 83.90, 96.85, 109.51, 127.01, 128.74, 128.83, 137.42. MS: m/z 376 (M^+), 378 (M^++2), 380 (M^++4), 382 (M^++6).

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4-(2-Furan-3-yl-ethyl)-2,2-dimethyl-5-phenyl-[1,3]dioxolane (14)

R_f = 0.40 (5% EtOAc in hexane)

^1H NMR (CDCl_3 , 400 MHz): δ 1.52 (s, 3H), 1.57 (s, 3H), 1.80-1.90 (m, 2H), 2.39-2.48 (m, 1H), 2.56-2.66 (m, 1H), 3.78-3.84 (m, 1H), 4.56 (d, 1H, J = 8.4 Hz). ^{13}C NMR (CDCl_3 , 75 MHz): δ

21.59, 27.26, 27.65, 32.09, 82.72, 83.56, 108.97, 111.07, 124.47, 127.05, 128.55, 128.80, 137.98, 139.04, 142.94. MS: m/z 272 (M^+).

Methyl 10-(2,2,2-Trichloro-ethoxy)-deca-5,8-diynoate (15)

R_f = 0.27 (10% hexane)

1H NMR ($CDCl_3$, 300 MHz): δ 1.77-1.87 (m, 2H), 2.20-2.28 (m, 2H), 2.44 (t, 2H, J = 7.5 Hz), 3.18-3.29 (m 2H), 3.68 (s, 3H), 4.16 (s, 2H), 4.45 (t, 2H, J = 2.4 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 10.06, 18.29, 23.96, 32.98, 51.76, 60.00, 74.21, 74.93, 80.13, 81.44, 82.95, 96.81, 173.75. MS: m/z 324 (M^+), 326 ($M^+ + 2$), 328 ($M^+ + 4$), 330 ($M^+ + 6$).

Methyl 8-Furan-3-yl-oct-5-ynoate (16)

R_f = 0.35 (10% EtOAc in hexane)

1H NMR ($CDCl_3$, 300 MHz): δ 1.74-1.84 (m, 2H), 2.18-2.25 (m, 2H), 2.34-2.44 (m, 4H), 2.61 (t, 2H, J = 7.2 Hz), 3.68 (s, 3H), 6.31-6.32 (m, 1H), 7.26-7.28 (m, 1H), 7.34 (t, 1H, J = 1.8 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 18.38, 20.03, 24.34, 24.92, 32.98, 51.73, 79.71, 80.68, 111.06, 124.02, 139.31, 142.88, 173.94. MS: m/z 220 (M^+).

3-(5-Benzyloxy-pentyl)-furan (17)

R_f = 0.16 (2% EtOAc in hexane)

1H NMR ($CDCl_3$, 300 MHz): δ 1.56-1.76 (m, 4H), 2.23-2.30 (m, 2H), 3.49 (t, 2H, J = 6.3 Hz), 4.15 (s, 2H), 4.43 (t, 2H, J = 2.1 Hz), 4.51 (s, 2H), 7.25-7.40 (m, 5H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 18.80, 25.47, 29.09, 60.23, 69.92, 73.13, 74.92, 81.32, 88.66, 96.97, 127.76, 127.81, 128.58, 138.72. MS: m/z 348 (M^+), 350 ($M^+ + 2$), 352 ($M^+ + 4$), 354 ($M^+ + 6$).

3-(5-Benzyloxy-pentyl)-furan (18)

R_f = 0.26 (2% EtOAc in hexane)

1H NMR ($CDCl_3$, 300 MHz): δ 1.36-1.46 (m, 2H), 1.52-1.68 (m, 4H), 2.41 (t, 2H, J = 7.2 Hz), 3.46 (t, 2H, J = 6.6 Hz), 4.43 (t, 2H, J = 2.1 Hz), 4.49 (s, 2H), 6.25 (m, 1H), 7.19 (m, 1H), 7.24-

7.34 (m, 6H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 24.89, 26.05, 29.75, 30.05, 70.53, 73.08, 111.21, 125.31, 127.70, 127.83, 128.55, 138.85, 138.95, 142.82. MS: m/z 244 (M^+).

7-(2,2,2-Trichloro-ethoxy)-hept-5-ynyl acetate (19)

R_f = 0.50 (15% EtOAc in hexane)

^1H NMR (CDCl_3 , 300 MHz): δ 1.56-1.65 (m, 2H), 1.71-1.80 (m, 2H), 2.05 (s, 3H), 2.27-2.33 (m, 2H), 4.09 (t, 2H, J = 6.6 Hz), 4.15-4.16 (m, 2H), 4.43-4.44 (m, 2H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 18.57, 21.13, 25.07, 27.89, 60.11, 64.00, 75.19, 81.28, 88.08, 96.88, 171.25. MS: m/z 300 (M^+), 302 ($\text{M}^+ + 2$), 304 ($\text{M}^+ + 4$), 306 ($\text{M}^+ + 6$).

5-Furan-3-yl-pentyl acetate (20)

R_f = 0.90 (65% EtOAc in hexane)

^1H NMR (CDCl_3 , 300 MHz): δ 1.33-1.44 (m, 2H), 1.53-1.72 (m, 4H), 2.04 (s, 3H), 2.42 (t, 2H, J = 7.2 Hz), 4.05 (t, 2H, J = 6.9 Hz), 6.25-6.26 (m, 1H), 7.20-7.21 (m, 1H), 7.34 (t, 1H, J = 1.8 Hz). ^{13}C NMR (CDCl_3 , 75 MHz): δ 21.16, 24.75, 25.68, 28.54, 29.75, 64.62, 111.10, 125.06, 138.94, 142.86, 171.37. MS: m/z 196 (M^+).

tert-Butyldiphenyl-[7-(2,2,2-trichloro-ethoxy)-hept-5-ynyloxy]-silane (21)

R_f = 0.70 (15% EtOAc in hexane)

^1H NMR (CDCl_3 , 300 MHz): δ 1.05 (s, 9H), 1.60-1.68 (m, 4H), 2.19-2.26 (m, 2H), 3.68 (t, 2H, J = 6.0 Hz), 4.15 (s, 2H), 4.42 (t, 2H, J = 2.1 Hz), 7.34-7.43 (m, 6H), 7.64-7.68 (m, 4H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 18.74, 19.42, 25.18, 27.07, 31.85, 60.22, 63.49, 74.80, 81.29, 88.85, 96.98, 127.83, 129.78, 134.12, 135.76. MS: m/z 496 (M^+), 498 ($\text{M}^+ + 2$), 500 ($\text{M}^+ + 4$), 502 ($\text{M}^+ + 6$).

tert-Butyl-(5-furan-3-yl-pentyloxy)-diphenylsilane (22)

R_f = 0.80 (15% EtOAc in hexane)

^1H NMR (CDCl_3 , 300 MHz): δ 1.04 (s, 9H), 1.33-1.43 (m, 2H), 1.45-1.62 (m, 4H), 2.39 (t, 2H, $J = 6.9$ Hz), 3.65 (t, 2H, $J = 6.6$ Hz), 6.22 (s, 1H), 7.17-7.19 (m, 1H), 7.32-7.43 (m, 7H), 7.64-7.68 (m, 4H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 19.44, 24.92, 25.66, 27.08, 29.95, 32.55, 64.07, 111.24, 125.37, 127.79, 129.72, 134.33, 135.72, 135.79, 138.95, 142.79. MS: m/z 392 (M^+).

7-(2,2,2-Trichloro-ethoxy)-hept-5-yn-1-ol (23)

$R_f = 0.23$ (30% EtOAc in hexane)

^1H NMR (CDCl_3 , 300 MHz): δ 1.56-1.72 (m, 5H), 2.26-2.33 (m, 2H), 3.67 (t, 2H, $J = 6.0$ Hz), 4.16 (s, 2H), 4.44 (t, 2H, $J = 2.1$ Hz). ^{13}C NMR (CDCl_3 , 75 MHz): δ 18.70, 24.92, 31.89, 60.15, 62.40, 74.98, 81.26, 88.52, 96.90. MS: m/z 258 (M^+), 260 ($\text{M}^+ + 2$), 262 ($\text{M}^+ + 4$), 264 ($\text{M}^+ + 6$).

5-Furan-3-yl-pentan-1-ol (24)

$R_f = 0.26$ (30% EtOAc in hexane)

^1H NMR (CDCl_3 , 300 MHz): δ 1.36-1.46 (m, 2H), 1.48 (br s, 1H, OH), 1.53-1.64 (m, 4H), 2.43 (t, 2H, $J = 7.2$ Hz), 3.64 (t, 2H, $J = 6.6$ Hz), 6.26 (s, 1H), 7.20-7.21 (m, 1H), 7.34 (t, 1H, $J = 1.8$ Hz). ^{13}C NMR (CDCl_3 , 75 MHz): δ 24.87, 25.56, 29.97, 32.71, 63.06, 111.16, 125.22, 138.95, 142.85. MS: m/z 154 (M^+).

3-(α -Deutero)-Octyl-furan (28):

^1H NMR (CDCl_3 , 400 MHz): δ 0.88 (t, 3H, $J = 6.8$ Hz), 1.20-1.40 (m, 10H), 2.45-2.60 (m, 2H), 2.40 (t, 1H, $J = 7.2$ Hz), 6.26 (d, 1H, $J = 0.8$ Hz), 7.20 (s, 1H), 7.34 (t, 1H, $J = 1.60$ Hz). MS: m/z 181 (M^+).