

Supporting Information

**Electrophilic aromatic substitutions of silylated
furans and thiophenes with retention of the
organosilyl group**

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General: Melting points are uncorrected. ^1H (300 MHz) and ^{13}C (75.5 MHz) NMR spectra of solutions in CDCl_3 ($\delta_{\text{H}} = 7.24$, $\delta_{\text{C}} = 77.0$) were calibrated to the solvent signal.

2-[Bis(4-methoxyphenyl)methyl]-5-(trimethylsilyl)furan

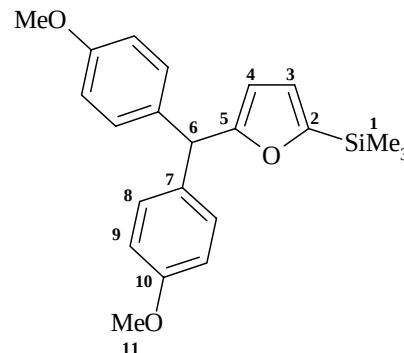
Separation and purification by column chromatography on basic alumina (activity III, pentane), colorless oil;

^1H NMR (CDCl_3 , 300 MHz): $\delta = 0.21$ (s, 9 H, 1-H), 3.77 (s, 6 H, 11-H), 5.37 (br s, 1 H, 6-H), 5.82 (dd, $^3J = 3.1$ Hz, $^4J = 0.8$ Hz, 1 H, 4-H), 6.52 (d, $^3J = 3.1$ Hz, 1 H, 3-H), 6.80-6.83 (AA'BB'-system, $J_{\text{AB}} = 8.7$ Hz, 4 H, 9-H), 7.03-7.06 (AA'BB'-system, $J_{\text{AB}} = 8.7$ Hz, 4 H, 8-H);

^{13}C NMR (CDCl_3 , 75.5 MHz): $\delta = -1.6$ (q, C-1), 49.3 (d, C-6), 55.2 (q, C-11), 108.2 (d, C-4), 113.6 (d, C-9), 120.1 (d, C-3), 129.6 (d, C-8), 134.9 (s, C-7), 158.1 (s, C-10), 159.5 (s, C-5), 161.6 (s, C-2);

MS (EI, 70 eV), m/z (%): 368, 367, 366 (M^+ , 5.2, 21, 100), 352, 351 ($\text{M}^+ - \text{CH}_3$, 4.0, 15), 337, 336, 335 ($\text{M}^+ - \text{OCH}_3$, 1.6, 3.6, 11), 325, 324, 323 ($\text{M}^+ - \text{CH}_3\text{Si}$, 1.5, 5.6, 23), 293 ($\text{M}^+ - \text{C}_3\text{H}_9\text{Si}$, 5.9), 265 (21), 259 (19), 73 ($\text{M}^+ - \text{C}_{19}\text{H}_{17}\text{O}_3$, 16);

Anal. Calcd. for $\text{C}_{22}\text{H}_{26}\text{O}_3\text{Si}$ (366.6): C, 72.09; H, 7.15. Found C, 72.47; H, 7.19.



2-[Bis(4-methoxyphenyl)methyl]-5-(trimethylsilyl)furan

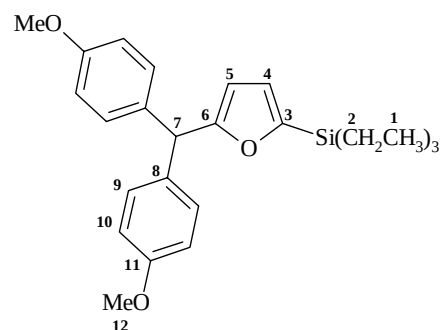
Separation and purification by column chromatography on basic alumina (activity III, pentane), colorless oil;

^1H NMR (CDCl_3 , 300 MHz): $\delta = 0.70$ (q, $^3J = 7.5$ Hz, 6 H, 2-H), 0.94 (t, $^3J = 7.5$ Hz, 9 H, 1-H), 3.77 (s, 6 H, 12-H), 5.36 (br s, 1 H, 7-H), 5.85 (dd, $^3J = 3.1$ Hz, $^4J = 0.8$ Hz, 1 H, 5-H), 6.54 (dd, $^3J = 3.1$ Hz, $^5J = 0.4$ Hz, 1 H, 4-H), 6.78-6.83 (AA'BB'-system, $J_{\text{AB}} = 8.8$ Hz, 4 H, 10-H), 7.02-7.07 (AA'BB'-system, $J_{\text{AB}} = 8.8$ Hz, 4 H, 9-H);

^{13}C NMR (CDCl_3 , 75.5 MHz): $\delta = 3.3$ (t, C-2), 7.3 (q, C-1), 49.4 (d, C-7), 55.2 (q, C-12), 108.0 (d, C-5), 113.6 (d, C-10), 121.3 (d, C-4), 129.7 (d, C-9), 135.0 (s, C-8), 157.4 (s, C-6), 158.2 (s, C-11), 161.5 (s, C-3);

MS (EI, 70 eV), m/z (%): 410, 409, 408 (M^+ , 8.8, 32, 100), 381, 380, 379 ($\text{M}^+ - \text{C}_2\text{H}_5$, 9.3, 32, 47), 366, 365 ($\text{M}^+ - \text{C}_3\text{H}_5$, 3.3, 12), 351, 352, ($\text{M}^+ - \text{C}_4\text{H}_9$, 4.6, 11), 293 ($\text{M}^+ - \text{C}_6\text{H}_{15}\text{Si}$, 3.1), 277 (18), 137 (11);

Anal. Calcd. for $\text{C}_{25}\text{H}_{32}\text{O}_3\text{Si}$ (408.2): C, 73.49; H, 7.89. Found: C, 73.43; H, 7.79.

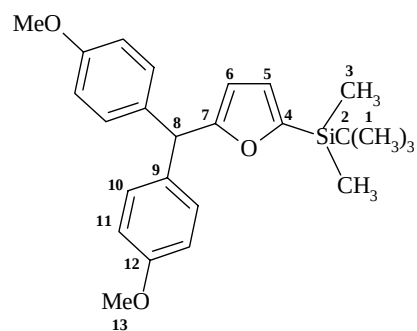


2-[Bis(4-methoxyphenyl)methyl]-5-(dimethyl-tert-butylsilyl)furan

Separation and purification by column chromatography on basic alumina (activity III, pentane), colorless oil;

^1H NMR (CDCl_3 , 300 MHz): $\delta = 0.18$ (s, 6 H, 3-H), 0.87 (s, 9 H, 1-H), 3.76 (s, 6 H, 13-H), 5.36 (br s, 1 H, 8-H), 5.86 (dd, $^3J = 3.2$ Hz, $^4J = 0.9$ Hz, 1 H, 6-H), 6.54 (dd, $^3J = 3.2$ Hz, $^5J = 0.4$ Hz, 1 H, 5-H), 6.79-6.82 (AA'BB'-system, $J_{\text{AB}} = 8.8$ Hz, 4 H, 11-H), 7.03-7.06 (AA'BB'-system, $J_{\text{AB}} = 8.8$ Hz, 4 H, 10-H);

^{13}C NMR (CDCl_3 , 75.5 MHz): $\delta = -6.3$ (q, C-3), 16.7 (s, C-2), 26.3 (q, C-1), 49.4 (d, C-8), 55.2 (q, C-13), 108.0 (d, C-6), 113.6 (d, C-11), 121.4 (d, C-5), 129.6 (d, C-10), 134.9 (s, C-9), 157.9 (s, C-7), 158.2 (s, C-12), 161.6 (s, C-4);



MS (EI, 70 eV), m/z (%): 410, 409, 408 (M^+ , 3.8, 15, 52), 353, 352, 351 ($M^+ - C_4H_9$, 7.9, 32, 100), 277 (20), 243 (15), 165 (16);

Anal. Calcd. for $C_{25}H_{32}O_3Si$ (408.2): C, 73.49; H, 7.89. Found: C, 73.23; H, 7.87.

2-[Bis(4-methoxyphenyl)methyl]-5-(trimethylsilyl)thiophene

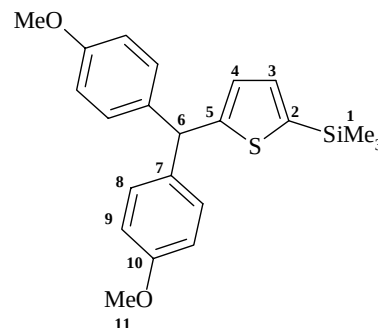
Separation and purification by column chromatography on basic alumina (activity III, pentane), colorless crystals, mp 67.5–68.5 °C;

1H NMR ($CDCl_3$, 300 MHz): δ = 0.26 (s, 9 H, 1-H), 3.78 (s, 6 H, 11-H), 5.59 (br s, 1 H, 6-H), 6.72 (dd, 3J = 3.3 Hz, 4J = 1.0 Hz, 1 H, 4-H), 6.81–6.84 (AA'BB'-system, J_{AB} = 8.8 Hz, 4 H, 9-H), 7.06 (d, 3J = 3.3 Hz, 1 H, 3-H), 7.11–7.14 (AA'BB'-system, J_{AB} = 8.8 Hz, 4 H, 8-H);

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = -0.4 (q, C-1), 50.7 (d, C-6), 55.2 (q, C-11), 113.7 (d, C-9), 127.5 (d, C-4), 129.7 (d, C-8), 133.7 (d, C-3), 136.5 (s, C-7), 139.2 (s, C-5), 154.3 (s, C-2), 158.2 (s, C-10);

MS (EI, 70 eV), m/z (%): 384, 383, 382 (M^+ , 8.0, 21, 100), 369, 368, 367 ($M^+ - CH_3$, 6.5, 17, 76), 351 (9.1), 311, 310, 309 ($M^+ - C_3H_9Si$, 3.5, 11, 66), 275.2 ($M^+ - C_7H_7O$, 16), 73.1 ($M^+ - C_{19}H_{17}SO_2$, 8.1).

Anal. Calcd. for $C_{22}H_{26}O_2SSi$ (382.1): C, 69.07; H, 6.85; S, 8.38. Found: C, 69.40; H, 6.90, S, 8.19.



2-(Ferrocenylphenylmethyl)-5-(trimethylsilyl)furan

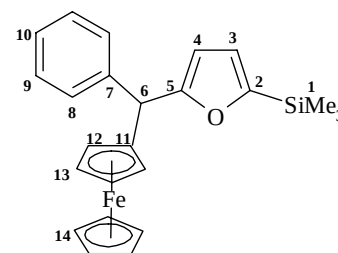
Separation and purification by column chromatography on basic alumina (activity III, pentane), beige powder; mp 61–62 °C;

1H NMR ($CDCl_3$, 300 MHz): δ = 0.28 (s, 9 H, 1-H), 4.05 (s, 5 H, 14-H), 4.05–4.19 (m, 4 H, 12-H, 13-H), 5.12 (br s, 1 H, 6-H), 5.95 (br s, 1 H, 4-H), 6.54 (br s, 1 H, 3-H), 7.18–7.24 (m, 5 H, 8-H, 9-H, 10-H);

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = -1.4 (q, C-1), 45.7 (d, C-6), 67.6, 68.3, 68.5, 68.9 (4 d, C-12, C-13), 68.9 (d, C-14), 90.4 (s, C-11), 106.6 (d, C-4), 120.3 (d, C-3), 126.3, (d, C-10), 128.0, 128.1 (2 d, C-8, C-9), 143.2 (s, C-7), 158.4 (s, C-5), 161.6 (s, C-2);

MS (EI, 70 eV), m/z (%): 416, 415, 414 (M^+ , 8.1, 31, 100), 200 (9), 73 (11);

Anal. Calcd. for $C_{24}H_{26}FeOSi$ (414.1): C, 69.56; H, 6.32. Found: C, 69.42; H, 6.48.



2-(Ferrocenylphenylmethyl)-5-(triethylsilyl)furan

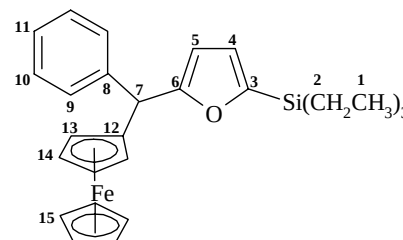
Separation and purification by column chromatography on basic alumina (activity III, pentane/ether = 20/1, v/v), yellow oil;

1H NMR ($CDCl_3$, 300 MHz): δ = 0.76 (q, 3J = 7.9 Hz, 6 H, 2-H), 1.00 (t, 3J = 7.9 Hz, 9 H, 1-H), 4.02 (s, 5 H, 15-H), 4.02–4.23 (m, 4 H, 13-H, 14-H), 5.11 (br s, 1 H, 7-H), 6.02 (d, 3J = 2.9 Hz, 1 H, 5-H), 6.58 (d, 3J = 2.9 Hz, 1 H, 4-H), 7.15–7.28 (m, 5 H, 9-H, 10-H, 11-H);

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 3.0 (t, C-2), 7.4 (q, C-1), 45.8 (d, C-7), 67.5, 67.6, 68.3, 68.5 (4 d, C-13, C-14), 68.8 (d, C-15), 90.2 (s, C-12), 106.4 (d, C-5), 121.5 (d, C-4), 126.3 (d, C-11), 128.0, 128.1 (2 d, C-9, C-10), 143.2 (s, C-8), 156.4 (s, C-6), 161.5 (s, C-3);

MS (EI, 70 eV), m/z (%): 458, 457, 456 (M^+ , 9.5, 38, 100), 275 (11);

Anal. Calcd. for $C_{27}H_{32}FeOSi$ (456.2): C, 71.04; H, 7.07. Found: C, 70.55; H, 7.08.



2-(Ferrocenylphenylmethyl)-5-(tributylsilyl)furan

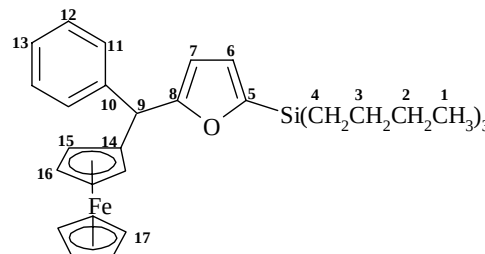
Separation and purification by column chromatography on basic alumina (activity III, pentane), yellow-orange oil;

^1H NMR (CDCl_3 , 300 MHz): δ = 0.73-1.37 (m, 27 H, 1-H, 2-H, 3-H, 4-H), 4.01 (s, 5 H, 17-H), 4.06-4.28 (m, 4 H, 15-H, 16-H), 5.09 (s, 1 H, 9-H), 6.04 (d, 3J = 3.1 Hz, 1 H, 7-H), 6.55 (d, 3J = 3.1 Hz, 1 H, 6-H), 7.14-7.23 (m, 5 H, 11-H, 12-H, 13-H);

^{13}C NMR (CDCl_3 , 75.5 MHz): δ = 12.1 (t, C-4), 13.8 (q, C-1), 26.0, 26.6 (2 t, C-2, C-3), 45.8 (d, C-9), 67.5, 67.7, 68.4, 68.5 (4 d, C-15, C-16), 68.8 (d, C-17), 90.2 (s, C-14), 106.3 (d, C-7), 121.2 (d, C-6), 126.3 (d, C-13), 128.0, 128.1 (2 d, C-11, C-12), 143.2 (s, C-10), 157.1 (s, C-8), 161.2 (s, C-5);

MS (EI, 70 eV), m/z (%): 542, 541, 540 (M^+ , 8.8, 33, 100);

Anal. Calcd. for $\text{C}_{33}\text{H}_{44}\text{FeOSi}$ (540.3): C, 73.31; H, 8.20. Found: C, 73.21; H, 8.39.

**2-(Ferrocenylphenylmethyl)-5-(dimethyl-*tert*-butylsilyl)furan**

Separation and purification by column chromatography on basic alumina (activity III, pentane), orange oil;

^1H NMR (CDCl_3 , 300 MHz): δ = 0.24 (s, 6 H, 3-H), 0.92 (s, 9 H, 1-H), 4.03 (s, 5 H, 16-H), 4.06-4.27 (m, 4 H, 14-H, 15-H), 5.10 (s, 1 H, 8-H), 6.03 (d, 3J = 3.1 Hz, 1 H, 6-H), 6.57 (d, 3J = 3.1 Hz, 1 H, 5-H), 7.13-7.24 (m, 5 H, 10-H, 11-H, 12-H);

^{13}C NMR (CDCl_3 , 75.5 MHz): δ = -6.1 (q, C-3), 16.8 (s, C-2), 26.4 (q, C-1), 45.8 (d, C-8), 67.6, 67.7, 68.4, 68.6 (4 d, C-14, C-15), 68.9 (d, C-16), 90.3 (s, C-13), 106.4 (d, C-6), 121.6 (d, C-5), 126.3 (d, C-12), 128.0, 128.1 (2 d, C-10, C-11), 143.2 (s, C-9), 157.0 (s, C-7), 161.5 (s, C-4);

MS (EI, 70 eV), m/z (%): 458, 457, 456 (M^+ , 9.2, 37, 100);

Anal. Calcd. for $\text{C}_{27}\text{H}_{32}\text{FeOSi}$ (456.2): C, 71.04; H, 7.07. Found: C, 70.99; H, 7.00.

