Supporting Information for

Selective synthesis of *E*-vinylsilanes and *E,E-*divinylsilanes via platinum-catalyzed hydrosilylation of alkynes with secondary silanes

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- 1. NMR spectra and analytical data of isolated *E*-vinylsilanes S2
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1. NMR spectra and analytical data of isolated *E*-vinylsilanes



Figure S2. ¹³C NMR (75 MHz, CDCl₃) of product 3



Figure S3. ²⁹Si NMR (79 MHz, CDCl₃) of product 3

Analytical data of product **3**:

Isolated yield: 92% (200.7 mg); ¹H NMR (CDCl₃, δ , ppm): 0.46 (d, 3H, *J*_{HH} = 3.8 Hz, *CH*₃), 0.97 (t, 3H, *J*_{HH} = 6.9 Hz, -(CH₂)₄*CH*₃), 1.32 – 1.53 (m, 6H, -(*CH*₂)₄CH₃), 2.14 – 2.31 (m, 2H, =CHCH₂), 4.57 – 4.71 (m, 1H, Si*H*), 5.76 – 5.88 (m, 1H, =*CH*Si), 6.32 (dt, 1H, *J*_{HH} = 18.5, 6.2 Hz, =*CH*CH₂), 7.34 – 7.47 (m, 3H, Ph), 7.55 – 7.68 (m, 2H, Ph); ¹³C NMR (CDCl₃, δ , ppm): -5.11 (*C*H₃), 14.03, 22.53, 28.22, 31.43, 36.83, 123.98, 127.82, 129.17, 134.50, 136.34, 151.63; ²⁹Si NMR (CDCl₃, δ , ppm): -22.23; MS: *m/z* (rel. intensity): 105 (21), 121 (42), 122 (11), 134 (11), 216 (15), 217 (100), 218 (38, M⁺); anal. calcd. for C₁₄H₂₂Si (%): C: 76.99, H: 10.15; found: C: 76.90, H: 10.11.



Figure S4. 1 H NMR (300 MHz, CDCl₃) of product 4



Figure S5. 13 C NMR (75 MHz, CDCl₃) of product 4



Figure S6. ²⁹Si NMR (79 MHz, CDCl₃) of product 4

Analytical data of product 4:

Isolated yield: 93% (260.5 mg); ¹H NMR (CDCl₃, δ , ppm): 0.98 (t, 3H, J_{HH} = 6.8 Hz, -(CH₂)₄CH₃), 1.33 – 1.56 (m, 6H, -(CH₂)₄CH₃), 2.24 – 2.36 (m, 2H, =CHCH₂), 5.19 (d, 1H, J_{HH} = 3.1 Hz, SiH), 5.95 – 6.01 (m, 1H, =CHSi), 6.39 (dt, 1H, J_{HH} = 18.5, 6.3 Hz, =CHCH₂), 7.39 – 7.70 (m, 10H, Ph); ¹³C NMR (CDCl₃, δ , ppm): 14.04, 22.50, 28.11, 31.41, 36.93, 121.89, 127.91, 129.50, 134.26, 135.41, 153.95; ²⁹Si NMR (CDCl₃, δ , ppm): -22.21; MS: *m/z* (rel. intensity): 53 (18), 105 (43), 106 (20), 107 (19), 131 (15), 145 (17), 180 (21), 181 (43), 182 (35), 183 (61), 184 (21), 203 (27), 251 (19), 259 (23), 267 (17), 279 (100), 280 (32, M⁺).



Figure S7. ¹H NMR (400 MHz, CDCl₃) of product 5



Figure S8. ¹³C NMR (75 MHz, CDCl₃) of product 5



Figure S9. ²⁹Si NMR (79 MHz, CDCl₃) of product 5

Analytical data od product 5:

Isolated yield: 90% (165.7 mg); ¹H NMR (CDCl₃, δ , ppm): 0.60 -0.66 (m, 4H, CH₃CH₂-), 0.89 (t, 3H, *J*_{HH} = 7.0 Hz, -(CH₂)₄CH₃), 0.99 (t, 6H, *J*_{HH} = 7.8 Hz, CH₃CH₂-), 1.26 - 1.32 (m, 4H, -(CH₂)₄CH₃), 1.38 - 1.44 (m, 2H, -(CH₂)₄CH₃), 2.10 - 2.16 (m, 2H, =CHCH₂), 3.78 - 3.89 (m, 1H, SiH), 5.52 - 5.62 (m, 1H, =CHSi), 6.17 (dt, 1H, *J*_{HH} = 18.6, 6.1 Hz, =CHCH₂); ¹³C NMR (CDCl₃, δ , ppm): 3.38 (CH₃), 8.05 (CH₂), 14.02, 22.54, 28.38, 31.40, 36.94, 123.58, 150.60; ²⁹Si NMR (CDCl₃, δ , ppm): -10.13; MS: *m/z* (rel. intensity): 59 (17), 85 (13), 87 (14), 95 (17), 97 (16), 99 (25), 113 (14), 127 (12), 155 (62), 182 (20), 183 (100), 184 (16, M⁺); anal. calcd. for C₁₁H₂₄Si (%): C: 71.65, H: 13.12; found: C: 71.70, H: 13.18.



Figure S10. 1 H NMR (400 MHz, CDCl₃) of product 6



Figure S11. 13 C NMR (100 MHz, CDCl₃) of product 6



Figure S12. ²⁹Si NMR (79 MHz, CDCl₃) of product 6

Analytical data od product 6:

Isolated yield: 92% (272.4 mg); ¹H NMR (CDCl₃, δ , ppm): 0.41 (d, 6H, J_{HH} = 3.8 Hz, CH_3), 0.50 (s, 6H, CH_3), 4.47 – 4.53 (m, 1H, SiH), 6.65 (dd, 1H, J_{HH} = 19.1, 1.1 Hz, =CHSi), 7.02 (d, 1H, J_{HH} = 19.1 Hz, =CH), 7.28 – 7.40 (m, 3H, Ph), 7.48 – 7.52 (m, 2H, Ph), 7.59 – 7.66 (m, 4H, Ph); ¹³C NMR (CDCl₃, δ , ppm): -3.78 (CH_3), -2.51 (CH_3), 126.57, 126.99, 127.06, 128.22, 128.24, 128.59, 133.37 (d, J = 2.5 Hz), 133.45 (d, J = 1.7 Hz), 138.22 (d, J = 1.7 Hz), 138.38, 138.58, 139.53, 139.74, 145.40, 145.44; ²⁹Si NMR (CDCl₃, δ , ppm): -10.32, -17.07; MS: m/z (rel. intensity): 59 (17), 135 (32), 145 (42), 236 (80), 237 (100), 238 (27), 281 (77), 282 (23), 296 (16, M⁺); anal. calcd. for C₁₈H₂₄Si₂ (%): C: 72.90, H: 8.16; found: C: 72.81, H: 8.12.



Figure S13. ¹H NMR (400 MHz, CDCl₃) of product 7



Figure S14. ¹³C NMR (100 MHz, CDCl₃) of product 7



Figure S15. ²⁹Si NMR (79 MHz, CDCl₃) of product 7

Analytical data of product 7:

Isolated yield: 89% (304.5 mg); ¹H NMR (CDCl₃, δ , ppm): 1.36 (s, 9H, (CH₃)₃), 5.29 (d, 1H, J_{HH} = 3.2 Hz, SiH), 6.71 (dd, 1H, J_{HH} = 19.0, 3.3 Hz, =CHSi), 7.13 (d, 1H, J_{HH} = 19.0 Hz, =CH), 7.39 – 7.49 (m, 10H, -C₆H₄- and Ph), 7.64 – 7.69 (m, 4H, Ph); ¹³C NMR (CDCl₃, δ , ppm): 31.25 (C(CH₃)₃), 34.66 (C(CH₃)₃), 120.36, 125.49, 126.47, 128.02, 129.69, 133.77, 135.52, 148.95, 151.85; ²⁹Si NMR (CDCl₃, δ , ppm): -21.03; MS: m/z (rel. intensity): 57 (24), 77 (14), 91 (14), 105 (39), 106 (17), 131 (29), 132 (30), 146 (14), 180 (19), 181 (48), 182 (28), 183 (45), 184 914), 200 (16), 207 (32), 208 (74), 209 (57), 210 (18), 224 (24), 250 (23), 252 (35), 264 (32), 285 (100), 288 (36), 327 (14), 342 (52, M⁺); anal. calcd. for C₂₄H₂₆Si (%): C: 84.15, H: 7.65; found: C: 84.09, H: 7.55.





Figure S17. ¹³C NMR (75 MHz, CDCl₃) of product 8



Figure S18. ²⁹Si NMR (79 MHz, CDCl₃) of product 8

Analytical data of product 8:

Isolated yield: 92% (257.7 mg); ¹H NMR (CDCl₃, δ , ppm): 0.59 (d, 3H, *J*_{HH} = 3.8 Hz, *CH*₃),1.40 (s, 9H, (*CH*₃)₃), 4.78 – 4.87 (m, 1H, Si*H*), 6.60 (dd, 1H, *J*_{HH} = 19.0, 3.3 Hz, =*CHS*i), 7.14 (d, 1H, *J*_{HH} = 19.0 Hz, =*CH*), 7.42 – 7.50 (m, 7H, -C₆H₄- and Ph), 7.64 – 7.71 (m, 2H, Ph); ¹³C NMR (CDCl₃, δ , ppm): -5.15 (*CH*₃), 31.26 (*C*(*CH*₃)₃), 34.64 (*C*(*CH*₃)₃), 122.58, 125.47, 126.31, 127.92, 129.38, 134.62, 146.97, 151.61; ²⁹Si NMR (CDCl₃, δ , ppm): -20.66; MS: *m/z* (rel. intensity): 57 (100), 105 (31), 106 (10), 115 (12), 121 (10), 143 (13), 145 (75), 146 (42), 147 (24), 148 (11), 187 (13), 209 (11), 221 (10), 222 (28), 223 (36), 224 (17), 263 (10), 265 (50), 266 (12), 279 (87), 280 (28, M⁺); anal. calcd. for C₁₉H₂₄Si (%): C: 81.36, H: 8.62; found: C: 81.45, H: 8.72.



Figure S20. ¹³C NMR (75 MHz, CDCl₃) of product 9



Figure S21. ²⁹Si NMR (79 MHz, CDCl₃) of product 9

Analytical data of product 9:

Isolated yield: 92% (239.4 mg); ¹H NMR (CDCl₃, δ , ppm): 0.66-0.84 (m, 4H, CH₃CH₂-), 0.88 –0.96 (m, 3H, -(CH₂)₄CH₃), 1.00-1.15 (m, 6H, CH₃CH₂-), 1.30 – 1.41 (m, 4H, -(CH₂)₄CH₃), 1.59 – 1.68 (m, 2H, -(CH₂)₄CH₃), 2.57 – 2.66 (m, 2H, -(CH₂)₄CH₃), 4.00 – 4.10 (m, 1H, SiH), 6.39 (dd, 1H, *J*_{HH} = 19.1, 3.4 Hz, =CHSi), 7.02 (d, 1H, *J*_{HH} = 19.2 Hz, =CH), 7.17 (d, 2H, *J*_{HH} = 8.0 Hz, -C₆H₄-), 7.39 (d, 2H, *J*_{HH} = 8.0 Hz, -C₆H₄-); ¹³C NMR (CDCl₃, δ , ppm): 3.38 (CH₃), 8.11 (CH₂), 14.01, 22.54, 31.10, 31.47, 35.68, 122.25, 126.34, 128.59, 135.78, 143.15, 146.33; ²⁹Si NMR (CDCl₃, δ , ppm): -8.32; MS: *m/z* (rel. intensity): 131 (12), 133 (18), 145 (11), 159 (10), 161 (100), 162 (24), 203 (34), 231 (41), 259 (14), 260 (26, M⁺); anal. calcd. for C₁₇H₂₈Si (%): C: 78.38, H: 10.83; found: C: 78.42, H: 10.88.



Figure S22. ¹H NMR (400 MHz, CDCl₃) of product 10



Figure S23. 13 C NMR (100 MHz, CDCl₃) of product 10



Figure S24. ²⁹Si NMR (79 MHz, CDCl₃) of product 10

Analytical data of product 10:

Isolated yield: 93% (279.1 mg); ¹H NMR (CDCl₃, δ , ppm): 2.39 (s, 3H, *CH*₃), 5.30 (d, 1H, *J*_{HH} = 3.2 Hz, Si*H*), 6.70 (dd, 1H, *J*_{HH} = 19.0, 3.2 Hz, =CHSi), 7.11 (d, 2H, *J*_{HH} = 19.1 Hz, =C*H*), 7.39 – 7.48 (m, 10H, -C₆*H*₄- and Ph), 7.66 – 7.69 (m, 4H, Ph); ¹³C NMR (CDCl₃, δ , ppm): 21.34 (*C*H₃), 120.11, 126.73, 128.10, 129.33, 129.78, 133.82, 135.25, 135.59, 138.66, 149.11; ²⁹Si NMR (CDCl₃, δ , ppm): -20.96; MS: *m/z* (rel. intensity): 53 (12), 78 (10), 105 (22), 106 (10), 180 (14), 181 (40), 182 (18), 195 (11), 196 (12), 207 (12), 208 (24), 221 (26), 222 (81), 223 (48), 224 (16), 299 (29), 300 (100, M⁺).



Figure S25. ¹H NMR (300 MHz, CDCl₃) of product 11



Figure S26. 13 C NMR (100 MHz, CDCl₃) of product 11



Figure S27. ²⁹Si NMR (79 MHz, CDCl₃) of product 11

Analytical data of product 11:

Isolated yield: 89% (325 mg); ¹H NMR (CDCl₃, δ , ppm): 5.28 (d, 1H, *J*_{HH} = 3.2 Hz, Si*H*), 6.77 (dd, 1H, *J*_{HH} = 19.0, 3.2 Hz, =CHSi), 7.14 (d, 1H, *J*_{HH} = 19.0 Hz, =CH), 7.37 - 7.48 (m, 10H, Ar), 7.53 - 7.68 (m, 9H, Ar); ¹³C NMR (CDCl₃, δ , ppm): 121.64, 127.01, 127.20, 127.28, 127.47, 128.10, 128.82, 129.81, 133.60, 135.56, 135.82, 136.85, 140.58, 141.36, 148.60; ²⁹Si NMR (CDCl₃, δ , ppm): -21.15; MS: *m/z* (rel. intensity): 105 (15), 181 (32), 206 (20), 208 (17), 284 (95), 286 (46), 362 (100, M⁺); anal. calcd. for C₂₆H₂₂Si (%): C: 86.14, H: 6.12; found: C: 86.22, H: 6.20.



Figure S28. ¹H NMR (300 MHz, CDCl₃) of product 12



Figure S29. 13 C NMR (100 MHz, CDCl₃) of product 12



Figure S30. ²⁹Si NMR (79 MHz, CDCl₃) of product 12

Analytical data of product 12:

Isolated yield: 87% (261.1 mg); ¹H NMR (CDCl₃, δ , ppm): 0.53 (d, 3H, J_{HH} = 3.8 Hz, CH₃), 4.71-4.78 (m, 1H, SiH), 6.60 (dd, 1H, J_{HH} = 19.0, 3.0 Hz, =CHSi), 7.09 (d, 1H, J_{HH} = 19.0 Hz, =CH), 7.31 – 7.46 (m, 6H, Ar), 7.50 – 7.63 (m, 8H, Ar); ¹³C NMR (CDCl₃, δ , ppm): -5.16, 123.88, 126.99, 127.05, 127.26, 127.41, 127.99, 128.80, 129.49, 134.65, 135.57, 136.96, 140.62, 141.13, 146.63; ²⁹Si NMR (CDCl₃, δ , ppm): -20.63; MS: *m/z* (rel. intensity): 105 (14), 121 (20), 146 (12), 178 (15), 222 (22), 223 (10), 285 (92), 286 (25), 299 (13), 300 (100, M⁺); anal. calcd. for C₂₁H₂₀Si (%): C: 83.94, H: 6.71; found: C: 83.99, H: 6.80.





Figure S32. ¹³C NMR (100 MHz, CDCl₃) of product 13



Figure S33. ²⁹Si NMR (79 MHz, CDCl₃) of product 13

Analytical data of product 13:

Isolated yield: 89% (244 mg); ¹H NMR (CDCl₃, δ , ppm): 0.68 (d, 3H, J_{HH} = 3.8 Hz, CH_3), 4.92 – 4.95 (m, 1H, Si*H*), 6.75 (dd, 1H, J_{HH} = 18.8, 3.0 Hz, =CHSi), 7.42 – 7.60 (m, 7H, =CH and Ar), 7.74 – 8.01 (m, 6H, Ar), 8.23 (d, 1H, J_{HH} = 7.7 Hz, Ar); ¹³C NMR (CDCl₃, δ , ppm): -5.06, 123.43, 123.81, 125.54, 125.72, 126.13, 127.84, 127.93, 128.00, 128.52, 129.49, 130.86, 133.59, 134.33, 134.64, 134.79, 135.51, 136.03, 144.40; ²⁹Si NMR (CDCl₃, δ , ppm): -20.77; MS: m/z (rel. intensity): 105 (15), 152 (14), 181 (26), 195 (27), 196 (24), 197 (11), 259 (87), 260 (29), 273 (28), 274 (100, M⁺); anal. calcd. for C₁₉H₁₈Si (%): C: 83.15, H: 6.01; found: C: 83.29, H: 6.22.



Figure S34. ¹H NMR (300 MHz, CDCl₃) of product 14



Figure S35. ¹³C NMR (100 MHz, CDCl₃) of product 14



Figure S36. ²⁹Si NMR (79 MHz, CDCl₃) of product 14

Analytical data of product 14:

Isolated yield: 87% (282 mg);¹H NMR (CDCl₃, δ , ppm): 0.68 (d, 3H, J_{HH} = 3.8 Hz, CH_3), 4.88 – 4.97 (m, 1H, SiH),6.79 (dd, 1H, J_{HH} = 18.7, 3.0 Hz, =CHSi), 7.42 – 7.55 (m, 3H, Ar), 7.59 – 7.79 (m, 6H, Ar), 7.86 – 7.98 (m, 3H, =CH and Ar), 8.18 – 8.24 (m, 1H, Ar), 8.67 – 8.77 (m, 2H, Ar); ¹³C NMR (CDCl₃, δ , ppm): -5.05 (*C*H₃), 122.48, 123.06, 124.32, 124.88, 126.44, 126.64 (d, *J* = 3.7 Hz), 126.72, 128.04, 128.43, 128.80, 129.53, 130.22, 130.33, 130.37, 131.67, 134.67, 135.23, 135.51, 145.11; ²⁹Si NMR (CDCl₃, δ , ppm): -20.91; MS: *m/z* (rel. intensity): 105 (10), 231 (14), 246 (10), 309 (98), 310 (37), 324 (100, M⁺); anal. calcd. for C₂₃H₂₀Si (%): C: 85.13, H: 6.21; found: C: 85.30, H: 6.42.



Figure S37. ¹H NMR (400 MHz, CDCl₃) of product 15



Figure S38. 13 C NMR (100 MHz, CDCl₃) of product 15



Figure S39. ²⁹Si NMR (79 MHz, CDCl₃) of product 15

Analytical data of product 15:

Isolated yield: 89% (343.7 mg); ¹H NMR (CDCl₃, δ , ppm): 5.41 (d, 1H, *JHH* = 3.2 Hz, Si*H*), 6.93 (dd, 1H, *J_{HH}* = 18.7, 3.2 Hz, =C*H*Si), 7.45 – 7.50 (m, 6H, =C*H* and Ar), 7.58 – 7.72 (m, 5H, Ar), 7.74 – 7.76 (m, 4H, Ar), 7.89 – 7.94 (m, 2H, Ar), 7.98 – 8.0 (m, 1H, Ar), 8.10 – 8.14 (m, 1H, Ar); ¹³C NMR (CDCl₃, δ , ppm): 122.57, 123.14, 124.39, 125.10, 126.26,126.56, 126.76, 126.85, 128.10, 128.22, 128.94, 129.93, 130.23, 130.38, 130.51, 131.69, 133.65, 134.79, 135.17, 135.22, 135.64, 147.25; ²⁹Si NMR (CDCl₃, δ , ppm): -21.46; MS: *m/z* (rel. intensity): 105 (14), 179 (18), 184 (13), 202 (21), 203 (13), 307 (28), 308 (57), 309 (31), 310 (11), 386 (100, M⁺); anal. calcd. for C₂₈H₂₂Si (%): C: 87.00, H: 5.74; found: C: 87.12, H: 5.82.





Figure S41. 13 C NMR (100 MHz, CDCl₃) of product 16



Figure S42. ²⁹Si NMR (79 MHz, CDCl₃) of product 16

Analytical data of product 16:

Isolated yield: 94% (191.9 mg); ¹H NMR (CDCl₃, δ , ppm): 0.52 (d, 3H, *J*_{HH} = 3.8 Hz, *CH*₃), 1.03 (d, 3H, *J*_{HH} = 7.2 Hz, -(CH₂)₃CH₃), 1.42 – 1.55 (m, 4H, -(CH₂)₂CH₃), 2.24 – 2.34 (m, 2H, =CHCH₂), 4.64 – 4.75 (m, 1H, Si*H*), 5.84 – 5.93 (m, 1H, =CHSi), 6.37 (dt, 1H, *J*_{HH} = 18.5, 6.3 Hz, =CHCH₂), 7.42 – 7.48 (m, 3H, Ph), 7.64 – 7.71 (m, 2H, Ph); ¹³C NMR (CDCl₃, δ , ppm): -5.11 (*C*H₃), 13.95, 22.26, 30.72, 36.55, 124.04, 127.83, 129.18, 134.50, 136.33, 151.66; ²⁹Si NMR (CDCl₃, δ , ppm): -22.21; MS: *m/z* (rel. intensity): 105 (17), 121 (30), 202 (10), 204 (100, M⁺); anal. calcd. for C₁₃H₂₀Si (%): C: 76.40, H: 9.86; found: C: 76.51, H: 9.90.



Figure S43. ¹H NMR (400 MHz, CDCl₃) of product 17



Figure S44. ¹³C NMR (100 MHz, CDCl₃) of product 17



Figure S45. ²⁹Si NMR (79 MHz, CDCl₃) of product 17

Analytical data of product 17:

Isolated yield: 92% (244.8 mg); ¹H NMR (CDCl₃, δ , ppm): 0.99 (t, 3H, J_{HH} = 7.2 Hz, -(CH₂)₃CH₃), 1.40 – 1.53 (m, 4H, -(CH₂)₂CH₃), 2.27 – 2.32 (m, 2H, =CHCH₂), 5.18 (d, 1H, J_{HH} = 3.0 Hz, Si*H*), 5.98 – 6.07 (m, 1H, =CHSi), 6.39 (dt, 1H, J_{HH} = 18.5, 6.2 Hz, =CHCH₂), 7.42 – 7.47 (m, 6h, Ph), 7.64 – 7.70 (m, 4H, Ph); ¹³C NMR (CDCl₃, δ , ppm): 13.92, 22.25, 30.62, 36.64, 121.94, 127.92, 129.49, 134.29, 135.41, 153.89; ²⁹Si NMR (CDCl₃, δ , ppm): -22.20; MS: *m/z* (rel. intensity): 53 (18), 105 (42), 106 (16), 145 (16), 146 (17), 181 (33), 183 (48), 184 (19), 188 (19), 189 (26), 259 (17), 265 (100), 266 (28, M⁺).



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

Figure S47. ¹³C NMR (100 MHz, CDCl₃) of product 18



Figure S48. ²⁹Si NMR (79 MHz, CDCl₃) of product 18

Analytical data of product 18:

Isolated yield: 91% (203.9 mg); ¹H NMR (CDCl₃, δ , ppm): 0.54 (d, 3H, *J*_{HH} = 3.8 Hz, *CH*₃), 4.75 (d, 1H, *J*_{HH} = 3.6 Hz, Si*H*), 6.58 (dd, 1H, *J*_{HH} = 19.1, 3.0 Hz, =CHSi), 7.07 (d, 1H, *J*_{HH} = 19.1 Hz, =CH), 7.28 – 7.42 (m, 6H, Ph), 7.45 – 7.50 (m, 2H, Ph), 7.60 – 7.64 (m, 2H, Ph); ¹³C NMR (CDCl₃, δ , ppm): -5.16 (*C*H₃), 123.75, 126.62, 127.99, 128.42, 128.58, 129.49, 134.65, 135.60, 137.97, 147.07; ²⁹Si NMR (CDCl₃, δ , ppm): -20.64; MS: *m/z* (rel. intensity): 105 (55), 106 (16), 120 (30), 121 (14), 131 (25), 145 (33), 146 (63), 147 (19), 209 (68), 210 (17), 223 (100), 224 (75, M⁺); anal. calcd. for C₁₅H₁₆Si (%): C: 80.30, H: 7.19; found: C: 80.45, H: 7.31.



Figure S49. 1 H NMR (300 MHz, CDCl₃) of product 19



Figure S50. 13 C NMR (75 MHz, CDCl₃) of product 19



Figure S51. ²⁹Si NMR (79 MHz, CDCl₃) of product 19

Analytical data of product 19:

Isolated yield: 90% (257.5 mg); ¹H NMR (CDCl₃, δ , ppm): 5.16 (d, 1H, *J*_{HH} = 3.1 Hz, Si*H*), 6.61 (dd, 1H, *J*_{HH} = 19.0, 3.2 Hz, =CHSi), 6.99 (d, 1H, *J*_{HH} = 19.0 Hz, =CH), 7.12 – 7.27 (m, 7H, Ph), 7.31 – 7.37 (m, 3H, Ph), 7.45 – 7.55 (m, 5H, Ph); ¹³C NMR (CDCl₃, δ , ppm): 121.62, 126.85, 128.19, 128.69, 129.90, 133.70, 135.65, 137.93, 149.25; ²⁹Si NMR(CDCl₃, δ , ppm): -22.10; MS: *m/z* (rel. intensity): 53 (10), 105 (27), 106 (12), 130 (19), 131 (19), 132 (12), 181 (14), 205 (12), 207 (19), 208 (29), 209 (32), 210 (34), 285 (78), 286 (100, M⁺).



Figure S52. 1 H NMR (300 MHz, CDCl₃) of product 20



Figure S53. ¹³C NMR (75 MHz, CDCl₃) of product 20


Figure S54. ²⁹Si NMR (79 MHz, CDCl₃) of product 20

Analytical data of product 20:

Isolated yield: 90% (171.1 mg); ¹H NMR (CDCl₃, δ , ppm): 0.71-0.83 (m, 4H, CH₃CH₂-), 1.03-1.12 (m, 6H, CH₃CH₂-), 4.01 – 4.07 (m, 1H, Si*H*), 6.46 (dd, 1H, *J*_{HH} = 19.3, 3.4 Hz, =CHSi), 7.05 (d, 1H, *J*_{HH} = 19.2 Hz, =CH), 7.26 – 7.40 (m, 3H, Ph), 7.46 – 7.50 (m, 2H, Ph); ¹³C NMR (CDCl₃, δ , ppm): 3.32 (*C*H₃), 8.09 (*C*H₂), 123.63, 126.41, 128.51, 138.22, 146.38; ²⁹Si NMR (CDCl₃, δ , ppm): -8.34; MS: *m/z* (rel. intensity): 58 (11), 105 (23), 131 (81), 132 (14), 133 (76), 134 (11), 149 (11), 159 (34), 161 (100), 162 (19), 190 (27, M⁺); anal. calcd. for C₁₂H₁₈Si (%): C: 75.71, H: 9.53; found: C: 75.80, H: 9.55.

1.2. NMR spectra and analytical data of symmetrical *E,E*-divinylsilanes



Figure S56. ¹³C NMR (100 MHz, CDCl₃) of product **21**



Figure S57. ²⁹Si NMR (79 MHz, CDCl₃) of product **21**

Analytical data of product 21:

Isolated yield: 92% (318 mg): ¹H NMR (CDCl₃, δ , ppm): 0.43 (s, 3H, *CH*₃), 0.95 (t, 6H, $J_{HH} = 6.8$ Hz, -(CH₂)₄CH₃), 1.29 – 1.38 (m, 8H, -(CH₂)₄CH₃), 1.44 – 1.51 (m, 4H, -(CH₂)₄CH₃), 2.18 – 2.24 (m, 4H, =CHCH₂), 5.83 (d, 2H, $J_{HH} = 18.5$ Hz, =CHSi), 6.19 (dt, 2H, $J_{HH} = 18.5$, 6.2 Hz, =CHCH₂), 7.37–7.40 (m, 3H, Ph), 7.55 – 7.60 (m, 2H, Ph); ¹³C NMR (CDCl₃, δ , ppm): -3.64 (CH₃), 14.12, 22.60, 28.37, 31.51, 36.91, 125.92, 127.68, 128.84, 134.46, 138.36, 150.57; ²⁹Si NMR (CDCl₃, δ , ppm): -19.46; MS: *m/z* (rel. intensity): 95 (20), 105 (21), 107 (15), 121 (66), 122 (19), 145 (43), 146 (20), 174 (17), 159 (25), 160 (17), 173 (27), 174 (22), 216 (19), 217 (42), 218 (15), 237 (99), 238 (27), 243 (82), 245 (31), 299 (100), 300 (25), 314 (2, M⁺); anal. calcd. for C₂₁H₃₄Si (%): C: 80.18, H: 10.89; found: C: 80.32, H: 10.99.



Figure S58. ¹H NMR (400 MHz, CDCl₃) of product 22



Figure S59. ¹³C NMR (100 MHz, CDCl₃) of product 22



Figure S60. ²⁹Si NMR (79 MHz, CDCl₃) of product 22

Analytical data of product 22:

Isolated yield: 90% (372.5 mg); ¹H NMR (CDCl₃, δ , ppm): 0.91 (t, 6H, $J_{HH} = 6.8$ Hz, $-(CH_2)_4CH_3$), 1.29 – 1.36 (m, 8H, $-(CH_2)_4CH_3$), 1.40 – 1.48 (m, 4H, $-(CH_2)_4CH_3$), 2.19 – 2.25 (m, 4H, =CHCH₂), 5.98 (d, 2H, $J_{HH} = 19.3$ Hz, =CHSi), 6.18 (dt, 2H, $J_{HH} = 18.5$, 6.2 Hz, =CHCH₂), 7.35 – 7.40 (m, 6H, Ph), 7.53 – 7.57 (m, 4H, Ph); ¹³C NMR (CDCl₃, δ , ppm): 14.10, 22.54, 28.27, 31.47, 36.97, 123.85, 127.68, 129.11, 135.34, 135.51, 136.10, 152.68; ²⁹Si NMR (CDCl₃, δ , ppm): -22.19; MS: m/z (rel. intensity): 105 (11), 183 (17), 279 (17), 280 (100), 281 (34), 299 (65), 300 (19), 305 (63), 306 (22), 376 (2, M⁺); anal. calcd. for C₂₆H₃₆Si (%): C: 82.91, H: 9.63; found: C: 82.80, H: 9.55.



Figure S62. ¹³C NMR (100 MHz, CDCl₃) of product 23



Figure S63. ²⁹Si NMR (79 MHz, CDCl₃) of product 23

Analytical data of product 23:

Isolated yield: 92% (283.6 mg); ¹H NMR (CDCl₃, δ , ppm): 0.53 – 0.68 (m, 4H, CH₃CH₂-), 0.86 – 1.00 (m, 12H, -(CH₂)₄CH₃), 1.25 – 1.45 (m, 12H, -(CH₂)₄CH₃), 2.07 – 2.20 (m, 4H, =CHCH₂), 5.58 (d, 2H, J_{HH} = 18.6 Hz, =CHSi), 6.08 (dt, 2H, J_{HH} = 18.6, 6.3 Hz, =CHCH₂); ¹³C NMR (CDCl₃, δ , ppm): 4.52 (CH₃), 7.38 (CH₂), 14.05, 22.56, 28.50, 31.43, 37.01, 125.32, 149.43; ²⁹Si NMR (CDCl₃, δ , ppm): -11.55; MS: *m/z* (rel. intensity): 59 (28), 83 915), 85 (18), 87 (18), 95 (27), 97 (36), 99 (32), 111 (30), 113 (25), 125 (38), 127 (17), 153 (25), 183 (17), 223 (40), 251 (100), 252 (21), 280 (2, M⁺); anal. calcd. for C₁₈H₃₆Si (%): C: 77.06, H: 12.96; found: C: 77.12, H: 12.99.





Figure S65. ¹³C NMR (100 MHz, CDCl₃) of product 24



Figure S66. ²⁹Si NMR (79 MHz, CDCl₃) of product 24

Analytical data of product 24:

Isolated yield: 94% (399.4 mg); ¹H NMR (CDCl₃, δ , ppm): 0.33 (s, 12H, *CH*₃), 0.91 (t, 6H, $J_{HH} = 6.7$ Hz, -(CH₂)₄CH₃), 1.28 – 1.46 (m, 12H, -(CH₂)₄CH₃), 2.12 – 2.20 (m, 4H, =CHCH₂), 5.77 (d, 2H, $J_{HH} = 18.6$ Hz, =CHSi), 6.16 (dt, 2H, $J_{HH} = 18.6$, 6.2 Hz, =CHCH₂), 7.50 – 7.54 (m, 4H, Ph); ¹³C NMR (CDCl₃, δ , ppm): -2.46 (CH₃), 14.09, 22.57, 28.36, 31.49, 36.83, 127.05, 133.09, 139.85, 149.35; ²⁹Si NMR (CDCl₃, δ , ppm): -12.20; MS: m/z (rel. intensity): 59 (41), 73 (28), 95 (17), 99 (16), 131 (19), 155 (25), 159 (16), 179 (21), 193 (17), 215 (17), 217 (16), 231 (63), 232 (23), 275 (15), 290 (60), 291 (20), 314 (17), 327 (20), 329 (27), 371 (100), 372 (38), 373 (15), 386 (2, M⁺); anal. calcd. for C₂₄H₄₂Si₂ (%): C: 74.53, H: 10.95; found: C: 74.60, H: 10.99.





Figure S68. ¹³C NMR (100 MHz, CDCl₃) of product 25



Figure S69. ²⁹Si NMR (79 MHz, CDCl₃) of product 25

Analytical data of product 25:

Isolated yield: 90% (422 mg); ¹H NMR (CDCl₃, δ , ppm): 0.42 (s, 12H, CH₃), 2.33 (s, 6H, CH₃), 6.56 (d, 2H, J_{HH} = 19.1 Hz, =CHSi), 7.01 (d, 2H, J_{HH} = 19.1 Hz, =CH), 7.05 (2H, J_{HH} = 6.9 Hz, -C₆H₄-), 7.17 – 7.23 (m, 3H, -C₆H₄-), 7.50 – 7.61 (m, 7H, -C₆H₄-); ¹³C NMR (CDCl₃, δ , ppm): -2.42 (SiCH₃), 21.46 (CH₃), 123.80, 126.79, 128.50, 129.03, 132.37 (d, *J* = 6.7 Hz), 133.32 (d, *J* = 7.9 Hz), 138.16 (d, *J* = 8.8 Hz), 139.57, 139.83, 140.64, 140.90, 145.53; ²⁹Si NMR (CDCl₃, δ , ppm): -10.42; MS: *m/z* (rel. intensity): 59 (19), 115 (10), 149 (11), 157 (16), 158 (25), 159 (65), 160 (24), 161 (12), 173 (20), 175 (36), 176 (16), 217 (11), 230 (13), 231 (21), 232 (100), 234 (51), 235 (20), 236 (12), 237 (12), 251 (34), 252 (22), 310 (15), 319 (12), 334 (30), 335 (13), 353 (15), 411 (83), 412 (34), 413 (14), 426 (6, M⁺); anal. calcd. for C₂₈H₃₄Si₂ (%): C: 78.81, H: 8.03; found: C: 78.95, H: 8.14.



Figure S71. ¹³C NMR (100 MHz, CDCl₃) of product 26



Figure S72. ²⁹Si NMR (79 MHz, CDCl₃) of product 26

Analytical data of product 26:

Isolated yield: 90% (412 mg); ¹H NMR (CDCl₃, δ , ppm): 2.38 (s, 6H, CH₃), 6.81 (d, 2H, J_{HH} = 19.1 Hz, =CHSi), 7.04 (d, 2H, J_{HH} = 19.1 Hz, =CH), 7.18 (d, 4H, J_{HH} = 7.9 Hz, -C₆H₄-), 7.39 – 7.48 (m, 10H, Ph), 7.63 – 7.71 (m, 4H, Ph); ¹³C NMR (CDCl₃, δ , ppm): 21.32 (CH₃), 121.86, 126.73, 127.95, 129.31, 129.54, 135.15, 135.47, 135.74, 138.50, 148.54; ²⁹Si NMR (CDCl₃, δ , ppm): -19.37; MS: m/z (rel. intensity): 105 (18), 144 (17), 181 (16), 219 (16), 220 (20), 221 (39), 222 (24), 234 (20), 235 (23), 299 (22), 312 (100), 313 (46), 314 (15), 324 (42), 325 (69), 326 (18), 338 (47), 339 (85), 340 928), 416 (18, M⁺); anal. calcd. for C₃₀H₂₈Si (%): C: 86.48, H: 6.77; found: C: 86.37, H: 6.66.



Figure S74. ¹³C NMR (100 MHz, CDCl₃) of product 27



Figure S75. ²⁹Si NMR (79 MHz, CDCl₃) of product 27

Analytical data of product 27:

Isolated yield: 89% (378 mg); ¹H NMR (CDCl₃, δ , ppm): 0.65 (s, 3H, *CH*₃), 3.87 (s, 6H, OC*H*₃), 6.57 (d, 2H, *J*_{HH} = 19.1 Hz, =CHSi), 6.94 (d, 4H, *J*_{HH} = 8.8 Hz, -C₆H₄-), 7.03 (d, 2H, *J*_{HH} = 19.1 Hz, =CH), 7.43 – 7.50 (m, 7H, -C₆H₄- and Ph), 7.69 – 7.73 (m, 2H, Ph); ¹³C NMR (CDCl₃, δ , ppm): -3.56 (*C*H₃), 55.35 (OCH₃), 113.97, 122.47, 127.92 (d, *J* = 3.8 Hz), 129.23, 131.22, 134.67, 137.44, 146.11, 159.85; ²⁹Si NMR (CDCl₃, δ , ppm): -16.42; MS: *m/z* (rel. intensity): 105 (13), 121 (29), 175 (16), 176 (14), 238 (21), 254 912), 264 (24), 265 (100), 266 (38), 267 (20), 278 (25), 296 (20), 310 (15), 371 (85), 372 (25), 386 (22, M⁺).





Figure S77. ¹³C NMR (100 MHz, CDCl₃) of product 28



Figure S78. ²⁹Si NMR (79 MHz, CDCl₃) of product 28

Analytical data of product 28:

Isolated yield: 91% (500.8 mg); ¹H NMR (CDCl₃, δ , ppm): 1.34 (s, 18H, C(*CH*₃)₃), 6.82 (d, 2H, J_{HH} = 19.1 Hz, =C*H*Si), 7.04 (d, 2H, J_{HH} = 19.1 Hz, =C*H*), 7.37 – 7.47 (m, 14H, -C₆H₄- and Ph), 7.62 – 7.69 (m, 4H, Ph); ¹³C NMR (CDCl₃, δ , ppm): 31.31 (C(*C*H₃)₃), 34.70 (*C*(CH₃)₃), 122.12, 125.52, 126.51, 127.91, 129.50, 135.15, 135.41, 135.71, 148.40, 151.74; ²⁹Si NMR (CDCl₃, δ , ppm): -19.38; MS: *m/z* (rel. intensity): 57 (39), 105 (10), 181 (12), 221 (17), 248 (12), 250 (26), 251 (10), 264 (174), 277 (14), 278 (32), 279 (15), 354 (100), 355 (47), 356 (11), 357 (17), 410 (59), 411 (22), 422 (18), 423 (34), 424 (13), 500 (15, M⁺); anal. calcd. for C₃₆H₄₀Si (%): C: 86.34, H: 8.05; found: C: 86.39, H: 8.12.



Figure S79. ¹H NMR (400 MHz, CDCl₃) of product 29



Figure S80. ¹³C NMR (100 MHz, CDCl₃) of product 29



Figure S81. ²⁹Si NMR (79 MHz, CDCl₃) of product 29

Analytical data of product 29:

Isolated yield: 92% (444 mg); ¹H NMR (CDCl₃, δ , ppm): 0.62 (s, 3H, CH₃), 1.36 (s, 18H, C(CH₃)₃), 6.66 (d, 2H, J_{HH} = 19.1 Hz, =CHSi), 7.04 (d, 2H, J_{HH} = 19.1 Hz, =CH), 7.37 – 7.48 (m, 11H, -C₆H₄- and Ph), 7.64 – 7.69 (m, 2H, Ph); ¹³C NMR (CDCl₃, δ , ppm): -3.64 (CH₃), 31.28 (C(CH₃)₃), 34.63 (*C*(CH₃)₃), 124.17, 125.45, 126.33, 127.83, 129.17, 134.62, 135.49, 137.22, 146.50, 151.49; ²⁹Si NMR (CDCl₃, δ , ppm): -16.32; MS: *m/z* (rel. intensity): 57 (36), 263 (11), 290 (10), 292 (100), 293 (43), 304 (12), 348 (23), 361 (24), 423 (21), 438 (12, M⁺).



Figure S82. ¹H NMR (400 MHz, CDCl₃) of product 30





Figure S83. ¹³C NMR (100 MHz, CDCl₃) of product 30



Figure S84. ²⁹Si NMR (79 MHz, CDCl₃) of product 30

Analytical data of product 30:

Isolated yield: 89% (528.9 mg); ¹H NMR (CDCl₃, δ , ppm): 6.92 (d, 2H, *J*_{HH} = 19.1 Hz, =CHSi), 7.11 (d, 2H, *J*_{HH} = 19.1 Hz, =CH), 7.34 – 7.49 (m, 12H, Ar), 7.60 – 7.71 (m, 16H, Ar); ¹³C NMR (CDCl₃, δ , ppm): 123.22, 126.99, 127.20, 127.26, 127.42, 127.98, 128.79, 129.62, 134.78, 135.69, 137.03, 140.61, 141.26, 148.16; ²⁹Si NMR (CDCl₃, δ , ppm): -19.36; MS: *m/z* (rel. intensity): 49 (21), 73 (45), 91 (49), 105 (20), 207 (60), 208 (23), 209 (29), 281 (37), 282 (20), 283 (32), 284 (36), 297 (34), 355 (35), 373 (100), 374 (100), 386 (30), 429 (30), 464 (24), 540 (14, M⁺); anal. calcd. for C₄₀H₃₂Si (%): C: 88.84, H: 5.96; found: C: 89.02, H: 6.12.





Figure S85. ¹H NMR (400 MHz, CDCl₃) of product **31**



Figure S86. ¹³C NMR (100 MHz, CDCl₃) of product **31**



Figure S87. ²⁹Si NMR (79 MHz, CDCl₃) of product **31**

Analytical data of product 31:

Isolated yield: 87% (457.6 mg); ¹H NMR (CDCl₃, δ , ppm): 0.64 (s, 3H, CH₃), 6.73 (d, 2H, J_{HH} = 19.1 Hz, =CHSi), 7.08 (d, 2H, J_{HH} = 19.1 Hz, =CH), 7.33 – 7.37 (m, 2H, Ar), 7.40 – 7.47 (m, 7H, Ar), 7.55 – 7.63 (m, 12H, Ar), 7.65 – 7.68 (m, 2H, Ar); ¹³C NMR (CDCl₃, δ , ppm): -3.83 (CH₃), 125.24, 126.94, 127.03, 127.21, 127.34, 127.90, 128.74, 129.30, 134.60, 137.11, 140.62, 141.05, 146.26; ²⁹Si NMR (CDCl₃, δ , ppm): -16.29; MS: m/z (rel. intensity): 105 (12), 208 (12), 221 (12), 222 (15), 284 (20), 312 (100), 312 (42), 314 (12), 324 (16), 360 (10), 387 (21), 388 (11), 400 (11), 402 (12), 478 (18, M⁺); anal. calcd. for C₃₅H₃₀Si (%): C: 87.82, H: 6.32; found: C: 87.75, H: 6.26.





Figure S88. ¹H NMR (400 MHz, CDCl₃) of product 32



Figure S89. ¹³C NMR (100 MHz, CDCl₃) of product 32



Figure S90. ²⁹Si NMR (79 MHz, CDCl₃) of product 32

Analytical data of product 32:

Isolated yield: 88% (430 mg); ¹H NMR (CDCl₃, δ , ppm): 0.86 (q, 4H, *J*_{HH} = 7.8 Hz, CH₃CH₂-), 1.09 (t, 6H, *J*_{HH} = 7.9 Hz, CH₃CH₂-), 6.58 (d, 2H, *J*_{HH} = 19.2 Hz, =CHSi), 7.05 (d, 2H, *J*_{HH} = 19.2 Hz, =CH), 7.33 – 7.37 (m, 2H, Ar), 7.43 – 7.47 (m, 4H, Ar), 7.55 – 7.64 (m, 12H, Ar); ¹³C NMR (CDCl₃, δ , ppm): 4.45 (CH₃), 7.46 (CH₂), 125.11, 126.88, 126.96, 127.22, 127.32, 128.76, 137.38, 140.71, 140.85, 145.42; ²⁹Si NMR (CDCl₃, δ , ppm): -8.14; MS: *m/z* (rel. intensity): 165 (16), 178 (18), 179 (12), 180 (28), 181 (36), 182 (11), 197 (15), 205 (18), 207 (12), 208 (21), 225 (25), 226 (14), 234 (19), 235 (100), 236 (32), 276 (16), 277 (57), 278 (27), 415 (85), 416 (24), 444 (2, M⁺); anal. calcd. for C₃₂H₃₂Si (%): C: 86.43, H: 7.25; found: C: 86.35, H: 7.18.



Figure S92. ¹³C NMR (100 MHz, CDCl₃) of product 33



Figure S93. ²⁹Si NMR (79 MHz, CDCl₃) of product 33

Analytical data of product 33:

Isolated yield: 91% (286.5 mg); ¹H NMR (CDCl₃, δ , ppm): 0.38 (s, 3H, *CH*₃), 0.92 (t, 6H, $J_{HH} = 7.2$ Hz, $-(CH_2)_3CH_3$), 1.32 – 1.46 (m, 8H, $-(CH_2)_2CH_3$), 2.11 – 2.24 (m, 4H, $=CHCH_2$), 5.79 (dt, 2H, $J_{HH} = 18.5$, 1.5 Hz, =CHSi), 6.15 (dt, 2H, $J_{HH} = 18.5$, 6.1 Hz, $=CHCH_2$), 7.34 – 7.39 (m, 3H, Ph), 7.52 – 7.57 (m, 2H, Ph); ¹³C NMR (CDCl₃, δ , ppm): -3.65 (*C*H₃), 13.98, 22.32, 30.86, 36.45, 125.91, 127.67, 128.83, 134.44, 138.34, 150.51; ²⁹Si NMR (CDCl₃, δ , ppm): -19.50; MS: m/z (rel. intensity): 59 (13), 105 (20), 109 (13), 119 (20), 121 (78), 122 (25), 123 (16), 135 (13), 145 (30), 146 (16), 147 (13), 159 (27), 160 (16), 161 (14), 173 (36), 174 (27), 187 (22), 189 (27), 201 (21), 202 (36), 203 (83), 204 (18), 209 (100), 210 (21), 229 (47), 230 (13), 271 (79), 272 (19), 286 (6, M⁺); anal. calcd. for C₁₉H₃₀Si (%): C: 79.64, H: 10.55; found: C: 79.81, H: 10.72.



Figure S95. ¹³C NMR (100 MHz, CDCl₃) of product 34



Figure S96. ²⁹Si NMR (79 MHz, CDCl₃) of product 34

Analytical data of product 34:

Isolated yield: 90% (344.7 mg); ¹H NMR (CDCl₃, δ , ppm): 1.02 – 1.07 (m, 6H, -(CH₂)₃CH₃), 1.43 – 1.57 (m, 8H, -(CH₂)₂CH₃), 2.32 – 2.40 (m, 4H, =CHCH₂), 6.03-6.20 (m, 2H, =CHSi), 6.21 – 6.40 (m, 2H, =CHCH₂), 7.46– 7.50 (m, 6H, Ph), 7.66 – 7.70 (m, 4H, Ph); ¹³C NMR (CDCl₃, δ , ppm): 14.09, 22.41, 30.89, 36.81, 124.02, 127.79, 129.21, 135.30, 135.60, 135.91, 136.16, 152.87; ²⁹Si NMR (CDCl₃, δ , ppm): -21.92; MS: *m/z* (rel. intensity): 105 (12), 183 (20), 266 (18), 271 (57), 272 (19), 291 (100), 292 (32), 348 (2, M⁺); anal. calcd. for C₂₄H₃₂Si (%): C: 82.69, H: 9.25; found: C: 82.81, H: 9.39.



Figure S98. ¹³C NMR (100 MHz, CDCl₃) of product 35



Figure S99. ²⁹Si NMR (79 MHz, CDCl₃) of product 35

Analytical data of product 35:

Isolated yield: 89% (245 mg); ¹H NMR (CDCl₃, δ , ppm): 0.59 (q, 4H, *J*_{HH} = 7.8 Hz, CH₃CH₂-), 0.90 (t, 6H, *J*_{HH} = 5.9 Hz, -(CH₂)₃CH₃), 0.94 (t, 6H, *J*_{HH} = 6.6 Hz, CH₃CH₂-), 1.28 - 1.42 (m, 8H, -(CH₂)₃CH₃), 2.10 - 2.18 (m, 4H, -(CH₂)₃CH₃), 5.57 (dt, 2H, *J*_{HH} = 18.6, 1.5 Hz, =CHSi), 6.07 (dt, 2H, *J*_{HH} = 18.6, 6.3 Hz, =CHCH₂); ¹³C NMR (CDCl₃, δ , ppm): 4.52 (*C*H₃), 7.37 (*C*H₂), 13.94, 22.21, 30.99, 36.69, 125.42, 149.37; ²⁹Si NMR (CDCl₃, δ , ppm): -11.58; MS: *m/z* (rel. intensity): 59 (11), 85 (14), 111 (15), 139 (11), 195 (32), 223 (100), 224 (19), 252 (1, M⁺); anal. calcd. for C₁₆H₃₂Si (%): C: 76.10, H: 12.77; found: C: 76.22, H: 12.82.



Figure S100. ¹H NMR (400 MHz, CDCl₃) of product 36



Figure S101. ^{13}C NMR (100 MHz, CDCl_3) of product 36



Figure S102. ²⁹Si NMR (79 MHz, CDCl₃) of product 36

Analytical data of product 36:

Isolated yield: 90% (322.9 mg); ¹H NMR (CDCl₃, δ , ppm): 0.86 (s, 3H, CH₃), 6.93 (d, 2H, J_{HH} = 19.1 Hz, =CHSi), 7.29 (d, 2H, J_{HH} = 19.1 Hz, =CH), 7.44 – 7.49 (m, 2H, Ph), 7.52 – 7.57 (m, 4H, Ph), 7.59 – 7.64 (m, 3H, Ph), 7.67 – 7.74 (m, 4H, Ph), 7.87 – 7.92 (m, 2H, Ph); ¹³C NMR (CDCl₃, δ , ppm): -3.78 (CH₃), 125.00, 126.55, 127.87, 128.27, 128.48, 129.27, 134.55, 136.72, 137.99, 146.74; ²⁹Si NMR (CDCl₃, δ , ppm): -16.06; MS: m/z (rel. intensity): 51 (15), 102 (17), 103 (26), 105 (21), 121 (23), 145 (48), 146 (21), 218 (16), 219 (19), 220 (26), 222 (41), 223 (59), 224 (25), 233 (16), 245 (16), 246 (19), 247 (20), 248 (66), 249 (68), 250 (30), 311 (98), 312 (25), 325 (28), 326 (100, M⁺).



Figure S104. ¹³C NMR (100 MHz, CDCl₃) of product 37



Figure S105. ²⁹Si NMR (79 MHz, CDCl₃) of product 37

Analytical data of product 37:

Isolated yield: 92% (392.8 mg); ¹H NMR (CDCl₃, δ , ppm): 7.04 (d, 2H, *J*_{HH} = 19.1 Hz, =CHSi), 7.04 (d, 2H, *J*_{HH} = 19.1 Hz, =CH), 7.36 – 7.68 (m, 16H, Ph), 7.79 – 7.86 (m, 4H, Ph); ¹³C NMR (CDCl₃, δ , ppm): 123.34, 126.98, 128.22, 128.75, 128.81, 129.85, 135.02, 135.92, 138.23, 148.93; ²⁹Si NMR (CDCl₃, δ , ppm): -19.19; MS: *m/z* (rel. intensity): 51 (13), 77 (13), 105 (37), 130 (36), 131 (13), 177 (13), 179 (16), 180 (33), 182 (14), 205 (41), 206 (39), 218 (15), 219 (45), 281 (14), 295 (100), 296 (29), 308 (44), 309 (21), 388 (4, M⁺).



Figure S107. ¹³C NMR (100 MHz, CDCl₃) of product 38


Figure S108. ²⁹Si NMR (79 MHz, CDCl₃) of product 38

Analytical data of product 38:

Isolated yield: 92% (295.7 mg); ¹H NMR (CDCl₃, δ , ppm): 0.80-0.90 (m, 4H, CH₃CH₂-), 1.04-1.12 (m, 6H, CH₃CH₂), 6.54 (d, 2H, *J*_{HH} = 19.2 Hz, =CHSi), 7.02 (d, 2H, *J*_{HH} = 19.2 Hz, =CH), 7.26 – 7.40 (m, 6H, Ph), 7.47 – 7.52 (m, 4H, Ph); ¹³C NMR (CDCl₃, δ , ppm): 4.44 (CH₃), 7.49 (CH₂), 124.95, 126.48, 128.12, 128.56, 131.55, 138.39, 145.94; ²⁹Si NMR (CDCl₃, δ , ppm): -8.24; MS: *m/z* (rel. intensity): 103 (10), 105 (14), 131 (27), 159 (17), 189 (12), 235 (19), 263 (100), 264 (24), 292 (28, M⁺); anal. calcd. for C₂₀H₂₄Si (%): C: 82.13, H: 8.27; found: C: 82.35, H: 8.42.



Figure S109. ¹H NMR (400 MHz, CDCl₃) of product 39





Figure S110. ¹³C NMR (100 MHz, CDCl₃) of product **39**

----2.52



Figure S111. ²⁹Si NMR (79 MHz, CDCl₃) of product 39

Analytical data of product 39:

Isolated yield: 92% (403 mg); ¹H NMR (CDCl₃, δ , ppm): 0.49 (overlapping s, 12H, CH₃), 6.64 (d, 2H, J_{HH} = 19.1 Hz, =CHSi), 7.01 (d, 2H, J_{HH} = 19.1 Hz, =CH), 7.27 – 7.41 (m, 6H, Ph), 7.45 – 7.55 (m, 4H, Ph), 7.57 – 7.68 (m, 4H, Ph); ¹³C NMR (CDCl₃, δ , ppm): -2.52 (CH₃), 126.56, 127.06, 128.21, 128.57, 133.34, 138.21, 139.52, 145.38; ²⁹Si NMR (CDCl₃, δ , ppm): -10.47; MS: *m/z* (rel. intensity): 135 (20), 145 (19), 161 (17), 237 (15), 294 (17), 296 (40), 297 (18), 340 (23), 383 (31), 398 (100, M⁺).

1.3. NMR spectra and analytical data of unsymmetrical *E,E*-divinylsilanes



Figure S113. ¹³C NMR (100 MHz, CDCl₃) of product 40



Figure S114. ²⁹Si NMR (79 MHz, CDCl₃) of product 40

Analytical data of product 40:

Isolated yield: 90% (317 mg); ¹H NMR (CDCl₃, δ , ppm): 0.60 (s, 3H, CH₃), 1.01 (t, 3H, *J*_{HH} = 6.4 Hz, -(CH₂)₄CH₃), 1.37 – 1.88 (m, 6H, -(CH₂)₄CH₃), 2.24 – 2.35 (m, 2H, =CHCH₂), 5.97 (d, 1H, *J*_{HH} = 18.5 Hz, =CHSi), 6.33 (dt, 1H, *J*_{HH} = 18.5, 6.2 Hz, =CHCH₂), 6.72 (d, 1H, *J*_{HH} = 19.1 Hz, =CHSi), 7.07 (d, 1H, *J*_{HH} = 19.1 Hz, =CHCH₂), 7.34 – 7.48 (m, 6H, Ph), 7.52 – 7.59 (m, 2H, Ph), 7.66 – 7.73 (m, 2H, Ph); ¹³C NMR (CDCl₃, δ , ppm): -3.75 (CH₃), 14.06, 22.53, 28.27, 31.45, 36.90, 125.21, 125.88, 126.53, 127.75, 128.14, 128.47, 128.75, 129.04, 134.49, 137.52, 138.21, 146.20, 151.20; ²⁹Si NMR (CDCl₃, δ , ppm): -17.84; MS: *m/z* (rel. intensity): 105 (23), 121 (42), 131 (18), 145 (38), 146 (16), 158 (20), 159 (21), 216 (15), 217 (31), 221 (16), 222 (19), 223 (21), 242 (29), 243 (100), 244 (48), 245 (18), 249 (23), 250 (48), 305 (69), 306 (18), 320 (39, M⁺); anal. calcd. for C₂₂H₂₈Si (%): C: 82.43, H: 8.80; found: C: 82.52, H: 8.88.



Figure S115. 1 H NMR (400 MHz, CDCl₃) of product **41**



Figure S116. ¹³C NMR (100 MHz, CDCl₃) of product 41



Figure S117. ²⁹Si NMR (79 MHz, CDCl₃) of product 41

Analytical data of product 41:

Isolated yield: 90% (378.4 mg); ¹H NMR (CDCl₃, δ , ppm): 0.65 (s, 3H, CH₃), 1.37 (s, 9H, C(CH₃)₃), 6.70 (dt, 2H, *J*_{HH} = 19.3, 1.6 Hz, =CHCH₂), 7.07 (d, 2H, *J*_{HH} = 19.1 Hz, =CHSi), 7.30 – 7.54 (m, 12H, Ph and –C₆H₄-), 7.64 – 7.75 (m, 2H, Ph); ¹³C NMR (CDCl₃, δ , ppm): -3.63 (CH₃), 31.35 (C(CH₃)₃), 34.71 (C(CH₃)₃), 124.02, 125.36, 125.54, 126.41, 126.67, 127.94, 128.34, 128.60, 129.32, 134.68, 135.48, 137.08, 138.19, 146.70 (d, *J* = 6.9 Hz), 151.60; ²⁹Si NMR (CDCl₃, δ , ppm): -16.32; MS: *m/z* (rel. intensity): 57 (50), 187 (30), 222 (21), 243 (25), 244 (29), 245 (26), 246 (31), 247 (37), 248 (34), 249 (30), 250 (33), 254 (20), 262 (22), 264 (47), 265 (30), 276 (20), 277 (24), 279 (34), 280 (47), 281 (31), 288 (23), 289 (56), 290 (46), 292 (83), 293 (42), 294 (20), 302 (18), 303 (27), 304 (77), 305 (100), 306 (59), 307 (24), 326 (30), 327 (23), 362 (24), 366 (31), 367 (96), 368 (58), 370 (27), 380 (23), 382 (24, M⁺); anal. calcd. for C₂₇H₃₀Si (%): C: 84.76, H: 7.90; found: C: 84.85, H: 8.02.



Figure S119. ¹³C NMR (100 MHz, CDCl₃) of product 42



Figure S120. ²⁹Si NMR (79 MHz, CDCl₃) of product 42

Analytical data of product 42:

Isolated yield: 88% (441.6 mg); ¹H NMR (CDCl₃, δ , ppm): 0.54 (s, 3H, CH₃), 0.89 – 0.94 (m, 3H, -(CH₂)₄CH₃), 1.27 – 1.51 (m, 8H, -(CH₂)₄CH₃), 2.20 – 2.26 (m, 2H, =CHCH₂), 5.87 (dt, 1H, J_{HH} = 18.6, 1.5 Hz, =CHSi), 6.26 (dt, 1H, J_{HH} = 18.6, 6.3 Hz, =CHCH₂), 6.81 (d, 1H, J_{HH} = 19.1 Hz, =CHSi), 6.97 (d, 1H, J_{HH} = 19.1 Hz, =CHCH₂), 7.39 – 7.43 (m, 3H, Ph), 7.57 – 7.61 (m, 2H, Ph), 7.75 – 7.77 (m, 1H, -C₆H₃-), 7.83 – 7.89 (m, 2H, -C₆H₃-); ¹³C NMR (CDCl₃, δ , ppm): -4.02 (CH₃), 14.02, 22.52, 28.22, 31.47, 36.93, 121.33 (m, CF₃), 121.99, 124.24, 124.69, 126.34, 126.36, 127.95, 129.41, 131.74, 131.86, 132.07, 133.91, 134.46, 136.42, 140.15, 142.74, 152.09; ²⁹Si NMR (CDCl₃, δ , ppm):-17.56; MS: *m/z* (rel. intensity): 227 (15), 228 (12), 277 (12), 278 (43), 279 (17), 298 (100), 299 (30), 341 (28), 437 (15), 441 (8), 456 (3, M⁺); anal. calcd. for C₂₄H₂₆F₆Si(%): C: 63.14, H: 5.74; found: C: 63.30, H: 5.88.





Figure S122. ¹³C NMR (100 MHz, CDCl₃) of product 43



Figure S123. ²⁹Si NMR (79 MHz, CDCl₃) of product 43

Analytical data of product 43:

Isolated yield: 92% (457.7 mg); ¹H NMR (CDCl₃, δ , ppm): 0.89 – 1.08 (m, 6H, -(CH₂)₄CH₃), 1.36 – 1.72 (m, 12H, -(CH₂)₄CH₃), 2.26 – 2.40 (m, 2H, -(CH₂)₄CH₃), 2.61 – 2.72 (m, 2H, =CHCH₂), 6.13 (d, 1H, J_{HH} = 18.5 Hz, =CHSi), 6.33 (dt, 1H, J_{HH} = 18.5, 6.1 Hz, =CHCH₂), 6.81 (d, 1H, J_{HH} = 19.1 Hz, =CHSi), 7.04 (d, 1H, J_{HH} = 19.1 Hz, =CHCH₂), 7.23 (d, 2H, J_{HH} = 8.0 Hz, -C₆H₄-) 7.42 – 7.50 (m, 8H, Ph and -C₆H₄-), 7.63 – 7.71 (m, 4H, Ph); ¹³C NMR (CDCl₃, δ , ppm): 14.01, 14.04, 22.52, 28.22, 31.08, 31.44, 35.68, 37.00, 122.35, 123.46, 126.60, 127.76, 128.58, 129.27, 135.57, 143.40, 148.12, 153.30; ²⁹Si NMR (CDCl₃, δ , ppm): -20.67; MS: *m/z* (rel. intensity): 105 (15), 253 (31), 276 (18), 278 (60), 279 (40), 280 (28), 291 (24), 304 (17), 355 (35), 356 (22), 375 (20), 376 (78), 377 (42), 378 (16), 381 (47), 382 (28), 452 (100, M⁺); anal. calcd. for C₃₂H₄₀Si (%): C: 84.89, H: 8.91; found: C: 84.95, H: 8.99.



Figure S124. ¹H NMR (400 MHz, CDCl₃) of product 44



Figure S125. ¹³C NMR (100 MHz, CDCl₃) of product 44



Figure S126. ²⁹Si NMR (79 MHz, CDCl₃) of product 44

Analytical data of product 44:

Isolated yield: 90% (372.5 mg); ¹H NMR (CDCl₃, δ , ppm): 0.53 (s, 3H, *CH*₃), 0.95 (t, 3H, *J*_{HH} = 7.0 Hz, -(CH₂)₄CH₃), 1.32 - 1.35 (m, 15H, C(*CH*₃)₃ and -(CH₂)₄CH₃), 2.18 - 2.28 (m, 2H, =CHCH₂), 5.19 (d, 1H, *J*_{HH} = 18.5 Hz, =CHSi), 6.25 (dt, 1H, *J*_{HH} = 18.6, 6.3 Hz, =CHCH₂), 6.61 (d, 1H, *J*_{HH} = 19.1 Hz, =CHSi), 6.99 (d, 1H, *J*_{HH} = 19.1 Hz, =CHCH₂), 7.29 - 7.53 (m, 7H, Ph and -C₆H₄-), 7.58 - 7.68 (m, 2H, Ph); ¹³C NMR (CDCl₃, δ , ppm): -3.66 (*C*H₃), 14.06, 22.54, 28.30, 31.29, 31.46, 34.62, 36.90, 124.81, 125.42, 126.28, 126.63, 127.73, 128.99, 134.52, 135.69, 137.77, 146.04, 151.11, 151.35; ²⁹Si NMR (CDCl₃, δ , ppm): -17.84; MS: *m/z* (rel. intensity): 57 (76), 105 (14), 121 (33), 122 (10), 145 (27), 146 (14), 147 (11), 158 (13), m159 (15), 171 (11), 172 (10), 177 (11), 187 (11), 215 (21), 216 (14), 217 (20), 221 (11), 235 (12), 250 (18), 264 (18), 278 (12), 280 (19), 291 (21), 298 (14), 230 (26), 305 (32), 306 (24), 319 (10), 361 (100), 362 (33), 376 (98, M⁺); anal. calcd. for C₂₆H₃₆Si (%): C: 82.91, H: 9.63; found: C: 82.99, H: 9.71.



Figure S127. ¹H NMR (400 MHz, CDCl₃) of product 45



Figure S128. ¹³C NMR (100 MHz, CDCl₃) of product 45



Figure S129. ²⁹Si NMR (79 MHz, CDCl₃) of product 45

Analytical data of product 45:

Isolated yield: 86% (495.8 mg); ¹H NMR (CDCl₃, δ , ppm): 6.92 (d, 1H, *J*_{HH} = 19.1 Hz, =CHSi), 7.01 – 7.21 (m, 3H, =CHSi and =CHCH₂), 7.35 – 7.97 (m, 18H, Ph and –C₆H₃-); ¹³C NMR (CDCl₃, δ , ppm): 121.66 (m, *C*F₃), 121.93, 125.11, 126.54 (d, *J* = 3.1 Hz), 126.79, 128.15, 128.63, 128.75, 129.13, 129.94, 131.75, 132.20, 133.76, 135.56, 135.94, 137.76, 139.87, 145.03, 149.39; ²⁹Si NMR (CDCl₃, δ , ppm): -19.23; MS: *m/z* (rel. intensity): 51 (22), 77 (29), 103 (23), 104 (20), 181 (22), 183 (36), 201 (22), 219 (19), 227 (17), 278 (77), m279 (28), 362 (17), 421 (100), 422 (29), 446 (15), 447 (19), 505 (53), 506 (17), 524 (13, M⁺); anal. calcd. for C₃₀H₂₂F₆Si (%): C: 68.69, H: 4.23; found: C: 68.80, H: 4.31.



Figure S130. ¹H NMR (400 MHz, CDCl₃) of product 46



Figure S131. ¹³C NMR (100 MHz, CDCl₃) of product 46



Figure S132. ²⁹Si NMR (79 MHz, CDCl₃) of product 46

Analytical data of product 46:

Isolated yield: 88% (447.3 mg); ¹H NMR (CDCl₃, δ , ppm): 0.72 (s, 3H, *CH*₃), 6.74 (d, 1H, *J*_{HH} = 19.2 Hz, =*CH*Si), 6.94 (d, 1H, *J*_{HH} = 19.1 Hz, =*CH*Si), 7.11 (d, 1H, *J*_{HH} = 19.1 Hz, =*CH*CH₂), 7.12 (d, 1H, *J*_{HH} = 19.2 Hz, =*CH*CH₂), 7.35 – 7.56 (m, 8H, Ph), 7.68 – 7.74 (m, 2H, Ph), 7.81 – 7.85 (m, 1H, -C₆H₄-), 7.93 – 7.96 (m, 2H, -C₆H₄-); ¹³C NMR (CDCl₃, δ , ppm): -4.04 (*C*H₃), 121.53 (m, *C*F₃), 123.85, 125.15, 126.43 (d, *J* = 2.9 Hz), 126.67, 128.11, 128.31, 128.59, 128.61, 129.68, 131.04, 131.72, 132.16, 134.58, 135.73, 137.85, 140.00, 143.29, 143.94, 147.50; ²⁹Si NMR (CDCl₃, δ , ppm): -15.82; MS: *m/z* (rel. intensity): 51 (11), 91 (11), 105 (20), 139 (26), 145 (14), 219 (10), 278 (10), 283 (12), 284 (13), 303 (24), 304 (100), 305 (18), 443 (40), 444 (11), 462 (12, M⁺); anal. calcd. for C₂₅H₂₀F₆Si (%): C: 64.92, H: 4.36; found: C: 65.12, H: 4.52.





Figure S133. ¹H NMR (400 MHz, CDCl₃) of product 47



Figure S134. ¹³C NMR (100 MHz, CDCl₃) of product 47



Figure S135. ²⁹Si NMR (79 MHz, CDCl₃) of product 47

Analytical data of product 47:

Isolated yield: 90% (392.3 mg); ¹H NMR (CDCl₃, δ , ppm): 0.73 (s, 3H, *CH*₃), 1.02 (t, 3H, *J*_{HH} = 6.9 Hz, -(CH₂)₄CH₃), 1.37 - 1.50 (m, 4H, -(CH₂)₄CH₃), 1.67 - 1.80 (m, 2H, -(CH₂)₄CH₃), 2.66 - 2.76 (m, 2H, =CHCH₂), 6.75 (d, 1H, *J*_{HH} = 19.1 Hz, =CHSi), 6.81 (d, 1H, *J*_{HH} = 19.1 Hz, =CHSi), 7.15 (d, 1H, *J*_{HH} = 19.1 Hz, =CHCH₂), 7.16 (d, 1H, *J*_{HH} = 19.1 Hz, =CHCH₂), 7.28 (d, 2H, *J*_{HH} = 8.1 Hz, -C₆H₄-) 7.35 - 7.54 (m, 10H, Ph and -C₆H₄-), 7.57 - 7.62 (m, 2H, Ph); ¹³C NMR (CDCl₃, δ , ppm): -3.73 (*C*H₃), 14.02, 22.52, 31.05, 31.43, 31.66, 123.66, 125.27, 126.55 (d, *J* = 3.6 Hz), 127.86, 128.25, 128.50, 128.59, 129.23, 131.48, 134.59, 135.63, 136.97, 128.11, 143.34, 146.66, 146.75; ²⁹Si NMR (CDCl₃, δ , ppm): -16.35; MS: *m/z* (rel. intensity): 105 (18), 249 (19), 250 (24), 277 (38), 291 (15), 292 (25), 293 (44), 294 (20), 304 (17), 305 (73), 307 (44), 308 (18), 317 (18), 318 (70), 319 (100), 320 (51), 321 (23), 381 (54), 383 (36), 384 (17), 389 (18), 396 (26, M⁺); anal. calcd. for C₂₈H₃₂Si (%): C: 84.79, H: 8.13; found: C: 84.92, H: 8.28.

Product 48





Figure S137. ¹³C NMR (100 MHz, CDCl₃) of product 48



Figure S138. ²⁹Si NMR (79 MHz, CDCl₃) of product 48

Analytical data of product 48:

Isolated yield: 92% (477.9 mg); ¹H NMR (CDCl₃, δ , ppm): 0.98 (t, 3H, *J*_{HH} = 6.9 Hz, -(CH₂)₄CH₃), 1.33 – 1.44 (m, 4H, -(CH₂)₄CH₃), 1.62 – 1.74 (m, 2H, -(CH₂)₄CH₃), 2.43 (s, 3H, CH₃), 2.62 – 2.73 (m, 2H, =CHCH₂), 6.88 (d, 1H, *J*_{HH} = 19.1 Hz, =CHSi), 6.92 (d, 1H, *J*_{HH} = 19.1 Hz, =CHCH₂), 7.11 (d, 1H, *J*_{HH} = 19.2 Hz, =CHSi), 7.12 (d, 1H, *J*_{HH} = 19.2 Hz, =CHCH₂), 7.18 – 7.25 (m, 2H, Ar), 7.28 – 7.542 (m, 12H, Ar), 7.68 – 7.77 (m, 4H, Ar); ¹³C NMR (CDCl₃, δ , ppm): 14.02, 21.34, 22.52, 31.07, 31.44, 35.69, 121.71, 122.94, 123.90, 126.67, 127.43, 127.89, 128.44, 128.61, 129.23, 129.48, 135.01, 135.66, 138.00, 138.08, 143.56, 148.59, 148.69; ²⁹Si NMR (CDCl₃, δ , ppm): -19.30; MS: *m/z* (rel. intensity): 105 (21), 181 (22), 206 (16), 220 (18), 221 (43), 222 (28), 234 (15), 235 (23), 278 (22), 279 (23), 291 (31), 292 (18), 311 (62), 612 (25), 324 (28), 105 (21), 181 (22), 206 (16), 220 (18), 221 (31), 292 (18), 311 (62), 312 (25), 324 (28), 394 (91), 395 (100), 472 (285, M⁺); anal. calcd. for C₃₄H₃₆Si (%): C: 86.38, H: 7.68; found: C: 86.26, H: 7.52.