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Formal [3 + 2] Additions of Acceptor-Substituted Cyclopropylmethylsilanes with arylacetylenes

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General. ^{1}H and ^{13}C spectra were recorded on JEOL JNM-LA400 instrument using solutions in $CDCl_3$. The ^{1}H and ^{13}C spectra were referred, respectively, to TMS used as an internal standard and the central line for $CDCl_3$. Elemental (C, H, N) analyses were done on Perkin-Elmer 240-C automatic elemental analyzer. All the reactions were carried out using freshly distilled and dry solvents from solvent stills. Column chromatography was performed over silica gel (100-200 mesh) from Acme Chemicals using hexanes and ethyl acetate mixtures as eluent. The separation of isomers and their rigorous purification were achieved by radial chromatography using plates coated with silica gel PF_{254} (E-Merck). Except a few mixtures, all other mixtures could be separated by radial chromatography. Solvents were removed under reduced pressure on a rotovap. Organic extracts were dried with anhydrous Na_2SO_4.

General procedure for cyclopropanation of allyl *tert*-butyldiphenylsilane with diazo compounds. A solution of the diazo compound (2 mmol) in $CHCl_3$ (2 mL) was added over a period of 10 h using a syringe pump to a stirred solution of allyl *tert*-butyldiphenylsilane (1.120 g, 4 mmol) and $Rh_2(OAc)_4$ (43 mg, 0.01 mmol) in anhydrous $CHCl_3$ (0.5 mL) under nitrogen. The reaction mixture was stirred further for 5 h and the solvent was removed. The residue was chromatographed to obtain the pure product **1** and the unreacted allylsilane.

1a: 75% yield, colorless dense liquid (*trans*:*cis* = 2.4:1)
1b: 60% yield, colorless dense liquid (*trans*:*cis* = 2.1:1)
1c: 60% yield, colorless dense liquid (*trans*:*cis* = 2:1)

***trans*-1a**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71-7.69 (2H, m), 7.61-7.55 (4H, m), 7.51-7.47 (1H, m), 7.38-7.23 (8H, m), 2.31-2.27 (1H, m), 1.67-1.58 (1H, m), 1.45-1.39 (1H, dd, J = 15.0, 6.5 Hz), 1.37-1.31 (2H, m), 1.05 (9H, s), 0.78-0.73 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.3, 137.6, 135.8, 135.7, 134.2, 134.0, 132.1, 129.0, 128.9, 128.0, 127.7, 127.4, 27.7, 27.3, 23.2, 21.7, 17.8, 15.6. Anal Calcd for $C_{27}H_{30}OSi$: C, 81.36; H, 7.59. Found: C, 81.22; H, 7.45.

***cis*-1a** . ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94-7.91 (2H, m), 7.69-7.67 (2H, m), 7.69-7.28 (11H, m), 2.67-2.62 (1H, m), 1.60-1.50 (1H, m), 1.42-1.35 (1H, dd, J = 15.1, 9.8 Hz), 1.31-1.26 (1H, dd, J = 15.1, 3.9 Hz), 1.23-1.17 (1H, m), 1.02 (9H, s), 0.95-

0.90 (1H, dt, *J* = 7.8, 4.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.8, 139.0, 136.1, 135.9, 134.6, 134.5, 132.3, 129.0, 128.9, 128.3, 127.9, 127.5, 27.7, 24.8, 22.5, 18.1, 16.7, 7.4. Anal Calcd for $C_{27}H_{30}OSi$: C, 81.36; H, 7.59. Found: C, 81.25; H, 7.50.

***trans*-1b**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.56 (4H, m), 7.41-7.31 (6H, m), 2.21-2.13 (1H, ddd, *J* = 16.4, 8.3, 6.6 Hz), 2.06-1.98 (1H, ddd, *J* = 16.4, 8.3, 6.6 Hz), 1.52-1.48 (1H, m), 1.43-1.16 (7H, m), 1.11-1.07 (1H, m), 1.04 (9H, s), 0.84 (3H, t, *J* = 7.3 Hz), 0.59-0.54 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.3, 136.0, 135.9, 134.6, 134.2, 129.1, 129.08, 127.6, 43.0, 30.9, 27.8, 25.9, 22.2, 21.5, 20.4, 18.0, 15.5, 13.8. Anal Calcd for $C_{25}H_{34}OSi$: C, 79.31; H, 9.05. Found: C, 79.20; H, 8.90.

***cis*-1b**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66-7.59 (4H, m), 7.40-7.32 (6H, m), 2.43-2.35 (1H, ddd, *J* = 16.4, 8.3, 6.6 Hz), 2.28-2.20 (1H, ddd, *J* = 16.4, 8.3, 6.6 Hz), 1.91-1.86 (1H, m), 1.57-1.22 (8H, m), 1.03 (9H, s), 0.90 (3H, t, *J* = 7.3 Hz), 0.81-0.76 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.0, 136.2, 136.1, 134.9, 134.6, 129.0, 128.97, 127.5, 127.46, 44.6, 27.8, 27.1, 26.1, 22.4, 21.4, 18.1, 16.9, 13.9, 7.2. Anal Calcd for $C_{25}H_{34}OSi$: C, 79.31; H, 9.05. Found: C, 79.15; H, 8.90.

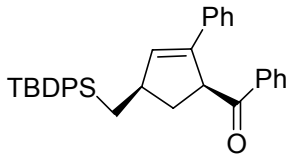
***trans*-1c**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64-7.58 (4H, m), 7.39-7.32 (6H, m), 1.89-1.85 (1H, m), 1.59-1.54 (1H, dd, *J* = 14.9, 4.6 Hz), 1.40-1.33 (2H, m), 1.27-1.21 (1H, m), 1.07 (9H, s), 1.06 (9H, s), 0.57-0.53 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 214.5, 136.0, 135.9, 134.5, 134.47, 129.1, 127.6, 127.5, 43.6, 27.8, 26.8, 26.2, 21.6, 21.0, 18.0, 15.7. Anal Calcd for $C_{25}H_{34}OSi$: C, 79.31; H, 9.05. Found: C, 79.23; H, 8.94.

***cis*-1c**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68-7.66 (2H, m), 7.63-7.60 (2H, m), 7.41-7.32 (6H, m), 2.21-2.16 (1H, m), 1.37-1.25 (2H, m), 1.21-1.02 (1H, m), 1.17 (9H, s), 1.04 (9H, s), 0.95-0.88 (1H, m), 0.76-0.71 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 213.3, 136.2, 136.0, 134.9, 134.6, 129.0, 128.97, 127.5, 127.4, 44.2, 27.8, 26.3, 23.1, 21.5, 18.1, 16.5, 7.3. Anal Calcd for $C_{25}H_{34}OSi$: C, 79.31; H, 9.05. Found: C, 79.16; H, 8.94.

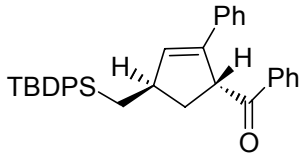
***trans*-12**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.56 (4H, m), 7.40-7.32 (6H, m), 2.30-2.15 (2H, m), 1.78-1.64 (7H, m), 1.49-1.33 (3H, m), 1.07(9H, s), 0.09-0.07 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.5, 136.0, 135.9, 134.5, 134.4, 129.1, 127.6, 127.5, 39.7, 33.6, 28.1, 27.9, 26.1, 26.0, 23.8, 23.6, 18.2, 10.0. Anal Calcd for $C_{25}H_{32}OSi$: C, 79.73; H, 8.56. Found: C, 79.60; H, 8.45.

***cis*-12**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66-7.56 (4H, m), 7.40-7.32 (6H, m), 2.04-1.88 (2H, m), 1.76-1.65 (3H, m), 1.25-0.98 (7H, m), 1.02 (9H, s), 0.41-0.35 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.8, 136.1, 136.0, 134.8, 134.4, 129.0, 127.6, 127.5, 42.0, 36.0, 35.8, 29.3, 27.8, 25.1, 23.9, 20.3, 18.1, 8.6. Anal Calcd for $C_{25}H_{32}OSi$: C, 79.73; H, 8.56. Found: C, 79.56; H, 8.46.

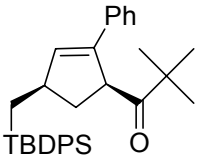
General procedure for the intermolecular [3 + 2] addition of cylopropylmethylsilanes, 1a-1c and 12, with arylacetylenes. A solution of $TiCl_4$ (61 mg, 0.326 mmol) in anhydrous CH_2Cl_2 (0.5 mL) was added slowly under nitrogen to a stirred solution of cylopropylmethylsilane (0.251 mmol) and arylacetylene (0.326 mmol) in anhydrous CH_2Cl_2 (0.8 mL) at – 78 °C. The reaction mixture turned deep red. After stirring for 3 h at – 78 °C, it was warmed slowly over 1 h to – 40 °C. The stirring was continued at this temperature for 2 h and the reaction mixture was taken in Et_2O (20 mL). The ethereal solution was washed with saturated aqueous NH_4Cl (2 x 7 mL) and water (7 mL). The combined aqueous washings were extracted with Et_2O (2 x 7 mL). The combined organic extracts were washed with brine, dried, and concentrated. Purification of the crude residue by silica gel column chromatography (EtOAc/hexanes) gave pure product. Separation of the *cis* and *trans* isomers was achieved by radial chromatography over silica gel.



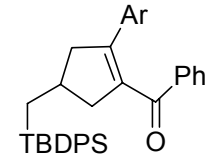
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97-7.95 (2H, m), 7.71-7.69 (2H, m), 7.62-7.54 (3H, m), 7.47-7.22 (8H, m), 7.16-7.05 (5H, m), 5.98-5.97 (1H, m), 4.75-4.71 (1H, dd, *J* = 10.0, 5.9 Hz), 2.98-2.95 (1H, m), 2.54-2.45 (1H, ddd, *J* = 13.2, 10.0, 8.5 Hz), 1.65-1.60 (1H, td, *J* = 13.2, 5.2 Hz), 1.53-1.47(1H, dd, *J* = 14.9, 8.0 Hz), 1.38-1.33 (1H, dd, *J* = 14.9, 6.9 Hz), 1.01 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.7, 139.6, 136.6, 136.3, 136.1, 135.6, 134.8, 134.6, 132.9, 129.1, 129.0, 128.6, 128.2, 127.6, 127.5, 126.8, 125.7, 53.1, 41.6, 39.4, 27.8, 18.1, 17.6. Anal Calcd for $C_{35}H_{36}OSi$: C, 83.96; H, 7.25. Found: C, 83.80; H, 7.15.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90-7.87 (2H, m), 7.66-7.63 (4H, m), 7.57-7.53 (1H, m), 7.46-7.30 (8H, m), 7.20-7.04 (5H, m), 6.03 (1H, broad s), 4.81-4.79 (1H, m), 3.13-3.08 (1H, m), 2.04-1.89 (2H, m), 1.50-1.44 (1H, dd, *J* = 14.9, 7.6 Hz), 1.38-1.32 (1H, dd, *J* = 14.9, 7.3 Hz), 1.04 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.8, 139.2, 136.7, 136.2, 136.1, 135.3, 134.74, 134.7, 132.9, 129.2, 129.1, 128.5, 128.2, 127.6, 126.9, 125.7, 53.1, 40.9, 40.3, 27.9, 18.2, 17.9. Anal Calcd for $C_{35}H_{36}OSi$: C, 83.96; H, 7.25. Found: C, 83.85; H, 7.20.

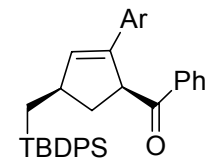


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71-7.65 (4H, m), 7.45-7.32 (6H, m), 7.20-7.04 (5H, m), 5.82-5.81 (1H, m), 4.33-4.28 (1H, m), 2.92-2.87 (1H, m), 2.29-2.21 (1H, ddd, *J* = 12.9, 9.0, 8.8 Hz), 1.55-1.50 (1H, dd, *J* = 14.9, 7.6 Hz), 1.34-1.28 (2H, m), 1.09 (9H, s), 1.02 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 216.8, 140.5, 137.1, 136.5, 136.4, 136.2, 134.9, 134.7, 129.1, 129.0, 128.0, 127.6, 126.7, 125.9, 52.4, 44.2, 41.4, 40.2, 27.8, 26.8, 18.2, 17.7. Anal Calcd for $C_{33}H_{40}OSi$: C, 82.45; H, 8.39. Found: C, 82.32; H, 8.27.



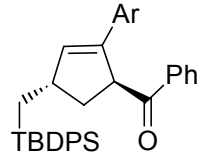
Ar = *p*-MeO-C_6H_4-

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68-7.65 (6H, m), 7.42-7.32(7H, m), 7.24-7.20 (2H, m), 6.88-6.84(2H, m), 6.56-6.52 (2H, m), 3.65(3H, s), 2.79-2.40 (5H, m), 1.58-1.53 (1H, dd, *J* = 14.9, 6.3 Hz), 1.53-1.47 (1H, dd, *J* = 14.9, 7.3 Hz), 1.05 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.2, 159.0, 145.2, 136.7, 136.14, 136.1, 135.0,134.6, 132.5, 129.3, 129.1, 128.4, 128.1, 127.6, 127.5, 113.2, 55.1, 47.0, 46.7, 33.7, 27.9, 18.2, 17.2. Anal Calcd for $C_{36}H_{38}O_2Si$: C, 81.47; H, 7.22. Found: C, 81.35; H, 7.14.



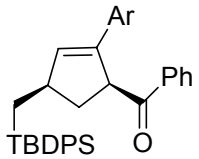
Ar = *p*-MeO-C_6H_4-

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98-7.96 (2H, m), 7.71-7.55 (5H, m), 7.48-7.23 (8H, m), 7.0-6.97 (2H, m), 6.70-6.67 (2H, m), 5.86-5.85 (1H, m), 4.72-4.68 (1H, dd, *J* = 10.0, 5.6 Hz), 3.72 (3H, s), 2.97-2.94 (1H, m), 2.53-2.45 (1H, ddd, *J* = 13.2, 10.0, 8.3 Hz), 1.64-1.58 (1H, td, *J* = 13.2, 4.9 Hz), 1.51-1.46 (1H, dd, *J* = 14.9, 8.0 Hz), 1.37-1.31 (1H, dd, *J* = 14.9, 7.0 Hz), 1.00 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.9, 158.5, 138.9, 136.6, 136.4, 136.1, 134.8, 134.7, 134.3, 132.9, 129.0, 128.9, 128.6, 128.4, 128.3, 127.5, 127.51, 126.9, 114.2, 113.6, 55.1, 53.2, 41.5, 39.4, 27.8, 18.1, 17.6. Anal Calcd for $C_{36}H_{38}O_2Si$: C, 81.47; H, 7.22. Found: C, 81.30; H, 7.10.



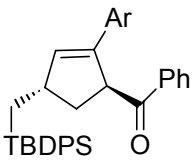
Ar = *p*-MeO-C_6H_4-

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89-7.87 (2H, m), 7.68-7.53 (5H, m), 7.45-7.28 (8H, m), 7.00-6.97 (2H, m), 6.70-6.68 (2H, m), 5.89 (1H, broad s), 4.78-4.74 (1H, m), 3.72(3H, s), 3.11-3.06 (1H, m), 2.03-1.87 (2H, m), 1.49-1.43 (1H, dd, *J* = 14.9, 7.6 Hz), 1.37-1.31 (1H, dd, *J* = 14.9, 7.3 Hz), 1.03 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.0, 158.6, 138.6, 136.4, 136.2, 136.1, 134.8, 134.6, 132.9, 129.1, 128.5, 128.1, 127.6, 126.9, 113.7, 55.2, 53.3, 40.9, 40.3, 27.9, 18.2, 18.1. Anal Calcd for $C_{36}H_{38}O_2Si$: C, 81.47; H, 7.22. Found: C, 81.35; H, 7.12.



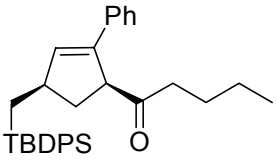
Ar = *p*-Cl-C_6H_4-

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96-7.94 (2H, m), 7.70-7.68 (2H, m), 7.62-7.56 (3H, m), 7.49-7.24 (8H, m), 7.10 (2H, d, *J* = 8.6 Hz), 6.95 (2H, d, *J* = 8.6 Hz), 5.92 (1H, broad s), 4.71-4.68 (1H, dd, *J* = 10.0, 5.6 Hz), 2.99-2.94 (1H, m), 2.56-2.48 (1H, ddd, *J* = 13.2, 10.0, 8.5 Hz), 1.66-1.60 (1H, td, *J* = 13.2, 5.2 Hz), 1.50- 1.44 (1H, dd, *J* = 14.9, 8.0 Hz), 1.37-1.32 (1H, dd, *J* = 14.9, 6.8 Hz), 1.00 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.5, 138.4, 136.9, 136.4, 136.3, 136.1, 134.7, 134.5, 134.2, 133.1, 132.4, 129.1, 129.0, 128.6, 128.5, 127.6, 127.5, 127.0, 53.0, 41.6, 39.5, 27.8, 18.1, 17.6. Anal Calcd for $C_{35}H_{35}ClOSi$: C, 78.62; H, 6.60. Found: C, 78.50; H, 6.48.

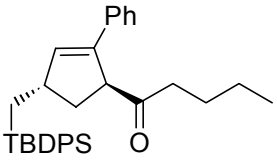


Ar = *p*-Cl-C_6H_4-

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88-7.85 (2H, m), 7.65-7.63 (4H, m), 7.59-7.52 (1H, m), 7.46-7.31 (8H, m), 7.13-7.09 (2H, m), 6.97-6.94 (2H, m), 5.98 (1H, broad s), 4.76-4.74 (1H, m), 3.12-3.05 (1H, m), 2.06-1.91 (2H, m), 1.48-1.43 (1H, dd, *J* = 14.9, 7.6 Hz), 1.39-1.33 (1H, dd, *J* = 14.9, 7.1 Hz), 1.04 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.6, 138.2, 137.4, 136.2, 136.1, 134.7, 134.6, 133.9,133.1, 132.6, 129.2, 128.62, 128.6, 128.4, 127.7, 126.9, 53.1, 41.0, 40.3, 27.9, 18.2, 17.9. Anal Calcd for $C_{35}H_{35}ClOSi$: C, 78.62; H, 6.60. Found: C, 78.45; H, 6.44.

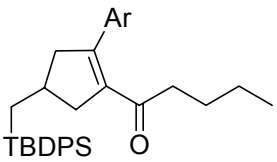


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70-7.68 (4H, m), 7.44-7.35 (6H, m), 7.22-7.15 (3H, m), 7.07-7.06 (2H, m), 5.84 (1H, broad s), 3.88-3.84 (1H, m), 2.96-2.93 (1H, m), 2.49-2.41 (1H, ddd, *J* = 17.1, 8.3, 6.6 Hz), 2.33-2.25 (1H, ddd, *J* = 13.2, 9.3, 8.5 Hz), 2.19-2.11 (1H, ddd, *J* = 17.1, 8.3, 6.3 Hz), 1.54-1.32 (5H, m), 1.20-1.11 (2H, sextet, *J* = 7.3 Hz), 1.05 (9H, s), 0.81 (3H, t, *J* = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 213.1, 139.6, 137.0, 136.3, 136.1, 135.7, 134.8, 134.6, 129.2, 128.3, 127.7, 127.6, 127.1, 125.6, 59.1, 41.3, 39.0, 38.1, 27.8, 25.7, 22.2, 18.2, 18.0, 13.8. Anal Calcd for $C_{33}H_{40}OSi$: C, 82.45; H, 8.39. Found: C, 82.30; H, 8.30.



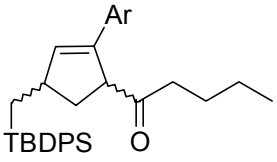
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70-7.66 (4H, m), 7.42-7.34 (6H, m), 7.22-7.05 (5H, m), 5.97 (1H, broad s), 3.88-3.84 (1H, m), 3.09-3.06 (1H, m), 2.48-2.40 (1H, ddd, *J* = 17.1, 8.3, 6.6 Hz), 2.17-2.09 (1H, ddd, *J* = 17.1, 8.3, 6.3 Hz), 1.93-1.88 (1H, m), 1.78-1.70 (1H, m), 1.54-1.33 (4H, m), 1.10-1.01 (2H, m), 1.05 (9H, s), 0.74 (3H, t, *J* = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.8, 139.3, 136.8, 136.2, 136.1, 135.2, 134.7, 134.6, 129.2, 128.4, 127.64, 127.6, 127.2, 125.6, 59.3, 41.3, 38.6, 38.3,

27.8, 25.5, 22.1, 18.0, 17.8, 13.7. Anal Calcd for $C_{33}H_{40}OSi$: C, 82.45; H, 8.39. Found: C, 82.35; H, 8.35.



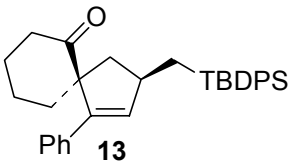
Ar = *p*-MeO-C_6H_4-

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66-7.63 (4H, m), 7.43-7.32 (6H, m), 7.04-7.01 (2H, m), 6.81-6.77 (2H, m), 3.79(3H, s), 2.66-2.51 (2H, m), 2.44-2.30 (3H, m), 2.17-2.12 (2H, dt, *J* = 7.3, 2.6 Hz), 1.45-1.34 (4H, m), 1.15-1.07 (2H, sextet, *J* = 7.3 Hz), 1.03 (9H, s), 0.76 (3H, t, *J* = 7.3 Hz), ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.3, 159.4, 148.9, 137.1, 136.2, 134.9, 134.7, 129.5, 129.1, 129.06, 127.6, 127.57, 113.5, 52.2, 49.0, 45.1, 41.4, 33.3, 27.9, 26.5, 22.2, 18.2, 17.1, 13.8. Anal Calcd for $C_{34}H_{42}O_2Si$: C, 79.95; H, 8.29. Found, C, 79.80; H, 8.16.



Ar = *p*-MeO-C_6H_4-

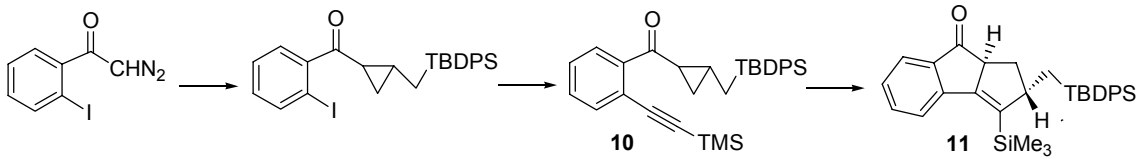
Mixture of the *trans*- and *cis*-isomers. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70-7.65 (m), 7.45-7.31 (m), 7.09-7.06 (m), 7.02-6.98 (m), 6.77-6.72 (m), 5.83 (broad s), 5.73-5.72 (m), 3.86-3.78 (m), 3.76 (s), 3.75 (s), 3.10-3.03 (m), 2.99-2.92 (m), 2.49-2.41 (ddd, *J* = 17.2, 8.4, 6.8 Hz), 2.32-2.03 (m), 1.92-1.86 (m), 1.76-1.68 (m), 1.53-1.26 (m), 1.21-1.12 (sextet, *J* = 7.3 Hz), 1.08-1.01 (m), 1.04 (s), 1.042 (s), 0.82 (t, *J* = 7.3 Hz), 0.74 (t, *J* = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 213.3, 213.1, 158.9, 158.7, 139.0, 138.7, 136.3, 136.2, 136.1, 135.0, 134.8, 134.7, 129.2, 128.5, 128.0, 127.6, 126.9, 126.8, 113.8, 113.7, 59.6, 59.3, 55.2, 41.4, 41.3, 38.74, 38.7, 38.1, 38.0, 27.9, 25.7, 25.6, 22.3, 22.1, 18.2, 18.0, 13.8, 13.7. Anal Calcd for $C_{34}H_{42}O_2Si$: C, 79.95; H, 8.29. Found: C, 79.75; H, 8.14.



13

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68-7.62 (4H, m), 7.41-7.30 (6H, m), 7.21-7.07 (5H, m), 5.86 (1H, d, *J* = 2.4 Hz), 2.84-2.80 (1H, m), 2.46-2.42 (1H, m), 2.28-2.17 (1H, m), 1.97-1.92 (3H, m), 1.67-1.63 (2H, m), 1.53-1.40 (4H, m), 1.25-1.16 (1H, m),

1.00 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 214.0, 143.6, 136.3, 136.29, 136.2, 135.2, 135.0, 134.5, 129.1, 127.9, 127.6, 127.4, 126.7, 63.9, 46.2, 39.9, 39.2, 35.8, 27.8, 25.6, 22.2, 18.1, 17.0. Anal Calcd for $C_{33}H_{38}OSi$: C, 82.79; H, 8.00. Found: C, 82.68; H, 7.85.



Procedure for the preparation of 2-(*t*-butyldiphenylsilylmethyl)cyclopropyl(2-iodophenyl) ketone. A solution of (2-iodophenyl)diazomethyl ketone (1.897 g, 7 mmol) in $CHCl_3$ (6 mL) was added to a stirred solution of allyl *tert*-butyldiphenylsilane (3.920 g, 14 mmol) and $Rh_2(OAc)_4$ (150 mg, 0.035 mmol) in anhydrous $CHCl_3$ (1 mL) over a period of 10 h using a syringe pump under nitrogen. The reaction mixture was stirred further for 5 h and the solvent was removed. The residue was chromatographed over silica gel to obtain the *trans*-product (0.907 g) and the *cis*-product (0.478 g) in a combined 40% yield. The ratio of the *trans*- and the *cis*-products was 1.9:1.

***trans*-product** (colorless dense liquid). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87-7.85 (1H, m), 7.64-7.56 (4H, m), 7.38-7.28 (7H, m), 7.12-7.04 (2H, m), 2.09-2.05 (1H, m), 1.77-1.69 (1H, m), 1.63-1.58 (1H, m), 1.44-1.40 (1H, m), 1.18-1.13 (1H, dd, J = 14.9, 8.3 Hz), 1.06 (9H, s), 0.82-0.78 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.9, 140.1, 136.0, 135.9, 134.3, 134.2, 131.2, 129.2, 129.1, 128.3, 127.9, 127.6, 91.3, 31.7, 27.8, 25.4, 23.3, 18.1, 15.9. Anal Calcd for $C_{27}H_{29}IOSi$: C, 61.83; H, 5.57. Found: C, 61.65; H, 5.45.

***cis*-product**. The *cis*-isomer was contaminated with another product (uncharacterized) that was inseparable. However, some characteristic ^{1}H absorptions for the *cis*-isomer are: δ 2.45-2.39 (m), 1.27-1.23 (m), 1.06 (s).

Procedure for the preparation of 10. A pressure tube was charged with the above *trans*-product (178 mg, 0.34 mmol), Cu_2I_2 (6 mg, 0.0034 mmol), $Pd(PPh_3)_4$ (20 mg, 0.017 mmol) and Et_3N (2 mL). The content of the pressure tube was purged with nitrogen for 10 min. Trimethylsilylacetylene (40 mg, 0.407 mmol) was added to the flask. The flask was sealed with a Teflon cap and stirred at 80-90 °C for 6 h. The reaction

mixture was then allowed to cool to 25 °C and filtered. The filtrate was concentrated and the residue was chromatographed over silica gel to obtain the product **10**, 115 mg, 69%, colorless dense liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61-7.54 (4H, m), 7.50-7.49 (1H, m), 7.38-7.23 (9H, m), 2.55-2.51 (1H, m), 1.74-1.67 (1H, m), 1.49-1.44 (1H, dd, *J* = 15.0, 6.0 Hz), 1.37-1.32 (1H, m), 1.23-1.17 (1H, dd, *J* = 15.0, 7.6 Hz), 1.04 (9H, s), 0.76-0.71 (1H, m), 0.22 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.7, 142.6, 136.0, 135.9, 134.4, 134.3, 133.9, 130.3, 129.1, 129.0, 128.3, 127.9, 127.7, 127.5, 120.9, 103.5, 100.0, 31.6, 27.9, 24.4, 23.4, 18.1, 16.0, -0.10. Anal Calcd for $C_{32}H_{38}OSi_2$: C, 77.69; H, 7.74. Found: C, 77.56; H, 7.60.

Procedure for the preparation of 11. A solution of $TiCl_4$ (47 mg, 0.25 mmol) in anhydrous CH_2Cl_2 (0.5 mL) was added under nitrogen to a stirred solution of **10** (95 mg, 0.192 mmol) in anhydrous CH_2Cl_2 (0.8 mL) at - 78 °C. The reaction mixture turned deep red. After stirring for 2 h at – 78 °C, it was warmed slowly to – 40 °C. Stirring was continued at this temperature for 2 h and the reaction mixture was taken in Et_2O (20 mL). The ethereal layer was washed with saturated aqueous NH_4Cl (2 x 7 mL) and water (7 mL). The combined aqueous washings were extracted with Et_2O (2 x 7 mL). The combined organic extracts were washed with brine, dried, and concentrated. Purification of the crude residue by silica gel column chromatography (EtOAc/hexanes) gave pure product **11**, 76 mg, 85% yield, colorless dense liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68-7.65 (3H, m), 7.62-7.53 (4H, m), 7.41-7.31 (7H, m), 3.98-3.94 (1H, dd, *J* = 11.0, 7.3 Hz), 3.06-3.01 (1H, m), 1.77-1.72 (1H, dd, *J* = 12.2, 7.3 Hz), 1.48-1.24 (3H, m), 1.04 (9H, s), 0.20 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.8, 150.2, 144.2, 143.3, 141.7, 136.2, 136.07, 134.8, 134.2, 134.0, 129.22, 129.2, 128.3, 127.7, 127.6, 124.2, 123.7, 60.9, 52.7, 30.5, 27.8, 18.2, 14.6, -0.4. Anal. Calcd. for $C_{32}H_{38}OSi_2$: C, 77.69; H, 7.75. Found: C, 77.55; H, 7.65.