

Electronic Supplementary Information for

Silver-Catalyzed Silicon-Hydrogen Bond Functionalization by Carbene Insertion

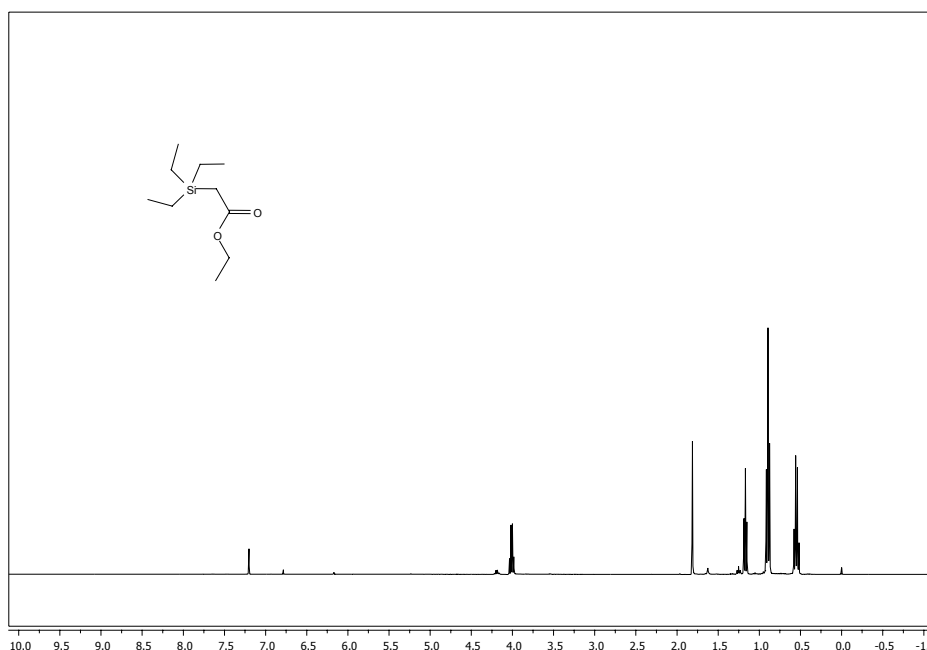
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Selected NMR data for compounds **3-13**, those of the competition experiments with different silanes and EDA, and those with other diazocompounds.

Ethyl 2-(triethylsilyl)acetate (3**):**

O. Andrey, Y. Landais, D. Planchenault, D. Weber, *Tetrahedron*, 1995, **51**, 12083.

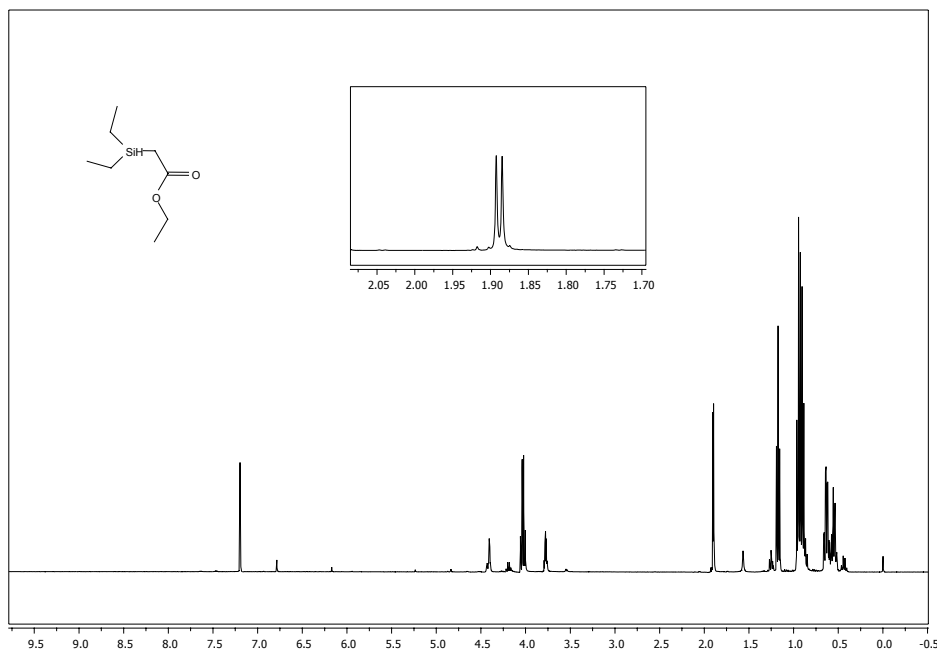
¹H NMR (400 MHz, CDCl₃): δ 0.55 (q, 2H, *J* = 7.9 Hz, SiCH₂CH₃), 0.89 (t, 3H, *J* = 7.9 Hz, SiCH₂CH₃), 1.17 (t, 3H, *J* = 7.1 Hz, CO₂CH₂CH₃), 1.81 (s, 2H, SiCH₂), 4.01 (q, 2H, *J* = 7.1 Hz, CO₂CH₂CH₃).



Ethyl-2-(diethylsilyl)acetate (4):

R. I. Pal'ChicK, L. L. Schchkovskaya, A. I. Kol'tsov. *Zhurnal Obschei Khimi*, 1969, **39**, 1792.

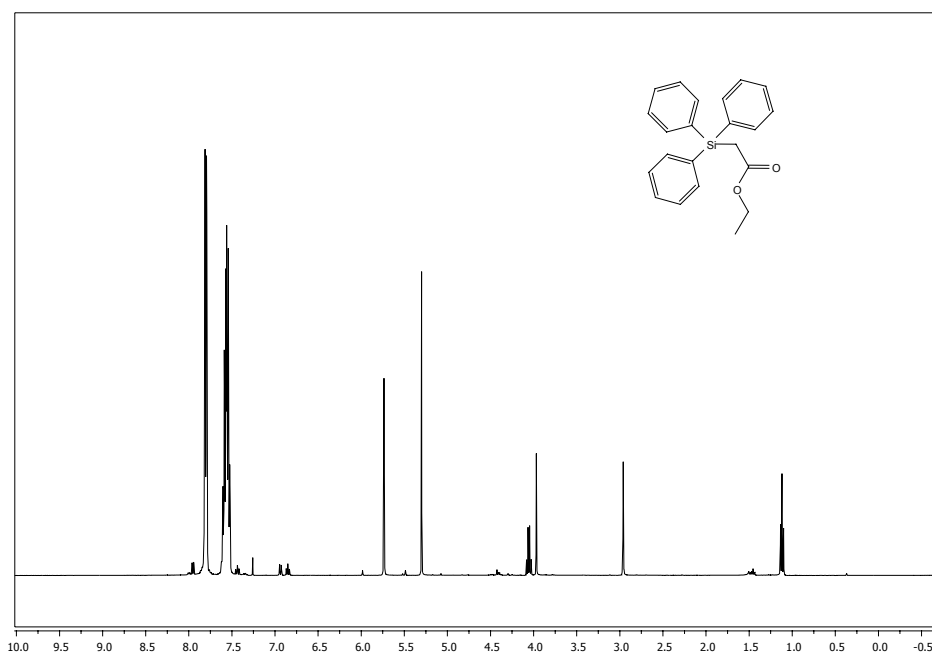
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 0.62 (q, 2H, $J = 7.9$ Hz, SiCH_2CH_3), 0.93 (t, 3H, $J = 7.9$ Hz, SiCH_2CH_3), 1.16 (t, 3H, $J = 7.1$ Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$) 1.89 (d, 2H, $J = 3.1$ Hz, SiCH_2), 3.78 (m, 1H, SiH), 4.02 (q, 2H, $J = 7.1$ Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$).



Ethyl 2-(triphenylsilyl)acetate (5):

O. Andrey, Y. Landais, D. Planchenault, D. Weber, *Tetrahedron*, 1995, **51**, 12083.

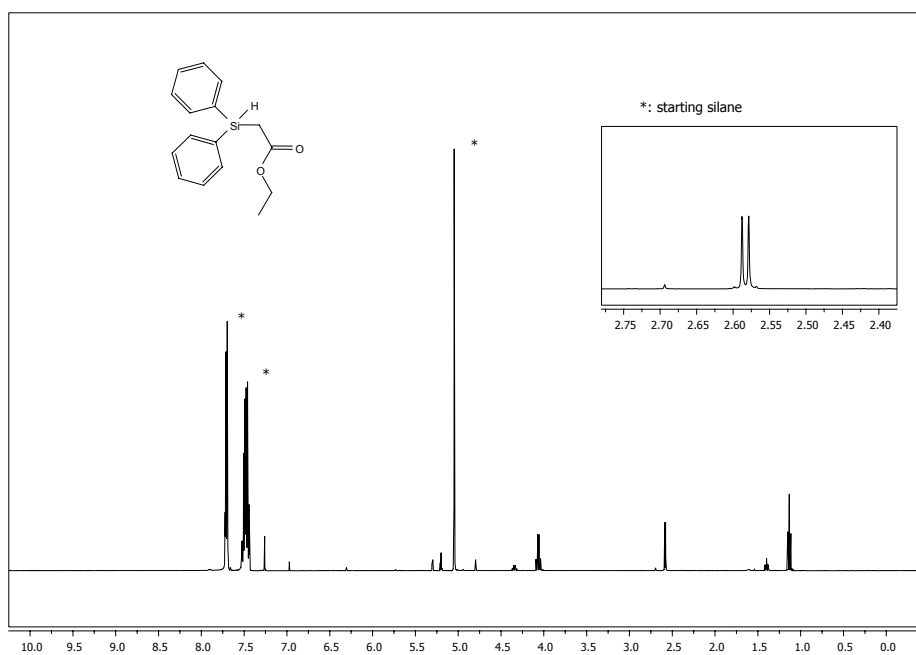
^1H NMR (400 MHz, CDCl_3): δ 1.12 (t, 3H, $J = 7.1$ Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$), 2.96 (s, 2H, SiCH_2), 4.06 (q, 2H, $J = 7.1$ Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$), 7.52-7.60 (m, 9H, CH_{Ar}), 7.39-7.81 (m, 6H, CH_{Ar}).



Ethyl 2-(diphenylsilyl)acetate (6):

K. A. W. Kramer, A. N. Wright, *J. Chem. Soc.*, 1963, 3604.

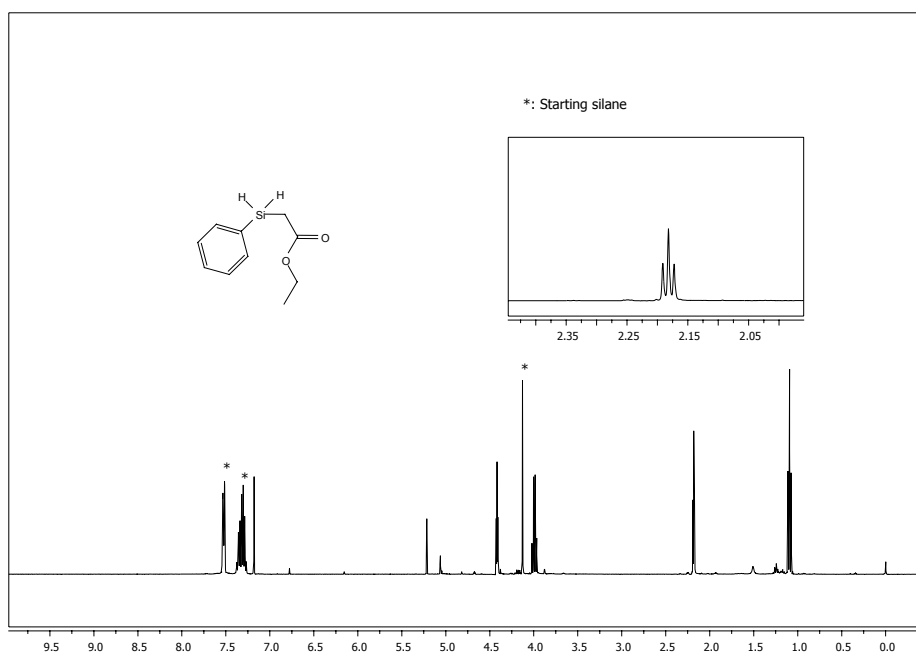
^1H NMR (400 MHz, CDCl_3): δ 1.13 (t, 3H, $J = 7.1$ Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$), 2.58 (d, 2H, $J = 3.6$ Hz, SiCH_2), 4.06 (q, 2H, $J = 7.1$ Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$), 5.20 (t, 1H, $J = 3.6$ Hz, SiH), 7.44-7.51 (m, 9H, CH_{Ar}), 7.69-7.72 (m, 6H, CH_{Ar}).



Ethyl 2-(phenylsilyl)acetate (7):

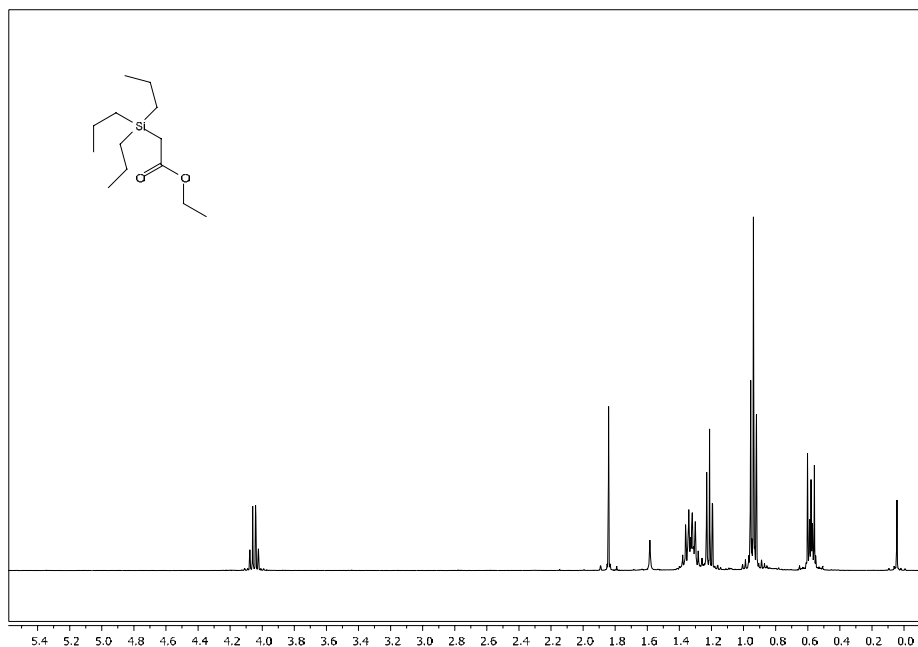
K. A. W. Kramer, A. N. Wright, *J. Chem. Soc.*, 1963, 3604.

^1H NMR (400 MHz, CDCl_3): δ 1.09 (t, 3H, $J = 7.1$ Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$), 2.18 (t, 2H, $J = 4.0$ Hz, SiCH_2), 3.99 (q, 2H, $J = 7.1$ Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$), 4.42 (t, 2H, $J = 4.0$ Hz, SiH), 7.25-7.40 (m, 9H, CH_{Ar}), 7.50-7.55 (m, 6H, CH_{Ar}).



Ethyl-2-(tripropylsilyl)acetate (8)

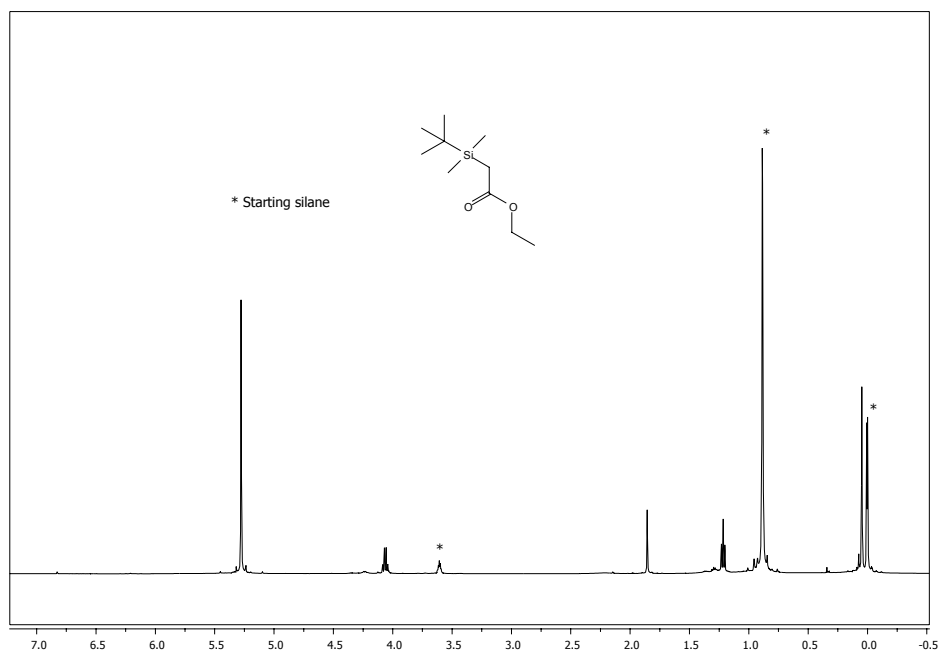
^1H NMR (400 MHz, CDCl_3): δ 0.58 (m, 2H, $\text{SiCH}_2\text{CH}_2\text{CH}_3$), 0.94 (t, 3H, $J = 7.0$ Hz, $\text{SiCH}_2\text{CH}_2\text{CH}_3$), 1.21 (t, 3H, $J = 7.1$ Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$), 1.28-1.38 (m, 2H, $\text{SiCH}_2\text{CH}_2\text{CH}_3$), 1.84 (s, 2H, CH_2Si), 4.05 (q, 2H, $J = 7.1$ Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$).



Ethyl-2-(*tert*-butyldimethylsilyl)acetate (**9**)

R. Green James, *Science of Synthesis*, 2006, 8a, 427.

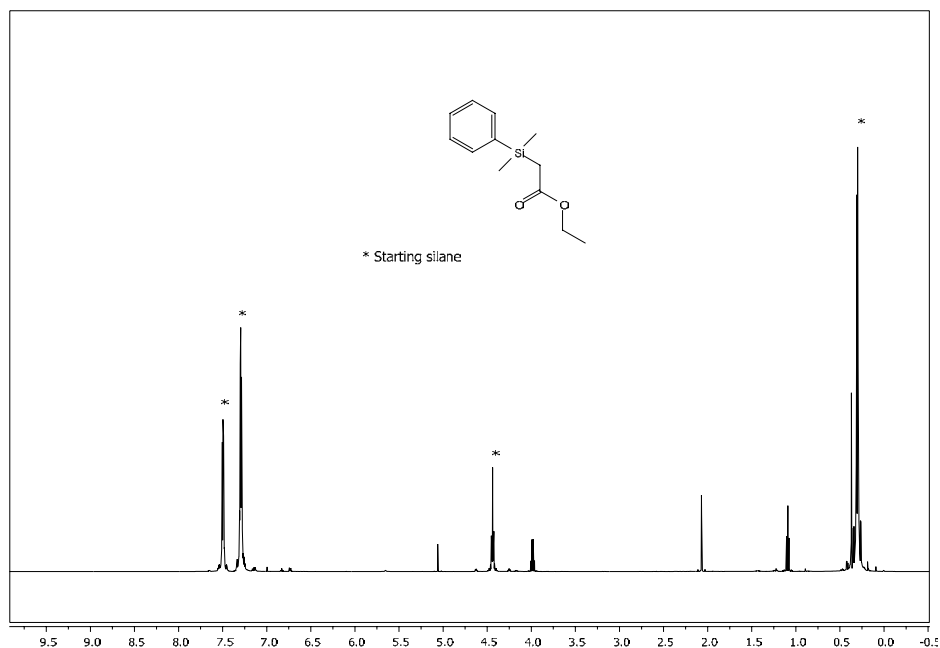
^1H NMR (400 MHz, CDCl_3): δ 0.05 (s, 6H, SiCH_3), 0.89 (s, 9H, $\text{SiC}(\text{CH}_3)_3$), 1.22 (t, 3H, $J = 7.1$ Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$), 1.86 (s, 2H, CH_2Si), 4.06 (q, $J = 7.1$ Hz, 2H, $\text{CO}_2\text{CH}_2\text{CH}_3$)



Ethyl-2-(dimethyl(phenyl)silyl)acetate (10)

R. J. Fessenden, S. Fessenden, *J. Org. Chem.*, 1967, **32**, 3235.

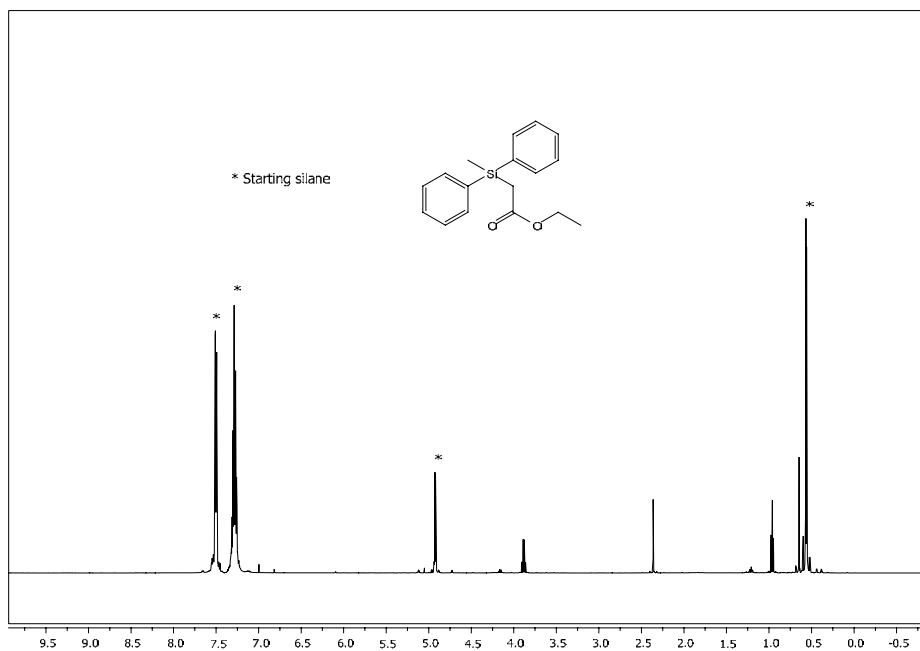
^1H NMR (400 MHz, CDCl_3): δ 0.30 (s, 6H, SiCH_3), 1.09 (t, 3H, $J = 7.1$ Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$), 2.07 (s, 2H, CH_2Si), 3.99 (q, 2H, $J = 7.1$ Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$), 7.28-7.30 (m, 3H, CH_{Ar}), 7.49-7.51 (m, 2H, CH_{Ar}).



Ethyl-2-(methyldiphenylsilyl)acetate (**11**)

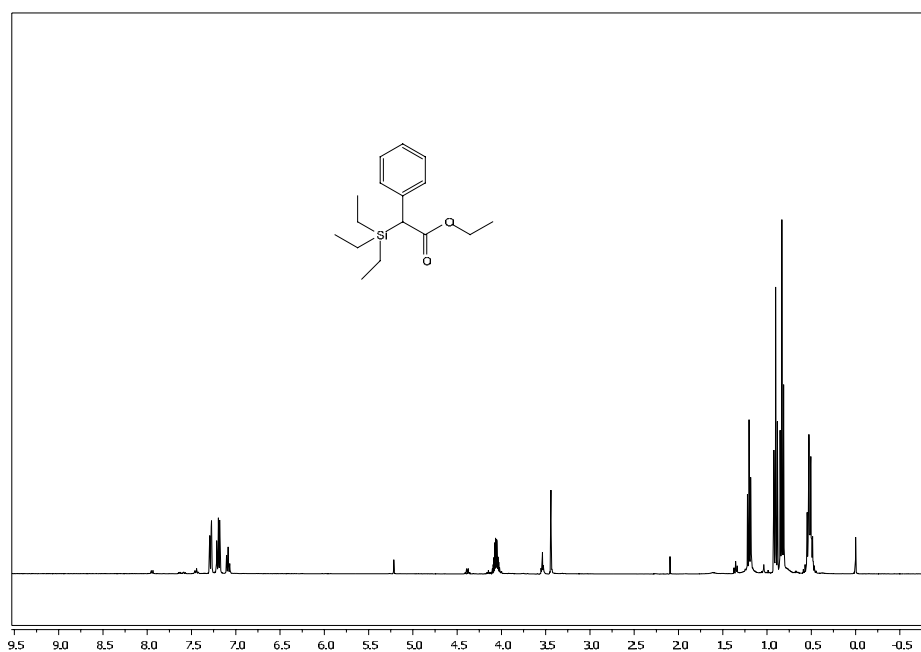
R. J. Fessenden, S. Fessenden, *J. Org. Chem.*, 1967, **32**, 3235.

^1H NMR (400 MHz, CDCl_3): δ 0.56 (s, 3H, SiCH_3), 0.96 (t, 3H, $J = 7.1$ Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$), 2.36 (s, 2H, CH_2Si), 3.88 (q, 2H, $J = 7.1$ Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$), 7.23-7.34 (m, 6H, CH_{Ar}), 7.59 (d, 4H, $J = 9.6$ Hz, CH_{Ar}).



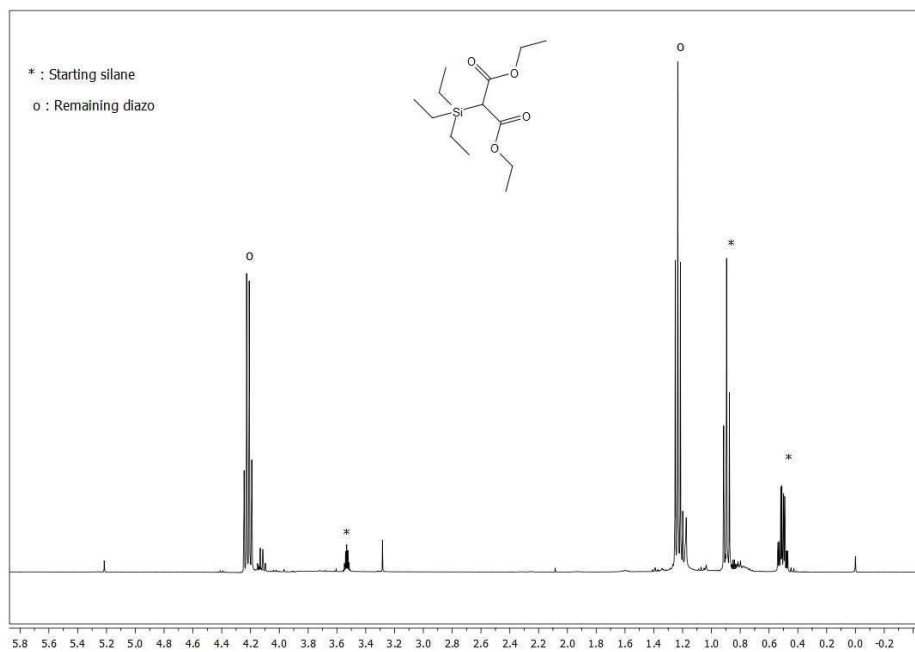
Ethyl-2-phenyl(2-triethylsilyl)acetate (12)

^1H NMR (400 MHz, CDCl_3): δ 0.52 (q, 6H, $J = 7.9$ Hz, CH_2CH_3), 0.83 (t, 9H, $J = 7.9$ Hz, CH_2CH_3), 1.20 (t, 3H, $J = 7.9$ Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$), 3.42 (s, 1H, SiCH), 4.06 (q, 2H, $J = 7.9$ Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$), 7.09 (t, 1H, $J = 7.9$ Hz, CH_{Ar}), 7.19 (t, 2H, $J = 7.9$ Hz, CH_{Ar}), 7.29 (d, 2H, $J = 7.9$ Hz, CH_{Ar}).



Diethyl-2-(triethylsilyl)malonate (13)

^1H NMR (400 MHz, CDCl_3): δ 0.45 (q, 2H, $J = 7.0$ Hz, SiCH_2CH_3), 0.84 (t, 3H, $J = 7.0$ Hz, SiCH_2CH_3), 1.20 (t, 3H, $J = 7.0$ Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$), 3.28 (s, 1H, CHSi), 4.12 (q, 2H, $J = 7.0$ Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$).



COMPETITION EXPERIMENTS WITH PHENYL (TOP) AND ETHYLSILANES
(BOTTOM)

