Electronic Supplementary Material (ESI) for ChemComm.

Organocatalytic Silyl Transfer from Silylborane to Nitroalkenes for the Synthesis of β-silyl nitroalkanes and β-Silyl Amines

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1. General Information.

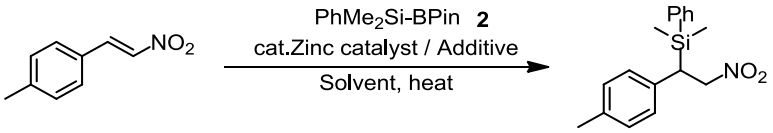
Components were visualized by UV and/or Phosphomolybdic acid staining. ^{1}H-, ^{13}C- and ^{29}Si-NMR were recorded on a Bruker Ascend^{TM} 400 spectrometers. Chemical shifts (in ppm) were referenced to internal solvent peaks (^{1}H, ^{13}C). Toluene, DCM, Et_2O, THF were removed from *Solvent Processing System*. All reagent were commercial available or synthesized according to literature reports.[1, 2]

2. Reaction Optimization.

General Procedure for Optimization: 0.1 mmol of nitroalkene **1b** and 0.15 mmol $Me_2PhSiBPin$ **2** were added into an over-dried thick-wall pressure vessel (10 mL) after catalyst and additives were added. Then 0.5 mL toluene/water (v/v = 4/1) mixed solvent was added. The reaction was heated at 50^{o}C for 12 h. After the reaction was over, yield was determined by ^{1}H NMR, using 4-acetylnitrobenzene as internal standard.

2.1 Effect of Zn(II) salts

Table S1a Optimization of zinc salts. [a, b]



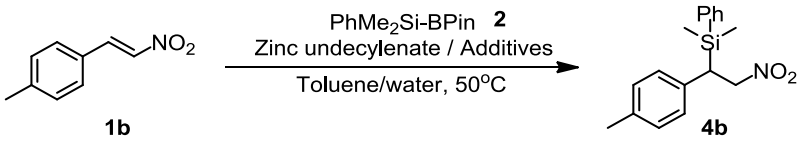
1b **4b**

Entry	Catalyst	Additives	Temp.[°C]	Solvent	Yield[%]
1	$ZnCl_2$	None	50	Dioxane/water	nr
2	$Zn(OAc)_2$	None	50	Dioxane/water	9
3	$Zn(acac)_2$	None	50	Dioxane/water	Trace
4	$Zn(OTf)_2$	None	50	Dioxane/water	Trace
5	Zinc undecylenate	None	50	Dioxane/water	13
6	Zinc undecylenate	**A1**	50	Dioxane/water	70
7	Zinc undecylenate	**B1**	50	Dioxane/water	25
8	Zinc undecylenate	**A1** + **B1**	50	Dioxane/water	77
9	$ZnCl_2$	**A1** + **B1**	50	Dioxane/water	nr
10	$Zn(OAc)_2$	**A1** + **B1**	50	Dioxane/water	69
11	$Zn(acac)_2$	**A1** + **B1**	50	Dioxane/water	47
12	$Zn(OTf)_2$	**A1** + **B1**	50	Dioxane/water	46
13	$Zn(OH)_2$	**A1** + **B1**	50	Dioxane /water	Trace
14	Zinc methacrylate	**A1** + **B1**	50	Toluene/water	93
15	Zinc undecylenate	**A1** + **B1**	50	MeOH	Trace
16	Zinc undecylenate	**A1** + **B1**	50	DCM/water	70
17 [c]	Zinc undecylenate	**A1** + **B1**	50	Toluene/water	>95

[a]General procedure: Nitroalkene **1b** (0.1 mmol), $Me_2PhSiBPin$ **2** (1.5 equiv), and 10 mol% catalyst with 20 mol% **A1** or/and 20 mol% **B1** in 0.5 mL toluene/water (v/v = 4/1) mix solvent for 12 h. [b]400M ^{1}H-NMR was used to determine the yields. 4-acetylnitrobenzene was used as internal standard. [c]Reaction underwent with 5 mol% **A1** and 5 mol% **B1**.

2.2 Effect of Additives

Table S1b Optimization of additives. [a, b]



1b 4b

Entry	Catalyst	Additives	Temp.[°C]	Solvent	Yield[%]
1	Zinc undecylenate	**A2** + **B1**	50	Toluene/water	89
2	Zinc undecylenate	**A1** + **B2**	50	Toluene/water	51
3	Zinc undecylenate	**A1** + **B3**	50	Toluene/water	84
4	Zinc undecylenate	**A1** + **B4**	50	Toluene/water	39
5	Zinc undecylenate	**A1** + **B5**	50	Toluene/water	46
6	Zinc undecylenate	**A1** + **B6**	50	Toluene/water	51
7	Zinc undecylenate	**A1** + **B7**	50	Toluene/water	82
8	Zinc undecylenate	**A1** + **B8**	50	Toluene/water	59
9	Zinc undecylenate	**A1** + **B9**	50	Toluene/water	nr
10	Zinc undecylenate	**A1** + **B10**	50	Toluene/water	nr
11	Undecylenic acid	**A1** + **B1**	50	Toluene/water	93
12	Undecylenic acid	**A1**	50	Toluene/water	60
13	Undecylenic acid	**B1**	50	Toluene/water	20
14	Undecylenic acid	--	50	Toluene/water	nr
15	Undecylenic acid	**A2** + **B1**	50	Toluene/water	24

[a]General procedure: Nitroalkene **1b** (0.1 mmol), $Me_2PhSiBPin$ **2** (1.5 equiv), 10 mol% zinc undecylenate with 5 mol% **A1** and 5 mol% **B1** in 0.5 mL toluene/water (v/v = 4/1) mix solvent for 12 h. [b]400M ^{1}H-NMR was used to determine the yields. 4-acetylnitrobenzene was used as internal standard.

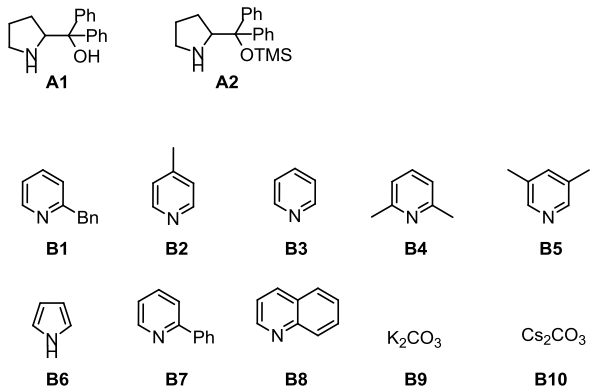
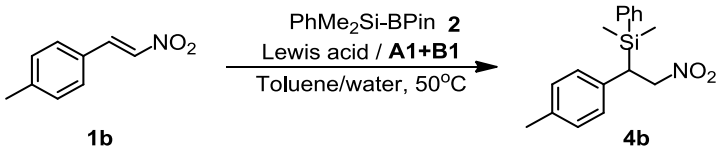


Figure S1 Additives in optimization.

2.3 Effect of Other Lewis acids

Table S1c Optimization of Lewis acids. [a, b]



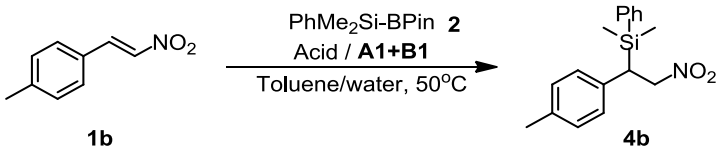
1b **4b**

Entry	Catalyst	Additives	Temp.[°C]	Solvent	Yield[%]
1	$AlCl_3$	**A1** + **B1**	50	Dioxane/water	NR
2	$TiCl_4$	**A1** + **B1**	50	Dioxane/water	NR
3	Ag_2CO_3	**A1** + **B1**	50	Dioxane/water	35
4	$AgNO_3$	**A1** + **B1**	50	Dioxane/water	NR
5	CF_3COOAg	**A1** + **B1**	50	Dioxane/water	NR
6	PhCOOAg	**A1** + **B1**	50	Dioxane/water	54
7	$Co(OAc)_2$	**A1** + **B1**	50	Dioxane/water	Trace
8	$TiCl_2Cp_2$	**A1** + **B1**	50	Dioxane/water	NR
9	$Mn(OAc)_2$	**A1** + **B1**	50	Dioxane/water	90
10	AgOAc	**A1** + **B1**	50	Dioxane/water	94
11	Ti(O*i*-Pr)$_4$	**A1** + **B1**	50	Dioxane/water	92

[a]General procedure: Nitroalkene **1b** (0.1 mmol), $Me_2PhSiBPin$ **2** (1.5 equiv), and 10 mol% catalyst with 5 mol% **A1** and 5 mol% **B1** in 0.5 mL toluene/water (v/v = 4/1) mix solvent for 12 h. [b]400M ^{1}H-NMR was used to determine the yields. 4-acetylnitrobenzene was used as internal standard.

2.4 Effect of Other Protic Acids

Table S1d Optimization of acids. [a, b]



1b 4b

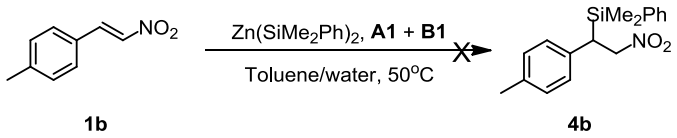
Entry	Catalyst	Additives	Temp.[°C]	Solvent	Yield[%]
1	AcOH	**A1** + **B1**	50	Dioxane/water	39
2	HBF_4	**A1** + **B1**	50	Dioxane/water	NR
3	Undecylenate acid	**A1** + **B1**	50	Dioxane/water	61
4	Undecylenate acid	**A1** + **B1**	50	Toluene/water	93
5	Undecanoic acid	**A1** + **B1**	50	Toluene/water	85
6	None	**A1** + **B1**	50	Dioxane/water	NR

[a]General procedure: Nitroalkene **1b** (0.1 mmol), $Me_2PhSiBPin$ **2** (1.5 equiv), and 10 mol% acid catalyst with 5 mol% **A1** and 5 mol% **B1** in 0.5 mL toluene/water (v/v = 4/1) mix solvent for 12 h. [b]400M ^{1}H-NMR was used to determine the yields. 4-acetylnitrobenzene was used as internal standard.

3. Preliminary Mechanistic Study.

3.1 Silylation Using Putative $Zn(SiMe_2Ph)_2$

Table S2 Optimization with $Zn(SiMePh)_2$.



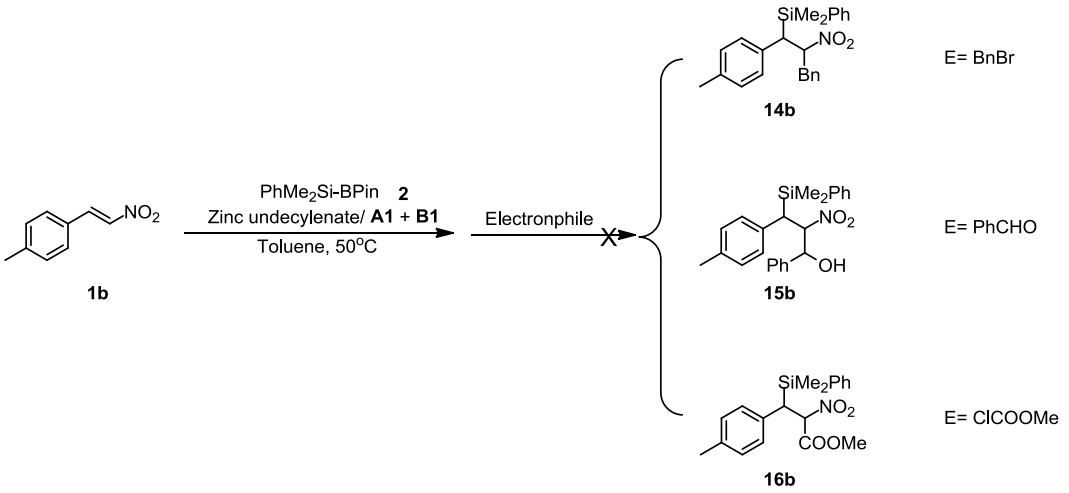
1b **4b**

Entry	Catalyst	Additives	Temp.[°C]	Solvent	Yield[%]
1	None	**A1**	50	Dioxane/water	NR
2	None	**B1**	50	Dioxane/water	NR
3	None	**A1** + **B1**	50	Dioxane/water	NR
4	Undecylenate acid	None	50	Dioxane/water	NR
5	Undecylenate acid	**A1** + **B1**	50	Dioxane/water	NR

General procedure: Nitroalkene **1b** (0.1 mmol), $Zn(SiMePh)_2$ (2.0 equiv), and 10 mol% undecylenate acid catalyst with 5 mol% **A1** and 5 mol% **B1** in 0.5 mL dioxane/water (v/v = 4/1) mix solvent for 12 h.

$Zn(SiMe_2Ph)_2$ was prepared and verified the reactivity according to work of Oestreich's.[3] 1.0 equiv of Nitroalkene **1b** (0.1 mmol) was added into an over-dried thick-wall pressure vessel (10 mL) in 0.5 mL dioxane/water (v/v = 4/1) under Ar protection. 2.0 equiv of $Zn(SiMe_2Ph)_2$ was added by syringe in a little amount of toluene afterwards. The reaction was heated for 12 h at 50°C, and monitored by TLC.

3.2 Attempts to Trapping with Electronphiles[4]

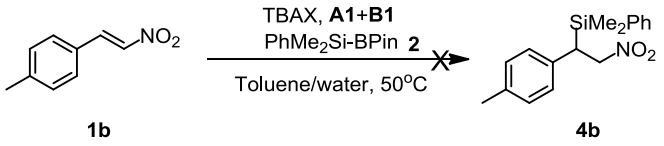


1b **14b** **15b** **16b**

Nitroalkene **1b** (0.1 mmol), $Me_2PhSiBPin$ **2** (1.5 equiv), and 10 mol% zinc undecylenate with 5 mol% **A1** and 5 mol% **B1** in 0.5 mL toluene were added into an over-dried thick-wall pressure vessel (10 mL) under Ar protection. Electronphile was added using a syringe after heated for 2 h at 50°C. The reaction was heated for another 12 h at 50°C. After the reaction was over, water was

added to the mixed system to quench the reaction. After another 30 mins stirring, yield was determined by ^{1}H NMR, using 4-acetylnitrobenzene as internal standard.

3.3 Test with Phase Transfer Agents and Surfactants

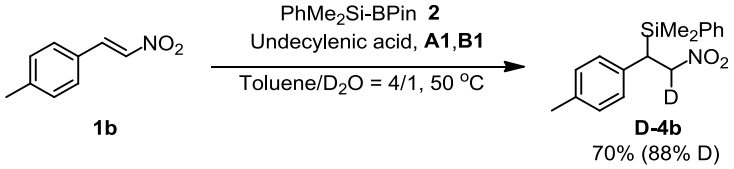


1b **4b**

TBAX = TBAC, or TBAB, or TBAI

Nitroalkene **1b** (0.1 mmol), $Me_2PhSiBPin$ **2** (1.5 equiv), and 10 mol% TBAX (TBAX = TBAC, or TBAB, or TBAI), with 5 mol% **A1** and 5 mol% **B1** in 0.5 mL toluene/water (v/v = 4/1) were added into an over-dried thick-wall pressure vessel (10 mL) under Ar protection. The reaction was heated for 12 h at 50°C. After the reaction was over, yield was determined by ^{1}H NMR, using 4-acetylnitrobenzene as internal standard.

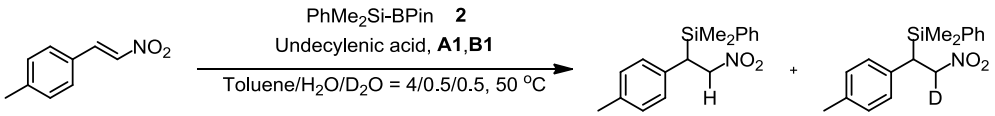
3.4 Deuterium Labeled Experiments



1b **D-4b**

70% (88% D)

Nitroalkene **1b** (0.1 mmol), 10 mol% undecylenate acid, 5 mol% **A1**, 5 mol% **B1**, 1.5 equiv $Me_2PhSiBPin$ **2** were added into an over-dried thick-wall pressure vessel (10 mL) under Ar protection. Next, 0.2 M toluene/D_2O (v/v = 4/1) mixed solvent was added to vessel. The reaction was heated at 50°C for 12 h, monitored by TLC. After the reaction was over, the resulted mixture was extracted 3 times with DCM. The organic phases were collected, dried with $MgSO_4$, filtered and the solvent was evaporated in vacuo. The resulting oil was purified with silica gel chromatography. A mobile phase consisting of petroleum ether/ethyl acetate (v/v) 60/1 was used as eluent.



1b **4b** : **D-4b**

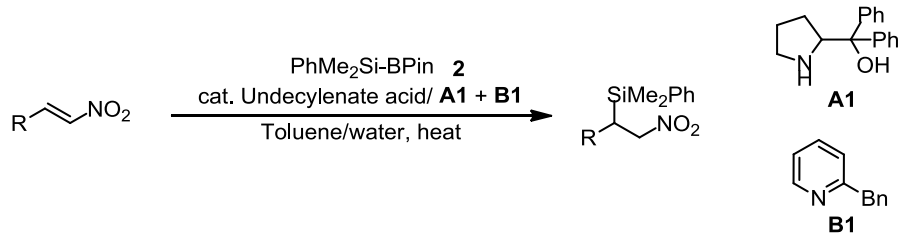
100 : 5

91%

Nitroalkene **1b** (0.1 mmol), 10 mol% undecylenate acid, 5 mol% **A1**, 5 mol% **B1**, 1.5 equiv $Me_2PhSiBPin$ **2** were added into an over-dried thick-wall pressure vessel (10 mL). Next, 0.2 M toluene/H_2O/D_2O (v/v/v = 4/0.5/0.5) mixed solvent was added to vessel. The reaction was heated at 50°C for 12 h, monitored by TLC. After the reaction was over, the resulted mixture was extracted 3 times with DCM. The organic phases were collected, dried with $MgSO_4$, filtered and the solvent was evaporated in vacuo. The resulting oil was purified with silica gel chromatography. A mobile phase consisting of petroleum ether/ethyl acetate (v/v) 60/1 was used as eluent

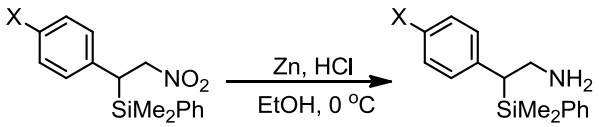
4. General Procedure for β-Silylation and Reduction of β-Silyl Nitroalkane.

4.1 General Procedure I: β-Silylation.



1.0 equiv of nitroalkene **1**, 10 mol% undecylenate acid, 5 mol% **A1**, 5 mol% **B1**, 1.5 equiv $Me_2PhSiBPin$ **2** were added into an over-dried thick-wall pressure vessel (10 mL). Next, 0.2 M toluene/water (v/v = 4/1) mixed solvent was added to vessel. The reaction was heated at 50°C for 4 to 12 h, monitored by TLC. After the reaction was over, the resulted mixture was extracted 3 times with DCM. The organic phases were collected, dried with $MgSO_4$, filtered and the solvent was evaporated in vacuo. The resulting oil was purified with silica gel chromatography. A mobile phase consisting of petroleum ether/ethyl acetate (v/v) from 100/1 to 4/1 can be used as eluent.

4.2 General Procedure II: Reduction of β-Silyl Nitroalkane.



4b: X = Me
4i: X = Br

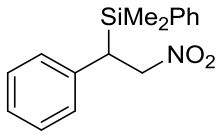
13b: 95% yield
13i: 79% yield

10 equiv zinc powder was added to a solution of 1 equiv **4** in 0.17M EtOH to an over-dried round-bottomed flask. Next, 15 equiv of 0.48M hydrochloric acid was added by drop at 0°C. The reaction was tracked by TLC. After the reaction was over, the resulted mixture was extracted with DCM 3 times. The organic phases were collected, dried with $MgSO_4$, filtered and the solvent was evaporated in vacuo. The sample was purified using silica gel chromatography with a mobile phase consisting of DCM/MeOH (v/v) from 30/1 to 10/1.

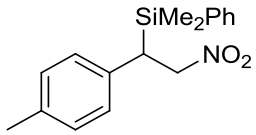
5. References.

1. (a) C. Xu, J. Du, L. Ma, G. Li, M. Tao and W. Zhang, *Tetrahedron*, 2013, **69**, 4749-4757. (b)D. M. Mampreian and A. H. Hoveyda, *Org. Lett.* 2004, **6**, 2829-2832.
2. M. Suginome, T. Matsuda and Y. Ito, *Organometallics*, 2000, **19**, 4647-4649.
3. (a) C. K. Hazra and M. Oestreich, *Org. Lett.* 2012, **14**, 4010-4013. (b) E. S. Schmidtmann and M. Oestreich, *Chem. Commun.*2006, 3643-3645.
4. J. Rae, Y. C. Hu and D. J. Procter, *Chem. Eur. J.* 2014, **20**, 13143-13145.

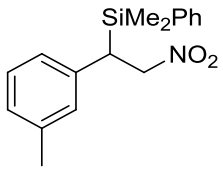
6. Spectroscopic Data of Key Compounds.



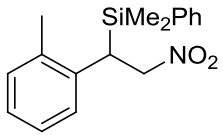
Dimethyl(2-nitro-1-phenylethyl)(phenyl)silane (**4a**): Following General Procedure **I**, 44.8 mg **1a** was converted into 76.1 mg of **4a** as a light yellow oil (89.3% yield). TLC: 20/1 Petroleum ether/Ethyl acetate, R_f = 0.55. **^{1}H-NMR** ($CDCl_3$, 400M, ppm): δ7.44-7.37 (m,5H), 7.26-7.13 (m, 3H), 7.00-6.97 (m, 2H), 4.86-4.80 (t, *J* = 13.51 Hz, 1H), 4.53-4.48 (dd, *J* = 3.76, 13.51 Hz, 1H), 3.29-3.25 (dd, *J* = 3.76, 13.51 Hz, 1H), 0.31 (s, 3H), 0.29 (s, 3H) ; **^{13}C-NMR** ($CDCl_3$, 101M, ppm): δ137.68, 135.00, 134.05, 130.15, 128.72, 128.33, 127.45, 126.23, 77.04, 36.25, -3.81, -5.32 ; **^{29}Si-NMR** ($CDCl_3$, 80M, ppm): δ-2.02. HRMS [ESI, $(M+Na)^+$]: for $C_{16}H_{19}NO_2Si$ found 308.1074, calcd. 308.1077.



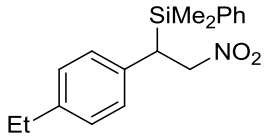
Dimethyl(2-nitro-1-(p-tolyl)ethyl)(phenyl)silane (**4b**): Following General Procedure **I**, 49.0 mg **1b** was converted into 83.2 mg **4b** as a light yellow oil (92.6% yield). TLC: 20/1 Petroleum ether/Ethyl acetate, R_f = 0.55. **^{1}H-NMR** ($CDCl_3$, 400M, ppm): δ7.46-7.37 (m, 5H), 7.06-7.04 (d, *J* = 7.92 Hz, 2H), 6.89-6.87 (d, *J* = 7.92 Hz, 2H), 4.83-4.78 (t, *J* = 13.45 Hz, 1H), 4.51-4.46 (dd, *J* = 3.8, 13.45 Hz, 1H), 3.25-3.20 (dd, *J* = 3.8, 13.45 Hz, 1H), 2.30 (s, 3H), 0.30 (s, 3H), 0.29 (s, 3H) ; **^{13}C-NMR** ($CDCl_3$, 101M, ppm): δ135.71, 135.21, 134.45, 134.06, 130.09, 129.44, 128.32, 127.34, 77.21, 35.79, 21.10, -3.74, -5.32 ; **^{29}Si-NMR** ($CDCl_3$, 80M, ppm): δ-2.24. HRMS [ESI, $(M+Na)^+$]: for $C_{17}H_{21}NO_2Si$ found 322.1237, calcd. 322.1234.



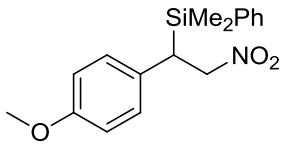
Dimethyl(2-nitro-1-(m-tolyl)ethyl)(phenyl)silane (**4c**): Following General Procedure **I**, 81.5 mg **1c** was converted into 116.3 mg **4c** as a light yellow oil (77.0% yield). TLC: 20/1 Petroleum ether/Ethyl acetate, R_f = 0.55. **^{1}H-NMR** ($CDCl_3$, 400M, ppm): δ7.46-7.39 (m, 5H), 7.17-7.13 (t, *J* = 7.54 Hz, 1H), 7.00-6.98 (d, *J* = 7.54 Hz, 1H), 6.83-6.81 (d, *J* = 7.54 Hz, 1H), 6.81-6.78 (s, 1H), 4.87-4.80 (t, *J* = 13.44 Hz, 1H), 4.54-4.49 (dd, *J* = 3.76, 13.44 Hz, 1H), 3.27-3.23 (dd, *J* = 3.76, 13.44 Hz, 1H), 2.29 (s, 3H), 0.32 (s, 3H), 0.31 (s, 3H) ; **^{13}C-NMR** ($CDCl_3$, 101M, ppm): δ138.15, 137.51, 135.11, 134.05, 130.07, 128.50, 128.32, 128.24, 126.97, 124.39, 77.02, 36.01, 21.53, -3.85, -5.33 ; **^{29}Si-NMR** ($CDCl_3$, 80M, ppm): δ-2.14. HRMS [ESI, $(M+Na)^+$]: for $C_{17}H_{21}NO_2Si$ found 322.1234, calcd. 322.1234.



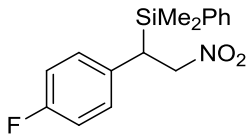
Dimethyl(2-nitro-1-(o-tolyl)ethyl)(phenyl)silane (**4d**): Following General Procedure **I**, 81.5 mg **1d** was converted into 116.0 mg **4d** as a light yellow oil (76.8% yield). TLC: 20/1 Petroleum ether/Ethyl acetate, R_f = 0.55. **^{1}H-NMR** ($CDCl_3$, 400M, ppm): δ7.45-7.36 (m, 5H), 7.12-7.03 (m, 3H), 6.90-6.90 (m, 1H), 4.85-4.79 (t, *J* = 13.52 Hz, 1H), 4.56-4.52 (dd, *J* = 3.68, 13.52 Hz, 1H), 3.60-3.55 (dd, *J* = 3.68, 13.52 Hz, 1H), 2.25 (s, 3H), 0.35 (s, 3H), 0.27 (s, 3H) ; **^{13}C-NMR** ($CDCl_3$, 101M, ppm): δ136.36, 136.27, 135.30, 134.04, 131.03, 130.16, 128.33, 126.23, 125.96, 125.54, 77.70, 30.66, 20.30, -3.75, -5.21 ; **^{29}Si-NMR** ($CDCl_3$, 80M, ppm): δ-1.90. HRMS [ESI, $(M+Na)^+$]: for $C_{17}H_{21}NO_2Si$ found 322.1230, calcd. 322.1234.



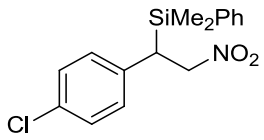
(1-(4-ethylphenyl)-2-nitroethyl)dimethyl(phenyl)silane (**4e**): Following General Procedure **I**, 88.5 mg **1e** was converted into 87.0 mg **4e** as a light yellow oil (55.1% yield). TLC: 20/1 Petroleum ether/Ethyl acetate, R_f = 0.55. **^{1}H-NMR** ($CDCl_3$, 400M, ppm): δ7.44-7.37 (m, 5H), 7.08-7.06 (d, *J* = 8.04 Hz, 2H), 6.91-6.89 (d, *J* = 8.04 Hz, 2H), 4.84-4.77 (t, *J* = 13.4 Hz, 1H), 4.50-4.46 (dd, *J* = 3.8, 13.4 Hz, 1H), 3.26-3.21 (dd, *J* = 3.8, 13.4 Hz, 1H), 263-2.57 (q, *J* = 7.6 Hz, 2H), 1.23-1.19 (t, *J* = 7.6 Hz, 3H), 0.30 (s, 3H), 0.28 (s, 3H) ; **^{13}C-NMR** ($CDCl_3$, 101M, ppm): δ142.04, 135.27, 134.65, 134.06, 130.09, 128.31, 128.19, 127.37, 77.21, 35.78, 28.45, 15.48, -3.71, -5.32 ; **^{29}Si-NMR** ($CDCl_3$, 80M, ppm): δ-2.21. HRMS [ESI, $(M+Na)^+$]: for $C_{18}H_{23}NO_2Si$ found 336.1392, calcd. 336.1390.



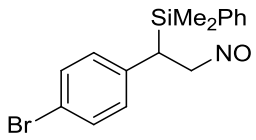
(1-(4-methoxyphenyl)-2-nitroethyl)dimethyl(phenyl)silane (**4f**): Following General Procedure **I**, 89.5 mg **1f** was converted into 130.1 mg **4f** as a yellow oil (81.8% yield). TLC: 20/1 Petroleum ether/Ethyl acetate, R_f = 0.30. **^{1}H-NMR** ($CDCl_3$, 400M, ppm): δ7.43-7.36 (m, 5H), 6.90-6.87 (dd, *J* = 2.04, 6.6 Hz, 2H), 6.80-6.77 (dd, *J* = 2.04, 6.6 Hz, 2H), 4.78-4.72 (t, *J* = 13.38 Hz, 1H), 4.51-4.47 (dd, *J* = 3.84, 13.38 Hz, 1H), 3.77 (s, 3H), 3.21-3.17 (dd, *J* = 3.84, 13.38 Hz, 1H), 0.30 (s, 3H), 0.28 (s, 3H) ; **^{13}C-NMR** ($CDCl_3$, 101M, ppm): δ158.07, 135.19, 134.07, 130.11, 129.46, 128.46, 128.32, 114.22, 77.42, 55.34, 35.35, -3.77, 5.24 ; **^{29}Si-NMR** ($CDCl_3$, 80M, ppm): δ-2.28. HRMS [ESI, $(M+Na)^+$]: for $C_{17}H_{21}NO_3Si$ found 338.1185, calcd. 338.1183.



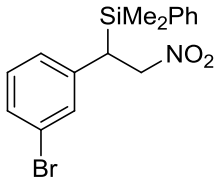
(1-(4-fluorophenyl)-2-nitroethyl)dimethyl(phenyl)silane (**4g**): Following General Procedure **I**, 50.3 mg **1g** was converted into 55.2 mg **4g** as a light yellow solid (60.9% yield). TLC: 20/1 Petroleum ether/Ethyl acetate, R_f = 0.50. MP: 55-59 ^{o}C.**^{1}H-NMR** ($CDCl_3$, 400M, ppm): δ7.46-7.37 (m, 5H), 6.95-6.93 (m, 4H), 4.80-4.73 (t, *J* = 13.48 Hz, 1H), 4.55-4.50 (dd, *J* = 3.8, 13.48 Hz, 1H), 3.27-3.23 (dd, *J* = 3.8, 13.48 Hz, 1H), 0.31 (s, 3H), 0.30 (s, 3H) ; **^{13}C-NMR** ($CDCl_3$, 101M, ppm): δ161.41 (d, *J* = 245 Hz), 134.65, 134.03, 133.38 (d, *J* = 3.0 Hz), 130.25, 128.81 (d, *J* = 7.0 Hz), 128.36, 115.63 (d, *J* = 21.0 Hz), 77.16, 35.61, -3.98, -5.28 ; **^{29}Si-NMR** ($CDCl_3$, 80M, ppm): δ-2.00. HRMS [ESI, $(M+Na)^+$]: for $C_{16}H_{18}FNO_2Si$ found 326.0983, calcd. 326.0983.



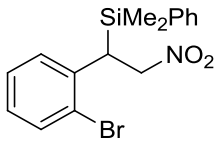
(1-(4-chlorophenyl)-2-nitroethyl)dimethyl(phenyl)silane (**4h**): Following General Procedure **I**, 41.7 mg **1h** was converted into 56.0 mg **4h** as a light yellow solid (67.9% yield). TLC: 20/1 Petroleum ether/Ethyl acetate, R_f = 0.50. MP: 78-81 ^{o}C. **^{1}H-NMR** ($CDCl_3$, 400M, ppm): δ7.45-7.37 (m, 5H), 7.22-7.20 (d, *J* = 8.4 Hz, 2H), 6.90-6.88 (d, *J* = 8.4 Hz, 2H), 4.79-4.72 (t, *J* = 13.52 Hz, 1H), 4.53-4.49 (dd, *J* = 3.76, 13.52 Hz, 1H), 3.26-3.21 (dd, *J* = 3.76, 13.52 Hz, 1H), 0.31 (s,3H), 0.30 (s,3H) ; **^{13}C-NMR** ($CDCl_3$, 101M, ppm): δ136.35, 134.48, 134.05, 132.01, 130.34, 128.91, 128.70, 128.43, 77.37, 35.91, -3.94, -5.27 ; **^{29}Si-NMR** ($CDCl_3$, 80M, ppm): δ-1.95. HRMS [ESI, $(M+Na)^+$]: for $C_{16}H_{18}ClNO_2Si$ found 342.0684, calcd. 342.0688.



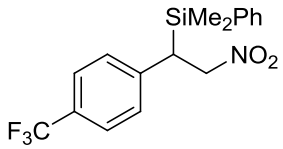
(1-(4-bromophenyl)-2-nitroethyl)dimethyl(phenyl)silane (**4i**): Following General Procedure **I**, 115.3 mg **1i** was converted into 117.1 mg **4i** as a yellow solid (63.5% yield). TLC: 20/1 Petroleum ether/Ethyl acetate, R_f = 0.50. MP: 73-76 ^{o}C.**^{1}H-NMR** ($CDCl_3$, 400M, ppm): δ7.47-7.35 (m, 7H), 6.84-6.82 (m, 2H), 4.79-4.72 (t, *J* = 13.58 Hz, 1H), 4.52-4.48 (dd, *J* = 3.68, 13.58 Hz, 1H), 3.24-3.20 (dd, *J* = 3.68, 13.58 Hz, 1H), 0.30 (s, 3H), 0.29 (s, 3H) ; **^{13}C-NMR** ($CDCl_3$, 101M, ppm): δ136.89, 134.42, 134.05, 131.84, 130.36, 129.07, 128.44, 119.99, 76.77, 35.97, -3.94, -5.28 ; **^{29}Si-NMR** ($CDCl_3$, 80M, ppm): δ-2.03. HRMS [ESI, $(M+Na)^+$]: for $C_{16}H_{18}BrNO_2Si$ found 388.0165, calcd. 388.0163.



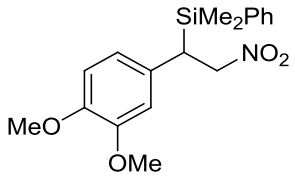
(1-(3-bromophenyl)-2-nitroethyl)dimethyl(phenyl)silane (**4j**): Following General Procedure **I**, 68.1 mg **1j** was converted into 66.8 mg **4j** as a yellow oil (61.5% yield). TLC: 20/1 Petroleum ether/Ethyl acetate, R_f = 0.50. **^{1}H-NMR** ($CDCl_3$, 400M, ppm): δ7.45-7.39 (m, 5H), 7.30-7.26 (d, *J* = 7.72 Hz, 1H), 7.13-7.08 (t, *J* = 7.72 Hz, 1H), 7.08 (s, 1H), 6.90-6.89 (d, *J* = 7.72 Hz, 1H), 4.79-4.72 (t, *J* = 13.54 Hz, 1H), 4.52-4.47 (dd, *J* = 3.72, 13.54 Hz, 1H), 3.24-3.19 (dd, *J* = 3.72, 13.54 Hz, 1H), 0.32 (s, 6H) ; **^{13}C-NMR** ($CDCl_3$, 101M, ppm): δ140.32, 134.32, 134.04, 130.49, 130.39, 130.21, 129.39, 128.43, 125.94, 122.85, 76.66, 36.12, -3.97, -5.29 ; **^{29}Si-NMR** ($CDCl_3$, 80M, ppm): δ-1.70. HRMS [ESI, $(M+Na)^+$]: for $C_{16}H_{18}BrNO_2Si$ found 388.0159, calcd. 388.0163.



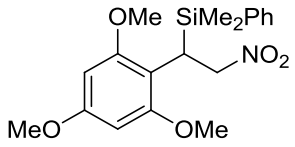
(1-(2-bromophenyl)-2-nitroethyl)dimethyl(phenyl)silane (**4k**): Following General Procedure **I**, 68.8 mg **1k** was converted into 100.6 mg **4k** as a yellow oil (91.7% yield). TLC: 20/1 Petroleum ether/Ethyl acetate, R_f = 0.50. **^{1}H-NMR** ($CDCl_3$, 400M, ppm): δ7.58-7.57 (dd, *J* = 1.36, 7.8 Hz, 1H), 7.56-7.38 (m, 5H), 7.23-7.18 (ddd, *J* = 1.36, 7.8, 15.4 Hz, 1H), 7.05-7.00 (ddd, *J* = 1.36, 7.8, 15.4 Hz, 1H), 6.94-6.91 (dd, *J* = 1.36, 7.8 Hz, 1H), 4.79-4.71 (t, *J* = 13.83 Hz, 1H), 4.52-4.47 (dd, *J* = 3.82, 13.83 Hz, 1H), 3.24-3.19 (dd, *J* = 3.82, 13.83 Hz, 1H), 0.34 (s, 3H), 0.33 (s, 3H) ; **^{13}C-NMR** ($CDCl_3$, 101M, ppm): δ137.83, 134.74, 134.12, 133.71, 130.32, 128.42, 127.69, 127.52, 126.74, 125.31, 77.36, 34.21, -3.55, -5.49 ; **^{29}Si-NMR** ($CDCl_3$, 80M, ppm): δ-0.97. HRMS [ESI, $(M+Na)^+$]: for $C_{16}H_{18}BrNO_2Si$ found 388.0159, calcd. 388.0163.



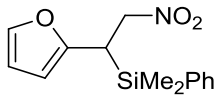
Dimethyl(2-nitro-1-(4-(trifluoromethyl)phenyl)ethyl)(phenyl)silane (**4l**): Following General Procedure **I**, 64.5 mg **1l** was converted into 55.4 mg **4l** as a colorless oil (53.0% yield). TLC: 9/1 Petroleum ether/Ethyl acetate, R_f = 0.40. **^{1}H-NMR** ($CDCl_3$, 400M, ppm): δ7.51-7.39 (m, 7H), 7.08-7.06 (m, 2H), 4.86-4.79 (t, *J* = 13.6 Hz, 1H), 4.56-4.52 (dd, *J* = 3.76, 13.6 Hz, 1H), 3.36-3.31 (dd, *J* = 3.76, 13.6 Hz, 1H), 0.32 (s, 3H), 0.31 (s, 3H) ; **^{13}C-NMR** ($CDCl_3$, 101M, ppm): δ142.27, 134.14, 134.02, 130.47, 128.54 (q, *J* = 32.6 Hz), 128.49, 127.60, 125.70 (q, *J* = 3.8 Hz), 124.98 (q, *J* = 274 Hz), 76.56, 36.59, -3.98, -5.30 ; **^{29}Si-NMR** ($CDCl_3$, 80M, ppm): δ-1.61. HRMS [ESI, $(M+Na)^+$]: for $C_{17}H_{18}F_3NO_2Si$ found 376.0949, calcd. 376.0951.



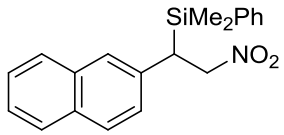
(1-(3,4-dimethoxyphenyl)-2-nitroethyl)dimethyl(phenyl)silane (**4m**): Following General Procedure **I**, 104.5 mg **1m** was converted into 129.8 mg **4m** as an orange solid (74.6% yield). TLC: 9/1 Petroleum ether/Ethyl acetate, R_f = 0.50. MP: 68-70 ^{o}C. **^{1}H-NMR** ($CDCl_3$, 400M, ppm): δ7.44-7.36 (m, 5H), 6.76-6.74 (d, *J* = 8.26 Hz, 1H), 6.55-6.53 (dd, *J* = 2.0, 8.26 Hz, 1H), 6.33-6.34 (d, *J* = 2.0 Hz, 1H), 4.80-4.73 (t, *J* = 13.36 Hz, 1H), 4.56-4.51 (dd, *J* = 3.84, 13.36 Hz, 1H), 3.83 (s, 3H), 3.69 (s, 3H), 3.20-3.16 (dd, *J* = 3.84, 13.36 Hz, 1H), 0.31 (s, 3H), 0.30 (s, 3H) ; **^{13}C-NMR** ($CDCl_3$, 101M, ppm): δ148.90, 147.45, 135.15, 134.13, 130.09, 129.98, 128.27, 119.29, 111.46, 111.04, 77.30, 55.94, 55.74, 35.80, -3.94, -5.03 ; **^{29}Si-NMR** ($CDCl_3$, 80M, ppm): δ-2.23. HRMS [ESI, $(M+Na)^+$]: for $C_{18}H_{23}NO_4Si$ found 368.1287, calcd. 368.1289.



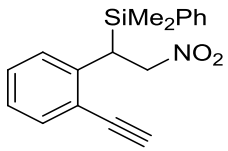
Dimethyl(2-nitro-1-(2,4,6-trimethoxyphenyl)ethyl)(phenyl)silane (**4n**): Following General Procedure **I**, 119.5 mg **1n** was converted into 162.3 mg **4n** as a brown oil (86.5% yield). TLC: 9/1 Petroleum ether/Ethyl acetate, R_f = 0.35. **^{1}H-NMR** ($CDCl_3$, 400M, ppm): δ7.47-7.46 (m, 2H), 7.36-7.35 (m, 3H), 6.07 (s, 2H), 5.21-5.15 (t, *J* = 12.5 Hz, 1H), 4.44-4.40 (dd, *J* = 4.52, 12.5 Hz, 1H), 3.93-3.89 (dd, *J* = 4.52, 12.5 Hz, 1H), 3.78 (s, 3H), 3.69 (s, 6H), 0.30 (s, 3H), 0.19 (s, 3H) ; **^{13}C-NMR** ($CDCl_3$, 101M, ppm): δ148.90, 147.45, 135.15, 134.13, 130.09, 129.98, 128.27, 119.29, 111.46, 111.04, 77.30, 55.94, 55.74, 35.80, -3.94, -5.03 ; **^{29}Si-NMR** ($CDCl_3$, 80M, ppm): δ-2.23. HRMS [ESI, $(M+Na)^+$]: for $C_{19}H_{25}NO_5Si$ found 398.1391, calcd. 398.1394.



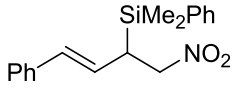
(1-(furan-2-yl)-2-nitroethyl)dimethyl(phenyl)silane (**4o**): Following General Procedure **I**, 41.7 mg **1o** was converted into 56.0 mg **4o** as a brown oil (67.9% yield). TLC: 9/1 Petroleum ether/Ethyl acetate, R_f = 0.50. **^{1}H-NMR** ($CDCl_3$, 400M, ppm): δ7.48-7.38 (m, 5H), 7.31-7.30 (d, *J* = 2.08 Hz, 1H), 6.29-6.28 (dd, *J* = 2.08, 2.9 Hz, 1H), 5.96-5.94 (d, *J* = 2.9 Hz, 1H), 4.74-4.68 (t, *J* = 13.4 Hz, 1H), 4.39-4.35 (dd, *J* = 3.52, 13.4 Hz, 1H), 3.42-3.38 (dd, *J* = 3.52, 13.4 Hz, 1H), 0.39 (s, 3H), 0.36 (s, 3H) ; **^{13}C-NMR** ($CDCl_3$, 101M, ppm): δ151.98, 141.54, 134.89, 133.87, 130.21, 128.37, 110.72, 105.94, 75.57, 29.67, -3.69, -4.91 ; **^{29}Si-NMR** ($CDCl_3$, 80M, ppm): δ-1.32. HRMS [ESI, $(M+Na)^+$]: for $C_{14}H_{17}NO_3Si$ found 298.0869, calcd. 298.0870.



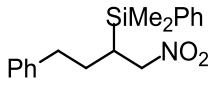
Dimethyl(1-(naphthalen-2-yl)-2-nitroethyl)(phenyl)silane (**4p**): Following General Procedure **I**, 60.3 mg **1p** was converted into 48.5 mg **4p** as a colorless oil (47.9% yield). TLC: 20/1 Petroleum ether/Ethyl acetate, R_f = 0.30. **^{1}H-NMR** ($CDCl_3$, 400M, ppm): δ8.14-8.12 (m, 1H), 7.86-7.84 (m, 1H), 7.71-7.69 (m, 1H), 7.54-7.36 (m, 8H), 7.12-7.10 (m, 1H), 5.04-4.97 (t, *J* = 13.5 Hz, 1H), 4.72-4.67 (dd, *J* = 3.94, 13.5 Hz, 1H), 4.32-4.28 (dd, *J* = 3.94, 13.5 Hz, 1H), 0.26 (s, 3H), 0.22 (s, 3H) ; **^{13}C-NMR** ($CDCl_3$, 101M, ppm): δ135.11, 134.51, 134.25, 134.05, 131.99, 130.18, 129.07, 128.35, 126.72, 126.08, 125.79, 125.19, 123.31, 122.84, 77.48, 29.41, -3.43, -5.29 ; **^{29}Si-NMR** ($CDCl_3$, 80M, ppm): δ-1.18. HRMS [ESI, $(M+Na)^+$]: for $C_{20}H_{21}NO_2Si$ found 358.1233, calcd. 358.1234.



(1-(2-ethynylphenyl)-2-nitroethyl)dimethyl(phenyl)silane (**4q**): Following General Procedure **I**, 51.6 mg **1q** was converted into 48.1 mg **4q** as a yellow oil (52.4% yield). TLC: 20/1 Petroleum ether/Ethyl acetate, R_f = 0.40. **^{1}H-NMR** ($CDCl_3$, 400M, ppm): δ7.51-7.38 (m, 6H), 7.27-7.23 (m, 1H), 7.14-7.10 (m, 1H), 6.94-6.92 (m, 1H), 4.86-4.79 (t, *J* = 13.5 Hz, 1H), 4.54-4.50 (dd, *J* = 3.84, 13.5 Hz, 1H), 4.13-4.09 (dd, *J* = 3.84, 13.5 Hz, 1H), 3.38 (s, 1H), 0.32 (s, 6H) ; **^{13}C-NMR** ($CDCl_3$, 101M, ppm): δ140.75, 135.02, 134.09, 133.74, 130.21, 129.10, 128.37, 125.82, 125.28, 122.12, 82.56, 82.19, 76.69, 33.27, -3.53, -5.56 ; **^{29}Si-NMR** ($CDCl_3$, 80M, ppm): δ-0.68. HRMS [ESI, $(M+Na)^+$]: for $C_{18}H_{19}NO_2Si$ found 332.1074, calcd. 332.1077.



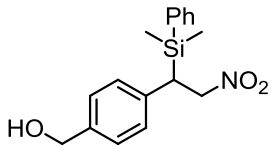
(E)-dimethyl(1-nitro-4-phenylbut-3-en-2-yl)(phenyl)silane (**4r**): Following General Procedure **I**, 52.5 mg **1r** was converted into 40.9 mg **4r** as a brown oil (44.0% yield). TLC: 20/1 Petroleum ether/Ethyl acetate, R_f = 0.40. **^{1}H-NMR** ($CDCl_3$, 400M, ppm): δ7.50-7.40 (m, 5H), 7.33-7.21 (m, 5H), 6.36-6.32 (d, *J* = 15.84 Hz, 1H), 6.07-6.05 (dd, *J* = 13.48, 15.84 Hz, 1H), 4.49-4.43 (t, *J* = 12.54 Hz, 1H), 4.40-4.36 (dd, *J* = 3.8, 12.54 Hz, 1H), 2.92-2.86 (ddd, *J* = 3.8, 12.54, 13.48 Hz, 1H), 0.43 (s, 3H), 0.42 (s, 3H) ; **^{13}C-NMR** ($CDCl_3$, 101M, ppm): δ159.45, 158.69, 137.71, 133.84, 129.38, 127.93, 106.80, 90.94, 76.15, 55.52, 55.39, 24.71, -3.10, -3.89 ; **^{29}Si-NMR** ($CDCl_3$, 80M, ppm): δ-1.65. HRMS [ESI, $(M+Na)^+$]: for $C_{18}H_{21}NO_2Si$ found 334.1232, calcd. 334.1234.



Dimethyl(1-nitro-4-phenylbutan-2-yl)(phenyl)silane (**4s**): Following General Procedure **I**, 88.5 mg

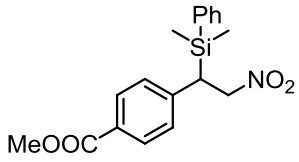
1s was converted into 85.0 mg **4s** as a yellow oil (54.3% yield). TLC: 20/1 Petroleum ether/Ethyl acetate, R_f = 0.50. **^{1}H-NMR** ($CDCl_3$, 400M, ppm): δ7.52-7.49 (m, 2H), 7.44-7.37 (m, 3H), 7.28-7.18 (m, 3H), 7.07-7.05 (m, 2H), 4.44-4.32 (m, *2*H), 2.64-2.48 (m, 2H), 1.94-1.80 (m, 2H), 1.77-1.67 (m, 1H), 0.40 (s, 6H) ; **^{13}C-NMR** ($CDCl_3$, 101M, ppm): δ141.53, 135.99, 133.88, 129.93, 128.55, 128.41, 128.36, 126.16, 78.25, 34.89, 30.61, 25.93, -3.94, -4.29 ; **^{29}Si-NMR** ($CDCl_3$, 80M, ppm): δ-0.66. HRMS [ESI, $(M+Na)^+$]: for $C_{18}H_{23}NO_2Si$ found 336.1396, calcd. 336.1390.

(1-cyclohexyl-2-nitroethyl)dimethyl(phenyl)silane (**4t**): Following General Procedure **I**, 77.5 mg **1t** was converted into 61.6 mg **4t** as a light yellow oil (42.3% yield). TLC: 20/1 Petroleum ether/Ethyl acetate, R_f = 0.65. **^{1}H-NMR** ($CDCl_3$, 400M, ppm): δ7.52-7.49 (m, 2H), 7.39-7.37 (m, 3H), 4.48-4.42 (dd, *J* = 11.0, 13.32 Hz, 1H), 4.27-4.22 (dd, *J* = 3.36, 13.32 Hz, 1H), 1.95-1.90 (dt, *J* = 3.36, 11.0 Hz, 1H), 1.70-1.50 (m, 6H), 1.19-1.03 (m, 5H), 0.41 (s, 3H), 0.39 (s, 3H) ; **^{13}C-NMR** ($CDCl_3$, 101M, ppm): δ137.15, 133.84, 129.71, 128.29, 75.96, 38.46, 32.89, 32.76, 31.48, 27.00, 26.93, 26.23, -1.94, -3.01 ; **^{29}Si-NMR** ($CDCl_3$, 80M, ppm): δ-1.28. HRMS [ESI, $(M+Na)^+$]: for $C_{16}H_{25}NO_2Si$ found 314.1542, calcd. 314.1547.

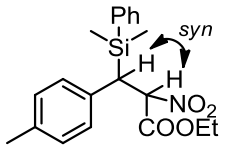


(4-(1-(dimethyl(phenyl)silyl)-2-nitroethyl)phenyl)methanol (**4u**): Following General Procedure **I**, 17.9 mg **1u** was converted into 6.0 mg **4u** as a colorless oil (19.0% yield). TLC: 1/1 Petroleum ether/Ethyl acetate, R_f = 0.65. **^{1}H-NMR** ($CDCl_3$, 400M, ppm): δ7.44-7.37 (m, 5H), 7.26-7.24 (d, *J* = 7.92 Hz, 2H), 6.99-6.97 (d, *J* = 7.92 Hz, 2H), 4.84-4.77 (t, *J* = 13.52 Hz, 1H), 4.65-4.63 (d, *J* = 4.32 Hz,

2H), 4.52-4.47 (dd, *J* = 3.76, 13.52 Hz, 1H), 3.29-3.24 (dd, *J* = 3.76, 13.52 Hz, 1H), 0.30 (s, 3H), 0.29 (s, 3H) ; **^{13}C-NMR** ($CDCl_3$, 101M, ppm): δ138.76, 137.20, 134.89, 134.05, 130.21, 128.37, 127.63, 127.51, 77.06, 65.21, 36.08, -3.78, -5.32. HRMS [ESI, $(M+Na)^+$]: for $C_{17}H_{21}NO_3Si$ found 338.1183, calcd. 338.1183.

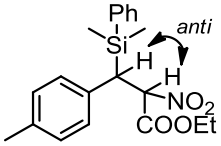


Methyl 4-(1-(dimethyl(phenyl)silyl)-2-nitroethyl)benzoate (**4v**): Following General Procedure **I**, 20.7 mg **1v** was converted into 17.9 mg **4v** as a colorless oil (52.1% yield). TLC: 10/1 Petroleum ether/Ethyl acetate, R_f = 0.50. **^{1}H-NMR** ($CDCl_3$, 400M, ppm): δ7.93-7.90 (d, *J* = 8.20 Hz, 2H), 7.46-7.37 (m, 5H), 7.04-7.01 (d, *J* = 8.20 Hz, 2H), 4.88-4.802 (t, *J* = 13.64 Hz, 1H), 4.55-51 (dd, *J* = 3.60, 13.64 Hz, 1H), 3.89 (s, 3H), 3.37-3.32 (dd, *J* = 3.60, 13.64 Hz, 1H), 0.31 (s, 3H), 0.30 (s, 3H) ; **^{13}C-NMR** ($CDCl_3$, 101M, ppm): δ166.97, 143.53, 134.22, 134.02, 130.40, 130.04, 128.43, 128.15, 127.30, 76.49, 52.19, 36.81, -3.98, -5.29. HRMS [ESI, $(M+H)^+$]: for $C_{18}H_{21}NO_4Si$ found 344.1313, calcd. 344.1313.

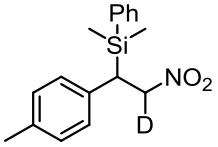


Ethyl 3-(dimethyl(phenyl)silyl)-2-nitro-3-(p-tolyl)propanoate (**4w1**): Following General Procedure **I**, 23.5 mg **1w** was converted into 4.2 mg **4w1** as a colorless oil (11.3% yield). TLC: 20/1 Petroleum ether/Ethyl acetate, R_f = 0.60. **^{1}H-NMR** ($CDCl_3$, 400M, ppm): δ7.45-7.34 (m, 5H), 7.01-6.99 (d, *J* = 7.80 Hz, 2H), 6.79-6.77 (d, *J* = 7.80 Hz, 2H), 5.43-5.41 (d, *J* = 9.48 Hz, 1H), 4.00-3.94 (q, *J* = 7.88 Hz, 2H), 3.38-3.35 (d, *J* = 9.48 Hz, 1H), 2.28 (s, 3H), 1.04-1.00 (t, 7.88 Hz, 3H), 0.30 (s, 3H), 0.29 (s, 3H) ;

^{13}C-NMR ($CDCl_3$, 101M, ppm): δ164.27, 136.12, 135.42, 134.50, 133.51, 129.99, 129.80, 129.23, 128.90, 90.43, 62.81, 38.10, 21.09, 13.67, -3.13, -3.69. HRMS [ESI, $(M+Na)^+$]: for $C_{16}H_{25}NO_2Si$ found 394.1444, calcd. 394.1445.

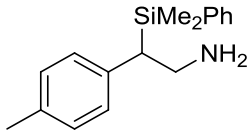


Ethyl 3-(dimethyl(phenyl)silyl)-2-nitro-3-(p-tolyl)propanoate (**4w2**): Following General Procedure **I**, 23.5 mg **1w** was converted into 16.8 mg **4w2** as a colorless oil (45.2% yield). TLC: 20/1 Petroleum ether/Ethyl acetate, R_f = 0.60. **^{1}H-NMR** ($CDCl_3$, 400M, ppm): δ7.45-7.34 (m, 5H), 7.05-7.03 (d, *J* = 7.76 Hz, 2H), 6.91-6.89 (d, *J* = 7.76 Hz, 2H), 5.59-5.55 (d, *J* = 12.88 Hz, 1H), 3.75-3.70 (q, *J* = 7.15 Hz, 2H), 3.50-3.47 (d, *J* = 12.88 Hz, 1H), 2.28 (s, 3H), 1.15-1.11 (t, 7.14 Hz, 3H), 0.33 (s, 3H), 0.16 (s, 3H) ; **^{13}C-NMR** ($CDCl_3$, 101M, ppm): δ163.99, 136.04, 135.34, 134.40, 134.07, 129.85, 129.48, 127.94, 127.85, 91.82, 62.94, 37.66, 21.09, 13.67, -2.15, -4.76. HRMS [ESI, $(M+Na)^+$]: for $C_{16}H_{25}NO_2Si$ found 394.1444, calcd. 394.1445.

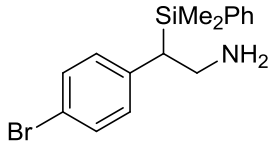


d-Dimethyl(2-nitro-1-(p-tolyl)ethyl)(phenyl)silane (D-**4b**): Following General Procedure **I**, 16.3 mg **1b** was converted into 21.0 mg D-**4b** as a light yellow oil (70% yield). TLC: 20/1 Petroleum ether/Ethyl acetate, R_f = 0.55. **^{1}H-NMR** (d_6-acetone, 400M, ppm): δ7.53-7.51 (m, 2H), 7.45-7.37 (m, 3H), 7.06-7.04 (d, *J* = 7.84 Hz , 2H), 6.98-6.96 (d, *J* = 7.84 Hz , 2H), 5.03-4.99 (m, 0.45 H), 4.74-4.70 (m, 0.67 H), 3.35-3.30 (m, 1 H), 2.25 (s, 3H), 0.35 (s, 3H), 0.30 (s, 3H) ; **^{13}C-NMR** (d_6-acetone, 101M, ppm): δ136.41, 136.13, 135.92, 134.91, 130.56, 129.82, 128.83, 128.27, 77.45

(t, *J* = 24.0 Hz), 36.36, 20.91, -3.92, -5.18. HRMS [ESI, $(M+H)^+$]: for $C_{17}H_{20}DNO_2Si$ found 301.1493, calcd. 301.1493.



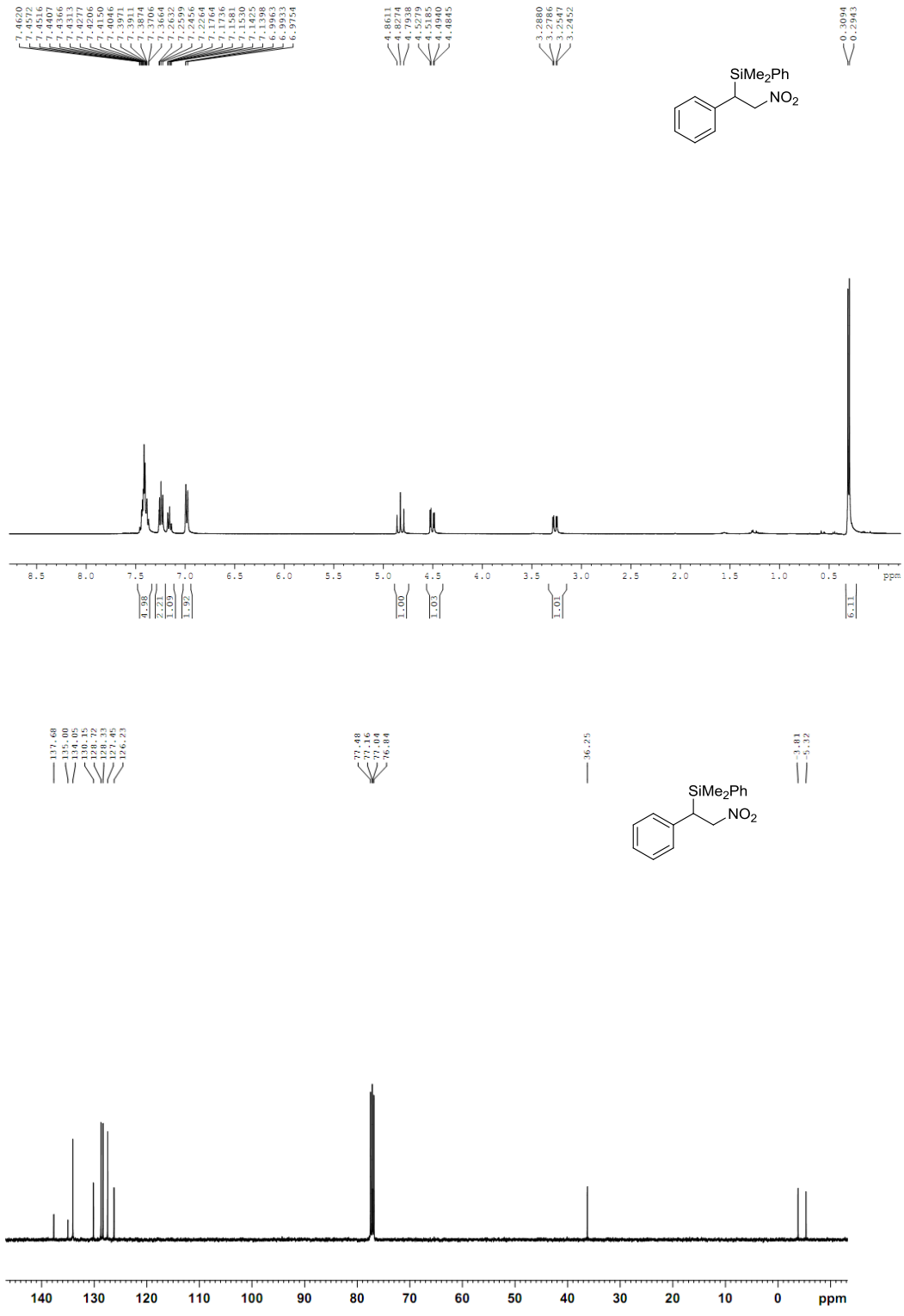
2-(dimethyl(phenyl)silyl)-2-(p-tolyl)ethanamine (**13b**): Following General Procedure **II**, 100 mg **4b** was converted into 256 mg **13b** as a white plate (95% yield). TLC: 1/15 MeOH/DCM, R_f = 0.30. MP: 135-142 ^oC. **^{1}H-NMR** (CD_3OD, 400M, ppm): δ7.46-7.34 (m, 5H), 7.14-7.13 (d, *J* = 8.0 Hz, 2H), 6.97-6.95 (d, *J* = 8.0 Hz, 2H), 4.86 (s, 2H), 3.47-3.41 (t, *J* = 13.4 Hz, 1H), 3.29-3.25 (dd, *J* = 3.4, 13.4 Hz, 1H), 2.66-2.62 (dd, *J* = 3.4, 13.4 Hz, 1H), 2.31 (s, 3H), 0.29 (s, 3H), 0.25 (s, 3h); **^{13}C-NMR** (CD_3OD, 101M, ppm): δ137.07, 136.65, 135.38, 135.15, 130.77, 130.59, 129.05, 129.05, 41.93, 36.73, 21.00, -4.05, -5.40 ; **^{29}Si-NMR** (CD_3OD, 80M, ppm): δ-2.45. **HRMS** [ESI, $(M+H)^+$]: for $C_{17}H_{23}NSi$ found 270.1670, calcd. 270.1673.



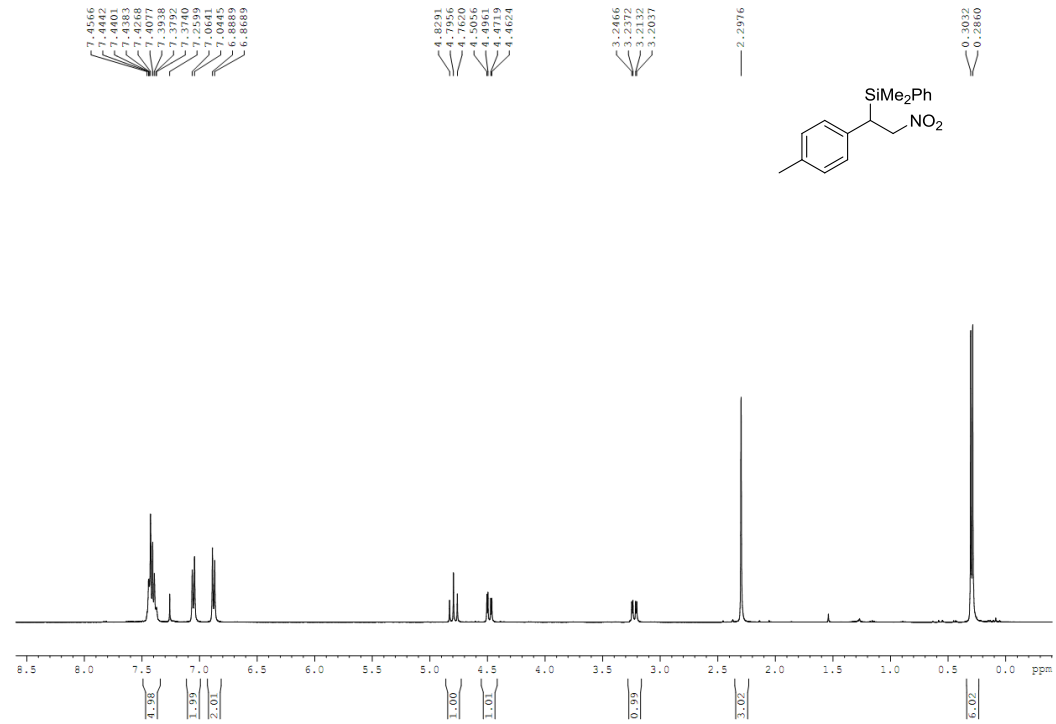
2-(4-bromophenyl)-2-(dimethyl(phenyl)silyl)ethanamine (**13i**): Following General Procedure **II**, 120 mg **4i** was converted into 87 mg **13i** as a gray plate (79% yield). TLC: 1/15 MeOH/DCM, R_f = 0.30. MP: 125-130 ^oC. **^{1}H-NMR** (CD_3OD, 400M, ppm): δ7.44-7.34 (m, 7H), 6.99-6.96 (m, 2H), 4.87 (s, 2H), 3.47-3.40 (t, *J* = 13.1 Hz, 1H), 3.31-3.27 (dd, *J* = 2.7, 13.1 Hz, 1H), 2.73-2.69 (dd, *J* = 2.7, 13.1 Hz, 1H), 0.31 (s, 3H), 0.28 (s, 3H) ; **^{13}C-NMR** (CD_3OD, 101M, ppm): δ140.65, 137.33, 135.12, 132.54, 131.14, 130.52, 128.90, 119.89, 42.28, 40.85, -4.03, -5.07 ; **^{29}Si-NMR** (CD_3OD, 80M, ppm): δ-3.18. **HRMS** [ESI, $(M+H)^+$]: for $C_{16}H_{20}BrNSi$ found 334.0623, calcd. 334.0621.

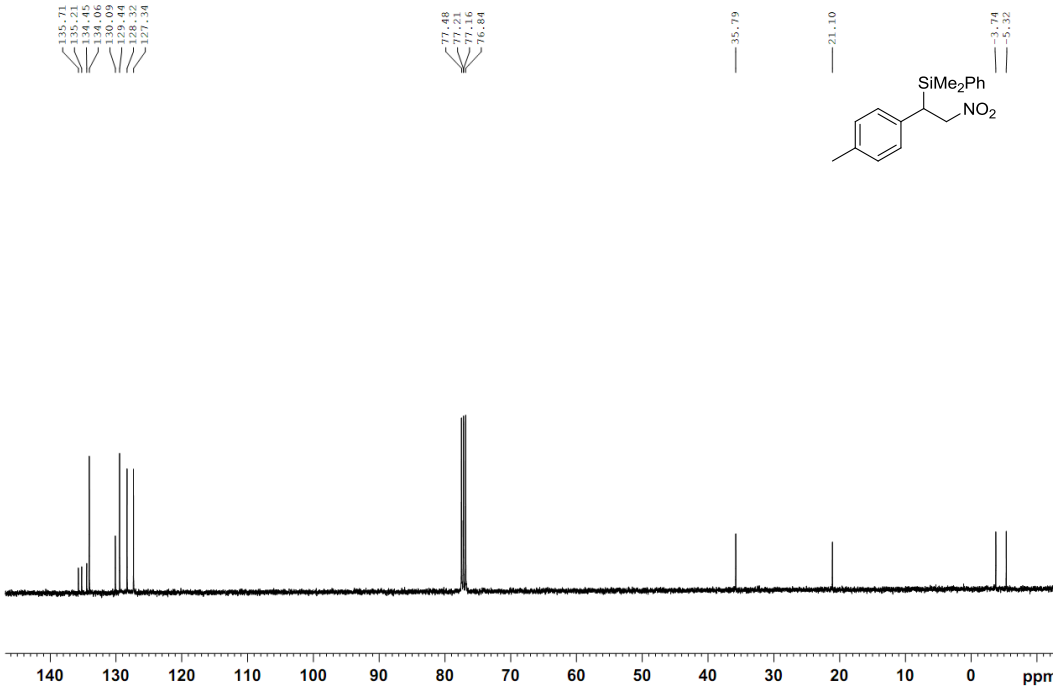
7. Copy of NMR spectra

4a ^{1}H-NMR ($CDCl_3$, 400M, ppm); **^{13}C-NMR** ($CDCl_3$, 101M, ppm)

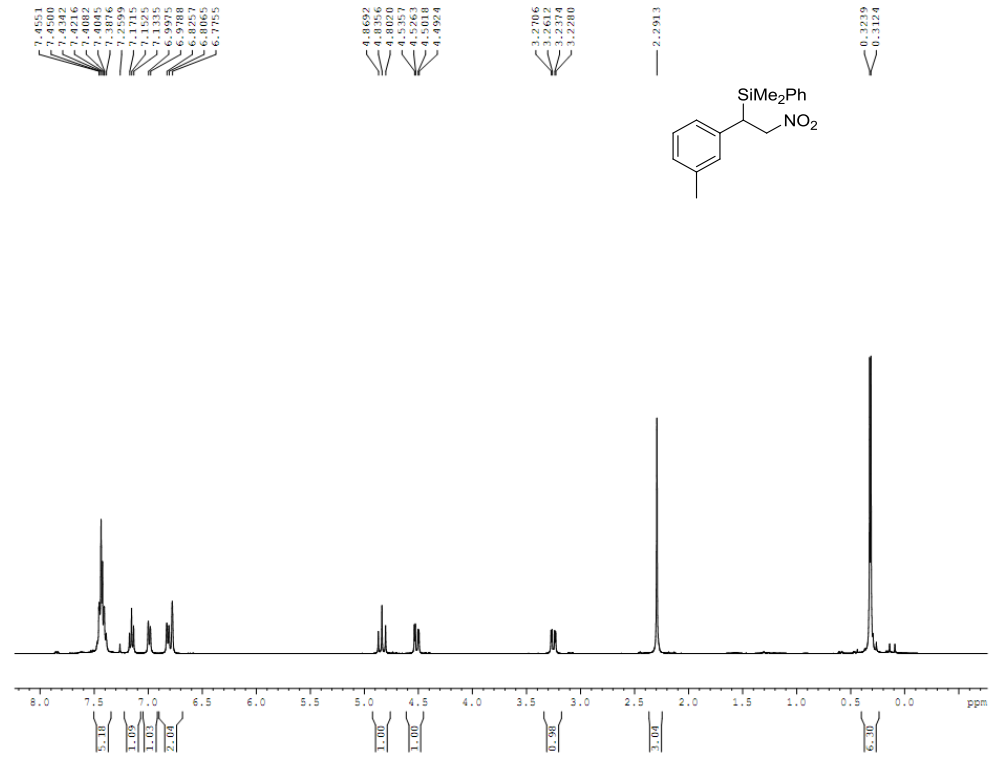


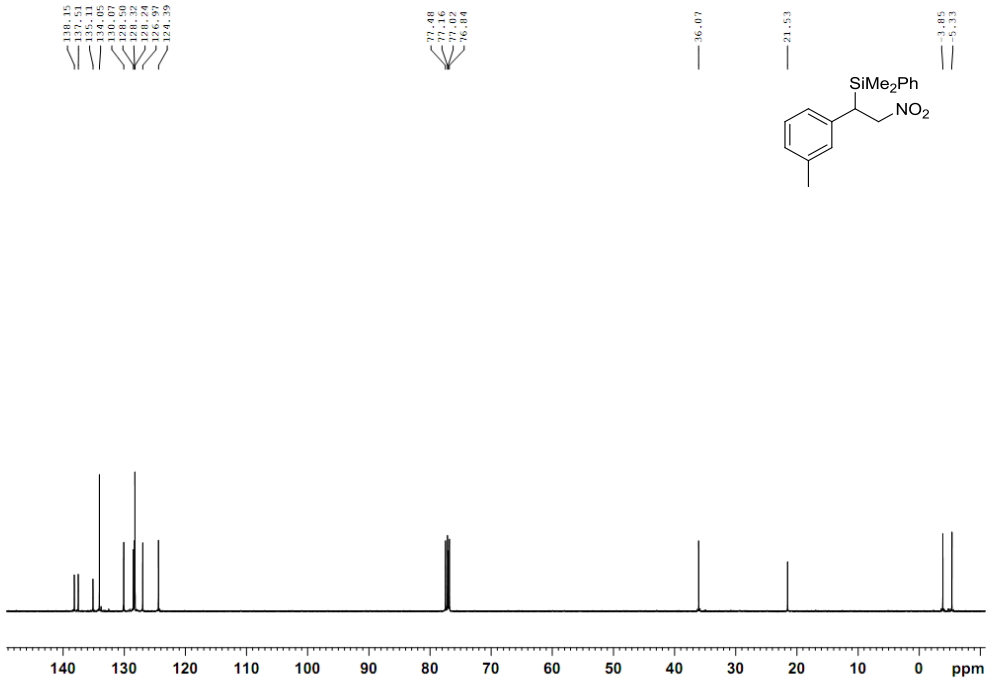
4b **^{1}H-NMR** ($CDCl_3$, 400M, ppm); **^{13}C-NMR** ($CDCl_3$, 101M, ppm)



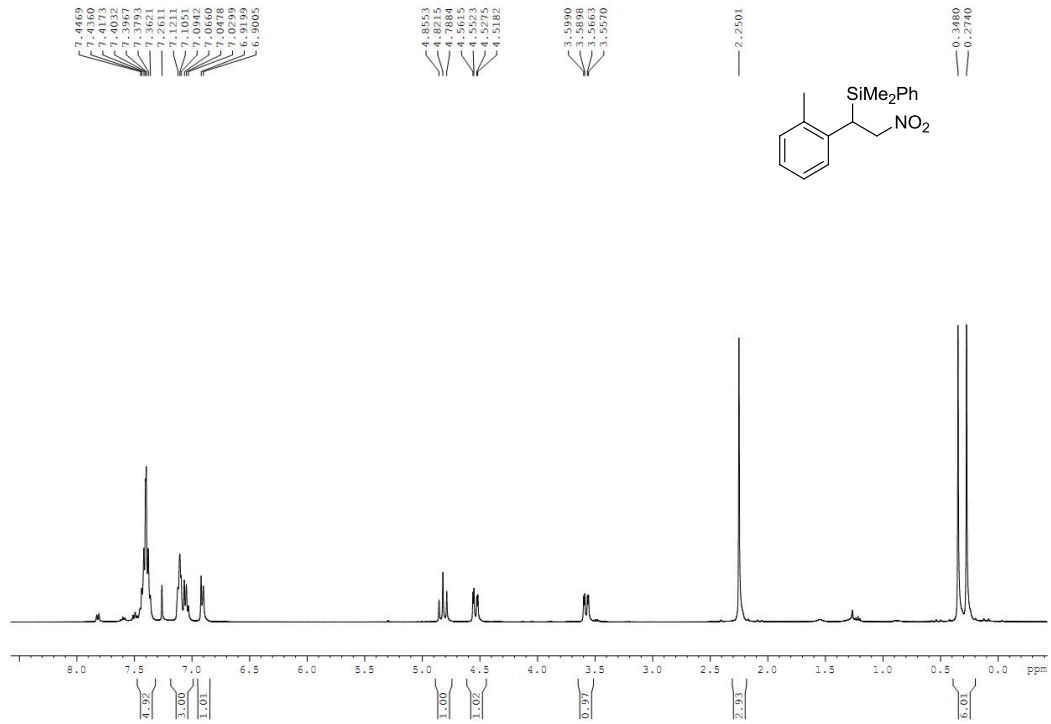


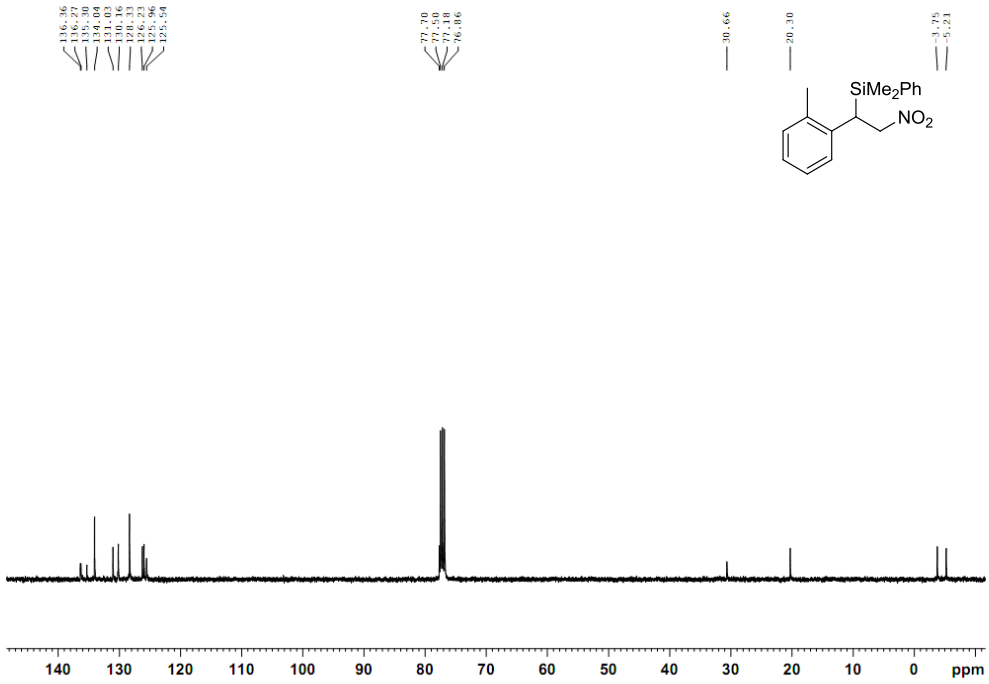
4c **^{1}H-NMR** ($CDCl_3$, 400M, ppm); **^{13}C-NMR** ($CDCl_3$, 101M, ppm)



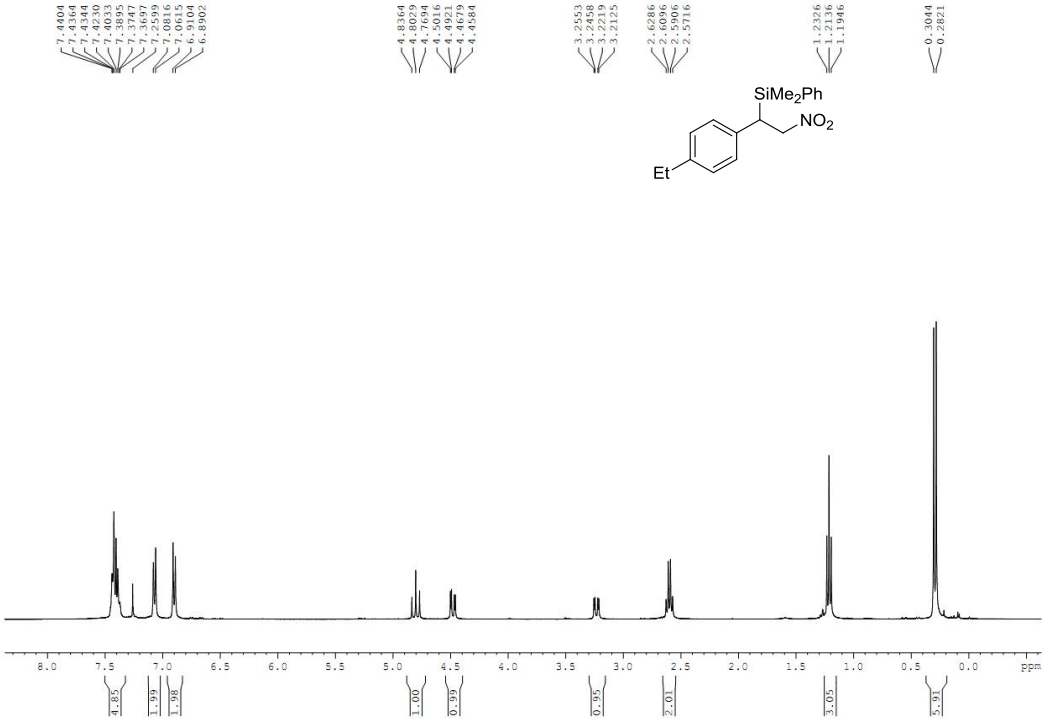


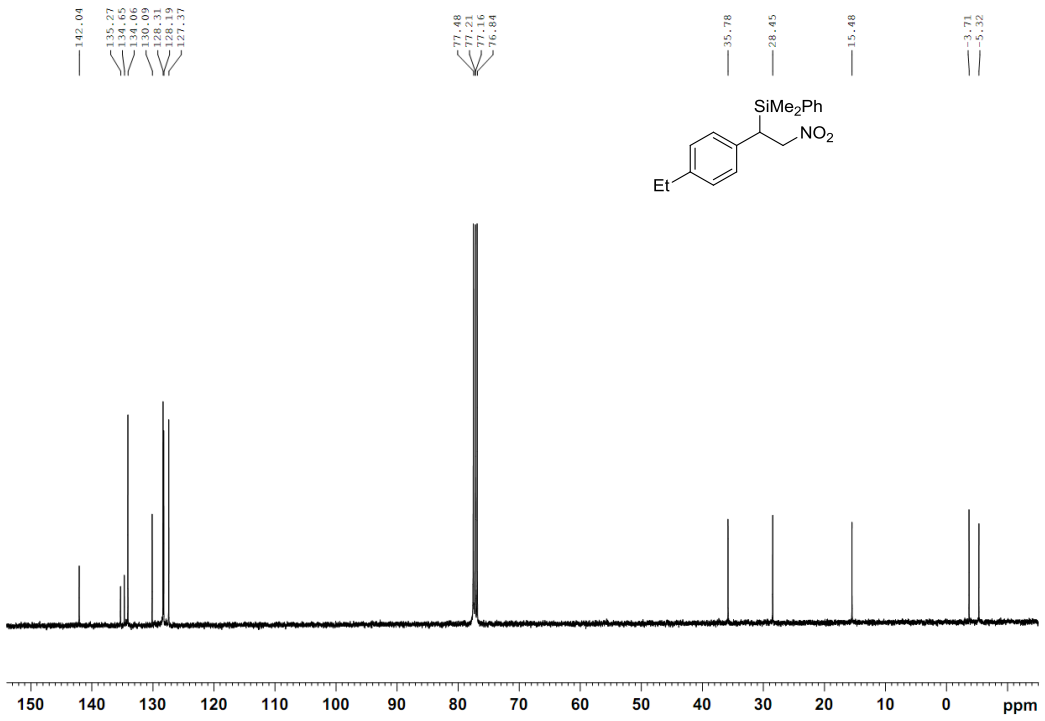
4d **^{1}H-NMR** ($CDCl_3$, 400M, ppm); **^{13}C-NMR** ($CDCl_3$, 101M, ppm)



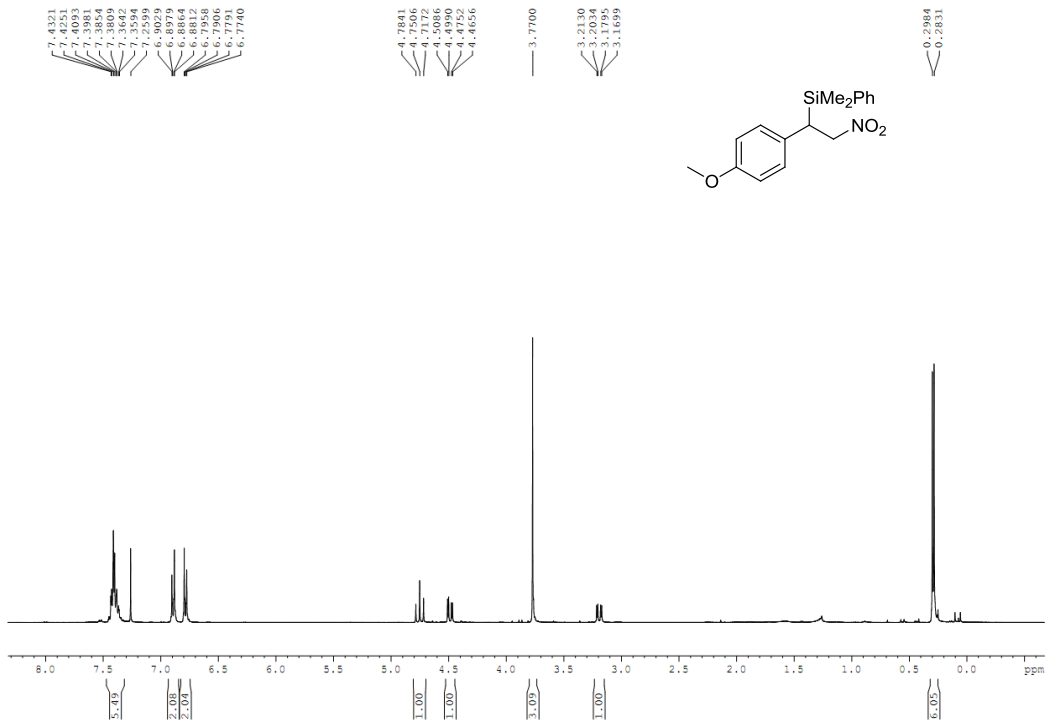


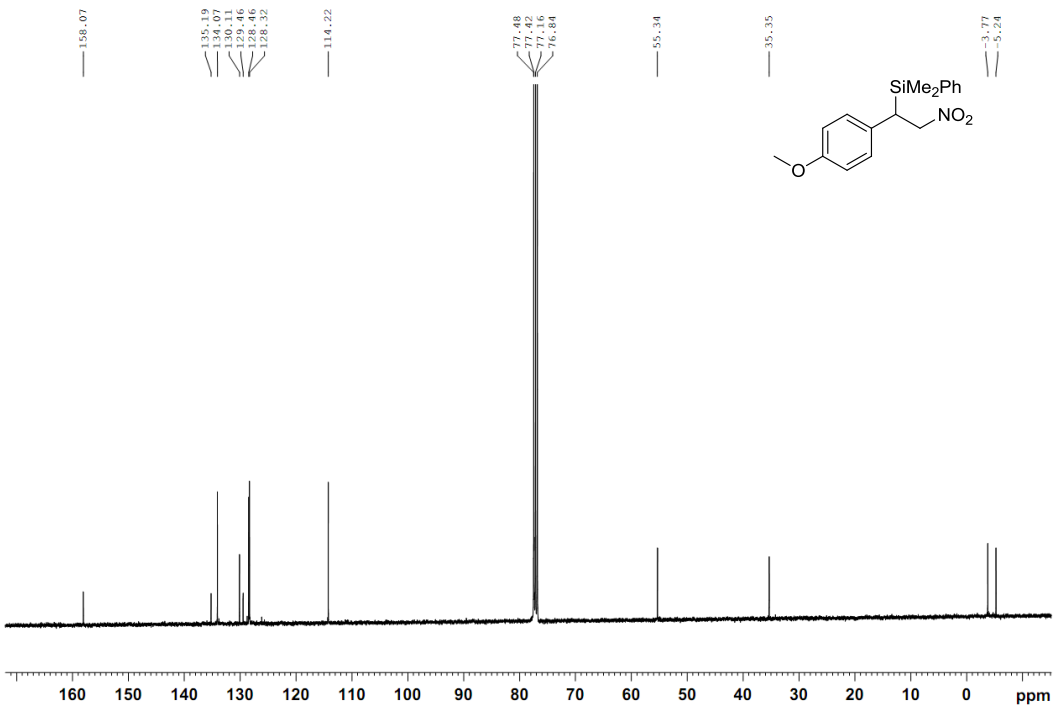
4e **^{1}H-NMR** ($CDCl_3$, 400M, ppm); **^{13}C-NMR** ($CDCl_3$, 101M, ppm)



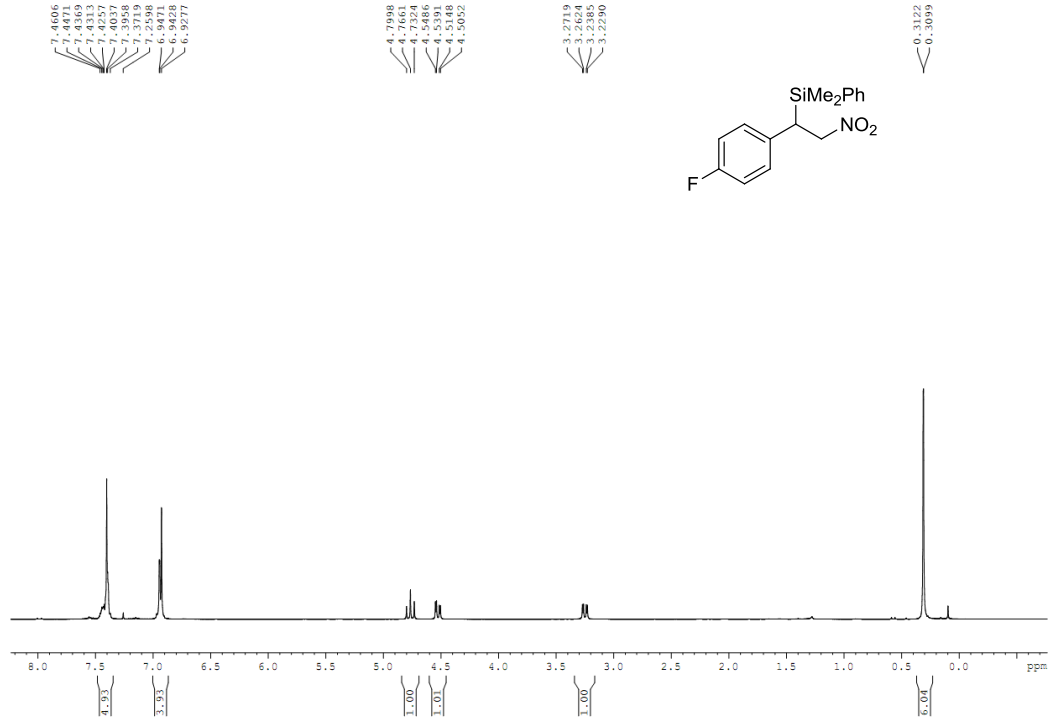


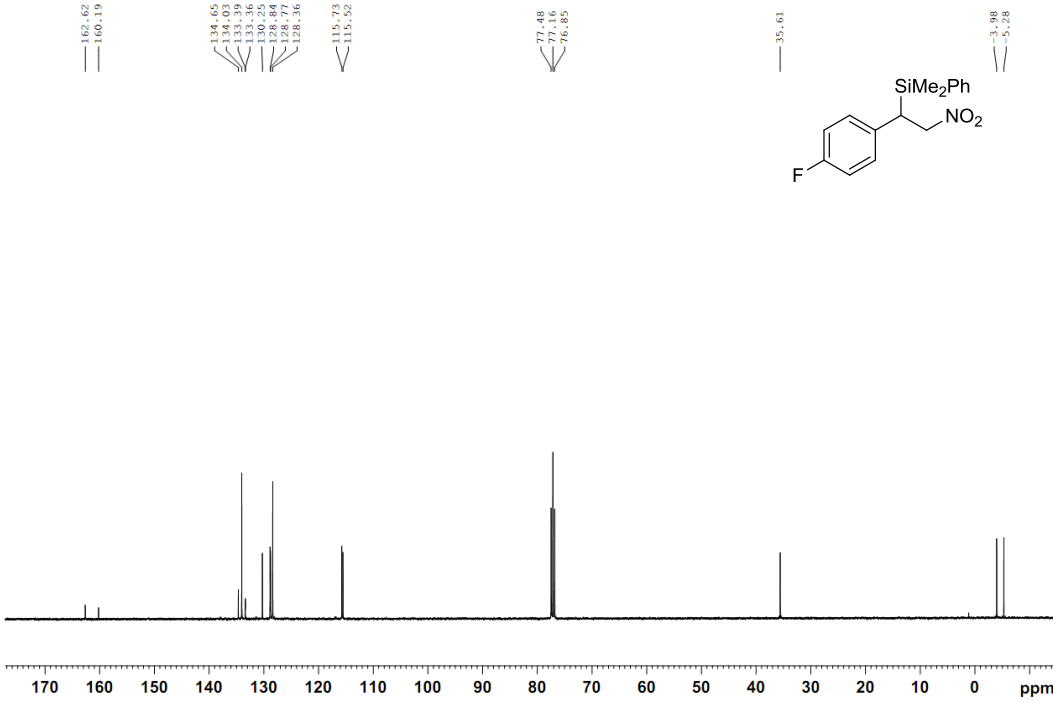
4f **^{1}H-NMR** ($CDCl_3$, 400M, ppm); **^{13}C-NMR** ($CDCl_3$, 101M, ppm)



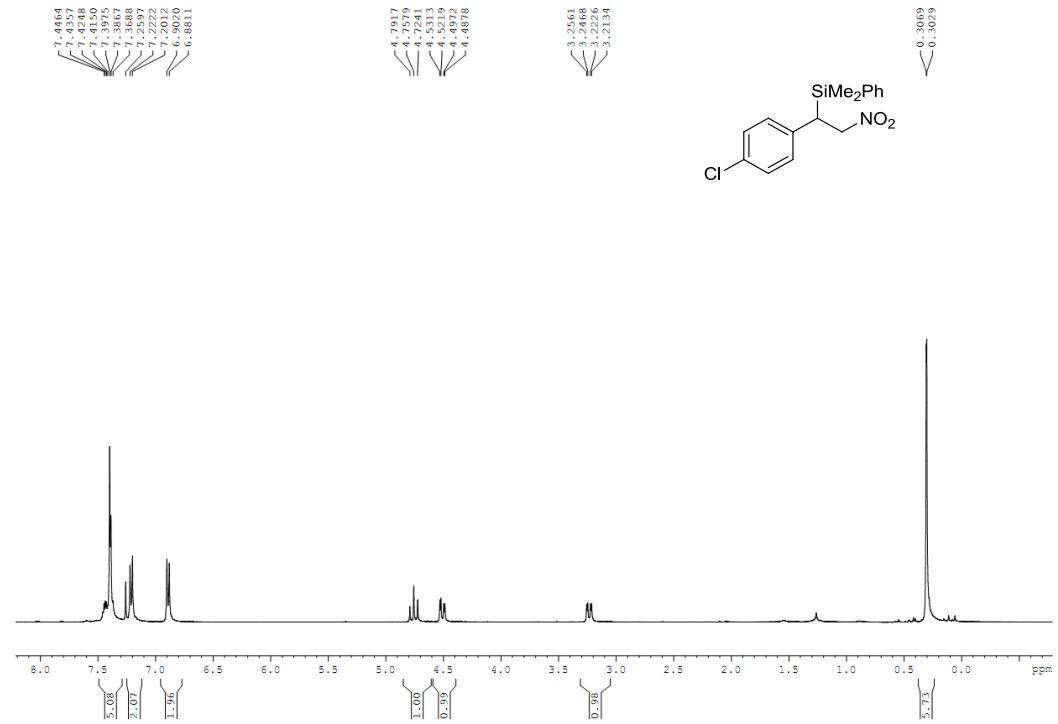


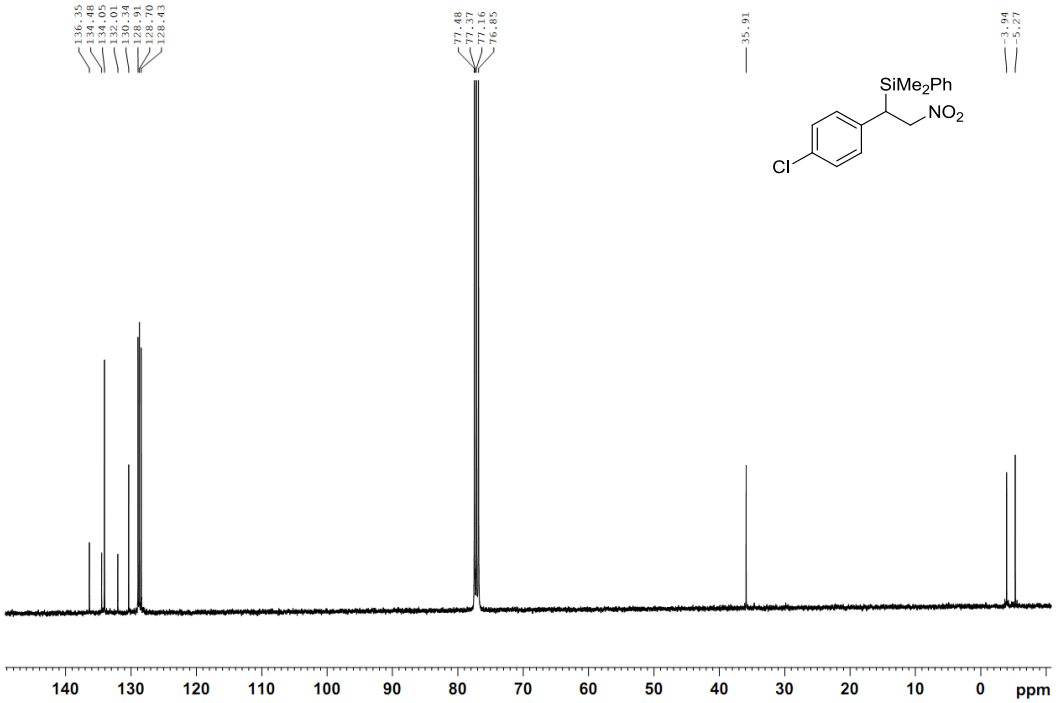
4g **^{1}H-NMR** ($CDCl_3$, 400M, ppm); **^{13}C-NMR** ($CDCl_3$, 101M, ppm)



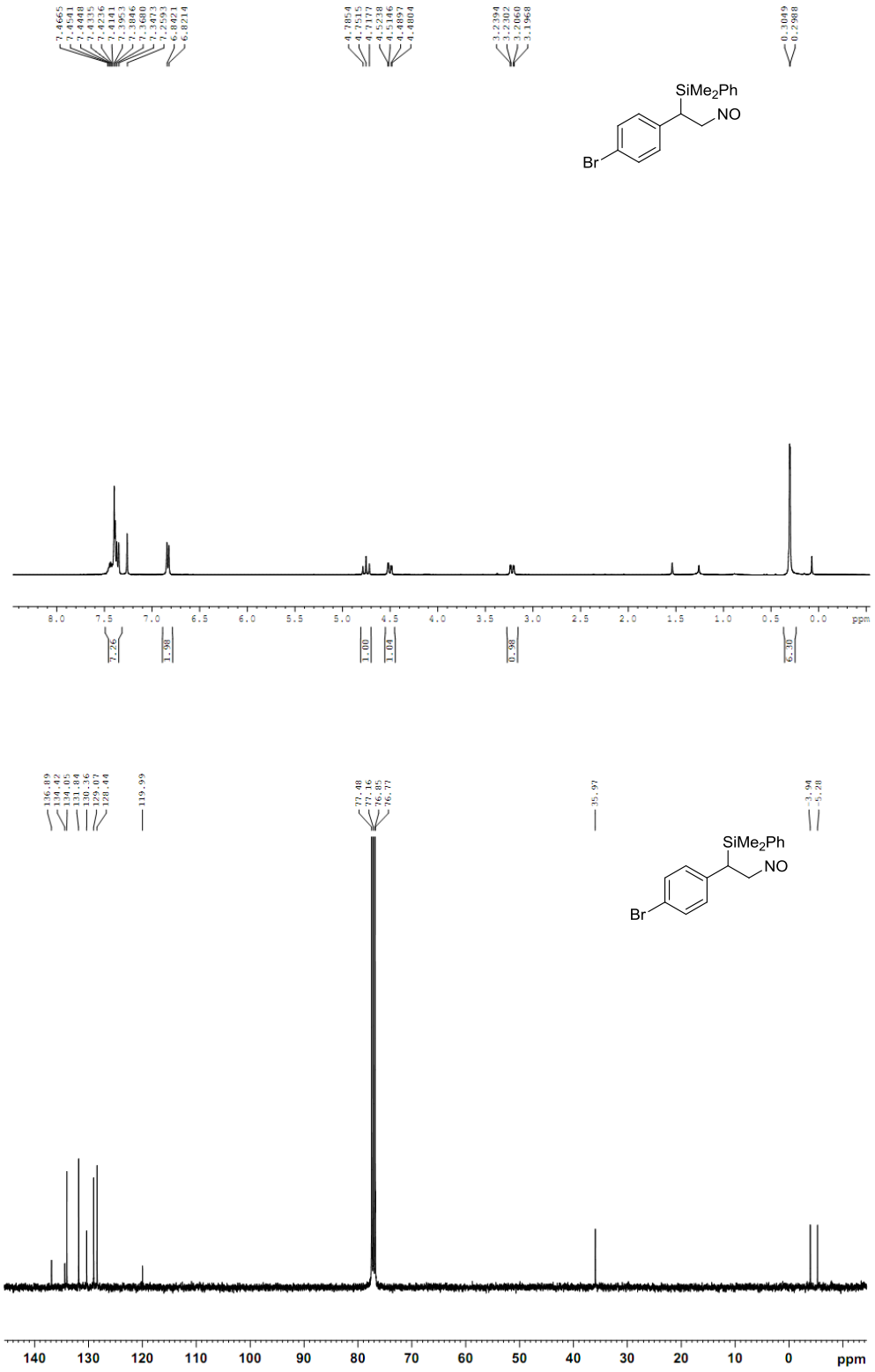


4h **^{1}H-NMR** ($CDCl_3$, 400M, ppm); **^{13}C-NMR** ($CDCl_3$, 101M, ppm)

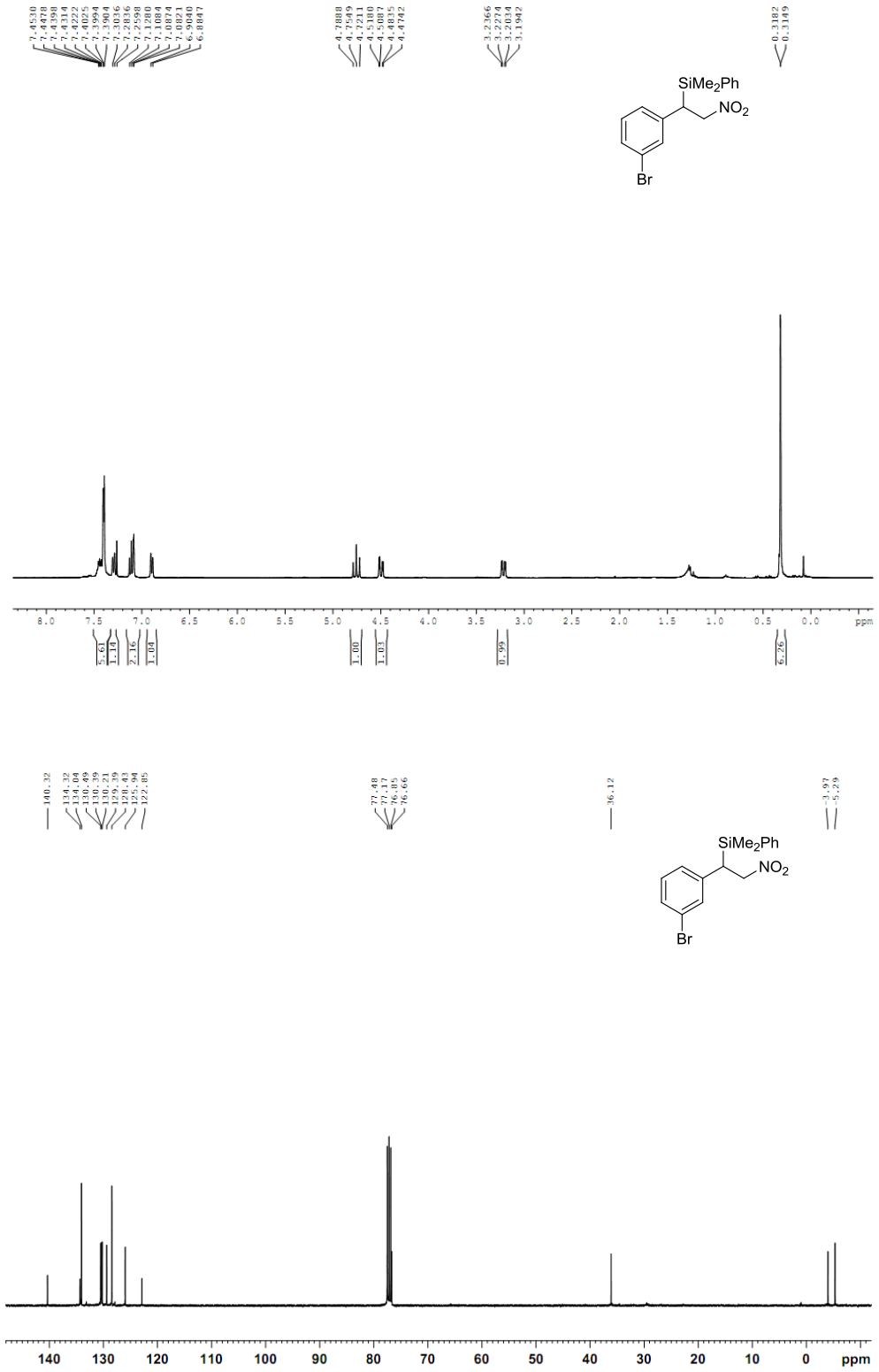




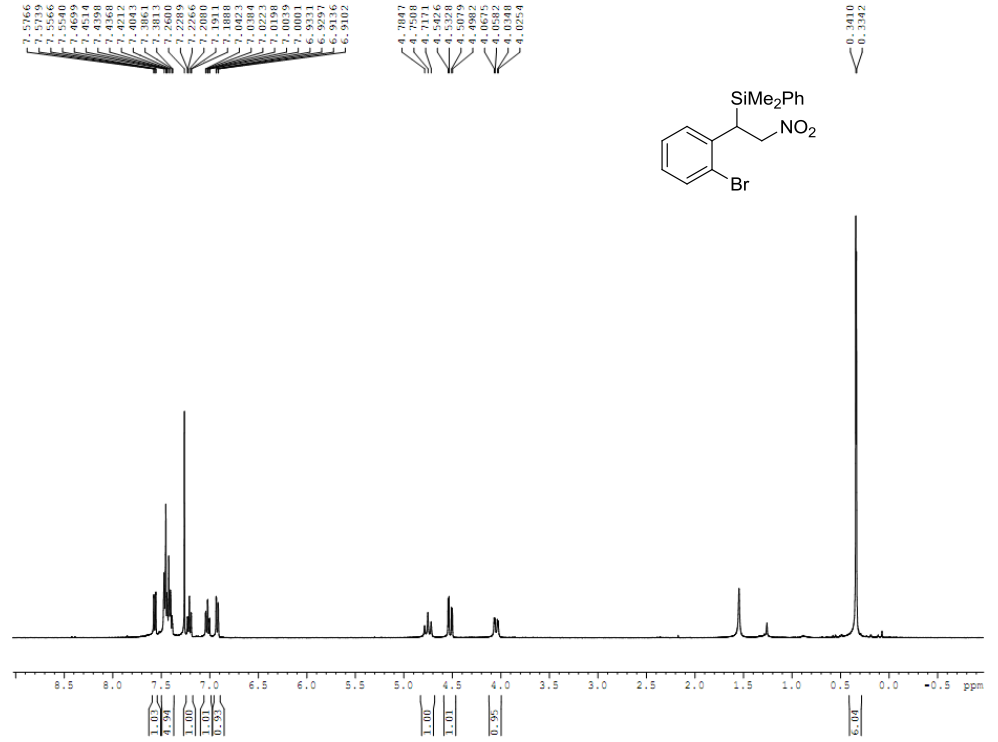
4i **^{1}H-NMR** ($CDCl_3$, 400M, ppm); **^{13}C-NMR** ($CDCl_3$, 101M, ppm)

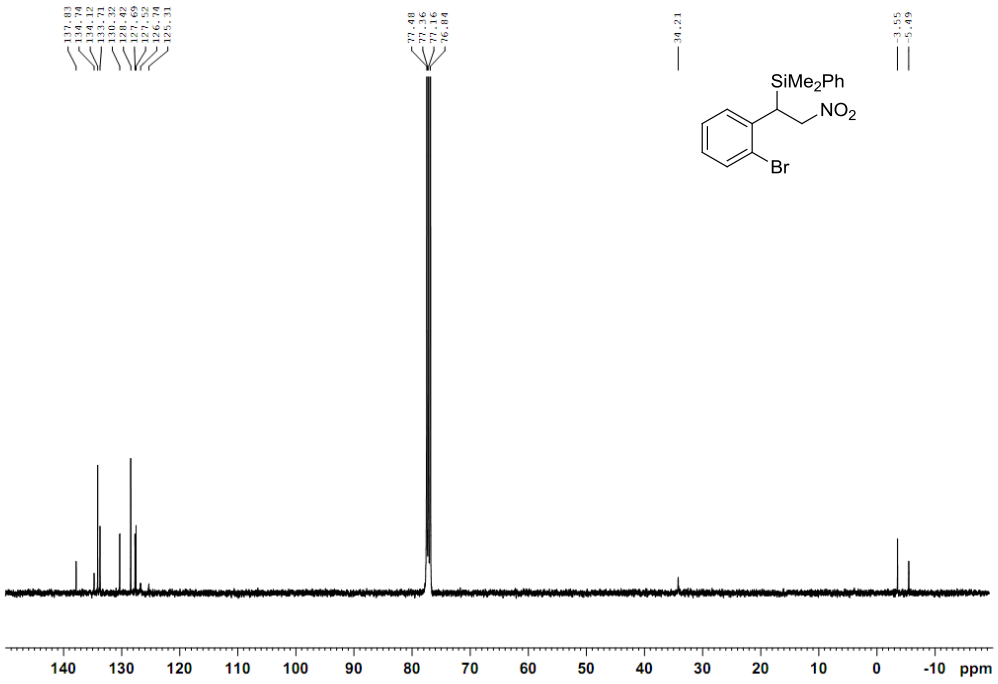


4j **^{1}H-NMR** ($CDCl_3$, 400M, ppm); **^{13}C-NMR** ($CDCl_3$, 101M, ppm)

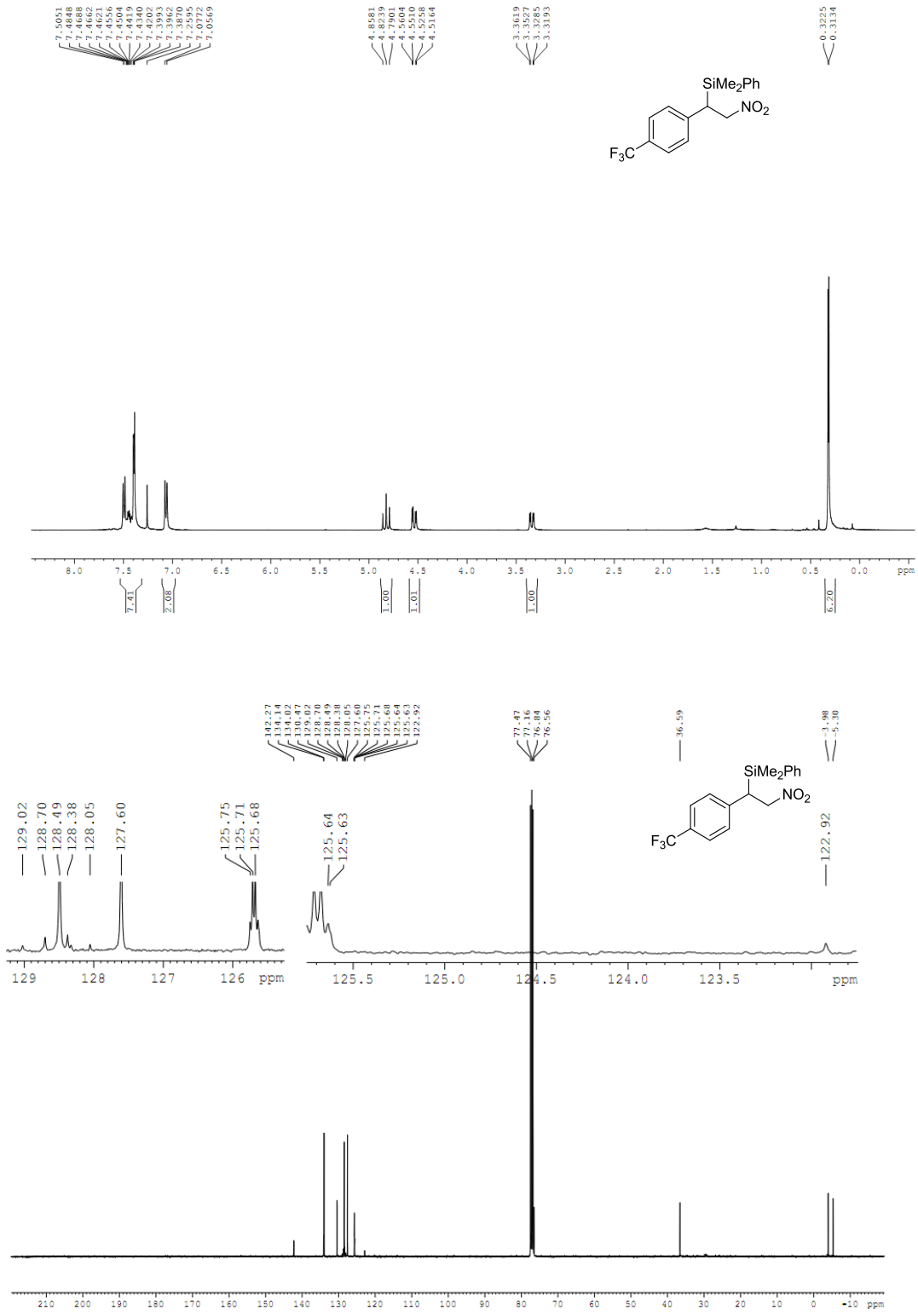


4k **^{1}H-NMR** ($CDCl_3$, 400M, ppm); **^{13}C-NMR** ($CDCl_3$, 101M, ppm)

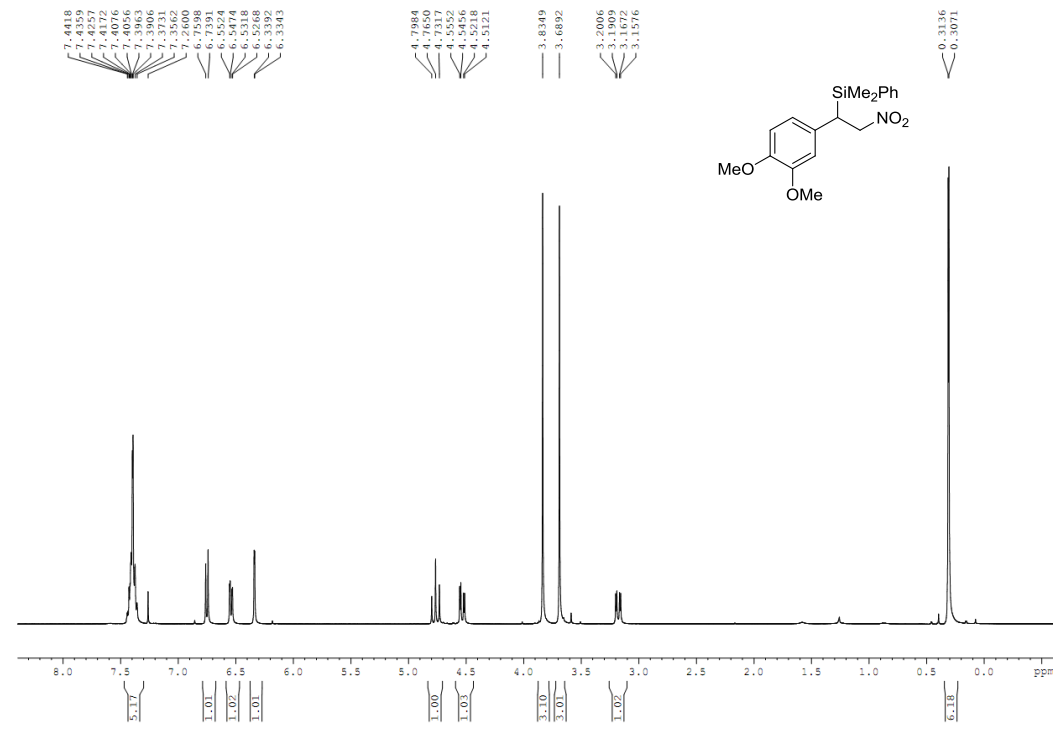


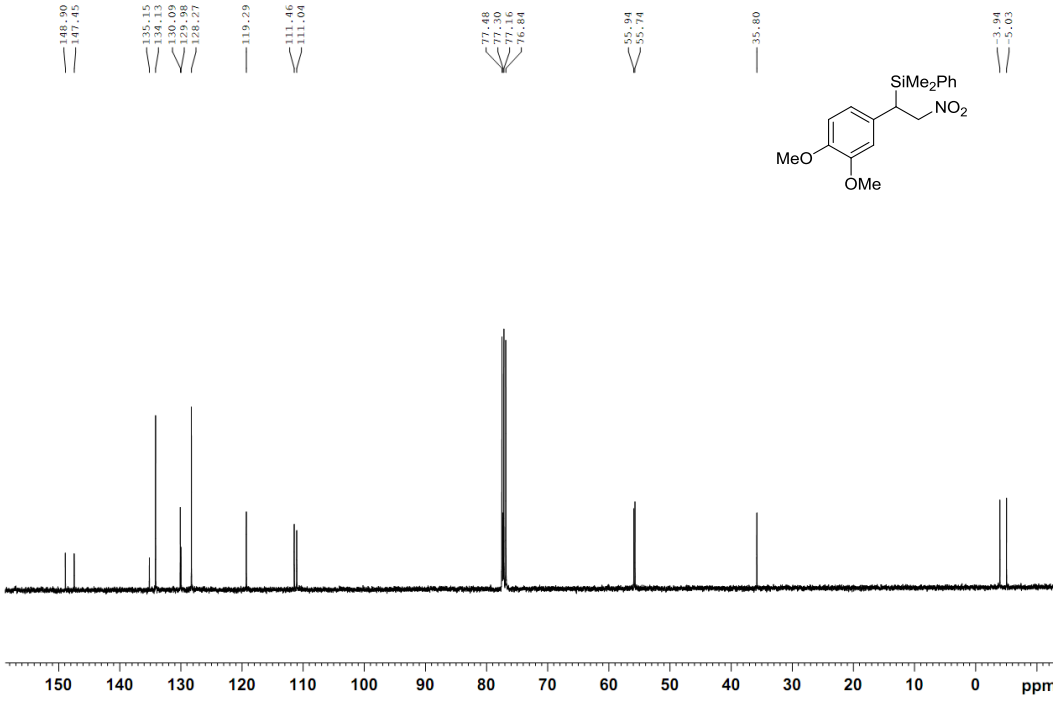


4l **^{1}H-NMR** ($CDCl_3$, 400M, ppm); **^{13}C-NMR** ($CDCl_3$, 101M, ppm)

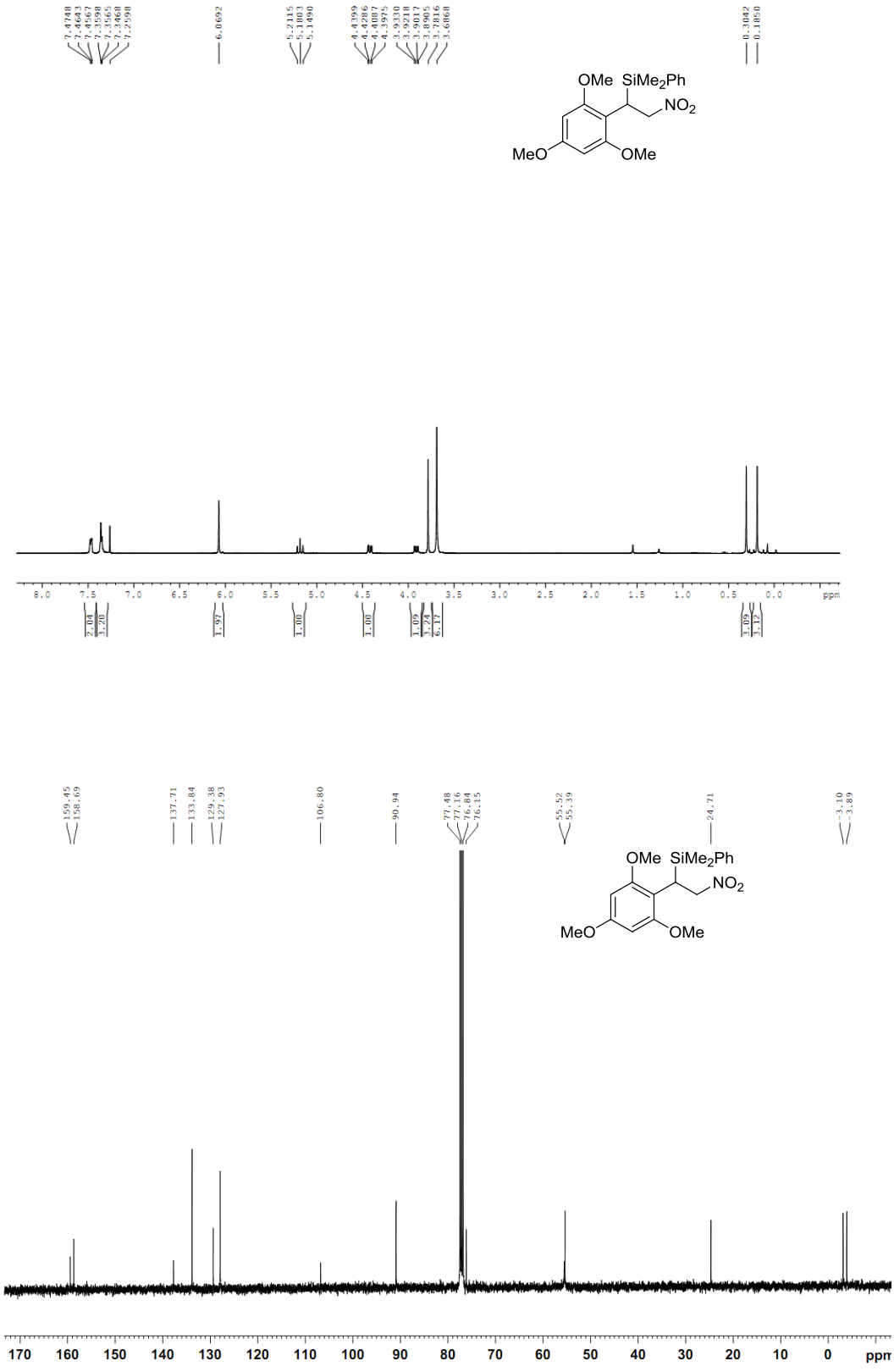


4m **^{1}H-NMR** ($CDCl_3$, 400M, ppm); **^{13}C-NMR** ($CDCl_3$, 101M, ppm)

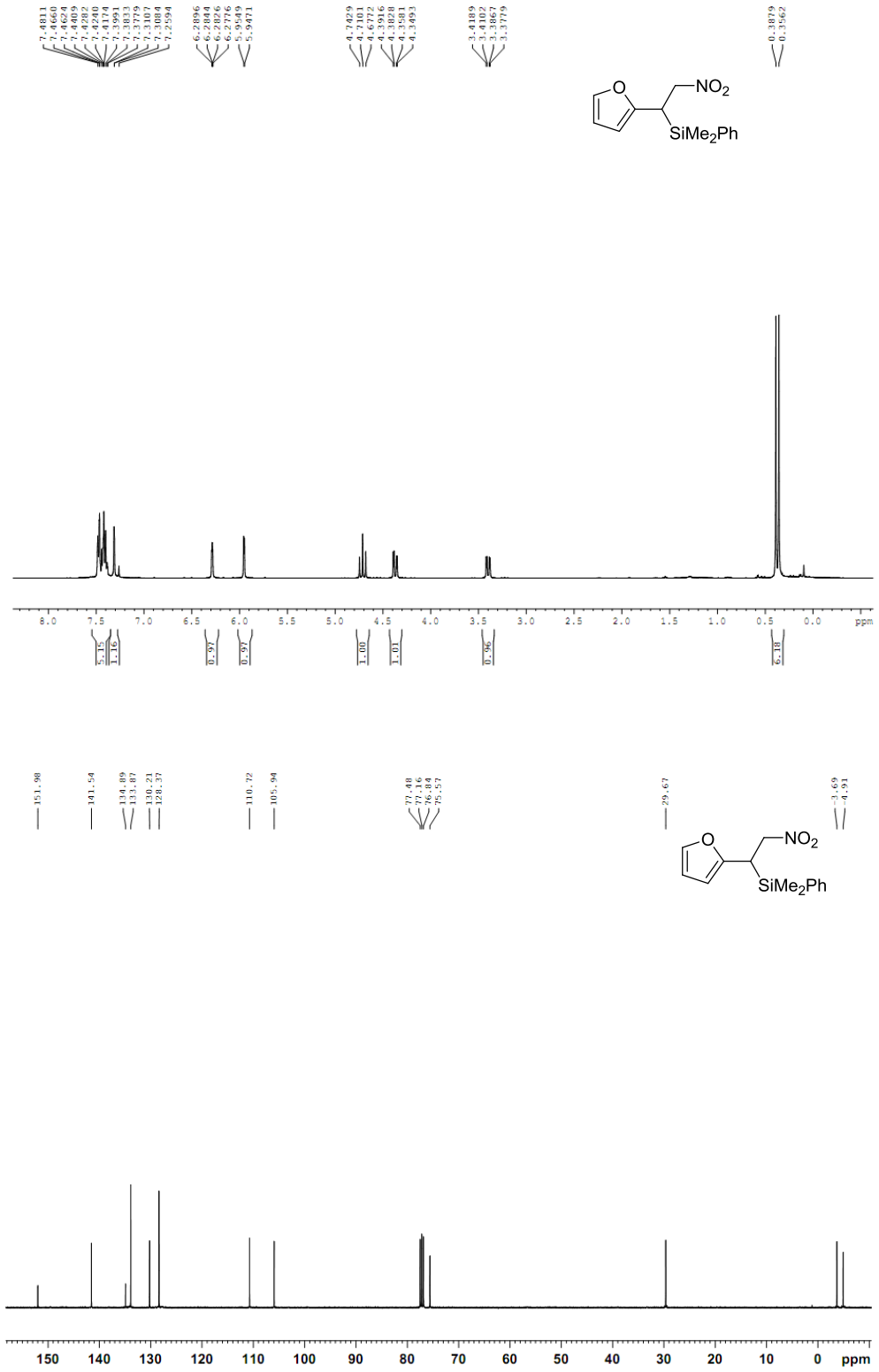




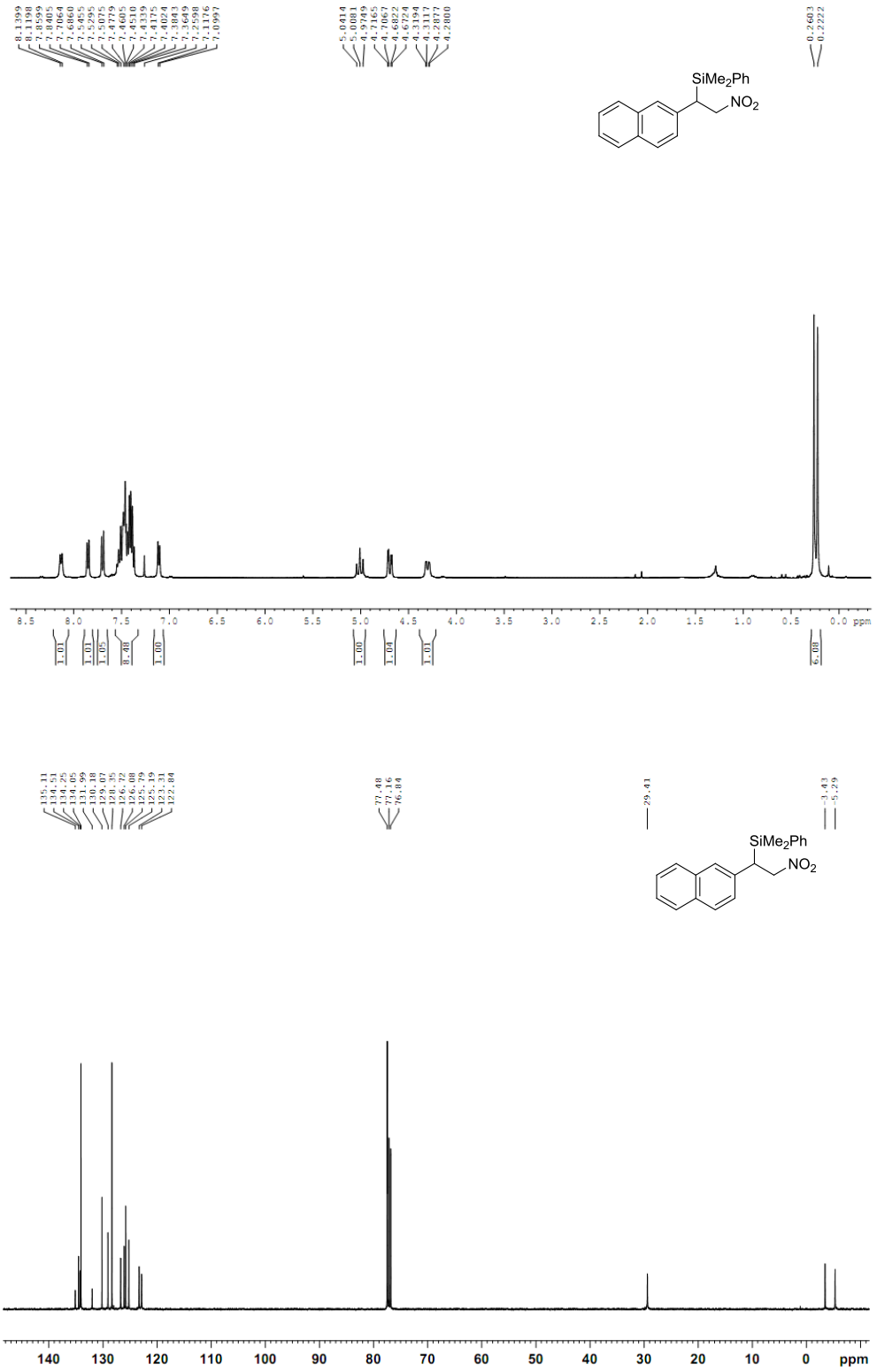
4n **^{1}H-NMR** ($CDCl_3$, 400M, ppm); **^{13}C-NMR** ($CDCl_3$, 101M, ppm)



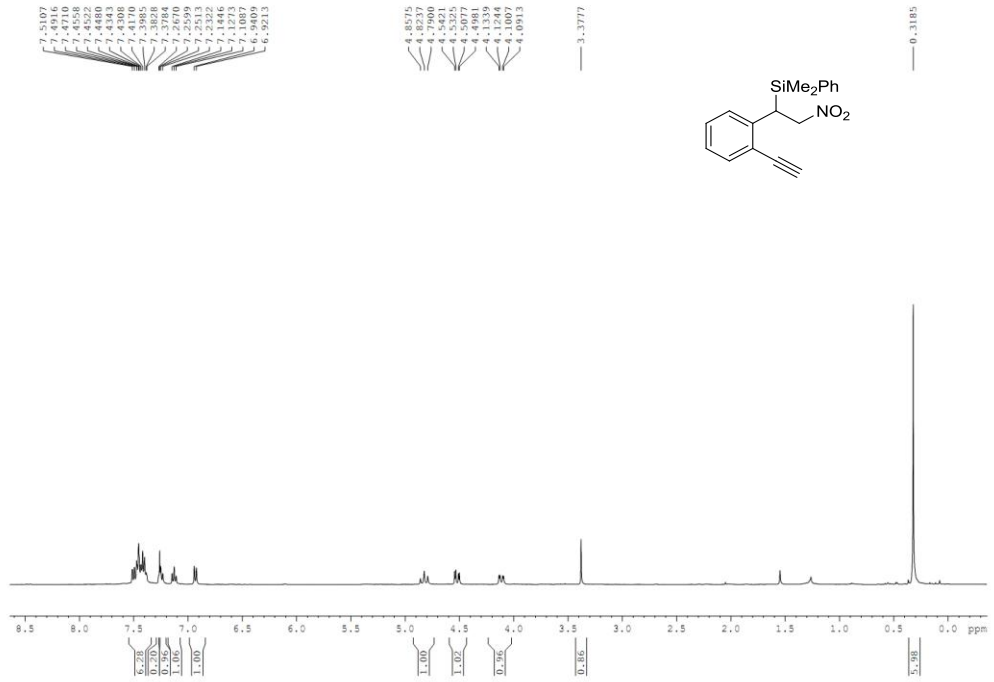
4o **^{1}H-NMR** ($CDCl_3$, 400M, ppm); **^{13}C-NMR** ($CDCl_3$, 101M, ppm)

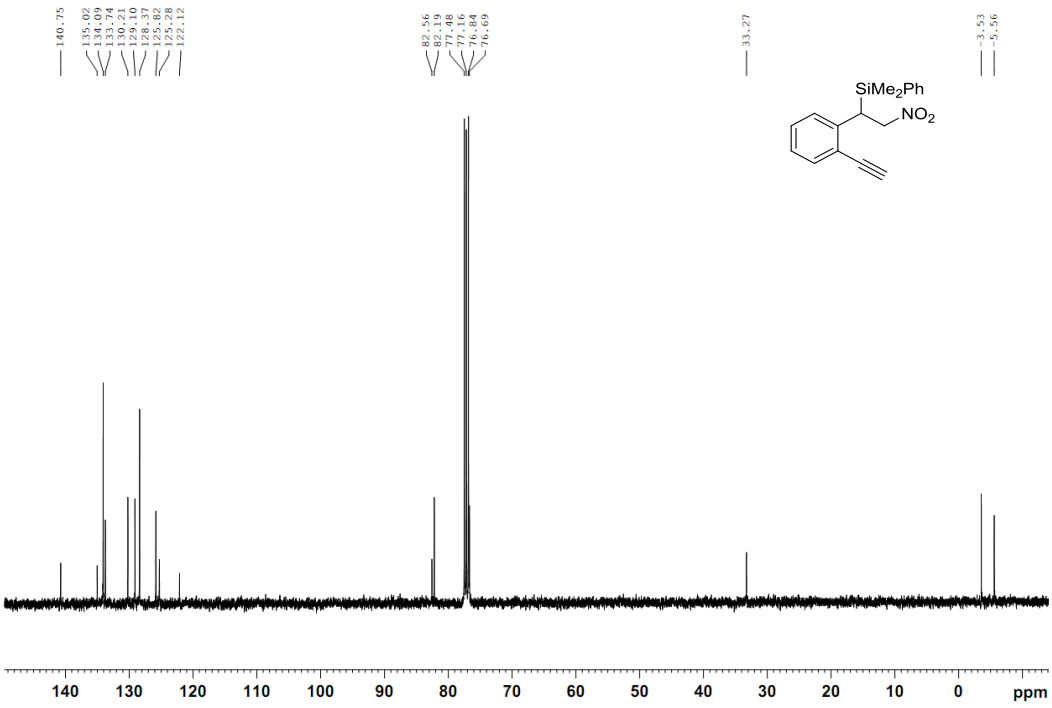


4p **^{1}H-NMR** ($CDCl_3$, 400M, ppm); **^{13}C-NMR** ($CDCl_3$, 101M, ppm)

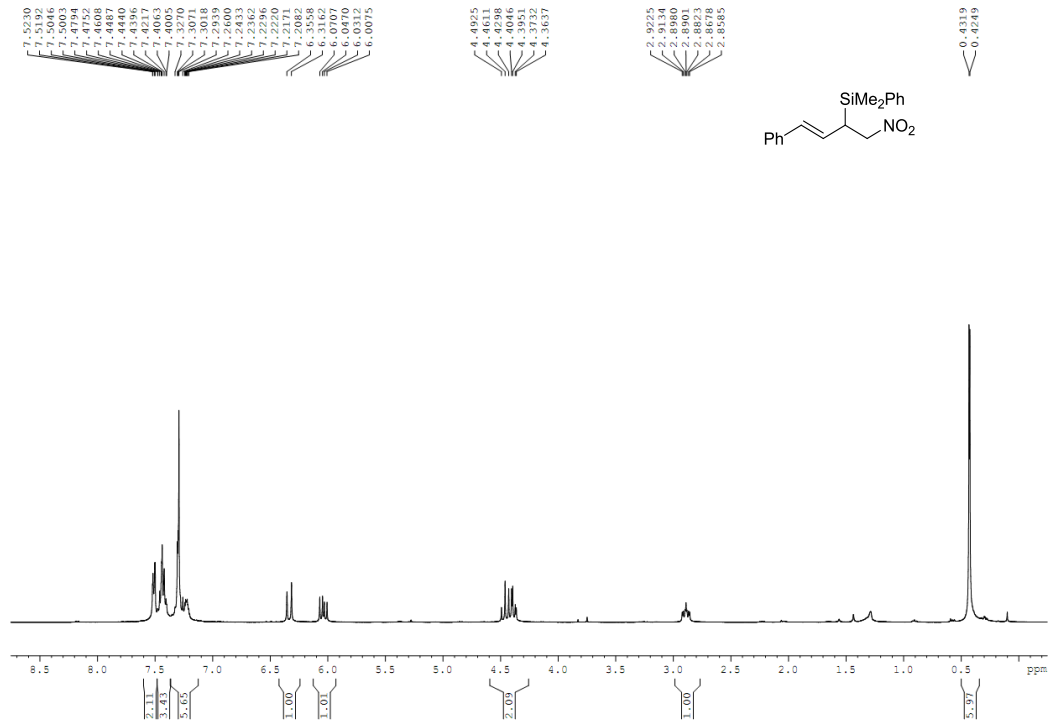


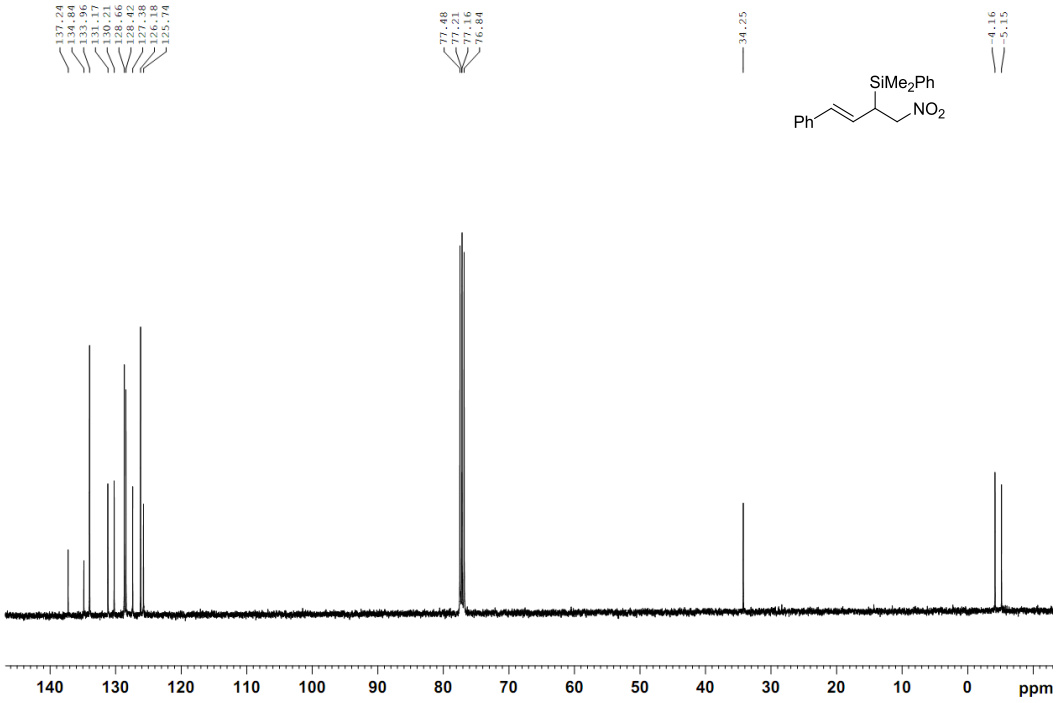
4q **^{1}H-NMR** ($CDCl_3$, 400M, ppm); **^{13}C-NMR** ($CDCl_3$, 101M, ppm)



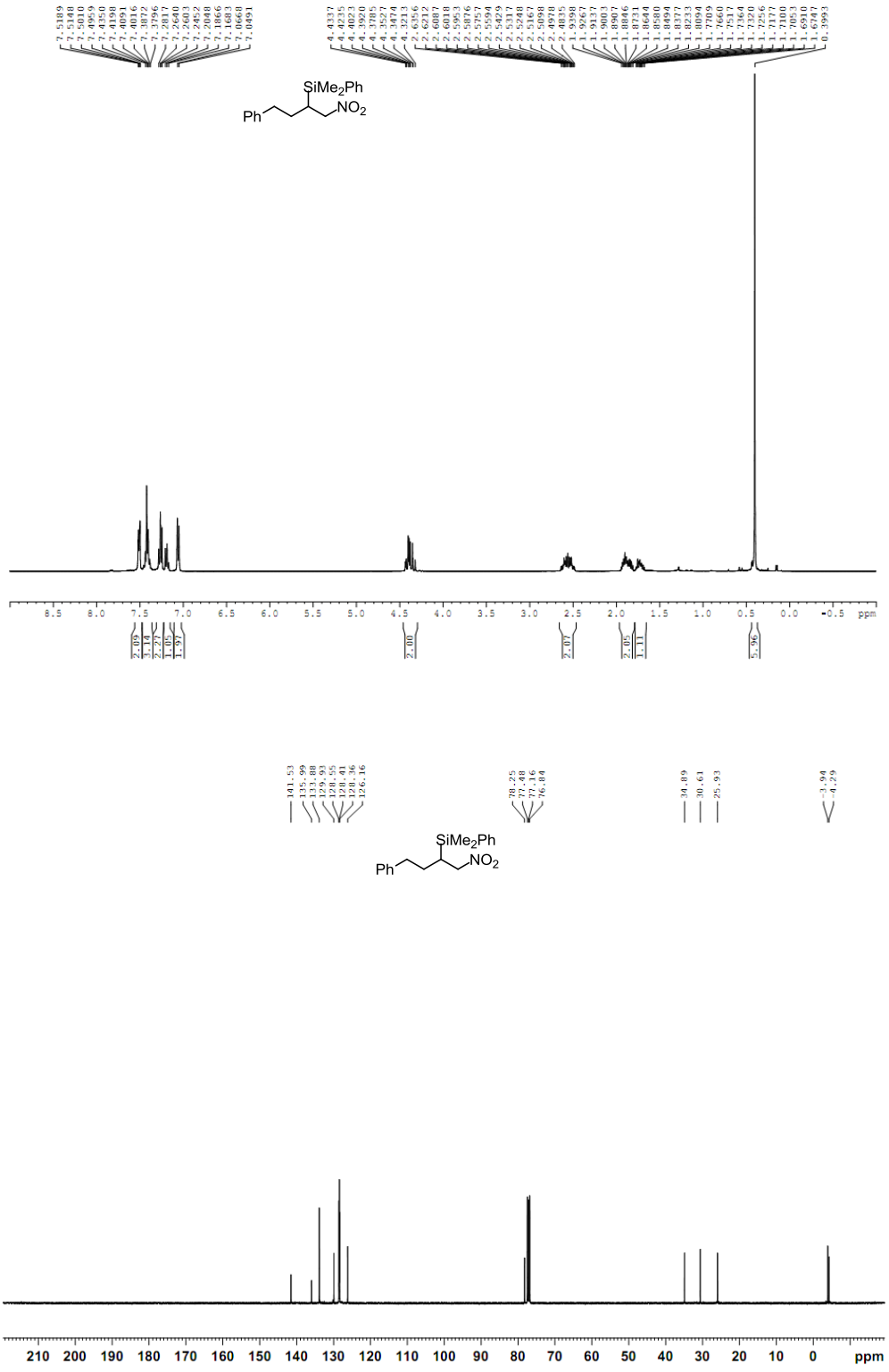


4r **^{1}H-NMR** ($CDCl_3$, 400M, ppm); **^{13}C-NMR** ($CDCl_3$, 101M, ppm)

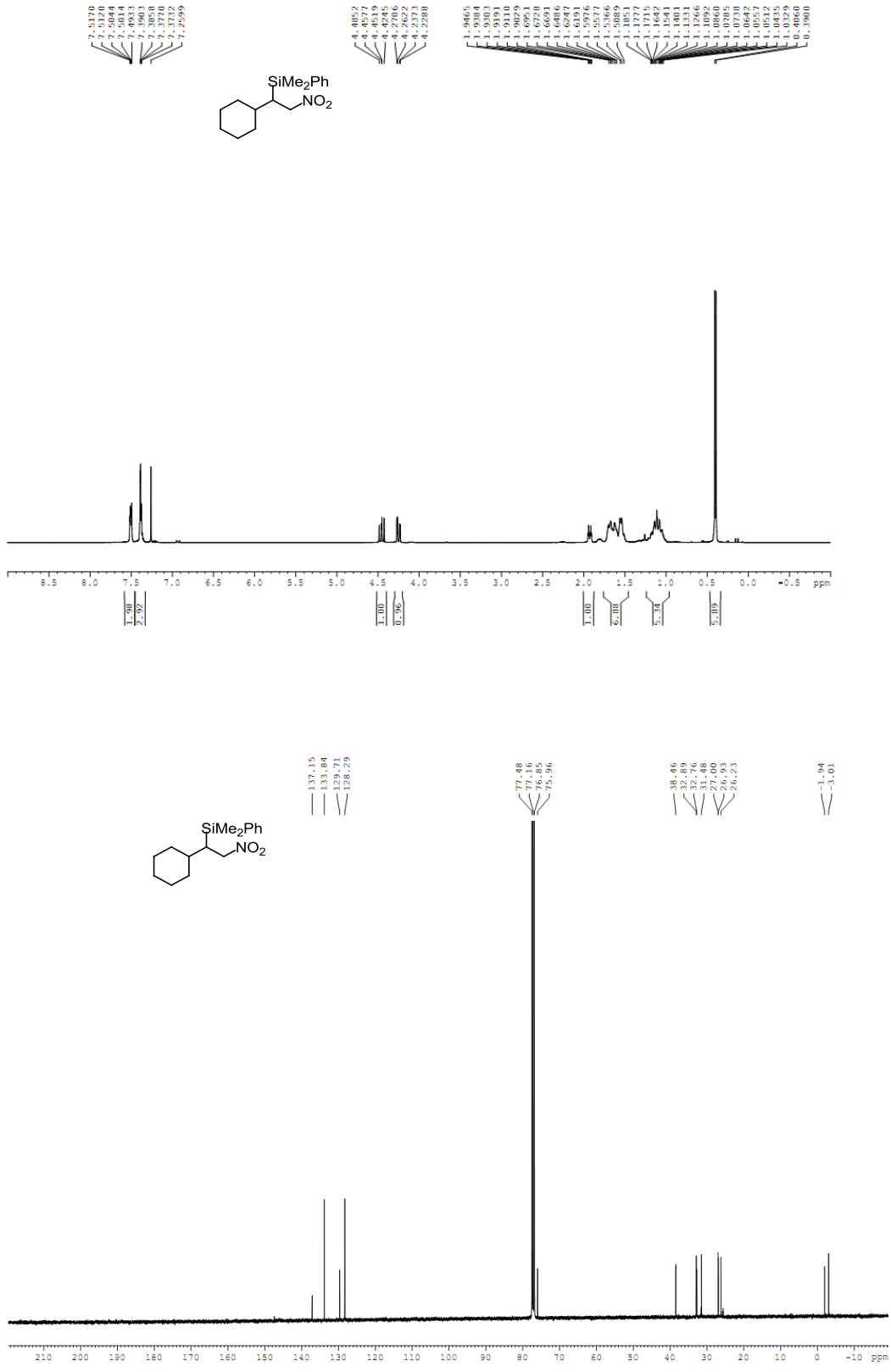




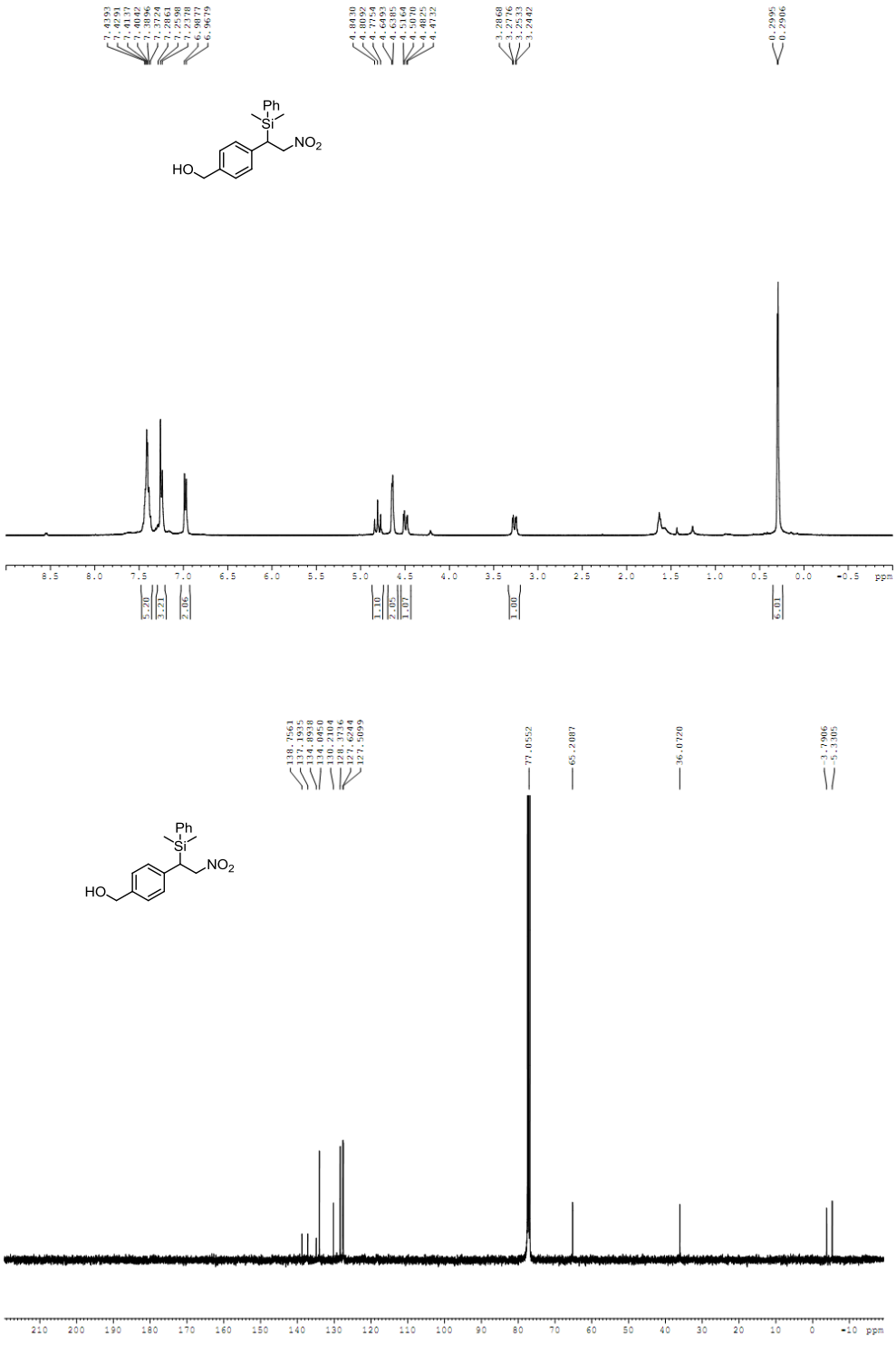
4s **^{1}H-NMR** ($CDCl_3$, 400M, ppm); **^{13}C-NMR** ($CDCl_3$, 101M, ppm)



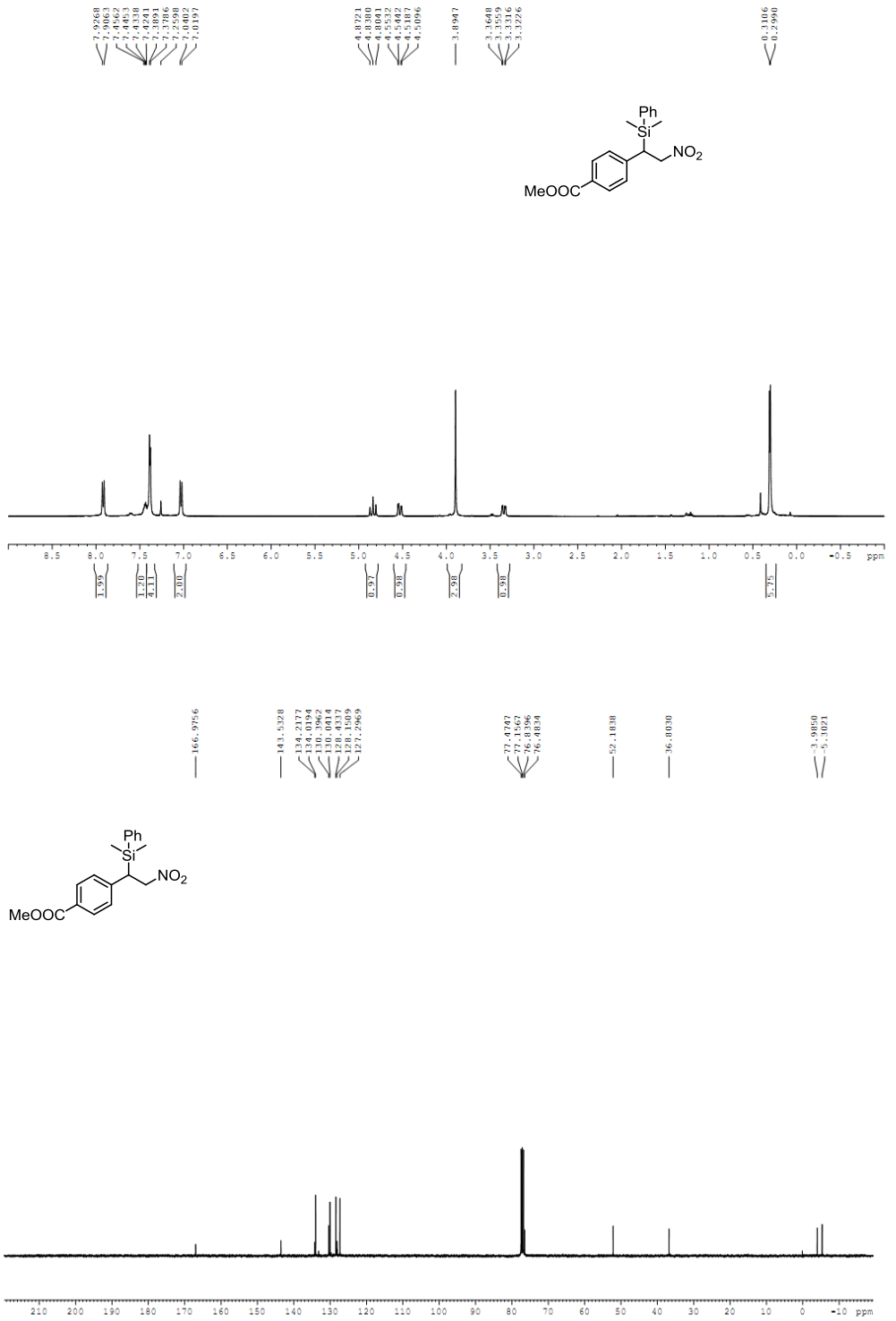
4t **^{1}H-NMR** ($CDCl_3$, 400M, ppm); **^{13}C-NMR** ($CDCl_3$, 101M, ppm)



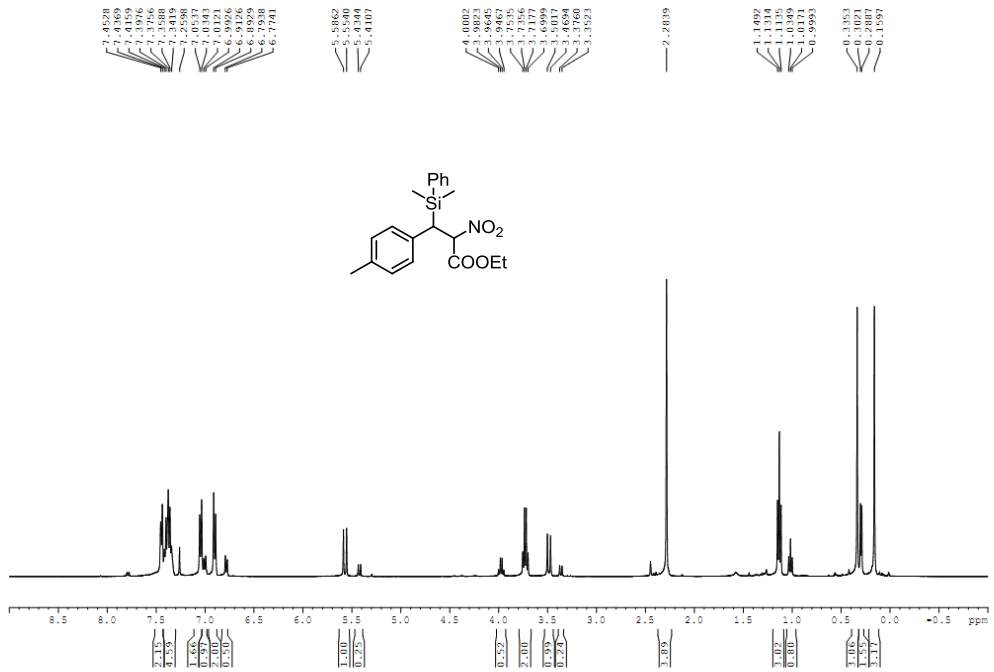
4u **^{1}H-NMR** ($CDCl_3$, 400M, ppm); **^{13}C-NMR** ($CDCl_3$, 101M, ppm)

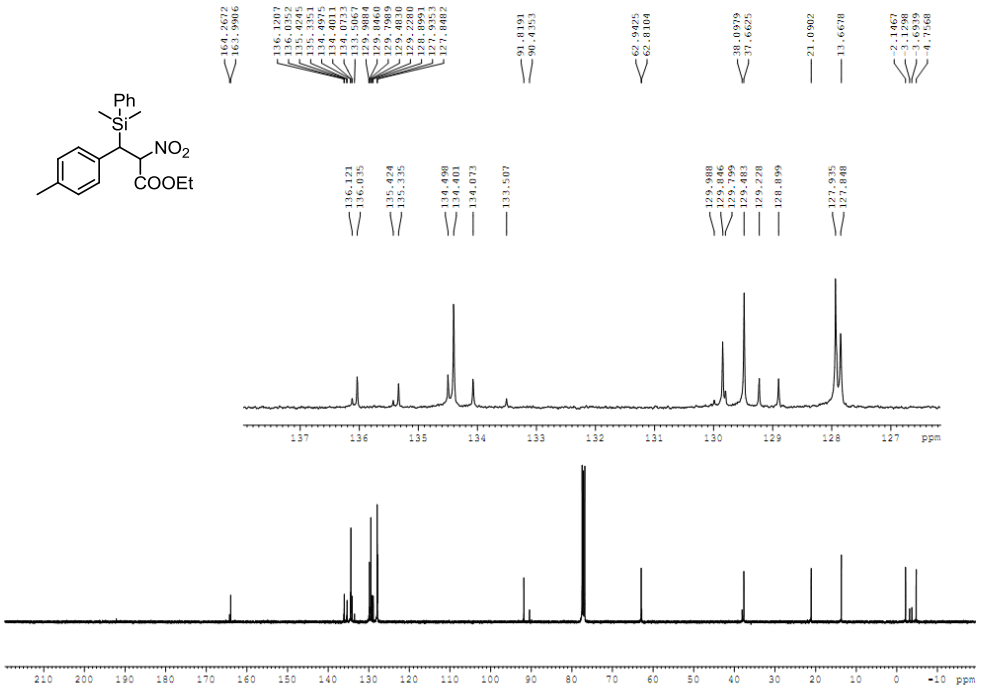


4v ^{1}**H-NMR** ($CDCl_3$, 400M, ppm); ^{13}**C-NMR** ($CDCl_3$, 101M, ppm)

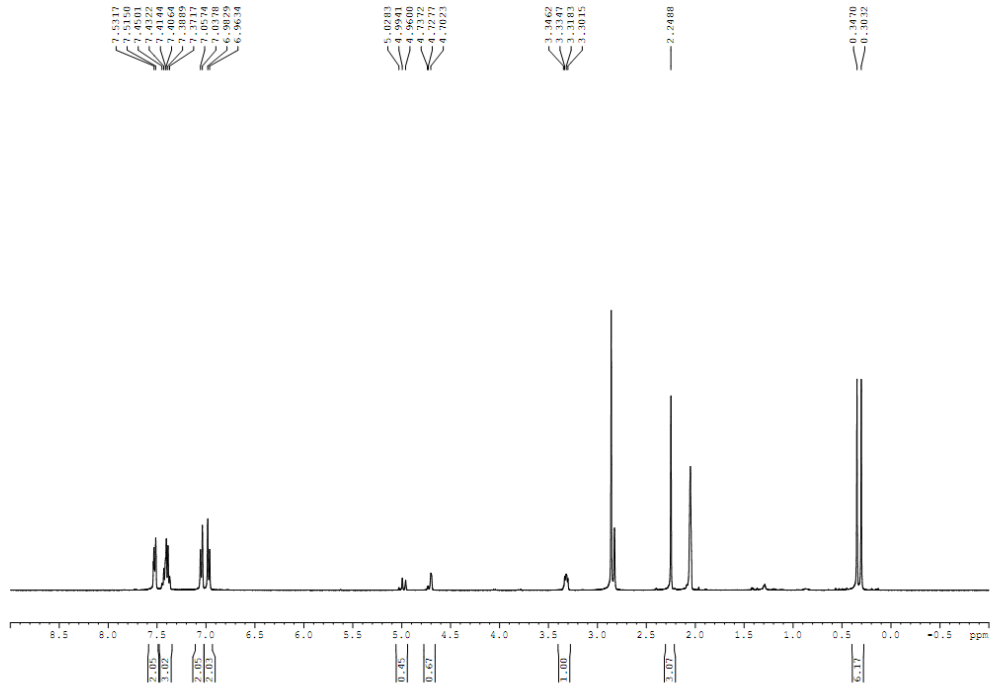


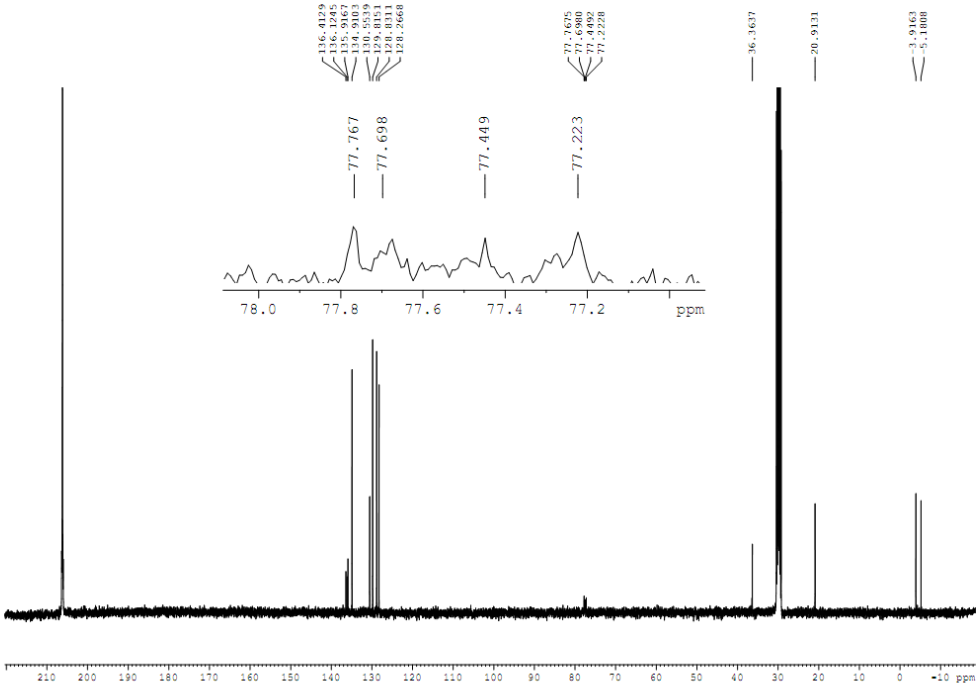
4w ^{1}**H-NMR** ($CDCl_3$, 400M, ppm); ^{13}**C-NMR** ($CDCl_3$, 101M, ppm)



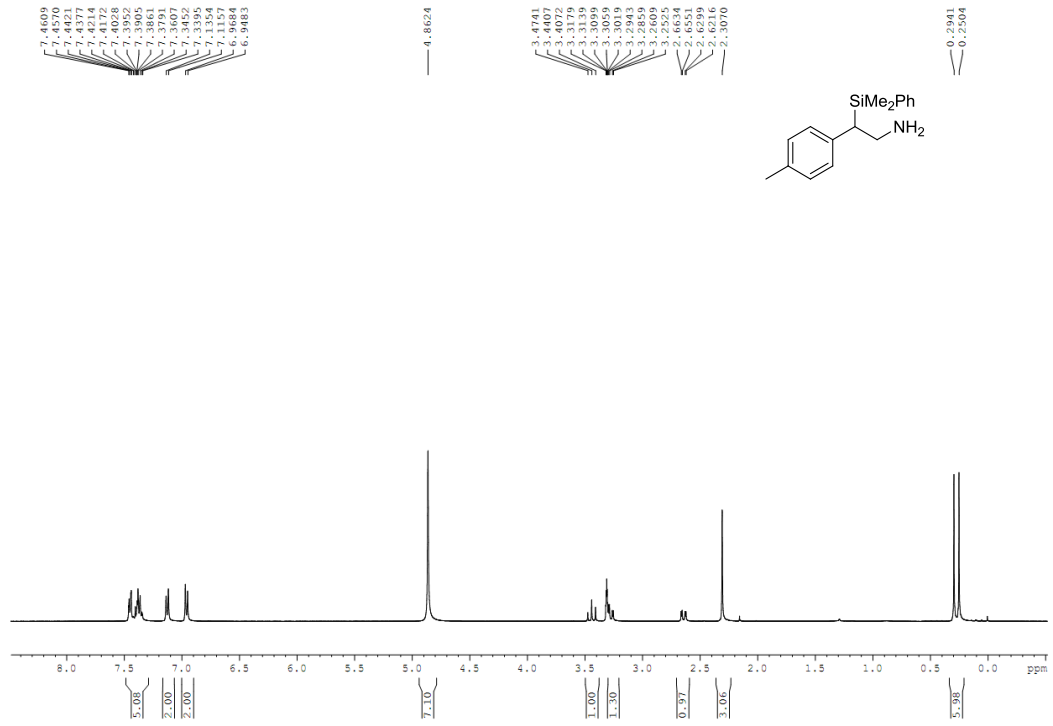


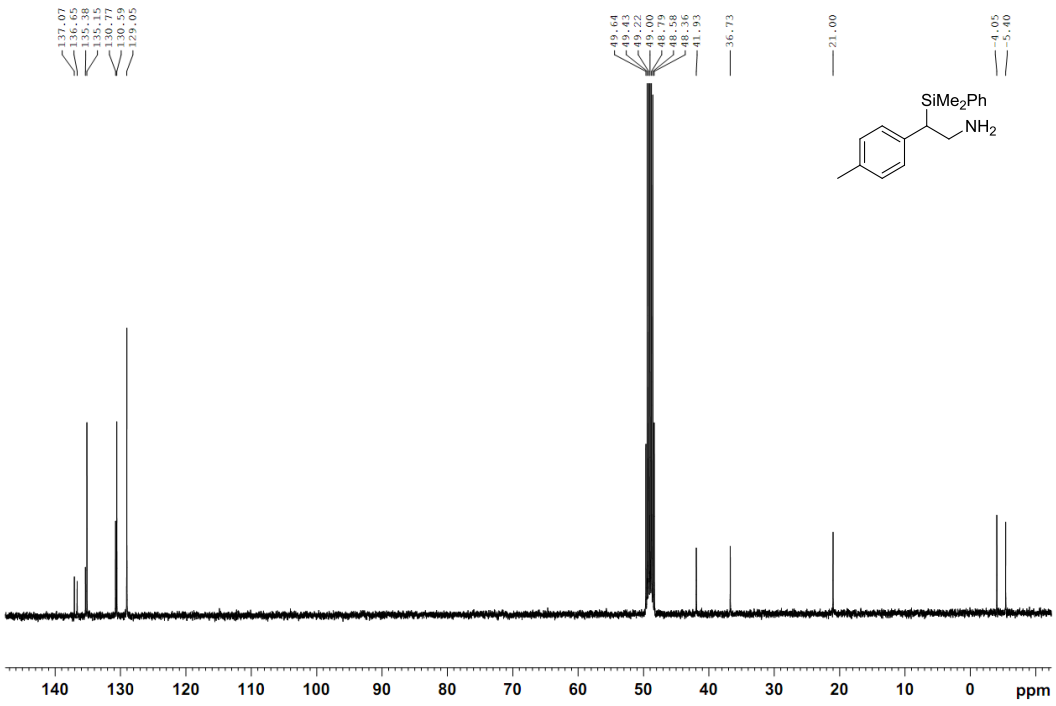
D-**4b** ^{1}**H-NMR** (d_6-acetone, 400M, ppm); ^{13}**C-NMR** (d_6-acetone, 101M, ppm)





13b ^{1}H-NMR (CD_3OD, 400M, ppm); **^{13}C-NMR** (CD_3OD, 101M, ppm)





13i ^{1}**H-NMR** (CD_3OD, 400M, ppm); ^{13}**C-NMR** (CD_3OD, 101M, ppm)