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Cooperative Organocatalysis of Mukaiyama-Type Aldol Reactions by Thioureas and Nitro Compounds

Supporting Information

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1. Nomenclature and abbreviations

Table S1. Nomenclature and abbreviations

Abbreviation	Name/description
INEPT	Insensitive nuclei enhanced by polarization transfer
HMDS	Hexamethyldisilazane
HPLC	High Performance Liquid Chromatography
HRMS	High Resolution Mass Spectrometry
NMR	Nuclear Magnetic Resonance
rps	Revolutions per second
TBS	tert-Butyldimethylsilyl
TIPS	Triisopropylsilyl
THF	Tetrahydrofuran
wt. %	Weight Percent

2. Materials and methods

Materials and Synthetic Techniques

All reagents and solvents were provided by commercial suppliers (Sigma-Aldrich, Fisher Scientific and VWR) and used without further purification unless otherwise noted. Reactions requiring anhydrous conditions were performed under positive argon or nitrogen pressure using standard Schlenk line techniques. Nitromethane was distilled in the presence of P_2O_5 and stored over 4Å molecular sieves under argon. 1,3-Bis-(3,5-bis(trifluoromethyl)phenyl)thiourea (**1a**)[1] and 1-ethoxy-1-[(*tert*-butyldimethylsilyl)oxy]-1-ethoxyethene (**3a**)[2] were synthesized by previously reported techniques.

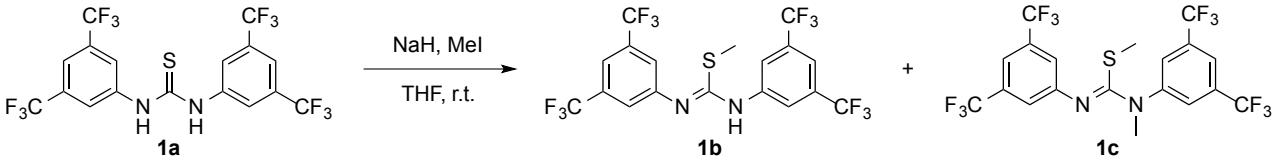
High Resolution Mass Spectrometry

HRMS analyses were performed by KAUST Analytical Core Labs (4700 King Abdullah University of Science and Technology, Thuwal, 23955-6900, Saudi Arabia).

NMR Spectroscopy

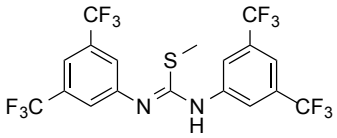
Data for routine characterization of small molecules and polymers were recorded at room temperature on Bruker Avance-III 400 MHz and 600 MHz NMR spectrometers equipped with a Z-axis gradient BBO probe. NMR chemical shifts are reported in ppm and are calibrated against residual solvent signals of $CDCl_3$ (^{1}H δ 7.26, ^{13}C δ 77.16). ^{29}Si NMR experiments were run using INEPT to enhance ^{29}Si NMR signals for no-selective polarization transfer.

3. Synthesis of Thiourea Catalysts



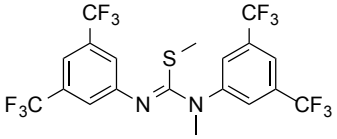
Sodium hydride (72.4 mg, 3 mmol, 60 *wt*. % dispersion in mineral oil, 1.5 eq.) was added to a solution of 1,3-bis-(3,5-bis(trifluoromethyl)phenyl)thiourea (**1a**)[1] (1.01 g, 2 mmol, 1 eq.) in 10 mL of dry THF under an argon atmosphere. The reaction mixture was stirred for 15 min at room temperature and iodomethane (856 mg, 0.376 mL, 6 mmol, 3 eq.) was added. The resulting mixture was stirred overnight at room temperature under argon. After this time, the solvent was removed in *vacuo*, and the residue was taken up in hexane (100 mL). The obtained suspension was filtered and evaporated. The crude mixture of products was purified by column chromatography (hexane:ethyl acetate, 100:1->80:20). Methyl (*Z*)-N,N'-bis-(3,5-bis(trifluoromethyl)phenyl)-N-methylcarbamimidothioate (**1c**) (323 mg, 31 %) was obtained as the first fraction. Methyl (*Z*)-N,N'-bis-(3,5-bis(trifluoromethyl)phenyl)-carbamimidothioate (**1b**) (374 mg, 36 %) was obtained as the second fraction.

Methyl (*Z*)-N,N'-bis-(3,5-bis(trifluoromethyl)phenyl)-carbamimidothioate (1b)



White solid. Isolated yield 36 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (s, 5H), 6.74 (s, 1H), 2.36 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.90, 151.50, 132.52 (q, *J* = 33.4 Hz), 123.27 (q, *J* = 272.8 Hz), 121.19, 117.29, 15.15. ^{19}F NMR (377 MHz, $CDCl_3$): δ -63.02 (s, 12F) ppm. HRMS (ESI+) calculated for $[C_{18}H_{11}N_2F_{12}S]^+$: 515.04458, found: 515.04500.

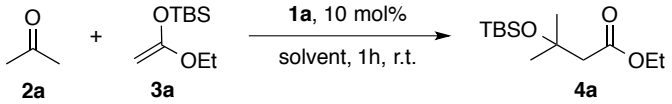
Methyl (*Z*)-N,N'-bis-(3,5-bis(trifluoromethyl)phenyl)-N-methylcarbamimidothioate (1c)



White solid. Isolated yield 31 %. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (s, 1H), 7.53 (s, 2H), 7.42 (s, 1H), 7.24 (s, 2H), 3.49 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.08, 150.03, 146.77, 132.66 (q, *J* = 33.8 Hz), 132.05 (q, *J* = 33.2 Hz), 124.74, 124.56, 123.20 (q, *J* = 272.7 Hz), 122.78 (q, *J* = 272.9 Hz), 121.33, 118.79, 116.06, 116.02, 115.98, 41.13, 15.71. ^{19}F NMR (377 MHz, $CDCl_3$): δ -63.16 (s, 6F), -63.19 (s, 6F) ppm. HRMS (ESI+) calculated for $[C_{19}H_{13}N_2F_{12}S]^+$: 529.06023, found: 529.06018.

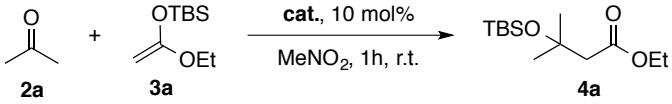
4. Catalytic reactions

Screening of solvents



Acetone (10 μL, 7.86 mg, 135 μmol, 1 eq.) and **1a** (6.77 mg, 13.5 μmol, 0.1 eq.) in 80 μL of solvent (see table 1, main text) were combined in an HPLC vial (1.8 ml), followed by the addition of **3a** (46 μL, 41 mg, 203 μmol, 1.5 eq.) under air; **3a** was added in a single portion. The vial was closed by screw cap and the reaction was stirred at room temperature for 1 hour. After this time 0.5 mL of $CDCl_3$ was added; the resulting solution was analyzed by NMR directly. Conversion was estimated by the ratio of ^1H signals at 1.35 (s, 6H) for ethyl 3-((*tert*-butyldimethylsilyl)oxy)-3-methylbutanoate (**4a**) and 2.17 (s, 6H) for acetone (**2a**).

Screening of catalysts



Acetone (10 μL, 7.86 mg, 135 μmol, 1 eq.), catalyst **1** (13.5 μmol, 0.1 eq., see table 2, main text) and nitromethane (73 μL, 82.61 mg, 1.35 mmol, 10 eq.) were combined in an HPLC vial (1.8 ml), followed by the addition of **3a** (46 μL, 41 mg, 203 μmol, 1.5 eq.) under air; **3a** was added in a single portion. The vial was closed by screw cap and the reaction was stirred at room temperature for 1 hour. 0.5 mL of $CDCl_3$ was added after this time and the resulting solution was analyzed by NMR directly. Conversion was estimated by the ratio of ^1H signals at 1.35 (s, 6H) for ethyl 3-((*tert*-butyldimethylsilyl)oxy)-3-methylbutanoate (**4a**) and 2.17 (s, 6H) for acetone (**2a**).

5. Kinetic experiments

General procedure

The compounds were mixed in a vial until the reaction mixture became homogeneous (10 – 20 seconds) and then the solution was transferred into an NMR tube equipped with a thinner internal tube (the internal tube was filled with 0.02 mL of HMDS (^{29}Si NMR δ = 2.2 ppm) in 0.1 mL of $CDCl_3$). The combined tubes were placed into a Bruker 600 MHz NMR spectrometer, spun at 20 rps and analyzed every 2-20 minutes. The first recorded point of each analysis was ~5 minutes after the reaction started.

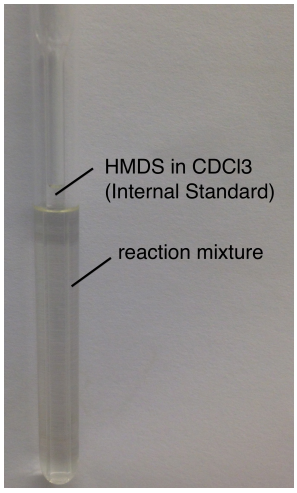
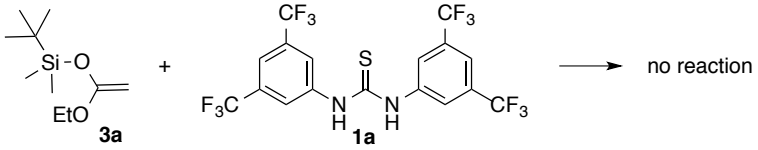


Figure S1. NMR tube set-up for kinetic experiments.

Reaction 3a with 1a



Thiourea **1a** (49 mg, 0.097 mmol, 1 eq.) was dissolved in **3a** (334 µL, 298 mg, 1.470 mmol, 15 eq.) and analyzed via ^{29}Si NMR every 20 minutes for 17 hours. No degradation was observed (figure S2).

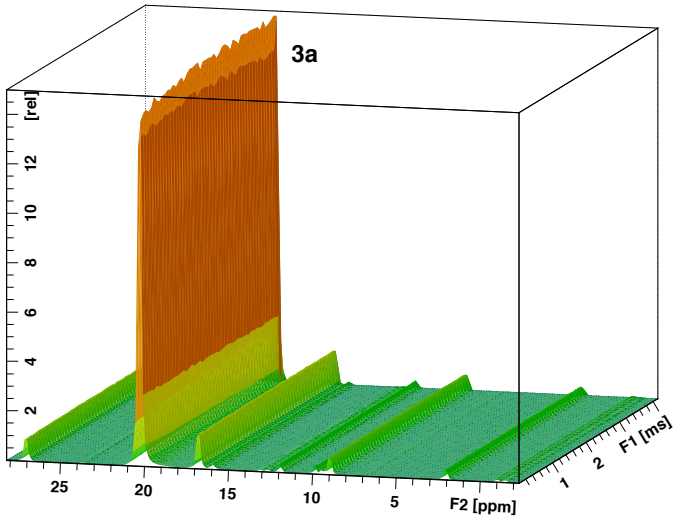
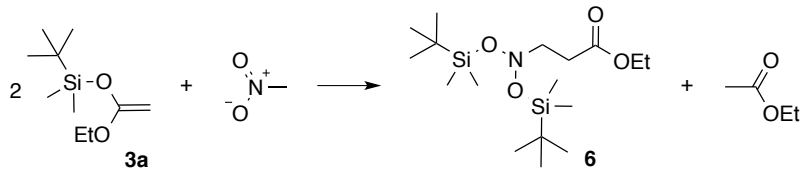


Figure S2. ^{29}Si NMR spectra showing the stability of 3a in presence of thiourea 1a. Z axis: time from 0.1-17 hours.

Reaction of 3a with nitromethane



Nitromethane (302 µL, 341 mg, 5.590 mmol, 10 eq.) was mixed with **3a** (190 µL, 170 mg, 0.838 mmol, 1.5 eq.) and analyzed by ^{29}Si NMR every 20 minutes for 17 hours (Figure S3).

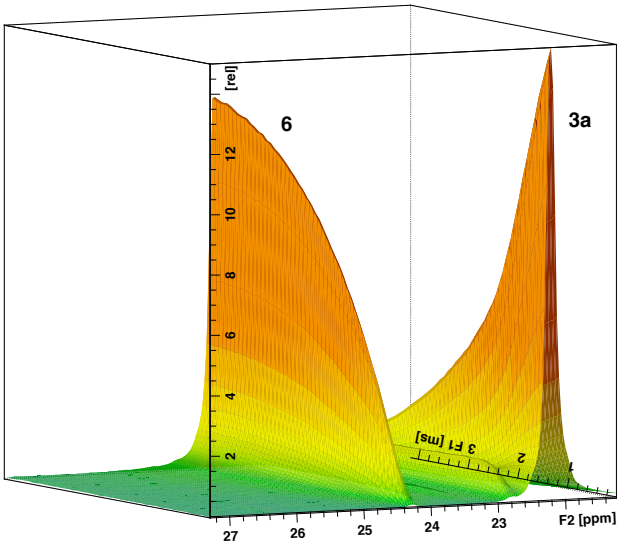
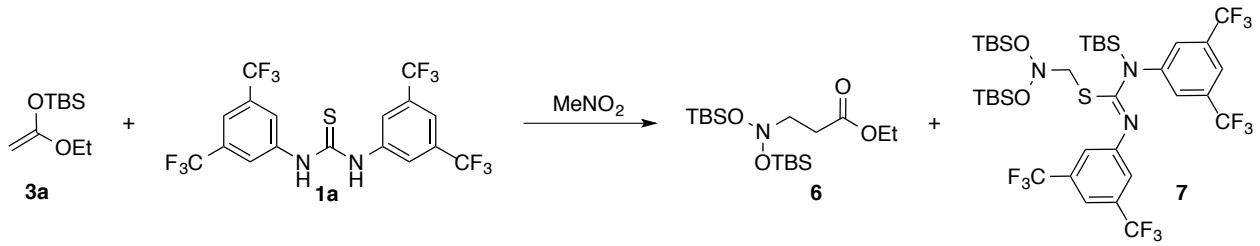


Figure S3. ^{29}Si NMR spectra for degradation of 3a in nitromethane. Z axis: time from 0.1-17 hours.

After 23 hours 0.1 mL of the reaction mixture was diluted with 0.5 mL of $CDCl_3$ and analyzed by ^{1}H NMR (Figure S12). The molar ratio between **6** (peak at 3.27 ppm, 2H) and ethyl acetate (peak at 2.03 ppm, 3H) is 1:1. The peak at 5.73 ppm corresponds to **5**. A similar structure (TIPS instead of TBS) was synthetized previously[3] and has the same shift (δ = 5.75 ppm, s, 2H) for CH_2=N protons. The reaction mixture was evaporated under vacuum yielding 120 mg (76 %) of ethyl 3-(bis((tert-butyldimethylsilyl)oxy)amino)propanoate (**6**) as slightly yellow oil. ^{1}H NMR (600 MHz; $CDCl_3$): δ 4.11 (q, *J* = 7.1 Hz, 2H), 3.27 (t, *J* = 6.9 Hz, 2H), 2.60 (t, *J* = 6.9 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H), 0.88 (s, 18H), 0.15 (s, 6H), 0.13 (s, 6H). ^{13}C NMR (151 MHz; $CDCl_3$): δ 172.3, 62.2, 60.5, 29.9, 26.1, 17.9, 14.3, -3.8, -4.5. ^{29}Si NMR (119 MHz; $CDCl_3$): δ 23.7 (s, 2Si). HRMS (ESI$^+$) calculated for $[C_{17}H_{39}NO_4Si_2K]^+$: 416.20492, found: $[C_{17}H_{39}NO_4Si_2K]^+$: 416.20492.

Reaction of 3a with nitromethane in the presence of 1a



Thiourea **1a** (28 mg, 0.056 mmol, 0.1 eq.) was dissolved in nitromethane (302 µL, 341 mg, 5.590 mmol, 10 eq.). The resulting mixture was mixed with **3a** (190 µL, 170 mg, 0.838 mmol, 1.5 eq.) and analyzed by ^{29}Si NMR every 5 minutes for 17 hours (Figure S4).

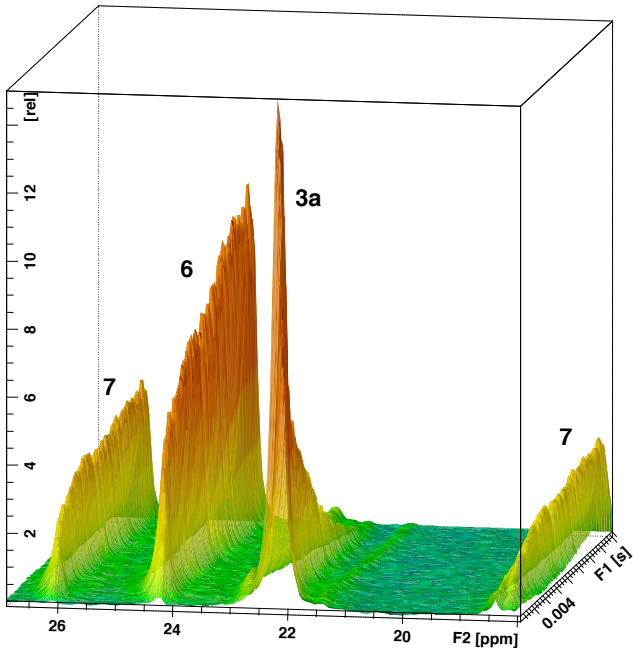
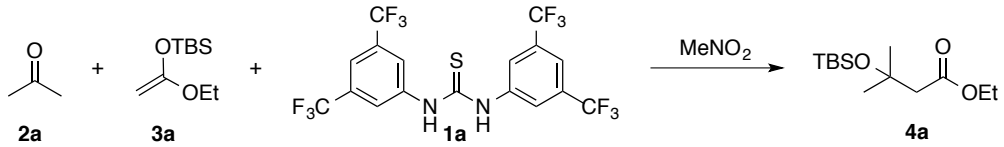


Figure S4. ^{29}Si NMR spectra for the degradation of 3a in nitromethane in presence of 1a. Z axis: time from 0.1-17 hours.

After 17 hours the reaction mixture was evaporated under high vacuum (0.8 mBar) at 120 °C to give a 110 mg of mixture of **6** and **7** as a yellow oil. Purification of **7** via column chromatography failed and therefore the structure of **7** was determined by NMR in as a mixture with **6**. (Bis((tert-butyldimethylsilyl)oxy)amino)methyl (Z)-N,N'-bis(3,5-bis(trifluoromethyl)phenyl) -N-(tert-butyldimethylsilyl) carbamimido thioate (**7**): ^{1}H NMR (600 MHz; $CDCl_3$): δ 7.77 (s, 1H), 7.64 (s, 2H), 7.48 (s, 1H), 7.37 (s, 2H), 3.74 (s, 2H), 1.02 (s, 9H), 0.76 (s, 18H), 0.14 (s, 6H), 0.05 (s, 6H), -0.09 (s, 6H). ^{13}C NMR (101 MHz; $CDCl_3$): δ 159.9, 149.38, 145.44, 132.64, 130.59, 124.7, 121.61, 120.79, 115.99, 115.94, 68.4, 28.3, 25.8, 20.2, 17.85, -1.8, -4.5, -4.9. ^{29}Si NMR (119 MHz; $CDCl_3$): δ 25.4 (s, 2Si), 17.0 (s, 1Si). ^{19}F NMR (377 MHz; $CDCl_3$): δ -63.1 (s, 12F).

Mukaiyama reaction



Acetone (41.3 µL, 32.46 mg, 0.558 mmol, 1 eq.) and thiourea **1a** (28 mg, 0.056 mmol, 0.1 eq.) was dissolved in nitromethane (302 µL, 341 mg, 5.590 mmol, 10 eq.). The resulting mixture was combined with **3a** (190 µL, 170 mg, 0.838 mmol, 1.5 eq.) and analyzed by ^{29}Si NMR every 2 minutes for 2 hours (Figure S5). The reaction completed after 60 minutes.

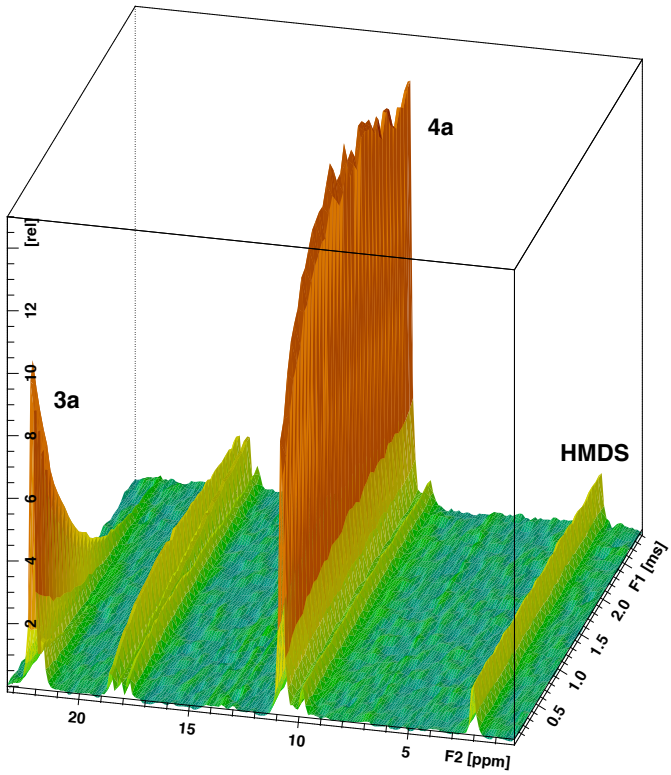
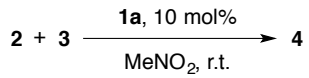


Figure S5. ^{29}Si NMR spectra for the Mukaiyama reaction. Z axis; time from 5-120 minutes.

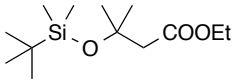
6. Exploration of Scope

General procedure



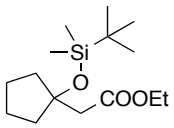
A solution of carbonyl compound **2** (1 mmol, 1 eq., see table 3, main text) and **1a** (50 mg, 0.1 mmol, 0.1 eq.) in 0.54 mL of nitromethane were combined in an HPLC vial (1.8 mLl). **3** (1.5 mmol, 1.5 eq.) was then added in one portion under air. The vial was closed by screw cap and the reaction was stirred at room temperature. After the reaction was complete, nitromethane was evaporated in *vacuo*. The products were purified by column chromatography.

Ethyl 3-((*tert*-butyldimethylsilyl)oxy)-3-methylbutanoate (4a)



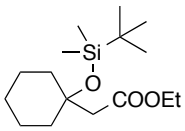
Colorless oil. Isolated yield: 88 %. Purification by column chromatography, hexane:ethyl acetate, 100:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.10 (q, *J* = 7.2 Hz, 2H), 2.44 (s, 2H), 1.35 (s, 6H), 1.25 (t, *J* = 7.2 Hz, 3H), 0.83 (s, 9H), 0.07 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.4, 72.7, 60.2, 49.8, 30.3, 25.8, 18.1, 14.3, -2.1. HRMS (ESI+) calculated for $[C_{13}H_{29}O_3Si]^+$: 261.18805, found: 261.18803.

Ethyl 2-(1-((tert-butyldimethylsilyl)oxy)cyclopentyl)acetate (4b)



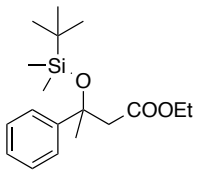
Colorless oil. Isolated yield: 56 %. Purification by column chromatography, hexane:ethyl acetate, 100:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.10 (q, *J* = 7.1 Hz, 2H), 2.58 (s, 2H), 1.85-1.65 (m, 6H), 1.64-1.51 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.83 (s, 9H), 0.08 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.5, 82.9, 60.2, 46.2, 39.8, 25.6, 23.3, 18.0, 14.1, -2.5. HRMS (ESI^+) calculated for $[C_{15}H_{30}O_3SiNa]^+$: 309.18564, found: $[C_{15}H_{30}O_3SiNa]^+$: 309.18534.

Ethyl 2-(1-((tert-butyldimethylsilyl)oxy)cyclohexyl)acetate (4c)



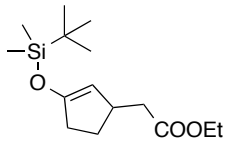
Colorless oil. Isolated yield: 88 %. Purification by column chromatography, hexane:ethyl acetate, 100:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.10 (q, *J* = 7.1 Hz, 2H), 2.51 (s, 2H), 1.78-1.70 (m, 2H), 1.70-1.61 (m, 2H), 1.61-1.50 (m, 2H), 1.45-1.31 (m, 4H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.86 (s, 9H), 0.09 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.6, 74.8, 60.4, 46.6, 38.7, 26.1, 25.8, 23.1, 18.5, 14.4, -1.7. NMR data corresponded to peaks previously reported.[4]

Ethyl 3-((*tert*-butyldimethylsilyl)oxy)-3-phenylbutanoate (4d)



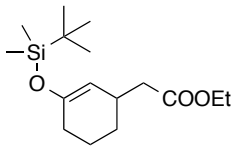
Colorless oil. Isolated yield: 71 %. Purification by column chromatography, hexane:ethyl acetate, 100:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47-7.45 (m, 2H), 7.33-7.21 (m, 3H), 3.97 (q, *J* = 7.0 Hz, 2H), 2.75 (dd, *J* = 51.0, 13.5 Hz, 2H), 1.82 (s, 3H), 1.09 (t, *J* = 7.2 Hz, 3H), 0.93 (s, 9H), 0.08 (s, 3H), -0.12 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.5, 147.5, 127.9, 127.0, 125.5, 75.8, 60.2, 51.3, 28.5, 26.1, 18.5, 14.1, -1.9, -2.4. HRMS (ESI$^+$) calculated for $[C_{18}H_{30}O_3SiNa]^+$: 345.18564, found: $[C_{18}H_{30}O_3SiNa]^+$: 345.18549.

Ethyl 2-(3-((tert-butyldimethylsilyl)oxy)cyclopent-2-en-1-yl)acetate (4e)



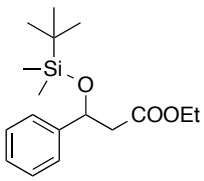
Colorless oil. Isolated yield: 87 %. Purification by column chromatography, hexane:ethyl acetate:triethylamine, 98:1:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.60 (d, *J* = 1.8 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.05-3.00 (m, 1H), 2.34-2.22 (m, 4H), 2.14-2.07 (m, 1H), 1.52-1.43 (m, 1H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.90 (s, 9H), 0.13 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.5, 156.5, 106.5, 60.6, 42.3, 39.1, 33.5, 28.5, 26.1, 18.7, 14.8, -4.1, -4.2. NMR data corresponded to peaks previously reported.[5]

Ethyl 2-(3-((tert-butyldimethylsilyl)oxy)cyclohex-2-en-1-yl)acetate (4f)



Colorless oil. Isolated yield: 99 %. Purification by column chromatography, hexane:ethyl acetate:triethylamine, 98:1:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.85-4.69 (m, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.70-2.57 (m, 1H), 2.33-2.18 (m, 2H), 2.04-1.90 (m, 2H), 1.75-1.70 (m, 2H), 1.62-1.52 (m, 1H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.22-1.06 (m, 1H), 0.90 (s, 9H), 0.11 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 151.8, 107.9, 60.3, 41.7, 32.0, 29.9, 28.7, 25.8, 21.3, 18.2, 14.4, -4.26, -4.34. NMR data corresponded to peaks previously reported.[6]

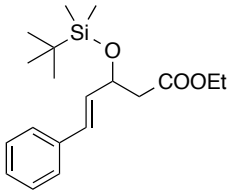
Ethyl 3-((*tert*-butyldimethylsilyl)oxy)-3-phenylpropanoate (4g)



Colorless oil. Isolated yield: 99 %. Purification by column chromatography, hexane:ethyl acetate, 100:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.24 (m, 5H), 5.14 (dd, *J* = 9.4, 4.0 Hz, 1H), 4.17-4.08 (m, 2H), 2.72 (dd, *J* = 14.6, 9.4 Hz, 1H), 2.54 (dd, *J* = 14.6, 4.0 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 3H), 0.84 (s, 9H), 0.02 (s, 3H), -0.18 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.7,

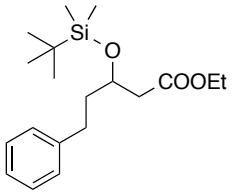
144.1, 128.4, 127.7, 125.9, 72.4, 60.8, 46.7, 25.8, 18.2, 14.3, -4.6, -5.2. NMR data corresponded to peaks previously reported.[7]

Ethyl (*E*)-3-((*tert*-butyldimethylsilyl)oxy)-5-phenylpent-4-enoate (4h)



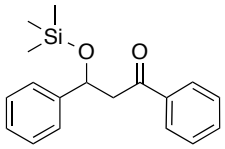
Colorless oil. Isolated yield: 99 %. Purification by column chromatography, hexane:ethyl acetate, 100:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.22 (m, 5H), 6.58 (d, *J* = 15.9 Hz, 1H), 6.20 (dd, *J* = 15.9, 6.7 Hz, 1H), 4.78 (qd, *J* = 6.6, 1.2 Hz, 1H), 4.16-4.12 (m, 2H), 2.66-2.50 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 3H), 0.90 (s, 9H), 0.09 (s, 3H), 0.07 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.2, 136.8, 131.8, 130.0, 128.7, 127.7, 126.6, 70.9, 60.6, 44.2, 25.9, 18.2, 14.4, -4.1, -4.9. NMR data corresponded to peaks previously reported.[8]

Ethyl 3-((*tert*-butyldimethylsilyl)oxy)-5-phenylpentanoate (4i)



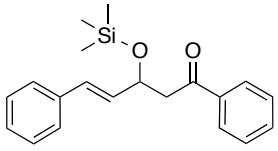
Colorless oil. Isolated yield: 41 %. Purification by column chromatography, hexane:ethyl acetate, 100:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.26 (m, 2H), 7.20-7.17 (m, 3H), 4.22 (dd, *J* = 6.6, 5.9 Hz, 1H), 4.13 (qd, *J* = 7.1, 2.6 Hz, 2H), 2.71-2.64 (m, 2H), 2.50 (qd, *J* = 12.9, 6.3 Hz, 2H), 1.89-1.80 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 3H), 0.94-0.85 (m, 9H), 0.07 (d, *J* = 13.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.8, 142.3, 128.52, 128.43, 125.9, 69.2, 60.5, 42.8, 39.5, 31.5, 25.9, 18.2, 14.3, -4.4, -4.6. HRMS (ESI$^+$) calculated for $[C_{19}H_{32}O_3SiNa]^+$: 359.20129, found: $[C_{19}H_{32}O_3SiNa]^+$: 359.20114.

1,3-Diphenyl-3-((trimethylsilyl)oxy)propan-1-one (4k)



Colorless oil. Isolated yield: 99 %. Purification by column chromatography, hexane:ethyl acetate, 100:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98-7.96 (m, 2H), 7.57-7.53 (m, 1H), 7.47-7.42 (m, 4H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.28-7.24 (m, 1H), 5.40 (dd, *J* = 8.8, 3.8 Hz, 1H), 3.57 (dd, *J* = 15.6, 8.8 Hz, 1H), 3.03 (dd, *J* = 15.6, 3.8 Hz, 1H), -0.02 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.6, 144.8, 137.7, 133.1, 128.56, 128.49, 128.43, 127.4, 125.8, 71.7, 49.8, 0.0. NMR data corresponded to peaks previously reported.[9]

(*E*)-1,5-diphenyl-3-((trimethylsilyl)oxy)pent-4-en-1-one (4l)



Colorless oil. Isolated yield: 99 %. Purification by column chromatography, hexane:ethyl acetate, 100:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99-7.96 (m, 2H), 7.58-7.21 (m, 8H), 6.62 (d, *J* = 15.8 Hz, 1H), 6.29 (dd, *J* = 15.8, 6.0 Hz, 1H), 5.02-4.97 (m, 1H), 3.42 (dd, *J* = 15.5, 7.8 Hz, 1H), 3.03 (dd, *J* = 15.5, 4.9 Hz, 1H), 0.07 (s, 8H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.7, 137.8, 137.0, 133.3, 132.3, 129.8, 128.82, 128.78, 128.66, 127.8, 126.7, 70.5, 47.4, 0.4. HRMS (ESI^+) calculated for $[C_{20}H_{24}O_2SiNa]^+$: 347.14378, found: $[C_{20}H_{24}O_2SiNa]^+$: 347.14339.

7. NMR spectra

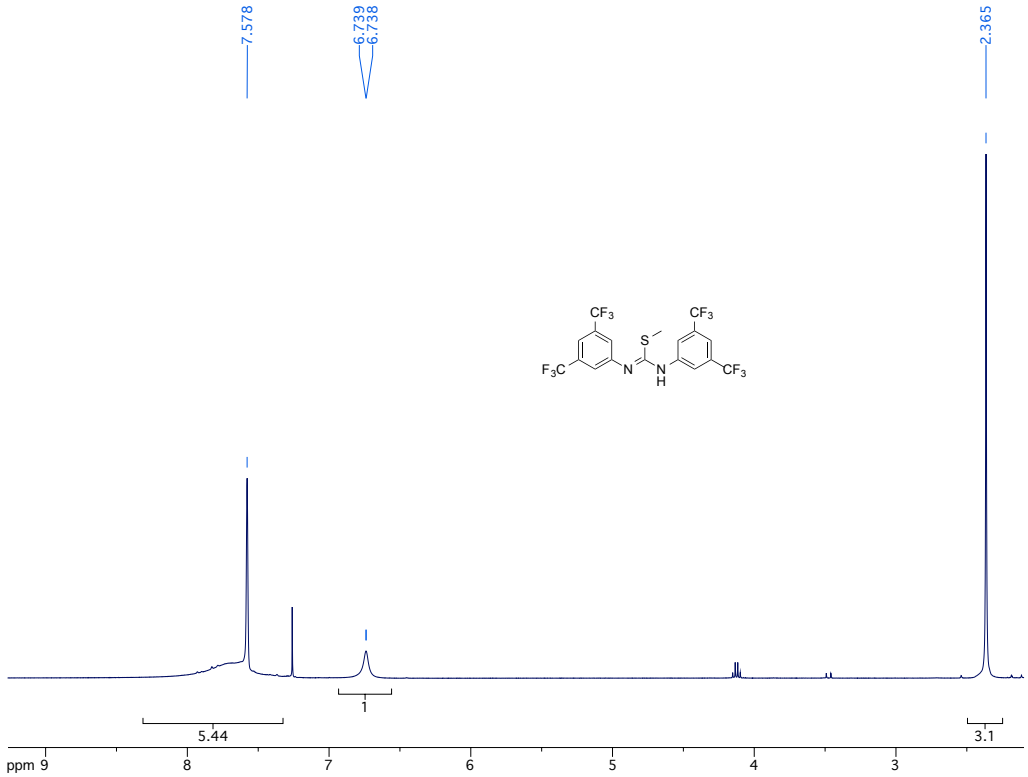


Figure S6. ^{1}H-NMR spectrum of 1b in $CDCl_3$.

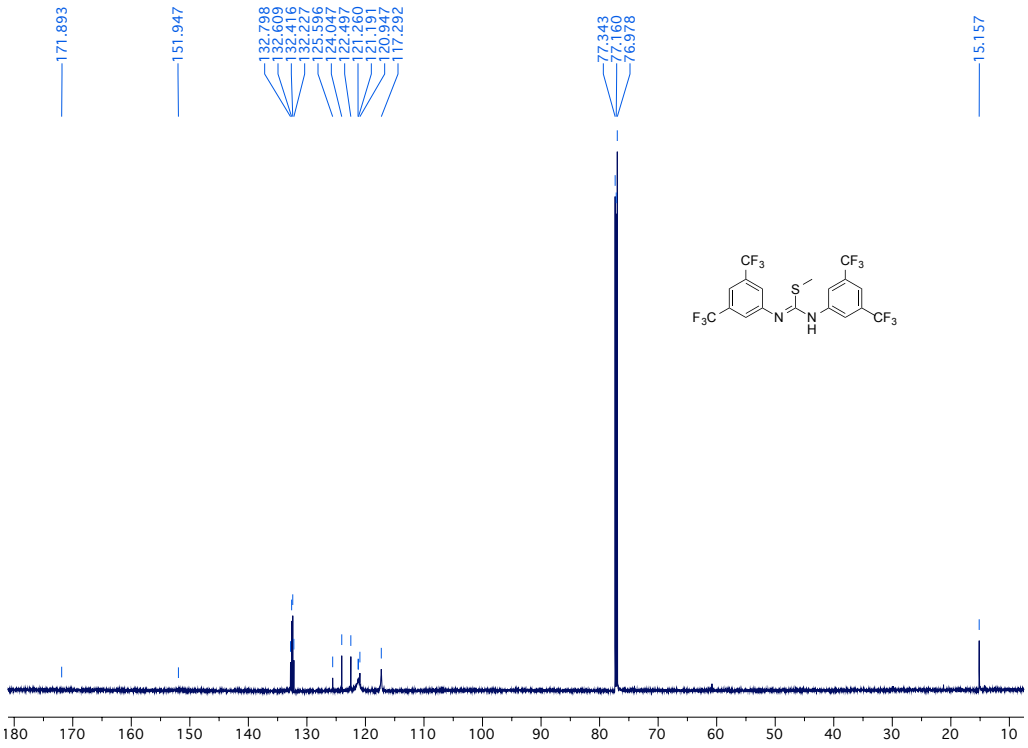


Figure S7. ^{13}C-NMR spectrum of 1b in $CDCl_3$.

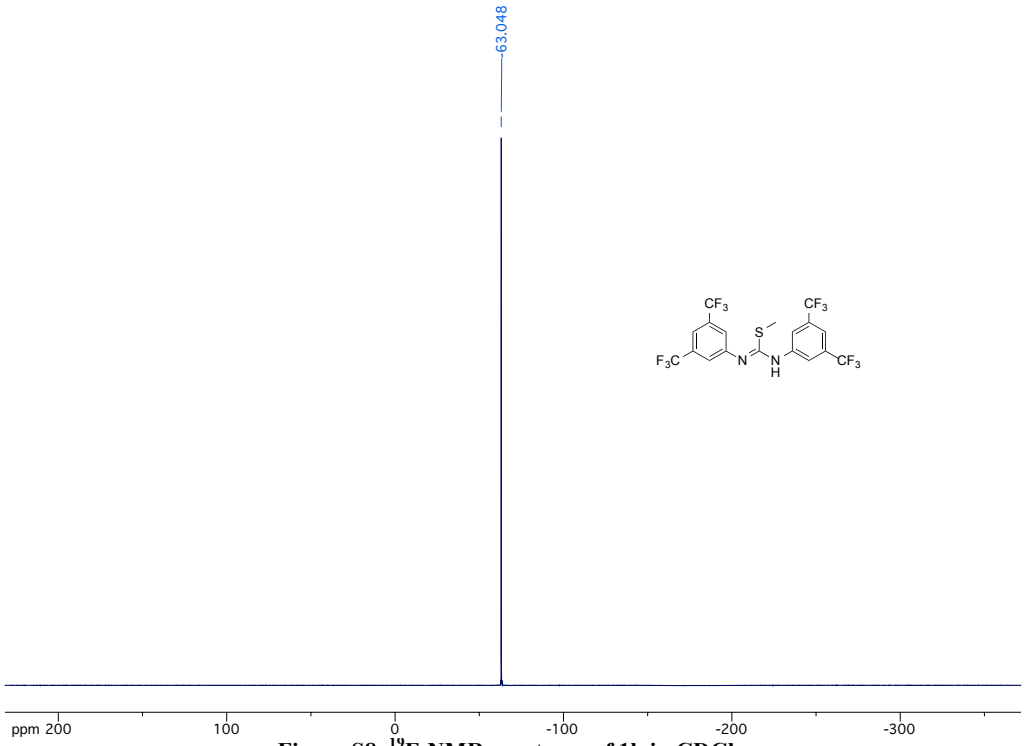


Figure S8. ^{19}F-NMR spectrum of 1b in $CDCl_3$.

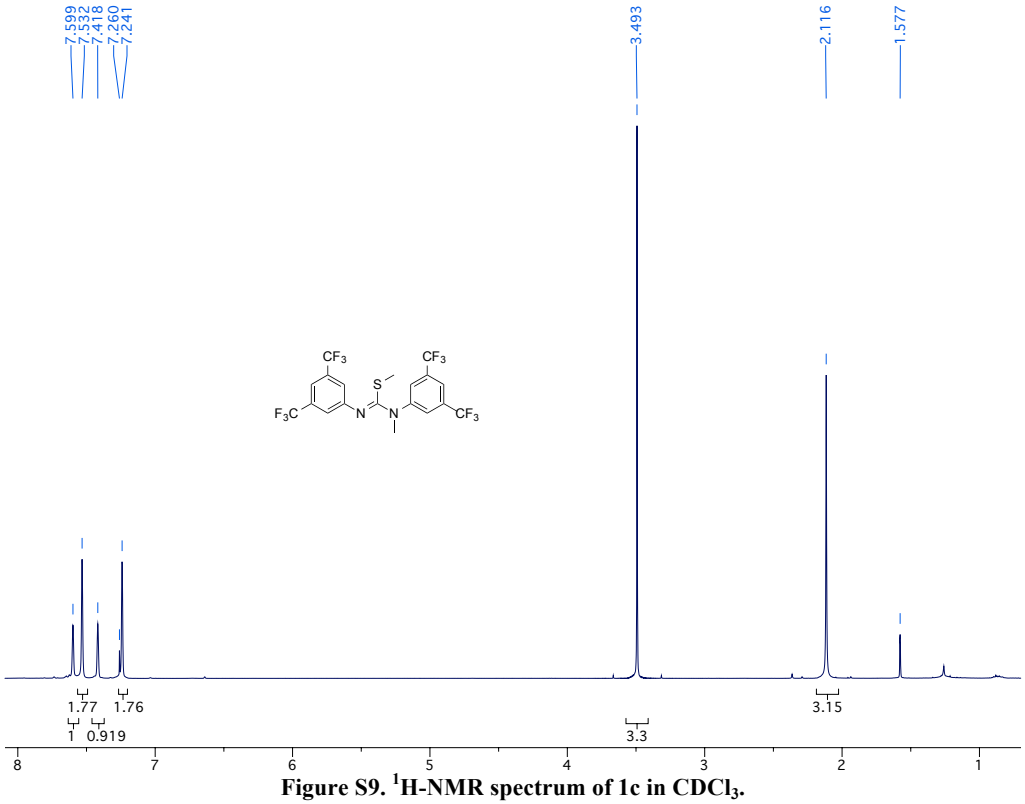


Figure S9. ^{1}H-NMR spectrum of 1c in $CDCl_3$.

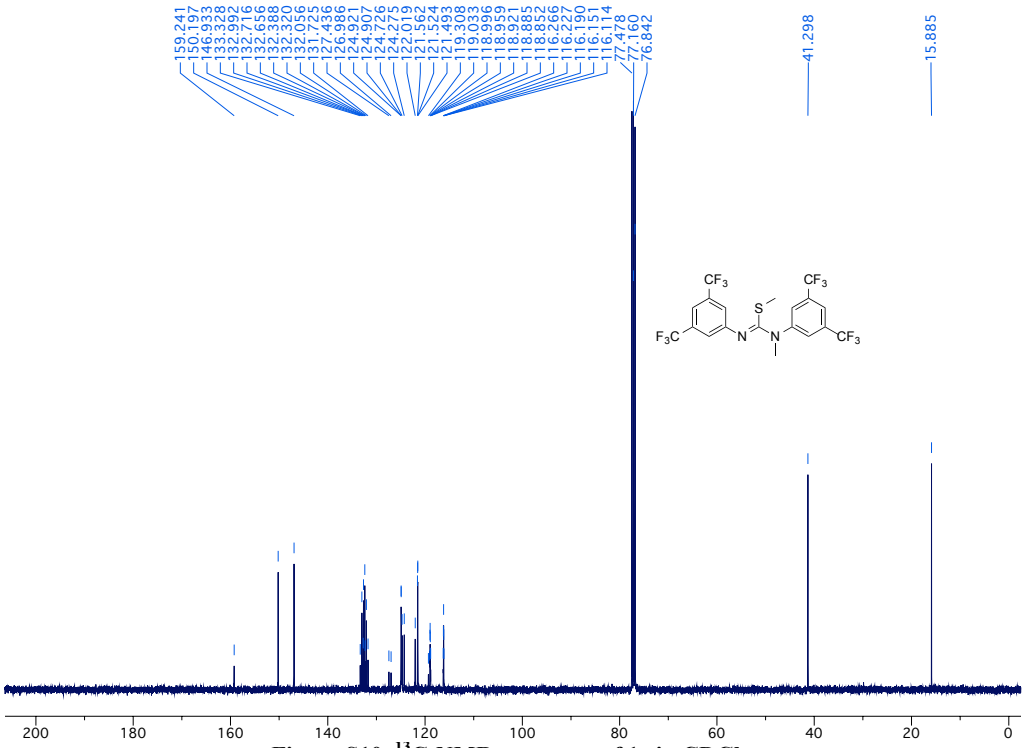


Figure S10. ^{13}C-NMR spectrum of 1c in $CDCl_3$.

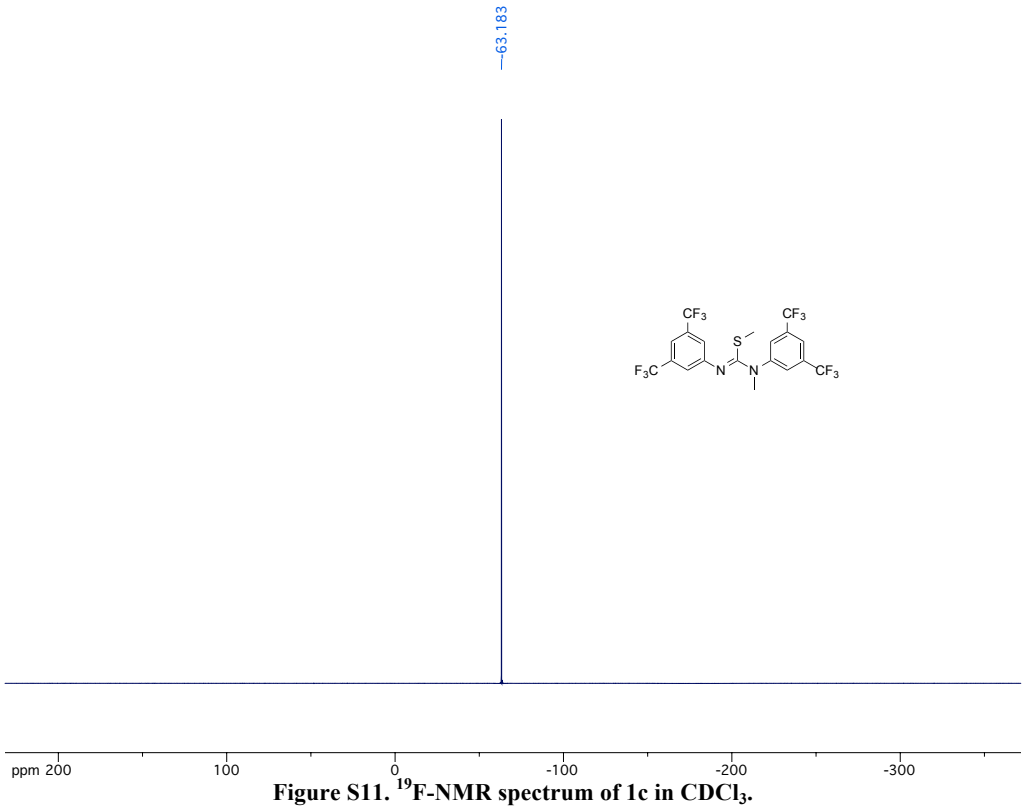


Figure S11. ^{19}F-NMR spectrum of 1c in $CDCl_3$.

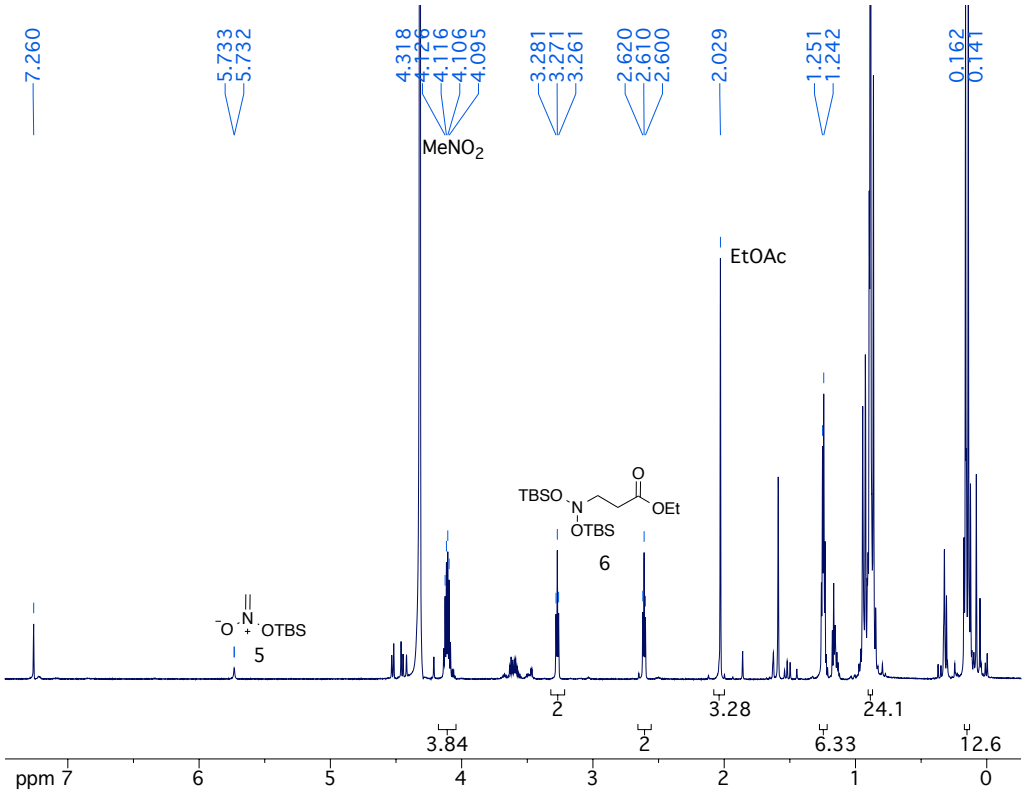


Figure S12. ^{1}H NMR spectra for the reaction mixture of degradation of 3a in nitromethane after 23 hours in $CDCl_3$.

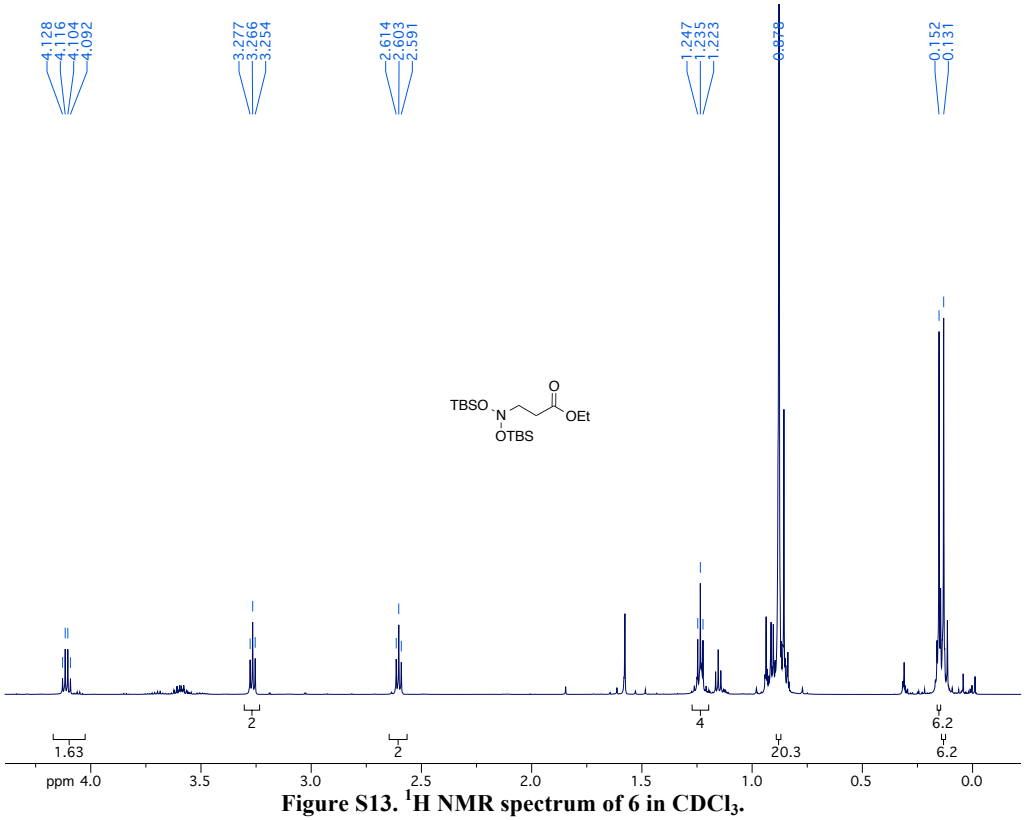


Figure S13. ^{1}H NMR spectrum of 6 in $CDCl_3$.

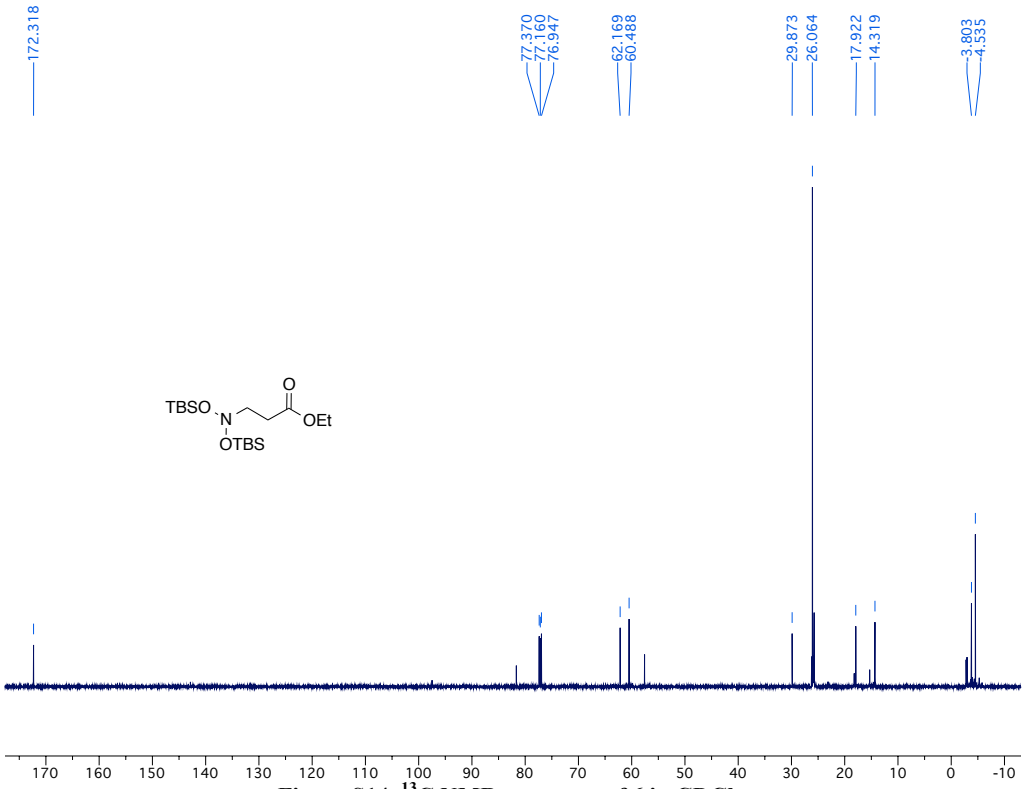


Figure S14. ^{13}C NMR spectrum of 6 in $CDCl_3$.

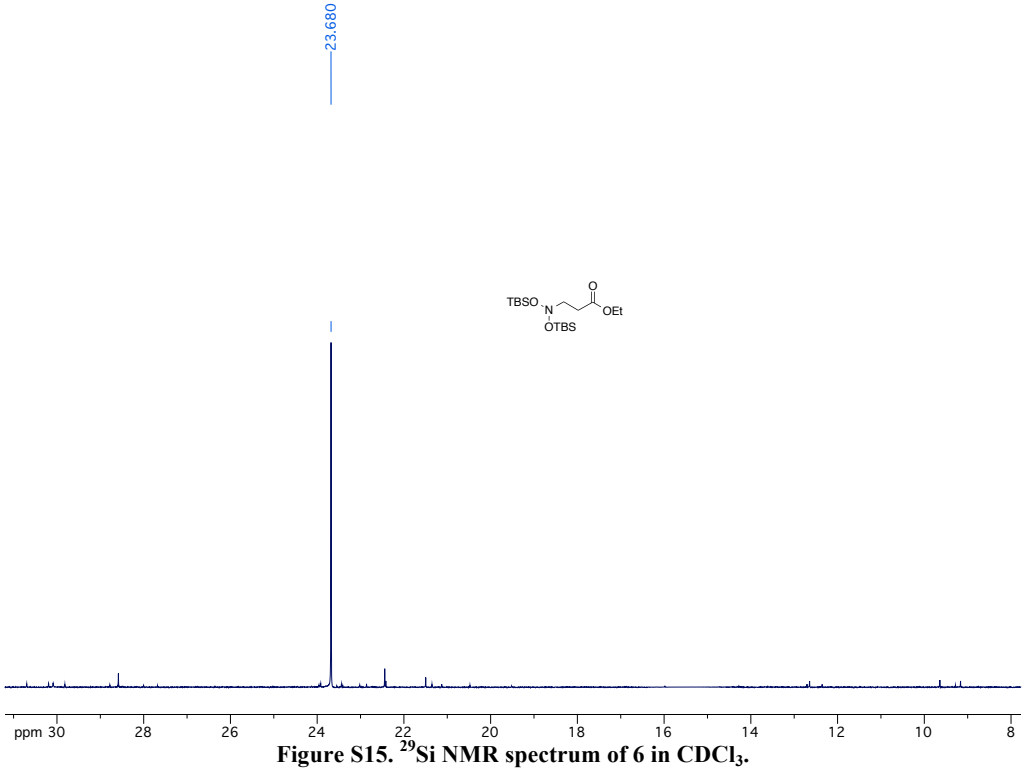


Figure S15. ^{29}Si NMR spectrum of 6 in $CDCl_3$.

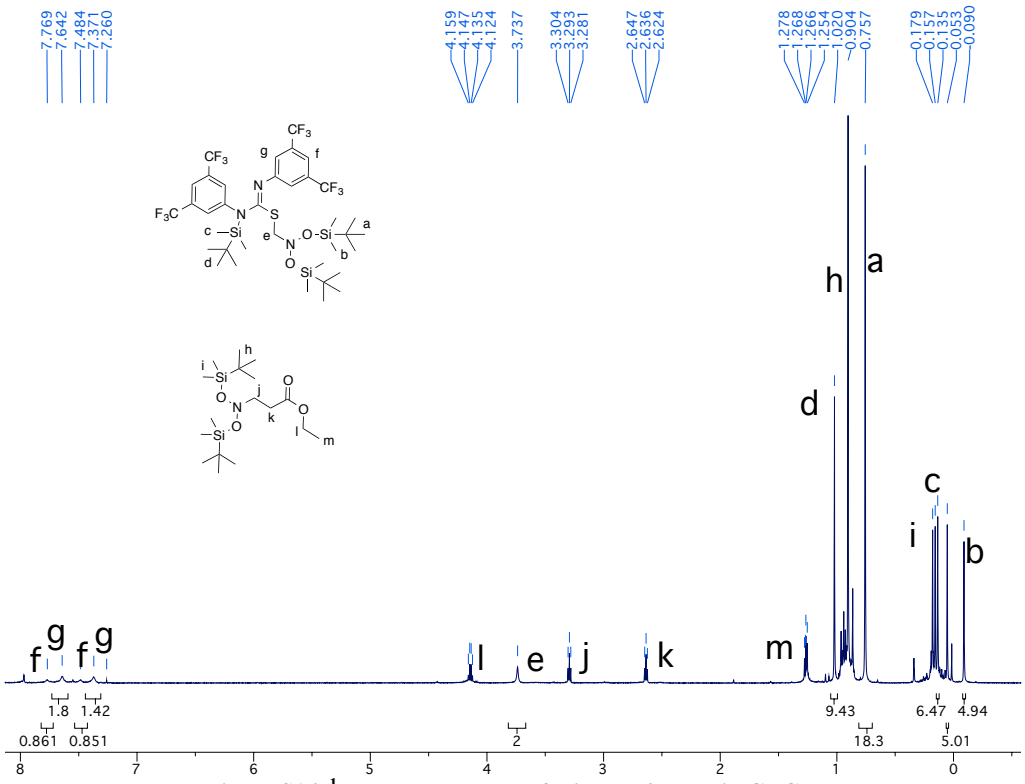


Figure S16. ^{1}H NMR spectrum of mixture 6 and 7 in $CDCl_3$.

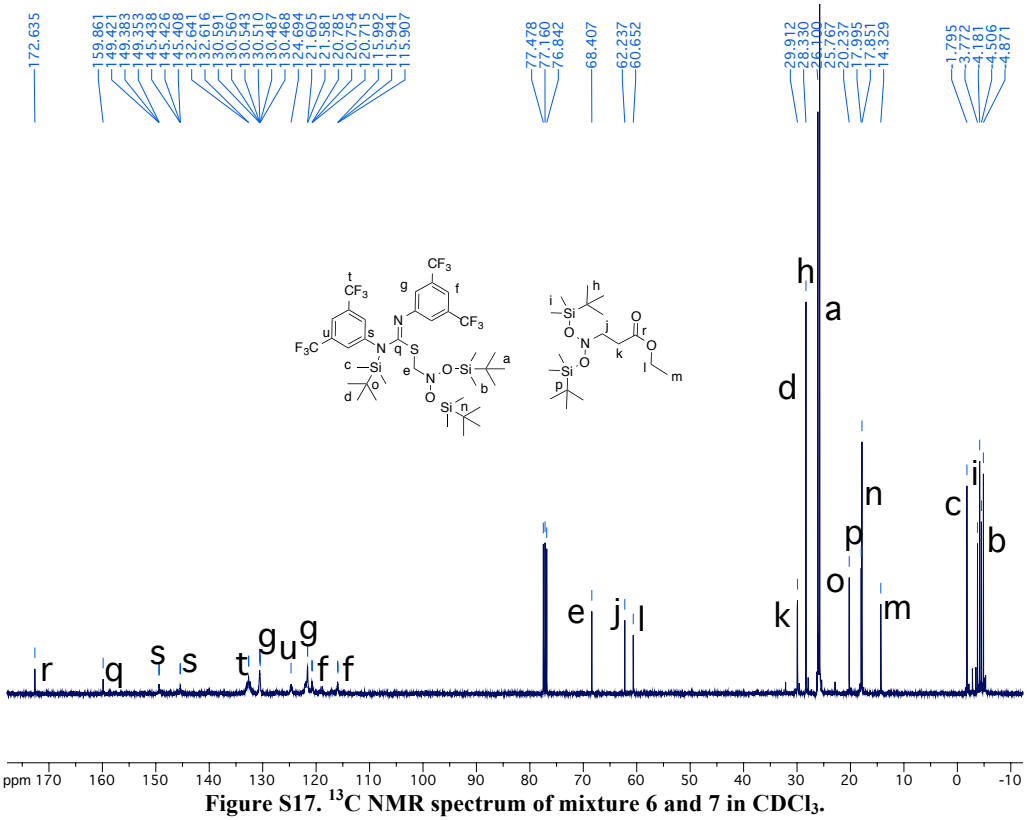


Figure S17. ^{13}C NMR spectrum of mixture 6 and 7 in $CDCl_3$.

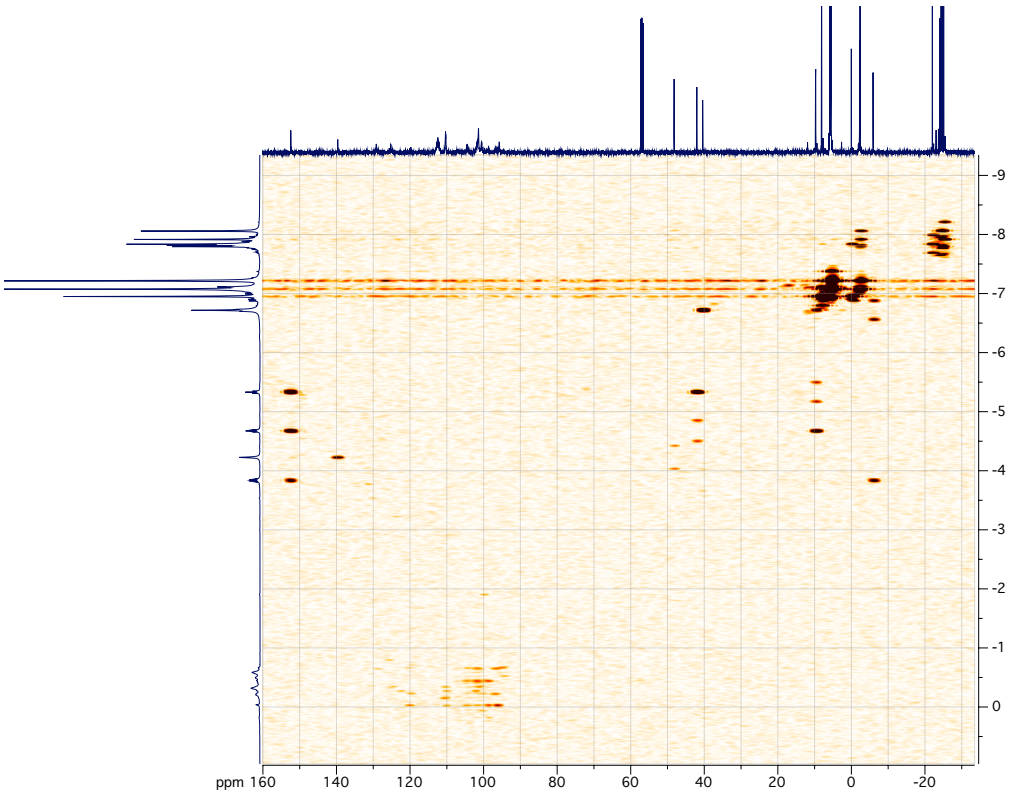


Figure S18. HMBC spectrum of mixture 6 and 7 in $CDCl_3$.

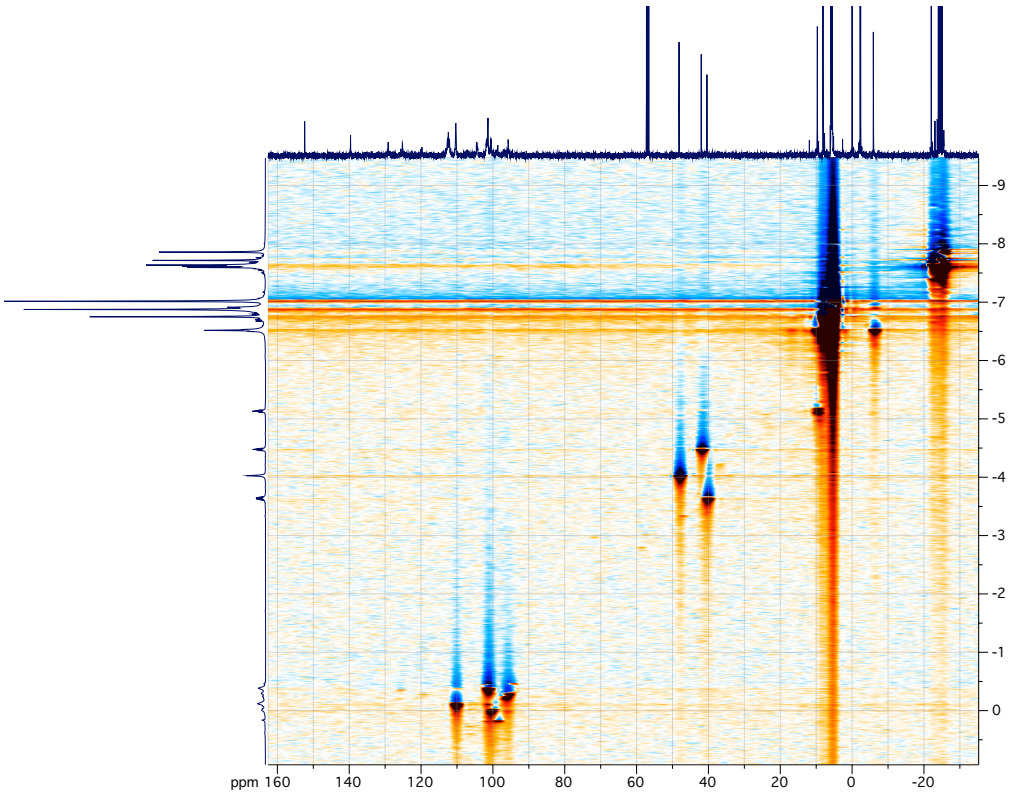


Figure S19. HSQC spectrum of mixture 6 and 7 in $CDCl_3$.

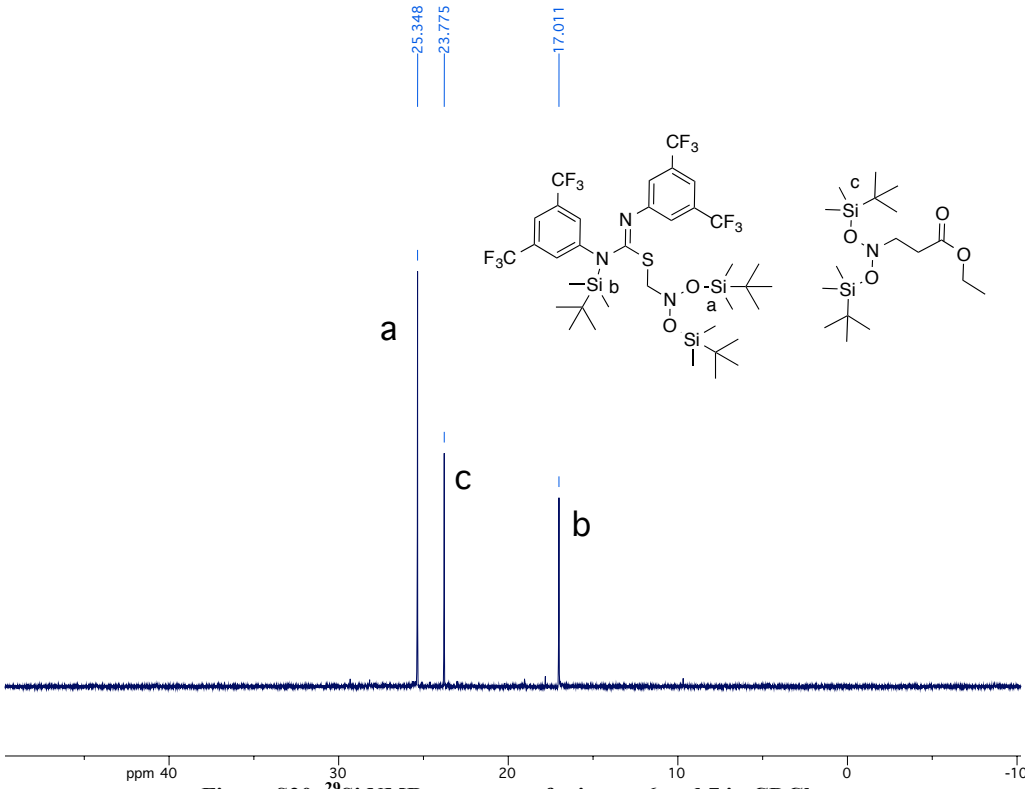


Figure S20. ^{29}Si NMR spectrum of mixture 6 and 7 in $CDCl_3$.

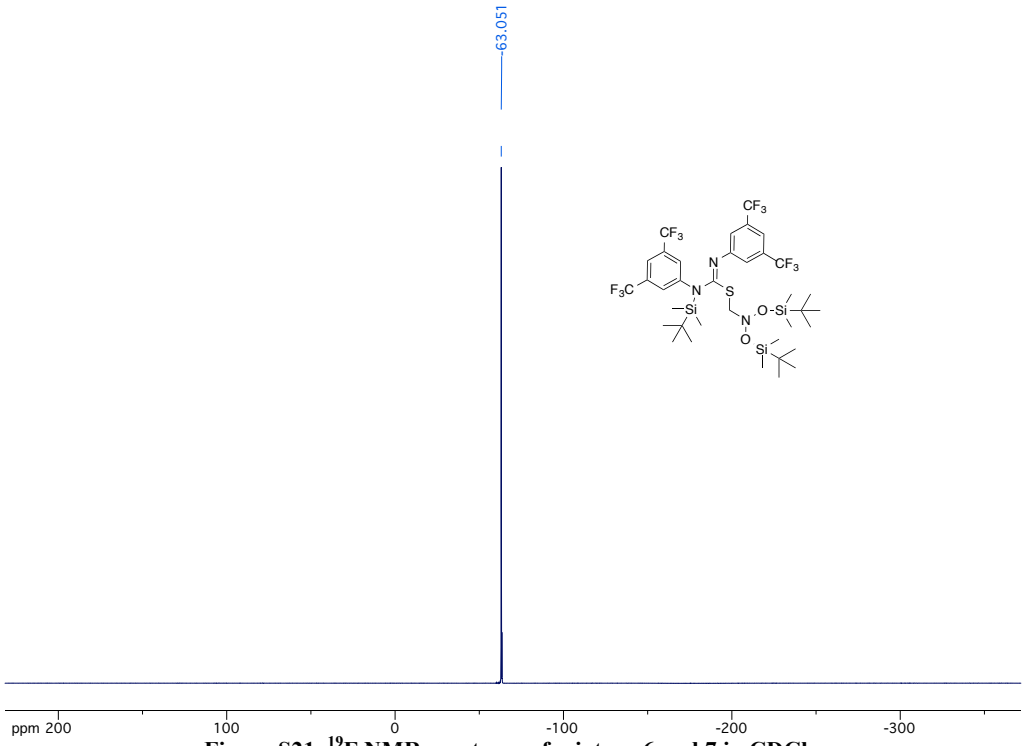


Figure S21. ^{19}F NMR spectrum of mixture 6 and 7 in $CDCl_3$.

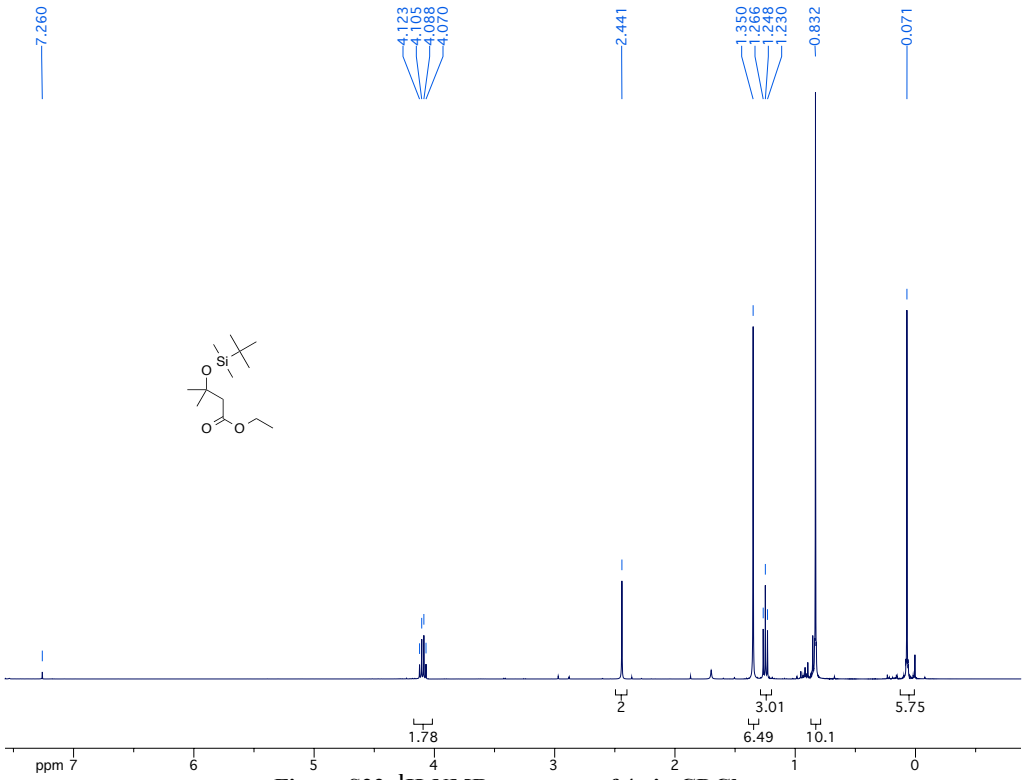


Figure S22. ^{1}H-NMR spectrum of 4a in $CDCl_3$.

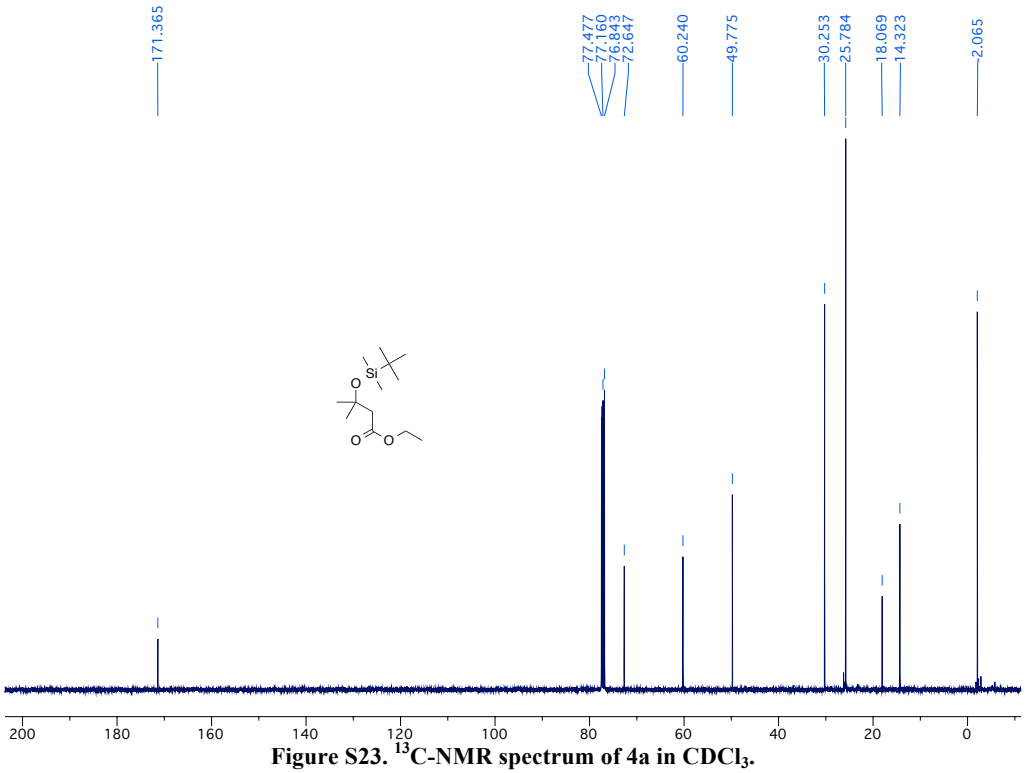


Figure S23. ^{13}C-NMR spectrum of 4a in $CDCl_3$.

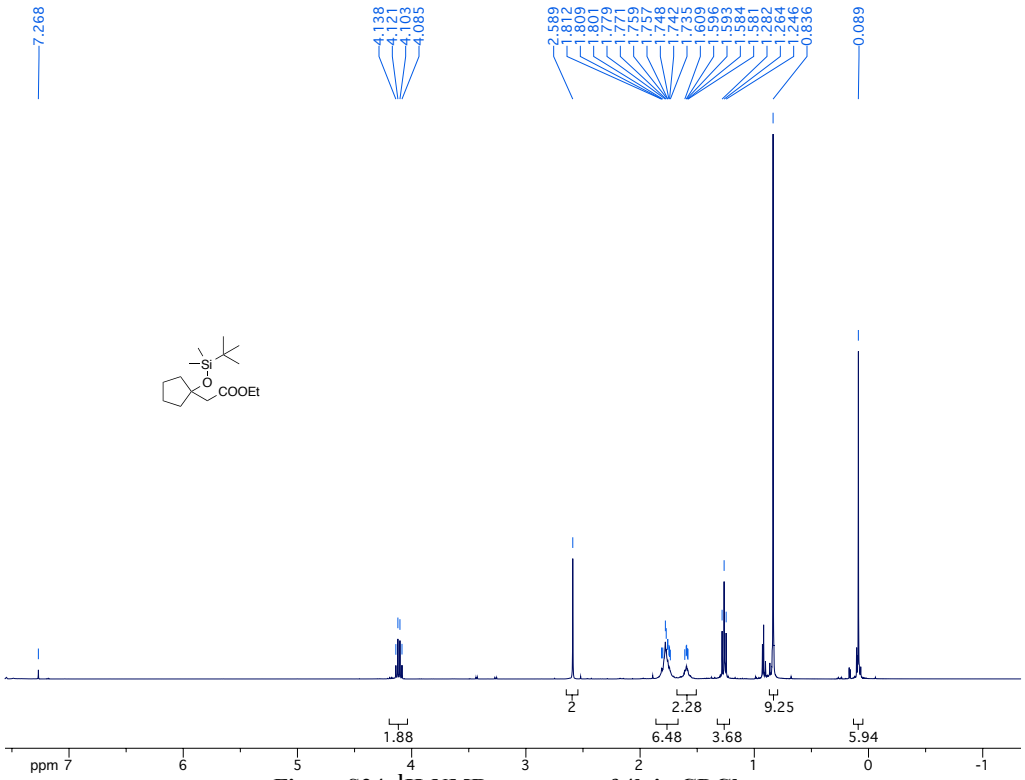


Figure S24. ^{1}H-NMR spectrum of 4b in $CDCl_3$.

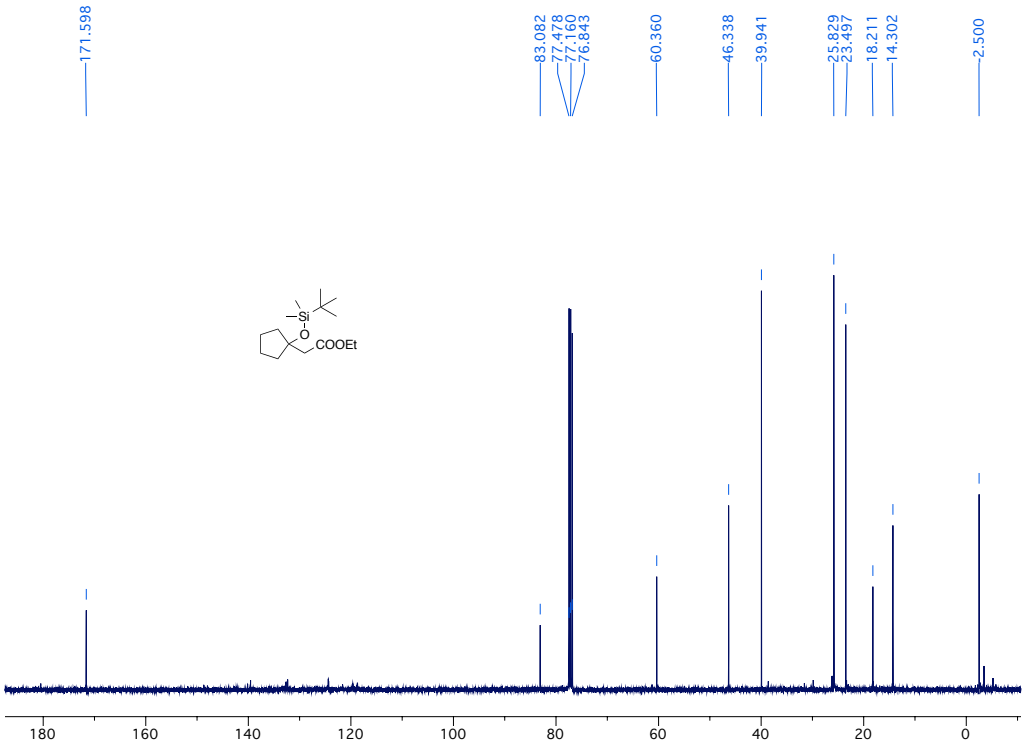


Figure S25. ^{13}C-NMR spectrum of 4b in $CDCl_3$.

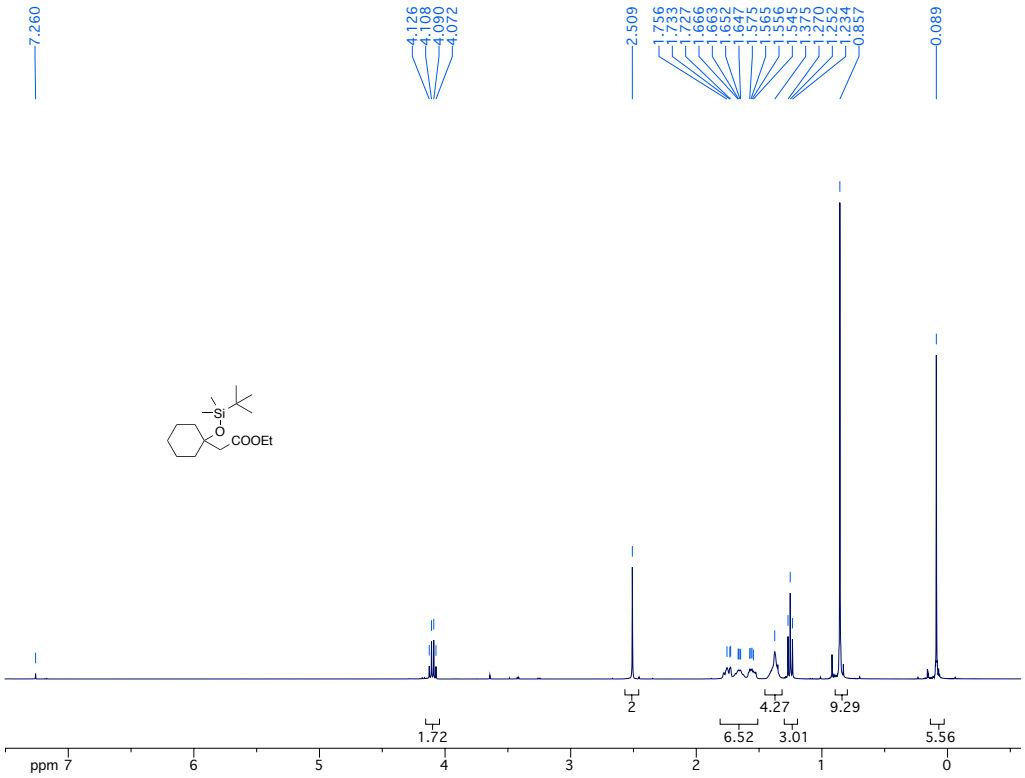


Figure S26. ^{1}H-NMR spectrum of 4c in $CDCl_3$.

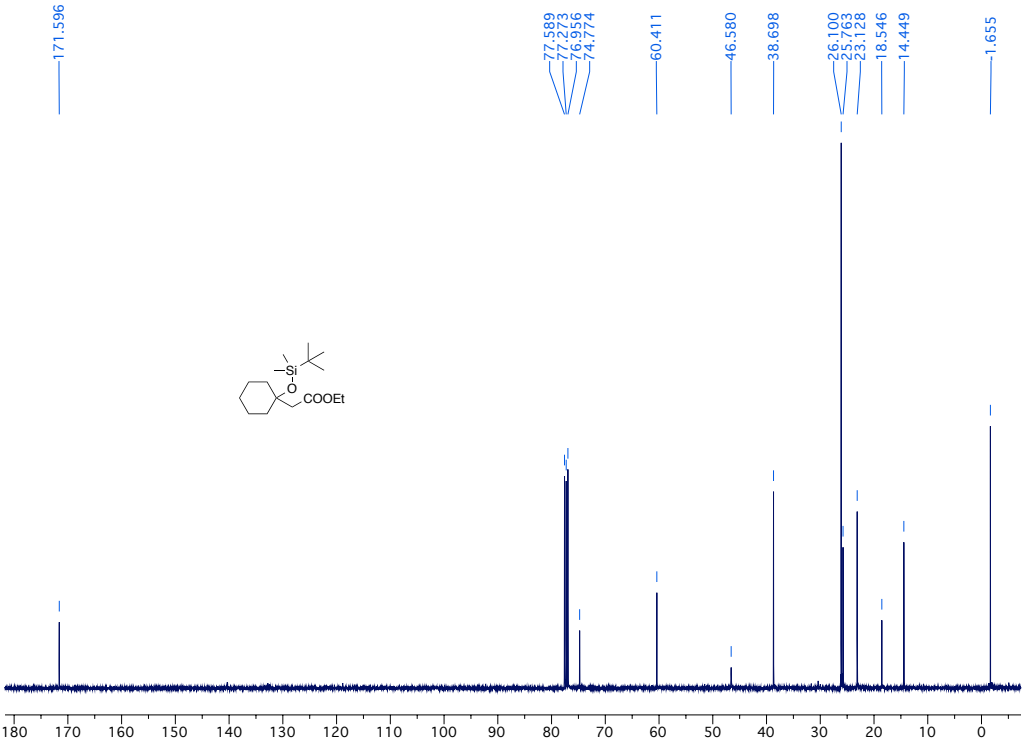


Figure S27. ^{13}C-NMR spectrum of 4c in $CDCl_3$.

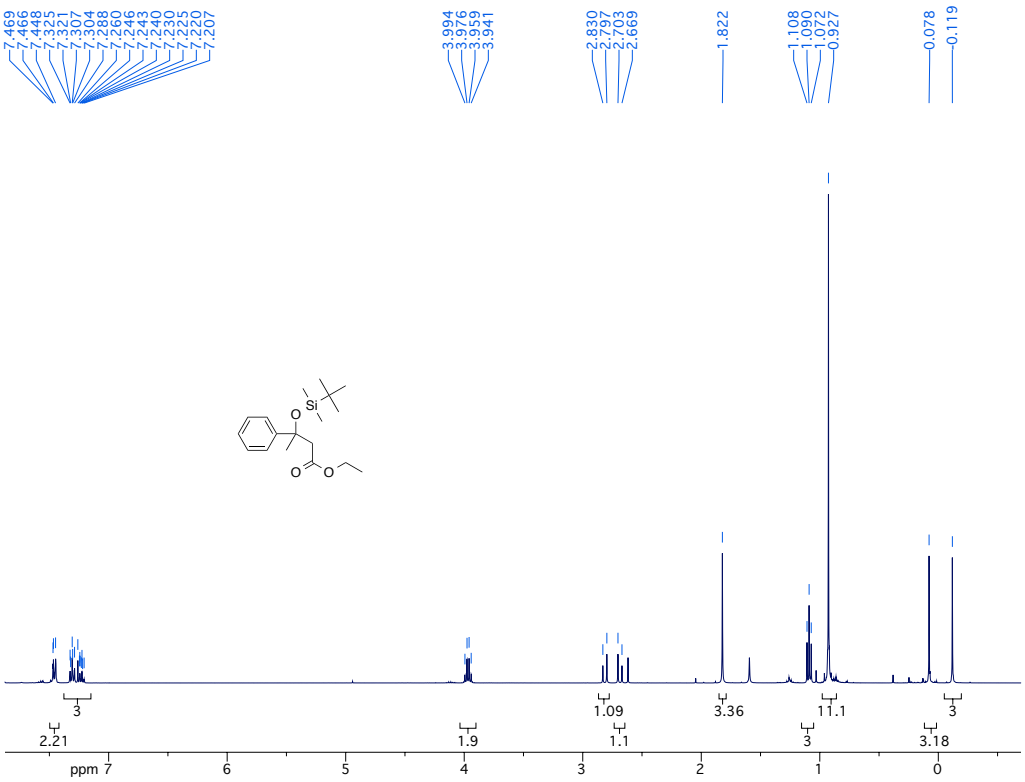


Figure S28. ^{1}H-NMR spectrum of 4d in $CDCl_3$.

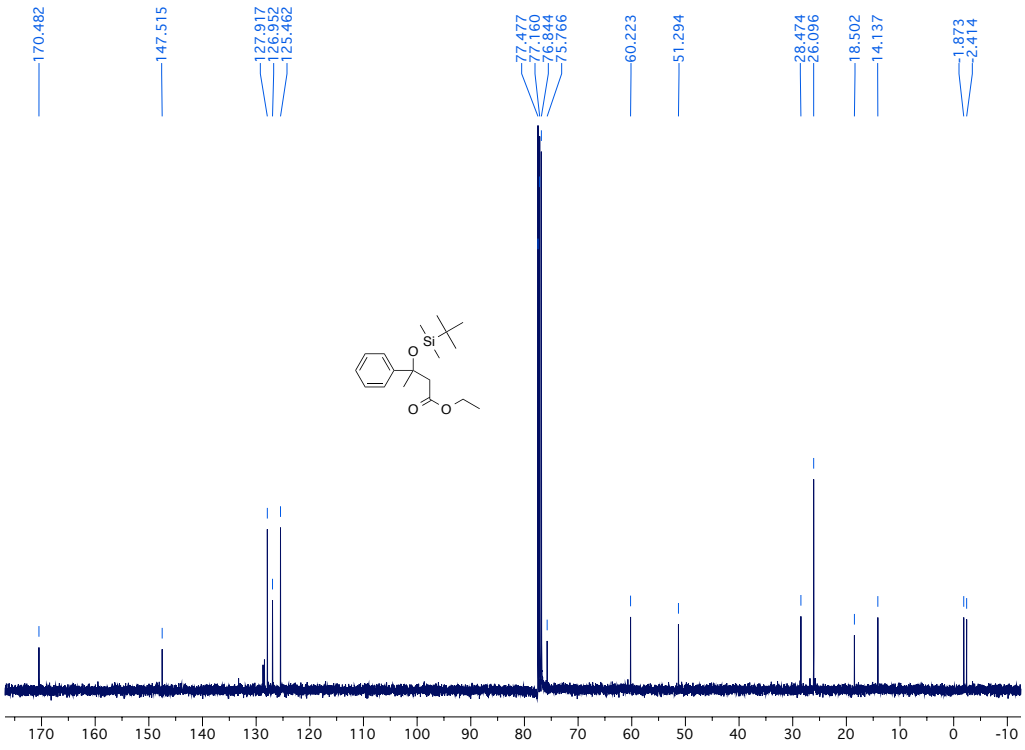


Figure S29. ^{13}C-NMR spectrum of 4d in $CDCl_3$.

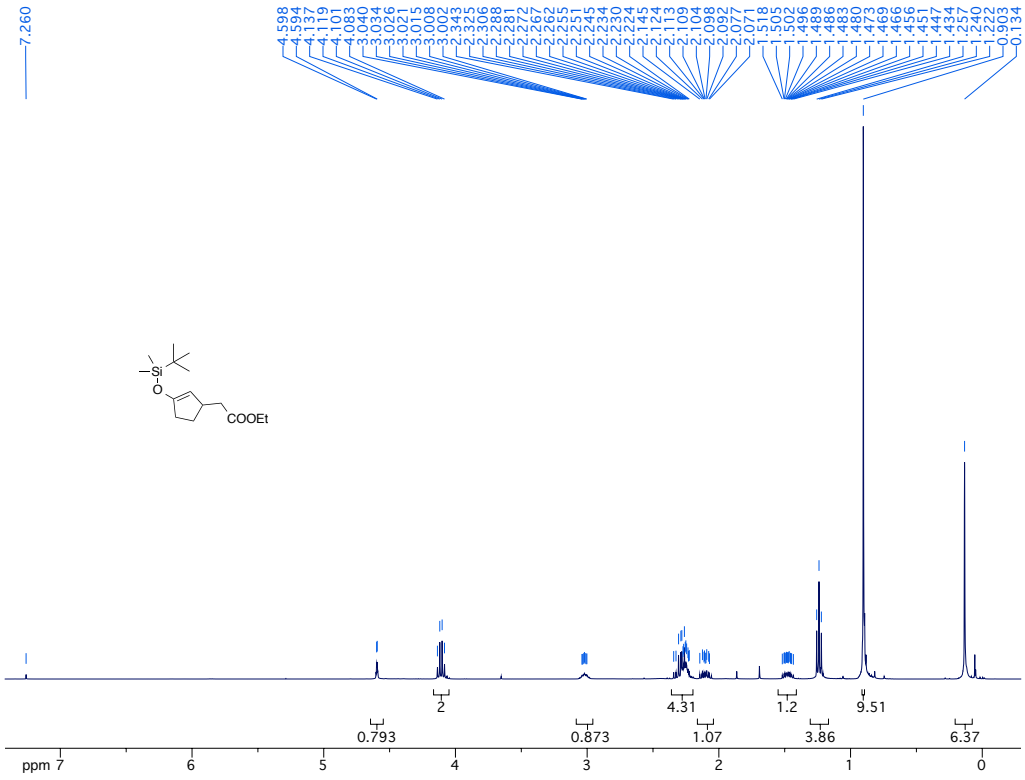


Figure S30. ^{1}H-NMR spectrum of 4e in $CDCl_3$.

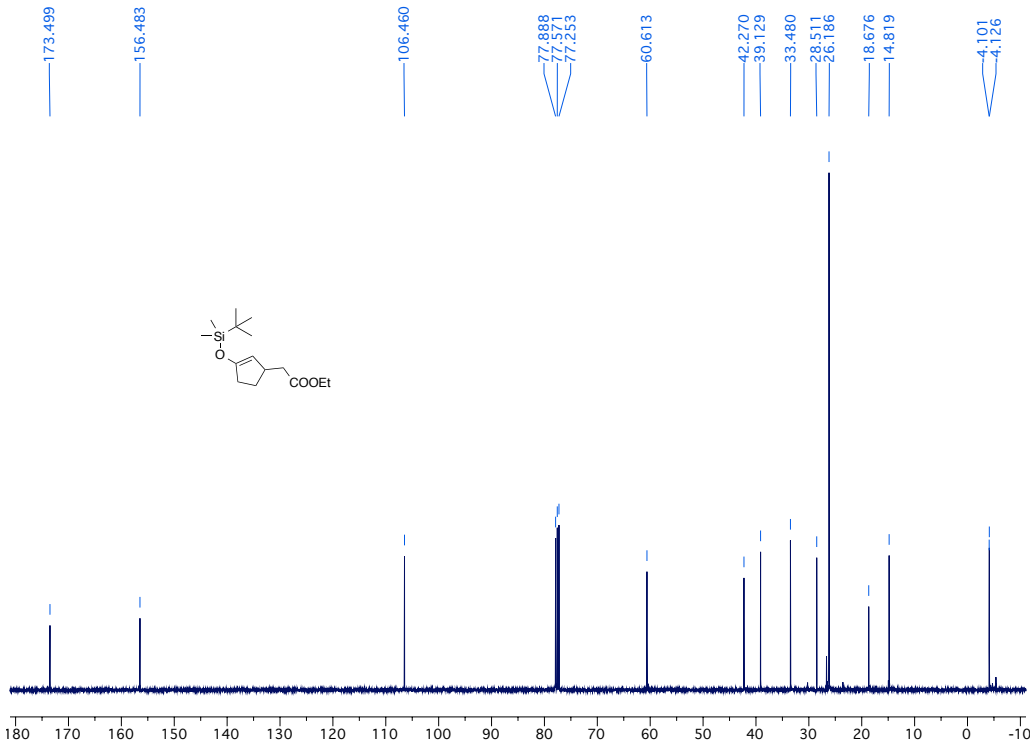


Figure S31. ^{13}C-NMR spectrum of 4e in $CDCl_3$.

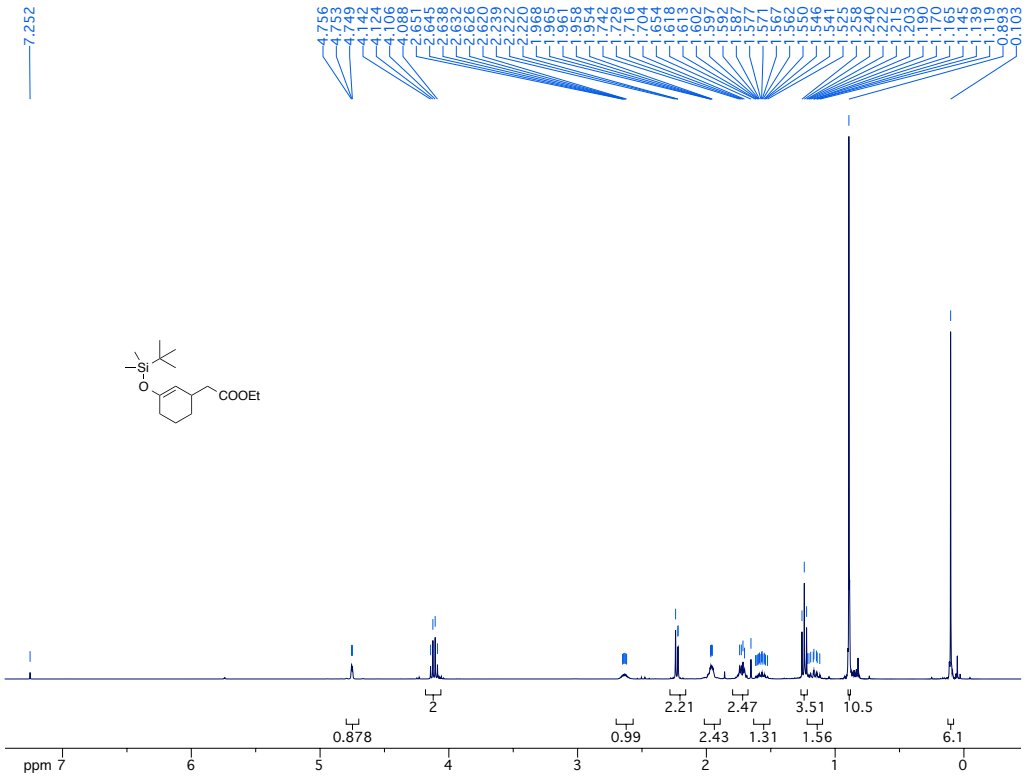


Figure S32. ^{1}H-NMR spectrum of 4f in $CDCl_3$.

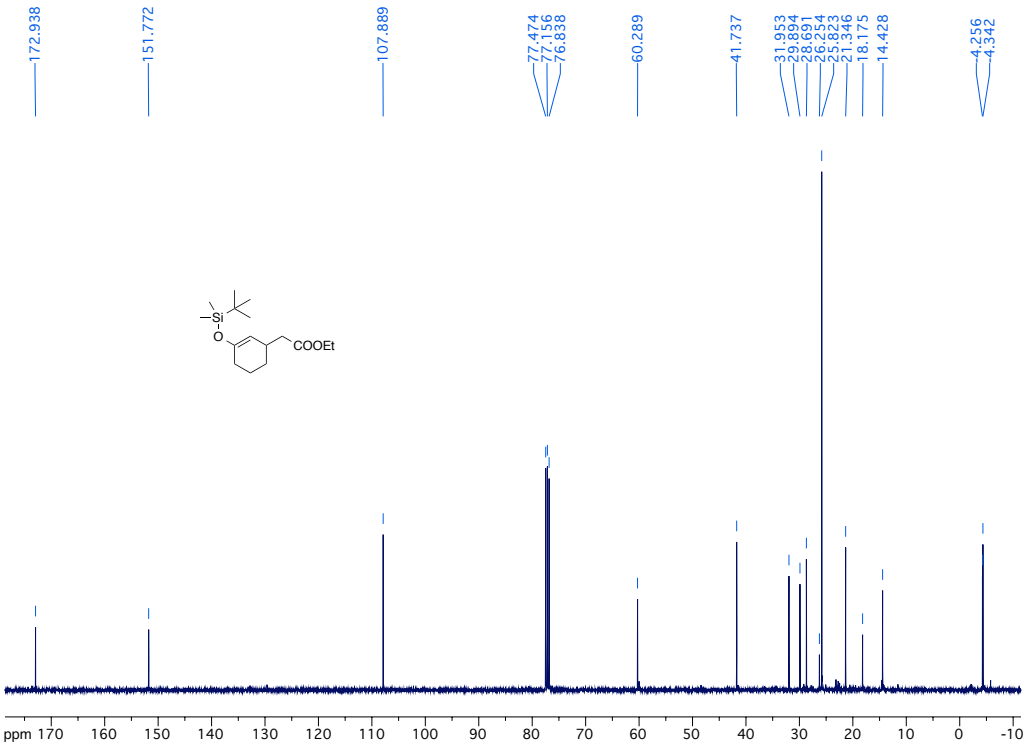


Figure S33. ^{13}C-NMR spectrum of 4f in $CDCl_3$.

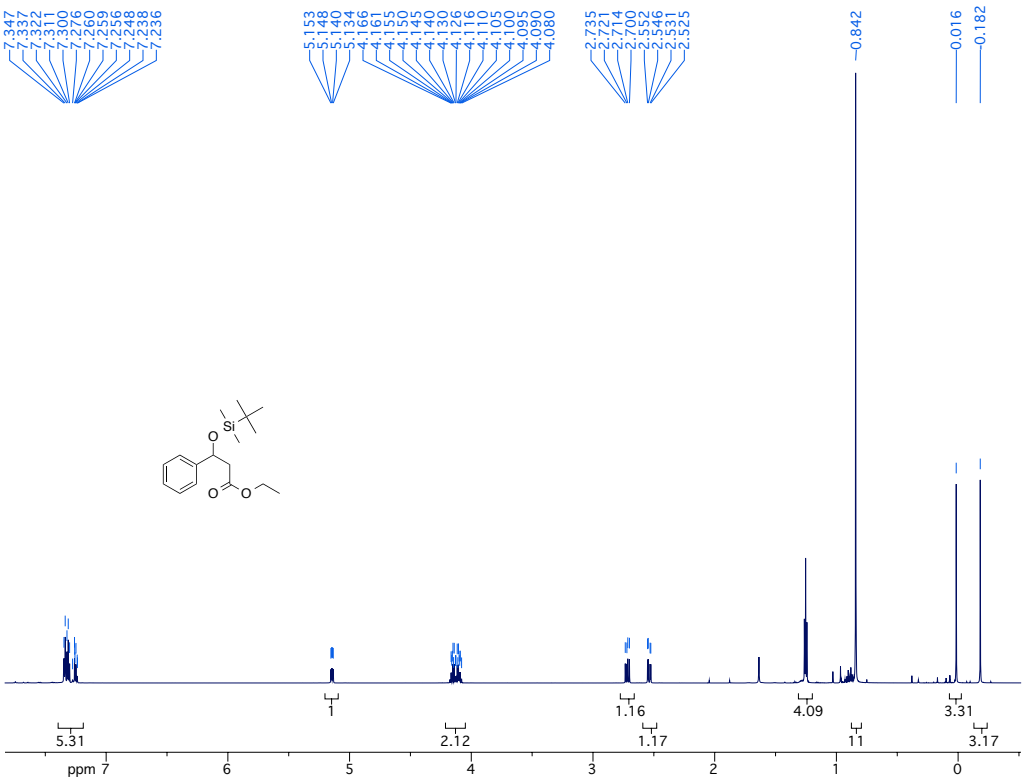


Figure S34. ^{1}H-NMR spectrum of 4g in $CDCl_3$.

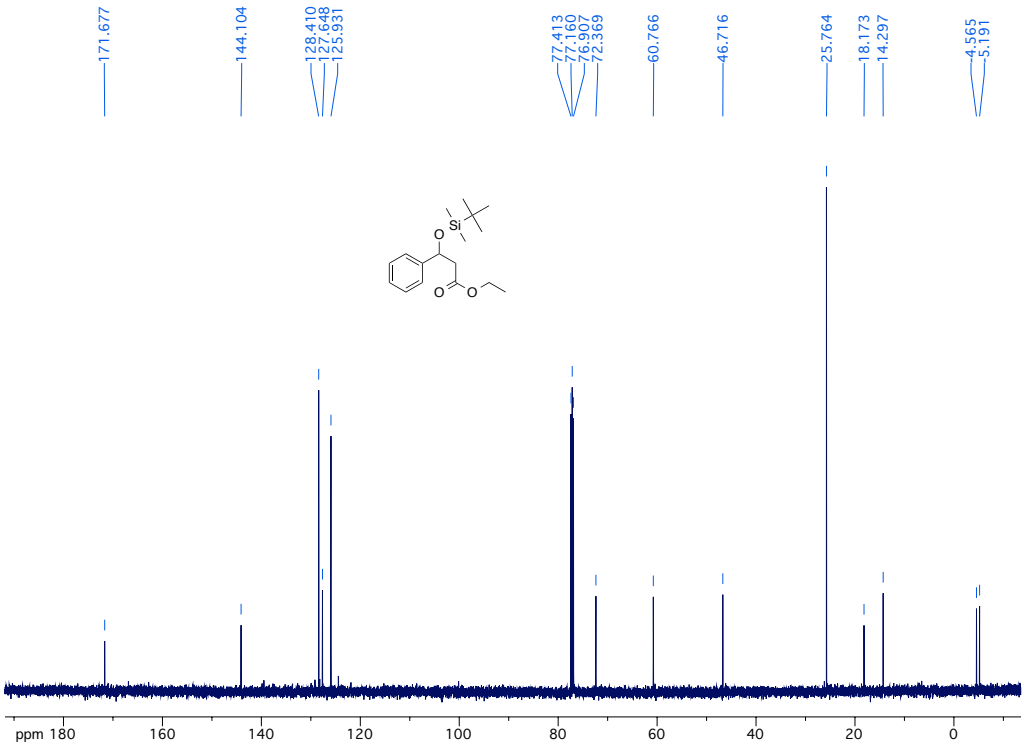


Figure S35. ^{13}C-NMR spectrum of 4g in $CDCl_3$.

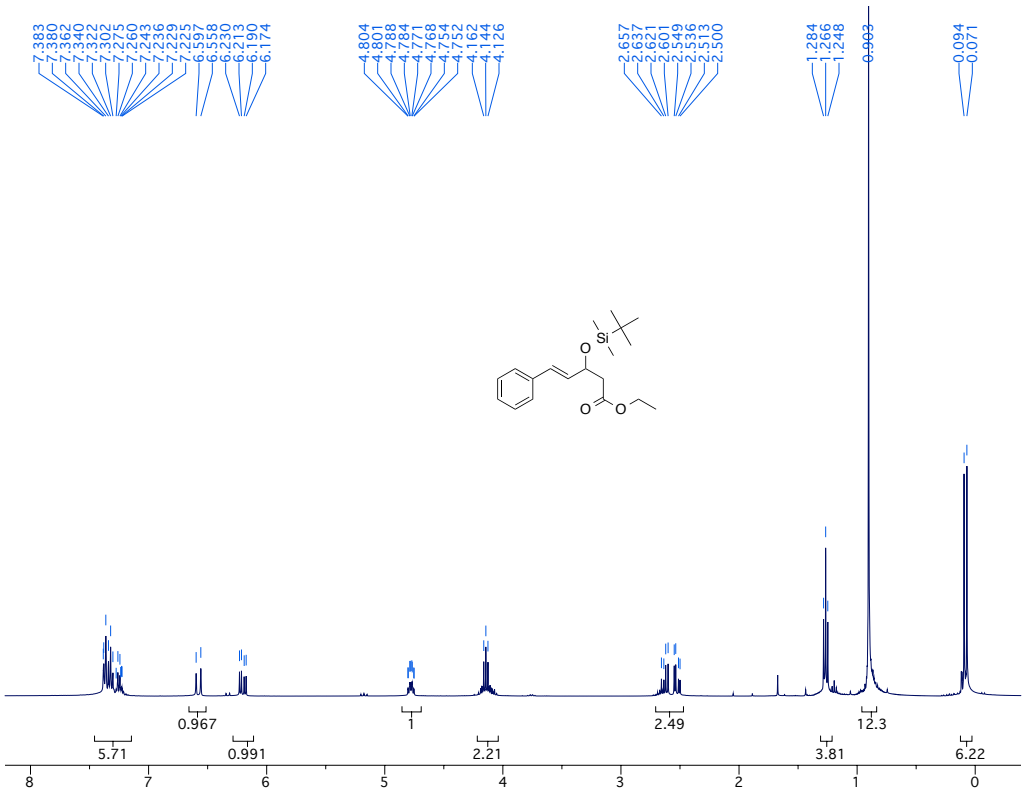


Figure S36. ^{1}H-NMR spectrum of 4h in $CDCl_3$.

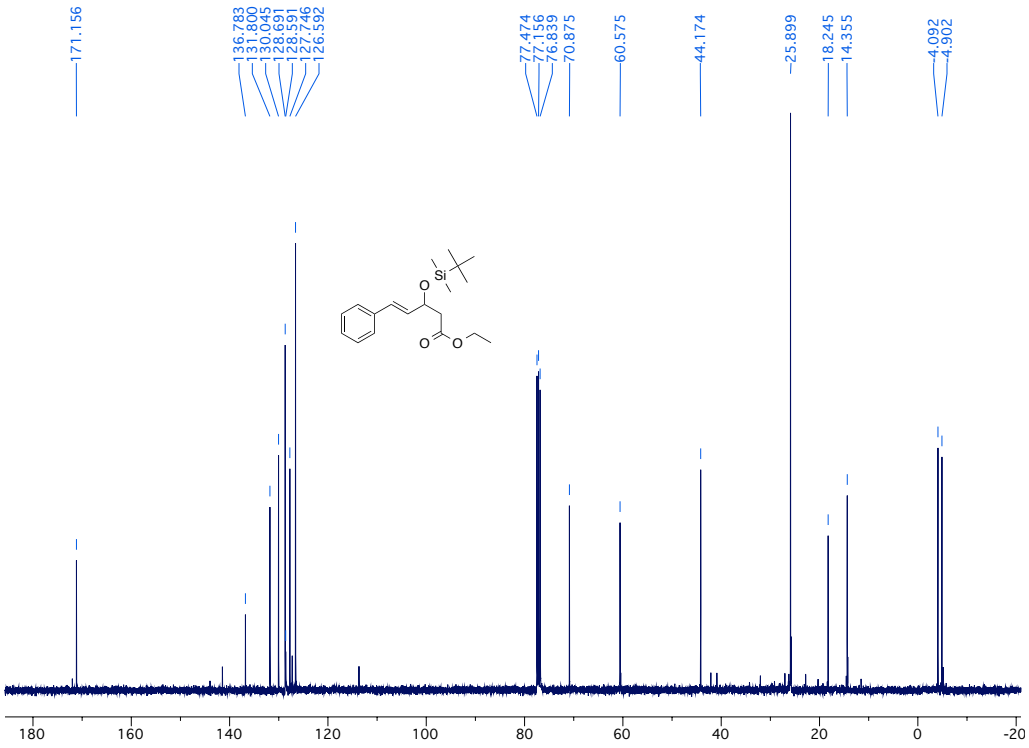


Figure S37. ^{13}C-NMR spectrum of 4h in $CDCl_3$.

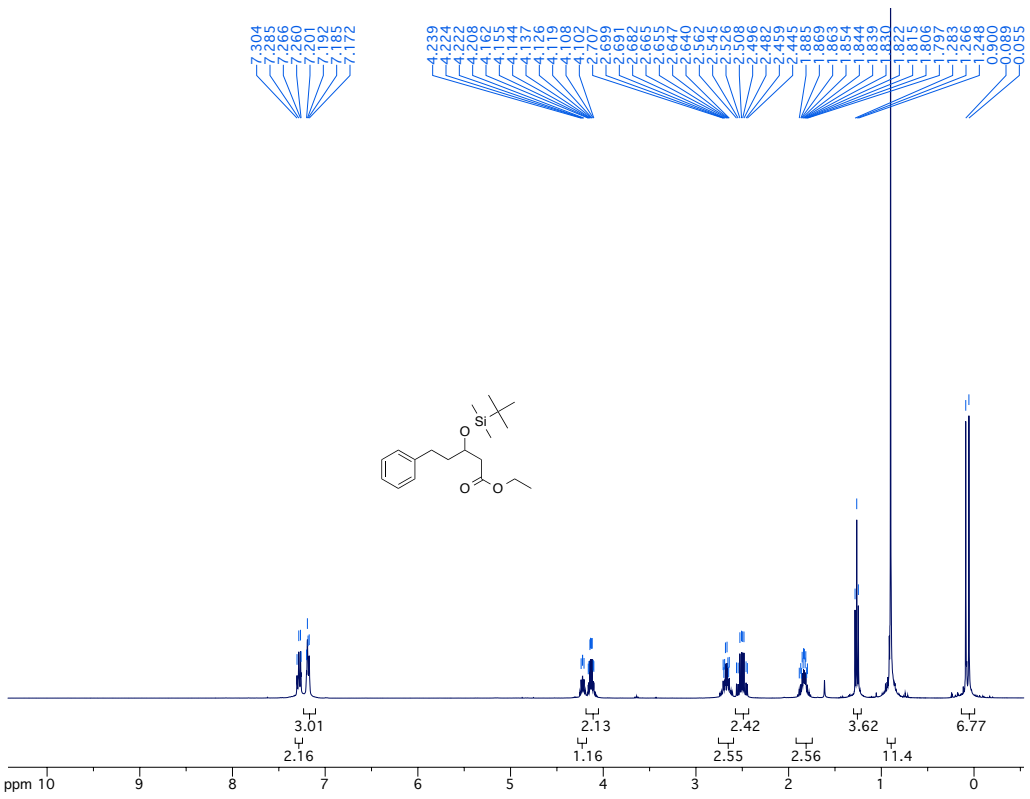


Figure S38. ^{1}H-NMR spectrum of 4i in $CDCl_3$.

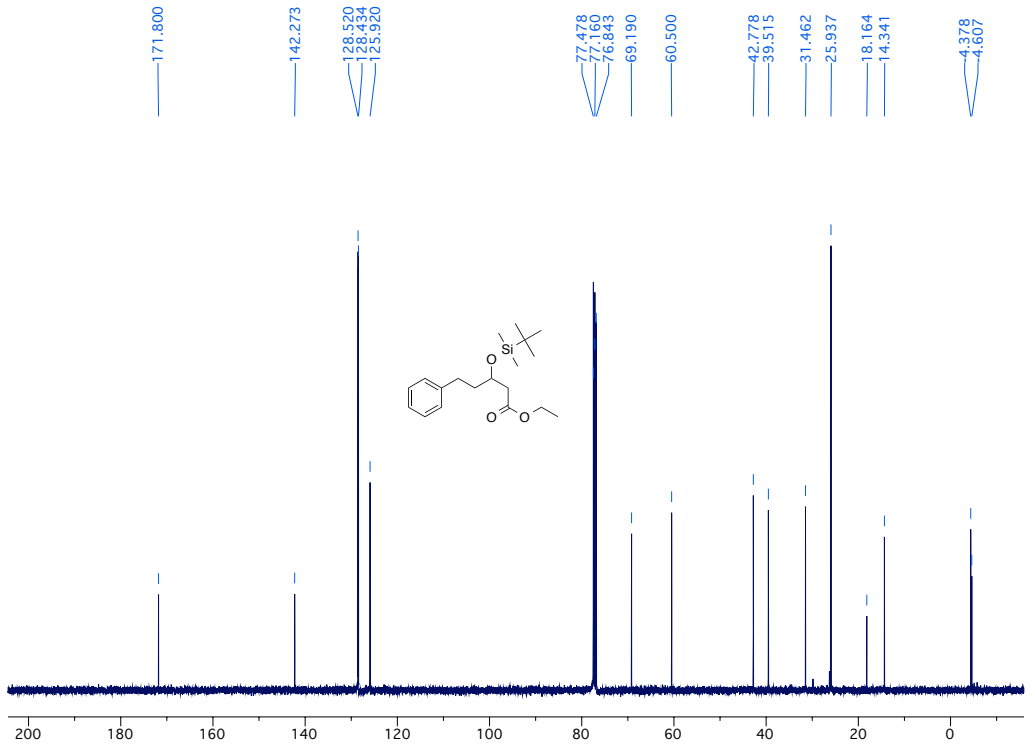


Figure S39. ^{13}C-NMR spectrum of 4i in $CDCl_3$.

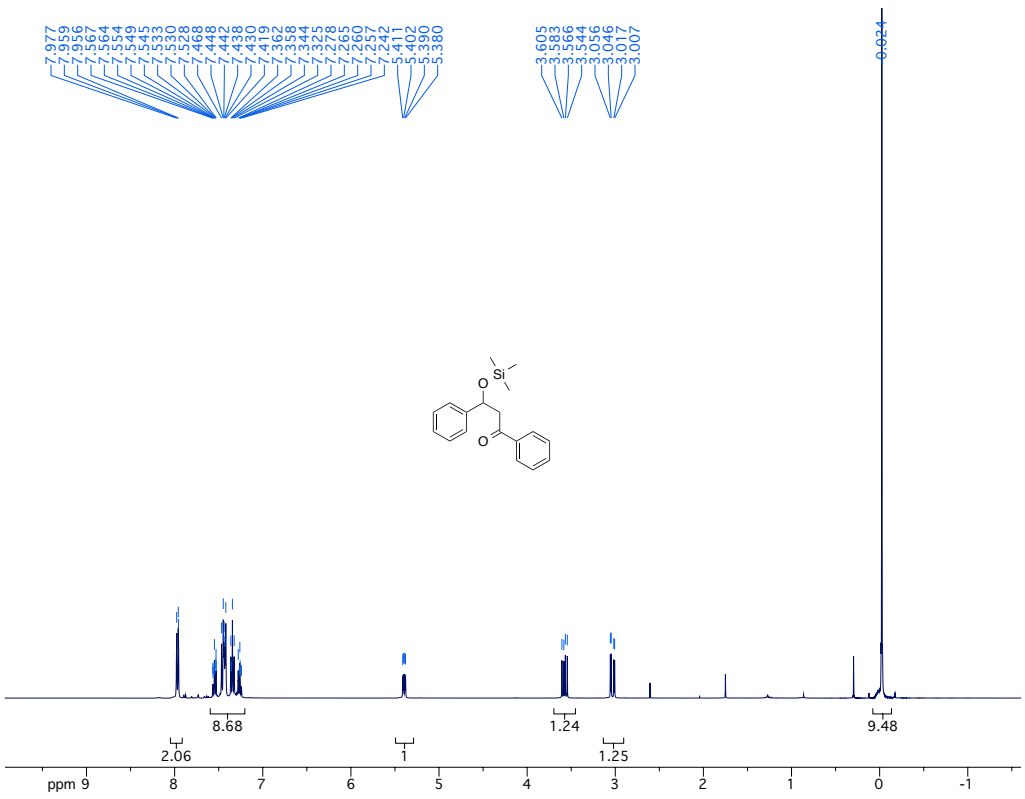


Figure S40. ^{1}H-NMR spectrum of 4k in $CDCl_3$.

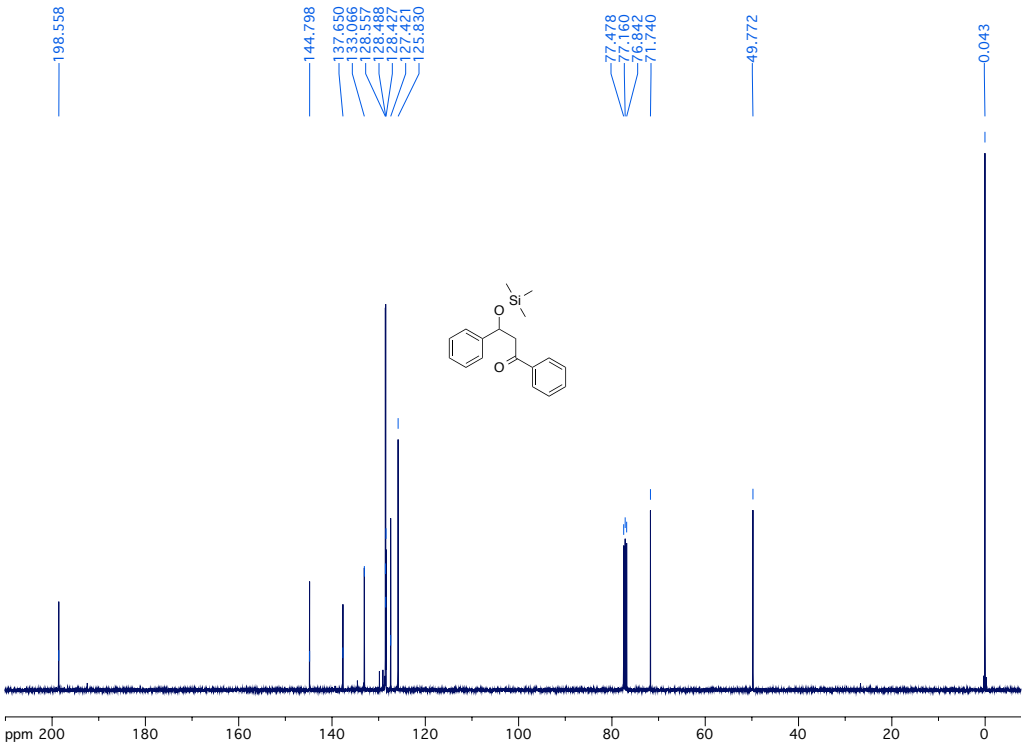


Figure S41. ^{13}C-NMR spectrum of 4k in $CDCl_3$.

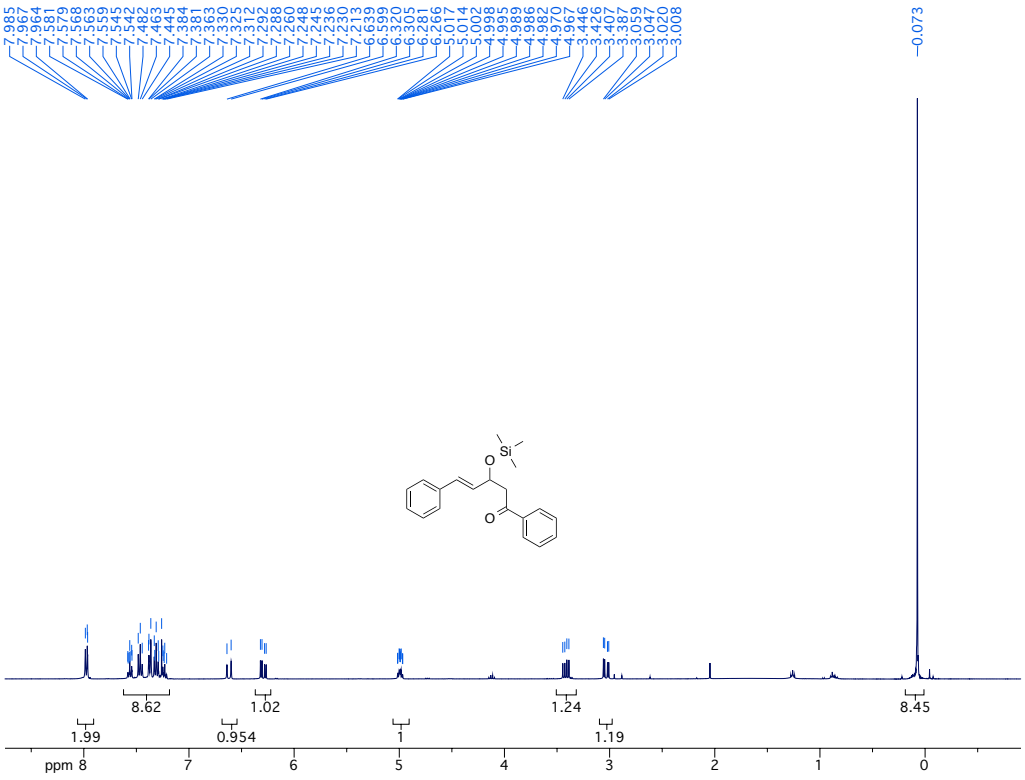


Figure S42. ^{1}H-NMR spectrum of 4l in $CDCl_3$.

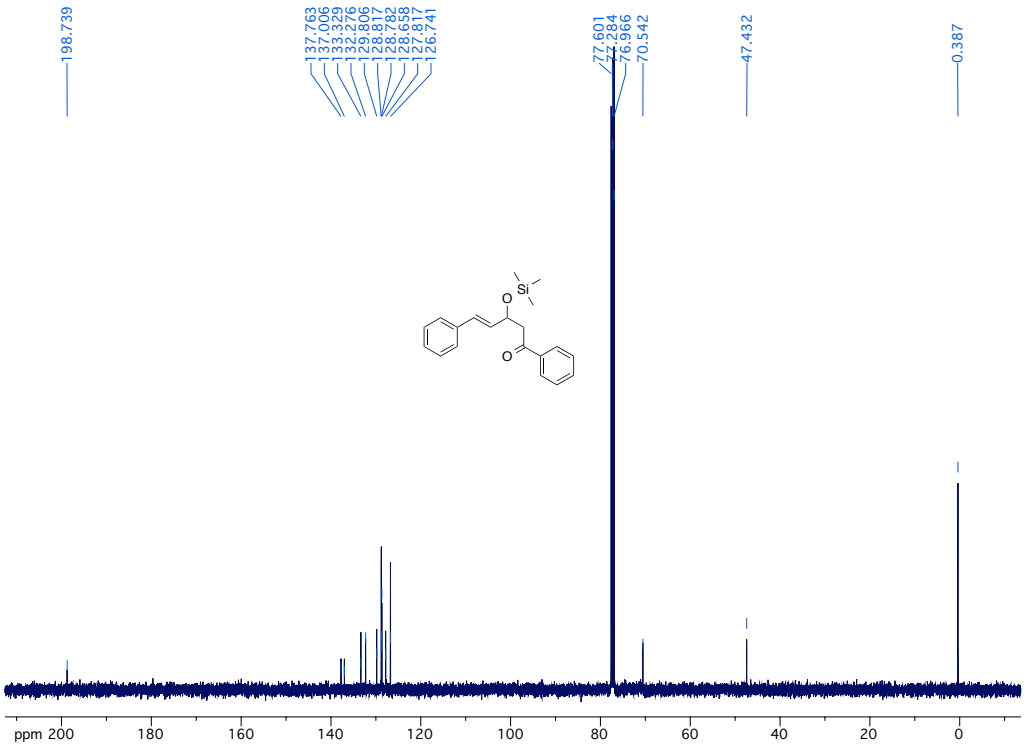


Figure S43. ^{13}C-NMR spectrum of 4l in $CDCl_3$.

9. References

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