

Rhodium(II)-Catalyzed Stereoselective Synthesis of Allylsilanes

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Supporting Information

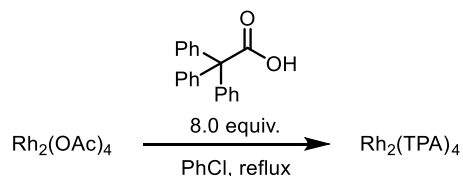
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1 – General Considerations

All solvents were degassed with argon and purified and dried by a *Glass Contour Solvent System* unless otherwise stated. ^1H and ^{13}C NMR spectra were recorded at either 400 MHz (^{13}C at 100 MHz) or 600 MHz (^{13}C at 150 MHz) on an INOVA-400, Varian-400, or INOVA-600 spectrometer, as indicated. NMR spectra were run in solutions of deuterated chloroform (CDCl_3) with residual chloroform taken as an internal standard (7.27 ppm for ^1H , and 77.23 ppm for ^{13}C), and were reported in parts per million (ppm). Abbreviations for signal multiplicity are as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, dd = doublet of doublet, etc. Coupling constants (J values) were calculated directly from the spectra. IR spectra were collected on a Nicolet iS10 FT-IR spectrometer. Mass spectra were taken on a Thermo Finnigan LTQ-FTMS spectrometer with APCI, ESI or NSI. Thin layer chromatographic analysis was performed with silica gel plates, visualizing with UV light and/or staining with PMA or aqueous KMnO_4 stain.

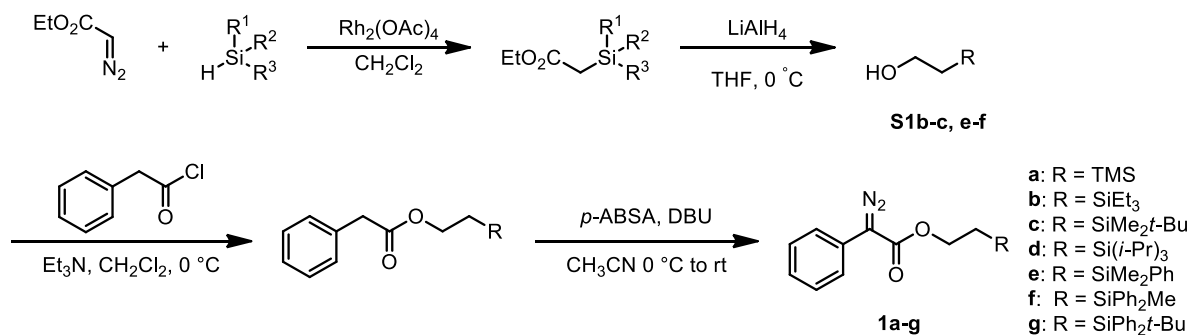
2 – Experimental Data



dirhodium(II) tetrakis(triphenylacetate): $\text{Rh}_2(\text{OAc})_4$ (700 mg, 1.58 mmol, 1.0 equiv.) and triphenylacetic acid (3.6 g, 12.5 mmol, 8.0 equiv.) were dissolved in chlorobenzene (150 mL) in a 250 mL round-bottomed flask equipped with a magnetic stir bar. A soxhlet extractor was attached, containing potassium carbonate, and a reflux condenser. The mixture was heated at reflux overnight (16 hours). CH_2Cl_2 (150 mL) was added and the mixture was washed with saturated aqueous sodium bicarbonate solution (2 x 150 mL) and brine (100 mL), dried over MgSO_4 and concentrated. The green residue was purified by column chromatography (eluent: CH_2Cl_2) to give the product as a green solid. This was dissolved in a minimal quantity of benzene and flash frozen with liquid nitrogen. The frozen solution was freeze-dried on a high vacuum pump overnight to give the product as a fluffy light green solid (1.4 g, 61% yield). The spectral data matched those reported in the literature.¹

2.1 Synthesis of Achiral Diazos

All diazos **1a-g** were prepared by direct diazo transfer to the ester according to Scheme SI-1.



Scheme SI-1

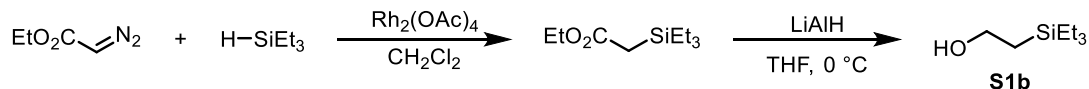
2.1.1 Preparation of 2-silylethanols

Alcohol **S1a** was purchased from Alfa Aesar and used as received. Alcohol **S1g** was prepared according to a literature procedure.² Alcohols **S1b-c** and **S1e-f** were prepared by Si-H insertion with ethyl diazoacetate according to Scheme SI-1. The preparation of **S1d** is described below.

Synthesis of alcohols S1b-c and S1e-f:

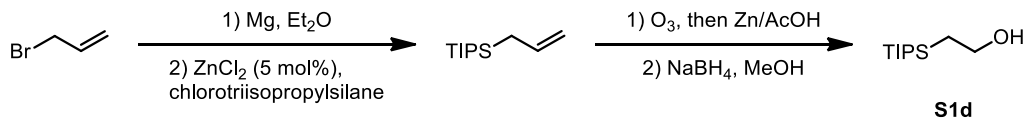
Alcohols **S1b-c** and **S1e-f** were prepared by Si-H insertion with ethyl diazoacetate according to Scheme SI-1 above. The procedure for **S1b** is shown below. Alcohols **S1c,e** and **f** were prepared in a manner analogous to **S1b**, and spectral data for these compounds were consistent with those reported.³⁻⁵

The synthesis of S1b is representative:



2-(triethylsilyl)ethanol (S1b): A solution of ethyl diazoacetate (2.5 g, 80% by mass in CH_2Cl_2 , 17.5 mmol, 1.0 equiv.) in CH_2Cl_2 (20 mL) was added dropwise over 4 hours to a solution of triethylsilane (5.7 mL, 35.1 mmol, 2.0 equiv.) and $\text{Rh}_2(\text{OAc})_4$ (77 mg, 0.18 mmol, 1 mol %) in CH_2Cl_2 (40 mL). The mixture was stirred overnight and the volatiles removed by rotary evaporation. The crude residue was filtered through a short plug of silica to remove the catalyst, eluting with 95:5 pentane: Et_2O . The filtrate was concentrated to give crude ethyl triethylsilylacetate as a pale oil. This oil was dissolved in 15 mL THF and added dropwise to a suspension of lithium aluminum hydride (1.3 g, 35 mmol, 2.0 equiv.) in THF (20 mL) at 0°C . The mixture was stirred overnight at room temperature. The mixture was cooled again to 0°C and water added carefully (1.3 mL), followed by dropwise addition of 15% aqueous NaOH (1.3 mL). THF (40 mL) was added to break up the solids, followed by water (4.5 mL). The slurry was stirred vigorously until the solids became a white precipitate (approx. 30 mins). The solids were removed by filtration, washing with EtOAc. The filtrate was dried over MgSO_4 and concentrated to give the crude 2-(triethylsilyl)ethanol (2.3 g, 80% yield over 2 steps), pure enough for the next step. The spectral data were consistent with those previously reported.⁶

Synthesis of 2-(triisopropylsilyl)ethanol



2-(triisopropylsilyl)ethanol (S1d):

Synthesis of allyltriisopropylsilane – by a modified literature procedure⁷: A flame dried, 3-necked, 500 mL round-bottomed flask was fitted with a glass stopper, reflux condenser, addition funnel and magnetic stirring bar. The flask was cooled under a stream of argon, which was then maintained throughout the reaction. The flask was charged with magnesium turnings (15.1 g, 630 mmol, 3.15 equiv.) followed by Et_2O (100 mL). The addition funnel was charged with allyl bromide (51.9 mL, 600 mmol, 3.0 equiv.) and 150 mL Et_2O and stirred until well mixed. While the magnesium suspension was stirred vigorously, a small portion of the allyl bromide solution (10 mL) was carefully added to the flask. The reaction initiated almost immediately, and the allyl bromide solution was added dropwise at such a rate as to maintain a gentle reflux. When the addition was complete, the mixture was stirred overnight (16 hours) at room temperature. To another flask was added zinc(II) chloride (1.4 g, 10 mmol, 5 mol %) followed by THF (300 mL) and triisopropylchlorosilane (42.8 mL, 200 mmol, 1.0 equiv.). To this solution was carefully added the Grignard solution via cannula, under argon. The solution was stirred 4 hours and quenched carefully by adding water dropwise (10 mL). A solution of HCl (1M, 200 mL) was added, and the layers separated. The organic layer was washed with water (100 mL), dried over MgSO_4 , filtered and concentrated. The crude residue was purified by passing through a small plug of silica, eluting with hexanes. Allyltriisopropylsilane was

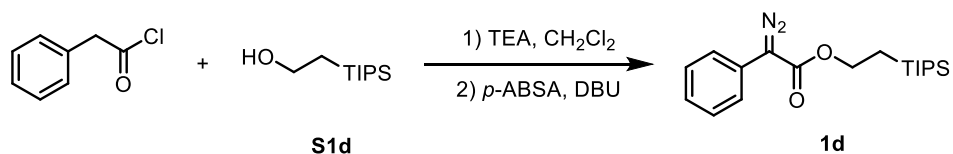
collected as a colorless oil (39.1 g, 98% yield). The spectral data matched those in the literature.⁷

Synthesis of 2-(triisopropylsilyl)ethanol (S1d): allyltriisopropylsilane (20.0 g, 101 mmol, 1.0 equiv.) was dissolved in 300 mL CH₂Cl₂ in a 1000 mL graduated cylinder. The solution was cooled to -78 °C and ozone was bubbled through the solution until a blue color persisted. Argon was bubbled through the system until the solution became colorless. The reaction mixture was allowed to warm to room temperature and concentrated. The crude residue was dissolved in AcOH/H₂O 10:1 (150 mL). Zinc dust (7.8 g, 120 mmol, 1.2 equiv.) was added carefully and the mixture stirred for 2 hours. Water (200 mL) was added and the mixture extracted with Et₂O (200 mL). The organic layer was washed with water (100 mL), saturated aqueous sodium bicarbonate (100 mL), and brine (100 mL), dried over MgSO₄, filtered and concentrated to give cleanly the aldehyde (18 g, 89 % yield), which was used without further purification. The aldehyde (10.0 g, 49.9 mmol, 1.0 equiv.) was dissolved in 150 mL of methanol and cooled to 0 °C. Sodium borohydride pellets (2.1 g, 54.9 mmol, 1.2 equiv.) were added and the mixture stirred for 3 hours. Then saturated sodium bicarbonate solution was added (100 mL) followed by Et₂O (150 mL) and the mixture stirred vigorously. Water was added (100 mL) and the layers separated. The aqueous layer was extracted with Et₂O (75 mL). The organic layers were combined and dried (MgSO₄), filtered and concentrated. The biphasic crude residue was dissolved in Et₂O (150 mL) and washed with H₂O (2 x 100 mL), brine (100 mL), and dried over MgSO₄, filtrated and concentrated to give the alcohol **S1d** as a colorless oil (8.3 g, 82% yield). The spectral data were consistent with those previously reported for this compound.⁶

2.1.2 Preparation of Diazos 1a-g

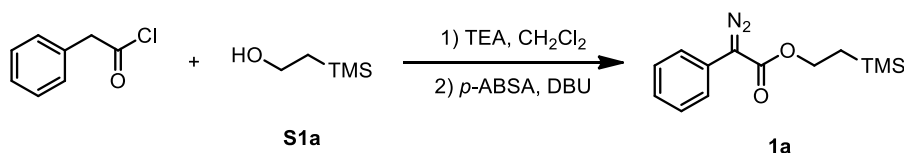
Diazos **1a-g** were prepared from the corresponding alcohols (**S1a-g**, the preparation of which have been described above) and phenylacetyl chloride, followed by direct diazo transfer with *p*-ABSA and DBU (according to scheme SI-1).

Preparation of 1d is representative:

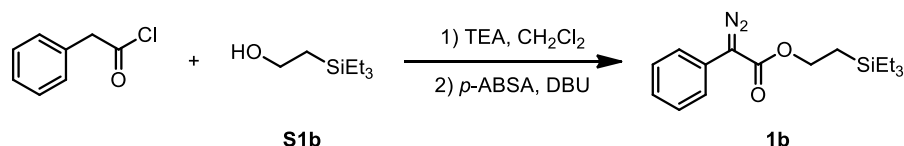


2-(triisopropylsilyl)ethyl 2-diazo-2-phenylacetate (1d): To a solution of 2-(triisopropylsilyl)ethanol (2.0 g, 9.9 mmol, 1.2 equiv.) and triethylamine (2.3 mL, 16.4 mmol, 2.0 equiv.) in CH₂Cl₂ (20 mL) was added phenylacetyl chloride (1.1 mL, 8.2 mmol, 1.0 equiv.) carefully dropwise. The mixture was stirred overnight at room temperature, before it was quenched with 1M HCl (15 mL). The organic layer was separated and washed with brine (20 mL), dried over MgSO₄, filtered and concentrated. The crude product was passed through a short column of silica gel (3% Et₂O in pentane) to remove the excess alcohol. This gave 2-(triisopropylsilyl)ethyl phenylacetate as a colorless oil (1.7 g, 65% yield), which was used immediately in the next step. This product (1.7 g, 5.3 mmol, 1.0 equiv.) was dissolved in acetonitrile (15 mL) along with *p*-acetamidobenzenesulfonyl azide [*p*-ABSA] (1.9 g, 8.0 mmol, 1.5 equiv.) and cooled to 0 °C. Then 1,8-diazabicycloundec-7-ene [DBU] (1.6 mL, 10.6 mmol, 2.0 equiv.) was added dropwise. The mixture was allowed to warm to room temperature over several hours and then stirred for 48 hours. The mixture was quenched by addition of saturated aqueous NH₄Cl (15 mL) and water (5 mL). The mixture was extracted with Et₂O (20 mL).

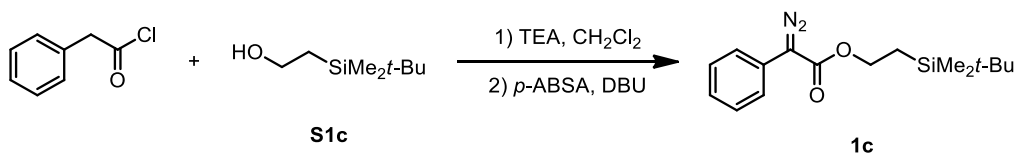
The organic layer was washed with brine (15 mL) and dried over MgSO₄, filtered and concentrated. The crude material was purified by column chromatography (3% Et₂O in pentane). This gave diazo **1d** as a thick orange oil (1.3 g, 72 % yield) that solidified in the freezer (-25 °C). ¹H NMR (400 MHz; CDCl₃) δ 7.53-7.48 (m, 2H), 7.42-7.36 (m, 2H), 7.21-7.16 (m, 1H), 4.47-4.40 (m, 2H), 1.23-1.14 (m, 2H), 1.09 (m, 21H); ¹³C NMR (100 MHz, CDCl₃) δ 165.6, 129.1, 125.9, 124.2, 63.7, 18.9, 11.4, 11.1 (the resonance resulting from the diazo carbon was not detected); IR (neat): 2939, 2863, 2082, 1697 cm⁻¹; HRMS (NSI) calcd for C₁₃H₃₀O₂N₂NaSi ([M+Na]⁺) 369.1969, found 369.1964;



2-(trimethylsilyl)ethyl 2-diazo-2-phenylacetate (1a): Prepared analogously to **1d**. *Step 1:* From phenylacetyl chloride (6.2 mL, 46.6 mmol, 1.1 equiv.), **S1a** (5.0 g, 42.3 mmol, 1.0 equiv.) and triethylamine (8.8 mL, 63.5 mmol, 1.5 equiv.). After work-up, the crude was used without purification in *Step 2:* From the crude ester, *p*-ABSA (15.2 g, 63.5 mmol, 1.5 equiv.), and DBU (12.6 mL, 84.6 mmol, 2.0 equiv.). The crude was purified by column chromatography (5% Et₂O in pentane) to give the diazo as a red oil (5.5 g, 50% yield over 2 steps). ¹H NMR (400 MHz; CDCl₃) δ 7.51 (dd, 2H, *J* = 8.5, 1.1 Hz), 7.40 (t, 2H, *J* = 7.9 Hz), 7.19 (m, 1H), 4.43-4.37 (m, 2H), 1.14-1.07 (m, 2H), 0.09 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 165.5, 129.0, 129.8, 125.9, 124.1, 63.5, 17.8, -1.3 (the resonance resulting from the diazo carbon was not detected); IR (neat): 2954, 2080, 1698, 1150 cm⁻¹; HRMS (NSI) calcd for C₁₃H₁₈O₂N₂NaSi ([M+Na]⁺) 285.1029, found 285.1032;

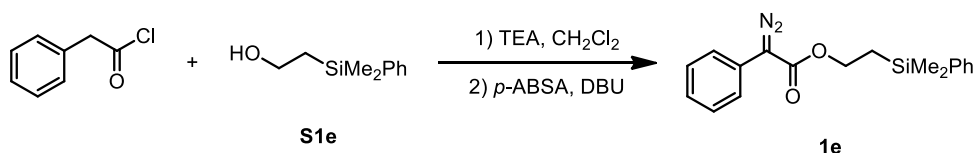


2-(triethylsilyl)ethyl 2-diazo-2-phenylacetate (1b): Prepared analogously to **1d**. *Step 1:* From phenylacetyl chloride (1.6 mL, 11.7 mmol, 1.0 equiv.), **S1b** (2.3 g, 14.1 mmol, 1.2 equiv.), and triethylamine (3.3 mL, 23.4 mmol, 2.0 equiv.) to give the ester (1.7 g). *Step 2:* From the ester (1.7 g, 6.0 mmol, 1.0 equiv.), *p*-ABSA (2.2 g, 9.0 mmol, 1.5 equiv.), and DBU (1.8 mL, 12.0 mmol, 2.0 equiv.). The crude was purified by column chromatography (2% Et₂O in pentane) to give the diazo as a red oil (1.2 g, 33% yield over two steps). ¹H NMR (400 MHz; CDCl₃) δ 7.51 (dd, 2H, *J* = 8.6, 1.2 Hz), 7.42-7.37 (m, 2H), 7.19 (tt, 1H, *J* = 7.8, 1.2 Hz), 4.41-4.36 (m, 2H), 1.15-1.09 (m, 2H), 0.98 (t, 9H, *J* = 7.9 Hz), 0.58 (q, 6H, *J* = 7.9 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 165.6, 129.1, 125.9 (2 signals), 124.2, 63.5, 13.1, 7.6, 3.6 (the resonance resulting from the diazo carbon was not detected); IR (film): 2953, 2874, 2080, 1699, 1150 cm⁻¹; HRMS (NSI) calcd for C₁₆H₂₄O₂N₂Si ([M]⁺) 304.1602, found 304.1588;

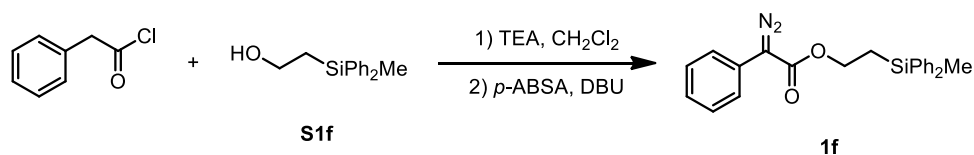


2-(tert-butyl)dimethylsilyl ethyl 2-diazo-2-phenylacetate (1c): Prepared analogously to **1d**. *Step 1:* From phenylacetyl chloride (2.3 mL, 17.7 mmol, 1.1 equiv.), **S1c** (2.6 g, 16.1 mmol, 1.0 equiv.) and triethylamine (3.3 mL, 24 mmol, 1.5 equiv.) to give the ester (3.2 g). *Step 2:* From the ester (3.2 g, 11.3 mmol, 1.0 equiv.), *p*-ABSA (4.1 g, 17 mmol, 1.5 equiv.) and DBU (3.2 mL, 22.6 mmol, 2.0 equiv.). The crude was purified by column

chromatography (4% Et₂O in pentane) to give the diazo as a red oil (2.3 g, 47% yield over two steps). ¹H NMR (600 MHz; CDCl₃) δ 7.51 (dd, 2H, *J* = 8.5, 1.0 Hz), 7.40 (t, 2H, *J* = 8 Hz), 7.19 (t, 1H, *J* = 7.4 Hz), 4.42-4.37 (m, 2H), 1.13-1.09 (m, 2H), 0.92 (s, 9H), 0.03 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 165.6, 129.1, 125.9 (2 signals), 124.2, 63.8, 26.6, 16.6, 14.1, -5.8 (the resonance resulting from the diazo carbon was not detected); IR (neat): 2953, 2856, 2080, 1699 cm⁻¹; HRMS (NSI) calcd for C₁₆H₂₄O₂N₂NaSi ([M+Na]⁺) 327.1499, found 327.1501;



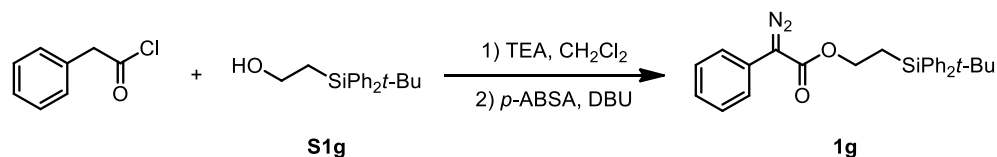
2-(dimethyl(phenyl)silyl)ethyl 2-diazo-2-phenylacetate (1e): Prepared analogously to **1d**. *Step 1:* From phenylacetyl chloride (0.78 mL, 6.0 mmol, 1.0 equiv.), **S1e** (1.3 g, 7.2 mmol, 1.2 equiv.), and triethylamine (1.7 mL, 12 mmol, 2.0 equiv.) to give the ester (1.2 g). *Step 2:* From the ester (1.2 g, 3.9 mmol, 1.0 equiv.), *p*-ABSA (1.2 g, 5.9 mmol, 1.5 equiv.) and DBU (1.2 mL, 7.8 mmol, 2.0 equiv.). The crude was purified by column chromatography (3% Et₂O in pentane) to give the diazo as a red oil (870 mg, 46% yield over two steps). ¹H NMR (400 MHz; CDCl₃) δ 7.55-7.50 (m, 2H), 7.47 (d, 2H, *J* = 8.8 Hz), 7.41-7.33 (m, 5H), 7.17 (td, 1H, *J* = 7.4, 1.2 Hz), 4.37 (m, 2H), 1.34 (m, 2H), 0.35 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 165.5, 138.0, 133.6, 129.4, 129.1, 128.1, 125.9, 125.8, 124.1, 63.2, 17.1, -2.7 (the resonance resulting from the diazo carbon was not detected); IR (film): 2954, 2080, 1697, 1243, 1150 cm⁻¹; HRMS (NSI) calcd for C₁₈H₂₀O₂N₂NaSi ([M+Na]⁺) 347.1186, found 347.1187;



2-(methyldiphenylsilyl)ethyl 2-diazo-2-phenylacetate (1f): Prepared analogously to **1d**.

Step 1: From phenylacetyl chloride (1.0 mL, 7.9 mmol, 1.1 equiv.), **S1f** (1.7 g, 7.2 mmol, 1.0 equiv.), and triethylamine (1.5 mL, 10.8 mmol, 1.5 equiv.) to give the ester (2.6 g).

Step 2: From the ester (2.6 g, 7.2 mmol, 1.0 equiv.), *p*-ABSA (2.6 g, 10.8 mmol, 1.5 equiv.) and DBU (2.0 mL, 14.4 mmol, 2.0 equiv.). The crude was purified by column chromatography (3% EtOAc in hexanes) to give the diazo as a red oil (1.9 g, 68% yield over two steps). ¹H NMR (400 MHz; CDCl₃) δ 7.58-7.53 (m, 4H), 7.49-7.44 (m, 2H), 7.43-7.35 (m, 8H), 7.22-7.17 (m, 1H), 4.48-4.41 (m, 2H), 1.71-1.64 (m, 2H), 0.65 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 165.4, 136.0, 134.5, 129.7, 129.1, 128.2, 125.9, 125.8, 124.1, 63, 15.8, -3.9 (the resonance resulting from the diazo carbon was not detected); IR (neat): 3068, 2955, 2081, 1696, 1150 cm⁻¹; HRMS (NSI) calcd for C₂₃H₂₂O₂N₂NaSi ([M+Na]⁺) 409.1343, found 409.1343;



2-(tert-butyldiphenylsilyl)ethyl 2-diazo-2-phenylacetate (1g): Prepared analogously to

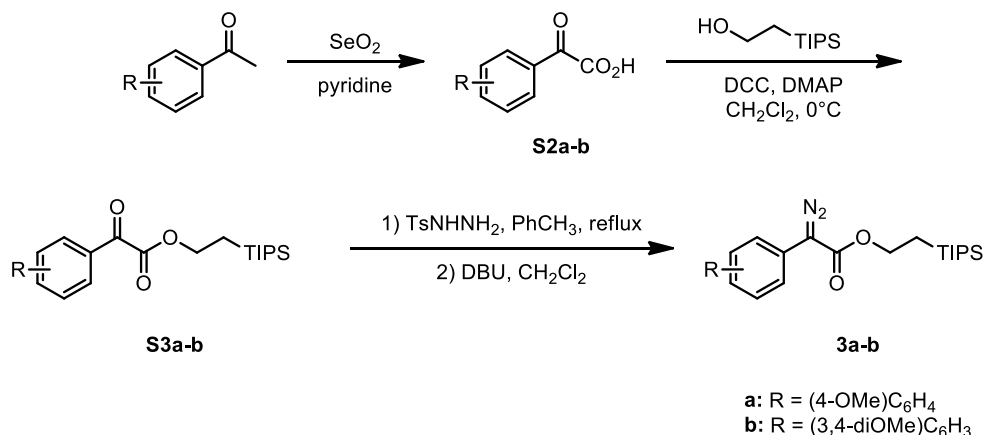
1d. *Step 1:* From phenylacetyl chloride (1.9 mL, 14.7 mmol, 1.0 equiv.), **S1g** (4.6 g, 16.2 mmol, 1.1 equiv.) and triethylamine (4.5 mL, 32.4 mmol, 2.0 equiv.) to give the ester (4.0 g). *Step 2:* From the ester (4.0 g, 9.9 mmol, 1.0 equiv.), *p*-ABSA (3.6 g, 14.9 mmol, 1.5 equiv.) and DBU (3.0 mL, 19.8 mmol, 2.0 equiv.). The crude was purified by column

chromatography (2% Et₂O in pentane) to give the diazo as a thick red oil (2.3 g, 37% yield over two steps). ¹H NMR (400 MHz; CDCl₃) δ 7.71-7.65 (m, 4H), 7.51-7.36 (m, 10H), 7.23-7.16 (m, 1H), 4.38-4.31 (m, 2H), 1.79-1.72 (m, 2H), 1.09 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 165.5, 136.0, 133.7, 129.6, 129.1, 128.0, 125.9, 125.9, 124.2, 63.6, 27.8, 18.2, 12.3 (the resonance resulting from the diazo carbon was not detected); IR (neat): 2929, 2856, 2081, 1698, 1149 cm⁻¹; HRMS (NSI) calcd for C₂₆H₂₈O₂N₂NaSi ([M+Na]⁺) 451.1812, found 451.1813;

2.1.3 Preparation of Diazos 3a-l and S5

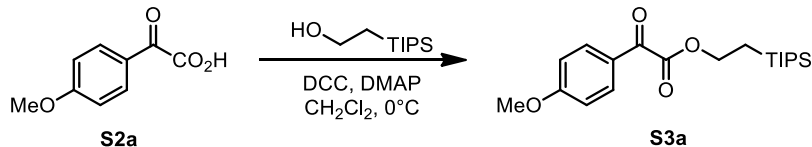
Preparation of Diazos 3a-b

Diazos **3a,b** were prepared according to Scheme SI-2. Acids **S2a-b** were prepared by oxidation of the corresponding acetophenones, according to a literature procedure.⁸

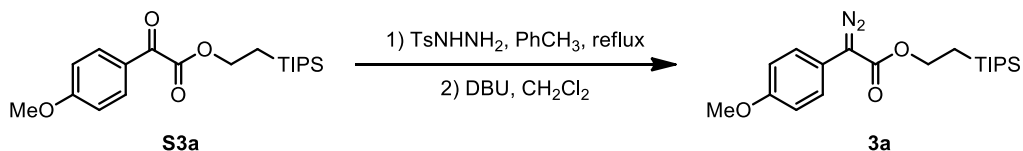


Scheme SI-2

The preparation of **3a** is representative:

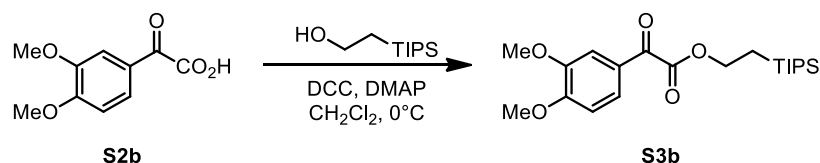


2-(triisopropylsilyl)ethyl 2-(4-methoxyphenyl)-2-oxoacetate (S3a): To a 0 °C solution of acid **S2a** (1.1 g, 6.1 mmol, 1.0 equiv.), alcohol **S1d** (1.9 g, 9.2 mmol, 1.5 equiv.), and DMAP (74 mg, 0.61 mmol, 0.1 equiv.) in CH₂Cl₂ (6 mL) was added a solution of dicyclohexylcarbodiimide [DCC] (1.4 g, 6.7 mmol, 1.1 equiv.) in CH₂Cl₂ (5 mL). The mixture was stirred overnight, and allowed to warm to room temperature over that time. The precipitate was removed by filtration, washing with copious quantities of Et₂O. The filtrate was concentrated by rotary evaporation and purified by column chromatography (5% Et₂O in pentane) to give the ester as a colorless oil (1.6 g, 73% yield). ¹H NMR (400 MHz; CDCl₃) δ 8.06-8.00 (m, 2H), 7.00-6.96 (m, 2H), 4.56-4.49 (m, 2H), 3.90 (s, 3H), 1.30-1.22 (m, 2H), 1.14-1.03 (m, 21H); ¹³C NMR (100 MHz, CDCl₃) δ 185.2, 165.1, 164.4, 132.8, 125.8, 114.4, 65.1, 55.8, 18.9, 13.2, 11.1; IR (neat): 2941, 2865, 1729, 1675, 1597 cm⁻¹; HRMS (NSI) calcd for C₂₀H₃₂O₄NaSi ([M+Na]⁺) 387.1962, found 387.1966;



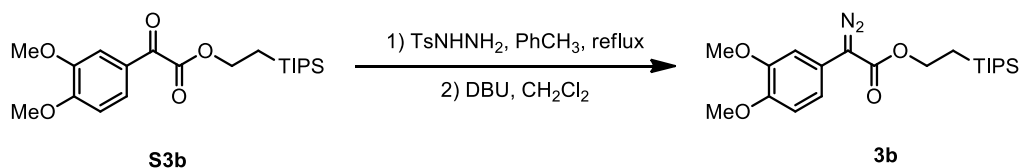
2-(triisopropylsilyl)ethyl 2-diazo-2-(4-methoxyphenyl)acetate (3a): A solution of the ketone (1.6 g, 4.4 mmol, 1.0 equiv.) and *p*-toluenesulfonyl hydrazide (900 mg, 4.8 mmol, 1.1 equiv.) in toluene (30 mL) was heated to reflux in a dean-stark apparatus overnight.

The solution was allowed to cool to room temperature and the toluene removed by rotary evaporation. The crude residue was dissolved in CH₂Cl₂ (30 mL) and DBU (2.0 mL, 13.2 mmol, 3.0 equiv.) added. The mixture was stirred at room temperature for 24 hours. The orange solution was quenched with saturated aqueous NH₄Cl (30 mL) and the aqueous phase extracted with CH₂Cl₂ (20 mL). The organic extracts were combined and dried over MgSO₄, filtered and concentrated. The crude residue was purified by column chromatography (4% Et₂O in pentane) to give the product as a red oil (980 mg, 59% yield). ¹H NMR (400 MHz; CDCl₃) δ 7.43-7.38 (m, 2H), 6.98-6.92 (m, 2H), 4.45-4.38 (m, 2H), 3.82 (s, 3H), 1.21-1.03 (m, 23H); ¹³C NMR (100 MHz, CDCl₃) δ 166.2, 158.2, 126.2, 117.3, 114.8, 63.6, 55.6, 18.9, 11.4, 11.2 (the resonance resulting from the diazo carbon was not detected); IR (neat): 2941, 2865, 2077, 1694, 1512 cm⁻¹; HRMS (NSI) calcd for C₂₀H₃₂O₃N₂NaSi ([M+Na]⁺) 399.2074, found 399.2075;



2-(triisopropylsilyl)ethyl 2-(3,4-dimethoxyphenyl)-2-oxoacetate (S3b): Prepared analogously to **S3a**. From carboxylic acid **S2b** (1.5 g, 7.1 mmol, 1.0 equiv.), alcohol **S1d** (1.7 g, 8.5 mmol, 1.2 equiv.), DCC (1.6 g, 7.8 mmol, 1.1 equiv.) and DMAP (87 mg, 0.71 mmol, 0.1 equiv.). The crude was purified by column chromatography (9:1 hexanes:EtOAc) to give the product as a slightly yellow oil (2.1 g, 75% yield). ¹H NMR (400 MHz; CDCl₃) δ 7.67 (dd, 1H, *J* = 8.5, 2.0 Hz), 7.58 (d, 1H, *J* = 2.0 Hz), 6.93 (d, 1H, *J* = 8.5 Hz), 4.57-4.48 (m, 2H), 3.98 (s, 3H), 3.95 (s, 3H), 1.30-1.23 (m, 2H), 1.14-1.05 (m, 21H); ¹³C NMR (100 MHz, CDCl₃) δ 185.3, 164.4, 155.1, 149.5, 126.5, 125.9, 110.9,

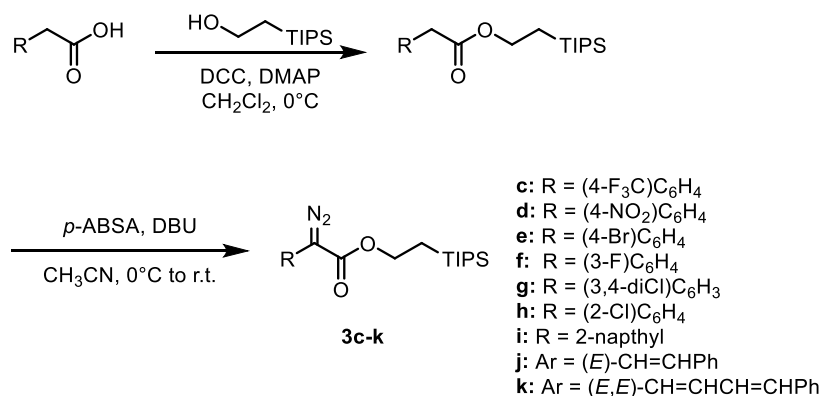
110.4, 65.1, 56.4, 56.3, 18.9, 11.1 (2 signals); IR (neat): 2940, 2864, 1729, 1672, 1514 cm^{-1} ; HRMS (NSI) calcd for $\text{C}_{21}\text{H}_{34}\text{O}_5\text{NaSi}$ ($[\text{M}+\text{Na}]^+$) 417.2068, found 417.2072;



2-(triisopropylsilyl)ethyl 2-diazo-2-(3,4-dimethoxyphenyl)acetate (3b): Prepared analogously to **3a**. From the ketone (2.1 g, 5.3 mmol, 1.0 equiv.), *p*-toluenesulfonyl hydrazide (1.1 g, 5.9 mmol, 1.1 equiv.) and DBU (2.4 mL, 15.9 mmol, 3.0 equiv.). The crude was purified by column chromatography (10-15% Et_2O in pentane) to give the product as a fluffy red solid (1.3 g, 59% yield). ^1H NMR (400 MHz; CDCl_3) δ 7.21 (s, 1H), 6.92-6.86 (m, 2H), 4.46-4.37 (m, 2H), 3.91 (s, 3H), 3.89 (s, 3H), 1.20-1.13 (m, 2H), 1.12-1.02 (m, 21H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.1, 149.6, 147.4, 117.8, 116.7, 111.8, 108.5, 63.6, 56.2, 56.1, 18.9, 11.3, 11.2 (the resonance resulting from the diazo carbon was not detected); IR (neat): 2940, 2864, 2077, 1694, 1519 cm^{-1} ; HRMS (NSI) calcd for $\text{C}_{21}\text{H}_{34}\text{O}_4\text{N}_2\text{Si}$ (M^+) 406.2282, found 406.2284;

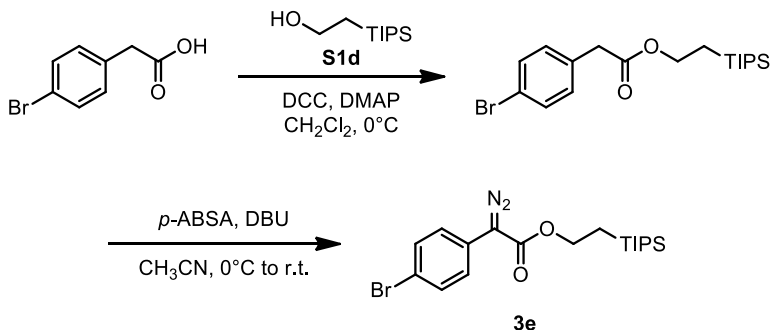
Preparation of Diazos 3c-k

Diazos **3c-k** were prepared by direct diazo transfer to the ester, according to Scheme SI-3 below:



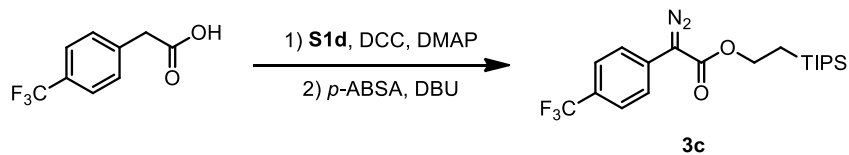
Scheme SI-3

The preparation of **3e** is representative:



2-(triisopropylsilyl)ethyl 2-(4-bromophenyl)-2-diazoacetate (3e): A solution of 4-bromophenylacetic acid (1.1 g, 4.95 mmol, 1.0 equiv.), *N,N*-dimethyl-4-aminopyridine (DMAP) (60 mg, 0.50 mmol, 10 mol %), and 2-(triisopropylsilyl)ethanol **S1d** (1.2 g, 5.9 mmol, 1.2 equiv.) in CH₂Cl₂ (4 mL) was cooled to 0 °C. Then a solution of *N,N*-dicyclohexylcarbodiimide (DCC) (1.1 g, 5.4 mmol, 1.1 equiv.) in CH₂Cl₂ (2 mL) was added over 2 minutes. The mixture was stirred for 3 hours, and the white precipitate was removed by filtration, washing several times with Et₂O. The filtrate was concentrated by

rotary evaporation and the crude residue purified by column chromatography (5% Et₂O in pentane). The ester intermediate was isolated as a colorless oil (1.8 g) and used immediately in the diazo transfer: The ester (1.8 g, 4.4 mmol, 1.0 equiv.) was dissolved in CH₃CN (10 mL), followed by *p*-ABSA (1.6 g, 6.6 mmol, 1.5 equiv.). The mixture was cooled to 0 °C. Then DBU (1.3 mL, 8.8 mmol, 2.0 equiv.) was added. The mixture was allowed to warm to room temperature and stirred for 72 hours. The reaction was quenched with saturated aqueous NH₄Cl (15 mL) and H₂O (5 mL). The mixture was extracted with Et₂O (20 mL). The ether layer was washed with brine, dried over MgSO₄, filtered and concentrated. The crude residue was purified by column chromatography (2% Et₂O in pentane) to give the diazo **3e** as a thick orange/red oil (1.7 g, 79 % yield over two steps), which solidified as an orange solid in the freezer (-25 °C). ¹H NMR (400 MHz; CDCl₃) δ 7.52-7.47 (m, 2H), 7.40-7.36 (m, 2H), 4.46-4.39 (m, 2H), 1.21-1.13 (m, 2H), 1.13-1.02 (m, 21H); ¹³C NMR (100 MHz, CDCl₃) δ 165.2, 132.2, 125.5, 125.2, 119.4, 63.9, 18.9, 11.4, 11.2 (the resonance resulting from the diazo carbon was not detected); IR (neat): 2939, 2862, 2091, 1690 cm⁻¹; HRMS (NSI) calcd for C₁₉H₂₉O₂N₂BrNaSi ([M+Na]⁺) 447.1074, found 447.1070;

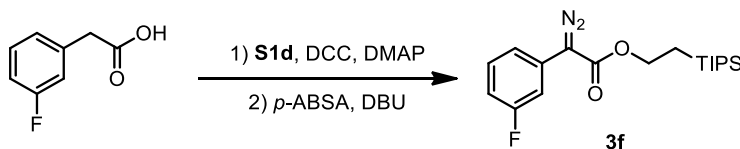


2-(triisopropylsilyl)ethyl 2-diazo-2-(4-(trifluoromethyl)phenyl)acetate (3c): Prepared analogously to **3e**. *Step 1:* From 4-(trifluoromethyl)phenylacetic acid (1.0 g, 4.9 mmol, 1.0 equiv.), **S1d** (1.2 g, 5.9 mmol, 1.2 equiv.), DCC (1.1 g, 5.4 mmol, 1.1 equiv.) and DMAP (72 mg, 0.59 mmol, 0.1 equiv.) to give the intermediate ester (810 mg). *Step 2:*

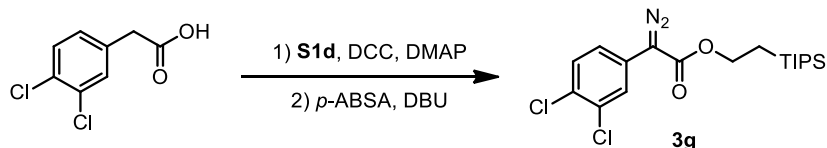
From the ester (0.81 g, 2.1 mmol, 1.0 equiv.), *p*-ABSA (0.77 g, 3.2 mmol, 1.5 equiv.), and DBU (0.59 mL, 4.2 mmol, 2.0 equiv.). The crude was purified by chromatography (2% Et₂O in pentane) to give the product **3c** as an orange solid (730 mg, 37% yield over two steps). ¹H NMR (400 MHz; CDCl₃) δ 7.63 (s, 4H), 4.49-4.41 (m, 2H), 1.22-1.15 (m, 2H), 1.11-1.06 (m, 21H); ¹³C NMR (100 MHz, CDCl₃) δ 164.8, 130.6, 127.6 (q, *J* = 32.8 Hz), 126 (q, *J* = 3.7 Hz), 124.3 (q, *J* = 271.6 Hz), 123.6, 64.1, 18.9, 11.4, 11.2 (the resonance resulting from the diazo carbon was not detected); IR (neat): 2943, 2866, 2087, 1702, 1322 cm⁻¹; HRMS (NSI) calcd for C₂₀H₂₉O₂N₂F₃NaSi ([M+Na]⁺) 437.1843, found 437.1838;

2-(triisopropylsilyl)ethyl 2-diazo-2-(4-nitrophenyl)acetate (3d): Prepared analogously to **3e**. *Step 1:* From 4-nitrophenylacetic acid (910 mg, 5.0 mmol, 1.0 equiv.), **S1d** (1.2 g, 5.9 mmol, 1.2 equiv.), DCC (1.1 g, 5.5 mmol, 1.1 equiv.) and DMAP (61 mg, 0.5 mmol, 0.1 equiv.) to give the ester (1.2 g). *Step 2:* From the ester (1.2 g, 3.2 mmol, 1.0 equiv.), *p*-ABSA (1.2 g, 4.8 mmol, 1.5 equiv.) and DBU (0.90 mL, 6.4 mmol, 2.0 equiv.). The crude was purified by column chromatography (2% Et₂O in pentane) to give the diazo as an orange solid (870 mg, 44% yield over two steps). ¹H NMR (400 MHz; CDCl₃) δ 8.23-8.18 (m, 2H), 7.69-7.63 (m, 2H), 4.47-4.40 (m, 2H), 1.20-0.99 (m, 23H); ¹³C NMR (100 MHz, CDCl₃) δ 164.1, 145.1, 134.4, 124.5, 123.3, 64.4, 18.9, 11.4, 11.1 (the resonance resulting from the diazo carbon was not detected); IR (film): 2942, 2846, 2091, 1697,

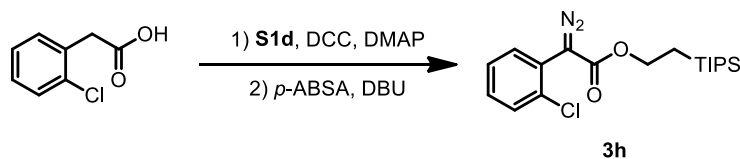
1330 cm^{-1} ; HRMS (NSI) calcd for $\text{C}_{19}\text{H}_{29}\text{O}_4\text{N}_2\text{NaSi}$ ($[\text{M}+\text{Na}]^+$) 414.1820, found 414.1815;



2-(triisopropylsilyl)ethyl 2-diazo-2-(3-fluorophenyl)acetate (3f): Prepared analogously to **3e**. *Step 1:* From 3-fluorophenylacetic acid (760 mg, 4.9 mmol, 1.0 equiv.), **S1d** (1.2 g, 5.9 mmol, 1.2 equiv.), DCC (1.1 g, 5.4 mmol, 1.1 equiv.) and DMAP (72 mg, 0.59 mmol, 0.1 equiv.) to give the ester (1.0 g). *Step 2:* From the ester (1.0 g, 3.0 mmol, 1.0 equiv.), *p*-ABSA (1.1 g, 4.5 mmol, 1.5 equiv.) and DBU (0.84 mL, 6.0 mmol, 2.0 equiv.). The crude was purified by column chromatography (1% Et_2O in pentane) to give the diazo as an orange oil (900 mg, 50% yield over two steps). ^1H NMR (400 MHz; CDCl_3) δ 7.41-7.30 (m, 2H), 7.18 (ddd, 1H, $J = 8.0, 1.8, 0.9$ Hz), 6.86 (tdd, 1H, $J = 8.3, 2.5, 0.9$ Hz), 4.48-4.40 (m, 2H), 1.25-1.03 (m, 23H); ^{13}C NMR (100 MHz, CDCl_3) δ 165, 163.4 (d, $^1J_{\text{CF}} = 245$ Hz), 130.5 (d, $^3J_{\text{CF}} = 8.8$ Hz), 128.5 (d, $^3J_{\text{CF}} = 9.4$ Hz), 119 (d, $^4J_{\text{CF}} = 2.6$ Hz), 112.5 (d, $^2J_{\text{CF}} = 21.3$ Hz), 111.3 (d, $^2J_{\text{CF}} = 25.3$ Hz), 63.9, 18.9, 11.4, 11.1; IR (film): 2942, 2865, 2082, 1700, 1244 cm^{-1} ; HRMS (NSI) calcd for $\text{C}_{19}\text{H}_{29}\text{O}_2\text{N}_2\text{FNaSi}$ ($[\text{M}+\text{Na}]^+$) 387.1875, found 387.1879;

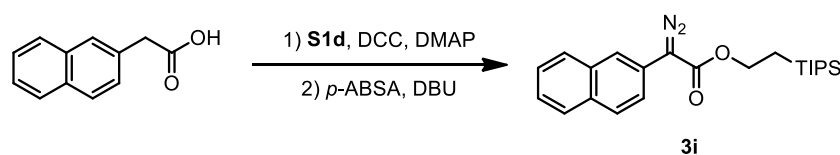


2-(triisopropylsilyl)ethyl 2-diazo-2-(3,4-dichlorophenyl)acetate (3g): Prepared analogously to **3e**. *Step 1:* From 3,4-dichlorophenylacetic acid (1.0 g, 5.0 mmol, 1.0 equiv.), **S1d**, (1.2 g, 5.9 mmol, 1.2 equiv.), DCC (1.1 g, 5.5 mmol, 1.1 equiv.) and DMAP (61 mg, 0.5 mmol, 0.1 equiv.) to give the ester (1.5 g). *Step 2:* From the ester (1.5 g, 3.8 mmol, 1.0 equiv.), *p*-ABSA (1.4 g, 5.7 mmol, 1.5 equiv.) and DBU (1.1 mL, 7.6 mmol, 2.0 equiv.). The crude was purified by column chromatography (0.5% Et₂O in pentane) to give the diazo as an orange solid (1.4 g, 67% yield over two steps). ¹H NMR (400 MHz; CDCl₃) δ 7.66 (d, 1H, *J* = 2.3 Hz), 7.42 (d, 1H, *J* = 8.6 Hz), 7.30 (dd, 1H, *J* = 8.6, 2.3 Hz), 4.47-4.39 (m, 2H), 1.21-1.04 (m, 23H); ¹³C NMR (100 MHz, CDCl₃) δ 164.7, 133.4, 130.8, 129.4, 126.5, 125.4, 122.8, 64.1, 18.9, 11.4, 11.1; IR (film): 2941, 2865, 2085, 1699, 1159 cm⁻¹; HRMS (APCI) calcd for C₁₉H₂₉O₂N₂Cl₂Si ([M+H]⁺) 415.1370, found 415.1360; Anal. calcd for C₁₉H₂₈N₂O₂SiCl₂: C 54.93, H 6.79, N 6.74, Found C 54.92, H 6.80, N 6.66;



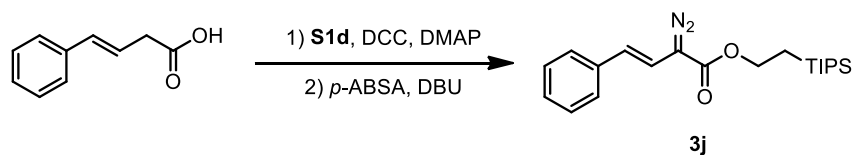
2-(triisopropylsilyl)ethyl 2-(2-chlorophenyl)-2-diazoacetate (3h): Prepared analogously to **3e**. *Step 1:* From 2-chlorophenylacetic acid (850 mg, 5.0 mmol, 1.0 equiv.), **S1d** (1.2 g, 5.9 mmol, 1.2 equiv.), DCC (1.1 g, 5.5 mmol, 1.1 equiv.), DMAP (61 mg, 0.5 mmol, 0.1 equiv.) to give the ester (1.2 g). *Step 2:* From the ester (1.2 g, 3.3 mmol, 1.0 equiv.),

p-ABSA (1.2 g, 5.0 mmol, 1.5 equiv.) and DBU (0.93 mL, 6.6 mmol, 2.0 equiv.). The crude was purified by column chromatography (1% Et₂O in pentane) to give the diazo as a yellow oil (1.1g, 58% yield over two steps). ¹H NMR (400 MHz; CDCl₃) δ 7.55 (dd, 1H, *J* = 7.7, 1.8 Hz), 7.40 (dd, 1H, *J* = 7.9, 1.6 Hz), 7.34-7.22 (m, 2H), 4.42-4.35 (m, 2H), 1.18-1.01 (m, 23H); ¹³C NMR (100 MHz, CDCl₃) δ 165.9, 133.9, 132.5, 130.2, 129.7, 127.3, 124.3, 64.0, 18.9, 11.4, 11.2; IR (neat): 2941, 2865, 1093, 1698, 1239 cm⁻¹; HRMS (NSI) calcd for C₁₉H₂₉O₂N₂ClNaSi ([M+Na]⁺) 403.1579, found 403.1577; Anal. calcd for C₁₉H₂₉N₂O₂SiCl: C 59.90, H 7.67, N 7.35, Found C 60.12, H 7.59, N 7.17;

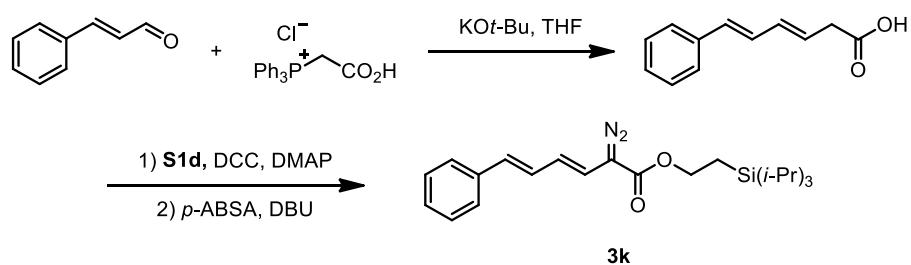


2-(triisopropylsilyl)ethyl 2-diazo-2-(naphthalen-2-yl)acetate (3i): Prepared analogously to **3e**. *Step 1:* From 2-naphthylacetic acid (1.2 g, 6.2 mmol, 1.0 equiv.), **S1d** (1.5 g, 7.4 mmol, 1.2 equiv.), DCC (1.4 g, 6.8 mmol, 1.1 equiv.) and DMAP (76 mg, 0.62 mmol, 0.1 equiv.) to give the ester (1.6 g). *Step 2:* From the ester (1.6 g, 4.3 mmol, 1.0 equiv.), *p*-ABSA (1.6 g, 6.5 mmol, 1.5 equiv.) and DBU (1.3 mL, 8.6 mmol, 2.0 equiv.). The crude was purified by column chromatography (1% Et₂O in pentane) to give the diazo as a red oil (1.5 g, 60% yield over two steps) that solidified upon storage in a freezer (-25 °C). ¹H NMR (400 MHz; CDCl₃) δ 8.05 (s, 1H), 7.86 (d, 1H, *J* = 8.7 Hz), 7.85-7.78 (m, 2H), 7.56 (d, 1H, *J* = 8.7 Hz), 7.53-7.41 (m, 2H), 4.51-4.45 (m, 2H), 1.25-1.19 (m, 2H), 1.17-1.04 (m, 21H); ¹³C NMR (100 MHz, CDCl₃) δ 165.7, 133.8, 131.6, 128.8, 127.8, 127.8, 126.8, 125.9, 123.1, 122.7, 122.1, 63.8, 18.9, 11.4, 11.2 (the resonance resulting from the

diazo carbon was not detected); IR (neat): 2962, 2939, 2862, 2083, 1698 cm^{-1} ; HRMS (NSI) calcd for $\text{C}_{23}\text{H}_{32}\text{O}_2\text{N}_2\text{NaSi}$ ($[\text{M}+\text{Na}]^+$) 419.2125, found 419.2125;



(*E*)-2-(triisopropylsilyl)ethyl 2-diazo-4-phenylbut-3-enoate (3j): Prepared analogously to **3e**. *Step 1:* From *trans*-styrylacetic acid (1.0 g, 6.2 mmol, 1.0 equiv.), **S1d** (1.5 g, 7.4 mmol, 1.2 equiv.), DCC (1.4 g, 6.8 mmol, 1.1 equiv.) and DMAP (76 mg, 0.62 mmol, 0.1 equiv.) to give the ester (1.3 g). *Step 2:* From the ester (1.3 g, 3.8 mmol, 1.0 equiv.), *p*-ABSA (1.3 g, 5.2 mmol, 1.5 equiv.) and DBU (1.1 mL, 7.0 mmol, 2.0 equiv.), the reaction mixture was stirred for 3.5 hours before it was quenched. The diazo was purified by chromatography (2% Et_2O in pentane) to give the product as a red oil. This was dissolved in benzene (8 mL), flash frozen with liquid N_2 , and placed under vacuum (160 mTorr) overnight (16 hours) to furnish the diazo as a red solid (1.1 g, 48% yield over two steps). ^1H NMR (400 MHz; CDCl_3) δ 7.41-7.29 (m, 4H), 7.25-7.17 (m, 1H), 6.52 (d, 1H, $J = 16.3$ Hz), 6.20 (d, 1H, $J = 16.3$ Hz), 4.45-4.38 (m, 2H), 1.20-1.14 (m, 2H), 1.12-1.05 (m, 21H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.5, 137.1, 128.9, 127.2, 126.0, 123.0, 111.8, 64.1, 18.9, 11.4, 11.2 (the resonance resulting from the diazo carbon was not detected); IR (neat): 2937, 2865, 2079, 1698 cm^{-1} ; HRMS (NSI) calcd for $\text{C}_{21}\text{H}_{32}\text{O}_2\text{N}_2\text{NaSi}$ ($[\text{M}+\text{Na}]^+$) 395.2125, found 395.2124;

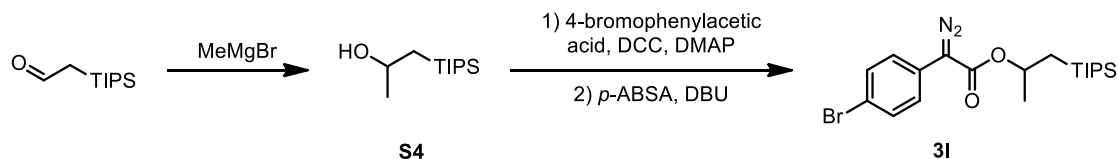


(3E,5E)-2-(triisopropylsilyl)ethyl 2-diazo-6-phenylhexa-3,5-dienoate (3k): To a flame-dried, 500 mL round-bottomed flask was added (carboxymethyl)triphenylphosphonium chloride⁹ (26.7 g, 72 mmol, 1.2 equiv.). The flask was evacuated under high vacuum and back-filled with argon (2x). Then cinnamaldehyde (7.5 mL, 60 mmol, 1.0 equiv.) and THF (130 mL) were added. The mixture was stirred vigorously and cooled to 0 °C. A solution of KO*t*-Bu (16.8 g, 150 mmol, 2.5 equiv.) in THF (80 mL) was added dropwise over a period of 30 minutes *via* cannula. The mixture was allowed to stir for 2 hours, over which time it warmed to room temperature. The solution was quenched by the addition of saturated aqueous NH₄Cl (150 mL) and H₂O (50 mL). Each of the two layers had become homogenous. The aqueous layer was removed and the organic layer extracted with 0.5 M NaOH (100 mL x 2). The aqueous layer was acidified to pH = 1.0 with concentrated HCl and extracted with Et₂O (200 mL). The ethereal layer was dried over MgSO₄ and concentrated. This gave the crude, impure acid as a sticky reddish oil. A portion of this crude product was used without further purification. The procedure above for the synthesis of **3e** was then followed, using a portion of the crude acid (1.2 g, ~ 6.2 mmol, 1.0 equiv.), **S1d** (1.5 g, 7.4 mmol, 1.2 equiv.), DCC (1.4 g, 6.8 mmol, 1.1 equiv.) and DMAP (76 mg, 0.62 mmol, 0.1 equiv.) to give the ester (860 mg). *Step 2:* From the ester (860 mg, 2.3 mmol, 1.0 equiv.), *p*-ABSA (840 mg, 3.5 mmol, 1.5 equiv.) and DBU (0.69 mL, 4.6 mmol, 2.0 equiv.), the reaction mixture was stirred for 3 hours before it was quenched. The crude was purified by column chroma-

tography (2% Et₂O in pentane) to give the diazo as a thick red oil (360 mg, 14% yield over last two steps). ¹H NMR (400 MHz; CDCl₃) δ 7.39 (d, 2H, *J* = 7.6 Hz), 7.32 (dd, 2H, *J* = 7.6, 7.1 Hz), 7.22 (t, 1H, *J* = 7.1 Hz), 6.89 (dd, 1H, *J* = 15.5, 8.8 Hz), 6.47 (d, 1H, *J* = 15.6 Hz), 6.17-6.02 (m, 2H), 4.43-4.36 (m, 2H), 1.19-1.13 (m, 2H), 1.12-1.04 (m, 21H); ¹³C NMR (100 MHz, CDCl₃) δ 165.4, 137.5, 130.4, 128.8, 128.6, 127.5, 126.4, 124.0, 114.9, 64.1, 18.9, 11.3, 11.1 (the resonance resulting from the diazo carbon was not detected); IR (film): 2941, 2890, 2865, 2072, 1698 cm⁻¹; HRMS (NSI) calcd for C₂₃H₃₄O₂N₂NaSi ([M+Na]⁺) 421.2282, found 421.2291;

Preparation of Diazo **3l**

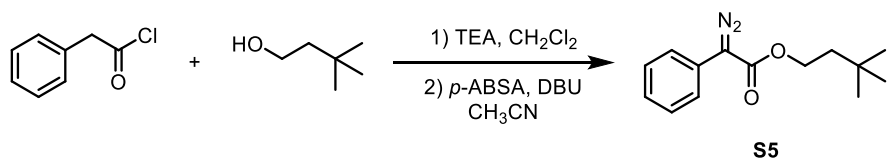
Diazo **3l** was prepared as shown below:



1-(triisopropylsilyl)propan-2-ol (S4): To a solution of 2-triisopropylacetaldehyde (see preparation of **S1d** above) (2.0 g, 10.0 mmol, 1.0 equiv.) in Et₂O (20 mL) at -78 °C was added methylmagnesium bromide solution (6.7 mL, 3.0 M in Et₂O, 20 mmol, 2.0 equiv.) dropwise. The mixture was stirred at this temperature for 1 hour and then quenched with H₂O (3 mL) and allowed to warm to room temperature. 1M aqueous HCl (15 mL) was added and the layers separated. The organic layer was washed with H₂O (10 mL) and brine (10 mL). The organic was dried over MgSO₄ and concentrated to give the crude alcohol **S4** as a colorless oil (1.9 g, 86% yield), which was used without further purification.

1-(triisopropylsilyl)propan-2-yl 2-(4-bromophenyl)-2-diazoacetate (3l): Prepared analogously to **3e**. *Step 1:* From 4-bromophenylacetic acid (1.2 g, 5.8 mmol, 1.0 equiv.), alcohol **S4** (1.5 g, 6.9 mmol, 1.2 equiv.), DCC (1.3 g, 6.4 mmol, 1.1 equiv.), and DMAP (71 mg, 0.56 mmol, 0.1 equiv.) to give the ester as a colorless oil (2.0 g). *Step 2:* From the ester (2.0 g, 4.9 mmol, 1.0 equiv.), *p*-ABSA (1.8 g, 7.3 mmol, 1.5 equiv.) and DBU (1.5 mL, 9.8 mmol, 2.0 equiv.). The crude was purified by column chromatography (1% Et₂O in pentane) to give the diazo **3l** as an orange solid (1.7 g, 68% yield over two steps). ¹H NMR (400 MHz; CDCl₃) δ 7.52-7.47 (m, 2H), 7.41-7.36 (m, 2H), 5.41-5.32 (m, 1H), 1.39 (d, 3H, *J* = 6.1 Hz), 1.23 (dd, 1H, *J* = 14.6, 7.0 Hz), 1.11-1.04 (m, 21H), 1.01 (dd, 1H, *J* = 14.6, 7.5 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 164.5, 132.1, 125.6, 125.2, 119.3, 71.6, 24.1, 19.0, 19.0, 18.4, 11.5 (the resonance resulting from the diazo carbon was not detected); IR (neat): 2957, 2938, 2862, 2085, 1691 cm⁻¹; HRMS (NSI) calcd for C₂₀H₃₁O₂N₂BrNaSi ([M+Na]⁺) 461.123, found 461.1241;

Preparation of Diazo **S5**



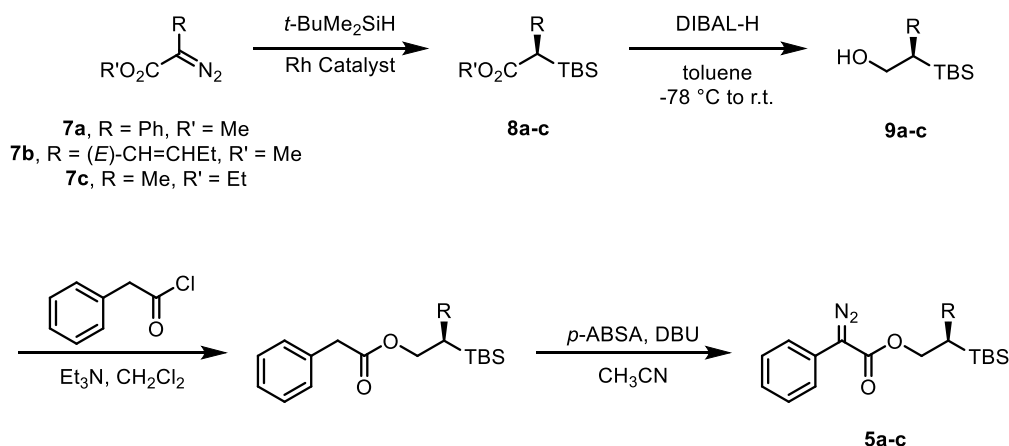
3,3-dimethylbutyl 2-diazo-2-phenylacetate (S5): To a solution of 3,3-dimethyl-1-butanol (1.5 mL, 12 mmol, 1.5 equiv.) and triethylamine (2.3 mL, 16 mmol, 2.0 equiv.) in CH₂Cl₂ (20 mL) at 0 °C was added phenylacetyl chloride (1.1 mL, 8.0 mmol, 1.0 equiv.) dropwise slowly. The mixture was stirred overnight and quenched by washing with 1M HCl and dried over MgSO₄. The crude mixture was concentrated and used immediately in the next step. To a solution of the crude ester and *p*-ABSA (3.8 g, 15.7

mmol, 2.0 equiv.) in acetonitrile (20 mL) at 0 °C was added DBU (3.1 mL, 20.8 mmol, 2.6 equiv.). The mixture was allowed to warm to room temperature overnight, and quenched with saturated aqueous NH₄Cl (25 mL). The mixture was extracted with Et₂O (20 mL). The ethereal layer was washed with brine (25 mL) and dried over MgSO₄, filtered and concentrated. The crude residue was purified by column chromatography (3% Et₂O in pentane) to give the diazo as a red oil (910 mg, 46% yield over 2 steps). ¹H NMR (400 MHz; CDCl₃) δ 7.53-7.48 (m, 2H), 7.43-7.37 (m, 2H), 7.19 (tt, 1H, *J* = 7.7, 1.2 Hz), 4.35 (t, 2H, *J* = 7.3 Hz), 1.65 (t, 2H, *J* = 7.3 Hz), 0.98 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 165.6, 129.1, 125.9, 125.8, 124.1, 62.9, 42.1, 30.0, 29.8; IR (neat): 2956, 2867, 2080, 1700, 1240 cm⁻¹; HRMS (NSI) calcd for C₁₄H₁₈N₂O₂Na ([M+Na]⁺) 269.1261, found 269.1259;

2.2 Synthesis of Chiral Diazos 5a-c

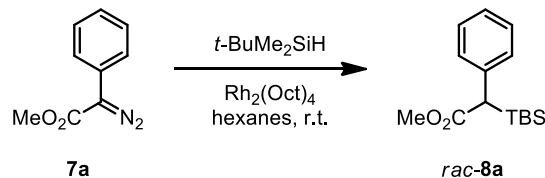
Chiral diazos **5a-c** were synthesized according to the general reaction scheme SI-

4. Diazos **7a**¹⁰, **7b**¹¹, and **7c**¹² were prepared according to known literature procedures.

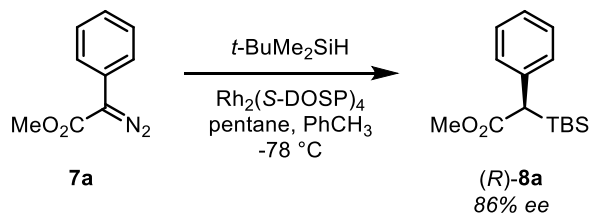


Scheme SI-4

2.2.1 Synthesis of 8a-c

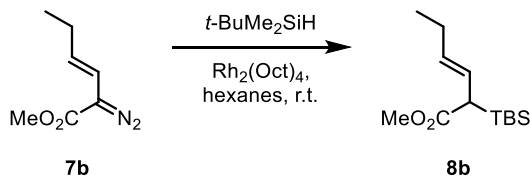


(*R/S*)-methyl 2-(*tert*-butyldimethylsilyl)-2-phenylacetate (*rac*-8a): To a solution of Rh₂(Oct)₄ (219 mg, 0.284 mmol, 1 mol %) and *tert*-butyldimethylsilane (9.4 mL, 56.8 mmol, 2.0 equiv.) in hexanes (40 mL) at room temperature was added a solution of **7a** (5.0 g, 28.4 mmol, 1.0 equiv.) dropwise over 2 hours. The mixture was allowed to stir at room temperature overnight. The solvent was removed by rotary evaporation and the crude residue purified by column chromatography (3% Et₂O in pentane). The product was isolated as a pale yellow oil (6.7 g, 89 % yield). See (*R*)-**8a** below for characterization data.

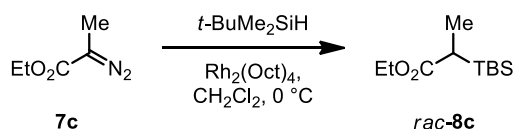


(*R*)-methyl 2-(*tert*-butyldimethylsilyl)-2-phenylacetate ((*R*)-8a): *tert*-butyldimethylsilane (15.1 mL, 90.9 mmol, 4.0 equiv.), and Rh₂(*S*-DOSP)₄ (1.3 g, 0.68 mmol, 3 mol %) were dissolved in a mixture of pentane (135 mL) and toluene (11mL). The green solution was cooled to -78 °C in an acetone/dry ice bath. Diazo **7a** (4.0 g, 22.7 mmol, 1.0 equiv.) was dissolved in 75 mL pentane. The orange solution was then added dropwise to the reaction mixture over 2 hours. The mixture was stirred an additional 2 hours before it was allowed to warm to room temperature. The solvent was removed by

rotary evaporation and the crude residue purified by column chromatography (3% Et₂O in pentane). The product was isolated as a colorless oil (5.3 g, 88% yield, 86% ee). [α]_D²⁰: 15.9 (c. 1.8, CHCl₃); ¹H NMR (400 MHz; CDCl₃) δ 7.36 (d, 2H, J = 7.5 Hz), 7.26 (dd, 2H, J = 7.5, 7.3 Hz), 7.16 (t, 1H, J = 7.3 Hz), 3.65 (s, 3H), 3.55 (s, 1H), 0.86 (s, 9H), 0.11 (s, 3H), -0.12 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 174.0, 137.2, 128.9, 128.3, 125.9, 51.6, 43.1, 26.8, 18.0, -6.3, -6.8; IR (neat): 2951, 2930, 2884, 2858, 1720 cm⁻¹; HRMS (NSI) calcd for C₁₅H₂₅O₂Si ([M+H]⁺) 265.1618, found 265.1624; The ee was determined by chiral HPLC: OD column, 1 mL/min, 0.5 % iPrOH in hexanes. Major: 4.2 min, Minor: 9.9 min, 86 % ee

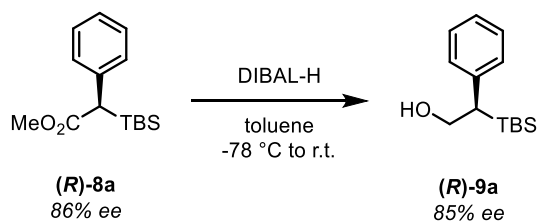


methyl (E)-2-(*tert*-butyldimethylsilyl)hex-3-enoate (8b): The diazo **7b** (2.9 g, 18.8 mmol, 1.0 equiv.), in pentane (45 mL), was added dropwise over 1 hour to a solution of Rh₂(Oct)₄ (145 mg, 0.188 mmol, 1 mol%) and *t*-BuMe₂SiH (9.3 mL, 56.4 mmol, 3.0 equiv.) in 45 mL pentane. The mixture was stirred for 15 minutes and concentrated. The crude mixture was purified by column chromatography (3% Et₂O in pentane). The product **8b** was isolated as a colorless oil (3.5 g, 76% yield). ¹H NMR (400 MHz; CDCl₃) δ 5.61 (ddt, 1H, J = 15.3, 10.4, 1.4 Hz), 5.36 (dt, 1H, J = 15.3, 6.4 Hz), 3.63 (s, 3H), 2.96 (d, 1H, J = 10.4 Hz), 2.07-1.98 (m, 2H), 0.96 (t, 3H, J = 7.5 Hz), 0.91 (s, 9H), 0.03 (s, 3H), 0.01 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 174.5, 132.1, 124.3, 51.3, 41.0, 26.9, 25.9, 18.1, 14.0, -6.5, -6.7; IR (neat): 2958, 2930, 2858, 1721, 1131 cm⁻¹; HRMS (NSI) calcd for C₁₃H₂₇O₂Si ([M+H]⁺) 243.1775, found 243.1776;



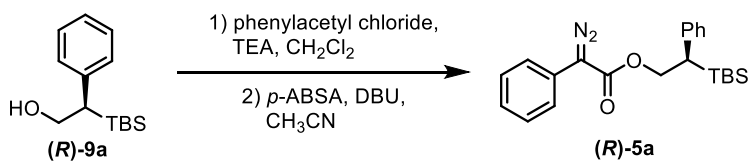
ethyl 2-(tert-butyldimethylsilyl)propanoate (*rac*-8c): *tert*-butyldimethylsilane (19.4 mL, 117 mmol, 3.0 equiv.) and $\text{Rh}_2(\text{Oct})_4$ (300 mg, 0.39 mmol, 1 mol %) were dissolved in CH_2Cl_2 (100 mL). The mixture was cooled to 0 °C. The diazo **7c** (5.0 g, 39 mmol, 1.0 equiv.), as a solution in CH_2Cl_2 (100 mL) was added to the reaction mixture dropwise over 3 hours. The reaction mixture was stirred at room temperature overnight (16 hours). The solvent was removed and the crude residue purified by column chromatography (5% Et_2O in pentane). The product was isolated as a slightly green-tinged oil (7.9 g, 94% yield). ^1H NMR (400 MHz; CDCl_3) δ 4.15-4.01 (m, 2H), 2.14 (q, 1H, $J = 7.2$ Hz), 1.28-1.20 (m, 6H), 0.92 (s, 9H), 0.05 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 177.1, 59.9, 27.6, 26.9, 17.8, 14.5, 12.7, -6.7, -6.8; IR (neat): 2957, 2931, 2883, 2859, 1717 cm^{-1} ; HRMS (APCI-methanol) calcd for $\text{C}_{11}\text{H}_{25}\text{O}_2\text{Si}$ ($[\text{M}+\text{H}]^+$) 217.1618, found 217.1619;

2.2.2 Synthesis of Diazos 9a-c



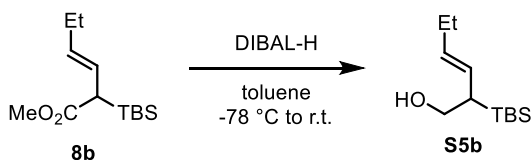
(*R*)-2-(tert-butyldimethylsilyl)-2-phenylethanol (*R*-S5a): To a solution of (*R*)-**8a** (4.0 g, 15.1 mmol, 1.0 equiv.) in toluene at -78 °C was added diisobutylaluminum hydride (DIBAL-H) (38 mL, 1.0 M in toluene, 37.8 mmol, 2.5 equiv.) dropwise slowly. The mixture was stirred at this temperature for 30 minutes, allowed to warm to room tempera-

ture, and stirred for 2 hours. The mixture was carefully quenched with MeOH (5 mL), and stirred until the bubbling ceased. A concentrated aqueous solution of Rochelle salt (25 mL) was added followed by H₂O (25 mL) and toluene (25 mL). The biphasic mixture was stirred vigorously overnight. The aqueous phase was drained and the organic phase dried over MgSO₄ and concentrated. The crude was passed through a short plug of silica, eluting with 3:1 hexanes:EtOAc. The product was isolated as a colorless oil (3.2 g, 89% yield.). $[\alpha]_D^{20}$: 5.4 (c. 1.2, CHCl₃); ¹H NMR (400 MHz; CDCl₃) δ 7.30-7.23 (m, 2H), 7.17-7.09 (m, 3H), 4.08 (ddd, 1H, J = 11.7, 11.2, 3.2 Hz), 3.99 (ddd, 1H, J = 11.2, 9.0, 4.3 Hz), 2.58 (dd, 1H, J = 11.7, 4.3 Hz), 1.39 (dd, 1H, J = 9.0, 3.2 Hz), 0.82 (s, 9H), 0.02 (s, 3H), -0.22 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 141.2, 128.9, 128.6, 125.6, 64.3, 39.1, 27.1, 17.6, -6.1, -6.8; IR (film): 3379, 2954, 2927, 2882, 2856 cm⁻¹; HRMS (NSI) calcd for C₁₄H₂₄ONaSi ([M+Na]⁺) 259.1489, found 259.1490; The ee was determined by chiral HPLC: ADH column, 1 mL/min, 1 % iPrOH in hexanes. Major: 11.5 min, Minor: 13 min, 85 % ee.



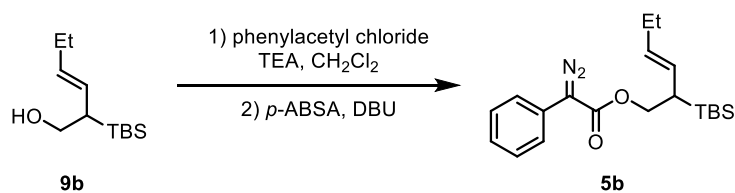
(R)-2-(tert-butyldimethylsilyl)-2-phenylethyl 2-diazo-2-phenylacetate (R-5a): To a solution of alcohol **(R)-9a** (3.2 g, 13.5 mmol, 1.05 equiv.) and triethylamine (3.6 mL, 25.7 mmol, 2.0 equiv.) in CH₂Cl₂ (40 mL) at 0 °C was added phenylacetyl chloride (1.7 mL, 12.9 mmol, 1.0 equiv.) dropwise. The mixture was stirred 4 hours and quenched with saturated NH₄Cl (50 mL). The organic phase was washed with aqueous 1M HCl (30 mL) and saturated aqueous NaHCO₃ (30 mL), dried over MgSO₄ and concentrated. The

crude residue was purified by column chromatography (9:1 hexanes:EtOAc) to give the ester (2.7 g). This ester was immediately dissolved in acetonitrile (35 mL), along with *p*-ABSA (2.7 g, 11.4 mmol, 1.5 equiv.) and cooled to 0 °C. Then DBU (2.3 mL, 15.2 mmol, 2.0 equiv.) was added dropwise. The mixture was allowed to warm to room temperature over a few hours and stirred a total of 36 hours. The mixture was quenched by addition of NH₄Cl (40 mL). The aqueous phase was extracted with Et₂O (30 mL). The ethereal layer was dried over MgSO₄ and concentrated. The crude material was purified by column chromatography (3% Et₂O in pentane) to give the diazo as an orange oil (1.9 g, 39% yield over two steps). $[\alpha]_D^{20}$: 4.2 (c. 1.4, CHCl₃); ¹H NMR (400 MHz; CDCl₃) δ 7.30-7.22 (m, 6H), 7.17-7.08 (m, 4H), 4.78 (dd, 1H, *J* = 11.2, 4.2 Hz), 4.65 (dd, 1H, *J* = 12.2, 11.2 Hz), 2.76 (dd, 1H, *J* = 12.2, 4.2 Hz), 0.88 (s, 9H), 0.11 (s, 3H), -0.15 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 165.8, 141.4, 129.0, 128.6, 128.2, 125.8, 125.7, 125.4, 124.1, 67.2, 35.0, 27.1, 17.6, -6.1, -6.8 (the resonance resulting from the diazo carbon was not detected); IR (film): 2954, 2928, 2882, 2856, 2083, 1698 cm⁻¹; HRMS (NSI) calcd for C₂₂H₂₈O₂N₂NaSi ([M+Na]⁺) 403.1812, found 403.1819; The ee was determined by chiral HPLC: OJ column, 1 mL/min, 0.5 % iPrOH in hexanes. Major: 7.6 min, Minor: 11.5 min, 86% ee.



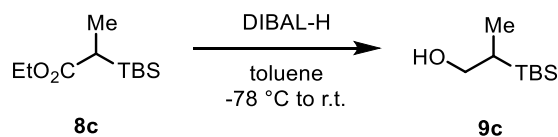
(*E*)-2-(*tert*-butyldimethylsilyl)hex-3-en-1-ol (9b): To a -78 °C solution of the ester **8b** (3.5 g, 14.4 mmol, 1.0 equiv.) in toluene (50 mL) was added a solution of DIBAL-H (36 mL, 1.0 M in toluene, 36.0 mmol, 2.5 equiv.) dropwise. The mixture was stirred for 1.5

hours at this temperature, allowed to warm to room temperature and stirred for 1 hour. The mixture was quenched by careful addition of MeOH (5 mL), and stirred until bubbling had ceased. Then toluene (50 mL) and a saturated aqueous solution of Rochelle salt (50 mL) was added. The mixture was stirred vigorously until both layers had become homogenous, about 30 min. The layers were separated and the organic layer dried over MgSO₄ and concentrated. This gave the crude alcohol as a colorless oil (3.0 g, 97% yield). ¹H NMR (600 MHz; CDCl₃) δ 5.51 (dt, 1H, *J* = 15.2, 6.4 Hz), 5.28 (dd, 1H, *J* = 15.2, 10.1 Hz), 3.74 (ddd, 1H, *J* = 10.7, 9.1, 3.8 Hz), 3.58 (ddd, 1H, *J* = 11.6, 10.7, 2.3 Hz), 2.12-2.03 (m, 2H), 1.98 (ddd, 1H, *J* = 11.6, 10.1, 3.8 Hz), 1.65 (dd, 1H, *J* = 9.1, 2.3 Hz), 0.99 (t, 3H, *J* = 7.5 Hz), 0.90 (s, 9H), -0.04 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 134.5, 127.7, 62.6, 36.3, 27.2, 26.1, 17.6, 14.3, -6.7, -6.8; IR (film): 3366, 2957, 2928, 2856, 1248 cm⁻¹; HRMS (NSI) calcd for C₁₂H₂₇OSi ([M+H]⁺) 215.1826, found 215.1828;



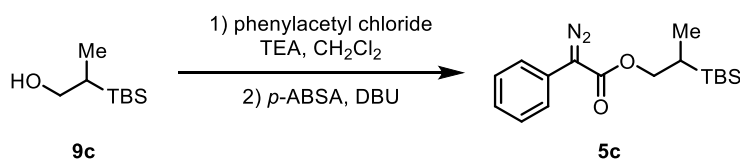
(E)-2-(tert-butyldimethylsilyl)hex-3-en-1-yl 2-diazo-2-phenylacetate (5b): To a solution of the alcohol **9b** (3.0 g, 14.0 mmol) and triethylamine (3.9 mL, 28.0 mmol, 2.0 equiv.) in CH₂Cl₂ (50 mL) at 0 °C was added phenylacetyl chloride (3.0 mL, 22.4 mmol, 1.6 equiv.) dropwise. The mixture was allowed to warm to room temperature overnight and was diluted with CH₂Cl₂ (50 mL). The solution was washed with 1M HCl (50 mL) and 1M NaOH (50 mL). The mixture was dried over MgSO₄ and concentrated to give the crude ester as a yellow oil (4.6 g). This was immediately dissolved in acetonitrile (55 mL) with *p*-ABSA (5.0 g, 20.7 mmol, 1.5 equiv.) and cooled to 0 °C. DBU (4.1 mL, 2.0

equiv.) was added dropwise, and the mixture allowed to warm to room temperature over several hours, and stirred for a total of 72 hours. The reaction was quenched with saturated aqueous NH_4Cl (70 mL) and extracted with Et_2O (75 mL). The ethereal layer was washed with brine (50 mL), dried over MgSO_4 and concentrated. The crude material was purified by column chromatography (2% Et_2O in pentane) to give the diazo as an orange oil (1.6 g, 31% yield over two steps). ^1H NMR (400 MHz; CDCl_3) δ 7.49 (d, 2H, $J = 7.5$ Hz), 7.38 (dd, 2H, $J = 7.5, 7.4$ Hz), 7.18 (t, 1H, $J = 7.4$ Hz), 5.46-5.28 (m, 2H), 4.53 (dd, 1H, $J = 10.9, 3.9$ Hz), 4.31 (dd, 1H, $J = 11.6, 10.6$ Hz), 2.19 (ddd, 1H, $J = 11.6, 9.2, 3.9$ Hz), 2.09-1.99 (m, 2H), 1.01-0.93 (m, 12H), 0.03 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.7, 132.5, 129.1, 127.6, 126.0, 125.8, 124.1, 66.4, 32.6, 27.3, 26.1, 17.7, 14.3, -6.5, -6.7 (the resonance resulting from the diazo carbon was not detected); IR (neat): 2957, 2929, 2856, 2081, 1699 cm^{-1} ; HRMS (NSI) calcd for $\text{C}_{20}\text{H}_{31}\text{O}_2\text{Si}$ ($[\text{M}+\text{H}-\text{N}_2]^+$) 331.2088, found 331.2086;



2-(*tert*-butyldimethylsilyl)propan-1-ol (9c): To a solution of the ester **8c** (3.0 g, 13.9 mmol, 1.0 equiv.) in CH_2Cl_2 (20 mL) at -78 $^\circ\text{C}$ was added a solution of DIBAL-H (35 mL, 1.0 M in CH_2Cl_2 35 mmol, 2.5 equiv.) dropwise. The mixture was stirred for 2 hours, warmed to room temperature, and stirred for 1 hour. The mixture was quenched by careful addition of MeOH (5 mL), and stirred until bubbling ceased. An aqueous solution of Rochelle salt (25 mL) was added followed by CH_2Cl_2 (20 mL). The mixture was stirred vigorously for 1 hour. The layers were separated and the organic layer dried over MgSO_4

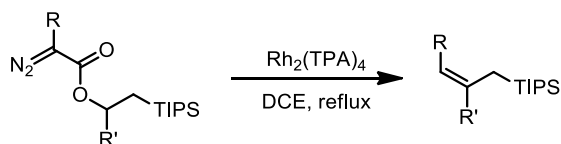
and concentrated. This gave the product as a colorless oil (2.2 g, 92% yield). ^1H NMR (400 MHz; CDCl_3) δ 3.89-3.82 (m, 1H), 3.55-3.47 (m, 1H), 1.50-1.43 (m, 1H), 1.17-1.05 (m, 4H), 0.91 (s, 9H), -0.04 (s, 3H), -0.05 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 66.5, 27.4, 22.6, 17.4, 13.1, -6.8, -6.9; IR (neat): 3322, 2954, 2928, 2857 cm^{-1} ; HRMS (APCI) calcd for $\text{C}_9\text{H}_{21}\text{Si}$ ($[\text{M}+\text{H}-\text{H}_2\text{O}]^+$) 157.1413, found 157.1408;



2-(tert-butyldimethylsilyl)propyl 2-diazo-2-phenylacetate (5c): To a solution of the alcohol **S5c** (1.5 g, 8.6 mmol, 1.2 equiv.) and triethylamine (2.0 mL, 14.4 mmol, 2.0 equiv.) in CH_2Cl_2 (30 mL) at 0 °C was added phenylacetyl chloride (0.95 mL, 7.2 mmol, 1.0 equiv.) dropwise. The mixture was allowed to warm to room temperature overnight and quenched by washing with saturated aqueous NaHCO_3 (30 mL), and 1M HCl (30 mL). The mixture was dried over MgSO_4 and concentrated. The crude mixture was purified by column chromatography (5% Et_2O in pentane) to give the ester as a colorless oil (1.5 g). This was immediately dissolved in acetonitrile (15 mL) with *p*-ABSA (1.9 g, 7.8 mmol, 1.5 equiv.) and cooled to 0 °C. DBU (1.6 mL, 10.4 mmol, 2.0 equiv.) was added dropwise, and the mixture allowed to warm to room temperature over several hours, and stirred for a total of 48 hours. The reaction was quenched with saturated aqueous NH_4Cl (20 mL) and extracted with Et_2O (25 mL). The ethereal layer was washed with brine (20 mL), dried over MgSO_4 and concentrated. The crude material was purified by column chromatography (5% Et_2O in pentane) to give the diazo as an orange oil (1.2 g, 52% yield over two steps). ^1H NMR (400 MHz; CDCl_3) δ 7.51 (d, 2H, $J = 8.6$ Hz), 7.39 (dd, 2H, $J =$

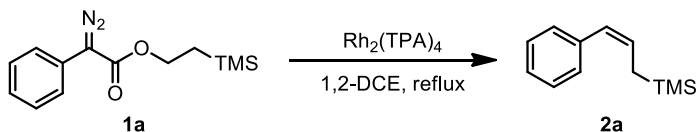
8.6, 7.4 Hz), 7.19 (t, 1H, $J = 7.4$ Hz), 4.56 (dd, 1H, $J = 10.8, 3.7$ Hz), 4.15 (app t, 1H, $J = 10.8$ Hz), 1.43-1.32 (m, 1H), 1.11 (d, 3H, $J = 7.3$ Hz), 0.95 (s, 9H), 0.00 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.7, 129.1, 125.9, 125.9, 124.2, 69.4, 27.3, 19.1, 17.4, 13.6, -6.8, -7.0; IR (film): 2953, 2928, 2856, 2080, 1699 cm^{-1} ; HRMS (NSI) calcd for $\text{C}_{17}\text{H}_{26}\text{O}_2\text{N}_2\text{NaSi}$ ($[\text{M}+\text{Na}]^+$) 341.1656, found 341.1660;

2.3 General Procedure for Allyl Silane Reaction

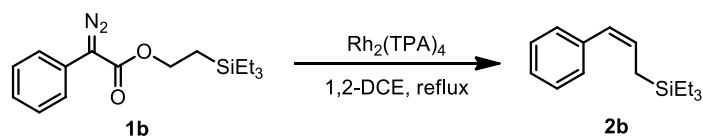


A solution of the diazo (0.3 – 0.5 mmol) in 4 mL 1,2-dichloroethane (DCE) was added dropwise over 2 hours to a solution of $\text{Rh}_2(\text{TPA})_4$ (1 mol %) in DCE (2 mL) at reflux. The mixture was stirred at reflux for an additional 30 minutes, cooled to room temperature and concentrated. The crude was purified by chromatography.

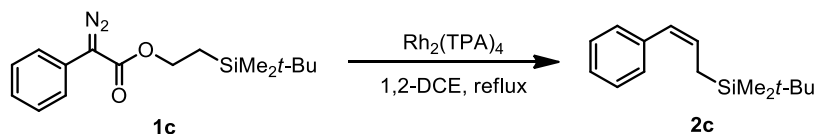
2.4 Experimental Data for Allyl Silanes



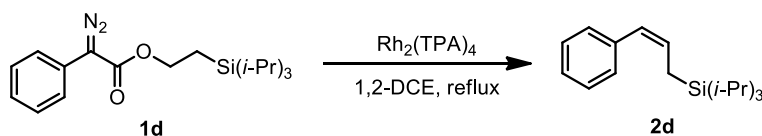
(Z)-trimethyl(3-phenylallyl)silane (2a): The general procedure for allyl silane formation was followed, with **1a** (131 mg, 0.5 mmol, 1.0 equiv.) and $\text{Rh}_2(\text{TPA})_4$ (7 mg, 0.005 mmol, 1 mol %), purifying by column chromatography (pentane) to give **2a** as a colorless oil (72 mg, 76% yield) as a 89:11 mixture of *Z*:*E* isomers. Both the Z^{13} and E^{14} isomers of this compound are known in the literature.



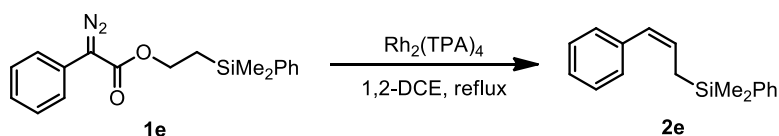
(Z)-triethyl(3-phenylallyl)silane (2b): The general procedure for allyl silane formation was followed, with **1b** (152 mg, 0.5 mmol, 1.0 equiv.) and $\text{Rh}_2(\text{TPA})_4$ (7 mg, 0.005 mmol, 1 mol %), purifying by column chromatography (pentane) to give **2b** as a colorless oil (86 mg, 76% yield) as a 91:9 mixture of *Z:E* isomers. ^1H NMR (400 MHz; CDCl_3) δ 7.37-7.31 (m, 4H), 7.25-7.18 (m, 1H), 6.34 (dt, 1H, $J = 11.6, 1.6$ Hz), 5.76 (dt, 1H, $J = 11.6, 9.1$ Hz), 1.89 (dd, 2H, $J = 9.1, 1.6$ Hz), 0.94 (t, 9H, $J = 7.9$ Hz), 0.58 (q, 6H, $J = 7.9$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 138.4, 129.4, 128.8, 128.3, 126.9, 126.2, 14.8, 7.5, 3.6; IR (neat): 2951, 2909, 2874, 1446 cm^{-1} ; HRMS (APCI) calcd for $\text{C}_{15}\text{H}_{25}\text{Si}$ ($[\text{M}+\text{H}]^+$) 233.1720, found 233.1718;



(Z)-tert-butyltrimethyl(3-phenylallyl)silane (2c): The general procedure for allyl silane formation was followed, with **1c** (152 mg, 0.5 mmol, 1.0 equiv.) and $\text{Rh}_2(\text{TPA})_4$ (7 mg, 0.005 mmol, 1 mol %), purifying by column chromatography (pentane) to give **2c** as a colorless oil (92 mg, 79% yield) as a 95:5 mixture of *Z:E* isomers. ^1H NMR (400 MHz; CDCl_3) δ 7.37-7.29 (m, 4H), 7.23-7.18 (m, 1H), 6.34 (d, 1H, $J = 11.6$ Hz), 5.75 (dt, 1H, $J = 11.6, 9.1$ Hz), 1.88 (dd, 2H, $J = 9.1, 1.4$ Hz), 0.90 (s, 9H), 0.00 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.4, 129.6, 128.8, 128.3, 127.0, 126.2, 26.7, 17.1, 15.7, -6.0; IR (neat): 2952, 2927, 2882, 2855, 1248 cm^{-1} ; HRMS (APCI) calcd for $\text{C}_{15}\text{H}_{25}\text{Si}$ ($[\text{M}+\text{H}]^+$) 233.1720, found 233.1722;

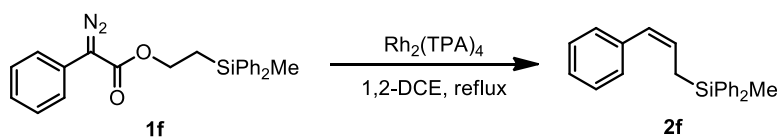


(Z)-triisopropyl(3-phenylallyl)silane (2d): The general procedure for allyl silane formation was followed, with **1d** (173 mg, 0.5 mmol, 1.0 equiv.) and $\text{Rh}_2(\text{TPA})_4$ (7 mg, 0.005 mmol, 1 mol %), purifying by column chromatography (pentane) to give **2d** as a colorless oil (112 mg, 82% yield). ^1H NMR (400 MHz; CDCl_3) δ 7.35-7.27 (m, 4H), 7.22-7.15 (m, 1H), 6.29 (dt, 1H, $J = 11.6, 1.8$ Hz), 5.81 (dt, 1H, $J = 11.6, 8.8$ Hz), 1.92 (dd, 2H, $J = 8.8, 1.8$ Hz), 1.11-0.97 (m, 21H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.4, 130.0, 128.9, 128.3, 127.0, 126.2, 18.9, 12.1, 11.3; IR (neat): 2940, 2889, 2864, 1462, 881 cm^{-1} ; HRMS (APCI) calcd for $\text{C}_{18}\text{H}_{31}\text{Si}$ ($[\text{M}+\text{H}]^+$) 275.2190, found 275.2186;

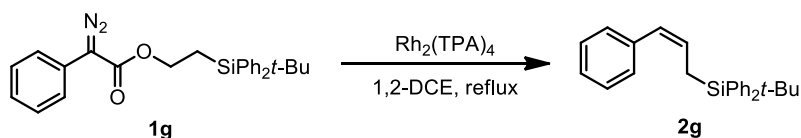


(Z)-dimethyl(phenyl)(3-phenylallyl)silane (2e): The general procedure for allyl silane formation was followed, with **1e** (162 mg, 0.5 mmol, 1.0 equiv.) and $\text{Rh}_2(\text{TPA})_4$ (7 mg, 0.005 mmol, 1 mol %), purifying by column chromatography (0.1% Et_2O in pentane) to give **2e** as a colorless oil (101 mg, 80% yield) as a 84:16 mixture of *Z*:*E* isomers. The *E* isomer has been characterized previously.¹⁴ Characterization data for *Z* isomer: ^1H NMR (400 MHz; CDCl_3) (Note: Aryl hydrogens appeared as groups of multiplets, and the signals resulting from the minor *E* isomer could not be distinguished from those of the *Z*. The other peaks could be easily distinguished by comparison to published spectra for the *E* isomer¹⁴) δ 7.57-7.52 (m, 2H), 7.42-7.28 (m, 5H), 7.27-7.17 (m, 3H), 6.38 (d, 1H, $J = 11.6$ Hz), 5.73 (dt, 1H, $J = 11.6, 9.0$ Hz), 2.10 (dd, 2H, $J = 9.0, 1.3$ Hz), 0.34 (s, 6H); ^{13}C

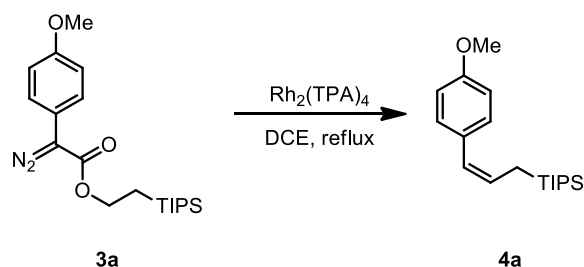
NMR (100 MHz, CDCl₃) (The peaks for the *Z* isomer could be distinguished from those for the *E* by comparison to the published spectrum for the *E* isomer¹⁴) δ 138.7, 138.2, 133.8, 129.3, 128.8, 128.5, 128.3, 128.0, 127.7, 126.3, 18.9, -2.9; IR (neat): 3068, 3008, 2955, 1248, 1112 cm⁻¹; HRMS (NSI) calcd for C₁₇H₂₁Si ([M+H]⁺) 253.1407, found 253.1411;



(Z)-methyldiphenyl(3-phenylallyl)silane (2f): The general procedure for allyl silane formation was followed, with **1f** (139 mg, 0.36 mmol, 1.0 equiv.) and Rh₂(TPA)₄ (5 mg, 0.0036 mmol, 1 mol %), purifying by column chromatography (1% Et₂O in pentane) to give **2f** as a colorless oil (79 mg, 70% yield) as a 89:11 mixture of *Z*:*E* isomers. The compound was characterized as the mixture of isomers. NMR peaks for the major and minor isomers were assigned as closely as possible: ¹H NMR (400 MHz; CDCl₃) δ 7.60-7.51 (m, 4H, major and minor), 7.45-7.15 (m, 11H, major and minor), 6.40 (d, 1H, *J* = 11.6 Hz, major), 6.34 (m, 2H, minor), 5.76 (dt, 1H, *J* = 11.6, 8.8 Hz, major), 2.40 (dd, 2H, *J* = 8.8, 1.6 Hz, major), 2.26 (d, 2H, *J* = 7.1 Hz, minor), 0.62 (s, 3H, minor), 0.60 (s, 3H, major); ¹³C NMR (100 MHz, CDCl₃) δ 138.1 (major), 136.6 (minor), 134.8 (major), 129.9 (minor), 129.7 (major), 128.9 (major), 128.7 (minor), 128.5 (major), 128.4 (major), 128.2 (major), 127.9 (major, 2 signals), 126.8 (minor), 126.6 (minor), 126.5 (major, 2 signals), 125.9 (minor), 21.8 (minor), -4.2 (major), -4.3 (minor); IR (neat): 3067, 3009, 1427, 1110, 694 cm⁻¹; HRMS (NSI) calcd for C₂₂H₂₂NaSi ([M+Na]⁺) 337.1383, found 337.1386;

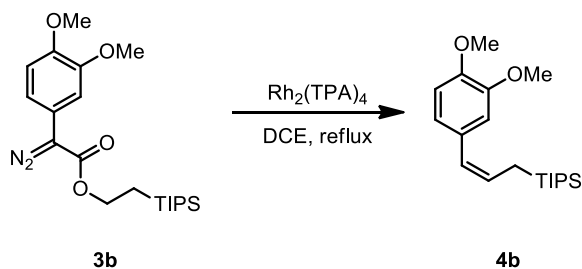


(Z)-tert-butyldiphenyl(3-phenylallyl)silane (2g): The general procedure for allyl silane formation was followed, with **1g** (154 mg, 0.36 mmol, 1.0 equiv.) and $\text{Rh}_2(\text{TPA})_4$ (5 mg, 0.0036 mmol, 1 mol %), purifying by column chromatography (1% Et_2O in pentane) to give **2g** as a colorless oil (87 mg, 68% yield) as a 95:5 mixture of *Z:E* isomers. ^1H NMR (400 MHz; CDCl_3) δ 7.62-7.57 (m, 4H), 7.44-7.29 (m, 8H), 7.26-7.17 (m, 3H), 6.32 (d, 1H, $J = 11.5$ Hz), 5.73 (dt, 1H, $J = 11.5, 8.4$ Hz), 2.47 (dd, 2H, $J = 8.4, 1.5$ Hz), 1.05 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.1, 136.2, 134.3, 129.3 (2 signals), 128.8, 128.4, 128.3, 127.8, 126.4, 28.0, 18.6, 13.3; IR (neat): 3012, 2928, 2856, 1426, 696 cm^{-1} ; HRMS (APCI) calcd for $\text{C}_{25}\text{H}_{29}\text{Si}$ ($[\text{M}+\text{H}]^+$) 357.2033, found 357.2029;

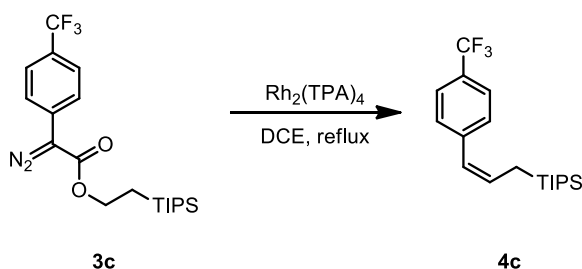


(Z)-triisopropyl(3-(4-methoxyphenyl)allyl)silane (4a): The general procedure for allyl silane formation was followed, with **3a** (132 mg, 0.35 mmol, 1.0 equiv.) and $\text{Rh}_2(\text{TPA})_4$ (5 mg, 1 mol %), purifying by column chromatography (1% Et_2O in pentane) to give **4a** as a colorless oil (81 mg, 76% yield). ^1H NMR (600 MHz; CDCl_3) δ 7.29 (d, 2H, $J = 8.6$ Hz), 6.92-6.86 (m, 2H), 6.25 (d, 1H, $J = 11.5$ Hz), 5.74 (dt, 1H, $J = 11.5, 8.7$ Hz), 3.83 (s, 3H), 1.91 (dd, 2H, $J = 8.7, 1.8$ Hz), 1.12-1.00 (m, 21H); ^{13}C NMR (150 MHz, CDCl_3) δ 157.95, 131.08, 129.98, 128.46, 126.57, 113.73, 55.4, 18.88, 11.9, 11.36; IR (neat): 2940,

2889, 2864, 1509, 1242 cm^{-1} ; HRMS (APCI) calcd for $\text{C}_{19}\text{H}_{33}\text{OSi}$ ($[\text{M}]^+$) 304.2217, found 304.2215;

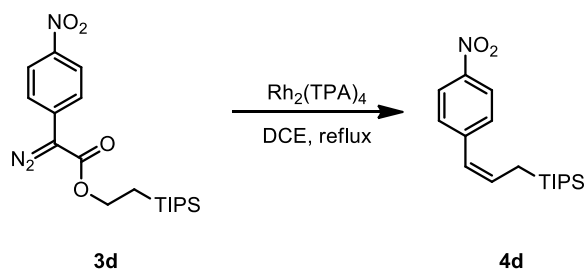


(Z)-3-(3,4-dimethoxyphenyl)allyl triisopropylsilane (4b): The general procedure for allyl silane formation was followed, with **3b** (122 mg, 0.3 mmol, 1.0 equiv.) and $\text{Rh}_2(\text{TPA})_4$ (4 mg, 0.0035 mmol, 1 mol %), purifying by column chromatography (5% Et_2O in pentane) to give **4b** as a colorless oil (77 mg, 77% yield). ^1H NMR (400 MHz; CDCl_3) δ 6.95-6.81 (m, 3H), 6.23 (d, 1H, $J = 11.5$ Hz), 5.74 (dt, 1H, $J = 11.5, 8.7$ Hz), 3.90 (s, 3H), 3.88 (s, 3H), 1.92 (dd, 2H, $J = 8.7, 1.7$ Hz), 1.13-0.98 (m, 21H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.6, 147.4, 131.4, 128.8, 126.7, 121.3, 112.1, 111.0, 56.0, 56.0, 18.9, 12.0, 11.3; IR (neat): 2939, 2864, 1512, 1235 cm^{-1} ; HRMS (APCI) calcd for $\text{C}_{20}\text{H}_{35}\text{O}_2\text{Si}$ ($[\text{M}+\text{H}]^+$) 335.2401, found 335.2404;

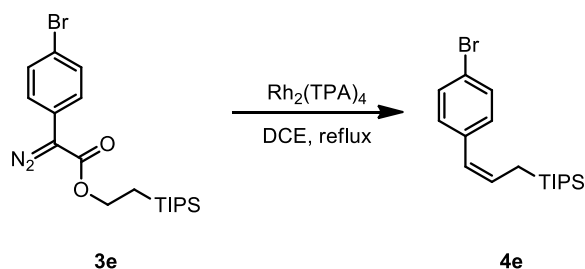


(Z)-3-(4-(trifluoromethyl)phenyl)allyl triisopropylsilane (4c): The general procedure for allyl silane formation was followed, with **3c** (145 mg, 0.35 mmol, 1.0 equiv.) and

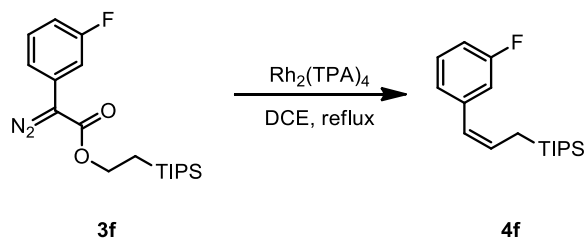
Rh₂(TPA)₄ (5 mg, 0.0035 mmol, 1 mol %), purifying by column chromatography (pentane) to give **4c** as a colorless oil (88 mg, 73% yield). ¹H NMR (400 MHz; CDCl₃) δ 7.59 (d, 2H, *J* = 8.2 Hz), 7.43 (d, 2H, *J* = 8.2 Hz), 6.31 (d, 1H, *J* = 11.7 Hz), 5.94 (dt, 1H, *J* = 11.7, 8.9 Hz), 1.92 (dd, 2H, *J* = 8.9, 1.8 Hz), 1.13-0.98 (m, 21H); ¹³C NMR (100 MHz, CDCl₃) δ 142.1, 132.4, 129.1, 128.2 (q, *J* = 32 Hz), 125.8, 125.3 (q, *J* = 3.7 Hz), 124.6 (q, *J* = 272 Hz), 18.8, 12.5, 11.4; IR (film): 2942, 2866, 1323, 1123 cm⁻¹; HRMS (APCI) calcd for C₁₉H₂₉F₂Si ([M+H-HF]⁺) 323.2001, found 323.2002;



(Z)-triisopropyl(3-(4-nitrophenyl)allyl)silane (4d): The general procedure for allyl silane formation was followed, with **3d** (150 mg, 0.38 mmol, 1.0 equiv.) and Rh₂(TPA)₄ (5 mg, 0.004 mmol, 1 mol %), purifying by column chromatography (1% Et₂O in pentane) to give the allylsilane **4d** as a colorless oil (72 mg, 60% yield). ¹H NMR (600 MHz; CDCl₃) δ 8.20 (d, 2H, *J* = 8.7 Hz), 7.47 (d, 2H, *J* = 8.7 Hz), 6.32 (d, 1H, *J* = 11.6 Hz), 6.03 (dt, 1H, *J* = 11.6, 9.0 Hz), 1.95 (dd, 2H, *J* = 9.0, 1.8 Hz), 1.12-0.96 (m, 21H); ¹³C NMR (100 MHz, CDCl₃) δ 146.0, 145.5, 134.5, 129.4, 125.0, 123.8, 18.8, 13.0, 11.3; IR (neat): 2941, 2889, 2864, 1514, 1338 cm⁻¹; HRMS (APCI) calcd for C₁₈H₃₀O₂NSi ([M+H]⁺) 320.2040, found 320.2044;

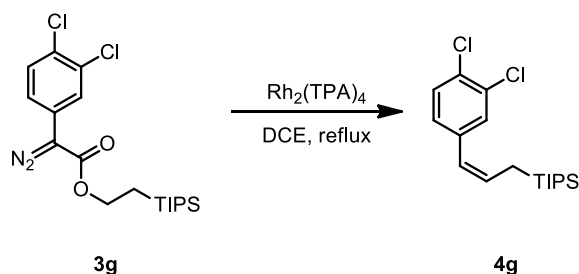


(Z)-(3-(4-bromophenyl)allyl)triisopropylsilane (4e): The general procedure for allyl silane formation was followed, with **3e** (149 mg, 0.35 mmol, 1.0 equiv.) and $\text{Rh}_2(\text{TPA})_4$ (5 mg, 0.0035 mmol, 1 mol %), purifying by column chromatography (pentane) to give **4e** as a colorless oil (91 mg, 73% yield) ^1H NMR (400 MHz; CDCl_3) δ 7.46-7.40 (m, 2H), 7.21-7.15 (m, 2H), 6.19 (dt, 1H, $J = 11.6, 1.9$ Hz), 5.83 (dt, 1H, $J = 11.6, 8.8$ Hz), 1.86 (dd, 2H, $J = 8.8, 1.8$ Hz), 1.13-0.93 (m, 21H); ^{13}C NMR (100 MHz, CDCl_3) δ 137.3, 131.5, 130.9, 130.5, 125.9, 119.9, 18.8, 12.2, 11.3; IR (film): 2940, 2889, 2864, 1486 cm^{-1} ; HRMS (APCI) calcd for $\text{C}_{18}\text{H}_{30}\text{BrSi}$ ($[\text{M}+\text{H}]^+$) 353.1295, found 353.1291;

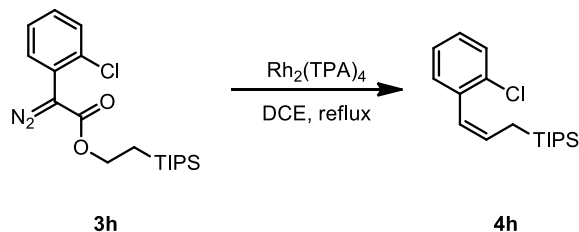


(Z)-(3-(3-fluorophenyl)allyl)triisopropylsilane (4f): The general procedure for allyl silane formation was followed, with **3f** (146 mg, 0.4 mmol, 1.0 equiv.) and $\text{Rh}_2(\text{TPA})_4$ (6 mg, 1 mol %), purifying by column chromatography (pentane) to give **4f** as a colorless oil (87 mg, 74% yield). ^1H NMR (600 MHz; CDCl_3) δ 7.26 (q, 1H, $J = 7.2$ Hz), 7.08 (d, 1H, $J = 7.7$ Hz), 7.02 (d, 1H, $J = 10.1$ Hz), 6.88 (t, 1H, $J = 8.4$ Hz), 6.24 (d, 1H, $J = 11.6$ Hz), 5.88-5.81 (m, 1H), 1.90 (d, 2H, $J = 8.8$ Hz), 1.09-0.98 (m, 21H); ^{13}C NMR (150 MHz, CDCl_3) δ 163 (d, $J = 245$ Hz), 140.7 (d, $J = 7.7$ Hz), 131.3, 129.7 (d, $J = 8.4$ Hz),

125.9 (d, $J = 1.7$ Hz), 124.6, 115.5 (d, $J = 21.2$ Hz), 113.1 (d, $J = 21.1$ Hz), 18.8, 12.3, 11.3; IR (neat): 2941, 2865, 1580, 880 cm^{-1} ; HRMS (APCI) calcd for $\text{C}_{18}\text{H}_{30}\text{FSi}$ ($[\text{M}+\text{H}]^+$) 293.2095, found 293.2097;

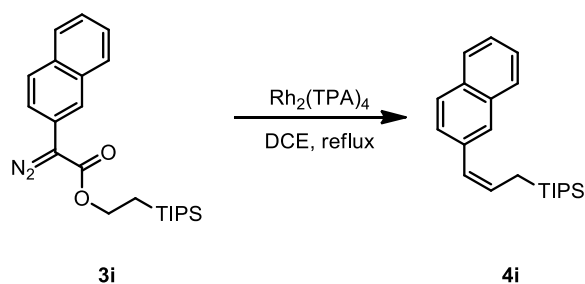


(Z)-(3-(3,4-dichlorophenyl)allyl)triisopropylsilane (4g): The general procedure for allyl silane formation was followed, with **3g** (166 mg, 0.4 mmol, 1.0 equiv.) and $\text{Rh}_2(\text{TPA})_4$ (6 mg, 1 mol %), purifying by column chromatography (pentane) to give **4g** as a colorless oil (87 mg, 64% yield). ^1H NMR (600 MHz; CDCl_3) δ 7.42 (s, 1H), 7.39 (d, 1H, $J = 8.3$ Hz), 7.17 (d, 1H, $J = 8.3$ Hz), 6.18 (d, 1H, $J = 11.4$ Hz), 5.89 (dt, 1H, $J = 11.4, 8.9$ Hz), 1.88 (d, 2H, $J = 8.9$ Hz), 1.12-1.00 (m, 21H); ^{13}C NMR (150 MHz, CDCl_3) δ 138.5, 132.3, 132.2, 130.6, 130.3, 129.9, 128.2, 124.7, 18.8, 12.4, 11.4; IR (neat): 2941, 2864, 1470 cm^{-1} ; HRMS (APCI) calcd for $\text{C}_{18}\text{H}_{29}\text{Cl}_2\text{Si}$ ($[\text{M}+\text{H}]^+$) 343.1410, found 343.1415;

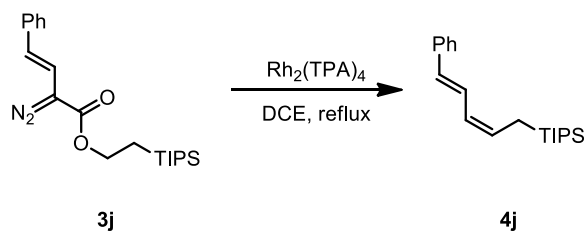


(Z)-(3-(2-chlorophenyl)allyl)triisopropylsilane (4h): The general procedure for allyl silane formation was followed, with **3h** (152 mg, 0.4 mmol, 1.0 equiv.) and $\text{Rh}_2(\text{TPA})_4$ (6

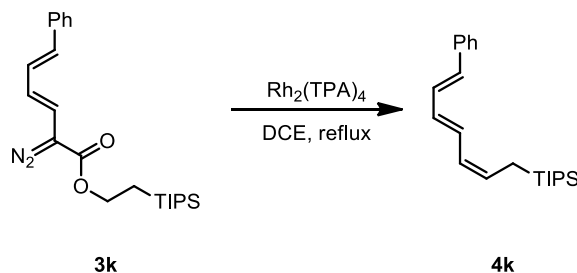
mg, 1 mol %), purifying by column chromatography (pentane) to give **4h** as a colorless oil (95 mg, 77% yield). ^1H NMR (600 MHz; CDCl_3) δ 7.44 (dd, 1H, $J = 7.6, 1.5$ Hz), 7.39 (dd, 1H, $J = 7.9, 1.2$ Hz), 7.24 (td, 1H, $J = 7.6, 1.2$ Hz), 7.17 (td, 1H, $J = 7.9, 1.5$ Hz), 6.36 (d, 1H, $J = 11.4$ Hz), 5.96 (dt, 1H, $J = 11.4, 8.7$ Hz), 1.82 (dd, 2H, $J = 8.7, 1.7$ Hz), 1.14-0.97 (m, 21H); ^{13}C NMR (150 MHz, CDCl_3) δ 136.4, 134.0, 131.3, 130.8, 129.7, 127.8, 126.3, 124.4, 18.8, 12.0, 11.3; IR (neat): 2940, 2864, 1469 cm^{-1} ; HRMS (APCI) calcd for $\text{C}_{18}\text{H}_{30}\text{ClSi}$ ($[\text{M}+\text{H}]^+$) 309.1800, found 309.1803;



(Z)-triisopropyl(3-(naphthalen-2-yl)allyl)silane (4i): The general procedure for allyl silane formation was followed, with **3i** (139 mg, 0.35 mmol, 1.0 equiv.) and $\text{Rh}_2(\text{TPA})_4$ (5 mg, 1 mol %), purifying by column chromatography (pentane) to give **4i** as a colorless oil (84 mg, 74% yield). ^1H NMR (600 MHz; CDCl_3) δ 7.84-7.77 (m, 4H), 7.52-7.42 (m, 3H), 6.45 (d, 1H, $J = 11.6$ Hz), 5.92 (td, 1H, $J = 11.6, 8.8$ Hz), 2.02 (d, 2H, $J = 8.8$ Hz), 1.14-1.00 (m, 21H); ^{13}C NMR (150 MHz, CDCl_3) δ 136.0, 133.7, 132.2, 130.6, 128.0, 127.8, 127.8, 127.6, 127.3, 127.0, 126.1, 125.6, 18.9, 12.4, 11.4; IR (film): 2940, 2888, 2863, 1462 cm^{-1} ; HRMS (APCI) calcd for $\text{C}_{22}\text{H}_{33}\text{Si}$ ($[\text{M}+\text{H}]^+$) 325.2346, found 325.2348;

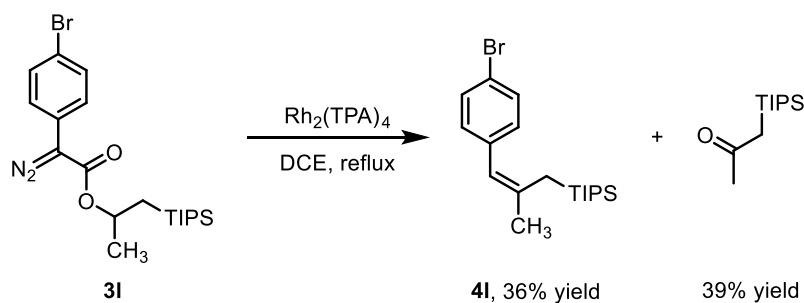


triisopropyl((2Z,4E)-5-phenylpenta-2,4-dien-1-yl)silane (4j): The general procedure for allyl silane formation was followed, with **3j** (100 mg, 0.27 mmol, 1.0 equiv.) and $\text{Rh}_2(\text{TPA})_4$ (4 mg, 1 mol %), purifying by column chromatography (pentane) to give **4j** as a colorless oil (49 mg, 60% yield). ^1H NMR (600 MHz; CDCl_3) δ 7.41 (d, 2H, $J = 7.8$ Hz), 7.31 (dd, 2H, $J = 7.8, 7.3$ Hz), 7.20 (t, 1H, $J = 7.3$ Hz), 7.14 (dd, 1H, $J = 15.5, 11.0$ Hz), 6.49 (d, 1H, $J = 15.5$ Hz), 6.06 (dd, 1H, $J = 11.0, 10.7$ Hz), 5.67 (dt, 1H, $J = 10.7, 9.0$ Hz), 1.86 (d, 2H, $J = 9$ Hz), 1.14-1.04 (m, 21H) (Note: The peak at 5.67 appears as a quartet. The coupling between protons at 6.06 ppm and 5.67 ppm was determined by a homonuclear decoupling NMR experiment, irradiating the doublet at 1.86 ppm. In this experiment, the peak at 5.67 is a doublet, with a coupling constant of 10.7 ppm.); ^{13}C NMR (150 MHz, CDCl_3) δ 138.2, 130.9 (2 signals), 128.8, 127.2, 126.6, 126.3, 124.8, 18.9, 12.7, 11.4; IR (neat): 2940, 2889, 2864, 1462 cm^{-1} ; HRMS (APCI) calcd for $\text{C}_{20}\text{H}_{33}\text{Si}$ ($[\text{M}+\text{H}]^+$) 301.2346, found 301.2349;



triisopropyl((2Z,4E,6E)-7-phenylhepta-2,4,6-trien-1-yl)silane (4k): The general procedure for allyl silane formation was followed, with **3k** (120 mg, 0.3 mmol, 1.0 equiv.)

and $\text{Rh}_2(\text{TPA})_4$ (4 mg, 1 mol %), purifying by column chromatography (pentane) to give **4k** as a slightly yellow oil (36 mg, 37% yield). ^1H NMR (600 MHz; CDCl_3) δ 7.42 (d, 2H, $J = 7.5$ Hz), 7.32 (t, 2H, $J = 7.7$ Hz), 7.22 (t, 1H, $J = 7.4$ Hz), 6.90 (dd, 1H, $J = 15.5$, 10.8 Hz), 6.71 (dd, 1H, $J = 14.7$, 11.4 Hz), 6.54 (d, 1H, $J = 15.5$ Hz), 6.36 (dd, 1H, $J = 14.7$, 10.8 Hz), 6.01 (dd, 1H, $J = 11.4$, 10.5 Hz), 5.66 (dt, 1H, $J = 10.5$, 9.0 Hz), 1.83 (d, 2H, $J = 9.0$ Hz), 1.15-1.05 (m, 21H) (Note: The peak at 5.66 appears as a quartet. The coupling between 6.01 ppm and 5.66 ppm was determined by a homonuclear decoupling NMR experiment, irradiating the doublet at 1.83 ppm. The peak at 5.66 became a doublet, with a coupling constant of 10.5 ppm); ^{13}C NMR (100 MHz, CDCl_3) δ 137.8, 131.7, 131.5, 131.1, 129.9, 129.4, 128.8, 127.4, 126.6, 126.4, 18.9, 12.8, 11.4; IR (neat): 2940, 2888, 2863, 1594, 1461 cm^{-1} ; HRMS (APCI) calcd for $\text{C}_{22}\text{H}_{35}\text{Si}$ ($[\text{M}+\text{H}]^+$) 327.2503, found 327.2504;

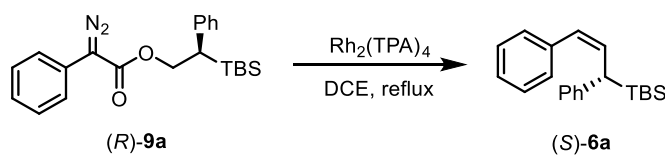
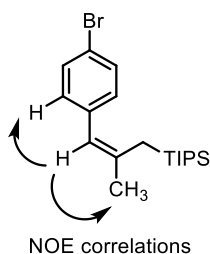


(Z)-(3-(4-bromophenyl)-2-methylallyl)triisopropylsilane (4l): The general procedure for allyl silane formation was followed, with **3l** (132 mg, 0.3 mmol, 1.0 equiv.) and $\text{Rh}_2(\text{TPA})_4$ (4 mg, 1 mol %). The two products formed in the reaction were isolated by column chromatography (**4l**: 100% pentane; 1-(triisopropylsilyl)-2-propanone: 5% Et_2O in pentane) to give **4l** as a colorless oil (40 mg, 36% yield), and 1-triisopropylsilyl-2-propanone as a colorless oil (25 mg, 39% yield).

Characterization data for **4l**: ^1H NMR (400 MHz; CDCl_3) δ 7.42 (d, 2H, $J = 8.4$ Hz), 7.13 (d, 2H, $J = 8.4$ Hz), 6.05 (s, 1H), 1.94 (s, 3H), 1.89 (s, 2H), 1.04-0.97 (m, 21H); ^{13}C NMR (100 MHz, CDCl_3) δ 139.6, 138.5, 131.4, 130.6, 122.5, 119.3, 27.8, 18.9, 15.8, 12.1; IR (film): 2941, 2888, 2864, 1485 cm^{-1} ; HRMS (NSI) calcd for $\text{C}_{19}\text{H}_{32}\text{BrSi}$ ($[\text{M}+\text{H}]^+$) 367.1451, found 367.1451;

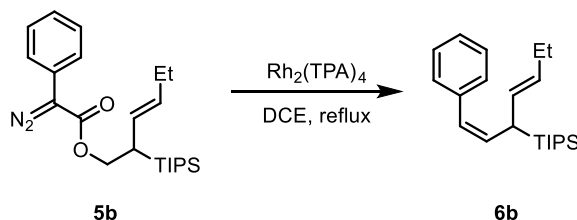
Characterization data for 1-(triisopropylsilyl)-2-propanone: ^1H NMR (400 MHz; CDCl_3) δ 2.25 (s, 2H), 2.18 (s, 3H), 1.16-1.06 (m, 21H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.9, 32.6, 31.4, 18.6, 11.6; IR (neat): 2942, 2866, 1692 cm^{-1} ; HRMS (NSI) calcd for $\text{C}_{12}\text{H}_{27}\text{OSi}$ ($[\text{M}+\text{H}]^+$) 215.1826, found 215.1819 ¹⁵

The alkene geometry of **4l** was determined by NOE correlations:



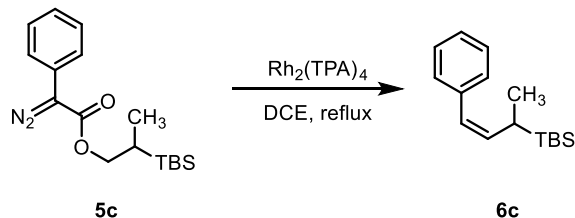
(S,Z)-tert-butyl(1,3-diphenylallyl)dimethylsilane (S-6a): The diazo (133 mg, 0.35 mmol, 1.0 equiv.) in 4 mL 1,2-dichloroethane (DCE) was added dropwise over 2 hours to a solution of $\text{Rh}_2(\text{TPA})_4$ (5 mg, 1 mol %) in 2 mL DCE at reflux. The mixture was allowed to cool to room temperature and the solvent was removed. The solvent was replaced with PhCF_3 (5 mL) and the solution heated at reflux overnight. The solution was allowed to cool to room temperature and the solvent removed. The crude residue was

purified by column chromatography (pentane) to give the product as a colorless oil (56 mg, 52% yield). The reaction with the racemic diazo was run in an identical manner to give 59 mg of the product (55% yield). $[\alpha]_D^{20}$: 183.7 (c. 1.3, CHCl_3); ^1H NMR (400 MHz; CDCl_3) δ 7.37-7.09 (m, 10H), 6.46 (d, 1H, $J = 11.3$ Hz), 6.17 (dd, 1H, $J = 12.4$, 11.3 Hz), 3.67 (d, 1H, $J = 12.4$ Hz), 0.71 (s, 9H), -0.01 (s, 3H), -0.20 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.9, 137.9, 132.8, 128.9, 128.7, 128.4, 127.9, 127.7, 126.6, 124.8, 35.6, 27.1, 18.0, -6.4, -7.6; IR (neat): 3022, 2927, 2882, 2855, 1247 cm^{-1} ; HRMS (NSI) calcd for $\text{C}_{21}\text{H}_{29}\text{Si}$ ($[\text{M}+\text{H}]^+$) 309.2033, found 309.2034; The ee was determined by chiral HPLC: OJ column, 0.5 mL/min, 0 % iPrOH in hexanes, $\lambda = 230$ nm. tR: Major: 15.6 min, Minor: 9.3 min, 86% ee.

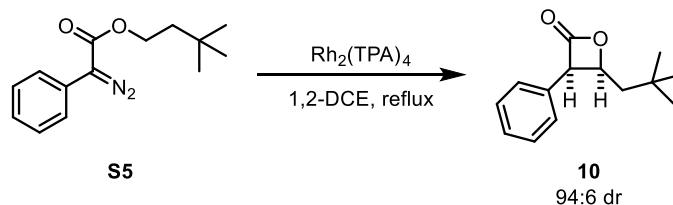


triisopropyl((1Z,4E)-1-phenylhepta-1,4-dien-3-yl)silane (6b): The diazo (143 mg, 0.4 mmol, 1.0 equiv.), in 4 mL DCE, was added dropwise over 2 hours to a solution of $\text{Rh}_2(\text{TPA})_4$ (6 mg, 1 mol %) in 2 mL DCE at reflux. The solution was allowed to cool to room temperature before the solvent was removed. The crude was dissolved in PhCF_3 (5 mL) and heated at reflux for 16 hours. The solvent was again removed and the crude purified by column chromatography (pentane) to give the product as a colorless oil (54 mg, 47% yield). ^1H NMR (400 MHz; CDCl_3) δ 7.33-7.25 (m, 4H), 7.21-7.16 (m, 1H), 6.35 (d, 1H, $J = 11.5$ Hz), 5.73 (dd, 1H, $J = 12.0$, 11.5 Hz), 5.52 (dd, 1H, $J = 15.3$, 7.5 Hz), 5.41 (dt, 1H, $J = 15.3$, 6.2 Hz), 3.24 (dd, 1H, $J = 12.0$, 7.5 Hz), 2.11-2.02 (m, 2H), 0.99 (t, 3H,

$J = 7.4$ Hz), 0.82 (s, 9H), -0.06 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.3, 132.7, 129.7, 128.9, 128.7, 128.3, 126.6, 126.4, 32.3, 27.3, 26.2, 18.1, 14.4, -6.8, -7.1; IR (film): 2958, 2928, 2882, 2855 cm^{-1} ; HRMS (NSI) calcd for $\text{C}_{19}\text{H}_{31}\text{Si}$ ($[\text{M}+\text{H}]^+$) 287.2190, found 287.2189;

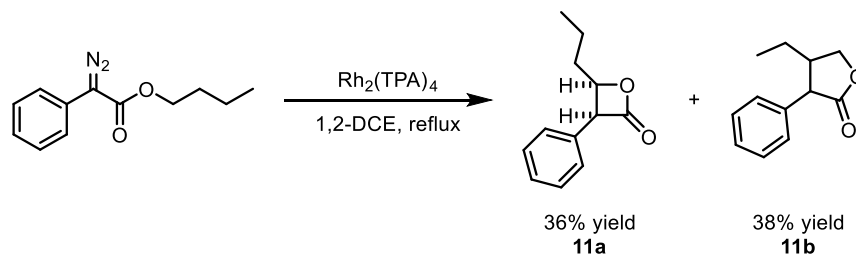


(Z)-tert-butyl dimethyl(4-phenylbut-3-en-2-yl)silane (6c): The diazo (127 mg, 0.4 mmol, 1.0 equiv.), in 4 mL DCE, was added dropwise over 2 hours to a solution of $\text{Rh}_2(\text{TPA})_4$ (6 mg, 1 mol %) in 2 mL DCE at reflux. The solution was allowed to cool to room temperature and the solvent removed. The crude residue was purified by column chromatography (pentane) to give the product as a 90:10 mixture of *Z:E* alkene isomers (67 mg, 68% yield). ^1H NMR (600 MHz; CDCl_3) δ 7.36-7.29 (m, 4H), 7.24-7.20 (m, 1H), 6.31 (d, 1H, $J = 11.4$ Hz), 5.62 (dd, 1H, $J = 12.3, 11.4$ Hz), 2.53 (m, 1H), 1.20 (d, 3H, $J = 7.2$ Hz), 0.87 (s, 9H), -0.02 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.5, 137.4, 128.7, 128.3, 126.3, 125.8, 27.4, 20.3, 17.8, 16.8, -7.1, -7.3; IR (neat): 2954, 2928, 2856, 1248 cm^{-1} ; HRMS (NSI) calcd for $\text{C}_{16}\text{H}_{27}\text{Si}$ ($[\text{M}+\text{H}]^+$), found 247.1879;



4-neopentyl-3-phenyloxetan-2-one (10): A solution of the diazo **S5** (123 mg, 0.5 mmol, 1.0 equiv.) in DCE (4 mL) was added dropwise over 2 hours to a solution of $\text{Rh}_2(\text{TPA})_4$ catalyst (7 mg, 0.005 mmol, 1 mol %) in 2 mL DCE at reflux. The mixture was allowed to stir for 20 minutes at reflux before it was allowed to cool to room temperature. The solvent was removed, and the crude mixture was purified by column chromatography (9:1 hexanes:EtOAc) to give the product as a slightly green-tinged solid (92 mg, 84% yield). ^1H NMR (400 MHz; CDCl_3) δ 7.43-7.31 (m, 3H), 7.24-7.19 (m, 2H), 5.06 (d, 1H, $J = 6.8$ Hz), 4.97 (ddd, 1H, $J = 10.0, 6.8, 2.2$ Hz), 1.36 (dd, 1H, $J = 15.3, 10.0$ Hz), 1.15 (dd, 1H, $J = 15.3, 2.2$ Hz), 0.91 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.3, 130.8, 129.1, 129.0, 128.4, 74.9, 59.5, 44.4, 30.3, 29.8; IR (neat): 2953, 2912, 1800, 1143 cm^{-1} ; HRMS (NSI) calcd for $\text{C}_{14}\text{H}_{18}\text{O}_2\text{Na}$ ($[\text{M}+\text{Na}]^+$) 241.1199, found 241.1198;

The *cis* stereochemistry of β -lactone **10** was determined by the diagnostic coupling constant ($J_{\text{cis}} = 6.8$ Hz).^{16,17}



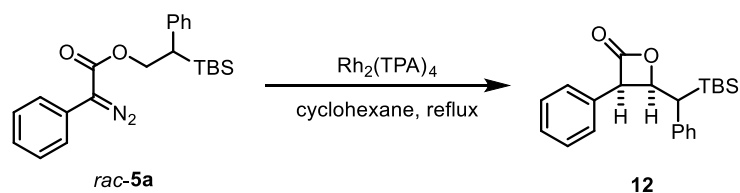
The diazo (87 mg, 0.4 mmol, 1.0 equiv.) in 4 mL DCE was added dropwise over 2 hours to a solution of $\text{Rh}_2(\text{TPA})_4$ (6 mg, 1 mol %) in 2 mL DCE at reflux. The mixture was al-

lowed to heat at reflux for an additional 30 minutes and the solution was cooled. The solvent was removed and the crude mixture was purified by column chromatography (10-15% EtOAc in hexanes). The two products were isolated separately as slightly green-tinged oils (**11a**: 27 mg, 36% yield; **11b**: 29 mg, 38% yield).

Characterization data for **11a**: ^1H NMR (400 MHz; CDCl_3) δ 7.41-7.31 (m, 3H), 7.26-7.21 (m, 2H), 5.04 (d, 1H, $J = 6.7$ Hz), 4.80 (ddd, 1H, $J = 9.1, 6.7, 4.2$ Hz), 1.51-1.20 (m, 4H), 0.83 (t, 3H, $J = 7.1$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 170.2, 130.7, 129.0, 128.9, 128.3, 76.9, 58.6, 33.2, 18.5, 13.8; IR (neat): 2961, 2874, 1811, 1124 cm^{-1} ; HRMS (NSI) calcd for $\text{C}_{12}\text{H}_{15}\text{O}_2$ ($[\text{M}+\text{H}]^+$) 191.1067, found 191.1068;

The *cis* stereochemistry of β -lactone **11a** was determined by the diagnostic coupling constant ($J_{\text{cis}} = 6.7$ Hz).^{16,17}

Characterization data for **11b**: ^1H NMR (400 MHz; CDCl_3) δ 7.41-7.28 (m, 3H), 7.21-7.16 (m, 2H), 4.47 (dd, 1H, $J = 9.1, 6.8$ Hz), 4.15 (dd, 1H, $J = 9.1, 6.1$ Hz), 3.96 (d, 1H, $J = 8.4$ Hz), 2.73-2.62 (m, 1H), 1.21-0.98 (m, 2H), 0.83 (t, 3H, $J = 7.4$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 177.8, 133.9, 129.3, 128.9, 127.7, 71.1, 50.3, 43.0, 21.5, 11.9; IR (neat): 2963, 2933, 2877, 1766, 1154 cm^{-1} ; HRMS (NSI) calcd for $\text{C}_{12}\text{H}_{15}\text{O}_2$ ($[\text{M}+\text{H}]^+$) 191.1067, found 191.1068;

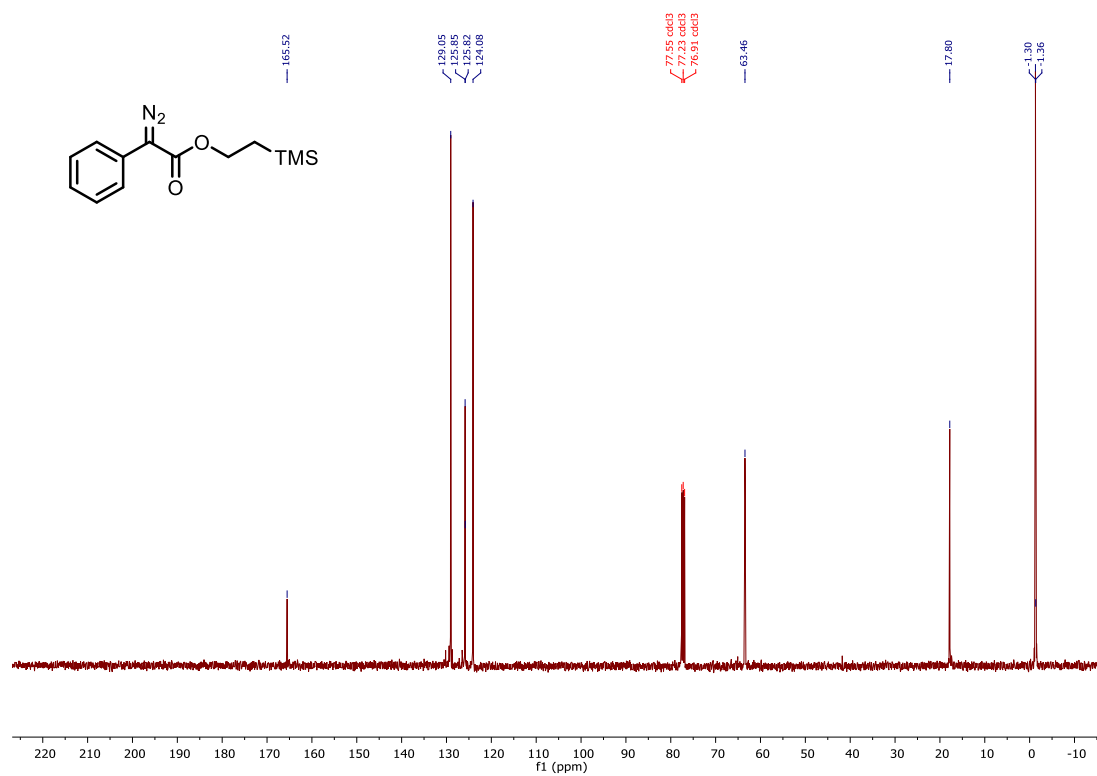
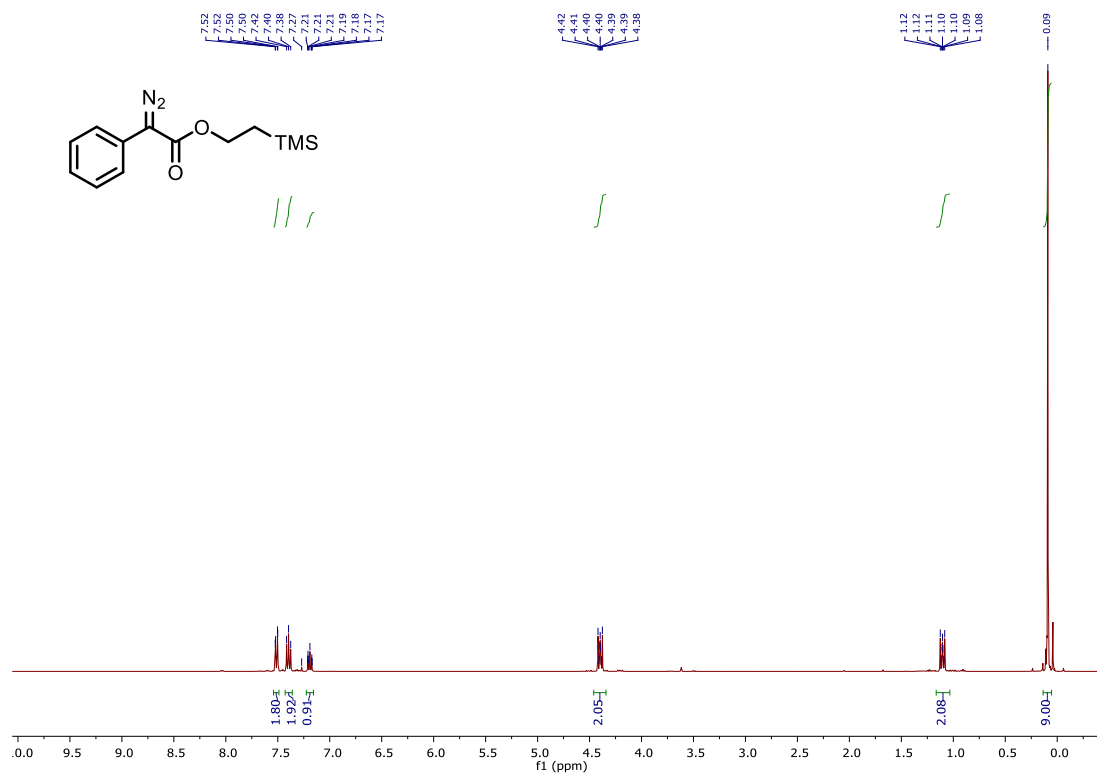


4-((tert-butyldimethylsilyl)(phenyl)methyl)-3-phenyloxetan-2-one (12): The diazo (133 mg, 0.35 mmol, 1.0 equiv.), in 4 mL cyclohexane, was added dropwise over 2 hours to a solution of $\text{Rh}_2(\text{TPA})_4$ catalyst (5 mg, 0.0035 mmol, 1 mol %) in 2 mL cyclohexane at reflux. The mixture was allowed to cool to room temperature and the solvent removed. The crude residue was purified by column chromatography (5% Et_2O in pentane) to give the product as a white solid (53 mg, 43% yield). ^1H NMR (400 MHz; CDCl_3) δ 7.25-7.19 (m, 1H), 7.13 (t, 2H, $J = 7.5$ Hz), 6.97-6.90 (m, 3H), 6.78 (d, 2H, $J = 7.3$ Hz), 6.40-6.30 (m, 2H), 5.28 (dd, 1H, $J = 12.3, 6.1$ Hz), 4.94 (d, 1H, $J = 6.1$ Hz), 2.48 (d, 1H, $J = 12.3$ Hz), 0.76 (s, 9H), 0.17 (s, 3H), -0.26 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.2, 138.5, 130.4, 129.6, 128.3 (2 signals), 128.2, 128.1, 125.3, 78.2, 60.7, 34.6, 27.1, 17.7, -5.5, -5.6; IR (neat): 2957, 2927, 2853, 1818, 1122 cm^{-1} ; HRMS (NSI) calcd for $\text{C}_{22}\text{H}_{29}\text{O}_2\text{Si}$ ($[\text{M}+\text{H}]^+$) 353.1931, found 353.1933;

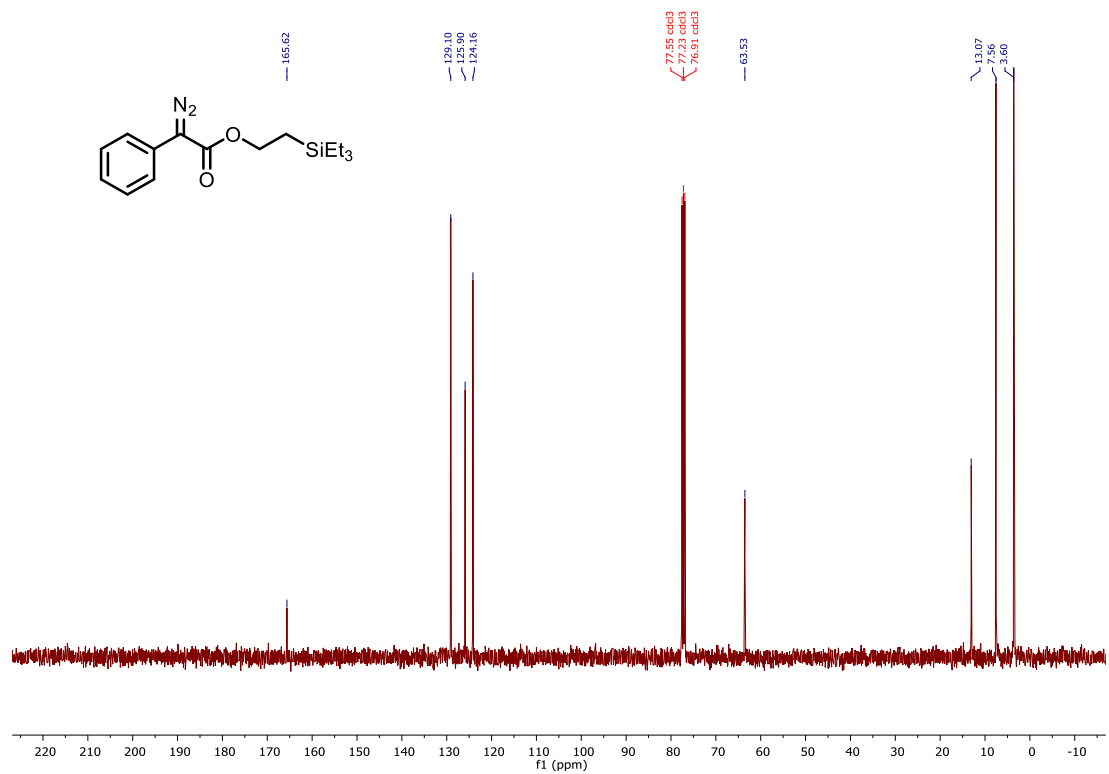
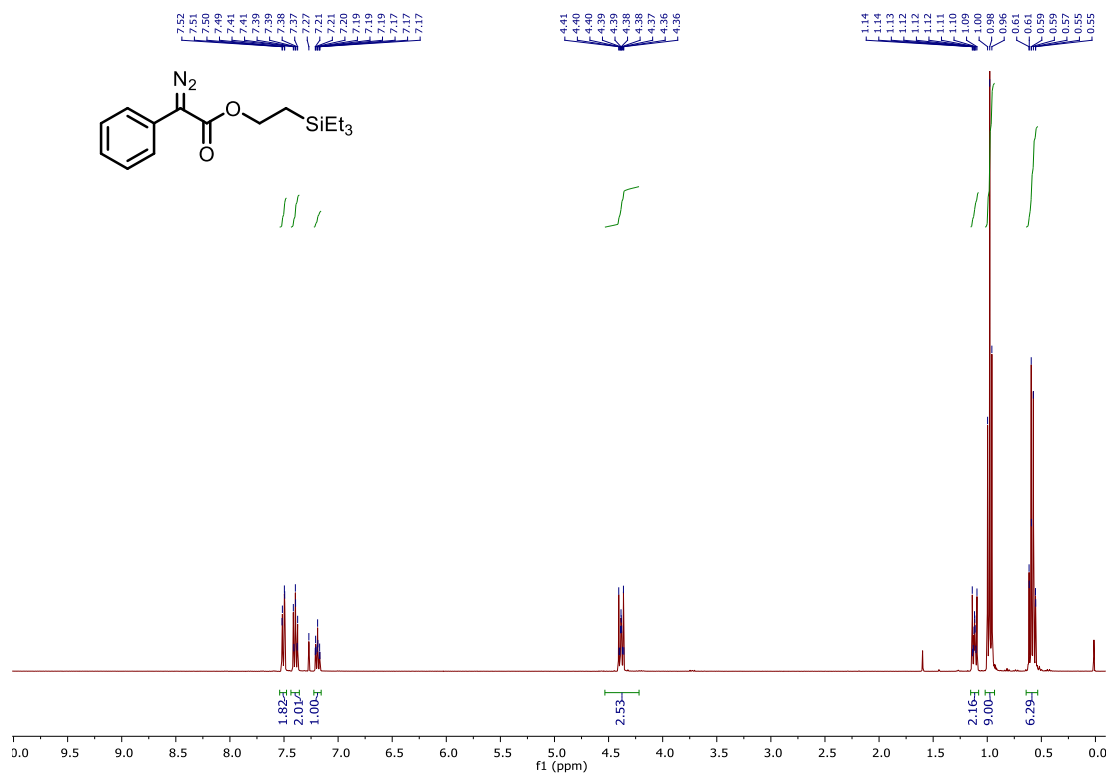
The internal *cis* stereochemistry of β -lactone **12** was determined by the diagnostic coupling constant ($J_{\text{cis}} = 6.1$ Hz).^{16,17}

3 – Spectral Data

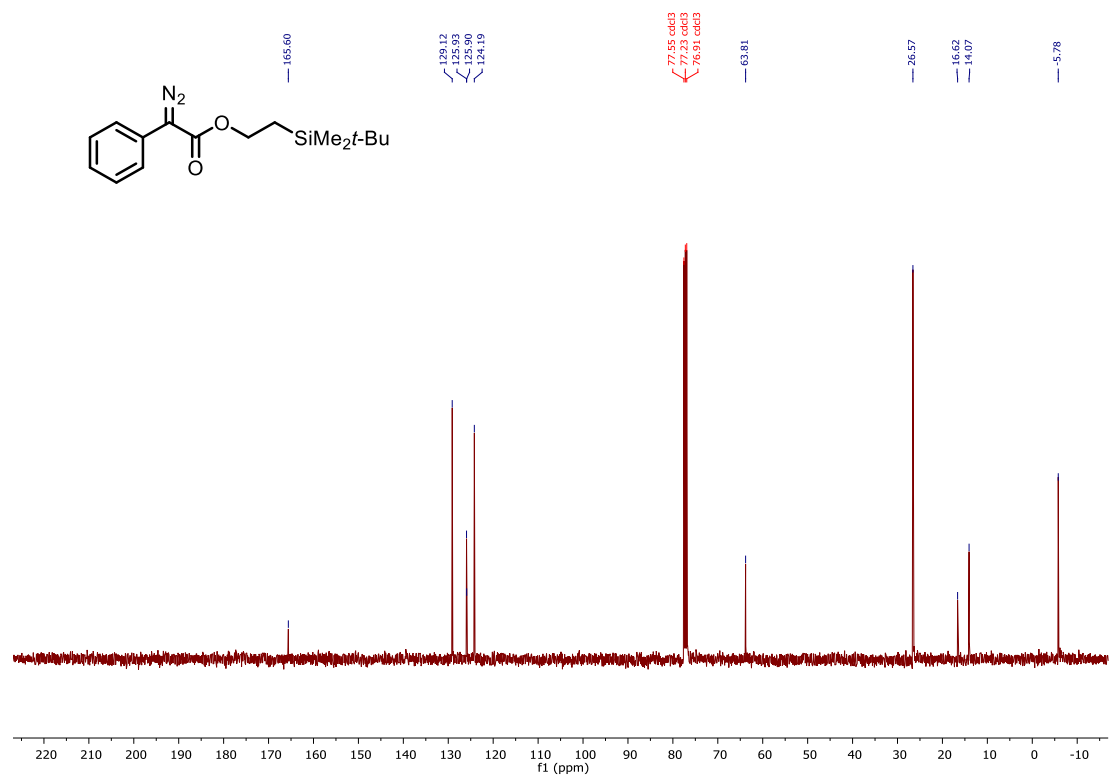
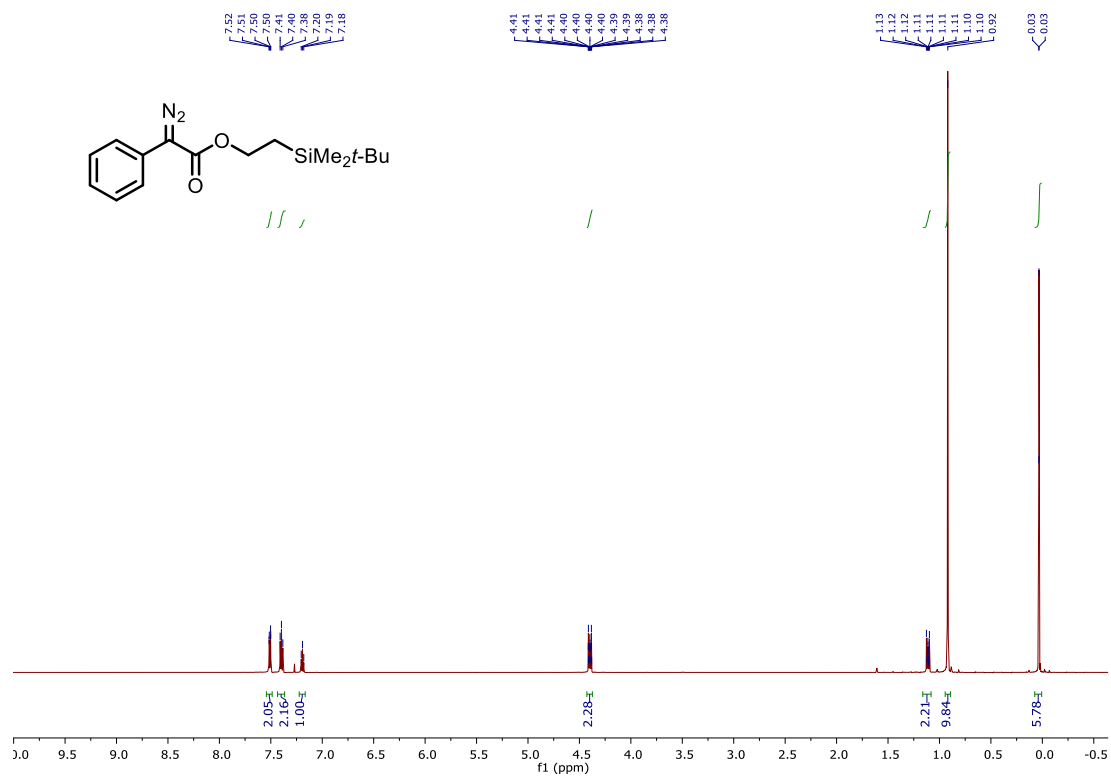
3.1 NMR Data



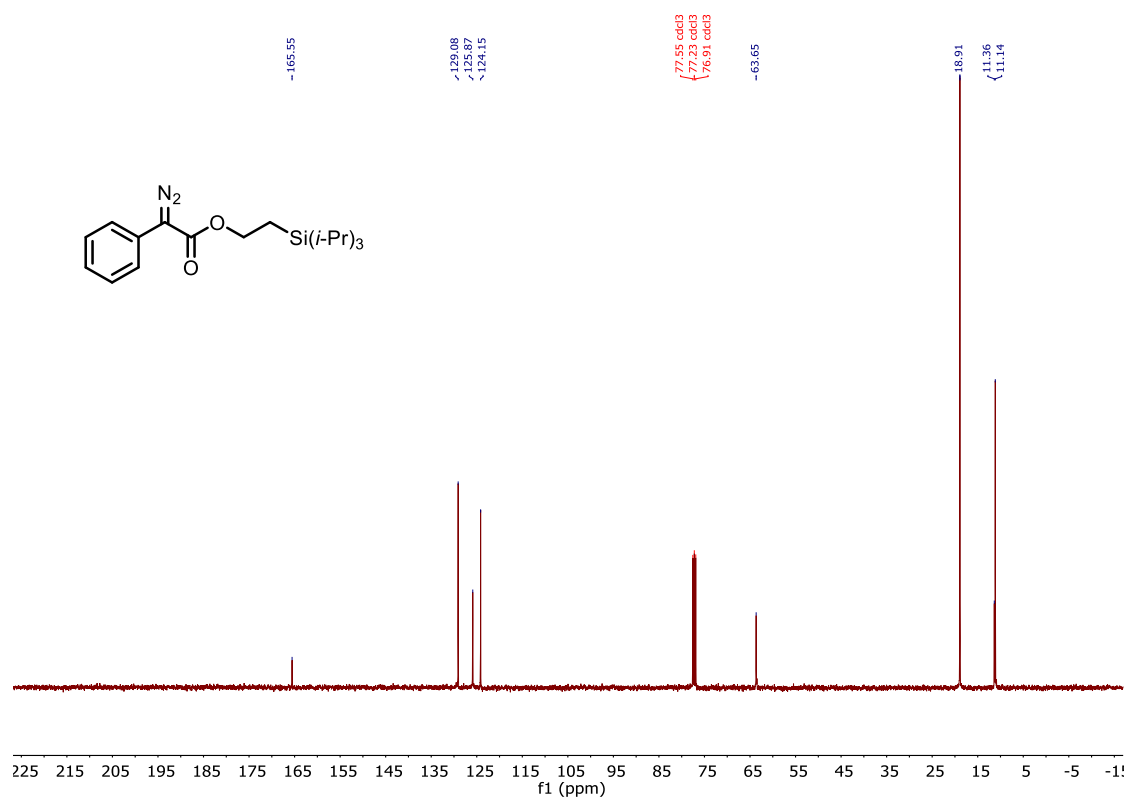
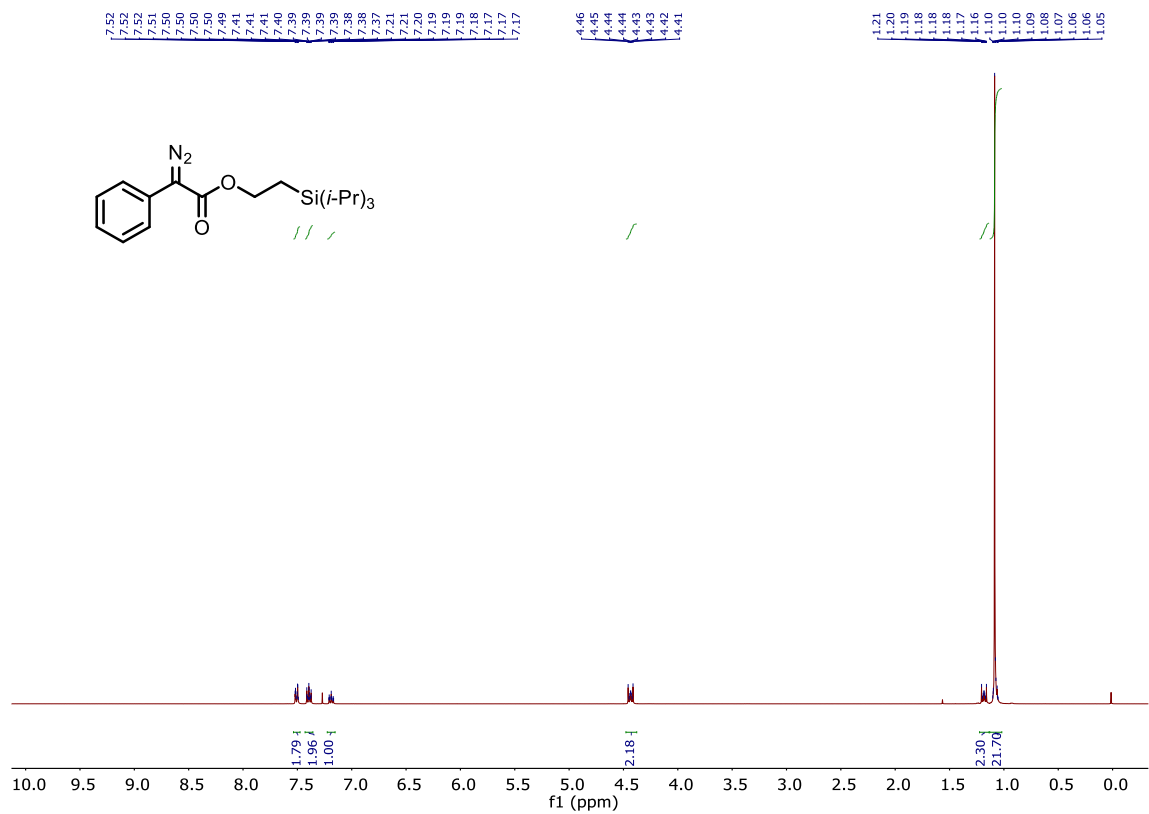
¹H and ¹³C NMR for compound **1a**



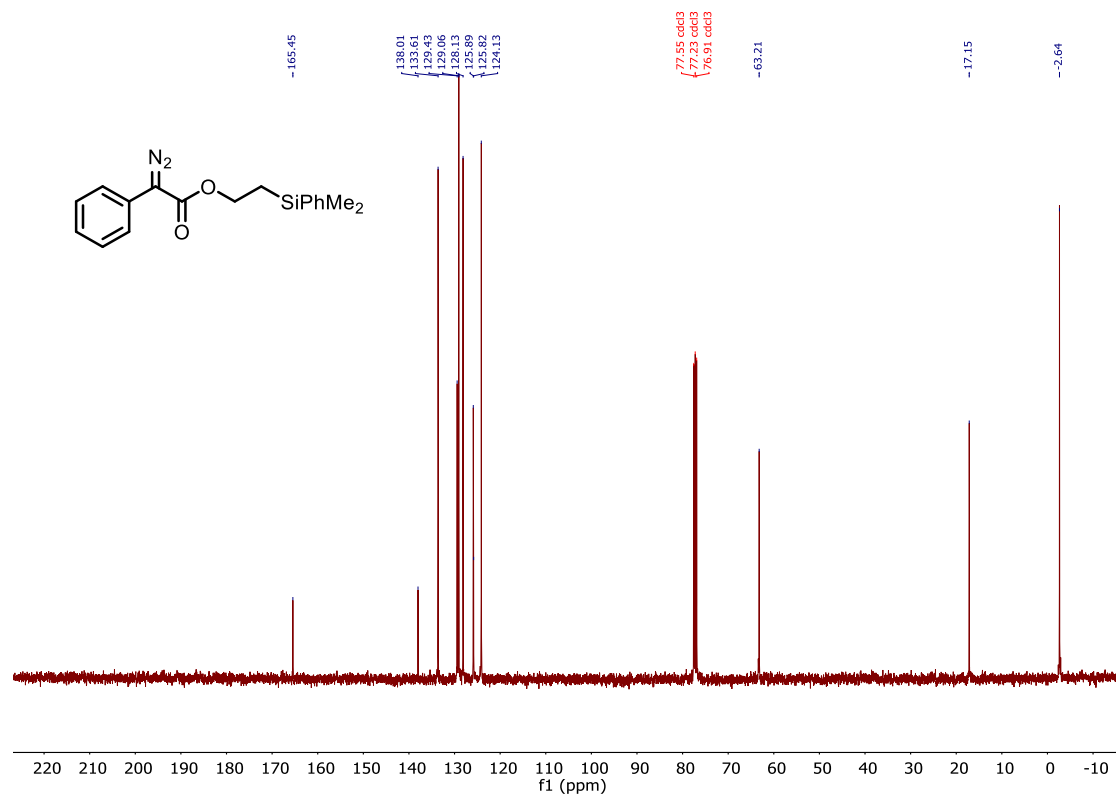
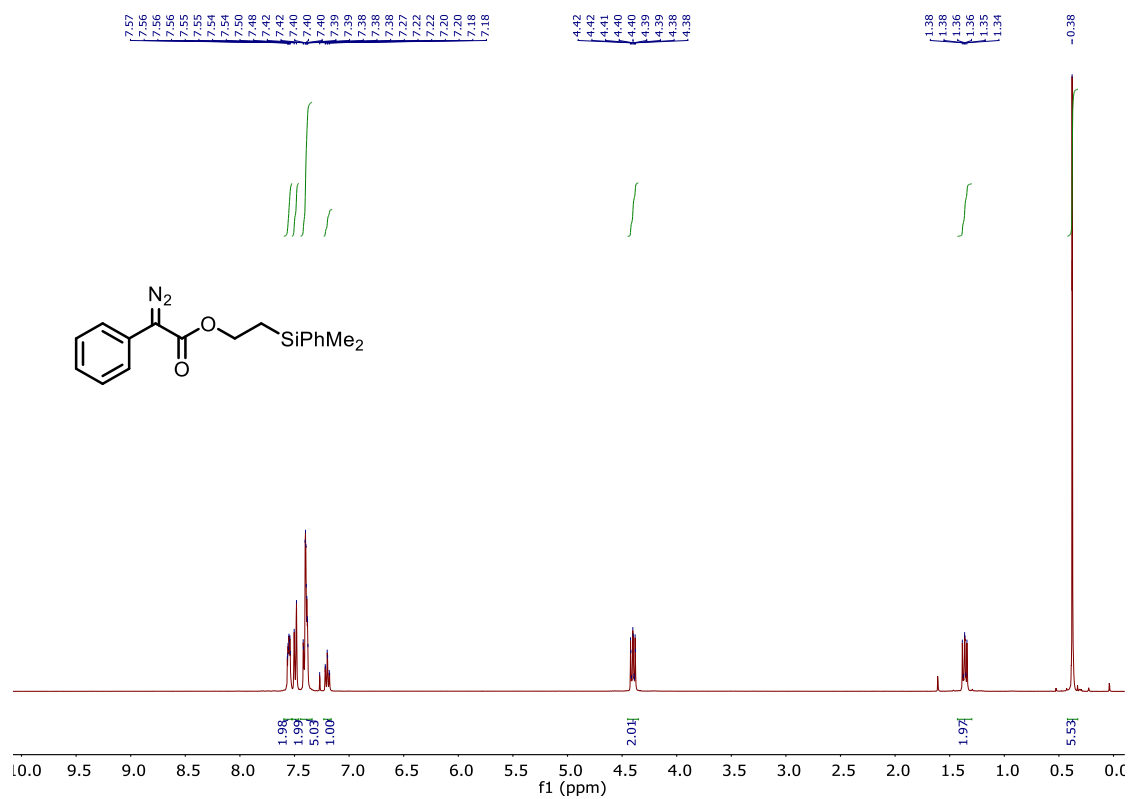
¹H and ¹³C NMR for compound **1b**



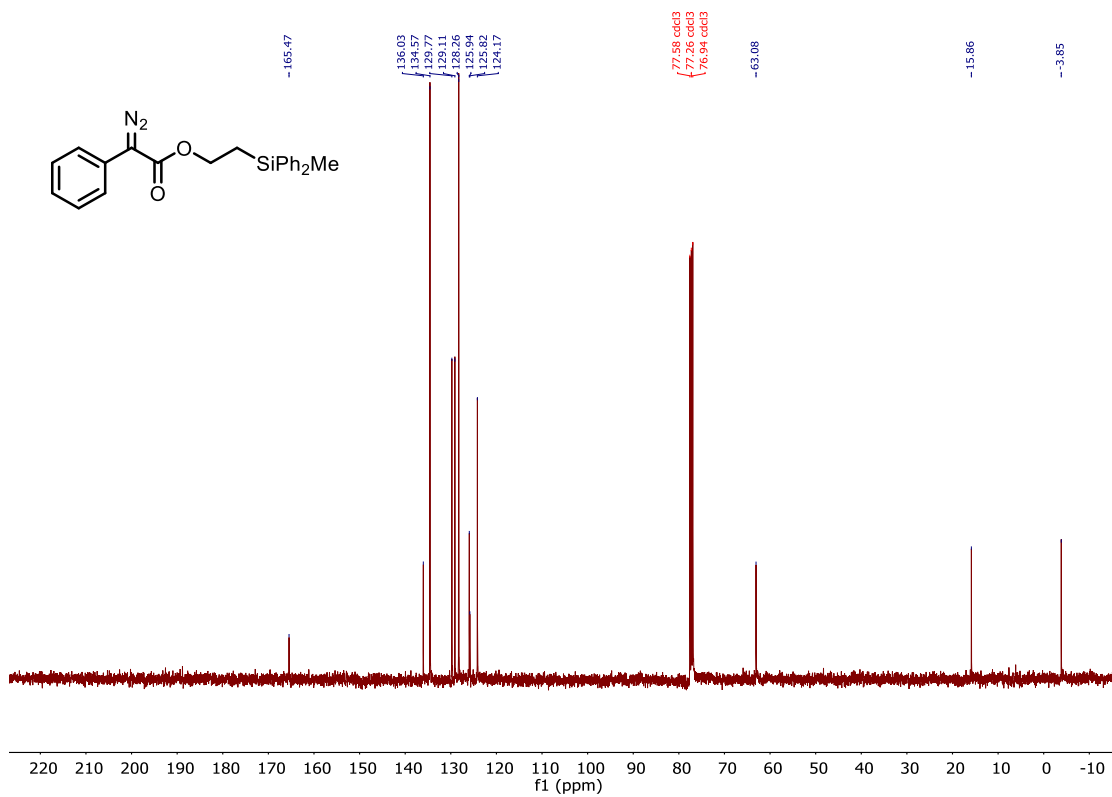
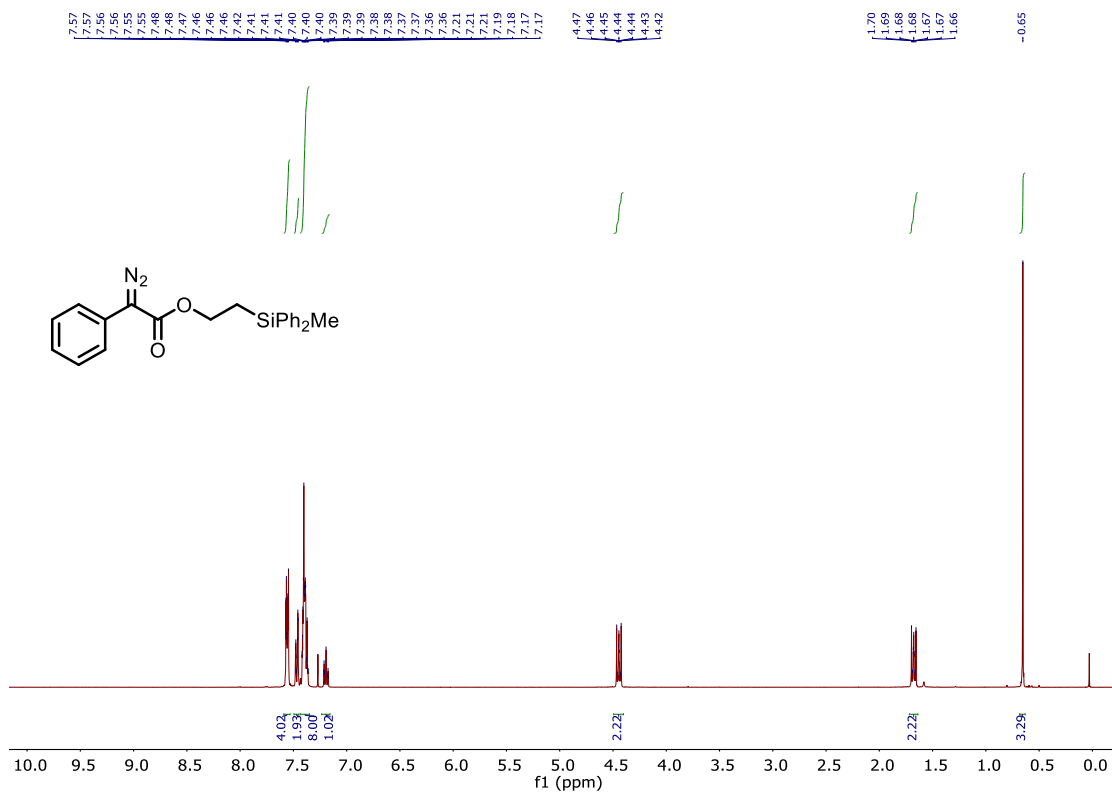
¹H and ¹³C NMR for compound **1c**



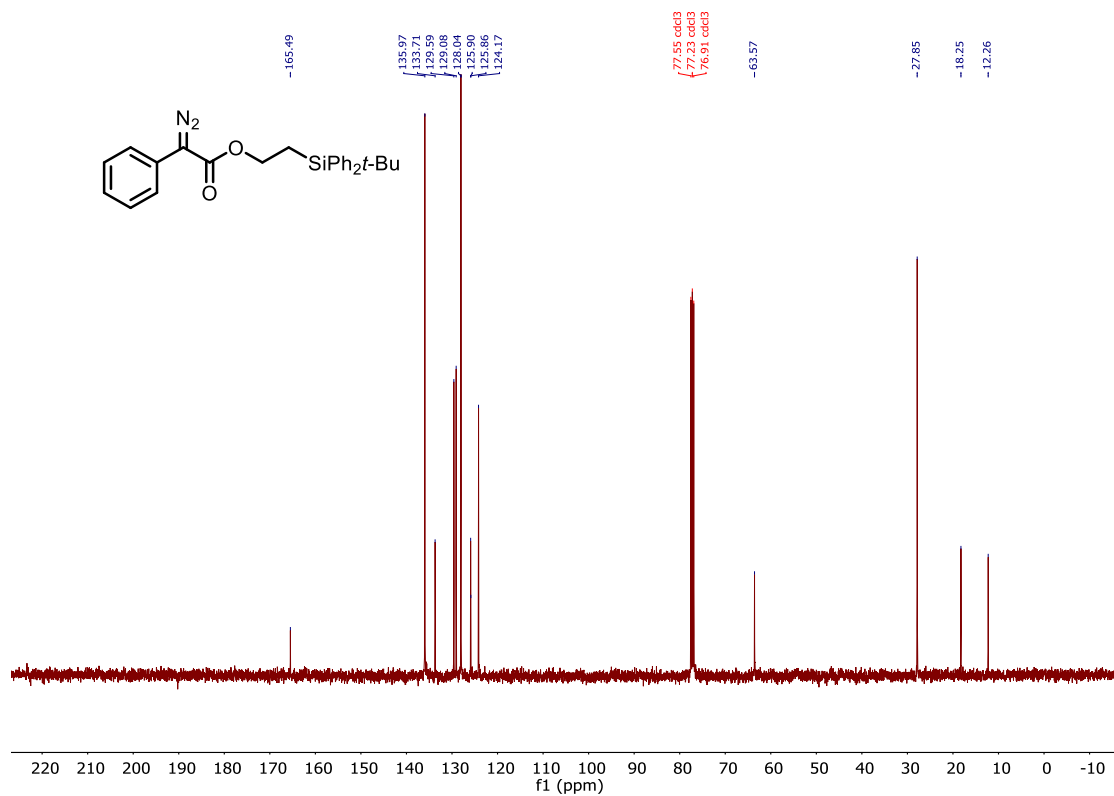
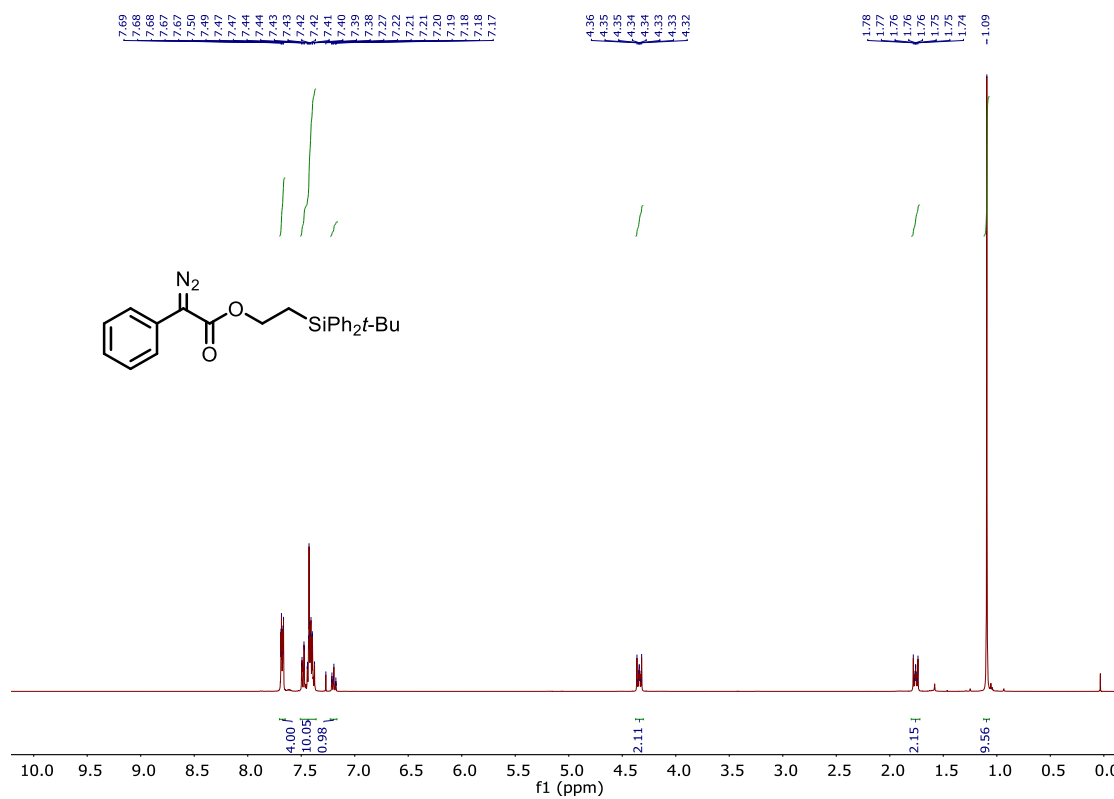
¹H and ¹³C NMR for compound **1d**



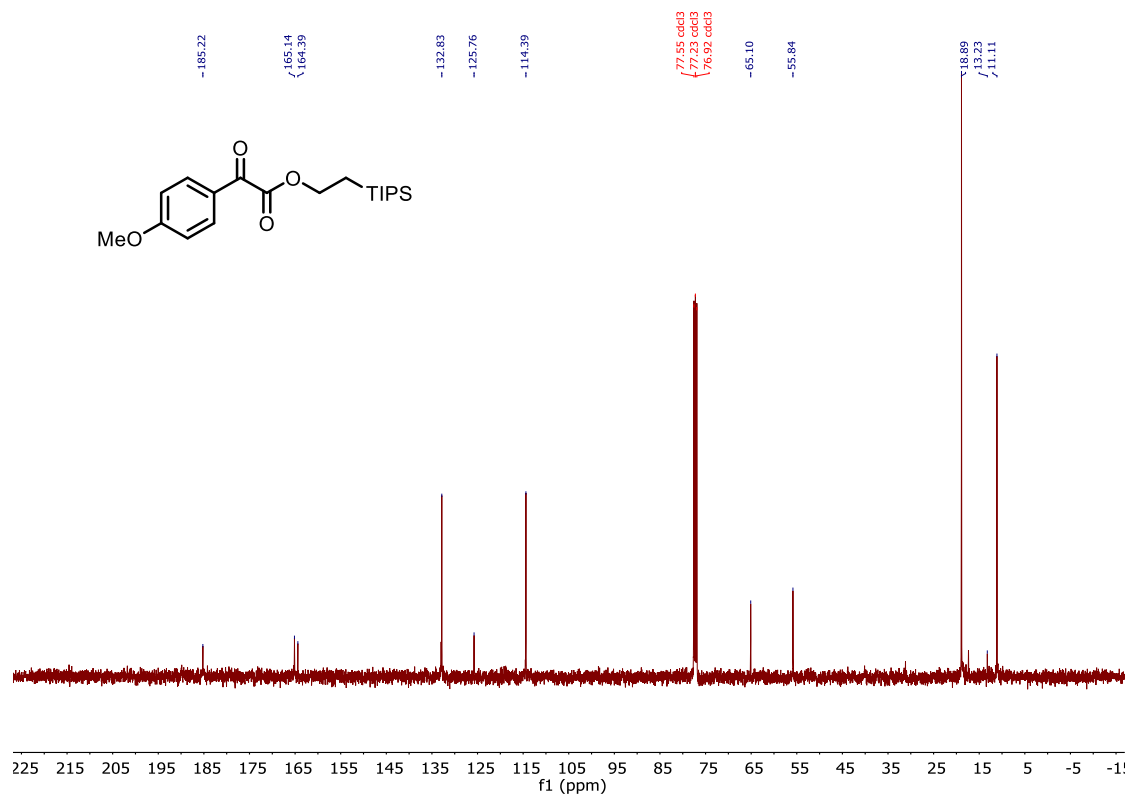
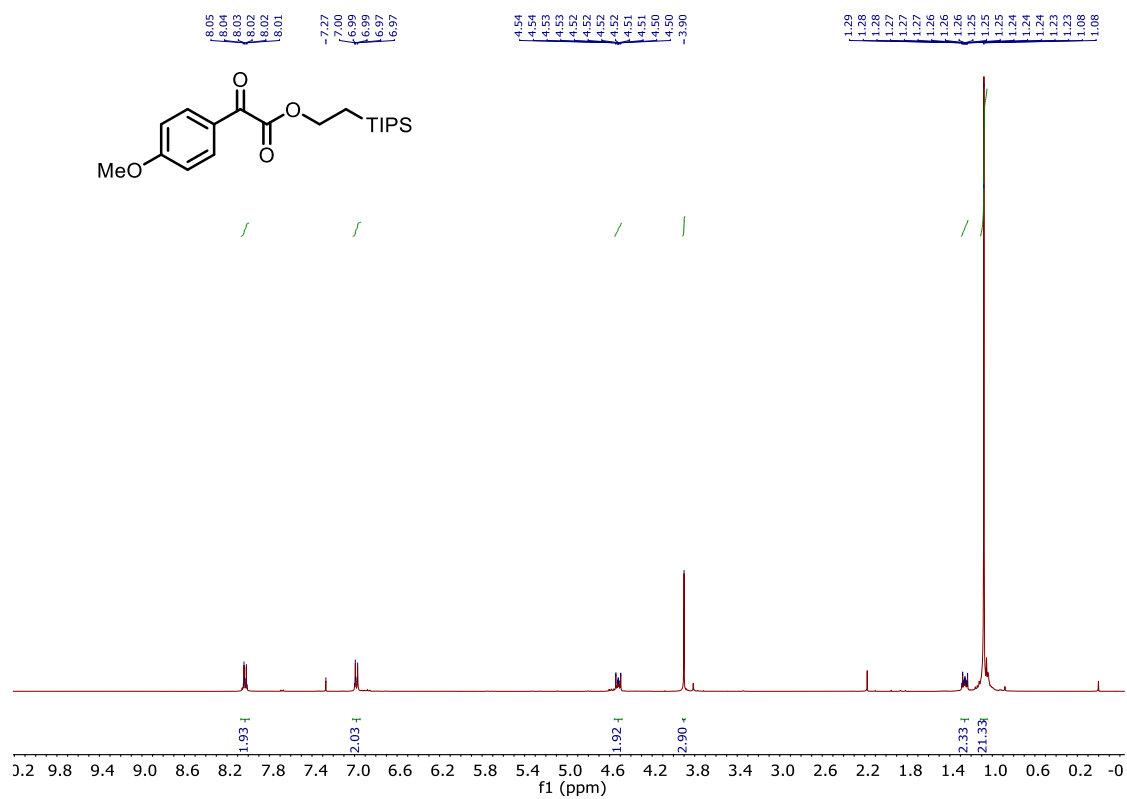
¹H and ¹³C NMR for compound **1e**



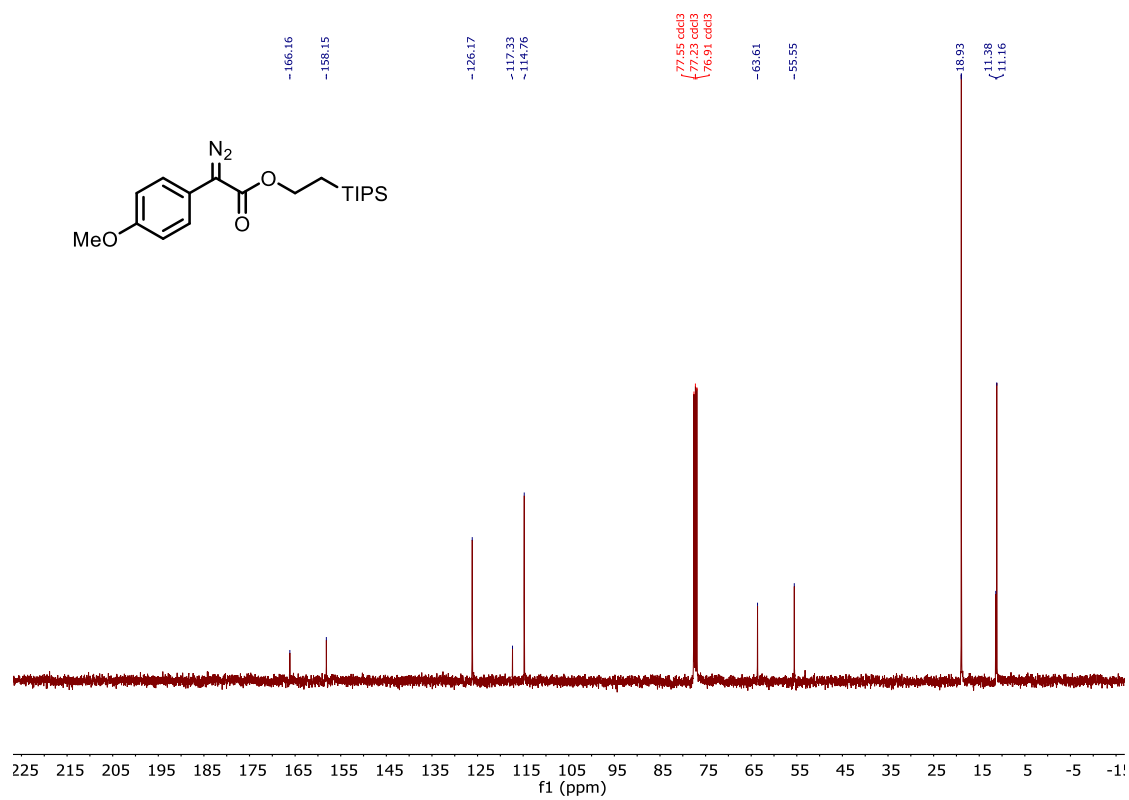
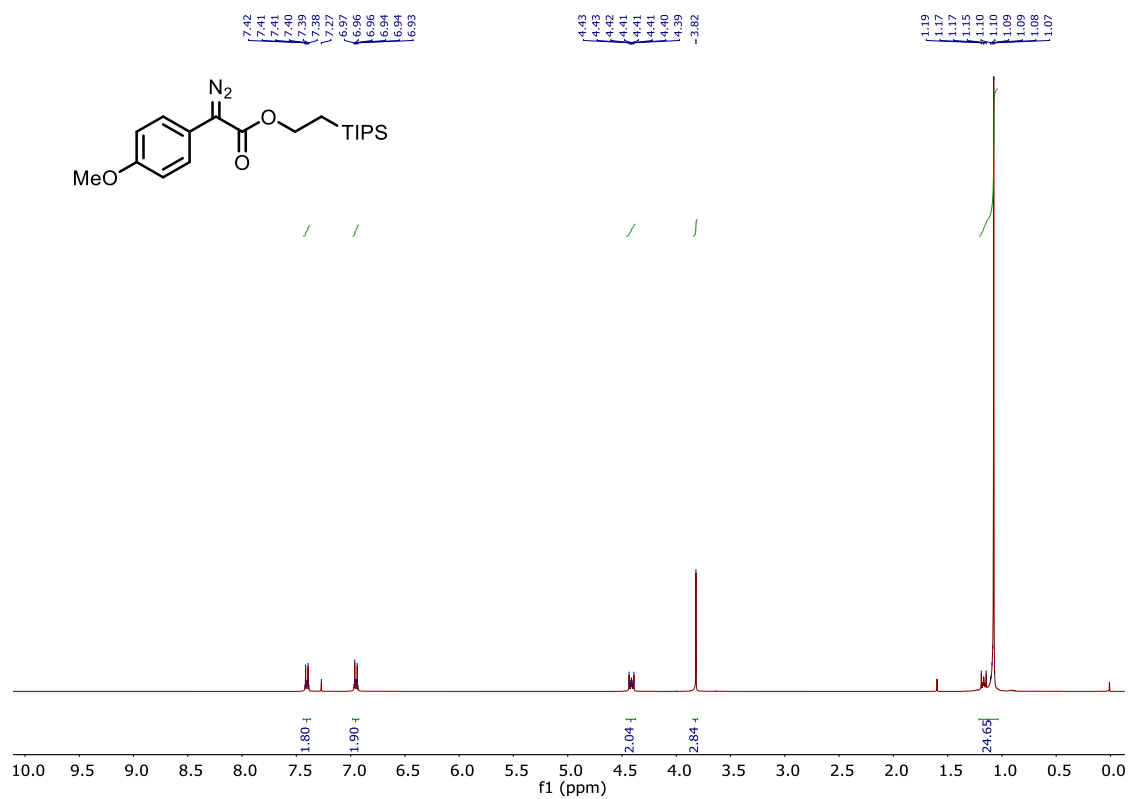
¹H and ¹³C NMR for compound **1f**



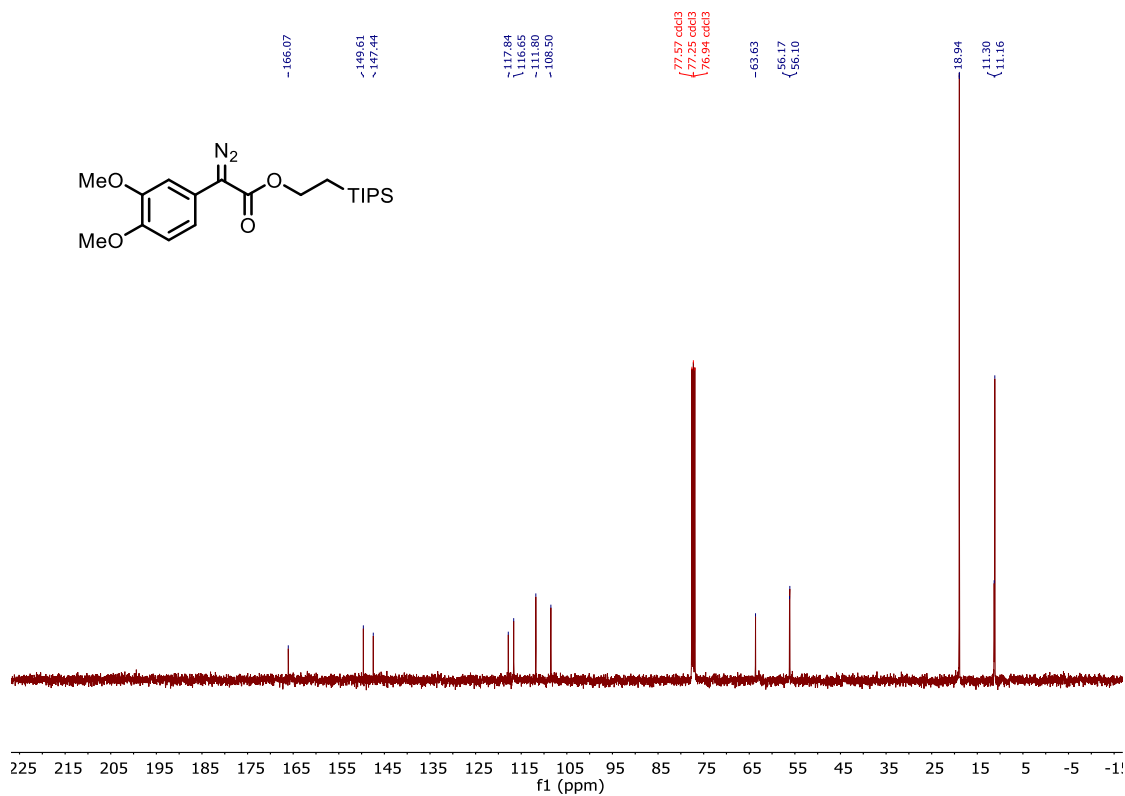
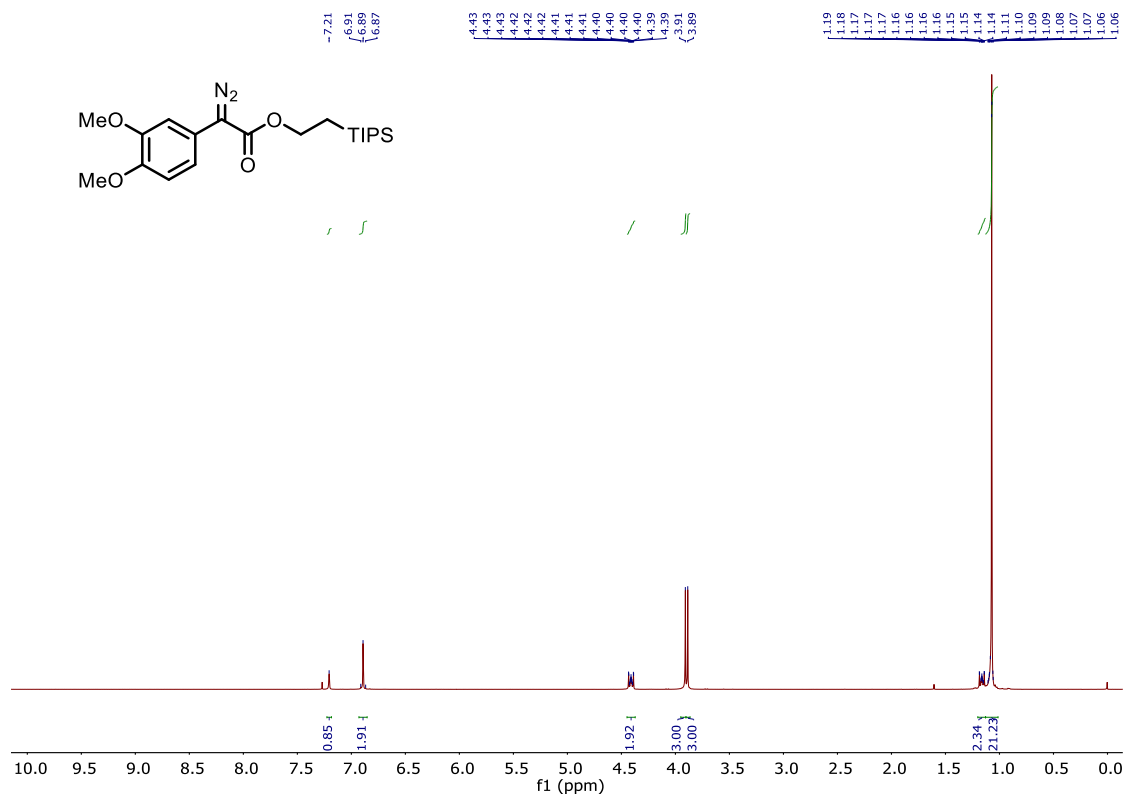
¹H and ¹³C NMR for compound **1g**



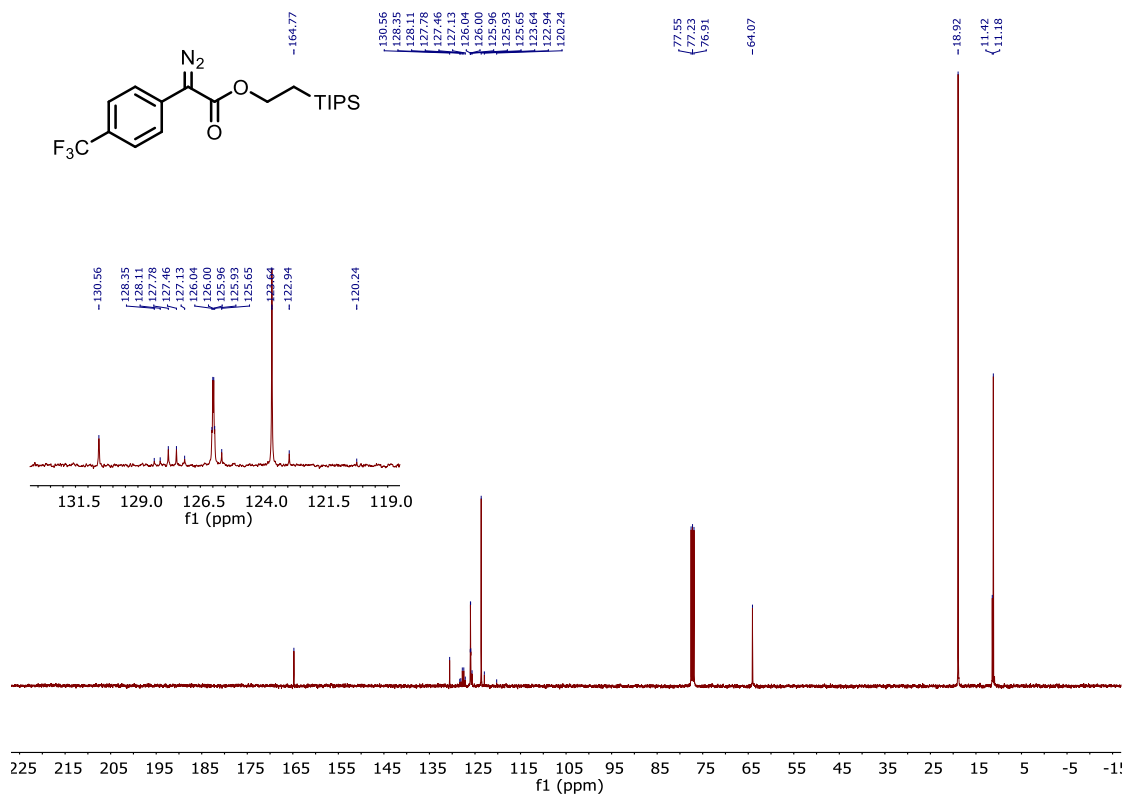
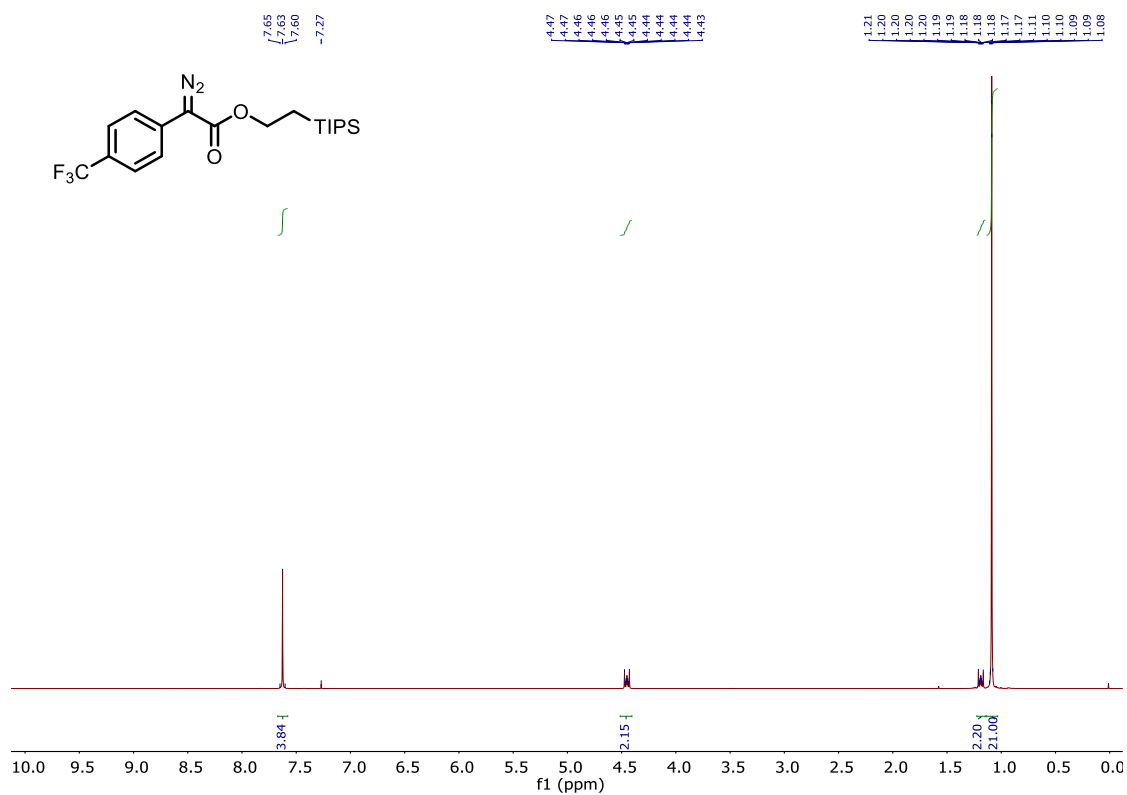
¹H and ¹³C NMR for compound S3a



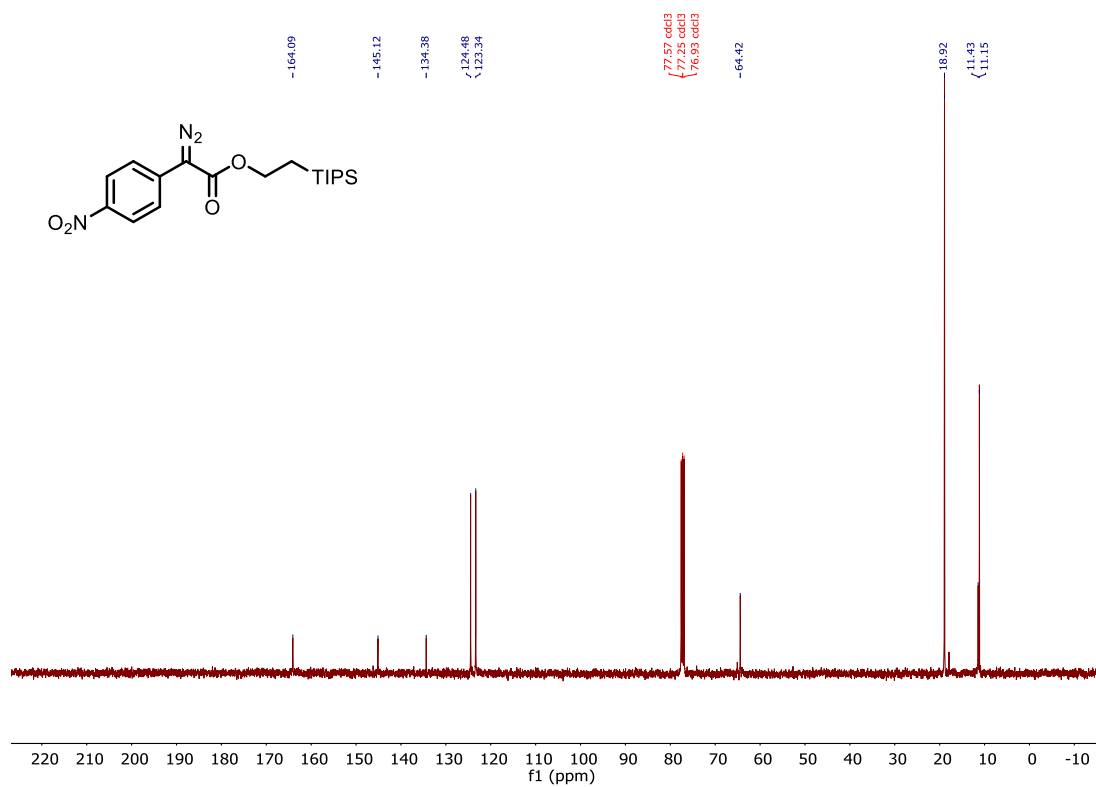
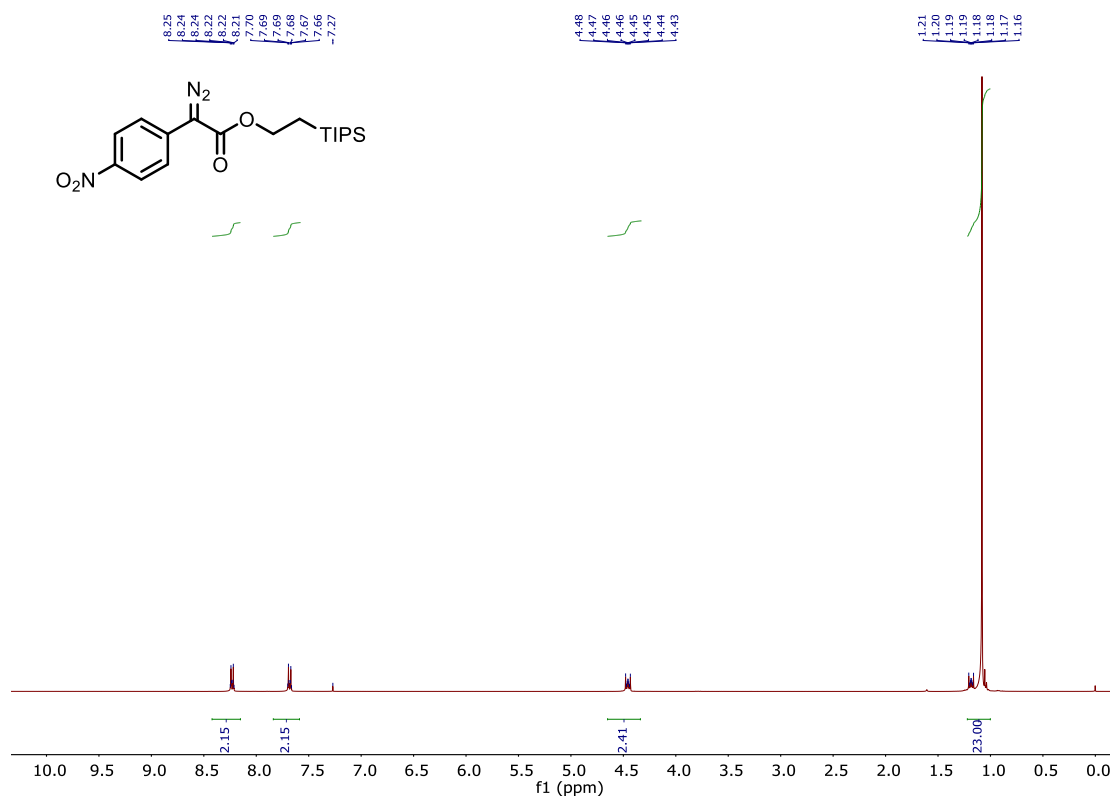
^1H and ^{13}C NMR for compound **3a**



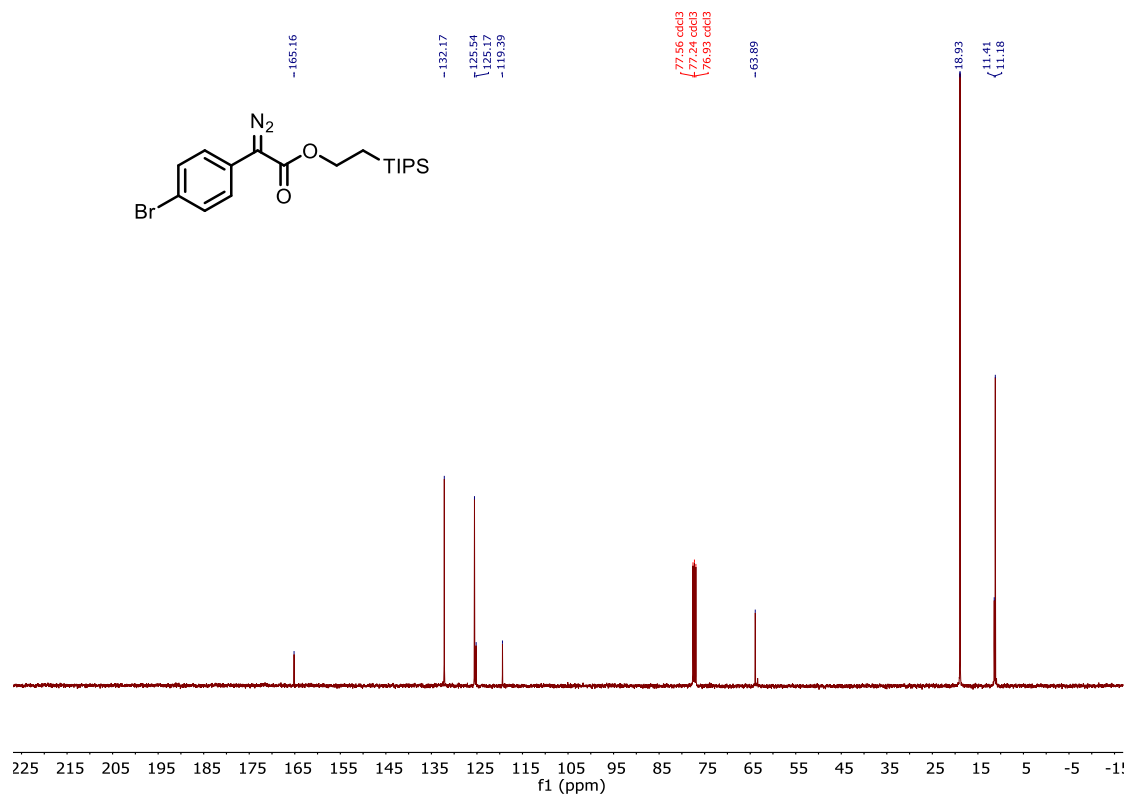
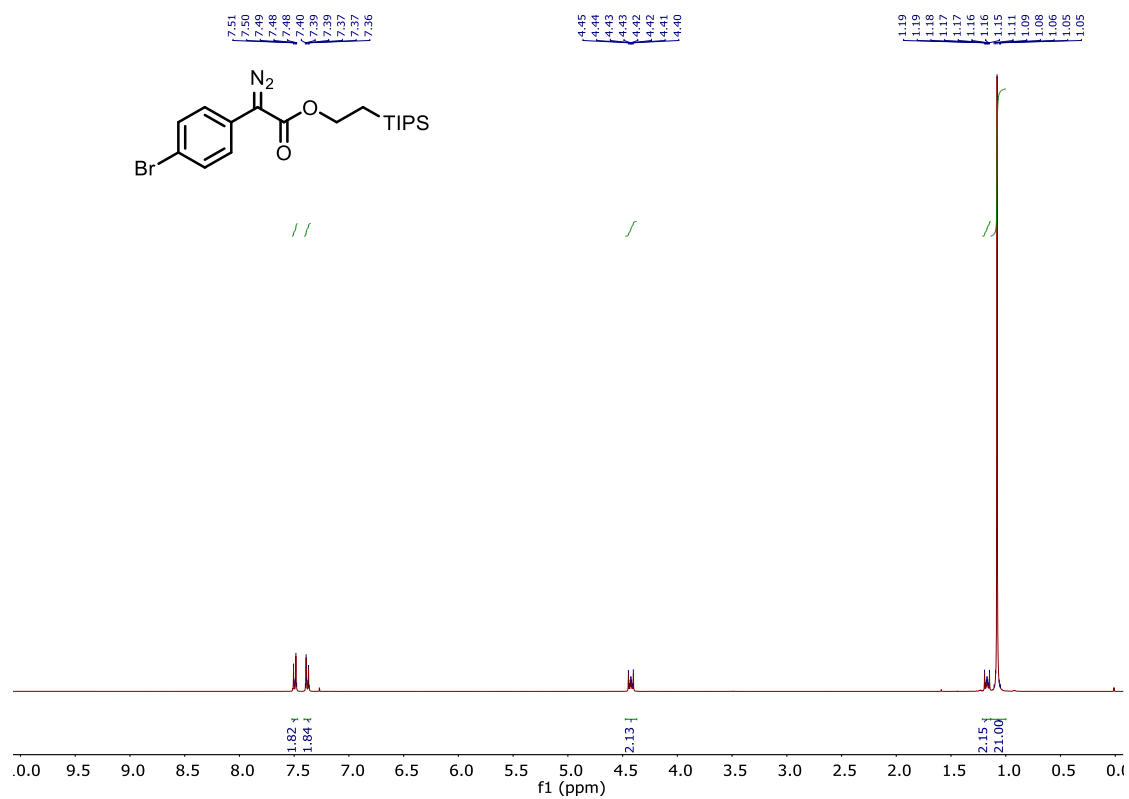
¹H and ¹³C NMR for compound **3b**



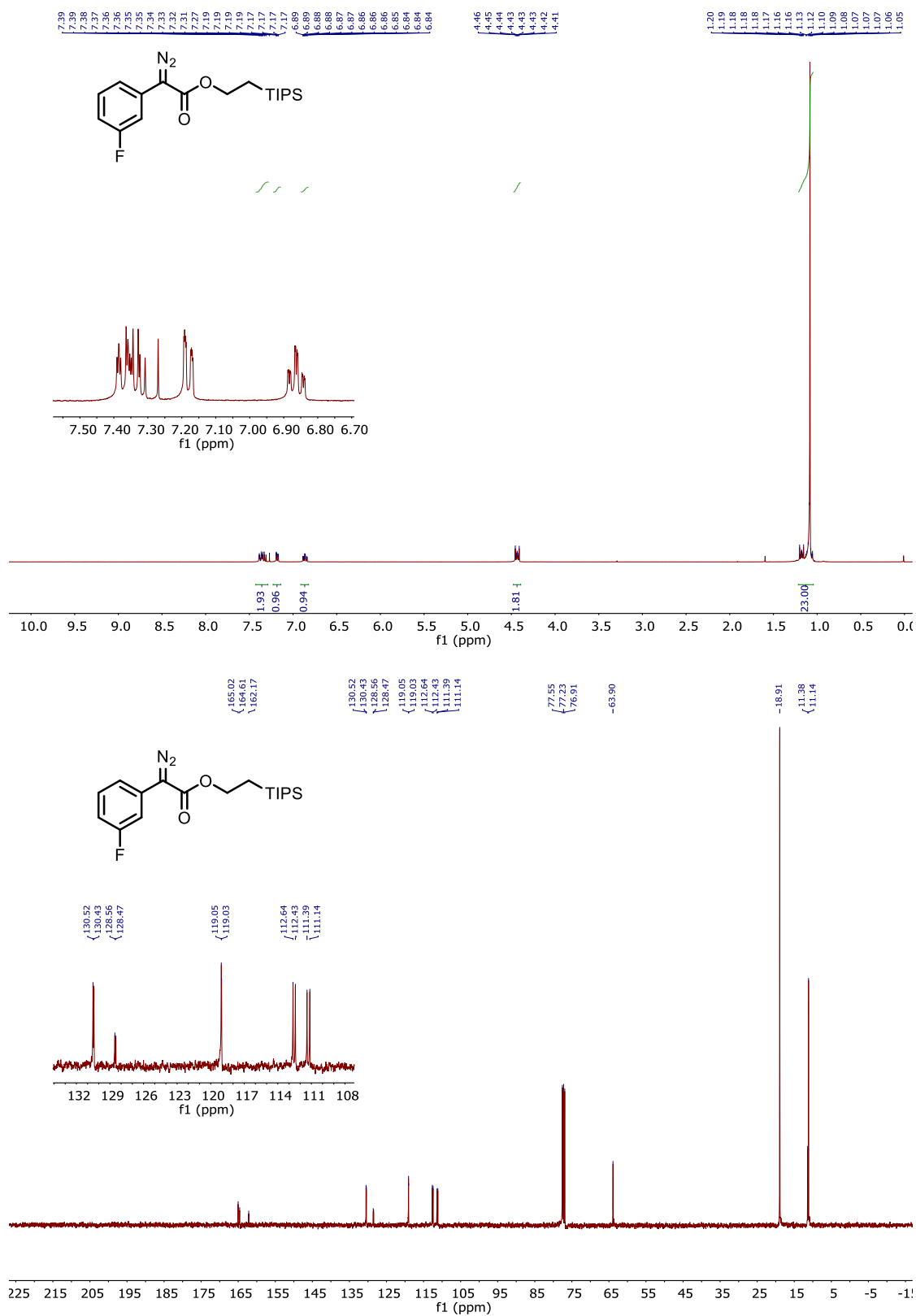
¹H and ¹³C NMR for compound **3c**



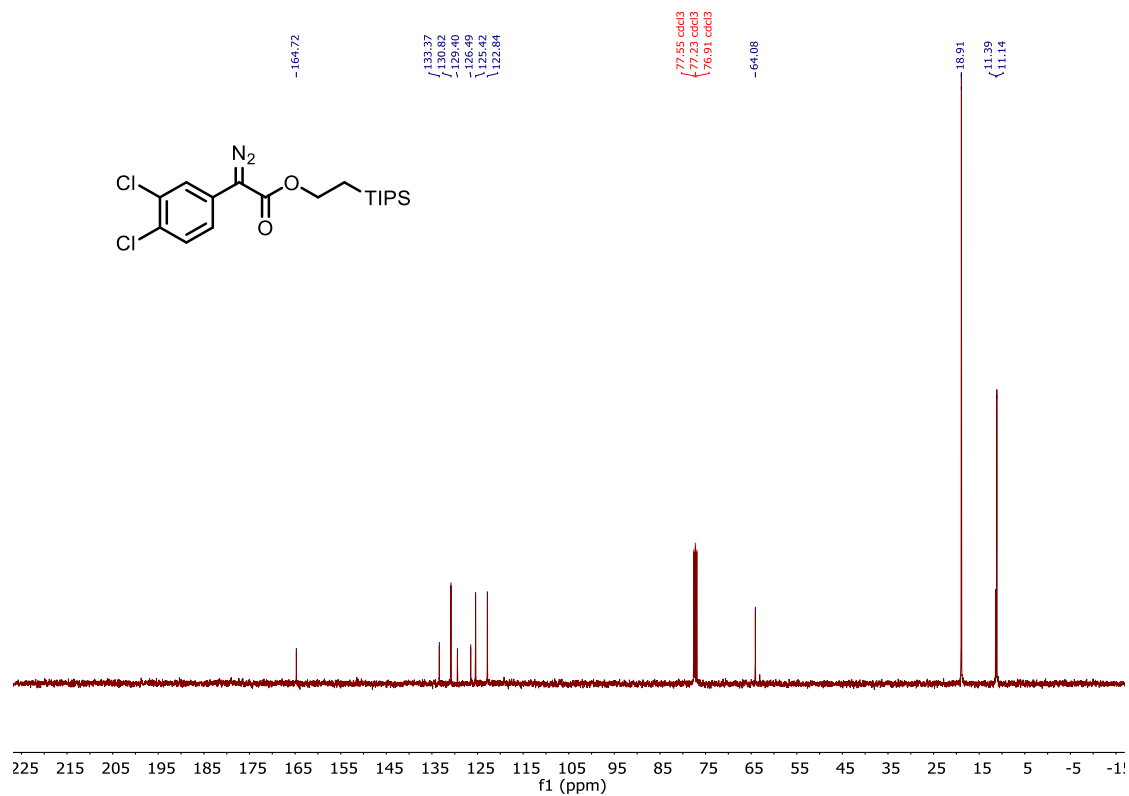
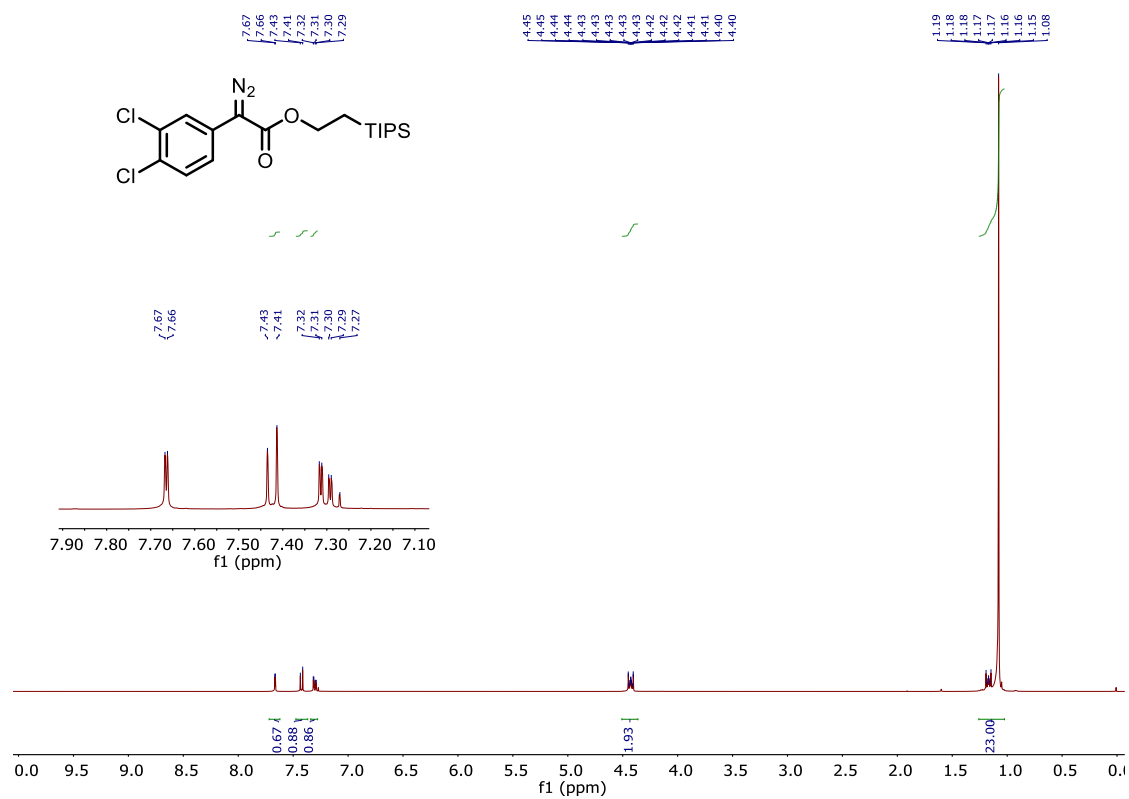
¹H and ¹³C NMR for compound **3d**



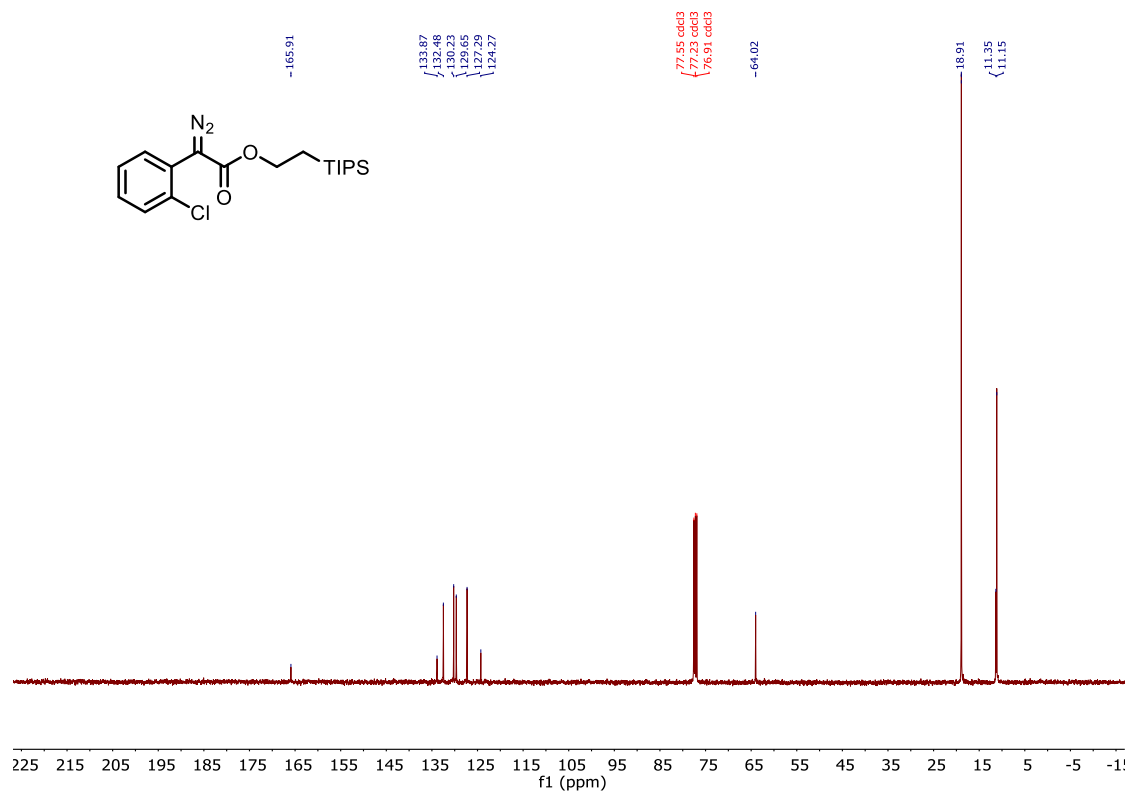
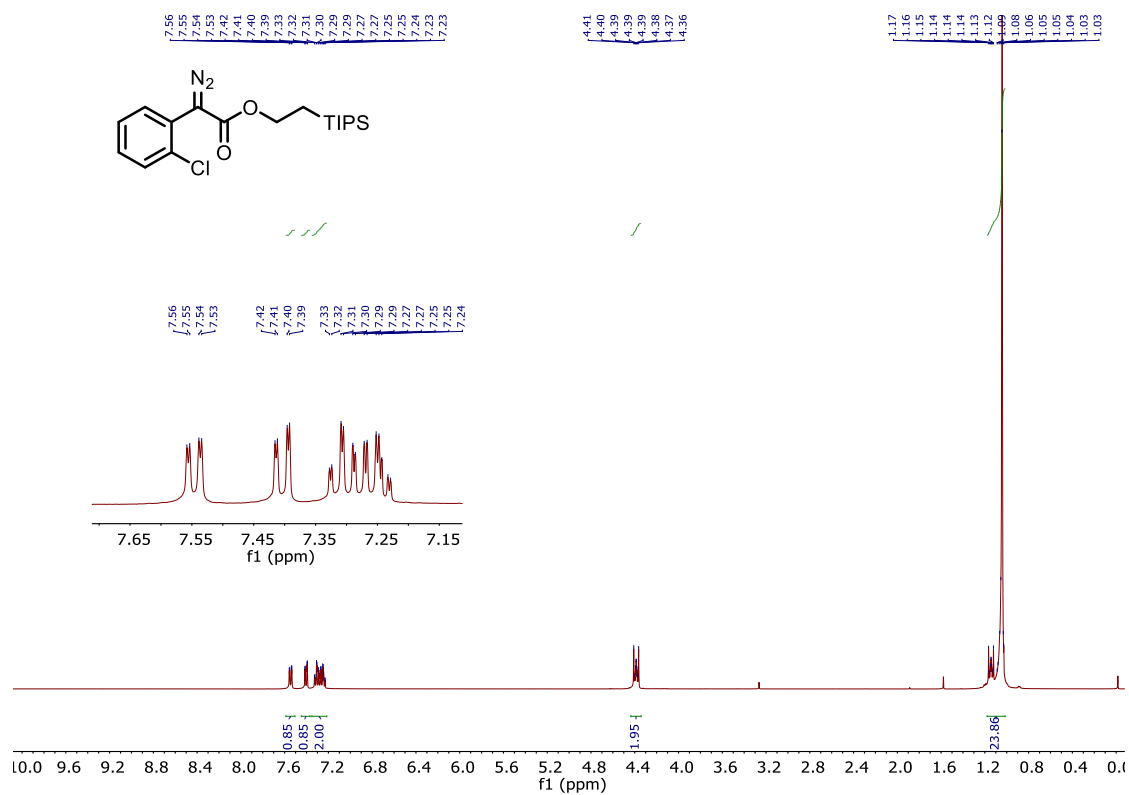
¹H and ¹³C NMR for compound **3e**



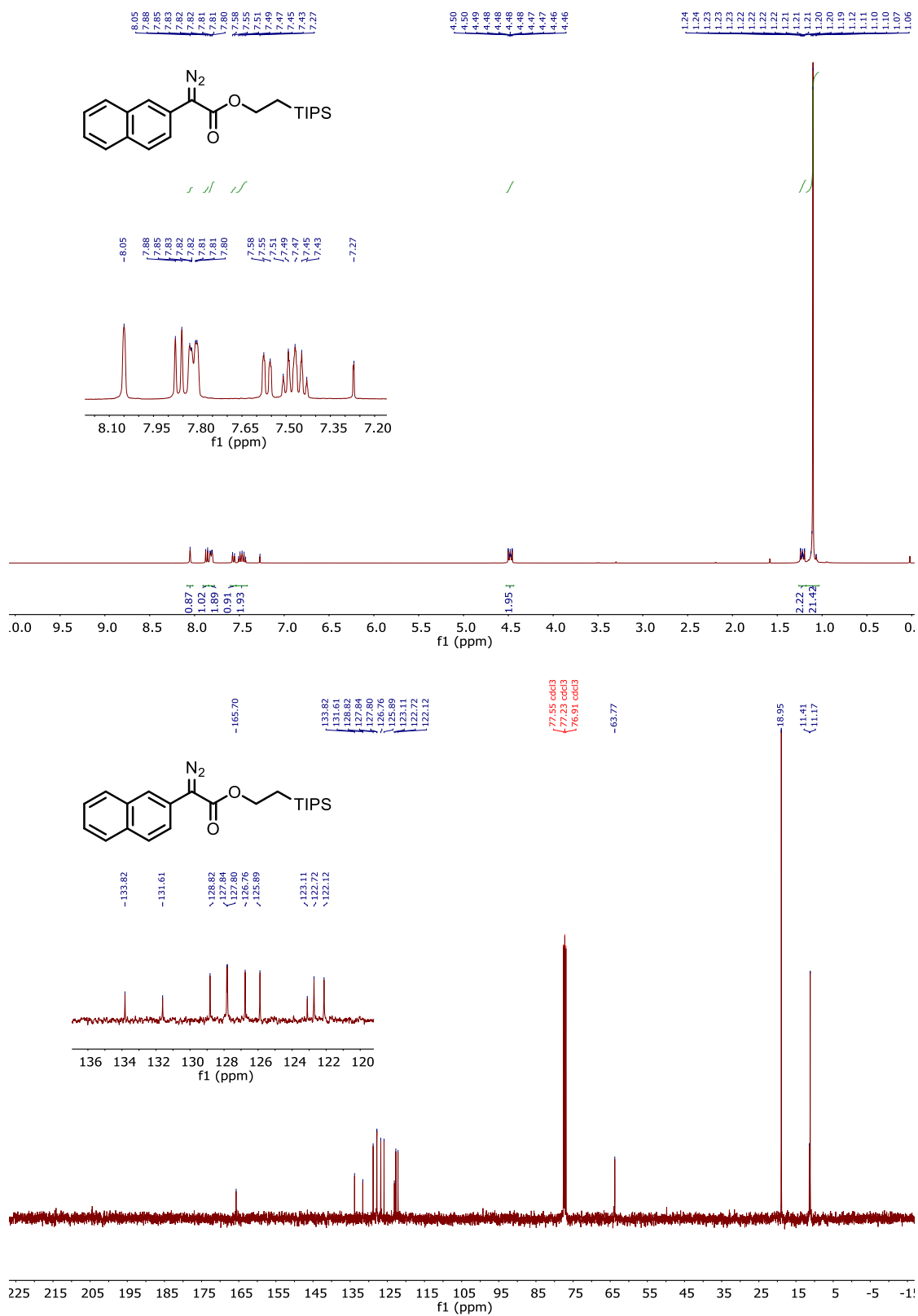
¹H and ¹³C NMR for compound **3f**



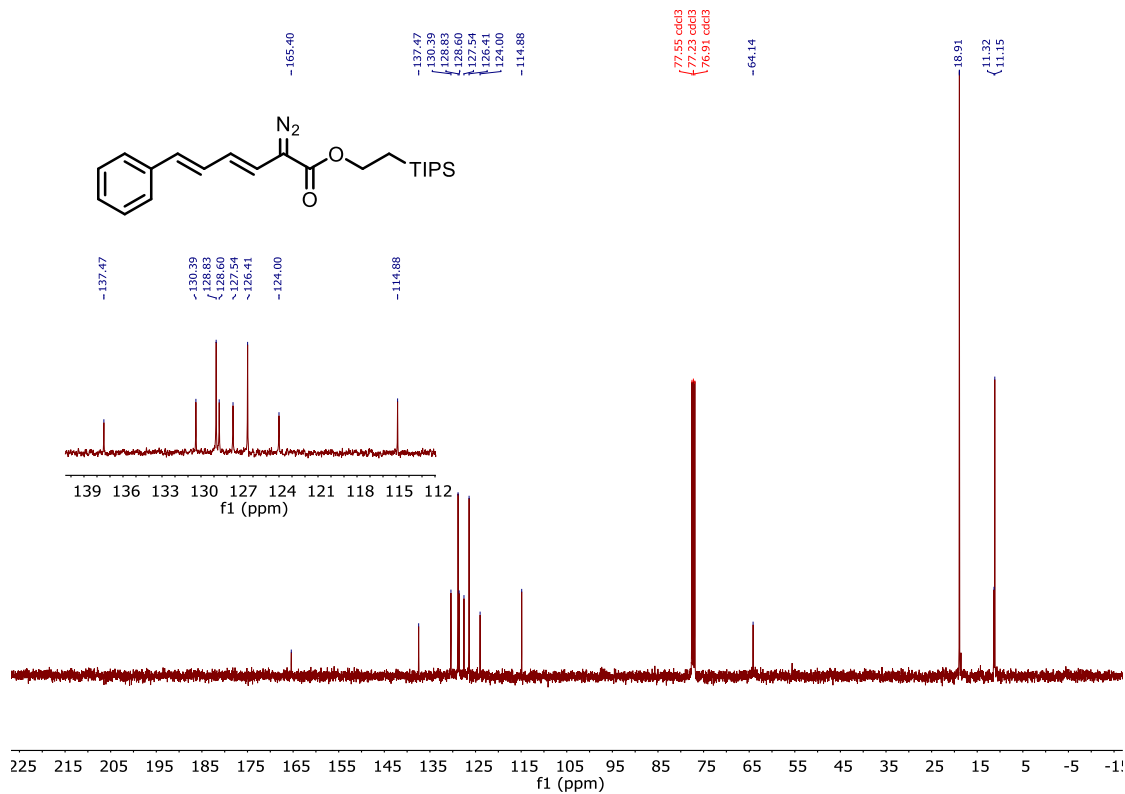
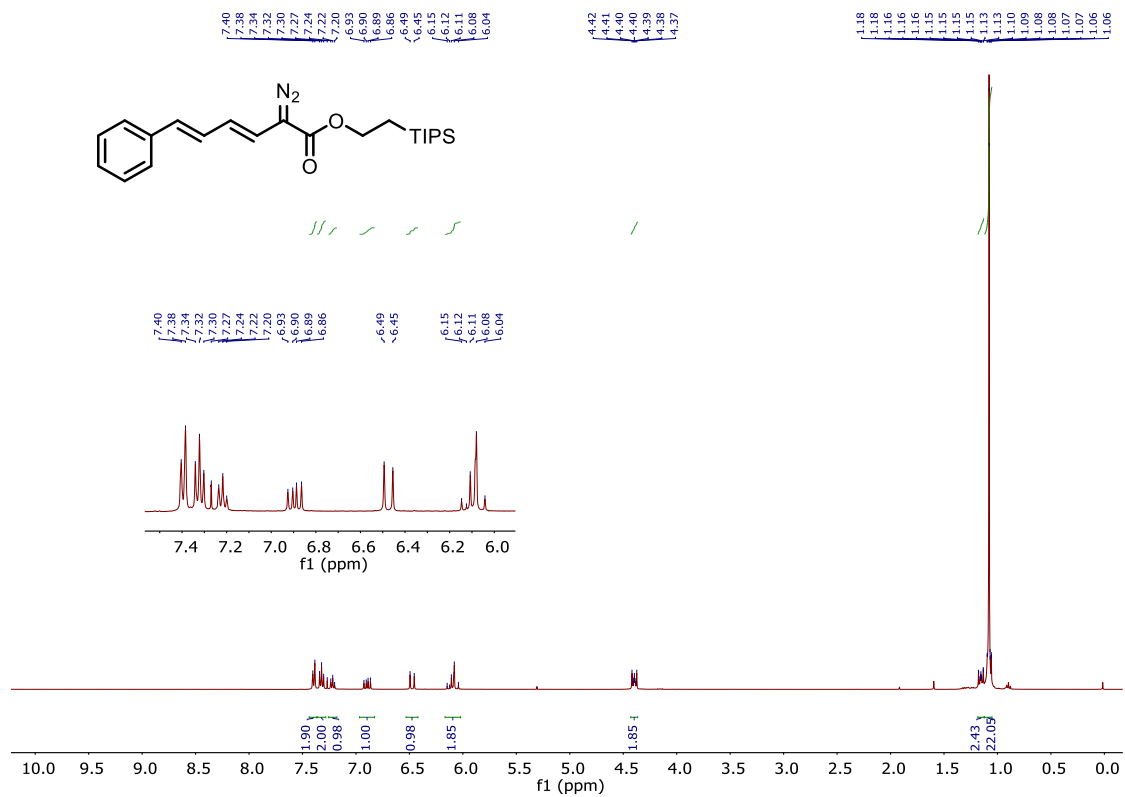
¹H and ¹³C NMR for compound **3g**



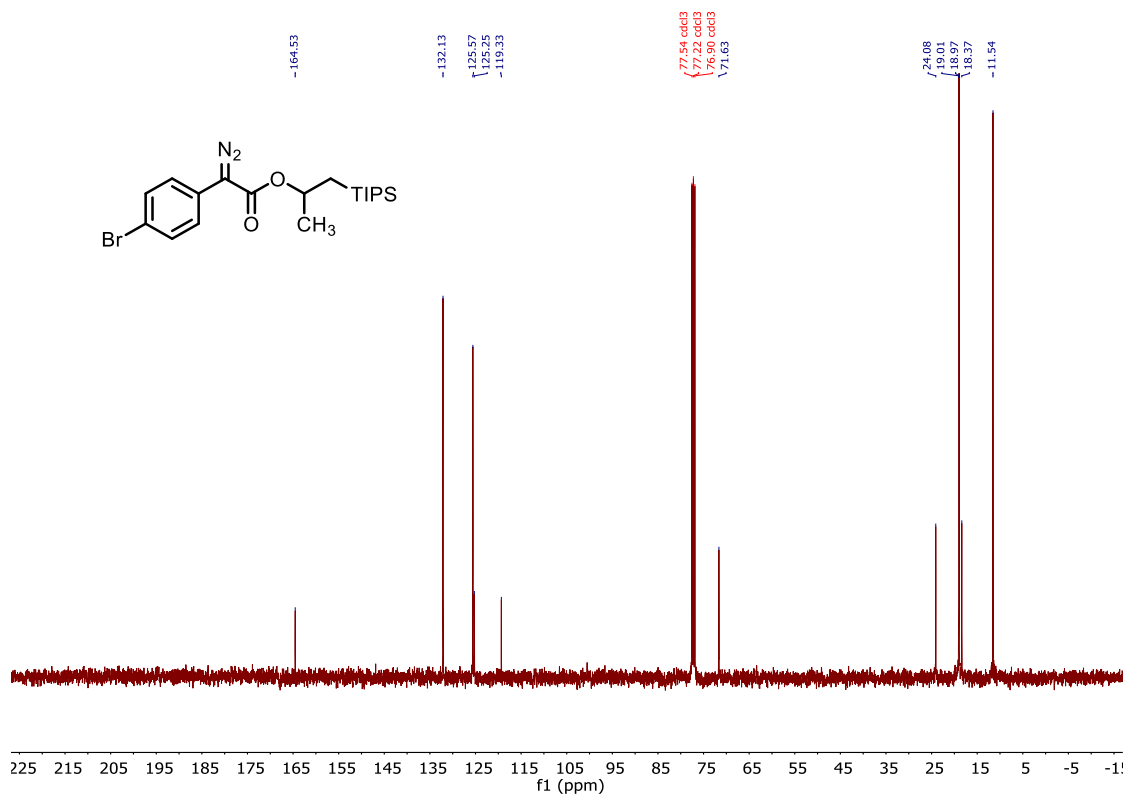
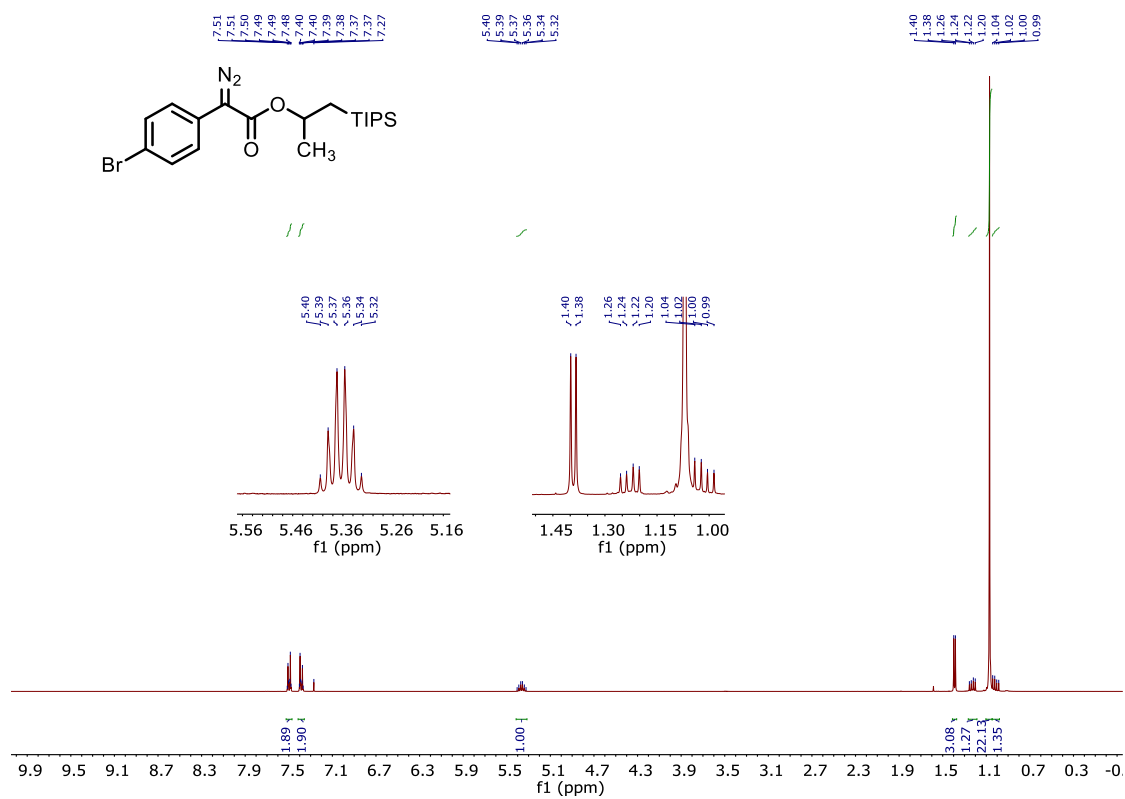
¹H and ¹³C NMR for compound **3h**



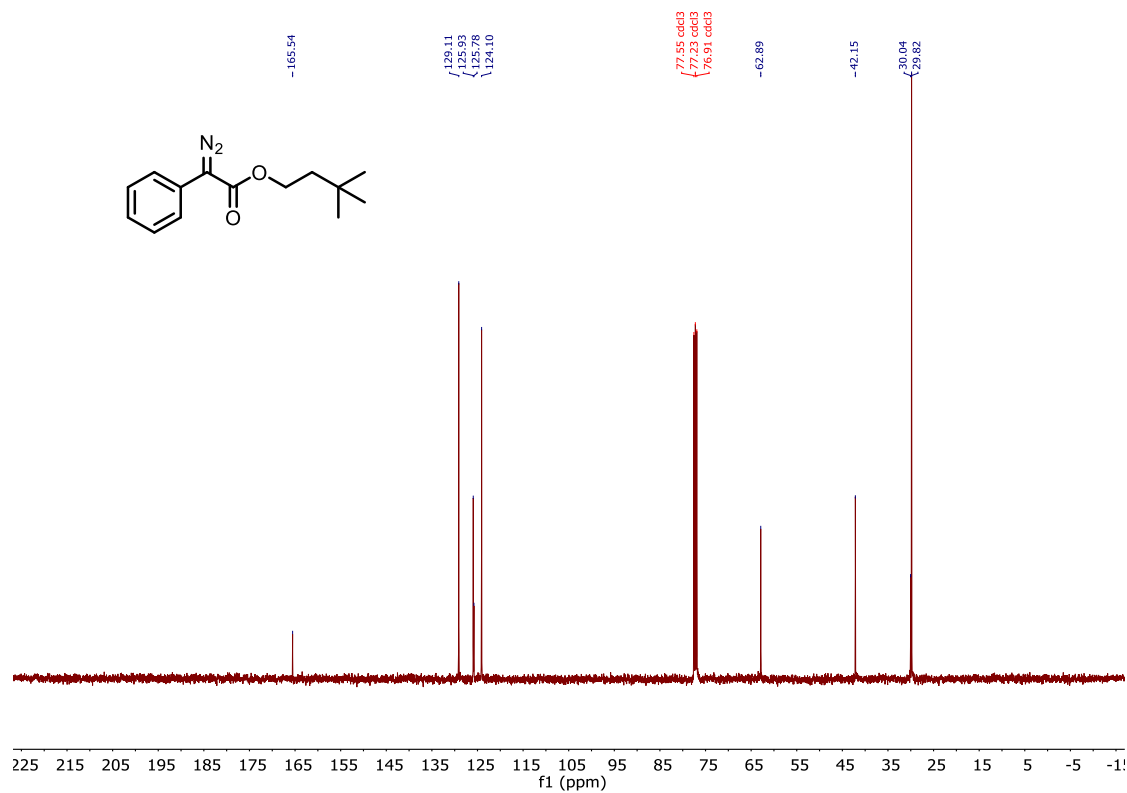
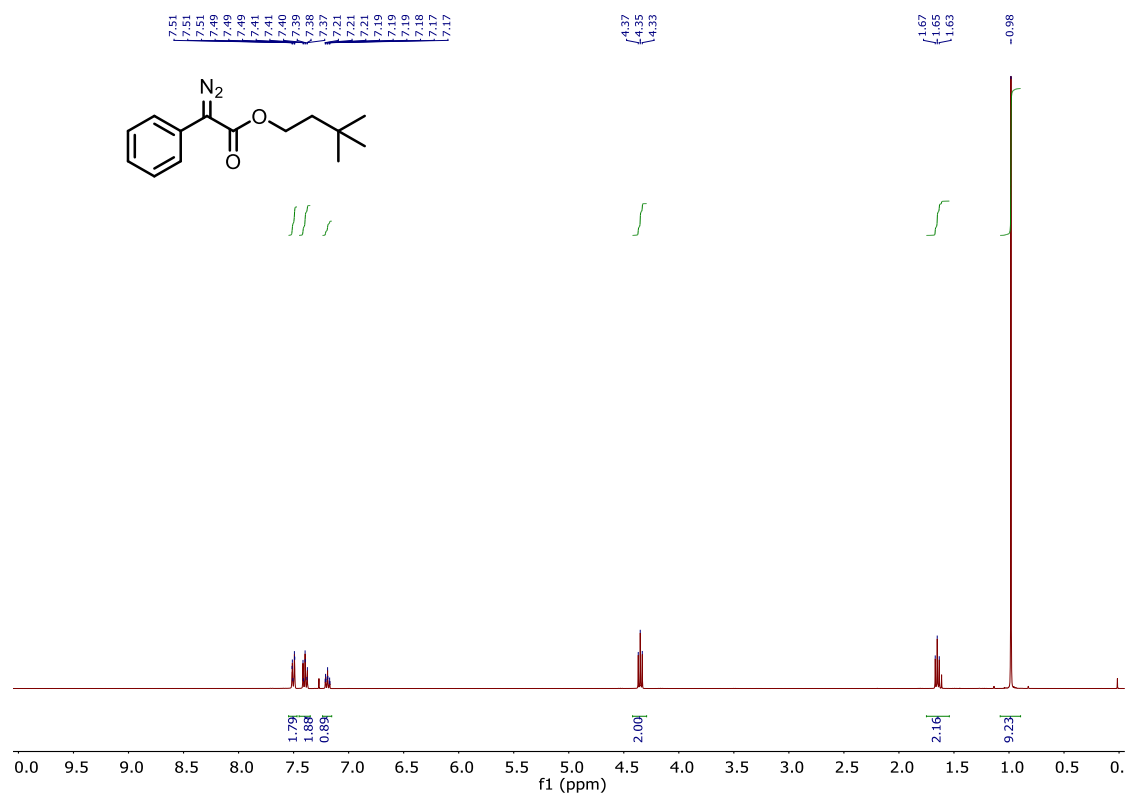
¹H and ¹³C NMR for compound 3i



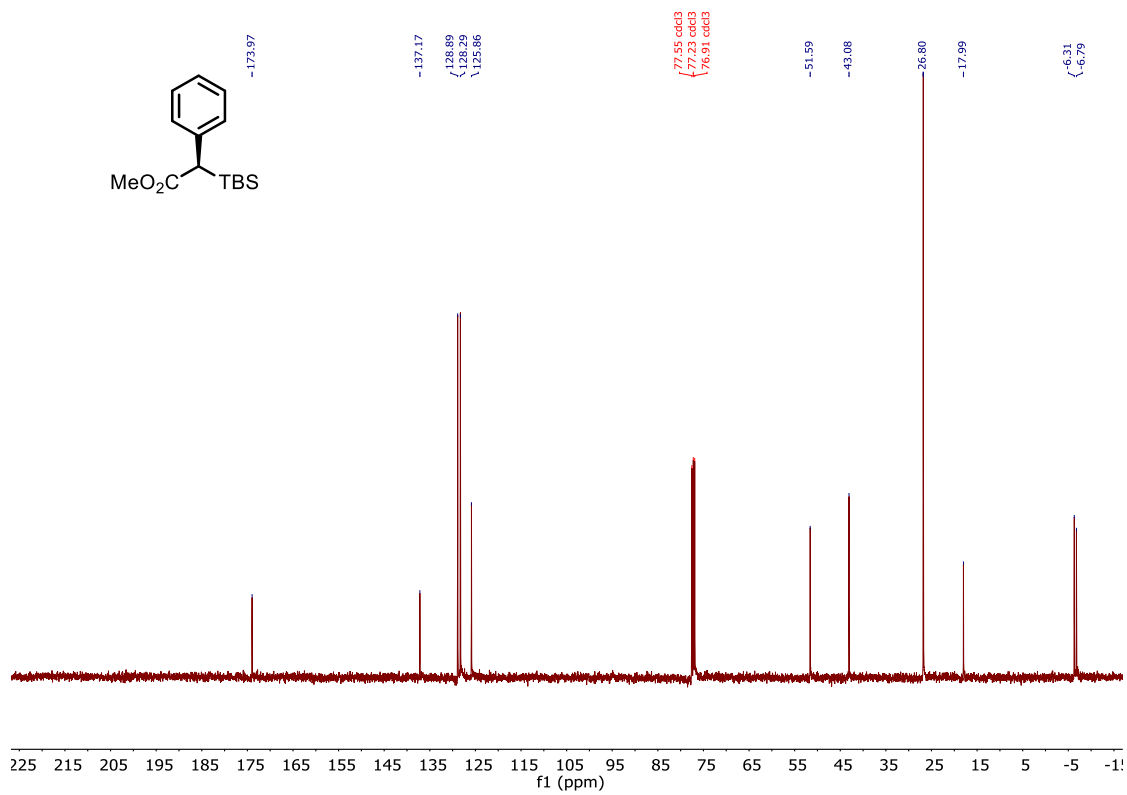
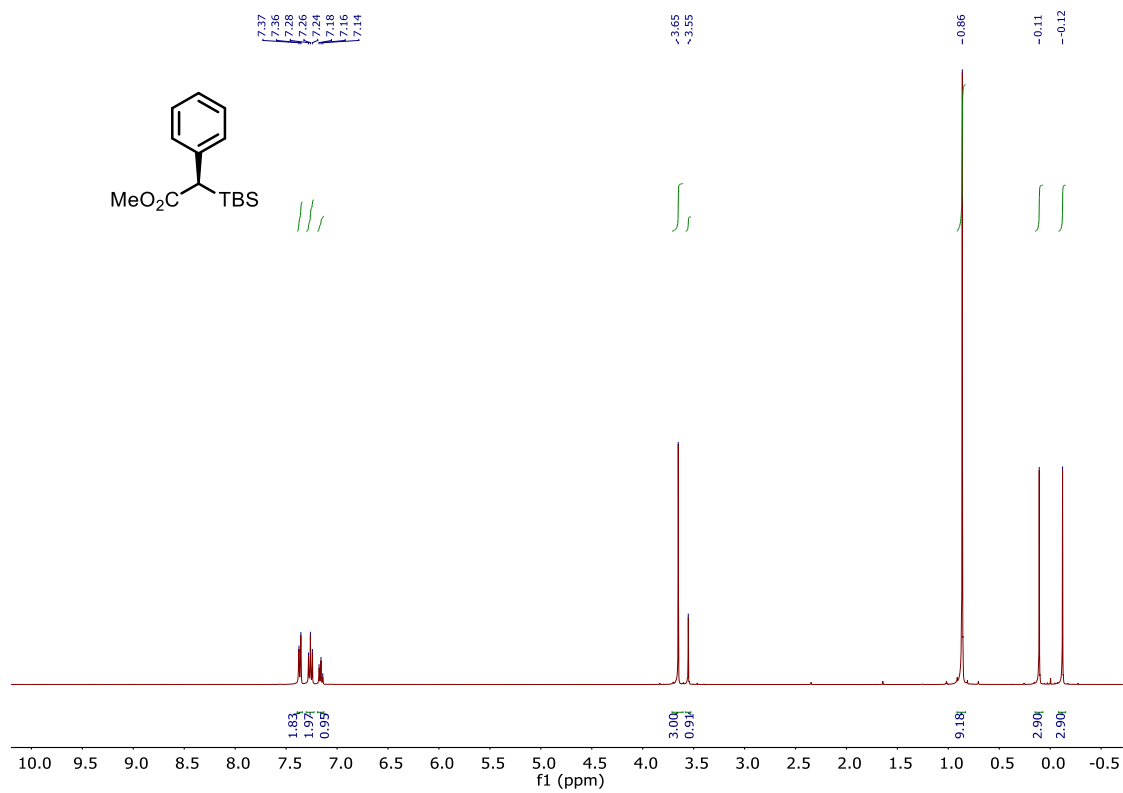
¹H and ¹³C NMR for compound **3k**



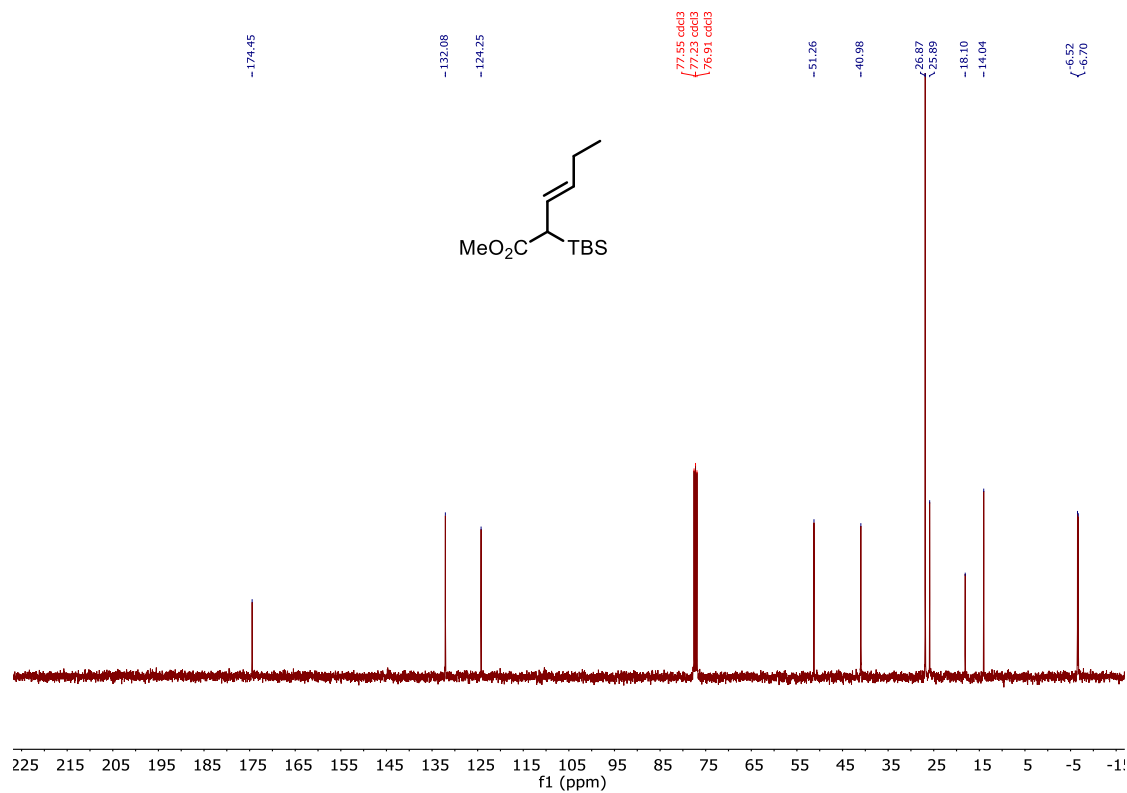
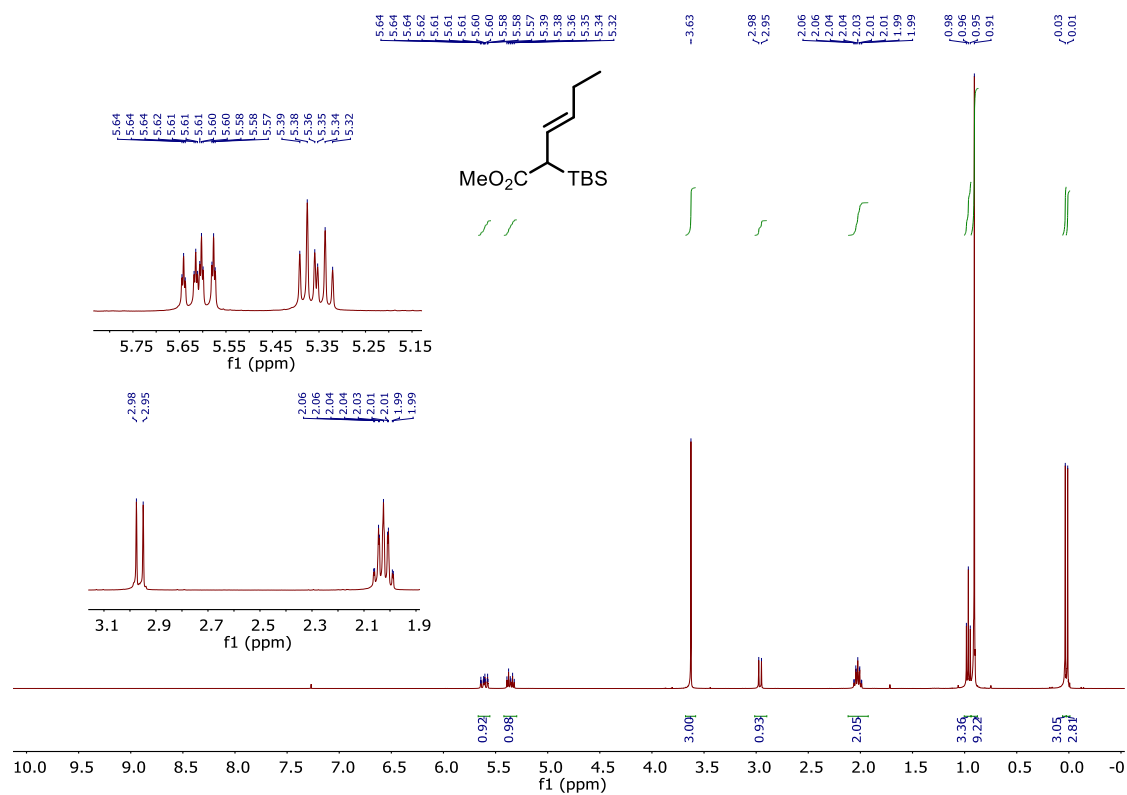
¹H and ¹³C NMR for compound **31**

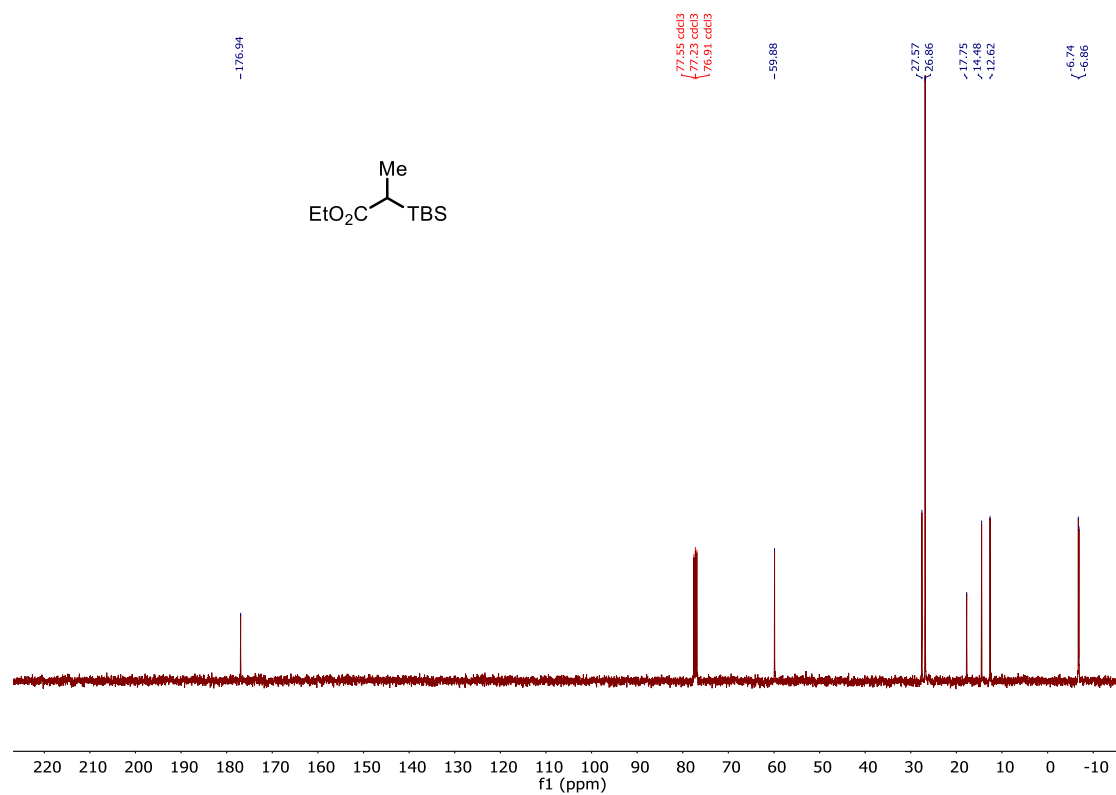
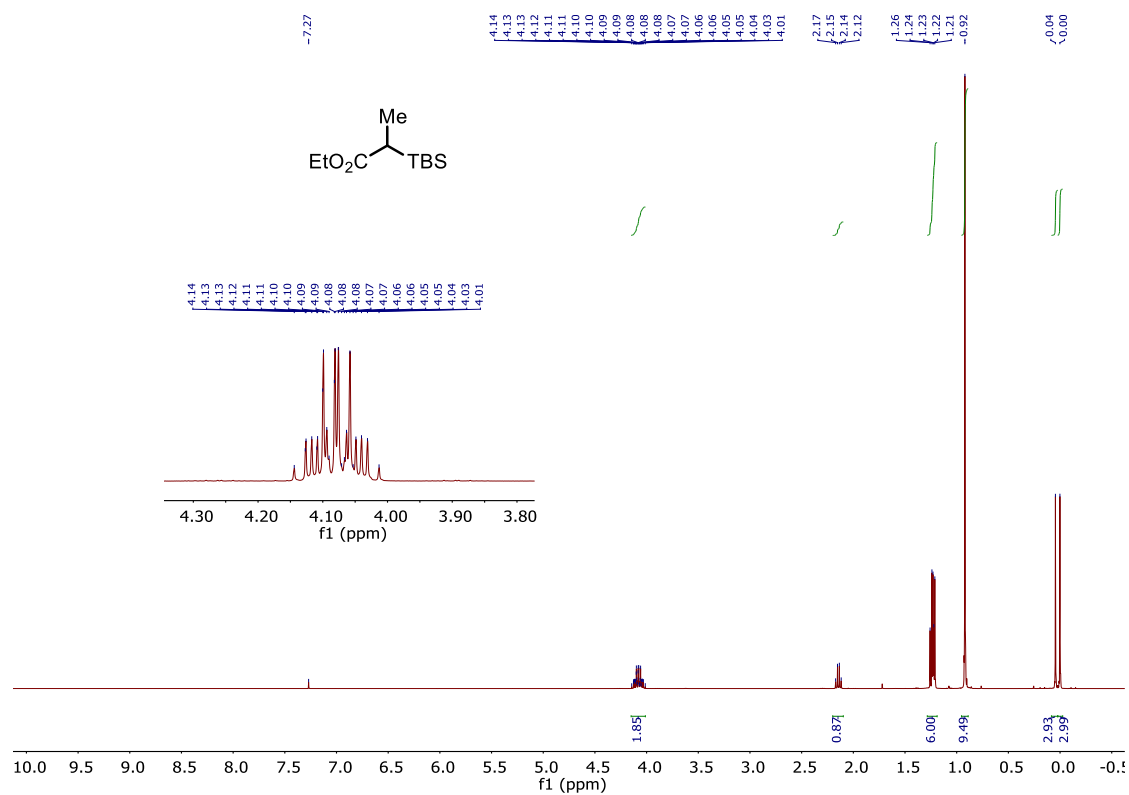


¹H and ¹³C NMR for compound S5

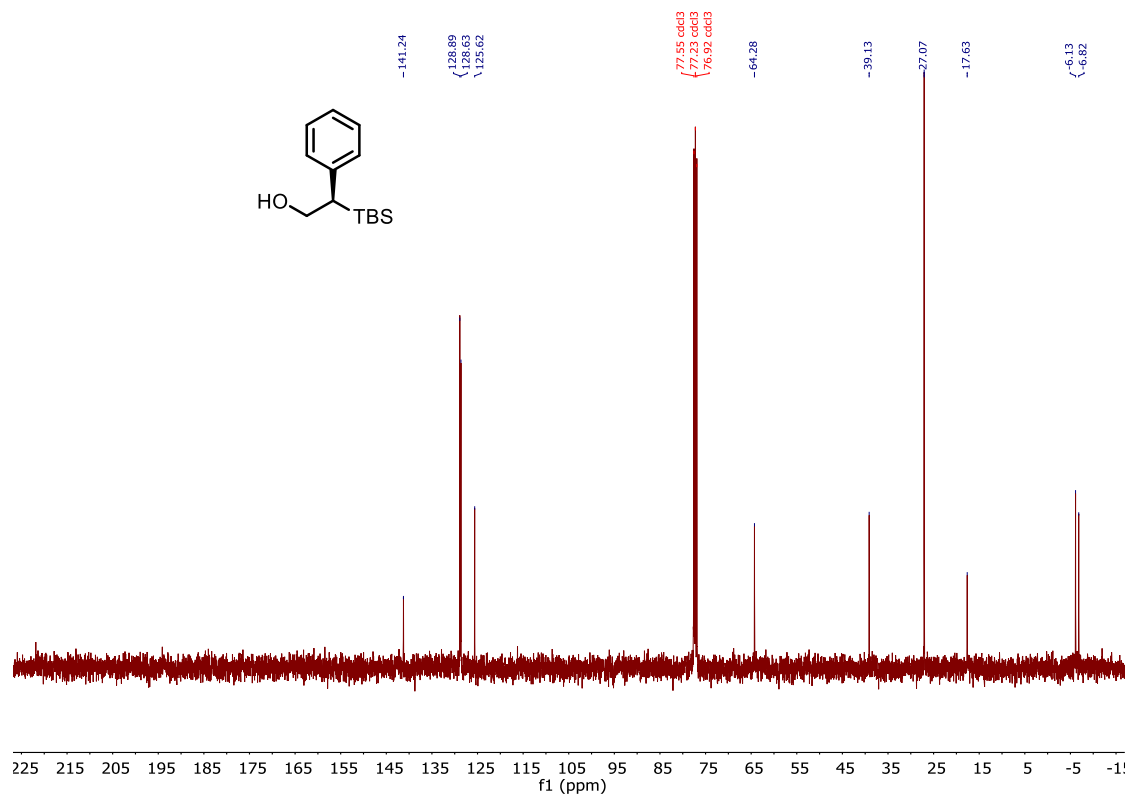
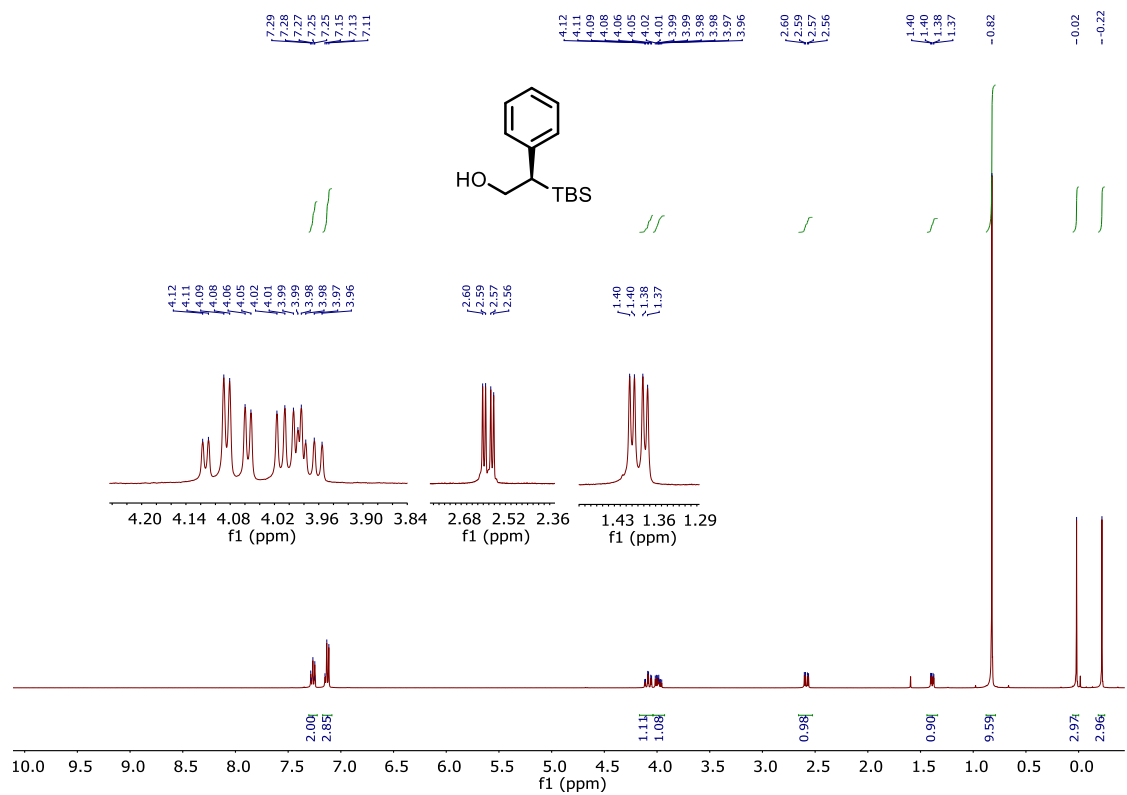


¹H and ¹³C NMR for compound **(R)-8a**

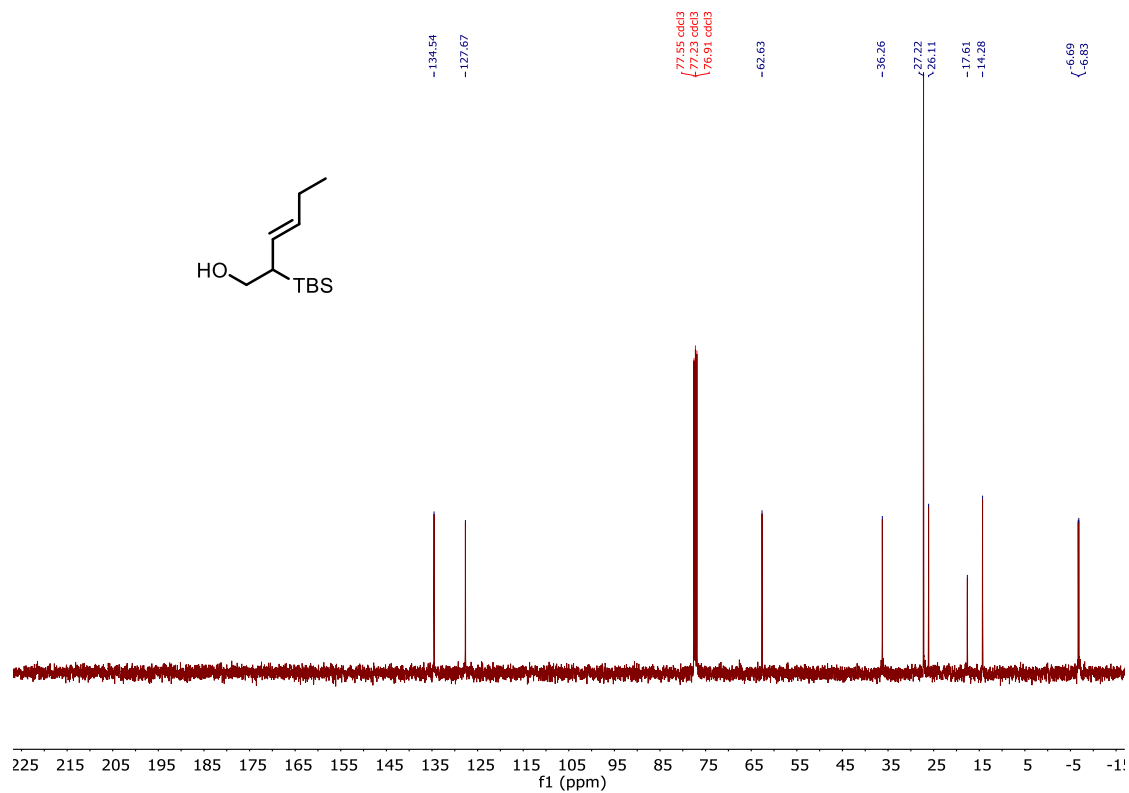
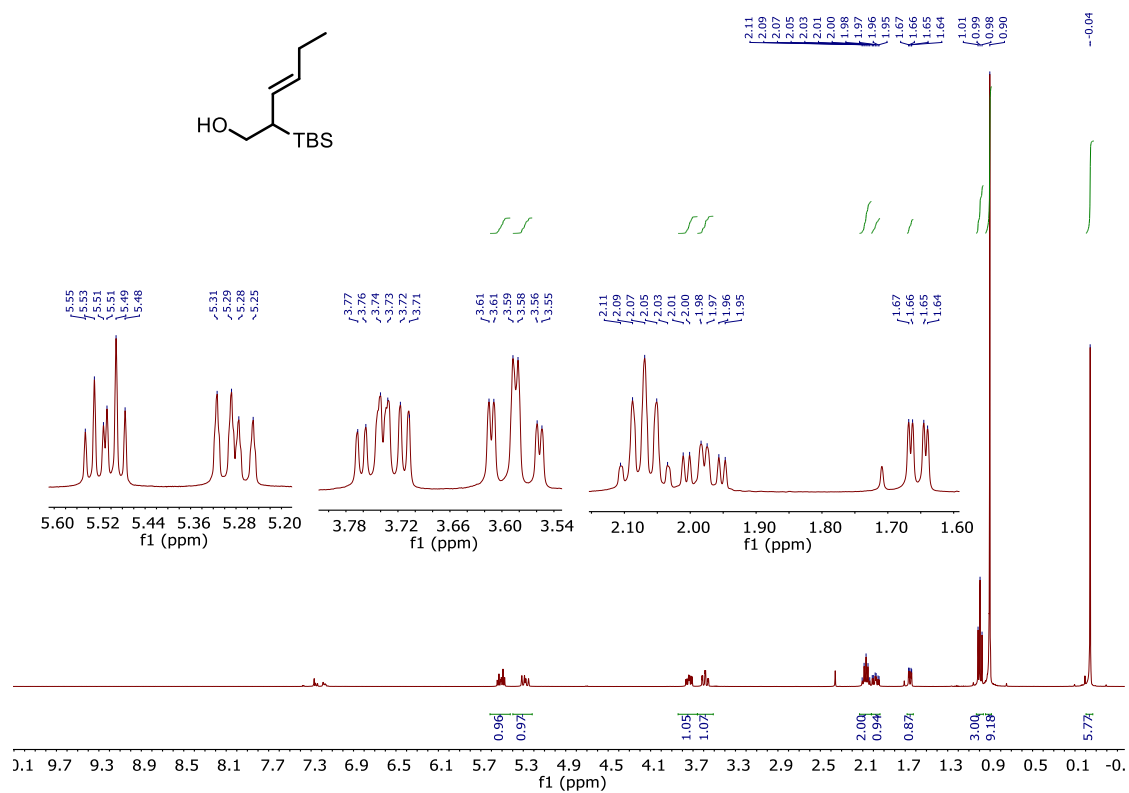
¹H and ¹³C NMR for compound **8b**



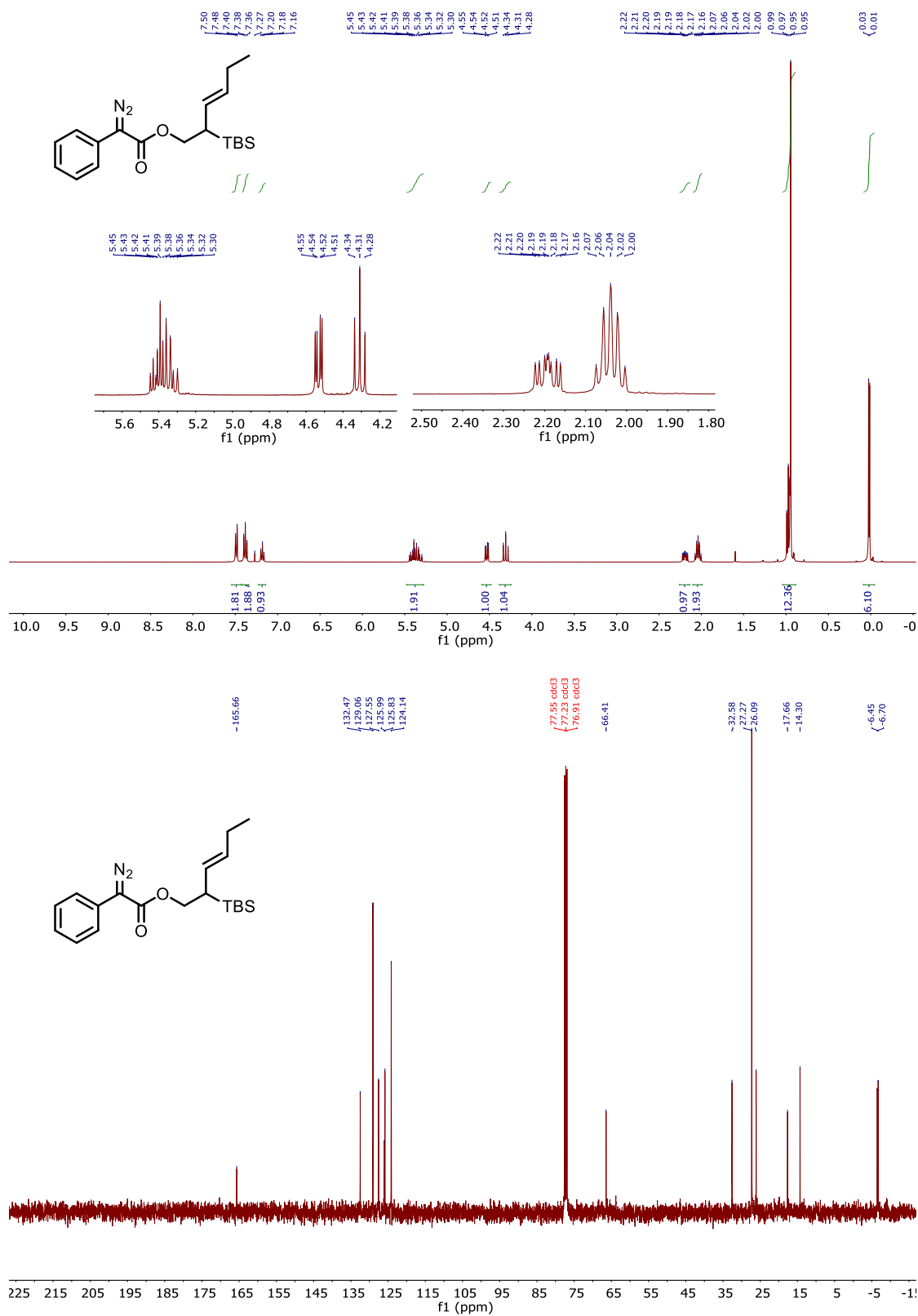
¹H and ¹³C NMR for compound **8c**



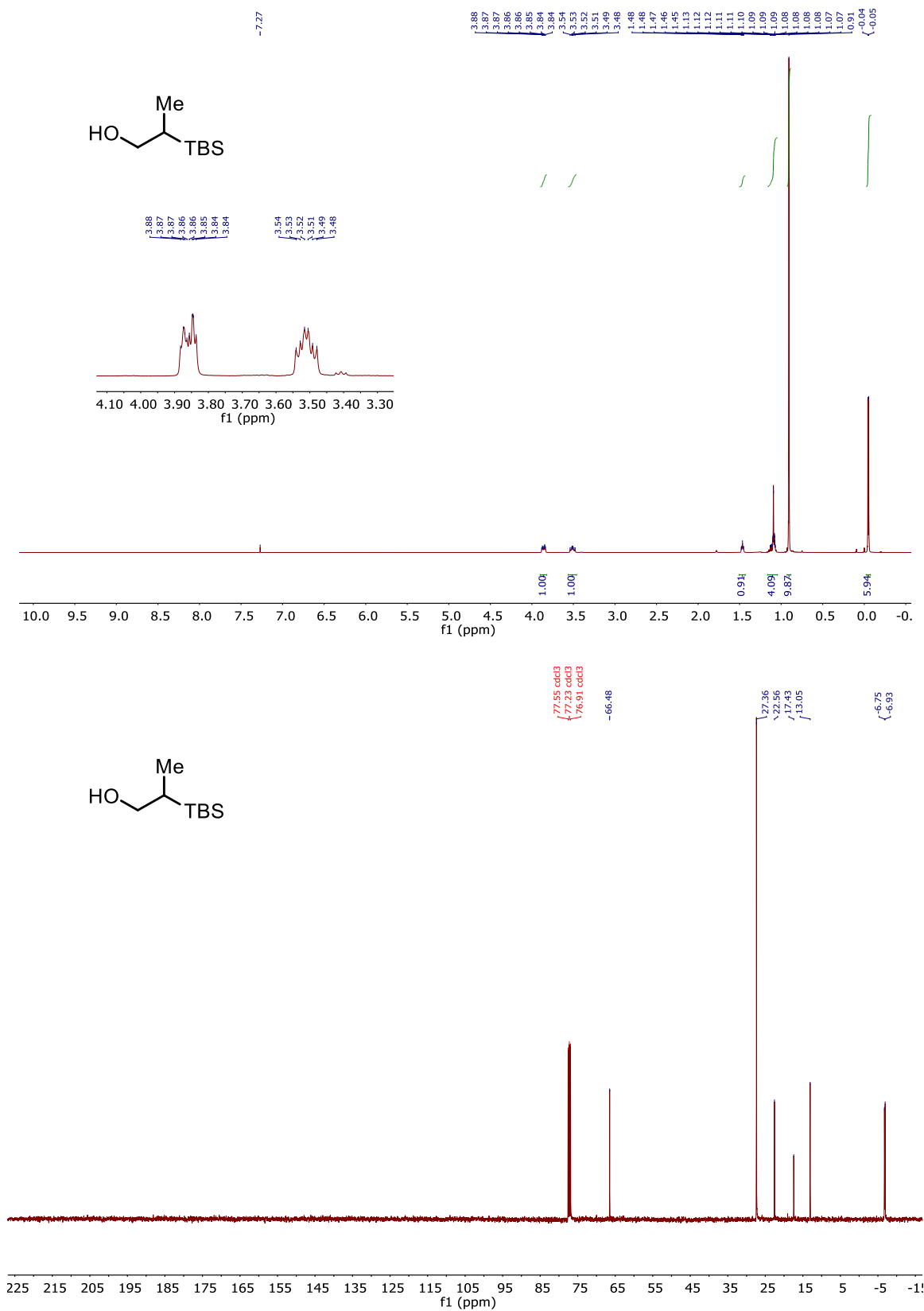
¹H and ¹³C NMR for compound (R)-9a



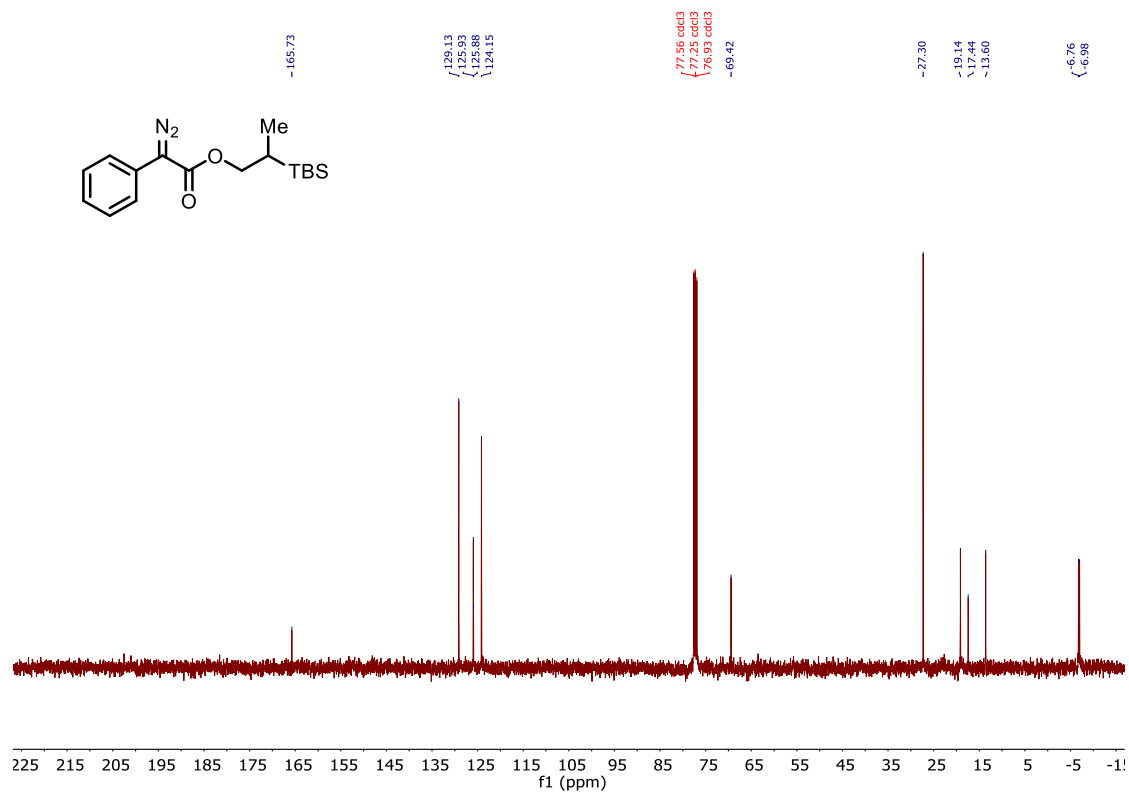
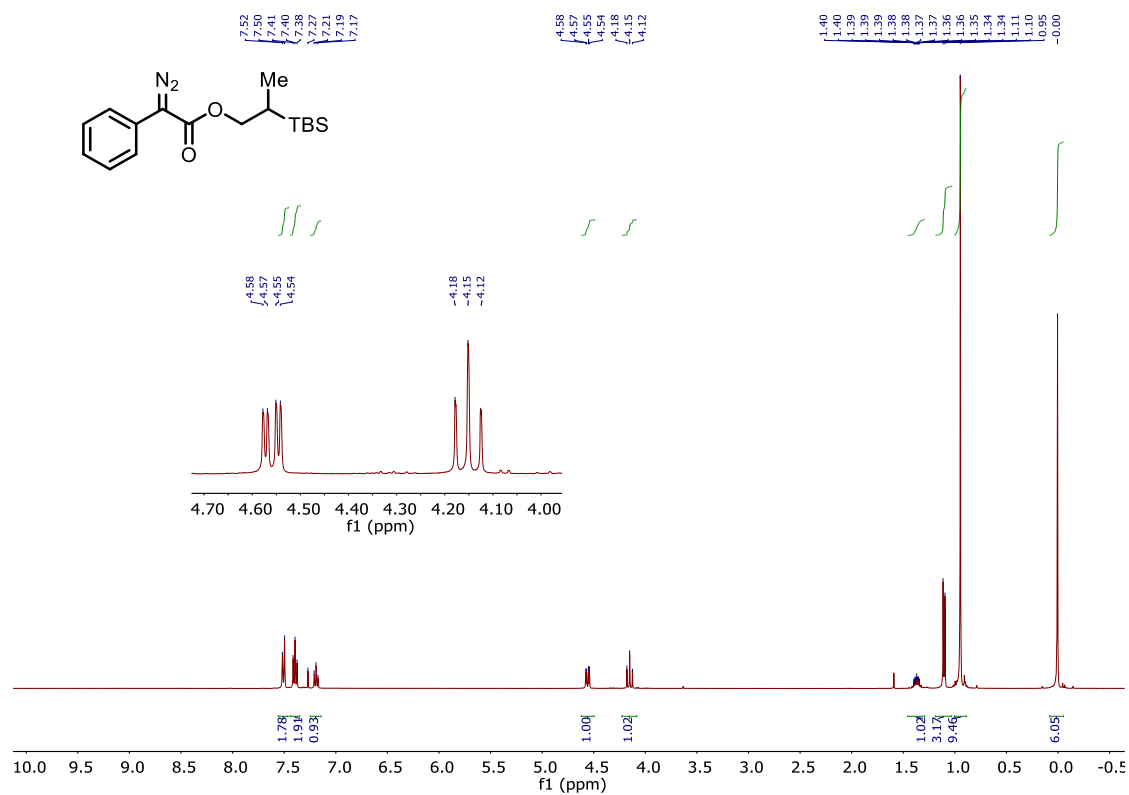
¹H and ¹³C NMR for compound **9b**



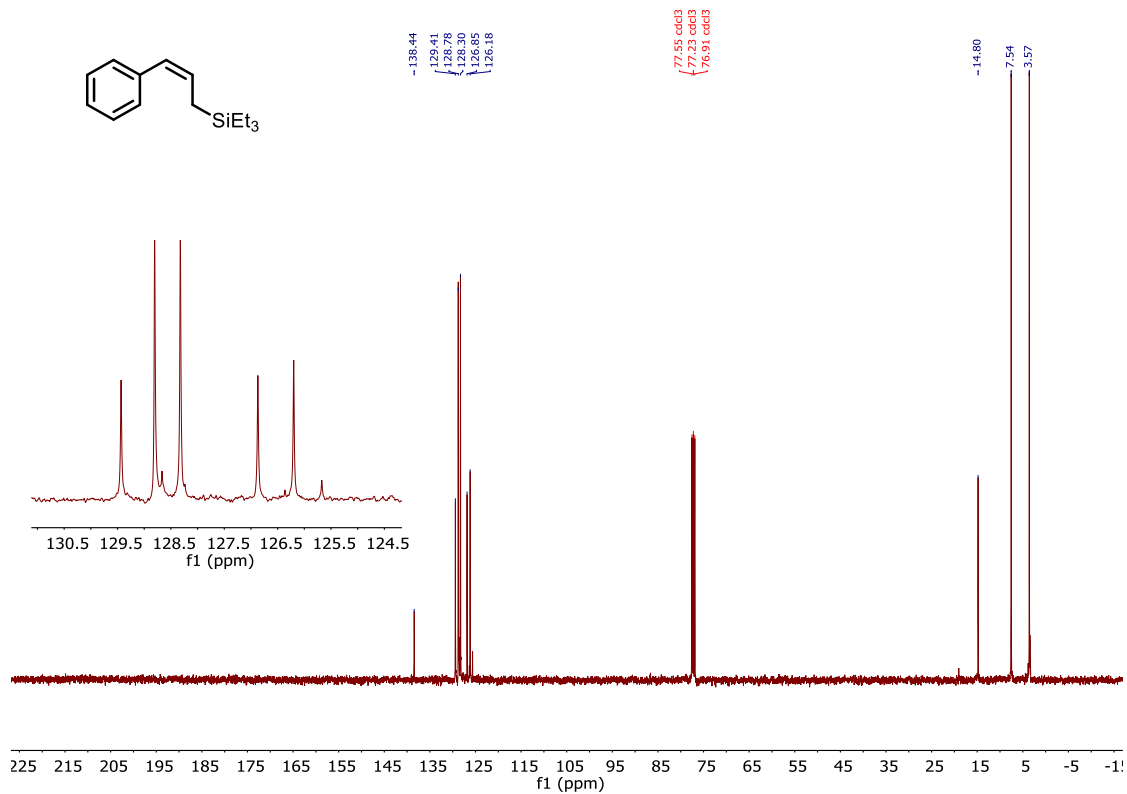
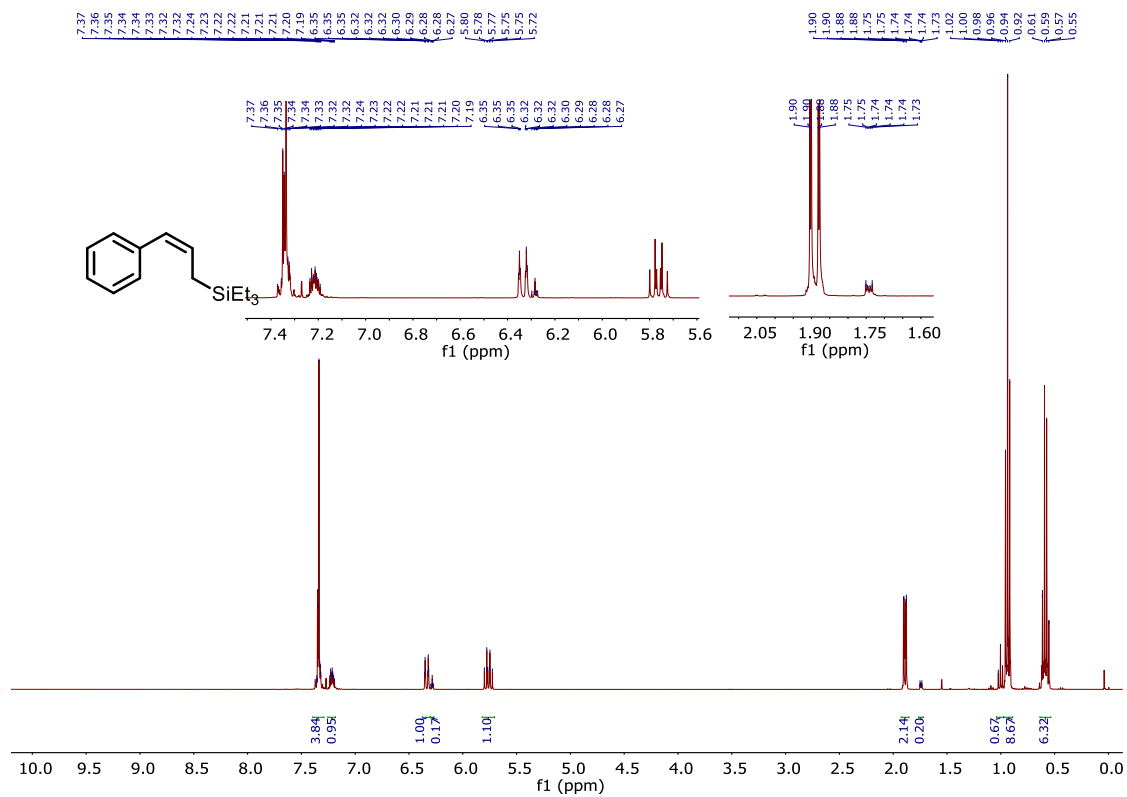
^1H and ^{13}C NMR for compound **5b**



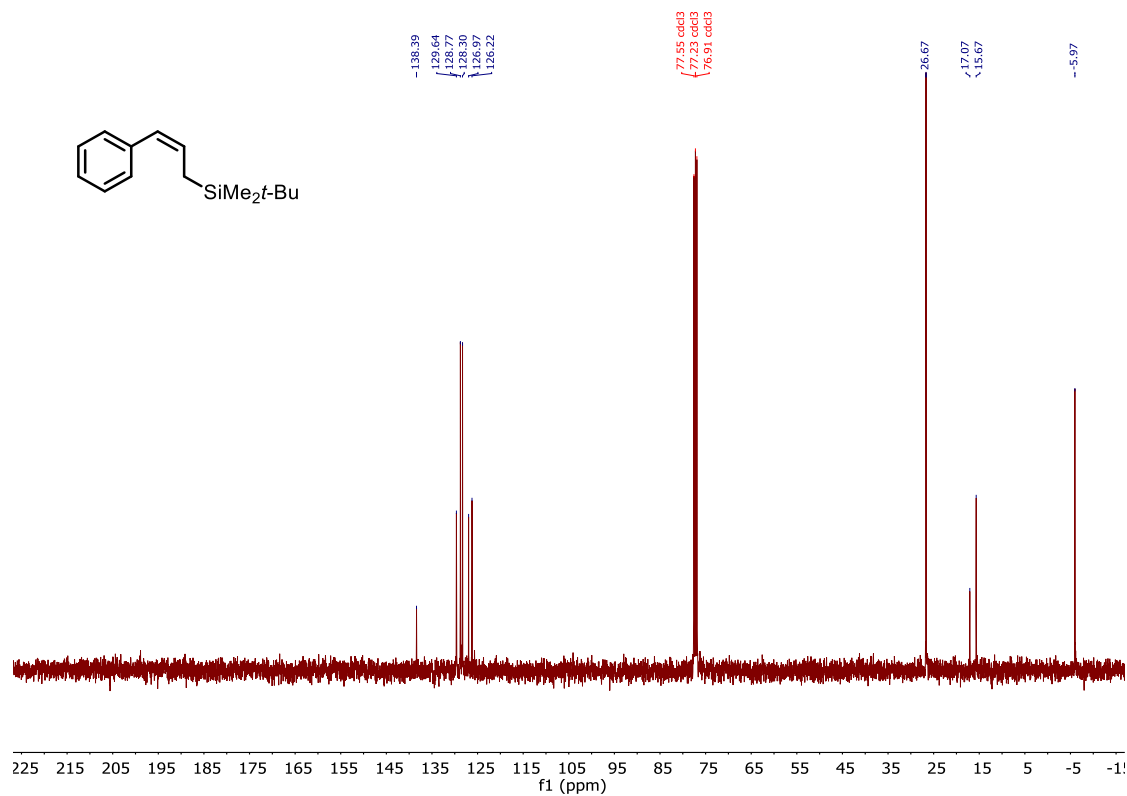
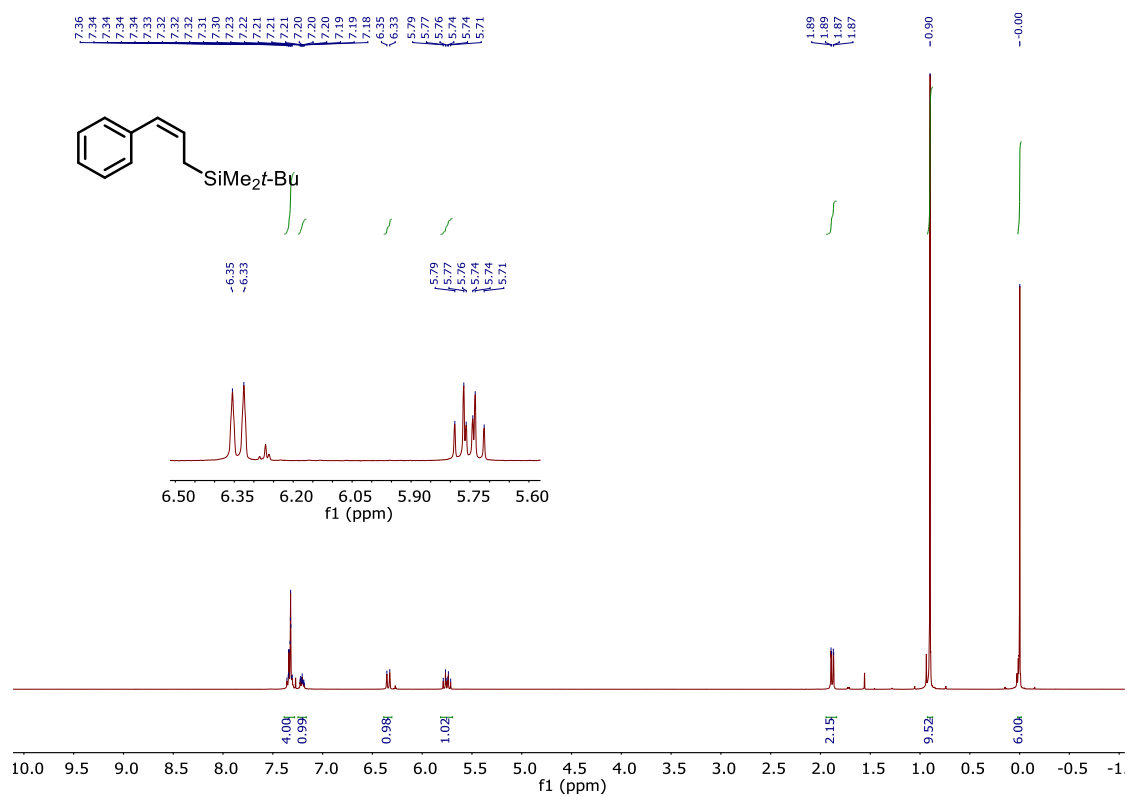
¹H and ¹³C NMR for compound **9c**



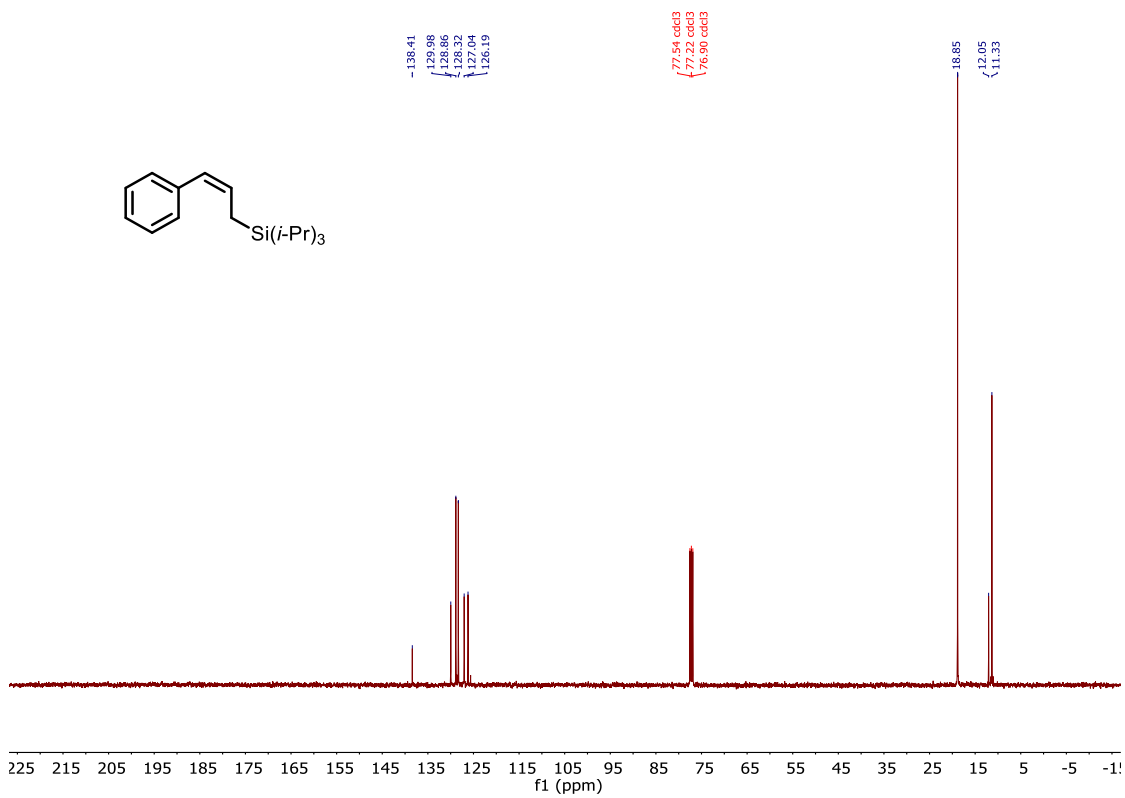
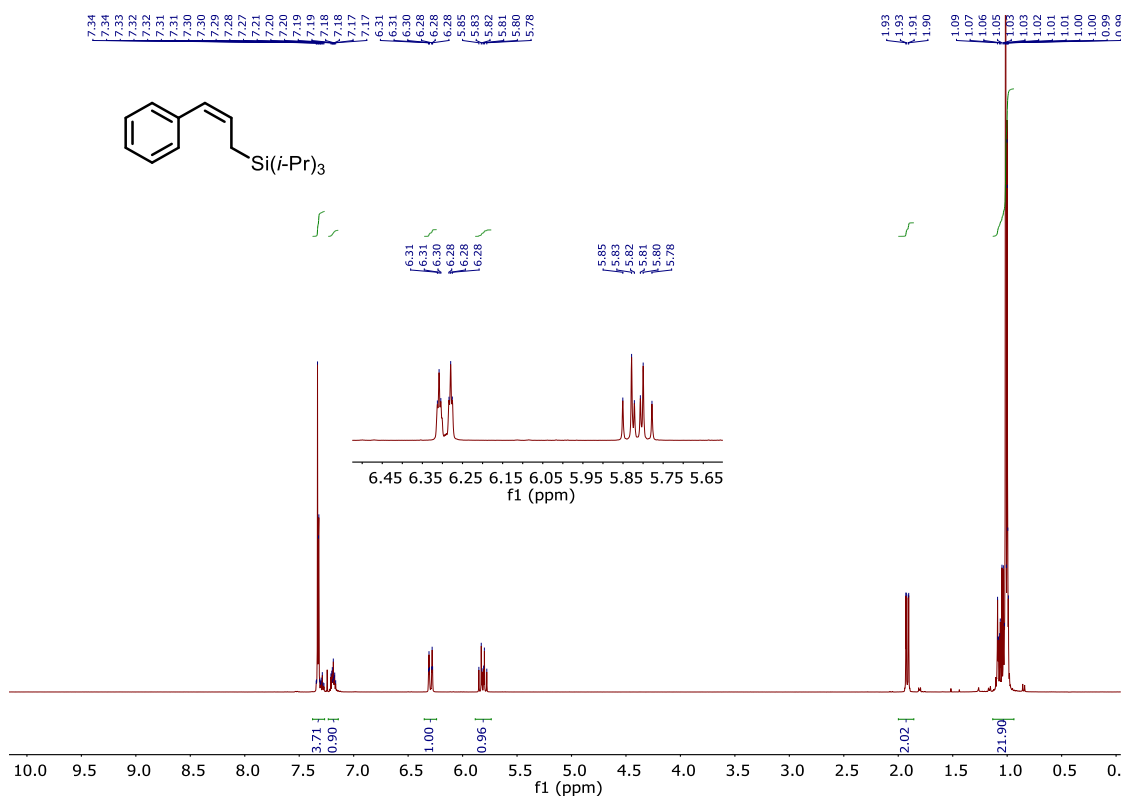
^1H and ^{13}C NMR for compound **5c**



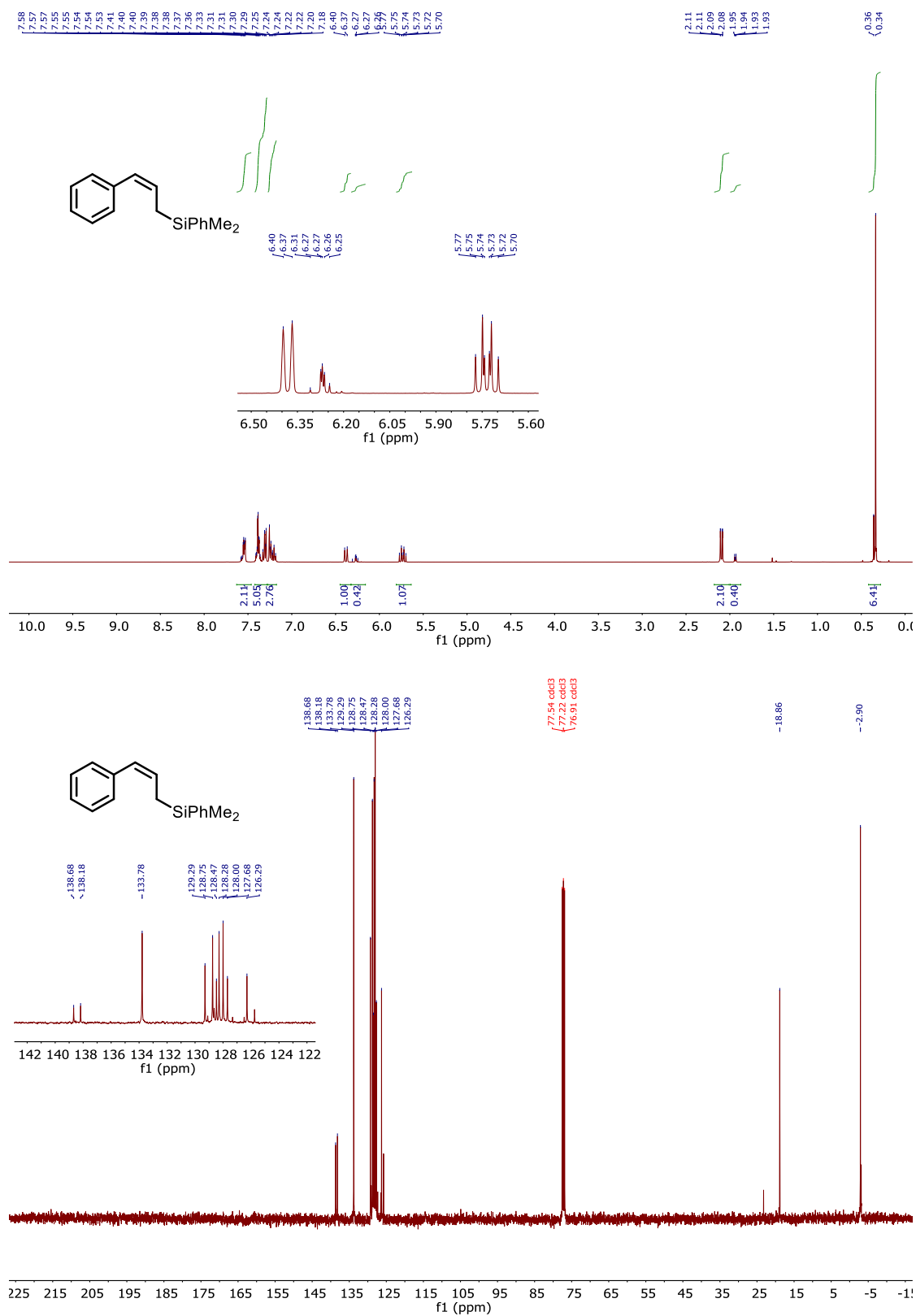
¹H and ¹³C NMR for compound **2b**



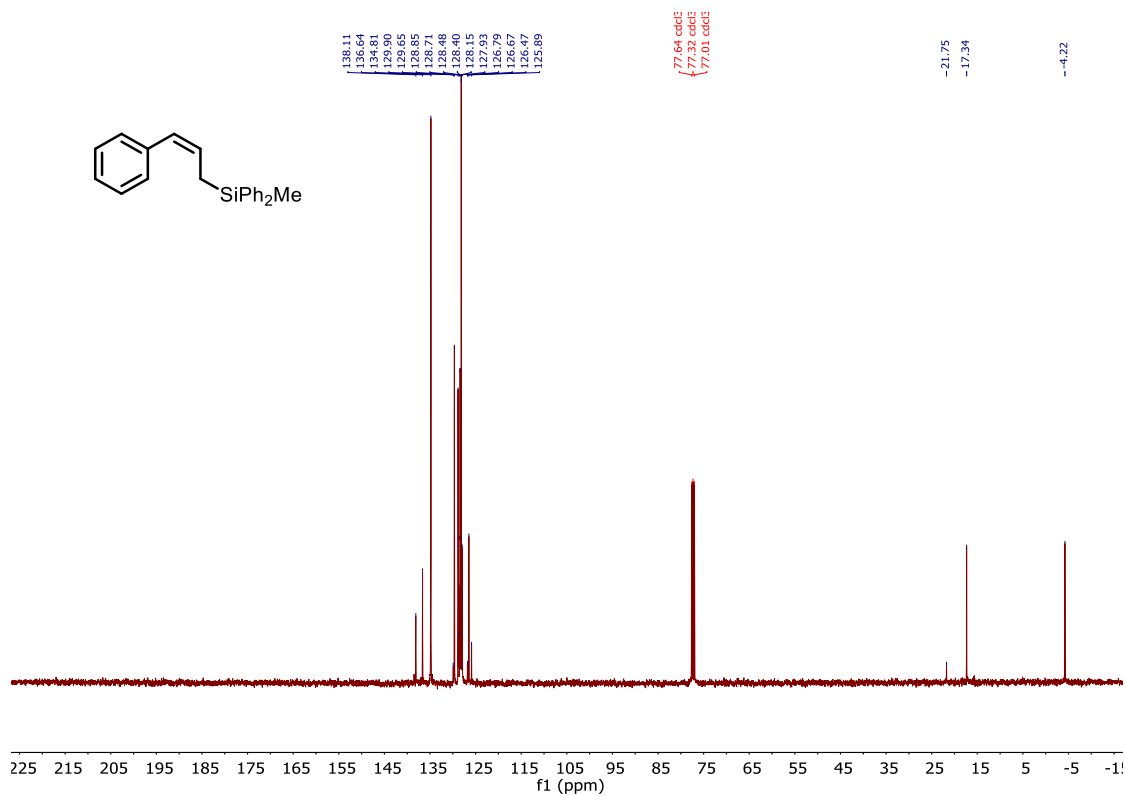
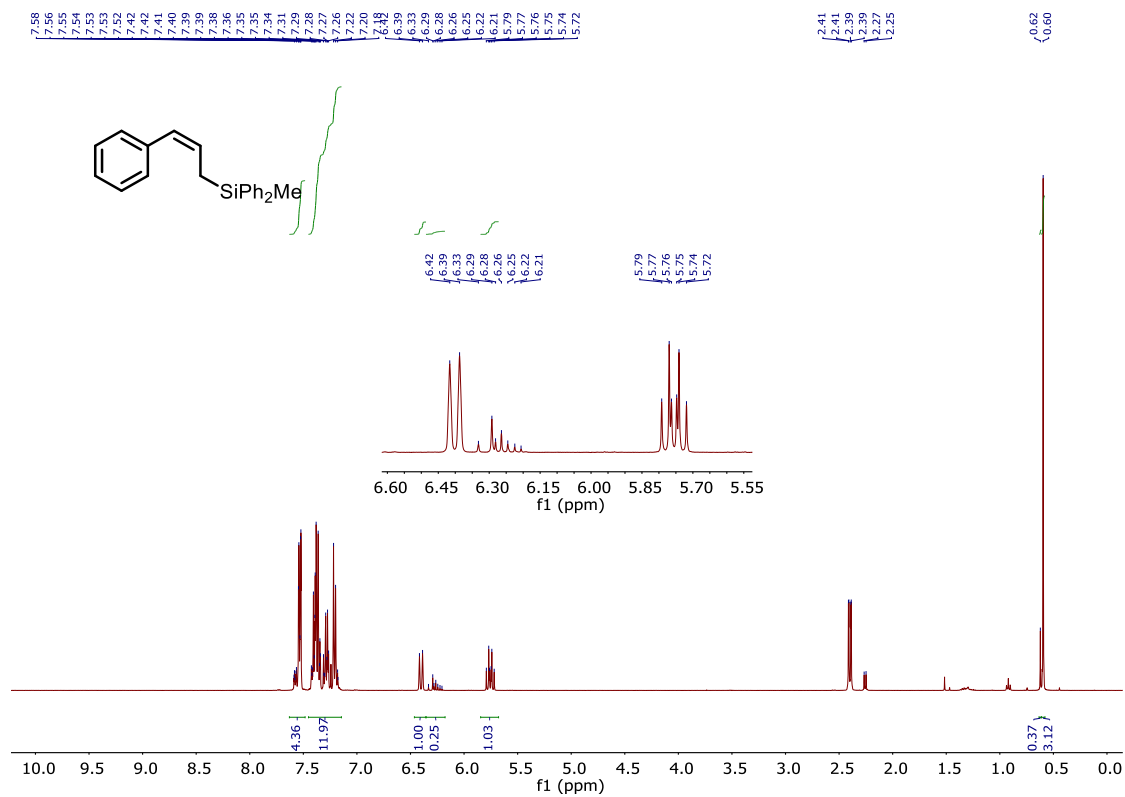
¹H and ¹³C NMR for compound **2c**



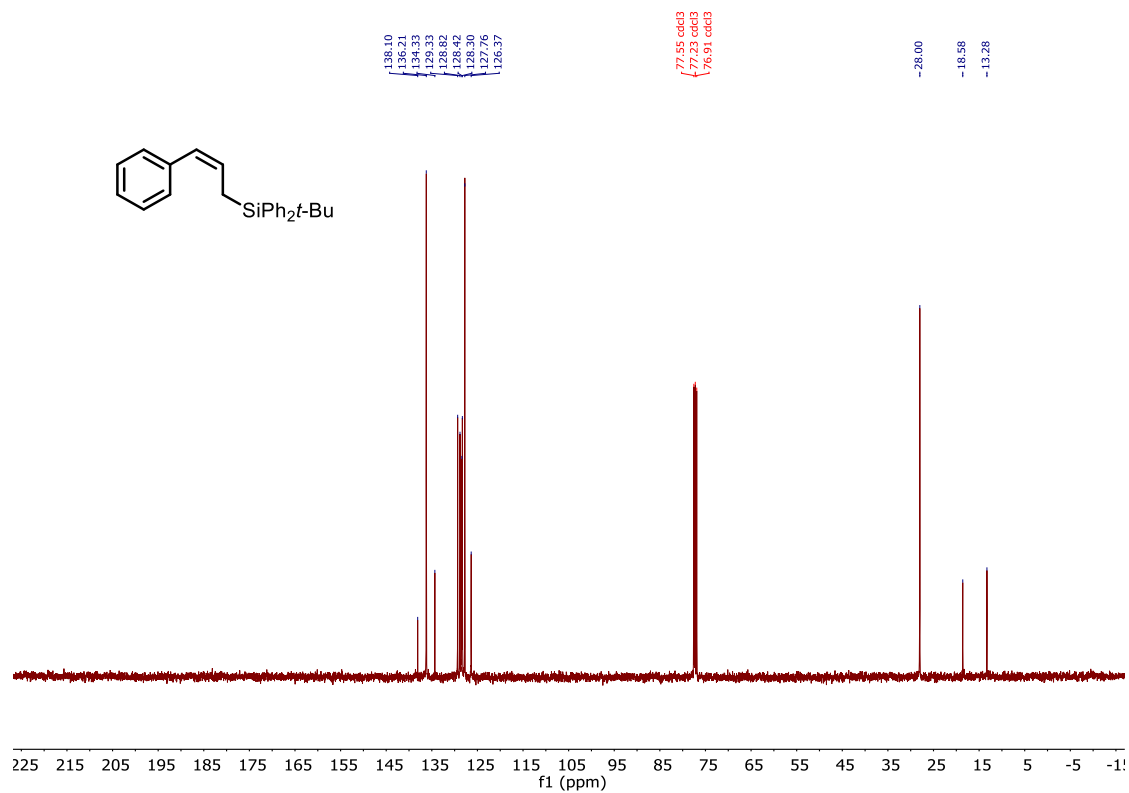
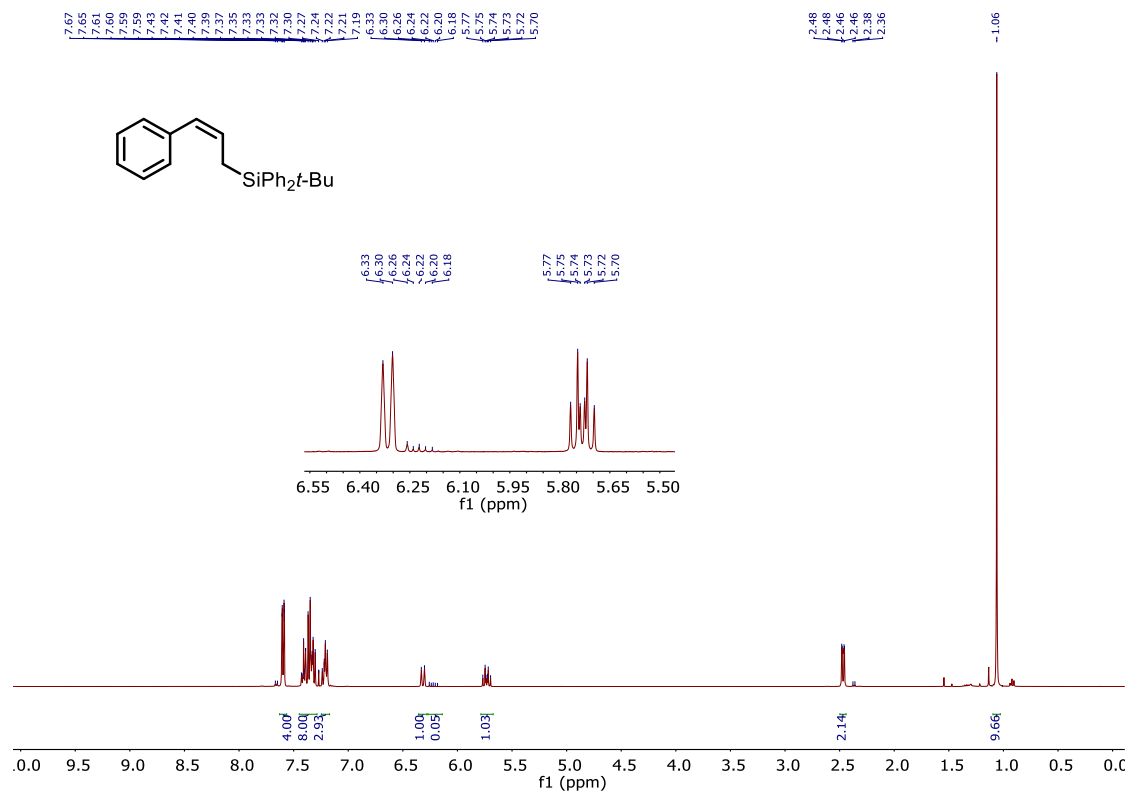
¹H and ¹³C NMR for compound **2d**



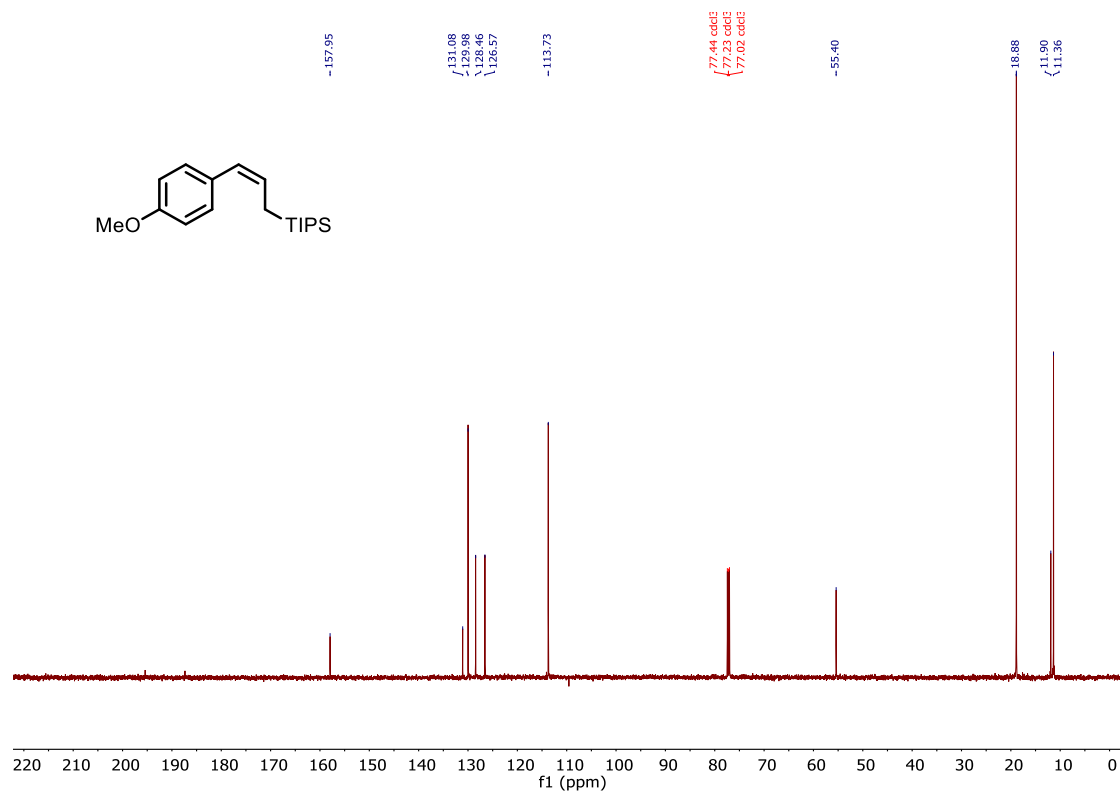
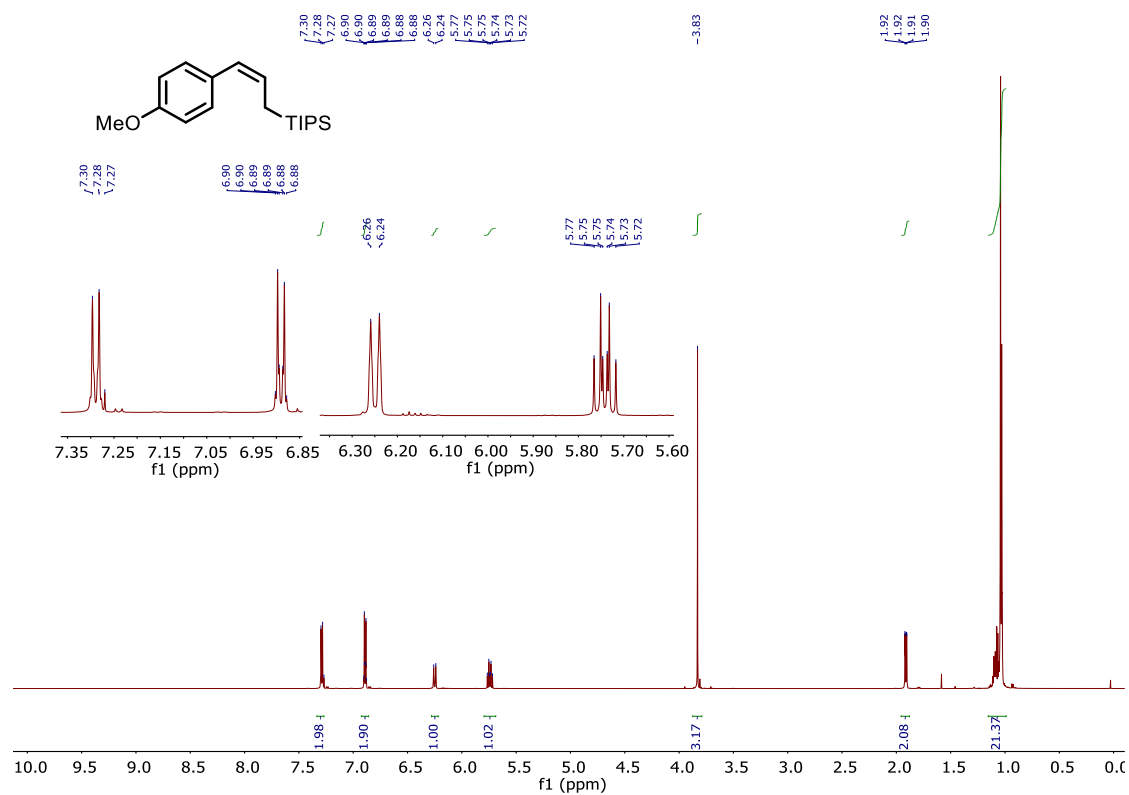
¹H and ¹³C NMR for compound 2e



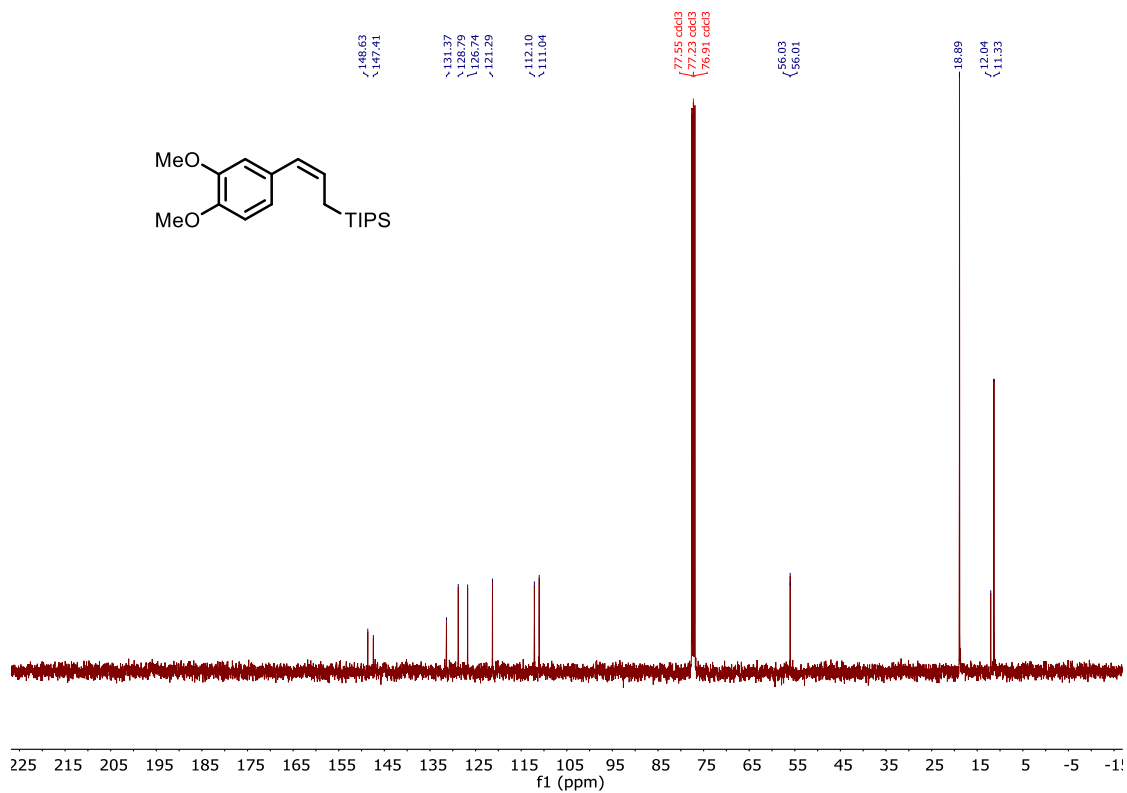
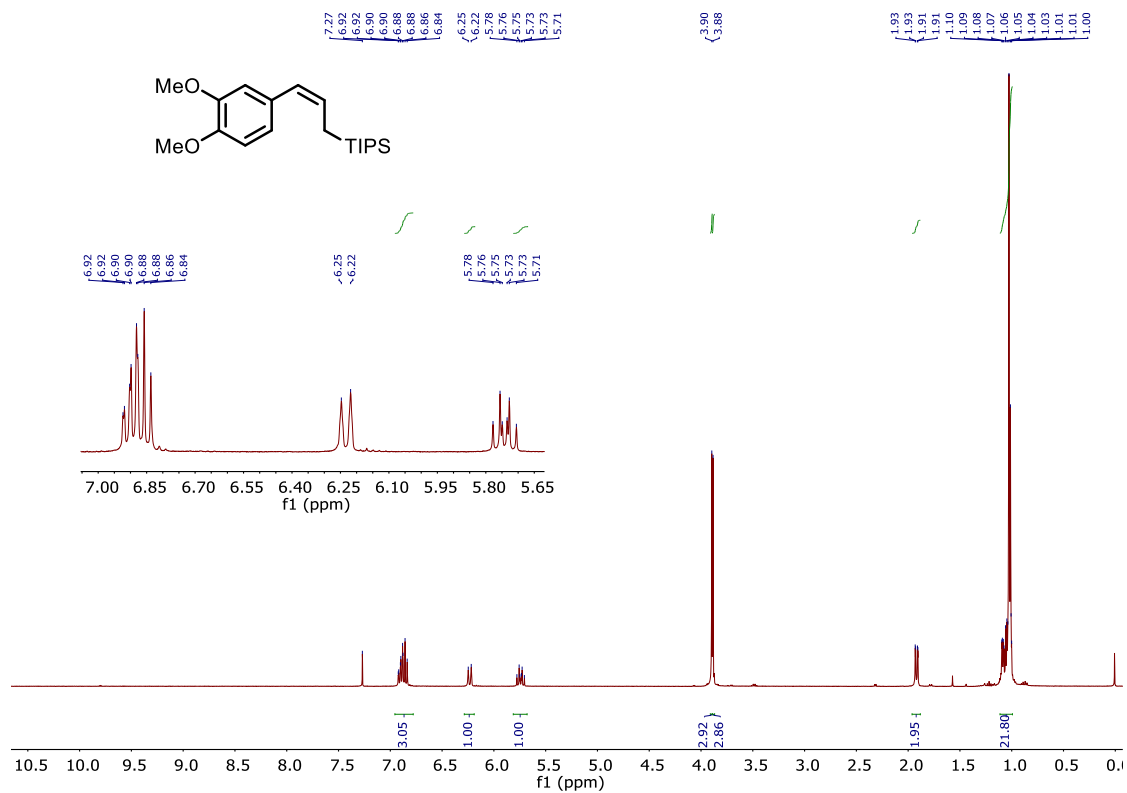
¹H and ¹³C NMR for compound **2f**



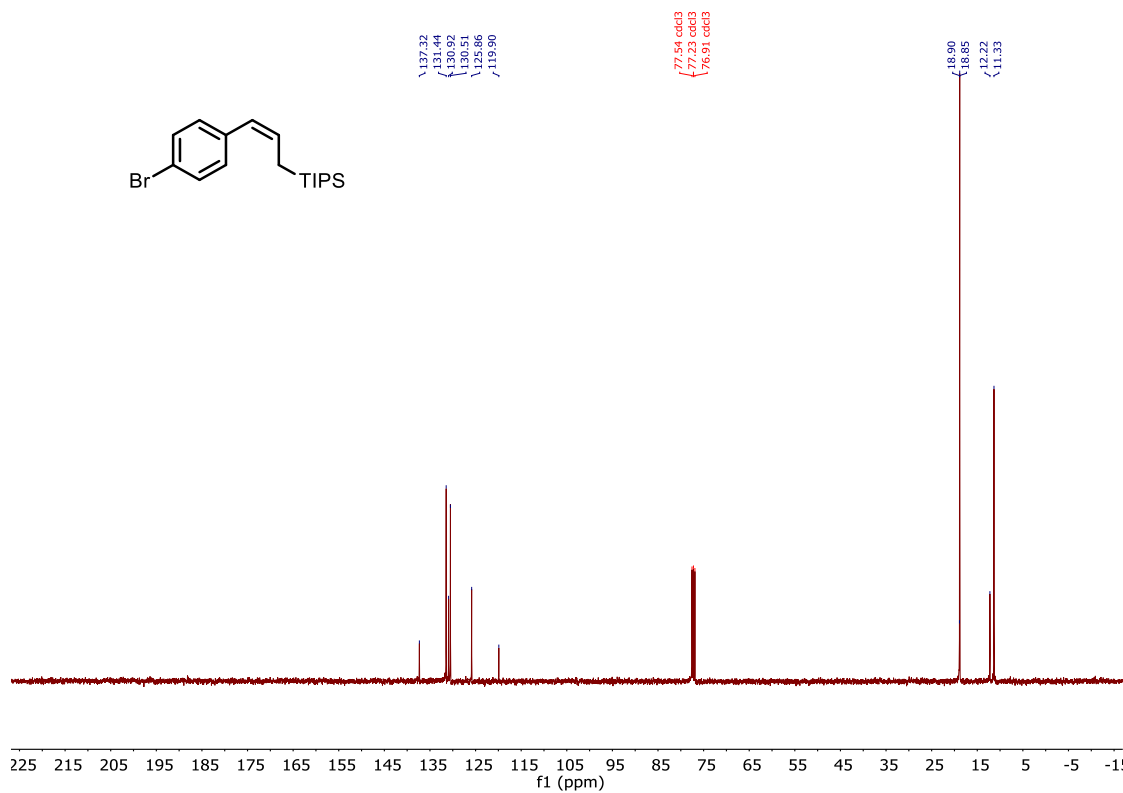
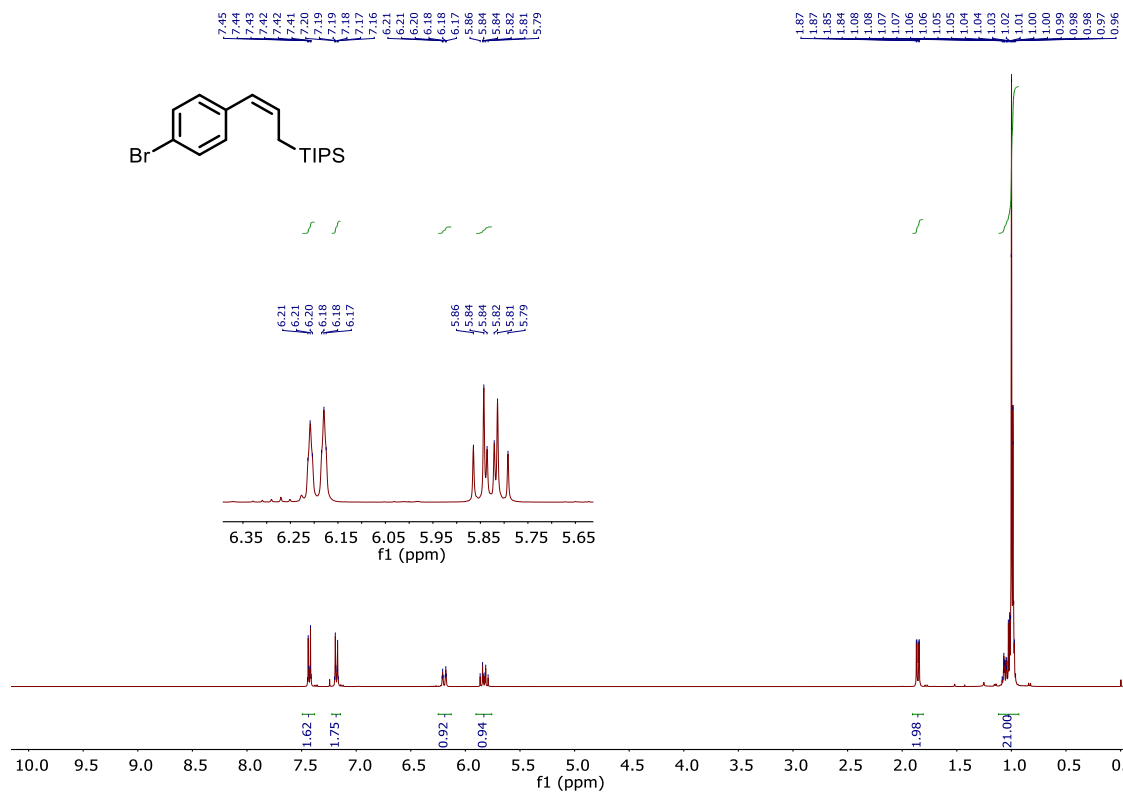
¹H and ¹³C NMR for compound **2g**



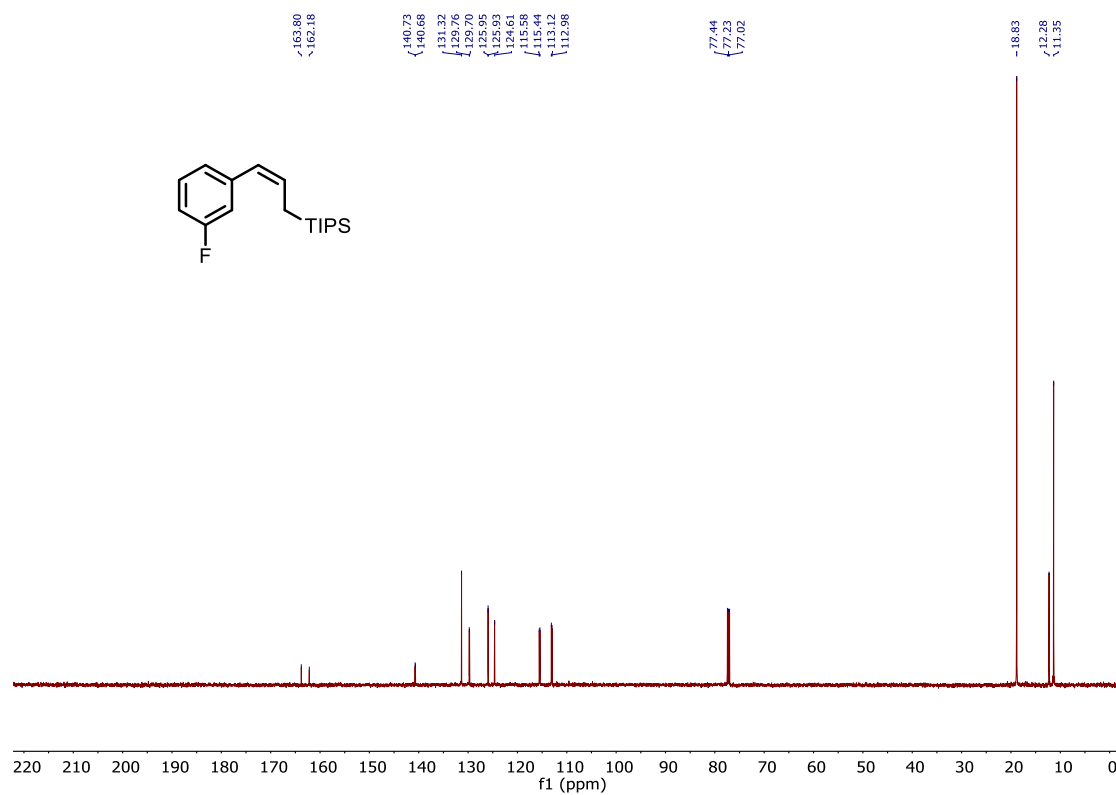
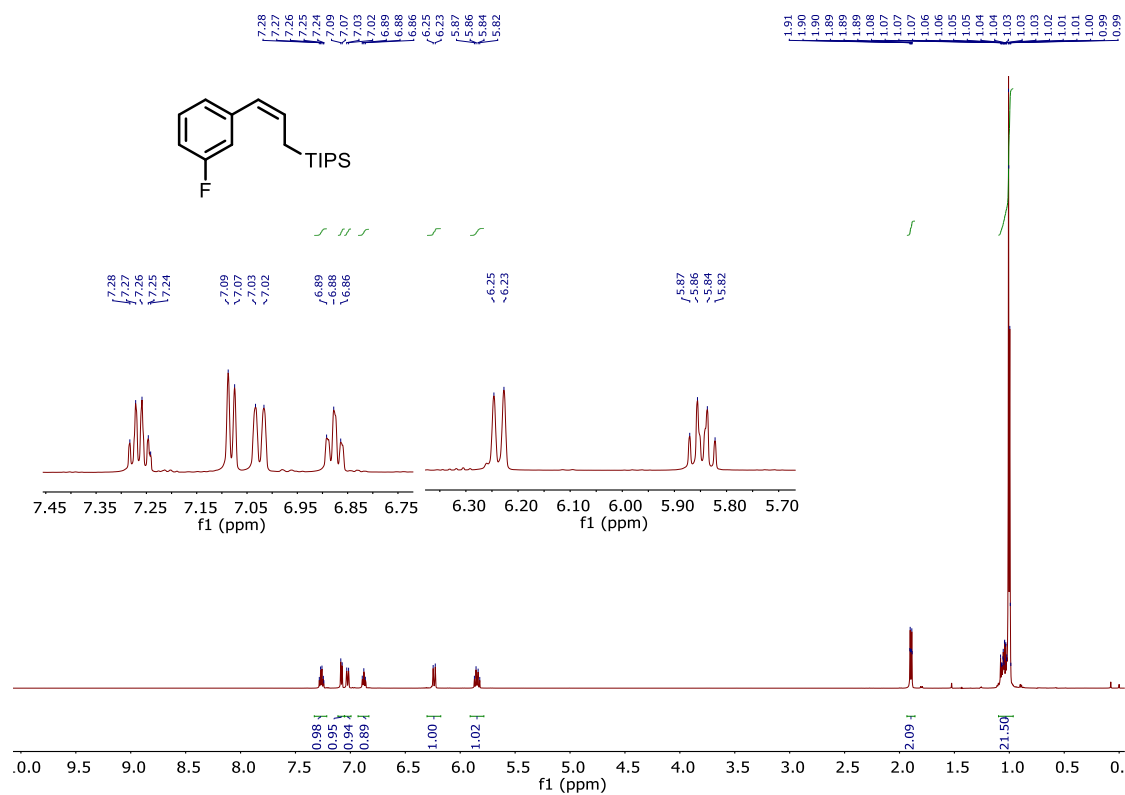
^1H and ^{13}C NMR for compound **4a**



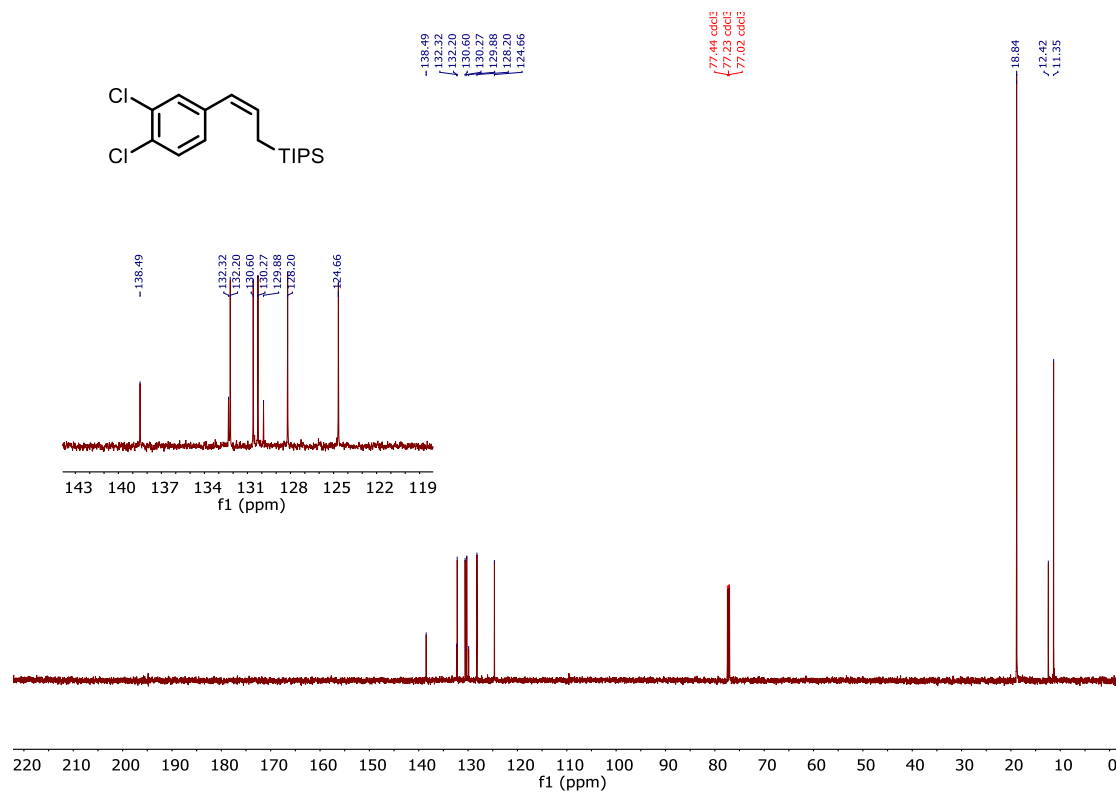
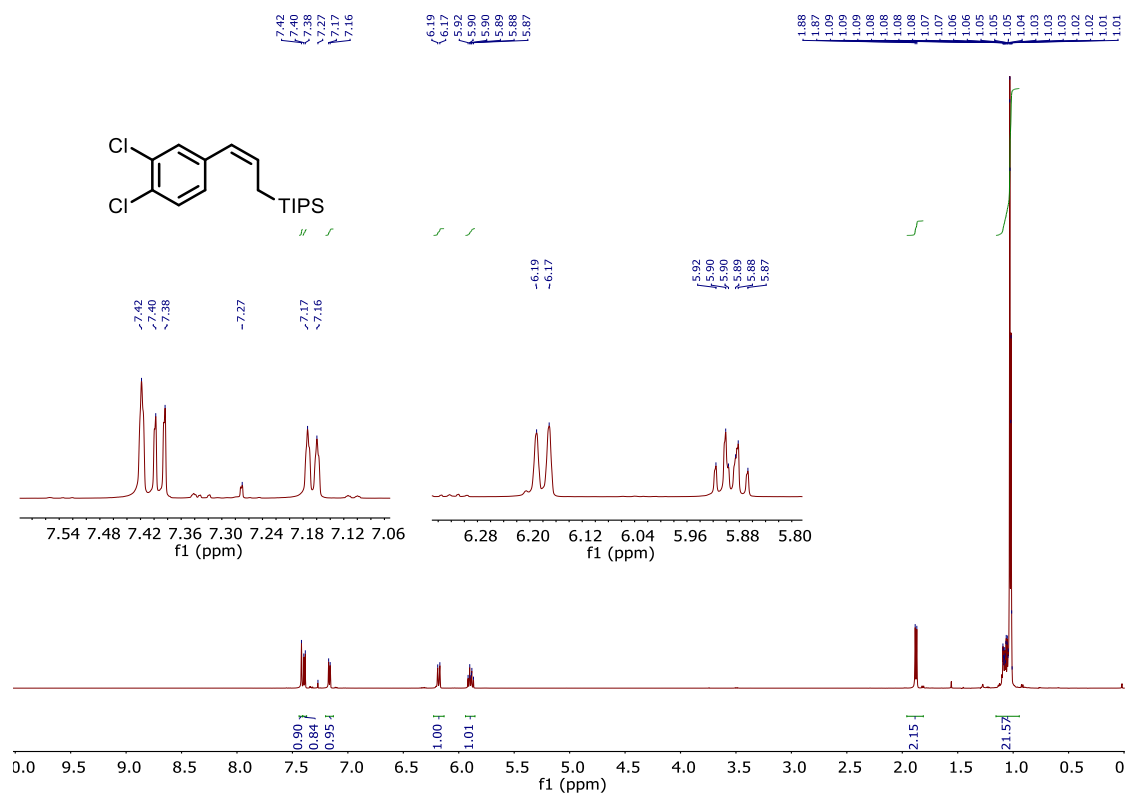
^1H and ^{13}C NMR for compound **4b**



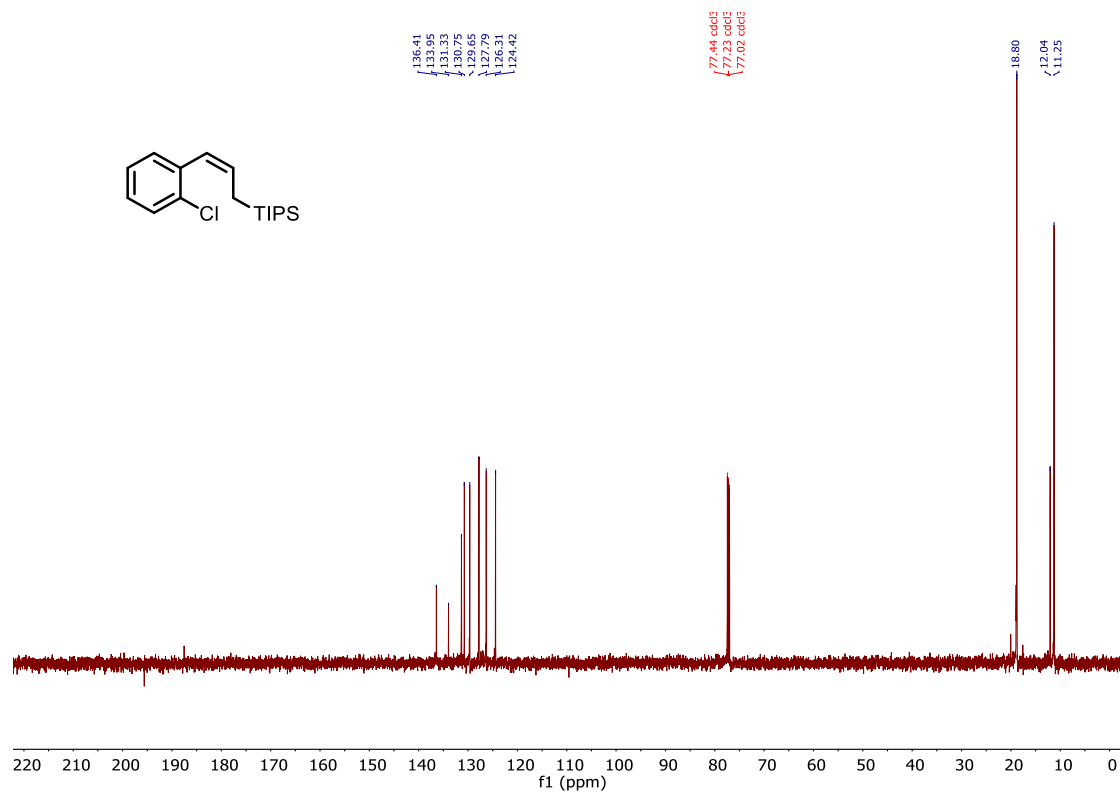
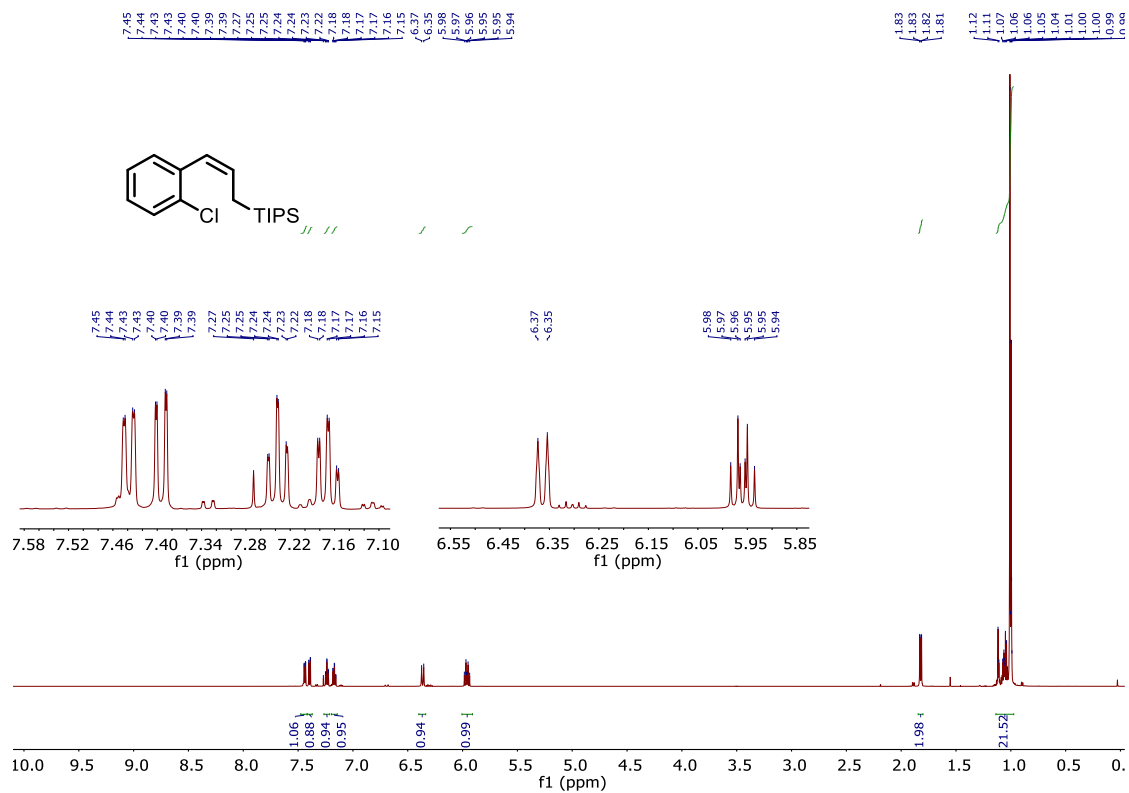
¹H and ¹³C NMR for compound **4e**



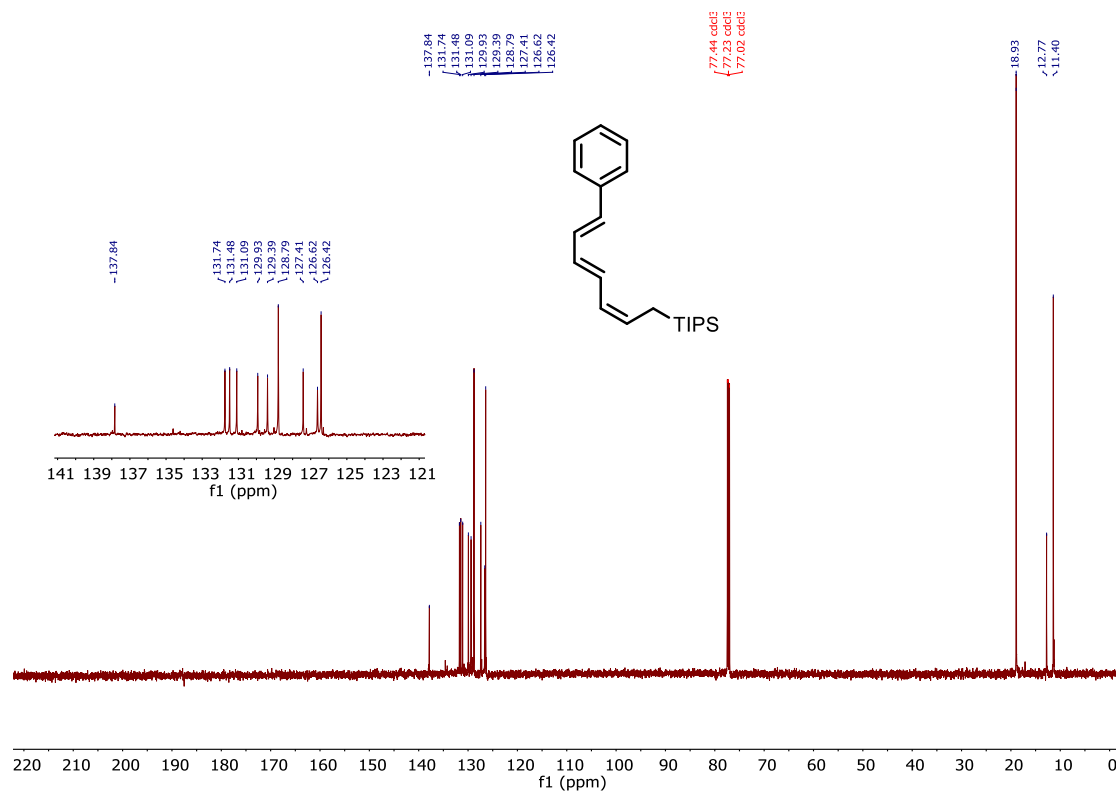
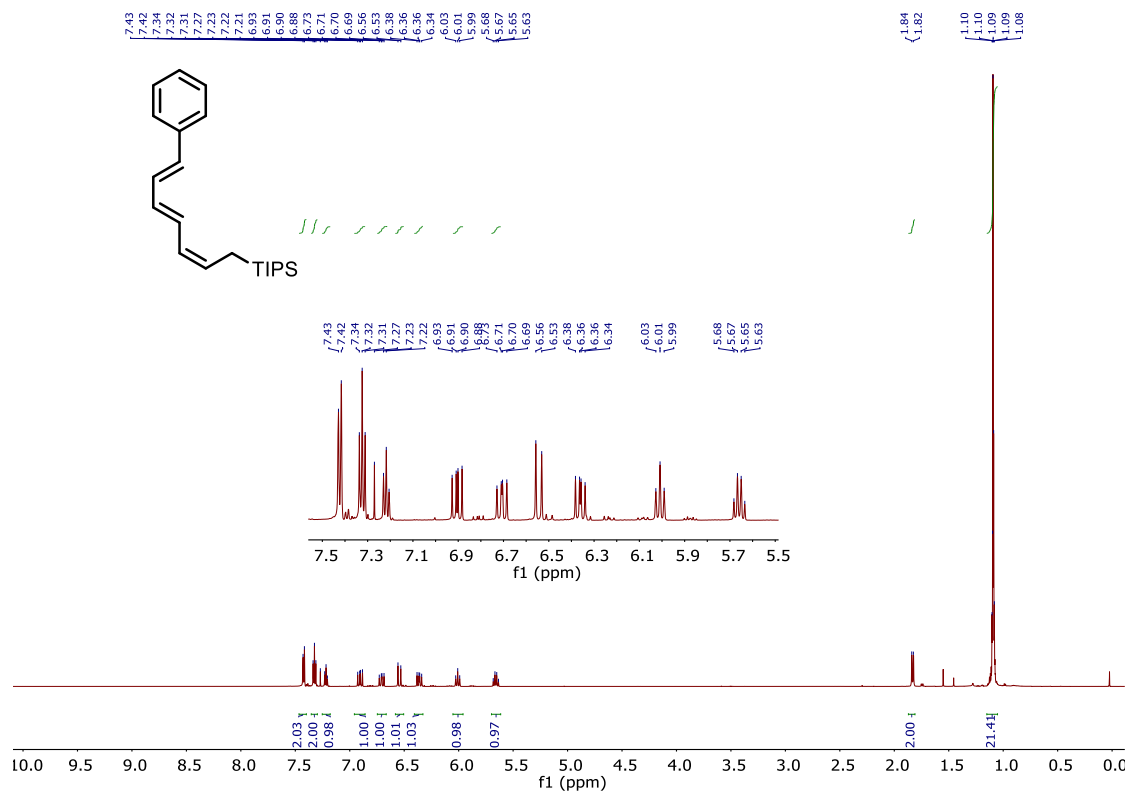
^1H and ^{13}C NMR for compound **4f**

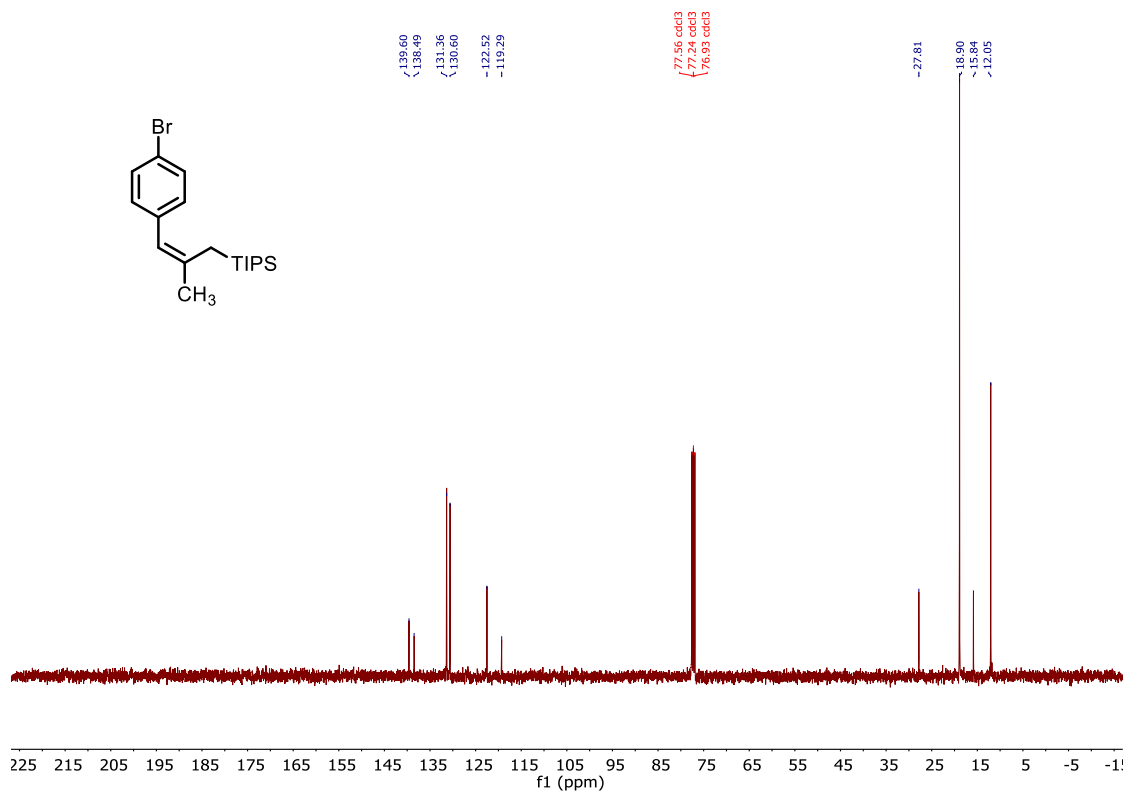
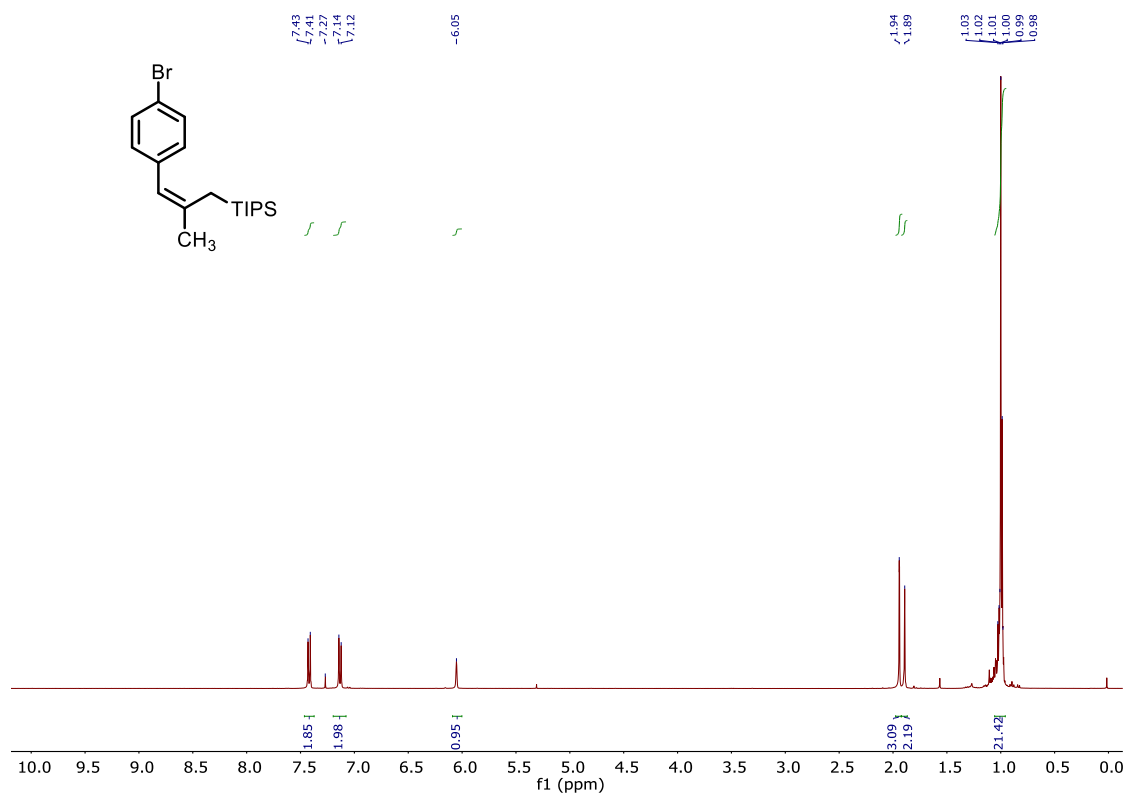


^1H and ^{13}C NMR for compound **4g**

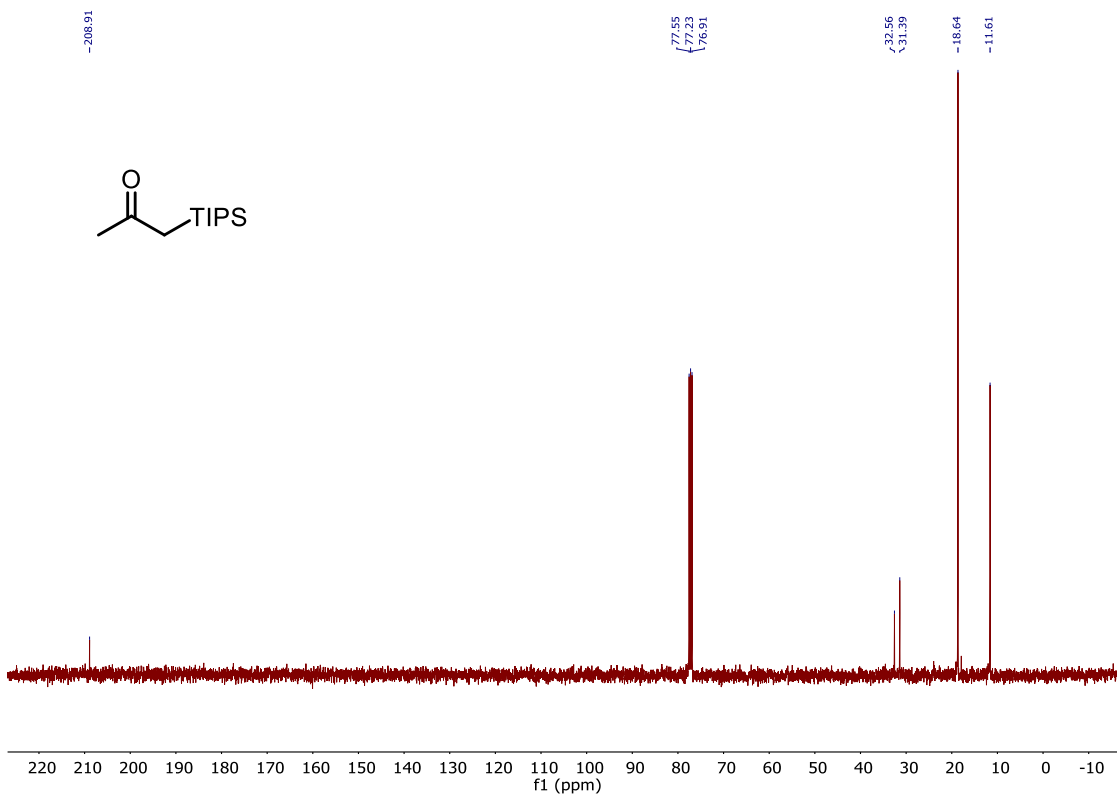
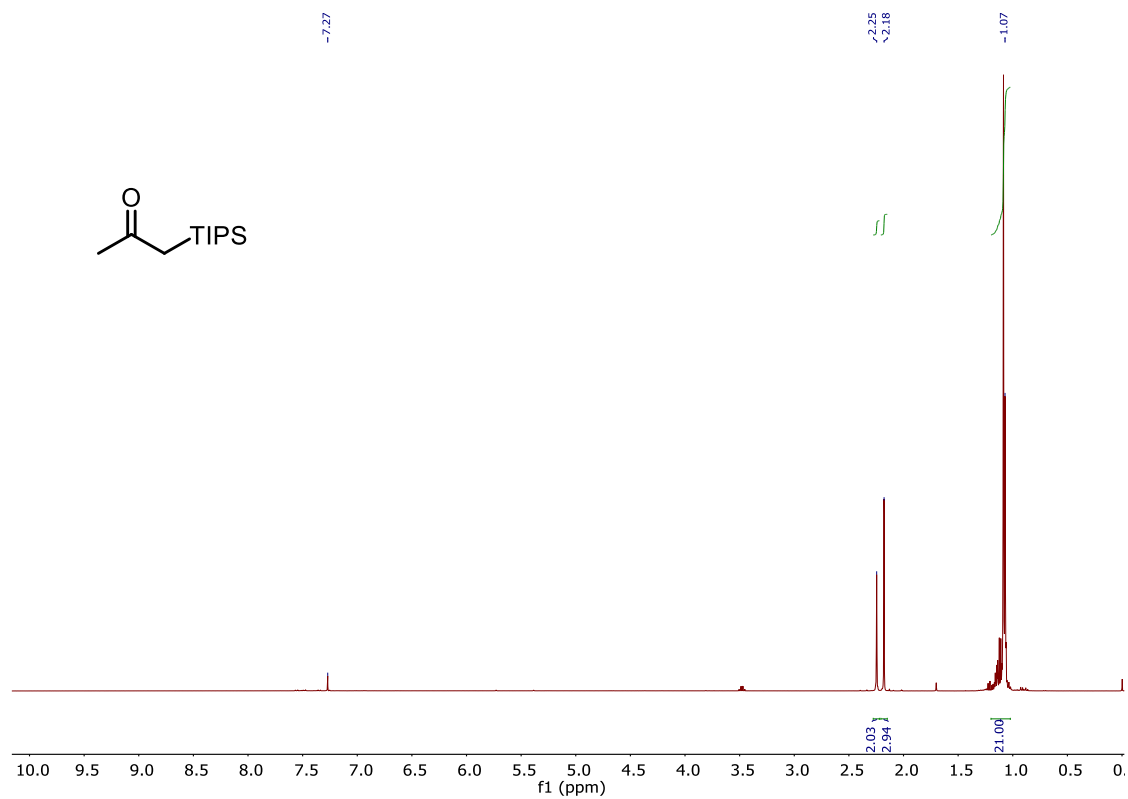


^1H and ^{13}C NMR for compound **4h**

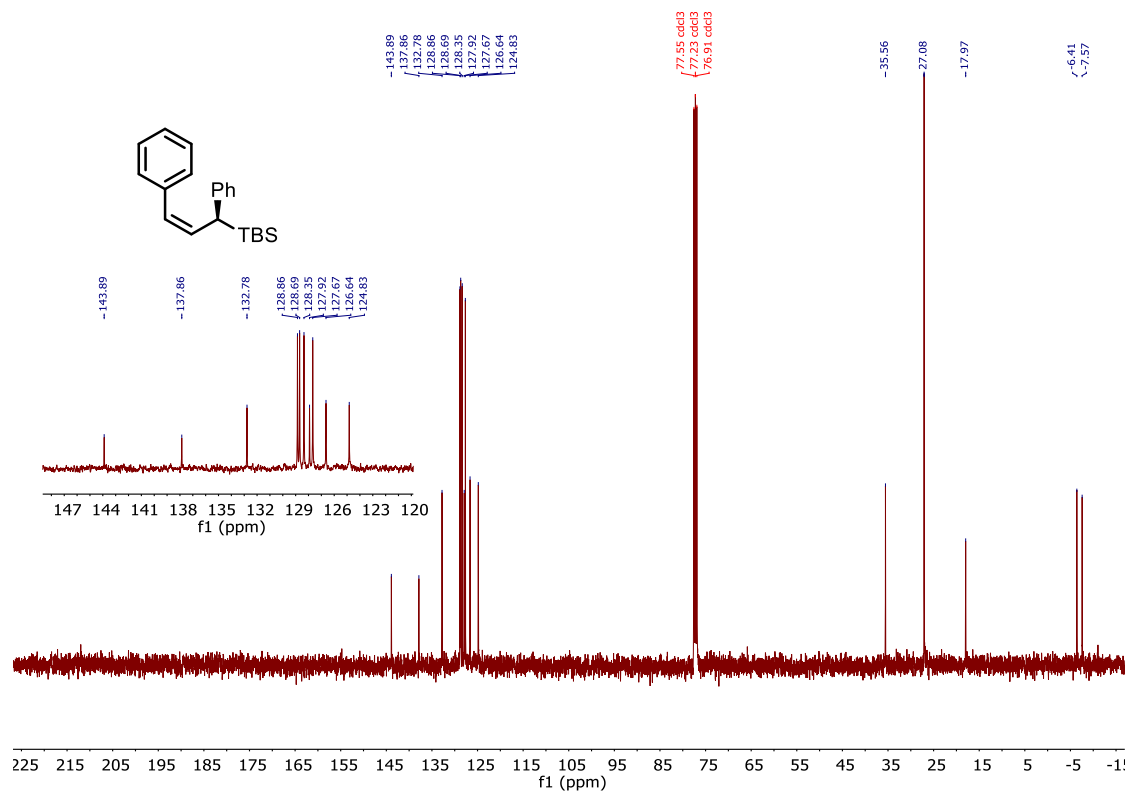
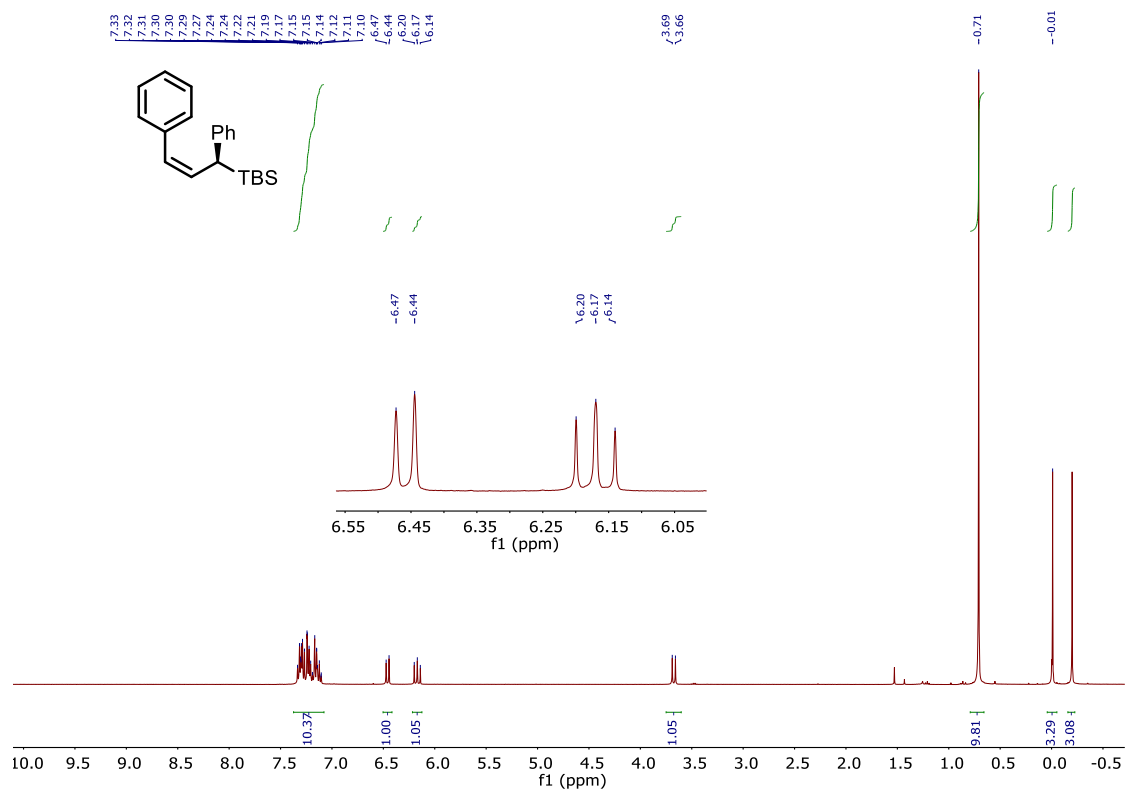
¹H and ¹³C NMR for compound **4k**

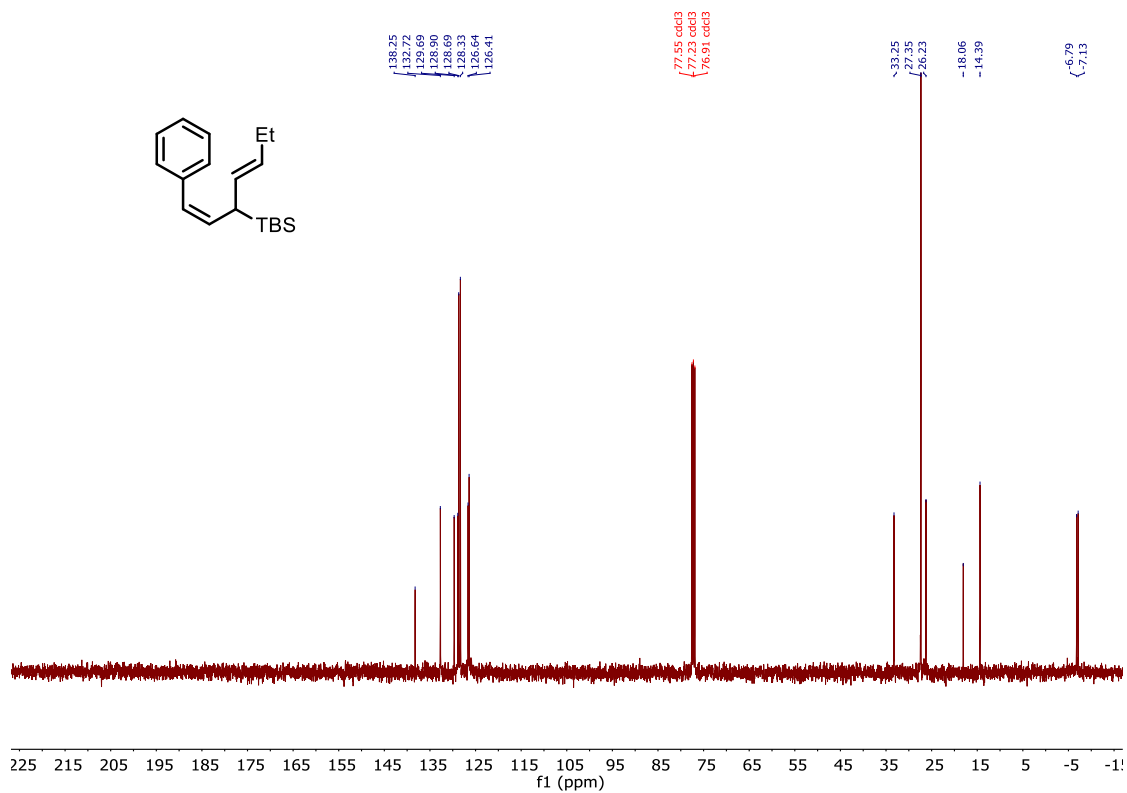
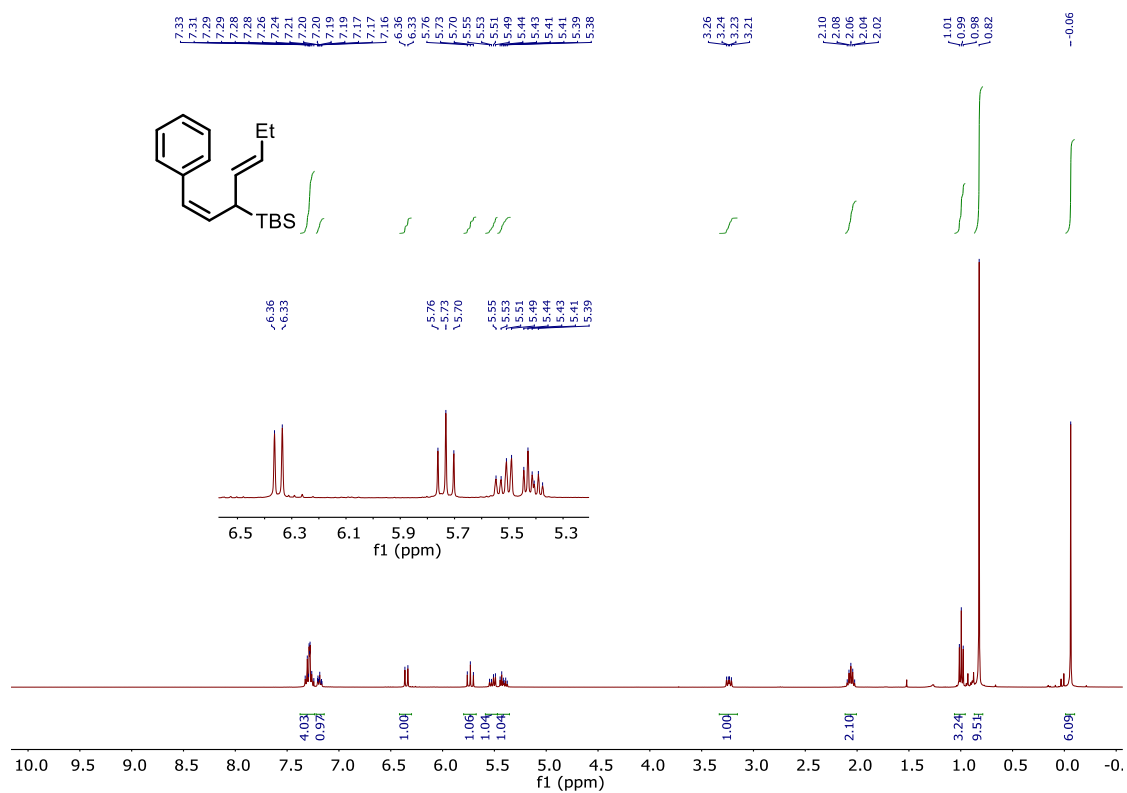


¹H and ¹³C NMR for compound **4l**

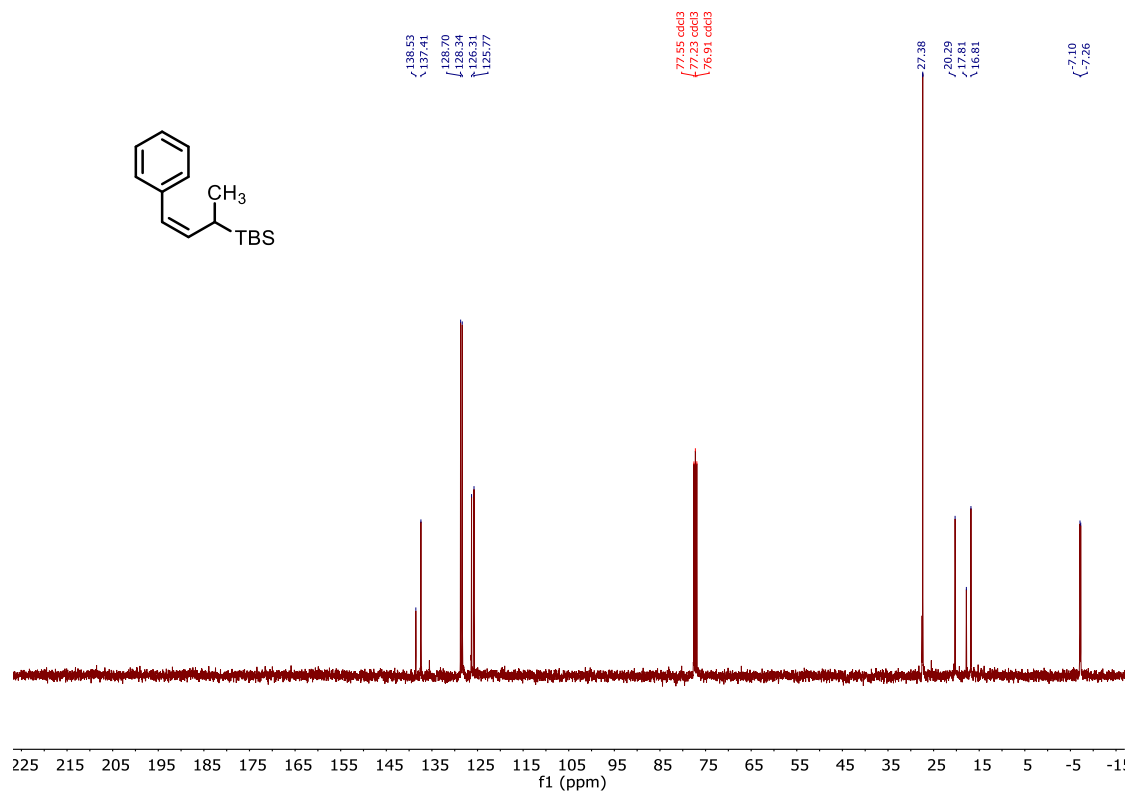
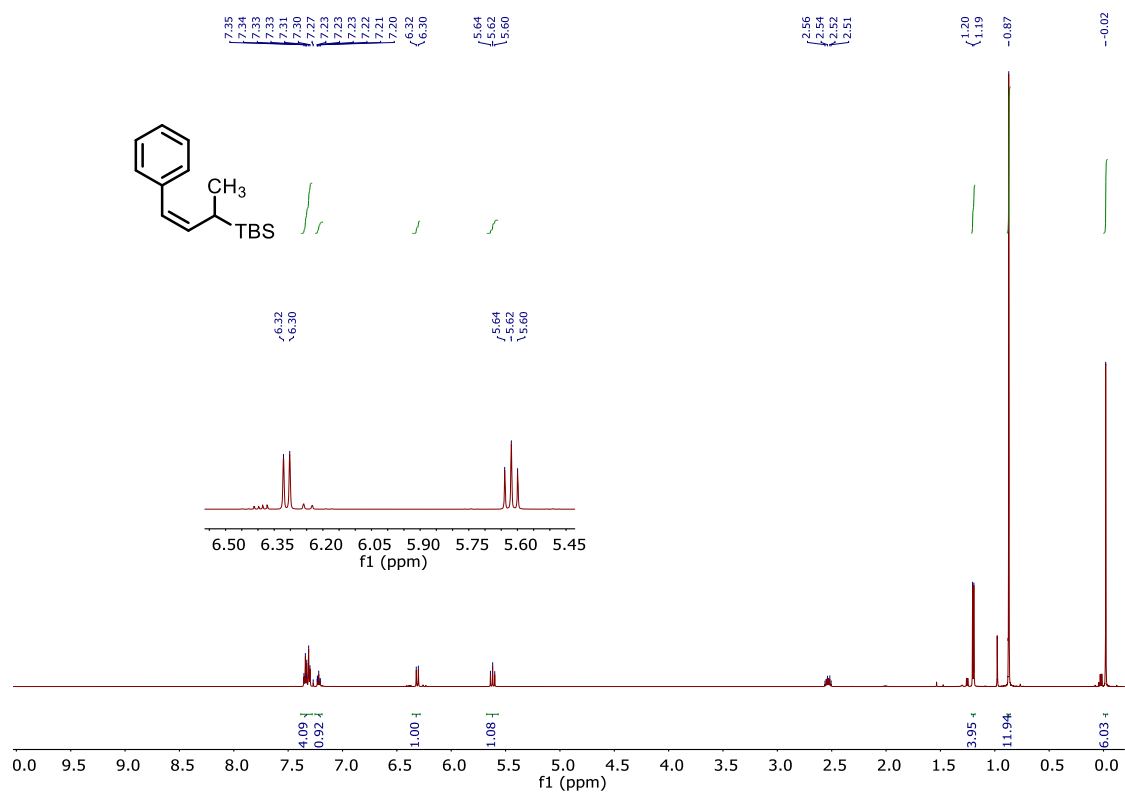


¹H and ¹³C NMR for 1-(triisopropylsilyl)-2-propanone

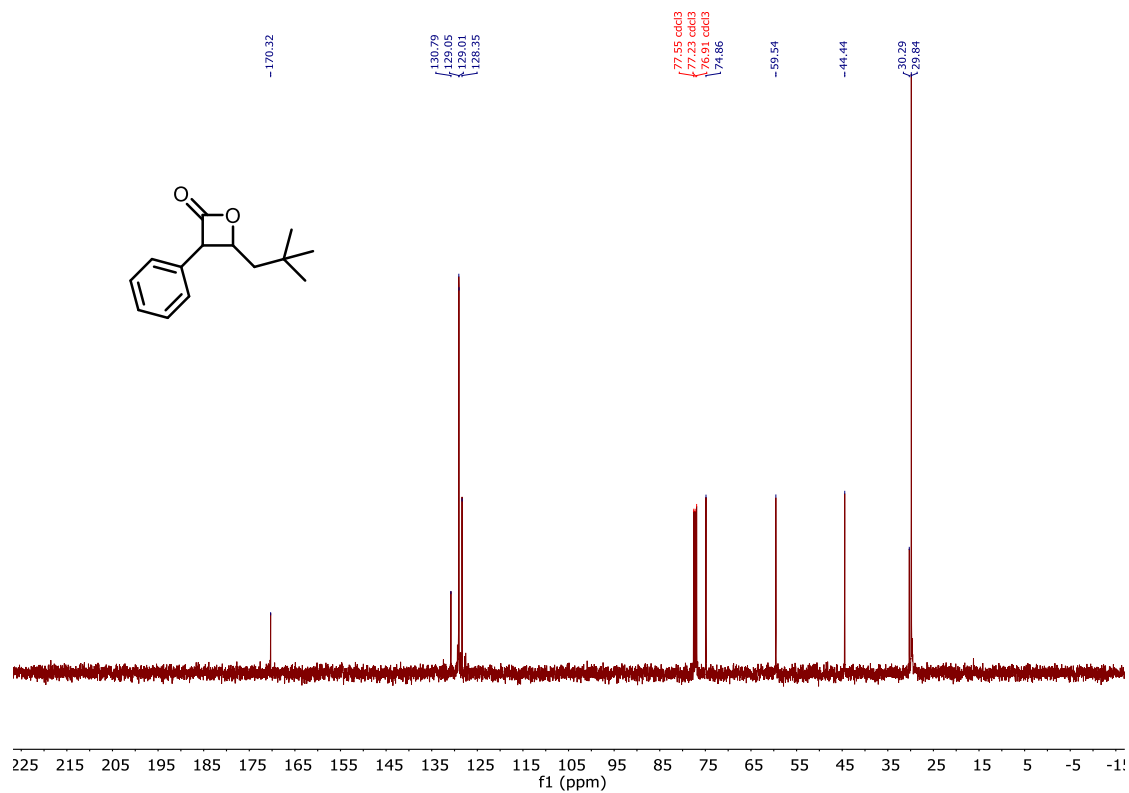
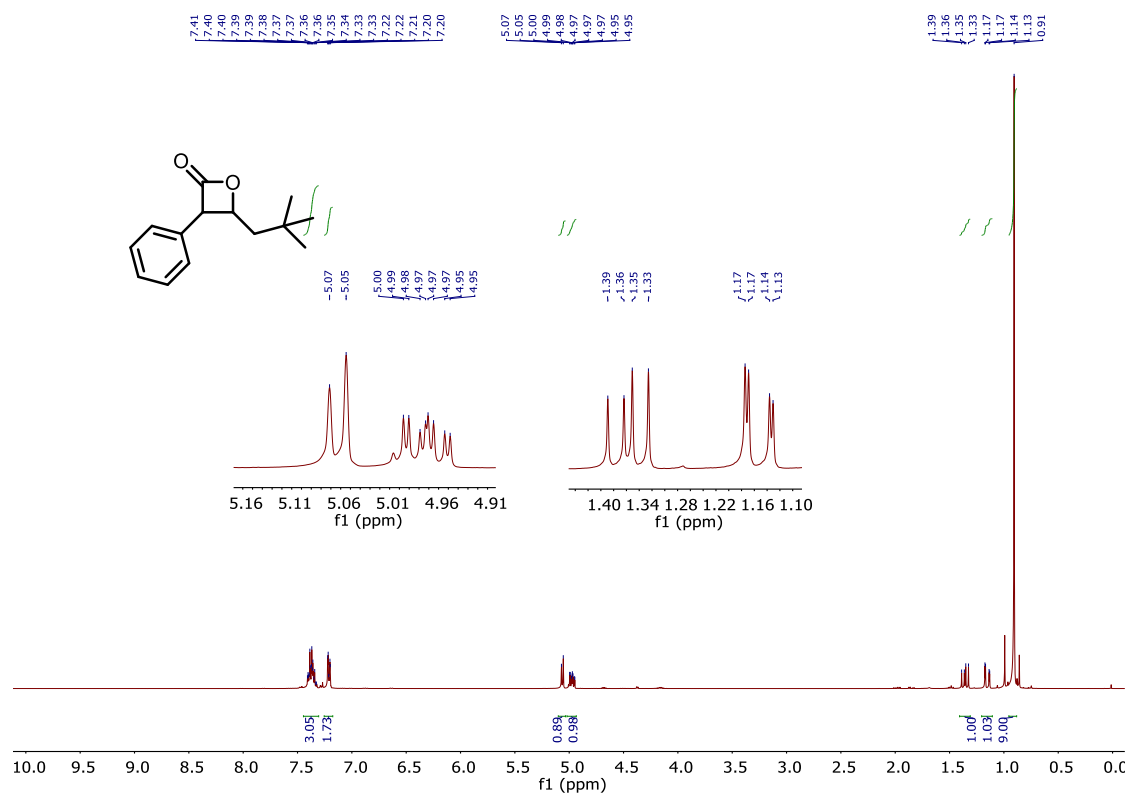
 ^1H and ^{13}C NMR for compound (*R*)-6a



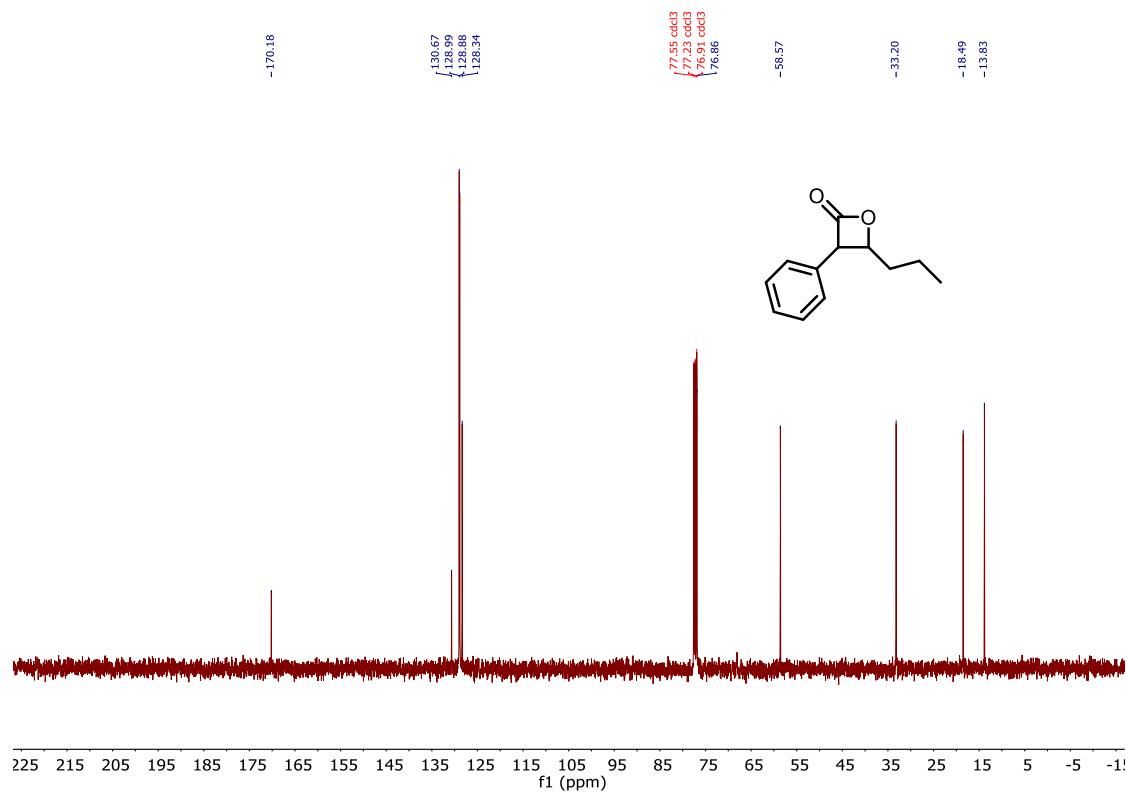
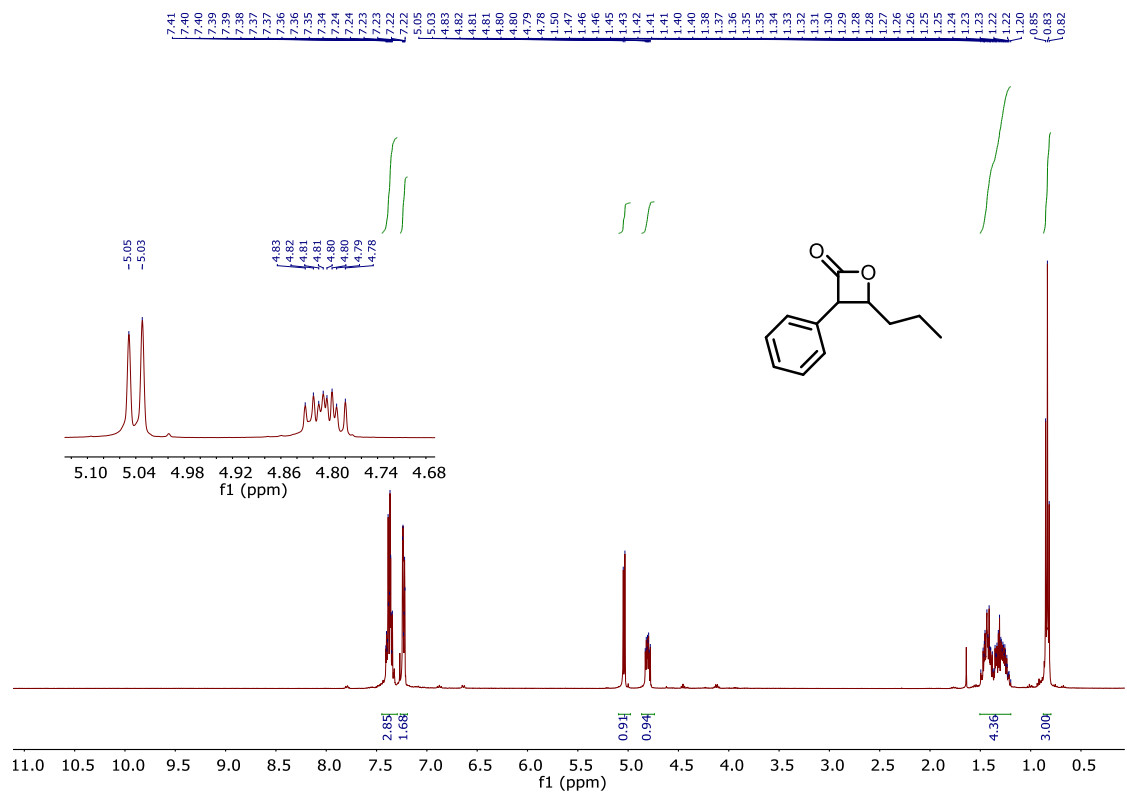
¹H and ¹³C NMR for compound **6b**

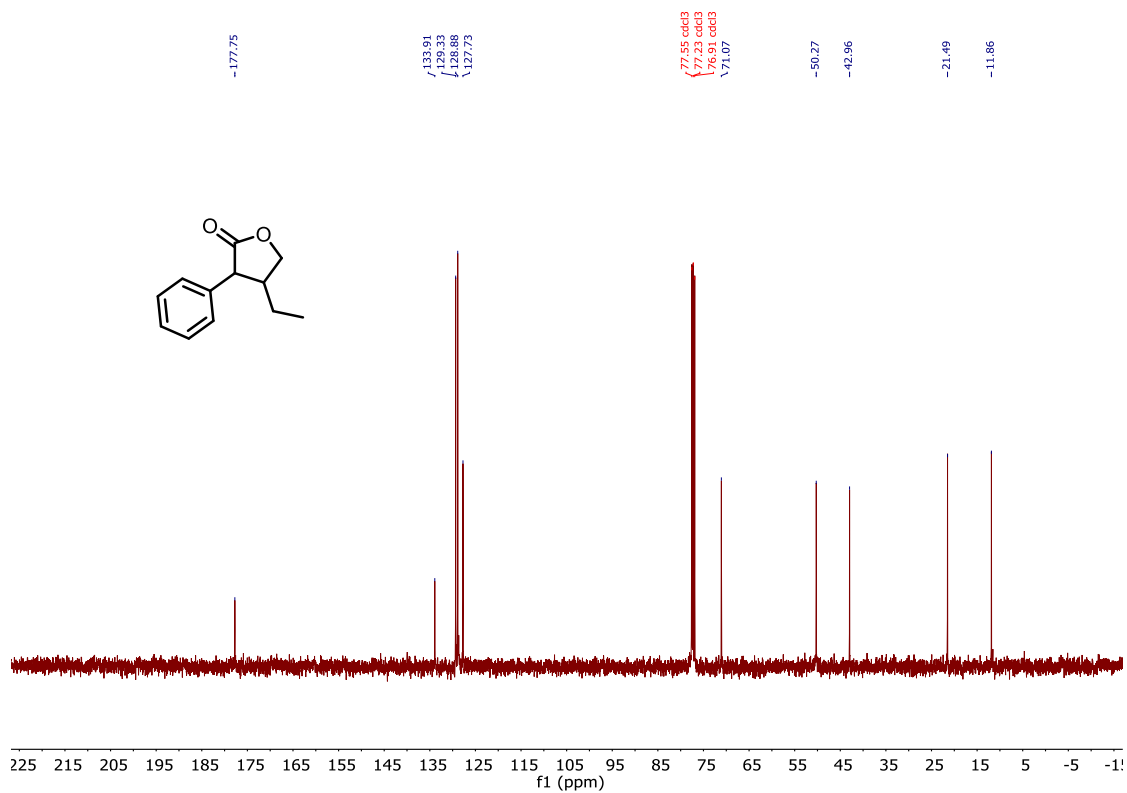
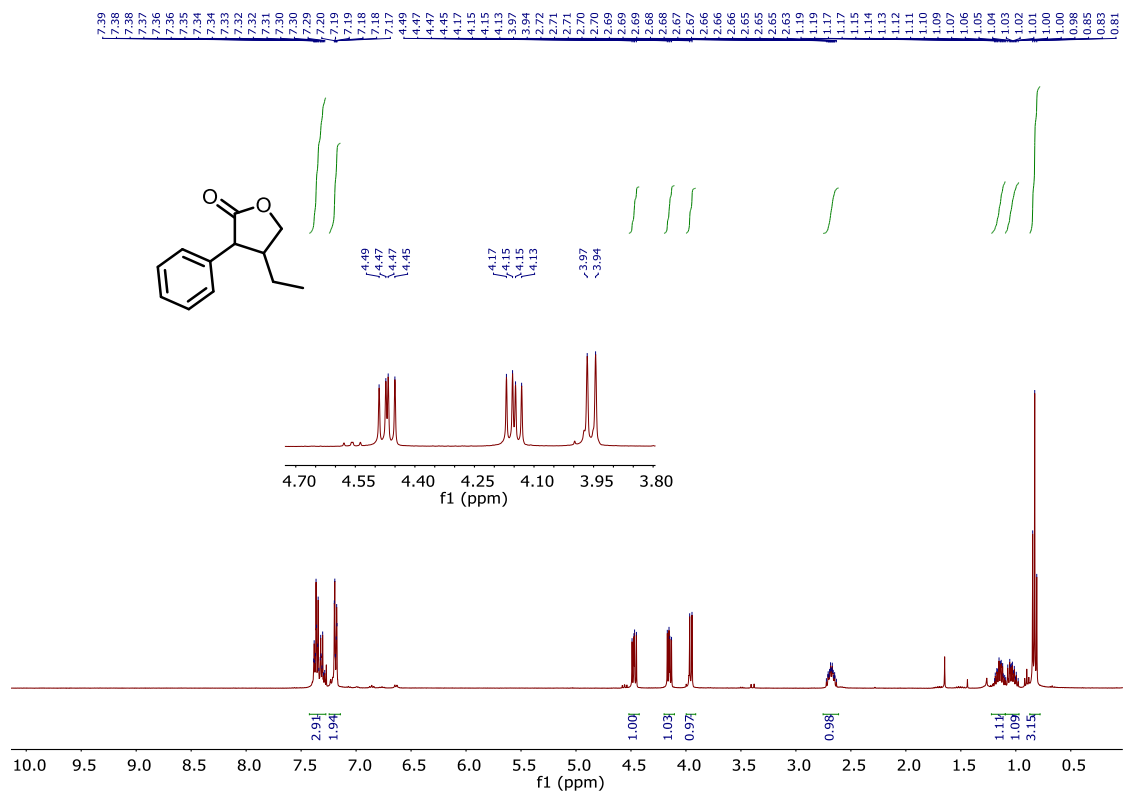


¹H and ¹³C NMR for compound **6c**

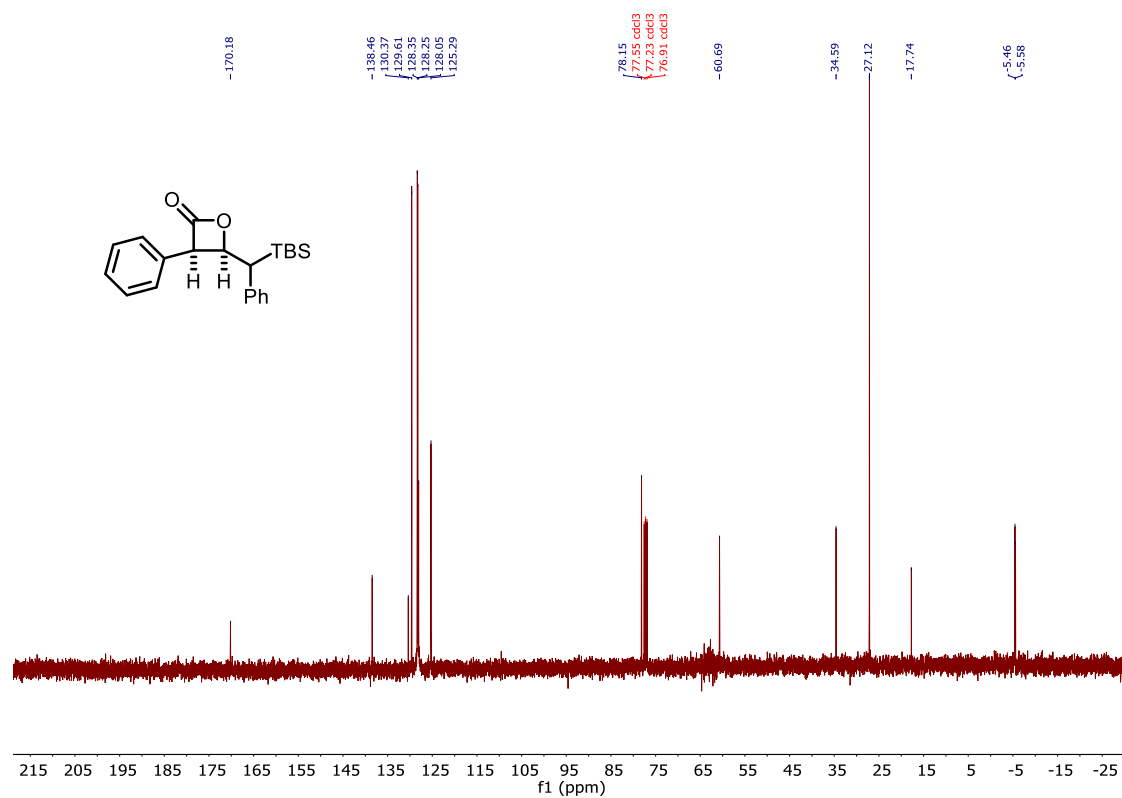
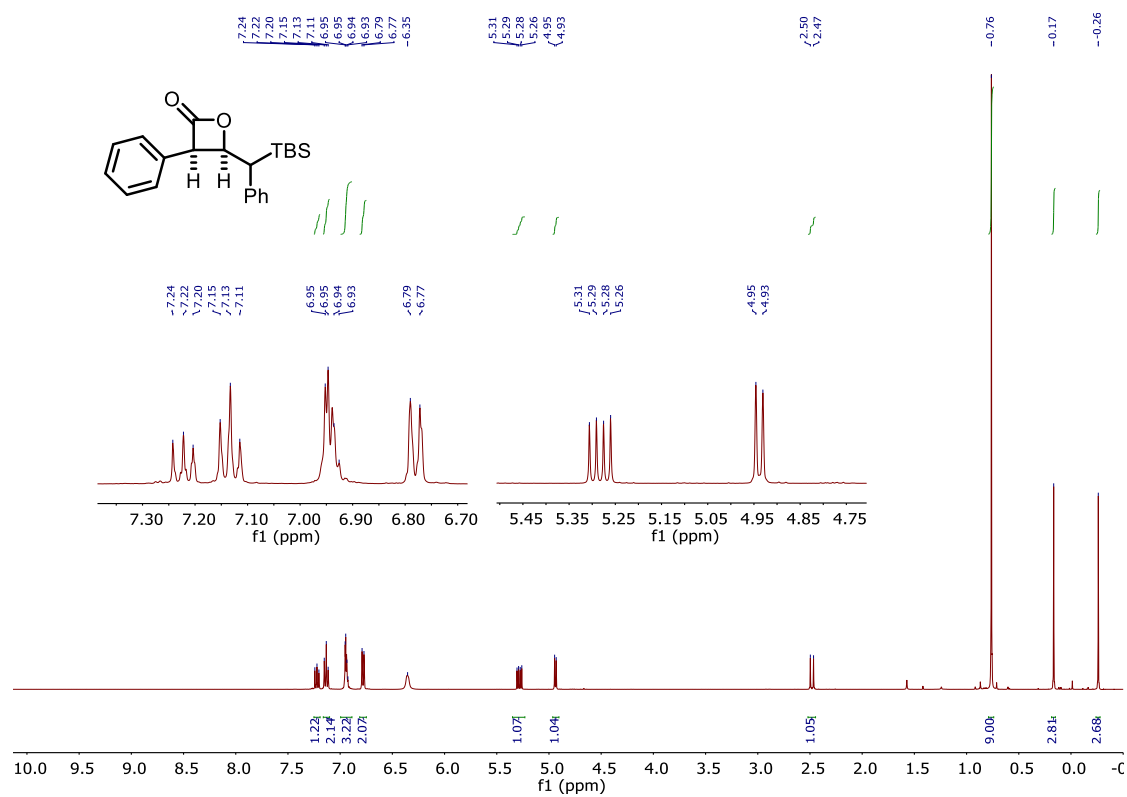


¹H and ¹³C NMR for compound **10**

¹H and ¹³C NMR for compound **11a**

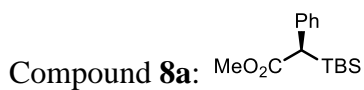


¹H and ¹³C NMR for compound **11b**

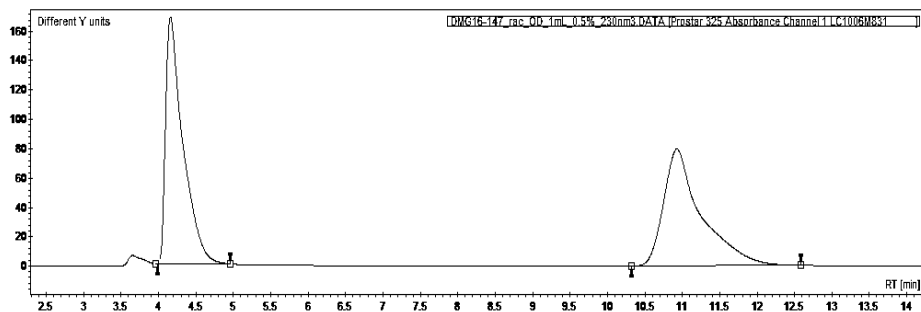


¹H and ¹³C NMR for compound 12

3.2 HPLC Chromatograms

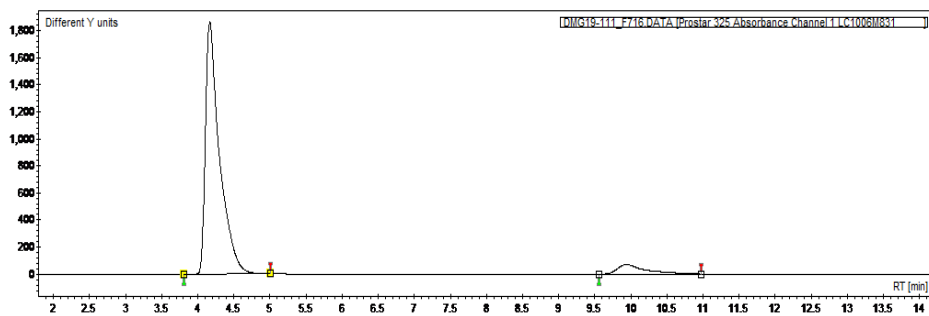


Racemic:

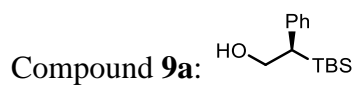


#	Time	Area %
1	4.16 min	43.953
2	10.93 min	56.047

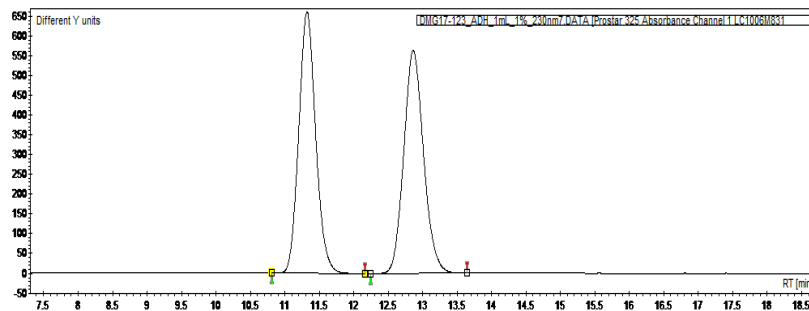
Enantioenriched:



#	Time	Area %
1	4.17 min	92.961
2	9.94 min	7.039
		86% ee

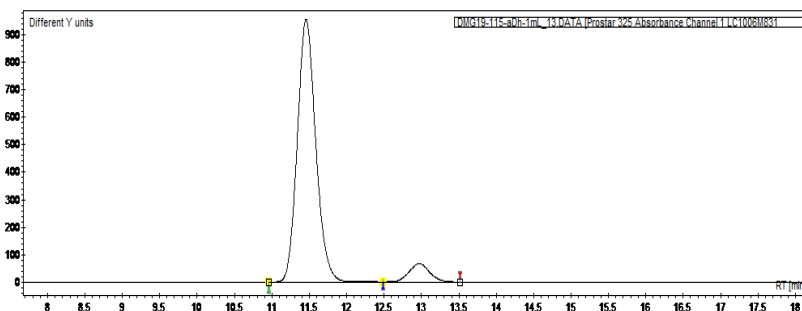


Racemic:



#	Time	Area %
1	11.32 min	50.041
2	12.86 min	49.959

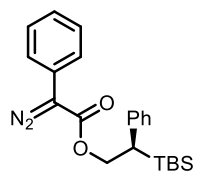
Enantioenriched:



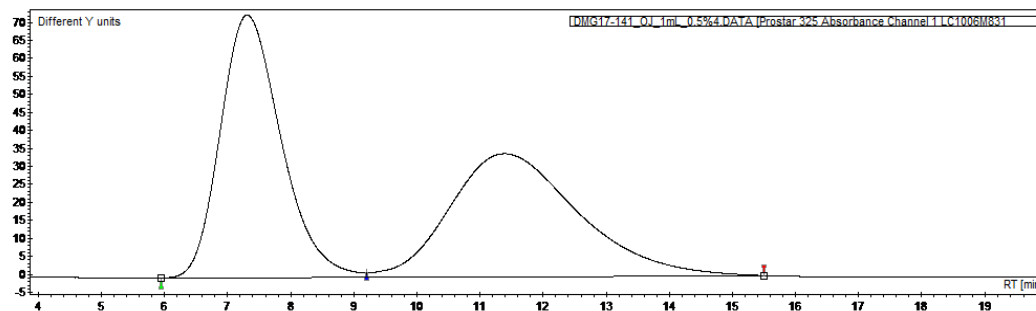
#	Time	Area % [%]
1	11.46 min	92.659
2	12.97 min	7.341

85% ee

Compound (*R*)-5a:

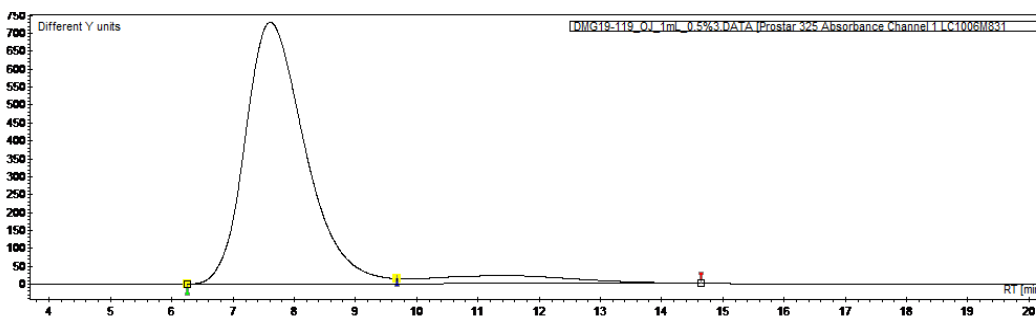


Racemic:

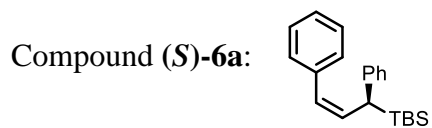


#	Time	Area % [%]
1	7.31 min	50.271
2	11.39 min	49.729

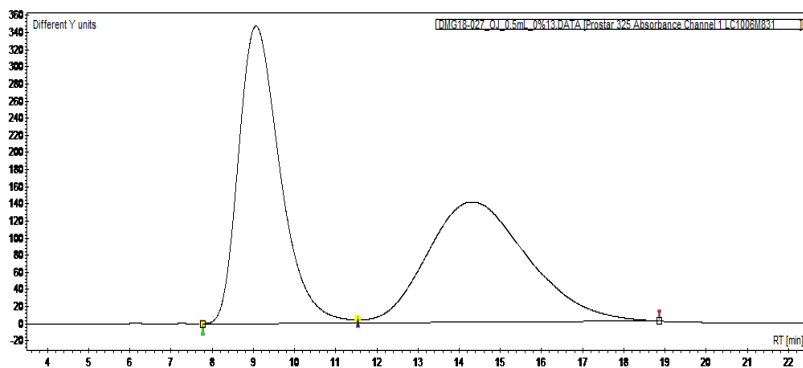
Enantioenriched:



#	Time	Area %
1	7.61 min	92.955
2	11.46 min	7.045
		86% ee

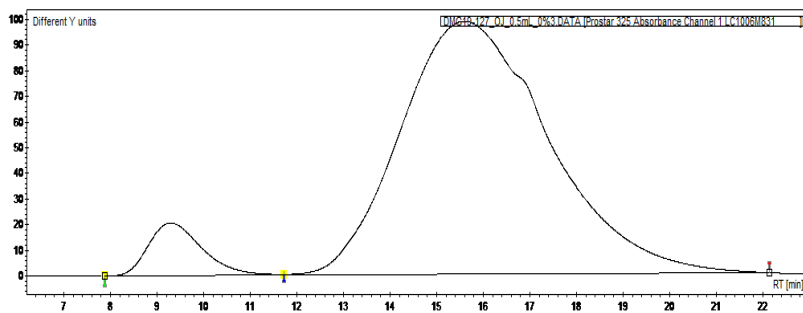


Racemic:



#	Time	Area %
1	9.06 min	50.420
2	14.30 min	49.580

Enantioenriched:



#	Time	Area %
1	9.29 min	6.972
2	15.59 min	93.028
		86% ee

4 – References

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