Supporting Information for

Aliphatic C-H Bond Oxidation with Hydrogen Peroxide Catalyzed by Manganese Complexes. Directing Selectivity through Torsional Effects

Michela Milan[1], Massimo Bietti[2*] and Miquel Costas[1*]

[1] QBIS Research Group, Institut de Química Computacional i Catàlisi (IQCC) and Departament de Química, Universitat de Girona, Campus Montilivi, Girona E-17071, Cata*l*onia, Spain.

[2] Dipartimento di Scienze e Tecnologie Chimiche, Università "Tor Vergata", Via della Ricerca Scientifica, 1 I-00133 Rome, Italy.

e-mail: miquel.costas@udg.edu

bietti@uniroma2.it

Contents

1. Experimental Section

1.1 Materials

Reagents and solvents used were of commercially available reagent quality unless stated otherwise. Solvents were purchased from SDS and Scharlab. Solvents were purified and dried by passing through an activated alumina purification system (M-Braun SPS-800) or by conventional distillation techniques.

1.2 Instrumentation

Oxidation products were identified by comparison of their GC retention times and GC/MS with those of authentic compounds, and/or by ^{1}H and $^{13}C\{^{1}H\}$-NMR analyses. NMR spectra were taken on BrukerDPX300 and DPX400 spectrometers using standard conditions. High resolution mass spectra (HRMS) were recorded on a Bruker MicroTOF-Q IITM instrument with a ESI source at Serveis Tècnics of the University of Girona. Samples were introduced into the mass spectrometer ion source by direct infusion through a syringe pump and were externally calibrated using sodium formate. Chromatographic resolution of enantiomers was performed on an AgilentGC-7820-A chromatograph using a CYCLOSIL-B column and HPLC 1200 series Agilent technologies using CHIRALPAK-IA and CHIRALPAK-IC columns. The configuration of the major enantiomer was determined by chemical correlation.

2. Synthesis of the complexes

***(S,S)*-[Mn(CF_3SO_3)$_2$(pdp)],**[1] **(*S,S*)**, **(*R,R*)** or the racemic mixture of **[Mn(CF_3SO_3)$_2$(^{TIPS}mcp)]**[2] and **(*S,S*)-[Mn(CF_3SO_3)$_2$(^{TIPS}ecp)]**[2] complexes were prepared according to the reported procedures.

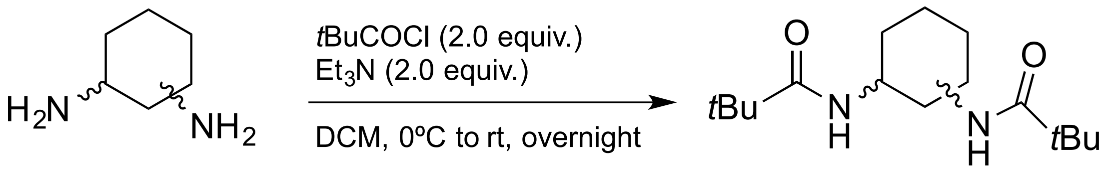
3. Synthesis of the substrates

The following substrates were prepared according to the reported procedures:

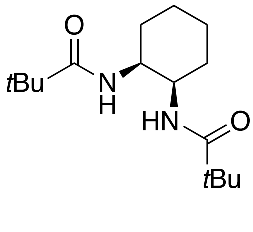
trans-**4**[3]

4-9[4]

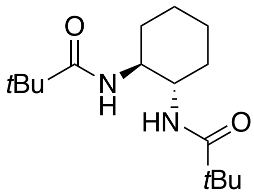
Substrates *cis*/*trans*-**1-3** were synthetized according to the following procedure:



A round-bottom flask equipped with a septum and kept under nitrogen was charged with a 0.20 M solution of the diamine (1.0 equiv) in dichloromethane and cooled to 0 °C. Triethylamine (2.0 equiv) was added to the reaction flask. The pivaloyl chloride (2.0 equiv) was added dropwise and the reaction was stirred overnight at room temperature. At this point, a saturated aqueous Na_2CO_3 solution was added until pH~10-11 and then diluted with dichloromethane. The organic layer was separated from the basic aqueous layer. The aqueous layer was extracted with dichloromethane (2x) and the organic layers were combined. The organic layer was washed with 1N HCl and dried over anhydrous sodium sulfate (Na_2SO_4). The organic layer was evaporated to dryness and the crude amine was purified by flash chromatography over silica gel.

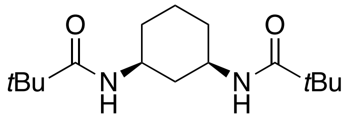


(*cis*-1): A round-bottom flask equipped with a septum and kept under nitrogen was charged with a 0.20 M solution of *cis*-1,2-diaminocyclohexane (3.7 mmol, 0.43 g, 1.0 equiv) in dichloromethane and cooled to 0 °C. Triethylamine (7.4 mmol, 1.0 mL, 2.0 equiv) was added to the reaction flask. The pivaloyl chloride (7.4 mmol, 1.0 mL, 2.0 equiv) was added dropwise and the reaction was stirred overnight at room temperature. At this point, a saturated aqueous Na_2CO_3 solution was added until pH~10-11 and then diluted with dichloromethane. The organic layer was separated from the basic aqueous layer. The aqueous layer was extracted with dichloromethane (2x) and the organic layers were combined. The organic layer was washed with 1N HCl and dried over anhydrous sodium sulfate (Na_2SO_4). The organic layer was evaporated to dryness and the crude amine was purified by flash chromatography over silica gel using CH_2Cl_2/MeOH 3% and the product was concentrated to dryness. The product was isolated as a white solid (0.81 g, 77% yield). ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 6.51 (s, 2H), 4.08 – 3.88 (m, 2H), 1.91 (q, J = 6.9, 3.7 Hz, 2H), 1.6 - 1.41 (m, 6H), 1.20 (s, 9H). ^{13}C-NMR 179.3, 50.6, 38.8, 28.3, 27.5, 22.3. HRMS(ESI+) *m/z* calculated for $C_{16}H_{30}N_2O_2$ [M+Na]+ 305.2199 , found 305.2206.



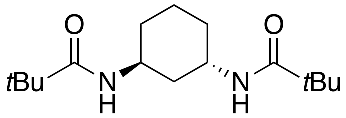
(*trans*-**1**): Following the general conditions, the crude mixture was purified by flash chromatography over silica using CH_2Cl_2/MeOH 2% and the product was concentrated to dryness. The product was isolated as a white solid (0.93 g, 81% yield).

^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 6.17 (s, 2H), 3.71 – 3.54 (m, 2H), 2.07 (dt, *J* = 12.8, 2.7 Hz, 2H), 1.44 – 1.27 (m, 2H), 1.23 (s, 3H), 1.17 (s, 18H). ^{13}C-NMR 179.1, 53.7, 38.5, 32.4, 27.6, 24.7. HRMS(ESI+) *m/z* calculated for $C_{16}H_{30}N_2O_2$ [M+Na]+ 305.2199, found 305.2204.



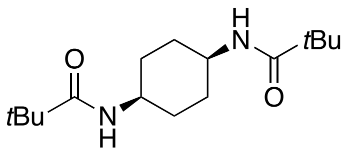
(*cis*-**2**): Following the general conditions, the crude mixture was purified by flash chromatography over silica using hexane:ethyl acetate 3:1 and the product was concentrated to dryness. The product was isolated as a white solid (0.71 g, 73% yield).

^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.42 (d, J = 7.7 Hz, 2H), 3.81 (tdt, J = 11.7, 7.9, 3.9 Hz, 2H), 2.28 – 2.26 (m, 1H), 2.08 – 1.92 (m, 2H), 1.81 (dp, J = 14.0, 3.4 Hz, 1H), 1.56 – 1.37 (m, 1H), 1.19 (s, 18H), 1.11 – 0.96 (m, 3H). ^{13}C-NMR 177.5, 47.4, 39.5, 38.5, 32.3, 27.6, 22.9. HRMS(ESI+) m/z calculated for $C_{16}H_{30}N_2O_2$ [M+Na]+ 305.2199, found 305.2206.



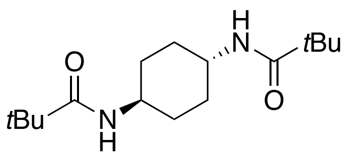
(*trans*-2): Following the general conditions, the crude mixture was purified by flash chromatography over silica using hexane:ethyl acetate 3:1 and the product was concentrated to dryness. The product was isolated as a white solid (0.64 g, 74% yield).

^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.67 (d, J = 5.6 Hz, 2H), 4.18 – 3.89 (m, 2H), 1.71 (dt, J = 11.6, 6.0 Hz, 4H), 1.62 – 1.52 (m, 2H), 1.52 – 1.37 (m, 2H), 1.20 (s, 18H). ^{13}C-NMR 177.8, 44.6, 38.6, 36.6, 27.6, 20.1. HRMS(ESI+) *m/z* calculated for $C_{16}H_{30}N_2O_2$ [M+Na]+ 305.2199 , found 305.2207.



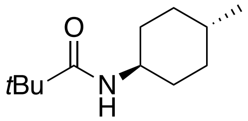
(*cis*-3): Following the general conditions, the crude mixture was purified by flash chromatography over silica using hexane:ethyl acetate 1:1 and the product was concentrated to dryness. The product was isolated as a white solid (0.46 g, 47% yield).

^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.69 (d, J = 7.5 Hz, 2H), 3.81 (dt, J = 7.5, 3.8 Hz, 2H), 1.67 (td, J = 7.5, 6.2, 3.9 Hz, 4H), 1.47 (qd, J = 10.7, 9.7, 4.5 Hz, 4H), 1.11 (s, 18H). ^{13}C-NMR 177.6, 45.4, 38.6, 28.3, 27.5. HRMS(ESI+) *m/z* calculated for $C_{16}H_{30}N_2O_2$ [M+Na]+ 305.2199, found 305.2198.



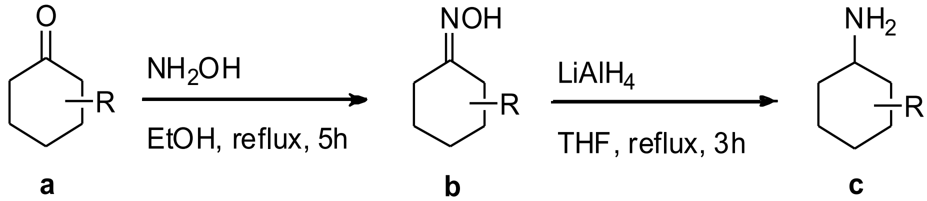
(*trans*-3): Following the general conditions, the crude mixture was purified by flash chromatography over silica using hexane:ethyl acetate 1:2 and the product was concentrated to dryness. The product was isolated as a white solid (0.51 g, 55% yield).

^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.42 (d, *J* = 8.0 Hz, 2H), 3.76 (m, 2H), 2.08 – 1.91 (m, 4H), 1.30 – 1.22 (m, 4H), 1.20 (s, 18H). ^{13}C-NMR 177.8, 47.5, 38.6, 31.8, 27.6. HRMS(ESI+) *m/z* calculated for $C_{16}H_{30}N_2O_2$ [M+Na]+ 305.2199, found 305.2197.

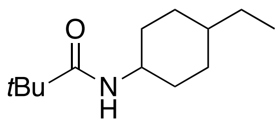


(*trans*-4): Following the general conditions, the crude mixture was purified by flash chromatography over silica using hexane:ethyl acetate 2:1 and the product was concentrated to dryness. The product was isolated as a white solid (0.58 g, 83% yield).

^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.39 (s, 1H), 3.67 (ddq, J = 11.8, 8.1, 4.2 Hz, 1H), 1.96 (dt, J = 7.8, 3.5 Hz, 2H), 1.71 (dt, J = 7.8, 3.5 Hz, 2H), 1.37 – 1.27 (m, 1H), 1.18 (s, 9H), 1.16 – 0.98 (m, 4H), 0.90 (d, J = 6.4 Hz, 3H). ^{13}C-NMR 177.6, 48.2, 38.5, 33.9, 33.2, 32.0, 27.6, 22.2. HRMS(ESI+) *m/z* calculated for $C_{12}H_{23}NO$ [M+Na]+ 220.1672, found 220.1671.

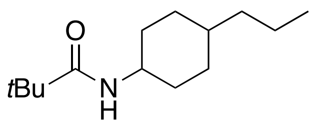


Hydroxylamine hydrochloride (1.2 equiv) followed by pyridine (3.0 equiv) was added to a solution of ketone (**a**) (1.0 equiv) in absolute ethanol and the reaction mixture was heated to reflux temperature under stirring for 5 hours. The reaction was then quenched with water and the product extracted with ethyl acetate (2 x 50 mL). The organic fractions were washed with water and dried over anhydrous $MgSO_4$. The solvent was removed under vacuum to obtain the oxime (**b**) that was used in the next step without further purification. To a stirred solution of lithium aluminium hydride (0.5 equiv) in anhydrous THF under N_2, was added a solution of intermediate **b** drop wise. The reaction was slowly heated to reflux temperature for 3 hours. After this, the reaction mixture was quenched with 1M NaOH solution at 5°C. After filtration through Celite© and extraction with ethyl acetate (2 x 50 mL) the organic fractions were dried over anhydrous $MgSO_4$, the solvent removed under vacuum and the obtained intermediate **c** was used in the next acylation step without further purification to give the corresponding amide.



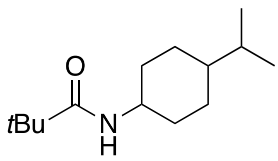
(5): Hydroxylamine hydrochloride (6.7 mmol, 0.47 g, 1.2 equiv) followed by pyridine (16.8 mmol, 1 mL, 3.0 equiv) was added to a solution of 4-ethylcyclohexanone (**a**) (5.6 mmol, 0.71 g, 1.0 equiv) in absolute ethanol and the reaction mixture was heated to reflux temperature under stirring for 5 hours. The reaction was then quenched with water and the product extracted with ethyl acetate (2 x 50 mL). The organic fractions were washed with water and dried over anhydrous $MgSO_4$. The solvent was removed under vacuum to obtain the oxime (**b**) that was used in the next step without further purification. To a stirred solution of lithium aluminium hydride (11.2 mmol, 0.43 g, 0.5 equiv) in anhydrous THF under N_2, was added a solution of intermediate **b** drop wise. The reaction was slowly heated to reflux temperature for 3 hours. After this, the reaction mixture was quenched with 1M NaOH solution at 5°C. After filtration through Celite© and extraction with ethyl acetate (2 x 50 mL) the organic fractions were dried over anhydrous $MgSO_4$, the solvent removed under vacuum and the obtained 4-ethylcyclohexylamine was used in the next acylation step without further purification to give the amide **5**. The crude mixture was purified by flash chromatography over silica using CH_2Cl_2/MeOH 1% and the product was concentrated to dryness. The product was isolated as a white solid (0.62 g, 71% yield, *cis*:*trans* = 1:1.2).

^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.72 (s, 1H), 5.40 (s, 1H), 2.04 – 1.91 (m, 2H), 1.84 – 1.72 (m, 2H), 1.69 – 1.51 (m, 5H), 1.37 – 1.24 (m, 4H), 1.21 (s, 8H), 1.19 (s, 9H), 1.14 – 1.01 (m, 6H), 0.89 (td, J = 7.3, 6.3 Hz, 6H). ^{13}C-NMR 177.6, 177.4, 48.6, 45.2, 38.7, 38.5, 37.5, 33.2, 31.4, 29.5, 29.3, 28.2, 27.8, 27.64, 27.6, 11.59, 11.56. HRMS(ESI+) m/z calculated for $C_{13}H_{25}NO$ [M+Na]+ 234.1828, found 234.1834.



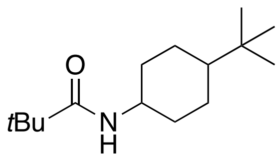
(6): Following the general conditions, the crude mixture was purified by flash chromatography over silica using CH_2Cl_2/MeOH 1% and the product was concentrated to dryness. The product was isolated as a white solid (0.32 g, 33% yield, *cis*:*trans* = 1:2).

^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.70 (bs, 1H), 5.42 (d, J = 8.0 Hz, 1H), 4.00 – 3.93 (m, 0.5H) 3.65 (dtt, J = 11.7, 8.1, 4.0 Hz, 1H), 2.03 – 1.84 (m, 2H), 1.73 (dt, J = 11.1, 2.3 Hz, 2H), 1.67 – 1.49 (m, 3H), 1.39 – 1.20 (m, 5H), 1.16 (d, J = 6.5 Hz, 18H), 1.09 – 0.95 (m, 4H), 0.86 (td, J = 7.1, 5.9 Hz, 5H). ^{13}C-NMR 177.5, 177.3, 48.5, 45.2, 39.1, 38.6, 38.5, 37.8, 36.6, 35.3, 33.2, 31.8, 29.3, 28.1, 27.60, 27.57, 20.1, 14.31, 14.29. HRMS(ESI+) *m/z* calculated for $C_{14}H_{27}NO$ [M+Na]+ 248.1985, found 248.1987.



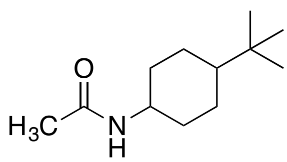
(7): Following the general conditions, the crude mixture was purified by flash chromatography over silica using hexane:ethyl acetate 4:1 and the product was concentrated to dryness. The product was isolated as a white solid (0.43 g, 85% yield, *cis*:*trans* = 1:1.4).

^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.79 (s, 1H), 5.48 (d, *J* = 8.1 Hz, 1H), 4.00 – 3.93 (m, 1H), 3.67 – 3.54 (m, 1H), 1.94 – 1.88 (m, 2H), 1.74 – 1.61 (m, 4H), 1.57 – 1.33 (m, 6H), 1.23 – 1.21 (m, 1H), 1.14 (s, 9H), 1.11 (s, 9H), 1.07 – 0.97 (m, 6H), 0.81 (dd, *J* = 10.8, 6.8 Hz, 12H). ^{13}C-NMR 182.3, 177.7, 177.4, 48.6, 44.7, 43.2, 42.7, 38.6, 38.4, 38.3, 33.2, 32.5, 31.5, 29.6, 28.4, 27.54, 27.51, 27.1, 26.4, 24.8, 19.9, 19.8. HRMS(ESI+) *m/z* calculated for $C_{14}H_{27}NO$ [M+Na]+ 248.1985, found 248.1985.



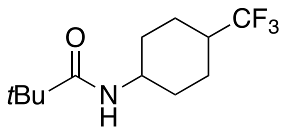
(8): Following the general conditions, the crude mixture was purified by flash chromatography over silica using CH_2Cl_2/MeOH 0.5% and the product was concentrated to dryness. The product was isolated as a white solid (2.3 g, 54% yield, *cis*:*trans* = 1:2).

^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.77 (bs, 0.5H), 5.41 (bs, 1H), 4.07 – 4.01 (m, 0.5H), 3.69 – 3.56 (m, 1H), 1.99 - 1.96 (m, 2H), 1.85 - 1.74 (m, 3H), 1.66 – 1.62 (m, 1H), 1.52 – 1.43 (m, 1H), 126 – 1.23 (m, 2H), 1.18 (s, 4.5H), 1.15 (s, 9H), 1.08 – 1.00 (m, 5H), 0.84 (s, 4.5H), 0.82 (s, 9H). ^{13}C-NMR 177.5, 177.3, 48.5, 47.41, 47.36, 38.7, 38.5, 33.6, 32.4, 32.3, 30.3, 27.62, 27.58, 27.55, 27.4, 27.3, 26.1, 21.8. HRMS(ESI+) *m/z* calculated for $C_{15}H_{29}NO$ [M+Na]+ 262.2141, found 262.2142.



(9): Following the general conditions, the crude mixture was purified by flash chromatography over silica using hexane:ethyl acetate 1:1 and the product was concentrated to dryness. The product was isolated as a white solid (0.54 g, 64% yield, *cis*:*trans* = 1:1.4).

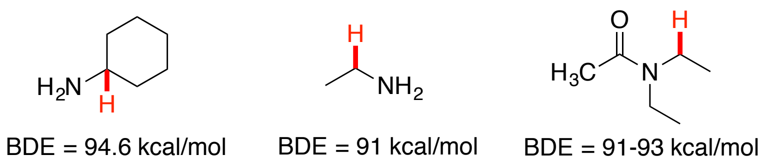
^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 6.10 (bs, 1.5H), 4.04 – 4.02 (m, 0.7H), 3.61 – 3.54 (m, 1H), 1.94 (s, 3H), 1.89 (s, 3H), 1.82 - 1.71 (m, 3H), 1.60 – 1.55 (m, 1H), 1.48 – 1.39 (m, 1H), 1.07 – 0.98 (m, 6H), 0.81 (s, 6H), 0.78 (s, 9H). ^{13}C-NMR 169.4, 48.7, 47.7, 47.2, 44.2, 33.5, 32.4, 32.3, 30.6, 27.5, 27.4, 27.3, 26.1, 23.5, 23.4, 21.9. HRMS(ESI+) *m/z* calculated for $C_{12}H_{23}NO$ [M+Na]+ 220.1672, found 220.1671.



(10): Following the general conditions, the crude mixture was purified by flash chromatography over silica using hexane:ethyl acetate 2:1 and the product was concentrated to dryness. The product was isolated as a white solid (0.46 g, 34% yield, *cis*:*trans* = 1:2.4).

^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.66 (bs, 0.5H), 5.40 (bs, 1H), 4.11 – 4.07 (m, 0.5H), 3.80 – 3.71 (m, 1H), 2.13 - 2.10 (m, 2H), 2.02 – 1.99 (m, 3H), 1.87 – 1.84 (m, 1H), 1.55 – 1.42 (m, 2.5H), 1.31 - 1.26 (m, 1H), 1.23 (s, 2H), 1.21 (s, 9H), 1.15 – 1.08 (m, 2H). ^{13}C-NMR 177.7, 128.9, 47.4, 43.8, 41.0, 38.5, 31.4, 28.2, 27.53, 27.49, 23.99, 23.97, 23.94, 23.91, 20.29, 20.26. HRMS(ESI+) *m/z* calculated for $C_{12}H_{20}F_3NO$ [M+Na]+ 274.1389, found 274.1389.

4. Estimation of the Tertiary C-H Bond BDE of *N*-Cyclohexylacetamide



There is no value for the *N*-cyclohexylamides. The Luo book gives **94.6 kcal/mole** for the tertiary C-H bond of cyclohexylamine.[5] The α-C-H bonds of ethylamine have a BDE of **91 kcal mol**[6] while those of the C-H bonds α- to N in *N,N*-diethylacetamide are between **91** and **93 kcal/mol**[7]. If we assume that amide α-C-H bonds are about **1 kcal/mol** stronger than those of amines, and take **94.6 kcal/mole** for the tertiary C-H bond of cyclohexylamine as a reference value, we would estimate a value between **95** and **96 kcal/mol** for the tertiary C-H bond of *N*-cyclohexylacetamide.

5. Oxidation reactions

Hydrogen peroxide solutions employed in the oxidation reactions were prepared by diluting commercially available hydrogen peroxide (30% H_2O_2 solution in water, Aldrich) in acetonitrile to achieve a 1.5 M. Commercially available glacial acetic acid (99-100%) purchased from Riedel-de-

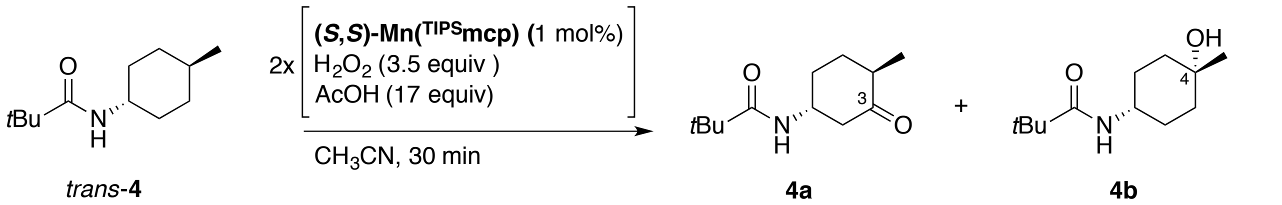
Haën was employed. The purity of the amide substrates synthetized as described above was in all cases >99%. Cyclopropane carboxylic acid was purchased from Aldrich.

5.1 Reaction protocol for catalysis

An acetonitrile solution (400 µL) of the substrate (0.25 M) and the corresponding complex (2.5 mM) was prepared in a vial (10 mL) equipped with a stir bar cooled at -40 ºC, in a CH_3CN/N_2(liq) bath. 98 µL (neat, 17 equiv.) of acetic acid were added directly to the solution. Then, 236 µL of a 1.5 M hydrogen peroxide solution in CH_3CN (3.5 equiv.) were added by syringe pump over a period of 30 min. At this point, an internal standard (biphenyl) was added and the solution was quickly filtered through a basic alumina plug, which was subsequently rinsed with 2 x 1 mL AcOEt. GC analysis of the solution provided substrate conversions and product yields relative to the internal standard integration. Isomer ratio was determined by GC or ^{1}H-NMR. Commercially unavailable products were identified by a combination of ^{1}H, ^{13}C{^{1}H}-NMR analysis, and HRMS. The oxidized products were identified by comparison to the GC retention time of racemate products obtained with the racemic mixture of **Mn(^{TIPS}mcp)**.

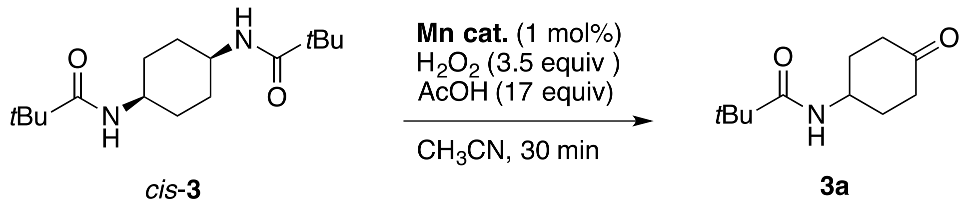
5.2 Optimization Experiments

The majority of the optimization experiments have been already reported in a previous work.[8]



T (ºC)	Conv (%)	Yield C3 (%)	Yield C4 (%)	ee C3 (%)
0	98	42	11	64
-40	>99	78[a]	14[a]	78

Conversions and yields determined by GC analysis. [a]Isolated yield.

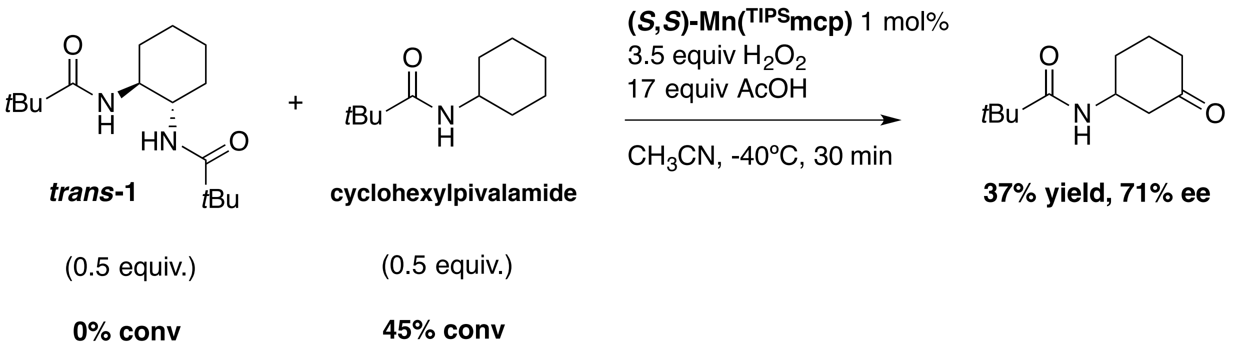


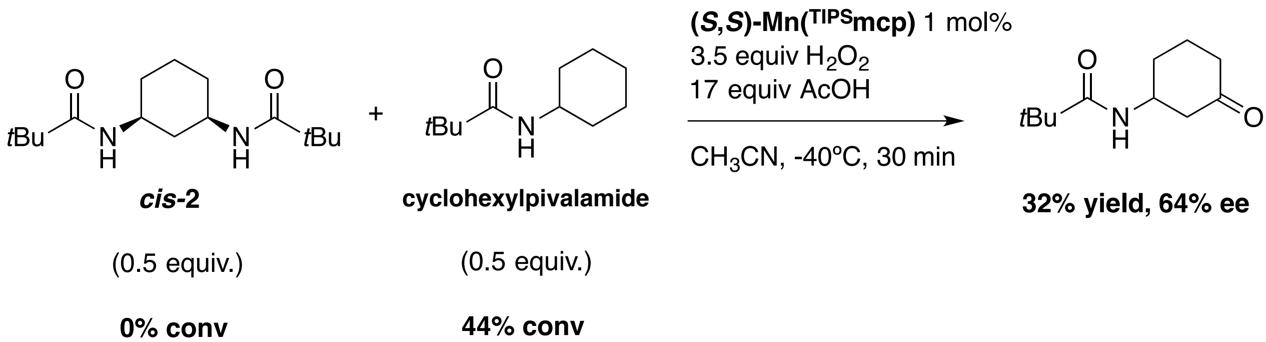
Cat.	T (ºC)	Conv (%)	Yield (%)
Mn(pdp)	-40	70	48
Mn(^{TIPS}ecp)	-40	49	29
Mn(^{TIPS}mcp)	-40	99	50
Mn(^{TIPS}mcp)	0	98	23

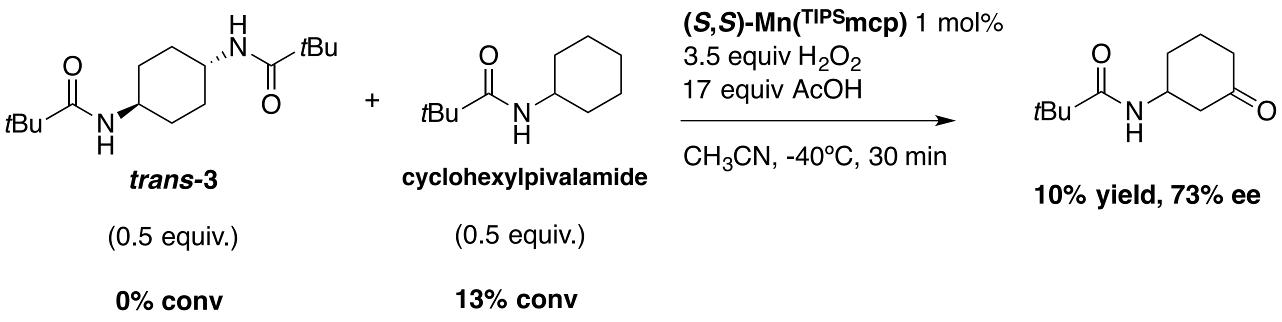
Conversions and yields determined by GC analysis.

5.3 Competition Experiments

Conversions and yields determined by GC analysis using the correspondent response factor:

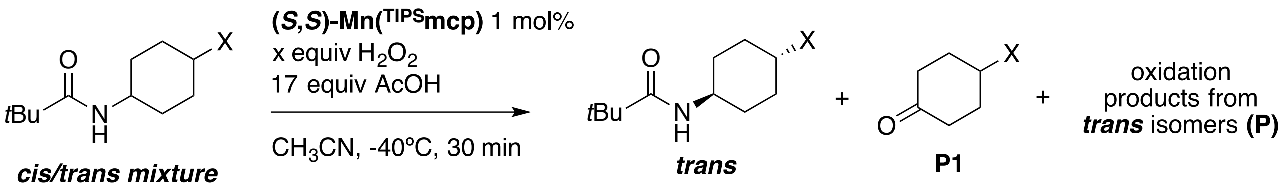






5.4 Reaction optimization for the isolation of the *trans* isomer

The following table reports the small scale catalysis using substrates **5**-**10**:



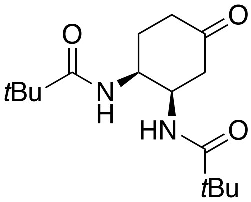
Sub	*trans:cis*	H_2O_2 (equiv.)	Conv *cis* (%)[a]	Conv *trans* (%)[a]	Yield P1 (%)[a]	Yield P (%)[a]
5	1.2:1	2.0	>99	32	31	31
6	2:1	2.5	>99	30	43	24
7	1.4:1	3.0	>99	26	46	10
8	2:1	3.5	>99	0	93	-
9[b]	1.4:1	3.5	>99	36	78	5
10	2.4:1	3.0	>99	10	81	5

[a]Conversions and yields determined from crude reaction mixtures by GC and ^{1}H-NMR analysis. [b]**Mn(^{TIPS}ecp)** (1 mol%) and cyclopropane carboxylic acid.

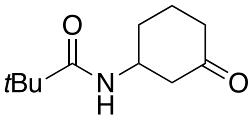
5.5 General Procedure for product isolation

A 25 mL round bottom flask was charged with: catalyst (6 µmol, 1.0 mol%), substrate (1 equiv.), CH_3CN (3.3 mL) and a magnetic stir bar. The carboxylic acid of choice was the added (17 equiv.) and the mixture was cooled at -40 ºC in an CH_3CN/N_2(liq) bath under magnetic stirring. Then, 1.4 mL of a 1.5 M hydrogen peroxide solution in CH_3CN (3.5 equiv.) were added by syringe pump over a period of 30 min at -40°C. At this point, 15 mL of an aqueous $NaHCO_3$ saturated solution were added to the mixture. The resultant solution was extracted with CH_2Cl_2 (3 x 10 mL). Organic fractions were combined, dried over $MgSO_4$, and the solvent was removed under reduced pressure to afford the oxidized product. This residue was filtered by silica gel column to obtain the pure product.

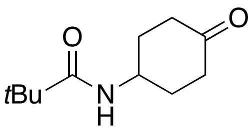
6. Characterization of the isolated products



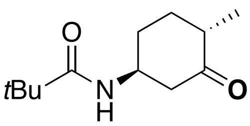
(1a), purification by flash chromatography (SiO_2; hexane:AcOEt 2:1→1:1) gave the product as a white solid (76 mg, 74% yield, 60% ee); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 7.30 (bs, 1H), 5.93 (bs, 1H), 4.54 (s, 1H), 4.35 – 4.21 (m, 1H), 2.90 (dd, *J* = 14.5, 4.6 Hz, 1H), 2.70 – 2.52 (m, 1H), 2.50 – 2.38 (m, 2H), 1.76 – 1.65 (m, 2H), 1.22 (s, 9H), 1.20 (s, 9H). ^{13}C-NMR 208.8, 180.5, 179.4, 51.9, 51.5, 45.5, 39.0, 27.5, 27.4, 26.3. HRMS(ESI+) *m/z* calculated for $C_{16}H_{28}N_2O_3$ [M+Na]+ 319.1922, found 319.1983.



(2a), purification by flash chromatography (SiO_2; hexane:AcOEt 1:1) gave the product as a white solid (55 mg, 61% yield); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.60 (bs, 1H), 4.33 - 4.15 (m, 1H), 2.69 (ddt, *J* = 13.9, 4.8, 1.5 Hz, 1H), 2.49 - 2.20 (m, 3H), 2.14 – 1.97 (m, 1H), 1.99 – 1.59 (m, 3H), 1.18 (s, 6H). ^{13}C-NMR 209.0, 177.7, 48.4, 47.6, 41.0, 38.6, 30.7, 27.5, 22.2. HRMS(ESI+) *m/z* calculated for $C_{11}H_{19}NO_2$ [M+Na]+ 220.1308, found 220.1307.

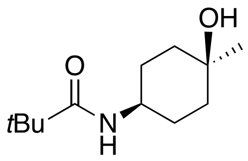


(3a), purification by flash chromatography (SiO_2; CH_2Cl_2/MeOH 3%) gave the product as a white solid (41 mg, 46% yield); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.57 (s, 1H), 4.24 (tdt, J = 11.2, 7.7, 3.9 Hz, 1H), 2.55 – 2.33 (m, 4H), 2.33 – 2.17 (m, 2H), 1.76 – 1.56 (m, 2H), 1.21 (s, 9H). ^{13}C-NMR 209.7, 178.0, 46.3, 39.2, 38.7, 32.0, 27.6. HRMS(ESI+) m/z calculated for $C_{11}H_{19}NO_2$ [M+Na]+ 220.1308, found 220.1307.

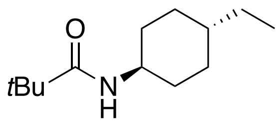


(4a), purification by flash chromatography (SiO_2; hexane:AcOEt 2:1) gave the product as a white solid (86 mg, 78% yield, 78% ee); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.59 (d, J = 7.9 Hz, 1H), 4.17 – 4.02 (m, 1H), 2.72 (ddd, J = 13.1, 4.7, 2.2 Hz, 1H), 2.36 – 2.17 (m, 3H), 2.06

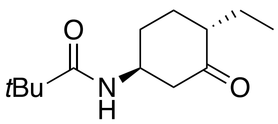
(ddt, J = 12.9, 5.9, 3.5 Hz, 1H), 1.61 (tdd, J = 12.7, 11.5, 3.5 Hz, 1H), 1.45 – 1.31 (m, 1H), 1.19 (s, 9H), 1.05 (d, J = 6.5 Hz, 3H). ^{13}C-NMR 209.2, 177.5, 49.0, 47.9, 44.4, 38.6, 32.1, 31.2, 27.5, 14.2. HRMS(ESI+) m/z calculated for $C_{12}H_{21}NO_2$ [M+Na]+ 234.1465, found 234.1477.



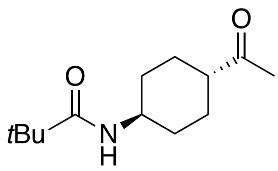
(4b), purification by flash chromatography (SiO_2; hexane:AcOEt 1:1) gave the product as a white solid (16 mg, 14% yield); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.48 (d, J = 7.6 Hz, 1H), 3.74 – 3.69 (m, 1H), 1.77 (dq, J = 7.6, 4.9, 4.0 Hz, 2H), 1.66 (td, J = 10.9, 9.5, 5.5 Hz, 2H), 1.57 – 1.45 (m, 4H), 1.25 (s, 3H), 1.18 (s, 9H). ^{13}C-NMR 209.2, 177.7, 68.4, 47.5, 38.5, 37.5, 31.0, 28.3, 27.6. HRMS(ESI+) m/z calculated for $C_{12}H_{23}NO_2$ [M+Na]+ 236.1621, found 236.1628.



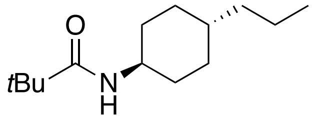
(*trans*-5), purification by flash chromatography (SiO_2; hexane:AcOEt 5:1) gave the product as a white solid (66 mg, 68% yield); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.41 (s, 1H), 3.75 – 3.65 (m, 1H) 2.01 – 1.89 (m, 2H), 1.83 – 1.71 (m, 2H), 1.28 – 1.20 (m, 2H), 1.18 (s, 9H), 1.13 – 0.97 (m, 5H), 0.88 (t, J = 7.4 Hz, 3H). ^{13}C-NMR 177.5, 48.5, 38.6, 38.4, 33.1, 31.4, 29.4, 27.6, 11.6. HRMS(ESI+) *m/z* calculated for $C_{13}H_{25}NO$ [M+Na]+ 234.1828, found 234.1834.



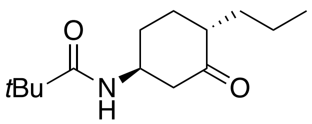
(5a), purification by flash chromatography (SiO_2; hexane:AcOEt 1:1) gave the product as a white solid (60 mg, 65% yield, 86% ee); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.59 (d, *J* = 7.8 Hz, 1H), 4.19 – 4.01 (m, 1H), 2.71 (ddd, *J* = 13.0, 4.7, 2.1 Hz, 1H), 2.22 – 2.16 (m, 1H), 2.16 – 2.07 (m, 2H), 1.82 (ddd, *J* = 13.7, 7.5, 5.8 Hz, 1H), 1.60 (tdd, *J* = 12.3, 11.0, 3.4 Hz, 1H), 1.43 – 1.24 (m, 3H), 1.20 (s, 9H), 0.92 (t, *J* = 7.5 Hz, 3H). ^{13}C-NMR 209.0, 177.6, 51.3, 49.1, 48.0, 38.6, 31.7, 28.5, 27.6, 21.8, 11.6. HRMS(ESI+) *m/z* calculated for $C_{13}H_{23}NO_2$ [M+Na]+ 248.1621, found 248.1626.



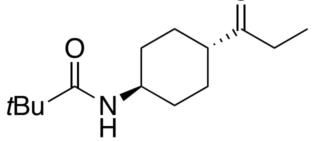
(5b), purification by flash chromatography (SiO_2; hexane:AcOEt 1:1) gave the product as a white solid (12 mg, 13% yield); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.55 – 5.29 (m, 1H), 3.72 (tdt, J = 11.8, 8.0, 4.0 Hz, 1H), 2.33 – 2.21 (m, 1H), 2.15 (s, 3H), 2.11 – 2.03 (m, 2H), 2.03 – 1.91 (m, 2H), 1.53 – 1.39 (m, 2H), 1.18 (s, 9H), 1.13-1.02 (m, 1H). ^{13}C-NMR 211.2, 177.7, 50.6, 47.7, 38.5, 32.3, 27.9, 27.6, 27.2, 22.7, 14.1. HRMS(ESI+) *m/z* calculated for $C_{13}H_{23}NO_2$ [M+Na]+ 248.1621, found 248.1612.



(*trans*-6), purification by flash chromatography (SiO_2; hexane:AcOEt 1:1) gave the product as a white solid (103 mg, 91% yield); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.40 (d, J = 7.9 Hz, 1H), 3.68 (ddp, J = 11.7, 8.1, 4.0 Hz, 1H), 2.02 – 1.91 (m, 2H), 1.76 (dt, J = 12.5, 3.0 Hz, 2H), 1.36 – 1.22 (m, 4H), 1.21 (d, J = 2.7 Hz, 1H), 1.18 (s, 10H), 1.12 – 0.95 (m, 4H), 0.88 (t, J = 7.3 Hz, 3H). ^{13}C-NMR 177.5, 48.5, 39.1, 38.5, 36.6, 33.2, 31.8, 27.6, 20.1, 14.3. HRMS(ESI+) *m/z* calculated for $C_{14}H_{27}NO$ [M+Na]+ 248.1985, found 248.1994.

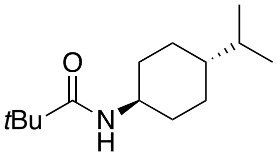


(6a), purification by flash chromatography (SiO_2; hexane:AcOEt 1:1) gave the product as a white solid (43 mg, 42% yield, 90% ee); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.60 (d, *J* = 7.7 Hz, 1H), 4.19 – 4.00 (m, 1H), 2.71 (ddd, *J* = 13.0, 4.7, 2.0 Hz, 1H), 2.23 – 2.14 (m, 2H), 2.13 – 2.04 (m, 1H), 1.78 (ddt, *J* = 13.4, 8.8, 5.9 Hz, 1H), 1.60 (tdd, *J* = 12.6, 11.1, 3.6 Hz, 1H), 1.42 – 1.20 (m, 5H), 1.19 (s, 9H), 0.91 (t, *J* = 7.3 Hz, 3H). ^{13}C-NMR 209.1, 177.6, 49.5, 49.1, 47.9, 38.6, 31.6, 31.0, 28.9, 27.5, 20.2, 14.2. HRMS(ESI+) *m/z* calculated for $C_{14}H_{25}NO_2$ [M+Na]+ 262.1778, found 262.1777.

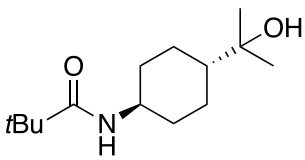


(6b), purification by flash chromatography (SiO_2; hexane:AcOEt 1:1) gave the product as a white solid (4 mg, 4% yield); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.38 (d, *J* =

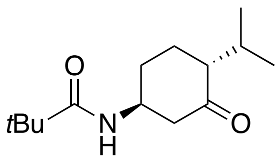
7.8 Hz, 1H), 3.71 (tdt, *J* = 11.8, 8.0, 4.0 Hz, 1H), 2.46 (q, *J* = 7.3 Hz, 2H), 2.28 (tt, *J* = 12.1, 3.5 Hz, 1H), 2.11 – 2.01 (m, 2H), 1.92 (dt, *J* = 13.2, 2.9 Hz, 2H), 1.48 (qd, *J* = 13.3, 3.4 Hz, 2H), 1.17 (s, 9H), 1.15 – 1.07 (m, 2H), 1.03 (t, *J* = 7.3 Hz, 3H). ^{13}C-NMR 213.7, 177.7, 49.7, 47.7, 38.5, 33.7, 32.4, 29.7, 27.6, 27.4, 7.7, 1.1. HRMS(ESI+) *m/z* calculated for $C_{14}H_{25}NO_2$ [M+Na]+ 262.1778, found 262.1777.



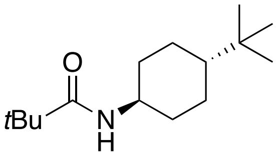
(*trans*-7), purification by flash chromatography (SiO_2; hexane:AcOEt 5:1) gave the product as a white solid (91 mg, 75% yield); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.38 (d, J = 7.6 Hz, 1H), 3.61 (dtq, J = 11.7, 8.1, 4.0 Hz, 1H), 1.93 (dt, J = 11.1, 3.7 Hz, 2H), 1.69 (dt, J = 10.7, 3.0 Hz, 2H), 1.45 – 1.31 (m, 1H), 1.13 (s, 9H), 1.09 – 0.93 (m, 5H), 0.81 (d, J = 6.9 Hz, 6H). ^{13}C-NMR 177.5, 48.5, 43.3, 38.4, 33.3, 32.5, 28.4, 27.6, 19.8. HRMS(ESI+) *m/z* calculated for $C_{14}H_{27}NO$ [M+Na]+ 248.1985, found 248.1985.



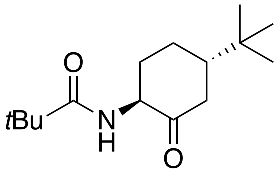
(7a), purification by flash chromatography (SiO_2; hexane:AcOEt 2:1) gave the product as a white solid (37 mg, 45% yield); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.40 (s, 1H), 3.69 – 3.67 (m, 1H) , 2.00 (dd, J = 12.3, 3.6 Hz, 2H), 1.89 – 1.77 (m, 2H), 1.55 (s, 1H), 1.24 – 1.20 (m, 3H), 1.14 (s, 15H), 1.11 – 0.98 (m, 2H). ^{13}C-NMR 177.6, 72.6, 48.4, 48.3, 38.5, 33.2, 27.6, 27.1, 26.2. HRMS(ESI+) *m/z* calculated for $C_{14}H_{27}NO_2$ [M+Na]+ 264.1934, found 264.1934.



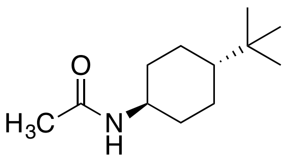
(7b), purification by flash chromatography (SiO_2; hexane:AcOEt 2:1) gave the product as a white solid (11 mg, 14% yield, 4% ee); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.48 – 5.31 (m, 1H), 3.65 (dtt, J = 11.4, 7.6, 4.0 Hz, 1H), 2.00 (dd, J = 12.3, 3.6 Hz, 2H), 1.92 – 1.86 (m, 1H), 1.79 – 1.75 (m, 1H), 1.35 – 1.23 (m, 6H), 1.19 (s, 9H), 1.11 – 0.98 (m, 3H). ^{13}C-NMR 177.6, 72.5, 48.4, 48.2, 38.5, 33.2, 27.6, 27.0, 26.2. HRMS(ESI+) *m/z* calculated for $C_{14}H_{25}NO_2$ [M+Na]+ 262.1778, found 262.1760.



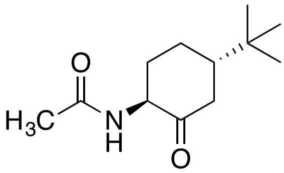
(*trans*-8), purification by flash chromatography (SiO_2; hexane:AcOEt 5:1) gave the product as a white solid (101 mg, 66% yield); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.38 (d, J = 7.9 Hz, 1H), 3.71 – 3.61 (m, 1H), 2.09 – 1.93 (m, 2H), 1.86 – 1.70 (m, 2H), 1.19 (s, 9H), 1.17 – 1.01 (m, 4H), 0.96 (tt, J = 11.8, 3.2 Hz, 1H), 0.86 (s, 9H). ^{13}C-NMR 177.6, 48.5, 47.4, 38.5, 33.7, 32.4, 27.61, 27.58, 26.2. HRMS(ESI+) *m/z* calculated for $C_{15}H_{29}NO$ [M+Na]+ 262.2141, found 262.2142.



(8a), purification by flash chromatography (SiO_2; hexane:AcOEt:MeOH 99:1:0.01) gave the product as a white solid (60 mg, 34% yield, 70% ee); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 6.68 (s, 1H), 4.40 (dtd, *J* = 12.3, 6.1, 1.3 Hz, 1H), 2.70 (ddt, *J* = 12.7, 6.3, 3.2 Hz, 1H), 2.60 (ddd, *J* = 12.5, 3.4, 2.5 Hz, 1H), 2.23 – 2.14 (m, 1H), 1.94 (dq, *J* = 9.5, 3.4 Hz, 1H), 1.61 – 1.53 (m, 3H), 1.23 (s, 9H), 0.93 (s, 9H). ^{13}C-NMR 208.8, 178.2, 57.7, 51.0, 42.7, 38.8, 33.9, 32.9, 27.5, 27.2, 25.1. HRMS(ESI+) *m/z* calculated for $C_{15}H_{27}NO_2$ [M+Na]+ 276.1934, found 276.1932.

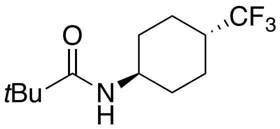


(*trans*-9), purification by flash chromatography (SiO_2; hexane:AcOEt 1:1) gave the product as a white solid (90 mg, 84% yield); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.42 (s, 1H), 3.67 (dtd, *J* = 11.4, 7.5, 4.0 Hz, 1H), 2.07 – 2.00 (m, 2H), 1.96 (d, *J* = 0.8 Hz, 3H), 1.83 – 1.75 (m, 2H), 1.18 – 1.04 (m, 4H), 0.85 (d, *J* = 0.9 Hz, 9H). ^{13}C-NMR 169.2, 48.8, 47.3, 33.7, 32.3, 27.5, 26.1, 23.6. HRMS(ESI+) *m/z* calculated for $C_{12}H_{23}NO$ [M+Na]+ 220.1672, found 220.1670.

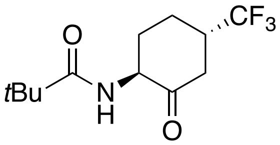


(9a), purification by flash chromatography (SiO_2; hexane:AcOEt 1:1) gave the product collected with low amount of the substrate (32 mg, 46% ee); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 6.42 (s, 1H), 4.49 – 4.34 (m, 1H), 2.66 (d, J = 19.0 Hz, 1H), 2.56 (d, J = 12.7 Hz, 1H), 2.16 (d, J = 25.4 Hz, 1H), 2.01 (s, 3H), 1.57 (d, J = 39.8 Hz, 2H), 1.26 (d, J = 28.8 Hz, 2H), 0.89 (s, 9H).

^{13}C-NMR 208.5, 169.8, 57.8, 50.9, 42.6, 34.0, 32.9, 27.5, 27.2, 25.1. HRMS(ESI+) *m/z* calculated for $C_{12}H_{21}NO_2$ [M+Na]+ 234.1465, found 234.1468.

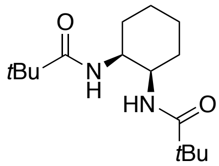


(*trans*-10), purification by flash chromatography (SiO_2; hexane:AcOEt 5:1) gave the product as a white solid (88 mg, 96% yield); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 5.45 (d, J = 6.7 Hz, 1H), 3.72 (tdt, J = 11.8, 8.0, 4.0 Hz, 1H), 2.08 (dd, J = 12.8, 3.7 Hz, 2H), 2.02 – 1.88 (m, 3H), 1.55 – 1.32 (m, 2H), 1.17 (s, 9H), 1.15 – 1.02 (m, 2H). ^{13}C-NMR 177.8, 129.3, 47.5, 38.5, 31.4, 27.6, 23.98, 23.94. HRMS(ESI+) *m/z* calculated for $C_{12}H_{20}F_3NO$ [M+Na]+ 274.1389, found 274.1389.

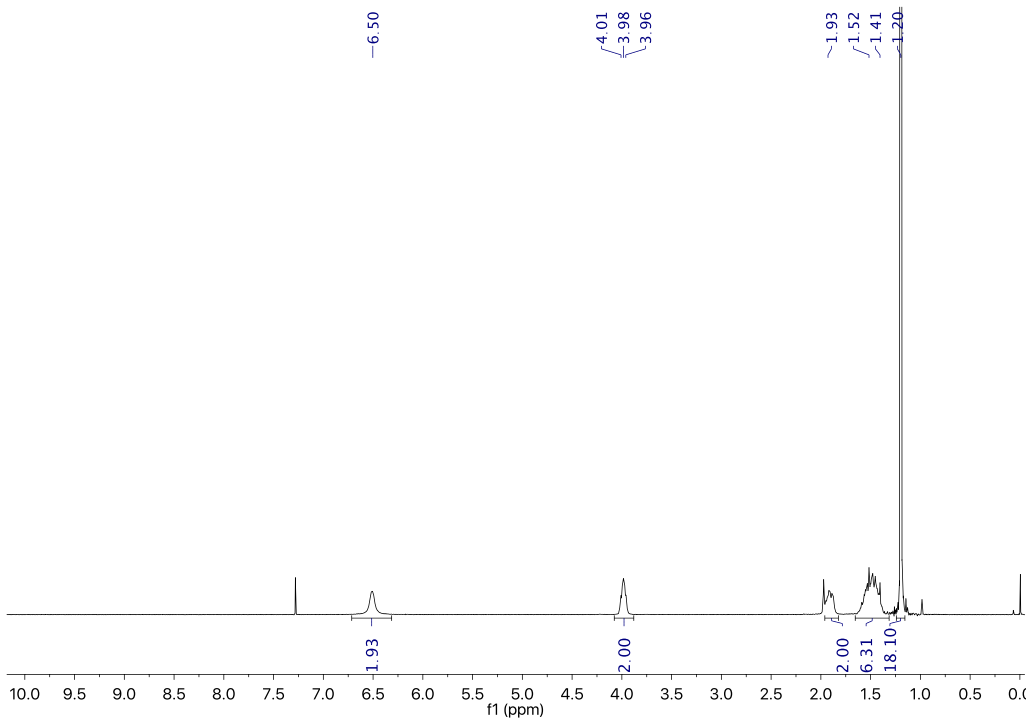


(10a), purification by flash chromatography (SiO_2; hexane:AcOEt 1:1) gave the product collected with the substrate (66 mg, 40% ee); ^{1}H-NMR ($CDCl_3$, 400 MHz, 300K) δ, ppm: 6.60 (bs, 1H), 4.48 – 4.42 (m, 1H), 2.78 – 2.72 (m, 2H), 2.52 – 2.45 (m, 2H), 2.34 – 2.22 (m, 1H), 1.84 – 1.78 (m, 2H), 1.21 (s, 9H). ^{13}C-NMR 204.0, 178.3, 131.6, 128.9, 126.1, 123.3, 57.4, 41.6, 41.3, 41.1, 40.8, 39.5, 38.8, 31.9, 27.4, 27.3. HRMS(ESI+) *m/z* calculated for $C_{12}H_{18}F_3NO_2$ [M+Na]+ 288.1182, found 288.1175.

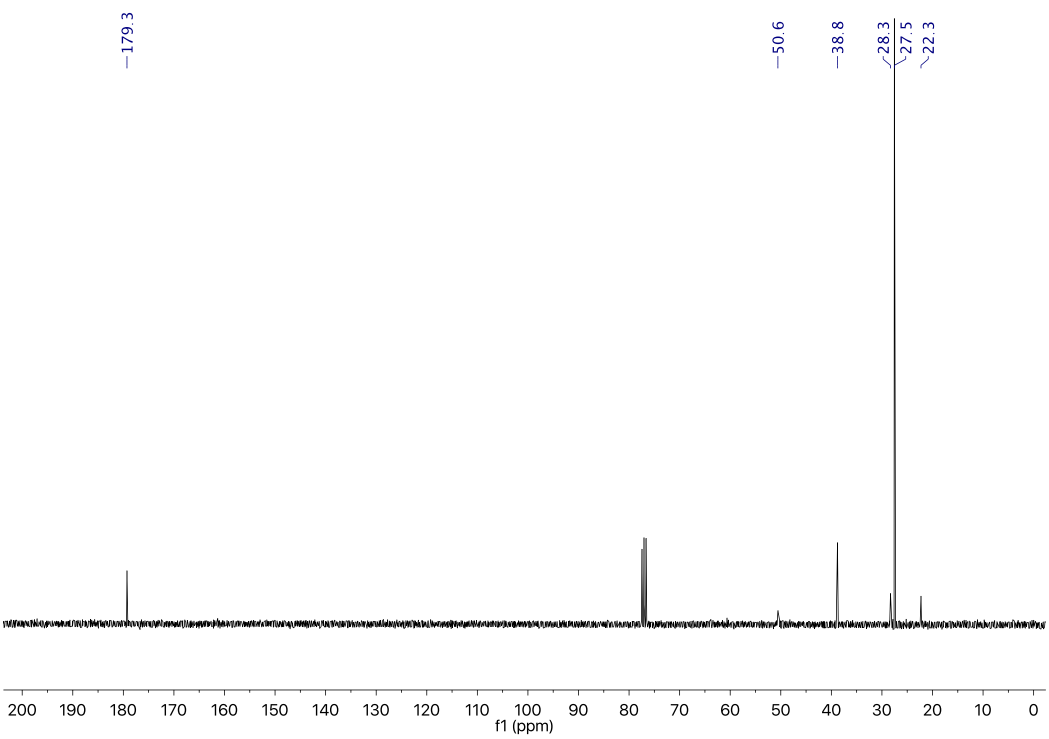
A1 ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of substrates

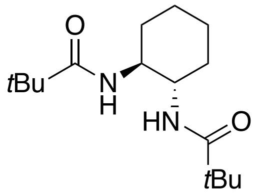


^{1}H-NMR of *cis*-**1** in $CDCl_3$

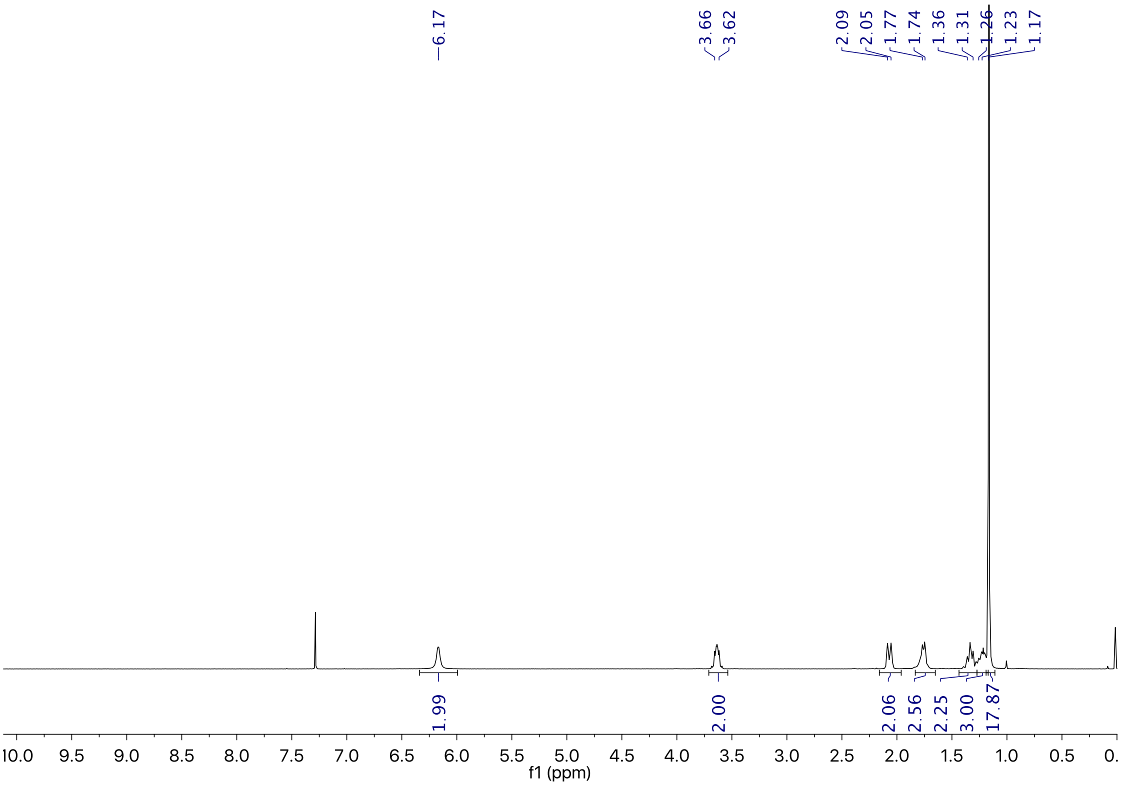


$^{13}C\{^{1}H\}$-NMR of *cis*-**1** in $CDCl_3$

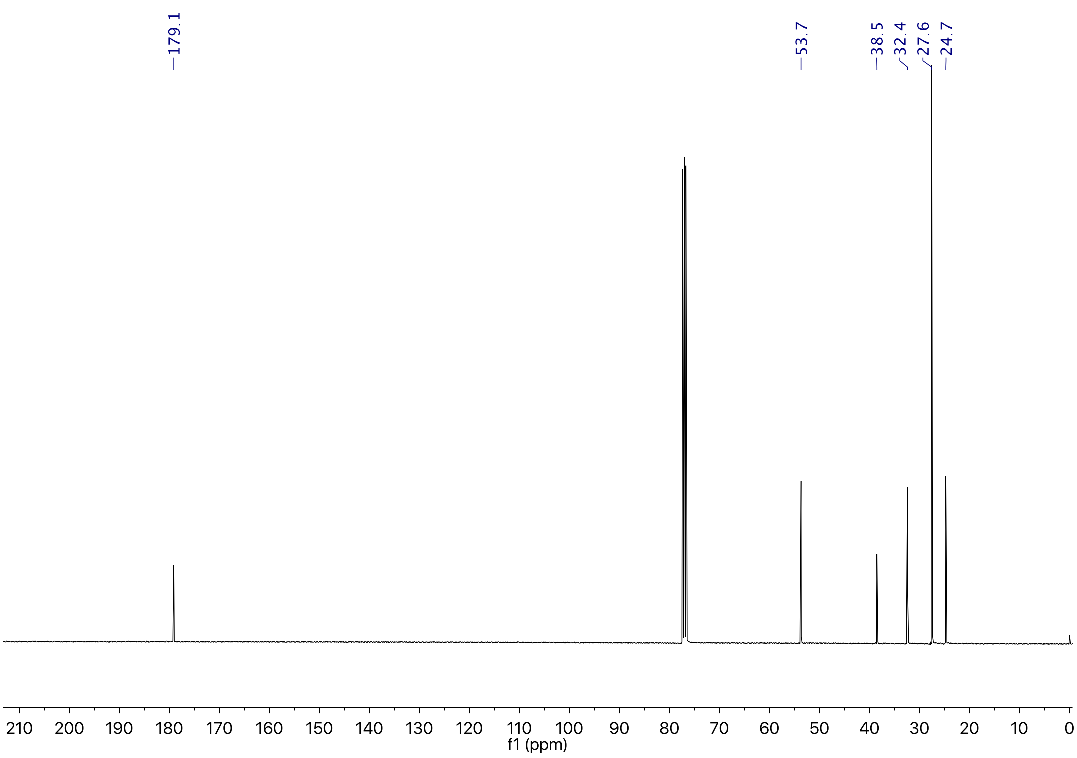


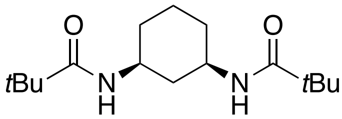


^{1}H-NMR of *trans*-**1** in $CDCl_3$

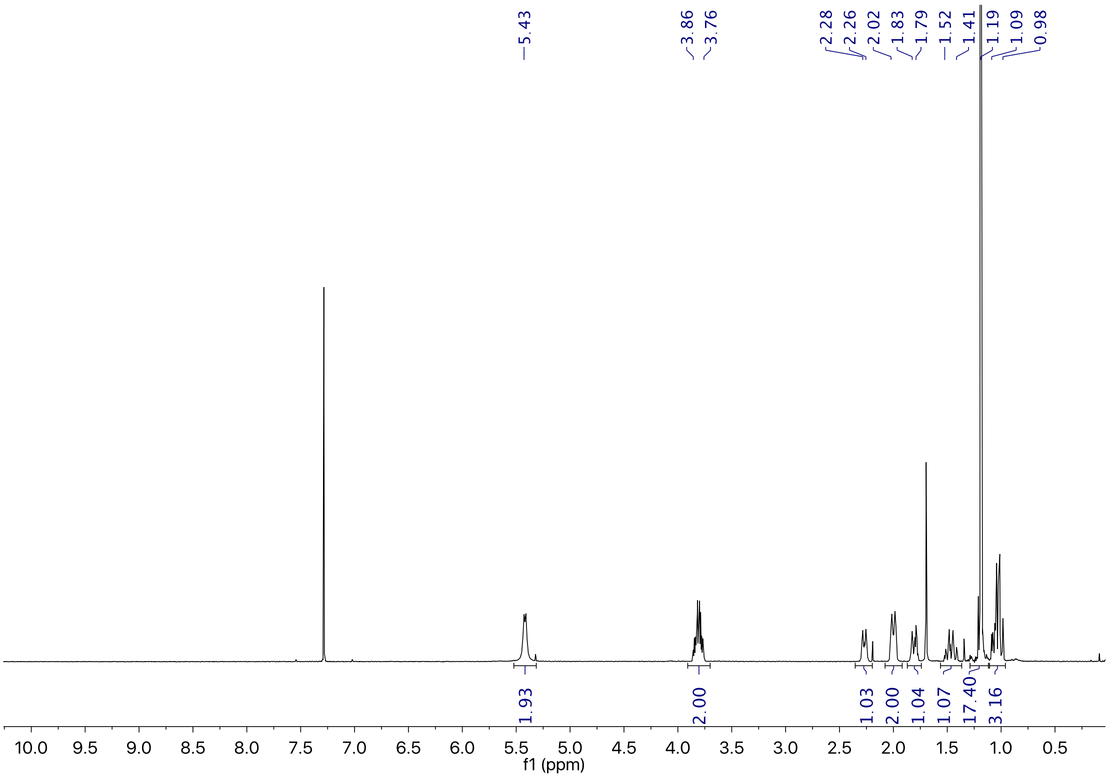


$^{13}C\{^1H\}$-NMR of *trans*-**1** in $CDCl_3$

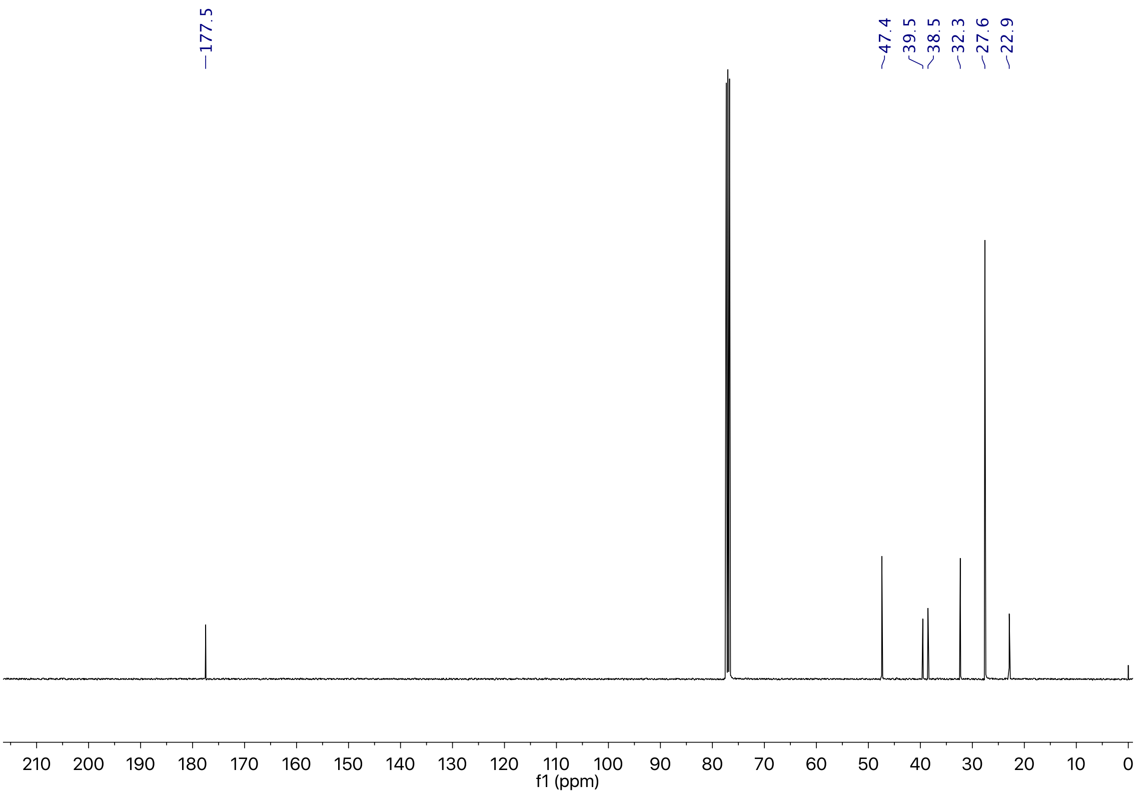


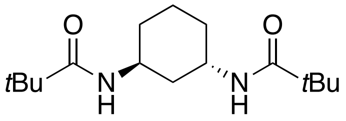


^{1}H-NMR of *cis*-**2** in $CDCl_3$

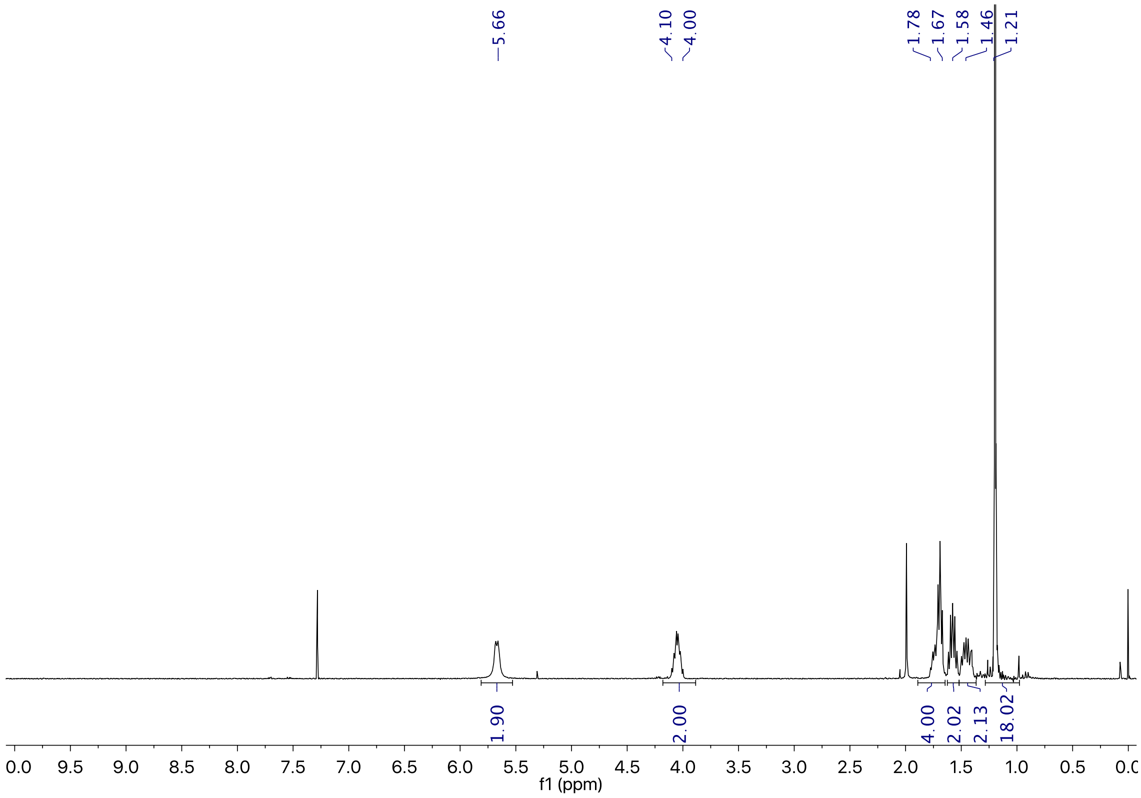


^{13}C{^{1}H}-NMR of *cis*-**2** in $CDCl_3$

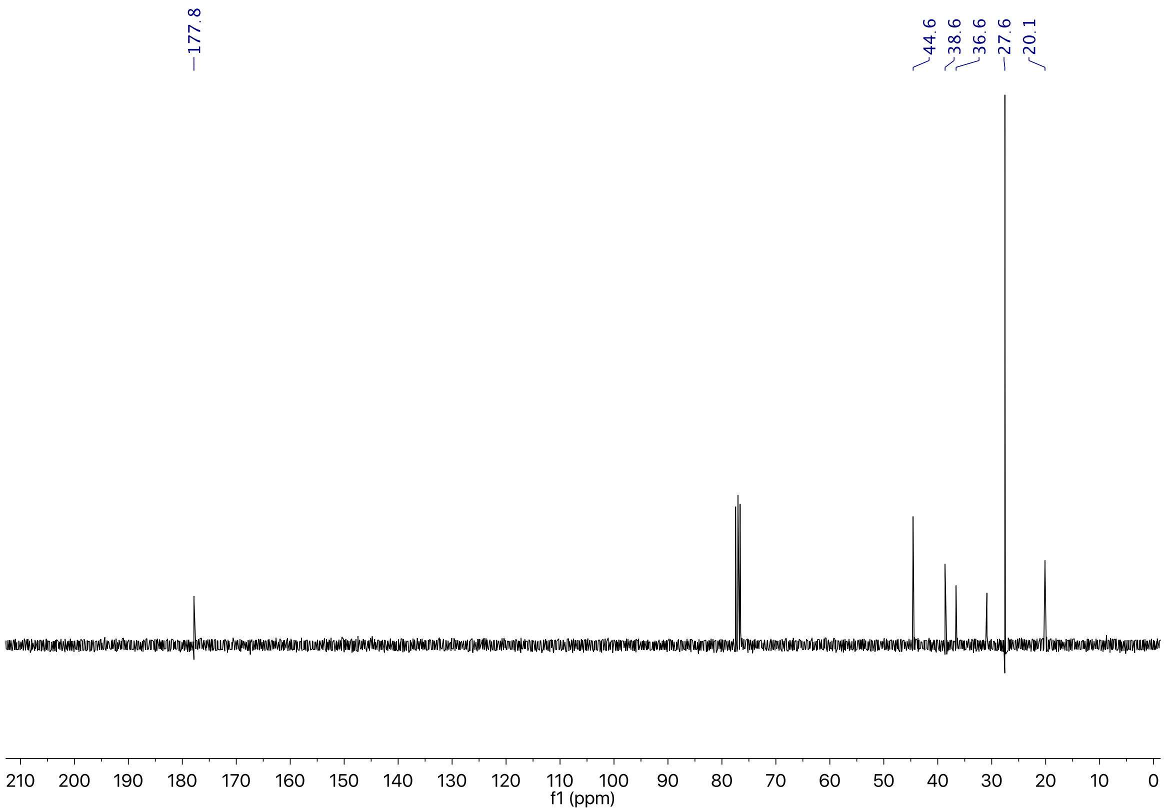


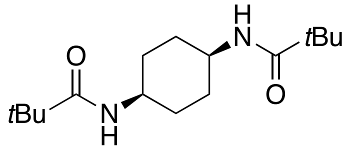


^{1}H-NMR of *trans*-**2** in $CDCl_3$

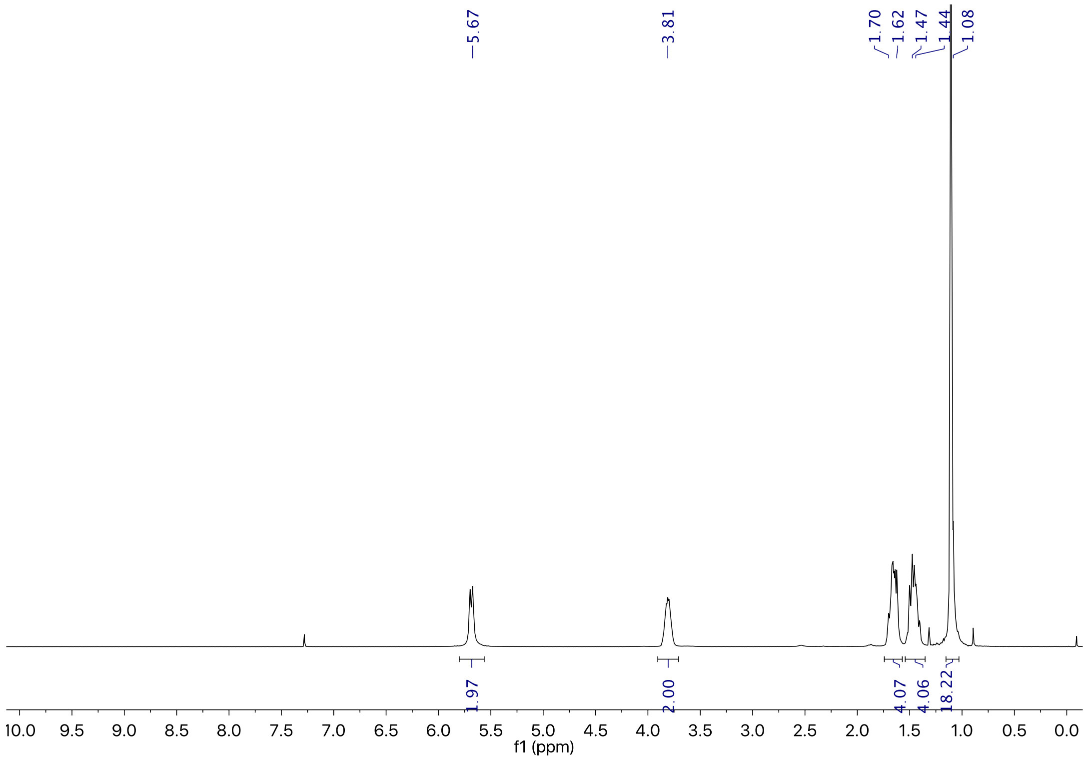


^{13}C{^{1}H}-NMR of *trans*-**2** in $CDCl_3$

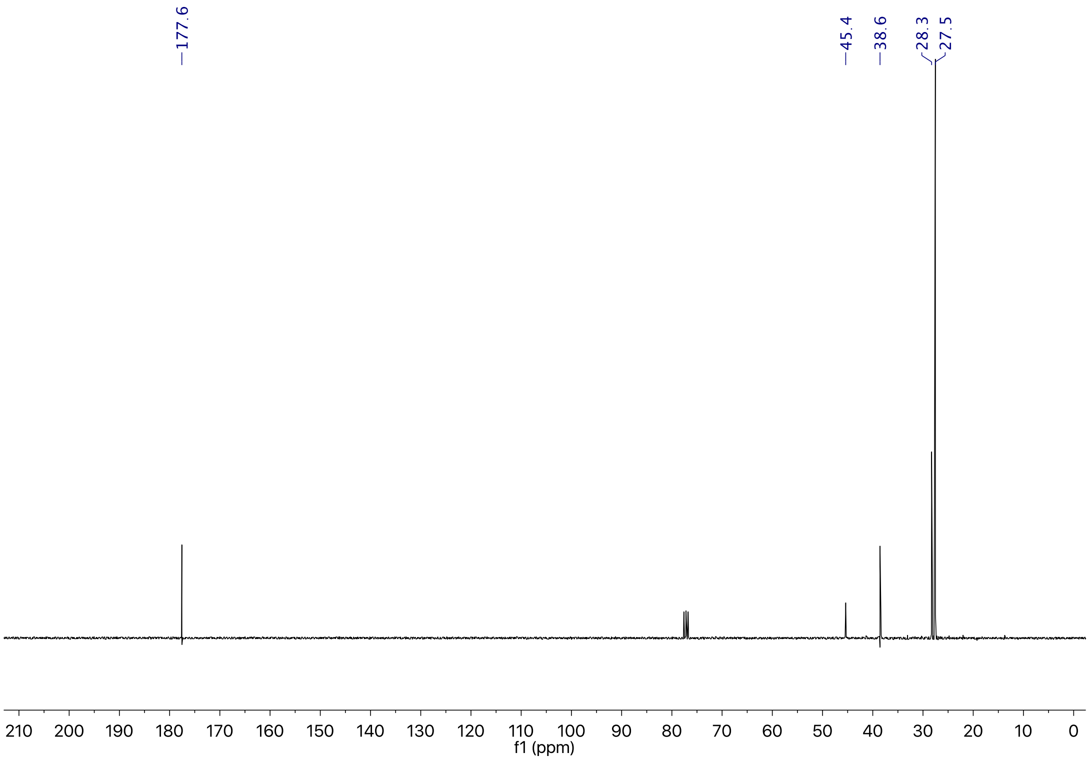


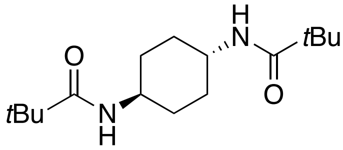


^{1}H-NMR of *cis*-**3** in $CDCl_3$

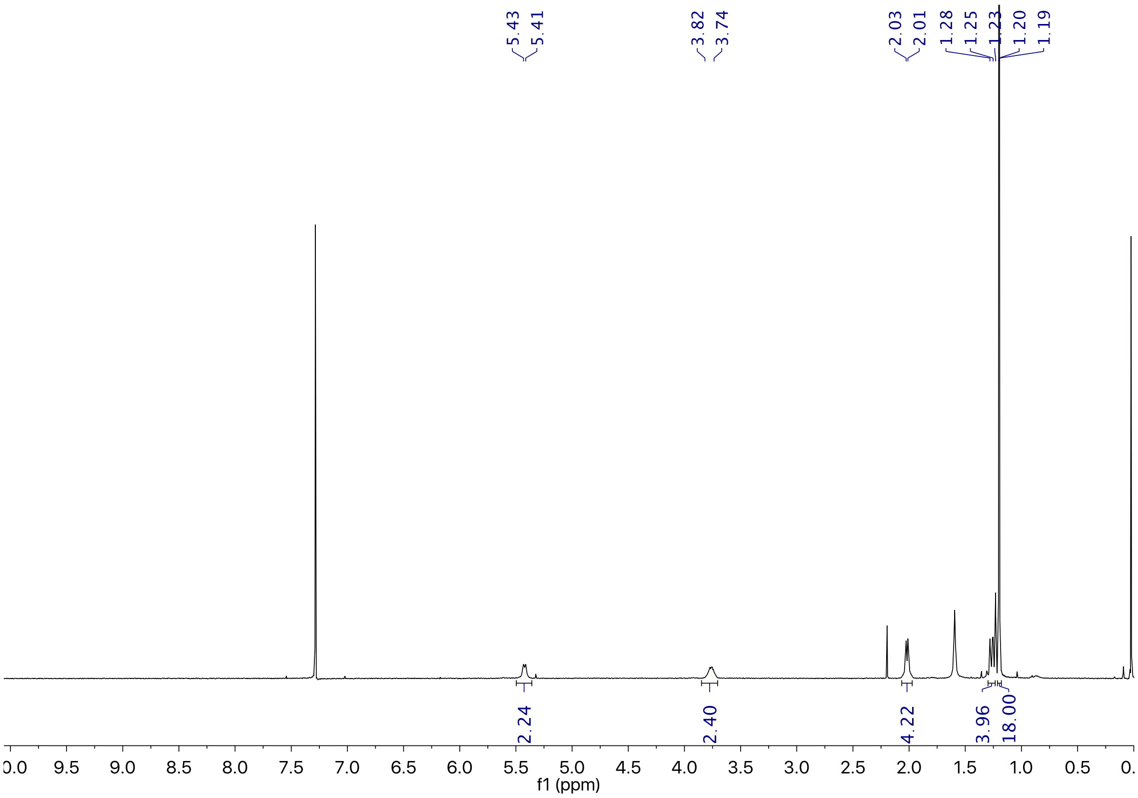


^{13}C{^{1}H}-NMR of *cis*-**3** in $CDCl_3$

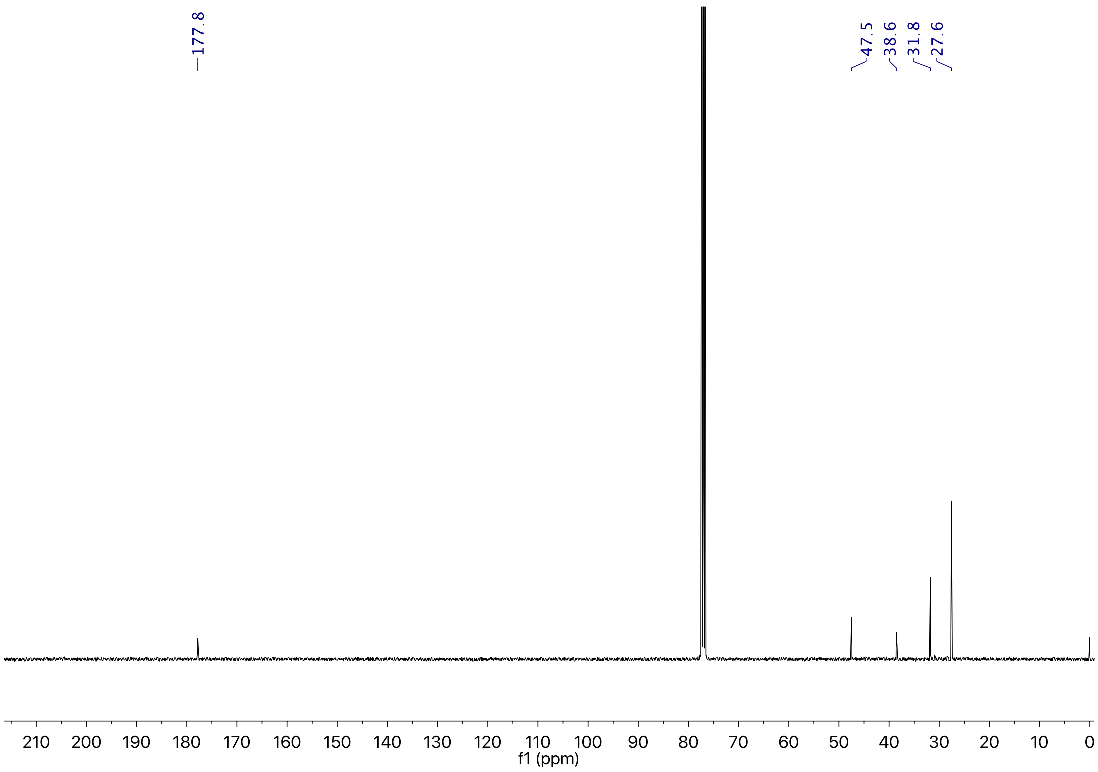


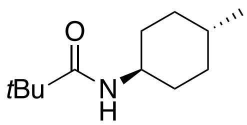


^{1}H-NMR of *trans*-**3** in $CDCl_3$

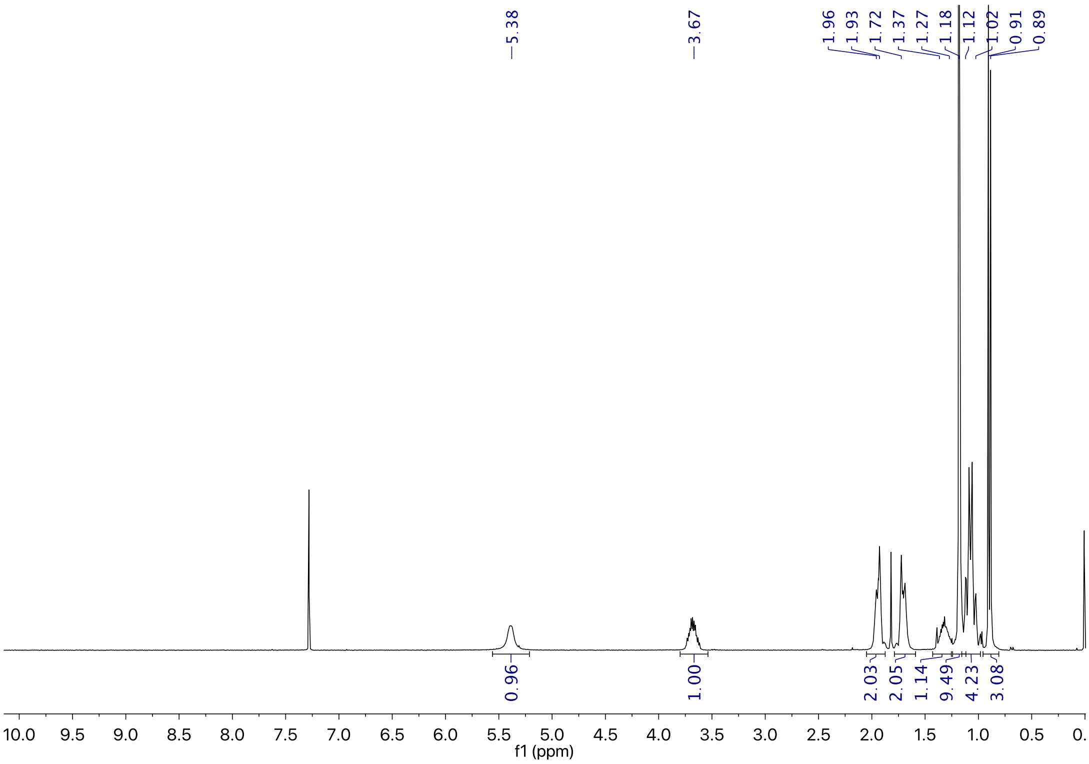


^{13}C{^{1}H}-NMR of *trans*-**3** in $CDCl_3$

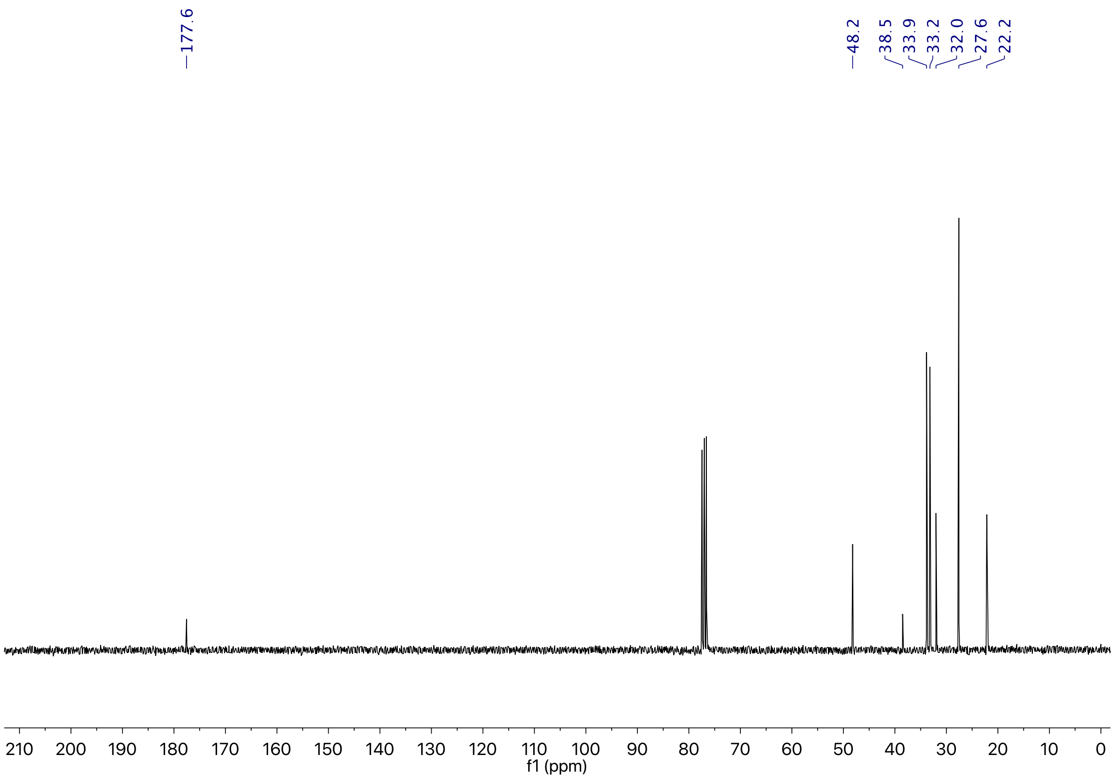


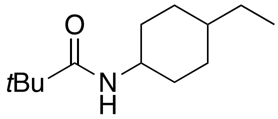


^{1}H-NMR of *trans*-**4** in $CDCl_3$

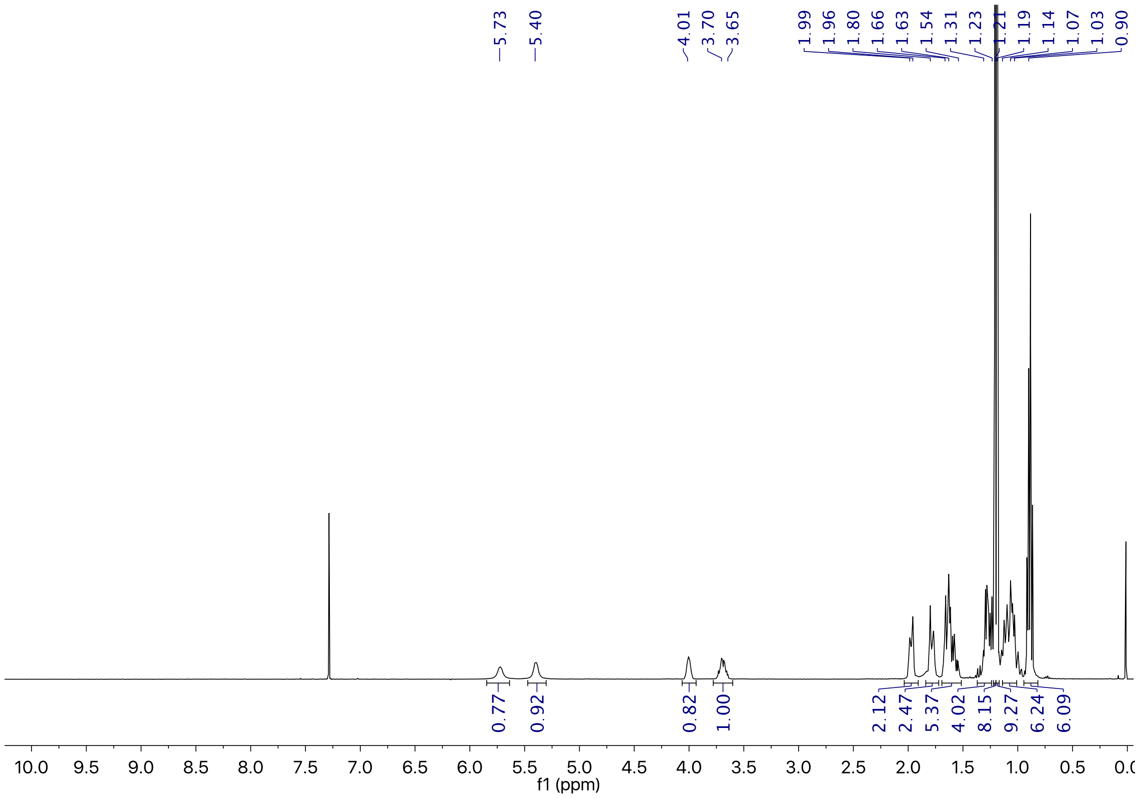


^{13}C{^{1}H}-NMR of *trans*-**4** in $CDCl_3$

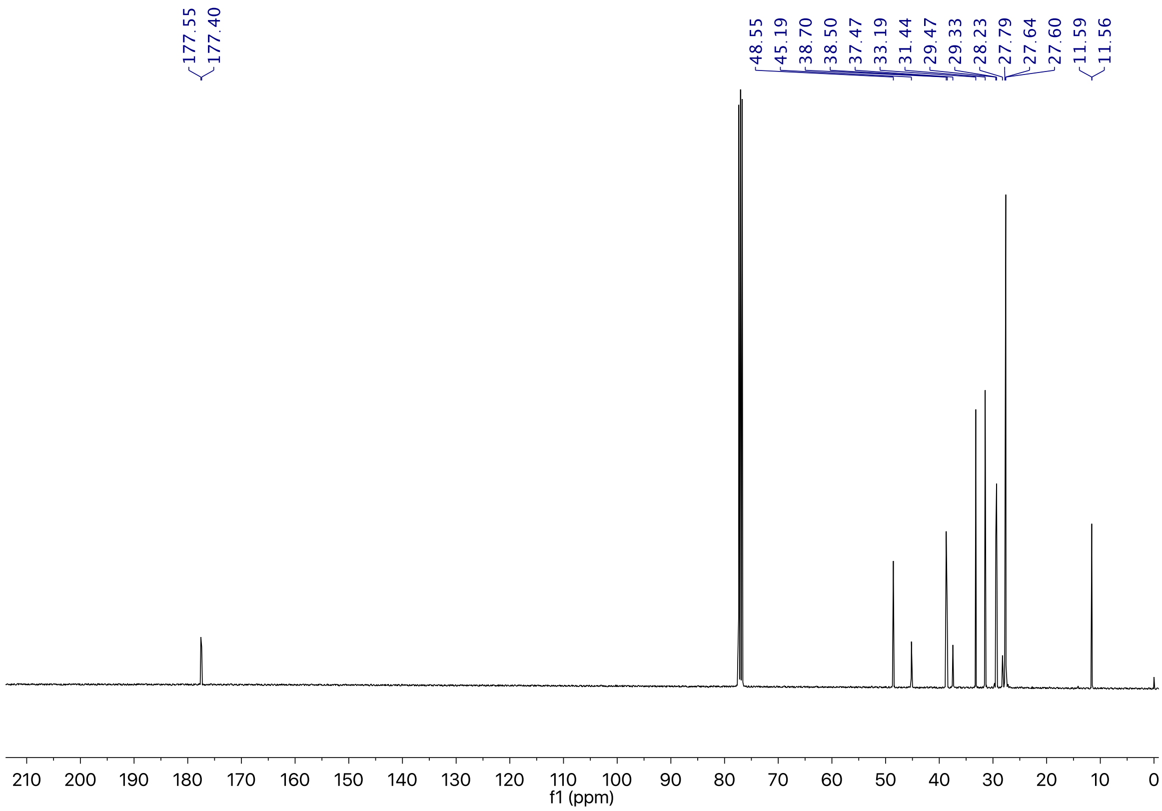


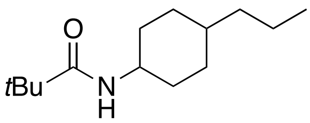


^{1}H-NMR of **5** in $CDCl_3$

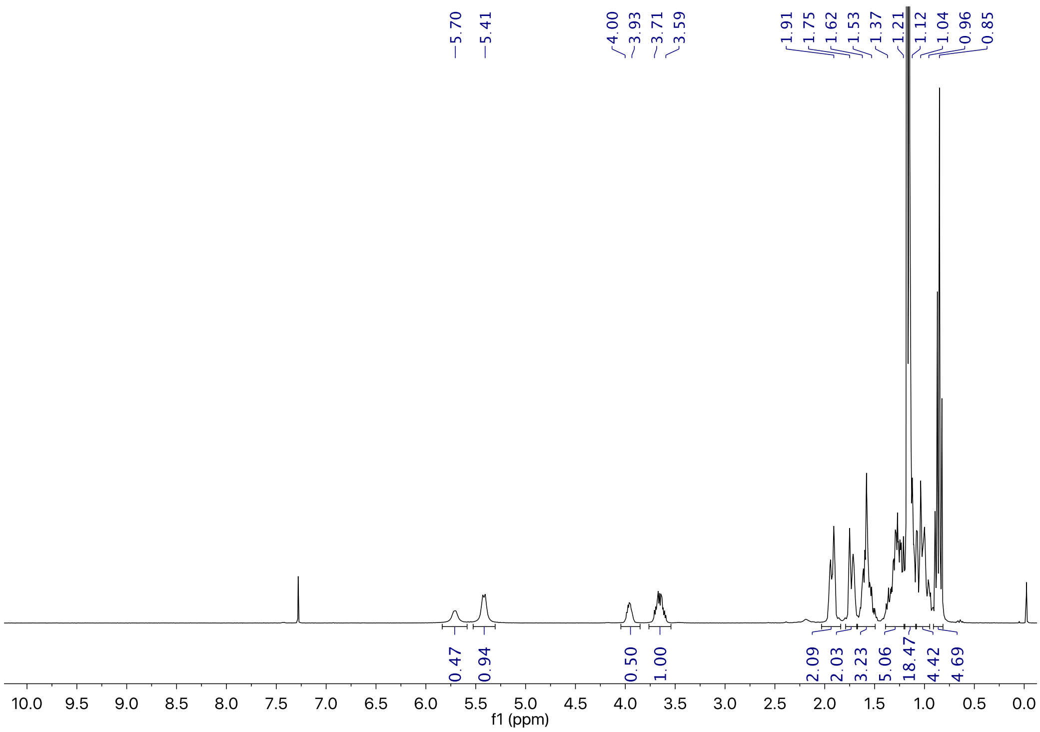


^{13}C{^{1}H}-NMR of **5** in $CDCl_3$

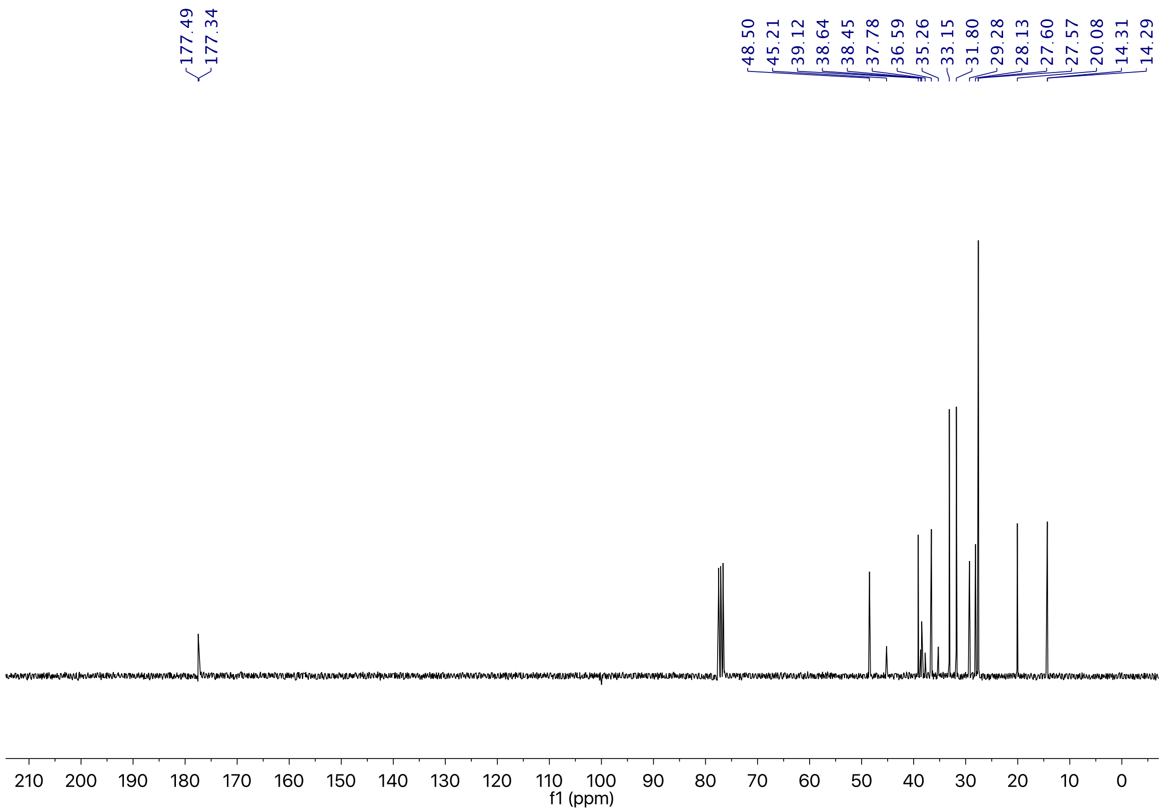


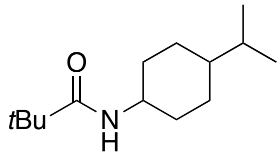


^{1}H-NMR of **6** in $CDCl_3$

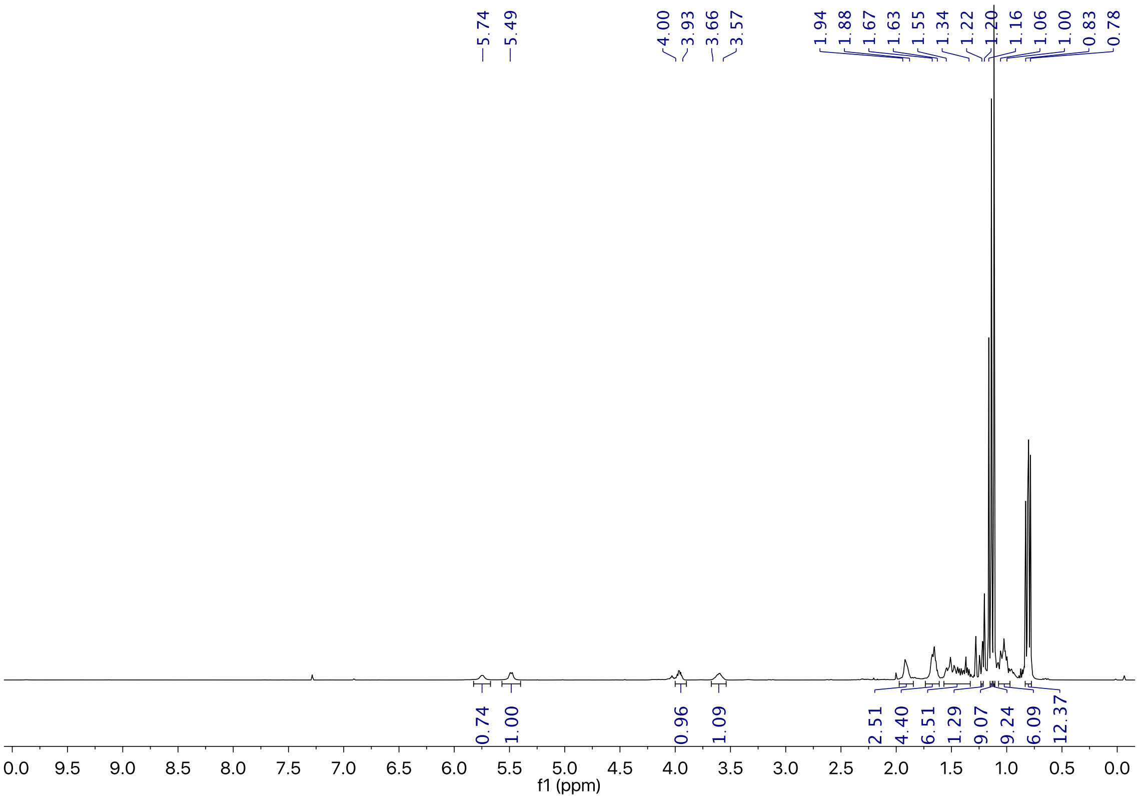


$^{13}C\{^1H\}$-NMR of **6** in $CDCl_3$

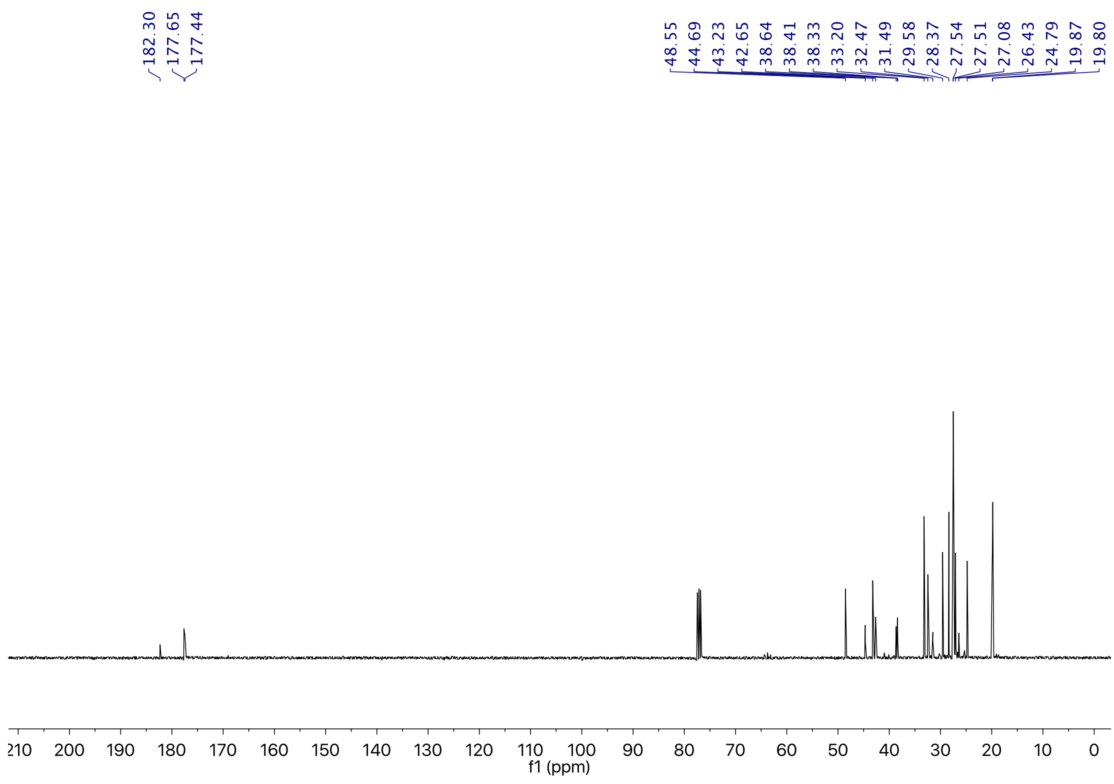


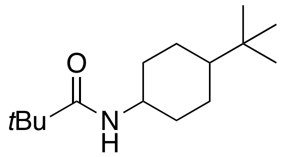


^{1}H-NMR of **7** in $CDCl_3$

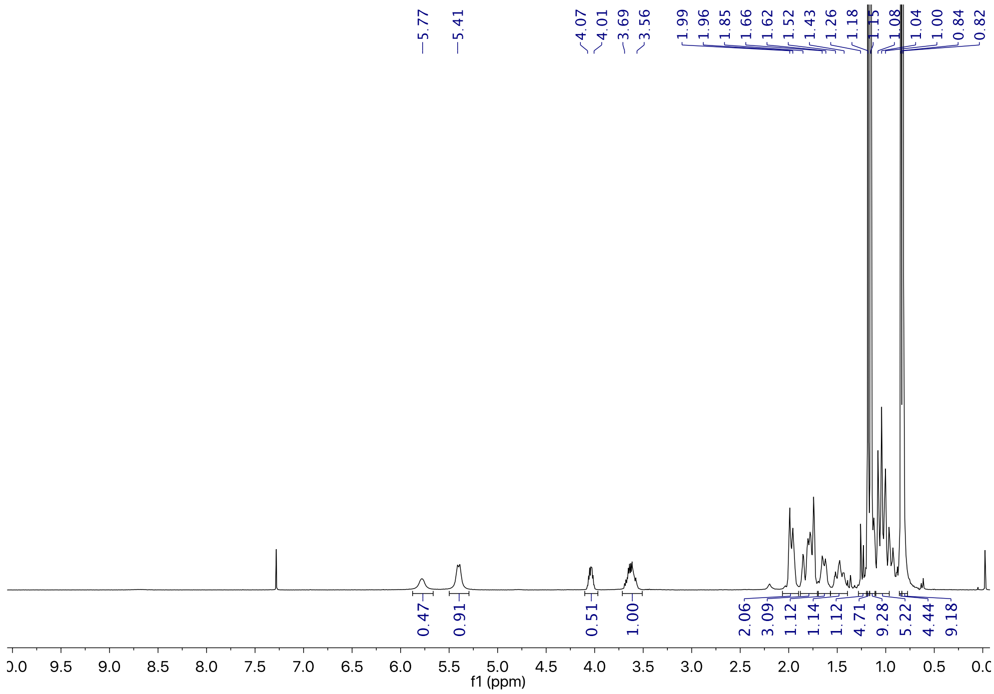


^{13}C{^{1}H}-NMR of **7** in $CDCl_3$

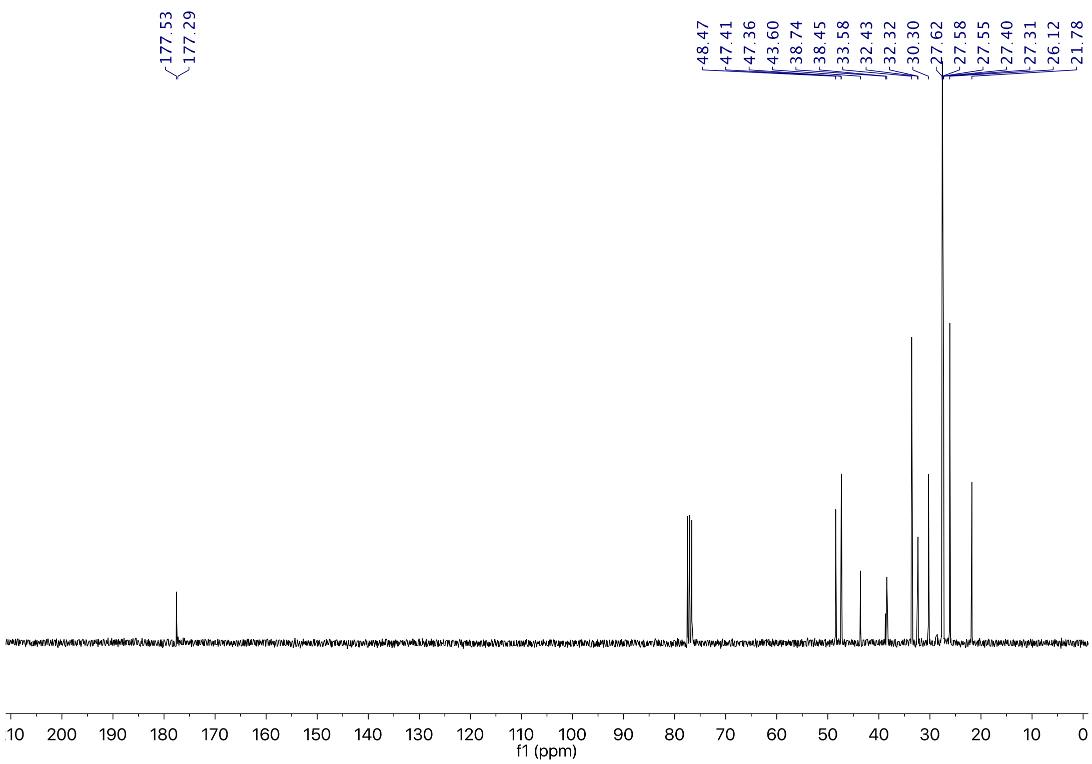


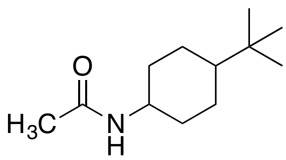


^{1}H-NMR of **8** in CDCl$_3$

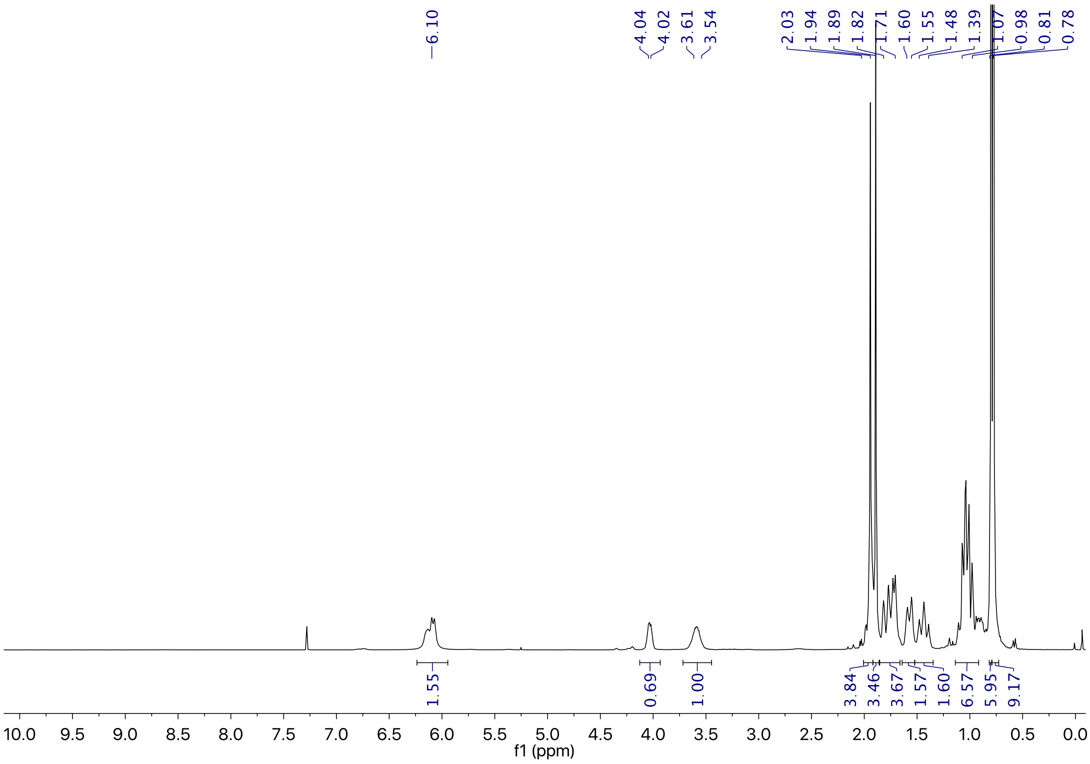


^{13}C{^{1}H}-NMR of **8** in CDCl$_3$

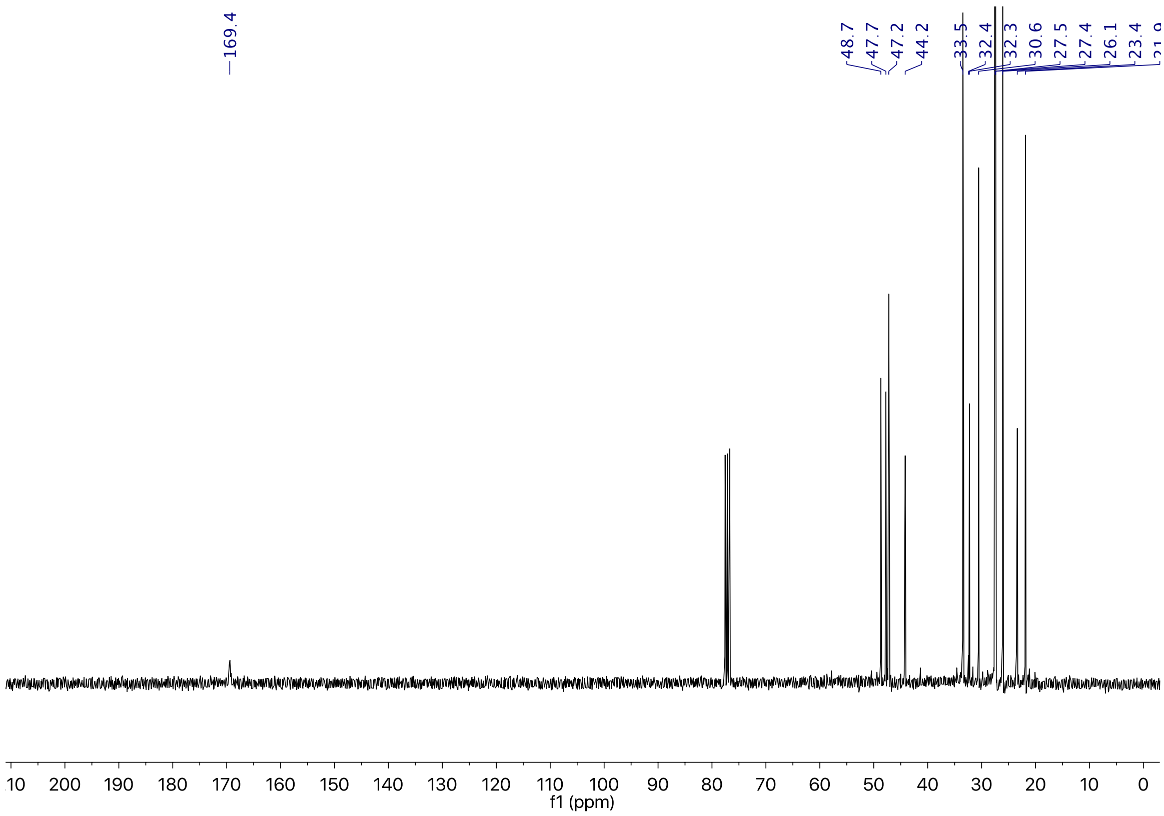


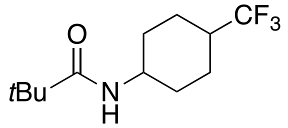


^{1}H-NMR of **9** in $CDCl_3$

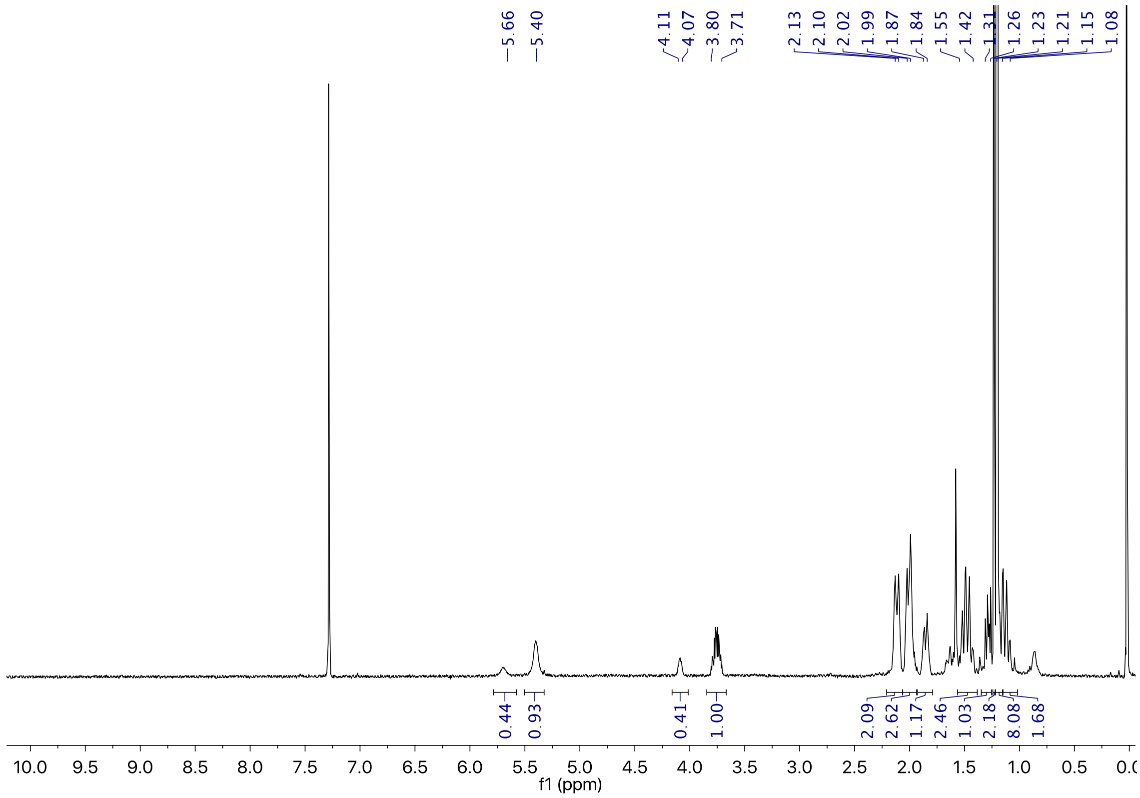


^{13}C{^{1}H}-NMR of **9** in $CDCl_3$

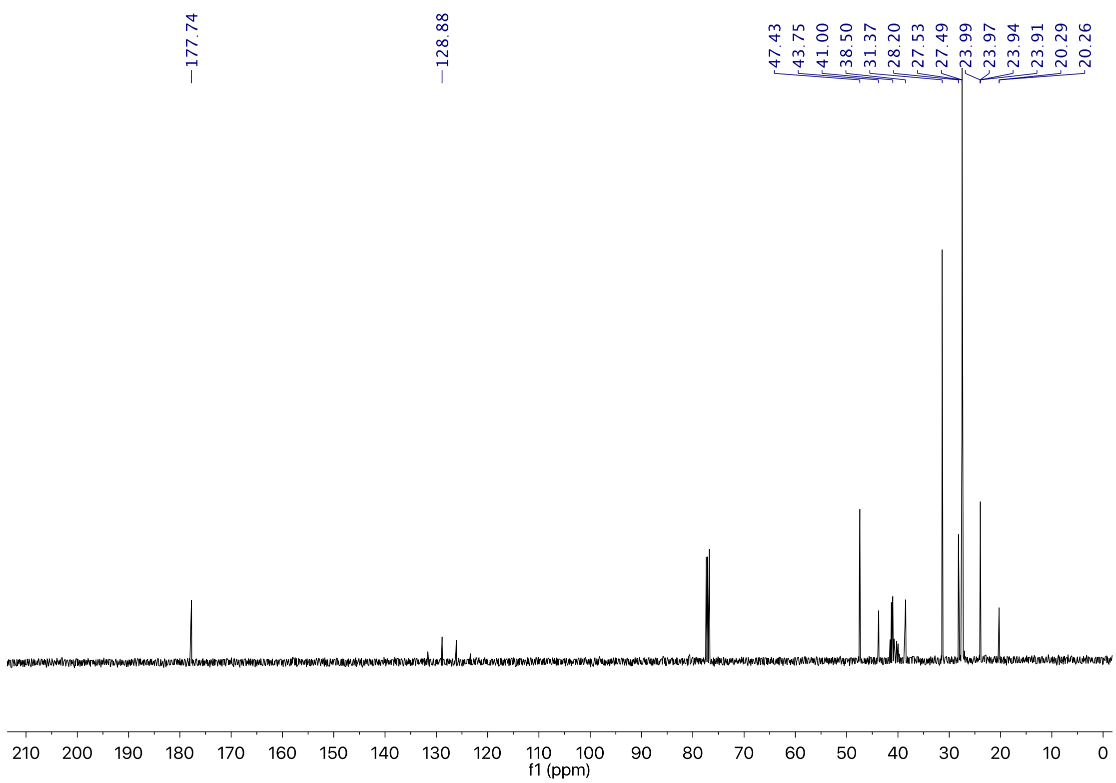




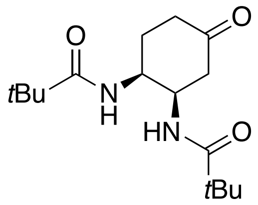
1H-NMR of **10** in $CDCl_3$



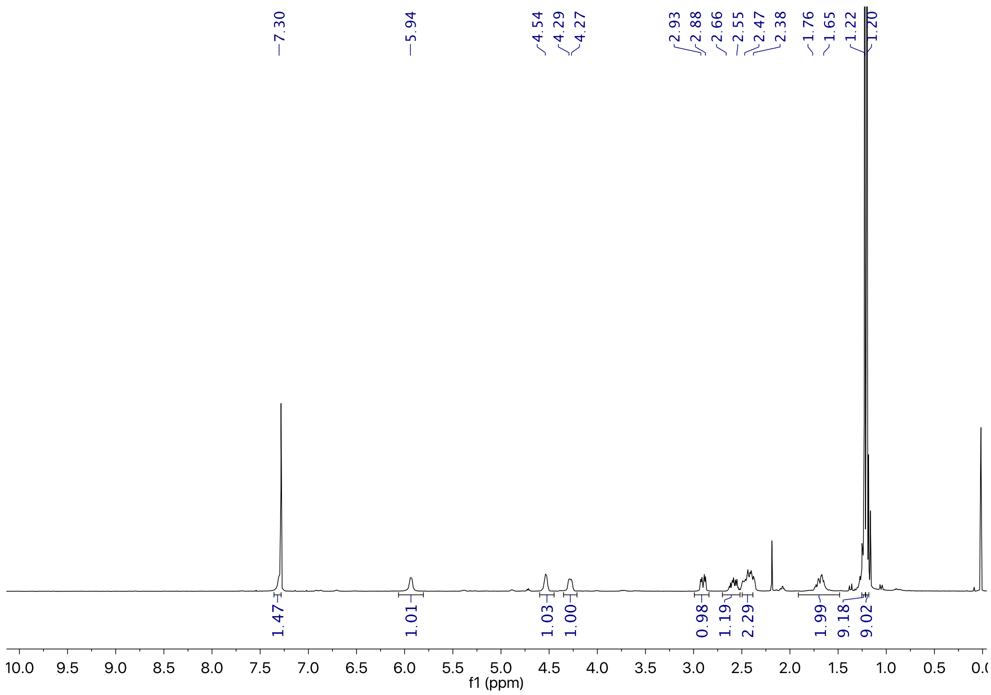
13C{1H}-NMR of **10** in $CDCl_3$



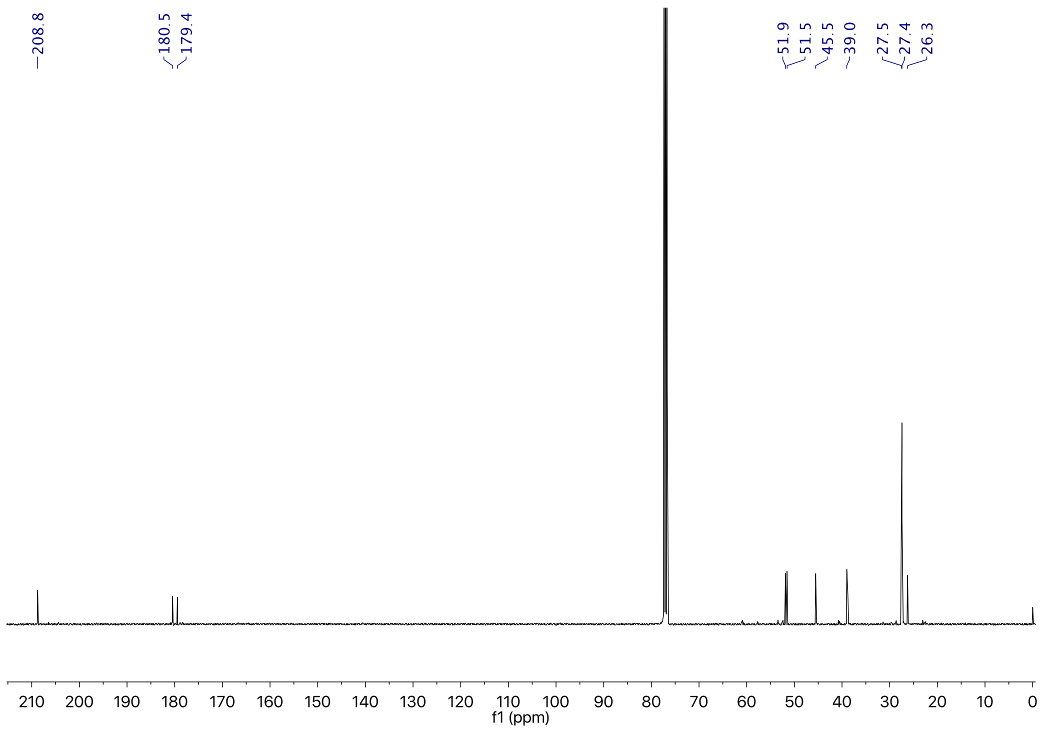
A2 ^{1}H and ^{13}C{^{1}H} NMR spectra of isolated products

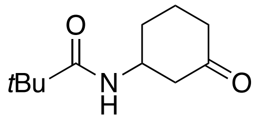


^{1}H-NMR of **1a** in $CDCl_3$

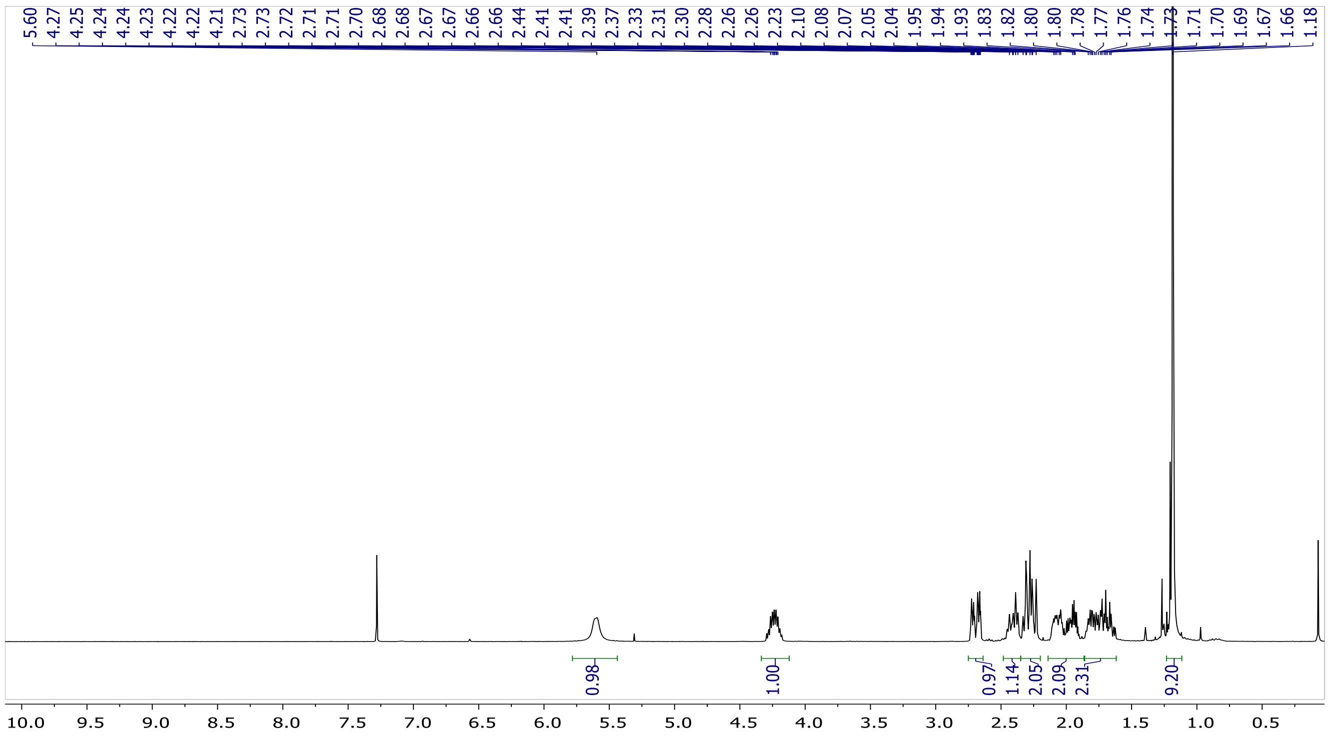


^{13}C{^{1}H}-NMR of **1a** in $CDCl_3$

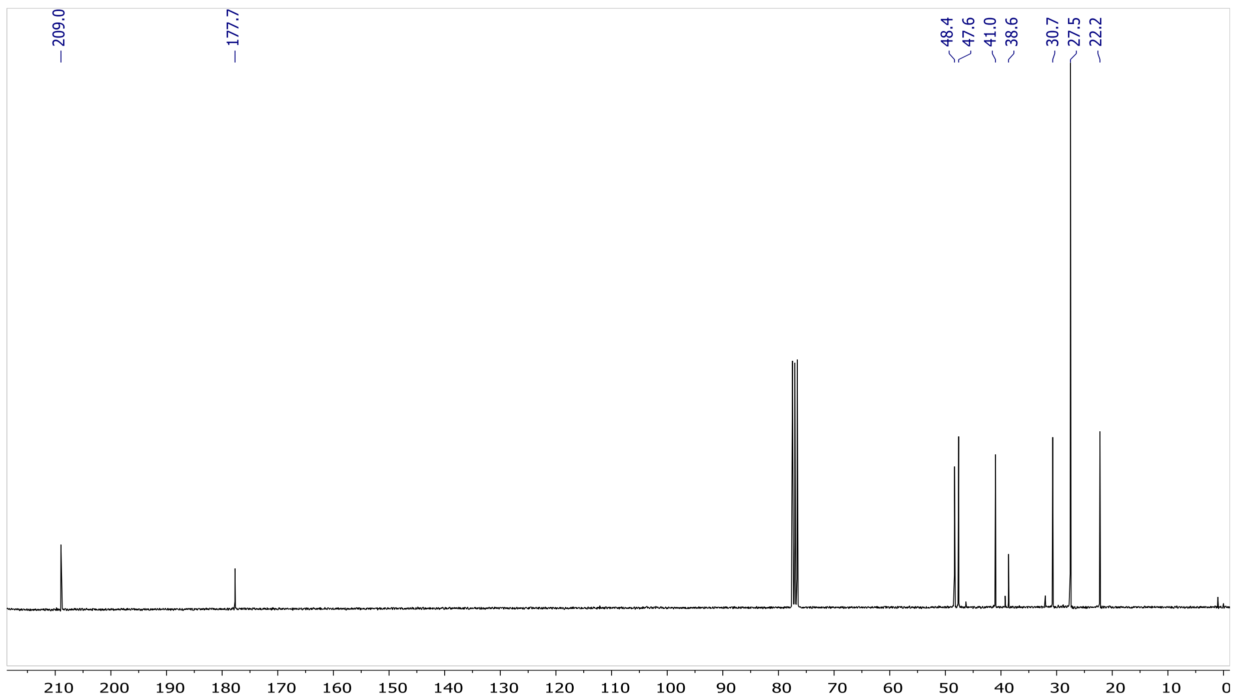


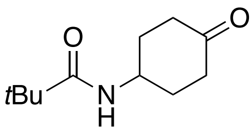


^{1}H-NMR of **2a** in $CDCl_3$

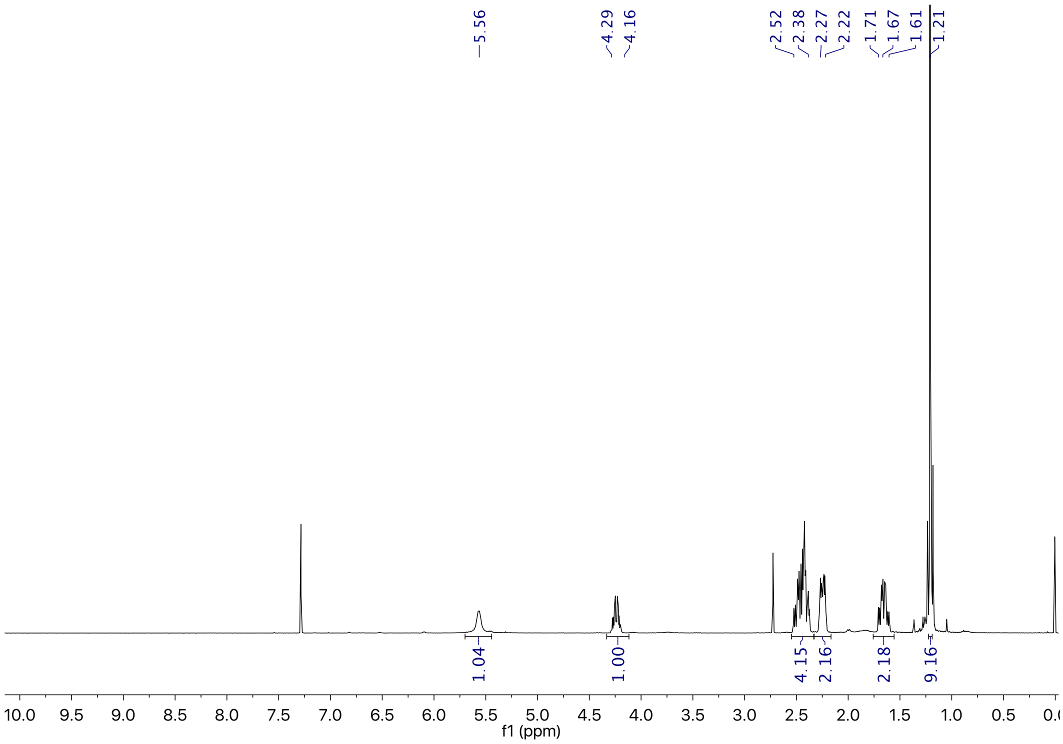


^{13}C{^{1}H}-NMR of **2a** in $CDCl_3$

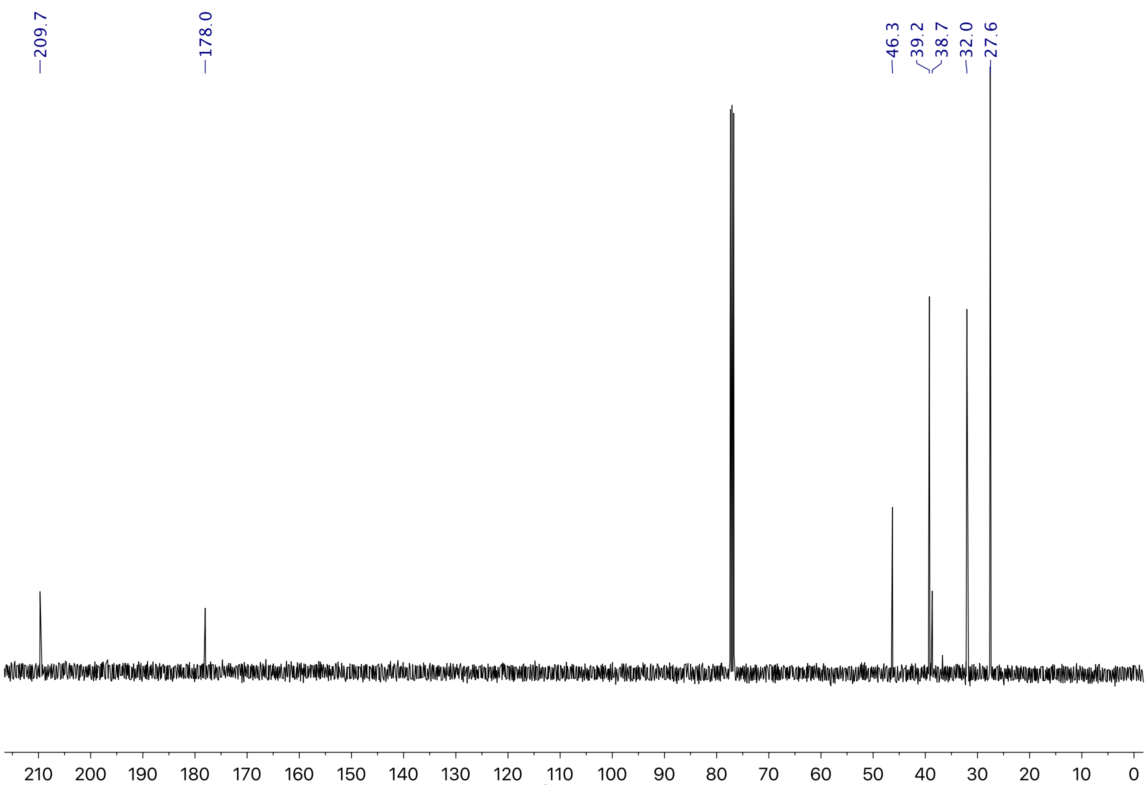


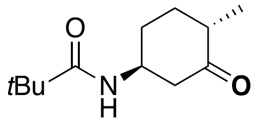


^{1}H-NMR of **3a** in $CDCl_3$

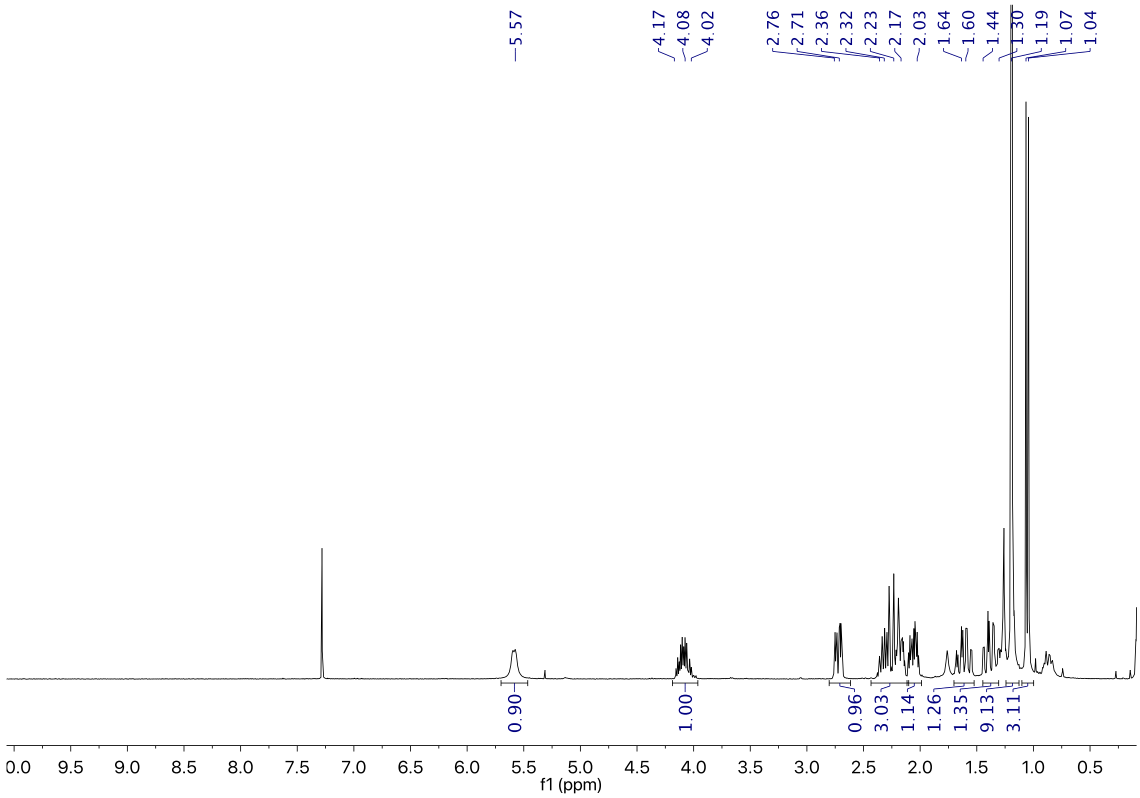


$^{13}C\{^{1}H\}$-NMR of **3a** in $CDCl_3$

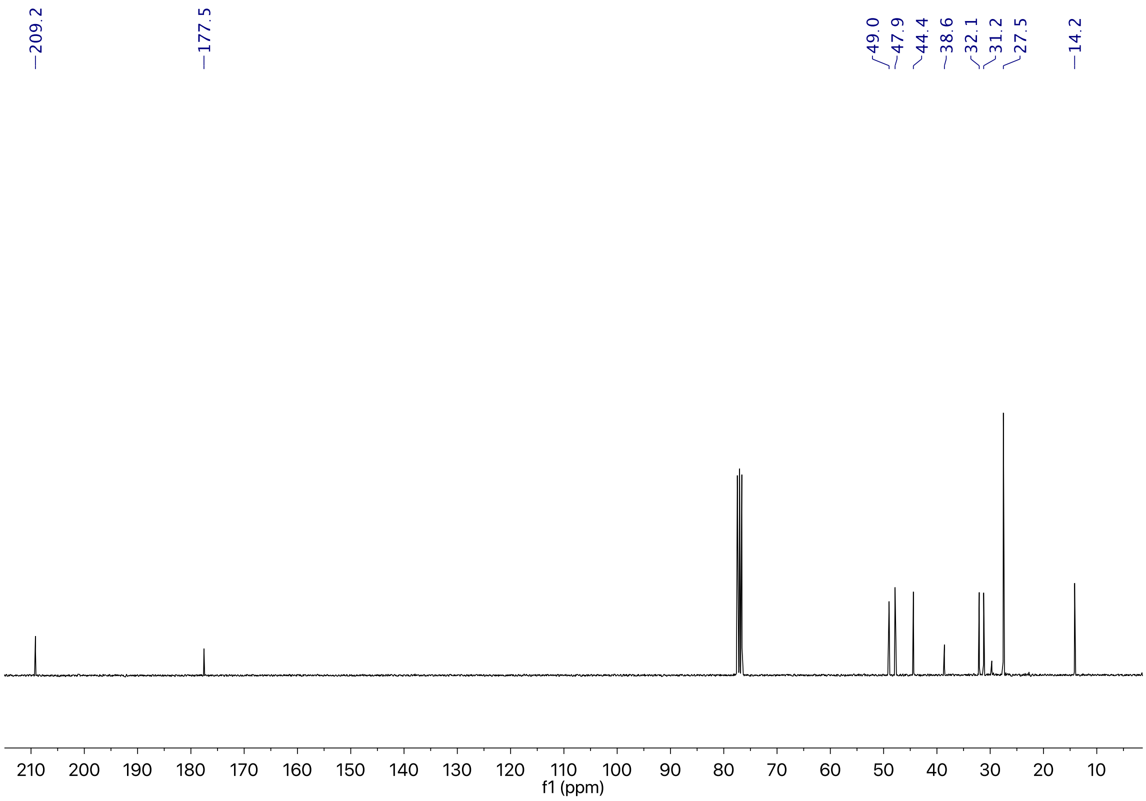


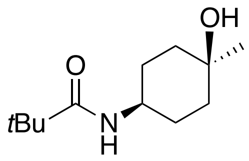


^{1}H-NMR of **4a** in $CDCl_3$

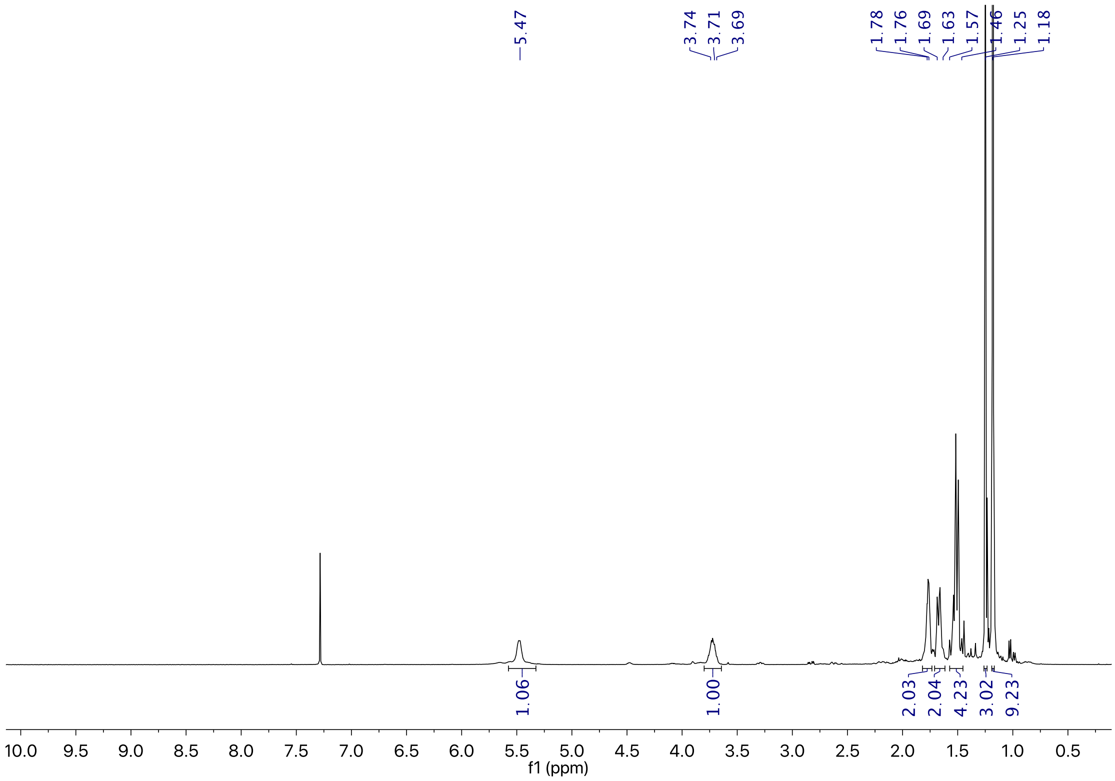


^{13}C{^{1}H}-NMR of **4a** in $CDCl_3$

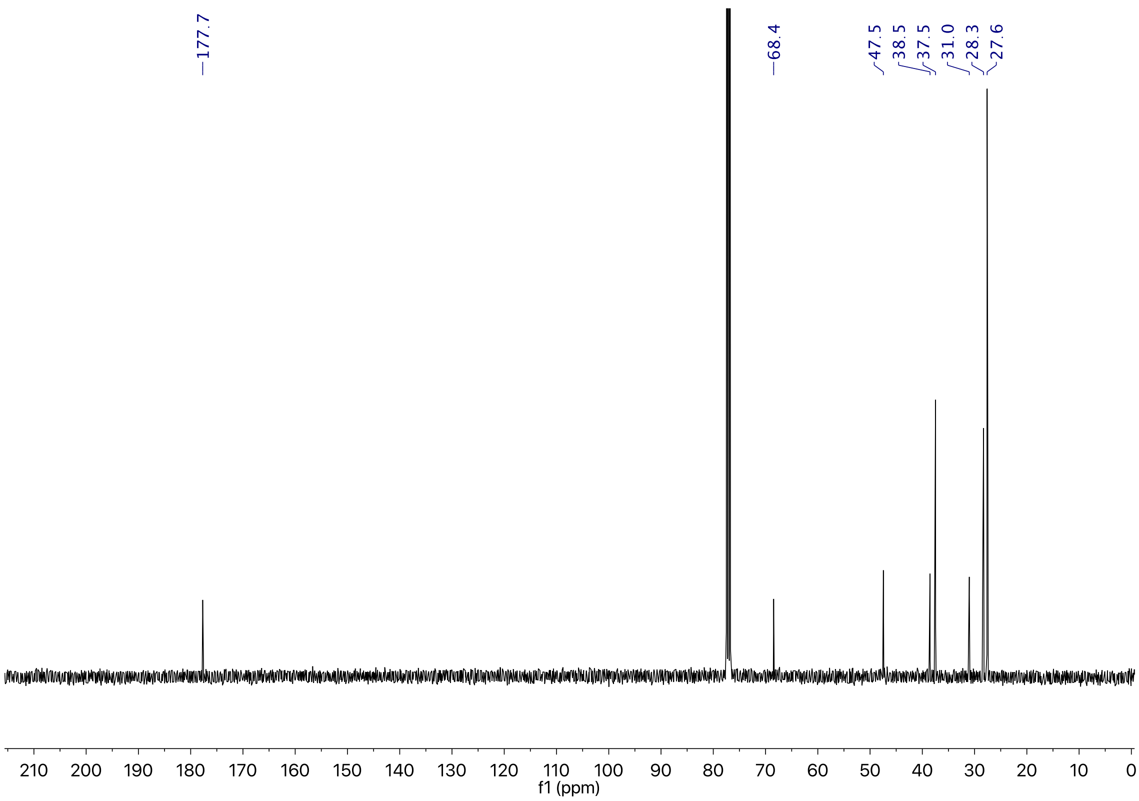


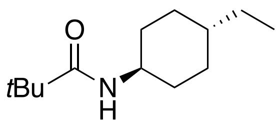


^{1}H-NMR of **4b** in $CDCl_3$

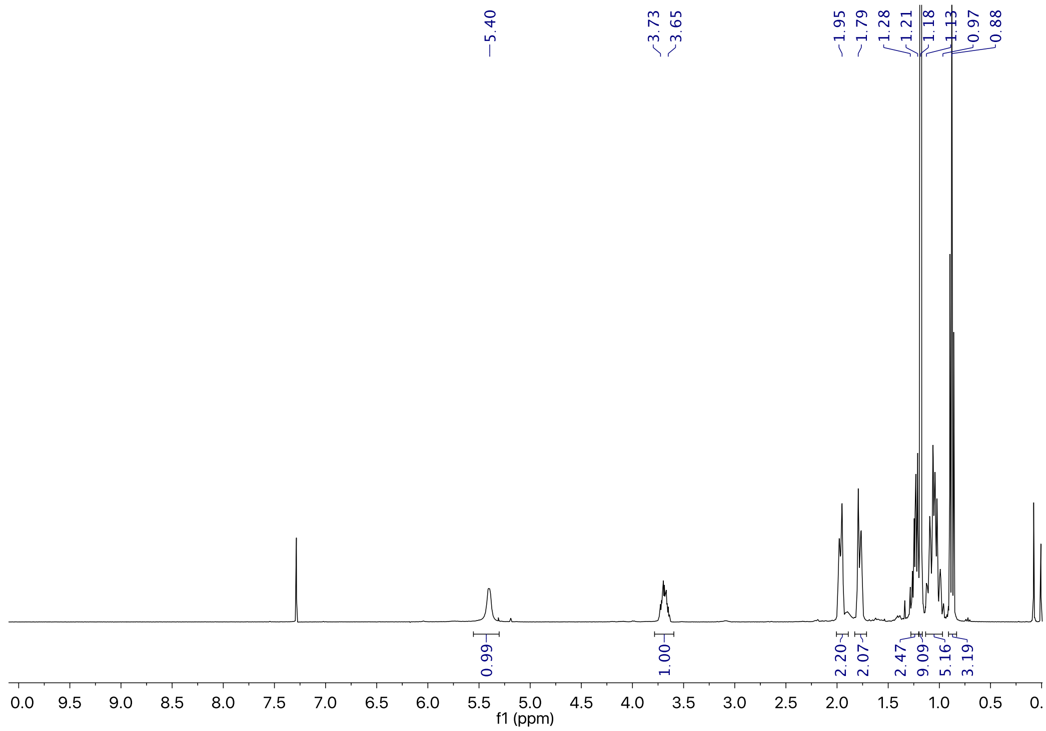


$^{13}C\{^{1}H\}$-NMR of **4b** in $CDCl_3$

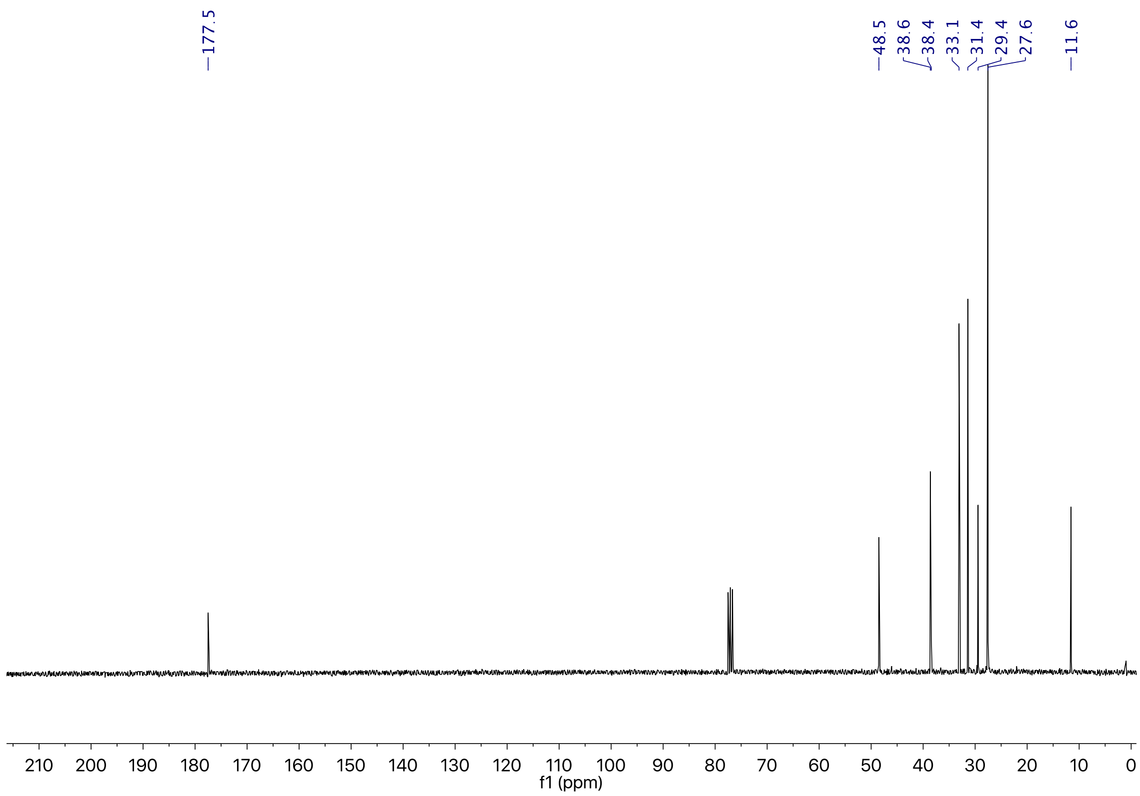


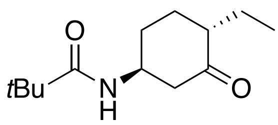


^{1}H-NMR of *trans*-**5** in $CDCl_3$

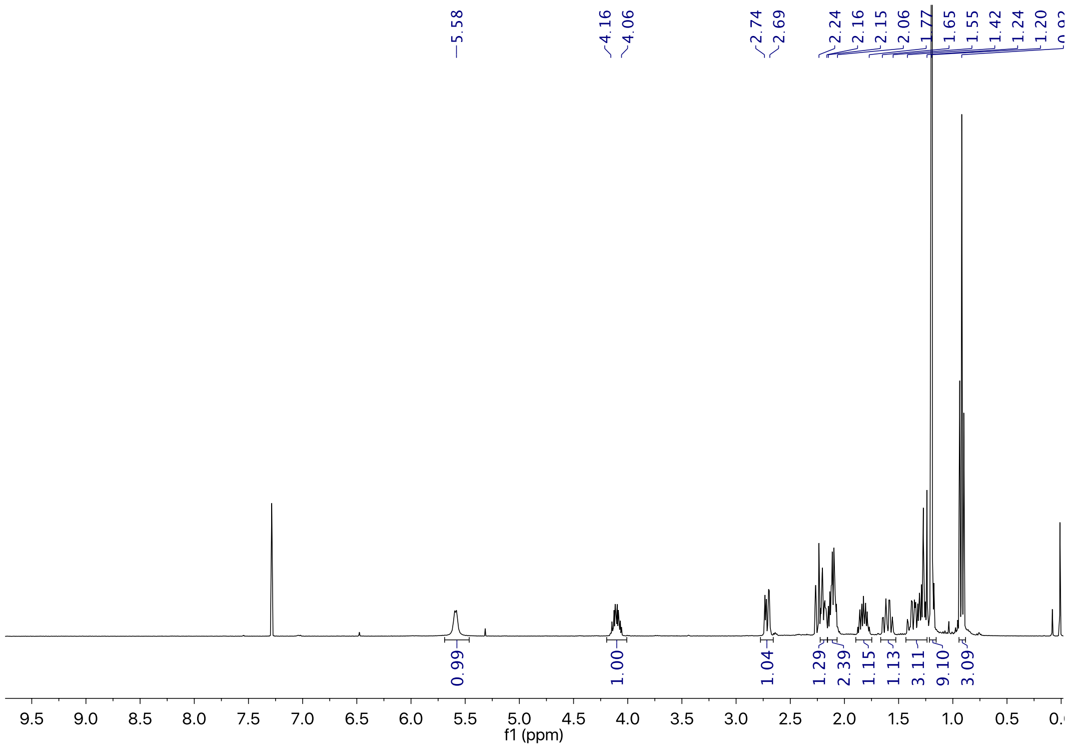


$^{13}C\{^1H\}$-NMR of *trans*-**5** in $CDCl_3$

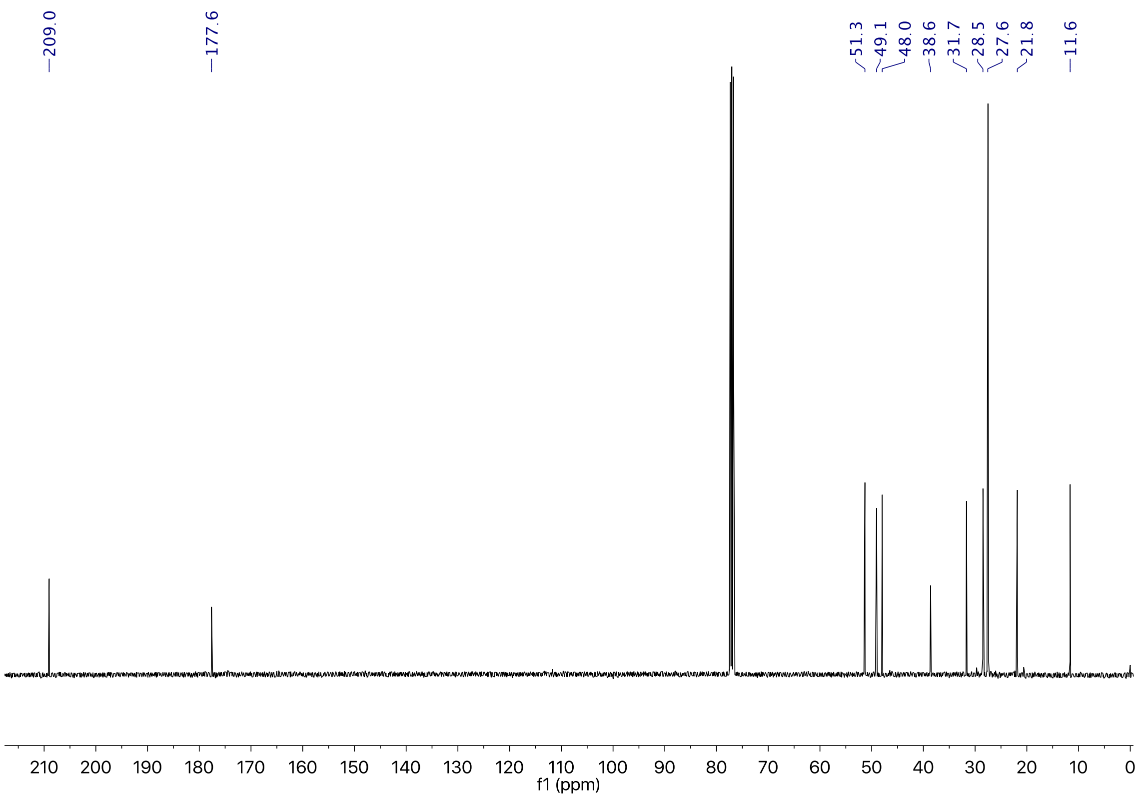


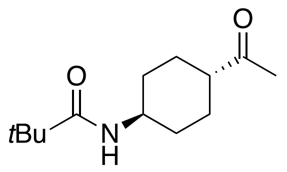


^{1}H-NMR of **5a** in $CDCl_3$

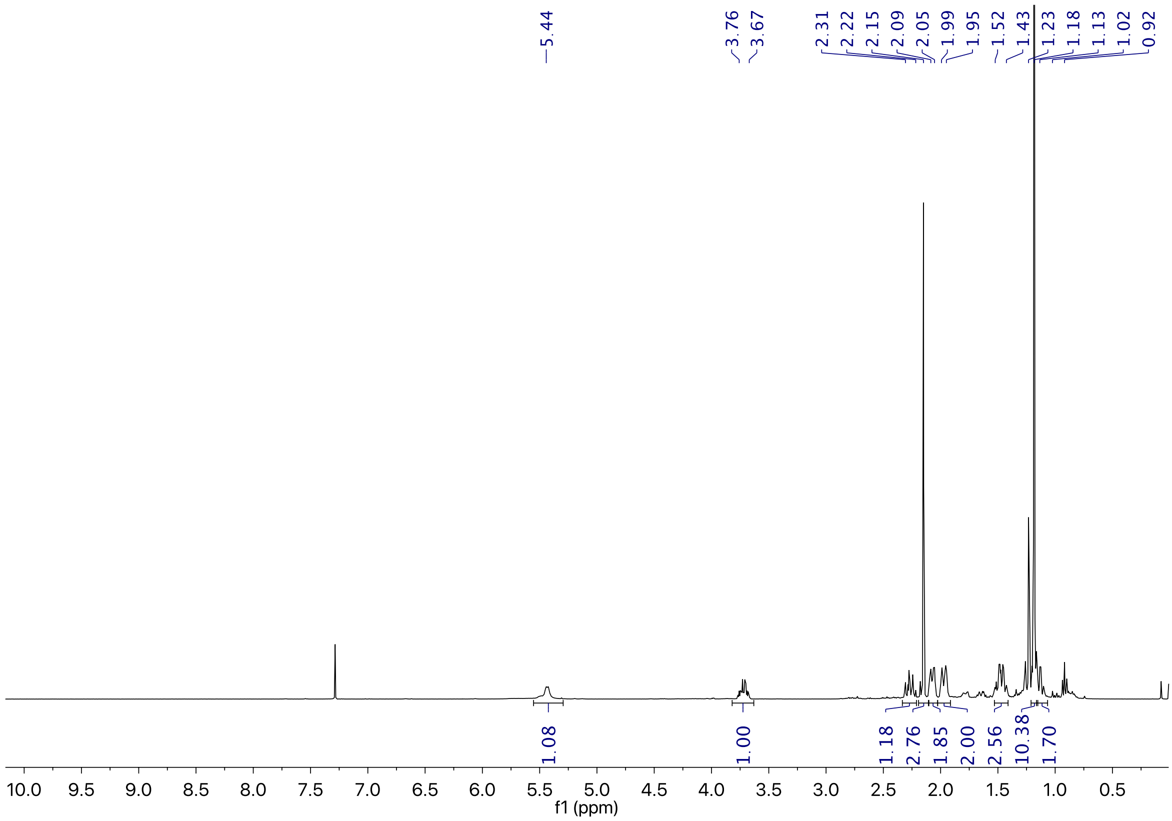


^{13}C{^{1}H}-NMR of **5a** in $CDCl_3$

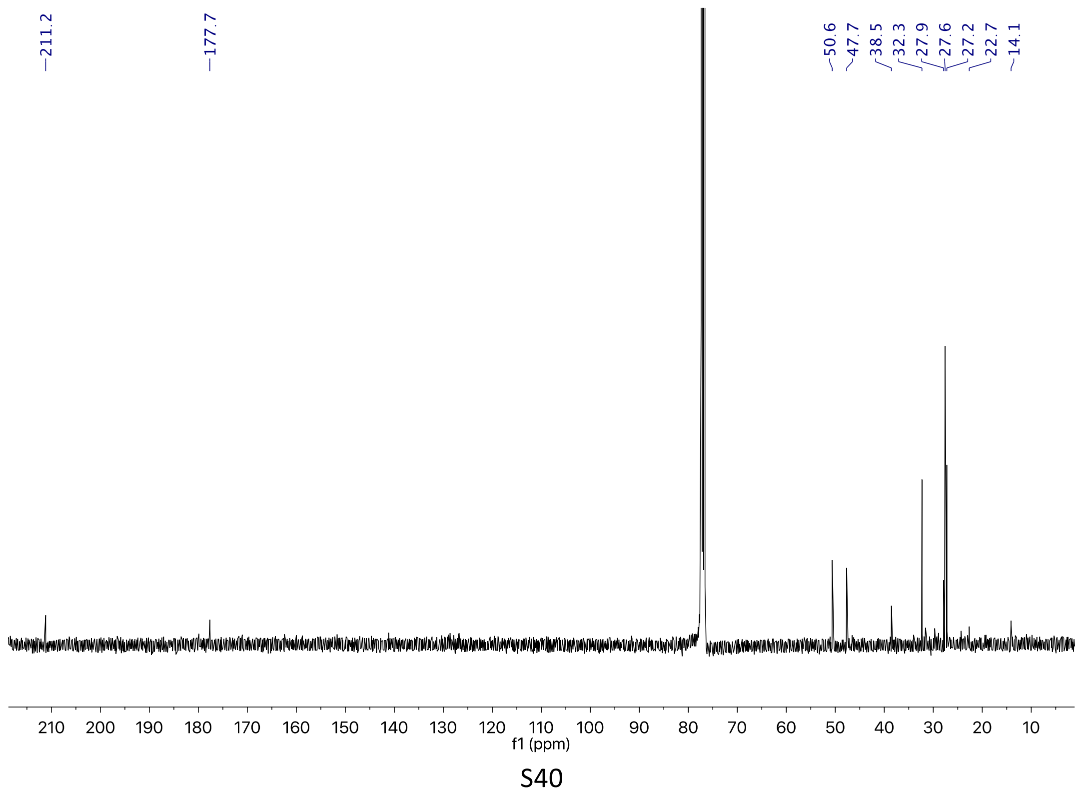


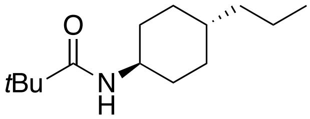


^{1}H-NMR of **5b** in $CDCl_3$

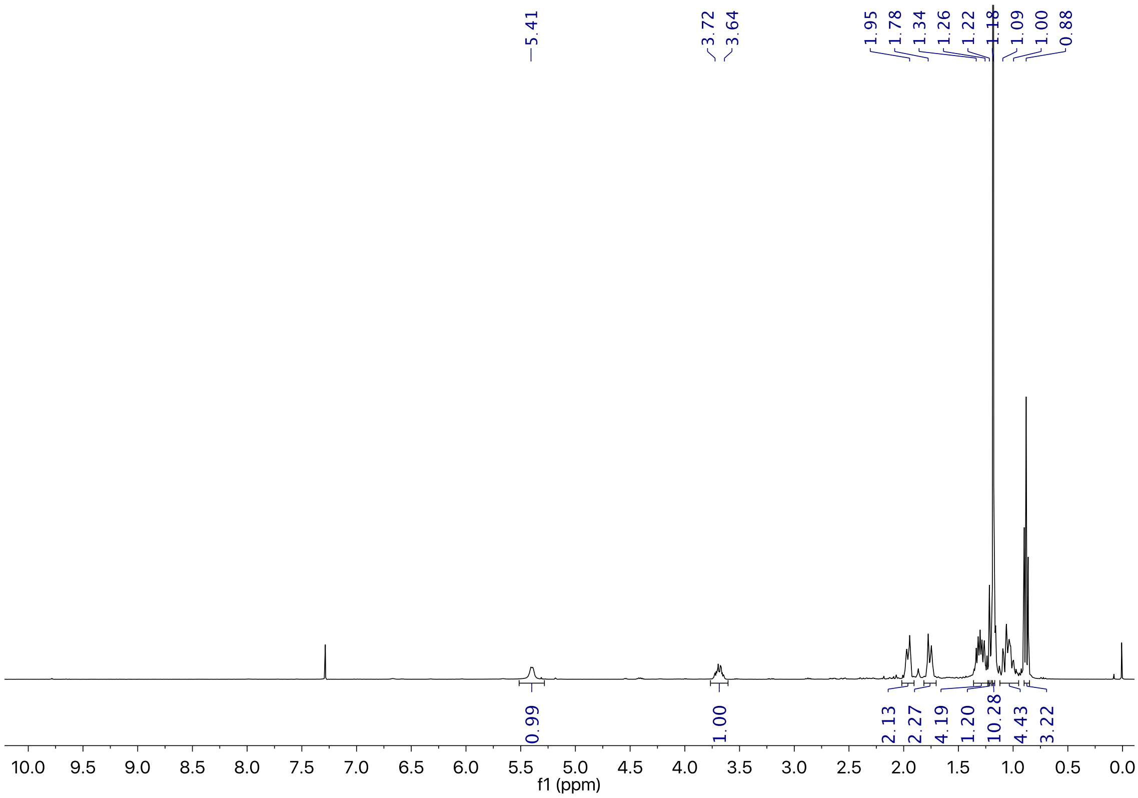


^{13}C{^{1}H}-NMR of **5b** in $CDCl_3$

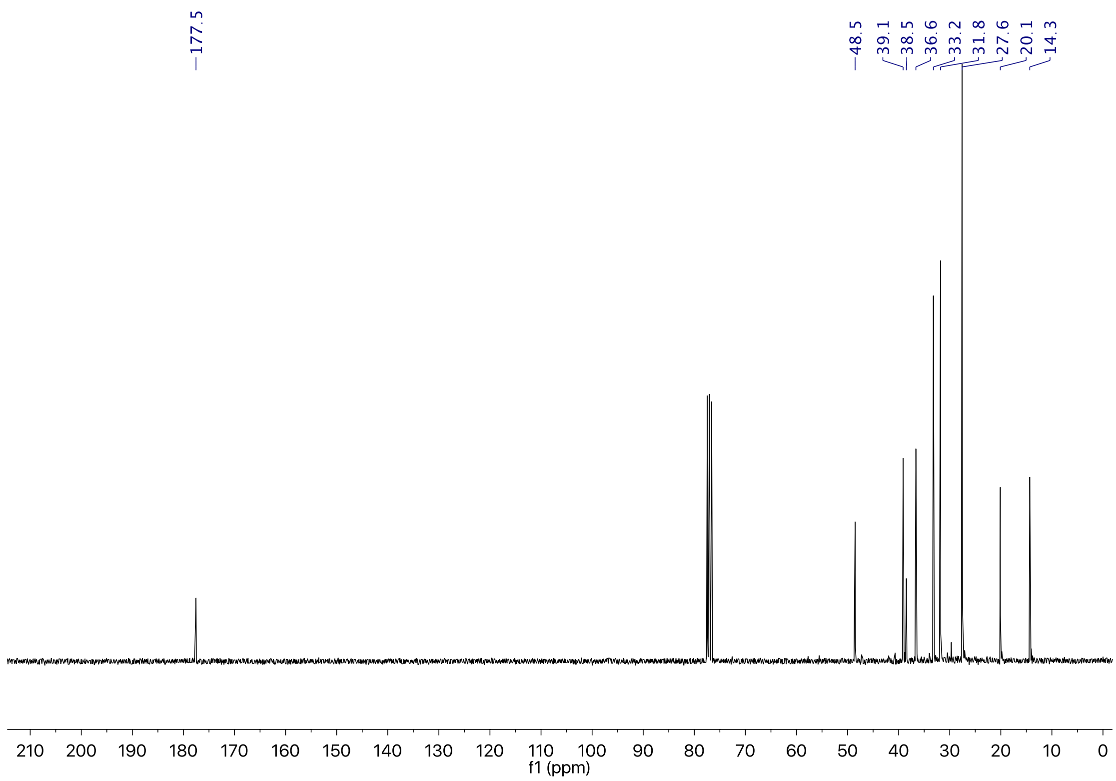


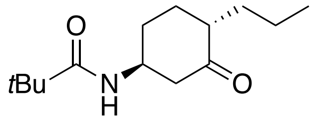


^{1}H-NMR of *trans*-**6** in $CDCl_3$

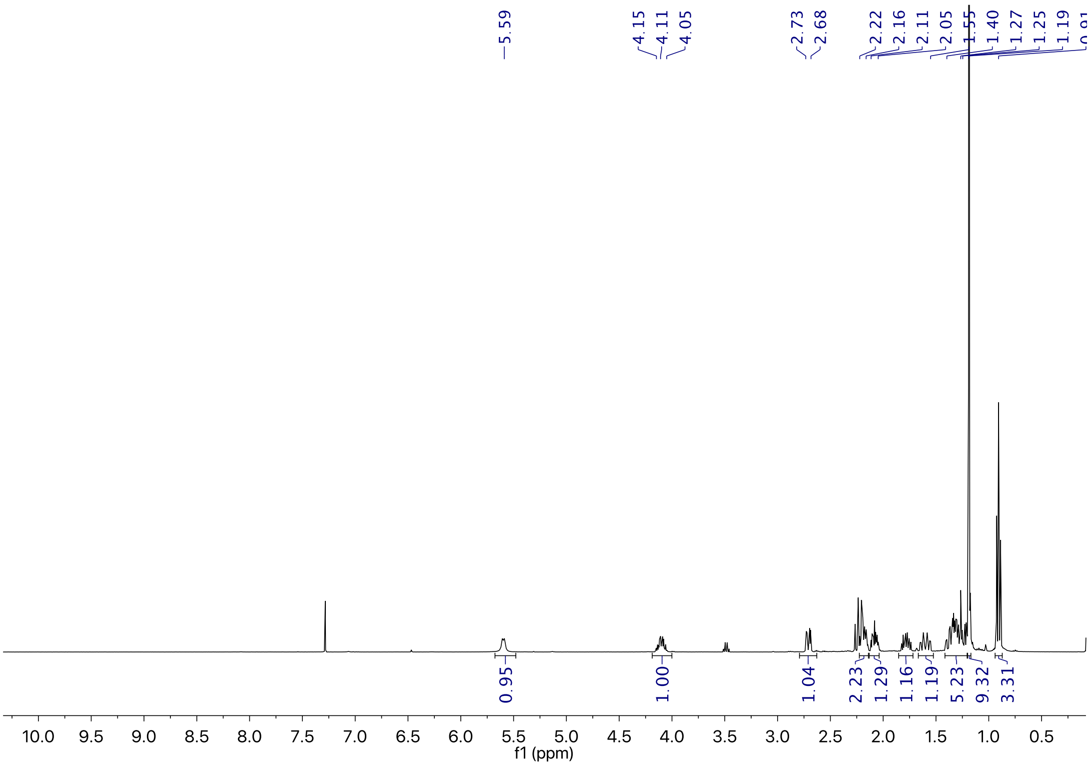


^{13}C{^{1}H}-NMR of *trans*-**6** in $CDCl_3$

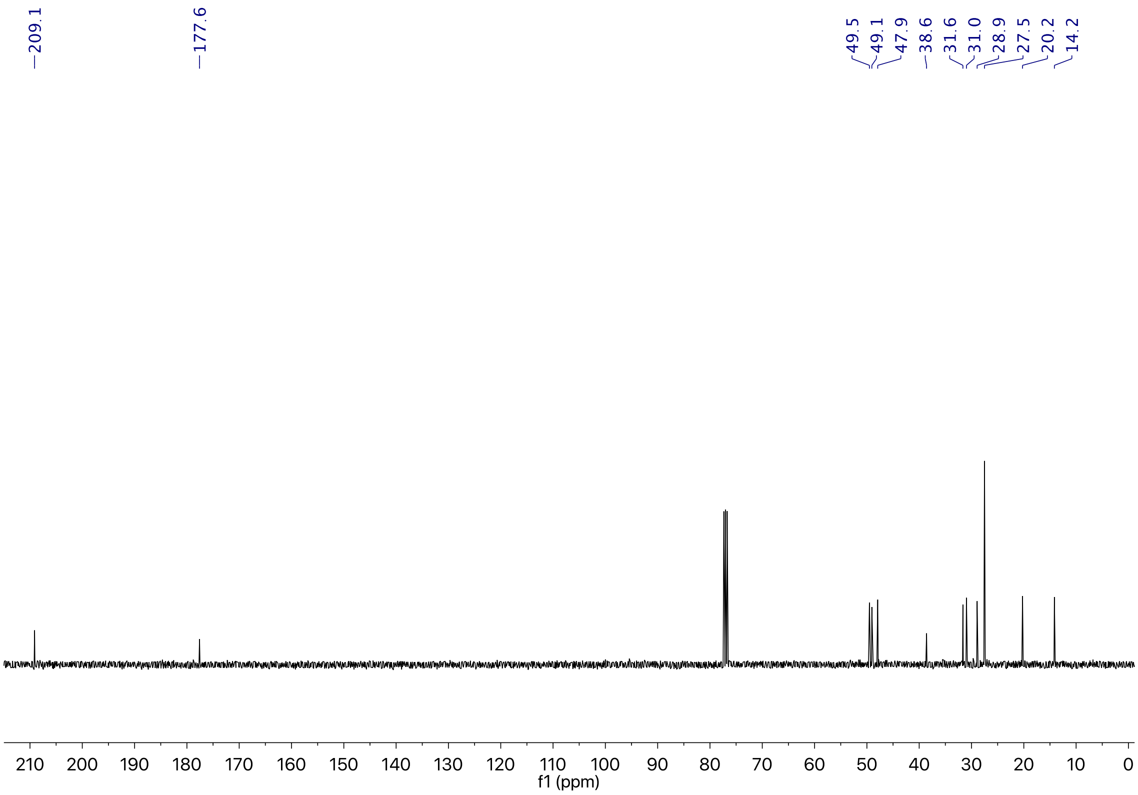


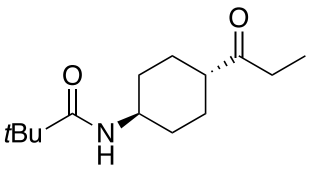


^{1}H-NMR of **6a** in $CDCl_3$

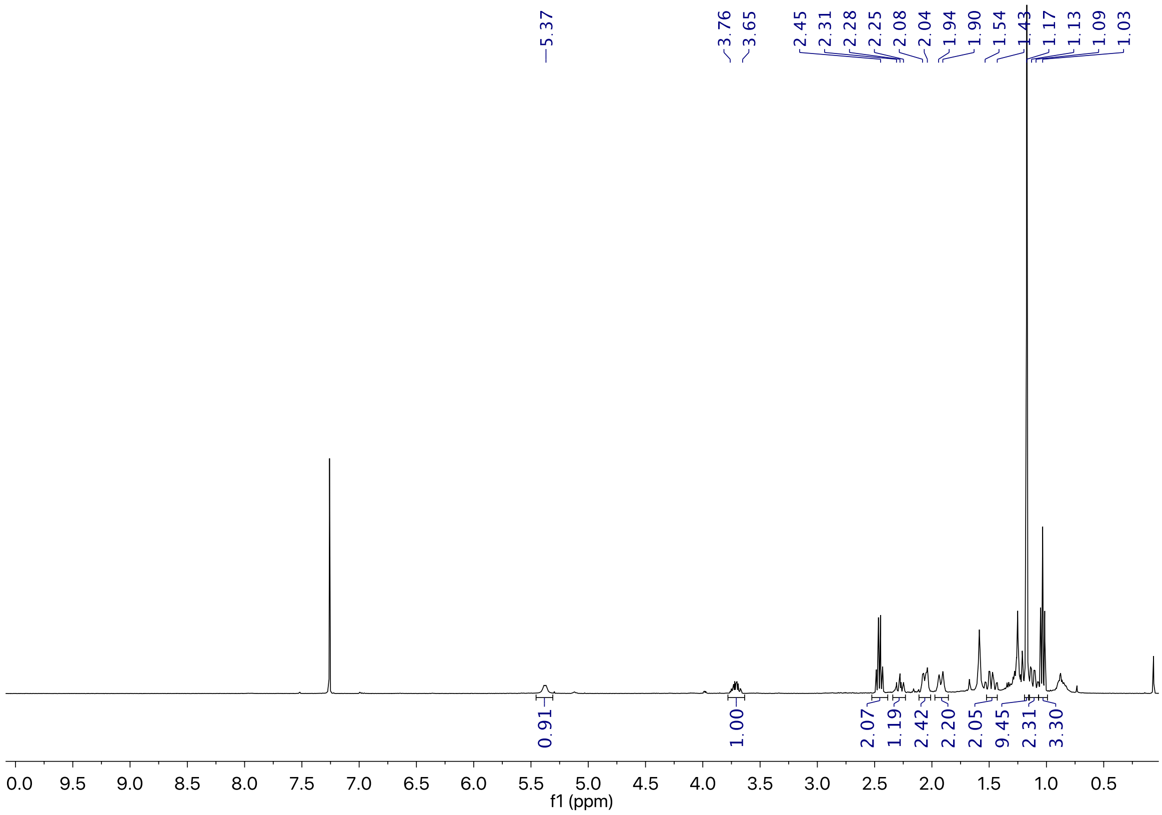


^{13}C{^{1}H}-NMR of **6a** in $CDCl_3$

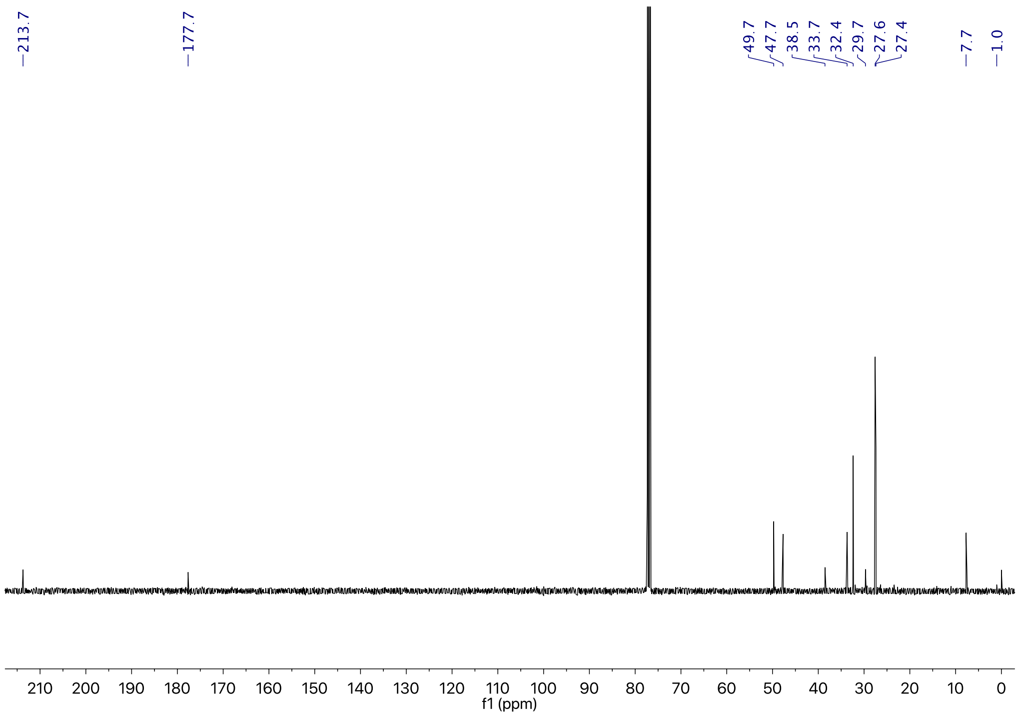


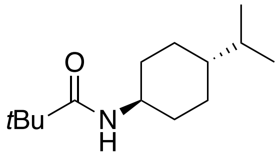


^{1}H-NMR of **6b** in $CDCl_3$

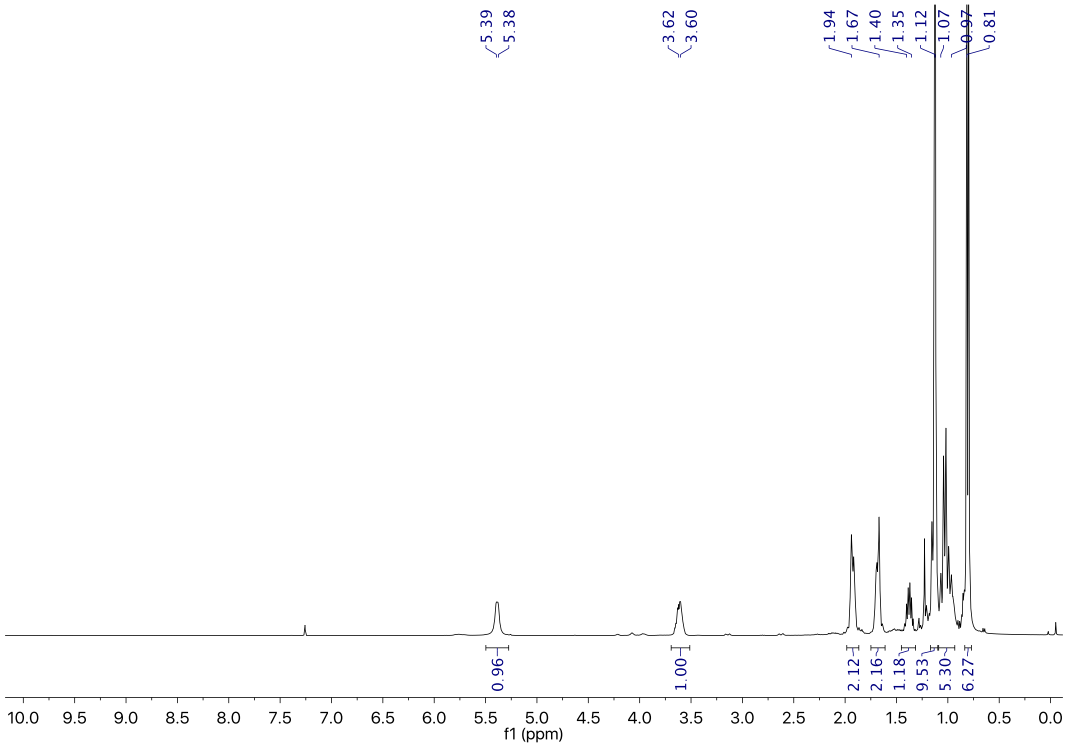


^{13}C{^{1}H}-NMR of **6b** in $CDCl_3$

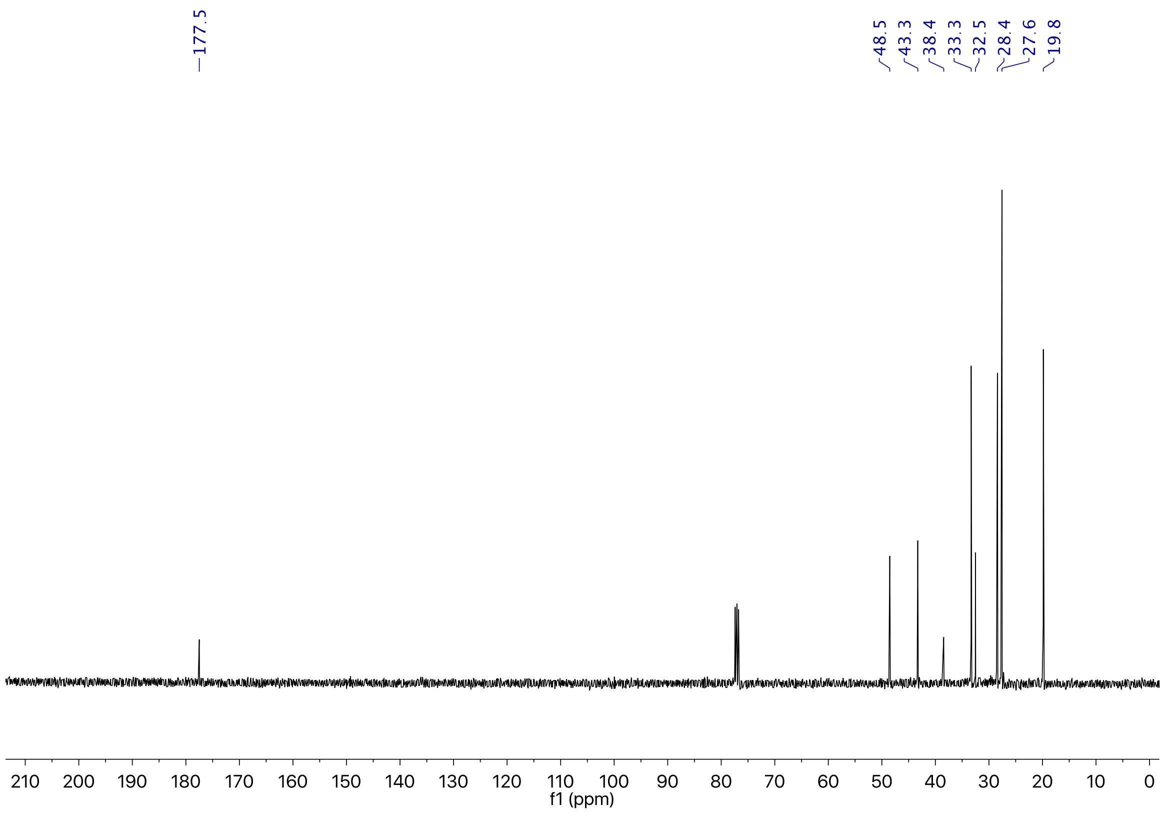


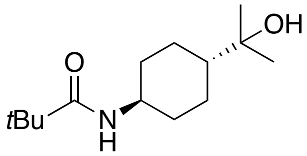


^{1}H-NMR of *trans*-**7** in $CDCl_3$

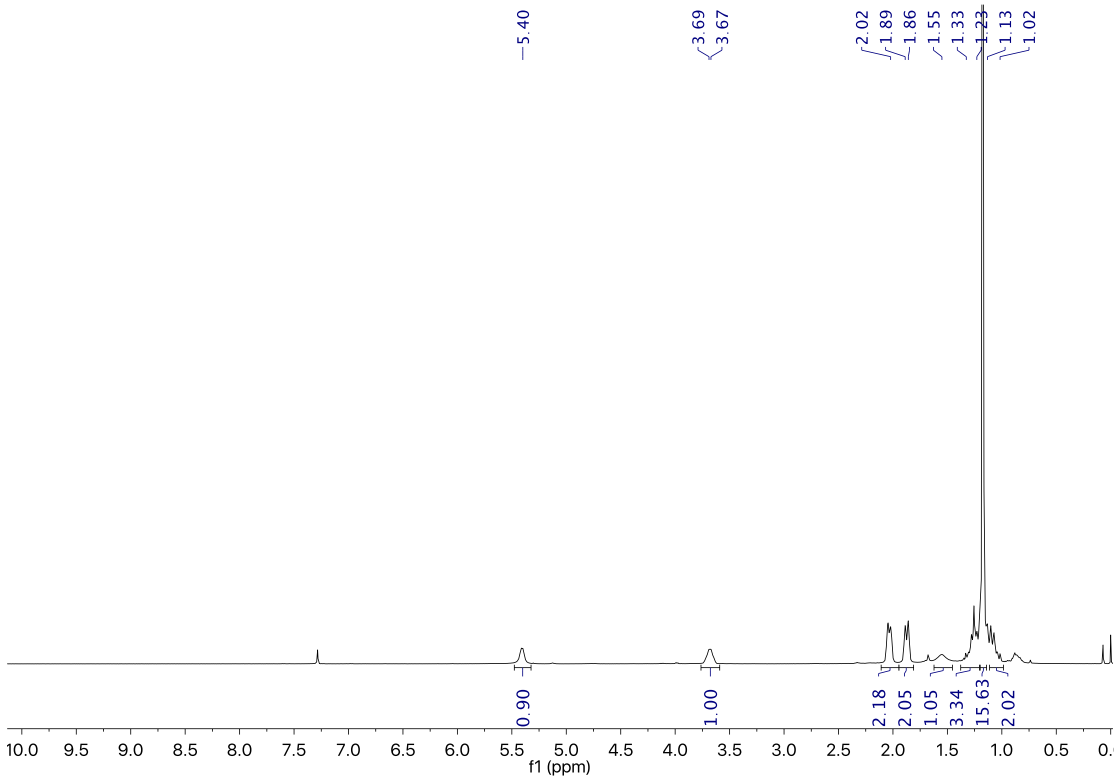


^{13}C{^{1}H}-NMR of *trans*-**7** in $CDCl_3$

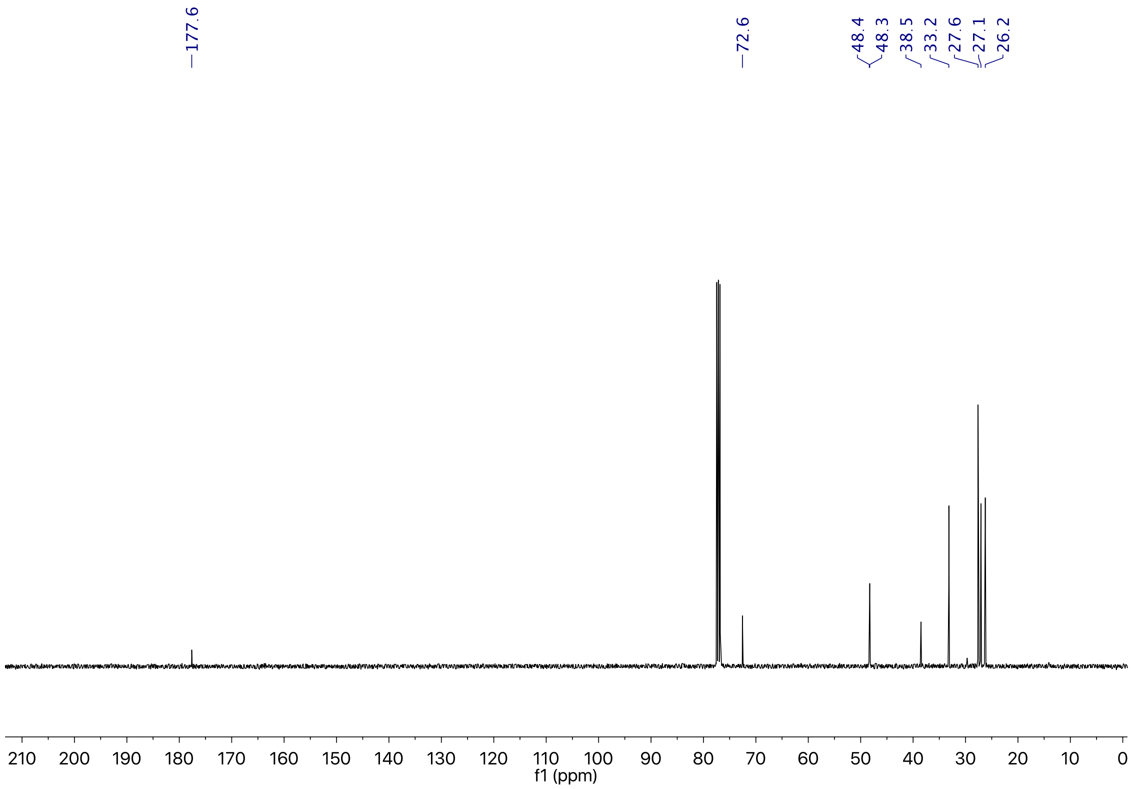


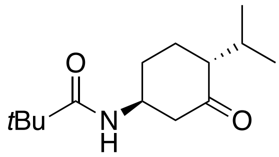


^{1}H-NMR of **7a** in $CDCl_3$

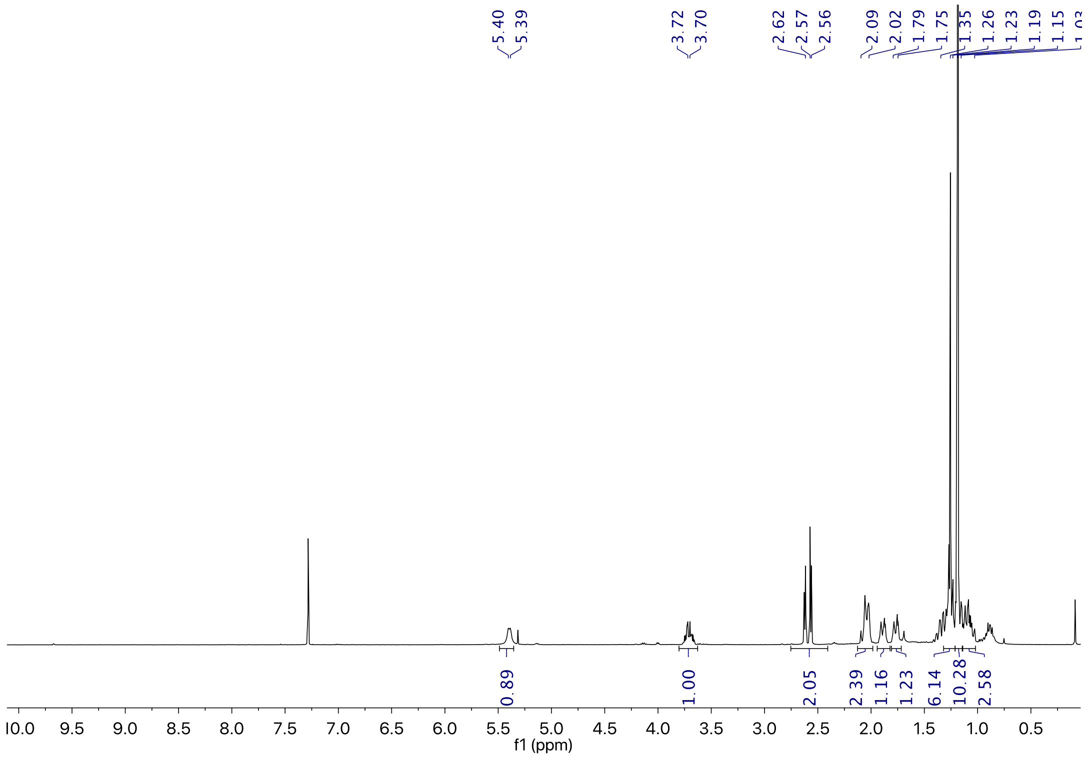


^{13}C{^{1}H}-NMR of **7a** in $CDCl_3$

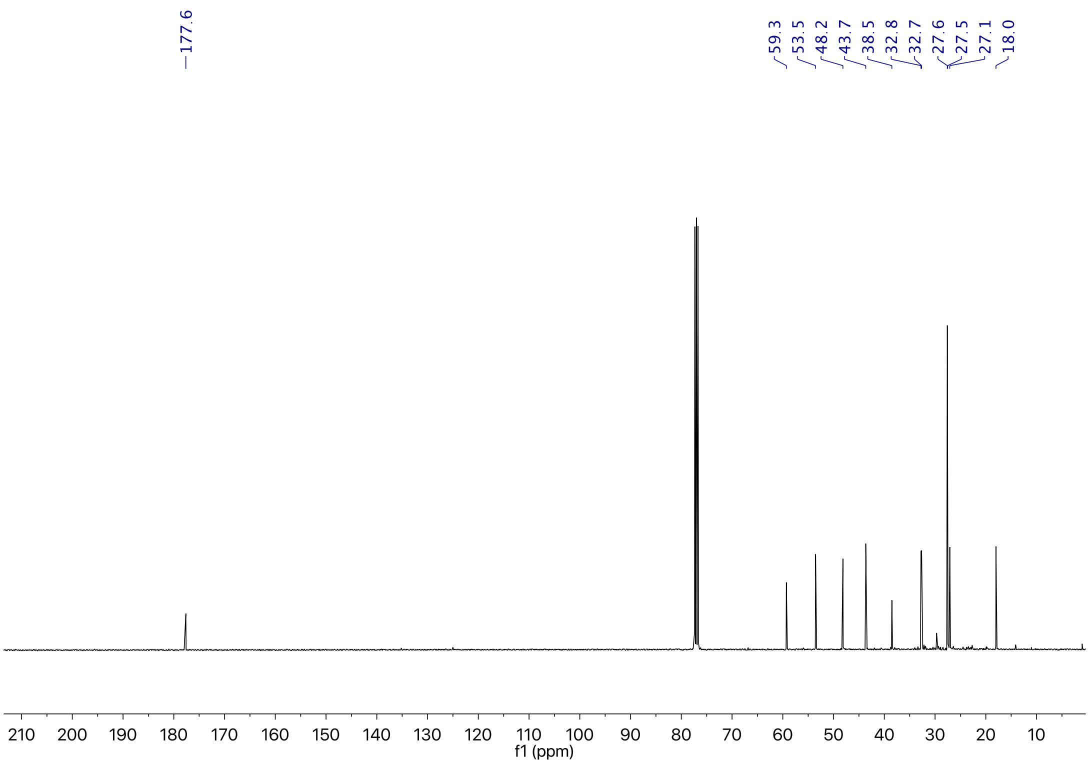


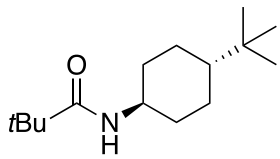


^{1}H-NMR of **7b** in $CDCl_3$

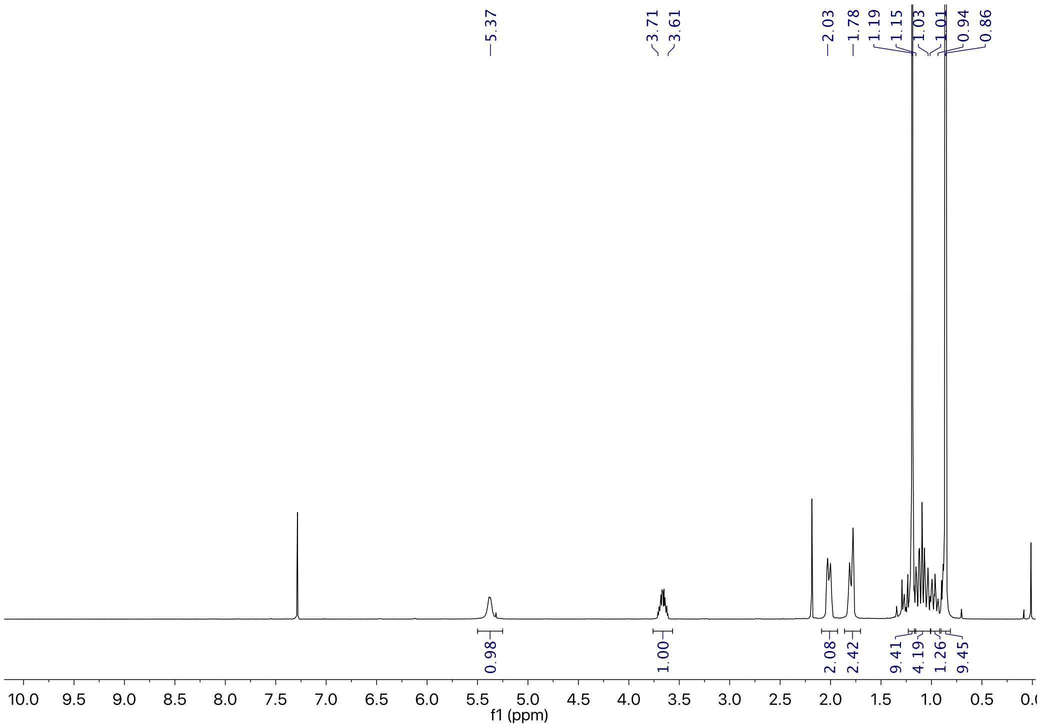


^{13}C{^{1}H}-NMR of **7b** in $CDCl_3$

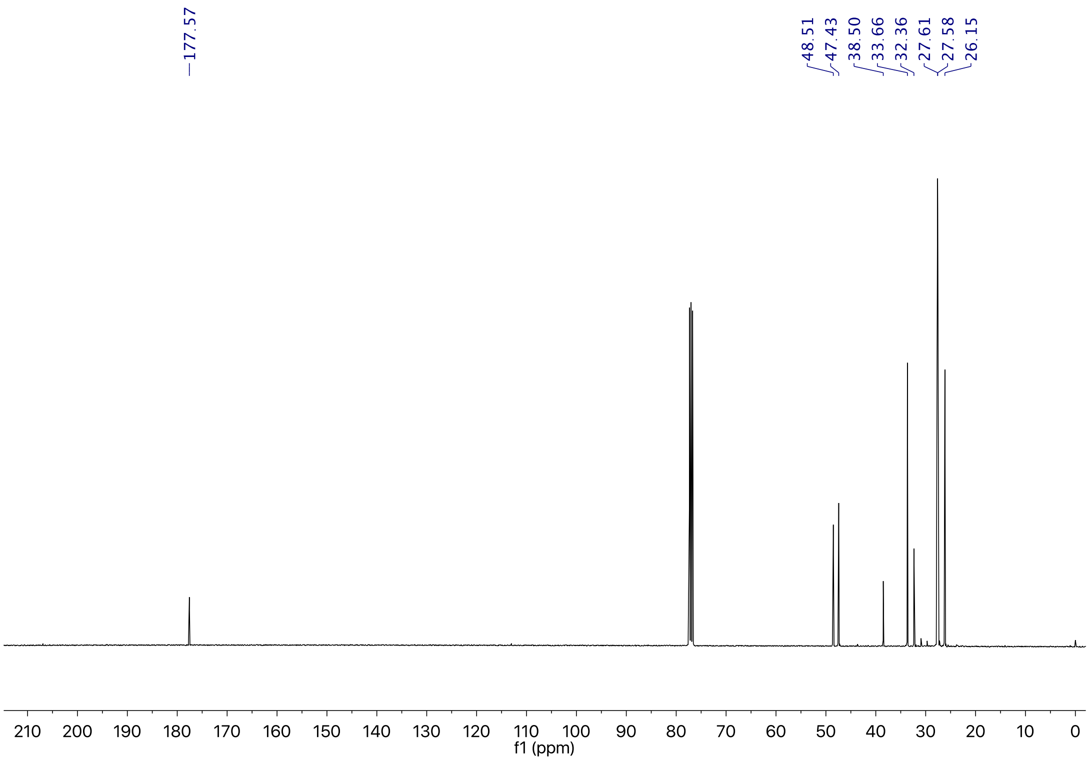


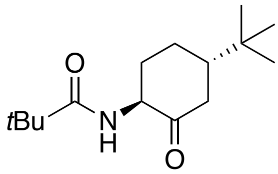


^{1}H-NMR of *trans*-**8** in $CDCl_3$

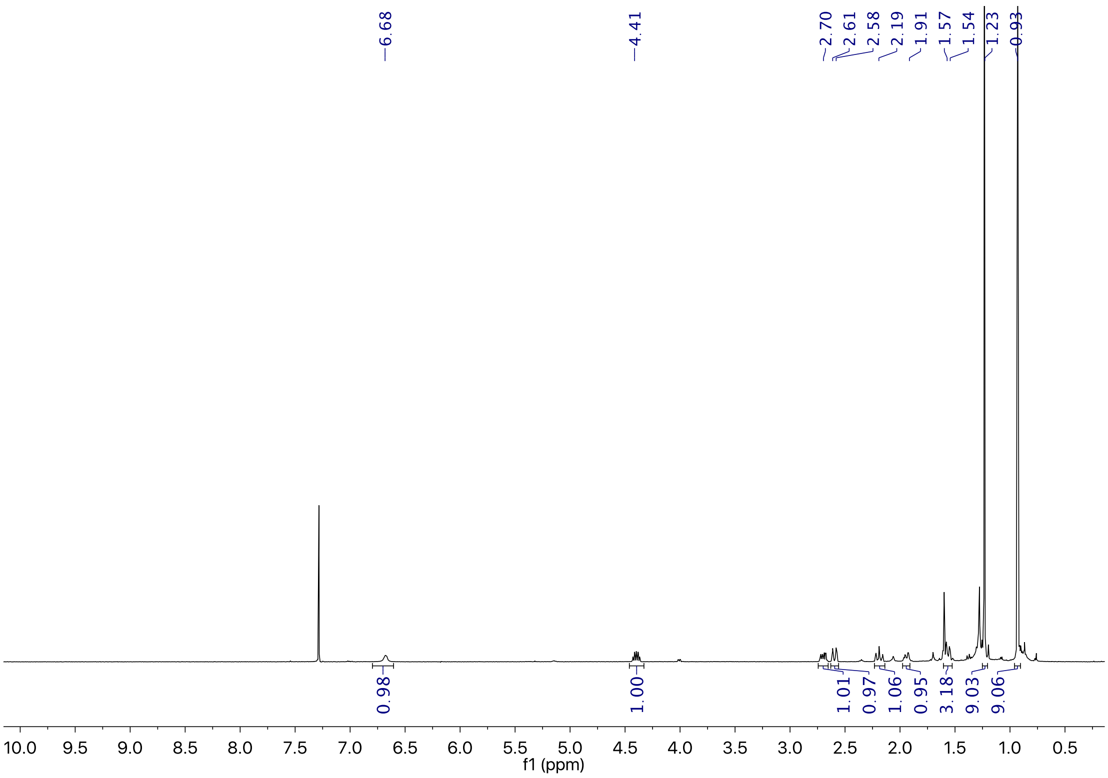


^{13}C{^{1}H}-NMR of *trans*-**8** in $CDCl_3$

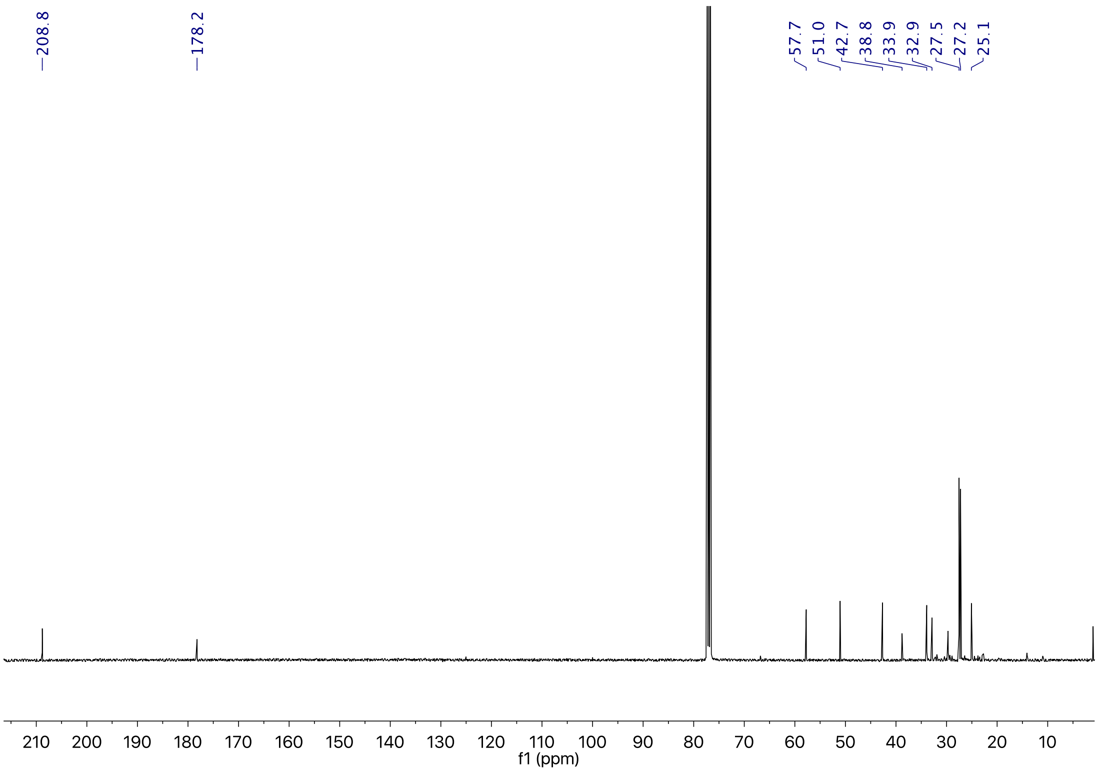


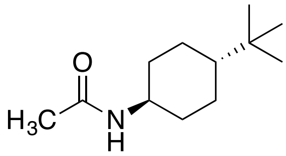


^{1}H-NMR of **8a** in $CDCl_3$

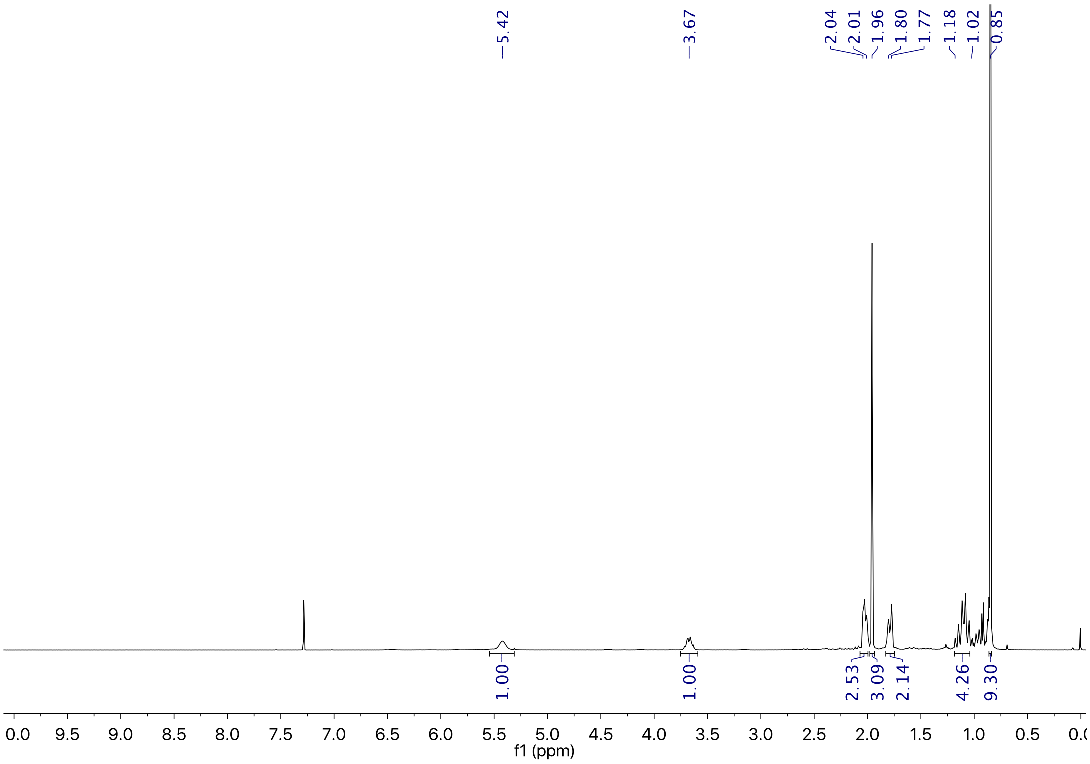


^{13}C{^{1}H}-NMR of **8a** in $CDCl_3$

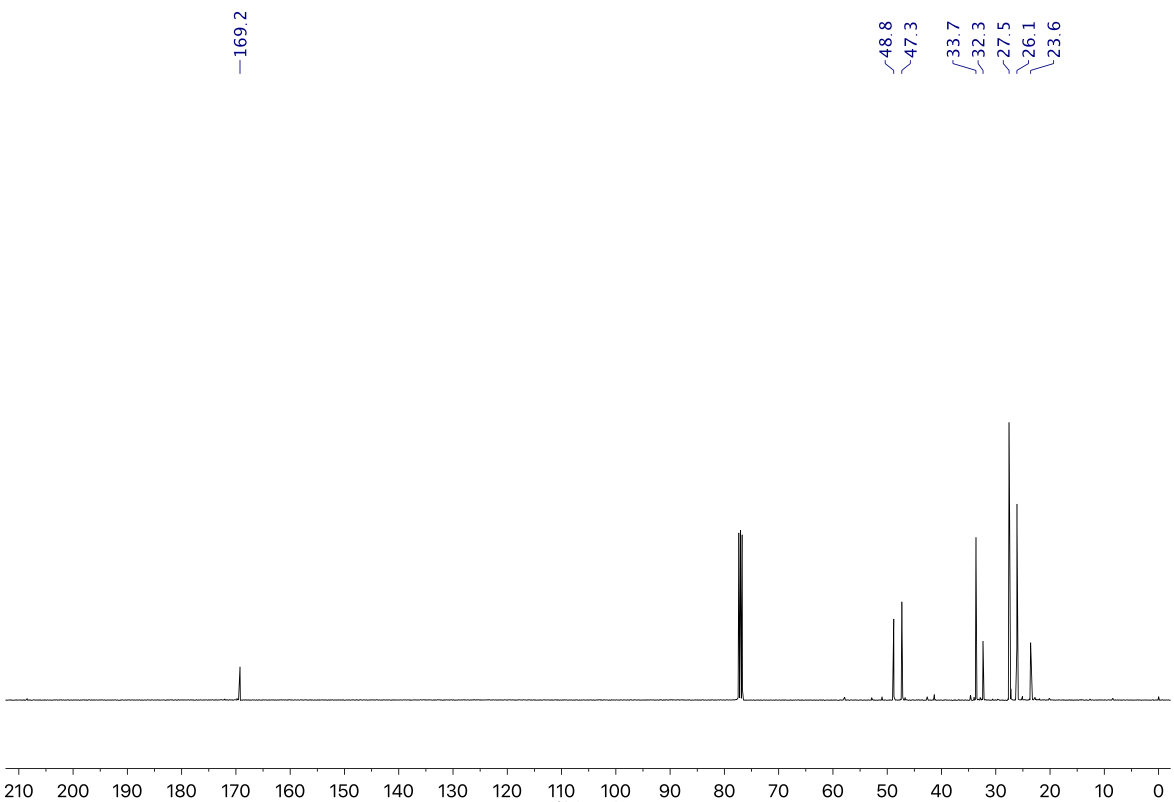


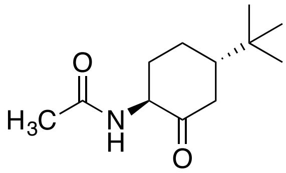


[1]H-NMR of *trans*-**9** in $CDCl_3$

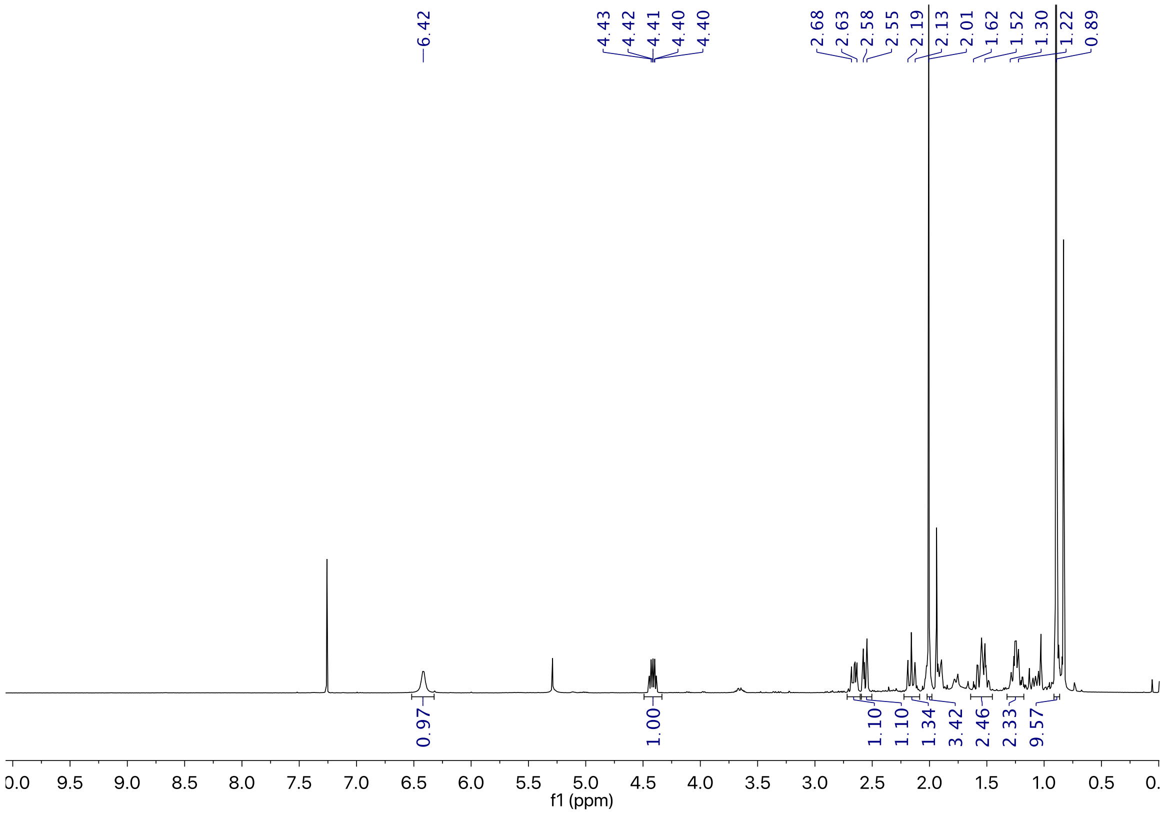


[13]C{[1]H}-NMR of *trans*-**9** in $CDCl_3$

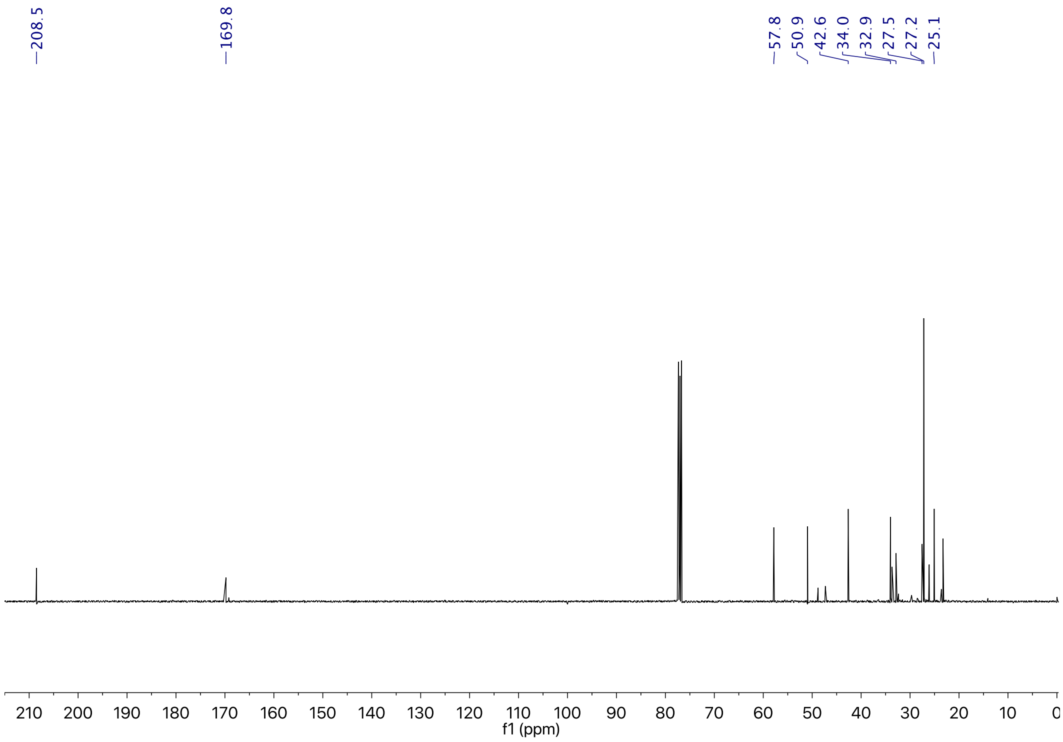


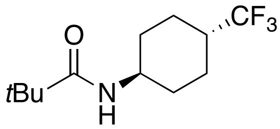


[1]H-NMR of **9a** in $CDCl_3$

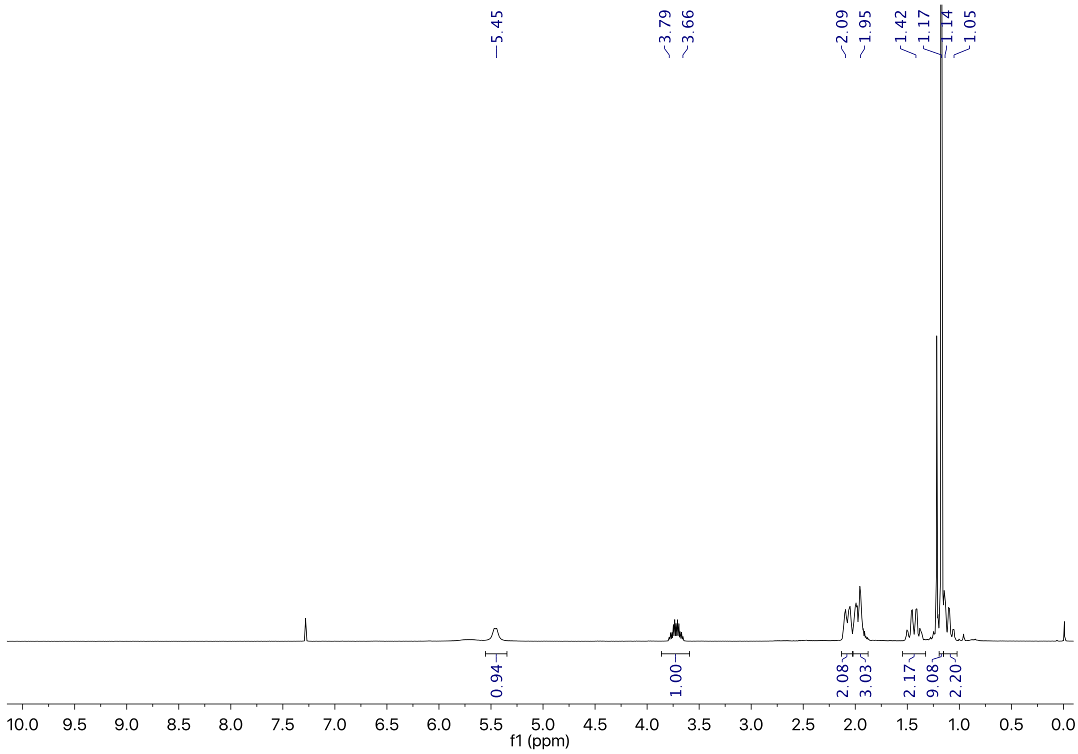


[13]C{[1]H}-NMR of **9a** in $CDCl_3$

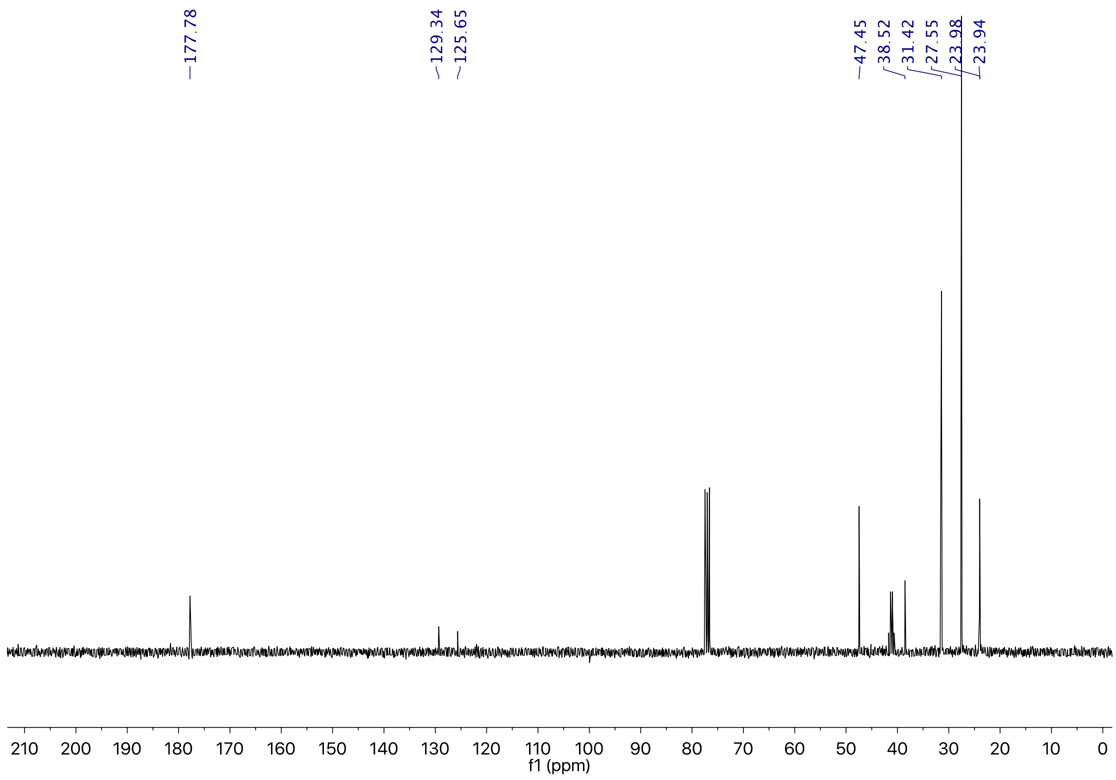


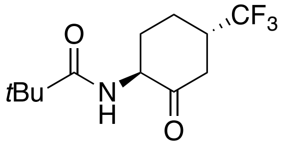


^{1}H-NMR of *trans*-**10** in $CDCl_3$

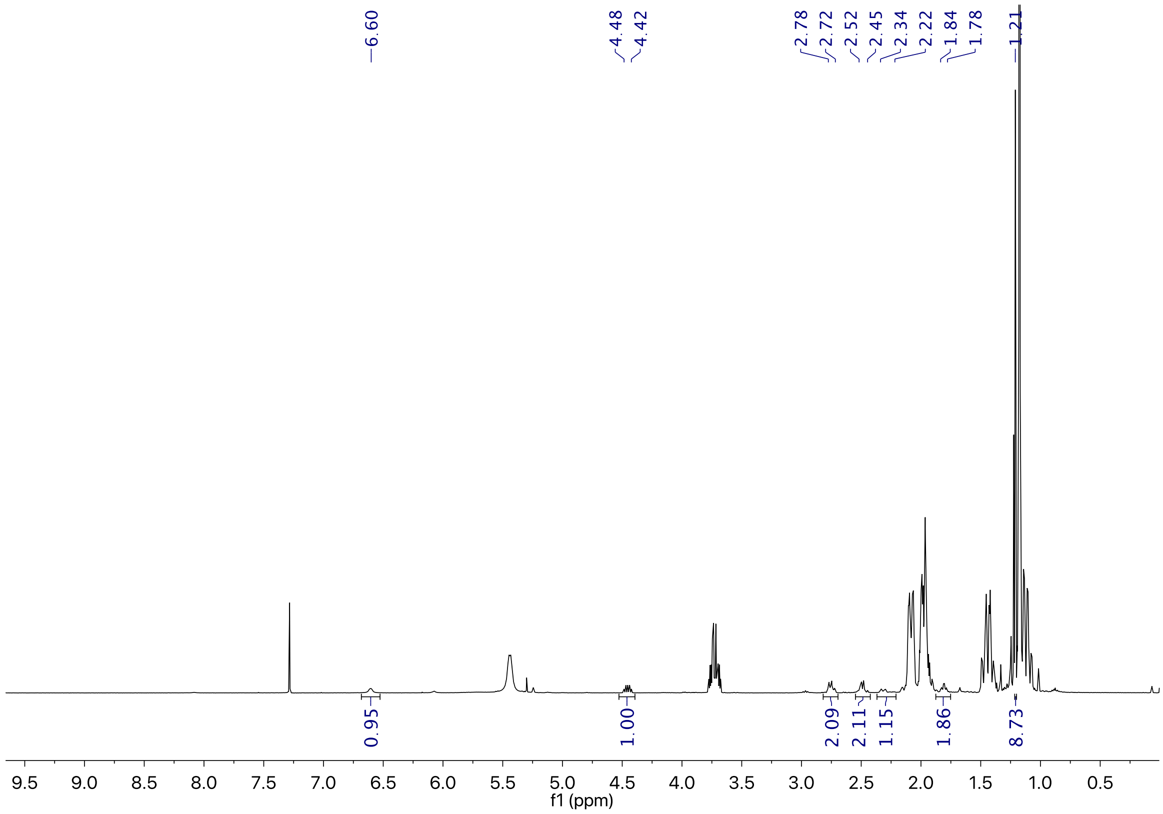


$^{13}C\{^{1}H\}$-NMR of *trans*-**10** in $CDCl_3$

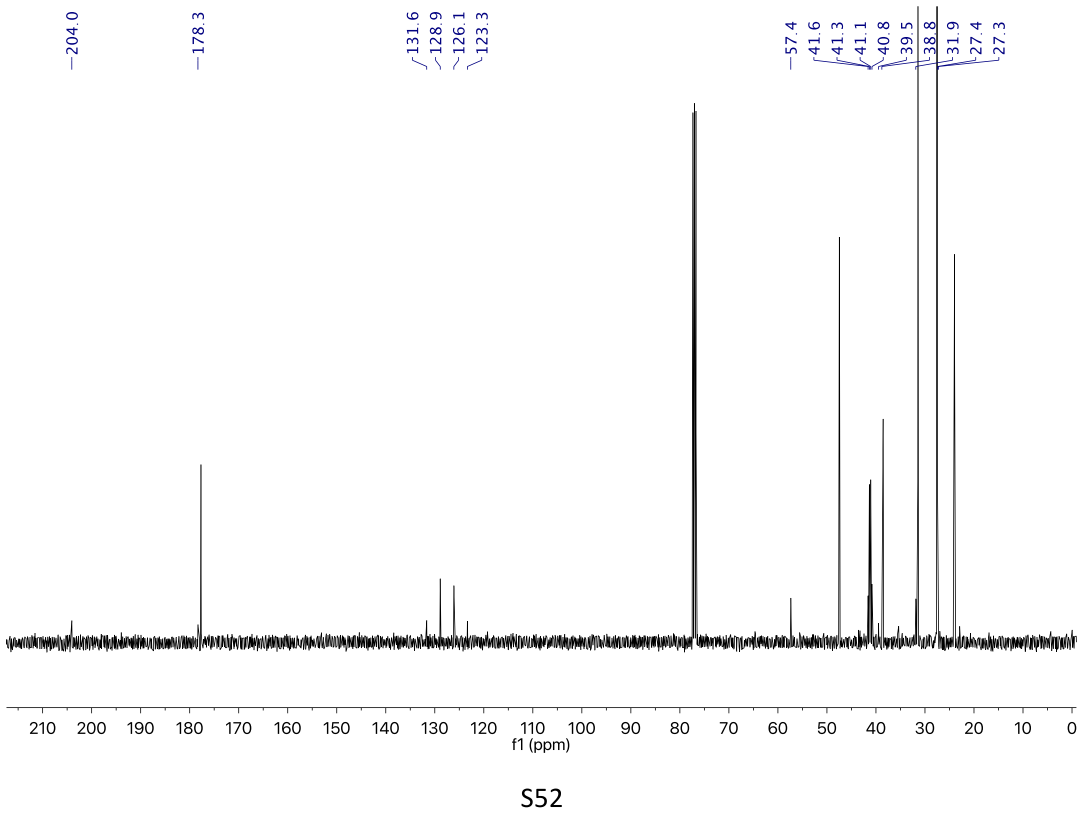




^{1}H-NMR of **10a** in $CDCl_3$

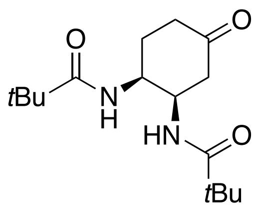


^{13}C{^{1}H}-NMR of **10a** in $CDCl_3$

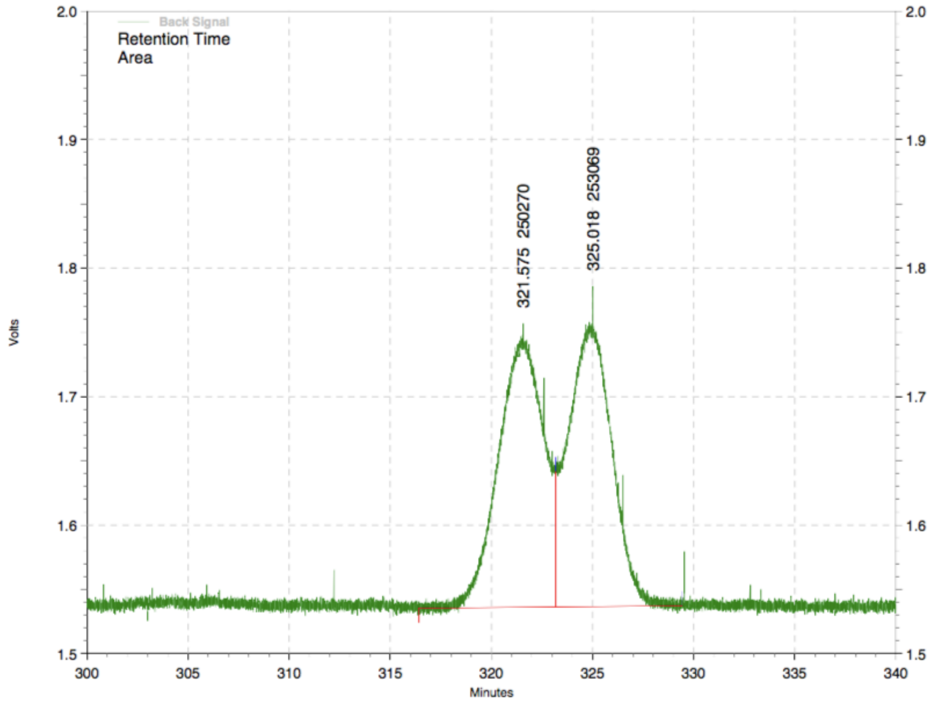


A3 GC spectra of products

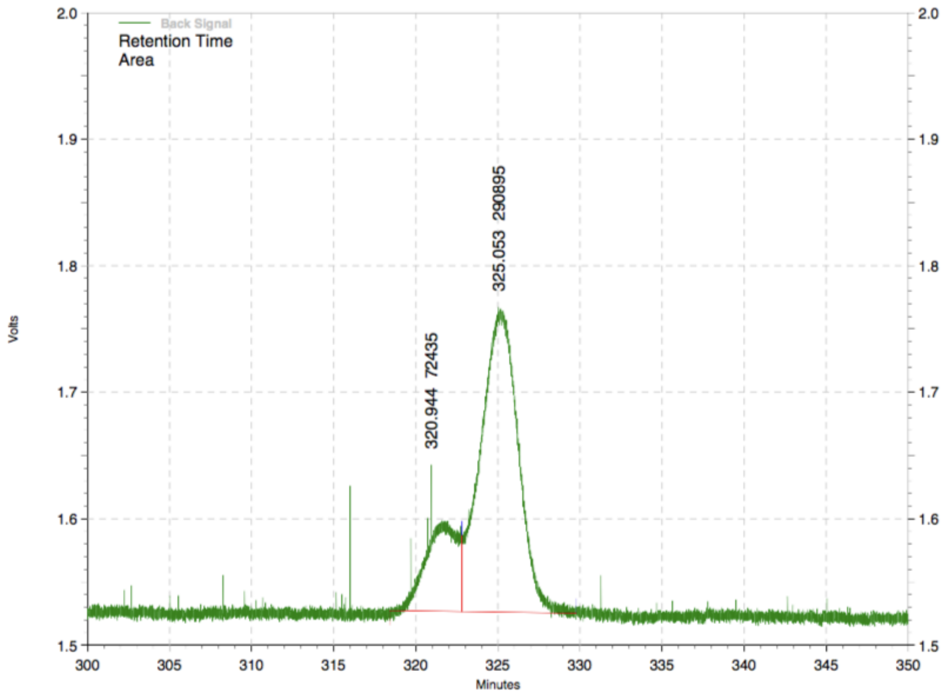
The racemic products were obtained by using the racemic **[Mn(CF_3SO_3)$_2$(^{TIPS}mcp)]** complex.

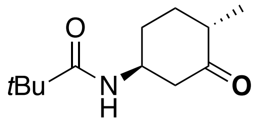


Rac

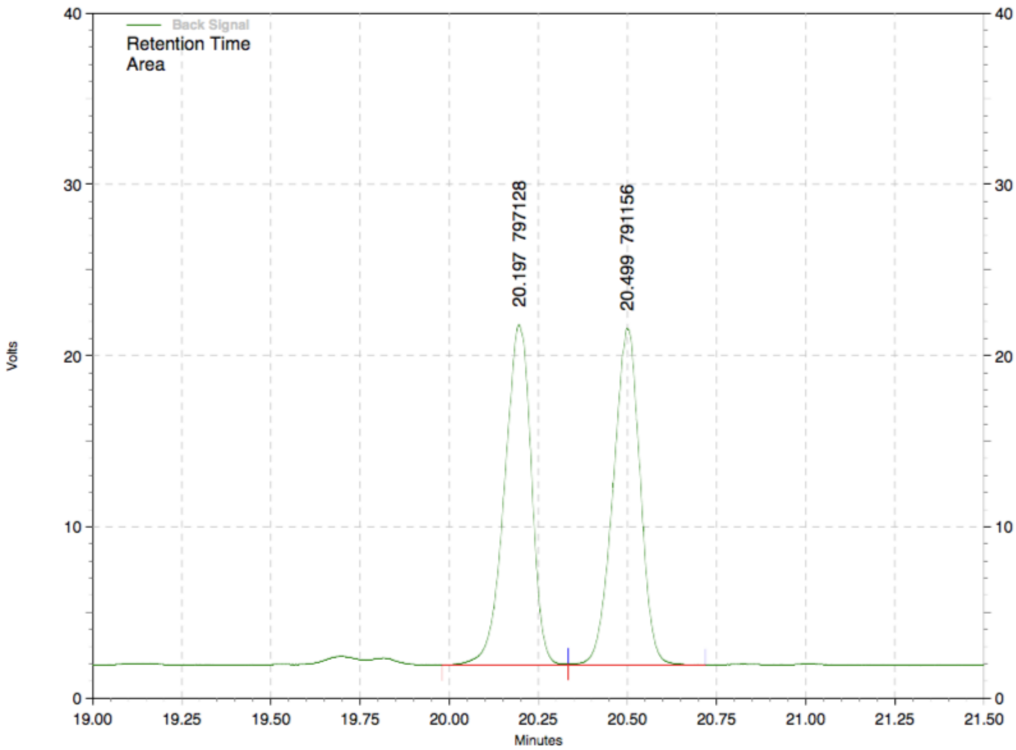


1a (*S,S*)-Mn(^{TIPS}mcp)

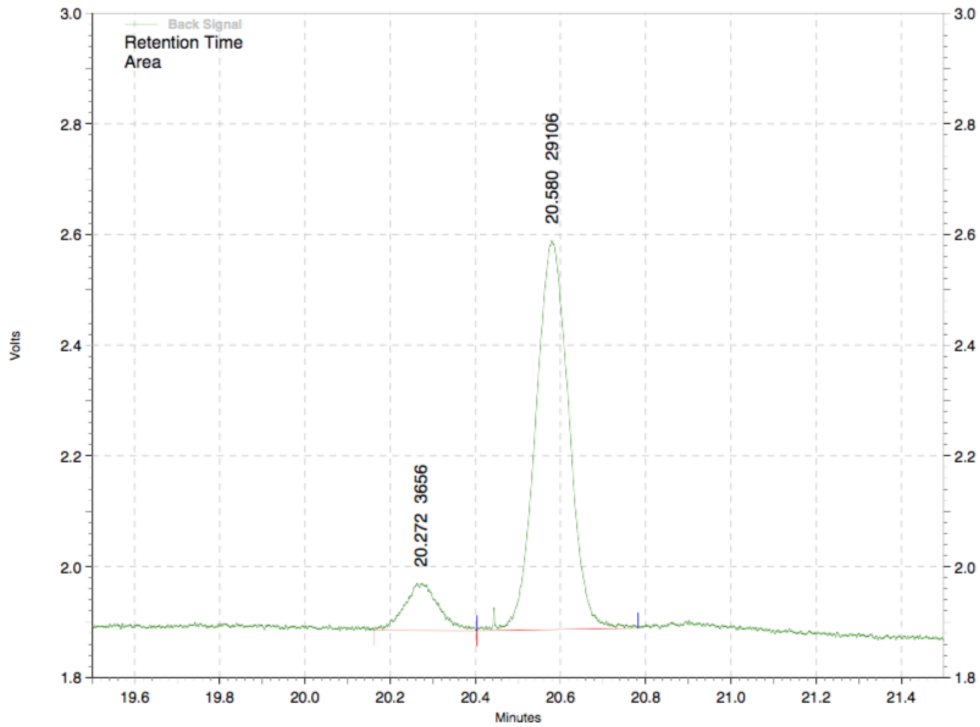




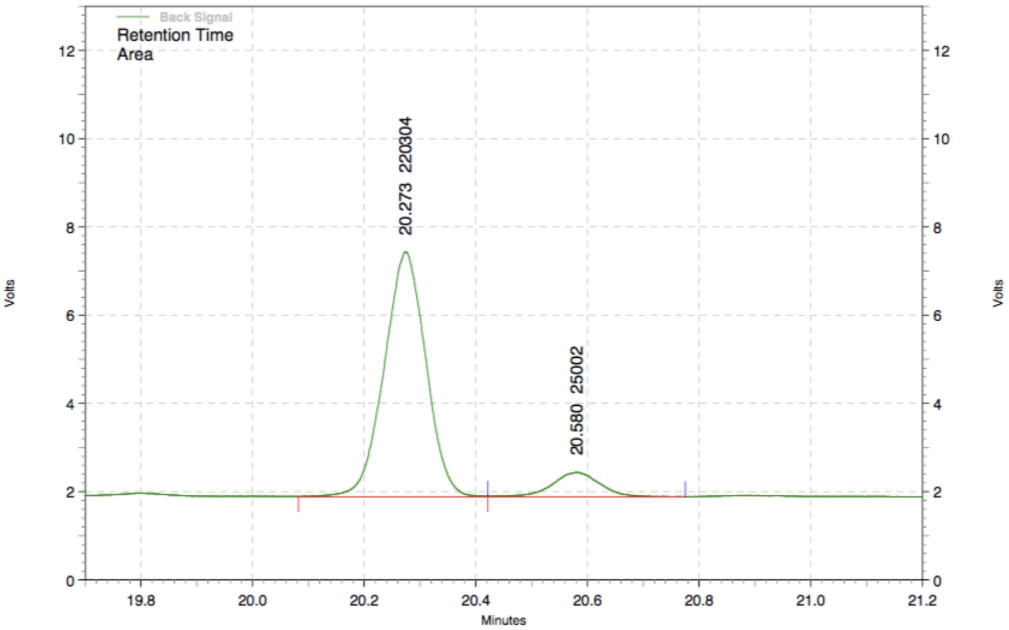
Rac

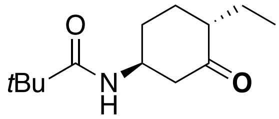


4a (*S*,*S*)-Mn(^{TIPS}mcp)

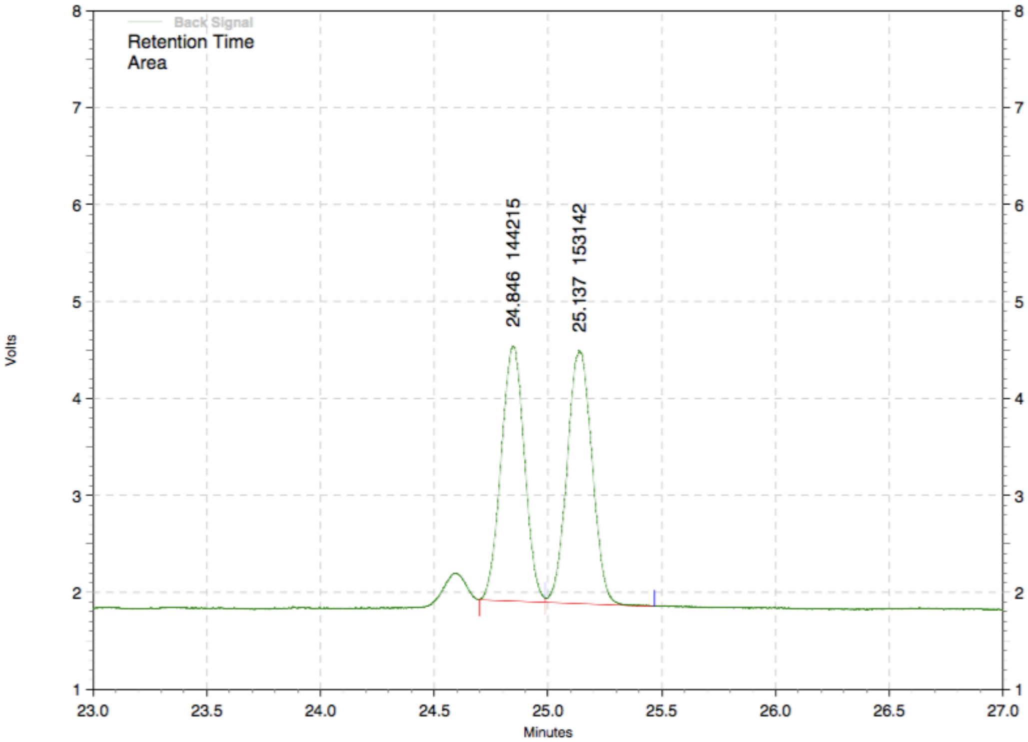


4a (*R*,*R*)-Mn(^{TIPS}mcp)

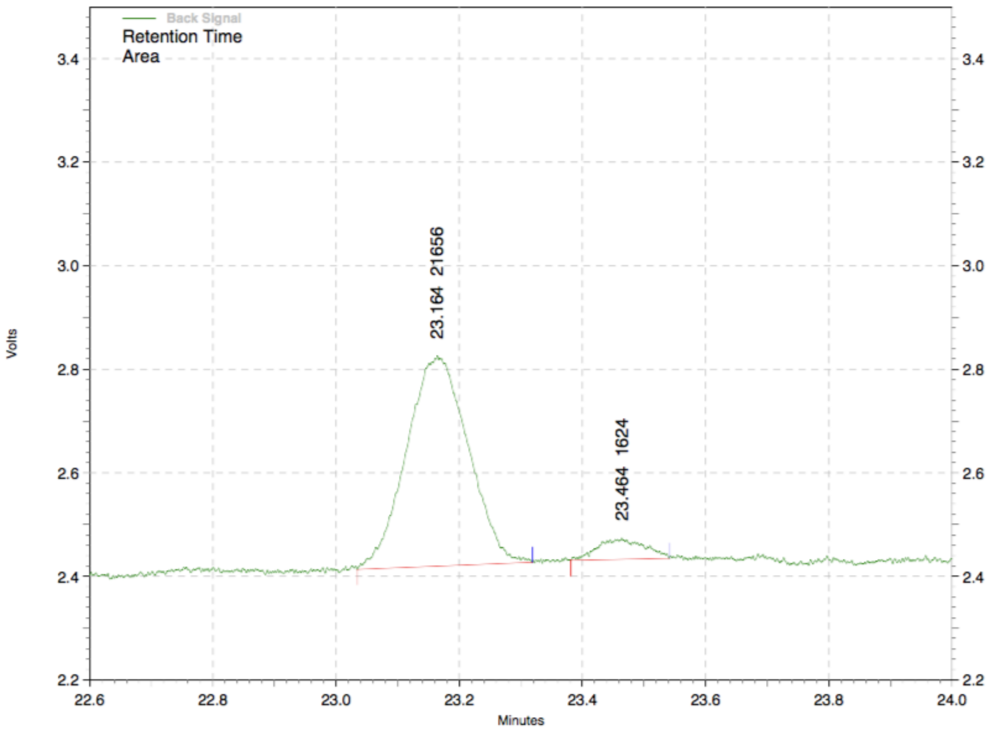


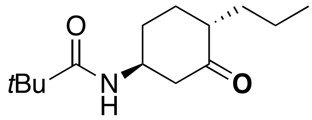


Rac

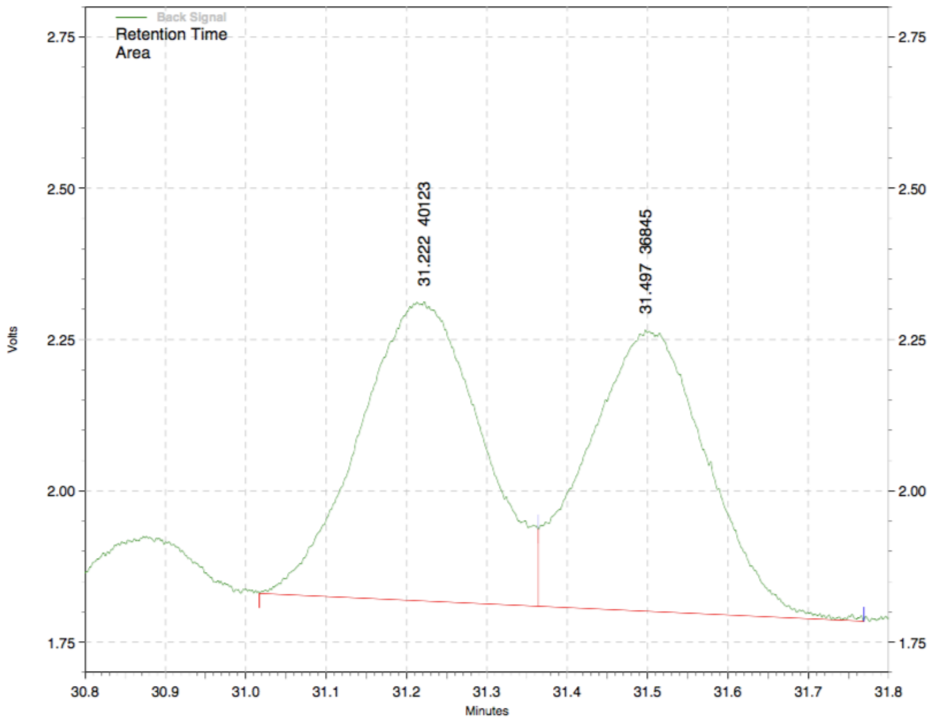


5a (*R*,*R*)-Mn(^{TIPS}mcp)

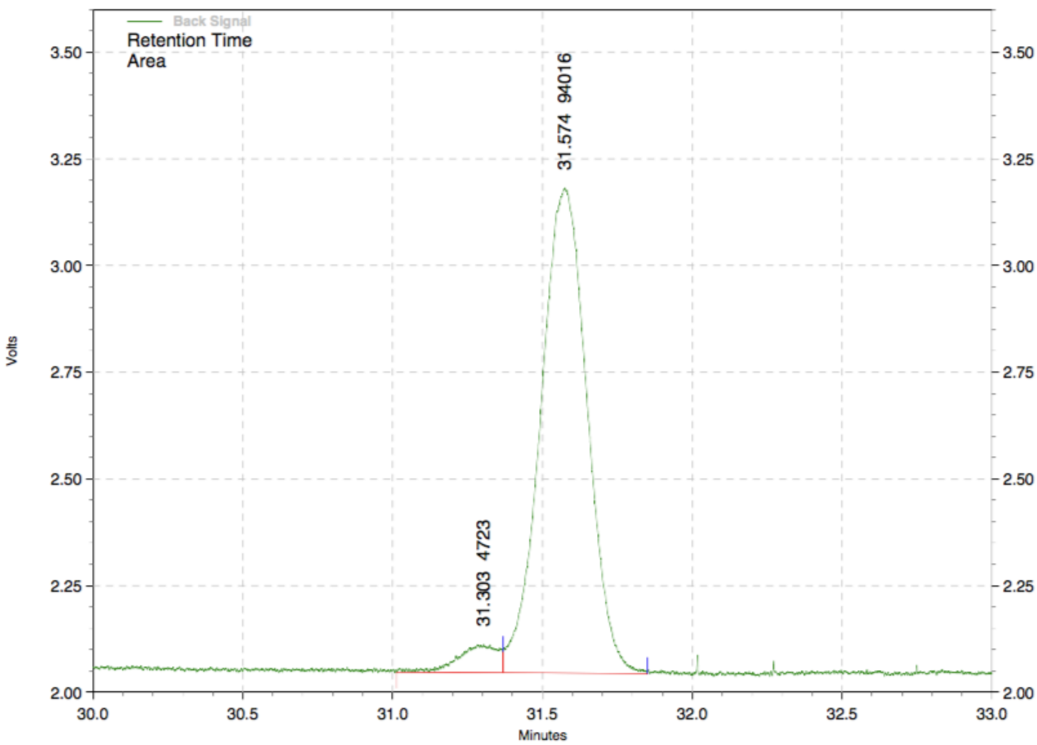


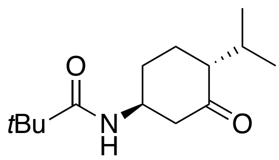


Rac

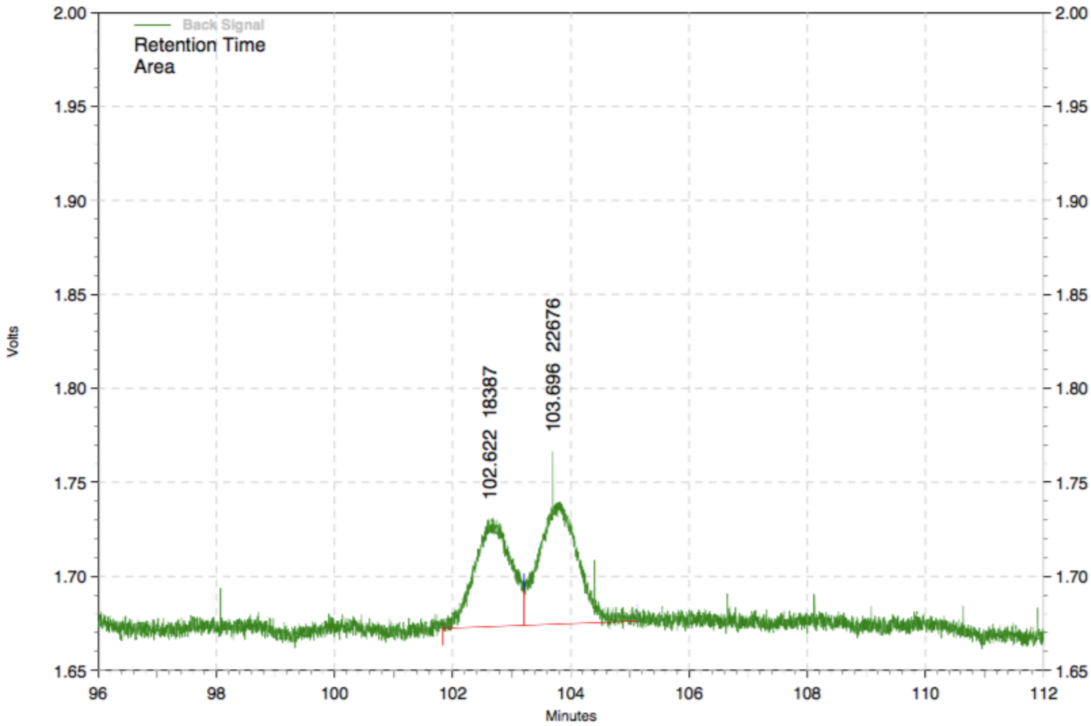


6a (*S*,*S*)-Mn(^{TIPS}mcp)

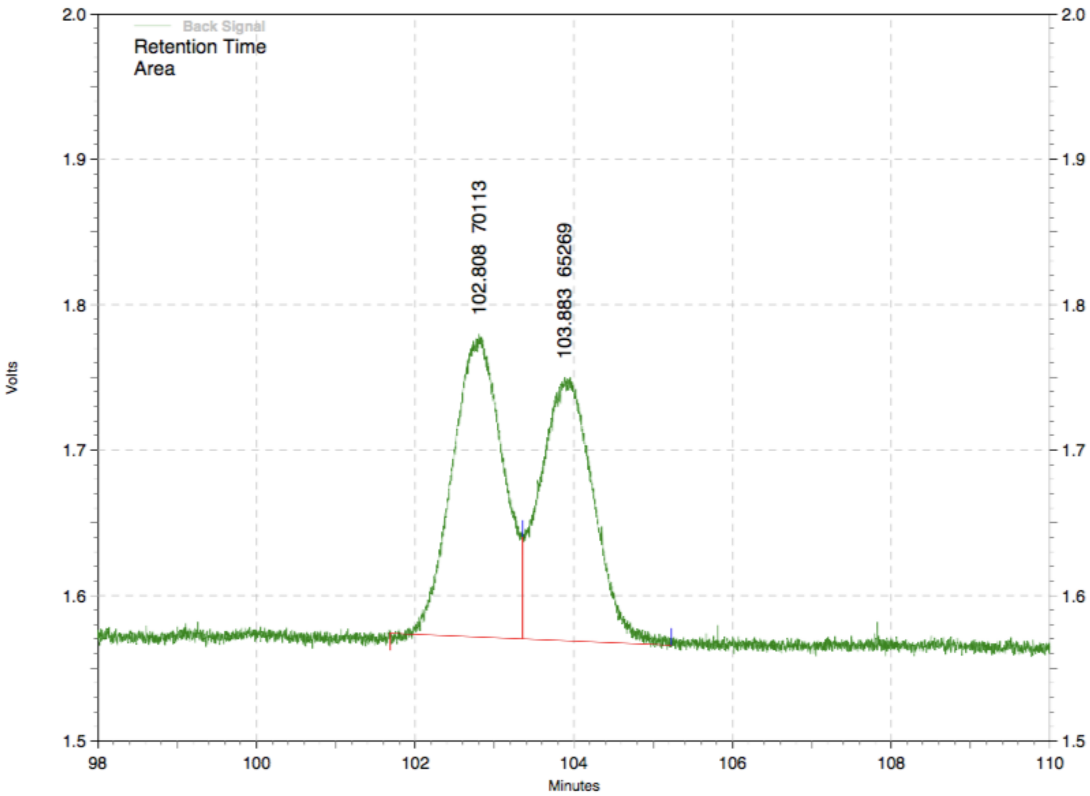


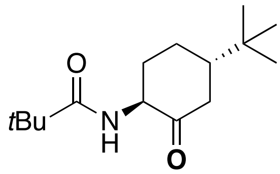


Rac

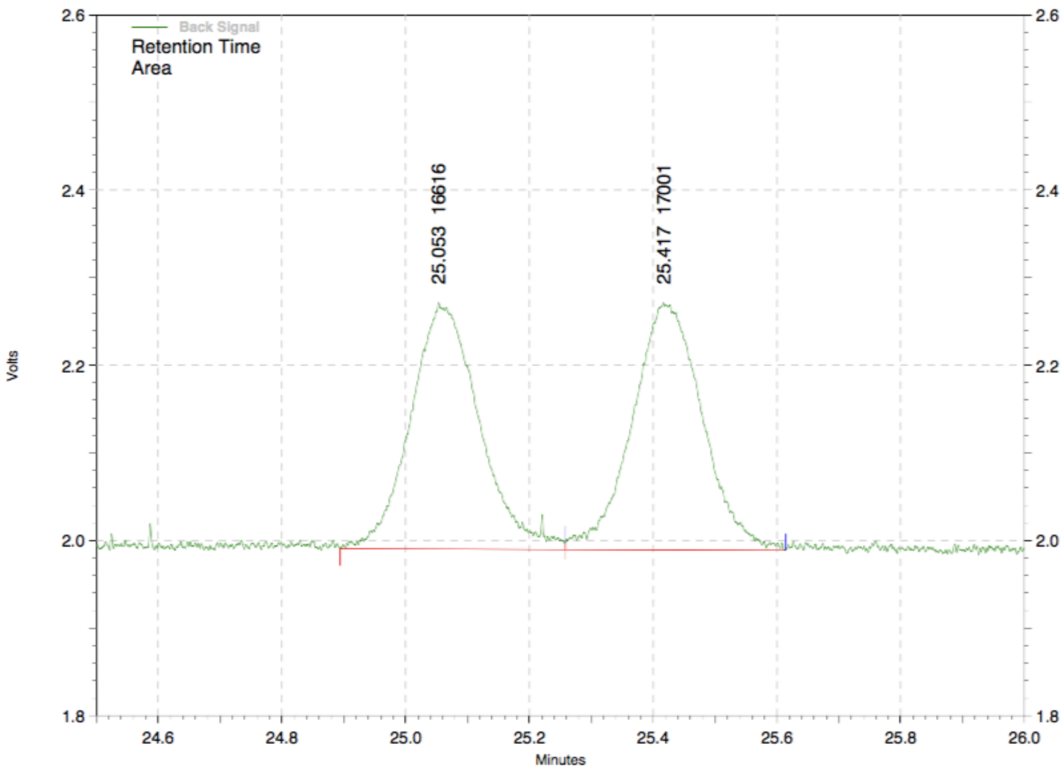


7a (*R*,*R*)-Mn(^{TIPS}mcp)

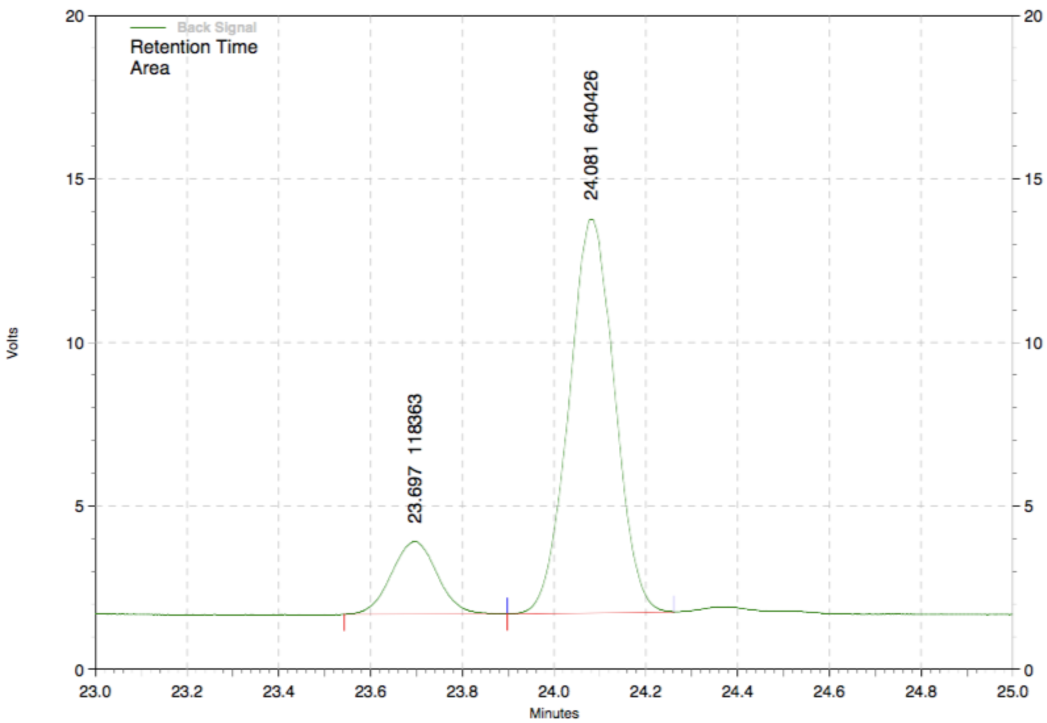


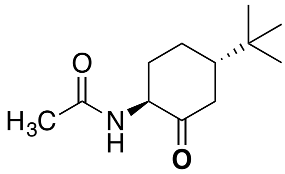


Rac

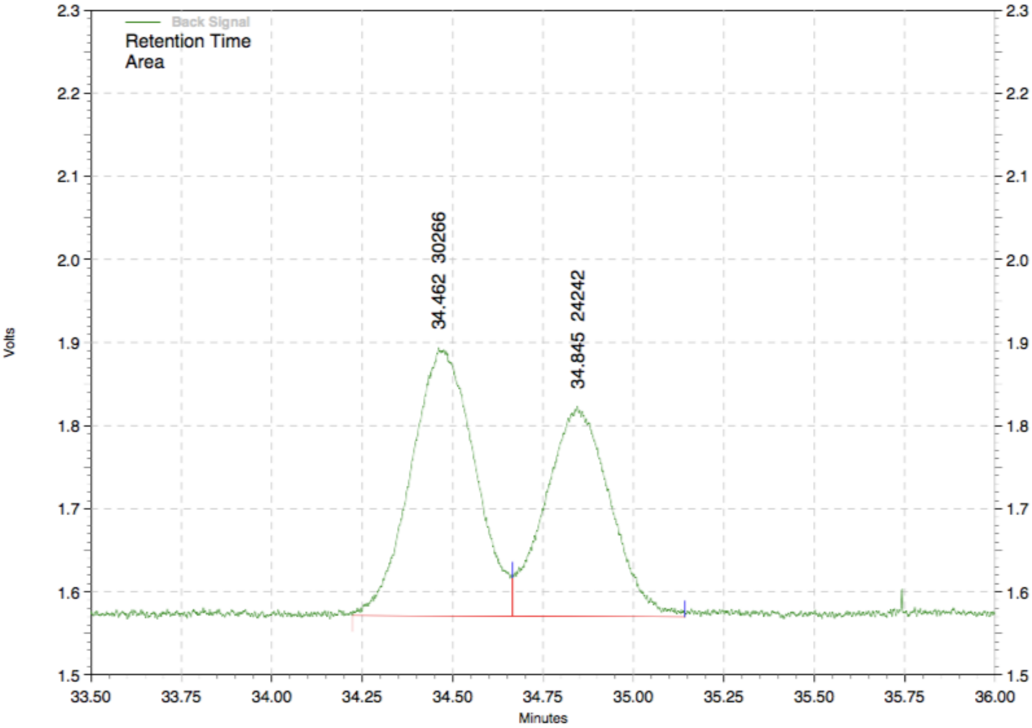


8a (*S*,*S*)-Mn(pdp)

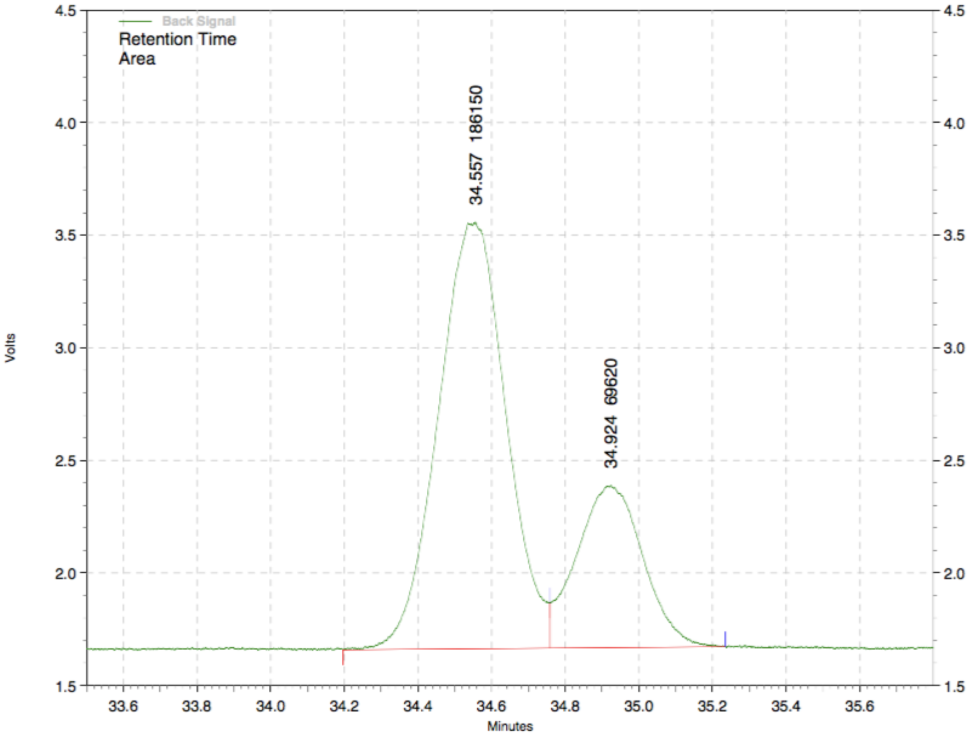


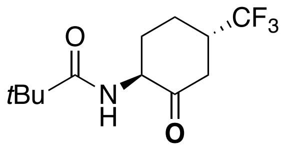


Rac

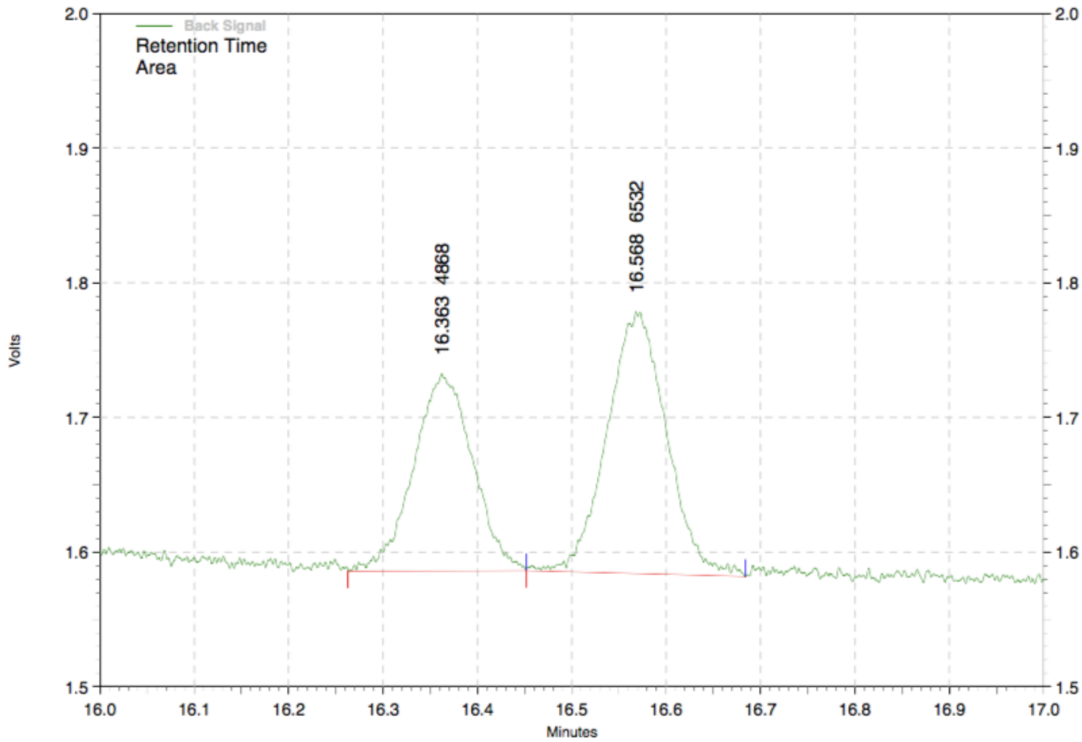


9a (*R*,*R*)-Mn(^{TIPS}mcp)

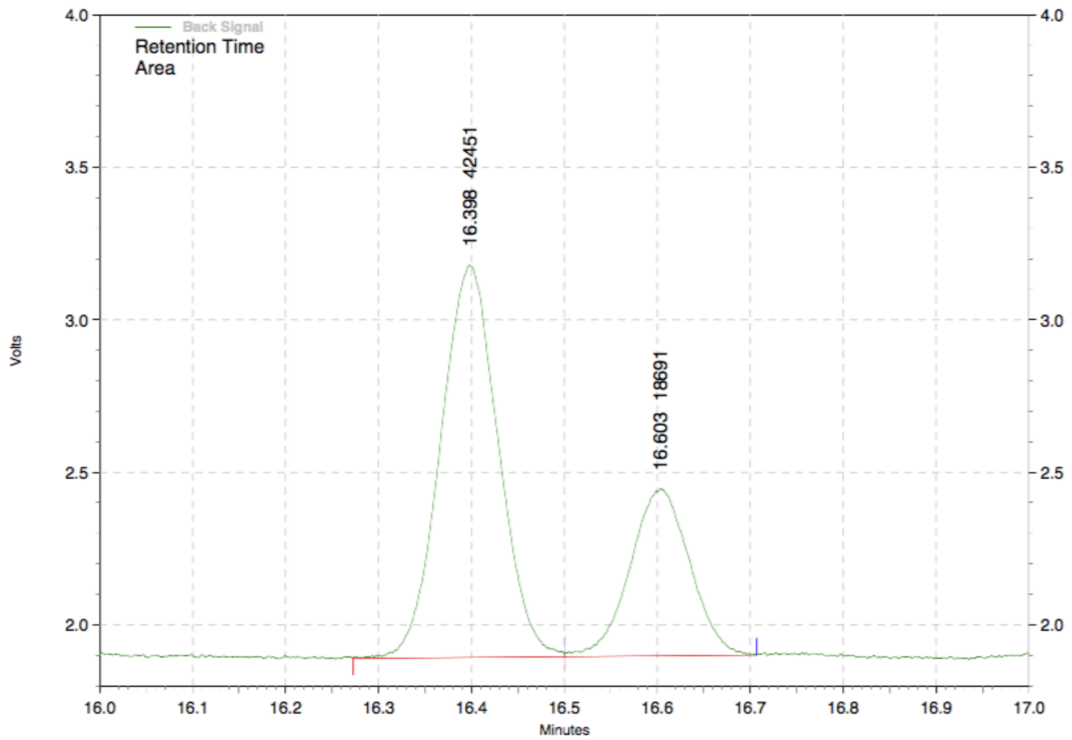




Rac



10a (*R*,*R*)-Mn(^{TIPS}mcp)



References

1. Ottenbacher, R. V.; Bryliakov, K. P.; Talsi, E. P., *Adv. Synth. Catal.* **2011,** *353*, 885-889.
2. Milan, M.; Bietti, M.; Costas, M., *ACS Cent. Sci.* **2017,** *3*, 196-204.
3. Bechara, W. S.; Khazhieva, I. S.; Rodriguez, E.; Charette, A. B., *Org. Lett.* **2015,** *17*, 1184-1187.
4. Nirogi, R. V. S.; Konda, J. B.; Kambhampati, R.; Shinde, A.; Bandyala, T. R.; Gudla, P.; Kandukuri, K. K.; Jayarajan, P.; Kandikere, V.; Dubey, P. K., *Bioorg. Med. Chem. Lett.* **2012,** *22*, 6980-6985.
5. Luo, Y.-R. C. H. o. C. B. E., CRC Press, Boca Raton, FL., **2007**.
6. Salamone, M.; DiLabio, G. A.; Bietti, M., *J. Am. Chem. Soc.* **2011,** *133*, 16625-16634.
7. Salamone, M.; Milan, M.; DiLabio, G. A.; Bietti, M., *J. Org. Chem.* **2014,** *79*, 7179-7184.
8. Milan, M.; Bietti, M.; Costas, M., *ACS Cent. Sci.* **2017,** *3*, 196-204.