Supplementary data

Stereoselective synthesis of highly functionalized (*Z*)-chloroalkene dipeptide isosteres containing an α,α-disubstituted amino acid

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I. General information

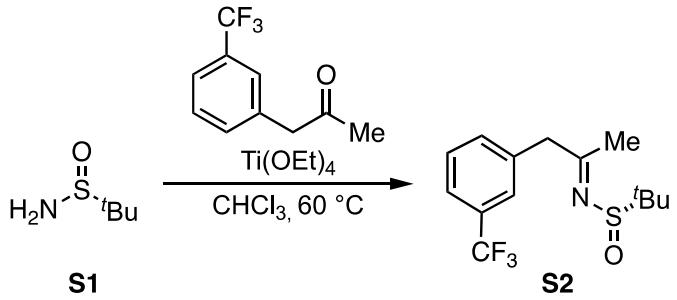
General Methods. All reactions utilizing air- or moisture-sensitive reagents were performed in dried glassware under a nitrogen atmosphere, using commercially supplied solvents and reagents unless otherwise noted. Thin-layer chromatography (TLC) was performed on Merck 60F254 precoated silica gel plates which were visualized by fluorescence quenching under UV light and by staining with phosphomolybdic acid, p-anisaldehyde, or ninhydrin. Flash column chromatography was carried out using silica gel 60 N (Kanto Chemical Co., Inc.).

Characterization data. 1H NMR (400 MHz) and 13C NMR (100 MHz) spectra were recorded using a Bruker Biospin AVANCE III HD. Chemical shifts are reported in δ (ppm) relative to Me4Si (in $CDCl_3$) as internal standard. Infrared (IR) spectra were recorded on a JASCO FT/IR 6300, and are reported as wavenumber (cm–1). Low- and high-resolution mass spectra were recorded on a Bruker Daltonics compact (ESI-MS) spectrometers in the positive and negative detection mode. Optical rotations were measured on a JASCO DIP-370 polarimeter operating at the sodium D line with a 100 mm path length cell, and were reported as follows: [α]D (concentration (g/100 mL), solvent).

HPLC conditions

Analytical high performance liquid chromatography (HPLC) was performed on a JASCO PU-2089 Plus (JASCO corporation, Ltd., Tokyo, Japan) equipped with a JASCO UV-2075 Plus (JASCO corporation, Ltd., Tokyo, Japan) variable wavelength UV detector using a CHIRALPAK IC (0.46 cm X 25 cm) or YMC CHIRAL Amylose-SC (0.46 cm X 25 cm) chiral column.

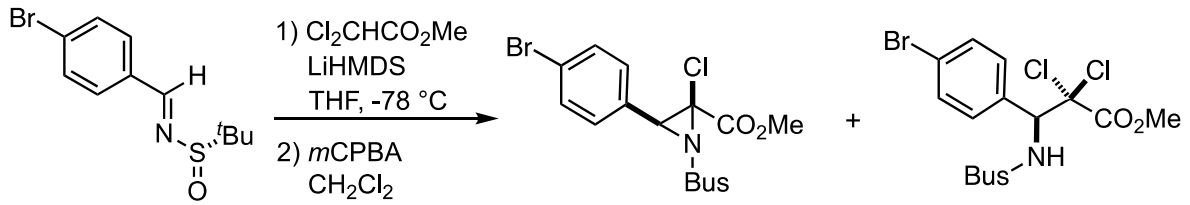
II. Experimental procedures of imines S2



S1 **S2**

(S,*E*)-2-methyl-N-(1-(3-(trifluoromethyl)phenyl)propan-2-ylidene)propane-2-sulfinamide (S2): To a solution of *tert*-butylsulfinamide **S1** (812.0 mg, 6.70 mmol) in $CHCl_3$ (27.0 mL) were added 3-(Trifluoromethyl)phenylacetone (1.66 mL, 10.0 mmol) and $Ti(OEt)_4$ (4.20 mL, 3.00 mmol) under nitrogen, and the mixture was stirred at room temperature for 51 h. After cooling to 0 °C, the reaction was quenched with crashed ice while rapidly stirring. Then resulting suspension was filtered through a plug of celite, and the filter cake was washed with EtOAc. The filtrate was transferred to separatory funnel where the organic layer was washed with brine and dried over $MgSO_4$. Concentration under reduced pressure followed by flash chromatography over silica gel with *n*-hexane-EtOAc (3:1) gave the title compound **S2** as a white solid (1.68 g, 82%).: IR (ATR) ν 1628 (CN), 1075 (NSO) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.14 (s, 9H), 2.36 (s, 3H), 3.76 (d, J = 4.9 Hz, 2H), 7.39–7.53 (m 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.9 (3C), 22.4, 49.3, 56.7, 124.0 (q, J = 273 Hz, 1C), 123.7 (q, J = 4 Hz, 1C), 126.3 (q, J = 4 Hz, 1C), 128.9, 130.7 (q, J = 32 Hz, 1C), 132.8, 136.6, 182.0; HRMS (ESI), *m/z* calcd for $C_{14}H_{19}F_3NOS$ $[M+H]^+$ 306.1134, found 306.1133

III. Experimental procedures of 2-chloroaziridines 2, 4a-d and β-amino ester 3

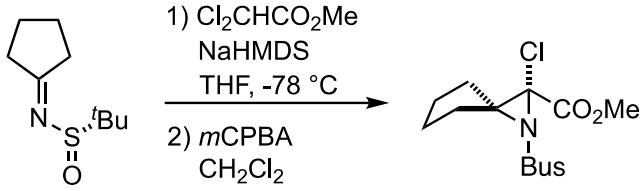


1 **2** **3**

Methyl (*Z*)-*N*-(*tert*-buthylsulfonyl)-2-chloro 3-(4-bromophenyl)aziridine 2-carboxylate (2) and Methyl N-(tert-buthylsulfonyl)-3-(4-bromophenyl)-2,2-dichloro 3-aminobutanoate (3): To a solution of methyl dichloroacetate (455.0 μL, 4.50 mmol) in THF (30.0 mL) was added LiHMDS (3.45 mL, 4.50 mmol) at -78 °C under nitrogen, and the mixture was stirred for 30 min at -78 °C. To the solution was added *N*-sulfinyl imine **1**[S1] in THF (3.00 mL) at -78 °C, and the mixture was stirred for 30 min at -78 °C. The reaction was quenched with anhydrous MeOH and slowly warmed up to room temperature. Concentration under reduced pressure gave *N*-sulfinyl methyl ester as an oily product, which was used immediately in next step without purification. To a solution of *N*-sulfinyl methyl ester in CH_2Cl_2 (15.0 mL) was added *m*CPBA (887.7 mg, 3.60 mmol) and the mixture was stirred for 16 h at room temperature. The reaction was quenched with saturated aqueous of $Na_2S_2O_3$ solution and saturated aqueous of $NaHCO_3$ solution. The reaction mixture was extracted with EtOAc, washed with brine and dried over $MgSO_4$, filtered and concentrated. To this residue was added a solution of 1,3,5-dimethoxybenzene (200 μL of a stock solution of 100.8 mg in 1200 μL) as an internal standard; the title compounds **2** yield was 45% in 3 steps and **3** yield was 13% in 3 steps; the yields were calculated by ^{1}H NMR analysis.

2-chloroaziridine 2: Prepared by the above procedure and isolated as a white solid (28.3 mg, 5% in 2 steps). IR (ATR) ν1753 (CO), 1335 (SO_2), 1130 (SO_2) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.51 (s, 9H), 3.93 (s, 3H), 4.88 (s, 1H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.8 (3C), 50.7, 54.6, 61.4, 65.6, 123.7, 129.5, 129.9 (2C), 131.6 (2C), 163.3.; HRMS (ESI), *m/z* Calcd for $C_{14}H_{17}BrClNO_4S$ $[M+Na]^+$ 431.9642, found 431.9662.

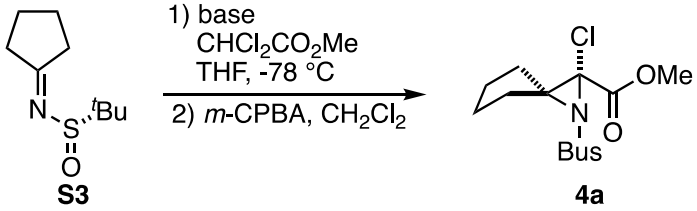
β-amino ester 3: Prepared by the above procedure and isolated as a white solid (19.3 mg, 3% in 2 steps). IR (ATR) ν 3290 (NH), 1763 (CO), 1318 (NSO), 1133 (NSO) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (s, 9H), 3.90 (s, 3H), 5.19 (d, *J* = 5.2, 1H), 5.30 (d, *J* = 5.2, 1H), 7.30 (d, *J* = 8.5, 2H), 7.53 (d, *J* = 8.5, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.0 (3C), 55.0, 60.6, 65.3, 86.3, 123.7, 130.8 (2C), 131.6 (2C), 130.1, 164.9; HRMS (ESI), *m/z* calcd for $C_{14}H_{19}BrCl_2NO_4S$ $[M+H]^+$ 445.9590, found 445.9586.



S3 **4a**

Methyl (2*R*)-*N*-(*tert*-buthylsulfonyl)-2-chloro-3- azaspiro[2.4] heptane-2-carboxylate (4a): To a solution of methyl dichloracetate (5.50 mL) in THF (275 mL) was added NaHMDS (28.0 mL, 53.1 mmol) at -78 ℃ under nitrogen, and the mixture was stirred for 30 min at -78 ℃. To the solution of enolate was added dropwise a solution of *N*-sulfinyl imine **S3**[S2] (5.53 g, 29.5 mmol) in THF (20.0 mL) at -78 ℃, and the mixture was stirred for 30 min at -78 ℃. The reaction was quenched with saturated aqueous of NH_4Cl solution. The reaction mixture was extracted with EtOAc, washed with brine and dried over $MgSO_4$. Concentration under reduced pressure gave *N*-sulfinyl methyl ester as an oily product, which was used immediately in next step without purification. To a solution of *N*-sulfinyl methyl ester in CH_2Cl_2 (150 mL) was added *m*CPBA (11.1 g, 45.0 mmol), and the mixture was stirred for 30 min at room temperature. The reaction was quenched with saturated aqueous solution of $Na_2S_2O_3$ and saturated aqueous solution of $NaHCO_3$. The reaction mixture was extracted with CH_2Cl_2, washed with brine and dried over $MgSO_4$. Concentration under reduced pressure followed by flash chromatography over silica gel with *n*-hexane-EtOAc (4:1) gave the title compound **4a** (6.48 g, 71% in 2 steps) as an yellow oil.: IR (ATR) ν1752 (CO), 1326 (NSO), 1129 (NSO) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.48 (s, 9H), 1.64–2.28 (m, 8H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.7(3C), 24.7, 25.7, 53.7, 61.3, 65.1, 164.3; HRMS (ESI), *m/z* calcd for $C_{12}H_{20}ClNNaO_4S$ $[M+Na]^+$ 332.0694, found 332.0694.

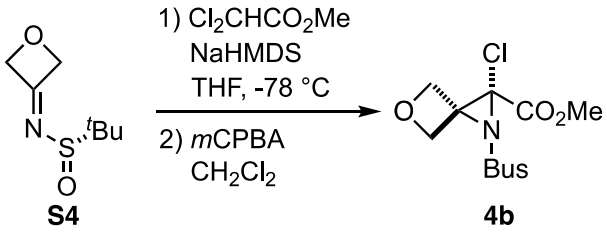
Table S1. Reaction optimization of aza-Darzens condensation



S3 **4a**

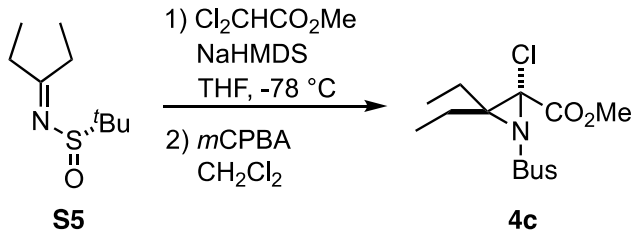
entry	base	yield (%)[a]
1	LiHMDS	27%
2	NaHMDS	71%
3	KHMDS	n. r.[b]

a Determined by ^1H-NMR with *tert*-butylanisole as an internal standard
b No reaction.



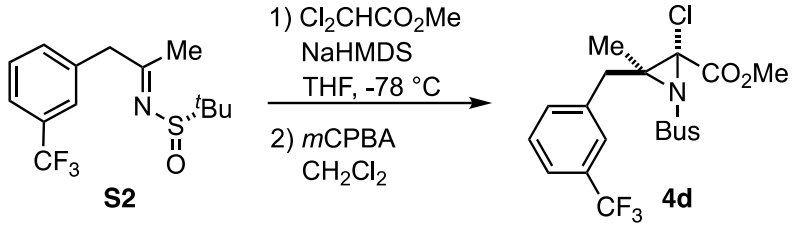
S4 **4b**

Methyl (2*R*)-*N*-(*tert*-buthylsulfonyl)-2-chloro-5-oxa-1-azaspiro[2.3]hexane-2-carboxylate (4b): To a solution of methyl dichloracetate (311.0 μL) in THF (20.0 mL) was added NaHMDS (2.54 mL, 3.30 mmol) at -78 °C under nitrogen, and the mixture was stirred for 30 min at -78 °C. To the solution of enolate was added dropwise a solution of *N*-sulfinyl imine **S4**[S3] (357.6 mg, 2.04 mmol) in THF (4.00 mL) at -78 °C, and the mixture was stirred for 30 min at -78 °C. The reaction was quenched with anhydrous MeOH and slowly warmed up to room temperature. Concentration under reduced pressure gave *N*-sulfinyl methyl ester as an oily product, which was used immediately in next step without purification. To a solution of *N*-sulfinyl methyl ester in CH_2Cl_2 (10.0 mL) was added *m*CPBA (591.8 mg, 2.40 mmol), and the mixture was stirred for 1 h at room temperature. The reaction was quenched with saturated aqueous solution of $Na_2S_2O_3$ and saturated aqueous solution of $NaHCO_3$. The reaction mixture was extracted with CH_2Cl_2, washed with brine and dried over $MgSO_4$. Concentration under reduced pressure followed by flash chromatography over silica gel with *n*-hexane-EtOAc (4:1) gave the title compound **4b** (212.3 mg, 37% in 2 step) as an yellow oil.: IR (ATR) ν 1759 (CO), 1336 (NSO), 1133 (NSO) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.52 (s, 9H), 3.88 (s, 3H), 4.92–4.94 (m, 2H), 5.04–5.06 (m, 1H), 5.39–5.41 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.5 (3C), 54.3, 58.5, 61.7, 73.5, 75.0, 77.4, 163.0; HRMS (ESI), *m/z* calcd for $C_{10}H_{16}ClNNaO_5S$ $[M+Na]^+$ 320.0330, found 320.0339.



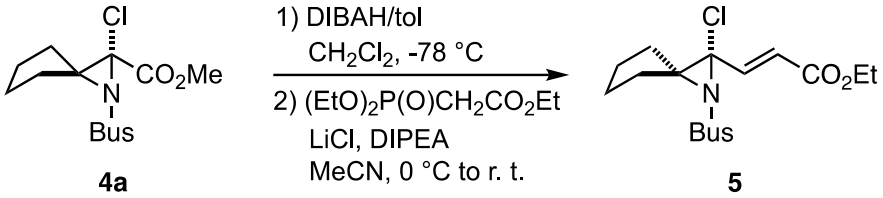
S5 **4c**

Methyl *N*-(*tert*-butylsulfonyl)-2-chloro-3,3-diethylaziridine-2-carboxylate (4c): By use of a procedure similar to that described for the preparation of **4a**, the corresponding imine **S5**[S4] (977.1 mg, 5.16 mmol) was converted into the title compound **4c** (1.28 g, 80% in 2 steps) as a yellow oil.: IR (ATR) ν1734 (CO), 1318 (NSO), 1129 (NSO) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.08 (t, *J* = 7.5 Hz, 3H), 1.10 (t, *J* = 7.5 Hz, 3H), 1.48 – 1.54 (m, 1H), 1.52 (s, 9H), 1.90 (dq, *J* = 14.7, 7.5 Hz, 1H), 2.07 (dq, *J* = 14.7, 7.5 Hz, 1H), 2.13 – 2.22 (m, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.6 (2C), 22.2, 23.8 (3C), 24.2, 53.4, 61.7, 67.1, 77.2, 164.4; HRMS (ESI), *m/z* calcd for $C_{12}H_{22}ClNNaO_4S$ $[M+Na]^+$ 334.0850, found 334.0850.

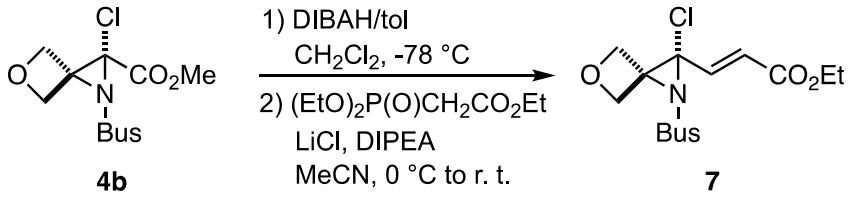


Methyl (*E*)-N-(tert-buthylsulfonyl)-2-chloro-3-methyl-3-(3-(trifluoromethyl)benzyl) aziridin-2-carboxylate (4d): By use of a procedure similar to that described for the preparation of **4b**, the corresponding imine **S2** (292.6 mg, 0.96 mmol) was converted into the title compound **4d** (193.3 mg, 63% in 2 steps) as a white solid.: IR (ATR) ν1751 (CO), 1330 (NSO), 1133 (NSO) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.54 (s, 9H), 1.67 (s, 3H), 2.98 (d, *J* = 14.7 Hz, 1H), 3.10 (d, J = 14.7 Hz, 1H), 3.88 (s, 3H), 7.42–7.48 (m, 3H), 7.51–7.57 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.7, 23.7 (3C), 41.1, 53.8, 55.3, 61.8, 65.9, 124.1 (q, *J* = 270 Hz, 1C), 124.2 (q, *J* = 4 Hz, 1C), 124.2 (q, *J* = 3 Hz, 1C), 129.0, 130.8 (q, *J* = 33 Hz, 1C), 133.1, 136.2, 164.6; HRMS (ESI), m/z calcd for $C_{17}H_{21}ClF_3NNaO_4S$ [M+Na]+ 450.0724, found 450.0724.

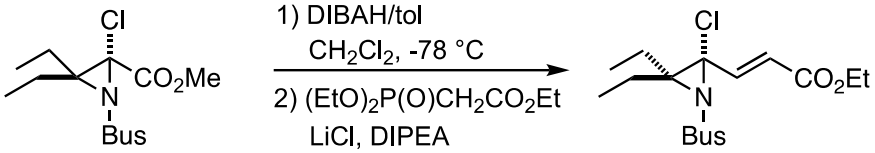
IV. Experimental procedures of enoates 5, 7, 9 and 11.



Ethyl (S,*E*)-3-(1-(tert-butylsulfonyl)-2-chloro-1-azaspiro[2.4]heptan-2-yl)acrylate (5): To a solution of the ester **4a** (2.63 g, 8.50 mmol) in CH_2Cl_2 (85.0 mL) was added dropwise a solution of DIBAH in toluene (1.00 M, 17.0 mL, 17.0 mmol) at -78 ºC under nitrogen, and the mixture was stirred for 1 h at -78 ºC. The reaction was quenched with saturated aqueous of Rochelle salt solution and extracted with Et_2O. The extract was washed with brine and dried over $MgSO_4$. Concentration under reduced pressure gave an oily aldehyde, which was used immediately in next step without purification. To a stirred solution of LiCl (900.8 mg, 21.3 mmol) in MeCN (38.0 mL) were added Ethyl diethylphosphonoacetate (2.50 mL, 12.8 mmol) and DIPEA (3.80 mL, 21.3 mmol) at 0℃ under nitrogen. After being stirred for 30 min at 0℃, a solution of the above aldehyde in MeCN (5.00 mL) was added to the mixture, and the mixture was stirred for 30 min at room temperature. The reaction mixture was quenched by saturated aqueous of NH_4Cl solution and extracted with EtOAc. The extract was washed with brine and dried over $MgSO_4$. Concentration under reduced pressure followed by flash chromatography over silica gel with *n*-hexane-EtOAc (4:1) gave the compound **11** (2.09 g, 70% in 2 steps) as an yellow oil.: IR (ATR) ν 1723 (CO), 1321 (NSO), 1128 (NSO) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.31 (t, J = 7.1 Hz, 3H), 1.44 (s, 9H), 1.64–2.08 (m, 6H), 2.22–2.32 (m, 1H), 2.38–2.50 (m, 1H), 4.23 (q, J = 7.1 Hz, 2H), 6.48 (d, J = 15.0 Hz, 1H), 7.22 (d, J = 15.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 23.6 (3C), 24.5, 26.1, 28.3, 33.5, 60.6, 67.2, 69.4, 77.2, 127.2, 140.5, 165.0; HRMS (ESI), *m/z* calcd for $C_{15}H_{24}ClNNaO_4S$ $[M+Na]^+$ 372.1007, found 372.1003.

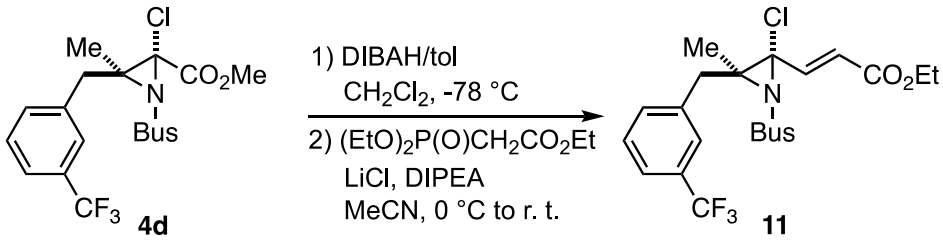


Ethyl (4*R, E*)-*N*-(*tert*-butylsulfonyl)-4-chloro-5-oxa-7-azaspiro[2.3]hexan-2-yl)acrylate (7): By use of a procedure similar to that described for the preparation of **5**, the ester **4b** (147.6 mg, 0.52 mmol) was converted into the title compound **7** (117.9 mg, 67% in 2 steps) as an colorless oil.: IR (ATR) ν 1721 (CO), 1328, 1134 (SO_2) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.31 (t, J = 7.1 Hz, 3H), 1.53 (s, 9H), 4.24 (q, J = 7.1 Hz, 2H), 4.84 (dd, J = 8.4, 1.3 Hz, 1H), 4.92 (dd, J = 8.4, 1.3 Hz, 1H), 5.04 (d, J = 8.3 Hz, 1H), 5.31 (d, J = 8.3 Hz, 1H), 6.53 (d, J = 15.0 Hz, 1H), 6.88 (d, J = 15.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 23.7 (3C), 57.6, 58.4, 61.0, 61.2, 64.3, 72.9, 73.7, 75.5, 75.8, 77.3, 128.5, 137.6, 164.0, 164.5; HRMS (ESI), *m/z* calcd for $C_{13}H_{20}ClNNaO_5S$ $[M+Na]^+$ 360.0643, found 360.0633.



4c **9**

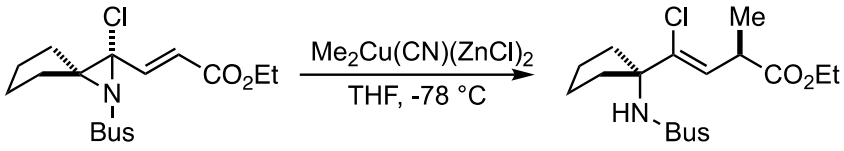
Ethyl (4*R, E*)-*N*-(*tert*-butylsulfonyl)-4-chloro-5,5-diethylaziridine-2-yl)acrylate (9): By use of a procedure similar to that described for the preparation of **5**, the ester **4c** (1.12 g, 3.60 mmol) was converted into the title compound **9** (869.9 mg, 70% in 2 steps) as an colorless oil.: IR (ATR) ν1722 (CO), 1318 (NSO), 1129 (NSO) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.04 (t, *J* = 7.5 Hz, 3H), 1.10 (t, *J* = 7.5 Hz, 3H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.44 (s, 9H), 1.94–2.01 (m, 3H), 2.19–2.28 (m, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 6.53 (d, *J* = 15.0 Hz, 1H) , 7.42 (d, *J* = 15.0 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 9.5, 10.4, 14.2, 22.1, 23.7 (3C), 25.3, 60.9, 64.0, 72.0, 77.2, 127.7, 140.2, 165.2; HRMS (ESI), *m/z* calcd for $C_{15}H_{26}ClNNaO_4S$ $[M+Na]^+$ 374.1163, found 374.1163.



4d **11**

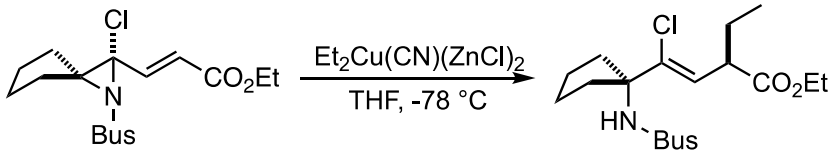
Ethyl (4*R, E*)-*N*-(*tert*-butylsulfonyl)-4-chloro-5-methyl-5-(3-(trifluoromethyl)benzyl)aziridin-2-yl)acrylate (11): By use of a procedure similar to that described for the preparation of **5**, the ester **4d** (452.3 mg, 1.06 mmol) was converted into the title compound **9** (211.2 mg, 43% in 2 steps) as an colorless oil.: IR (ATR) ν1721 (CO), 1325 (NSO), 1127 (NSO) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.31 (t, *J* = 7.1 Hz, 3H), 1.48 (s, 9H), 1.59 (s, 3H), 3.40 (s, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 6.59 (d, *J* = 15.0 Hz, 1H), 7.32–7.37 (m, 1H), 7.39–7.47 (m, 2H), 7.43 (d, *J* = 15.0 Hz, 1H), 7.50–7.55 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 20.7, 24.0 (3C), 38.7, 59.5, 61.4, 70.6, 77.6, 124.3 (q, *J* = 270 Hz, 1C), 124.4, 126.7, 128.4, 129.6, 132.4 (q, *J* = 33 Hz, 1C), 132.8, 137.0, 140.7, 165.2; HRMS (ESI), *m/z* calcd for $C_{20}H_{25}ClF_3NNaO_4S$ $[M+Na]^+$ 490.1037, found 490.1018.

V. Experimantal procedure of ααAA-containing CADIs 6a-6f, 8, 10, 12



5 **6a**

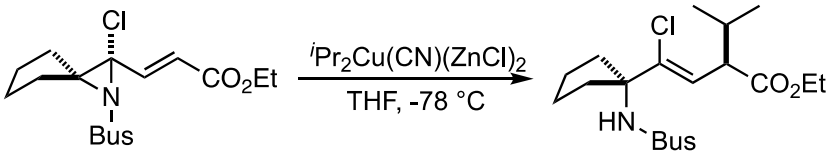
Ac$_5$c-Ala-type CADI (6a): To a suspension of $ZnCl_2$ (237.8 mg, 1.72 mmol) and LiCl (182.3 mg, 4.30 mmol) in THF (1.70 mL) was added a solution of methyl lithium (1.20 M, 1.40 mL, 1.72 mmol) at -78 ºC under nitrogen, and the mixture was stirred for 30 min at 0 ºC to provide ca. 0.82 M solution of methylzinc chloride in THF. In another flask, to a suspension of CuCN (77.0 mg, 0.86 mmol) in THF (8.60 mL) was added a solution of methylzinc chloride in THF at -78 ºC under nitrogen, and the mixture was stirred for 10 min at 0 ºC. To the solution of organocuprate was added dropwise a solution of ester **5** (114.6 mg, 0.33 mmol) in THF (4.00 mL) at -78 ºC. After stirred for 30 min at 0 ºC, the reaction mixture was quenched by addition of a 3:2 saturated NH_4Cl-28% NH_3 aqueous solution with additional stirring for 30 min at room temperature. The mixture was extracted with Et_2O and the extract was washed with brine and dried over $MgSO_4$. Concentration under reduced pressure followed by flash chromatography over silica gel with *n*-hexane-EtOAc (3:1) gave the title compound **6a** (47.4 mg, 40 %, >20:1 dr) as a colorless oil.: IR (ATR) ν1730 (CO), 1307 (NSO), 1126 (NSO) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (t, *J* = 7.1 Hz, 3H), 1.30 (d, *J* = 7.2 Hz, 3H), 1.39 (s, 9H), 1.64 – 1.95 (m, 4H), 1.97 – 2.31 (m, 4H), 3.61 (dq, *J* = 8.9, 7.2 Hz, 1H), 4.03 (s, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 5.99 (d, *J* = 8.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 16.9, 21.9, 22.7, 24.2 (3C), 36.8, 39.0, 40.1, 60.1, 60.8, 71.4, 126.1, 138.2, 173.9; HRMS (ESI), *m/z* calcd for $C_{16}H_{29}ClNO_4S$ $[M+H]^+$ 366.1500, found 366.1491.



5 **6b**

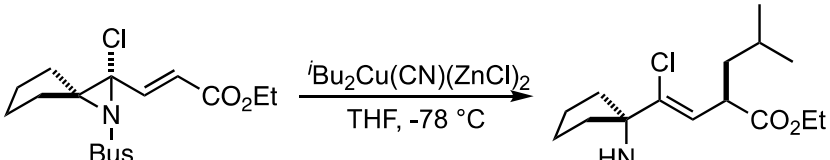
Ac$_5$c-Ethylgly-type CADI (6b): To a suspension of CuCN (215.0 mg, 2.40 mmol) and LiCl (203.5 mg, 4.80 mmol) in THF (2.70 mL) was added a solution of diethylzinc (1.09 M, 2.20 mL, 2.40 mmol) at -78 ºC under nitrogen, and the mixture was stirred for 10 min at 0 ºC. To the solution of the above organocuprate was added dropwise a solution of the enoate **5** (130.2 mg, 0.37 mmol) in THF (5.00 mL) at -78 °C. After being stirred for 1 h at -78 °C, the reaction mixture was quenched by addition of a 3:2 saturated NH_4Cl-28% NH_3 aqueous solution with additional stirring for 30 min at room temperature. The mixture was extracted with Et_2O and the extract was washed with brine and dried over $MgSO_4$. Concentration under reduced pressure followed by flash chromatography over silica gel with *n*-hexane-EtOAc (3:1) gave the title compound **6b** (113.1 mg, 0.30 mmol, 80 %, >20:1 dr) as a colorless oil.**:** IR (ATR) ν1724 (CO), 1306 (NSO), 1126 (NSO) cm^{-1}; ^{1}H NMR (400

MHz, $CDCl_3$) δ 0.89 – 1.03 (m, 3H), 1.17 – 1.32 (m, 3H), 1.39 (s, 9H), 1.62 – 1.78 (m, 3H), 1.78 – 1.95 (m, 3H), 1.96 – 2.12 (m, 2H), 2.12 – 2.35 (m, 2H), 3.31 – 3.62 (m, 1H), 4.05 (s, 1H), 4.09 – 4.20 (m, 2H), 5.86 – 6.08 (m, 1H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.4, 14.2, 22.0, 22.6, 24.2 (3C), 25.7, 36.8, 39.0, 47.2, 60.1, 60.7, 71.4, 125.0, 138.9, 173.3; HRMS (ESI), *m/z* calcd for $C_{17}H_{30}ClNO_4S$ $[M+H]^+$ 380.1657, found 380.1641.



5 **6c**

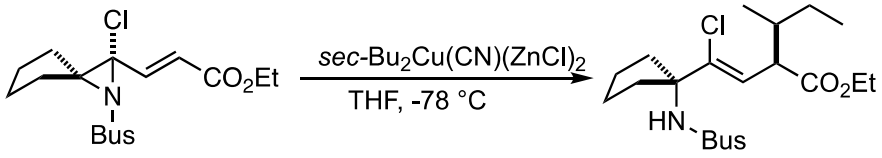
Ac$_5$c-Val-type CADI (6c): To a suspension of $ZnCl_2$ (340.7 mg, 2.50 mmol) and LiCl (212.0 mg, 5.00 mmol) in THF (2.50 mL) was added a solution of isopropylmagnesium chloride (1.10 M, 2.40 mL, 2.50 mmol) at -78 ºC under nitrogen, and the mixture was stirred for 30 min at 0 ºC to provide isopropylzinc chloride solution in THF. In another flask, to a suspension of CuCN (112.0 mg, 1.25 mmol) in THF (12.5 mL) was added a solution of isopropylzinc chloride in THF at -78 ºC under nitrogen, and the mixture was stirred for 10 min at 0 ºC. To the solution of organocuprate was added dropwise a solution of enoate **5** (184.9 mg, 0.53 mmol) in THF (5.00 mL) at -78 ºC. After stirred at 0 ºC for 30 min, the reaction mixture was quenched by addition of a 3:2 saturated NH_4Cl-28% NH_3 aqueous solution with additional stirring at room temperature for 30 min. The mixture was extracted with Et_2O and the extract was washed with brine and dried over $MgSO_4$. Concentration under reduced pressure followed by flash chromatography over silica gel with *n*-hexane-EtOAc (3:1) gave the title compound **6c** (195.6 mg, 0.50 mmol, 94 %, >20:1 dr) as a colorless oil.: IR (ATR) ν3282 (NH), 1726 (CO), 1308 (NSO), 1126 (NSO) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 (d, J = 6.8 Hz, 3H), 0.98 (d, J = 6.8 Hz, 3H), 1.21 – 1.32 (m, 3H), 1.39 (s, 9H), 1.61 – 1.96 (m, 5H), 2.00 – 2.17 (m, 2H), 2.17 – 2.28 (m, 2H), 3.31 – 3.43 (m, 1H), 4.09 (s, 1H), 4.10 – 4.22 (m, 2H), 5.89 – 6.04 (m, 1H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 19.6, 20.5, 22.1, 22.6, 24.2 (3C), 31.7, 37.0, 39.0, 52.7, 60.2, 60.6, 71.5, 124.1, 139.4, 172.8; HRMS (ESI), *m/z* calcd for $C_{18}H_{33}ClNO_4S$ $[M+H]^+$ 394.1813, found 394.1812.



5 **6d**

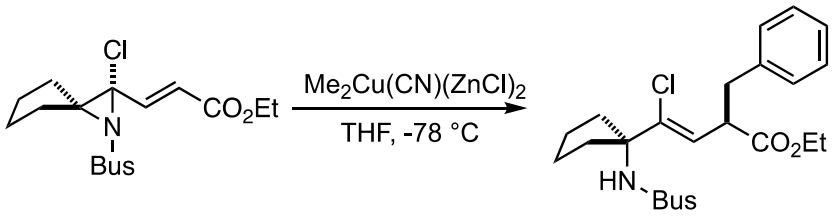
Ac$_5$c-Leu-type CADI (6d): To a suspension of $ZnCl_2$ (204.4 mg, 1.50 mmol) and LiCl (127.2 mg, 3.00 mmol) in THF (1.50 mL) was added a solution of isobuthylmagnesium bromide (0.90 M, 1.70 mL, 1.50 mmol) at -78 ºC under nitrogen, and the mixture was stirred for 30 min at 0 ºC to provide methylzinc chloride solution in THF. In another flask, to a suspension of CuCN (67.2 mg, 0.75 mmol) in THF (7.50 mL) was added a solution of methylzinc chloride in THF at -78 ºC under nitrogen, and the mixture was stirred at 0 ºC for 10

min. To the solution of organocuprate was added dropwise a solution of enoate **5** (107.8 mg, 0.30 mmol) in THF (3.00 mL) at -78 ºC. After stirred at 0 ºC for 30 min, the reaction mixture was quenched by addition of a 3:2 saturated NH_4Cl-28% NH_3 aqueous solution with additional stirring at room temperature for 30 min. The mixture was extracted with Et_2O and the extract was washed with brine and dried over MgSO4. Concentration under reduced pressure followed by flash chromatography over silica gel with *n*-hexane-EtOAc (3:1) gave the title compound **12d** (121.0 mg, 96 %, >20:1 dr) as a colorless oil.: IR (ATR) ν3282 (NH), 1726 (CO), 1308 (NSO), 1126 (NSO) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.90 – 0.91 (m, 3H), 0.93 – 0.95 (m, 3H), 1.24 – 1.27 (m, 3H), 1.38 (s, 9H), 1.45 – 1.51 (m, 1H), 1.57 – 1.88 (m, 6H), 2.05 – 2.10 (m, 2H), 2.16 – 2.21 (m, 2H), 3.60 – 3.66 (m, 1H), 4.06 (s, 1H), 4.11 – 4.17 (m, 2H), 5.87 – 5.89 (d, J = 9.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 19.6, 20.5, 22.1, 22.6, 24.2 (3C), 31.7, 37.0, 39.0, 52.7, 60.2, 60.6, 71.5, 124.1, 139.4, 172.8; HRMS (ESI), *m/z* calcd for $C_{18}H_{33}ClNO_4S$ $[M+H]^+$ 394.1813, found 394.1812.



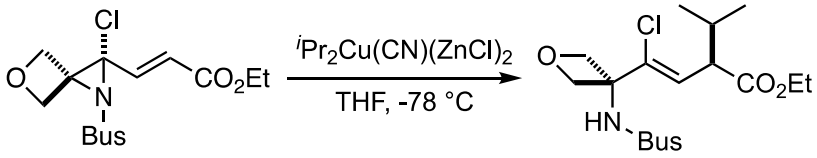
5 **6e**

Ac_5c-Ile-type CADI (**6e**): To a suspension of $ZnCl_2$ (204.4 mg, 1.50 mmol) and LiCl (127.2 mg, 3.00 mmol) in THF (1.50 mL) was added a solution of *sec*-buthylmagnesium bromide (0.90 M, 1.70 mL, 1.50 mmol) at -78 ºC under nitrogen, and the mixture was stirred for 30 min at 0 ºC to provide *sec*-buthylzinc chloride solution in THF. In another flask, to a suspension of CuCN (112.0 mg, 1.25 mmol) in THF (12.5 mL) was added a solution of *sec*-buthylzinc chloride in THF at -78 ºC under nitrogen, and the mixture was stirred at 0 ºC for 10 min. To the solution of organocuprate was added dropwise a solution of enoate **5** (104.8 mg, 0.30 mmol) in THF (1.50 mL) at -78 ºC. After stirred for 30 min at 0 ºC, the reaction mixture was quenched by addition of a 3:2 saturated NH_4Cl-28% NH_3 aqueous solution with additional stirring for 30 min at room temperature. The mixture was extracted with Et_2O and the extract was washed with brine and dried over $MgSO_4$. Concentration under reduced pressure followed by flash chromatography over silica gel with *n*-hexane-EtOAc (3:1) gave the title compound **6e** (78.6 mg, 0.19 mmol, 74 %, 3.8:1 dr) as a colorless oil.: IR (ATR) ν 1724 (CO), 1307 (NSO), 1126 (NSO) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.82 – 1.00 (m, 6H), 1.16 – 1.31 (m, 5H), 1.38 (s, 9H), 1.64 – 1.99 (m, 5H), 2.00 – 2.15 (m, 2H), 2.21 (s, 2H), 3.37 – 3.66 (m, 1H), 4.07 (s, 1H), 4.09 – 4.27 (m, 2H), 5.84 – 6.06 (m, 1H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.3, 11.6, 14.2, 14.3, 16.0, 16.6, 22.0, 22.0, 22.6, 24.2, 26.3, 27.3, 37.0, 37.1, 37.9, 38.0, 38.8, 38.9, 50.9, 51.2, 60.1, 60.6, 71.5, 123.7, 124.5, 139.1, 139.4, 172.7, 173.0; HRMS (ESI) , *m/z* calcd for $C_{19}H_{34}ClNaO_4S$ $[M+Na]^+$ 430.1790, found 430.7189.



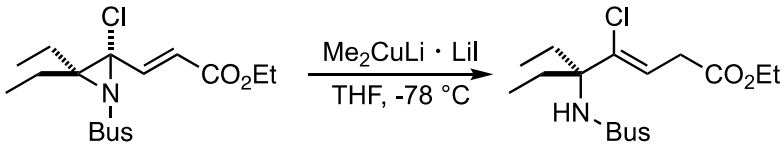
5 **6f**

Ac$_5$c-Phe-type CADI (6f): To a suspension of $ZnCl_2$ (204.4 mg, 1.50 mmol) and LiCl (127.2 mg, 3.00 mmol) in THF (1.50 mL) was added a solution of phenylmagnesium chloride (0.30 M, 5.00 mL, 1.50 mmol) at -78 ºC under nitrogen, and the mixture was stirred for 30 min at 0 ºC to provide phenylzinc chloride solution in THF. In another flask, to a suspension of CuCN (67.2 mg, 0.75 mmol) in THF (5.00 mL) was added a solution of phenylzinc chloride in THF at -78 ºC under nitrogen, and the mixture was stirred for 10 min at 0 ºC. To the solution of organocuprate was added dropwise a solution of enoate **5** (97.8 mg, 0.28 mmol) in THF (1.50 mL) at -78 ºC. After stirred for 30 min at 0 ºC, the reaction mixture was quenched by addition of a 3:2 saturated NH_4Cl-28% NH_3 aqueous solution with additional stirring for 30 min at room temperature. The mixture was extracted with Et_2O and the extract was washed with brine and dried over $MgSO_4$. Concentration under reduced pressure followed by flash chromatography over silica gel with *n*-hexane-EtOAc (3:1) gave the title compound **6f** (111.0 mg, 90%, >20:1 dr) as a colorless oil.: IR (ATR) ν 1727 (CO), 1303 (NSO), 1126 (NSO) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ1.13 (t, J = 7.1 Hz, 3H), 1.37 (s, 9H), 1.53–1.69 (m, 2H), 1.77–1.82 (m, 2H), 2.01–2.17 (m, 4H), 2.95 (dd, J = 13.6, 6.7 Hz, 1H), 3.06 (dd, J = 13.6, 8.1 Hz, 1H), 3.86 (ddd, J = 9.2, 8.1, 6.7 Hz, 1H), 4.01 (s, 1H), 4.06 (q, J = 7.1 Hz, 2H), 5.97 (d, J = 9.2 Hz, 1H), 7.18–7.28 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.5, 19.6, 19.7, 21.7 (3C), 35.0, 35.5, 35.6, 45.2, 57.6, 58.3, 68.9, 122.0, 124.0, 125.7 (2C), 126.6 (2C), 135.5, 135.8, 169.9; HRMS (ESI), *m/z* calcd for $C_{22}H_{33}ClNO_4S$ $[M+H]^+$ 442.1814, found 442.1805.



7 **8**

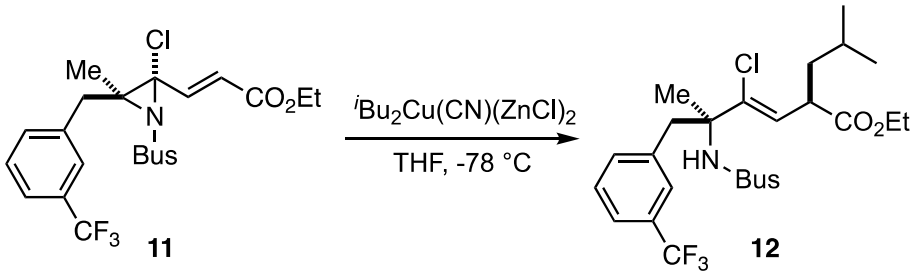
Oxetane-Val-type CADI (8): To a suspension of $ZnCl_2$ (443.5 mg, 3.30 mmol) and LiCl (275.5 mg, 6.50 mmol) in THF (3.30 mL) was added a solution of isopropylmagnesium chloride (0.42 M, 7.90 mL, 3.30 mmol) at -78 ºC under nitrogen, and the mixture was stirred for 30 min at 0 ºC to provide isopropylzinc chloride solution in THF. In another flask, to a suspension of CuCN (145.5 mg, 1.60 mmol) in THF (25.0 mL) was added a solution of isopropylzinc chloride in THF at -78 ºC under nitrogen, and the mixture was stirred for 10 min at 0 ºC. To the solution of organocuprate was added dropwise a solution of ester **7** (197.2 mg, 0.65 mmol) in THF (6.50 mL) at -78 ºC. After stirred at 0 ºC for 30 min, the reaction mixture was quenched by addition of a 3:2 saturated NH_4Cl-28% NH_3 aqueous solution with additional stirring at room temperature for 30 min. The mixture was extracted with Et_2O and the extract was washed with brine and dried over $MgSO_4$. Concentration under reduced pressure followed by flash chromatography over silica gel with *n*-hexane-EtOAc (3:1) gave the title compound **8** (136.0 mg, 61%, >20:1 dr) as a colorless oil.: IR (ATR) ν 3267 (NH), 1732 (CO), 1308 (NSO), 1124 (NSO) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.97 (d, J = 6.9 Hz, 3H), 0.99 (d, J = 6.9 Hz, 3H), 1.28 (t, J = 7.2 Hz, 3H), 1.44 (s, 9H), 2.16 (tq, J = 6.9 Hz, 1H), 3.38 (dd, J = 9.8, 6.9 Hz, 1H), 4.18 (q, J = 7.2 Hz 2H), 4.71 (d, J = 7.0 Hz, 1H), 4.78 (d, J = 7.3, 1H), 4.82 (d, J = 7.0, 1H), 4.91 (d, J = 7.3Hz, 1H), 4.94 (br, 1H), 6.20 (d, J = 9.8Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.4, 19.7, 20.6, 24.2, 32.0, 52.8, 60.4, 61.0, 63.4, 78.5, 79.4, 126.7, 135.8, 172.5; HRMS (ESI), *m/z* calcd for $C_{16}H_{28}ClNNaO_5S$ $[M+Na]^+$ 404.1269, found 404.1269.



9 **10**

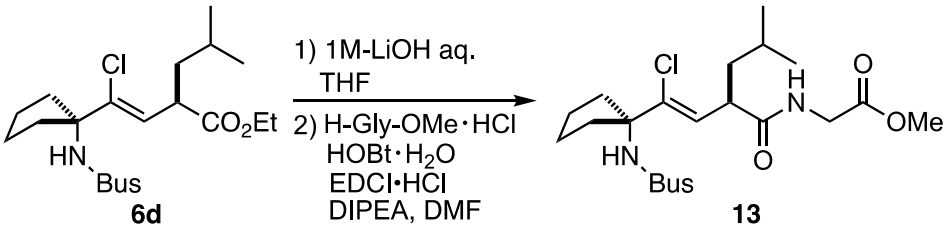
Deg-Gly-type CADI (10): To a stirred solution of CuI (761.8 mg, 4.00 mmol) in THF (15.0 mL) was added dropwise MeLi in Et_2O (1.20 M, 8.00 mL, 9.60 mmol) at -78 °C under nitrogen, and the mixture was stirred for 10 min at 0 °C. To the solution of the above organocuprate was added dropwise a solution of the enoate **9** (324.4 mg, 0.92 mmol) in THF (5.00 mL) at -78 °C. After being stirred for 30 min at -78 °C, the reaction was quenched by addition of a 3:2 saturated NH_4Cl-28% NH_3 aqueous solution with additional stirring for 30 min at room temperature. The mixture was extracted with Et_2O and the extract was washed with brine and dried over $MgSO_4$. Concentration under reduced pressure followed by flash chromatography over silica gel with *n*-hexane-EtOAc (2:1) gave the title compound **10** (265.5 mg, 73%) as colorless oil.: IR (ATR) ν3291 (NH), 1737 (CO), 1308 (NSO), 1122 (NSO) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, J = 7.3 Hz, 6H), 1.27 (t, J = 7.1 Hz, 3H), 1.41 (s, 9H), 1.92 (dq, J = 14.5, 7.3 Hz, 2H), 2.04 (dq, J = 14.5, 7.3 Hz, 2H), 3.32 (d, J = 6.4

Hz, 2H), 3.63 (s, 1H), 4.16 (q, J = 7.1 Hz, 2H), 6.06 (t, J = 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 8.0 (2C), 14.2, 24.3 (3C), 27.6 (2C), 34.7, 60.7, 60.9, 68.0, 121.2, 139.6, 170.6; HRMS (ESI), *m/z* calcd for $C_{15}H_{29}ClNO_4S$ $[M+H]^+$ 354.1500, found 354.1493.

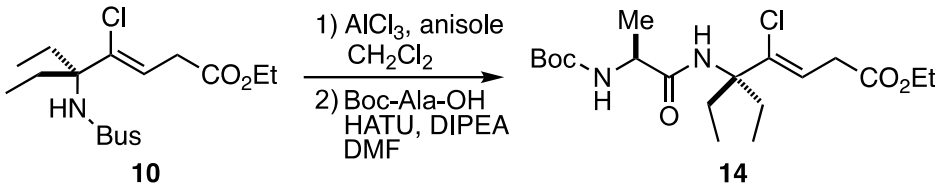


(αMe)$_3$-CF$_3$-Phe-Leu-type CADI (12): To a suspension of $ZnCl_2$ (102.2 mg, 0.75 mmol) and LiCl (63.6 mg, 0.75 mmol) in THF (750.0 μL) was added a solution of isobuthylmagnesium bromide (0.90 M, 675.0 μL, 0.75 mmol) at -78 ºC under nitrogen, and the mixture was stirred for 30 min at 0 ºC to provide methylzinc chloride solution in THF. In another flask, to a suspension of CuCN (34.0 mg, 0.38 mmol) in THF (1.50 mL) was added a solution of methylzinc chloride in THF at -78 ºC under nitrogen, and the mixture was stirred at 0 ºC for 10 min. To the solution of organocuprate was added dropwise a solution of ester **11** (56.8 mg, 0.12 mmol) in THF (3.80 mL) at -78 ºC. After stirred at 0 ºC for 30 min, the reaction mixture was quenched by addition of a 3:2 saturated NH_4Cl-28% NH_3 aqueous solution with additional stirring at room temperature for 30 min. The mixture was extracted with Et2O and the extract was washed with brine and dried over MgSO4. Concentration under reduced pressure followed by flash chromatography over silica gel with *n*-hexane-EtOAc (3:1) gave the title compound **12** (38.9 mg, 56%, >20:1 dr) as a colorless oil.: IR (ATR) ν3286 (NH), 1732 (CO), 1329 (NSO), 1128 (NSO) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89–0.94 (m, 3H), 0.92–0.94 (m, 3H), 1.91–1.22 (m, 3H), 1.37–1.40 (m, 1H), 1.39 (s, 9H), 1.50–1.63 (m, 2H), 1.63 (s, 3H), 3.11 (d, J = 13.3 Hz, 1H), 3.16 (d, J = 13.3 Hz, 1H), 3.61–3.67 (m, 1H), 4.05–4.11 (m, 2H), 4.08 (s, 1H), 5.67–5.70 (d, J = 9.2 Hz, 1H), 7.33–7.41 (m, 2H), 7.43 (m, 1H), 7.48–7.55 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.3, 22.5, 22.6, 24.3 (3C), 25.8, 41.4, 44.5, 46.4, 60.5, 60.7, 64.2, 124.0 (q, J = 252 Hz, 1C), 124.1 (q, J = 16 Hz, 1C), 126.9, 127.2, (q, J = 12 Hz, 1C), 128.6, 130.5 (q, J = 32 Hz, 1C), 134.0, 136.0, 138.4, 173.1; HRMS (ESI), m/z calcd for $C_{24}H_{35}ClF_3NNaO_4S$ $[M+Na]^+$ 548.1820, found 548.1814.

VI. Experimantal procedure of ααAA-containing CADIs (13,14) N/C terminal condensations

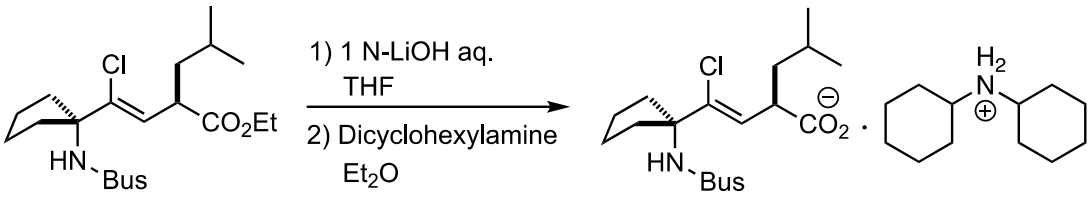


Bus-Ac$_5$c-Ψ^{Cl}-Leu-Gly-OMe (13): To a solution of CADI **6d** (204.0 mg, 0.50 mmol) in THF (5.00 mL) was added 1.0 M aqueous solution of LiOH (2.00 mL), and the mixture was stirred at room temperature for 50 h. The reaction mixture was diluted with EtOAc, washed with 0.1 M aqueous solution of HCl and dried over $MgSO_4$. The reaction mixture was concentrated under reduced pressure to give the carboxylic acid as colorless oil, which was used immediately in the next step without purification. To a solution of crude carboxylic acid in DMF (5.00 mL) was added H-Gly-OMe hydrochloride (81.6 mg, 0.65 mmol), HOBt•H_2O (99.5 mg, 0.65 mmol) and EDCI•H_2O (124.6 mg, 0.65 mmol) and cooled to 0 °C. DIEPA (223.0 μL, 1.25 mmol) were added, and the reaction was stirred for 5.5 h. The reaction mixture was diluted with EtOAc, and washed with NH_4Cl, $NaHCO_3$, and brine and dried over $MgSO_4$. Concentration under reduced pressure followed by flash chromatography over silica gel with Hexane-EtOAc (2:1) gave the title compound **13** as a colorless solid (72.2 mg, 32%): IR (ATR) ν 3448 (NH), 3371 (NH), 1700 (CO), 1655 (CO); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 – 0.91 (m, 3H), 0.91 – 0.96 (m, 3H), 1.39 (s, 9H), 1.44 – 1.59 (m, 2H), 1.59 – 1.76 (m, 1H), 1.76 – 1.84 (m, 2H), 1.84 – 1.97 (m, 3H), 1.97 – 2.14 (m, 1H), 2.14 – 2.40 (m, 2H), 3.47 – 3.61 (m, 1H), 3.72 (s, 3H), 3.89 (dd, *J* = 17.6, 5.8 Hz, 1H), 4.01 (dd, *J* = 17.6, 5.8 Hz, 1H), 4.10 (s, 1H), 5.72 – 5.93 (m, 1H), 6.85 (m, 1H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 21.4, 21.6, 23.0, 23.4, 24.1 (3C), 26.1, 36.0, 39.9, 40.2, 41.3, 44.7, 52.1, 60.3, 71.5, 125.9, 141.0, 170.2, 172.7.; HRMS (ESI), *m*/*z* calcd for $C_{20}H_{36}ClN_2O_5S$ $[M+H]^+$ 451.2028, found 451.2022.



Boc-Ala-Deg-Ψ^{Cl}-Gly-OEt (14): To a solution of the CADI **10** (78.8 mg, 0.20 mmol) in CH_2Cl_2 (2.00 mL) were added Anisole (43.5 µL, 0.40 mmol) and $AlCl_3$ (120.0 mg, 0.90 mmol), and the mixture was stirred at room temperature for 3.5 h under nitrogen. The reaction mixture was quenched by saturated aqueous of NH_4Cl solution and extracted with CH_2Cl_2. The extract was washed with brine and dried over $MgSO_4$. The reaction mixture was concentrated under reduced pressure to give the deprotected amine as colorless oil, which was used immediately in the next step without purification. To a solution of Boc-L-Ala-OH (75.7 mg, 0.40 mmol), HATU (152.1 mg, 0.40 mmol) and DIPEA (71.4 µL, 0.40 mmol) in DMF (1.50 mL) was added crude amine in DMF (500.0 µL), and the reaction was stirred for 24 h. The reaction mixture was diluted with EtOAc, and washed with NH_4Cl, $NaHCO_3$, and brine and dried over $MgSO_4$. Concentration under reduced pressure followed by flash chromatography over silica gel with Hexane-EtOAc (1:2) gave the title compound **14** as a colorless solid (25.3 mg, 31%): $[a]_D^{23.2}$ = -18.2 (*c* 1.00, $CHCl_3$); IR (ATR) ν 3323 (NH), 1728 (CO), 1673 (CO); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.79 (t, *J* = 7.4 Hz, 3H), 0.81 (t, *J* = 7.4 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.31 – 1.36 (m, 3H), 1.45 (s, 9H), 1.79 (dq, *J* = 14.1, 7.4 Hz, 2H), 2.01 (dq, *J* = 14.1, 7.4 Hz, 2H), 3.31 (d, *J* = 6.5 Hz, 2H), 3.98 – 4.10 (m, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 4.95 (s, 1H), 5.95 (t, *J* = 6.5 Hz, 1H), 6.18 (s, 1H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 7.5, 7.6, 14.2, 25.8, 26.0, 28.3 (3C), 34.6, 60.8, 63.5, 77.2, 119.4, 128.2, 129.2, 139.3, 170.9, 171.1, 172.8.; HRMS (ESI), *m*/*z* calcd for $C_{19}H_{34}ClN_2O_5$ $[M+H]^+$ 405.2151, found 405.2155.

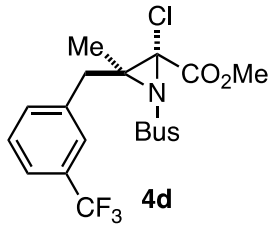
VII. Experimantal procedure of Ac5c-Leu-type CADI dicyclohexylammonium salt S6



6d **S6**

Ac5c-Leu-type CADI dicyclohexylammonium salt (**S6**): To a solution of chloroalkene **6d** (125.6 mg, 0.31 mmol) in THF (3.00 mL) was added 1 M LiOH aqueous (1.50 mL, 1.50 mmol) and the mixture was stirred for 22 h at room tempetature.The mixture was dilluted with EtOAc and washed with 0.1 N HCl aqueous and the organic later was washed with brine and dried over $MgSO_4$. Concentration under reduced pressure gave N-sulfonyl carboxylic acid as a solid compound, which was used in next step without purification. After to a solution of N-sulfonyl carboxylic acid in Et_2O (1.20 mL) was added dicyclohexylamine (80 μL), the precipitate was appeared immidiately. The precipitate was filtered and the solvent was removed under reduced pressure gave the title compound **S6** dicyclohexylammonium salt (43.4 mg, 25%) as a solid.: IR (ATR) ν1623 (CO), 1304 (NSO), 1126 (NSO) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.90–0.95 (m, 6H), 1.14–1.46 (m, 10H), 1.38 (s, 9H), 1.61–1.79 （m, 11H）, 1.97–1.99 (m, 4H), 2.06–2.09 (m, 2H), 2.13– 2.28 (m, 2H), 2.84–2.91 (m, 2H), 3.42– 3.48 (m, 1H), 4.11 (s, 1H), 5.95– 5.98 (m, 1H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.9, 22.5, 22.6, 23.0, 24.3 (3C), 24.9 (4C), 25.4 (2C), 26.0 (2C), 30.3, 36.7, 38.8, 42.3, 47.3, 52.7 (2C), 71.6 (2C), 77.2, 128.9, 136.0, 178.4.; HRMS (ESI), *m/z* calcd for $C_{29}H_{54}ClN_2O_4S$ $[M+H]^+$ 561.3487, found 561.3489.

VIII. Chiral HPLC analysis of compounds 4d, 5, 7, 9

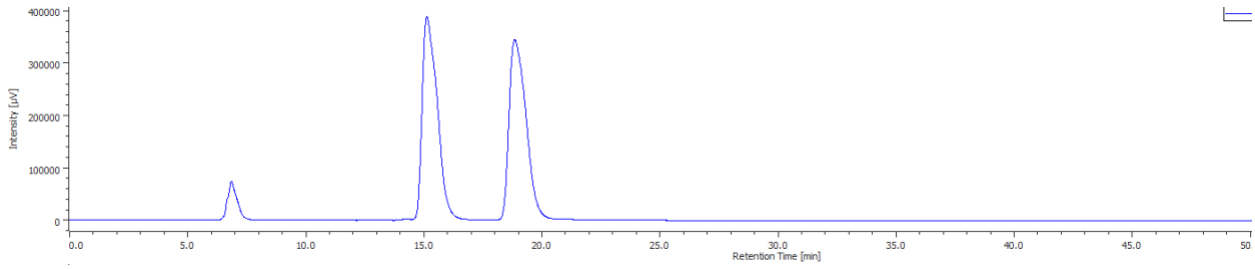


4d

Enantiomeric ratio was measured by HPLC

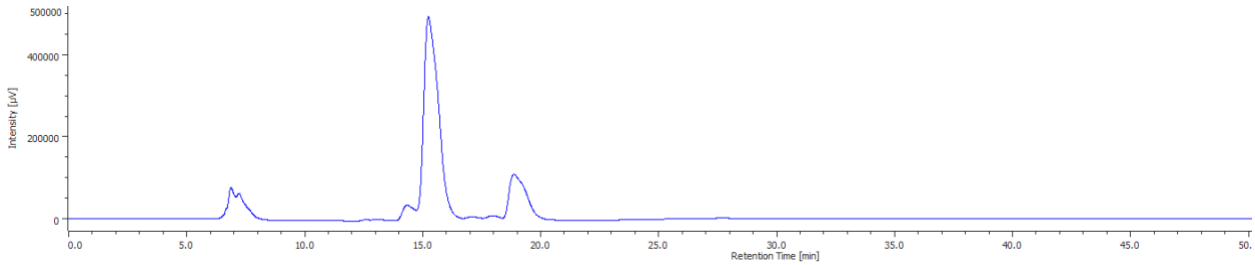
(CHIRALPACK IC, 5% IPA/hexanes, 0.5 mL/min, 210 nm).

・Racemic aziridine **4d**



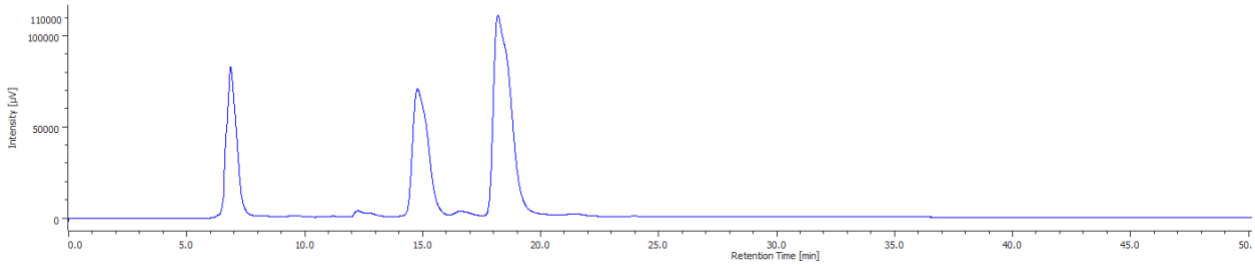
	Ret. time [min]	Area	Height	Area%
1	15.117	16857577	385069	**49.821**
2	18.842	16978802	341893	**50.179**

・Chiral aziridine **4d (NaHMDS)**

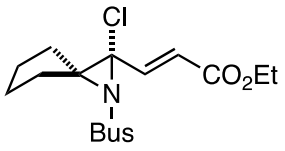


	Ret. time [min]	Area	Height	Area%
1	15.242	19672368	474448	**79.008**
2	18.858	5226746	107358	**20.992**

・Chiral aziridine **4d (LiHMDS)**



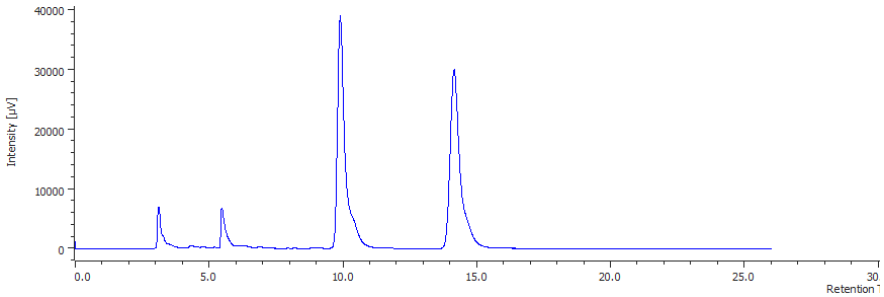
	Ret. time [min]	Area	Height	Area%
1	14.800	2528030	63420	**35.670**
2	17.850	4559147	87171	**64.330**



5

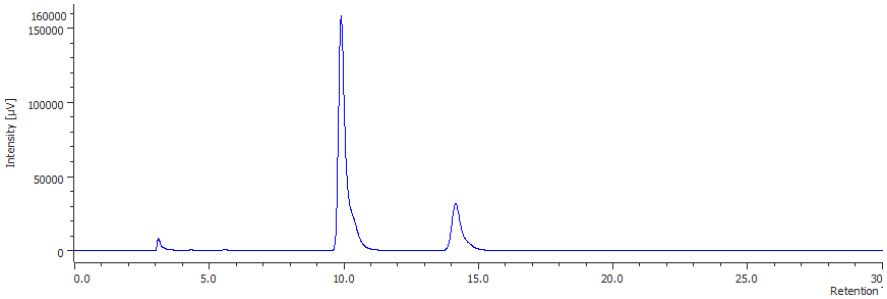
Enantiomeric ratio was measured by HPLC (YMC CHIRAL Amylose-SC, 20% IPA/hexanes, 1.0 mL/min, 220 nm).

- Racemic enoate **5**



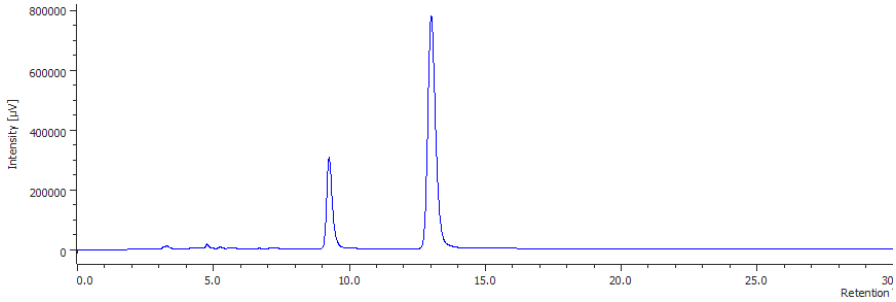
	Ret. time [min]	Area	Height	Area%
1	9.900	786194	38785	**49.672**
2	14.150	796582	29848	**50.328**

- Chiral enoate **5 (NaHMDS)**

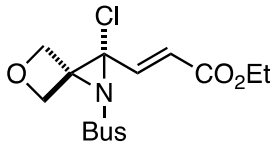


	Ret. time [min]	Area	Height	Area%
1	9.892	3112665	157060	**79.136**
2	14.150	820633	31410	**20.864**

- Chiral enoate **5 (LiHMDS)**



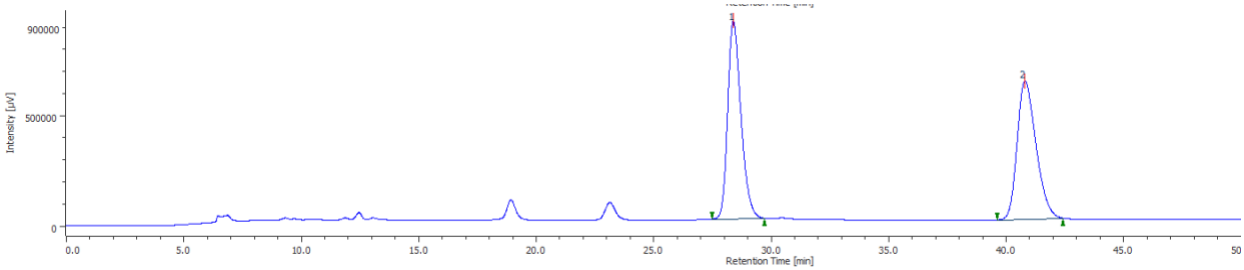
	Ret. time [min]	Area	Height	Area%
1	9.250	4522907	303610	**22.388**
2	13.008	15679097	771154	**77.612**



7

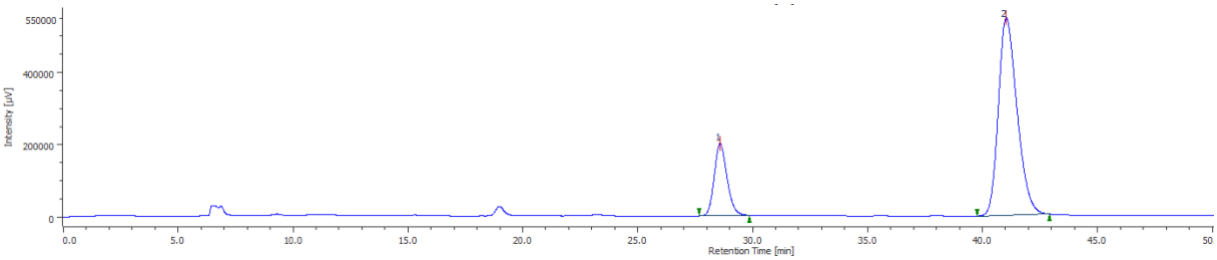
Enantiomeric ratio was measured by HPLC (CHIRALPACK IC, 15% IPA/hexanes, 0.5 mL/min, 210 nm).

・Racemic enoate **7**



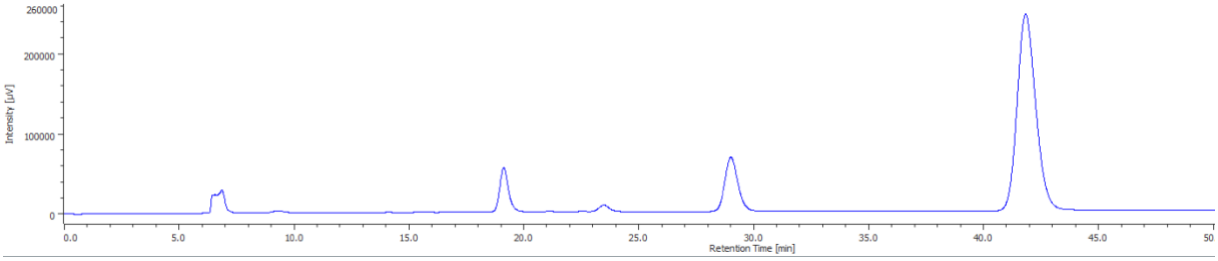
	Ret. time [min]	Area	Height	Area%
1	28.375	34966903	892298	**50.145**
2	40.783	3476314	624462	**49.855**

・Chiral enoate **7 (NaHMDS)**

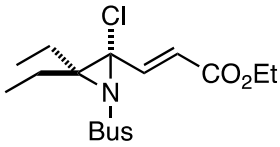


	Ret. time [min]	Area	Height	Area%
1	28.567	7742232	199740	**20.165**
2	41.008	30642735	543670	**79.835**

・Chiral enoate **7 (LiHMDS)**



	Ret. time [min]	Area	Height	Area%
1	29.000	2643996	67132	**16.151**
2	41.808	13726748	244061	**83.849**

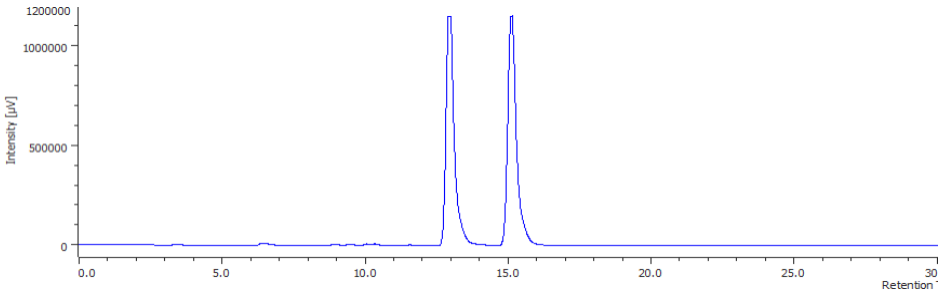


Enantiomeric ratio was measured by HPLC

(YMC CHIRAL Amylose-SC, 15% IPA/hexanes, 0.5 mL/min, 220 nm).

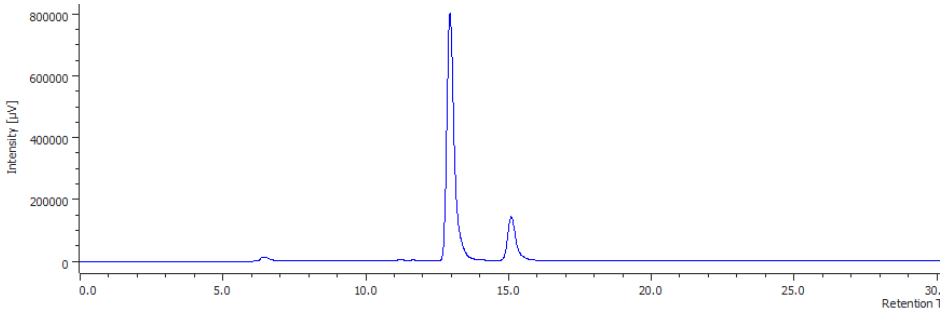
9

・Racemic enoate **9**



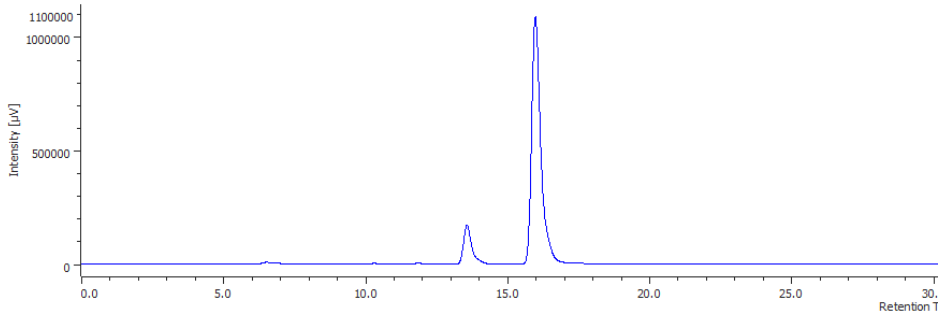
	Ret. time [min]	Area	Height	Area%
1	12.983	23548902	1148524	**49.115**
2	15.125	24397136	1147809	**50.885**

・Chiral enoate **9 (NaHMDS)**



	Ret. time [min]	Area	Height	Area%
1	12.942	14640152	796478	**83.964**
2	15.092	2796117	139654	**16.036**

・Chiral enoate **9 (LiHMDS)**



	Ret. time [min]	Area	Height	Area%
1	13.558	3544166	172217	**12.610**
2	15.967	24562302	1083470	**87.390**

IX. X-ray crystallographic data

Crystals of aziridine **2** [$C_{14}H_{17}BrClNO_4S$, code: 2064227], β-aminoester **3** [$C_{14}H_{18}BrCl_2NO_4S$, code: 2064228], aziridine **4d** [$C_{17}H_{21}ClF_3NO_4S$, code: 2064229] and enoate **11** [$C_{15}H_{24}ClNO_4S$, code: 2065548] were obtained by recrystallization from EtOAc/*n*-hexanae and CADI ammonium salt **15** [$2(C_{17}H_{29}ClNO_4S^-)$, $2(C_{12}H_{24}N^+)$, C_6H_{14}, code: 2064230] were obtained by recrystallization from EtOH/*n*-hexanae. A suitable single crystals of **2, 3, 4d, 11, 15** were selected and measured on a Rigaku XtaLAB mini (Mo) CCD diffractometer. Using Olex2,[S5] the structure was solved with the SHELXT [S6] structure solution program using Direct Methods and refined with the SHELXL[S7] refinement package using Least Squares minimization.

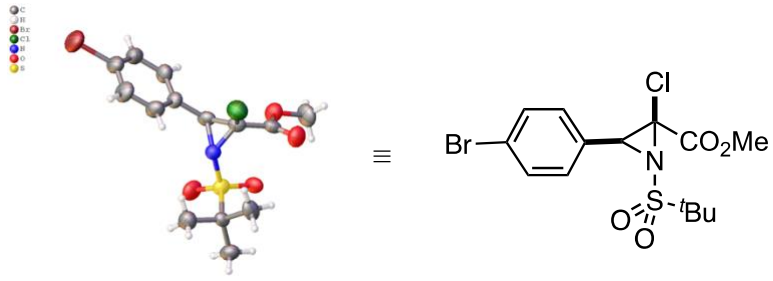


Figure S1. ORTEP representation of **2.**

Table S2. Crystal data and structure refinement for **2**, CCDC Number: 2064227

Identification code	SIM17-011			
Emipircal formula	$C_{14}H_{17}BrClNO_4S$			
Formula wight	410.71			
Temperature	293(2)			
Crystal system	monoclinic			
Sapce group	$P2_1/c$			
Unit cell Dimensions	a/Å	6.5794(9)	alpha/°	90
	b/Å	8.0509(19)	beta/°	90.055(14)
	c/Å	33.122(6)	gamma/°	90
Volume/Å^3	1754.5(6)			
Z	4			
ρ_{calc}g/cm^3	1.555			
μ/mm^{-1}	2.629			
F(000)	832.0			
Crystal size/mm^3	0.8 × 0.72 × 0.5			
Radiation	MoKα (λ = 0.71073)			
2Θ range for data collection/°	5.208 to 50.7			
Index ranges	$-7 \le h \le 7$, $-9 \le k \le 9$, $-39 \le l \le 37$			
Reflections collected	9634			
Independent refletions	3193 [Rint = 0.1007, Rsigma = 0.0840]			
Data/restraints/parameters	3193/0/204			
Goodness-of-fit on F^2	1.052			
Final R indexes [I>2σ (I)]	R_1 = 0.0857, wR_2 = 0.2062			
Final R indexes [all data]	R_1 = 0.1033, wR_2 = 0.2216			
Largest diff. peak/hole/e Å^{-3}	0.50/-0.64			

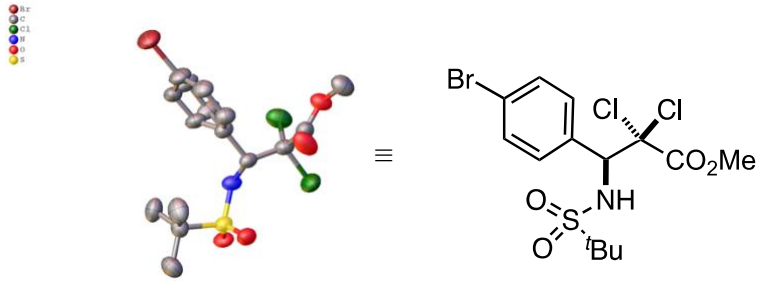


Figure S2. ORTEP representation of **3.**

Table S3. Crystal data and structure refinement for **3**, CCDC Number: 2064228

Identification code	SIM17-011			
Emipircal formula	$C_{14}H_{18}BrCl_2NO_4S$			
Formula wight	447.16			
Temperature	293(2)			
Crystal system	monoclinic			
Sapce group	$P2_1/c$			
Unit cell Dimensions	a/Å	12.396(4)	alpha/°	90
	b/Å	14.044(4)	beta/°	118.17(4)
	c/Å	11.920(3)	gamma/°	90
Volume/Å^3	1829.3(11)			
Z	4			
ρ_{calc}g/cm^3	1.624			
μ/mm^{-1}	2.670			
F(000)	904.0			
Crystal size/mm^3	0.12 × 0.09 × 0.06			
Radiation	MoKα (λ = 0.71073)			
2Θ range for data collection/°	4.724 to 50.696			
Index ranges	$-14 \le h \le 14$, $-16 \le k \le 16$, $-14 \le l \le 14$			
Reflections collected	15794			
Independent refletions	3349 [Rint = 0.1016, Rsigma = 0.0773]			
Data/restraints/parameters	3349/18/234			
Goodness-of-fit on F^2	1.026			
Final R indexes [I>2σ (I)]	R_1 = 0.0527, wR_2 = 0.0960			
Final R indexes [all data]	R_1 = 0.1256, wR_2 = 0.1205			
Largest diff. peak/hole/e Å^{-3}	0.44/-0.51			

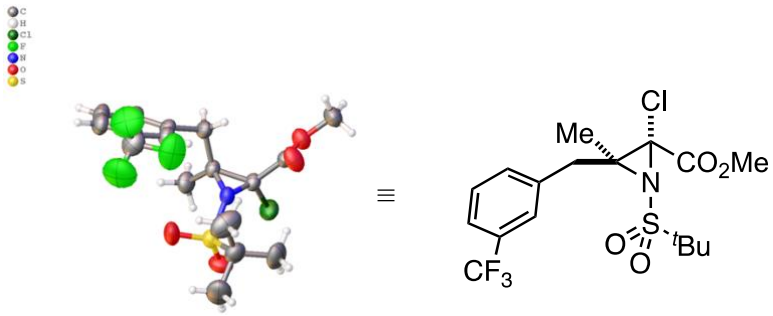


Figure S3. ORTEP representation of **4d.**

Table S4. Crystal data and structure refinement for **4d**, CCDC Number: 2064229.

Identification code	SIM17-009			
Emipircal formula	$C_{17}H_{21}ClF_3NO_4S$			
Formula wight	427.86			
Temperature	293(2)			
Crystal system	triclinic			
Sapce group	P-1			
Unit cell Dimensions	a/Å	7.3770(8)	alpha/°	90.570(10)
	b/Å	11.8839(13)	beta/°	106.868(11)
	c/Å	12.4930(17)	gamma/°	100.186(9)
Volume/Å^3	1029.4(2)			
Z	2			
ρ_{calc}g/cm^3	1.380			
μ/mm^{-1}	0.335			
F(000)	444.0			
Crystal size/mm^3	0.561 × 0.235 × 0.206			
Radiation	MoKα (λ = 0.71073)			
2Θ range for data collection/°	4.72 to 65.892			
Index ranges	$-10 \le h \le 10$, $-17 \le k \le 18$, $-16 \le l \le 19$			
Reflections collected	12539			
Independent refletions	6632 [Rint = 0.1067, Rsigma = 0.0889]			
Data/restraints/parameters	6632/120/277			
Goodness-of-fit on F^2	1.020			
Final R indexes [I>2σ (I)]	R_1 = 0.0992, wR_2 = 0.2428			
Final R indexes [all data]	R_1 = 0.1380, wR_2 = 0.2750			
Largest diff. peak/hole/e Å^{-3}	0.39/-0.48			

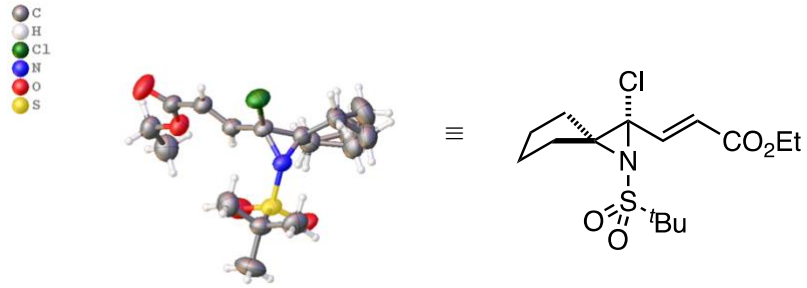


Figure S4. ORTEP representation of **5.**

Table S5. Crystal data and structure refinement for **5**, CCDC Number: 2065548.

Identification code	SIM17-032			
Emipircal formula	$C_{15}H_{24}ClNO_4S$			
Formula wight	349.86			
Temperature	293			
Crystal system	triclinic			
Sapce group	P-1			
Unit cell Dimensions	a/Å	7.0093(11)	alpha/°	93.204(8)
	b/Å	8.932(9)	beta/°	99.536(10)
	c/Å	14.7723(15)	gamma/°	96.869(10)
Volume/$Å^3$	909.0(2)			
Z	2			
$\rho_{calc}g/cm^3$	1.278			
μ/mm^{-1}	0.340			
F(000)	372.0			
Crystal size/mm^3	0.261 × 0.233 × 0.085			
Radiation	MoKα (λ = 0.71073)			
2Θ range for data collection/°	4.576 to 50.246			
Index ranges	$-8 \leq h \leq 8, -10 \leq k \leq 10, -17 \leq l \leq 17$			
Reflections collected	7608			
Independent refletions	7608 [Rint = 0.0350, Rsigma = 0.0456]			
Data/restraints/parameters	3211/72/222			
Goodness-of-fit on F^2	1.132			
Final R indexes [I>2σ (I)]	$R_1 = 0.0568$, $wR_2 = 0.1324$			
Final R indexes [all data]	$R_1 = 0.0764$, $wR_2 = 0.1423$			
Largest diff. peak/hole/e $Å^{-3}$	0.25/-0.24			

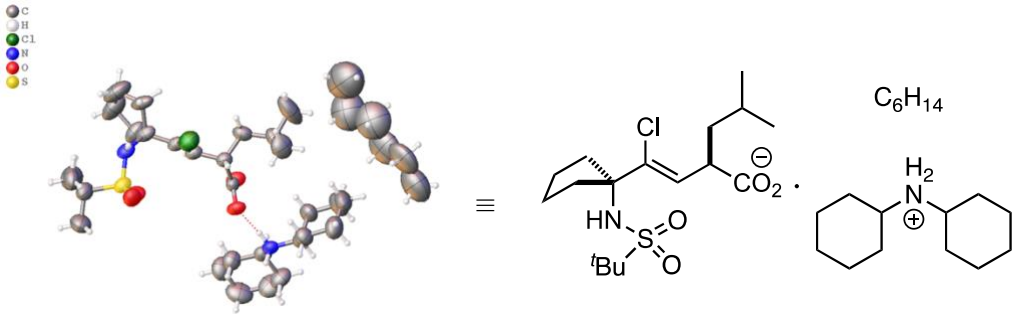


Figure S5. ORTEP representation of **S6.**

Table S6. Crystal data and structure refinement for **S6**, CCDC Number: 2064230.

Identification code	SIM21-032			
Emipircal formula	$C_{32}H_{60}ClN_2O_4S$			
Formula wight	604.33			
Temperature	293			
Crystal system	monoclinic			
Sapce group	I2/a			
Unit cell Dimensions	a/Å	14.1676(19)	alpha/°	90
	b/Å	21.601(3)	beta/°	90.248(13)
	c/Å	23.423(4)	gamma/°	90
Volume/Å^3	7148.8(17)			
Z	8			
ρ_{calc}g/cm^3	1.123			
μ/mm^{-1}	0.200			
F(000)	2648.0			
Crystal size/mm^3	0.354 × 0.225 × 0.145			
Radiation	MoKα (λ = 0.71073)			
2Θ range for data collection/°	4.748 to 50.698			
Index ranges	$-17 \leq h \leq 17$, $-26 \leq k \leq 26$, $-28 \leq l \leq 28$			
Reflections collected	31587			
Independent refletions	6551 [Rint = 0.0845, Rsigma = 0.0646]			
Data/restraints/parameters	6551/67/382			
Goodness-of-fit on F^2	1.017			
Final R indexes [I>2σ (I)]	R_1 = 0.0619, wR_2 = 0.1515			
Final R indexes [all data]	R_1 = 0.1362, wR_2 = 0.1905			
Largest diff. peak/hole/e Å^{-3}	0.31/-0.23			

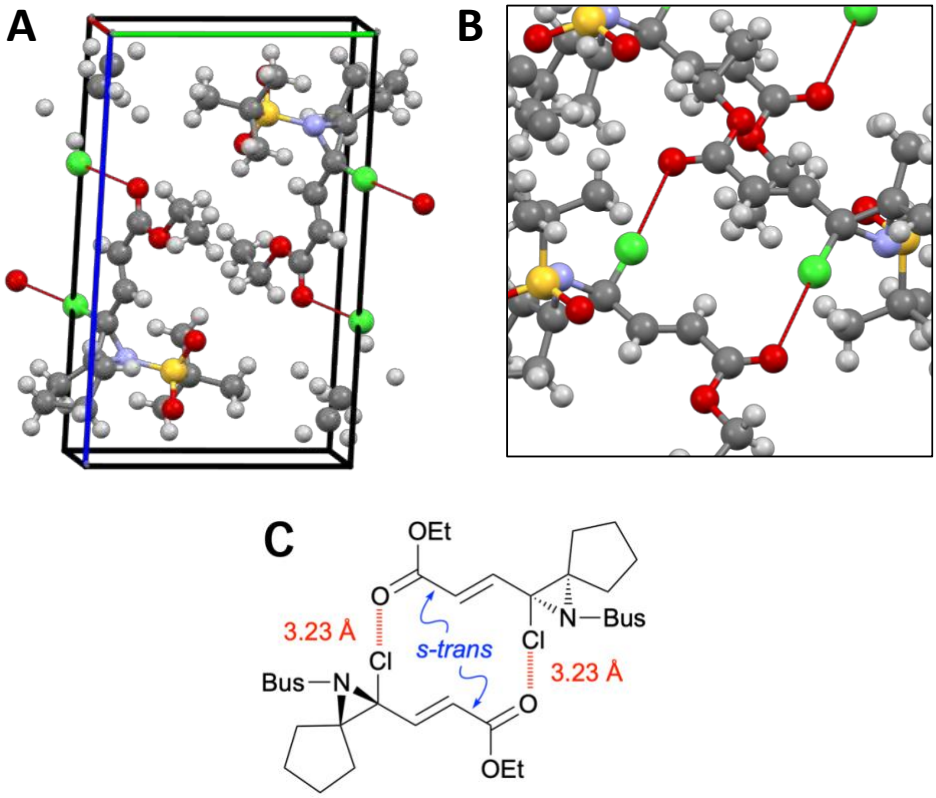


Figure S6. (A) Packing model of enoate (**5**). (B) Enlarged view of the packing model of **5** focusing the distance between C-Cl···O=C. (C) Schematic view of the packing model of **5**.

Th The distance between the carbonyl oxygen atom and the chlorine atom is 3.23 Å, which is less than the sum of the van der Waals radii of oxygen (1.52 Å) and that of chlorine (1.75 Å), indicating that there is an attractive interaction between carbonyl oxygen and the chlorine. Those intermolecular interactions such as halogen bonding between C-Cl…O=C contribute to the s-trans conformation over s-cis conformation.

X. Natural bond orbital (NBO) analysis data

The positions of hydrogen atoms of the X-ray crystal structure of **5** were optimized at the wB97XD/6-311G(d) level of theory as implemented by Gaussian 16.[S8] The DFT-optimized geometry were subjected to analysis with NBO 7.0[S9] at the wB97XD/6-311++G(d,p) level of theory in the gas phase implemented in Gaussian 16.

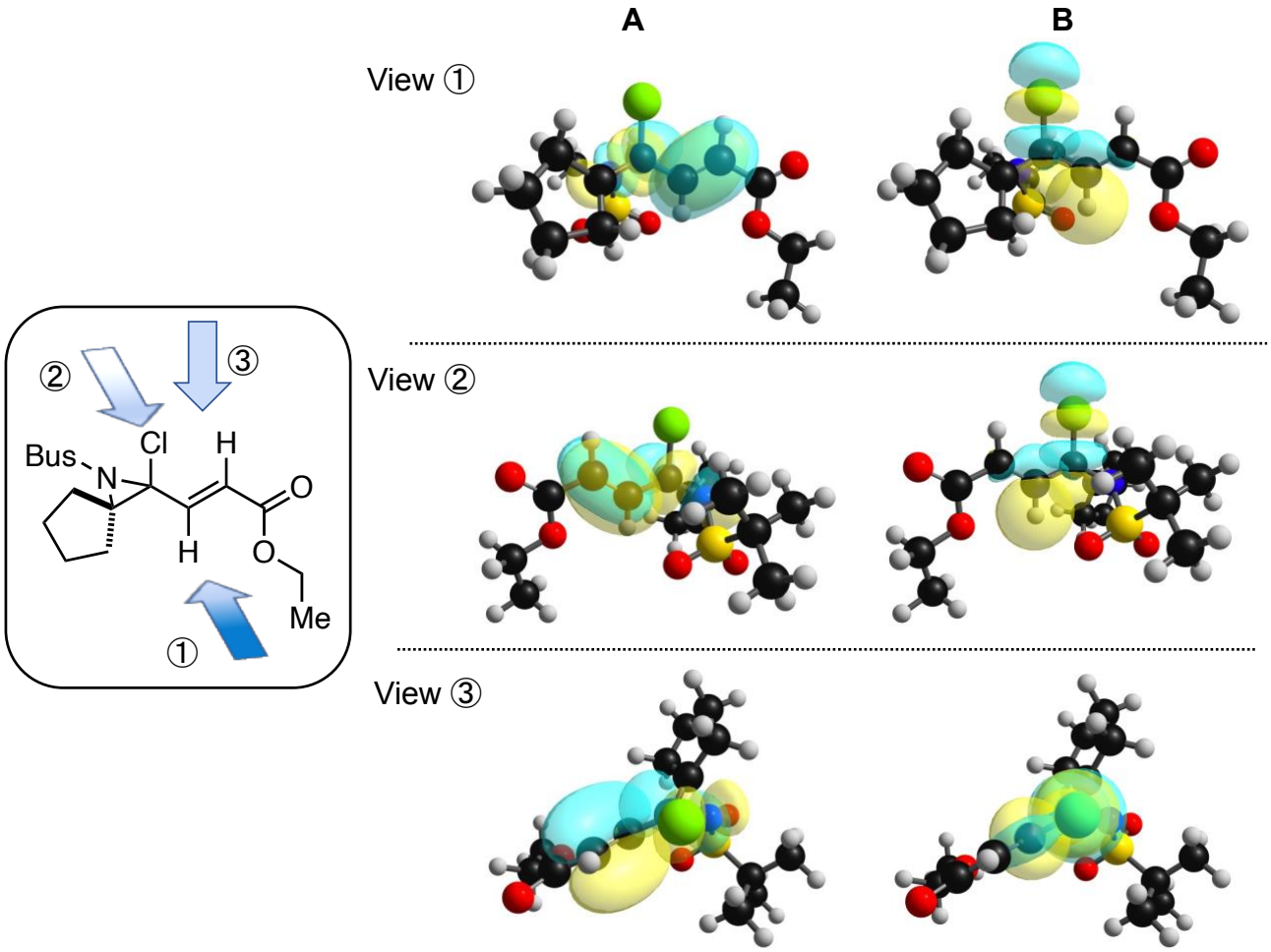


Figure S7. NBO analysis characterized by overlap of the C=C π orbital and C-N σ* orbital (A), C-H σ orbital and C-Cl σ* orbital (B) from three-position angles.

Optimized geometry of Acsc-type enoate 5 (Corrected SCF Energy = -1799.907935)

16	1.504850000	2.066900000	2.306754000
17	3.166277000	-1.101932000	0.180700000
8	-0.693966000	1.371841000	-2.400915000
7	1.906351000	0.501556000	1.917142000
8	0.876152000	2.741792000	1.233582000
8	0.809649000	1.986465000	3.541686000
8	0.735956000	0.776184000	-3.988067000
6	0.953720000	0.370843000	-0.473002000
6	1.723270000	-0.210565000	0.655103000
6	0.981696000	-0.654508000	1.894239000
6	1.218612000	0.201733000	-1.748228000
6	-0.525228000	-0.512440000	2.018904000
6	0.419843000	0.799559000	-2.832407000
6	-1.522567000	2.016917000	-3.380293000
6	-2.795572000	2.420517000	-2.712119000
6	3.140734000	2.759247000	2.582730000
6	1.409240000	-1.837271000	2.724760000
6	3.819328000	2.018283000	3.720548000
6	3.950722000	2.642136000	1.289820000
6	2.895944000	4.231896000	2.965384000
6	-0.882676000	-1.297092000	3.226253000
6	0.212669000	-2.217399000	3.466936000
1	0.101944000	0.973392000	-0.182151000
1	2.075773000	-0.361277000	-2.097159000
1	-0.969511000	-0.951599000	1.116627000
1	-0.858734000	0.524365000	2.052841000
1	-1.692030000	1.322129000	-4.206005000
1	-0.976722000	2.874928000	-3.781952000
1	-2.606863000	3.105647000	-1.882626000
1	-3.327660000	1.549711000	-2.322213000
1	-3.448682000	2.924890000	-3.428715000
1	2.248084000	-1.537952000	3.355137000
1	1.782890000	-2.636213000	2.079155000
1	3.976237000	0.967147000	3.473075000
1	3.237013000	2.077107000	4.641594000
1	4.795621000	2.474968000	3.904873000
1	3.448917000	3.132086000	0.453254000
1	4.135836000	1.598591000	1.027069000
1	4.919515000	3.126779000	1.435513000
1	2.288410000	4.310079000	3.868850000
1	2.401725000	4.778336000	2.160470000
1	3.861242000	4.705517000	3.160085000
1	0.421171000	-2.312225000	4.537503000
1	-0.085624000	-3.232775000	3.174959000
1	-1.849343000	-1.794741000	3.121249000
1	-0.996781000	-0.603837000	4.067132000

XI. Energy diagram of aza-Darzens condensation

All calculations were performed with the Gaussian 16[S8] software package. Geometry optimizations were performed with the B3LYP[S10] density functional and the 6-31+G(d) basis set using the PCM[S11] solvent model for THF. Frequency calculations (195 K) were used to confirm the presence of local minimum (no imaginary frequencies) and transition states (one imaginary frequency). To obtain more accurate energetics, single-point energy calculations were performed on the optimized structures at the M06[S12] /6-311++G(d,p) level of theory using the PCM solvent model for THF. For all transition states, the intrinsic reaction coordinate (IRC) was followed to ensure it connects the reactants and products. Visualizations of the structures of the transition states were created using the CYLview[S13] software package.

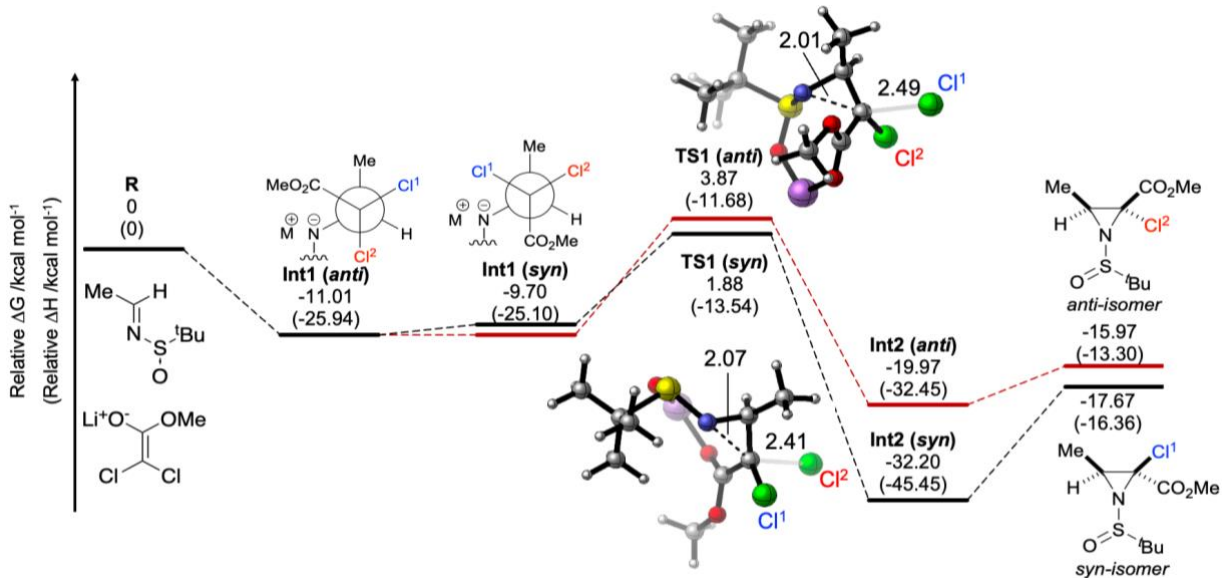


Figure S8. DFT calculations for aza-Darzens condensation with aldimine reactant. Each relative *ΔG* value and *ΔH* value given in kcal/mol are shown.

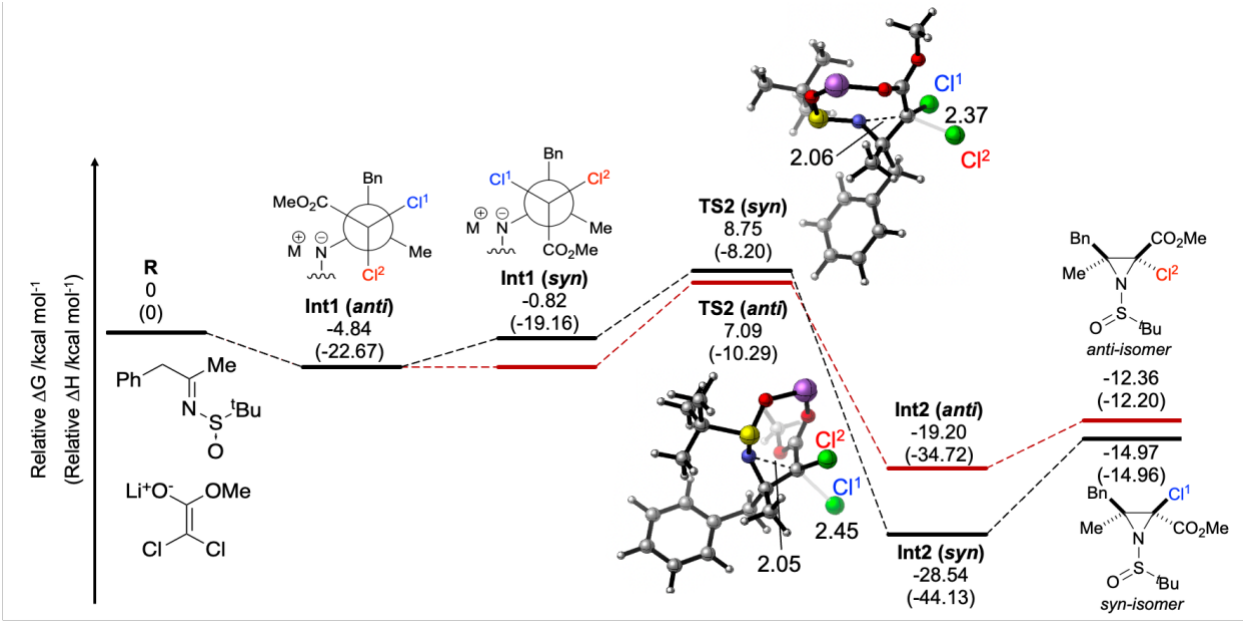
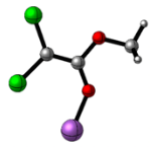


Figure S9. DFT calculations for aza-Darzens condensation with ketimine reactant. Each relative *ΔG* value and *ΔH* value given in kcal/mol are shown.

Optimized geometry of all compounds, intermediate and transition states

1. Common Reactant

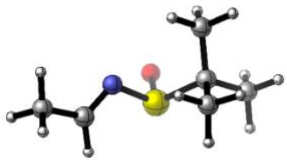
1.1 Lithium enolate



6	0.609222000	-0.146528000	-0.000007000
17	1.910852000	1.040861000	0.000014000
17	1.123324000	-1.821642000	-0.000011000
6	-0.700111000	0.268736000	-0.000001000
8	-1.099747000	1.484176000	-0.000012000
8	-1.637935000	-0.743493000	0.000017000
6	-3.010453000	-0.338085000	0.000006000
1	-3.253230000	0.247557000	-0.892352000
1	-3.253215000	0.247653000	0.892304000
1	-3.582668000	-1.267937000	0.000059000
3	-0.327456000	3.138595000	-0.000035000

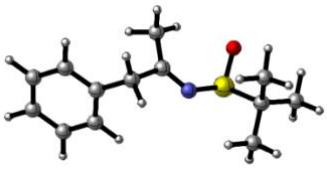
2. Uncommon Reactant

2.1 Aldimine



6	0.190512000	-0.969892000	-0.133157000
6	-1.216676000	-1.189208000	0.374822000
7	-0.039454000	0.414955000	0.237483000
6	1.271950000	-1.647137000	0.735982000
1	1.069324000	-1.425840000	1.789477000
1	1.182159000	-2.736091000	0.604341000
17	-1.816194000	-3.349214000	-0.225403000
17	-1.436555000	-1.302611000	2.103051000
6	-2.407069000	-0.640676000	-0.369503000
8	-2.429486000	-0.418261000	-1.568094000
8	-3.453092000	-0.459390000	0.413897000
6	-4.652584000	-0.003369000	-0.220812000
1	-4.951695000	-0.703891000	-1.006308000
1	-4.498890000	0.994530000	-0.645482000
1	-5.403245000	0.032908000	0.568953000
16	0.326561000	1.664846000	-0.777563000
6	-0.188600000	3.038614000	0.384285000
6	0.719813000	2.985574000	1.602109000
1	0.557831000	2.068395000	2.181033000
1	0.503580000	3.848864000	2.248305000
1	1.781455000	3.040823000	1.317494000
6	0.034832000	4.329249000	-0.391918000
1	-0.607142000	4.385127000	-1.278910000
1	1.081592000	4.432418000	-0.712864000
1	-0.201161000	5.184092000	0.257356000
6	-1.646773000	2.865017000	0.765514000
1	-1.798058000	1.948150000	1.349451000
1	-1.961554000	3.721558000	1.379479000
1	-2.292002000	2.833139000	-0.123298000
8	-0.626589000	1.866503000	-1.976025000
6	0.439038000	-1.321718000	-1.594836000
1	1.375416000	-0.848945000	-1.918727000
1	0.550433000	-2.407105000	-1.702634000
1	-0.365764000	-0.997072000	-2.253440000
6	2.662664000	-1.183598000	0.407216000
6	3.504511000	-1.916209000	-0.434774000
6	3.144100000	0.011301000	0.951790000
6	4.785953000	-1.460663000	-0.738046000
6	4.421011000	0.475473000	0.647246000
6	5.246507000	-0.259305000	-0.202199000
1	3.150161000	-2.858647000	-0.855808000
1	2.502145000	0.577906000	1.626523000
1	5.427993000	-2.048259000	-1.393124000
1	4.775533000	1.409805000	1.081795000
1	6.248275000	0.097322000	-0.437538000
3	-2.027238000	1.006669000	-2.852391000

2.2 Ketimine

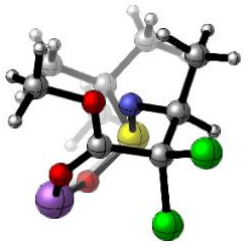


6	0.268142000	-0.742752000	0.345913000
7	-0.708791000	0.080075000	0.204831000
6	1.363567000	-0.306902000	1.316862000
1	0.991135000	0.549089000	1.887612000
1	1.549339000	-1.127351000	2.021155000
16	-2.007370000	-0.080627000	-0.921459000
6	-3.364699000	0.539363000	0.257267000
6	-3.044875000	1.993486000	0.619909000
1	-2.132924000	2.069245000	1.217016000
1	-3.878257000	2.402393000	1.205171000
1	-2.929397000	2.617490000	-0.274624000
6	-4.652922000	0.453320000	-0.574754000
1	-4.876736000	-0.577588000	-0.864641000
1	-4.592162000	1.066311000	-1.482339000
1	-5.488818000	0.829431000	0.027168000
6	-3.435458000	-0.367839000	1.486295000
1	-2.528114000	-0.292243000	2.093469000
1	-4.287686000	-0.063674000	2.107192000
1	-3.583667000	-1.414050000	1.198660000
8	-2.384128000	-1.517740000	-1.271192000
6	0.482358000	-2.081746000	-0.318595000
1	1.489734000	-2.112097000	-0.749746000
1	0.442048000	-2.870070000	0.445074000
1	-0.259103000	-2.300643000	-1.084195000
6	2.663016000	0.056196000	0.612515000
6	3.800482000	-0.755863000	0.722955000
6	2.741895000	1.222044000	-0.166159000
6	4.990869000	-0.413940000	0.071644000
6	3.928479000	1.566159000	-0.818621000
6	5.057924000	0.747794000	-0.702541000
1	3.758195000	-1.659980000	1.326646000
1	1.868883000	1.864157000	-0.258945000
1	5.863341000	-1.054736000	0.171954000
1	3.972172000	2.473912000	-1.415276000
1	5.981833000	1.015926000	-1.208435000

3. Intermediates, transition states, products

3.1 For *anti*-product from aldimine

3.1.1 Intermediate 1



6	-0.518927000	-0.538865000	1.129830000
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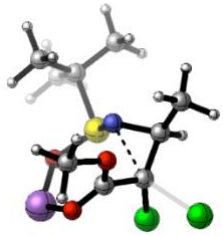
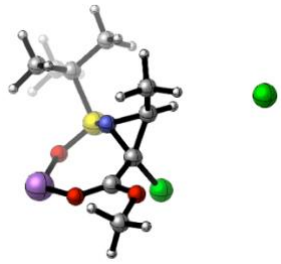
7	0.557382000	0.180485000	0.467961000
6	-0.844569000	0.139428000	2.470014000
1	-1.115357000	1.189943000	2.328996000
1	-1.648385000	-0.366031000	3.012599000
17	-1.509106000	-1.911370000	-1.068344000
17	-3.358707000	-0.879964000	0.940466000
6	-1.817936000	0.765151000	-0.652205000
8	-1.430666000	0.907748000	-1.804068000
8	-2.336168000	1.732884000	0.076396000
6	-2.379232000	3.057810000	-0.516473000
1	-2.992667000	3.036961000	-1.418974000
1	-1.365367000	3.387030000	-0.750836000
1	-2.829156000	3.690183000	0.246668000
16	1.747469000	-0.742544000	-0.155431000
6	3.295744000	0.252899000	0.295394000
6	3.433484000	0.178637000	1.820066000
1	2.591098000	0.667726000	2.318265000
1	4.357699000	0.684066000	2.128591000
1	3.488683000	-0.860016000	2.170557000
6	4.475341000	-0.448272000	-0.391979000
1	4.374827000	-0.417993000	-1.480780000
1	4.557955000	-1.497556000	-0.081357000
1	5.410630000	0.056305000	-0.116580000
6	3.151858000	1.698158000	-0.183373000
1	2.288593000	2.180846000	0.284723000
1	4.054350000	2.262601000	0.086525000
1	3.036305000	1.744274000	-1.271477000
8	1.750947000	-0.620467000	-1.731390000
3	0.252392000	0.145943000	-2.480903000
1	0.063486000	0.101527000	3.079788000
1	-0.293665000	-1.598140000	1.331955000

3.1.2 Transition state



6	-0.473978000	-0.857484000	1.115368000
6	-1.343125000	-0.540599000	-0.052186000
7	0.485973000	0.088027000	0.507071000
6	-0.887971000	-0.491279000	2.531517000
1	-1.156531000	0.562738000	2.611759000
1	-1.742343000	-1.100698000	2.838497000
17	-1.237980000	-1.628409000	-1.419817000
17	-3.710318000	-1.059529000	0.523162000
6	-1.634047000	0.892282000	-0.435067000
8	-1.529901000	1.302930000	-1.590479000
8	-2.007731000	1.643138000	0.580628000
6	-2.227562000	3.049302000	0.310158000
1	-3.022028000	3.164827000	-0.429383000
1	-1.303454000	3.507408000	-0.049304000
1	-2.524398000	3.474502000	1.267409000
16	1.683046000	-0.563678000	-0.504641000
6	3.234806000	0.067500000	0.388934000
6	3.270532000	-0.637786000	1.749185000
1	2.441344000	-0.320074000	2.388574000
1	4.207671000	-0.381787000	2.258292000
1	3.237289000	-1.729296000	1.645177000
6	4.408138000	-0.374980000	-0.496936000
1	4.365471000	0.095417000	-1.484008000
1	4.432355000	-1.463469000	-0.627621000
1	5.347633000	-0.074699000	-0.016711000
6	3.175555000	1.588391000	0.528014000
1	2.325896000	1.899374000	1.142406000
1	4.098026000	1.935337000	1.010510000
1	3.100678000	2.072782000	-0.450653000
8	1.631348000	0.282640000	-1.804729000
3	0.107150000	1.020251000	-2.642047000
1	-0.045204000	-0.696439000	3.201055000
1	-0.177125000	-1.910795000	1.070755000

3.1.3 Intermediate 2



6	0.634195000	-0.852079000	0.023271000
6	0.622079000	0.590566000	0.397148000
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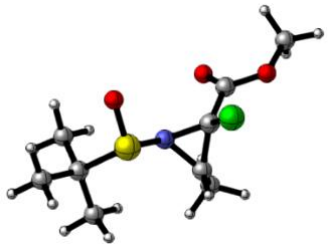
6	1.307664000	-1.413456000	-1.202250000
1	1.309174000	-0.693923000	-2.026256000
1	2.340170000	-1.686511000	-0.953219000
17	0.705995000	0.984351000	2.155822000
17	4.694748000	-2.833704000	0.172081000
6	1.186411000	1.758631000	-0.390492000
8	0.461290000	2.638891000	-0.842758000
8	2.493855000	1.722368000	-0.496265000
6	3.147249000	2.829722000	-1.179499000
1	2.940756000	3.758053000	-0.644146000
1	2.784479000	2.889868000	-2.206808000
1	4.207028000	2.586392000	-1.150735000
16	-2.065544000	0.042274000	0.720724000
6	-3.087382000	-1.108841000	-0.374847000
6	-2.489074000	-2.514130000	-0.233553000
1	-1.514894000	-2.598739000	-0.722373000
1	-3.164676000	-3.227877000	-0.718935000
1	-2.388068000	-2.817622000	0.815045000
6	-4.489155000	-1.041530000	0.255907000
1	-4.910632000	-0.033043000	0.201257000
1	-4.484340000	-1.366000000	1.302939000
1	-5.150616000	-1.716356000	-0.299119000
6	-3.096055000	-0.612967000	-1.820183000
1	-2.101755000	-0.660014000	-2.272175000
1	-3.768427000	-1.254397000	-2.402350000
1	-3.469965000	0.413655000	-1.887482000
8	-2.541365000	1.469443000	0.427860000
3	-1.523693000	2.809001000	-0.582807000
1	0.788883000	-2.320121000	-1.532432000
1	0.606312000	-1.509927000	0.891896000

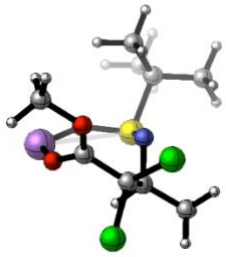
3.1.4 *anti*-product



6	0.461657000	0.806390000	-1.316639000
6	1.175294000	-0.141465000	-0.396693000
7	-0.158845000	0.303713000	-0.072482000
6	0.763994000	2.281670000	-1.427121000
1	1.052056000	2.704769000	-0.461768000
1	1.578500000	2.438301000	-2.143858000
17	1.452193000	-1.805406000	-1.045389000
6	2.273166000	0.329732000	0.547952000
8	2.071253000	1.096058000	1.467303000
8	3.469988000	-0.144280000	0.199072000
6	4.592768000	0.287933000	1.005003000
1	4.448845000	-0.024955000	2.041254000
1	4.694297000	1.374124000	0.952179000
1	5.460247000	-0.204768000	0.568457000
16	-1.496619000	-0.886962000	-0.139290000
6	-2.895561000	0.324219000	0.262833000
6	-2.964601000	1.366800000	-0.857936000
1	-2.120751000	2.060375000	-0.820195000
1	-3.882596000	1.954376000	-0.736487000
1	-3.000170000	0.902866000	-1.851486000
6	-4.147847000	-0.569644000	0.255554000
1	-4.093291000	-1.346763000	1.024337000
1	-4.303549000	-1.049657000	-0.718207000
1	-5.025356000	0.053436000	0.464732000
6	-2.663559000	0.950267000	1.637771000
1	-1.771463000	1.582473000	1.645799000
1	-3.532125000	1.569226000	1.895117000
1	-2.553651000	0.180302000	2.407702000
8	-1.314100000	-1.751437000	1.085692000
1	-0.114710000	2.821173000	-1.797000000
1	0.145245000	0.323878000	-2.243838000

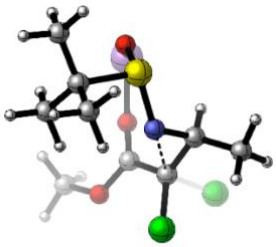
3.2 For *syn*-product from aldimine

3.2.1 Intermediate 1



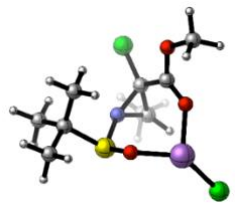
6	-0.536453000	-1.171845000	-0.560366000
6	-1.797234000	-0.482825000	0.018127000
7	0.573161000	-0.483383000	0.103126000
6	-0.529792000	-2.697673000	-0.396934000
1	-0.455762000	-2.974289000	0.658652000
1	-1.420309000	-3.168093000	-0.830319000
17	-3.304867000	-0.948322000	-0.934102000
17	-2.075099000	-0.932099000	1.742115000
6	-1.673337000	1.048029000	-0.160815000
8	-1.334026000	1.541458000	-1.230972000
8	-2.059514000	1.754317000	0.880706000
6	-2.028299000	3.198945000	0.748556000
1	-2.664943000	3.507408000	-0.082723000
1	-1.001080000	3.531263000	0.586373000
1	-2.411953000	3.574116000	1.695520000
16	1.901545000	-0.395626000	-0.836979000
6	3.199463000	0.009484000	0.471961000
6	3.319265000	-1.218821000	1.382126000
1	2.389268000	-1.395264000	1.928642000
1	4.127537000	-1.055285000	2.106805000
1	3.562672000	-2.122829000	0.809630000
6	4.509929000	0.249269000	-0.290967000
1	4.425879000	1.104330000	-0.968205000
1	4.801849000	-0.630273000	-0.878307000
1	5.313873000	0.454919000	0.427092000
6	2.781540000	1.252922000	1.258564000
1	1.835933000	1.084660000	1.781053000
1	3.555596000	1.488417000	2.000846000
1	2.670669000	2.118701000	0.596814000
8	1.896140000	0.908429000	-1.744529000
3	0.351306000	1.816993000	-2.135920000
1	-0.601816000	-0.952130000	-1.638835000
1	0.349960000	-3.094308000	-0.914866000

3.2.2 Transition state



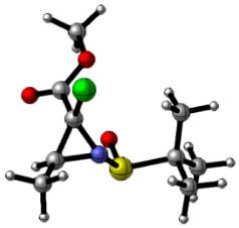
6	-0.619132000	-1.431642000	-0.541899000
6	-1.408092000	-0.413283000	0.226519000
7	0.586110000	-0.977963000	0.134269000
6	-0.968461000	-2.905075000	-0.363978000
1	-0.918830000	-3.197305000	0.688464000
1	-1.970321000	-3.116376000	-0.750471000
17	-3.601503000	-0.538477000	-0.772803000
17	-1.790723000	-0.763983000	1.885627000
6	-1.331084000	1.035231000	-0.169365000
8	-0.977425000	1.412133000	-1.282183000
8	-1.718603000	1.861588000	0.788586000
6	-1.766140000	3.270704000	0.459616000
1	-2.454995000	3.432135000	-0.372026000
1	-0.767284000	3.627336000	0.199660000
1	-2.127674000	3.757454000	1.363775000
16	1.939369000	-0.723449000	-0.807454000
6	3.030702000	0.147272000	0.469801000
6	3.259142000	-0.840742000	1.620269000
1	2.327895000	-1.060699000	2.147401000
1	3.968217000	-0.398587000	2.331542000
1	3.689518000	-1.784439000	1.263689000
6	4.345629000	0.444792000	-0.265518000
1	4.191682000	1.128958000	-1.105338000
1	4.814820000	-0.471386000	-0.644046000
1	5.046188000	0.914427000	0.435330000
6	2.352686000	1.432640000	0.945235000
1	1.414073000	1.216566000	1.463465000
1	3.020570000	1.951215000	1.644612000
1	2.150554000	2.109278000	0.108057000
8	1.770288000	0.317538000	-1.955725000
3	0.367296000	1.318036000	-2.625529000
1	-0.674625000	-1.163206000	-1.603977000
1	-0.242100000	-3.506191000	-0.921666000

3.2.3 Intermediate 2



6	-0.729422000	0.449685000	1.733843000
6	-0.198389000	1.265434000	0.573126000
7	0.495104000	0.081388000	1.028912000
6	-0.629225000	0.873469000	3.177322000
1	0.288866000	1.431882000	3.372501000
1	-1.491887000	1.494731000	3.442260000
17	-3.686698000	-2.439075000	0.317535000
17	0.666373000	2.803713000	0.885273000
6	-1.037675000	1.267795000	-0.701442000
8	-1.845737000	0.385833000	-0.947982000
8	-0.827205000	2.315121000	-1.474947000
6	-1.619441000	2.400550000	-2.690877000
1	-2.680361000	2.423293000	-2.436292000
1	-1.400911000	1.544952000	-3.332381000
1	-1.308344000	3.331756000	-3.160244000
16	0.842087000	-1.464811000	0.313824000
6	2.542002000	-1.061922000	-0.418195000
6	3.464859000	-0.695574000	0.749711000
1	3.167568000	0.242628000	1.224565000
1	4.483655000	-0.577985000	0.361482000
1	3.489094000	-1.483010000	1.512024000
6	2.976194000	-2.383991000	-1.073062000
1	2.313888000	-2.663709000	-1.897270000
1	3.007822000	-3.208058000	-0.350788000
1	3.987283000	-2.254073000	-1.475532000
6	2.428945000	0.057744000	-1.454178000
1	2.194228000	1.021796000	-0.993964000
1	3.395627000	0.161709000	-1.961630000
1	1.677293000	-0.175621000	-2.214991000
8	-0.040056000	-1.785969000	-0.893798000
3	-1.977122000	-1.616525000	-0.964485000
1	-1.625967000	-0.114521000	1.473171000
1	-0.643186000	-0.016800000	3.815574000

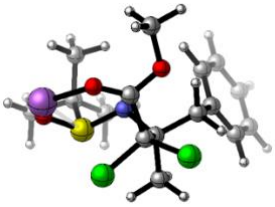
3.2.4 *syn*-product



6	1.058838000	1.611233000	-1.015956000
6	1.246668000	0.587790000	0.053869000
7	-0.083083000	1.045319000	-0.270466000
6	1.341007000	3.084336000	-0.860631000
1	1.151204000	3.423442000	0.160552000
1	2.386568000	3.292150000	-1.115492000
17	1.849915000	1.064800000	1.688652000
6	1.781384000	-0.791092000	-0.349011000
8	2.367327000	-0.981817000	-1.395491000
8	1.568899000	-1.706340000	0.591797000
6	2.028617000	-3.046543000	0.298139000
1	3.108422000	-3.044046000	0.133907000
1	1.513637000	-3.425638000	-0.587133000
1	1.772432000	-3.634149000	1.178517000
16	-1.332582000	0.096104000	-1.076761000
6	-2.485723000	-0.111961000	0.411589000
6	-2.991594000	1.286170000	0.785143000
1	-2.183625000	1.921977000	1.157028000
1	-3.743866000	1.187454000	1.577311000
1	-3.469593000	1.786920000	-0.065460000
6	-3.628359000	-0.986249000	-0.130647000
1	-3.272086000	-1.978986000	-0.421789000
1	-4.123107000	-0.524437000	-0.993729000
1	-4.380410000	-1.110085000	0.657435000
6	-1.760034000	-0.800659000	1.567551000
1	-0.976757000	-0.165554000	1.991106000
1	-2.486710000	-1.016087000	2.360957000
1	-1.313786000	-1.748146000	1.250680000
8	-0.812383000	-1.284461000	-1.430232000
1	1.232568000	1.205314000	-2.014023000
1	0.703886000	3.656152000	-1.544389000

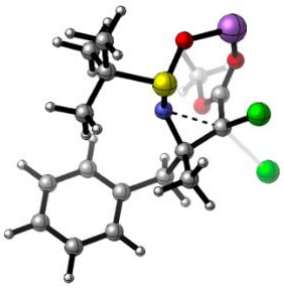
3.3 For *anti*-product from ketimine

3.3.1 Intermediate 1



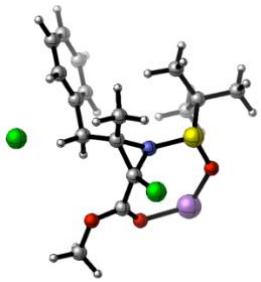
6	-0.361796000	-0.634228000	-0.629233000
6	-1.959518000	-0.764833000	-0.478558000
7	0.020449000	0.556002000	0.124256000
6	0.287504000	-1.869860000	0.099141000
1	-0.075425000	-1.886811000	1.127388000
1	-0.072088000	-2.782190000	-0.384868000
17	-2.821590000	0.366109000	-1.613436000
17	-2.630822000	-2.440614000	-0.855635000
6	-2.420023000	-0.382363000	0.958577000
8	-2.980911000	0.664802000	1.247563000
8	-2.175661000	-1.337158000	1.835063000
6	-2.528580000	-1.070303000	3.217669000
1	-3.604294000	-0.902737000	3.296695000
1	-1.979560000	-0.197422000	3.575383000
1	-2.232968000	-1.967310000	3.758884000
16	0.061073000	1.993328000	-0.655770000
6	1.601774000	2.807901000	0.087492000
6	2.809463000	2.051736000	-0.476841000
1	2.808722000	1.006343000	-0.159248000
1	3.734194000	2.521690000	-0.116968000
1	2.825306000	2.084143000	-1.573812000
6	1.601545000	4.261307000	-0.406470000
1	0.740468000	4.813964000	-0.020970000
1	1.583265000	4.314335000	-1.502574000
1	2.517424000	4.760492000	-0.063649000
6	1.555329000	2.739617000	1.614157000
1	1.517915000	1.701741000	1.956259000
1	2.456259000	3.212828000	2.027462000
1	0.681790000	3.271167000	2.006540000
8	-1.068207000	2.953516000	-0.102729000
6	0.023205000	-0.690330000	-2.120633000
1	1.112029000	-0.641432000	-2.202762000
1	-0.315596000	-1.627049000	-2.577273000
1	-0.392048000	0.139091000	-2.694062000
6	1.801989000	-1.911566000	0.130016000
6	2.533569000	-2.558624000	-0.879642000
6	2.512966000	-1.375940000	1.215802000
6	3.928110000	-2.649324000	-0.820337000
6	3.906011000	-1.468734000	1.285708000
6	4.621249000	-2.102045000	0.263911000
1	2.006194000	-3.008058000	-1.718253000
1	1.964161000	-0.881521000	2.012356000
1	4.470002000	-3.156048000	-1.615447000
1	4.432653000	-1.047344000	2.138922000
1	5.704623000	-2.176881000	0.316783000
3	-2.663628000	2.462190000	0.602071000

3.3.2 Transition state



6	-0.214913000	-0.713695000	-0.678964000
6	-1.701218000	-0.640413000	-0.433177000
7	-0.125925000	0.535024000	0.123801000
6	0.495606000	-1.894829000	0.048371000
1	0.104202000	-1.968288000	1.060578000
1	0.190242000	-2.804667000	-0.477570000
17	-2.687872000	0.172256000	-1.646321000
17	-2.697048000	-2.854964000	-0.732076000
6	-2.271854000	-0.442005000	0.963058000
8	-3.139075000	0.395855000	1.204938000
8	-1.784066000	-1.256049000	1.876935000
6	-2.263068000	-1.080485000	3.233382000
1	-3.341028000	-1.248548000	3.269288000
1	-2.022848000	-0.075121000	3.585353000
1	-1.733668000	-1.833614000	3.814629000
16	-0.235745000	2.040428000	-0.660491000
6	1.299357000	2.906131000	0.041015000
6	2.516617000	2.224551000	-0.592244000
1	2.606635000	1.181785000	-0.277066000
1	3.424348000	2.753274000	-0.275873000
1	2.476449000	2.261479000	-1.687723000
6	1.177675000	4.361854000	-0.433172000
1	0.297428000	4.850886000	-0.006455000
1	1.122121000	4.431257000	-1.526334000
1	2.068767000	4.913362000	-0.108508000
6	1.306709000	2.814406000	1.566643000
1	1.386105000	1.777588000	1.902647000
1	2.170159000	3.372455000	1.950643000
1	0.399920000	3.255419000	1.992857000
8	-1.406477000	2.796546000	0.029915000
6	0.202173000	-0.686189000	-2.152837000
1	1.288339000	-0.581727000	-2.214384000
1	-0.083554000	-1.628597000	-2.631171000
1	-0.249173000	0.132394000	-2.713088000
6	2.007093000	-1.812056000	0.113324000
6	2.817101000	-2.395170000	-0.875313000
6	2.638998000	-1.200097000	1.208184000
6	4.211739000	-2.351712000	-0.785022000
6	4.033032000	-1.154676000	1.305291000
6	4.825734000	-1.727240000	0.305588000
1	2.352392000	-2.900911000	-1.718742000
1	2.029841000	-0.762269000	1.994721000
1	4.816948000	-2.813582000	-1.561317000
1	4.498975000	-0.677551000	2.164204000
1	5.909817000	-1.697455000	0.380891000
3	-3.121040000	2.178467000	0.439117000

3.3.3 Intermediate 2



6	0.391054000	-0.451469000	-0.455087000
6	-0.592485000	-1.543446000	-0.162001000
7	-1.007748000	-0.175122000	0.053827000
6	1.497408000	-0.204135000	0.583217000
1	1.133352000	-0.510633000	1.568762000
1	2.314767000	-0.883595000	0.306440000
17	-1.240355000	-2.539167000	-1.525523000
17	4.313304000	-2.017881000	-1.467494000
6	-0.659502000	-2.415466000	1.081489000
8	-1.616678000	-2.376731000	1.848558000
8	0.378008000	-3.210485000	1.206148000
6	0.386470000	-4.141136000	2.325054000
1	-0.470746000	-4.812100000	2.246322000
1	0.353541000	-3.584921000	3.263354000
1	1.322506000	-4.686202000	2.224924000
16	-2.426144000	0.381530000	-0.836568000
6	-2.430713000	2.204964000	-0.348237000
6	-1.215714000	2.857447000	-1.017728000
1	-0.273616000	2.536567000	-0.566591000
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1	-1.185255000	2.657047000	-2.095112000
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1	-3.767216000	2.584752000	-2.052725000
1	-3.812956000	3.799671000	-0.766294000
6	-2.430308000	2.358038000	1.171685000
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1	-2.506506000	3.424944000	1.413440000
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8	-3.541279000	-0.280421000	-0.017703000
6	0.770826000	-0.161003000	-1.893461000
1	1.063187000	0.887645000	-1.993914000
1	1.635776000	-0.779156000	-2.158373000
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6	2.025624000	1.215018000	0.674623000
6	3.039620000	1.664863000	-0.187012000
6	1.543606000	2.093981000	1.656703000
6	3.535700000	2.967829000	-0.086134000
6	2.039229000	3.397273000	1.762293000
6	3.033489000	3.840749000	0.885037000
1	3.457773000	0.979857000	-0.920689000
1	0.783859000	1.750738000	2.355421000
1	4.324208000	3.296094000	-0.758684000
1	1.654963000	4.060728000	2.533262000
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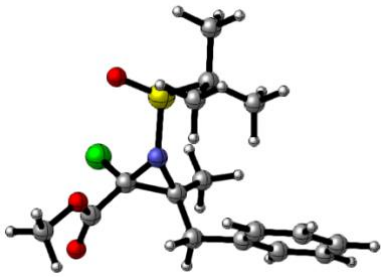
3.3.4 *anti*-product



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1	0.751109000	-2.757363000	-0.680938000
17	-2.785458000	-0.583088000	-1.819657000
6	-2.146403000	-1.861798000	0.464880000
8	-2.381218000	-3.012895000	0.150412000
8	-2.363664000	-1.335268000	1.667465000
6	-2.945036000	-2.216278000	2.659747000
1	-2.280387000	-3.063607000	2.841824000
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16	-1.153608000	1.891524000	-0.521429000
6	0.237282000	2.807999000	0.376215000
6	1.555802000	2.456234000	-0.320037000
1	1.843202000	1.414493000	-0.159390000
1	2.352322000	3.085508000	0.095517000
1	1.511191000	2.652056000	-1.398222000
6	-0.116697000	4.288043000	0.148147000
1	-1.070236000	4.550791000	0.615583000
1	-0.167761000	4.538380000	-0.918563000
1	0.667970000	4.907585000	0.598317000
6	0.233631000	2.461867000	1.864682000
1	0.494758000	1.414948000	2.035778000
1	0.971299000	3.092903000	2.376077000
1	-0.747142000	2.655073000	2.310895000
8	-2.424934000	2.197000000	0.237407000
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1	1.312630000	-0.062946000	-2.317778000
1	0.349488000	-1.436087000	-2.886087000
1	-0.373726000	0.177472000	-2.804060000
6	2.273855000	-1.414926000	0.024037000
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6	2.727973000	-0.838800000	1.220659000
6	4.552716000	-1.305919000	-0.835170000
6	4.071902000	-0.491378000	1.388058000
6	4.988628000	-0.718996000	0.357406000
1	2.886985000	-2.129272000	-1.920157000
1	2.024297000	-0.668109000	2.032164000
1	5.259865000	-1.501913000	-1.637242000
1	4.401788000	-0.048503000	2.324492000
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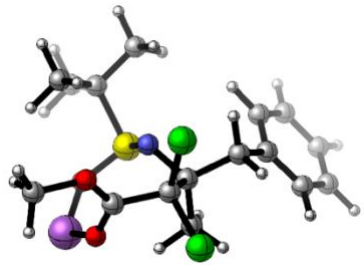
3.4 For *syn*-product from ketimine

3.4.1 Intermediate 1



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1	1.038476000	-1.101039000	1.804755000
1	1.171422000	-2.542601000	0.798346000
17	-1.445244000	-3.317230000	-0.507385000
17	-1.469700000	-1.861242000	2.026515000
6	-2.454997000	-0.794503000	-0.322816000
8	-2.591072000	-0.585197000	-1.526377000
8	-3.367920000	-0.466514000	0.573421000
6	-4.525367000	0.260868000	0.098618000
1	-5.037664000	-0.314889000	-0.674759000
1	-4.216836000	1.233384000	-0.291808000
1	-5.158287000	0.384158000	0.975978000
16	0.208122000	1.701140000	-0.737854000
6	-0.171541000	3.157283000	0.414939000
6	0.739567000	3.038444000	1.640888000
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1	0.568748000	3.897880000	2.302239000
1	1.798713000	3.044308000	1.356866000
6	0.167138000	4.422333000	-0.386645000
1	-0.470176000	4.516465000	-1.270483000
1	1.214624000	4.425297000	-0.712914000
1	0.011147000	5.304224000	0.247680000
6	-1.647652000	3.137226000	0.814791000
1	-1.893454000	2.223755000	1.363039000
1	-1.858417000	4.001057000	1.459015000
1	-2.294373000	3.206787000	-0.066362000
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6	0.465119000	-1.173373000	-1.603040000
1	1.303219000	-0.529108000	-1.882007000
1	0.788102000	-2.208806000	-1.738930000
1	-0.363088000	-0.983915000	-2.284436000
6	2.649649000	-1.054086000	0.405980000
6	3.449822000	-1.894805000	-0.386090000
6	3.217134000	0.141214000	0.875400000
6	4.761744000	-1.544625000	-0.718400000
6	4.528292000	0.498748000	0.546152000
6	5.305814000	-0.341377000	-0.256895000
1	3.044055000	-2.839597000	-0.741461000
1	2.626244000	0.792295000	1.512092000
1	5.360089000	-2.214637000	-1.331302000
1	4.944150000	1.430012000	0.923752000
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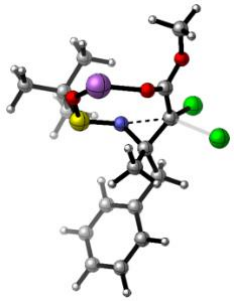
3	-2.119755000	0.957725000	-2.592487000

3.4.2 Transition state



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1	1.208590000	-2.507008000	0.804196000
17	-1.501322000	-3.472969000	-0.228616000
17	-1.394910000	-1.362012000	2.129737000
6	-2.431768000	-0.824758000	-0.359072000
8	-2.473035000	-0.582620000	-1.561255000
8	-3.508198000	-0.818405000	0.412414000
6	-4.778225000	-0.564640000	-0.231803000
1	-4.958472000	-1.315569000	-1.003682000
1	-4.783633000	0.436863000	-0.667293000
1	-5.516169000	-0.641408000	0.565046000
16	0.105907000	1.820037000	-0.779313000
6	-0.247915000	3.243175000	0.417044000
6	0.824413000	3.213515000	1.511521000
1	0.750761000	2.306091000	2.116041000
1	0.685626000	4.081404000	2.168527000
1	1.834608000	3.275239000	1.089065000
6	-0.122232000	4.519083000	-0.429645000
1	-0.874195000	4.550014000	-1.223007000
1	0.870925000	4.605916000	-0.887260000
1	-0.268921000	5.391624000	0.218431000
6	-1.655484000	3.094762000	0.996919000
1	-1.743488000	2.180285000	1.590377000
1	-1.866493000	3.952887000	1.647793000
1	-2.410004000	3.078309000	0.203657000
8	-1.016330000	2.008181000	-1.852344000
6	0.512323000	-1.139413000	-1.568786000
1	1.419934000	-0.610661000	-1.873434000
1	0.687477000	-2.212060000	-1.681025000
1	-0.301834000	-0.858856000	-2.231790000
6	2.759250000	-1.087738000	0.373276000
6	3.532668000	-2.012506000	-0.346890000
6	3.345846000	0.141803000	0.714587000
6	4.844731000	-1.715607000	-0.728086000
6	4.656285000	0.445875000	0.333159000
6	5.410866000	-0.481461000	-0.392786000
1	3.104918000	-2.978320000	-0.607295000
1	2.771865000	0.862121000	1.290384000
1	5.424708000	-2.450050000	-1.281789000
1	5.090153000	1.403801000	0.610163000
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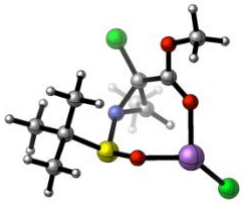
3.4.3 Intermediate 2



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1	2.274861000	-1.100659000	1.672209000
1	2.368787000	-2.512866000	0.621230000
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17	-0.214176000	-1.350701000	2.747646000
6	-1.684069000	-1.600443000	0.491992000
8	-2.616064000	-0.921002000	0.097857000
8	-1.701412000	-2.919992000	0.579266000
6	-2.938034000	-3.591361000	0.208584000
1	-3.166860000	-3.388459000	-0.838856000
1	-3.749910000	-3.242457000	0.848922000
1	-2.738758000	-4.649085000	0.369018000
16	-0.203249000	1.514059000	-0.482909000
6	-0.677743000	2.724855000	0.902116000
6	0.593899000	2.976466000	1.720963000
1	0.907623000	2.084000000	2.268443000
1	0.385138000	3.769858000	2.448524000
1	1.424299000	3.315512000	1.090862000
6	-1.103450000	3.990988000	0.140211000
1	-1.996758000	3.817798000	-0.466583000
1	-0.304610000	4.367276000	-0.509536000
1	-1.334423000	4.773183000	0.872416000
6	-1.821415000	2.182516000	1.758876000
1	-1.531448000	1.286255000	2.313827000
1	-2.097697000	2.951632000	2.490596000
1	-2.710554000	1.964134000	1.161010000
8	-1.463039000	1.290426000	-1.313606000
6	0.639464000	-1.589691000	-1.378484000
1	1.357314000	-1.107826000	-2.049635000
1	0.795593000	-2.671870000	-1.437967000
1	-0.364590000	-1.360379000	-1.745054000
6	3.393079000	-0.775696000	-0.134293000
6	4.107221000	-1.487267000	-1.110249000
6	3.760631000	0.553883000	0.127030000
6	5.153483000	-0.884816000	-1.815968000
6	4.804887000	1.160385000	-0.576906000
6	5.503460000	0.443204000	-1.553670000
1	3.847692000	-2.523407000	-1.316828000
1	3.231316000	1.115059000	0.893001000
1	5.695793000	-1.454392000	-2.566430000
1	5.076400000	2.190054000	-0.357946000
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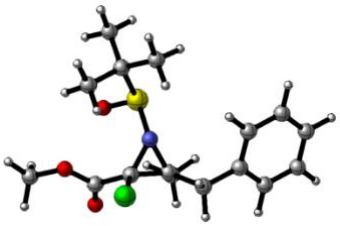
3.4.4 *syn*-product



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1	1.483649000	-1.118830000	1.799837000
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6	-2.039577000	-1.753228000	-0.355631000
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8	-3.187007000	-1.209705000	0.040109000
6	-4.383081000	-1.676905000	-0.625204000
1	-4.502785000	-2.751388000	-0.469159000
1	-4.321758000	-1.455952000	-1.693013000
1	-5.199906000	-1.125328000	-0.161952000
16	-0.726449000	1.308780000	-0.949610000
6	-1.455715000	2.579965000	0.253929000
6	-0.312754000	3.052841000	1.159012000
1	0.032508000	2.254347000	1.821116000
1	-0.676856000	3.880412000	1.780176000
1	0.540817000	3.423906000	0.579171000
6	-1.933780000	3.714406000	-0.668040000
1	-2.734893000	3.380932000	-1.334467000
1	-1.116672000	4.119247000	-1.277486000
1	-2.322552000	4.530570000	-0.047715000
6	-2.617177000	1.982218000	1.046714000
1	-2.280313000	1.197045000	1.729454000
1	-3.079319000	2.777256000	1.645529000
1	-3.380899000	1.566981000	0.383247000
8	-1.868170000	0.810521000	-1.816392000
6	0.775100000	-1.442479000	-1.601706000
1	1.615314000	-0.846091000	-1.971929000
1	1.039012000	-2.499733000	-1.706026000
1	-0.096091000	-1.246343000	-2.226426000
6	3.015839000	-0.677309000	0.363513000
6	4.042301000	-1.354267000	-0.311821000
6	3.196598000	0.683108000	0.661457000
6	5.215310000	-0.691491000	-0.687718000
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6	5.379694000	0.665102000	-0.392564000
1	3.925614000	-2.411100000	-0.542595000
1	2.418623000	1.220627000	1.197434000
1	5.999555000	-1.236202000	-1.207545000
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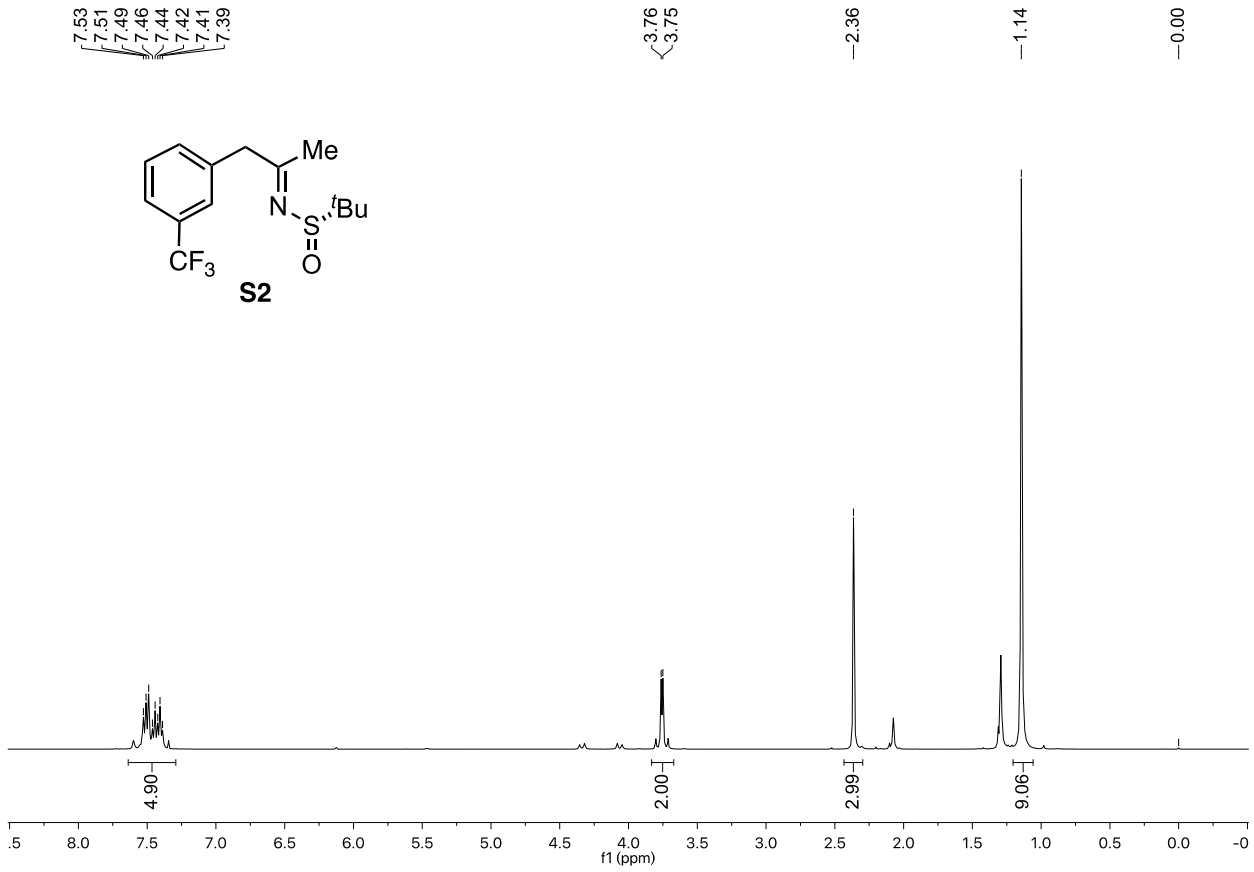
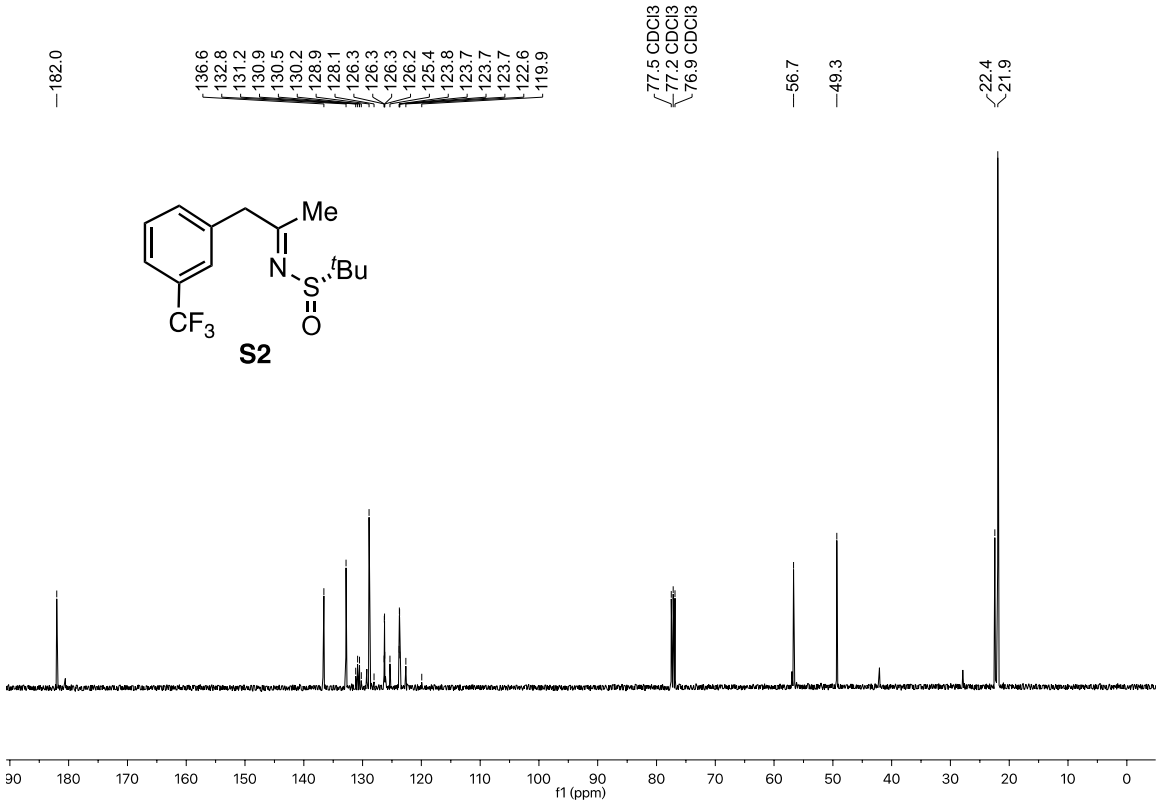
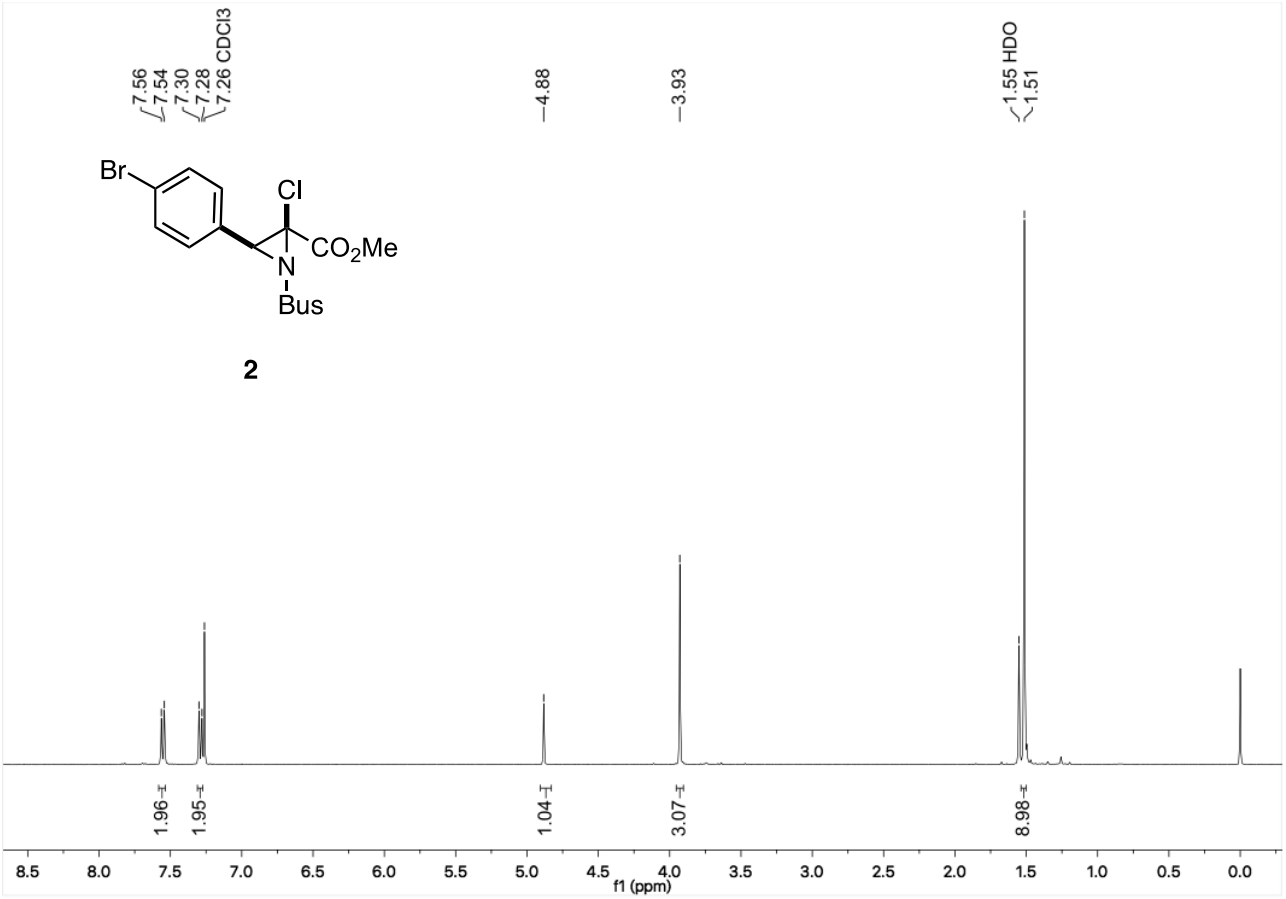
XII. ^{1}H NMR and ^{13}C NMR charts



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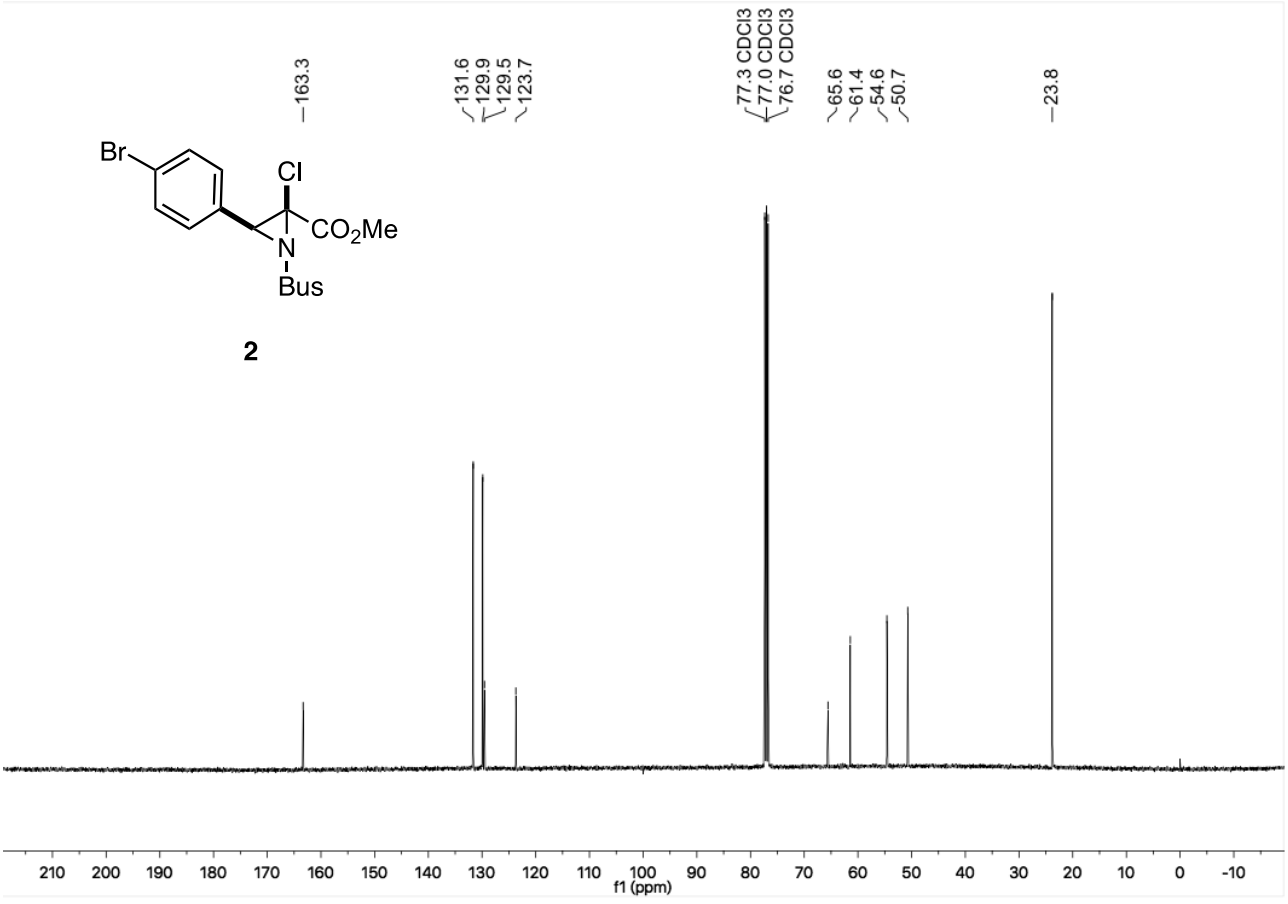
7.54
7.30
7.28
7.26 CDCl3
4.88
3.93
1.55 HDO
1.51
Br
Cl
CO2Me
N
Bus
1.96
1.95
1.04
3.07
8.98
f1 (ppm)

2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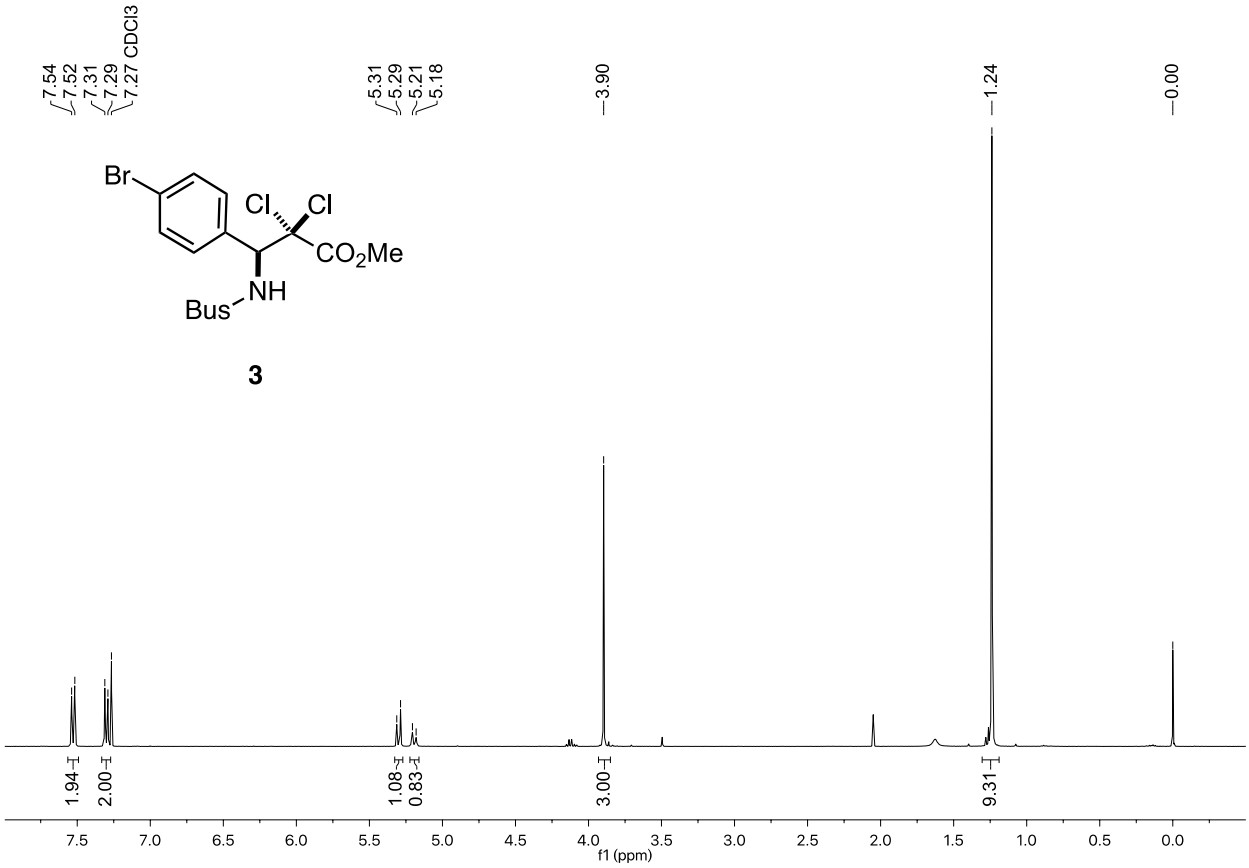
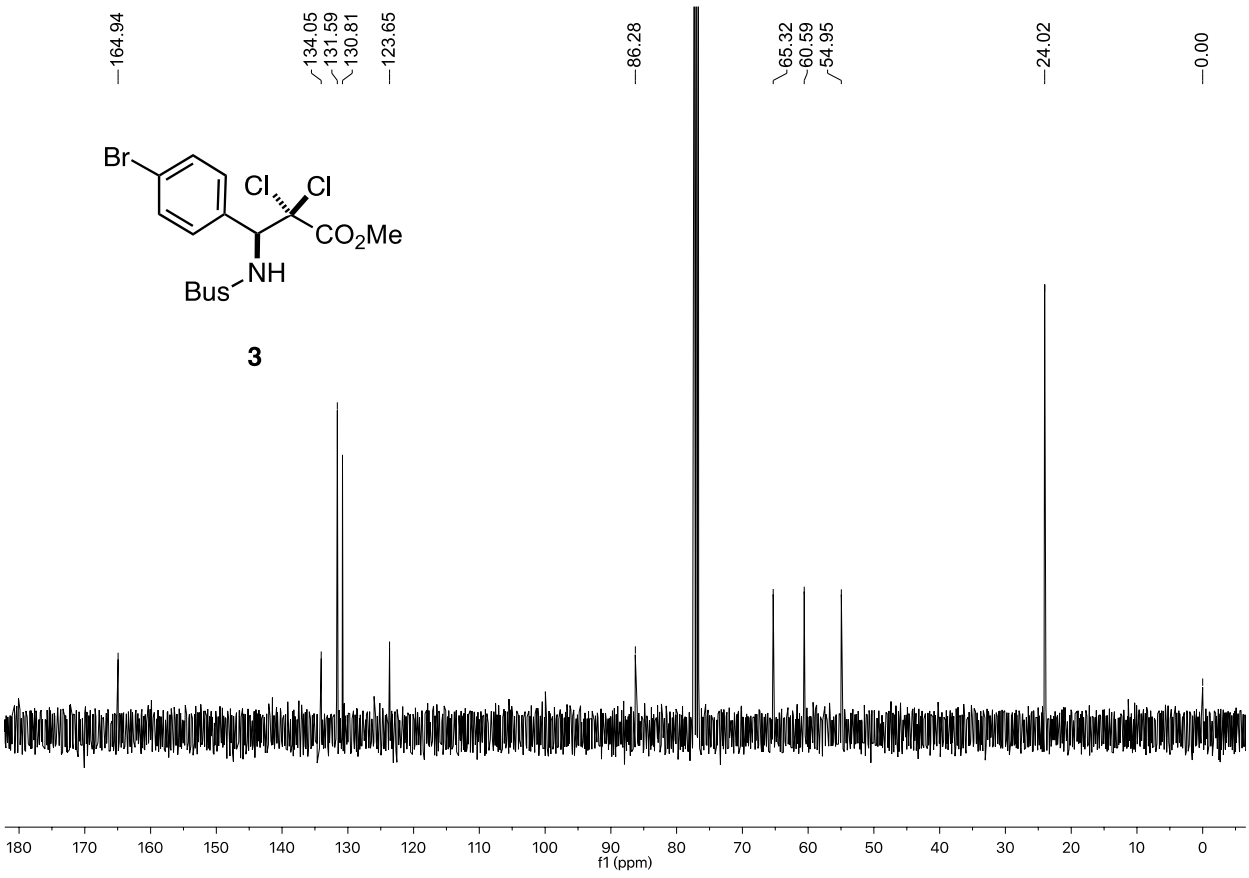
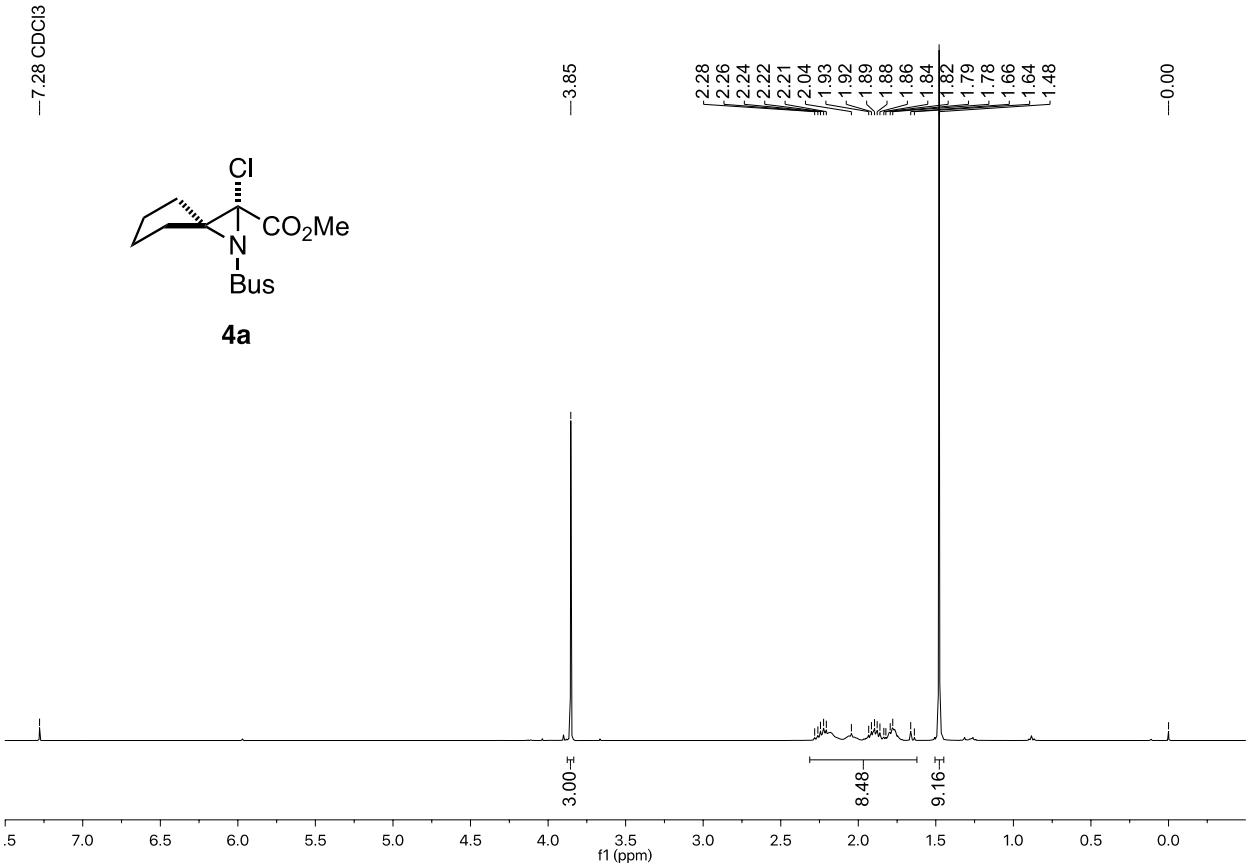
131.6
129.9
129.5
123.7
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
65.6
61.4
54.6
50.7
23.8
Br
Cl
CO2Me
N
Bus
f1 (ppm)

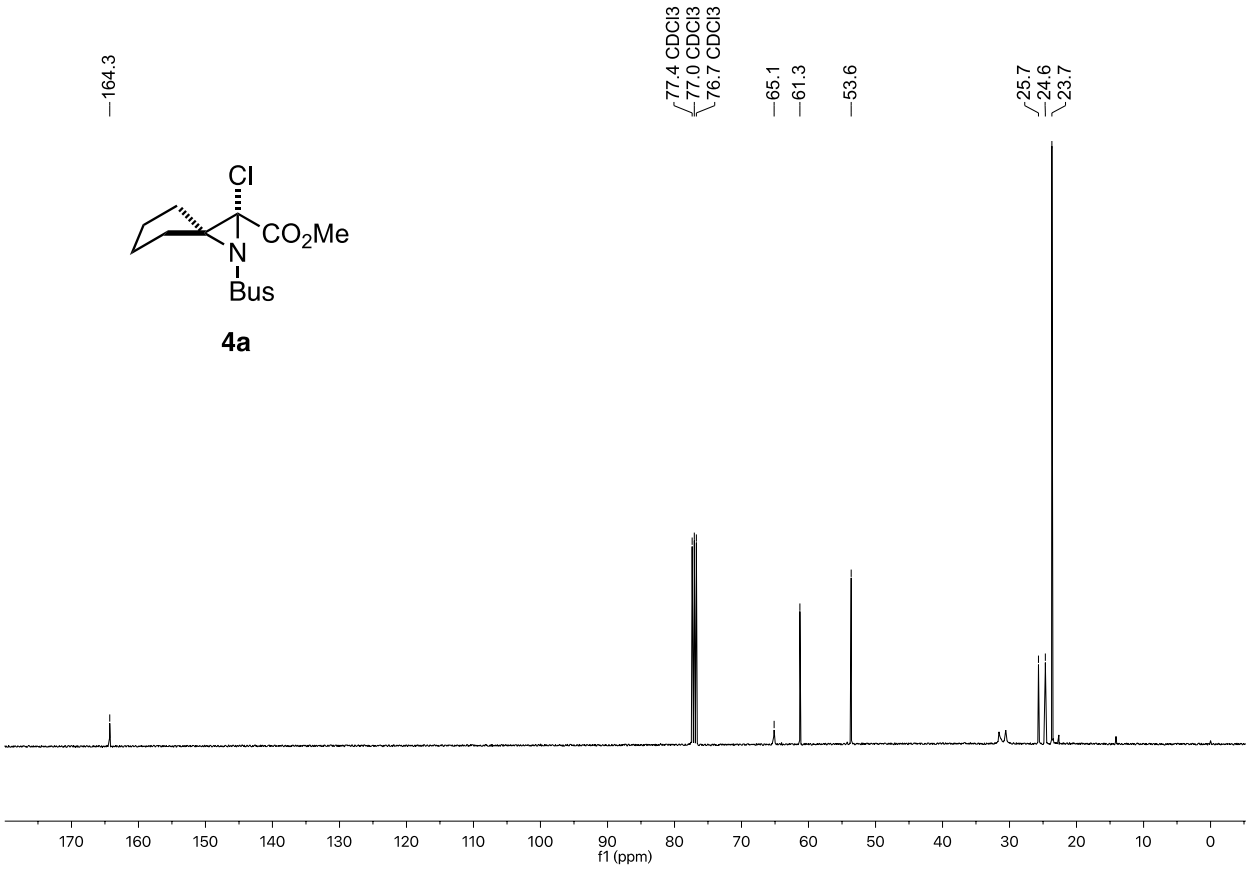
2


7.54
7.52
7.31
7.29
7.27 CDCl3
5.31
5.29
5.21
5.18
3.90
1.24
0.00
Br
Cl
Cl
CO2Me
NH
Bus
3
1.94
2.00
1.08
0.83
3.00
9.31
f1 (ppm)

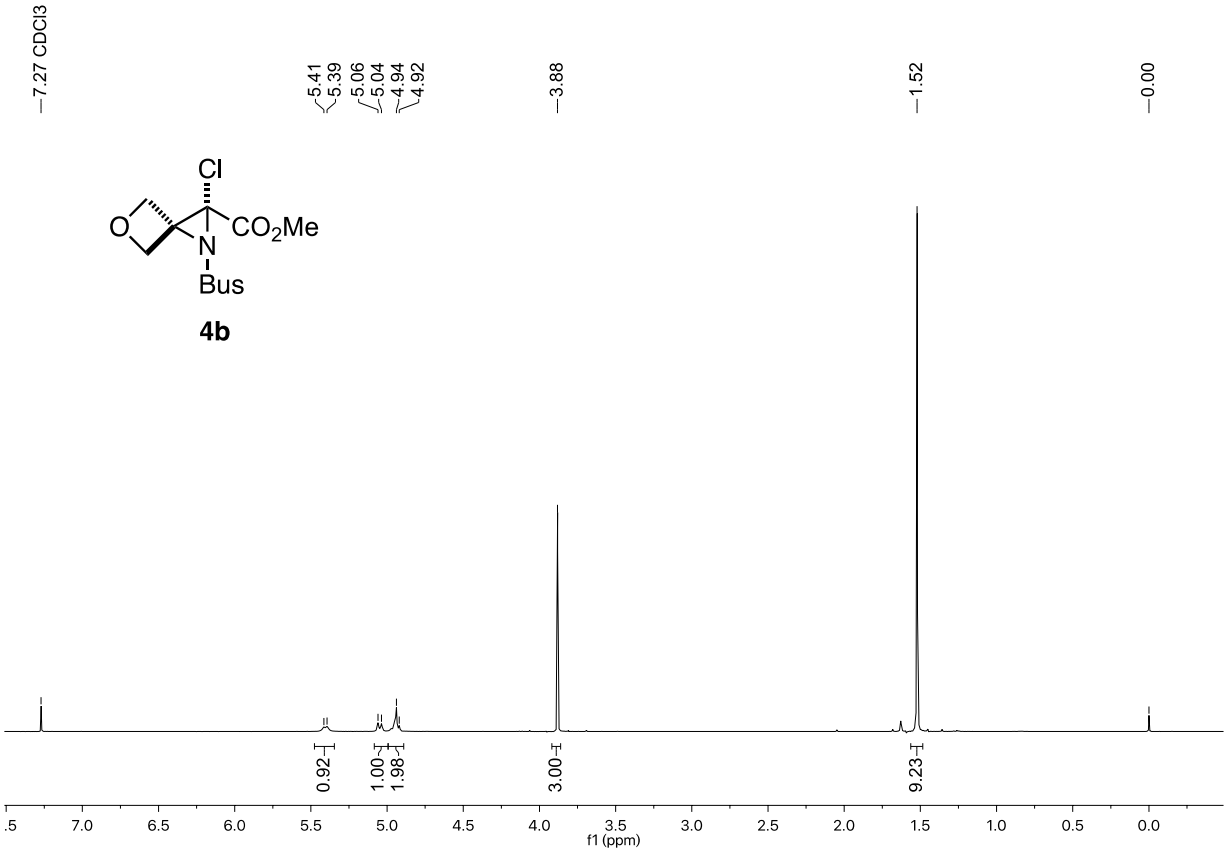

164.94
134.05
131.59
130.81
123.65
86.28
65.32
60.59
54.95
24.02
0.00
Br
Cl
Cl
CO2Me
NH
Bus
3
f1 (ppm)

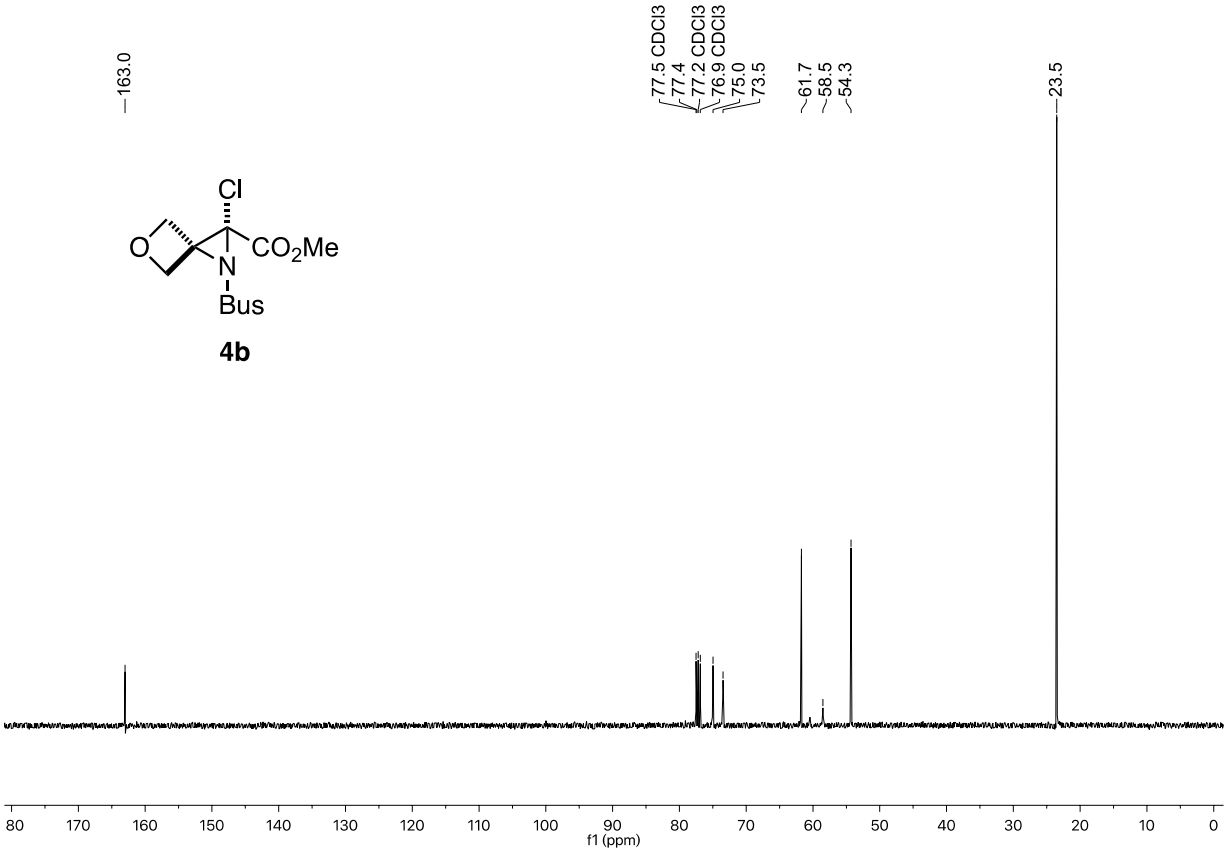

7.28 CDCl3
3.85
2.28
2.26
2.24
2.22
2.21
2.04
1.93
1.92
1.89
1.88
1.86
1.84
1.82
1.79
1.78
1.66
1.64
1.48
0.00
Cl
CO2Me
N
Bus
3.00
8.48
9.16
f1 (ppm)

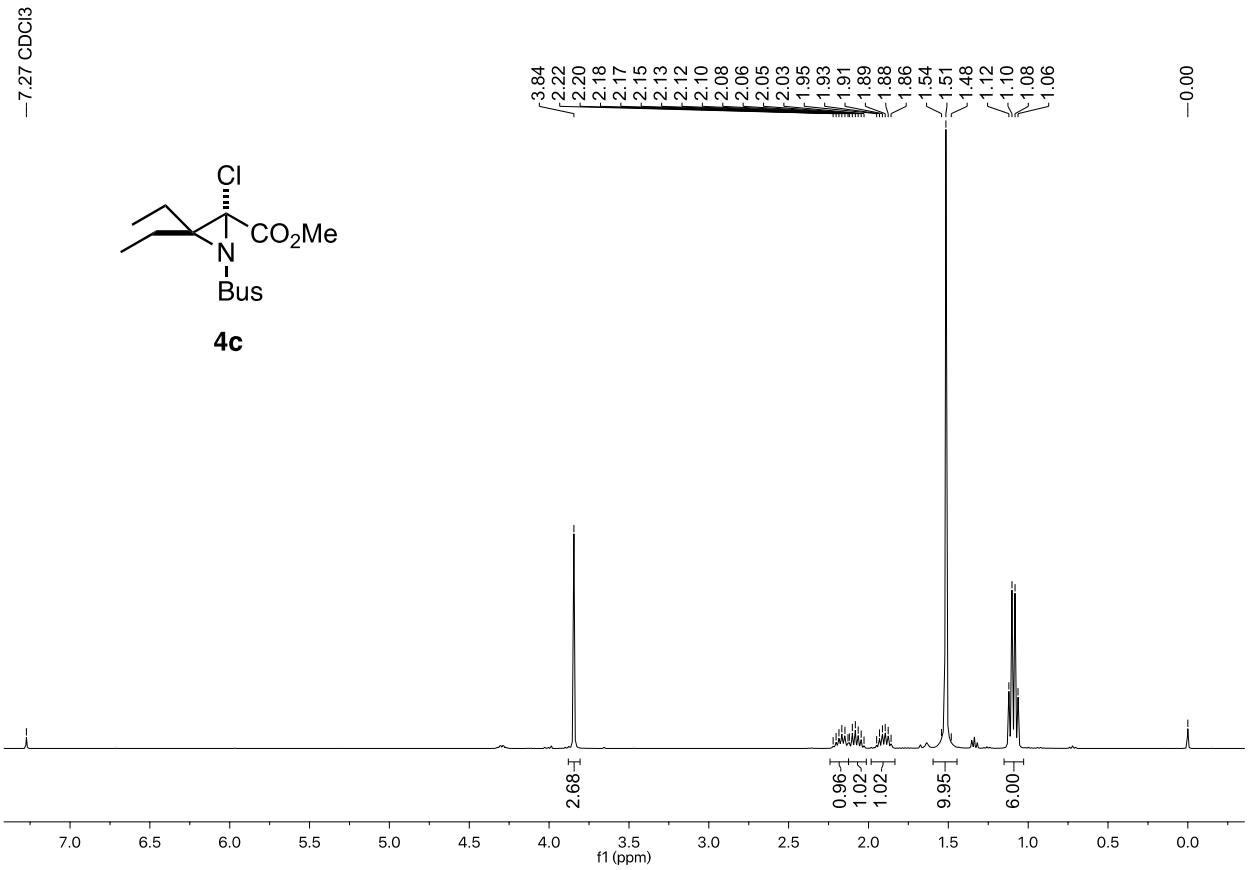
4a

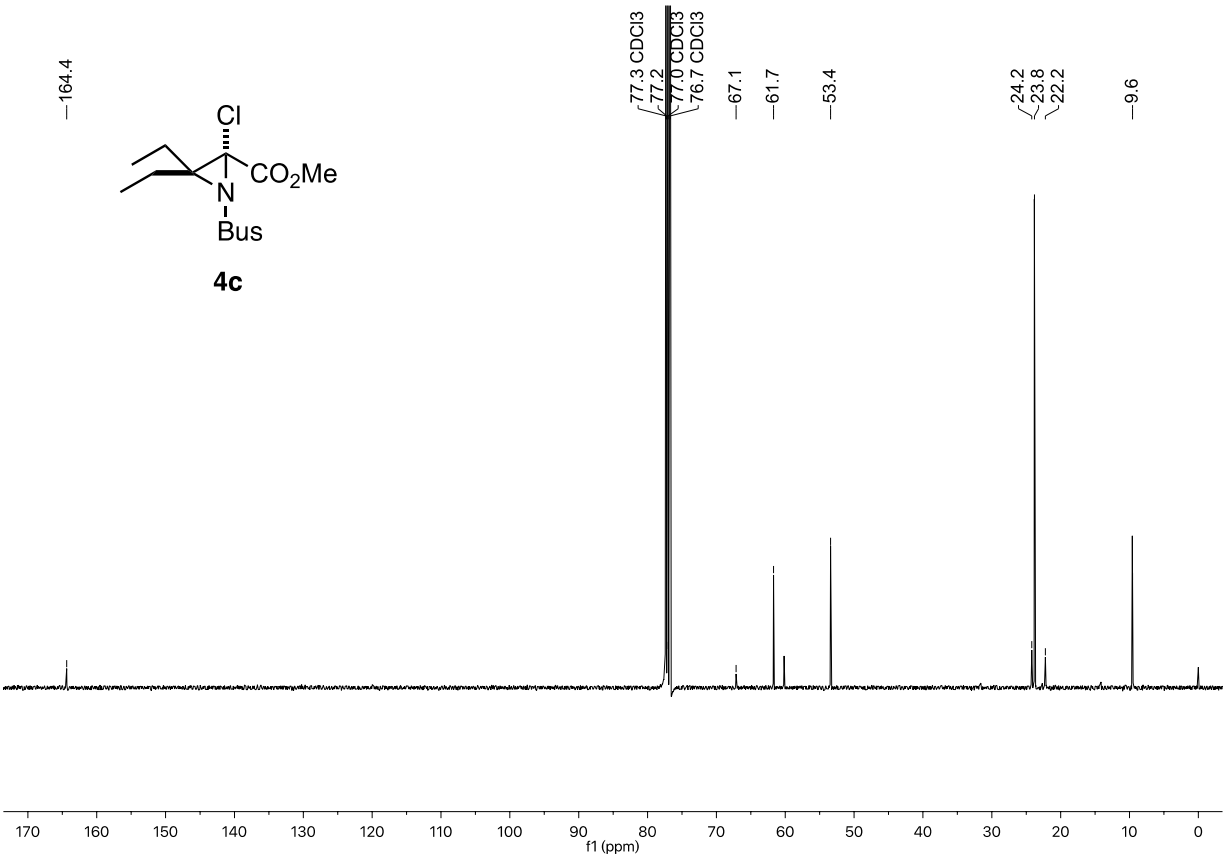

164.3
77.4 CDCl3
77.0 CDCl3
76.7 CDCl3
65.1
61.3
53.6
25.7
24.6
23.7
Cl
CO2Me
N
Bus
f1 (ppm)

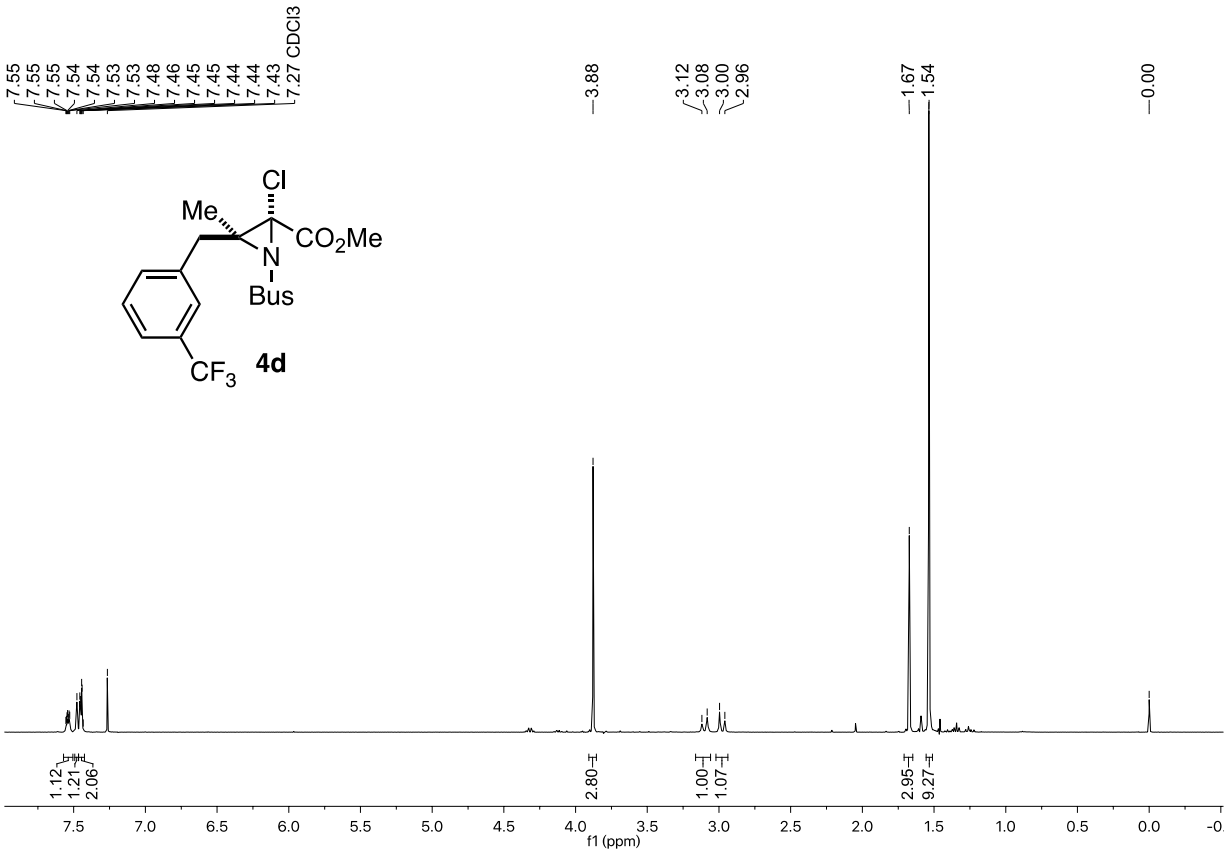
4a

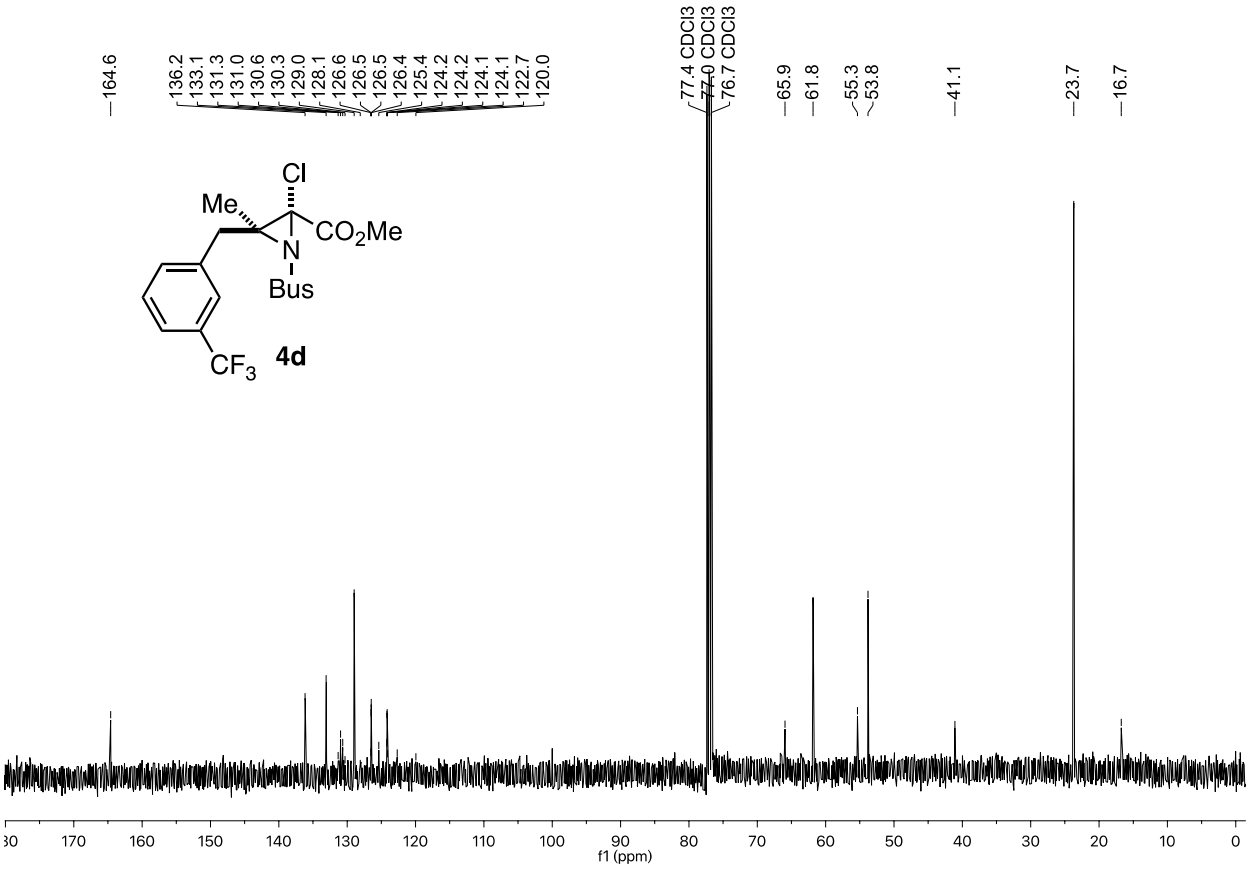

7.27 CDCl3
5.41
5.39
5.06
5.04
4.94
4.92
3.88
1.52
0.00
Cl
O
CO2Me
N
Bus
4b
0.92
1.00
1.98
3.00
9.23
f1 (ppm)

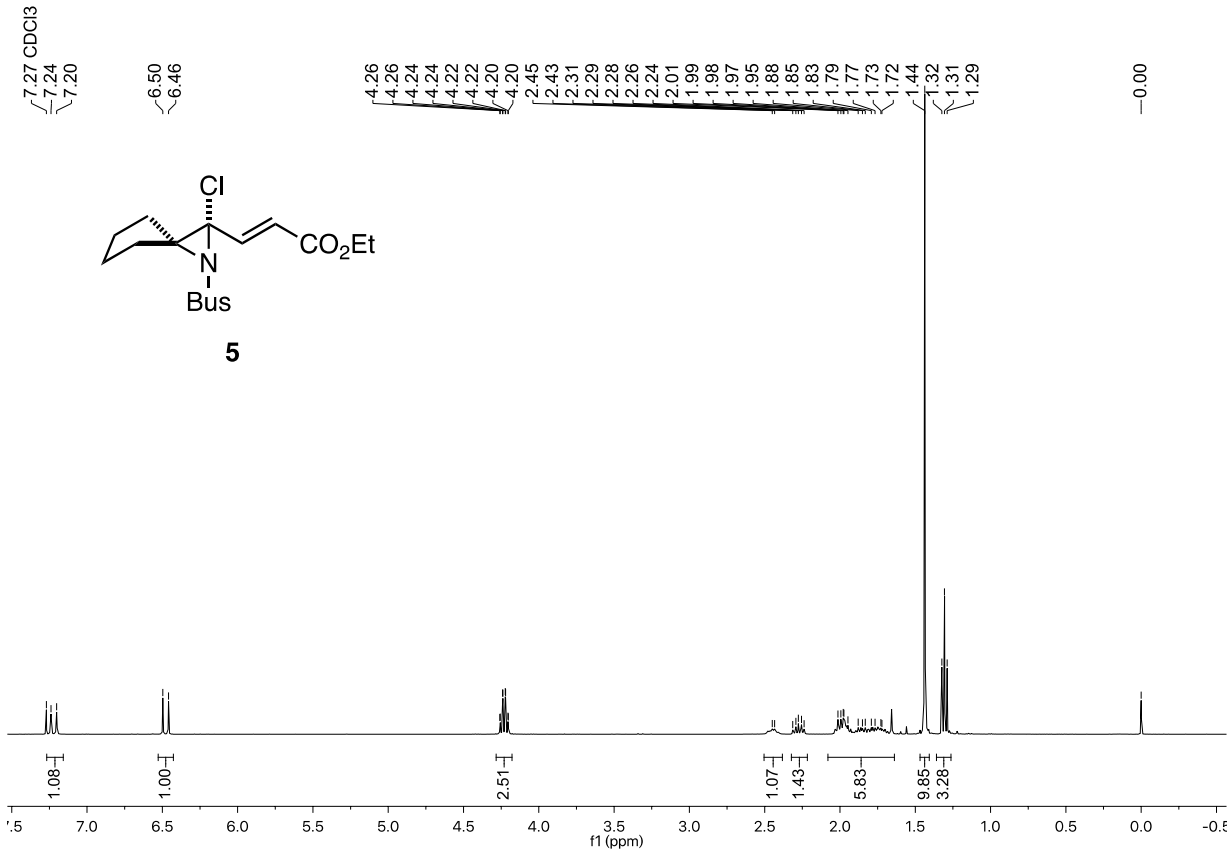

163.0
77.5 CDCl3
77.4
77.2 CDCl3
76.9 CDCl3
75.0
73.5
61.7
58.5
54.3
23.5
Cl
O
CO2Me
N
Bus
4b
f1 (ppm)


7.27 CDCl3
3.84
2.22
2.20
2.18
2.17
2.15
2.13
2.12
2.10
2.08
2.06
2.05
2.03
1.95
1.93
1.91
1.89
1.88
1.86
1.54
1.51
1.48
1.12
1.10
1.08
1.06
0.00
Cl
CO2Me
N
Bus
4c
2.68
0.96
1.02
1.02
9.95
6.00
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

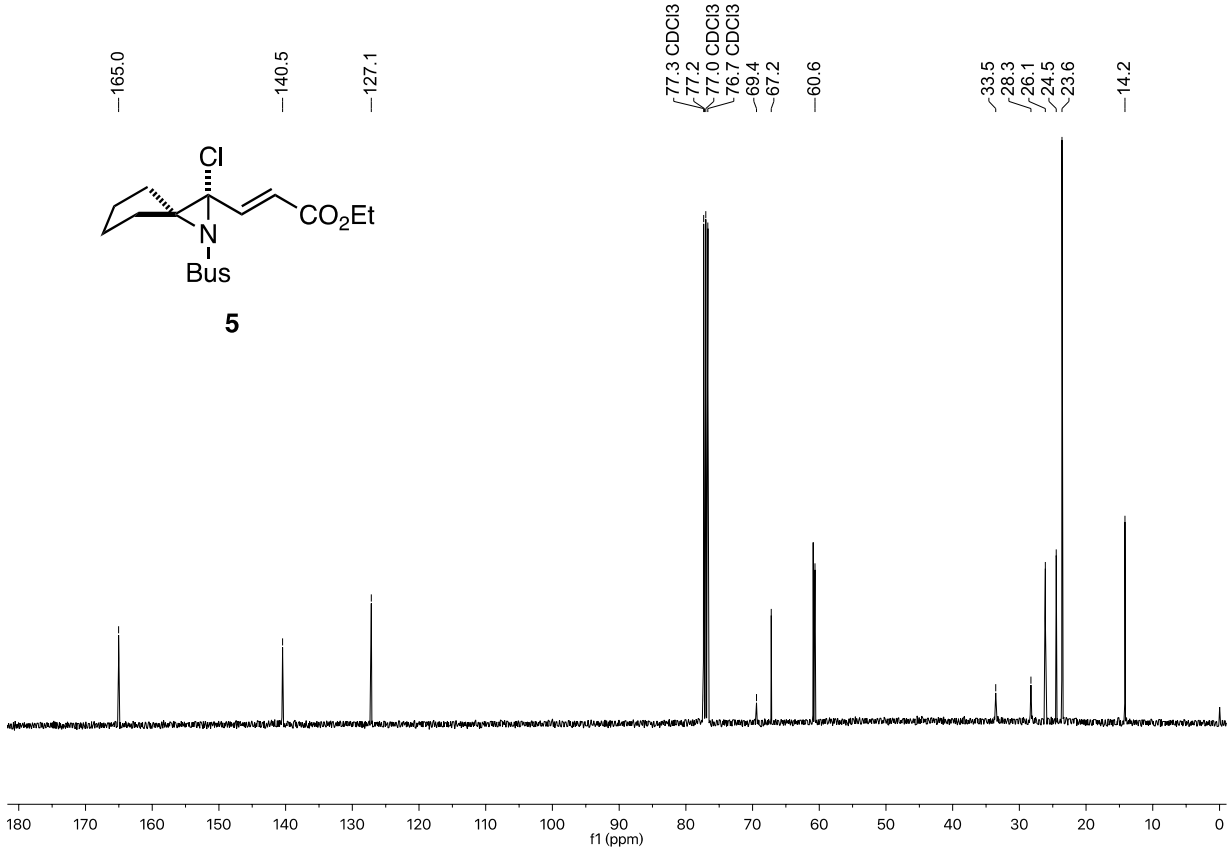

164.4
77.3 CDCl3
77.2
77.0 CDCl3
76.7 CDCl3
67.1
61.7
53.4
24.2
23.8
22.2
9.6
Cl
CO2Me
N
Bus
4c
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.55
7.55
7.55
7.54
7.54
7.53
7.53
7.48
7.46
7.45
7.45
7.44
7.44
7.43
7.27 CDCl3
3.88
3.12
3.08
3.00
2.96
1.67
1.54
0.00
Cl
Me
CO2Me
N
Bus
CF3
4d
1.12
1.21
2.06
2.80
1.00
1.07
2.95
9.27
f1 (ppm)

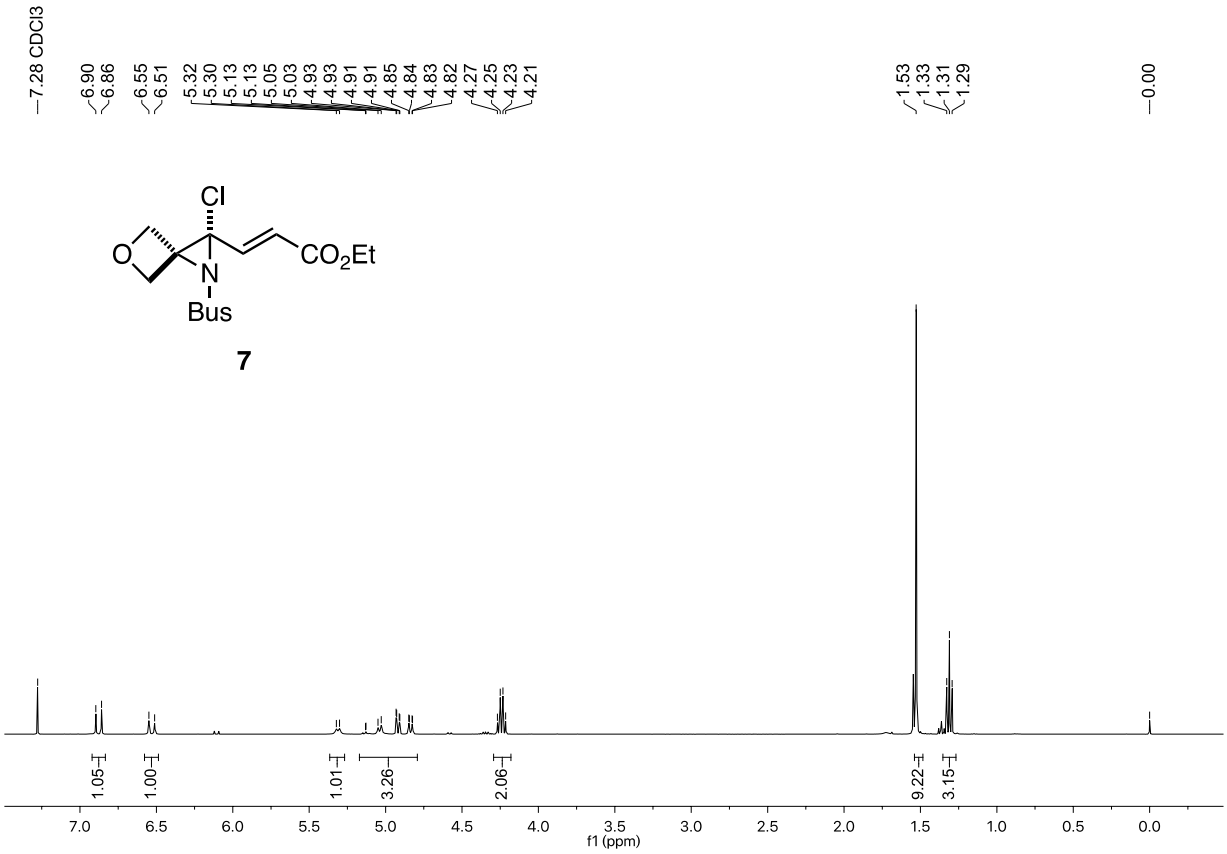

164.6
136.2
133.1
131.3
131.0
130.6
130.3
129.0
128.1
126.6
126.5
126.5
126.4
125.4
124.2
124.2
124.1
124.1
122.7
120.0
77.4 CDCl3
77.0 CDCl3
76.7 CDCl3
65.9
61.8
55.3
53.8
41.1
23.7
16.7
Cl
Me
CO2Me
N
Bus
CF3
4d
f1 (ppm)

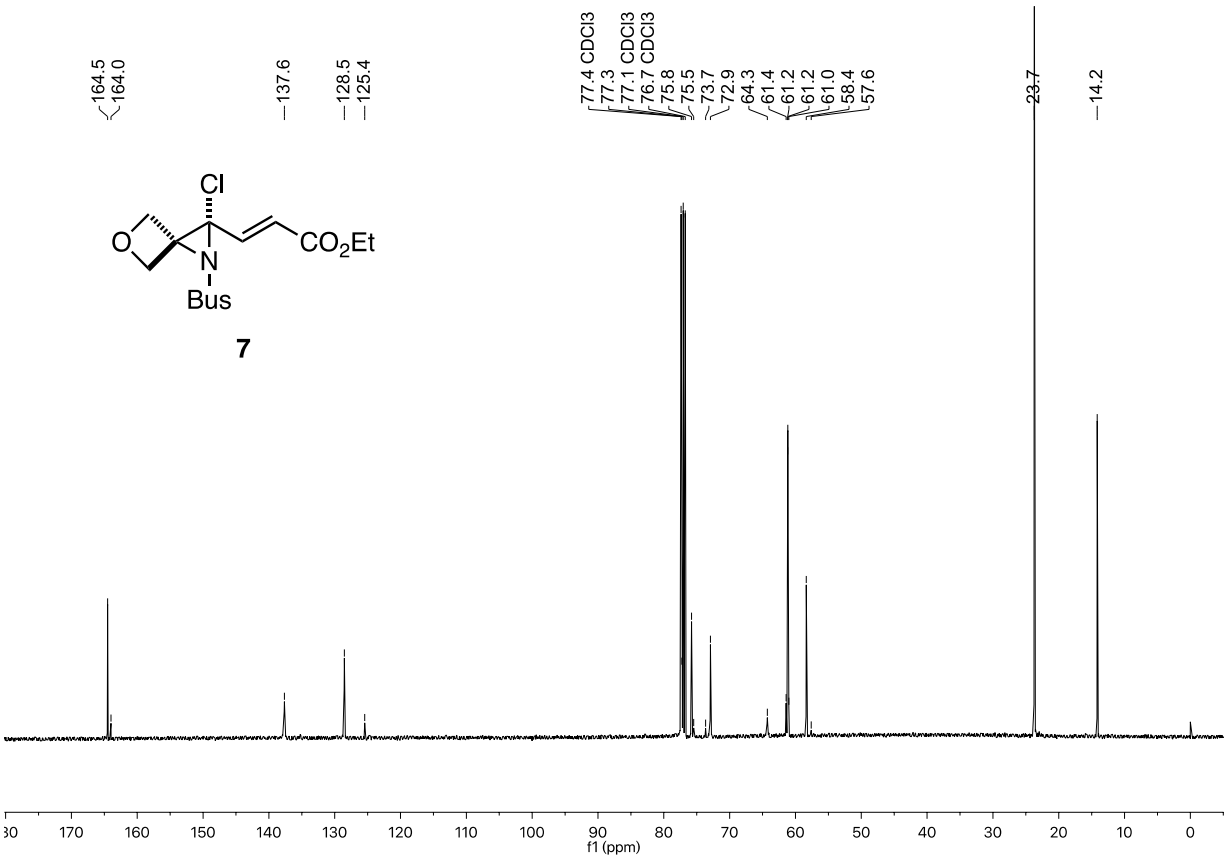

7.27 CDCl3
7.24
7.20
6.50
6.46
4.26
4.26
4.24
4.24
4.22
4.22
4.20
4.20
2.45
2.43
2.31
2.29
2.28
2.26
2.24
2.01
1.99
1.98
1.97
1.95
1.88
1.85
1.83
1.79
1.77
1.73
1.72
1.44
1.32
1.31
1.29
0.00
Cl
CO2Et
N
Bus
1.08
1.00
2.51
1.07
1.43
5.83
9.85
3.28
f1 (ppm)

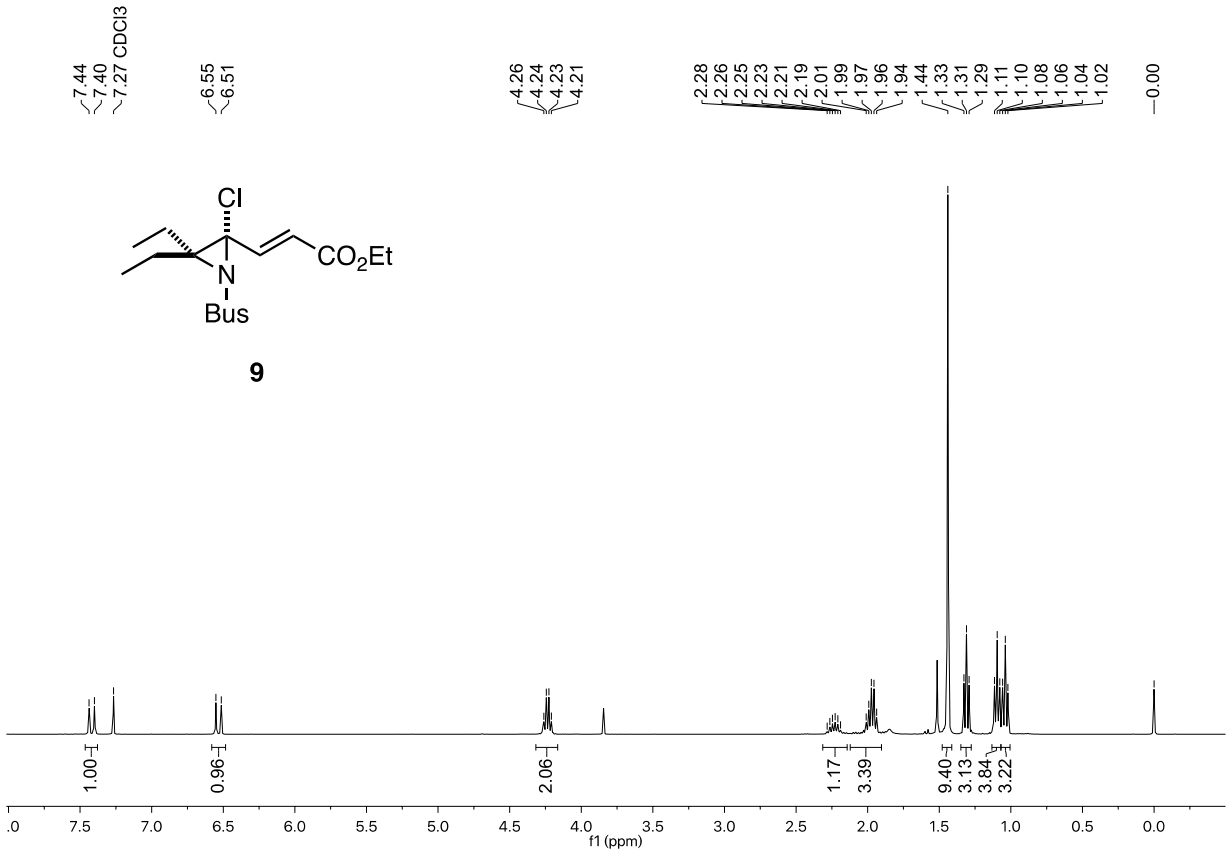
5


165.0
140.5
127.1
77.3 CDCl3
77.2
77.0 CDCl3
76.7 CDCl3
69.4
67.2
60.6
33.5
28.3
26.1
24.5
23.6
14.2
Cl
CO2Et
N
Bus
f1 (ppm)

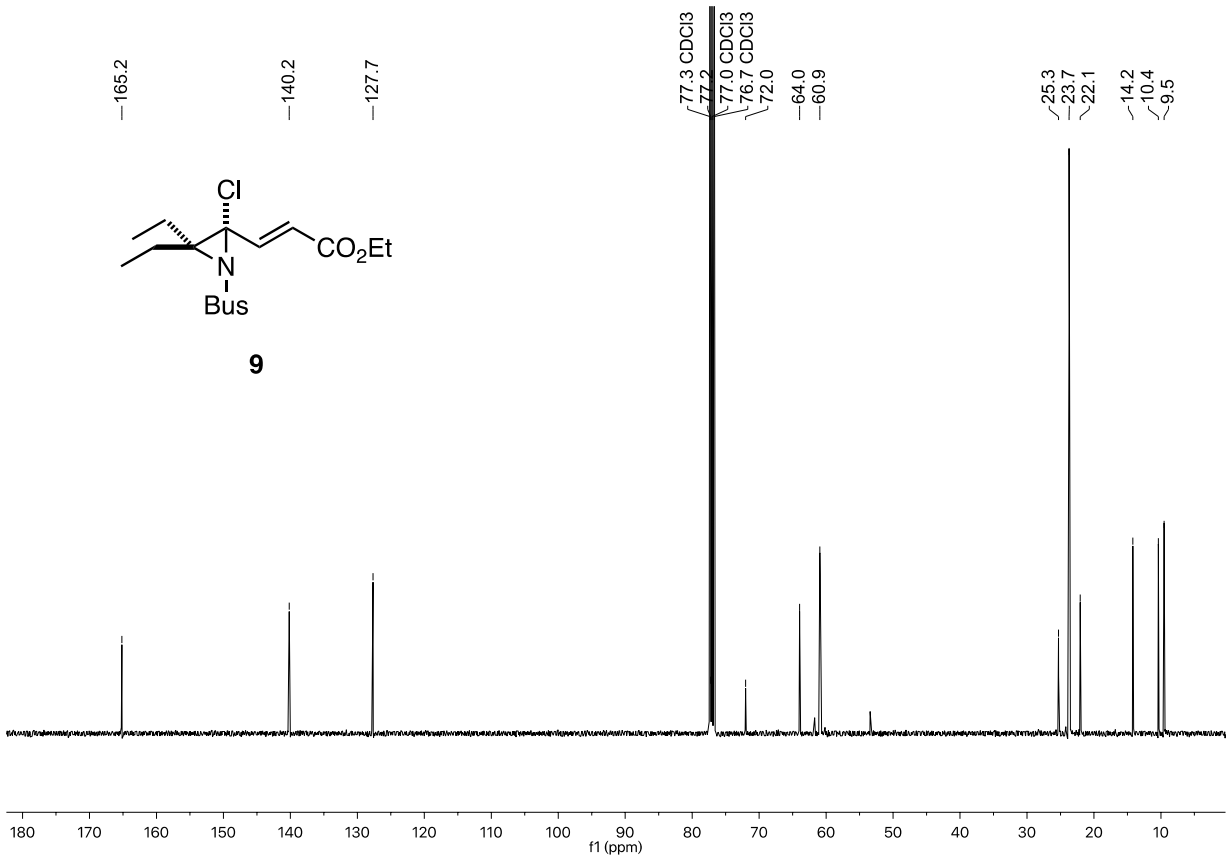
5


7.28 CDCl3
6.90
6.86
6.55
6.51
5.32
5.30
5.13
5.13
5.05
5.03
4.93
4.93
4.91
4.91
4.85
4.84
4.83
4.82
4.27
4.25
4.23
4.21
1.53
1.33
1.31
1.29
0.00
Cl
O
N
Bus
CO2Et
7
1.05
1.00
1.01
3.26
2.06
9.22
3.15
f1 (ppm)

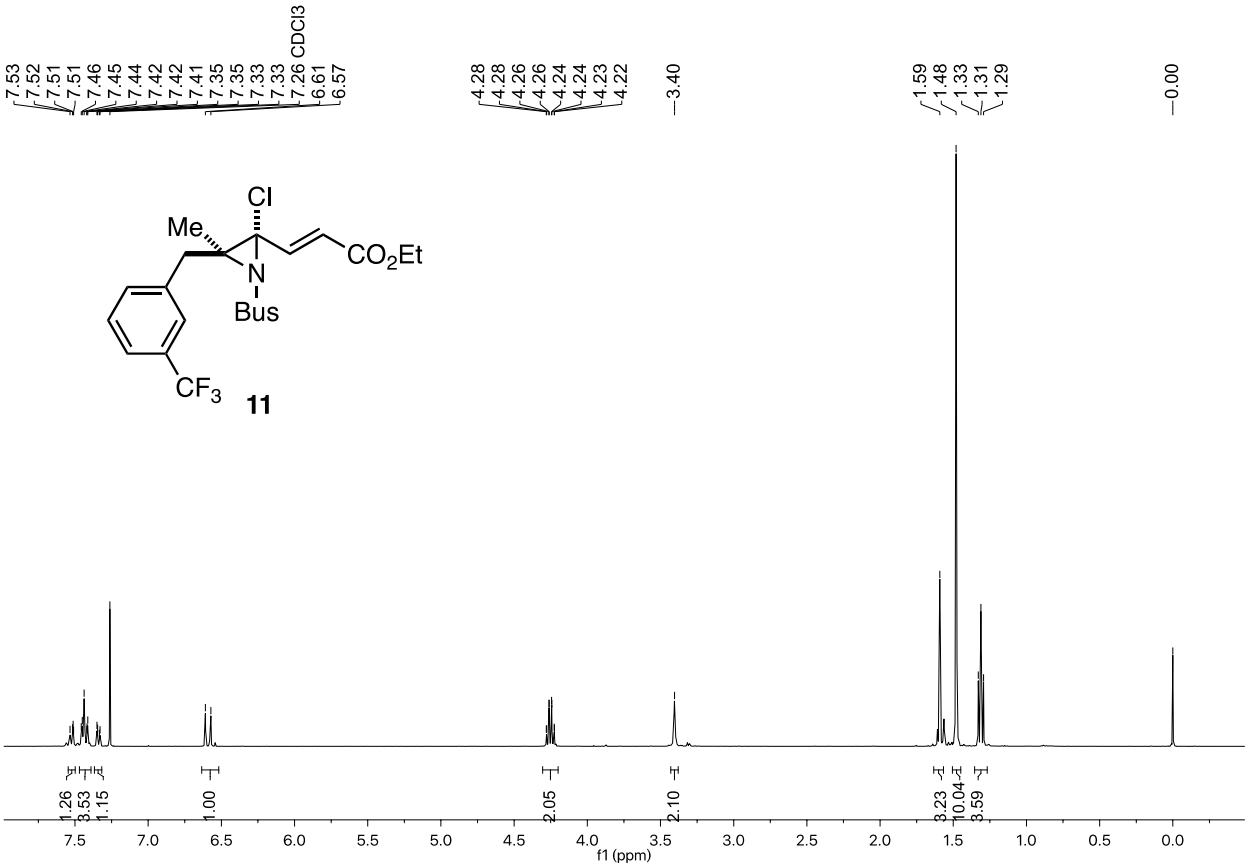

164.5
164.0
137.6
128.5
125.4
77.4 CDCl3
77.3
77.1 CDCl3
76.7 CDCl3
75.8
75.5
73.7
72.9
64.3
61.4
61.2
61.2
61.0
58.4
57.6
23.7
14.2
Cl
O
N
Bus
CO2Et
7
f1 (ppm)

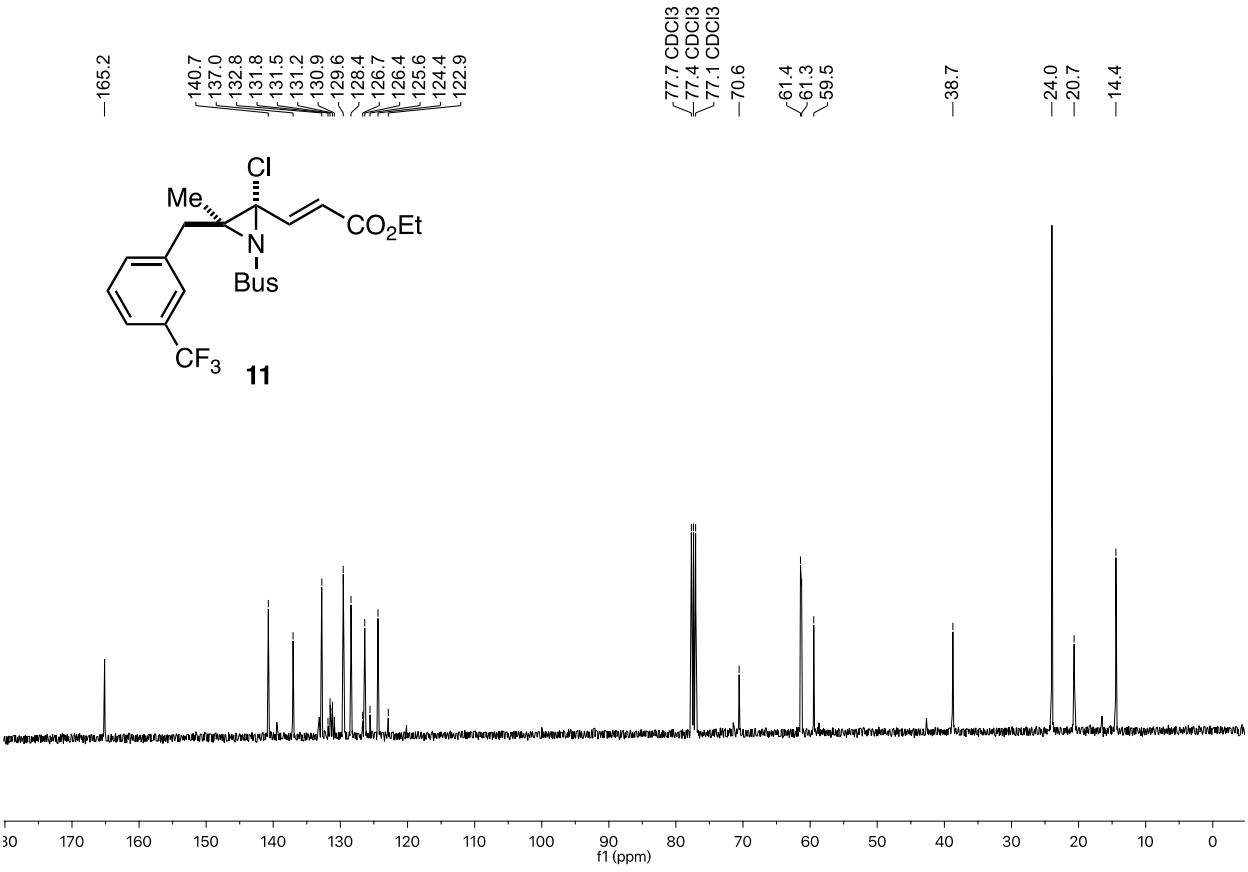

7.44
7.40
7.27 CDCl3
6.55
6.51
4.26
4.24
4.23
4.21
2.28
2.26
2.25
2.23
2.21
2.19
2.01
1.99
1.97
1.96
1.94
1.44
1.33
1.31
1.29
1.11
1.10
1.08
1.06
1.04
1.02
0.00
Cl
CO2Et
N
Bus
1.00
0.96
2.06
1.17
3.39
9.40
3.13
3.84
3.22
f1 (ppm)

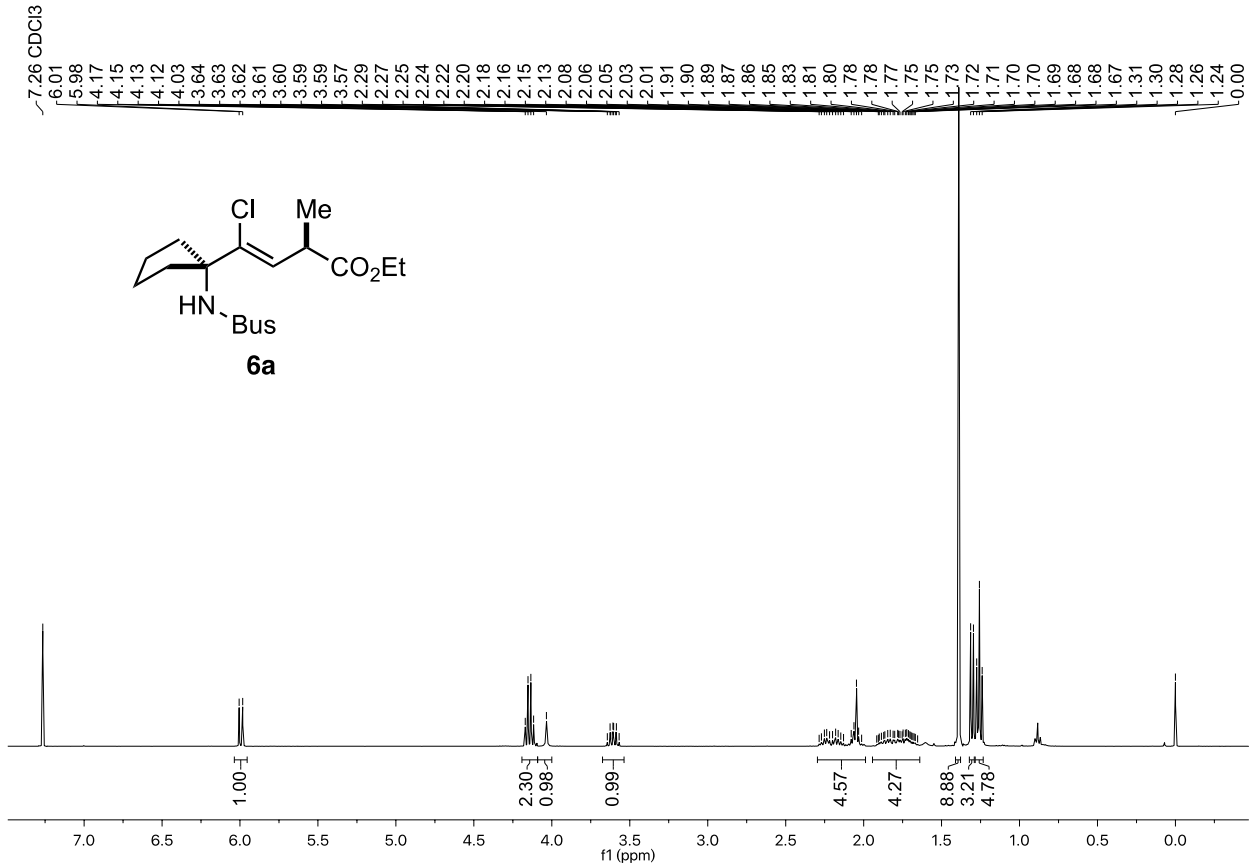
9

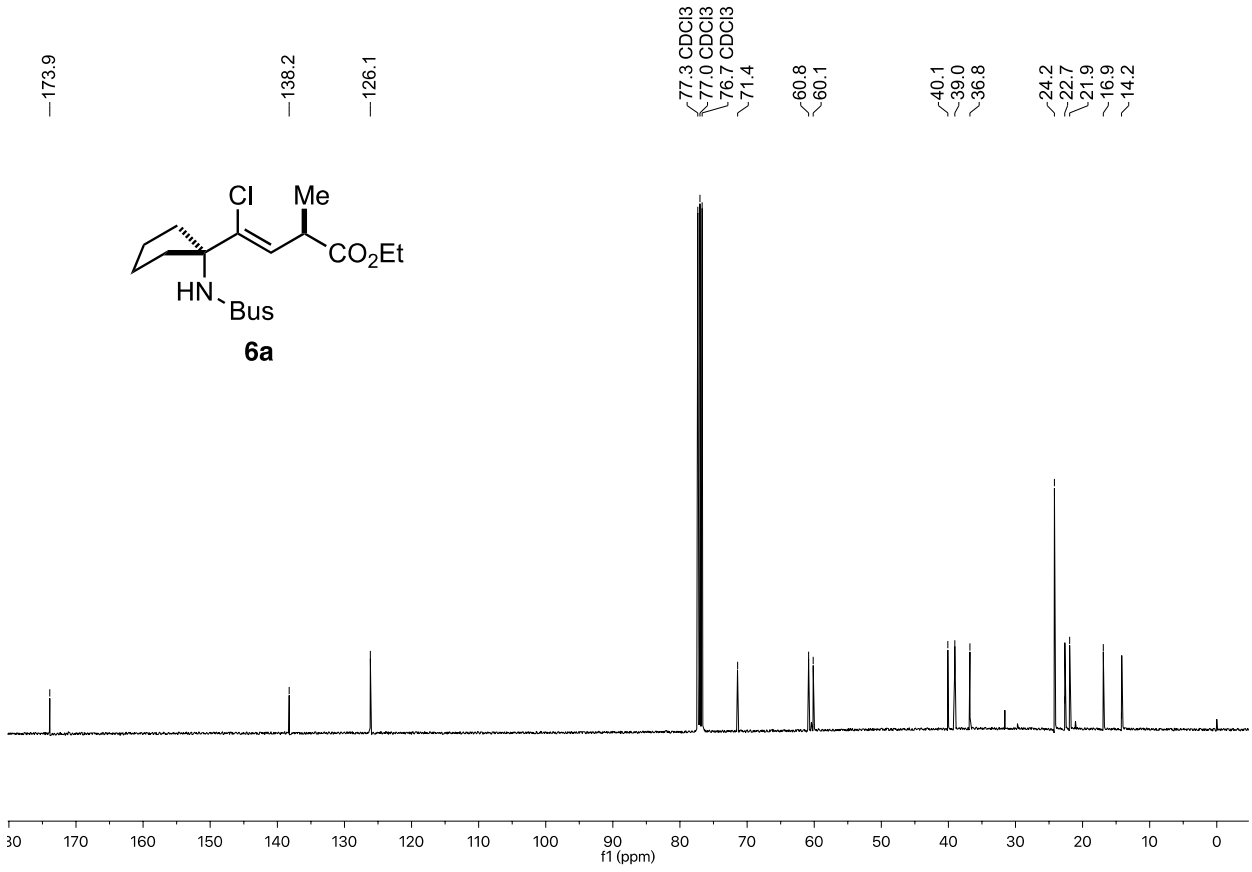

165.2
140.2
127.7
77.3 CDCl3
77.2
77.0 CDCl3
76.7 CDCl3
72.0
64.0
60.9
25.3
23.7
22.1
14.2
10.4
9.5
Cl
CO2Et
N
Bus
f1 (ppm)

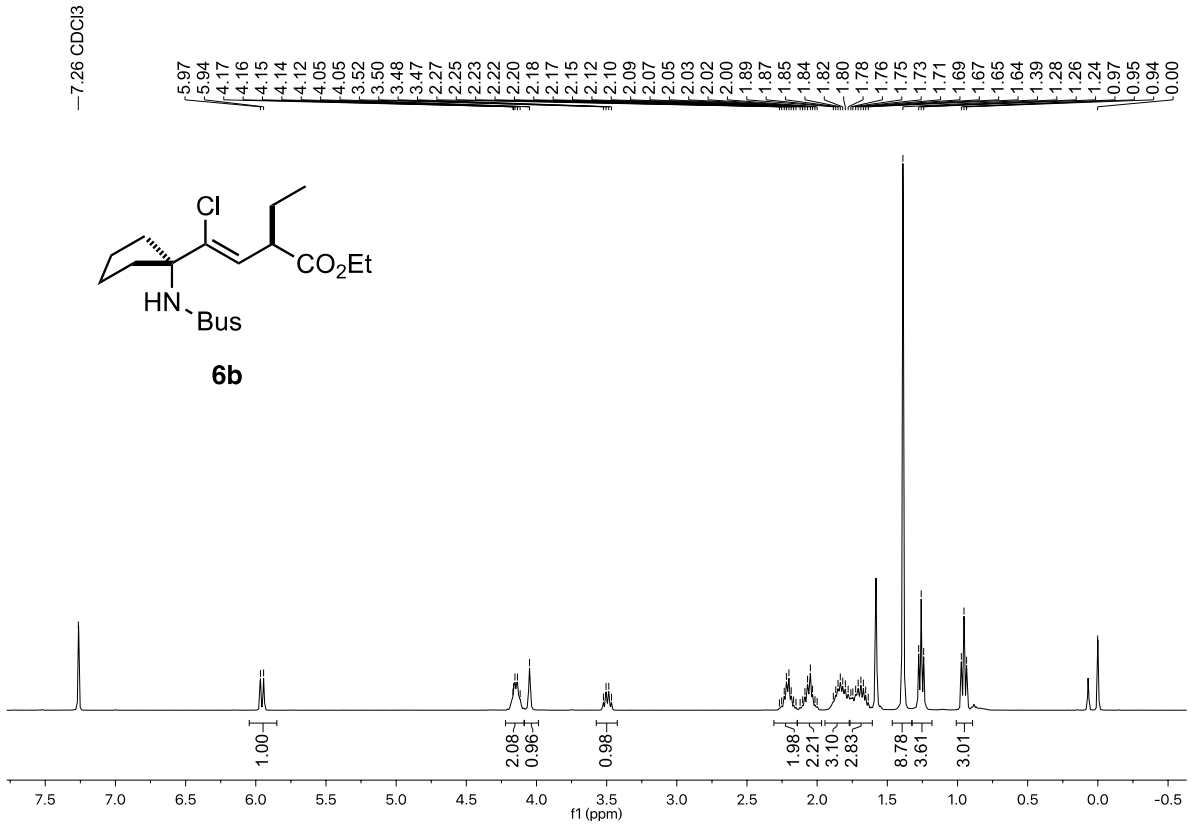
9

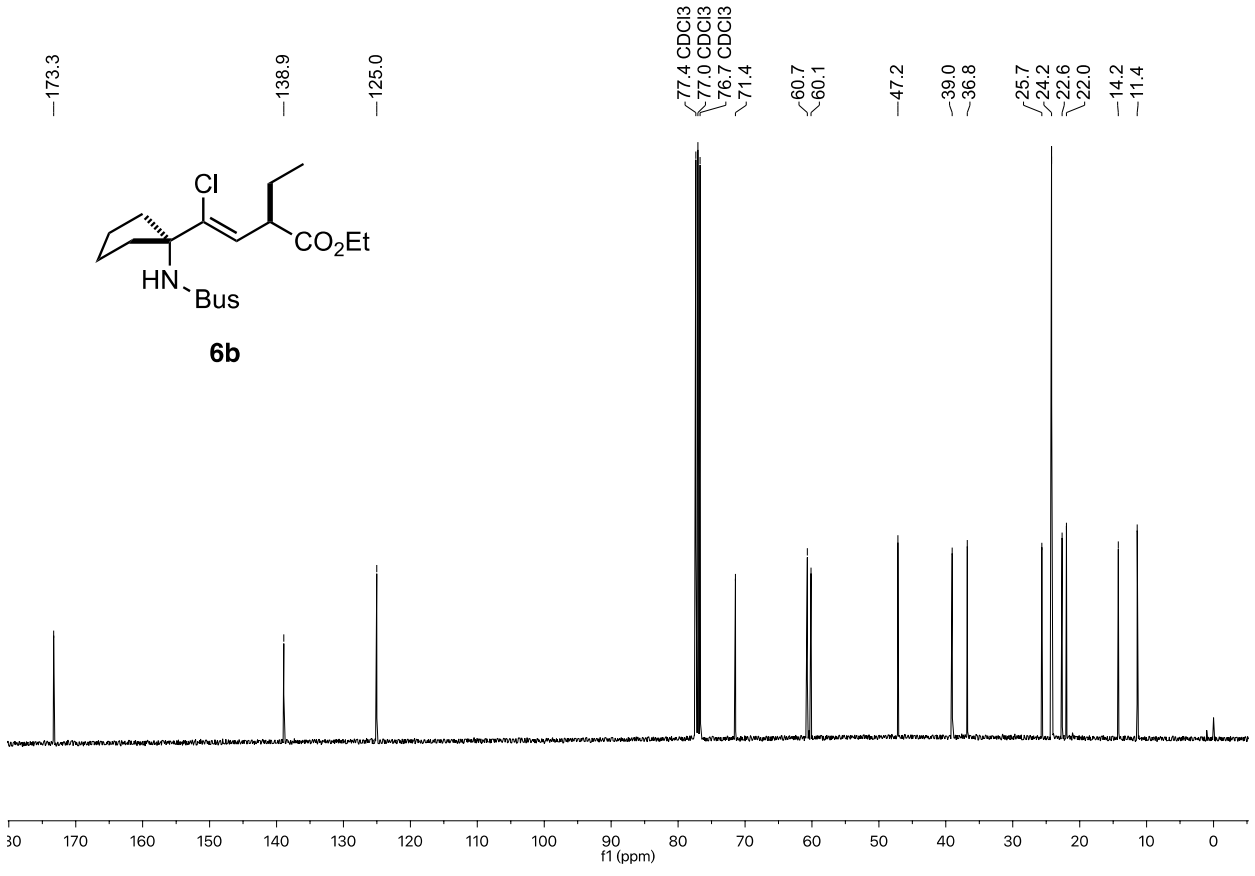

7.53
7.52
7.51
7.51
7.46
7.45
7.44
7.42
7.42
7.41
7.35
7.35
7.33
7.33
7.26 CDCl3
6.61
6.57
4.28
4.28
4.26
4.26
4.24
4.24
4.23
4.22
3.40
1.59
1.48
1.33
1.31
1.29
0.00
Cl
Me
N
Bus
CO2Et
CF3
11
1.26
3.53
1.15
1.00
2.05
2.10
3.23
10.04
3.59
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

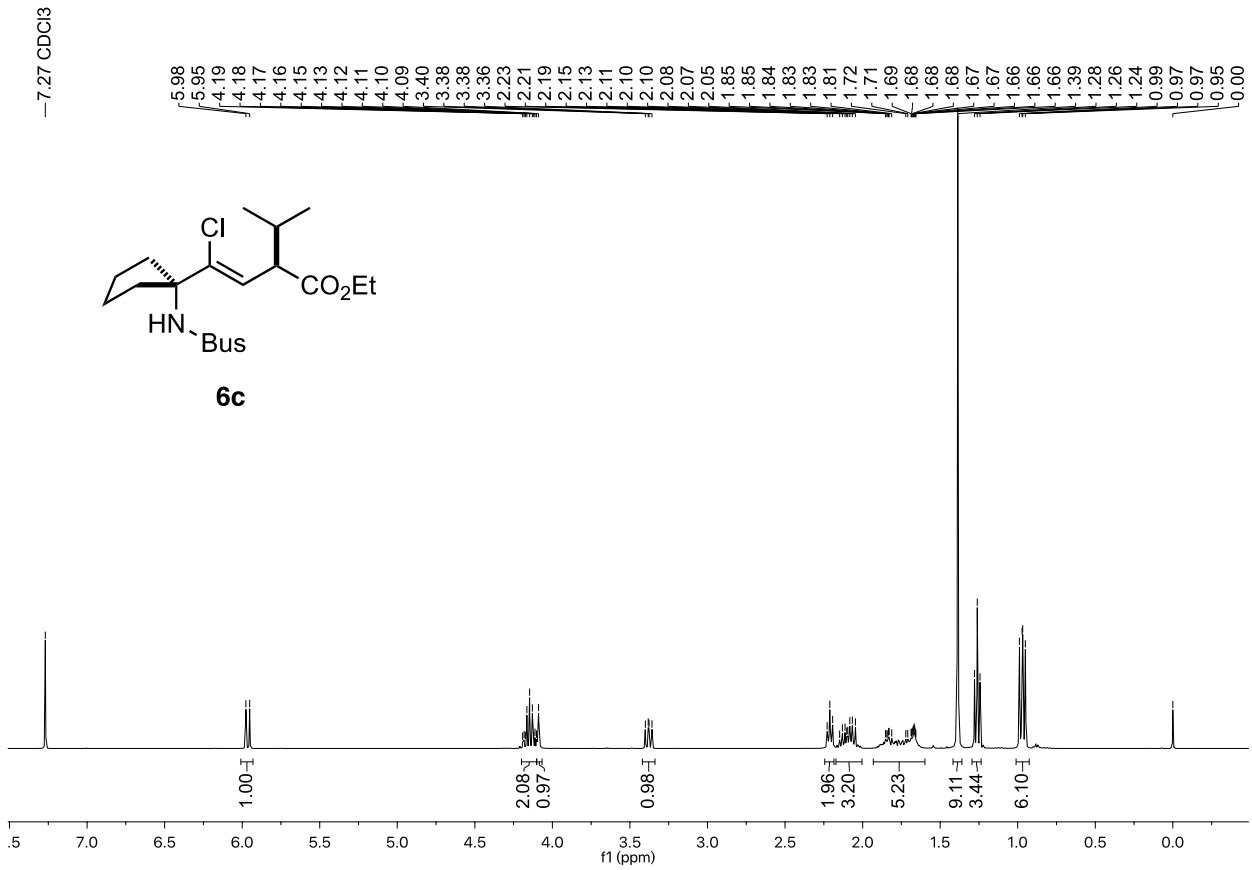

165.2
140.7
137.0
132.8
131.8
131.5
131.2
130.9
129.6
128.4
126.7
126.4
125.6
124.4
122.9
77.7 CDCl3
77.4 CDCl3
77.1 CDCl3
70.6
61.4
61.3
59.5
38.7
24.0
20.7
14.4
Cl
Me
N
Bus
CO2Et
CF3
11
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

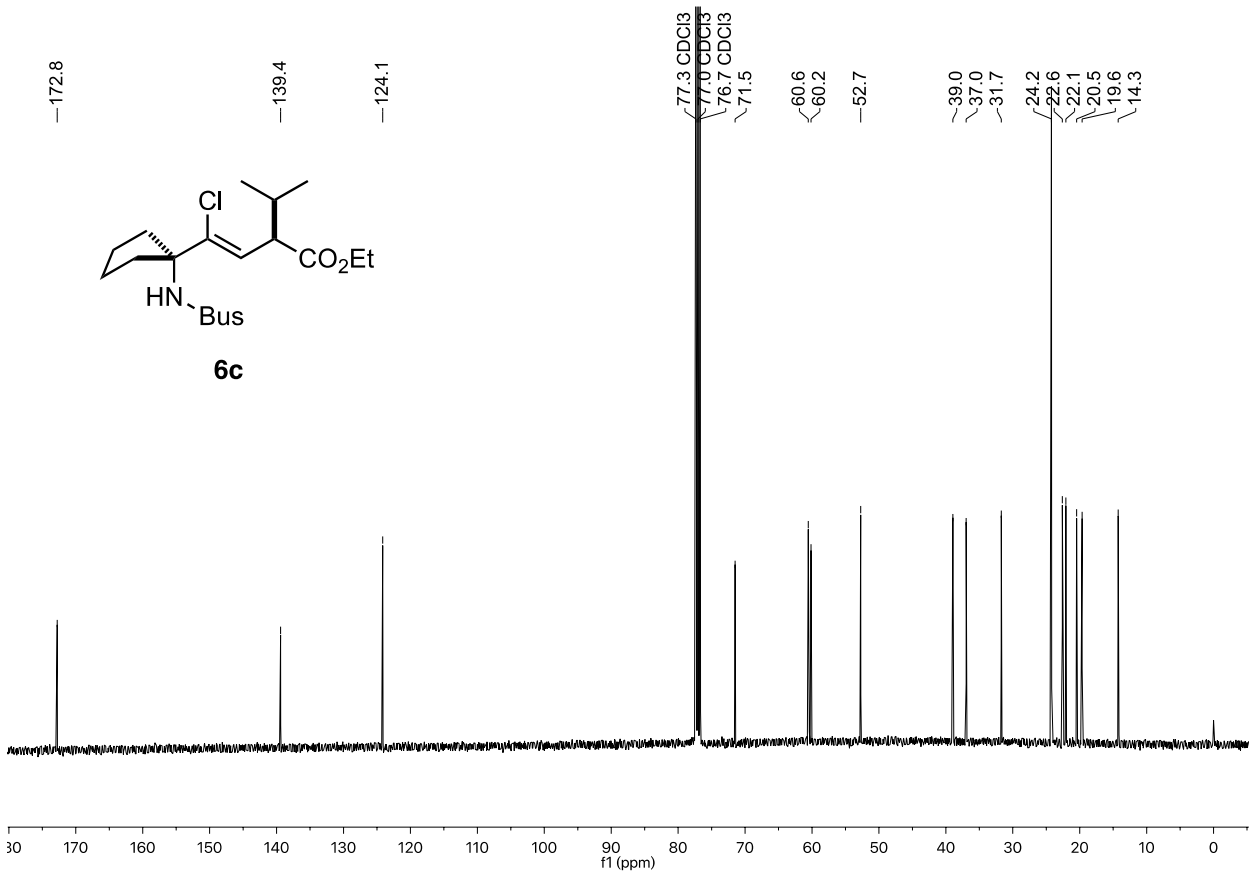

7.26 CDCl3
6.01
5.98
4.17
4.15
4.13
4.12
4.03
3.64
3.63
3.62
3.61
3.60
3.59
3.59
3.57
2.29
2.27
2.25
2.24
2.22
2.20
2.18
2.16
2.15
2.13
2.08
2.06
2.05
2.03
2.01
1.91
1.90
1.89
1.87
1.86
1.85
1.83
1.81
1.80
1.78
1.78
1.77
1.75
1.75
1.73
1.72
1.71
1.70
1.70
1.69
1.68
1.68
1.67
1.31
1.30
1.28
1.26
1.24
0.00
Cl
Me
CO2Et
HN
Bus
6a
1.00
2.30
0.98
0.99
4.57
4.27
8.88
3.21
4.78
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

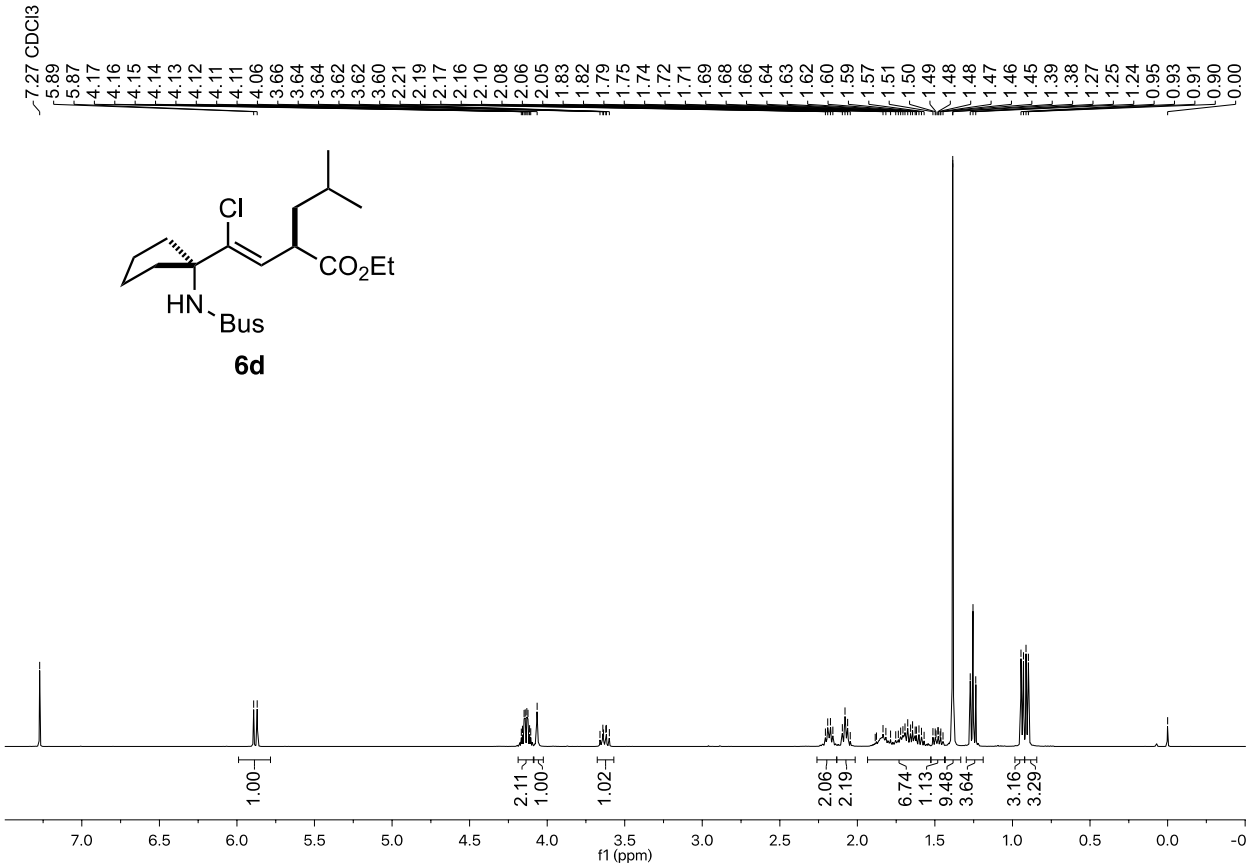

173.9
138.2
126.1
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
71.4
60.8
60.1
40.1
39.0
36.8
24.2
22.7
21.9
16.9
14.2
Cl
Me
CO2Et
HN
Bus
6a
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

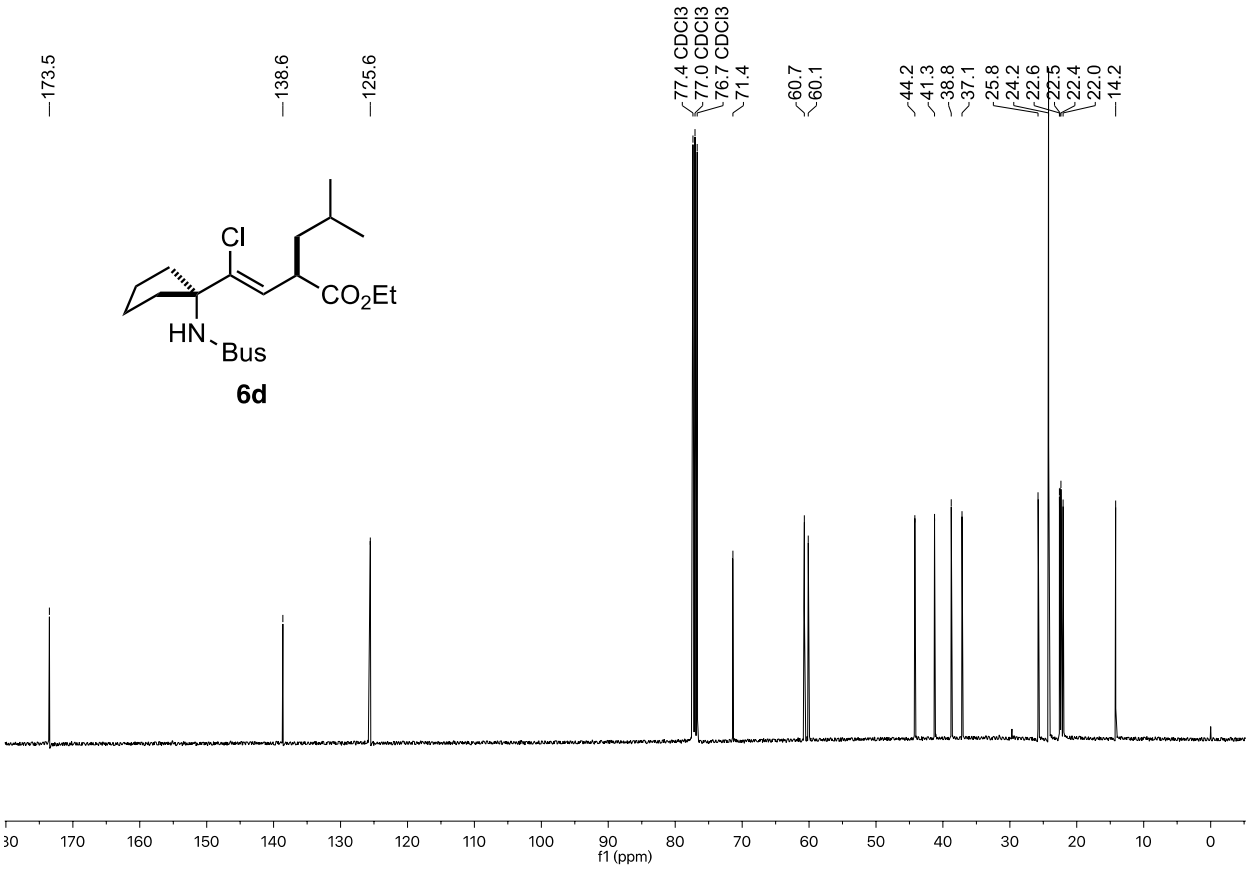

7.26 CDCl3
5.97
5.94
4.17
4.16
4.15
4.14
4.12
4.05
3.52
3.50
3.48
3.47
2.27
2.25
2.23
2.22
2.20
2.18
2.17
2.15
2.12
2.10
2.09
2.07
2.05
2.03
2.02
2.00
1.89
1.87
1.85
1.84
1.82
1.80
1.78
1.76
1.75
1.73
1.71
1.69
1.67
1.65
1.64
1.39
1.28
1.26
1.24
0.97
0.95
0.94
0.00
Cl
CO2Et
HN
Bus
6b
1.00
2.08
0.96
0.98
1.98
2.21
3.10
2.83
8.78
3.61
3.01
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

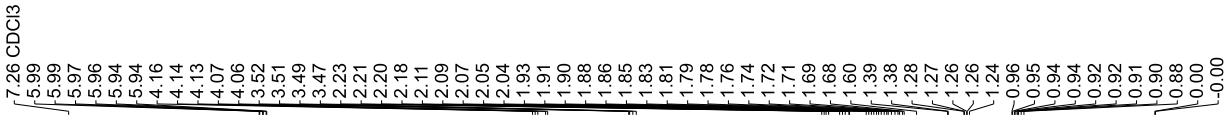

173.3
138.9
125.0
77.4 CDCl3
77.0 CDCl3
76.7 CDCl3
71.4
60.7
60.1
47.2
39.0
36.8
25.7
24.2
22.6
22.0
14.2
11.4
Cl
CO2Et
HN
Bus
6b
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.27 CDCl3
5.98
5.95
4.19
4.18
4.17
4.16
4.15
4.13
4.12
4.11
4.10
4.09
3.40
3.38
3.38
3.36
2.23
2.21
2.19
2.15
2.13
2.11
2.10
2.10
2.08
2.07
2.05
1.85
1.85
1.84
1.83
1.83
1.81
1.72
1.71
1.69
1.68
1.68
1.68
1.67
1.67
1.66
1.66
1.66
1.39
1.28
1.26
1.24
0.99
0.97
0.97
0.95
0.00
Cl
CO2Et
HN
Bus
6c
1.00
2.08
0.97
0.98
1.96
3.20
5.23
9.11
3.44
6.10
f1 (ppm)


172.8
139.4
124.1
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
71.5
60.6
60.2
52.7
39.0
37.0
31.7
24.2
22.6
22.1
20.5
19.6
14.3
Cl
CO2Et
HN
Bus
6c
f1 (ppm)


7.27 CDCl3
5.89
5.87
4.17
4.16
4.15
4.14
4.13
4.12
4.11
4.11
4.06
3.66
3.64
3.64
3.62
3.62
3.60
2.21
2.19
2.17
2.16
2.10
2.08
2.06
2.05
1.83
1.82
1.79
1.75
1.74
1.72
1.71
1.69
1.68
1.66
1.64
1.63
1.62
1.60
1.59
1.57
1.51
1.50
1.49
1.48
1.48
1.47
1.46
1.45
1.39
1.38
1.27
1.25
1.24
0.95
0.93
0.91
0.90
0.00
Cl
CO2Et
HN
Bus
6d
1.00
2.11
1.00
1.02
2.06
2.19
6.74
1.13
9.48
3.64
3.16
3.29
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


173.5
138.6
125.6
77.4 CDCl3
77.0 CDCl3
76.7 CDCl3
71.4
60.7
60.1
44.2
41.3
38.8
37.1
25.8
24.2
22.6
22.5
22.4
22.0
14.2
Cl
CO2Et
HN
Bus
6d
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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4.13
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4.06
3.52
3.51
3.49
3.47
2.23
2.21
2.20
2.18
2.11
2.09
2.07
2.05
2.04
1.93
1.91
1.90
1.88
1.86
1.85
1.83
1.81
1.79
1.78
1.76
1.74
1.72
1.71
1.69
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1.60
1.39
1.38
1.28
1.27
1.26
1.26
1.24
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0.94
0.92
0.92
0.91
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0.88
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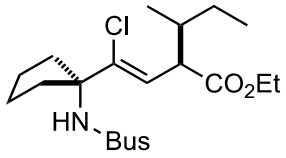
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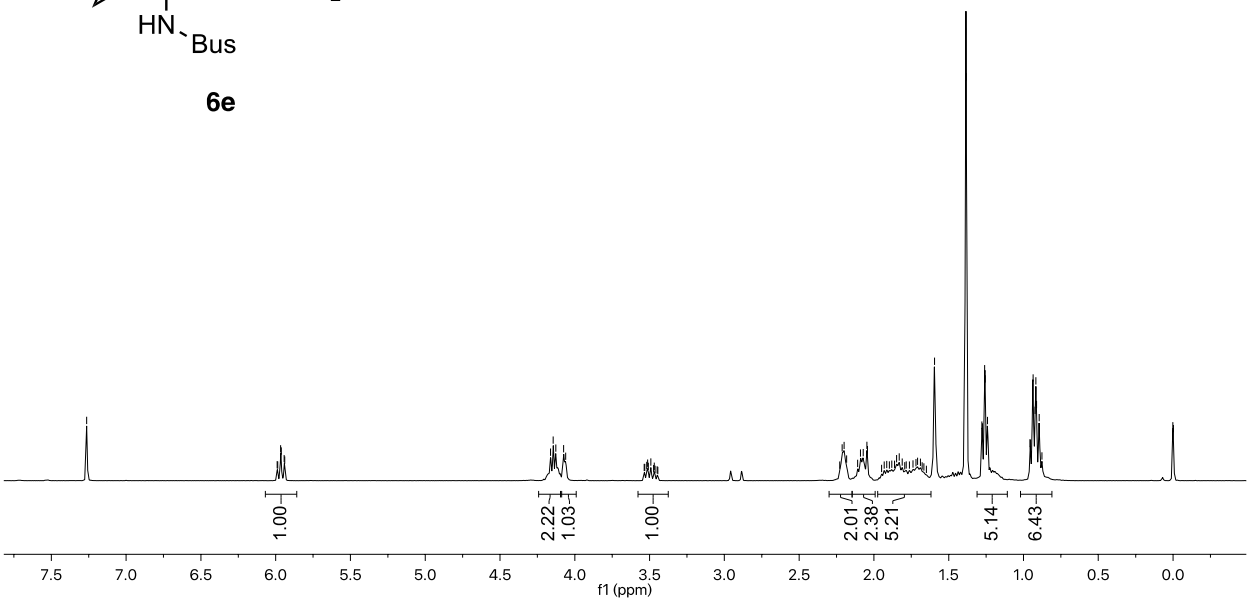
CO2Et
HN
Bus

6e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2.38
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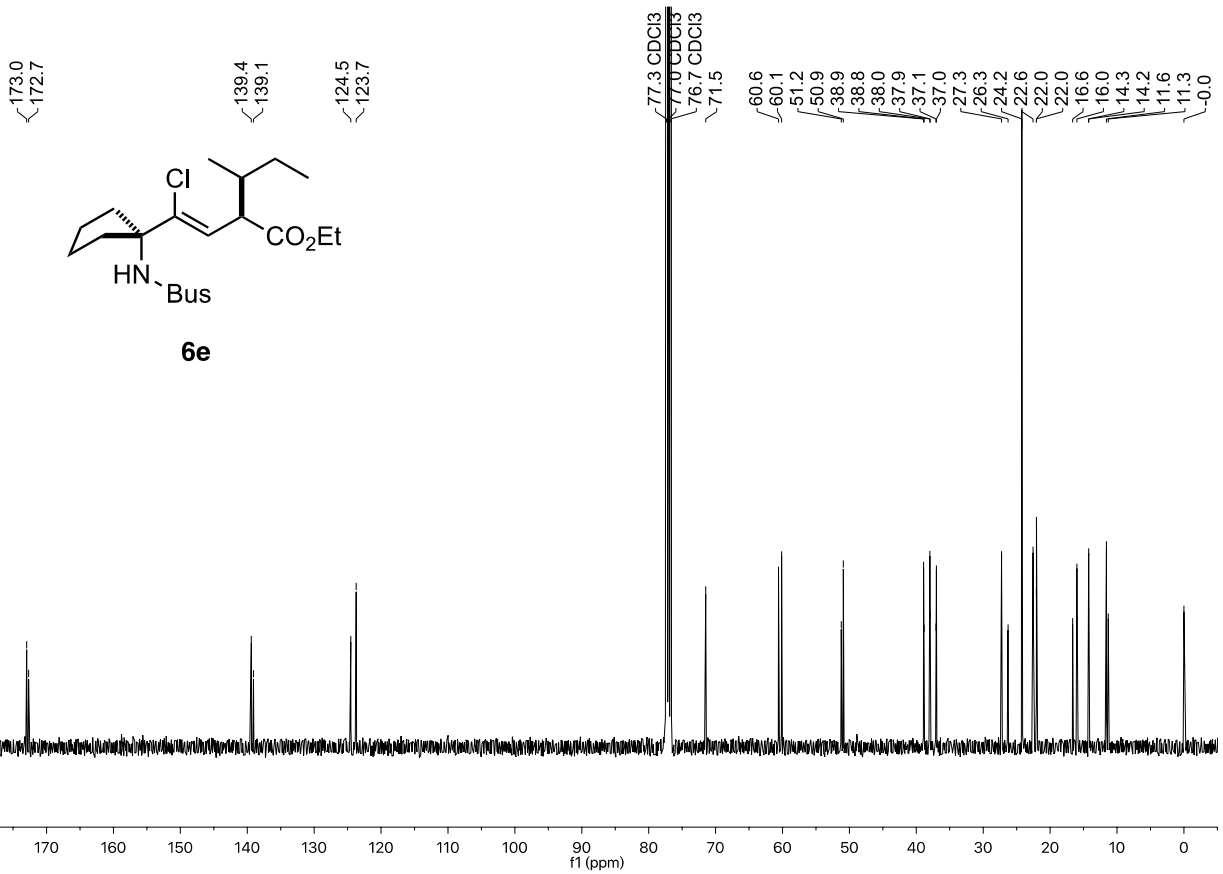
5.14
6.43
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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172.7
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123.7
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
71.5
60.6
60.1
51.2
50.9
38.9
38.8
38.0
37.9
37.1
37.0
27.3
26.3
24.2
22.6
22.0
22.0
16.6
16.0
14.3
14.2
11.6
11.3
-0.0
Cl
CO2Et
HN
Bus
30
170
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140
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120
110
100
90
80
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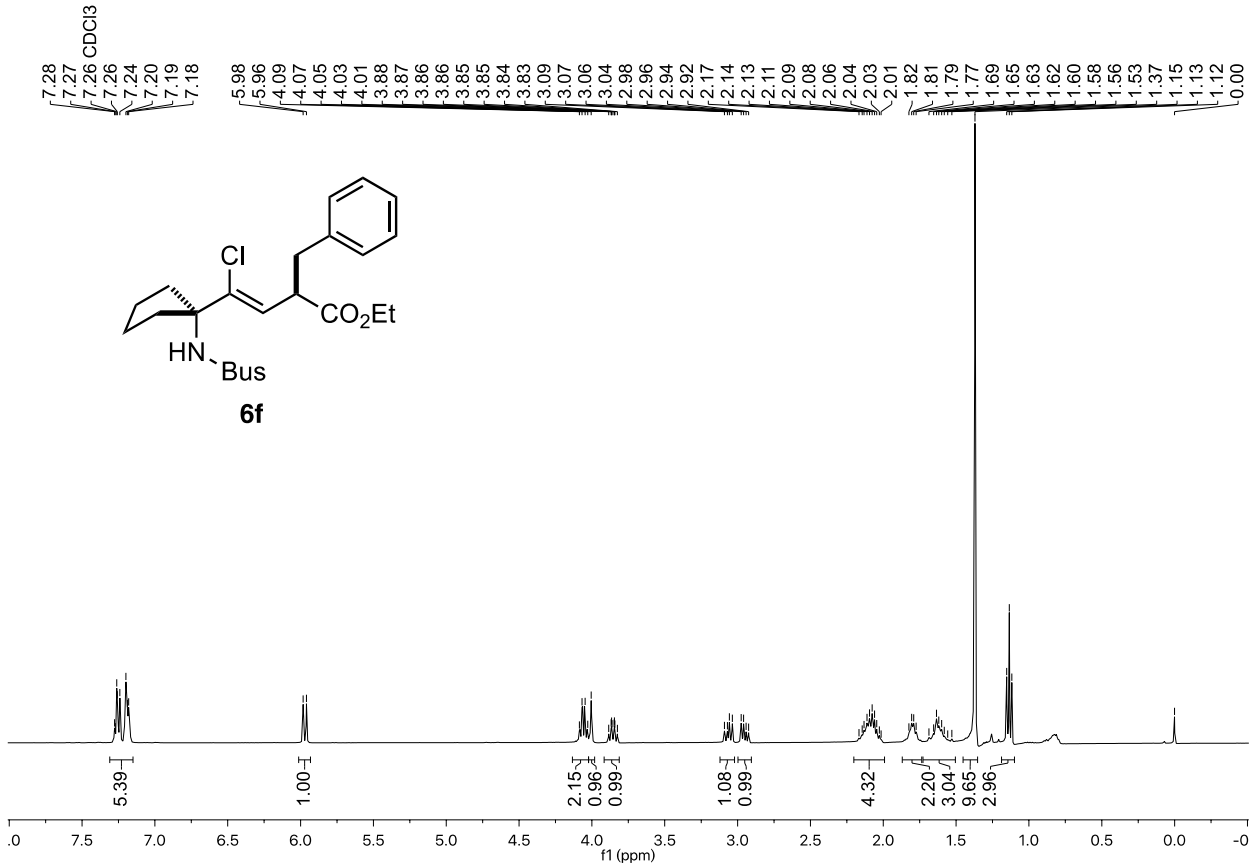
60
50
40
30
20
10
0
f1 (ppm)

6e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7.26 CDCl3
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7.18
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5.96
4.09
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4.01
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3.85
3.84
3.83
3.09
3.07
3.06
3.04
2.98
2.96
2.94
2.92
2.17
2.14
2.13
2.11
2.09
2.08
2.06
2.04
2.03
2.01
1.82
1.81
1.79
1.77
1.69
1.65
1.63
1.62
1.60
1.58
1.56
1.53
1.37
1.15
1.13
1.12
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Cl
CO2Et
HN
Bus
6f
5.39
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1.08
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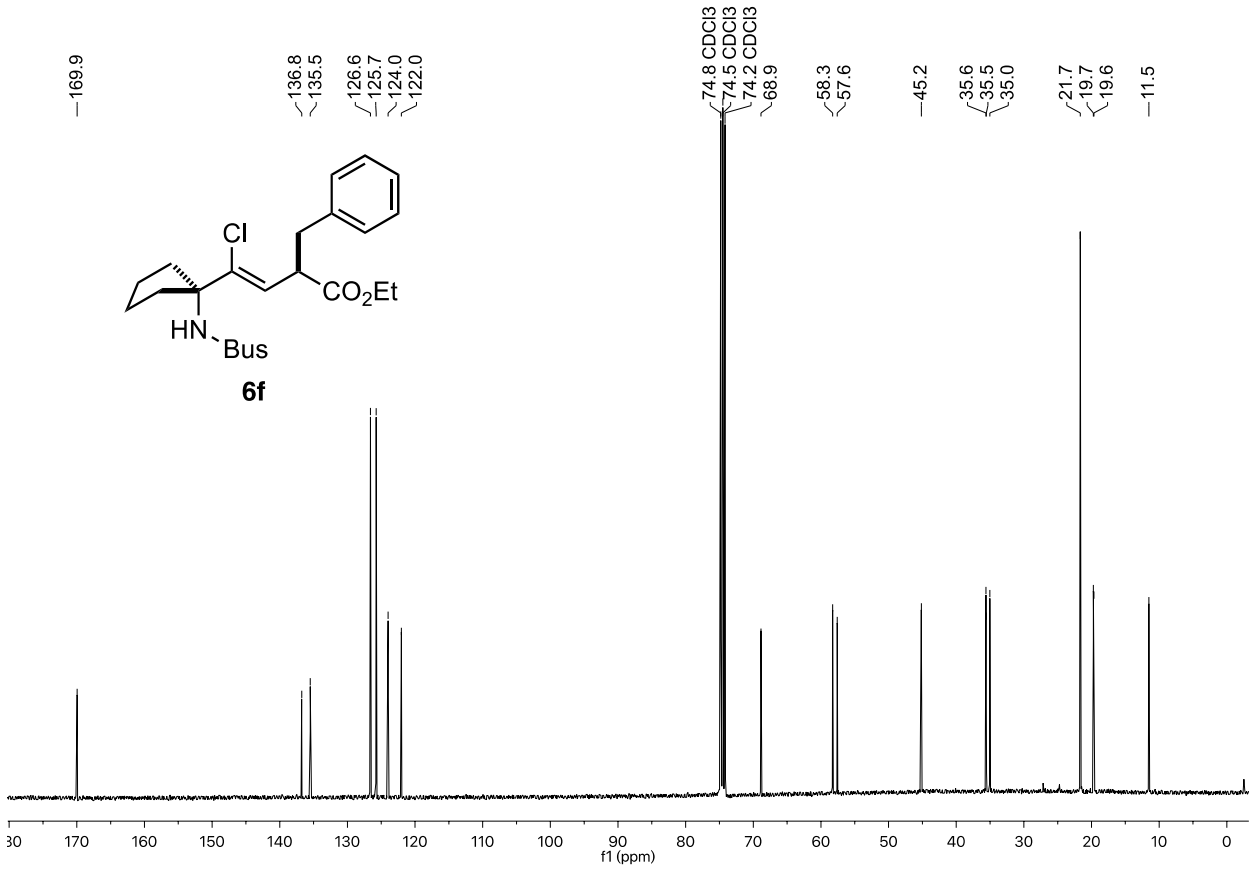
3.04
9.65
2.96
f1 (ppm)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135.5
126.6
125.7
124.0
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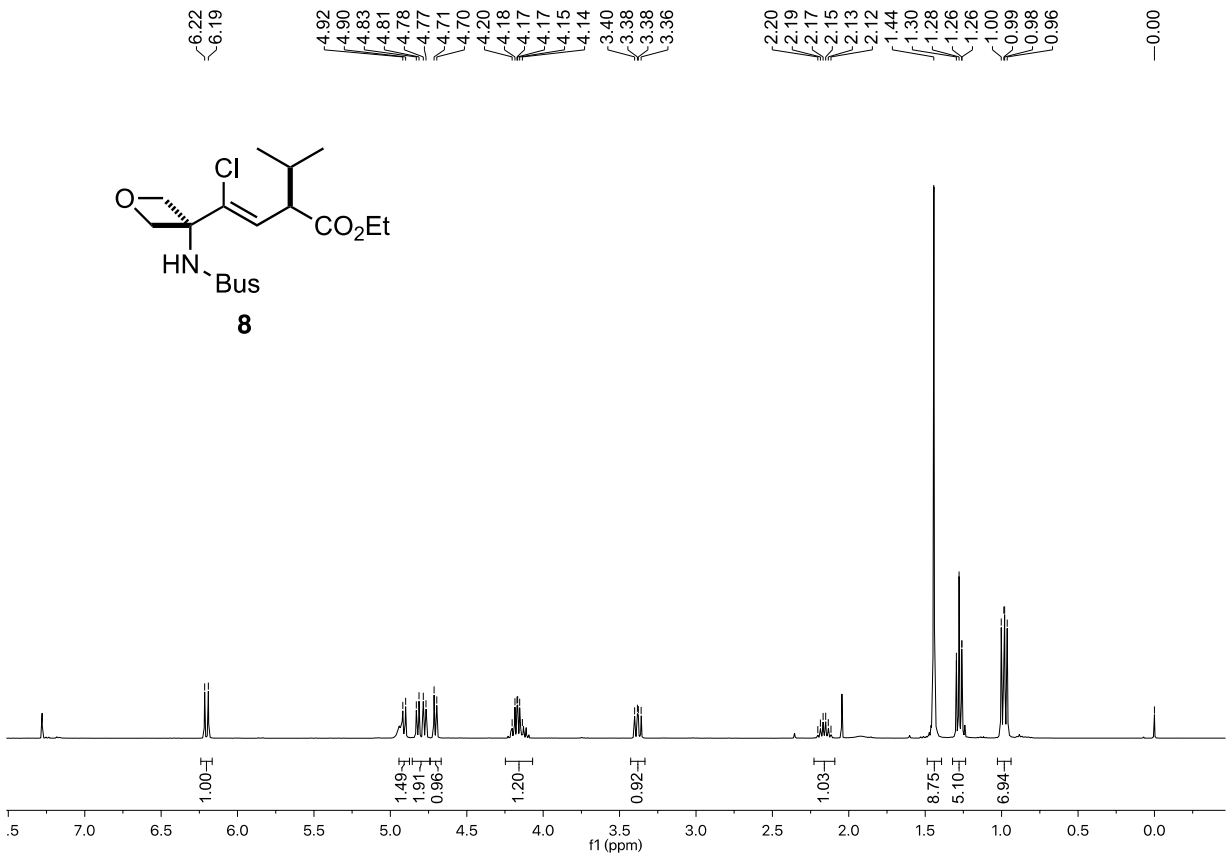
74.8 CDCl3
74.5 CDCl3
74.2 CDCl3
68.9
58.3
57.6
45.2
35.6
35.5
35.0
21.7
19.7
19.6
11.5
Cl
CO2Et
HN
Bus
6f
f1 (ppm)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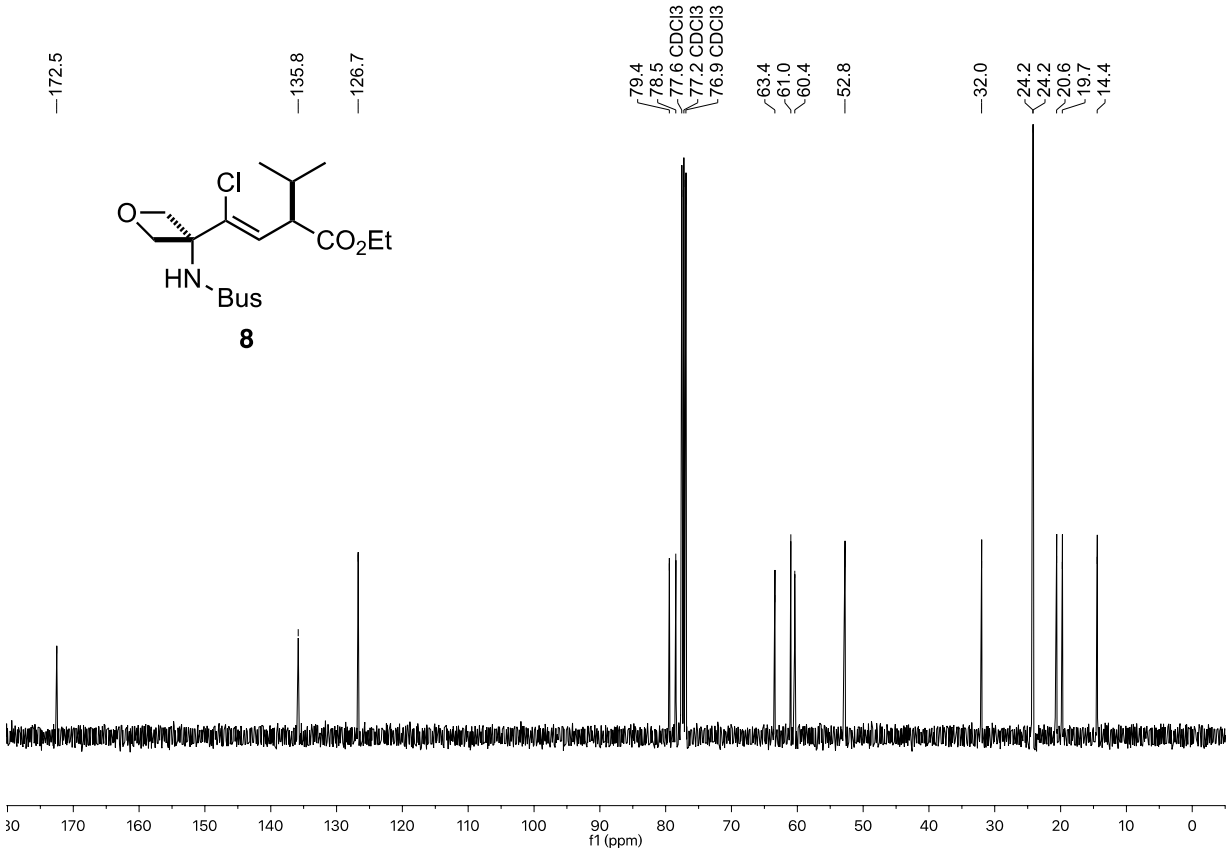
6.19
4.92
4.90
4.83
4.81
4.78
4.77
4.71
4.70
4.20
4.18
4.17
4.17
4.15
4.14
3.40
3.38
3.38
3.36
2.20
2.19
2.17
2.15
2.13
2.12
1.44
1.30
1.28
1.26
1.26
1.00
0.99
0.98
0.96
0.00
Cl
O
CO2Et
HN
Bus
8
1.00
1.49
1.91
0.96
1.20
0.92
1.03
8.75
5.10
6.94
f1 (ppm)


172.5
135.8
126.7
79.4
78.5
77.6 CDCl3
77.2 CDCl3
76.9 CDCl3
63.4
61.0
60.4
52.8
32.0
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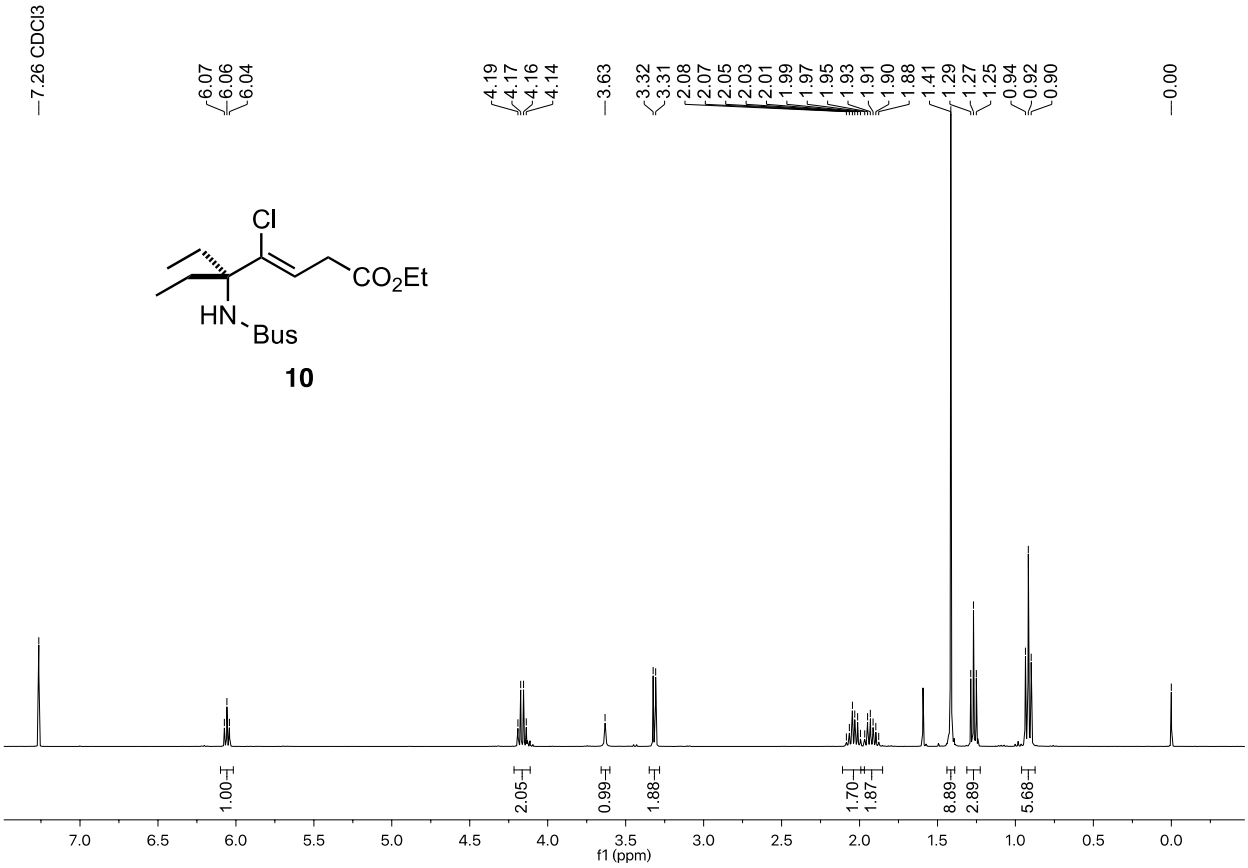
24.2
20.6
19.7
14.4
Cl
O
CO2Et
HN
Bus
8
f1 (ppm)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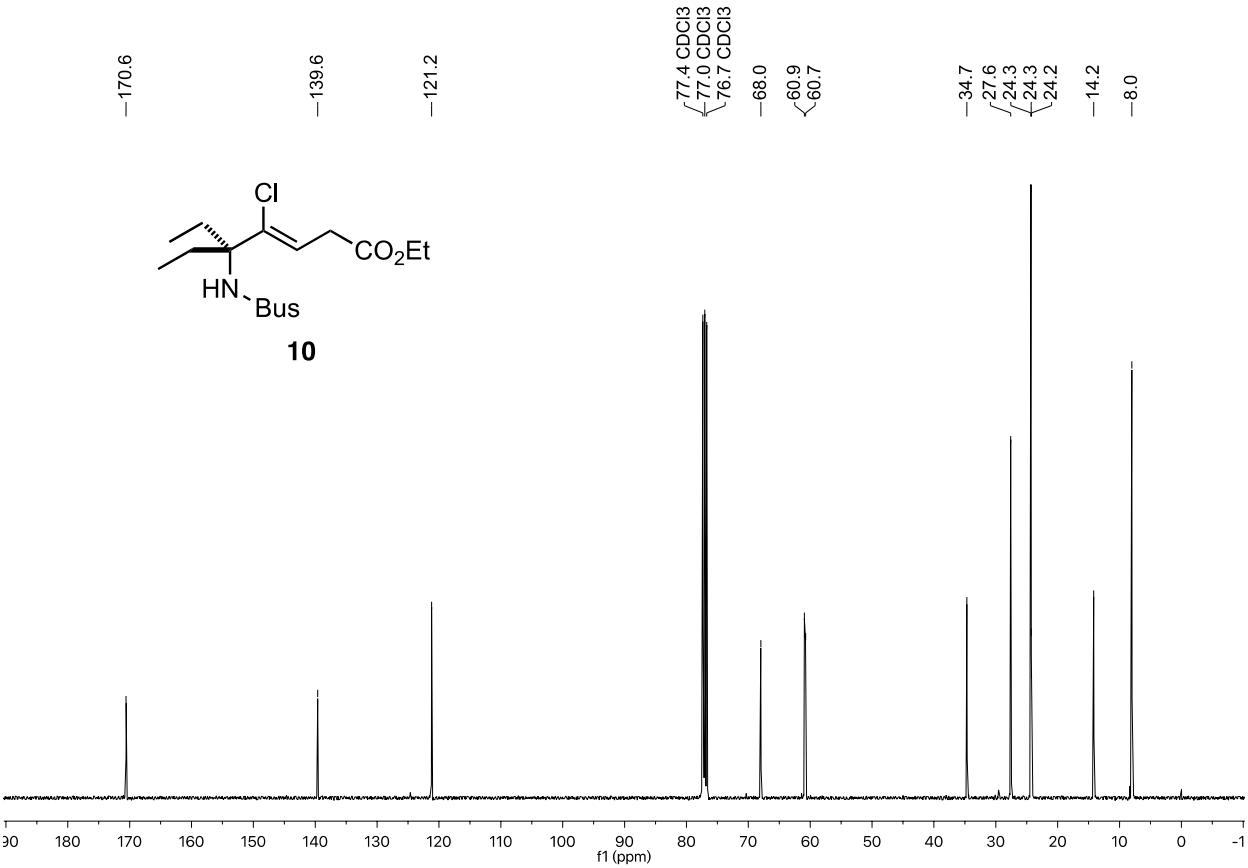
6.07
6.06
6.04
4.19
4.17
4.16
4.14
3.63
3.32
3.31
2.08
2.07
2.05
2.03
2.01
1.99
1.97
1.95
1.93
1.91
1.90
1.88
1.41
1.29
1.27
1.25
0.94
0.92
0.90
0.00
Cl
CO2Et
HN
Bus
10
1.00
2.05
0.99
1.88
1.70
1.87
8.89
2.89
5.68
f1 (ppm)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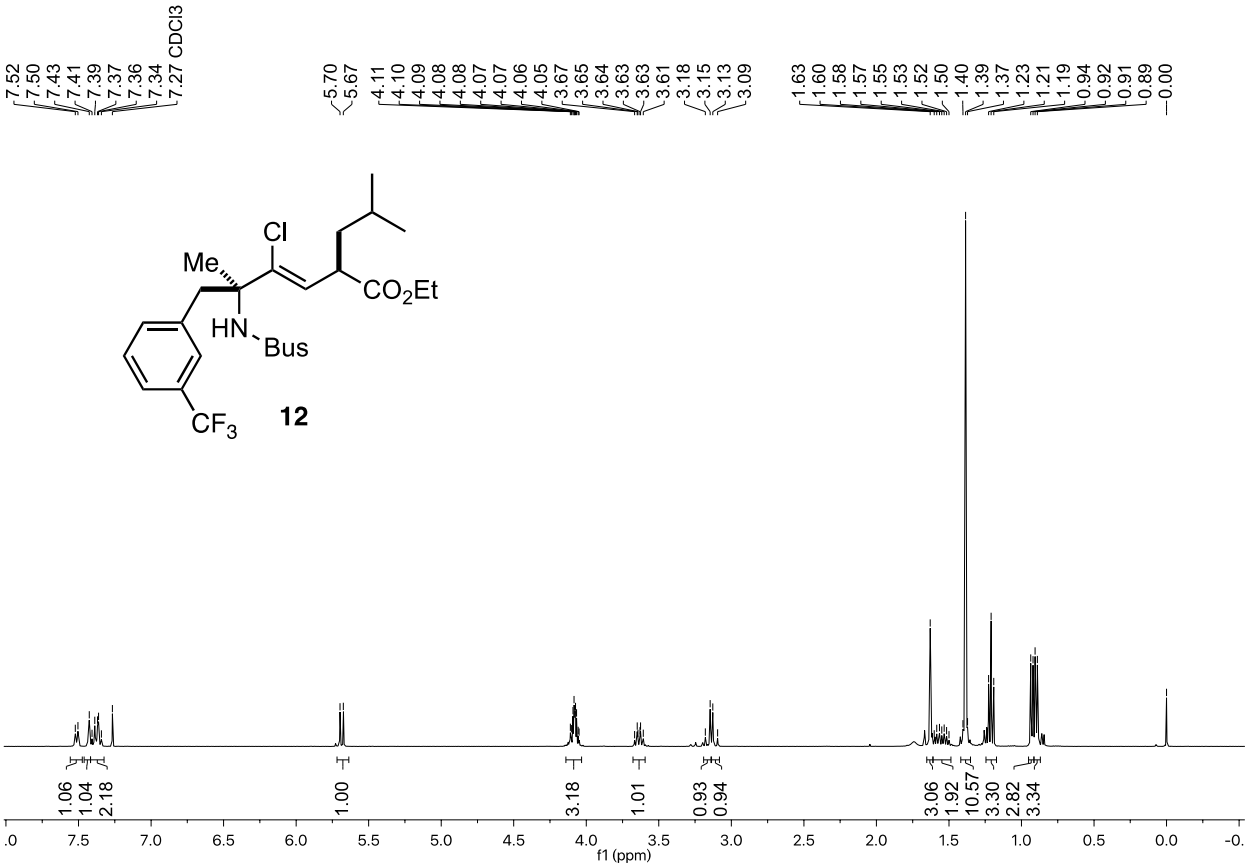
139.6
121.2
77.4 CDCl3
77.0 CDCl3
76.7 CDCl3
68.0
60.9
60.7
34.7
27.6
24.3
24.3
24.2
14.2
8.0
Cl
CO2Et
HN
Bus
10
f1 (ppm)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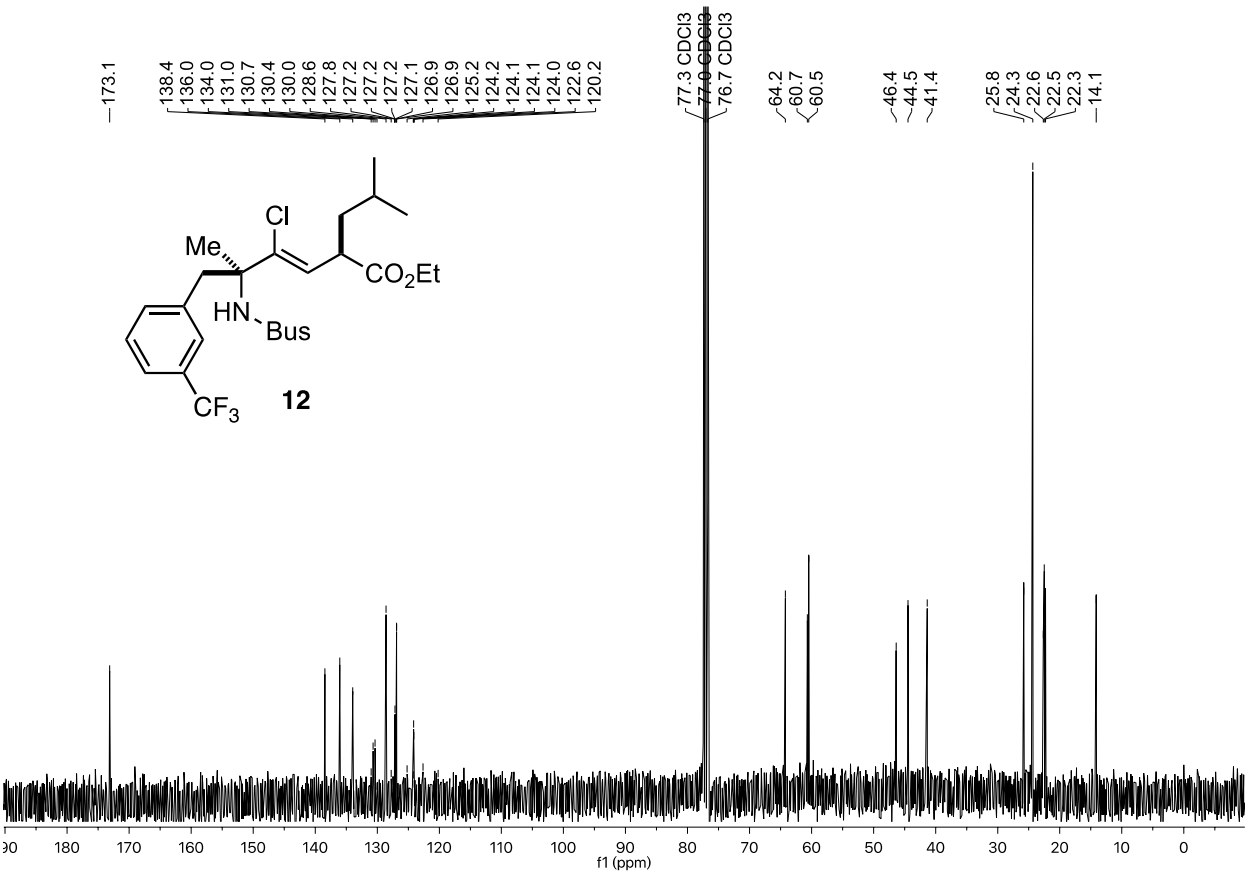
7.50
7.43
7.41
7.39
7.37
7.36
7.34
7.27 CDCl3
5.70
5.67
4.11
4.10
4.09
4.08
4.08
4.07
4.07
4.06
4.05
3.67
3.65
3.64
3.63
3.63
3.61
3.18
3.15
3.13
3.09
1.63
1.60
1.58
1.57
1.55
1.53
1.52
1.50
1.40
1.39
1.37
1.23
1.21
1.19
0.94
0.92
0.91
0.89
0.00
Cl
Me
CO2Et
HN
Bus
CF3
12
1.06
1.04
2.18
1.00
3.18
1.01
0.93
0.94
3.06
1.92
10.57
3.30
2.82
3.34
f1 (ppm)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131.0
130.7
130.4
130.0
128.6
127.8
127.2
127.2
127.2
127.1
126.9
126.9
125.2
124.2
124.1
124.1
124.0
122.6
120.2
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
64.2
60.7
60.5
46.4
44.5
41.4
25.8
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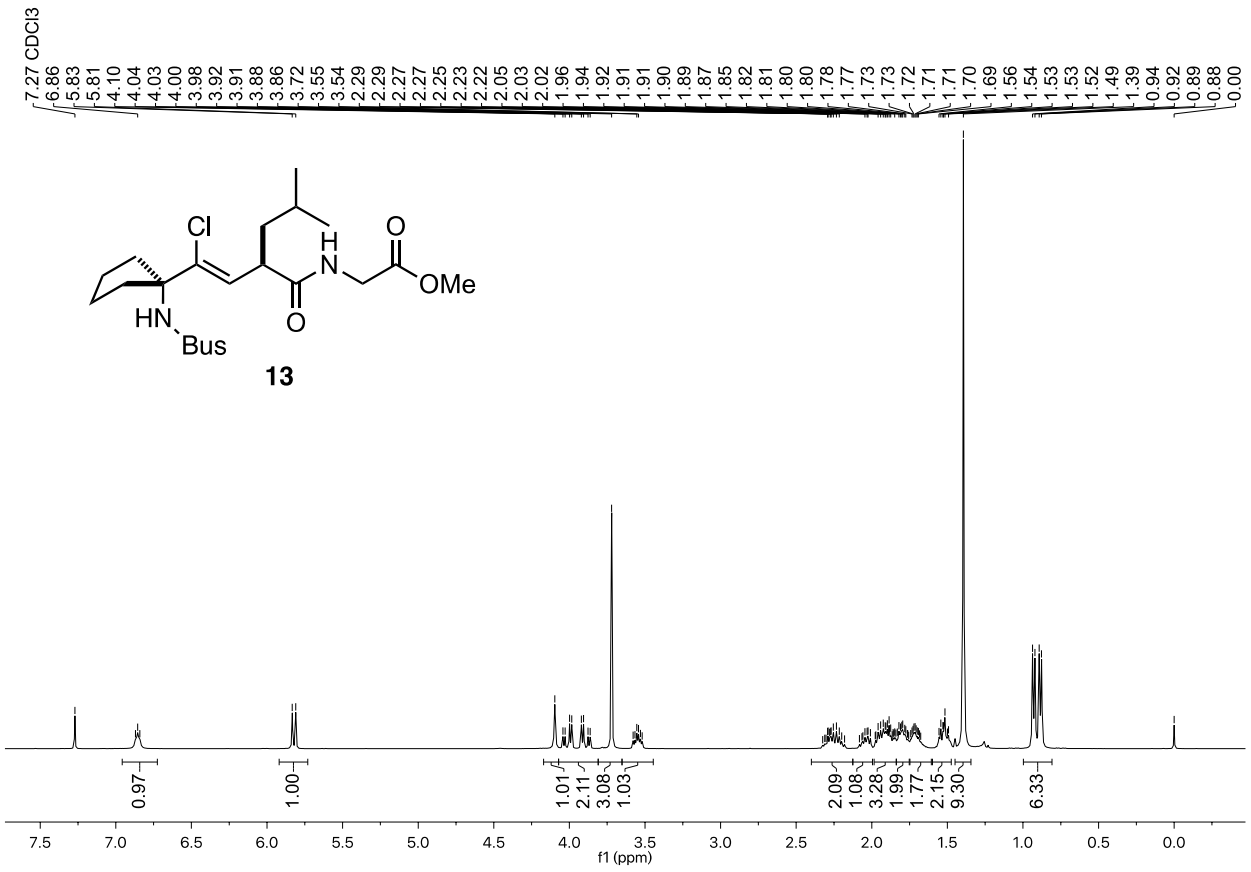
22.6
22.5
22.3
14.1
Cl
Me
CO2Et
HN
Bus
CF3
12
f1 (ppm)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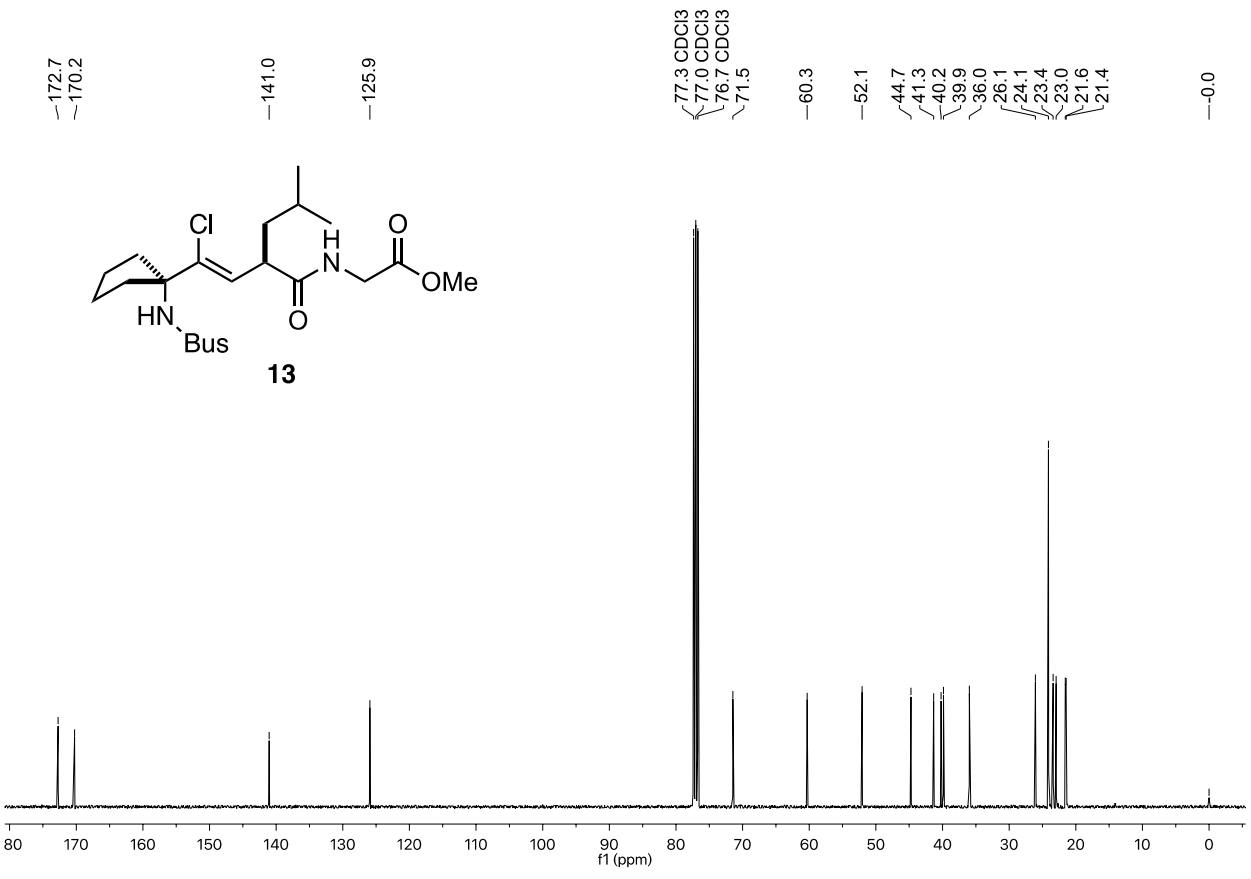
4.00
3.98
3.92
3.91
3.88
3.86
3.72
3.55
3.54
2.29
2.29
2.27
2.27
2.25
2.23
2.22
2.05
2.03
2.02
1.96
1.94
1.92
1.91
1.91
1.90
1.89
1.87
1.85
1.82
1.81
1.80
1.80
1.78
1.77
1.73
1.73
1.72
1.71
1.71
1.70
1.69
1.56
1.54
1.53
1.53
1.52
1.49
1.39
0.94
0.92
0.89
0.88
0.00
Cl
H
N
O
OMe
HN
Bus
O
13
0.97
1.00
1.01
2.11
3.08
1.03
2.09
1.08
3.28
1.99
1.77
2.15
9.30
6.33
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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125.9
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
71.5
60.3
52.1
44.7
41.3
40.2
39.9
36.0
26.1
24.1
23.4
23.0
21.6
21.4
0.0
Cl
H
N
O
OMe
HN
Bus
O
13
80
170
160
150
140
130
120
110
100
90
80
70
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50
40
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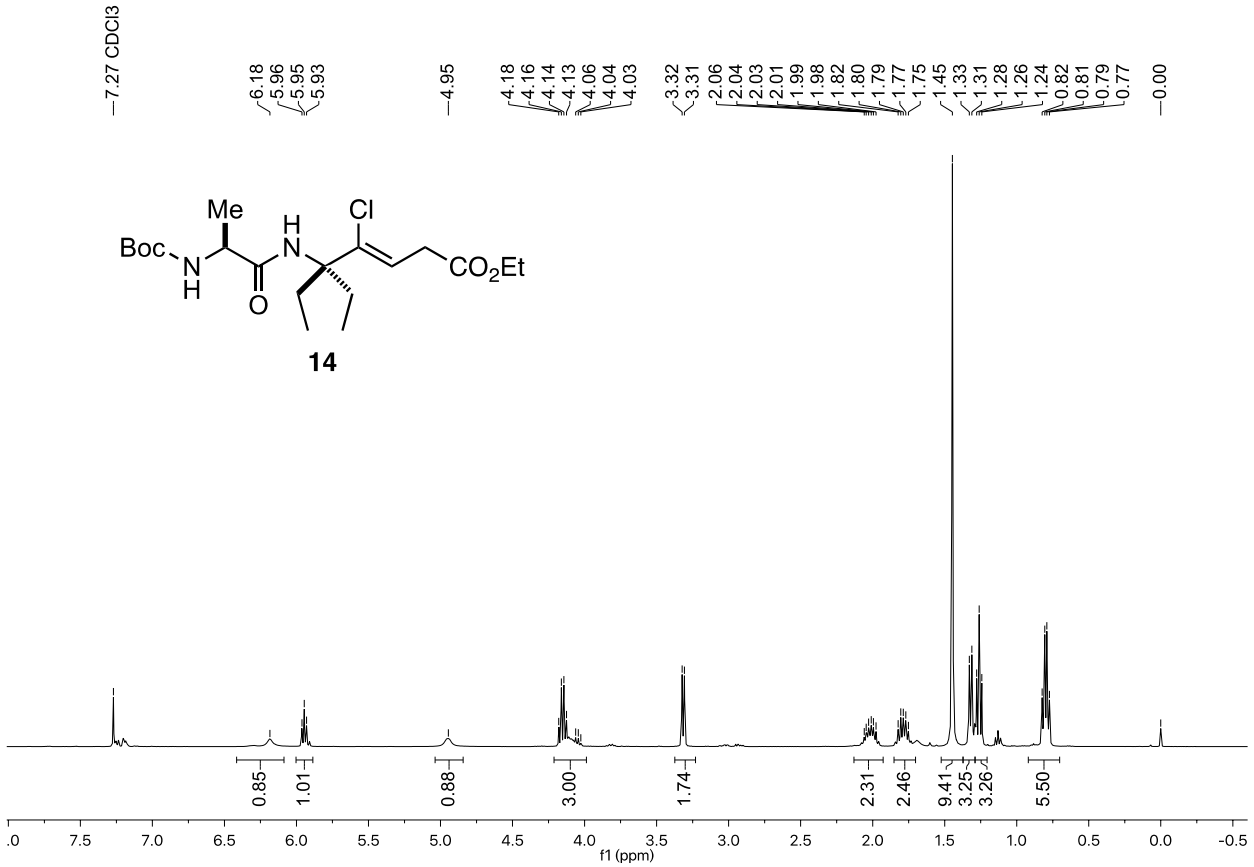
20
10
0
f1 (ppm)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4.14
4.13
4.06
4.04
4.03
3.32
3.31
2.06
2.04
2.03
2.01
1.99
1.98
1.82
1.80
1.79
1.77
1.75
1.45
1.33
1.31
1.28
1.26
1.24
0.82
0.81
0.79
0.77
0.00
Me
H
N
Cl
Boc
N
H
O
CO2Et
14
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3.00
1.74
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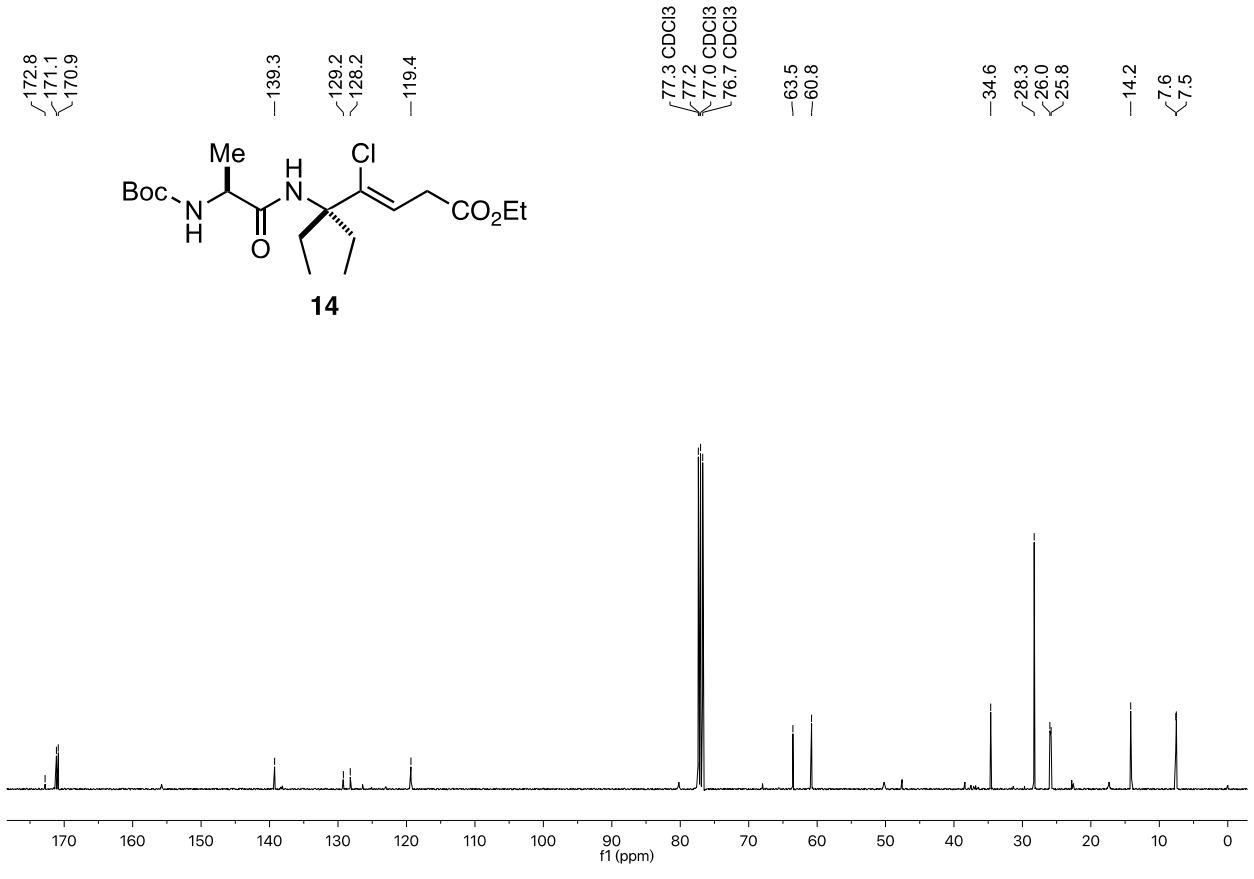
9.41
3.25
3.26
5.50
f1 (ppm)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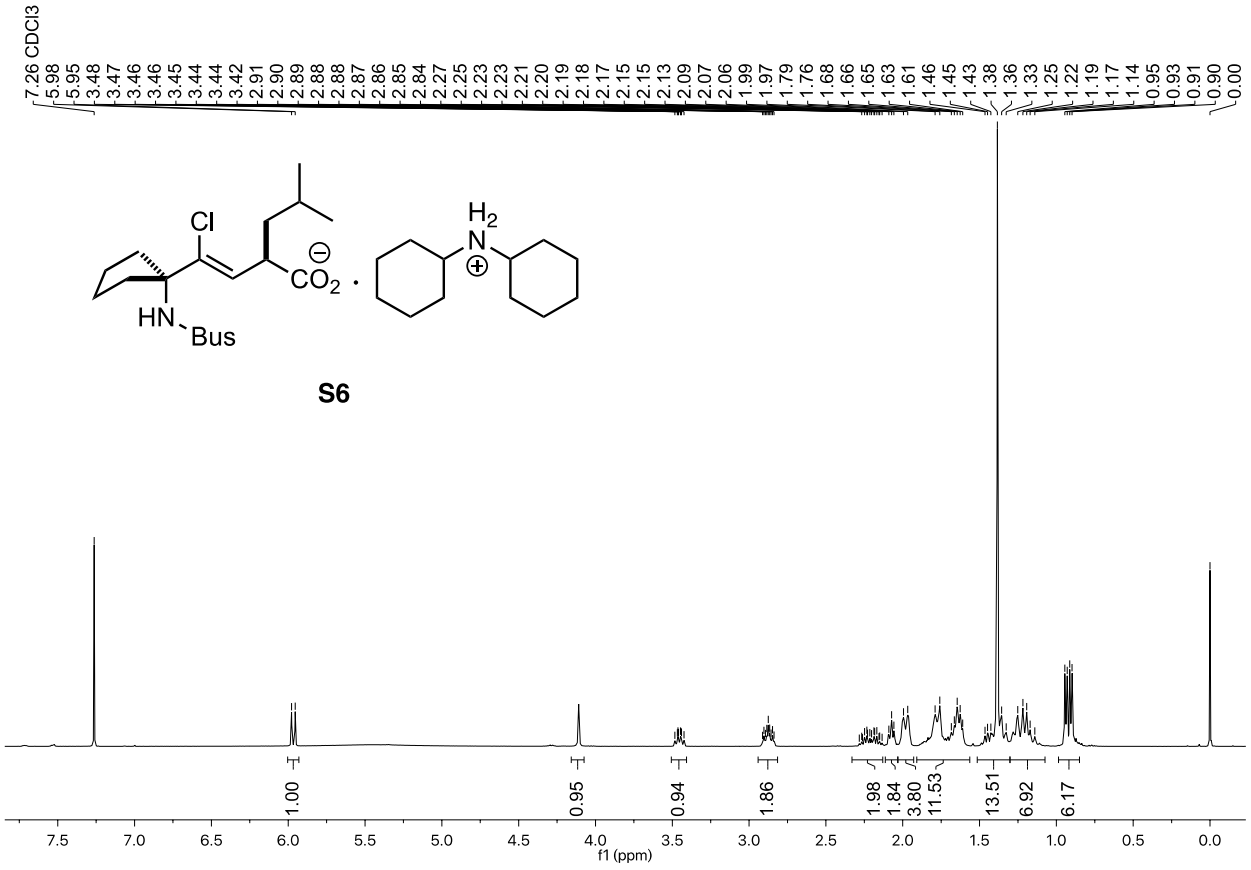
171.1
170.9
139.3
129.2
128.2
119.4
77.3 CDCl3
77.2
77.0 CDCl3
76.7 CDCl3
63.5
60.8
34.6
28.3
26.0
25.8
14.2
7.6
7.5
Me
H
N
Cl
Boc
N
H
O
CO2Et
14
f1 (ppm)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5.98
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3.47
3.46
3.46
3.45
3.44
3.44
3.42
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2.90
2.89
2.88
2.88
2.87
2.86
2.85
2.84
2.27
2.25
2.23
2.23
2.21
2.20
2.19
2.18
2.17
2.15
2.15
2.13
2.09
2.07
2.06
1.99
1.97
1.79
1.76
1.68
1.66
1.65
1.63
1.61
1.46
1.45
1.43
1.38
1.36
1.33
1.25
1.22
1.19
1.17
1.14
0.95
0.93
0.91
0.90
0.00
Cl
CO2
H2
N
HN
Bus
S6
1.00
0.95
0.94
1.86
1.98
1.84
3.80
11.53
13.51
6.92
6.17
7.5
7.0
6.5
6.0
5.5
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3.5
3.0
2.5
2.0
1.5
1.0
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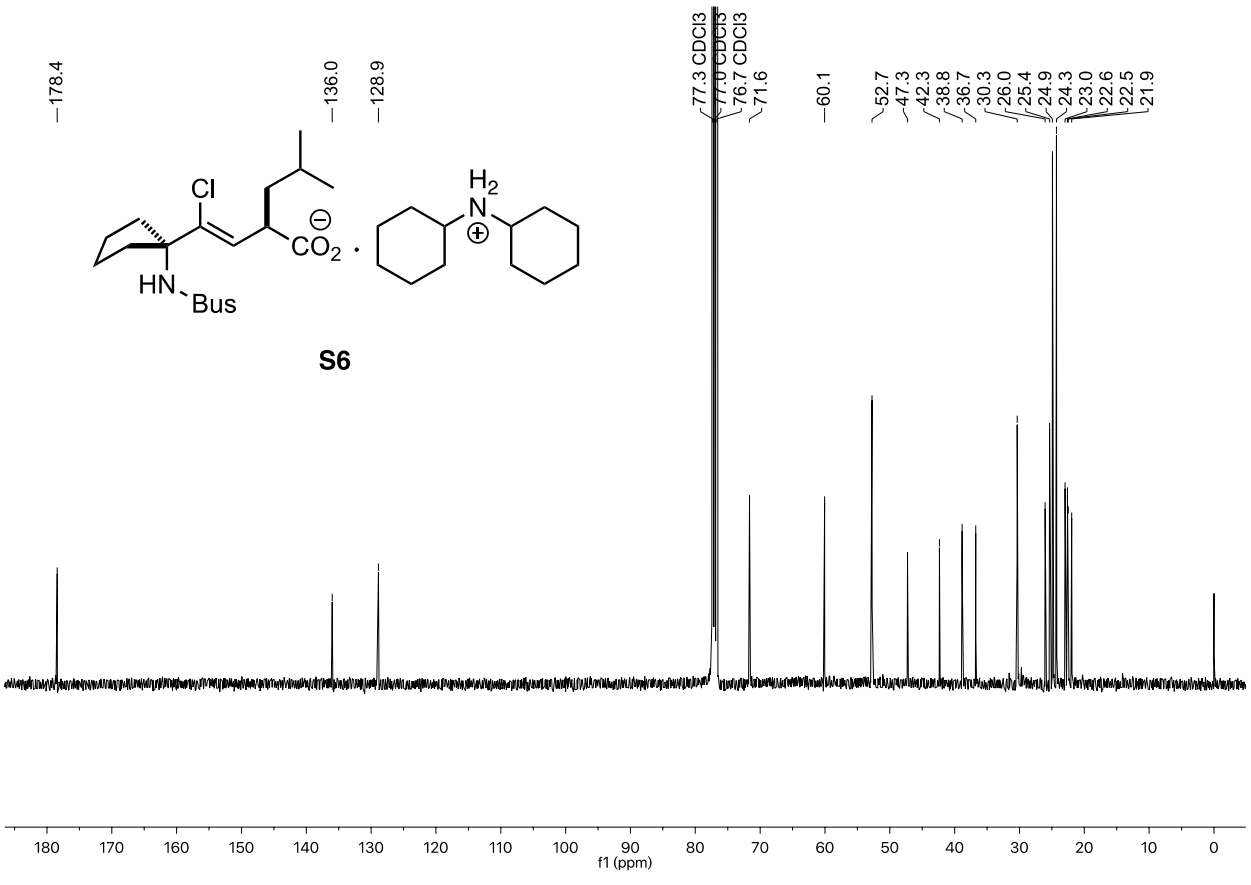
0.0
f1 (ppm)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77.0 CDCl3
76.7 CDCl3
71.6
60.1
52.7
47.3
42.3
38.8
36.7
30.3
26.0
25.4
24.9
24.3
23.0
22.6
22.5
21.9
Cl
CO2
H2
N
HN
Bus
S6
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

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