Supporting Information

Skeletal Rearrangement of Enynones by Aluminum Halides: Construction of Bicyclo[3.1.0]hexanes with Introducing Halides

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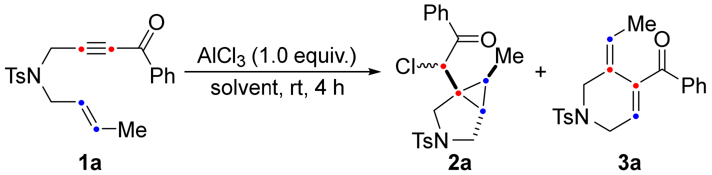
1. Evaluation of Solvents for the AlCl3-Mediated Formation of 2a

Table S1. Evaluation of Solvents for the $AlCl_3$-Mediated Formation of **2a**



entry	Solvent	**2a** [%]	dr[a]	**3a** [%]	**1a**[b] [%]
1	CH_2Cl_2	78	60:40	trace	0
2	CH_2Br_2	53	59:41	0	0
3	$ClCH_2CH_2Cl$	62	57:43	trace	0
4	$CHCl_3$	65	60:40	trace	0
5	CCl_4	40[b]	60:40	0	0
6	toluene	35	60:40	trace	0
7	CH_3NO_2	20	65:35	19	0
8	CH_3CN	47	59:41	trace	0[c]
9	THF	0	-	0	96

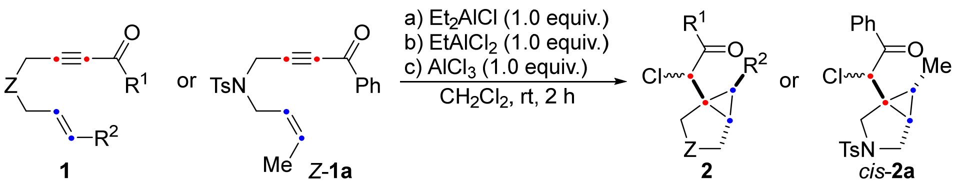
[a] Diastereomeric ratio. [b] Determined by ^{1}H NMR analysis using AcOMe as an internal standard.
[c] (*Z*)-isomer of **1a**: 7%.

2. General Information

All reactions were carried out under an argon atmosphere. 7-En-2-ynones **1a-n** and *Z*-**1a** were prepared by the method reported in the literatures.[1] Unless otherwise noted, materials and catalysts are commercially available. All solvents were purchased as the "anhydrous" and used without further purification. For the thin-layer chromatography (TLC) analysis, Merck precoated TLC plates (silica gel 60 F254) were used. Column chromatography was performed on silica gel 60N (63-200 µm, neutral, Kanto Kagaku Co., Ltd.). Medium pressure liquid chromatography (MPLC) was carried out with YAMAZEN EPCLC-Wprep 2XY.

^{1}H and ^{13}C NMR spectra were measured at 500 and 125 MHz in $CDCl_3$ and the chemical shifts are given in ppm using $CHCl_3$ (7.26 ppm) in $CDCl_3$ for ^{1}H NMR and $CDCl_3$ (77.0 ppm) for ^{13}C NMR as an internal standard, respectively. Splitting patterns of an apparent multiplet associated with an averaged coupling constant were designed as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broadened). Mass spectra and HRMS were recorded on double-focusing magnetic sector by FAB or ESI methods.

3. Skeletal Rearrangement of 1a-l using $Et_nAlCl_{(3-n)}$ and Characterization of 2a-l and cis-2a



To a solution of enynones **1a-l** (0.4 mmol) or *Z*-**1a** (147.0 mg, 0.4 mmol) in CH_2Cl_2 (2 mL) was added Et_2AlCl (1.0 M in hexane solution, 0.4 mL, 0.4 mmol, method **a**), $EtAlCl_2$ (1.0 M in hexane solution, 0.4 mL, 0.4 mmol, method **b**) or $AlCl_3$ (53.3 mg, 0.4 mmol, method **c**) at 0 ºC. After being stirred at room temperature until the consumption of **1** (by TLC analysis), the reaction mixture was quenched with sat. $NaHCO_3$ and sat. Rochelle salt, and extracted with AcOEt. The organic layer was dried over $MgSO_4$ and concentrated in vacuo to dryness. The residue was purified by MPLC (hexane:AcOEt = 92:8 to 75:25) to give **2a-**

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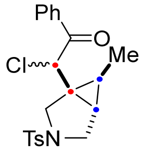
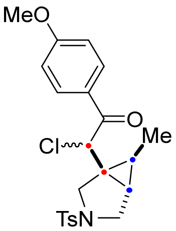
[1] D. Sato, Y. Watanabe, K. Noguchi, J. Kanazawa, K. Miyamoto, M. Uchiyama, A. Saito, *Org. Lett.* **2020**, *22*, 4063–4067.

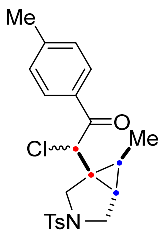
l or *cis*-**2a** as an epimeric mixture. In cases of **2a**, **2b**, **2e**, **2g** and **2i-k**, since major epimer-rich and/or minor epimer-rich products were separated, yields were determined by adding these products together.



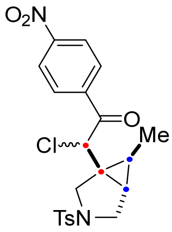
2-Chloro-2-[(1*S,5*S**,6*S**)-6-methyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl]-1-phenylethan-1-one (2a)**: (**a**) 151.7 mg (94%, 56:44), (**b**) 143.0 mg (89%, 56:44), (**c**) 126.0 mg (78%, 60:40). **[major]** R_f = 0.41 (hexane:AcOEt = 2:1). White solid. Mp 178-179 °C. IR (KBr) ν cm^{-1}; 1685, 1596, 1342, 1163, 667, 598, 549. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm; 7.92 (d, J = 7.5 Hz, 2H), 7.72 (d, J = 8.0 Hz, 2H), 7.61 (t, J = 7.5 Hz, 1H), 7.49 (dd, J = 7.5, 7.5 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 5.07 (s, 1H), 3.90 (d, J = 9.7 Hz, 1H), 3.56 (d, J = 9.7 Hz, 1H), 3.54 (d, J = 9.7 Hz, 1H), 3.15 (dd, J = 9.7, 3.4 Hz, 1H), 2.43 (s, 3H), 1.35-1.29 (m, 2H), 1.02 (d, J = 5.7 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ ppm; 192.4, 143.4, 134.0, 133.8, 133.7, 129.6, 128.9, 127.5, 58.5, 50.2, 49.2, 33.5, 30.8, 23.2, 21.5, 12.5 (note that two carbon peaks overlap with each other). HRMS (ESI, m/z): calcd. for $C_{21}H_{23}ClNO_3S^+$ $[M + H]^+$, 404.1082; found, 404.1084. **[minor]** R_f = 0.38 (hexane:AcOEt = 2:1). Pale yellow solid. Mp 148-149 °C. IR (KBr) ν cm^{-1}; 1697, 1598, 1337, 1165, 668, 606, 551. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm; 7.64 (d, J = 8.0 Hz, 2H), 7.59-7.52 (m, 3H), 7.40-7.34 (m, 4H), 5.06 (s, 1H), 3.55 (d, J = 9.2 Hz, 1H), 3.50 (d, J = 9.7 Hz, 1H), 3.22 (d, J = 9.7 Hz, 1H), 2.77 (dd, J = 9.2, 4.0 Hz, 1H), 2.49 (s, 3H), 1.30 (td, J = 6.3, 4.0 Hz, 1H), 1.22 (d, J = 6.3 Hz, 3H), 0.98 (dd, J = 4.0, 4.0 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ ppm; 192.9, 143.5, 135.3, 133.6, 133.0, 129.6, 128.7, 128.3, 127.6, 58.9, 50.9, 50.2, 33.4, 31.9, 21.6, 20.3, 12.0. HRMS (ESI, m/z): calcd. for $C_{21}H_{23}ClNO_3S^+$ $[M + H]^+$, 404.1082; found, 404.1079.



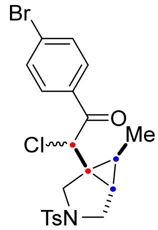
2-Chloro-1-(4-methoxyphenyl)-2-[(1*S,5*S**,6*S**)-6-methyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl]ethan-1-one (2b)**: (**a**) 143.3 mg (83%, 64:36), (**b**) 122.4 mg (71%, 58:42), (**c**) ^{1}H NMR analysis (15%, 57:43). **[major]** R_f = 0.32 (hexane:AcOEt = 2:1). White solid. Mp 170-171 °C. IR (KBr) ν cm^{-1}; 1673, 1600, 1341, 1271, 1198, 1162, 665, 611, 549. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm; 7.90 (d, J = 8.6 Hz, 2H), 7.70 (d, J = 8.6 Hz, 2H), 7.30 (d, J = 8.6 Hz, 2H), 6.93 (d, J = 8.6 Hz, 2H), 5.05 (s, 1H), 3.89 (d, J = 9.5 Hz, 1H), 3.86 (s, 3H), 3.55 (d, J = 10.3 Hz, 1H), 3.53 (d, J = 10.3 Hz, 1H), 3.41 (dd, J = 9.5, 4.0 Hz, 1H), 2.40 (s, 3H), 1.32 (dd, J = 4.0, 4.0 Hz, 1H), 1.25 (qd, J = 6.9, 4.0 Hz, 1H), 1.00 (d, J = 6.9 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ ppm; 190.9, 164.2, 143.3, 133.7, 131.3, 129.6, 127.4, 126.5, 114.1, 58.2, 55.5, 50.3, 49.2, 33.6, 30.7, 23.1, 21.5, 12.4. HRMS (FAB, m/z): calcd. for $C_{22}H_{25}ClNO_4S$ [M + H], 434.1193; found, 434.1182. **[minor]** R_f = 0.29 (hexane:AcOEt = 2:1). White solid. Mp 139-141 °C. IR (KBr) ν cm^{-1}; 1681, 1600, 1341, 1265, 1182, 1166, 665, 605, 549. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm; 7.64 (d, J = 8.6 Hz, 4H), 7.34 (d, J = 8.6 Hz, 2H), 6.85 (d, J = 8.6 Hz, 2H), 5.03 (s, 1H), 3.85 (s, 3H), 3.54 (d, J = 6.3 Hz, 1H), 3.52 (d, J = 6.3 Hz, 1H), 3.30 (d, J = 9.5 Hz, 1H), 2.89 (dd, J = 9.5, 4.0 Hz, 1H), 2.47 (s, 3H), 1.25 (qd, J = 5.7, 4.0 Hz, 1H), 1.21 (d, J = 5.7 Hz, 3H), 1.03 (dd, J = 4.0, 4.0 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ ppm; 190.9, 163.9, 143.3, 133.3, 130.9, 129.6, 127.6, 127.5, 113.9, 57.9, 55.5, 51.0, 50.2, 33.5, 31.6, 21.5, 20.3, 11.9. HRMS (FAB, m/z): calcd. for $C_{22}H_{25}ClNO_4S$ [M + H], 434.1193; found, 434.1189.



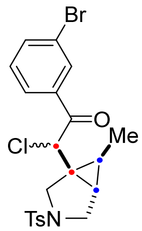
2-Chloro-2-[(1*S,5*S**,6*S**)-6-methyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl]-1-(p-tolyl)ethan-1-one (2c)**: (**a**) 160.7 mg (96%, 54:46), (**b**) 131.2 mg (78%, 31:69), (**c**) 131.0 mg (78%, 57:43). R_f = 0.46 (hexane:AcOEt = 2:1). White solid. Mp 180-181 °C. IR (KBr) ν cm^{-1}; 1683, 1604, 1342, 1163, 666, 609, 549. ^{1}H NMR (500 MHz, $CDCl_3$, 69:31 mixture of epimers) δ ppm; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm; 7.81 (d, J = 8.0 Hz, 0.6H), 7.69 (d, J = 8.0 Hz, 0.6H), 7.62 (d, J = 8.0 Hz, 1.4H), 7.47 (d, J = 8.0 Hz, 1.4H), 7.34 (d, J = 8.0 Hz, 1.4H), 7.30 (d, J = 8.0 Hz, 0.6H), 7.26 (d, J = 8.0 Hz, 0.6H), 7.15 (d, J = 8.0 Hz, 1.4H), 5.07 (s, 0.3H), 5.06 (s, 0.7H), 3.88 (d, J = 9.7 Hz, 0.3H), 3.54 (d, J = 9.7 Hz, 0.3H), 3.52 (d, J = 9.7 Hz, 1H), 3.48 (d, J = 9.2 Hz, 0.7H), 3.24 (d, J = 9.2 Hz, 0.7H), 3.14 (dd, J = 9.7, 4.0 Hz, 0.3H), 2.78 (dd, J = 9.2, 4.0 Hz, 0.7H), 2.47 (s, 2.1H), 2.401 (s, 0.9H), 2.396 (s, 0.9H), 2.37 (s, 2.1H), 1.32 (dd, J = 4.0, 4.0 Hz, 0.3H), 1.27-1.22 (m, 1H), 1.20 (d, J = 5.7 Hz, 2.1H), 1.01 (dd, J = 4.0, 4.0 Hz, 0.7H), 0.99 (d, J = 6.3 Hz, 0.9H). ^{13}C-NMR (125 MHz, $CDCl_3$, 69:31 mixture of epimers) δ ppm; 192.3 (major), 192.0 (minor), 145.1 (minor), 144.6 (major), 143.4 (major), 143.3 (minor), 133.6 (minor), 133.0 (major), 132.5 (major), 131.1 (minor), 129.53 (minor), 129.50 (major + minor), 129.3 (major), 128.9 (minor), 128.5 (major), 127.5 (major), 127.4 (minor), 58.7 (major), 58.3 (minor), 50.8 (major), 50.2 (minor), 50.1 (major), 49.2 (minor), 33.5 (minor), 33.4 (major), 31.8 (major), 30.6 (minor), 23.1 (minor), 21.64 (minor), 21.60 (major), 21.5 (major), 21.4 (minor), 20.3 (major), 12.3 (minor), 11.8 (major). HRMS (FAB, m/z): calcd. for $C_{22}H_{25}ClNO_3S$ [M + H], 420.1214; found, 420.1204.



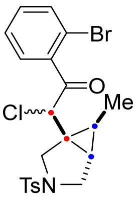
2-Chloro-2-[(1*S,5*S**,6*S**)-6-methyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl]-1-(4-nitrophenyl) ethan-1-one (2d)**: (**a**) 92.9 mg (52%, 65:35), (**b**) 127.7 mg (71%, 71:29), (**c**) 102.5 mg (57%, 53:47). R_f = 0.35 (hexane:AcOEt = 2:1). Yellow solid. Mp 179-181 °C. IR (KBr) ν cm^{-1}; 1697, 1600, 1525, 1343, 1163, 665, 600, 549. ^{1}H NMR (500 MHz, $CDCl_3$, 71:29 mixture of epimers) *δ* ppm; ^{1}H NMR (500 MHz, $CDCl_3$) *δ* ppm; 8.31 (d, *J* = 8.6 Hz, 0.6H), 7.21 (d, *J* = 8.6 Hz, 1.4H), 8.09 (d, *J* = 8.6 Hz, 0.6H), 7.83 (d, *J* = 8.6 Hz, 1.4H), 7.69 (d, *J* = 8.6 Hz, 0.6H), 7.66 (d, *J* = 8.6 Hz, 1.4H), 7.37 (d, *J* = 8.6 Hz, 1.4H), 7.32 (d, *J* = 8.6 Hz, 0.6H), 5.03 (s, 0.3H), 4.98 (s, 0.7H), 3.91 (d, *J* = 10.0 Hz, 0.3H), 3.57 (d, *J* = 9.2 Hz, 0.7H), 3.55 (d, *J* = 9.2 Hz, 0.3H), 3.54 (d, *J* = 9.7 Hz, 0.7H), 3.47 (d, *J* = 10.0 Hz, 0.3H), 3.25 (d, *J* = 9.7 Hz, 0.7H), 3.14 (dd, *J* = 9.2, 4.0 Hz, 0.3H), 2.96 (dd, *J* = 9.2, 4.0 Hz, 0.7H), 2.50 (s, 2.1H), 2.42 (s, 0.9H), 1.37 (dd, *J* = 4.0, 4.0 Hz, 0.3H), 1.31-1.24 (m, 1H), 1.22 (d, *J* = 6.3 Hz, 2.1H), 1.06 (dd, *J* = 4.0, 4.0 Hz, 0.7H), 1.02 (d, *J* = 6.3 Hz, 0.9H). ^{13}C-NMR (125 MHz, $CDCl_3$, 71:29 mixture of epimers) *δ* ppm; 191.3 (major), 190.9 (minor), 150.6 (minor), 150.3 (major), 143.6 (major), 143.5 (minor), 139.7 (major), 138.4 (minor), 133.6 (minor), 133.2 (major), 130.6 (minor), 130.0 (major), 129.6 (major + minor), 127.5 (major), 127.4 (minor), 124.0 (minor), 123.7 (major), 58.8 (minor), 58.3 (major), 51.1 (major), 50.2 (major), 49.9 (minor), 49.1 (minor), 33.1 (minor), 32.9 (major), 31.7 (major), 30.7 (minor), 23.1 (minor), 21.6 (major), 21.5 (minor), 20.2 (major), 12.4 (minor), 11.9 (major). HRMS (FAB, m/z): calcd. for $C_{21}H_{22}ClN_2O_5S$ [M + H], 449.0938; found, 449.0916.



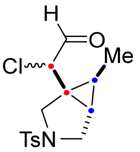
1-(4-Bromophenyl)-2-chloro-2-[(1*S,5*S**,6*S**)-6-methyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl]ethan-1-one (2e)**: (**a**) 193.1 mg (quant., 51:49), (**b**) 175.6 mg (91%, 53:47), (**c**) 157.1 mg (81%, 41:59). **[major]** R_f = 0.51 (hexane:AcOEt = 2:1). White solid. Mp 143-144 °C. IR (KBr) ν cm^{-1}; 1702, 1581, 1351, 1163, 1104, 670, 599, 549. ^{1}H NMR (500 MHz, $CDCl_3$) *δ* ppm; 7.64 (d, *J* = 8.6 Hz, 2H), 7.53-7.48 (m, 4H), 7.35 (d, *J* = 8.6 Hz, 2H), 4.96 (s, 1H), 3.54 (d, *J* = 4.8 Hz, 1H), 3.52 (d, *J* = 4.8 Hz, 1H), 3.24 (d, *J* = 9.2 Hz, 1H), 2.89 (dd, *J* = 9.2, 4.0 Hz, 1H), 2.48 (s, 3H), 1.26 (qd, *J* = 6.3, 4.0 Hz, 1H), 1.20 (d, *J* = 6.3 Hz, 3H), 1.02 (dd, *J* = 4.0, 4.0 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$) *δ* ppm; 191.7, 143.5, 133.7, 133.1, 131.9, 130.0, 129.6, 128.8, 127.5, 58.2, 51.0, 50.2, 33.2, 31.7, 21.6, 20.3, 11.9. HRMS (FAB, m/z): calcd. for $C_{21}H_{22}BrClNO_3S$ [M + H], 482.0192; found, 482.0174. **[minor]** R_f = 0.47 (hexane:AcOEt = 2:1). White solid. Mp 177-178 °C. IR (KBr) ν cm^{-1}; 1685, 1584, 1341, 1163, 1100, 665, 601, 549. ^{1}H NMR (500 MHz, $CDCl_3$) *δ* ppm; 7.79 (d, *J* = 8.6 Hz, 2H), 7.70 (d, *J* = 8.6 Hz, 2H), 7.61 (d, *J* = 8.6 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 5.00 (s, 1H), 3.90 (d, *J* = 9.5 Hz, 1H), 3.54 (d, *J* = 9.5 Hz, 1H), 3.50 (d, *J* = 9.5 Hz, 1H), 3.14 (dd, *J* = 9.5, 3.4 Hz, 1H), 2.42 (s, 3H), 1.37-1.24 (m, 2H), 1.00 (d, *J* = 6.3 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) *δ* ppm; 191.4, 143.4, 133.6, 133.4, 132.2, 130.3, 129.6, 129.4, 127.4, 58.4, 50.1, 49.2, 33.3, 30.7, 23.1, 21.5, 12.4. HRMS (FAB, m/z): calcd. for $C_{21}H_{22}BrClNO_3S$ [M + H], 482.0192; found, 482.0192.



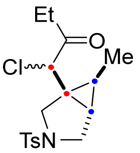
1-(3-Bromophenyl)-2-chloro-2-[(1*S,5*S**,6*S**)-6-methyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl]ethan-1-one (2f)**: (**a**) 175.7 mg (91%, 61:39), (**b**) 166.9 mg (86%, 61:39), (**c**) 152.2 mg (79%, 66:34). R_f = 0.39 (hexane:AcOEt = 2:1). Pale yellow solid. Mp 137-141 °C. IR (KBr) ν cm^{-1}; 1696, 1567, 1345, 1165, 1113, 666, 600, 550. ^{1}H NMR (500 MHz, $CDCl_3$, 61:39 mixture of epimers) *δ* ppm; ^{1}H NMR (500 MHz, $CDCl_3$) *δ* ppm; 8.01 (t, *J* = 1.7 Hz, 0.6H), 7.81 (d, *J* = 8.0 Hz, 0.6H), 7.72 (t, *J* = 1.7 Hz, 0.4H), 7.71-7.60 (m, 3H), 7.54 (d, *J* = 8.0 Hz, 0.4H), 7.36-7.27 (m, 2.6H), 7.24 (d, *J* = 6.9 Hz, 0.4H), 4.96 (s, 0.6H), 4.93 (s, 0.4H), 3.85 (d, *J* = 10.0 Hz, 0.6H), 3.53 (d, *J* = 5.2 Hz, 0.4H), 3.52 (d, *J* = 9.5 Hz, 0.6H), 3.51 (d, *J* = 5.2 Hz, 0.4H), 3.46 (d, *J* = 9.5 Hz, 0.6H), 3.22 (d, *J* = 9.2 Hz, 0.4H), 3.11 (dd, *J* = 10.0, 4.0 Hz, 0.6H), 2.89 (dd, *J* = 9.2, 4.0 Hz, 0.4H), 2.45 (s, 1.2H), 2.39 (s, 1.8H), 1.31 (dd, *J* = 4.0, 4.0 Hz, 0.6H), 1.30-1.25 (m, 1H), 1.18 (d, *J* = 6.3 Hz, 1.2H), 0.99 (d, *J* = 6.3 Hz, 1.8H), 0.98 (dd, *J* = 4.0, 4.0 Hz, 0.4H). ^{13}C-NMR (125 MHz, $CDCl_3$, 61:39 mixture of epimers) *δ* ppm; 191.3 (minor), 191.1 (major), 143.5 (minor), 143.4 (major), 136.82 (major), 136.78 (minor), 136.5 (minor), 135.5 (major), 133.6 (major), 133.1 (minor), 131.8 (major), 131.4 (minor), 130.4 (major), 130.2 (minor), 129.64 (minor), 129.60 (major), 127.5 (minor), 127.4 (major), 127.3 (major), 127.0 (minor), 123.1 (major), 123.0 (minor), 58.5 (major), 58.1 (minor), 51.0 (major), 50.2 (minor), 50.1 (major), 49.2 (minor), 33.3 (major), 33.1 (minor), 31.6 (minor), 30.7 (major), 23.1 (major), 21.6 (minor), 21.5 (major), 20.3 (minor), 12.4 (major), 11.9 (minor). HRMS (FAB, m/z): calcd. for $C_{21}H_{22}BrClNO_3S$ [M + H], 482.0192; found, 482.0192.



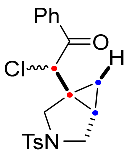
1-(2-Bromophenyl)-2-chloro-2-[(1*S,5*S**,6*S**)-6-methyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl]ethan-1-one (2g)**: (**a**) 156.0 mg (81%, 55:45), (**b**) 115.6 mg (60%, 58:42), (**c**) 132.8 mg (69%, 60:40). **[major]** R_f = 0.41 (hexane:AcOEt = 2:1). White solid. Mp 169-170 °C. IR (KBr) ν cm^{-1}; 1707, 1582, 1339, 1161, 1098, 670, 601, 549. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm; 7.69 (d, J = 8.6 Hz, 2H), 7.59 (d, J = 8.0 Hz, 1H), 7.41 (dd, J = 8.0, 6.9 Hz, 1H), 7.38-7.31 (m, 4H), 5.15 (s, 1H), 3.55 (d, J = 9.7 Hz, 1H), 3.53 (d, J = 9.2 Hz, 1H), 3.40 (d, J = 9.7 Hz, 1H), 2.89 (dd, J = 9.2, 4.0 Hz, 1H), 2.43 (s, 3H), 1.26 (qd, J = 6.3, 4.0 Hz, 1H), 1.26 (dd, J = 4.0, 4.0 Hz, 1H), 0.80 (d, J = 6.3 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ ppm; 196.2, 143.6, 138.9, 133.4, 133.2, 132.4, 129.7, 129.2, 127.7, 127.5, 118.7, 63.6, 49.5, 49.3, 34.0, 30.5, 23.7, 21.5, 12.5. HRMS (FAB, m/z): calcd. for $C_{21}H_{22}BrClNO_3S$ [M + H], 482.0192; found, 482.0192. **[minor]** R_f = 0.38 (hexane:AcOEt = 2:1). Pale yellow oil. IR (neat) ν cm^{-1}; 1716, 1586, 1348, 1167, 1108, 665, 598, 550. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm; 7.67 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 8.0 Hz, 1H), 7.39 (d, J = 8.0 Hz, 2H), 7.27 (ddd, J = 8.0, 7.5, 1.7 Hz, 1H), 7.09 (dd, J = 7.5, 7.5 Hz, 1H), 6.63 (dd, J = 7.5, 1.7 Hz, 1H), 5.27 (s, 1H), 3.57 (d, J = 9.7 Hz, 1H), 3.42 (d, J = 9.2 Hz, 1H), 3.00 (d, J = 9.7 Hz, 1H), 2.63 (dd, J = 9.2, 4.0 Hz, 1H), 2.47 (s, 3H), 1.29 (qd, J = 6.3, 4.0 Hz, 1H), 1.16 (d, J = 6.3 Hz, 3H), 0.80 (dd, J = 4.0, 4.0 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ ppm; 195.7, 143.8, 139.7, 133.6, 132.7, 132.4, 129.7, 128.8, 127.8, 127.4, 118.4, 63.2, 50.4, 50.1, 33.6, 31.5, 21.6, 20.0, 11.6. HRMS (FAB, m/z): calcd. for $C_{21}H_{22}BrClNO_3S$ [M + H], 482.0192; found, 482.0174.



2-Chloro-2-[(1*S,5*S**,6*S**)-6-methyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl]acetaldehyde (2h)**: (**a**) 33.2 mg (25%, 43:57), (**b**) 67.4 mg (51%, 60:40), (**c**) 34.7 mg (26%, 55:45). R_f = 0.30 (hexane:AcOEt = 2:1). Colorless oil. IR (neat) ν cm^{-1}; 1732, 1598, 1344, 1164, 666, 605, 549. ^{1}H NMR (500 MHz, $CDCl_3$, 60:40 mixture of epimers) δ ppm; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm; 9.50 (s, 0.4H), 9.46 (s, 0.6H), 7.65 (d, J = 8.0 Hz, 1.2H), 7.63 (d, J = 8.0 Hz, 0.8H), 7.32 (d, J = 8.0 Hz, 1.2H), 7.31 (d, J = 8.0 Hz, 0.8H), 4.24 (s, 0.6H), 4.09 (s, 0.4H), 3.62 (d, J = 9.2 Hz, 0.4H), 3.56 (d, J = 9.2 Hz, 0.4H), 3.53 (d, J = 9.7 Hz, 0.6H), 3.50 (d, J = 9.2 Hz, 0.6H), 3.22 (d, J = 9.2 Hz, 0.6H), 3.19 (dd, J = 9.7, 4.0 Hz, 0.4H), 3.08 (dd, J = 9.7, 4.0 Hz, 0.6H), 2.94 (d, J = 9.7 Hz, 0.4H), 2.42 (s, 3H), 1.37 (dd, J = 4.0, 4.0 Hz, 0.4H), 1.36-1.30 (m, 1H), 1.21-1.15 (m, 0.6H), 1.11 (d, J = 6.3 Hz, 1.2H), 1.10 (d, J = 6.3 Hz, 1.8H). ^{13}C NMR (125 MHz, $CDCl_3$, 60:40 mixture of epimers) δ ppm; 194.4 (minor), 192.7 (major), 143.7 (minor), 143.6 (major), 133.38 (minor), 133.36 (major), 129.7, 127.4 (major), 127.3 (minor), 65.0 (major), 63.5 (minor), 50.7 (major), 50.2 (minor), 49.4 (major), 48.9 (minor), 33.0 (major), 32.9 (minor), 30.4 (minor), 30.1 (major), 22.9 (major), 21.5, 18.7 (minor), 12.6 (major), 11.5 (minor). HRMS (ESI, m/z): calcd. for $C_{15}H_{19}ClNO_3S^+$ $[M + H]^+$, 328.0769; found, 328.0770.

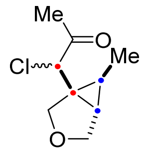


1-Chloro-1-[(1*S,5*S**,6*S**)-6-methyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl]butan-2-one (2i)**: (**a**) 121.1 mg (85%, 59:41), (**b**) 105.2 mg (74%, 60:40), (**c**) 88.8 mg (62%, 62:38). **[major]** R_f = 0.49 (hexane:AcOEt = 2:1). White solid. Mp 116-117 °C. IR (KBr) ν cm^{-1}; 1722, 1598, 1338, 1163, 668, 604, 550. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm; 7.66 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 4.28 (s, 1H), 3.52 (d, J = 9.2 Hz, 1H), 3.50 (d, J = 9.2 Hz, 1H), 3.27 (d, J = 9.2 Hz, 1H), 3.07 (dd, J = 9.2, 4.0 Hz, 1H), 2.66 (dq, J = 18.3, 7.2 Hz, 1H), 2.57 (dq, J = 18.3, 7.2 Hz, 1H), 2.42 (s, 3H), 1.33 (qd, J = 6.9, 4.0 Hz, 1H), 1.24 (dd, J = 4.0, 4.0 Hz, 1H), 1.13 (d, J = 6.9 Hz, 3H), 1.08 (t, J = 7.2 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ ppm; 203.4, 143.5, 133.5, 129.6, 127.4, 64.4, 49.5, 49.2, 34.3, 33.0, 30.5, 23.4, 21.5, 12.7, 7.7. HRMS (FAB, m/z): calcd. for $C_{17}H_{23}ClNO_3S$ [M + H], 356.1087; found, 356.1103. **[minor]** R_f = 0.41 (hexane:AcOEt = 2:1). White solid. Mp 146-148 °C. IR (KBr) ν cm^{-1}; 1734, 1598, 1344, 1168, 666, 606, 549. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm; 7.62 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 4.16 (s, 1H), 3.59 (d, J = 9.2 Hz, 1H), 3.50 (d, J = 9.2 Hz, 1H), 3.17 (dd, J = 9.2, 4.0 Hz, 1H), 2.93 (d, J = 9.2 Hz, 1H), 2.60 (dq, J = 18.3, 7.2 Hz, 1H), 2.41 (s, 3H), 2.39 (dq, J = 18.3, 7.2 Hz, 1H), 1.34-1.30 (m, 1H), 1.14-1.08 (m, 4H), 0.89 (t, J = 7.2 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ ppm; 204.3, 143.6, 133.2, 129.6, 127.3, 63.9, 50.9, 50.3, 34.1, 33.5, 31.6, 21.4, 19.5, 11.6, 7.5. HRMS (FAB, m/z): calcd. for $C_{17}H_{23}ClNO_3S$ [M + H], 356.1087; found, 356.1103.

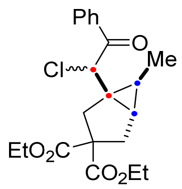


2-Chloro-1-phenyl-2-[(1*S,5*S**)-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl]ethan-1-one (2j)**: (**a**) 113.1 mg (73%, 60:40), (**b**) 116.5 mg (75%, 53:47), (**c**) 115.4 mg (74%, 44:56). **[major]** R_f = 0.49 (hexane:AcOEt = 2:1). Pale yellow solid. Mp 162-163 °C. IR (KBr) ν cm^{-1}; 1691, 1597, 1342, 1164, 664, 593, 550. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm; 7.89 (d, J = 7.5 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H), 7.60 (t, J = 7.5 Hz, 1H), 7.47 (dd, J = 7.5, 7.5 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 4.89 (s, 1H), 3.84 (d, J = 9.7 Hz, 1H), 3.52 (d, J = 9.7 Hz, 1H), 3.43 (d, J = 9.7 Hz, 1H), 3.17 (dd, J = 9.7, 4.0 Hz, 1H), 2.42 (s, 3H), 1.62-1.57 (m, 1H), 0.91 (s, 1H), 0.89 (d, J = 2.3 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ ppm; 191.9, 143.5, 134.1, 133.5, 129.6, 128.84, 128.82, 127.4, 61.4, 49.4, 49.1, 29.8, 23.3, 21.5, 16.3 (note that two carbon peaks overlap with each other). HRMS (FAB, m/z): calcd. for $C_{20}H_{21}ClNO_3S$ [M +

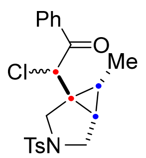
H], 390.0931; found, 390.0918. **[minor]** R_f = 0.43 (hexane:AcOEt = 2:1). White solid. Mp 107-108 °C. IR (KBr) ν cm^{-1}; 1697, 1596, 1338, 1161, 670, 597, 549. ^{1}H NMR (500 MHz, $CDCl_3$) *δ* ppm; 7.76 (d, *J* = 7.5 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.42 (dd, *J* = 7.5, 7.5 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 5.11 (s, 1H), 3.60 (d, *J* = 9.7 Hz, 1H), 3.51 (d, *J* = 9.7 Hz, 1H), 3.25 (d, *J* = 9.2 Hz, 1H), 3.04 (dd, *J* = 9.2, 4.0 Hz, 1H), 2.45 (s, 3H), 1.56 (td, *J* = 5.7, 4.0 Hz, 1H), 0.91 (d, *J* = 5.7 Hz, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$) *δ* ppm; 192.1, 143.6, 134.6, 133.9, 133.2, 129.6, 128.8, 128.6, 127.4, 60.2, 50.8, 49.8, 29.7, 22.4, 21.5, 14.7. HRMS (FAB, m/z): calcd. for $C_{20}H_{21}ClNO_3S$ [M + H], 390.0931; found, 390.0921.



1-Chloro-1-[(1*S,5*S**,6*S**)-6-methyl-3-oxabicyclo[3.1.0]hexan-1-yl]propan-2-one (2k)**: (**a**) 51.3 mg (68%, 51:49), (**b**) 50.4 mg (67%, 61:39), (**c**) 64.5 mg (85%, 51:49). **[major]** R_f = 0.56 (hexane:AcOEt = 2:1). Colorless oil. IR (neat) ν cm^{-1}; 1726, 1358, 1061, 645, 588. ^{1}H NMR (500 MHz, $CDCl_3$) *δ* ppm; 4.48 (s, 1H), 3.90 (d, *J* = 8.0 Hz, 1H), 3.80 (d, *J* = 8.6 Hz, 1H), 3.77 (d, *J* = 8.0 Hz, 1H), 3.72 (dd, *J* = 8.6, 2.9 Hz, 1H), 2.33 (s, 3H), 1.40 (dd, *J* = 5.2, 2.9 Hz, 1H), 1.30 (qd, *J* = 6.3, 5.2 Hz, 1H), 1.19 (d, *J* = 6.3 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) *δ* ppm; 201.1, 69.3, 68.6, 64.9, 35.0, 32.2, 27.1, 22.6, 12.7. HRMS (ESI, m/z): calcd. for $C_9H_{13}O_2^+$ [M - Cl]$^+$, 153.0910; found, 153.0914. **[minor]** R_f = 0.48 (hexane:AcOEt = 2:1). Colorless oil. IR (neat) ν cm^{-1}; 1731, 1359, 1059, 654, 560. ^{1}H NMR (500 MHz, $CDCl_3$) *δ* ppm; 4.41 (s, 1H), 3.88 (d, *J* = 8.6 Hz, 1H), 3.82 (d, *J* = 8.0 Hz, 1H), 3.79 (dd, *J* = 8.0, 2.9 Hz, 1H), 3.62 (d, *J* = 8.6 Hz, 1H), 2.38 (s, 3H), 1.50 (dd, *J* = 4.0, 2.9 Hz, 1H), 1.19 (d, *J* = 5.7 Hz, 3H), 1.14 (qd, *J* = 5.7, 4.0 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$) *δ* ppm; 201.8, 70.3, 70.0, 64.7, 35.2, 33.4, 28.2, 18.6, 11.6. HRMS (ESI, m/z): calcd. for $C_9H_{13}O_2^+$ [M - Cl]$^+$, 153.0910; found, 153.0909.

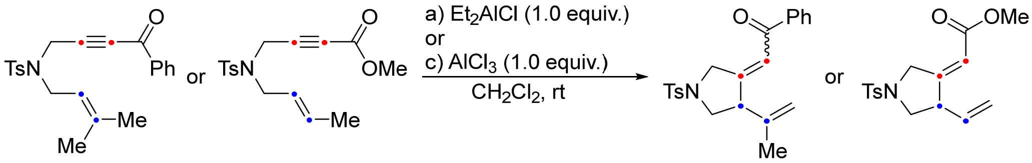


Diethyl (1*S,5*S**,6*S**)-1-(1-chloro-2-oxo-2-phenylethyl)-6-methylbicyclo[3.1.0]hexane-3,3-dicarboxylate (2l)**: (**a**) 71.4 mg (45%, 64:36). (**b**) 42.1 mg (27%, 60:40). (**c**) ^{1}H NMR analysis (20%, 63:37). **[major]** R_f = 0.59 (hexane:AcOEt = 2:1). Colorless oil. IR (neat) ν cm^{-1}; 1729, 1694, 1597, 1251, 1181, 738, 689. ^{1}H NMR (500 MHz, $CDCl_3$) *δ* ppm; 7.93 (d, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.46 (dd, *J* = 7.5, 7.5 Hz, 2H), 5.11 (s, 1H), 4.16 (q, *J* = 7.0 Hz, 2H), 4.14 (q, *J* = 7.0 Hz, 2H), 2.96 (d, *J* = 14.3 Hz, 1H), 2.84 (d, *J* = 14.3 Hz, 1H), 2.59 (dd, *J* = 13.8, 5.2 Hz, 1H), 2.44 (d, *J* = 13.8 Hz, 1H), 1.26 (dd, *J* = 5.2, 4.6 Hz, 1H), 1.22 (t, *J* = 7.0 Hz, 3H), 1.20 (t, *J* = 7.0 Hz, 3H), 1.01-0.94 (m, 1H), 0.97 (d, *J* = 4.6 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) *δ* ppm; 193.2, 172.7, 171.5, 134.5, 133.6, 128.70, 128.67, 61.6, 61.5, 61.1, 60.8, 37.3, 35.8, 35.5, 33.7, 25.5, 13.92, 13.89, 13.5. HRMS (ESI, m/z): calcd. for $C_{21}H_{26}ClO_5^+$ [M + H]$^+$, 393.1463; found, 393.1474. **[minor]** R_f = 0.56 (hexane:AcOEt = 2:1). Colorless oil. IR (neat) ν cm^{-1}; 2980, 2936, 1731, 1697, 1250, 1181. ^{1}H NMR (500 MHz, $CDCl_3$) *δ* ppm; 7.83 (d, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.47 (dd, *J* = 7.5, 7.5 Hz, 2H), 5.18 (s, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.67 (d, *J* = 14.3 Hz, 1H), 2.64 (d, *J* = 14.3 Hz, 1H), 2.43 (d, *J* = 14.3 Hz, 1H), 2.18 (dd, *J* = 14.3, 4.6 Hz, 1H), 1.22 (t, *J* =7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H), 1.20 (d, *J* = 6.3 Hz, 3H), 0.97 (dd, *J* = 4.6, 4.6 Hz, 1H), 0.86 (qd, *J* = 6.3, 4.6 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$) *δ* ppm; 193.6, 172.6, 171.2, 136.1, 133.3, 128.64, 128.56, 61.7, 61.6, 61.5, 59.6, 37.2, 36.3, 35.4, 34.8, 22.5, 14.0, 13.9, 13.0. HRMS (ESI, m/z): calcd. for $C_{21}H_{26}ClO_5^+$ [M + H]$^+$, 393.1463; found, 393.1475.



2-Chloro-2-[(1*S,5*S**,6*R**)-6-methyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl]-1-phenylethan-1-one (*cis*-2a)**: (**a**) 98.2 mg (61%, 65:35). **[major]** R_f = 0.39 (hexane:AcOEt = 2:1). White solid. Mp 139-141 °C. IR (KBr) ν cm^{-1}; 1690, 1339, 1164, 667. ^{1}H NMR (500 MHz, $CDCl_3$) *δ* ppm; 7.87 (d, *J* = 7.4 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.46 (dd, *J* = 7.4, 7.4 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.75 (s, 1H), 3.71 (d, *J* = 10.3 Hz, 1H), 3.65 (d, *J* = 10.3 Hz, 1H), 3.44 (dd, *J* = 9.7, 5.2 Hz, 1H), 3.37 (d, *J* = 9.7 Hz, 1H), 2.41 (s, 3H), 1.62 (dd, *J* = 8.6, 5.2 Hz, 1H), 1.22-1.16 (m, 1H), 0.94 (d, *J* = 6.4 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) *δ* ppm; 192.1, 143.4, 134.01, 133.96, 133.7, 129.6, 128.82, 128.78, 127.4, 63.8, 47.0, 46.6, 34.0, 27.1, 24.5, 21.5, 6.1. HRMS (ESI, m/z): calcd. for $C_{21}H_{23}ClNO_3S^+$ [M + H]$^+$, 404.1082; found, 404.1081. **[minor]** R_f = 0.37 (hexane:AcOEt = 2:1). White solid. Mp 149-151 °C. IR (KBr) ν cm^{-1}; 1693, 1339, 1164, 668. ^{1}H NMR (500 MHz, $CDCl_3$) *δ* ppm; 7.70 (d, *J* = 7.4 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.42 (dd, *J* = 7.4, 7.4 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 5.05 (s, 1H), 3.48 (d, *J* = 9.7 Hz, 1H), 3.44 (d, *J* = 9.7 Hz, 1H), 3.39 (d, *J* = 9.7 Hz, 1H), 3.27 (dd, *J* = 9.7, 5.2 Hz, 1H), 2.47 (s, 3H), 1.54 (dd, *J* = 8.6, 5.2 Hz, 1H), 1.29-1.23 (m, 1H), 1.08 (d, *J* = 6.3 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) *δ* ppm; 192.1, 143.5, 134.9, 133.8, 133.5, 129.6, 128.7, 128.5, 127.5, 62.0, 48.5, 47.2, 33.3, 25.9, 22.0, 21.5, 6.0. HRMS (ESI, m/z): calcd. for $C_{21}H_{23}ClNO_3S^+$ [M + H]$^+$, 404.1082; found, 404.1089.

4. Ene-type Reaction of 1m and 1n using $Et_nAlCl_{(3-n)}$ and Characterization of 4m and 4n



1m **1n** **4m** **4n**

Preparation of (*Z*)- and (*E*)-1-Phenyl-2-(4-(prop-1-en-2-yl)-1-tosylpyrrolidin-3-ylidene)ethan-1-one (4m)

To a solution of enynone **1m** (152.6 mg, 0.4 mmol) in CH_2Cl_2 (2 mL) was added Et_2AlCl (1.0 M in hexane solution, 0.4 mL, 0.4 mmol, method **a**) at 0 ºC. After being stirred at room temperature for 1 h, the reaction mixture was quenched with s sat. $NaHCO_3$ and sat. Rochelle salt, and extracted with AcOEt. The organic layer was dried over $MgSO_4$ and concentrated in vacuo to dryness. The residue was purified by MPLC (hexane:AcOEt = 85:15) to give **4m** (113.7 mg, 75%) as a mixture of geometric isomers in 90:10 ratio. The major isomer of **4m** was determined to be the *Z*-isomer by NOESY spectra analysis (See page S11).

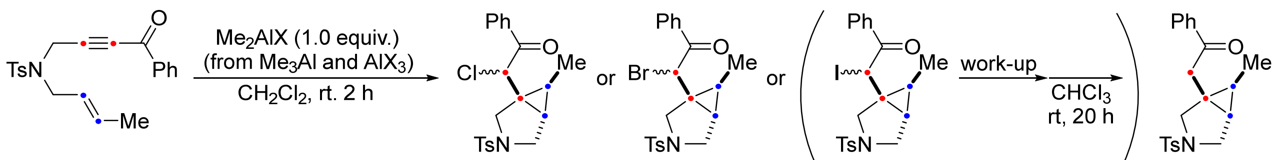
4m: R_f = 0.48 (hexane:AcOEt = 2:1). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$, 90:10 mixture of geometric isomers) δ ppm: 7.87 (d, J = 7.4 Hz, 2H), 7.76 (d, J = 8.0 Hz, 1.8H), 7.62 (d, J = 8.0 Hz, 0.2H), 7.57 (t, J = 7.4 Hz, 0.1H), 7.54 (t, J = 7.4 Hz, 0.9H), 7.44 (dd, J = 7.4, 7.4 Hz, 2H), 7.33 (d, J = 8.0 Hz, 1.8H), 7.27 (d, J = 8.0 Hz, 0.2H), 6.82 (ddd, J = 2.7, 2.7, 1.7 Hz, 0.9H), 6.41 (ddd, J = 1.2, 1.2, 1.2 Hz, 0.1H), 4.99 (br.s, 0.9H), 4.95 (br.s, 0.9H), 4.71 (br.s, 0.1H), 4.64 (br.s, 0.1H), 4.56 (dd, J = 18.9, 2.7 Hz, 0.9H), 4.29 (ddd, J = 18.9, 2.7, 2.7 Hz, 0.9H), 3.61-3.56 (m, 2.1H), 3.42 (d, J = 17.2 Hz, 0.1H), 3.35 (ddd, J = 5.2, 4.6, 4.6 Hz, 0.1H) , 3.13-3.05 (m, 0.9H), 2.41 (s, 3H), 1.62 (s, 2.7H), 1.36 (s, 0.3H). ^{13}C NMR (125 MHz, $CDCl_3$, 90:10 mixture of geometric isomers) δ ppm: 196.4 (minor), 189.5 (major), 160.7, 143.8 (major), 143.0 (minor), 141.7, 138.0 (major), 136.3 (minor), 133.3 (minor), 132.9 (major), 132.4 (minor), 132.2 (major), 129.7 (major), 129.6 (minor), 128.9 (minor), 128.6 (major), 128.2 (minor), 128.1 (major), 127.9 (major), 127.7 (minor), 120.1 (minor), 117.0 (major), 116.2 (major), 114.2 (minor), 53.7 (major), 52.9 (major), 52.6 (minor), 51.5 (minor), 50.3 (major), 35.7 (minor), 21.5, 18.7(major), 17.7 (minor). The ^{1}H and ^{13}C NMR spectra of **4m** were identical to data reported in the literature.[1]

Preparation of (*Z*)-Methyl 2-(1-tosyl-4-vinylpyrrolidin-3-ylidene)acetate (4n)

To a solution of enynone **1n** (128.6 mg, 0.4 mmol) in CH_2Cl_2 (2 mL) was added $AlCl_3$ (53.3 mg, 0.4 mmol, method **c**) at 0 ºC. After being stirred at room temperature for 24 h, the reaction mixture was quenched with sat. $NaHCO_3$ and sat. Rochelle salt, and extracted with AcOEt. The organic layer was dried over $MgSO_4$ and concentrated in vacuo to dryness. The residue was purified by MPLC (hexane:AcOEt = 85:15) to give **4m** (100.3 mg, 78%). Considering the stereochemistry of major isomer of **4m**, **4n** was determined to be the *Z*-isomer

4n: R_f = 0.47 (hexane:AcOEt = 2:1). Colorless oil. IR (neat) ν cm^{-1}; 1715, 1351, 1218, 1164. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm; 7.73 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.3 Hz, 2H), 5.66 (ddd, J = 2.9, 2.3, 2.3 Hz, 1H), 5.48 (ddd, J = 17.2, 10.3, 8.3 Hz, 1H), 5.21 (d, J = 10.4 Hz, 1H), 5.18 (d, J = 17.2 Hz, 1H), 4.48 (dd, J = 18.3, 2.3 Hz, 1H), 4.08 (ddd, J = 18.3, 2.3, 2.3 Hz, 1H), 3.69 (s, 3H), 3.68 (dd, J = 9.3, 7.7 Hz, 1H), 3.43-3.48 (m, 1H), 2.79 (dd, J = 9.3, 9.3 Hz, 1H), 2.43 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ ppm; 166.1, 160.1, 143.9, 134.1, 132.2, 129.8, 128.0, 119.8, 114.1, 52.4, 51.9, 51.4, 49.1, 21.5. HRMS (ESI, m/z): calcd. for $C_{16}H_{20}NO_4S^+$ [M + H]$^+$, 322.1108; found, 322.1098.

5. Skeletal Rearrangement of 1a using $Me_nAlX_{(3-n)}$ and Characterization of 5 and 7



1a **2a** **5** **6** **7**

To a solution of Me_2AlX, which was generated from Me_3Al (1.4 M in hexane solution, 0.19 mL, 0.266 mmol) and AlX_3 (X = Cl, 17.8 mg; X = Br, 35.5 mg; 0.133 mmol) at 60 ºC for 30 min,[2] was added CH_2Cl_2 (2 mL) and enynone **1a** (147.0 mg, 0.4 mmol) at 0 ºC. After being stirred at room temperature for 2 h, the reaction mixture was quenched with sat. $NaHCO_3$ and sat. Rochelle salt, and extracted with AcOEt. The organic layer was dried over $MgSO_4$ and concentrated in vacuo to dryness. The residue was purified by MPLC (hexane:AcOEt = 88:12) to give **2a** (142.7 mg, 88%, 55:45) or **5** (164.2 mg, 91%, 50:50) as an epimeric mixture. The ^{1}H NMR spectra of the obtained **2a** were identical to data of the above-mentioned **2a**.

【The case of the iodinated **6**】In the similar manner, the crude product including **6** were prepared from **1a** (147.0 mg, 0.4 mmol) using Me_3Al (1.4 M in hexane solution, 0.19 mL, 0.266 mmol) and AlI_3 (54.3 mg, 0.133 mmol) in CH_2Cl_2 (4 mL). Notably, the molecular ion peak of **6** (HRMS: m/z calcd. for $C_{21}H_{23}INO_3S^+$ [M + H]$^+$, 496.0438; found, 496.0443) was detected

[2] O. T. Beachley, Jr., L. Victoriano, *Organometallics* **1988**, *7*, 63–67.

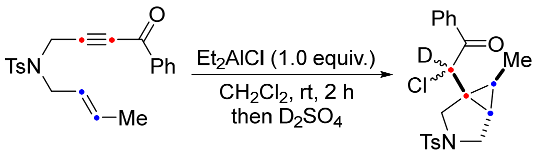
in ESI-Mass spectrum of the crude product. After the above-mentioned wok-up, the crude product (191.0 mg) was dissolved in $CHCl_3$ (20 mL) and then the resulting solution was allowed to stand at rt for 20 h. During this time, the color of the solution changed from pale yellow to brown. Subsequently, the solution was quenched with 20% $Na_2S_2O_3$ aq. and extracted with CH_2Cl_2. After the organic layer was dried over $MgSO_4$ and concentrated in vacuo to dryness, the purification of the residue using MPLC (hexane:AcOEt = 88:12) afforded **7** (60.6 mg, 41%).

2-Bromo-2-[(1*S,5*S**,6*S**)-6-methyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl]-1-phenylethan-1-one (5)**: R_f = 0.42 (hexane:AcOEt = 2:1). Colorless amorphous. IR (neat) ν cm^{-1}; 1685, 1341, 1165, 667, 548. ^1H NMR (500 MHz, $CDCl_3$, 50:50 mixture of epimers) δ ppm; 7.92 (d, J = 7.4 Hz, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.70 (d, J = 7.4 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.59 (t, J = 7.4 Hz, 0.5H), 7.55 (t, J = 7.4 Hz, 0.5H), 7.47 (dd, J = 7.4, 7.4 Hz, 1H), 7.40 (dd, J = 7.4, 7.4 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.32 (d, J = 8.0 Hz, 1H), 5.20 (s, 0.5H), 5.06 (s, 0.5H), 3.98 (d, J = 9.7 Hz, 0.5H), 3.63 (d, J = 9.7 Hz, 0.5H), 3.61 (d, J = 9.7 Hz, 0.5H), 3.56 (d, J = 9.2 Hz, 0.5H), 3.53 (d, J = 9.2 Hz, 0.5H), 3.52 (d, J = 9.2 Hz, 0.5H), 3.16 (dd, J = 9.2, 4.0 Hz, 0.5H), 3.01 (dd, J = 9.7, 4.0 Hz, 0.5H), 2.48 (s, 1.5H), 2.42 (s, 1.5H), 1.45-1.40 (m, 0.5H), 1.33-1.28 (m, 1H), 1.21 (d, J = 6.3 Hz, 1.5H), 1.04-1.02 (m, 0.5H), 1.02 (d, J = 6.3 Hz, 1.5H). ^{13}C-NMR (125 MHz, $CDCl_3$, 50:50 mixture of epimers) δ ppm; 192.01, 191.99, 143.4, 143.3, 134.6, 133.9, 133.7, 133.6, 133.5, 129.61, 129.59, 128.9, 128.70, 128.67, 128.5, 127.52, 127.49, 52.4, 51.6, 50.7, 49.7, 49.0, 47.1, 33.6, 33.1, 32.3, 32.2, 24.9, 21.6, 21.5, 20.6, 12.5, 11.5 (note that one carbon peak of each isomer overlaps with each other). HRMS (ESI, m/z): calcd. for $C_{21}H_{23}BrNO_3S^+$ [M + H]$^+$, 448.0577; found, 448.0588.

2-[(1*S,5*S**,6*S**)-6-methyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl]-1-phenylethan-1-one (7)**: R_f = 0.47 (hexane:AcOEt = 2:1). Colorless amorphous. IR (neat) ν cm^{-1}; 1686, 1340, 1164, 667. ^1H NMR (500 MHz, $CDCl_3$) δ ppm; 7.86 (d, J = 7.5 Hz, 2H), 7.65 (d, J = 8.0 Hz, 2H), 7.55 (t, J = 7.5 Hz, 1H), 7.43 (dd, J = 7.5, 7.5 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 3.76 (d, J = 9.2 Hz, 1H), 3.54 (d, J = 9.2 Hz, 1H), 3.18 (dd, J = 9.2, 3.4 Hz, 1H), 3.16 (d, J = 18.3 Hz, 1H), 3.10 (d, J = 18.3 Hz, 1H), 2.93 (d, J = 9.2 Hz, 1H), 2.41 (s, 3H), 1.03-0.95 (m, 2H), 0.96 (d, J = 5.7 Hz, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ ppm; 198.2, 143.2, 136.6, 133.7, 133.2, 129.5, 128.6, 127.7, 127.4, 54.3, 50.1, 37.7, 28.4, 27.7, 21.5, 18.5, 12.6. HRMS (ESI, m/z): calcd. for $C_{21}H_{24}NO_3S^+$ [M + H]$^+$, 370.1471; found, 370.1478.

6. Quenching of Aluminum Enolate with Electrophiles and Characterization of d-2a, 8 and 9

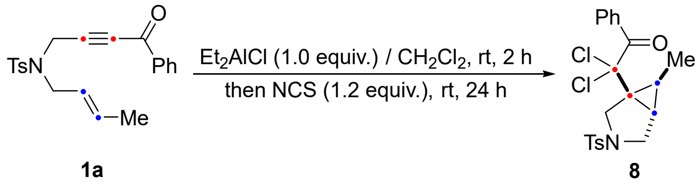
(a) Deuteration of aluminum enolate



To a solution of enynone **1a** (73.5 mg, 0.2 mmol) in CH_2Cl_2 (1 mL) was added Et_2AlCl (1.0 M in hexane solution, 0.2 mL, 0.2 mmol) at 0 ºC. After being stirred at room temperature for 2 h, D_2SO_4 (96-98 wt.% in D_2O, 99.5%D, 1 mL) was added at 0 ºC. After being stirred at room temperature for 1 h, the reaction mixture was quenched with sat. $NaHCO_3$ and sat. Rochelle salt, and extracted with AcOEt. The organic layer was dried over $MgSO_4$ and concentrated in vacuo to dryness. The residue was purified by MPLC (hexane:AcOEt = 80:20) to give **d-2a** (82.1 mg, quant. >99%D) as an epimeric mixture (72:28).

2-Chloro-2-[(1*S,5*S**,6*S**)-6-methyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl]-1-phenylethan-1-one-2-*d* (d-2a)**: R_f = 0.40 (hexane:AcOEt = 2:1). White solid. Mp 157-162 °C. IR (KBr) ν cm^{-1}; 1686, 1596, 1340, 1164, 667, 592, 549. ^1H NMR (500 MHz, $CDCl_3$, 72:28 mixture of epimers) δ ppm; 7.91 (d, J = 8.0 Hz, 1.4H), 7.70 (d, J = 8.0 Hz, 1.4H), 7.63 (d, J = 8.6 Hz, 0.6H), 7.59 (t, J = 8.0 Hz, 0.7H), 7.56-7.51 (m, 0.9H), 7.47 (dd, J = 8.0, 8.0 Hz, 1.4H), 7.38-7.33 (m, 1.2H), 7.30 (d, J = 8.0 Hz, 1.4H), 3.89 (d, J = 9.7 Hz, 0.7H), 3.57-3.52 (m, 1.7H), 3.48 (d, J = 9.2 Hz, 0.3H), 3.21 (d, J = 9.2 Hz, 0.3H), 3.14 (dd, J = 9.7, 4.0 Hz, 0.7H), 2.73 (dd, J = 9.2, 3.4 Hz, 0.3H), 2.48 (s, 0.9H), 2.40 (s, 2.1H), 1.34 (dd, J = 4.0, 4.0 Hz, 0.7H), 1.30-1.23 (m, 1H), 1.21 (d, J = 5.7 Hz, 0.9H), 1.02-0.98 (m, 0.3H), 1.00 (d, J = 6.3 Hz, 2.1H). ^{13}C-NMR (125 MHz, $CDCl_3$, 72:28 mixture of epimers) δ ppm; 192.9 (minor), 192.5 (major), 143.4 (minor), 143.3 (major), 135.3 (minor), 134.0 (major), 133.7 (major), 133.6 (major), 133.5 (minor), 132.9 (minor), 129.6, 128.81 (major), 128.77 (major), 128.6 (minor), 128.2 (minor), 127.5 (minor), 127.4 (major), 58.0 (t, J = 21.6 Hz), 50.8 (minor), 50.2 (major), 50.1 (minor), 49.2 (major), 33.34 (major), 33.31 (minor), 31.8 (minor), 30.6 (major), 23.1 (major), 21.51 (minor), 21.46 (major), 20.4 (minor), 12.4 (major), 11.8 (minor).. HRMS (ESI, m/z): calcd. for $C_{21}H_{22}DClNO_3S^+$ [M + H]$^+$, 405.1144; found, 405.1137.

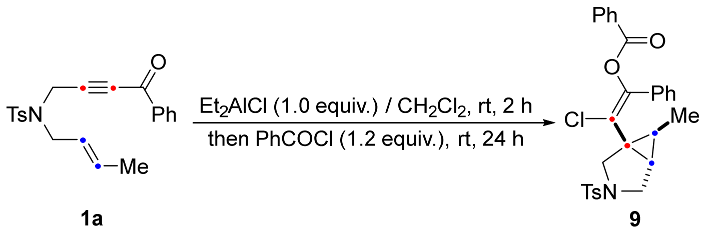
(b) Chlorination of aluminum enolate



To a solution of enynone **1a** (147 mg, 0.4 mmol) in CH_2Cl_2 (2 mL) was added Et_2AlCl (1.0 M in hexane solution, 0.4 mL, 0.4 mmol) at 0 ºC. After being stirred at room temperature for 2 h, *N*-chlorosuccinimide (NCS, 64.1 mg, 0.48 mmol) was added at 0 ºC. After being stirred at room temperature for 24 h, the reaction mixture was quenched with sat. $NaHCO_3$ and sat. Rochelle salt, and extracted with AcOEt. The organic layer was dried over $MgSO_4$ and concentrated in vacuo to dryness. The residue was purified by MPLC (hexane:AcOEt = 80:20) to give **8** (126.2 mg, 72%).

2,2-Dichloro-2-[(1*S,5*S**,6*S**)-6-methyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl]-1-phenylethan-1-one (8)**: R_f = 0.55 (hexane:AcOEt = 2:1). Colorless amorphous. IR (neat) ν cm^{-1}; 1701, 1597, 1348, 1168, 667, 609, 550. ^1H NMR (500 MHz, $CDCl_3$) δ ppm; 8.05 (dd, *J* = 8.0, 1.1 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.38 (dd, *J* = 8.0, 7.4 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 3.62 (d, *J* = 9.2 Hz, 1H), 3.55 (d, *J* = 9.2 Hz, 1H), 3.21 (dd, *J* = 9.2, 4.0 Hz, 1H), 3.18 (d, *J* = 9.2 Hz, 1H), 2.44 (s, 3H), 1.96 (dd, *J* = 5.2, 4.0 Hz, 1H), 1.42 (d, *J* = 6.3 Hz, 3H), 1.36 (dq, *J* = 6.3, 5.2 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$, 72:28 mixture of epimers) δ ppm; 187.4, 143.5, 133.5, 133.3, 131.8, 130.6, 129.6, 128.1, 127.4, 89.4, 54.0, 50.2, 41.4, 32.2, 24.4, 21.5, 12.1. HRMS (ESI, m/z): calcd. for $C_{21}H_{22}Cl_2NO_3S^+$ $[M + H]^+$, 438.0692; found, 438.0693.

(c) Acylation of aluminum enolate

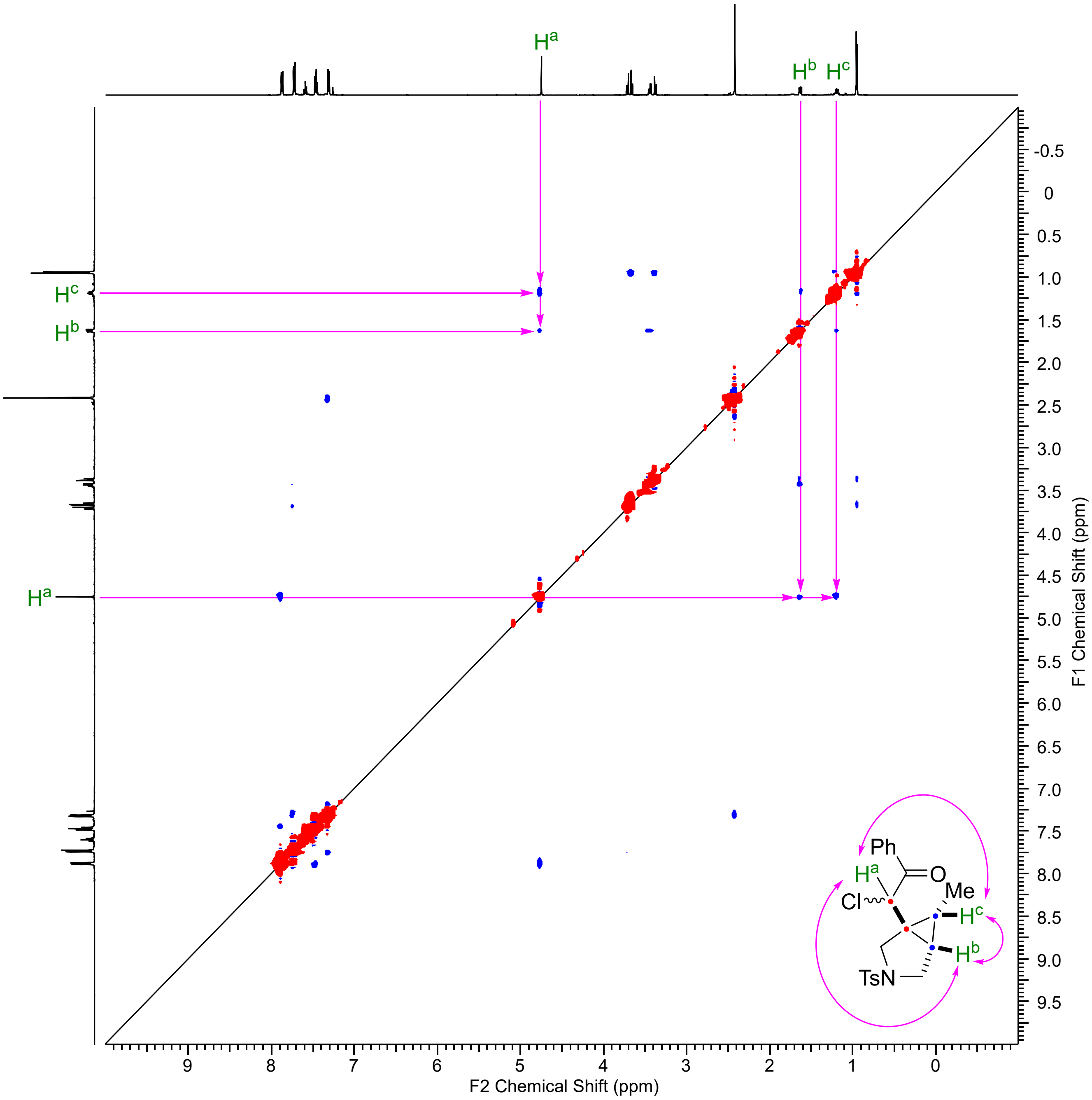


To a solution of enynone **1a** (147 mg, 0.4 mmol) in CH_2Cl_2 (2 mL) was added Et_2AlCl (1.0 M in hexane solution, 0.4 mL, 0.4 mmol) at 0 ºC. After being stirred at room temperature for 2 h, benzoyl chloride (55.7 μL, 0.48 mmol) was added at 0 ºC. After being stirred at room temperature for 24 h, the reaction mixture was quenched with sat. $NaHCO_3$ and sat. Rochelle salt, and extracted with AcOEt. The organic layer was dried over $MgSO_4$ and concentrated in vacuo to dryness. The residue was purified by MPLC (hexane:AcOEt = 80:20) to give **8** (183.6 mg, 90%).

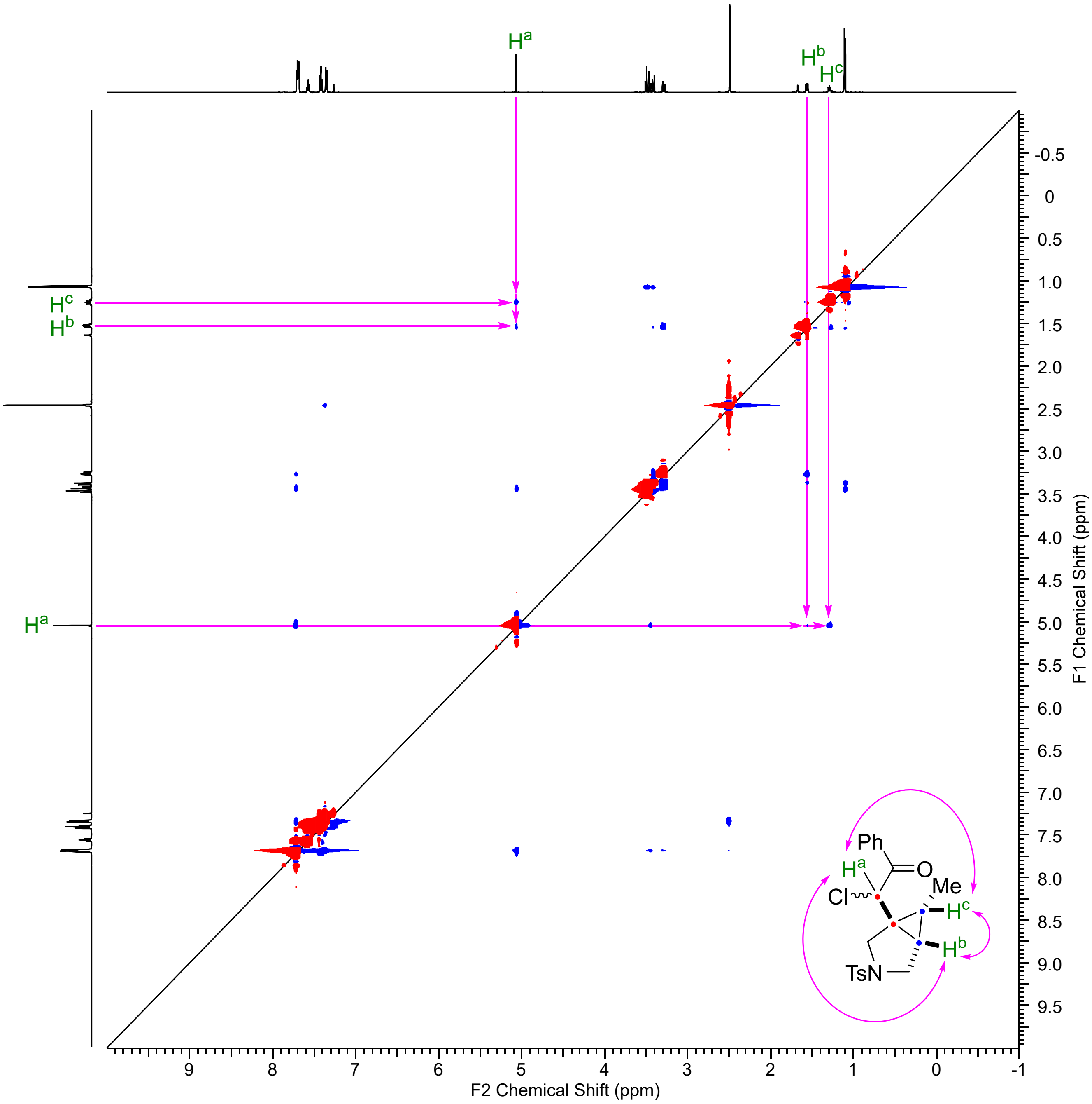
(*Z*)-2-Chloro-2-[(1*S,5*S**,6*S**)-6-methyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl]-1-phenylvinyl benzoate (9)**: R_f = 0.54 (hexane:AcOEt = 2:1). White solid. Mp 192 °C. IR (KBr) ν cm^{-1}; 1735, 1343, 1166, 667, 606, 546.
^1H NMR (500 MHz, $CDCl_3$) δ ppm; 8.11 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.46 (dd, *J* = 8.0, 7.4 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.34-7.28 (m, 1H), 7.23-7.07 (m, 4H), 3.86 (d, *J* = 9.7 Hz, 1H), 3.43 (d, *J* = 9.2 Hz, 1H), 3.37 (d, *J* = 9.2 Hz, 1H), 2.95-2.85 (m, 1H), 2.49 (s, 3H), 1.23 (dq, *J* = 6.3, 5.2 Hz, 1H), 1.09-0.95 (m, 3H), 0.90-0.74 (m, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ ppm; 163.7, 146.9, 143.7, 134.1, 133.7, 133.5, 130.2, 129.7, 129.6, 129.0, 128.6, 128.4, 128.3, 127.8, 123.7, 54.6, 50.1, 36.0, 33.5, 24.1, 21.5, 12.6. HRMS (ESI, m/z): calcd. for $C_{28}H_{26}ClNNaO_4S^+$ $[M + Na]^+$, 530.1163; found, 530.1160.

7. NOESY Spectra Analysis of cis-2a and 4m

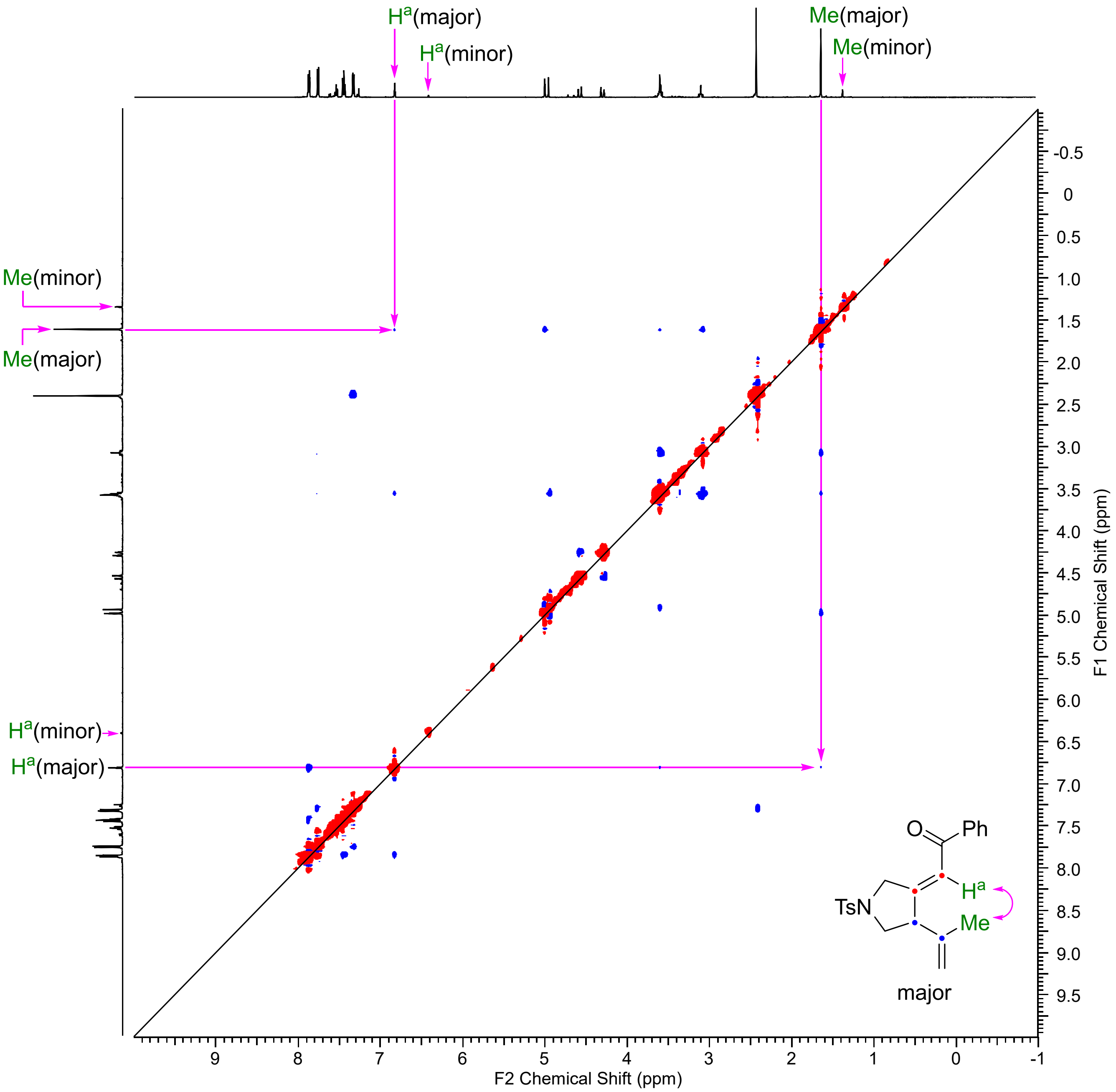
cis-**2a** (major epimer)



cis-**2a** (minor epimer)



4m



H^a(major)
H^a(minor)
Me(major)
Me(minor)
Me(minor)
Me(major)
H^a(minor)
H^a(major)
F2 Chemical Shift (ppm)
F1 Chemical Shift (ppm)
O
Ph
TsN
H^a
Me
major

8. X-ray structure of 2a

Crystals were grown from a solution of **2a-major** in hexane-CH_2Cl_2. Crystal: colorless block (size: 0.60 x 0.25 x 0.15 mm). Formula: $C_{21}H_{22}ClNO_3S$. Formula weight = 403.90. Crystal system: monoclinic. Space group: $P2_1/c$ (No. 14). Cell: a = 7.92368(14) Å, b = 37.6716(7) Å, c = 7.55990(14) Å, α = 90º, β = 121.2790(7)º, γ = 90º, V = 1928.61(6) Å^3, Z = 4.
D_X = 1.391 Mg m^{-3}, μ(CuKα) = 2.945 mm^{-1}, T = 203(2) K.

The diffraction data were collected using graphite monochromatized CuKα radiation with Rigaku R-AXIS RAPID diffractometer (ω-scan mode). The unit cell dimensions were determined using 31518 reflections with 3.52 ≤ θ ≤ 68.22°. The diffraction data of 34311 within 4.70 ≤ θ ≤ 68.22° were collected and merged to give 3519 unique reflections with the Rint of 0.0475. The structure was solved by a direct method and refined on F2 by a least-squares method by the programs SIR2004 and SHELXL2014, respectively. The final R(F) and the wR(F2) values are 0.0519 and 0.1367 for all reflections, respectively.

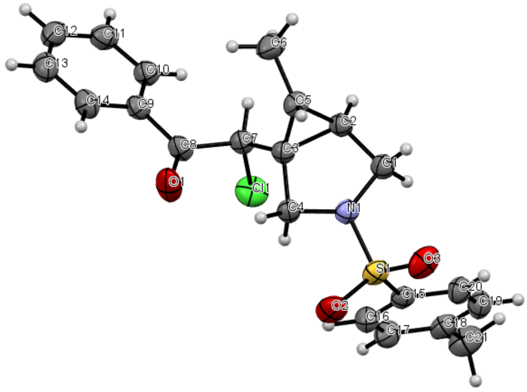


Figure S1. ORTEP representation of **2a-major** (CCDC 2210449), with thermal ellipsoids at the 50% probability level.

Crystals were grown from a solution of **2a-minor** in hexane-CH_2Cl_2. Crystal: colorless block (size: 0.45 x 0.45 x 0.30 mm). Formula: $C_{21}H_{22}ClNO_3S$. Formula weight = 403.90. Crystal system: orthorhombic. Space group: $Pbca$ (No. 61). Cell: a = 7.83618(14) Å, b = 18.4100(3) Å, c = 28.3095(5) Å, α = 90º, β = 90º, γ = 90º, V = 4084.04(13) Å^3, Z = 8.
D_X = 1.314 Mg m^{-3}, μ(CuKα) = 2.781 mm^{-1}, T = 203(2) K.

The diffraction data were collected using graphite monochromatized CuKα radiation with Rigaku R-AXIS RAPID diffractometer (ω-scan mode). The unit cell dimensions were determined using 66871 reflections with 3.12 ≤ θ ≤ 68.18°. The diffraction data of 67774 within 3.12 ≤ θ ≤ 68.18° were collected and merged to give 3735 unique reflections with the Rint of 0.0446. The structure was solved by a direct method and refined on F2 by a least-squares method by the programs SIR2004 and SHELXL2014, respectively. The final R(F) and the wR(F2) values are 0.0421 and 0.1065 for all reflections, respectively.

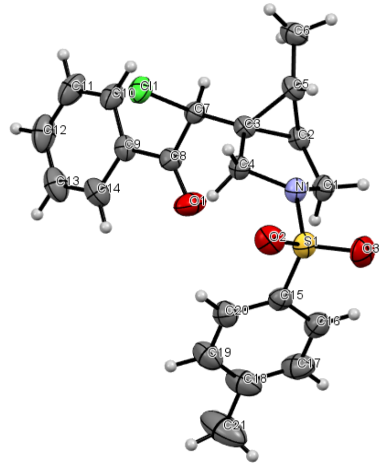


Figure S2. ORTEP representation of **2a-minor** (CCDC 2210451), with thermal ellipsoids at the 50% probability level.

9. Computational Details

All calculations were carried with the Gaussian 16 program package,[3] GRRM11,[4] and GRRM17[5] program. Structure optimizations were carried out at the M062X level[6] in the gas phase using the 6-31+G* basis set for **INT1a**–**INT4a'** and **INT2b**. The vibrational frequencies were computed at the same level to check whether each optimized structure is an energy minimum (no imaginary frequency) or a transition state (one imaginary frequency) and to evaluate its zero-point vibrational energy (ZPVE) and thermal corrections at 298 K. Intrinsic reaction coordinates (IRC) were calculated to confirm the connection between the transition states and the reactants/products. The Gibbs free energy used for discussion in this study was calculated by adding the gas-phase Gibbs free energy correction.

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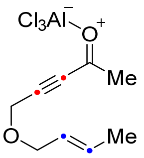
[3] Gaussian 16, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.
[4] Maeda, S.; Osada, Y.; Morokuma, K.; and Ohno, K. GRRM11, version 11.01, 2011.
[5] Maeda, S.; Harabuchi, Y.; Sumiya, Y.; Takagi, M.; Suzuki, K.; Hatanaka, M.; Osada, Y.; Taketsugu, T.; Morokuma, K.; Ohno, K. GRRM17, see http://iqce.jp/GRRM/index_e.shtml (accessed date 24 August, 2018); Maeda, S.; Ohno, K.; Morokuma, K. *Phys. Chem. Chem. Phys.* **2013**, *15*, 3683.
[6] Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215–241.

10. Cartesian Coordinates and Absolute Electronic Energies of Intermediates and Transition States

INT1a

Gibbs Free Energy = –2123.325031 A.U.



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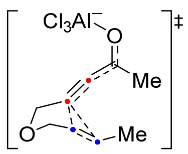
H	2.07408294	-2.15391185	-0.09716768
H	3.54585687	-2.31685058	0.87276601
C	2.87545239	-1.58964927	0.40023428
C	3.02234923	-0.65347550	-1.78258627
H	3.75012699	-0.15807544	-2.43041800
C	2.29640844	-0.66701726	1.43640038
C	1.81070460	0.18620647	-1.66745973
C	0.76855056	0.79966866	-1.59645979
C	-0.47237184	1.49977590	-1.55966005
O	-1.45416575	1.06961960	-0.93077464
C	-0.59049978	2.78816138	-2.30353992
H	-0.26545064	2.64782255	-3.33885931
H	0.08759387	3.51807073	-1.84681024
H	-1.61778893	3.14952189	-2.26202174
H	2.70459796	-1.58968928	-2.26974334
H	1.58469390	-1.12766197	2.12245034
C	2.61052412	0.62197326	1.56152591
H	3.32516978	1.05212828	0.85894249
H	2.85625361	2.02222403	3.17293626
C	2.05077821	1.53713161	2.60982941
H	1.44729537	2.33333668	2.15637169
H	1.41046216	0.99532849	3.31015792
Al	-1.86612051	-0.40423458	0.18466332
Cl	-1.22544065	0.30853136	2.07077435
Cl	-0.75177249	-2.04558930	-0.58346761
Cl	-3.94874192	-0.57363739	-0.09207354

TS1a

Gibbs Free Energy = –2123.311206 A.U.



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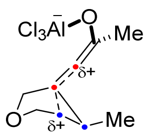
H	3.70805540	-2.05309453	1.34499012
C	2.96736702	-1.66476277	0.64043392
C	2.77490479	-0.77510357	-1.47398472
H	3.36589891	-0.29335593	-2.25585387
C	2.27257790	-0.43912072	1.17417690
C	1.81628947	0.21830874	-0.87522965
C	0.79063988	0.90628738	-1.04798892
C	-0.38319824	1.60495960	-1.18767312
O	-1.52266129	1.08107676	-0.93413801
C	-0.38710147	3.02131140	-1.67465824
H	0.61812396	3.37605622	-1.90475958
H	-0.84113543	3.65247706	-0.90383353
H	-1.01940846	3.08248450	-2.56589031
H	2.15463303	-1.57050837	-1.91361551
H	1.29730682	-0.55478479	1.64639177
C	2.82432365	0.80047017	1.06173277
H	3.82145579	0.88990771	0.62918892
H	2.67984238	2.41709660	2.43995986
C	2.15292541	2.03851262	1.55588563
H	2.18650502	2.82695452	0.79556248
H	1.11175972	1.84319986	1.82833864
Al	-1.92463122	-0.42119050	0.03983022
Cl	-1.24490194	0.12138862	2.00571463
Cl	-0.76584303	-2.05704733	-0.72305766
Cl	-4.00905965	-0.67528884	-0.14076499

INT2a

Gibbs Free Energy = –2123.326304 A.U.



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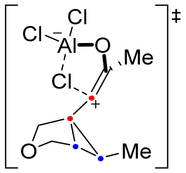
H	3.45567529	-2.07220153	1.33238165
C	2.80365103	-1.71332394	0.53140457
C	2.83297430	-0.58648751	-1.44815614
H	3.51696167	-0.02015110	-2.08439483
C	2.08833275	-0.43302244	0.92553998
C	1.98987263	0.30594819	-0.53809814
C	0.79430409	0.83190939	-0.84897284
C	-0.32628198	1.49120231	-1.11224509
O	-1.54663673	1.04670527	-0.95693113
C	-0.18255359	2.89280490	-1.65472994
H	0.86075701	3.19340676	-1.77676275
H	-0.68563970	3.57598945	-0.96465411
H	-0.69005459	2.93394840	-2.62265701
H	2.16102122	-1.19916177	-2.06267733
H	1.14855055	-0.48705355	1.47171277
C	2.76190873	0.82524289	0.77966280
H	3.82530743	0.78253660	0.54392999
H	2.73541276	2.15669330	2.43917157
C	2.24867761	2.06477911	1.46317028
H	2.47830979	2.96095671	0.88011823
H	1.16903037	2.00631920	1.62663108
Al	-1.97821494	-0.38545144	0.04767033
Cl	-1.31270128	0.14741936	2.03079837
Cl	-0.67488768	-1.94819568	-0.68615241
Cl	-4.03739491	-0.77759920	-0.13529795

TS2a

Gibbs Free Energy = –2123.320176 A.U.



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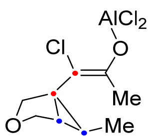
H	-4.11909000	-2.09233500	-1.11319100
C	-3.17178700	-1.81256400	-0.64604500
C	-2.30932800	-1.01342700	1.30971600
H	-2.64165300	-0.62320400	2.27461800
C	-2.70345200	-0.42108600	-1.04395400
C	-2.00541100	0.07855800	0.28220800
C	-0.80996800	0.73882100	0.20209400
C	0.19353700	1.53958400	0.55349400
O	1.45736000	1.47316900	0.24809600
C	-0.22990300	2.72654700	1.39678100
H	-1.29831500	2.73321300	1.62278400
H	0.03726400	3.63724400	0.85337400
H	0.34345800	2.68749500	2.32705600
H	-1.41173500	-1.63221300	1.44359100
H	-2.12207000	-0.28945300	-1.95190500
C	-3.29289800	0.73068300	-0.39501800
H	-4.14438400	0.53650400	0.25678800
H	-3.21771800	2.88196100	-0.22657300
C	-3.19720100	2.10688600	-0.99784300
H	-2.28234200	2.22001500	-1.58521800
H	-4.05275000	2.26639100	-1.66182600
Al	2.23417400	-0.11678700	-0.10146000
Cl	0.61053300	-0.98848800	-1.28010200
Cl	2.35128400	-1.17019300	1.74287700
Cl	4.02615100	0.15647200	-1.16795200

INT3a

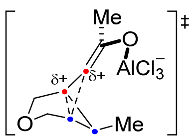
Gibbs Free Energy = –2123.343355 A.U.



O	-4.03624898	-1.23185491	0.50388824
H	-3.32135415	-2.57645208	-0.91793663
H	-4.65979027	-1.49855905	-1.41264616
C	-3.72761788	-1.55675293	-0.84462259
C	-2.85059261	-0.76707467	1.12332981
H	-3.14459849	-0.12333248	1.95831708
C	-2.67948048	-0.54305332	-1.26359806
C	-2.06853258	-0.04114846	0.02955906
C	-0.63004181	0.17345534	0.21558383
C	0.03779116	1.17940135	0.81364554
O	1.36506425	1.20802686	0.92738102
C	-0.66606985	2.35671597	1.41793941
H	-1.75013253	2.28097664	1.32021759
H	-0.31599666	3.27405136	0.93431030
H	-0.40082185	2.41728851	2.47803107
H	-2.24743820	-1.60439141	1.50784234
H	-2.04639687	-0.74525499	-2.12382816
C	-2.90527724	0.87440353	-0.85091237
H	-3.89100124	1.09862016	-0.44257309
H	-2.12864917	2.88800826	-1.04755548
C	-2.25671027	1.98136744	-1.64751915
H	-1.27116564	1.67989625	-2.01581716
H	-2.87809249	2.23533061	-2.51212172
Al	2.42080242	0.01210442	0.20186456
Cl	0.43458956	-1.17484521	-0.37430613
Cl	3.51373989	-1.20769963	1.50325089
Cl	3.31901860	0.54748296	-1.61446509

TS2a'

Gibbs Free Energy = –2123.315828 A.U.



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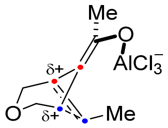
H	2.13237451	-2.67886609	0.34053173
C	2.07536151	-1.80003259	-0.30509100
C	3.39843711	-0.19469571	-1.27094318
H	4.43786462	0.14043166	-1.28667122
C	1.65861716	-0.56437703	0.48140790
C	2.55815016	0.60594430	-0.26524417
C	1.25769412	0.92486535	-0.54480346
C	0.13495466	1.40852288	-1.08454747
O	-1.02596062	0.81805973	-1.12134487
C	0.19589155	2.78539714	-1.69599438
H	1.20185810	3.20972314	-1.67636289
H	-0.48784706	3.43757597	-1.14485557
H	-0.15669114	2.71527921	-2.72894681
H	2.95036628	-0.11060363	-2.26813693
H	0.68851419	-0.49696047	0.98172698
C	2.76788978	0.24496619	1.16392284
H	3.68737768	-0.31861911	1.31353635
H	2.13921915	0.58323008	3.18876203
C	2.34074550	1.16300292	2.28429856
H	3.13415035	1.88320178	2.50146019
H	1.42849946	1.70450583	2.01967120
Al	-1.98874011	-0.18841393	0.00462636
Cl	-1.36884949	0.52188838	1.95234750
Cl	-1.29884906	-2.21586311	-0.21188535
Cl	-4.03394526	0.07977839	-0.43197109

INT3a'

Gibbs Free Energy = –2123.316843 A.U.



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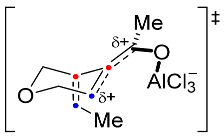
H	1.32702287	-1.89361351	-1.24487772
H	2.01290441	-2.63319450	0.22903665
C	1.99921755	-1.73856954	-0.39474039
C	3.43683490	-0.13539740	-1.23464769
H	4.49147775	0.14654429	-1.19081169
C	1.55605254	-0.50111163	0.39449135
C	2.59155102	0.65186075	-0.22408442
C	1.22334215	0.81386455	-0.47765007
C	0.15939193	1.35715549	-1.09425042
O	-1.03177285	0.82602004	-1.13233410
C	0.29404303	2.69235670	-1.77301445
H	1.31969291	3.06669014	-1.75316057
H	-0.36628986	3.40972569	-1.27682617
H	-0.04312959	2.59011255	-2.80876925
H	3.03389311	0.01683152	-2.24251397
H	0.74561702	-0.54035768	1.13247642
C	2.77549833	0.27602509	1.16266045
H	3.64186262	-0.35934376	1.34133091
H	2.02944476	0.48210817	3.16816176
C	2.29262583	1.11632896	2.31786376
H	3.09309759	1.79460342	2.62750645
H	1.41300664	1.70147975	2.03808733
Al	-1.97517082	-0.18323377	0.00691542
Cl	-1.35898104	0.52194526	1.96201814
Cl	-1.28743970	-2.21481294	-0.19664598
Cl	-4.02697721	0.07288019	-0.41074354

TS3a'

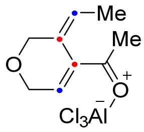
Gibbs Free Energy = –2123.31428 A.U.



O	0.88438262	0.94740688	-0.35133470
H	-0.87754180	0.18426657	0.45593038
H	0.54797471	-0.89838211	0.45121672
C	0.20890152	0.12773293	0.59023132
C	0.80310457	2.28765650	0.09471790
H	1.56620464	2.86135088	-0.43656026
C	0.53380884	0.64616348	2.00012273
C	1.05792644	2.23375192	1.60280322
C	-0.06101840	1.89246473	2.48239689
C	-0.92948577	2.39525354	3.38496031
O	-1.74743476	1.66646112	4.10020262
C	-1.04572924	3.87641170	3.60300813
H	-0.37158867	4.44204624	2.95568319
H	-2.07858846	4.18422386	3.41426640
H	-0.82250757	4.10075574	4.65074849
H	-0.18956917	2.71494208	-0.09122286
H	1.01854373	-0.01721800	2.72127927
C	2.31550271	1.80114507	2.01403344
H	3.04364369	1.62101008	1.21879007
H	3.49158284	2.53669259	3.57577043
C	2.79893206	1.69910525	3.41601199
H	1.98506095	1.76519899	4.14141414
H	3.36750471	0.77866954	3.57595564
Al	-1.61717816	-0.04686108	4.59757426
Cl	-3.11661926	-0.45682232	6.02432657
Cl	-1.76339974	-1.25761124	2.81182249
Cl	0.40701849	-0.24802238	5.34704183

INT4a'

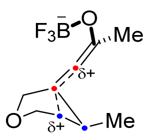
Gibbs Free Energy = –2123.386482 A.U.



O	1.74914938	0.61684624	0.13481940
H	-0.10516367	0.11442891	-0.64256659
H	0.65961276	-1.05396051	0.44771603
C	0.48718218	0.01606445	0.28470525
C	1.72749891	2.02135369	0.34051101
H	2.73461880	2.37911727	0.12048541
C	-0.32136373	0.55500638	1.41910708
C	1.33665283	2.30846168	1.76926346
C	0.07848609	1.62694619	2.13834474
C	-0.87187485	2.17052808	3.11263330
O	-1.59034640	1.43471824	3.82113207
C	-1.10811115	3.64461527	3.22214561
H	-0.40350508	4.22257346	2.62568260
H	-2.13047239	3.83248256	2.87413093
H	-1.06502776	3.94470896	4.27306409
H	1.01877060	2.48801319	-0.36338234
H	-1.27976314	0.07313099	1.60668400
C	2.12190988	2.99296337	2.61159995
H	3.03456599	3.42215999	2.19819886
H	1.59381696	4.21555562	4.31541508
C	1.91483304	3.19214381	4.08348008
H	1.18849697	2.49057623	4.50674914
H	2.85899963	3.02769546	4.61173617
Al	-1.62097626	-0.29677621	4.53437157
Cl	-2.42438155	0.01181096	6.45962267
Cl	-2.87027377	-1.36590211	3.18500944
Cl	0.42094072	-0.89042537	4.50670501

INT2b

Gibbs Free Energy = –824.642142 A.U.

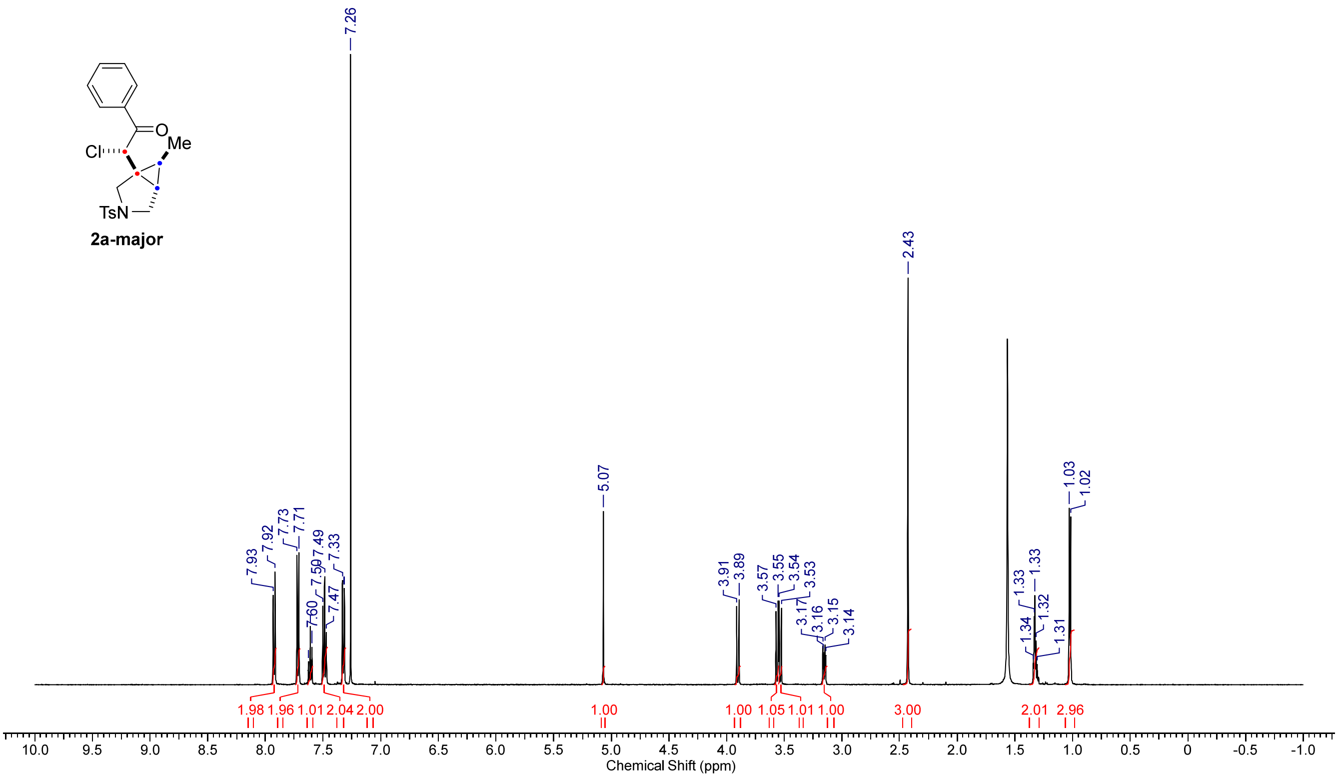


O	0.96822289	0.71224603	-0.37014823
H	-0.25126064	-0.67323427	0.60429597

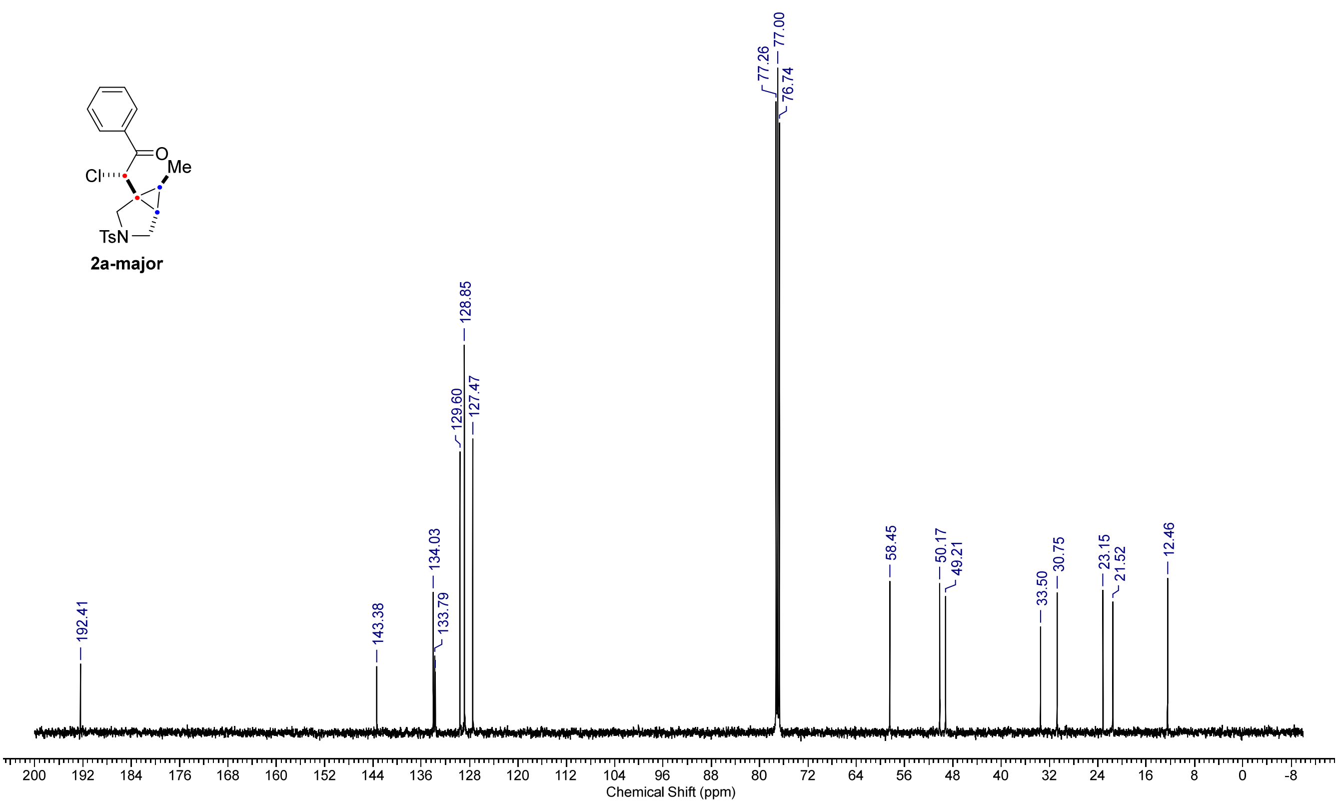
H	1.47456263	-1.11091473	0.38257393	H	0.65037506	-0.08828723	2.85027466
C	0.77919416	-0.29639483	0.60375712	C	2.06794618	1.38512916	2.03873561
C	0.36105045	1.89417705	0.12352286	H	2.71419743	1.51638314	1.17112869
H	0.82471516	2.74003234	-0.38960576	H	2.89905342	2.85013349	3.38682080
C	1.07448093	0.34345285	1.94584414	C	2.61862538	1.79299535	3.38141436
C	0.62177567	1.89387563	1.62934056	H	1.88779848	1.61105663	4.17421374
C	-0.24951659	2.32386354	2.56193492	H	3.51109992	1.19922620	3.60062402
C	-0.90734612	2.73424370	3.63997889	B	-1.78771133	0.54341078	4.07265865
O	-1.77369187	2.03538628	4.32196962	F	-0.55610841	0.03868396	4.53318945
C	-0.66531288	4.14718684	4.10616562	F	-2.85996843	0.01311564	4.72247630
H	0.06554657	4.67300482	3.48742536	F	-1.83484821	0.35202119	2.67369424
H	-0.31453902	4.10726817	5.14103088				
H	-1.61756501	4.68422766	4.07976548				
H	-0.72212271	1.89380235	-0.05113391				

11. ^{1}H and ^{13}C NMR Spectra of Compounds 2a-2l, 4m, 4n, 5, 6 and d-2a

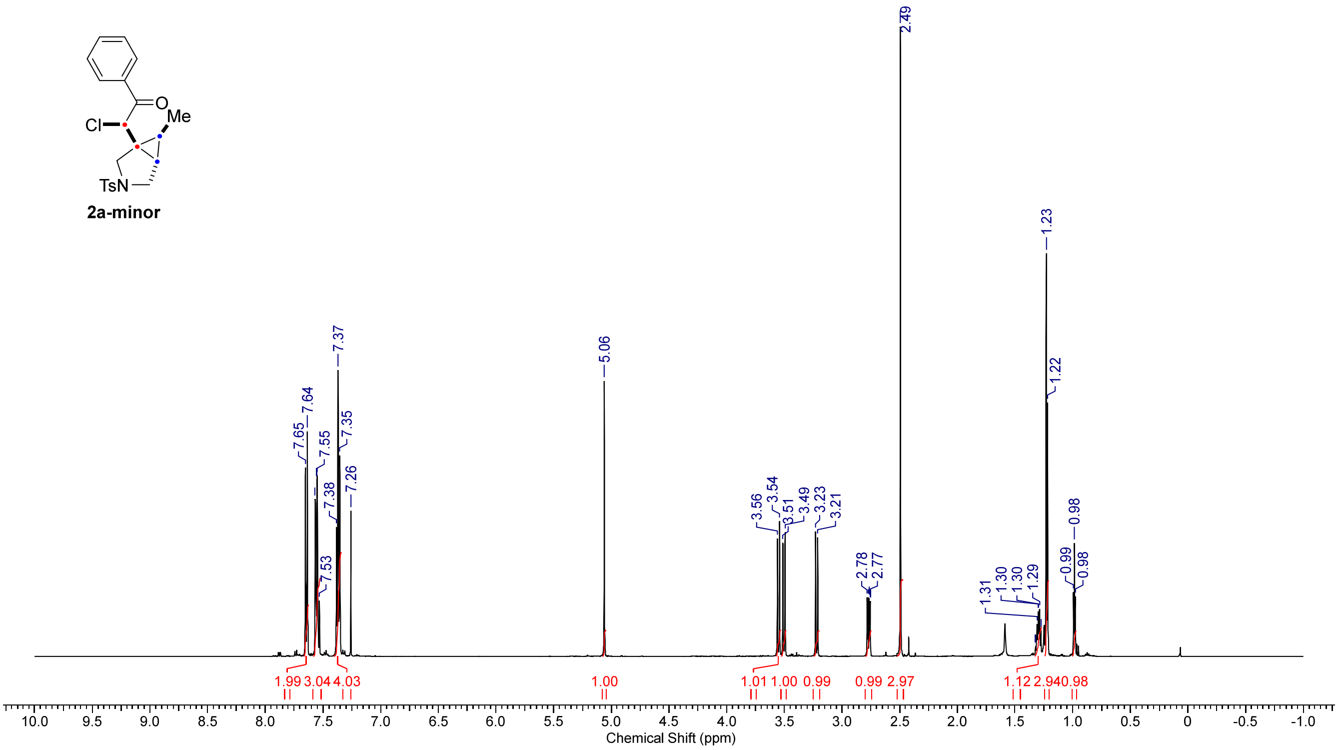
^{1}H NMR (500 MHz, $CDCl_3$) of **2a** (major epimer)



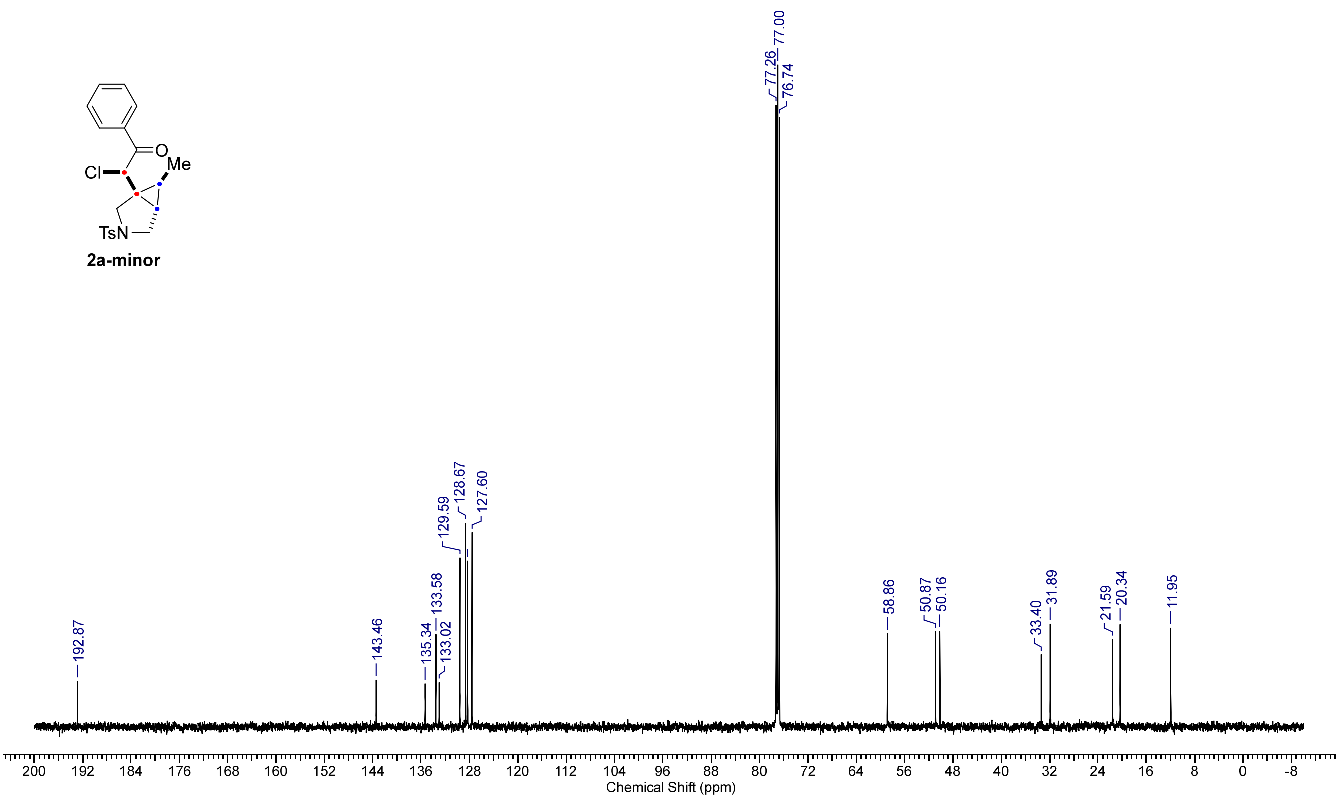
^{13}C NMR (125 MHz, $CDCl_3$) of **2a** (major epimer)



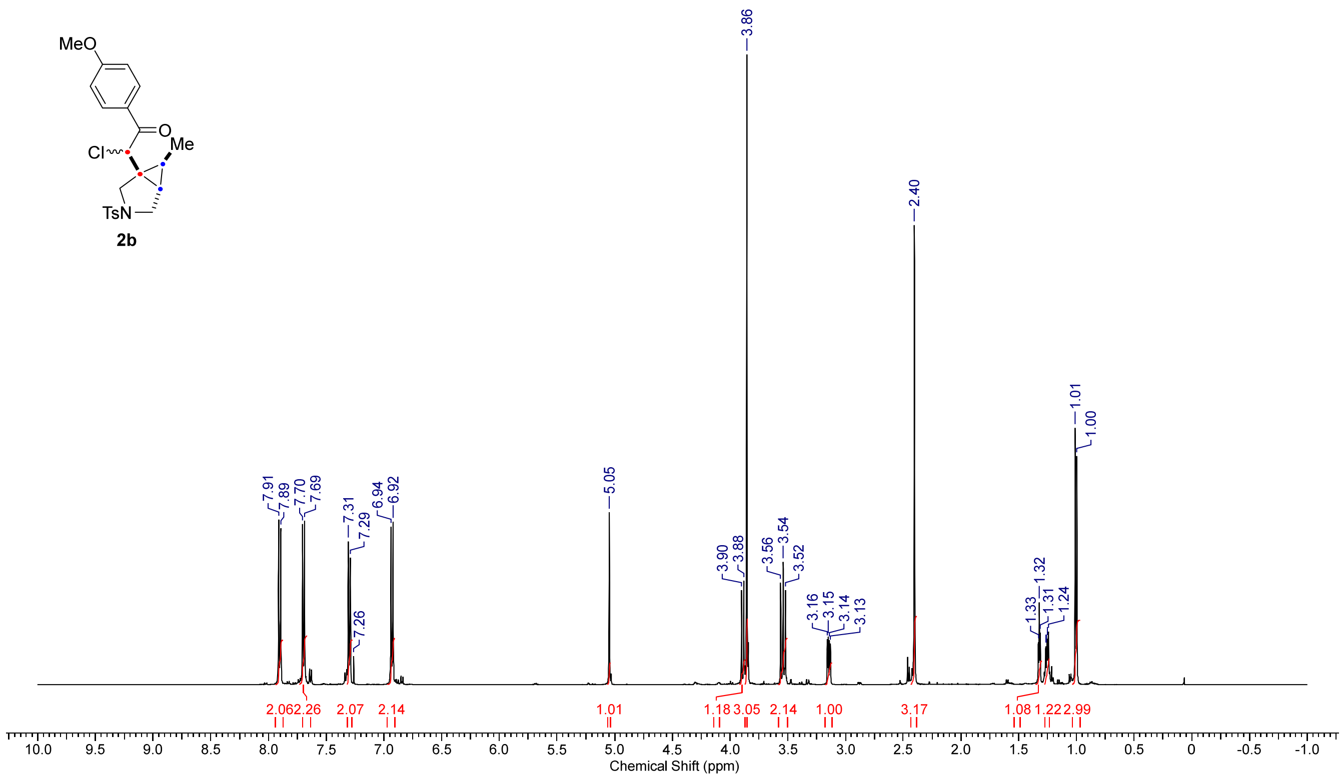
^{1}H NMR (500 MHz, $CDCl_3$) of **2a** (minor epimer)



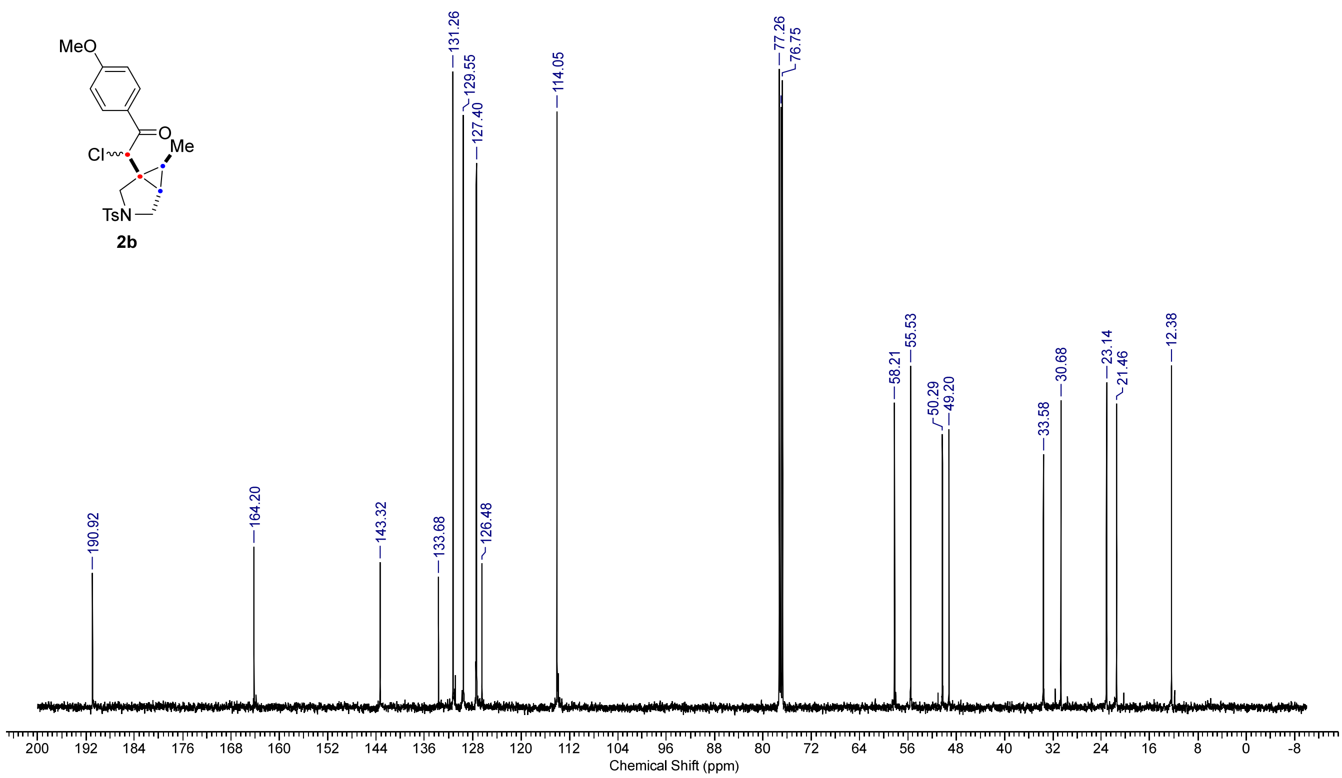
^{13}C NMR (125 MHz, $CDCl_3$) of **2a** (minor epimer)



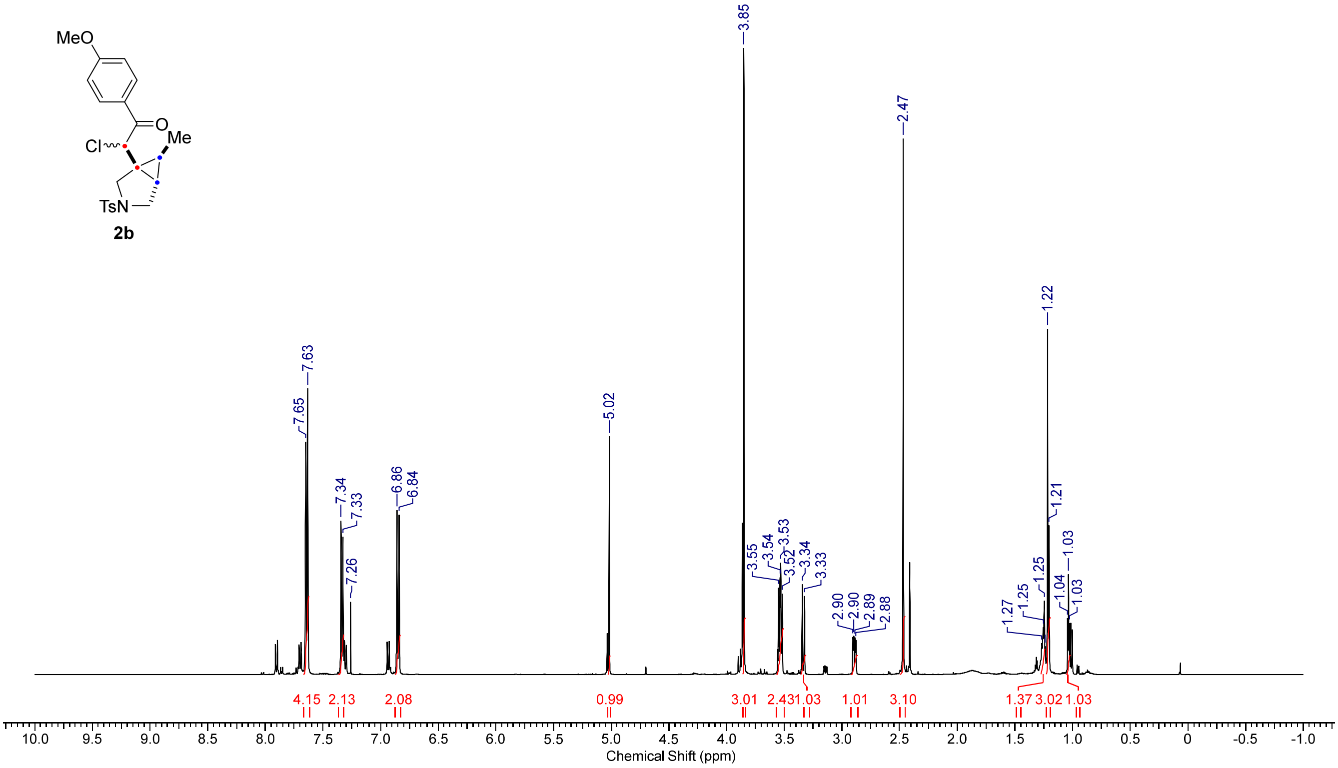
^{1}H NMR (500 MHz, $CDCl_3$) of **2b** (major epimer-rich)



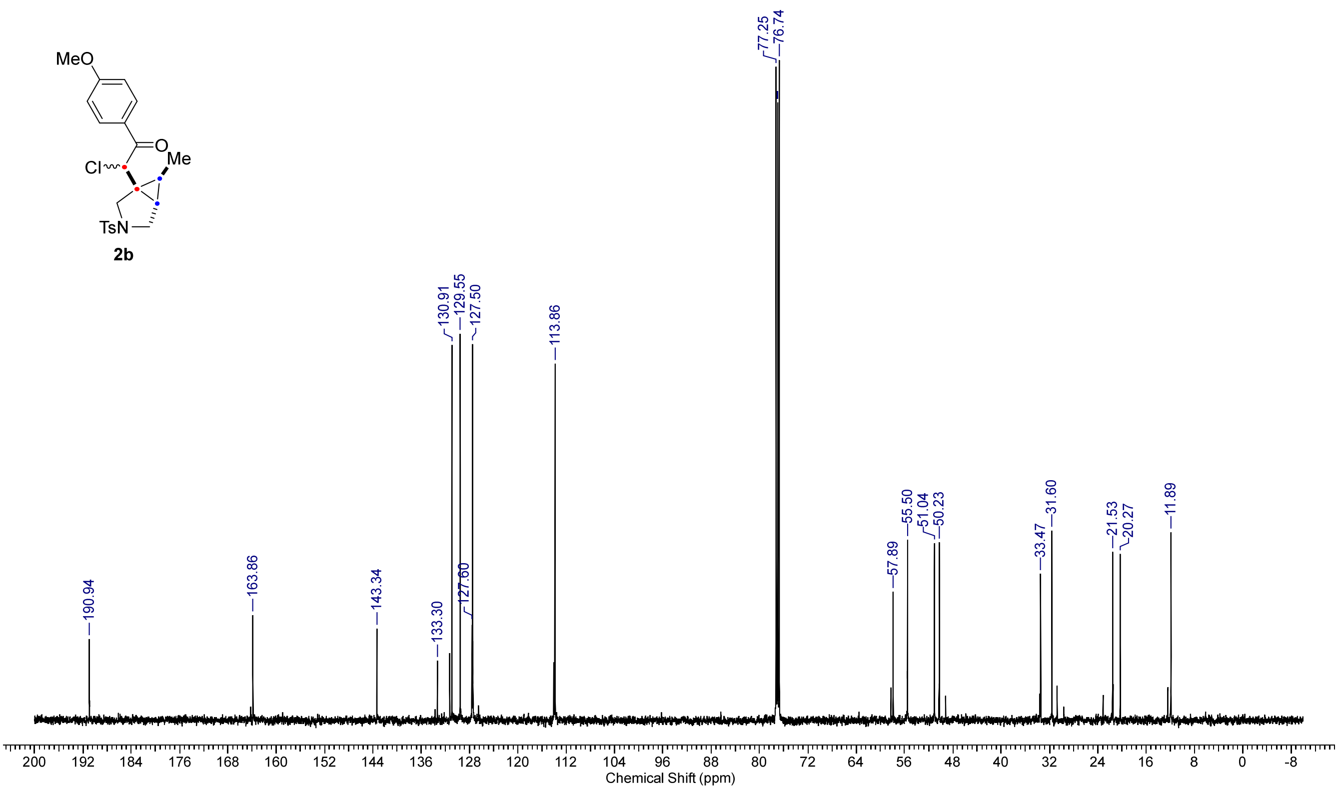
^{13}C NMR (125 MHz, $CDCl_3$) of **2b** (major epimer-rich)



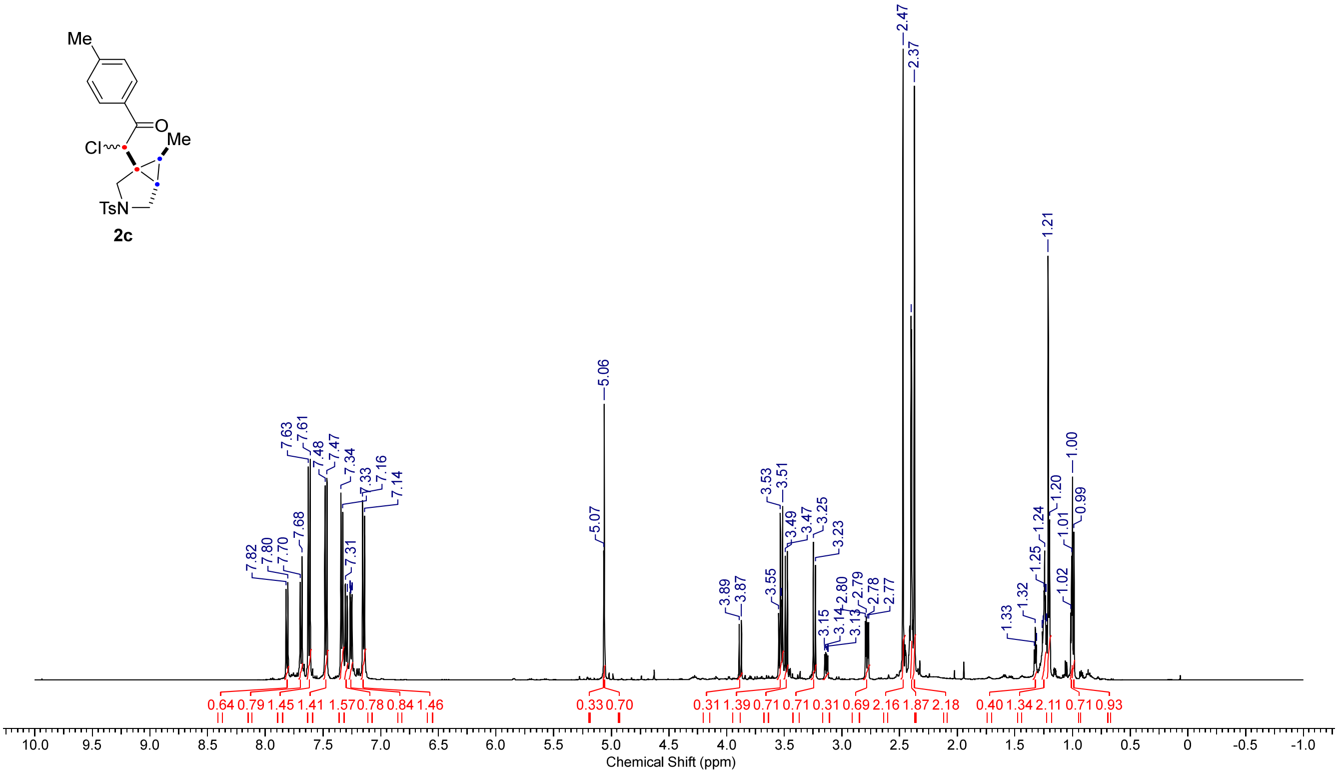
^{1}H NMR (500 MHz, $CDCl_3$) of **2b** (minor epimer-rich)



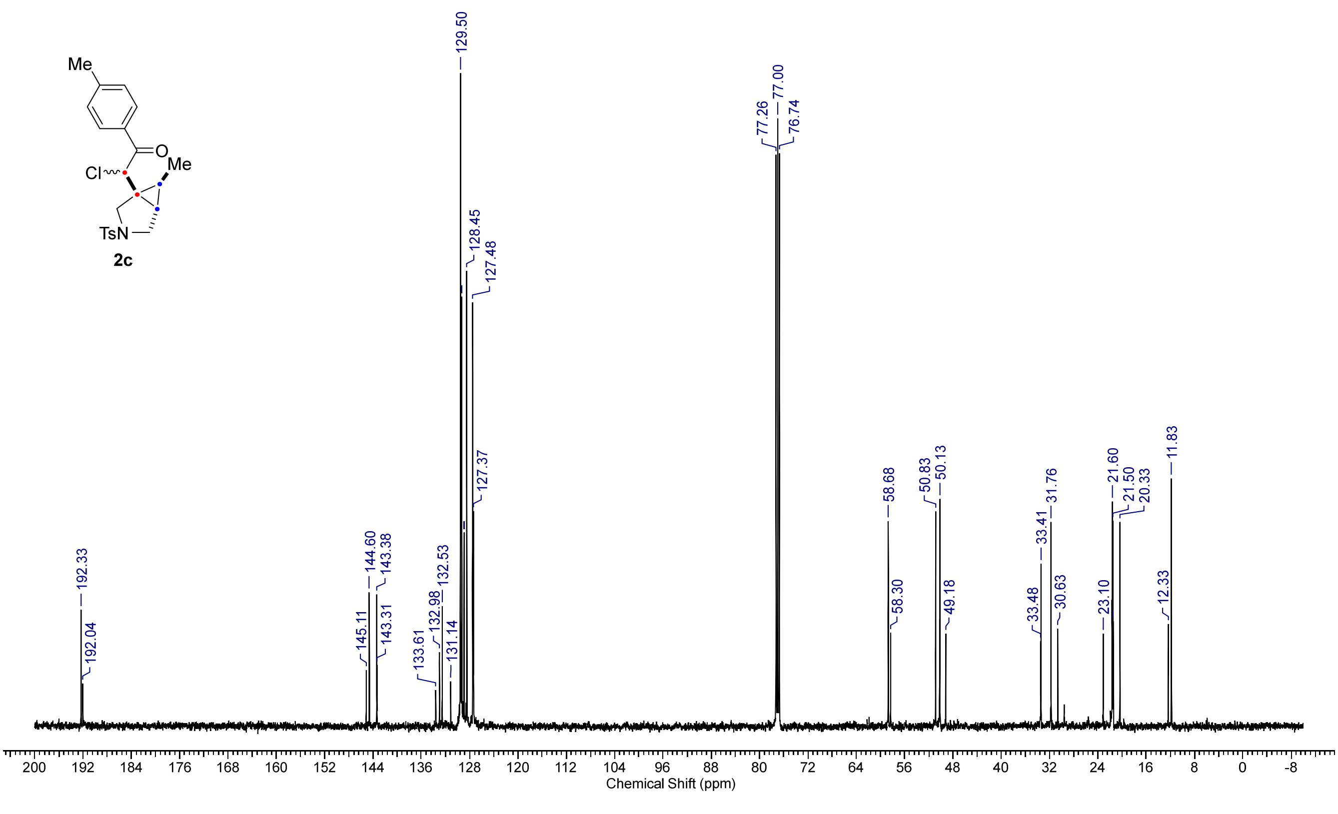
^{13}C NMR (125 MHz, $CDCl_3$) of **2b** (minor epimer-rich)



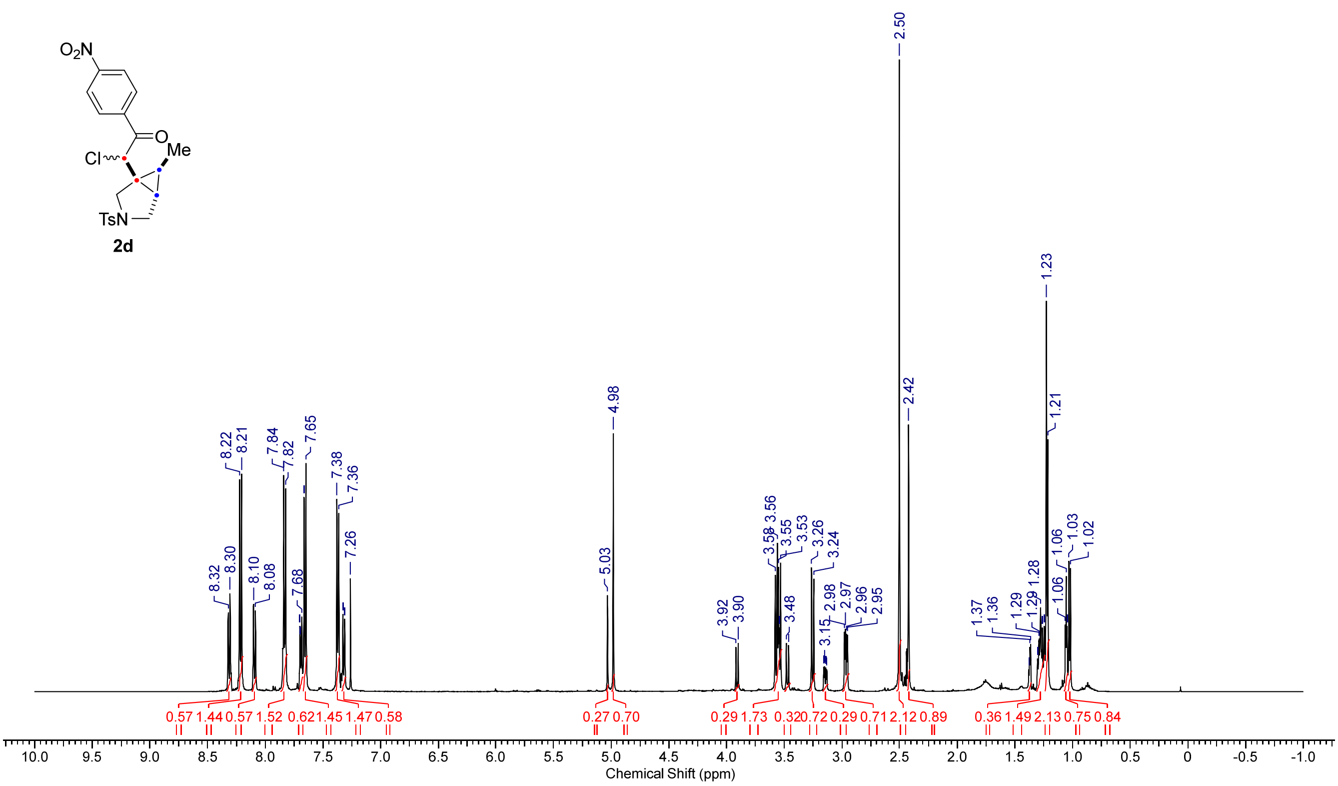
^{1}H NMR (500 MHz, $CDCl_3$) of **2c** (69:31 mixture of epimers)



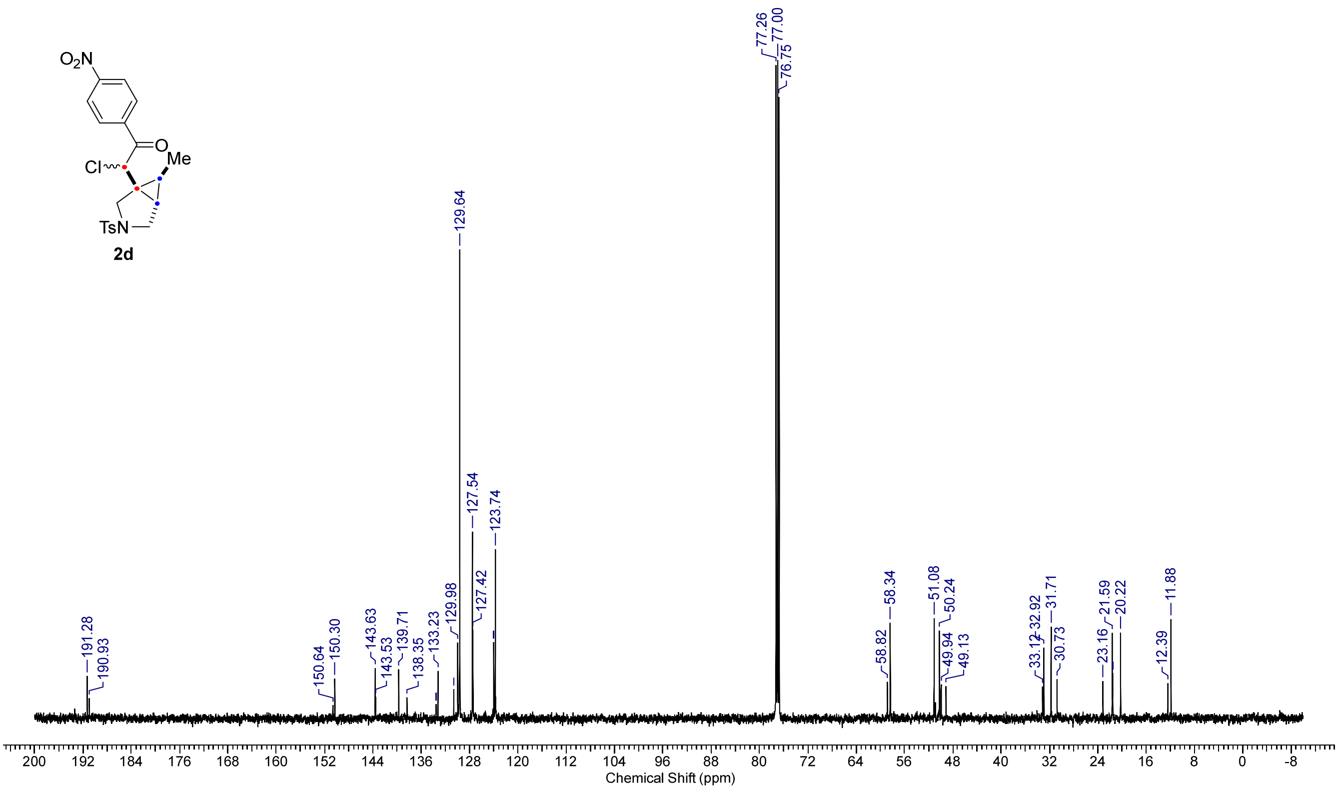
^{13}C NMR (125 MHz, $CDCl_3$) of **2c** (69:31 mixture of epimers)



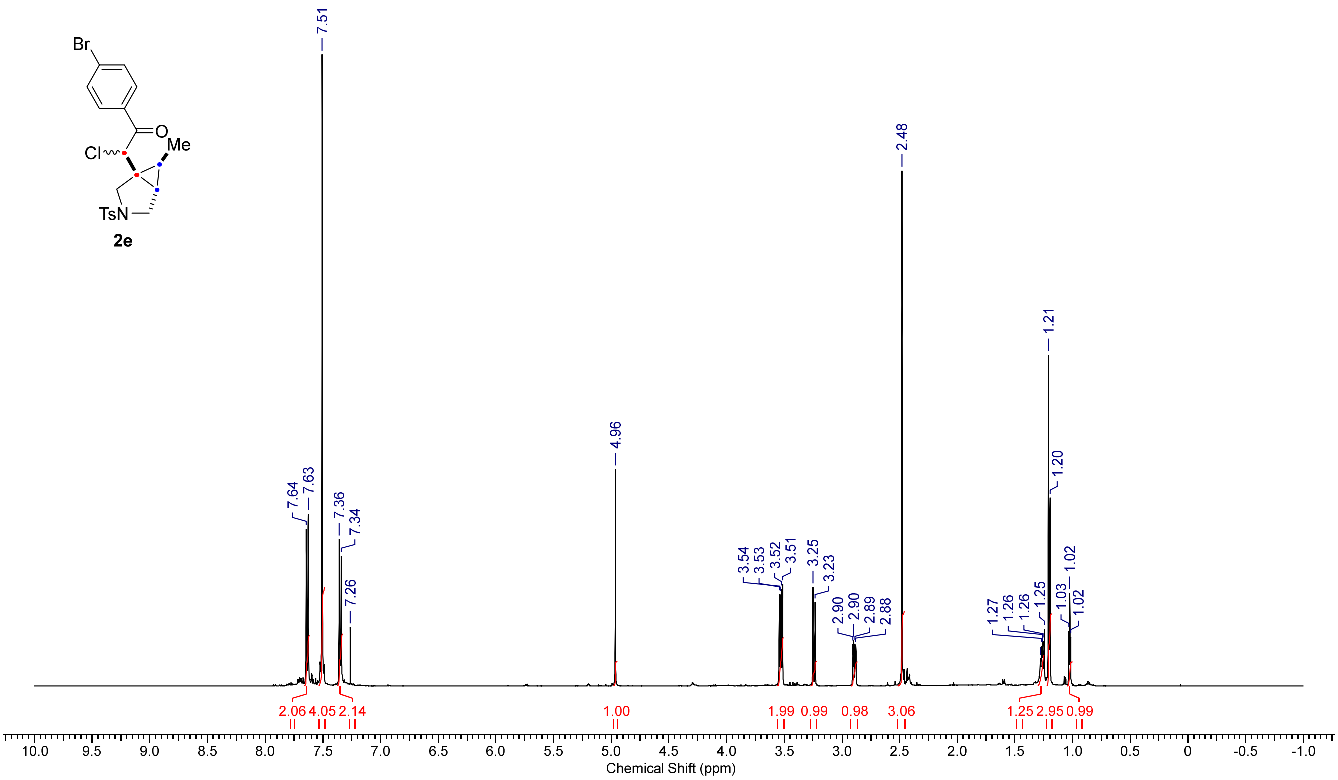
[1]H NMR (500 MHz, $CDCl_3$) of **2d** (71:29 mixture of epimers)



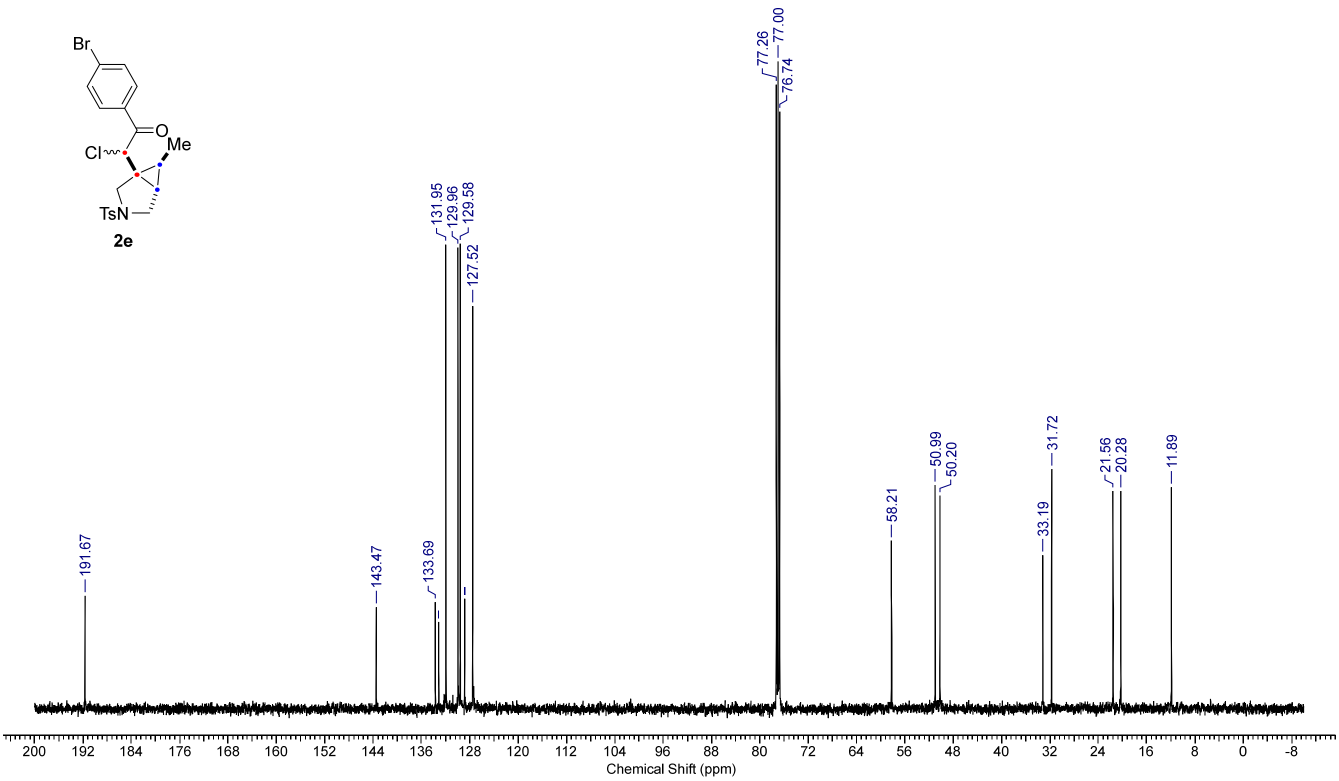
[13]C NMR (125 MHz, $CDCl_3$) of **2d** (71:29 mixture of epimers)



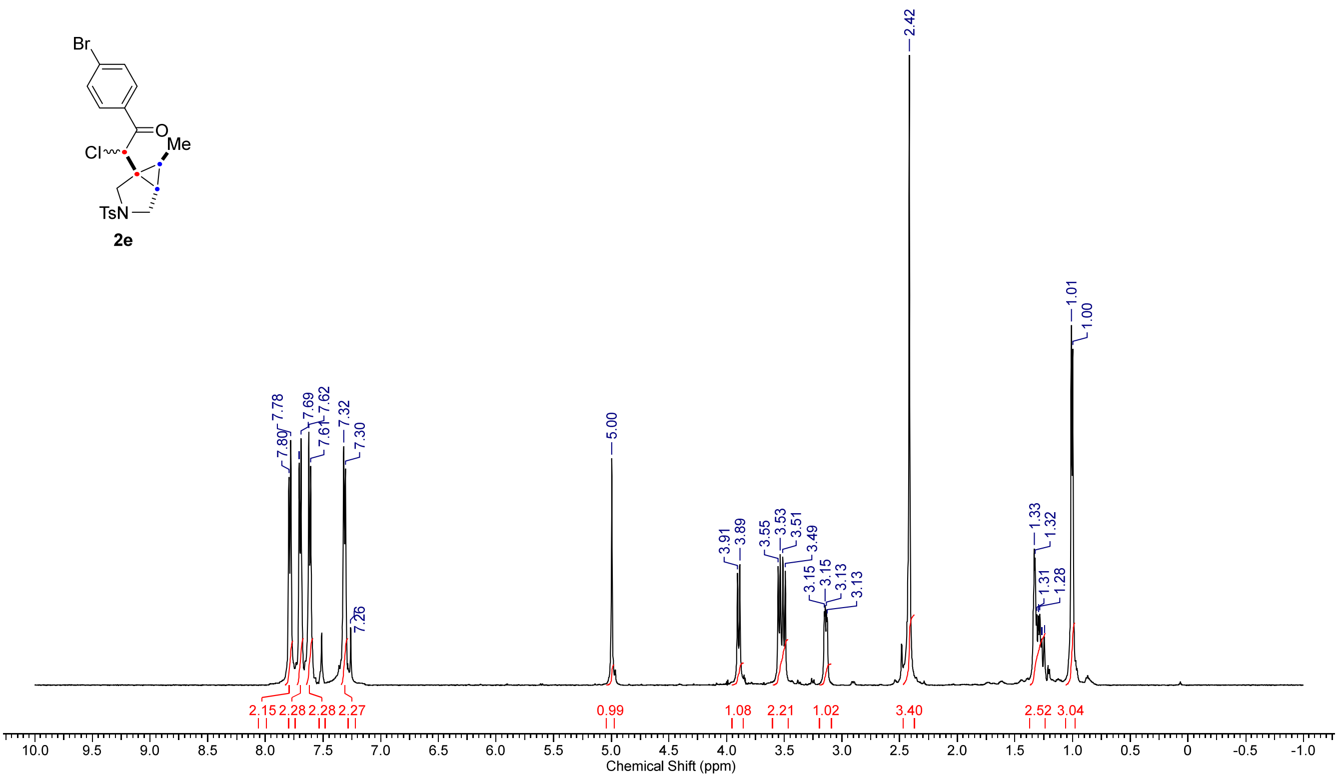
^1H NMR (500 MHz, $CDCl_3$) of **2e** (major epimer-rich)



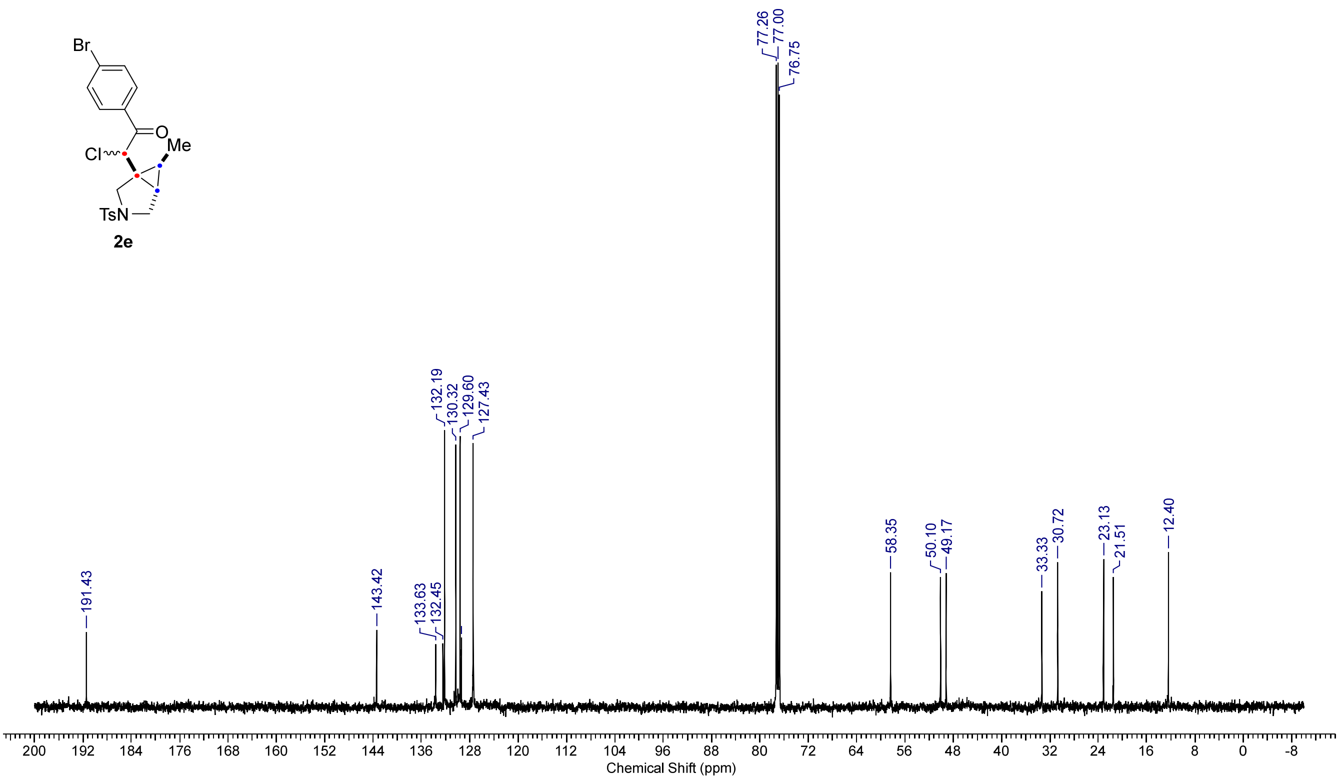
^{13}C NMR (125 MHz, $CDCl_3$) of **2e** (major epimer-rich)



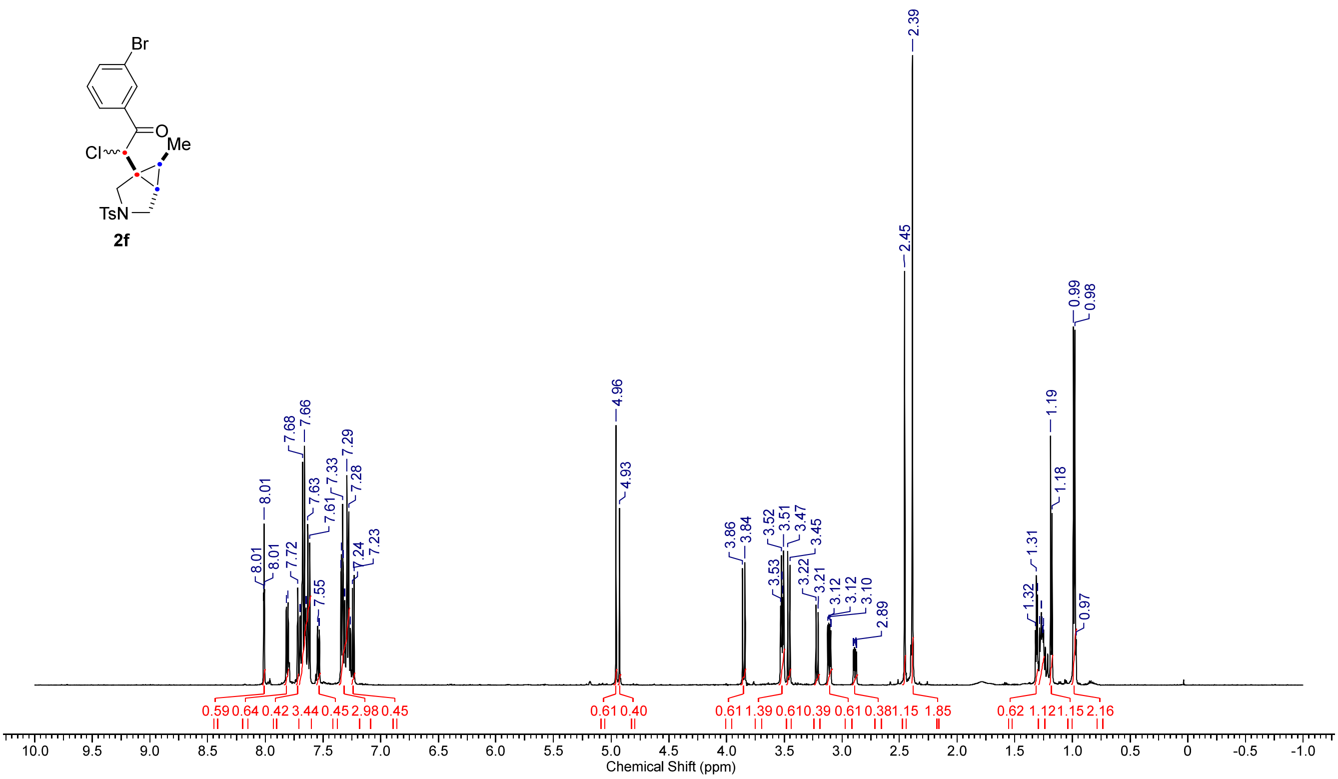
[1]H NMR (500 MHz, $CDCl_3$) of **2e** (minor epimer-rich)



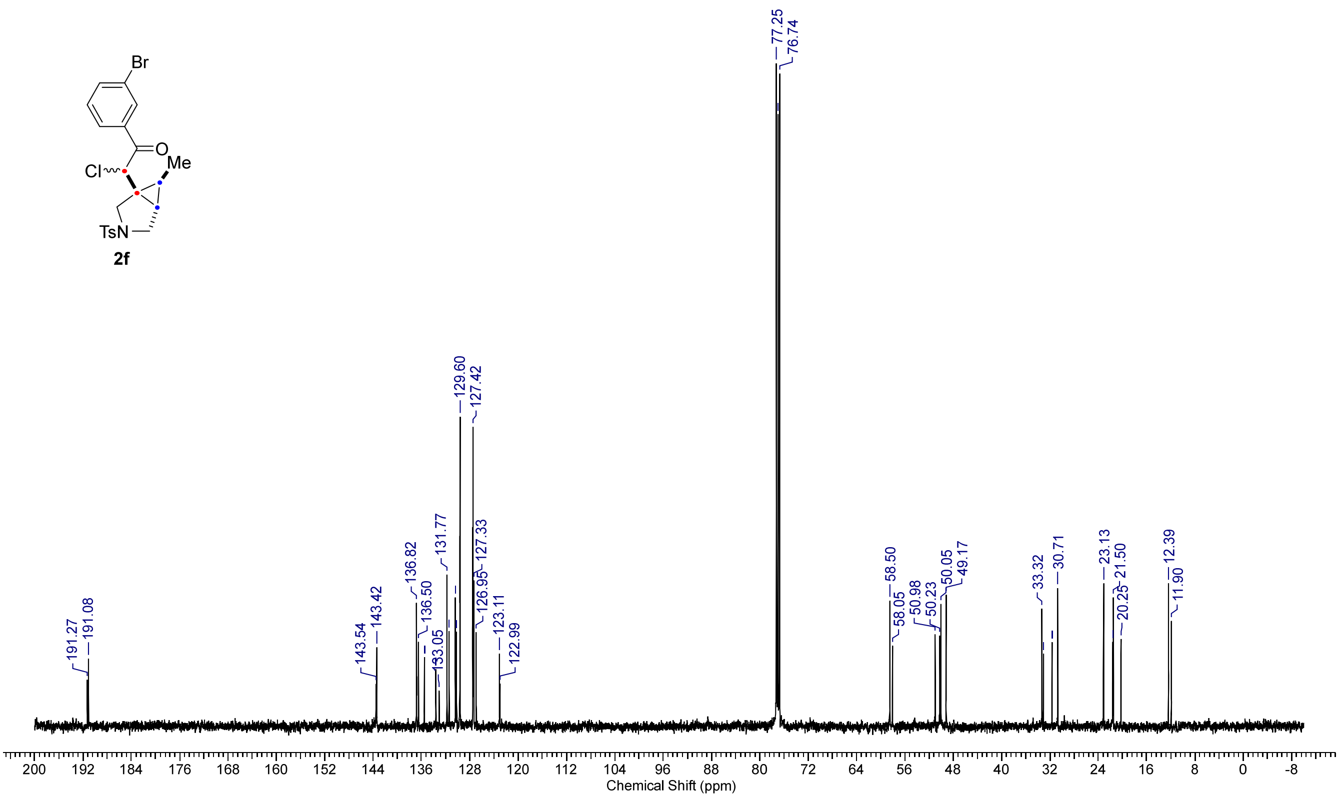
[13]C NMR (125 MHz, $CDCl_3$) of **2e** (minor epimer-rich)



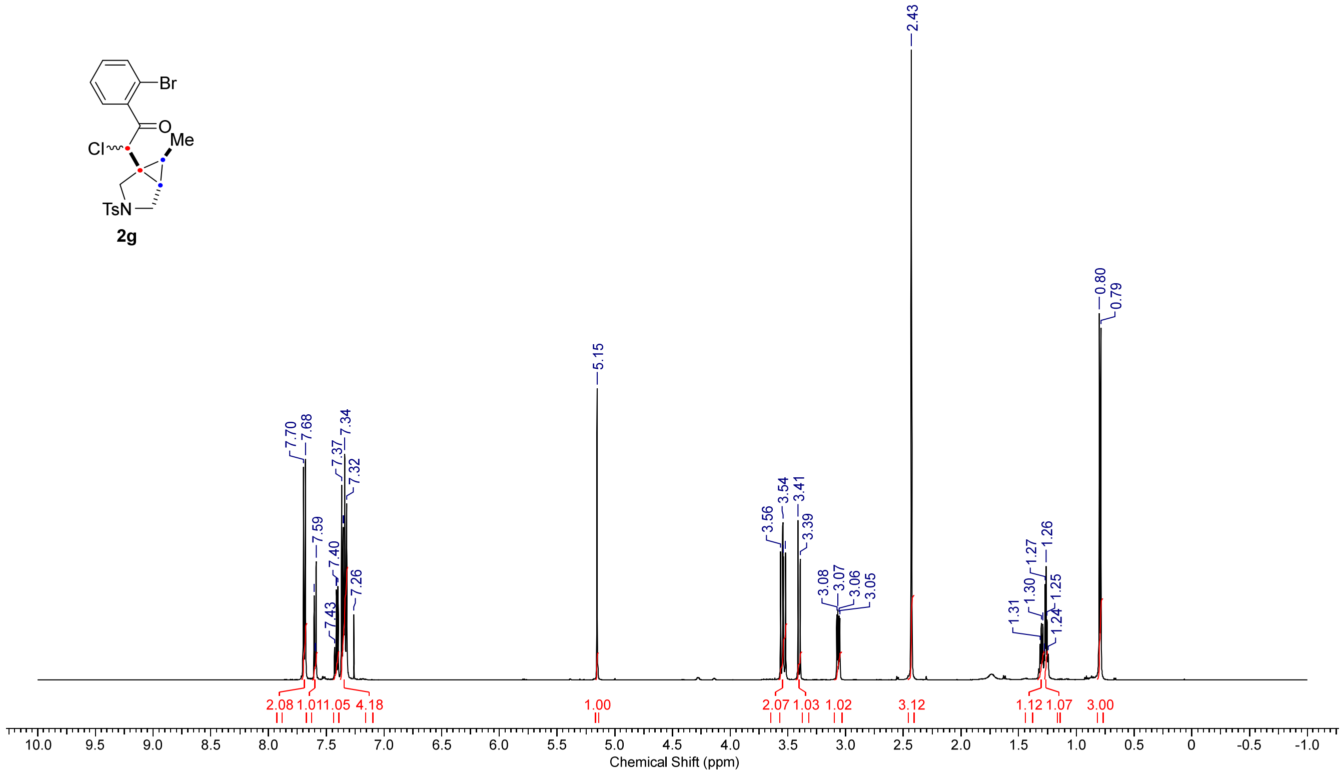
[1]H NMR (500 MHz, $CDCl_3$) of **2f** (61:39 mixture of epimers)



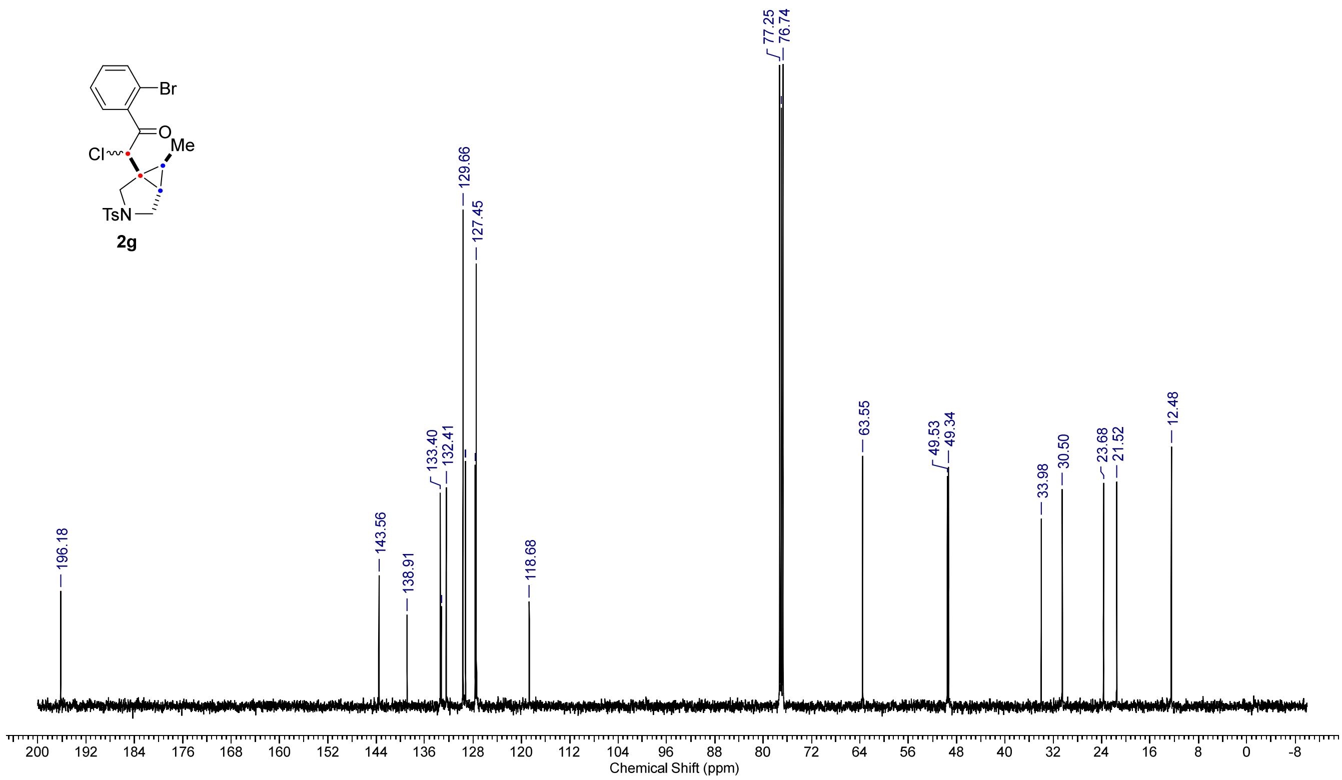
[13]C NMR (125 MHz, $CDCl_3$) of **2f** (61:39 mixture of epimers)



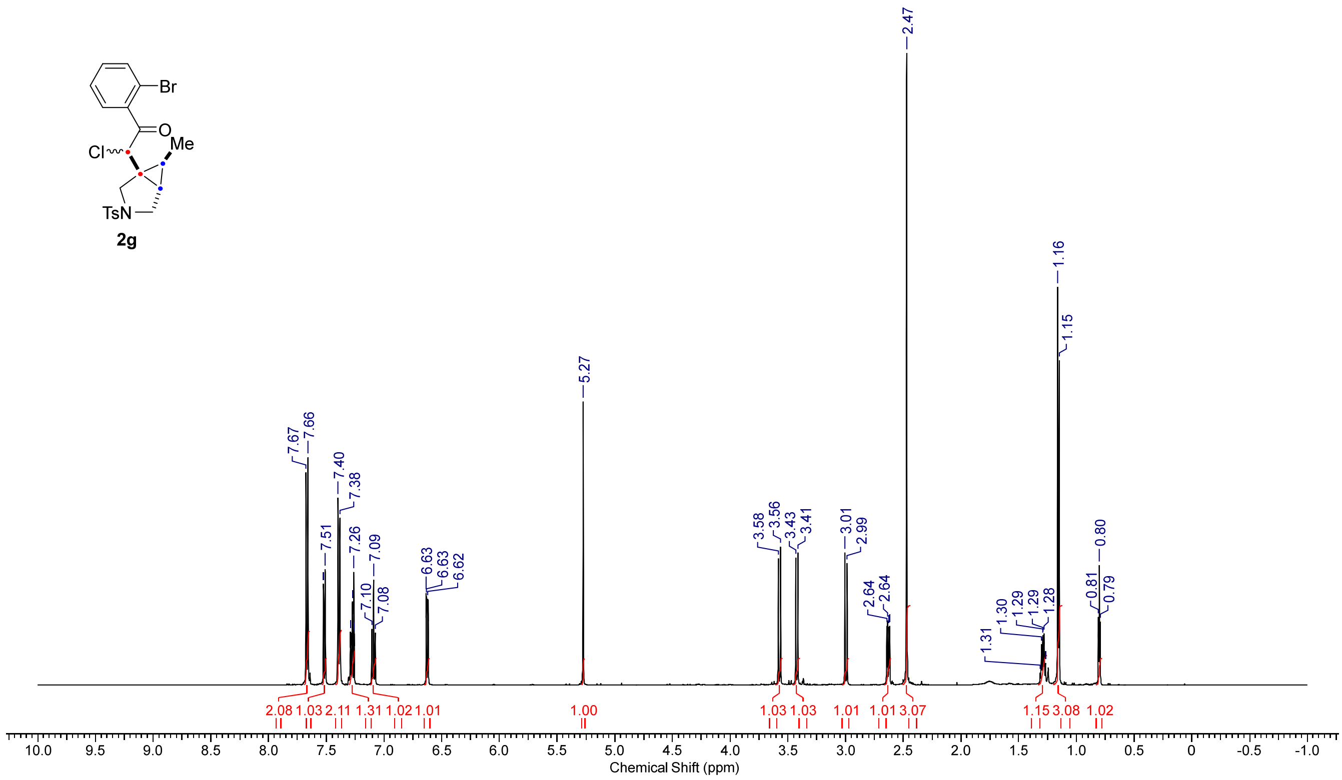
^{1}H NMR (500 MHz, $CDCl_3$) of **2g** (major epimer)



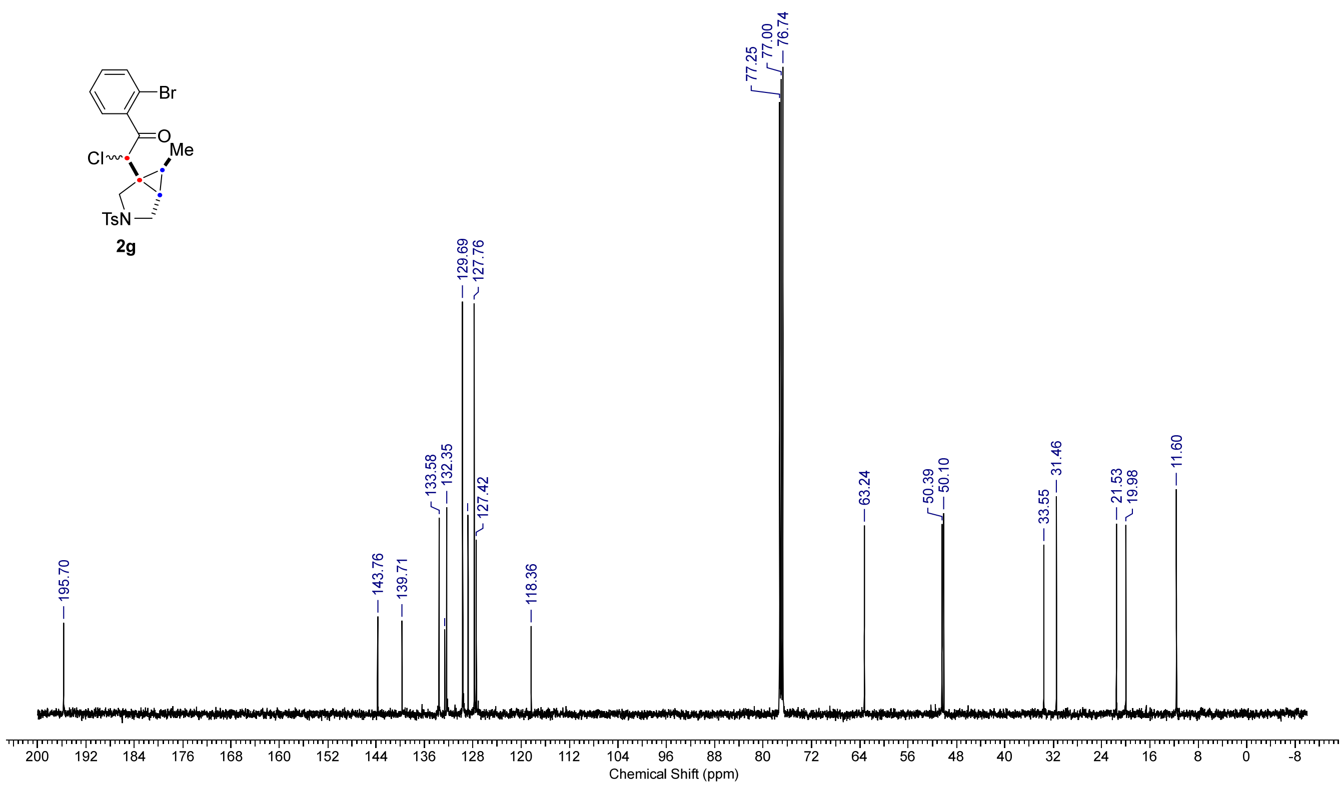
^{13}C NMR (125 MHz, $CDCl_3$) of **2g** (major epimer)



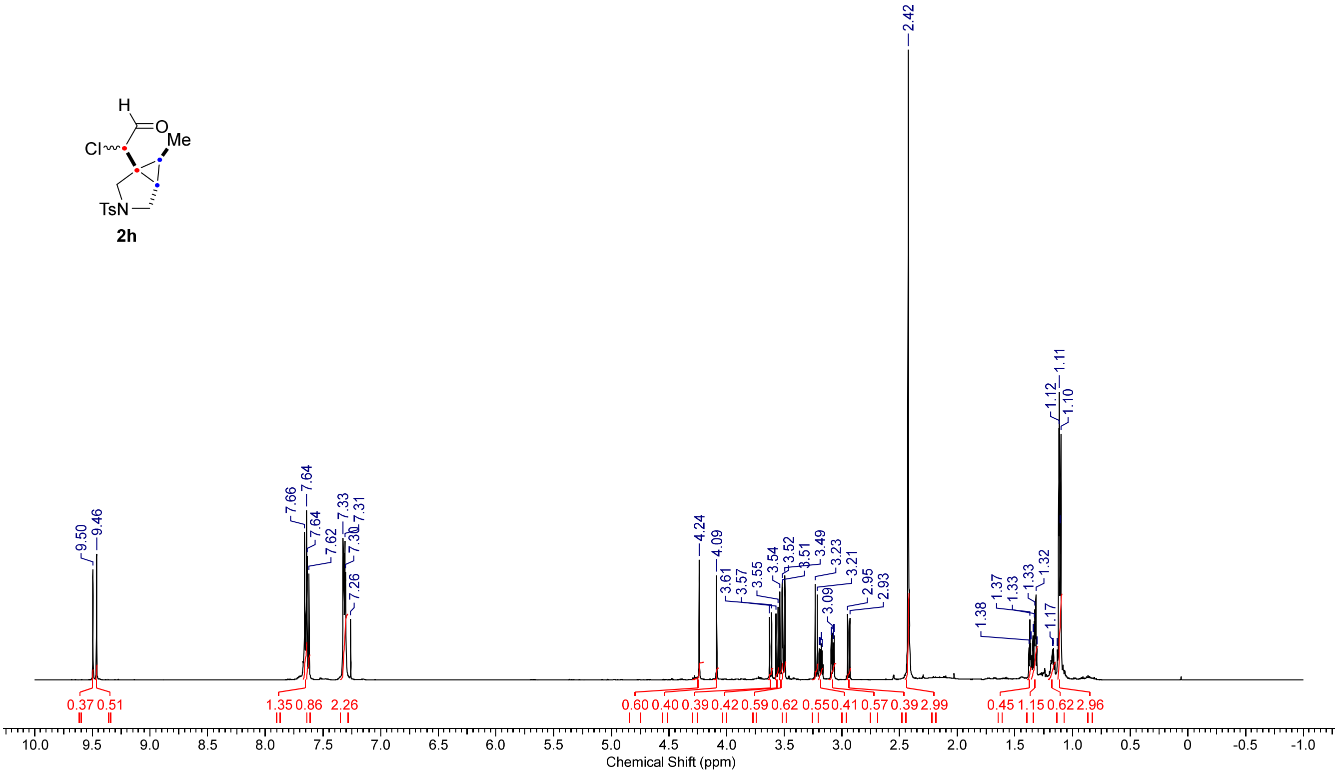
^{1}H NMR (500 MHz, $CDCl_3$) of **2g** (minor epimer)



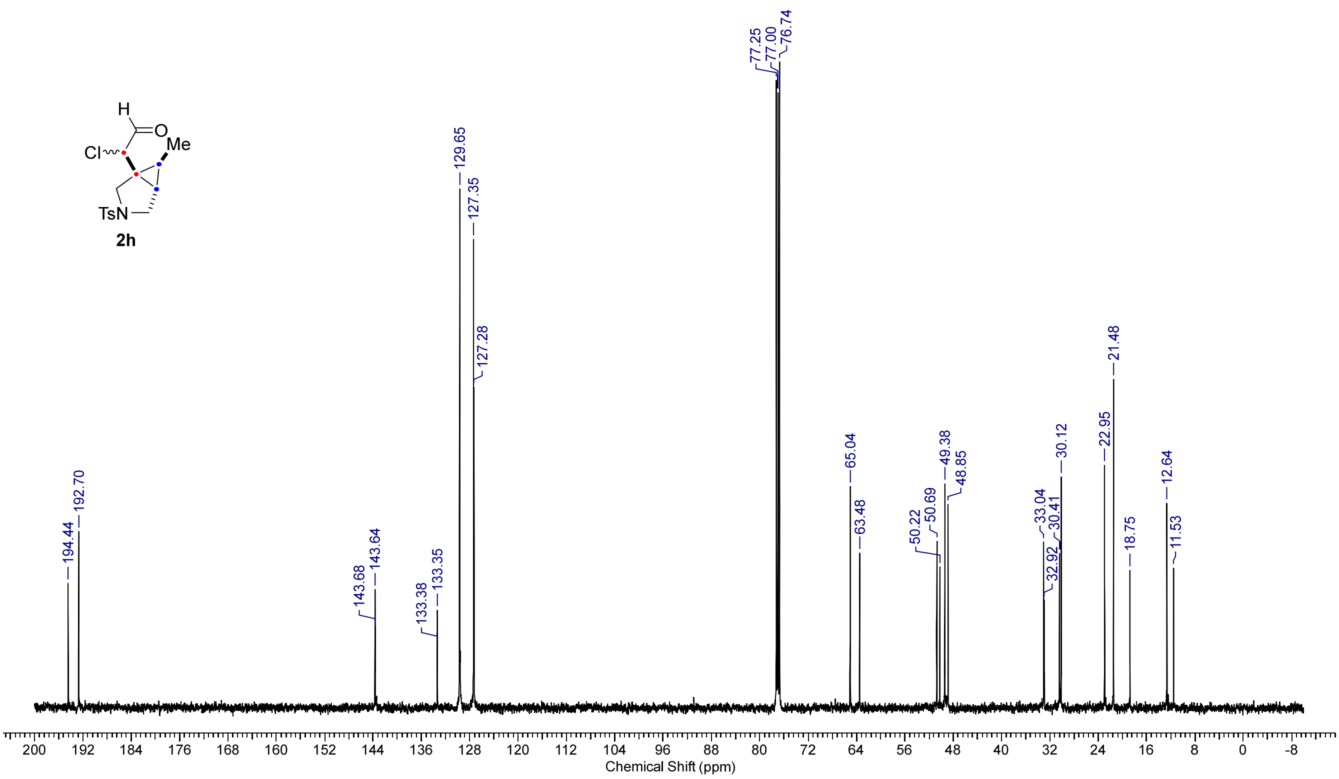
^{13}C NMR (125 MHz, $CDCl_3$) of **2g** (minor epimer)



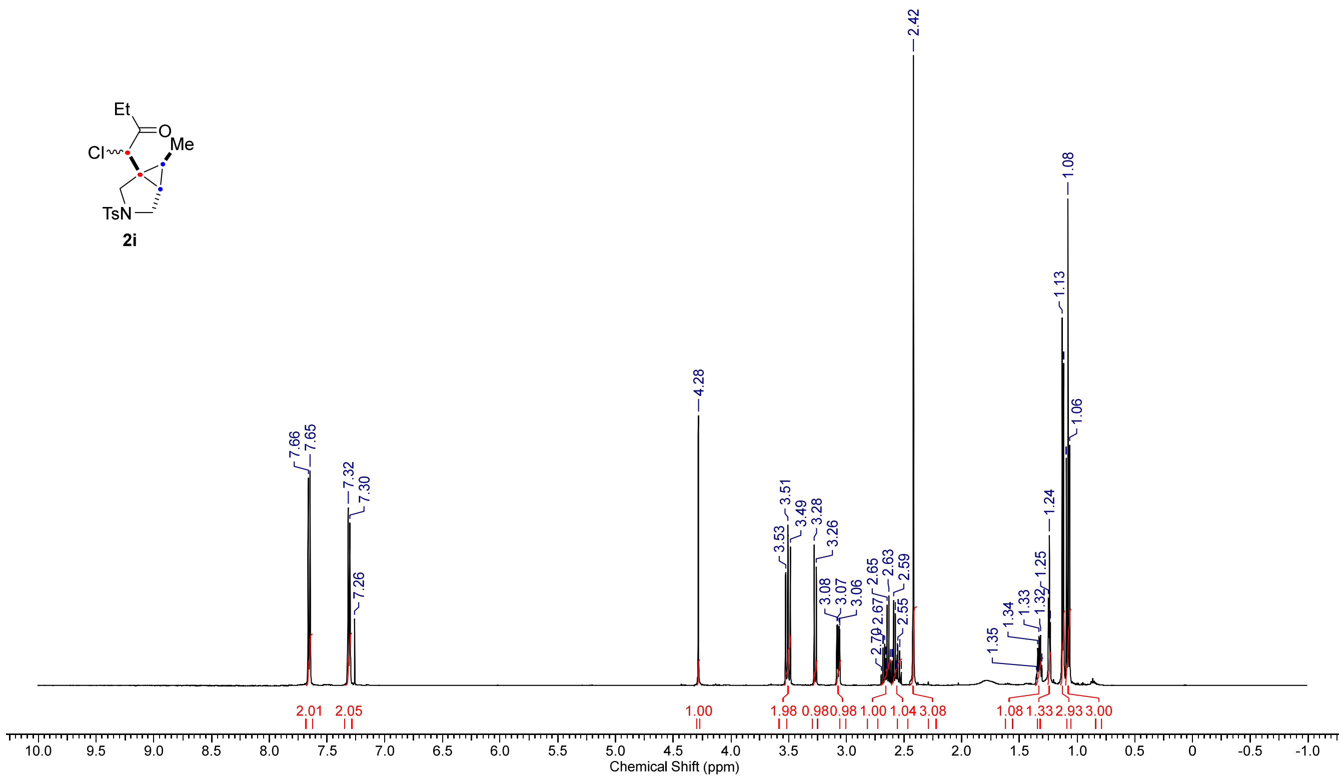
[1]H NMR (500 MHz, $CDCl_3$) of **2h** (60:40 mixture of epimers)



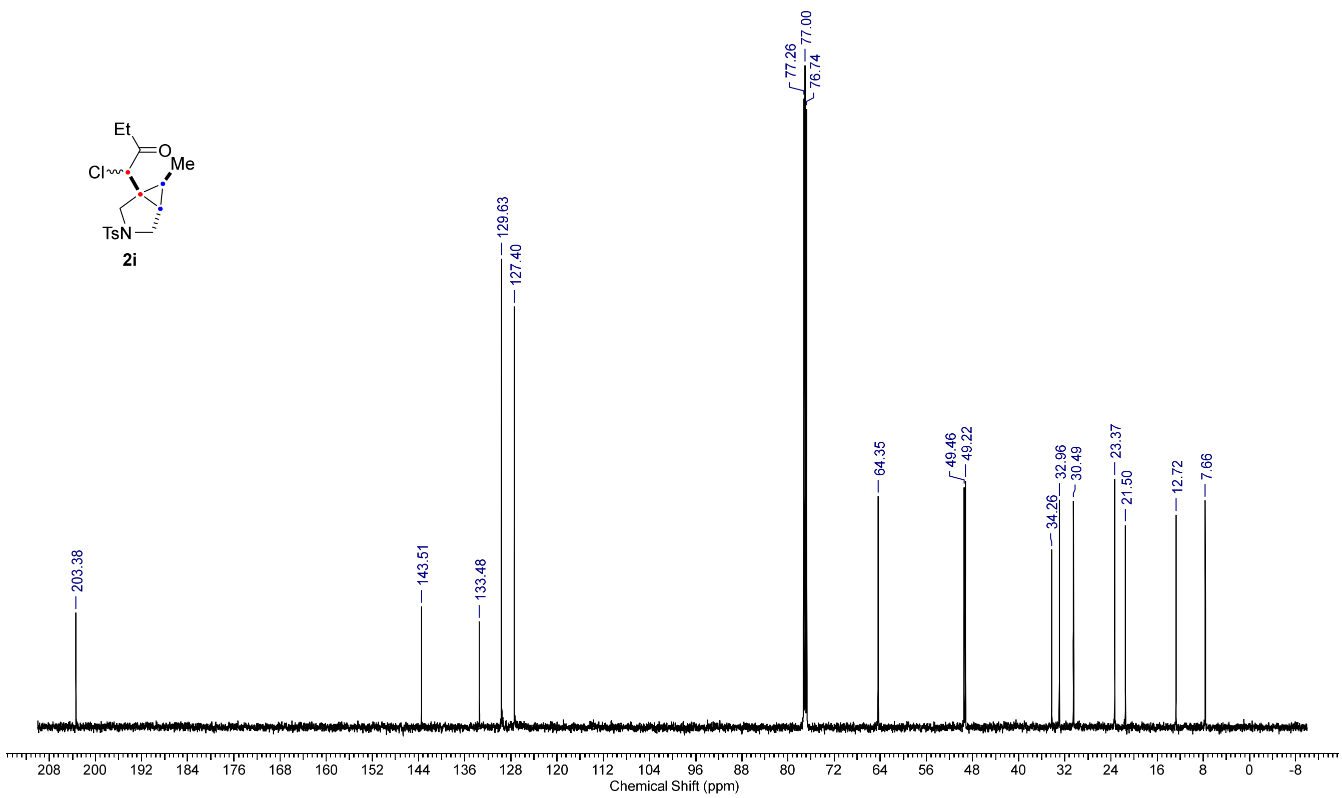
[13]C NMR (125 MHz, $CDCl_3$) of **2h** (60:40 mixture of epimers)



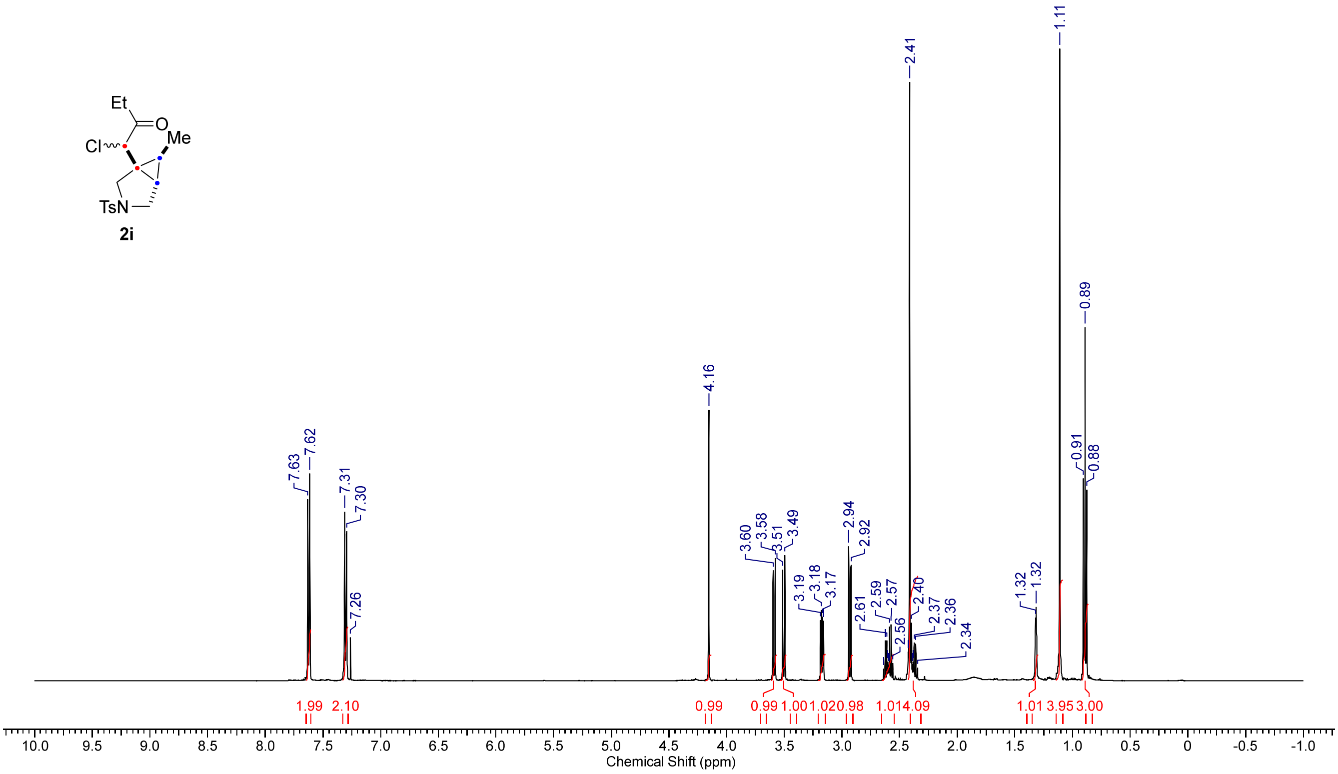
^{1}H NMR (500 MHz, $CDCl_3$) of **2i** (major epimer)



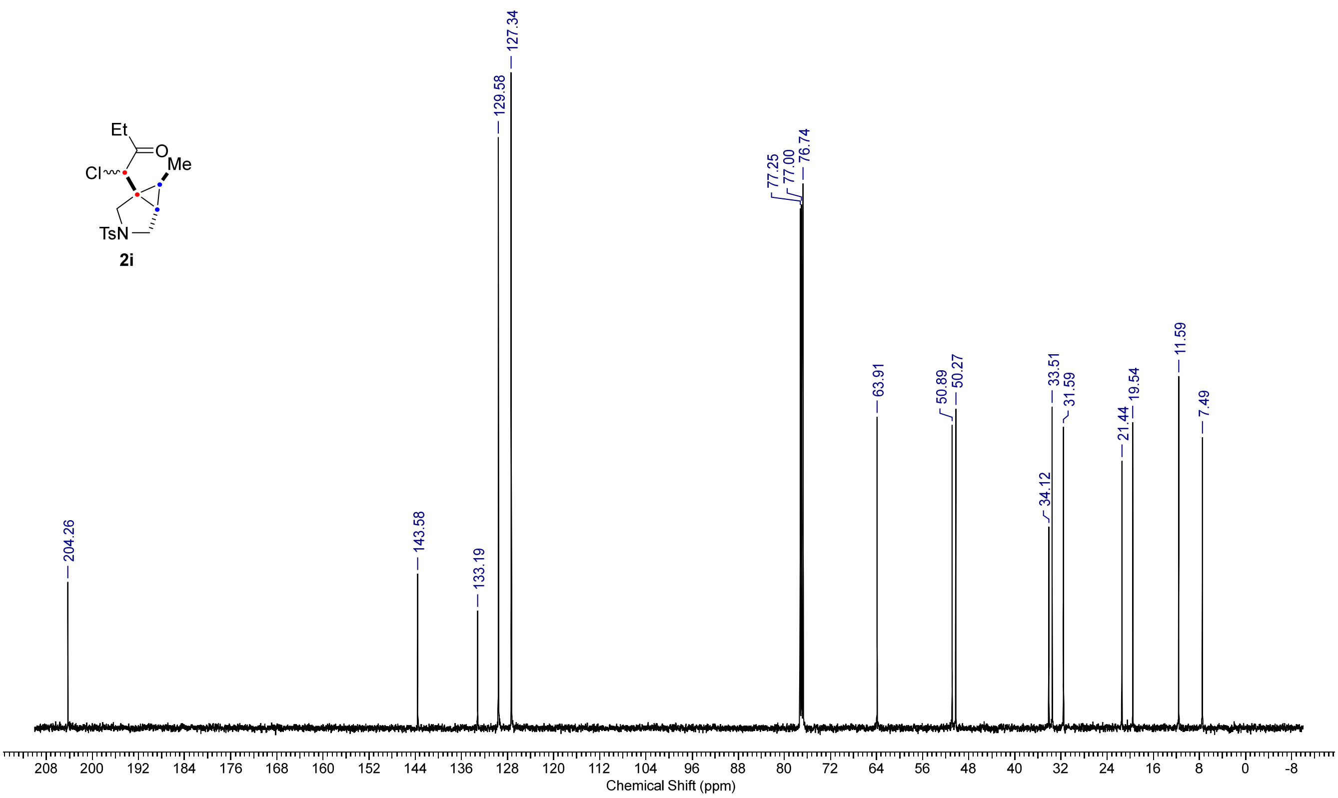
^{13}C NMR (125 MHz, $CDCl_3$) of **2i** (major epimer)



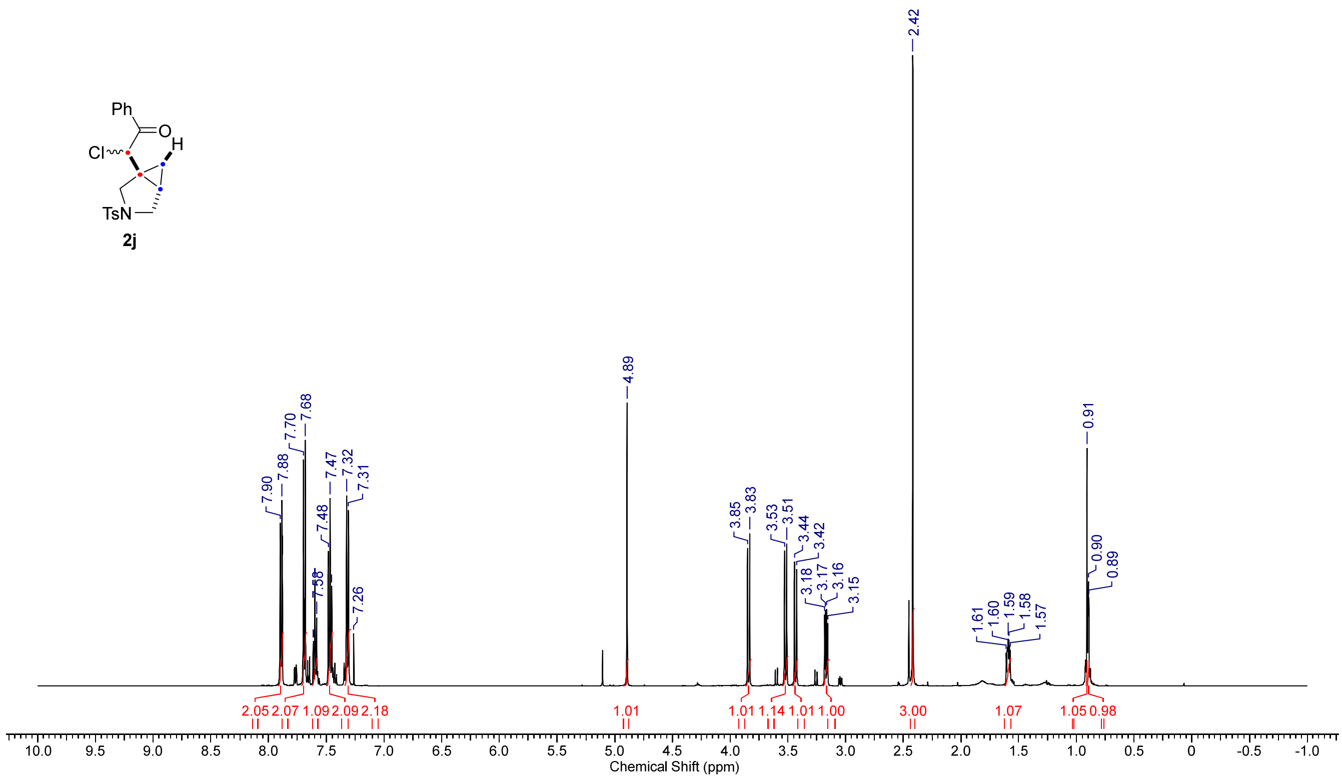
^{1}H NMR (500 MHz, $CDCl_3$) of **2i** (minor epimer)



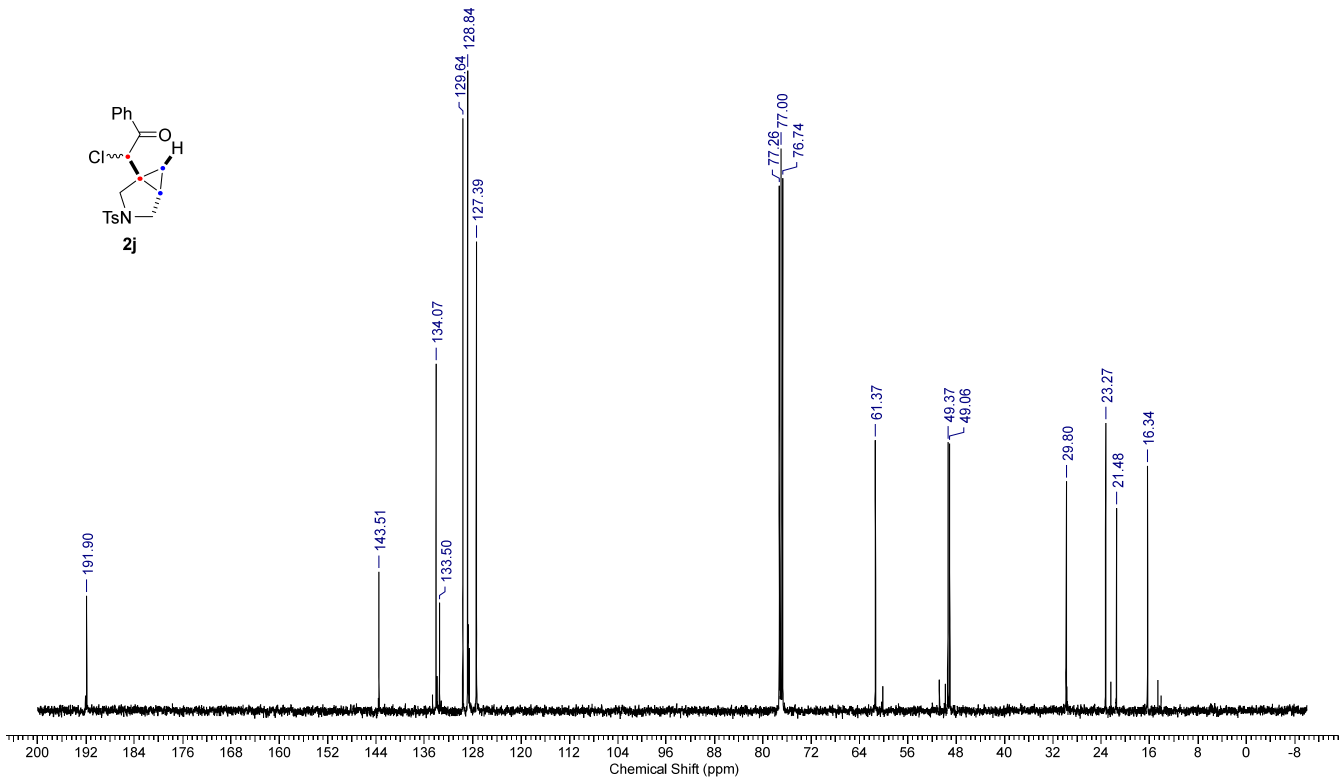
^{13}C NMR (125 MHz, $CDCl_3$) of **2i** (minor epimer)



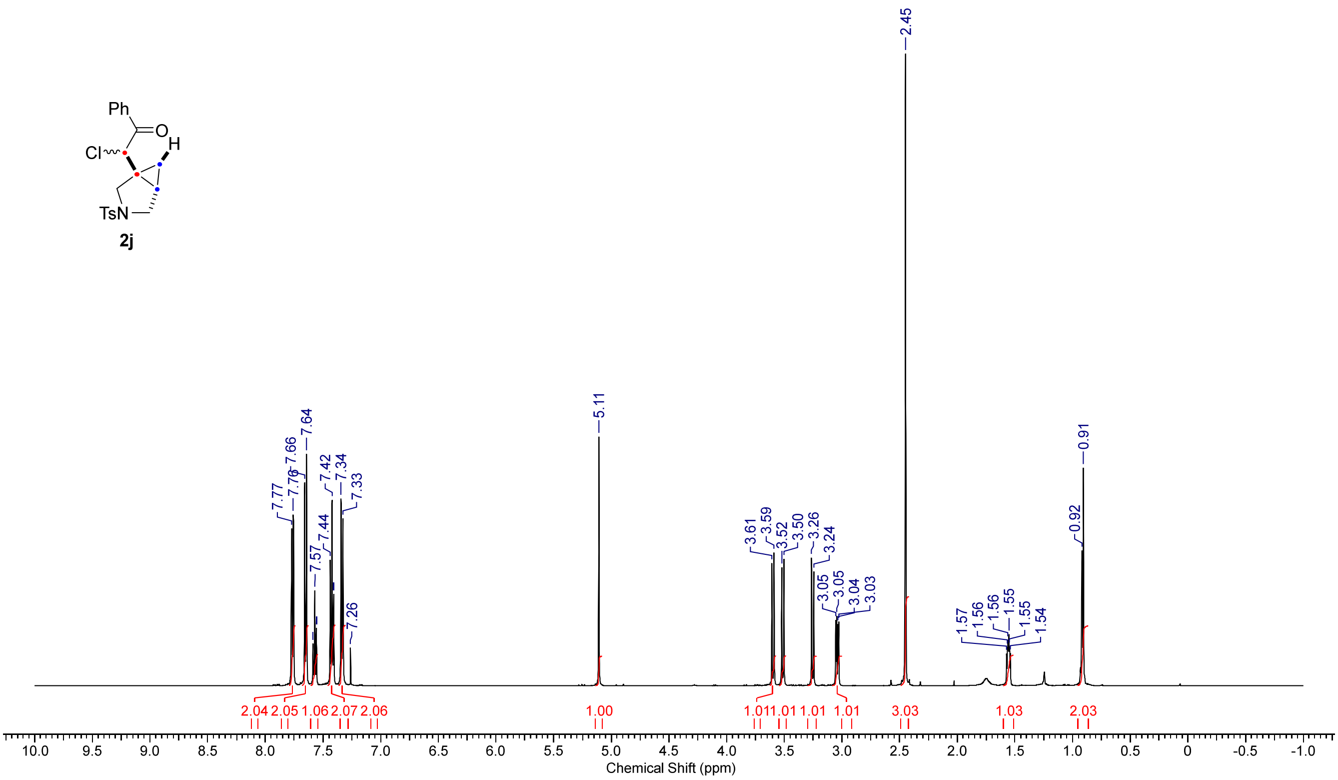
^{1}H NMR (500 MHz, $CDCl_3$) of **2j** (major epimer-rich)



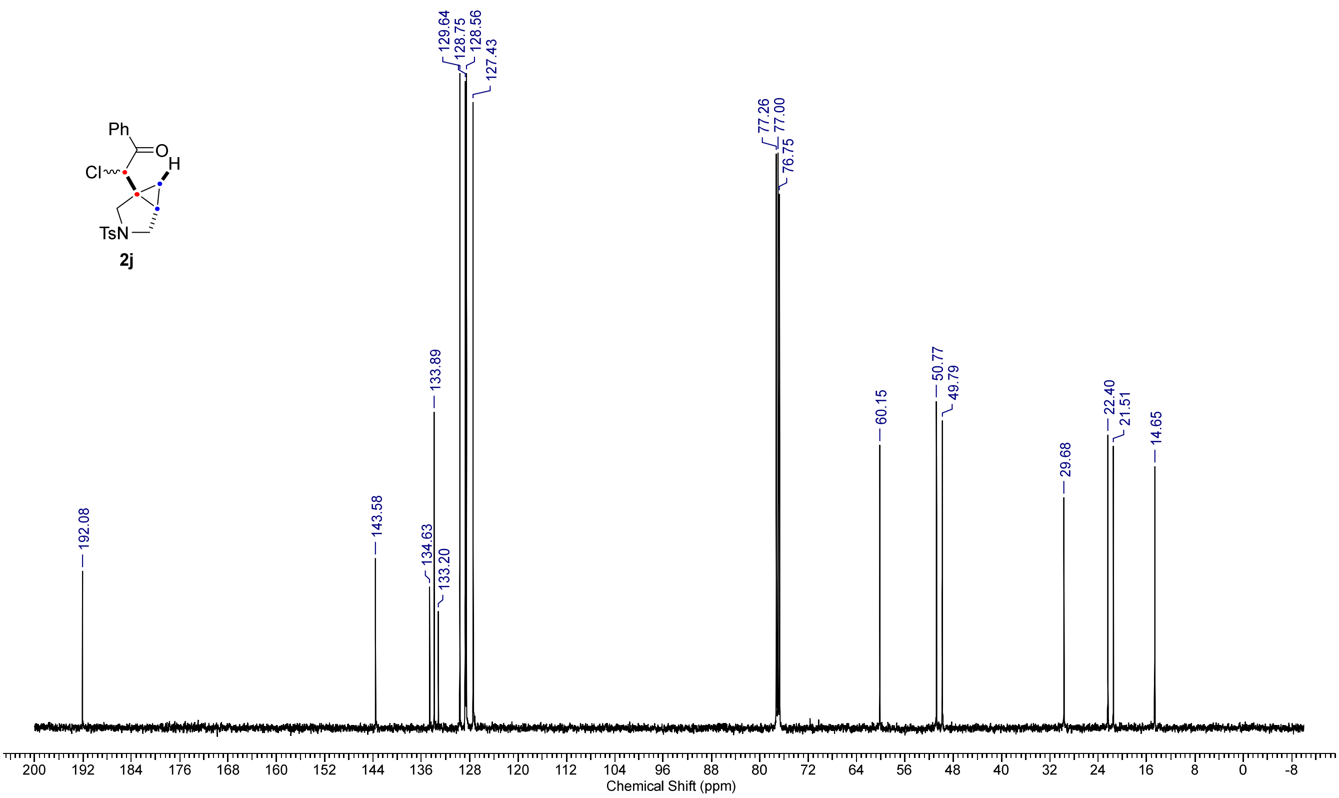
^{13}C NMR (125 MHz, $CDCl_3$) of **2j** (major epimer-rich)



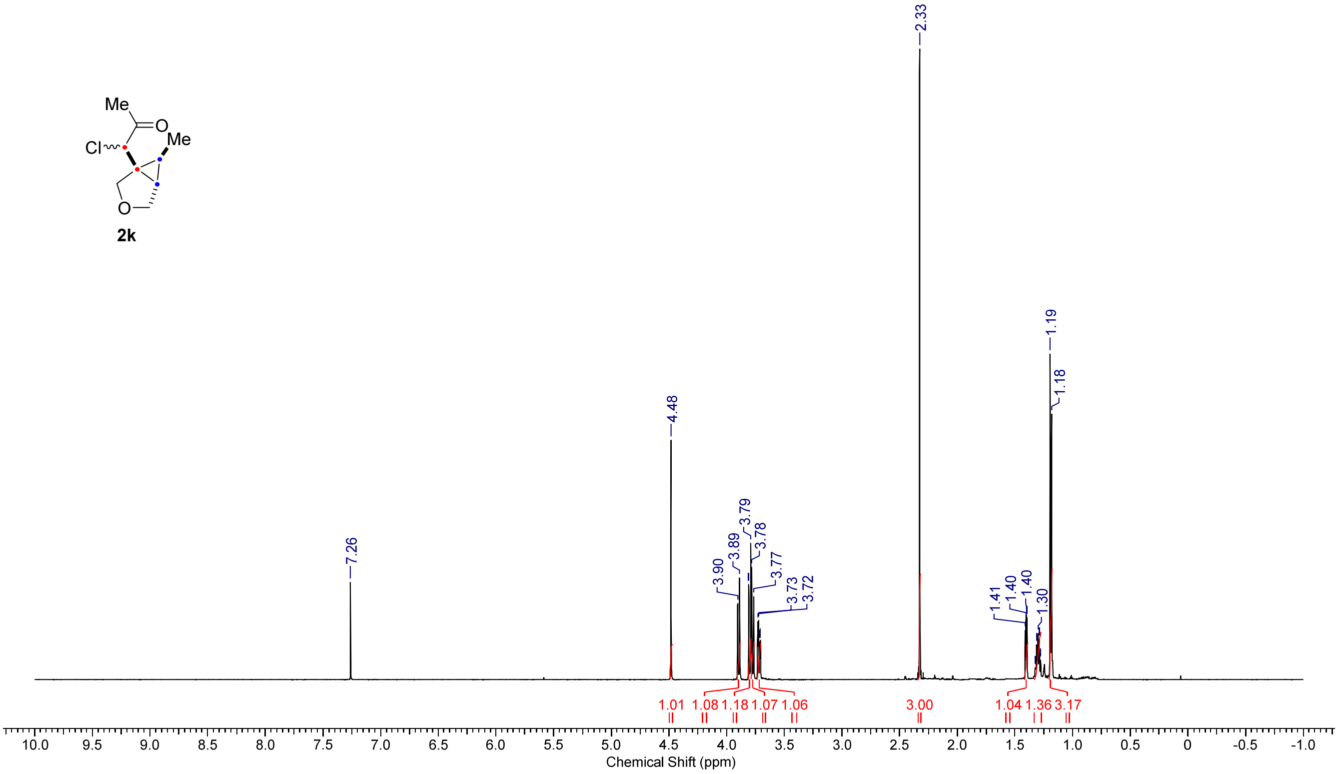
^{1}H NMR (500 MHz, $CDCl_3$) of **2j** (minor epimer)



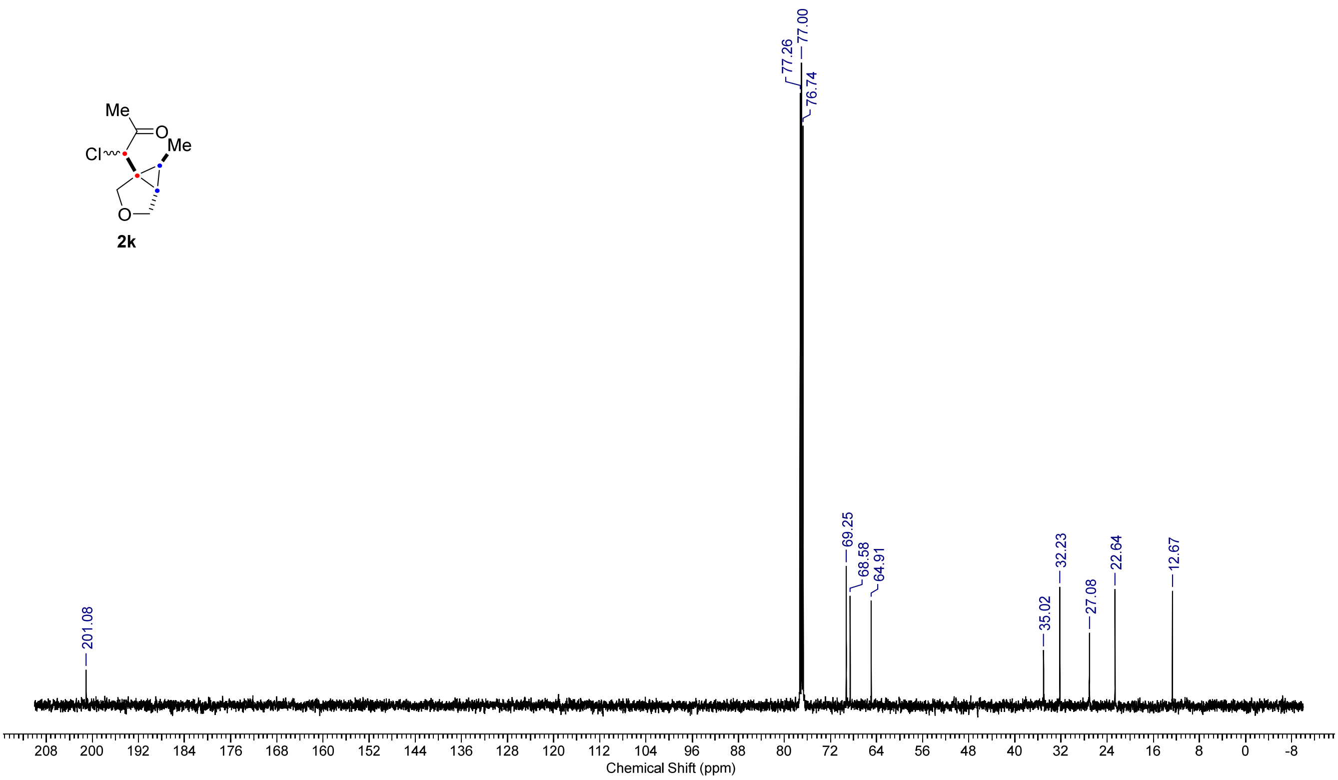
^{13}C NMR (125 MHz, $CDCl_3$) of **2j** (minor epimer)



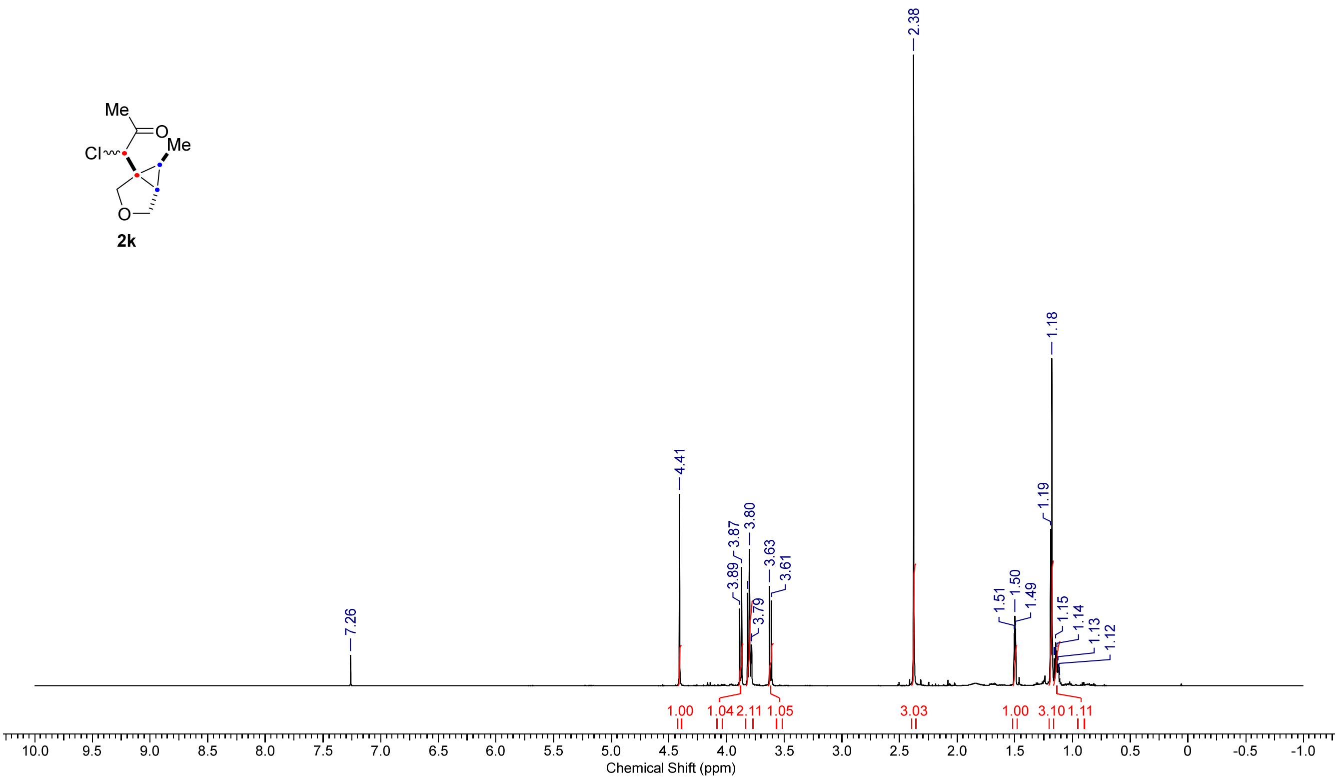
[1]H NMR (500 MHz, $CDCl_3$) of **2k** (major epimer)



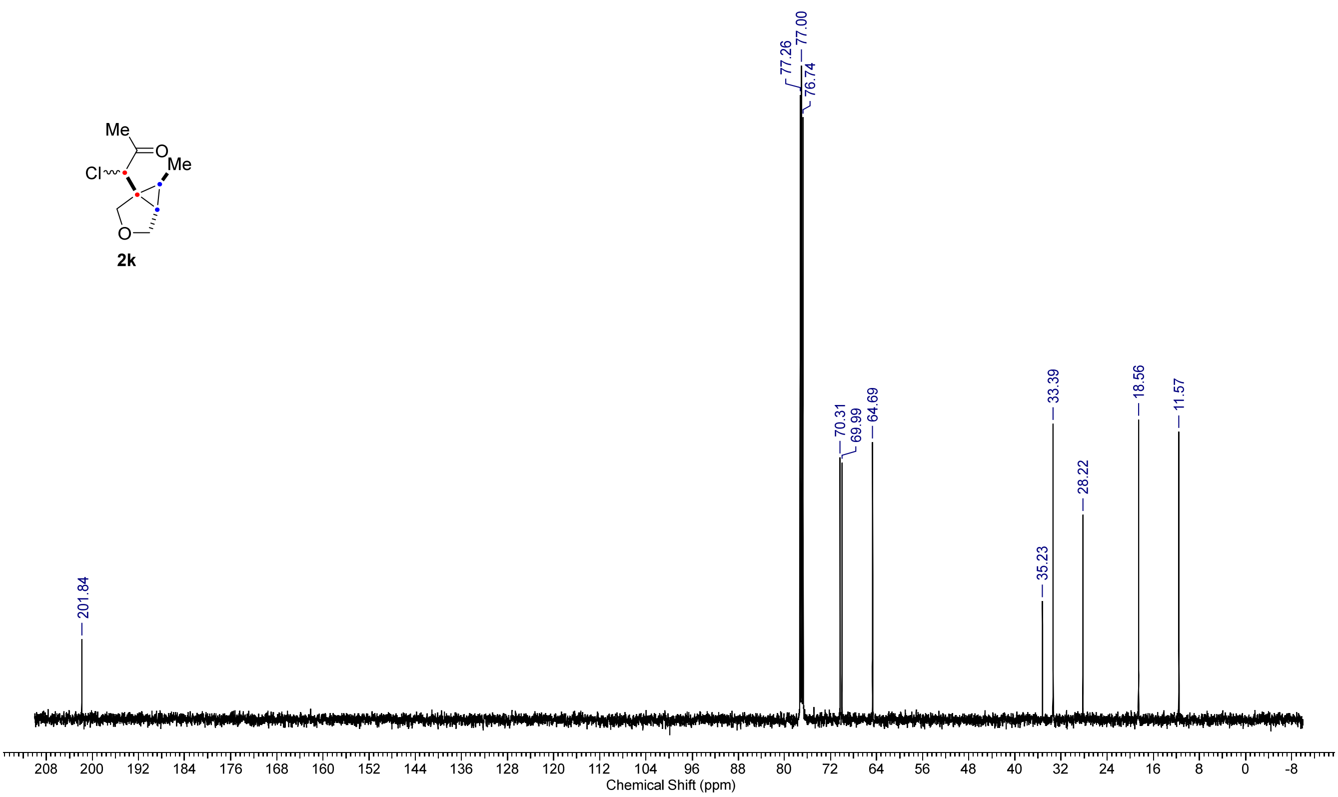
[13]C NMR (125 MHz, $CDCl_3$) of **2k** (major epimer)



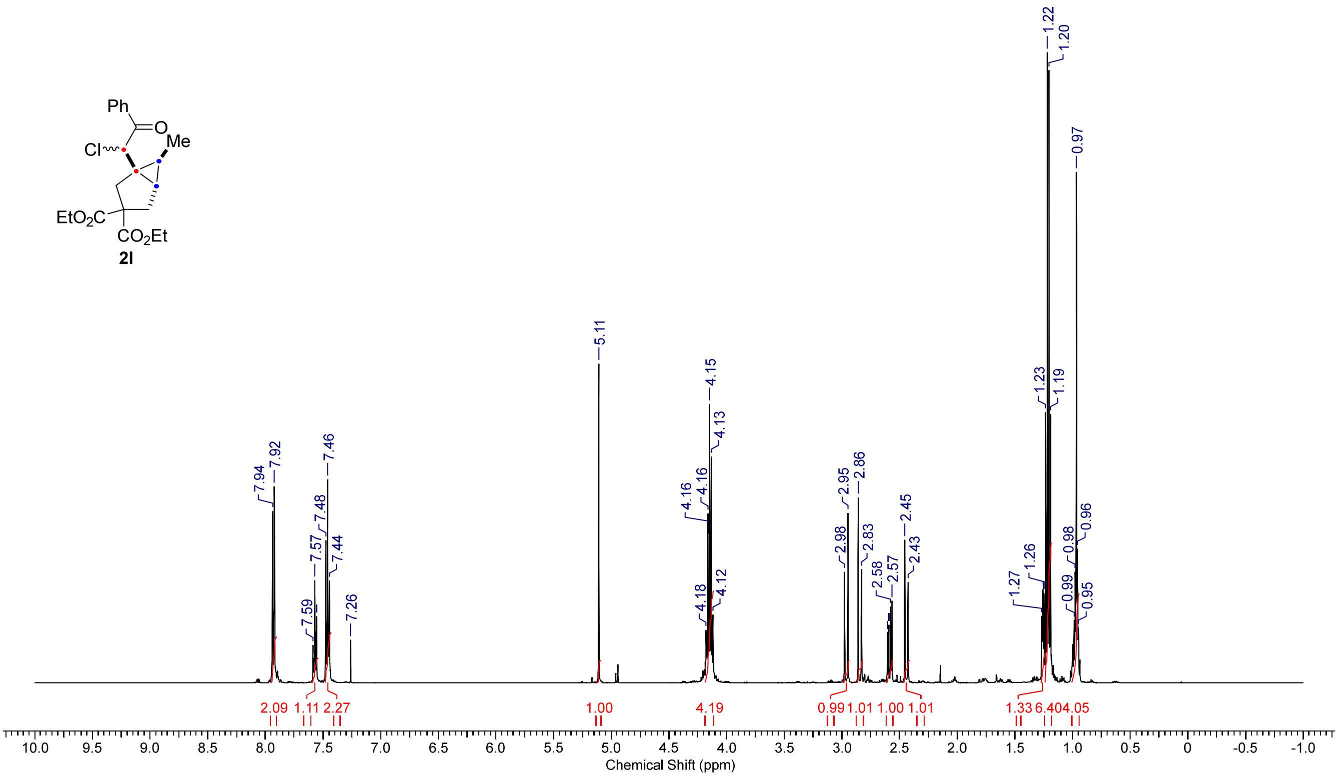
^{1}H NMR (500 MHz, $CDCl_3$) of **2k** (minor epimer)



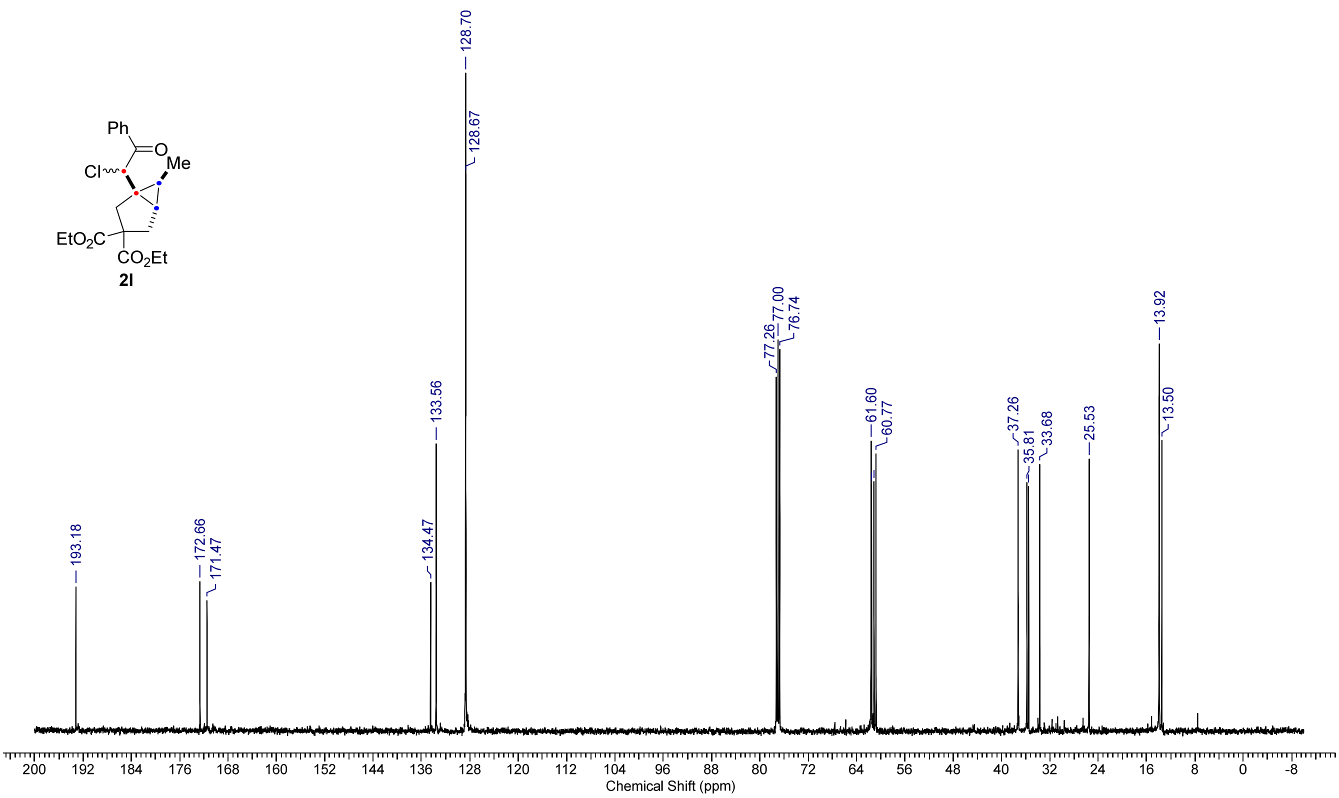
^{13}C NMR (125 MHz, $CDCl_3$) of **2k** (minor epimer)



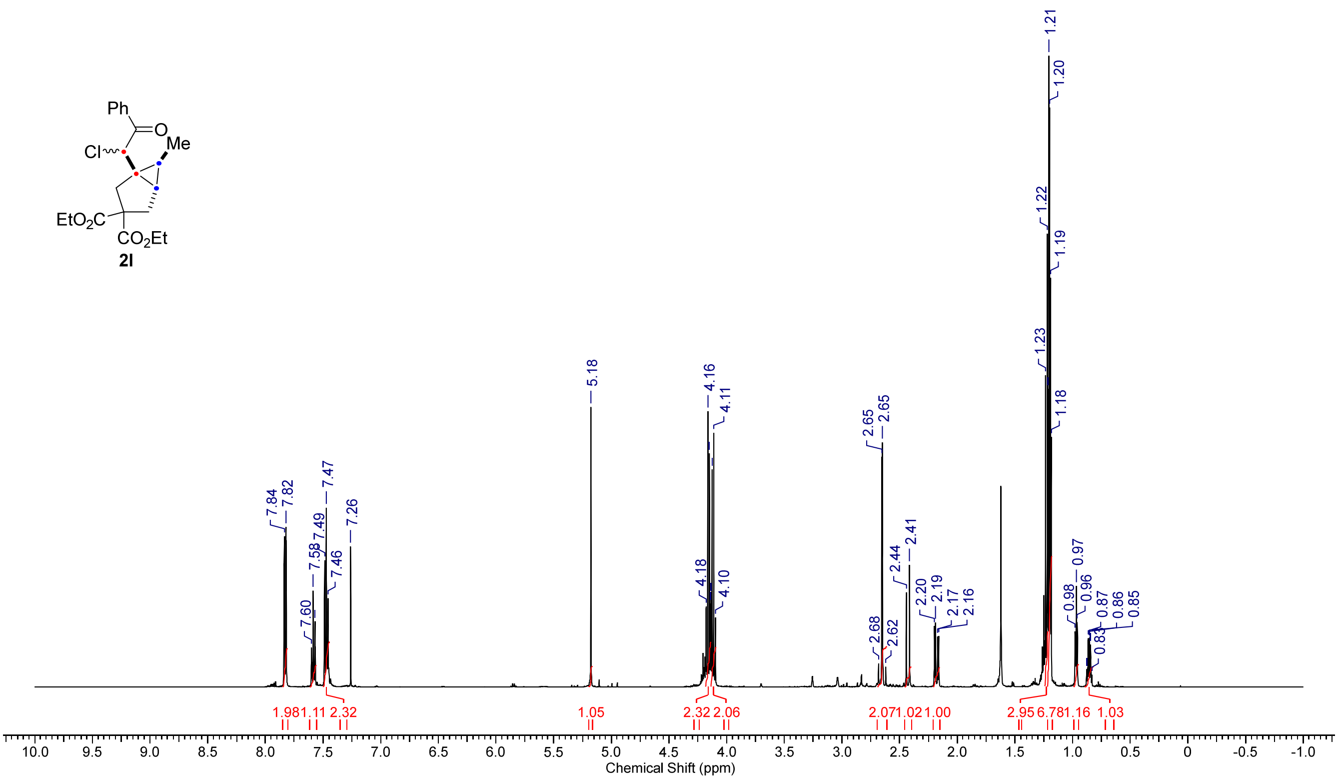
^{1}H NMR (500 MHz, $CDCl_3$) of **2l** (major epimer-rich)



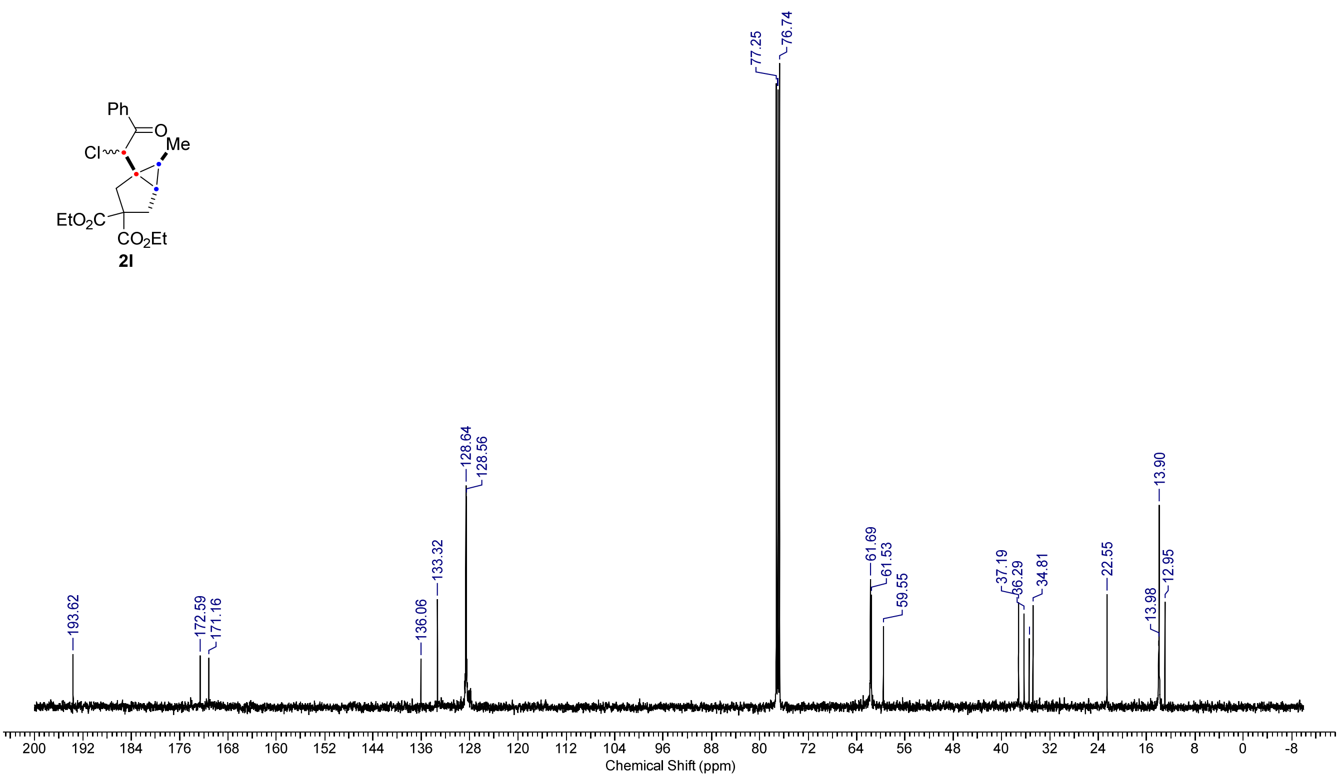
^{13}C NMR (125 MHz, $CDCl_3$) of **2l** (major epimer-rich)



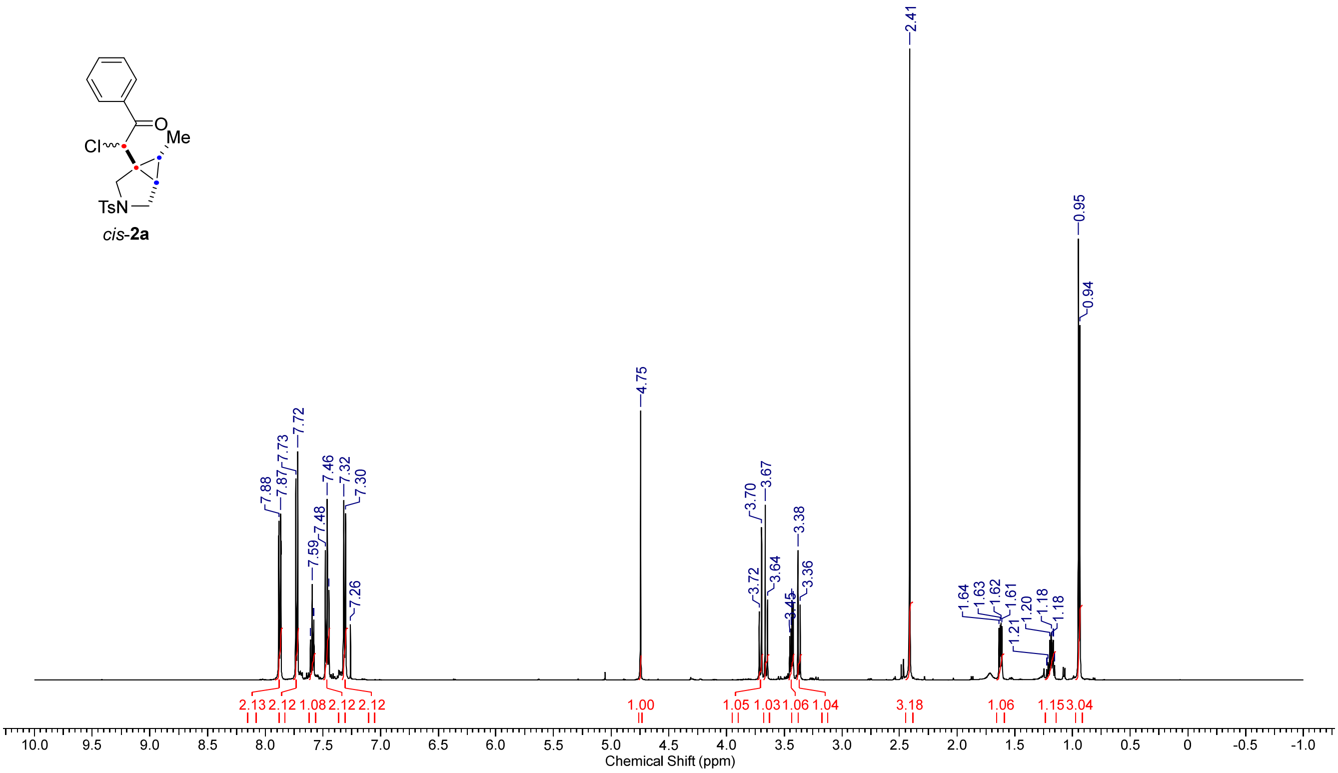
[1]H NMR (500 MHz, $CDCl_3$) of **2l** (minor epimer-rich)



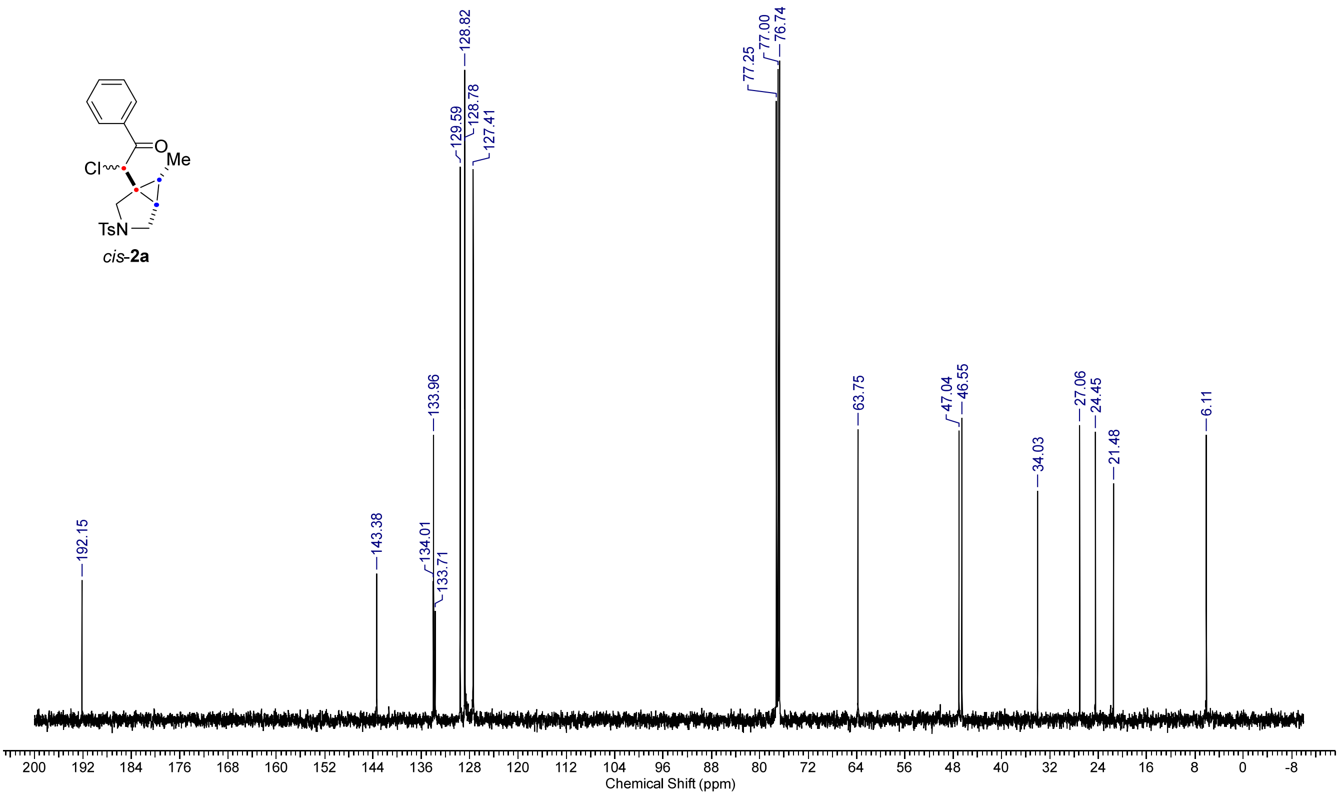
[13]C NMR (125 MHz, $CDCl_3$) of **2l** (minor epimer-rich)



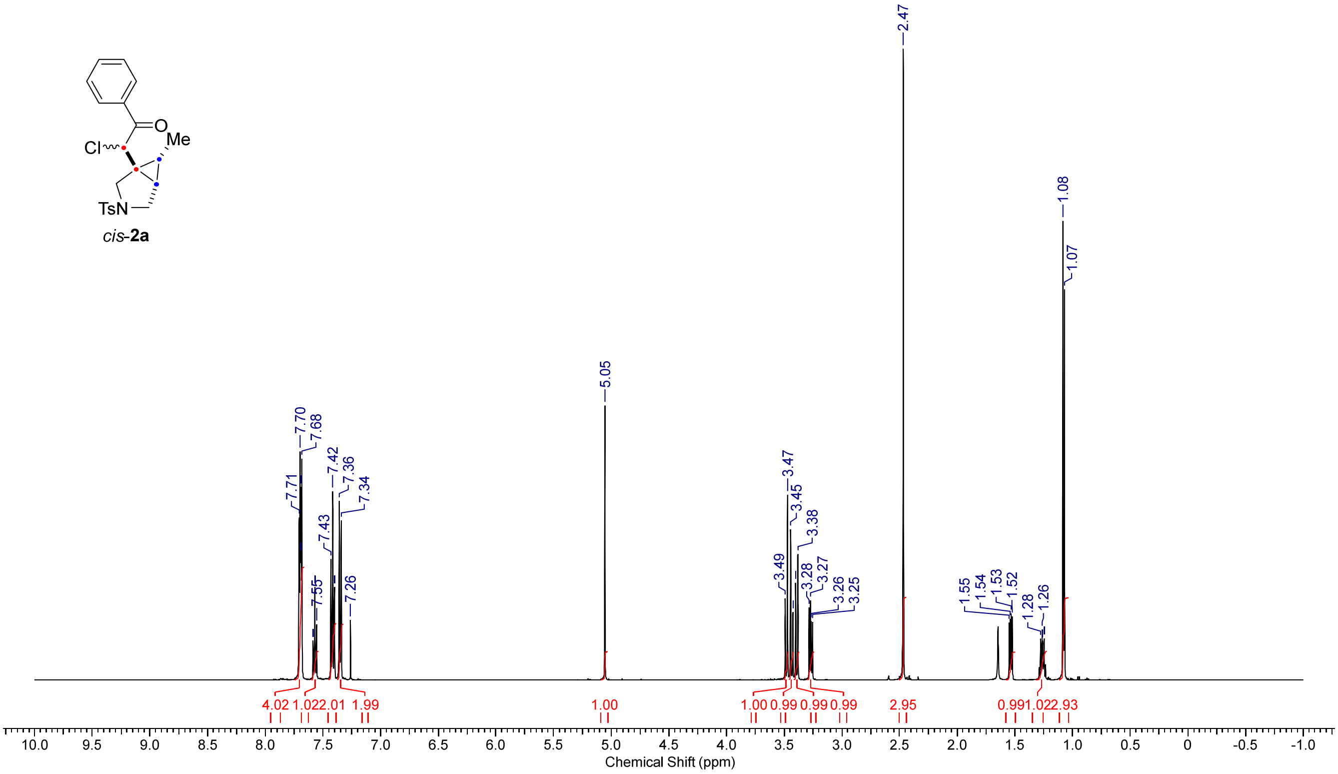
[1]H NMR (500 MHz, $CDCl_3$) of *cis*-**2a** (major epimer-rich)



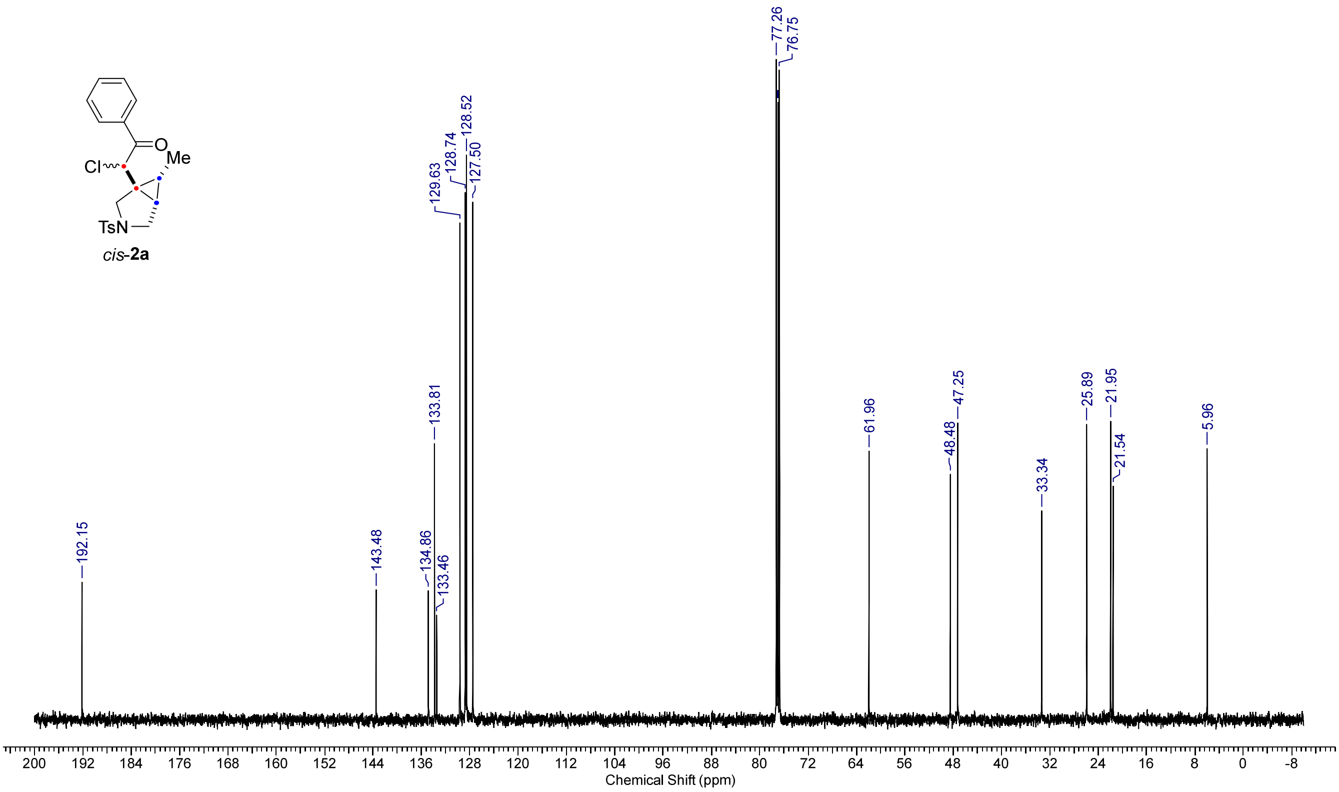
[13]C NMR (125 MHz, $CDCl_3$) of *cis*-**2a** (major epimer-rich)



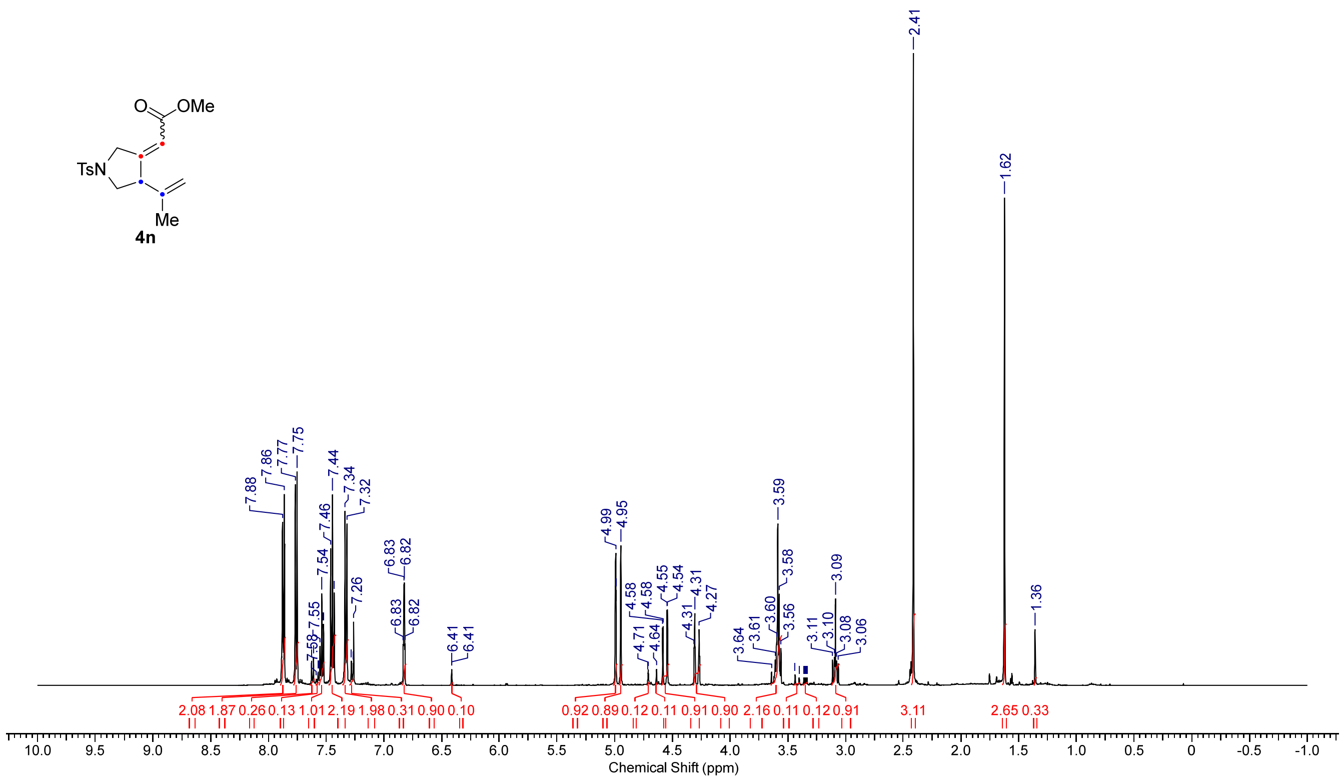
[1]H NMR (500 MHz, $CDCl_3$) of *cis*-**2a** (minor epimer)



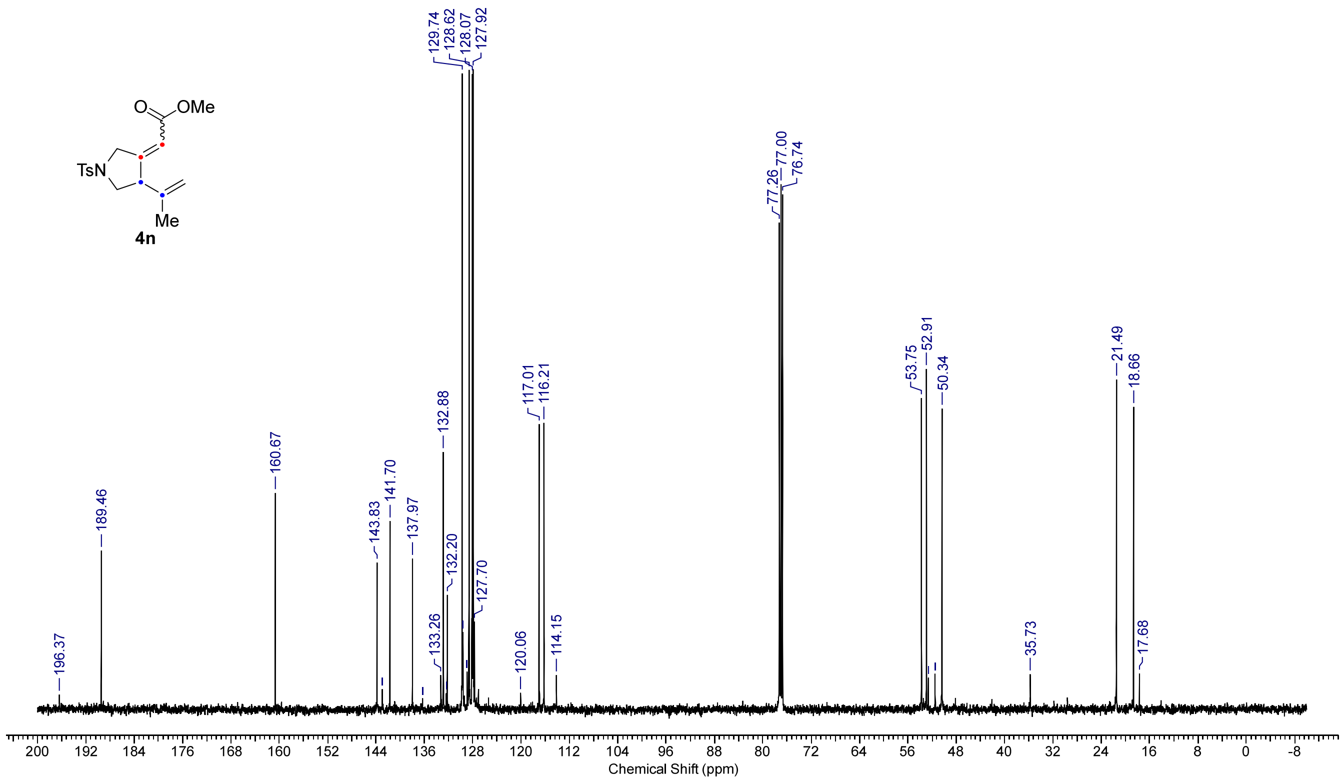
[13]C NMR (125 MHz, $CDCl_3$) of *cis*-**2a** (minor epimer)



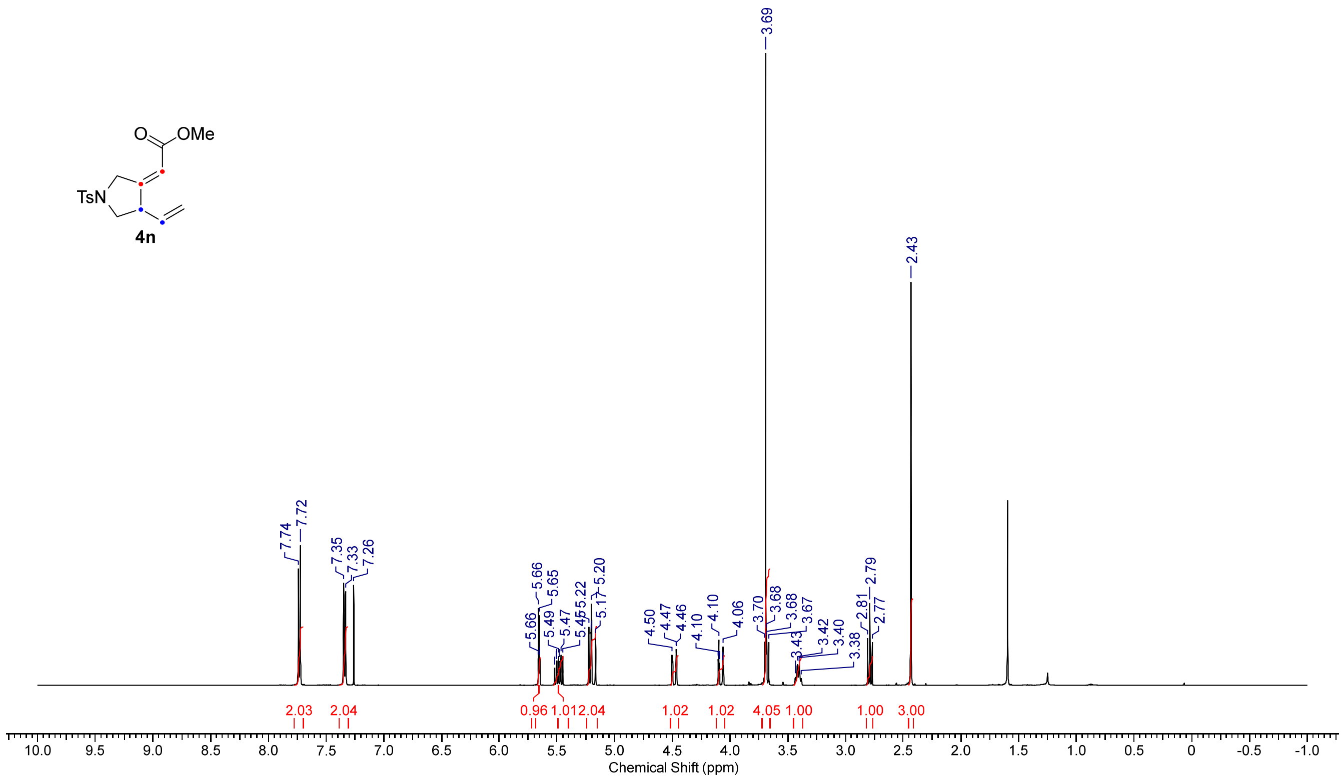
[1]H NMR (500 MHz, $CDCl_3$) of **4m** (90:10 mixture of geometric isomers)



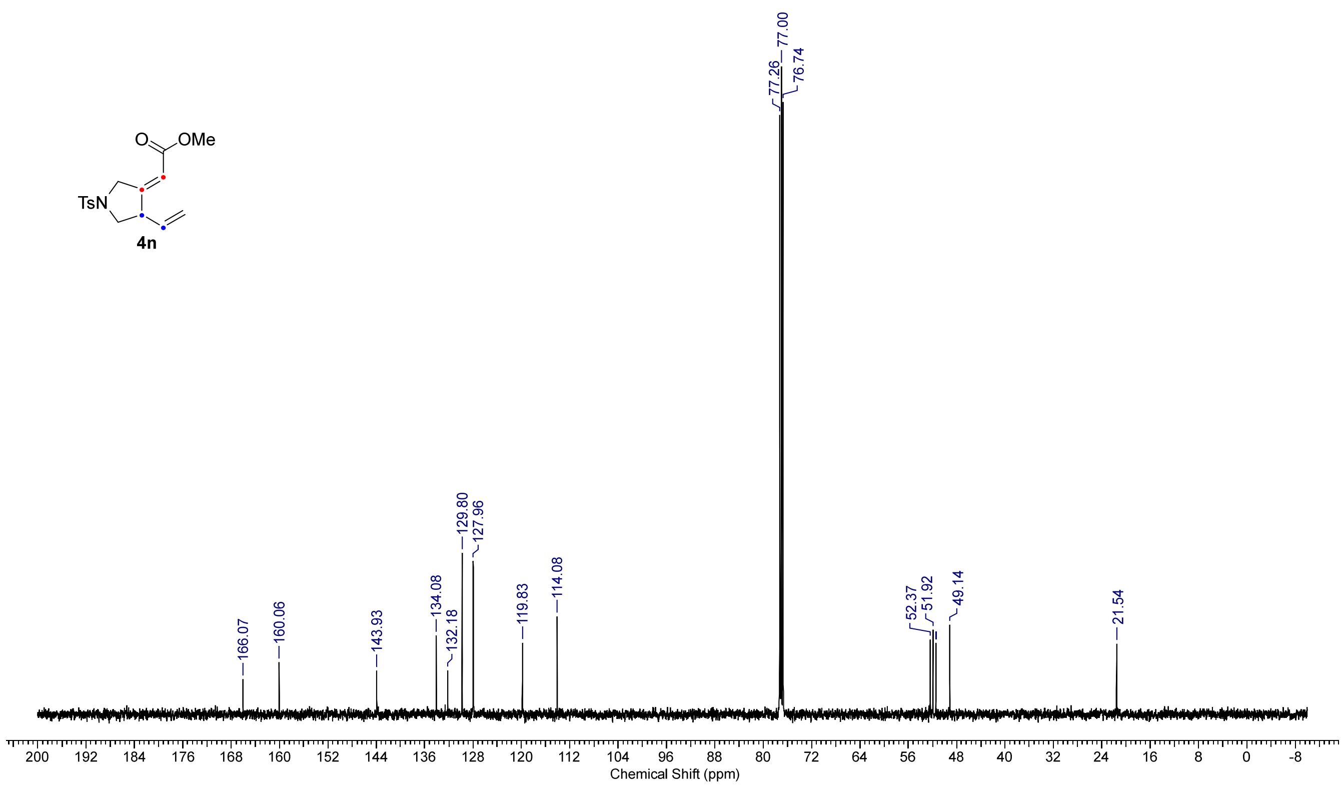
[13]C NMR (125 MHz, $CDCl_3$) of **4m** (90:10 mixture of geometric isomers)



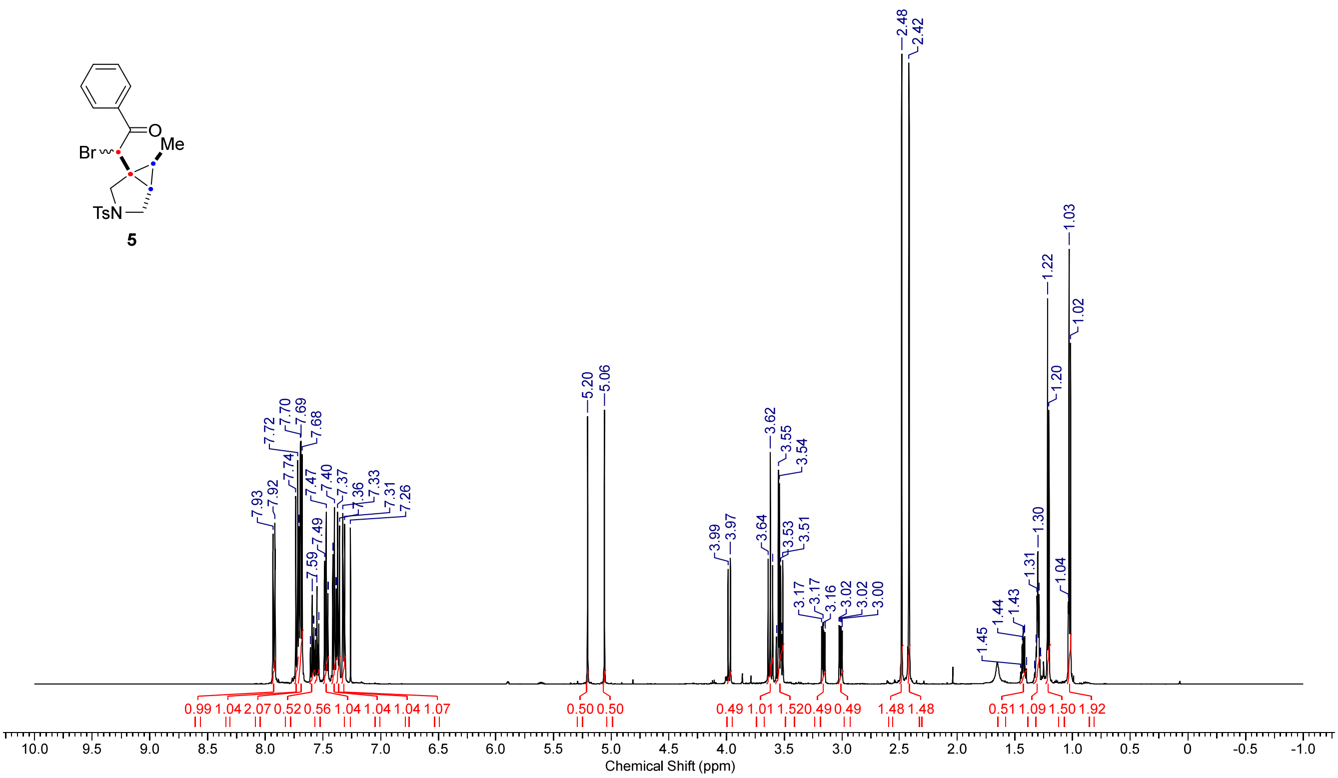
[1]H NMR (500 MHz, $CDCl_3$) of **4n**



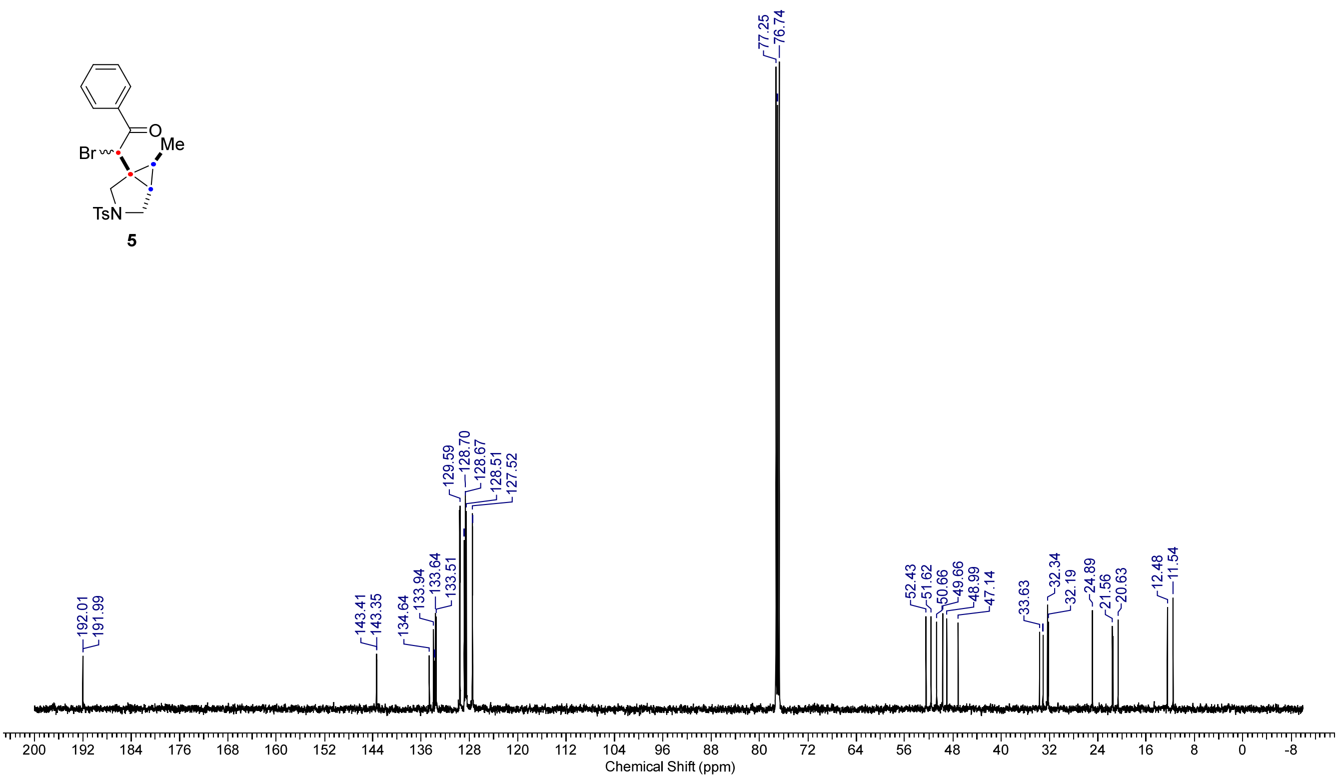
[13]C NMR (125 MHz, $CDCl_3$) of **4n**



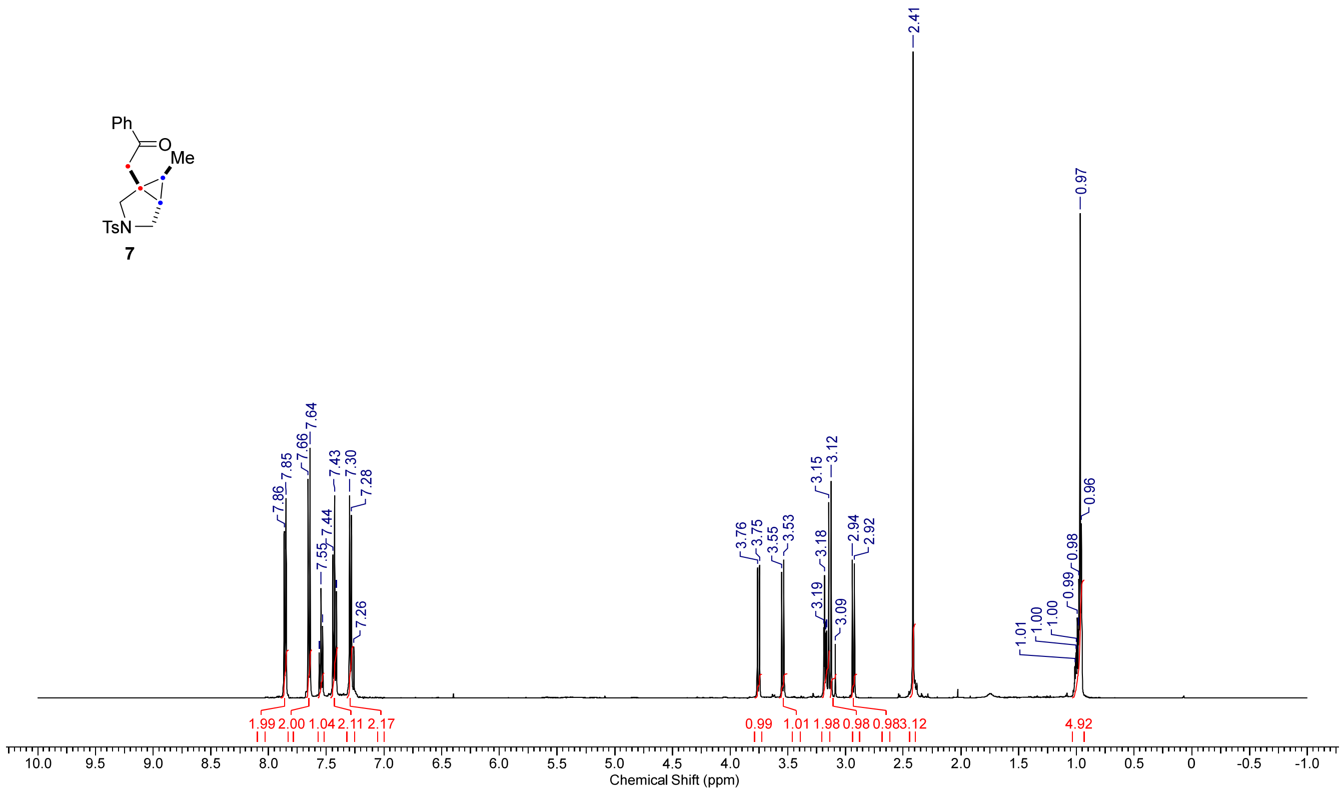
^{1}H NMR (500 MHz, $CDCl_3$) of **5** (50:50 mixture of epimers)



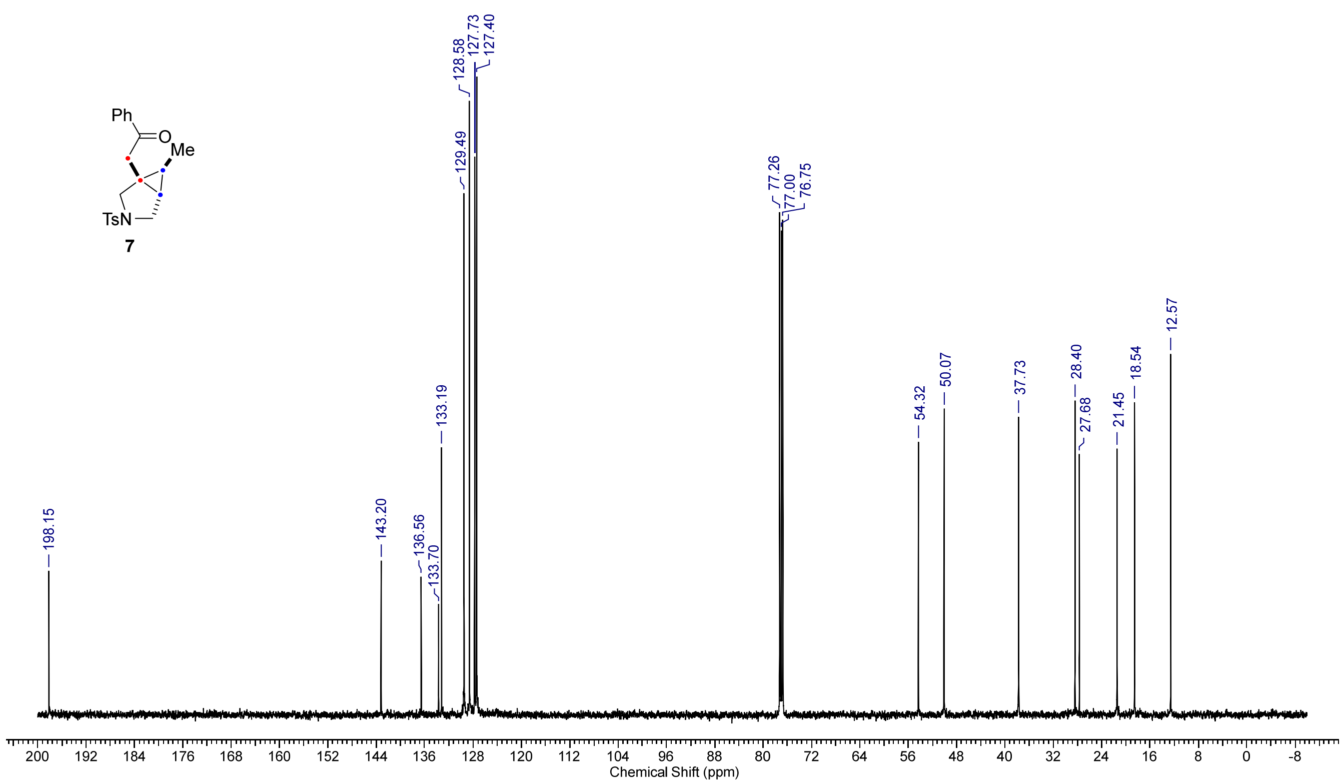
^{13}C NMR (125 MHz, $CDCl_3$) of **5** (50:50 mixture of epimers)



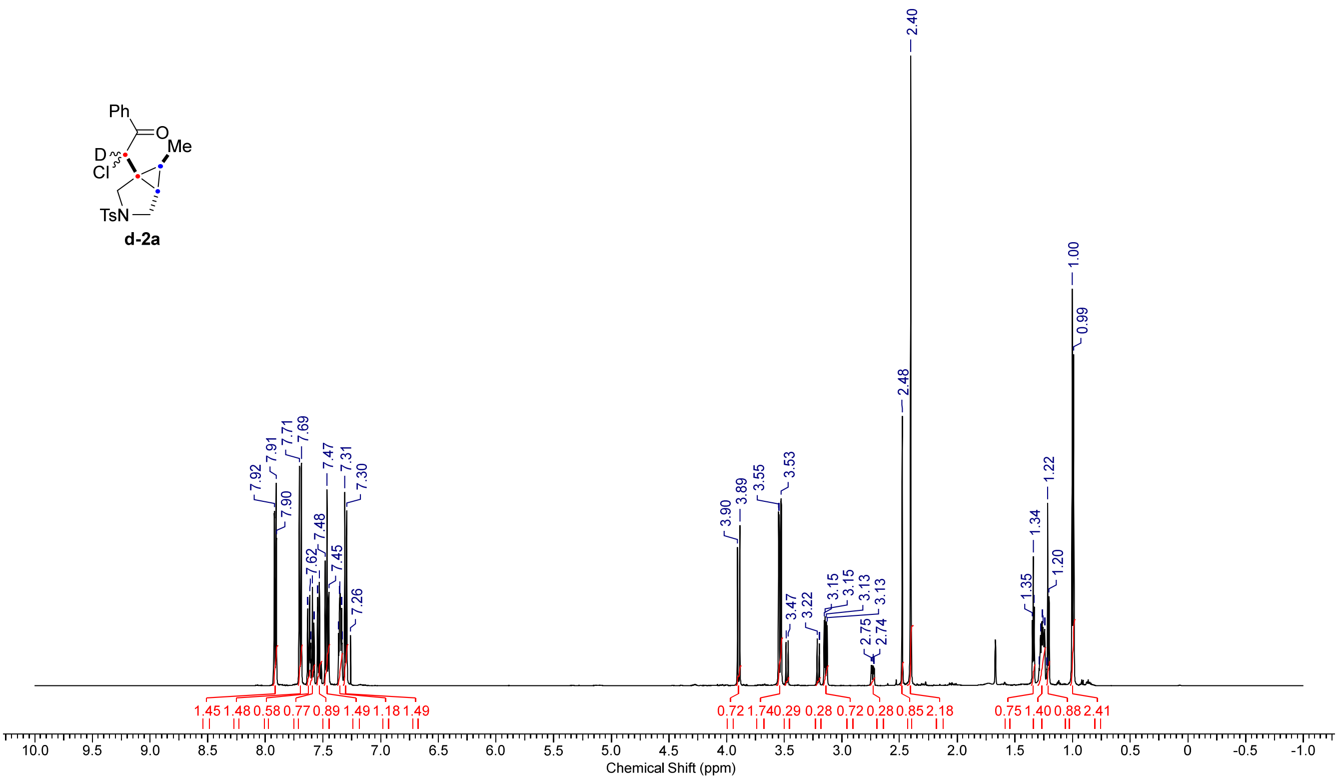
^{1}H NMR (500 MHz, $CDCl_3$) of **7**



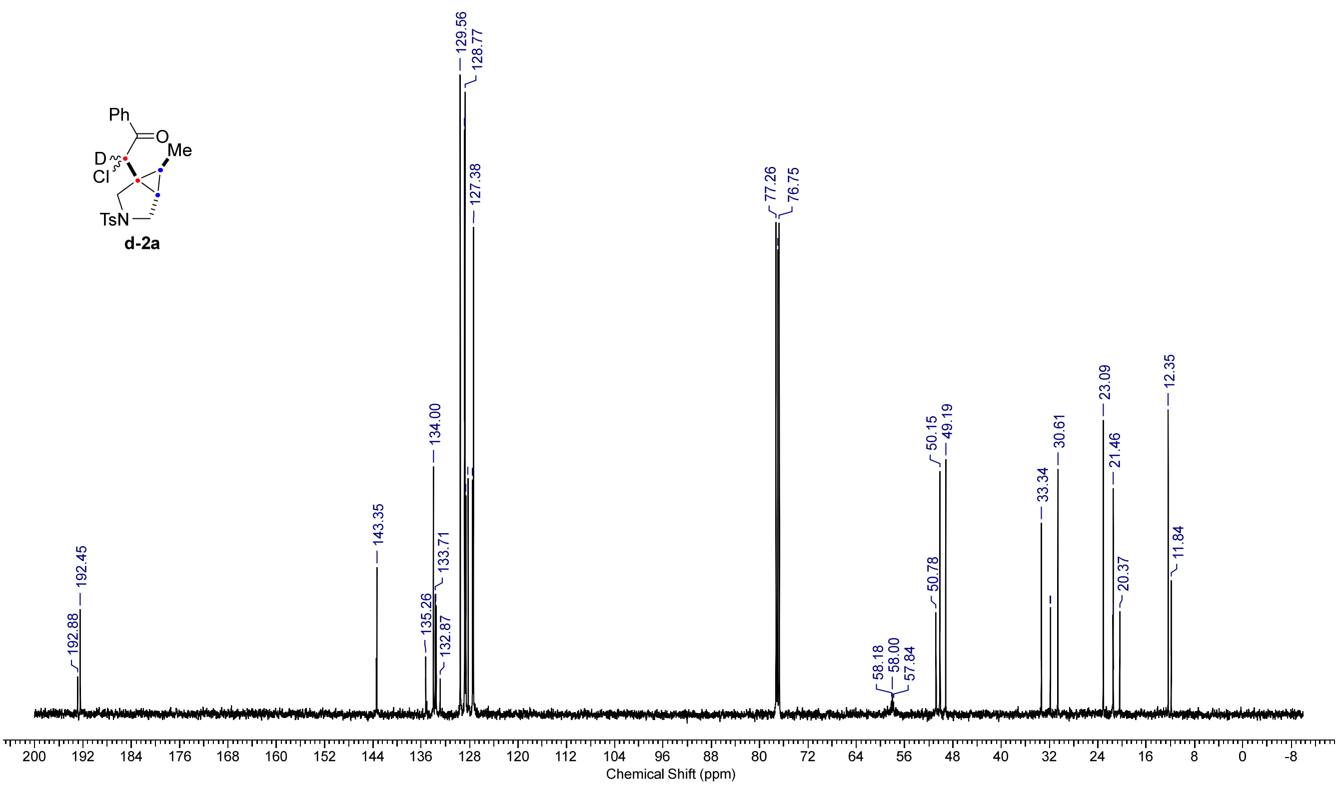
^{13}C NMR (125 MHz, $CDCl_3$) of **7**



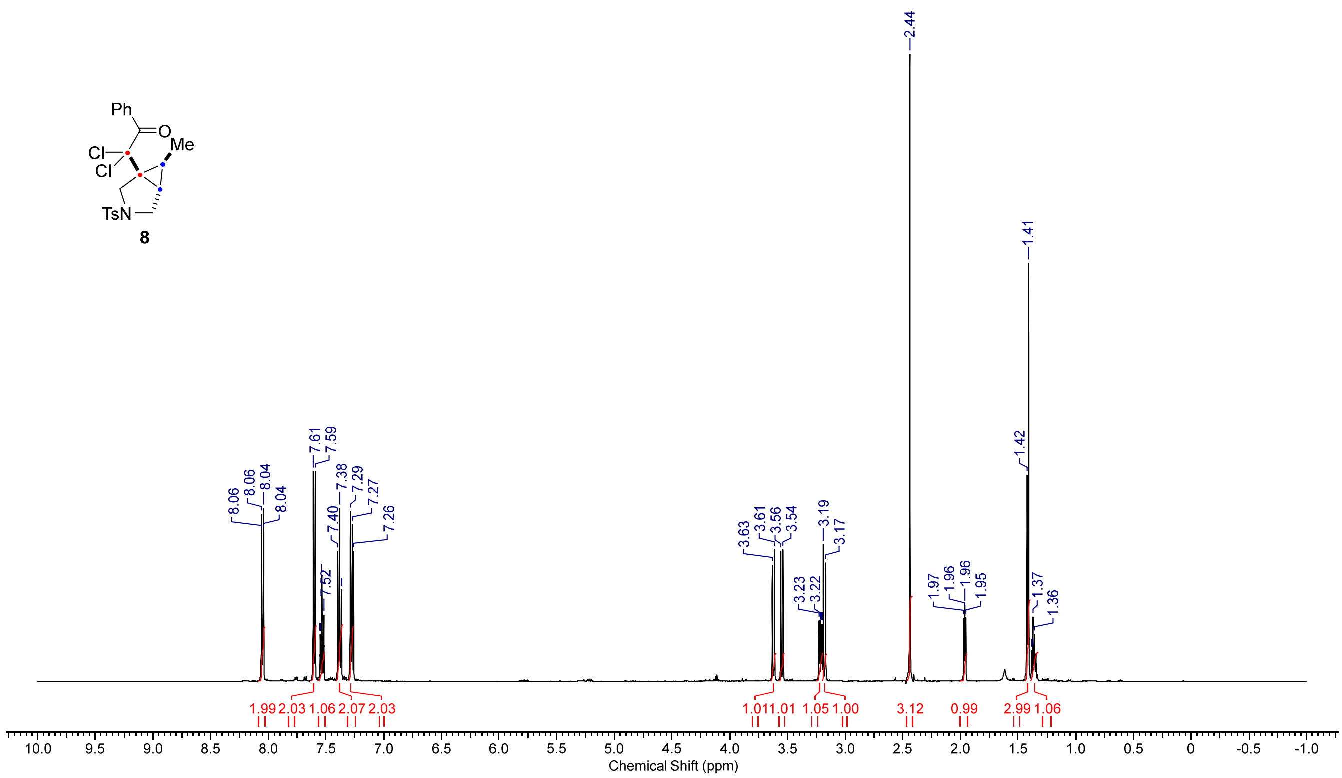
^{1}H NMR (500 MHz, $CDCl_3$) of **d-2a** (72:28 mixture of epimers)



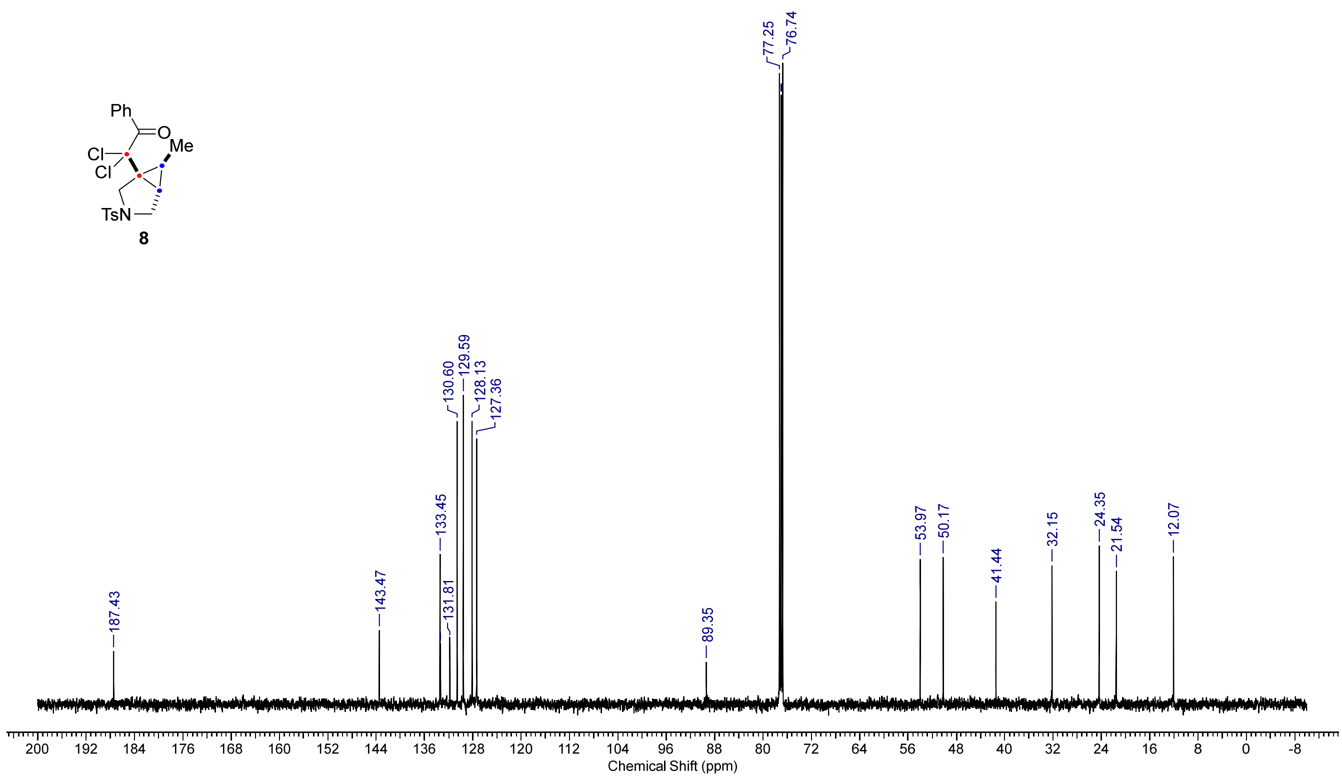
^{13}C NMR (125 MHz, $CDCl_3$) of **d-2a** (72:28 mixture of epimers)



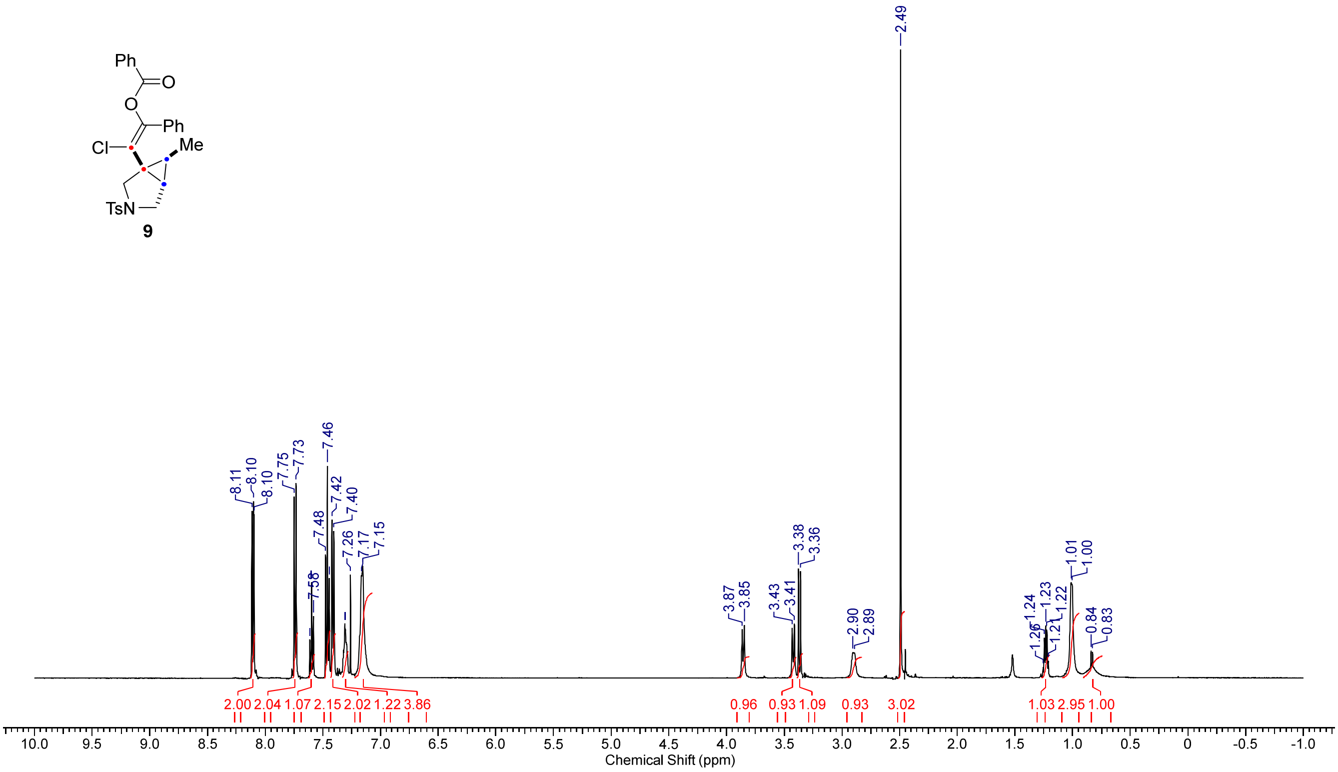
^{1}H NMR (500 MHz, $CDCl_3$) of **8**



^{13}C NMR (125 MHz, $CDCl_3$) of **8**



^{1}H NMR (500 MHz, $CDCl_3$) of **9**



^{13}C NMR (125 MHz, $CDCl_3$) of **9**