

Supporting Information

“Pt(II)/SnX₂ (X = Cl, Br)-Catalyzed Cyclization: Completely Different Reactivity of the Pt Complex toward 1,6-Haloenynes and 1,6-Enynes”

Min-Soo Jang, Xi Wang, Woo-Young Jang, Hye-Young Jang*

Division of Energy Systems Research

Ajou University

Suwon, 443-749

Korea

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Experimental Section

General. All reactions were run under an atmosphere of argon, unless otherwise indicated. Anhydrous solvents were transferred by an oven-dried syringe. Flasks were flame-dried and cooled under a stream of nitrogen. Dichloroethane was distilled from calcium hydride. Product **8b** and **9b** exhibited spectral properties consistent with previous literature reports.¹ The products were obtained as an inseparable mixture of *Z/E* isomers. The relative stereochemical assignments were made in analogous to those previously reported.²

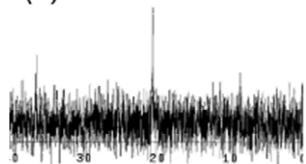
Representative Experimental Procedure for Cycloisomerization of haloenynes. To a premixed solution of Pt(II) (5 mol%), Phosphine (5 mol%), and SnBr₂ (25 mol%) under H₂ (1 atm) in dichloroethane (0.1 M) was added haloenynes under N₂ (1 atm) at room temperature. The resulting mixture was allowed to run at 80 °C until the starting material was completely consumed.

Representative Experimental Procedure for Cycloreduction of enynes. To a premixed solution of Pt(II) (5 mol%), Phosphine (5 mol%), and SnCl₂ (25 mol%), in dichloromethane (0.1 M) was added enynes under H₂ (1 atm) at room temperature. The resulting mixture was allowed to run at 40 °C until the starting material was completely consumed.

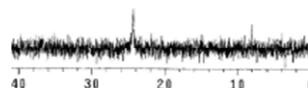
¹ Jang, H.-Y.; Krische, M. J. *J. Am. Chem. Soc.* **2004**, *126*, 7875.

² (a) Zhu, G.; Zhang, Z. *J. Org. Chem.* **2005**, *70*, 3339. (b) Cook G. R.; Hayashi, R. *Org. Lett.* **2006**, *8*, 1045.

(a)

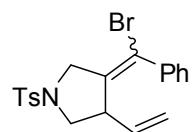


(b)



(a) ^{31}P NMR of $\text{P}(\text{Ph}-2,4,6-\text{OMe}_3)_3$ in CDCl_3 ; δ 20.7 ppm

(b) ^{31}P NMR of the CDCl_3 solution of PtBr_2 (1eq) and $\text{P}(\text{Ph}-2,4,6-\text{OMe}_3)_3$ (1eq) ; δ 24.3 ppm



3-(bromo(phenyl)methylene)-1-tosyl-4-vinylpyrrolidine (1b)

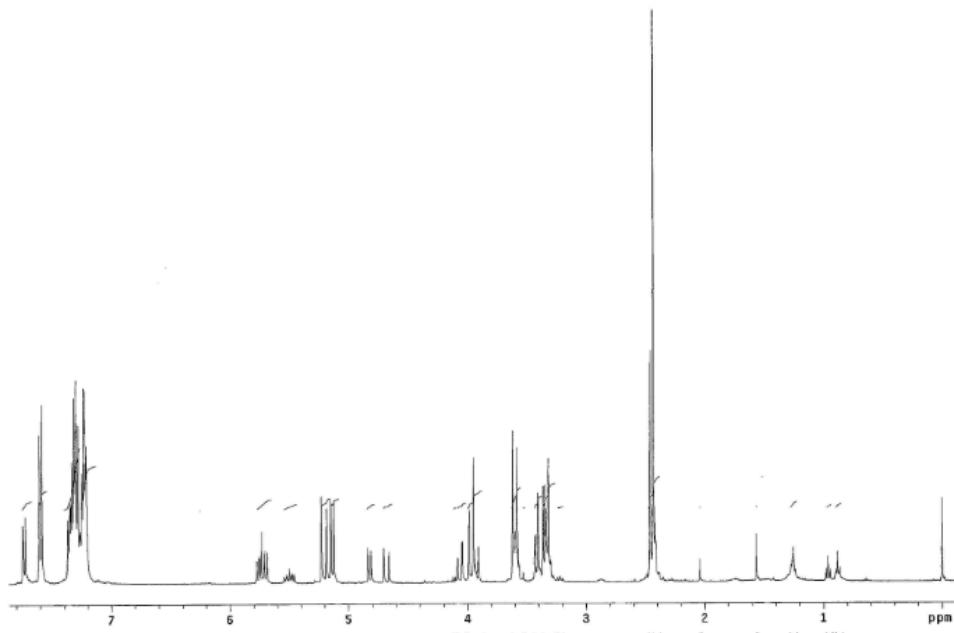
Z/E = 1:0.6

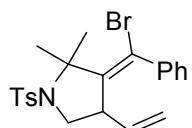
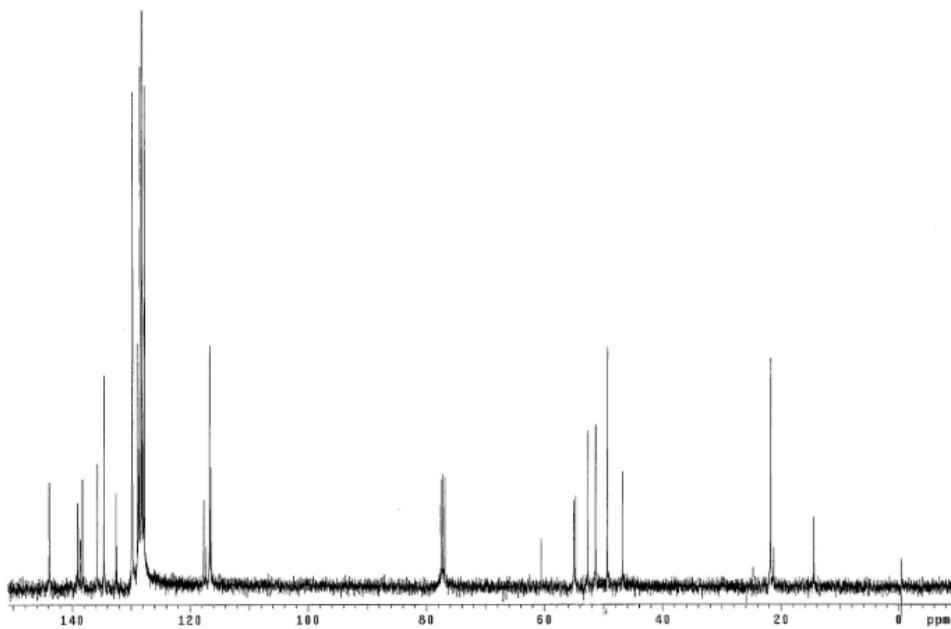
¹H-NMR (400 MHz, CDCl₃) : δ 7.73 (d, *J* = 8.4 Hz, 2×0.6H), 7.73 (d, *J* = 8 Hz, 2×0.4H), 7.37-7.20 (m, 7H), 5.57-5.68 (m, 1×0.6H), 5.51-5.47 (m, 1×0.4H), 5.21 (d, *J* = 16.4 Hz, 1×0.6H), 5.14 (d, *J* = 9.6 Hz, 1×0.6H), 4.82 (d, *J* = 10.0 Hz 1×0.4H), 4.68 (d, *J* = 17.2 Hz 1×0.4H), 4.01-3.90 (m, 2H), 3.06-3.58 (m, 1H), 3.43-3.29 (m, 2H), 2.46 (s, 3×0.6H), 2.43 (s, 3×0.4H)

¹³C-NMR (100 MHz, CDCl₃) : δ 143.9, 143.8, 139.1, 138.9, 138.6, 138.2, 135.6, 138.2, 135.6, 134.5, 132.5, 132.3, 129.8, 129.7, 128.9, 128.7, 128.5, 128.1, 127.9, 127.7, 117.6, 117.3, 116.6, 116.4, 60.5, 55.0, 54.7, 52.6, 51.3, 49.3, 46.7, 21.8, 14.4

HRMS : Calcd for C₂₀H₂₀BrNO₂S [M⁺] 418.3543, found. 418.3535.

IR(neat): 1017, 1047, 1093, 1162, 1265, 1348, 1443, 1597, 3057 cm⁻¹





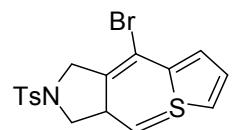
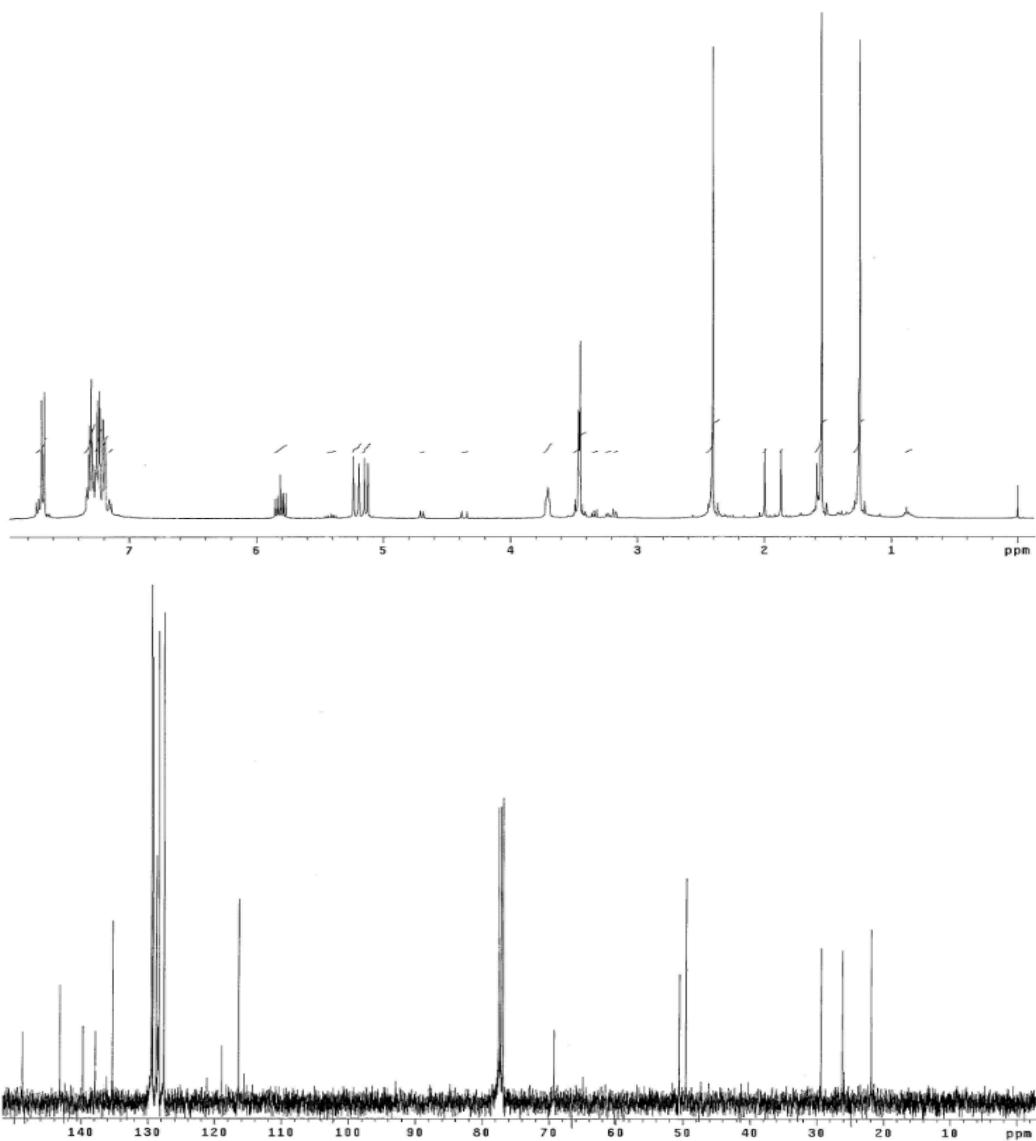
(Z)-3-(bromo(phenyl)methylene)-2,2-dimethyl-1-tosyl-4-vinylpyrrolidine (2b)

¹H-NMR (400 MHz, CDCl₃) : δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.24 (m, 7H), 5.81 (m, 1H), 5.22 (d, *J* = 16.8 Hz, 1H), 5.14 (d, *J* = 10.4 Hz, 1H), 3.70 (m, 1H), 3.46 (m, 2H), 2.41 (s, 3H), 1.55 (s, 3H), 1.25 (s, 3H)

¹³C-NMR (100 MHz, CDCl₃) : δ 148.8, 143.2, 139.7, 137.8, 135.2, 129.4, 129.2, 128.7, 128.5, 128.5, 128.4, 127.6, 118.9, 116.4, 69.2, 50.5, 49.5, 29.4, 26.2, 25.9, 21.8

HRMS : Calcd for C₂₂H₂₄BrNO₂S [M⁺] 446.0789, found 446.0791.

IR(neat): 1091, 1160, 1265, 1336, 1442, 1598, 1711, 2874, 2986, 3054cm⁻¹



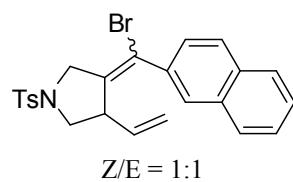
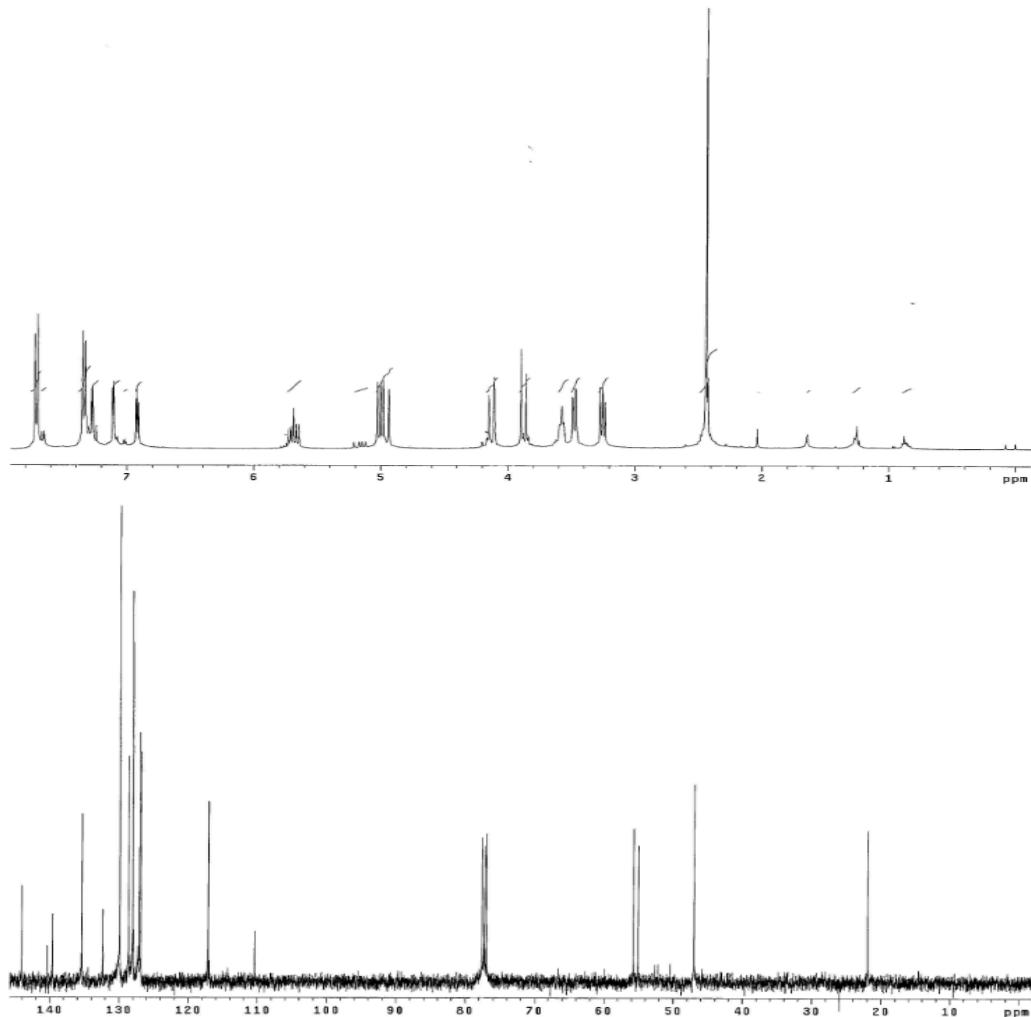
(Z)-3-(bromo(thiophen-2-yl)methylene)-1-tosyl-4-vinylpyrrolidine (3b)

¹H-NMR (400 MHz, CDCl₃) : δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.8 Hz, 2H), 7.27 (d, *J* = 5.2 Hz, 1H), 7.11 (d, *J* = 3.6 Hz, 1H), 6.92 (t, *J* = 3.6 Hz, 1H), 5.69 (m, 1H), 5.02 (d, *J* = 10.4 Hz, 1H), 4.96 (d, *J* = 17.2 Hz, 1H), 4.13 (d, *J* = 15.6 Hz, 1H), 3.88 (d, *J* = 15.6 Hz, 1H), 3.59 (m, 1H), 3.48 (dd, *J* = 11.2, 2.0 Hz, 1H), 3.25 (dd, *J* = 9.2, 6.0 Hz, 1H), 2.44 (s, 3H)

¹³C-NMR (100 MHz, CDCl₃) : δ 144.0, 140.3, 139.6, 135.4, 132.3, 129.9, 128.6, 128.5, 128.0, 127.9, 127.2, 127.0, 126.8, 117.1, 110.4, 55.7, 55.0, 47.0, 26.0, 22.0

HRMS : Calcd for C₁₈H₁₈BrNO₂S₂[M⁺] 424.0041, found 424.0038.

IR(neat): 1050, 1161, 1265, 1347, 1423, 1447, 2856, 2925, 3081cm⁻¹



3-(bromo(naphthalen-2-yl)methylene)-1-tosyl-4-vinylpyrrolidine (4b)

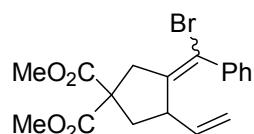
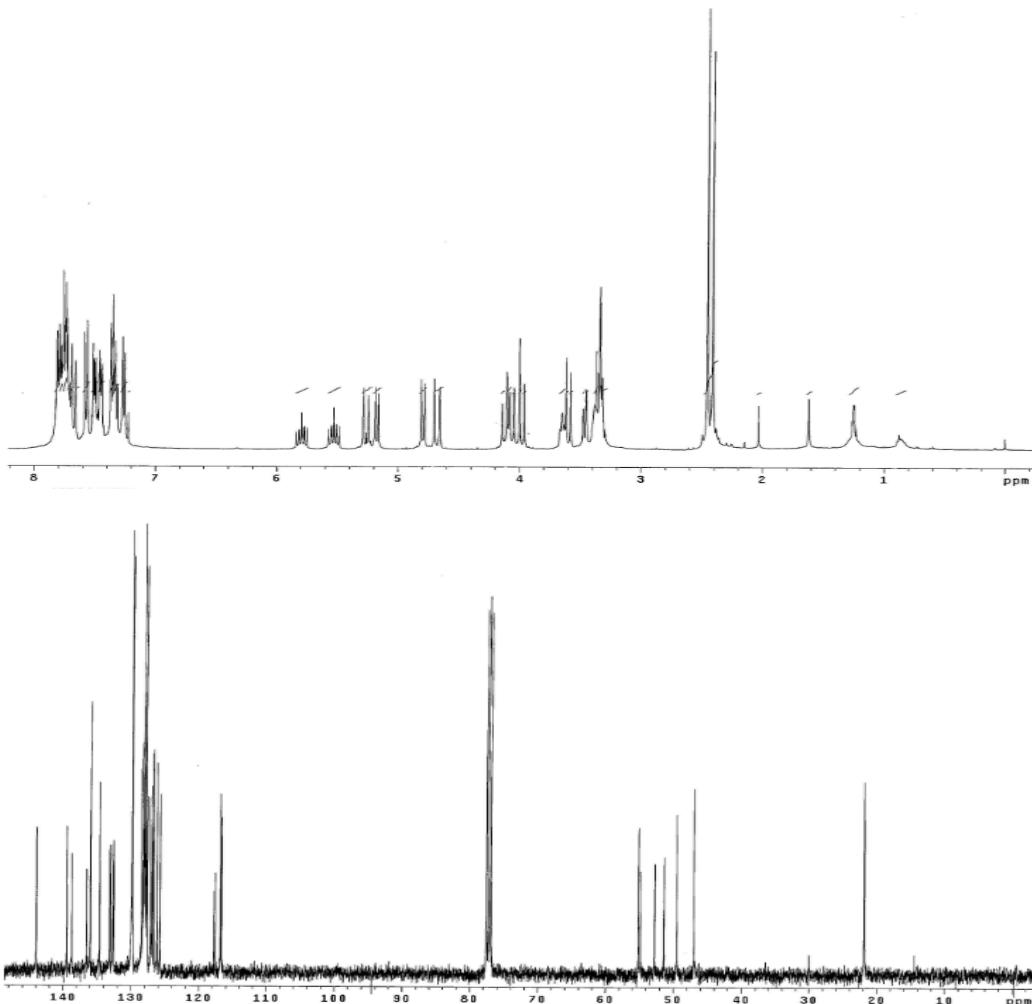
¹H-NMR (400 MHz, CDCl₃) : δ 7.82-7.66 (m, 5H), 7.57 (d, *J* = 8.0Hz, 1H), 7.52-7.43 (m, 2H), 7.36-7.31 (m, 2H), 7.26 (d, *J* = 8.0 Hz, 1H), 5.83-5.75 (m, 1×0.5H), 5.57-5.48 (m, 1×0.5H), 5.27 (d, *J* = 17.2 Hz 1×0.5H), 5.18 (d, *J* = 10.4 Hz 1×0.5H), 4.80 (d, *J* = 10.4 Hz 1×0.5H), 4.68 (d, *J* = 17.2 Hz 1×0.5H), 4.41-3.96 (m, 2H), 3.66-3.58 (m, 1H), 3.48-3.29 (m, 2H), 2.45 (s, 3×0.5H), 2.41 (s, 3×0.5H)

¹³C-NMR (100 MHz, CDCl₃) : δ 143.9, 139.4, 138.7, 136.5, 135.9, 134.6, 133.1, 133.0, 132.7, 132.6,

132.5, 129.9, 129.8, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.1, 126.9, 126.8, 126.6, 126.1, 125.7, 117.7, 117.5, 116.7, 116.6, 55.1, 54.8, 52.7, 51.4, 49.5, 47.0, 21.9, 21.8

HRMS : Calcd for C₂₄H₂₂BrNO₂S [M⁺] 468.0633, found 468.0634.

IR(neat): 1047, 1092, 1161, 1270, 1450, 1596, 1637, 3058, 3418 cm⁻¹



dimethyl 3-(bromo(phenyl)methylene)-4-vinylcyclopentane-1,1-dicarboxylate (5b)

Z/E = 1:1

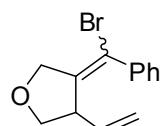
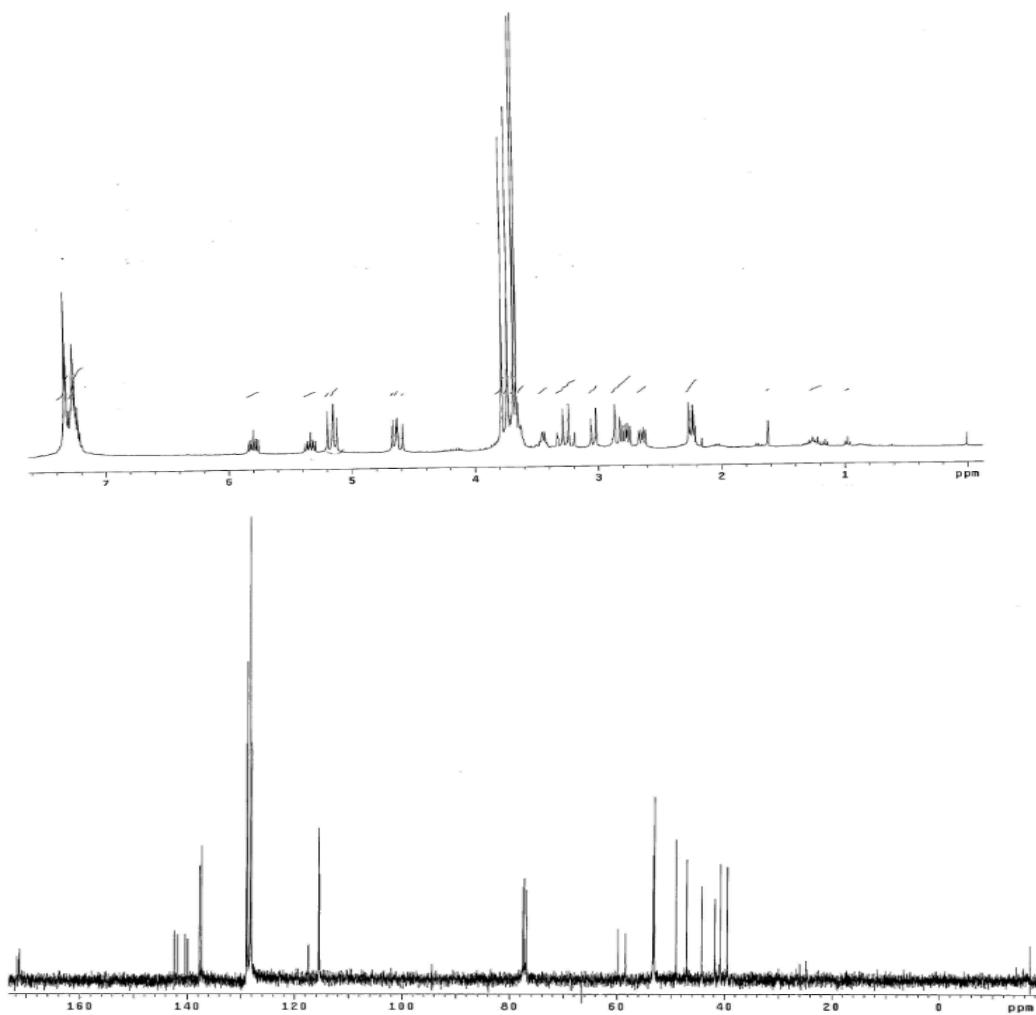
¹H-NMR (400 MHz, CDCl₃) : δ 7.34-7.19 (m, 5H), 5.84-5.75 (m, 1×0.5H), 5.37-5.29 (m, 1×0.5H), 5.15 (m, 2×0.5H), 4.65 (d, *J* = 11.6 Hz 1×0.5H), 4.60 (d, *J* = 17.6 Hz 1×0.5H), 3.78 (s, 3×0.5H), 3.73 (s,

3×0.5H), 3.68 (s, 3×0.5H), 3.66 (s, 3×0.5H), 3.47-3.41 (m, 1×0.5H), 3.33-3.19 (m, 1H), 3.05-2.96 (m, 1×0.5H), 2.88-2.61 (m, 2H), 2.63-2.21 (m, 1H)

¹³C-NMR (100 MHz, CDCl₃) : δ 171.7, 171.4, 171.2, 142.3, 141.8, 140.4, 139.8, 137.6, 137.3, 128.9, 128.8, 128.2, 127.9, 117.5, 117.3, 115.5, 115.4, 59.7, 58.3, 53.2, 53.0, 48.9, 46.9, 44.1, 41.7, 40.7, 39.4

HRMS : Calcd for C₁₈H₁₉BrO₄ [M⁺] 379.0545, found 379.0547.

IR(neat): 1733, 2942, 2989, 3051 cm⁻¹



3-(bromo(phenyl)methylene)-4-vinyltetrahydrofuran (6b)

Z/E = 1:0.7

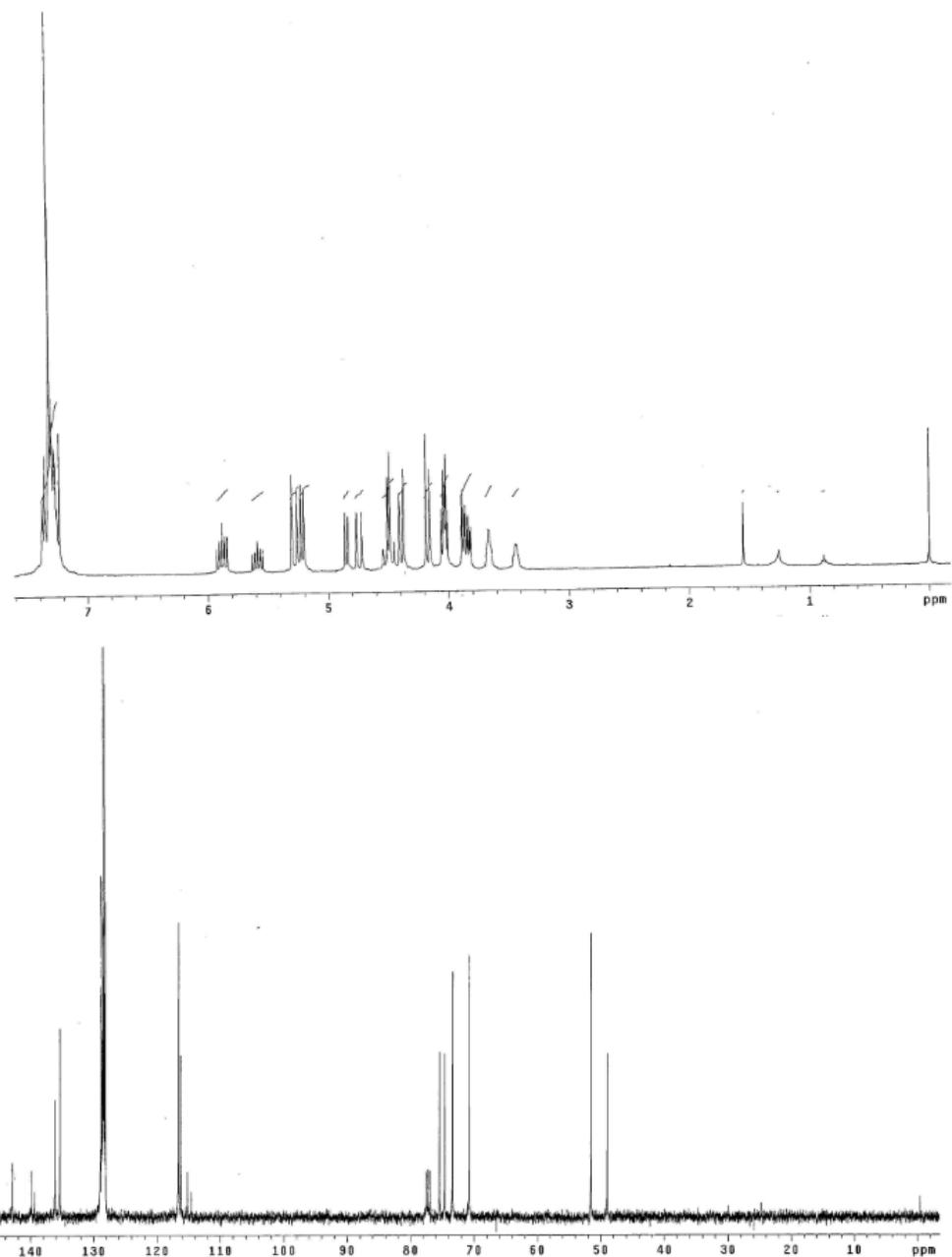
¹H-NMR (400 MHz, CDCl₃) : δ 7.37-7.23 (m, 5H), 5.92-5.83 (m, 1×0.6H), 5.63-5.54 (m, 1×0.4H), 5.28

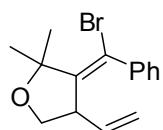
(d, $J = 16.8$ Hz 1×0.6H), 5.21 (d, $J = 12.4$ Hz 1×0.6H), 4.85 (d, $J = 12.0$ Hz 1×0.4H), 4.74 (d, $J = 16.0$ Hz 1×0.4H), 4.49 (m, 1H), 4.39 (d, $J = 13.6$ Hz 1×0.6H), 4.17 (d, $J = 13.2$ Hz 1×0.6H), 4.05-4.00 (m, 1H), 3.89-3.81 (m, 2×0.4H), 3.67-3.65 (m, 1×0.6H), 3.45-3.42 (m, 1×0.4H)

¹³C-NMR (100 MHz, CDCl₃) : δ 142.8, 139.7, 139.2, 136.0, 135.3, 128.7, 128.6, 128.4, 128.3, 128.2, 128.0, 116.5, 116.2, 115.1, 114.5, 75.4, 74.6, 73.3, 70.7, 51.4, 48.9

HRMS : Calcd for C₁₃H₁₁BrO [M-2]⁺ 263.0072, found 263.0074.

IR(neat): 1443, 1419, 1597, 1636, 2852, 2976, 3079 cm⁻¹





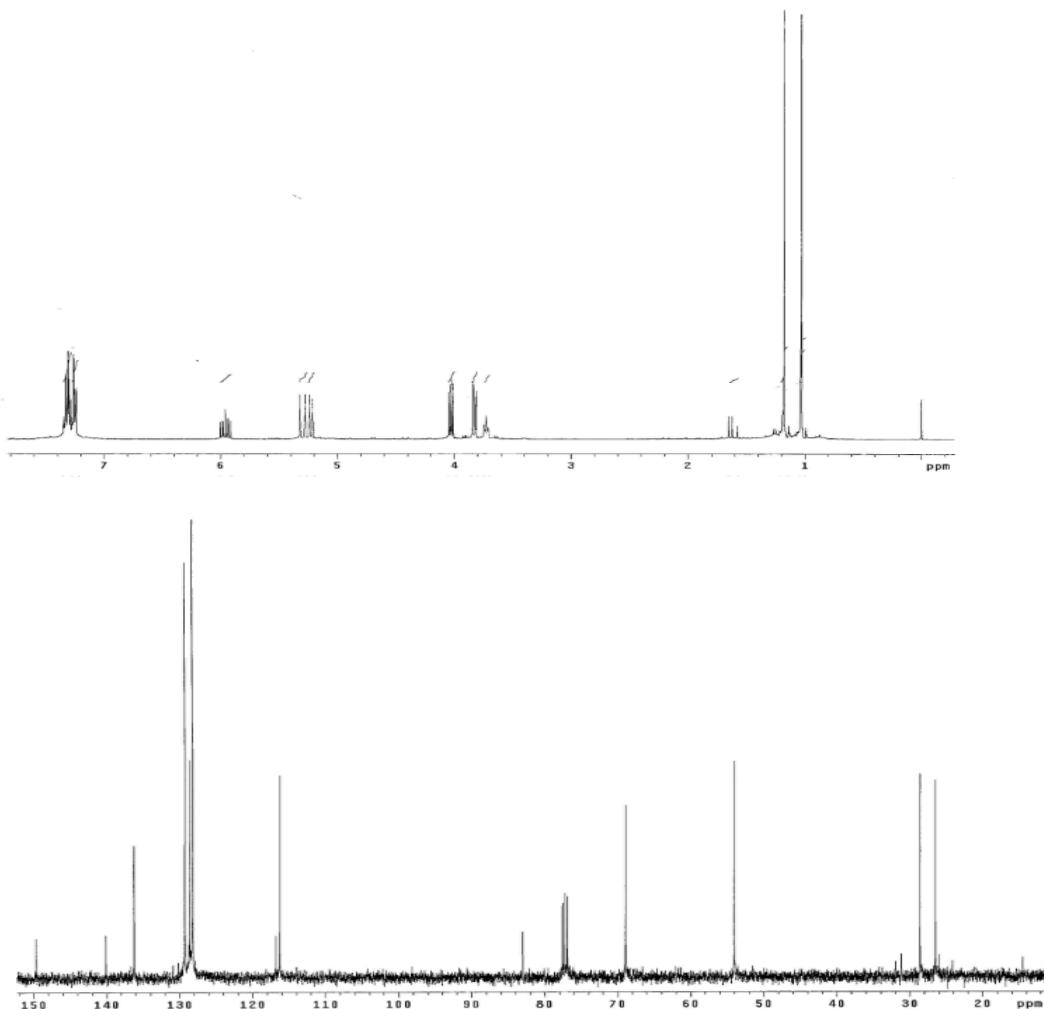
(Z)-3-(bromo(phenyl)methylene)-2,2-dimethyl-4-vinyltetrahydrofuran (7b)

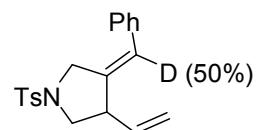
¹H-NMR (400 MHz, CDCl₃) : δ 7.25 (m, 5H), 5.96 (m, 1H), 5.30 (d, *J* = 17.2 Hz, 1H), 5.22 (d, *J* = 10.0 Hz, 1H), 4.03 (dd, *J* = 9.2, 6.0 Hz, 1H), 3.83 (dd, *J* = 8.8, 6.8 Hz, 1H), 3.73 (m, 1H), 1.18 (s, 3H), 1.04 (s, 3H)

¹³C-NMR (100 MHz, CDCl₃) : δ 149.7, 140.1, 136.2, 129.3, 128.7, 128.6, 128.2, 116.8, 116.3, 83.0, 69.0, 54.0, 31.9, 31.2, 28.6, 26.5, 26.0, 24.1

HRMS : Calcd for C₁₅H₁₇BrO [M]⁺ 293.0541, found 293.0545.

IR(neat): 1053, 1149, 1265, 1362, 1443, 1636, 1659, 1713, 2864, 2932, 2977, 3054, 3081 cm⁻¹





Deutero-9b

¹H-NMR (400 MHz, CDCl₃) : δ 7.70 (m, 2H), 7.20 (m, 7H), 6.17 (d, *J* = 2.8 Hz, 0.5H), 5.56 (m, 1H), 5.18 (m, 2H), 4.30 (d, *J* = 13.6 Hz, 1H), 3.98 (d, *J* = 13.8 Hz, 1H), 3.63 (dd, *J* = 8.0, 9.2 Hz, 1H), 3.42 (m, 1H), 2.84(dd, *J*= 9.2 Hz, 1H) 2.40 (s, 3H).

