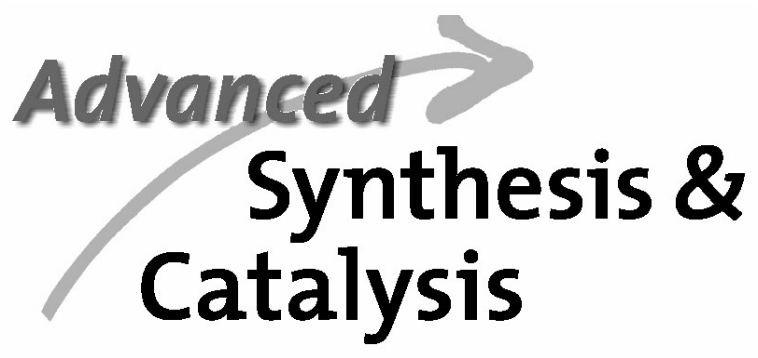

Supporting Information

Supporting Information

Gold(I)- and Acid-Catalyzed Intermolecular Ring-Opening of Unactivated Vinylcyclopropanes with Sulfonamide

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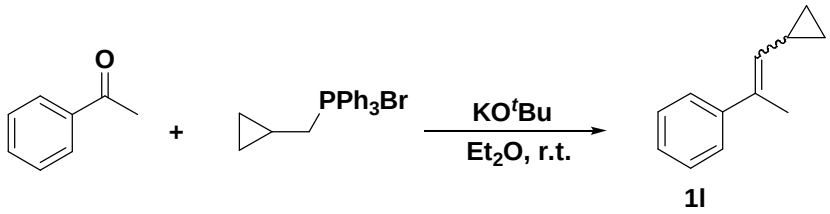
General remarks.

All reactions and manipulation were performed using standard Schlenk techniques under an Ar atmosphere. All solvents were distilled prior to use. Gold complexes $AuCl(PPh_3)$, $AuCl(PEt_3)$ and $AuCl_3$ were commercial products. Other gold(I) complexes were prepared by treating one equiv of $AuCl(SMe_2)$ with the corresponding phosphine ligands in DCM at room temperature, and $AuCl(SMe_2)$ was synthesized according to the reported procedure.[1] All unactivated VCPs **1** were prepared from the corresponding ketones by using Wittig reaction, unless otherwise stated.[2] $TsND_2$ was prepared as reported.[3] ^{1}H and ^{13}C NMR spectra were recorded on Bruker AVANCE spectrometers DPX 200, DPX 250, DPX 300, and DPX 700. HRMS was performed by the MS-Service of the Laboratory of Organic Chemistry, ETH Zurich.

1. General procedure for the synthesis of new substrates (General procedure A).

b-Methyl-b-phenyl vinylcyclopropane (1l)

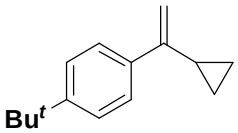


1l

To a mixture of cyclopropylmethyl triphenylphosphonium bromide (3.0 g, 7.5 mmol) and acetophenone (600 mg, 5.0 mmol) in 20 mL of ether, KO^{t}Bu (842 mg, 7.5 mmol) was added in one portion at room temperature under an Ar atmosphere. The suspension was stirred overnight, filtered, concentrated and purified by silica gel chromatography using *n*-hexane as eluent to afford 640 mg of colorless liquid **1l** (80 % yield).

^{1}H NMR (300 MHz, $CDCl_3$): 7.51-7.30 (m, 5H, Ar-*H*), 5.31 (dd, *J* = 1.2 Hz, *J* = 9.3 Hz, 0.18H, C*H*, minor), 4.97 (dd, *J* = 1.2 Hz, *J* = 9.6 Hz, 0.82H, C*H*, major), 2.28 (d, *J* = 1.2 Hz, 0.54H, CH_3, minor), 2.15 (d, *J* = 1.5 Hz, 2.46H, CH_3, major), 1.80-1.72 (m, 0.18H, C*H*, minor), 1.64-1.52 (m, 0.82H, C*H*, major), 0.98-0.92 (spt, 0.36H, CH_2, minor), 0.80-0.71 (spt, 1.64H, CH_2, major), 0.59-0.54 (m, 0.36H, CH_2, minor), 0.51-0.46 (m, 1.64H, CH_2, major). ^{13}C NMR (75.5 MHz, $CDCl_3$): 143.8, 142.3, 134.3, 133.3, 132.7, 131.9, 128.3, 128.2, 128.1, 126.5, 126.4, 125.4, 25.1, 16.1, 11.3, 7.4. HRMS (EI) Calcd for $C_{12}H_{16}$: 158.1090. Found: 158.1089.

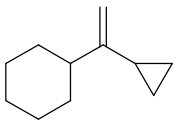
a-(4-*tert*-Butyl)phenyl vinylcyclopropane (1c)



According to **General procedure A**, α-(4-*tert*-butyl)-phenyl vinylcyclopropane **1c** was obtained from the corresponding ketone. Colorless liquid, 96% yield.

^{1}H NMR (300 MHz, $CDCl_3$): d 7.69 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 7.50 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 5.41 (s, 1H, C*H*), 5.03 (s, 1H, C*H*), 1.83-1.74 (spt, 1H, C*H*), 1.47 (s, 9H, CH_3), 0.98-0.92 (spt, 2H, CH_2), 0.75-0.70 (m, 2H, CH_2). ^{13}C NMR (75.5 MHz, $CDCl_3$): d 150.5, 149.1, 125.8, 125.1, 108.4, 34.6, 31.5, 15.7, 6.7.HRMS (EI) Calcd for $C_{15}H_{20}$: 200.1560. Found: 200.1562.

a-Cyclohexyl vinylcyclopropane (1m)



According to **General procedure A**, α-cyclohexyl vinylcyclopropane **1m** was obtained from the corresponding ketone. Colorless liquid, 50% yield.

^{1}H NMR (300 MHz, $CDCl_3$): 4.62 (s, 1H, C*H*), 4.52 (s, 1H, C*H*), 2.01-1.70 (m, 6H), 1.39-1.17 (m, 6H), 0.68-0.62 (spt, 2H, CH_2), 0.45-0.40 (m, 2H, CH_2). ^{13}C NMR (75.5 MHz,

$CDCl_3$): 156.8, 104.5, 45.3, 32.7, 26.8, 26.4, 14.8, 6.4. HRMS (EI) Calcd for $C_{11}H_{18}$: 150.1403. Found: 150.1404.

2. General procedure for the gold(I) or HOTf catalyzed intermolecular ring-opening of unactivated VCPs 1 with sulfonamides (General procedure B).

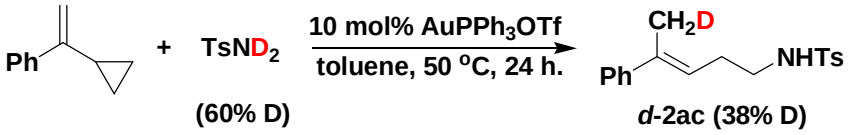
For Gold(I)-catalyzed ring-opening reaction:

To a suspension of $AuPPh_3OTf$, prepared *in situ* from $AuCl(PPh_3)$ (10.0 mg, 0.02 mmol) and AgOTf (5.6 mg, 0.02 mmol) in 2 mL of toluene, TsNHMe was added (39 mg, 0.2 mmol), followed by α-phenyl vinylcyclopropane **1a** (88 mg, 0.6 mmol). The resulting mixture was stirred for 24 h at 50 ^oC. Then, the reaction mixture was cooled to room temperature, evaporated under vacuum, and the residue was purified by silica gel column chromatography (eluent: EtOAc/petroleum ether = 1/3) to afford the product **2ae** (63 mg, 97% yield) as colorless liquid.

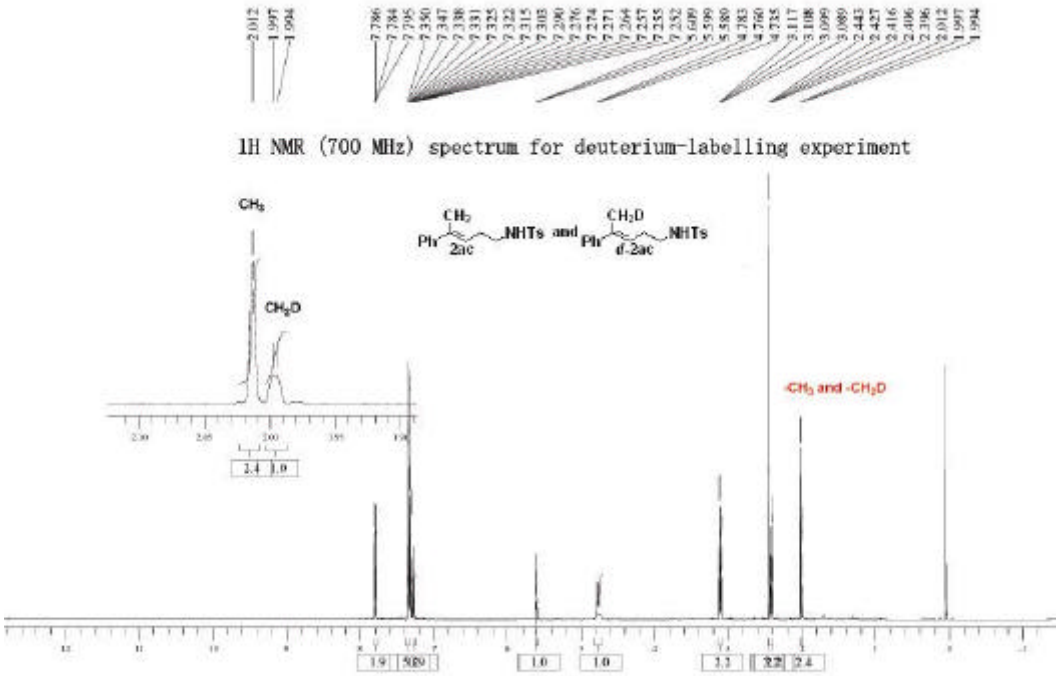
For HOTf catalyzed ring-opening reaction:

To the solution of α-phenyl vinylcyclopropane **1a** (88 mg, 0.6 mmol) and TsNHMe (39 mg, 0.2 mmol) in 2 mL toluene at 50 ^oC, HOTf (3.0 mg, 0.02 mmol) was added using Micro-syringe. The resulted solution was stirred for 24 h. Then, the reaction mixture was cooled to room temperature, evaporated and purified by silica gel column chromatography (eluent: EtOAc/petroleum ether = 1/3) to afford the product **2ae** (60 mg, 92% yield) as colorless liquid.

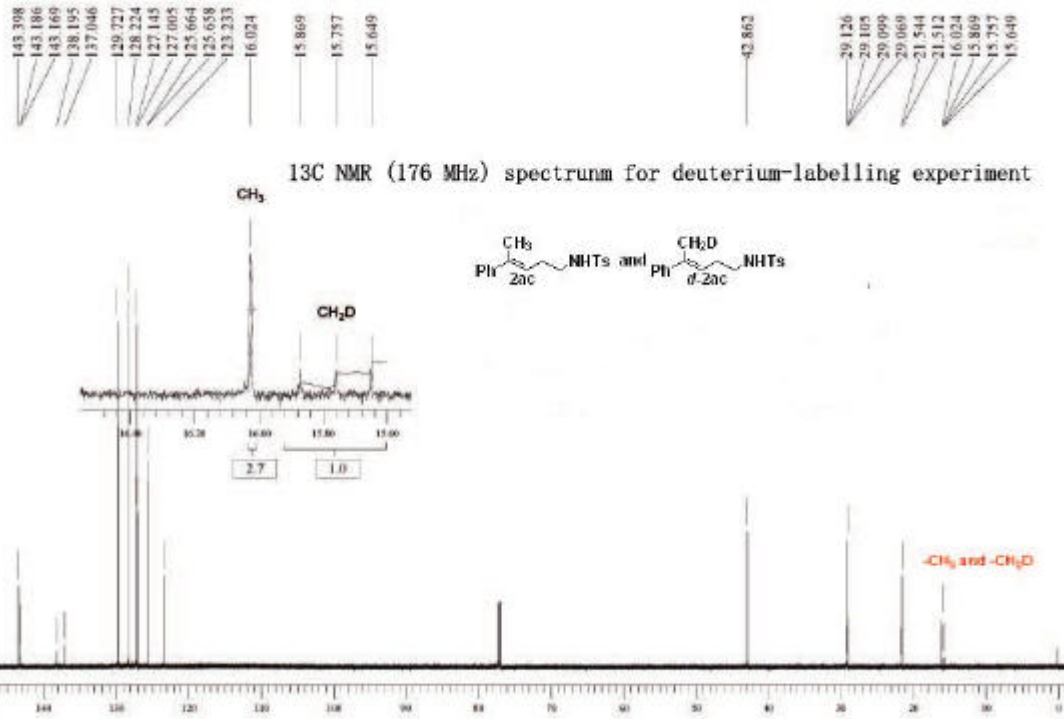
3. Deuterium labelling experiment with $TsND_2$. [4]



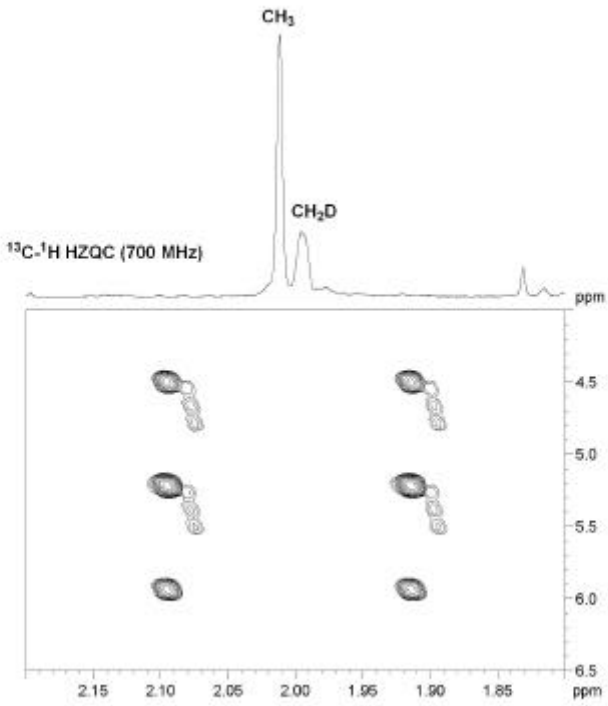
By adopting $AuPPh_3OTf$ as catalyst, the experiment with $TsND_2$ (60% deuterium, 40 mg, 0.2 mmol) and α-phenyl vinylcyclopropane **1a** (88 mg, 0.6 mmol) was carried out according to the above **General procedure B,** yielding 25 mg (40% yield) of the product *d*-**2ac** as colorless liquid and with a deuterium content of 38% at the methyl group exclusively, as shown in the equation. The deuterium incorporation of the products was analyzed by ^1H (700 MHz), ^{13}C NMR (176.0 MHz) and ^{13}C-^1H HZQC NMR spectroscopy.

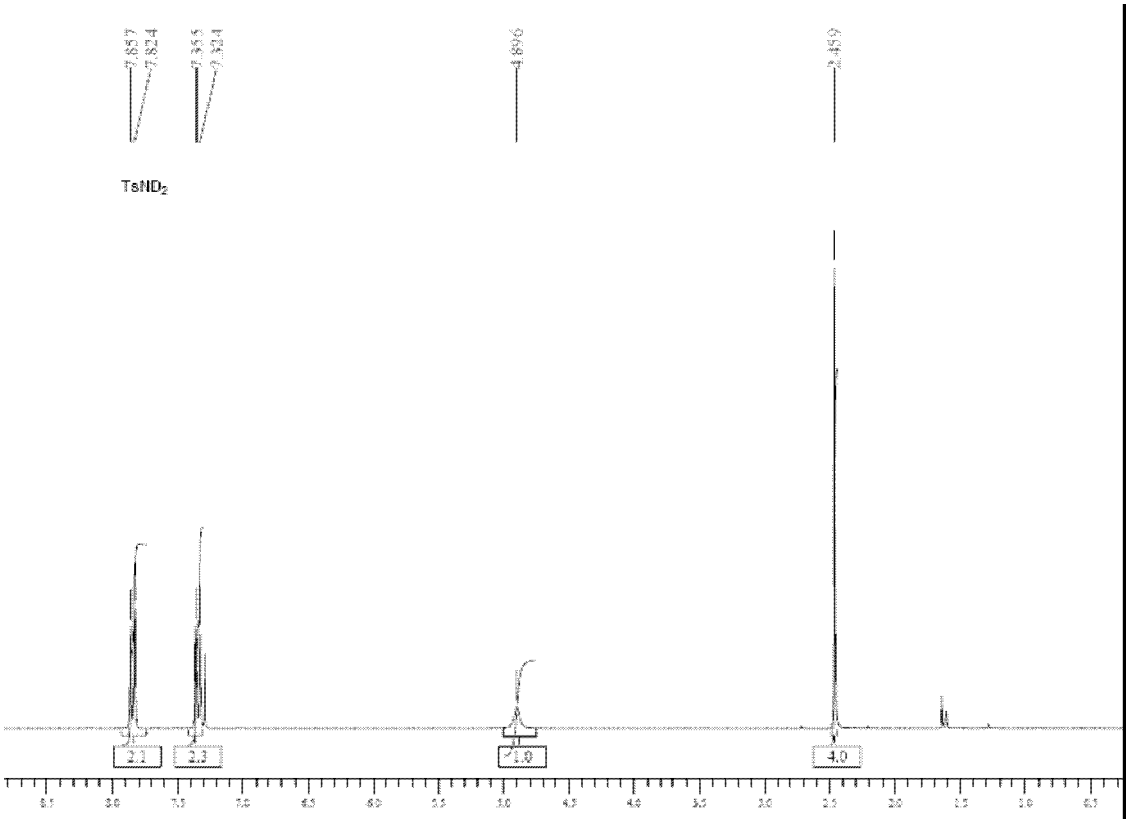


1H NMR (700 MHz) spectrum for deuterium-labelling experiment



13C NMR (176 MHz) spectrunm for deuterium-labelling experiment


CH3
CH2D
13C-1H HZQC (700 MHz)
ppm
4.5
5.0
5.5
6.0
6.5
2.15
2.10
2.05
2.00
1.95
1.90
1.85
ppm


7.857
7.824
7.355
7.334
1.896
2.459
TsND2
2.1
2.3
1.0
4.0

4. General procedure for competition experiments (Hammett study). [5]

Using PPh_3AuOTf as catalyst:

To a suspension of $AuPPh_3OTf$, prepared *in situ* from $AuCl(PPh_3)$ (10.0 mg, 0.02 mmol) and AgOTf (5.6 mg, 0.02 mmol) in 2 mL toluene, TsNHMe was added (39 mg, 0.2 mmol), followed by α-phenyl vinylcyclopropane **1a** (88 mg, 0.6 mmol) and α-(4-chloro)-phenyl vinylcyclopropane **1d** (108 mg, 0.6 mmol), and then the resulted mixture was stirred for 24 h at 50 ^oC. Then, the reaction mixture was cooled to room temperature, evaporated under vacuum, and the residue was purified by silica gel column chromatography (eluent: EtOAc/petroleum ether = 1/3) to afford a mixture of **2ae** and **2da** (61 mg) as colorless liquid. The ratio of the two products (1.0: 2.1) was determined by ^1H NMR (700 MHz) spectroscopy by integration of the methyl signal and corresponds to $\boldsymbol{K_{rel} = k_R/k_H}$. Data are shown in Table 1.

Table 1. Data of the Hammett study using PPh_3AuOTf as catalyst

entry	R	s_p of R	$k_{rel} = k_R/k_H$	$\log k_{rel}$
1	CF_3	0.54	1/15.6	-1.19
2	Cl	0.23	1.0/2.1	-0.32
3	F	0.06	1.0/1.3	-0.12
4	H	0	1.0	0
5	Me	-0.14	2.2/1	0.34
6	^{t}Bu	-0.2	2.6/1.0	0.41

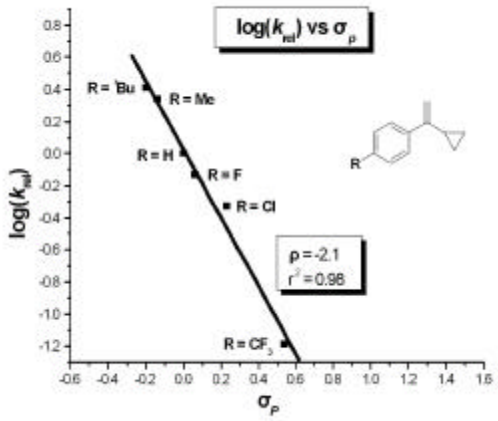
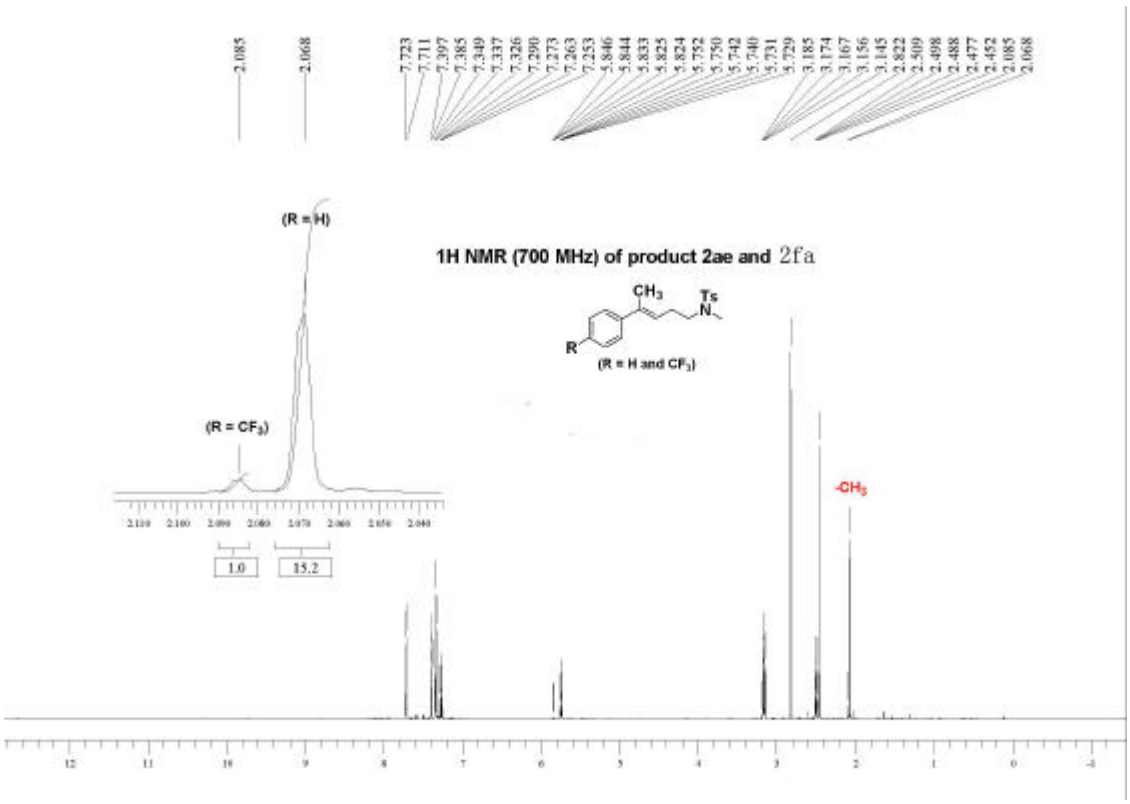
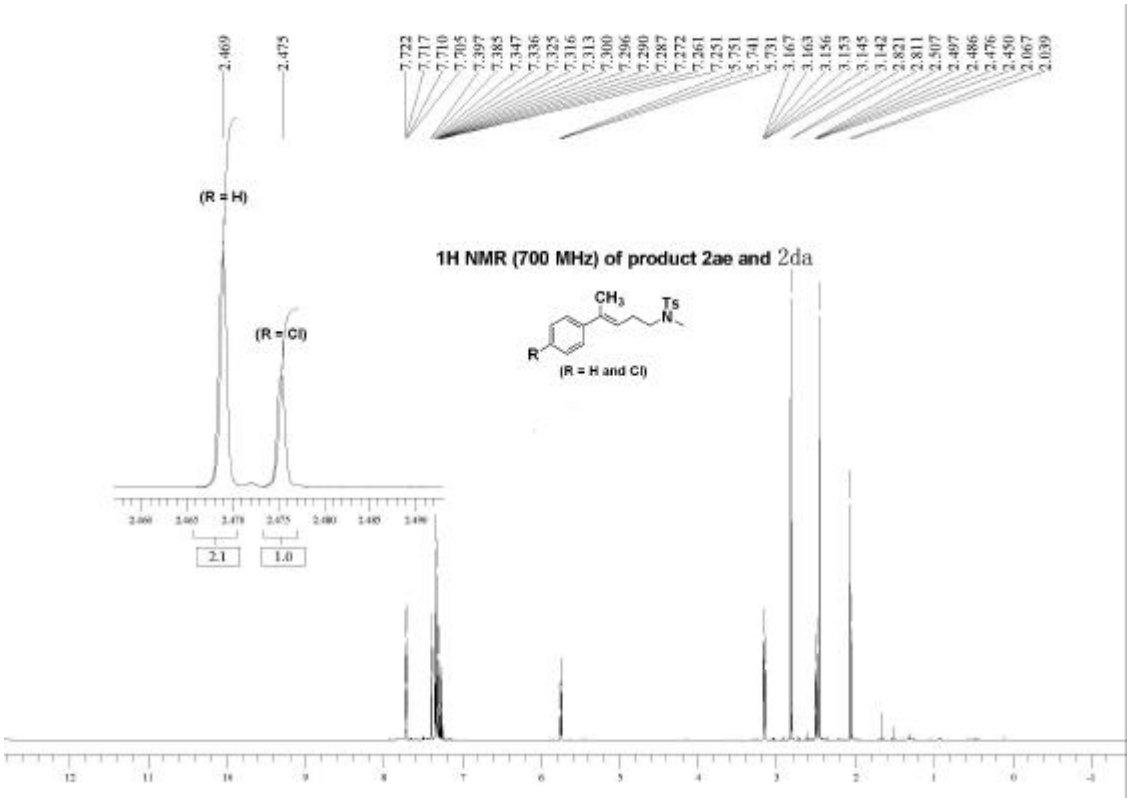
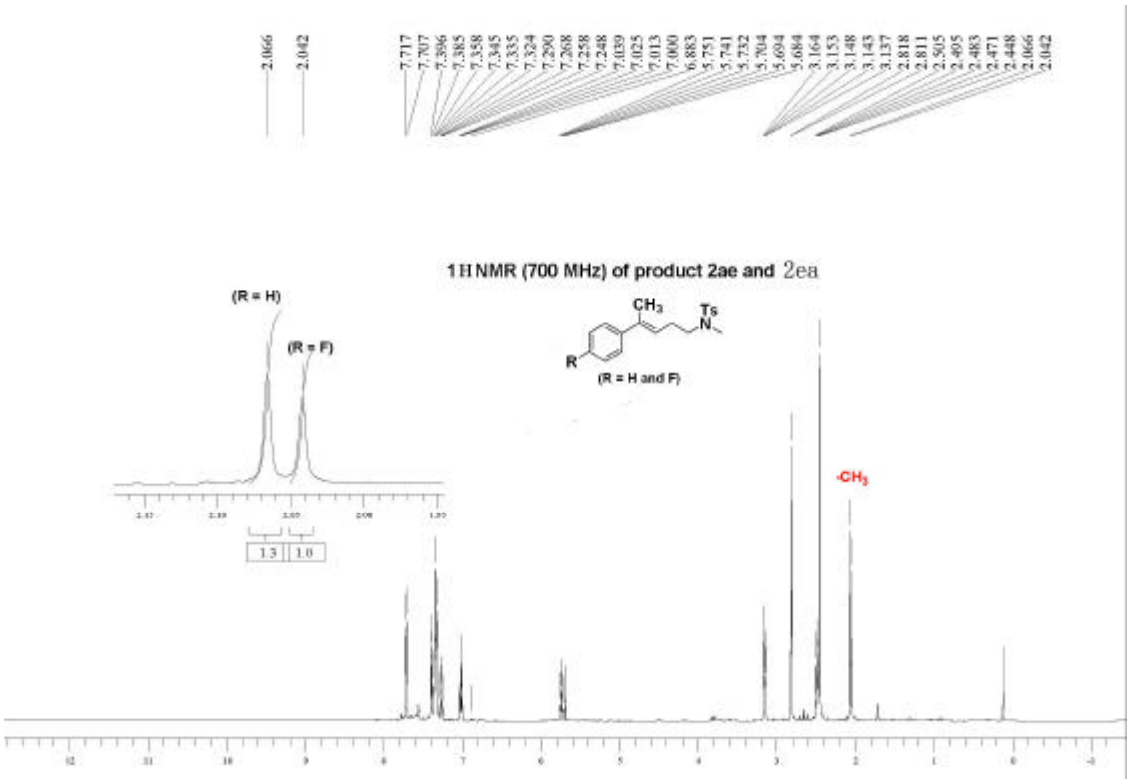


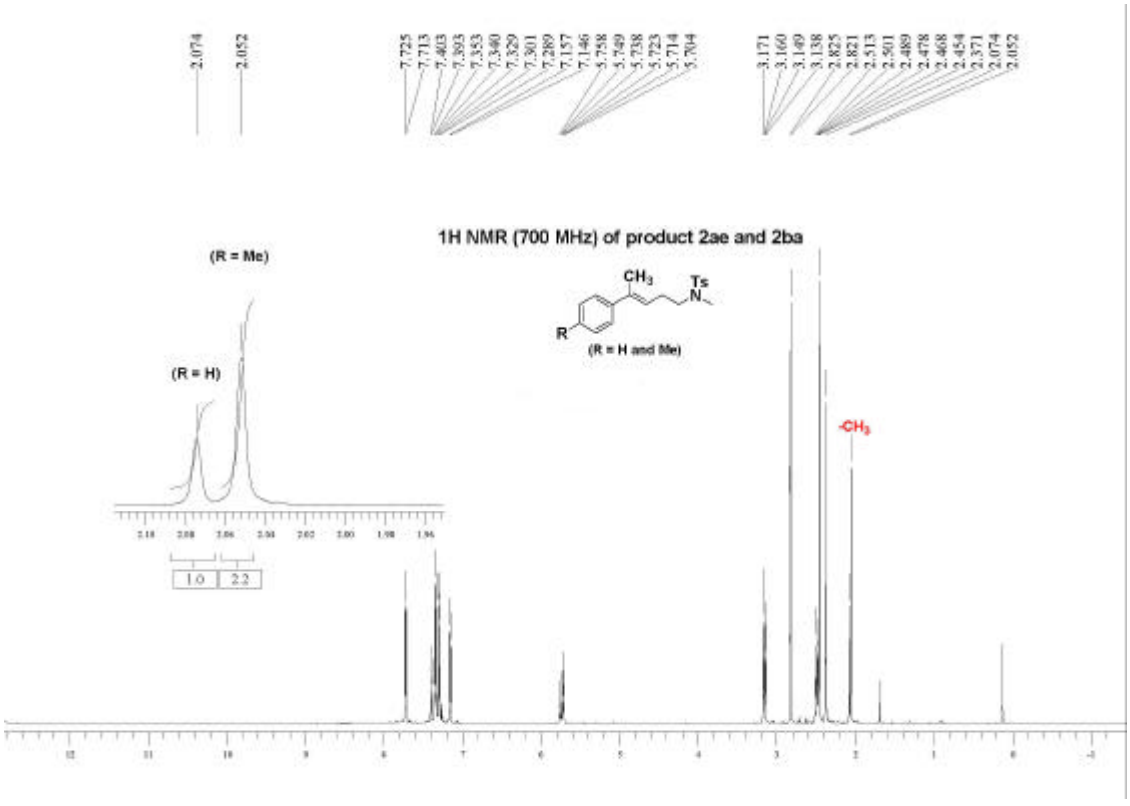
Figure 1. Hammett plot of ring-opening of **1a-f** with TsNHMe using PPh_3AuOTf as catalyst.

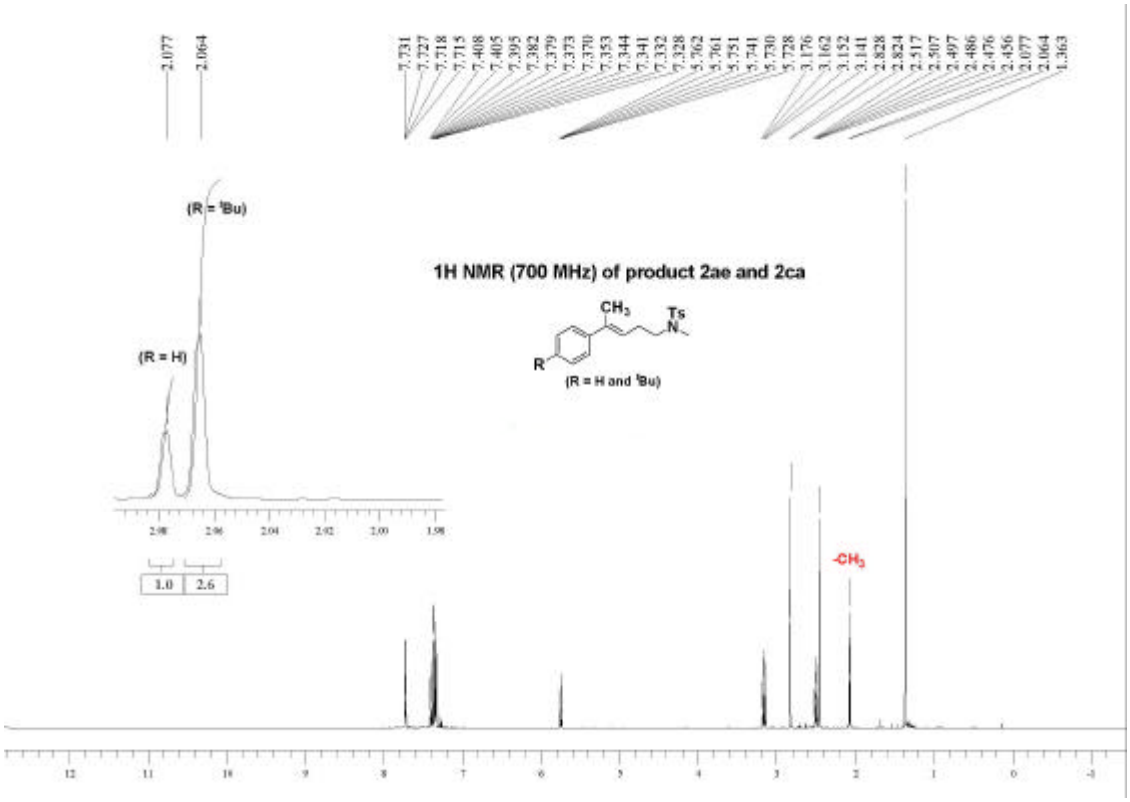
^{1}H NMR spectra of product mixtures of competition experiments using PPh_3AuOTf as catalyst.






2.066
2.042
7.717
7.707
7.396
7.385
7.358
7.345
7.335
7.324
7.290
7.268
7.258
7.248
7.039
7.025
7.013
7.000
6.883
5.751
5.741
5.732
5.704
5.694
5.684
3.164
3.153
3.148
3.143
3.137
2.818
2.811
2.505
2.495
2.483
2.471
2.448
2.066
2.042
1H NMR (700 MHz) of product 2ae and 2ea
(R = H)
(R = F)
1.3
1.0
CH3
Ts
N
R
(R = H and F)
CH3


2.074
2.052
7.725
7.713
7.403
7.393
7.353
7.340
7.329
7.301
7.289
7.157
7.146
5.758
5.749
5.738
5.723
5.714
5.704
3.171
3.160
3.149
3.138
2.825
2.821
2.513
2.501
2.489
2.478
2.468
2.454
2.371
2.074
2.052
1H NMR (700 MHz) of product 2ae and 2ba
(R = Me)
(R = H)
1.0
2.2
CH3
Ts
N
R
(R = H and Me)
CH3



Using HOTf as catalyst:

To the solution of α-phenyl vinylcyclopropane **1a** (88 mg, 0.6 mmol), α-(4-chloro)-phenyl vinylcyclopropane **1d** (108 mg, 0.6 mmol) and TsNHMe (39 mg, 0.2 mmol) in 2 mL toluene at 50 ^{o}C, HOTf (3.0 mg, 0.02 mmol) was added using Micro-syringe. The resulted solution was stirred for 24 h. Then, the reaction mixture was cooled to room temperature, evaporated and purified by silica gel column chromatography (eluent: EtOAc/petroleum ether = 1/3) to afford a mixture of product **2ae** and **2da** (60 mg) as colorless liquid. The ratio of the two products (1.0: 2.0) was determined by ^{1}H NMR (700 MHz) spectroscopy by integration of the methyl signal and corresponds to $\boldsymbol{K_{rel} = k_R/k_H}$. Data are shown in Table 2.

Table 2. Data of the Hammett study using HOTf as catalyst

entry	R	s_p of R	$k_{rel} = k_R/k_H$	$\log k_{rel}$
1	Cl	0.23	1.0/2.0	-0.30
2	F	0.06	1.0/1.3	-0.11
3	H	0	1.0	0
4	Me	-0.14	2.1/1	0.32
5	^{t}Bu	-0.2	2.7/1.0	0.43

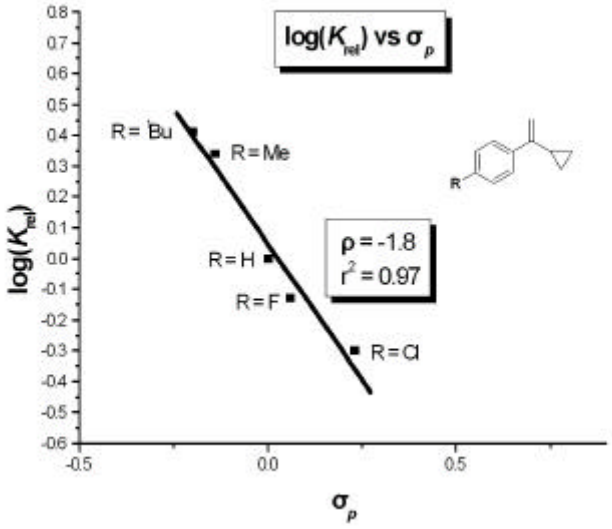
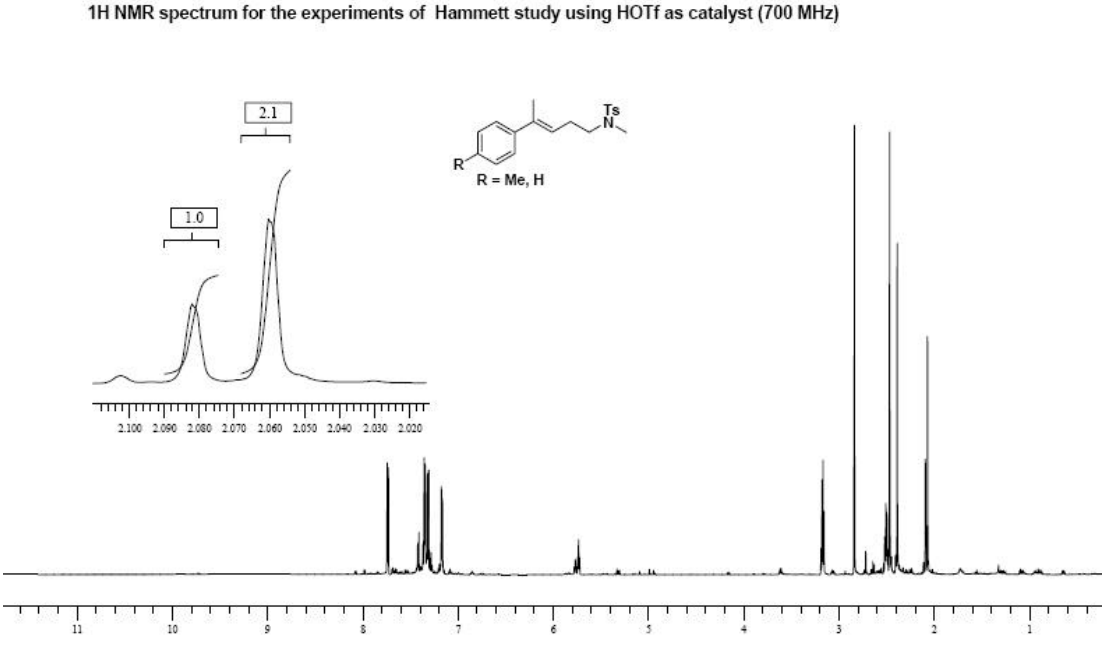
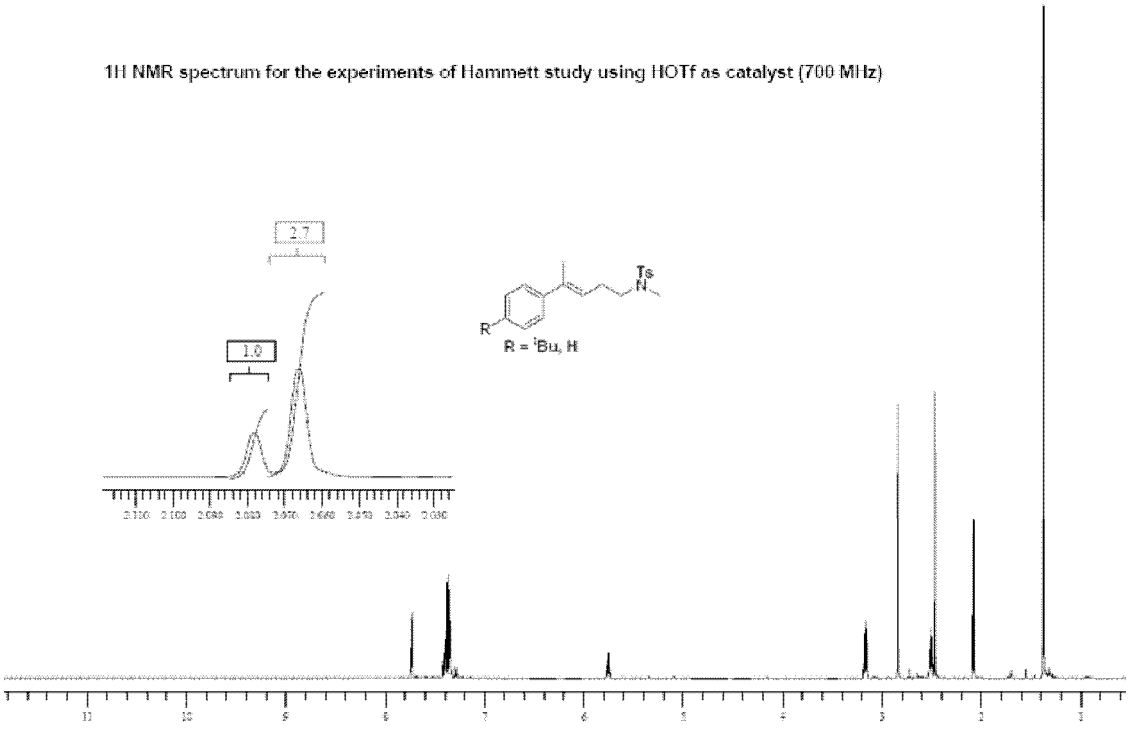


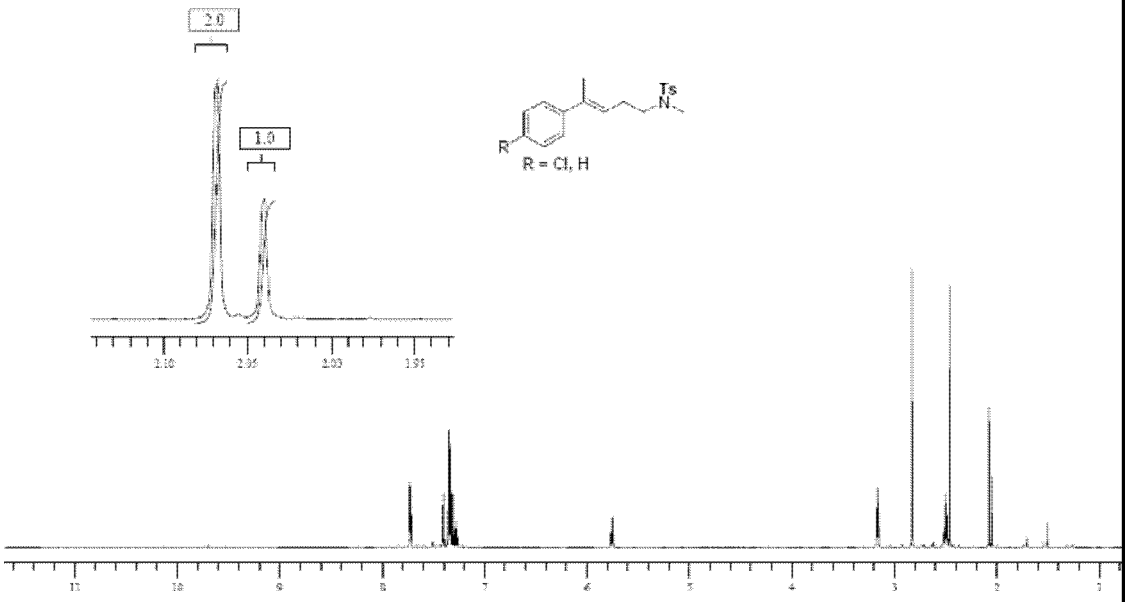
Figure 2. Hammett plot of ring-opening of **1a-e** with TsNHMe using HOTf as catalyst



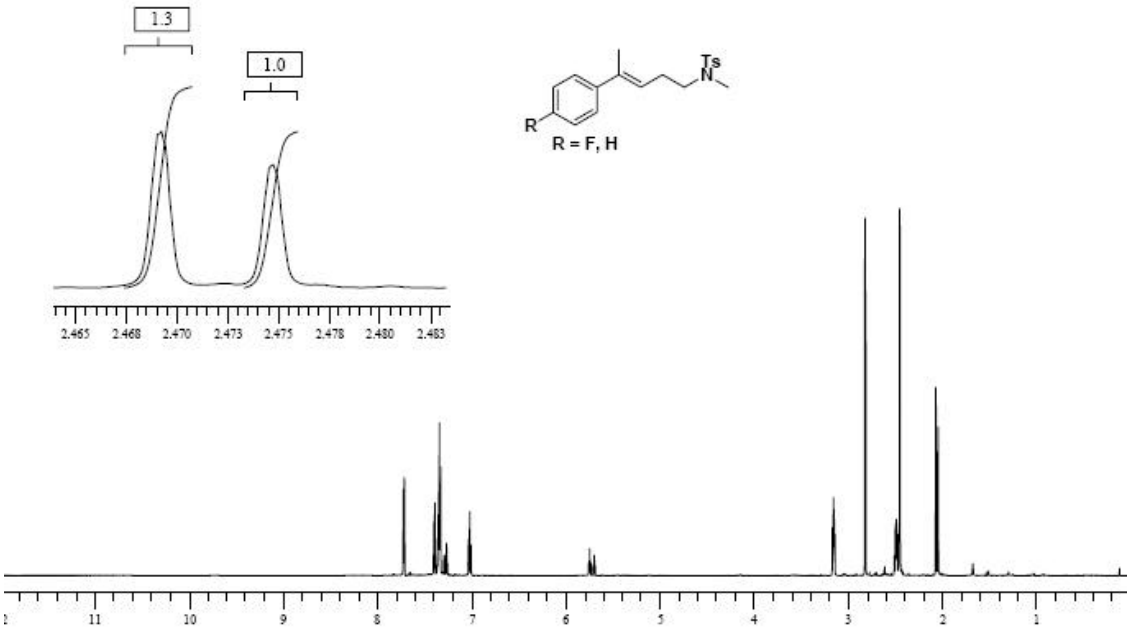
1H NMR spectrum for the experiments of Hammett study using HOTf as catalyst (700 MHz)



1H NMR spectrum for the experiments of Hammett study using HOTs as catalyst (700 MHz)

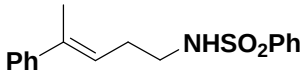


1H NMR spectrum for the experiments of Hammett study (700 MHz)



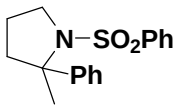
5. Analytical data of new products.

(*E*)-*N*-(4-Phenylpent-3-enyl)benzenesulfonamide (2aa)



73% yield. Colorless liquid.
^{1}H NMR (250 MHz, $CDCl_3$): d 7.92-7.90 (m, 2H, Ar-*H*), 7.63-7.23 (m, 8H, Ar-*H*), 5.60 (td, *J* = 7.2 Hz, 1H, C*H*), 4.66 (t, *J* = 6.0 Hz, 1H, N*H*), 3.12 (q, *J* = 6.9 Hz, 2H, CH_2-N), 2.41 (dd, *J* = 6.9 Hz, 2H, CH_2), 2.01 (s, 3H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): d 143.1, 138.3, 132.6, 129.1, 128.2, 127.1, 125.7, 123.1, 42.9, 29.1, 16.0. HRMS (EI) Calcd for $C_{17}H_{19}NO_2S$: 301.1131. Found: 301.1130.

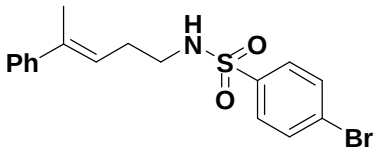
2-Methyl-2-phenyl-1-(phenylsulfonyl)pyrrolidine (3aa)



^{1}H NMR (300 MHz, $CDCl_3$): d 7.72 (d, *J* = 7.2 Hz, 2H, Ar-*H*), 7.56-7.24 (m, 8H, Ar-*H*), 3.79-3.72 (m, 1H, CH_2-N), 3.66-3.58 (m, 1H, CH_2-N), 2.21-2.13 (m, 1H, CH_2), 2.05-1.99 (m, 1H, CH_2), 1.93 (s, 3H, CH_3), 1.91-1.81 (m, 2H, CH_2). ^{13}C NMR (75.5 MHz, $CDCl_3$): d

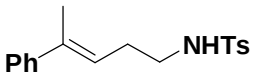
146.3, 141.3, 132.0, 128.7, 128.1, 127.0, 126.7, 125.9, 70.0, 50.0, 45.8, 26.5, 22.5. HRMS (EI) Calcd for $C_{17}H_{19}NO_2S$: 301.1131. Found: 301.1128.

(*E*)-4-Bromo-*N*-(4'-phenylpent-3'-enyl)benzenesulfonamide (**2ab**)



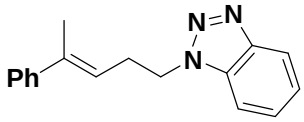
30% yield. White solid. M.P. 101-103 ^{o}C.
^{1}H NMR (250 MHz, $CDCl_3$): d 7.77-7.63 (m, 4H, Ar-*H*), 7.35-7.25(m, 5H, Ar-*H*), 5.58 (td, *J* = 7.3 Hz, 1H, Ar-*H*), 4.60 (t, *J* = 6.0 Hz, 1H, N*H*), 3.13 (q, *J* = 6.8 Hz, 2H, CH_2-N), 2.43 (q, *J* = 6.8 Hz, 2H, CH_2), 2.01 (s, 3H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): d 143.0, 139.1, 138.6, 132.4, 128.6, 128.3, 127.6, 127.1, 125.6, 122.8, 42.9, 29.0, 16.1. HRMS (EI) Calcd for $C_{17}H_{18}BrNO_2S$: 379.0236. Found: 379.0233.

(*E*)-4-Methyl-*N*-(4?-phenylpent-3?-enyl)benzenesulfonamide (**2ac**)



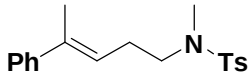
33% yield. Colorless liquid.
^{1}H NMR (250 MHz, $CDCl_3$): d 7.78 (d, *J* = 8.3 Hz, 2H, Ar-*H*), 7.34-7.26 (m, 7H, Ar-*H*), 5.58 (td, *J* = 7.3 Hz, 1H, C*H*), 4.48 (t, *J* = 6.0 Hz, 1H, N*H*), 3.11 (q, *J* = 6.8 Hz, 2H, CH_2-N), 2.45 (s, 3H, CH_3-Ar), 2.41 (dd, *J* = 7.0 Hz, 2H, CH_2), 2.02 (s, 3H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): d 143.4, 143.1, 138.4, 136.9, 129.7, 128.2, 127.13, 127.07, 125.6, 123.1, 42.8, 29.1, 21.5, 16.1. HRMS (EI) Calcd for $C_{18}H_{21}NO_2S$: 315.1288. Found: 315.1289.

(*E*)-1-(4?-Phenylpent-3?-enyl)-1*H*-benzotriazole (**2ad**)



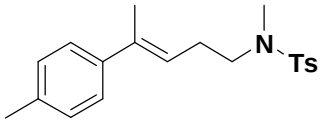
10% yield. Pale yellow liquid.
^{1}H NMR (200 MHz, $CDCl_3$): d 8.11 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.60-7.25 (m, 8H, Ar-*H*), 5.77 (t, *J* = 7.4 Hz, 1H, C*H*), 4.80 (t, *J* = 7.0 Hz, 2H, CH_2-N), 2.96 (dd, *J* = 7.2 Hz, 2H, CH_2), 1.89 (s, 3H, CH_3). ^{13}C NMR (63.0 MHz, $CDCl_3$): d 146.0, 143.2, 138.8, 128.2, 127.2, 127.1, 125.7, 123.8, 122.3, 120.1, 47.8, 29.4, 15.9. HRMS (EI) Calcd for $C_{17}H_{17}N_3$: 263.1417. Found: 263.1416.

(*E*)-4-Methyl-*N*-methyl-*N*-(4'-phenylpent-3'-enyl)benzenesulfonamide (**2ae**)



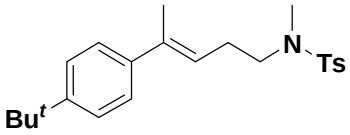
97% yield. Colorless liquid.
^{1}H NMR (250 MHz, $CDCl_3$): d 7.72 (d, *J* = 8.3 Hz, 2H, Ar-*H*), 7.42-7.26 (m, 7H, Ar-*H*), 5.74 (bt, *J* = 7.0 Hz, 1H, C*H*), 3.15 (t, *J* = 7.3 Hz, 2H, CH_2-N), 2.82 (s, 3H, CH_3-N), 2.49 (dd, *J* = 7.5 Hz, 2H, CH_2), 2.45 (s, 3H, Ar-CH_3), 2.07 (s, 3H, CH_3). ^{13}C NMR (63.0 MHz, $CDCl_3$): d 143.38, 143.30, 137.3, 134.8, 129.7, 128.2, 127.4, 126.9, 126.0, 125.7, 123.6, 49.8, 34.9, 27.6, 21.5, 16.0. HRMS (EI) Calcd for $C_{19}H_{23}NO_2S$: 329.1444. Found: 329.1443.

(*E*)-4-Methyl-*N*-methyl-*N*-[4?-(4??-methylphenyl)pent-3?-enyl]benzenesulfonamide (**2ba**)



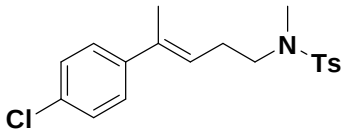
99% yield. Colorless liquid.
^{1}H NMR (700 MHz, $CDCl_3$): d 7.72 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 7.33 (d, *J* = 7.7 Hz, 2H, Ar-*H*), 7.29 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 7.5 (d, *J* = 7.7 Hz, 2H, Ar-*H*), 5.71 (t, *J* = 7.0 Hz, 1H, C*H*), 3.15 (t, *J* = 7.7 Hz, 2H, CH_2-N), 2.82 (s, 3H, CH_3-N), 2.48 (dd, *J* = 7.0 Hz, 2H, CH_2), 2.45 (s, 3H, CH_3-Ar), 2.37 (s, 3H, CH_3-Ar). ^{13}C NMR (63 MHz, $CDCl_3$): d 143.2, 140.5, 137.1, 136.6, 134.9, 129.7, 128.9, 127.4, 125.5, 122.7, 49.8, 34.9, 27.6, 21.5, 21.0, 16.0. HRMS (EI) Calcd for $C_{20}H_{25}NO_2S$: 343.1601. Found: 343.1599.

(*E*)-4-Methyl-*N*-methyl-*N*-[4?-(4??-*tert*-butylphenyl)pent-3?-enyl]benzenesulfonamide (**2ca**)



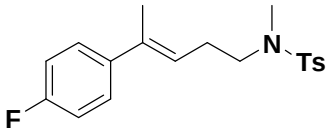
90% yield. Colorless liquid.
^{1}H NMR (700 MHz, $CDCl_3$): d 7.72 (d, *J* = 8.3 Hz, 2H, Ar-*H*), 7.38-7.32 (m, 6H, Ar-*H*), 5.72 (td, *J* = 7.5 Hz, 1H, C*H*), 3.14 (t, *J* = 7.3 Hz, 2H, CH_2-N), 2.81 (s, 3H, CH_3-N), 2.47 (dd, *J* = 7.8 Hz, 2H, CH_2), 2.45 (s, 3H, CH_3-Ar), 2.06 (s, 3H, CH_3), 1.36 (s, 9H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): d 149.8, 143.2, 140.4, 136.9, 134.9, 129.7, 127.4, 125.3, 125.1, 122.9, 49.8, 34.9, 34.4, 31.3, 27.6, 21.5, 15.9. HRMS (EI) Calcd for $C_{23}H_{31}NO_2S$: 385.2070. Found: 385.2073.

(*E*)-4-Methyl-*N*-methyl-*N*-[4?-(4??-chlorophenyl)pent-3?-enyl]benzenesulfonamide (2da)



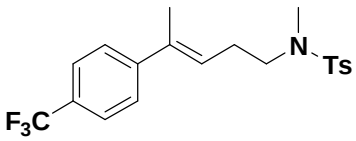
96% yield. Colorless liquid.
^{1}H NMR (250 MHz, $CDCl_3$): d 7.70 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.34-7.26 (m, 6H, Ar-*H*), 5.73 (bt, *J* = 7.0 Hz, 1H, C*H*), 3.14 (t, *J* = 7.3 Hz, 2H, CH_2-N), 2.80 (s, 3H, CH_3-N), 2.48 (dd, *J* = 7.3 Hz, 2H, CH_2), 2.44 (s, 3H, CH_3-Ar), 2.03 (s, 3H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): d 143.3, 141.8, 136.1, 134.8, 132.6, 129.7, 128.3, 127.4, 127.0, 124.2, 49.7, 34.9, 27.6, 21.5, 15.9. HRMS (EI) Calcd for $C_{19}H_{22}ClNO_2S$: 363.1054. Found: 363.1053.

(*E*)-4-Methyl-*N*-methyl-*N*-[4?-(4??-fluorophenyl)pent-3?-enyl]benzenesulfonamide (2ea)



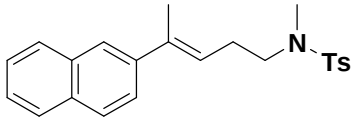
96% yield. Colorless liquid.
^{1}H NMR (700 MHz, $CDCl_3$): d 7.71 (d, 2H, *J* = 8.4 Hz, Ar-*H*), 7.37-7.31 (m, 4H, Ar-*H*), 7.05-7.0 (m, 2H, Ar-*H*), 5.68 (td, *J* = 7.4 Hz, 1H, C*H*), 3.14 (t, *J* = 7.0 Hz, 2H, CH_2-N), 2.81 (s, 3H, CH_3-N), 2.47 (dd, *J* = 7.0 Hz, 2H, CH_2), 2.45 (s, 3H, CH_3-Ar), 2.04 (s, 3H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): d 143.2, 140.5, 137.0, 136.5, 134.9, 129.7, 128.9, 127.4, 125.5, 122.7,49.8, 34.9, 27.6, 21.5, 21.0, 16.0. HRMS (EI) Calcd for $C_{19}H_{22}FNO_2S$: 347.1350. Found: 347.1351.

(*E*)-4-Methyl-*N*-methyl-*N*-[4?-(4??-trifluoromethylphenyl)pent-3?-enyl]benzenesulfonamide (2fa)



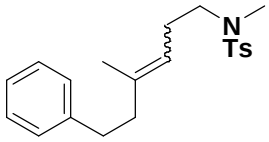
58% yield. Colorless liquid.
^{1}H NMR (250 MHz, $CDCl_3$): d 7.71 (d, *J* = 8.3 Hz, 2H, Ar-*H*), 7.58 (d, *J* = 8.5 Hz, 2H, Ar-*H*), 7.48 (d, *J* = 8.5 Hz, 2H, Ar-*H*), 7.33 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 5.83 (td, *J* = 7.1 Hz, 1H, C*H*), 3.16 (t, *J* = 7.3 Hz, 2H, CH_2-N), 2.81 (s, 3H, CH_3-N), 2.50 (dd, *J* = 7.3 Hz, 2H, CH_2), 2.45 (s, 3H, CH_3-Ar), 2.08 (s, 3H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): d 146.9, 143.3, 136.2, 134.8, 129.7, 127.4, 125.94, 125.86, 125.21, 125.16, 125.11, 125.06, 49.6, 34.9, 27.6, 21.5, 15.9. MS (EI, m/z): 378.14, 242.11, 198.06, 155.01, 91.06. Anal. Calcd for $C_{20}H_{22}F_3NO_2S$: C, 60.44; H, 5.58; N, 3.52. Found: C, 60.45; H, 5.64; N, 3.63.

(*E*)-4-Methyl-*N*-methyl-*N*-[4?-(naphthalene-2??-yl)pent-3?-enyl]benzenesulfonamide (**2ha**)



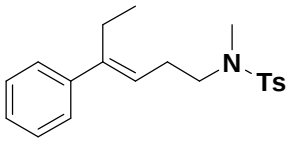
99% yield. Colorless liquid.
^{1}H NMR (300 MHz, $CDCl_3$): d 7.85-7.30 (m, 11H, Ar-*H*), 5.90 (td, *J* = 7.2 Hz, 1H, C*H*), 3.19 (t, *J* = 7.2 Hz, 2H, CH_2), 2.84 (s, 3H, CH_3-N), 2.55 (dd, *J* = 7.8 Hz, 2H, CH_2), 2.43 (s, 3H, CH_3), 2.17 (s, 3H, CH_3-Ar). ^{13}C NMR (75.5 MHz, $CDCl_3$): d 143.3, 140.5, 137.1, 134.9, 133.4, 132.5, 129.7, 128.1, 127.7, 127.5, 127.4, 126.1, 125.6, 124.3, 124.2, 124.1, 49.8, 38.0, 35.0, 27.8, 21.5, 16.0. HRMS (EI) Calcd for $C_{23}H_{25}NO_2S$: 379.1601. Found: 379.1617.

(*Z*/*E*)-4-Methyl-*N*-methyl-*N*-[4?-methyl-6?-phenylhex-3?-enyl]benzenesulfonamide (2ia)



80% yield. Colorless liquid. d.r. = 80:20.
^{1}H NMR (250 MHz, $CDCl_3$): d 7.72-7.66 (m, 2H, Ar-*H*), 7.36-7.18 (m, 7H, Ar-*H*), 5.38 (td, *J* = 7.0 Hz, 0.2H, C*H*, minor), 5.10 (td, *J* = 6.8 Hz, 0.8H, C*H*, major), 3.40-3.35 (t, 0.4H, CH_2, minor), 3.05-2.95 (m, 1.6H, CH_2, major), 2.90-2.83 (t, 0.4H, CH_2, minor), 2.76-2.67 (m, 1.6H, CH_2, major), 2.74 (s, 3H, CH_3-N), 2.46 (s, 3H, CH_3-Ar), 2.34-2.21 (m, 3.2H, CH_2, major), 2.11-2.06 (m, 0.8H, CH_2, minor), 1.68 (s, 2.4 H, CH_3, major), 1.67 (s, 0.6H, CH_3, minor). ^{13}C NMR (75.5 MHz, $CDCl_3$): d 143.2, 142.2, 137.3, 129.6, 128.44, 128.38, 128.31, 128.29, 128.25, 127.4, 125.82, 125.76, 125.71,123.75, 121.5, 120.5,49.95, 49.89, 41.48, 36.5, 34.80, 34.77, 34.70, 34.5, 34.24, 34.21, 34.1, 26.8, 26.4, 26.0, 23.4, 21.5, 16.3. HRMS (EI) Calcd for $C_{21}H_{27}NO_2S$: 357.1757. Found: 357.1755.

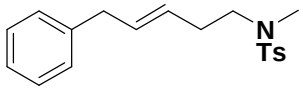
(*E*)-4-Methyl-*N*-methyl-*N*-(4'-phenylhex-3'-enyl)benzenesulfonamide (**2ja**)



76% yield. Colorless liquid.
^{1}H NMR (300 MHz, $CDCl_3$): d 7.71 (d, *J* = 8.3 Hz, 2H, Ar-*H*), 7.37-7.25 (m, 7H, Ar-*H*), 5.57 (t, *J* = 7.3 Hz, 1H, C*H*), 3.14 (t, *J* = 7.3 Hz, 2H, CH_2-N), 2.82 (s, 3H, CH_3-N), 2.59-2.46 (m, 4H, CH_2), 2.44 (s, 3H, CH_3), 1.0 (t, *J* = 7.5 Hz, 3H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): d 144.2, 143.4, 143.1, 137.3, 129.7, 128.2, 127.4, 126.8, 126.3, 123.2, 50.1, 34.9, 27.3, 23.1, 21.5, 13.6. HRMS (EI) Calcd for $C_{20}H_{25}NO_2S$: 343.1601. Found:

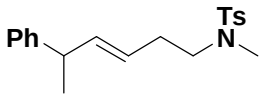
343.1597.

4-Methyl-*N*-methyl-*N*-(5?-phenylpent-3?-enyl)benzenesulfonamide (**2ka**)



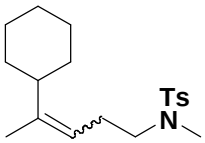
57% yield. Colorless liquid.
^{1}H NMR (250 MHz, $CDCl_3$): d 7.70 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.35-7.18 (m, 7H, Ar-*H*), 5.73-5.62 (m, 1H, C*H*), 5.52-5.41 (m, 1H, C*H*), 3.35 (d, *J* = 6.8 Hz, 2H, CH_2-Ar), 3.08 (t, *J* = 7.5 Hz, 2H, CH_2), 2.75 (s, 3H, CH_3-N), 2.45 (s, 3H, CH_3), 2.30 (dd, *J* = 7.3 Hz, 3H, CH_2). ^{13}C NMR (75.5 MHz, $CDCl_3$): d 143.2, 140.4, 134.9, 129.6, 128.5, 128.4, 127.4, 126.0, 50.0, 39.0, 34.8, 31.1, 21.5. HRMS (EI) Calcd for $C_{19}H_{23}NO_2S$: 329.1444. Found: 329.1445.

4-Methyl-*N*-methyl-*N*-(5-phenylhex-3-enyl)benzenesulfonamide (2la)



54% yield. Colorless liquid.
^{1}H NMR (250 MHz, $CDCl_3$): d 7.69 (d, *J* = 8.3 Hz, 1H, Ar-*H*), 7.35-7.20 (m, 7H, Ar-*H*), 5.74-5.65 (q, 1H, C*H*), 5.48-5.36 (m, 1H, C*H*), 3.45 (pentet, 1H, C*H*), 3.07 (t, *J* = 7.0 Hz, 2H, CH_2), 2.74 (s, 3H, CH_3-N), 2.45 (s, 3H, CH_3), 1.36 (d, *J* = 7.3 Hz, 3H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): d 145.9, 143.2, 137.8, 135.0, 129.6, 128.3, 127.4, 127.2, 126.1, 124.7, 50.0, 42.3, 34.8, 31.2,21.5, 21.3. HRMS (EI) Calcd for $C_{20}H_{25}NO_2S$: 343.1601. Found: 343.1600.

(*E*)-4-Methyl-*N*-methyl-*N*-[4?-cyclohexylpent-3?-enyl]benzenesulfonamide (**2ma**)



99% yield. Colorless liquid. d.r. = 86:14.
^{1}H NMR (300 MHz, $CDCl_3$): d 7.67 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 7.31 (d, *J* = 8.1 Hz, 2H, Ar-*H*), 5.06 (t, *J* = 6.8 Hz, 0.86H, C*H*, major), 4.98 (t, *J* = 6.8 Hz, 0.14H, C*H*, minor), 3.0 (t, *J* = 7.5 Hz, 2H, CH_2), 2.75 (s, 3H, CH_3-N), 2.43 (s, 3H, CH_3-Ar), 2.23 (q, *J* = 7.5 Hz, 2H, CH_2), 1.78-1.61 (m, 6H), 1.57 (s, 3H, CH_3), 1.36-1.08 (m, 5H). ^{13}C NMR (75.5 MHz, $CDCl_3$, major product): d 143.2, 143.1, 135.0, 129.6, 127.4, 117.8, 50.0, 47.3, 34.8, 31.9, 31.7, 26.7, 26.4, 14.5. HRMS (EI) Calcd for $C_{19}H_{29}NO_2S$: 335.1914. Found: 335.1914.

6. Crystal and structure data for product 2ab.

Empirical formula	C17 H18 Br N O2 S
Formula weight	380.29
Temperature	294(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/n
Unit cell dimensions	a = 5.1841(6) A alpha = 90 deg.
	b = 29.677(3) A beta = 91.127(2) deg.
	c = 11.2315(12) A gamma = 90 deg
Volume	1727.6(3) A^3
Z, Calculated density	4, 1.462 Mg/m^3
Absorption coefficient	2.506 mm^-1
F(000)	776
Crystal size	0.26 x 0.20 x 0.05 mm
Theta range for data collection	1.37 to 26.37 deg.
Limiting indices	-6<=h<=6, -37<=k<=36, -14<=l<=14
Reflections collected / unique	13907 / 3535 [R(int) = 0.0531]
Completeness to theta = 26.37	99.7 %
Absorption correction	Empirical
Max. and min. transmission	0.8849 and 0.5619
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3535 / 0 / 199
Goodness-of-fit on F^2	1.029
Final R indices [I>2sigma(I)]	R1 = 0.0610, wR2 = 0.1789
R indices (all data)	R1 = 0.1366, wR2 = 0.2233
Max. and min. transmission	0.8849 and 0.5619

Reference

1. Kaesz, H.D. *Inorg*. *Synth*. **1989**, *26*, 85.
2. Ohta, T.; Ikegami, H.; Miyake, T.; Takaya, J. *J*. *Organomet. Chem.* **1995**, *502*, 169.
3. Chen, Y.; Shi, M. *J*. *Org*. *Chem*. **2004**, *69*, 426.
4. As for ^{13}C-^{1}H HZQC NMR, please see: Ollerenshaw, J. E.; Tuqarino, V.; Skrynnikov, N. R.; Kay, L. E., *J*. *Biomol*. *NMR*. **2005**, *33*, 25.
5. s_p values are as reported: Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev*. **1991**, *91*, 165.