Electronic Supplementary Material (ESI) for ChemComm.

Brönsted Acid-Catalyzed α-Halogenation of Ynamides from Halogenated Solvents and Pyridine-*N*-Oxides

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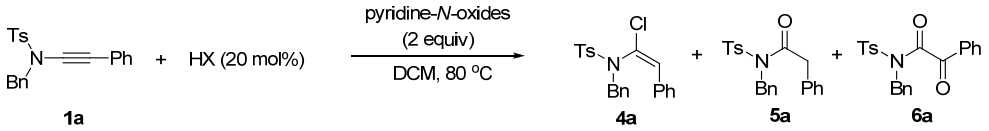
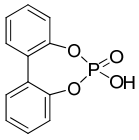
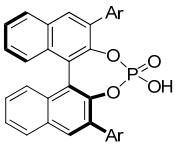
1. General Information

All solvents were dried and distilled according to standard methods before use.[1] Pyridine-*N*-oxides[2] and ynamides[3] were prepared according to the literature procedures. Ynamides were prepared according to the literature. All other chemicals were purchased from commercial sources and was used as received. TLC (this-layer chromatography) analysis was carried out on Merck silica gel 60 F254 TLC plates and was visualized with UV lamp and $KMnO_4$ solution. Flash chromatography was performed on Kieselgel 60 (230-400 mesh). ^1H and ^{13}C NMR spectra were recorded on a Varian (400 MHz) or Bruker (400 MHz) spectrometer with TMS as an internal standard. High resolution mass spectra (HRMS) were obtained from Korea Basic Science Institute (KBSI, Daegu).

2. Optimization Study

Table S1. Screening of Acid Catalysts[a]



entry	HX	time	yield (%)[b] (**4a**/**5a**/**6a**)		
1		60 h	69	8	-
2	 (*S*)-TCyP (Ar = 2,4,6-(*c*Hex)$_3$C$_6$H$_2$) (10 mol %)	60 h	48	-	-
3	MsOH	28 h	-	15	85
4	CSA[b]	72 h	(messy)	-	-
5	citric acid	80 h	59	40	-
6	PhCOOH	80 h	83	7	-
7	HCOOH	60 h	46	22	-
8	lactic acid	60 h	30	30	-
9	PPTS	60 h	28	-	27
10	4- nitrophenol	60 h	37	-	-

[a]All reactions were conducted in CH_2Cl_2 (0.1 M); Yields were determined based on the ^1H NMR spectra with CH_2Br_2 as an internal standard. [b]CSA: (1*S*)-(+)-10-camphorsulfonic acid. [c]PPTS: pyridinium *p*-toluenesulfonate.

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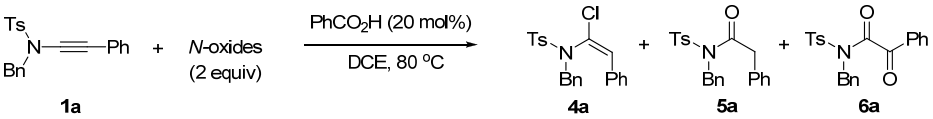
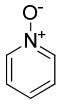
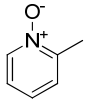
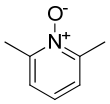
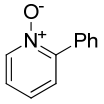
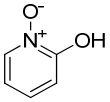
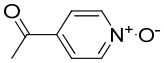
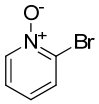
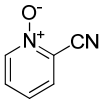
[1] Armarego, W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals*; Elsevier: Oxford, **2009**.

[2] (a) Kokatla, H. P.; Thomson, P. F.; Bae, S.; Doddi, V. R.; Lakshman, M. K. *J. Org. Chem.* **2011**, *76*, 7842. (b) Bering, L.; Antonchick, A. P.; *Org. Lett*. **2015**, *17*, 3134.

[3] Alexandre, H.; Pascal, R.; Vincent, G.; Kevin, C.; Robert H. D. *Angew. Chem,. Int. Ed.* **2014**, *53*, 8333.

Table S2. Screening of *N*-Oxides



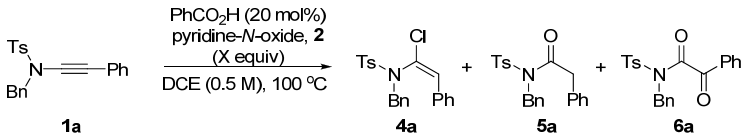
entry	*N*-oxides	time	yield (%)[b] (**4a**/**5a**/**6a**)		
1		70 h	92(89)	-	-
2		36 h	76 (73)	12	12
3		65 h	59	13	34
4		60 h	53	7	19
5		15 h	-	-	-
6		65 h	32	20	25
7		70 h	trace (messy)	-	-
8		70 h	trace (messy)	-	-
9	$Ph_3P{=}O$	40 h	-	-	-
10	$Me_3N^+\text{-}O^-$	15 h	26	-	-

3. Kinetic Study

Initially, the efficiency of conversion of **1a** into **4a** was inspected varying amount of pyridine-*N*-oxide **2**. Trends in Table S3 shows that the amount of **2** had relatively negligible effect on the formation of side products **5a** and **6a**, but the trend in the reaction time for consumption of starting **1a** indicated the rate is inversely related to [**2**]. We carried out the detailed kinetic study as described below.

Ynamide **1a** (0.2 mmol, 0.5 M) and 20 mol% of PhCOOH was dissolved in DCE (0.4 mL) and was mixed with five different loadings of pyridine-*N*-oxide **2** (0.25 M, 0.50 M, 0.75 M, 1.0 M, and 1.25 M). These solutions were independently heated at 100 °C and time-dependent formation of the product **4a** was measured by GLC (with *n*-dodecane as an internal standard). The plot of [**4a**] vs. time showed zeroth-order dependence on [**4a**] (a linear plot). These time evolutions were shown in Figure S1-S5 after averaging duplicate experiments for each figures.

Table S3. Effect of pyridine *N*-Oxide (equivalent)



entry	**2** (equiv)	time (h)	yield (%) (**1a**/**4a**/**5a**/**6a**)			
1	0.5	156	35	51	6	
2	1.0	130	-	63	13	-
3	2.0	70	-	92	4	-
4	3.0	40	-	78	5	17
5	5.0	24	-	71	6	23

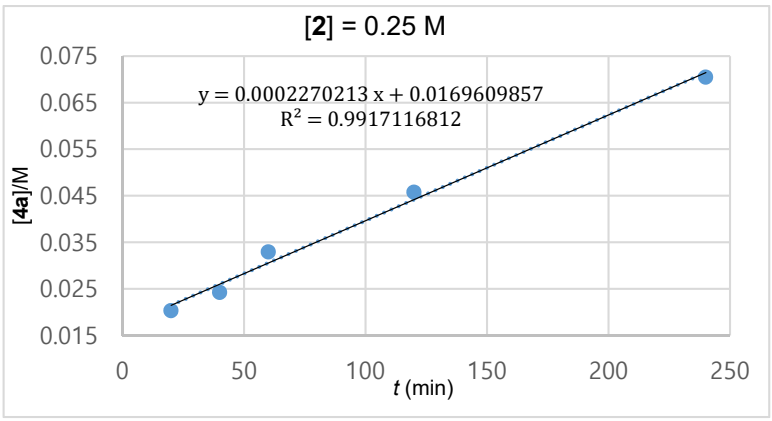


Figure S1.

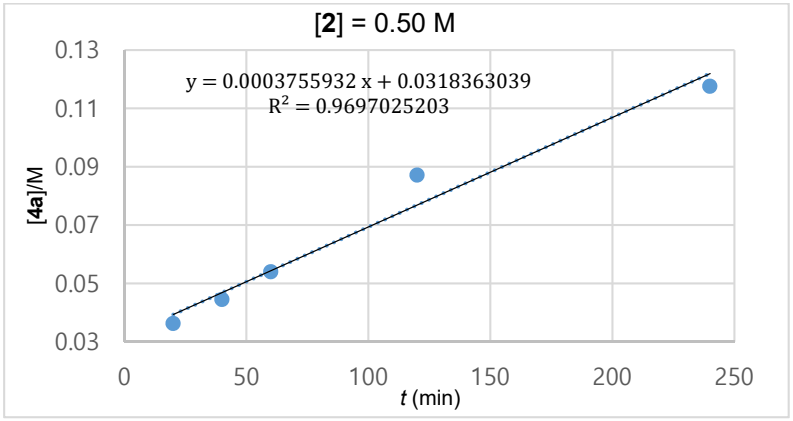


Figure S2

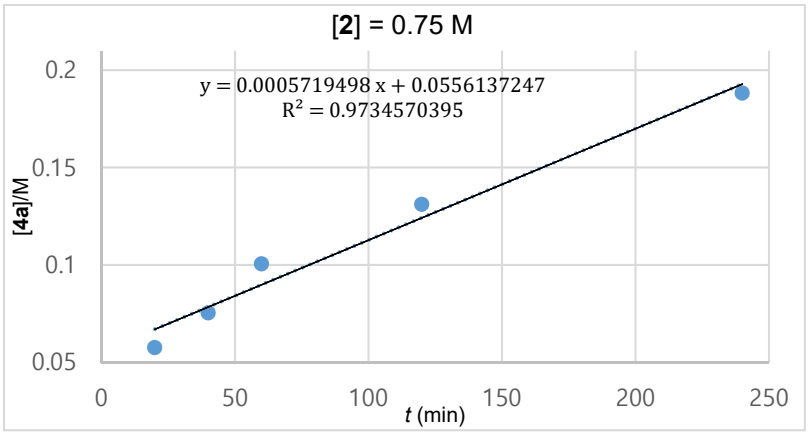


Figure S3

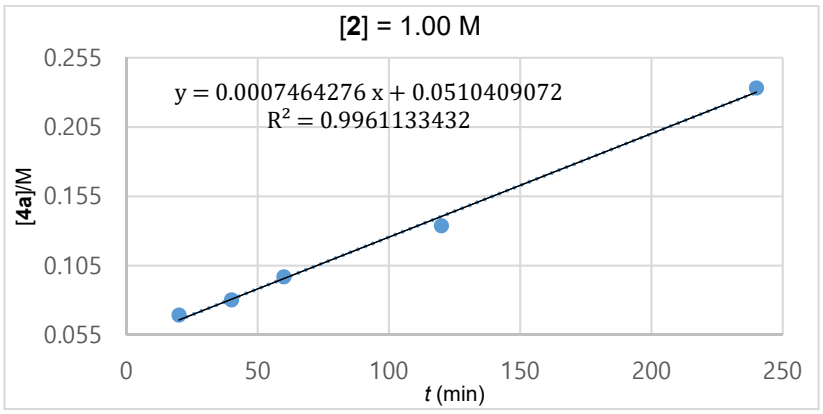


Figure S4

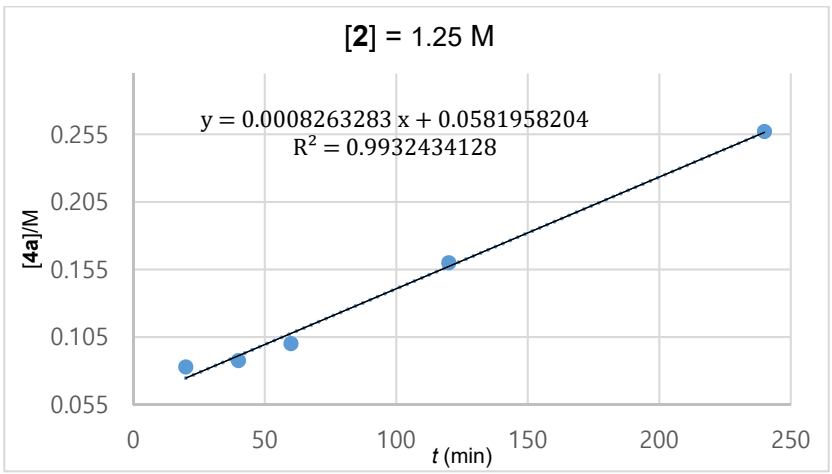


Figure S5

A linear plot in the Figure S1-S5 as well as the rate dependency on [**1a**] (Figure S6) shows that the formation of **4a** is 0^{th} order in ynamide **1a**. The rates of the formation of **4a** ($M{\cdot}h^{-1}$) in each concentration of [**2**], was calculated from the least-square fit of the slopes in Figure S1-S5 which was then plotted against [**2**] in Figure

S7.

The first-order rate dependence on pyridine-*N*-oxide **2** indicates that the rate-determining step is the attack of **2** on the halonium **H** (Scheme 3 of manuscript). The rate was not affected by the concentration of ynamide **1a** (Figure S6), which indicates the formation of keteniminium **D** as well as halonium **H** is fast and reversible processes and the concentration of **D** in the reaction mixture is limited by the concentration of the acid catalyst, [PhCOOH].

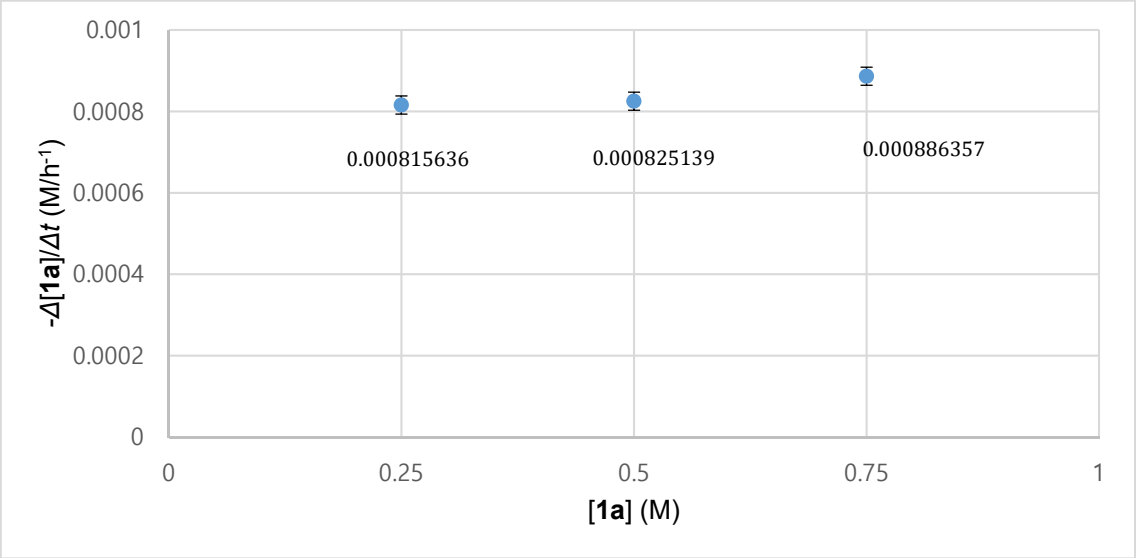


Figure S6 The rate dependence on ynamide **1a**

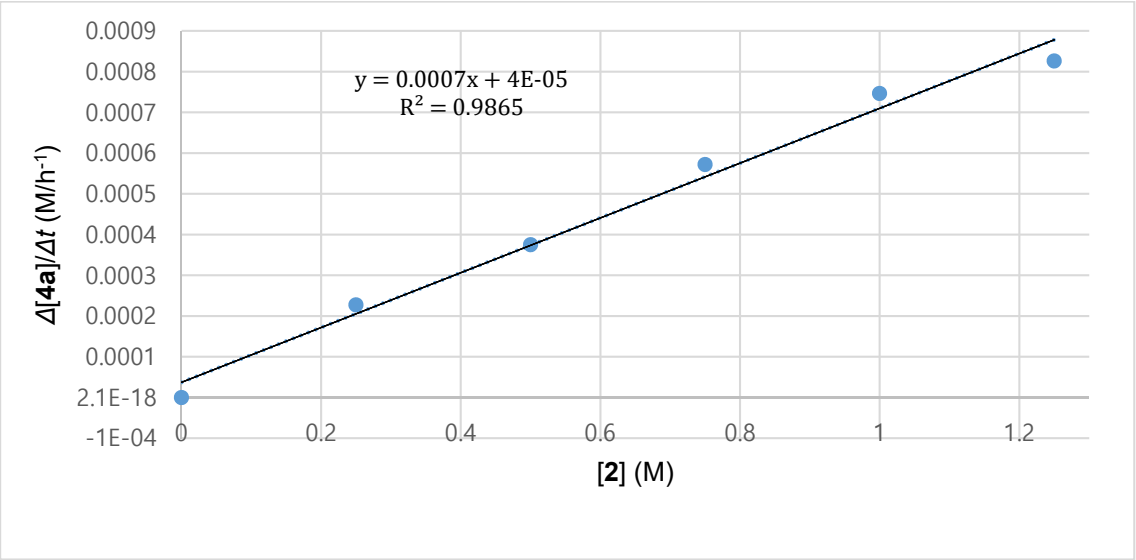
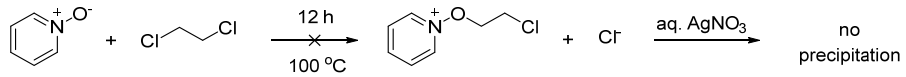


Figure S7 The rate dependence on pyridine-*N*-oxide **2**

4. Halide Test

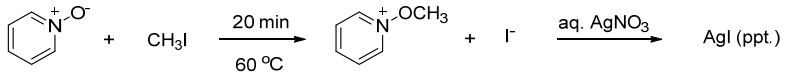
Mechanistically, there is a possibility that the current halogenation may actually occur by the halide anion liberated from the reaction of pyridine-*N*-oxide and halogenated solvents. To exclude such a possibility, pyridine-*N*-oxide was heated in 1,2-DCE (1.0 M) for 12 h at 100 ºC and an aliquot (0.2 mL) of the reaction mixture was mixed with saturated aqueous $AgNO_3$ solution. We did not observe the formation of precipitates in this text (left picture below).

(Mixture A)



On the other hand, a similar experiment was repeated with CH_3I as solvent. This time, the reaction mixture that was heated for 20 min at 65 ºC generated iodide anion, which was confirmed by the positive $AgNO_3$ test (right picture below).

(Mixture B)



Mixture A

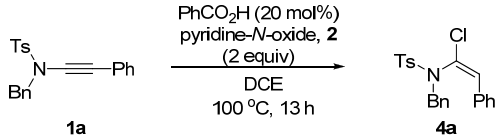
(no precipitation observed)

Mixture B

(yellow precipitation of AgI observed)

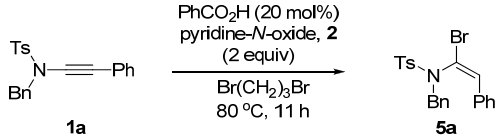
5. General Procedure

General Procedure A: Hydrochlorination



Ynamide **1a** (0.1 mmol) was added in a 10 ml screw-capped test tube. Pyridine *N*-oxide (0.2 mmol), benzoic acid (0.02 mmol) and 1,2-dichloroethane (0.2 ml) was added sequentially under air. The reaction mixture was stirred at 100 °C for 13 h. Solvent was removed under vacuum and the residue was purified by column chromatography (EtOAc:*n*Hex = 1:15~1:7).

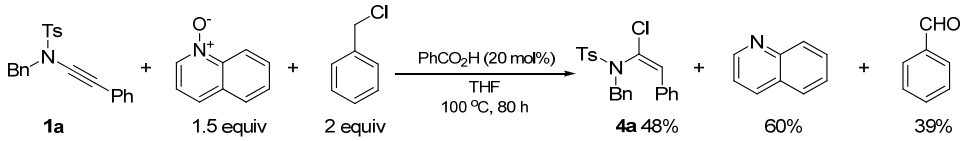
General Procedure B: Hydrobromination



Ynamide **1a** (0.1 mmol) was added in a 10 ml screw-capped test tube. Pyridine *N*-oxide (0.2 mmol), benzoic acid (0.02 mmol) and 1,3-dibromoropropane (0.2 ml) was added sequentially under air. The reaction mixture was stirred at 80 °C for 11 h. Solvent was removed under vacuum and the residue was purified by column chromatography (EtOAc:*n*Hex = 1:20~1:10).

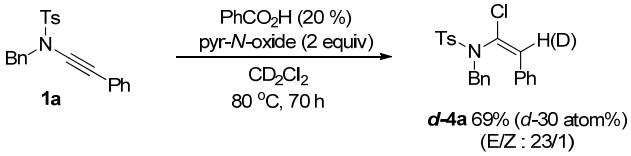
6. Mechanistic Studies (Scheme 2)

(Eq. 2)



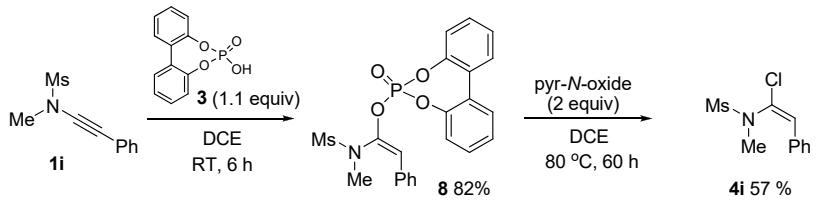
Similar procedure to General Procedure A was followed (ynamide **1a** (0.1 mmol), quinoline *N*-oxide (0.15 mmol), benzyl chloride (0.2 mmol) and benzoic acid (0.02 mmol) in THF (0.2 ml)), leading to isolation of **4a** (48%) along with quinolone (60%) and benzaldehyde (39%). The identity of the latter two was confirmed by GC-MS. The smaller yield of benzaldehyde than that of **4a** is presumably due to the volatility. The slightly higher yield of quinoline is likely due to the oxygenation of ynamides leading to α-ketoamide **6a** which was observed in a trace amount in the crude ^{1}H NMR spectrum.

(Eq. 3)



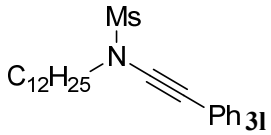
Similar procedure to General Procedure A was followed (ynamide **1a** (0.1 mmol), pyridine *N*-oxide (0.2 mmol) and benzoic acid (0.02 mmol) in CD_2Cl_2 (1 ml)). The %D incorporation in ***d*-4a** was based on its ^{1}H-NMR spectrum.

(Eqs. 4 and 5)



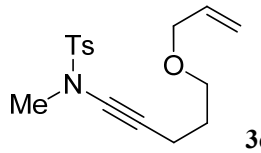
Ynamide **1i** (0.1 mmol) was stirred with diarylphosphoric acid **3** (0.11 mmol) in 1,2-dichloroethane (1 ml) at RT for 6 h. Solvent was removed and the residue was purified by column chromatography (EtOAc:*n*Hex = 1:3) to obtain **8**. Subsequently, the adduct **8** was mixed with pyridine-N-oxide (2 equiv.) in 1,2-dichloroethane (0.5 M) and was heated at 80 °C for 60 h. The purification of the mixture afforded **4i** in 57 % yield. For the formation of **9** and its reaction to afford **4c**, a similar procedure was followed under the reaction conditions described in the manuscript.

7. Characterization of Substrates and Products



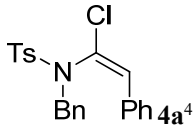
3l

yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.40 (m, 2H), 7.32-7.29 (m, 3H), 3.53 (t, *J* = 7.3 Hz, 2H), 3.13 (s, 3H), 1.83-1.76 (m, 2H), 1.45-1.26 (m, 18H), 0.88 (t, *J* = 6.9 Hz 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.5, 128.3, 128.0, 122.7, 81.7, 71.0, 51.7, 38.2, 31.9, 29.64, 29.62, 29.56, 29.5, 29.4, 29.1, 28.3, 26.3, 22.7, 14.1; HRMS (EI) Calcd for $C_{21}H_{33}NO_2S$ $[M]^+$ 363.2227; found 363.2228.



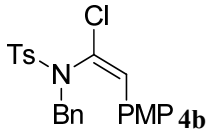
3q

colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 5.91 (ddt, *J* = 10.4, 17.2, 5.6 Hz, 1H), 5.27 (dq, *J* = 17.2, 1.64 Hz, 1H), 5.17 (dq, *J* = 10.4, 1.7 Hz, 1H), 3.96 (dt, *J* = 5.6, 1.4 Hz, 2H), 3.48 (t, *J* = 6.2 Hz, 2H), 3.01 (s, 3H), 2.46 (s, 3H), 2.35 (t, *J* = 7.1 Hz, 2H), 1.79-1.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.5, 134.9, 133.2, 129.7, 127.8, 116.8, 75.1, 71.9, 68.7, 68.0, 39.3, 29.1, 21.6, 15.2; HRMS (EI) Calcd for $C_{16}H_{21}NO_3S$ $[M]^+$ 307.1237; found 307.1237.



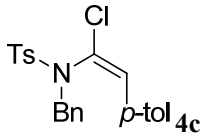
4a[4]

white solid (35.4 mg); mp 126-130 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.34-7.31 (m, 4H), 7.21-7.19 (m, 5H), 7.14-7.10 (m, 3H), 6.60 (s, 1H), 4.79 (d, *J* = 10.6 Hz, 1H), 4.03 (d, *J* = 10.0 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 135.0, 134.9, 133.3, 132.9, 129.8, 129.6, 128.9, 128.8, 128.5, 128.3, 128.2, 128.1, 127.5, 52.4, 21.7; HRMS (EI) Calcd for $C_{22}H_{20}ClNO_2S$ $[M]^+$ 397.0898, found 397.0898.



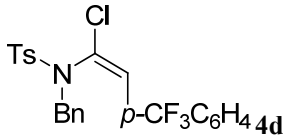
4b

yellow solid (28.7 mg); mp 128-132 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.3 Hz, 2H), 7.35-7.32 (m, 4H), 7.24(d, *J* = 5.6 Hz, 2H), 7.14-7.12 (m, 3H), 6.73 (d, *J* = 8.9 Hz, 2H), 6.52 (s, 1H), 4.81 (d, *J* = 13.0 Hz, 1H), 4.03 (d, *J* = 13.0 Hz, 1H), 2.46(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 144.5, 135.0, 134.5, 133.5, 130.3, 129.8, 129.6, 128.9, 128.3, 128.2, 125.6, 125.4, 113.5, 55.2, 52.4, 21.7; HRMS (EI) Calcd for $C_{23}H_{22}ClNO_3S$ $[M]^+$ 427.1003, found 427.1003.



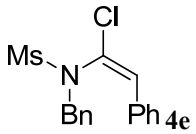
4c

white solid (33.4 mg); mp 116-122 °C; ^{1}H NMR (400 MHz, CDCl3): δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.25-7.23 (m, 3H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.56 (s, 1H), 4.80 (d, *J* = 12.8 Hz, 1H), 4.04 (d, *J* = 12.8 Hz, 1H), 2.46 (s, 3H) 2.29(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.5, 138.6, 135.0, 134.9, 133.5, 130.1, 129.8, 129.6, 128.9, 128.8, 128.7, 128.3, 128.2, 126.6, 52.4, 21.7, 21.3; HRMS (EI) Calcd for $C_{23}H_{22}ClNO_2S$ $[M]^+$ 411.1054, found 411.1053.



4d

pale yellow solid (41.0 mg); mp 120-124 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 2H), 7.36-7.34 (m, 5H), 7.20-7.10 (m, 4H), 6.64 (s, 1H), 4.81 (d, *J* = 12.9 Hz, H), 4.02 (d, *J* = 12.2 Hz, H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.9, 144.5, 136.3 (q, $^4J_{CF}$ = 1 Hz), 134.7, 133.7, 133.1, 129.8, 129.7, 128.88, 128.85 (q, $^2J_{CF}$ = 41 Hz), 128.77, 128.51, 128.31, 124.9 (q, $^3J_{CF}$ = 4 Hz), 124.0 (q, $^1J_{CF}$ = 271 Hz), 52.4, 21.7; HRMS (EI) Calcd for $C_{23}H_{19}ClF_3NO_2S$ $[M]^+$ 465.0772, found 465.0773.



4e

pale yellow liquid (26.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.26 (m, 4H), 7.20-7.14 (m, 6H), 6.56 (s, 1H), 4.71 (bs, 1H), 4.38 (bs, 1H), 3.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.6, 133.2, 132.6, 129.8, 128.7, 128.6, 128.5, 128.3, 128.2, 127.2, 53.0, 39.6; HRMS (EI) Calcd for $C_{16}H_{16}ClNO_2S$ $[M]^+$ 321.0585, found 321.0585.

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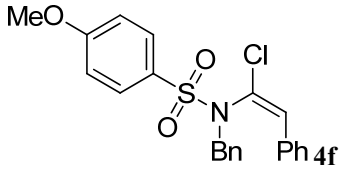
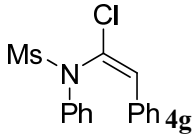
[4] Prabagar, B.; Nayak, S.; Mallick, R. K.; Prasad, R.; Sahoo, A. K. *Org. Chem. Front.,* **2016**, *3*, 110.



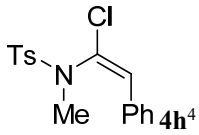
4f

pale yellow solid (33.5 mg); mp 122-126 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 9.0 Hz, 2H), 7.33 (d, *J* = 5.6 Hz, 2H), 7.31-7.18 (m, 5H), 7.14-7.10 (m, 2H), 6.95 (d, *J* = 9.0 Hz, 2H), 6.59 (s, 1H), 4.78 (d, *J* = 12.0 Hz, 1H), 4.03 (d, *J* = 12.8 Hz, 3H) 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.7, 134.9, 133.4, 132.9, 131.1, 129.8, 129.3, 128.8, 128.5, 128.3, 128.2, 128.1, 127.7, 114.1, 55.7, 52.4; HRMS (EI) Calcd for $C_{22}H_{20}ClNO_3S$ $[M]^+$ 413.0847, found 413.0847.



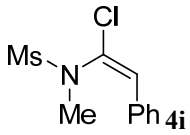
4g

white solid (27.0 mg); mp 126-130 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60-7.55 (m, 4H), 7.38-7.27 (m, 6H), 6.87 (s, H), 3.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.9, 133.6, 132.6, 129.6, 129.0, 128.7, 128.6, 128.1, 127.6, 124.3, 39.6; HRMS (EI) Calcd for $C_{15}H_{14}ClNO_2S$ $[M]^+$ 307.0428, found 307.0428.



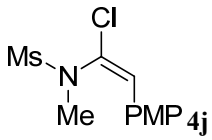
4h[4]

white solid (27.0 mg); mp 116-120 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.37-7.28 (m, 5H), 6.65 (s, H), 3.02 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.4, 134.2, 133.1, 132.4, 129.8, 129.5, 128.9, 128.8, 128.77, 128.68, 35.7, 21.7.



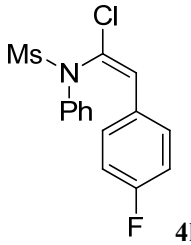
4i

colorless liquid (21.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60-7.56 (m, 2H), 7.40—7.33 (m, 3H), 6.72 (s, H), 3.17 (s, 3H), 3.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.7, 132.5, 129.5, 129.1, 128.8, 128.7, 38.1, 35.8; HRMS (EI) Calcd for $C_{10}H_{12}ClNO_2S$ $[M]^+$ 245.0272, found 245.0272.



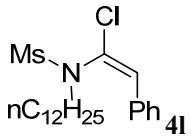
4j

pale yellow liquid (25.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.9 Hz, 2H), 6.61 (s, 1H), 3.81 (s, 3H) 3.14 (s, 3H), 3.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 132.11, 130.2, 126.9, 125.4, 114.2, 55.3, 38.0 35.6; HRMS (EI) Calcd for $C_{11}H_{14}ClNO_3S$ $[M]^+$ 275.0377, found 275.0377; 1D-NOE experiments were conducted to support the (E)-geometry.



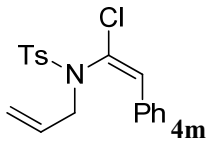
4k

Yellow sticky solid (19.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.51 (m, 4H), 7.37-7.27 (m, 3H), 7.05-7.00 (m, 2H), 6.80 (s, 1H), 3.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.8 (d, $^{1}J_{CF}$ = 249 Hz), 138.7, 132.4, 130.6 (d, $^{3}J_{CF}$ = 8 Hz), 129.6, 128.7 (d, $^{4}J_{CF}$ = 3 Hz), 128.0, 127.7, 124.2, 115.7 (d, $^{2}J_{CF}$ = 21 Hz), 39.6; HRMS (EI) Calcd for $C_{15}H_{13}ClFNO_2S$ $[M]^+$ 325.0334, found 325.0334.



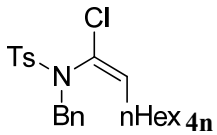
4l

yellow liquid (27.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 6.8 Hz, 2H), 7.36-7.29 (m, 3H), 6.81 (s, 1H), 3.50-3.36(bd, 2H), 1.84-1.77 (m, 2H), 1.57-1.15 (m, 18H), 0.88 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.5, 132.8, 129.1, 129.0, 128.6, 127.4, 49.0, 38.6, 31.9, 29.63, 29.59, 29.47, 29.4, 29.3, 29.1, 27.5, 26.8, 22.7, 14.1; HRMS (FAB) Calcd for $C_{21}H_{35}ClNO_2S$ $[M+H]^+$ 400.2072, found 400.2071.



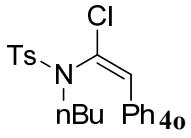
4m

pale yellow solid (21.2 mg); mp 112-116 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.3 Hz, 2H), 7.70 (d, *J* = 8.6 Hz, 2H), 7.40-7.33 (m, 5H), 6.76 (s, 1H), 5.73 (tdd, *J* = 7.0, 10.0, 17.0 Hz, H), 5.27 (app qd, *J* = 1.3, 17.0 Hz, 1H), 5.15 (app qd, *J* = 1.4, 10.0 Hz, 1H), 4.30 (bs, 1H), 3.65(bs, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 134.7, 134.4, 133.1, 130.6, 129.6, 129.1, 128.90, 128.85, 128.5, 127.6, 120.9, 51.6, 21.7; HRMS (EI) Calcd for $C_{18}H_{18}ClNO_2S$ $[M]^+$ 347.0741, found 347.0741.



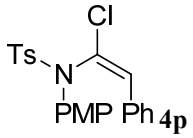
4n

colorless liquid (29.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.39-7.31 (m, 7H), 5.75-5.69 (m, 1H), 4.83 (d, *J* = 13.3 Hz, 1H), 3.94 (d, *J* = 13.4 Hz, 1H), 2.48 (s, 3H), 2.48-1.85 (m, 2H), 1.28-0.86 (m, 8H), 0.65 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.2, 138.1, 135.6, 134.5, 129.6, 128.43, 128.37, 128.2, 125.1, 51.3, 31.6, 29.5, 28.8, 28.2, 22.5, 21.7, 14.1; HRMS (EI) Calcd for $C_{22}H_{28}ClNO_2S$ $[M]^+$ 405.1524, found 405.1524.



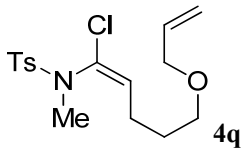
4o

pale yellow liquid (25.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 7.1 Hz, 2H) 7.38-7.31 (m, 5H), 6.77 (s, 1H), 3.56 (bs, 1H), 2.99 (bs, 1H), 1.59-1.56 (m, 2H), 1.52-1.50 (m, 2H), 0.81 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.4, 134.7, 134.4, 133.1, 129.6, 129.5, 129.1, 128.9, 128.5, 127.9, 48.3, 29.3, 21.6, 20.1, 13.6; HRMS (EI) Calcd for $C_{19}H_{22}ClNO_2S$ $[M]^+$ 363.1054, found 363.1054.



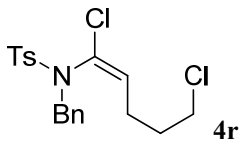
4p

yellow solid (34.3 mg); mp 122-126 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 7.2 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 9.1 Hz, 2H), 6.74 (s, 1H), 6.70 (d, *J* = 9.1 Hz, 2H), 3.73 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 144.4, 135.1, 133.0, 132.9, 131.6, 129.5, 129.2, 129.1, 128.9, 128.8, 128.6, 114.2, 55.4, 21.7; HRMS (EI) Calcd for $C_{22}H_{20}ClNO_3S$ $[M]^+$ 413.0847, found 413.0847.



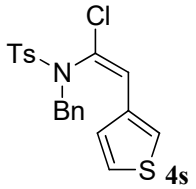
4q

colorless liquid (24.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 5.99-5.87 (m, 1H), 5.82 (t, *J* = 7.6 Hz, 1H), 5.28 (d, *J* = 17.2 Hz, 1H), 5.18 (d, *J* = 10.4 Hz, 1H), 3.97 (t, *J* = 4.8 Hz, 2H), 3.46 (t, *J* = 6.4 Hz, 2H), 2.92 (s, 3H), 2.44 (s, 3H), 2.44(m, 2H), 1.77-1.70 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.2, 134.9, 134.6, 134.4, 129.5, 128.5, 128.3, 116.8, 71.8, 69.6, 35.9, 28.6, 26.1, 21.6; HRMS (FAB) Calcd for $C_{16}H_{23}ClNO_3S$ $[M+H]^+$ 344.1082, found 344.1082.



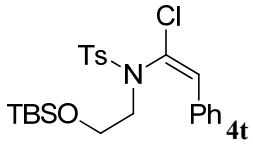
4r

white solid (29.2 mg); mp 98-102 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.38-7.30 (m, 7H), 5.72-5.67 (m, 1H), 4.82 (d, *J* = 13.2 Hz, 1H), 3.91 (d, *J* = 13.2 Hz, 1H), 3.19 (t, *J* = 6.8 Hz, 2H), 2.46 (s, 3H), 2.17-1.96 (m, 2H), 1.54-1.48 (m, 1H), 1.19-1.10 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.4, 135.9, 135.4, 134.4, 129.7, 128.7, 128.6, 128.4, 128.4, 126.5, 51.3, 44.0, 31.2, 26.9, 21.7; HRMS (FAB) Calcd for $C_{19}H_{22}Cl_2NO_2S$ $[M+H]^+$ 398.0743, found 398.0743.



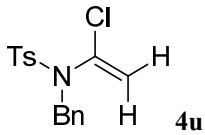
4s

white solid (37.2 mg); mp 110-112 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.3 Hz, 2H), 7.37-7.35 (m, 3H), 7.25-7.23 (m, 3H), 7.15-7.13 (m, 4H), 6.61 (s, 1H), 4.82 (d, *J* = 13.0 Hz, 1H), 3.99 (d, *J* = 13.0 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 134.8, 134.1, 133.4, 129.72, 129.66, 129.5, 128.9, 128.3, 128.2, 127.7, 126.5, 126.2, 125.0, 52.3, 21.7; HRMS (EI) Calcd for $C_{20}H_{18}ClNO_2S_2$ $[M]^+$ 403.0462, found 403.0462.



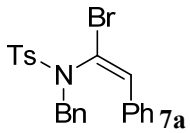
4t

sticky white liquid (36.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 6.8 Hz, 2H), 7.35-7.28 (m, 5H), 6.74 (s, 1H), 3.76 (d, *J* = 10.0 Hz, 1H), 3.71-3.62 (m, 2H), 3.22 (d, *J* = 9.6 Hz, 1H), 2.43 (s, 3H), 0.80 (s, 9H), -0.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 135.0, 134.3, 133.3, 129.7, 129.4, 128.99, 128.96, 128.6, 128.1, 60.5, 50.6, 26.0, 21.8, 18.4, -5.4; HRMS (FAB) Calcd for $C_{23}H_{33}ClNO_3SSi$ $[M+H]^+$ 466.1633, found 466.1634.



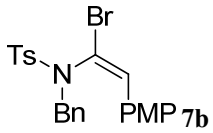
4u

colorless liquid (13.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.36-7.31 (m, 7H), 5.43 (d, *J* = 1.5 Hz, 1H), 5.31 (d, *J* = 1.5 Hz, 1H), 4.50 (s, 2H) , 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.4, 135.4, 134.8, 133.7, 129.7, 128.9, 128.5, 128.1, 128.1, 120.3, 51.2, 29.7, 21.7; HRMS (FAB) Calcd for $C_{16}H_{17}ClNO_2S$ $[M+H]^+$ 322.0663, found 322.0663.



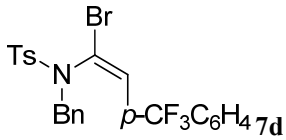
7a

white solid (37.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.2 Hz, 2H), 7.36-7.29 (m, 5H), 7.20-7.11 (m, 5H), 6.82 (s, 1H), 4.83 (d, *J* = 13.0 Hz, 1H), 3.94 (d, *J* = 13.0 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.8, 139.8, 134.3, 133.5, 133.2, 129.9, 129.6, 129.2, 128.7, 128.6, 128.3, 128.2, 128.0, 119.7, 53.4, 21.8; HRMS (FAB) Calcd for $C_{22}H_{21}BrNO_2S$ $[M+H]^+$ 442.0471, found 442.0471.



7b

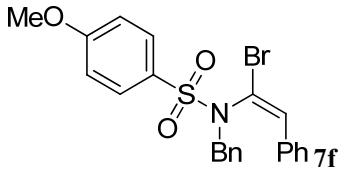
white solid (31.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.3 Hz, 2H), 7.36-7.28 (m, 6H), 7.16-7.12 (m, 3H), 6.73 (s, 1H), 6.72 (d, *J* = 8.9 Hz, 2H), 4.84 (d, *J* = 13.1 Hz, 1H), 3.94 (d, *J* = 13.0 Hz, 1H), 3.78 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 144.7, 139.2, 134.4, 133.4, 130.4, 129.9, 129.6, 129.2, 1128.3, 128.2, 126.4, 117.5, 113.5, 55.2, 53.3, 21.7; HRMS (FAB) Calcd for $C_{23}H_{23}BrNO_3S$ $[M+H]^+$ 472.0577, found 472.0577.



7d

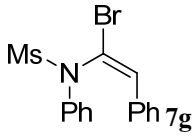
pale yellow sticky solid (40.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.41-7.31 (m, 7H),

7.24-7.11 (m, 4H), 6.86 (s, 1H), 4.84 (d, J = 13.1 Hz, 1H), 3.93 (d, J = 13.1 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.0, 138.4, 137.0 (q, $^4J_{CF}$ = 2 Hz), 134.1, 133.0, 129.9, 129.7, 129.2, 129.1, 128.7, 128.6, 128.5 (q, $^2J_{CF}$ = 32 Hz), 128.3, 124.9 (q, $^3J_{CF}$ = 4 Hz), 123.7 (q, $^1J_{CF}$ = 334 Hz), 53.4, 21.7; HRMS (FAB) Calcd for $C_{23}H_{20}BrF_3NO_2S$ $[M+H]^+$ 510.0345, found 510.0346.



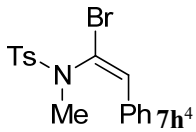
7f

white solid (38.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, J = 7.8 Hz, 2H), 7.38-7.27 (m, 4H), 7.24-7.10 (m, 6H), 7.00 (d, J = 7.8 Hz, 2H), 6.81 (s, 1H), 4.82 (d, J = 13.0 Hz, 1H), 3.93 (d, J = 13.1 Hz, 1H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.9, 139.7, 133.6, 133.3, 131.4, 129.9, 128.74, 128.69, 128.62, 128.3, 128.2, 128.1, 119.9, 114.1, 55.7, 53.4; HRMS (FAB) Calcd for $C_{22}H_{21}BrNO_2S$ $[M+H]^+$ 458.0420, found 458.0420.



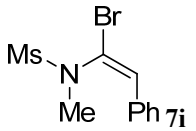
7g

pale yellow sticky solid (30.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.54 (m, 4H), 7.36-7.27 (m, 6H), 7.07 (s, H), 3.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.9, 138.6, 133.4, 129.6, 129.2, 128.7, 128.6, 127.5, 123.8, 118.0, 39.1; HRMS (FAB) Calcd for $C_{15}H_{15}BrNO_2S$ $[M+H]^+$ 352.0001, found 352.0001.



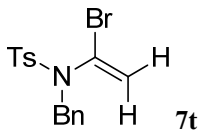
7h[4]

white solid (32.2 mg); E/Z = 1.8/1; ^{1}H NMR (400 MHz, $CDCl_3$) for only E isomer : δ 7.79-7.75 (m, 2H), 7.60-7.58 (m, 2H), 7.39-7.29 (m, 5H), 6.86 (s, H), 2.99 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for E/Z mixture : δ 137.1, 134.2, 134.0, 133.83, 133.77, 133.66, 129.6, 129.5, 129.3, 129.1, 129.0, 128.8, 128.7, 128.5, 128.2, 121.4, 120.5, 37.0, 36.7, 21.7; 1D-NOE experiments were conducted to support the (E)-geometry of the major isomer.



7i

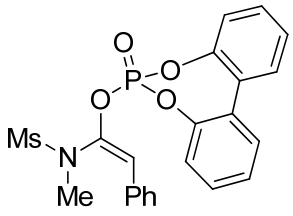
pale yellow sticky solid (22.3 mg); E/Z = 1.3/1; ^{1}H NMR (400 MHz, $CDCl_3$) for only E isomer : δ 7.57 (d, J = 8.0 Hz, 2H), 7.41-7.29 (m, 3H), 6.89 (s, H), 3.09 (s, 3H), 2.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for E/Z mixture : δ 137.3, 135.0, 133.5, 133.4, 129.3, 129.2, 129.0, 128.8, 128.7, 128.3, 120.5, 119.6, 37.4, 37.2, 37.1, 36.5; HRMS (FAB) Calcd for $C_{10}H_{13}BrNO_2S$ $[M+H]^+$ 289.9845, found 289.9845.



7t

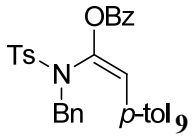
white solid (27.8 mg); mp 124-128 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J = 8.3 Hz, 2H), 7.36-7.29 (m, 7H), 5.72 (d, J = 1.3 Hz, 1H), 5.51 (d, J = 1.3 Hz, 1H), 4.47 (s, 2H) , 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$):

δ 144.5, 135.0, 134.7, 129.7, 129.0, 128.6, 128.3, 128.1, 125.3, 124.8, 52.2, 21.7; HRMS (FAB) Calcd for $C_{16}H_{17}BrNO_2S$ $[M+H]^+$ 366.0158, found 366.0158.



8

pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.49 (m, 6H), 7.46-7.30 (m, 7H), 3.17 (s, 3H), 2.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.5 (d, J_{CP} = 9.5 Hz), 139.7 (d, J_{CP} = 8.7 Hz), 131.4, 130.4, 130.2, 128.8, 128.70, 128.69, 128.0, 127.0, 121.4 (d, J_{CP} = 4.8 Hz), 117.7 (d, J_{CP} = 3.8 Hz), 39.0, 35.8; ^{31}P NMR (162 MHz, $CDCl_3$): δ 5.00; HRMS (FAB) Calcd for $C_{22}H_{21}NO_6PS$ $[M+H]^+$ 458.0822, found 458.0822.

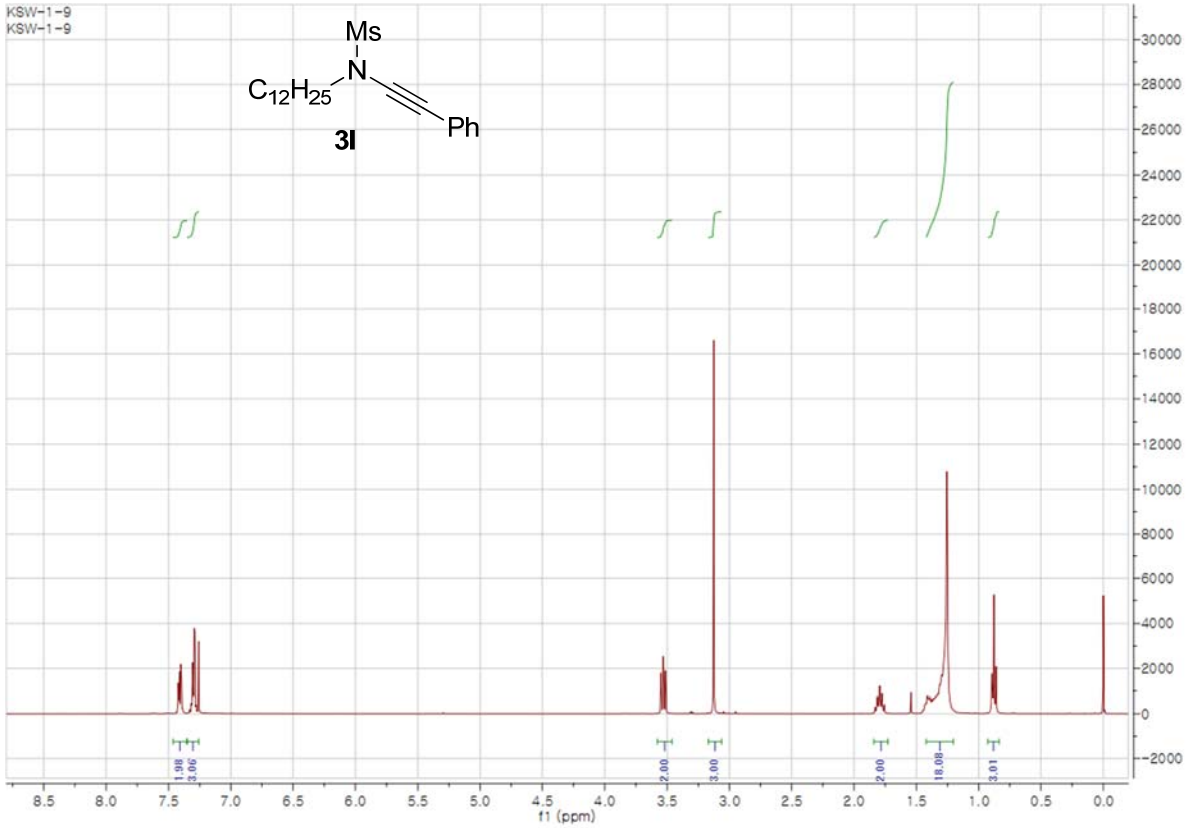


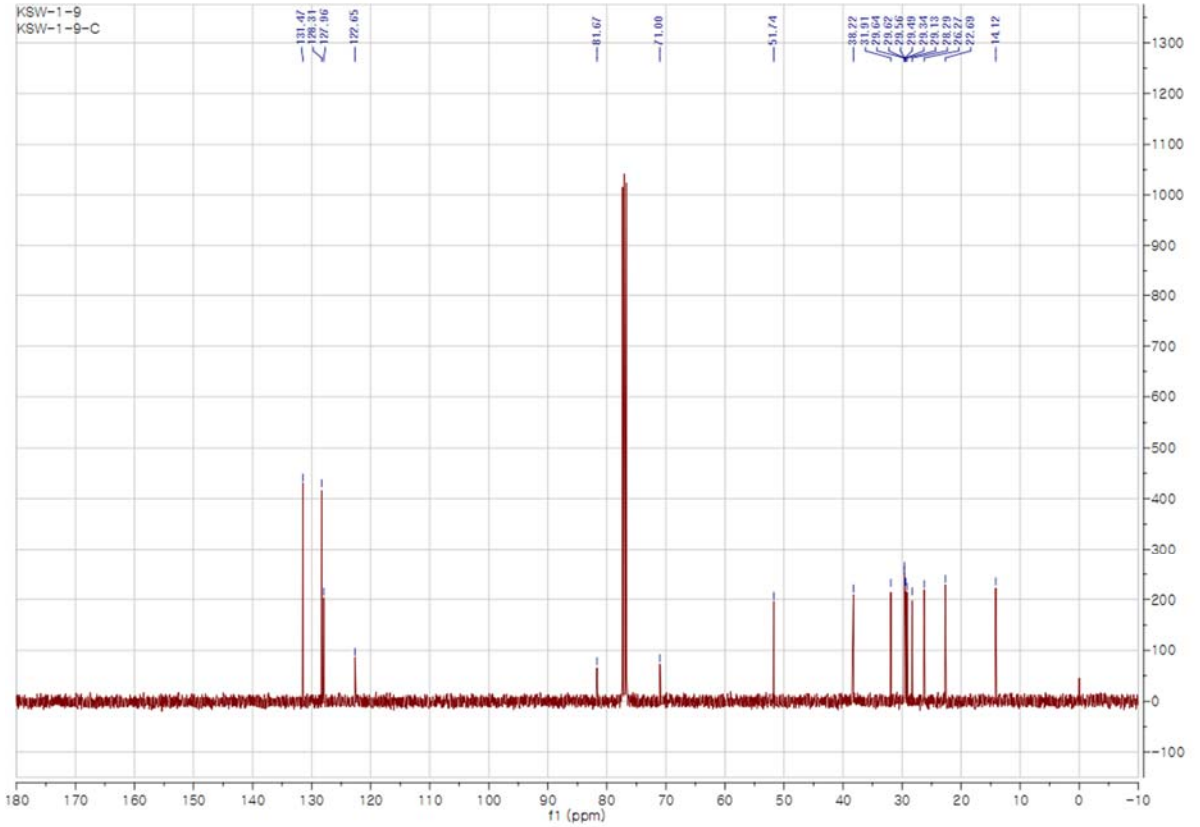
9

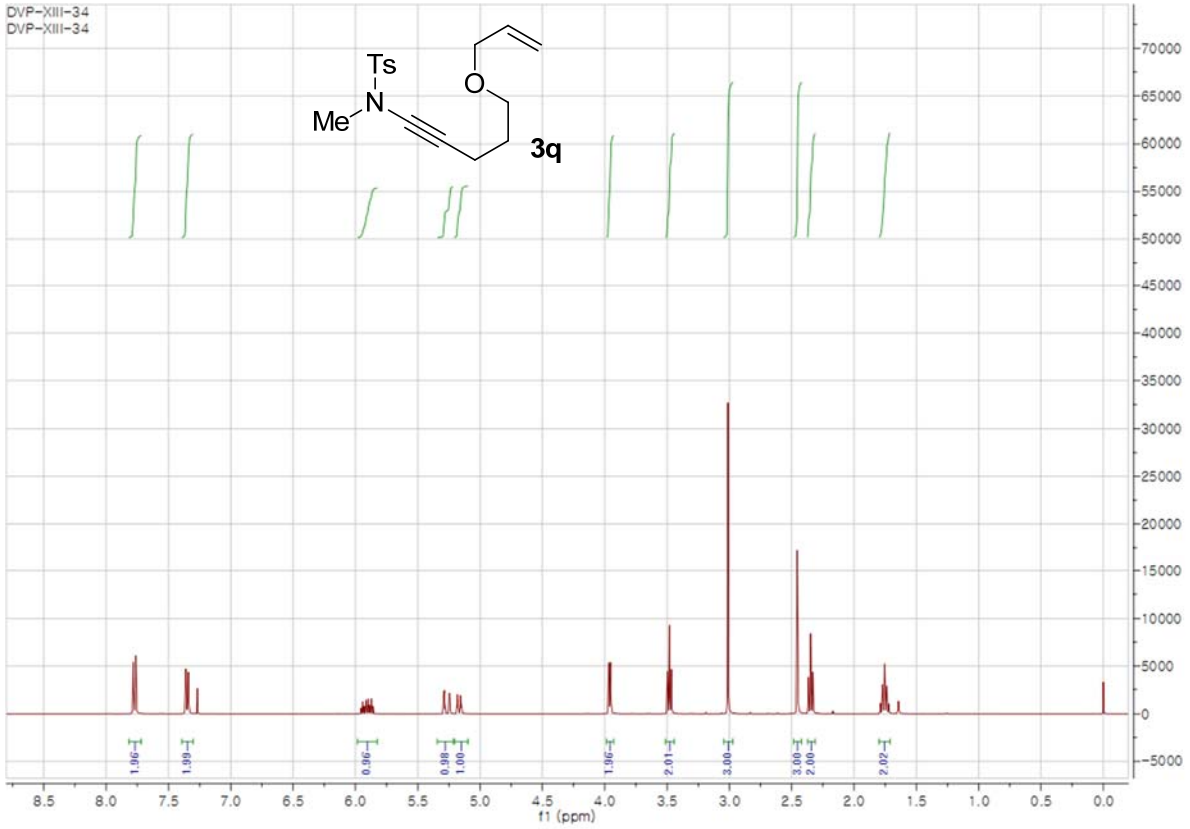
colorless to white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.70 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.57 (tt, *J* = 7.2, 1.2 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.27-7.23 (m, 4H), 7.18-7.11 (m, 5H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.47 (s, 1H), 4.51 (s, 2H), 2.33 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.0, 143.8, 138.0, 136.8, 136.3, 134.6, 133.6, 130.0, 129.7, 129.5, 129.1, 128.9, 128.7, 128.3, 128.2, 128.1, 128.0, 123.4, 52.8, 21.5, 21.3; HRMS (FAB) Calcd for $C_{30}H_{28}NO_4S$ $[M+H]^+$ 498.1734, found 498.1734.

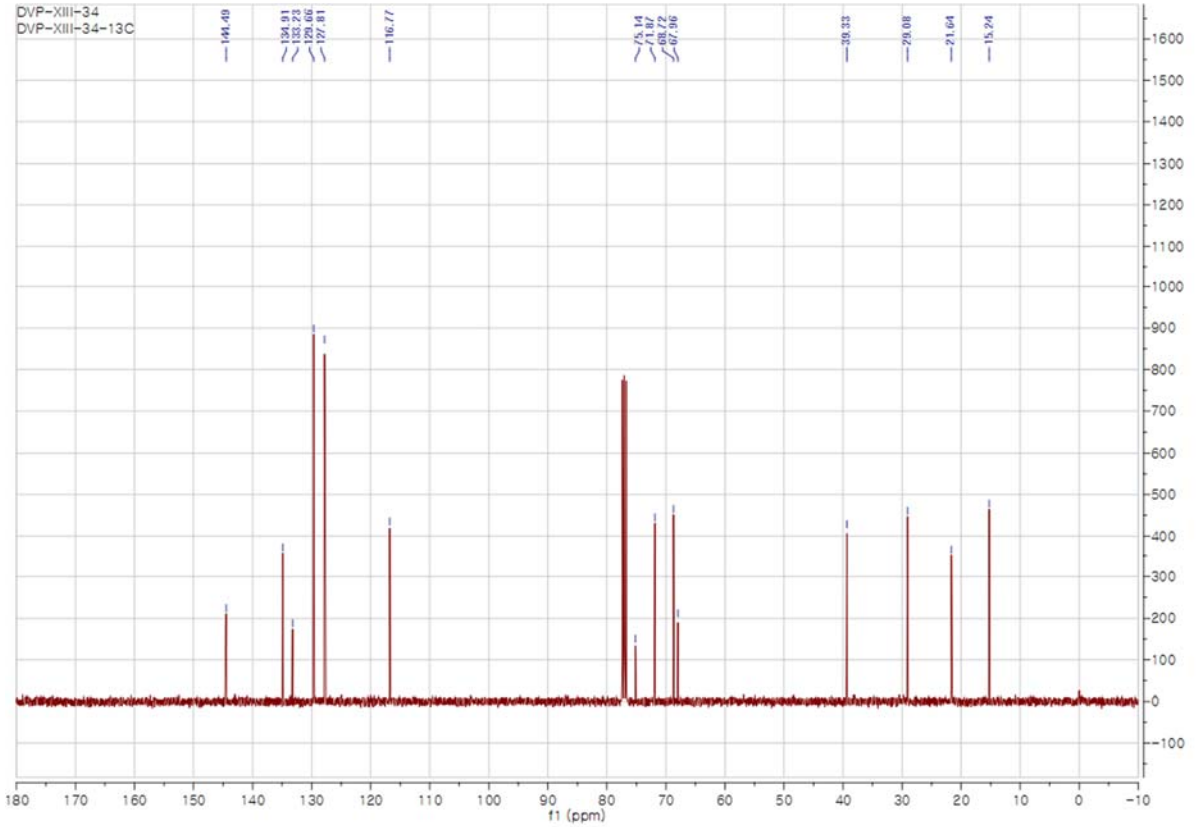
Appendix

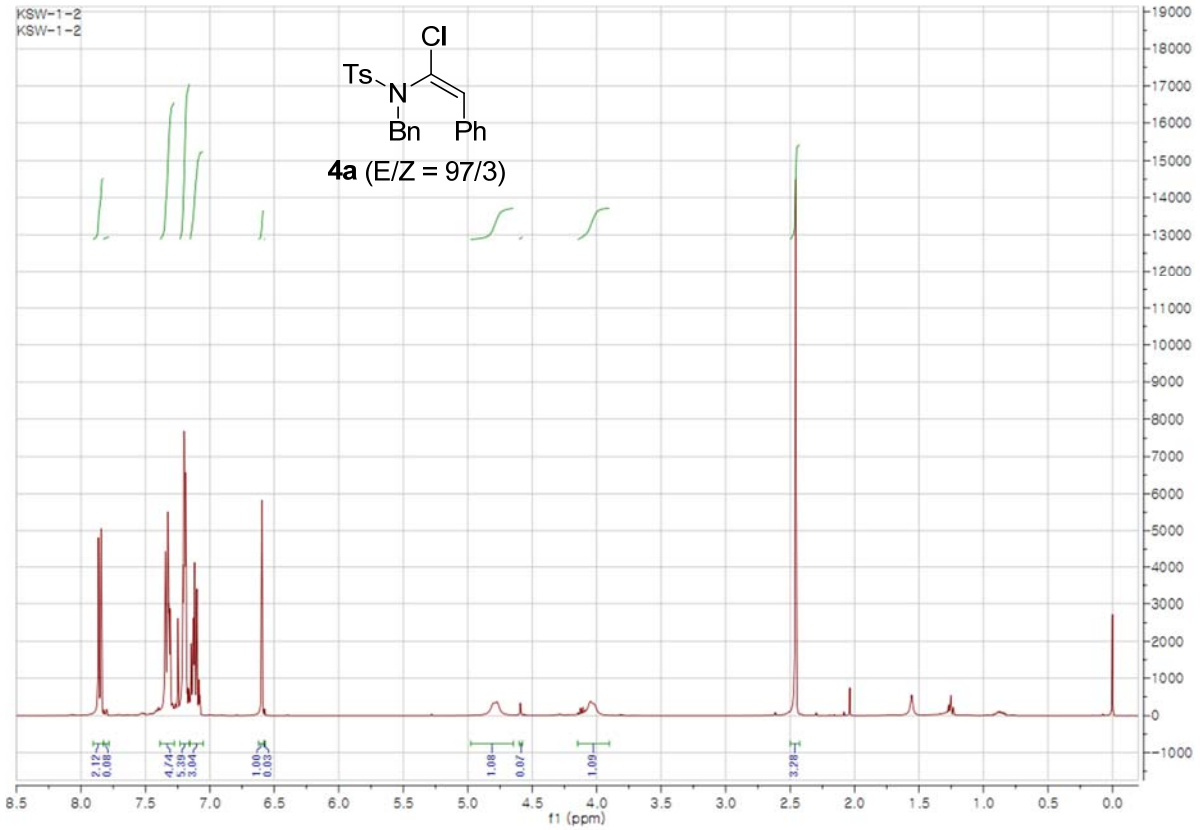
^{1}H and ^{13}C NMR spectra for all new compounds

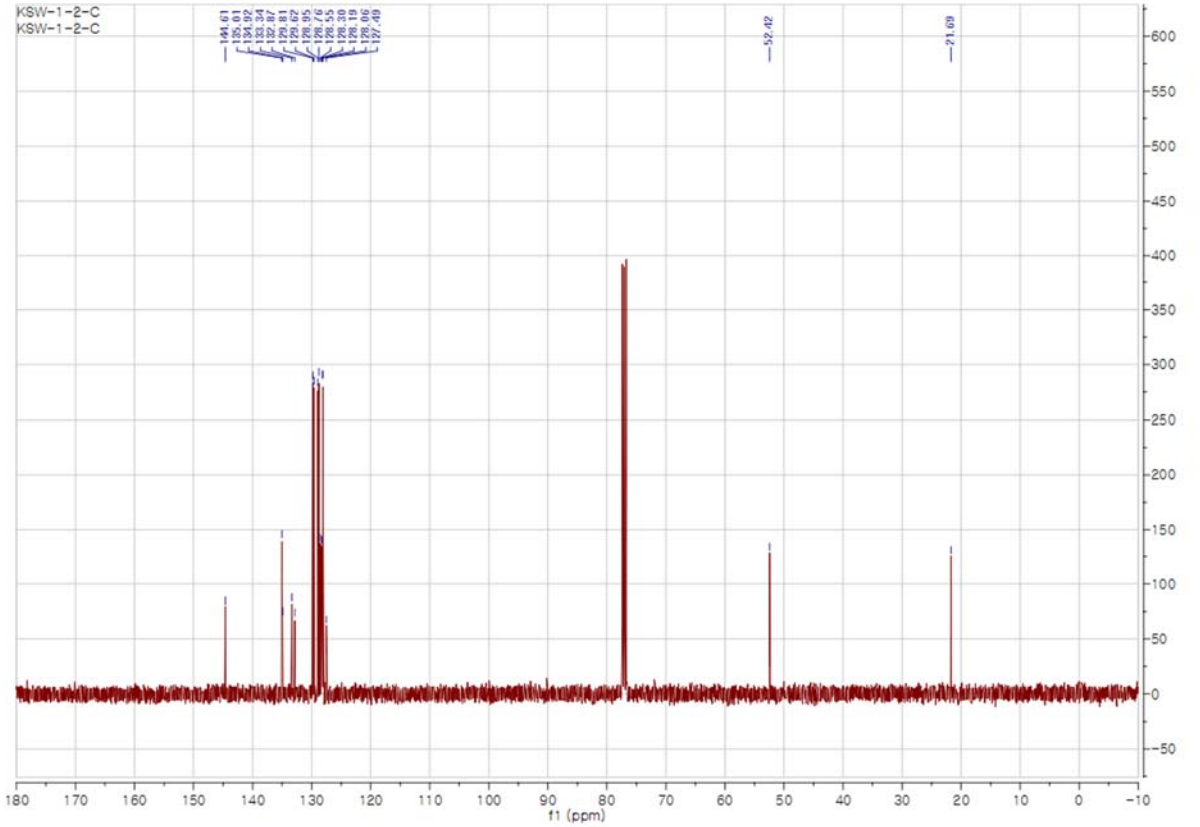

KSW-1-9
KSW-1-9
Ms
N
C12H25
Ph
3l
f1 (ppm)

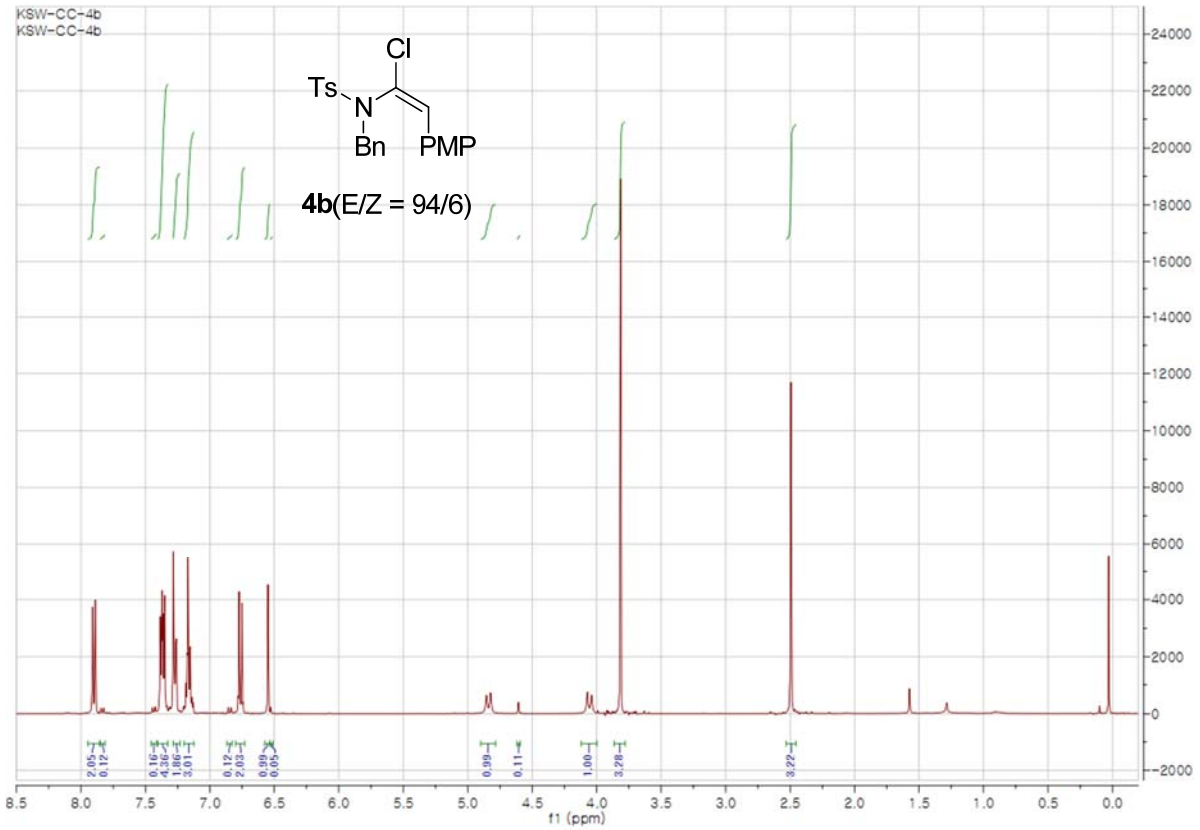

KSW-1-9
KSW-1-9-C
131.47
129.31
127.96
122.65
81.67
71.00
51.74
38.22
31.91
29.64
29.62
29.56
29.49
29.34
29.13
28.29
26.27
22.69
14.12
f1 (ppm)

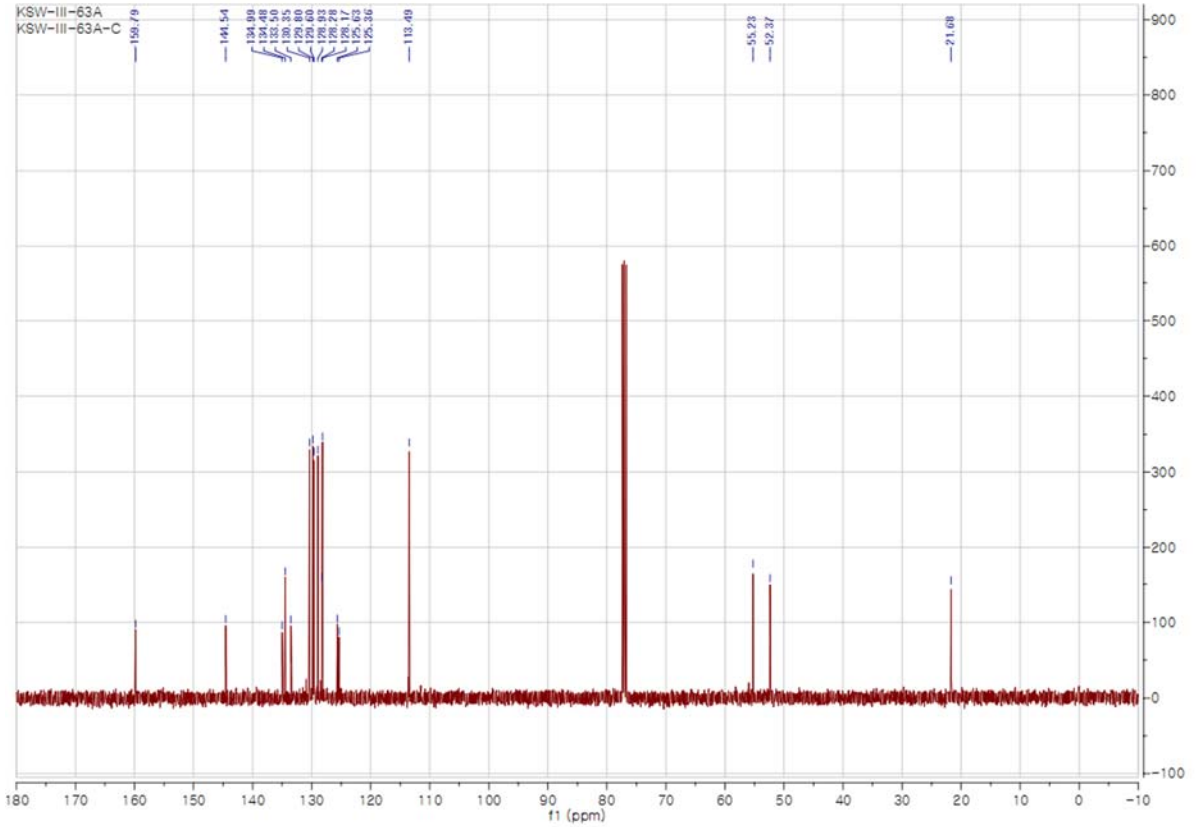

DVP-XIII-34
DVP-XIII-34
Ts
N
Me
O
3q
f1 (ppm)

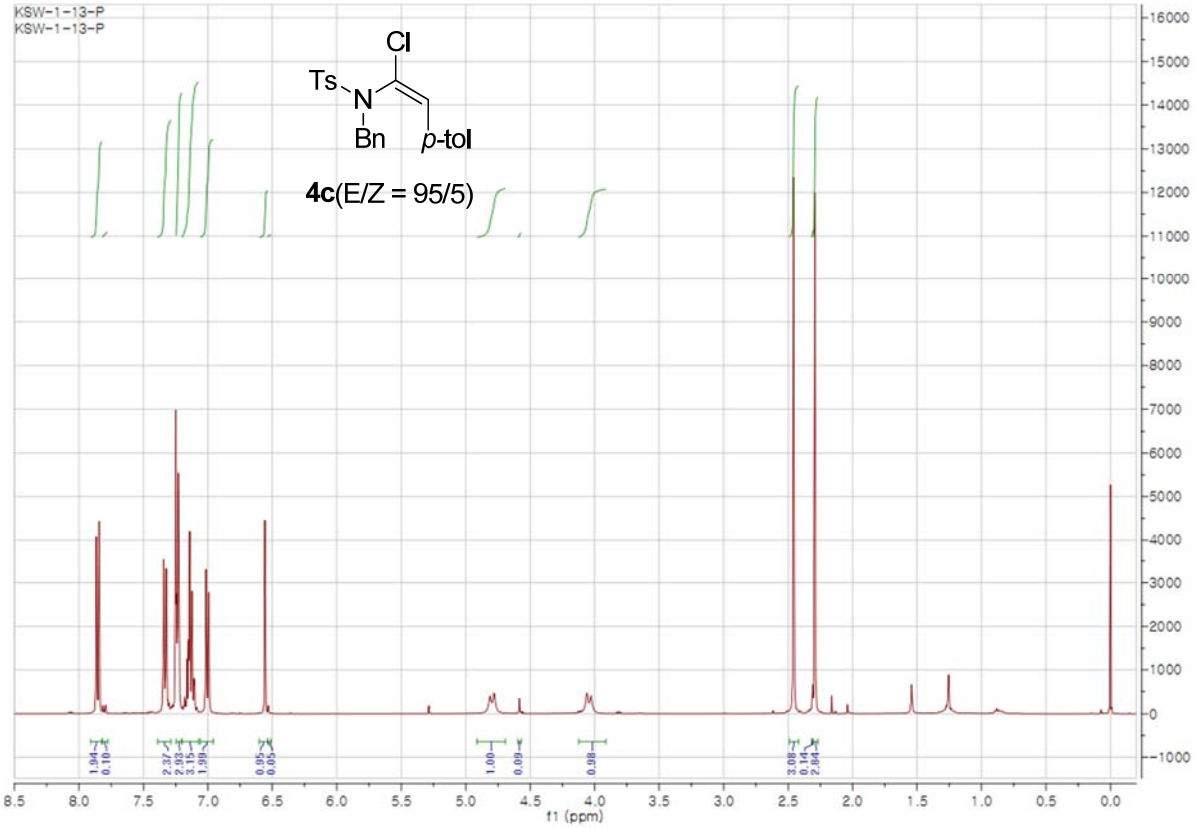

DVP-XIII-34
DVP-XIII-34-13C
144.49
134.91
133.23
129.66
127.81
116.77
75.14
71.97
68.72
67.96
39.33
29.08
21.64
15.24
f1 (ppm)

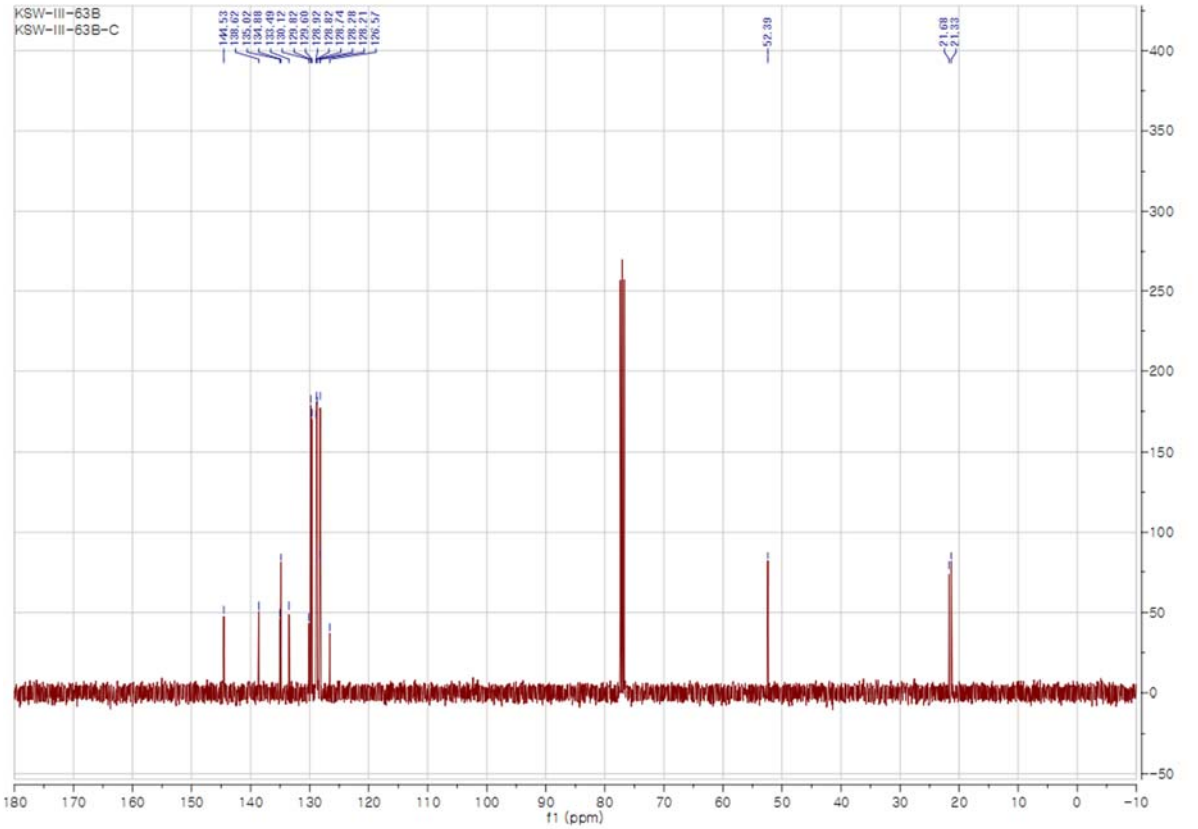

KSW-1-2
KSW-1-2
Cl
Ts
N
Bn
Ph
4a (E/Z = 97/3)
f1 (ppm)

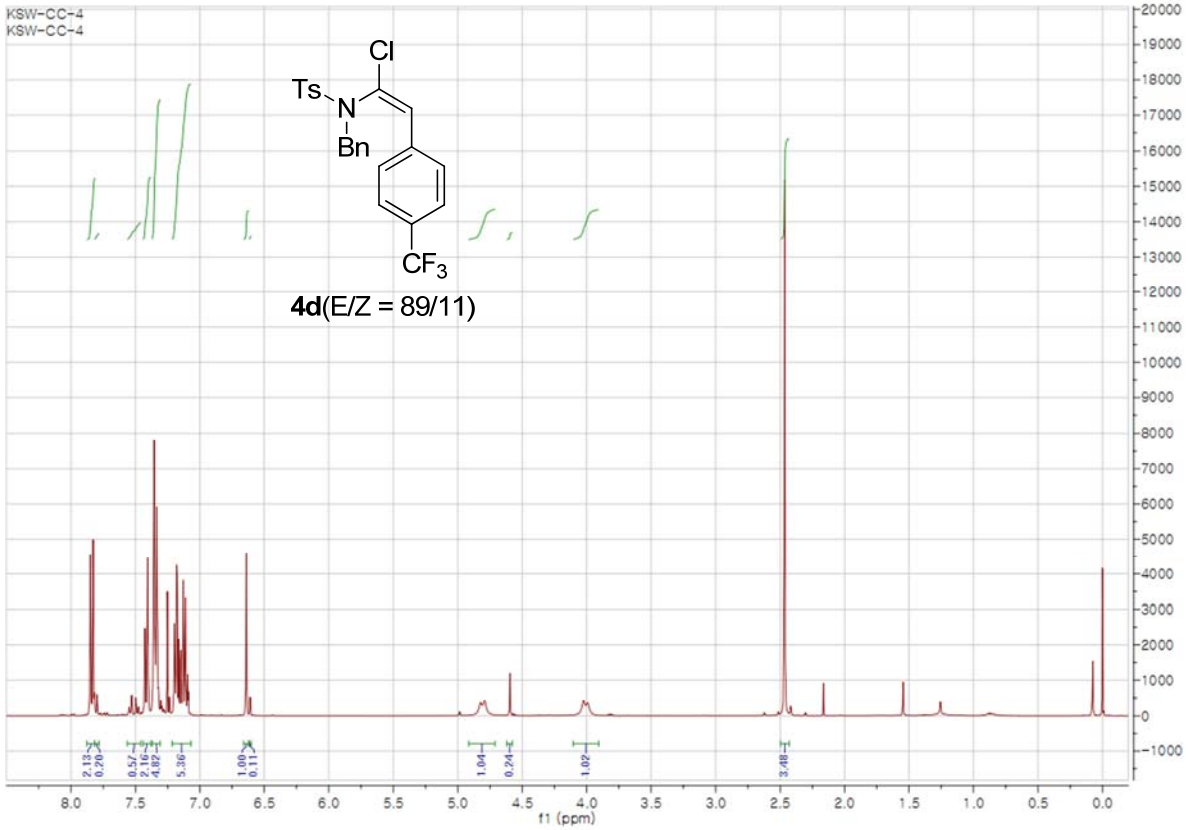

KSW-1-2-C
KSW-1-2-C
144.61
135.01
134.92
133.34
132.87
129.81
129.62
128.95
128.76
128.55
128.30
128.19
128.06
127.49
52.42
21.69
f1 (ppm)

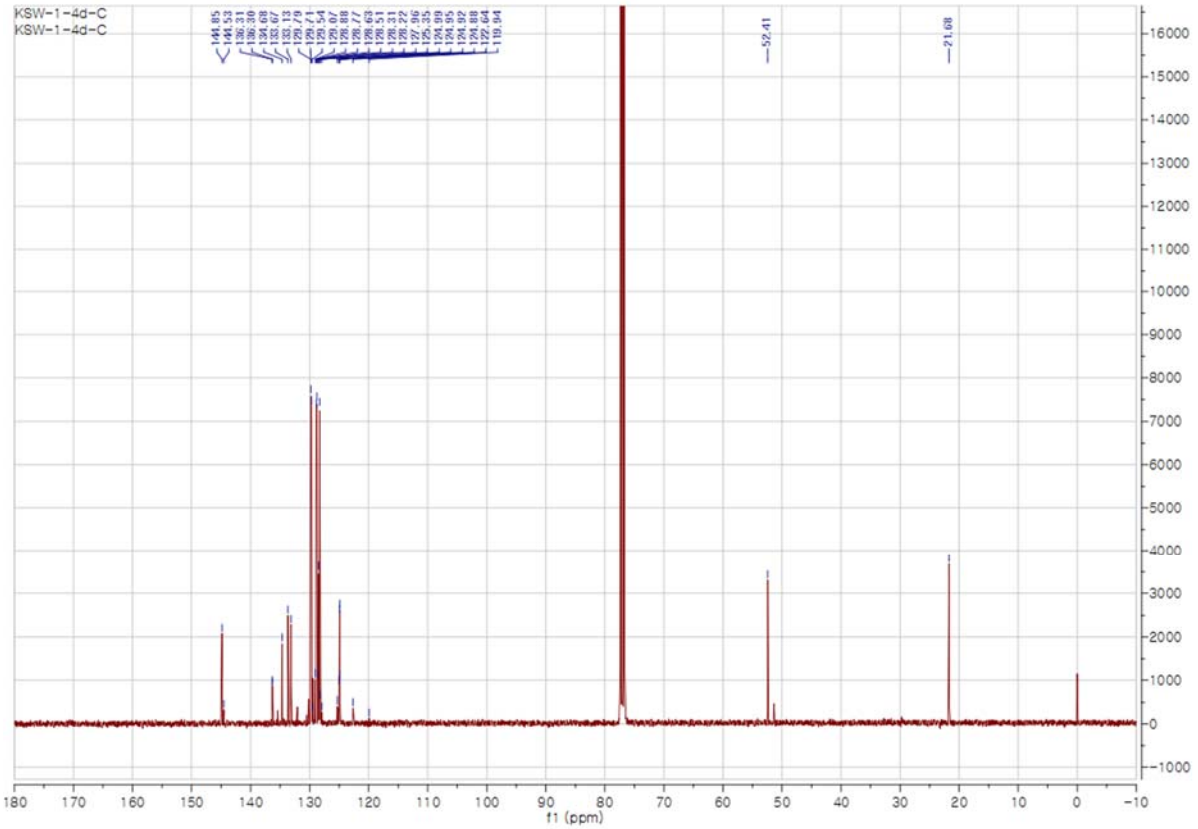

KSW-CC-4b
KSW-CC-4b
Cl
Ts
N
Bn
PMP
4b(E/Z = 94/6)
f1 (ppm)

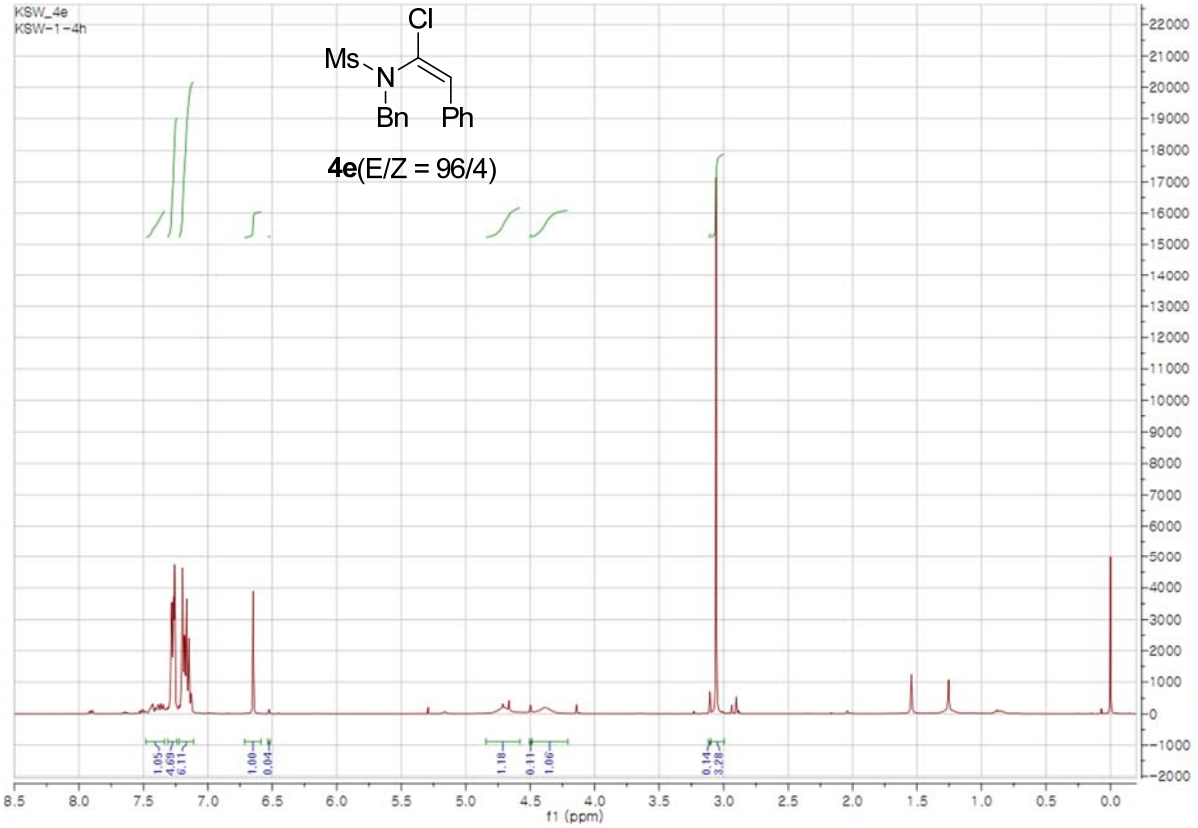

KSW-III-63A
KSW-III-63A-C
159.79
144.54
134.99
134.48
133.50
130.85
129.80
129.60
128.93
128.28
126.17
125.63
125.36
113.49
55.23
52.37
21.68
f1 (ppm)

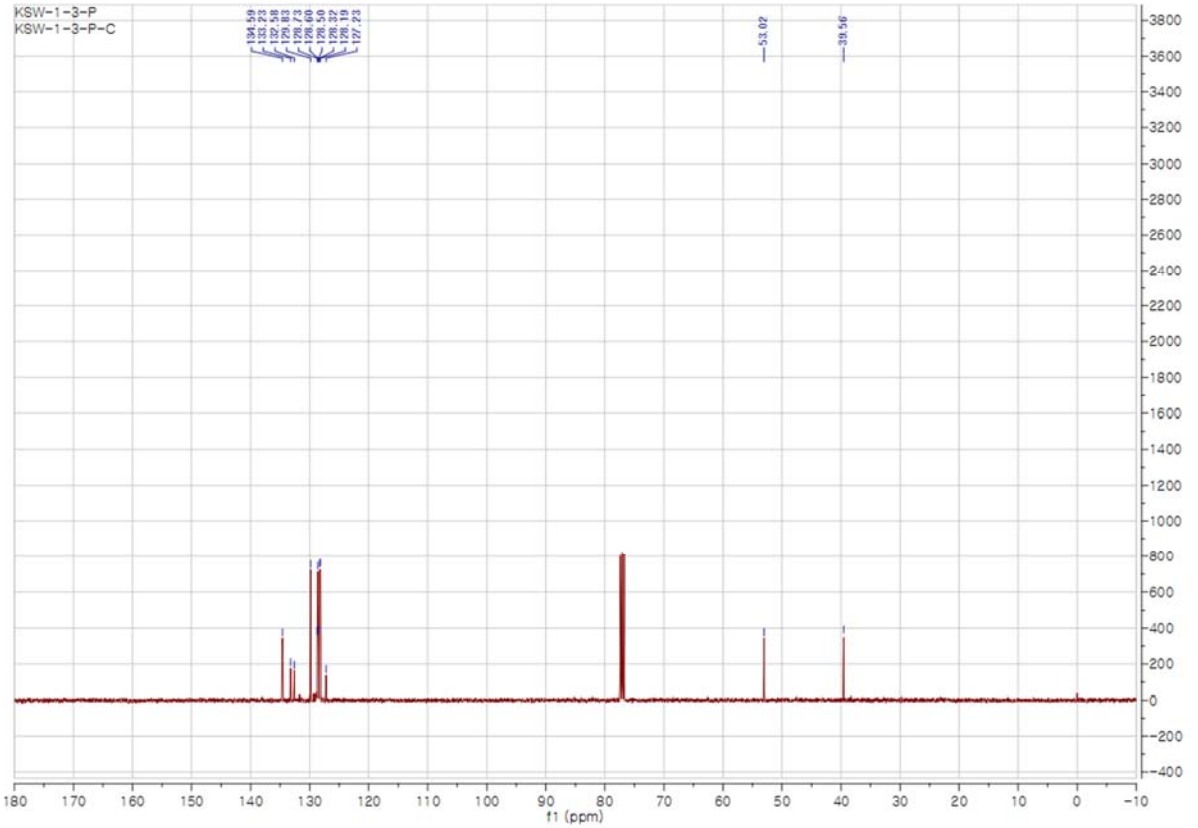

KSW-1-13-P
KSW-1-13-P
Cl
Ts
N
Bn
p-tol
4c(E/Z = 95/5)
f1 (ppm)

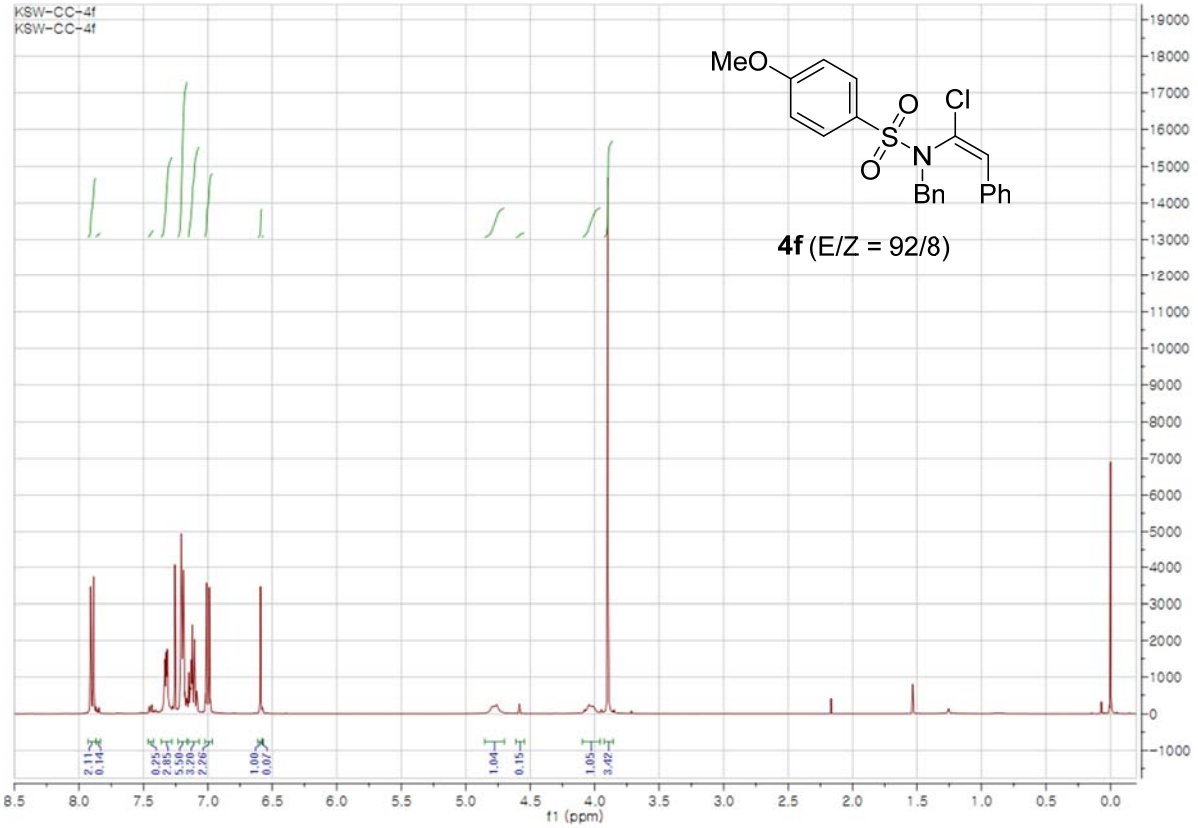

KSW-III-63B
KSW-III-63B-C
f1 (ppm)

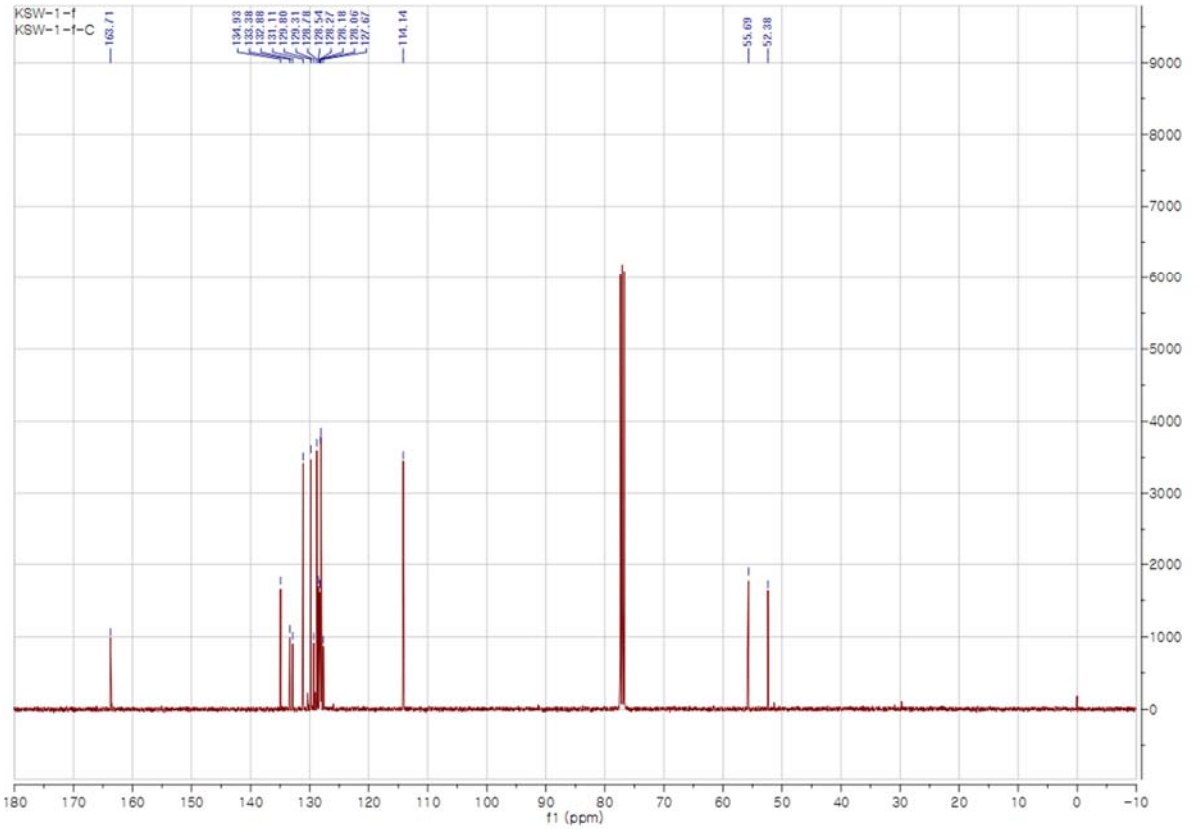

KSW-CC-4
KSW-CC-4
Cl
Ts
N
Bn
CF3
4d(E/Z = 89/11)
f1 (ppm)

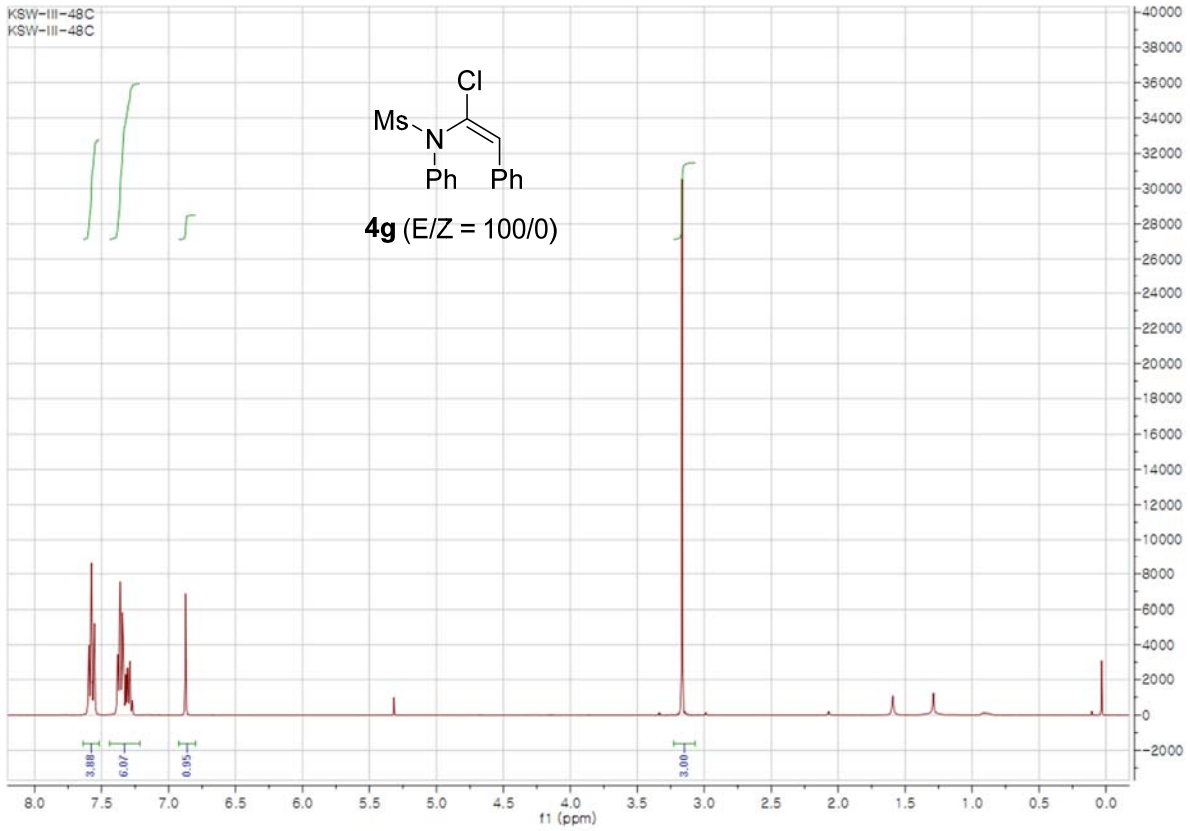

KSW-1-4d-C
KSW-1-4d-C
52.41
21.68
f1 (ppm)

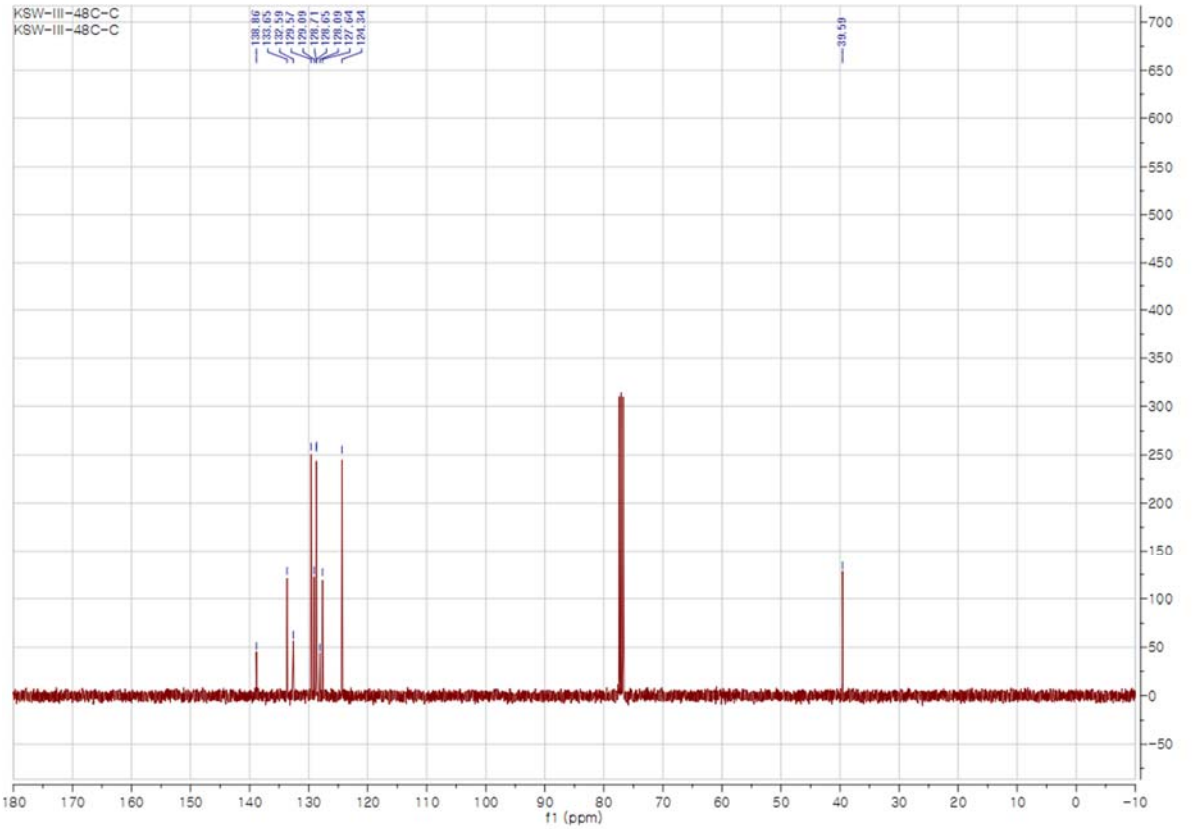

KSW_4e
KSW-1-4h
Cl
Ms
N
Bn
Ph
4e(E/Z = 96/4)
f1 (ppm)

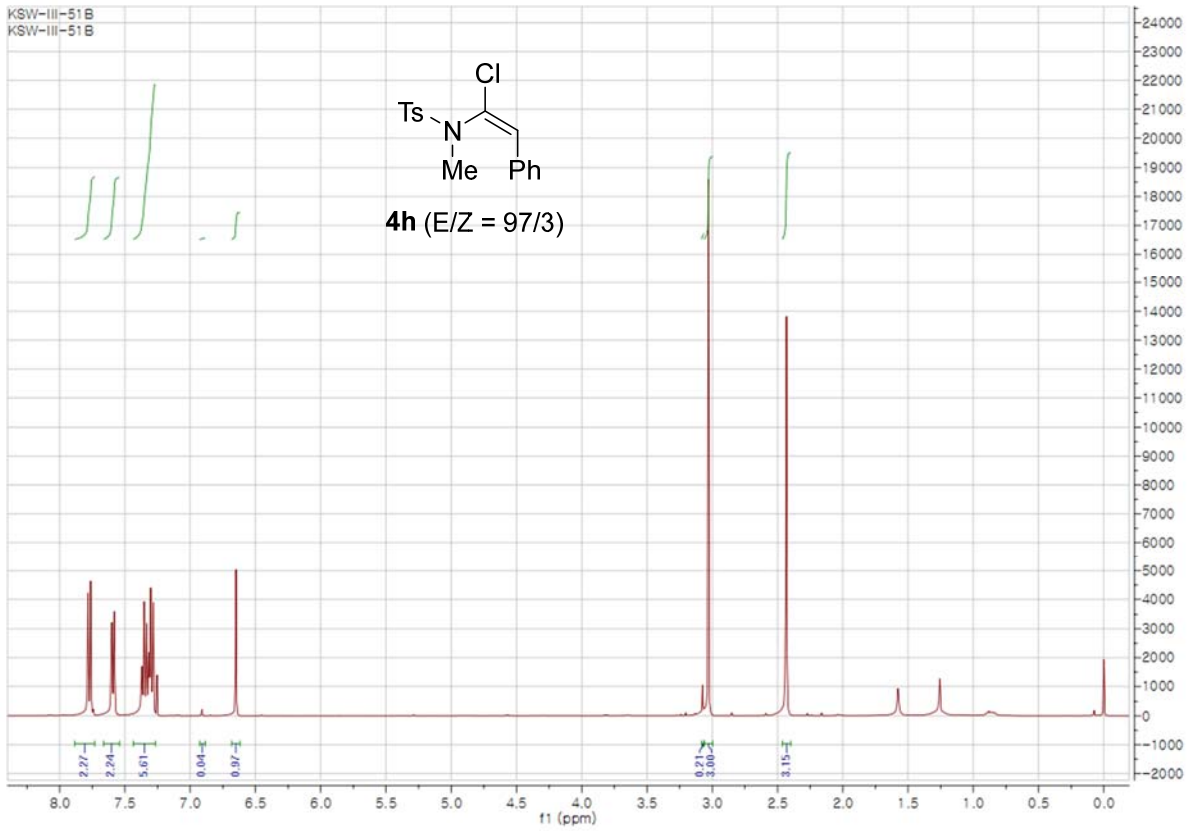

KSW-1-3-P
KSW-1-3-P-C
134.59
133.23
132.58
129.83
129.42
128.69
128.50
128.32
128.19
127.23
53.02
39.56
f1 (ppm)

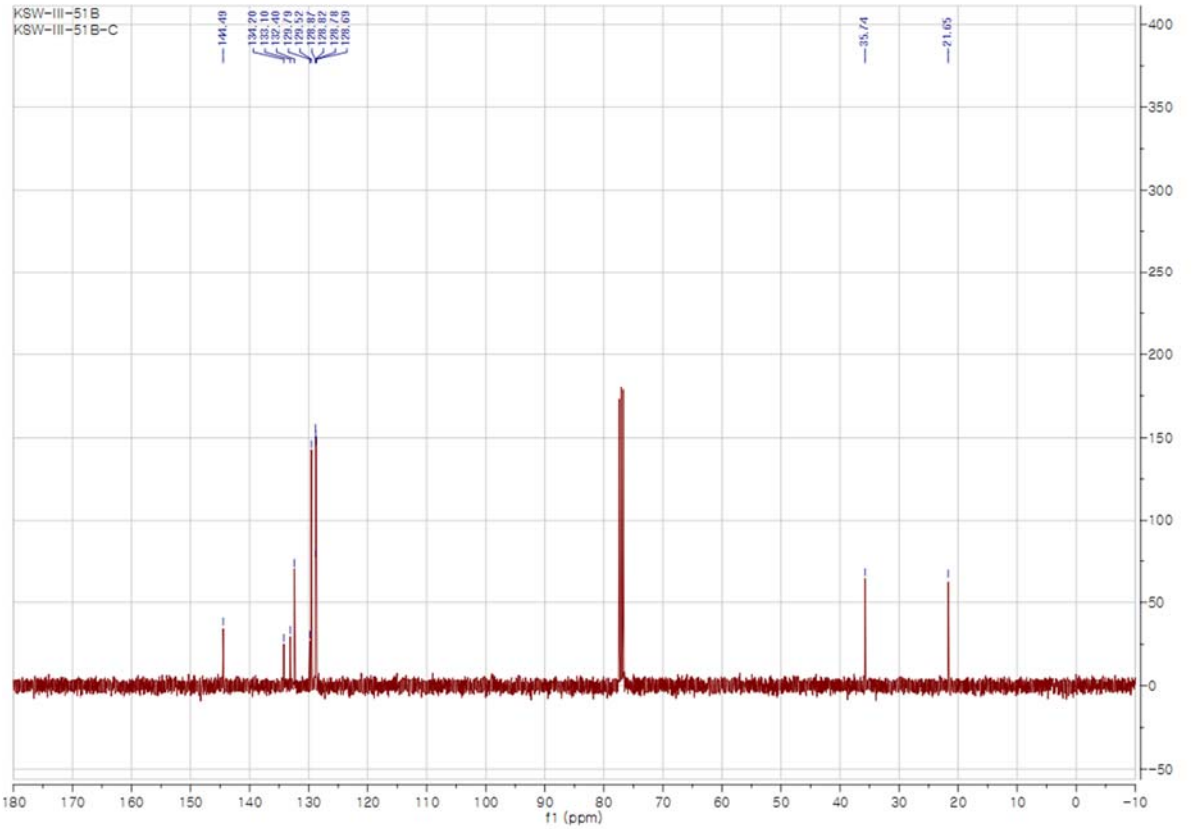

KSW-CC-4f
KSW-CC-4f
MeO
O
Cl
S
N
O
Bn
Ph
4f (E/Z = 92/8)
f1 (ppm)

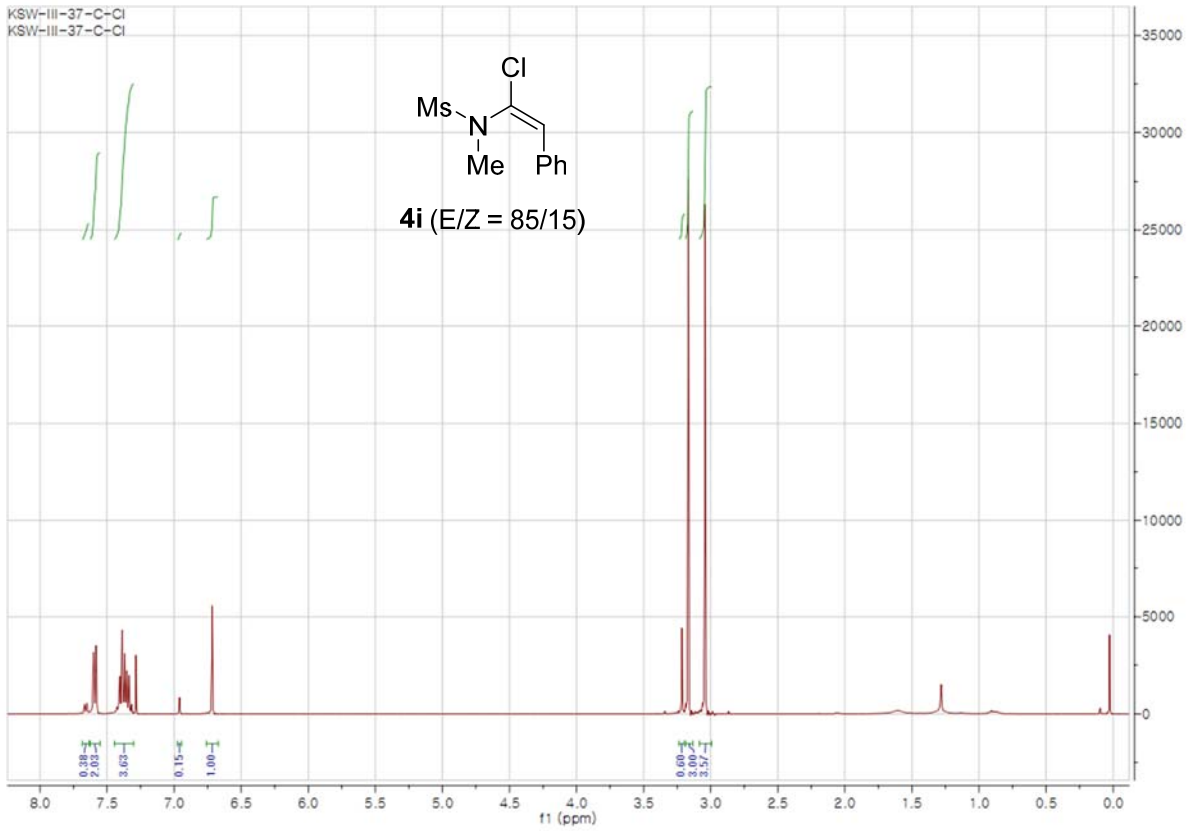

KSW-1-f
KSW-1-f-C
163.71
134.93
133.38
132.88
131.11
129.69
129.31
128.78
128.54
128.27
128.18
128.05
127.67
114.14
55.69
52.38
f1 (ppm)

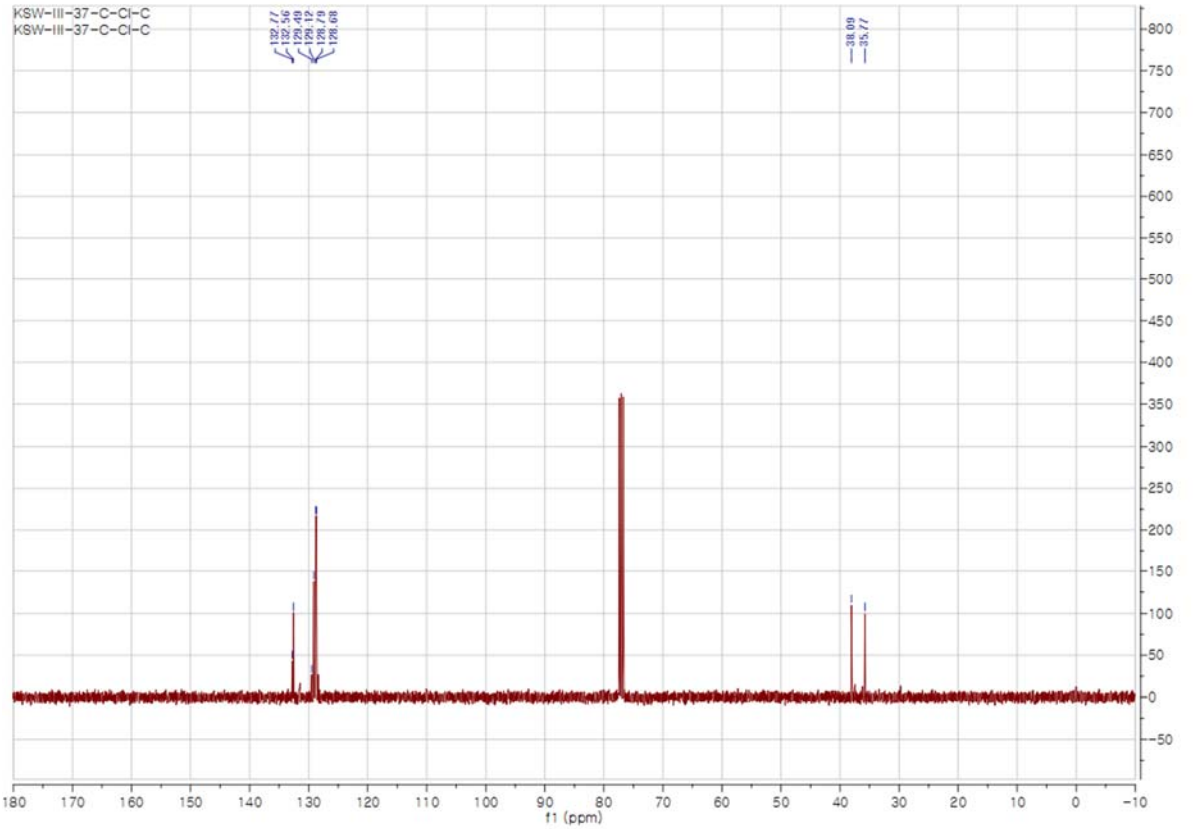

KSW-III-48C
KSW-III-48C
Cl
Ms
N
Ph
Ph
4g (E/Z = 100/0)
3.88
6.07
0.95
3.00
f1 (ppm)

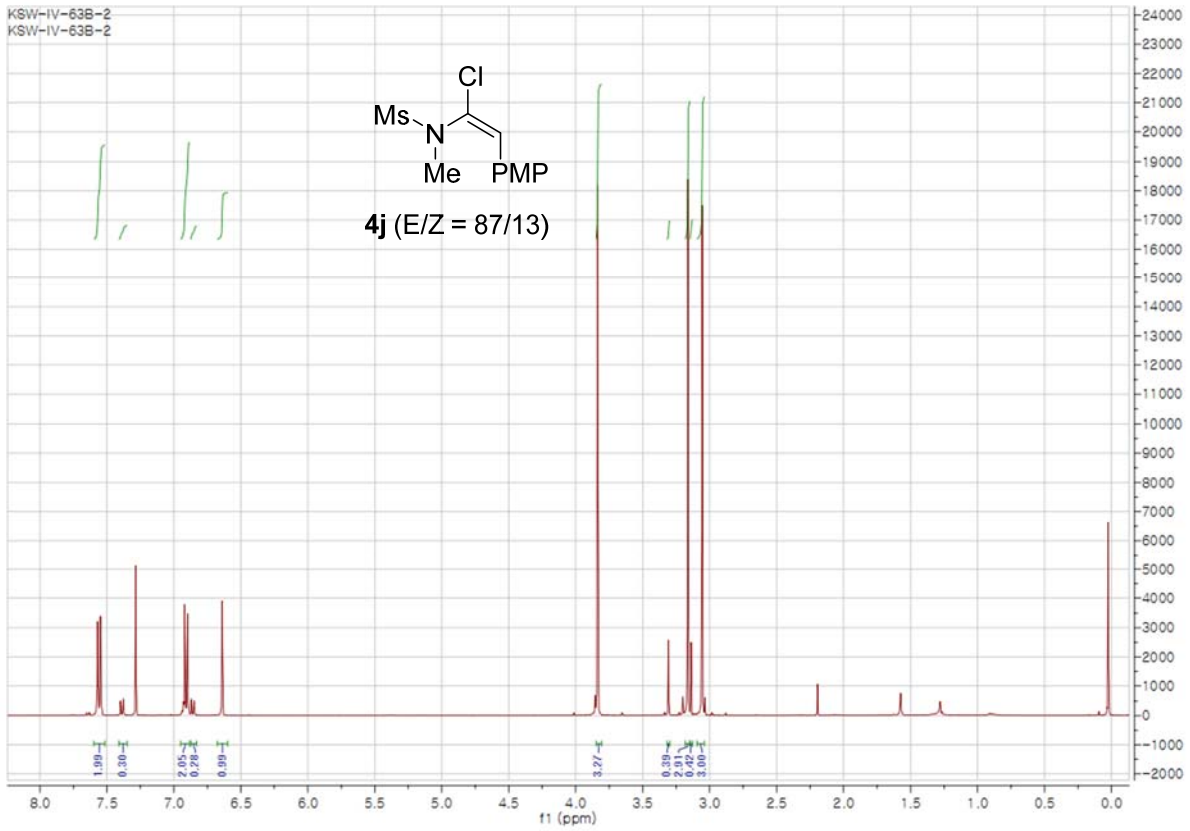

KSW-III-48C-C
KSW-III-48C-C
138.86
135.65
132.59
129.57
129.09
128.71
128.65
128.09
127.64
124.34
39.59
f1 (ppm)

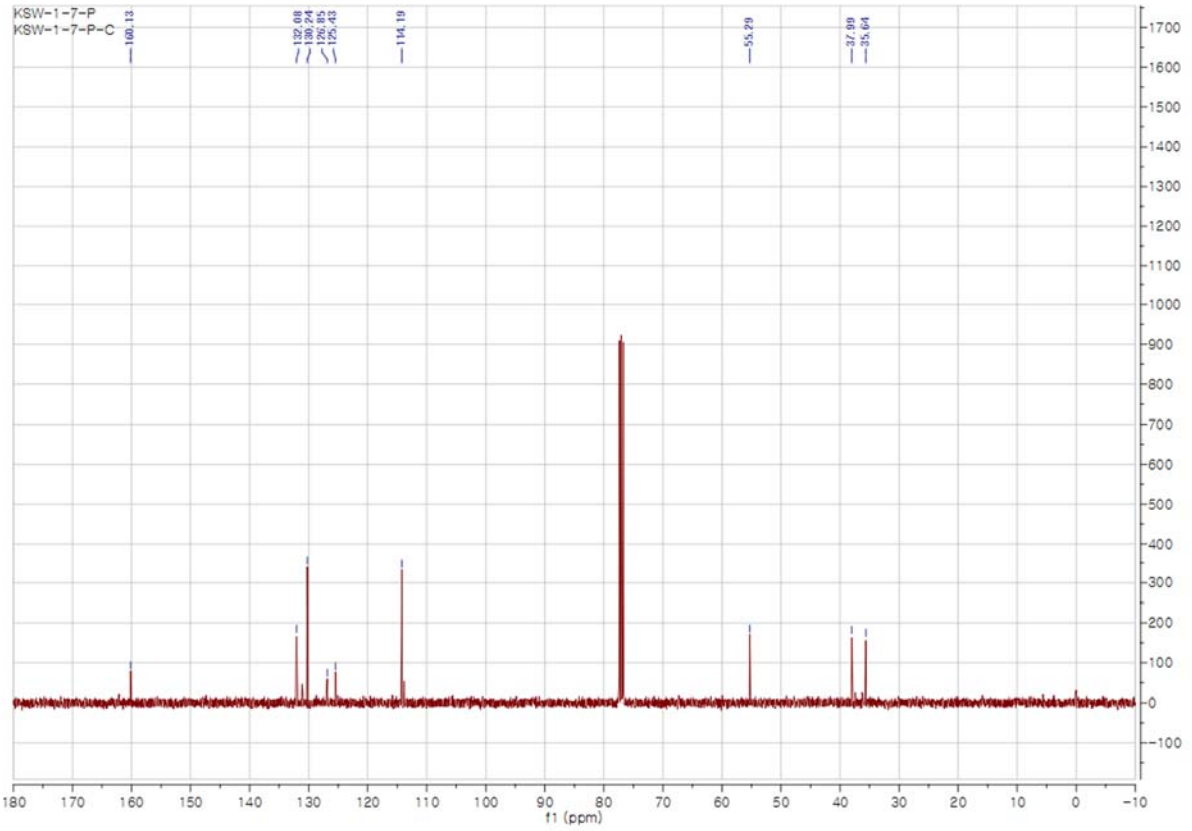

KSW-III-51B
KSW-III-51B
Cl
Ts
N
Me
Ph
4h (E/Z = 97/3)
f1 (ppm)

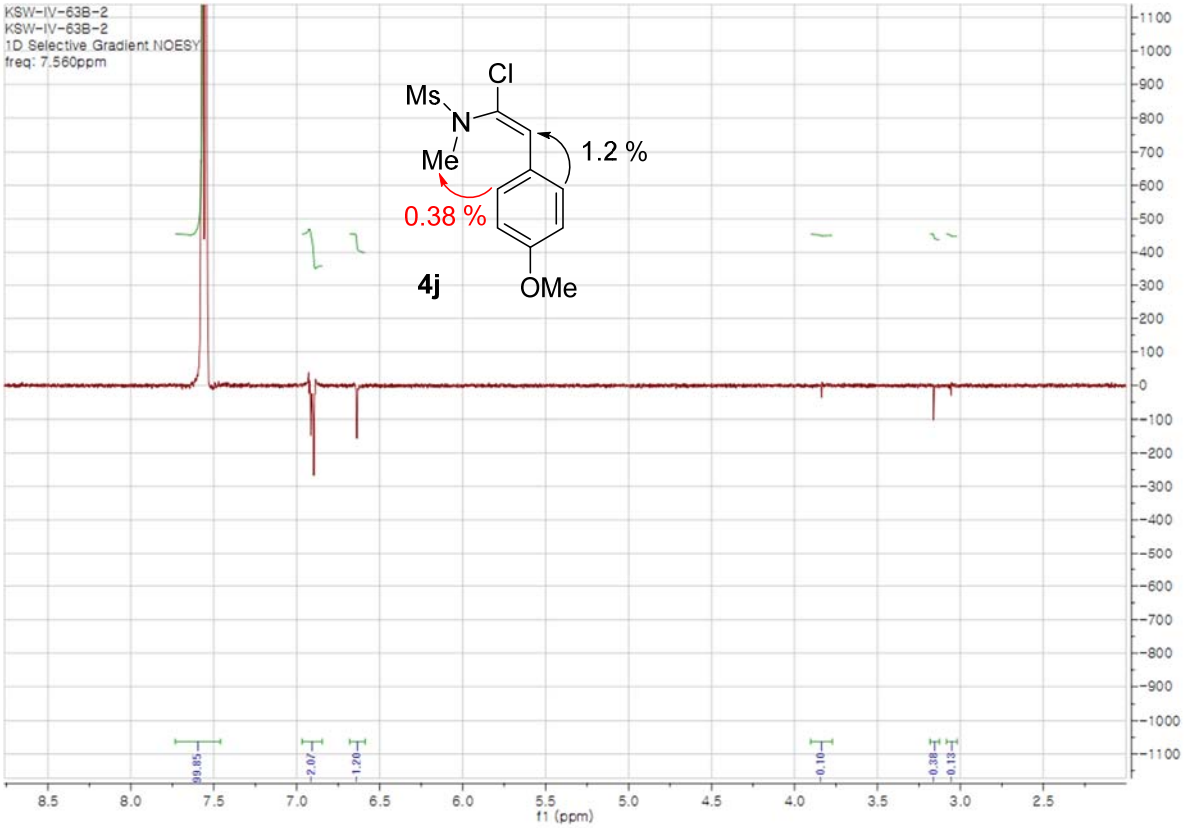

KSW-III-51B
KSW-III-51B-C
141.49
134.20
133.10
132.40
129.79
129.52
128.87
128.78
128.69
35.74
21.65
f1 (ppm)

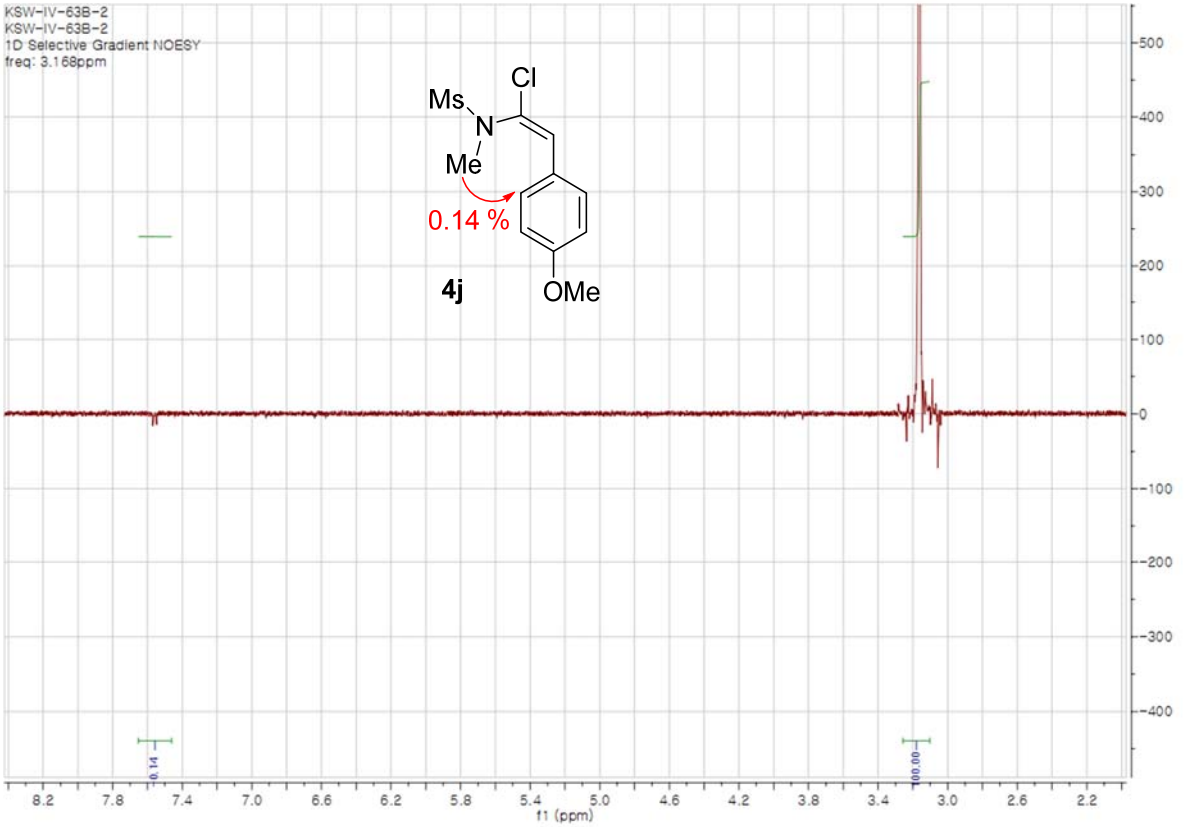

KSW-III-37-C-Cl
KSW-III-37-C-Cl
Cl
Ms
N
Me
Ph
4i (E/Z = 85/15)
f1 (ppm)

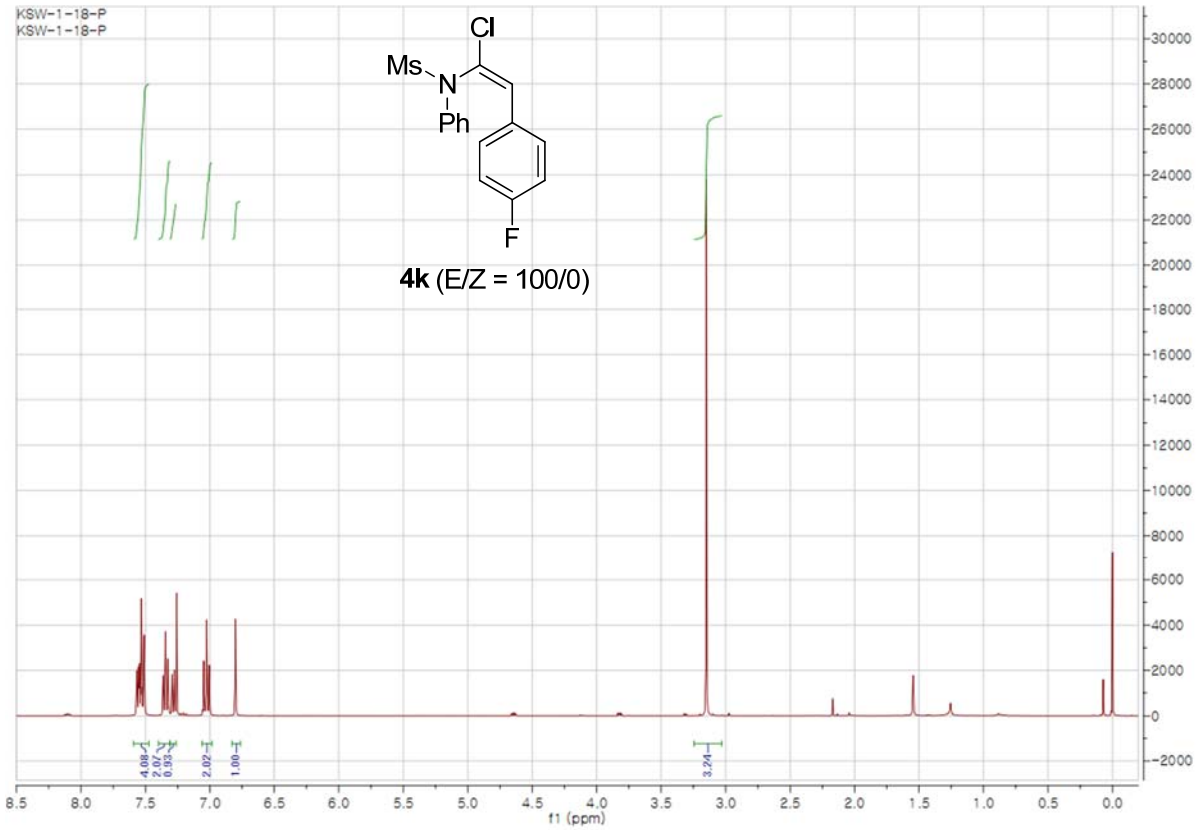

KSW-III-37-C-Cl-C
KSW-III-37-C-Cl-C
132.77
132.56
129.49
129.17
128.79
128.68
38.09
35.77
f1 (ppm)


KSW-IV-63B-2
KSW-IV-63B-2
Cl
Ms
N
Me
PMP
4j (E/Z = 87/13)
f1 (ppm)

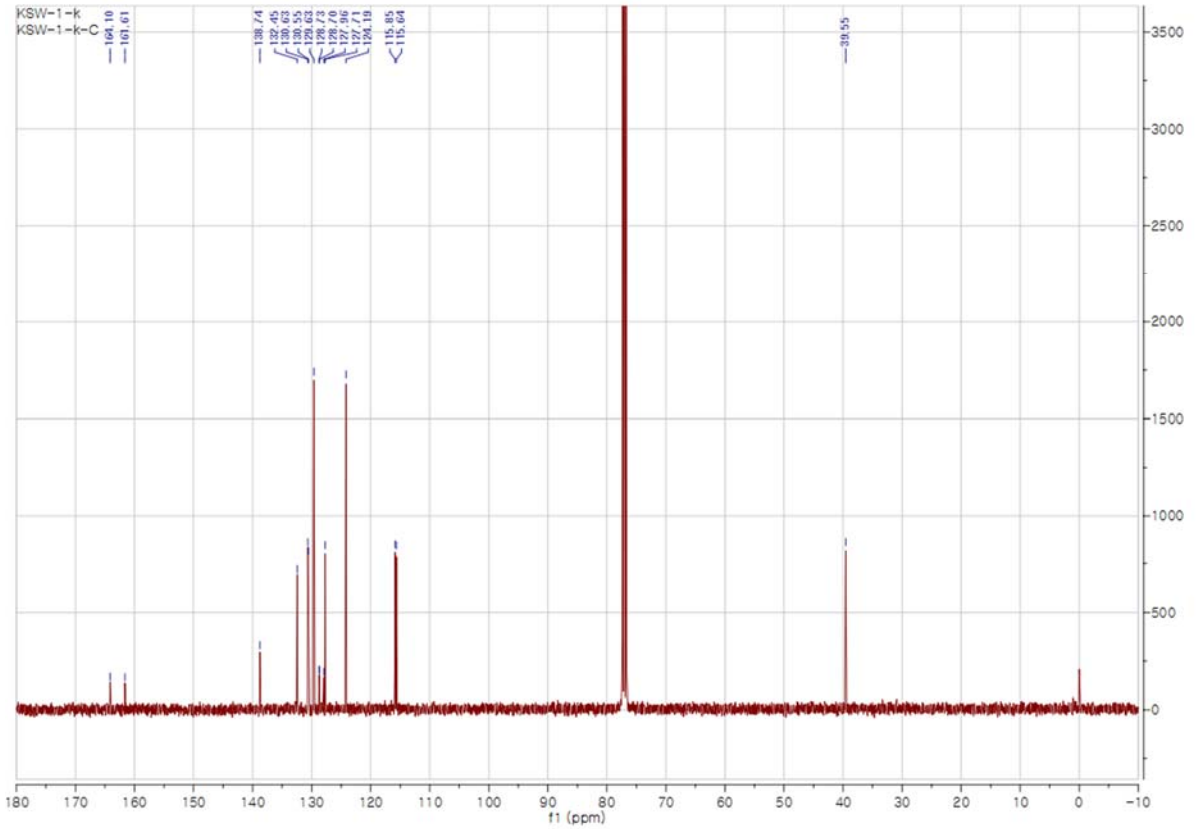

KSW-1-7-P
KSW-1-7-P-C
160.13
132.68
130.24
126.85
125.43
114.19
55.29
37.99
35.64
f1 (ppm)

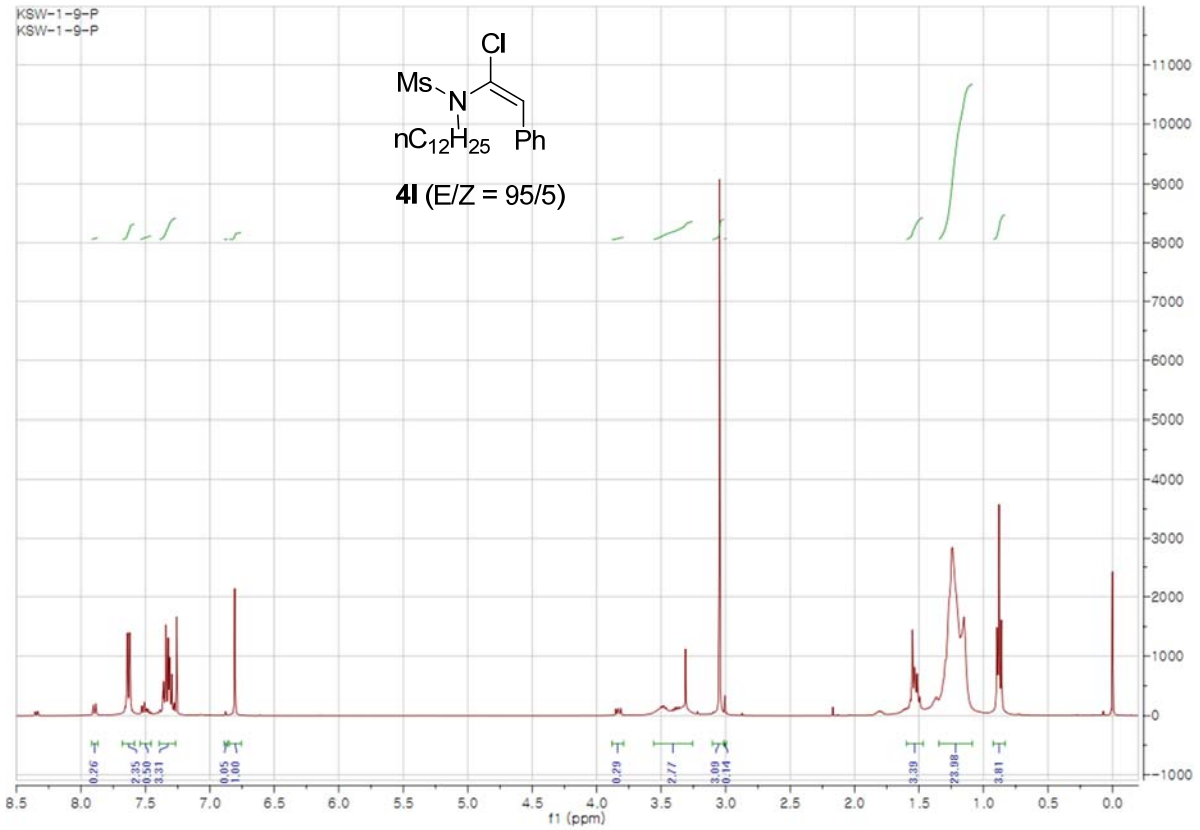

KSW-IV-63B-2
KSW-IV-63B-2
1D Selective Gradient NOESY
freq: 7.560ppm
Cl
Ms
N
Me
1.2 %
0.38 %
4j
OMe
f1 (ppm)

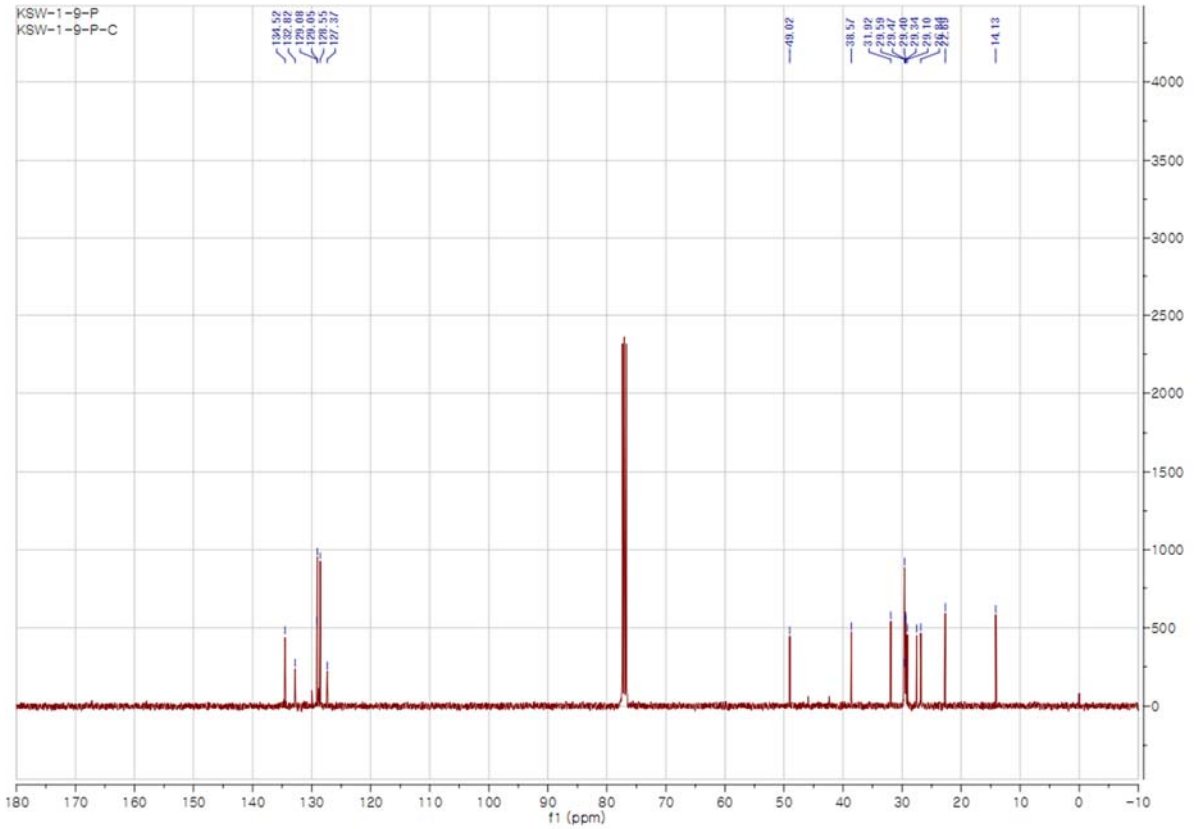

KSW-IV-63B-2
KSW-IV-63B-2
1D Selective Gradient NOESY
freq: 3.168ppm
Cl
Ms
N
Me
0.14 %
4j
OMe
f1 (ppm)

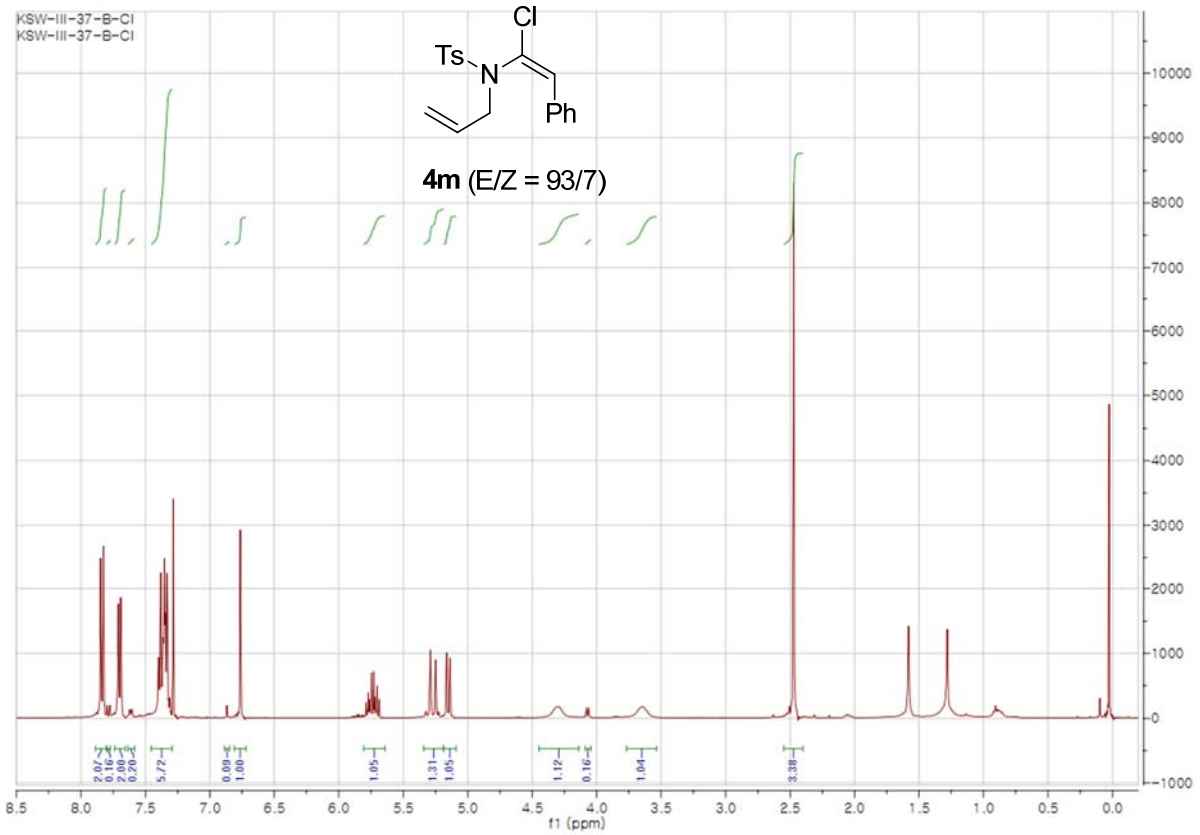

KSW-1-18-P
KSW-1-18-P
Cl
Ms
N
Ph
F
4.08
2.07
0.93
2.02
1.00
3.24
f1 (ppm)

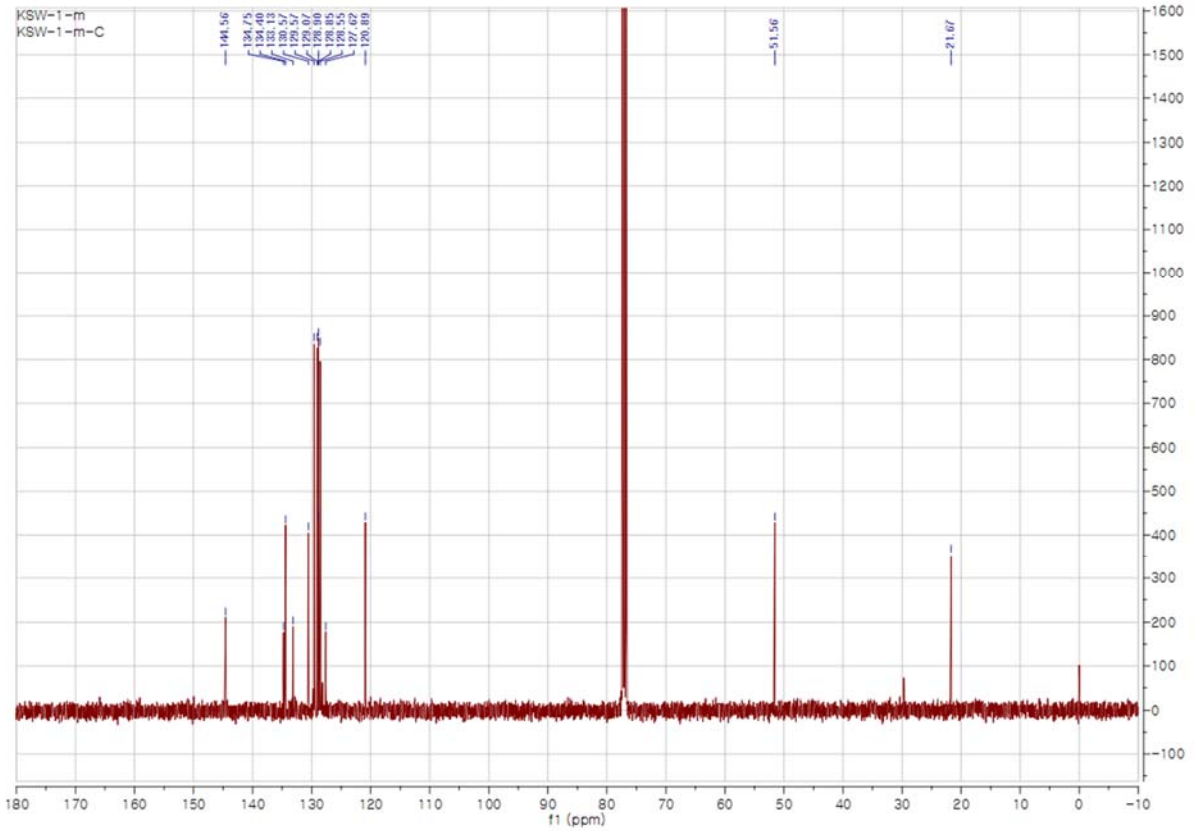
4k (E/Z = 100/0)

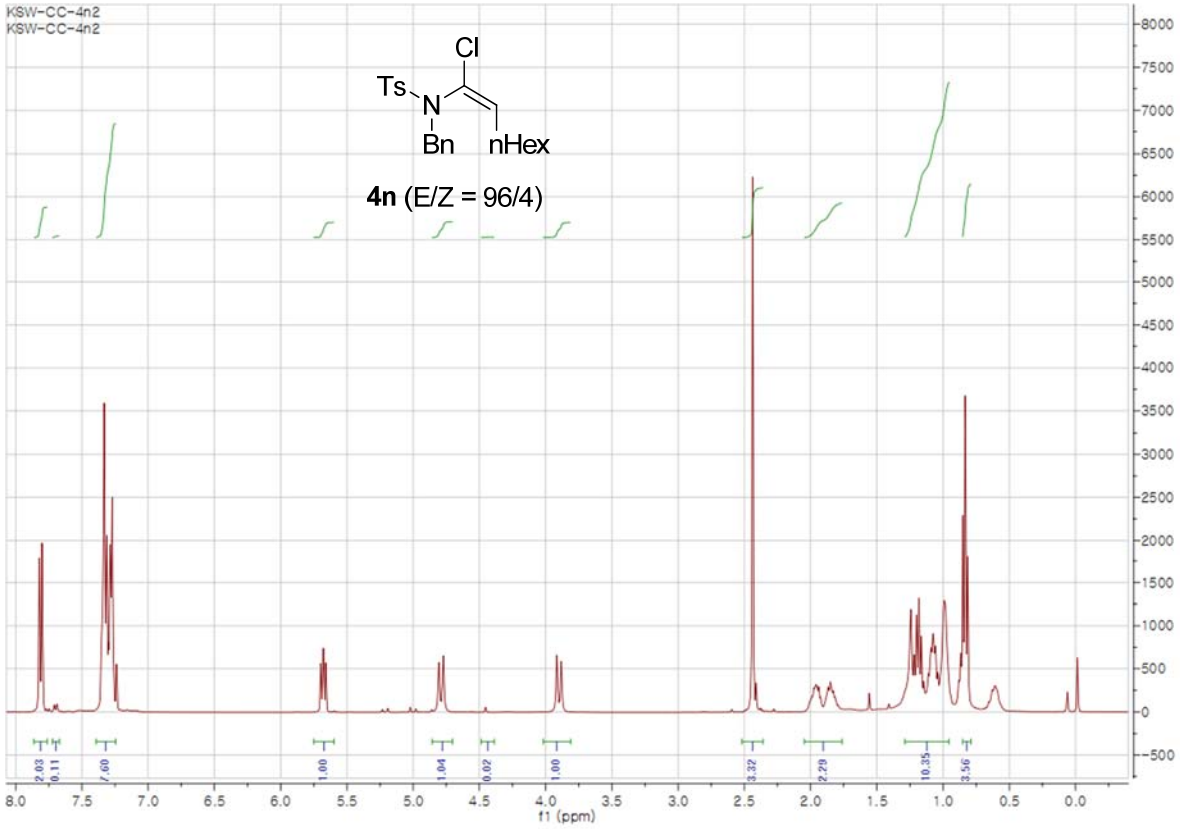

KSW-1-k
KSW-1-k-C
164.10
161.61
138.74
132.45
130.55
129.63
128.73
128.70
127.96
127.71
124.18
115.85
115.64
39.55
f1 (ppm)

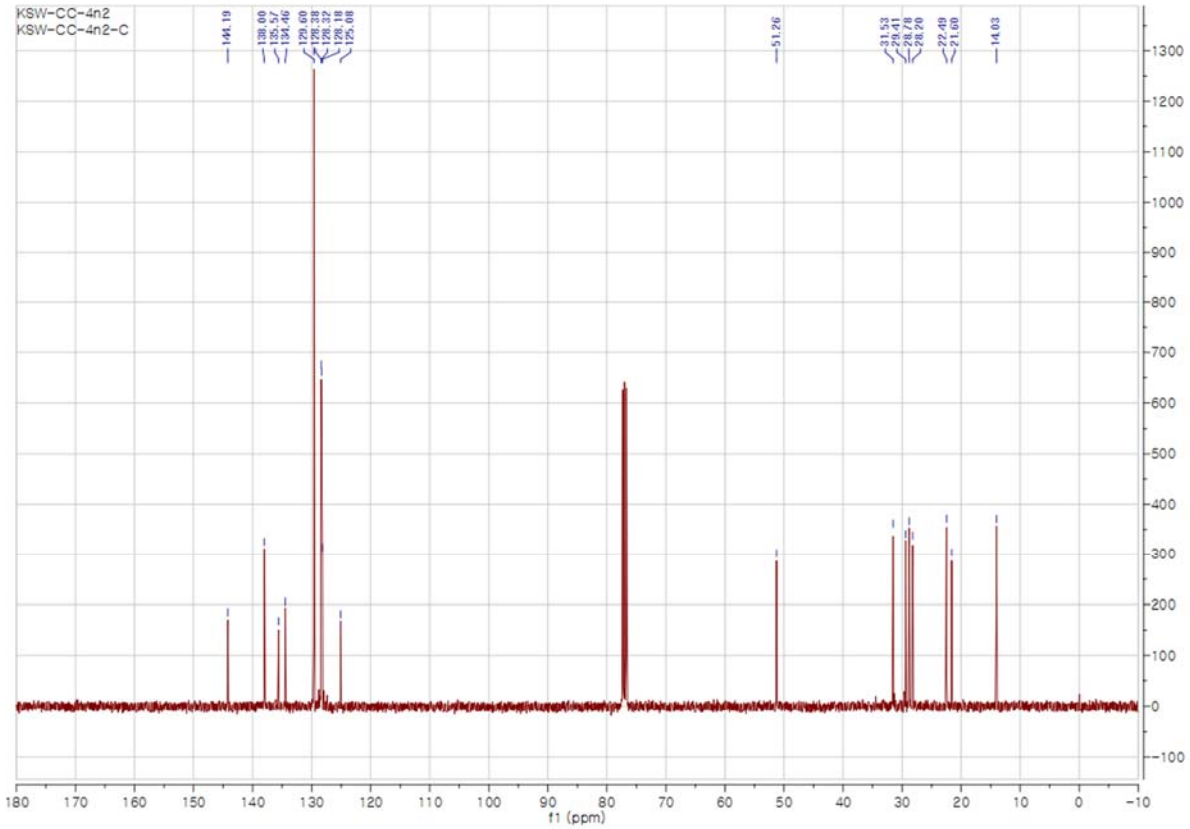

KSW-1-9-P
KSW-1-9-P
Cl
Ms
N
nC12H25
Ph
4l (E/Z = 95/5)
f1 (ppm)

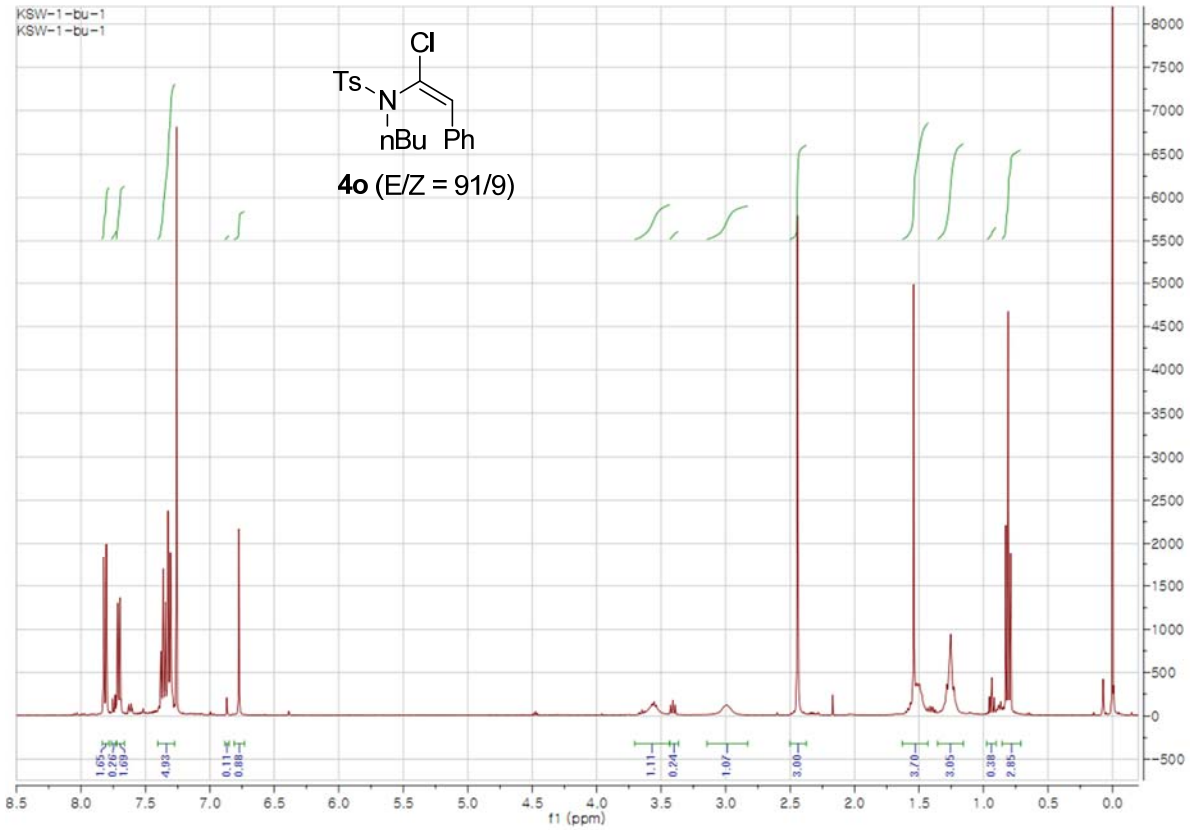

KSW-1-9-P
KSW-1-9-P-C
f1 (ppm)

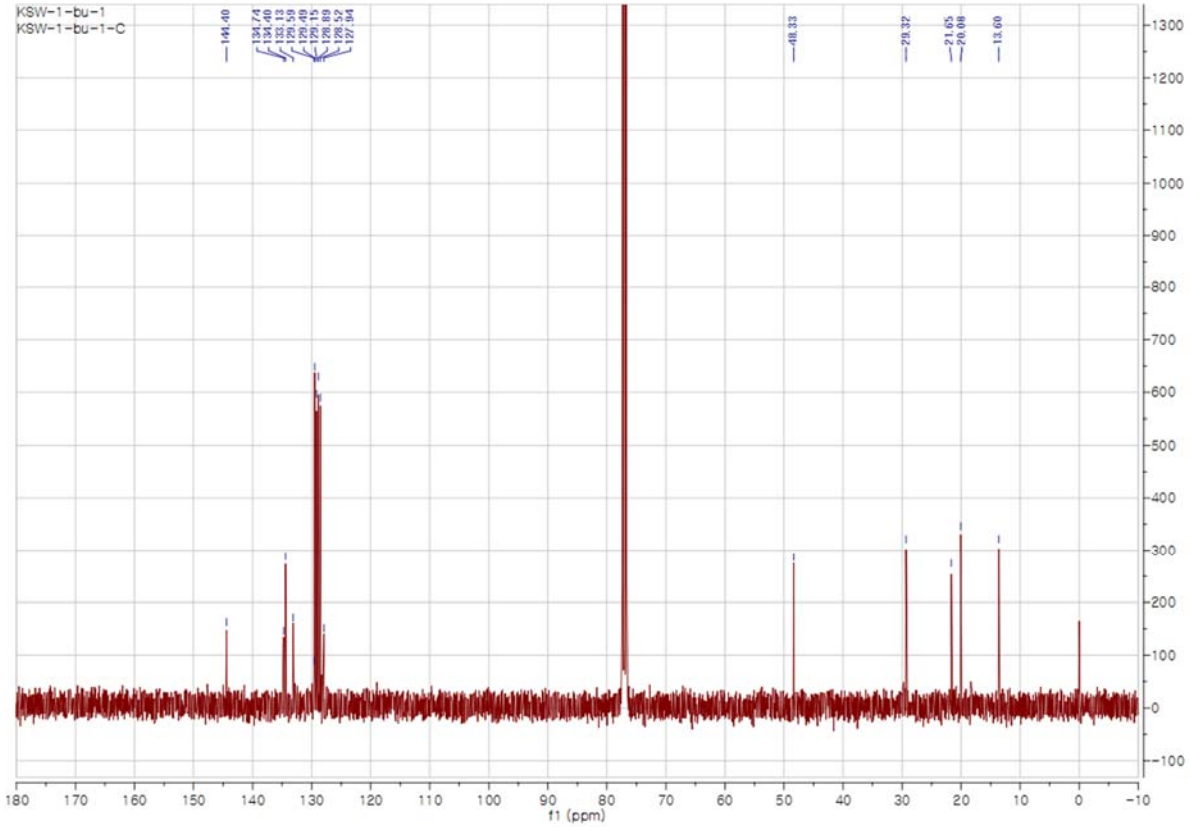

KSW-III-37-B-Cl
KSW-III-37-B-Cl
Cl
Ts
N
Ph
4m (E/Z = 93/7)
f1 (ppm)

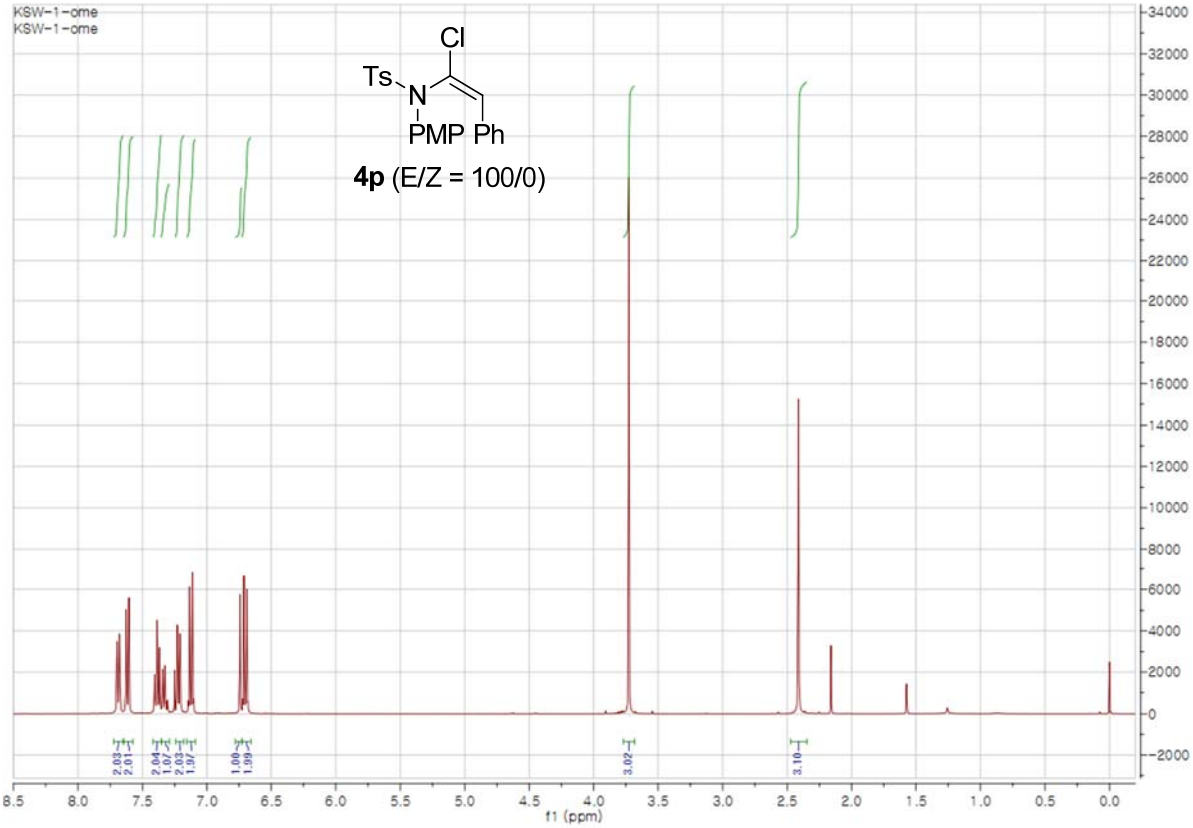

KSW-1-m
KSW-1-m-C
141.56
134.75
134.40
133.33
130.57
129.57
129.07
128.90
128.85
128.55
127.62
120.89
51.56
21.67
f1 (ppm)

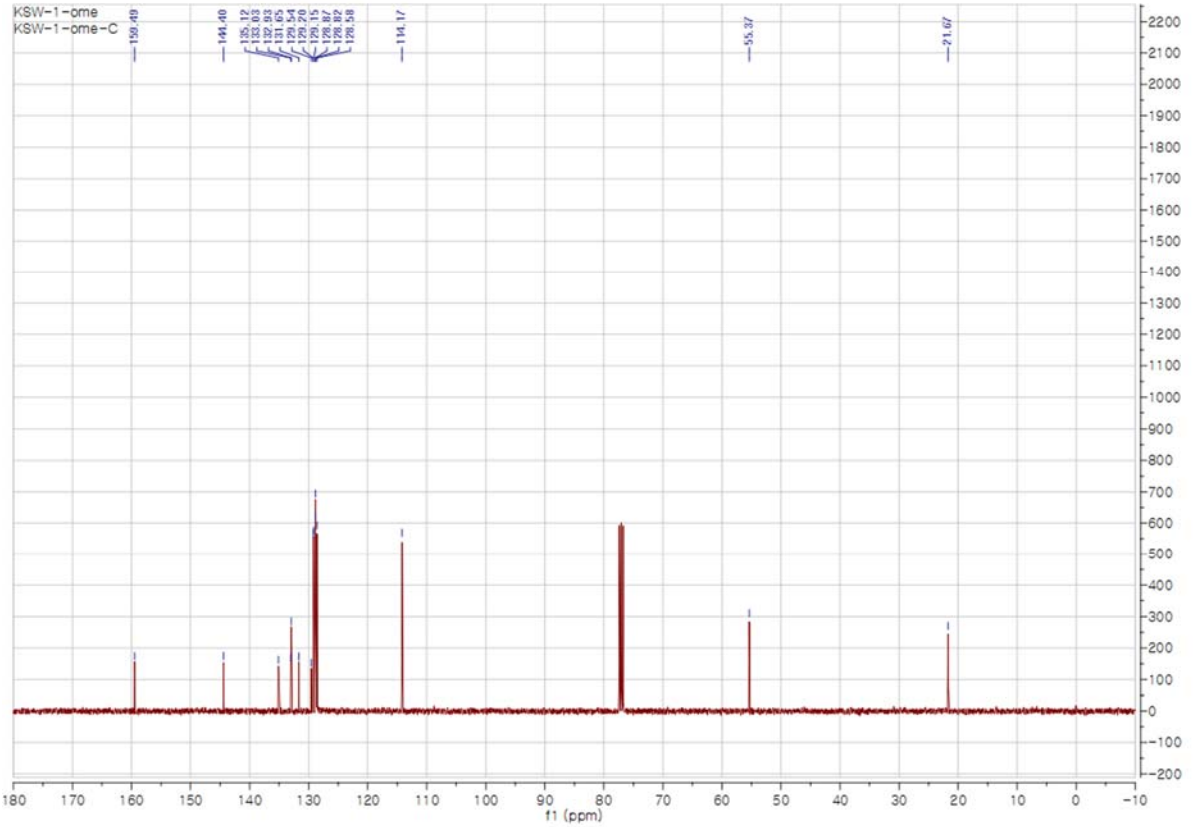

KSW-CC-4n2
KSW-CC-4n2
Cl
Ts
N
Bn
nHex
4n (E/Z = 96/4)
f1 (ppm)

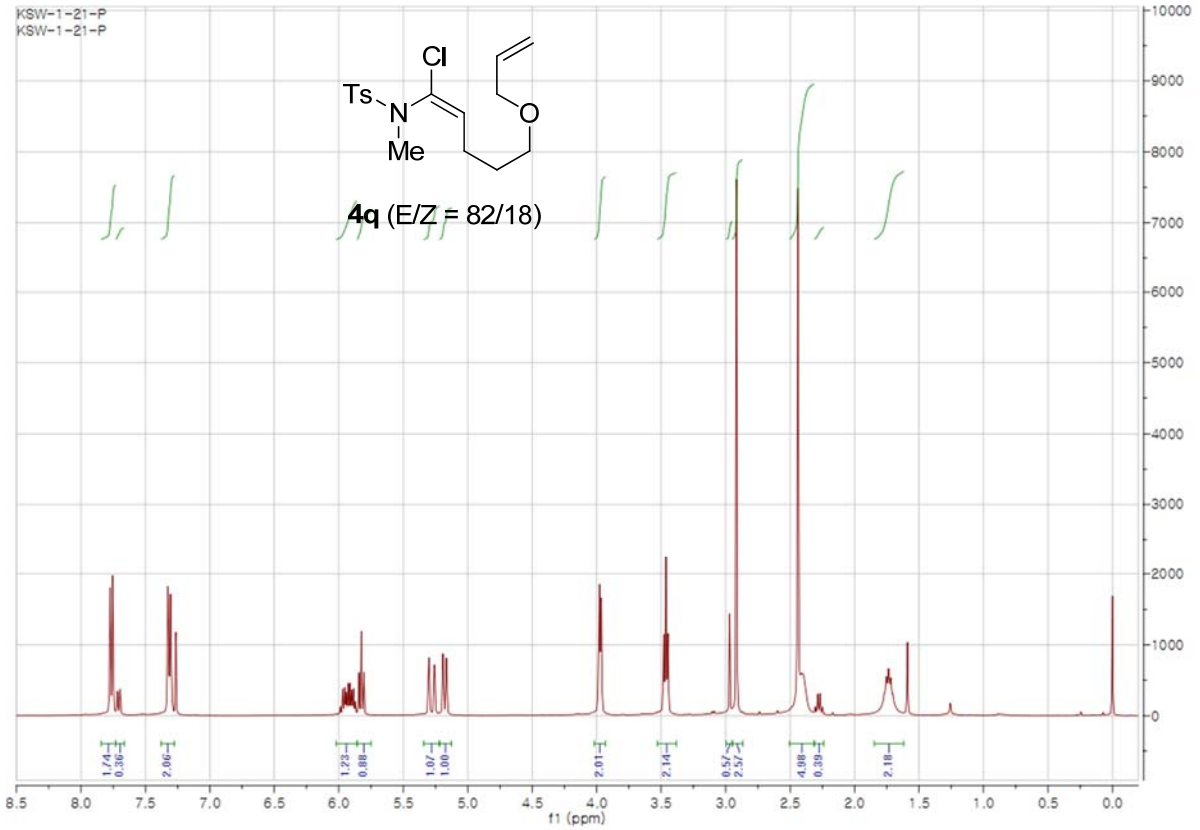

KSW-CC-4n2
KSW-CC-4n2-C
141.19
138.60
135.57
134.46
129.60
128.39
128.37
128.18
125.08
51.26
31.53
29.41
28.78
28.20
22.49
21.60
14.03
f1 (ppm)

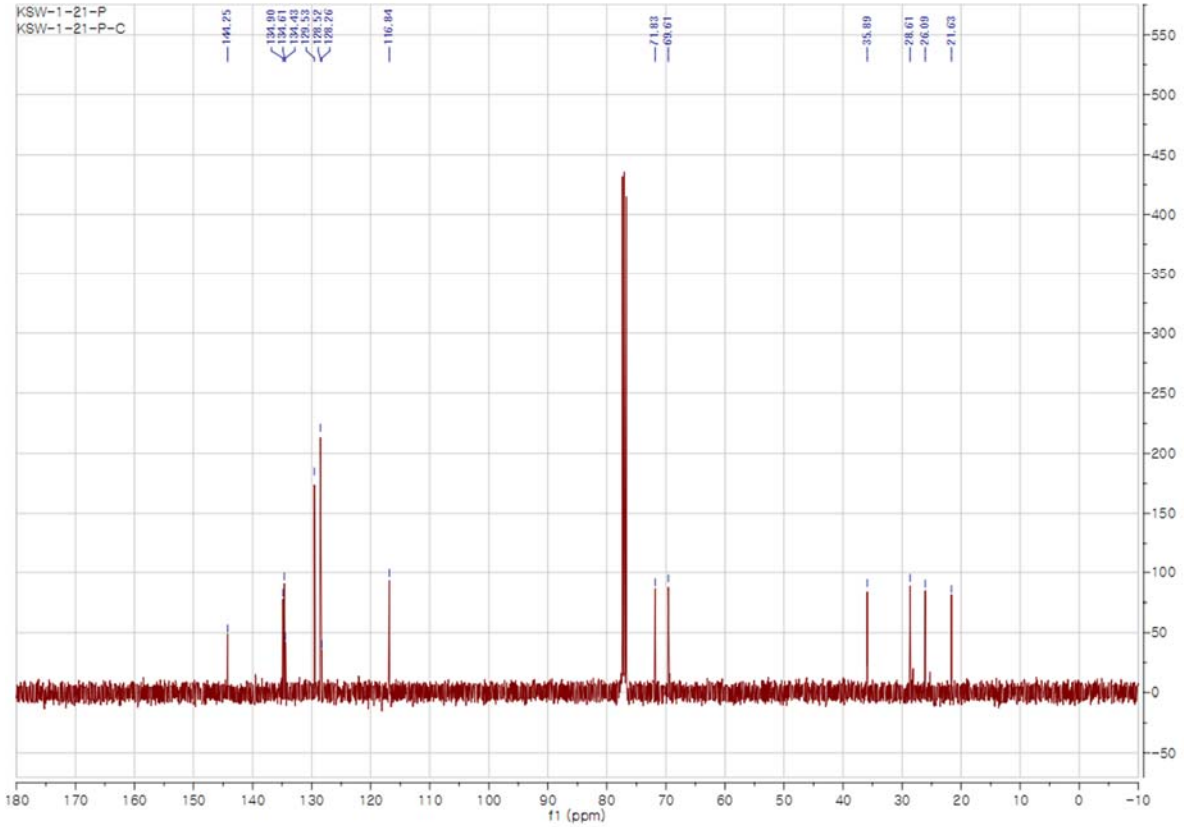

KSW-1-bu-1
KSW-1-bu-1
Cl
Ts
N
nBu
Ph
4o (E/Z = 91/9)
f1 (ppm)

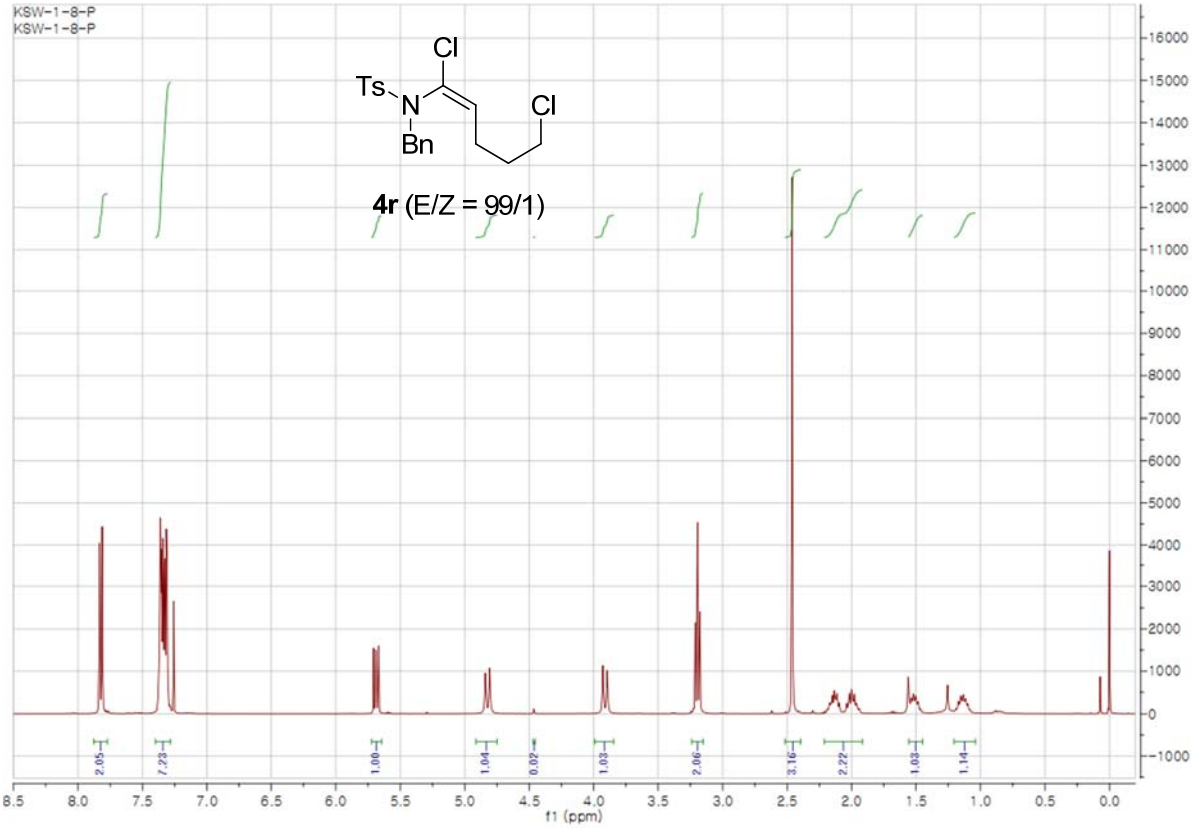

KSW-1-bu-1
KSW-1-bu-1-C
144.40
134.74
134.40
133.13
129.59
129.49
129.15
128.89
128.52
127.94
48.33
29.32
21.65
20.08
13.60
f1 (ppm)

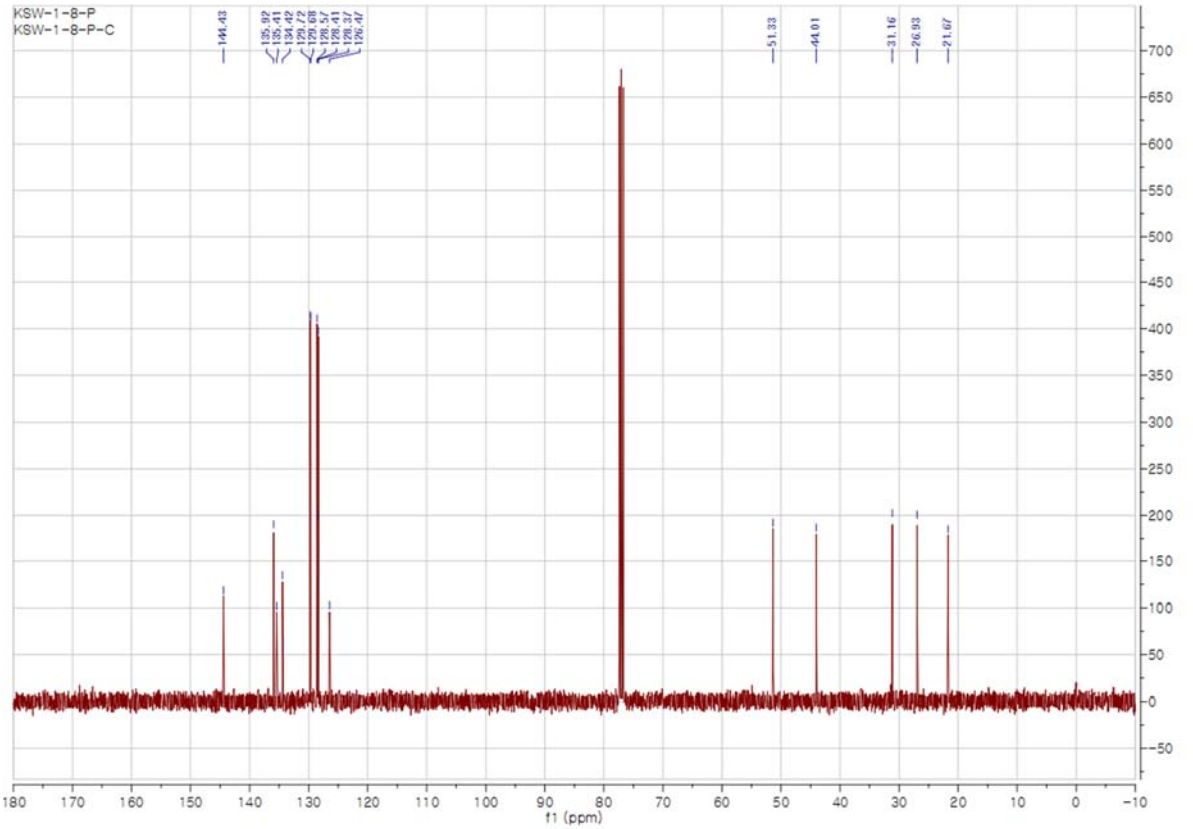

KSW-1-ome
KSW-1-ome
Cl
Ts
N
PMP
Ph
4p (E/Z = 100/0)
f1 (ppm)

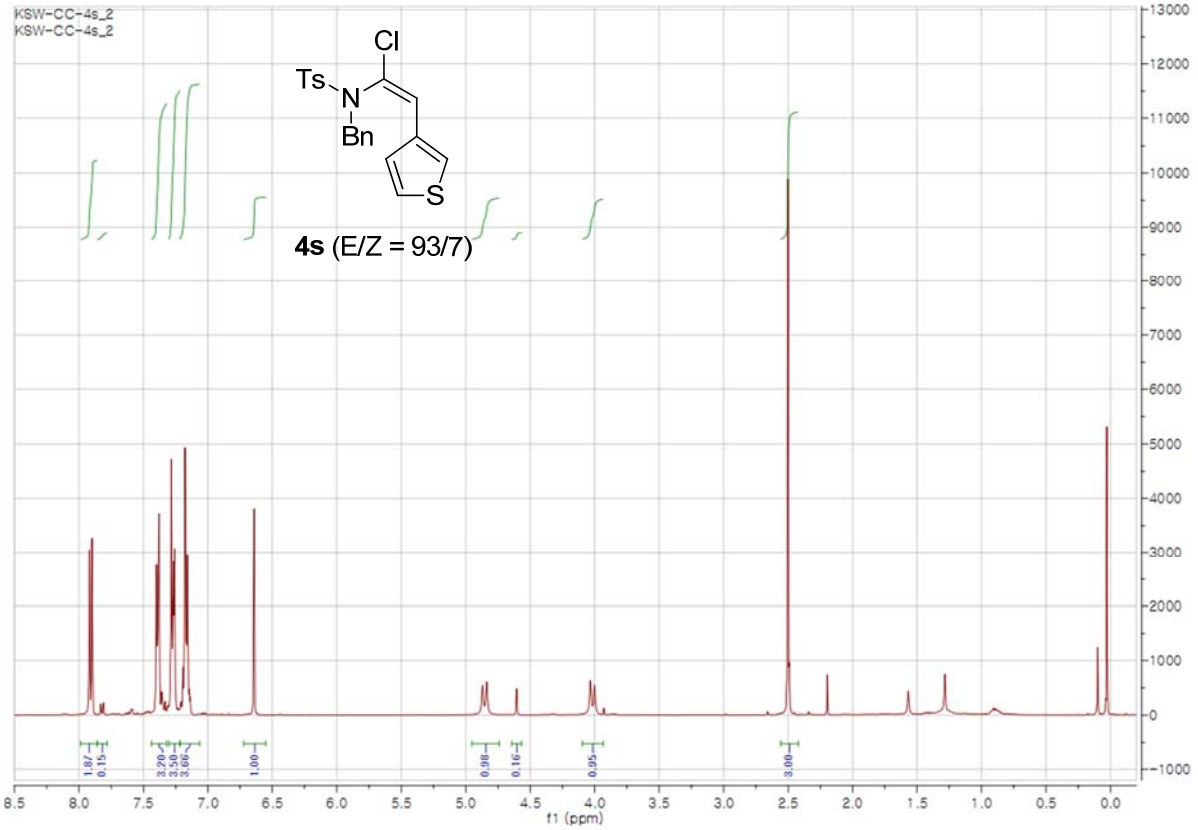

KSW-1-ome
KSW-1-ome-C
159.49
144.40
135.12
132.03
131.93
131.65
129.54
129.20
129.15
128.87
128.82
128.58
114.17
55.37
21.67
f1 (ppm)

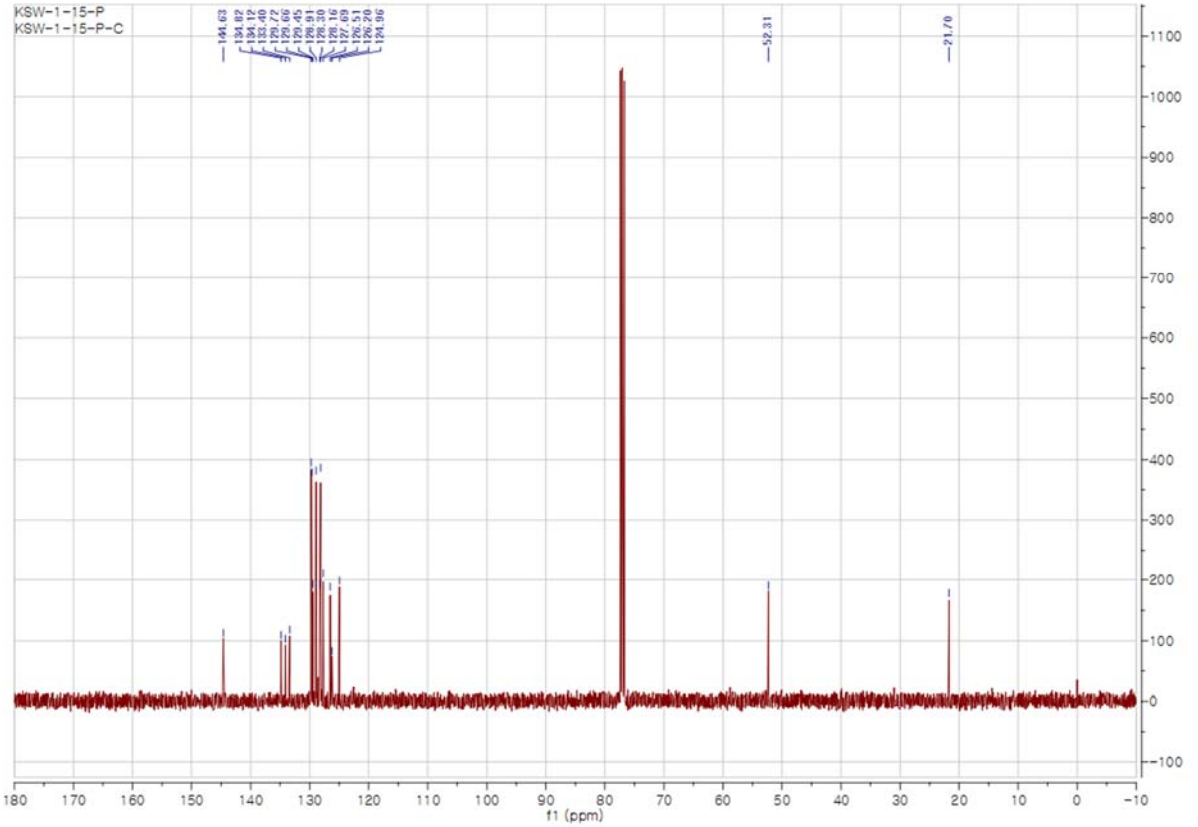

KSW-1-21-P
KSW-1-21-P
Cl
Ts
N
Me
O
4q (E/Z = 82/18)
f1 (ppm)

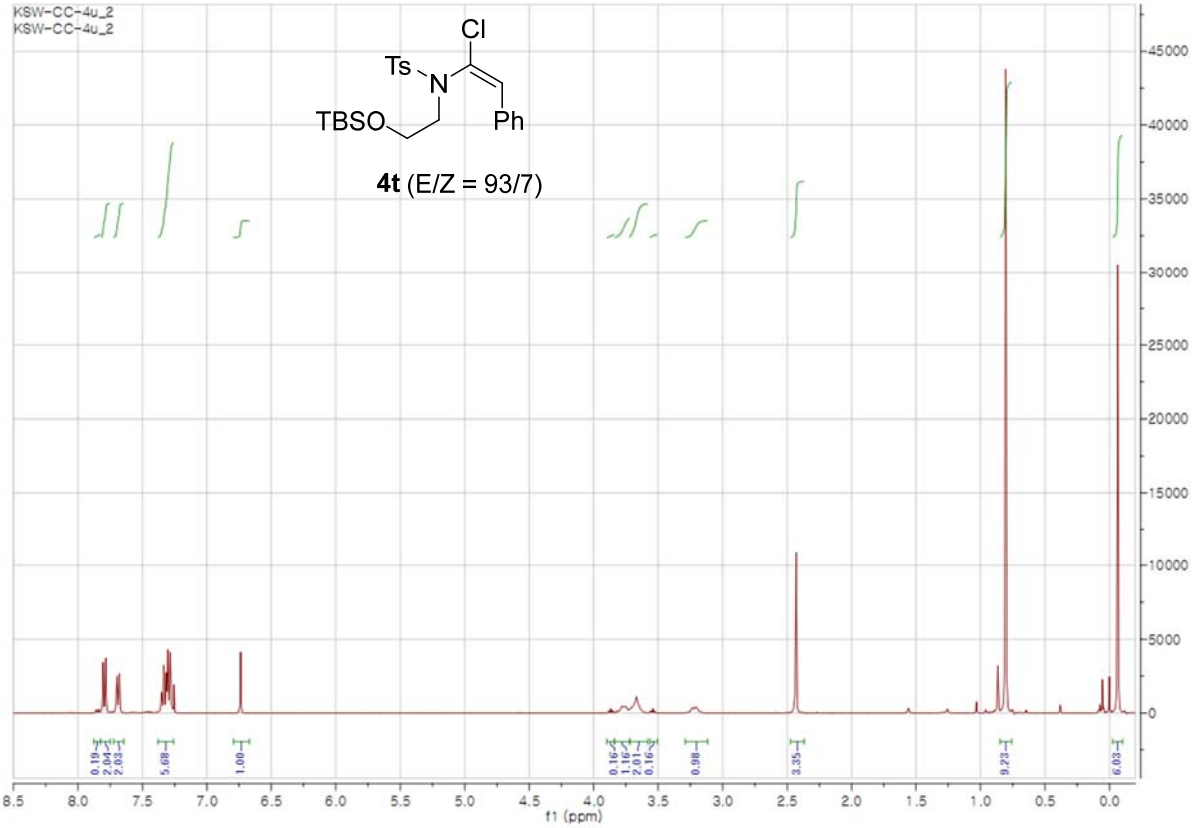

KSW-1-21-P
KSW-1-21-P-C
144.25
134.90
134.61
134.43
129.53
128.52
128.26
116.84
71.83
69.61
35.89
28.61
26.09
21.63
f1 (ppm)


KSW-1-8-P
KSW-1-8-P
Cl
Ts
N
Bn
Cl
4r (E/Z = 99/1)
f1 (ppm)

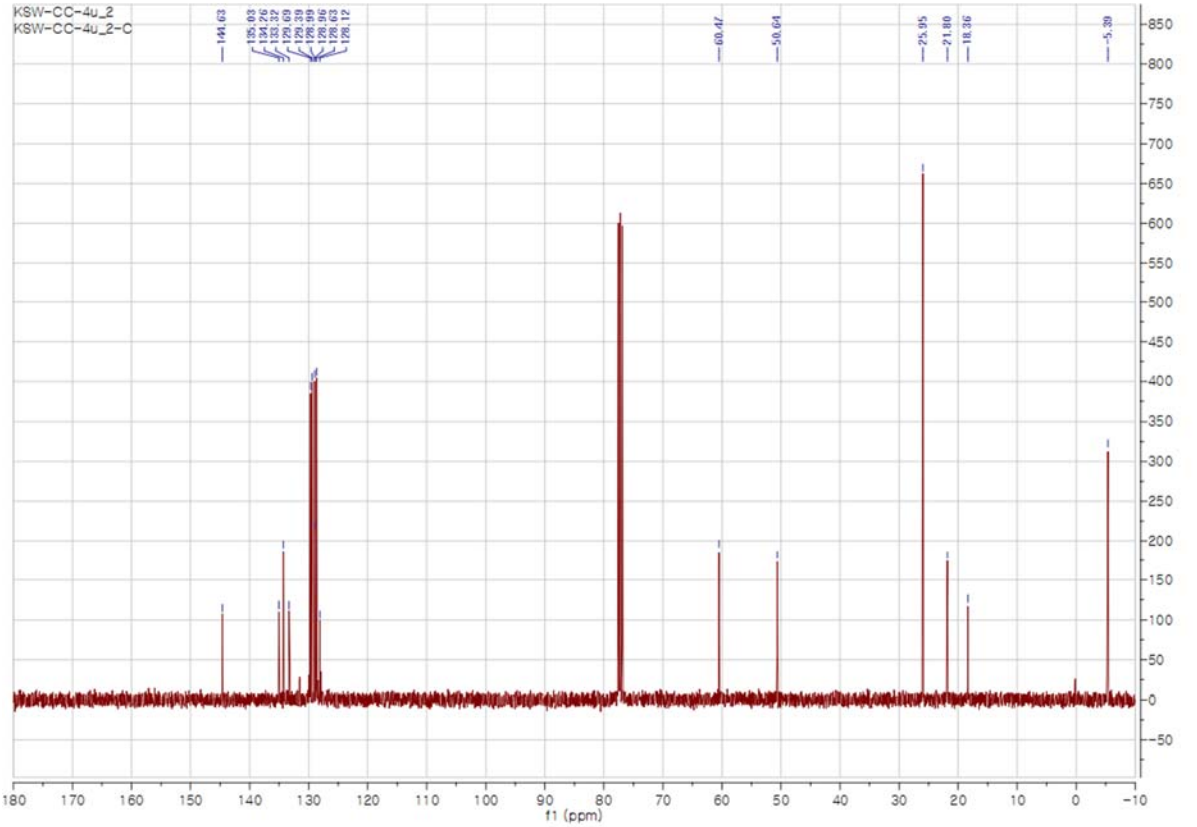

KSW-1-8-P
KSW-1-8-P-C
144.43
135.92
135.41
134.42
129.72
129.68
128.57
128.41
128.37
126.47
51.33
44.01
31.16
26.93
21.67
f1 (ppm)

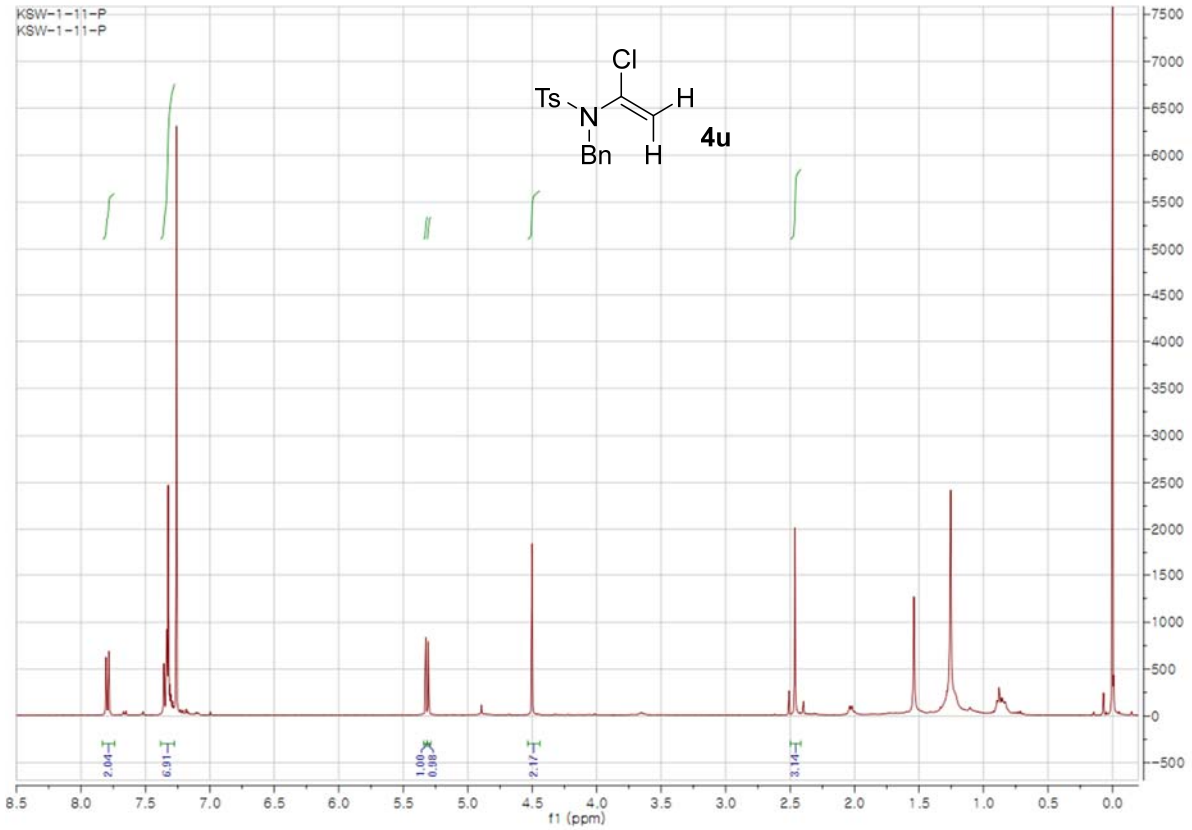

KSW-CC-4s_2
KSW-CC-4s_2
Cl
Ts
N
Bn
S
4s (E/Z = 93/7)
f1 (ppm)

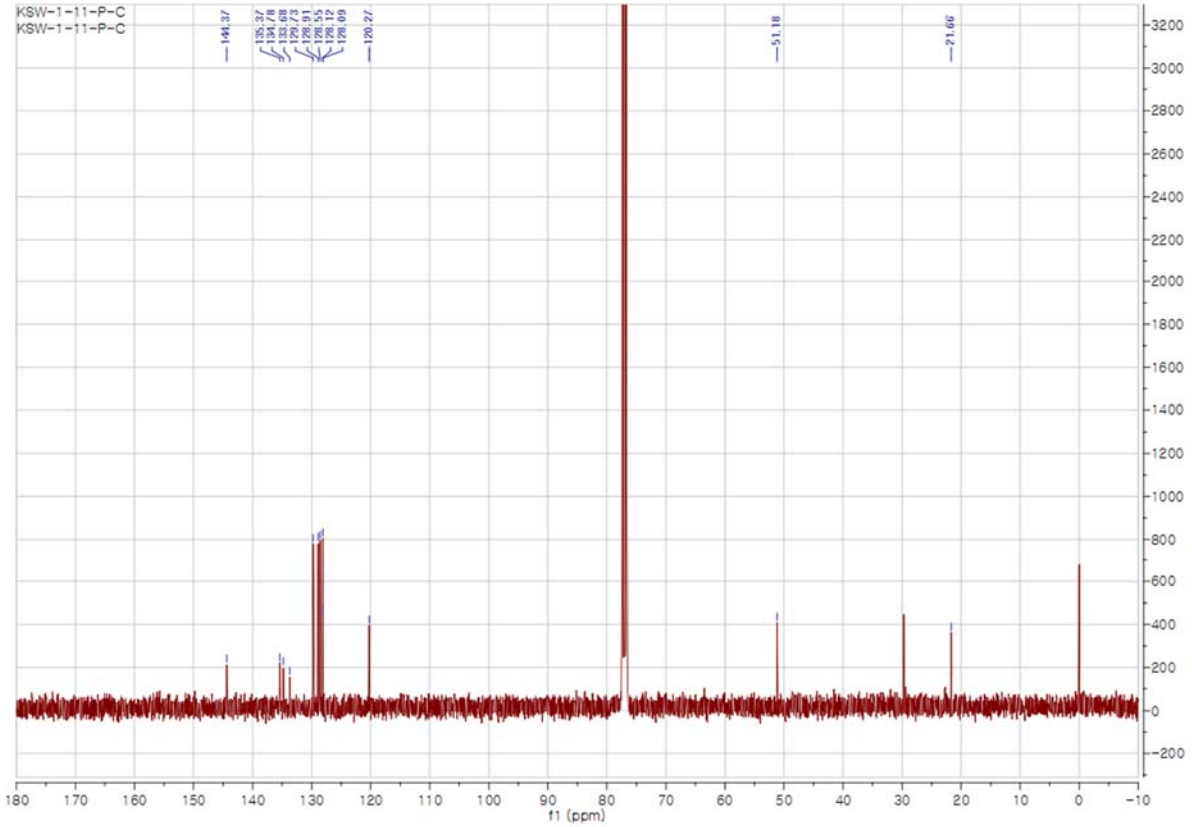

KSW-1-15-P
KSW-1-15-P-C
144.63
134.82
134.12
133.46
129.72
129.66
129.45
128.91
128.30
128.16
127.69
126.51
126.20
124.99
52.31
21.70
f1 (ppm)

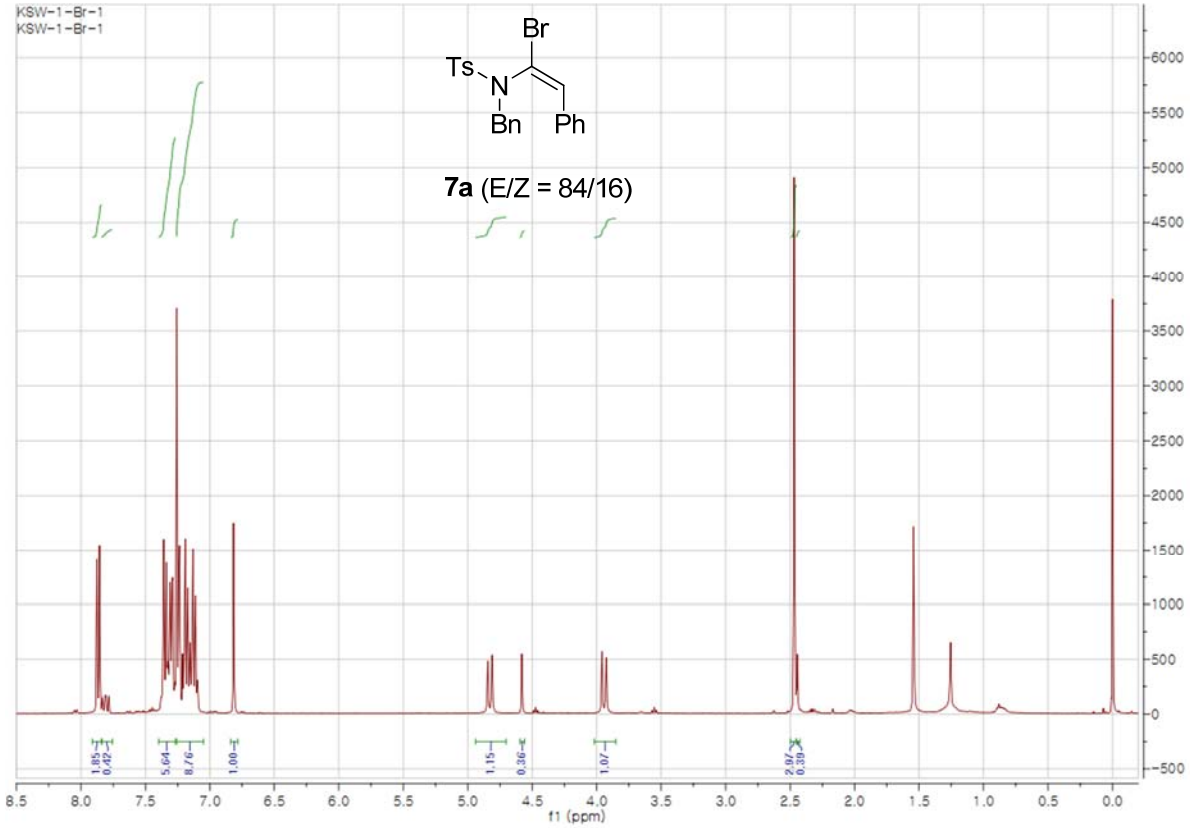

KSW-CC-4u_2
KSW-CC-4u_2
Cl
Ts
N
TBSO
Ph
f1 (ppm)

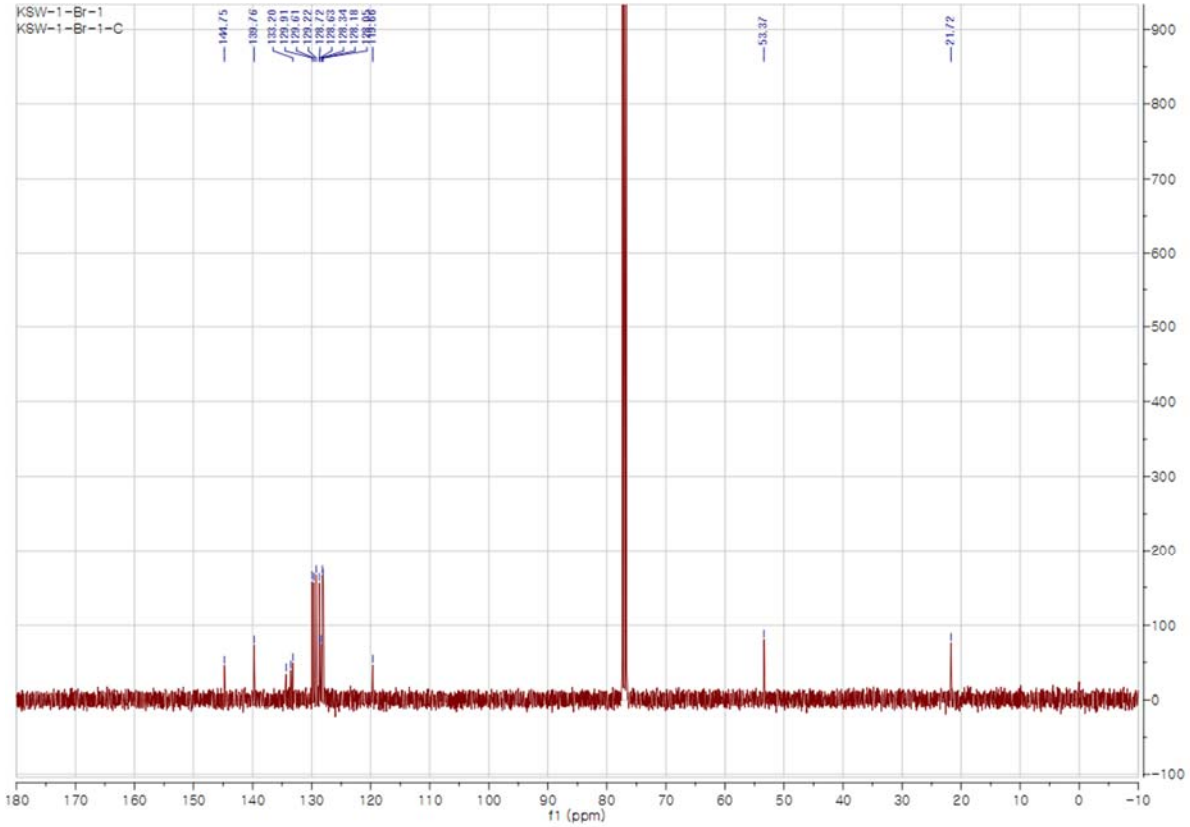
4t (E/Z = 93/7)

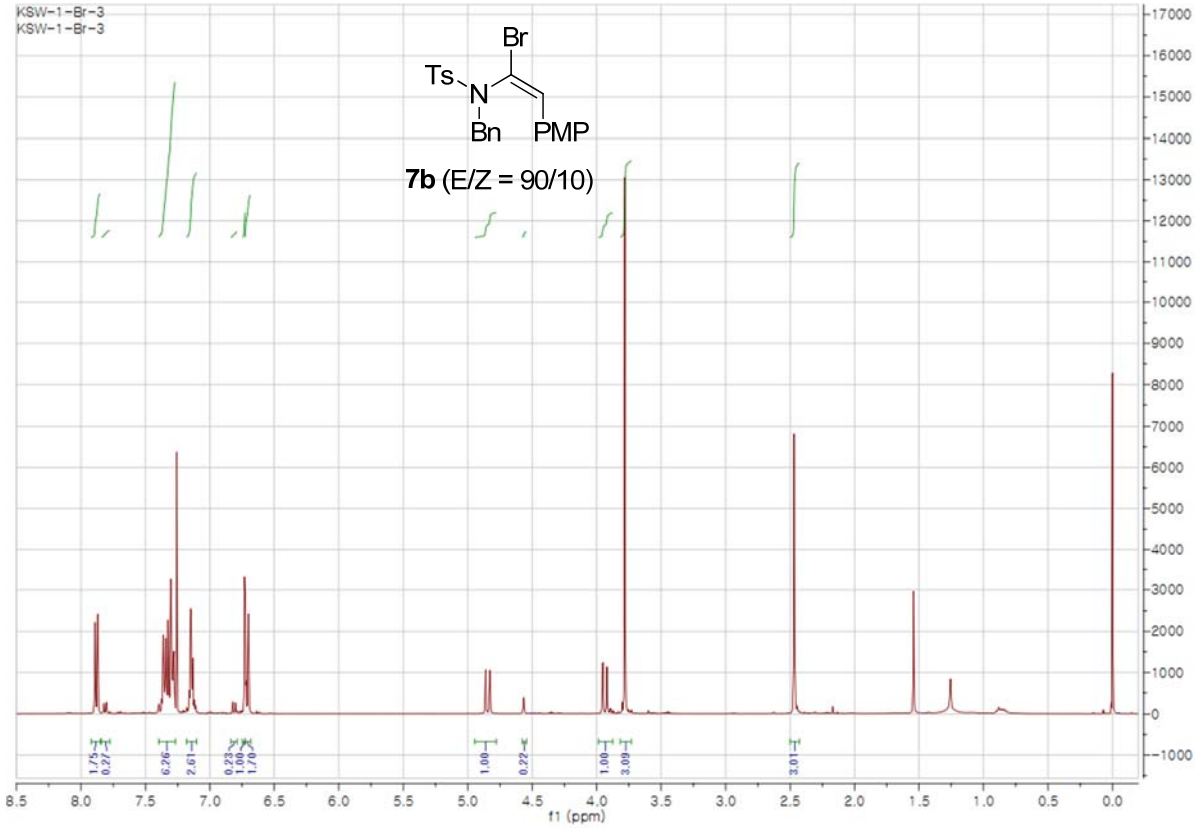

KSW-CC-4u_2
KSW-CC-4u_2-C
144.63
135.03
134.26
133.32
129.69
129.39
128.99
128.96
128.63
128.12
60.47
50.64
25.95
21.80
18.36
-5.39
f1 (ppm)

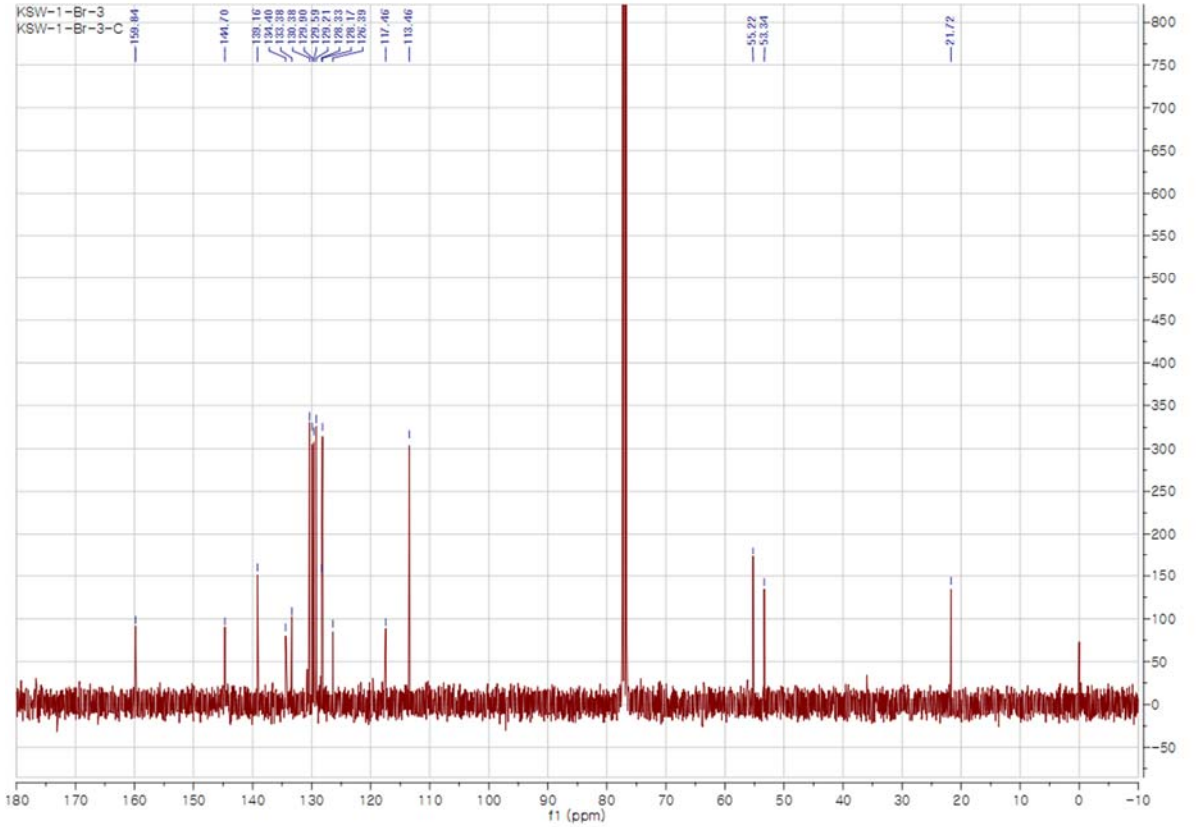

KSW-1-11-P
KSW-1-11-P
Cl
Ts
N
H
Bn
H
4u
2.04
6.91
1.00
0.98
2.17
3.14
f1 (ppm)

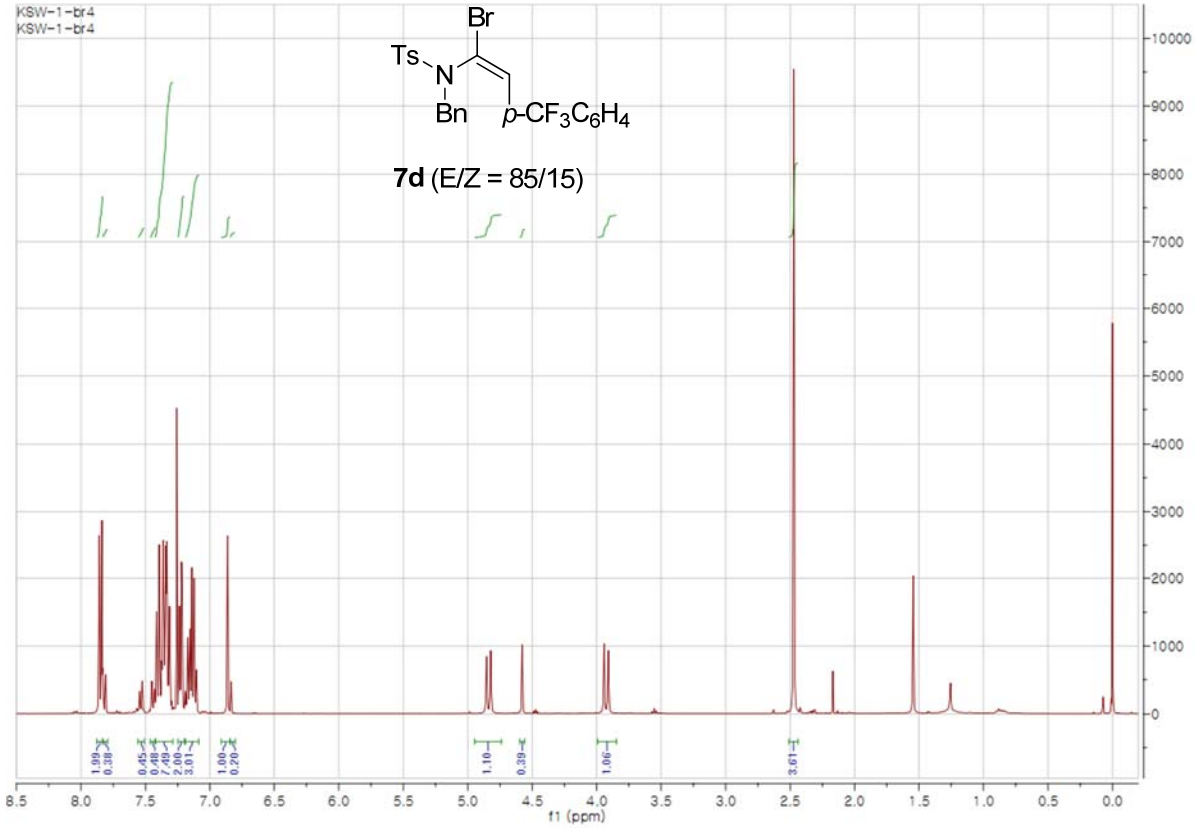

KSW-1-11-P-C
KSW-1-11-P-C
144.37
135.27
134.78
133.68
129.73
128.91
128.55
128.12
126.09
120.27
51.18
21.66
f1 (ppm)

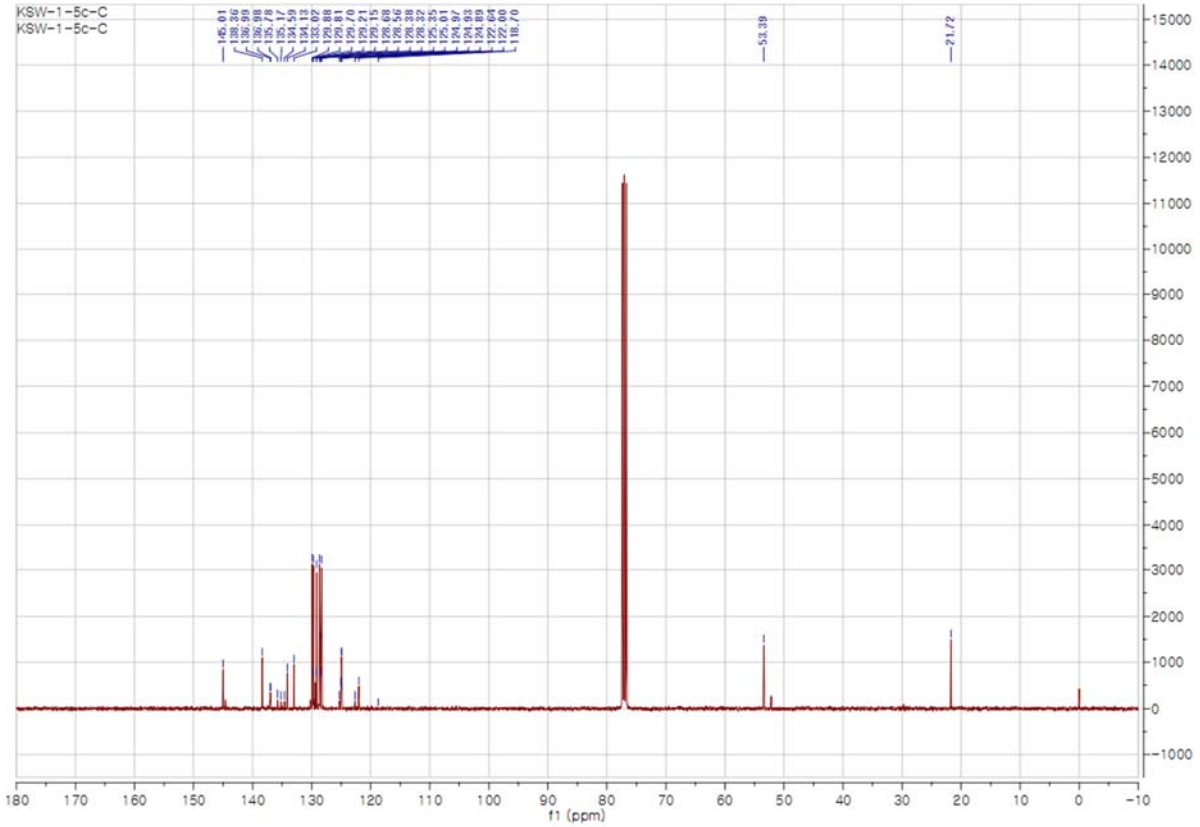

KSW-1-Br-1
KSW-1-Br-1
Br
Ts
N
Bn
Ph
7a (E/Z = 84/16)
f1 (ppm)

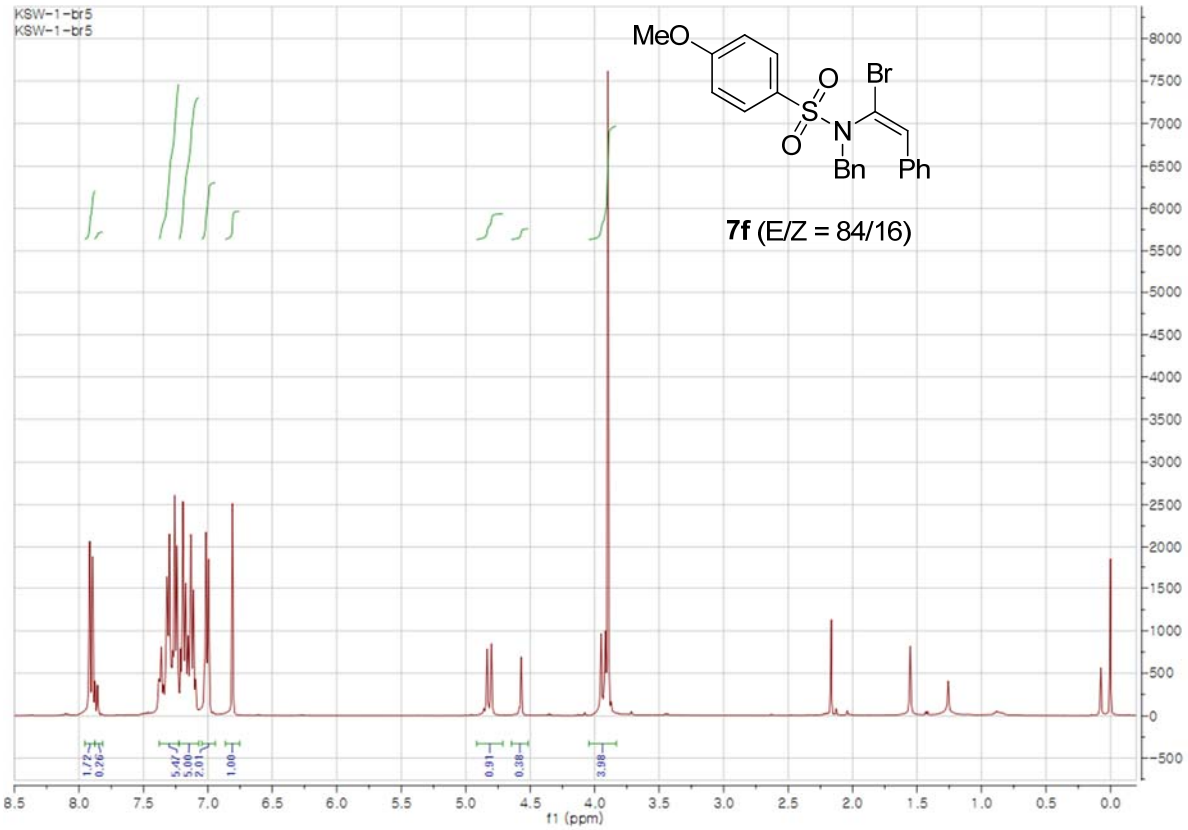

KSW-1-Br-1
KSW-1-Br-1-C
144.75
139.76
133.20
129.91
129.61
129.22
128.72
128.63
128.34
128.18
120.88
53.37
21.72
f1 (ppm)

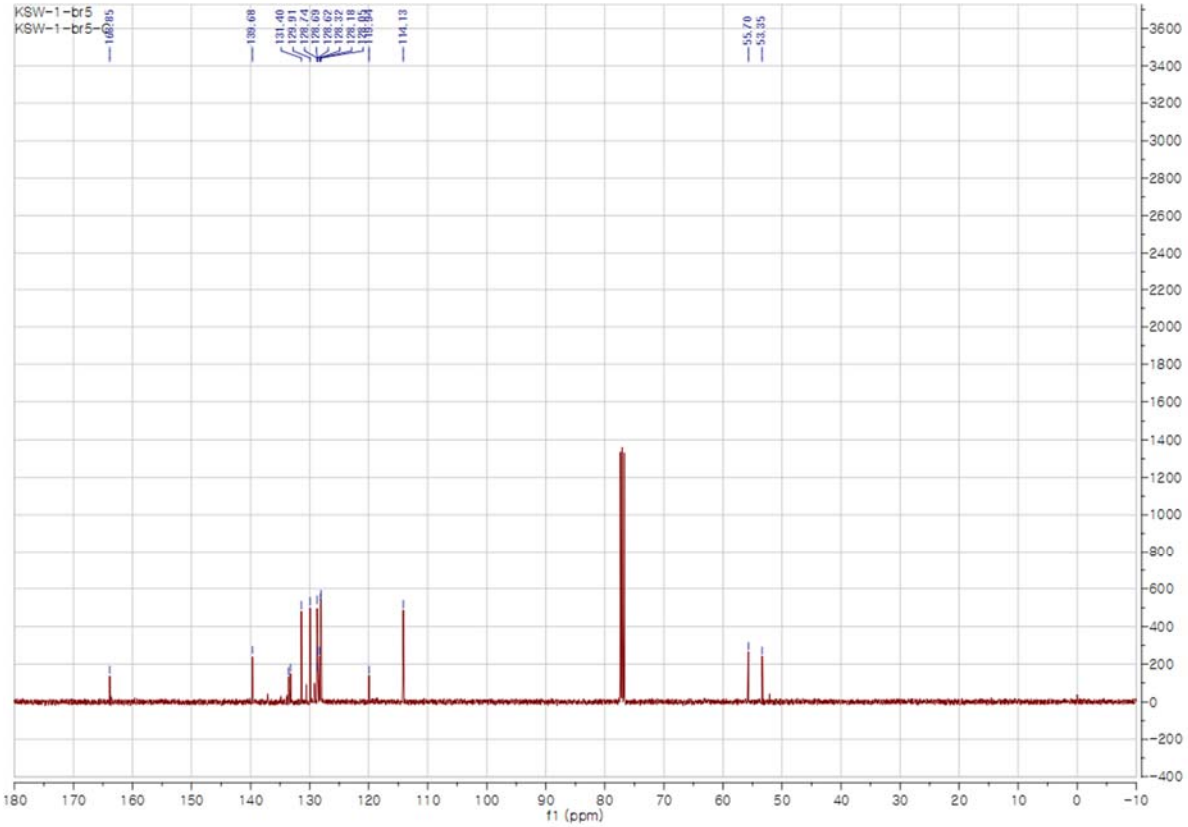

KSW-1-Br-3
KSW-1-Br-3
Br
Ts
N
Bn
PMP
7b (E/Z = 90/10)
f1 (ppm)

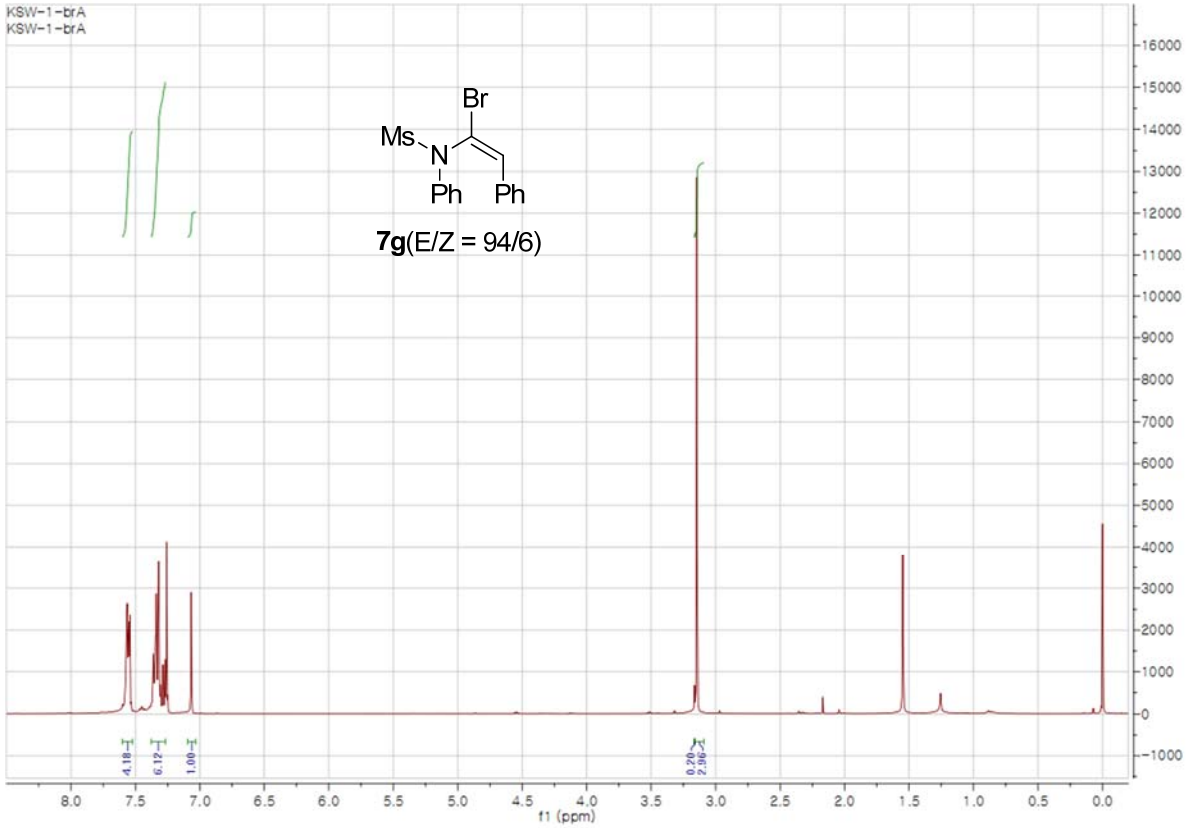

KSW-1-Br-3
KSW-1-Br-3-C
159.84
144.70
139.16
134.40
133.38
130.38
129.90
129.59
129.27
128.33
128.17
126.39
117.46
113.46
55.22
53.34
21.72
f1 (ppm)

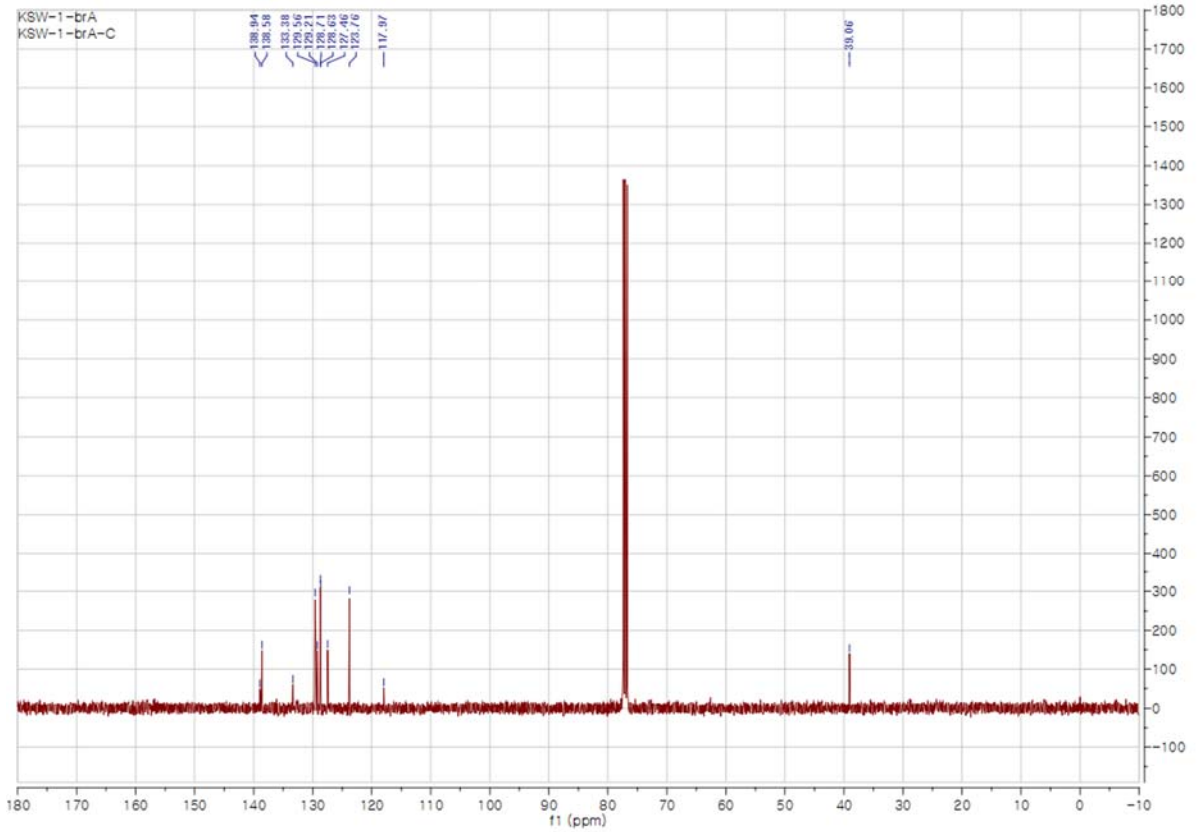

KSW-1-br4
KSW-1-br4
Br
Ts
N
Bn
p-CF3C6H4
7d (E/Z = 85/15)
f1 (ppm)

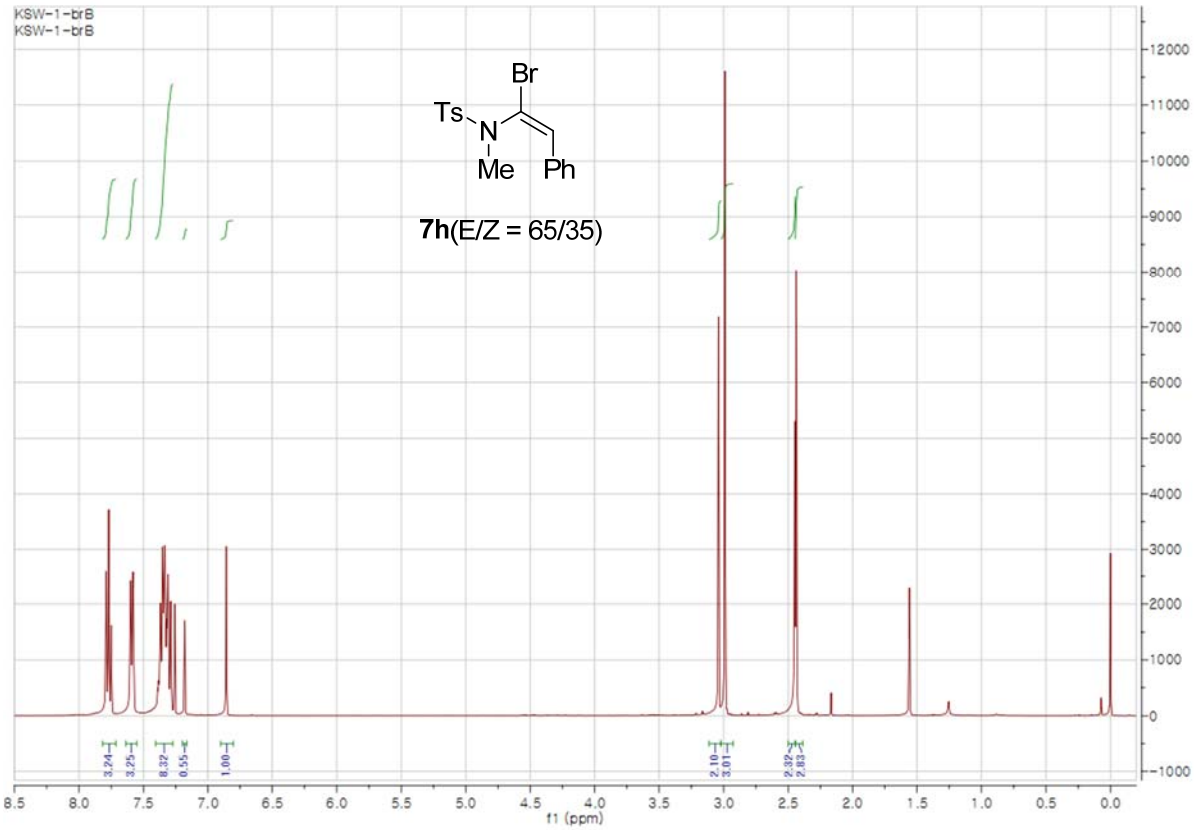

KSW-1-5c-C
KSW-1-5c-C
53.39
21.72
f1 (ppm)

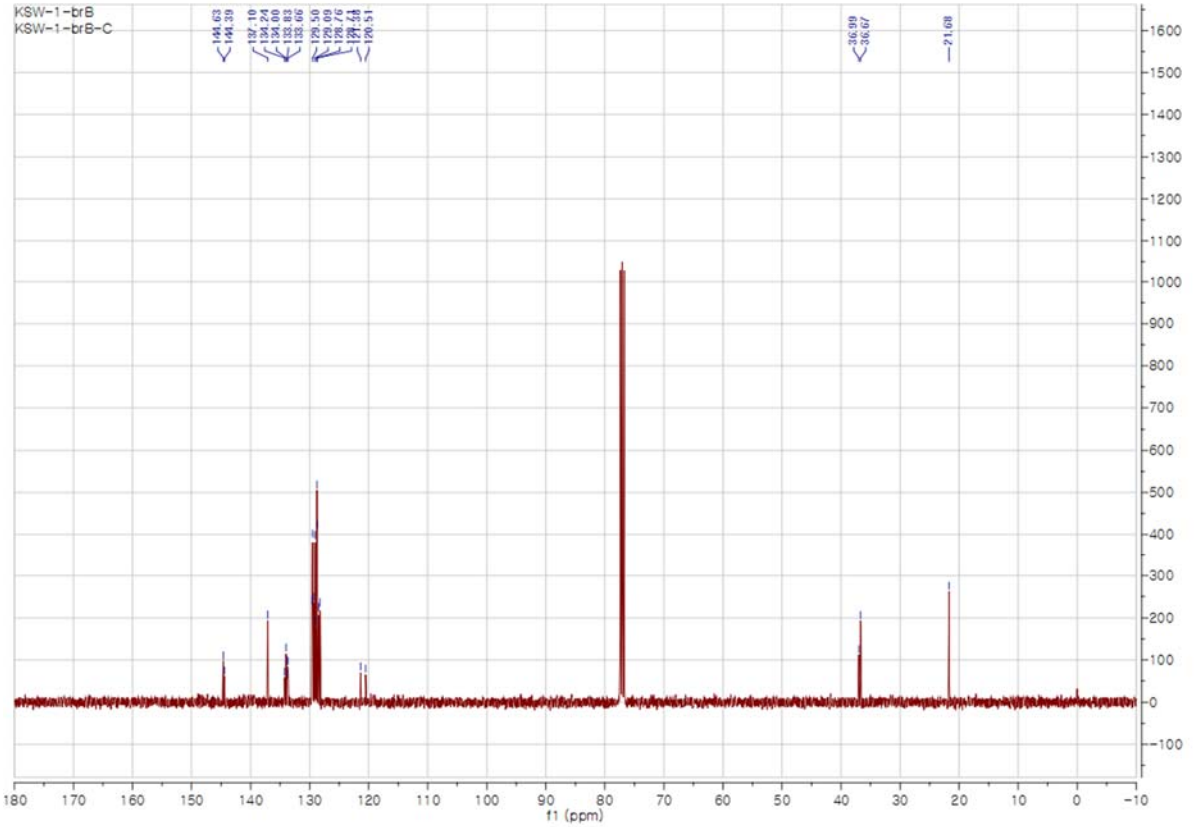

KSW-1-br5
KSW-1-br5
MeO
O
S
O
N
Br
Bn
Ph
7f (E/Z = 84/16)
f1 (ppm)

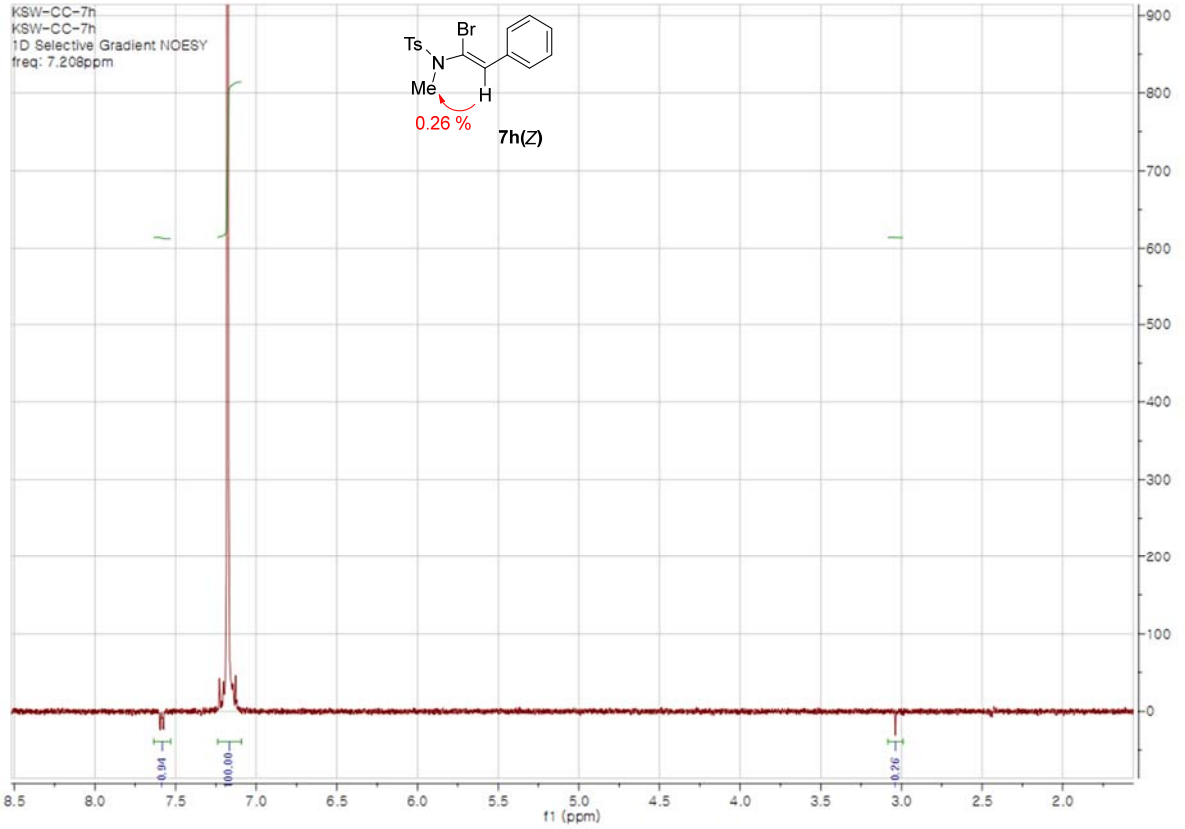

KSW-1-br5
KSW-1-br5
160.85
139.68
131.40
129.91
128.74
128.69
128.62
128.37
128.18
114.13
55.70
53.55
f1 (ppm)

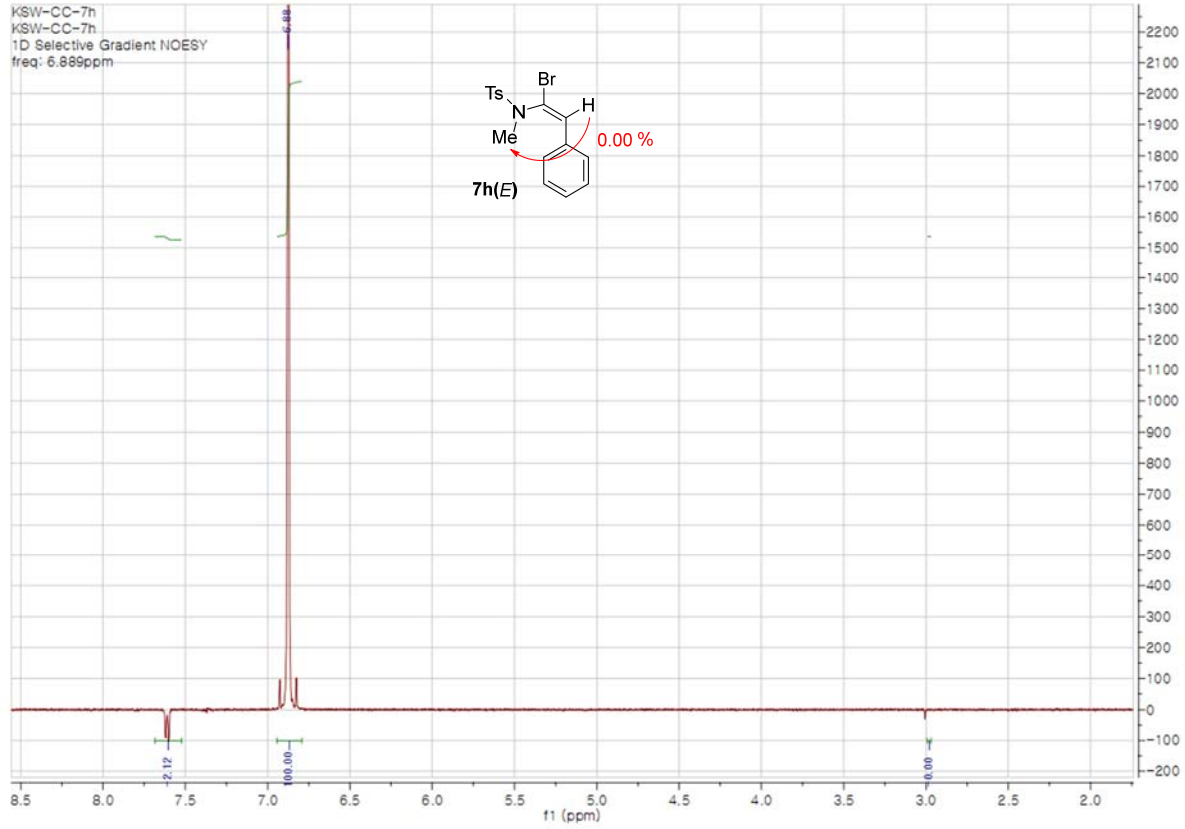

KSW-1-brA
KSW-1-brA
Br
Ms
N
Ph
Ph
7g(E/Z = 94/6)
4.18
6.12
1.00
0.20
2.96
f1 (ppm)

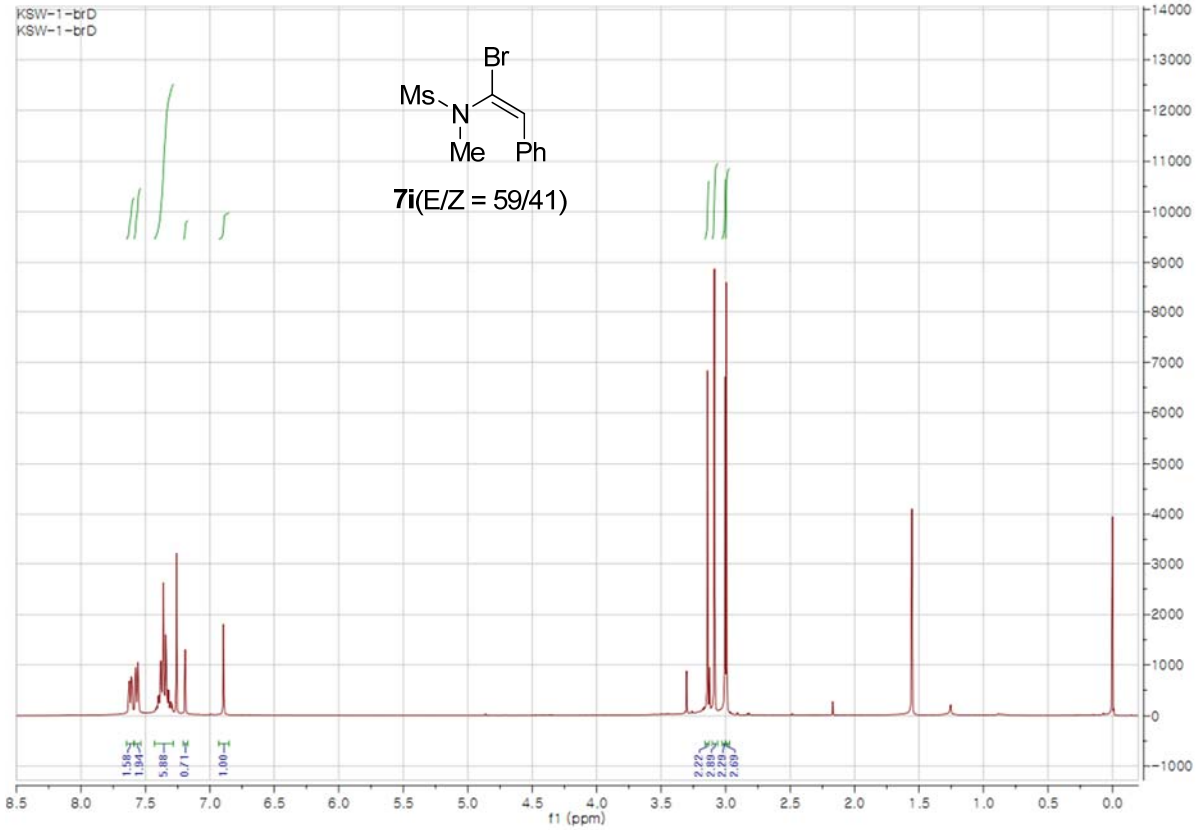

KSW-1-brA
KSW-1-brA-C
138.94
138.58
133.38
129.56
129.21
128.71
128.63
127.46
123.76
117.97
39.06
f1 (ppm)

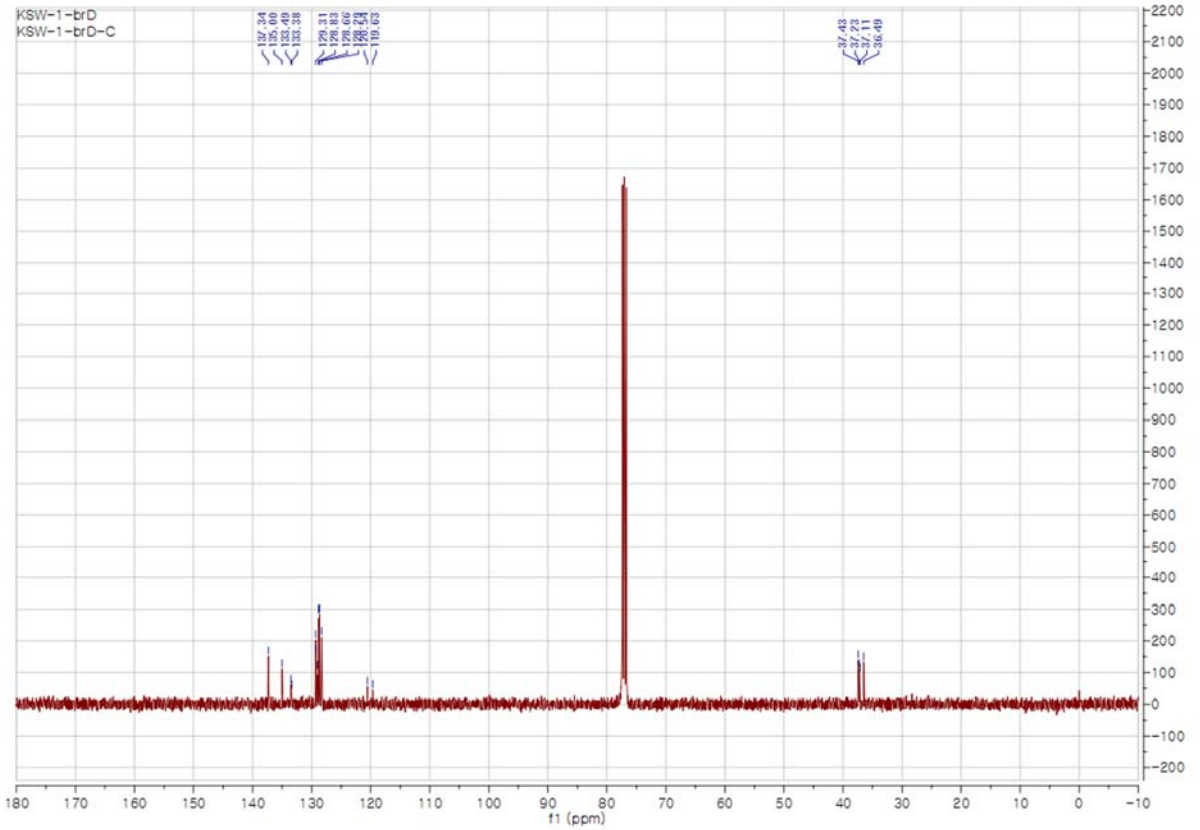

KSW-1-brB
KSW-1-brB
Br
Ts
N
Me
Ph
7h(E/Z = 65/35)
f1 (ppm)

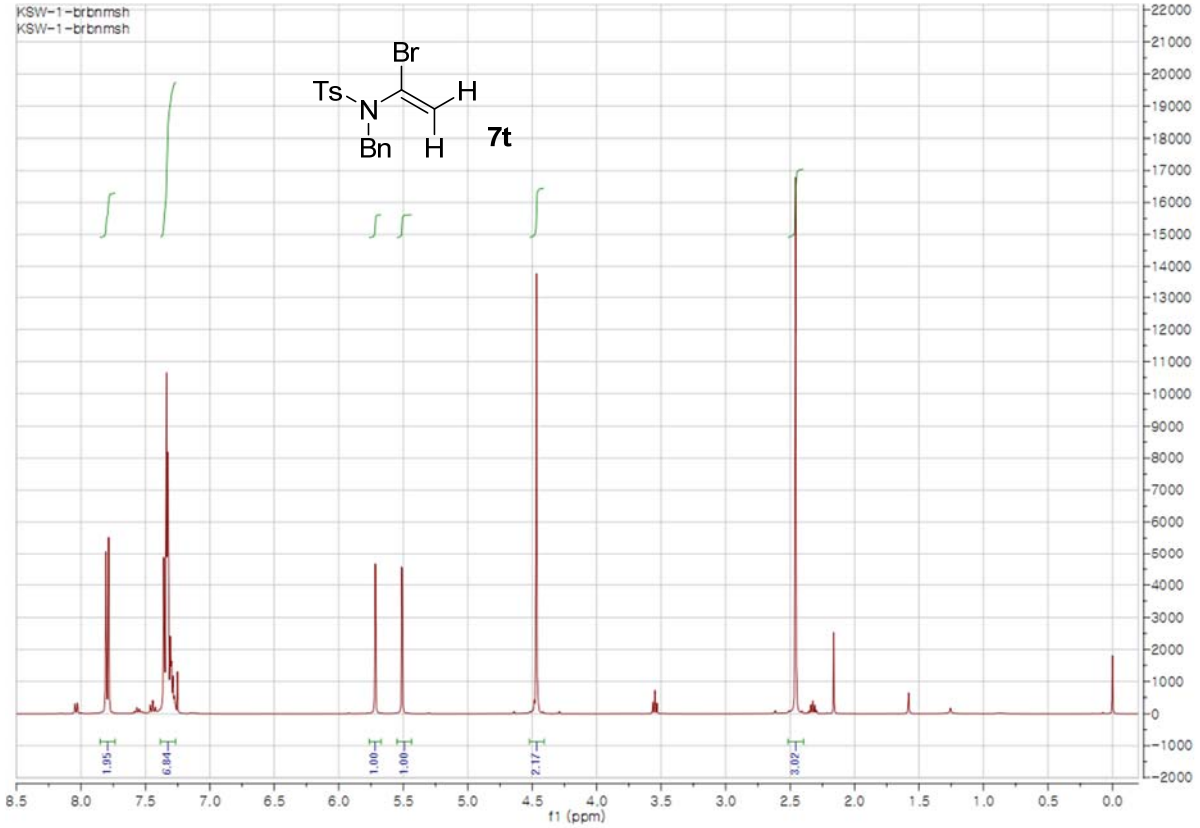

KSW-1-brB
KSW-1-brB-C
f1 (ppm)

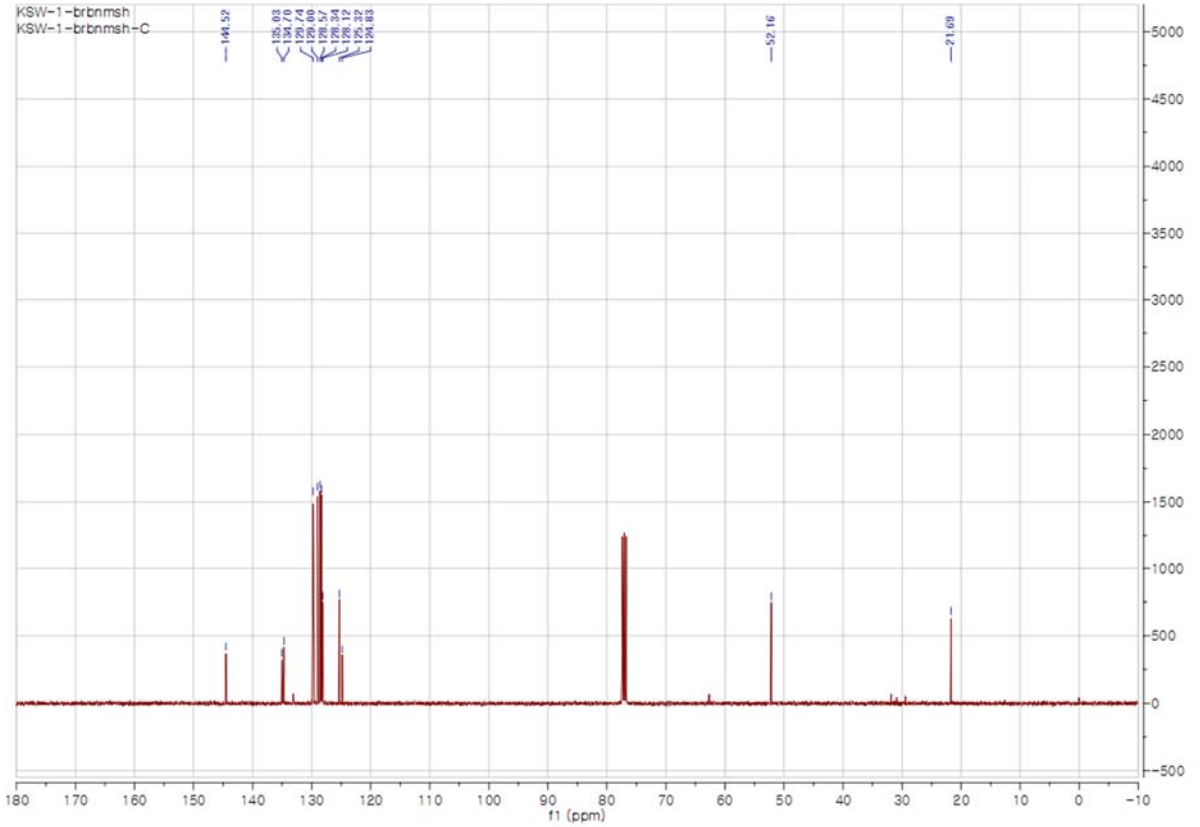

KSW-CC-7h
KSW-CC-7h
1D Selective Gradient NOESY
freq: 7.208ppm
Ts
N
Br
Me
H
0.26 %
7h(Z)
0.94
100.00
0.26
f1 (ppm)

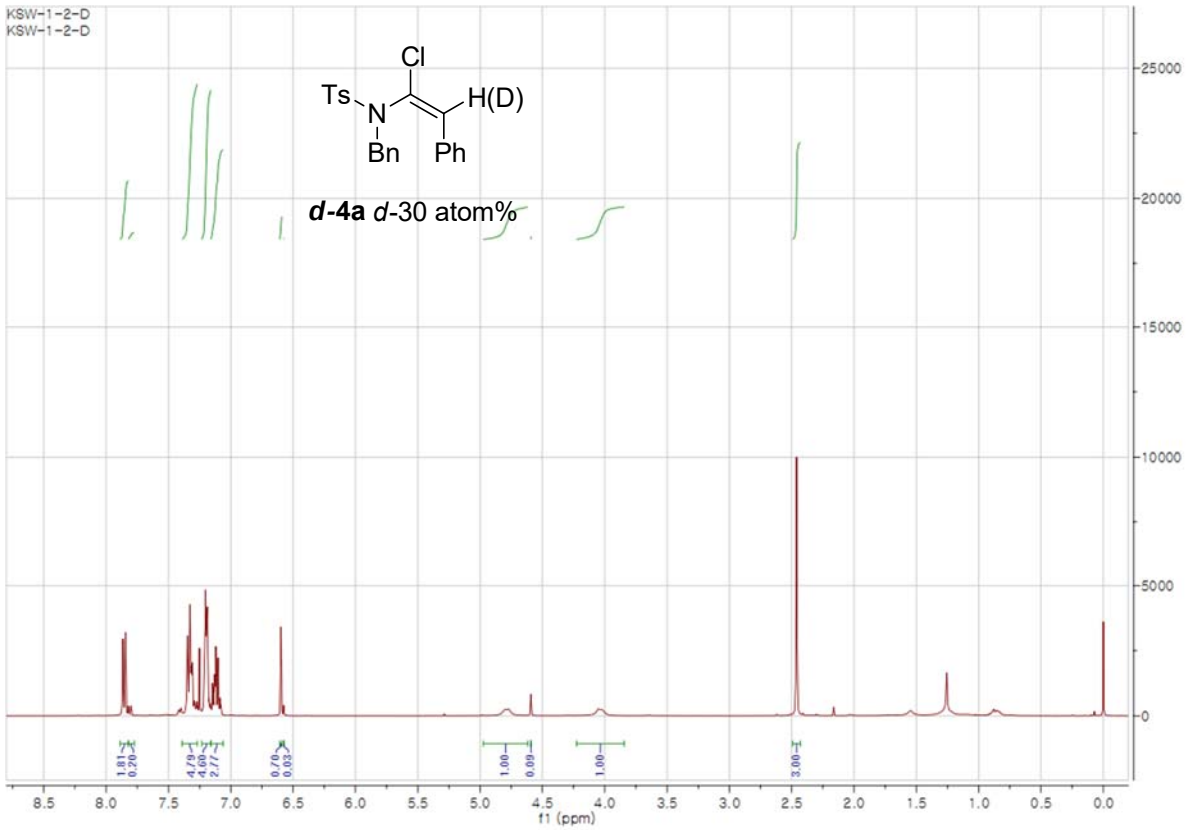

KSW-CC-7h
KSW-CC-7h
1D Selective Gradient NOESY
freq: 6.889ppm
Ts
N
Br
H
Me
0.00 %
7h(E)
2.12
100.00
0.00
f1 (ppm)

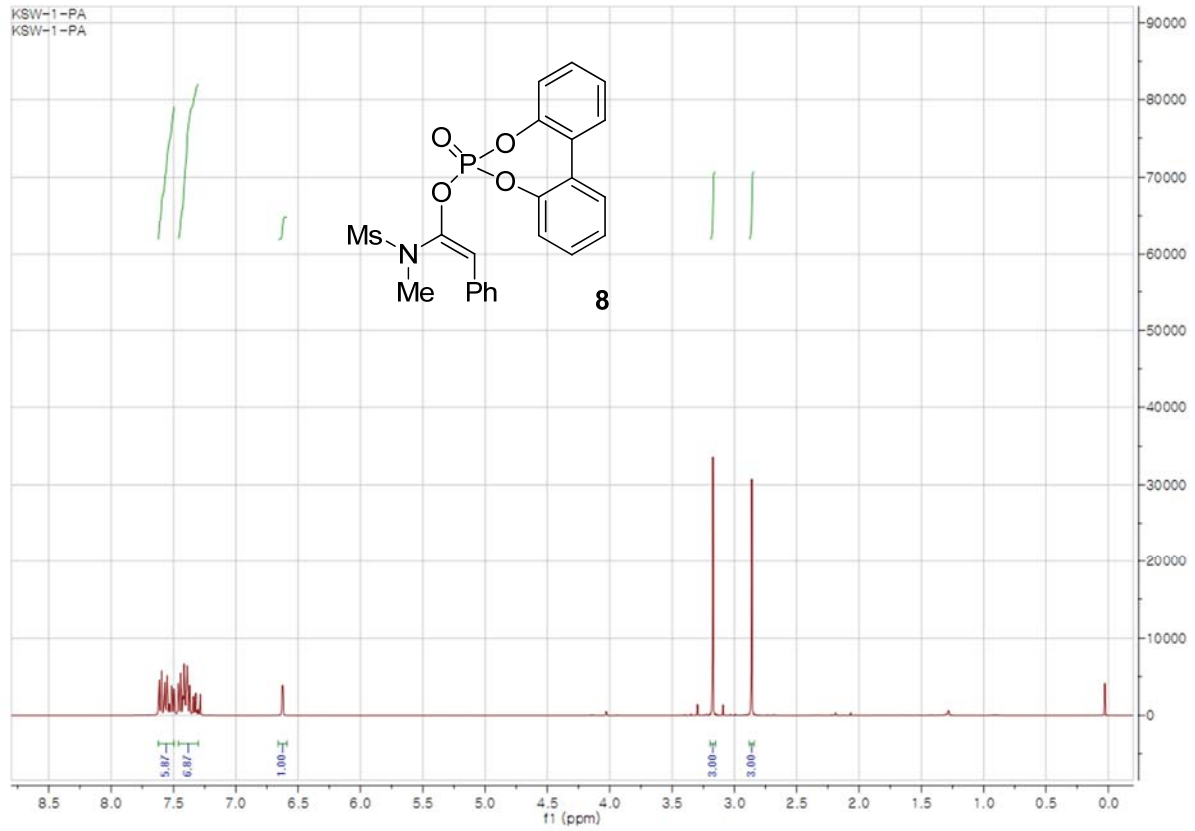

KSW-1-brD
KSW-1-brD
Br
Ms
N
Me
Ph
7i(E/Z = 59/41)
f1 (ppm)

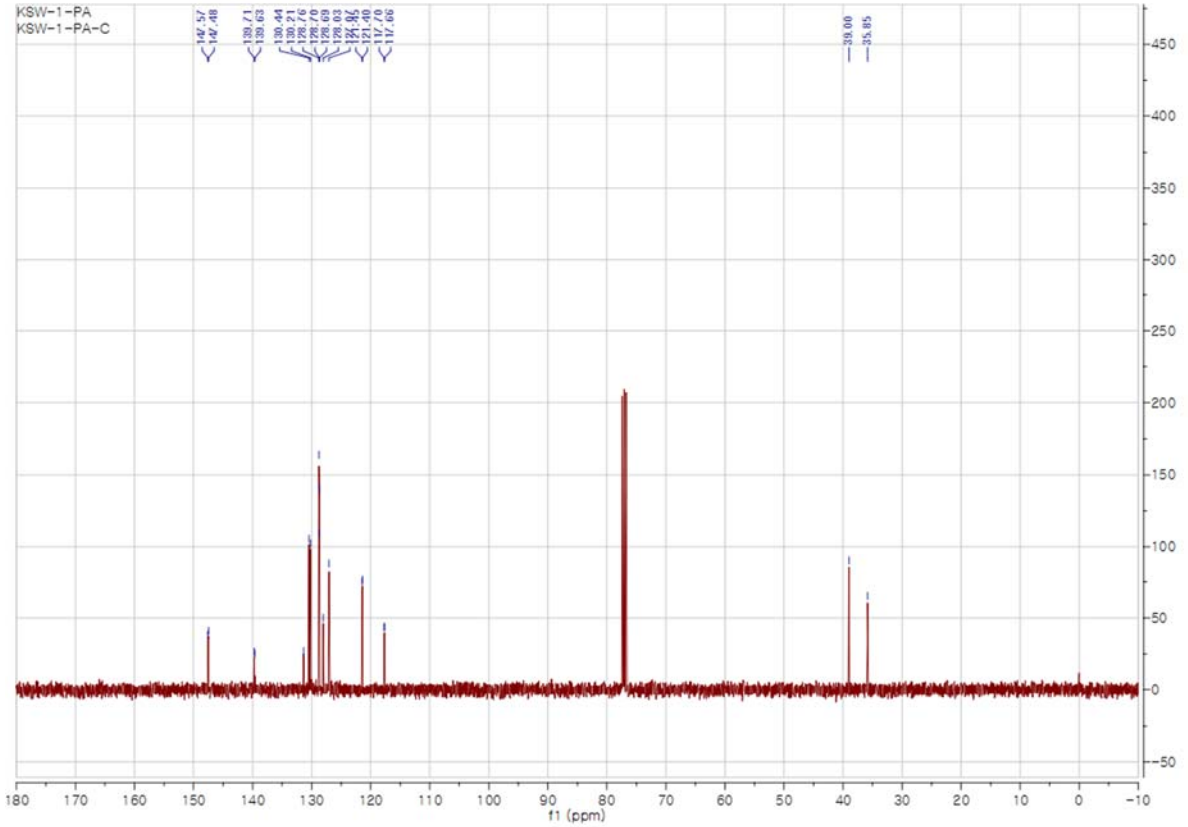

KSW-1-brD
KSW-1-brD-C
f1 (ppm)

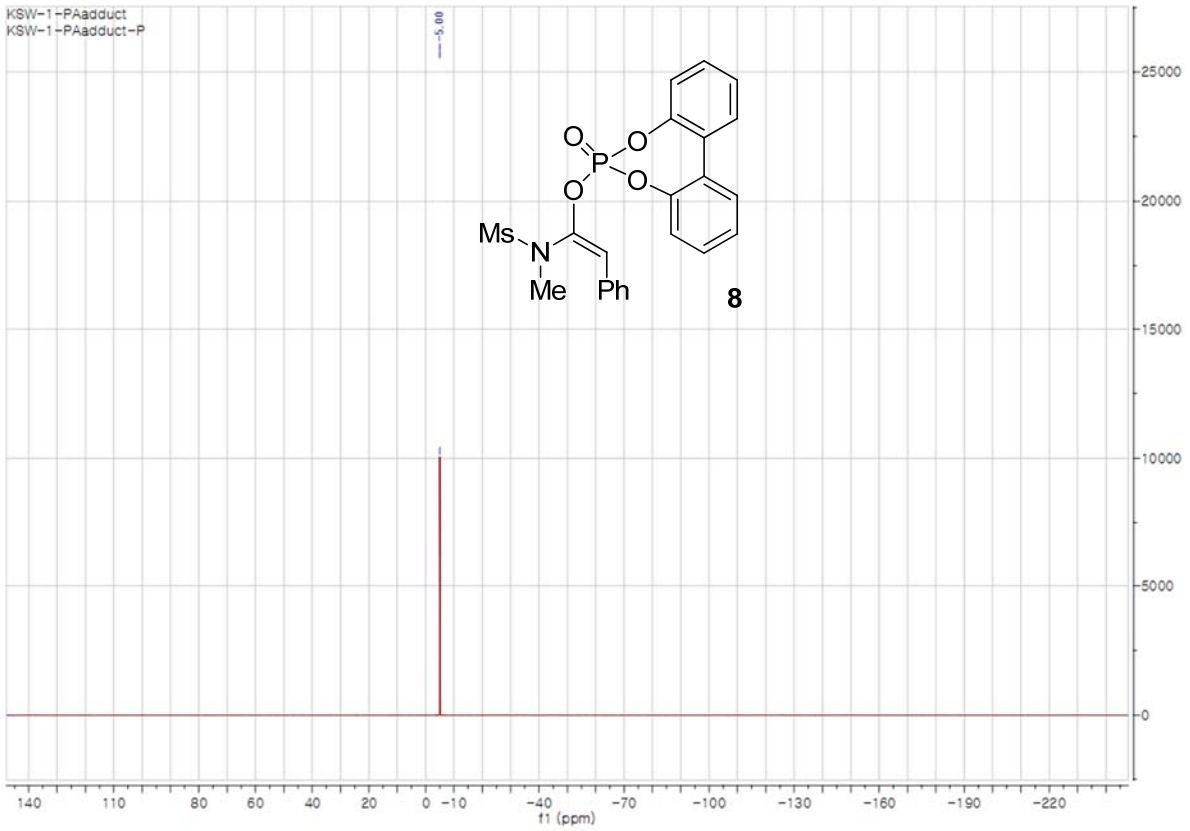

KSW-1-brbnmsh
KSW-1-brbnmsh
Br
Ts
N
H
Bn
H
7t
1.95
6.84
1.00
1.00
2.17
3.02
f1 (ppm)

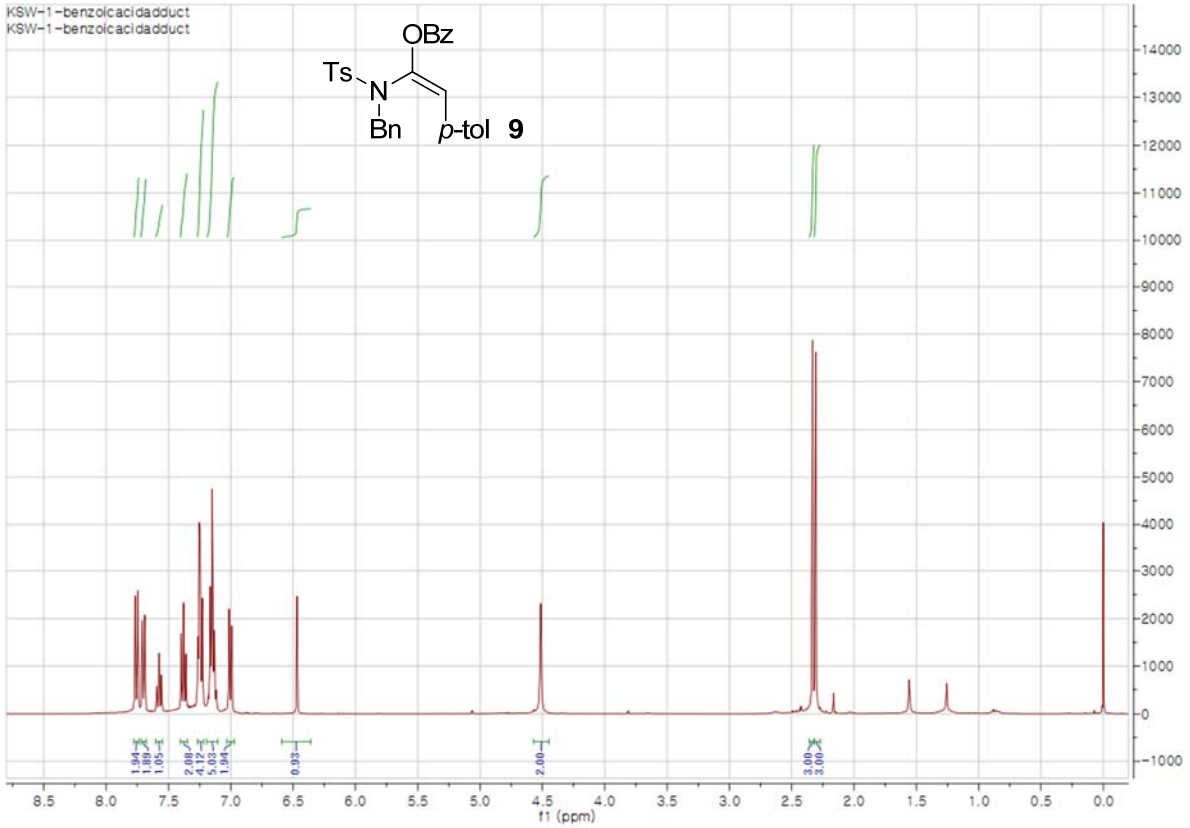

KSW-1-brbnmsh
KSW-1-brbnmsh-C
144.52
135.03
134.70
129.74
129.60
128.57
128.34
128.12
125.32
124.83
52.16
21.69
f1 (ppm)

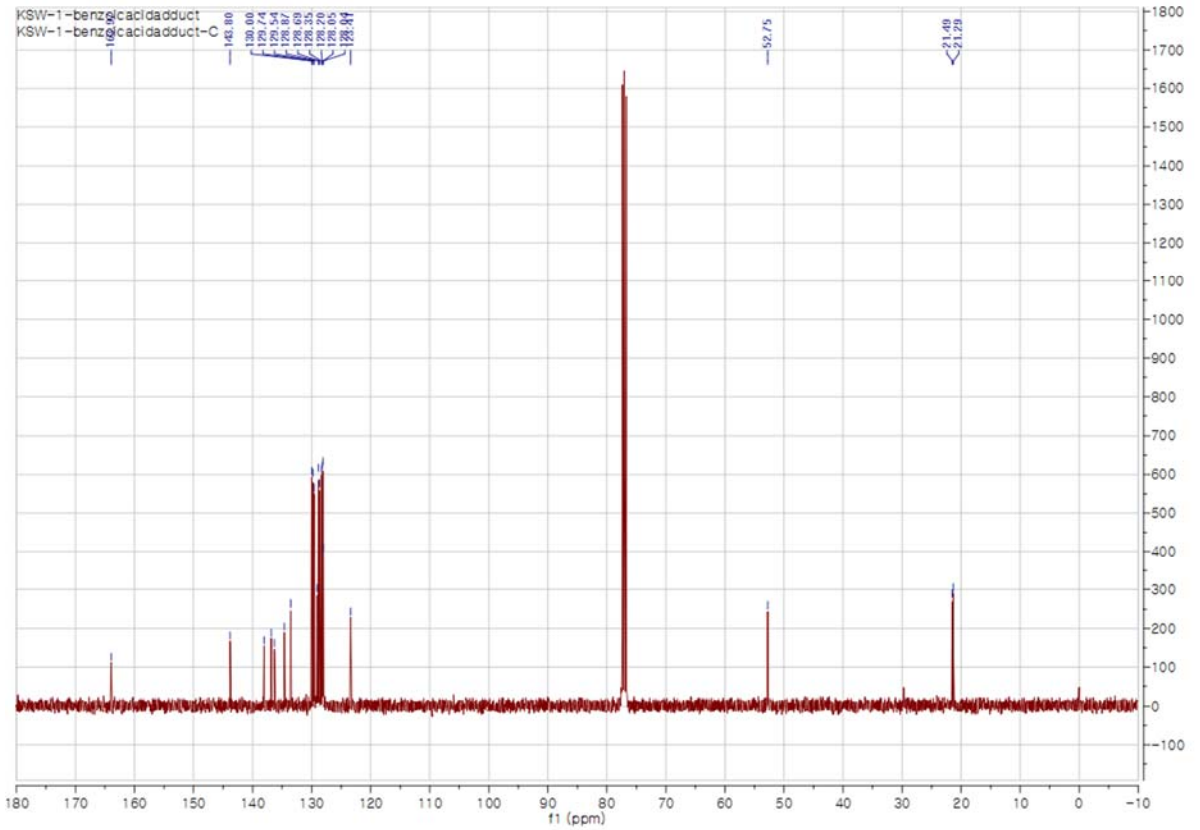

KSW-1-2-D
KSW-1-2-D
Cl
Ts
N
H(D)
Bn
Ph
***d*-4a** *d*-30 atom%
25000
20000
15000
10000
5000
0
1.81
0.20
4.79
4.60
2.77
0.70
0.03
1.00
0.09
1.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


KSW-1-PA
KSW-1-PA
O
P
O
O
O
Ms
N
Me
Ph
8
f1 (ppm)


KSW-1-PA
KSW-1-PA-C
f1 (ppm)


KSW-1-PAadduct
KSW-1-PAadduct-P
-5.69
O
P
O
O
O
Ms
N
Me
Ph
8
25000
20000
15000
10000
5000
0
140
110
80
60
40
20
0
-10
-40
-70
-100
-130
-160
-190
-220
f1 (ppm)


KSW-1-benzoicacidadduct
KSW-1-benzoicacidadduct
OBz
Ts
N
Bn
p-tol
9
f1 (ppm)


KSW-1-benzoicacidadduct
KSW-1-benzoicacidadduct-C
f1 (ppm)