Supplementary Materials

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Regio- and stereospecific synthesis of (*E*)-α-iodoenamide moieties from ynamides through the iodotrimethylsilane-mediated hydroiodation

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Contents

a) **General**: ^{1}H and ^{13}C NMR spectra were recorded on a BRUKER-SPECTROSPIN-400 with a 5 mm QNP probe at 400 MHz and 100 MHz, respectively. Chemical shift values, reported in parts per million (ppm), were indirectly referenced to external tetramethylsilane employing resonances due to trace monoprotio-solvent as an internal reference. Abbreviations are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Elemental analyses were performed at A RABBIT SCIENCE JAPAN Co., Ltd. (http://www.rabit-sc.jp/). Mass spectra were reported on a JEOL GC-mate II (for EI), and a Finnigan LCQ^{DECA} (for ESI). Column chromatography was carried out with silica gel, Silica Gel 60 N (Kanto Chemical Co.). Thin-layer chromategraphy analyses were performed on Merck silica gel 60 F_{254}. Reactions were performed in oven-dried glassware under an argon atmosphere unless otherwise noted.

b) **Materials**: Materials were purchased from Kanto Chemicals, Co., Inc., and Wako Pure Chemicals, and Tokyo Chemical Industry Co., LTD. All the chemical materials were used without further purification. Compounds of ynamides were prepared through the cross-coupling between appropriate alkynes and amines

according to the literature.[1] For the cross-coupling reactions, starting materials of amines, copper sulfate-pentahydrate, 1,10-phenanthroline, potassium phosphate were purchased from Wako Chemicals, Co., LTD., and Nacalai Tesque, Inc., and used without further purification.

c) **Representative procedure for preparation of ynamides, for 1 in Scheme 1 [1]:** To a solution of bromoethynylbenzene (1.4 g, 8.0 mmol) in 24 mL of anhydrous toluene in a reaction vial were added methyl phenylcarbamate (1.5 g, 9.6 mmol), K_3PO_4 (3.4 g, 16 mmol), copper sulfate-pentahydrate (400 mg, 16 mmol), and 1,10-phenanthroline (577 mg, 3.2 mmol). The reaction mixtures was capped under an argon atmosphere, and heated in an oil bath at 80 ºC for 15 h. The progress of the reaction was monitored using TLC analysis. Upon completion, the reaction mixture was allowed to cool to room temperature, and diluted with 15 mL of ethyl acetate. The mixture was filtered through a pad of celite, and the filtrate was concentrated *in vacuo*. The crude residue was purified by column chromatography with eluent of Hexane/ ethyl acetate = 19/1 to give 1.6 g of **1** in 80 % yield as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, J = 1.2, 8.6 Hz, 2H), 7.45-7.40 (m, 4H), 7.33-7.28 (m, 4H), 3.92 (s, 3H). ^{13}C NMR. (100 MHz, CDCl3) δ 154.9, 139.7, 131.5, 129.1, 128.4, 128.0, 127.2, 124.8, 123.0, 83.0, 70.3, 54.5.

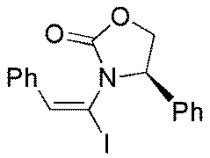
The ynamides in Scheme 2 (**3a**[4], **3b**[5], **3c**[5], **3d**[1a], **3e**[6], **3f**[6], **3g**[6], **3h**[7], **3i**[7], **3j**[8], **3k**[8], **3l**[7], **3m**[7], **3p**[8], **3q**[8], **3r**[4], **3s**[4], **3t**[5]) were known compounds, and ensured to show good match with physical data listed in the literatures.

d) **Representative procedure for (*E*)-1-halo-enamide moieties, for 2 (Table 1, entry 3)**: To a solution of **1** (1 mmol) in anhydrous CH_2Cl_2 (8 mL) at -78 ºC was added TMSI (1 M in CH_2Cl_2) dropwise over 5 min. After 15 min stirring, H_2O (20 mmol) was added, and the mixture was allowed to warm to 0 ºC over 50 min, and followed by additional stirring for 10 min. The reaction was quenched at 0 ºC with saturated aqueous sodium thiosulfate, stirred for 30 min, and allowed to warm to ambient temperature. To the mixture was added CH_2Cl_2, and organic phases were washed with brine, and then dried over Na_2SO_4, and concentrated to give a crude product. Purification by silica gel column chromatography afforded 375 mg of **2** in 99% yield as yellow viscous materials. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.28 (m, 10H), 7.17 (s, 1H), 3.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 142.2, 139.1, 135.2, 129.1, 129.02, 129.00, 127.7, 126.9, 124.5, 95.0, 54.0. MS (EI) *m/z*: 252 ($[M-I]^+$), 193 ($[M-I-CO_2CH_3]^+$). IR (neat): 3063, 2953, 1713 (C=O), 1622 (C=C), 1592 cm^{-1}. Anal. Calcd for $C_{16}H_{14}INO_2$: C, 50.68; H, 3.72; N, 3.69. Found: C, 50.66; H, 3.70; N, 3.76.

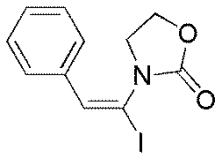
e) **Preparation of 1 M TMSI in CH_2Cl_2**: We purchased the seal-tubed TMSI (5 g) in neat form from Tokyo Chemical Industry Co., LTD, and it included a portion of Al metal inside the tube for inhibiting the decomposition of TMSI. 5 g of TMSI was added to 25 mL of dried CH_2Cl_2 along with the Al metal as a solid, thus providing colorless 1 M CH_2Cl_2 solution of TMSI for our experimental usage. The Al metal would not have a crucial role for the reactivity of the TMSI solution: actually, the reactivity of the freshly prepared TMSI solution was not influenced by with or without the metal. The stock solution in the presence of the Al metal was stable for at least two weeks, although it turned to slightly red colored solution.

f) **General procedure to make alkynyl bromide from terminal alkynes**[1, 2, 3]: To a solution of phenylacetylene (3.3 mL, 30 mmol) in dry acetone (60 mL) was added NBS (5.9 g, 33 mmol) and $AgNO_3$ (51 mg, 0.3 mmol). The reaction mixture was stirred at ambient temperature for *ca*. 2 h, monitoring by TLC analysis. When the starting alkyne was disappeared on TLC, the mixture was filtered through a pad of celite and florisil, and followed by the evaporation of all the volatiles. The residue was purified by short plug column chromatography as an eluent of hexane, giving the desired (bromoethynyl)benzene of 4.9 g in 91 %yield as a pale yellow oil. The (bromoethynyl)benzene was immediately served in next cross-coupling step without further purification because the bromide is liable to undergo rapid decomposition.

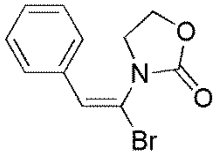
g) Characterization for (*E*)-1-halo-enamides 4a - 4t in Scheme 2.



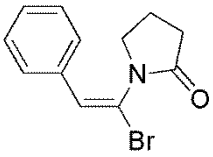
(*R*,*E*)-3-(1-iodo-2-phenylvinyl)-4-phenyloxazolidin-2-one (**4a**[4,8]); yellow solid, 99% (387 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.12 (m, 9H), 7.00 (d, J = 7.4 Hz, 2H), 4.78 (dd, J = 9.0, 9.0 Hz, 1H), 4.65 (dd, J = 9.0, 9.0 Hz, 1H), 4.24 (dd, J = 9.0, 9.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 145.8, 135.5, 134.1, 129.5, 129.0, 128.9, 128.7, 128.32, 128.28, 70.1, 63.6. MS (EI) *m/z*: 264 ($[M\text{-}I]^+$). IR (neat): 3045, 2954, 2901, 1760 (C=O), 1626 (C=C) cm^{-1}. Anal. Calcd for $C_{17}H_{14}INO_2$: C, 52.19; H, 3.61; N, 3.58. Found: C, 51.90; H, 3.50; N, 3.52.



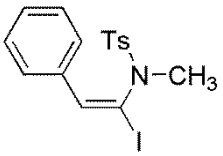
(*E*)-3-(1-iodo-2-phenylvinyl)oxazolidin-2-one (**4b**[5]); pale yellow solid, 87% (411 mg). After the isolation the compound immediately prior to the measurement of ^{13}C NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.24 (m, 4H), 7.18 (s, 1H), 7.14 (s, 1H), 4.36 (t, J = 8.0 Hz, 2H), 3.47 (t, J = 8.0 Hz, 2H).



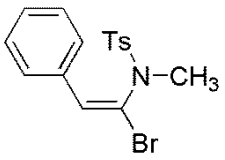
(*E*)-3-(1-bromo-2-phenylvinyl)oxazolidin-2-one (**4c**[5]); yellow solid, 99% (829 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.23 (m, 4H), 7.18 (s, 1H), 6.89 (s, 1H), 4.38 (t, J = 8.0 Hz, 2H), 3.66 (t, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 135.8, 133.9, 129.1, 128.2, 116.7, 63.0, 45.5. MS (EI) *m/z*: 267 (M^+), 188 ($[M\text{-}Br]^+$). IR (neat): 3283, 3032, 2920, 1754 (C=O), 1685 (C=C) cm^{-1}. Anal. Calcd for $C_{11}H_{10}BrNO_2$: C, 49.28; H, 3.76; N, 5.22. Found: C, 49.26; H, 3.73; N, 5.06.



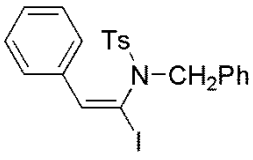
(*E*)-1-(1-bromo-2-phenylvinyl)pyrrolidin-2-one (**4d**[1a]); yellow oil, 99% (919 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.24 (m, 5H), 6.93 (s, 1H), 3.56 (t, J = 7.8 Hz, 2H), 2.43 (t, J = 7.8 Hz, 2H), 2.14 (tt, J = 7.8, 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 133.8, 133.5, 128.5, 128.3, 127.3, 117.0, 47.5, 30.6, 18.3. MS (EI) *m/z*: 266 ($[MH]^+$), 186 ($[MH\text{-}Br]^+$). IR (neat): 3059, 2930, 1685 (C=O), 1601 (C=C) cm^{-1}. Anal. Calcd for $C_{12}H_{12}BrNO$: C, 54.16; H, 4.54; N, 5.26. Found: C, 54.18; H, 4.40; N, 5.12.



(*E*)-*N*-(1-iodo-2-phenylvinyl)-*N*,4-dimethylbenzenesulfon amide (**4e**[6]); yellow solid, 99% (412 mg). The compound decomposed in the course of recrystallization, and was fragile even in solid state. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.3 Hz, 2H), 7.60-7.58 (m, 2H), 7.37-7.30 (m, 5H), 7.14 (s, 1H), 2.82 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 144.8, 135.1, 132.7, 129.6, 129.4, 129.1, 128.9, 128.7, 98.7, 38.4, 21.8.

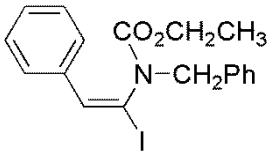


(*E*)-*N*-(1-bromo-2-phenylvinyl)-*N*,4-dimethylbenzene sulfonamide (**4f**[6]); pale yellow solid, 97% (1.26 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.2 Hz, 2H), 7.60-7.58 (m, 2H), 7.38-7.29 (m, 5H), 6.86 (s, 1H), 2.99 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 136.7, 133.6, 133.40, 133.38. 129.4, 128.8, 128.6, 128.5, 121.4, 36.5, 21.4. MS (EI) *m/z*: 285 ($[M\text{-}Br]^+$), 208 ($[M\text{-}Br\text{-}Ph]^+$). IR (neat): 3030, 1630 (C=C), 1357 (NSO_2), 1163 (NSO_2) cm^{-1}. Anal. Calcd for $C_{16}H_{16}BrNO_2S$: C, 52.47; H, 4.40; N, 3.82. Found: C, 52.25; H, 4.36; N, 3.69.

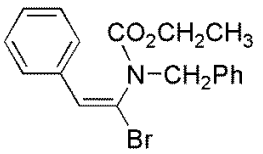


(*E*)-*N*-benzyl-*N*-(1-iodo-2-phenylvinyl)-4-methylbenzene sulfonamide (**4g**[6]); yellow solid, 93% (2.53 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.31-7.11 (m, 11H), 4.86 (d, J = 13.2 Hz, 1H),

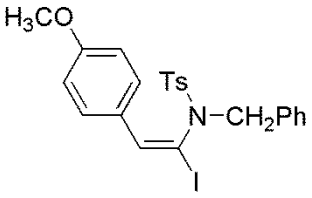
3.62 (d, J = 13.2 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 145.2, 135.1, 133.6, 133.2, 130.2, 129.9, 129.8, 129.04, 128.96, 128.6, 128.4, 128.2, 98.3, 55.4, 22.0. MS (ESI) *m/z*: 512 ($[MNa]^+$). IR (neat): 3029, 1594 (C=C), 1348 (NSO_2), 1164 (NSO_2), 1154 cm^{-1}. Anal. Calcd for $C_{22}H_{20}INO_2S$: C, 54.00; H, 4.12; N, 2.86. Found: C, 54.07; H, 4.00; N, 2.77.



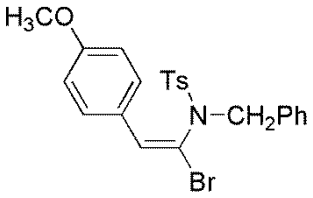
(*E*)-ethyl benzyl(1-iodo-2-phenylvinyl)carbamate (**4h**[7]); yellow viscous materials, 97% (393 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.25 (m, 2H), 7.21-7.13 (m, 6H), 7.00-6.97 (m, 3H), 4.64 (d, J = 14.3 Hz, 1H), 4.38 (d, J = 14.3 Hz, 1H), 4.30-4.17 (m, 2H), 1.23 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 142.2, 135.5, 134.8, 130.1, 128.6, 128.5, 128.4, 128.2, 128.0, 96.5, 63.2, 53.0, 14.8. MS (EI) *m/z*: 281 ($[MH-I]^+$), 207 ($[M-I-CO_2CH_2CH_3]^+$). IR (neat): 3029, 2979, 1707 (C=O), 1616 (C=C) cm^{-1}. Anal. Calcd for $C_{18}H_{18}INO_2$: C, 53.09; H, 4.46; N, 3.44. Found: C, 53.74; H, 4.61; N, 3.31.



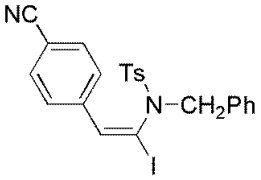
(*E*)-ethyl benzyl(1-bromo-2-phenylvinyl)carbamate (**4i**[7]); yellow viscous materials, 90% (329 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.27 (m, 2H), 7.22-7.15 (m, 6H), 7.02-7.00 (m, 2H), 6.72 (s, 1H), 4.66 (d, J = 14.3 Hz, 1H), 4.54 (d, J = 14.3 Hz, 1H), 4.25-4.19 (m, 2H), 1.19 (t, J = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 135.4, 134.4, 133.7, 129.9, 128.7, 128.45, 128.42, 128.1, 127.9, 121.2, 63.2, 52.3, 14.7. MS (EI) *m/z*: 359 (M^+), 279 ($[M-Br]^+$). IR (neat): 3062, 3030, 2979, 1712 (C=O), 1635 (C=C) cm^{-1}. Anal. Calcd for $C_{18}H_{18}BrNO_2$: C, 60.01; H, 5.04; N, 3.89. Found: C, 60.02; H, 4.87; N, 3.86.



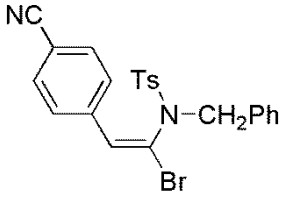
(*E*)-*N*-benzyl-*N*-(1-iodo-2-(4-methoxyphenyl) vinyl)-4-methylbenzenesulfonamide (**4j**[8]); yellow viscous materials, 99% (2.62 g). The compound immediately decomposed after the isolation by column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.3 Hz, 2H), 7.38-7.30 (m, 6H), 7.16-7.13 (m, 3H), 7.02 (s, 1H), 6.70-6.68 (m, 2H), 4.87 (d, J = 13.2 Hz, 1H), 3.78 (S, 3H), 3.61 (d, J = 13.2 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 147.7, 145.1, 133.6, 133.4, 130.8, 130.2, 129.9, 129.8, 128.6, 128.4, 128.0, 113.5, 95.7, 55.4, 55.3, 22.0.



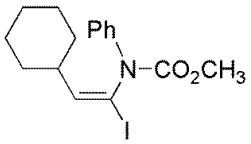
(*E*)-*N*-benzyl-*N*-(1-bromo-2-(4-methoxyphenyl) vinyl)-4-methylbenzenesulfonamide (**4k**[8]); yellow viscous materials, 99% (2.39 g). The compound immediately decomposed after the isolation by column chromatography. The stability of **4k** was comparable to that of **4j**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.3 Hz, 2H), 7.36-7.28 (m, 6H), 7.16-7.11 (m, 3H), 6.73-6.70 (m, 3H), 4.85 (d, J = 13.0 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 160.0, 144.9, 139.3, 134.5, 133.6, 130.6, 130.1, 129.8, 129.4, 128.5, 128.4, 126.6, 117.7, 113.7, 55.4, 55.3, 21.9.



(*E*)-*N*-benzyl-*N*-(2-(4-cyanophenyl)-1-iodovinyl)-4-methylbenzenesulfonamide (**4l**[7]); white solid, 88% (452 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.2 Hz, 2H), 7.43-7.38 (m, 4H), 7.32-7.27 (m, 4H), 7.21-7.13 (m, 4H), 4.87 (d, J = 13.2 Hz, 1H), 3.60 (d, J = 13.2 Hz, 1H), 2.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5, 145.5, 139.3, 133.2, 133.0, 132.0, 130.2, 130.0, 129.7, 129.2, 128.9, 128.6, 119.0, 111.8, 102.0, 55.6, 22.0. MS (ESI) *m/z*: 537 ([MNa]$^+$). IR (neat): 2223 (CN), 1598 (C=C), 1352 (NSO_2), 1166 (NSO_2) cm^{-1}. Anal. Calcd for $C_{23}H_{19}IN_2O_2S$: C, 53.70; H, 3.72; N, 5.45. Found: C, 53.74; H, 3.61; N, 5.39.

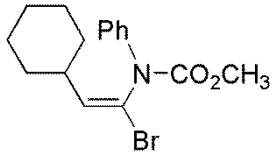


(*E*)-*N*-benzyl-*N*-(1-bromo-2-(4-cyanophenyl)vinyl)-4-methylbenzenesulfonamide (**4m**[7]); white solid, 99% (1.16 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 7.39-7.33 (m, 4H), 7.25-7.12 (m, 5H), 6.84 (s, 1H), 4.85 (d, J = 13.0 Hz, 1H), 3.91 (d, J = 13.0 Hz, 1H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 138.17, 138.16, 134.2, 133.2, 132.2, 130.1, 130.0, 129.4, 129.2, 128.9, 128.6, 123.2, 119.0, 111.9, 53.7, 22.0. MS (ESI) *m/z*: 489 ([MNa]$^+$). IR (neat): 2224 (CN), 1596 (C=C), 1353 (NSO_2), 1165 (NSO_2) cm^{-1}. Anal. Calcd for $C_{23}H_{19}BrN_2O_2S$: C, 59.11; H, 4.10; N, 5.99. Found: C, 59.12; H, 4.03; N, 5.77.

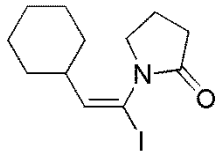


(*E*)-methyl 2-cyclohexyl-1-iodovinyl(phenyl) carbamate (**4n**); white solid, 88% (680 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.35 (m, 4H), 7.30-7.28 (m, 1H), 6.08 (d, J = 10.4 Hz, 1H), 3.83 (s, 3H), 2.39-2.30 (m, 1H), 1.68-1.49 (m, 5H), 1.18-1.08 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7, 149.8, 140.0, 129.0, 126.7, 124.8, 90.3, 53.7, 40.4, 31.3, 25.8, 25.5. MS (EI) *m/z*: 258 ([M-I]$^+$). IR (neat): 2922, 2886, 2844, 1703 (C=O), 1647 (C=C),

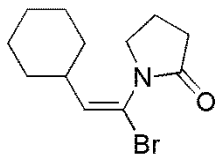
1439, 1382, 1281, 1250 cm^{-1}. Anal. Calcd for $C_{16}H_{20}INO_2$: C, 49.88; H, 5.23; N, 3.64. Found: C, 49.89; H, 5.15; N, 3.46.



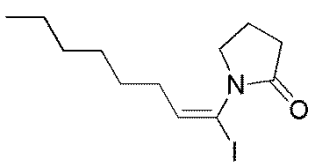
(*E*)-methyl 1-bromo-2-cyclohexylvinyl(phenyl) carbamate (**4o**); white solid, 85% (576 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 4.2 Hz, 4H), 7.30-7.24 (m, 1H), 5.82 (d, J = 10.4 Hz, 1H), 3.83 (s, 3H), 2.36-2.26 (m, 1H), 1.73-1.43 (m, 5H), 1.18-1.10 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 141.2, 140.1, 129.2, 126.9, 125.2, 116.8, 53.9, 39.4, 31.6, 26.0, 25.7. MS (EI) *m/z*: 338 ($[MH]^+$), 259 ($[MH\text{-}Br]^+$). IR (neat): 2924, 2846, 1722 (C=O), 1685 (C=C), 1491, 1436 cm^{-1}. Anal. Calcd for $C_{16}H_{20}BrNO_2$: C, 56.82; H, 5.96; N, 4.14. Found: C, 56.83; H, 5.75; N, 4.04.



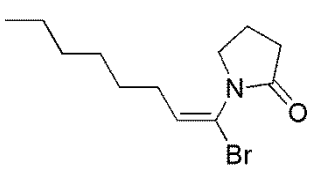
(*E*)-1-(2-cyclohexyl-1-iodovinyl)pyrrolidin-2-one (**4p**[8]); white solid, 81% (257 mg). The compound immediately decomposed after the isolation by column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.10 (d, J = 9.8 Hz, 1H), 3.37 (t, J = 6.4 Hz, 2H), 2.36 (t, J = 8.0 Hz, 2H), 2.18-2.05 (m, 3H), 1.70-1.59 (m, 5H), 1.27-1.05 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 150.6, 87.2, 49.4, 40.6, 32.3, 31.2, 25.9, 25.7, 18.1.



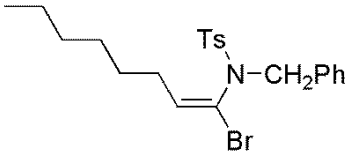
(*E*)-1-(1-bromo-2-cyclohexylvinyl)pyrrolidin-2-one (**4q**[8]); white solid, 67% (183 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84 (d, J = 10.0 Hz, 1H), 3.52 (t, J = 6.3 Hz, 2H), 2.43 (t, J = 8.2 Hz, 2H), 2.18-2.01 (m, 3H), 1.70-1.60 (m, 5H), 1.28-1.07 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 141.3, 113.1, 48.7, 39.3, 32.4, 30.9, 25.9, 25.7, 18.4. MS (EI) *m/z*: 273 ($[MH]^+$), 192 ($[M\text{-}Br]^+$). IR (neat): 2922, 2886, 2845, 1702 (C=O), 1647 (C=C), 1381, 1338, 1282, 1248 cm^{-1}. Anal. Calcd for $C_{12}H_{18}BrNO$: C, 52.95; H, 6.67; N, 5.15. Found: C, 52.94; H, 6.79; N, 5.29.



(*E*)-1-(1-iodooct-1-enyl)pyrrolidin-2-one (**4r**[4, 8]); yellow oil, 91% (585 mg). This is the known compound in ref. 8. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.19- 6.15 (m, 1H), 3.39 (t, J = 6.6 Hz, 2H), 2.33 (t, J = 8.2 Hz, 2H), 2.14-2.06 (m, 2H), 1.93 (q, J = 7.4 Hz, 2H), 1.34-1.20 (m, 8H), 0.85-0.81 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 145.1, 87.8, 49.2, 31.7, 31.2, 31.0, 29.0, 28.5, 22.7, 18.1, 14.3.

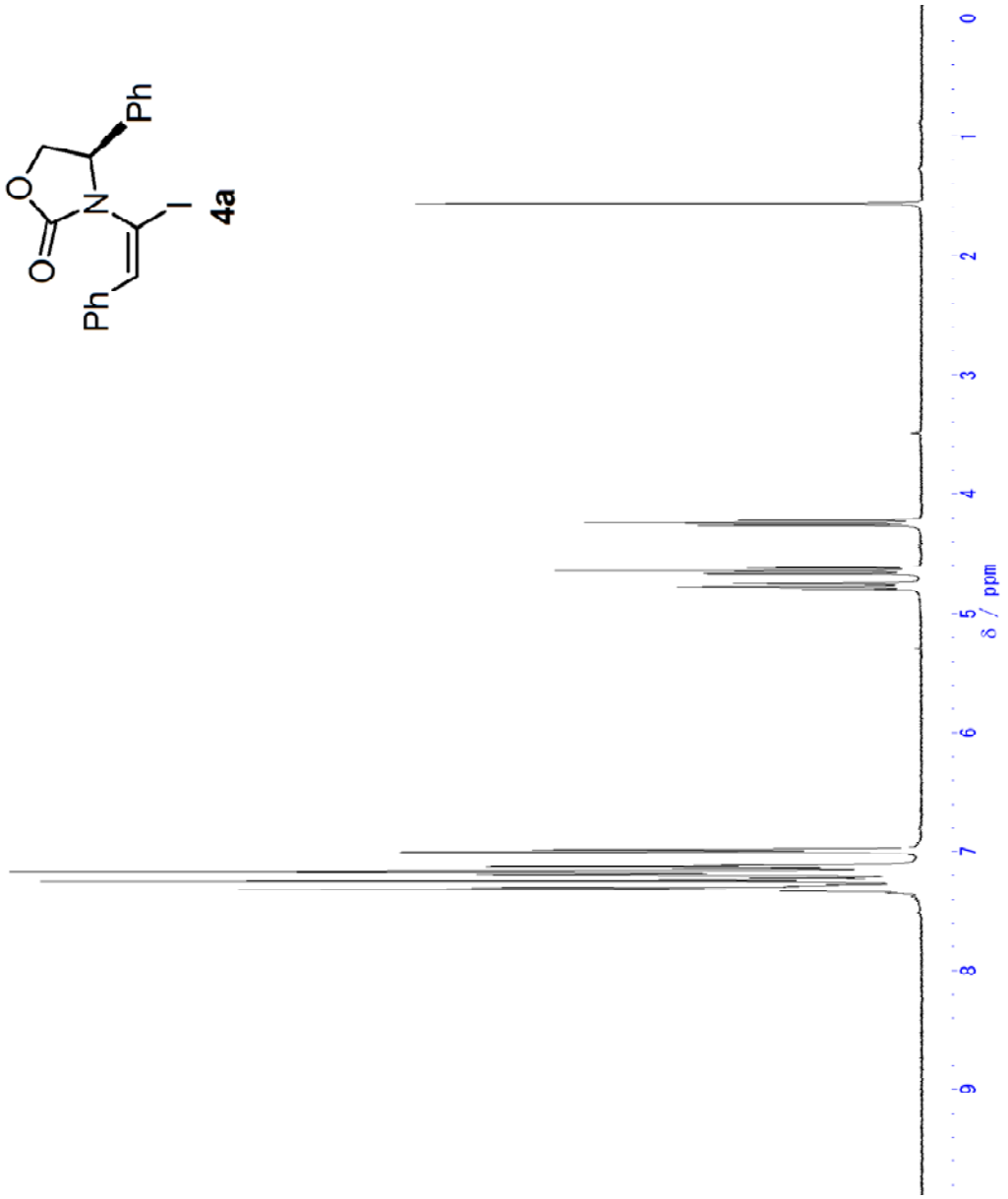


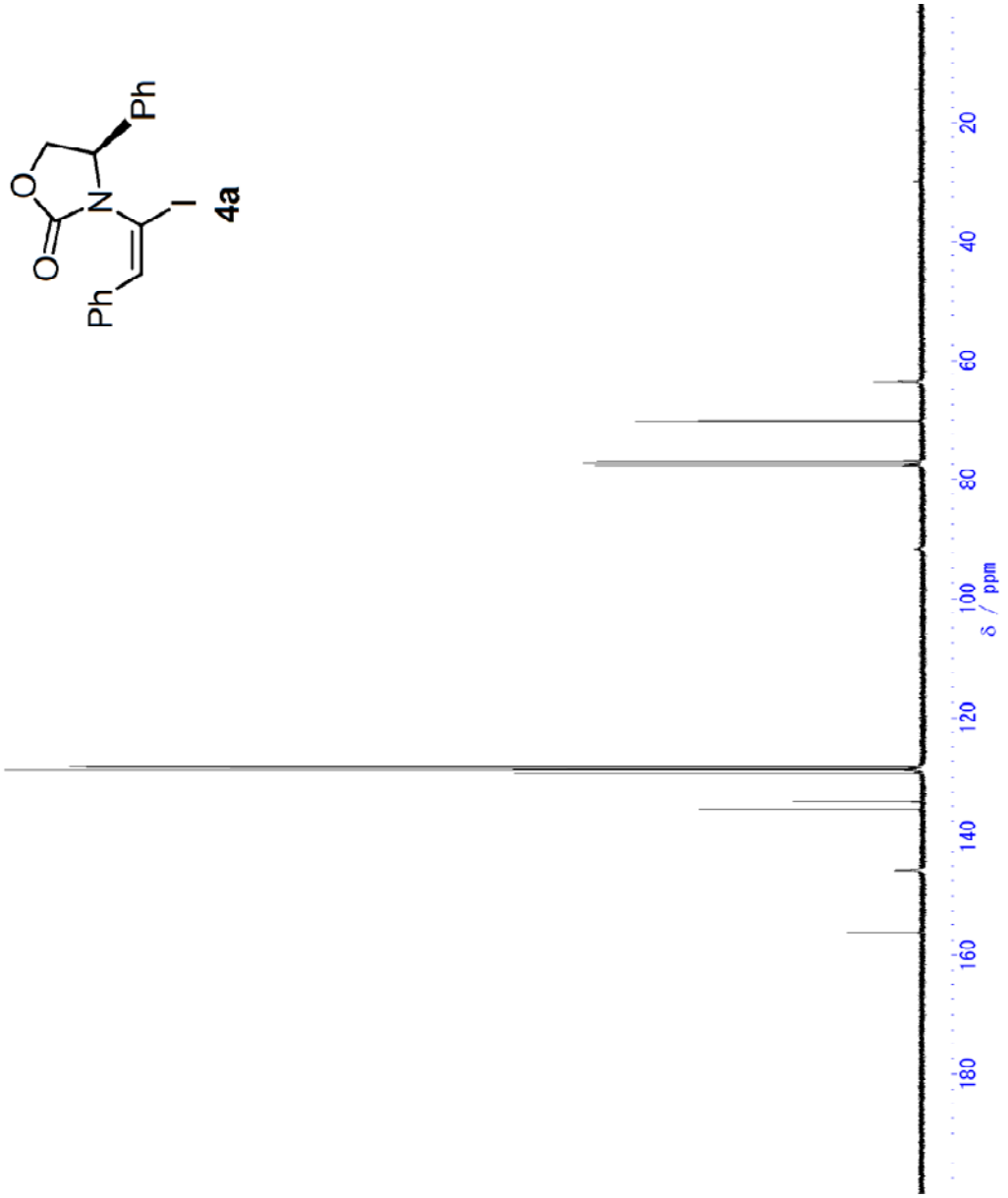
(*E*)-1-(1-bromooct-1-enyl)pyrrolidin-2-one (**4s**[4, 8]); pale yellow oil, 88% (478 mg). This is the known compound in ref. 8. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.95 (t, J = 7.5 Hz, 1H), 3.53 (t, J = 8.3 Hz, 2H), 2.43 (t, J = 8.3 Hz, 2H), 2.14 (tt, J = 8.3, 8.3 Hz, 2H), 1.96 (q, J = 7.5 Hz, 2H), 1.40-1.25 (m, 8H), 0.88 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 135.7, 113.8, 48.3, 31.7, 30.9, 29.7, 29.1, 28.6, 22.7, 18.4, 14.3. MS (EI) *m/z*: 194 ([MH-Br]$^{+}$). IR (neat): 2925, 2855, 1736 (C=O), 1692 (C=C), 1361 cm^{-1}. Anal. Calcd for $C_{16}H_{14}INO_2$: C, 50.68; H, 3.72; N, 3.69. Found: C, 50.66; H, 3.70; N, 3.76.



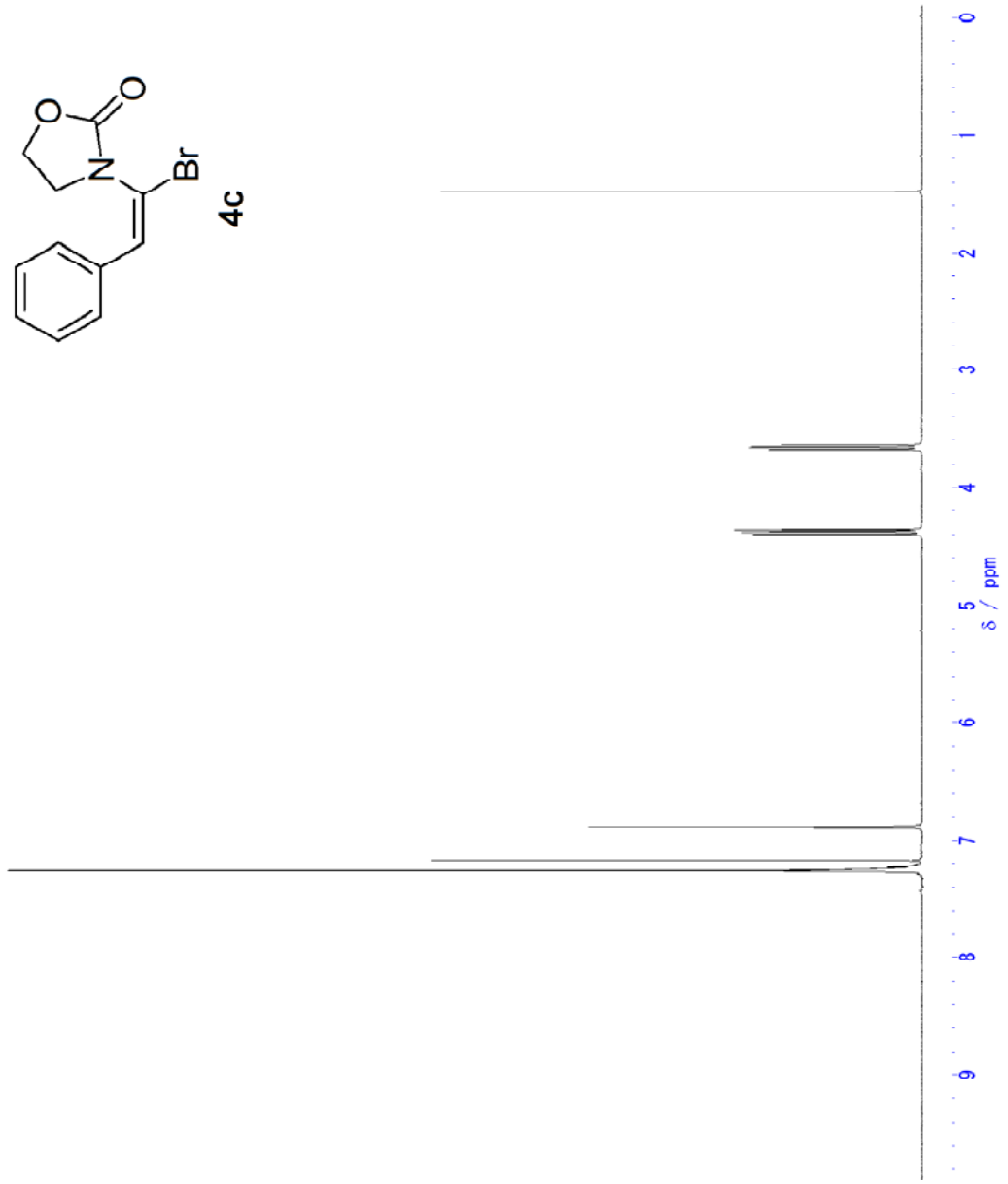
(*E*)-*N*-benzyl-*N*-(1-bromooct-1-enyl)-4-methyl benzenesulfonamide (**4t**[5]); colorless oil, 15% (68 mg). This compound was too fragile to isolate with column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.2 Hz, 2H), 7.40-7.27 (m, 7H), 5.90 (dd, J = 9.0, 5.8 Hz, 1H), 4.83 (d, J = 13.4 Hz, 1H), 3.84 (d, J = 13.4 Hz, 1H), 2.46 (s, 3H), 2.02-1.79 (m, 2H), 1.26-0.95 (m, 8H), 0.85 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 143.3, 135.5, 134.7, 130.03, 129.95, 128.9, 128.7, 128.6, 116.7, 52.5, 31.9, 30.9, 29.1, 28.4, 22.8, 22.0, 14.4.

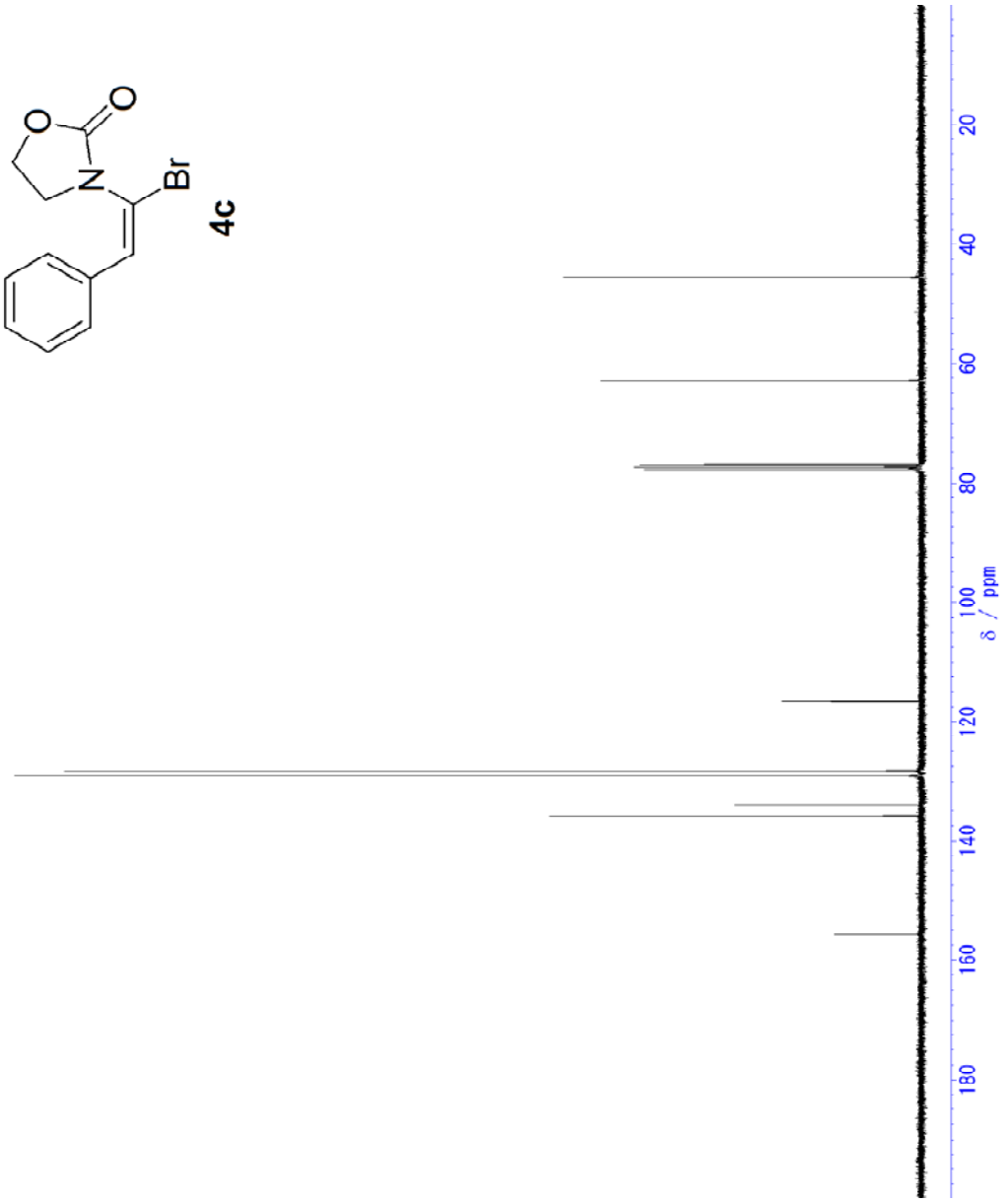
h) ^{1}H NMR and ^{13}C NMR spectra for (*E*)-1-halo-enamides 4a - 4t in Scheme 2.

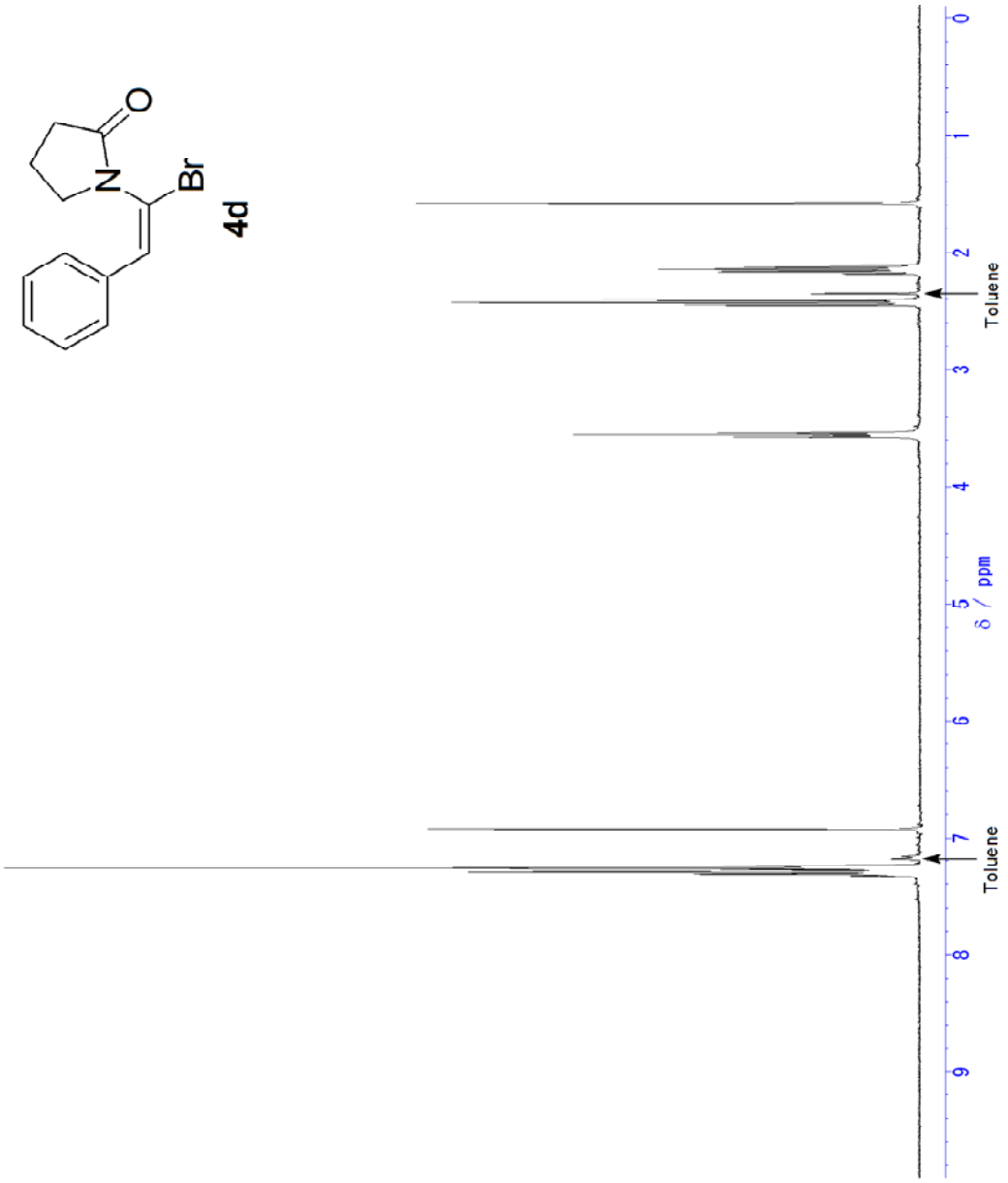


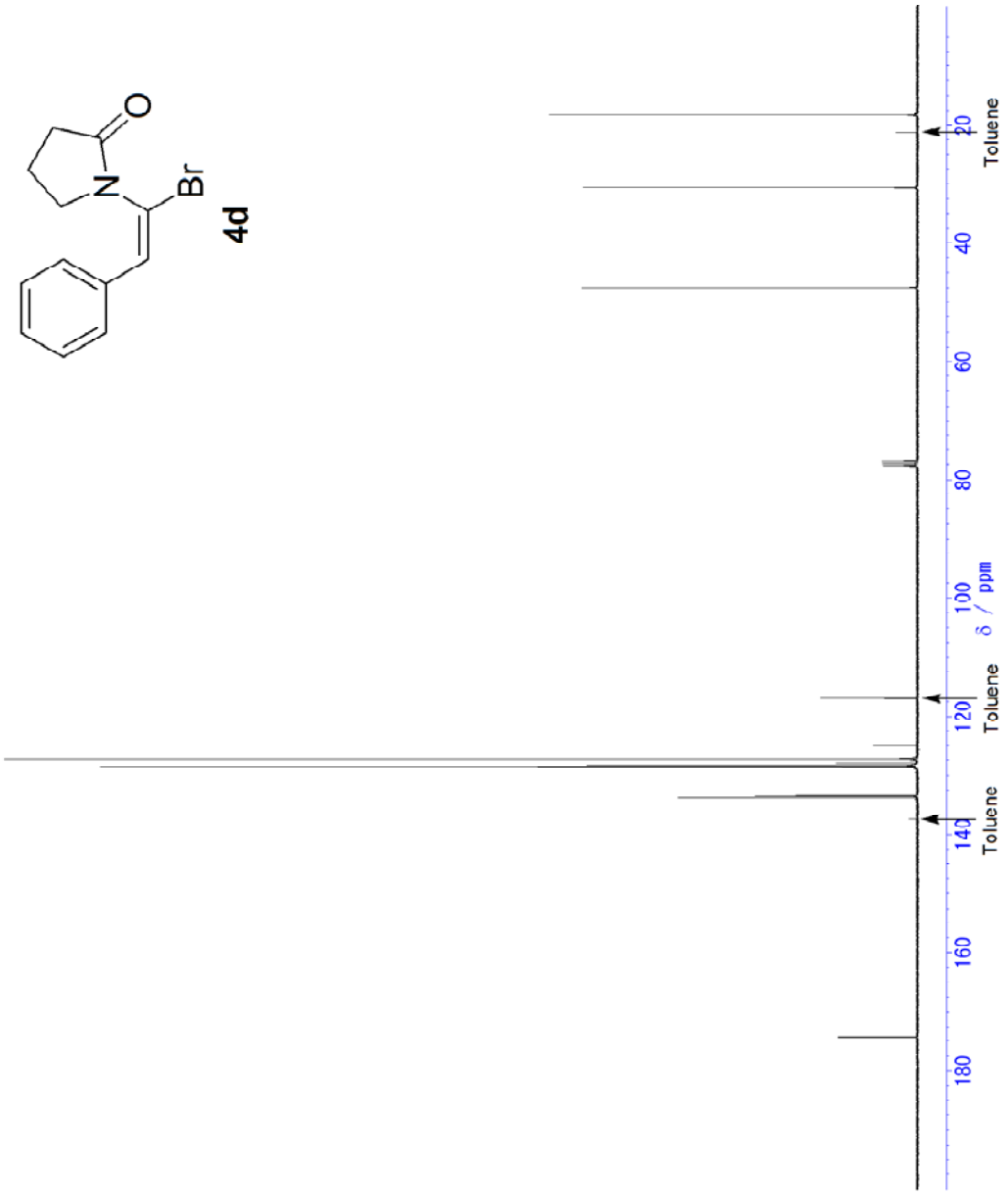

Ph
O
N
I
4a
O
Ph
20
40
60
80
100
120
140
160
180
δ / ppm

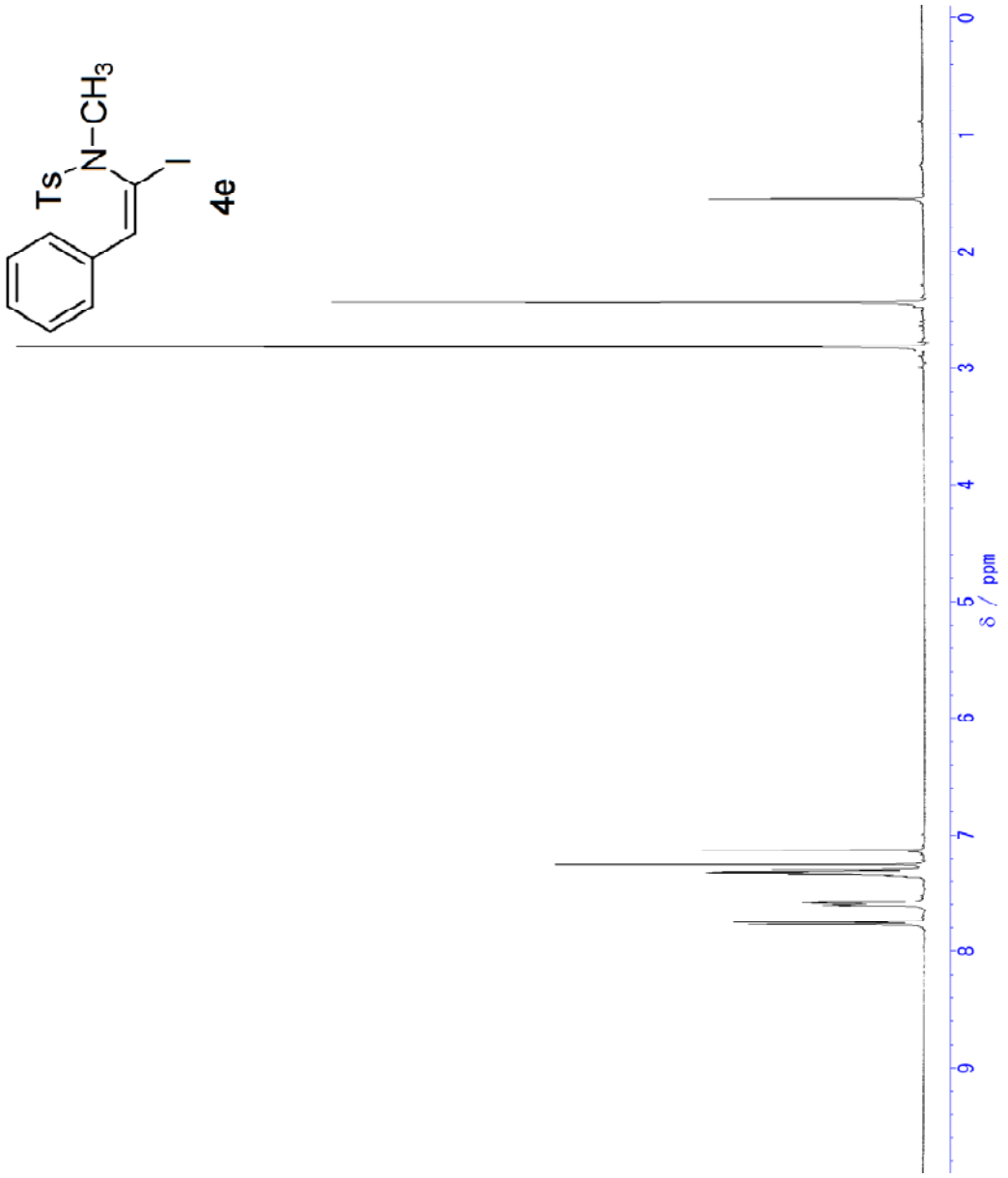

O
O
N
I
4b
δ / ppm
0
1
2
3
4
5
6
7
8
9

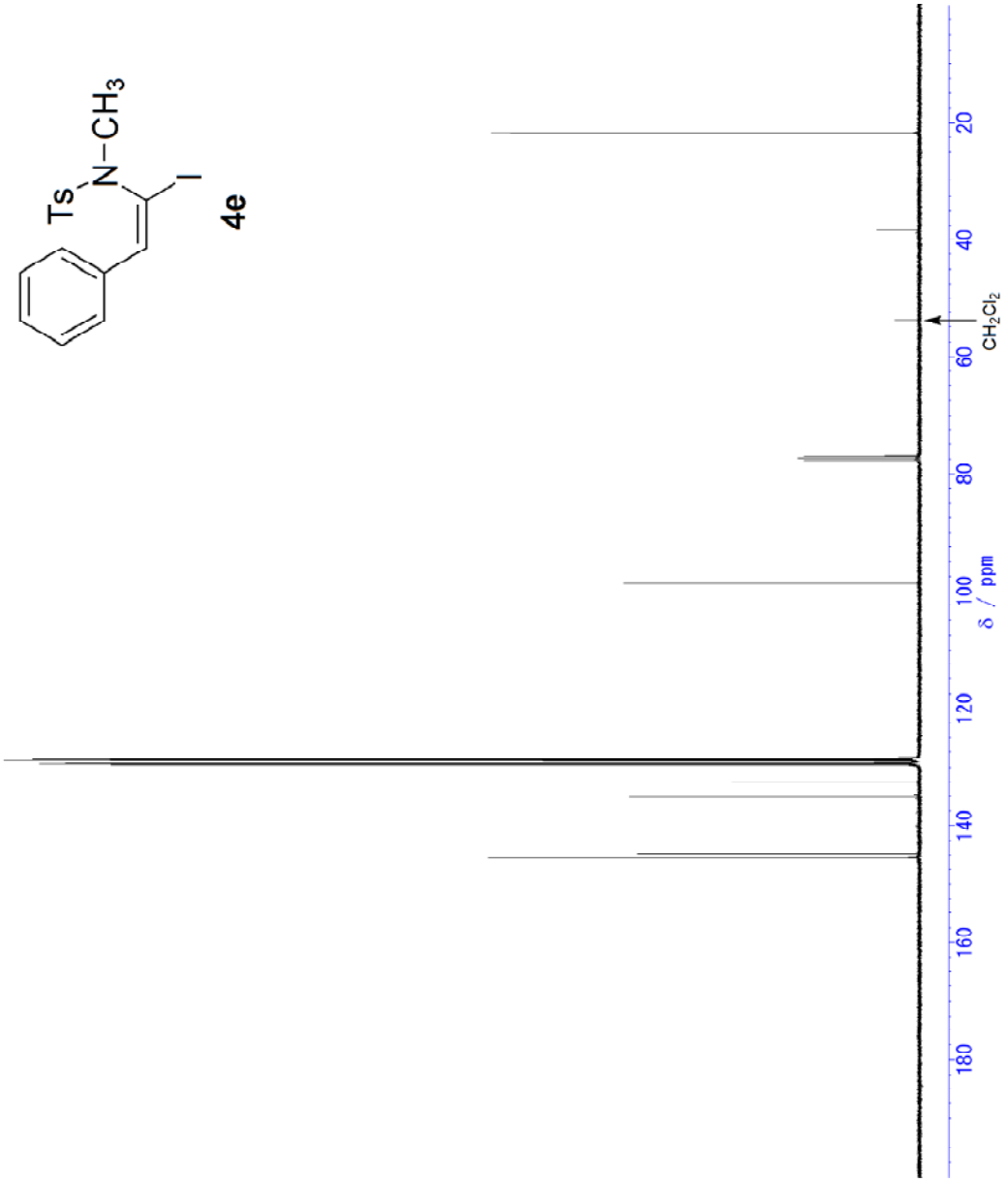

O
O
N
Br
4c
δ / ppm

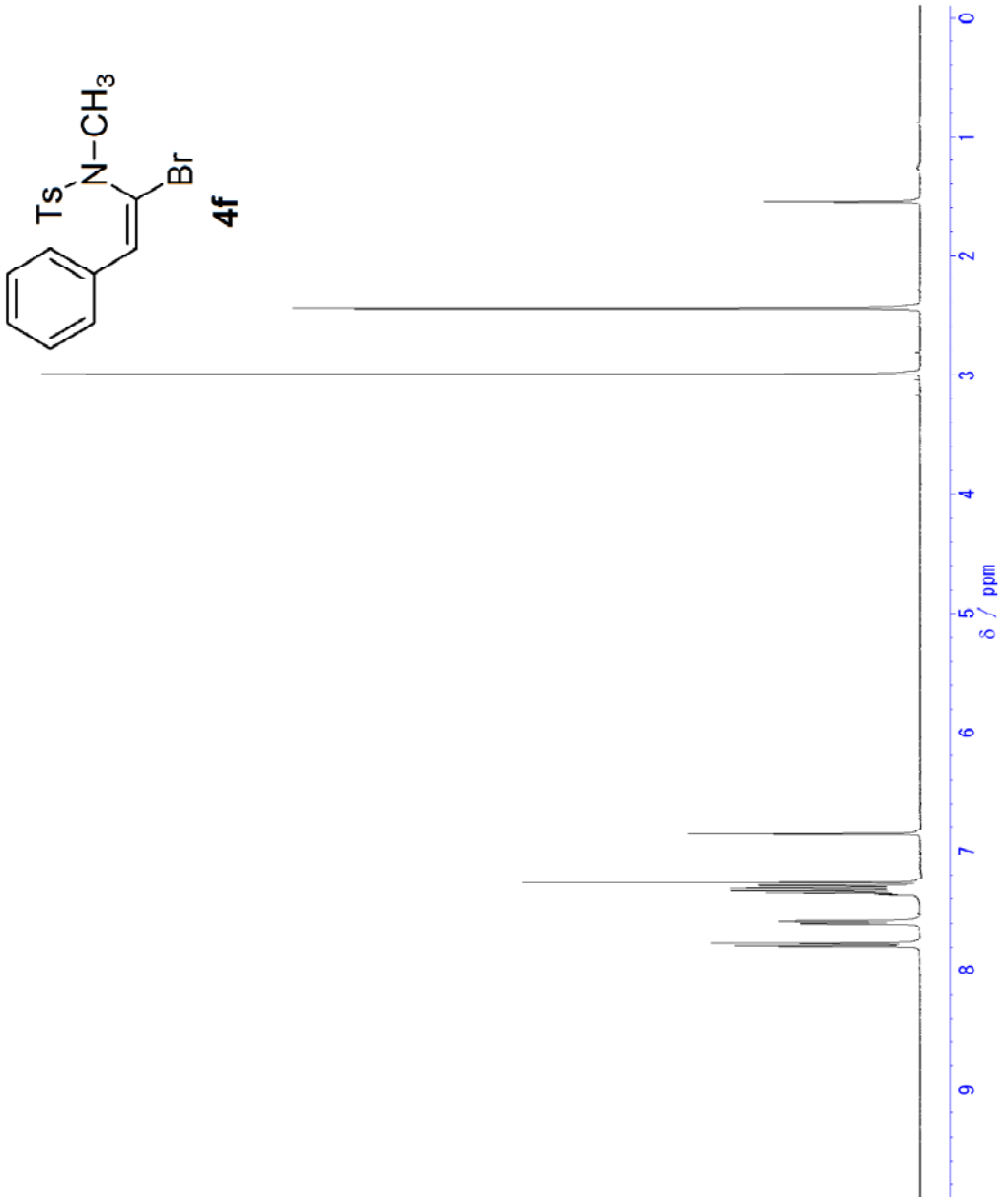

O
O
N
Br
4c
20
40
60
80
100
120
140
160
180
δ / ppm

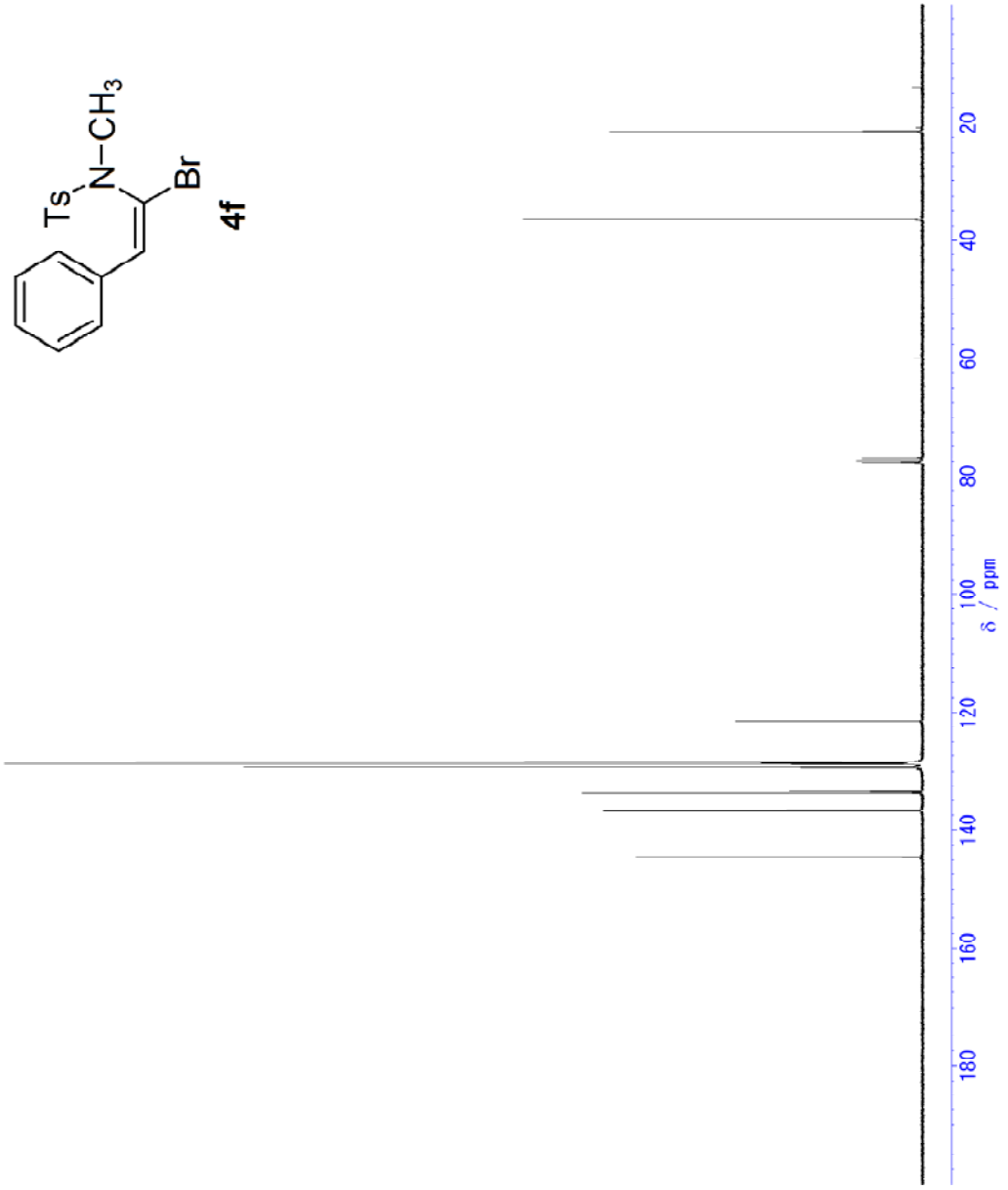

O
N
Br
4d
Toluene
Toluene
δ / ppm
0
1
2
3
4
5
6
7
8
9

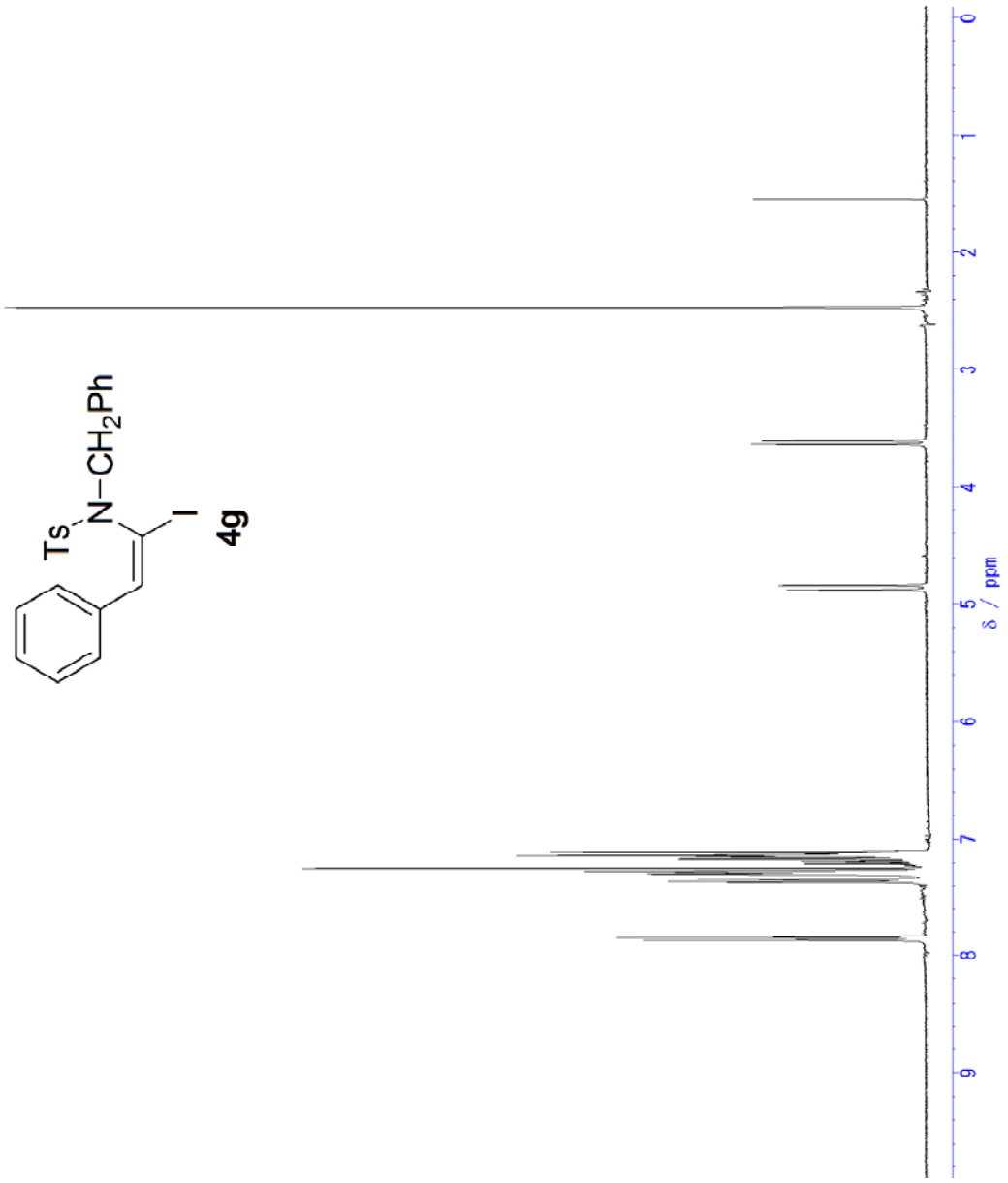

O
N
Br
4d
Toluene
Toluene
Toluene
δ / ppm
20
40
60
80
100
120
140
160
180

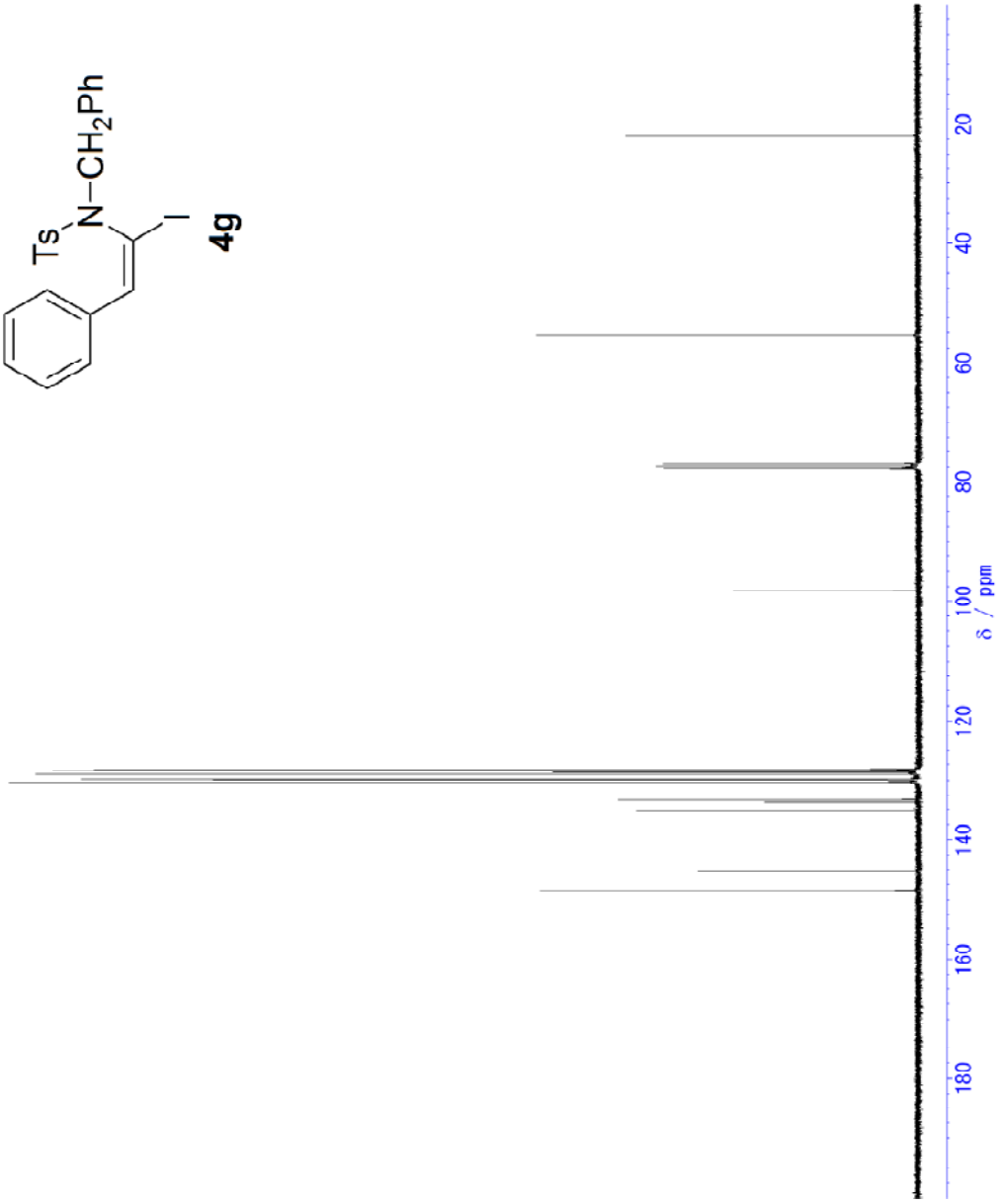

Ts
N–CH3
I
4e
δ / ppm

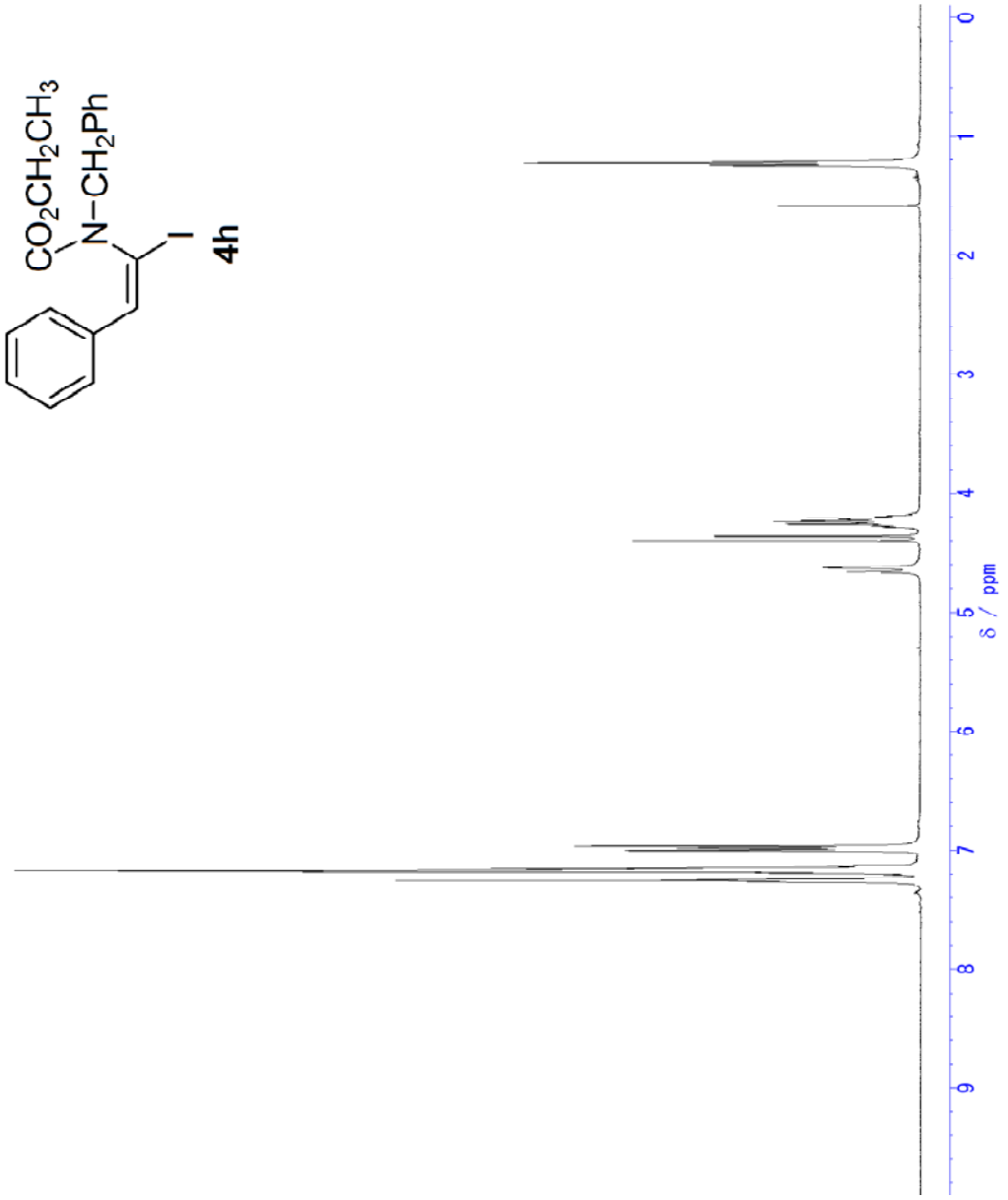

Ts
N–CH3
I
4e
CH2Cl2
δ / ppm
20
40
60
80
100
120
140
160
180

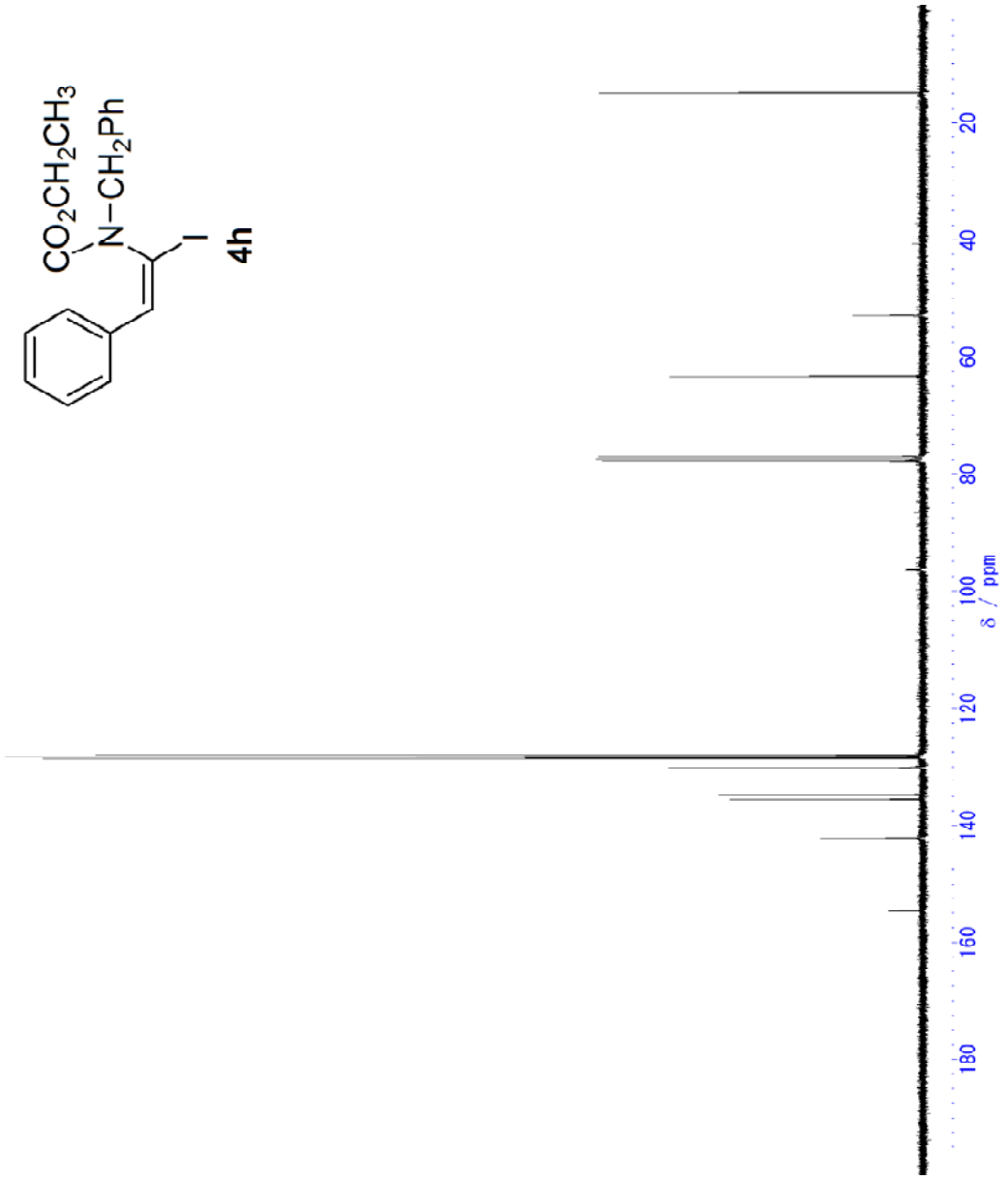

Ts
N–CH3
Br
4f
δ / ppm

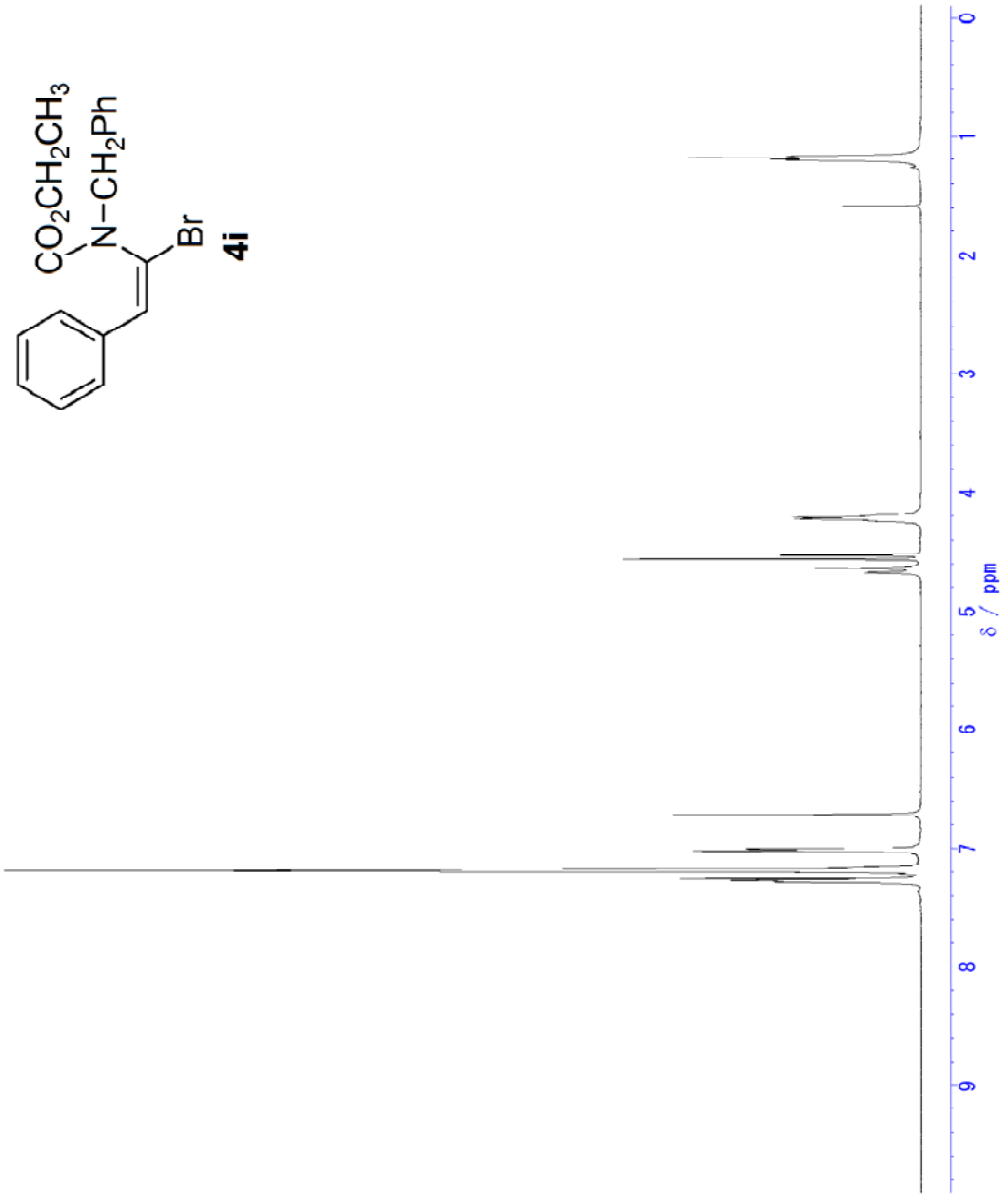

Ts
N–CH3
Br
4f
20
40
60
80
100
120
140
160
180
δ / ppm

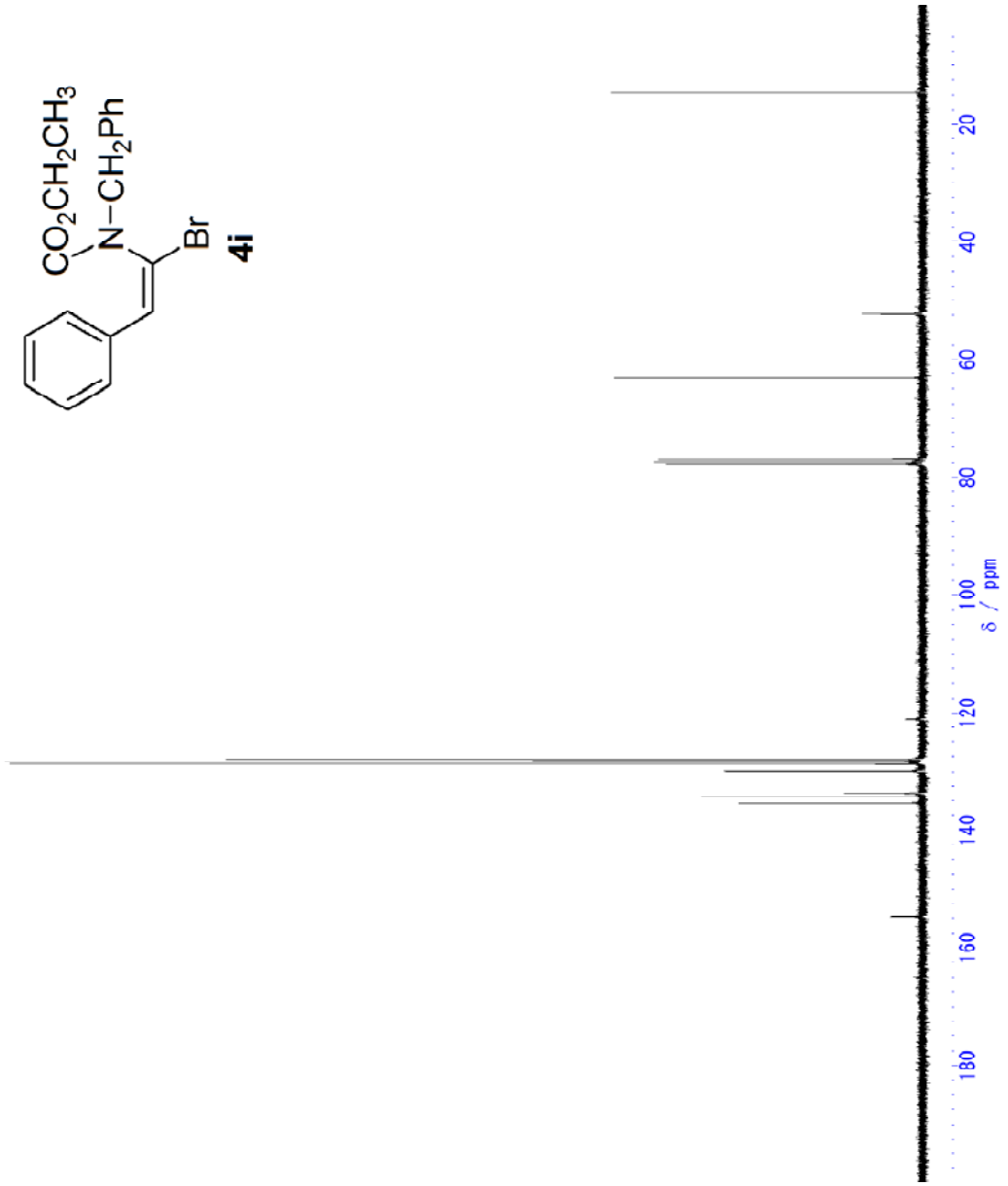

Ts
N–CH2Ph
I
4g
δ / ppm

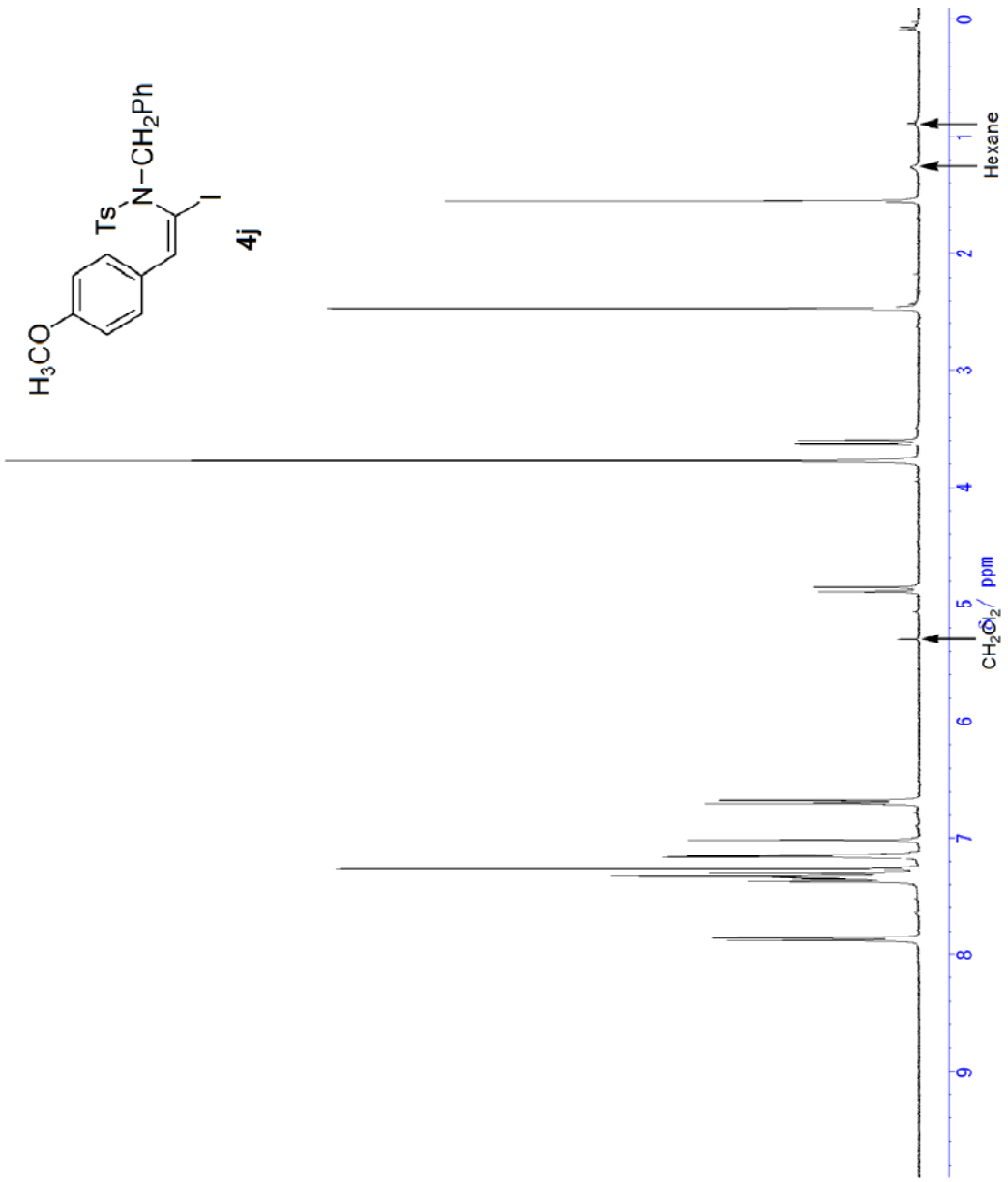

Ts
N–CH2Ph
I
4g
20
40
60
80
100
120
140
160
180
δ / ppm

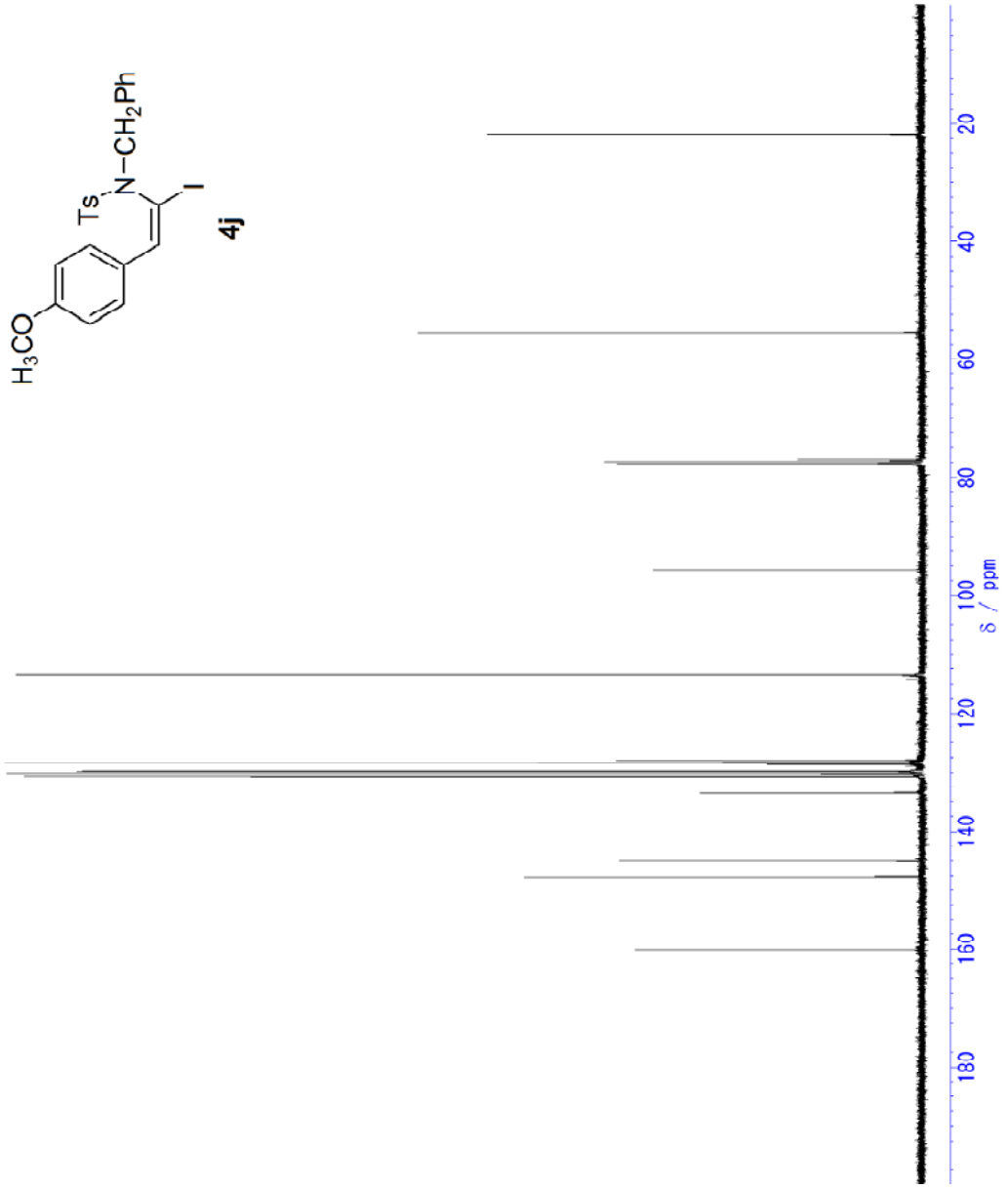

CO2CH2CH3
N–CH2Ph
I
4h
δ / ppm

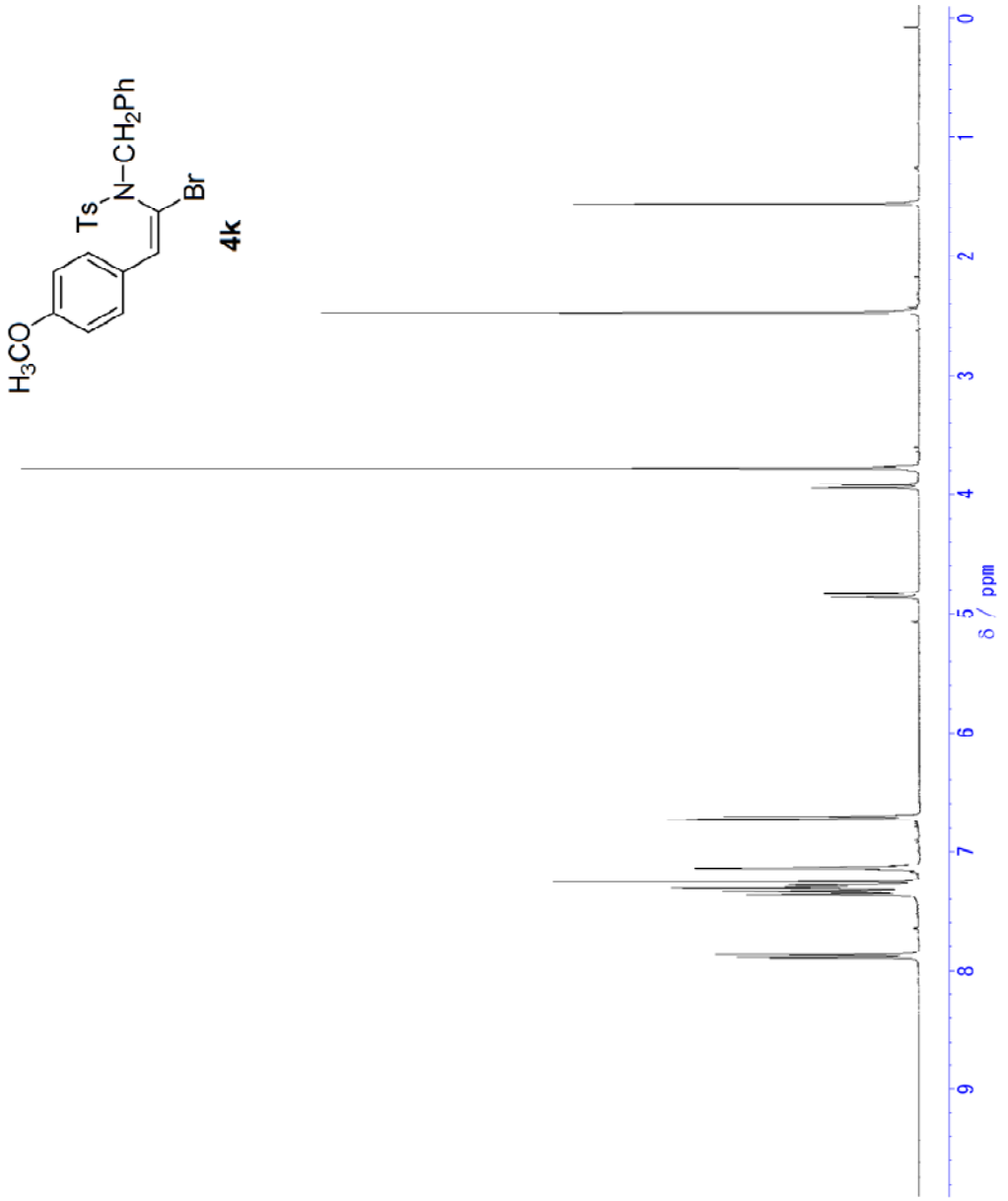

CO2CH2CH3
N–CH2Ph
I
4h
20
40
60
80
100
120
140
160
180
δ / ppm

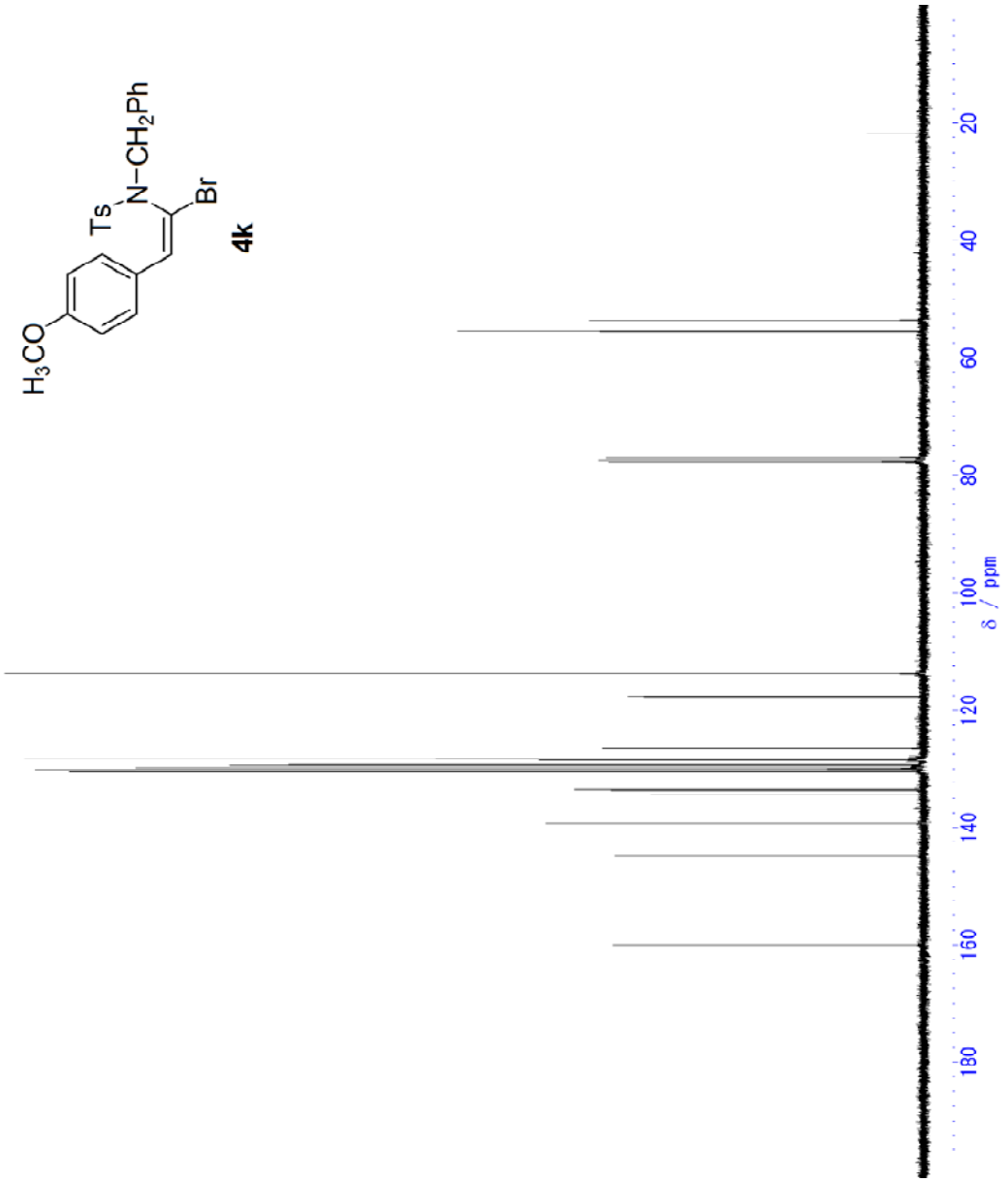

CO2CH2CH3
N–CH2Ph
Br
4i
δ / ppm

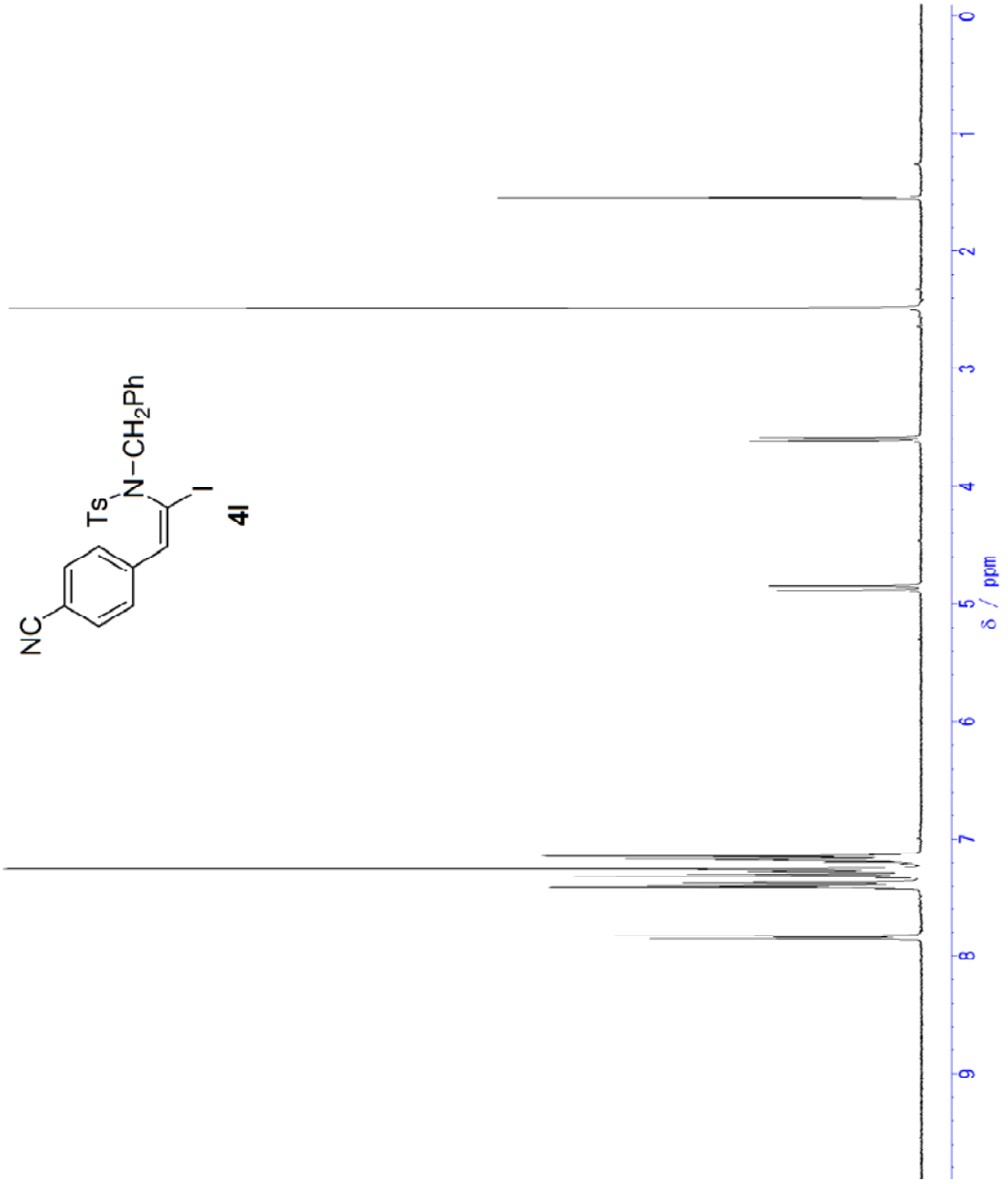

CO2CH2CH3
N–CH2Ph
Br
4i
δ / ppm

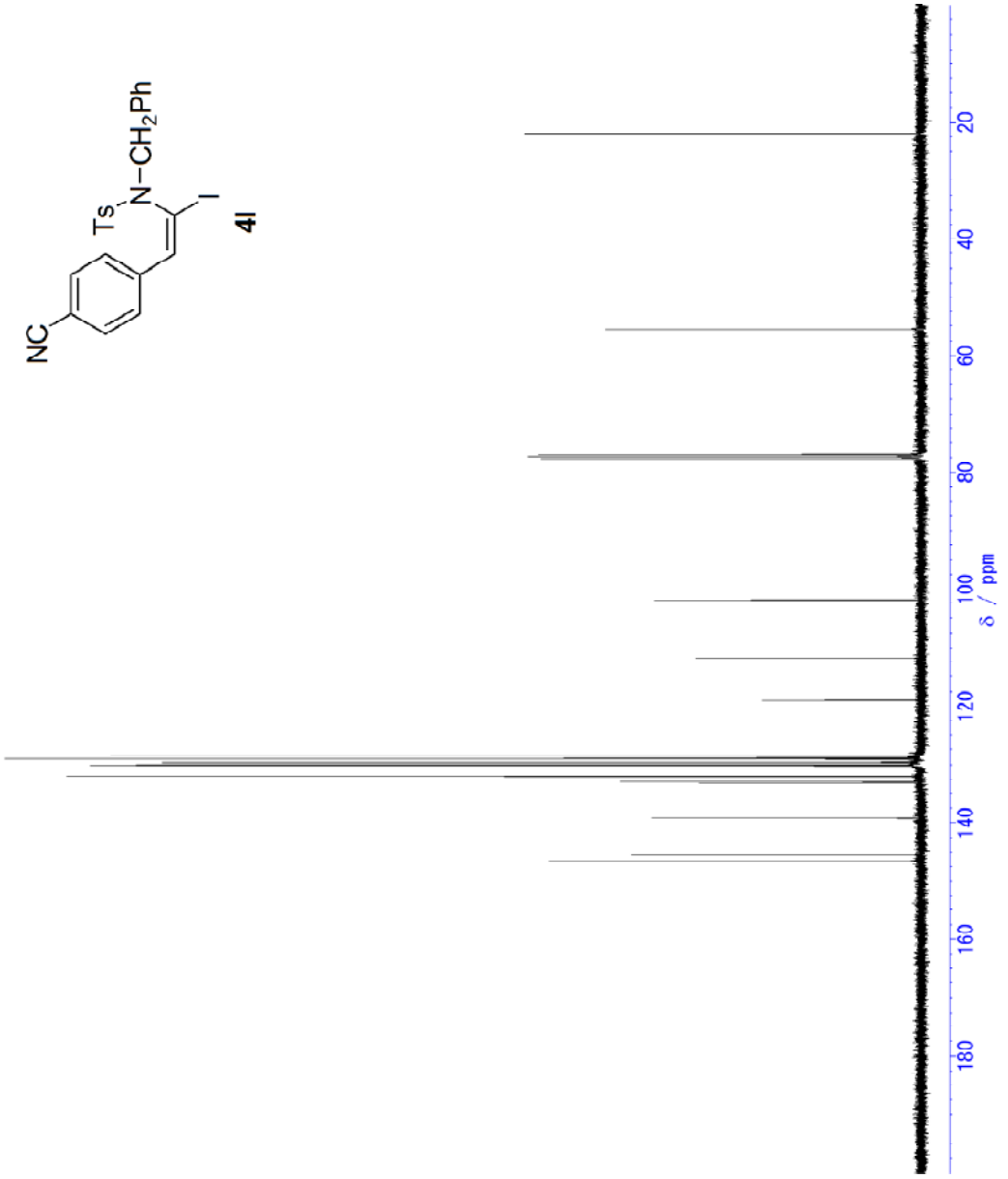

H3CO
Ts
N–CH2Ph
I
4j
Hexane
CH2Cl2
ppm

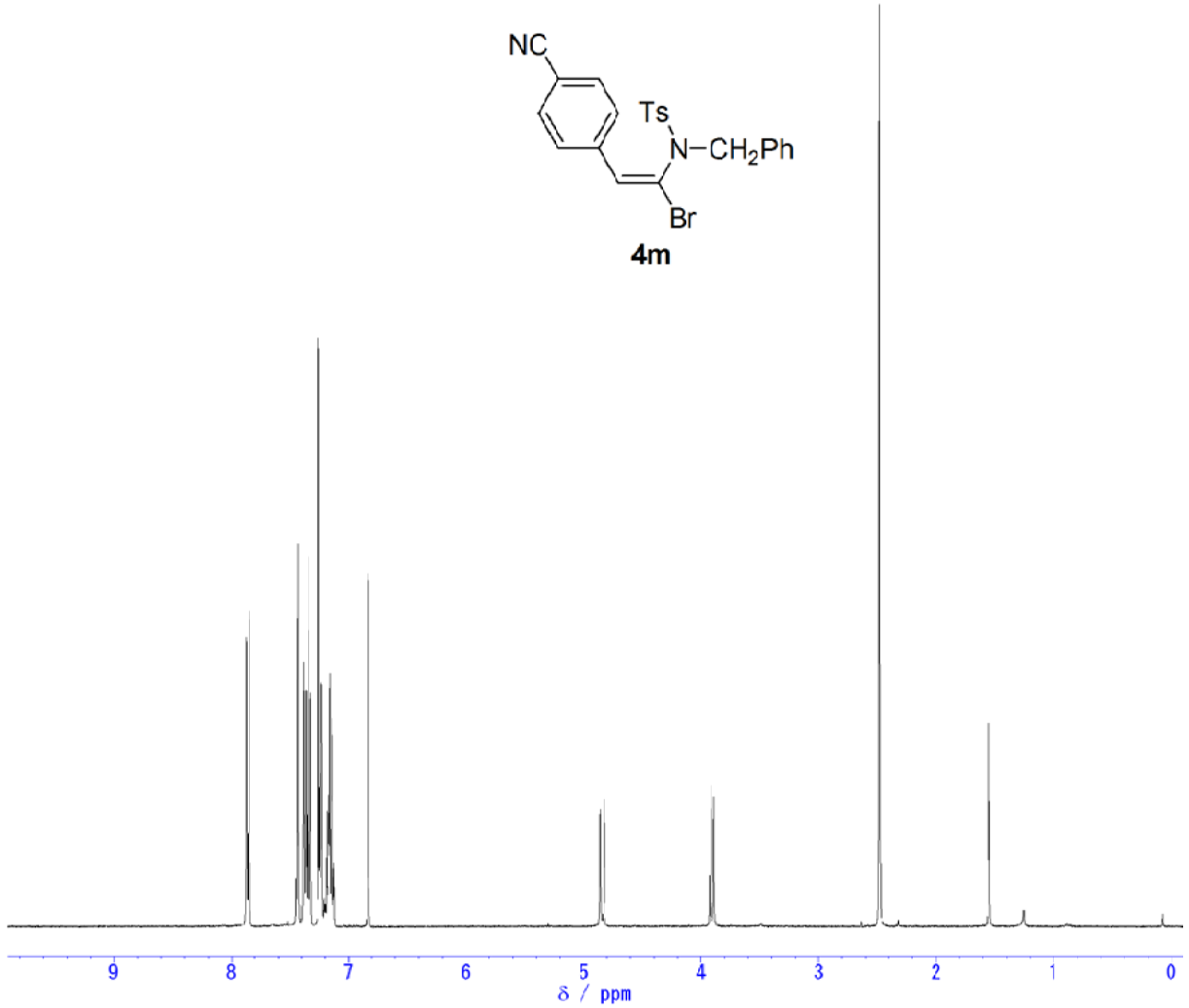

H3CO
Ts
N–CH2Ph
I
4j
20
40
60
80
100
120
140
160
180
δ / ppm

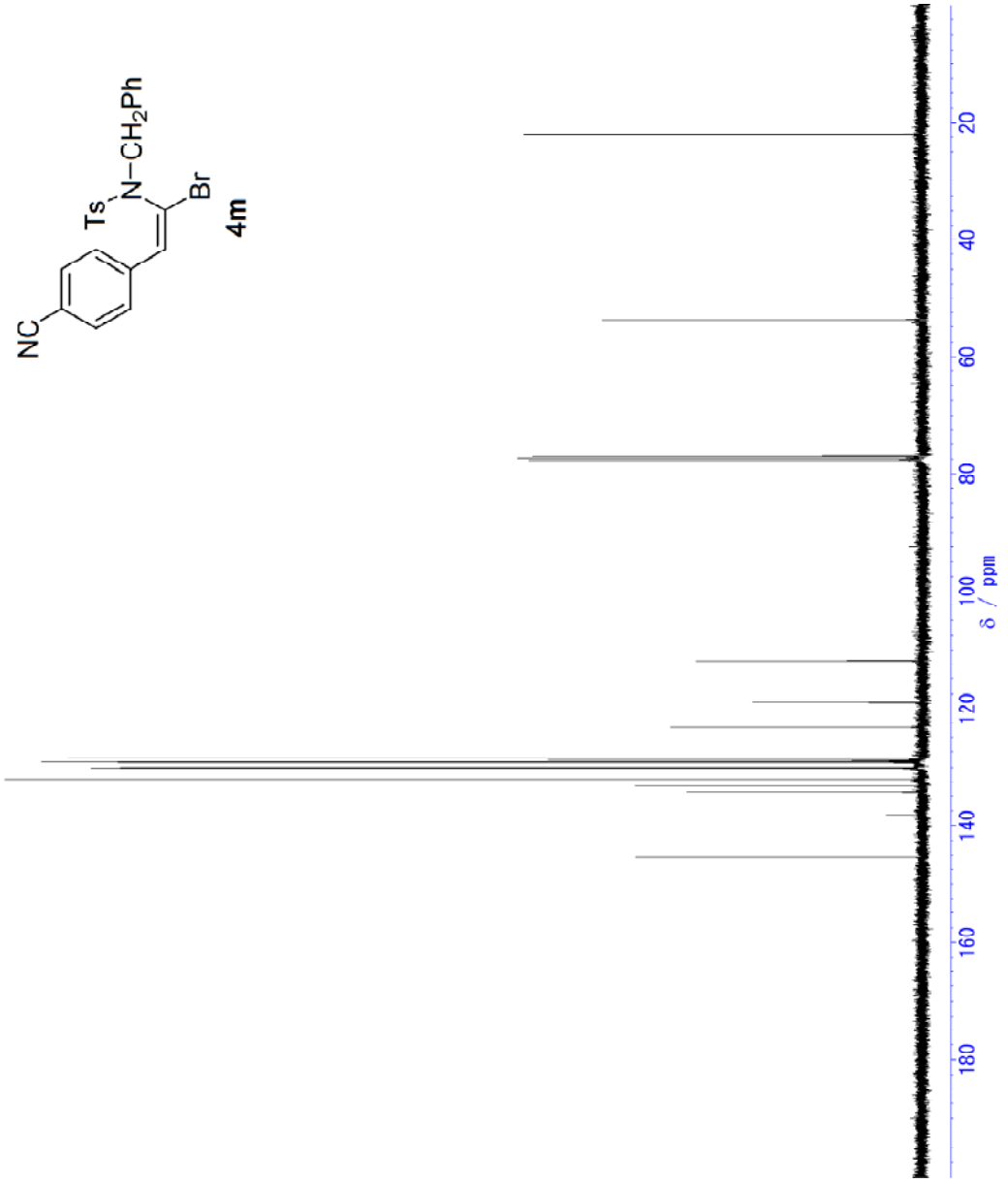

H3CO
Ts
N–CH2Ph
Br
4k
δ / ppm

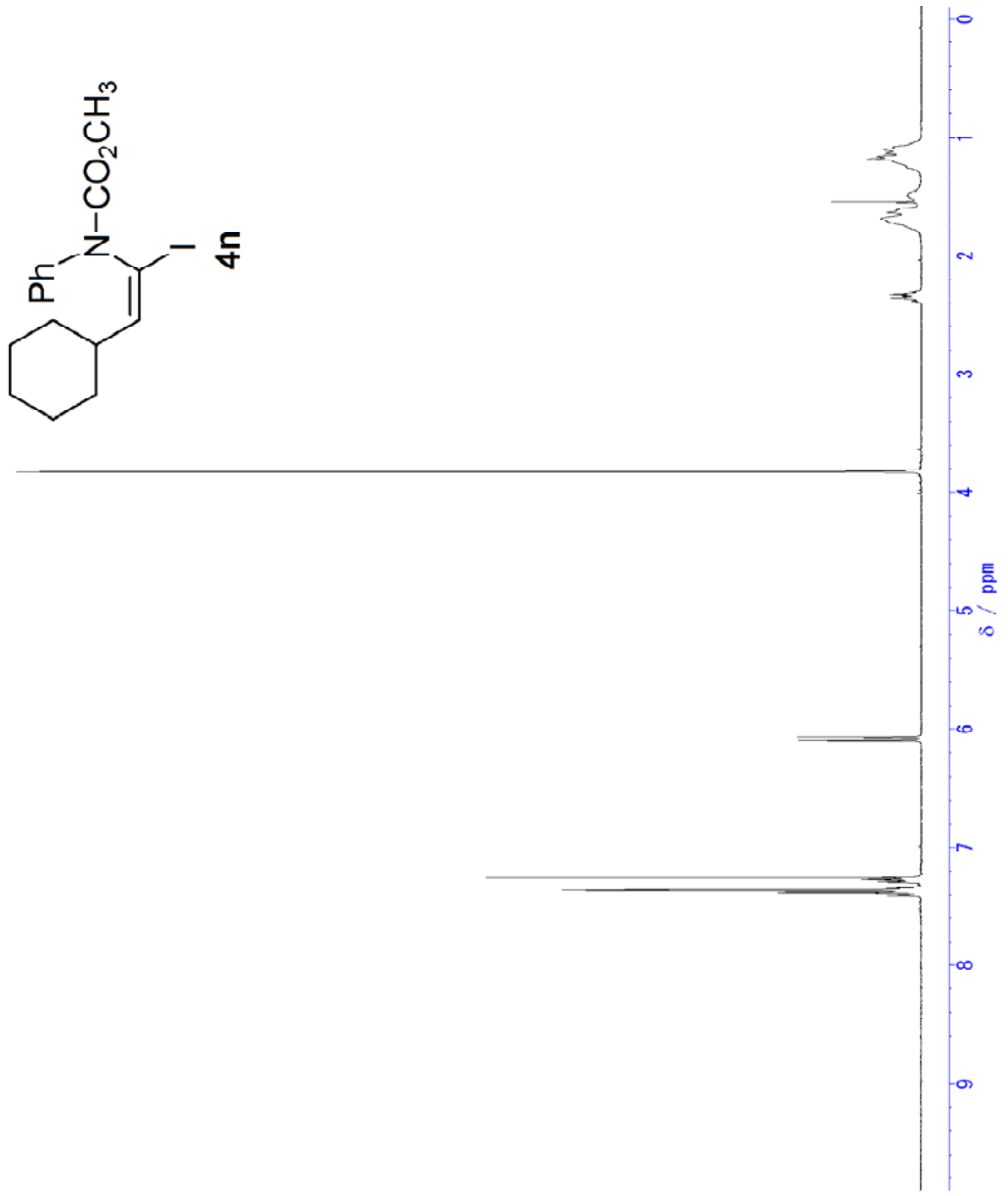

H3CO
Ts
N–CH2Ph
Br
4k
δ / ppm

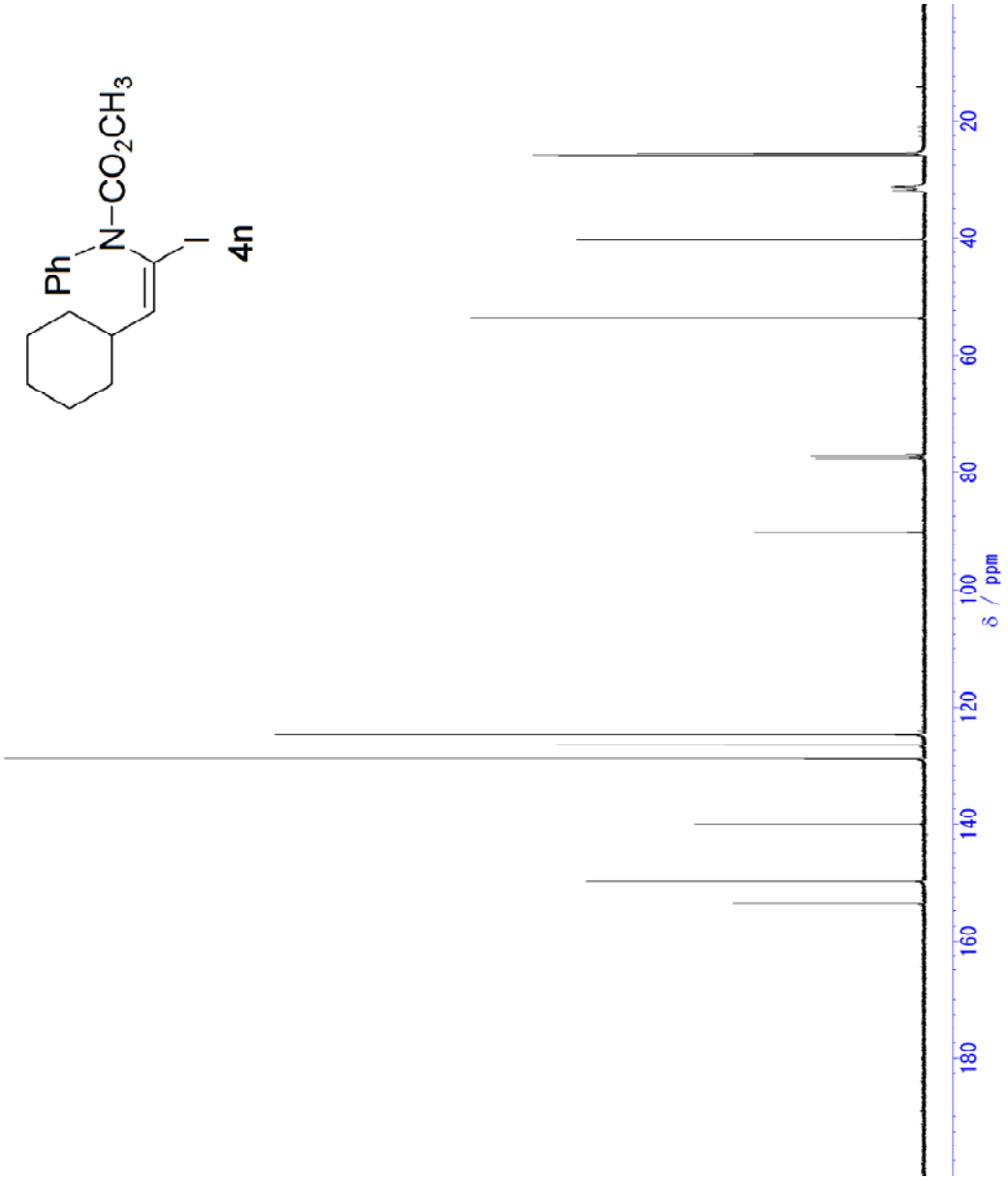

NC
Ts
N–CH2Ph
I
4l
δ / ppm

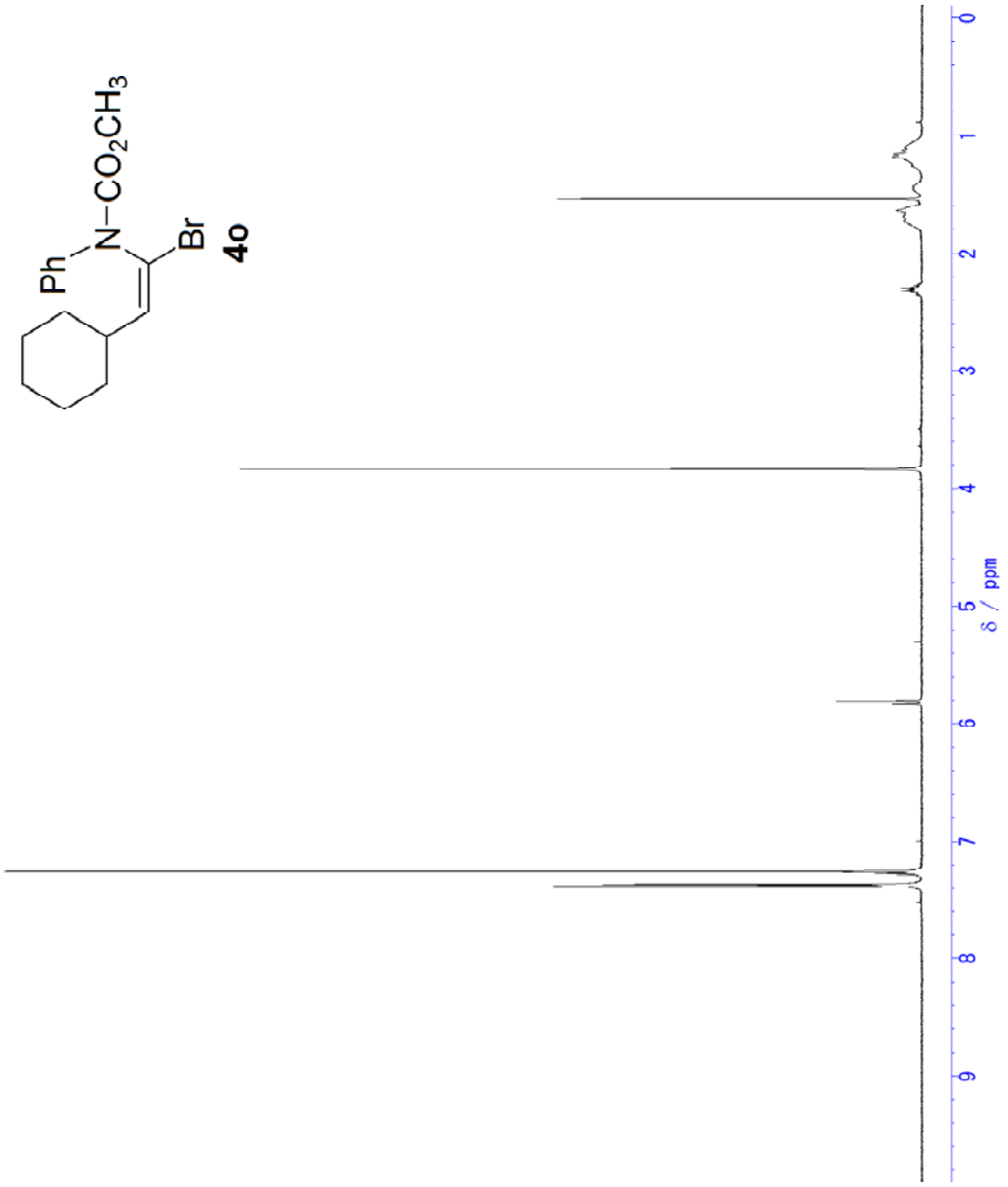

NC
Ts
N–CH2Ph
I
4l
20
40
60
80
100
120
140
160
180
δ / ppm

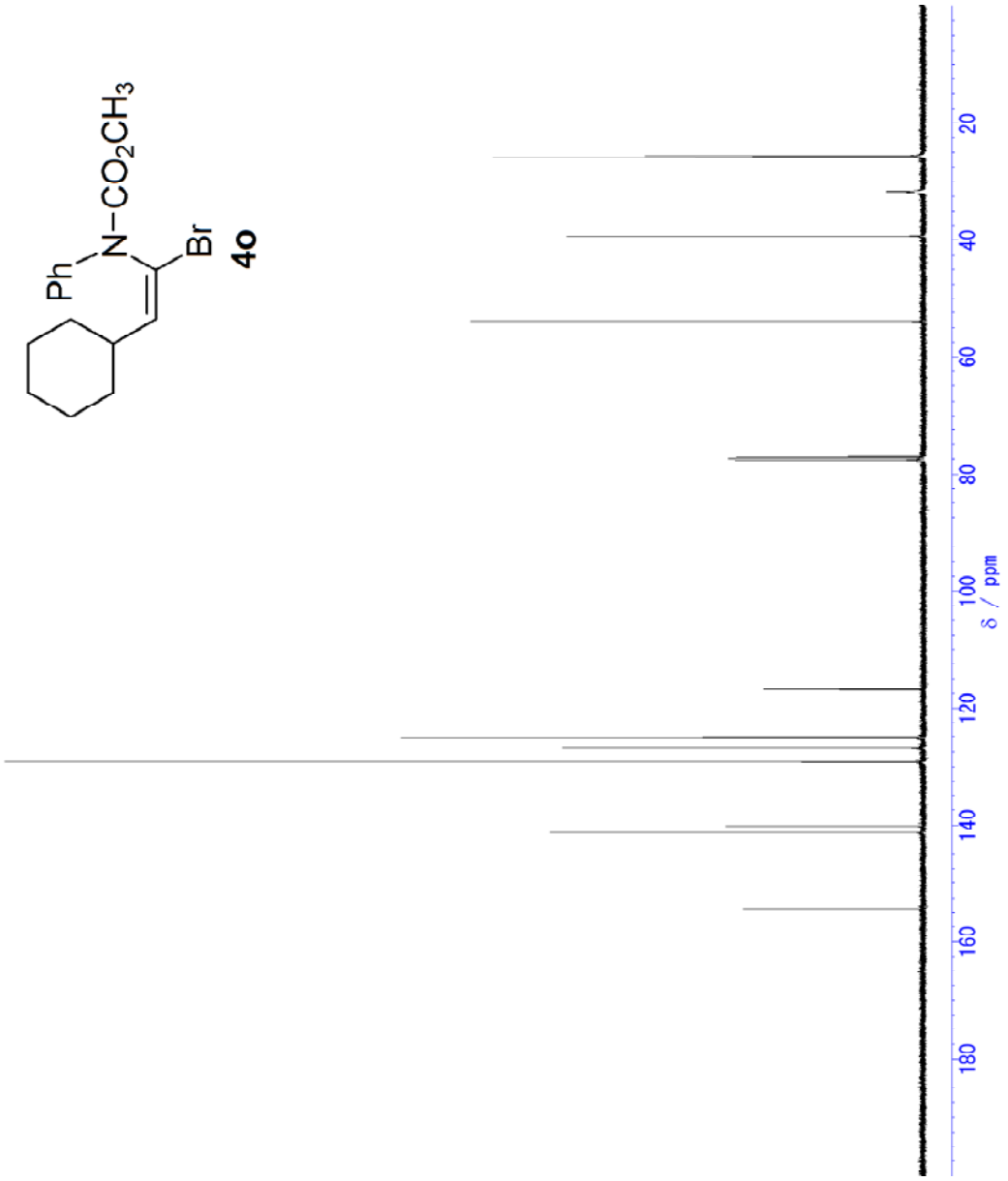

NC
Ts
N–CH2Ph
Br
4m
9
8
7
6
5
4
3
2
1
0
δ / ppm


NC
Ts
N–CH2Ph
Br
4m
20
40
60
80
100
120
140
160
180
δ / ppm

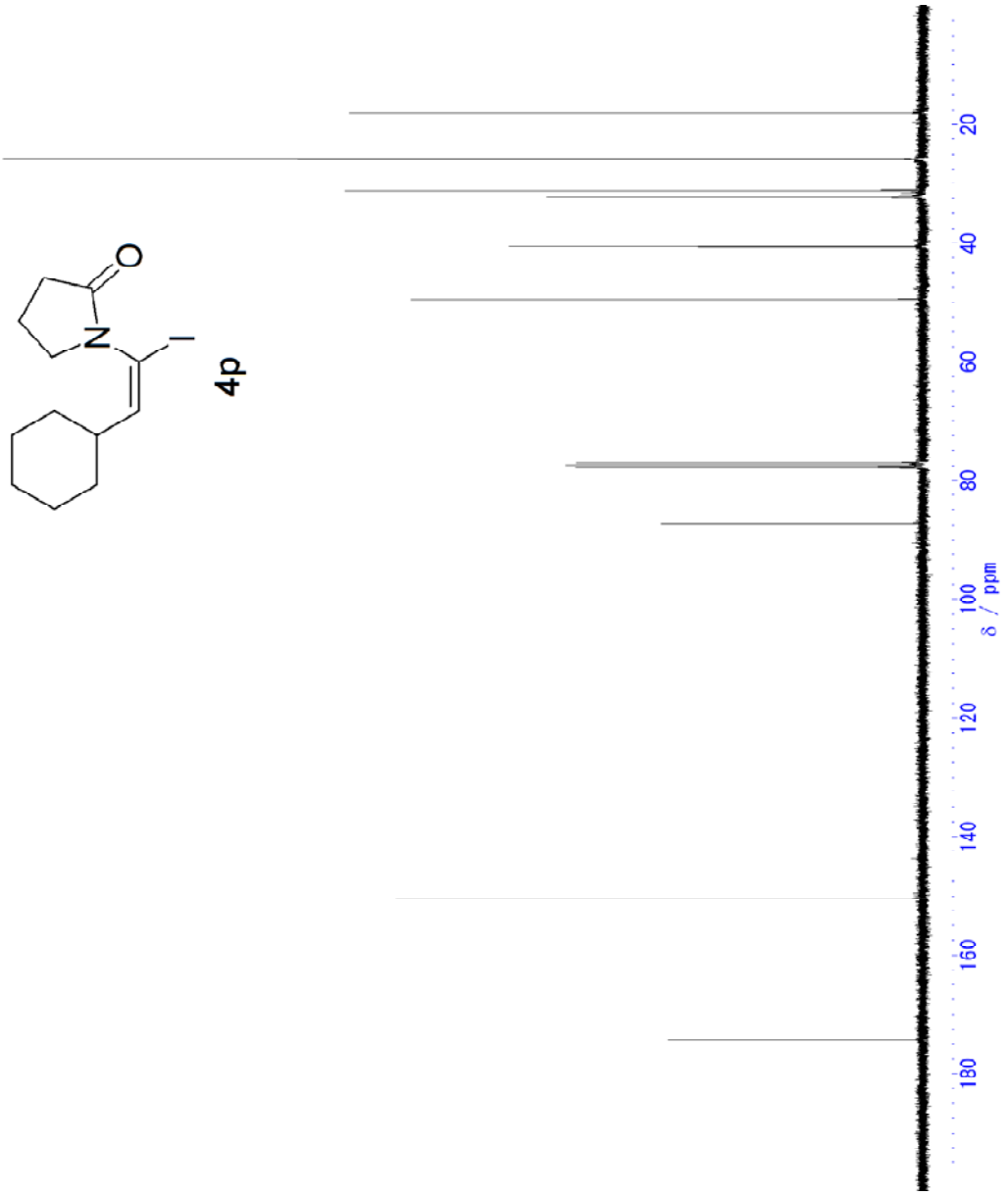

Ph
N–CO2CH3
I
4n
δ / ppm

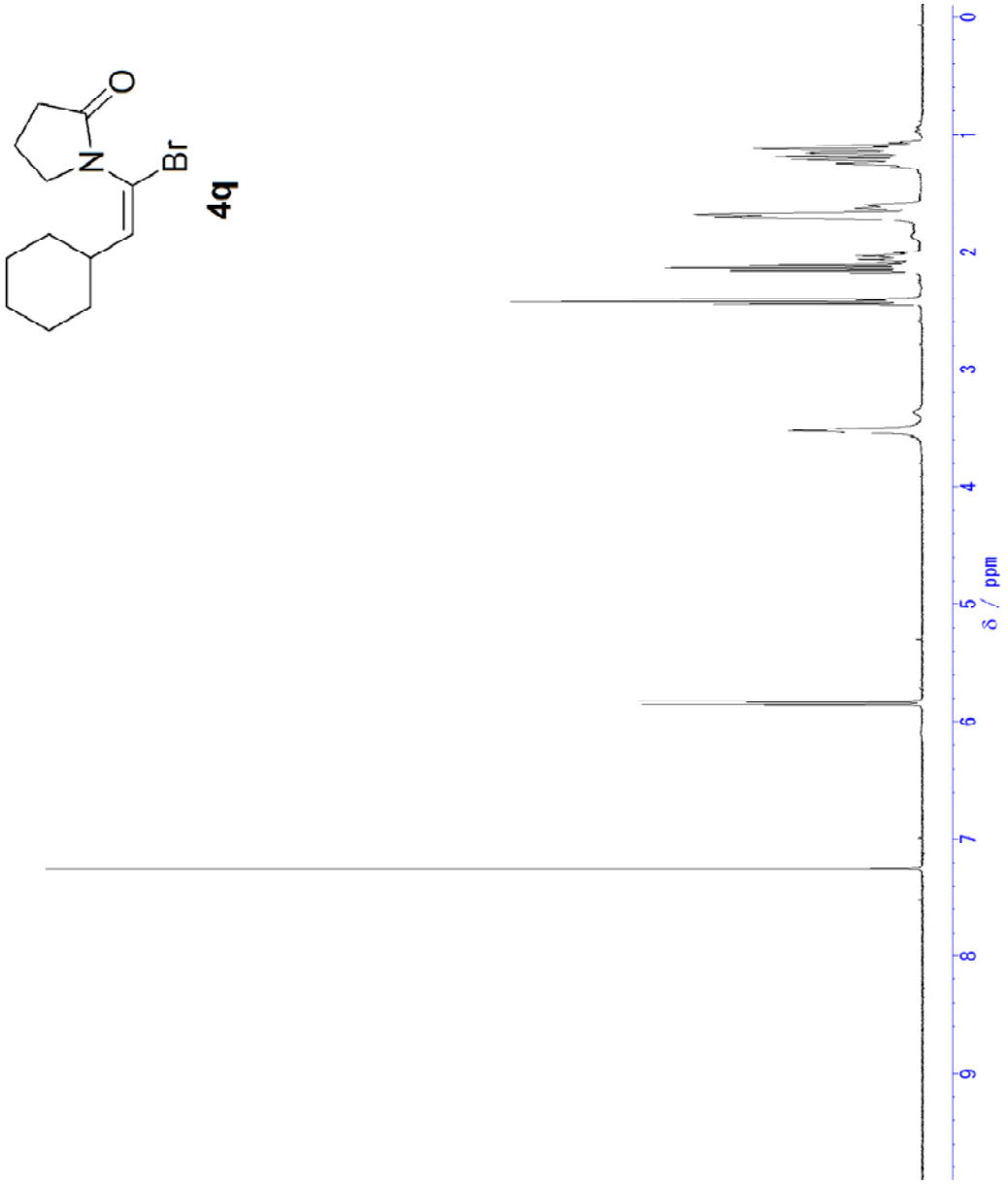

Ph
N–CO2CH3
I
4n
20
40
60
80
100
120
140
160
180
δ / ppm


Ph
N–CO2CH3
Br
4o
δ / ppm

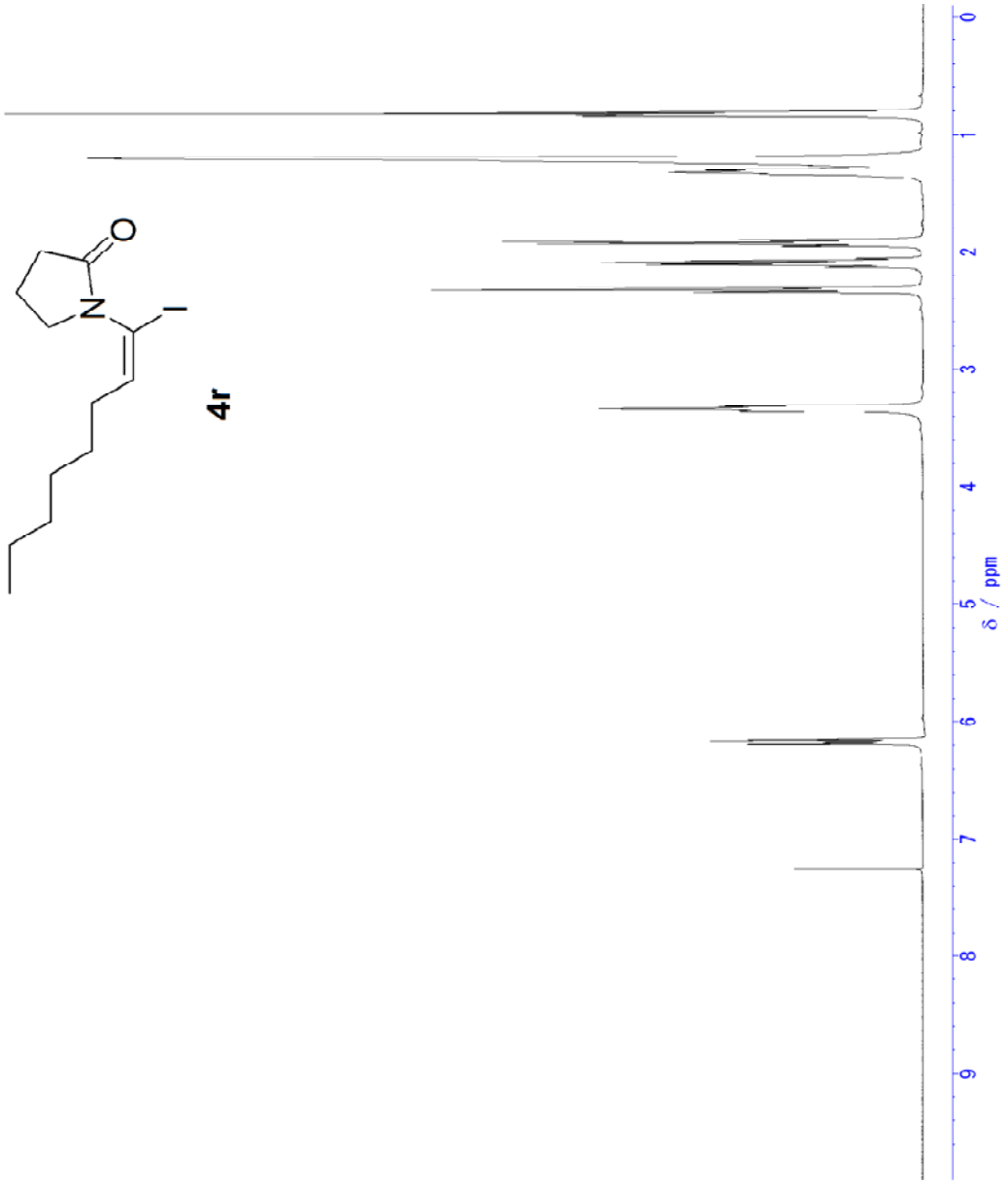

Ph
N–CO2CH3
Br
40
20
40
60
80
100
120
140
160
180
δ / ppm

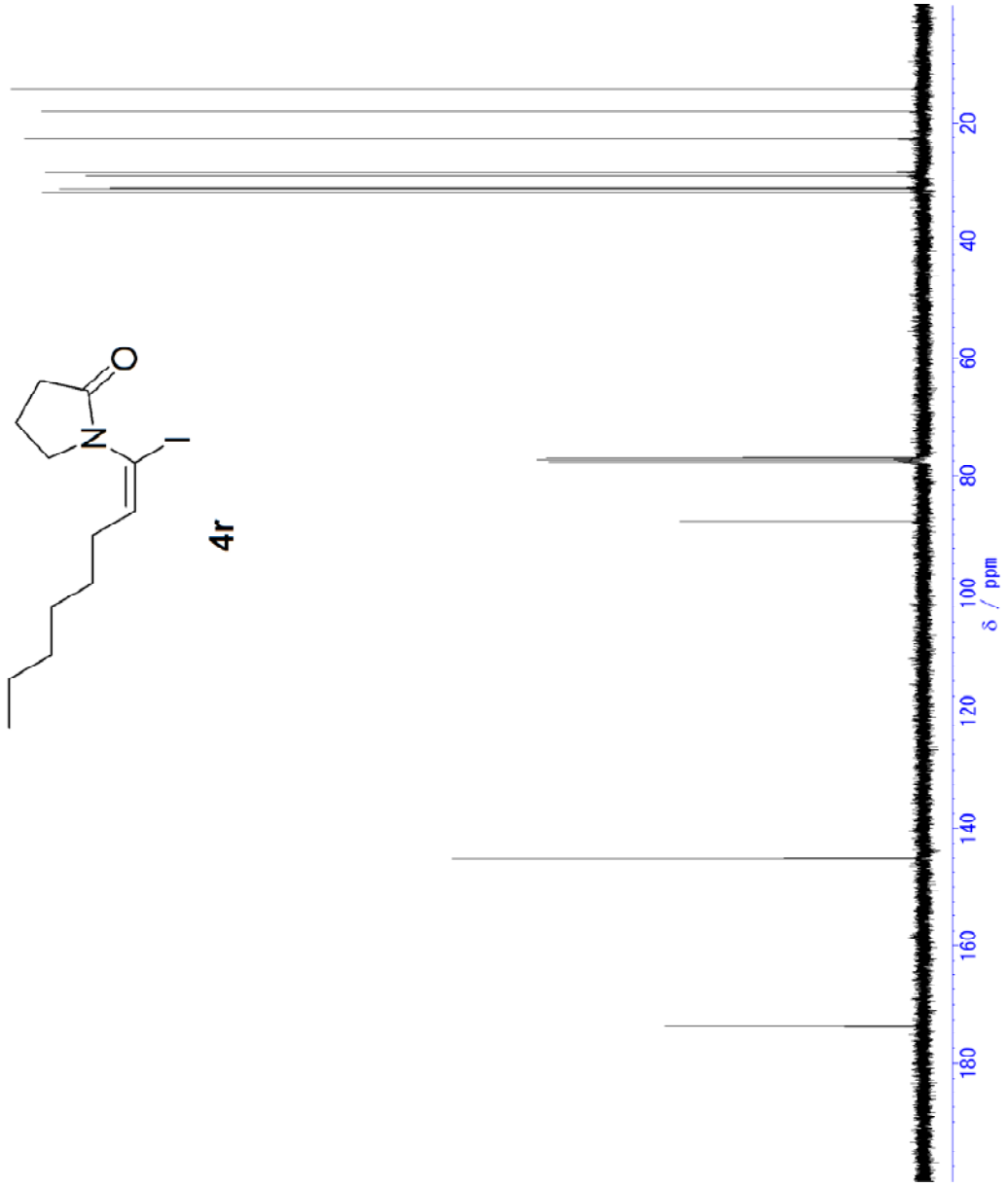

O
N
I
4p
δ / ppm

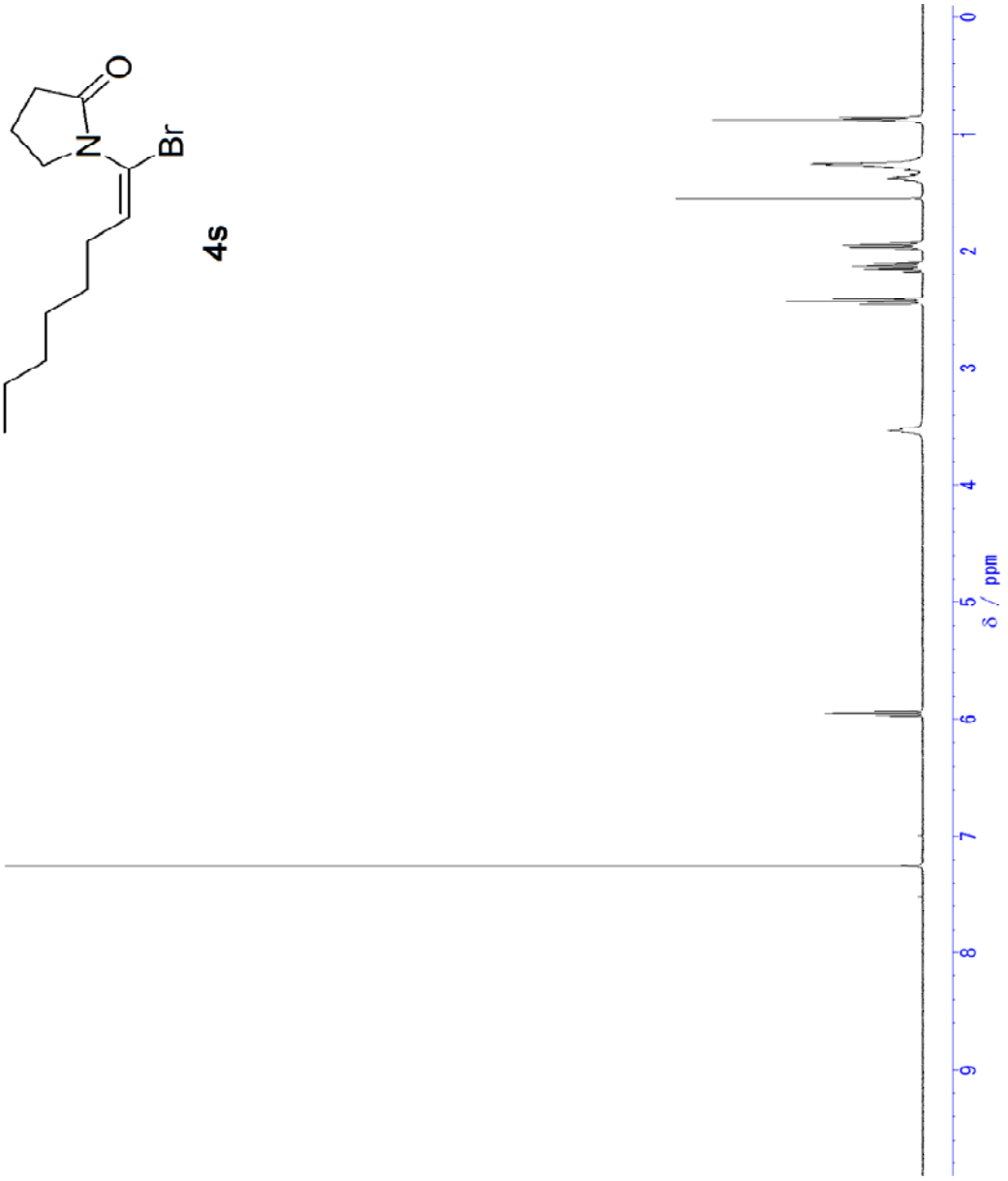

O
N
I
4p
20
40
60
80
100
120
140
160
180
δ / ppm

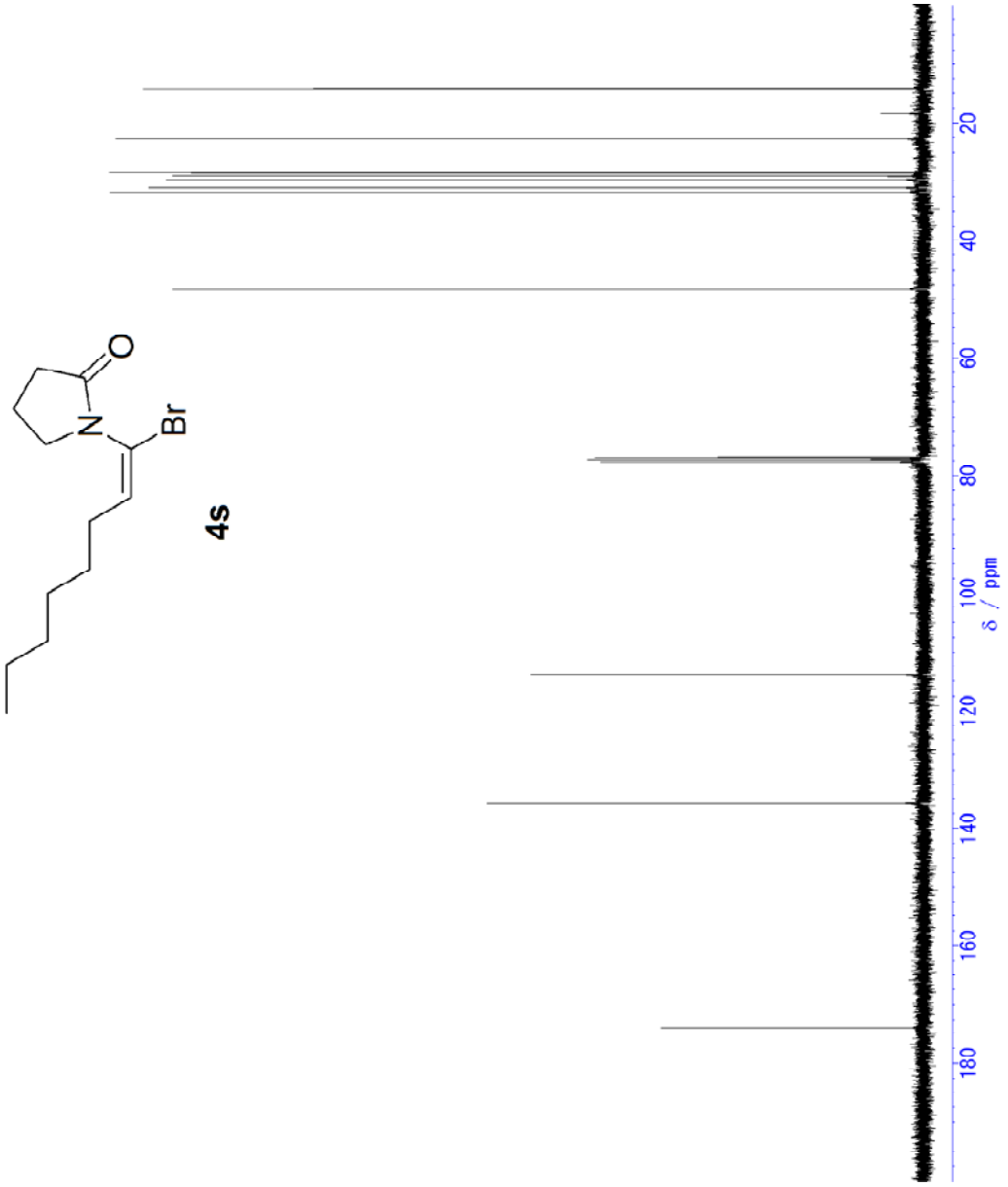

O
N
Br
4q
δ / ppm

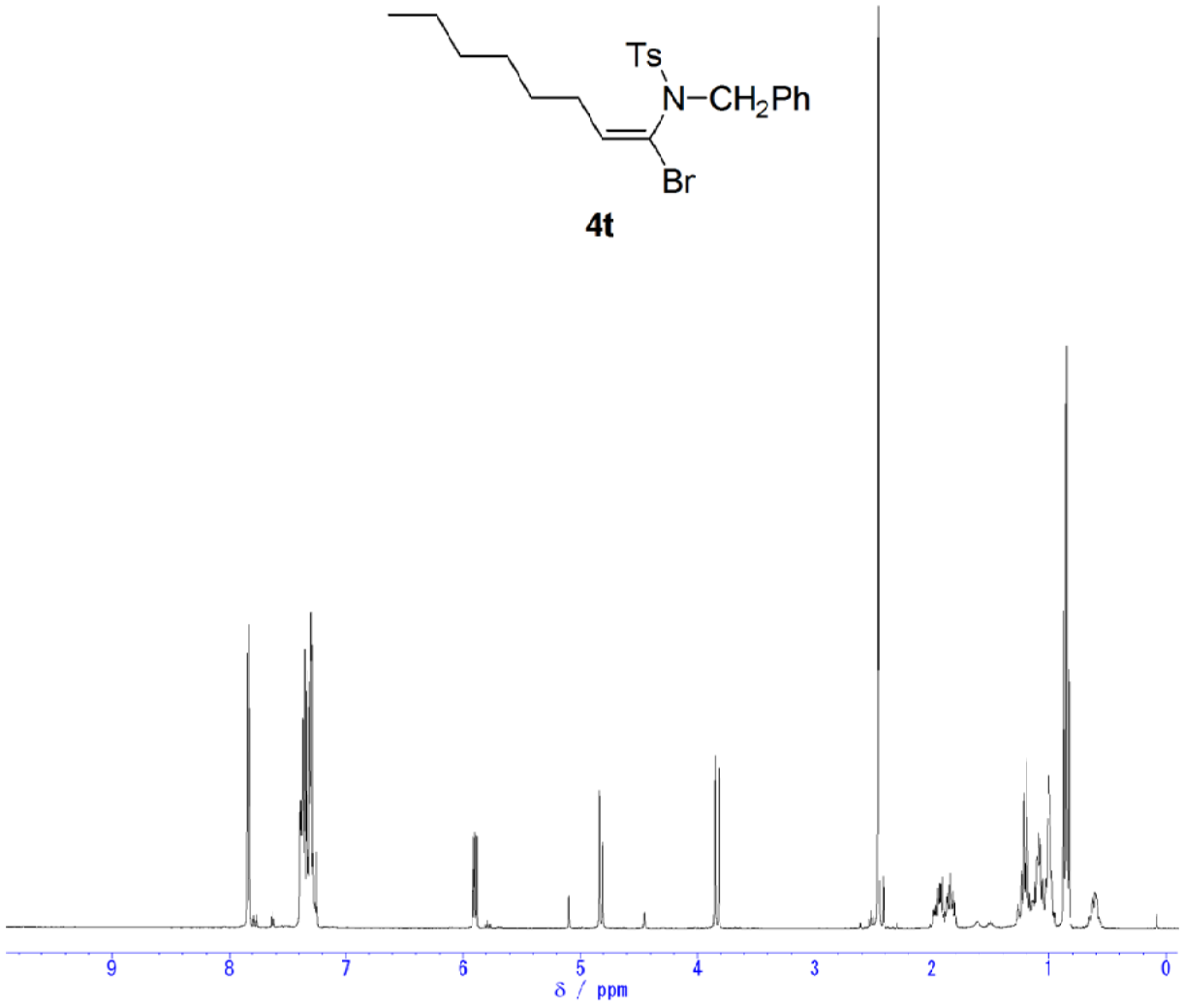

O
N
Br
4q
20
40
60
80
100
120
140
160
180
δ / ppm

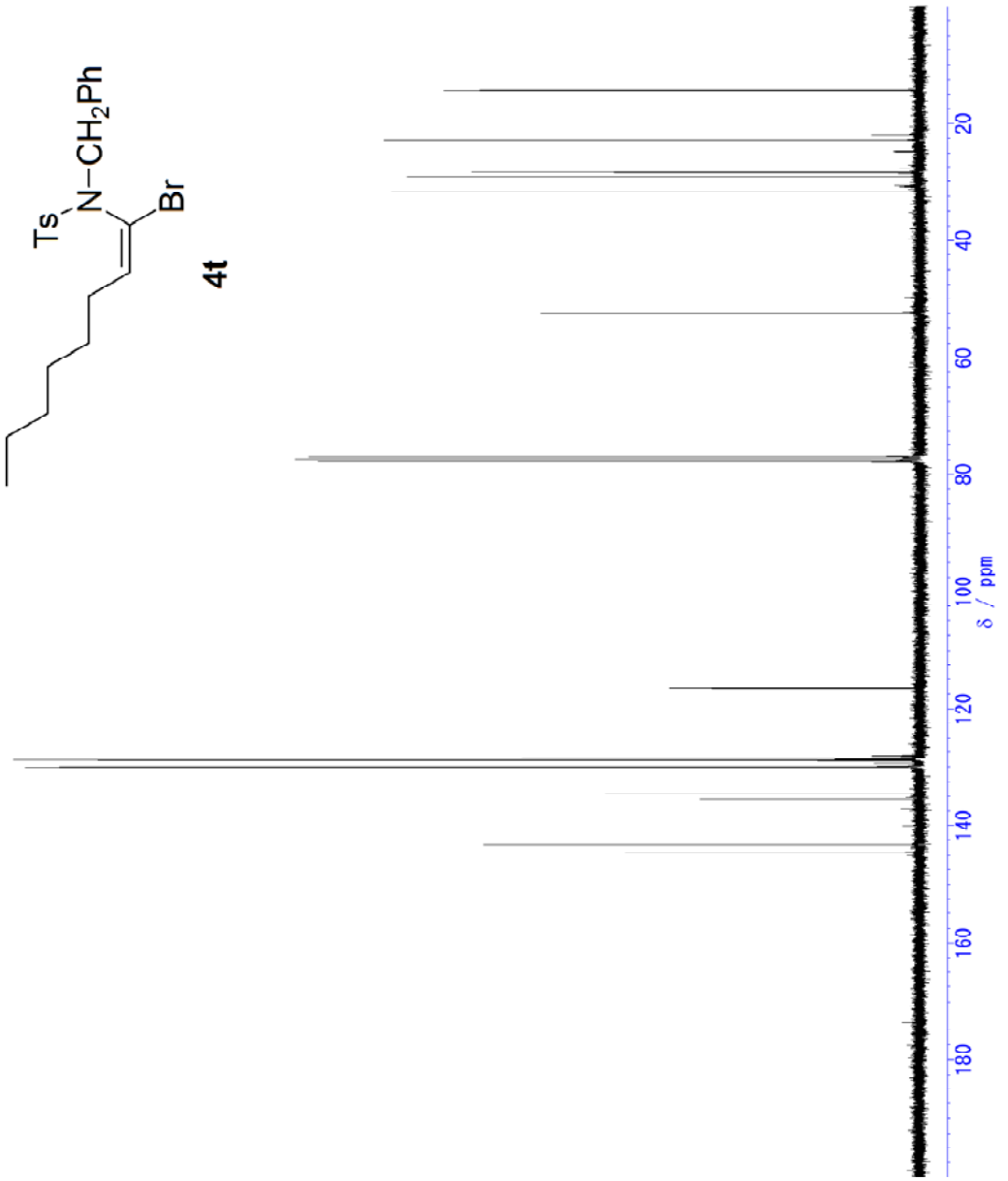

O
N
I
4r
δ / ppm


O
N
I
4r
20
40
60
80
100
120
140
160
180
δ / ppm


O
N
Br
4s
δ / ppm


O
N
Br
4s
20
40
60
80
100
120
140
160
180
δ / ppm


Ts
N–CH2Ph
Br
4t
9
8
7
6
5
4
3
2
1
0
δ / ppm


Ts
N–CH2Ph
Br
4t
20
40
60
80
100
120
140
160
180
δ / ppm

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