Supporting Information

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Regio- and stereoselective synthesis of 1-(1-halovinyl)-1*H*-indole moieties from 1-ethynyl-1*H*-indoles with *in situ* generated HX.

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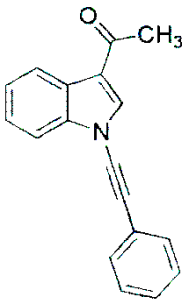
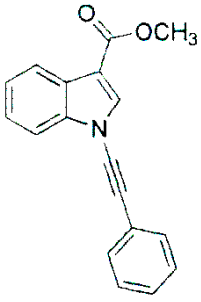
Contents

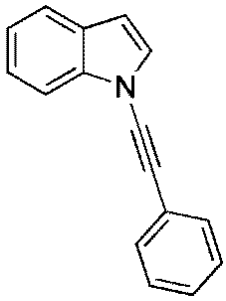
a) **General**: ^{1}H and ^{13}C NMR spectra were recorded on a BRUKER-SPECTROSPIN-400 with a 5 mm QNP probe at 400 MHz and 100 MHz, respectively. Chemical shift values, reported in parts per million (ppm), were indirectly referenced to external tetramethylsilane employing resonances due to trace monoprotio-solvent 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 chromatography 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

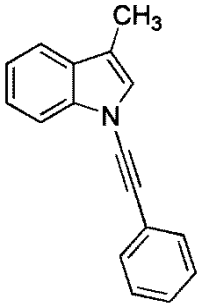
Wako Pure Chemicals, and Tokyo Chemical Industry Co., LTD. All the chemical materials were used without further purification. Compounds of 1-ethynyl-1*H*-indoles were prepared through the cross-coupling between appropriate alkynyl bromides and indoles according to the literature[1] and our modified procedure as described in section c) representative procedure. For the cross-coupling reactions, starting materials of indoles, 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 1-ethynyl-1*H*-indole, for 3 [1] in Scheme 1:**  The flask charged with $CuSO_4 \cdot 5H_2O$ (164.8 mg, 0.66 mmol) and 1,10-phenanthroline (237 mg, 1.32 mmol) was evacuated and backfilled with argon three times, and THF (13.2 mmol) was added. The mixture was stirred at 80 ºC for 10 min, and then charged with K_2CO_3 (1.82 g, 13.2 mmol), 3-acetylindole (1.05 g, 6 mmol), and bromoethynylbenzene (1.2 mL, 9.9 mmol). After stirring at 80 ºC for 17 h, the reaction mixture was allowed to cool to room temperature, and diluted with ethyl acetate (10 mL), and filtered through a pad of celite and florisil. To the mixture was added toluene (30 mL) and water (20 mL), and organic phase was extracted with toluene (10 mL x 3). Combined organic phases were washed with brine (20 mL), and then dried over Na_2SO_4, and concentrated to give the crude. The crude was purified by silica gel column chromatography (eluent, toluene only) to afford 1-(1-(phenylethynyl)-1*H*-indol-3-yl)ethanone (1.43 g, 84%) as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (dd, J = 6.8, 1.2 Hz, 1H), 7.94 (s, 1H), 7.65 (dd, J = 7.2, 1.2 Hz, 1H), 7.59-7.57 (m, 2H), 7.45-7.37 (m, 5H), 2.57 (s, 3H).

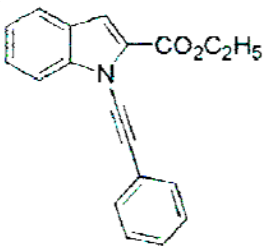
 **methyl 1-(phenylethynyl)-1*H*-indole-3-carboxylate, 1 [1a,c]:** white needles, 43% (2.07 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dd, J = 8.0, 0.8 Hz, 1H), 7.99 (s, 1H), 7.66 (dd, J = 8.3, 0.8 Hz, 1H), 7.59-7.56 (m, 2H), 7.43-7.35 (m, 5H), 3.94 (s, 3H).



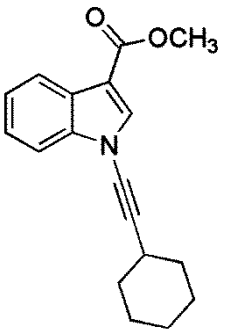
1-(phenylethynyl)-1*H*-indole, 5: The preparation of **5** caused a tremendous amount of 1,4-diphenylbuta-1,3-diyne that was produced through homo-coupling reaction of the starting bromoethynylbenzene. Unfortunately, the R_f values on TLC of both **5** and 1,4-diphenylbuta-1,3-diyne was very close, and thus the laborious operation for isolation of the target **5** in silica gel column chromatography (eluent; 1% Et_3N in hexane) was needed. Additional operation of recrystallization from hexane gave **5** in pure form. White needles, 26% (477 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, J = 8.0, 7.6 Hz, 2H), 7.57-7.55 (m, 2H), 7.41-7.33 (m, 4H), 7.29 (d, J = 3.4 Hz, 1H) 7.26-7.22 (m, 1H), 6.61 (d, J = 3.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 131.7, 129.1, 128.8, 128.3, 128.1, 123.9, 122.9, 122.3, 121.5, 111.6, 105.9, 81.1, 70.9. MS (EI) *m/z*: 217 (M^+). IR (neat): 3114, 3055, 2245 (C≡C) cm^{-1}. Anal. Calcd for $C_{16}H_{11}N$: C, 88.45; H, 5.10; N, 6.45. Found: C, 88.46; H, 5.11; N, 6.48.



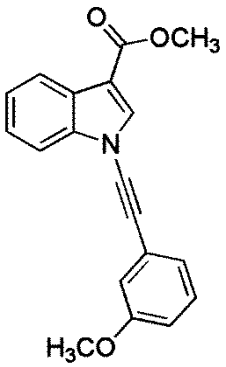
3-methyl-1-(phenylethynyl)-1*H*-indole, 7b: The preparation of **7b** caused a tremendous amount of 1,4-diphenylbuta-1,3-diyne that was produced through homo-coupling reaction of the starting bromoethynylbenzene. Unfortunately, the *Rf* values on TLC of both **7b** and 1,4-diphenylbuta-1,3-diyne was very close, and thus the laborious operation for isolation of the target **7b** in silica gel column chromatography (eluent; hexane only) was needed. Pale yellow oil, 12% (140 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 -7.52 (m, 4H), 7.39-7.31 (m, 4H), 7.24-7.22 (m, 1H), 7.05 (d, J = 1.1 Hz, 1H), 2.33 (d, J = 1.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 131.5, 129.0, 128.7, 128.0, 126.0, 123.8, 123.3, 121.8, 119.5, 115.1, 111.5, 81.5, 70.7, 9.8. MS (EI) *m/z*: 231 (M^+). IR (neat): 3056, 2916, 2860, 2247 (C≡C), 1456, 1405 cm^{-1}. Anal. Calcd for $C_{17}H_{13}N$: C, 88.28; H, 5.67; N, 6.06. Found: C, 88.28; H, 5.89; N, 6.05.



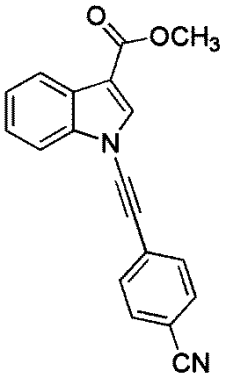
ethyl 1-(phenylethynyl)-1*H*-indole-2-carboxylate, 7c [1c]**:** white needles, 56% (1.25 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73-7.68 (m, 2H), 7.61 (dd, J = 7.2, 1.8, 2H), 7.48 (dd, J = 7.7, 7.2 Hz, 1H), 7.40-7.33 (m, 4H), 7.29 (dd, J = 7.5, 7.2 Hz, 1H), 4.45 (q, J = 7.1 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H).



methyl 1-(cyclohexylethynyl)-1*H*-indole-3-carboxylate, 7e: yellow oil, 68% (1.70 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dd, J = 7.6,1.6 Hz, 1H), 7.89 (s, 1H), 7.53 (d, J = 7.3 Hz, 1H), 7.39-7.30 (m, 2H), 3.92 (s, 3H), 2.71-2.66 (m, 1H), 1.93-1.90 (m, 2H), 1.81-1.77 (m, 2H), 1.60-1.55 (m, 3H), 1.43-1.41 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 138.4, 134.9, 125.3, 124.1, 123.2, 121.7, 111.2, 109.8, 75.6, 70.8, 51.0, 32.7, 28.7, 25.8, 24.8. MS (EI) *m/z*: 281 (M^+), 222 ([M-$COOCH_3$]$^+$). IR (neat): 2927, 2852, 2266 (C≡C), 1708 (C=O), 1460 cm^{-1}. Anal. Calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.98. Found: C, 76.82; H, 6.94; N, 5.09.

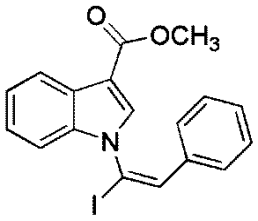


methyl 1-((3-methoxyphenyl)ethynyl)-1*H*-indole-3-carboxylate, 7g: pale yellow oil, 70% (1.40 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dd, J = 7.6, 1.4 Hz, 1H), 7.99 (s, 1H), 7.66 (d, J = 7.3 Hz, 1H), 7.42-7.37 (m, 2H), 7.30 (dd, J = 8.0 , 8.0 Hz) 7.17 (dd, J = 8.0, 1.9 Hz, 1H), 7.10-7.09 (m, 1H), 6.95 (dd, J = 8.0, 1.9 Hz, 1H), 3.94(s, 3H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 159.8, 138.6, 135.0, 129.9, 125.7, 124.8, 124.4, 124.0, 122.9, 122.2, 116.8, 115.3, 111.8, 111.3, 79.2, 72.1, 55.6, 51.6. MS (EI) *m/z*: 305 (M^+), 274 ([M-OCH_3]$^+$). IR (neat): 2996, 2950, 2256 (C≡C), 1708 (C=O), 1459 cm^{-1}. Anal. Calcd for $C_{19}H_{15}NO_3$: C, 74.74; H, 4.95; N, 4.59. Found: C, 74.73; H, 5.05; N, 4.65.



methyl 1-((4-cyanophenyl)ethynyl)-1*H*-indole-3-carboxylate, 7i: pale yellow needles, 40% (806 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J =7.0, Hz, 1H), 7.98 (s, 1H), 7.70-7.63 (m, 5H), 7.46-7.38 (m, 2H), 3.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 138.4, 134.7, 132.5, 131.8, 127.0, 125.8, 125.2, 124.4, 122.5, 118.6, 112.3, 111.9, 111.7, 83.5, 71.3, 51.8. MS (EI) *m/z*: 300 (M^+), 269 ([M-OCH_3]$^+$). IR (neat): 3120, 3072, 2256 (C≡C), 2224 (C≡N), 1708 (C=O), 1461 cm^{-1}. Anal. Calcd for $C_{19}H_{12}N_2O_2$: C, 75.99; H, 4.03; N, 9.33. Found: C, 75.98; H, 4.20; N, 9.34.

d) **Representative procedure for syntheses of 1-(1-halovinyl)-1*H*-indoles, (*E*)-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, and the mixture was stirred for 10 min. Then, H_2O (20 mmol) was added, and the cooling-bath was removed to warm to room temperature. After additional stirring for 50 min, the reaction was quenched at 0 ºC with saturated aqueous sodium thiosulfate, and 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 (eluent; Toluene/EtOAc = 100/1) afforded 403 mg of (*E*)-**2** in quantitative yield as pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, J = 8.4, 1.1 Hz, 1H), 7.79 (s, 1H), 7.45 (s, 1H), 7.42-7.30 (m, 3H), 7.26-7.16 (m, 1H), 7.12-7.09 (m, 2H), 6.76 (d, J = 7.3 Hz, 2H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 143.6, 135.4, 134.4, 133.4, 129.5, 129.1, 128.3, 127.0, 124.5, 123.7, 122.2, 112.3, 111.7, 84.1, 51.6. MS (EI) *m/z*: 403 (M^+), 372 ($[M-OCH_3]^+$), 276 ($[M-I]^+$). IR (neat): 3121, 3048, 1697 (C=O), 1621 (C=C) cm^{-1}. Anal. Calcd for $C_{18}H_{14}INO_2$: C, 53.62; H, 3.50; N, 3.47. Found: C, 53.46; H, 3.60; N, 3.73.

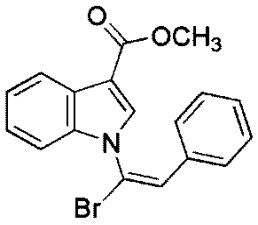


e) **Preparation of 1 M TMSI in CH_2Cl_2**: We purchased the seal-tubed TMSI (5 g) in neat form from Tokyo Chemical Industry Co., LTD, and it included a portion of Al metal inside the tube for inhibiting the decomposition of TMSI. 5 g of TMSI was added to 25 mL of dried CH_2Cl_2 along with the Al metal 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. However, in the case of 1 M toluene solution, unfortunately, complete decomposition on ^{1}H NMR spectra was observed only in 24 h.

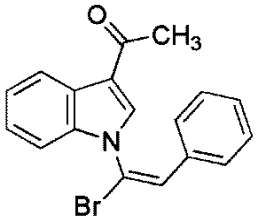
f) **General procedure to make alkynyl bromide from terminal alkynes** [1, 2, 3]: To a solution of phenylacetylene (3.3 mL, 30 mmol) in dry acetone (60 mL) was added NBS (5.9 g, 33 mmol) and $AgNO_3$ (51 mg, 0.3 mmol). The reaction mixture was stirred at ambient temperature for *ca*. 2 h, monitoring 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.

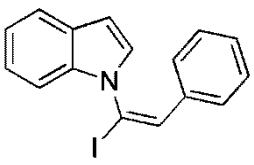
g) **Characterization for 1-(1-halovinyl)-1*H*-indoles in Table 1, 2 and 3.**



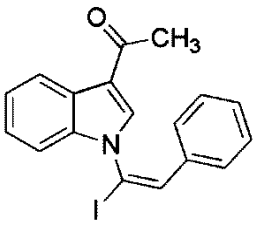
(*E*)-methyl 1-(1-bromo-2-phenylvinyl)-1*H*-indole-3-carboxylate, (*E*)-entry 19 in Table 1; yellowish white solid, quant. (355 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 7.2 Hz, 1H), 7.80 (s, 1H), 7.40 (d, J = 8.0 Hz, 1H), 7.36-7.28 (m, 2H), 7.21-7.10 (m, 4H), 6.76 (d, J = 7.5 Hz, 2H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 135.6, 134.6, 133.5, 133.1, 129.4, 129.1, 128.2, 126.9, 124.6, 123.7, 122.2, 113.0, 112.0, 111.9, 51.6. MS (EI) *m/z*: 355 (M^+), 276 ($[MH-Br]^+$). IR (neat): 3126, 3057, 1698 (C=O), 1633 (C=C), 1455 cm^{-1}. Anal. Calcd for $C_{18}H_{14}BrNO_2$: C, 60.69; H, 3.96; N, 3.93. Found: C, 60.62; H, 4.1; N, 4.15.



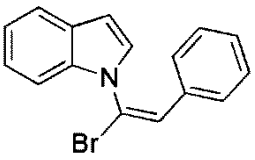
(*E*)-1-(1-(1-bromo-2-phenylvinyl)-1*H*-indol-3-yl) ethanone, (*E*)-entry 14 in Table 2; white needles, 75% (130 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (dd, J = 7.7, 1.4 Hz, 1H), 7.71 (s, 1H), 7.41-7.30 (m, 3H), 7.23-7.18 (m, 2H), 7.13 (dd, J = 7.4, 7.1 Hz, 2H), 6.77 (d, J = 7.4 Hz, 2H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 135.9, 134.7, 133.8, 133.1, 129.5, 129.2, 128.2, 126.6, 125.1, 124.2, 123.2, 121.0, 113.0, 111.9, 28.1. MS (EI) *m/z*: 339 (M^+), 260 ($[MH-Br]^+$). IR (neat): 3109, 1656 (C=O), 1604 (C=C), 1450 cm^{-1}. Anal. Calcd for $C_{18}H_{14}BrNO$: C, 63.55; H, 4.15; N, 4.12. Found: C, 63.57; H, 4.07; N, 4.22.



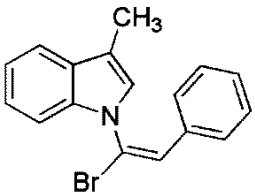
(*E*)-1-(1-iodo-2-phenylvinyl)-1*H*-indole, (*E*)-6 in Table 2; colorless cubes, 98% (3.15 g (*E*)-α only). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, J = 7.6, 1.6 Hz, 1H), 7.40-7.37 (m, 2H), 7.27-7.09 (m, 6H), 7.05 (d, J = 3.4 Hz, 1H), 6.82 (dd, J = 8.2, 1.5 Hz, 2H), 6.74 (d, J = 3.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 134.9, 129.5, 129.0, 128.9, 128.3, 127.6, 123.4, 121.9, 121.5, 112.3, 106.8, 88.4. MS (EI) *m/z*: 218 ($[M-I]^+$). IR (neat): 3097, 3039, 1619 (C=C) cm^{-1}. Anal. Calcd for $C_{16}H_{12}IN$: C, 55.67; H, 3.50; N, 4.06. Found: C, 55.65; H, 3.37; N, 4.13.



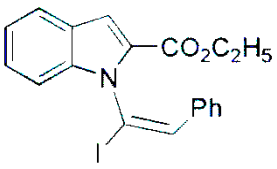
(*E*)-1-(1-(1-iodo-2-phenylvinyl)-1*H*-indol-3-yl)ethanone, (*E*)-4 in Table 2 and 3; yellow solid, 95% (1.48 g, *E*/*Z* = 98/2). Recrystallization from EtOH yielded only (*E*)-**4** of 1.24 g in 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (dd, *J* = 6.8, 1.5 Hz, 1H), 7.70 (s, 1H), 7.47 (s, 1H), 7.43-7.32 (m, 3H), 7.20 (m, 1H), 7.14-7.10 (m, 2H), 6.77 (dd, *J* = 7.8, 1.4 Hz, 2H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 143.7, 135.6, 134.3, 133.6, 129.6, 129.1, 128.2, 126.6, 124.9, 124.2, 123.2, 120.8, 112.1, 84.0, 28.0. MS (EI) *m/z*: 260 ($[M-I]^+$), 217 ($[M-I-COCH_3]^+$). IR (neat): 3113, 1658 (C=O), 1623 (C=C), 1605 (C=C), 1526 cm^{-1}. Anal. Calcd for $C_{18}H_{14}INO$: C, 55.83; H, 3.64; N, 3.62. Found: C, 55.80; H, 3.53; N, 3.69.



(*E*)-1-(1-bromo-2-phenylvinyl)-1*H*-indole, (*E*)-8a in Table 3; colorless needles and cubes, 99% (1.47 g (*E*)-*α* only). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 6.6, 1.5 Hz, 1H), 7.39 (d, *J* = 7.9 Hz, 1H), 7.24-7.09 (m, 7H), 7.07 (d, *J* = 3.3 Hz, 1H), 6.80 (dd, *J* = 7.9, 1.5 Hz, 2H), 6.70 (d, *J* = 3.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.2, 133.8, 133.0, 129.4, 128.94, 128.87, 128.3, 127.5, 123.5, 121.9, 121.4, 115.7, 111.9, 106.7. MS (EI) *m/z*: 297 (M^+), 217 ($[M-Br]^+$). IR (neat): 3106, 3047, 1633 (C=C) cm^{-1}. Anal. Calcd for $C_{16}H_{12}BrN$: C, 64.45; H, 4.06; N, 4.70. Found: C, 64.22; H, 3.87; N, 4.72.

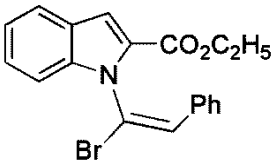


(*E*)-1-(1-bromo-2-phenylvinyl)-3-methyl-1*H*-indole, (*E*)-8b in Table 3; yellow oil, 97% (302 mg, (*E*)-*α* only). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.57 (m, 1H), 7.31-7.29 (m, 1H), 7.24-7.10 (m, 5H), 7.08 (s, 1H), 6.88-6.87 (m, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.6, 134.0, 132.4, 130.2, 128.9, 128.7, 128.3, 124.7, 123.5, 121.4, 119.5, 116.5, 116.3, 111.9, 10.1. MS (EI) *m/z*: 313 ($[MH]^+$), 232 ($[M-Br]^+$). IR (neat): 3053, 3025, 2916, 2859, 1636 (C=C), 1451 cm^{-1}. Anal. Calcd for $C_{17}H_{14}BrN$: C, 65.40; H, 4.52; N, 4.49. Found: C, 65.12; H, 4.51; N, 4.50.

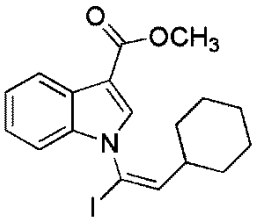


(*E*)-ethyl 1-(1-iodo-2-phenylvinyl)-1*H*-indole-2-carboxylate, (*E*)-8c in Table 3; pale yellow solid, 99% (405 mg, (*E*)-*α* only). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.57 (s, 1H), 7.47 (s, 1H), 7.37-7.36 (m, 2H), 7.27-7.23 (m, 1H), 7.14-7.07 (m, 3H), 6.87 (dd, *J* = 7.9, 1.6 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 143.0, 137.4, 135.1, 128.9, 128.5, 128.2, 127.5, 126.9,

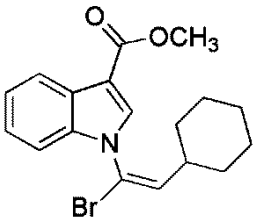
123.08, 123.06, 114.8, 112.5, 87.1, 61.4, 14.5. MS (EI) *m/z*: 290 ([M-I]$^+$), 217 ([M-I-COOC$_2$H$_5$]$^+$). IR (neat): 2976, 1706 (C=O), 1620 (C=C), 1453, 1442 cm^{-1}. Anal. Calcd for $C_{19}H_{16}INO_2$: C, 54.69; H, 3.87; N, 3.36. Found: C, 54.69; H, 3.87; N, 3.36.



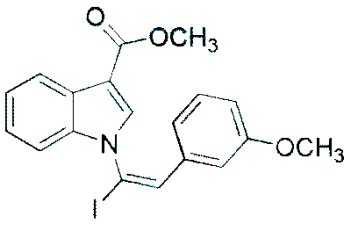
(*E*)-ethyl 1-(1-bromo-2-phenylvinyl)-1*H*-indole-2-carboxylate, (*E*)-8d in Table 3; pale yellow viscous materials, quant. (370 mg, (*E*)-*α* only). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, J = 8.0, 0.9 Hz, 1H), 7.52 (s, 1H), 7.38-7.32 (m, 2H), 7.25-7.22 (m, 2H), 7.16-7.08 (m, 3H), 6.85 (dd, *J* = 7.9, 1.6 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 137.8, 134.6, 133.9, 128.9, 128.8, 128.4, 128.1, 127.4, 126.9, 123.04, 122.97, 114.69, 114.68, 112.1, 61.3, 14.5. MS (EI) *m/z*: 289 ([MH-Br]$^+$). IR (neat): 3055, 2979, 1713 (C=O), 1640 (C=C), 1448 cm^{-1}. Anal. Calcd for $C_{19}H_{16}BrNO_2$: C, 61.64; H, 4.36; N, 3.78. Found: C, 61.61; H, 4.26; N, 3.91.



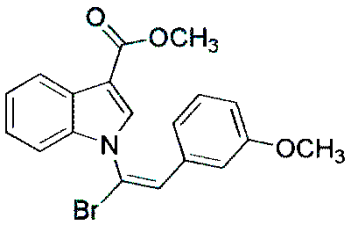
(*E*)-methyl 1-(2-cyclohexyl-1-iodovinyl)-1*H*-indole-3-carboxylate, (*E*)-8e in Table 3; pale yellow viscous materials, 84% (384 mg, (*E*)-*α* only). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19-8.17 (m, 1H), 7.75 (s, 1H), 7.41-7.26 (m, 3H), 6.49 (d, *J* = 10.0 Hz, 1H), 3.93 (s, 3H), 1.97-1.89 (m, 1H), 1.66-1.55 (m 5H) 1.28-1.00 (m 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 153.0, 136.4, 133.8, 126.5, 124.2, 123.3, 122.0, 111.8, 110.6, 80.7, 51.5, 40.2, 32.6, 32.3, 25.6, 25.4, 25.2. MS (EI) *m/z*: 409 (M$^+$), 378 ([M-OCH$_3$]$^+$), 282 ([M-I]$^+$). IR (neat): 3116, 2922, 2848, 1705 (C=O), 1633 (C=C), 1450 cm^{-1}. Anal. Calcd for $C_{18}H_{20}INO_2$: C, 52.83; H, 4.93; N, 3.42. Found: C, 52.97; H, 5.03; N, 3.43.



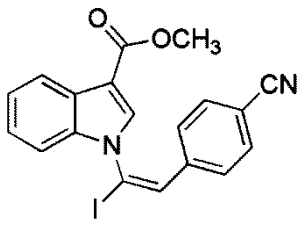
(*E*)-methyl 1-(1-bromo-2-cyclohexylvinyl)-1*H*-indole-3-carboxylate, (*E*)-8f in Table 3; pale yellow viscous materials, 99% (358 mg, (*E*)-*α* only). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20-8.17 (m, 1H), 7.77 (s, 1H), 7.43-7.40 (m, 1H), 7.37-7.33 (m, 2H), 6.23 (d, *J* = 10.1 Hz, 1H), 3.94 (s, 3H), 1.90-1.88 (m, 1H), 1.63-1.56 (m, 5H), 1.17-1.11 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 143.4, 136.7, 134.1, 126.5, 124.3, 123.3, 122.1, 111.5, 110.8, 110.3, 51.5, 39.1, 32.6, 25.7, 25.3. MS (EI) *m/z*: 361 (M$^+$), 302 ([M-COOCH$_3$]$^+$), 282 ([MH-Br]$^+$). IR (neat): 3122, 2924, 2849, 1707 (C=O), 1648 (C=C), 1451 cm^{-1}. Anal. Calcd for $C_{18}H_{20}BrNO_2$: C, 59.68; H, 5.56; N, 3.87. Found: C, 59.53; H, 5.78; N, 3.86.



(*E*)-methyl 1-(1-iodo-2-(3-methoxyphenyl)vinyl)-1*H*-indole-3-carboxylate, (*E*)-8g in Table 3; pale yellow needles, 96% (415 mg, *E*/*Z* = 96/4). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21-8.19 (m, 1H), 7.80 (s 1H), 7.43-7.41 (m, 2H), 7.35-7.31 (m, 2H), 7.04 (dd, *J* = 8.0, 8.0 Hz, 1H), 6.72 (dd, *J* = 8.0, 1.8 Hz, 1H) 6.43 (d, *J* = 8.0 Hz, 1H) 6.14-6.13 (m, 1H) 3.91 (s, 3H) 3.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 159.8, 143.7, 135.42, 135.40, 133.3, 129.9, 126.9, 124.5, 123.7, 122.2, 121.1, 116.2, 112.3, 111.5, 84.1, 55.0, 51.6. MS (EI) *m/z*: 306 ($[M-I]^+$), 275 ($[M-I-OCH_3]^+$), 247 ($[M-I-CO_2CH_3]^+$). IR (neat): 3121, 3048, 2835, 1697 (C=O), 1602 (C=C), 1448 cm^{-1}. Anal. Calcd for $C_{19}H_{16}INO_3$: C, 52.67; H, 3.72; N, 3.23. Found: C, 52.63; H, 3.71; N, 3.16.

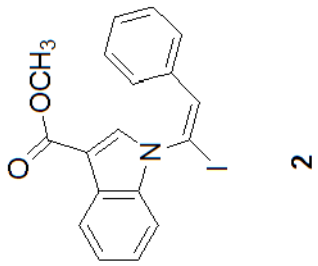


(*E*)-methyl 1-(1-bromo-2-(3-methoxyphenyl) vinyl)-1*H*-indole-3-carboxylate, (*E*)-8h in Table 3; white needles, 98% (376 mg, *E*/*Z* = 96/4). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.0 Hz, 1H), 7.81 (s, 1H), 7.41 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.36-7.29 (m, 2H), 7.19 (s, 1H), 7.04 (dd, *J* = 8.0, 8.0 Hz, 1H), 6.72 (dd, *J* = 8.0, 2.3 Hz, 1H), 6.43 (d, *J* = 8.0 Hz, 1H), 6.14 (s, 1H), 3.91 (s, 3H), 3.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 159.9, 135.7, 134.7, 134.2, 133.5, 130.0, 129.3, 128.5, 126.8, 125.6, 124.6, 123.7, 122.2, 121.1, 116.0, 113.1, 112.3, 112.0, 111.7, 55.0, 51.6. MS (EI) *m/z*: 385 (M^+), 354 ($[M-OCH_3]^+$), 326 ($[M-COOCH_3]^+$), 306 ($[MH-Br]^+$). IR (neat): 3117, 1708 (C=O), 1642 (C=C), 1453 cm^{-1}. Anal. Calcd for $C_{19}H_{16}BrNO_3$: C, 59.08; H, 4.18; N, 3.63. Found: C, 59.06; H, 4.15; N, 3.63.



(*E*)-methyl 1-(2-(4-cyanophenyl)-1-iodovinyl)-1*H*-indole-3-carboxylate, (*E*)-8i in Table 3; pale yellow needles, 97% (415 mg, *E*/*Z* = 99/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.75 (s, 1H), 7.47 (s, 1H), 7.40-7.32 (m, 5H), 6.84 (dd, *J* = 8.4, 0.5 Hz, 2H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 141.2, 138.4, 135.0, 132.81, 132.79, 128.5, 126.9, 124.8, 124.0, 122.4, 118.4, 112.6, 112.4, 112.1, 88.5, 51.7. MS (EI) *m/z*: 428 (M^+), 301 ($[M-I]^+$). IR (neat): 3139, 3054, 2226 (C≡N), 1699 (C=O), 1622 (C=C), 1448 cm^{-1}. Anal. Calcd for $C_{19}H_{13}IN_2O_2$: C, 53.29; H, 3.06; N, 6.54. Found: C, 53.26; H, 3.13; N, 6.59.

h) **^{1}H & ^{13}C NMR spectra for 1-(1-halovinyl)-1*H*-indoles in Table 1.**



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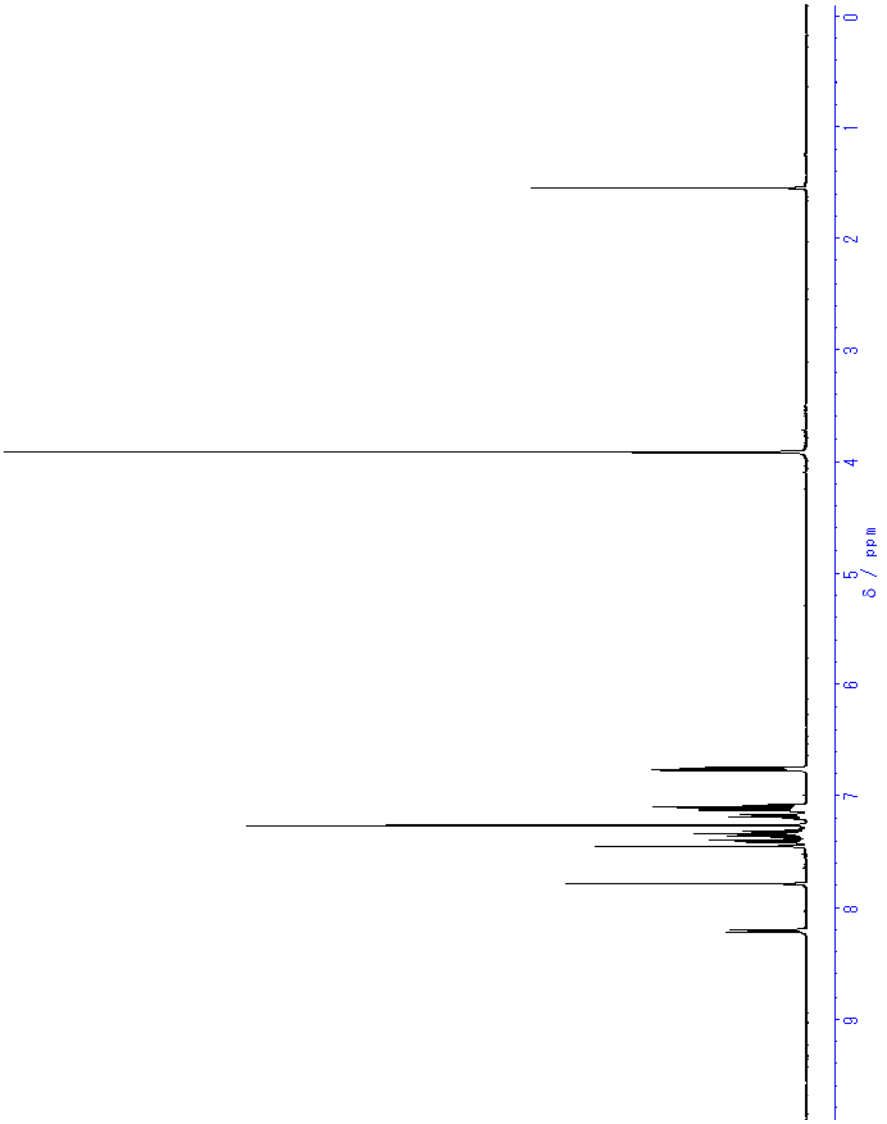

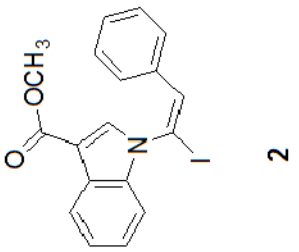

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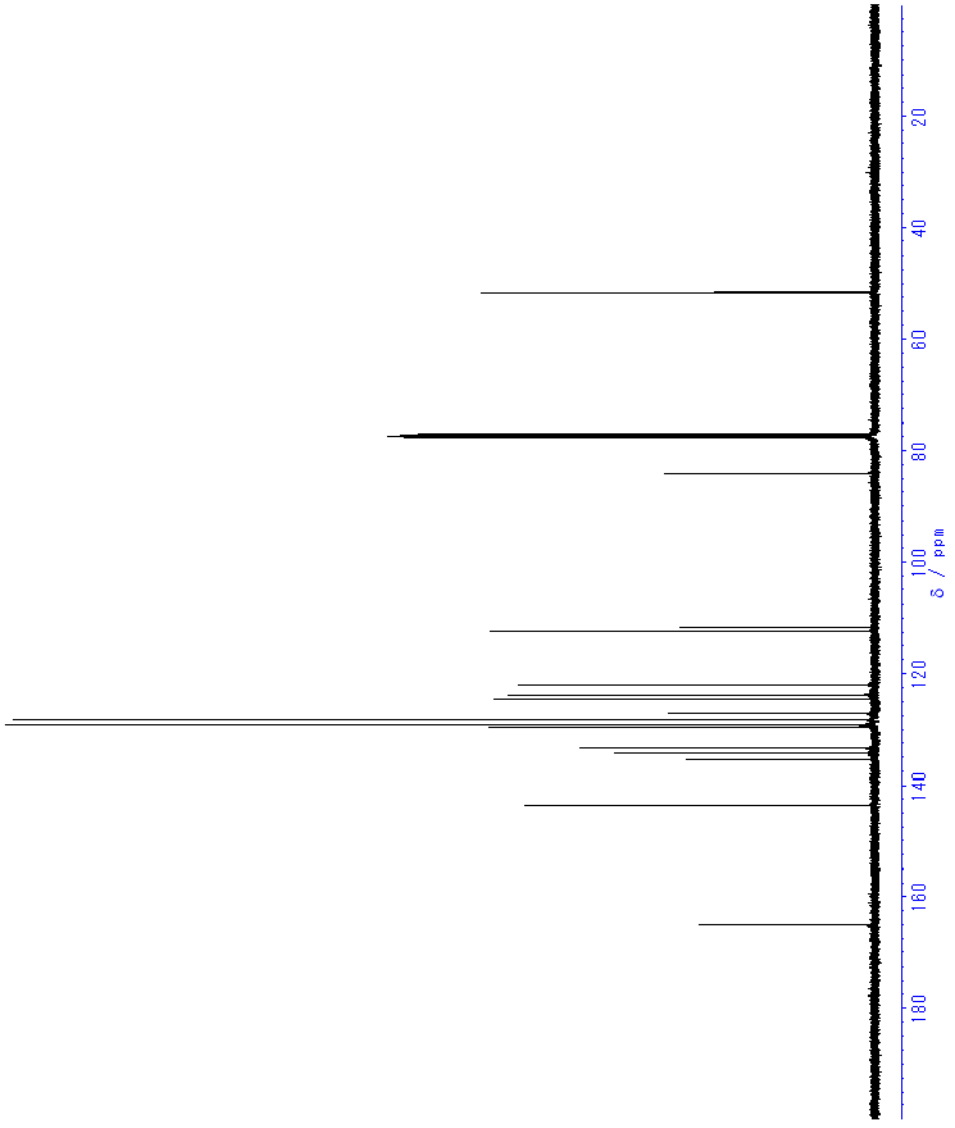


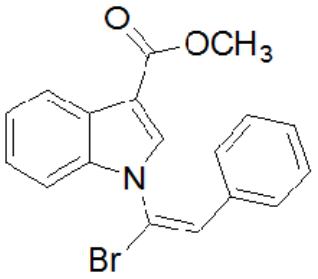
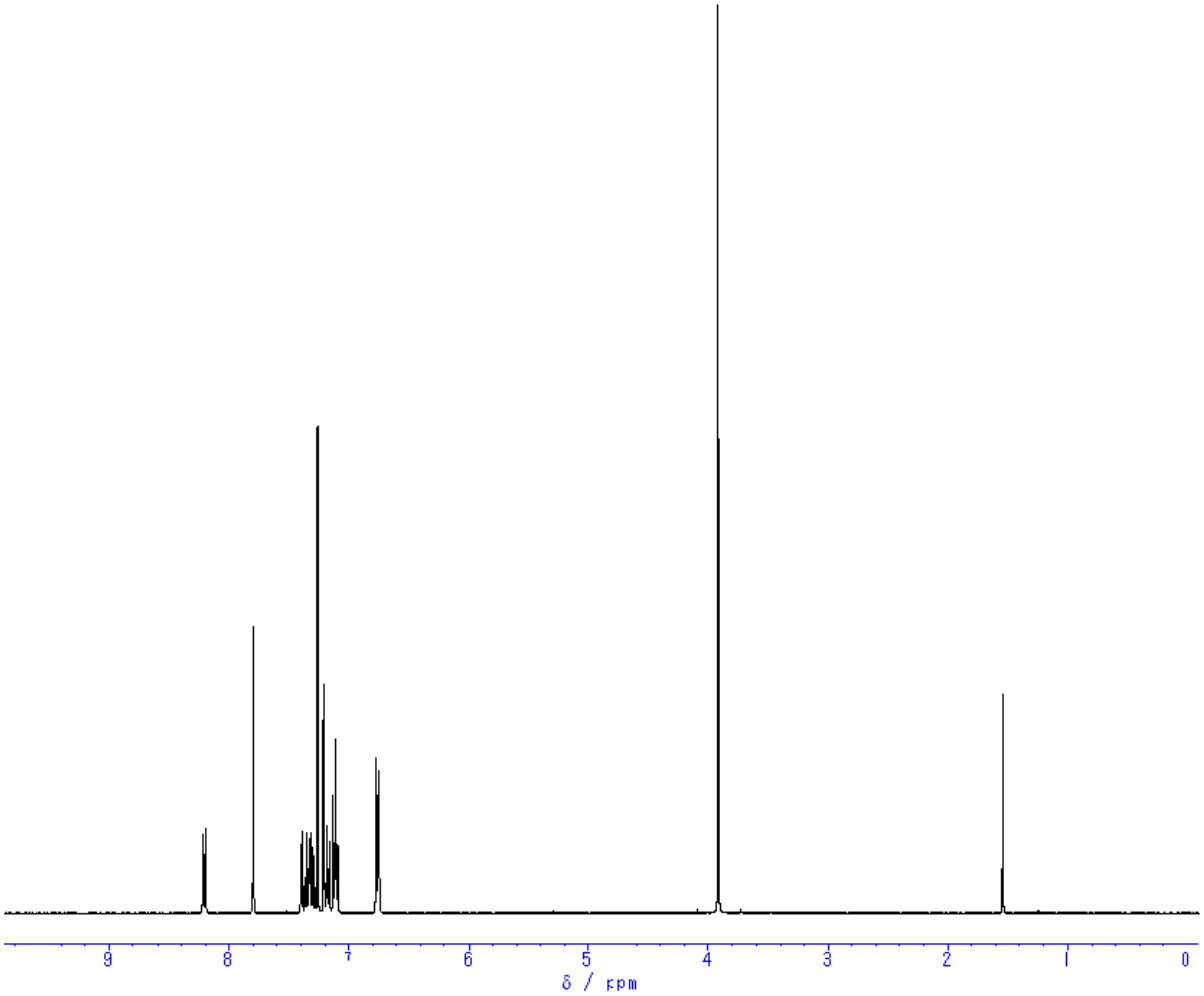


Table 1, entry 19



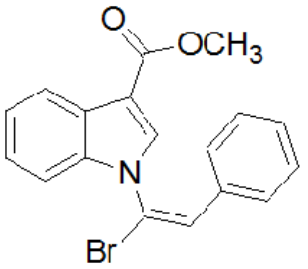
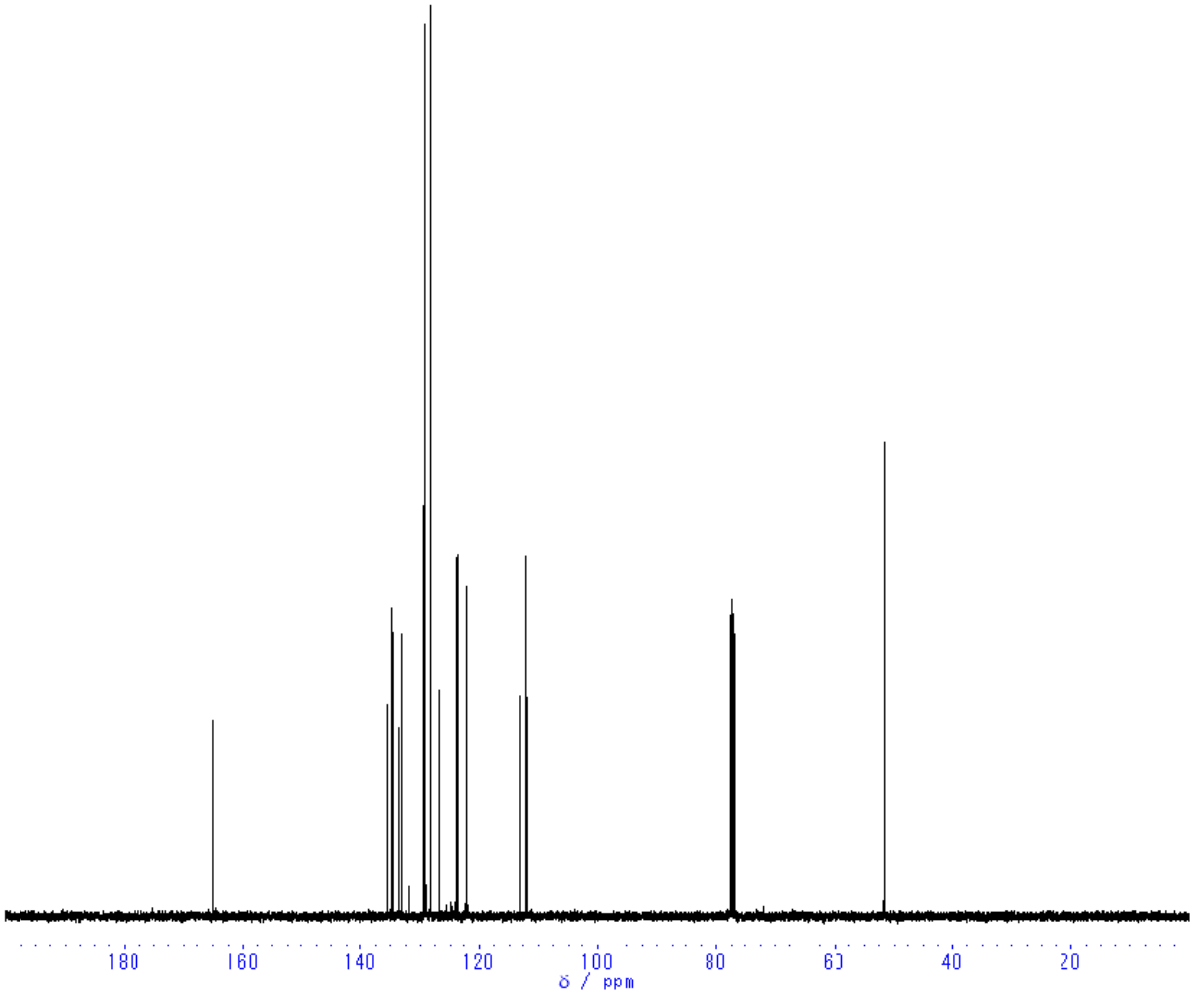
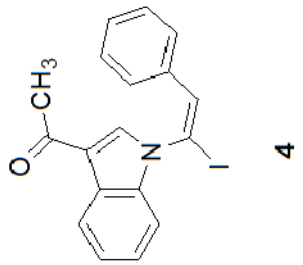


Table 1, entry 19

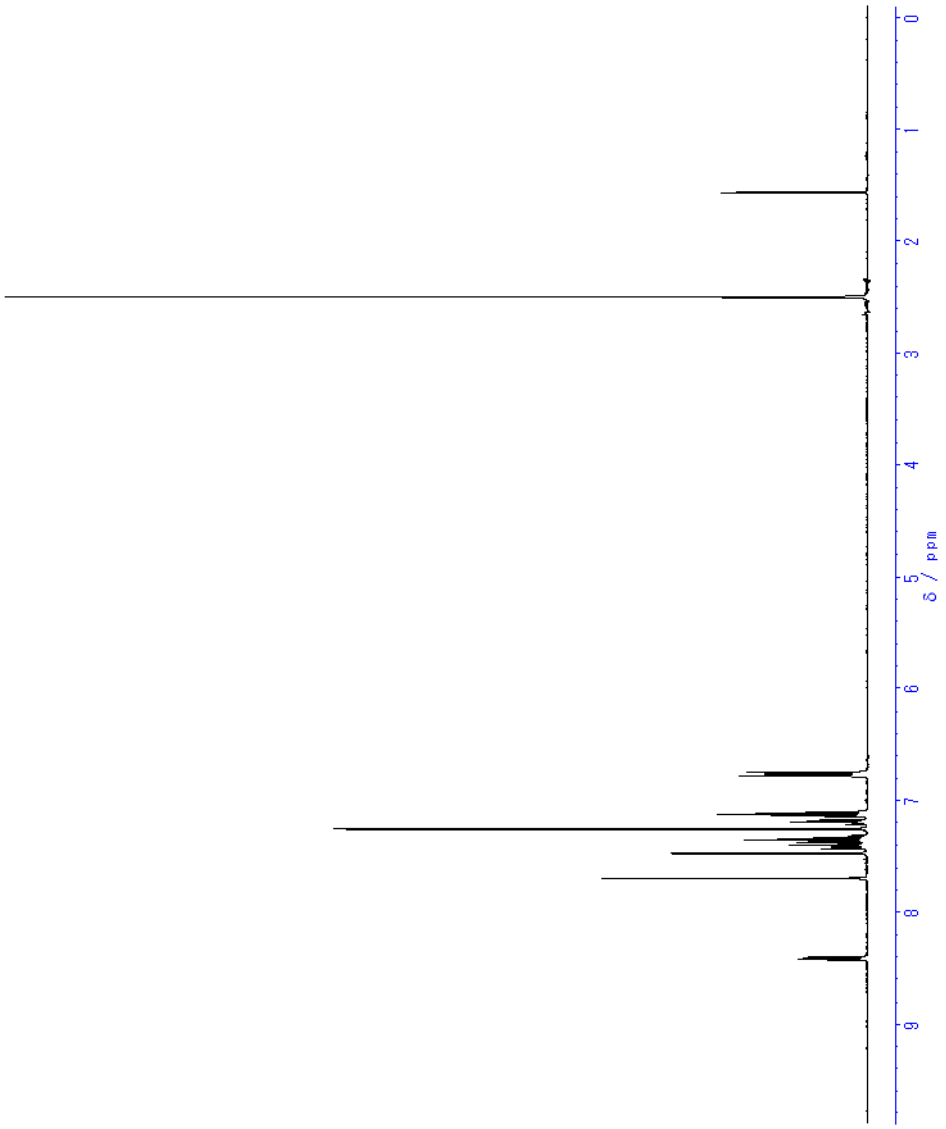


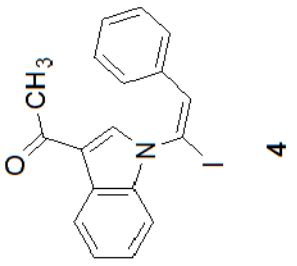
^{1}H & ^{13}C NMR spectra for 1-(1-halovinyl)-1*H*-indoles in Table 2.

Table 2, entry 1



4





4

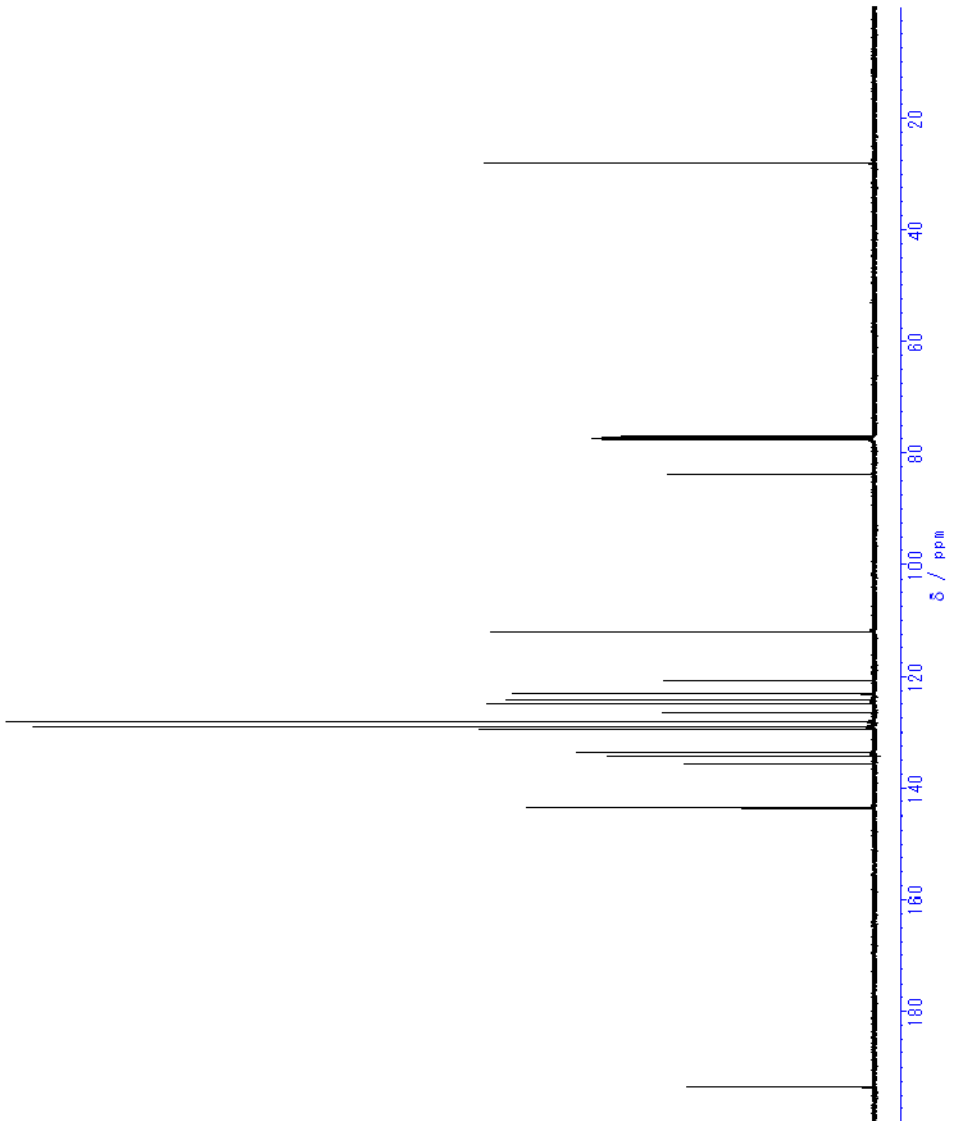
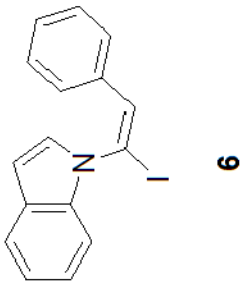
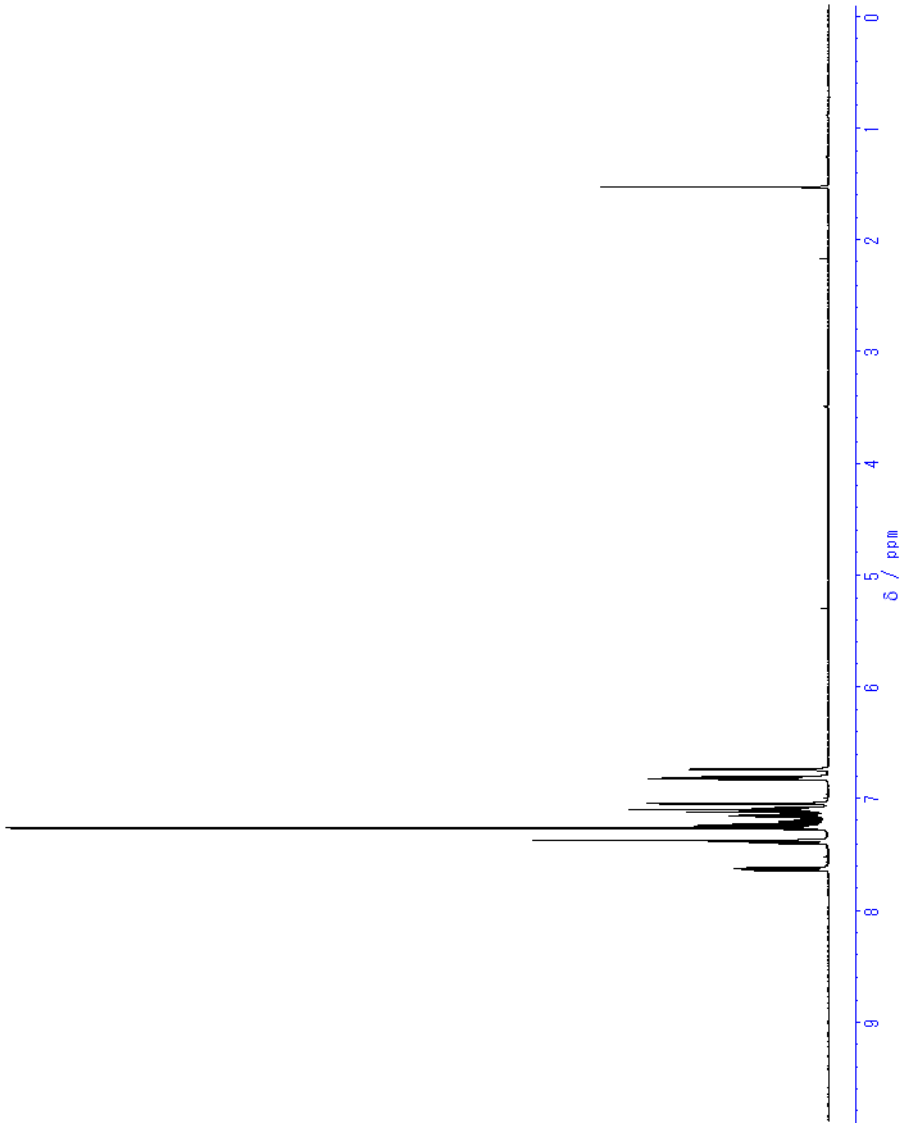
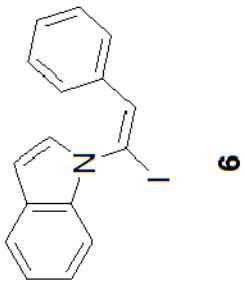


Table 2, entry 2



6





6

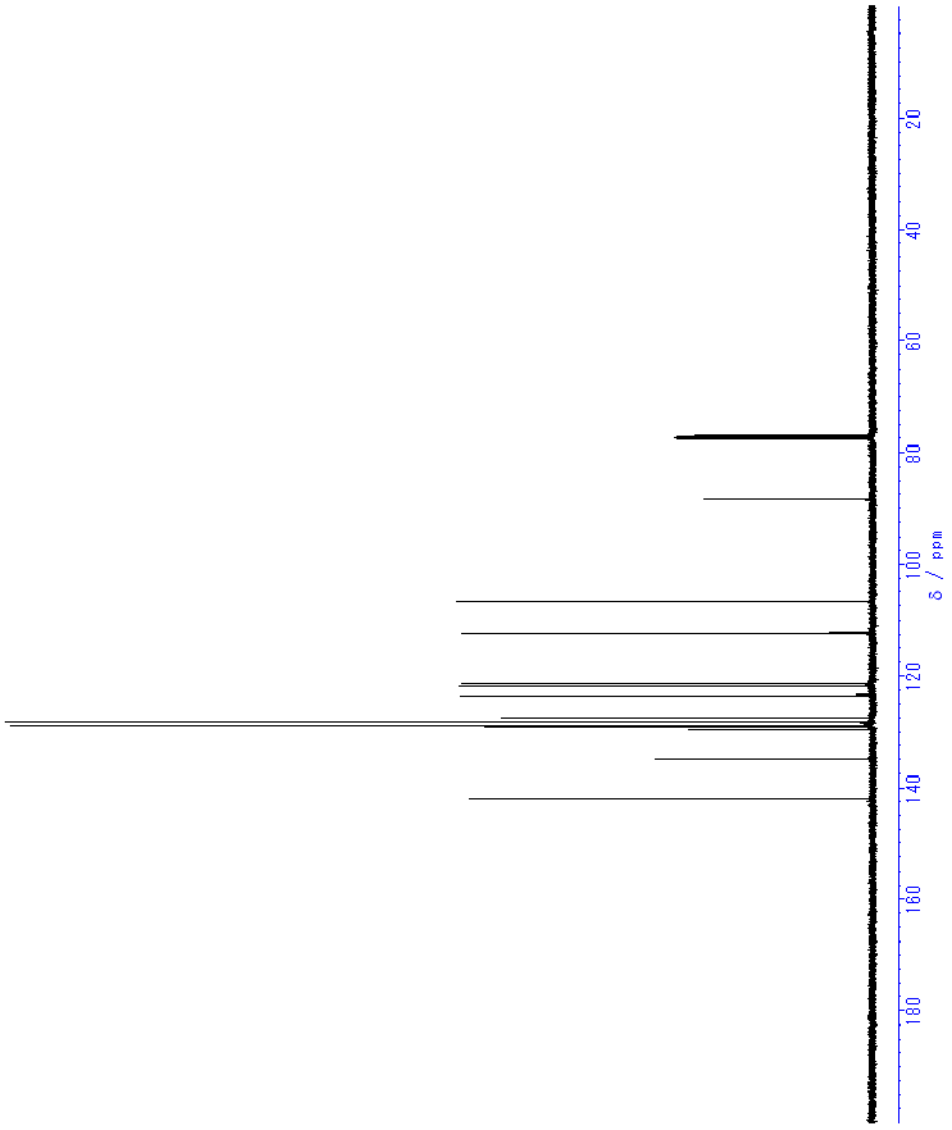
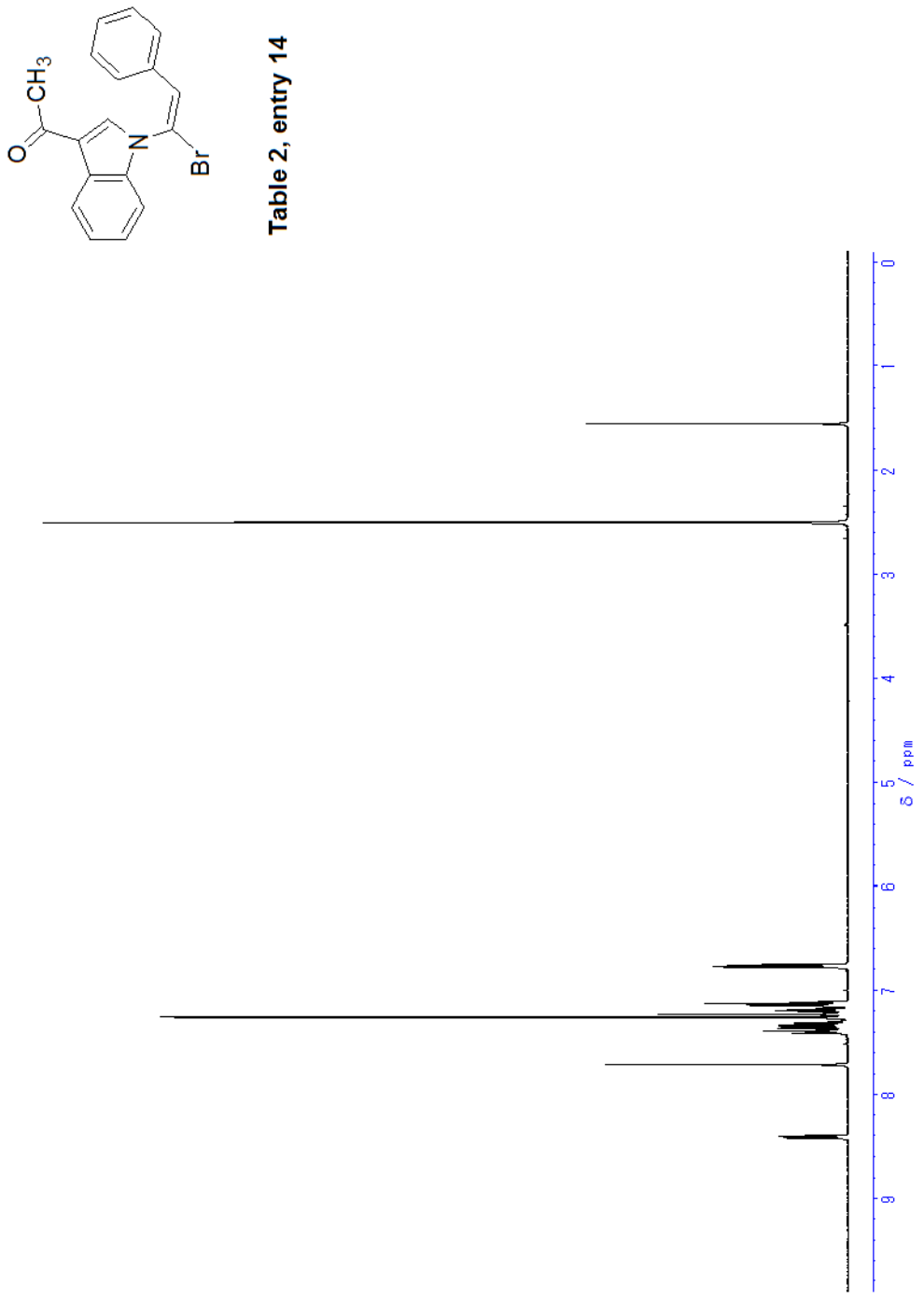


Table 2, entry 14



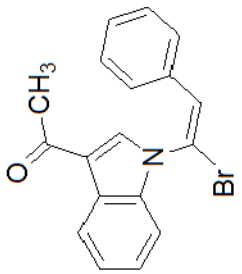


Table 2, entry 14

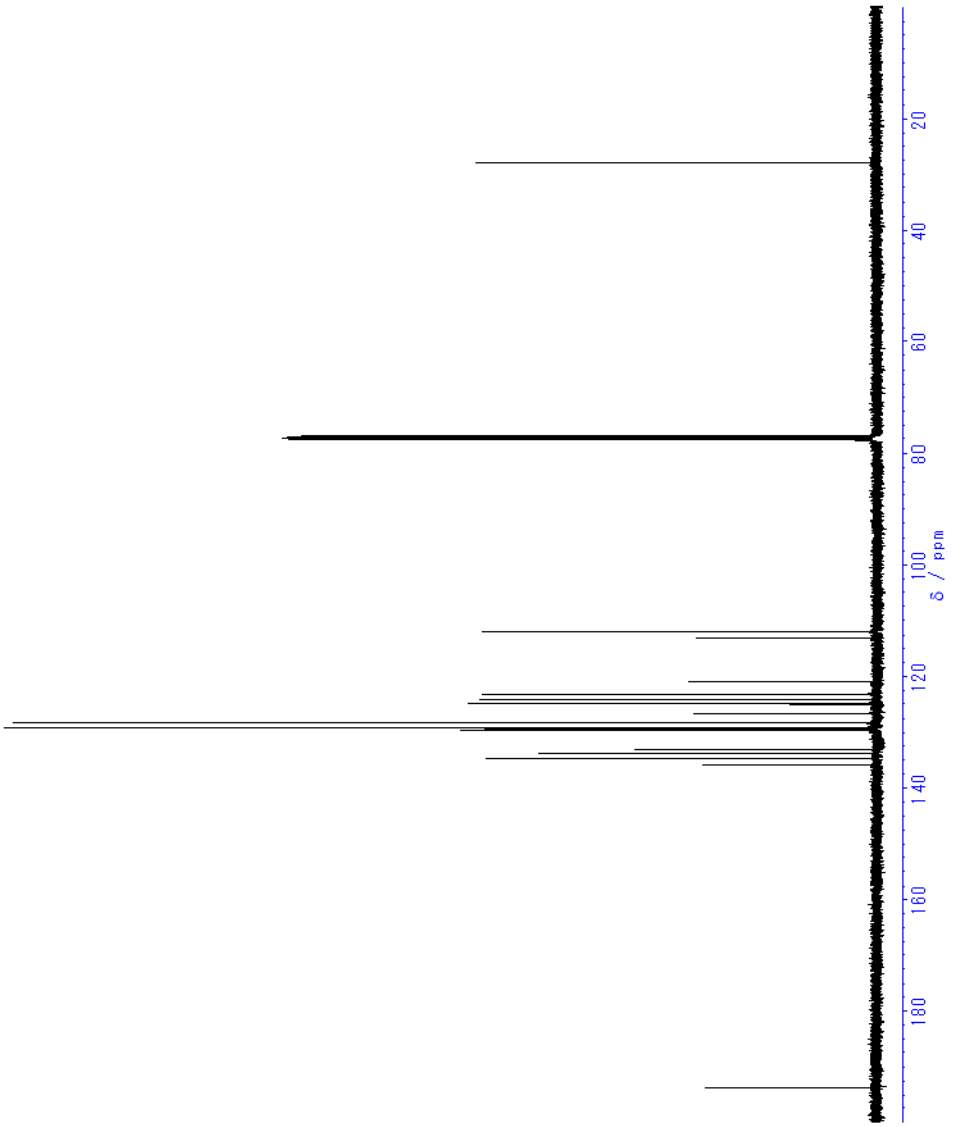
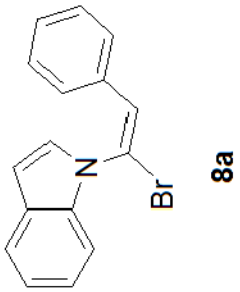
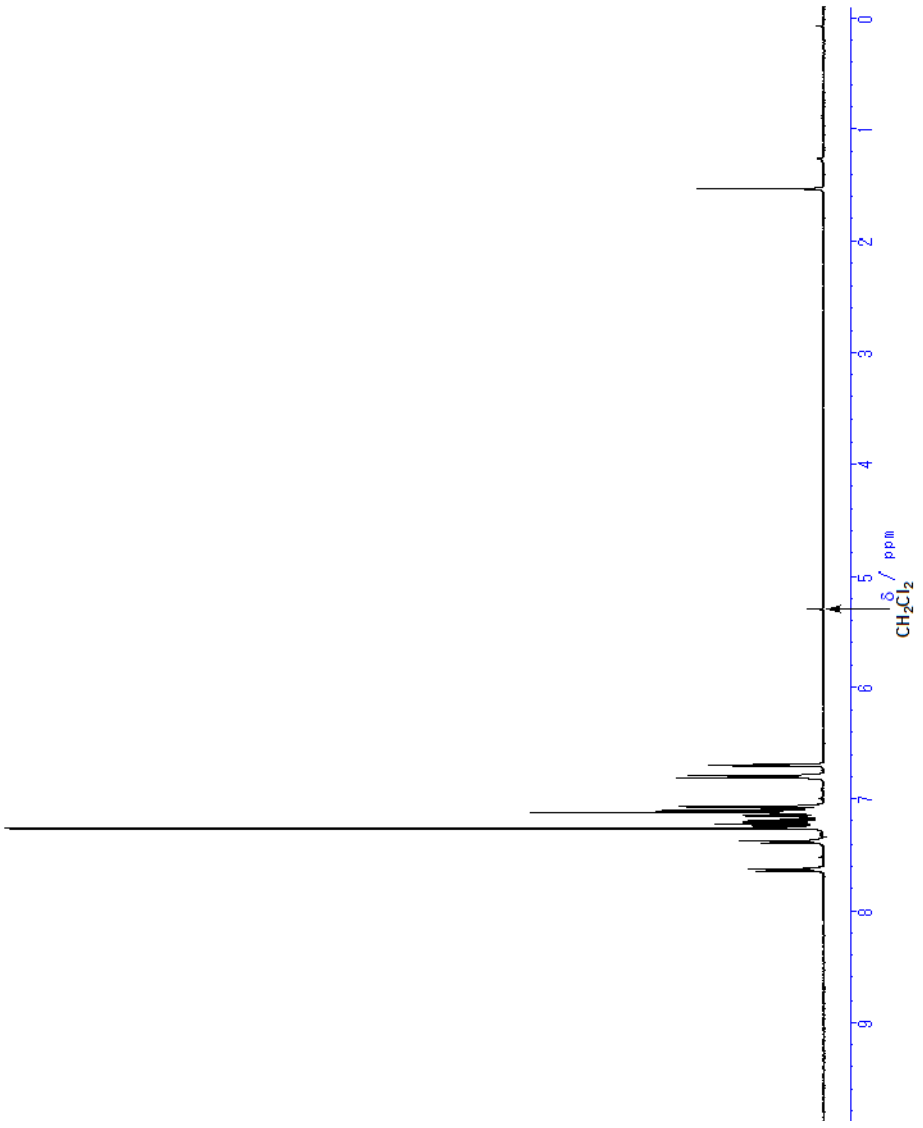
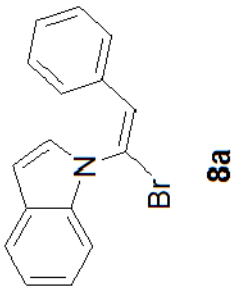


Table 2, entry 15



8a





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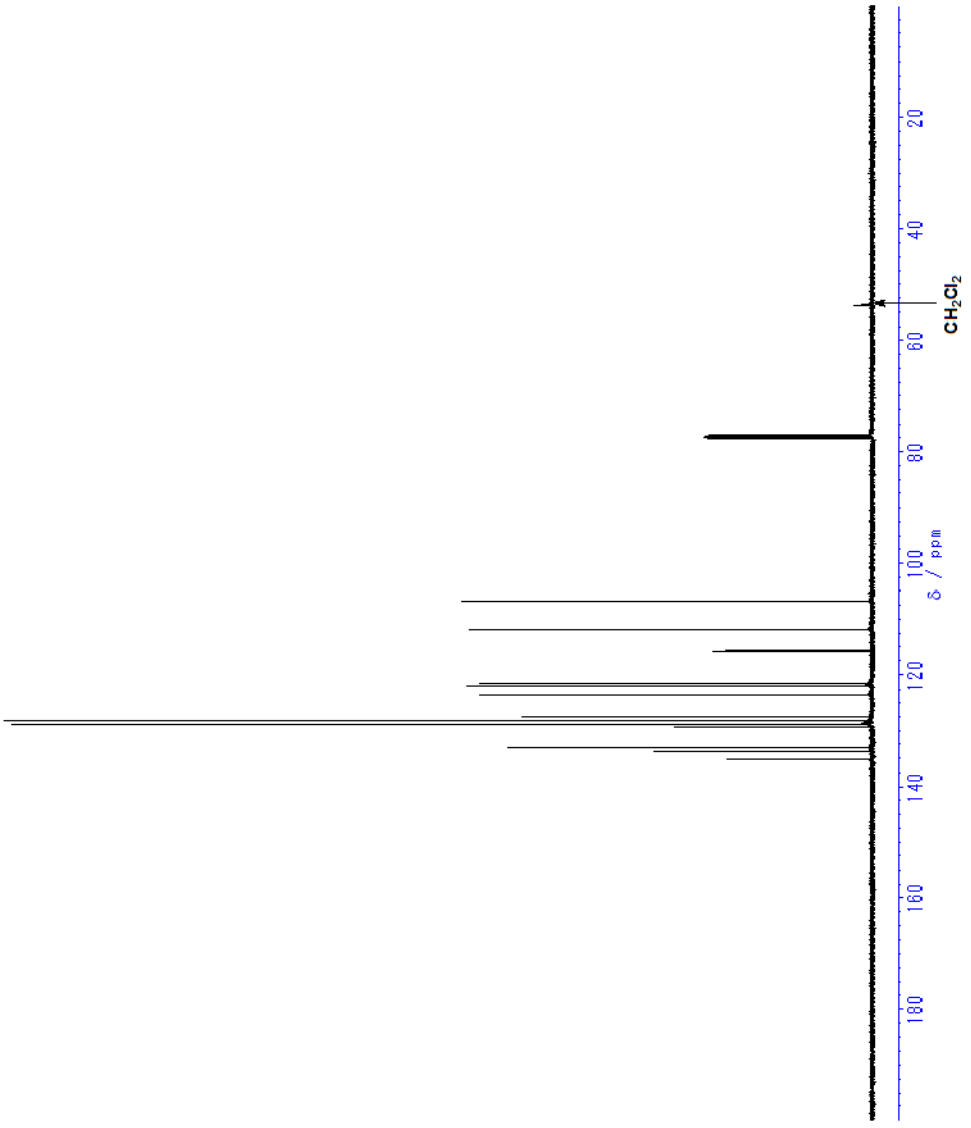
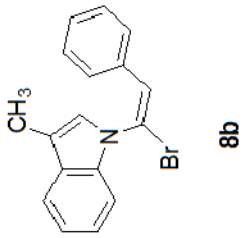


^{1}H & ^{13}C NMR spectra for 1-(1-halovinyl)-1*H*-indoles in Table 3.



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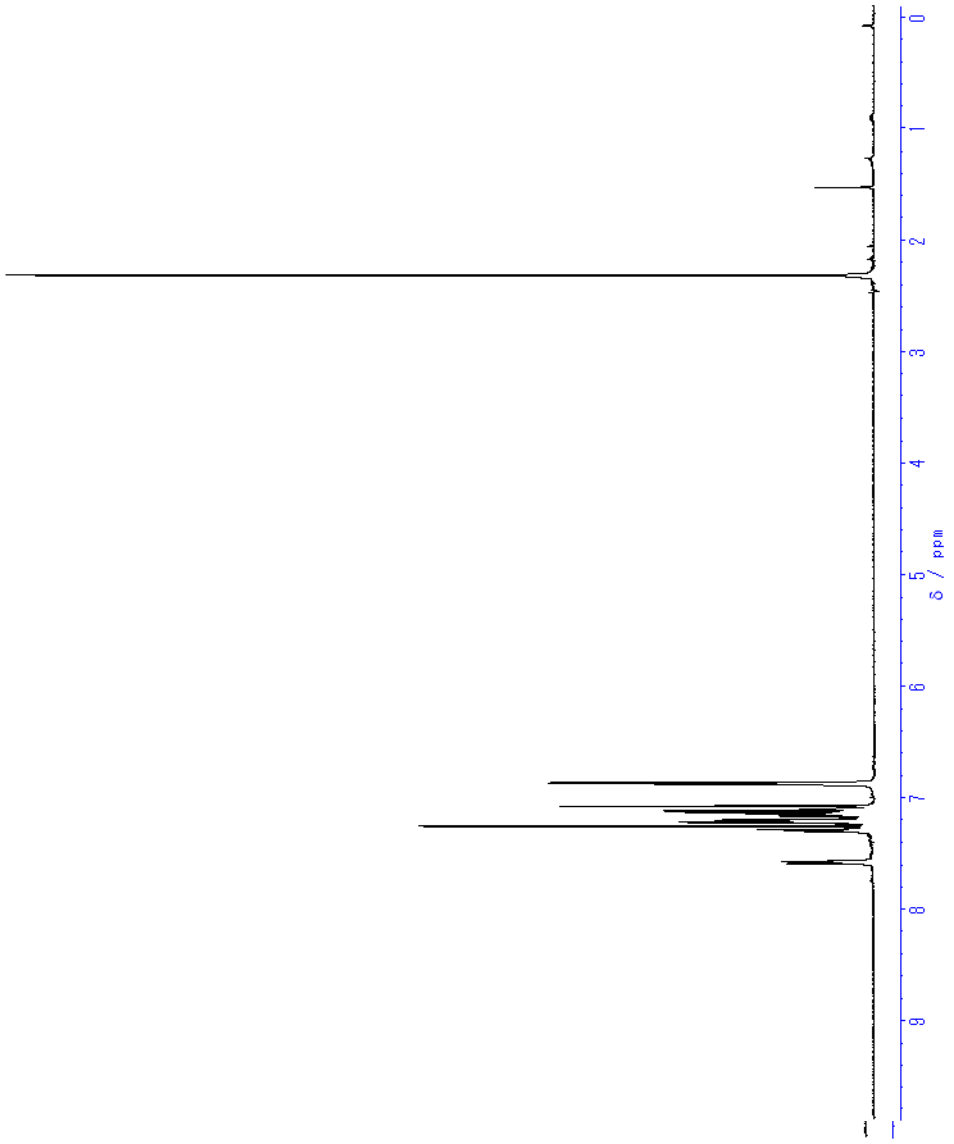

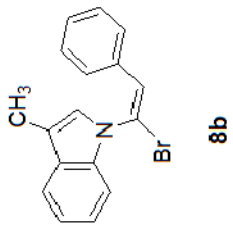

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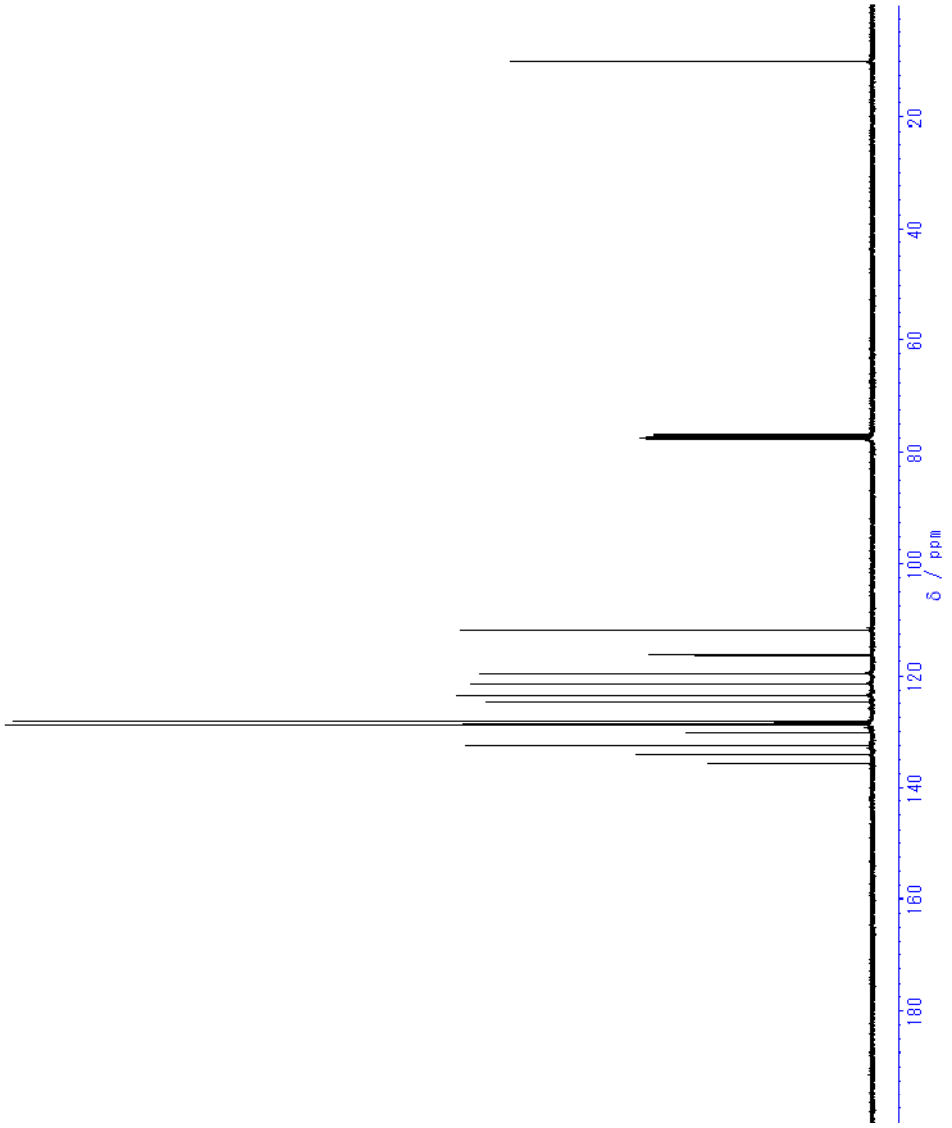

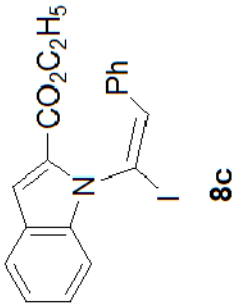

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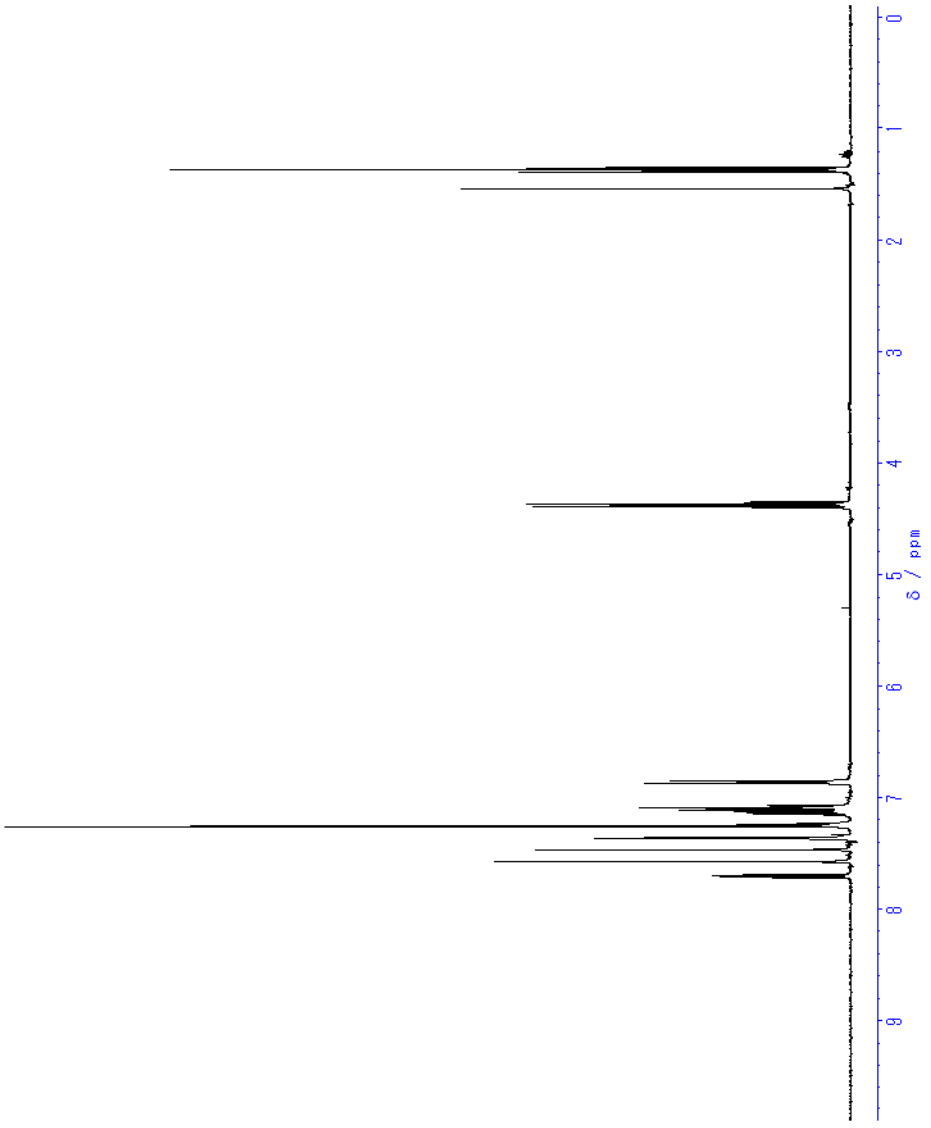

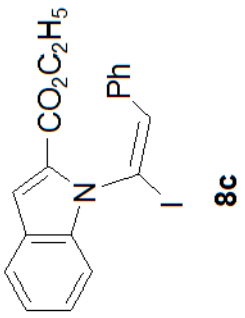

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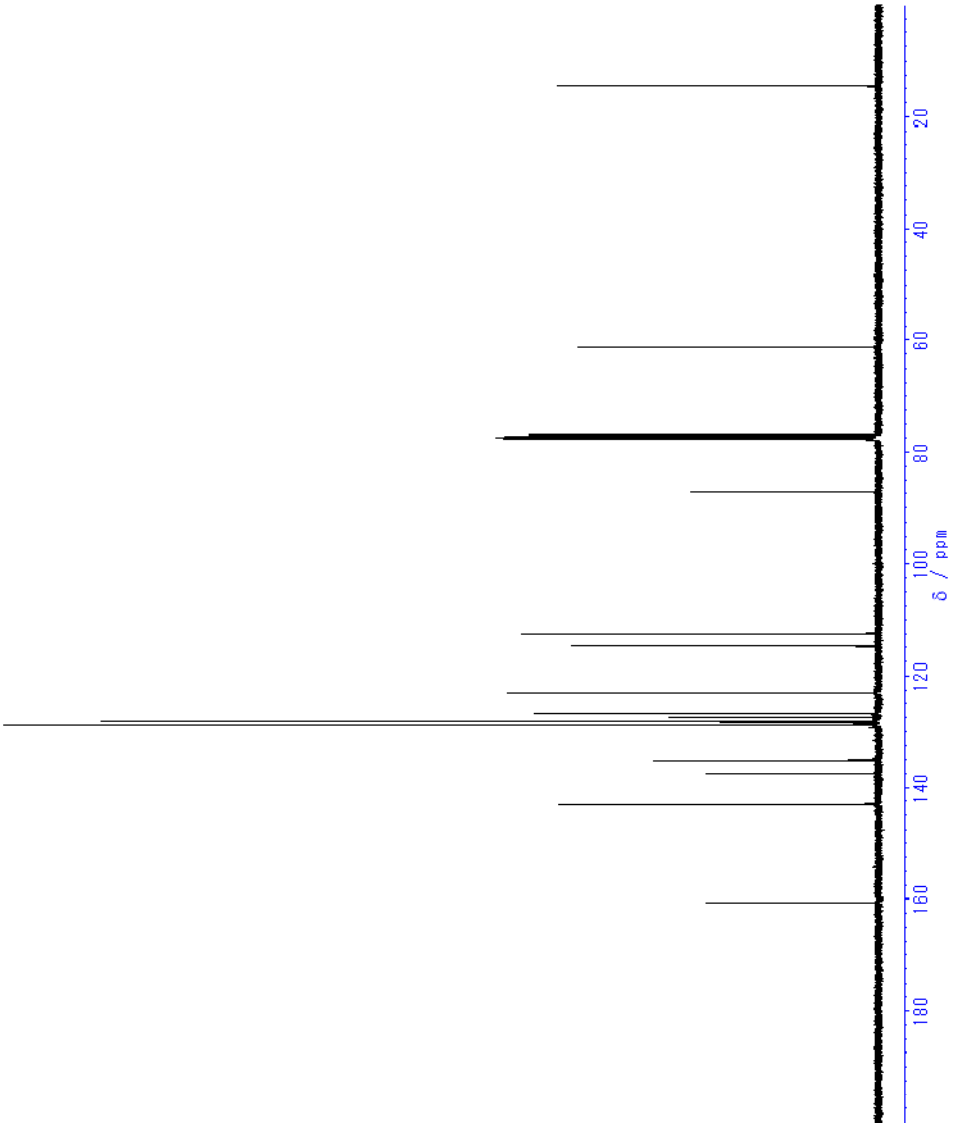

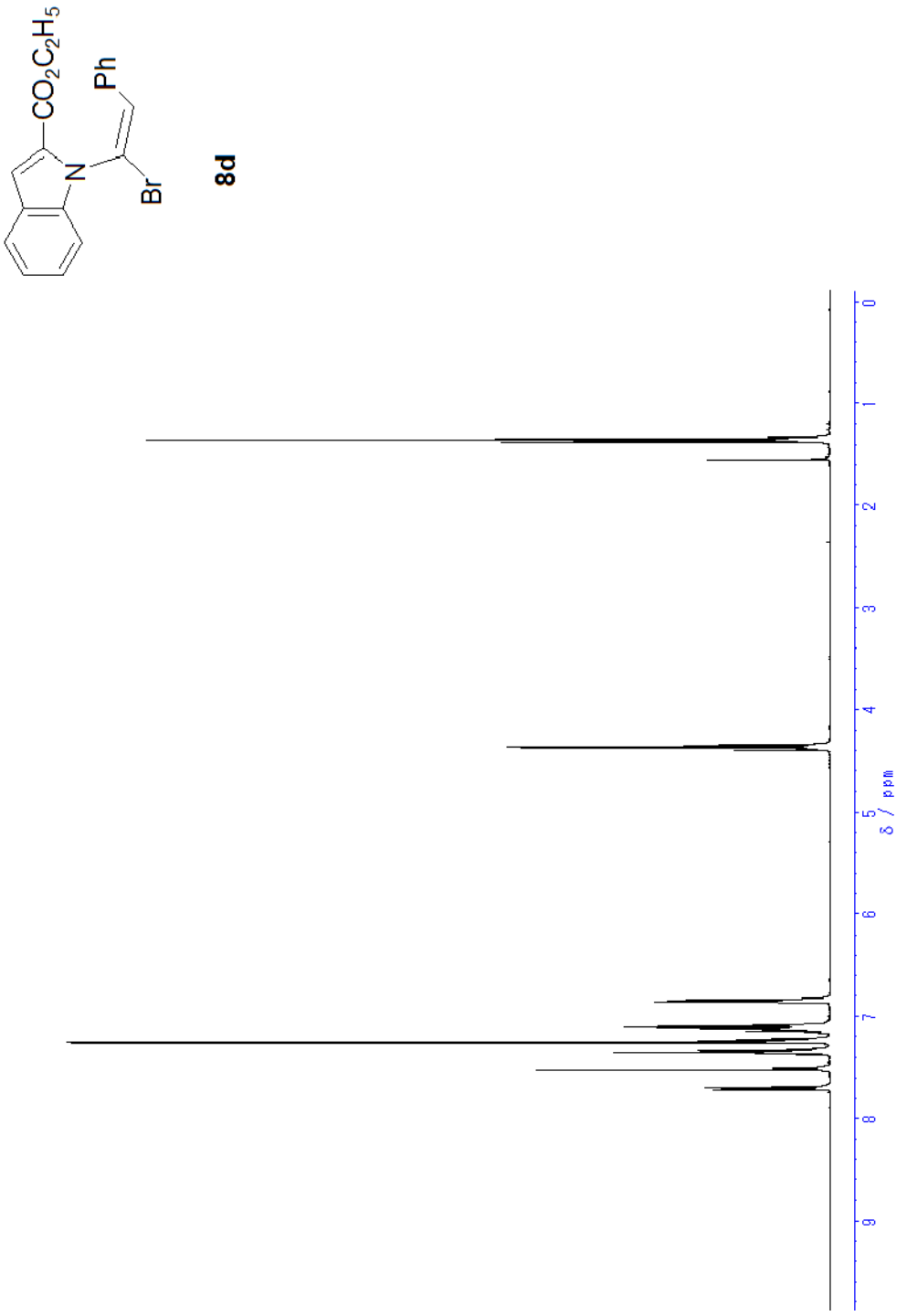
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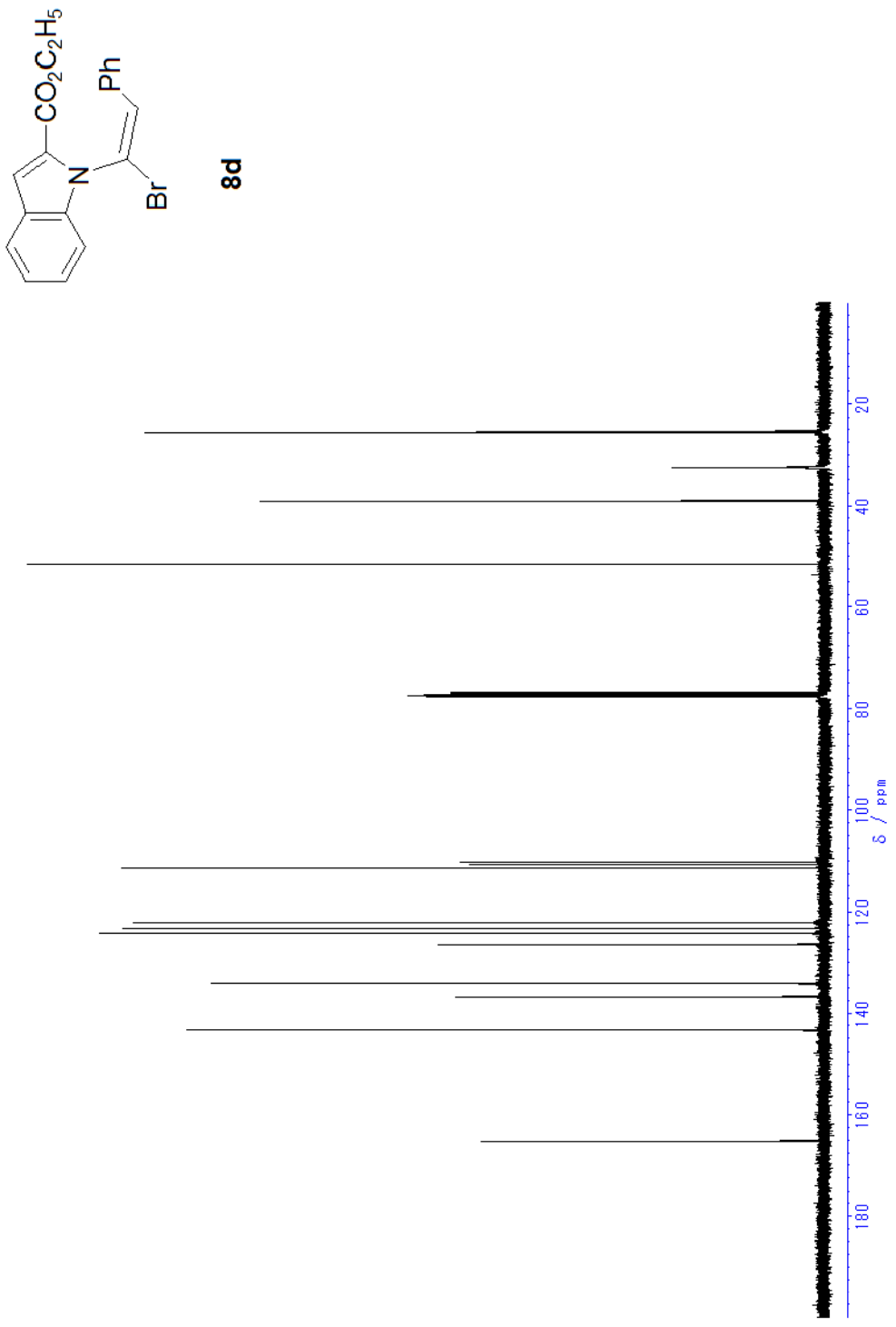
Ph
N
Br
8d
δ / ppm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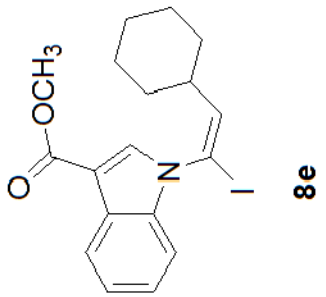
N
Br
8d
20
40
60
80
100
120
140
160
180
δ / ppm



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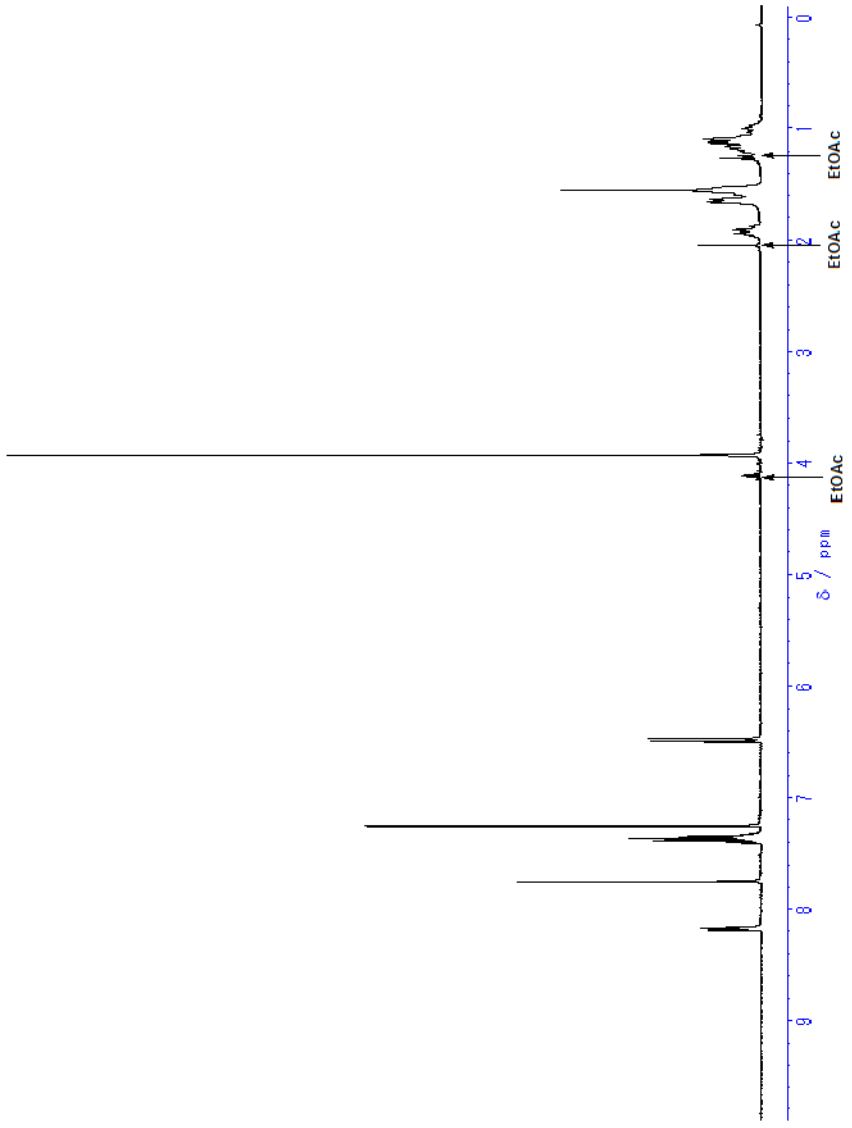

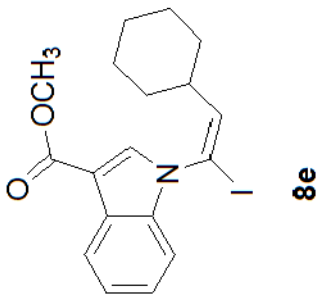

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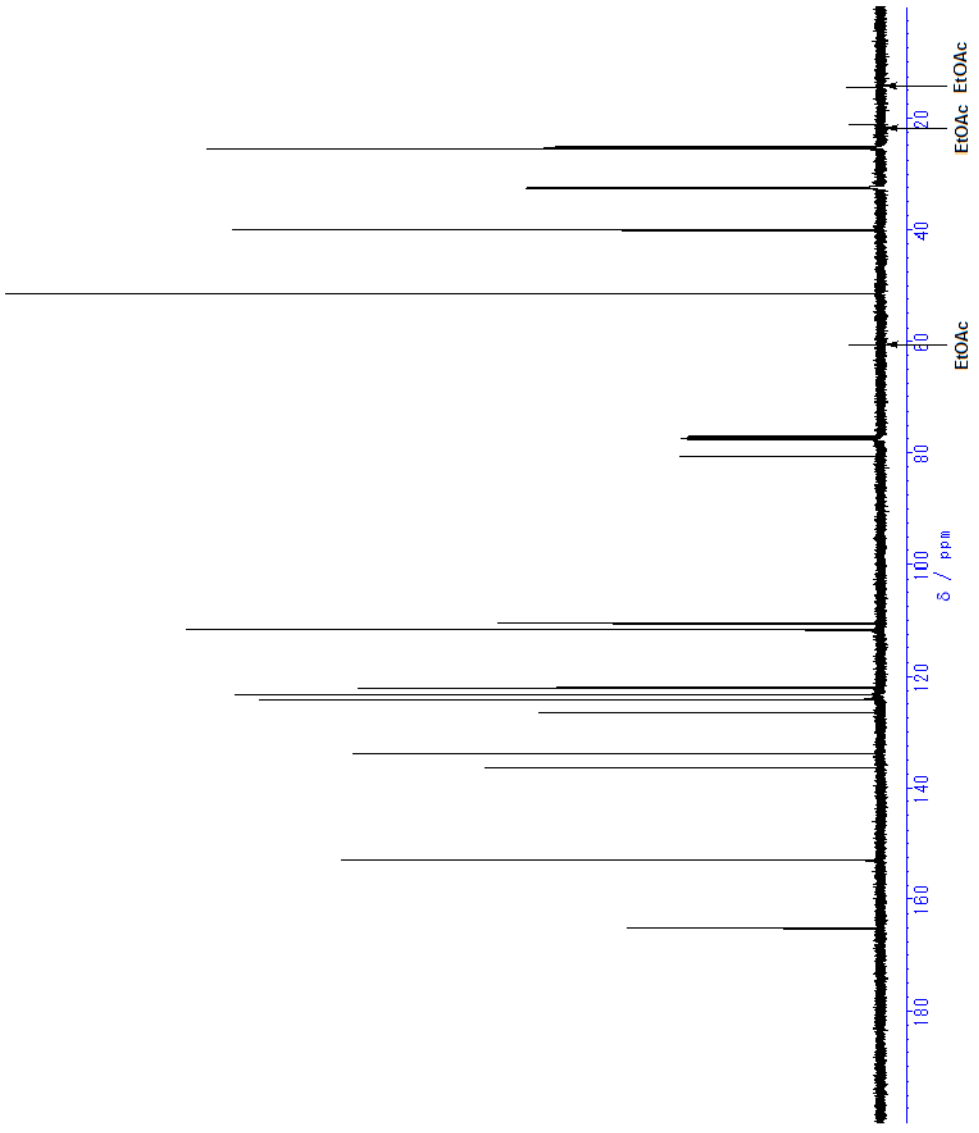

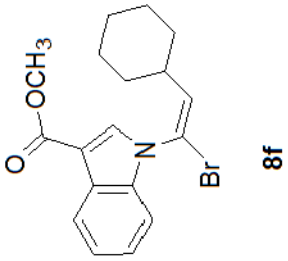

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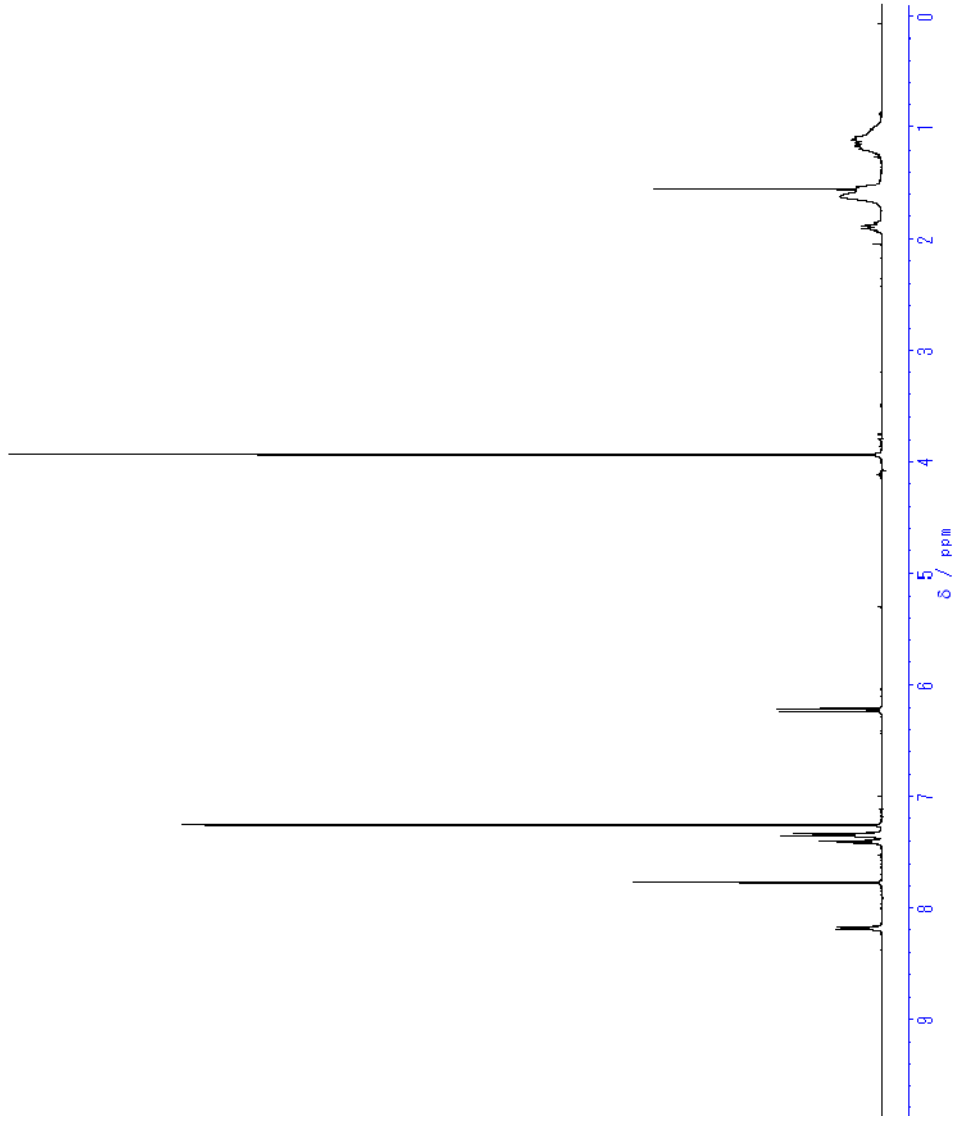

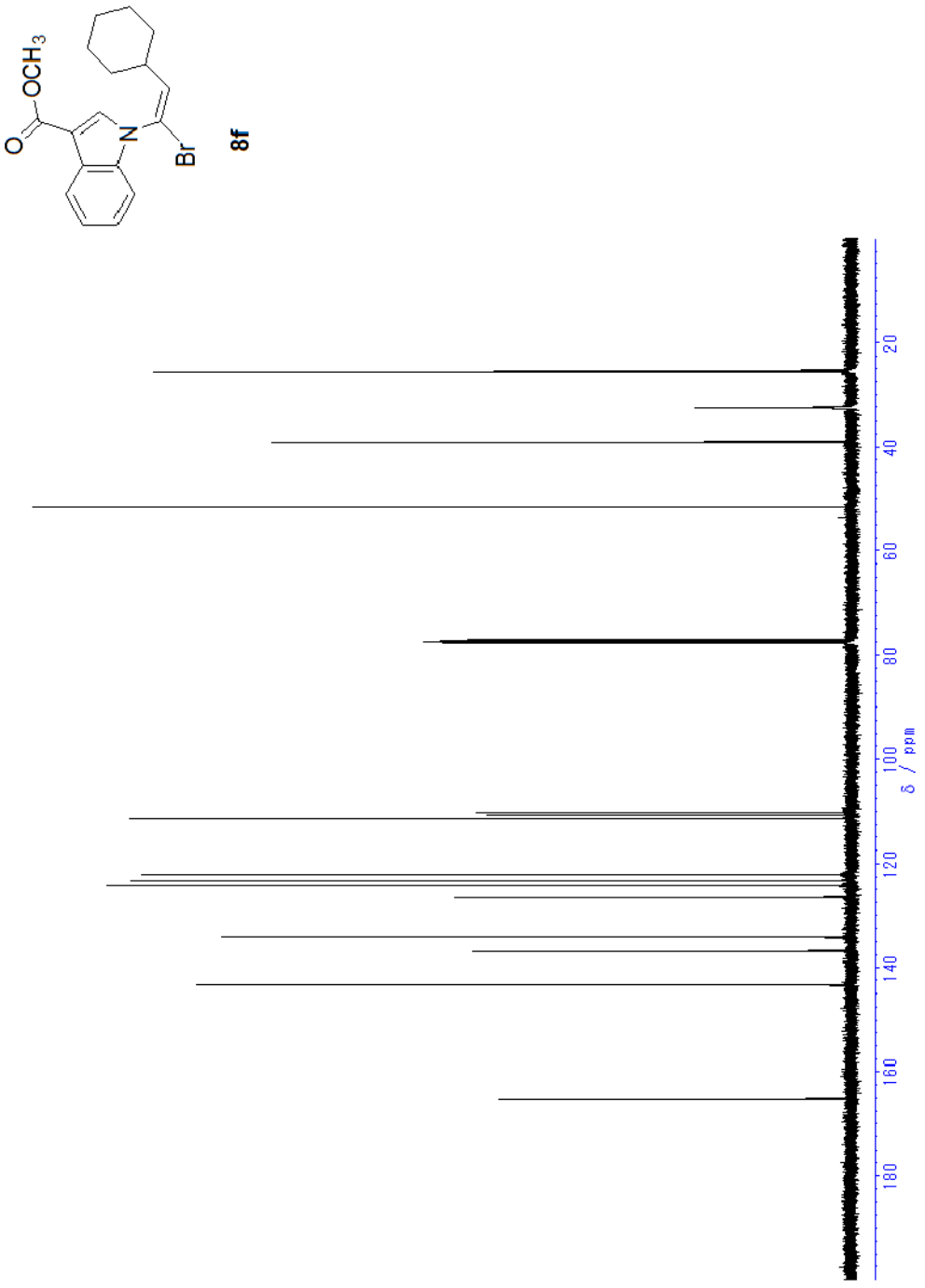
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O
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Br
8f
20
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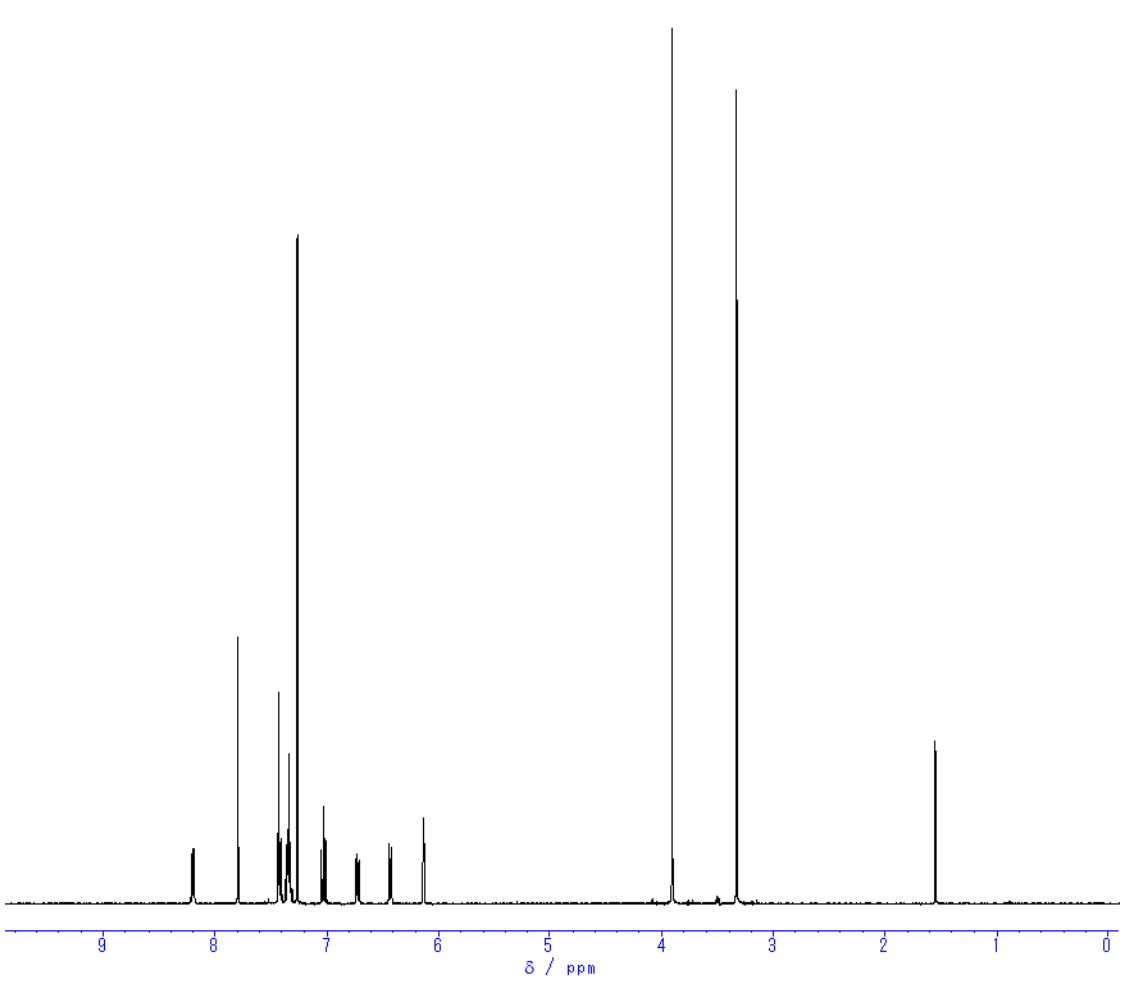
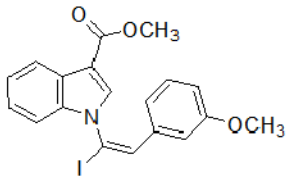
160
180
δ / ppm





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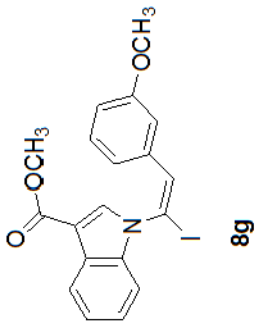

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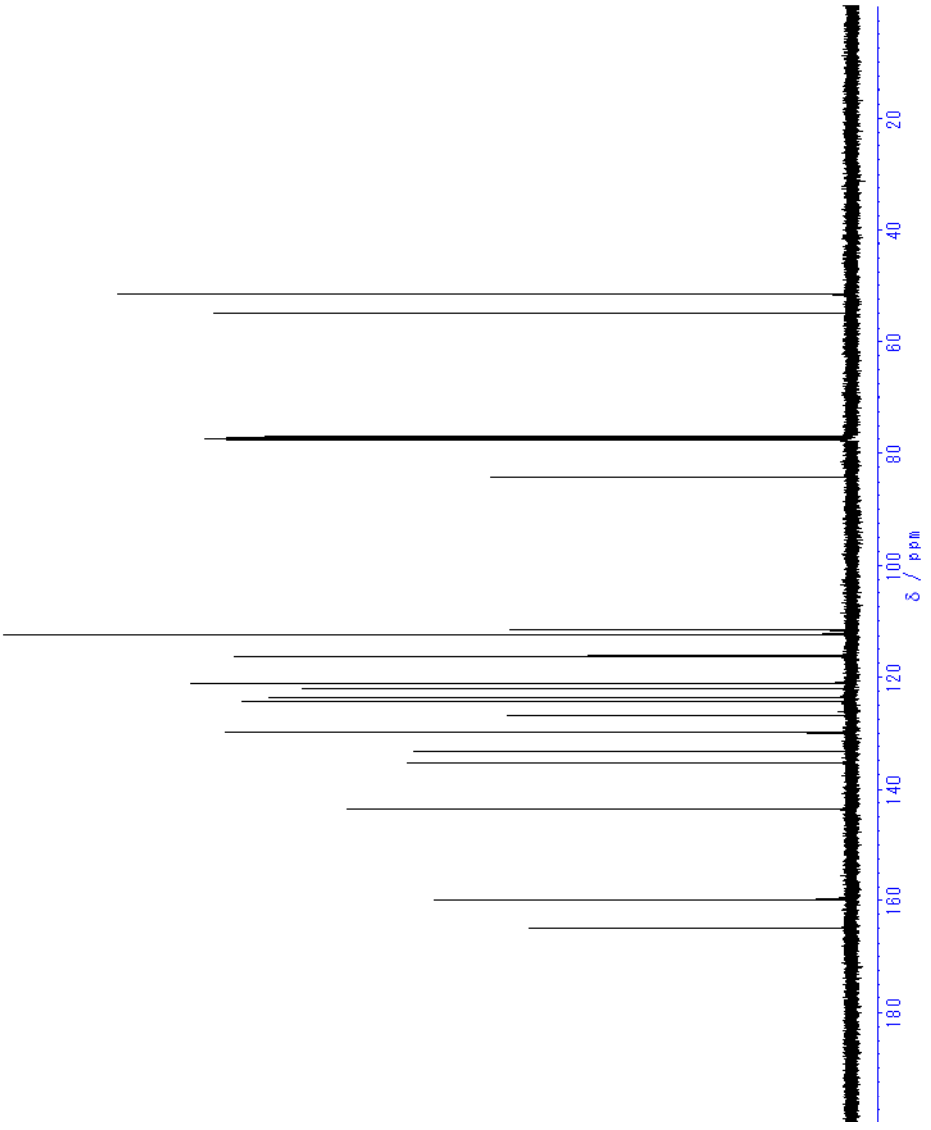

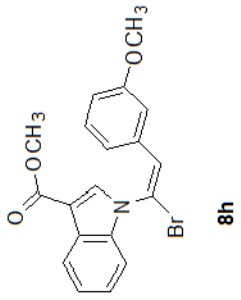

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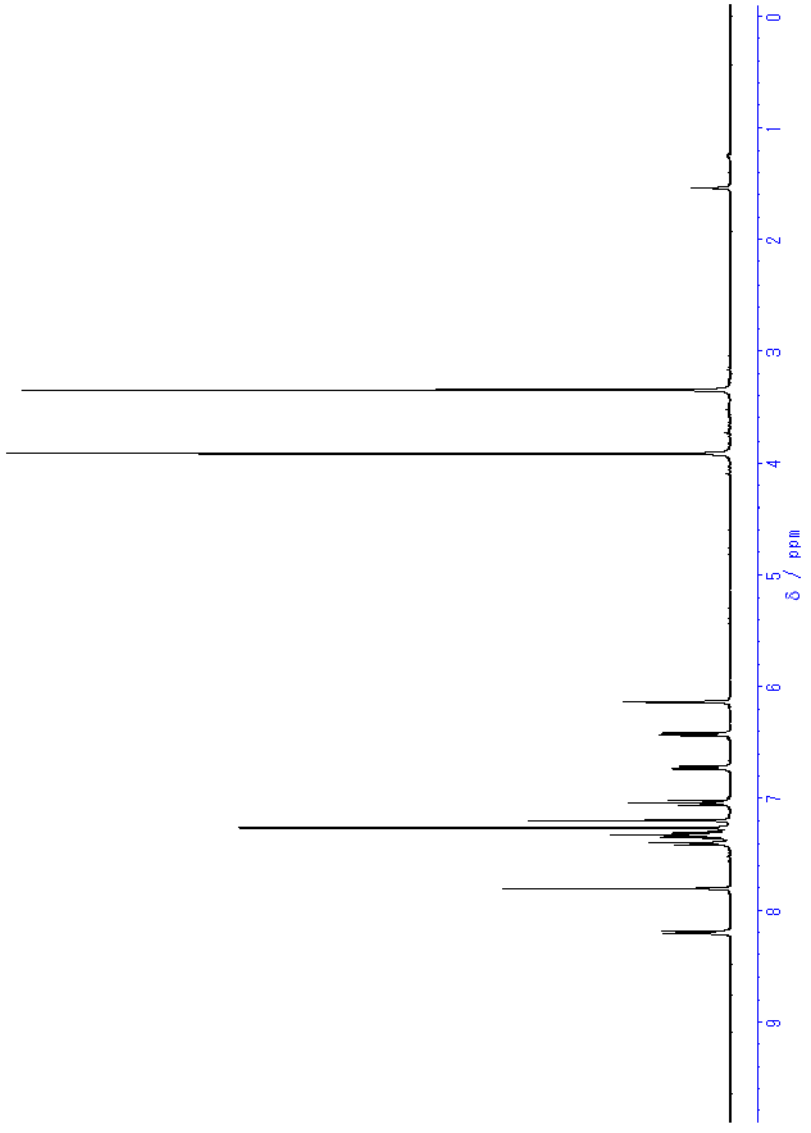

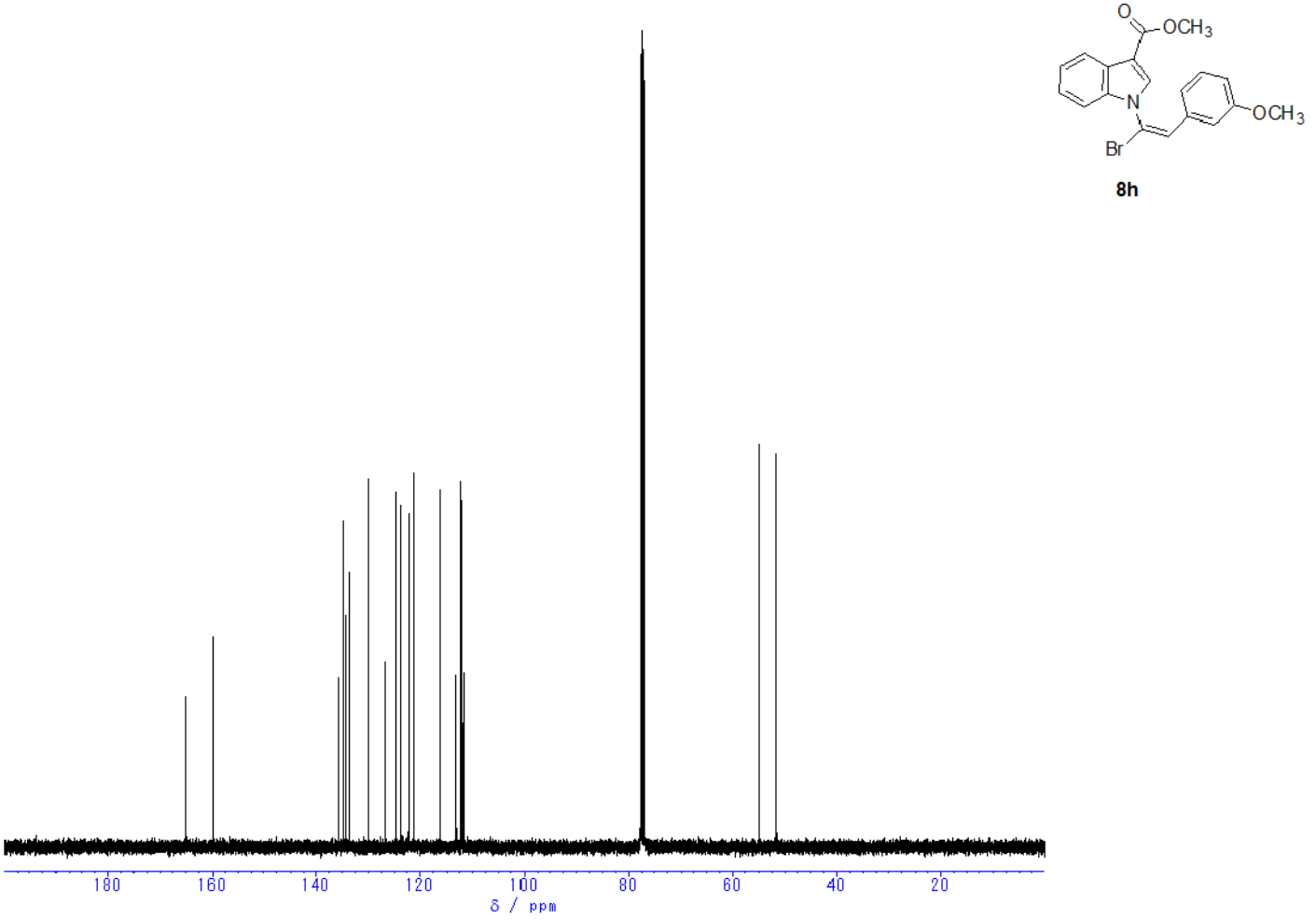

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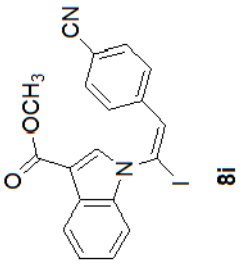

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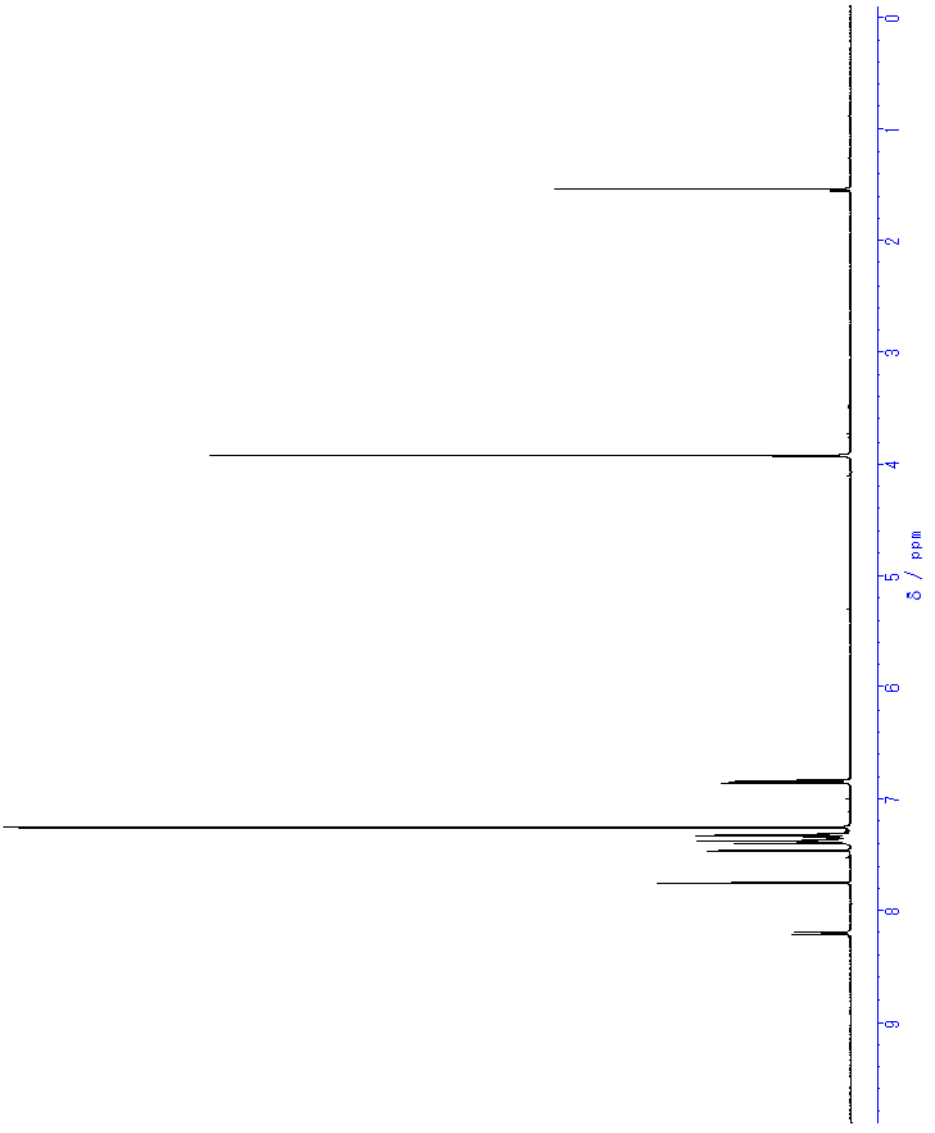

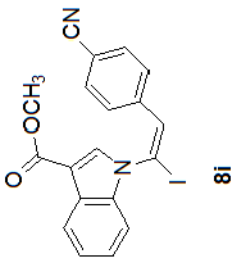

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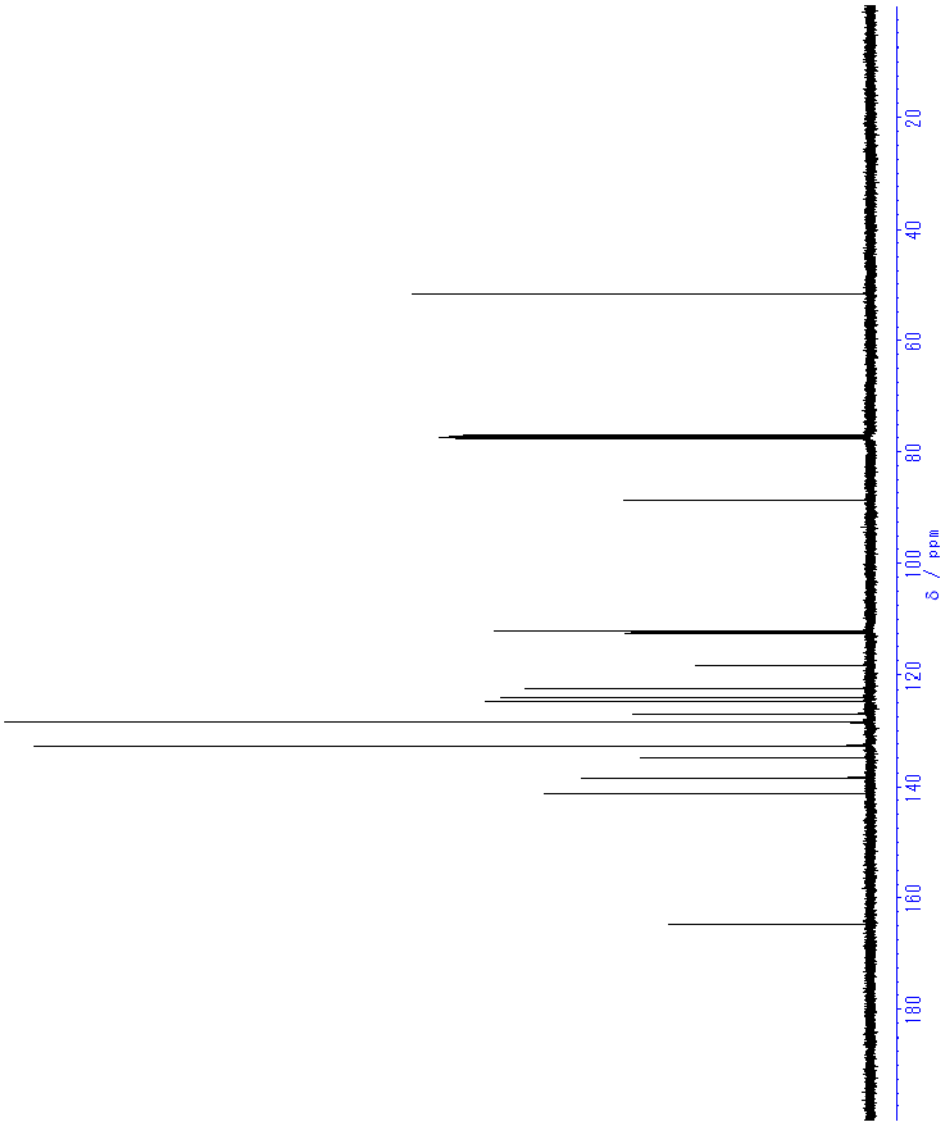

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1. (a) Zhang, Y.; Hsung, R. P.; Tracey, M. R.; Kurtz, K. C. M.; Vera, E. L. *Org. Lett.* **2004**, *6*, 1151-1154. (b) Zhang, X.; Zhang, Y.; Huang, J.; Hsung, R. P.; Kurtz, K. C. M.; Oppenheimer, J.; Petersen, M. E.; Sagamanova, I. K.; Schen, L.; Tracey, M. R. *J. Org. Chem.* **2006**, *71*, 4170-4177. (c) Jia, W.; Jiao, N. *Org. Lett.* **2010**, *12*, 2000-2003.
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