Supporting Information

Highly Efficient Vinylaromatics Generation *via* Iron-Catalyzed sp^3 C-H Bond Functionalization CDC Reaction: A Novel Approach to Preparing Substituted Benzo[α]phenazines

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General

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without purifications. $FeCl_3$ (>99.99%, trace metal basis) were purchased from Sigma-Aldrich. NEt_3 and DMA applied in the Heck closure were dried, distilled and degassed prior to use according to standard methods. Starting materials 2-aryl-3-methylquinoxalines and 2-phenyl-3-ethylquinoxaline (**1a–o**)[1,2], 2-methyl-3-phenoxyquinoxaline (**3b**)[3], 2-methoxy-3-methylquinoxaline (**3c**)[4], methyl 3-methylquinoxaline-2-carboxylate (**3d**)[5], 2-methyl-3-phenylpyrazine (**3e**)[6], 2-aryl-3-methylquinolines (**3g**, **3h**)[7], diethyl 2,6-dimethylpyridine-3,5-dicarboxylate (**3j**)[8], were synthesized according to the literature procedures. Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker AVANCE III 500 instrument in $CDCl_3$ using TMS as internal standard, operating at 500 MHz and 125 MHz, respectively. Chemical shifts (δ) are expressed in ppm and coupling constants (J) are given in Hz. GC-MS experiments were performed with an Agilent 6890N GC system equipped with a 5973N mass-selective detector. High resolution mass spectra (HRMS) of starting materials and products were obtained on a Water GCT Premier TOF MS with EI source. Electrospray ionization (ESI) mass experiments were performed on a Thermo LCQ fleet. High resolution mass spectra (HRMS) of CDC intermediate **9** was obtained on a Agilent 6210 TOF LC/MS with ESI source.

General synthesis of 2-(2-bromoaromatic)-3-methylquinoxalines (1p-1v)

O-methyl oximes **I** were synthesized according to the literature procedures[9]. Then, **I** (5.0 mmol) were combined with NBS (5.5 mmol, 1.1 equiv.), $Pd(OAc)_2$ (0.25 mmol, 5 mol%) and AcOH (30 mL), the mixture was heated at 100 °C for 12 h (monitored by TLC) to give **II** according to previous report by Sanford[10]. **II** underwent deprotection and α-bromination using general procedures. Finally, **III** were treated with *o*-PDA (*o*-phenylenediamine) as the preparation of substrates (**1a**-**1o**) to gain the desired **1p**-**1v**.

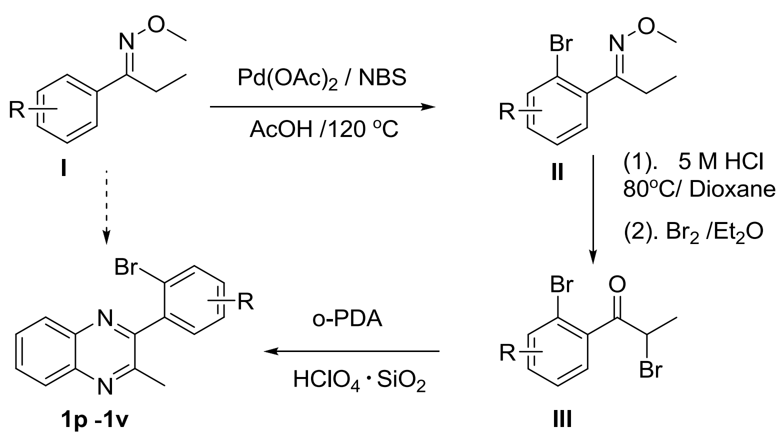
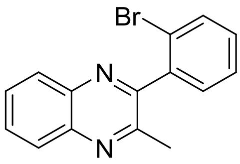


Figure 1. synthesis of substrates

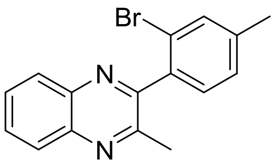
Characterization of some new reaction substrates

2-(2-bromophenyl)-3-methylquinoxaline (1j)



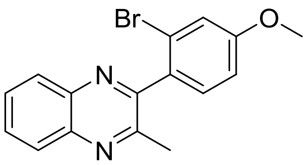
White solid; R_f =0.37 (petroleum ether-EtOAc= 6:1); mp 87-88℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.14-8.10 (m, 2H), 7.82-7.73 (m, 3H), 7.52-7.49 (m, 1H), 7.43-7.36 (m, 2H), 2.62 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.7, 153.0, 141.7, 140.6, 140.0, 132.9, 130.4, 130.2, 130.1, 129.3, 128.5, 127.9, 122.4, 23.1 ppm; MS (EI, 70eV): *m/z* (%) = 298 (60) [M+], 219 (100); HRMS (EI) for $C_{15}H_{11}N_2Br$: calcd. 298.0106, found 298.0099.

2-(2-bromo-4-methylphenyl)-3-methylquinoxaline (1p)



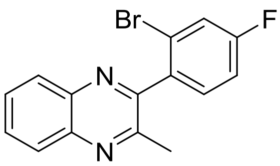
White solid; R_f =0.38 (petroleum ether-EtOAc= 6:1); mp 83-84℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.13-8.10 (m, 2H), 7.81-7.73 (m, 2H), 7.56 (s, 1H), 7.30 (s, 2H), 2.63 (s, 3H), 2.45 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.8, 153.2, 141.6, 140.8, 140.7, 137.1, 133.3, 130.0, 129.9, 129.3, 129.2, 128.6, 128.4, 122.1, 23.1, 21.0 ppm; MS (EI, 70eV): *m/z* (%) = 312 (52) [M+], 233 (100); HRMS (EI) for $C_{16}H_{13}N_2Br$: calcd. 312.0262, found 312.0282.

2-(2-bromo-4-methoxyphenyl)-3-methylquinoxaline (1q)



Pale yellow solid; R_f =0.21 (petroleum ether-EtOAc= 6:1); mp 88-89℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.13-8.10 (m, 2H), 7.80-7.73 (m, 2H), 7.33 (d, J = 8.5 Hz, 1H), 7.27 (d, J = 2.5 Hz, 1H), 7.03 (dd, J_1 = 8.5 Hz, J_2 = 2.5 Hz, 1H), 3.89 (s, 3H), 2.63 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.6, 154.6, 153.5, 141.6, 140.7, 132.3, 130.8, 130.0, 129.3, 129.2, 128.4, 122.8, 118.1, 114.0, 55.7, 23.2 ppm; MS (EI, 70eV): *m/z* (%) = 328 (100) [M+], 249 (83); HRMS (EI) for $C_{16}H_{13}N_2OBr$: calcd. 328.0211, found 328.0211.

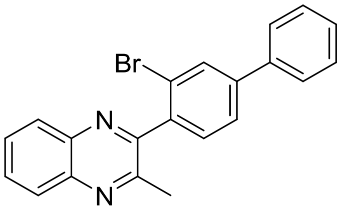
2-(2-bromo-4-fluorophenyl)-3-methylquinoxaline (1r)



White solid; R_f =0.34 (petroleum ether-EtOAc= 6:1); mp 103-104℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.13-8.10 (m, 2H), 7.83-7.75 (m, 2H), 7.49 (dd, J_1 = 8.3 Hz, J_2 = 2.3 Hz, 1H), 7.42 (dd, J_1 = 8.5 Hz, J_2 = 5.5 Hz, 1H), 7.23 (td, J_1 = 8.3 Hz, J_2 =

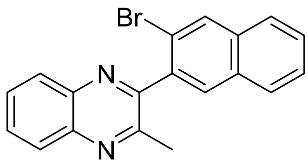
2.5 Hz, 1H), 2.62 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.6 (d, J = 251.5 Hz), 153.8, 152.9, 141.7, 140.6, 136.2, 131.3 (d, J = 8.5 Hz), 130.3, 129.4, 129.2, 128.4, 122.8 (d, J = 9.9 Hz), 120.3 (d, J = 24.4 Hz), 115.3 (d, J = 21.1 Hz), 23.1 ppm; MS (EI, 70eV): *m/z* (%) = 316 (77) [M+], 237 (100); HRMS (EI) for $C_{15}H_{10}N_2BrF$: calcd. 316.0011, found 315.9993.

2-(3-bromobiphenyl-4-yl)-3-methylquinoxaline (1s)



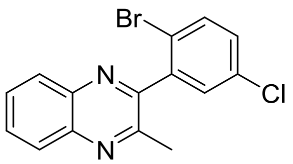
White solid; R_f =0.32 (petroleum ether-EtOAc= 6:1); mp 134-135℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.16-8.12 (m, 2H), 7.97 (d, J = 1.0 Hz, 1H), 7.83-7.71 (m, 3H), 7.65 (d, J = 7.5 Hz, 2H), 7.53-7.49 (m, 3H), 7.36 (t, J = 7.5 Hz, 1H), 2.69 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.6, 153.1, 143.8, 141.8, 140.7, 139.1, 138.7, 131.5, 130.5, 130.2, 129.3, 129.0, 128.5, 128.2, 127.2, 126.6, 122.8, 22.3 ppm; MS (EI, 70eV): *m/z* (%) = 374 (52) [M+], 295 (100); HRMS (EI) for $C_{21}H_{15}N_2Br$: calcd. 374.0419, found 374.0438.

2-(3-bromonaphthalen-2-yl)-3-methylquinoxaline (1t)



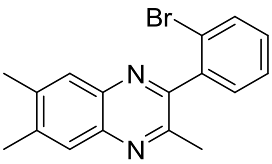
White solid; R_f =0.36 (petroleum ether-EtOAc= 6:1); mp 144-145℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.26 (s, 1H), 8.15 (td, J_1 = 8.2 Hz, J_2 = 1.0 Hz, 2H), 7.93 (s, 1H), 7.89-7.86 (m, 2H), 7.84-7.76 (m, 2H), 7.62-7.57 (m, 2H), 2.65 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.7, 153.3, 141.8, 140.6, 137.4, 134.4, 132.2, 131.6, 130.1, 129.6, 129.3, 139.3, 128.5, 128.1, 127.6, 127.0, 136.9, 119.4, 23.3 ppm; MS (EI, 70eV): *m/z* (%) = 348 (27) [M+], 269 (100); HRMS (EI) for $C_{19}H_{13}N_2Br$: calcd. 348.0262, found 348.0259.

2-(2-bromo-5-chlorophenyl)-3-methylquinoxaline (1u)



White solid; R_f =0.47 (petroleum ether-EtOAc= 6:1); mp 122-123℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.13-8.10 (m, 2H), 7.83-7.75 (m, 2H), 7.66 (d, J = 8.5 Hz, 1H), 7.43 (d, J = 2.5 Hz, 1H), 7.36 (dd, J_1 = 8.5 Hz, J_2 = 2.5 Hz, 1H), 2.64 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.3, 152.6, 141.9, 141.5, 140.5, 134.1, 134.0, 130.5, 130.4, 130.3, 129.5, 129.3, 128.5, 120.4, 23.0 ppm; MS (EI, 70eV): *m/z* (%) = 332 (48) [M+], 253 (100); HRMS (EI) for $C_{15}H_{10}N_2ClBr$: calcd. 331.9716, found 331.9712.

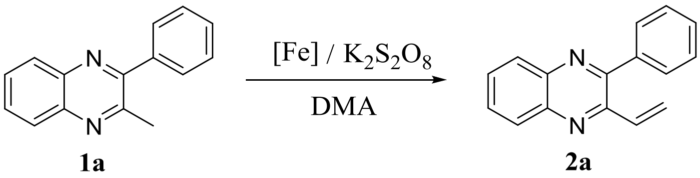
2-(2-bromophenyl)-3,6,7-trimethylquinoxaline (1v)



Yellow solid; R_f =0.35 (petroleum ether-EtOAc= 6:1); mp 119-120℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.86 (d, J = 7.5 Hz, 2H), 7.26-7.10 (m, 1H), 7.48 (td, J_1 = 7.6 Hz, J_2 = 0.9 Hz, 1H), 7.41 (dd, J_1 = 7.6 Hz, J_2 = 1.7 Hz, 1H), 7.36 (dd, J_1 = 7.8 Hz, J_2 = 1.7 Hz, 1H), 2.58 (s, 3H), 2.53 (s, 3H), 2.50 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.7, 151.8, 140.7, 140.6, 140.3, 139.7, 139.5, 132.8, 130.2, 130.2, 128.3, 127.8, 127.5, 122.6, 23.0, 20.4, 20.3 ppm; MS (EI, 70eV): m/z (%) = 326 (100) [M+], 247 (64); HRMS (EI) for $C_{17}H_{15}N_2Br$: calcd. 326.0419, found 326.0421.

Screening the different iron catalysts and oxidants

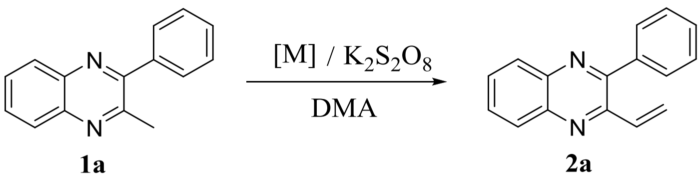
Table1. Screening of iron catalysts [a]



Entry	[Fe]	T (℃)	Time (hr)	Yield (%)[b]
1	$FeCl_3$	r.t.	24	0[c]
2	$FeCl_3$	60	24	27[c]
3	$FeCl_3$	110	3	94
4	$FeCl_3$· $6H_2O$	110	3	94
5	$FeCl_2$· $4H_2O$	110	3	91
6	$FeSO_4$· $7H_2O$	110	3	91
7	Fe Powder	110	3	35
8	Fe_2O_3	110	3	28
9	$Fe(acac)_3$	110	3	12
10	>99.99%, $FeCl_3$	110	3	94
11	—	110	3	4

[a] Reaction condition : **1a** (0.2 mmol), [Fe] (0.004 mmol), $K_2S_2O_8$ (0.4 mmol), DMA (1.5 mL), 110 ℃, $Fe(acac)_3$ = Ferric acetylacetonate. [b] GC-MS yield. [c] 10 mol % $FeCl_3$ was used, DMF severed as solvent.

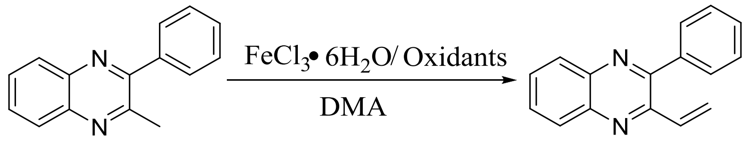
Table2. Screening of other metal catalysts [a]



Entry	[M]	T (℃)	Time (hr)	Yield (%)[b]
1	$CuCl_2$· $2H_2O$	110	3	83
2	$PdCl_2$	110	3	24
3	$AuCl_3$	110	3	33
4	$AlCl_3$	110	3	28

[a] Reaction condition : **1a** (0.2 mmol), [M] (0.004 mmol), $K_2S_2O_8$ (0.4 mmol), DMA (1.5 mL), 110 ℃. [b] GC-MS yield.

Table 3. Screening of oxidants [a]



1a **2a**

Entry	Oxidants	Time (hr)	Yield (%)[b]
1	$K_2S_2O_8$ (1.0 equiv)	8	88
2	$K_2S_2O_8$ (2.0 equiv)	3	94
3	$Na_2S_2O_8$ (2.0 equiv)	3	8
4	$(NH_4)_2S_2O_8$ (2.0 equiv)	3	52
5	OXONE (2.0 equiv)	3	11
6	BQ (2.0 equiv)	3	0
7	CAN (2.0 equiv)	3	0
8	O_2 (balloon)	3	0
9	$PhI(OAc)_2$ (2.0 equiv)	3	0
10	*t*-BuOOH (2.0 equiv)	3	0
11	DDQ (2.0 equiv)	3	0
12	H_2O_2 (2.0 equiv)	3	0
13	Ag_2O (2.0 equiv)	3	0
14	$NaIO_4$ (2.0 equiv)	3	0

[a] Reaction condition : **1a** (0.2 mmol), $FeCl_3\cdot 6H_2O$ (0.004 mmol), oxidant (0.4 mmol), DMA = N,N-dimethylacetamide (1.5 ml), 110 °C, BQ = 1,4-Benzoquinone, CAN = Ammonium ceric nitrate, DDQ = 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone. [b] GC-MS yield.

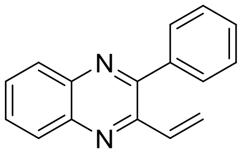
Typical experimental procedure for the synthesis of 2, 4 and 5

1 or **3** (0.2 mmol), $FeCl_3\cdot 6H_2O$ (1.1 mg, 0.004 mmol), $K_2S_2O_8$ (108 mg, 0.4 mmol) and DMA (1.5 mL) were sequentially added to a 10-mL tube under air. Then the tube was sealed and stirred at 110 °C for 3 h. Upon completion (monitored by TLC), the resulting mixture was diluted with Et_2O (15 mL) and washed by brine (10 mL × 3). The organic layer was then dried over Na_2SO_4, filtered and evaporated in *vacuo*, the residue was purified by column chromatography on silica gel (100-200 mesh) using petroleum ether-EtOAc as eluent to give desired products **2** or **4**.

To an oven-dried 10-mL tube were added **2j, 2p-2v** (0.15 mmol), $Pd(PPh_3)_4$ (7.3 mg, 0.0075 mmol) and Ag_2SO_4 (94 mg, 0.30 mmol) sequentially, then the tube was evacuated and backfilled with Argon, NEt_3 (61 mg, 0.6 mmol) and degassed DMA (2.0 mL) were added by syringe under Argon. The tube was heated at 140 °C with stirring for 3 hours, then the resulting mixture was diluted with Et_2O (10 mL) and washed by brine (10 mL × 3). The organic layer was then dried over Na_2SO_4, filtered and evaporated in *vacuo*, the residue was purified by column chromatography on silica gel (100-200 mesh) using petroleum ether-EtOAc as eluent to give desired products **5**.

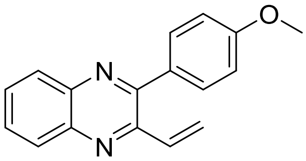
Characterization of all Products

2-phenyl-3-vinylquinoxaline (2a)



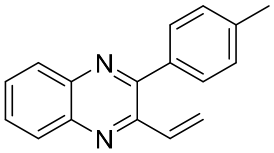
Orange oil; R_f =0.69 (petroleum ether-EtOAc= 6:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.13 (dt, J_1 = 7.5 Hz, J_2 = 2.0 Hz, 2H), 7.78-7.70 (m, 4H), 7.57-7.51 (m, 3H), 7.08 (dd, J_1 = 17.0 Hz, J_2 = 10.5 Hz, 1H), 6.67 (dd, J_1 = 16.8 Hz, J_2 = 1.75 Hz, 1H), 5.64 (dd, J_1 = 10.5 Hz, J_2 = 2.0 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.9, 148.9, 141.6, 141.4, 139.2, 135.4, 133.9, 129.7, 129.7, 129.6, 129.2, 128.1, 122.3 ppm; MS (EI, 70eV): *m/z* (%) = 231 (48) $[M-H]^+$; HRMS (EI) for $C_{16}H_{12}N_2$: calcd. 232.1000, found 232.1005.

2-(4-methoxyphenyl)-3-vinylquinoxaline (2b)



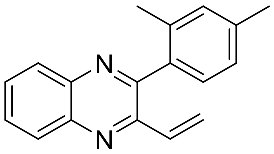
Yellow solid; R_f =0.38 (petroleum ether-EtOAc= 6:1); mp = 69-70℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.13-8.10 (m, 2H), 7.76-7.72 (m, 2H), 7.69 (dd, J_1 = 6.5 Hz, J_2 = 2.0 Hz, 2H), 7.11 (dd, J_1 = 17.0 Hz, J_2 = 10.5 Hz, 1H), 7.07 (dd, J_1 = 6.5 Hz, J_2 = 2.0 Hz, 2H), 6.65 (dd, J_1 = 17.0 Hz, J_2 = 2.0 Hz, 1H), 5.65 (dd, J_1 = 10.5 Hz, J_2 = 2.0 Hz, 1H), 3.91 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.5, 153.4, 148.9, 141.6, 141.3, 134.1, 131.2, 130.6, 129.6, 129.6, 129.1, 129.0, 122.2, 114.0, 55.4 ppm; MS (EI, 70eV): *m/z* (%) = 261 (100) $[M-H]^+$, 231 (45); HRMS (EI) for $C_{17}H_{13}N_2O$: calcd. 261.1028, found 261.1029.

2-p-tolyl-3-vinylquinoxaline (2c)



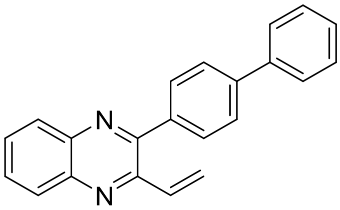
Orange solid; R_f = 0.59 (petroleum ether-EtOAc= 6:1); mp = 62-63℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.14-8.11 (m, 2H), 7.76-7.72 (m, 2H), 7.62 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.10 (dd, J_1 = 17.0 Hz, J_2 = 10.5 Hz, 1H), 6.66 (dd, J_1 = 17.0 Hz, J_2 = 1.5 Hz, 1H), 5.64 (dd, J_1 = 10.5 Hz, J_2 = 2.0 Hz, 1H), 2.47 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.8, 148.8, 141.5, 141.5, 138.2, 133.7, 129.9, 129.7, 129.6, 129.1, 129.1, 128.5, 122.4, 21.4 ppm; MS (EI, 70eV): *m/z* (%) = 245 (100) $[M-H]^+$, 231 (59); HRMS (EI) for $C_{17}H_{14}N_2$: calcd. 246.1157, found 246.1174.

2-(2,4-dimethylphenyl)-3-vinylquinoxaline (2d)



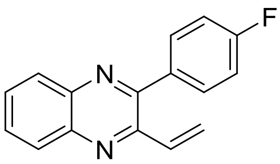
Yellow solid; R_f =0.58 (petroleum ether-EtOAc= 6:1); mp = 65-66℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.16-8.10 (m, 2H), 7.79-7.73 (m, 2H), 7.22 (d, J = 8.5 Hz, 1H), 7.17-7.15 (m, 2H), 6.77 (dd, J_1 = 17.0 Hz, J_2 = 10.5 Hz, 1H), 6.63 (dd, J_1 = 17.0 Hz, J_2 = 2.0 Hz, 1H), 5.56 (dd, J_1 = 10.5 Hz, J_2 = 2.0 Hz, 1H), 2.42 (s, 3H), 2.13 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.9, 149.4, 141.6, 141.5, 138.8, 136.1, 135.0, 133.0, 131.2, 129.9, 129.6, 129.2, 129.2, 126.8, 122.5, 21.3, 19.6 ppm; MS (EI, 70eV): m/z (%) = 259 (28) $[M\text{-}H]^+$, 245 (100); HRMS (EI) for $C_{18}H_{16}N_2$: calcd. 260.1313, found 260.1304.

2-(biphenyl-4-yl)-3-vinylquinoxaline (2e)



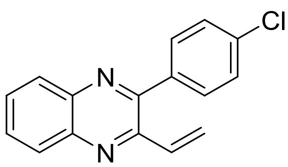
Yellow solid; R_f =0.63 (petroleum ether-EtOAc= 6:1); mp = 89-90℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.17-8.14 (m, 2H), 7.75-7.83 (m, 6H), 7.70 (d, J = 7.0 Hz, 2H), 7.51 (t, J = 7.5 Hz, 2H), 7.42 (t, J = 7.5 Hz, 1H), 7.17 (dd, J_1 = 17.0 Hz, J_2 = 11.0 Hz, 1H), 6.71 (dd, J_1 = 17.0 Hz, J_2 = 1.5 Hz, 1H), 5.69 (dd, J_1 = 10.5 Hz, J_2 = 2.0 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.4, 148.8, 142.0, 141.7, 141.5, 140.5, 137.1, 133.8, 130.2, 129.9, 129.8, 129.2, 128.9, 127.7, 127.3, 127.2, 122.5 ppm; MS (EI, 70eV): m/z (%) = 307 (100) $[M\text{-}H]^+$; HRMS (EI) for $C_{22}H_{16}N_2$: calcd. 308.1313, found 308.1315.

2-(4-fluorophenyl)-3-vinylquinoxaline (2f)



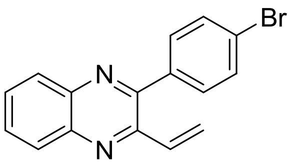
Orange solid; R_f =0.66 (petroleum ether-EtOAc= 6:1); mp = 68-69℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.15-8.10 (m, 2H), 7.78-7.71 (m, 4H), 7.28-7.22 (m, 2H), 7.05 (dd, J_1 = 17.0 Hz, J_2 = 11.0 Hz, 1.2H), 6.67 (dd, J_1 = 16.8 Hz, J_2 = 1.75 Hz, 1H), 5.67 (dd, J_1 = 11.0 Hz, J_2 = 2.0 Hz, 0.8H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.4 (d, J = 250.0 Hz), 152.6, 148.7, 141.5, 134.3, 133.6, 131.7 (d, J = 8.8 Hz), 130.0, 129.9, 129.2, 129.1, 128.8, 122.7, 115.6 (d, J = 21.3 Hz) ppm; MS (EI, 70eV): m/z (%) = 249 (100) $[M\text{-}H]^+$, 231 (100); HRMS (EI) for $C_{16}H_{11}N_2F$: calcd. 250.0906, found 250.0889.

2-(4-chlorophenyl)-3-vinylquinoxaline (2g)



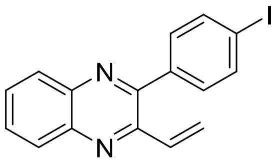
Yellow solid; R_f =0.69 (petroleum ether-EtOAc= 6:1); mp = 94-95℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.15-8.10 (m, 2H), 7.80-7.74 (m, 2H), 7.67 (dd, J_1 = 6.5 Hz, J_2 = 2.0 Hz, 2H), 7.53 (dd, J_1 = 6.5 Hz, J_2 = 2.0 Hz, 2H), 7.04 (dd, J_1 = 17.0 Hz, J_2 = 10.5 Hz, 1H), 6.67 (dd, J_1 = 17.0 Hz, J_2 = 1.5 Hz, 1H), 5.67 (dd, J_1 = 10.5 Hz, J_2 = 2.0 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.5, 148.6, 141.6, 141.5, 136.7, 135.4, 133.4, 131.1, 130.1, 129.9, 129.7, 129.2, 129.1, 128.8, 128.5, 122.8 ppm; MS (EI, 70eV): m/z (%) = 265 (49) $[M\text{-}H]^+$, 231 (100); HRMS (EI) for $C_{16}H_{11}N_2Cl$: calcd. 266.0611, found 266.0624.

2-(4-bromophenyl)-3-vinylquinoxaline (2h)



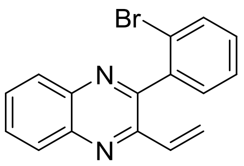
Yellow solid; R_f =0.67 (petroleum ether-EtOAc= 6:1); mp =105-106℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.15-8.10 (m, 2H), 7.80-7.74 (m, 2H), 7.69 (dd, J_1 = 6.5 Hz, J_2 = 2.0 Hz, 2H), 7.61 (dd, J_1 = 6.5 Hz, J_2 = 2.0 Hz, 2H), 7.03 (dd, J_1 = 17.0 Hz, J_2 = 11.0 Hz, 1H), 6.67 (dd, J_1 = 17.0 Hz, J_2 = 2.0 Hz, 1H), 5.67 (dd, J_1 = 10.75 Hz, J_2 = 1.75 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.5, 148.6, 141.6, 141.5, 137.2, 133.4, 131.7, 131.3, 130.2, 130.1, 129.9, 129.2, 129.1, 127.9, 123.7, 122.9 ppm; MS (EI, 70eV): *m/z* (%) = 311 (13) [M+], 231 (100); HRMS (EI) for $C_{16}H_{11}N_2Br$: calcd. 310.0106, found 310.0095.

2-(4-iodophenyl)-3-vinylquinoxaline (2i)



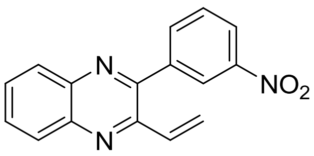
Yellow solid; R_f =0.58 (petroleum ether-EtOAc= 6:1); mp = 96-97℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.14-8.10 (m, 2H), 7.89 (d, J = 8.5 Hz, 2H), 7.80-7.75 (m, 2H), 7.47 (d, J = 8.0 Hz, 2H), 7.03 (dd, J_1 = 17.0 Hz, J_2 = 10.5 Hz, 1H), 6.67 (dd, J_1 = 17.0 Hz, J_2 = 2.0Hz, 1H), 5.66 (dd, J_1 = 10.75 Hz, J_2 = 1.75 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.6, 148.5, 141.6, 137.7, 137.7, 133.4, 131.5, 130.1, 129.9, 129.2, 129.1, 122.9, 95.5 ppm; MS (EI, 70eV): *m/z* (%) = 357 (10) $[M-H]^+$, 231 (100); HRMS (EI) for $C_{16}H_{11}N_2I$: calcd. 357.9967, found 357.9956.

2-(2-bromophenyl)-3-vinylquinoxaline (2j)



Pale yellow solid; R_f =0.58 (petroleum ether-EtOAc= 6:1); mp = 95-96℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.18-8.12 (m, 2H), 7.83-7.73 (m, 3H), 7.52-7.49 (m, 1H), 7.67 (dd, J_1 = 7.8 Hz, J_2 = 1.9 Hz, 1H), 7.39 (td, J = 7.8, 1.9 Hz, 1H), 6.73 (dd, J_1 = 17.0 Hz, J_2 = 10.5 Hz, 1H), 6.66 (dd, J_1 = 16.8 Hz, J_2 = 1.8 Hz, 1H), 5.60 (dd, J_1 = 10.3 Hz, J_2 = 2.3 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.5, 148.9, 142.0, 141.2, 139.3, 132.9, 132.6, 130.9, 130.5, 130.3, 129.8, 129.3, 129.2, 127.8, 122.9, 122.8 ppm; MS (EI, 70eV): *m/z* (%) = 310 (3) [M+], 231 (100); HRMS (EI) for $C_{16}H_{11}N_2Br$: calcd. 310.0106, found 310.0108.

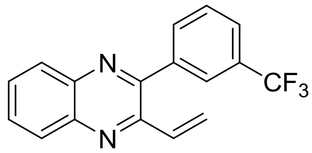
2-(3-nitrophenyl)-3-vinylquinoxaline (2k)



Yellow solid; R_f =0.38 (petroleum ether-EtOAc= 6:1); mp = 88-89℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.65 (t, J = 2.0 Hz, 1H), 8.39 (dd, J_1 = 8.5 Hz, J_2 = 1.5 Hz, 1H), 8.17 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 8.13 (dd, J_1 = 8.0 Hz, J_2 = 1.5 Hz, 1H), 8.08 (dd, J_1 = 6.5 Hz, J_2 = 1.0 Hz, 1H), 7.85-7.78 (m, 2H), 7.74 (t, J = 8.0 Hz, 1H), 7.00 (dd, J_1 = 17.0 Hz, J_2 = 10.5 Hz, 1H), 6.73 (dd, J_1 = 17.0 Hz, J_2 = 1.5 Hz, 1H), 5.73 (dd, J_1 = 10.75 Hz, J_2 = 1.75 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ =

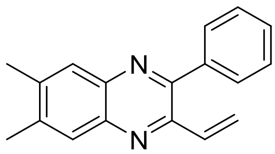
150.9, 148.4, 148.4, 141.9, 141.5, 140.0, 135.7, 132.8, 130.7, 130.3, 129.6, 129.3, 129.2, 124.9, 123.9, 123.8 ppm; MS (EI, 70eV): *m/z* (%) = 277 (50) [M+], 230 (100); HRMS (EI) for $C_{16}H_{11}N_3O_2$: calcd. 277.0851, found 277.0859.

2-(3-(trifluoromethyl)phenyl)-3-vinylquinoxaline (2l)



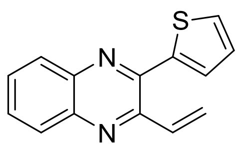
Orange oil; R_f =0.62 (petroleum ether-EtOAc= 6:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.17-8.13 (m, 2H), 8.03 (s, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.83-7.77 (m, 3H), 7.69 (t, J = 8.0 Hz, 1H), 7.01 (dd, J_1 = 17.0 Hz, J_2 = 11.0 Hz, 1H), 6.71 (dd, J_1 = 16.8 Hz, J_2 = 1.8 Hz, 1H), 5.70 (dd, J_1 = 10.5 Hz, J_2 = 2.0 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.1, 148.5, 141.7, 141.5, 139.1, 133.1, 133.0, 131.1 (q, J = 32.5 Hz), 130.4, 130.1, 129.3, 129.2, 129.0, 126.6 (q, J = 3.8 Hz), 125.9 (q, J = 3.8 Hz), 123.9 (q, J = 271.1 Hz), 123.2 ppm; MS (EI, 70eV): *m/z* (%) = 299 (100) $[M-H]^+$, 231 (41); HRMS (EI) for $C_{17}H_{11}N_2F_3$: calcd. 300.0874, found 300.0865.

6,7-dimethyl-2-phenyl-3-vinylquinoxaline (2m)



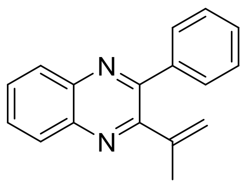
Yellow solid; R_f =0.53 (petroleum ether-EtOAc= 6:1); mp = 82-83℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.88 (d, J = 8.5 Hz, 2H), 7.69 (d, J = 7.0 Hz, 2H), 7.54-7.49 (m, 3H), 7.05 (dd, J_1 = 17.0 Hz, J_2 = 11.0 Hz, 1H), 6.61 (dd, J_1 = 17.0 Hz, J_2 = 1.5 Hz, 1H), 5.59 (dd, J_1 = 10.5 Hz, J_2 = 1.5 Hz, 1H), 2.52 (s, 3H), 2.51 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.9, 147.8, 140.6, 140.5, 140.4, 140.3, 138.6, 133.9, 129.7, 128.8, 128.4, 128.2, 128.2, 121.4, 20.4, 20.3 ppm; MS (EI, 70eV): *m/z* (%) = 259 (100) $[M-H]^+$; HRMS (EI) for $C_{18}H_{16}N_2$: calcd. 260.1313, found 260.1322.

2-(thiophen-2-yl)-3-vinylquinoxaline (2n)



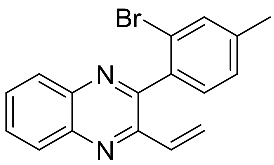
Brown oil; R_f =0.55 (petroleum ether-EtOAc= 6:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.10-8.07 (m, 2H), 7.74-7.72 (m, 2H), 7.63 (d, J = 4.0 Hz, 1H), 7.57 (d, J = 4.5 Hz, 1H), 7.41 (dd, J_1 = 16.8 Hz, J_2 = 10.75 Hz, 1H), 7.21 (dd, J_1 = 5.0 Hz, J_2 = 3.5 Hz, 1H), 6.64 (dd, J_1 = 17.0 Hz, J_2 = 2.0 Hz, 1H), 5.77 (dd, J_1 = 10.75 Hz, J_2 = 1.75 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.3, 147.0, 141.8, 141.4, 140.9, 134.0, 129.9, 129.8, 129.3, 129.1, 128.8, 127.8, 123.0 ppm; MS (EI, 70eV): *m/z* (%) = 237 (50) $[M-H]^+$; HRMS (EI) for $C_{14}H_{10}N_2S$: calcd. 238.0565, found 238.0560.

2-phenyl-3-(prop-1-en-2-yl)quinoxaline (2o)



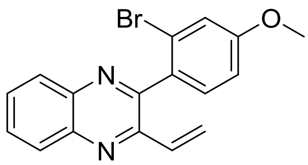
White solid; R_f =0.56 (petroleum ether-EtOAc= 6:1); mp = 118-119℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.16-8.13 (m, 2H), 7.80-7.75 (m, 4H), 7.51-7.47 (m, 3H), 5.42 (t, J = 1.3 Hz, 1H), 5.33 (s, 1H), 2.05 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.4, 152.9, 144.1, 141.2, 140.7, 139.4, 129.8, 129.8, 129.1, 129.1, 129.0, 128.5, 120.6, 21.9 ppm; MS (EI, 70eV): *m/z* (%) = 245 (30) $[M-H]^+$, 231 (100); HRMS (EI) for $C_{17}H_{14}N_2$: calcd. 246.1157, found 246.1151.

2-(2-bromo-4-methylphenyl)-3-vinylquinoxaline (2p)



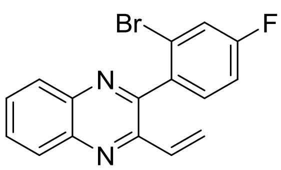
Isolated as yellow solid in 86% yield; R_f =0.57 (petroleum ether-EtOAc= 6:1); mp 115-116℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.17-8.11 (m, 2H), 7.82-7.74 (m, 2H), 7.56 (s, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.30 (d, J = 8.0 Hz, 1H), 6.75 (dd, J_1 = 17.0 Hz, J_2 = 10.5 Hz, 1H), 6.65 (dd, J_1 = 17.0 Hz, J_2 = 2.0 Hz, 1H), 5.59 (dd, J_1 = 10.5 Hz, J_2 = 2.0 Hz, 1H), 2.45 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.6, 149.1, 141.9, 141.3, 140.9, 136.4, 133.3, 132.3, 130.6, 130.2, 129.7, 129.3, 129.2, 128.6, 122.6, 122.5, 21.01 ppm; MS (EI, 70eV): *m/z* (%) = 324 (7) [M+], 245 (100); HRMS (EI) for $C_{17}H_{13}N_2Br$: calcd. 324.0262, found 324.0277.

2-(2-bromo-4-methoxyphenyl)-3-vinylquinoxaline (2q)



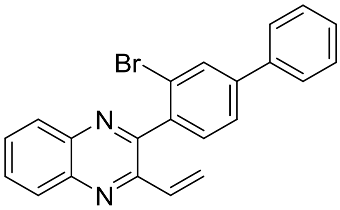
Isolated as pale yellow solid in 88% yield; R_f =0.31 (petroleum ether-EtOAc= 6:1); mp = 117-118℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.16-8.11 (m, 2H), 7.81-7.74 (m, 2H), 7.38 (d, J = 8.5 Hz, 1H), 7.27 (d, J = 8.0 Hz, 1H), 7.04 (dd, J_1 = 8.5 Hz, J_2 = 2.5 Hz, 1H), 6.77 (dd, J_1 = 17.0 Hz, J_2 = 10.5 Hz, 1H), 6.65 (dd, J_1 = 17.0 Hz, J_2 = 2.0 Hz, 1H), 5.60 (dd, J_1 = 10.5 Hz, J_2 = 2.0 Hz, 1H), 3.90 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.7, 153.4, 149.3, 141.9, 141.3, 132.9, 131.7, 131.5, 130.1, 129.6, 129.3, 129.2, 123.3, 122.6, 118.2, 113.9, 55.7 ppm; MS (EI, 70eV): *m/z* (%) = 340 (11) [M+], 261 (100); HRMS (EI) for $C_{17}H_{15}N_2Br$: calcd. 338.0419, found 338.0447.

2-(2-bromo-4-fluorophenyl)-3-vinylquinoxaline (2r)



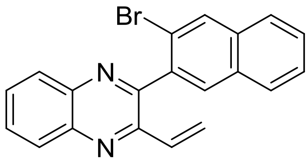
Isolated as pale yellow solid in 83% yield; R_f =0.58 (petroleum ether-EtOAc= 6:1); mp = 129-130℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.17-8.10 (m, 2H), 7.84-7.76 (m, 2H), 7.50-7.44 (m, 2H), 7.24 (td, J_1 = 8.3 Hz, J_2 =2.5 Hz, 1H), 6.71 (dd, J_1 = 17.0 Hz, J_2 = 9.5 Hz, 1H), 6.66 (dd, J_1 = 17.0 Hz, J_2 = 2.5 Hz, 1H), 5.62 (dd, J_1 = 9.8 Hz, J_2 = 2.8 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.7 (d, J = 252.5 Hz), 152.6, 149.0, 142.1, 141.2, 135.6 ((d, J = 3.5 Hz), 132.4, 132.1 (d, J = 8.7 Hz), 130.5, 130.0, 129.4, 129.2, 123.3 (d, J = 9.4 Hz), 123.1, 120.3 (d, J = 24.5 Hz), 115.2 (d, J = 21.6 Hz) ppm; MS (EI, 70eV): *m/z* (%) = 328 (7) [M+], 249 (100); HRMS (EI) for $C_{16}H_{10}N_2BrF$: calcd. 328.0011, found 328.0025.

2-(3-bromobiphenyl-4-yl)-3-vinylquinoxaline (2s)



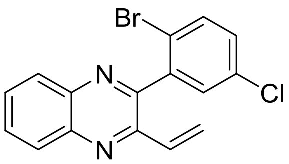
Isolated as yellow solid in 82% yield; R_f =0.48 (petroleum ether-EtOAc= 6:1); mp = 122-123℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.19-8.13 (m, 2H), 7.97 (d, J = 2.0 Hz, 1H), 7.84-7.76 (m, 2H), 7.72 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 7.67-7.65 (m, 2H), 7.54-7.50 (m, 3H), 7.45-7.43 (m, 1H), 6.83 (dd, J_1 = 16.8 Hz, J_2 = 10.8 Hz, 1H), 6.70 (dd, J_1 = 17.0 Hz, J_2 = 2.0 Hz, 1H), 5.64 (dd, J_1 = 10.8 Hz, J_2 = 1.8 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.4, 149.0, 143.8, 142.0, 141.2, 139.1, 137.9, 132.7, 131.4, 131.2, 130.4, 129.8, 129.3, 129.2, 129.0, 128.2, 127.2, 126.5, 123.2, 122.9 ppm; MS (EI, 70eV): m/z (%) = 386 (7) [M+], 307 (100); HRMS (EI) for $C_{22}H_{15}N_2Br$: calcd. 386.0419, found 386.0418.

2-(3-bromonaphthalen-2-yl)-3-vinylquinoxaline (2t)



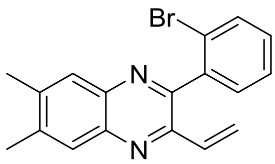
Isolated as yellow solid in 85% yield; R_f =0.56 (petroleum ether-EtOAc= 6:1); mp = 130-131℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.26 (s,1H), 8.20 (d, J = 8.5 Hz, 1H), 8.15 (d, J = 8.0 Hz, 1H), 7.97 (s,1H), 7.90-7.77 (m, 4H), 7.63-7.57 (m, 2H), 6.76 (dd, J_1 = 17.0 Hz, J_2 = 10.0 Hz, 1H), 6.67 (dd, J_1 = 17.0 Hz, J_2 = 2.0 Hz, 1H), 5.58 (dd, J_1 = 10.8 Hz, J_2 = 1.8 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.5, 149.3, 142.0, 141.2, 136.7, 134.5, 132.7, 132.2, 131.6, 130.4, 130.4, 129.9, 129.3, 129.3, 128.2, 127.7, 127.1, 126.9, 122.9, 119.8 ppm; MS (EI, 70eV): m/z (%) = 360 (4) [M+], 281 (100); HRMS (EI) for $C_{20}H_{13}N_2Br$: calcd. 360.0262, found 360.0257.

2-(2-bromo-5-chlorophenyl)-3-vinylquinoxaline (2u)



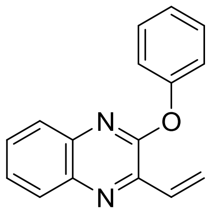
Isolated as yellow solid in 86% yield; R_f =0.65 (petroleum ether-EtOAc= 6:1); mp = 124-125℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.18-8.10 (m, 2H), 7.85-7.77 (m, 2H), 7.66 (d, J = 8.5 Hz, 1H), 7.47 (d, J = 2.5 Hz, 1H), 7.37 (dd, J_1 = 9.0 Hz, J_2 = 2.5 Hz, 1H), 6.72 (dd, J_1 = 17.0 Hz, J_2 = 9.0 Hz, 1H), 6.68 (dd, J_1 = 16.8 Hz, J_2 = 3.3 Hz, 1H), 5.64 (dd, J_1 = 9.0 Hz, J_2 = 3.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.2, 148.6, 142.1, 141.1, 140.7, 134.0, 132.2, 130.9, 130.6, 130.0, 129.4, 129.2, 123.3, 120.8 ppm; MS (EI, 70eV): m/z (%) = 344(1) [M+], 265 (100); HRMS (EI) for $C_{16}H_{10}N_2ClBr$: calcd. 343.9716, found 343.9748.

2-(2-bromophenyl)-6,7-dimethyl-3-vinylquinoxaline (2v)



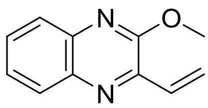
Isolated as yellow solid in 88% yield; R_f = 0.56 (petroleum ether-EtOAc= 6:1); mp = 114-115℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.92 (s, 1 H), 7.87 (s, 1 H), 7.72 (dd, J_1 = 8.0 Hz, J_2 = 1.0 Hz, 1 H), 7.49 (td, J_1 = 7.5 Hz, J_2 = 1.0 Hz, 1 H), 7.44 (dd, J_1 = 7.5 Hz, J_2 = 2.0 Hz, 1 H), 7.37 (td, J_1 = 7.5 Hz, J_2 = 2.0 Hz, 1 H), 6.70 (dd, J_1 = 17.0 Hz, J_2 = 10.5 Hz, 1 H), 6.59 (dd, J_1 = 17.0 Hz, J_2 = 2.0 Hz, 1 H), 5.54 (dd, J_1 = 10.5 Hz, J_2 = 2.0 Hz, 1 H), 2.53 (s, 3 H), 2.51 (s, 3 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.6, 147.9, 141.0, 140.9, 140.5, 140.2, 139.5, 132.8, 132.7, 130.9, 130.3, 128.2, 127.7, 123.0, 121.9, 20.4, 20.4 ppm; MS (EI, 70eV): *m/z* (%) = 338 (12) [M+], 259 (100); HRMS (EI) for $C_{18}H_{15}N_2Br$: calcd. 338.0419, found 338.0414.

2-phenoxy-3-vinylquinoxaline (4b)



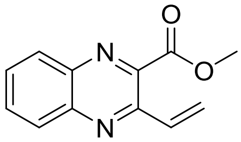
Yellow solid; R_f = 0.75 (petroleum ether-EtOAc= 6:1); mp = 75-76℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.06-8.04 (m, 1 H), 7.72-7.69 (m, 1 H), 7.62-7.58 (m, 2 H), 7.48 (t, J = 7.8 Hz, 2 H), 7.42 (dd, J_1 = 17.0 Hz, J_2 = 11.0 Hz, 1 H), 7.32-7.29 (m, 3 H), 6.80 (dd, J_1 = 17.3 Hz, J_2 = 1.8 Hz, 1 H), 5.83 (dd, J_1 = 11.0 Hz, J_2 = 1.5 Hz, 1 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.1, 153.0, 143.8, 139.7 (2C), 130.5, 129.6, 129.5, 128.8, 127.5, 127.3, 125.2, 123.6, 121.7 ppm; MS (EI, 70eV): *m/z* (%) = 248 (100) [M+], 219 (100); HRMS (EI) for $C_{16}H_{12}N_2O$: calcd. 248.0950, found 248.0962.

2-methoxy-3-vinylquinoxaline (4c)



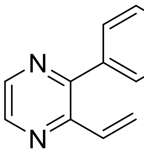
Yellow oil; R_f = 0.75 (petroleum ether-EtOAc= 6:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.00 (dd, J_1 = 8.3 Hz, J_2 = 1.3 Hz, 1 H), 7.83 (dd, J_1 = 8.3 Hz, J_2 = 1.3 Hz, 1 H), 7.63 (td, J_1 = 7.8 Hz, J_2 = 1.5 Hz, 1 H), 7.57-7.54 (m, 1 H), 7.23 (dd, J_1 = 17.5 Hz, J_2 = 11.0 Hz, 1 H), 6.67 (dd, J_1 = 17.5 Hz, J_2 = 2.0 Hz, 1 H), 5.74 (dd, J_1 = 11.0 Hz, J_2 = 2.0 Hz, 1 H), 4.15 (s, 3 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.8, 143.8, 140.2, 138.8, 130.8, 129.4, 128.8, 126.7, 126.6, 123.1, 53.7 ppm; MS (EI, 70eV): *m/z* (%) = 186 (100) [M+], 157 (43); HRMS (EI) for $C_{11}H_{10}N_2O$: calcd. 186.0793, found 186.0799.

methyl 3-vinylquinoxaline-2-carboxylate (4d)



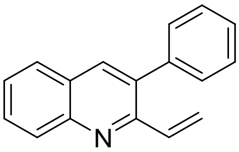
Orange solid; R_f = 0.32 (petroleum ether-EtOAc= 6:1); mp = 66-67℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.18 (dd, J_1 = 8.5 Hz, J_2 = 1.0 Hz, 1 H), 8.12 (dd, J_1 = 8.5 Hz, J_2 = 1.0 Hz, 1 H), 7.86 (ddd, J_1 = 8.3 Hz, J_2 = 6.9 Hz, J_3 = 1.5 Hz, 1 H), 7.79 (ddd, J_1 = 8.3 Hz, J_2 = 6.9 Hz, J_3 = 1.4 Hz, 1 H), 7.54 (dd, J_1 = 17.0 Hz, J_2 = 11.0 Hz, 1 H), 6.70 (dd, J_1 = 16.8 Hz, J_2 = 1.8 Hz, 1 H), 5.77 (dd, J_1 = 10.8 Hz, J_2 = 1.8 Hz, 1 H), 4.10 (s, 3 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.9, 148.9, 142.9 (2C), 140.4, 132.0 (2C), 130.4, 129.7, 129.3, 123.7, 53.3 ppm; MS (EI, 70eV): *m/z* (%) = 214 (86) [M+], 199 (59), 156 (100); HRMS (EI) for $C_{12}H_{10}N_2O_2$: calcd. 214.0742, found 214.0750.

2-phenyl-3-vinylpyrazine (4e)



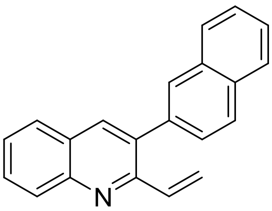
Yellow oil; R_f = 0.50 (petroleum ether-EtOAc= 6:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.56 (s, 2 H), 7.63-7.62 (m, 2 H), 7.53-7.48 (m, 3 H), 6.95 (dd, J_1 = 17.0 Hz, J_2 = 10.5 Hz, 1 H), 6.56 (dd, J_1 = 17.0 Hz, J_2 = 2.0 Hz, 1 H), 5.58 (dd, J_1 = 11.0 Hz, J_2 = 1.5 Hz, 1 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.6, 148.1, 142.5, 142.4, 137.5, 132.8, 129.6, 129.0, 128.4, 121.5 ppm; MS (EI, 70eV): *m/z* (%) = 181 (100) $[M-H]^+$; HRMS (EI) for $C_{12}H_{10}N_2$: calcd. 182.0844, found 182.0840.

3-phenyl-2-vinylquinoline (4g)



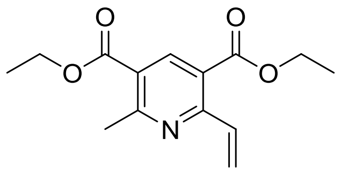
Yellow oil; R_f =0.63 (petroleum ether-EtOAc= 6:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.17 (d, J = 8.5 Hz, 1H), 8.05 (s, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.75-7.71 (m, 1H), 7.55-7.45 (m, 6H), 6.99 (dd, J_1 = 17.0 Hz, J_2 = 10.5 Hz, 1H), 6.61 (dd, J_1 = 17.0 Hz, J_2 = 2.0 Hz, 1H), 5.53 (dd, J_1 = 10.5 Hz, J_2 = 2.0 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.5, 147.3, 139.1, 136.7, 134.8, 134.7, 129.8, 129.5, 129.4, 128.4, 127.7, 127.5, 127.4, 126.5, 120.9 ppm; MS (EI, 70eV): *m/z* (%) = 230 (100) $[M-H]^+$; HRMS (EI) for $C_{17}H_{13}N$: calcd. 231.1048, found 231.1040.

3-(naphthalen-2-yl)-2-vinylquinoline (4h)



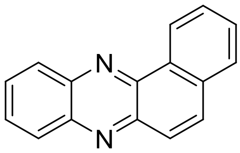
Pale yellow solid; R_f =0.58 (petroleum ether-EtOAc= 6:1); mp = 85-86℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.21 (d, J = 9.0 Hz, 1H), 7.92 (dd, J_1 = 9.0 Hz, J_2 = 5.5 Hz, 3H), 7.78-7.74 (m, 3H), 7.58-7.57 (m, 2H), 7.54-7.51 (m, 1H), 7.48-7.45 (m, 1H), 7.32 (ddd, J_1 = 8.2 Hz, J_2 = 6.8 Hz, J_3 = 1.2 Hz, 1H), 6.99 (d, J = 8.5 Hz, 1H), 6.86 (d, J = 2.0 Hz, 1H), 5.74 (d, J = 2.0 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.9, 148.1, 147.9, 138.6, 136.3, 133.7, 132.0, 129.8, 129.6, 128.3, 128.3, 127.5, 127.4, 126.3, 126.1, 125.9, 125.6, 121.6, 120.4 ppm; MS (EI, 70eV): *m/z* (%) = 280 (100) $[M-H]^+$; HRMS (EI) for $C_{21}H_{15}N$: calcd. 281.1204, found 281.1205.

diethyl 2-methyl-6-vinylpyridine-3,5-dicarboxylate (4j)



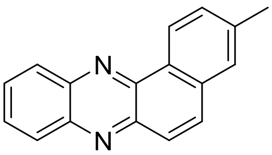
White solid; R_f = 0.63 (petroleum ether-EtOAc= 6:1); mp = 47-48℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.67 (s, 1 H), 7.67 (dd, J_1 = 16.9 Hz, J_2 = 10.6 Hz, 1 H), 6.66 (dd, J_1 = 16.9 Hz, J_2 = 2.3 Hz, 1 H), 5.68 (dd, J_1 = 10.6 Hz, J_2 = 2.3 Hz, 1 H), 4.44-4.39 (m, 4H), 2.89 (s, 3 H), 1.43 (t, J = 7.1 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.9 (2C), 162.3, 156.3, 141.3, 133.3, 123.9, 123.7, 121.8, 61.6, 61.4, 25.3, 14.3 (2C) ppm; MS (EI, 70eV): *m/z* (%) = 263 (48) [M+], 234 (93), 206 (100) HRMS (EI) for $C_{14}H_{17}NO_4$: calcd. 263.1158, found 263.1161.

benzo[a]phenazine (5j)



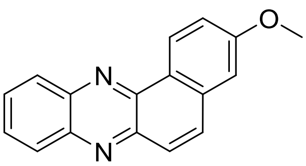
Yellow solid; R_f = 0.42 (petroleum ether-EtOAc= 6:1); mp = 142-143℃ (lit.[11] 142℃); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.41 (d, J = 8.5 Hz, 1H), 8.38-8.36 (m, 1H), 8.30-8.28 (m, 1H), 8.01 (d, J = 9.5 Hz, 1H), 7.97 (d, J = 9.5 Hz, 1H), 7.91-7.86 (m, 3H), 7.82-7.76 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.4, 142.7, 142.6, 142.0, 133.3, 133.2, 131.1, 130.0, 129.8 (2C), 129.7, 129.2, 128.2, 127.9, 127.1, 125.4 ppm; MS (EI, 70eV): *m/z* (%) = 230 (100) [M+].

3-methylbenzo[a]phenazine (5p)



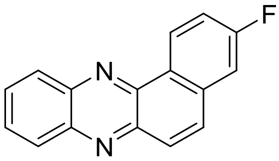
Yellow solid; R_f = 0.48 (petroleum ether-EtOAc= 6:1); mp = 186-187℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.29 (d, J = 8.0 Hz, 1H), 8.38-8.29 (m, 2H), 7.97 (s, 2H), 7.89-7.85 (m, 2H), 7.71 (s, 1H), 7.64 (dd, J_1 = 8.5 Hz, J_2 = 1.0 Hz, 1 H), 2.63 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.4, 142.9, 142.3, 142.1, 140.2, 133.4, 129.9, 129.8, 129. 7, 129.6, 129.1, 128.9, 128.2, 127.0, 125.4, 21.8 ppm; MS (EI, 70eV): *m/z* (%) = 244 (100) [M+]; HRMS (EI) for $C_{17}H_{12}N_2$: calcd. 244.1000, found 244.0977.

3-methoxybenzo[a]phenazine (5q)



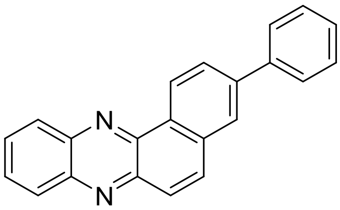
Yellow solid; R_f = 0.28 (petroleum ether-EtOAc= 6:1); mp = 166-167℃ (lit.[12]160-161℃); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.30 (d, J = 8.5 Hz, 1H), 8.33 (dd, J_1 = 7.3 Hz, J_2 = 2.3 Hz, 1H), 8.27 (dd, J_1 = 7.3 Hz, J_2 = 2.3 Hz, 1H), 7.96 (d, J = 9.0 Hz, 1H), 7.93 (d, J = 9.0 Hz, 1H), 7.87-7.82 (m, 2 H), 7.38 (dd, J_1 = 9.0 Hz, J_2 = 2.5 Hz, 1H), 7.28 (d, J = 2.5 Hz, 1H), 4.00 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 161.1, 142.8, 142.7, 142.1, 142.0, 134.9, 133.2, 129.8, 129.6, 129.5, 129.1, 127.6, 127.2, 124.8, 117.1, 109.7, 55.6 ppm; MS (EI, 70eV): *m/z* (%) = 260 (100) [M+], 245 (7).

3-fluorobenzo[a]phenazine (5r)



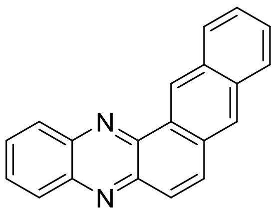
Yellow solid; R_f = 0.54 (petroleum ether-EtOAc= 6:1); mp = 195-196℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.42 (dd, J_1 = 9.0 Hz, J_2 = 6.0 Hz, 1H), 8.37-8.28 (m, 2H), 8.02 (d, J = 9.5 Hz, 1H), 7.95 (d, J = 9.0 Hz, 1H), 7.91-7.87 (m, 2H), 7.58-7.51 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.6 (d, J = 250.0 Hz), 143.2, 142.8, 142.2, 142.2, 135.0 (d, J = 9.1 Hz), 132.2, 130.1, 130.1, 129.7, 129.3, 128.7, 128.1 (d, J = 9.1 Hz), 127.7, 116.4 (d, J = 23.1 Hz), 113.1 (d, J = 21.5 Hz) ppm; MS (EI, 70eV): *m/z* (%) = 248 (100) [M+]; HRMS (EI) for $C_{16}H_9N_2F$: calcd. 248.0750, found 248.0748.

3-phenylbenzo[a]phenazine (5s)



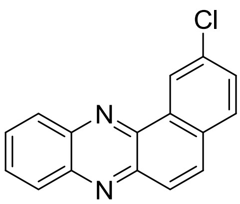
Yellow solid; R_f = 0.50 (petroleum ether-EtOAc= 6:1); mp = 179-180℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.44 (d, J = 8.5 Hz, 1H), 8.39-8.29 (m, 2H), 8.10 (d, J = 1.5 Hz, 1H), 8.11-8.04 (m, 2H), 8.00 (d, J = 9.5 Hz, 1H), 7.90-7.86 (m, 2H), 7.80 (d, J = 7.5 Hz, 2H), 7.55 (t, J = 7.8 Hz, 2H), 7.45 (t, J = 7.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.6, 142.6, 142.6, 142.1, 140.4, 133.6, 133.5, 130.1, 130.0, 129.9, 129.7, 129.1, 129.0, 128.0, 127.5, 127.0, 126.4, 126.0 ppm; MS (EI, 70eV): *m/z* (%) = 306 (100) [M+]; HRMS (EI) for $C_{22}H_{14}N_2$: calcd. 306.1157, found 306.1151.

naphtho[2,3-a]phenazine (5t)



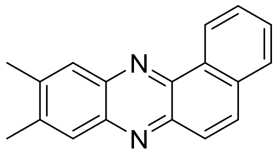
Yellow solid; R_f = 0.43 (petroleum ether-EtOAc= 6:1); mp = 225-226℃ (lit.[13] 220℃); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.80 (s, 1H), 8.37-8.35 (m, 1H), 8.28-8.23 (m, 3H), 8.05 (dd, J_1 = 8.5 Hz, J_2 = 3.5 Hz, 1 H), 7.98 (d, J = 9.5 Hz, 1H), 7.88-7.83 (m, 2H), 7.78 (d, J = 9.5 Hz, 1H), 7.65-7.62 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 144.6, 144.0, 142.4, 141.6, 134.2, 133.7, 132.4, 130.8, 129.8, 129.7, 129.5, 129.3, 129.0, 128.9, 128.1, 127.3, 127.2, 127.1, 126.7, 125.7 ppm; MS (EI, 70eV): *m/z* (%) = 280 (100) [M+].

2-chlorobenzo[a]phenazine (5u)



Yellow solid; R_f = 0.49 (petroleum ether-EtOAc= 6:1); mp = 208-209℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.34 (d, J = 2.0 Hz, 1H), 8.36-8.27 (m, 2H), 7.96 (s, 2H), 7.90-7.88 (m, 2H), 7.83 (d, J = 8.5 Hz, 1H), 7.71 (dd, J_1 = 8.5 Hz, J_2 = 2.0 Hz, 1 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.4, 143.0, 142.0, 141.5, 134.3, 132.4, 132.2, 131.4, 130.5, 130.1, 130.09, 129.8, 129.5, 129.2, 127.4, 125.0 ppm; MS (EI, 70eV): *m/z* (%) = 264 (100) [M+], 229 (24); HRMS (EI) for $C_{16}H_9N_2Cl$: calcd. 264.0454, found 264.0462.

9,10-dimethylbenzo[a]phenazine (5v)

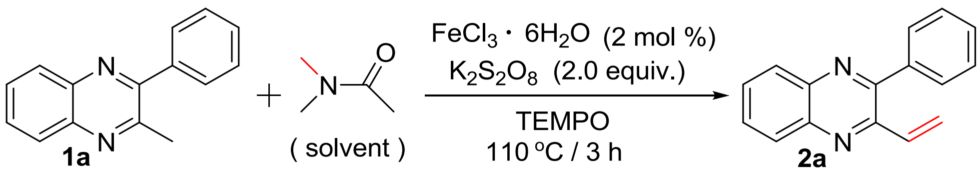


Pale yellow solid; R_f = 0.47 (petroleum ether-EtOAc= 6:1); mp = 211-212℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.39 (d, J = 8.0 Hz, 1H), 8.10 (s, 1H), 8.01 (s, 1H), 8.00-7.94 (m, 2H), 7.91 (d, J = 7.5 Hz, 1H), 7.81-7.74 (m, 2H), 2.58 (s, 3H), 2.57 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.0, 142.0, 142.0, 141.3, 141.1, 140.9, 133.1, 132.3, 131.4, 129.3, 128.4, 128.1, 127.9, 127. 7, 127.3, 125.1, 20.6, 20.5 ppm; MS (EI, 70eV): *m/z* (%) = 258 (100), 243 (30) [M+]; HRMS (EI) for $C_{18}H_{14}N_2$: calcd. 258.1157, found 258.1145.

Preliminary mechanistic studys

Effect of radical scavenger TEMPO on the reaction

Table 4. Effect of radical scavenger TEMPO [a]



Entry	TEMPO	Conversion (%)	Yields of **2a** (%)[b]
1	0	100	94
2	50 mol %	90	64[c]
3	200 mol %	97	5[c]

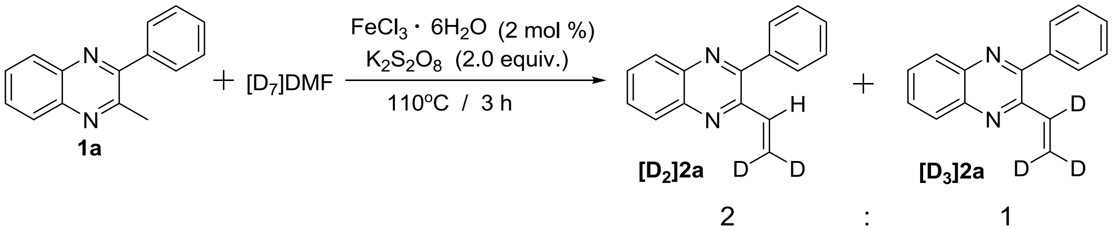
[a] Reaction condition : **1a** (0.2 mmol), $FeCl_3 \cdot 6H_2O$ (0.004 mmol), $K_2S_2O_8$ (0.4 mmol), DMA (1.5 mL), 110 ℃, under air, 3h. [b] GC-MS yields. [c] An oxidantion product 3-phenylquinoxaline -2-carbaldehyde was formed as a side product.

Deuterated experiments

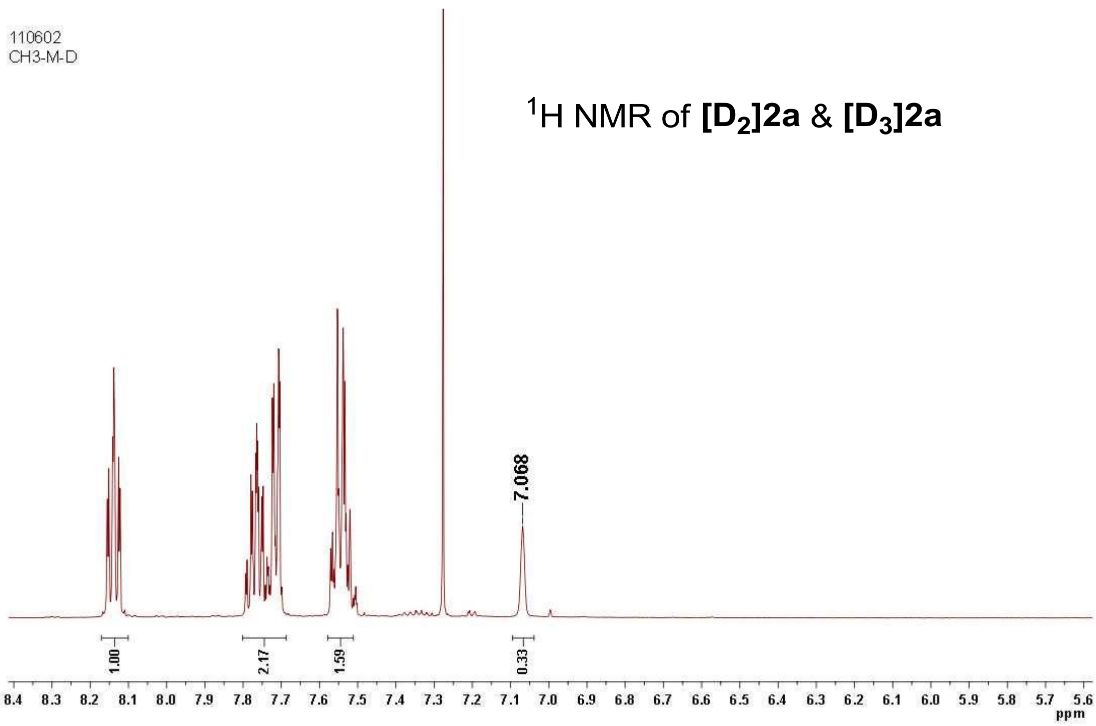
All the deuterated experiments were carried out twice.

(a) ***1a*** *treated with [D_7]DMF under the present condition*

1a (0.2 mmol), $FeCl_3 \cdot 6H_2O$ (1.1 mg, 0.004 mmol), $K_2S_2O_8$ (108 mg, 0.4 mmol) and [D_7] DMF (1.2 mL) were sequentially added to a 10-mL tube under air. Then the tube was sealed and stirred at 110 ºC for 3 h. Upon completion (monitored by TLC), the resulting mixture was diluted with Et_2O (15 mL) and washed by brine (10 mL × 3). The organic layer was then dried over Na_2SO_4, filtered and evaporated in *vacuo*, the residue was purified by column chromatography on silica gel (100-200 mesh) using petroleum ether-EtOAc as eluent to give **[D2]2a** and **[D3]2a** in the ratio 2 : 1.



Scheme 1. Synthesis of $[D_2]$2a and $[D_3]$2a



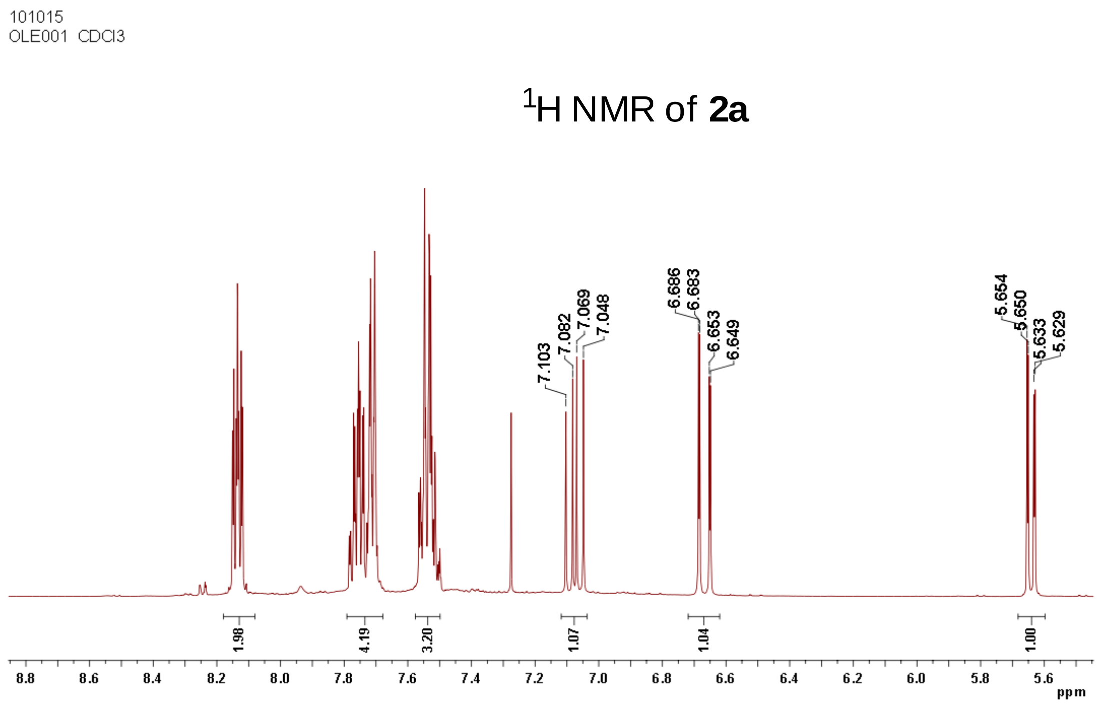
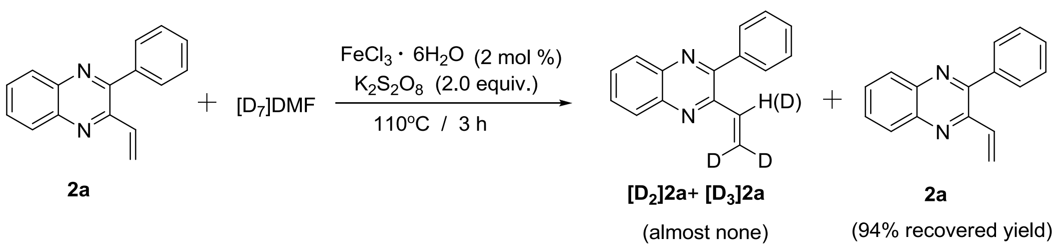


Figure 2. ^{1}H NMR spectra of deuterated products

*(b) **2a** treated with [D$_7$]DMF under the present condition*

2a (0.2 mmol), $FeCl_3 \cdot 6H_2O$ (1.1 mg, 0.004 mmol), $K_2S_2O_8$ (108 mg, 0.4 mmol) and [D$_7$] DMF (1.2 mL) were sequentially added to a 10-mL tube under air. Then the tube was sealed and stirred at 110 ºC for 3 h. The resulting mixture was diluted with Et_2O (15 mL) and washed by brine (10 mL × 3). The organic layer was then dried over Na_2SO_4, filtered and evaporated in *vacuo*, the residue was purified by column chromatography on silica gel (100-200 mesh) using petroleum ether-EtOAc as eluent. **2a** was recovered in 94% yield, and no obvious deuterated of **2a** were detected according to the ^{1}H NMR result.



Scheme 2. 2a treated with [D$_7$]DMF

Deuterated experiments (a) and (b) indicated that the C-H bond activation occurs on both coupling partners and the terminal vinyl carbon should be given by the N,N-dimethyl moiety of amides. In addition, the 2 : 1 ratio of **[D$_2$]2a** and **[D$_3$]2a** might be obtained through the following process. Firstly, the in-situ generated deuterium ion exchanged immediately with the benzylic hydrogen of [Fe]-promoted **1a** to form

[D$_1$]6a. Then **6a** or **[D$_1$]6a** fastly attacked the iminium **8**, intermediate **[D$_6$]9a** and **[D$_7$]9a** was thus generated respectively in the ratio of **1:2**. Then the **[D$_6$]9a** occurred elimination to form **[D$_2$]2a** entirely, meanwhile the **[D$_7$]9a** occurred elimination to give the product **[D$_3$]2a** and **[D$_2$]2a** in the ratio of **1:1**. To sum up, the ratio of **[D$_2$]2a** and **[D$_3$]2a** was eventually come to **2:1**.

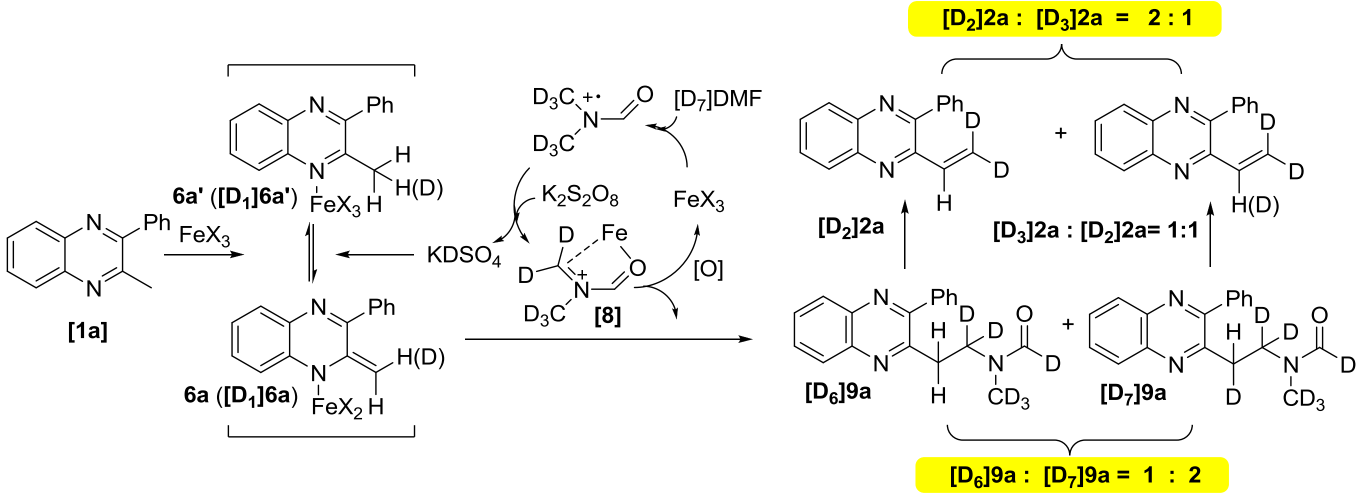
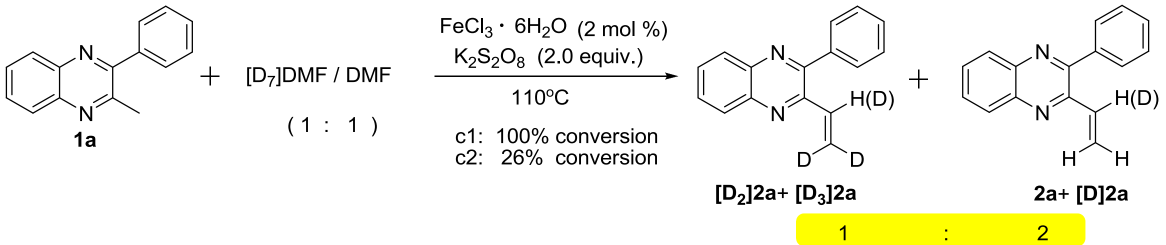


Figure 3. Deuterated experiments

(c) Competing reaction between [D$_7$]DMF and DMF

1a (0.2 mmol), $FeCl_3 \cdot 6H_2O$ (1.1 mg, 0.004 mmol), $K_2S_2O_8$ (108 mg, 0.4 mmol) and [D$_7$] DMF / DMF (0.6 mL / 0.6 mL) were sequentially added to a 10-mL tube under air. Then the tube was sealed and stirred at 110 ºC for 3 h. Upon completion (monitored by TLC), the resulting mixture was diluted with Et_2O (15 mL) and washed by brine (10 mL × 3). The organic layer was then dried over Na_2SO_4, filtered and evaporated in *vacuo*, the residue was purified by column chromatography on silica gel (100-200 mesh) using petroleum ether-EtOAc as eluent. A mixture of **[D$_2$]2a**, **[D$_3$]2a** and **2a** was determined on the basis of ^{1}H NMR analysis. Based on the integrations related to different hydrogen resonances, the kinetic isotope effect is calculated to be $\boldsymbol{k_H / k_D} \approx \boldsymbol{2.0}$, suggesting that the C-H bond cleavage of N, N-dimethyl amides is involved in the rate-determining step. Notablely, KIE value was also obtained when the reaction was stop at a lower conversion of 26%, the result was the same as it obtained after full conversion.



Scheme 3. Competing reaction between [D$_7$]DMF and DMF

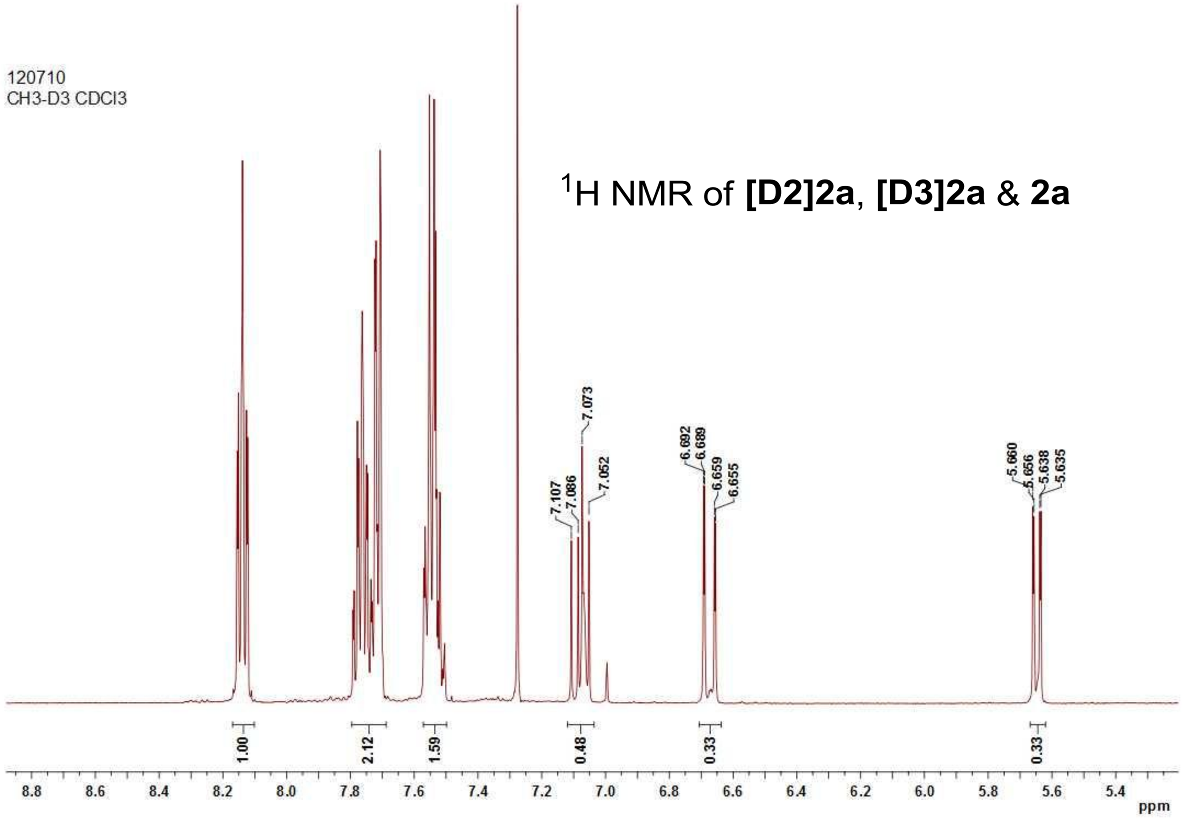


Figure 4. ^{1}H NMR spectra of KIE experiment (c1: 100% conversion of **1a**)

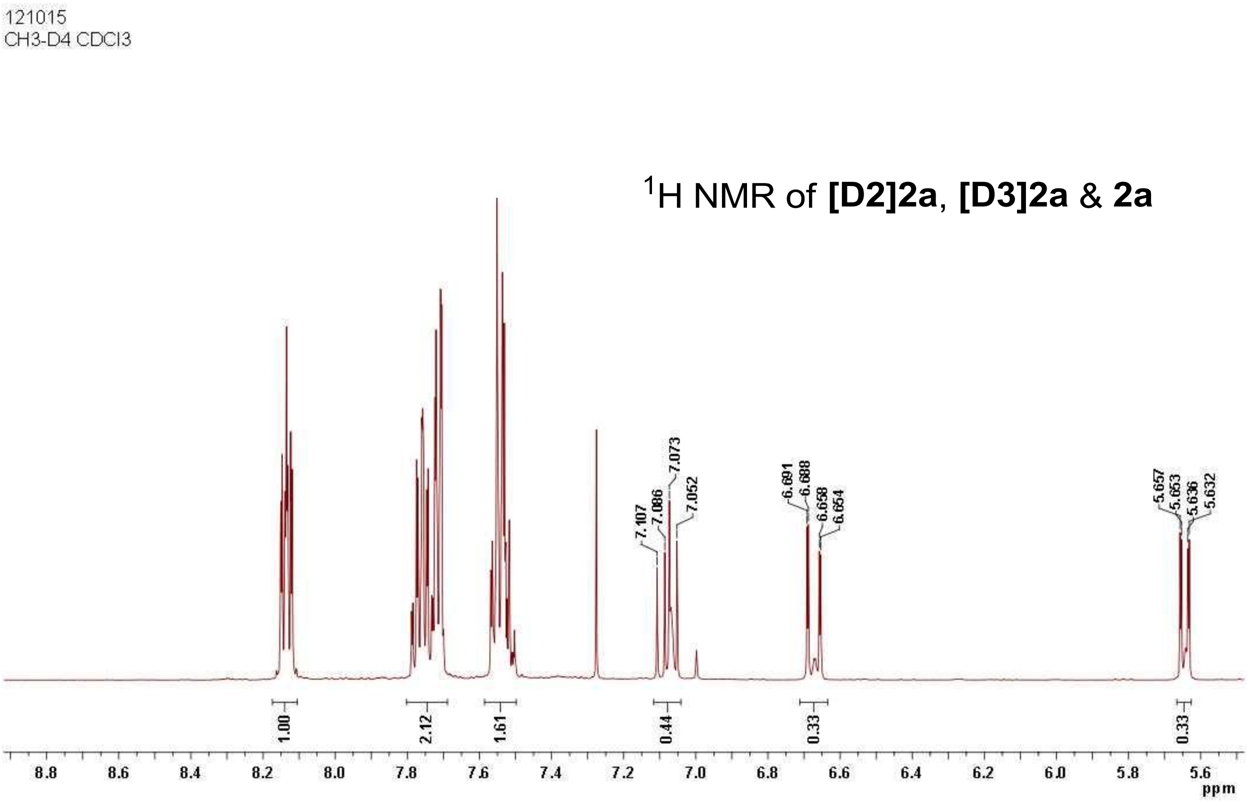


Figure 5. ^{1}H NMR spectra of KIE experiment (c2: 26% conversion of **1a**)

ESI-MS studies to capture the coupling intermediate

1a (0.2 mmol), $FeCl_3 \cdot 6H_2O$ (1.1 mg, 0.004 mmol), $K_2S_2O_8$ (108 mg, 0.4 mmol) and DMA (1.5 mL) were sequentially added to a 10-mL tube under air. Then the tube was sealed and stirred at 110 ºC. The mixture was stopped heating and cooled to room temperature when almost half of the starting material **1a** was converted to vinylation product **2a** (monitored by TLC). Then the mixture was diluted by methanol and subjected directly to ESI-MS analysis. From the mass spectrum we could find the starting material **1a** (m/z: 221) and the product **2a** (m/z: 233). Notably, the coupling intermediate between **1a** and N,N-dimethylacetamide (DMA) was detected (m/z: 306) and its structure was further confirmed by accurate mass data. The mass experiment result indicated that a key intermediate coupled between the substrate **1a** and DMA was generated during the process, which then underwent a tandem elimination to give the final vinylation product **2a**.

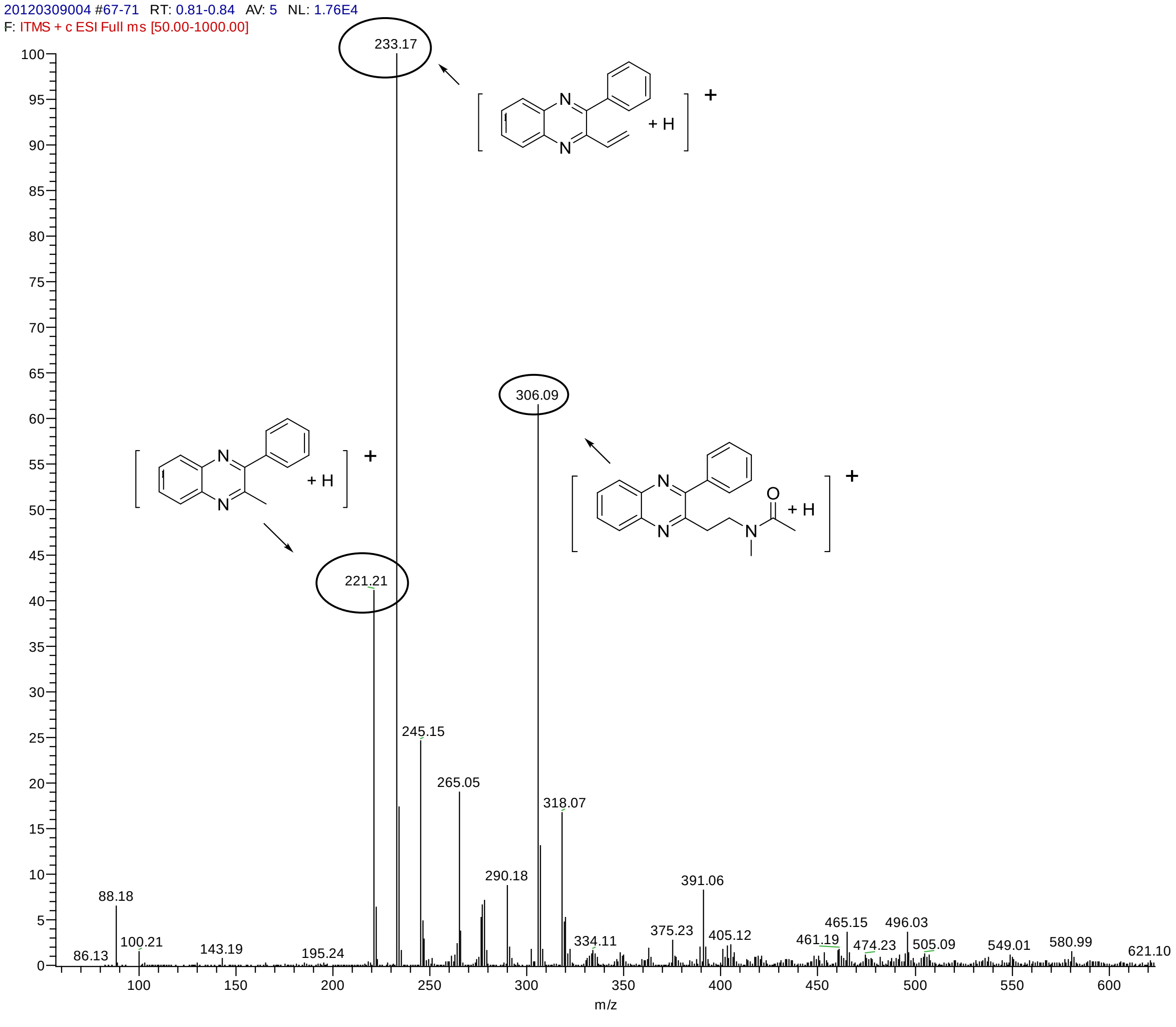
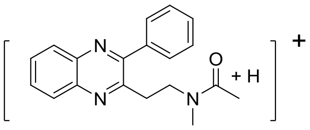


Figure 6. ESI-MS spectrum.



Ion Formula	m/z (measured)	m/z (caculated)	Diff (ppm)	DBE
C19 H20 N3 O	306.1598	306.1606	2.61	11.5

References

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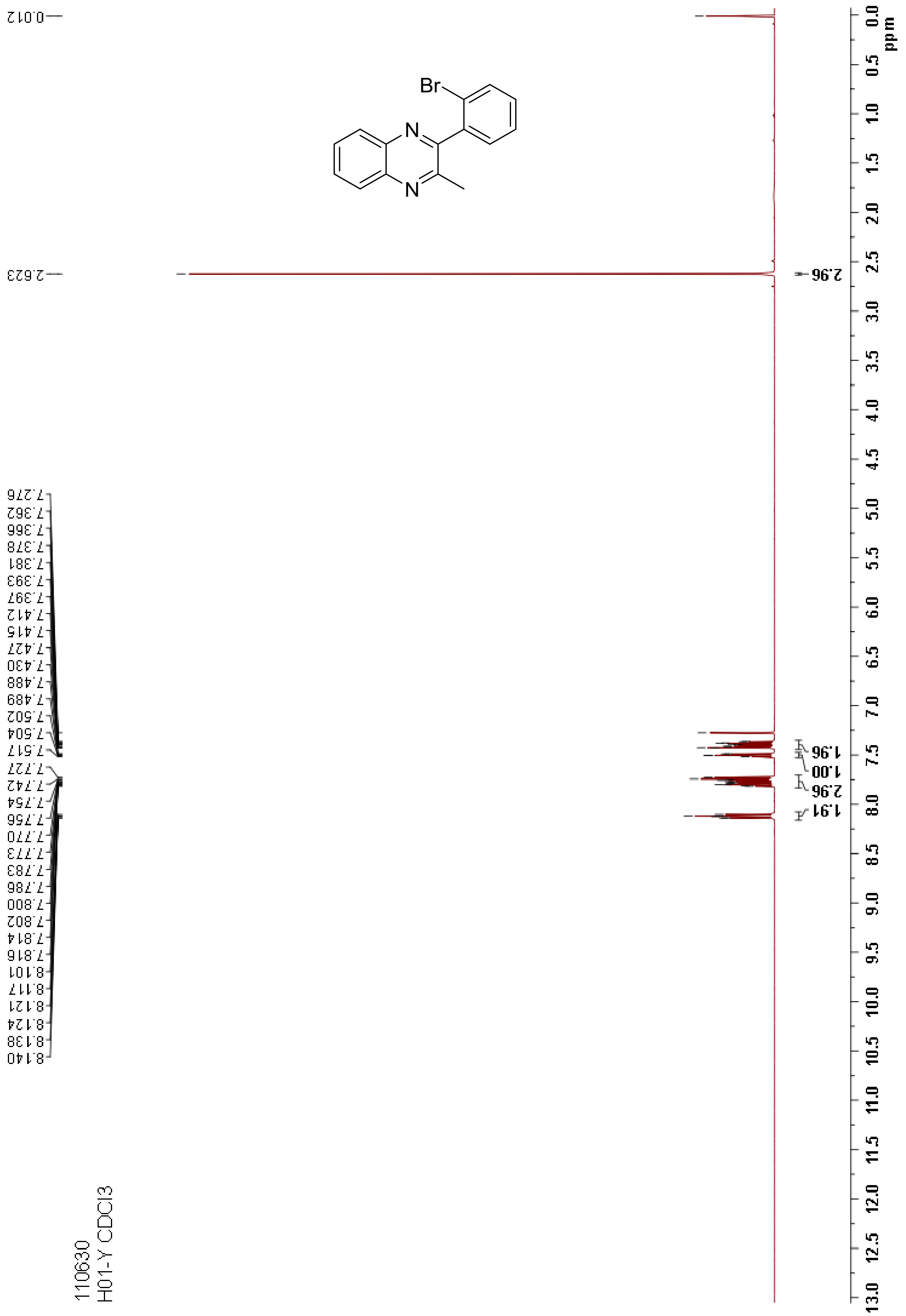
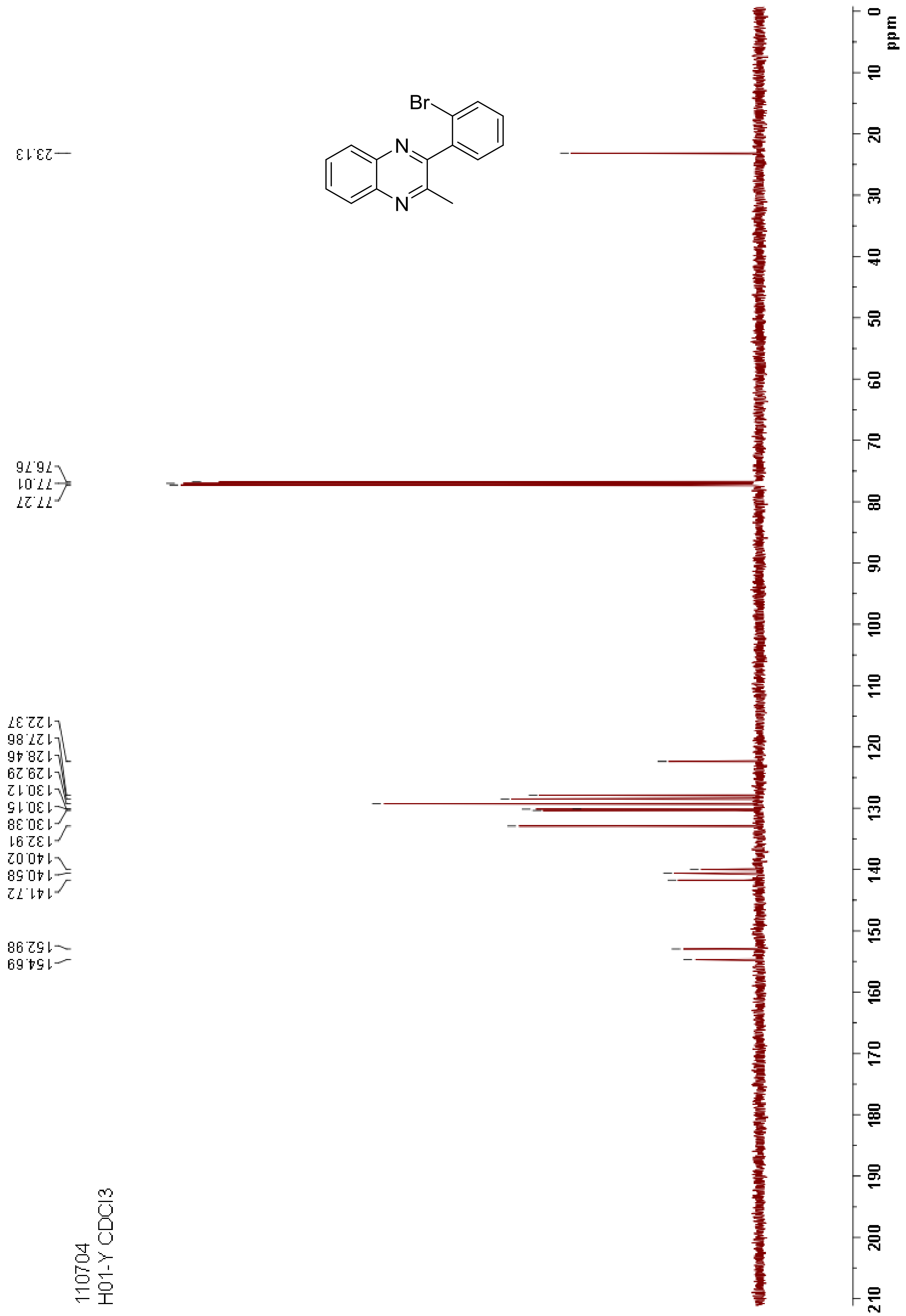
[1]H and [13]C NMR spectra of all products

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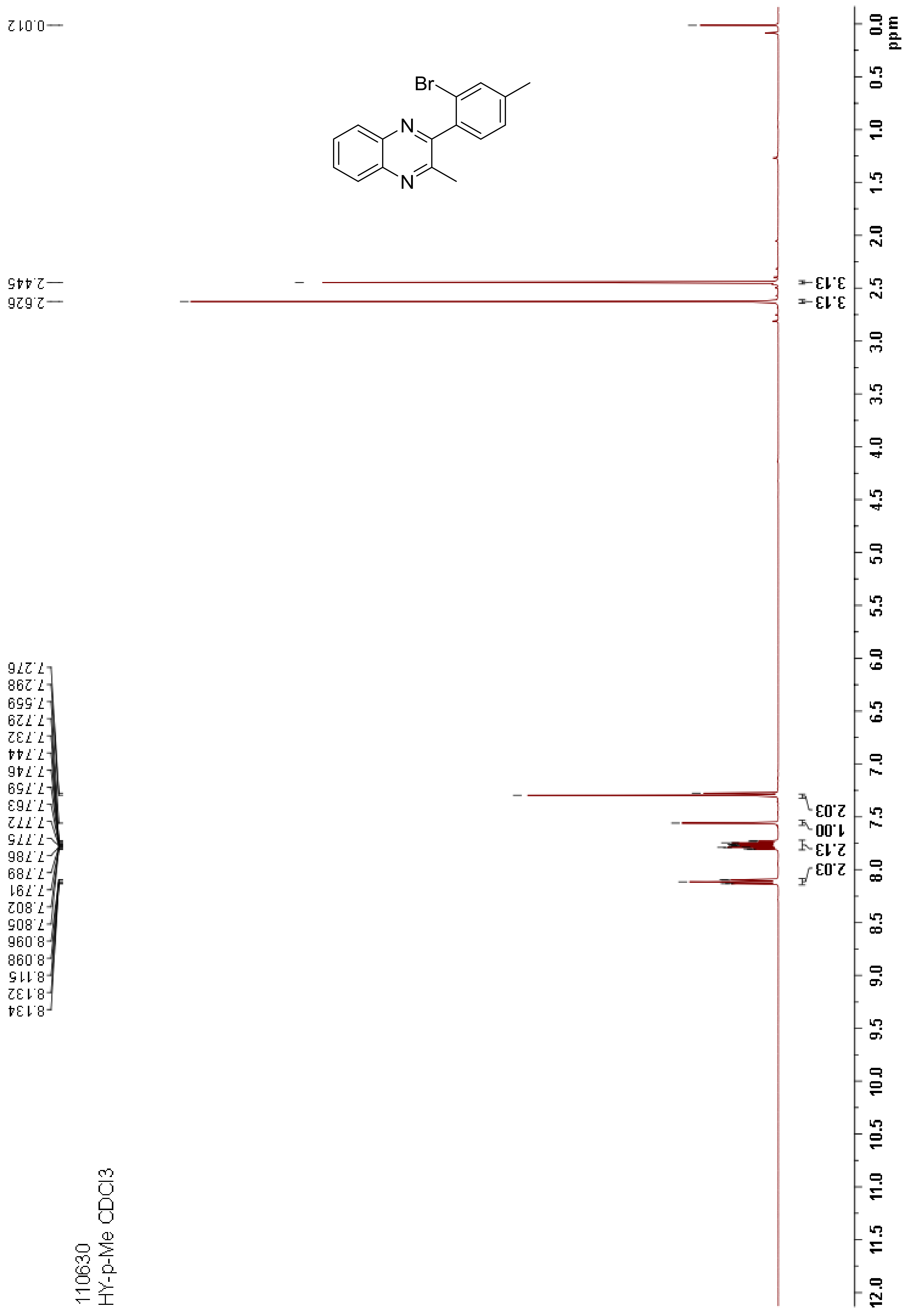
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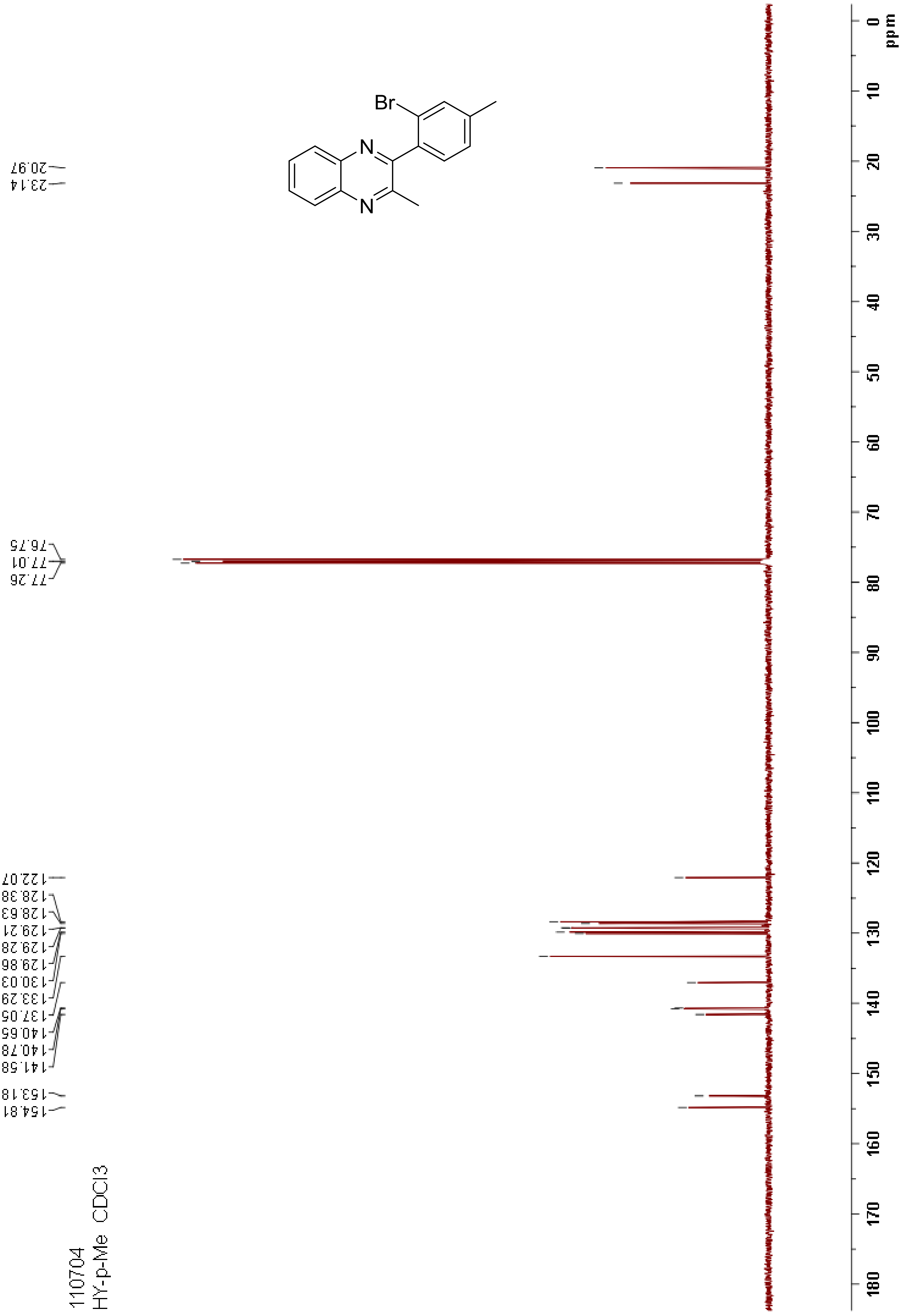
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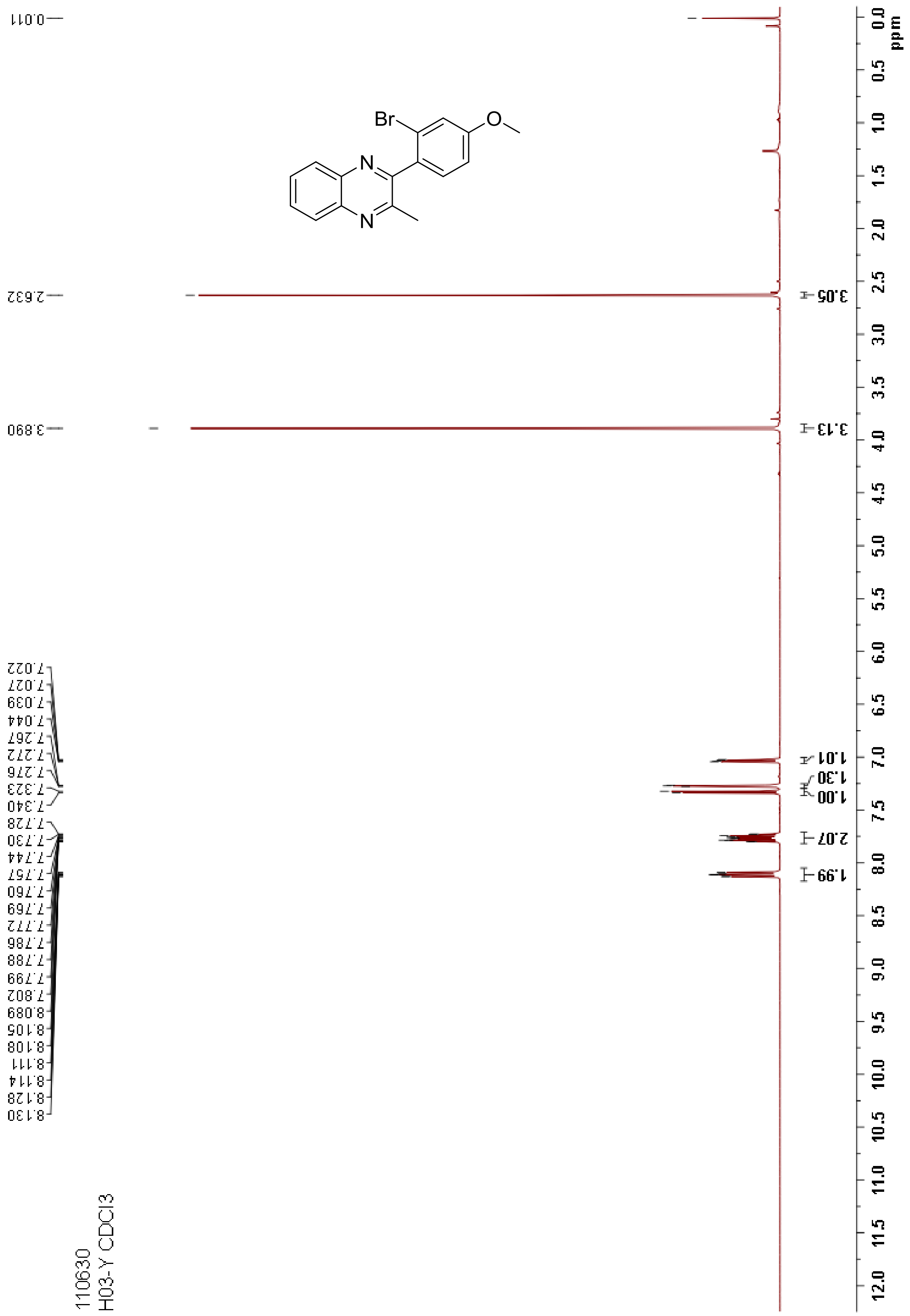
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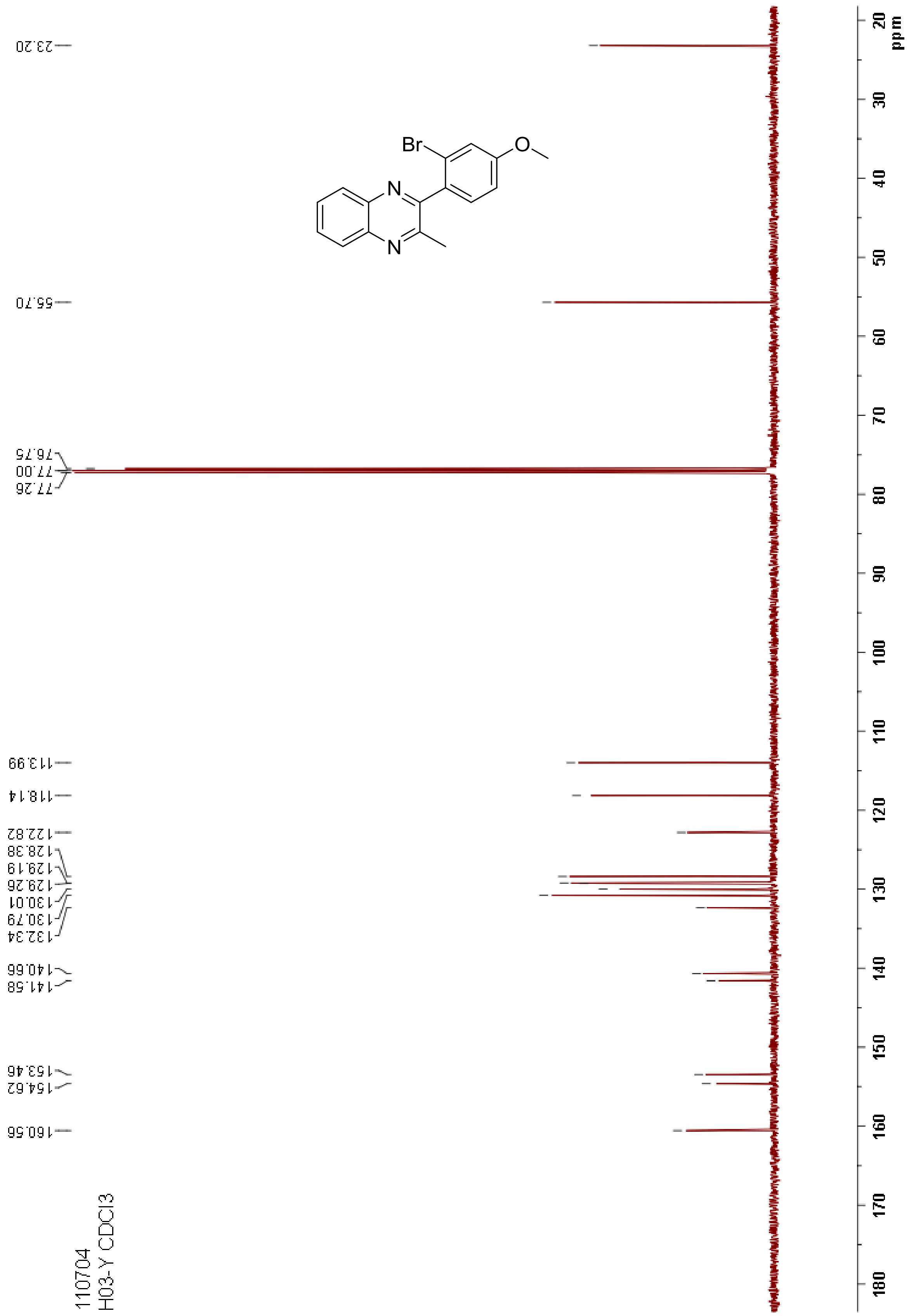
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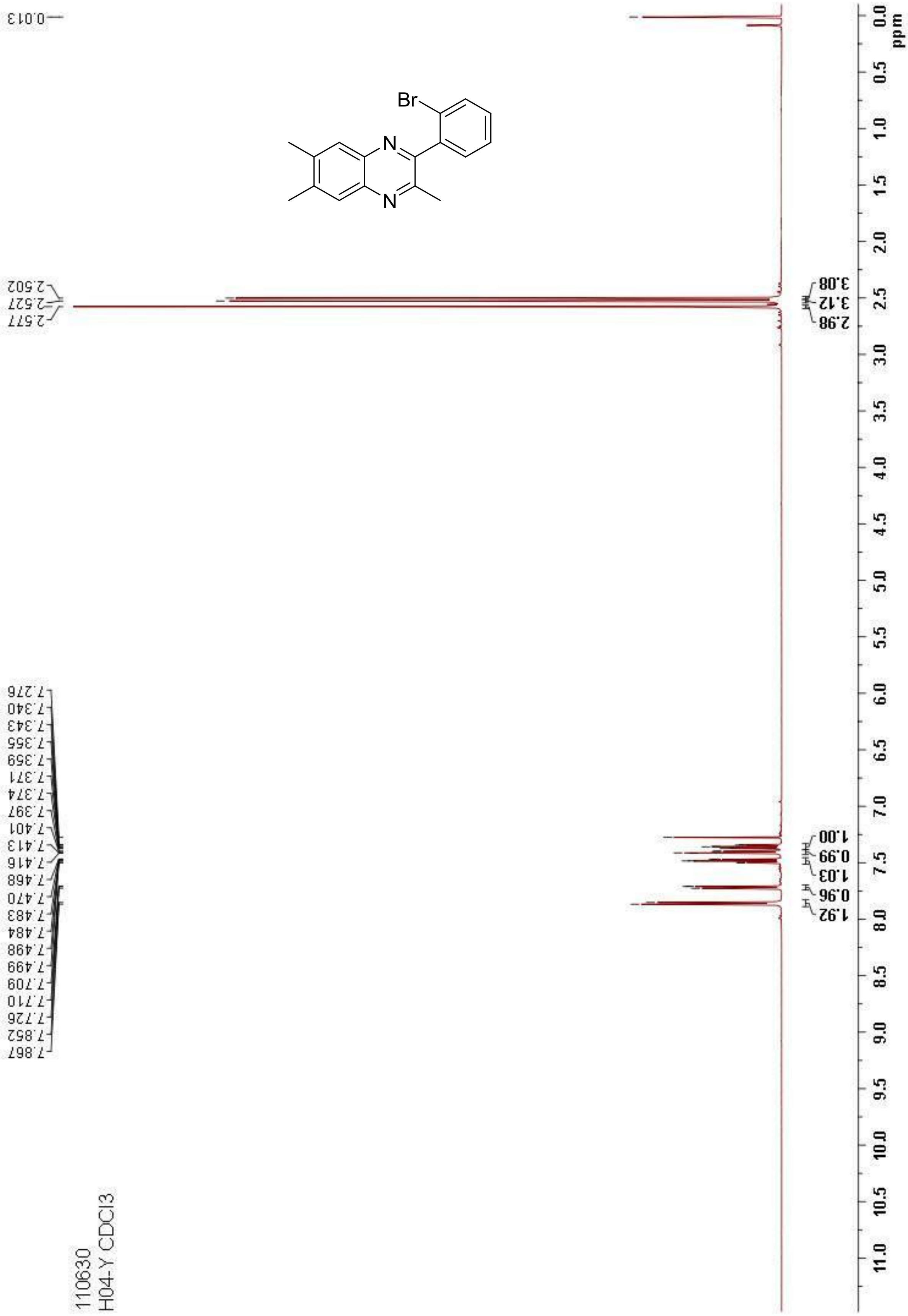
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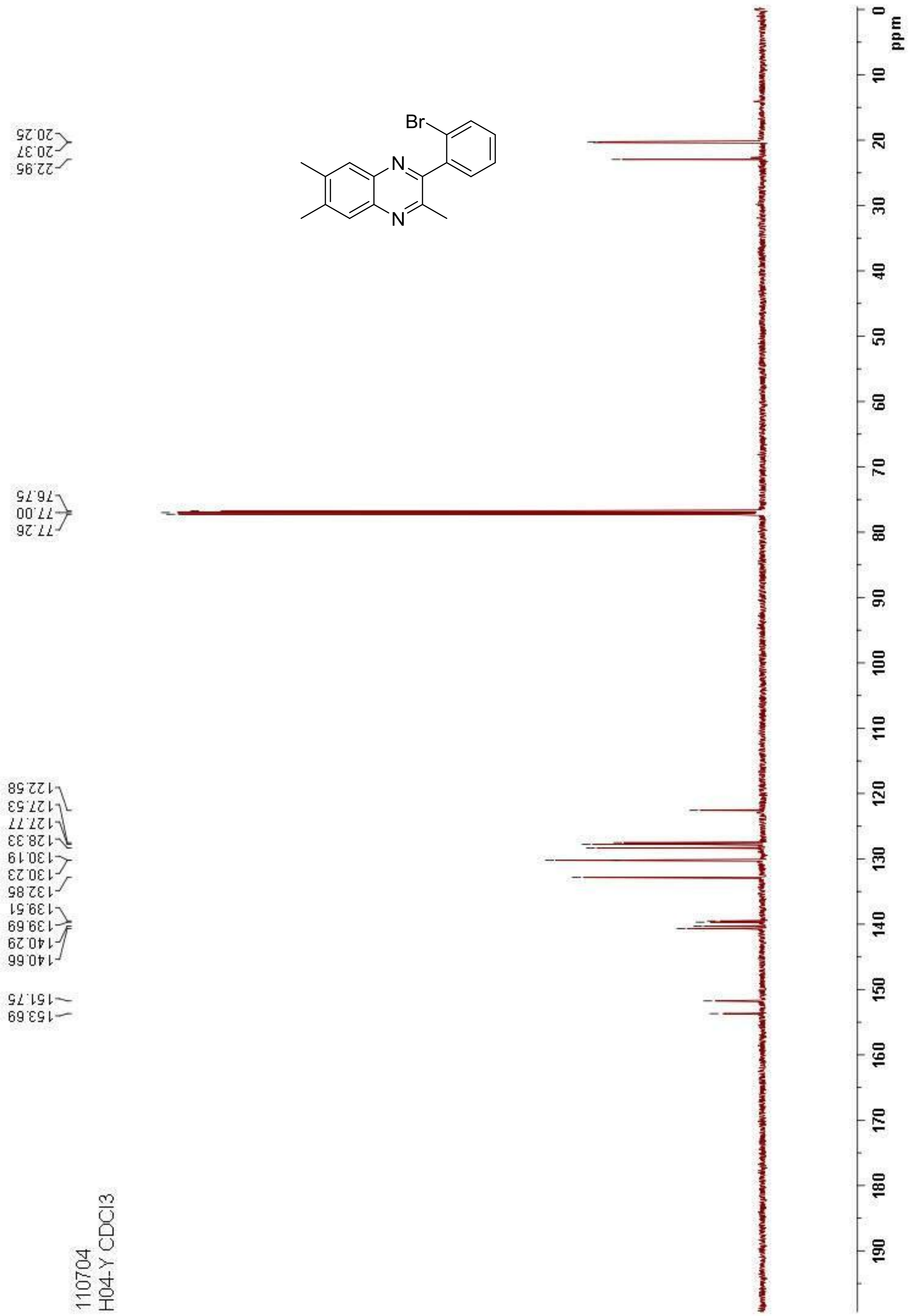
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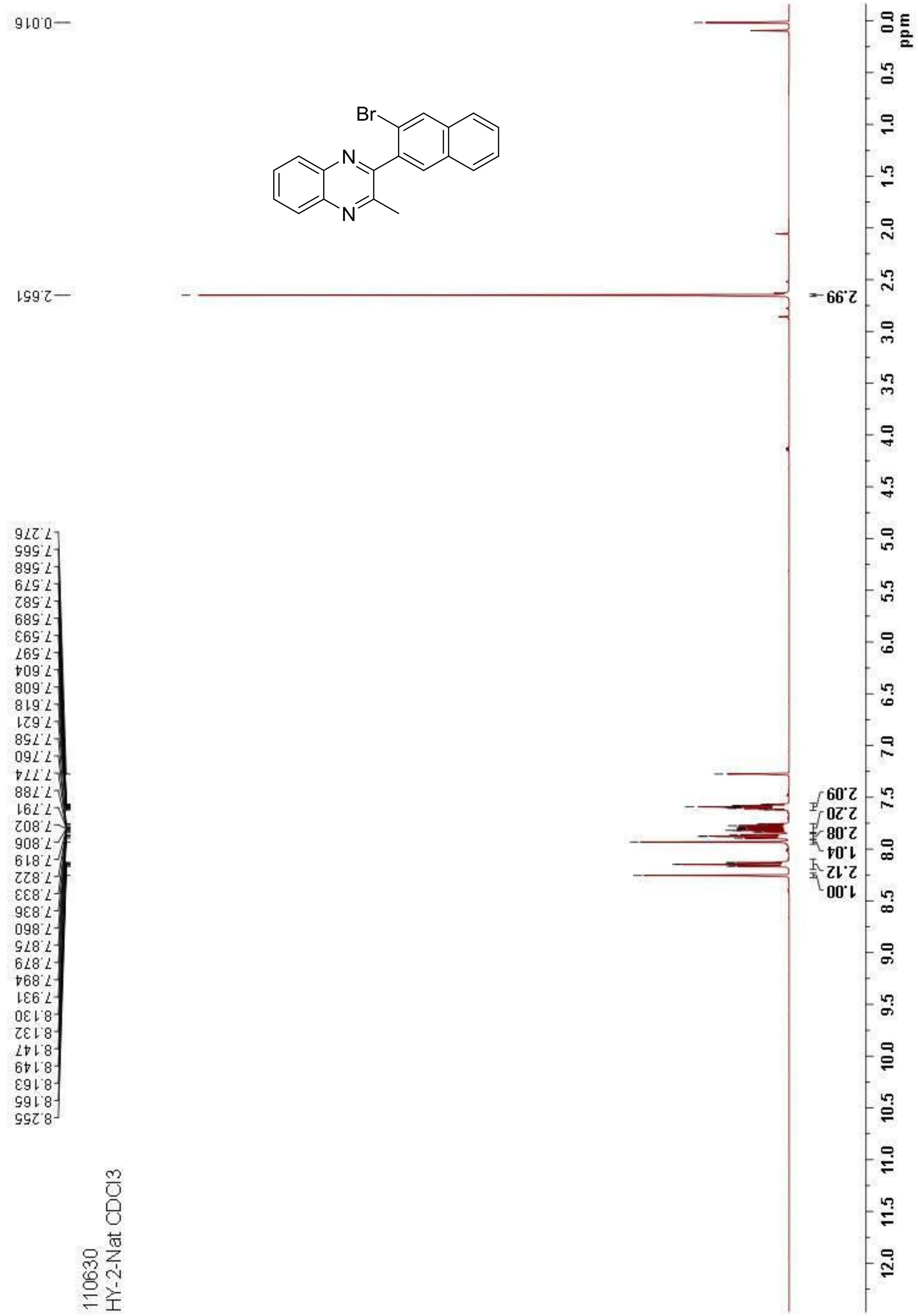
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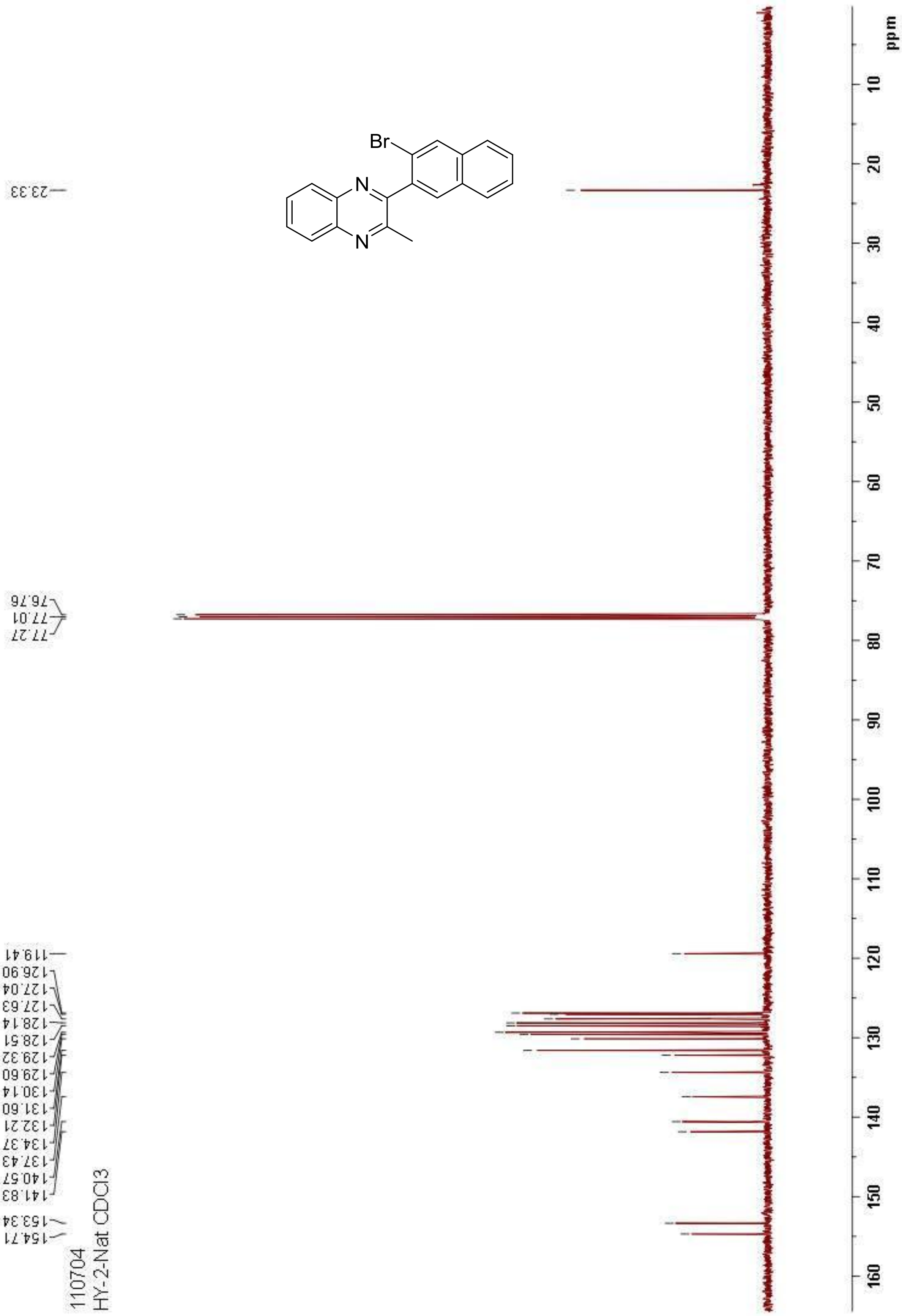
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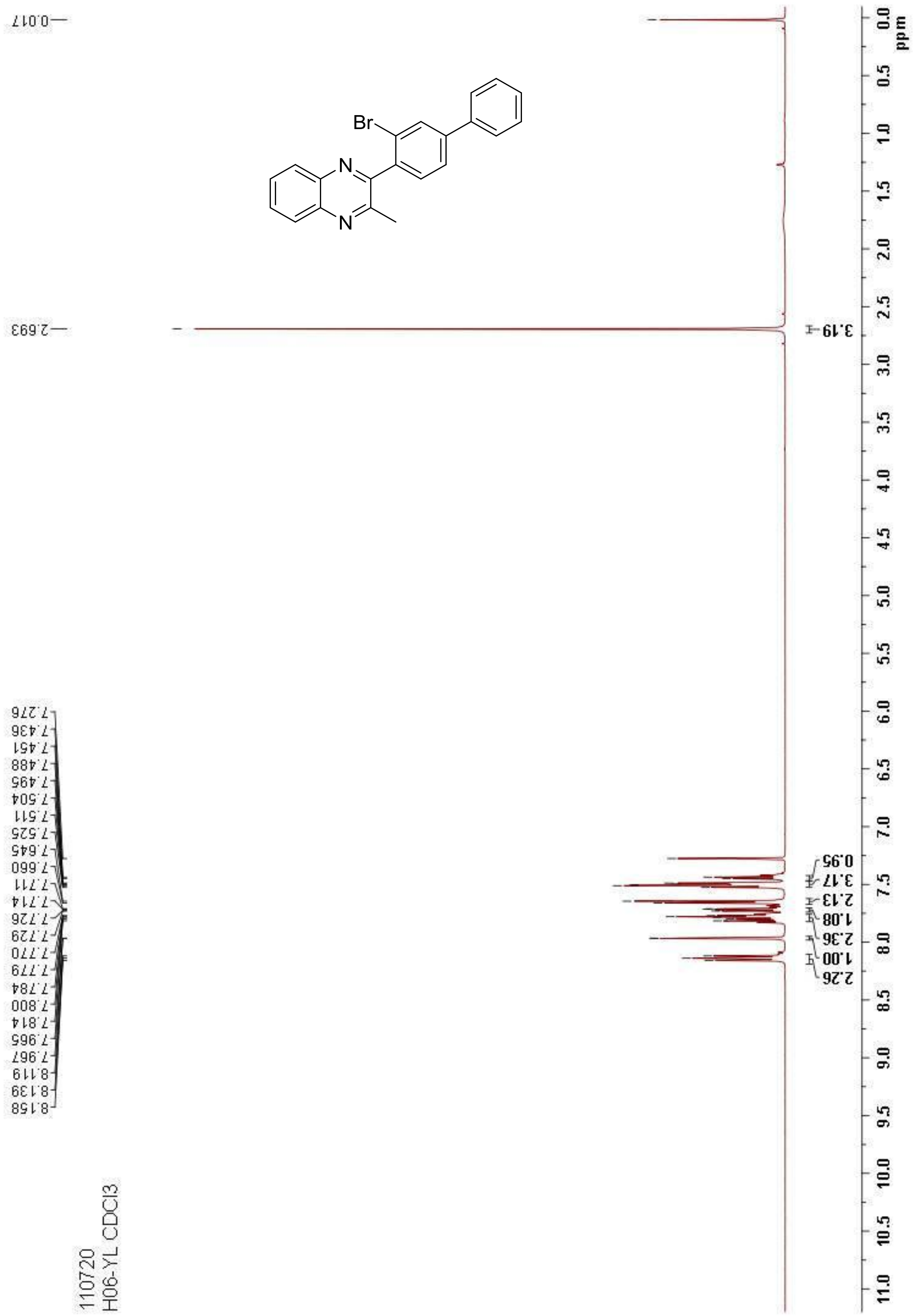
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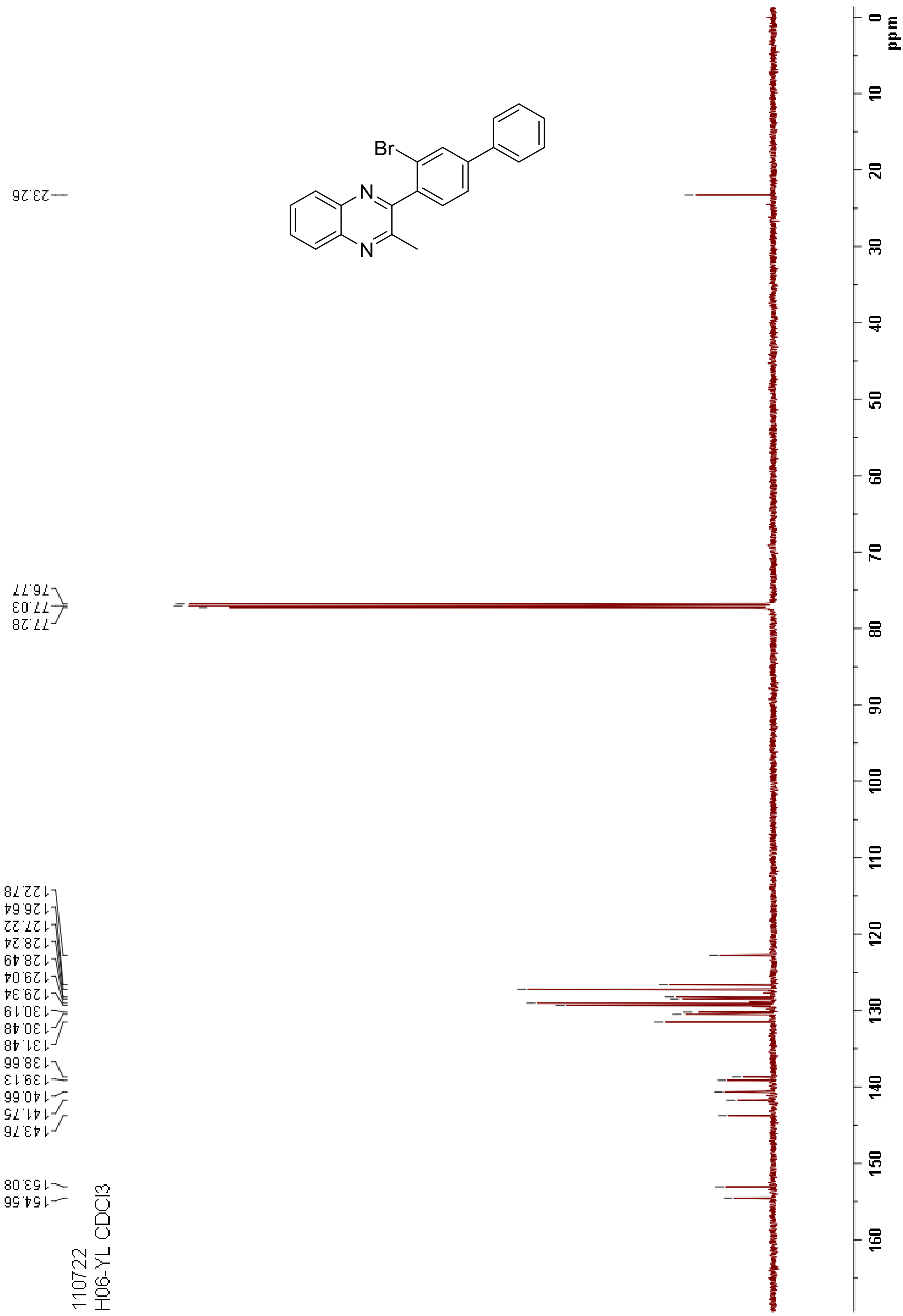
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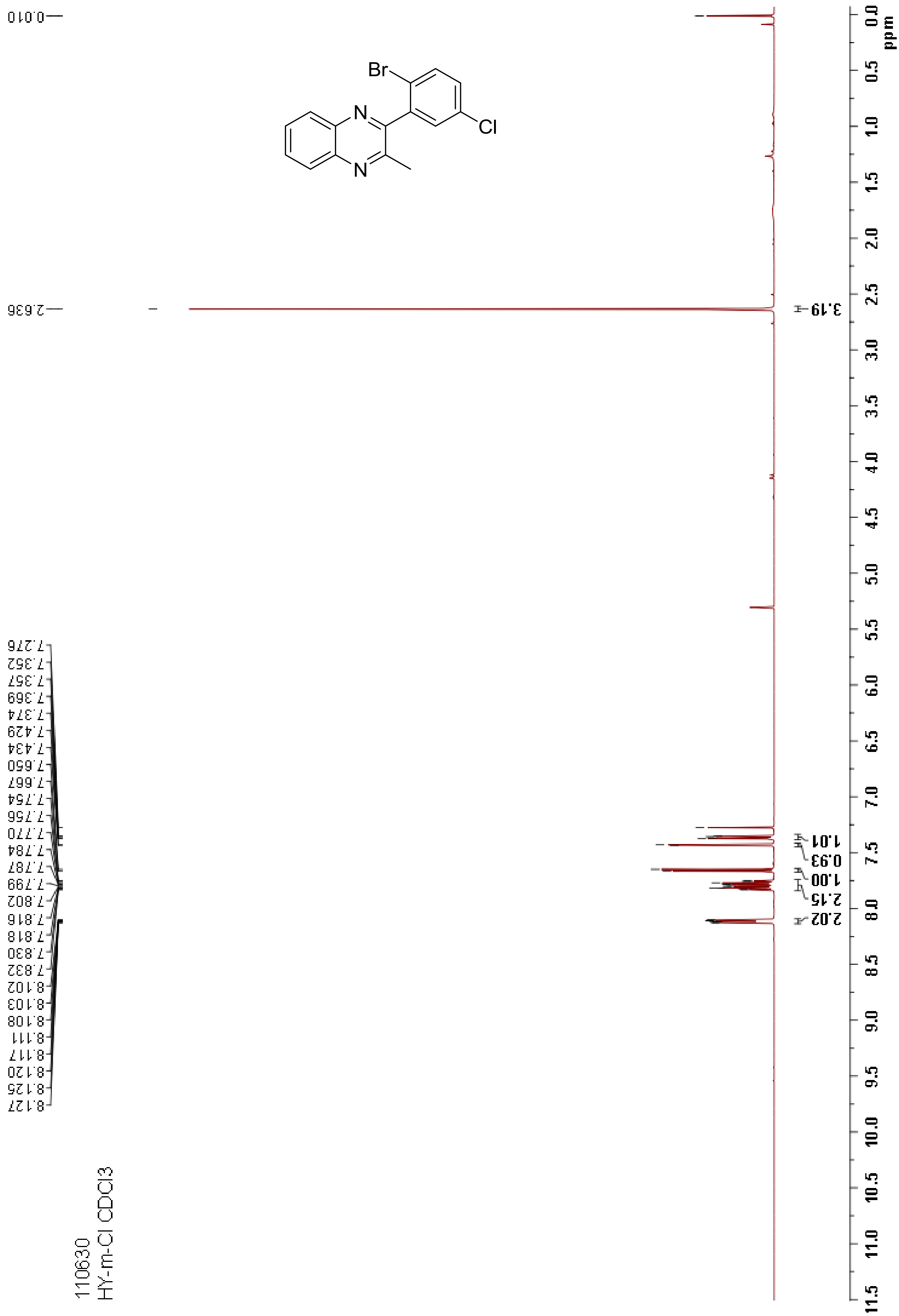
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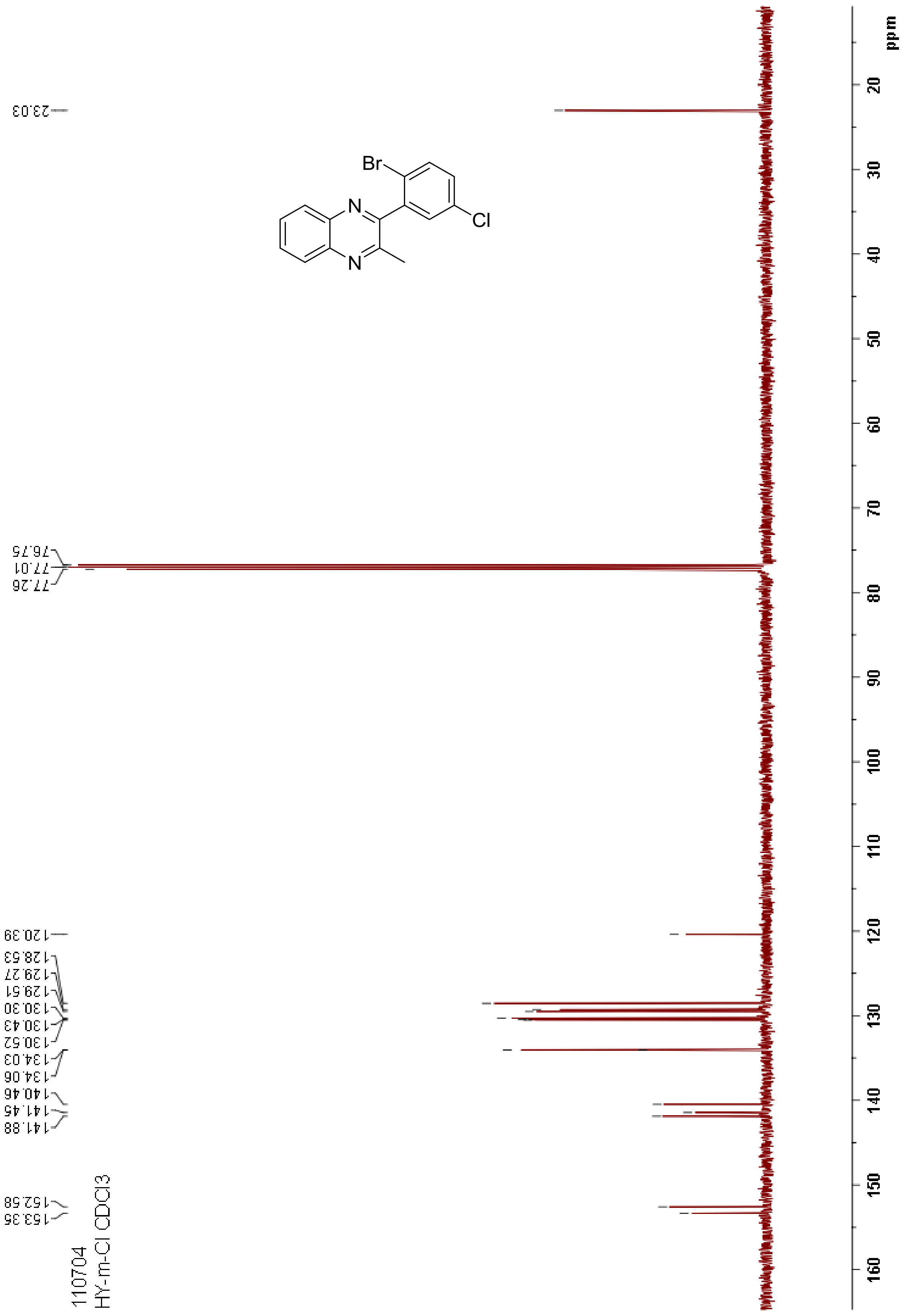
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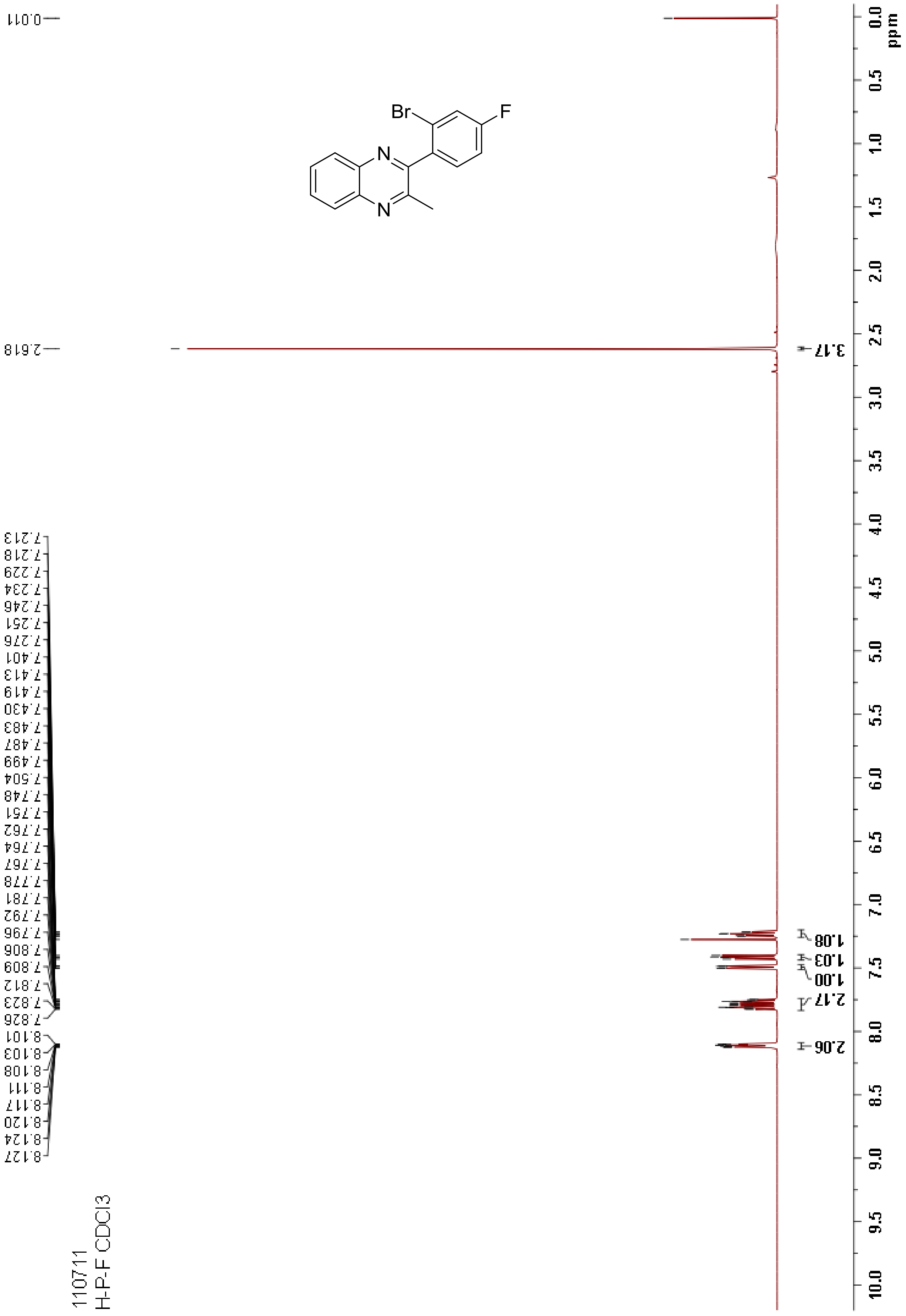
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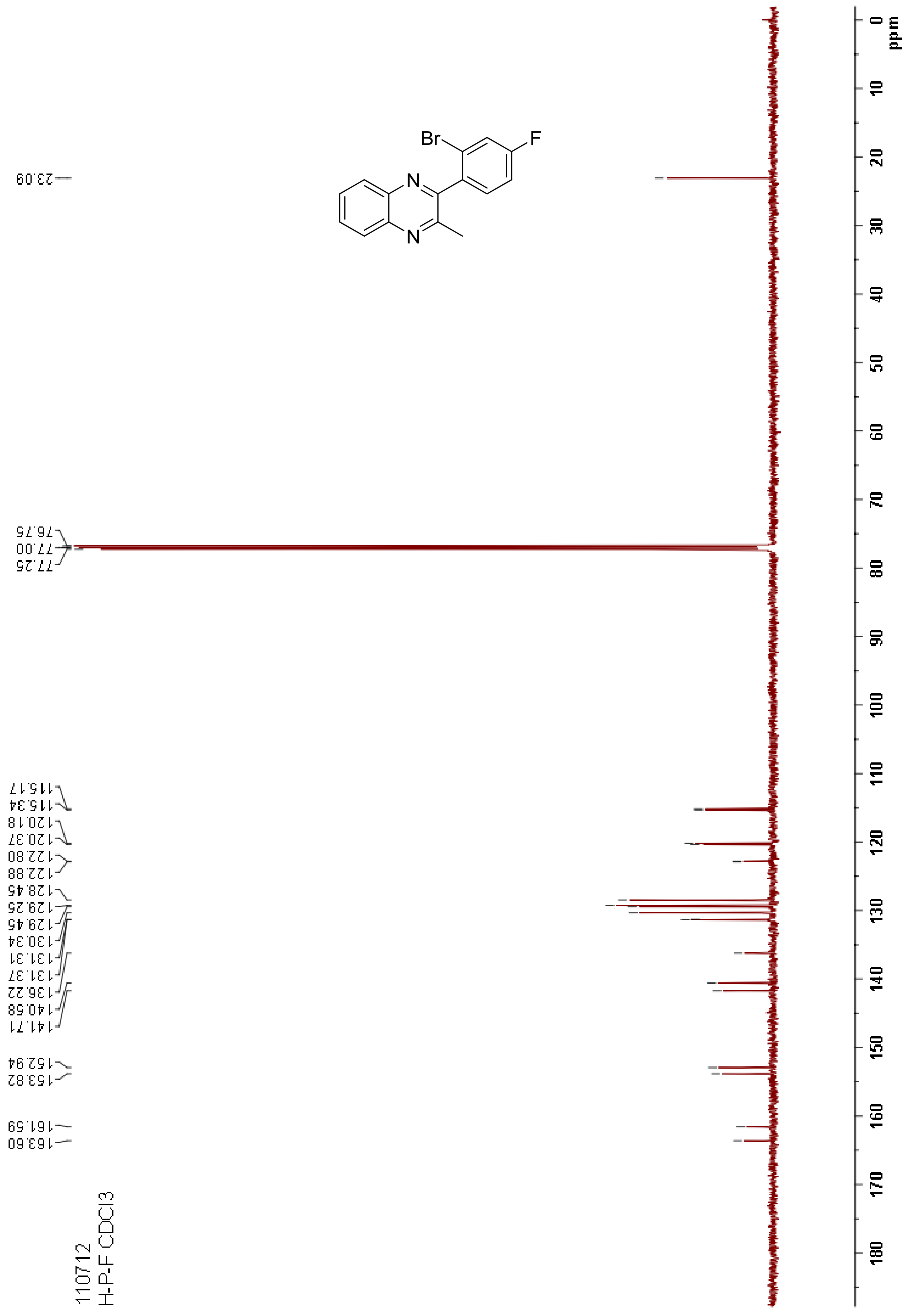
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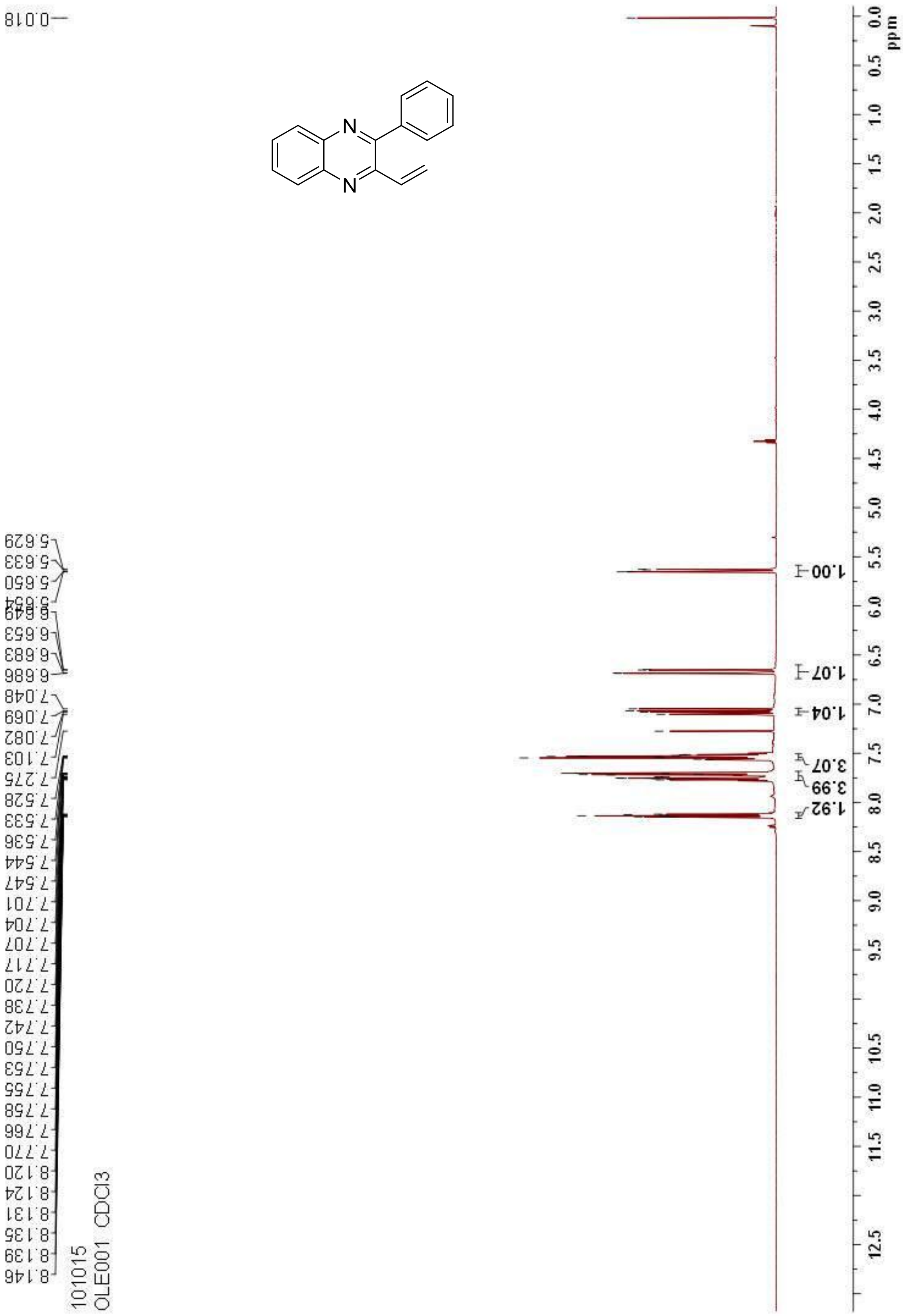
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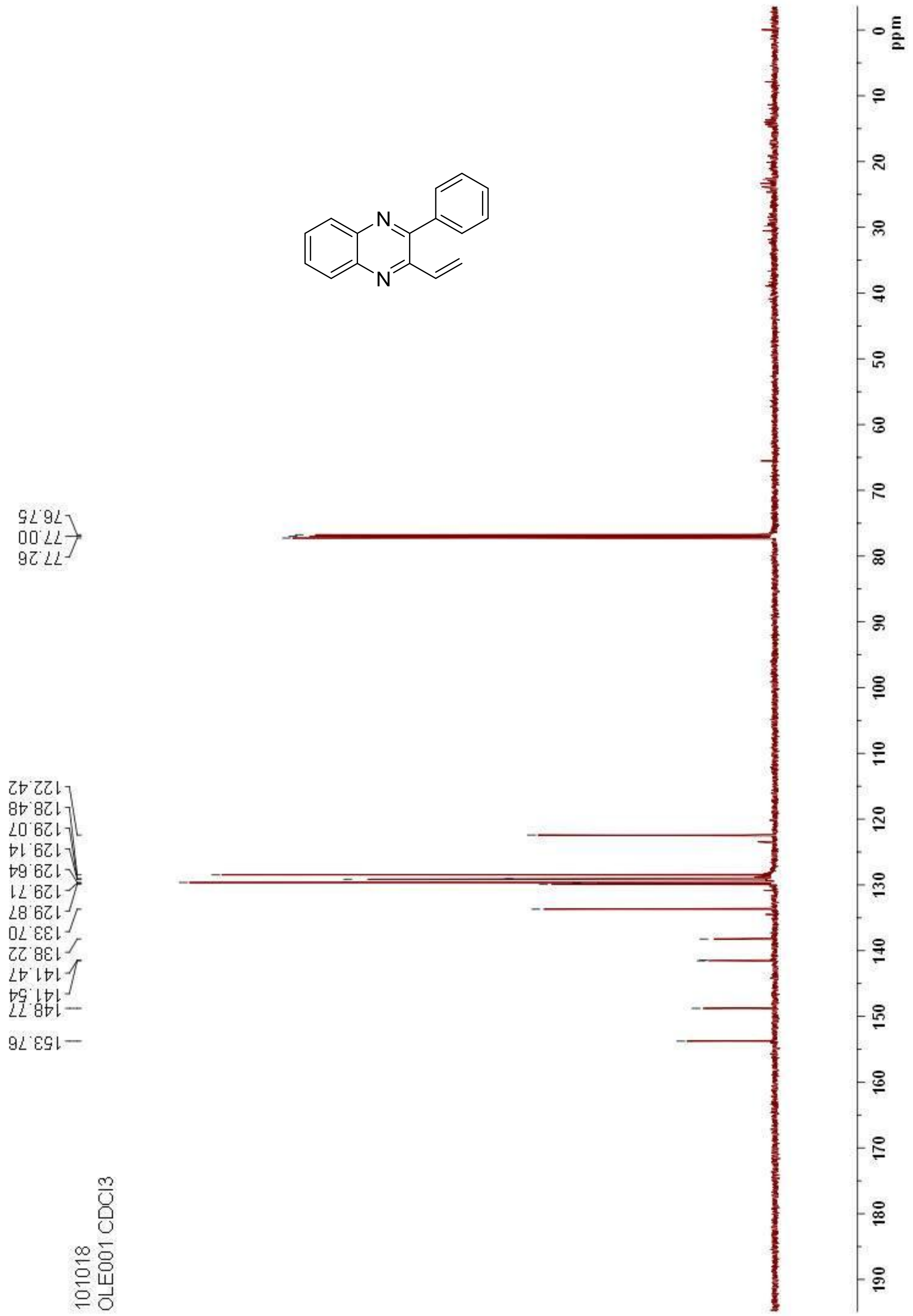
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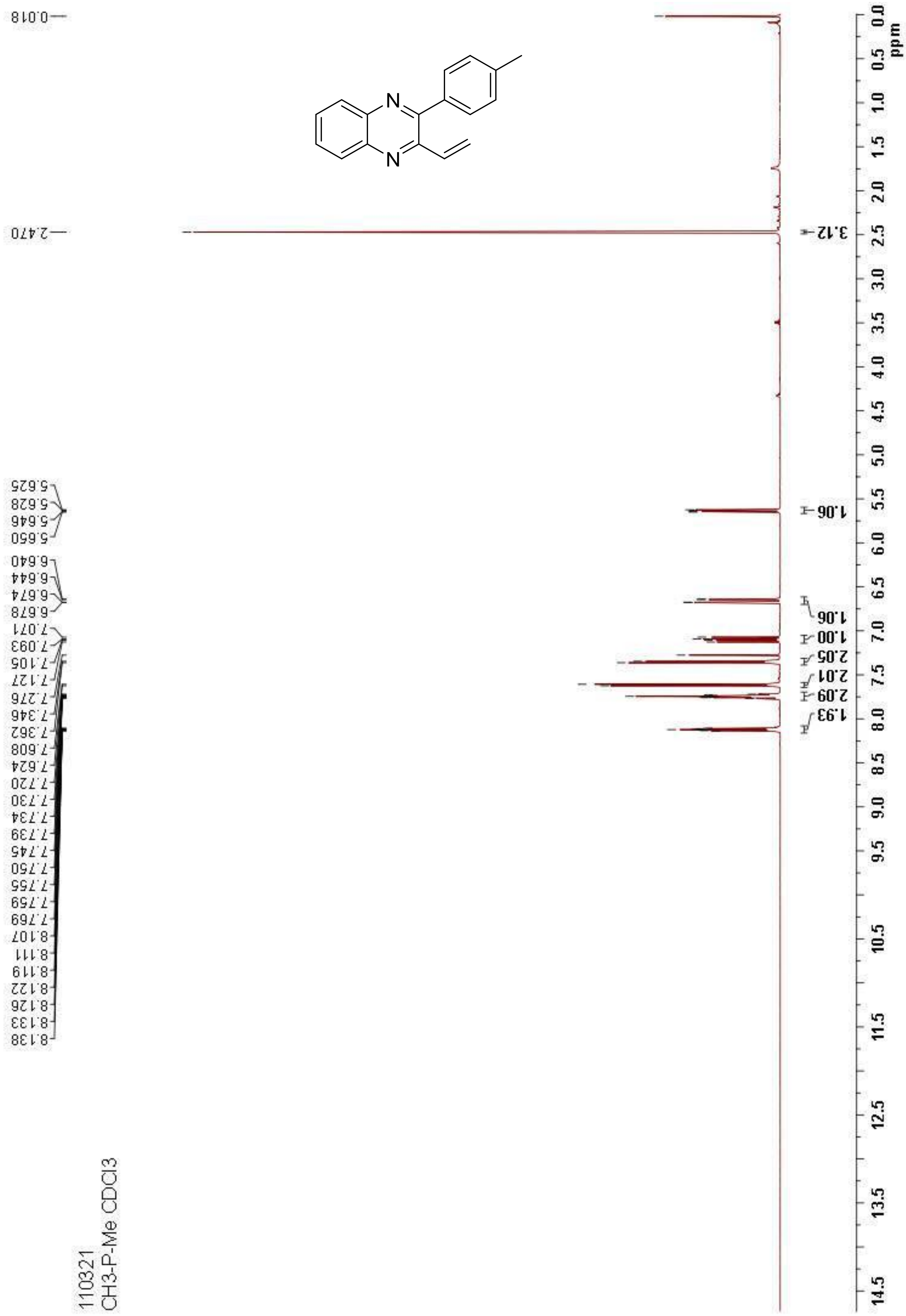
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6.644
6.674
6.678
7.071
7.093
7.105
7.127
7.276
7.346
7.362
7.608
7.624
7.720
7.730
7.734
7.739
7.745
7.750
7.755
7.759
7.769
8.107
8.111
8.119
8.122
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8.138
3.12
1.06
1.06
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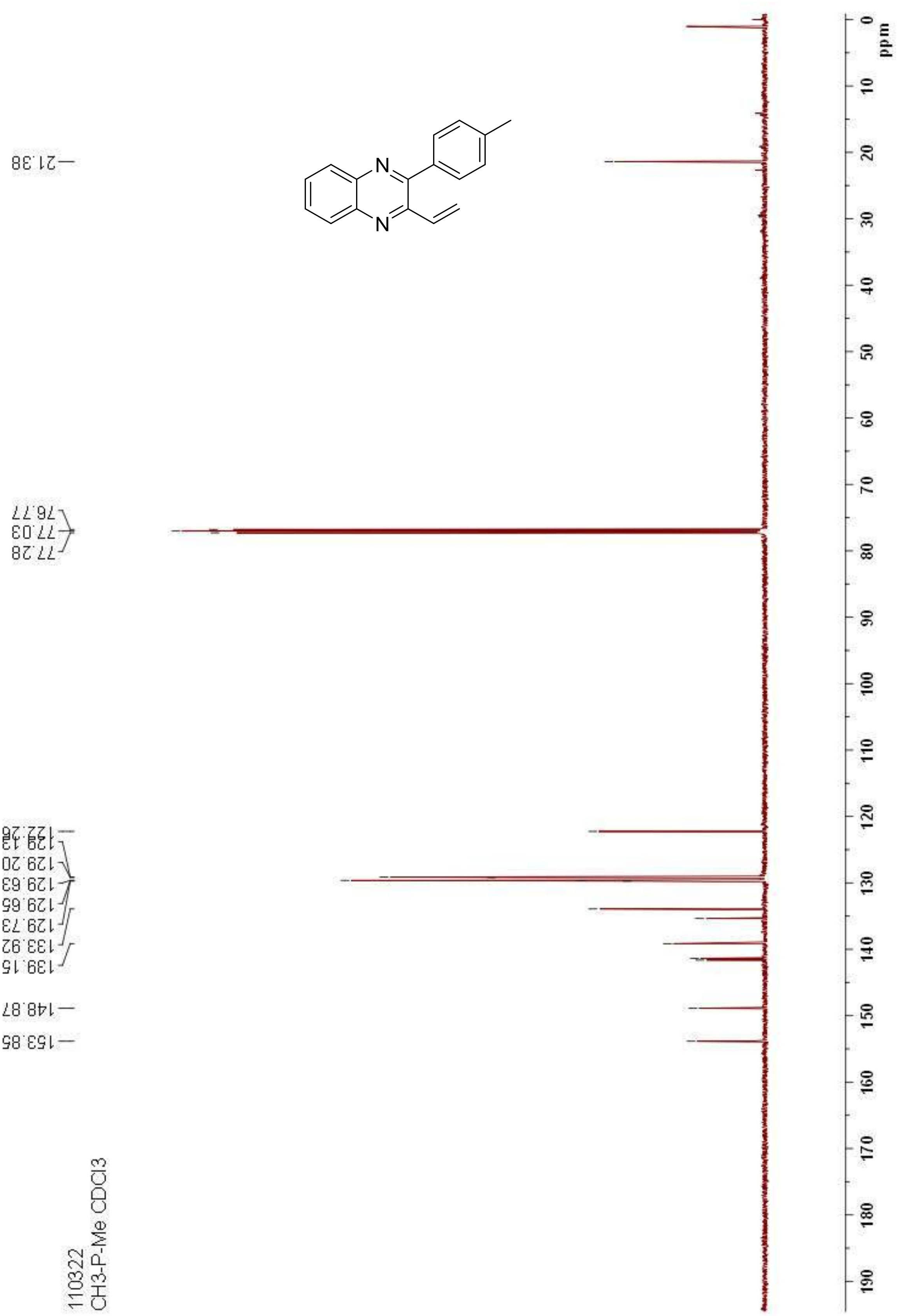
2.05
2.01
2.09
1.93
ppm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77.03
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133.92
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153.85
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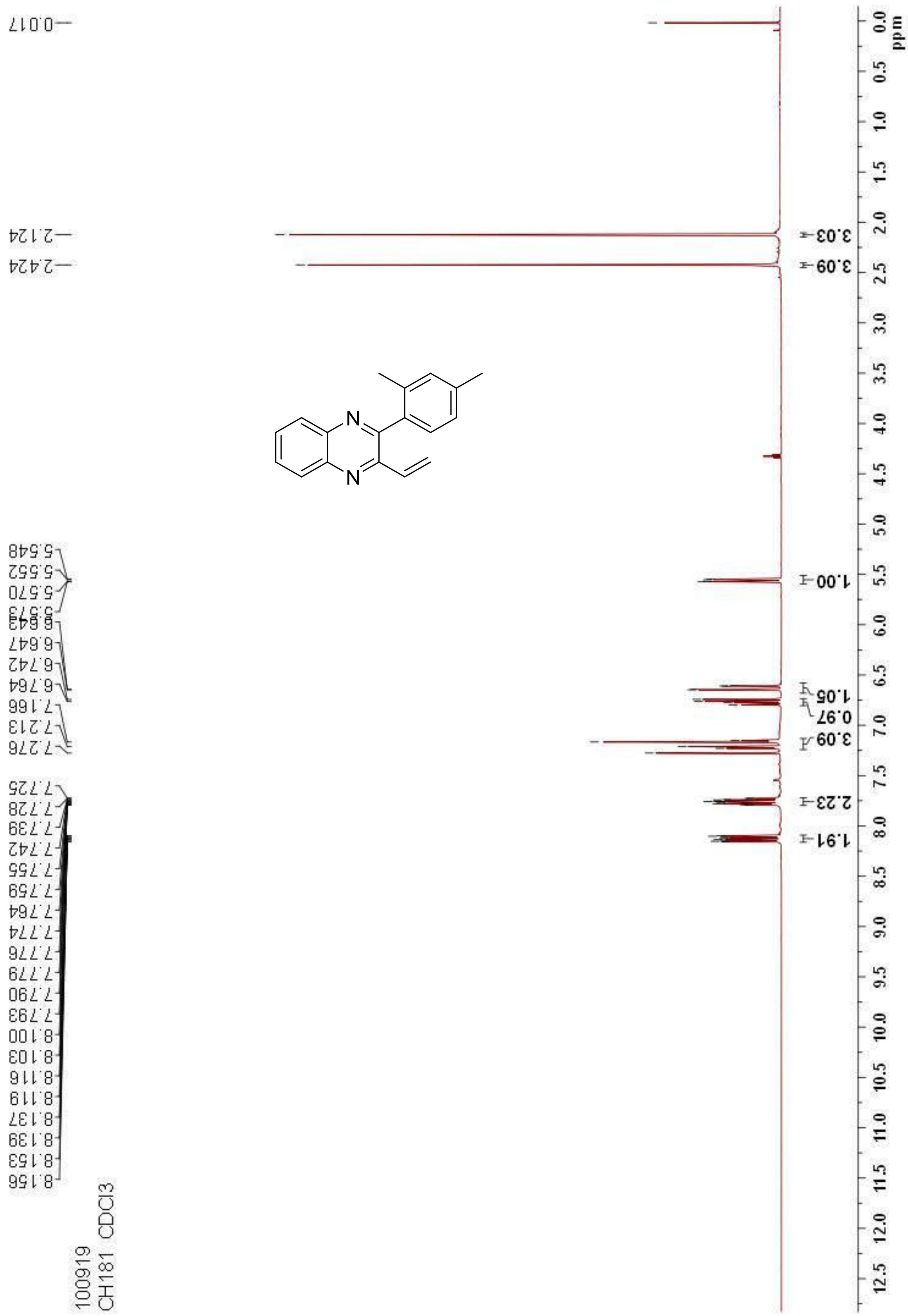
ppm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5.573
6.643
6.647
6.742
6.764
7.166
7.213
7.276
7.725
7.728
7.739
7.742
7.755
7.759
7.764
7.774
7.776
7.779
7.790
7.793
8.100
8.103
8.116
8.119
8.137
8.139
8.153
8.156
100919
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3.09
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1.05
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3.09
2.23
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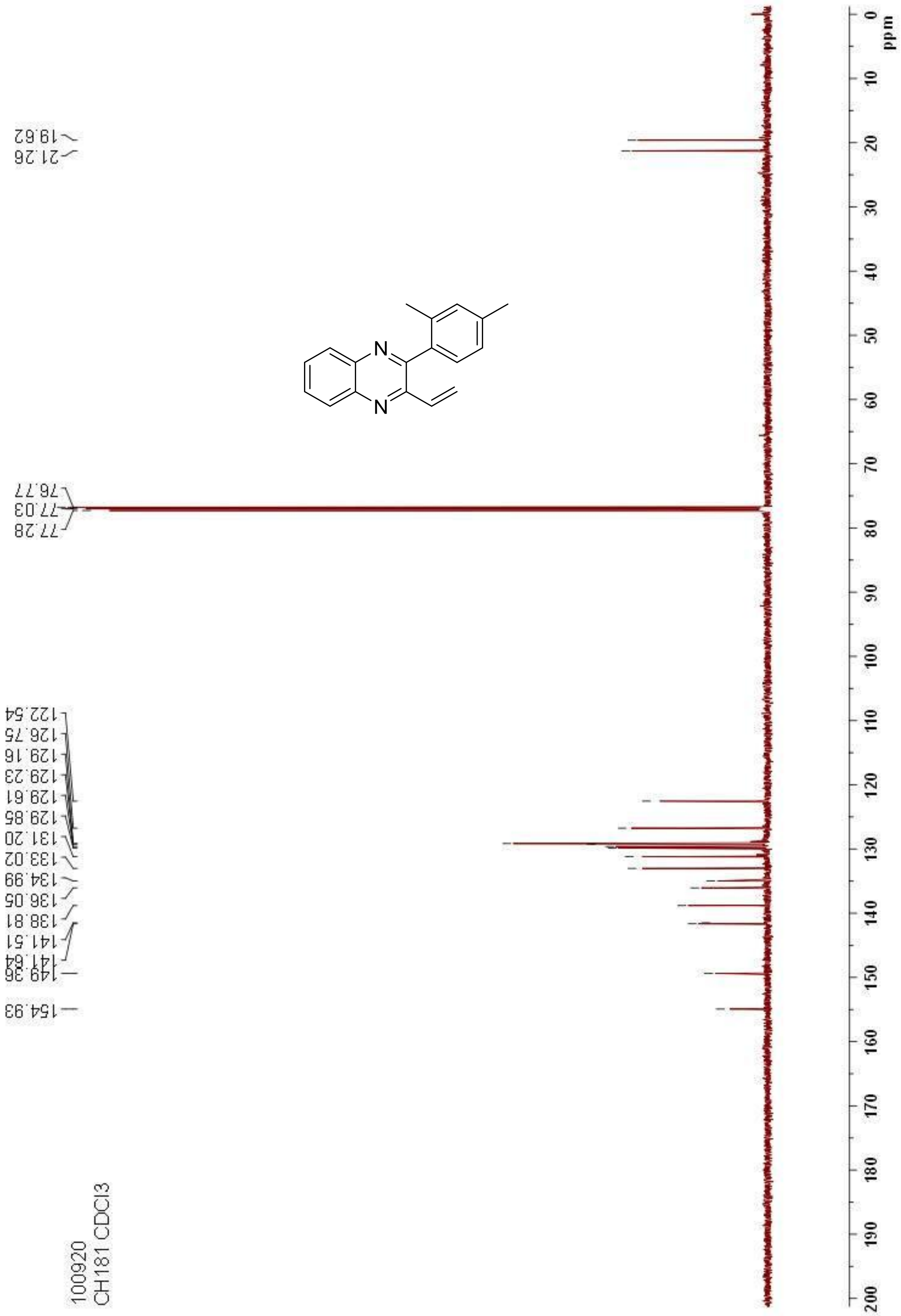
ppm
N
N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134.99
136.05
138.81
141.51
141.64
149.36
154.93
100920
CH181 CDCl3
ppm
0
10
20
30
40
50
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70
80
90
100
110
120
130
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150
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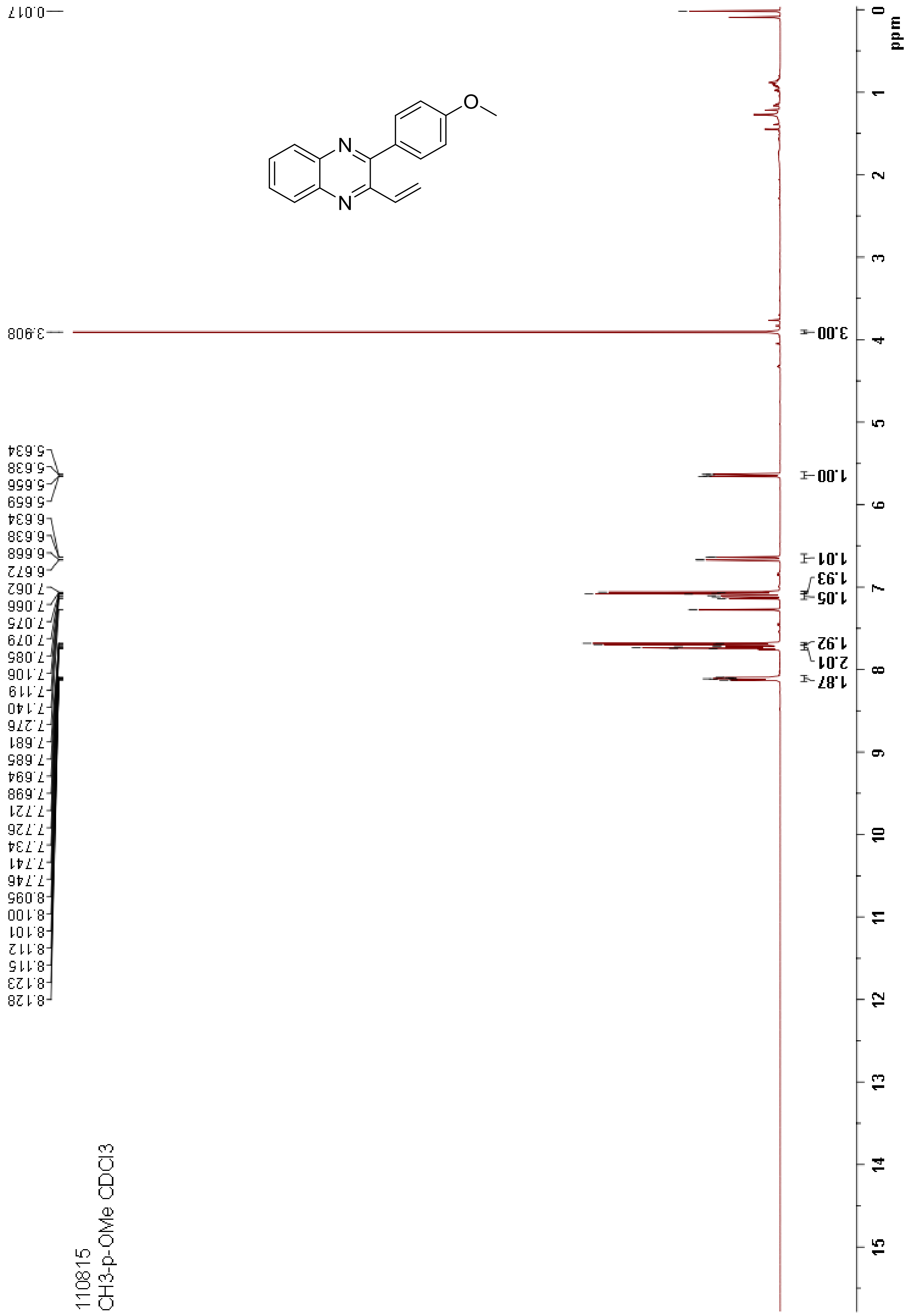
170
180
190
200
N
N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6.672
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7.066
7.075
7.079
7.085
7.106
7.119
7.140
7.276
7.681
7.685
7.694
7.698
7.721
7.726
7.734
7.741
7.746
8.095
8.100
8.101
8.112
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8.123
8.128
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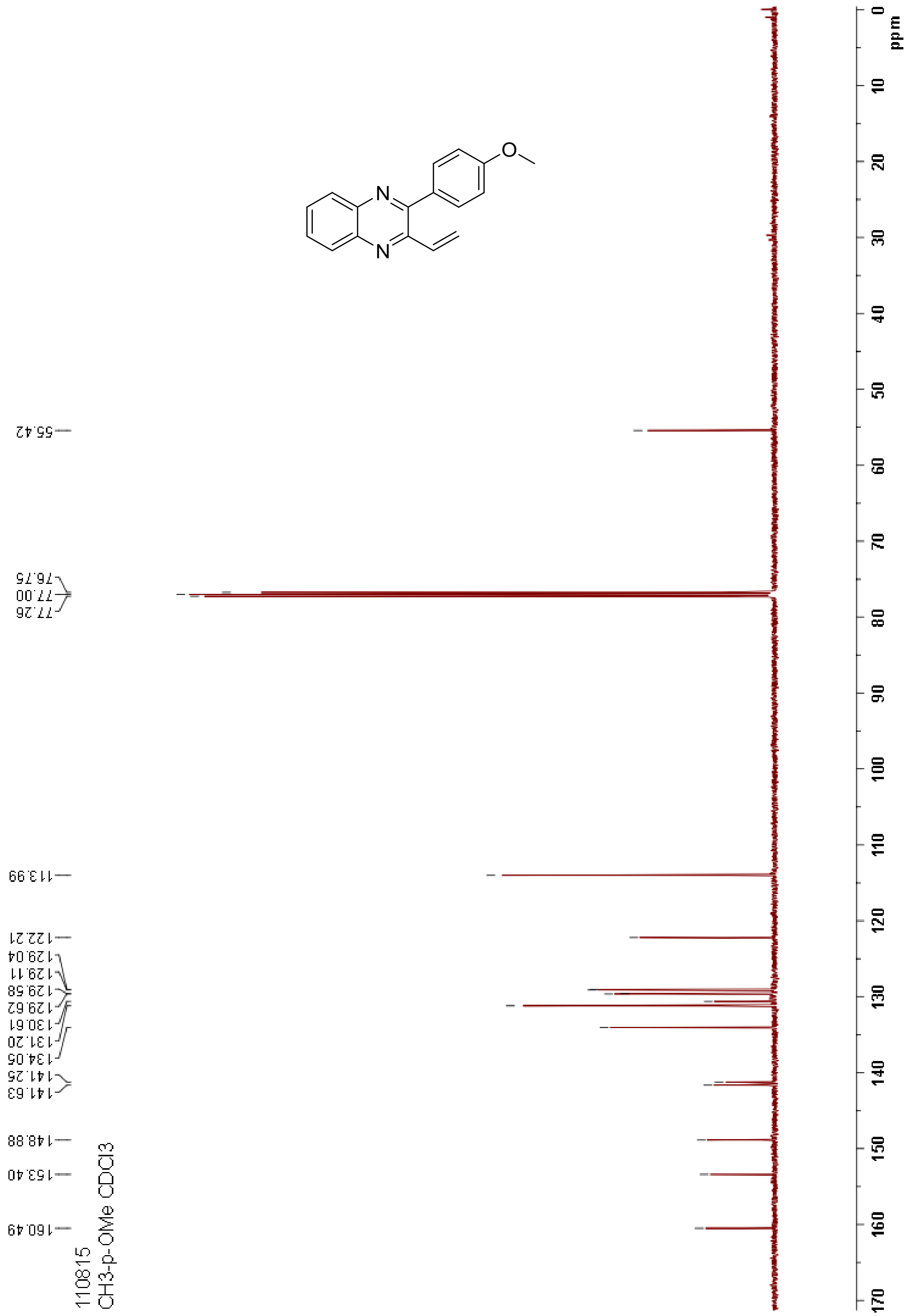
1.00
1.01
1.93
1.05
1.92
2.01
1.87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141.25
141.63
148.88
153.40
160.49
110815
CH3-p-OMe CDCl3
N
N
O
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160
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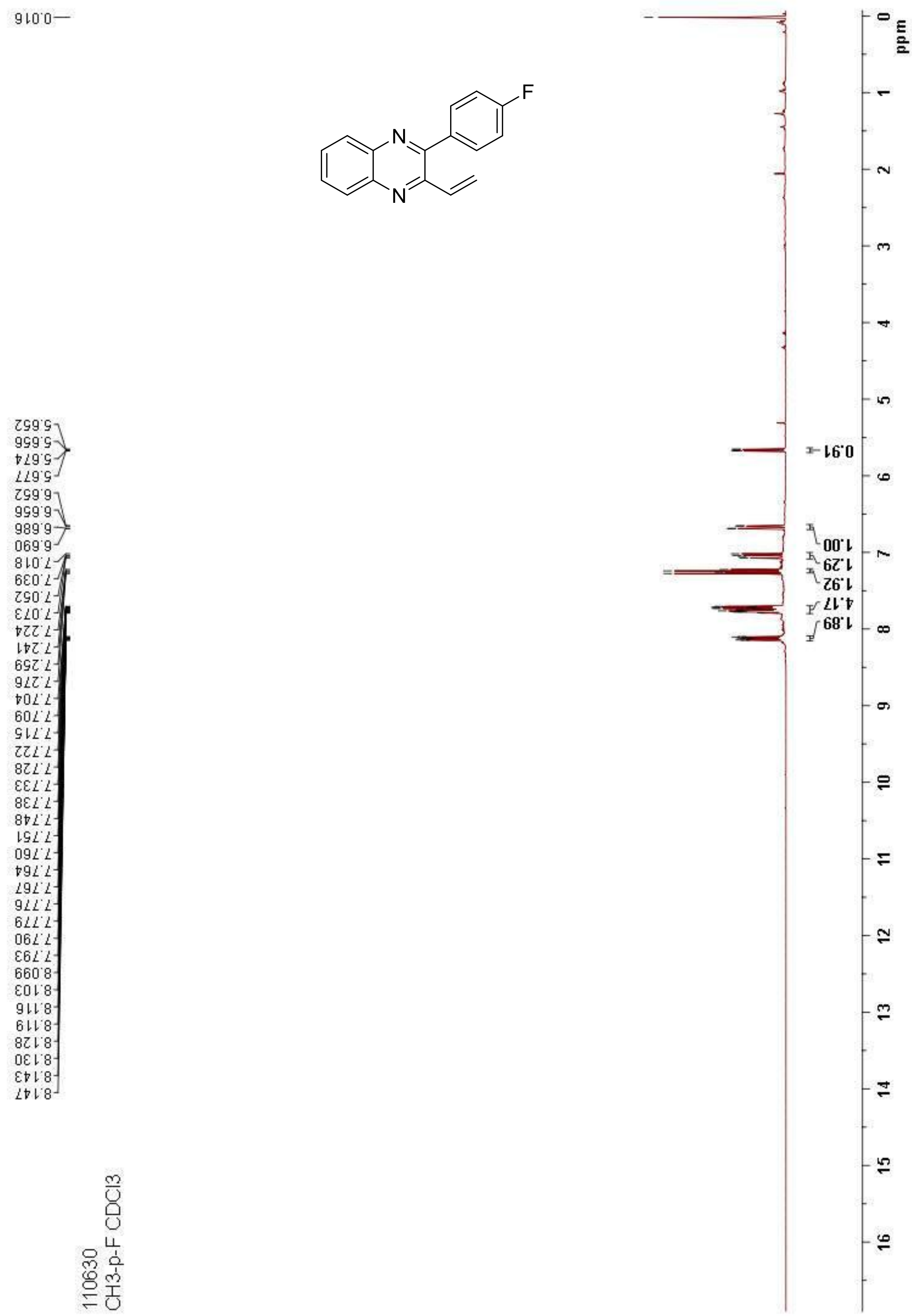
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6.690
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7.039
7.052
7.073
7.224
7.241
7.259
7.276
7.704
7.709
7.715
7.722
7.728
7.733
7.738
7.748
7.751
7.760
7.764
7.767
7.776
7.779
7.790
7.793
8.099
8.103
8.116
8.119
8.128
8.130
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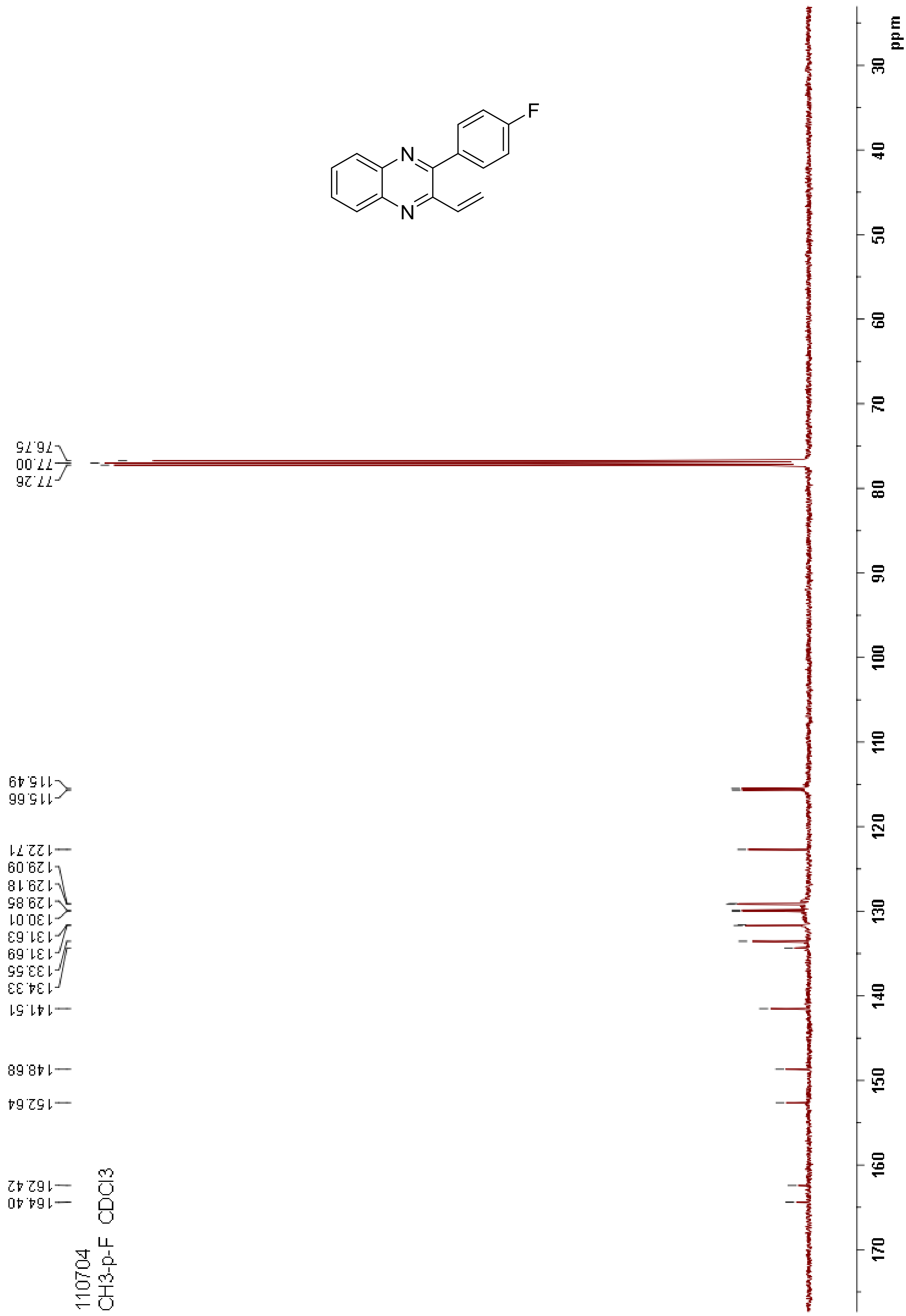
ppm



N
N
F
76.75
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77.26
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115.66
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129.18
129.85
130.01
131.63
131.69
133.55
134.33
141.51
148.68
152.64
162.42
164.40
110704
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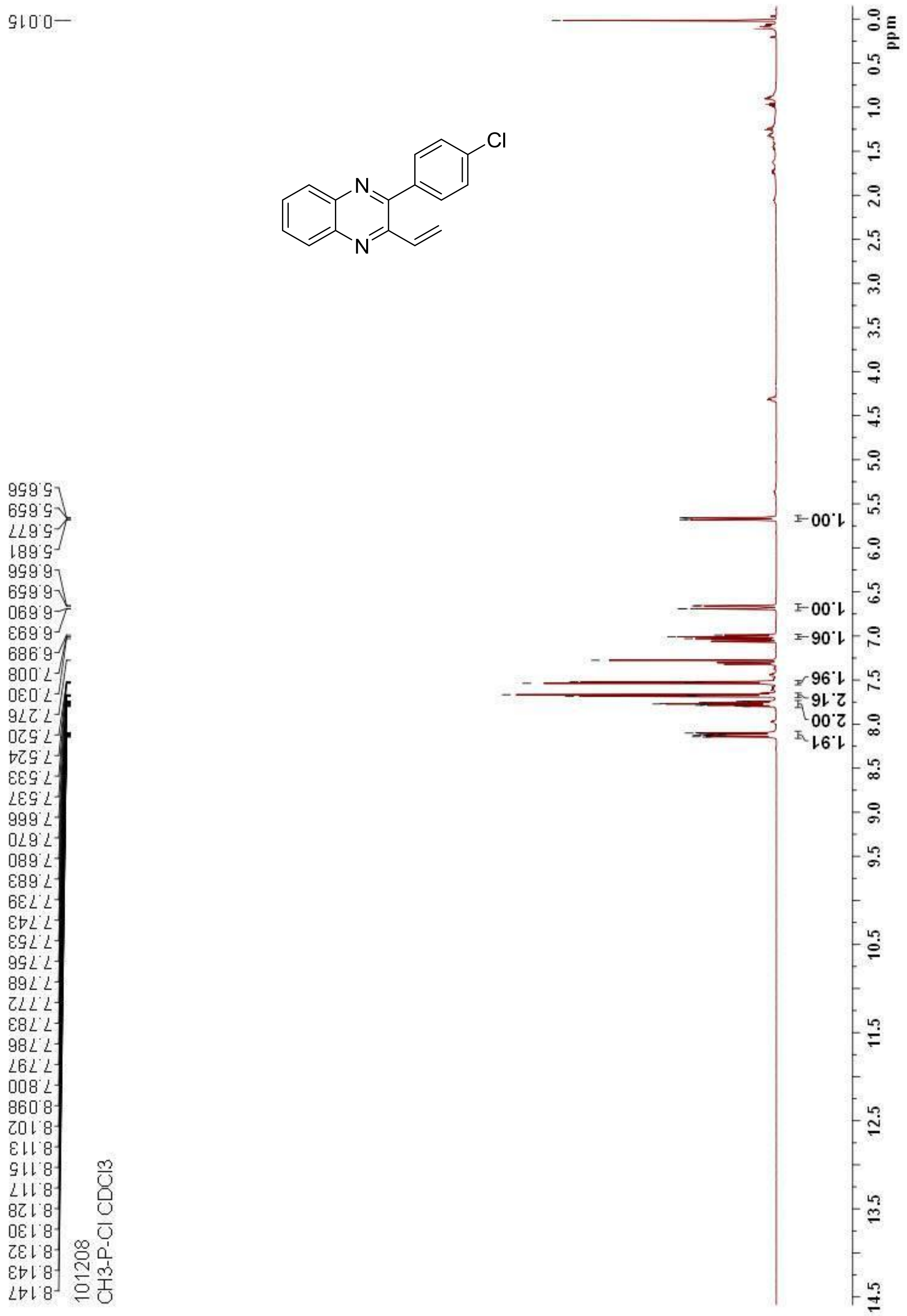
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N
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5.677
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6.690
6.693
6.989
7.008
7.030
7.276
7.520
7.524
7.533
7.537
7.666
7.670
7.680
7.683
7.739
7.743
7.753
7.756
7.768
7.772
7.783
7.786
7.797
7.800
8.098
8.102
8.113
8.115
8.117
8.128
8.130
8.132
8.143
8.147
101208
CH3-P-Cl CDCl3
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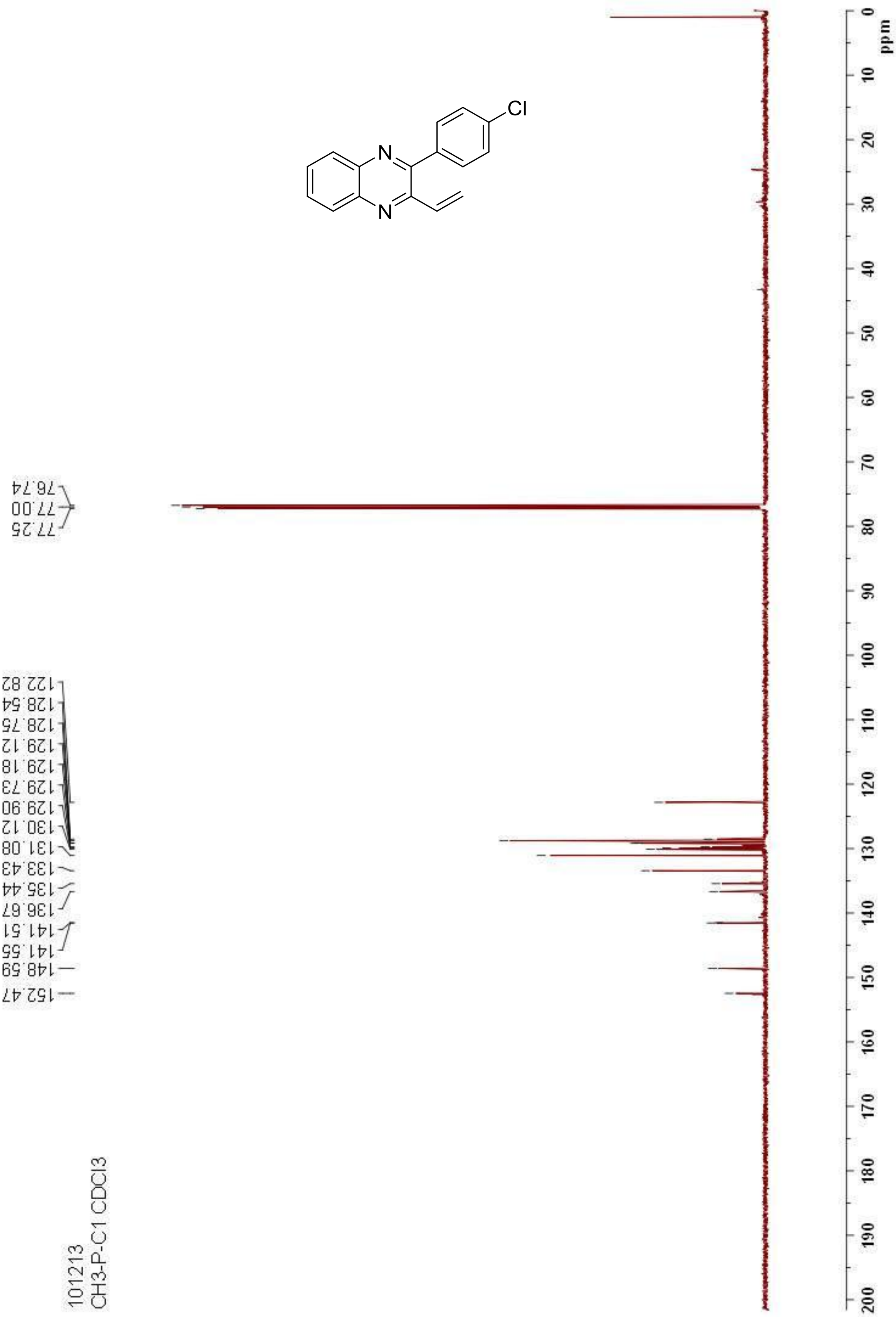
1.96
2.16
2.00
1.91
ppm


101213
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133.43
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130.12
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129.18
129.12
128.75
128.54
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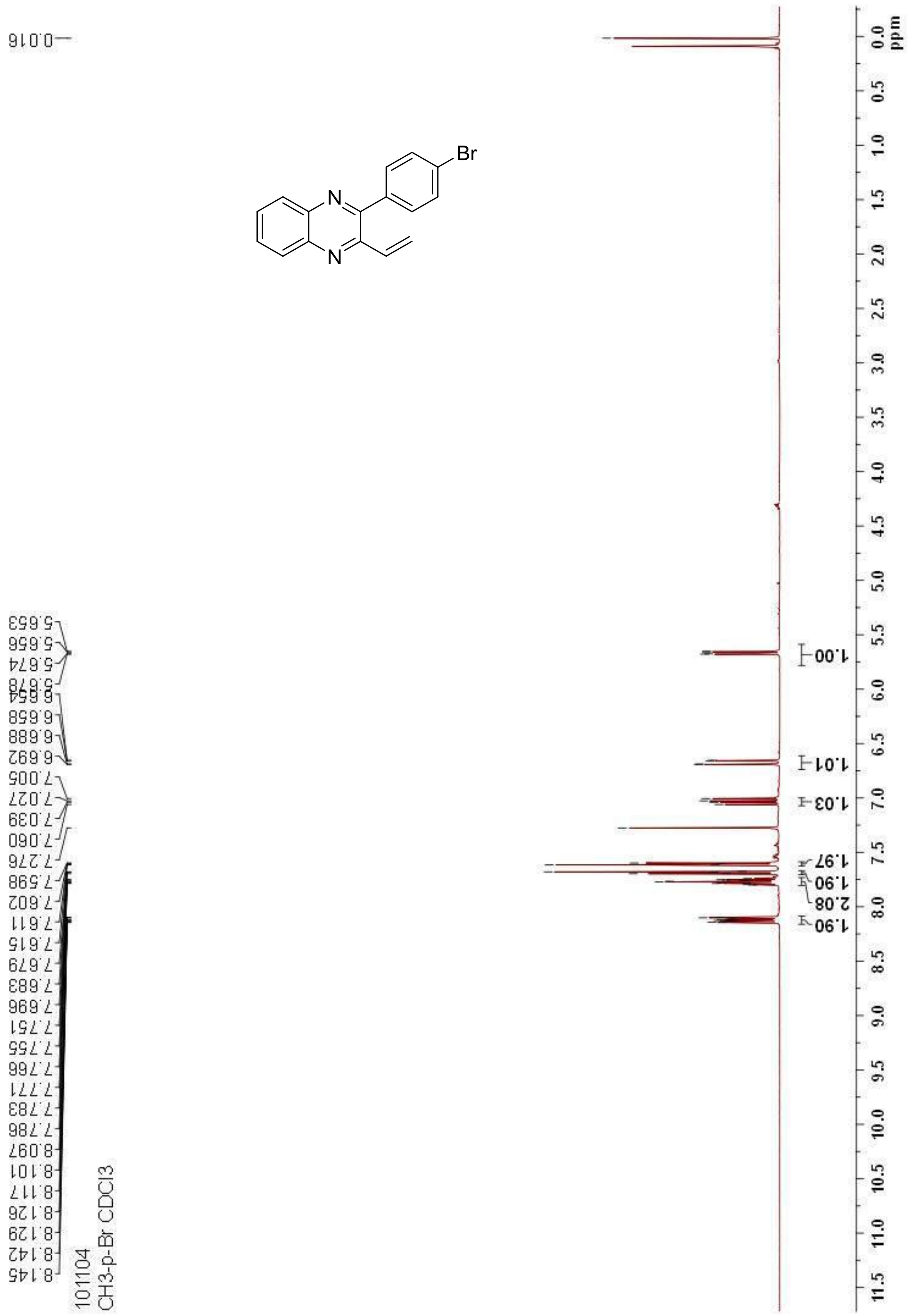
77.00
76.74
ppm
Cl
N
N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5.653
5.656
5.674
5.678
6.654
6.658
6.688
6.692
7.005
7.027
7.039
7.060
7.276
7.598
7.602
7.611
7.615
7.679
7.683
7.696
7.751
7.755
7.766
7.771
7.783
7.786
8.097
8.101
8.117
8.126
8.129
8.142
8.145
101104
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N
N
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1.97
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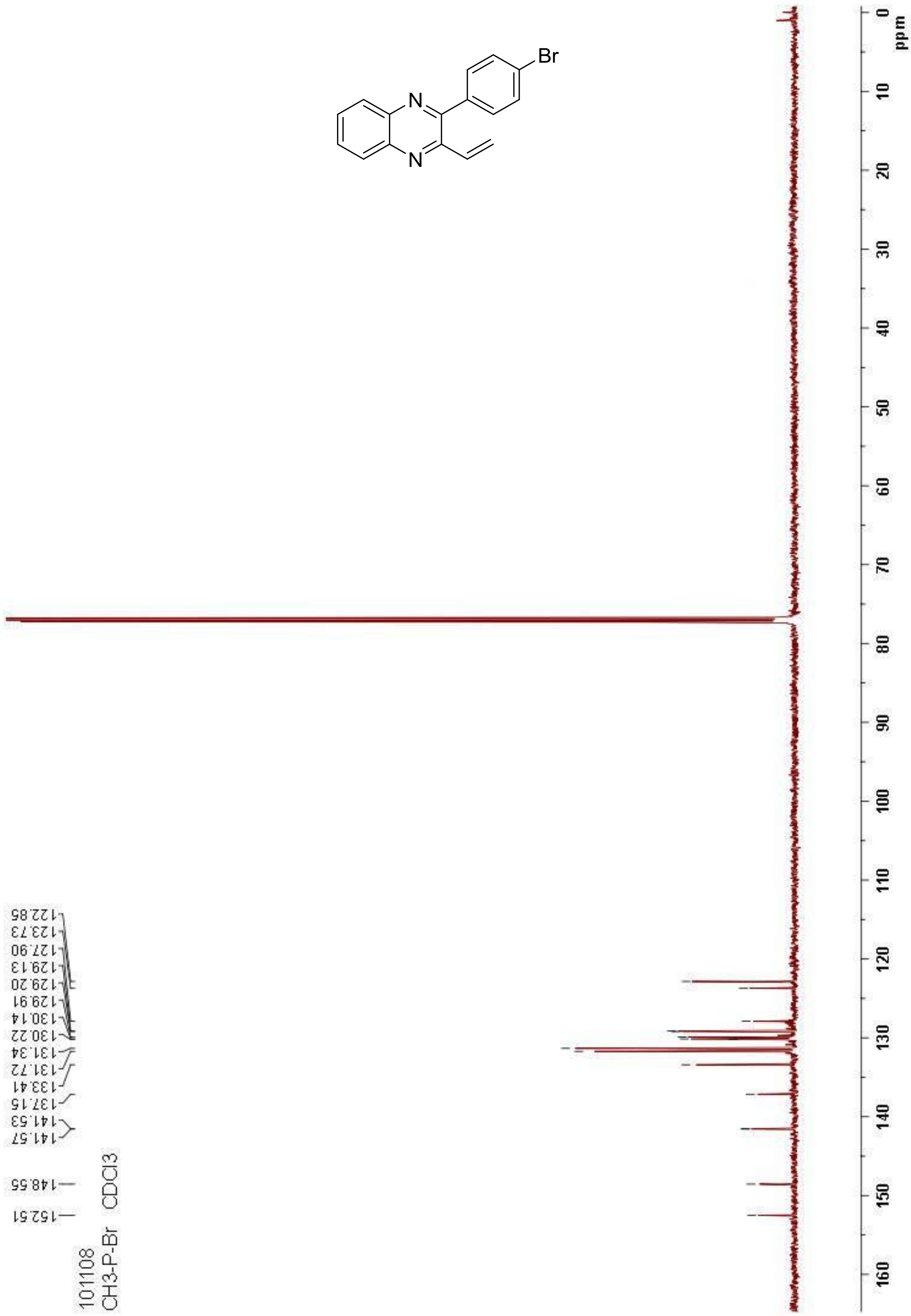
2.08
1.90
ppm


Br
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N
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141.57
141.53
137.15
133.41
131.72
131.34
130.22
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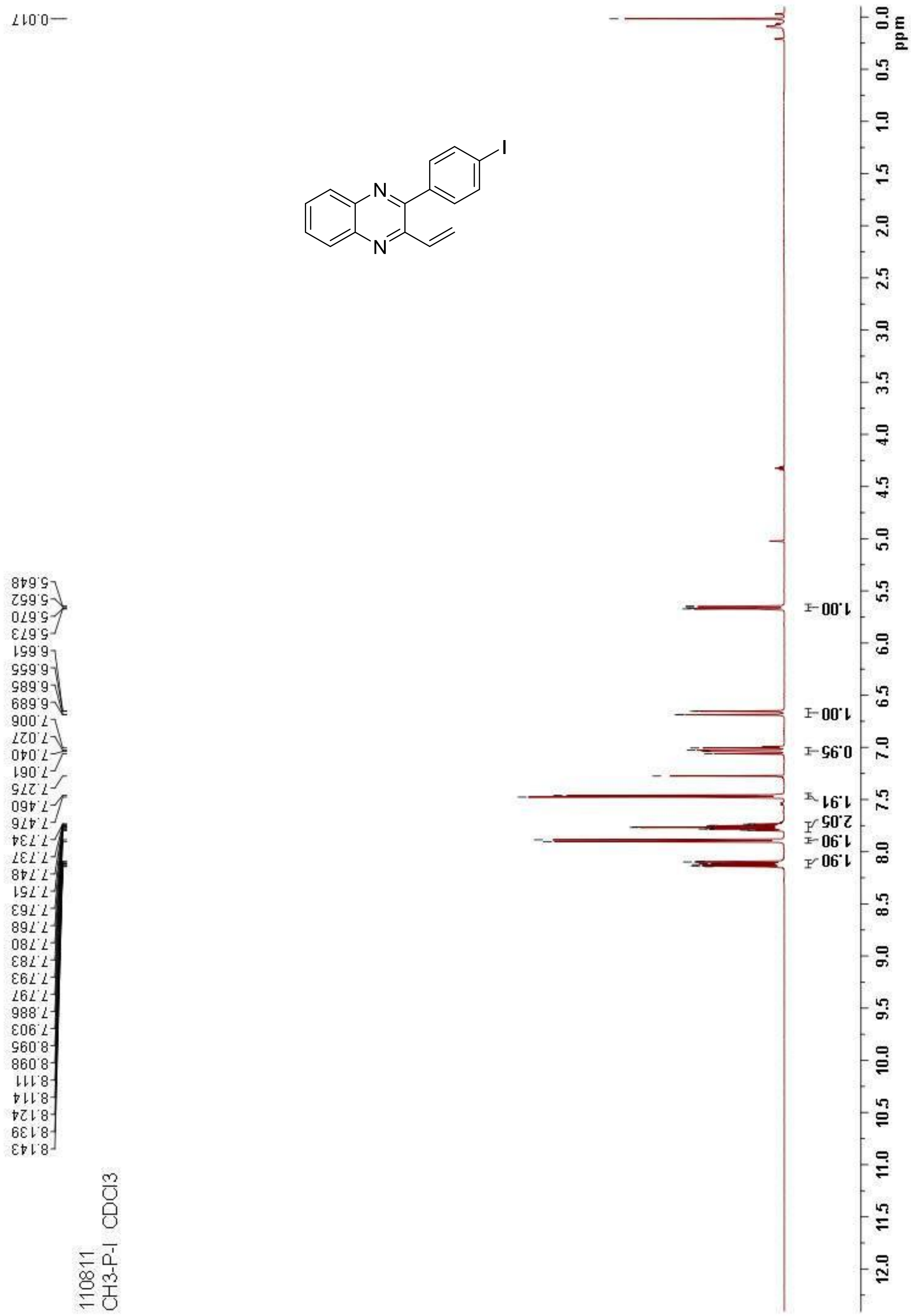
129.91
129.20
129.13
127.90
123.73
122.85
101108
CH3-P-Br CDCl3
ppm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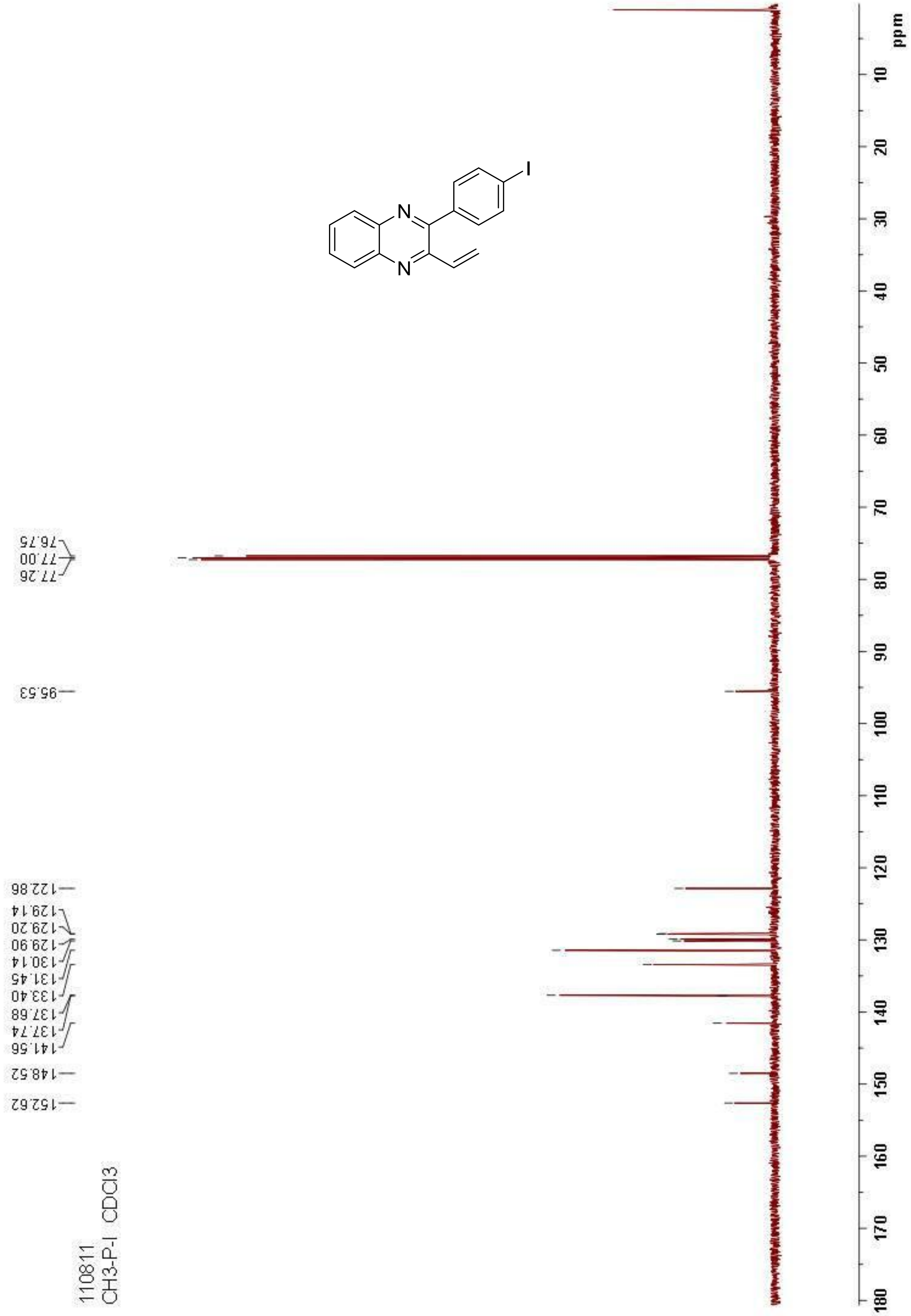
CH3-P-I CDCl3
ppm


76.75
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129.90
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133.40
137.68
137.74
141.56
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152.62
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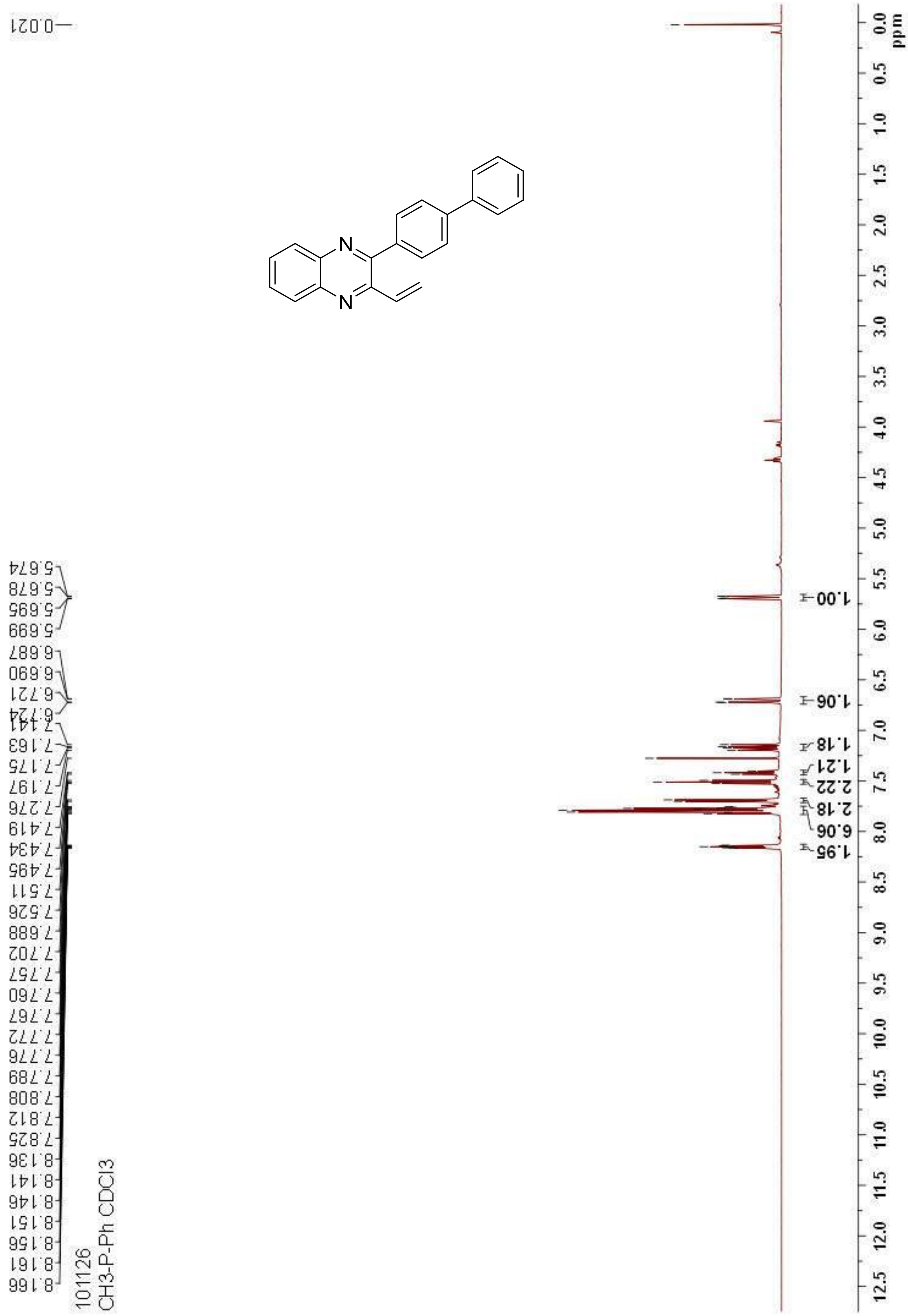
ppm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6.721
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7.141
7.163
7.175
7.197
7.276
7.419
7.434
7.495
7.511
7.526
7.688
7.702
7.757
7.760
7.767
7.772
7.776
7.789
7.808
7.812
7.825
8.136
8.141
8.146
8.151
8.156
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2.18
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ppm
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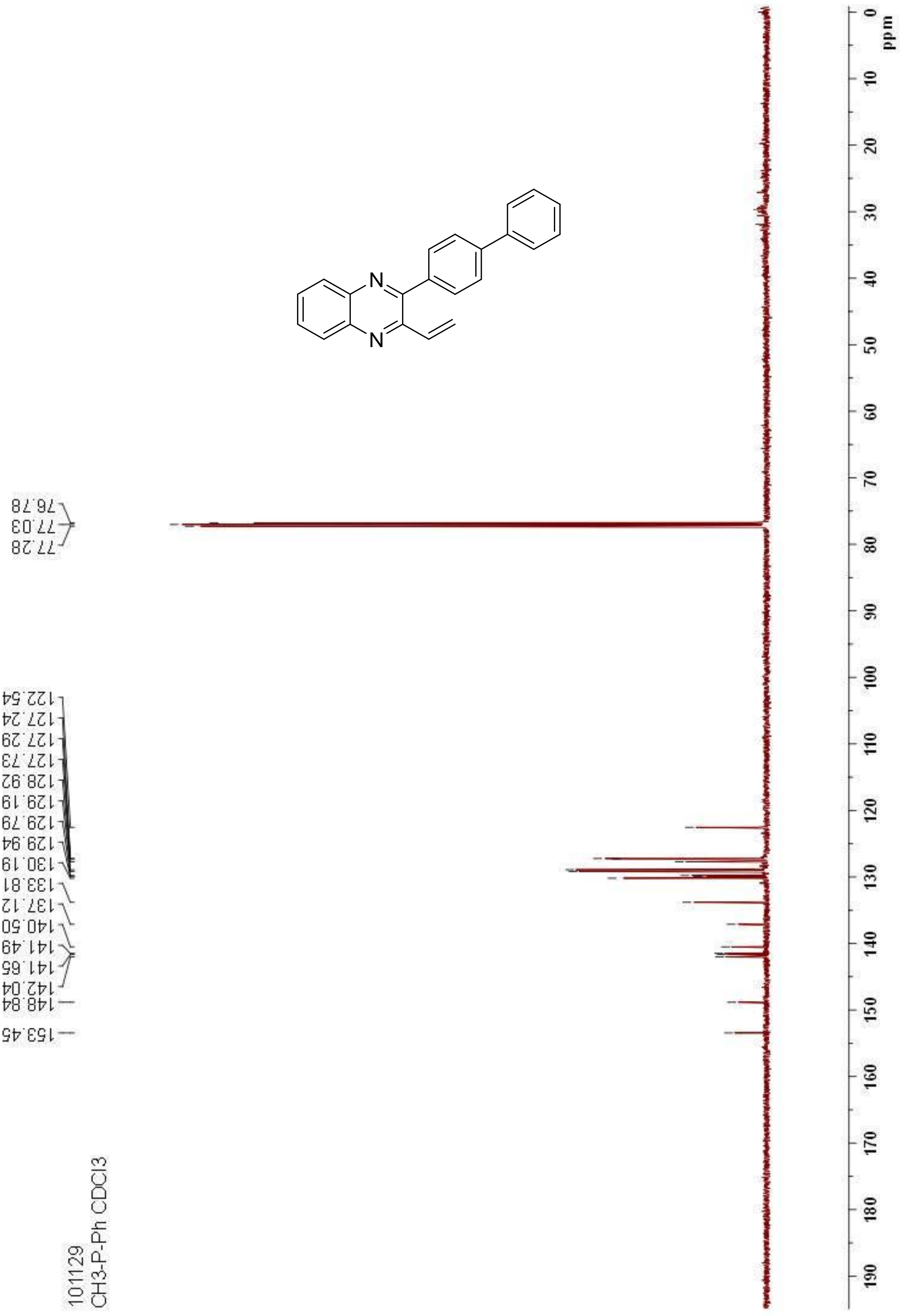
N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127.73
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130.19
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153.45
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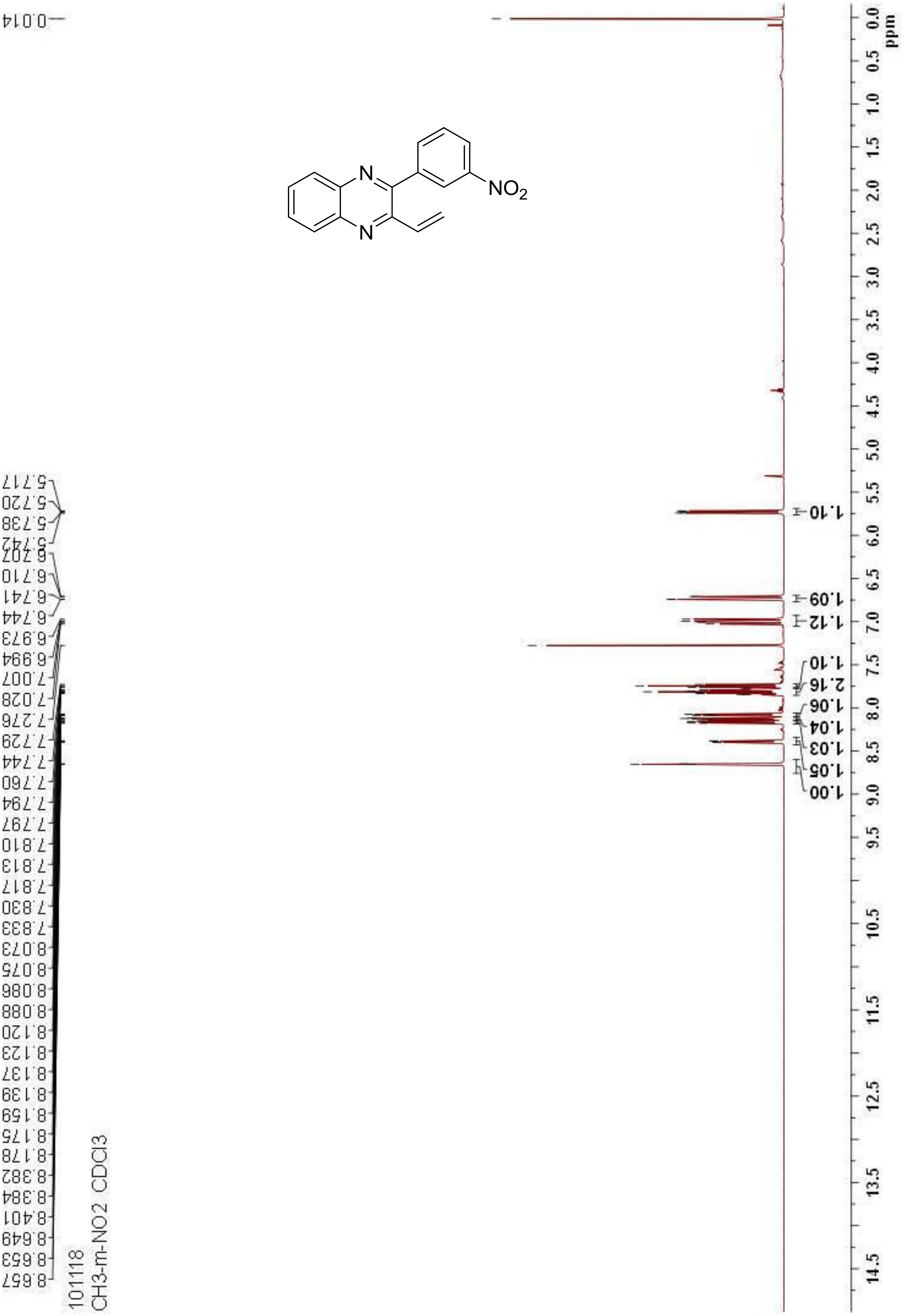
ppm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6.741
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6.973
6.994
7.007
7.028
7.276
7.729
7.744
7.760
7.794
7.797
7.810
7.813
7.817
7.830
7.833
8.073
8.075
8.086
8.088
8.120
8.123
8.137
8.139
8.159
8.175
8.178
8.382
8.384
8.401
8.649
8.653
8.657
101118
CH3-m-NO2 CDCl3
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1.09
1.12
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1.04
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1.00
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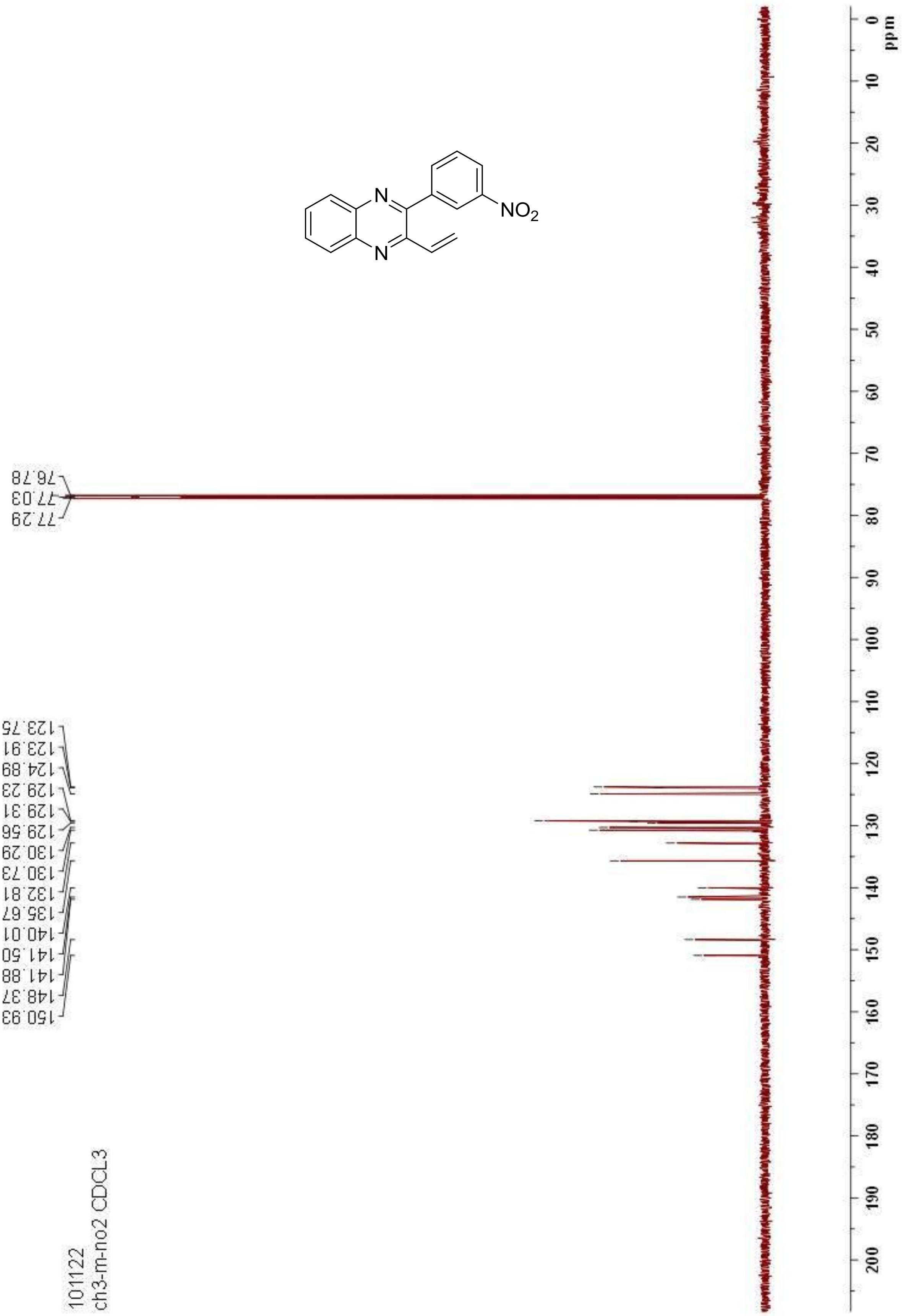
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135.67
140.01
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150.93
101122
ch3-m-no2 CDCL3
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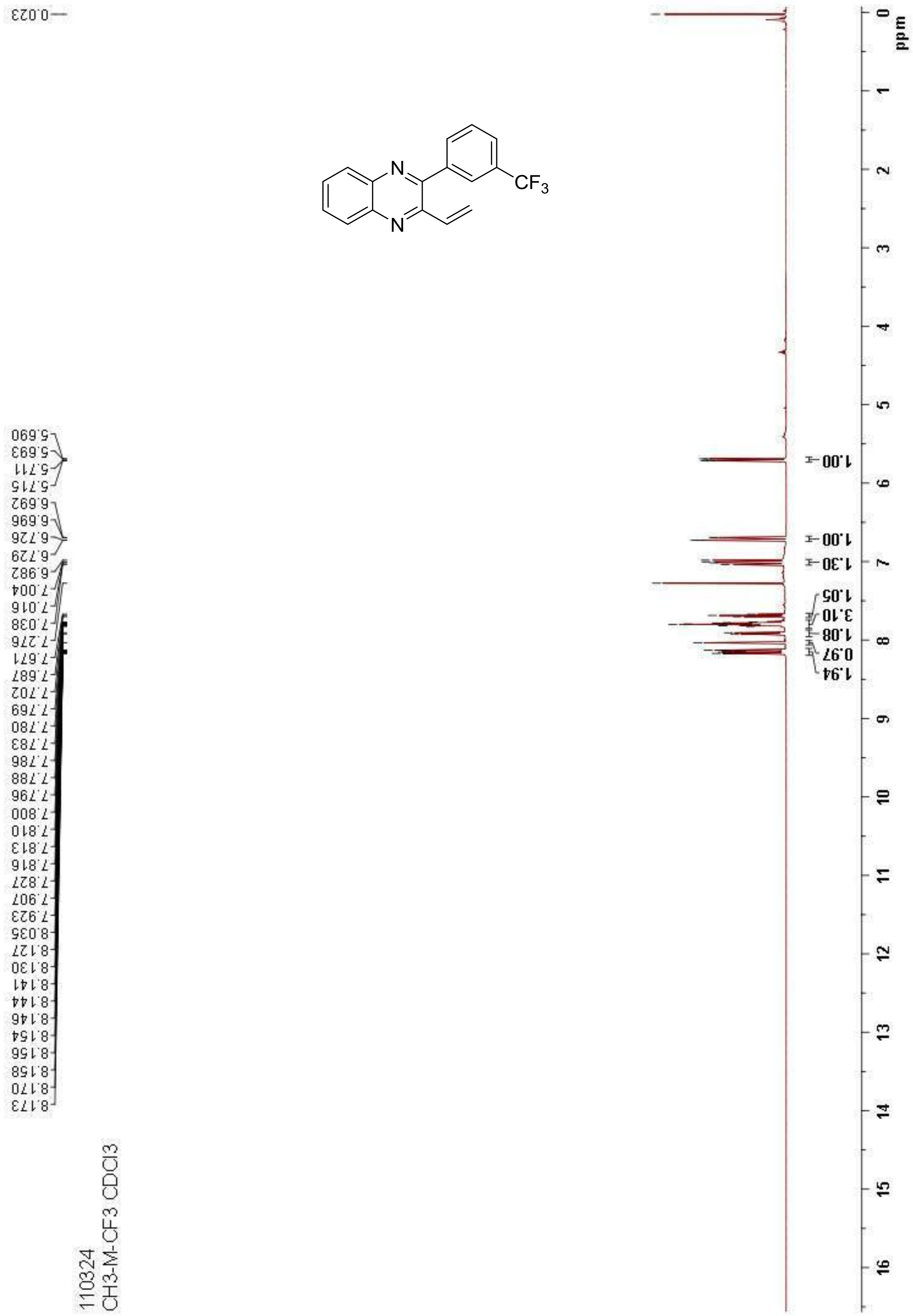
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6.729
6.982
7.004
7.016
7.038
7.276
7.671
7.687
7.702
7.769
7.780
7.783
7.786
7.788
7.796
7.800
7.810
7.813
7.816
7.827
7.907
7.923
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8.127
8.130
8.141
8.144
8.146
8.154
8.156
8.158
8.170
8.173
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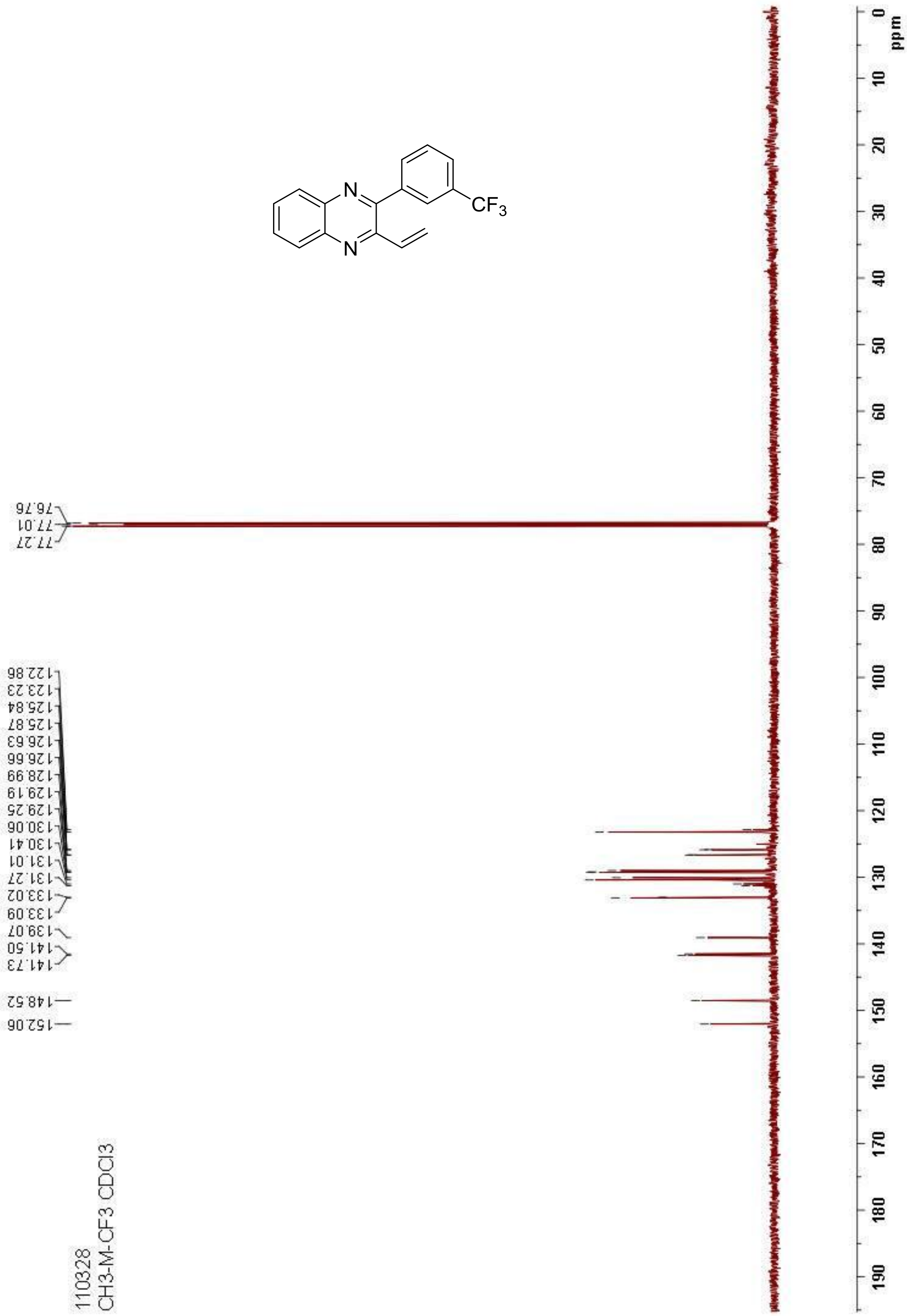
ppm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126.63
126.66
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129.19
129.25
130.06
130.41
131.01
131.27
133.02
133.09
139.07
141.50
141.73
148.52
152.06
110328
CH3-M-CF3 CDCl3
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60
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90
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130
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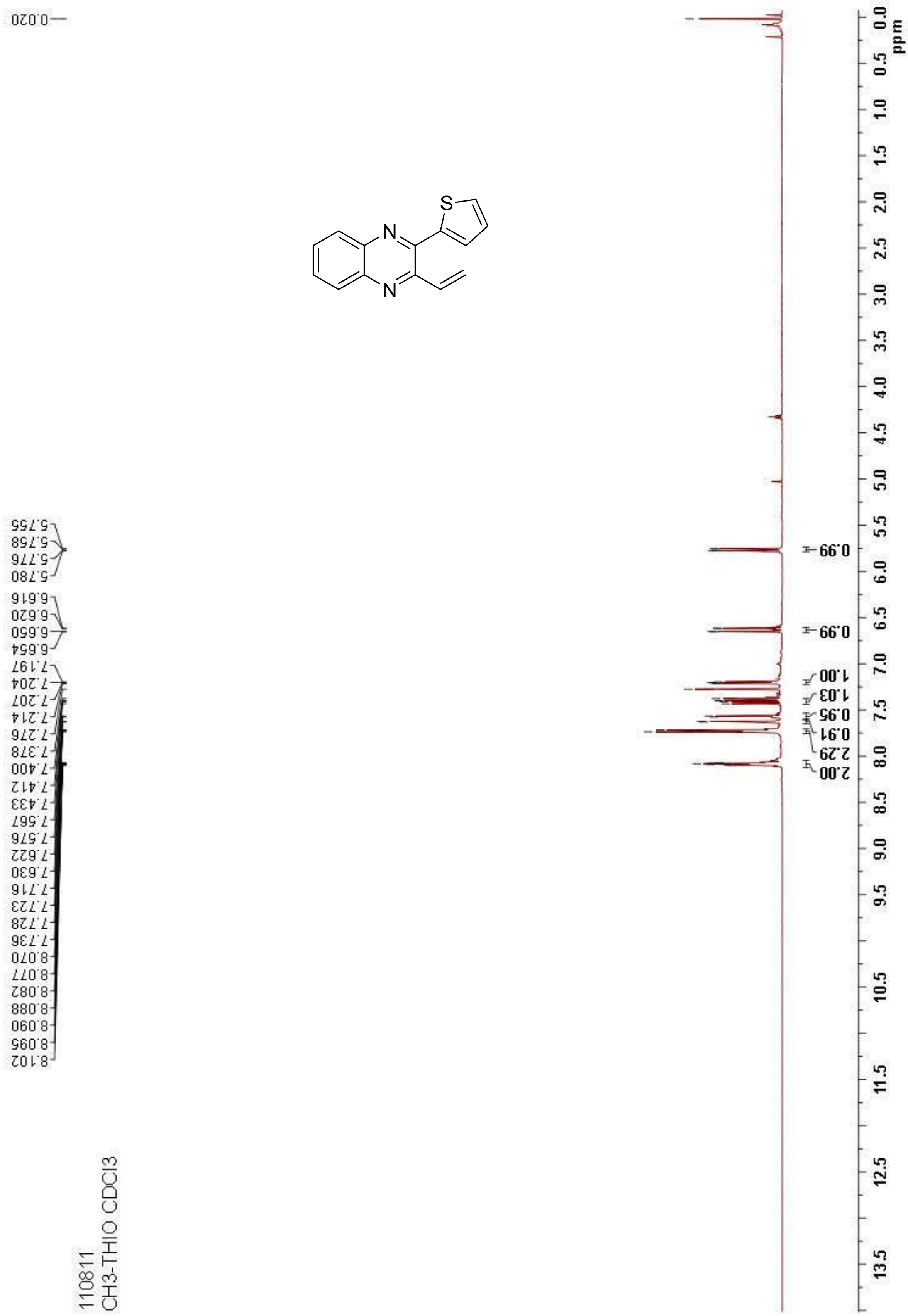
170
180
190
ppm



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6.620
6.650
6.654
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7.207
7.214
7.276
7.378
7.400
7.412
7.433
7.567
7.576
7.622
7.630
7.716
7.723
7.728
7.736
8.070
8.077
8.082
8.088
8.090
8.095
8.102
110811
CH3-THIO CDCl3
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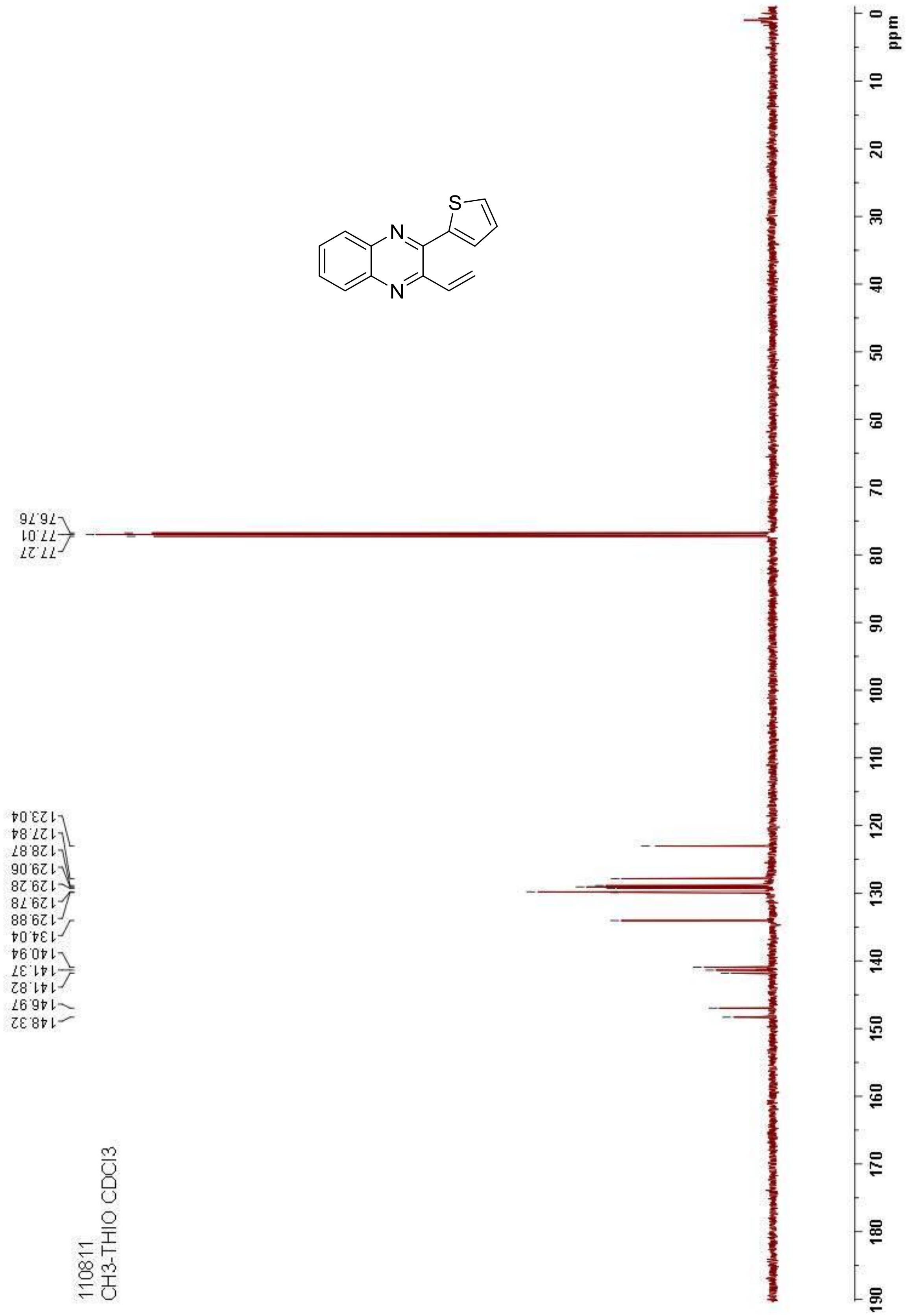
2.00
ppm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N
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77.27
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127.84
128.87
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134.04
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141.82
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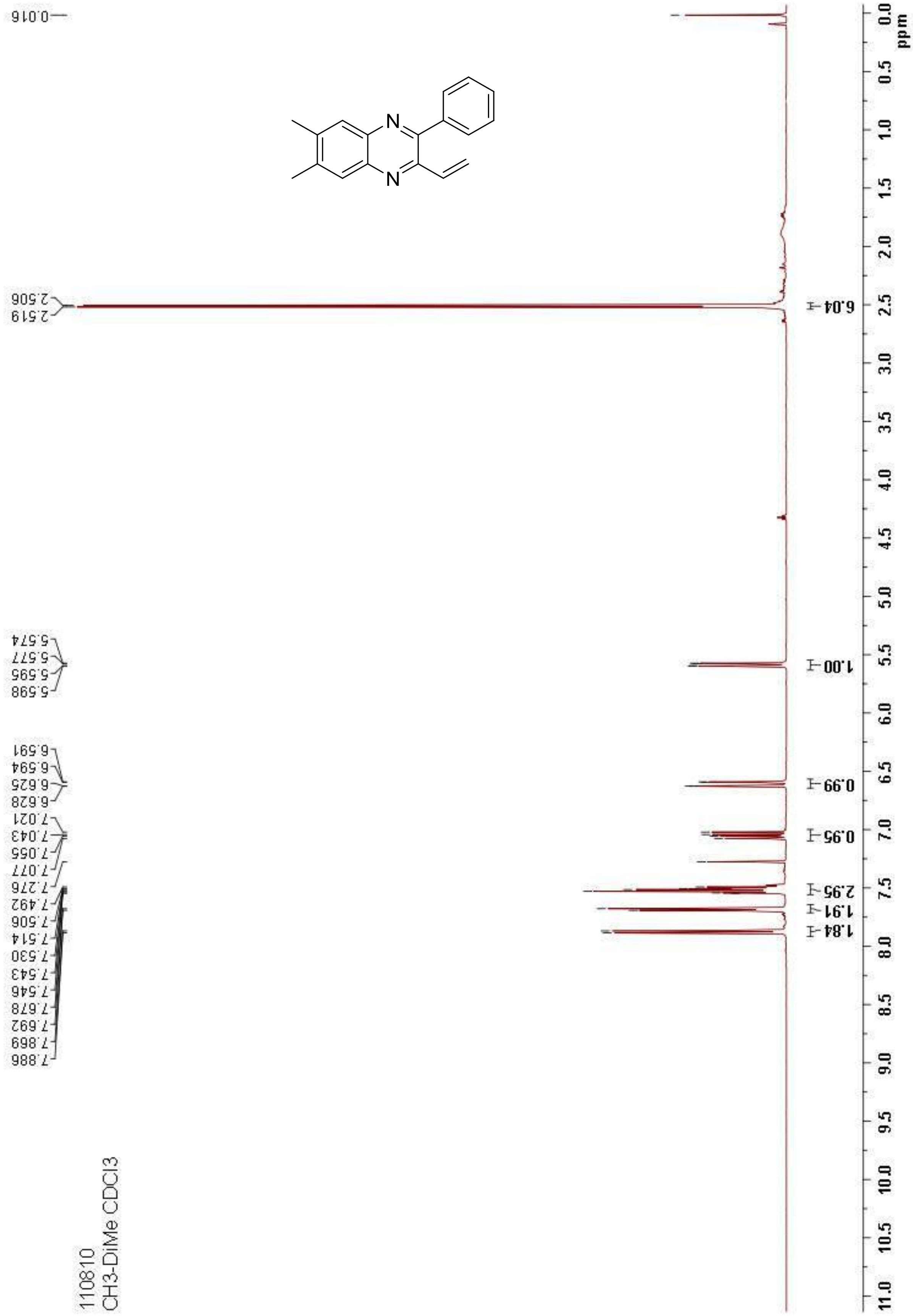
148.32
110811
CH3-THIO CDCl3
ppm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7.043
7.065
7.077
7.276
7.492
7.506
7.514
7.530
7.543
7.546
7.678
7.692
7.869
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ppm
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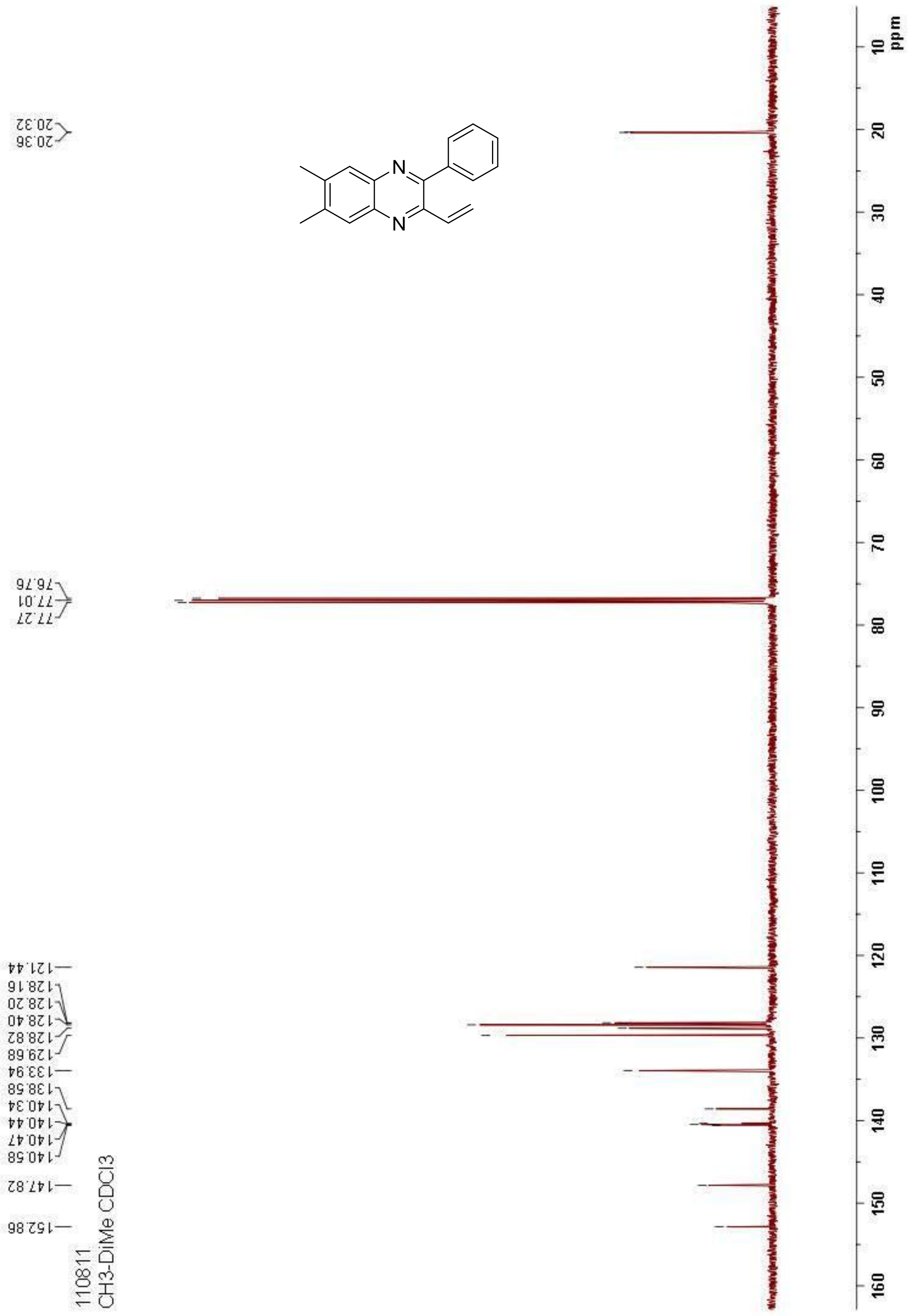
CH3-DiMe CDCl3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128.82
129.68
133.94
138.58
140.34
140.44
140.47
140.58
147.82
152.86
110811
CH3-DiMe CDCl3
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N
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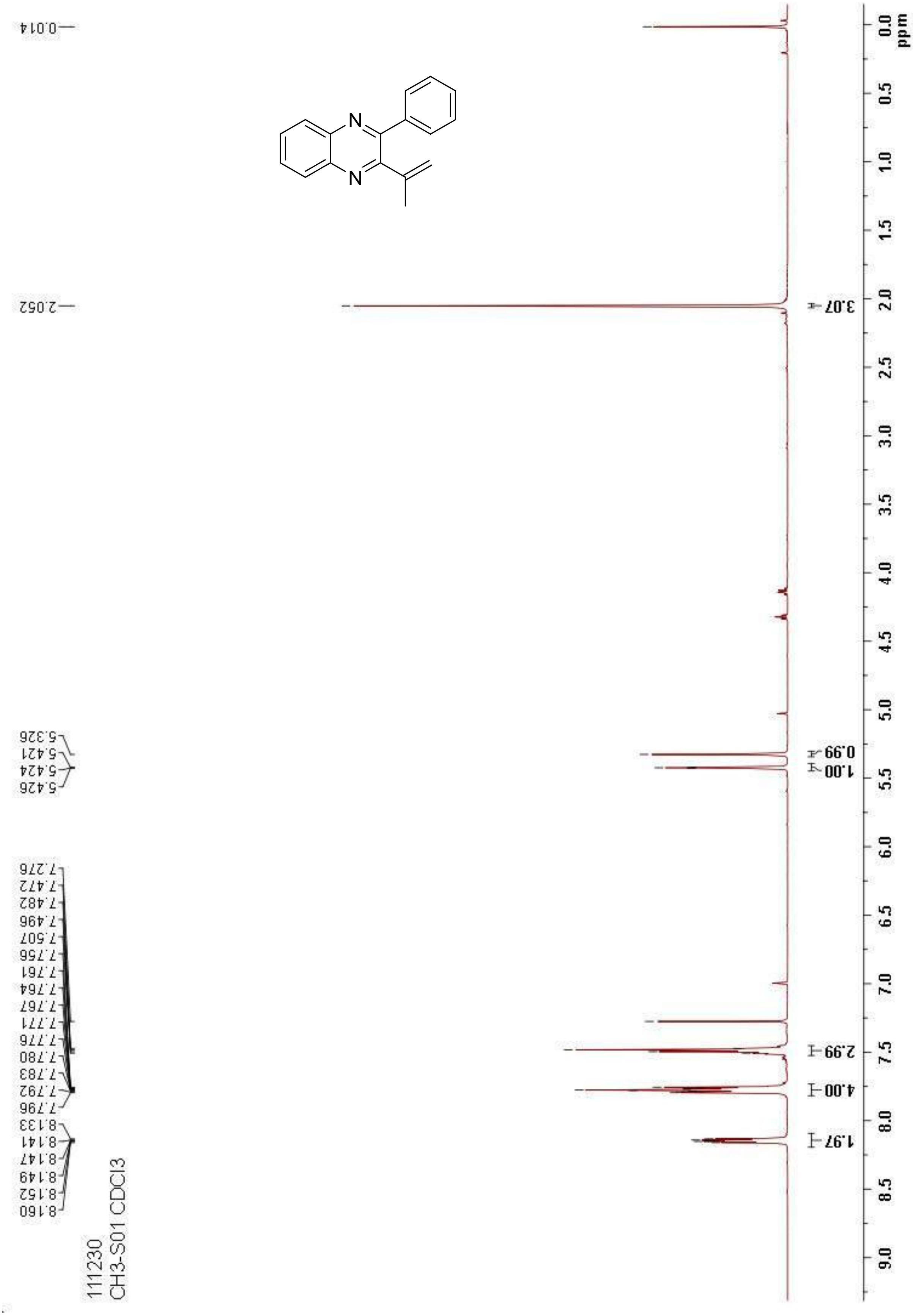
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
ppm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7.496
7.507
7.756
7.761
7.764
7.767
7.771
7.776
7.780
7.783
7.792
7.796
8.133
8.141
8.147
8.149
8.152
8.160
111230
CH3-S01 CDCl3
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1.00
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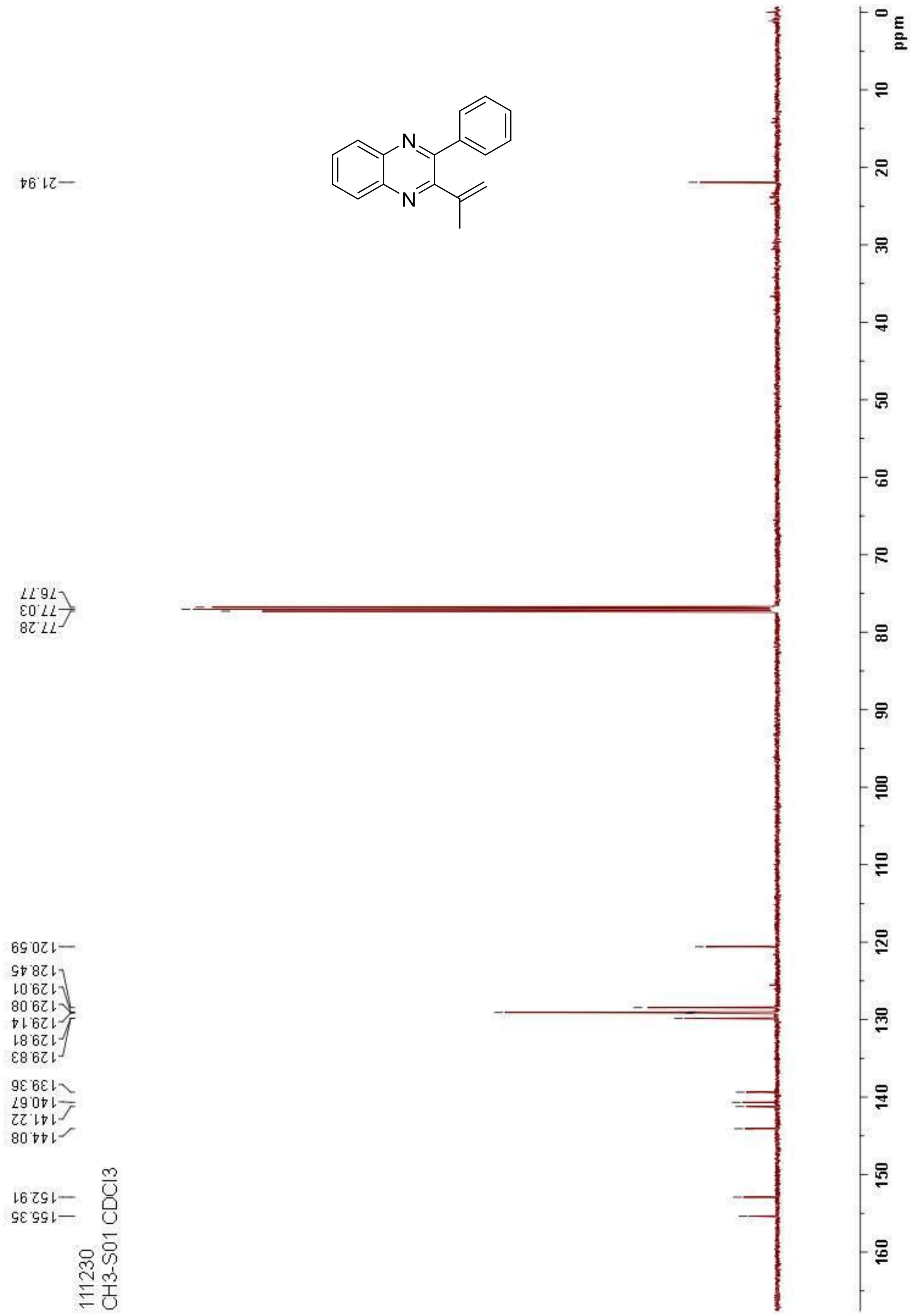
4.00
1.97
ppm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N
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139.36
140.67
141.22
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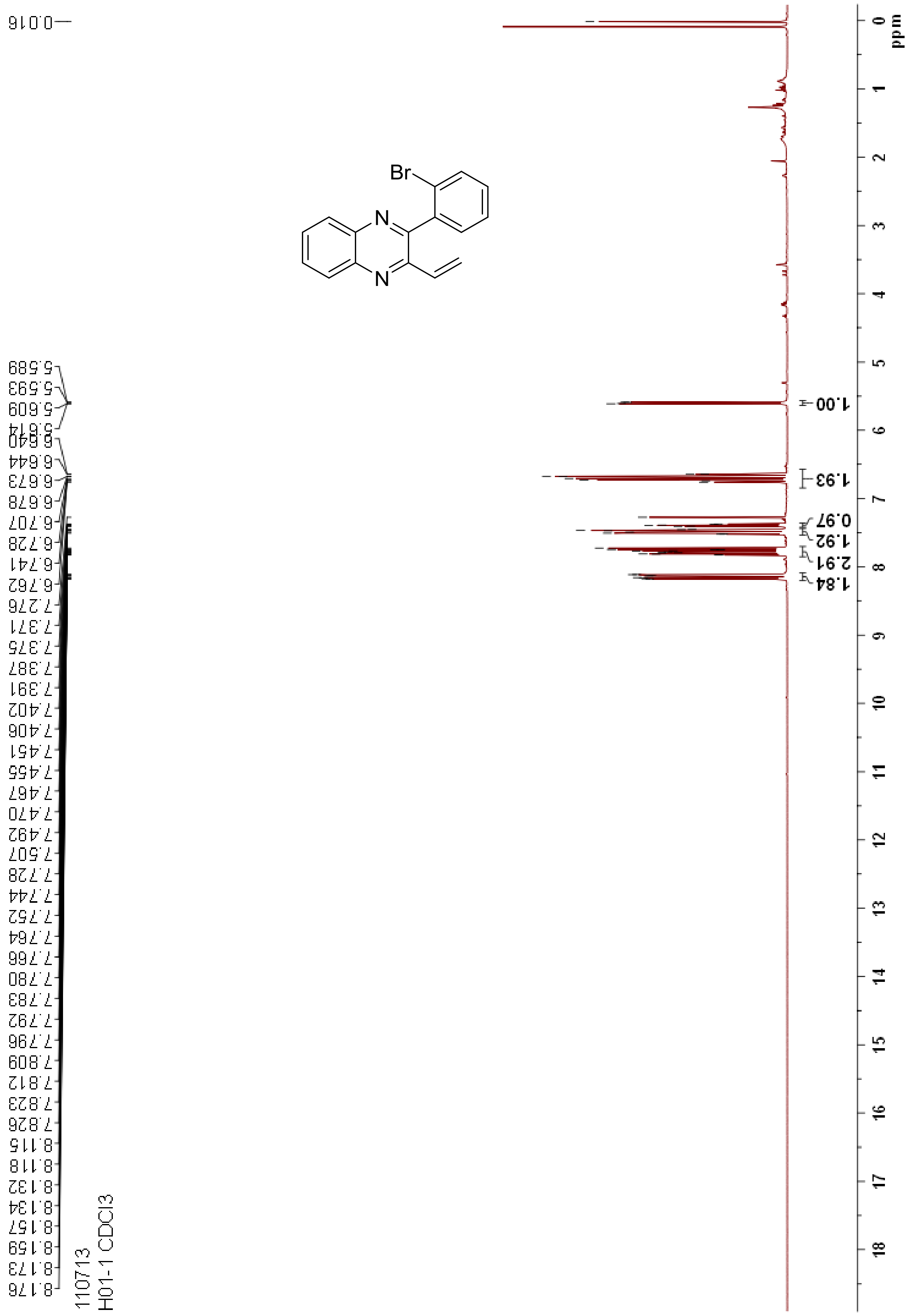
152.91
155.35
111230
CH3-S01 CDCl3
ppm


Br
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N
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5.593
5.609
5.614
6.640
6.644
6.673
6.678
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6.728
6.741
6.762
7.276
7.371
7.375
7.387
7.391
7.402
7.406
7.451
7.455
7.467
7.470
7.492
7.507
7.728
7.744
7.752
7.764
7.766
7.780
7.783
7.792
7.796
7.809
7.812
7.823
7.826
8.115
8.118
8.132
8.134
8.157
8.159
8.173
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110713
H01-1 CDCl3
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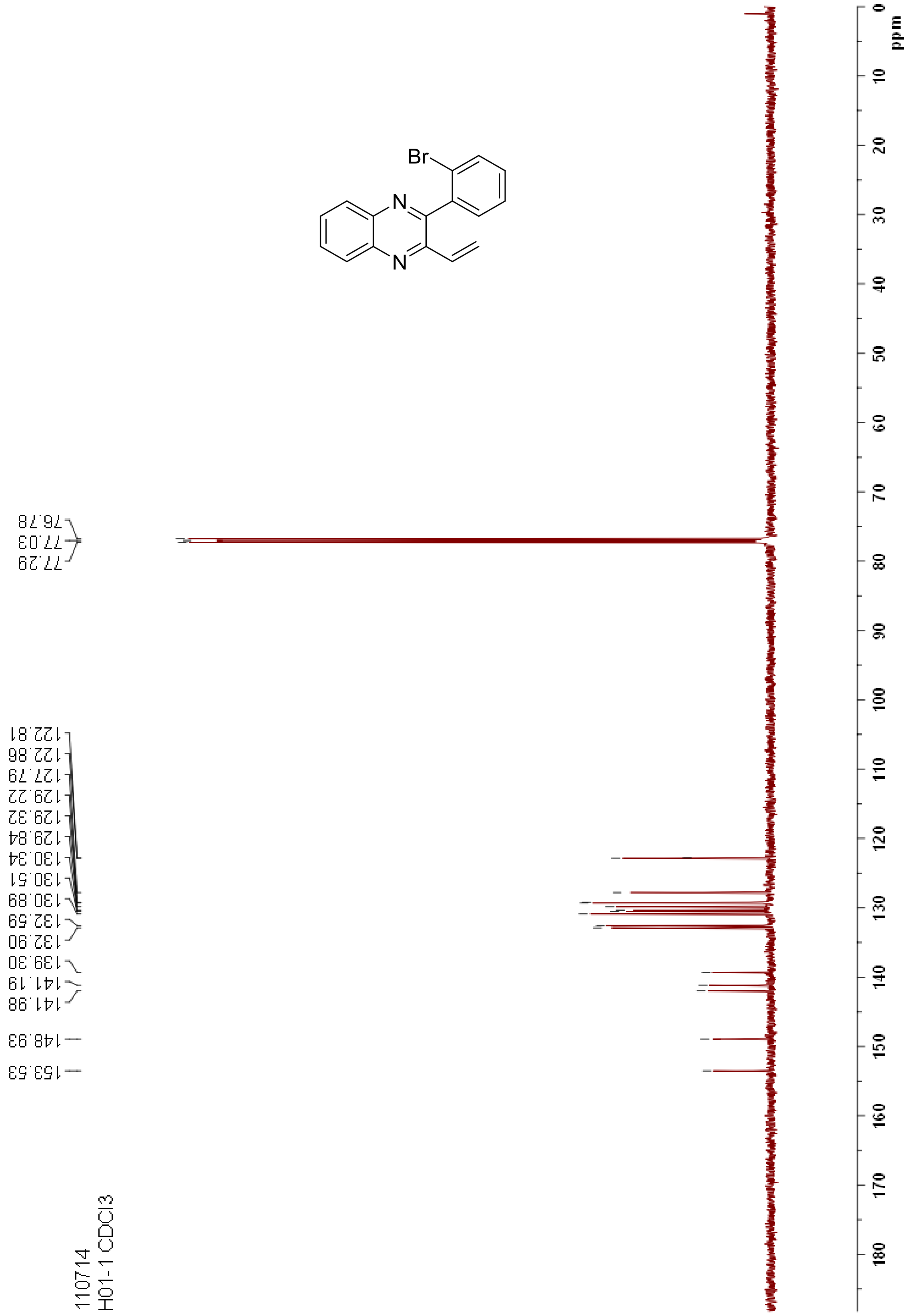
1.84
ppm


Br
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122.81
122.86
127.79
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130.51
130.89
132.59
132.90
139.30
141.19
141.98
148.93
153.53
110714
H01-1 CDCl3
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30
40
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90
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110
120
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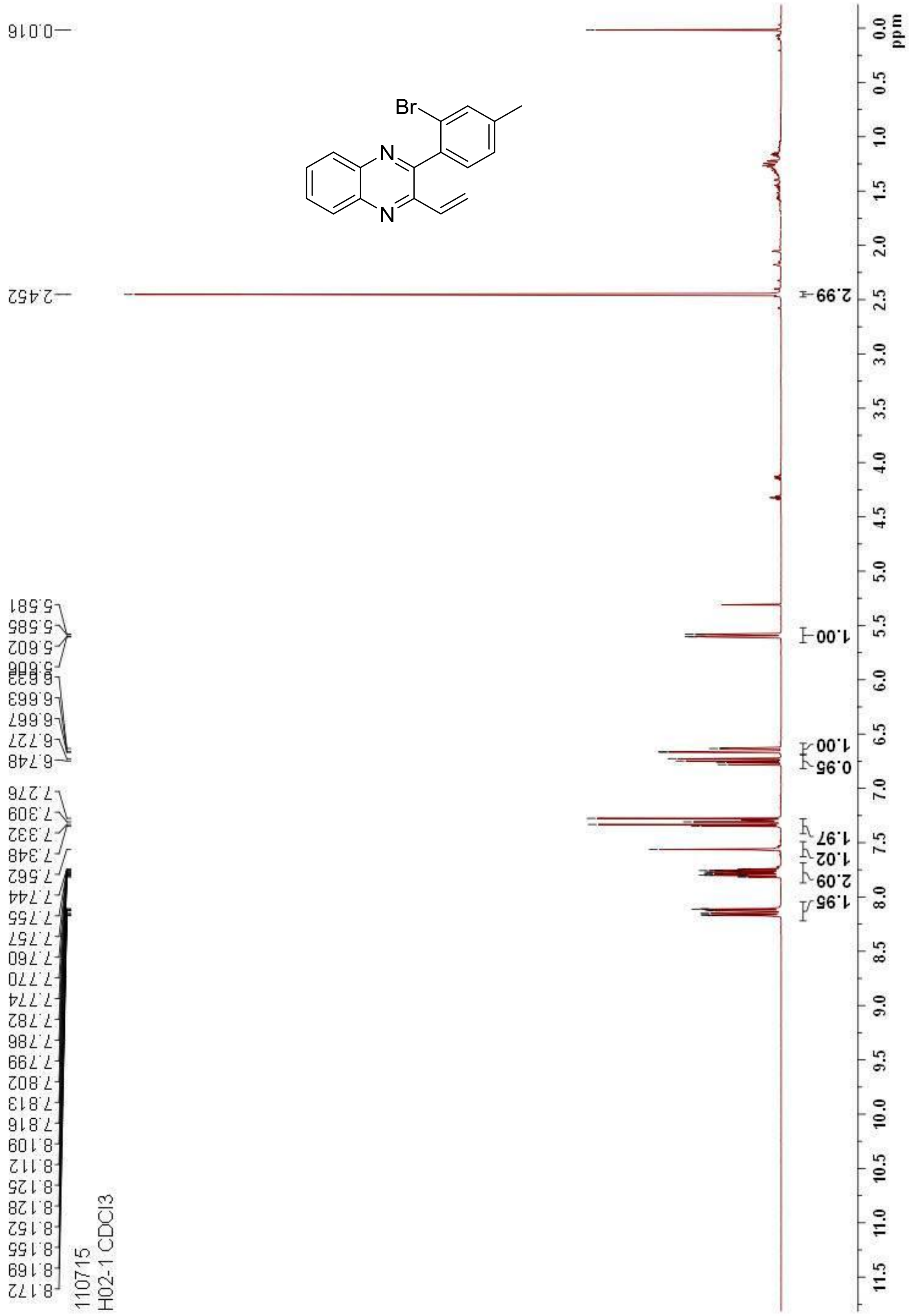
140
150
160
170
180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N
110715
H02-1 CDCl3
0.016
2.452
5.581
5.585
5.602
5.606
6.633
6.663
6.667
6.727
6.748
7.276
7.309
7.332
7.348
7.562
7.744
7.755
7.757
7.760
7.770
7.774
7.782
7.786
7.799
7.802
7.813
7.816
8.109
8.112
8.125
8.128
8.152
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8.172
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2.09
1.95
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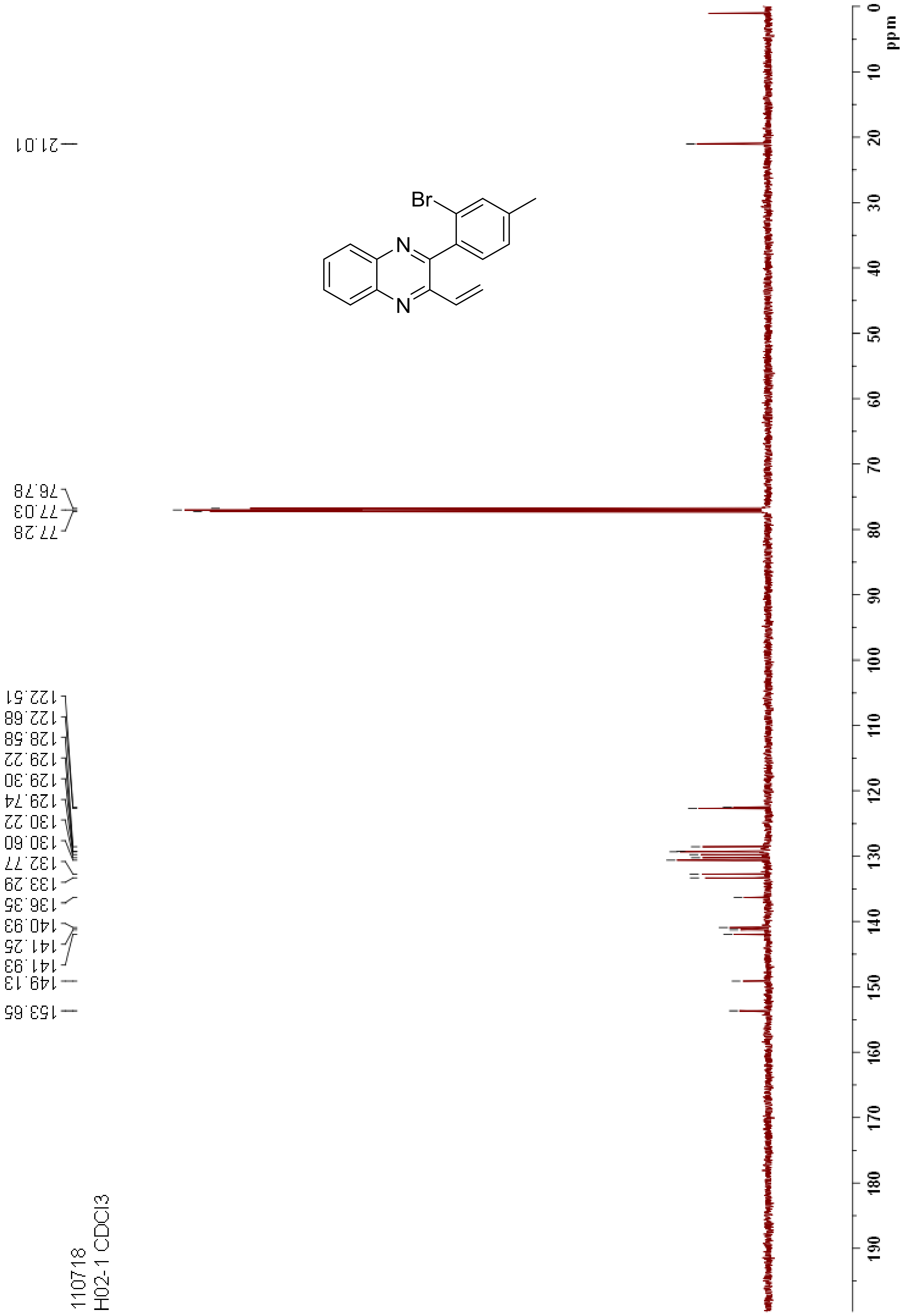
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H02-1 CDCl3
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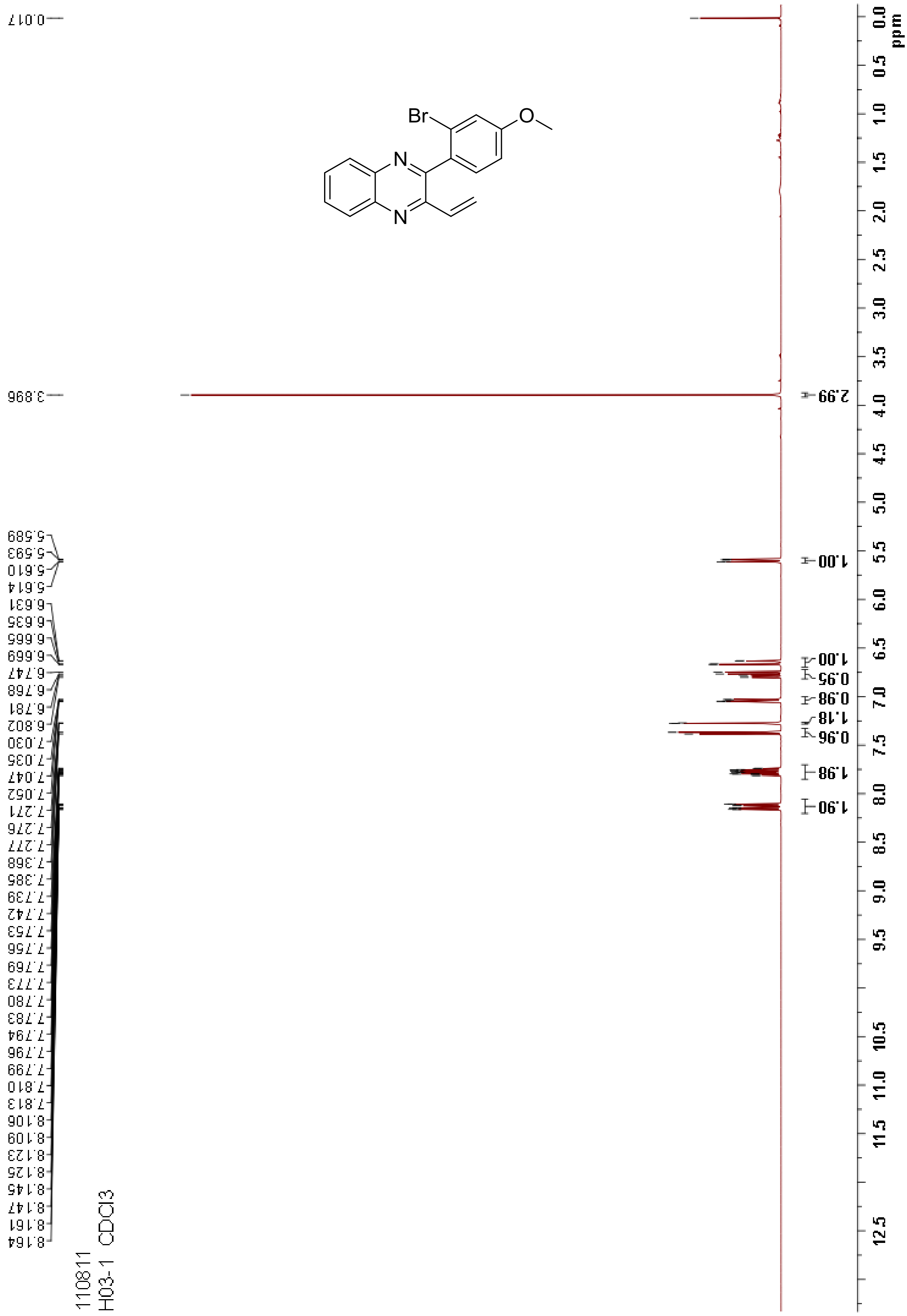
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O
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6.635
6.665
6.669
6.747
6.768
6.781
6.802
7.030
7.035
7.047
7.052
7.271
7.276
7.277
7.368
7.385
7.739
7.742
7.753
7.756
7.769
7.773
7.780
7.783
7.794
7.796
7.799
7.810
7.813
8.106
8.109
8.123
8.125
8.145
8.147
8.161
8.164
110811
H03-1 CDCl3
2.99
1.00
1.00
0.95
0.98
1.18
0.96
1.98
1.90
ppm
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
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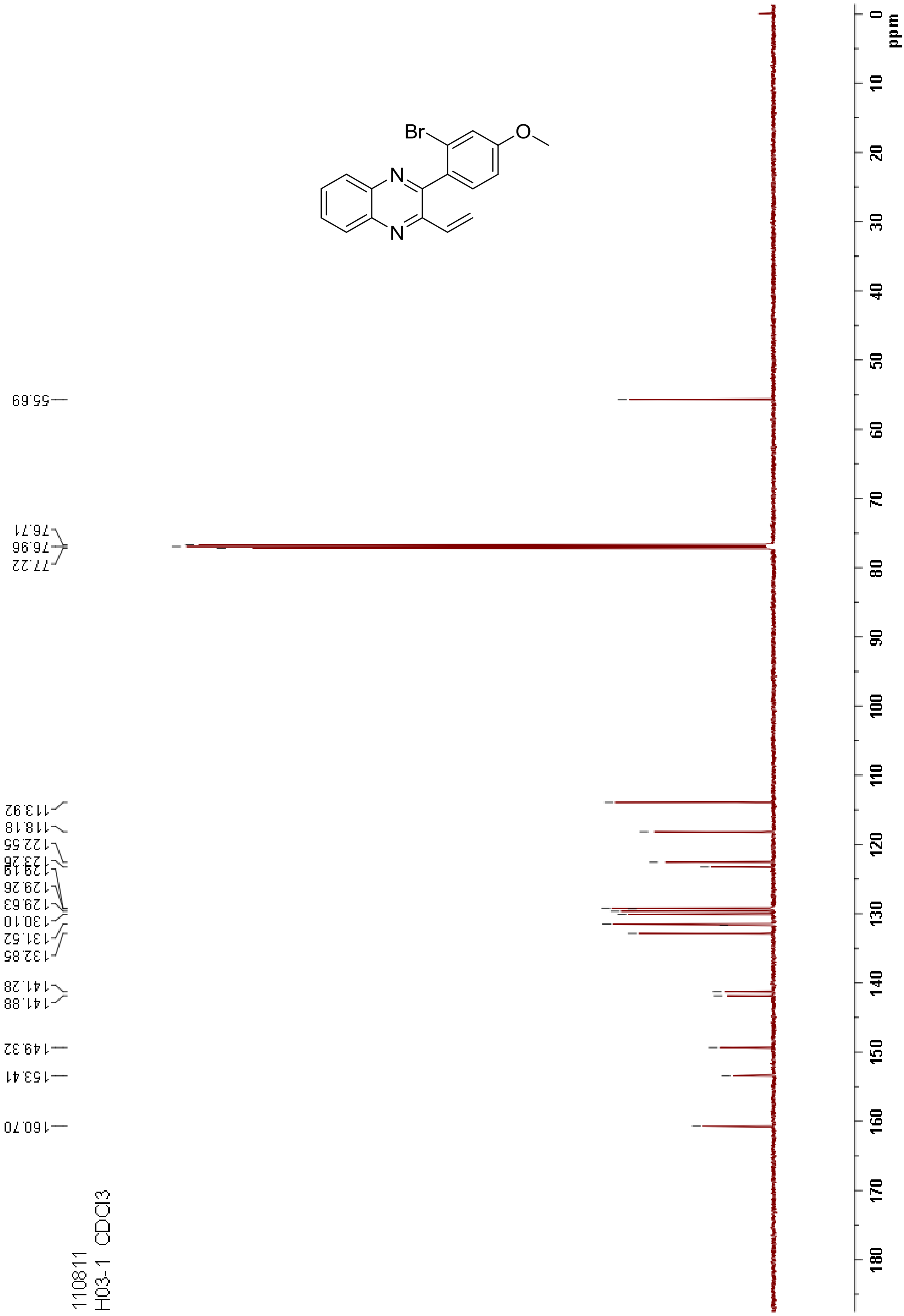
12.5


Br
N
N
O
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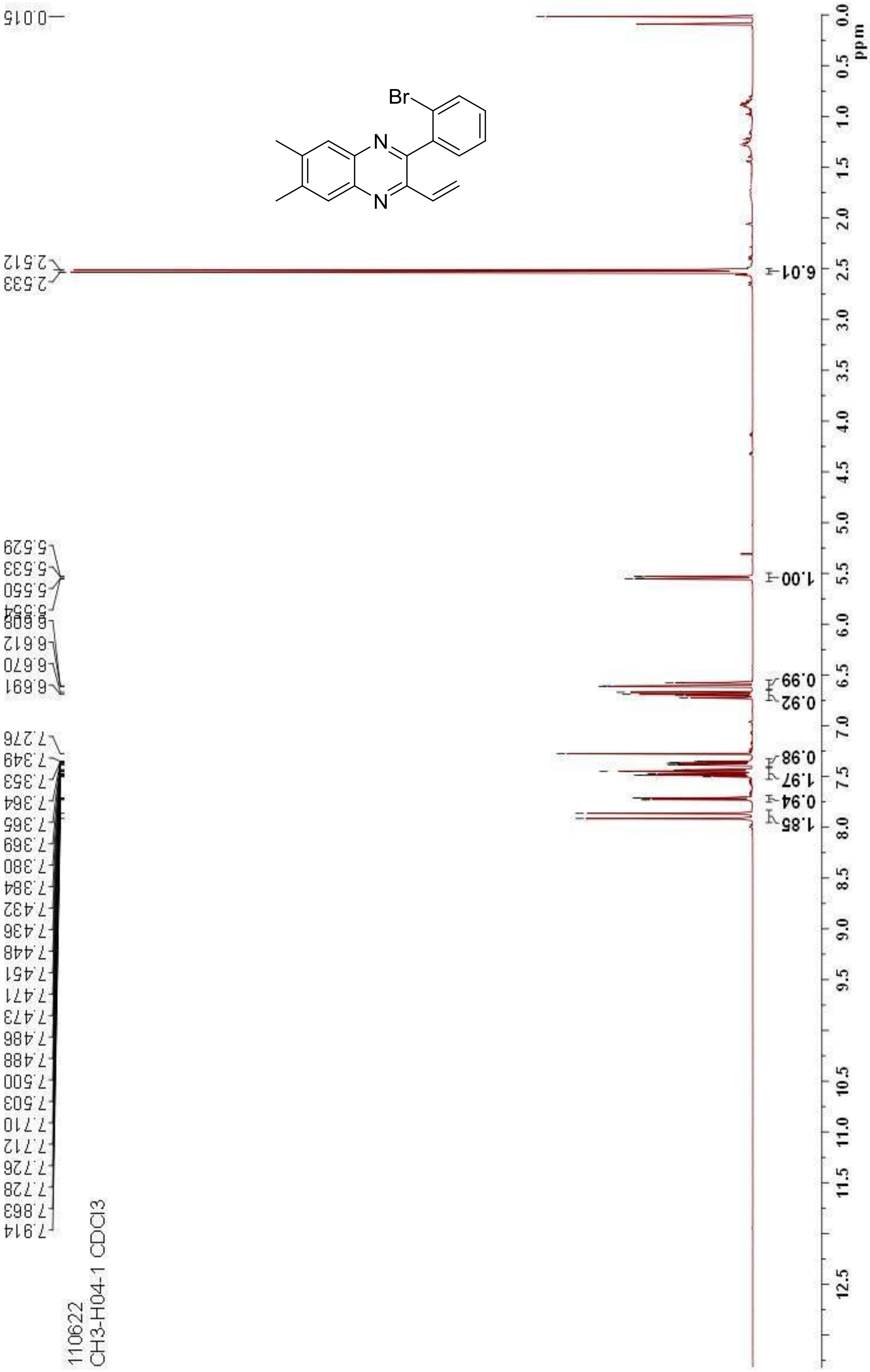
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N
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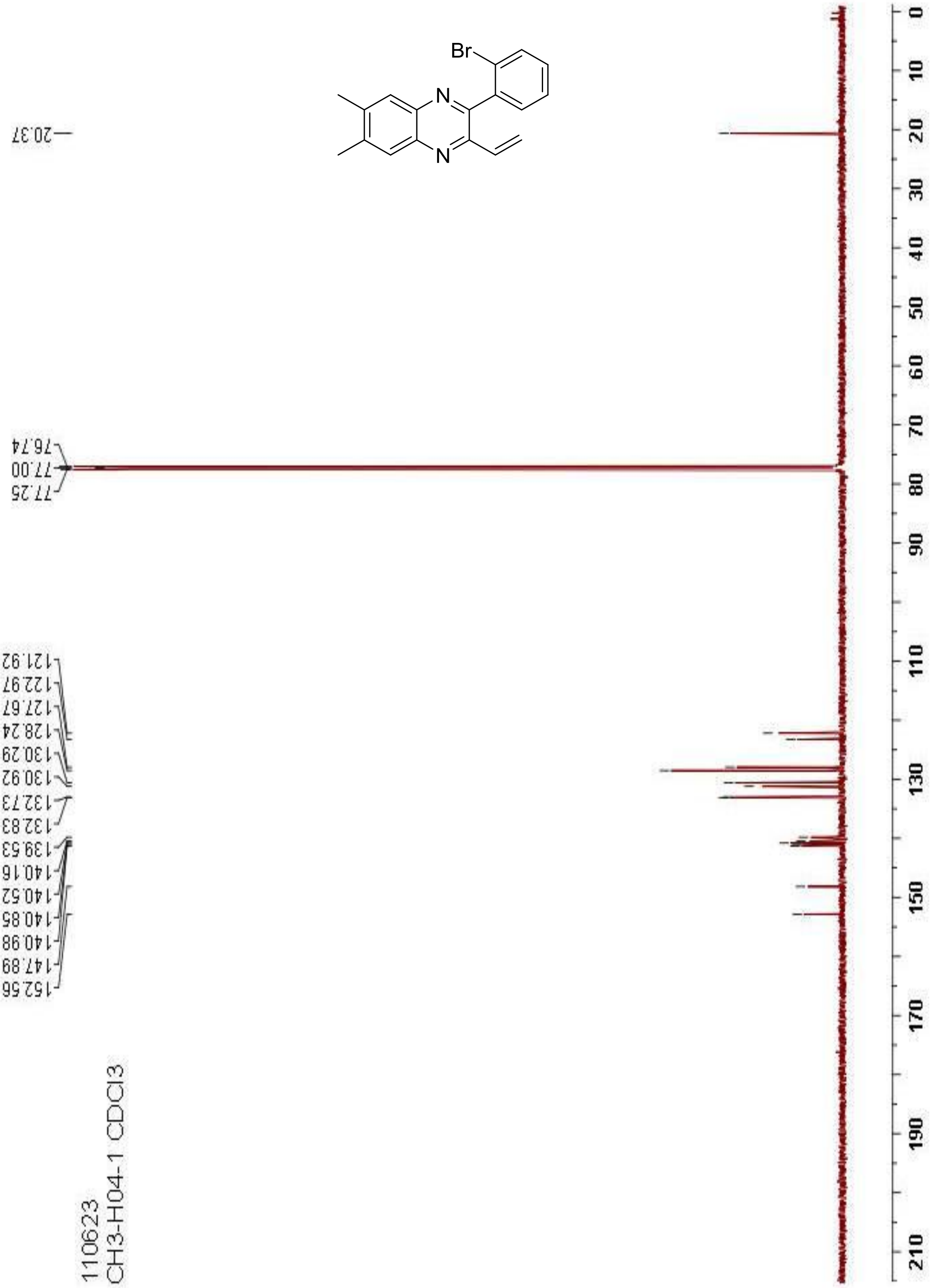
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N
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122.97
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130.92
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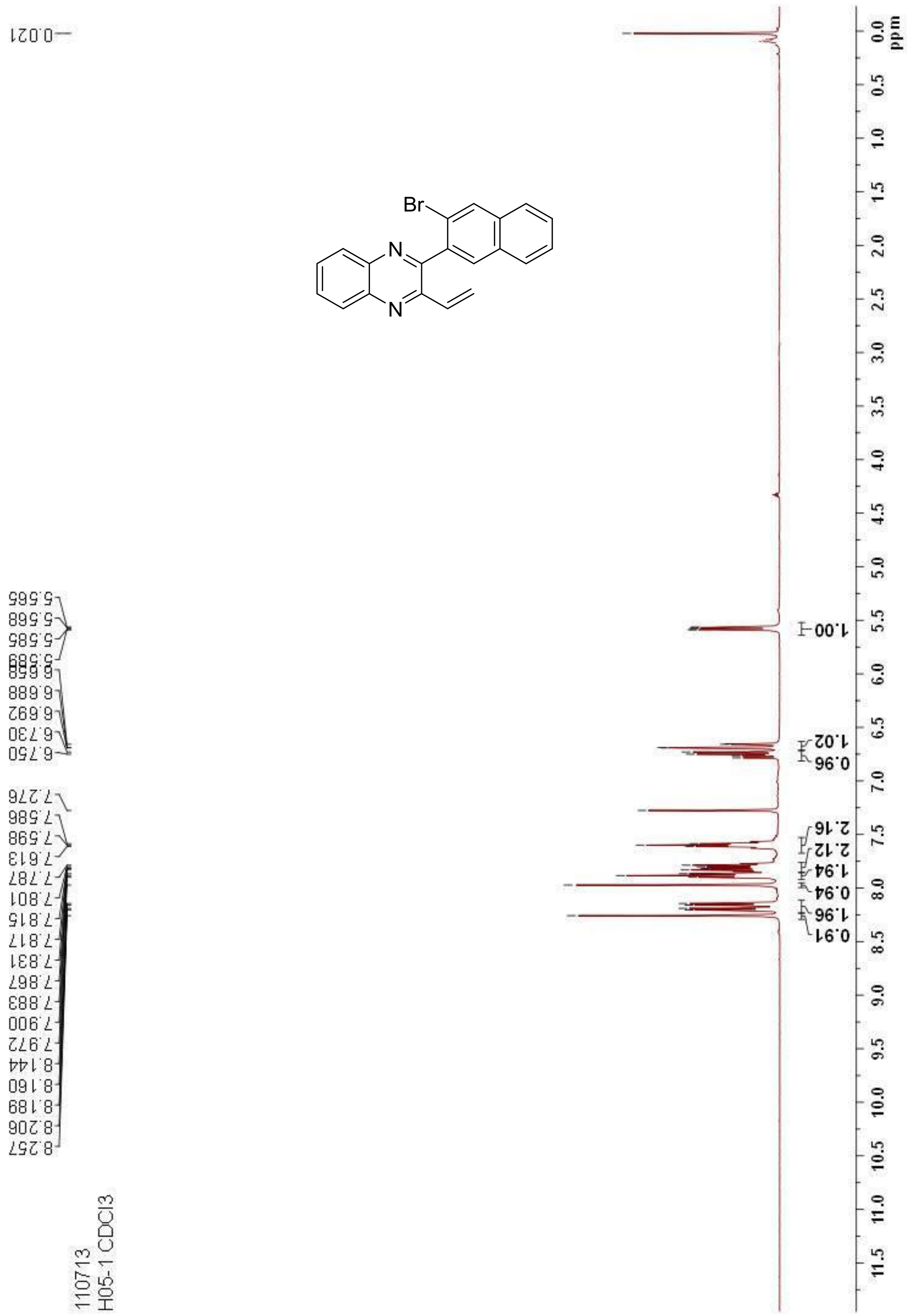
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6.730
6.750
7.276
7.586
7.598
7.613
7.787
7.801
7.815
7.817
7.831
7.867
7.883
7.900
7.972
8.144
8.160
8.189
8.206
8.257
110713
H05-1 CDCl3
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1.96
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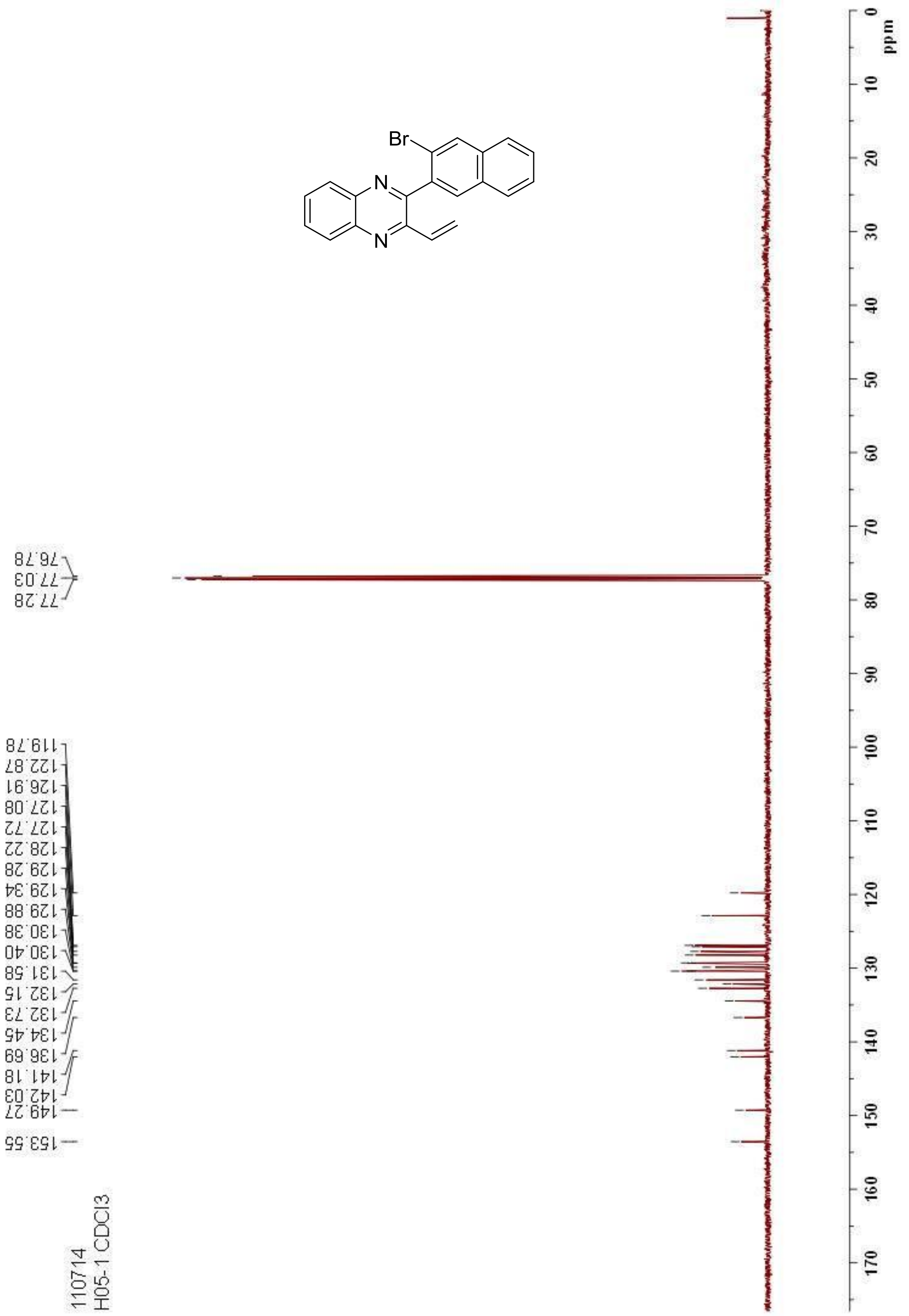
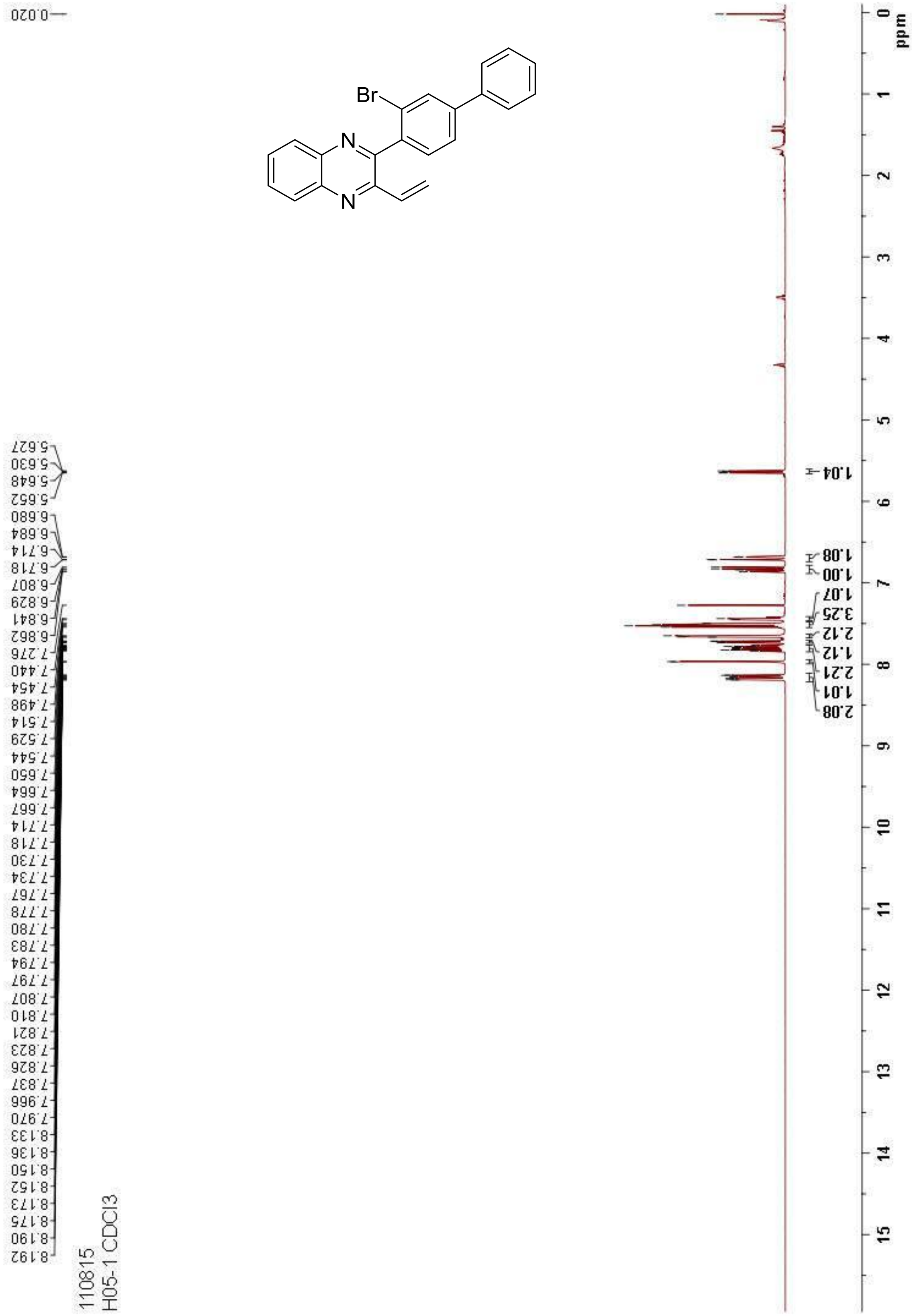
ppm

Electronic Supplementary Material (ESI) for Chemical Communications

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6.841
6.862
7.276
7.440
7.454
7.498
7.514
7.529
7.544
7.650
7.664
7.667
7.714
7.718
7.730
7.734
7.767
7.778
7.780
7.783
7.794
7.797
7.807
7.810
7.821
7.823
7.826
7.837
7.966
7.970
8.133
8.136
8.150
8.152
8.173
8.175
8.190
8.192
110815
H05-1 CDCl3
1.04
1.08
1.00
1.07
3.25
2.12
1.12
2.21
1.01
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2
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7
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9
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12
13
14
15
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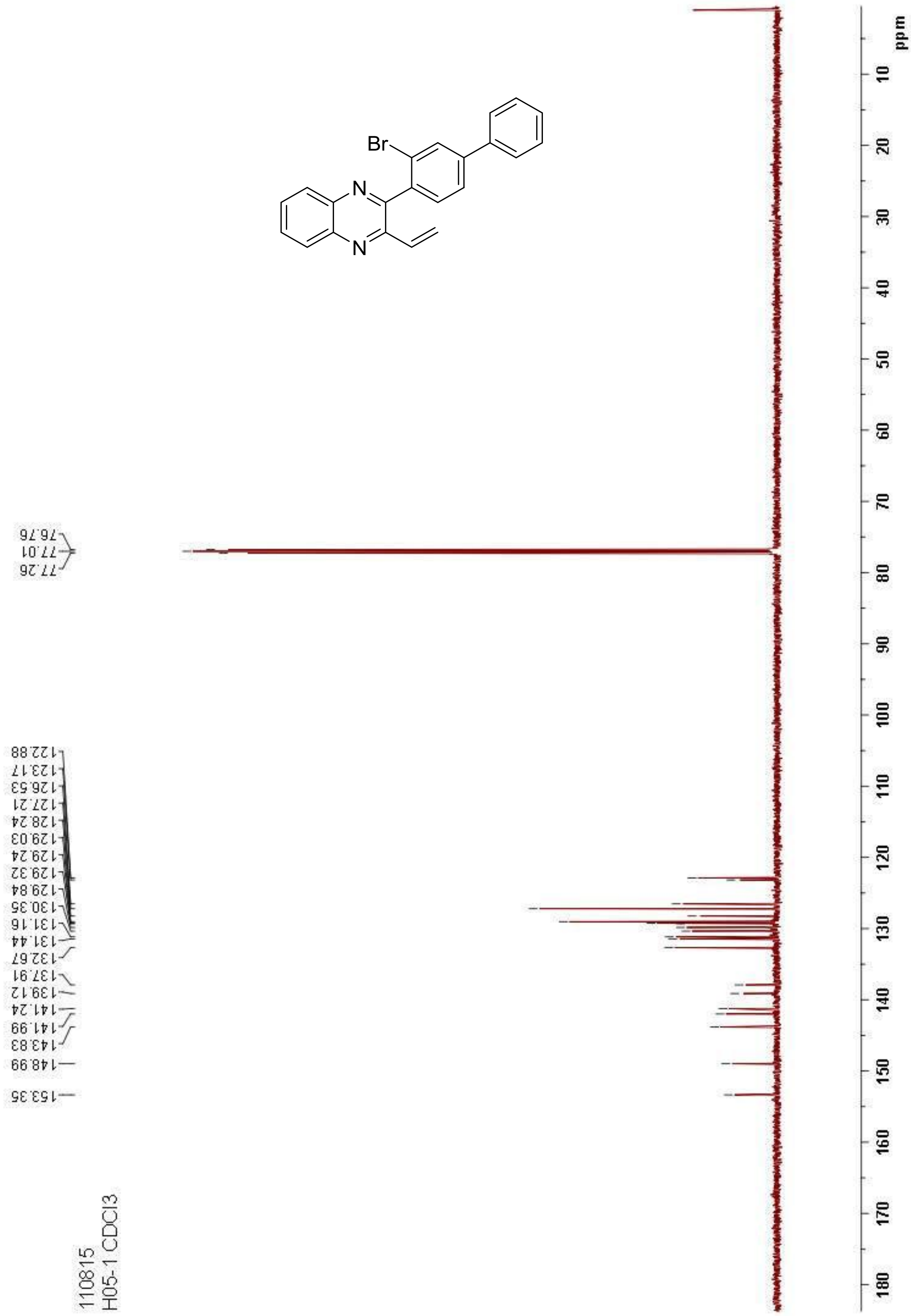
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129.84
130.35
131.16
131.44
132.67
137.91
139.12
141.24
141.99
143.83
148.99
153.35
110815
H05-1 CDCl3
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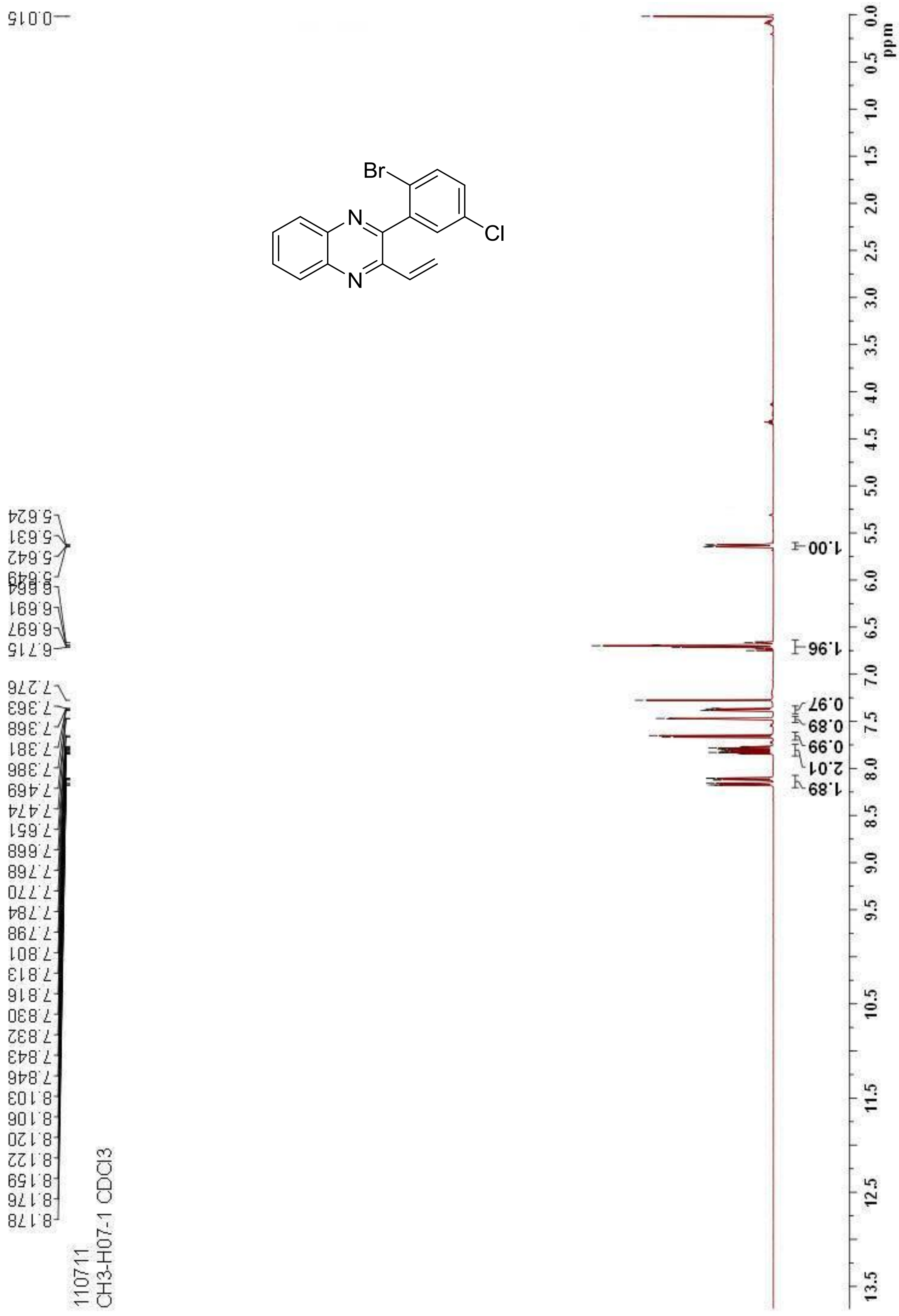
140
150
160
170
180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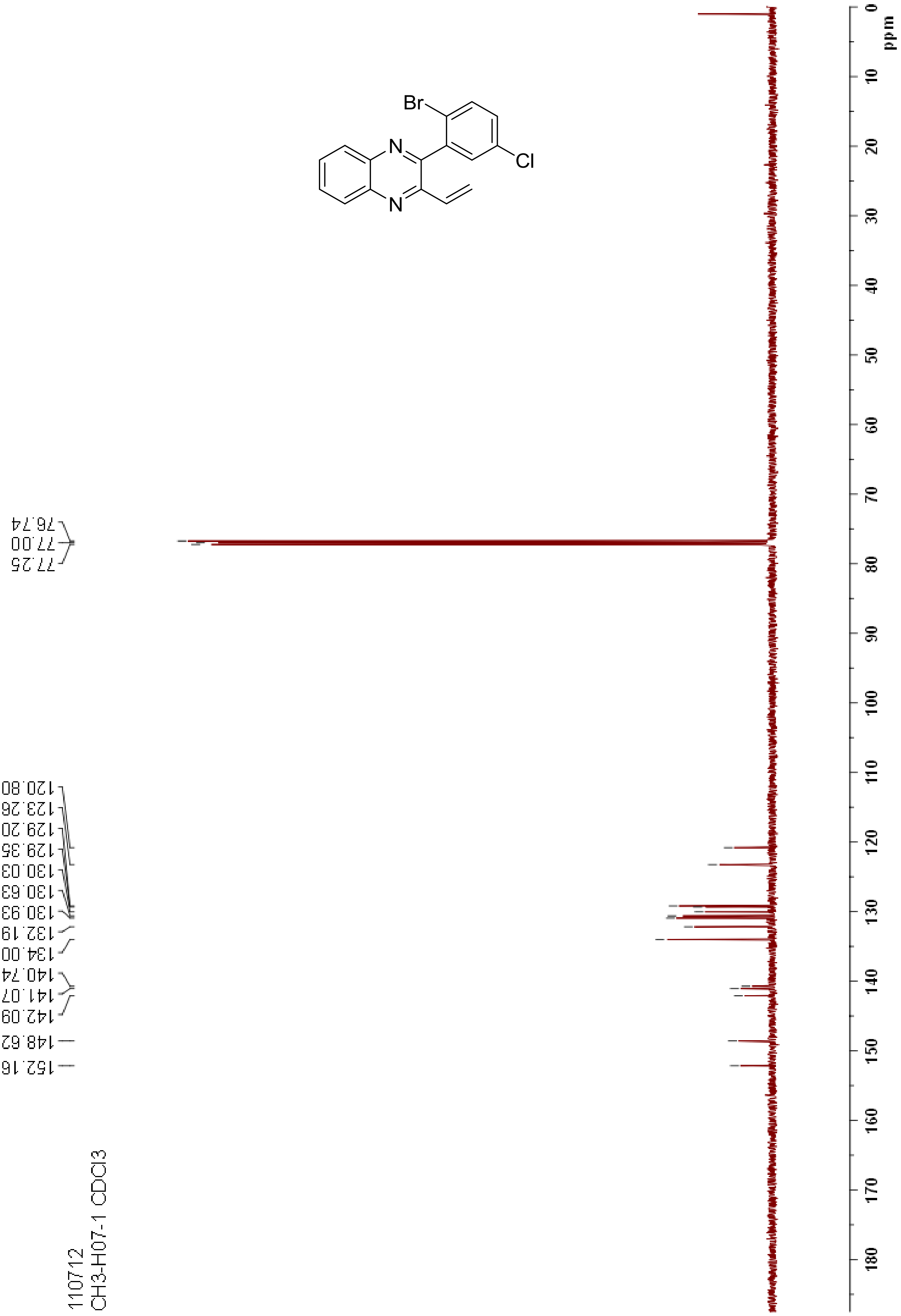
N
Cl
ppm
110711
CH3-H07-1 CDCl3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N
Cl
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129.20
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130.03
130.63
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132.19
134.00
140.74
141.07
142.09
148.62
152.16
110712
CH3-H07-1 CDCl3
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30
40
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70
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110
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150
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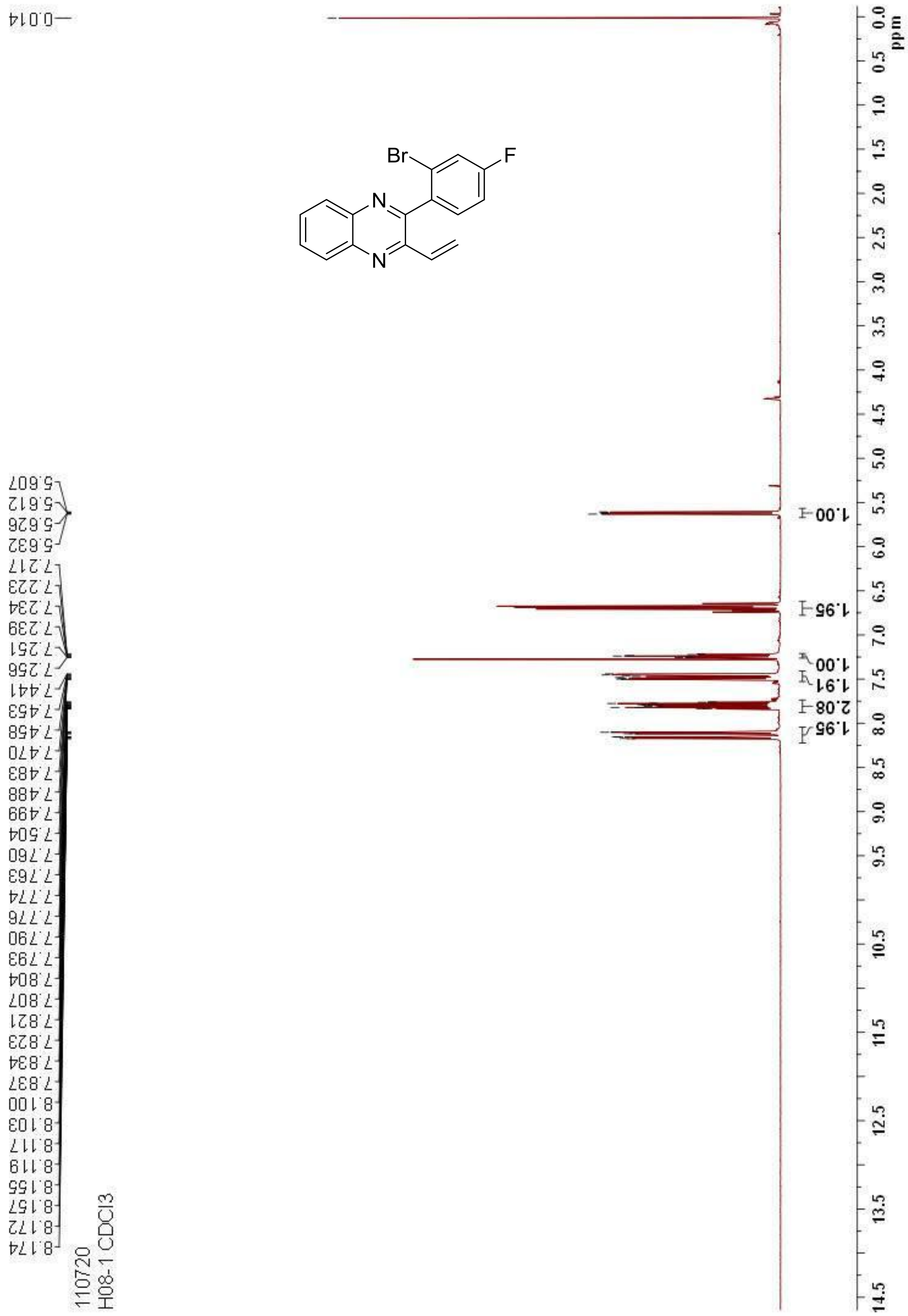
170
180


Br
F
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N
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H08-1 CDCl3
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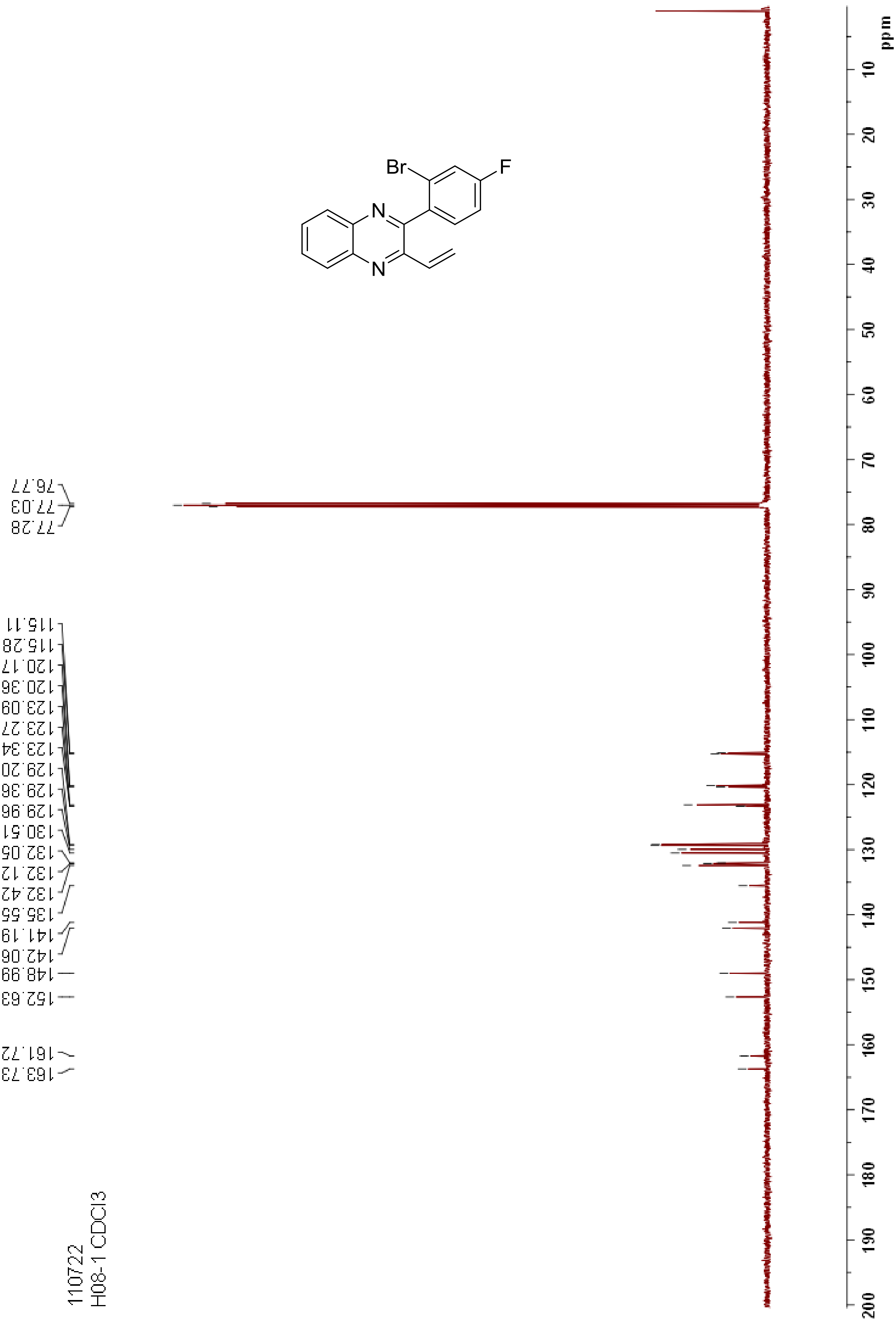
Br
F
N
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115.28
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123.09
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129.20
129.36
129.96
130.51
132.05
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141.19
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H08-1 CDCl3
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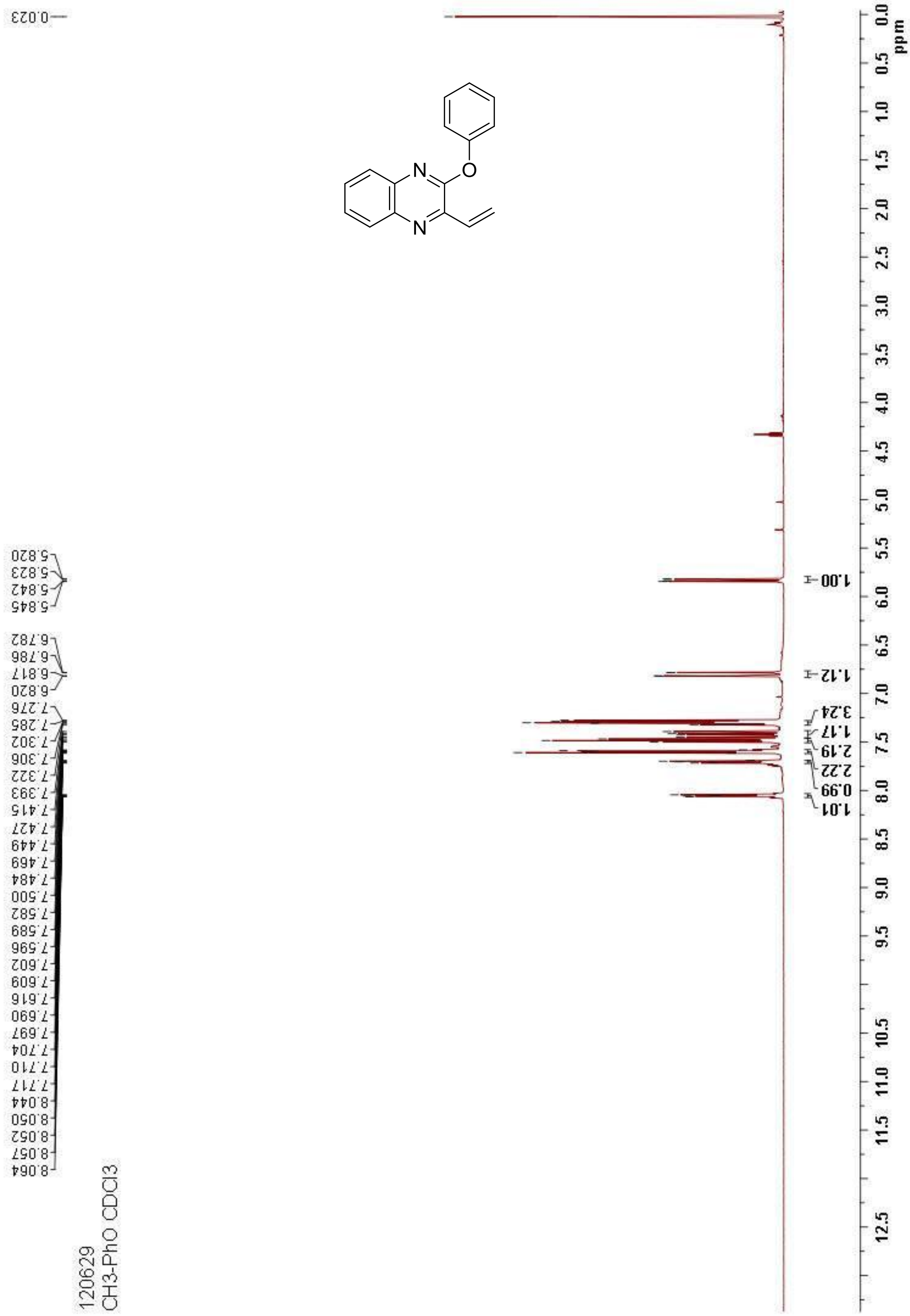
120629
CH3-PhO CDCl3
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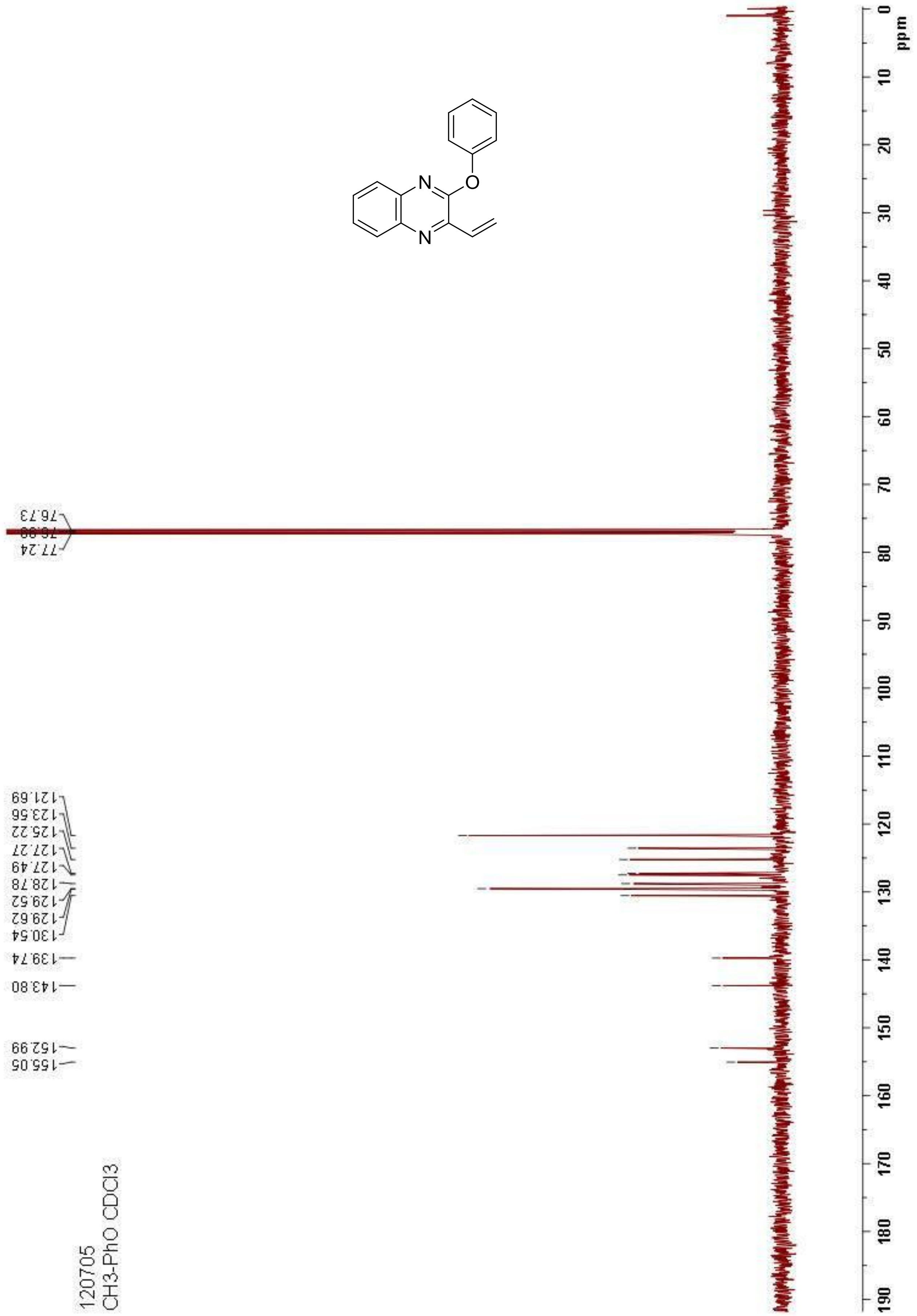

120705
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76.98
77.24
121.69
123.56
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127.27
127.49
128.78
129.52
129.62
130.54
139.74
143.80
152.99
155.05
ppm
0
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60
70
80
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100
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140
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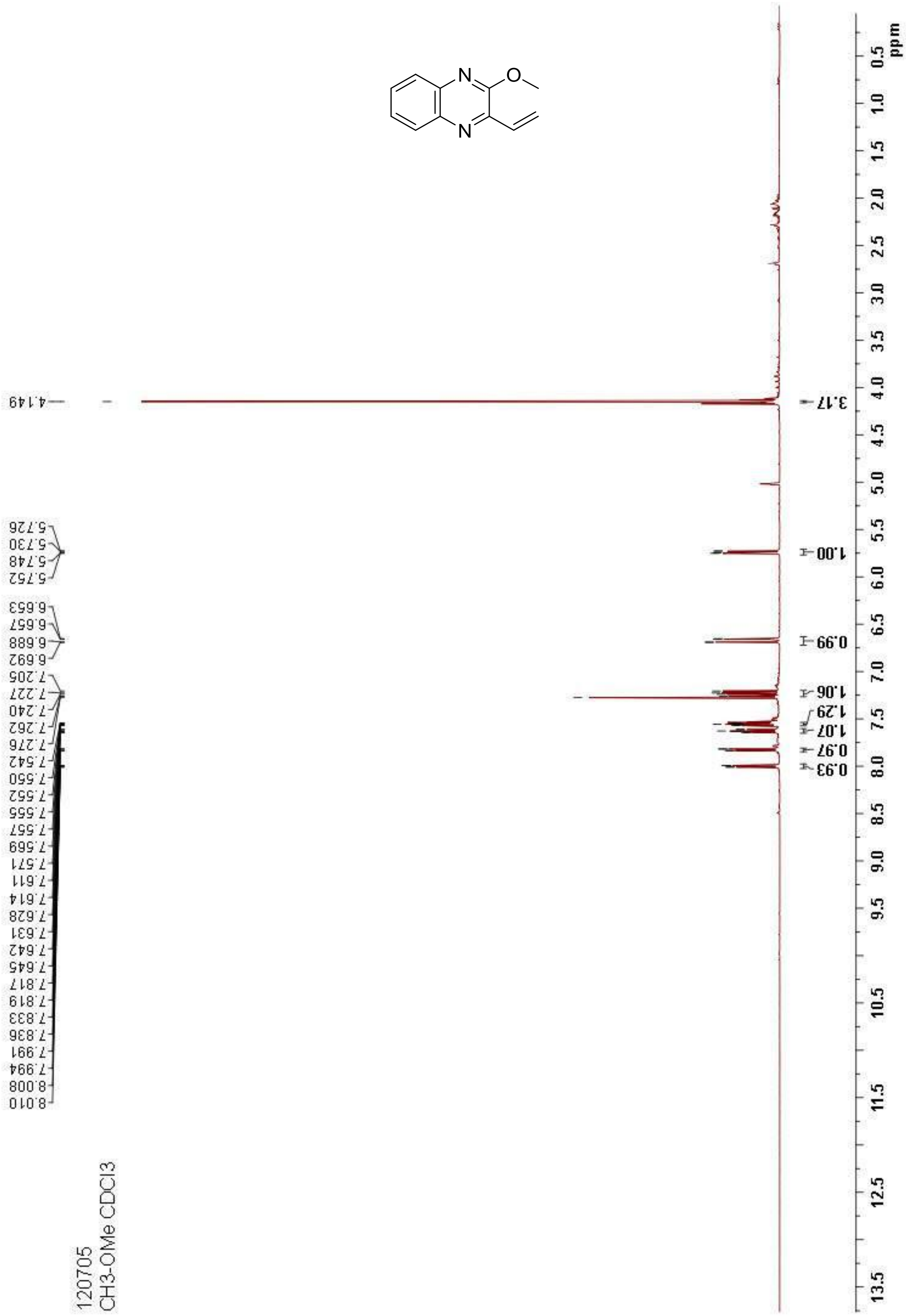
180
190
N
O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6.688
6.692
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7.227
7.240
7.262
7.276
7.542
7.550
7.552
7.555
7.557
7.569
7.571
7.611
7.614
7.628
7.631
7.642
7.645
7.817
7.819
7.833
7.836
7.991
7.994
8.008
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120705
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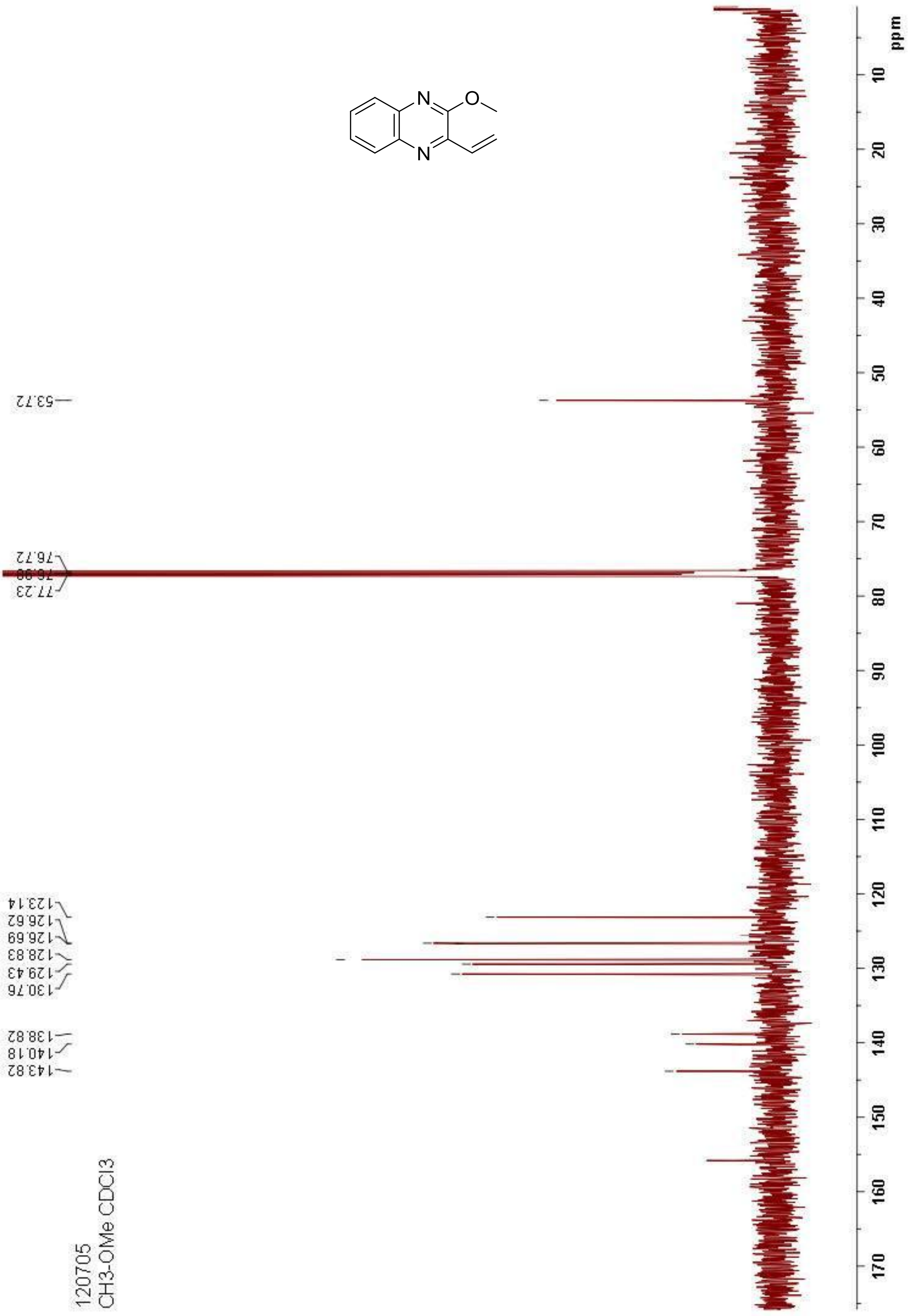
1.29
1.07
0.97
0.93
ppm


N
O
N
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77.23
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128.83
129.43
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138.82
140.18
143.82
120705
CH3-OMe CDCl3
ppm
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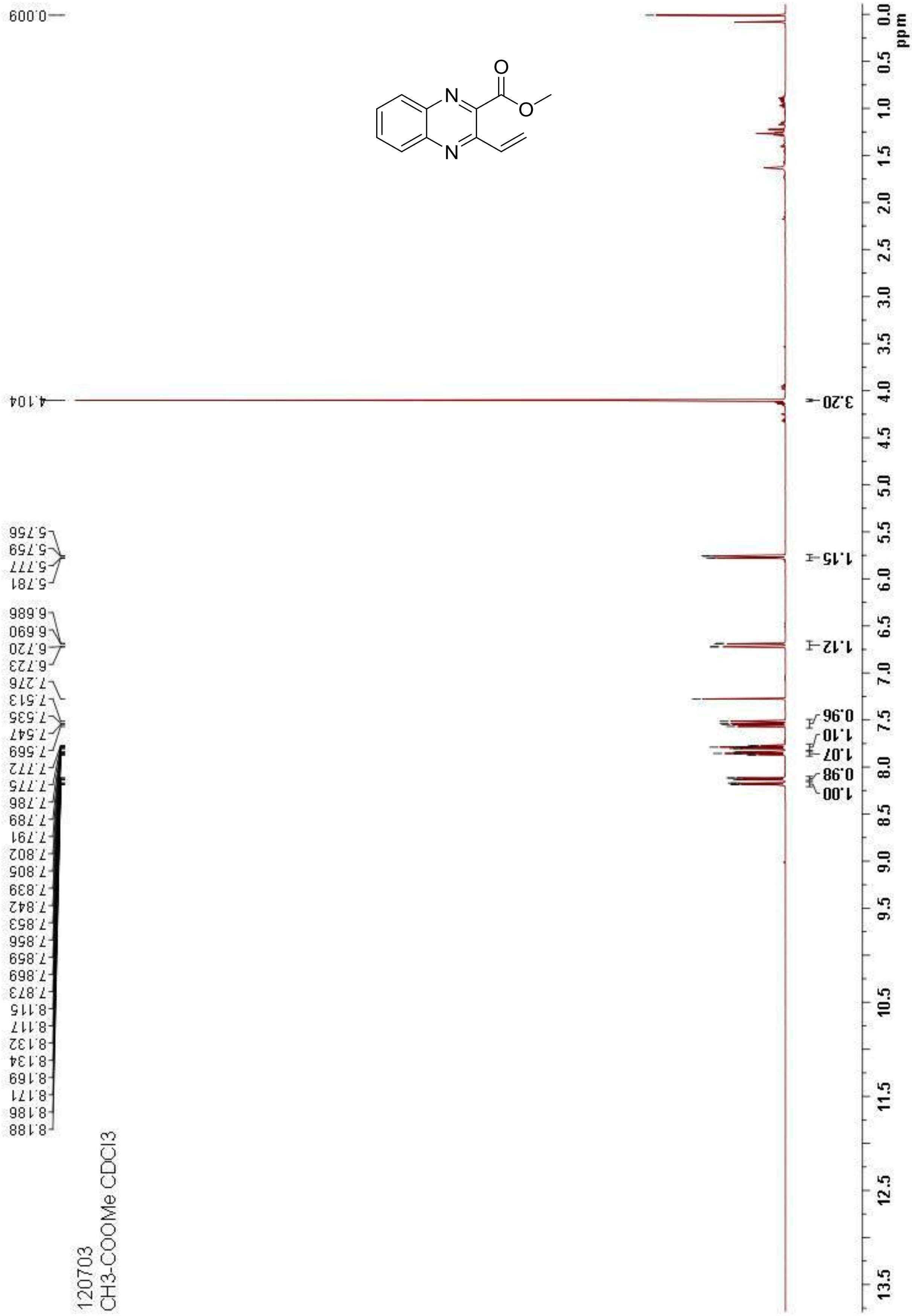
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170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6.720
6.723
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7.513
7.536
7.547
7.569
7.772
7.775
7.786
7.789
7.791
7.802
7.805
7.839
7.842
7.853
7.856
7.859
7.869
7.873
8.115
8.117
8.132
8.134
8.169
8.171
8.186
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1.10
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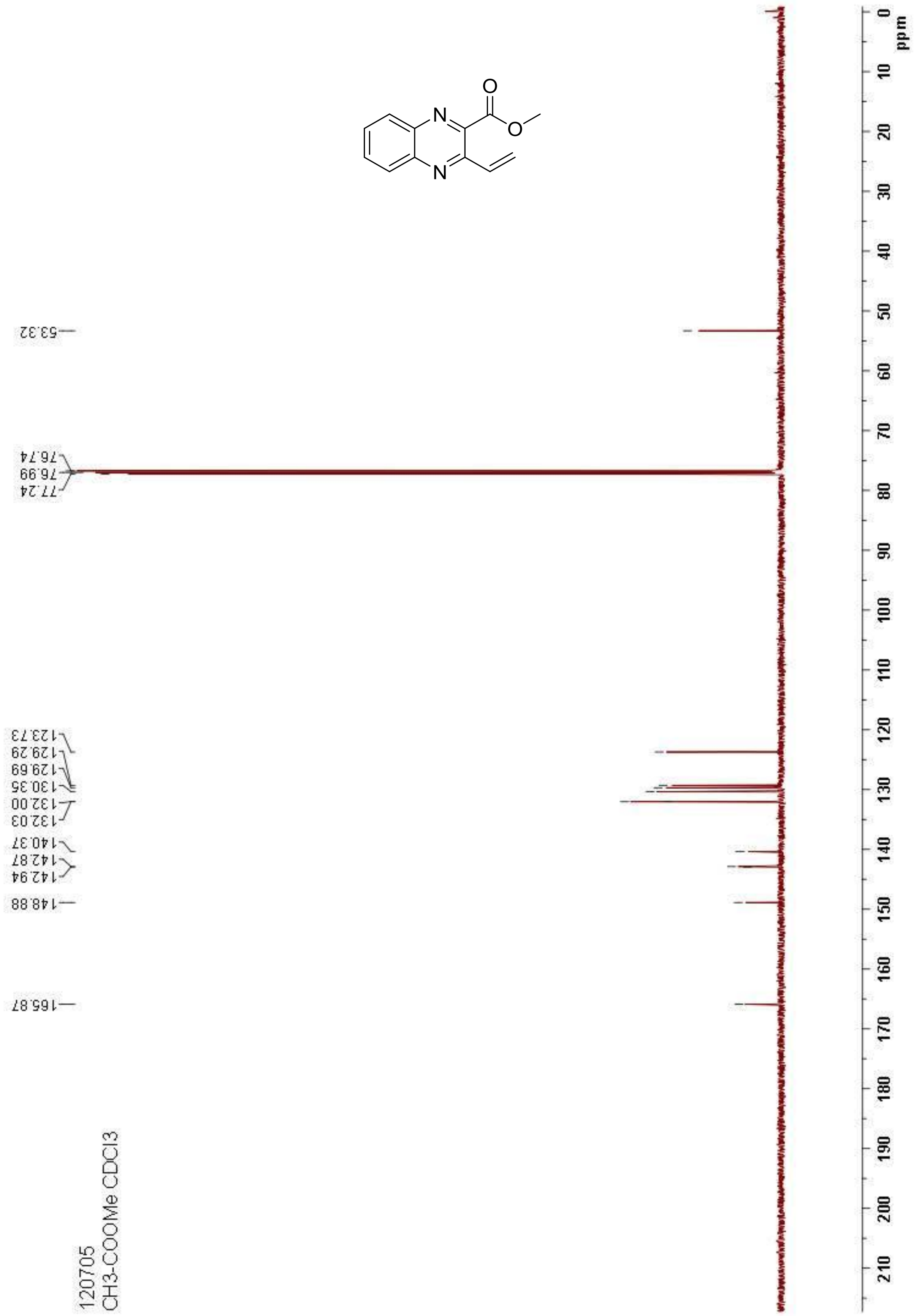
ppm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165.87
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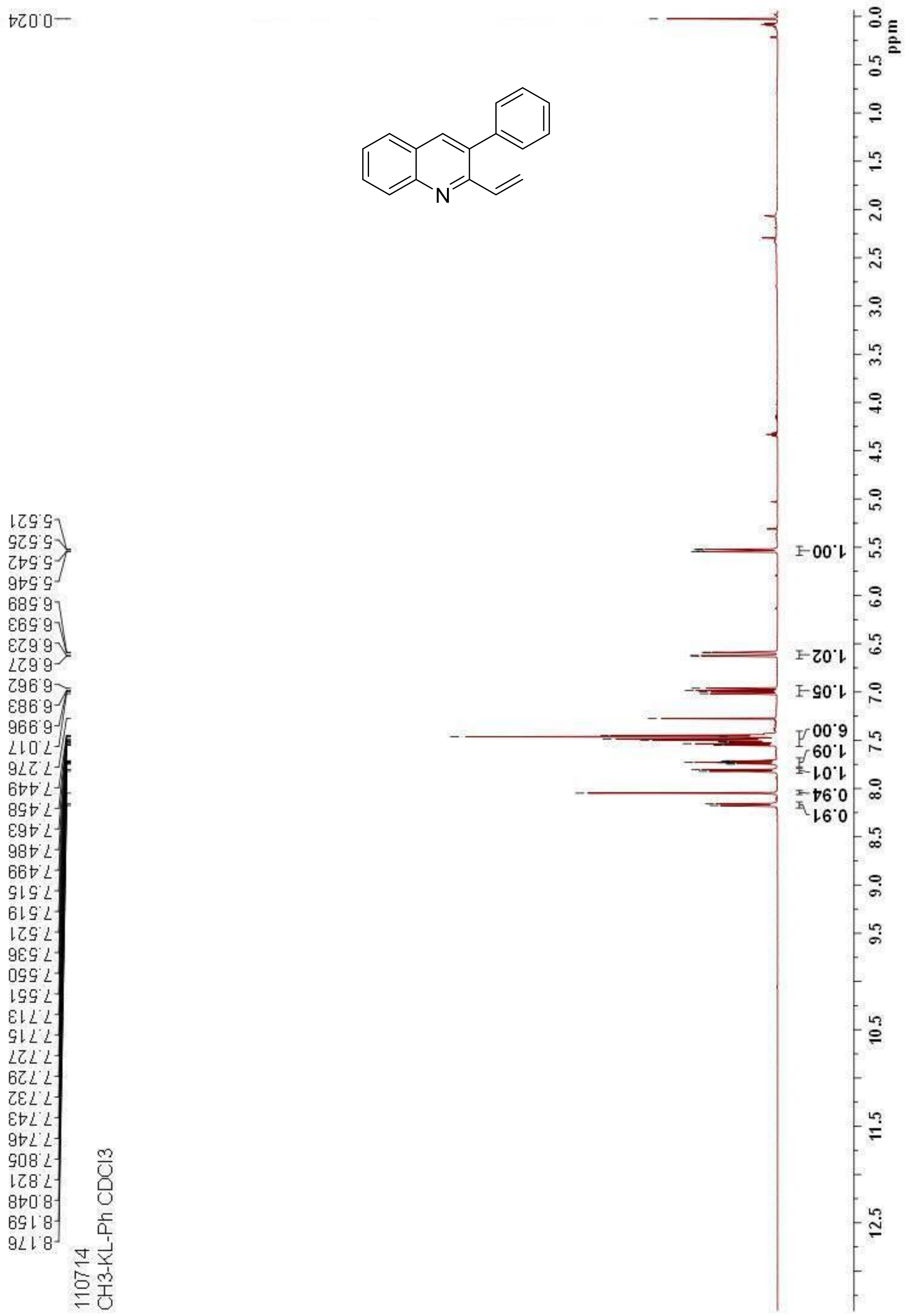
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6.983
6.996
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7.458
7.463
7.486
7.499
7.515
7.519
7.521
7.536
7.550
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7.715
7.727
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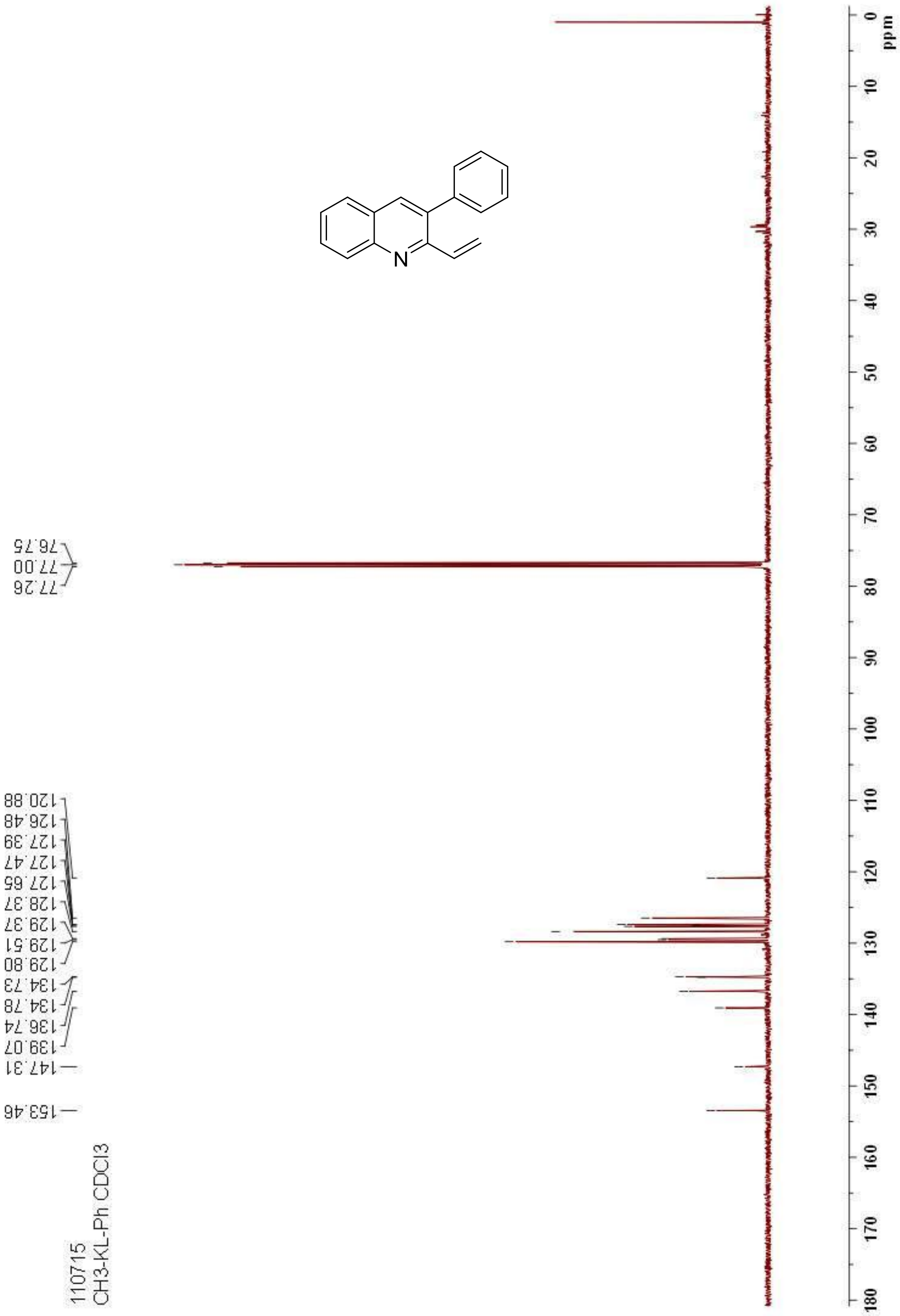
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CH3-KL-Ph CDCl3
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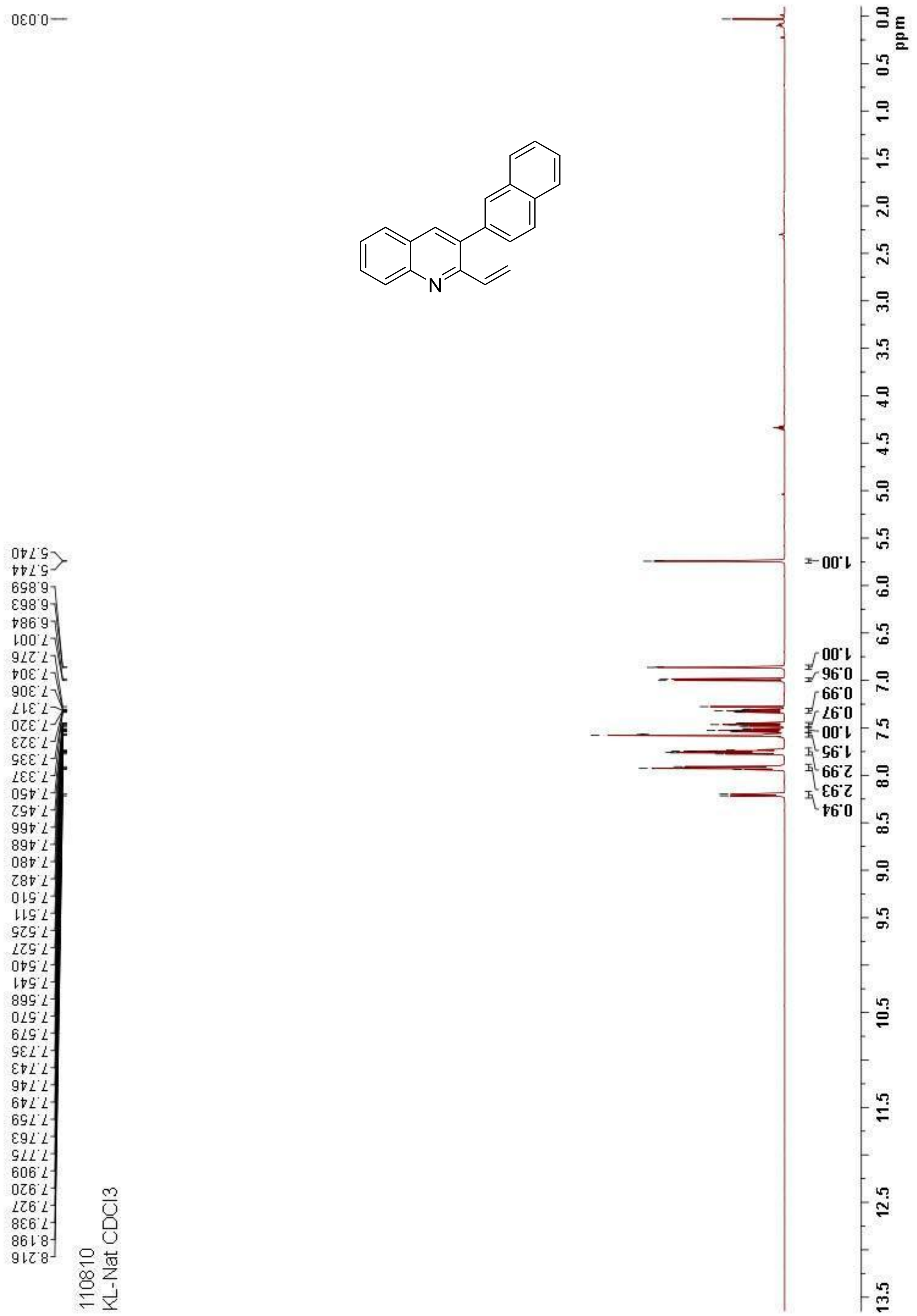
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7.482
7.510
7.511
7.525
7.527
7.540
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7.568
7.570
7.579
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7.743
7.746
7.749
7.759
7.763
7.775
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7.920
7.927
7.938
8.198
8.216
110810
KL-Nat CDCl3
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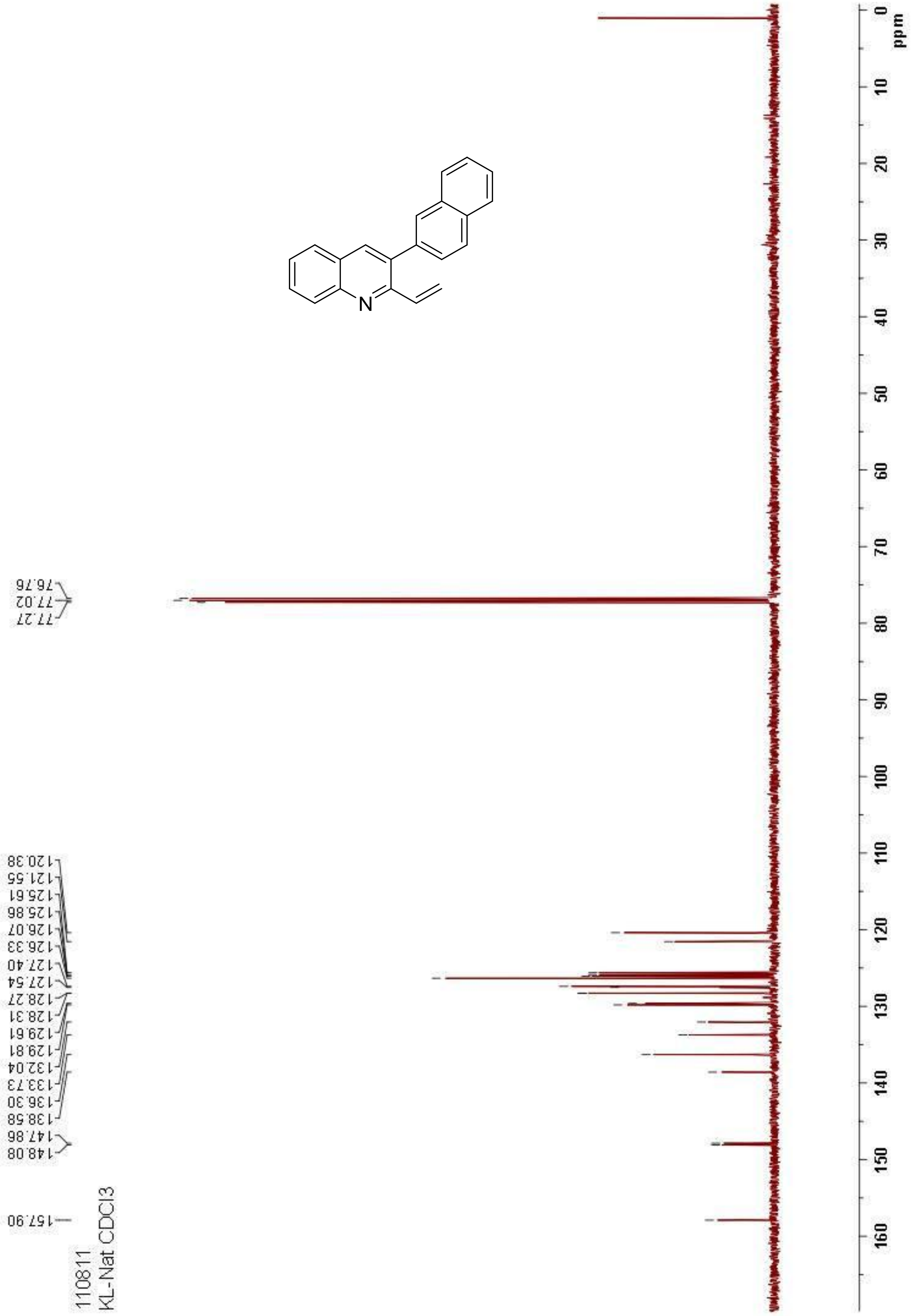
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127.54
128.27
128.31
129.61
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157.90
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KL-Nat CDCl3
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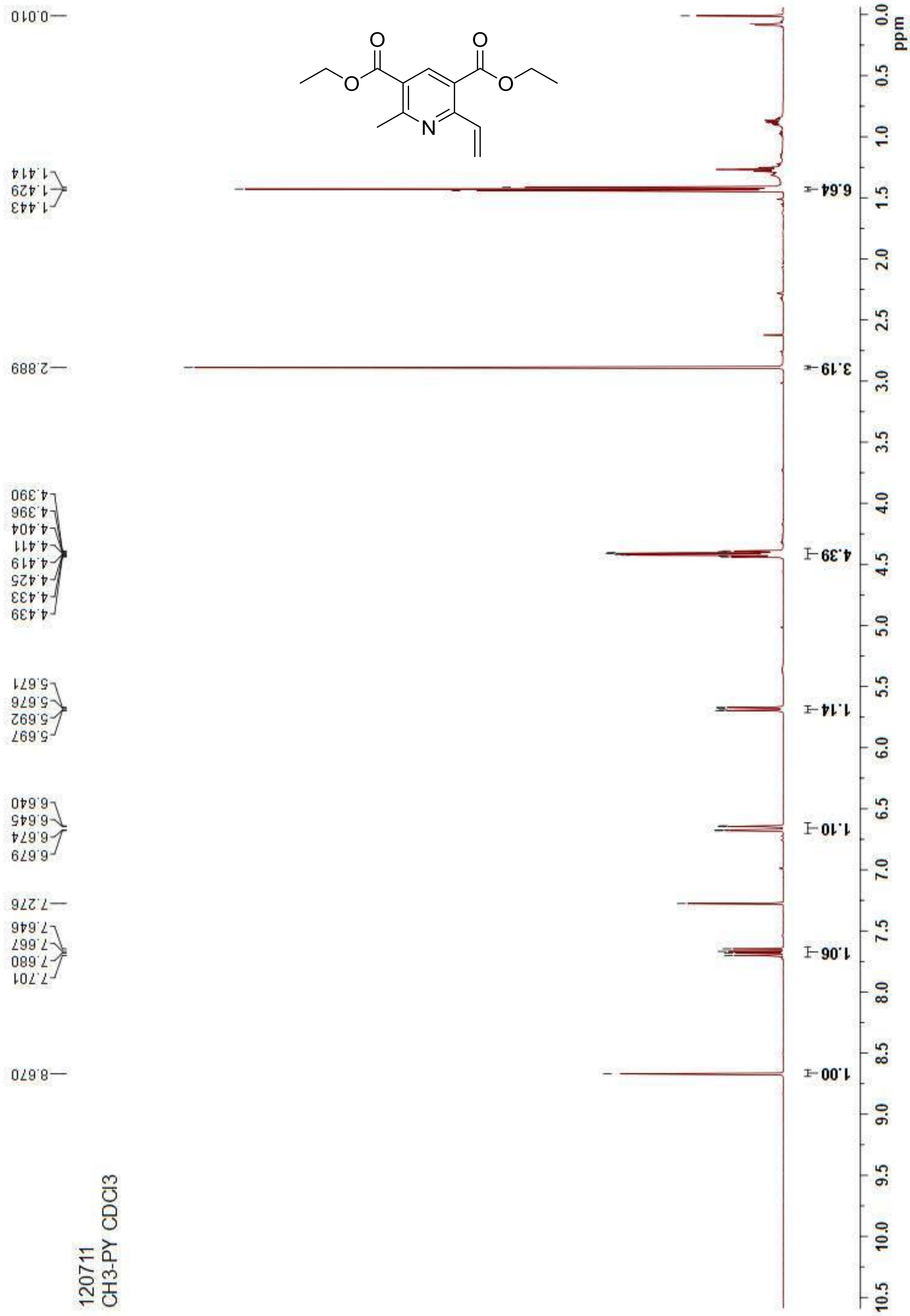
N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O
O
O
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4.419
4.425
4.433
4.439
5.671
5.676
5.692
5.697
6.640
6.645
6.674
6.679
7.276
7.646
7.667
7.680
7.701
8.670
120711
CH3-PY CDCl3
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1.14
1.10
1.06
1.00
ppm
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1.5
2.0
2.5
3.0
3.5
4.0
4.5
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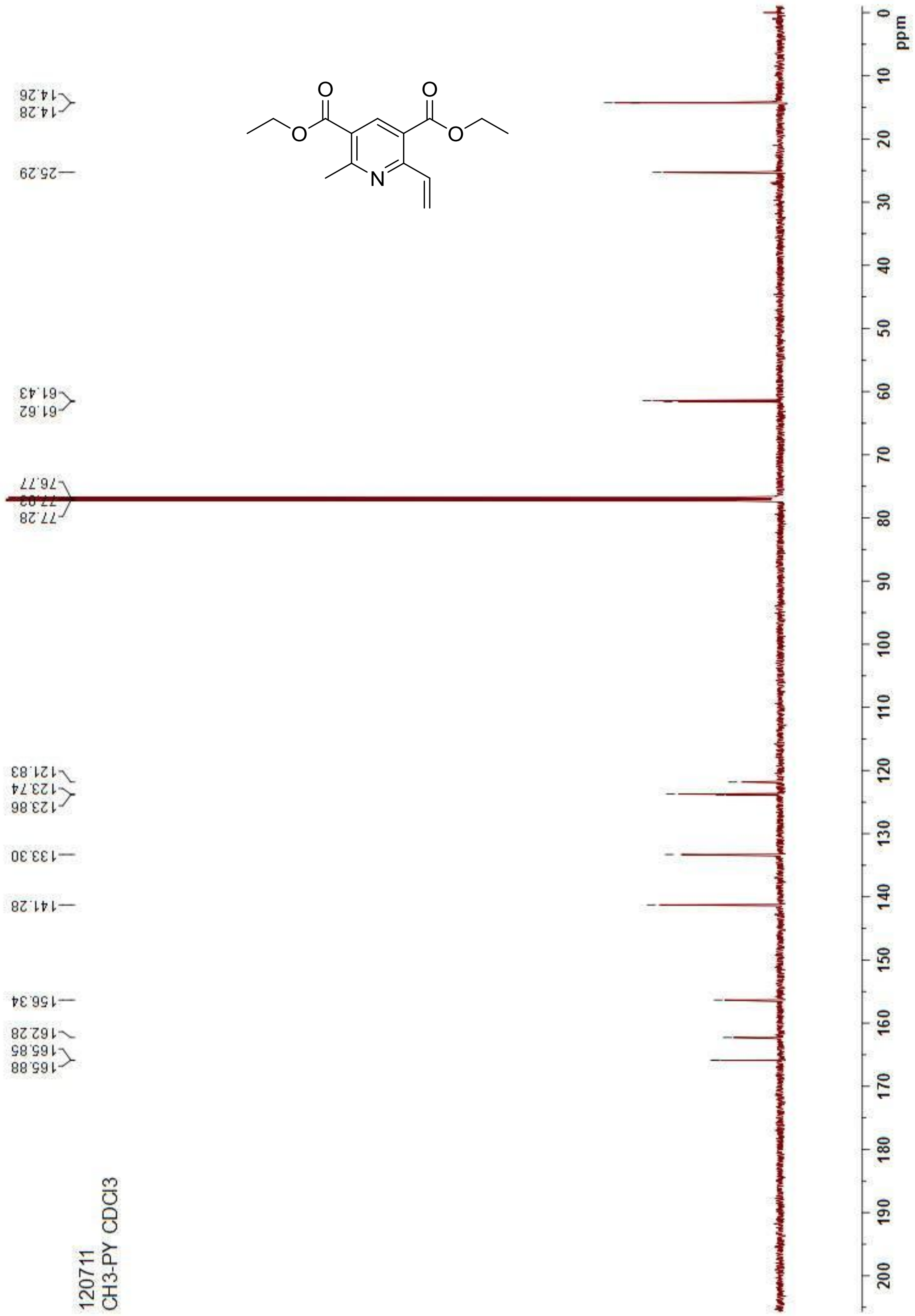
10.5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77.28
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141.28
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162.28
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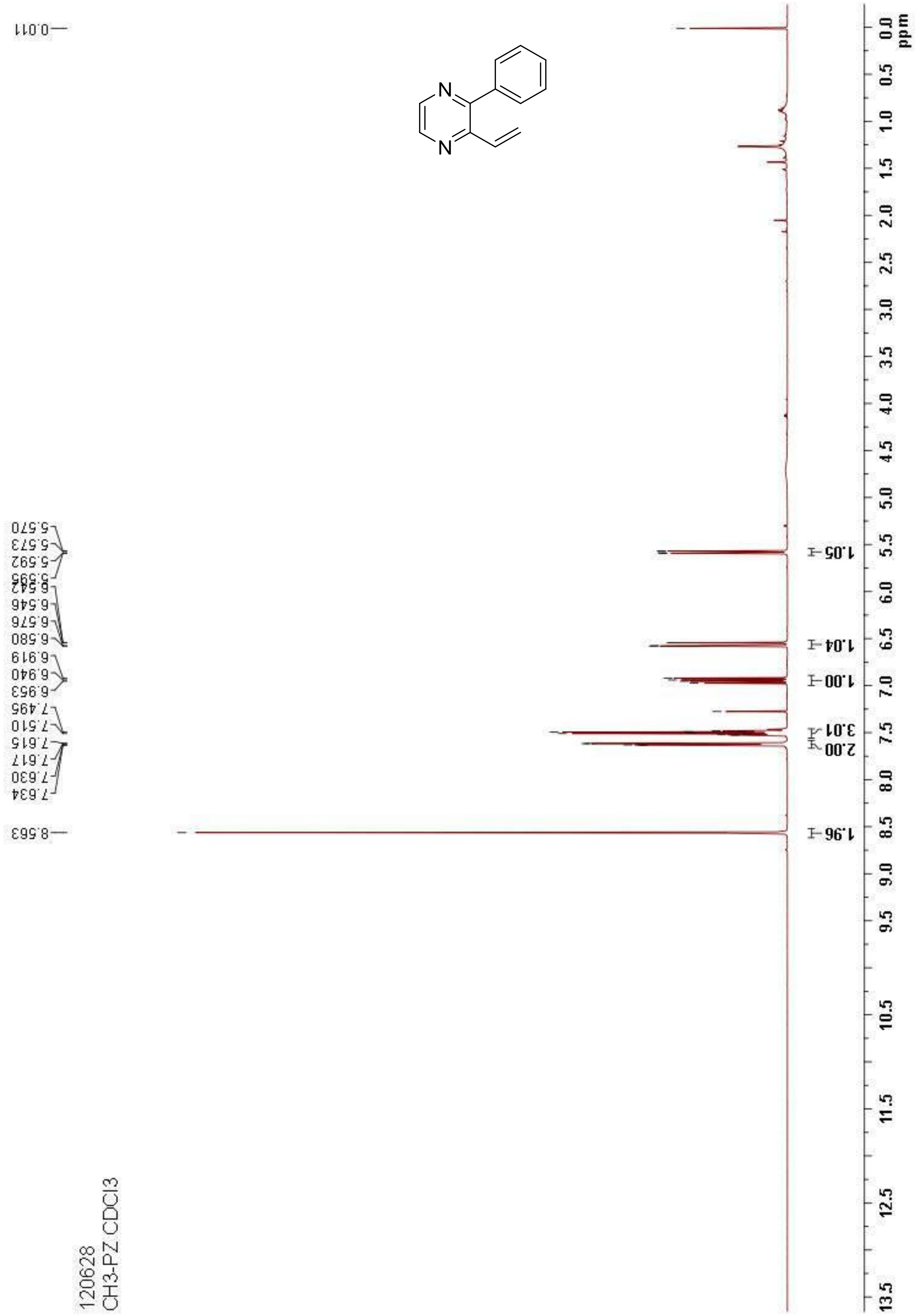
165.88
120711
CH3-PY CDCl3
ppm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6.940
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6.578
6.546
6.542
5.595
5.592
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1.05
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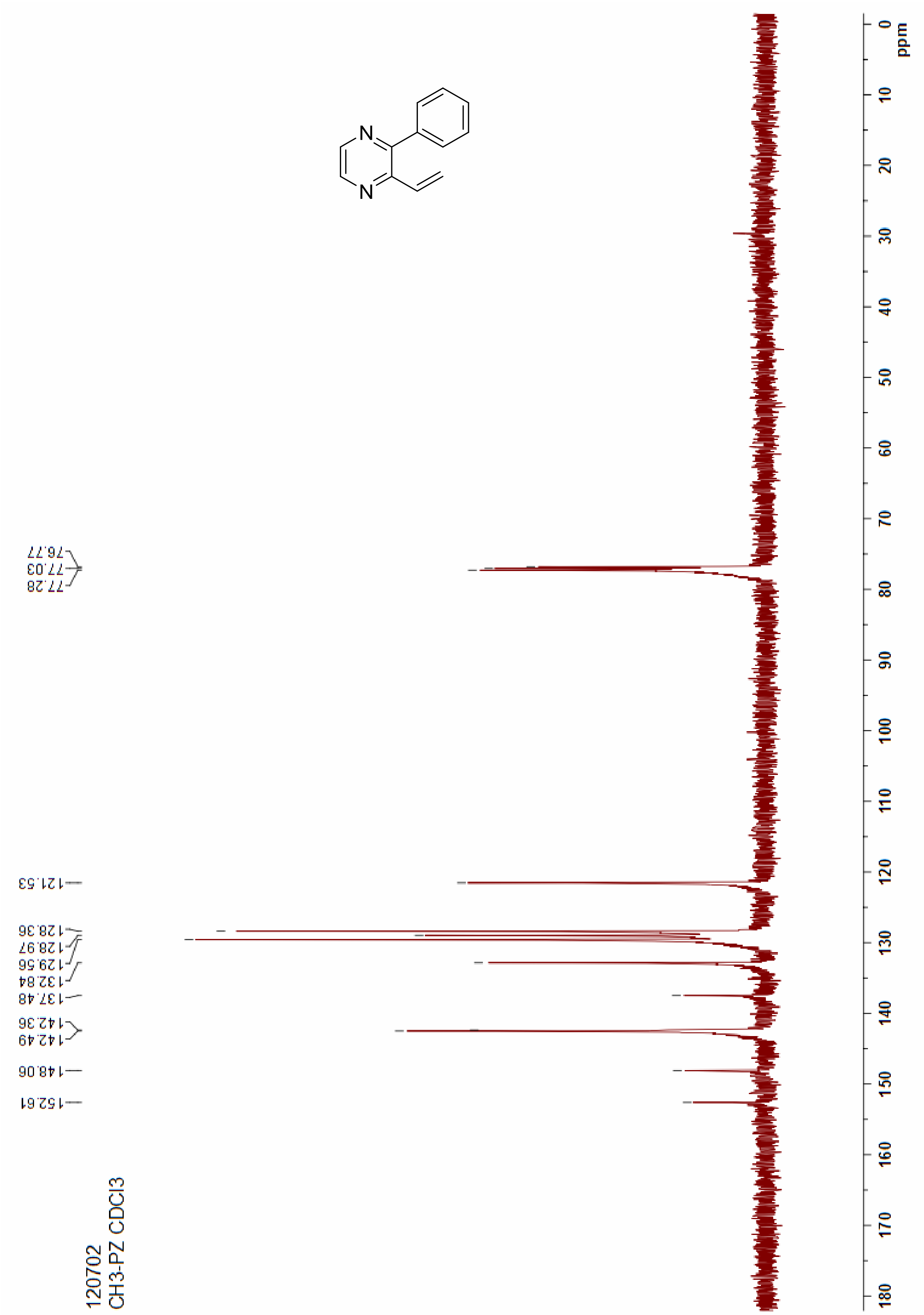
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129.56
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137.48
142.36
142.49
148.06
152.61
120702
CH3-PZ CDCl3
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110
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140
150
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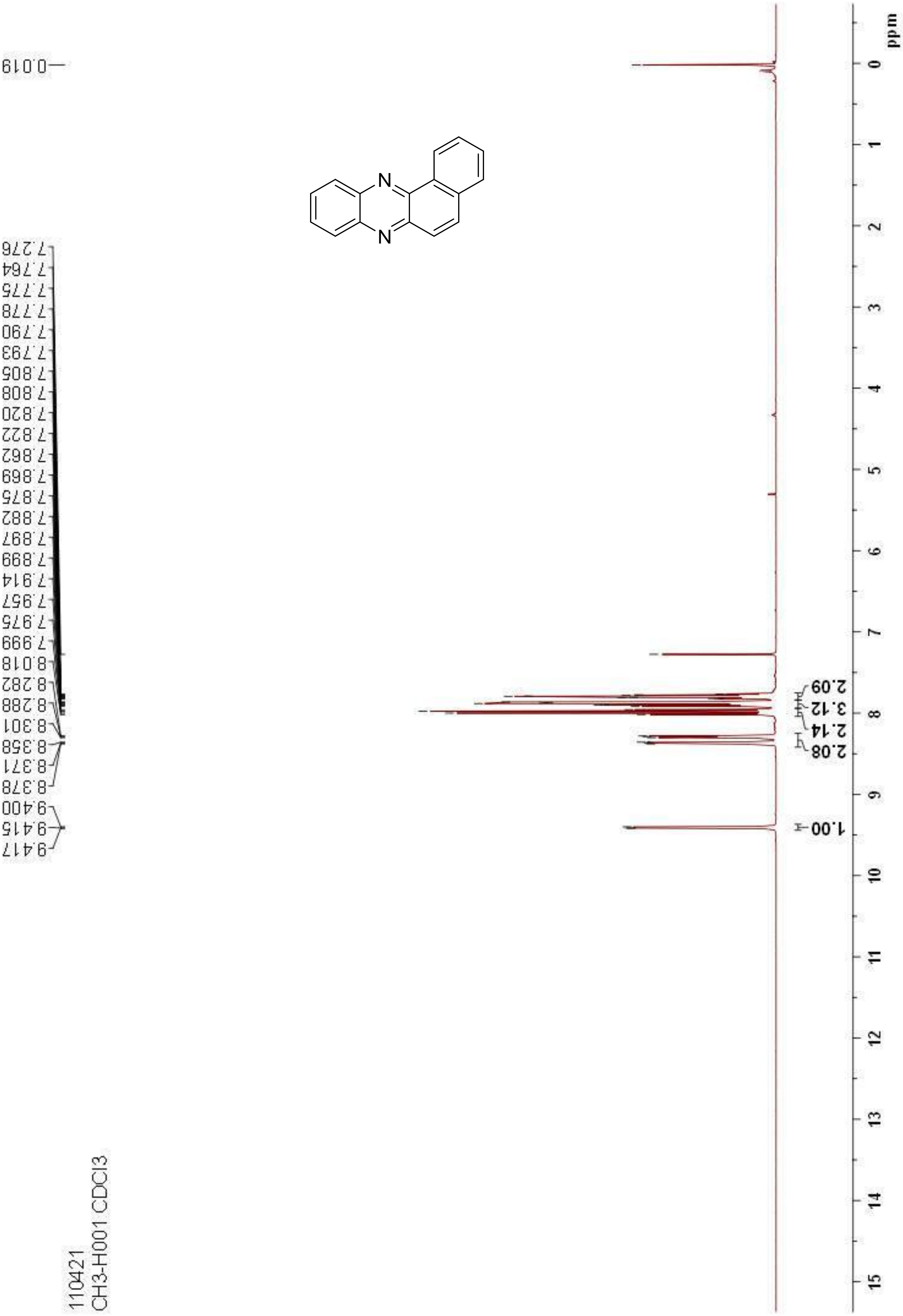
170
180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7.862
7.869
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7.882
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7.899
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7.957
7.975
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8.018
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8.288
8.301
8.358
8.371
8.378
9.400
9.415
9.417
N
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2.08
1.00
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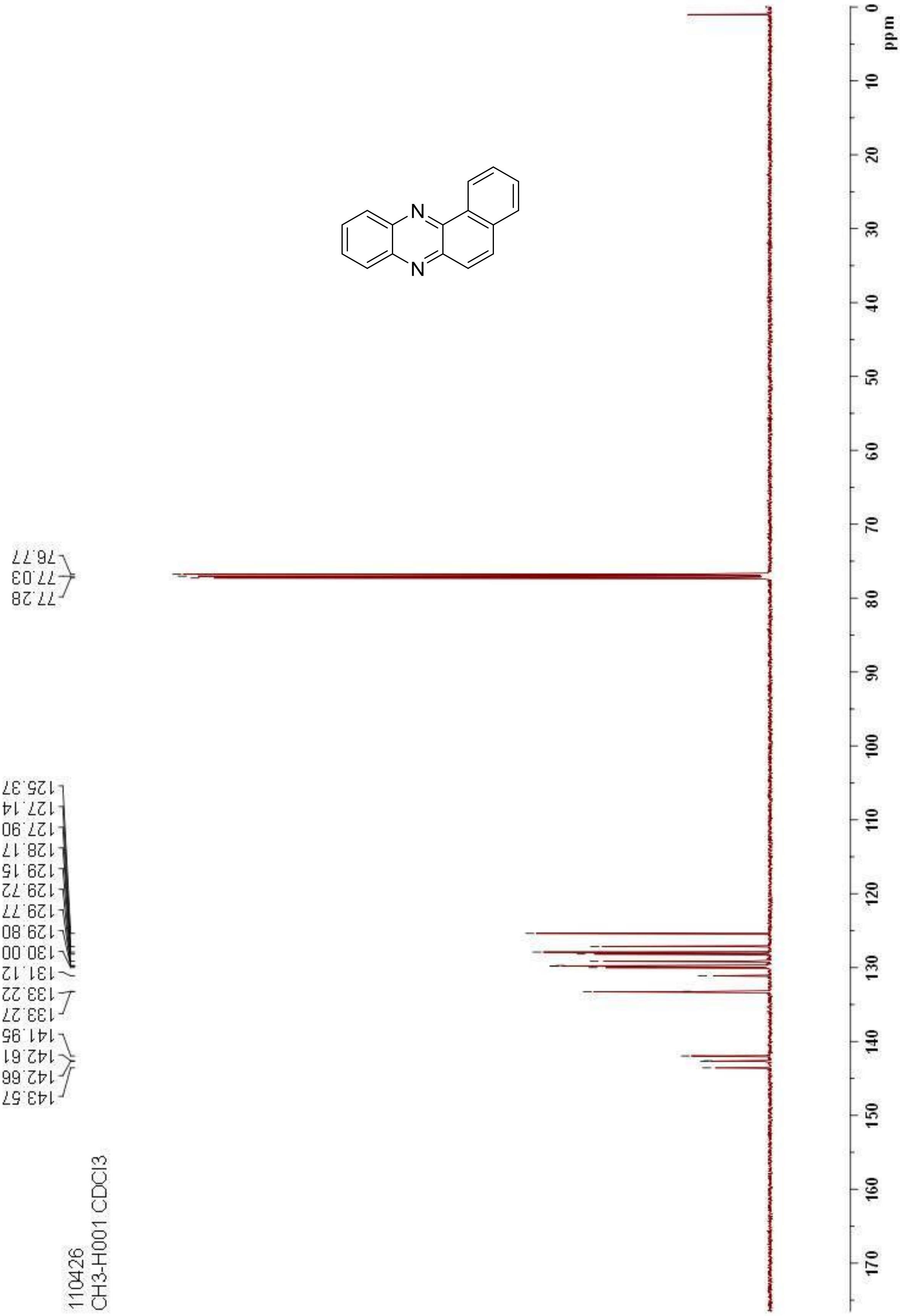
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127.90
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129.77
129.80
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131.12
133.22
133.27
141.95
142.61
142.66
143.57
110426
CH3-H001 CDCl3
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100
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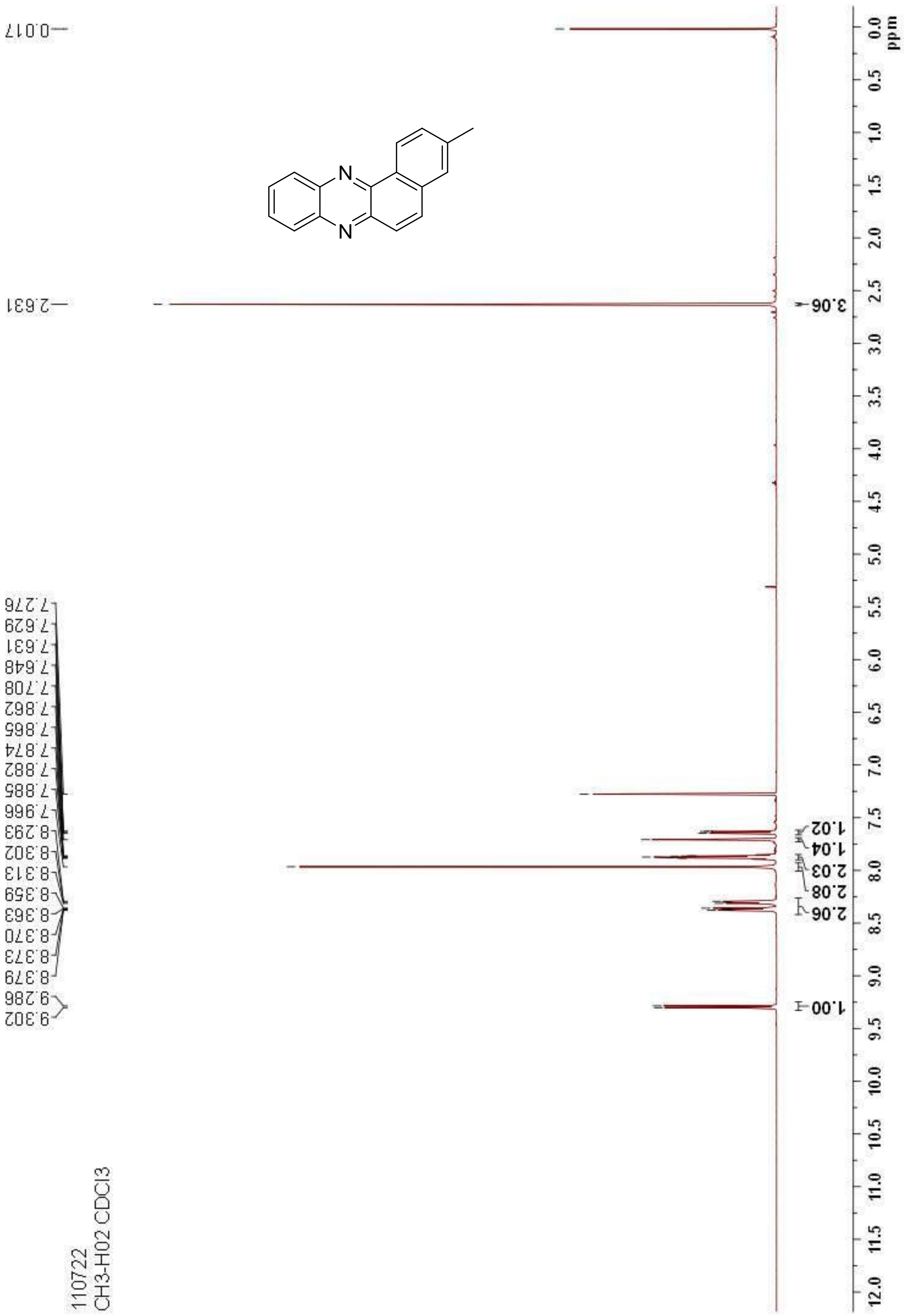
170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ppm
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2.631
7.276
7.629
7.631
7.648
7.708
7.862
7.865
7.874
7.882
7.885
7.966
8.293
8.302
8.313
8.359
8.363
8.370
8.373
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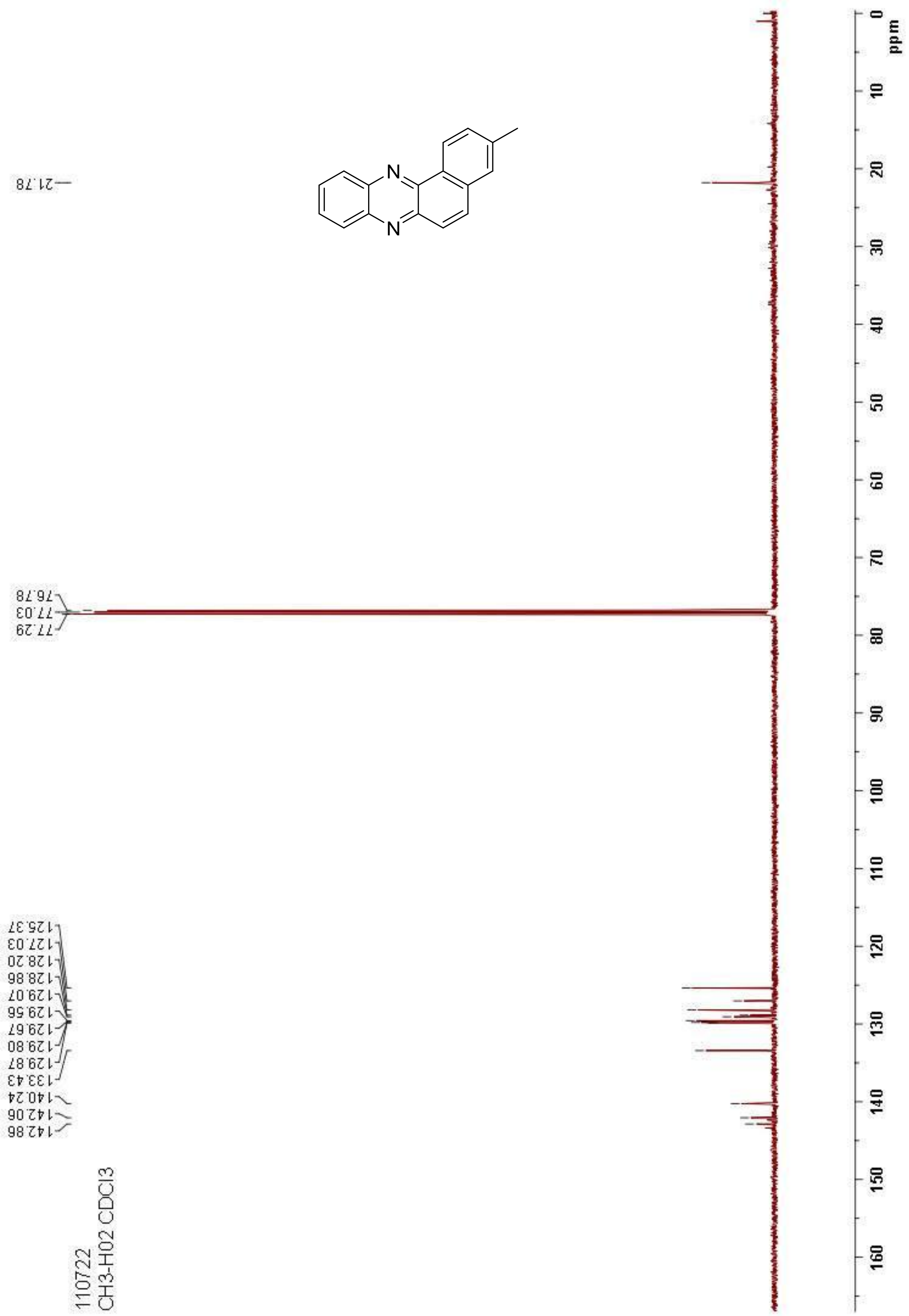
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CH3-H02 CDCl3
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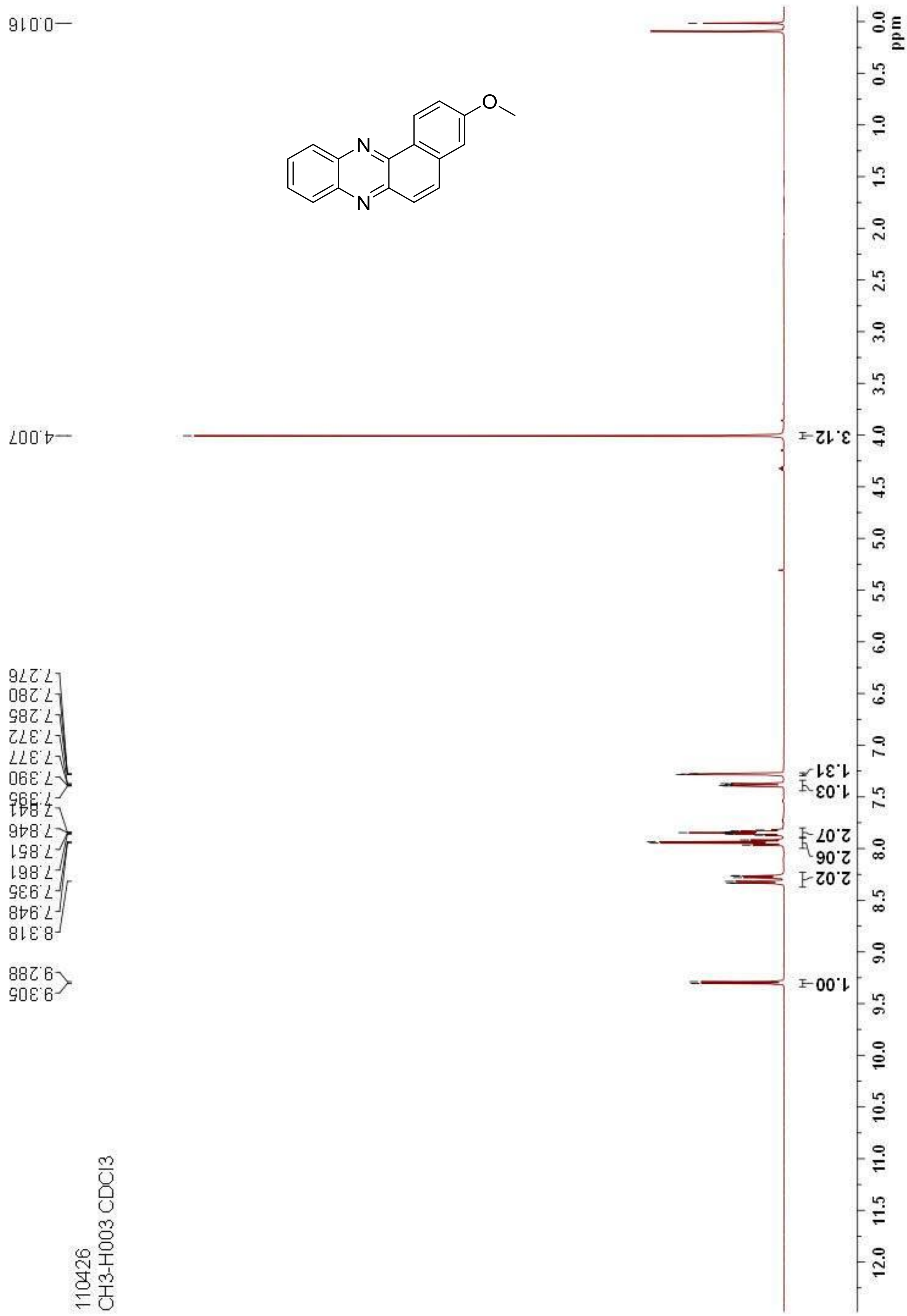
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7.935
7.948
8.318
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1.31
1.03
2.07
2.06
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1.00
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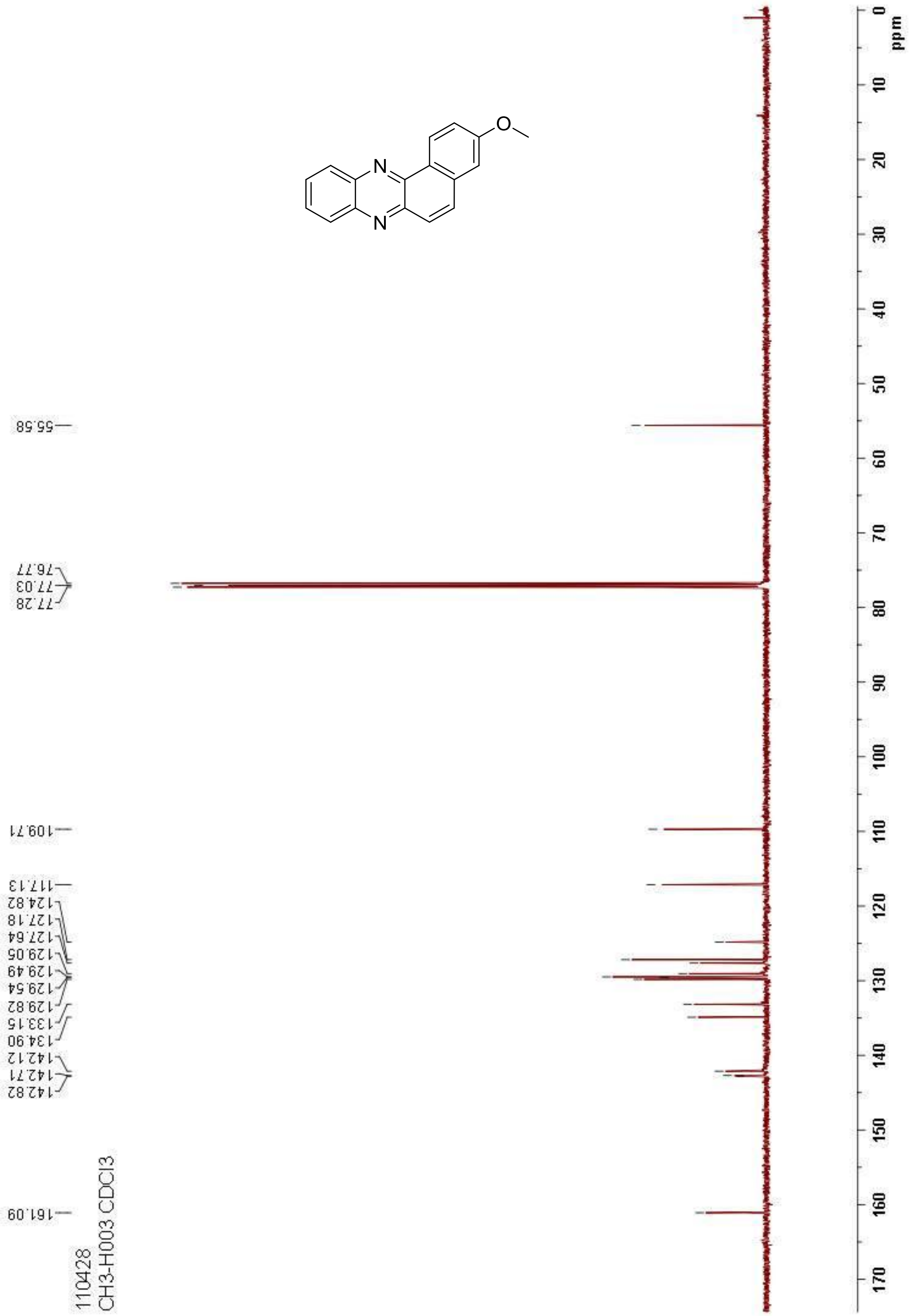
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133.15
134.90
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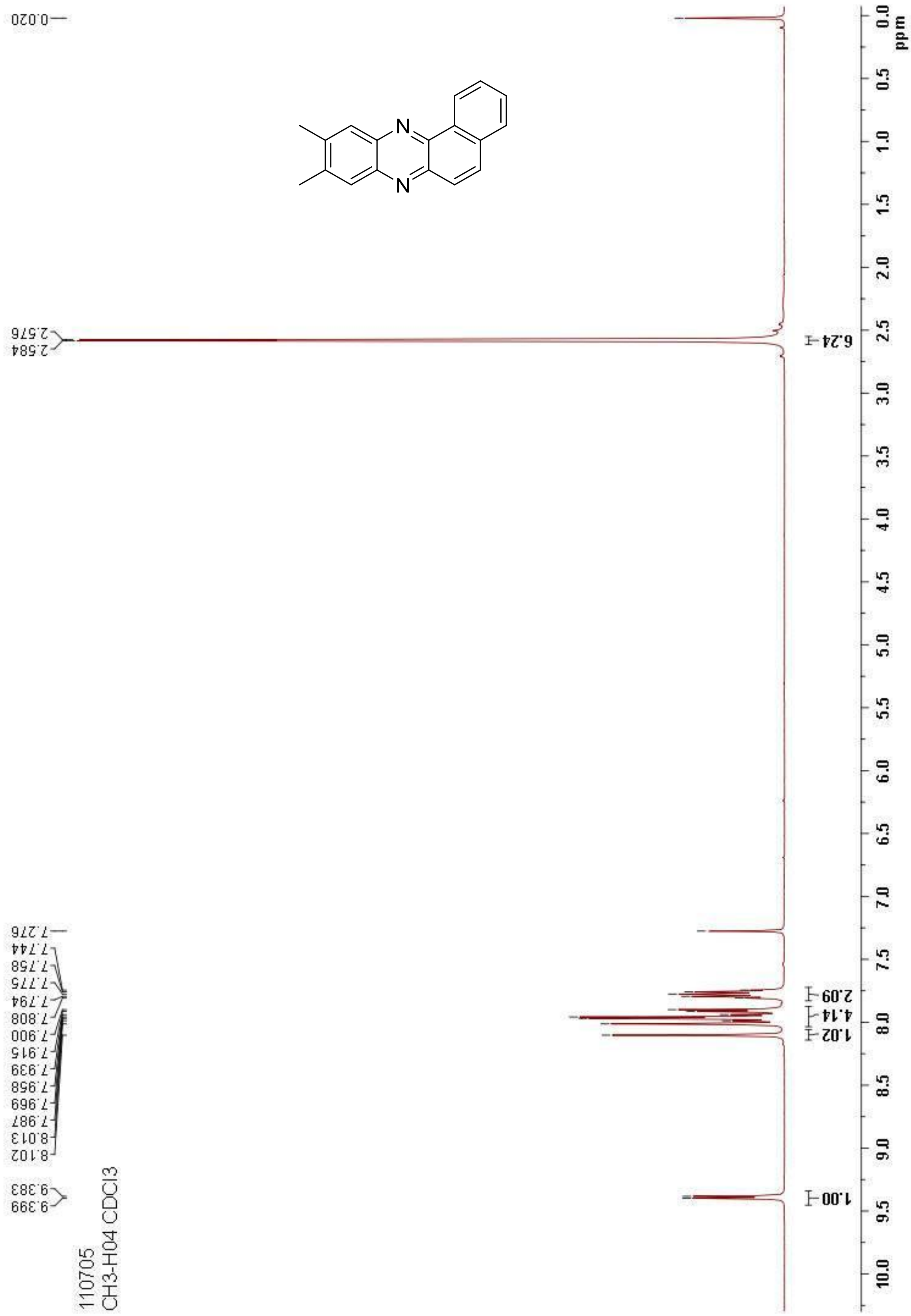
CH3-H003 CDCl3
ppm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7.969
7.987
8.013
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110705
CH3-H04 CDCl3
6.24
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4.14
1.02
1.00
ppm
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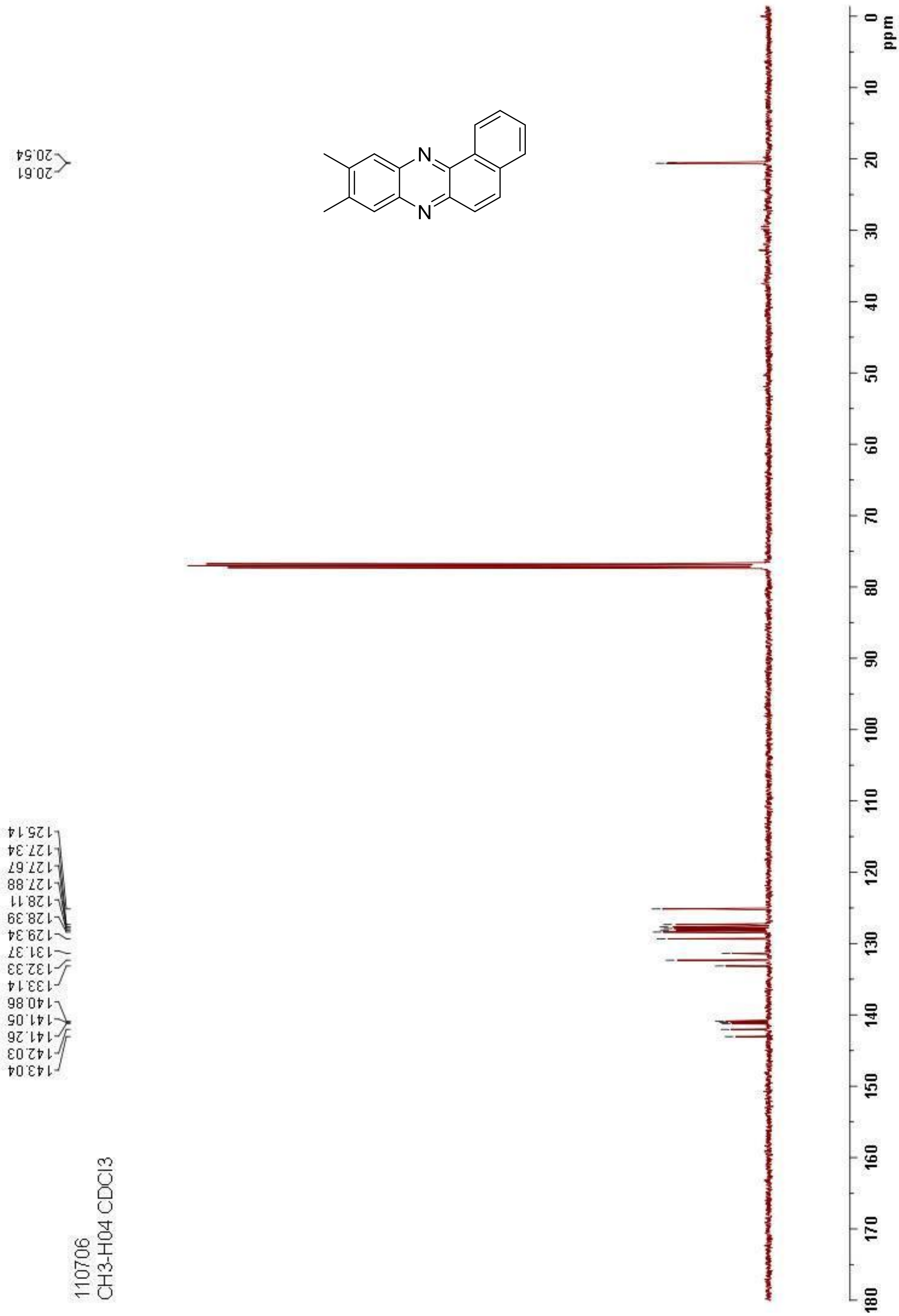
N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127.88
128.11
128.39
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131.37
132.33
133.14
140.86
141.05
141.26
142.03
143.04
110706
CH3-H04 CDCl3
N
N
ppm
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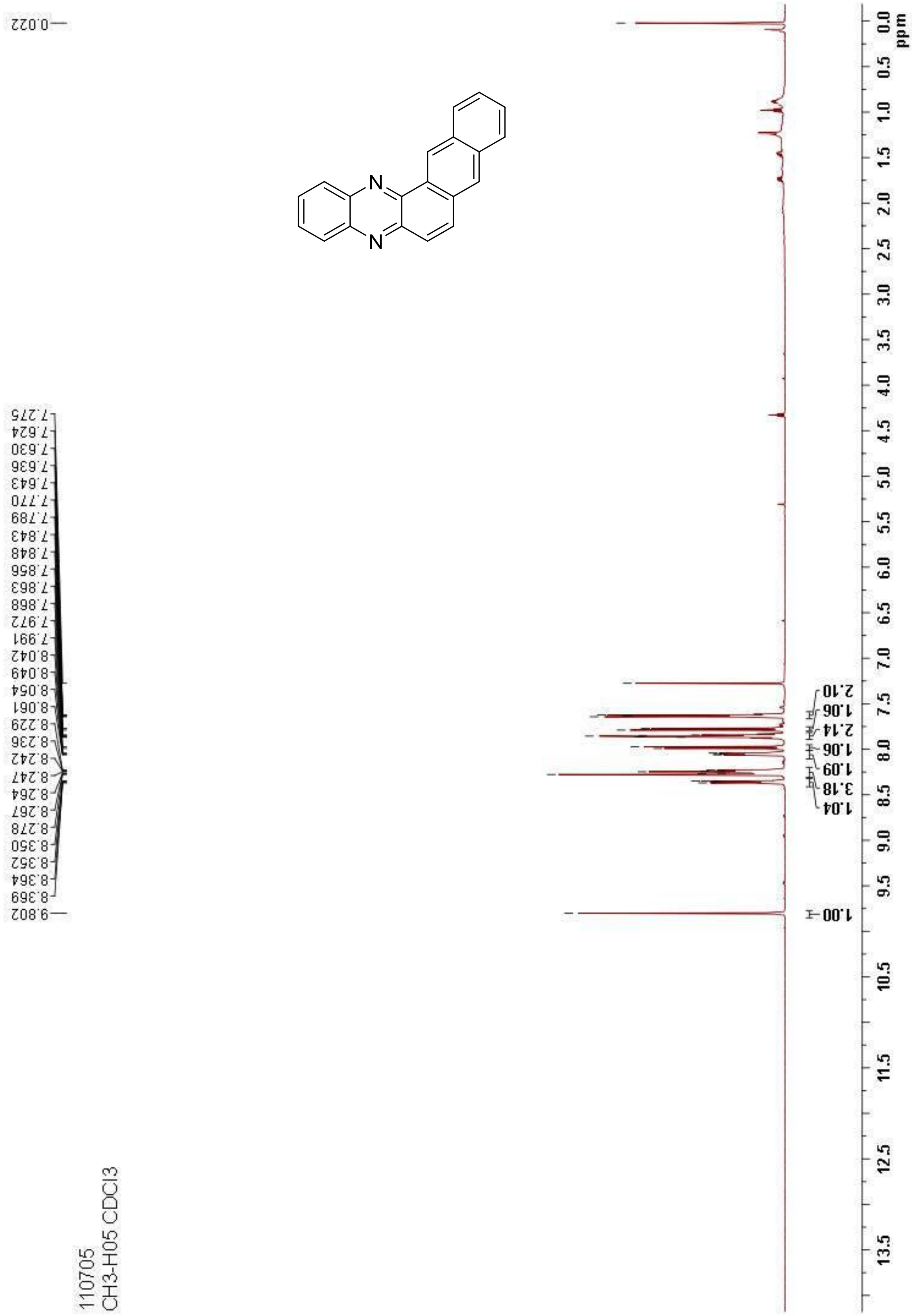
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180



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7.863
7.868
7.972
7.991
8.042
8.049
8.054
8.061
8.229
8.236
8.242
8.247
8.264
8.267
8.278
8.360
8.362
8.364
8.369
9.802
N
N
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2.14
1.06
1.09
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1.04
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ppm
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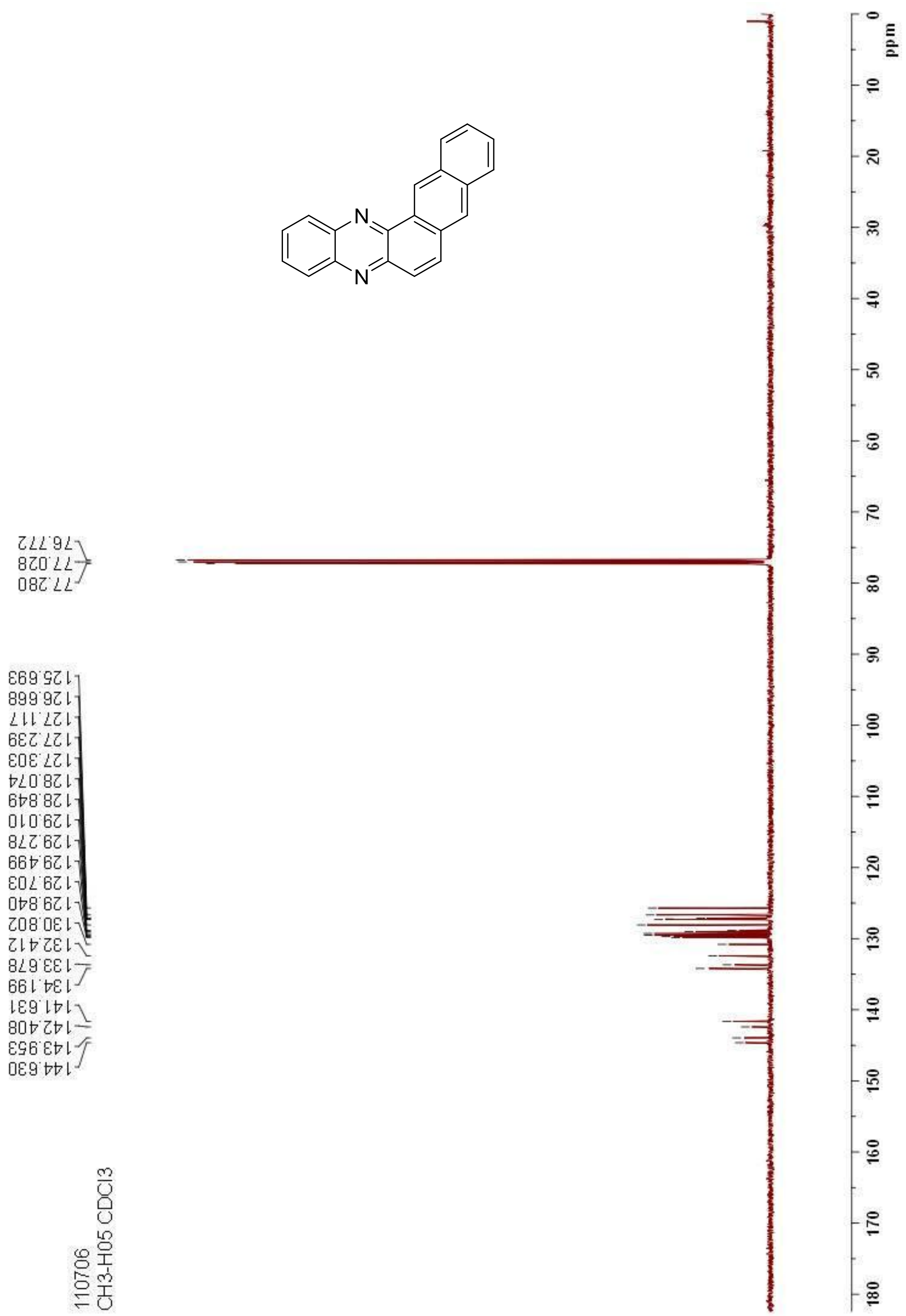
CH3-H05 CDCl3



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129.840
130.802
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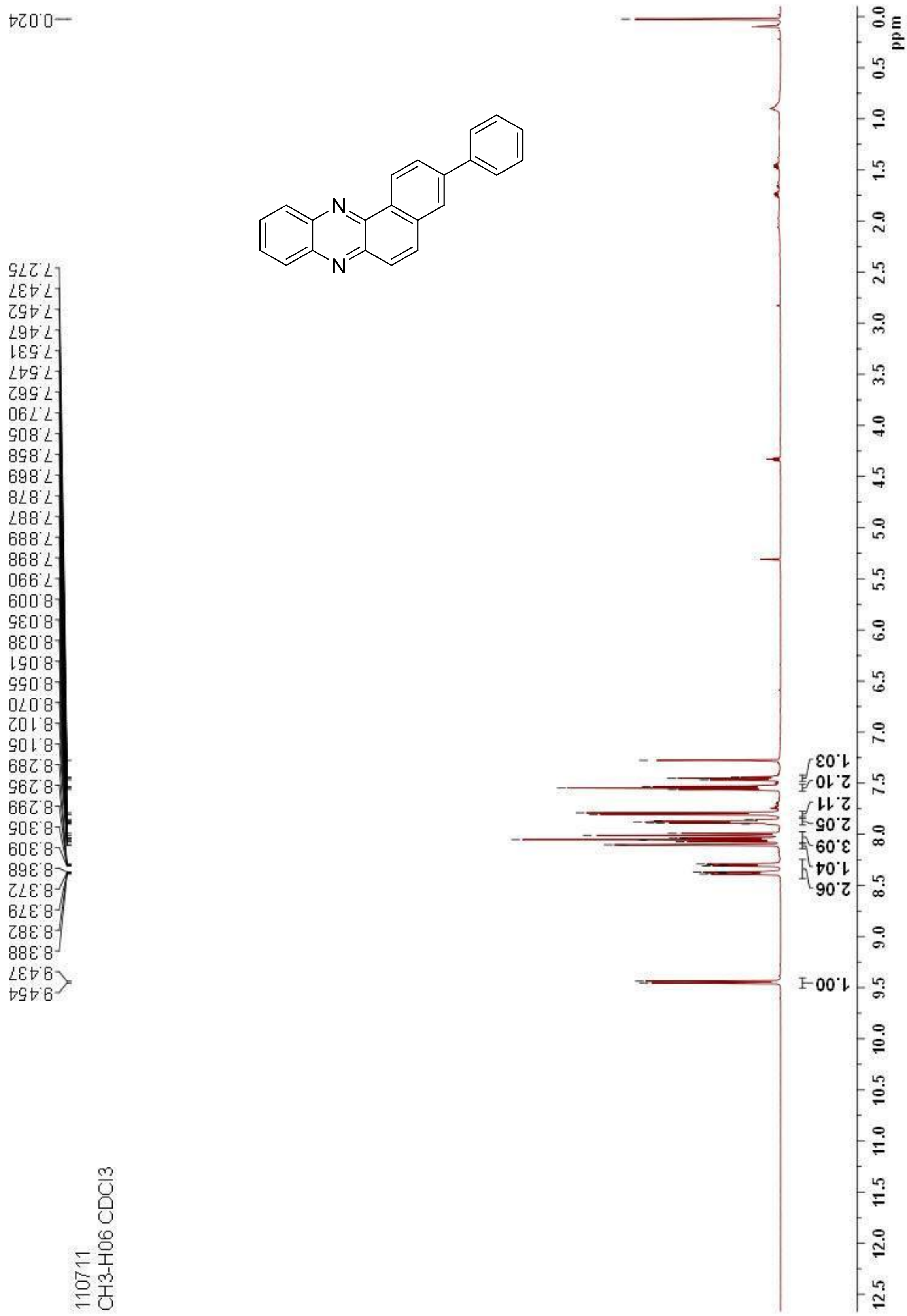
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7.889
7.898
7.990
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8.035
8.038
8.051
8.055
8.070
8.102
8.105
8.289
8.295
8.299
8.305
8.309
8.368
8.372
8.379
8.382
8.388
9.437
9.454
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N
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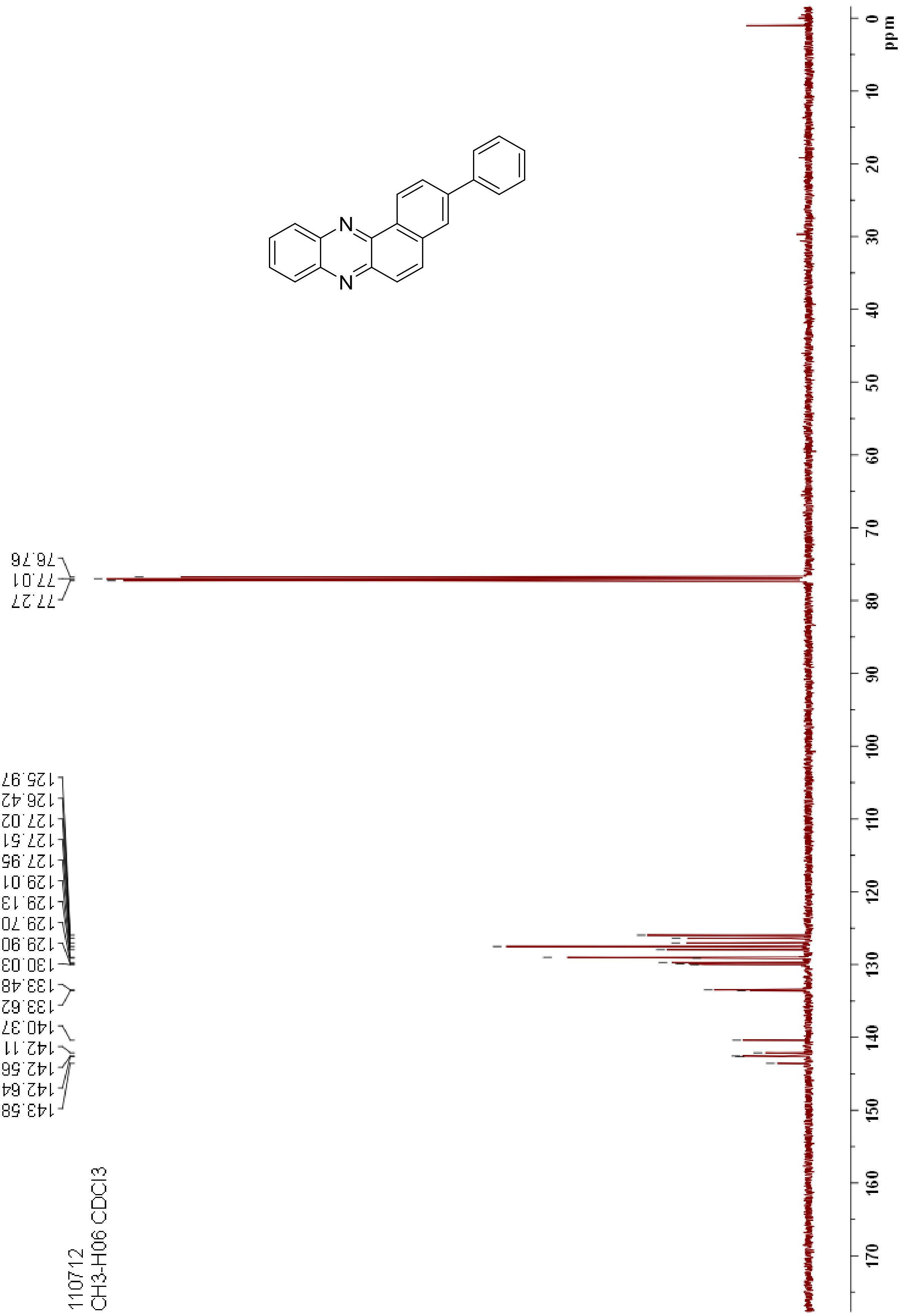
2.10
2.11
2.05
3.09
1.04
2.06
1.00
ppm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129.01
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129.70
129.90
130.03
133.48
133.62
140.37
142.11
142.56
142.64
143.58
110712
CH3-H06 CDCl3
ppm
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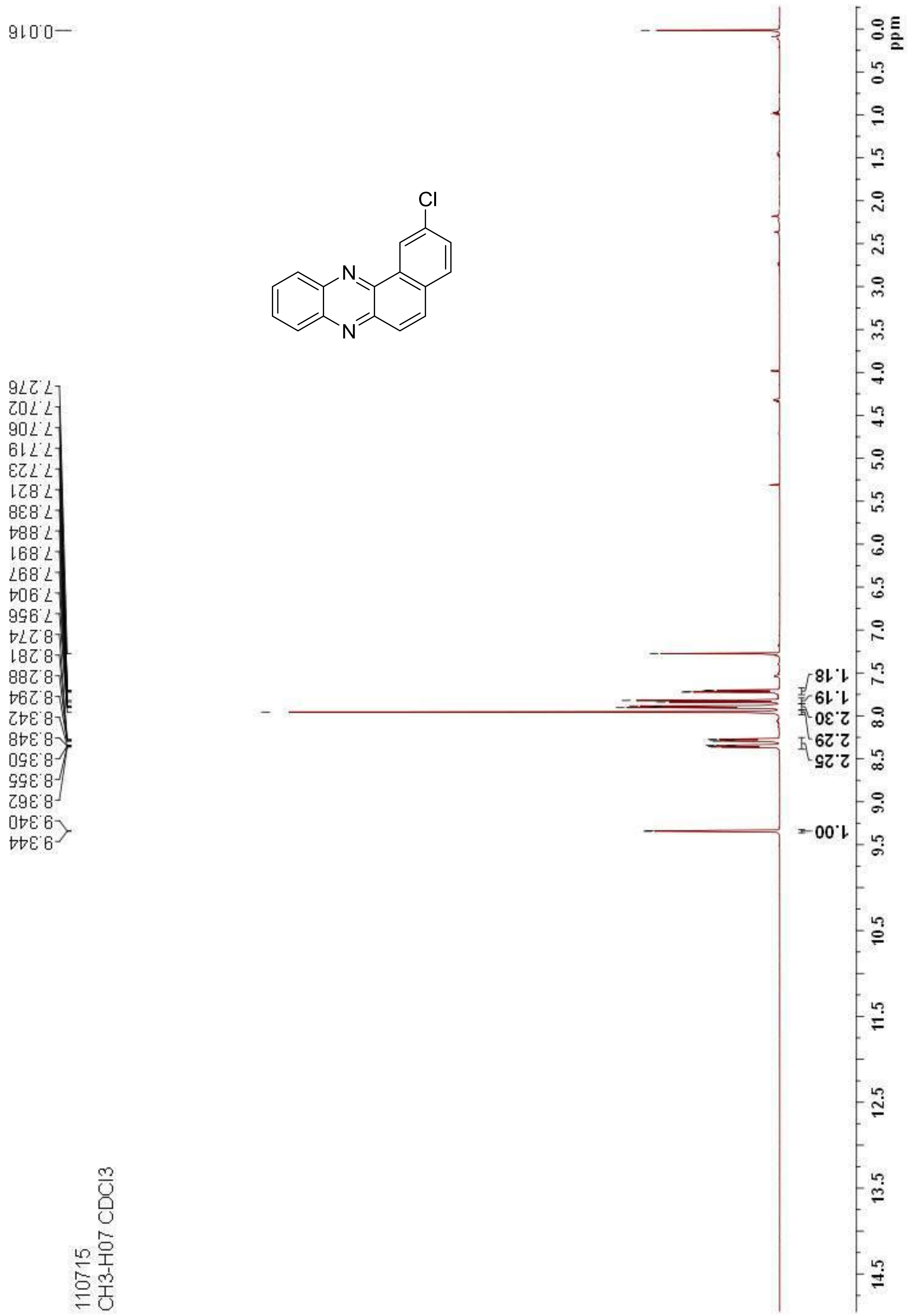
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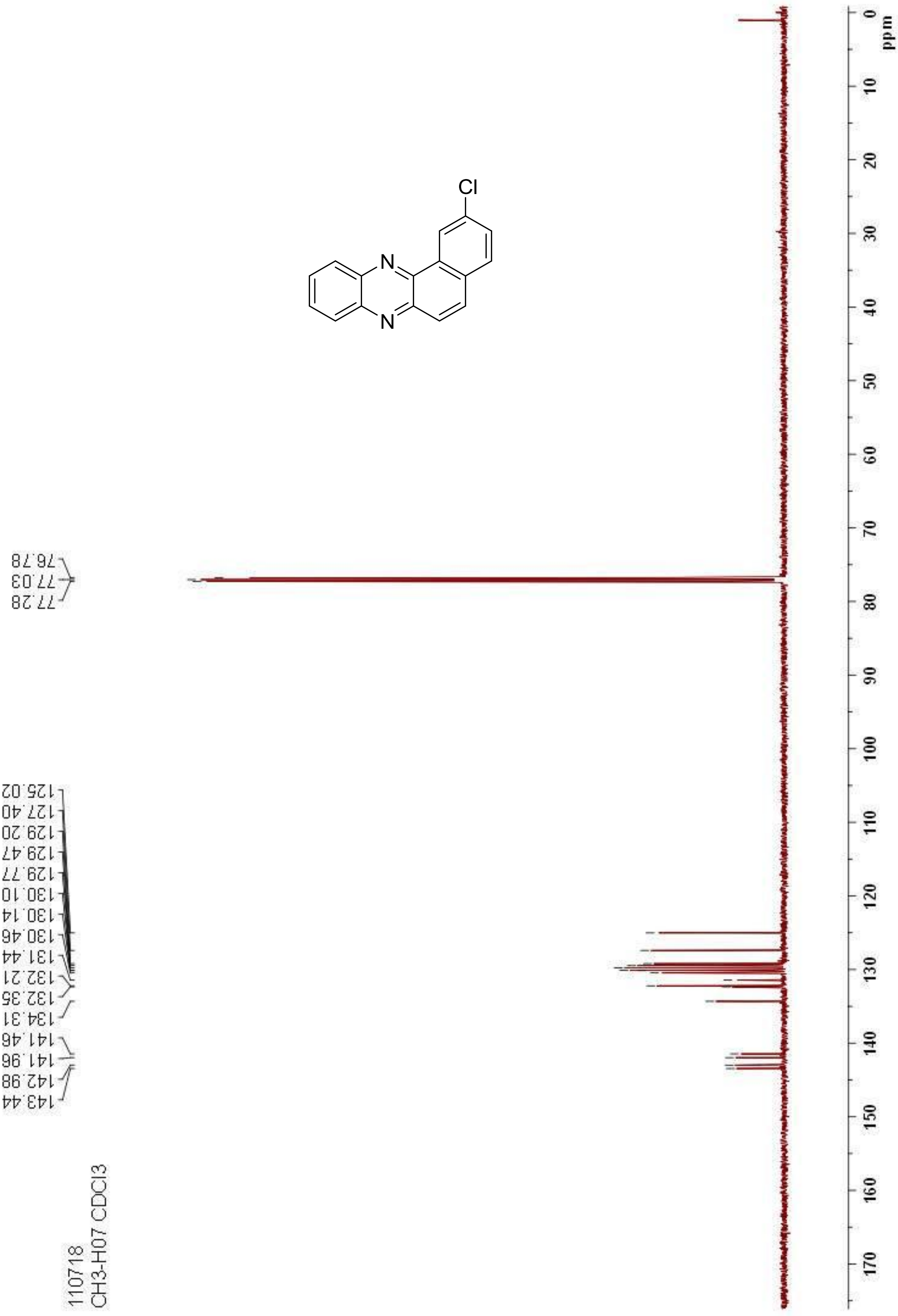
7.706
7.719
7.723
7.821
7.838
7.884
7.891
7.897
7.904
7.956
8.274
8.281
8.288
8.294
8.342
8.348
8.350
8.355
8.362
9.340
9.344
1.18
1.19
2.30
2.29
2.25
1.00
ppm
110715
CH3-H07 CDCl3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125.02
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129.20
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130.10
130.14
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132.35
134.31
141.46
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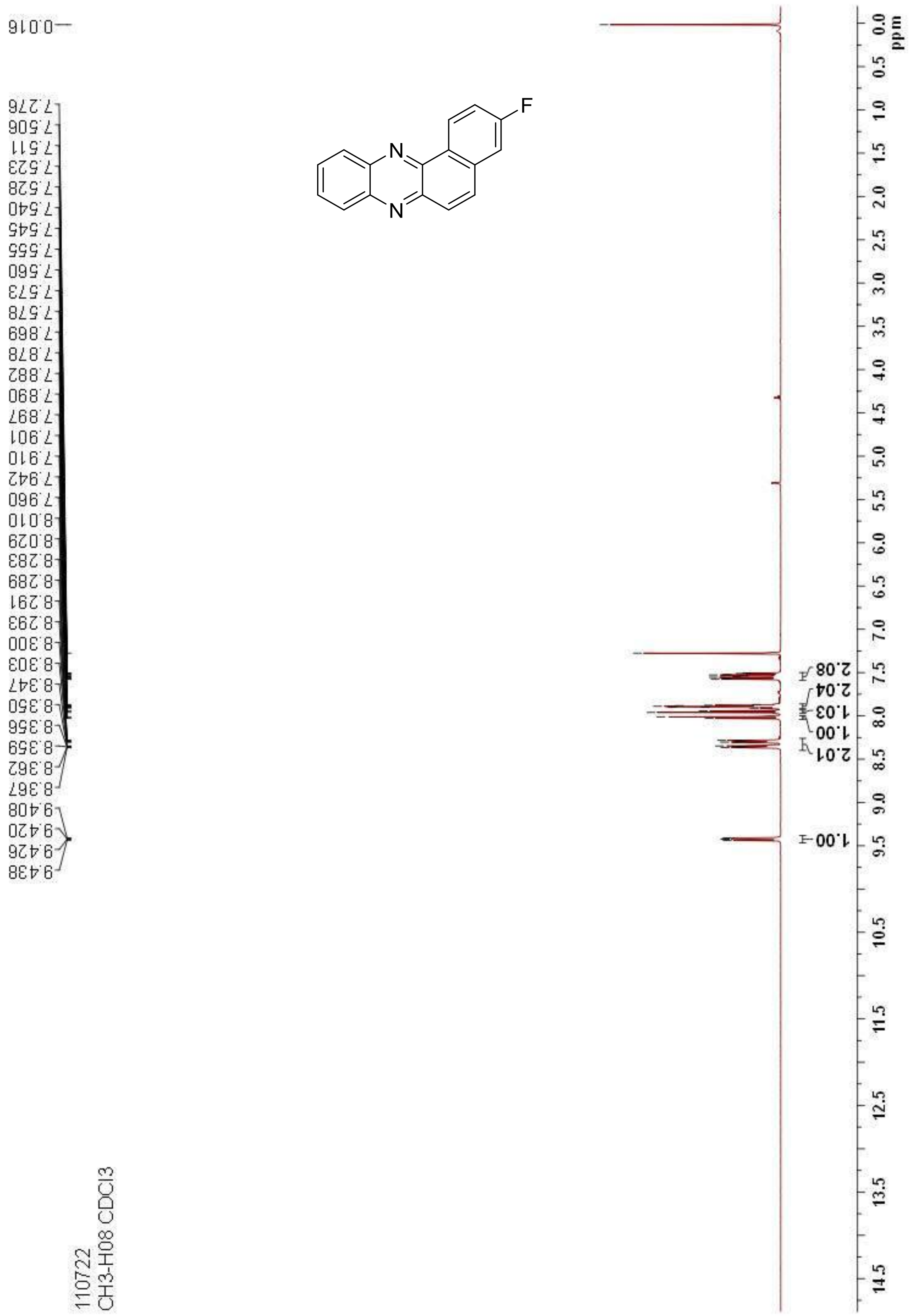
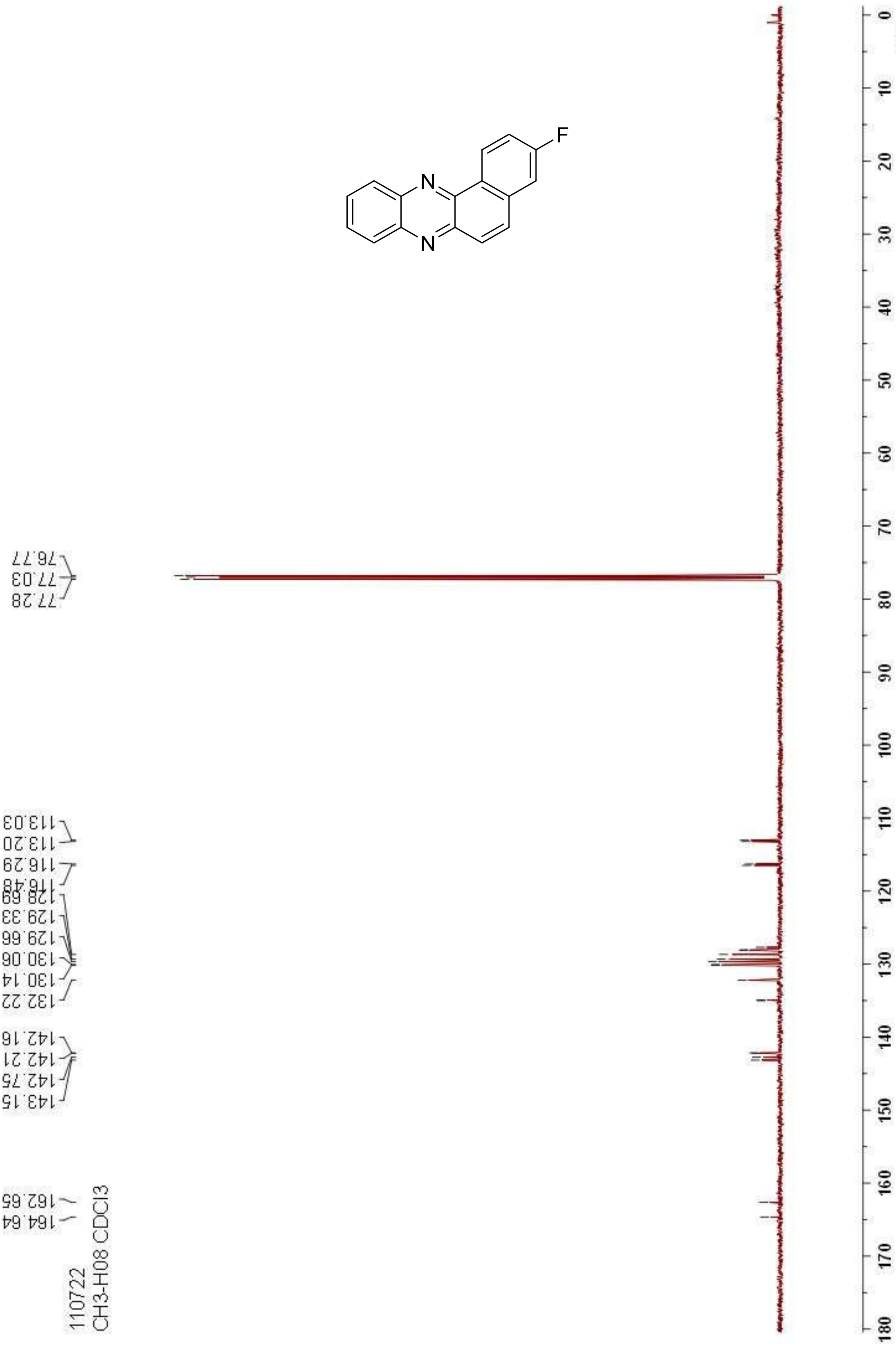
143.44
110718
CH3-H07 CDCl3
ppm


110722
CH3-H08 CDCl3
N
N
F
ppm


F
N
N
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77.03
77.28
113.03
113.20
116.29
116.48
128.69
129.33
129.66
130.06
130.14
132.22
142.16
142.21
142.75
143.15
162.65
164.64
110722
CH3-H08 CDCl3
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180