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A cascade formation of *N*-pyridylacrylamides from pyrido[1,2-*a*]pyrimidine diones and chromene aldehydes

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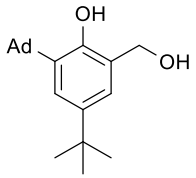
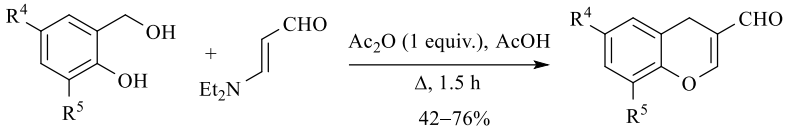
Solvents were purified and dried by standard procedures before use. ^{1}H and ^{13}C NMR spectra (400 and 100 MHz, respectively), as well as DEPT-135 spectra were acquired on a JEOL JNM-ECX400 spectrometer in DMSO-d_6 or $CDCl_3$ using residual solvent signals (DMSO-d_6: 2.50 ppm for ^{1}H nuclei, 39.5 ppm for ^{13}C nuclei; $CDCl_3$: 7.26 ppm for ^{1}H nuclei, 77.2 ppm for ^{13}C nuclei) as internal standards. Chemical shifts are reported in δ unit-parts per million (ppm). Splitting patterns are designated as s = singlet; br. s = broad singlet; d = doublet, t = triplet; m = multiplet. Elemental analysis was performed on a Euro Vector EA-3000 CHNS-analyzer. Melting points were determined by the capillary method on an SRS OptiMelt MPA100 apparatus. The starting chromenecarbaldehydes **2a**–**c**, **5f**, **7** [(a) D. V. Osipov, A. A. Artyomenko, V. A. Osyanin and Yu. N Klimochkin, *Chem. Heterocycl. Compd*., 2019, **55**, 261 (*Khim. Geterotsikl. Soedin*., 2019, **55**, 261). (b) A. V. Lukashenko, V. A. Osyanin, D. V. Osipov and Yu. N. Klimochkin, *Chem. Heterocycl. Compd*. 2016, **52**, 711 (*Khim. Geterotsikl. Soedin*., 2016, **52**, 711)], as well as 2*H*-pyrido[1,2-*a*]pyrimidine-2,4(3*H*)-diones **1a**–**c** [A. D. Dunn and R. Norrie, *Z. Chem*., 1990, **30**, 98.] were obtained by known methods.

2-(Adamantan-1-yl)-4-*tert*-butyl-6-(hydroxymethyl)phenol (9d).



Solid sodium borohydride (1.5 g, 40 mmol) was added to a suspension of 3-(adamantan-1-yl)-5-(*tert*-butyl)-2-hydroxybenzaldehyde (9.38 g, 30 mmol) in ethanol (100 ml) at room temperature over 15 min. Gas evolution was observed. The mixture was stirred at room temperature for 3 h and poured into 5% acetic acid (300 ml). The precipitated solid was filtered off, washed with water, dried at room temperature and recrystallized from hexane. Yield 8.05 g (85%), colorless solid, mp 157-159 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 1.20 (s, 9H, *t*-Bu), 1.70 (br. s, 6H, CH_2 Ad), 2.00 (br. s. 3H, CH Ad), 2.06 (br. s, 6H, CH_2 Ad), 4.59 (d, *J*=5.3 Hz, 2H, CH_2), 5.83 (t, *J*=5.3 Hz, 1H, $CH_2O\underline{H}$), 6.96 (d, *J*=2.5 Hz, 1H, Ar), 7.00 (d, *J*=2.5 Hz, 1H, Ar), 8.46 (s, 1H, OH). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 29.0 ($3CH_3$), 32.0 (3CH Ad), 34.4 (C *t*-Bu), 37.0 (C Ad), 37.2 ($3CH_2$ Ad), 40.7 ($3CH_2$ Ad), 62.8 (CH_2O), 122.0 (CH), 122.5 (CH), 127.1 (C), 136.2 (C), 141.1 (C), 152.7 (C−OH). Found (%): C, 80.25; H, 9.59. Calc. for $C_{21}H_{30}O_2$ (%): C, 80.21; H, 9.62.

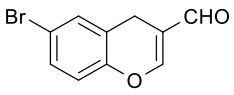
Synthesis of 4*H*-chromene-3-carbaldehydes (5a–e) (general procedure): Acetic anhydride (2.04 g, 20 mmol) was added to a solution of the corresponding *o*-hydroxybenzyl alcohol **9a**–**e** (20 mmol) and 3-(diethylamino)acrolein (2.8 g, 22 mmol) in AcOH (20 ml), and the mixture was refluxed for 1.5 h (compounds **5a**,**b**,**e**) or 4 h (compounds **5c**,**d**). The mixture was cooled to room temperature, and the formed precipitate was collected. The crude product was purified by recrystallization. In the cases where there was no precipitation (compounds **5c**,**d**), the mixture was concentrated under reduced pressure, and the residue was purified by column chromatography (silica gel, eluent CH_2Cl_2–hexane, 1:1) followed by recrystallization from methanol.



9a–e **5a–e**

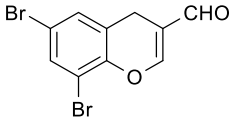
a R^4 = Br, R^5 = H
b R^4 = R^5= Br
c R^4 = R^5= Bu^t
d R^4 = Bu^t, R^5 = 1-adamantyl
e R^4 = 1-adamantyl, R^5 = Br

6-Bromo-4*H*-chromene-3-carbaldehyde (5a).



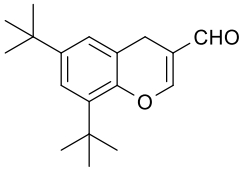
Yield 2.72 g (57%), colorless solid, mp 139-141 °C (AcOH). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.50 (s, 2H, CH_2), 6.87 (d, *J*=8.9 Hz, 1H, Ar), 7.26-7.30 (m, 2H, Ar), 7.35 (s, 1H, H-2), 9.44 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.6 (CH_2), 117.7 (C), 117.9 (C), 118.7 (CH), 121.8 (C), 131.1 (CH), 132.7 (CH), 149.3 (C), 158.8 (CH-2), 189.7 (CHO). Found (%): C, 50.15; H, 2.89. Calc. for $C_{10}H_7BrO_2$ (%): C, 50.24; H, 2.95.

6,8-Dibromo-4*H*-chromene-3-carbaldehyde (5b).



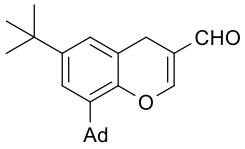
Yield 3.12 g (49%), colorless solid, mp 196-197 °C (AcOH). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.54 (s, 2H, CH_2), 7.23 (d, *J*=2.3 Hz, 1H, Ar), 7.42 (s, 1H, H-2), 7.56 (d, *J*=2.3 Hz, 1H, Ar), 9.48 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.1 (CH_2), 112.2 (C), 117.7 (C), 118.3 (C), 123.1 (C), 131.8 (CH), 134.4 (CH), 146.5 (C), 158.1 (CH-2), 189.4 (CHO). Found (%): C, 37.69; H, 1.88. Calc. for $C_{10}H_6Br_2O_2$ (%): C, 37.77; H, 1.90.

6,8-Di-*tert*-butyl-4*H*-chromene-3-carbaldehyde (5c).



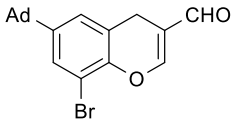
Yield 2.51 g (46%), colorless solid, mp 97-98 °C (MeOH). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.29 (s, 9H, *t*-Bu), 1.40 (s, 9H, *t*-Bu), 3.53 (s, 2H, CH_2), 6.99 (d, *J*=2.5 Hz, 1H, Ar), 7.21 (d, *J*=2.5 Hz, 1H, Ar), 7.44 (s, 1H, H-2), 9.46 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.2 (CH_2), 30.1 ($3CH_3$), 31.5 ($3CH_3$), 34.6 (C *t*-Bu), 35.1 (C *t*-Bu), 118.1 (C), 119.1 (C), 122.8 (CH), 124.8 (CH), 137.4 (C), 146.8 (C), 147.4 (C), 158.7 (CH-2), 190.1 (C=O). Found (%): C, 79.42; H, 8.87. Calc. for $C_{18}H_{24}O_2$ (%): C, 79.37; H, 8.88.

8-(Adamantan-1-yl)-6-*tert*-butyl-4*H*-chromene-3-carbaldehyde (5d).



Yield 2.94 g (42%), colorless solid, mp 138-140 °C (MeOH). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.29 (s, 9H, *t*-Bu), 1.78 (br. s, 6H, CH_2 Ad), 2.09 (br. s, 9H, CH_2 Ad, CH Ad), 3.53 (s, 2H, CH_2), 6.98 (d, *J*=2.3 Hz, 1H, Ar), 7.16 (d, *J*=2.3 Hz, 1H, Ar), 7.45 (s, 1H, H-2), 9.45 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.2 (CH_2), 29.1 ($3CH_3$), 31.5 (3CH Ad), 34.7 (C *t*-Bu), 37.0 ($3CH_2$ Ad), 37.3 (C Ad), 41.0 ($3CH_2$ Ad), 118.1 (C), 119.0 (C), 122.8 (CH), 124.7 (CH), 137.6 (C), 147.1 (C), 147.5 (C), 158.6 (CH-2), 190.1 (C=O). Found (%): C, 82.30; H, 8.58. Calc. for $C_{24}H_{30}O_2$ (%): C, 82.24; H, 8.63.

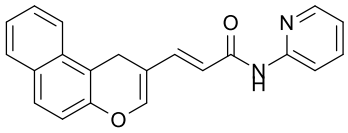
6-(Adamantan-1-yl)-8-bromo-4*H*-chromene-3-carbaldehyde (5e).



Yield 5.67 g (76%), light-yellow solid, mp 241-243 °C (1,2-dichloroethane). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.70-1.85 (m, 12H, CH_2 Ad), 2.09 (br. s, 3H, CH Ad), 3.54 (s, 2H, CH_2), 7.04 (d, *J*=2.3 Hz, 1H, Ar), 7.38 (d, *J*=2.3 Hz, 1H, Ar), 7.41 (s, 1H, H-2), 9.47 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.4 (CH_2), 28.9 (3CH Ad), 36.1 (C Ad), 36.6 ($3CH_2$ Ad), 43.1 ($3CH_2$ Ad), 110.9 (C), 118.6 (C), 120.7 (C), 125.7 (CH), 128.9 (CH), 144.9 (C), 149.7 (C), 158.8 (CH-2), 189.8 (CHO). Found (%): C, 64.42; H, 5.60. Calc. for $C_{20}H_{21}BrO_2$ (%): C, 64.35; H, 5.67.

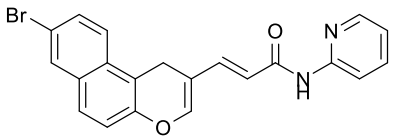
Synthesis of *N*-(pyridin-2-yl)acrylamides (4a–f, 6a–g, 8) (general procedure): A mixture of chromenecarbaldehyde **2a–c**, **5a–f**, **7** (1 mmol), 2*H*-pyrido[1,2-*a*]pyrimidine-2,4(3*H*)-dione **1a–c** (1 mmol) and $AcONH_4$ (77 mg, 1 mmol) in AcOH (4 ml) was stirred under reflux for 8 h. When the reaction was complete, the mixture was stored at 10 °C for 1 h, the solid was filtered off, washed by AcOH (1 ml) and ice-cold MeOH (2×3 ml) and dried at 120 °C for 10 h.

(*E*)-3-(1*H*-Benzo[*f*]chromen-2-yl)-*N*-(pyridin-2-yl)acrylamide (4a).



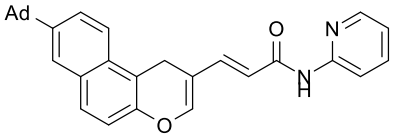
Yield 220 mg (67%), yellow solid, mp 220-222 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.81 (s, 2H, CH_2), 6.24 (d, *J*=15.1 Hz, 1H, CH=C<u>H</u>CO), 7.08 (t, *J*=6.2 Hz, 1H, Ar), 7.15 (s, 1H, $H_{α\text{-Pyran}}$), 7.17 (d, *J*=8.9 Hz, Ar), 7.48 (t, *J*=7.3 Hz, 1H, Ar), 7.59-7.63 (m, 2H, Ar, C<u>H</u>=CHCO), 7.72 (d, *J*=8.9 Hz, 1H, Ar), 7.79-7.85 (m, 2H, Ar), 7.90 (d, *J*=8.5 Hz, 1H, Ar), 8.15 (d, *J*=4.8 Hz, 1H, Ar), 8.50 (d, *J*=8.5 Hz, 1H, Ar), 10.58 (br. s, 1H, NH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.2 (CH_2), 111.6 (C), 111.8 (C), 115.4 (CH), 117.4 (CH), 117.6 (CH), 119.3 (CH), 122.6 (CH), 124.9 (CH), 127.0 (CH), 128.5 (2CH), 130.8 (C), 132.1 (C), 140.2 (CH), 141.6 (CH), 145.2 (CH), 146.9 (CH), 147.6 (C), 152.1 (C), 165.4 (C=O). Found (%): C, 76.88; H, 4.86; N, 8.46. Calc. for $C_{21}H_{16}N_2O_2$ (%): C, 76.81; H, 4.91; N, 8.53.

(*E*)-3-(8-Bromo-1*H*-benzo[*f*]chromen-2-yl)-*N*-(pyridin-2-yl)acrylamide (4b).



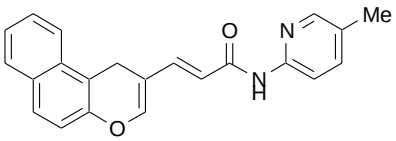
Yield 265 mg (65%), yellow solid, mp 263-265 °C. ^{1}H NMR (DMSO-d_6): δ 3.71 (s, 2H, CH_2), 6.56 (d, *J*=15.4 Hz, 1H, CH=C<u>H</u>CO), 7.05-7.08 (m, 1H, Ar), 7.29 (d, *J*=8.9 Hz, 1H, Ar), 7.46 (d, *J*=15.4 Hz, 1H, C<u>H</u>=CHCO), 7.51 (s, 1H, $H_{α\text{-Pyran}}$), 7.74-7.78 (m, 2H, Ar), 7.79 (td, *J*=8.9 Hz, *J*=1.6 Hz, 1H, Ar), 7.84 (d, *J*=8.9 Hz, 1H, Ar), 8.19 (d, *J*=8.3 Hz, 1H, Ar), 8.22 (d, *J*=1.6 Hz, 1H, Ar), 8.30 (d, *J*=3.9 Hz, 1H, Ar), 10.41 (s, 1H, NH). ^{13}C NMR (DMSO-d_6): δ 21.0 (CH_2), 112.2 (C), 112.3 (C), 114.1 (CH), 118.6 (C), 119.3 (CH), 119.8 (CH), 119.9 (CH), 125.1 (CH), 128.3 (CH), 130.5 (CH), 130.7 (CH, C), 132.1 (C), 138.6 (CH), 139.6 (CH), 146.5 (CH), 147.8 (C), 148.7 (CH), 152.8 (C), 164.9 (C=O). Found (%): C, 61.86; H, 3.65; N, 6.80. Calc. for $C_{21}H_{15}BrN_2O_2$ (%): C, 61.93; H, 3.71; N, 6.88.

(*E*)-3-[8-(Adamantan-1-yl)-1*H*-benzo[*f*]chromen-2-yl]-*N*-(pyridin-2-yl)acrylamide (4c).



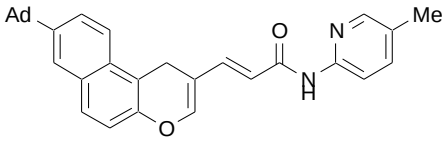
Yield 328 mg (71%), yellow solid, mp 267-269 °C. ^{1}H NMR (DMSO-d_6): δ 1.75 (br. s, 6H, CH_2 Ad), 1.96 (br. s, 6H, CH_2 Ad), 2.08 (br. s, 3H, CH Ad), 3.69 (s, 2H, CH_2), 6.56 (d, *J*=15.3 Hz, 1H, CH=C<u>H</u>CO), 7.05-7.08 (m, 1H, Ar), 7.19 (d, *J*=8.7 Hz, 1H, Ar), 7.47 (d, *J*=15.4 Hz, 1H, C<u>H</u>=CHCO), 7.49 (1H, s, $H_{α\text{-Pyran}}$), 7.74-7.83 (m, 5H, Ar), 8.20 (d, *J*=8.5 Hz, 1H, Ar), 8.30 (d, *J*=4.6 Hz, 1H, Ar), 10.45 (s, 1H, NH). ^{13}C NMR (DMSO-d_6): 21.1 (CH_2), 28.9 (3CH Ad), 36.4 (C Ad), 36.8 ($3CH_2$ Ad), 43.1 ($3CH_2$ Ad), 111.5 (C), 112.1 (C), 114.1 (CH), 117.6 (CH), 119.5 (CH), 119.8 (CH), 122.6 (CH), 123.9 (CH), 125.7 (CH), 129.1 (CH), 130.2 (C), 130.9 (C), 138.6 (CH), 140.0 (CH), 146.8 (CH), 147.1 (C), 148.0 (C), 148.7 (CH), 152.9 (C), 165.0 (C=O). Found (%): C, 80.55; H, 6.48; N, 5.98. Calc. for $C_{31}H_{30}N_2O_2$ (%): C, 80.49; H, 6.54; N, 6.06.

(*E*)-3-(1*H*-Benzo[*f*]chromen-2-yl)-*N*-(5-methylpyridin-2-yl)acrylamide (4d).



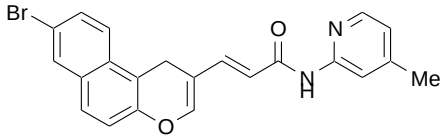
Yield 205 mg (60%), yellow solid, mp 225-227 °C. ^{1}H NMR (DMSO-d_6): δ 2.22 (s, 3H, CH_3), 3.71 (s, 2H, CH_2), 6.56 (d, *J*=15.3 Hz, 1H, CH=C<u>H</u>CO), 7.24 (d, *J*=8.7 Hz, 1H, Ar), 7.45 (d, *J*=15.3 Hz, 1H, C<u>H</u>=CHCO), 7.49-7.53 (m, 2H, Ar, $H_{α\text{-Pyran}}$), 7.57 (d, *J*=8.2 Hz, 1H, Ar), 7.64−7.68 (m, 1H, Ar), 7.82-7.85 (m, 2H, Ar), 7.93 (d, *J*=8.0 Hz, 1H, Ar), 8.10 (d, *J*=8.5 Hz, 1H, Ar), 8.13 (s, 1H, Ar), 10.34 (s, 1H, NH). ^{13}C NMR (DMSO-d_6): δ 17.8 (CH_3), 21.1 (CH_2), 111.9 (C), 112.2 (C), 113.6 (CH), 117.9 (CH), 119.8 (CH), 122.7 (CH), 125.4 (CH), 127.7 (CH), 128.6 (C), 128.95 (CH), 129.01 (CH), 130.8 (C), 132.0 (C), 139.0 (CH), 139.5 (CH), 146.4 (CH), 147.5 (C), 148.4 (CH), 150.7 (C), 164.8 (C=O). Found (%): C, 77.11; H, 5.25; N, 8.07. Calc. for $C_{22}H_{18}N_2O_2$ (%): C, 77.17; H, 5.30; N, 8.18.

(*E*)-3-(8-(Adamantan-1-yl)-1*H*-benzo[*f*]chromen-2-yl)-*N*-(5-methylpyridin-2-yl)acrylamide (4e).



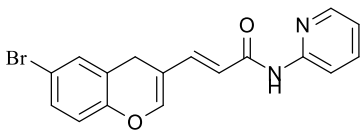
Yield 330 mg (69%), yellow solid, mp 260-262 °C (decomp.). ^{1}H NMR (DMSO-d_6): δ 1.75 (br. s, 6H, CH_2 Ad), 1.95 (br. s, 6H, CH_2 Ad), 2.07 (br. s, 3H, CH Ad), 2.29 (s, 3H, CH_3), 3.68 (s, 2H, CH_2), 6.55 (d, *J*=15.1 Hz, 1H, CH=C<u>H</u>CO), 6.90 (d, *J*=4.8 Hz, 1H, Ar), 7.18 (d, *J*=8.7 Hz, 1H, Ar), 7.45 (d, *J*=15.1 Hz, 1H, C<u>H</u>=CHCO), 7.48 (1H, s, $H_{α\text{-Pyran}}$), 7.76-7.82 (m, 4H, Ar), 8.06 (s, 1H, Ar), 8.15 (d, *J*=4.8 Hz, 1H, Ar), 10.35 (s, 1H, NH). ^{13}C NMR (DMSO-d_6): δ 21.1 (CH_2), 21.5 (CH_3), 28.9 (3CH Ad), 36.4 (C Ad), 36.7 (3CH_2 Ad), 43.1 (3CH_2 Ad), 111.5 (C), 112.1 (C), 114.5 (CH), 117.6 (CH), 119.6 (CH), 120.8 (CH), 122.6 (CH), 123.9 (CH), 125.7 (CH), 129.1 (CH), 130.2 (C), 130.9 (C), 139.8 (CH), 146.7 (CH), 147.1 (C), 147.9 (C), 148.3 (CH), 149.2 (C), 152.9 (C), 164.9 (C=O). Found (%): C, 80.56; H, 6.79; N, 5.79. Calc. for $C_{32}H_{32}N_2O_2$ (%): C, 80.64; H, 6.77; N, 5.88.

(*E*)-3-(8-Bromo-1*H*-benzo[*f*]chromen-2-yl)-*N*-(4-methylpyridin-2-yl)acrylamide (4f).



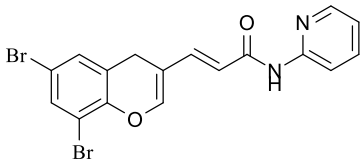
Yield 315 mg (75%), yellow solid, mp 274-275 °C. ^{1}H NMR (DMSO-d_6): δ 2.29 (s, 3H, CH_3), 3.69 (s, 2H, CH_2), 6.55 (d, *J*=15.1 Hz, 1H, CH=C<u>H</u>CO), 6.90 (d, *J*=3.7 Hz, 1H, Ar), 7.28 (d, *J*=8.5 Hz, 1H, Ar), 7.43 (d, *J*=15.1 Hz, 1H, C<u>H</u>=CHCO), 7.49 (s, 1H, $H_{α\text{-Pyran}}$), 7.72-7.85 (m, 3H, Ar), 8.04 (s, 1H, Ar), 8.15 (d, *J*=3.9 Hz, 1H, Ar), 8.21 (s, 1H, Ar), 10.31 (s, 1H, NH). Due to the poor solubility in the majority of organic solvents, ^{13}C NMR spectrum of the compound could not be obtained with satisfactory quality. Found (%): C, 62.70; H, 4.00; N, 6.55. Calc. for $C_{22}H_{17}BrN_2O_2$ (%): C, 62.72; H, 4.07; N, 6.65.

(*E*)-3-(6-Bromo-4*H*-chromen-3-yl)-*N*-(pyridin-2-yl)acrylamide (6a).



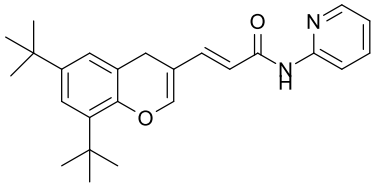
Yield 215 mg (60%), yellow solid, mp 217-219 °C. ^{1}H NMR (DMSO-d_6): δ 3.45 (s, 2H, CH_2), 6.29 (d, *J*=15.3 Hz, 1H, CH=C<u>H</u>CO), 6.94 (d, *J*=8.7 Hz, 1H, Ar), 7.05 (ddd, *J*=7.3 Hz, *J*=4.8 Hz, *J*=0.7 Hz, 1H, Ar), 7.33-7.38 (m, 3H, $H_{\alpha\text{-Pyran}}$, Ar, C<u>H</u>=CHCO), 7.43 (d, *J*=2.3 Hz, 1H, Ar), 7.71-7.75 (m, 1H, Ar), 8.17 (d, *J*=8.5 Hz, 1H, Ar), 8.28 (ddd, *J*=4.8 Hz, *J*=1.8 Hz, *J*=0.7 Hz, 1H, Ar), 10.53 (s, 1H, NH). ^{13}C NMR (DMSO-d_6): δ 23.0 (CH_2), 112.0 (C), 114.2 (CH), 116.1 (C), 119.2 (CH), 119.3 (CH), 119.8 (CH), 122.4 (C), 131.2 (CH), 132.8 (CH), 138.6 (CH), 139.6 (CH), 146.9 (CH), 148.6 (CH), 149.6 (C), 152.9 (C), 164.9 (C=O). Found (%): C, 57.22; H, 3.60; N, 7.75. Calc. for $C_{17}H_{13}BrN_2O_2$ (%): C, 57.16; H, 3.67; N, 7.84.

(*E*)-3-(6,8-Dibromo-4*H*-chromen-3-yl)-*N*-(pyridin-2-yl)acrylamide (6b).



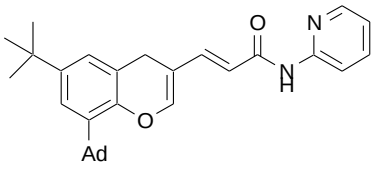
Yield 305 mg (70%), yellow solid, mp 252-253 °C (decomp.). ^{1}H NMR (DMSO-d_6): δ 3.50 (s, 2H, CH_2), 6.31 (d, *J*=15.3 Hz, 1H, CH=C<u>H</u>CO), 7.03-7.06 (m, 1H, Ar), 7.35 (d, *J*=15.3 Hz, 1H, C<u>H</u>=CHCO), 7.43 (s, 1H), 7.46 (s, 1H), 7.70 (s, 1H), 7.71-7.75 (m, 1H, Ar), 8.16 (d, *J*=8.2 Hz, 1H, Ar), 8.27-8.29 (m, 1H, Ar), 10.55 (s, 1H, NH). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 23.5 (CH_2), 111.7 (C), 112.7 (C), 114.2 (CH), 116.1 (C), 119.8 (CH), 120.2 (CH), 123.9 (C), 132.4 (CH), 133.7 (CH), 138.6 (CH), 139.0 (CH), 146.4 (CH), 146.7 (C), 148.6 (CH), 152.8 (C), 164.7 (C=O). Found (%): C, 46.90; H, 2.75; N, 6.34. Calc. for $C_{17}H_{12}Br_2N_2O_2$ (%): C, 46.82; H, 2.77; N, 6.42.

(*E*)-3-(6,8-Di-*tert*-butyl-4*H*-chromen-3-yl)-*N*-(pyridin-2-yl)acrylamide (6c).



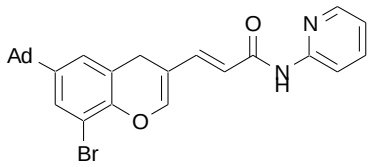
Yield 215 mg (55%), yellow solid, mp 234-235 °C. ^{1}H NMR (DMSO-d_6): δ 1.24 (s, 9H, t-Bu), 1.32 (s, 9H, *t*-Bu), 3.43 (s, 2H, CH_2), 6.28 (d, *J*=15.3 Hz, 1H, CH=C<u>H</u>CO), 7.02-7.06 (m, 2H, Ar), 7.12 (s, 1H), 7.36-7.40 (m, 2H, $H_{\alpha\text{-Pyran}}$, Ar), 7.72-7.76 (m, 1H, Ar), 8.18 (d, *J*=8.2 Hz, 1H, Ar), 8.28 (d, *J*=3.7 Hz, 1H, Ar), 10.48 (s, 1H, NH). ^{13}C NMR (DMSO-d_6): δ 23.9 (CH_2), 30.3 ($3CH_3$), 31.8 ($3CH_3$), 34.7 (C *t*-Bu), 35.1 (C *t*-Bu), 112.0 (C), 114.2 (CH), 118.5 (CH), 119.2 (C), 119.7 (CH), 122.3 (CH), 124.9 (CH), 136.6 (C), 138.6 (CH), 140.0 (CH), 146.1 (C), 146.8 (CH), 146.9 (C), 148.5 (CH), 152.9 (C), 165.1 (C=O). Found (%): C, 76.94; H, 7.70; N, 7.06. Calc. for $C_{25}H_{30}N_2O_2$ (%): C, 76.89; H, 7.74; N, 7.17.

(*E*)-3-[8-(Adamantan-1-yl)-6-*tert*-butyl-4*H*-chromen-3-yl]-*N*-(pyridin-2-yl)acrylamide (6d).



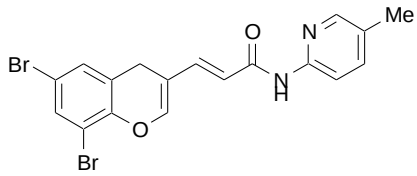
Yield 295 mg (63%), yellow solid, mp 252-253 °C. ^{1}H NMR (DMSO-d_6): δ 1.24 (s, 9H, *t*-Bu), 1.71 (br. s, 6H, CH_2 Ad), 2.01 (br. s, 6H, CH_2 Ad), 2.05 (s, 3H, CH Ad), 3.43 (s, 2H, CH_2), 6.28 (d, *J*=15.3 Hz, 1H, CH=C<u>H</u>CO), 7.01-7.07 (m, 3H, Ar), 7.37 (d, *J*=15.3 Hz, 1H, C<u>H</u>=CHCO), 7.39 (s, 1H, $H_{α\text{-Pyran}}$), 7.72-7.76 (m, 1H, Ar), 8.18 (d, *J*=8.2 Hz, 1H, Ar), 8.28 (d, *J*=4.1 Hz, 1H, Ar), 10.47 (s, 1H, NH). ^{13}C NMR (DMSO-d_6): δ 24.0 (CH_2), 28.9 ($3CH_3$), 31.8 (3CH Ad), 34.7 (C *t*-Bu), 36.9 ($3CH_2$ Ad), 37.9 (C Ad), 40.8 ($3CH_2$ Ad), 112.0 (C), 114.1 (CH), 118.5 (CH), 119.1 (C), 119.7 (CH), 122.2 (CH), 124.8 (CH), 136.9 (C), 138.6 (CH), 140.0 (CH), 146.2 (C), 146.7 (CH), 147.2 (C), 148.5 (CH), 152.9 (C), 165.1 (C=O). Found (%): C, 79.39; H, 7.79; N, 5.87. Calc. for $C_{31}H_{36}N_2O_2$ (%): C, 79.45; H, 7.74; N, 5.98.

(*E*)-3-[6-(Adamantan-1-yl)-8-bromo-4*H*-chromen-3-yl]-*N*-(pyridin-2-yl)acrylamide (6e).



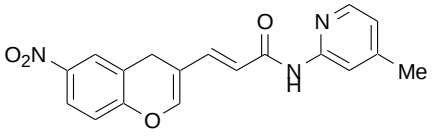
Yield 364 mg (74%), yellow solid, mp 242-244 °C. ^{1}H NMR ($CDCl_3$): δ 1.70-1.80 (m, 6H, CH_2 Ad), 1.84-1.86 (m, 6H, CH_2 Ad), 2.09 (br. s, 3H, CH Ad), 3.52 (s, 2H, CH_2), 5.96 (d, *J*=15.1 Hz, 1H, CH=C<u>H</u>CO), 7.05-7.09 (m, 3H, Ar, $H_{α\text{-Pyran}}$), 7.37 (d, *J*=2.3 Hz, 1H, Ar), 7.48 (d, *J*=15.1 Hz, 1H, C<u>H</u>=CHCO), 7.75-7.80 (m, 1H, Ar), 8.23 (d, *J*=4.1 Hz, 1H, Ar), 8.40 (d, *J*=8.5 Hz, 1H, Ar), 9.36 (br. s, 1H, NH). ^{13}C NMR ($CDCl_3$): δ 24.1 (CH_2), 28.9 (3CH Ad), 36.0 (C Ad), 36.7 ($3CH_2$ Ad), 43.2 ($3CH_2$ Ad), 110.7 (C), 111.9 (C), 115.0 (CH), 117.4 (CH), 119.6 (CH), 120.1 (C), 125.3 (CH), 128.6 (CH), 139.6 (CH), 141.2 (CH), 145.0 (C), 146.2 (CH), 147.2 (CH), 148.7 (C), 151.8 (C), 164.8 (C=O). Found (%): C, 66.05; H, 5.48; N, 5.60. Calc. for $C_{27}H_{27}BrN_2O_2$ (%): C, 65.99; H, 5.54; N, 5.70.

(*E*)-3-(6,8-Dibromo-4*H*-chromen-3-yl)-*N*-(5-methylpyridin-2-yl)acrylamide (6f).



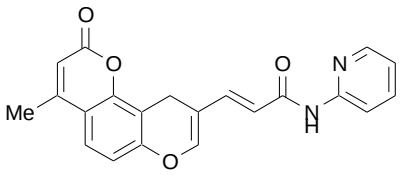
Yield 305 mg (68%), yellow solid, mp 265-267 °C (decomp.). ^{1}H NMR (DMSO-d_6): δ 2.27 (s, 3H, CH_3), 3.50 (s, 2H, CH_2), 6.31 (d, *J*=15.4 Hz, 1H, CH=C<u>H</u>CO), 6.89 (s, 1H, Ar), 7.33 (d, *J*=15.4 Hz, 1H, C<u>H</u>=CHCO), 7.43-7.46 (m, 2H), 7.71 (s, 1H), 8.01 (s, 1H), 8.13 (br. s, 1H, Ar), 10.48 (s, 1H, NH). ^{13}C NMR (DMSO-d_6): δ 21.5 (CH_3), 23.4 (CH_2), 111.7 (C), 112.7 (C), 114.6 (CH), 116.1 (C), 120.3 (CH), 120.9 (CH), 124.0 (C), 132.4 (CH), 133.7 (CH), 138.8 (CH), 146.3 (CH), 146.7 (C), 148.2 (CH), 149.2 (C), 152.9 (C), 164.7 (C=O). Found (%): C, 47.96; H, 3.19; N, 6.15. Calc. for $C_{18}H_{14}Br_2N_2O_2$ (%): C, 48.03; H, 3.14; N, 6.22.

(*E*)-*N*-(4-Methylpyridin-2-yl)-3-(6-nitro-4*H*-chromen-3-yl)acrylamide (6g).

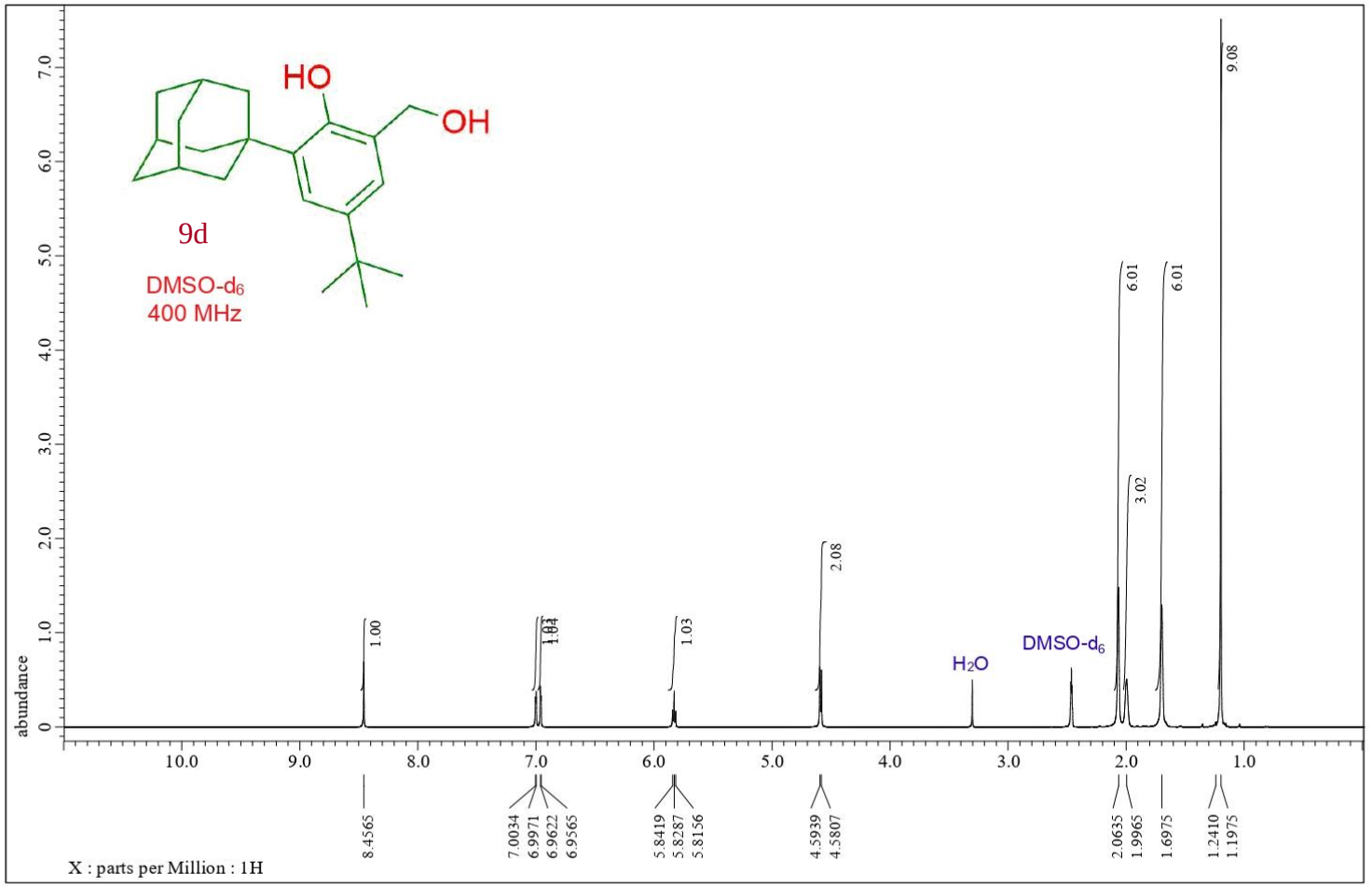


Yield 148 mg (44%), yellow solid, mp 286-289 °C (decomp.). ^{1}H NMR (DMSO-d_6): δ 2.28 (s, 3H, CH_3), 3.59 (s, 2H, CH_2), 6.35 (d, *J*=15.3 Hz, 1H, CH=C<u>H</u>CO), 6.90 (d, *J*=4.8 Hz, 1H, Ar), 7.21 (d, *J*=8.9 Hz, 1H, Ar), 7.36 (d, *J*=15.3 Hz, 1H, C<u>H</u>=CHCO), 7.42 (s, 1H, $H_{\alpha\text{-Pyran}}$), 8.02 (s, 1H, Ar), 8.06 (dd, *J*=8.9 Hz, *J*=2.7 Hz, 1H, Ar), 8.14 (d, *J*=5.0 Hz, 1H, Ar), 8.16 (d, *J*=2.3 Hz, 1H, Ar), 10.50 (s, 1H, NH). ^{13}C NMR (DMSO-d_6): δ 21.5 (CH_3), 23.1 (CH_2), 112.6 (C), 114.6 (CH), 118.1 (CH), 120.4 (CH), 120.9 (CH), 121.4 (C), 124.3 (CH), 126.5 (CH), 138.8 (CH), 143.8 (C), 146.1 (CH), 148.2 (CH), 149.3 (C), 152.9 (C), 155.1 (C), 164.6 (C=O). Found (%): C, 64.15; H, 4.52; N, 12.38. Calc. for $C_{18}H_{15}N_3O_4$ (%): C, 64.09; H, 4.48; N, 12.46.

(*E*)-3-(4-Methyl-2-oxo-2*H*,10*H*-pyrano[2,3-*f*]chromen-9-yl)-*N*-(pyridin-2-yl)acrylamide (8).



Yield 252 mg (70%), yellow solid, mp 319-320 °C. ^{1}H NMR (DMSO-d_6): δ 2.39 (s, 3H, CH_3), 3.47 (s, 2H, CH_2), 6.30 (s, 1H, H-3), 6.49 (d, *J*=15.3 Hz, 1H, CH=C<u>H</u>CO), 7.00-7.07 (m, 2H, Ar), 7.39 (d, *J*=15.3 Hz, 1H, C<u>H</u>=CHCO), 7.43 (s, 1H, H-8), 7.62 (d, *J*=8.9 Hz, 1H, Ar), 7.72-7.76 (m, 1H, Ar), 8.17 (d, *J*=8.5 Hz, 1H, Ar), 8.28 (d, *J*=3.9 Hz, 1H, Ar), 10.48 (s, 1H, NH). ^{13}C NMR (DMSO-d_6): δ 18.67 (CH_2), 18.74 (CH_3), 108.1 (C), 112.0 (C), 112.8 (CH), 113.1 (CH), 114.1 (CH), 116.2 (C), 119.8 (CH), 120.2 (CH), 125.0 (CH), 138.6 (CH), 139.1 (CH), 146.1 (CH), 148.7 (CH), 152.1 (C), 152.5 (C), 152.8 (C), 153.8 (C), 160.2 (OC=O), 164.8 (C=O). Found (%): C, 70.08; H, 4.41; N, 7.68. Calc. for $C_{21}H_{16}N_2O_4$ (%): C, 69.99; H, 4.48; N, 7.77.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DMSO-d6
400 MHz
abundance
H2O
DMSO-d6
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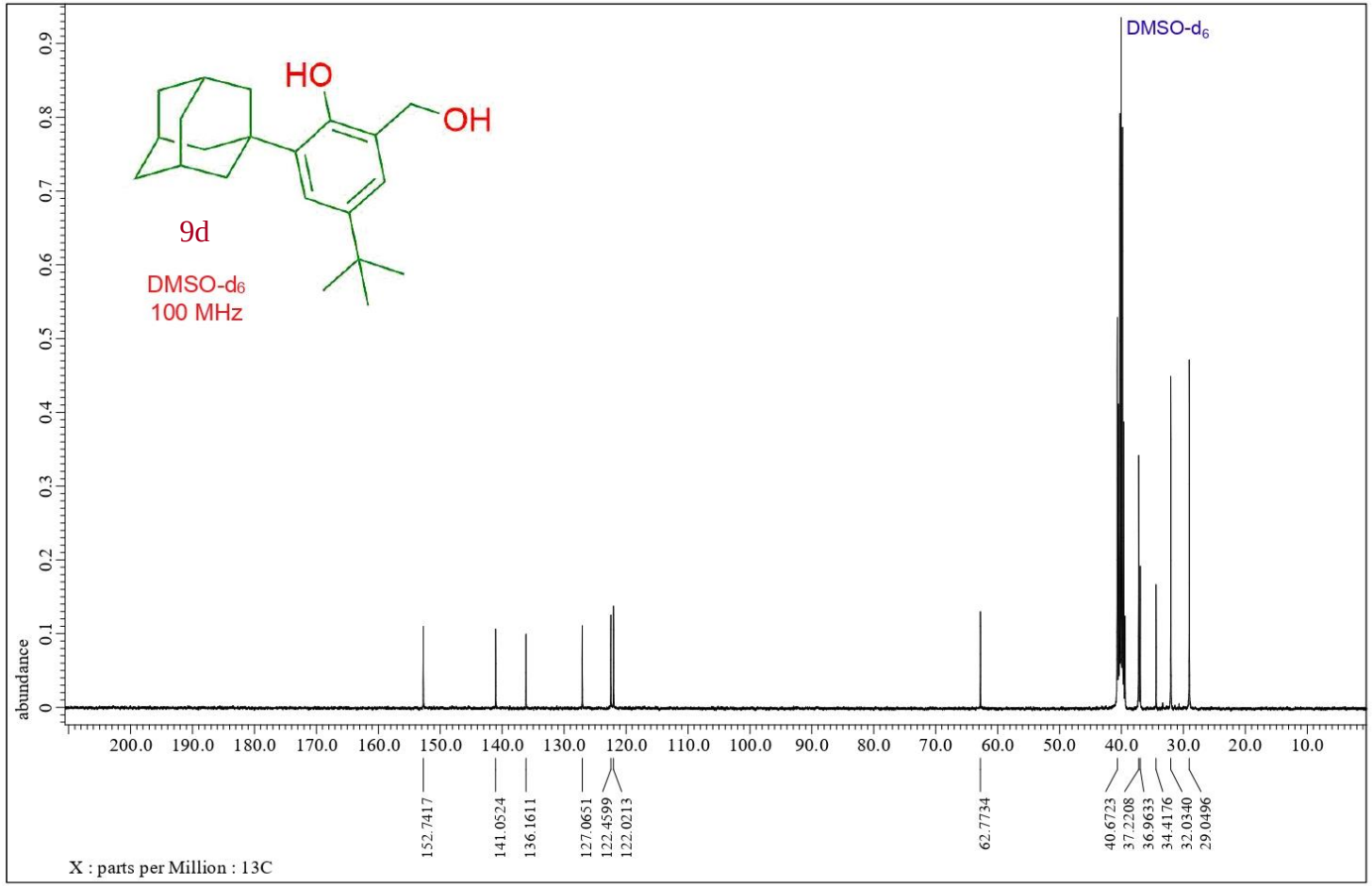
1.04
1.03
2.08
3.02
6.01
6.01
9.08
8.4565
7.0034
6.9971
6.9622
6.9565
5.8419
5.8287
5.8156
4.5939
4.5807
2.0635
1.9965
1.6975
1.2410
1.1975
X : parts per Million : 1H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OH
9d
DMSO-d6
100 MHz
DMSO-d6
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
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136.1611
127.0651
122.4599
122.0213
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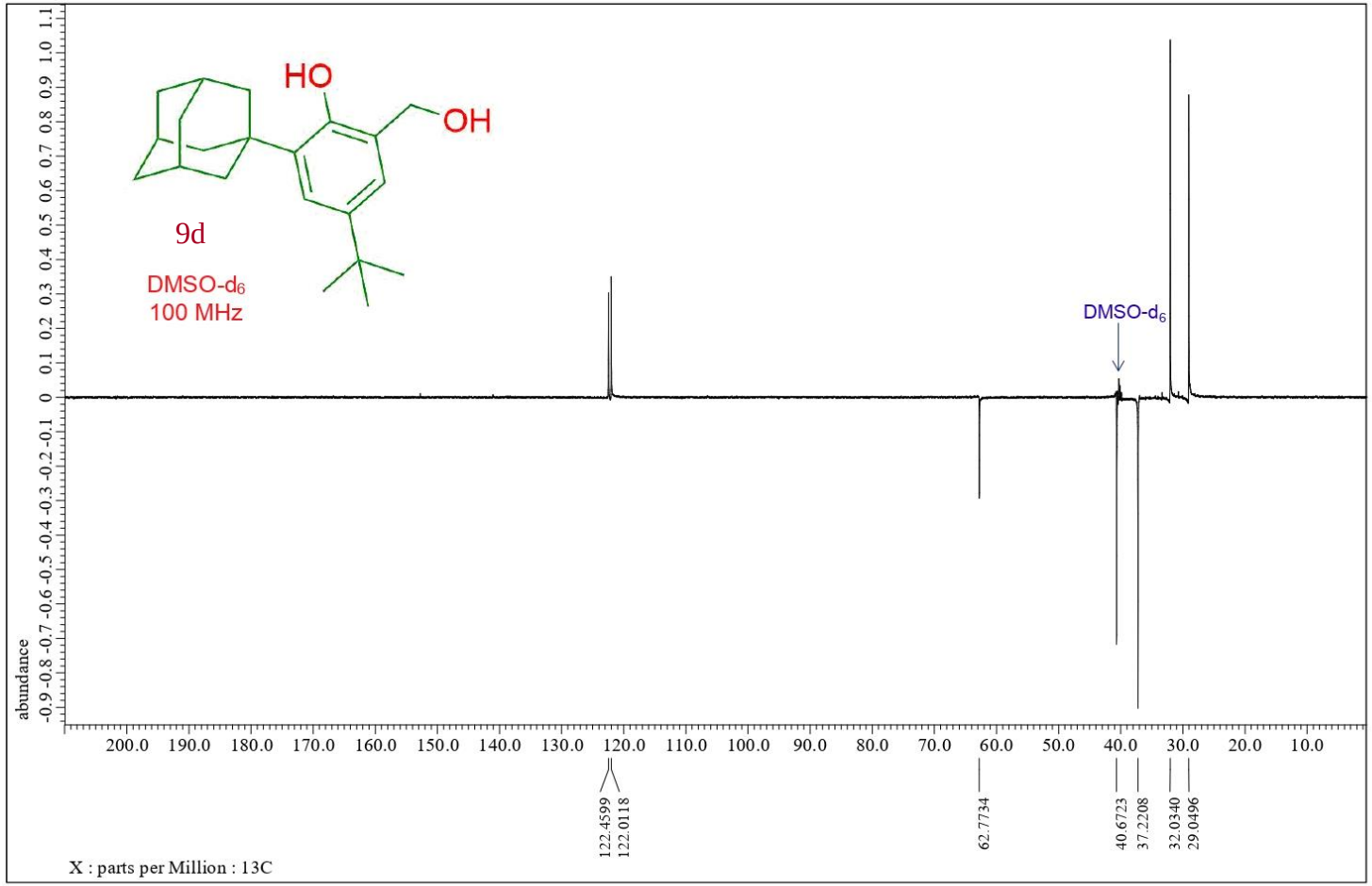
X : parts per Million : 13C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OH
9d
DMSO-d6
100 MHz
DMSO-d6
abundance
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200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0
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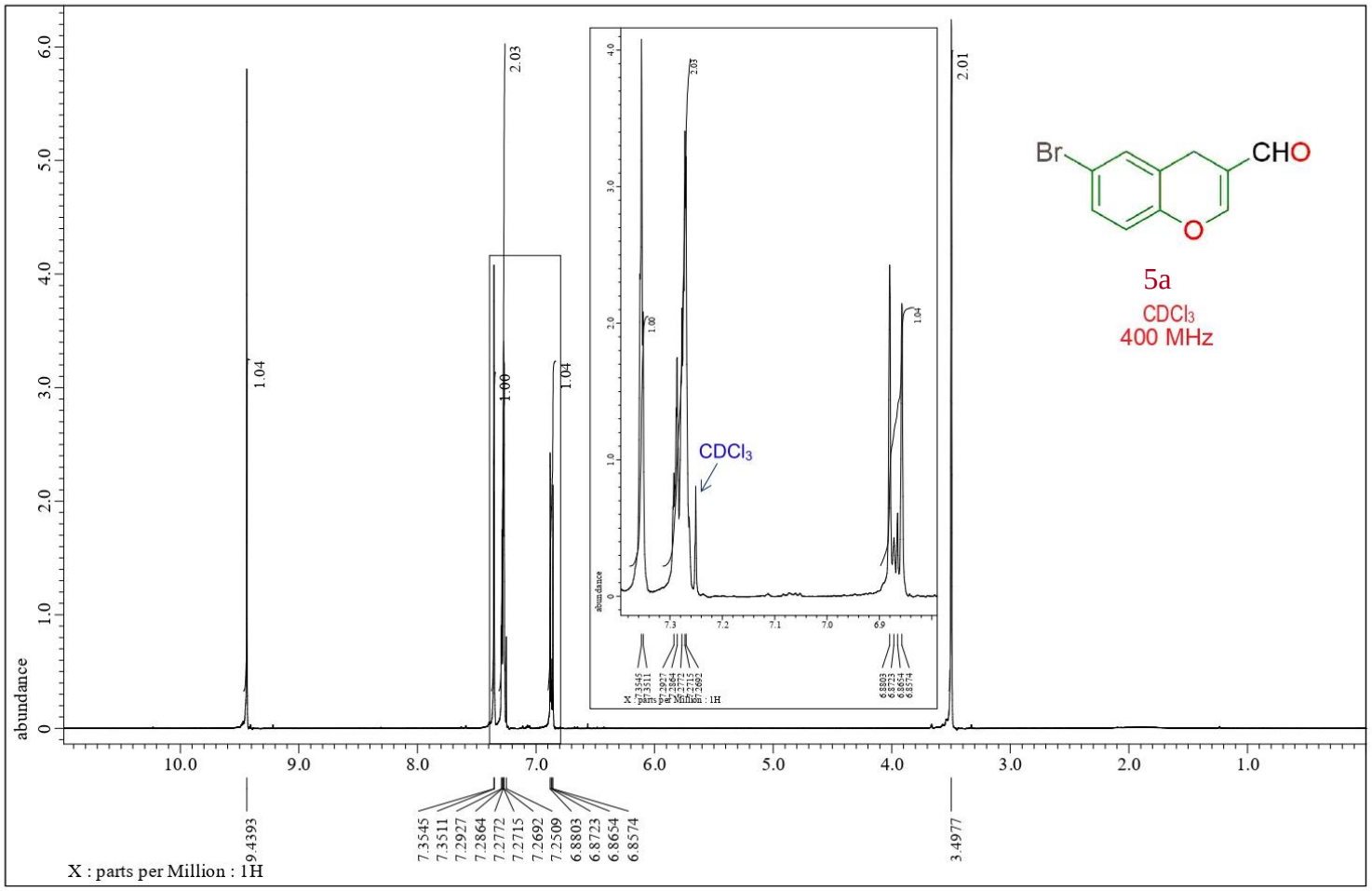
X : parts per Million : 13C


abundance
X : parts per Million : 1H
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7.2927
7.2864
7.2772
7.2715
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7.2509
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6.8723
6.8654
6.8574
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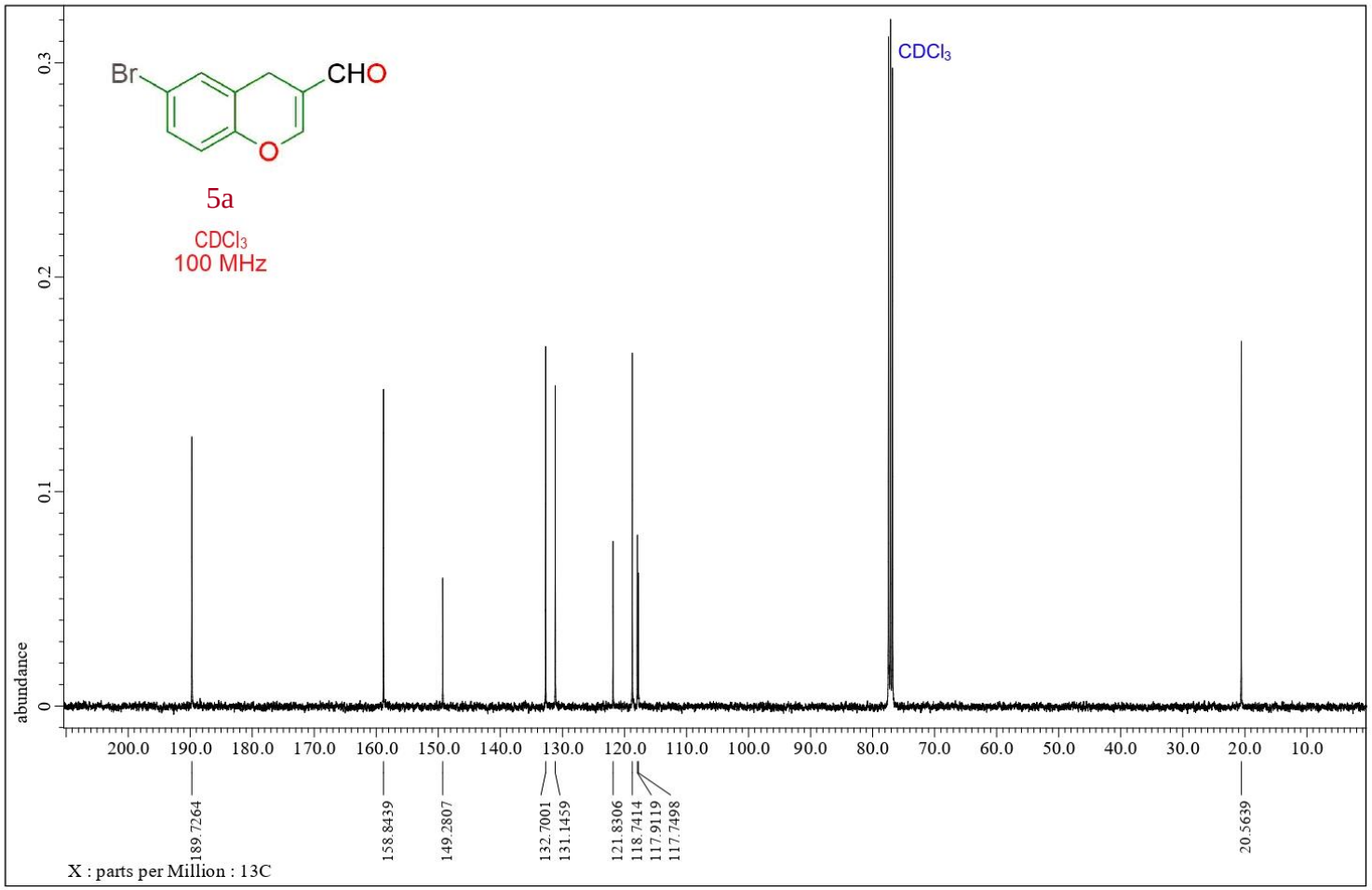
Br
CHO
O
5a
CDCl3
400 MHz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CHO
O
5a
CDCl3
100 MHz
CDCl3
abundance
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170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
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158.8439
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131.1459
121.8306
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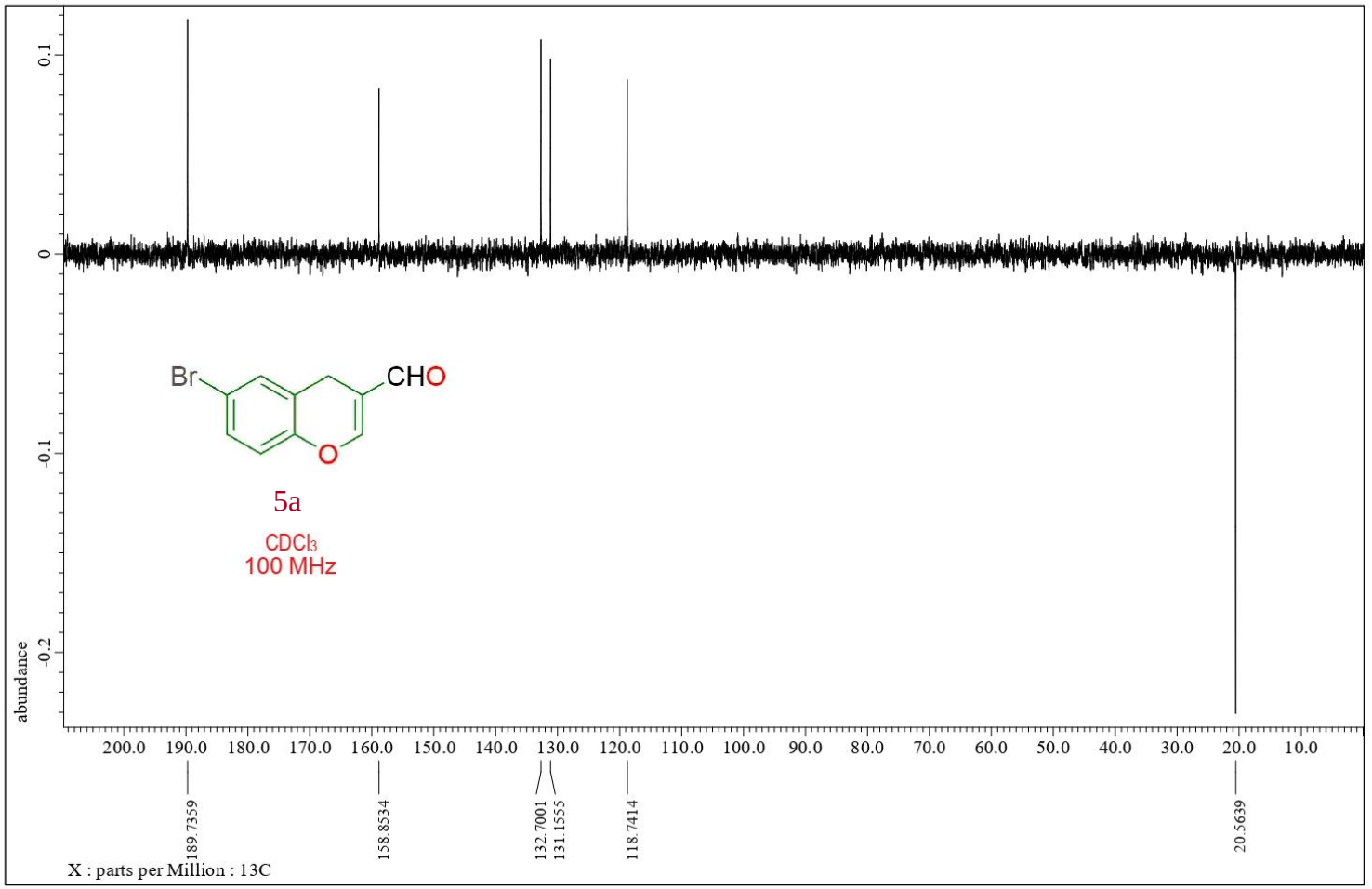
117.9119
117.7498
20.5639
X : parts per Million : 13C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0
-0.1
-0.2
abundance
Br
CHO
O
5a
CDCl3
100 MHz
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0
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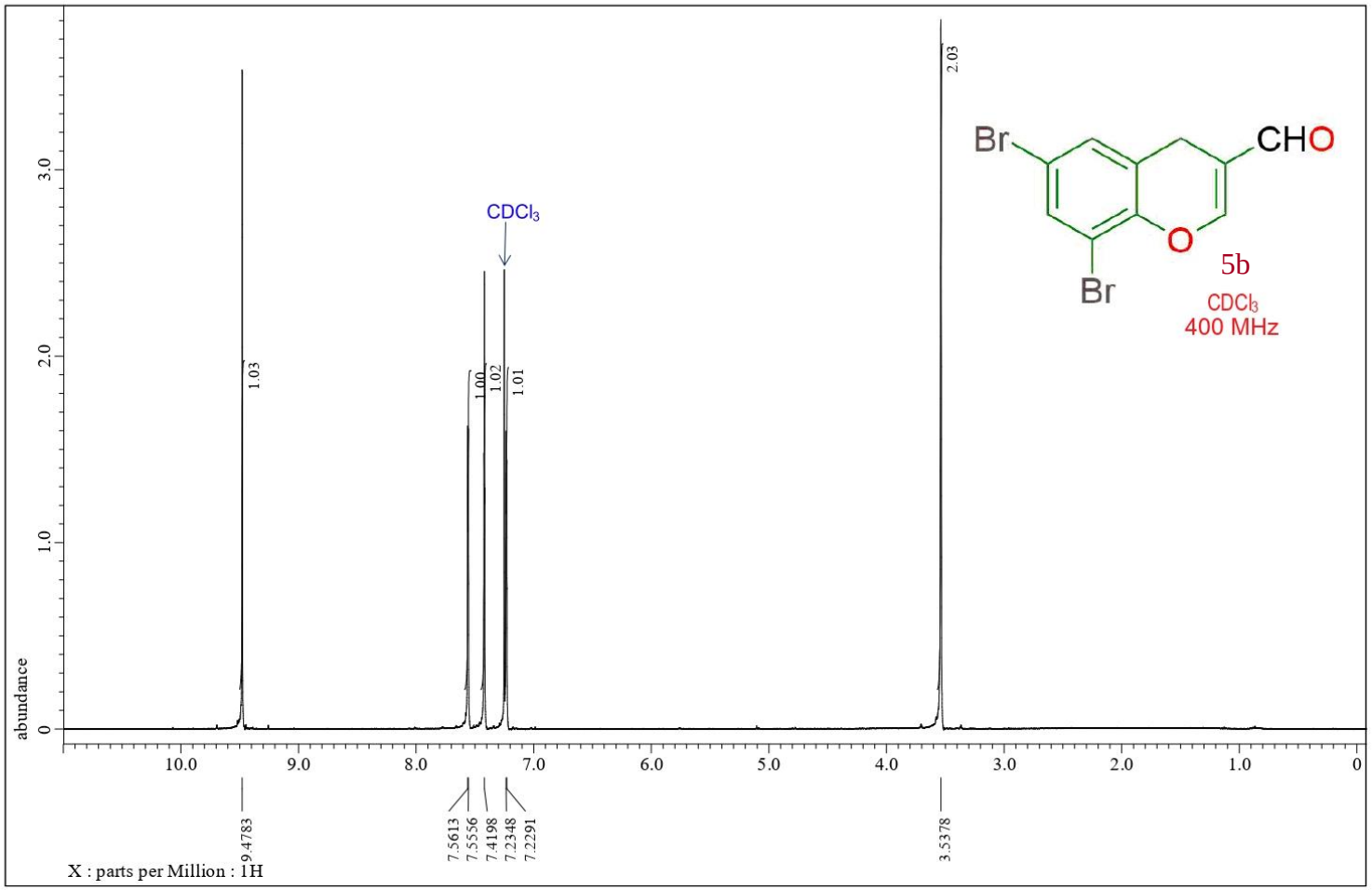
158.8534
132.7001
131.1555
118.7414
20.5639
X : parts per Million : 13C


abundance
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CDCl3
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1.00
1.02
1.01
2.03
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
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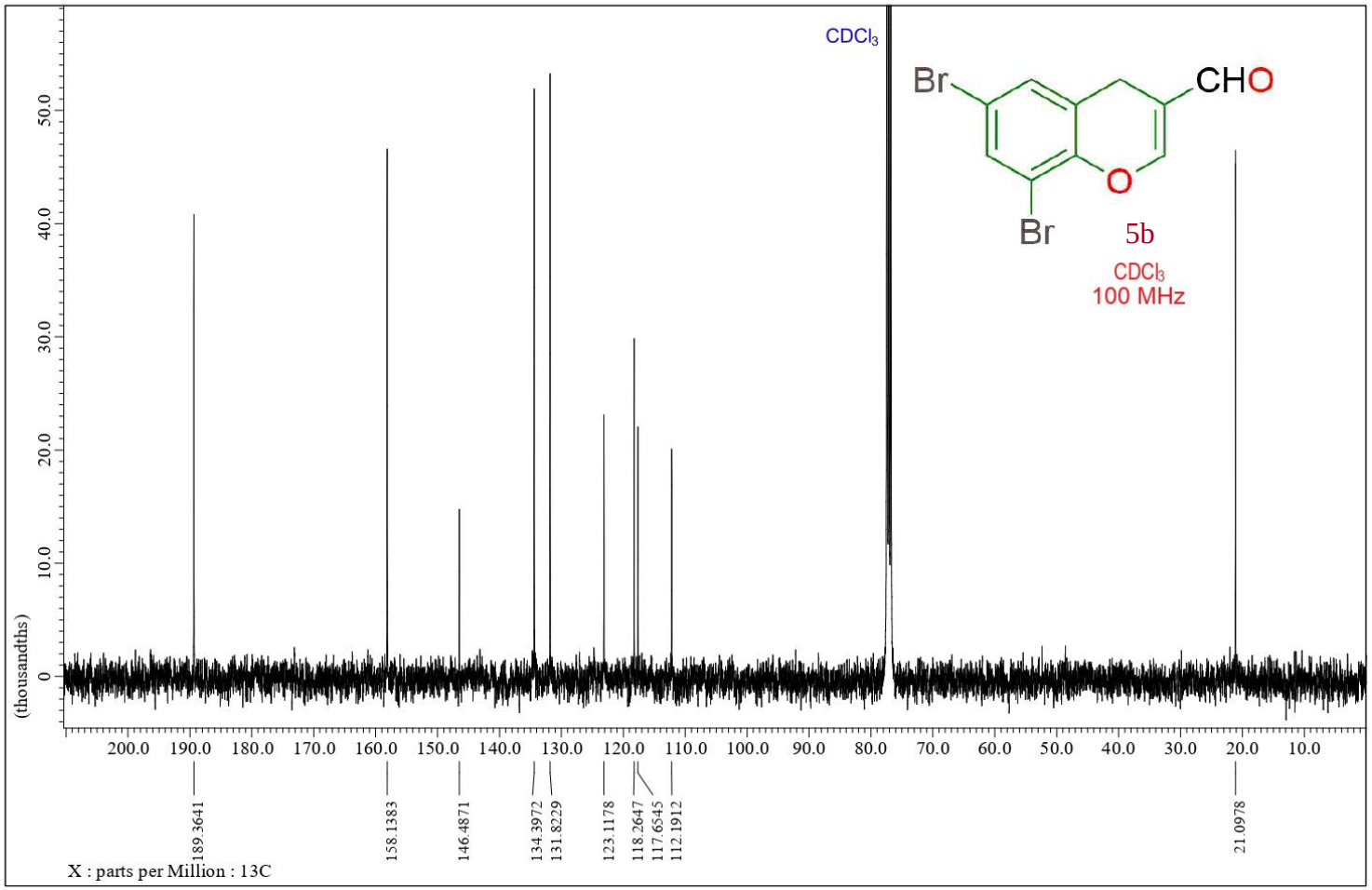
7.5613
7.5556
7.4198
7.2348
7.2291
3.5378
X : parts per Million : 1H
Br
CHO
O
Br
5b
CDCl3
400 MHz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Br
CHO
O
Br
5b
CDCl3
100 MHz
(thousandths)
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40.0
30.0
20.0
10.0
0
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0
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158.1383
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118.2647
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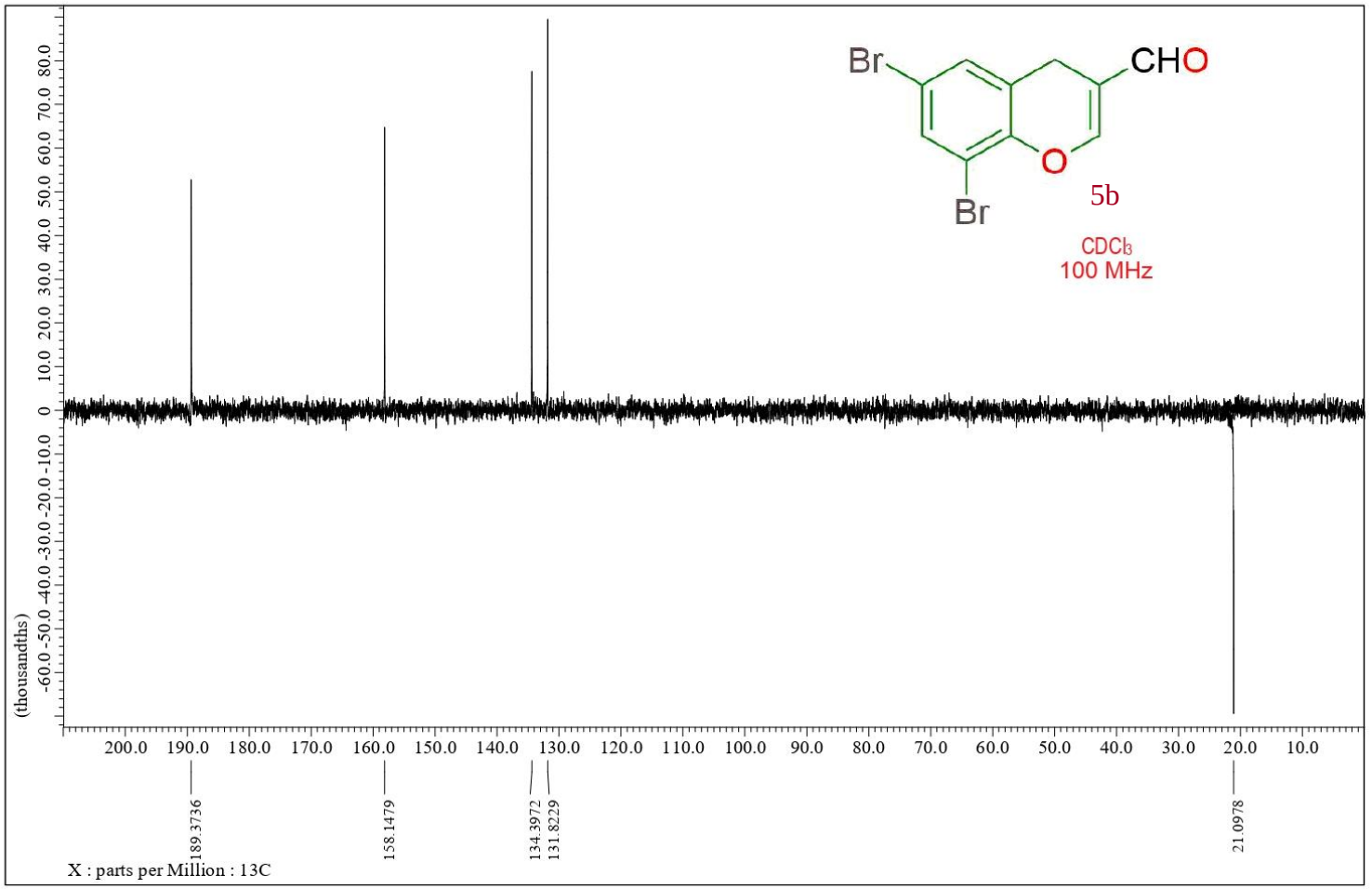
112.1912
21.0978
X : parts per Million : 13C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CHO
O
Br
5b
CDCl3
100 MHz
(thousandths)
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70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
-30.0
-40.0
-50.0
-60.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
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189.3736
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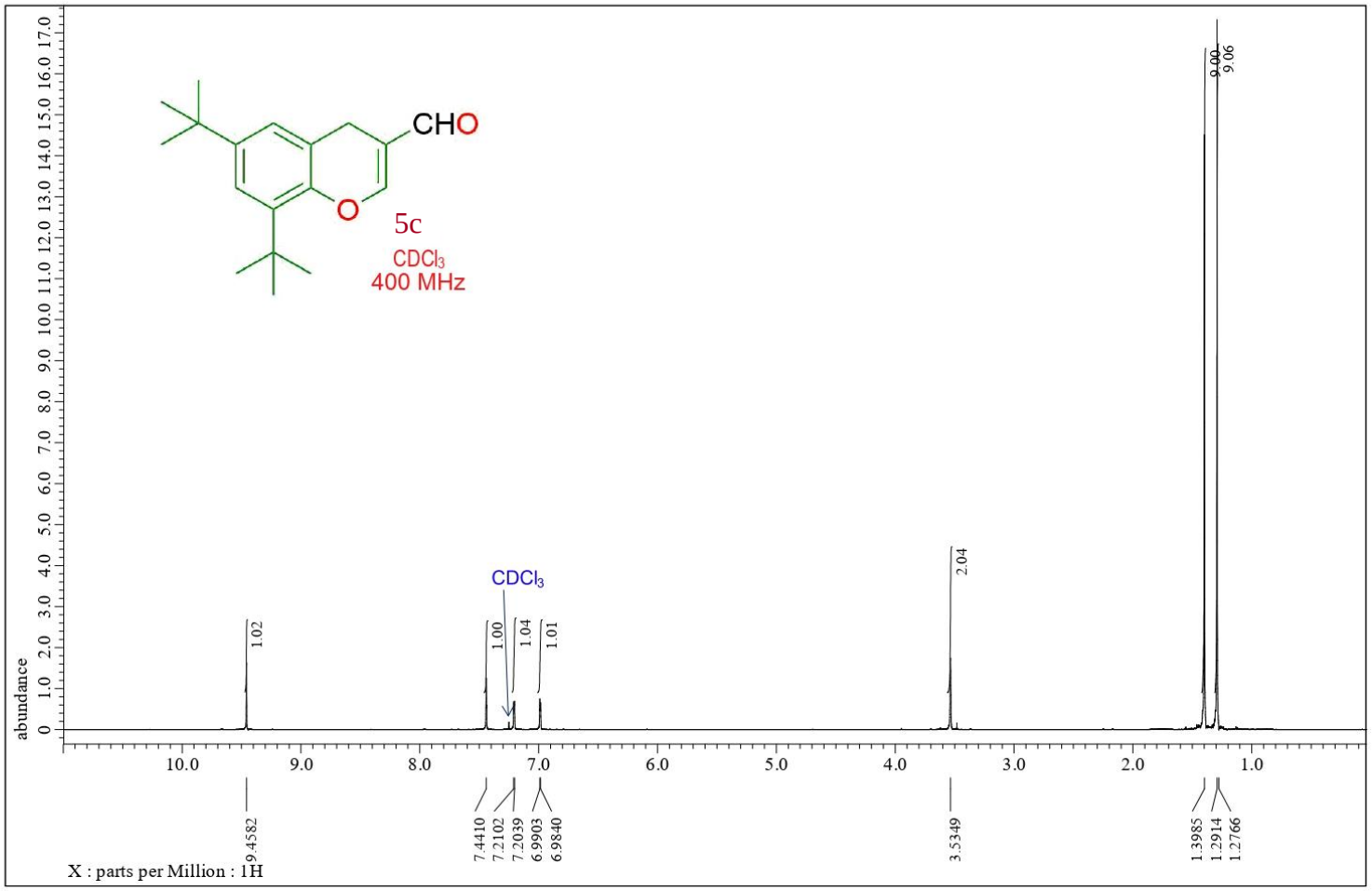
134.3972
131.8229
21.0978
X : parts per Million : 13C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O
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CDCl3
400 MHz
abundance
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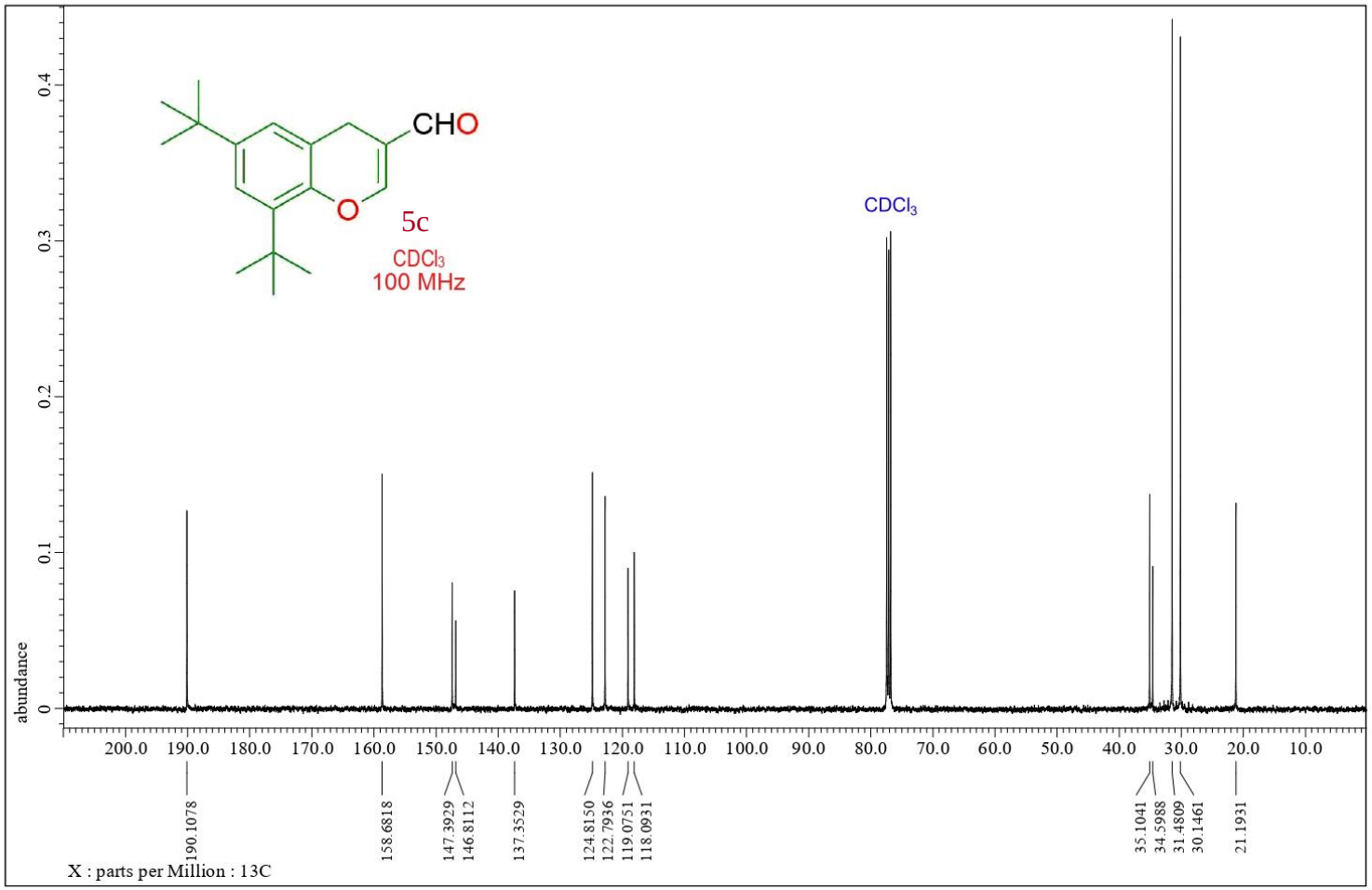
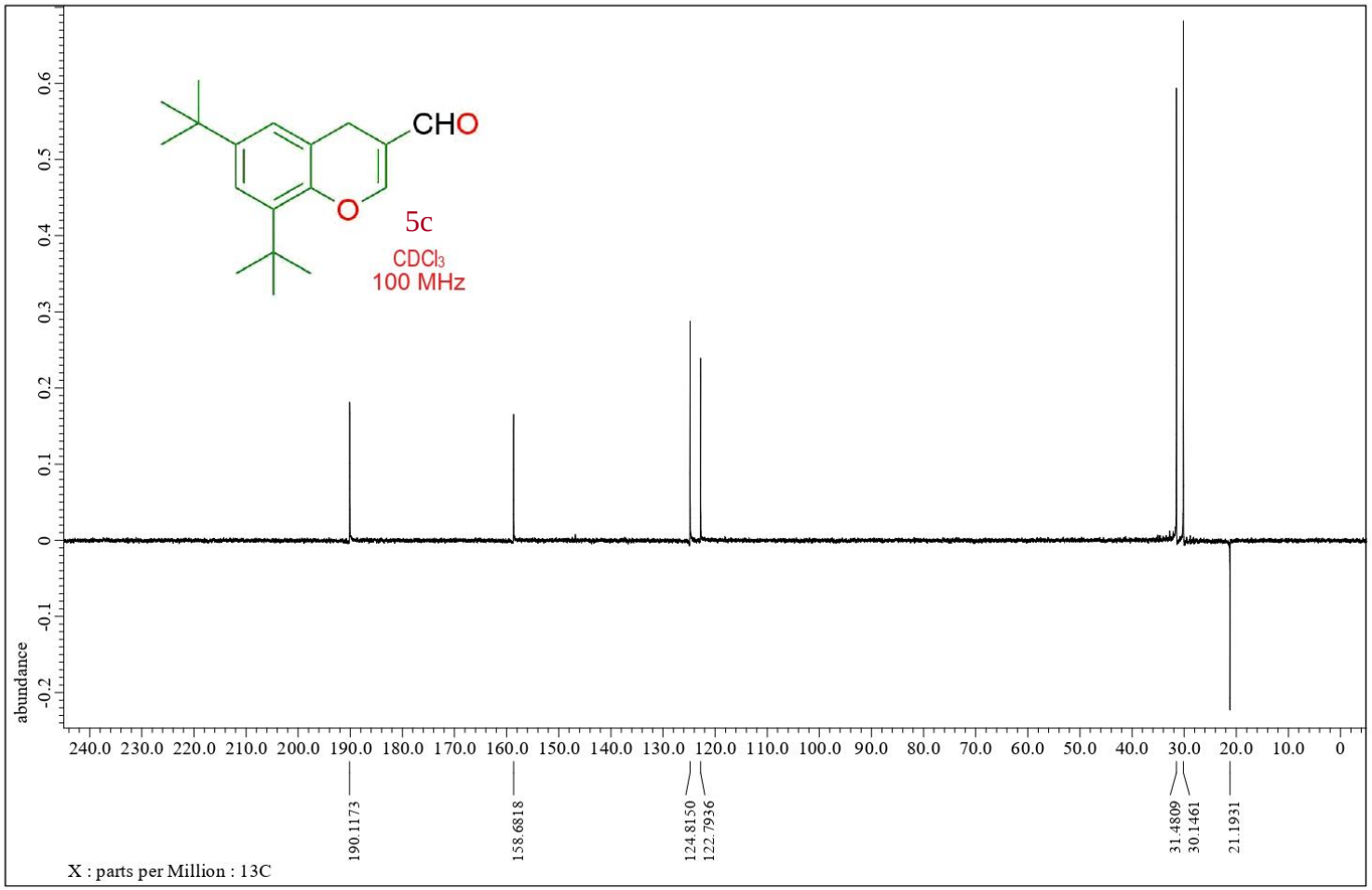
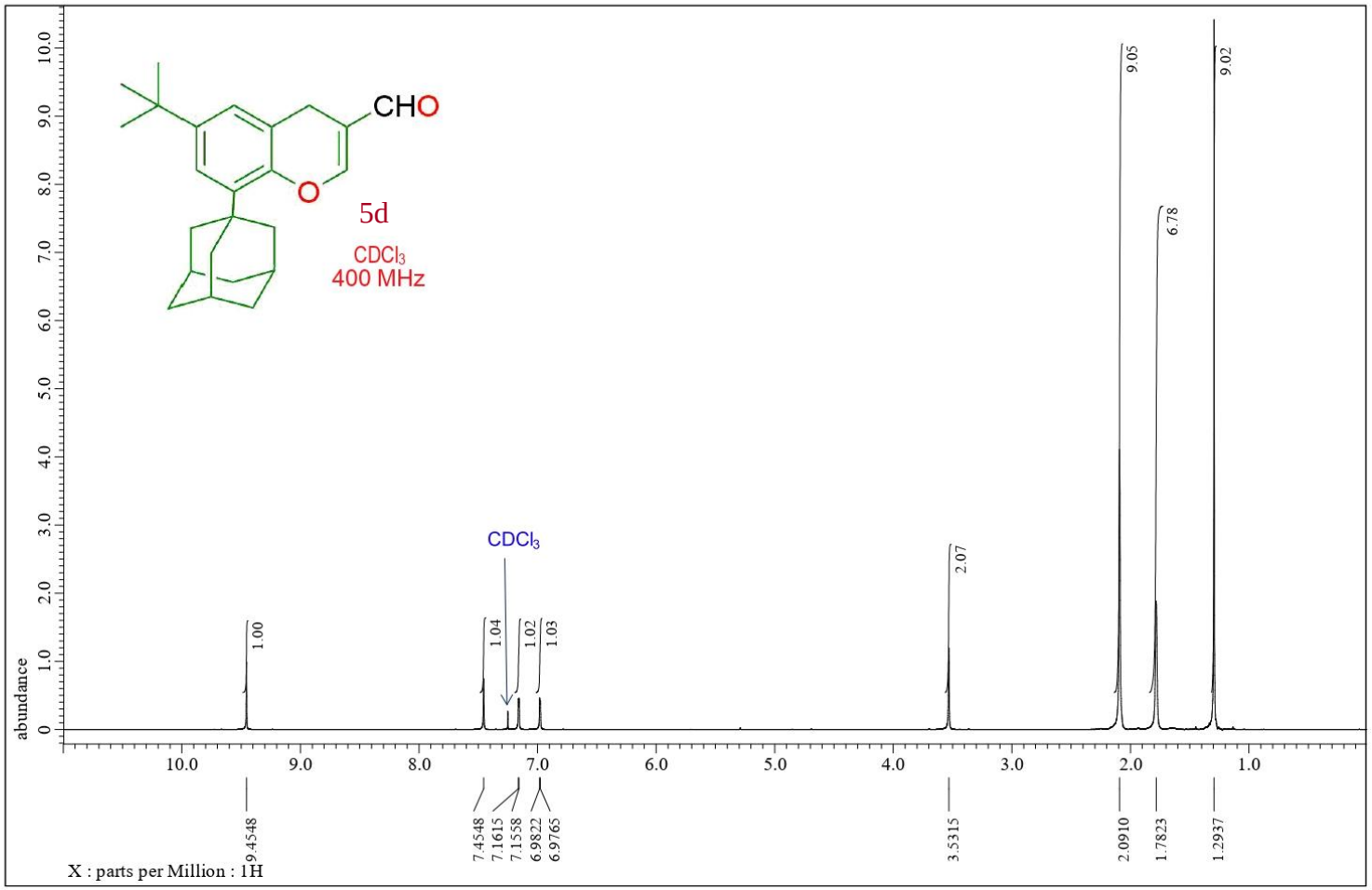
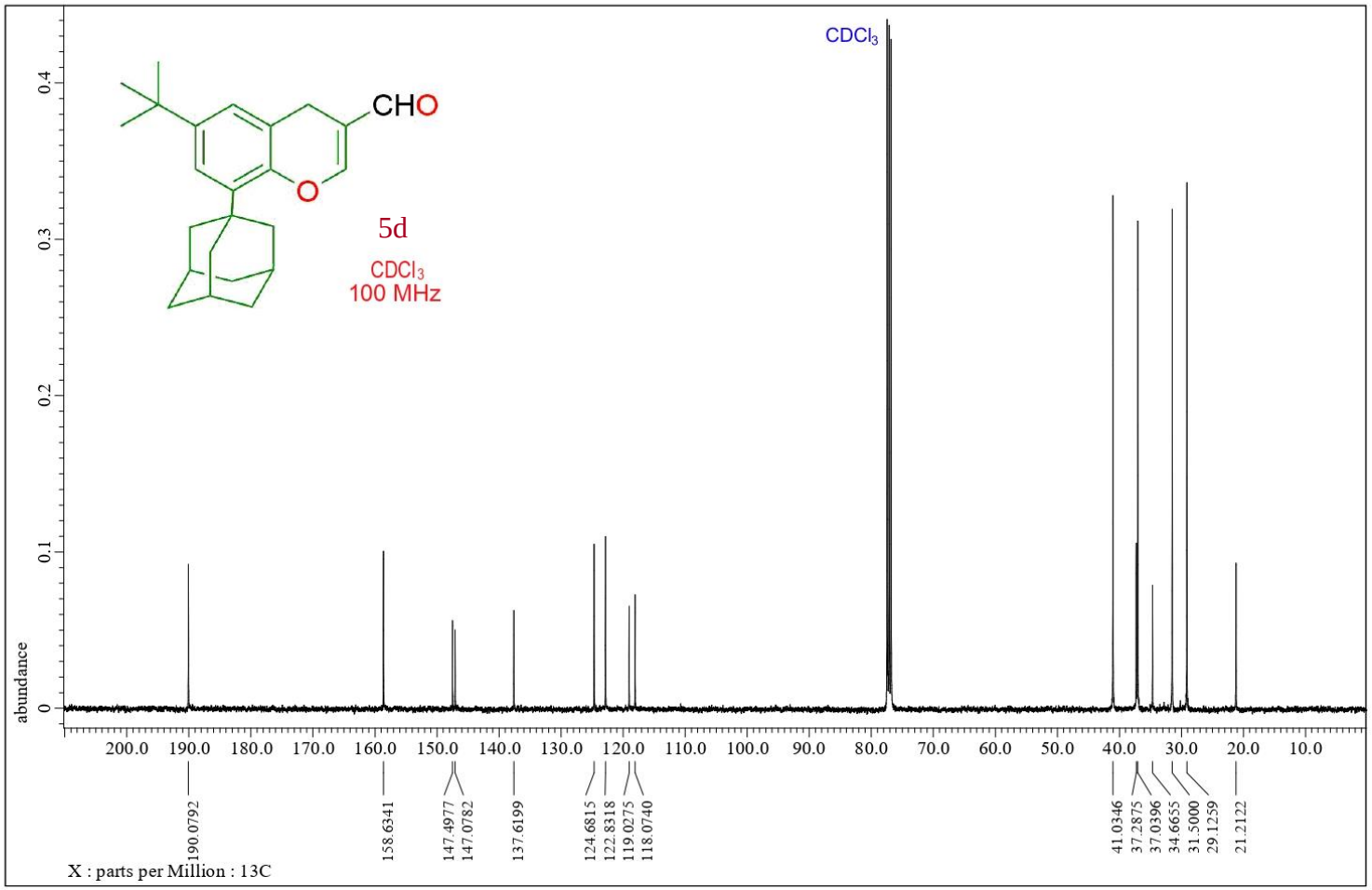
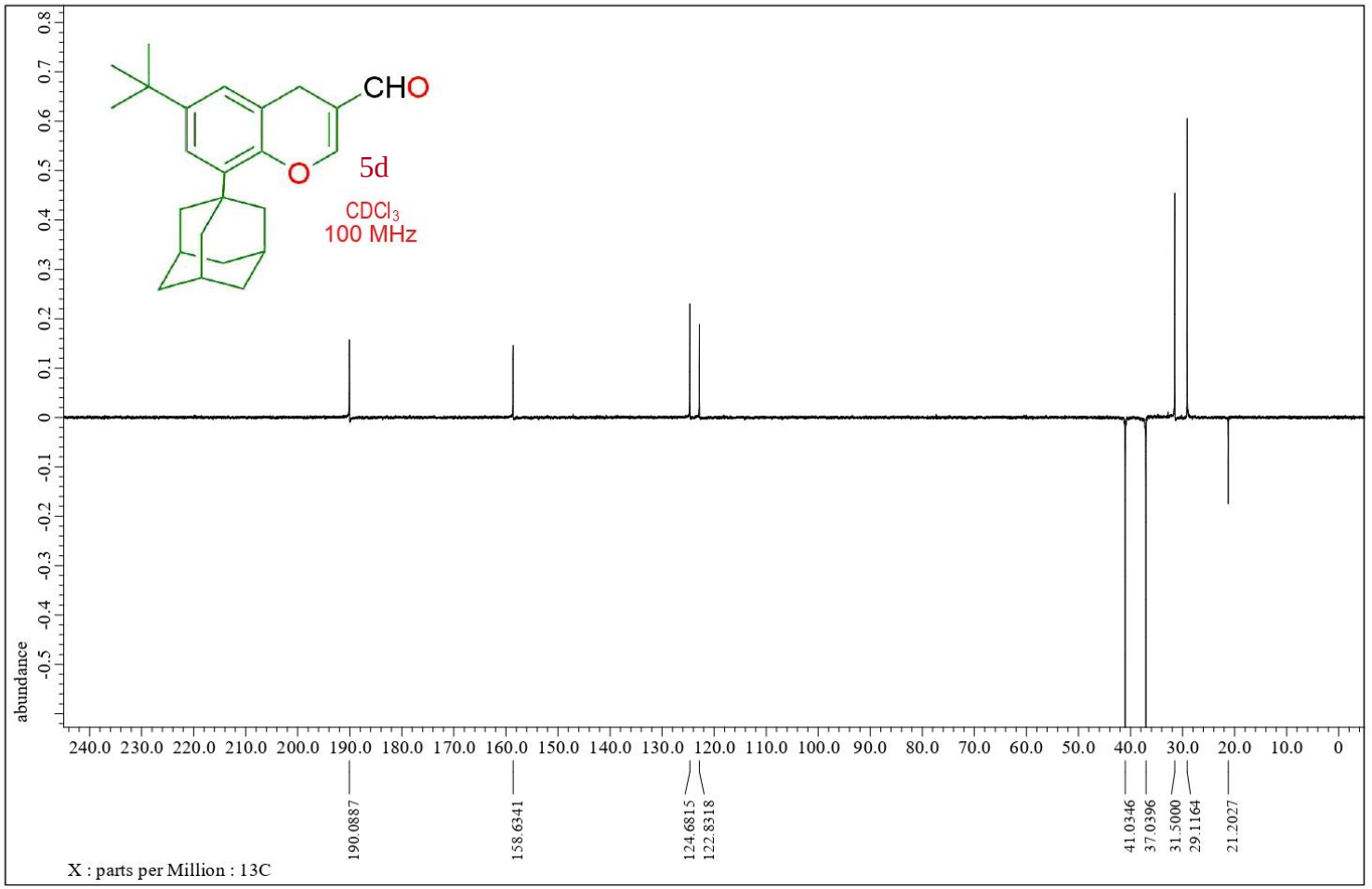
1.01
2.04
9.00
9.06
9.4582
7.4410
7.2102
7.2039
6.9903
6.9840
3.5349
1.3985
1.2914
1.2766
X : parts per Million : 1H

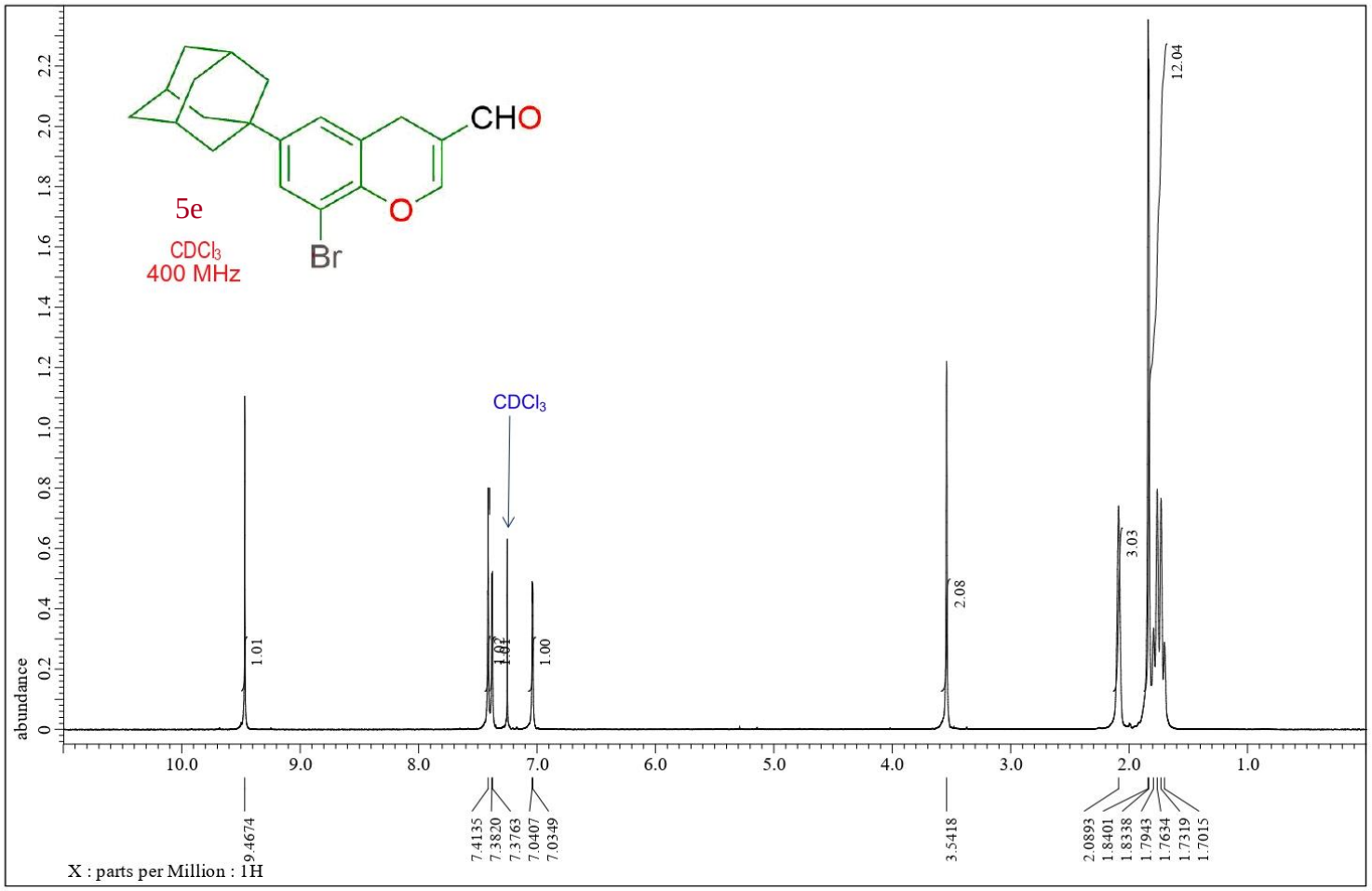

CHO
O
5c
CDCl3
100 MHz
CDCl3
abundance
0
0.1
0.2
0.3
0.4
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
190.1078
158.6818
147.3929
146.8112
137.3529
124.8150
122.7936
119.0751
118.0931
35.1041
34.5988
31.4809
30.1461
21.1931
X : parts per Million : 13C

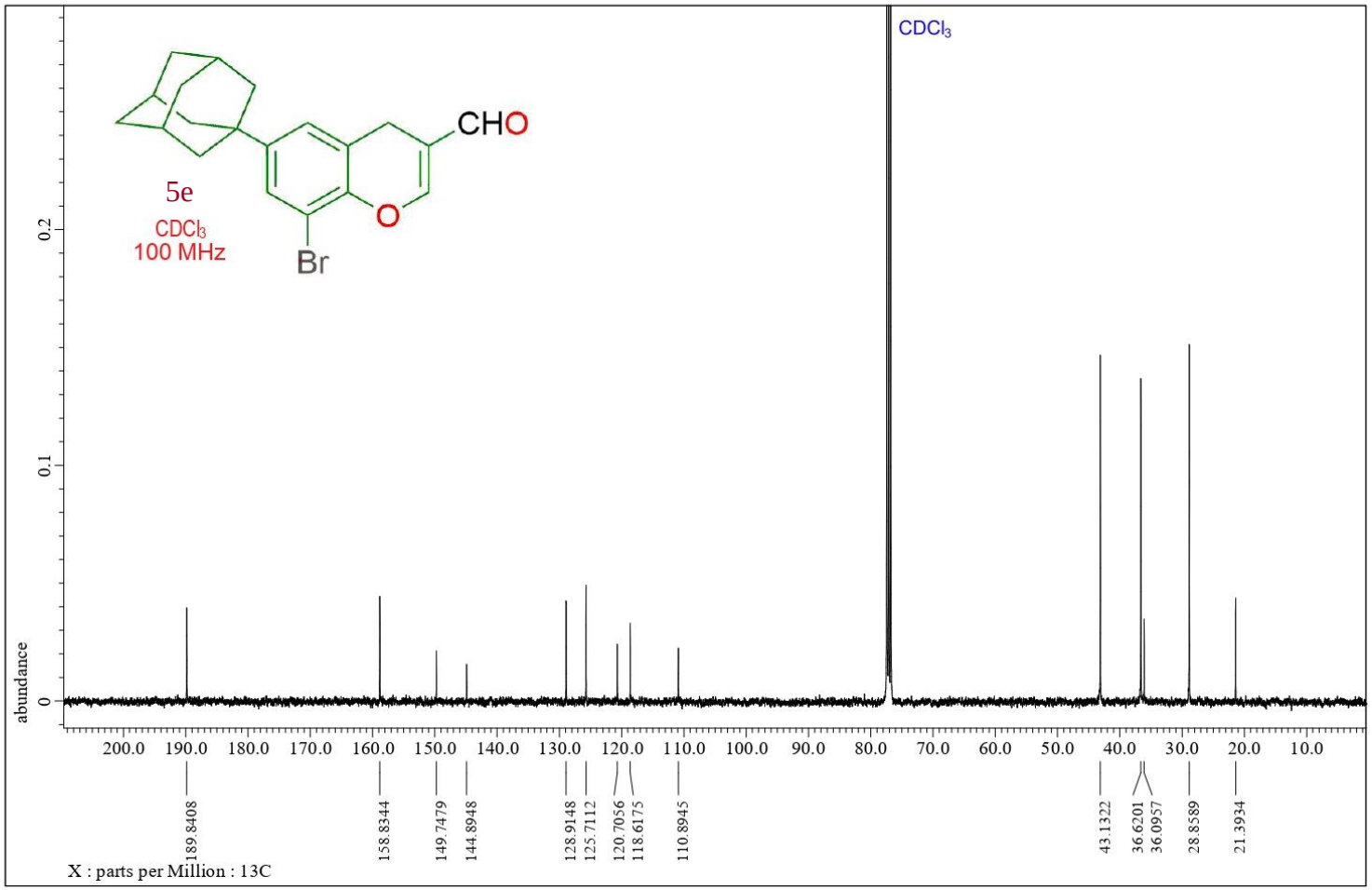

CHO
O
5c
CDCl3
100 MHz
abundance
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
240.0 230.0 220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
190.1173
158.6818
124.8150
122.7936
31.4809
30.1461
21.1931
X : parts per Million : 13C

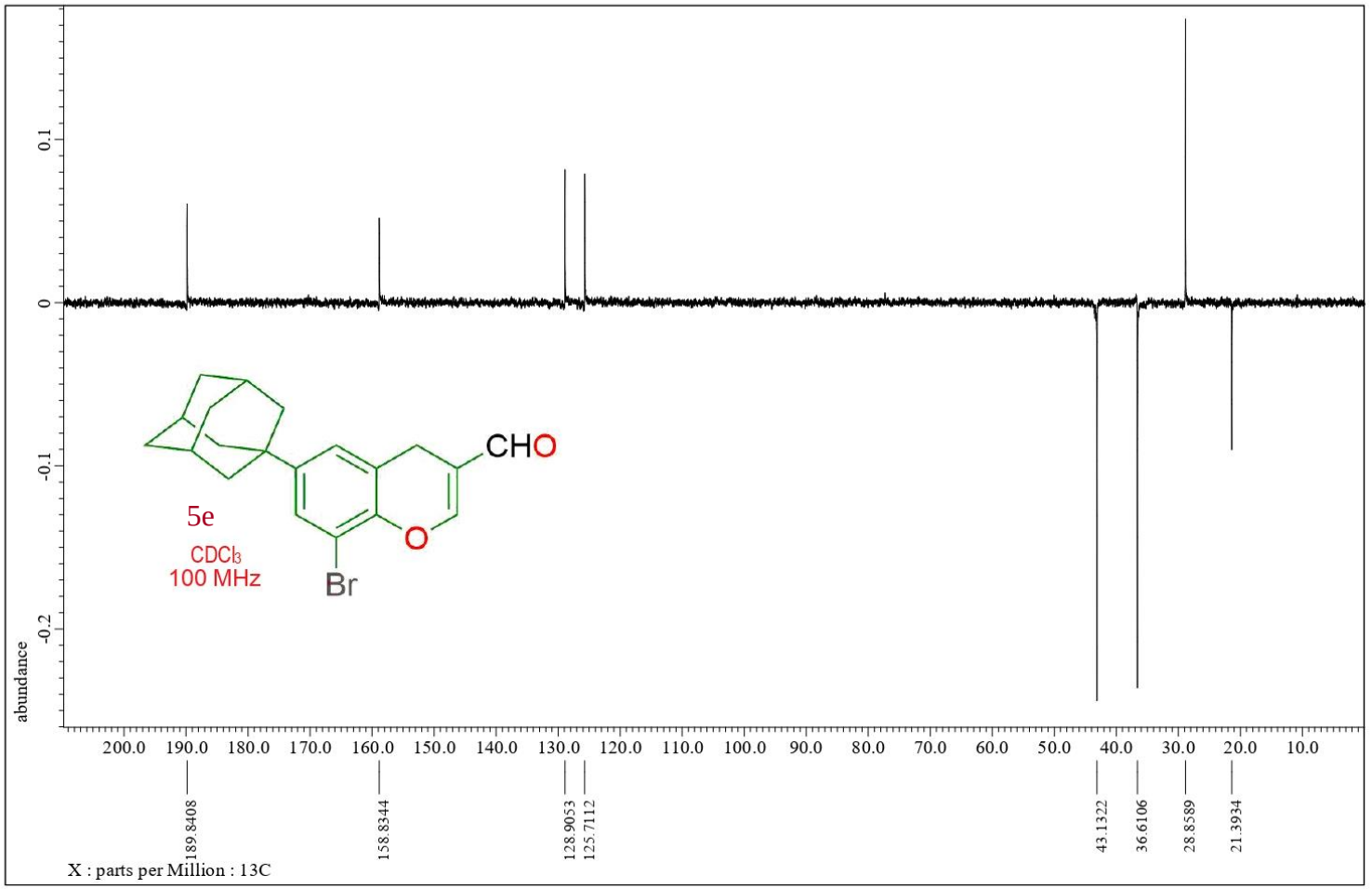

CHO
O
5d
CDCl3
400 MHz
abundance
CDCl3
1.00
1.04
1.02
1.03
2.07
9.05
6.78
9.02
9.4548
7.4548
7.1615
7.1558
6.9822
6.9765
3.5315
2.0910
1.7823
1.2937
X : parts per Million : 1H

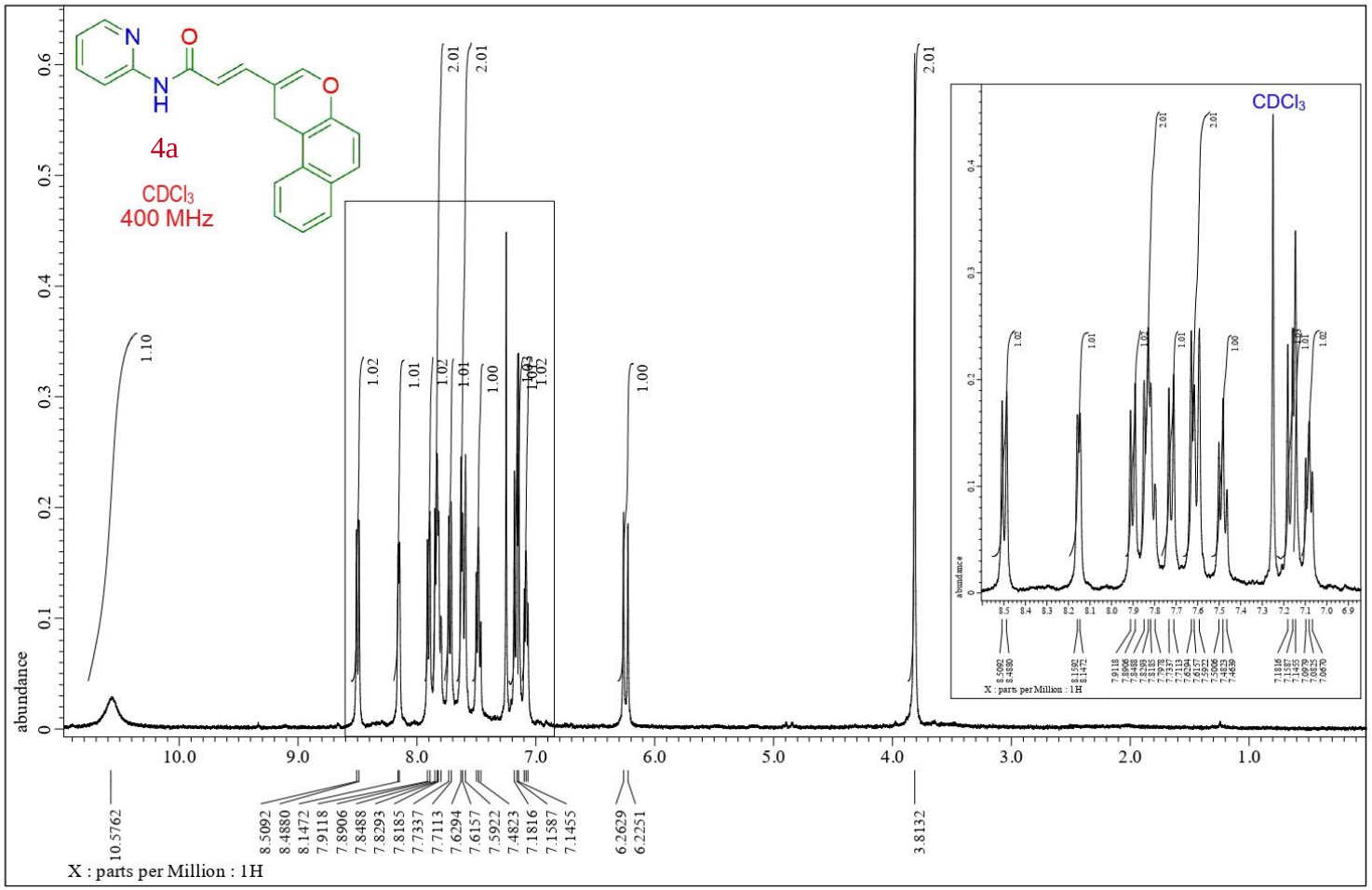

CDCl3
CHO
O
5d
CDCl3
100 MHz
abundance
0
0.1
0.2
0.3
0.4
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
190.0792
158.6341
147.4977
147.0782
137.6199
124.6815
122.8318
119.0275
118.0740
41.0346
37.2875
37.0396
34.6655
31.5000
29.1259
21.2122
X : parts per Million : 13C

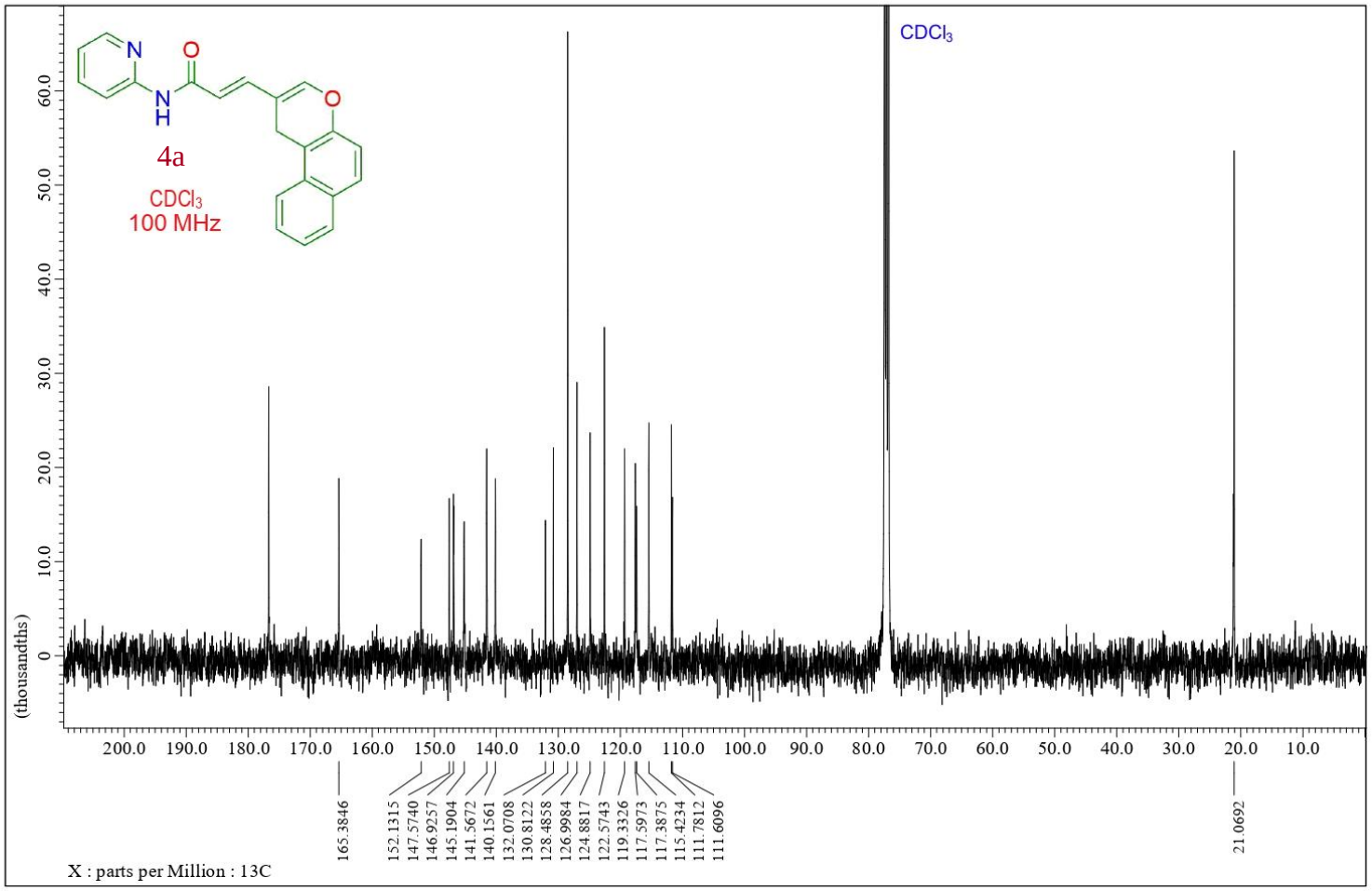

CHO
O
5d
CDCl3
100 MHz
abundance
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
-0.5
240.0 230.0 220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
190.0887
158.6341
124.6815
122.8318
41.0346
37.0396
31.5000
29.1164
21.2027
X : parts per Million : 13C

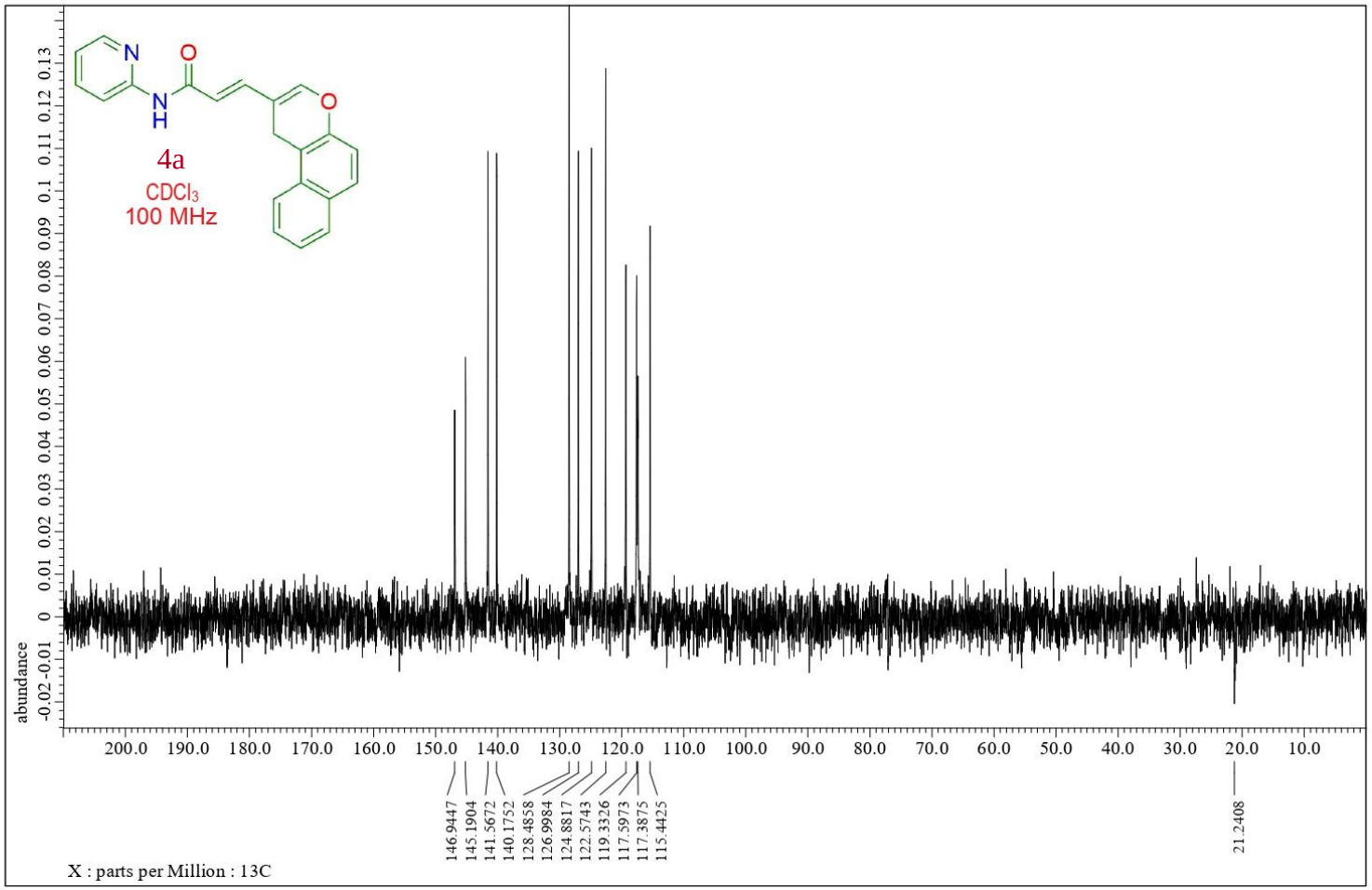

CHO
O
Br
5e
CDCl3
400 MHz
CDCl3
12.04
3.03
2.08
1.01
1.00
abundance
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
9.4674
7.4135
7.3820
7.3763
7.0407
7.0349
3.5418
2.0893
1.8401
1.8338
1.7943
1.7634
1.7319
1.7015
X : parts per Million : 1H

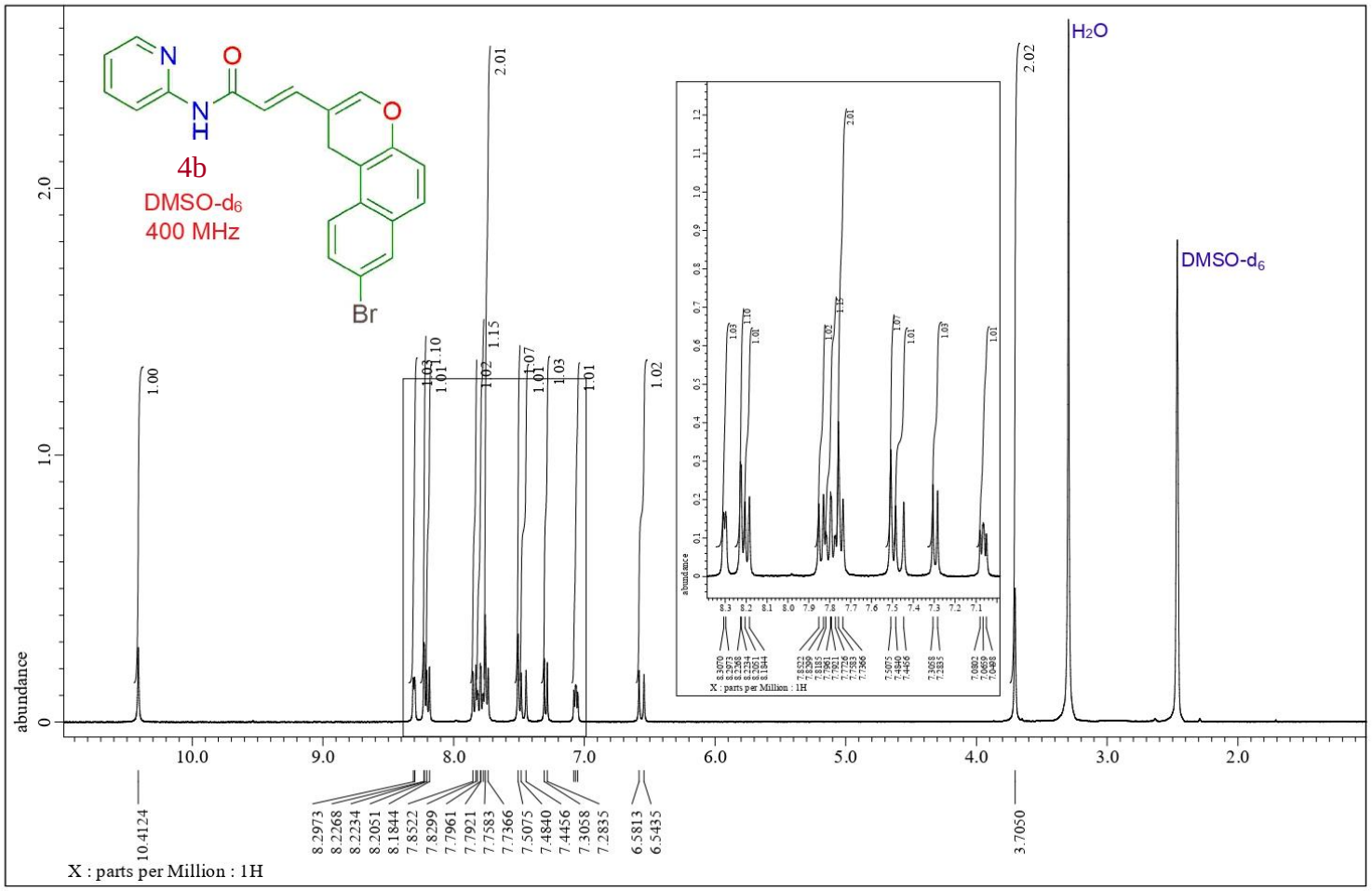

CDCl3
CHO
O
Br
5e
CDCl3
100 MHz
abundance
0.2
0.1
0
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0
189.8408
158.8344
149.7479
144.8948
128.9148
125.7112
120.7056
118.6175
110.8945
43.1322
36.6201
36.0957
28.8589
21.3934
X : parts per Million : 13C

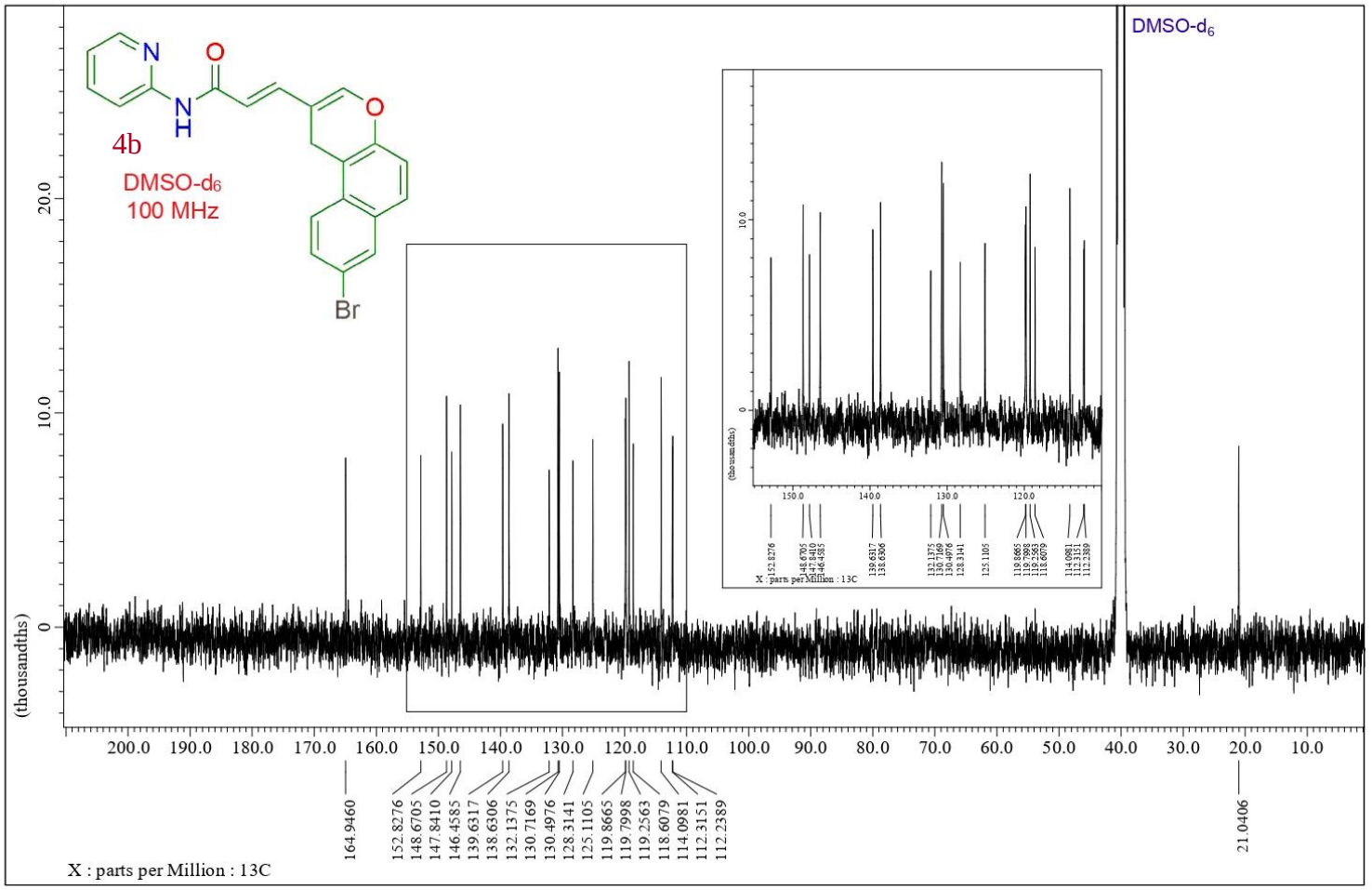

0.1
0
-0.1
-0.2
abundance
CHO
O
Br
5e
CDCl3
100 MHz
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0
189.8408
158.8344
128.9053
125.7112
43.1322
36.6106
28.8589
21.3934
X : parts per Million : 13C

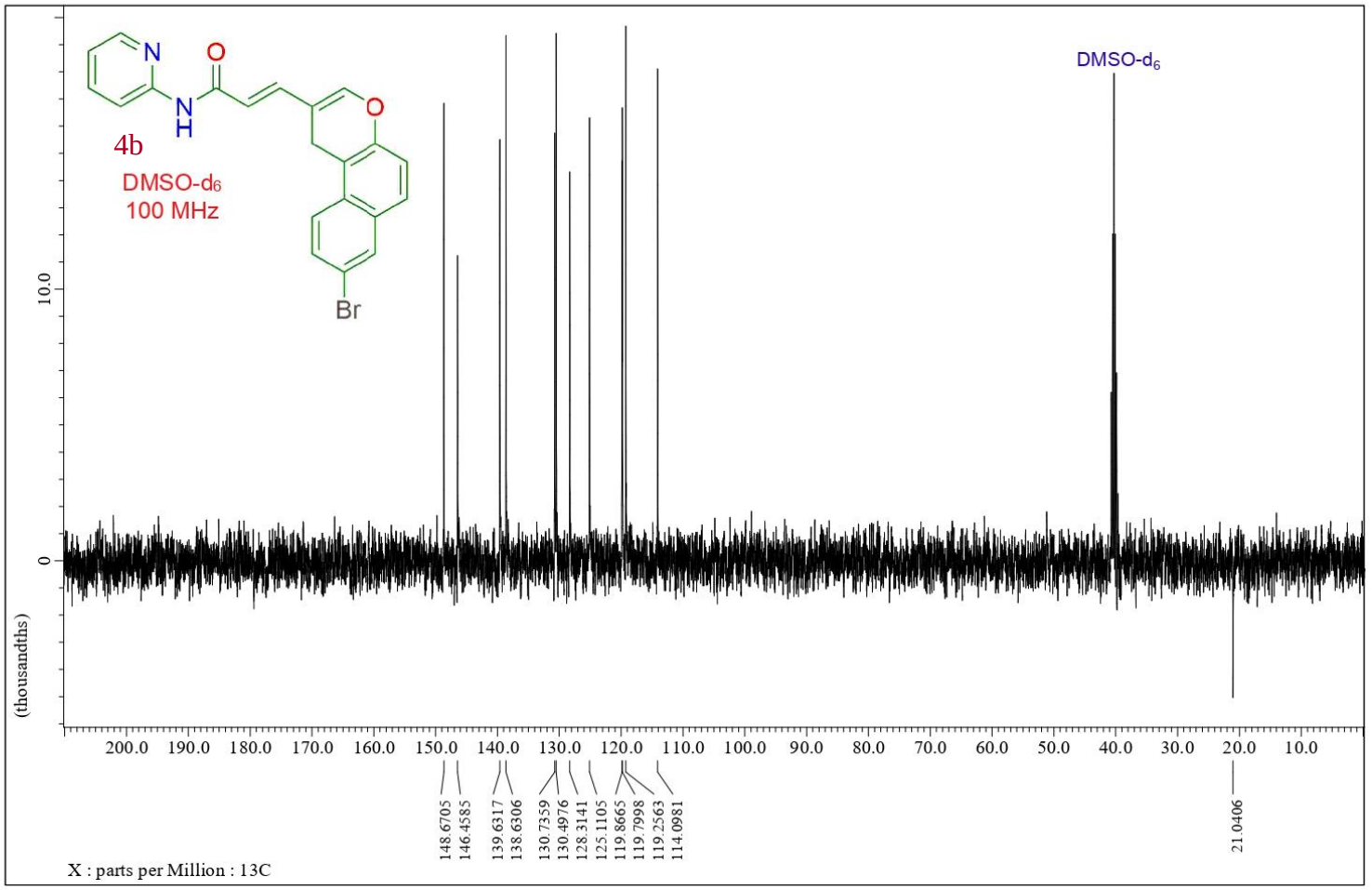

4a
CDCl3
400 MHz
abundance
X : parts per Million : 1H
CDCl3

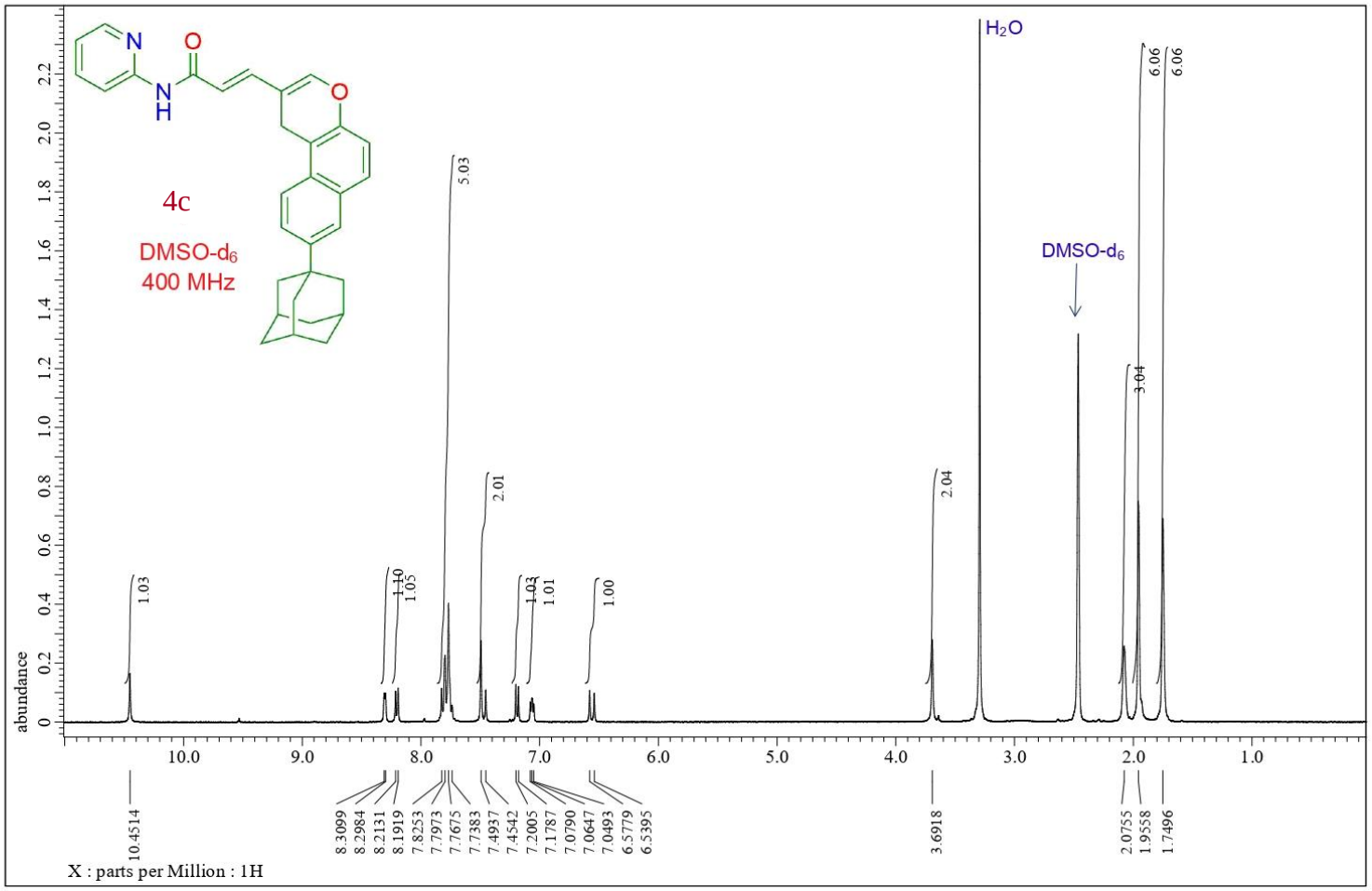

4a
CDCl3
100 MHz
CDCl3
(thousandths)
60.0
50.0
40.0
30.0
20.0
10.0
0
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0
165.3846
152.1315
147.5740
146.9257
145.1904
141.5672
140.1561
132.0708
130.8122
128.4858
126.9984
124.8817
122.5743
119.3326
117.5973
117.3875
115.4234
111.7812
111.6096
21.0692
X : parts per Million : 13C

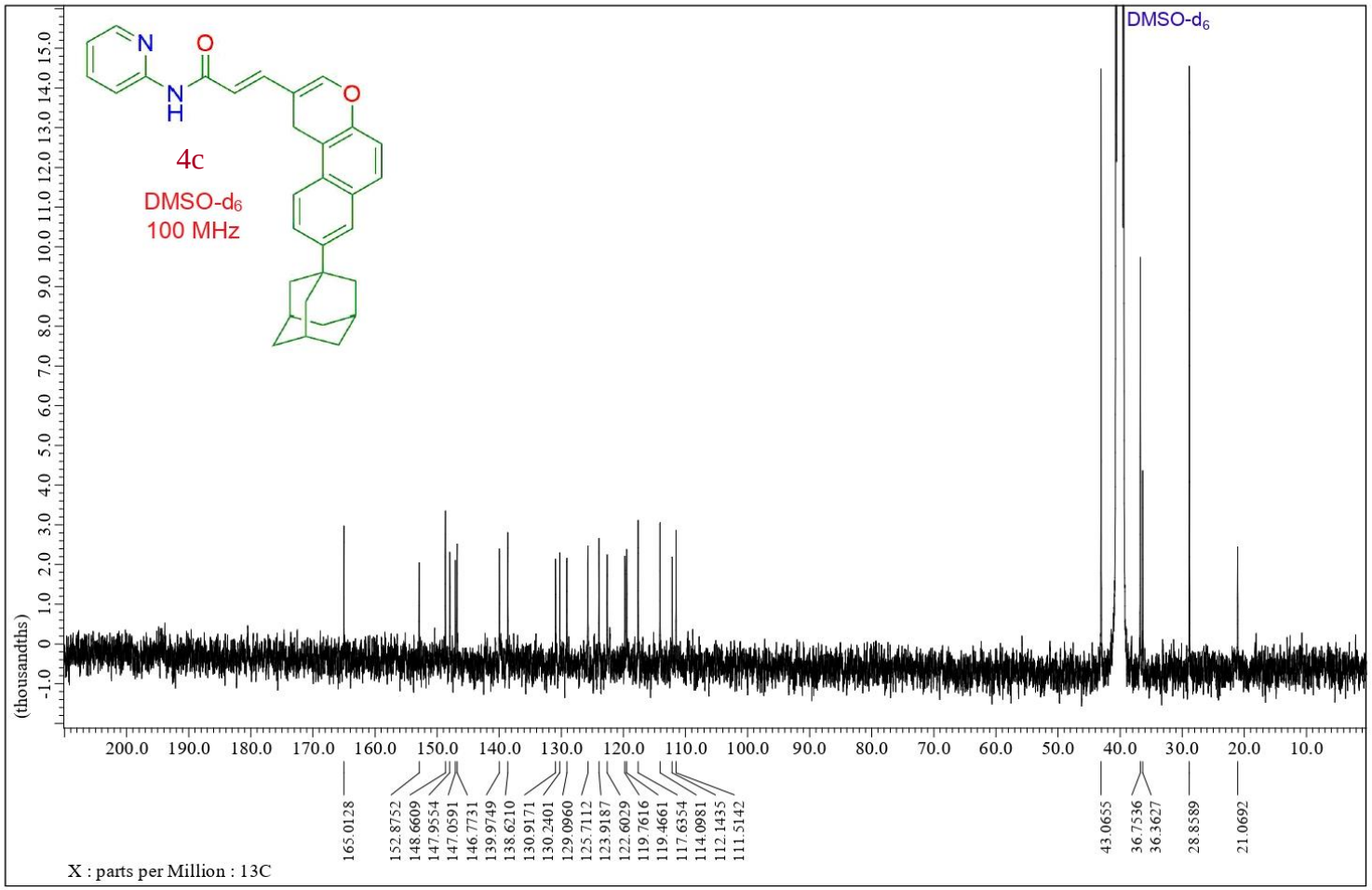

4a
CDCl3
100 MHz
abundance
-0.02 -0.01 0 0.01 0.02 0.03 0.04 0.05 0.06 0.07 0.08 0.09 0.1 0.11 0.12 0.13
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0
146.9447
145.1904
141.5672
140.1752
128.4858
126.9984
124.8817
122.5743
119.3326
117.5973
117.3875
115.4425
21.2408
X : parts per Million : 13C

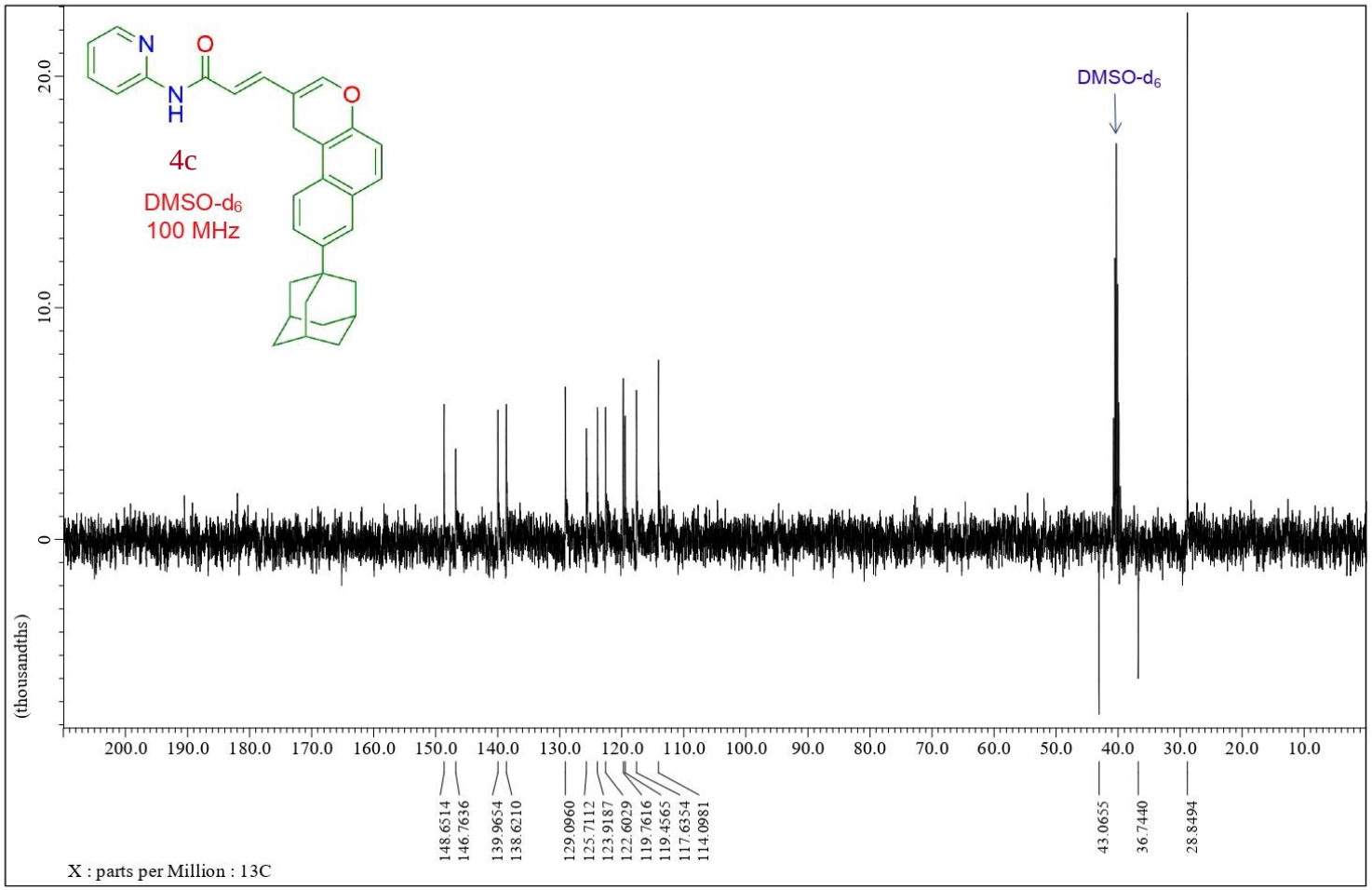

4b
DMSO-d6
400 MHz
Br
H2O
DMSO-d6
abundance
X : parts per Million : 1H
10.4124
8.2973
8.2268
8.2234
8.2051
8.1844
7.8522
7.8299
7.7961
7.7921
7.7583
7.7366
7.5075
7.4840
7.4456
7.3058
7.2835
6.5813
6.5435
3.7050

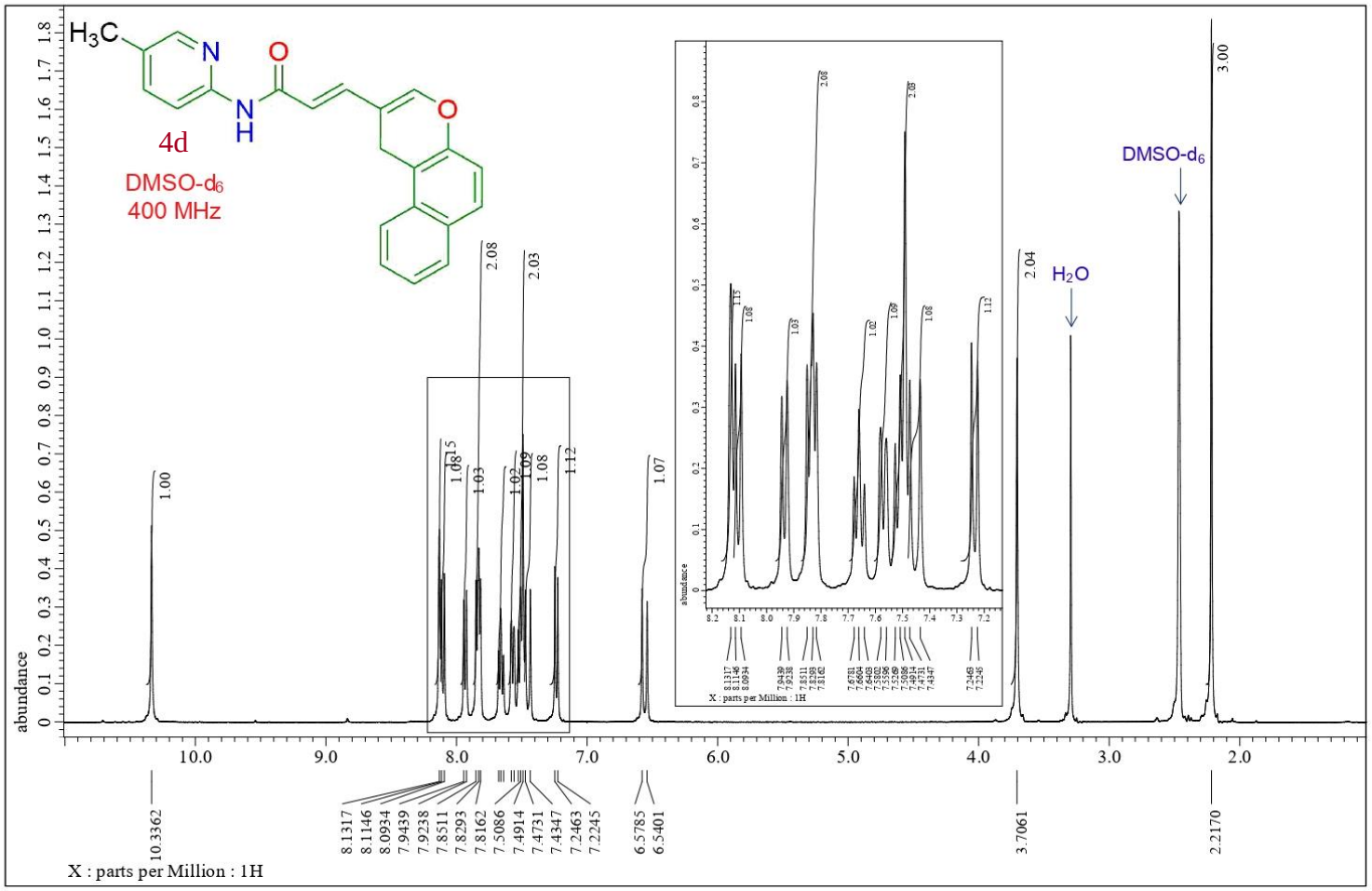

4b
DMSO-d6
100 MHz
DMSO-d6
(thousandths)
20.0
10.0
0
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0
164.9460
152.8276
148.6705
147.8410
146.4585
139.6317
138.6306
132.1375
130.7169
130.4976
128.3141
125.1105
119.8665
119.7998
119.2563
118.6079
114.0981
112.3151
112.2389
21.0406
X : parts per Million : 13C

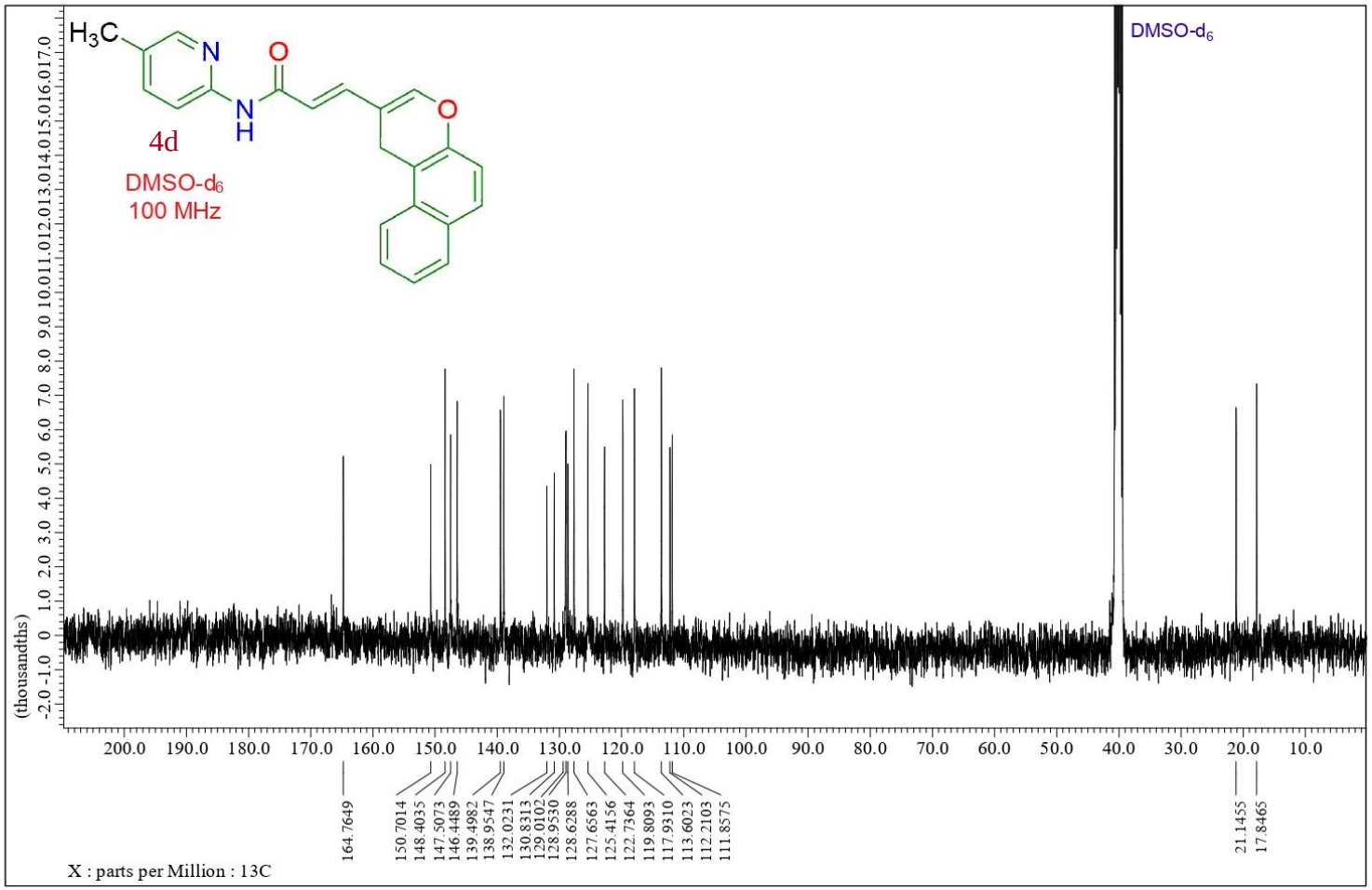

4b
DMSO-d6
100 MHz
DMSO-d6
10.0
0
(thousandths)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0
148.6705
146.4585
139.6317
138.6306
130.7359
130.4976
128.3141
125.1105
119.8665
119.7998
119.2563
114.0981
21.0406
X : parts per Million : 13C

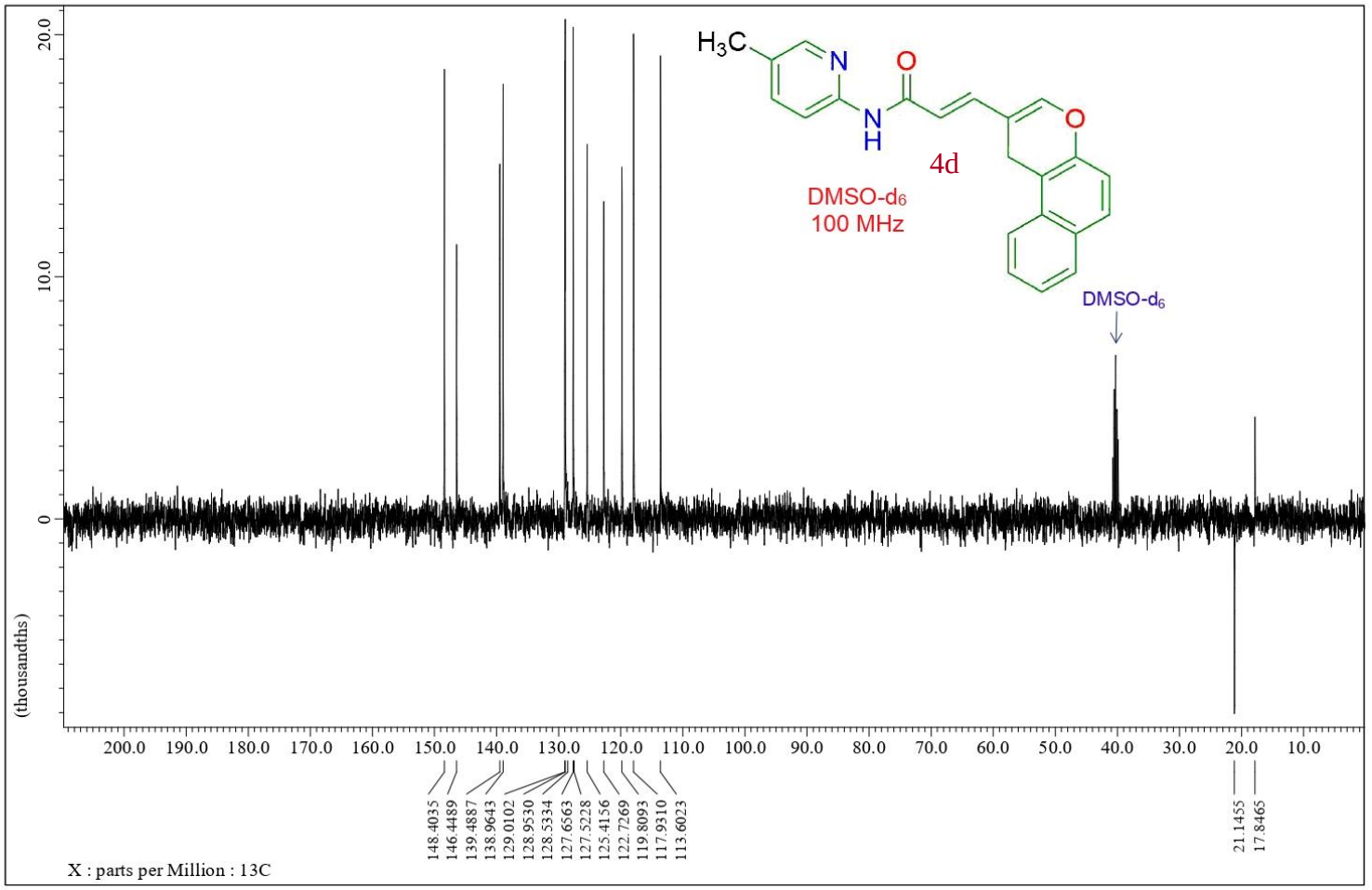

4c
DMSO-d6
400 MHz
H2O
DMSO-d6
abundance
X : parts per Million : 1H
10.4514
8.3099
8.2984
8.2131
8.1919
7.8253
7.7973
7.7675
7.7383
7.4937
7.4542
7.2005
7.1787
7.0790
7.0647
7.0493
6.5779
6.5395
3.6918
2.0755
1.9558
1.7496

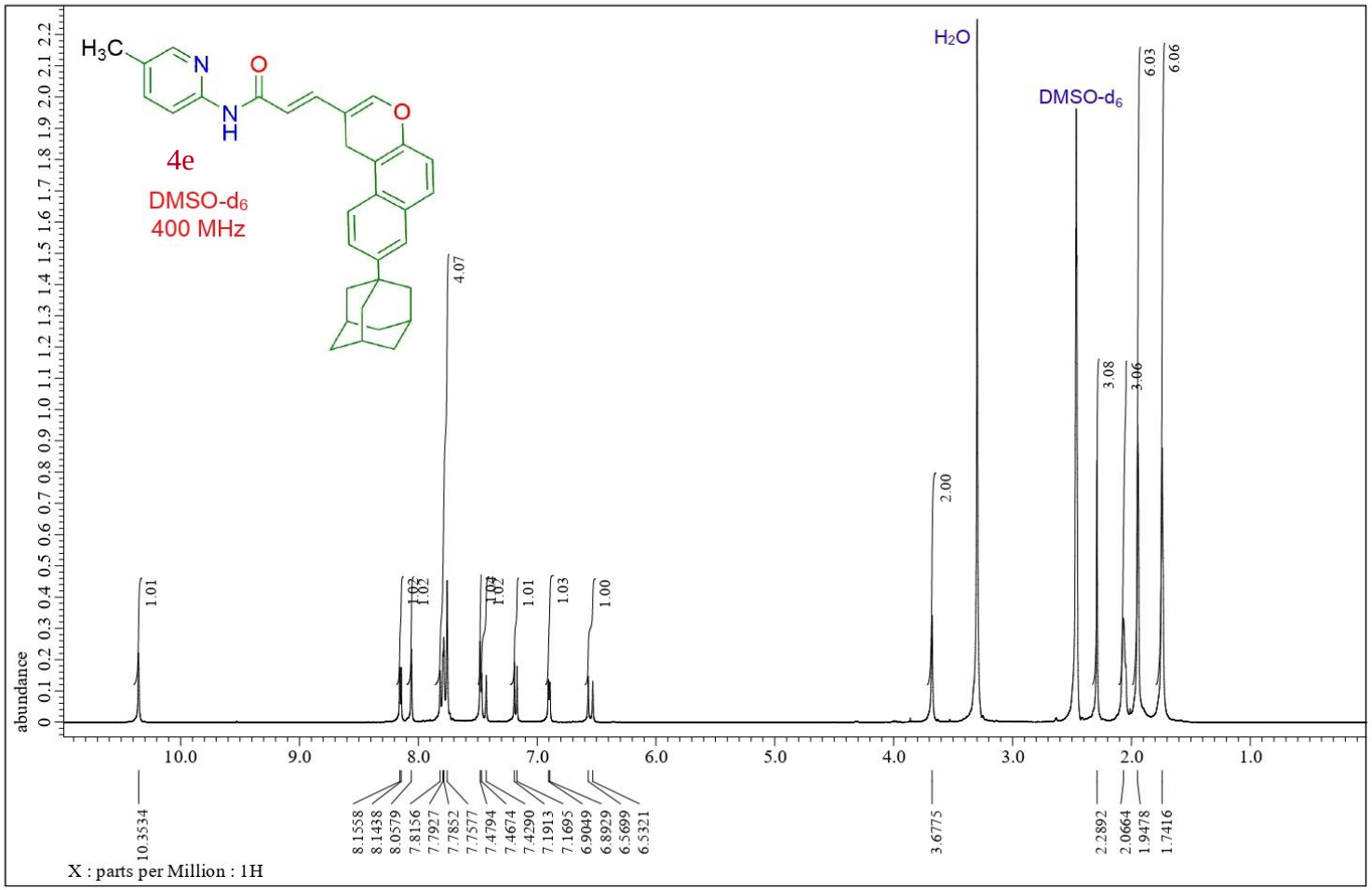

4c
DMSO-d6
100 MHz
DMSO-d6
(thousandths)
X : parts per Million : 13C
165.0128
152.8752
148.6609
147.9554
147.0591
146.7731
139.9749
138.6210
130.9171
130.2401
129.0960
125.7112
123.9187
122.6029
119.7616
119.4661
117.6354
114.0981
112.1435
111.5142
43.0655
36.7536
36.3627
28.8589
21.0692

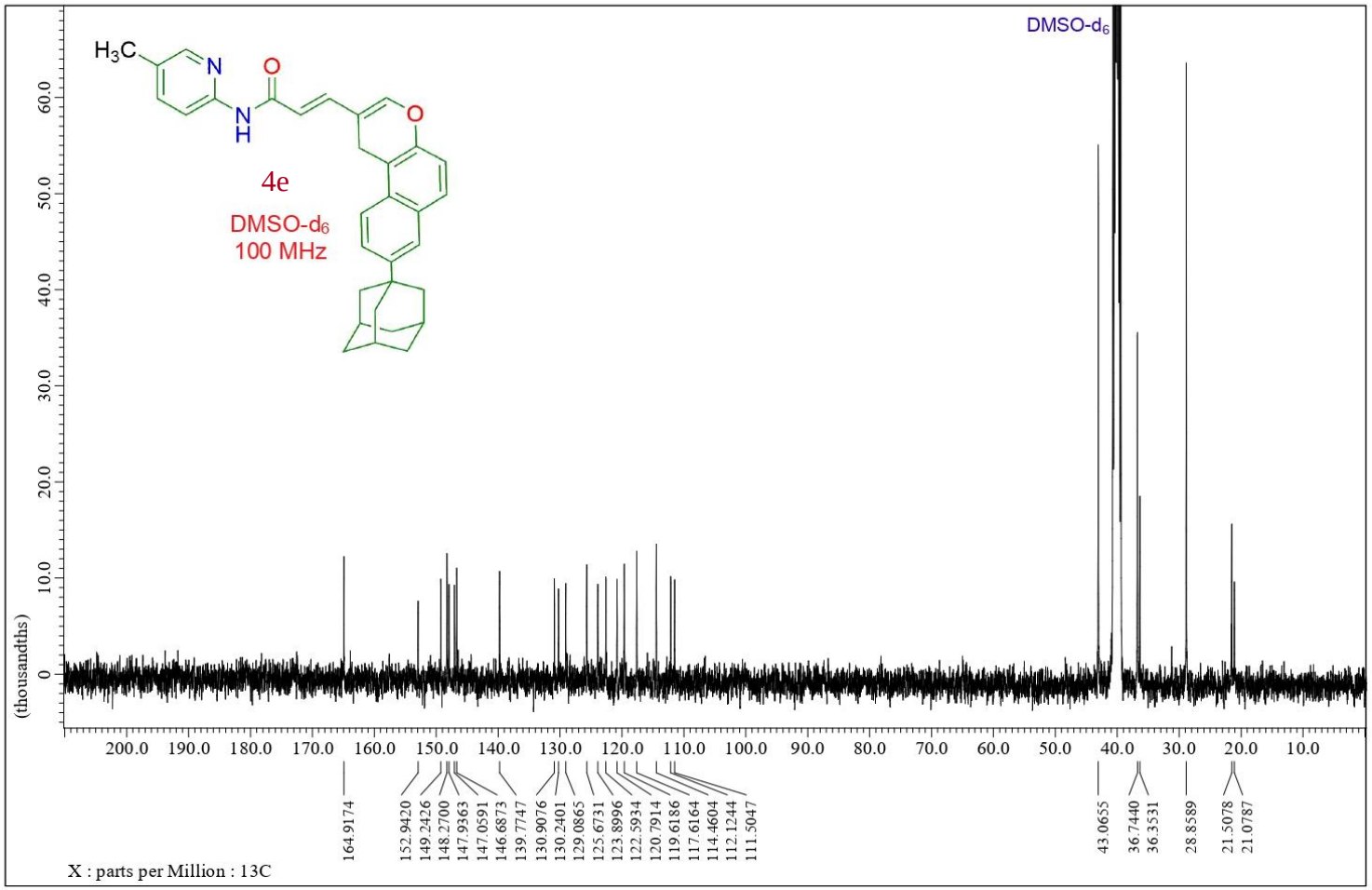

4c
DMSO-d6
100 MHz
DMSO-d6
20.0
10.0
0
(thousandths)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0
148.6514
146.7636
139.9654
138.6210
129.0960
125.7112
123.9187
122.6029
119.7616
119.4565
117.6354
114.0981
43.0655
36.7440
28.8494
X : parts per Million : 13C

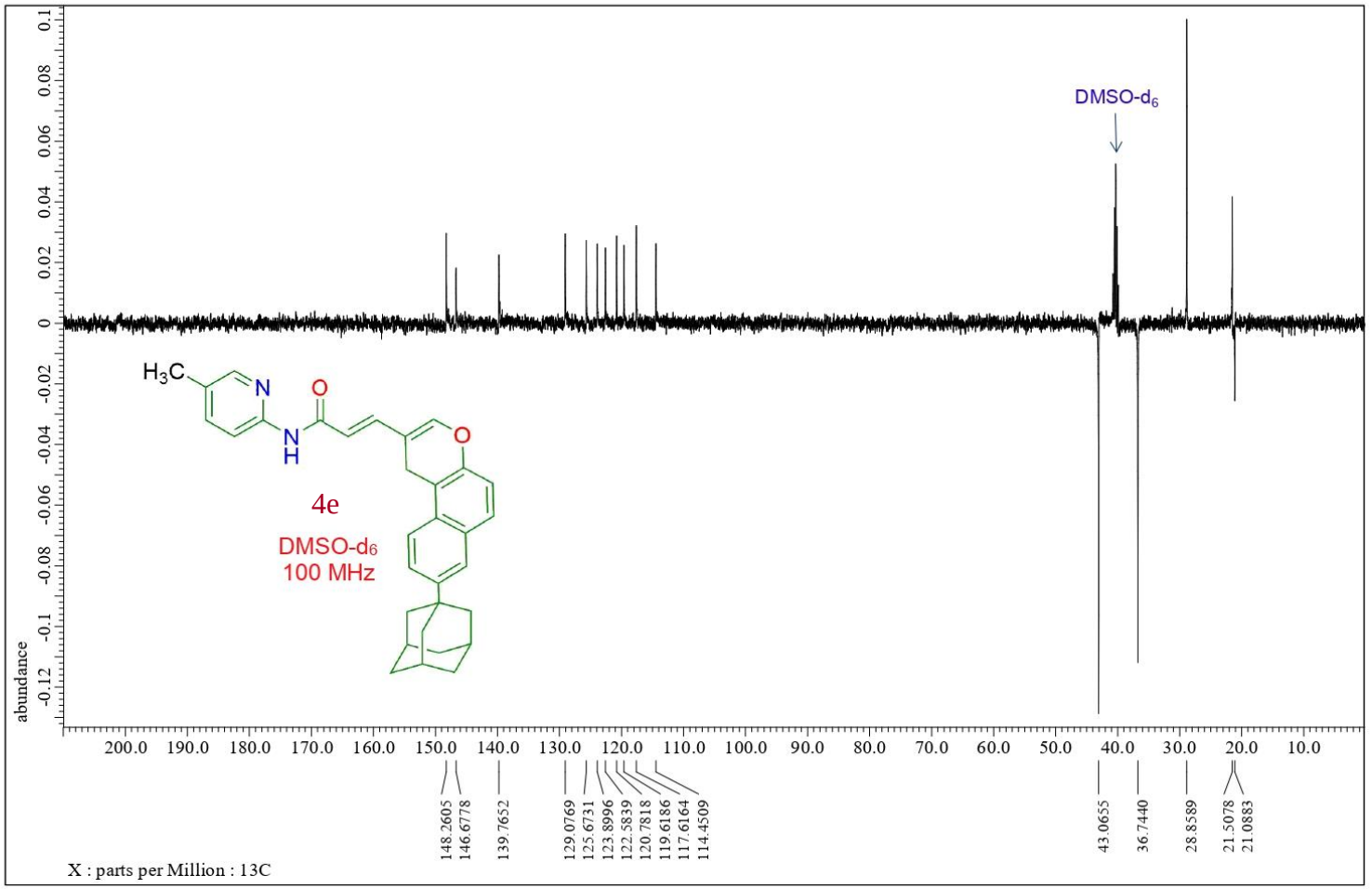

4d
DMSO-d6
400 MHz
DMSO-d6
H2O
abundance
X : parts per Million : 1H

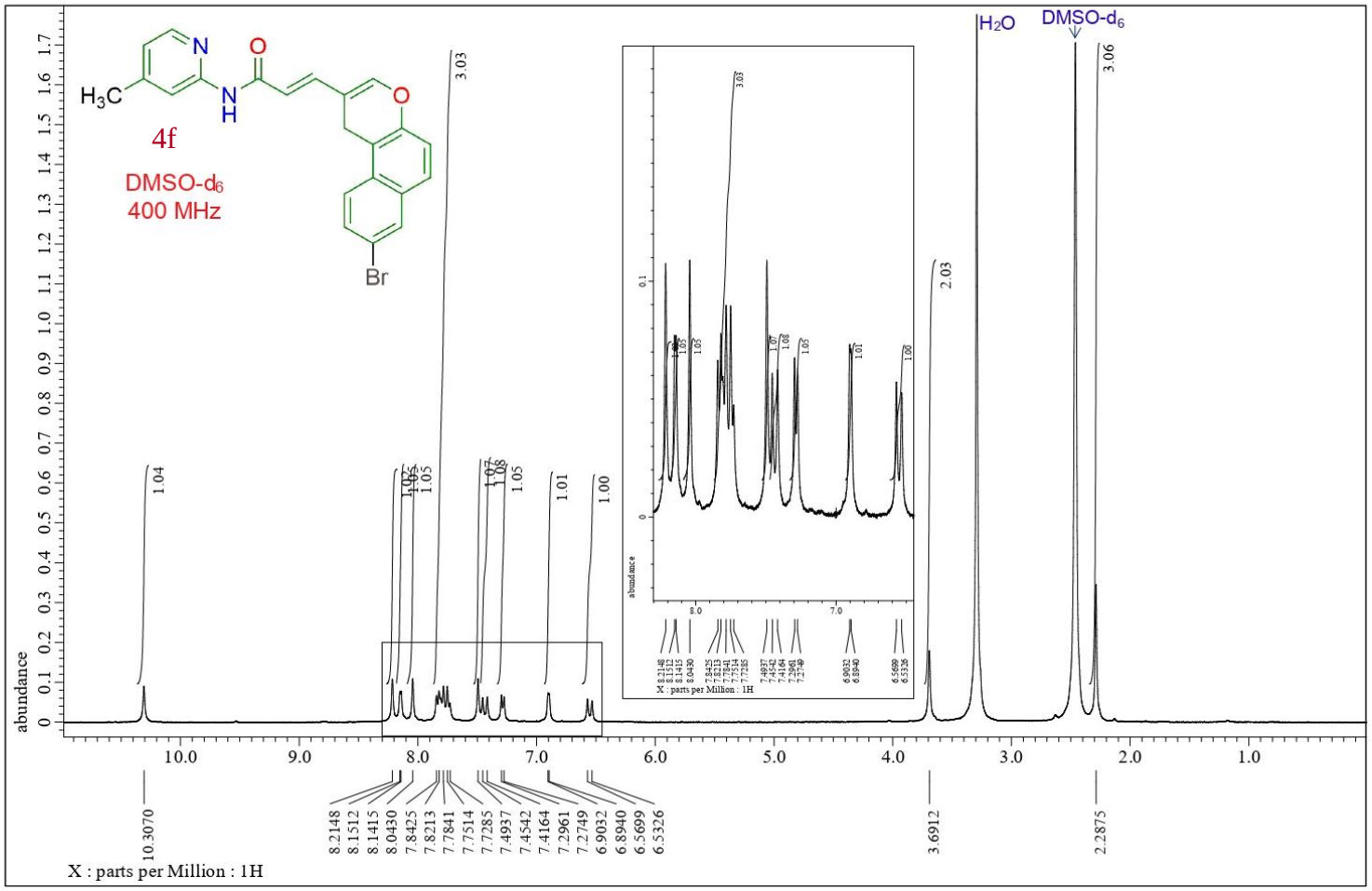

H3C
N
O
N
H
O
4d
DMSO-d6
100 MHz
DMSO-d6
(thousandths)
-2.0 -1.0 0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0 16.0 17.0
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0
164.7649
150.7014
148.4035
147.5073
146.4489
139.4982
138.9547
132.0231
130.8313
129.0102
128.9530
128.6288
127.6563
125.4156
122.7364
119.8093
117.9310
113.6023
112.2103
111.8575
21.1455
17.8465
X : parts per Million : 13C

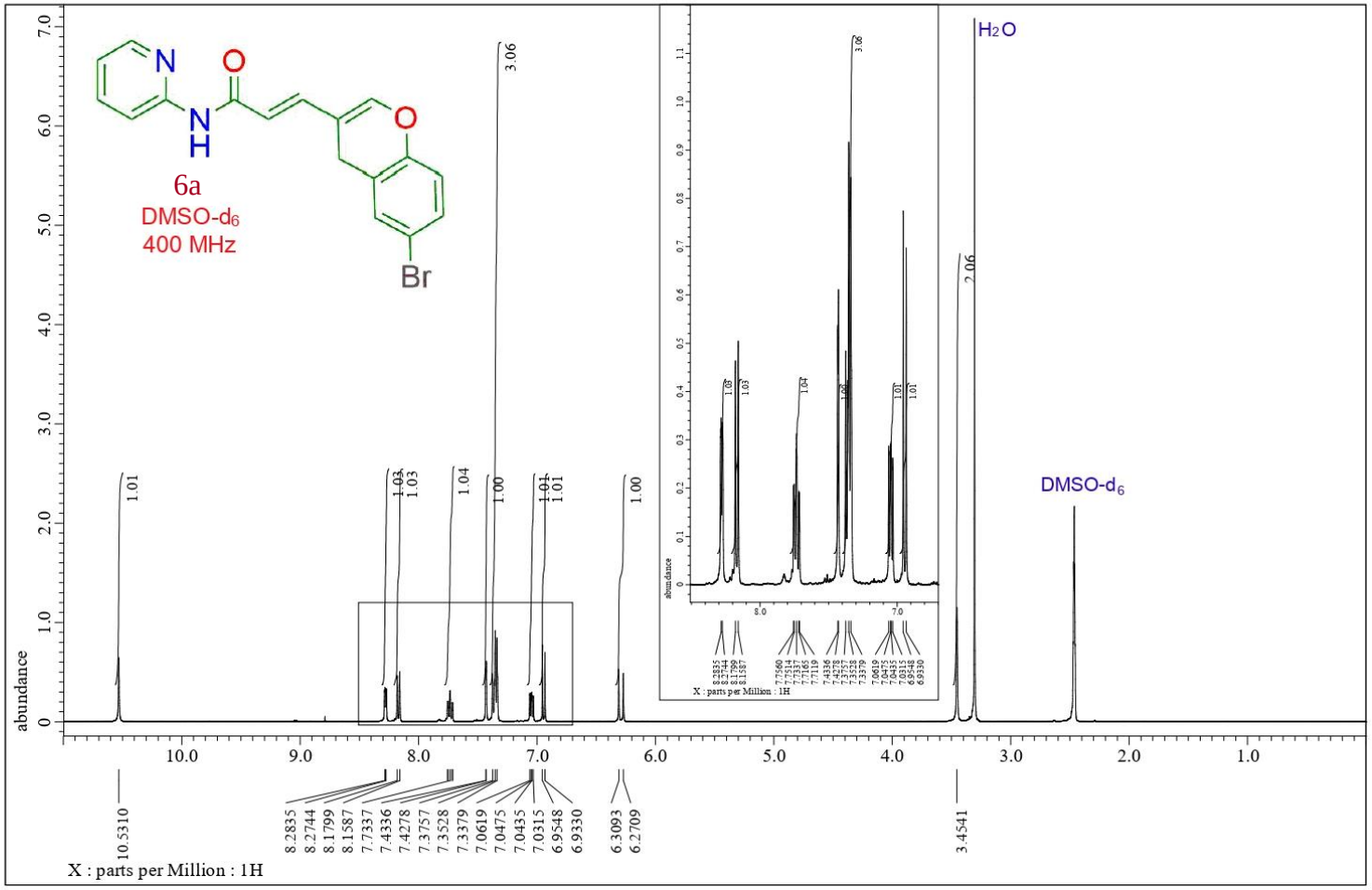

H3C
N
O
N
H
O
4d
DMSO-d6
100 MHz
DMSO-d6
20.0
10.0
0
(thousandths)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0
148.4035
146.4489
139.4887
138.9643
129.0102
128.9530
128.5334
127.6563
127.5228
125.4156
122.7269
119.8093
117.9310
113.6023
21.1455
17.8465
X : parts per Million : 13C

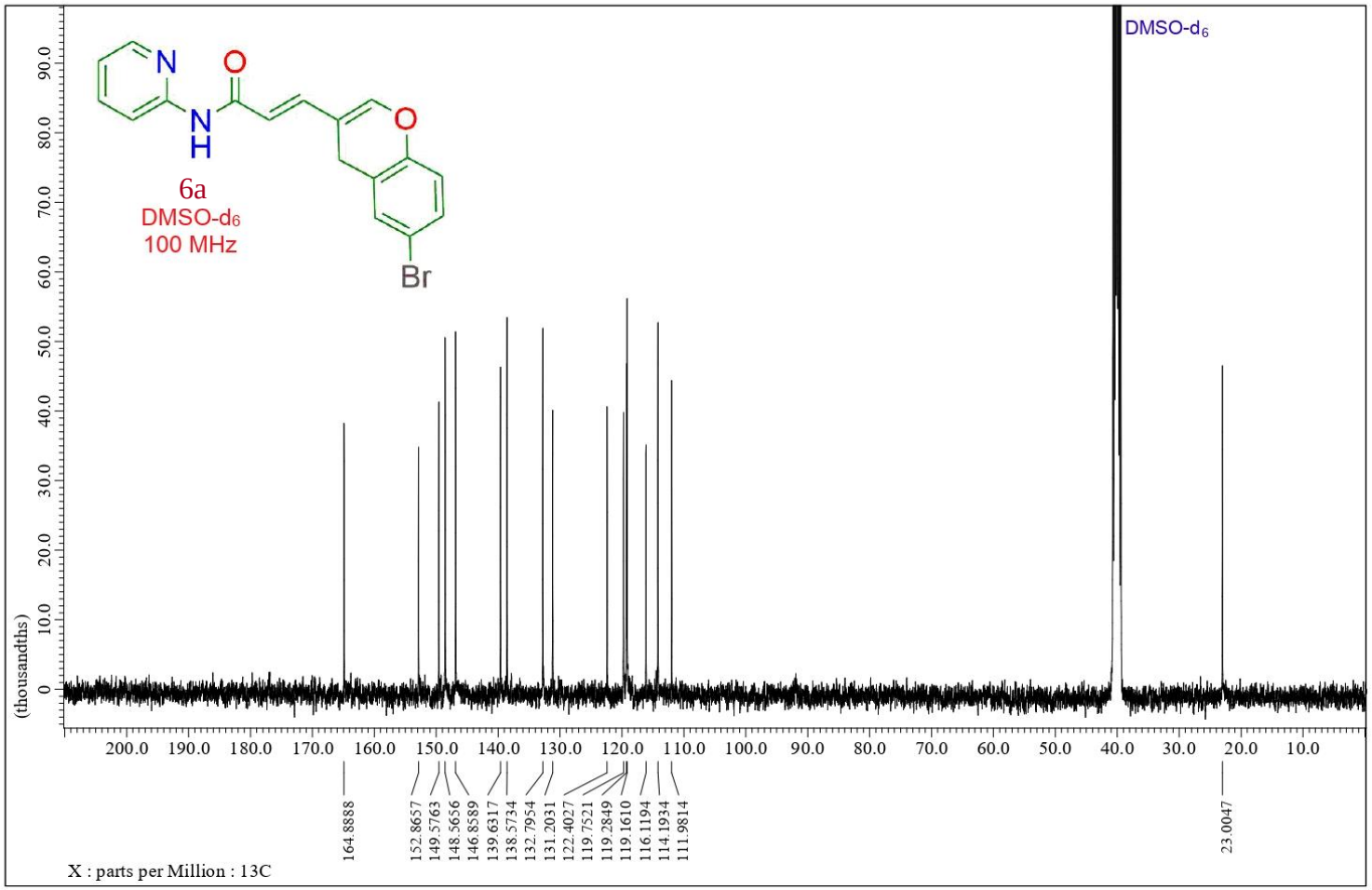

4e
DMSO-d6
400 MHz
H2O
DMSO-d6
abundance
X : parts per Million : 1H
10.3534
8.1558
8.1438
8.0579
7.8156
7.7927
7.7852
7.7577
7.4794
7.4674
7.4290
7.1913
7.1695
6.9049
6.8929
6.5699
6.5321
3.6775
2.2892
2.0664
1.9478
1.7416

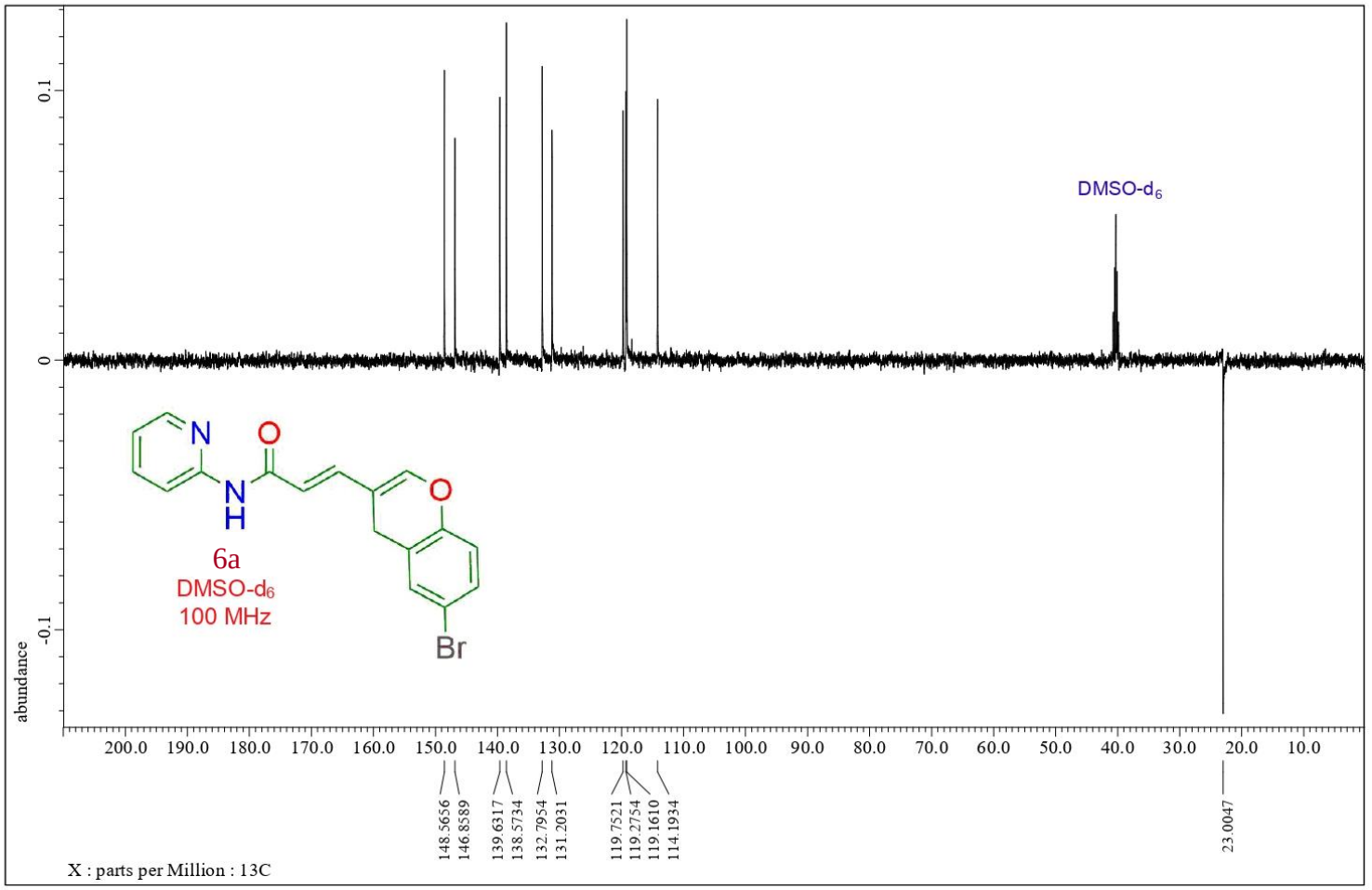

DMSO-d6
H3C
N
O
N
H
O
4e
DMSO-d6
100 MHz
(thousandths)
60.0
50.0
40.0
30.0
20.0
10.0
0
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0
164.9174
152.9420
149.2426
148.2700
147.9363
147.0591
146.6873
139.7747
130.9076
130.2401
129.0865
125.6731
123.8996
122.5934
120.7914
119.6186
117.6164
114.4604
112.1244
111.5047
43.0655
36.7440
36.3531
28.8589
21.5078
21.0787
X : parts per Million : 13C

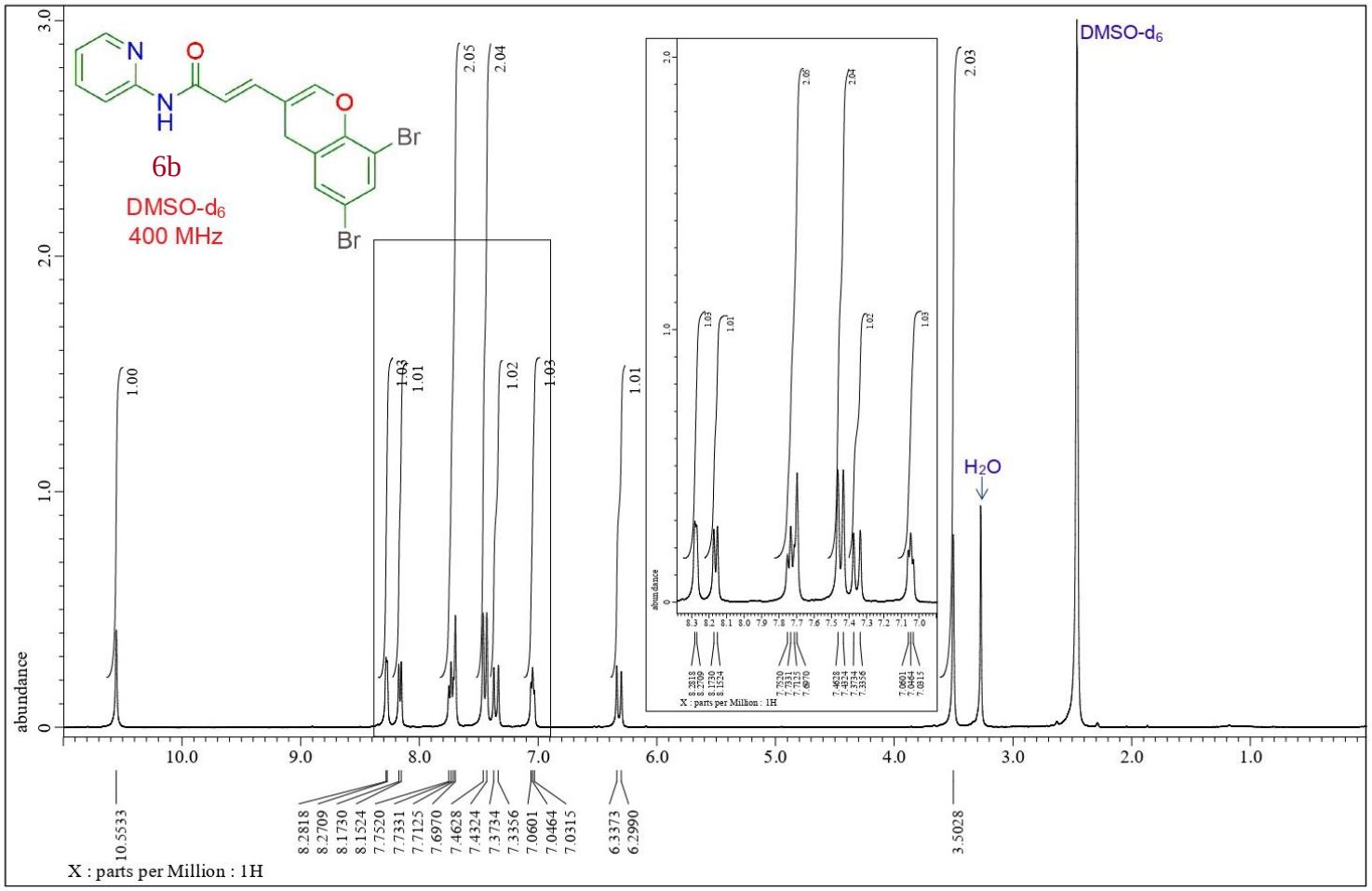

DMSO-d6
H3C
N
O
N
H
O
4e
DMSO-d6
100 MHz
abundance
0.1
0.08
0.06
0.04
0.02
0
-0.02
-0.04
-0.06
-0.08
-0.1
-0.12
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
148.2605
146.6778
139.7652
129.0769
125.6731
123.8996
122.5839
120.7818
119.6186
117.6164
114.4509
43.0655
36.7440
28.8589
21.5078
21.0883
X : parts per Million : 13C

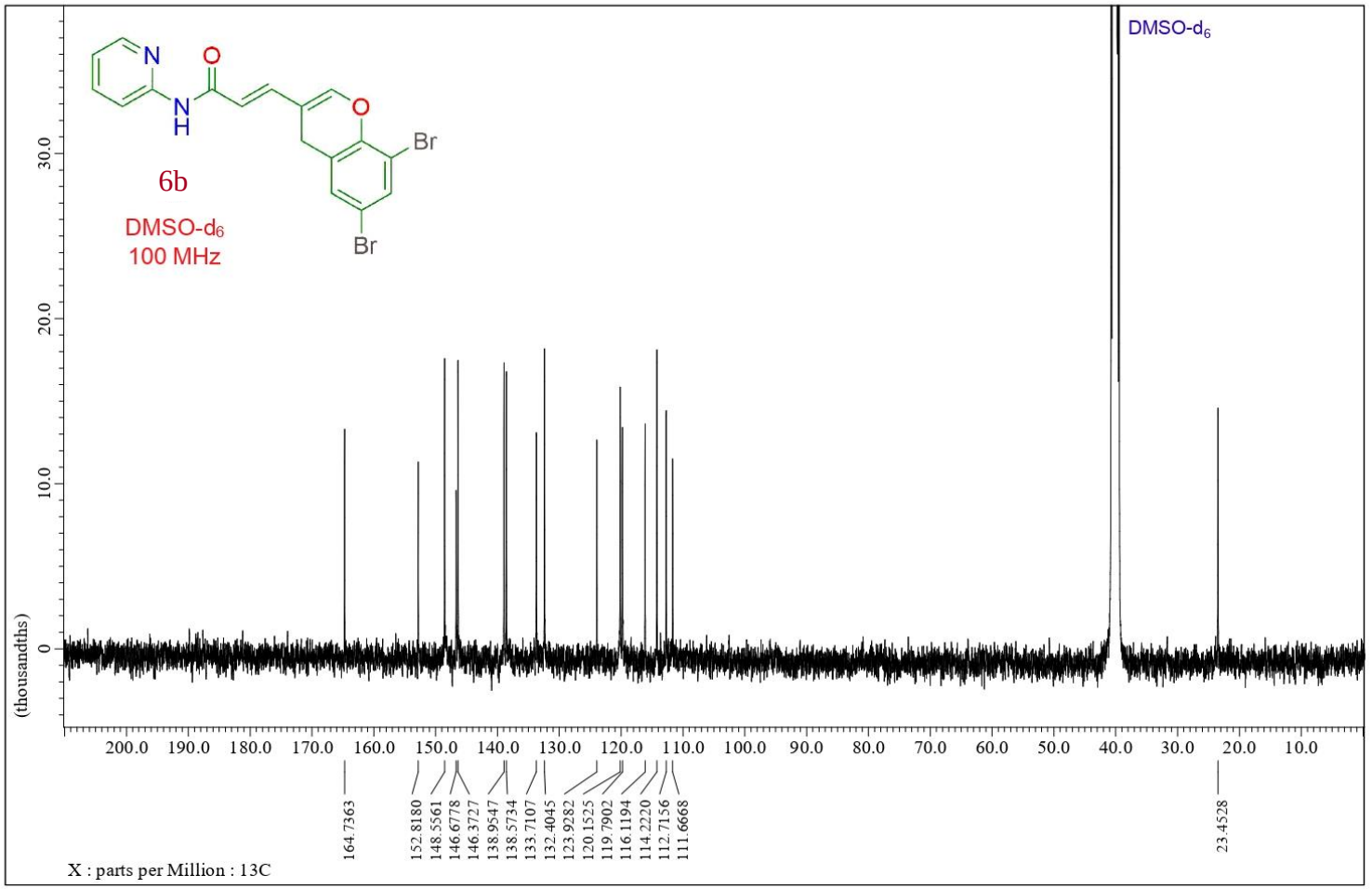

4f
DMSO-d6
400 MHz
H2O
DMSO-d6
abundance
X : parts per Million : 1H
10.3070
8.2148
8.1512
8.1415
8.0430
7.8425
7.8213
7.7841
7.7514
7.7285
7.4937
7.4542
7.4164
7.2961
7.2749
6.9032
6.8940
6.5699
6.5326
3.6912
2.2875

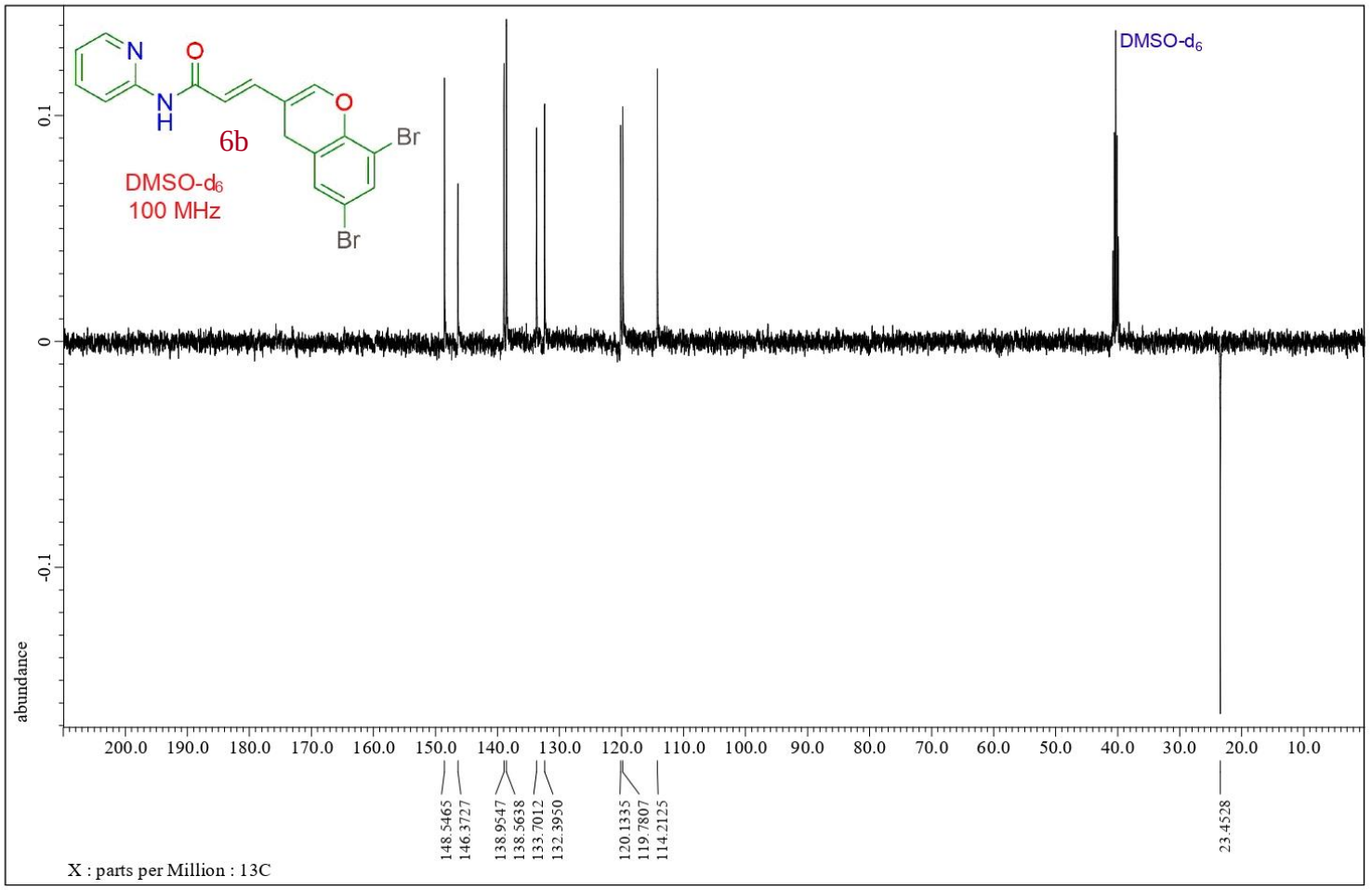

6a
DMSO-d6
400 MHz
Br
H2O
DMSO-d6
abundance
X : parts per Million : 1H
10.5310
8.2835
8.2744
8.1799
8.1587
7.7337
7.4336
7.4278
7.3757
7.3528
7.3379
7.0619
7.0475
7.0435
7.0315
6.9548
6.9330
6.3093
6.2709
3.4541

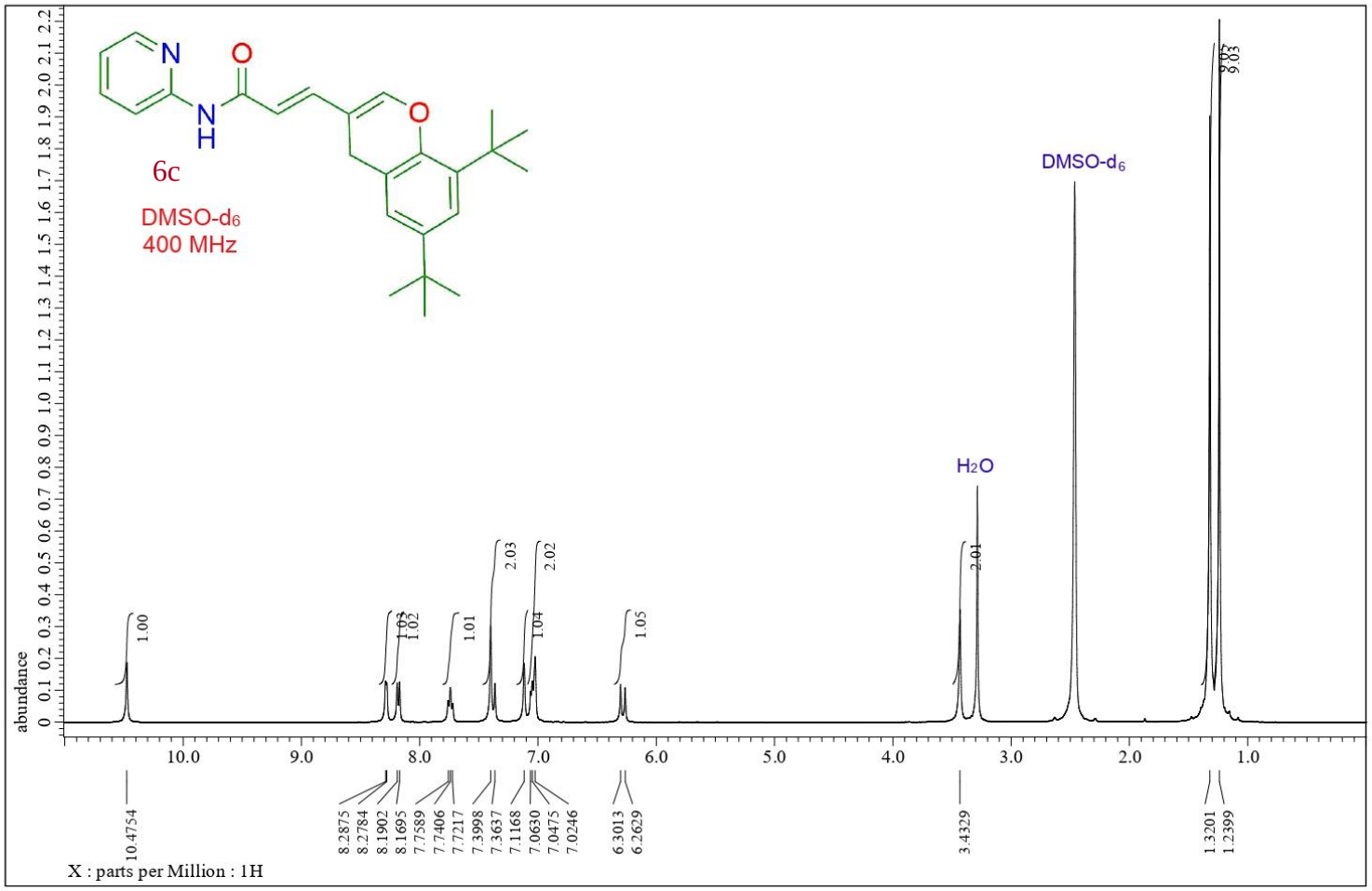

6a
DMSO-d6
100 MHz
Br
DMSO-d6
(thousandths)
0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
164.8888
152.8657
149.5763
148.5656
146.8589
139.6317
138.5734
132.7954
131.2031
122.4027
119.7521
119.2849
119.1610
116.1194
114.1934
111.9814
23.0047
X : parts per Million : 13C

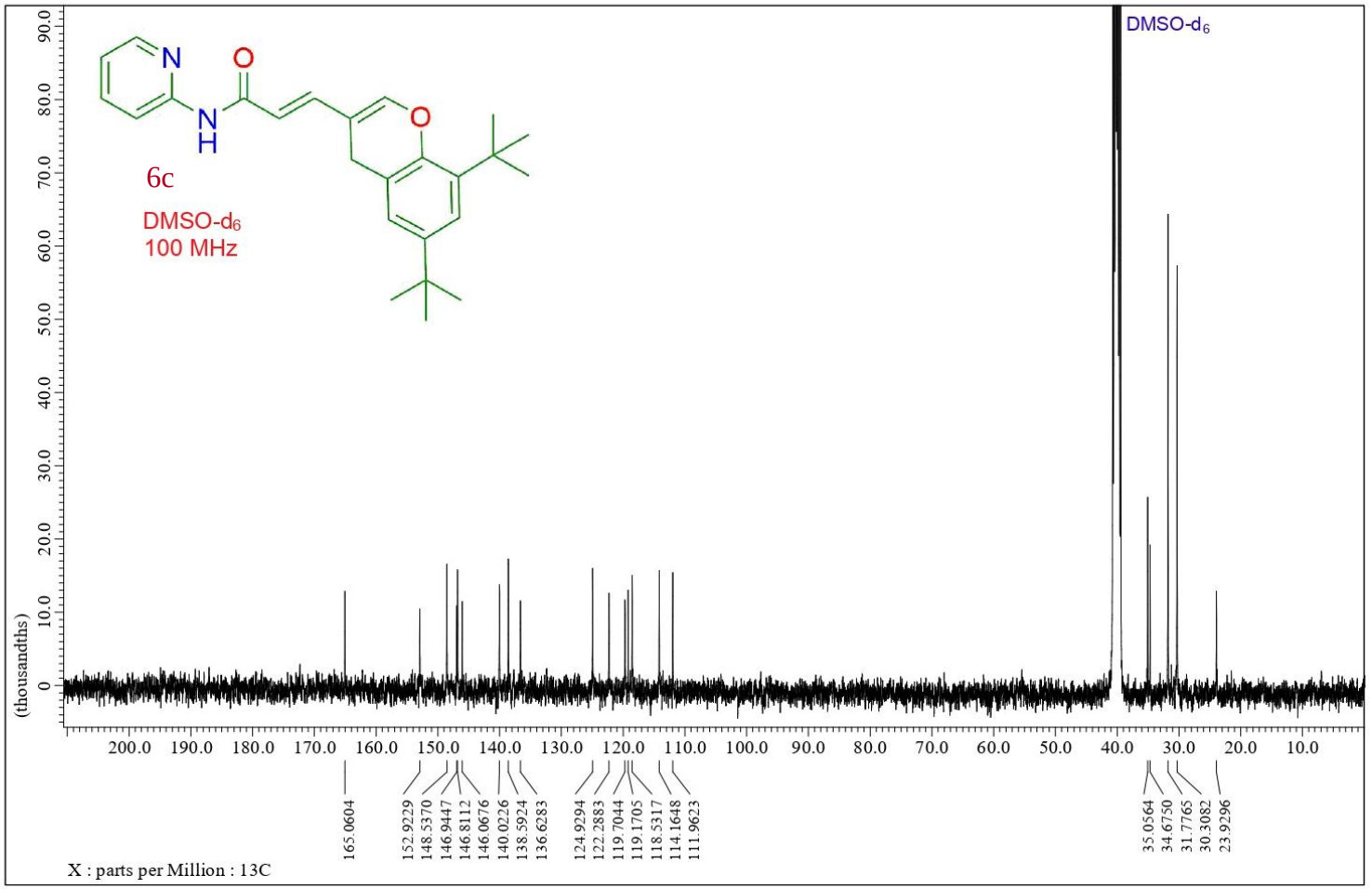

DMSO-d6
6a
DMSO-d6
100 MHz
Br
abundance
0.1
0
-0.1
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0
148.5656
146.8589
139.6317
138.5734
132.7954
131.2031
119.7521
119.2754
119.1610
114.1934
23.0047
X : parts per Million : 13C

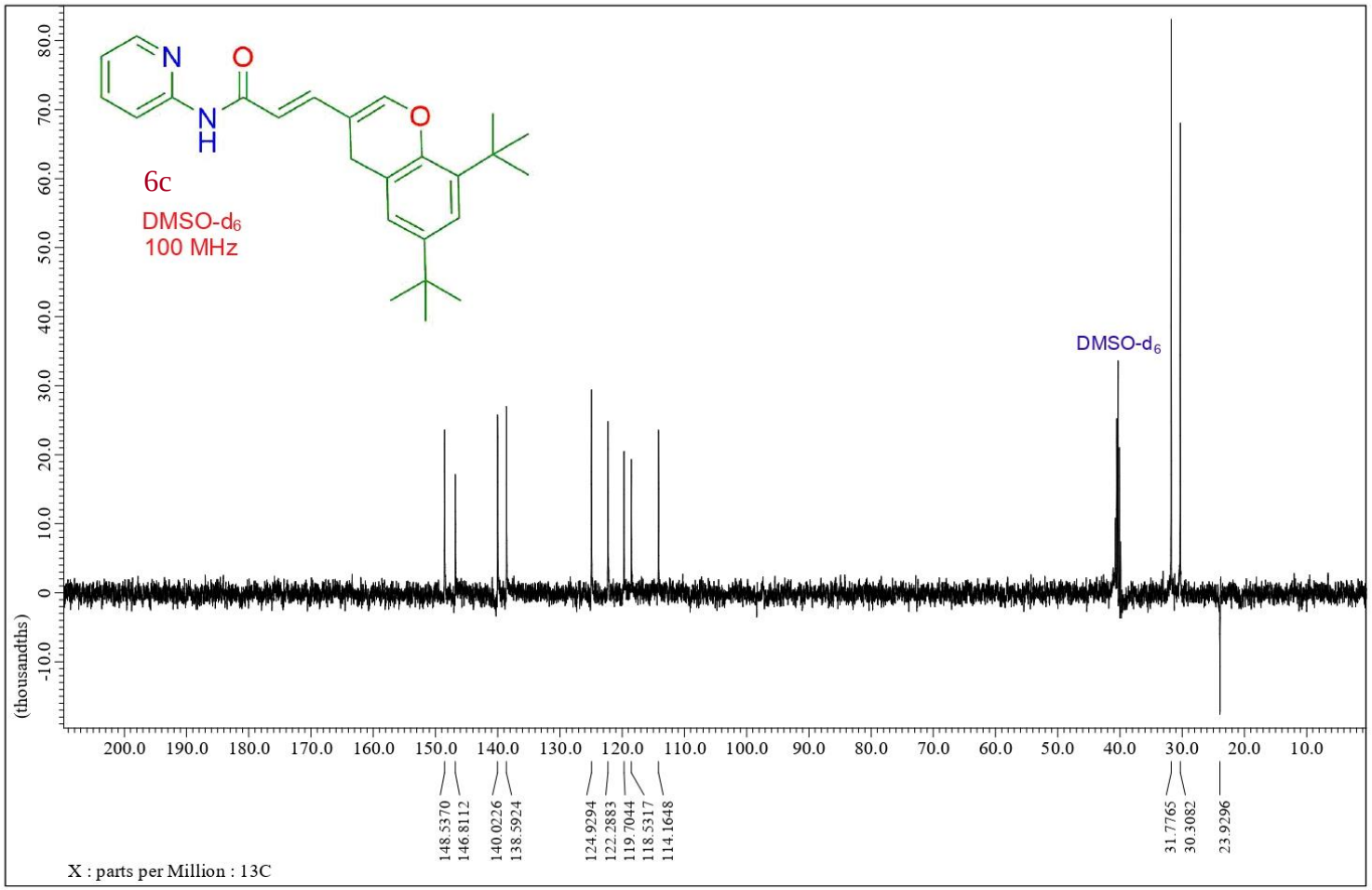

6b
DMSO-d6
400 MHz
DMSO-d6
H2O
abundance
X : parts per Million : 1H
10.5533
8.2818
8.2709
8.1730
8.1524
7.7520
7.7331
7.7125
7.6970
7.4628
7.4324
7.3734
7.3356
7.0601
7.0464
7.0315
6.3373
6.2990
3.5028

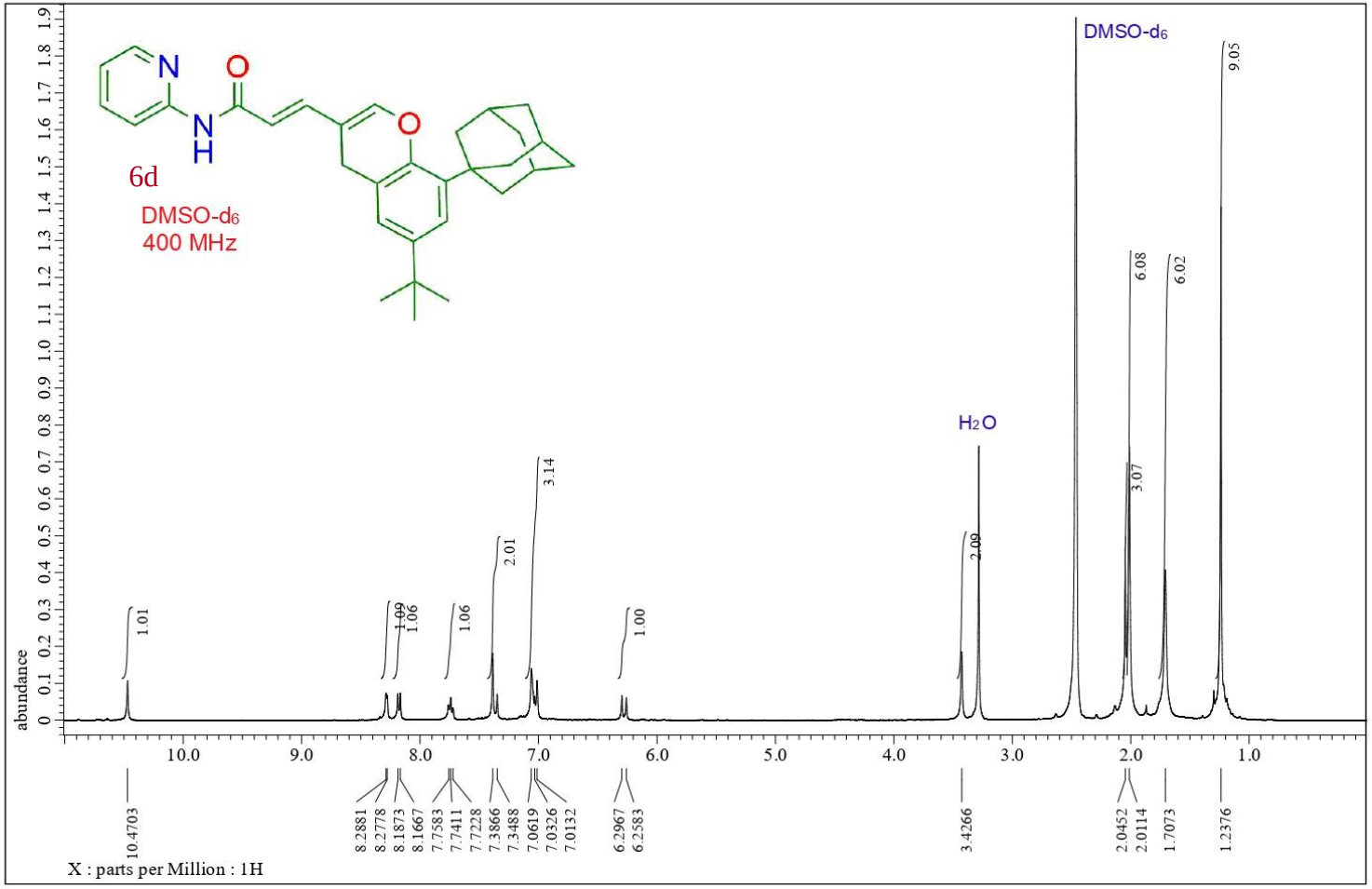

N
O
N
H
O
Br
Br
6b
DMSO-d6
100 MHz
DMSO-d6
30.0
20.0
10.0
0
(thousandths)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0
164.7363
152.8180
148.5561
146.6778
146.3727
138.9547
138.5734
133.7107
132.4045
123.9282
120.1525
119.7902
116.1194
114.2220
112.7156
111.6668
23.4528
X : parts per Million : 13C

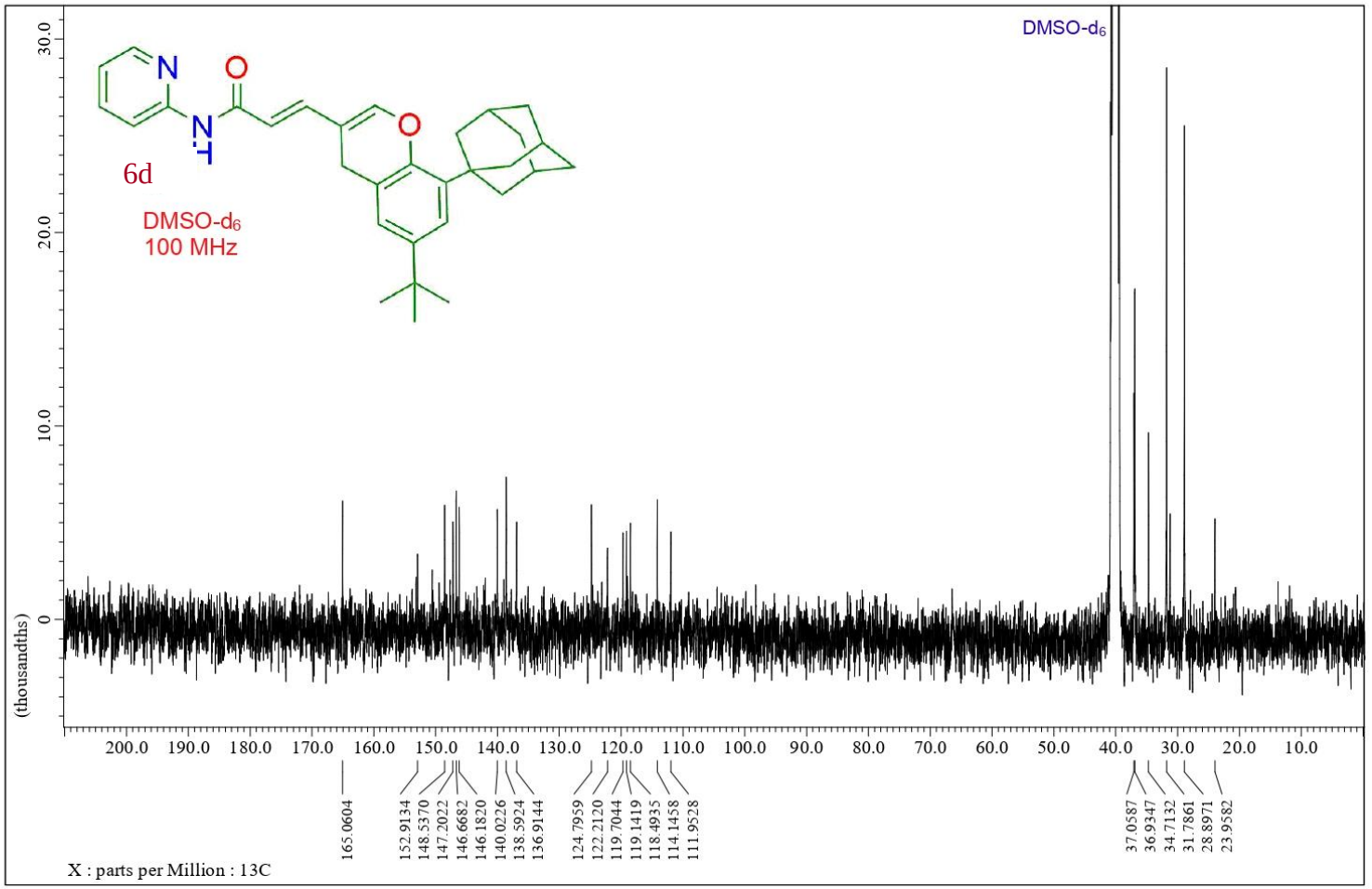

6b
DMSO-d6
100 MHz
DMSO-d6
abundance
0.1
0
-0.1
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0
148.5465
146.3727
138.9547
138.5638
133.7012
132.3950
120.1335
119.7807
114.2125
23.4528
X : parts per Million : 13C

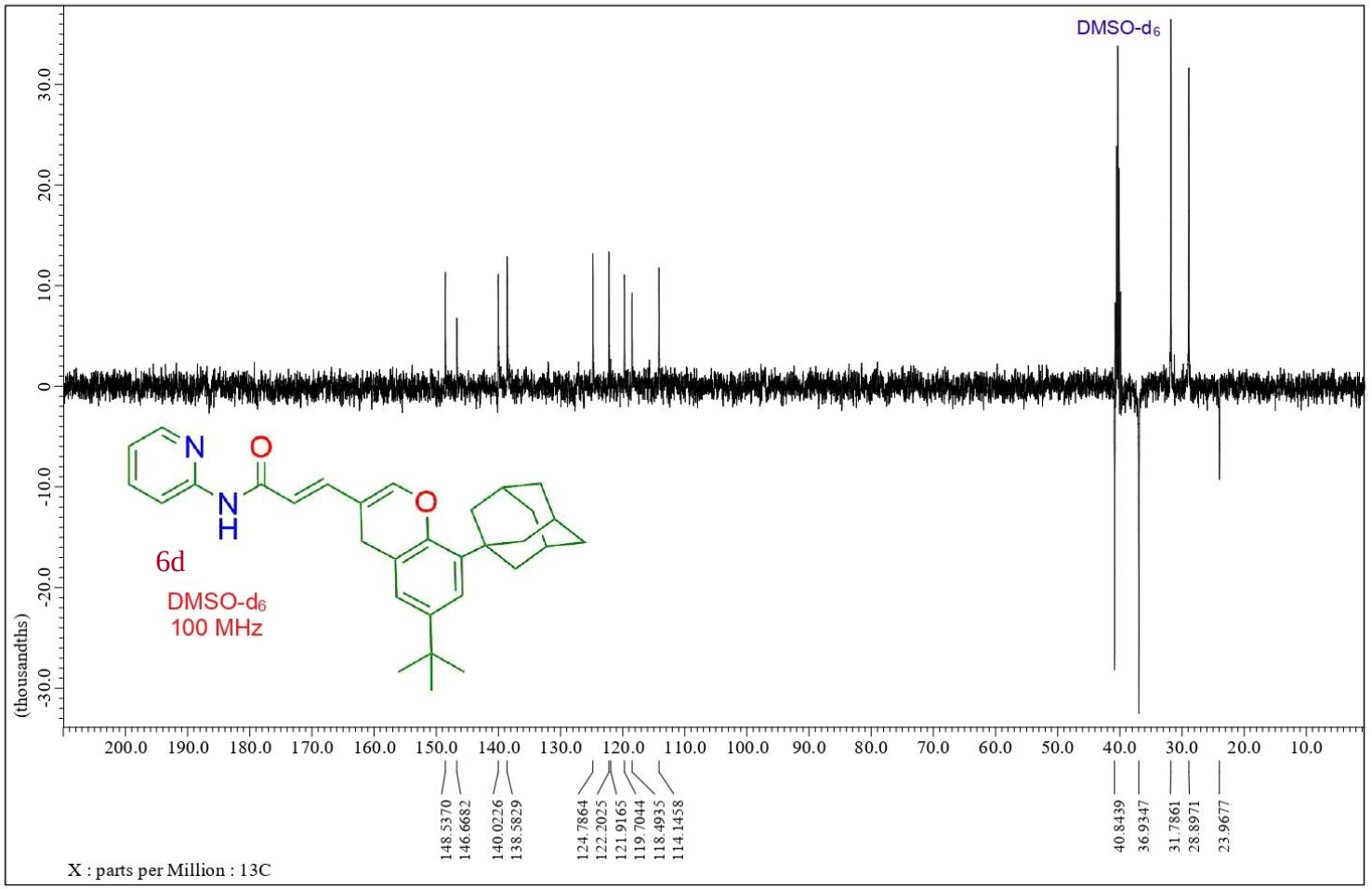

6c
DMSO-d6
400 MHz
DMSO-d6
H2O
abundance
X : parts per Million : 1H

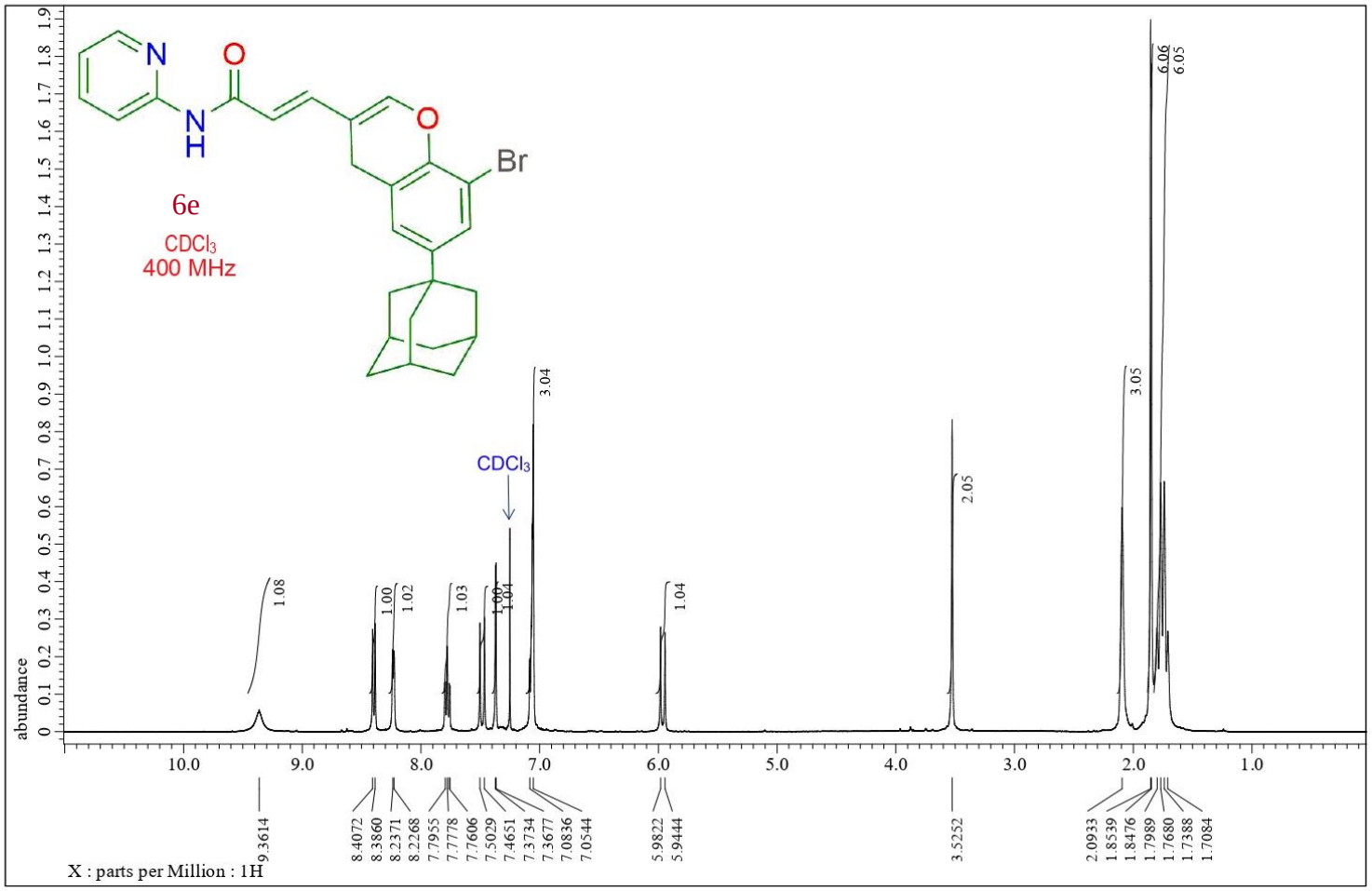

6c
DMSO-d6
100 MHz
DMSO-d6
(thousandths)
X : parts per Million : 13C
165.0604
152.9229
148.5370
146.9447
146.8112
146.0676
140.0226
138.5924
136.6283
124.9294
122.2883
119.7044
119.1705
118.5317
114.1648
111.9623
35.0564
34.6750
31.7765
30.3082
23.9296

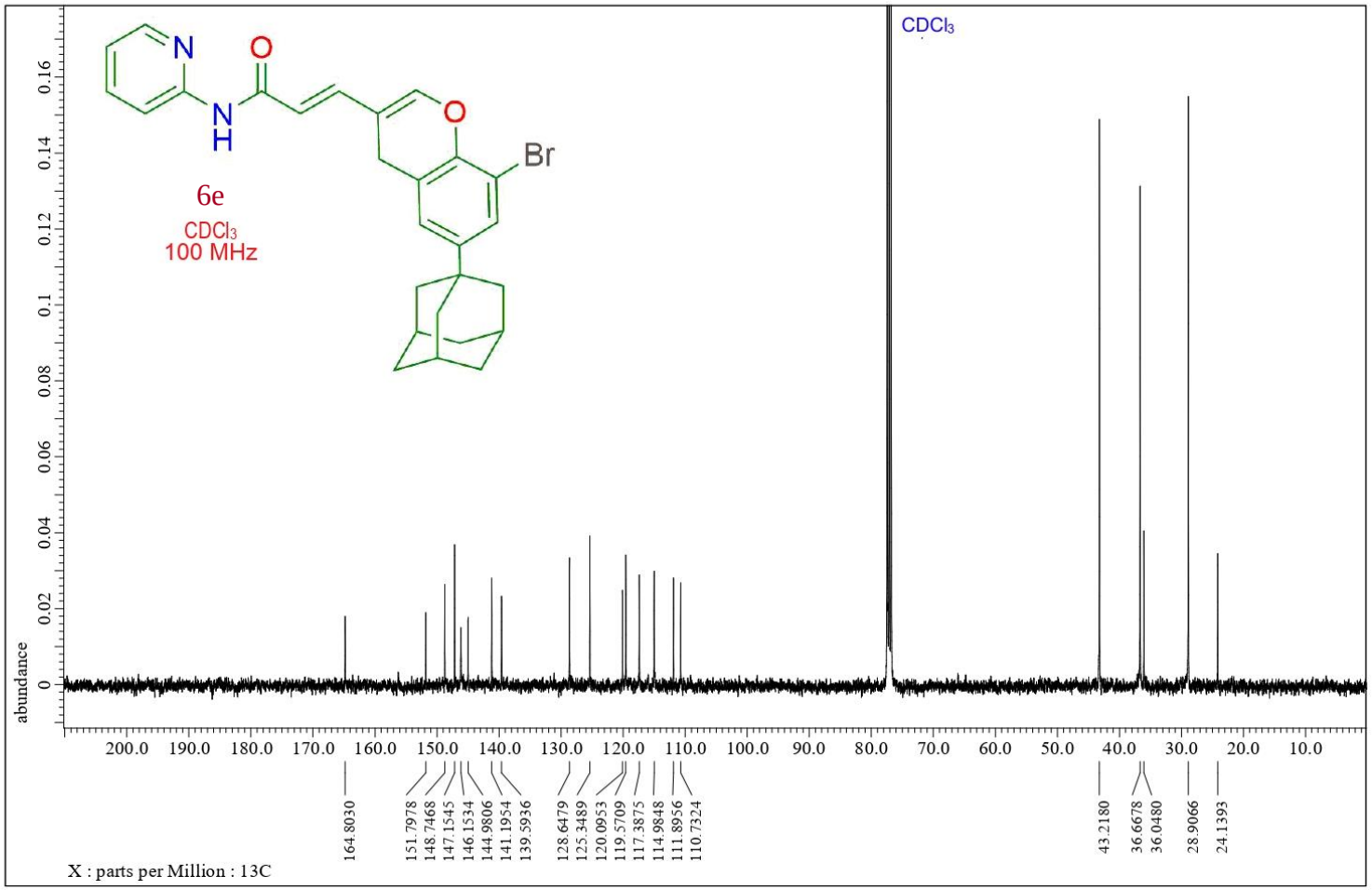

6c
DMSO-d6
100 MHz
DMSO-d6
(thousandths)
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
148.5370
146.8112
140.0226
138.5924
124.9294
122.2883
119.7044
118.5317
114.1648
31.7765
30.3082
23.9296
X : parts per Million : 13C

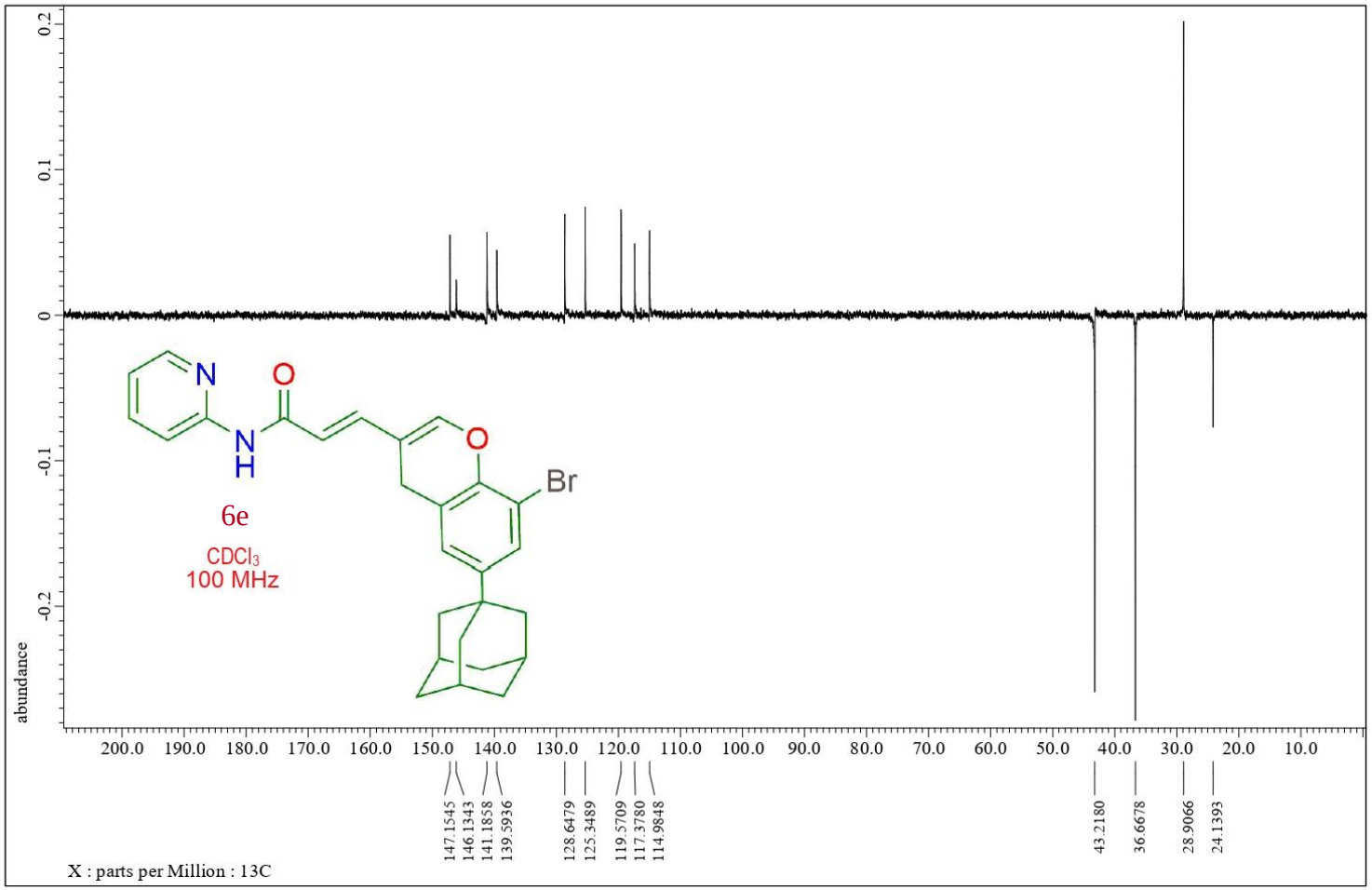

6d
DMSO-d6
400 MHz
DMSO-d6
H2O
abundance
X : parts per Million : 1H
10.4703
8.2881
8.2778
8.1873
8.1667
7.7583
7.7411
7.7228
7.3866
7.3488
7.0619
7.0326
7.0132
6.2967
6.2583
3.4266
2.0452
2.0114
1.7073
1.2376
1.01
1.09
1.06
1.06
2.01
3.14
1.00
2.09
3.07
6.08
6.02
9.05

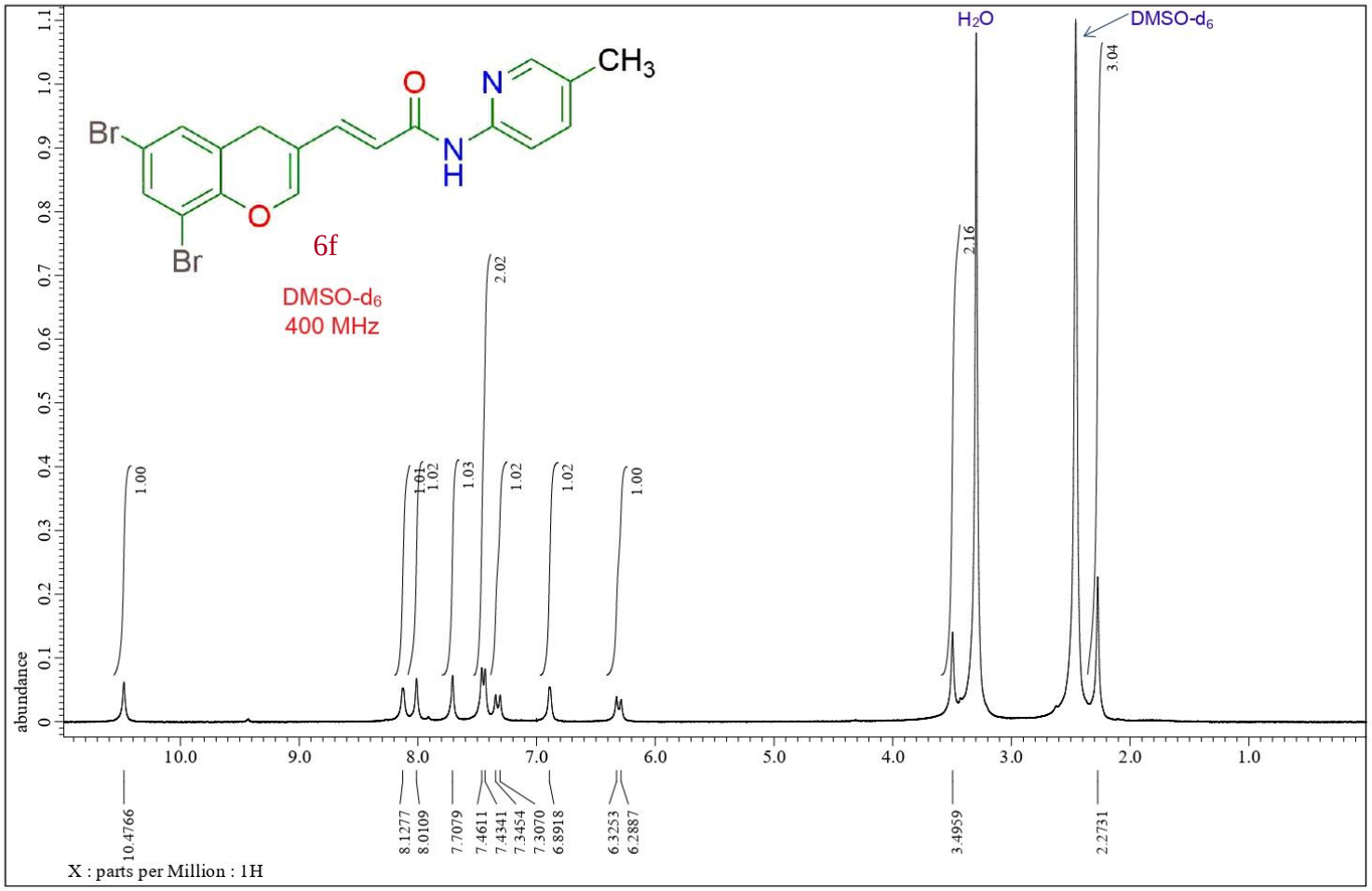

6d
DMSO-d6
100 MHz
DMSO-d6
(thousandths)
30.0
20.0
10.0
0
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0
165.0604
152.9134
148.5370
147.2022
146.6682
146.1820
140.0226
138.5924
136.9144
124.7959
122.2120
119.7044
119.1419
118.4935
114.1458
111.9528
37.0587
36.9347
34.7132
31.7861
28.8971
23.9582
X : parts per Million : 13C

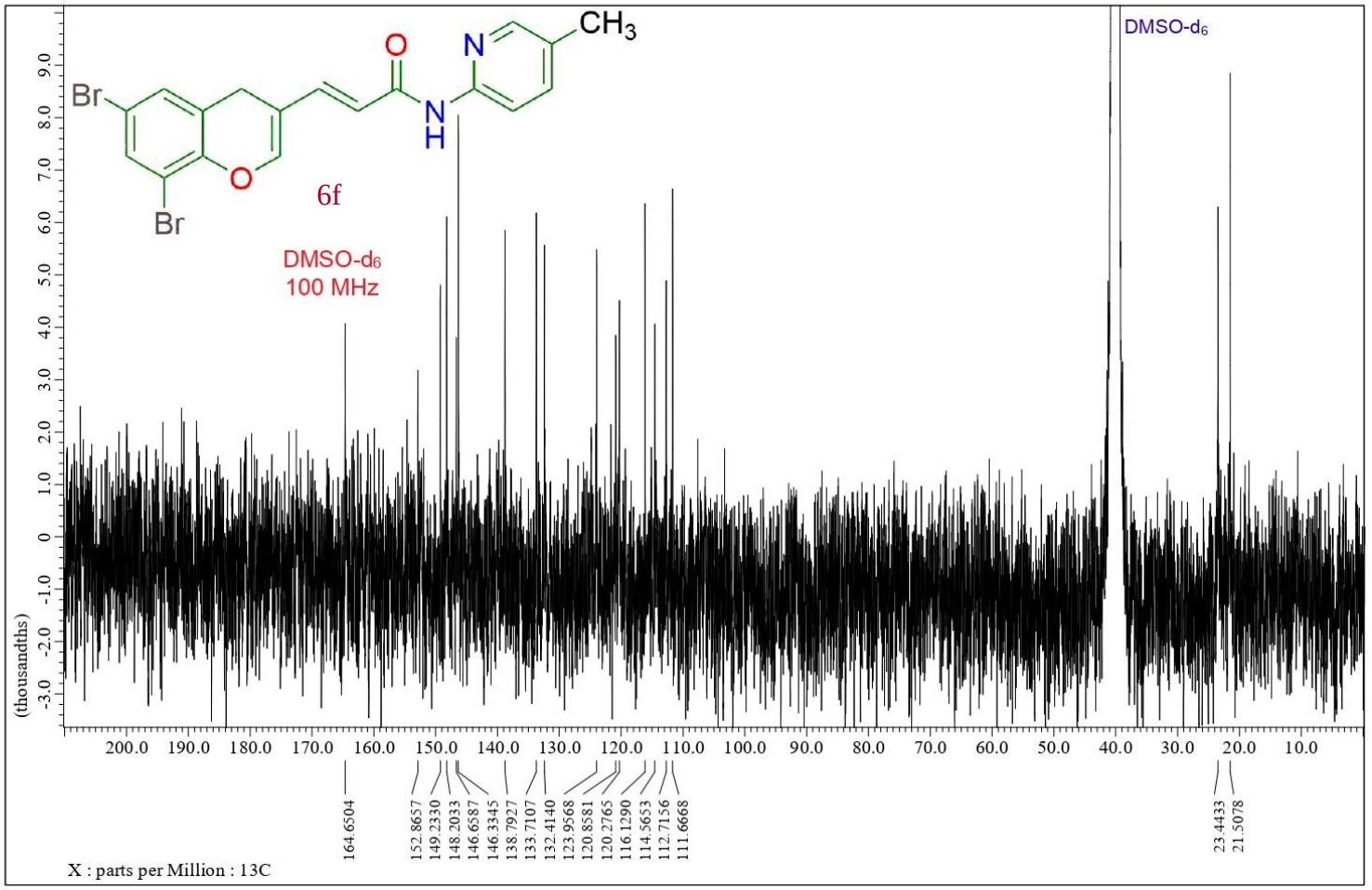

DMSO-d6
(thousandths)
30.0
20.0
10.0
0
-10.0
-20.0
-30.0
N
O
N
H
O
6d
DMSO-d6
100 MHz
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0
148.5370
146.6682
140.0226
138.5829
124.7864
122.2025
121.9165
119.7044
118.4935
114.1458
40.8439
36.9347
31.7861
28.8971
23.9677
X : parts per Million : 13C

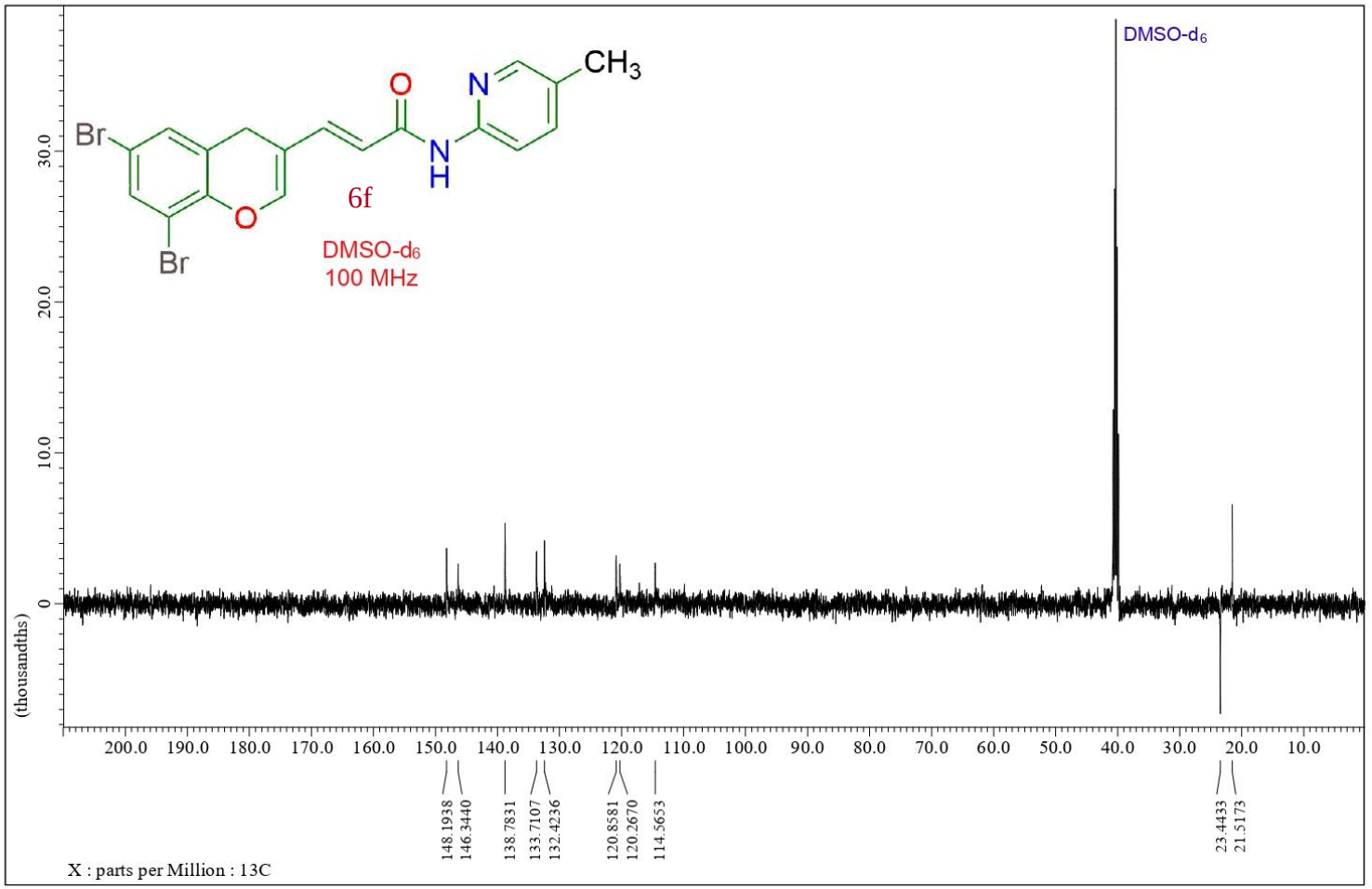

6e
CDCl3
400 MHz
Br
CDCl3
abundance
X : parts per Million : 1H
9.3614
8.4072
8.3860
8.2371
8.2268
7.7955
7.7778
7.7606
7.5029
7.4651
7.3734
7.3677
7.0836
7.0544
5.9822
5.9444
3.5252
2.0933
1.8539
1.8476
1.7989
1.7680
1.7388
1.7084
1.08
1.00
1.02
1.03
1.01
1.01
3.04
1.04
2.05
3.05
6.06
6.05

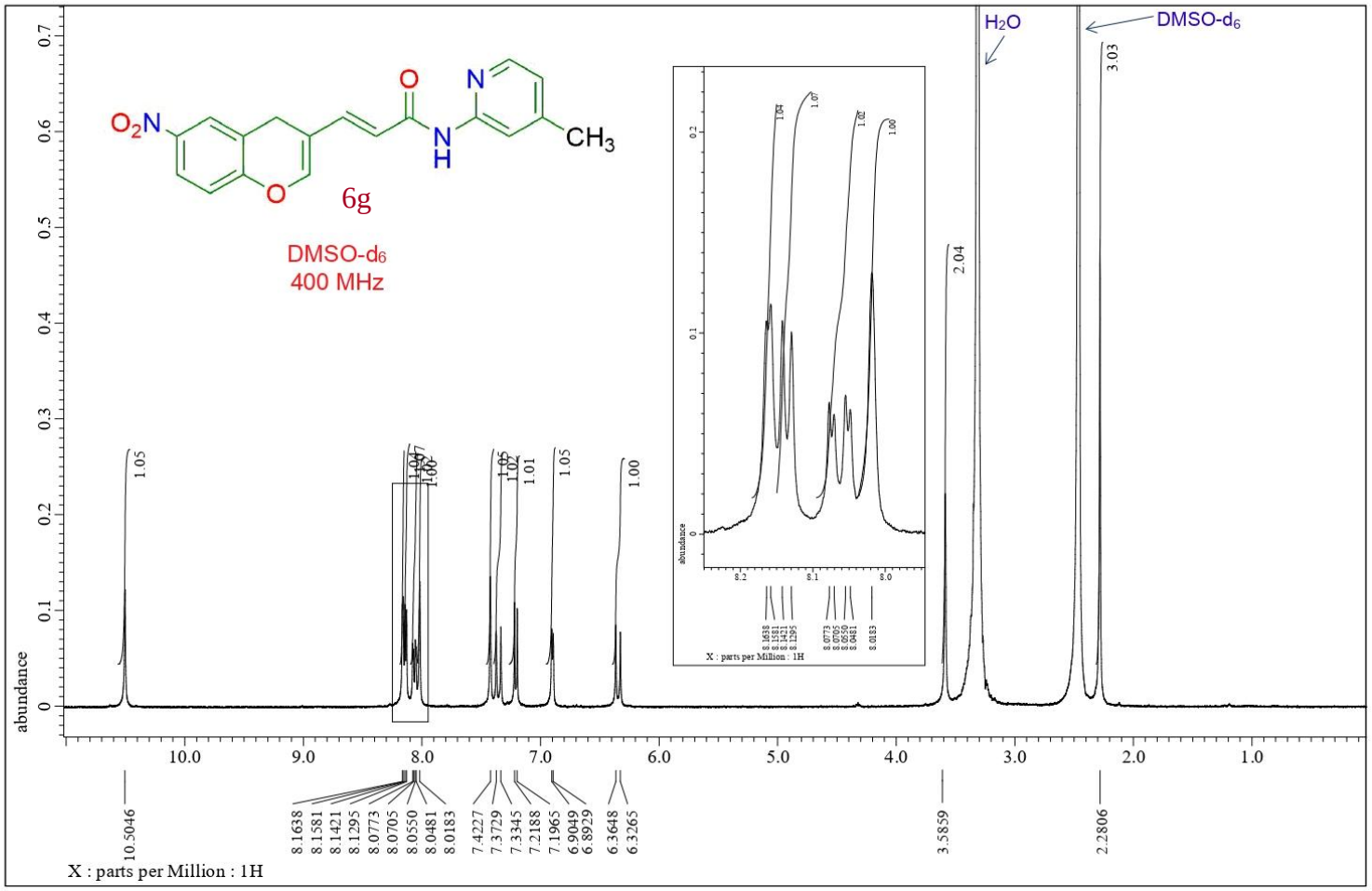

6e
CDCl3
100 MHz
CDCl3
Br
abundance
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
164.8030
151.7978
148.7468
147.1545
146.1534
144.9806
141.1954
139.5936
128.6479
125.3489
120.0953
119.5709
117.3875
114.9848
111.8956
110.7324
43.2180
36.6678
36.0480
28.9066
24.1393
X : parts per Million : 13C

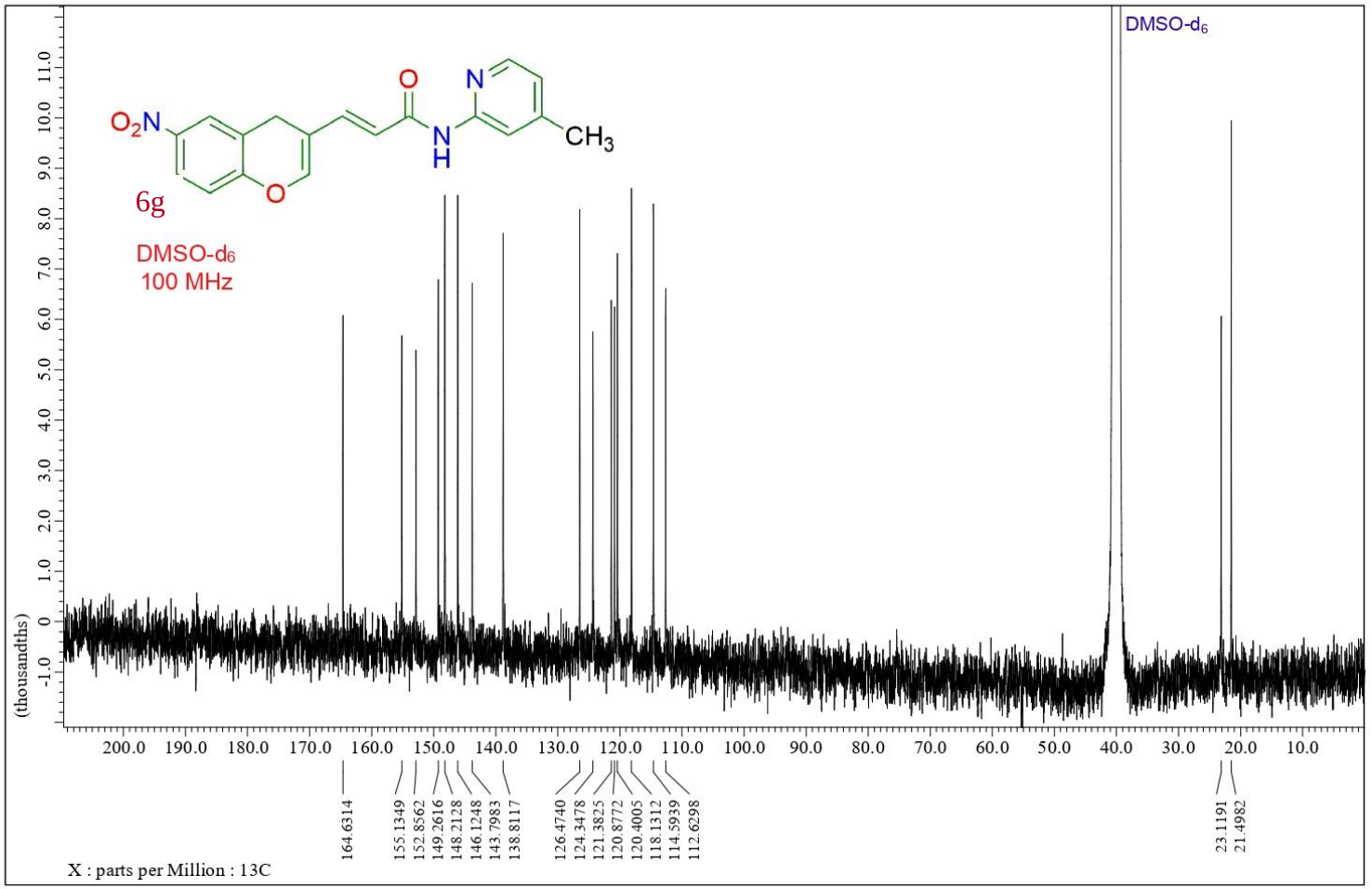

abundance
0.2
0.1
0
-0.1
-0.2
N
O
N
H
O
Br
6e
CDCl3
100 MHz
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0
147.1545
146.1343
141.1858
139.5936
128.6479
125.3489
119.5709
117.3780
114.9848
43.2180
36.6678
28.9066
24.1393
X : parts per Million : 13C

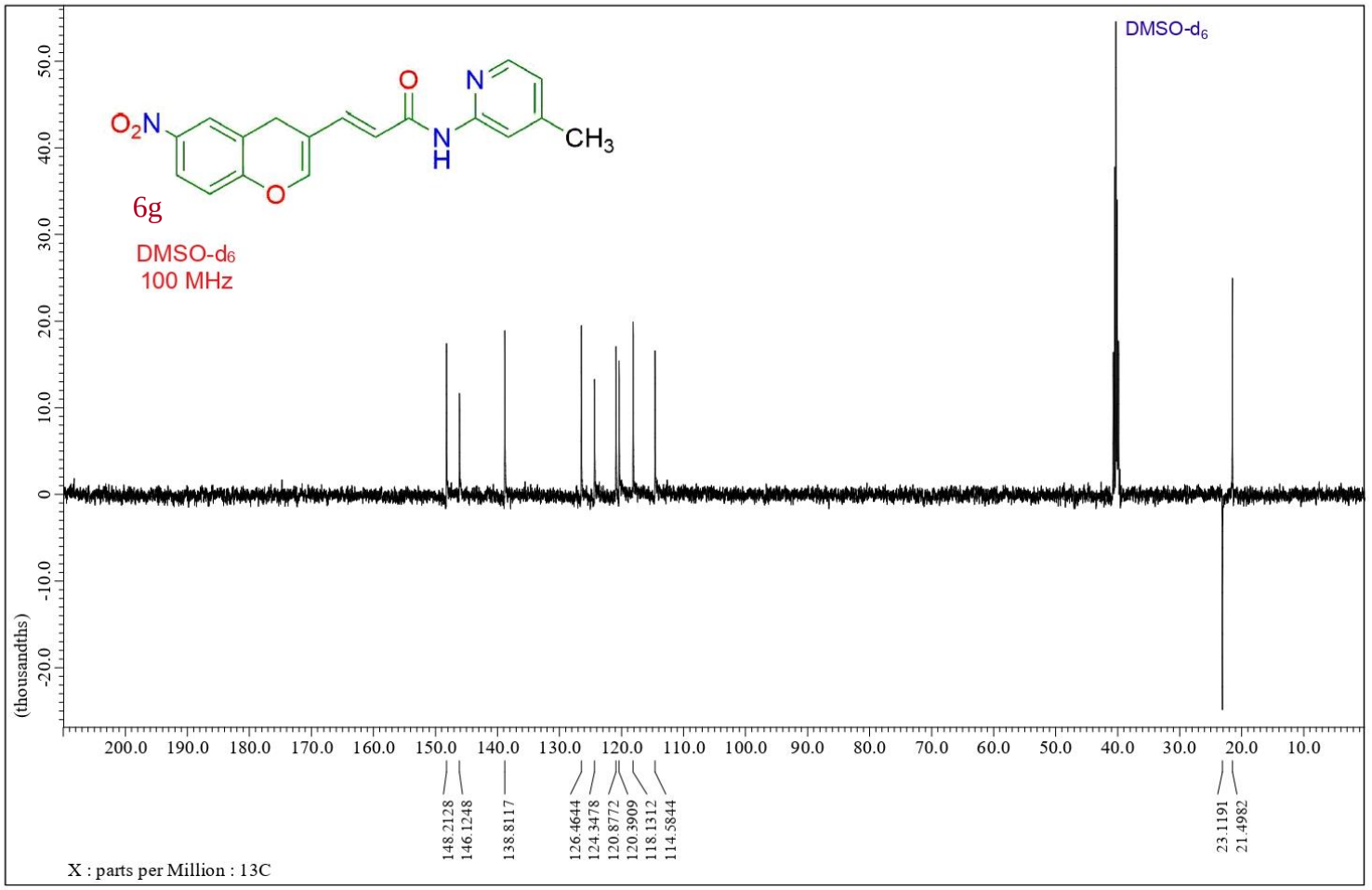

Br
O
N
CH3
N
H
O
Br
6f
DMSO-d6
400 MHz
H2O
DMSO-d6
3.04
2.16
2.02
1.00
1.01
1.02
1.03
1.02
1.02
1.00
abundance
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
10.4766
8.1277
8.0109
7.7079
7.4611
7.4341
7.3454
7.3070
6.8918
6.3253
6.2887
3.4959
2.2731
X : parts per Million : 1H

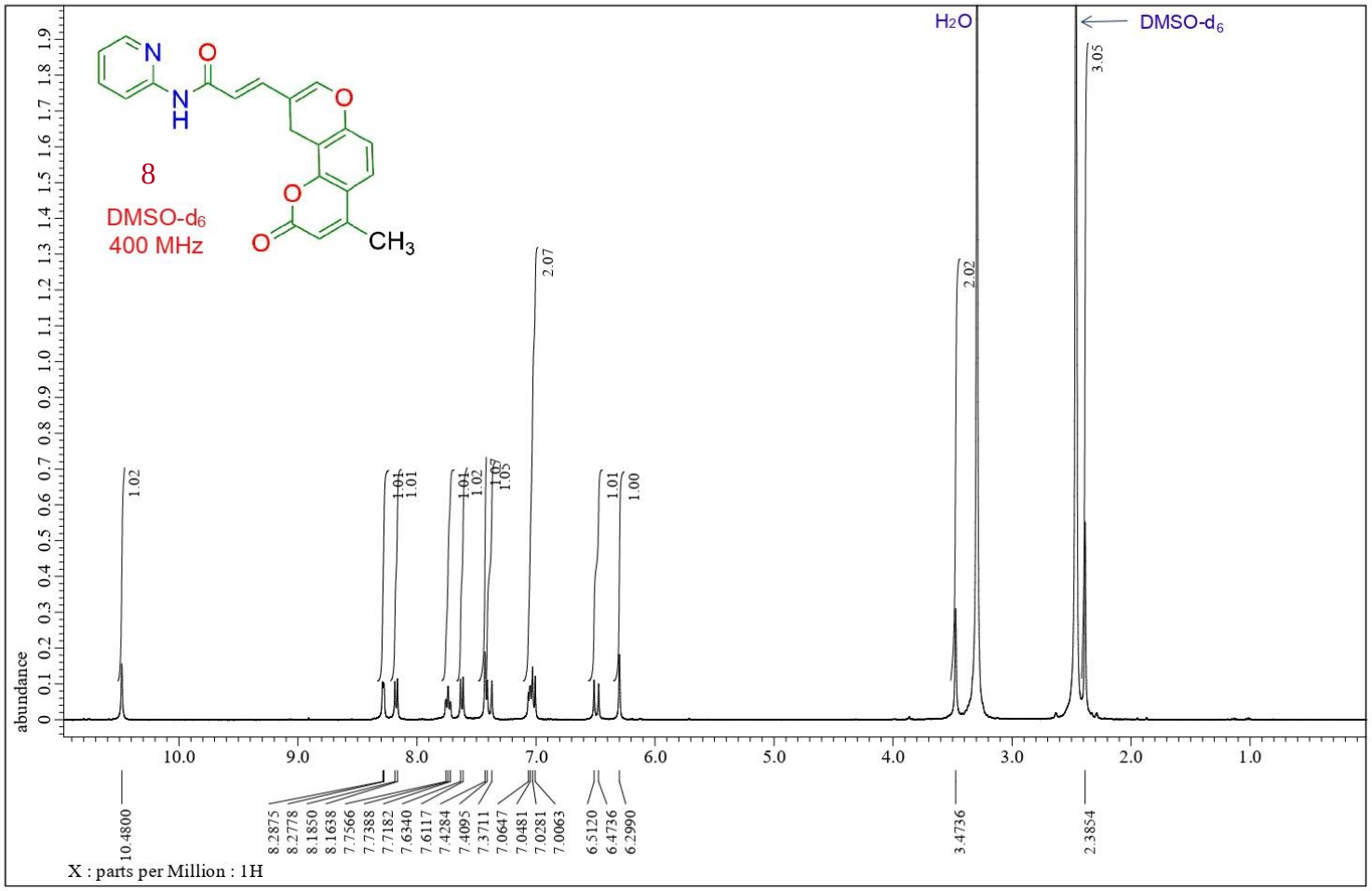

CH3
N
O
Br
N
H
O
Br
6f
DMSO-d6
100 MHz
DMSO-d6
(thousandths)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
-3.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
164.6504
152.8657
149.2330
148.2033
146.6587
146.3345
138.7927
133.7107
132.4140
123.9568
120.8581
120.2765
116.1290
114.5653
112.7156
111.6668
23.4433
21.5078
X : parts per Million : 13C

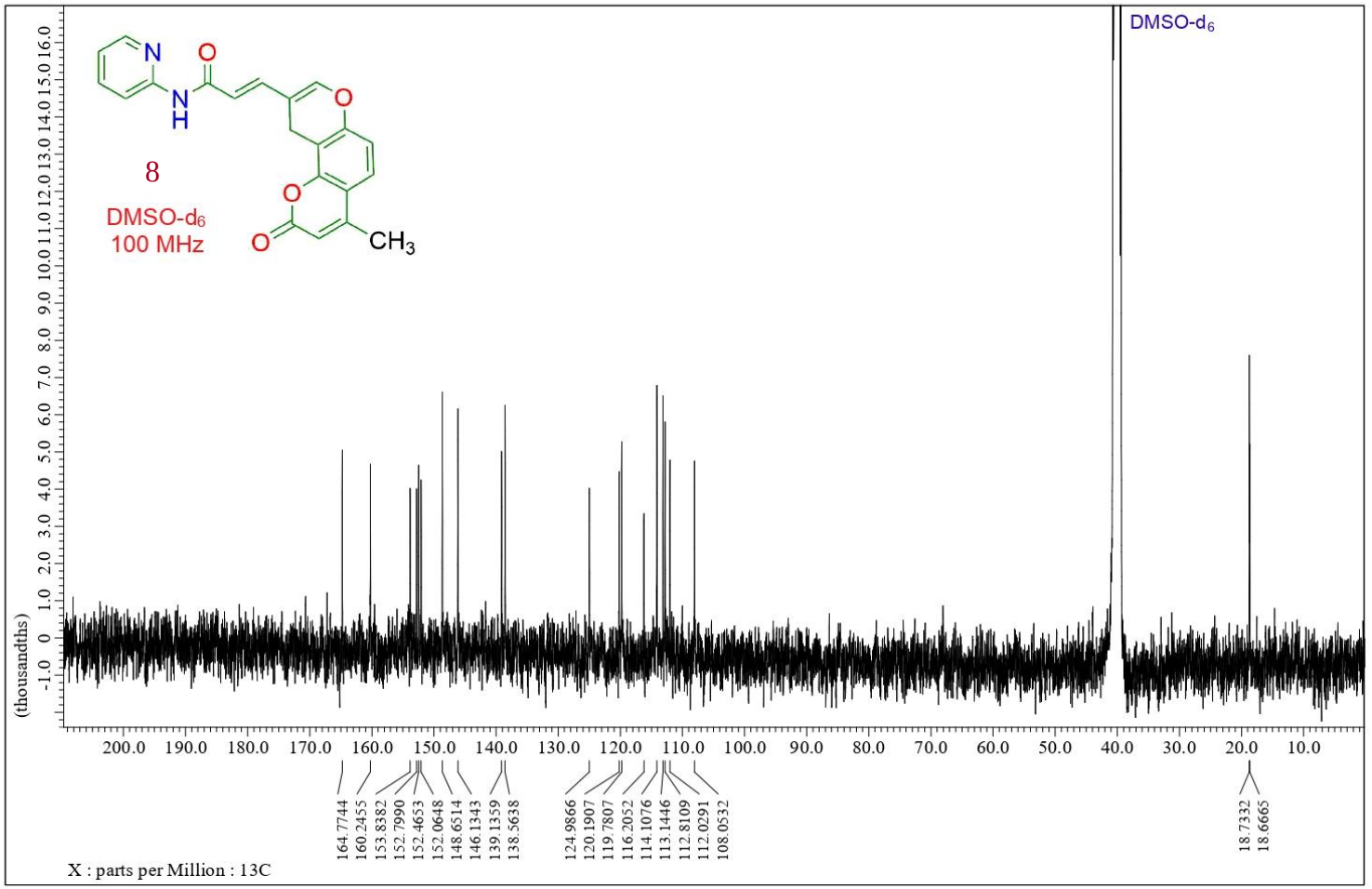

DMSO-d6
CH3
O
N
Br
N
H
O
Br
6f
DMSO-d6
100 MHz
30.0
20.0
10.0
0
(thousandths)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0
148.1938
146.3440
138.7831
133.7107
132.4236
120.8581
120.2670
114.5653
23.4433
21.5173
X : parts per Million : 13C

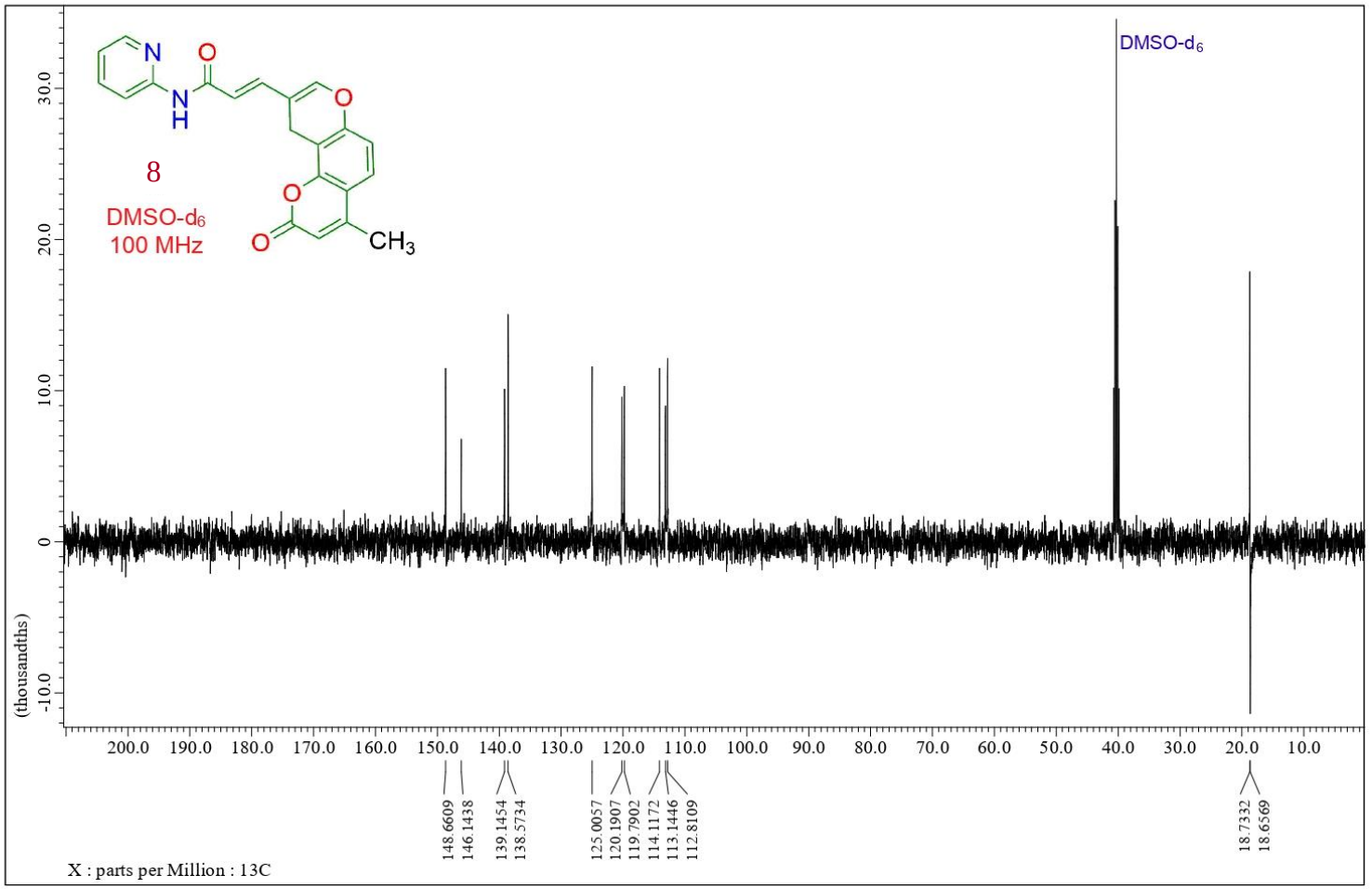

6g
DMSO-d6
400 MHz
H2O
DMSO-d6
abundance
X : parts per Million : 1H
10.5046
8.1638
8.1581
8.1421
8.1295
8.0773
8.0705
8.0550
8.0481
8.0183
7.4227
7.3729
7.3345
7.2188
7.1965
6.9049
6.8929
6.3648
6.3265
3.5859
2.2806


DMSO-d6
O2N
O
N
N
H
CH3
O
6g
DMSO-d6
100 MHz
(thousandths)
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
164.6314
155.1349
152.8562
149.2616
148.2128
146.1248
143.7983
138.8117
126.4740
124.3478
121.3825
120.8772
120.4005
118.1312
114.5939
112.6298
23.1191
21.4982
X : parts per Million : 13C


DMSO-d6
O2N
O
N
H
N
CH3
O
6g
DMSO-d6
100 MHz
(thousandths)
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0
148.2128
146.1248
138.8117
126.4644
124.3478
120.8772
120.3909
118.1312
114.5844
23.1191
21.4982
X : parts per Million : 13C


8
DMSO-d6
400 MHz
H2O
DMSO-d6
abundance
X : parts per Million : 1H
10.4800
8.2875
8.2778
8.1850
8.1638
7.7566
7.7388
7.7182
7.6340
7.6117
7.4284
7.4095
7.3711
7.0647
7.0481
7.0281
7.0063
6.5120
6.4736
6.2990
3.4736
2.3854


8
DMSO-d6
100 MHz
DMSO-d6
(thousandths)
X : parts per Million : 13C
164.7744
160.2455
153.8382
152.7990
152.4653
152.0648
148.6514
146.1343
139.1359
138.5638
124.9866
120.1907
119.7807
116.2052
114.1076
113.1446
112.8109
112.0291
108.0532
18.7332
18.6665


8
DMSO-d6
100 MHz
DMSO-d6
CH3
(thousandths)
30.0
20.0
10.0
0
-10.0
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0
148.6609
146.1438
139.1454
138.5734
125.0057
120.1907
119.7902
114.1172
113.1446
112.8109
18.7332
18.6569
X : parts per Million : 13C