Supporting Information

Divergent Transformation of *C,N*-Cyclic-*N′*-acyl Azomethine Imines by Reaction with Diazo Compounds

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1. General information

NMR spectra were recorded on JEOL ECS-400 (400 MHz for ^{1}H, 100 MHz for ^{13}C) using $CDCl_3$ as a solvent. Tetramethylsilane (δ = 0 ppm) for ^{1}H NMR and $CDCl_3$ (δ = 77.0 ppm) for ^{13}C NMR were used as internal standards. IR spectra were acquired on a JASCO FT/IR-230 spectrometer. Melting points were determined on a micromelting apparatus (AS-ONE ATM-02) and are uncorrected. Mass spectra were recorded on Bruker Daltonics micrOTOF II-KA1 (ESI). X-ray crystallography was performed on a Bruker SMART APEX II (with Cu Kα radiation). Purification of the products was performed by column chromatography on silica gel (Kanto Silica gel 60N, spherical, neutral or Fuji Silysia CHROMATOREX PSQ60B). Dehydrated solvents were purchased for the reactions and used without further desiccation.

C,N-Cyclic *N*'-acyl azomethine imines **1** were prepared according to the reported procedure.[1] Ethyl diazoacetate (containing CH_2Cl_2) and trimethylsilyldiazomethane (Et_2O solution) were purchased from Sigma-Aldrich and Oakwood Chemical, respectively, and used as they stand.

2. Procedure for the reaction with ethyl diazoacetate (Reaction A) and analytical data of **4**

Ethyl 2-(2-Benzamido-1,2,3,4-tetrahydroisoquinolin-1-yl)-2-diazoacetate (4a):[2] To a mixture of benzoyl(3,4-dihydroisoquinolin-2-ium-2-yl)amide (**1a**) (120 mg, 0.48 mmol) in benzene (12 mL) was added ethyl diazoacetate (328 mg, 85% with CH_2Cl_2, 2.49 mmol) and the mixture was heated at 60 °C (oil bath temperature) for 3 d. After being cooled to room temperature, xylene (10 mL) was added and the solvent and unreacted ethyl diazoacetate were removed under reduced pressure. The resulted crude products were purified by silica gel column chromatography (hexane/AcOEt = 3/1) to give **4a** (156 mg, 89% yield) as a solid. R_f = 0.6 (hexane/AcOEt = 1/1, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.78 (d, J = 7.3 Hz, 2H), 7.53–7.40 (m, 4H), 7.24–7.14 (m, 4H), 5.19 (s, 1H), 4.17 (q, J = 7.1 Hz, 2H), 3.48-3.42 (m, 1H), 3.38–3.24 (m, 2H), 2.93 (d, J = 15.6 Hz, 1H), 1.17 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 167.7, 165.7, 134.7, 133.5, 132.3, 131.5, 128.8, 128.5, 127.6, 127.1, 126.6, 62.5, 61.2, 60.2, 52.2, 29.1, 14.3. CCDC-2129155 contains the supplementary crystallographic data for **4a**.

In a similar manner, **4b**–**4g** were obtained from the corresponding *C,N*-cyclic-*N*'-acyl azomethine imines **1b**–**1g**.

Ethyl 2-Diazo-2-(2-(4-methylbenzamido)-1,2,3,4-tetrahydroisoquinolin-1-yl)acetate (4b): The reaction using **1b** (77 mg, 0.29 mmol) was carried out for 3 d. The compound **4b** (88 mg, 79% yield) was obtained as a solid after purification by silica gel column chromatography (hexane/AcOEt = 10/1, 6/1, 4/1 and then 3/1). R_f = 0.7 (hexane/AcOEt = 1/1, v/v). Mp. 137–139 °C ($CHCl_3$/hexane). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.68 (d, J = 8.2 Hz, 2H), 7.56 (s, 1H), 7.28–7.12 (m, 6H), 5.18 (s, 1H), 4.16 (q, J = 6.9 Hz, 2H), 3.48–3.42 (m, 1H), 3.38–3.22 (m, 2H), 2.90 (d, J = 15.6 Hz, 1H), 2.37 (s, 3H), 1.17 (t, J = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 167.7, 165.7, 141.9, 134.7, 132.3, 130.7, 129.1, 128.8, 127.6, 127.1, 126.5, 62.5, 61.1, 60.2, 52.3, 29.2, 21.4, 14.3; one signal overlaps. IR (KBr) 3250, 2979, 2929, 2105, 1692, 1648, 1542, 1374, 1292, 1260, 1101, 941, 914, 744 cm^{-1}. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{21}H_{22}N_4O_3Na$ 401.1590; Found 401.1601.

Ethyl 2-(2-(4-Chlorobenzamido)-1,2,3,4-tetrahydroisoquinolin-1-yl)-2-diazoacetate (4c): The reaction using **1c** (82 mg, 0.29 mmol) was carried out for 2 d. The compound **4c** (102 mg, 88% yield) was obtained as a solid after purification by silica gel column chromatography (hexane/AcOEt = 10/1, 6/1 and then 3/1). R_f = 0.8 (hexane/AcOEt = 1/1, v/v). Mp. 147–148 °C ($CHCl_3$/hexane). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.75 (s, 1H), 7.74 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 8.2 Hz, 2H), 7.24–7.11 (m, 4H), 5.18 (s, 1H), 4.17 (q, J = 7.1 Hz, 2H), 3.42 (dd, J = 9.2, 4.2 Hz, 1H), 3.36–3.21 (m, 2H), 2.91 (dd, J = 12.4, 4.2 Hz, 1H), 1.18 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 167.8, 164.6, 137.7, 134.6, 132.0, 131.9, 128.9, 128.7, 128.6, 127.7, 127.0, 126.6, 62.4, 61.2, 60.1, 52.1, 29.1, 14.3. IR (KBr) 3379, 2972, 2102, 1682, 1656, 1483, 1372, 1300, 1260, 1103, 1014, 845, 737 cm^{-1}. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{20}H_{19}N_4O_3ClNa$ 421.1043; Found 421.1014.

Ethyl 2-(2-Benzamido-5-methyl-1,2,3,4-tetrahydroisoquinolin-1-yl)-2-diazoacetate (4d): The reaction using **1d** (75 mg, 0.28 mmol) was carried out at 60 °C for 2 d and at 80 °C for 2 d. The compound **4d** (58 mg, 54% yield) was obtained as a solid after purification by silica gel column chromatography (hexane/AcOEt = 10/1, 6/1, 4/1, 3/1 and then 2/1). R_f = 0.7 (hexane/AcOEt = 1/1, v/v). Mp. 159–161 °C ($CHCl_3$/hexane). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.79 (d, J = 7.3 Hz, 2H), 7.58 (s, 1H), 7.49 (t, J = 7.3 Hz, 1H), 7.45–7.39 (m, 2H), 7.17–7.03 (m, 3H), 5.17 (s, 1H), 4.17 (q, J = 6.9 Hz, 2H), 3.54–3.45 (m, 1H), 3.31–3.22 (m, 1H), 3.14-3.03 (m, 1H), 2.88–2.78 (m, 1H), 2.24 (s, 3H), 1.17 (t, J = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 167.8, 165.6, 136.5, 133.5, 133.2, 132.1, 131.5, 129.0, 128.5, 127.1, 126.4, 124.8, 62.8, 61.2, 60.3, 52.0, 26.9, 19.3, 14.3. IR (KBr) 3364, 2960, 2937, 2855, 2092, 1684, 1656, 1515, 1379, 1294, 1106, 1031, 762, 714, 691 cm^{-1}. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{21}H_{22}N_4O_3Na$ 401.1590; Found 401.1594.

Ethyl 2-(2-Benzamido-7-methyl-1,2,3,4-tetrahydroisoquinolin-1-yl)-2-diazoacetate (4e): The reaction using **1e** (39 mg, 0.15 mmol) was carried out for 3 d. The compound **4e** (43 mg, 76% yield) was obtained as a solid after purification by silica gel column chromatography (hexane/AcOEt = 10/1, 6/1 and then 3/1). R_f = 0.7 (hexane/AcOEt = 1/1, v/v). Mp. 147–149 °C ($CHCl_3$/hexane). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.78 (d, J = 6.9 Hz, 2H), 7.53–7.38 (m, 3H), 7.48 (s, 1H), 7.06–7.00 (m, 2H), 6.99 (s, 1H), 5.13 (s, 1H), 4.23–4.13 (m, 2H), 3.43 (dd, J = 8.7, 4.6 Hz, 1H), 3.35–3.21 (m, 2H), 2.92–2.85 (m, 1H), 2.32 (s, 3H), 1.18 (t, J = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 167.8, 165.7, 136.2, 133.6, 132.0, 131.6, 131.6, 128.7, 128.6, 128.5, 127.4, 127.1, 62.6, 61.2, 60.3, 52.4, 28.7, 21.1, 14.3. IR (KBr) 3371, 2970, 2928, 2093, 1681, 1656, 1519, 1487, 1373, 1301, 1259, 1103, 802, 711, 693 cm^{-1}. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{21}H_{22}N_4O_3Na$ 401.1590; Found 401.1602.

Ethyl 2-(2-Benzamido-6-methoxy-1,2,3,4-tetrahydroisoquinolin-1-yl)-2-diazoacetate (4f): The reaction using **1f** (63 mg, 0.23 mmol) was carried out for 2 d. The compound **4f** (70 mg, 78% yield) was obtained as a solid after purification by silica gel column chromatography (hexane/AcOEt = 6/1, 3/1 and then 2/1). R_f = 0.4 (hexane/AcOEt = 1/1, v/v). Mp. 147–148 °C ($CHCl_3$/hexane). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.78 (d, J = 7.3 Hz, 2H), 7.57 (s, 1H), 7.49 (t, J = 7.3 Hz, 1H), 7.45–7.38 (m, 2H), 7.11 (d, J = 8.7 Hz, 1H), 6.77 (dd, J = 8.7, 2.3 Hz, 1H), 6.66 (d, J = 2.3 Hz, 1H), 5.12 (s, 1H), 4.16 (q, J = 7.0 Hz, 2H), 3.79 (s, 3H), 3.44 (dd, J = 9.2, 5.0 Hz, 1H), 3.35–3.20 (m, 2H), 2.92–2.84 (m, 1H), 1.17 (t, J = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 167.7, 165.6, 158.8, 136.1, 133.5, 131.5, 128.5, 128.2, 127.1, 124.3, 113.1, 113.0, 62.2, 61.1, 60.2, 55.2, 52.2, 29.4, 14.3. IR (KBr) 3369, 2968, 2931, 2091, 1679, 1656, 1522, 1505, 1372, 1261, 1110, 794, 704, 691 cm^{-1}. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{21}H_{22}N_4O_4Na$ 417.1539; Found 417.1530.

Ethyl 2-(2-Benzamido-7-bromo-1,2,3,4-tetrahydroisoquinolin-1-yl)-2-diazoacetate (4g): The reaction using **1g** (75 mg, 0.23 mmol) was carried out for 2 d. The compound **4g** (74 mg, 74% yield) was obtained as a solid after purification by silica gel column chromatography (hexane/AcOEt = 9/1, 6/1, 3/1 and then 2/1). R_f = 0.7 (hexane/AcOEt = 1/1, v/v). Mp. 150–152 °C ($CHCl_3$/hexane). ^{1}H

NMR ($CDCl_3$, 400 MHz): δ 7.77 (d, J = 7.3 Hz, 2H), 7.63 (s, 1H), 7.49 (t, J = 7.3 Hz, 1H), 7.40 (t, J = 7.3 Hz, 2H), 7.35–7.31 (m, 2H), 7.03 (d, J = 8.7 Hz, 1H), 5.17 (s, 1H), 4.16 (q, J = 7.3 Hz, 2H), 3.48–3.40 (m, 1H), 3.34–3.18 (m, 2H), 2.88–2.80 (m, 1H), 1.17 (t, J = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 167.4, 165.8, 134.7, 133.8, 133.4, 131.7, 130.8, 130.5, 129.8, 128.5, 127.1, 120.1, 62.0, 61.3, 60.0, 52.0, 28.8, 14.3. IR (KBr) 3369, 2974, 2090, 1685, 1655, 1520, 1487, 1373, 1305, 1257, 1102, 797, 711, 692 cm^{-1}. HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{20}H_{19}N_4O_3{}^{79}Br$ 465.0538; Found 465.0532. Calcd for $C_{20}H_{19}N_4O_3{}^{81}Br$ 467.0518; Found 467.0516.

3. Procedure for the reaction with trimethylsilyldiazomethane (Reaction B) and analytical data of **5**

3-Phenyl-6,7-dihydro-1*H*-1,5-methanobenzo[*g*][1,3,4]oxadiazonine (5a):[3] To a mixture of *C,N*-cyclic-*N*'-acyl azomethine imine **1a** (76 mg, 0.30 mmol) in butyronitrile (3 mL) and MeOH (0.3 mL) was added trimethylsilyldiazomethane (0.45 mL, 2 M solution in Et_2O, 0.90 mmol) and the mixture was stirred at rt for 1 d. After addition of acetic acid (0.06 mL) followed by toluene (3 mL) to the reaction mixture, the solvent was removed under reduced pressure. The resulted crude products were purified by silica gel column chromatography (hexane/AcOEt = 10/1, 8/1, 5/1, 2/1 and then 1/1) to give **5a** as a solid (52 mg, 65% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.89 (dd, J = 8.0, 1.6 Hz, 2H), 7.38–7.28 (m, 4H), 7.20–7.16 (m, 2H), 7.08–7.06 (m, 1H), 5.39 (d, J = 2.3 Hz, 1H), 3.80–3.72 (m, 1H), 3.67–3.58 (m, 2H), 3.48–3.39 (m, 2H), 2.56–2.47 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 155.5, 139.9, 138.0, 132.4, 131.4, 131.2, 129.9, 128.8, 127.9, 126.5, 126.0, 78.5, 54.0, 49.9, 33.6.

Addition of 1a in three separate parts: To a mixture of *C,N*-cyclic-*N*'-acyl azomethine imine **1a** (26 mg) in butyronitrile (3 mL) and MeOH (0.3 mL) was added trimethylsilyldiazomethane (0.45 mL, 2 M solution in Et_2O, 0.90 mmol) and the mixture was stirred at rt. After 2 h, **1a** (26 mg) was added to the reaction mixture. After 4 h, another **1a** (25 mg) was added (totally 0.31 mmol) and the mixture was stirred at rt for 1 d . After addition of acetic acid (0.06 mL) followed by similar work-up, **5a** (65 mg, 80% yield) was obtained as a solid.

In a similar manner of the former method for **5a** by one-pot addition of **1a**, **5b**–**5g** were obtained from the corresponding *C,N*-cyclic-*N*'-acyl azomethine imines **1b**–**1g**.

3-(*p*-Tolyl)-6,7-dihydro-1*H*-1,5-methanobenzo[*g*][1,3,4]oxadiazonine (5b):[3] The reaction of **1b** (80 mg, 0.30 mmol) with trimethylsilyldiazomethane (0.45 mL, 2 M solution in Et_2O, 0.90 mmol) was carried out for 1 d. The compound **5b** (64 mg, 77% yield) was obtained as an oil after purification by silica gel column chromatography (hexane/AcOEt = 8/1, 5/1, 2/1 and then 1/1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.78 (d, J = 8.2 Hz, 2H), 7.35–7.08 (m, 4H), 7.15 (d, J = 8.2 Hz, 2H), 5.39 (dd, J = 3.2, 2.3 Hz, 1H), 3.78–3.75 (m, 1H), 3.64–3.62 (m, 2H), 3.50–3.41 (m, 2H), 2.54–2.46 (m, 1H), 2.34 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 156.0, 140.1, 138.3, 131.4, 131.2, 129.7, 128.8, 128.7, 128.3, 126.5, 126.1, 78.8, 54.0, 50.1, 33.6, 21.3.

3-(4-Chlorophenyl)-6,7-dihydro-1*H*-1,5-methanobenzo[*g*][1,3,4]oxadiazonine (5c):[3] The reaction of **1c** (85 mg, 0.30 mmol) with trimethylsilyldiazomethane (0.45 mL, 2 M solution in Et_2O, 0.90 mmol) was carried out for 1 d. The compound **5c** (57 mg, 64% yield) was obtained as a solid after purification by silica gel column chromatography (hexane/AcOEt = 8/1, 5/1, 3/1, 2/1 and then 1/1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.82 (d, J = 8.7 Hz, 2H), 7.33–7.29 (m, 3H), 7.24–7.19 (m, 2H), 7.11–7.08 (m, 1H), 5.43 (d, J = 3.7 Hz, 1H), 3.80–3.74 (m, 1H), 3.68 (dd, J = 14.2, 0.9 Hz, 1H), 3.62 (dd, J = 14.2, 4.1 Hz, 1H), 3.51–3.35 (m, 2H), 2.56 (ddd, J = 15.6, 5.0, 2.3 Hz, 1H). ^{13}C{^{1}H} NMR

($CDCl_3$, 100 MHz): δ 154.5, 139.8, 137.9, 136.0, 131.5, 131.3, 130.9, 129.0, 128.2, 127.4, 126.7, 78.6, 54.1, 50.0, 33.7.

8-Methyl-3-phenyl-6,7-dihydro-1*H*-1,5-methanobenzo[*g*][1,3,4]oxadiazonine (5d):[3] The reaction of **1d** (79 mg, 0.30 mmol) with with trimethylsilyldiazomethane (0.45 mL, 2 M solution in Et_2O, 0.90 mmol) was carried out for 1 d. The compound **5d** (52 mg, 62% yield) was obtained as a solid after purification by silica gel column chromatography (hexane/AcOEt = 6/1, 4/1 and then 3/1). ^{1}H NMR ($CDCl_3$, 400 MHz): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.91 (dd, J = 7.8, 1.8 Hz, 2H), 7.41–7.33 (m, 3H), 7.17–7.07 (m, 3H) 5.44 (d, J = 3.7 Hz, 1H), 3.77 (ddd, J = 14.2, 5.0, 2.8 Hz, 1H), 3.67–3.58 (m, 2H), 3.42 (ddd, J = 14.2, 11.0, 1.8 Hz, 1H), 3.19 (ddd, J = 16.5, 11.0, 2.8 Hz, 1H), 2.78 (ddd, J = 16.5, 5.0, 1.8 Hz, 1H), 2.30 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 157.1, 138.7, 138.6, 137.1, 132.4, 131.3, 130.1, 129.6, 128.0, 126.3, 126.2, 79.8, 53.7, 50.0, 26.8, 21.3.

10-Methyl-3-phenyl-6,7-dihydro-1*H*-1,5-methanobenzo[*g*][1,3,4]oxadiazonine (5e):[3] The reaction of **1e** (79 mg, 0.30 mmol) with trimethylsilyldiazomethane (0.45 mL, 2 M solution in Et_2O, 0.90 mmol) was carried out for 1 d. The compound **5e** (68 mg, 81% yield) was obtained as an oil after purification by silica gel column chromatography (hexane/AcOEt = 6/1, 4/1 and then 3/1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.89 (d, J = 8.7 Hz, 2H), 7.40–7.32 (m, 3H), 7.13 (s, 1H), 7.03 (d, J = 7.8 Hz, 1H), 6.99 (d, J = 7.8 Hz, 1H), 5.37 (t, J = 2.5 Hz, 1H), 3.79–3.73 (m, 1H), 3.67–3.64 (m, 2H), 3.46–3.37 (m, 2H), 2.53–2.46 (m, 1H), 2.33 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 155.8, 138.0, 136.9, 136.1, 132.5, 132.4, 131.3, 123.0, 129.4, 128.0, 126.2, 78.8, 54.2, 50.2, 33.3, 20.7.

9-Methoxy-3-phenyl-6,7-dihydro-1*H*-1,5-methanobenzo[*g*][1,3,4]oxadiazonine (5f):[3] The reaction of **1f** (82 mg, 0.29 mmol) with trimethylsilyldiazomethane (0.45 mL, 2 M solution in Et_2O, 0.90 mmol) was carried out for 1 d. The compound **5f** (48 mg, 55% yield) was obtained as an oil after purification by silica gel column chromatography (hexane/AcOEt = 10/1, 8/1, 5/1, 3/1, 2/1 and then 1/1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.89 (dd, J = 8.0, 1.6 Hz, 2H), 7.32–7.39 (m, 3H), 7.25 (d, J = 8.7 Hz, 1H), 6.69 (dd, J = 8.7, 2.7 Hz, 1H), 6.63 (d, J = 2.7 Hz, 1H), 5.38 (t, J = 2.3 Hz, 1H), 3.79 (dd, J = 7.3, 2.3 Hz, 1H), 3.77 (s, 3H), 3.62 (d, J = 2.3 Hz, 2H), 3.38–3.49 (m, 2H), 2.43–2.52 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 159.5, 155.7, 141.6, 133.0, 132.5, 130.6, 129.9, 128.0, 126.1, 117.2, 110.7, 78.1, 55.1, 54.1, 50.4, 33.8.

10-Bromo-3-phenyl-6,7-dihydro-1*H*-1,5-methanobenzo[*g*][1,3,4]oxadiazonine (5g):[3] The reaction of **1g** (98 mg, 0.30 mmol) with trimethylsilyldiazomethane (0.45 mL, 2 M solution in Et_2O, 0.90 mmol) was carried out for 1 d. The compound **5g** (86 mg, 85% yield) was obtained as an oil after purification by silica gel column chromatography (hexane/AcOEt = 8/1, 5/1, 2/1 and then 1/1) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88 (dd, J = 8.2, 1.8 Hz, 2H), 7.46 (d, J = 2.3 Hz, 1H), 7.41–7.30 (m, 4H), 6.95 (d, J = 7.8 Hz, 1H), 5.34 (d, J = 2.3 Hz, 1H), 3.79–3.73 (m, 1H), 3.67–3.58 (m, 2H), 3.47–3.33 (m, 2H), 2.53–2.46 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 155.4, 140.1, 138.9, 134.2, 132.9, 132.2, 131.6, 130.1, 128.2, 128.1, 126.1, 120.0, 77.7, 53.8, 49.8, 33.2.

4. Procedure for the conversion of **4a** to **6** and analytical data of **6**

Ethyl 3-Benzamido-2,3-dihydro-1*H*-benzo[*d*]azepine-4-carboxylate (6): The mixture of the diazo compounds **4a** (53 mg, 0.15 mmol) and $Rh_2(OAc)_4$ (2 mg, 0.005 mmol) in CH_2Cl_2 (18 mL) was stirred at room temperature for 18 h.[4] The reaction mixture was passed through a pad of silica gel and the solution was condensed under reduced pressure. The resulted crude products were purified by silica gel column chromatography (hexane/AcOEt = 6/1, 3/1 and then 2/1) to give **6** as a solid (48 mg, 97% yield). R_f = 0.6 (hexane/AcOEt = 1/1, v/v). Mp. 191–192 °C (AcOEt/hexane). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.03 (s, 1H), 7.92 (d, J = 7.3 Hz, 2H), 7.61 (t, J = 7.3 Hz, 1H), 7.53 (t, J = 7.3 Hz, 2H), 7.13–7.16 (m, 2H), 7.06–6.96 (m, 1H), 6.62 (s, 1H), 6.50–6.44 (m, 1H), 3.78–3.71(m, 2H), 3.49–3.42 (m, 2H), 3.15–3.10 (m, 2H), 0.93–0.88 (m, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 167.2, 165.3, 141.4, 135.4, 133.3, 132.2, 132.0, 129.4, 128.7, 127.6 127.4, 126.1, 120.6, 61.7, 54.3, 35.0, 13.5; one signal overlaps. IR (KBr) 3230, 3054, 1716, 1655, 1620, 1542, 1302, 1251, 1215, 1067, 918, 774, 694 cm^{-1}. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{21}N_2O_3$ 337.1552; Found 337.1553. CCDC-2129011 contains the supplementary crystallographic data for **6**.

5. ORTEPs of **4a** and **6** (Ellipsoid contour percent probability level is 50%)

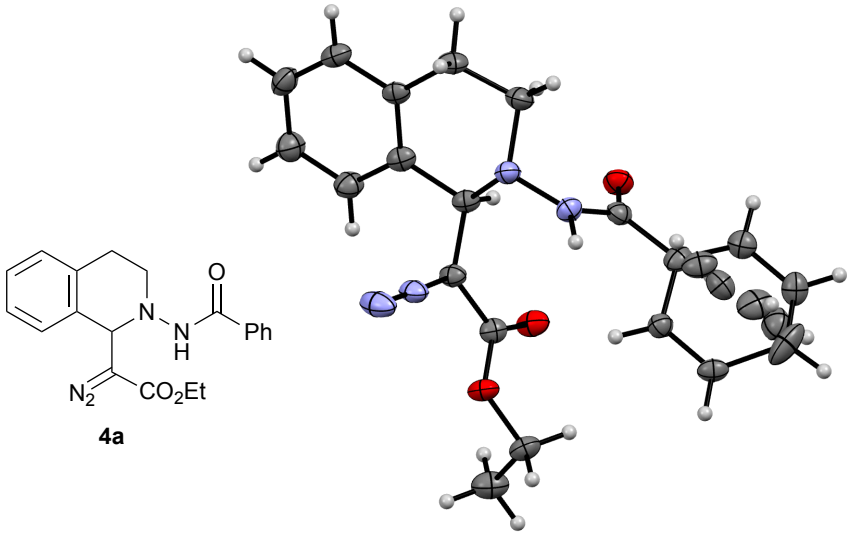

Figure S1. X-ray Structure of **4a** (CCDC-2129155)

Unit cell parameters: a = 4.9174(3), b = 16.0704(9), c = 11.6190(7), $P2_1$. R = 0.0562.

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 191207_rtakahashi4_2_0m_a

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 191207_rtakahashi4_2_0m_a

Bond precision: C-C = 0.0066 A Wavelength=1.54178

Cell: a=4.9174(3) b=16.0704(9) c=11.6190(7)
alpha=90 beta=90.199(3) gamma=90
Temperature: 90 K

	Calculated	Reported
Volume	918.18(9)	918.18(9)
Space group	P 21	P 21
Hall group	P 2yb	P 2yb
Moiety formula	C20 H20 N4 O3	?
Sum formula	C20 H20 N4 O3	C20 H20 N4 O3
Mr	364.40	364.40
Dx,g cm-3	1.318	1.318
Z	2	2
Mu (mm-1)	0.744	0.744
F000	384.0	384.0
F000'	385.19	
h,k,lmax	6,19,14	5,19,14
Nref	3648[1893]	3403
Tmin,Tmax	0.836,0.862	
Tmin'	0.743	

Correction method= Not given

Data completeness= 1.80/0.93 Theta(max)= 72.649

R(reflections)= 0.0562(3300) wR2(reflections)= 0.1597(3403)

S = 1.075 Npar= 286

The following ALERTS were generated. Each ALERT has the format
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Click on the hyperlinks for more details of the test.

Alert level B

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Alert level C

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PLAT241_ALERT_2_C High   'MainMol' Ueq as Compared to Neighbors of        C16 Check
PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ...............    0.00662 Ang.
PLAT353_ALERT_3_C Long   N-H (N0.87,N1.01A)  N1       - H24       .       1.02 Ang.
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600         28 Report
PLAT934_ALERT_3_C Number of (Iobs-Icalc)/Sigma(W) > 10 Outliers ..          1 Check
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Alert level G

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PLAT230_ALERT_2_G Hirshfeld Test Diff for    C16      --C21      .        8.4 s.u.
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PLAT300_ALERT_4_G Atom Site Occupancy of C18        Constrained at        0.5 Check
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PLAT300_ALERT_4_G Atom Site Occupancy of C21        Constrained at        0.5 Check
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PLAT300_ALERT_4_G Atom Site Occupancy of H21        Constrained at        0.5 Check
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                                                    x,y,z  =      1_555 Check
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PLAT913_ALERT_3_G Missing # of Very Strong Reflections in FCF ....          1 Note
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ...........        3.8 Low
PLAT965_ALERT_2_G The SHELXL WEIGHT Optimisation has not Converged     Please Check
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          2 Info
```

```
  0 ALERT level A = Most likely a serious problem - resolve or explain
  1 ALERT level B = A potentially serious problem, consider carefully

  6 ALERT level C = Check. Ensure it is not caused by an omission or oversight
 29 ALERT level G = General information/check it is not something unexpected

  1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  9 ALERT type 2 Indicator that the structure model may be wrong or deficient
  8 ALERT type 3 Indicator that the structure quality may be low
 18 ALERT type 4 Improvement, methodology, query or suggestion
  0 ALERT type 5 Informative message, check
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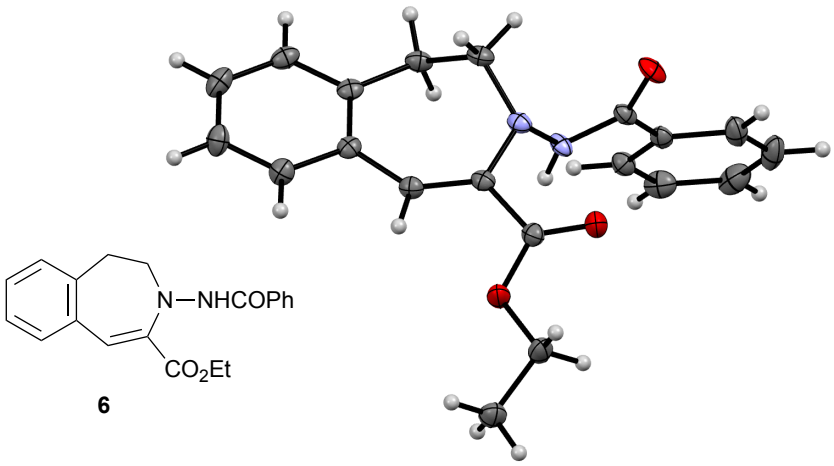

Figure S2. X-ray Structure of **6** (CCDC-2129011)

Unit cell parameters: a = 9.8436(4), b = 18.8060(7), c = 18.8060(7), *Pbca*. R = 0.0347.

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 210917_sakurai_0ma

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: 210917_sakurai_0ma

```
Bond precision:   C-C = 0.0016 A          Wavelength=1.54178

Cell:               a=9.8436(4)      b=18.8060(7)      c=18.8060(7)
                    alpha=90         beta=90           gamma=90
Temperature:        273 K
```

	Calculated	Reported
Volume	3481.3(2)	3481.3(2)
Space group	P b c a	P b c a
Hall group	-P 2ac 2ab	-P 2ac 2ab
Moiety formula	C20 H20 N2 O3	C20 H20 N2 O3
Sum formula	C20 H20 N2 O3	C20 H20 N2 O3
Mr	336.38	336.39
Dx,g cm-3	1.284	1.284
Z	8	8
Mu (mm-1)	0.705	0.705
F000	1424.0	1428.6
F000'	1428.34	
h,k,lmax	12,23,23	11,23,23
Nref	3445	3421
Tmin,Tmax	0.881,0.945	0.626,0.754
Tmin'	0.400	

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Correction method= # Reported T Limits: Tmin=0.626 Tmax=0.754
AbsCorr = MULTI-SCAN

Data completeness= 0.993          Theta(max)= 72.490

R(reflections)= 0.0347( 3203)                    wR2(reflections)=
                                                 0.0871( 3421)
S = 1.038                 Npar= 227
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The following ALERTS were generated. Each ALERT has the format
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Click on the hyperlinks for more details of the test.

Alert level B

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Maximum crystal size given = 1.300

Alert level C

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C20 H20 N2 O3
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Alert level G

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PLAT200_ALERT_1_G Reported _diffrn_ambient_temperature ..... (K) 273 Check
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0 **ALERT level A** = Most likely a serious problem - resolve or explain
1 **ALERT level B** = A potentially serious problem, consider carefully
2 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
13 **ALERT level G** = General information/check it is not something unexpected

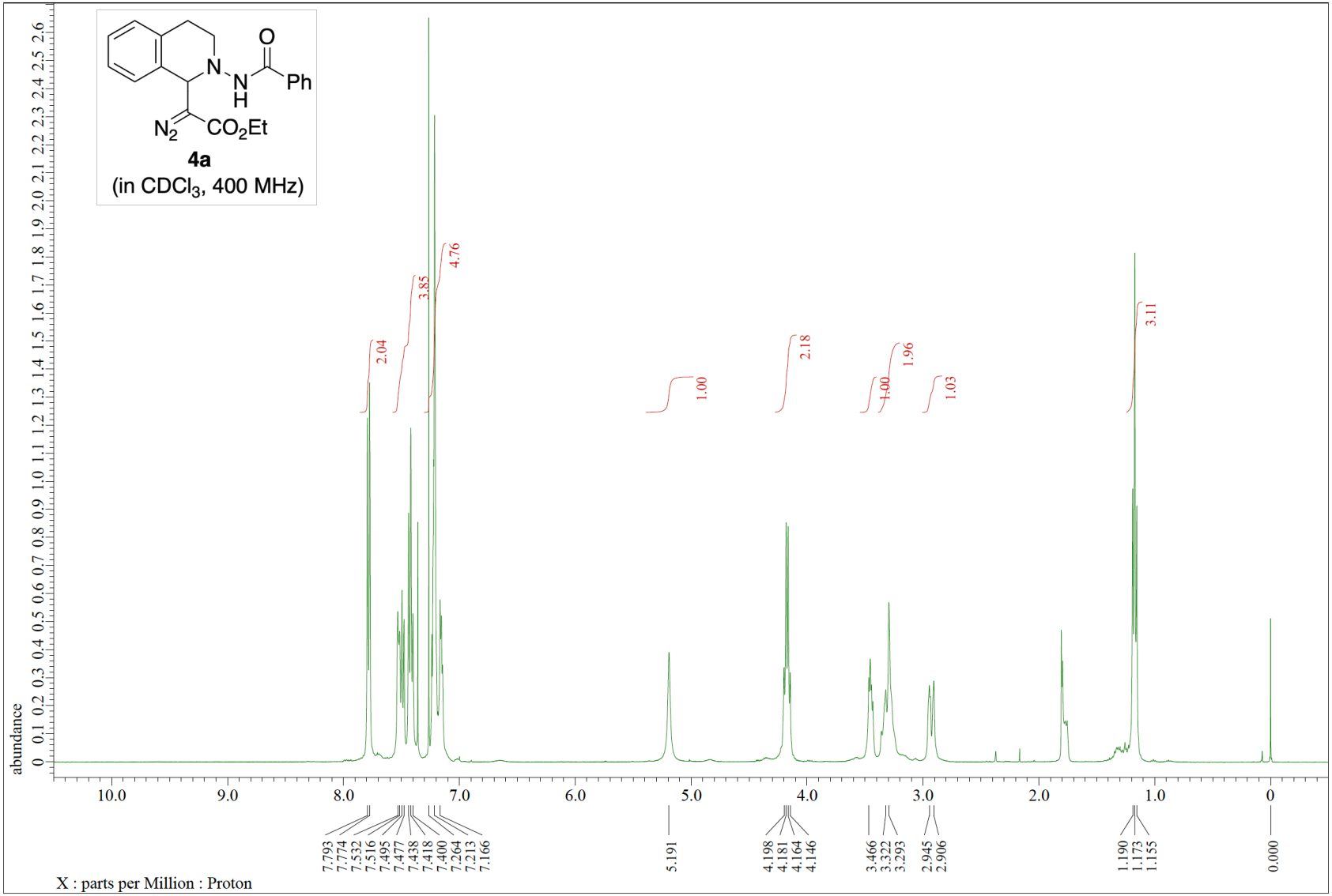
8 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
1 ALERT type 2 Indicator that the structure model may be wrong or deficient
3 ALERT type 3 Indicator that the structure quality may be low
4 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

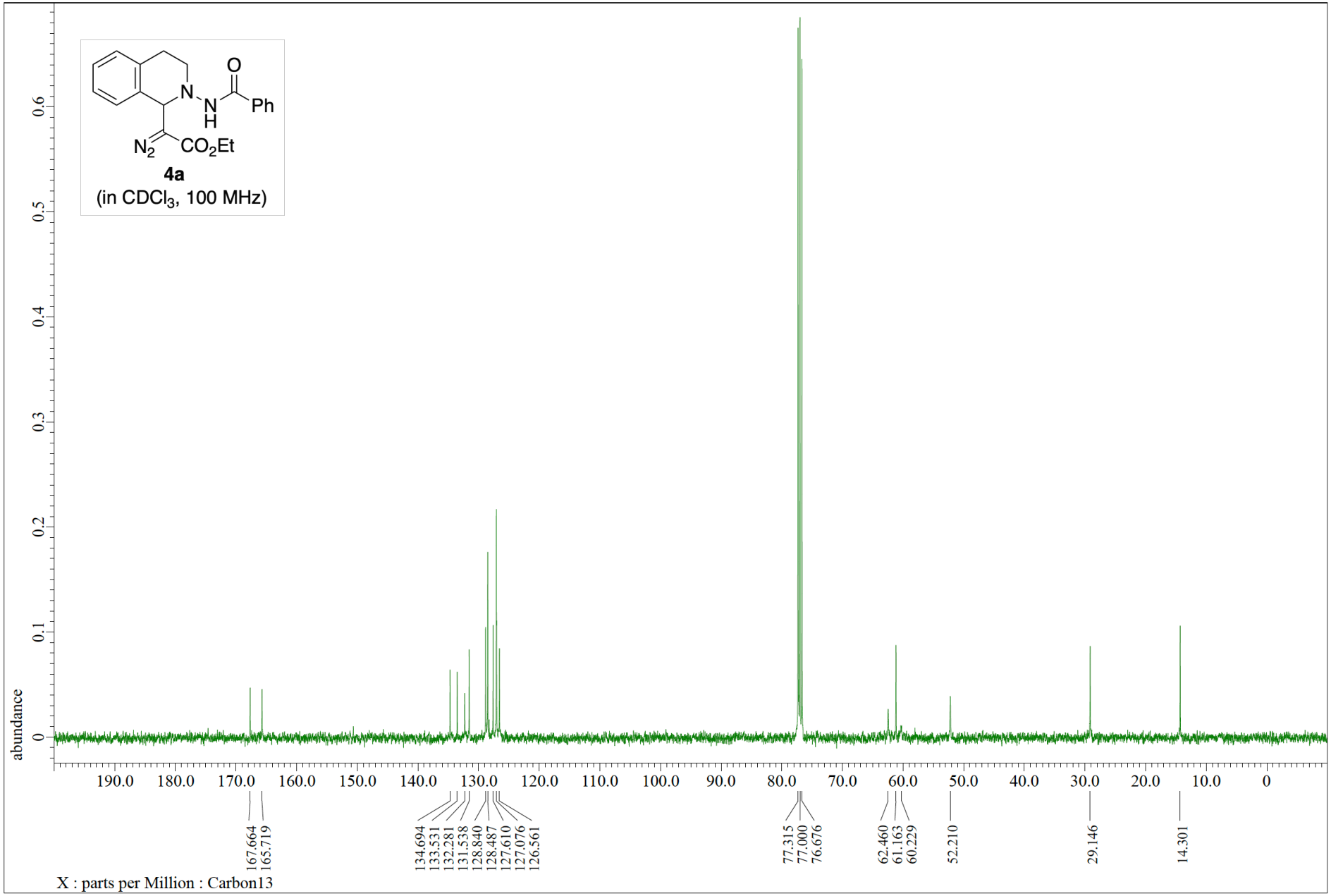
6. References

1. (a) T. Hashimoto, Y. Maeda, M. Omote, H. Nakatsu and K. Maruoka, *J. Am. Chem. Soc*., 2010, **132**, 4076; (b) K. Wang, Y. Li, X.Wang and B. Zhu, *ChemistrySelect*, 2019, **4**, 3340.
2. D. Zhang, J. Liu, Z. Kang, H. Qiu and W. Hu, *Org. Biomol. Chem*., 2019, **17**, 9844.
3. T. Soeta, T. Ohgai, T. Sakai, S. Fujinami and Y. Ukaji, *Org. Lett*., 2014, **16**, 4854.
4. J. Huang, L. Li, T. Xiao, Z.-W. Mao and L. Zhou, *Asian J. Org. Chem*., 2016, **5**, 1204.

7. NMR Spectra of compounds

1) ^{1}H and ^{13}C NMR spectra of α-diazoacetate moiety-introduced tetrahydroisoquinolines **4a**-**4g**

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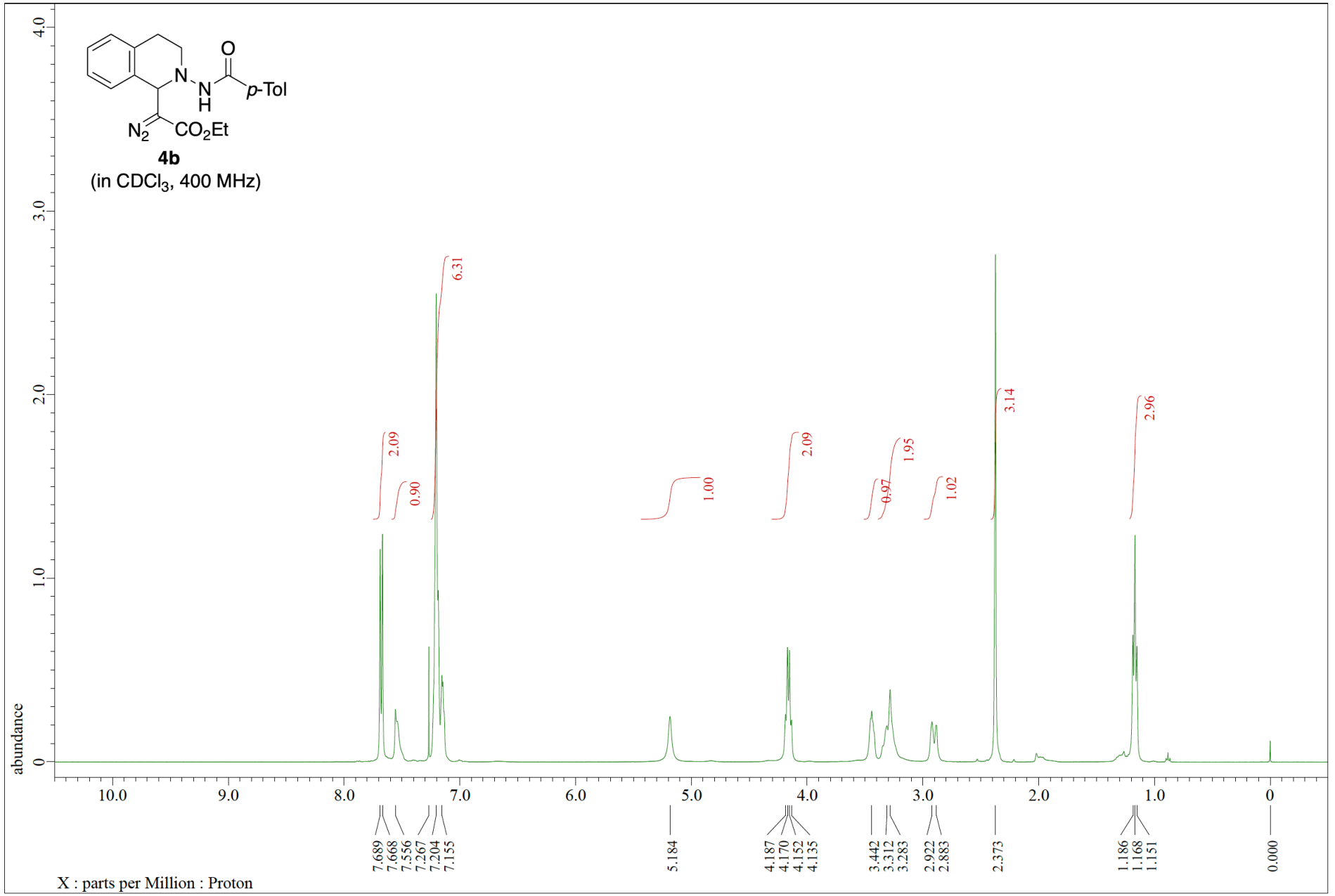
128.487
127.610
127.076
126.561
77.315
77.000
76.676
62.460
61.163
60.229
52.210
29.146
14.301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X : parts per Million : Proton
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2.09
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1.95
1.02
3.14
2.96
7.689
7.668
7.556
7.267
7.204
7.155
5.184
4.187
4.170
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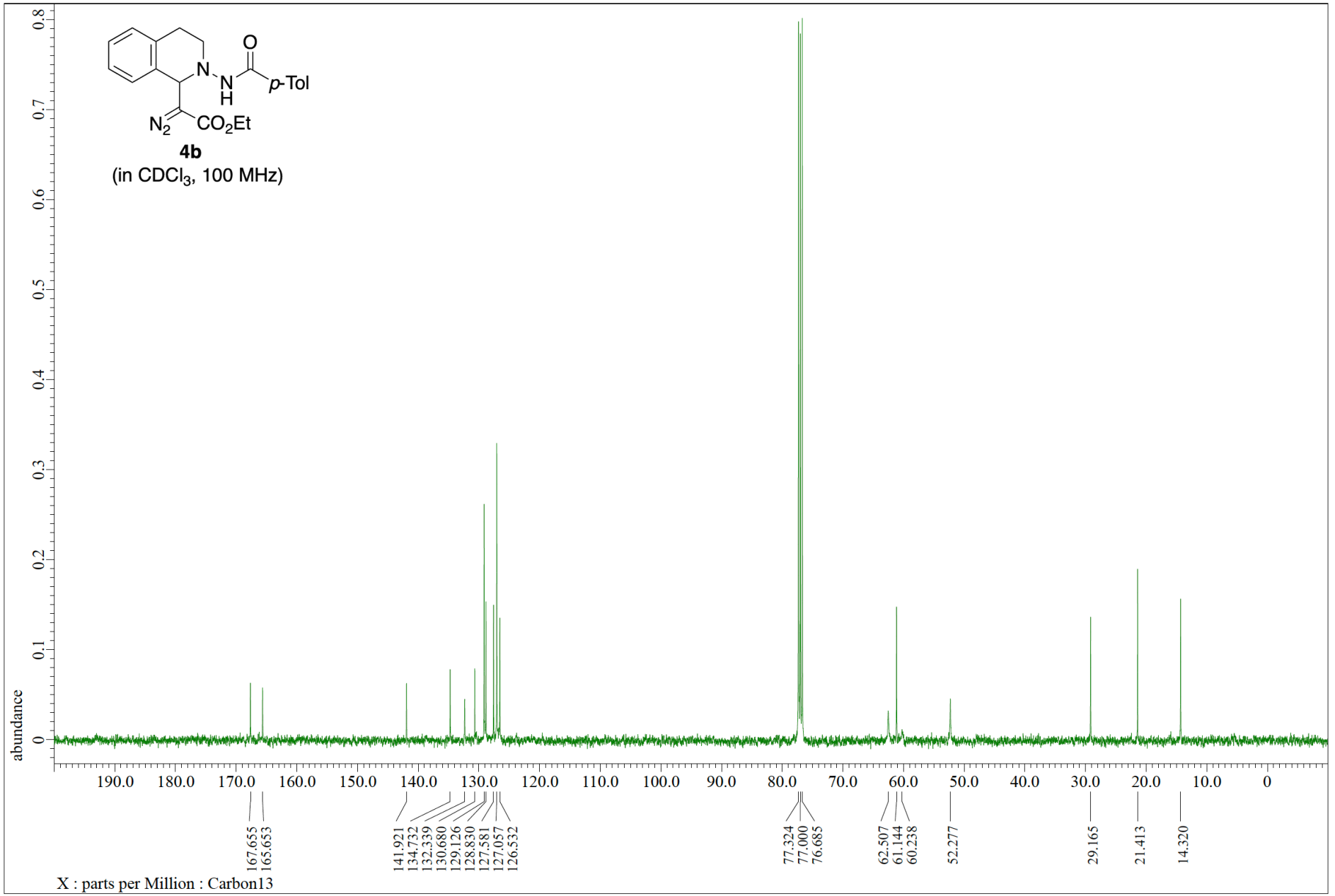
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127.581
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77.000
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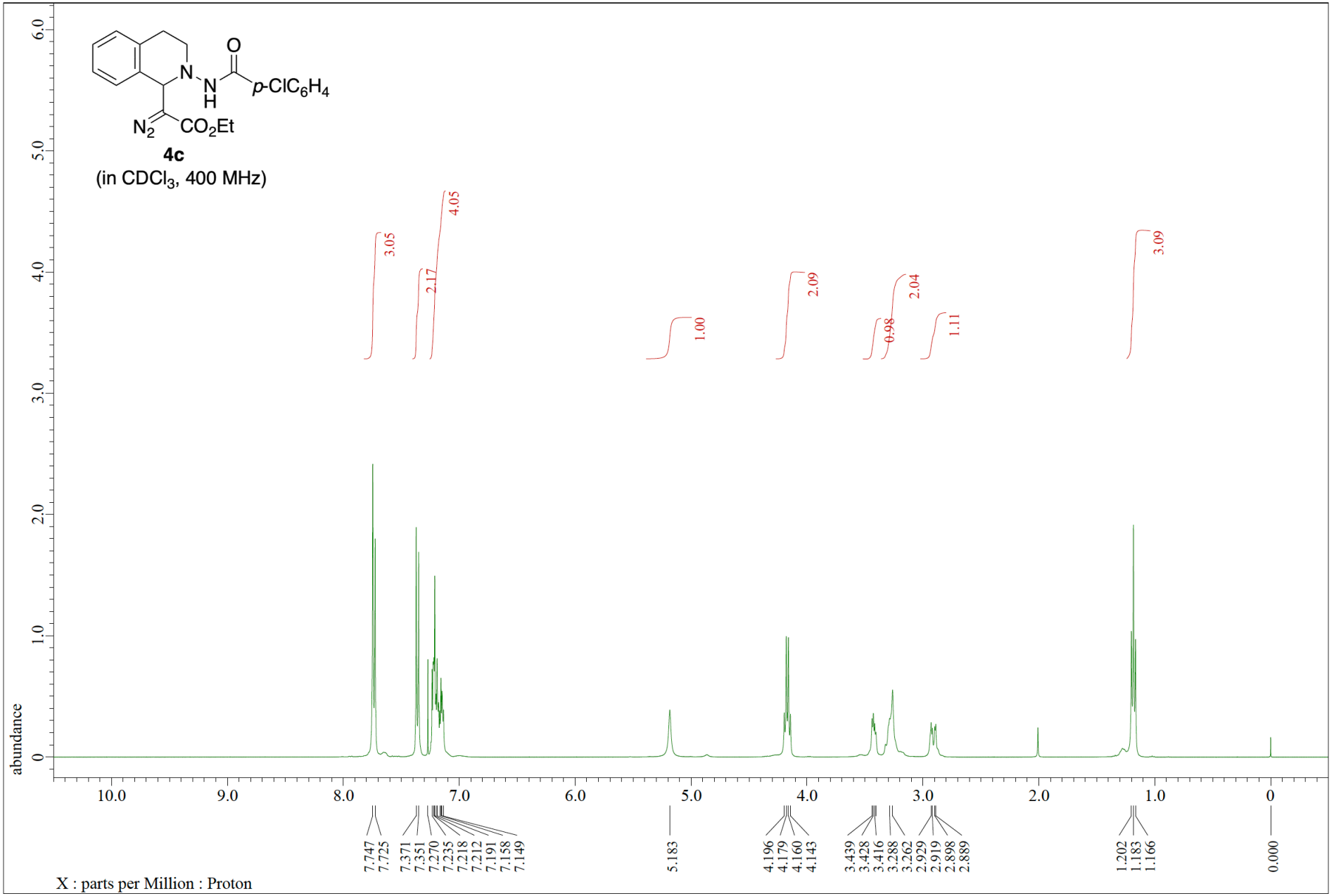
14.320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(in CDCl3, 400 MHz)
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2.17
4.05
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2.09
0.98
2.04
1.11
3.09
abundance
X : parts per Million : Proton
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7.725
7.371
7.351
7.270
7.235
7.218
7.212
7.191
7.158
7.149
5.183
4.196
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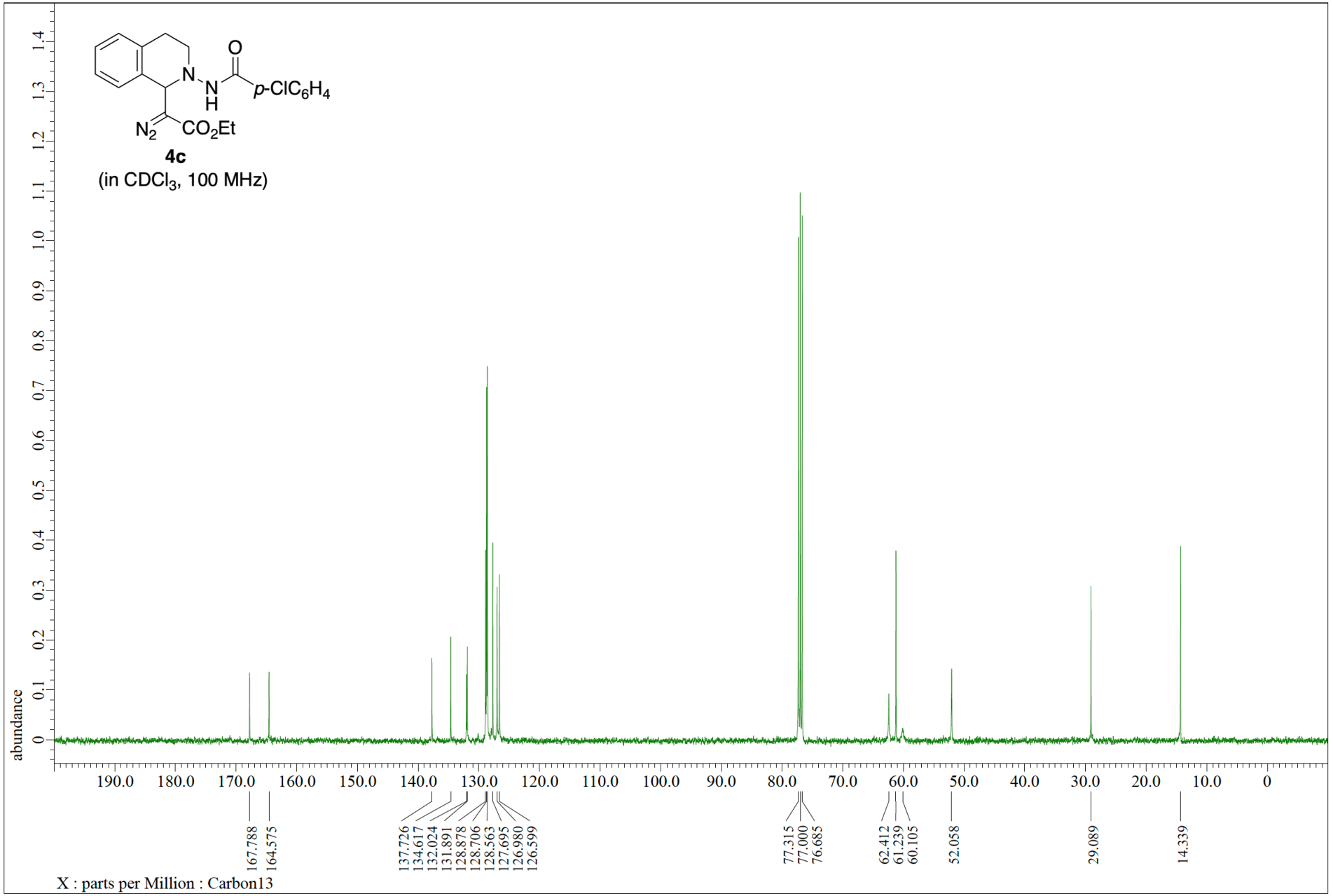
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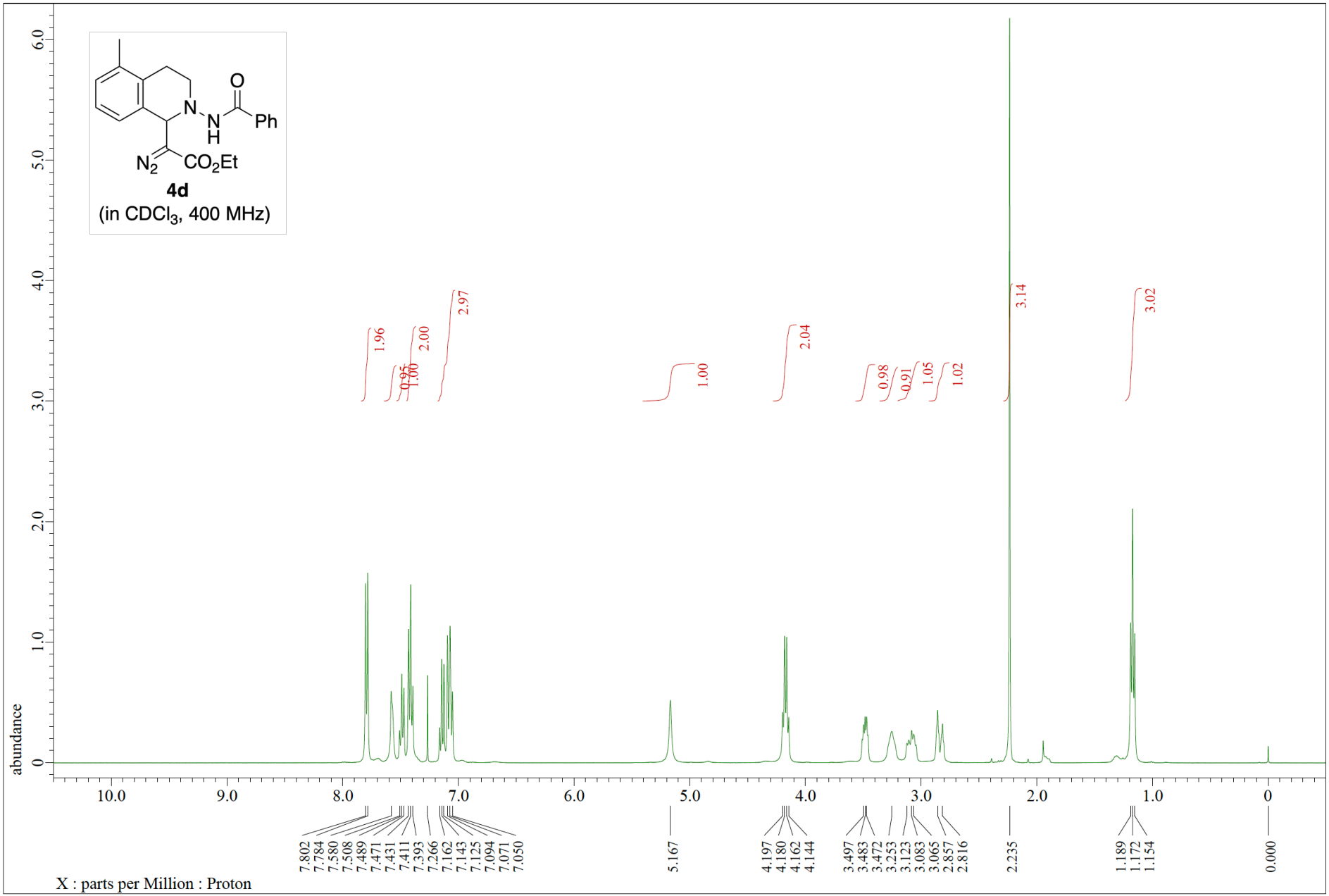
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0.91
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3.14
3.02
7.802
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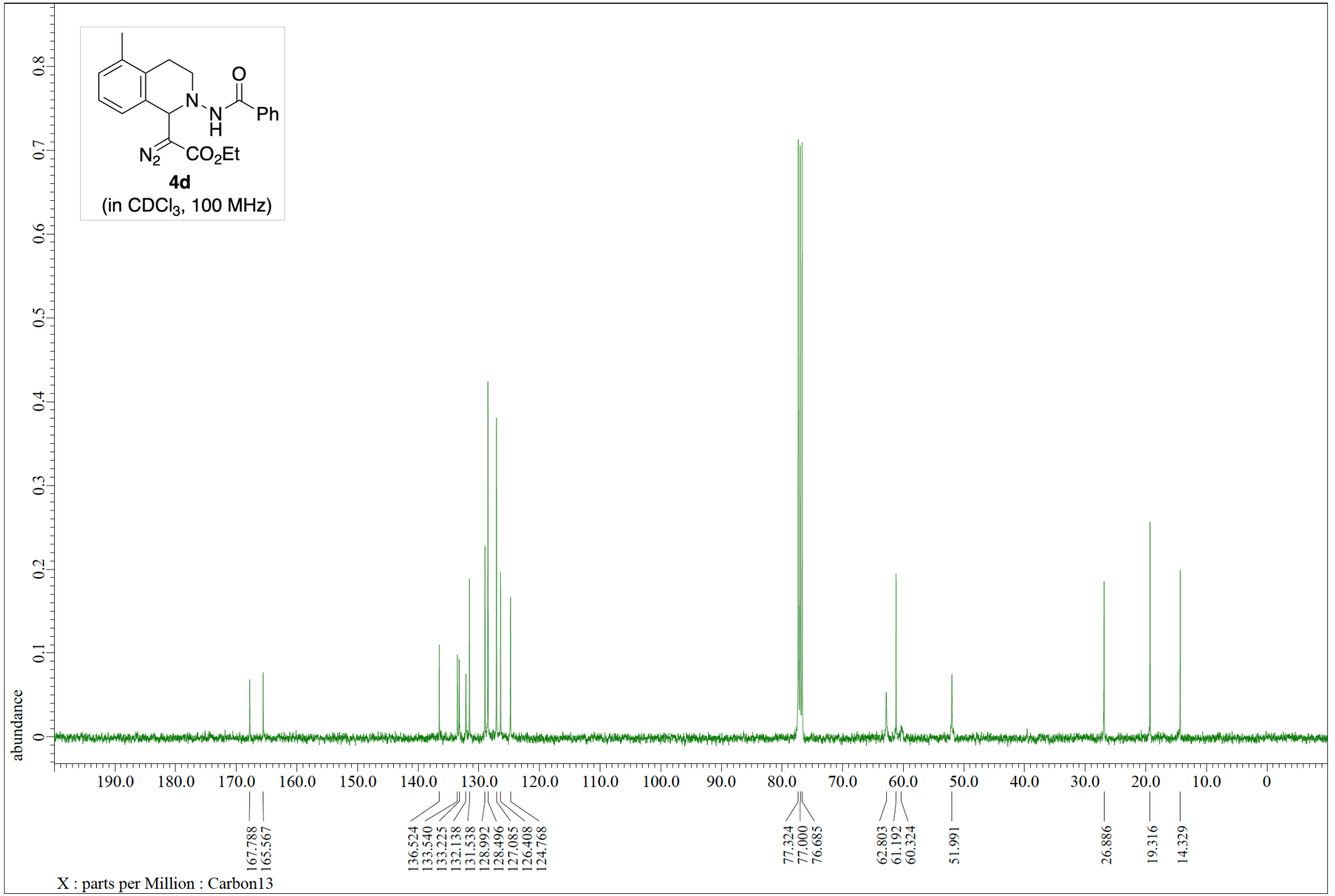
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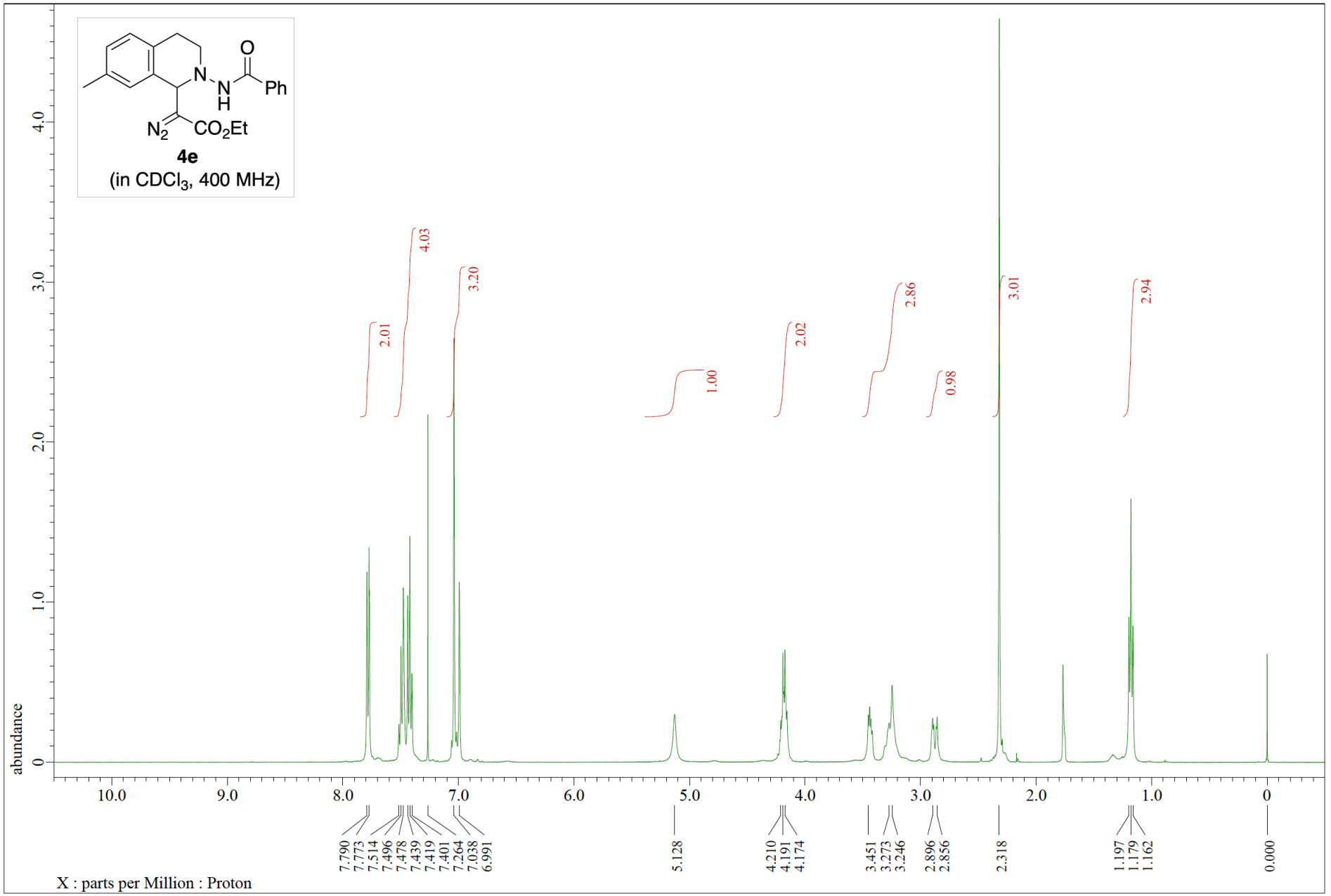
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0.98
3.01
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7.478
7.439
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4.210
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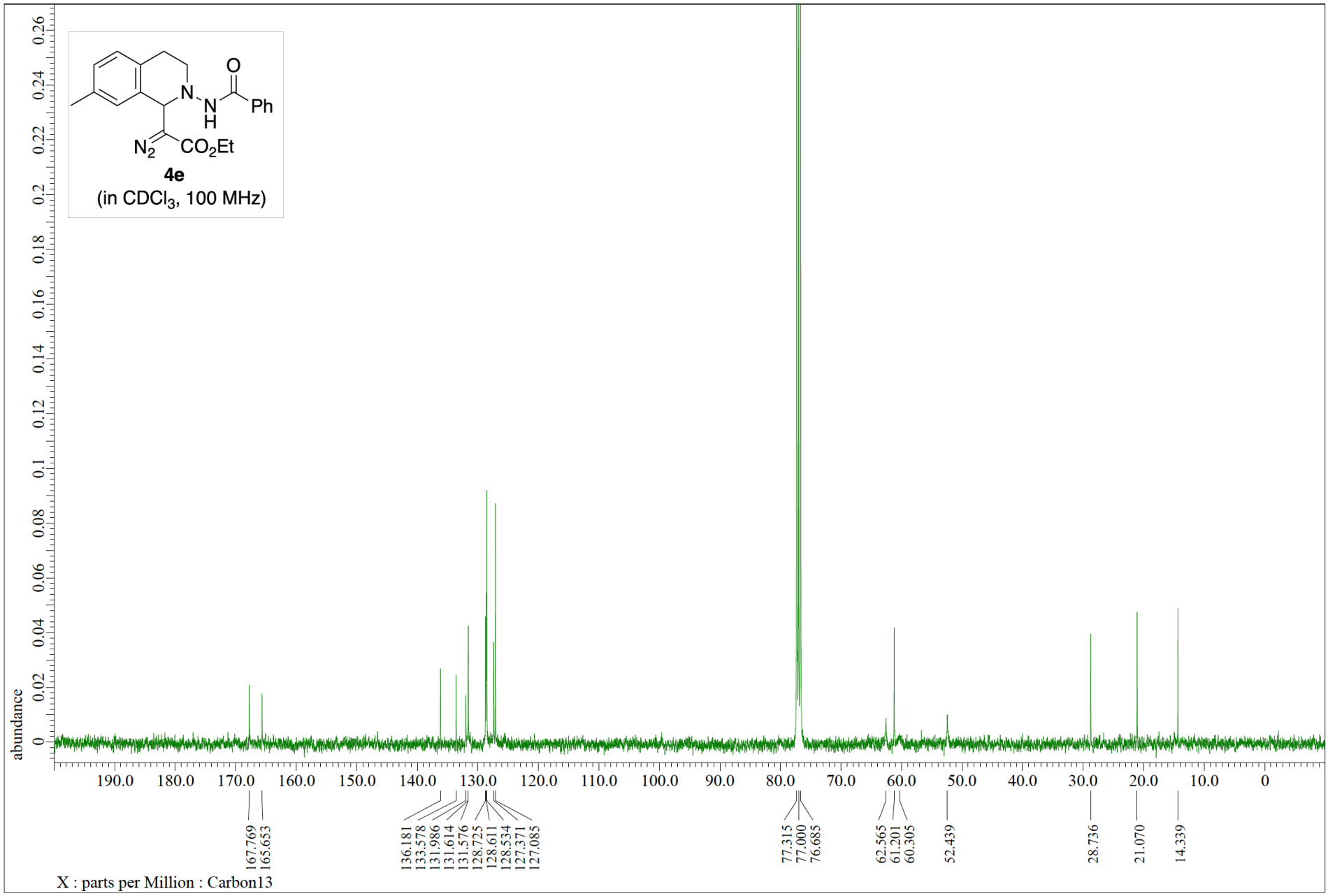
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(in CDCl3, 100 MHz)
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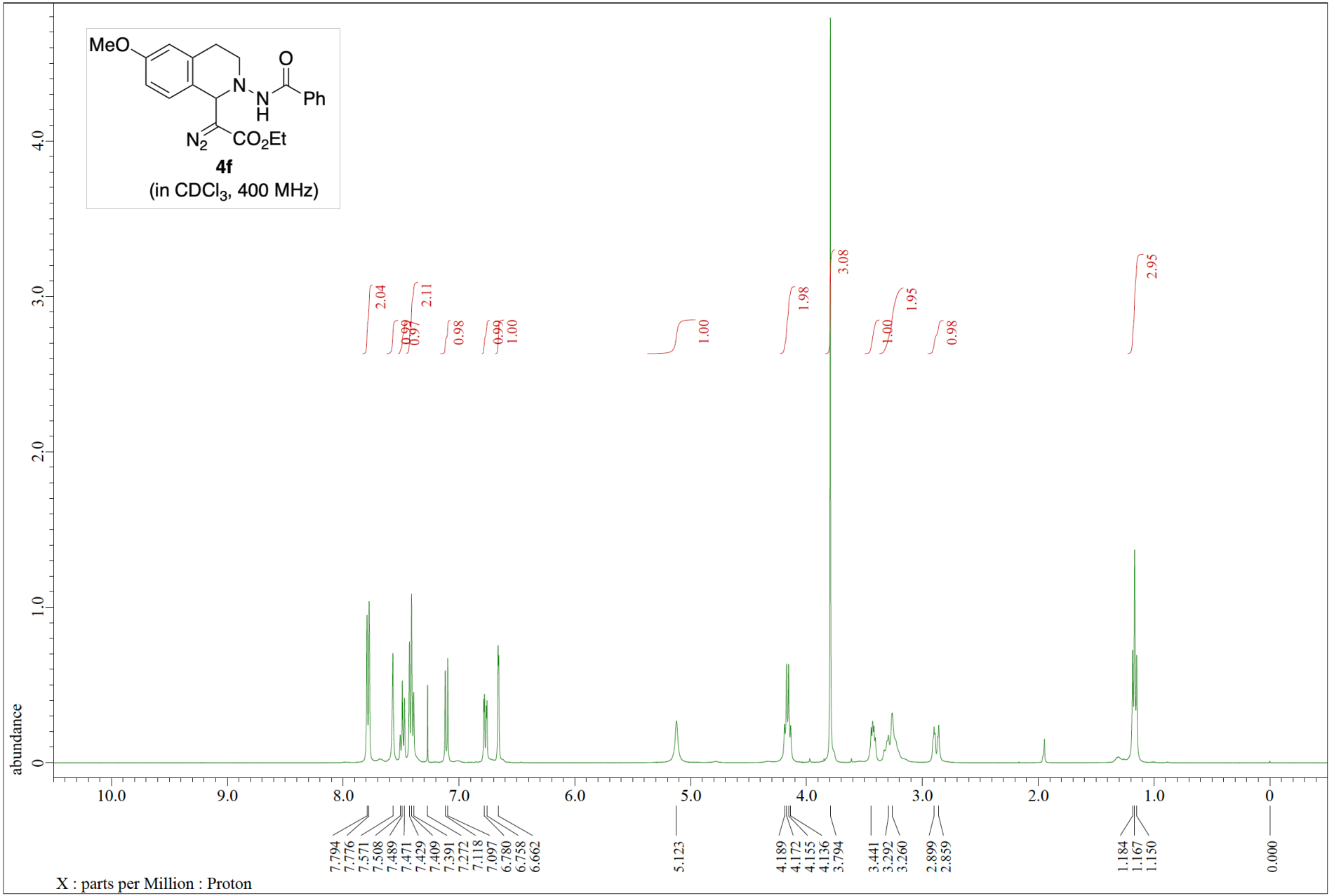
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O
N
N
H
Ph
N2
CO2Et
4f
(in CDCl3, 400 MHz)
abundance
X : parts per Million : Proton
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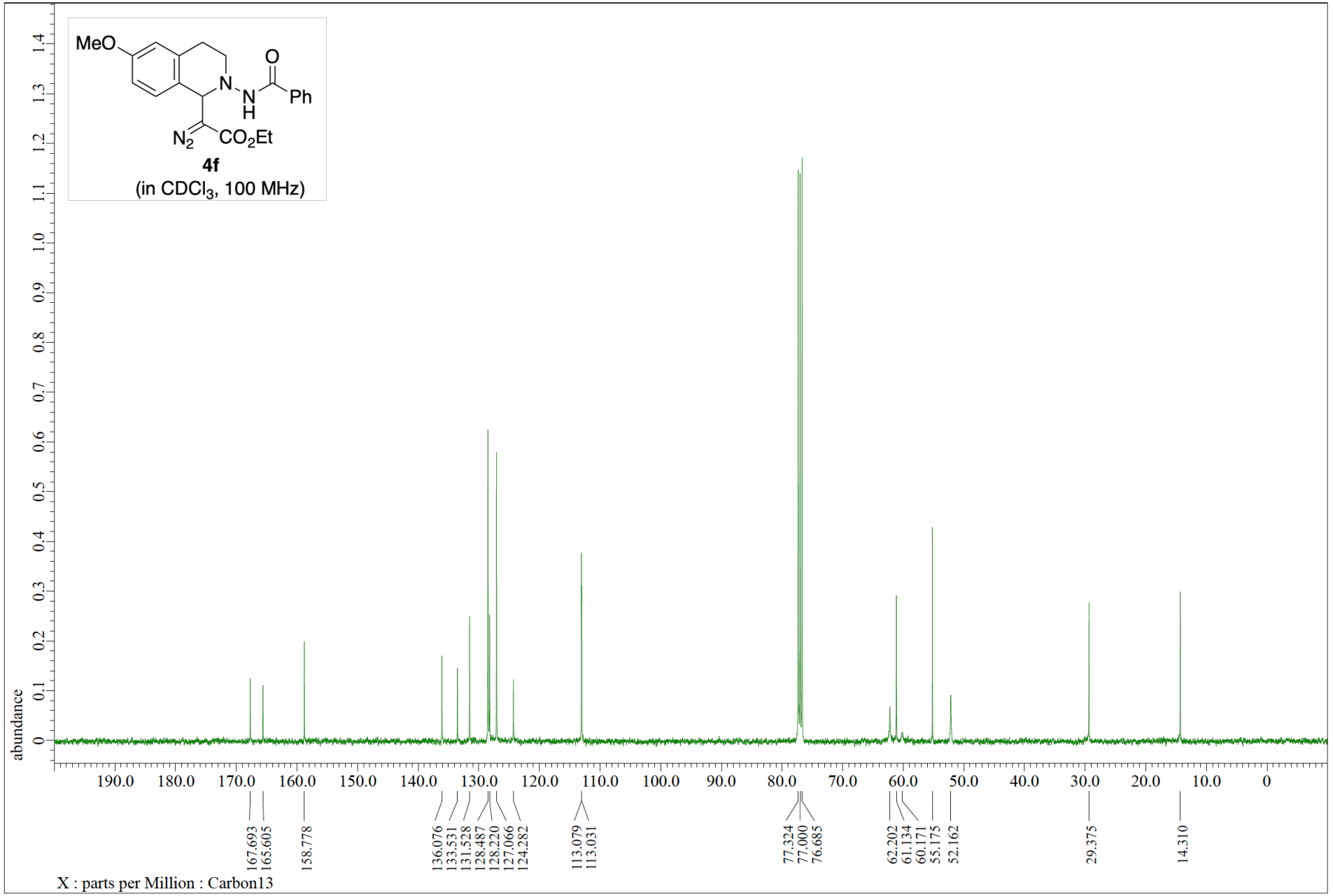
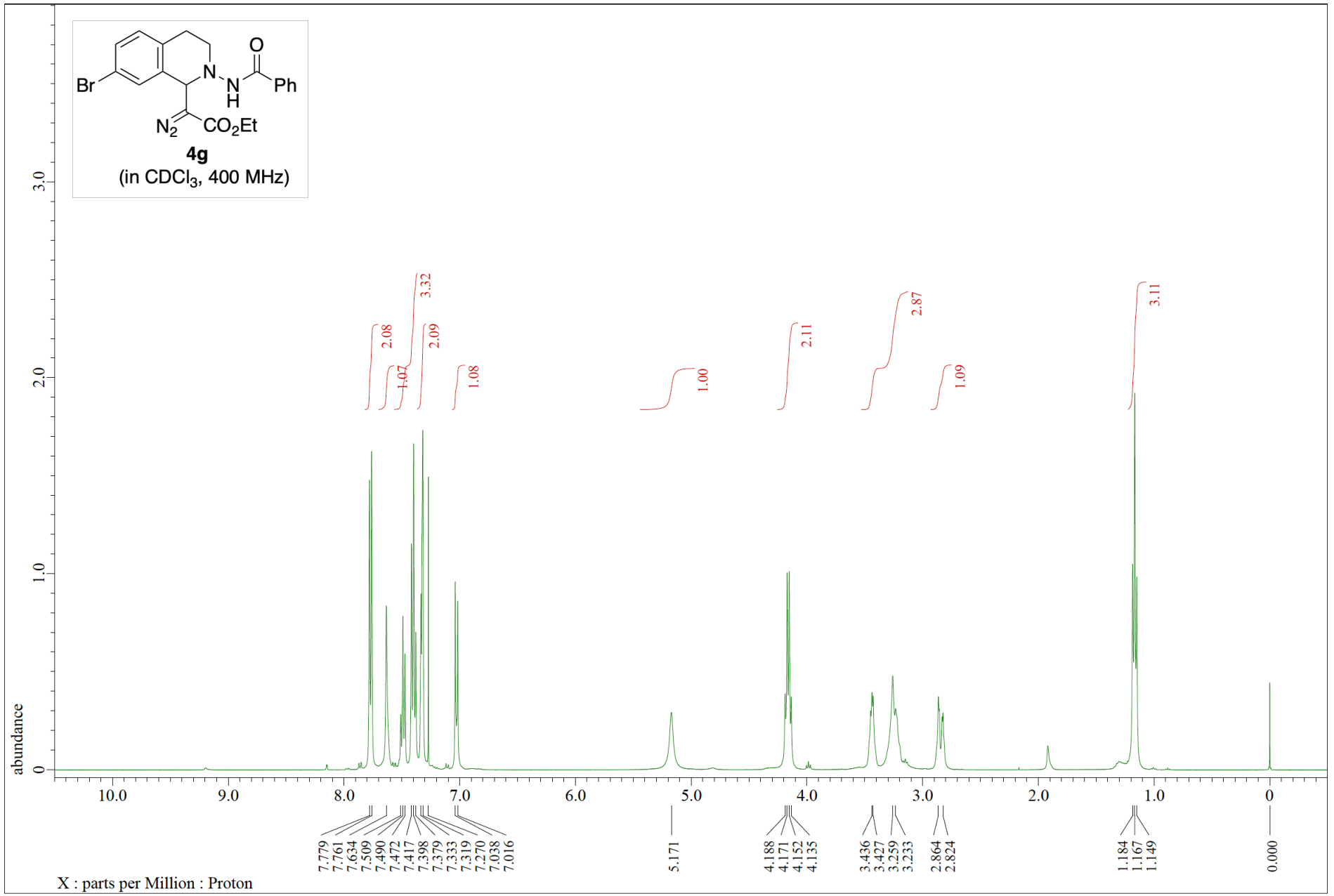
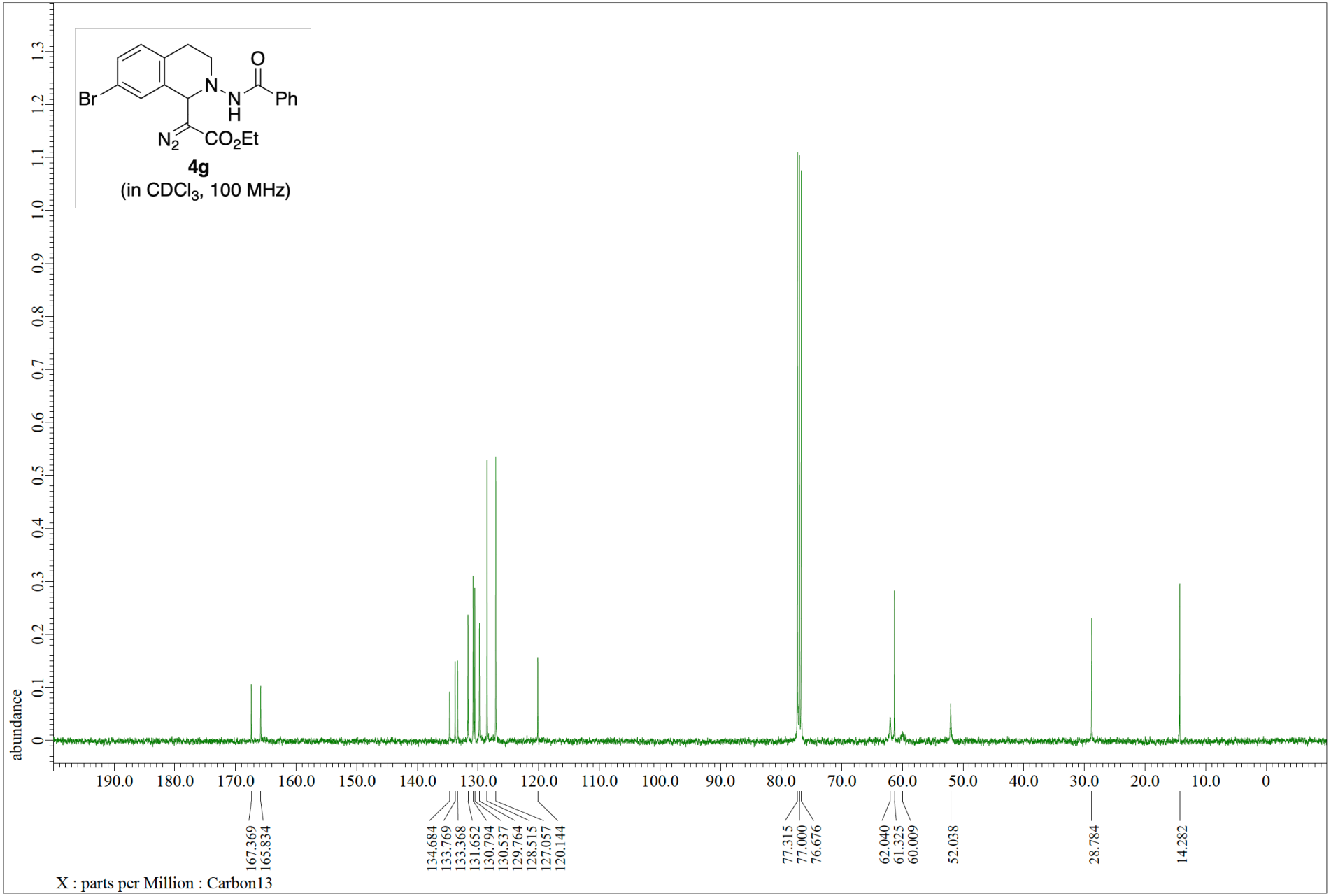
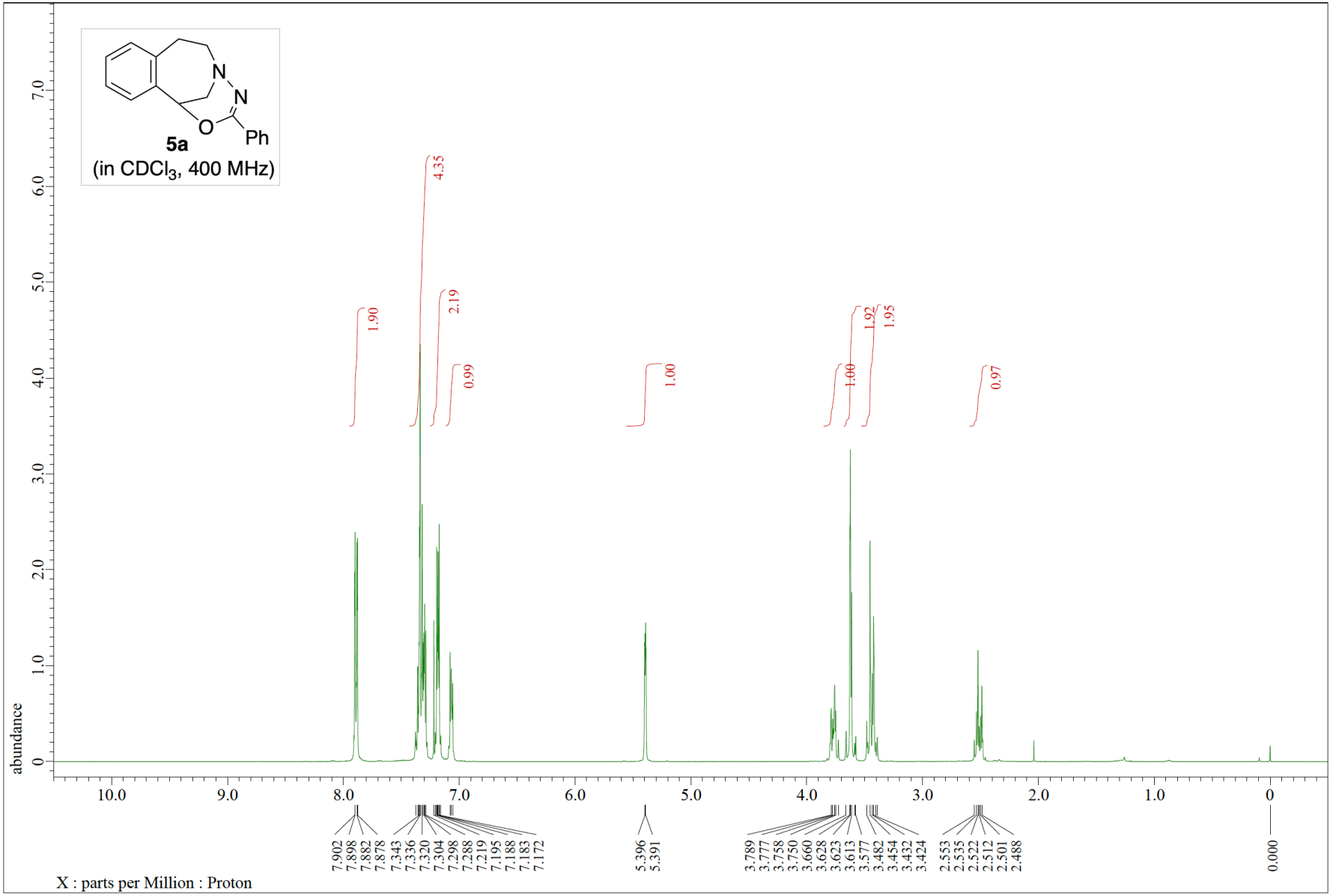
2.11
0.98
1.00
1.00
1.98
3.08
1.00
1.95
0.98
2.95
7.794
7.776
7.571
7.508
7.489
7.471
7.429
7.409
7.391
7.272
7.118
7.097
6.780
6.758
6.662
5.123
4.189
4.172
4.155
4.136
3.794
3.441
3.292
3.260
2.899
2.859
1.184
1.167
1.150
0.000

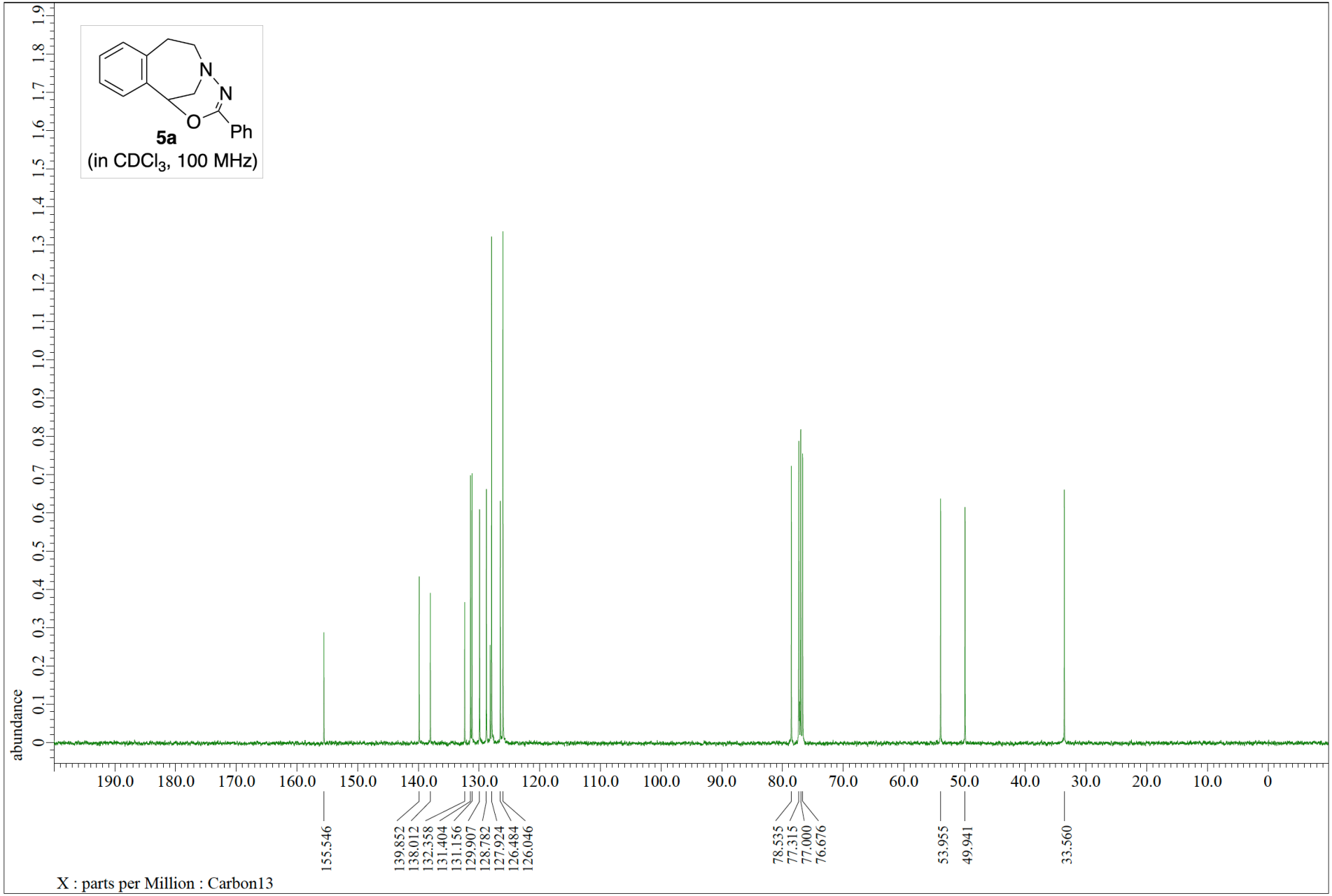

MeO
O
N
N
H
Ph
N2
CO2Et
4f
(in CDCl3, 100 MHz)
abundance
X : parts per Million : Carbon13
167.693
165.605
158.778
136.076
133.531
131.528
128.487
128.220
127.066
124.282
113.079
113.031
77.324
77.000
76.685
62.202
61.134
60.171
55.175
52.162
29.375
14.310

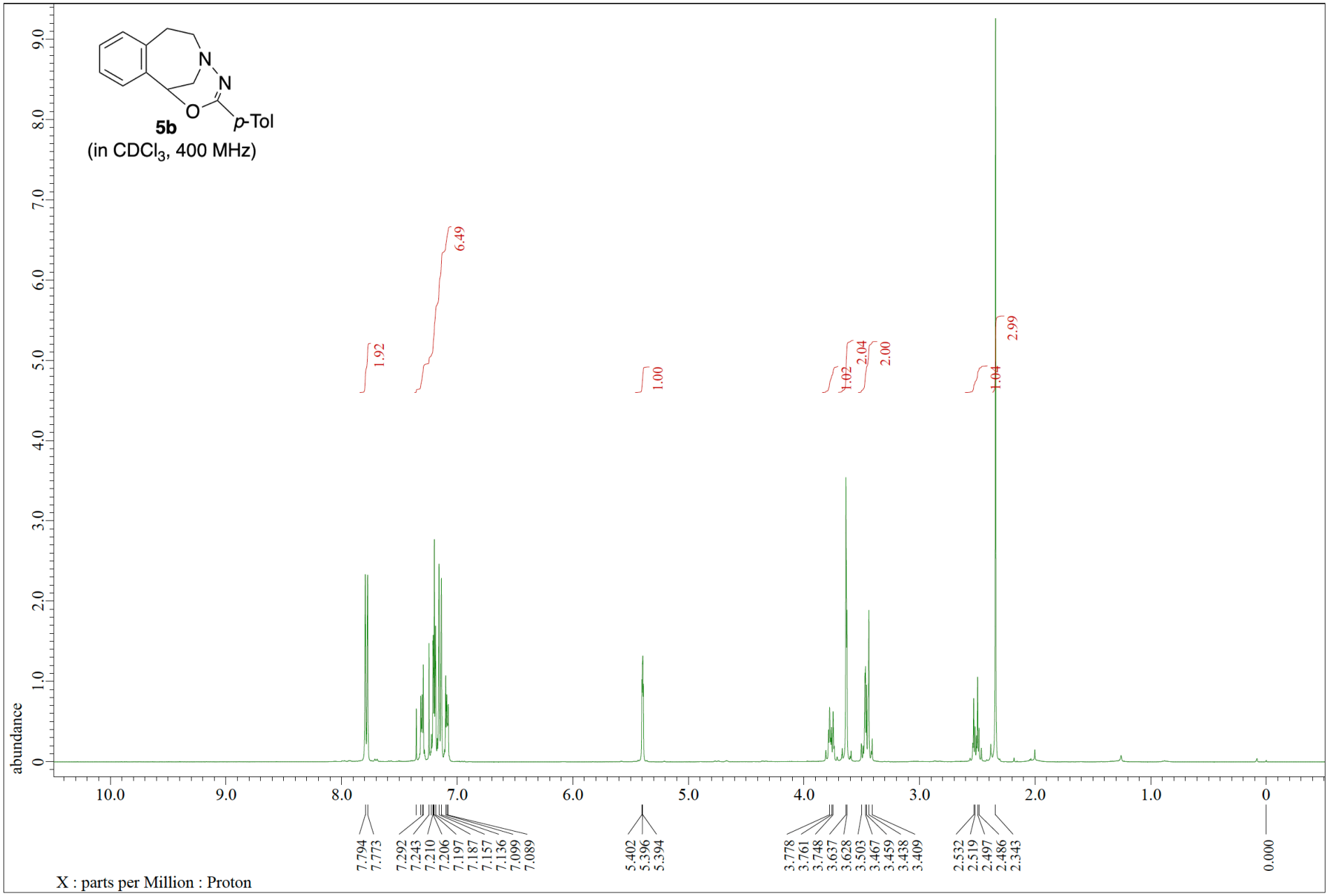

Br
N
N
H
O
Ph
N2
CO2Et
4g
(in CDCl3, 400 MHz)
abundance
X : parts per Million : Proton
2.08
1.07
3.32
2.09
1.08
1.00
2.11
2.87
1.09
3.11
7.779
7.761
7.634
7.509
7.490
7.472
7.417
7.398
7.379
7.333
7.319
7.270
7.038
7.016
5.171
4.188
4.171
4.152
4.135
3.436
3.427
3.259
3.233
2.864
2.824
1.184
1.167
1.149
0.000

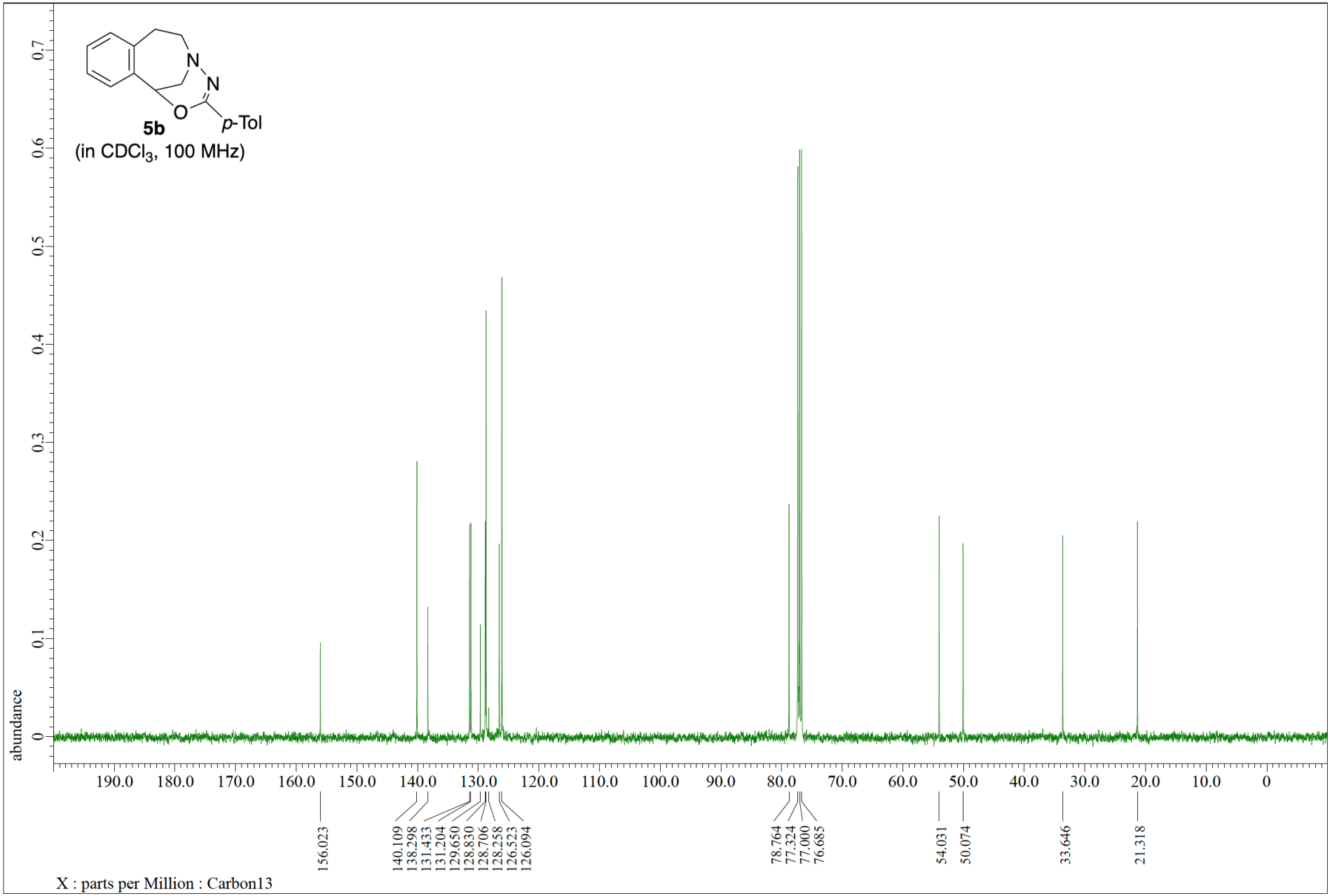

Br
N
N
H
O
Ph
N2
CO2Et
4g
(in CDCl3, 100 MHz)
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.369
165.834
134.684
133.769
133.368
131.652
130.794
130.537
129.764
128.515
127.057
120.144
77.315
77.000
76.676
62.040
61.325
60.009
52.038
28.784
14.282
X : parts per Million : Carbon13

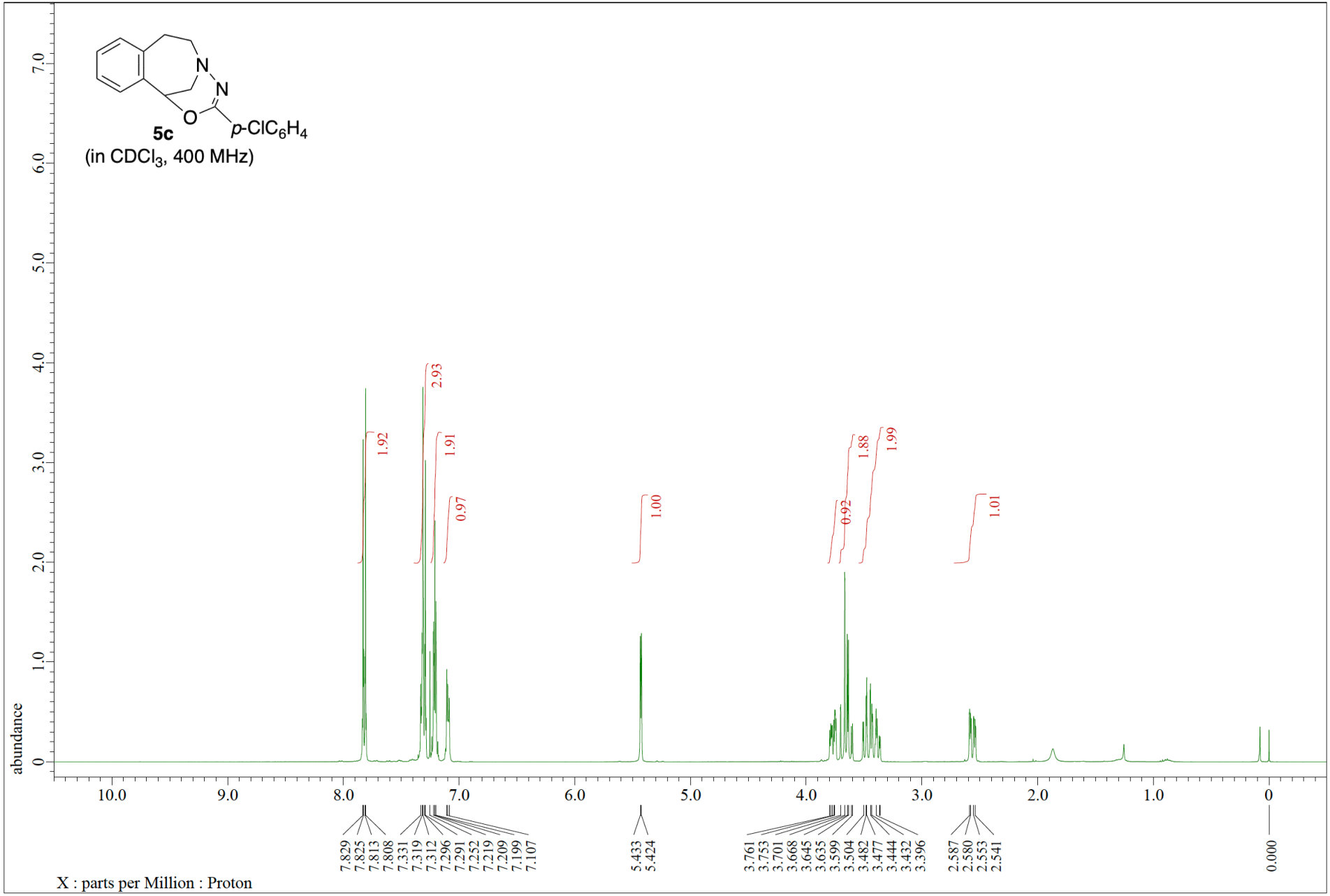
2) ^{1}H and ^{13}C NMR spectra of 3-benzazepine derivatives **5a-5g**

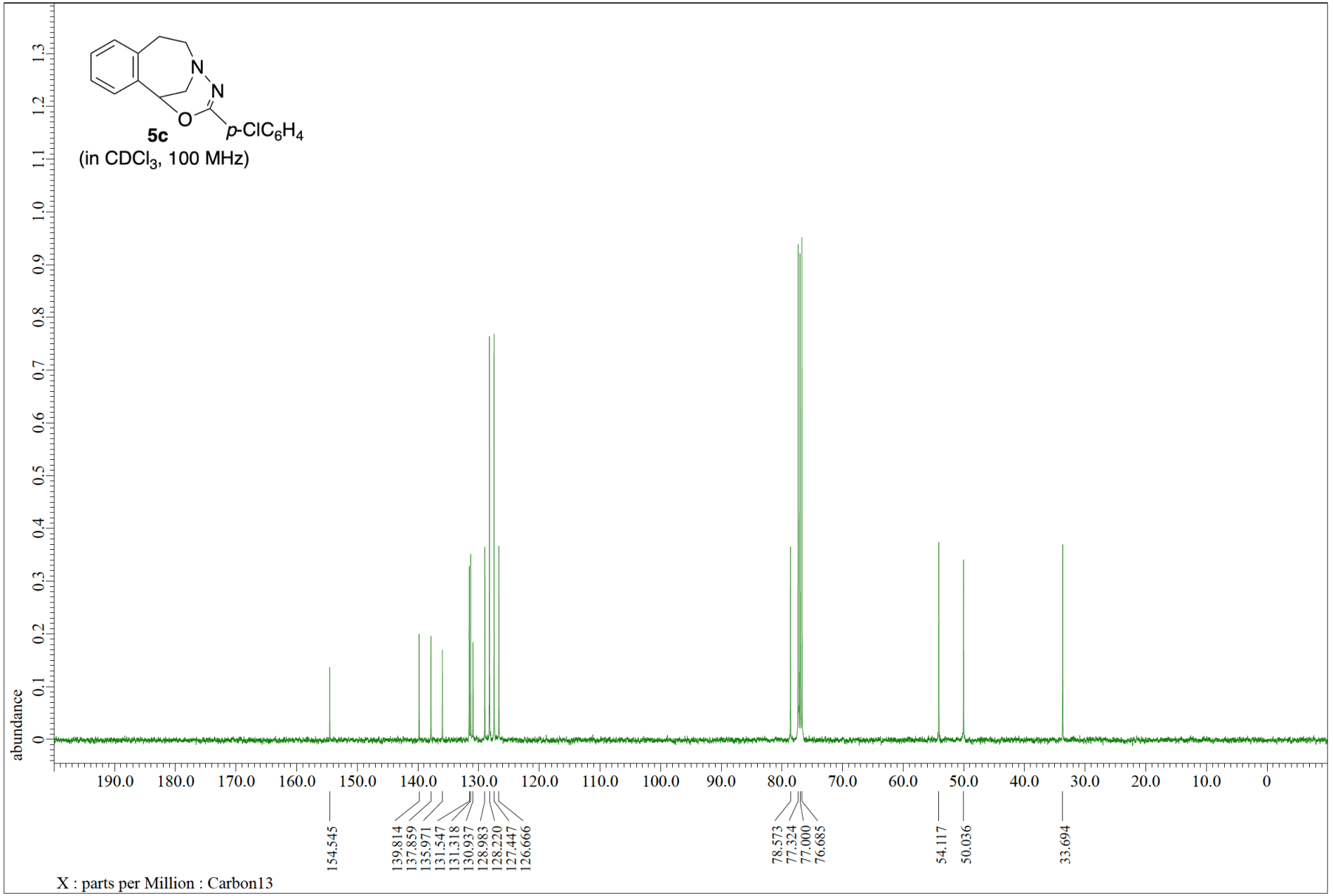


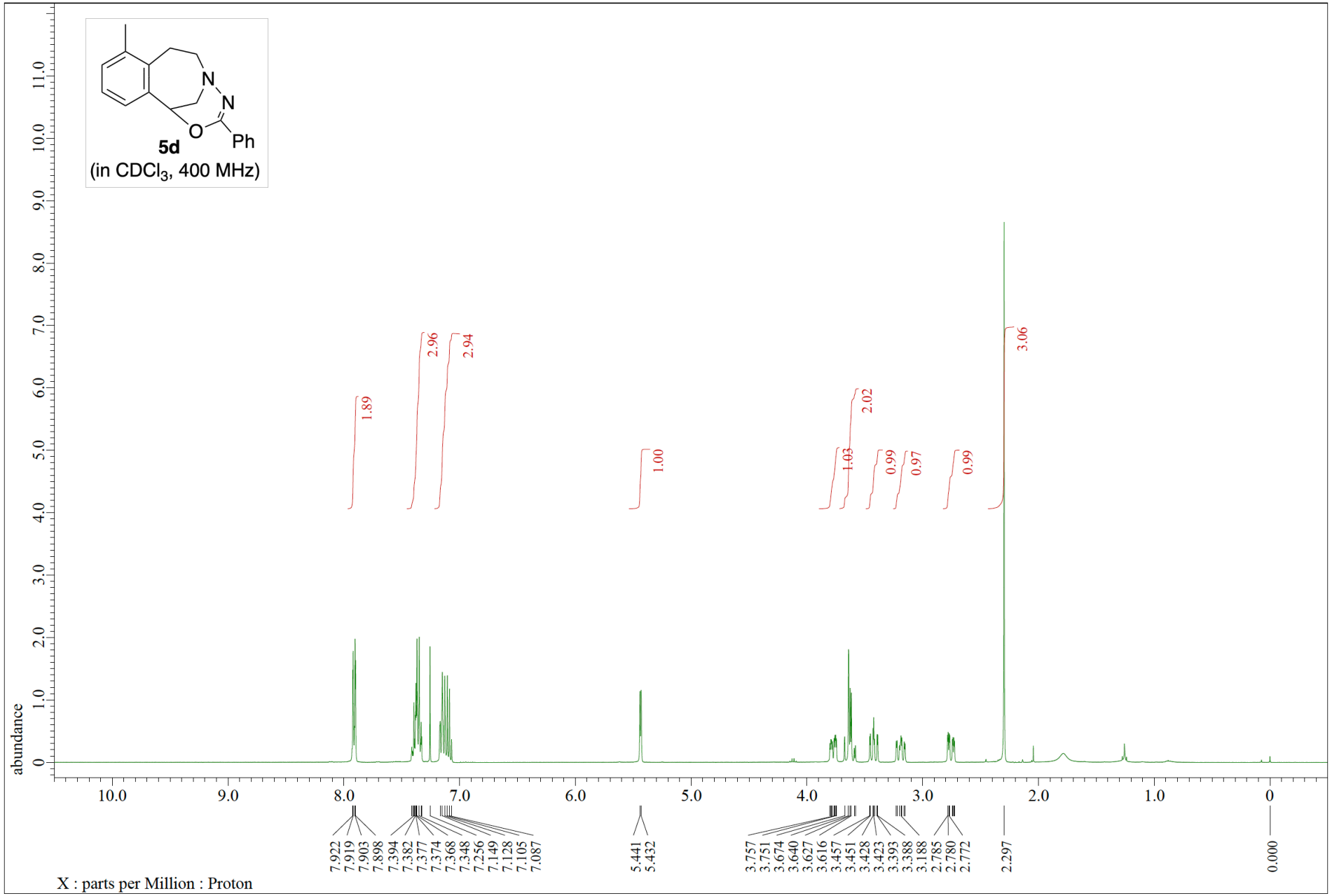

5a
(in CDCl3, 100 MHz)
abundance
X : parts per Million : Carbon13
155.546
139.852
138.012
132.358
131.404
131.156
129.907
128.782
127.924
126.484
126.046
78.535
77.315
77.000
76.676
53.955
49.941
33.560

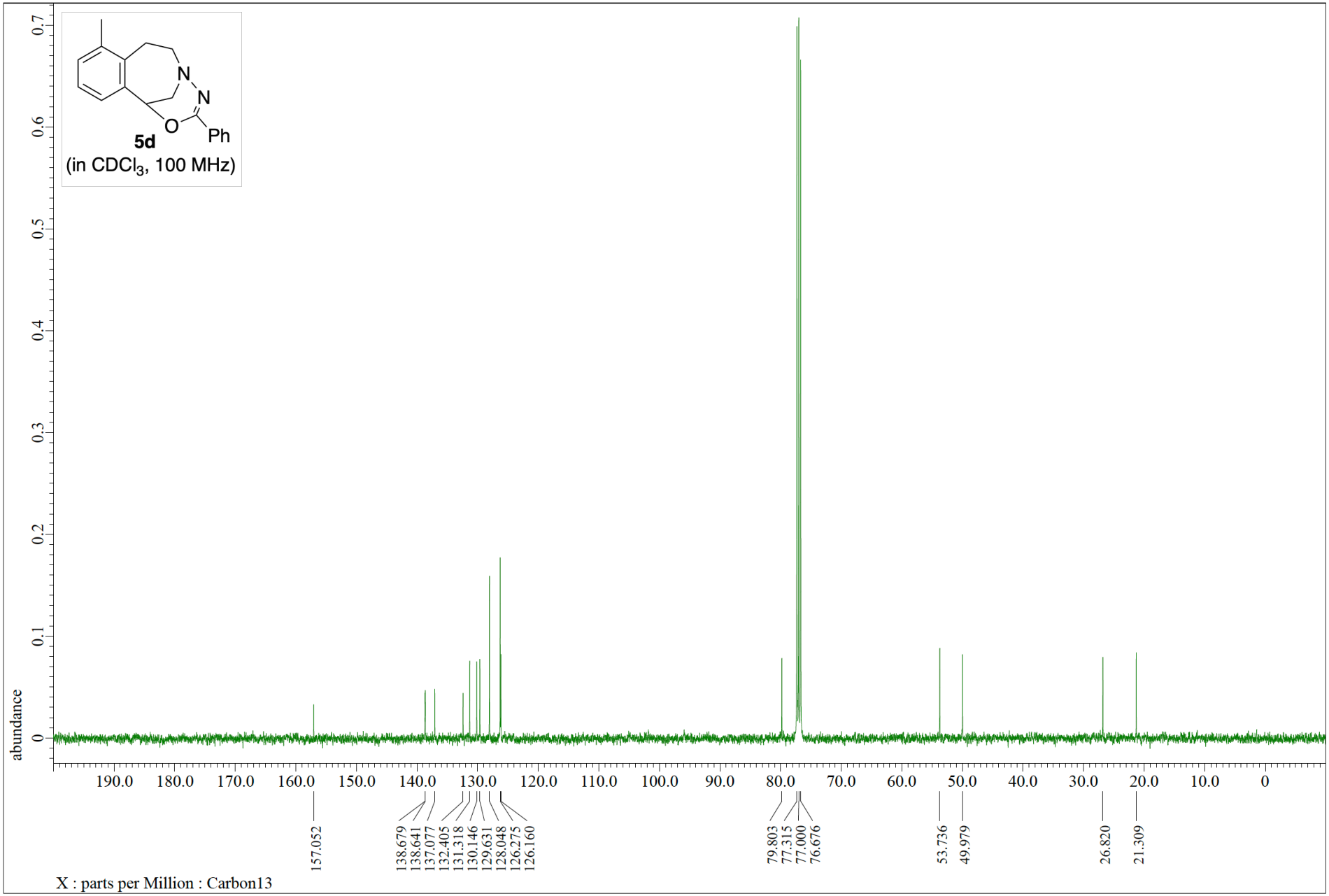

5b
(in CDCl3, 400 MHz)
p-Tol
abundance
X : parts per Million : Proton
1.92
6.49
1.00
1.02
2.04
2.00
1.04
2.99
7.794
7.773
7.292
7.243
7.210
7.206
7.197
7.187
7.157
7.136
7.099
7.089
5.402
5.396
5.394
3.778
3.761
3.748
3.637
3.628
3.503
3.467
3.459
3.438
3.409
2.532
2.519
2.497
2.486
2.343
0.000

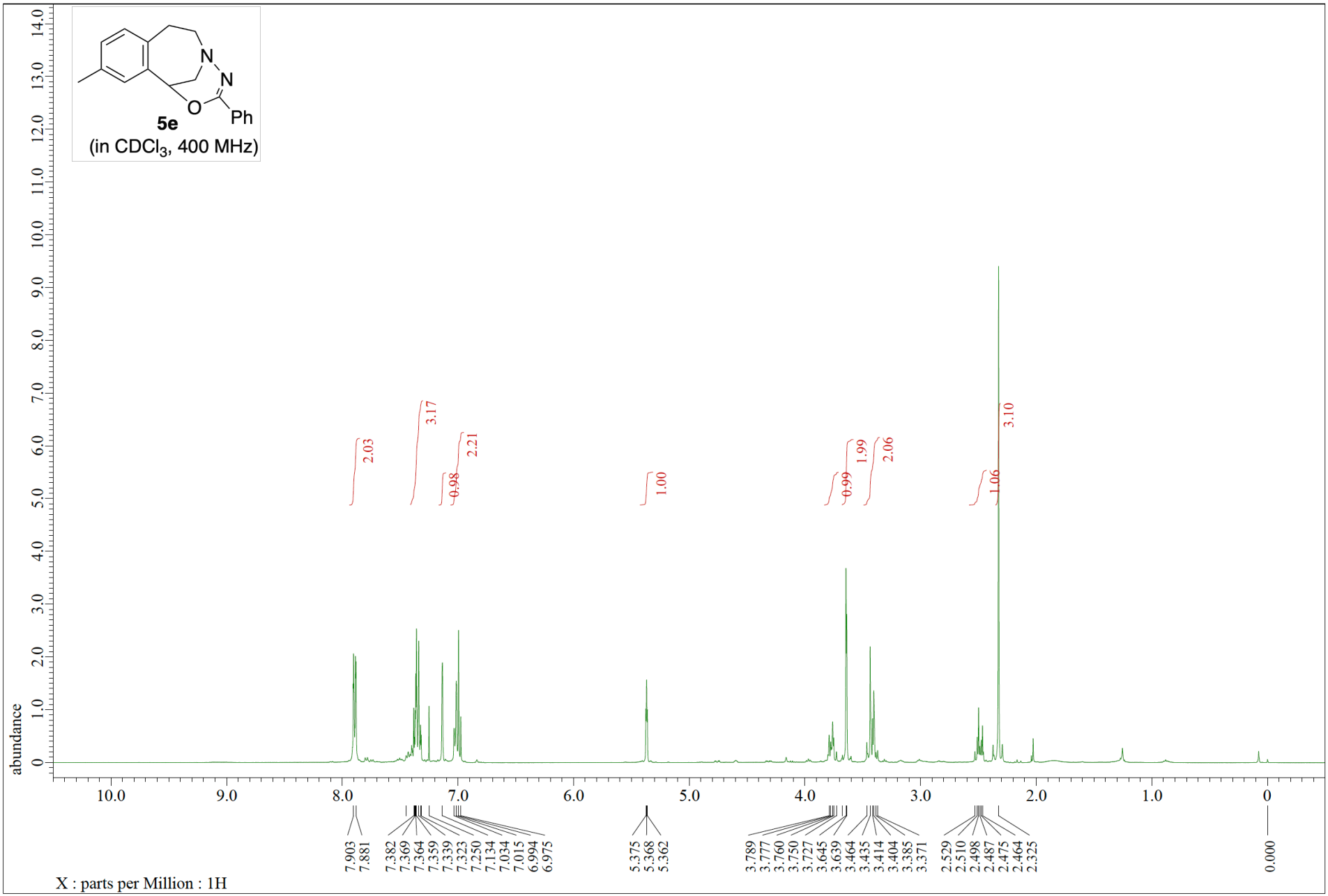

5b
(in CDCl3, 100 MHz)
p-Tol
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
156.023
140.109
138.298
131.433
131.204
129.650
128.830
128.706
128.258
126.523
126.094
78.764
77.324
77.000
76.685
54.031
50.074
33.646
21.318
X : parts per Million : Carbon13

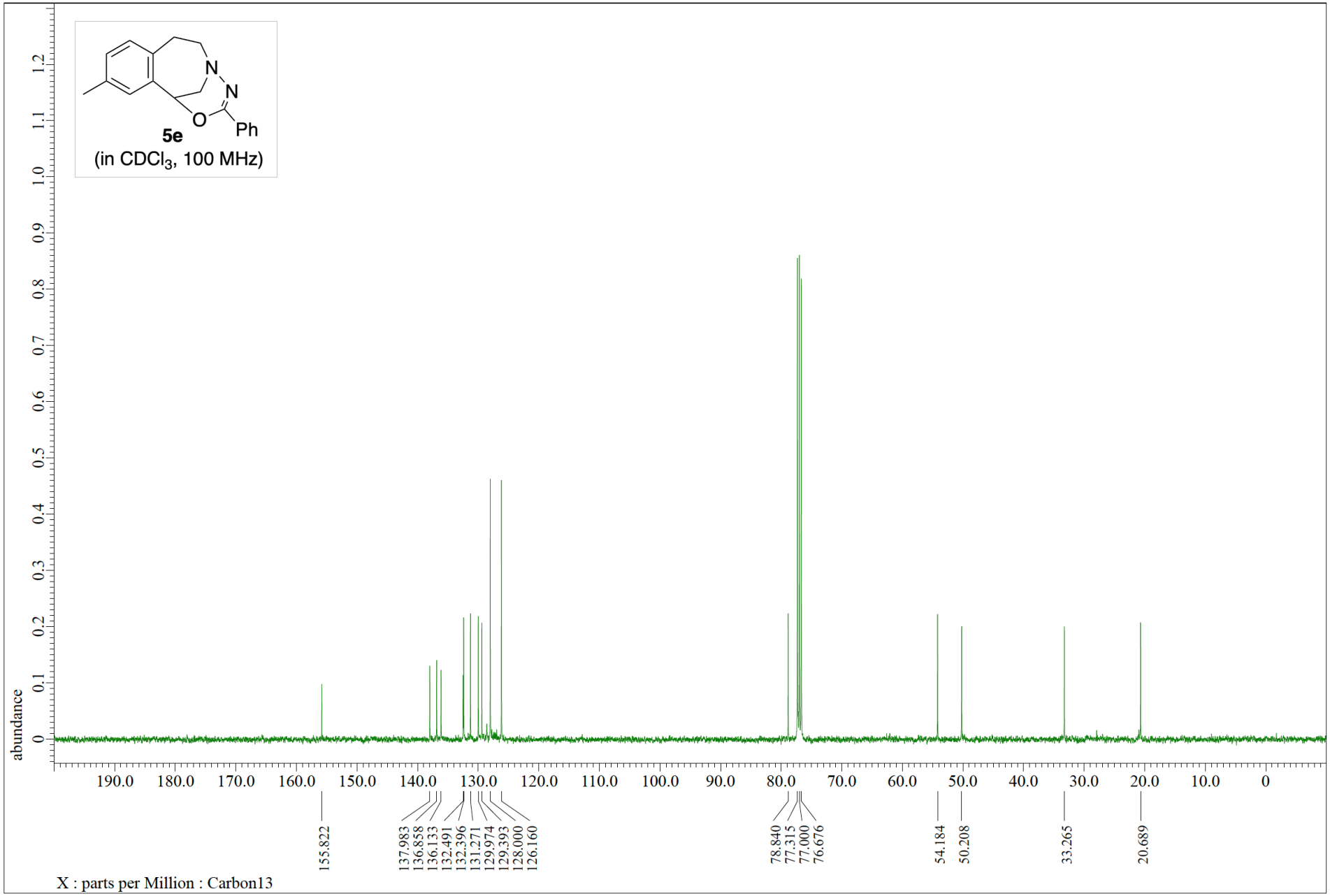

5c
p-ClC6H4
(in CDCl3, 400 MHz)
abundance
X : parts per Million : Proton
1.92
2.93
1.91
0.97
1.00
0.92
1.88
1.99
1.01
7.829
7.825
7.813
7.808
7.331
7.319
7.312
7.296
7.291
7.252
7.219
7.209
7.199
7.107
5.433
5.424
3.761
3.753
3.701
3.668
3.645
3.635
3.599
3.504
3.482
3.477
3.444
3.432
3.396
2.587
2.580
2.553
2.541
0.000

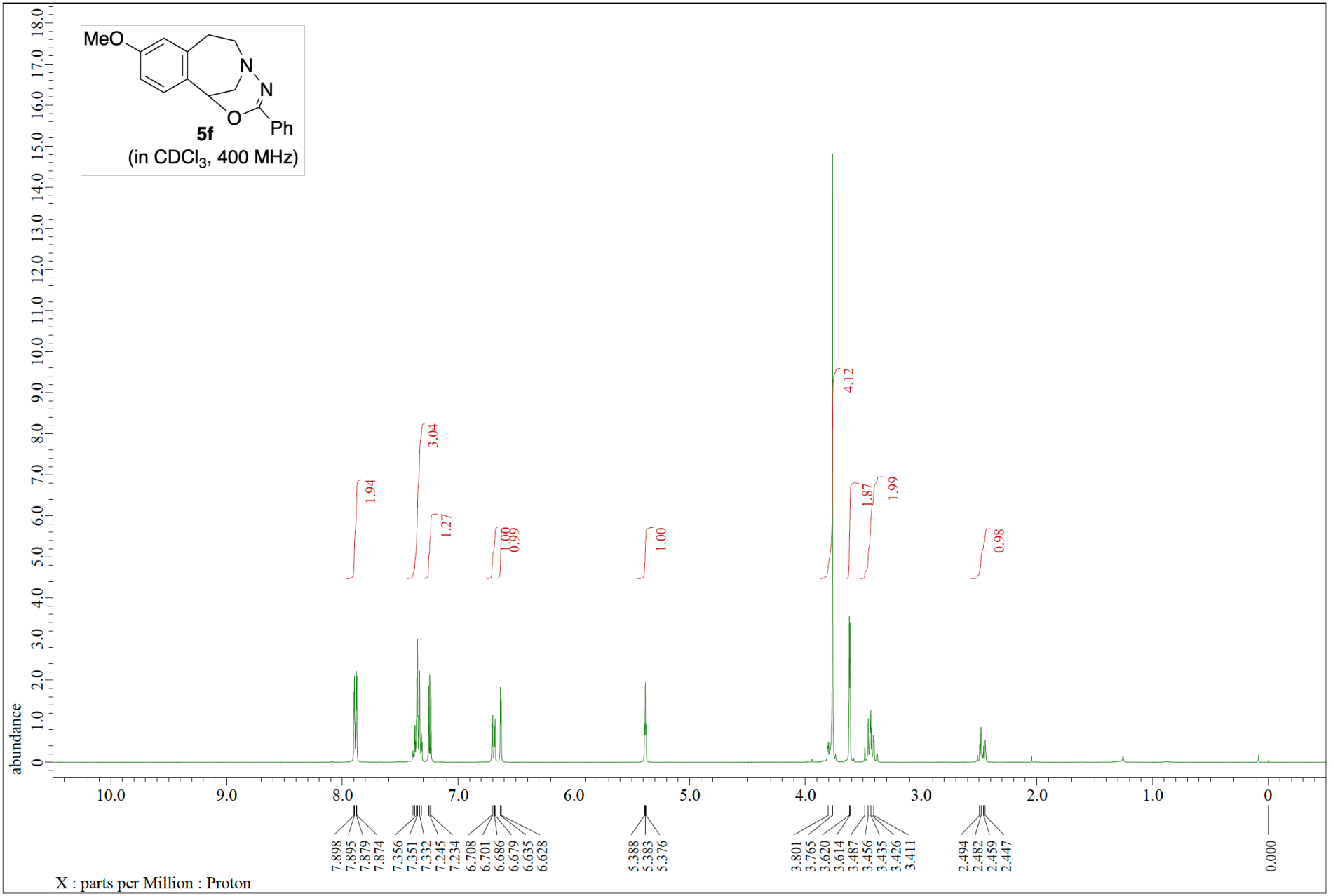

5c
p-ClC6H4
(in CDCl3, 100 MHz)
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
154.545
139.814
137.859
135.971
131.547
131.318
130.937
128.983
128.220
127.447
126.666
78.573
77.324
77.000
76.685
54.117
50.036
33.694
X : parts per Million : Carbon13

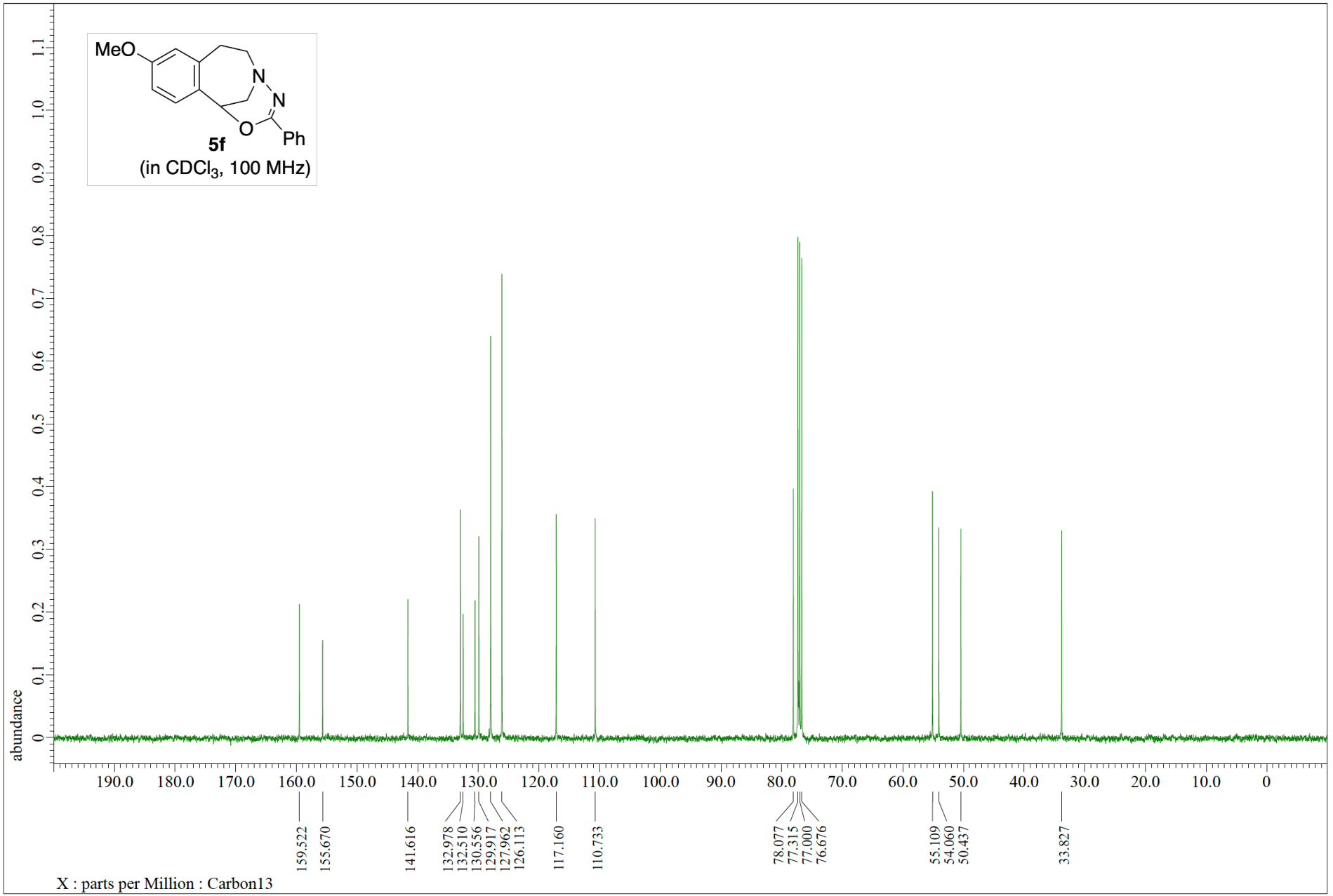

5d
(in CDCl3, 400 MHz)
abundance
X : parts per Million : Proton
1.89
2.96
2.94
1.00
1.03
2.02
0.99
0.97
0.99
3.06
7.922
7.919
7.903
7.898
7.394
7.382
7.377
7.374
7.368
7.348
7.256
7.149
7.128
7.105
7.087
5.441
5.432
3.757
3.751
3.674
3.640
3.627
3.616
3.457
3.451
3.428
3.423
3.393
3.388
3.188
2.785
2.780
2.772
2.297
0.000

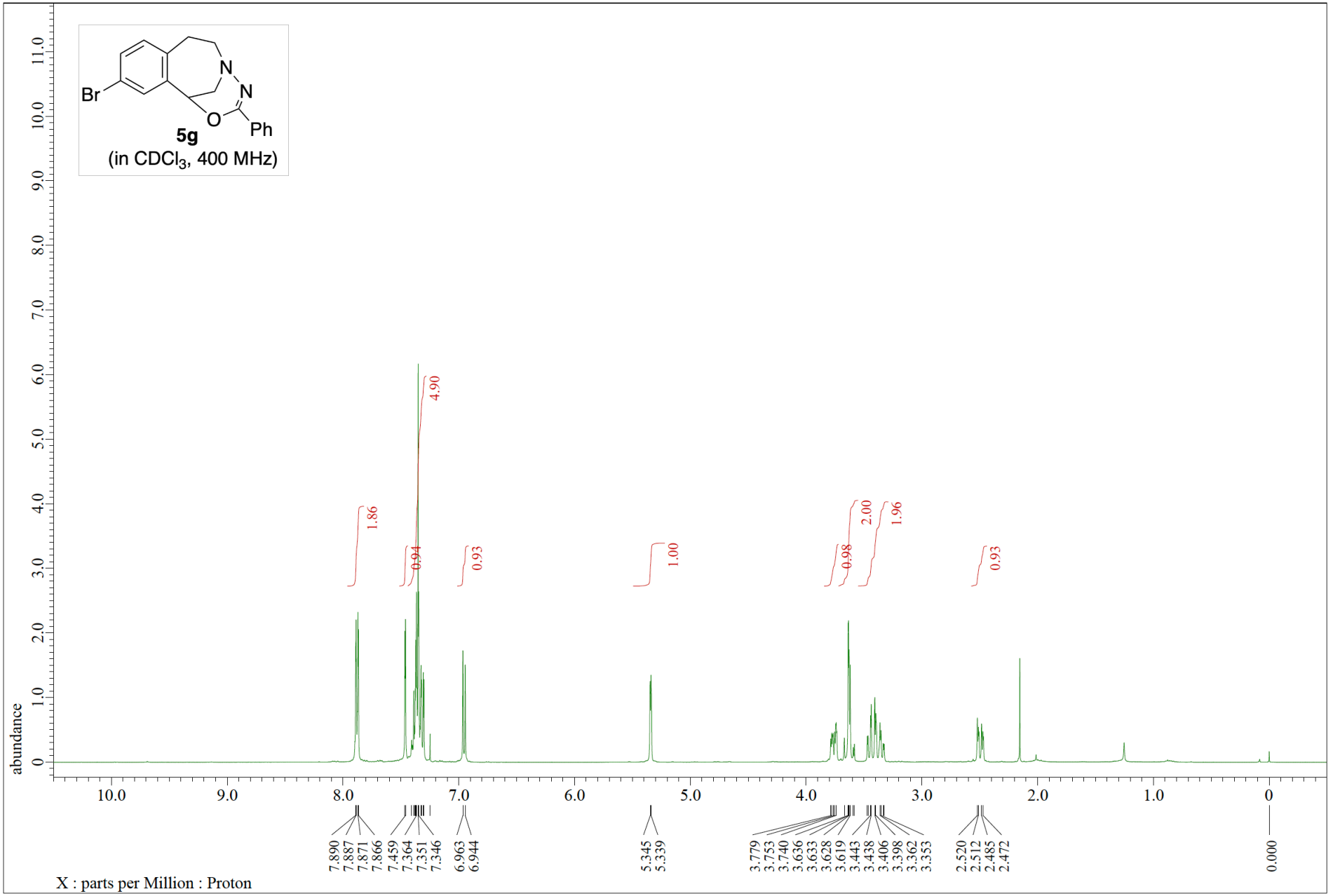

5d
(in CDCl3, 100 MHz)
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
157.052
138.679
138.641
137.077
132.405
131.318
130.146
129.631
128.048
126.275
126.160
79.803
77.315
77.000
76.676
53.736
49.979
26.820
21.309
X : parts per Million : Carbon13

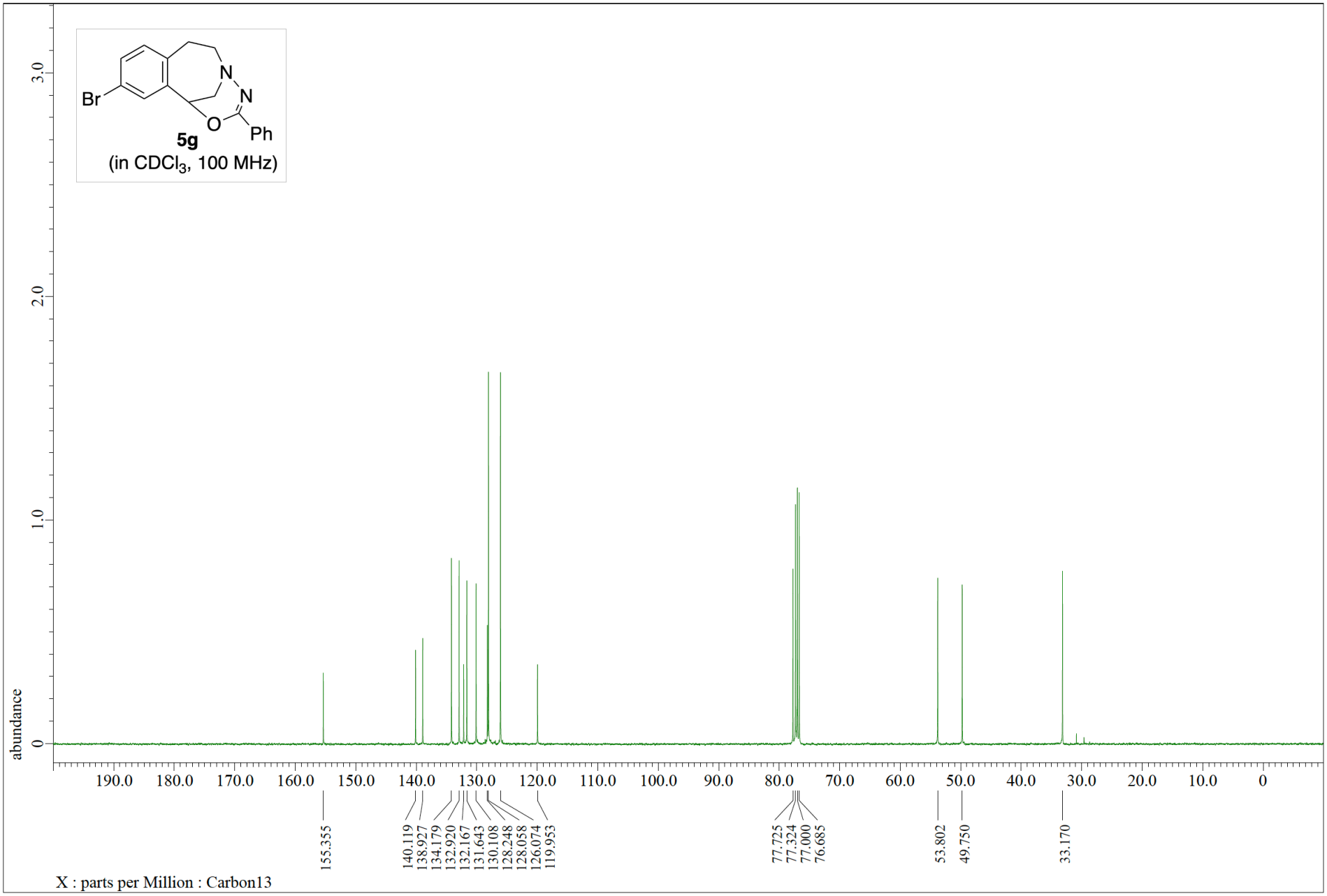

5e
(in CDCl3, 400 MHz)
abundance
X : parts per Million : 1H
2.03
3.17
0.98
2.21
1.00
0.99
1.99
2.06
1.06
3.10
7.903
7.881
7.382
7.369
7.364
7.359
7.339
7.323
7.250
7.134
7.034
7.015
6.994
6.975
5.375
5.368
5.362
3.789
3.777
3.760
3.750
3.727
3.645
3.639
3.464
3.435
3.414
3.404
3.385
3.371
2.529
2.510
2.498
2.487
2.475
2.464
2.325
0.000


5e
(in CDCl3, 100 MHz)
abundance
X : parts per Million : Carbon13
155.822
137.983
136.858
136.133
132.491
132.396
131.271
129.974
129.393
128.000
126.160
78.840
77.315
77.000
76.676
54.184
50.208
33.265
20.689

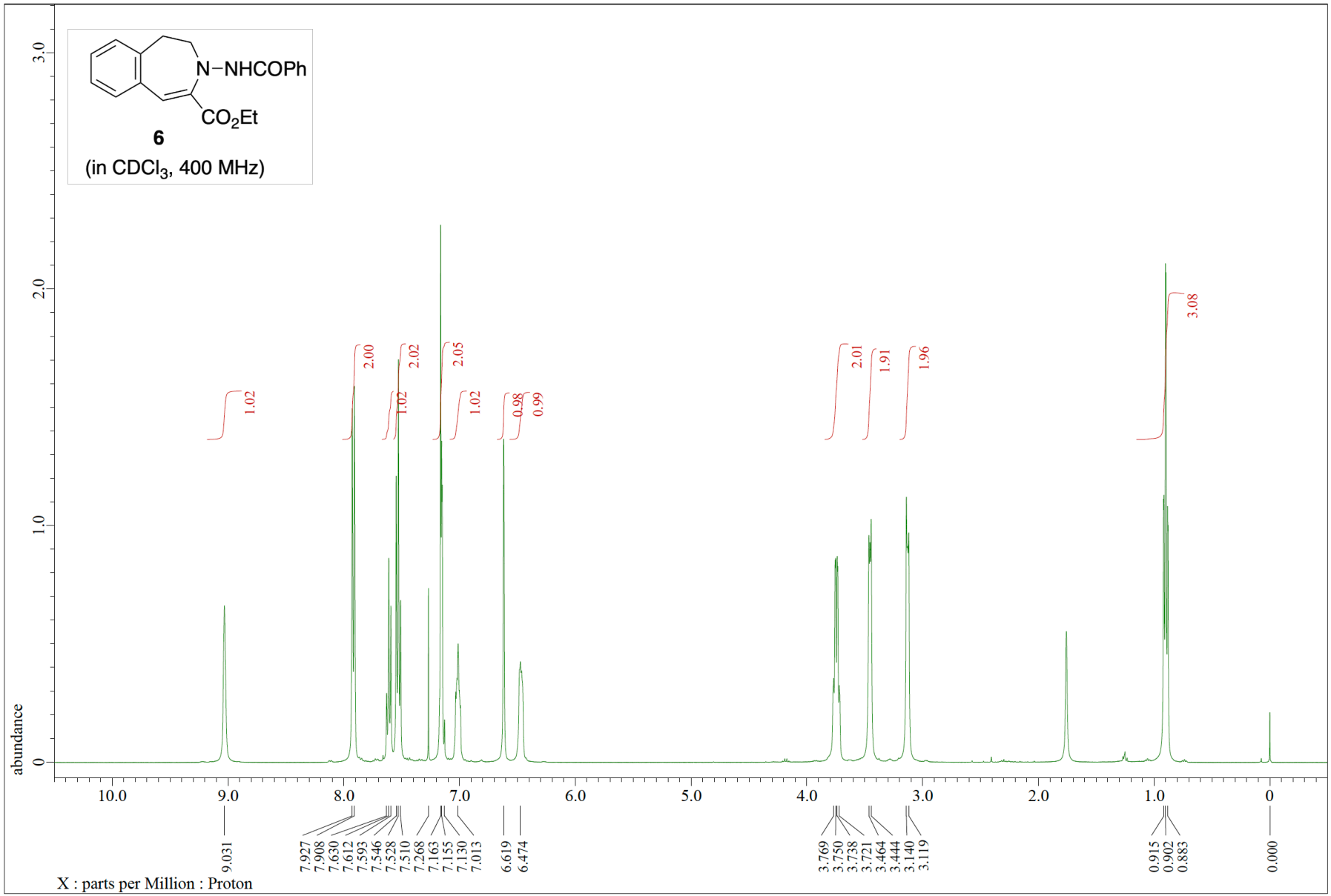

MeO
N
N
O
Ph
5f
(in CDCl3, 400 MHz)
abundance
X : parts per Million : Proton
1.94
3.04
1.27
1.00
0.98
1.00
4.12
1.87
1.99
0.98
7.898
7.895
7.879
7.874
7.356
7.351
7.332
7.245
7.234
6.708
6.701
6.686
6.679
6.635
6.628
5.388
5.383
5.376
3.801
3.765
3.620
3.614
3.487
3.456
3.435
3.426
3.411
2.494
2.482
2.459
2.447
0.000

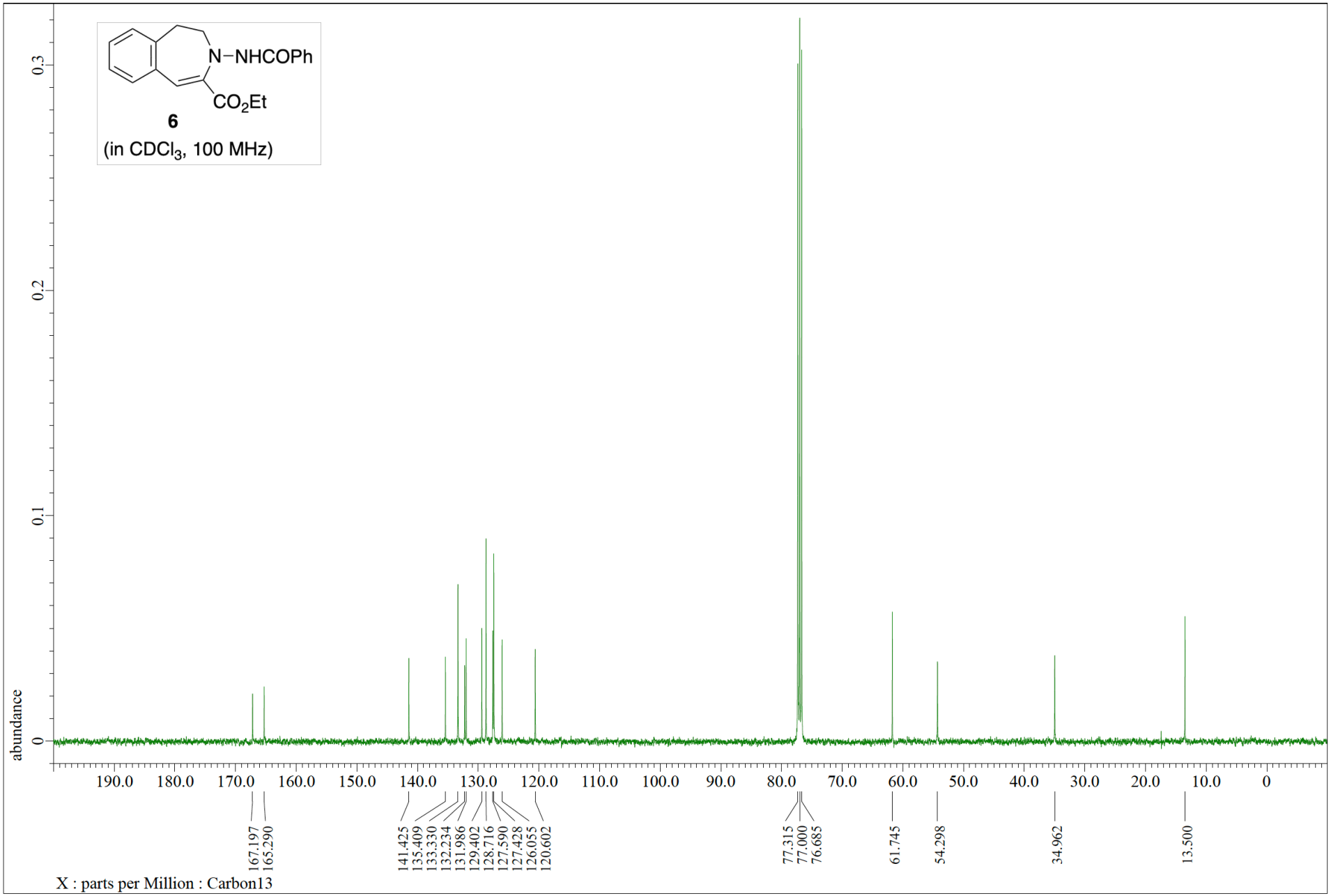

MeO
N
N
O
Ph
5f
(in CDCl3, 100 MHz)
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
159.522
155.670
141.616
132.978
132.510
130.556
129.917
127.962
126.113
117.160
110.733
78.077
77.315
77.000
76.676
55.109
54.060
50.437
33.827
X : parts per Million : Carbon13


Br
N
N
O
Ph
5g
(in CDCl3, 400 MHz)
abundance
X : parts per Million : Proton
1.86
0.94
4.90
0.93
1.00
0.98
2.00
1.96
0.93
7.890
7.887
7.871
7.866
7.459
7.364
7.351
7.346
6.963
6.944
5.345
5.339
3.779
3.753
3.740
3.636
3.633
3.628
3.619
3.443
3.438
3.406
3.398
3.362
3.353
2.520
2.512
2.485
2.472
0.000


Br
N
N
O
Ph
5g
(in CDCl3, 100 MHz)
abundance
3.0
2.0
1.0
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
155.355
140.119
138.927
134.179
132.920
132.167
131.643
130.108
128.248
128.058
126.074
119.953
77.725
77.324
77.000
76.685
53.802
49.750
33.170
X : parts per Million : Carbon13

3) ^{1}H and ^{13}C NMR spectra of **6**




N–NHCOPh
CO2Et
6
(in CDCl3, 100 MHz)
abundance
0.3
0.2
0.1
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
167.197
165.290
141.425
135.409
133.330
132.234
131.986
129.402
128.716
127.590
127.428
126.055
120.602
77.315
77.000
76.685
61.745
54.298
34.962
13.500
X : parts per Million : Carbon13