Azomethine Ylide Cycloaddition of 1,3- dienyl esters: Highly regio- and diastereoselective synthesis of functionalized pyrrolidinochromenes

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Supporting Information

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EXPERIMENTAL SECTION

General Information and Materials

Commercial reagents were used without further purification. IR spectra were recorded on a Perkin Elmer-FTIR spectrometer using solid samples as KBr plates. For compounds ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra were recorded in deuterochloroform ($CDCl_3$) on a Bruker 400 MHz spectrometer using tetramethylsilane (TMS, $\delta = 0$) as an internal standard at room temperature. Mass spectra were recorded on Agilent 1200 LC/MS-6110 mass spectrometer. The structures of all compounds (**8a-v, 10** and **11**) were confirmed by ^{1}H NMR, ^{13}C NMR spectrometry, and ESI-HRMS spectrometry. Spectral data of ^{1}H, ^{13}C NMR and ESI-HRMS of all compounds (**8a-v, 10 and 11**) are listed below.

Starting material **3a-c** and **4a-c** prepared by known procedure[1,2]

General Procedure for the Synthesis of compound (6a-o):

To a 25mL round bottom flask was added 2-hydroxyarylaldehyde **4** (1 mmol), K_2CO_3 (3.0 mmol), methyl (2*Z*,4*E*)-2-(bromomethyl)-5-phenylpenta-2,4-dienoate **5** (1 mmol) and acetonitrile (5 mL). The RB was stirred at room temperature for 3 hours. After the completion of the reaction as indicated by the TLC, EtOAc (10 mL) was added to the reaction mixture which was extracted with EtOAc and water (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, and filtered. The solvent was removed under reduced pressure, and the crude product was purified by silica gel chromatography (2:8; Ethyl Acetate/Hexane) to afford the product **6a-o** as solids.

General Procedure for the Synthesis of compounds (8a-v):

To a 25mL round bottom flask was added 1,3-diolefin aldehyde **6a** (0.3 mmol), N-methyl glycine ester **7a** (1.2 mmol), Et_3N (30 mol %) and toluene (5 mL) and the RB was kept under N_2 balloon at reflux for 8 hours. After the completion of the reaction as indicated

by the TLC, EtOAc (10 mL) was added to the reaction mixture which was extracted with EtOAc and water (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, and filtered. The solvent was removed under reduced pressure, and the crude product was purified by silica gel chromatography (1:8; Ethyl Acetate/Hexane) to afford the product **8a** as white color solid.

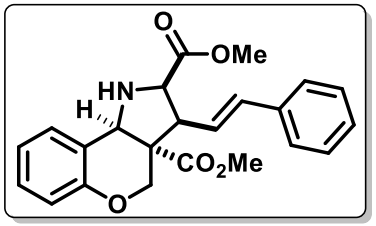
Typical experimental procedure for the synthesis of compound (10):

To a 25mL round bottom flask was added 1,3-diolefin aldehyde **8n** (0.2 mmol), pipecolinic acid **9** (0.8 mmol) and ethanol (5 mL) and the RB was kept at reflux for 12 hours. After the completion of the reaction as indicated by the TLC, EtOAc (10 mL) was added to the reaction mixture which was extracted with EtOAc and water (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, and filtered. The solvent was removed under reduced pressure, and the crude product was purified by silica gel chromatography (4:6; Ethyl Acetate/Hexane) to afford the product **10** as white color solid.

Typical experimental procedure for the synthesis of compound (8):

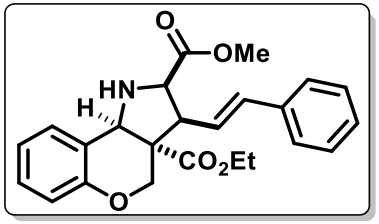
To a 25mL round bottom flask was added tricyclic compound **8a** (0.2 mmol), $NaBH_4$ (3 equiv.) in a mixture of THF: Methanol solvent system (5 mL, 1:1) and the RB were kept at reflux for 12 hours under N_2 balloon. After the completion of the reaction as indicated by the TLC, EtOAc (10 mL) was added to the reaction mixture which was extracted with EtOAc and water (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, and filtered. The solvent was removed under reduced pressure, and the crude product was purified by silica gel chromatography (4:6; Ethyl Acetate/Hexane) to afford the product **11** as colorless oil

Dimethyl (*E*)-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole-2,3a(4*H*)-dicarboxylate (8a)



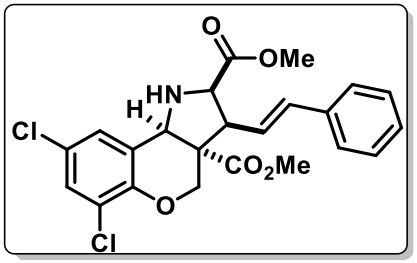
Physical state :White solid, yield : 91% (107 mg), M. P: 126-128 °C ; ^{1}H NMR (400 MHz, CDCl3) δ 7.40 (d, J = 7.6 Hz, 1H), 7.32 (d, J = 4.3 Hz, 4H), 7.29 – 7.23 (m, 2H), 7.24 – 7.18 (m, 1H), 6.97 (t, J = 7.5 Hz, 1H), 6.91 (d, J = 8.3 Hz, 1H), 6.55 (d, J = 15.4 Hz, 1H), 5.83 (dd, J = 15.4, 10.9 Hz, 1H), 4.58 (s, 1H), 4.51 (d, J = 11.3 Hz, 1H), 4.24 (d, J = 9.7 Hz, 1H), 4.00 (d, J = 11.2 Hz, 1H), 3.72 (s, 3H), 3.68 (d, J = 9.9 Hz, 1H), 3.63 (s, 3H).^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.1, 172.2, 154.3, 136.4, 136.0, 130.8, 129.3, 128.8, 128.2, 126.6, 121.4, 121.2, 120.7, 117.3, 64.3, 63.7, 59.5, 55.7, 55.3, 52.8, 52.4. HRMS (ESI): Calc. For $C_{23}H_{24}NO_5$ [M+H]+ 394.1654, measured 394.1647.

3a-Ethyl 2-methyl (*E*)-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole-2,3a(4*H*)-dicarboxylate (8b)



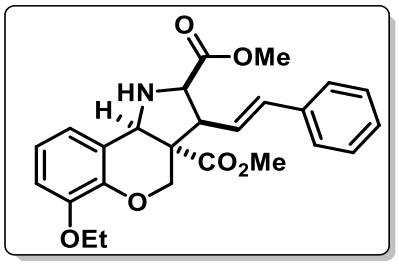
Physical state: White solid,Yield: 89% (111 mg) , M. P (°C) :124-126 ,^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.63 – 7.11 (m, 7H), 7.13 – 6.65 (m, 2H), 6.56 (d, *J* = 15.4 Hz, 1H), 5.84 (dd, *J* = 15.4, 10.9 Hz, 1H), 4.61 (s, 1H), 4.53 (d, *J* = 11.2 Hz, 1H), 4.23-4.28 (m, 3H), 4.01 (d, *J* = 11.2 Hz, 1H), 3.72 (d, *J* = 10.5 Hz, 1H).3.67 (s, 3H), 2.44 (s, 1H), 1.23 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.4, 172.2, 154.3, 136.4, 136.0, 130.8, 129.3, 128.8, 128.2, 126.5, 121.4, 121.2, 120.6, 117.2, 64.3, 63.5, 61.6, 59.2, 55.6, 55.2, 52.5, 14.3. HRMS (ESI): Calc. for $C_{24}H_{26}NO_5$ $[M+H]^+$ 408.1811, measured 408.1807.

Dimethyl (*E*)-6,8-dichloro-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole-2,3a(4*H*)-dicarboxylate (8c):



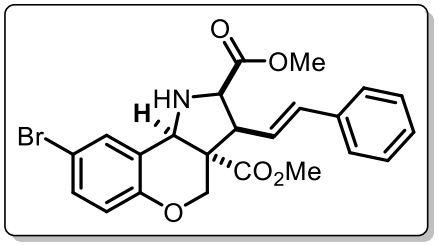
Physical state: White solid, Yield: 90% (125 mg), M. P (°C) :140-142, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.25 (m, 7H), 6.55 (d, *J* = 15.4 Hz, 1H), 5.78 (dd, *J* = 15.4, 10.8 Hz, 1H), 4.65 (dd, *J* = 11.3, 1.5 Hz, 1H), 4.53 (s, 1H), 4.21 (d, *J* = 9.7 Hz, 1H), 4.03 (d, *J* = 11.4 Hz, 1H), 3.73 (s, 3H), 3.69 (d, *J* = 2.6 Hz, 1H), 3.64 (s, 3H), 2.69 (s, 1H). ^{13}C NMR (100 MHz, CDCl3) δ 172.5, 172.1, 149.1, 136.4, 136.2, 129.6, 129.0, 128.9, 128.4, 126.6, 126.1, 123.6, 123.0, 120.5, 65.2, 63.4, 58.9, 55.2, 54.9, 53.0, 52.6. HRMS (ESI): Calc. For $C_{23}H_{22}Cl_2NO_5$ $[M+H]^+$ 462.0875, measured 462.0876.

Dimethyl (*E*)-6-ethoxy-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole-2,3a(4*H*)-dicarboxylate (8d)



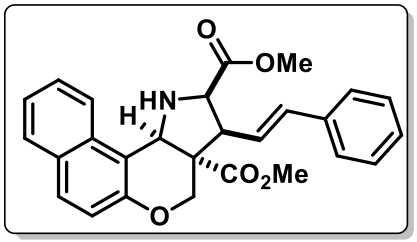
Physical state: White solid, Yield: 82 % (108 mg), M. P (°C) :128-130, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 6.82 (m, 7H), 6.55 (d, *J* = 15.4 Hz, 1H), 5.78 (dd, *J* = 15.4, 10.8 Hz, 1H), 4.67 (s, 1H), 4.65 (d, *J* = 1.3 Hz, 1H), 4.21 (d, *J* = 9.7 Hz, 1H), 4.03 (d, *J* = 11.4 Hz, 1H), 3.74 – 3.72 (m, 4H). 3.65 (s, 3H) 3.63 (d, *J* = 5.7 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.8, 171.8, 148.0, 144.2, 136.3, 136.2, 128.8, 128.2, 126.6, 122.3, 121.3, 121.2, 120.8, 112.5, 64.8, 64.5, 63.3, 59.0, 55.1, 55.0, 52.9, 52.6, 14.9, HRMS (ESI): Calc. for $C_{25}H_{28}NO_6$ $[M+H]^+$ 438.1917, measured 438.1916

Dimethyl (*E*)-8-bromo-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole-2,3a(4*H*)-dicarboxylate (8e):



Physical state: White solid, Yield: 85% (120 mg), M. P (°C) :132-134, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 2.5 Hz, 2H), 7.33 – 7.27 (m, 6H), 6.79 (d, *J* = 8.8 Hz, 1H), 6.54 (d, *J* = 15.4 Hz, 1H), 5.79 (dd, *J* = 15.4, 10.8 Hz, 1H), 4.52 (s, 1H), 4.49 (d, *J* = 1.5 Hz, 1H), 4.22 (d, *J* = 9.8 Hz, 1H), 3.97 (d, *J* = 11.2 Hz, 1H), 3.72 (s, 3H), 3.68 (d, *J* = 3.3 Hz, 1H), 3.64 (s, 3H) 2.54 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.7, 172.2, 153.4, 136.3, 136.2, 133.4, 132.2, 128.8, 128.3, 126.6, 122.8, 120.8, 119.1, 113.5, 64.4, 63.5, 59.0, 55.4, 55.0, 52.9, 52.5. HRMS (ESI): Calc. for $C_{23}H_{23}BrNO_5$ $[M+H]^+$ 472.0760, measured 472.0753, 474.0736.

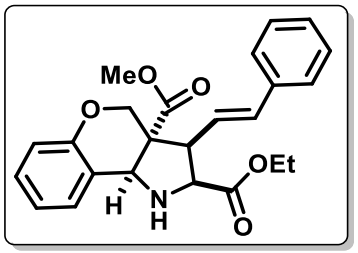
Dimethyl (*E*)-3-styryl-1,2,3,11c-tetrahydrobenzo[5,6]chromeno[4,3-b]pyrrole-2,3a(4*H*)-dicarboxylate (8f):



Physical state: White solid, Yield: 87 % (115 mg), M. P (°C): 140-142, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.5 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 9.0 Hz, 1H), 7.59 – 7.52 (m, 1H), 7.41 – 7.34 (m, 5H), 7.31 – 7.28 (m, 1H), 7.12 (d, *J* = 12.0 Hz 1H), 6.59 (d, *J* = 15.4 Hz, 1H), 5.85 (dd, *J* = 15.4, 10.9 Hz, 1H), 5.02 (s, 1H), 4.70 – 4.61 (m, 1H), 4.38 (d, *J* = 10.1 Hz, 1H), 4.18 (d, *J* = 11.1 Hz, 1H), 3.69 (s, 3H), 3.65 (s, 3H), 2.887 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.9, 172.7, 152.1, 136.4, 136.1, 133.5,

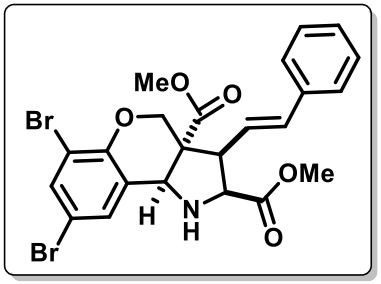
130.0, 129.4, 128.9, 128.4, 128.2, 127.1, 126.6, 124.0, 123.7, 121.1, 118.7, 112.7, 63.8, 63.7, 57.6, 55.6, 54.9, 52.8, 52.5. HRMS (ESI): Calc. for $C_{27}H_{26}NO_5$ $[M+H]^+$ 444.1811, measured 444.1812

2-Ethyl 3a-methyl (*E*)-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole-2,3a(4*H*)-dicarboxylate (8g)



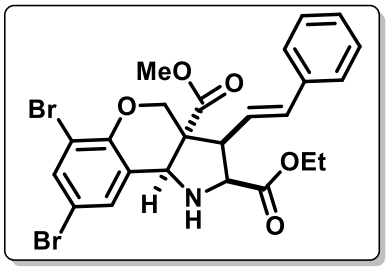
Physical state: White solid, Yield: 84% (103 mg), M. P (°C) :124-126, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 7.6, 1.7 Hz, 2H), 7.37 – 7.19 (m, 6H), 7.04 – 6.89 (m, 2H), 6.56 (d, *J* = 15.4 Hz, 1H), 5.86 (dd, *J* = 15.4, 10.9 Hz, 1H), 4.60 (d, *J* = 1.5 Hz, 1H), 4.54 (dd, *J* = 11.3, 1.5 Hz, 1H), 4.23 (d, *J* = 9.7 Hz, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 4.02 (d, *J* = 11.2 Hz, 1H), 3.74 (s, 3H), 3.71 (d, *J* = 10.3 Hz, 1H), 2.70 (s, 1H), 1.10 (t, *J* = 7.1 Hz, 3H).^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.1, 171.8, 154.3, 136.4, 135.9, 130.9, 129.3, 128.8, 128.2, 126.5, 121.5, 121.3, 120.8, 117.3, 64.3, 63.7, 61.6, 59.5, 55.8, 55.4, 52.8, 14.3. HRMS (ESI): Calc. for $C_{24}H_{26}NO_5$ $[M+H]^+$ 408.1811, measured 408.1807.

Dimethyl (*E*)-6,8-dibromo-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole-2,3a(4*H*)-dicarboxylate (8h)



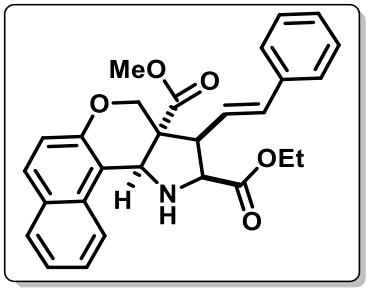
Physical state:White solid, Yield: 95% (153 mg), M. P (°C) :142-144, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 2.3 Hz, 1H), 7.51 (d, *J* = 2.3 Hz, 1H), 7.38 – 7.25 (m, 5H), 6.57 (d, *J* = 15.4 Hz, 1H), 5.80 (dd, *J* = 15.4, 10.8 Hz, 1H), 4.66 (dd, *J* = 11.3, 1.5 Hz, 1H), 4.56 (s, 1H), 4.23 (d, *J* = 9.6 Hz, 1H), 4.06 (d, *J* = 11.3 Hz, 1H), 3.75 (s, 3H), 3.71 (d, *J* = 10.2 Hz, 1H), 3.66 (s, 3H), 2.73 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.5, 172.1, 150.5, 136.4, 136.3, 135.1, 132.6, 128.9, 128.3, 126.6, 124.0, 120.6, 113.4, 112.1, 65.3, 63.4, 58.9, 55.2, 55.0, 53.0, 52.6. HRMS (ESI): Calc. for $C_{23}H_{22}Br_2NO_5$ $[M+H]^+$ 551.9844, measured 551.9852.

2-Ethyl 3a-methyl (*E*)-6,8-dibromo-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole-2,3a(4*H*)-dicarboxylate (8i)



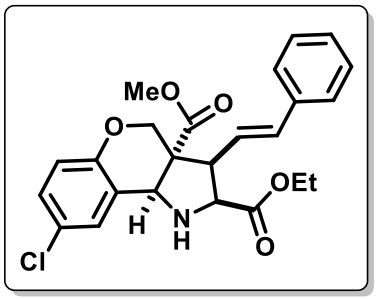
Physical state: White solid, Yield: 93 % (157 mg), M. P (°C) :144-146, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 2.3 Hz, 1H), 7.52 (d, *J* = 2.3 Hz, 1H), 7.37 – 7.25 (m, 5H), 6.57 (d, *J* = 15.4 Hz, 1H), 5.81 (dd, *J* = 15.5, 10.9 Hz, 1H), 4.67 (dd, *J* = 11.3, 1.5 Hz, 1H), 4.56 (d, *J* = 1.4 Hz, 1H), 4.20 (d, *J* = 9.7 Hz, 1H), 4.12 (dd, *J* = 7.1, 2.8 Hz, 2H), 4.06 (d, *J* = 11.3 Hz, 1H), 3.75 (s, 3H) 3.69 (d, *J* = 10.2 Hz, 1H), 1.09 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$,100 MHz):δ 172.5, 171.5, 150.5, 136.3, 136.2, 135.1, 132.6, 128.8, 128.6, 126.5, 124.0, 120.7, 113.4, 112.0, 65.3, 63.3, 61.7, 58.9, 55.2, 55.0, 53.0, 14.2. HRMS (ESI): Calc. for $C_{23}H_{22}Br_2NO_5$ $[M+H]^+$ 564.0021, measured 564.0030.

2-Ethyl 3a-methyl (*E*)-3-styryl-1,2,3,11c-tetrahydrobenzo[5,6]chromeno[4,3-b]pyrrole-2,3a(4*H*)-dicarboxylate (8j)



Physical state: White solid, Yield: 83% (114 mg), M. P (°C) :130-132, ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.34 (d, *J* = 8.4 Hz, 1H), 7.82 – 7.73 (m, 2H), 7.61 – 7.28 (m, 6H), 7.15 (d, *J* = 8.9 Hz, 1H), 6.63 (d, *J* = 15.4 Hz, 1H), 5.91 (dd, *J* = 15.4, 11.0 Hz, 1H), 5.06 (s, 1H), 4.70 (dd, *J* = 11.2, 1.6 Hz, 1H), 4.39 (d, *J* = 10.2 Hz, 1H), 4.23 (d, *J* = 11.2 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.86 (t, *J* = 10.6 Hz, 1H), 3.72 (s, 3H), 2.95 (s, 1H), 1.12 (t, *J* = 7.1 Hz, 3H).^{13}C NMR ($CDCl_3$, 100 MHz):δ 172.9, 172.2, 152.1, 136.3, 136.0, 133.5, 130.0, 129.3, 128.8, 128.3, 128.2, 127.1, 126.5, 124.0, 123.7, 121.3, 118.6, 112.7, 63.8, 63.7, 61.6, 57.6, 55.7, 54.9, 52.8, 14.3. HRMS (ESI): Calc. for $C_{28}H_{28}NO_5$ $[M+H]^+$ 458.1967, measured 458.1969.

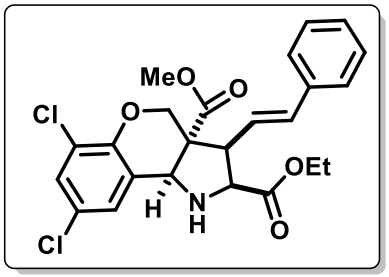
2-Ethyl 3a-methyl (*E*)-8-chloro-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole-2,3a(4*H*)-dicarboxylate (8k):



Physical state: White solid, Yield: 79% (105 mg), M. P (°C) :128-130, ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.42 (d, *J* = 2.6 Hz, 1H), 7.37 – 7.25 (m, 5H), 7.18 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.86 (d, *J* = 8.8 Hz, 1H), 6.57 (d, *J* = 15.4 Hz, 1H), 5.83 (dd, *J* = 15.4, 10.9 Hz, 1H), 4.56 (s, 1H), 4.53 (d, *J* = 11.3 Hz, 1H), 4.23 (d, *J* = 9.8 Hz, 1H), 4.13 (qd, *J* = 7.1, 1.2 Hz, 2H), 4.00 (d, *J* = 11.2 Hz, 1H), 3.74 (s, 3H), 3.70 (d, *J* = 10.3 Hz, 1H). 2.71 (s, 1H), 1.10 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.7, 171.6, 152.9, 136.2,

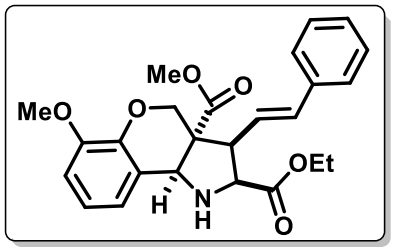
136.2, 130.4, 129.4, 128.8, 128.3, 126.5, 126.3, 122.1, 120.9, 118.7, 64.5, 63.4, 61.8, 59.0, 55.4, 55.0, 52.9, 14.3. HRMS (ESI): Calc. for $C_{24}H_{25}ClNO_5$ $[M+H]^+$ 442.1421, measured 442.1419.

2-Ethyl 3a-methyl (*E*)-6,8-dichloro-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole-2,3a(4*H*)-dicarboxylate (8l)



Physical state: White solid, Yield: 86 % (123 mg), M. P (°C) :134-136, ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36 – 7.28 (m, 7H), 6.58 (d, *J* = 15.5 Hz, 1H), 5.82 (dd, *J* = 15.4, 10.9 Hz, 1H), 4.67 (dd, *J* = 11.3, 1.4 Hz, 1H), 4.57 (s, 1H), 4.21 (d, *J* = 9.6 Hz, 1H), 4.12 (qd, *J* = 7.1, 2.2 Hz, 2H), 4.06 (d, *J* = 11.3 Hz, 1H), 3.75 (s, 3H), 3.70 (d, J = 10.2 Hz, 1H) 2.64 (s, 1H), 1.10 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.5, 171.5, 149.1, 136.3, 136.2, 129.6, 129.0, 128.8, 128.3, 126.5, 126.1, 123.5, 122.9, 120.6, 65.2, 63.3, 61.8, 58.9, 55.2, 54.9, 53.0, 14.3. HRMS (ESI): Calc. for $C_{24}H_{24}Cl_2NO_5$ $[M+H]^+$ 476.1032, measured 476.1031

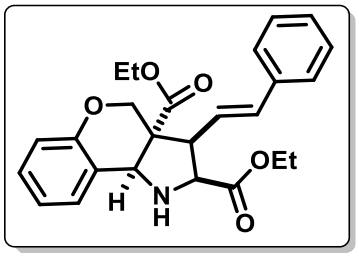
2-Ethyl 3a-methyl (*E*)-6-methoxy-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole-2,3a(4*H*)-dicarboxylate (8m)



Physical state: White solid, Yield: 88% (115 mg), M. P (°C) : 122-124, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.1 Hz, 1H), 7.30 (d, *J* = 11.0 Hz, 5H), 7.25 – 7.18 (m, 1H), 7.02 – 6.88 (m, 2H), 6.55 (d, *J* = 15.4 Hz, 1H), 5.82 (dd, *J* = 15.4, 10.9 Hz, 1H), 4.68 (s, 1H), 4.53 (d, *J* = 11.1 Hz, 1H), 4.28 (d, *J* = 9.7 Hz, 1H), 4.23 – 4.09 (m, 4H), 3.99 (d, *J* = 11.3 Hz, 1H), 3.72 (t, *J* = 10.3 Hz, 1H),

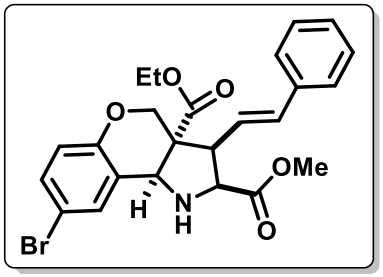
2.87s, 1H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.09 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.0, 171.6, 148.6, 143.9, 136.4, 136.0, 128.8, 128.1, 126.5, 122.4, 121.7, 121.2, 121.2, 110.9, 64.8, 63.6, 61.6, 59.2, 56.0, 55.6, 55.2, 52.8, 14.3 HRMS (ESI): Calc. for $C_{25}H_{28}NO_6$ $[M+H]^+$ 438.1917, measured 438.1918.

Diethyl (*E*)-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole-2,3a(4*H*)-dicarboxylate (8n)



Physical state: White solid, Yield: 80% (100 mg), M. P (°C) :122-124,^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.47 (d, *J* = 7.1 Hz, 1H), 7.40 – 7.20 (m, 5H), 7.00 – 6.90 (m, 2H), 6.55 (d, *J* = 15.4 Hz, 1H), 4.68 (s, 1H), 4.53 (d, *J* = 11.1 Hz, 1H), 4.28 (d, *J* = 9.7 Hz, 1H), 4.24-4.09 (m, 4H), 3.99 (d, *J* = 11.3 Hz, 1H), 3.72 (t, *J* = 10.3 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.09 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz):δ 172.0, 171.4, 154.33, 136.3, 136.2, 129.6, 128.8, 128.3, 126.3, 121.6, 120.9, 119.9, 117.3, 64.2, 63.1, 62.00, 61.90, 61.7, 59.1, 55.2, 55.03, 29.84, 14.9. HRMS (ESI): Calc. for $C_{25}H_{27}NO_5$ $[M+H]^+$ 422.1967, measured 422.1965.

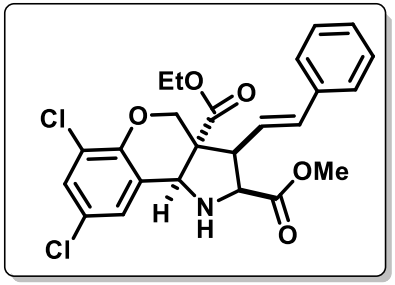
Ethyl 2-methyl (*E*)-8-bromo-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole-2,3a(4*H*)-dicarboxylate (8o)



Physical state:White solid, Yield: 89 % (124 mg), M. P (°C) : 130-132, ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.48 (d, *J* = 2.4 Hz, 1H), 7.28 – 7.21 (m, 6H), 6.74 (d, *J* = 8.7 Hz, 1H), 6.49 (d, *J* = 15.4 Hz, 1H), 5.74 (dd, *J* = 15.4, 10.9 Hz, 1H), 4.45 (dd, *J* = 13.2, 2.0 Hz,

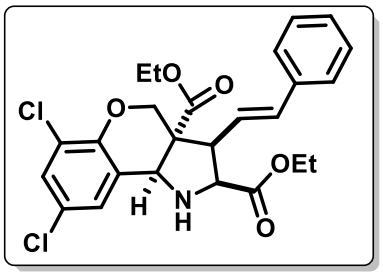
2H), 4.20 – 4.09 (m, 2H), 3.91 (d, *J* = 11.1 Hz, 1H), 3.63 (d, *J* = 12 Hz, 1H), 3.60 (s, 3H), 2.52 (s, 1H), 1.16 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz):δ 172.2, 172.1, 153.5, 136.3, 136.2, 133.4, 132.2, 128.9, 128.3, 126.5, 122.8, 120.9, 119.1, 113.5, 64.5, 63.4, 61.7, 58.8, 55.3, 54.9, 52.5, 14.3. HRMS (ESI): Calc. for $C_{24}H_{24}BrNO_5$ $[M+H]^+$ 486.0916, measured 486.0909.

Ethyl 2-methyl (*E*)-6,8-dichloro-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole-2,3a(4*H*)-dicarboxylate (8p)



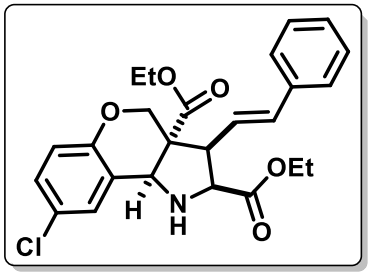
Physical state:White solid, Yield: 87 % (127 mg), M. P (°C) : 134-136, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 7H), 6.56 (d, *J* = 15.4 Hz, 1H), 5.78 (dd, *J* = 15.4, 10.9 Hz, 1H), 4.64 (d, *J* = 11.3 Hz, 1H), 4.53 (s, 1H), 4.24 - 415 (m, 3H), 4.03 (d, *J* = 11.3 Hz, 1H), 3.69 (d, *J* = 10.3 Hz, 1H), 3.65 (s, 3H), 2.64 (s, 1H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 171.7, 149.0, 136.4, 136.1, 129.5, 128.9, 128.8, 128.2, 126.4, 125.9, 123.5, 122.8, 120.5, 65.1, 63.2, 61.7, 58.7, 55.0, 54.7, 52.5, 14.2. HRMS (ESI): Calc. for $C_{24}H_{23}Cl_2NO_5$ $[M+H]^+$ 476.1031 measured 476.1029.

Diethyl (*E*)-6,8-dichloro-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole-2,3a(4*H*)-dicarboxylate (8q)



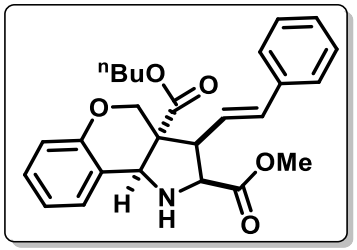
Physical state:White solid, Yield: 84 % (111 mg), M. P (°C) : 134-136, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 7H), 6.56 (d, *J* = 15.4 Hz, 1H), 5.79 (dd, *J* = 15.4, 10.9 Hz, 1H), 4.65 (dd, *J* = 11.3, 1.0 Hz, 1H), 4.54 (s, 1H), 4.25 – 4.09 (m, 4H), 4.03 (d, *J* = 11.3 Hz, 1H), 3.69 (t, *J* = 10.3 Hz, 1H), 2.56 (bs, 1H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.09 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 171.6, 149.1, 136.4, 136.2, 129.6, 129.0, 128.8, 128.3, 126.5, 126.0, 123.5, 122.9, 120.7, 65.2, 63.2, 61.8, 61.8, 58.7, 55.1, 54.8, 14.3. HRMS (ESI): Calc. for $C_{25}H_{25}ClNO_5$ $[M+H]^+$ 490.1188, measured 490.1186.

Diethyl (*E*)-8-chloro-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole-2,3a(4*H*)-dicarboxylate (8r)



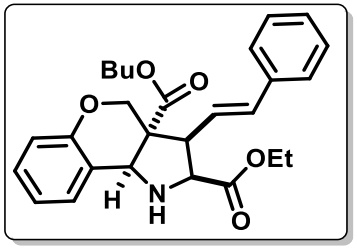
Physical state: White solid, Yield: 87 % (139 mg), M. P (°C) :128-130, ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40 (d, *J* = 2.5 Hz, 1H), 7.32 – 7.27 (m, 5H), 7.15 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 1H), 6.54 (d, *J* = 15.4 Hz, 1H), 5.80 (dd, *J* = 15.4, 10.9 Hz, 1H), 4.51 (dd, *J* = 13.6, 2.3 Hz, 2H), 4.30 – 4.05 (m, 5H), 3.96 (d, *J* = 11.2 Hz, 1H), 3.68 (t, *J* = 10.3 Hz, 1H), 2.59 (s, 1H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.09 (t, *J* = 7.1 Hz, 3H).^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.1, 171.7, 153.0, 136.3, 136.1, 130.4, 129.4, 128.8, 128.2, 126.5, 126.2, 122.2, 121.0, 118.7, 64.5, 63.4, 61.7, 61.7, 58.9, 55.4, 54.9, 14.4. HRMS (ESI): Calc. for $C_{25}H_{26}ClNO_6$ $[M+H]^+$ 456.1578, measured 456.1581.

Butyl 2-methyl (*E*)-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole-2,3a(4*H*)-dicarboxylate (8s)



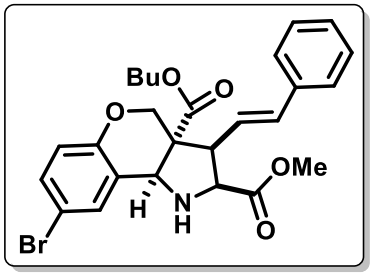
Physical state: White solid, Yield: 87% (112 mg), M. P (°C) :130-132, ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.41 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.33 – 7.27 (m, 5H), 7.23 – 7.16 (m, 1H), 6.97 (td, *J* = 7.5, 1.0 Hz, 1H), 6.90 (d, *J* = 8.2 Hz, 1H), 6.54 (d, *J* = 15.4 Hz, 1H), 5.82 (dd, *J* = 15.4, 10.9 Hz, 1H), 4.58 (s, 1H), 4.51 (dd, *J* = 11.2, 1.2 Hz, 1H), 4.25 (d, *J* = 9.8 Hz, 1H), 4.19 – 4.06 (m, 2H), 4.00 (d, *J* = 11.2 Hz, 1H), 3.70 (t, *J* = 10.3 Hz, 1H), 3.64 (s, 3H), 2.48 (s, 1H), 1.55 (dd, *J* = 9.7, 6.6 Hz, 2H), 1.31 – 1.22 (m, 2H), 0.82 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.3, 172.1, 154.2, 136.3, 136.0, 130.8, 129.2, 128.7, 128.1, 126.4, 121.3, 121.1, 120.4, 117.1, 65.3, 64.2, 63.4, 59.2, 55.5, 55.1, 52.4, 30.5, 19.0, 13.6. HRMS (ESI): Calc. for $C_{26}H_{29}NO_5$ $[M+H]^+$ 436.2124, measured 436.2120.

Butyl 2-ethyl (*E*)-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole-2,3a(4*H*)-dicarboxylate (8t)



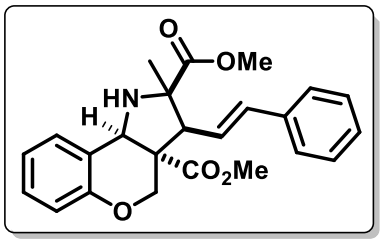
Physical state: White solid, Yield: 92% (124 mg), M. P (°C) :128-130, ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.18 – 7.17 (m, 4H), 7.17 – 6.87 (m, 1H), 6.57 (d, *J* = 15.4 Hz, 1H), 5.86 (dd, *J* = 15.5, 10.9 Hz, 1H), 4.60 (s, 1H), 4.54 (dd, *J* = 11.2, 1.4 Hz, 1H), 4.34 – 4.00 (m, 4H), 3.73 (t, *J* = 10.4 Hz, 1H), 2.61 (s, 1H), 1.80 – 1.49 (m, 2H), 1.42 – 1.25 (m, 2H), 1.11 (t, *J* = 7.1 Hz, 3H), 0.84 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.4, 171.7, 154.2, 136.2, 135.9, 130.8, 129.2, 128.7, 128.1, 126.4, 121.3, 121.2, 120.5, 117.1, 65.3, 64.2, 63.4, 61.6, 59.3, 55.5, 55.2, 30.6, 19.0, 14.2, 13.6. HRMS (ESI): Calc. for $C_{27}H_{31}NO_5$ $[M+H]^+$ 450.2280, measured 450.2279.

Butyl 2-methyl (*E*)-8-bromo-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole 2,3a(4*H*)- dicarboxylate (8u)



Physical state: White solid, Yield: 82% (121 mg), M. P (°C) :134-136, ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.56 (d, *J* = 2.2 Hz, 1H), 7.37 – 7.26 (m, 6H), 6.79 (d, *J* = 8.8 Hz, 1H), 6.55 (d, *J* = 15.4 Hz, 1H), 5.78 (dd, *J* = 15.4, 10.9 Hz, 1H), 4.56 (s, 1H), 4.50 (d, *J* = 11.3 Hz, 1H), 4.26 (d, *J* = 9.9 Hz, 1H), 4.20 – 4.05 (m, 2H), 3.98 (d, *J* = 11.3 Hz, 1H), 3.71 (d, *J* = 10.4 Hz, 1H), 3.66 (s, 3H), 1.64 – 1.49 (m, 2H), 1.36 – 1.21 (m, 2H), 0.83 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.1, 161.9, 153.5, 145.2, 136.3, 134.8, 132.4, 128.9, 127.8, 126.6, 123.4, 122.4, 119.1, 113.8, 113.5, 68.1, 65.6, 55.2, 54.9, 52.7, 30.6, 19.2, 13.7. HRMS (ESI): Calc. for $C_{26}H_{28}BrNO_5$ $[M+H]^+$ 514.1222, measured 514.1232.

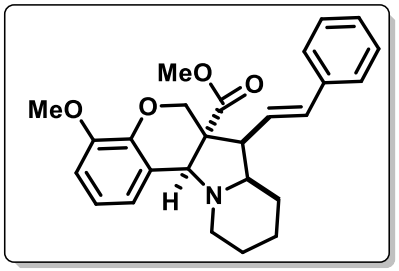
Dimethyl (*E*)-2-methyl-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole 2,3a(4*H*)-dicarboxylate (3v)



Physical state : Colorless liquid, yield : 64% (78 mg),^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 8, 1.4 Hz, 1H), 7.26-7.25 (m, 4H), 7.22 – 7.18 (m, 2H), 7.15 – 7.09 (m, 1H), 6.88 (td, *J* = 7.5, 1.1 Hz, 1H), 6.83 (d, *J* = 8 Hz, 1H), 6.42 (d, *J* = 16 Hz, 1H), 5.73 (dd, *J* = 16, 12 Hz, 1H), 4.60 (s, 1H), 4.46 (d, *J* = 12 Hz, 1H), 4.04 (d, *J* = 12 Hz, 1H), 3.61 (s, 3H), 3.57 (s, 3H), 3.18 (d, *J* = 12 Hz, 1H), 1.56 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.67, 172.85, 154.22, 136.35, 135.55, 130.98, 129.19, 128.77, 128.10, 126.46, 121.38,

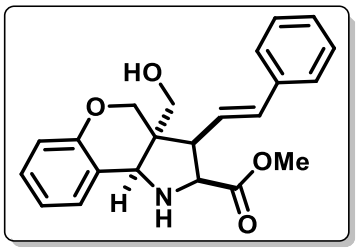
121.21, 120.28, 117.16, 69.69, 64.94, 63.29, 58.17, 56.82, 52.74, 52.69, 26.33. HRMS (ESI): Calc. For $C_{24}H_{25}NO_5$ $[M+Na]^+$ 430.1630, measured 430.1602.

Butyl 2-methyl (*E*)-8-bromo-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole 2,3a(4*H*)- dicarboxylate (10)



Physical state: White solid, Yield: 81% (83 mg), M. P (°C) :148-150, ^{1}H NMR ($CDCl_3$, 400 MHz): δ δ 7.39 – 7.27 (m, 6H), 6.90 – 6.88 (m, 2H), 6.77 (dd, *J* = 6.5, 3.1 Hz, 1H), 6.45 (d, *J* = 15.8 Hz, 1H), 6.11 (dd, *J* = 15.8, 8.6 Hz, 1H), 4.82 (dd, *J* = 10.9, 1.2 Hz, 1H), 4.34 – 4.24 (m, 1H), 3.84 (s, 3H), 3.67 (s, 3H), 3.20-3.26 (m, 1H), 3.16-3.10 (m, 1H), 2.95 (t, *J* = 9.1 Hz, 1H), 2.15 – 1.93 (m, 4H), 1.71 – 1.57 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.4, 148.6, 142.9, 136.7, 134.1, 129.6, 128.8, 128.0, 126.6, 123.6, 121.2, 121.1, 115.5, 110.9, 77.5, 77.2, 76.8, 68.0, 65.9, 65.1, 57.2, 56.9, 56.1, 55.7, 52.7, 31.3, 29.8, 26.8. HRMS (ESI): Calc. for $C_{26}H_{29}NO_4$ $[M+H]^+$ 420.2175, measured 420.2180.

Methyl (*E*)-3a-(hydroxymethyl)-3-styryl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-b]pyrrole-2-carboxylate (11)



Physical state: colorless oil, Yield: 89% (65 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.47 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.32 (d, *J* = 4.4 Hz, 4H), 7.28 – 7.20 (m, 4H), 6.98 (td, *J* = 7.5, 1.1 Hz, 1H), 6.92 – 6.89 (m, 1H), 6.64 (d, *J* = 15.4 Hz, 1H), 4.30 (d, *J* = 10.0 Hz, 1H),

4.24 (s, 1H), 4.04 (d, *J* = 11.6 Hz, 1H), 3.95 (d, *J* = 10.6 Hz, 1H), 3.76 (dd, *J* = 19.1, 8.7 Hz, 2H), 3.68 (s, 2H), 3.66 (s, 3H), 2.51 (s, 1H). ^{13}C NMR (100 MHz, CDCl3) δ 172.3, 154.1, 136.4, 135.9, 131.4, 129.9, 128.9, 128.2, 126.5, 121.9, 121.8, 119.8, 117.4, 65.0, 62.5, 62.4, 57.5, 52.8, 51.4, 49.5. HRMS (ESI): Calc. for $C_{22}H_{23}NO_4$ $[M+H]^+$ 366.1705, measured 366.1706

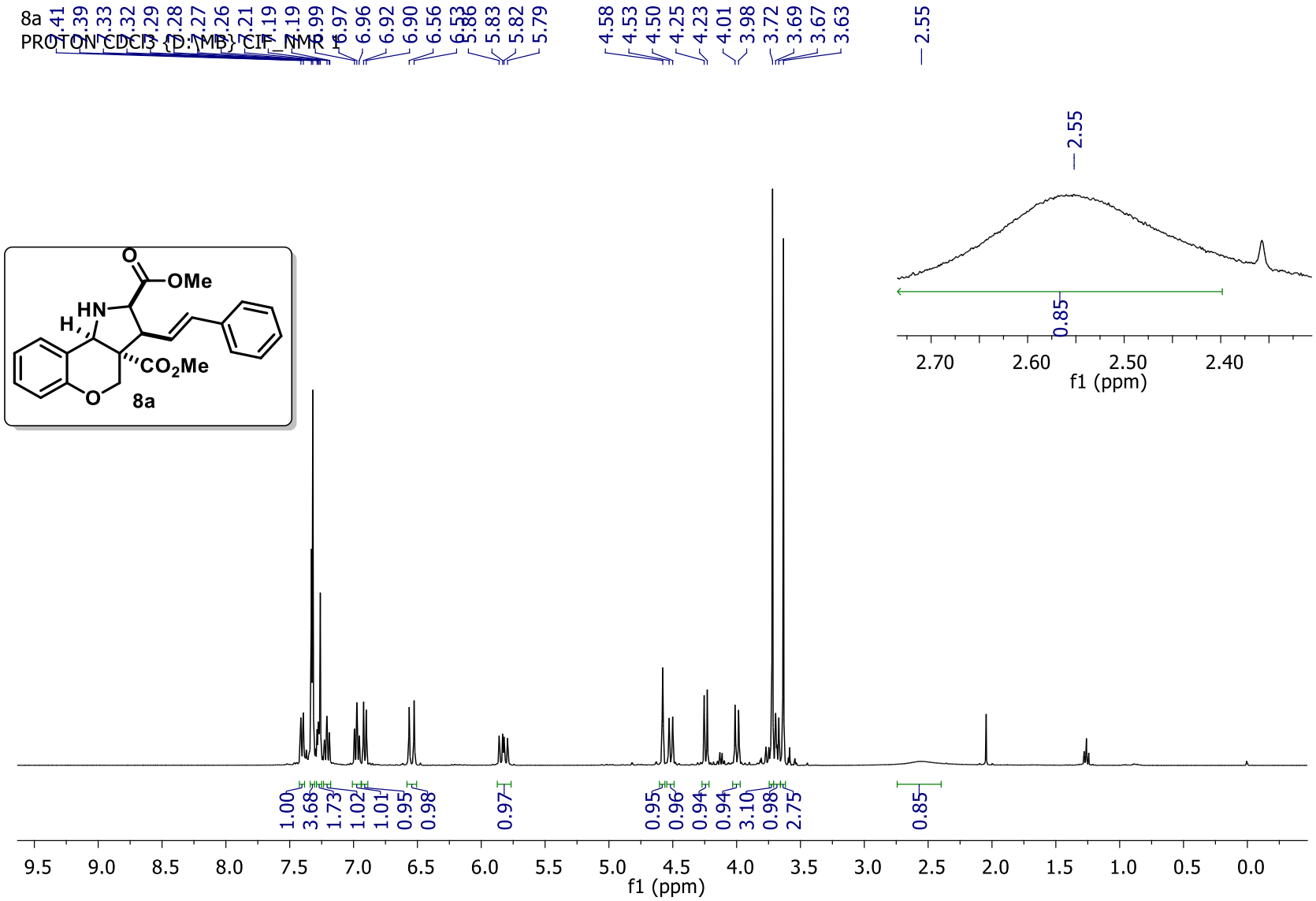
References:

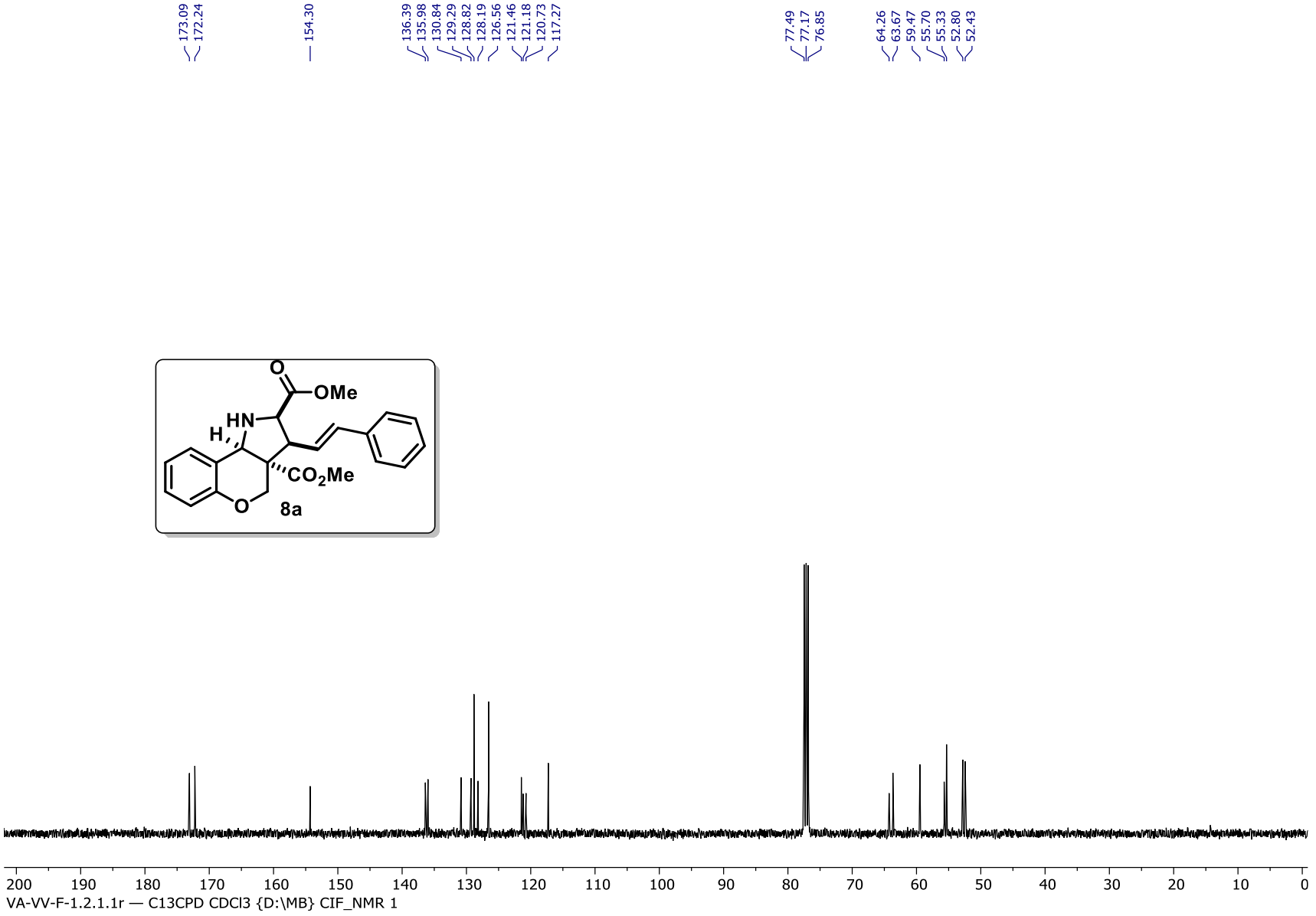
1. K. H. Kim, H. S. Lee, Y. M. Kim, J. N. Kim. Remarkable Rate Acceleration of Baylis-Hillman Reaction of Notorious α,β-Unsaturated Aldehydes Catalyzed by Proton Donor. *Bull. Korean Chem. Soc.* **2011**, *32*, 1087- 1090

2. K. H. Kim, S. H. Kim, S. Park, J. N. Kim. Palladium-catalyzed synthesis of indane and cyclobuta[a]indenes fromhomoallylic alcohols derived from BayliseHillman adducts: base-dependentstereoselectivity for the benzylidene group in cyclobuta[a]indene. *Tetrahedron***, 2011**, *67*, 3328- 3336

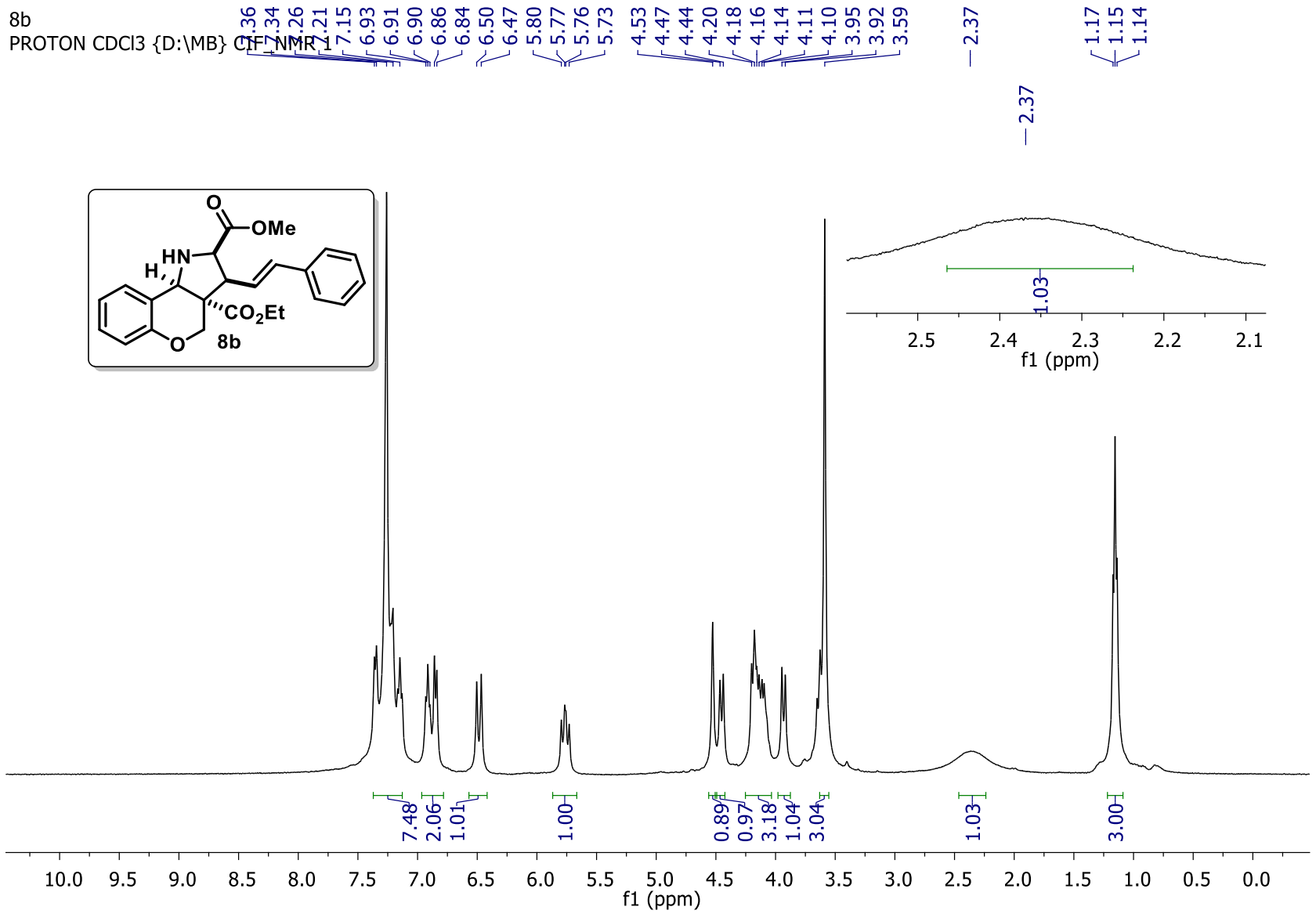
^{1}H and ^{13}C spectrums of the compounds

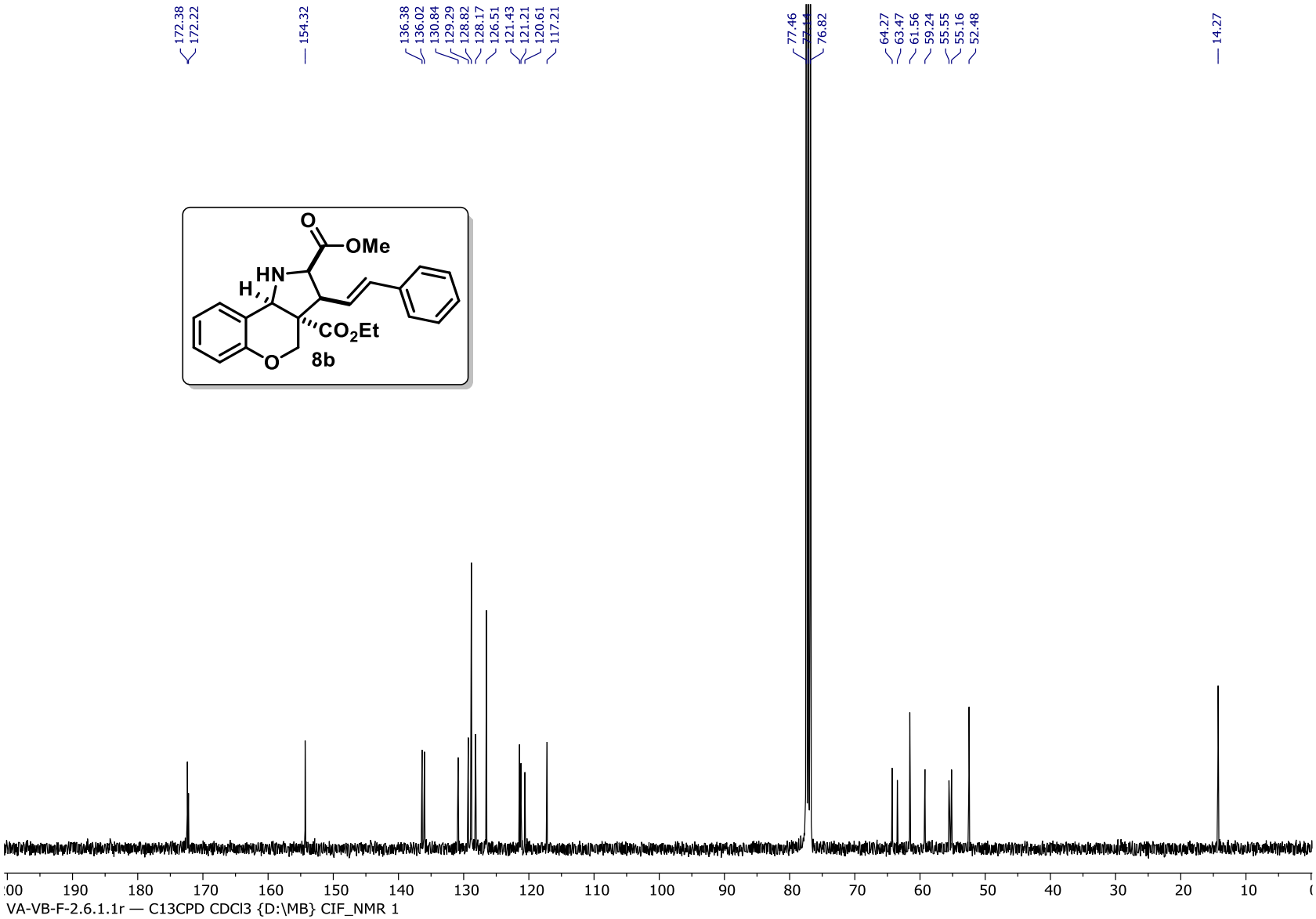
Dimethyl (*E*)-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole-2,3a(4*H*)-dicarboxylate (8a)



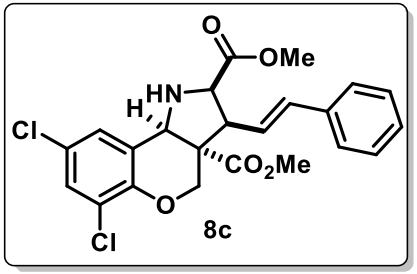

173.09
172.24
154.30
136.39
135.98
130.84
129.29
128.82
128.19
126.56
121.46
121.18
120.73
117.27
77.49
77.17
76.85
64.26
63.67
59.47
55.70
55.33
52.80
52.43
O
OMe
HN
H
CO2Me
O
8a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
VA-VV-F-1.2.1.1r — C13CPD CDCl3 {D:\MB} CIF_NMR 1

3a-Ethyl 2-methyl (*E*)-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole-2,3a(4*H*)-dicarboxylate (8b)



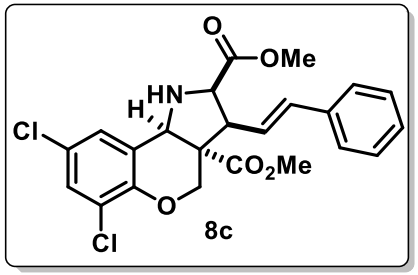

172.38
172.22
154.32
136.38
136.02
130.84
129.29
128.82
128.17
126.51
121.43
121.21
120.61
117.21
77.46
77.14
76.82
64.27
63.47
61.56
59.24
55.55
55.16
52.48
14.27
O
OMe
HN
H
CO2Et
O
8b
VA-VB-F-2.6.1.1r — C13CPD CDCl3 {D:\MB} CIF_NMR 1

Dimethyl (*E*)-6,8-dichloro-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole-2,3a(4*H*)-dicarboxylate (8c):

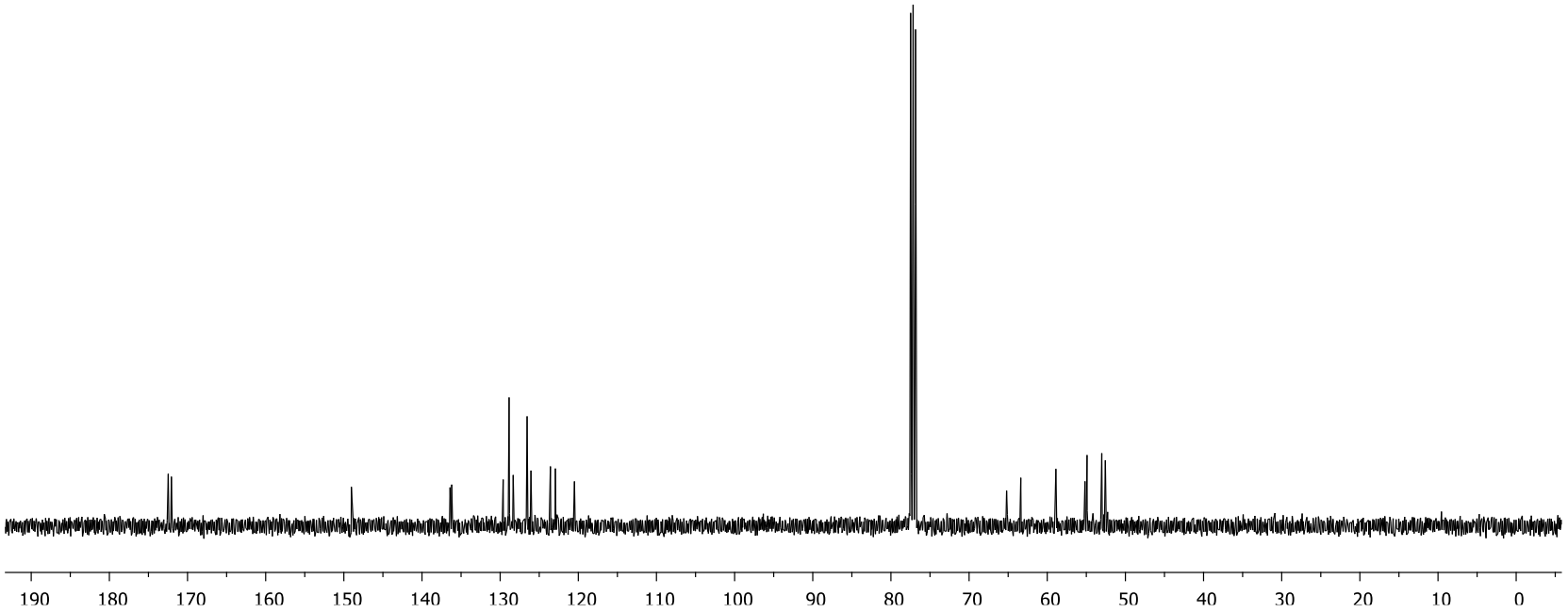


VA-VB-F-4.6.1.1r
C13CPD CDCl3 {D:\MB} CIF_NMR 1

152.49
142.08
149.06
136.43
136.22
129.63
128.96
128.87
128.35
126.57
126.07
123.58
122.95
120.51
77.49
77.17
76.86
65.21
63.40
58.90
55.19
54.92
53.04
52.58

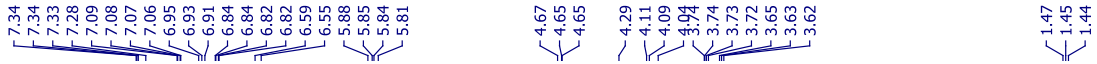


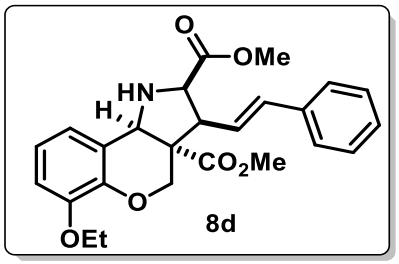
8c

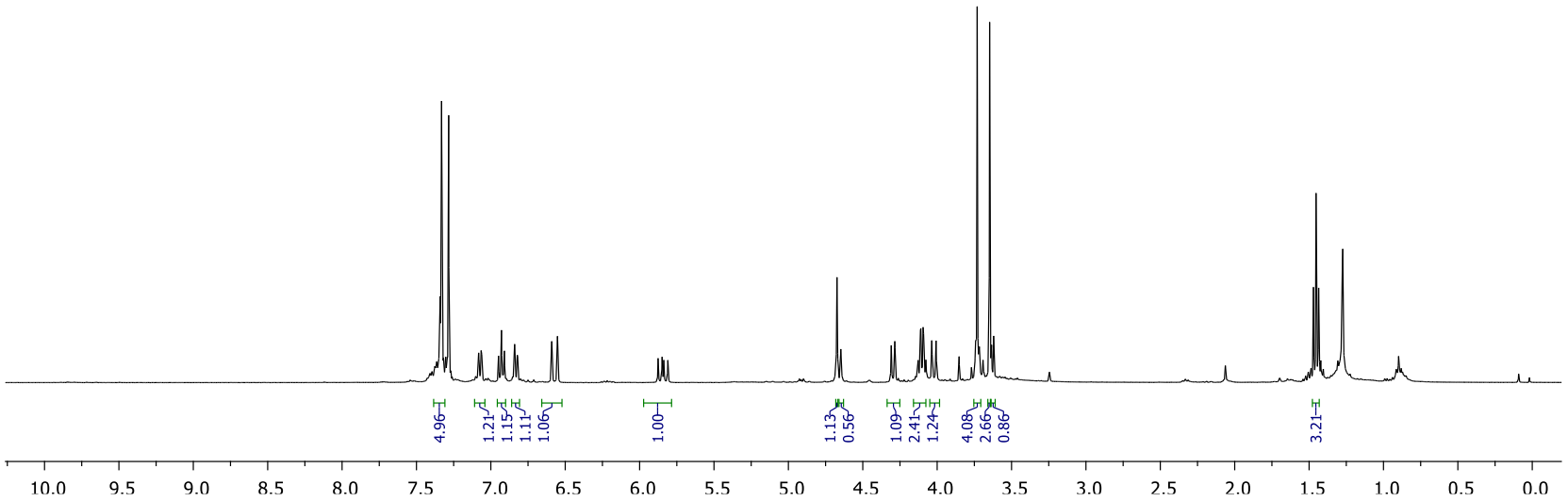


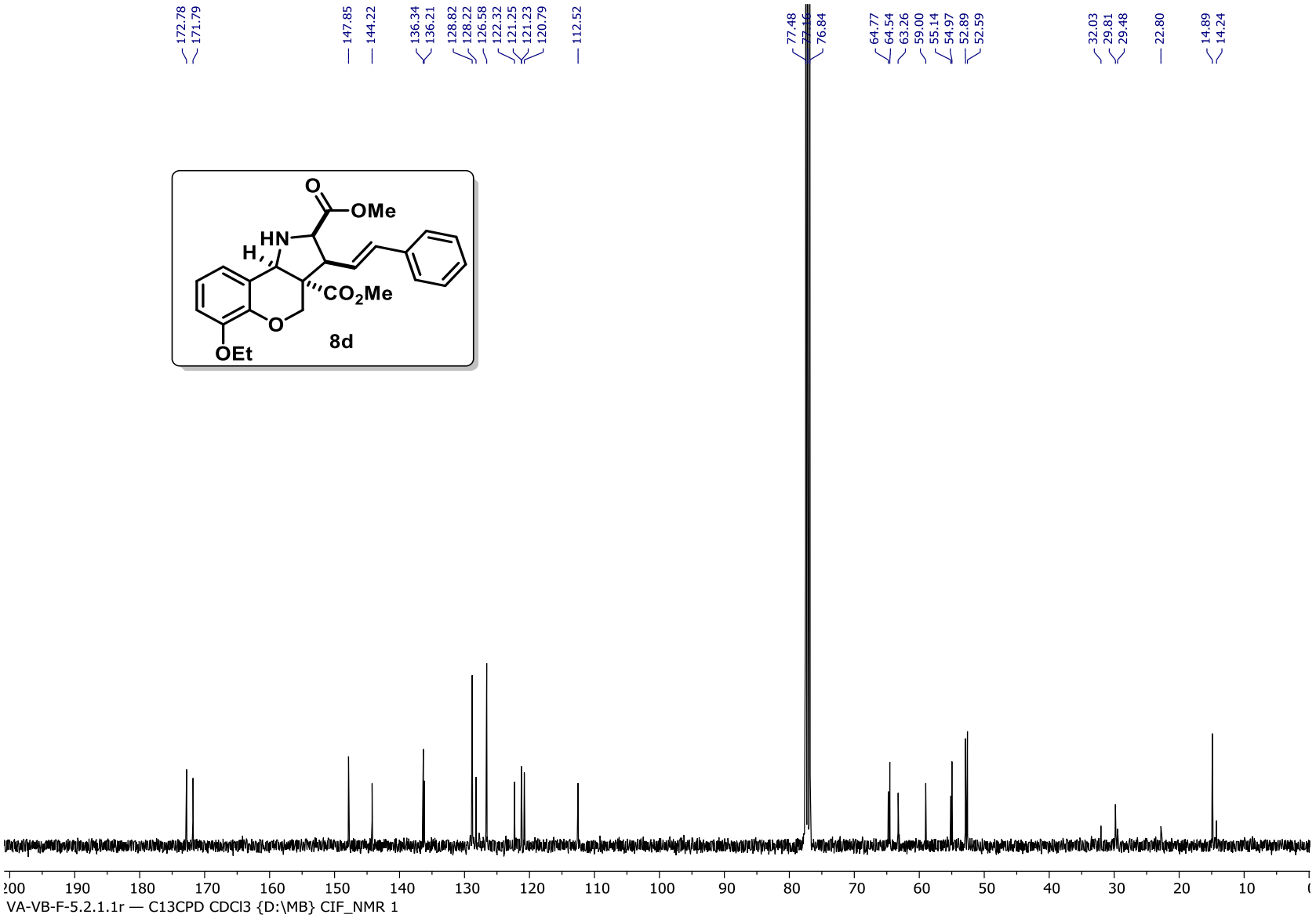
Dimethyl (*E*)-6-ethoxy-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole-2,3a(4*H*)-dicarboxylate (8d)

VA-VB-F-5.1.1.1r
PROTON CDCl3 {D:\MB} CIF_NMR 1

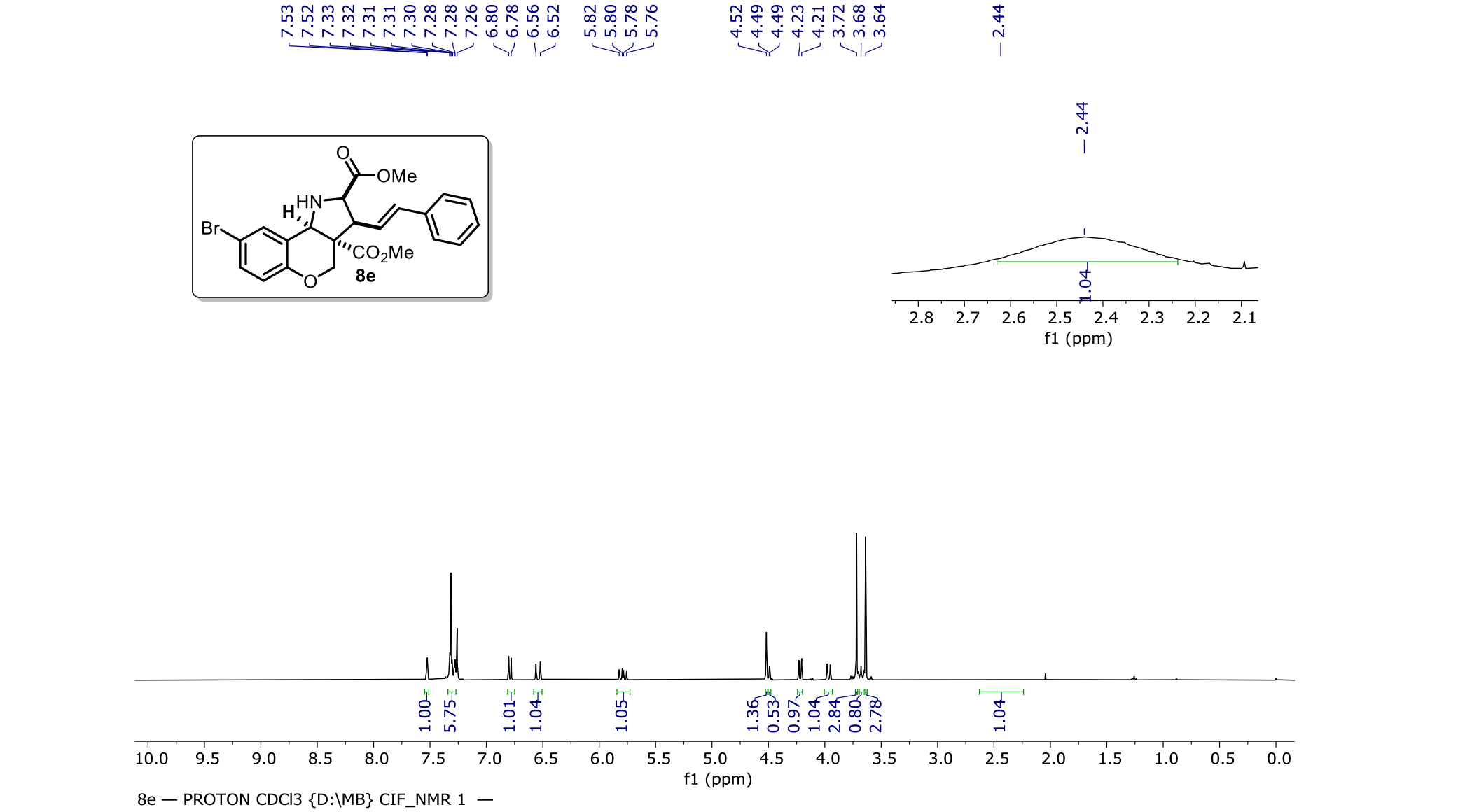




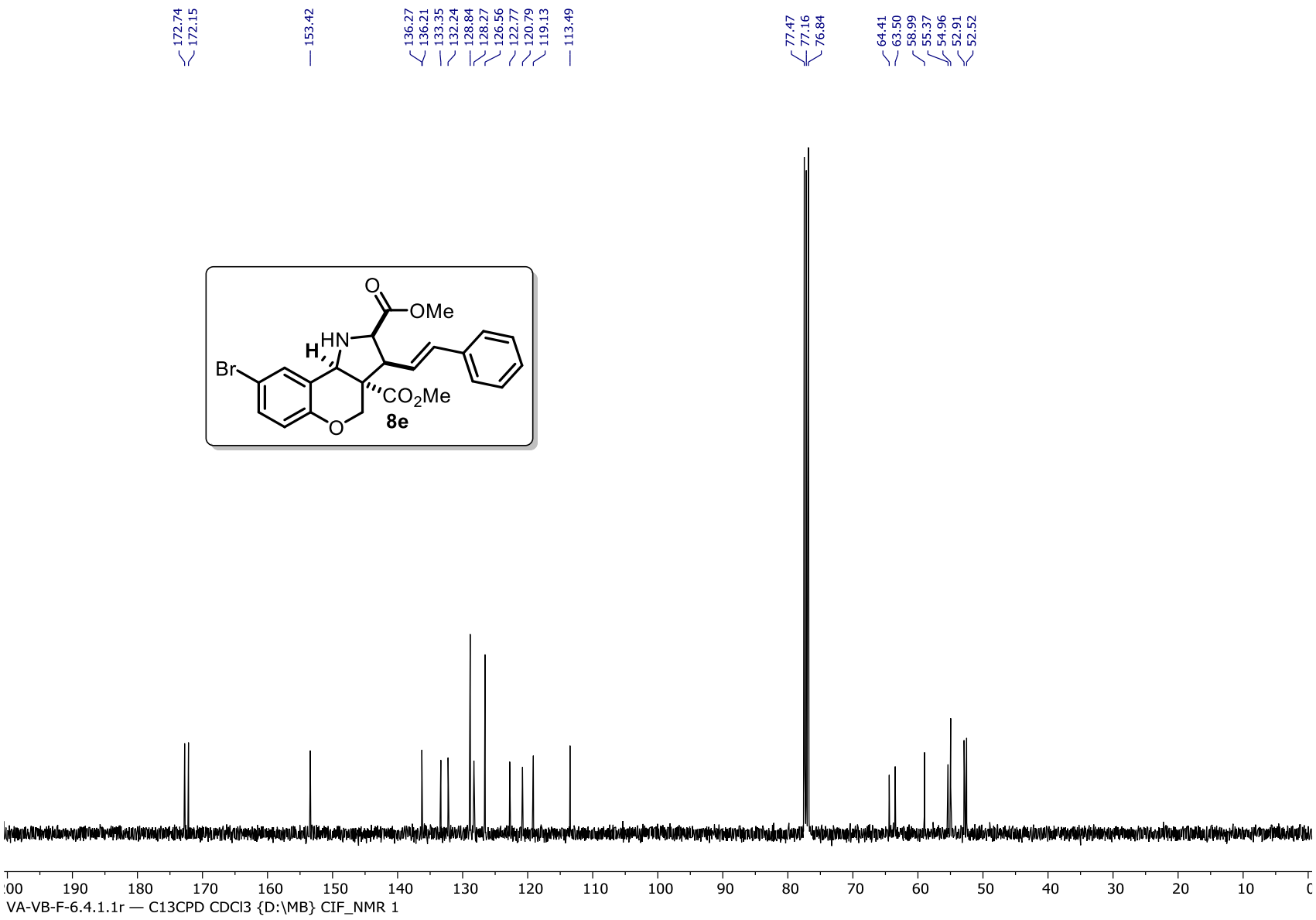



172.78
171.79
147.85
144.22
136.34
136.21
128.82
128.22
126.58
122.32
121.25
121.23
120.79
112.52
77.48
77.16
76.84
64.77
64.54
63.26
59.00
55.14
54.97
52.89
52.59
32.03
29.81
29.48
22.80
14.89
14.24
O
OMe
HN
H
CO2Me
O
OEt
8d
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
VA-VB-F-5.2.1.1r — C13CPD CDCl3 {D:\MB} CIF_NMR 1

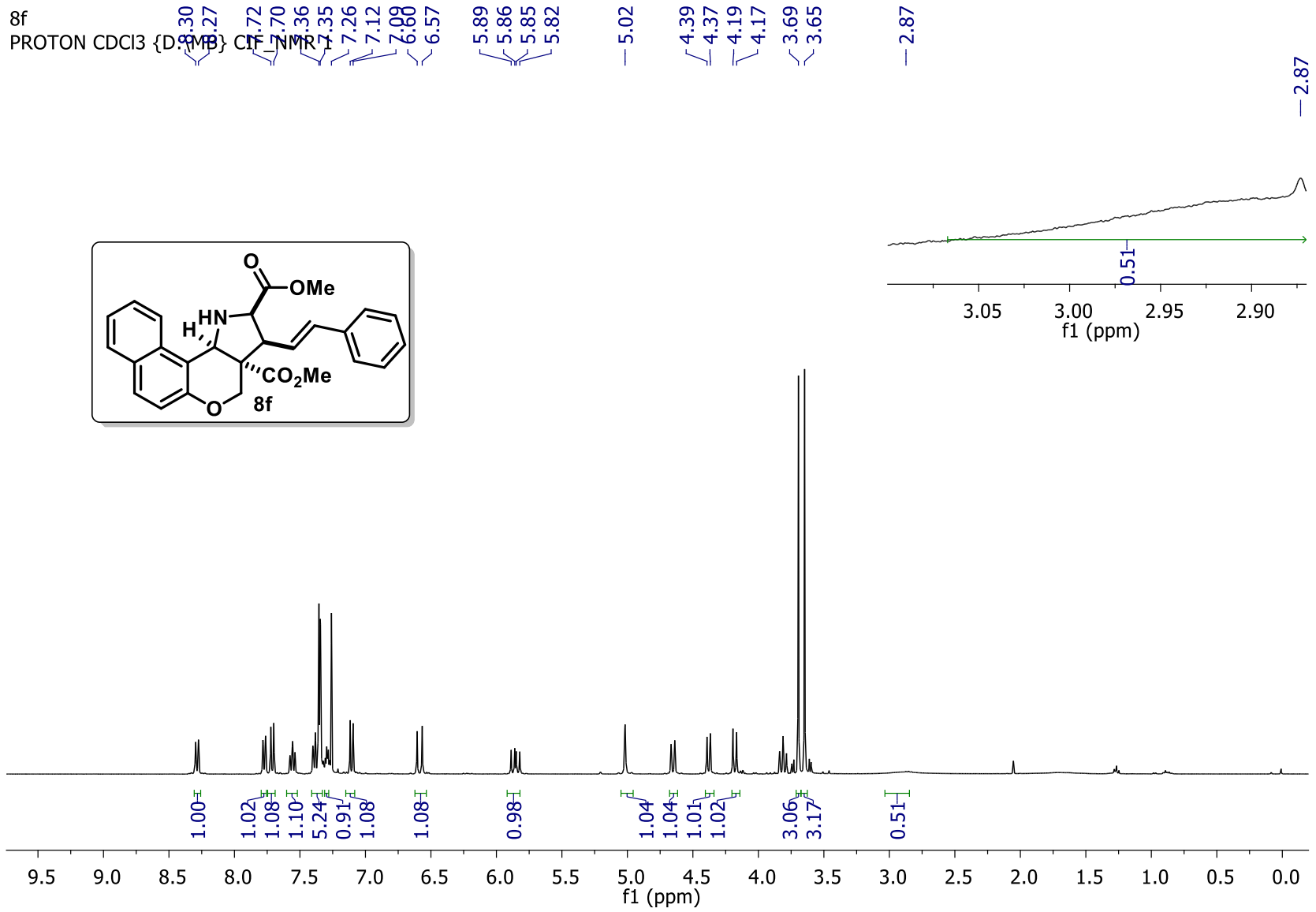
Dimethyl (*E*)-8-bromo-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole-2,3a(4*H*)-dicarboxylate (8e):

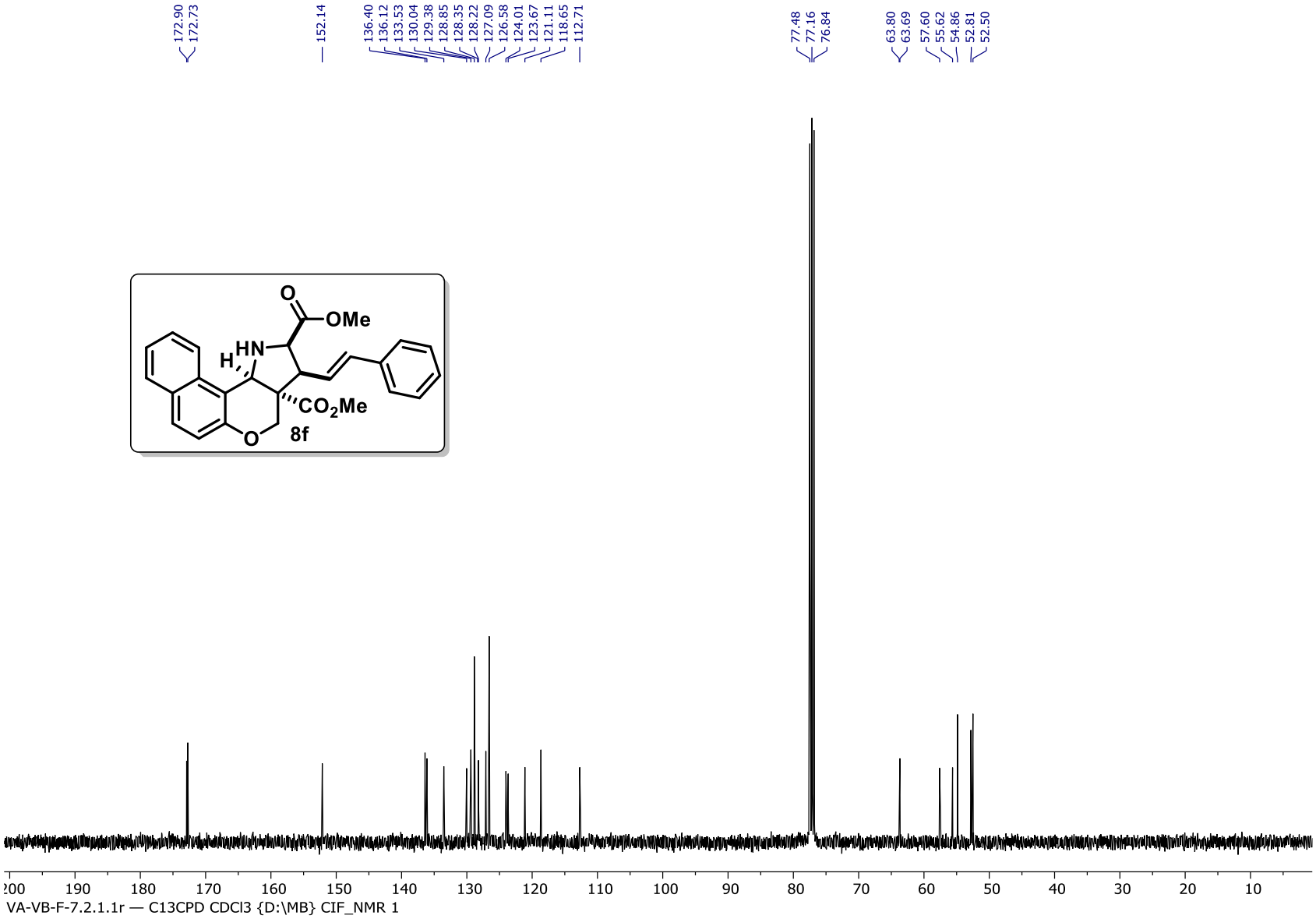


8e — PROTON CDCl3 {D:\MB} CIF_NMR 1 —

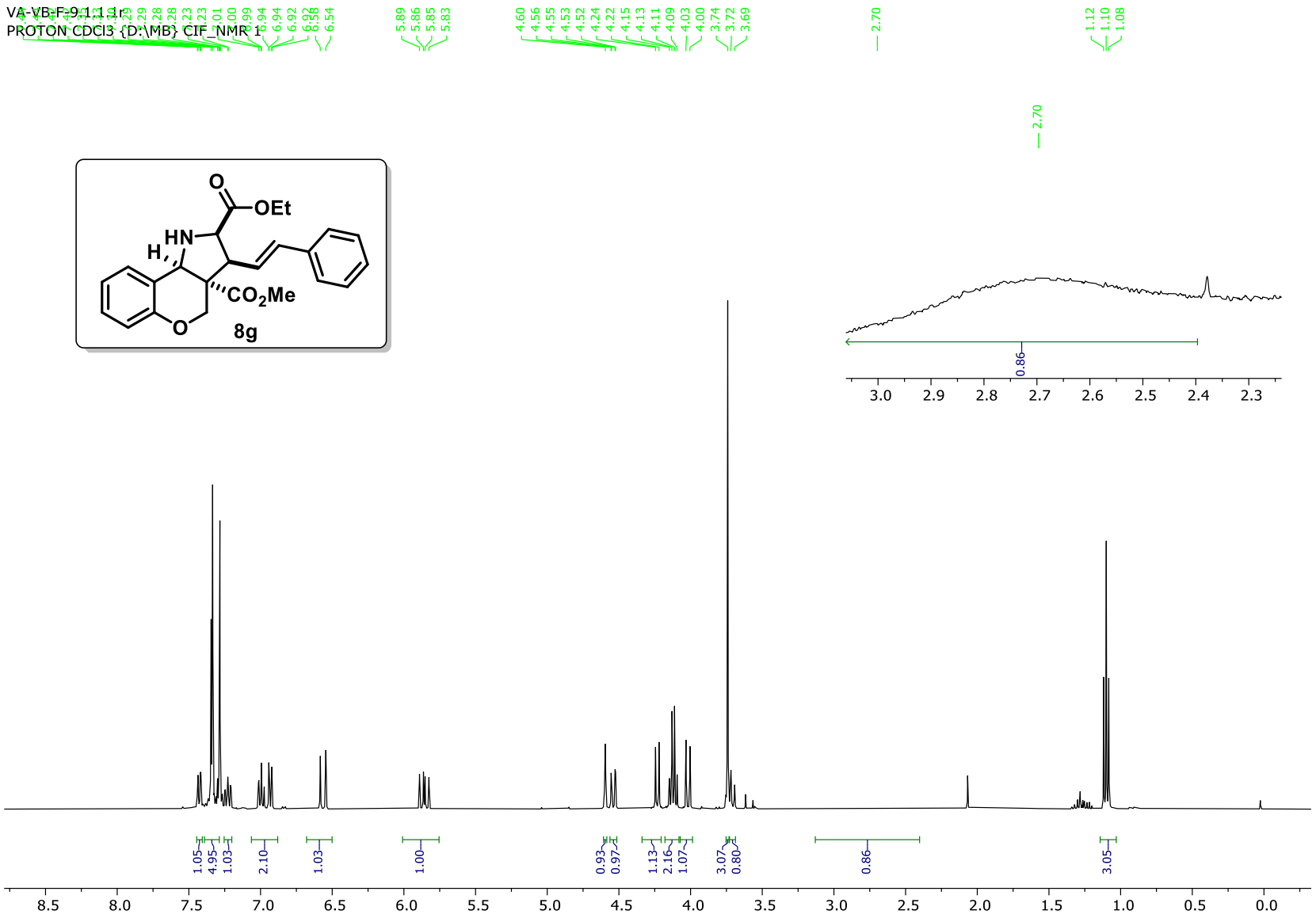

172.74
172.15
153.42
136.27
136.21
133.35
132.24
128.84
128.27
126.56
122.77
120.79
119.13
113.49
77.47
77.16
76.84
64.41
63.50
58.99
55.37
54.96
52.91
52.52
O
OMe
HN
H
Br
CO2Me
O
8e
VA-VB-F-6.4.1.1r — C13CPD CDCl3 {D:\MB} CIF_NMR 1

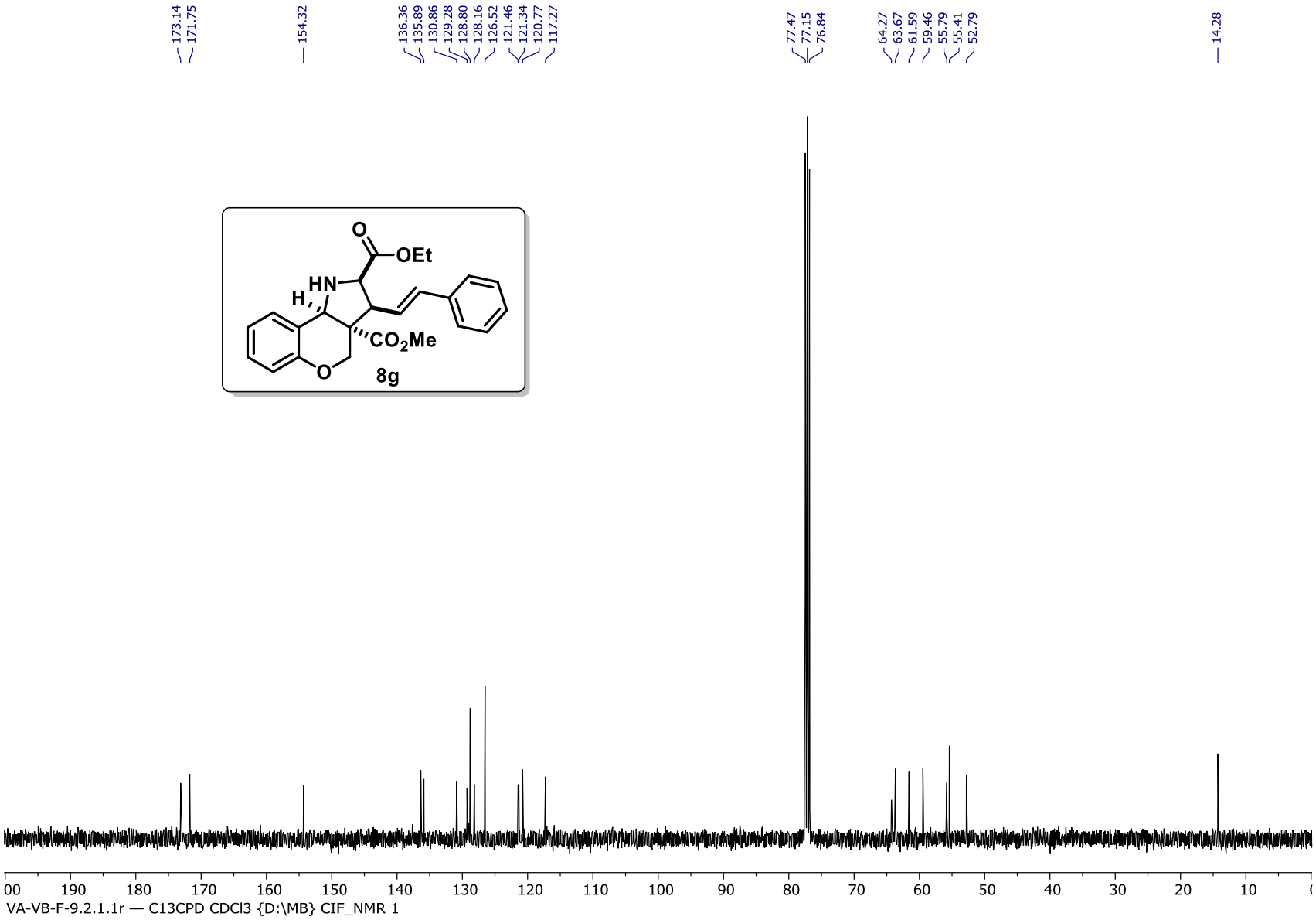
Dimethyl (*E*)-3-styryl-1,2,3,11c-tetrahydrobenzo[5,6]chromeno[4,3-b]pyrrole-2,3a(4*H*)-dicarboxylate (8f):



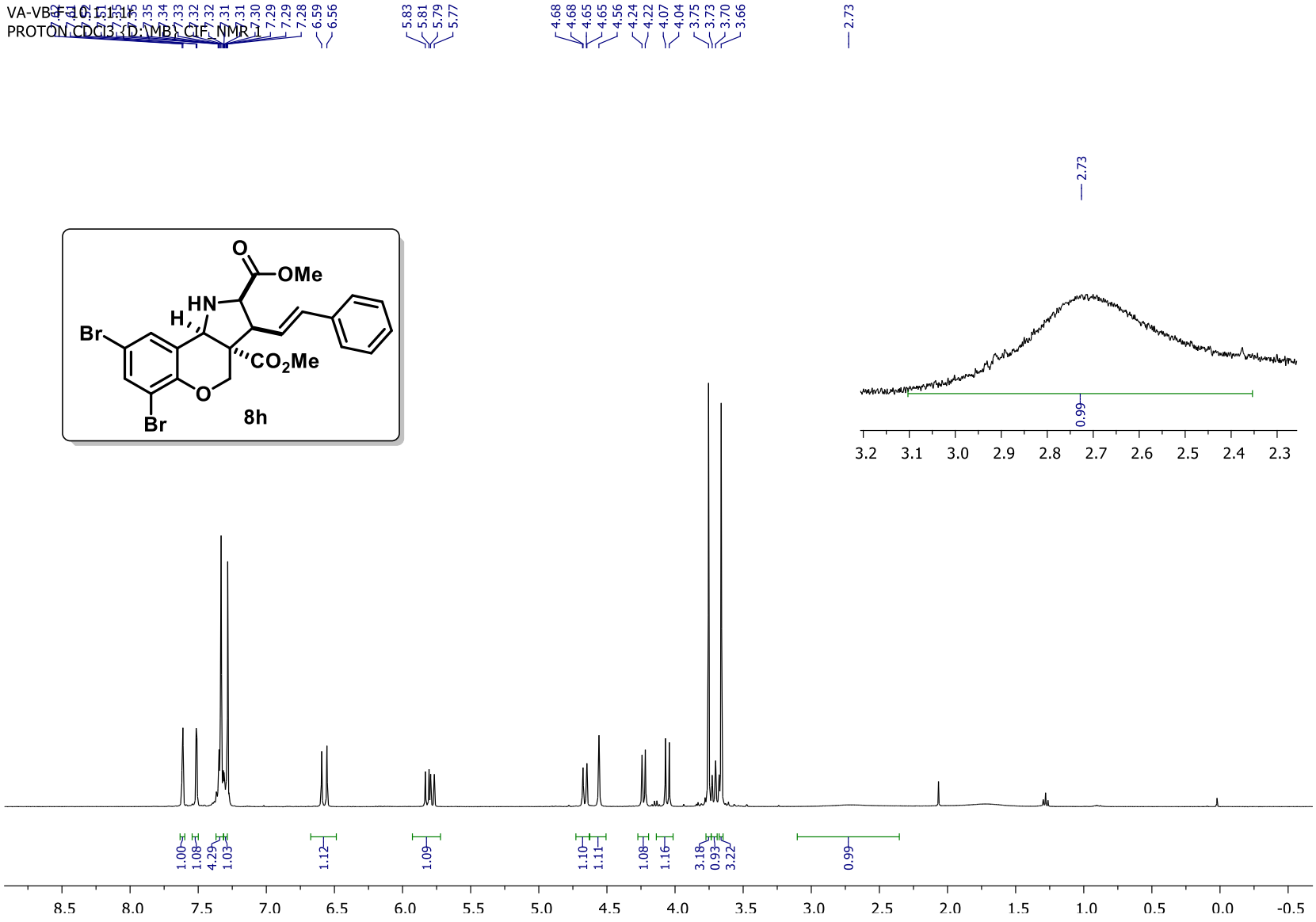

172.90
172.73
152.14
136.40
136.12
133.53
130.04
129.38
128.85
128.35
128.22
127.09
126.58
124.01
123.67
121.11
118.65
112.71
77.48
77.16
76.84
63.80
63.69
57.60
55.62
54.86
52.81
52.50
O
OMe
HN
H
CO2Me
O
8f
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
VA-VB-F-7.2.1.1r — C13CPD CDCl3 {D:\MB} CIF_NMR 1

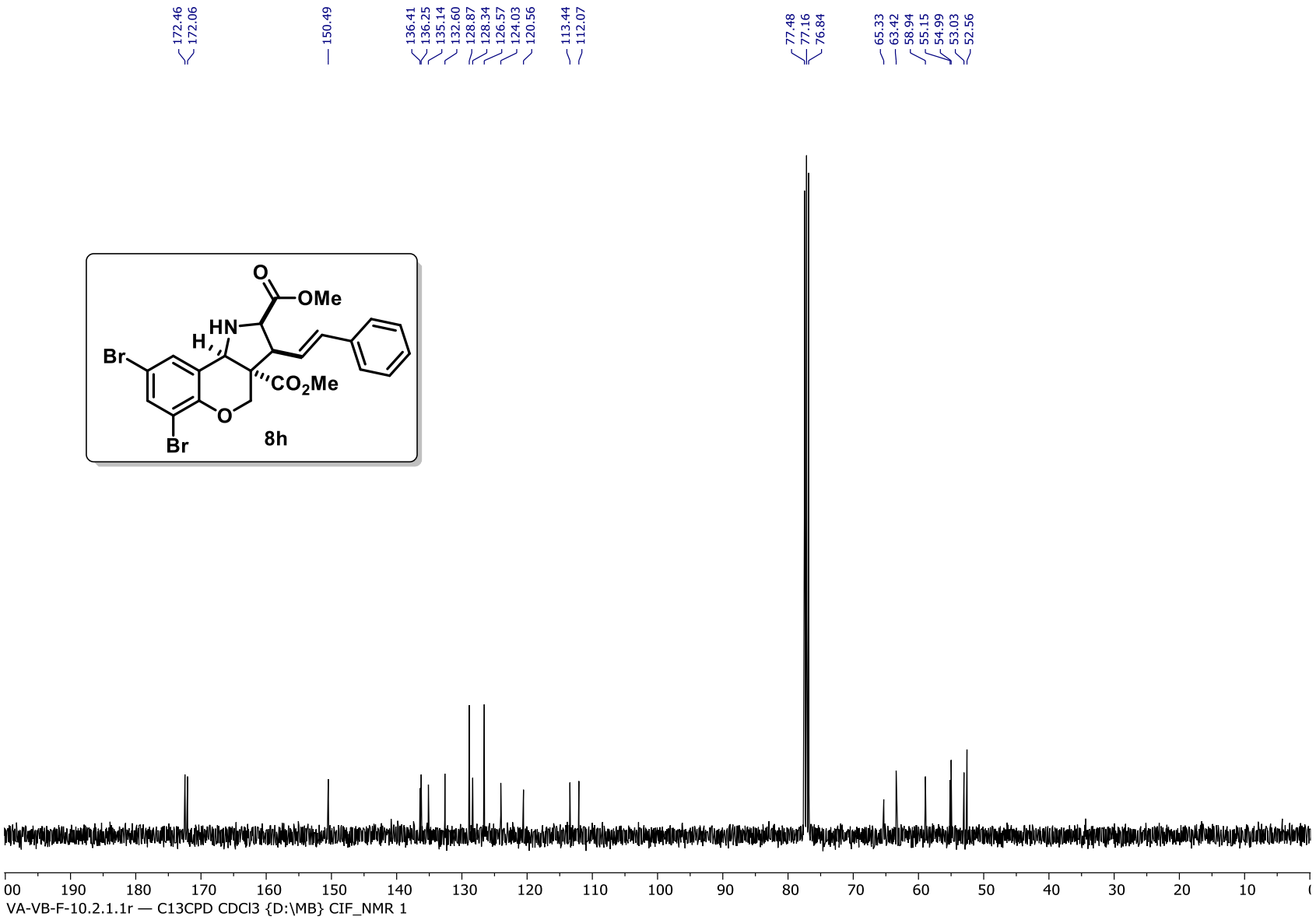
2-Ethyl 3a-methyl (*E*)-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole-2,3a(4*H*)-dicarboxylate (8g)



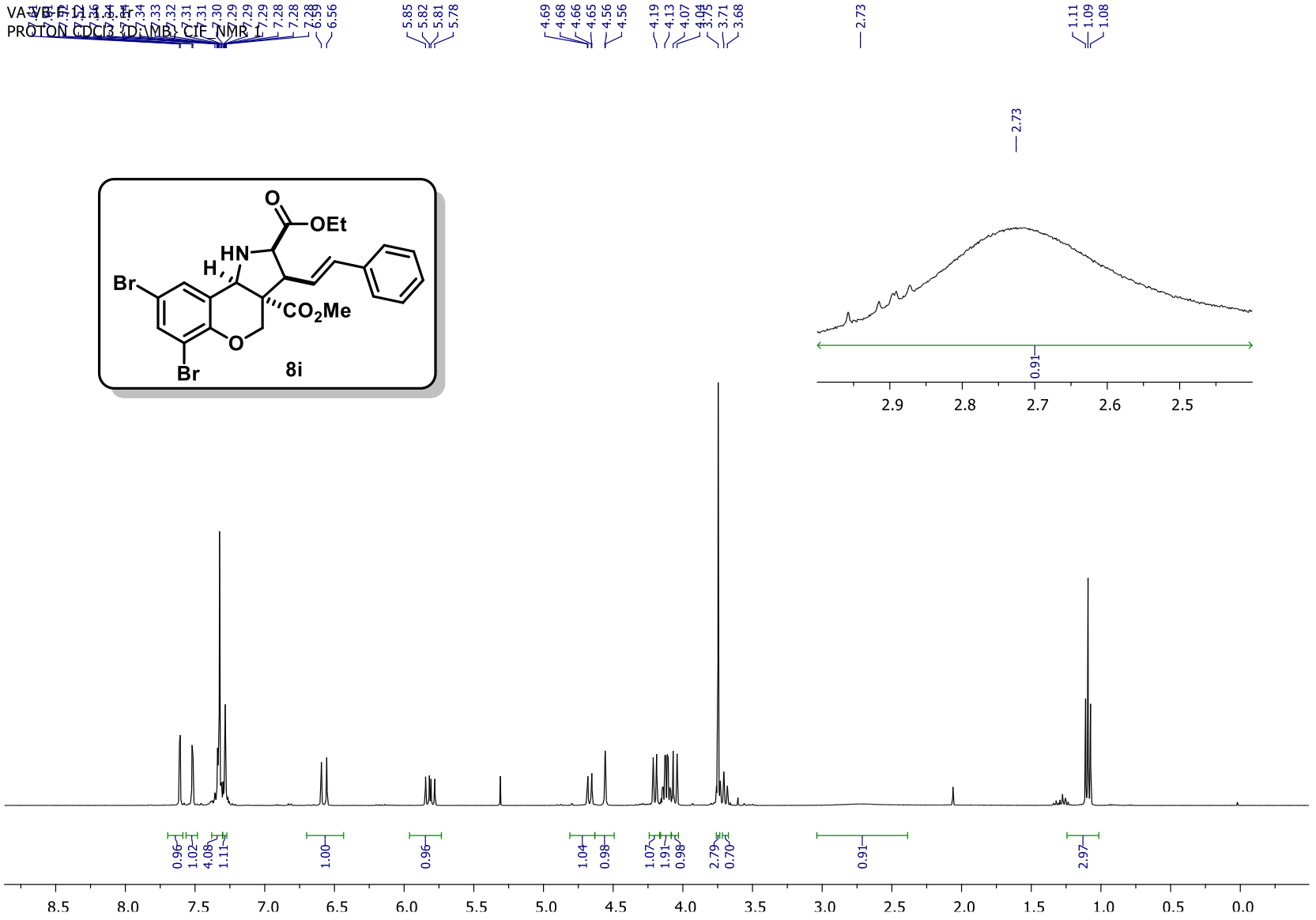

173.14
171.75
154.32
136.36
135.89
130.86
129.28
128.80
128.16
126.52
121.46
121.34
120.77
117.27
77.47
77.15
76.84
64.27
63.67
61.59
59.46
55.79
55.41
52.79
14.28
O
OEt
HN
H
CO2Me
O
8g
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
VA-VB-F-9.2.1.1r — C13CPD CDCl3 {D:\MB} CIF_NMR 1

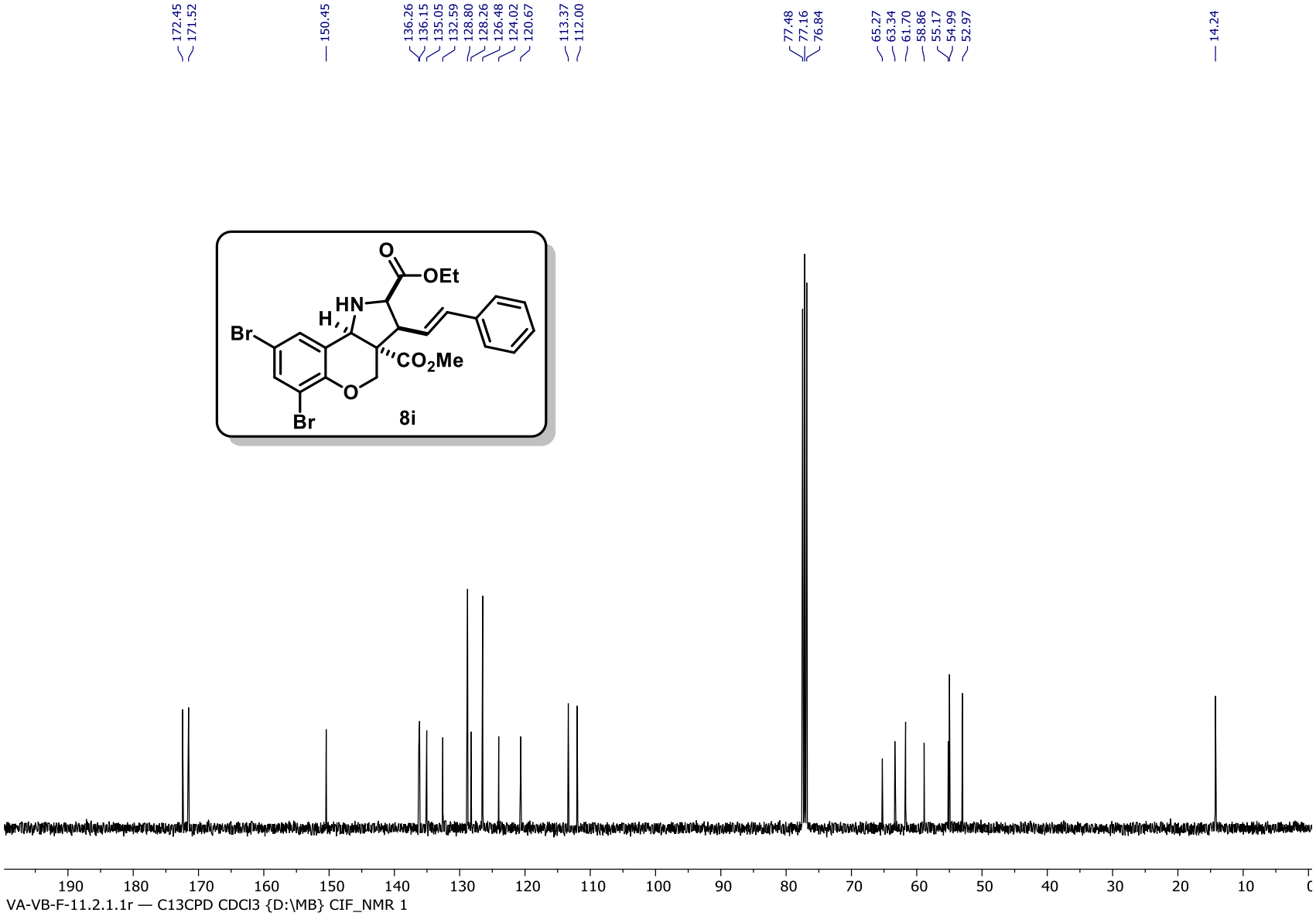
Dimethyl (*E*)-6,8-dibromo-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole-2,3a(4*H*)-dicarboxylate (8h)



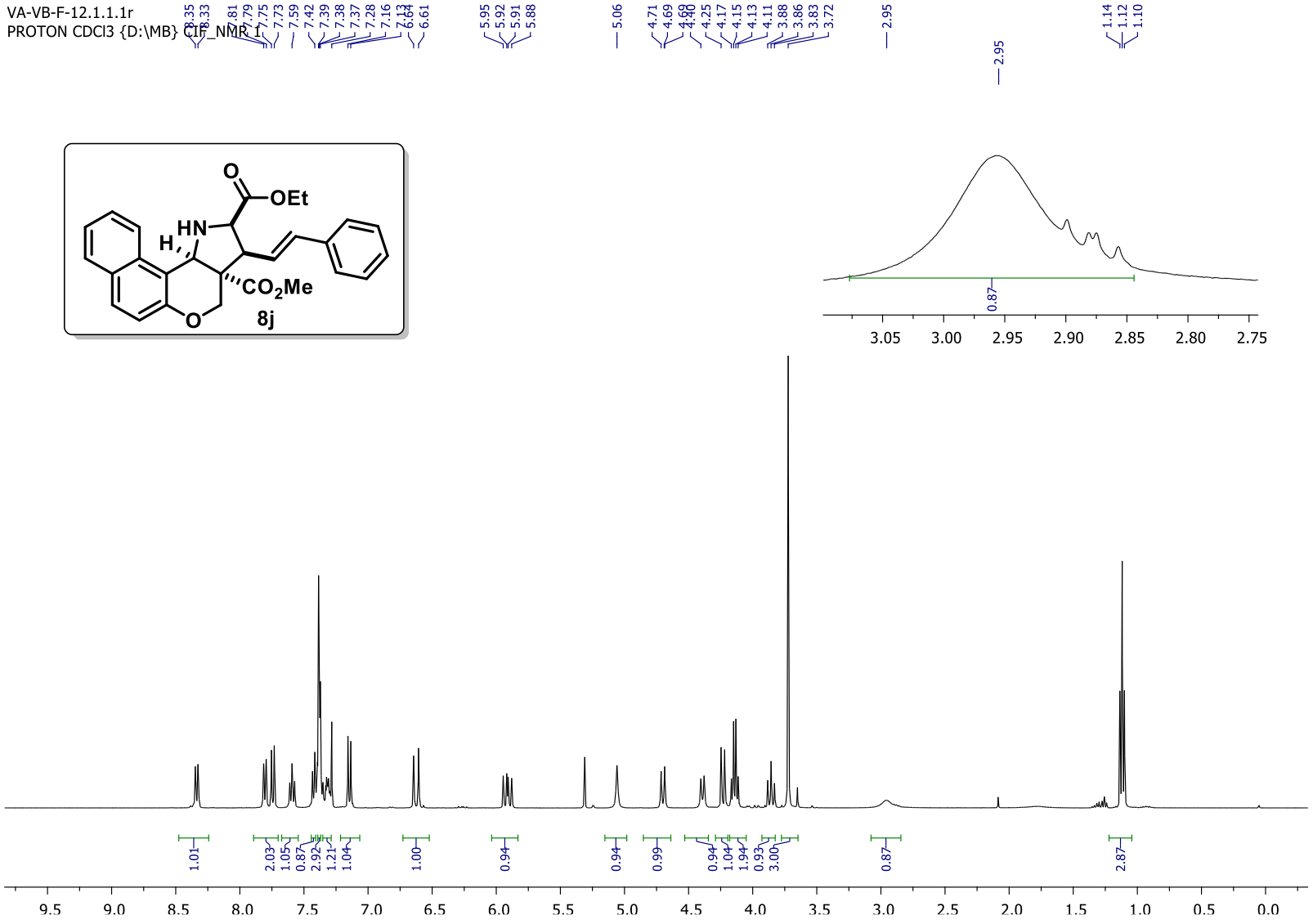

172.46
172.06
150.49
136.41
136.25
135.14
132.60
128.87
128.34
126.57
124.03
120.56
113.44
112.07
77.48
77.16
76.84
65.33
63.42
58.94
55.15
54.99
53.03
52.56
O
OMe
HN
H
Br
CO2Me
O
Br
8h
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
VA-VB-F-10.2.1.1r — C13CPD CDCl3 {D:\MB} CIF_NMR 1

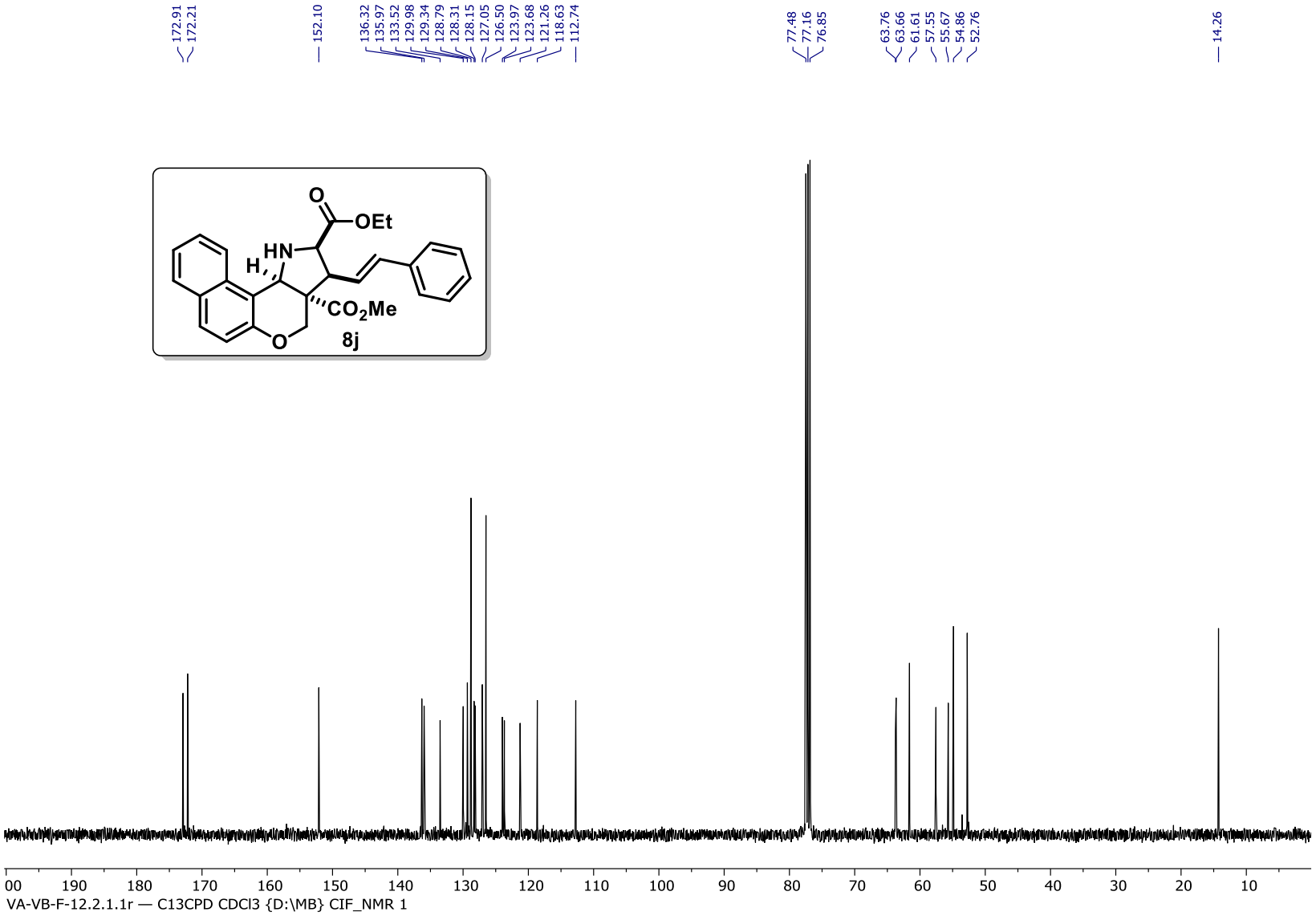
2-Ethyl 3a-methyl (*E*)-6,8-dibromo-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole-2,3a(4*H*)-dicarboxylate (8i)



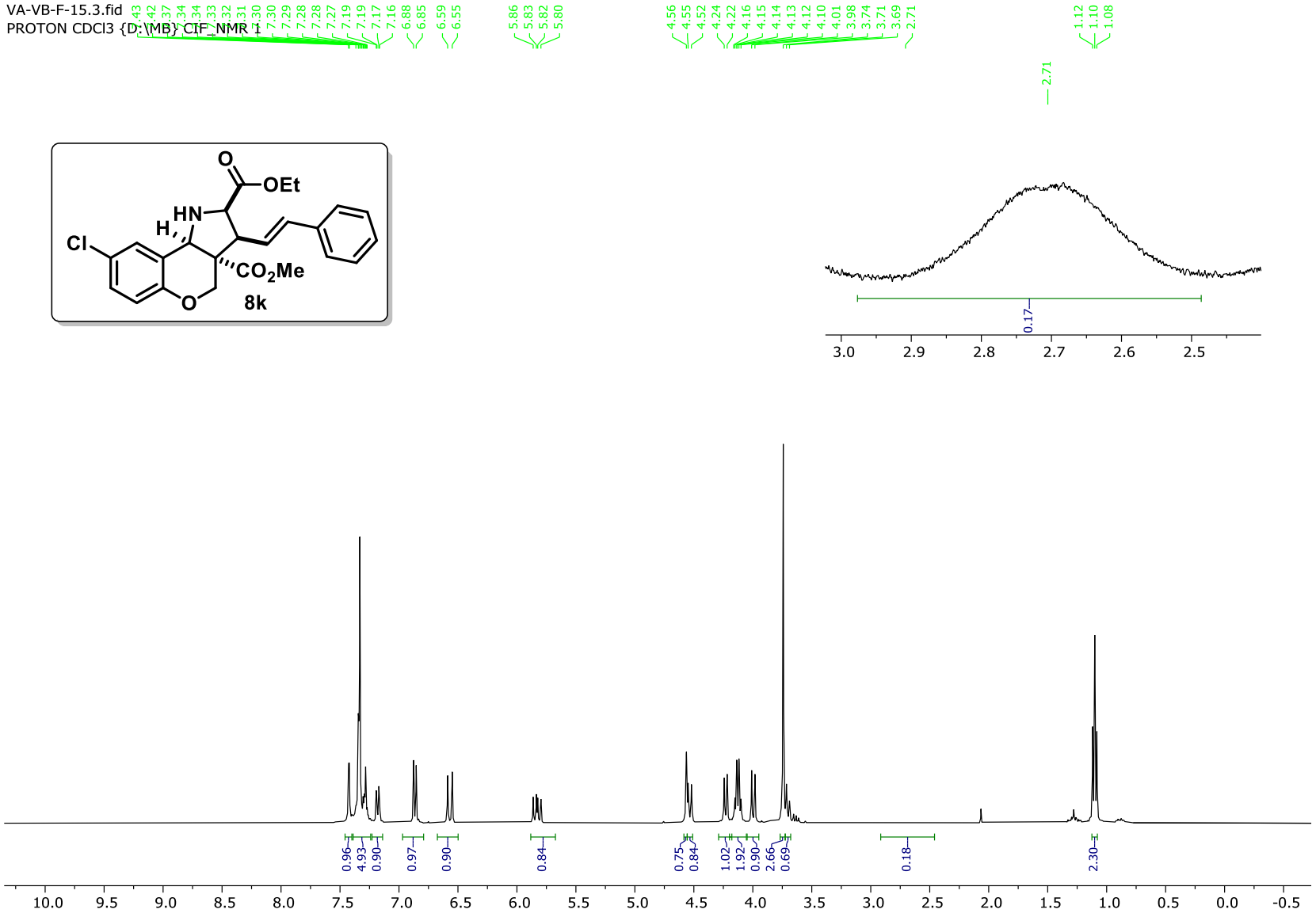

172.45
171.52
150.45
136.26
136.15
135.05
132.59
128.80
128.26
126.48
124.02
120.67
113.37
112.00
77.48
77.16
76.84
65.27
63.34
61.70
58.86
55.17
54.99
52.97
14.24
O
OEt
HN
H
Br
CO2Me
O
Br
8i
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
VA-VB-F-11.2.1.1r — C13CPD CDCl3 {D:\MB} CIF_NMR 1

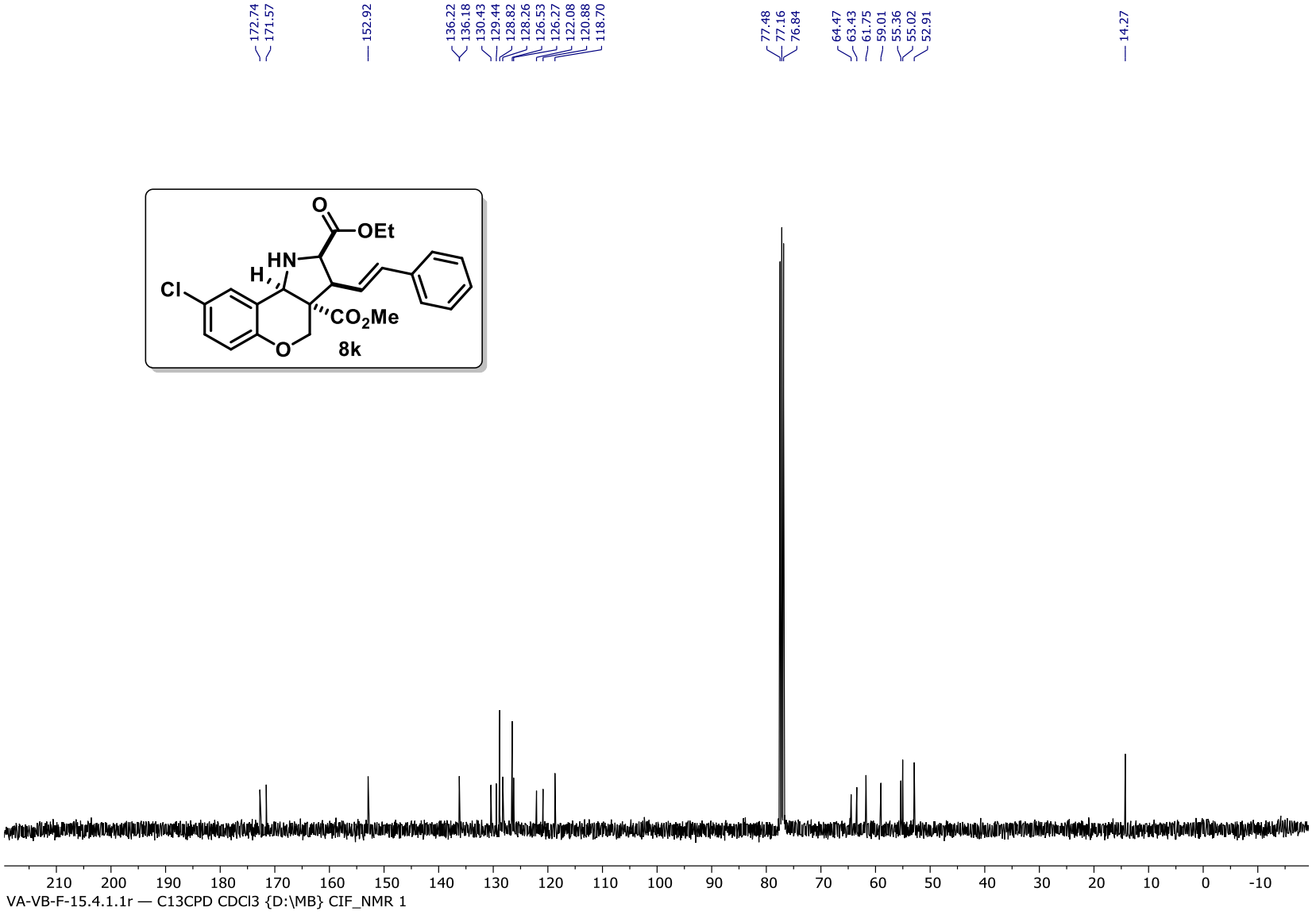
2-Ethyl 3a-methyl (*E*)-3-styryl-1,2,3,11c-tetrahydrobenzo[5,6]chromeno[4,3-b]pyrrole-2,3a(4*H*)-dicarboxylate (8j)



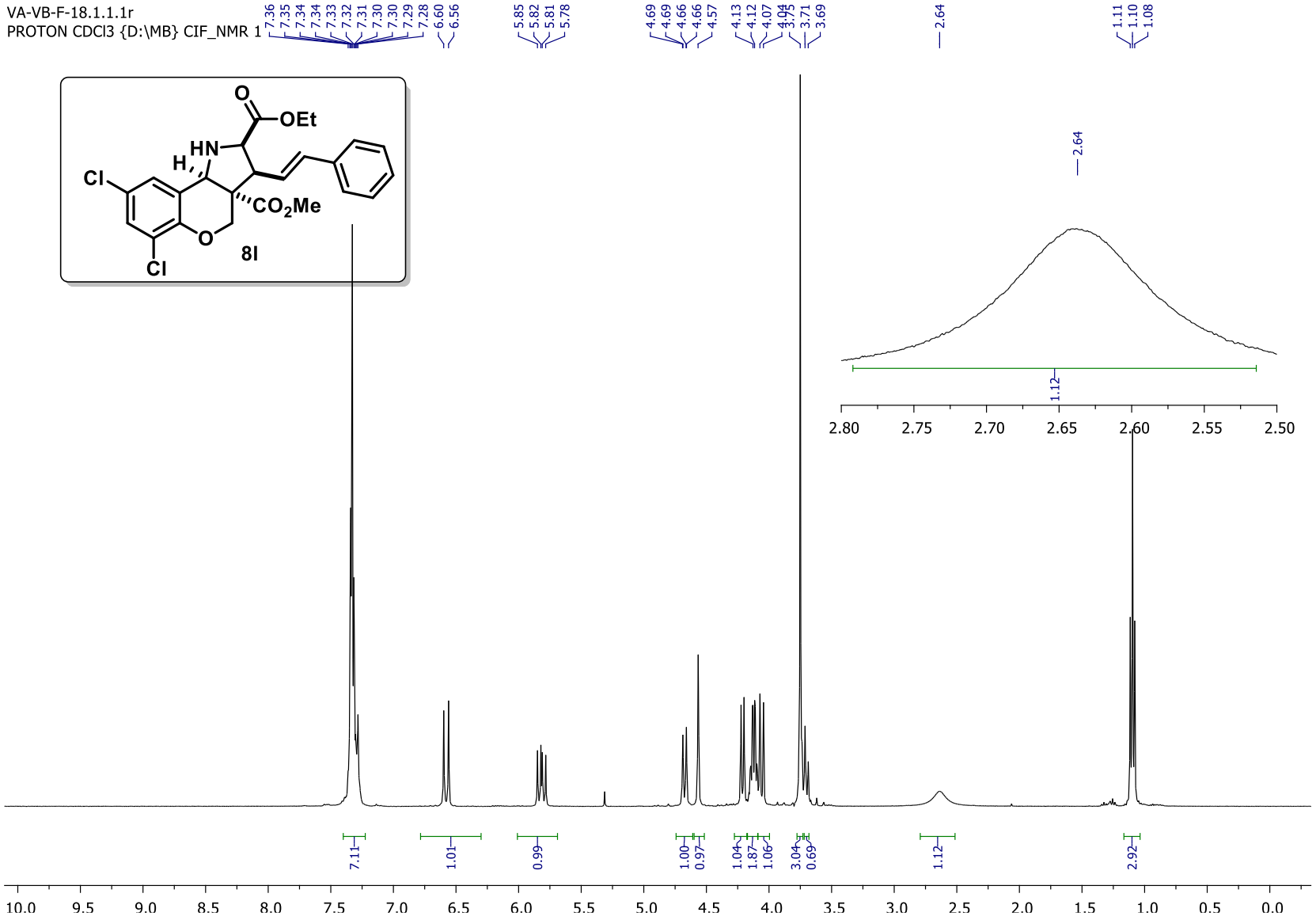

172.91
172.21
152.10
136.32
135.97
133.52
129.98
129.34
128.79
128.31
128.15
127.05
126.50
123.97
123.68
121.26
118.63
112.74
77.48
77.16
76.85
63.76
63.66
61.61
57.55
55.67
54.86
52.76
14.26
O
OEt
HN
H
CO2Me
O
8j
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
VA-VB-F-12.2.1.1r — C13CPD CDCl3 {D:\MB} CIF_NMR 1

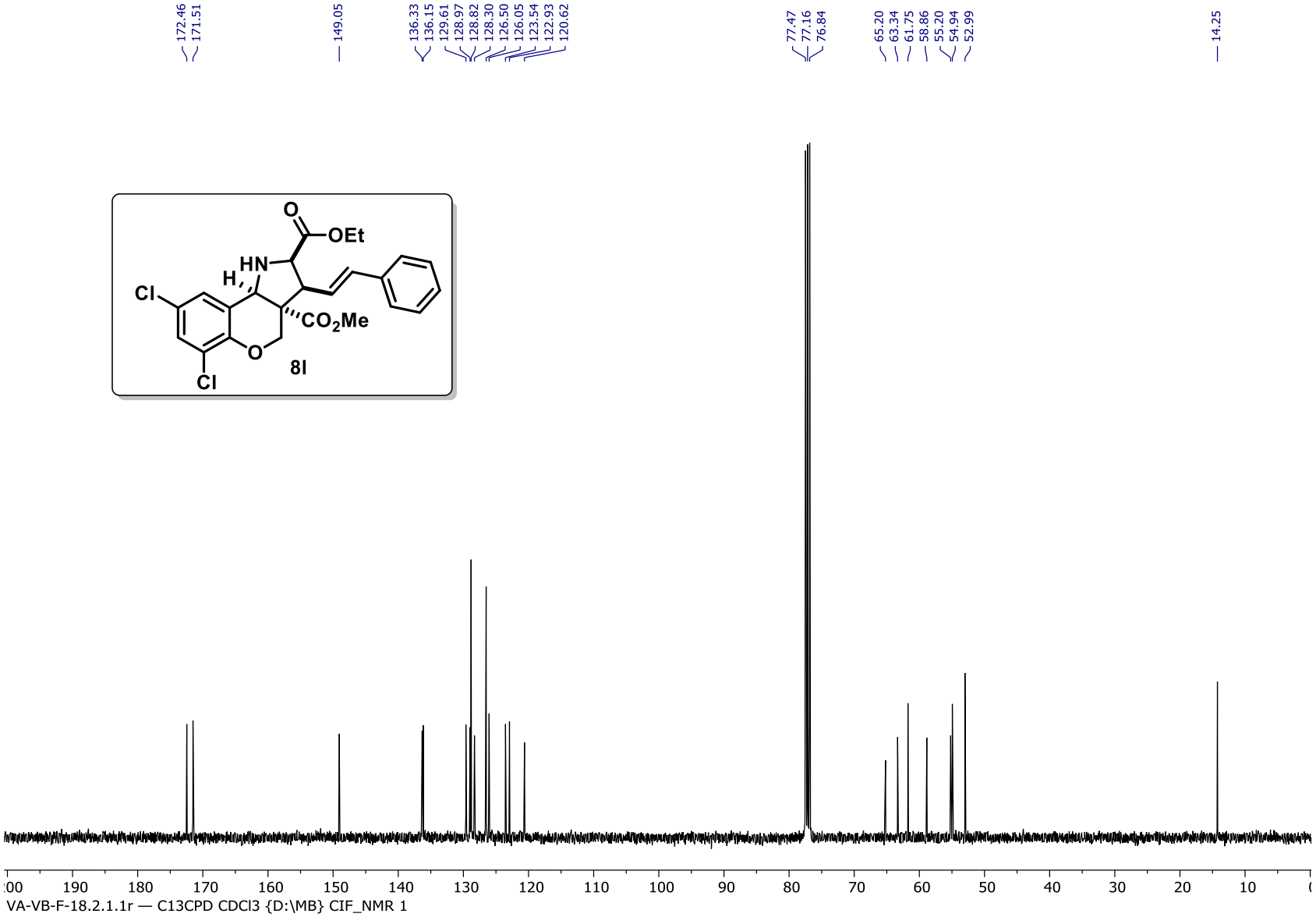
2-Ethyl 3a-methyl (*E*)-8-chloro-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole-2,3a(4*H*)-dicarboxylate (8k):



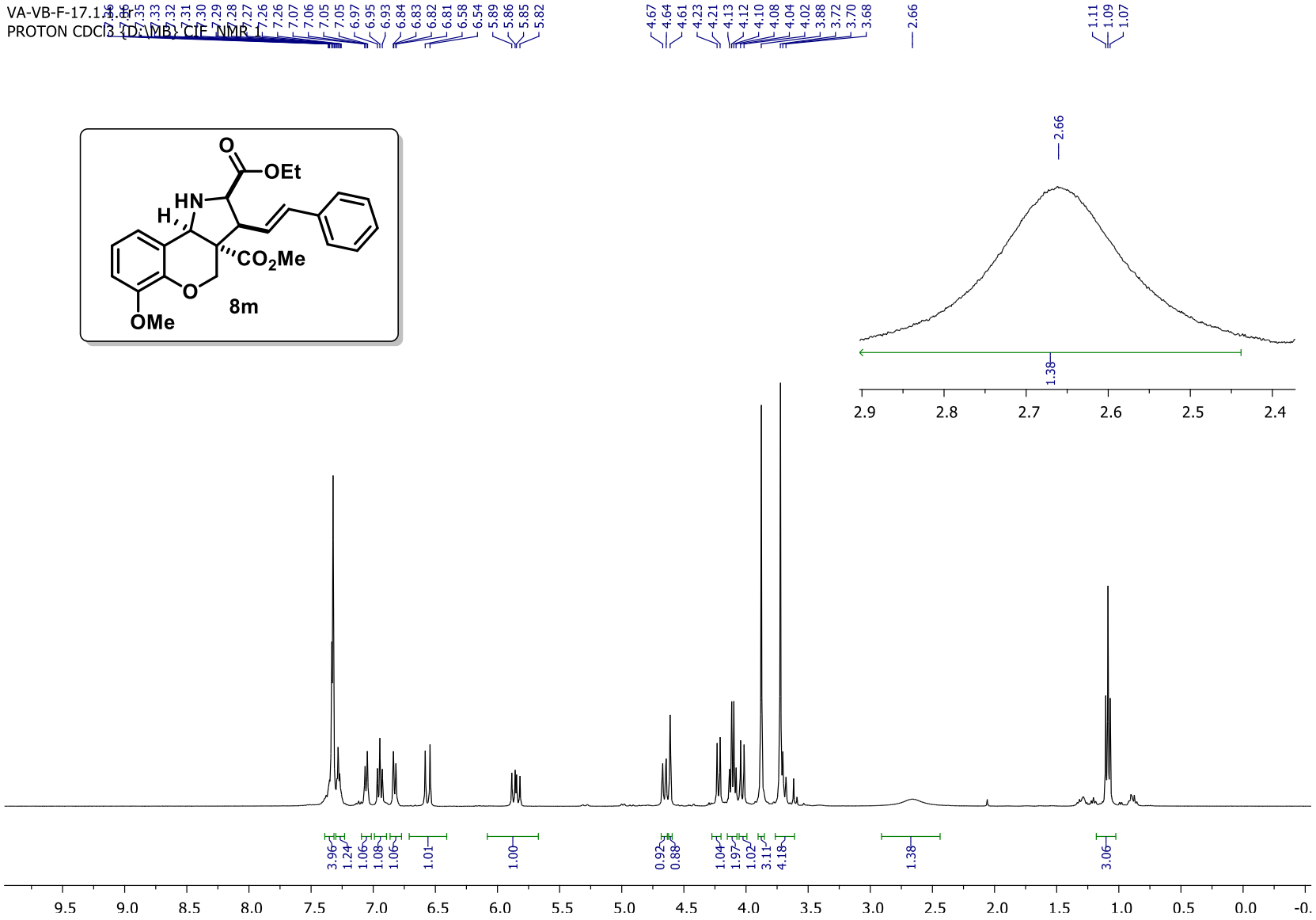

172.74
171.57
152.92
136.22
136.18
130.43
129.44
128.82
128.26
126.53
126.27
122.08
120.88
118.70
77.48
77.16
76.84
64.47
63.43
61.75
59.01
55.36
55.02
52.91
14.27
O
OEt
HN
H
Cl
CO2Me
O
8k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
VA-VB-F-15.4.1.1r — C13CPD CDCl3 {D:\MB} CIF_NMR 1

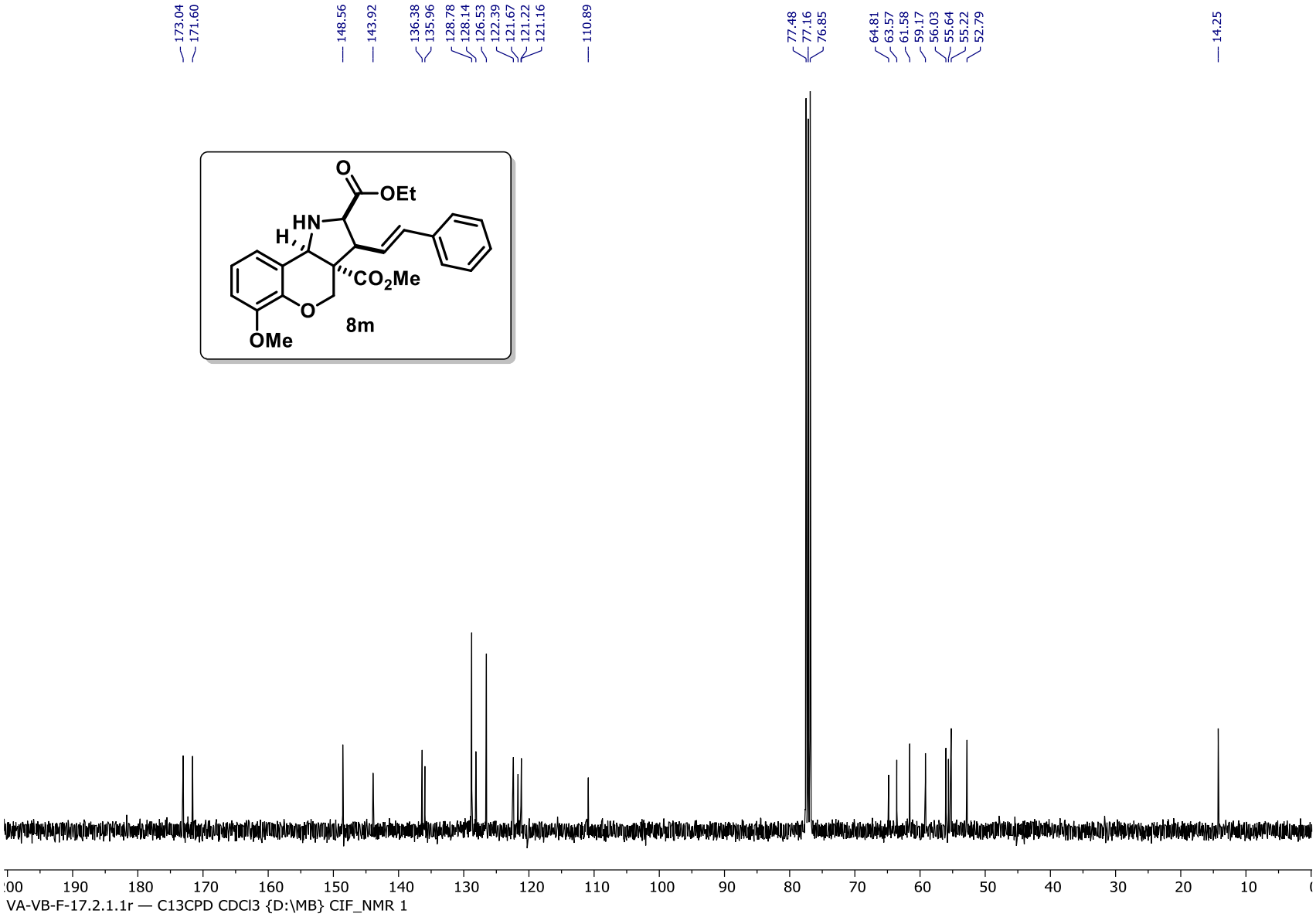
2-Ethyl 3a-methyl (*E*)-6,8-dichloro-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole-2,3a(4*H*)-dicarboxylate (8l)



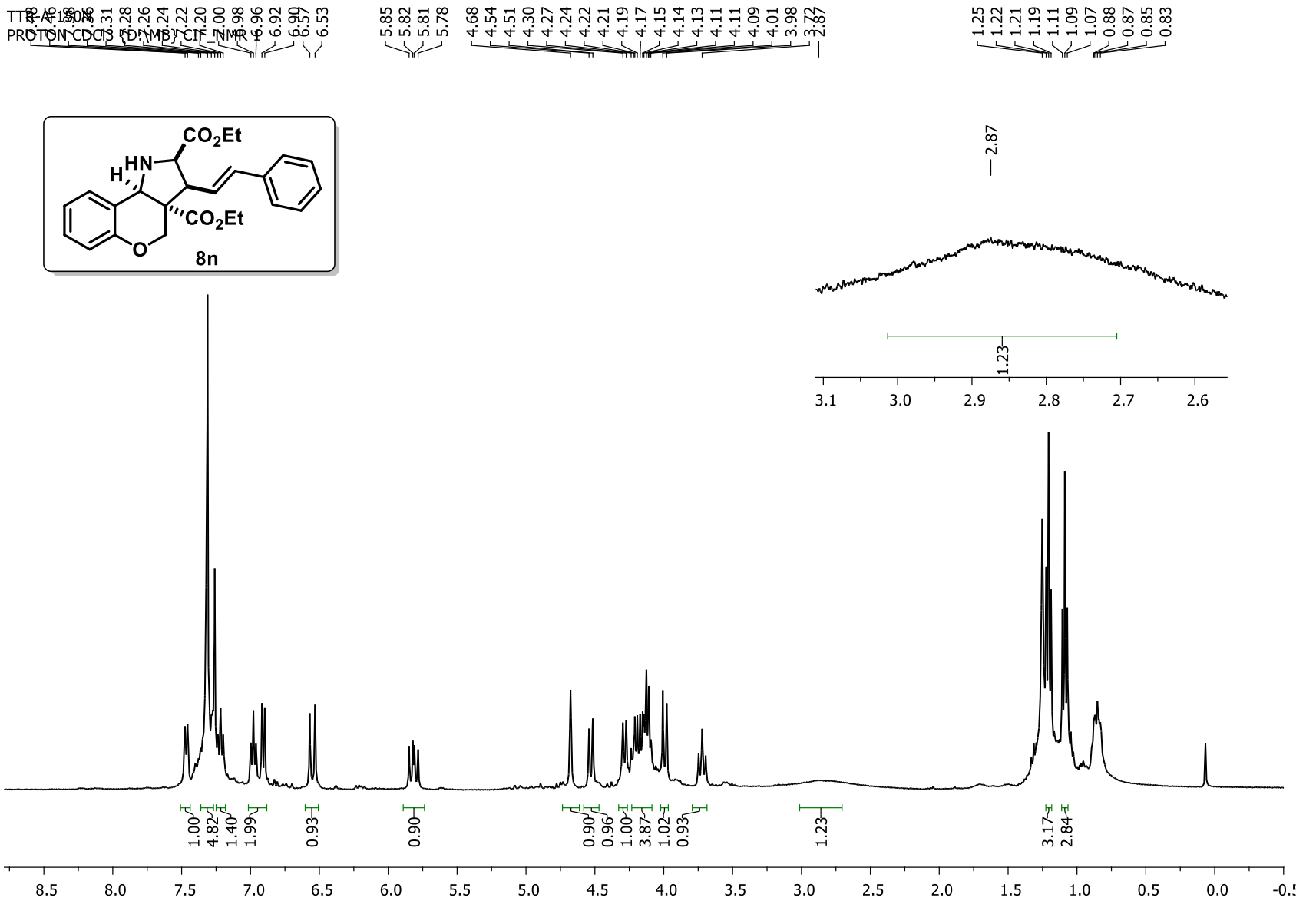

172.46
171.51
149.05
136.33
136.15
129.61
128.97
128.82
128.30
126.50
126.05
123.54
122.93
120.62
77.47
77.16
76.84
65.20
63.34
61.75
58.86
55.20
54.94
52.99
14.25
O
OEt
HN
H
Cl
CO2Me
O
Cl
8l
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
VA-VB-F-18.2.1.1r — C13CPD CDCl3 {D:\MB} CIF_NMR 1

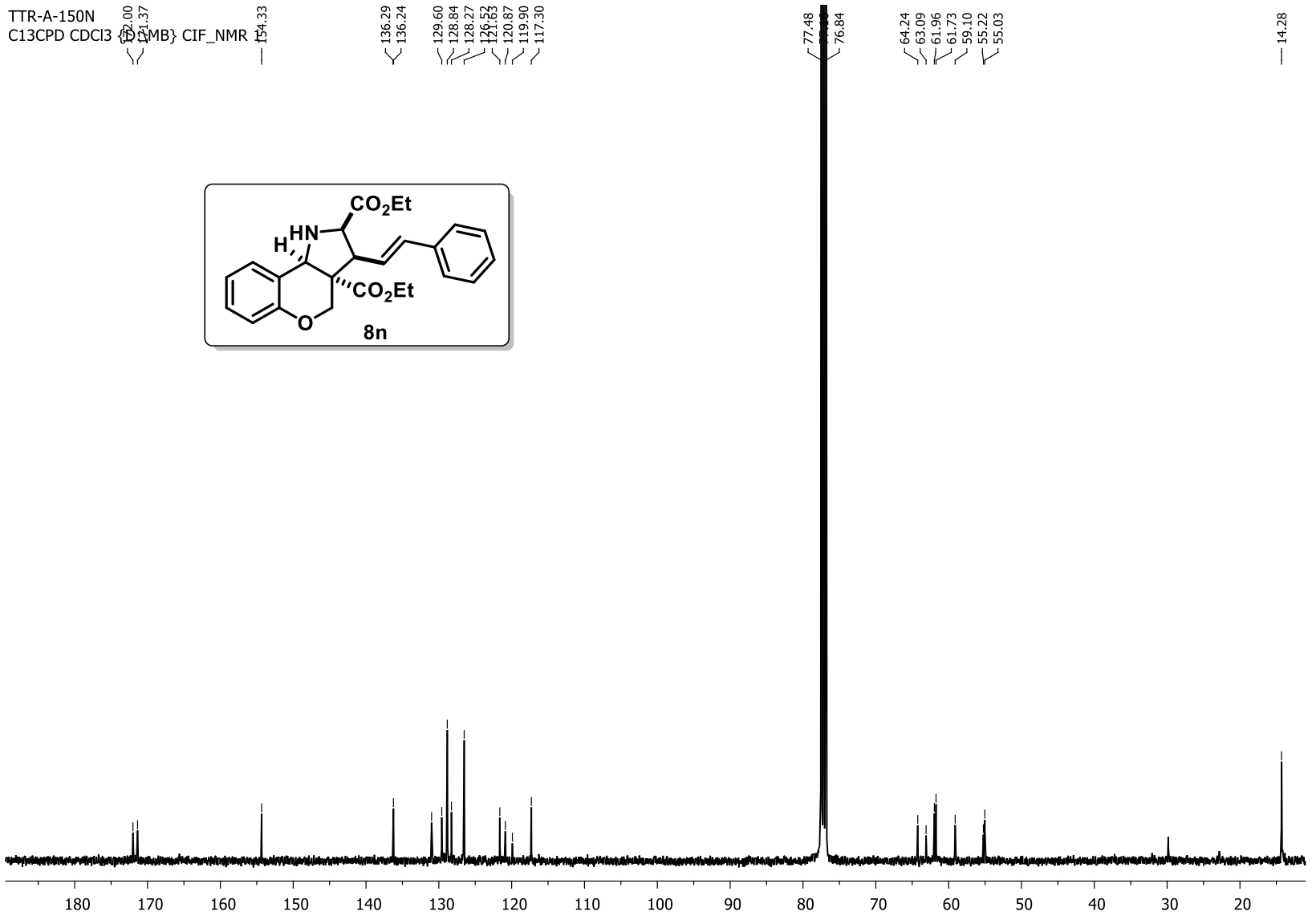
2-Ethyl 3a-methyl (*E*)-6-methoxy-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole-2,3a(4*H*)-dicarboxylate (8m)



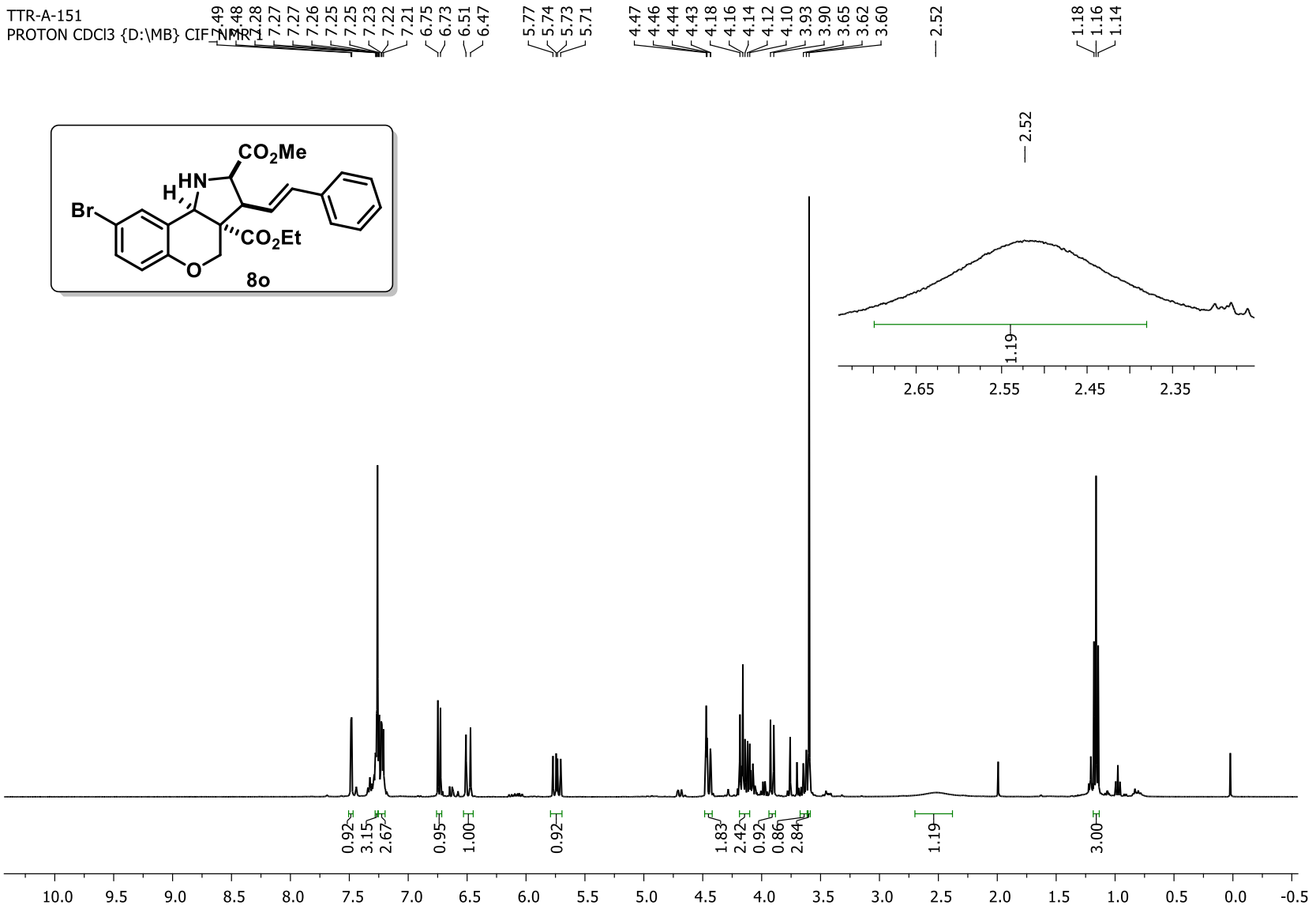

173.04
171.60
148.56
143.92
136.38
135.96
128.78
128.14
126.53
122.39
121.67
121.22
121.16
110.89
77.48
77.16
76.85
64.81
63.57
61.58
59.17
56.03
55.64
55.22
52.79
14.25
O
OEt
HN
H
CO2Me
O
OMe
8m
VA-VB-F-17.2.1.1r — C13CPD CDCl3 {D:\MB} CIF_NMR 1

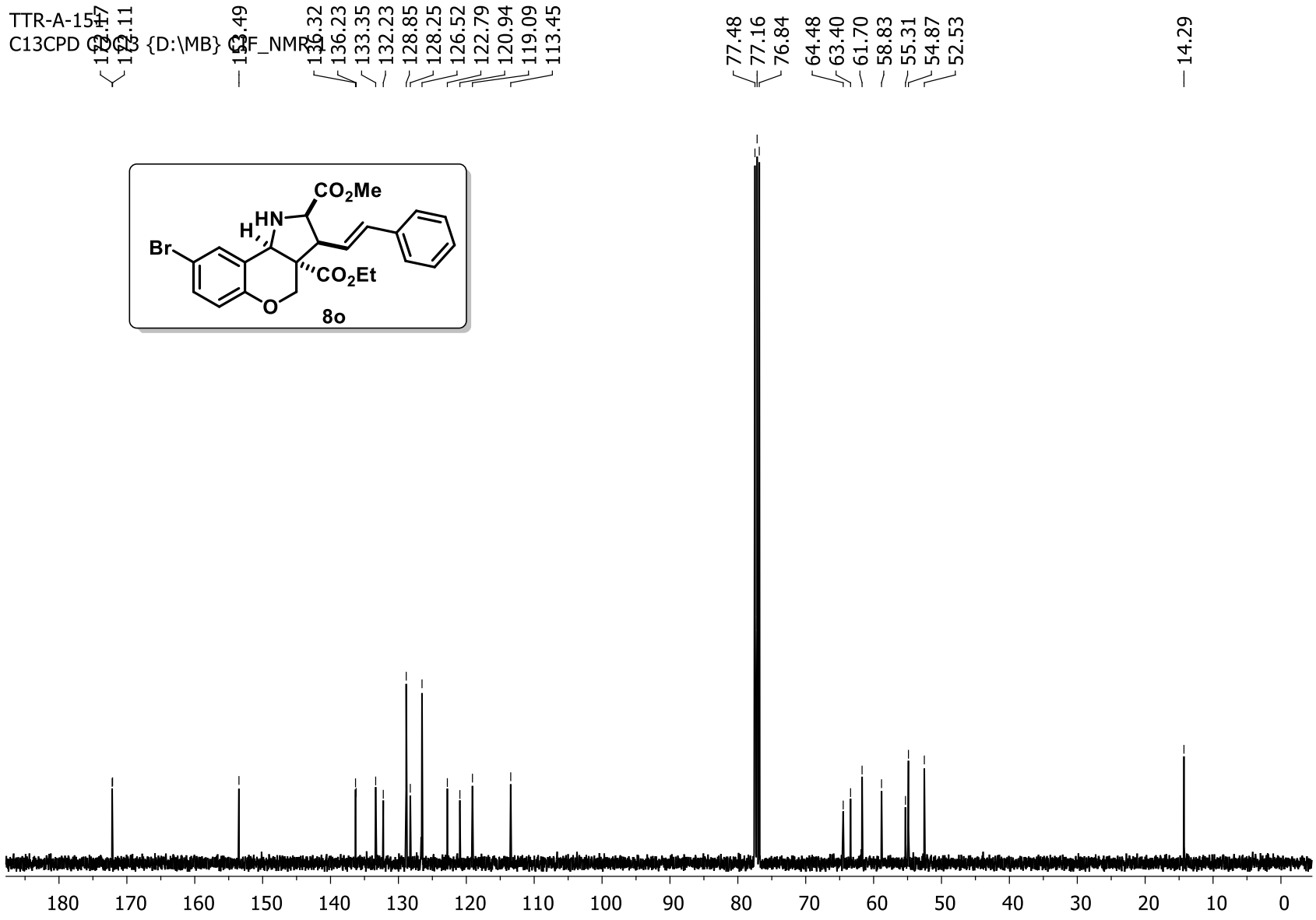
Diethyl (*E*)-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole-2,3a(4*H*)-dicarboxylate (8n)



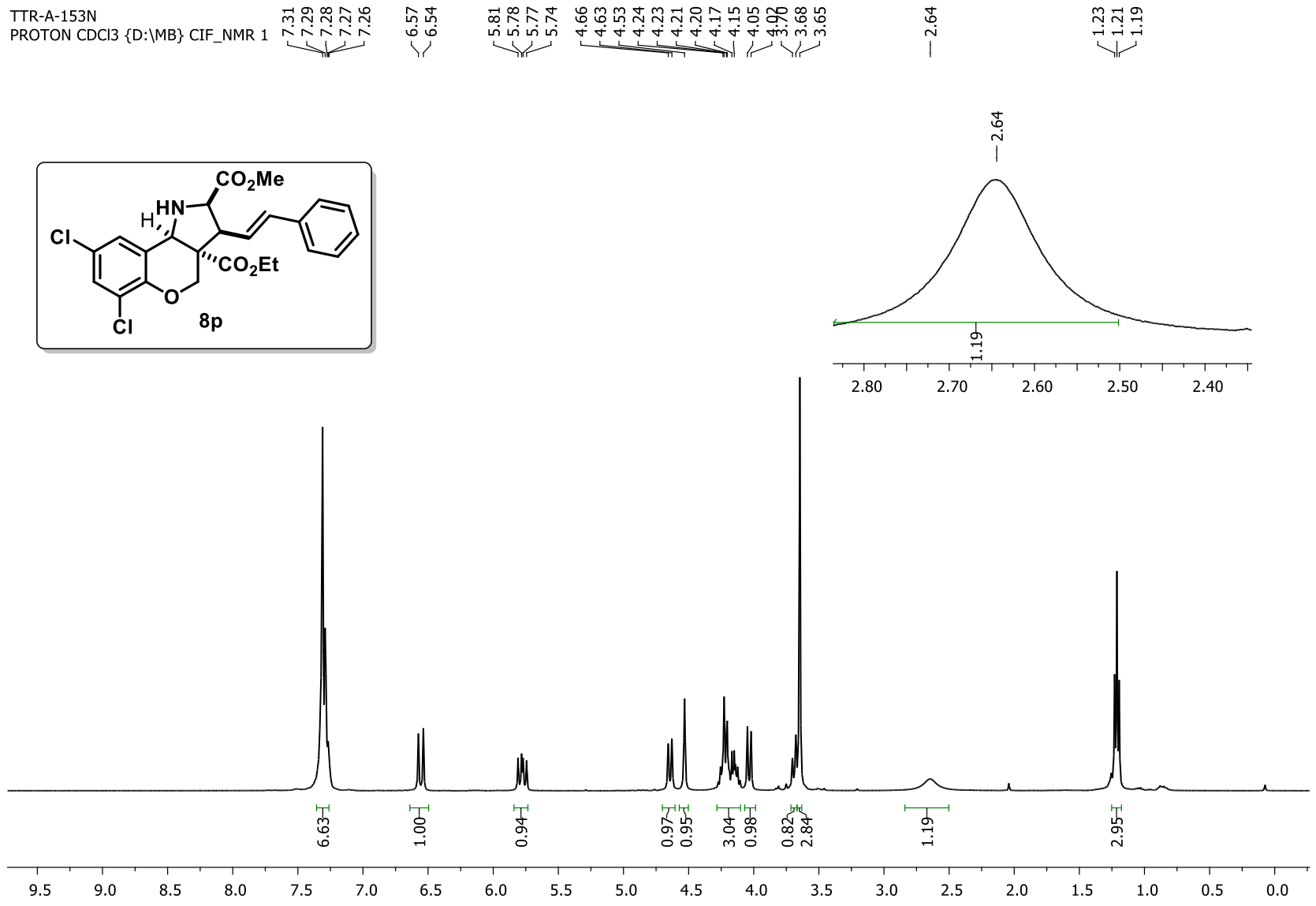

TTR-A-150N
C13CPD CDCl3 {D1MB} CIF_NMR 1
172.00
171.37
154.33
136.29
136.24
129.60
128.84
128.27
126.52
121.63
120.87
119.90
117.30
77.48
76.84
64.24
63.09
61.96
61.73
59.10
55.22
55.03
14.28
CO2Et
HN
H
CO2Et
O
8n
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20

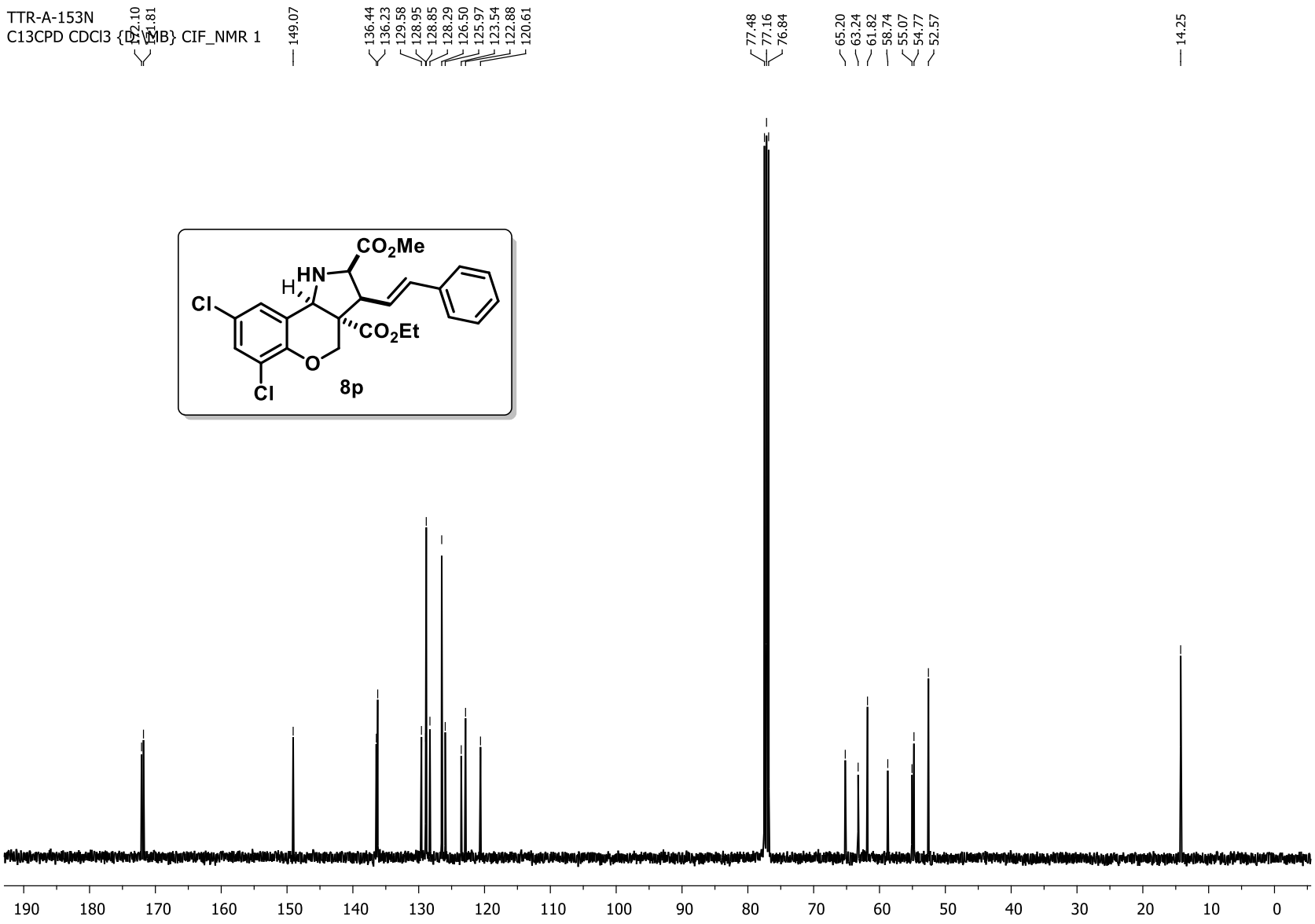
Ethyl 2-methyl (*E*)-8-bromo-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole-2,3a(4*H*)-dicarboxylate (8o)



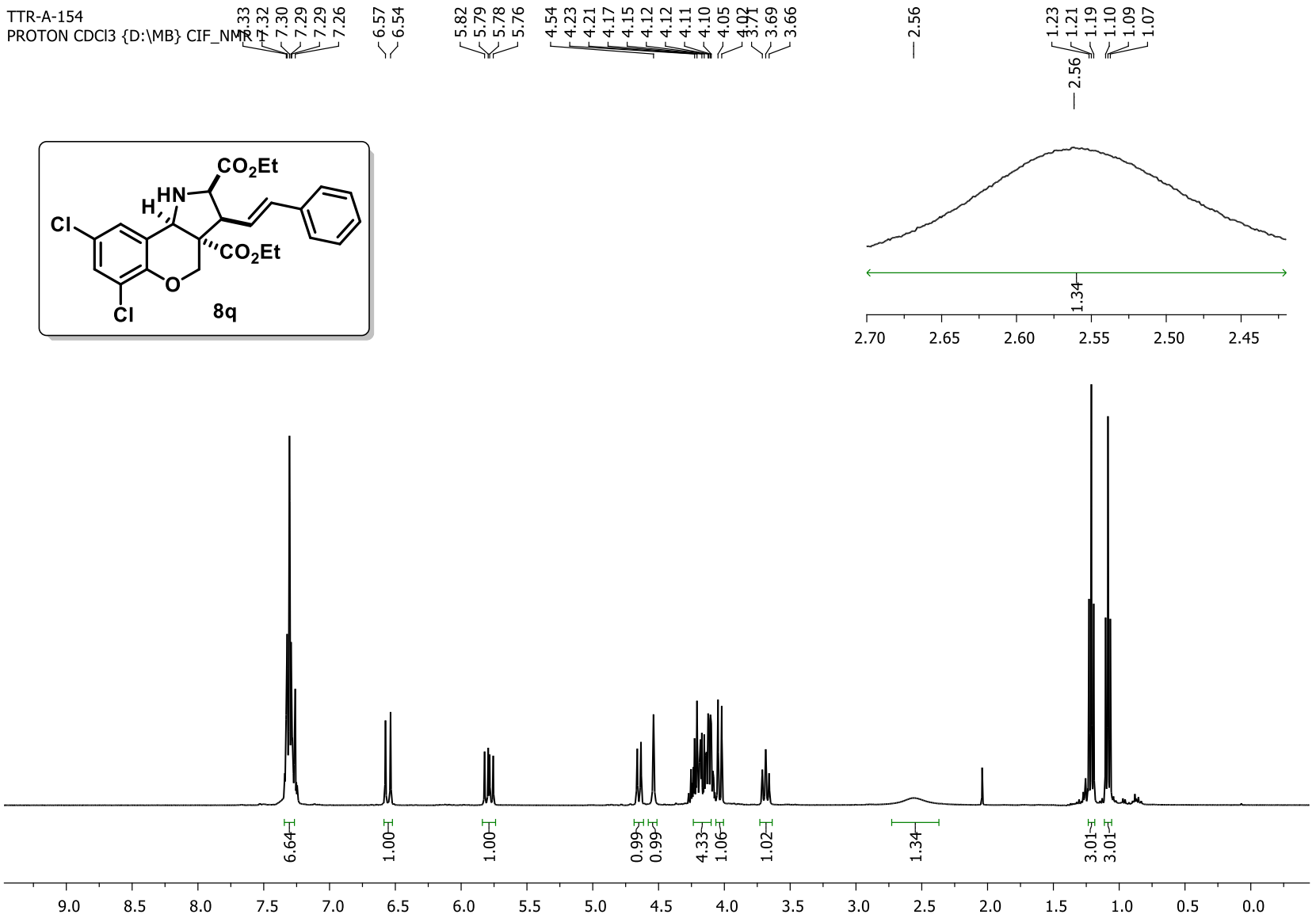

TTR-A-154
C13CPD CDCl3 {D:\MB} C13F_NMR
172.17
172.11
153.49
136.32
136.23
133.35
132.23
128.85
128.25
126.52
122.79
120.94
119.09
113.45
77.48
77.16
76.84
64.48
63.40
61.70
58.83
55.31
54.87
52.53
14.29
CO2Me
HN
H
Br
CO2Et
O
8o
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

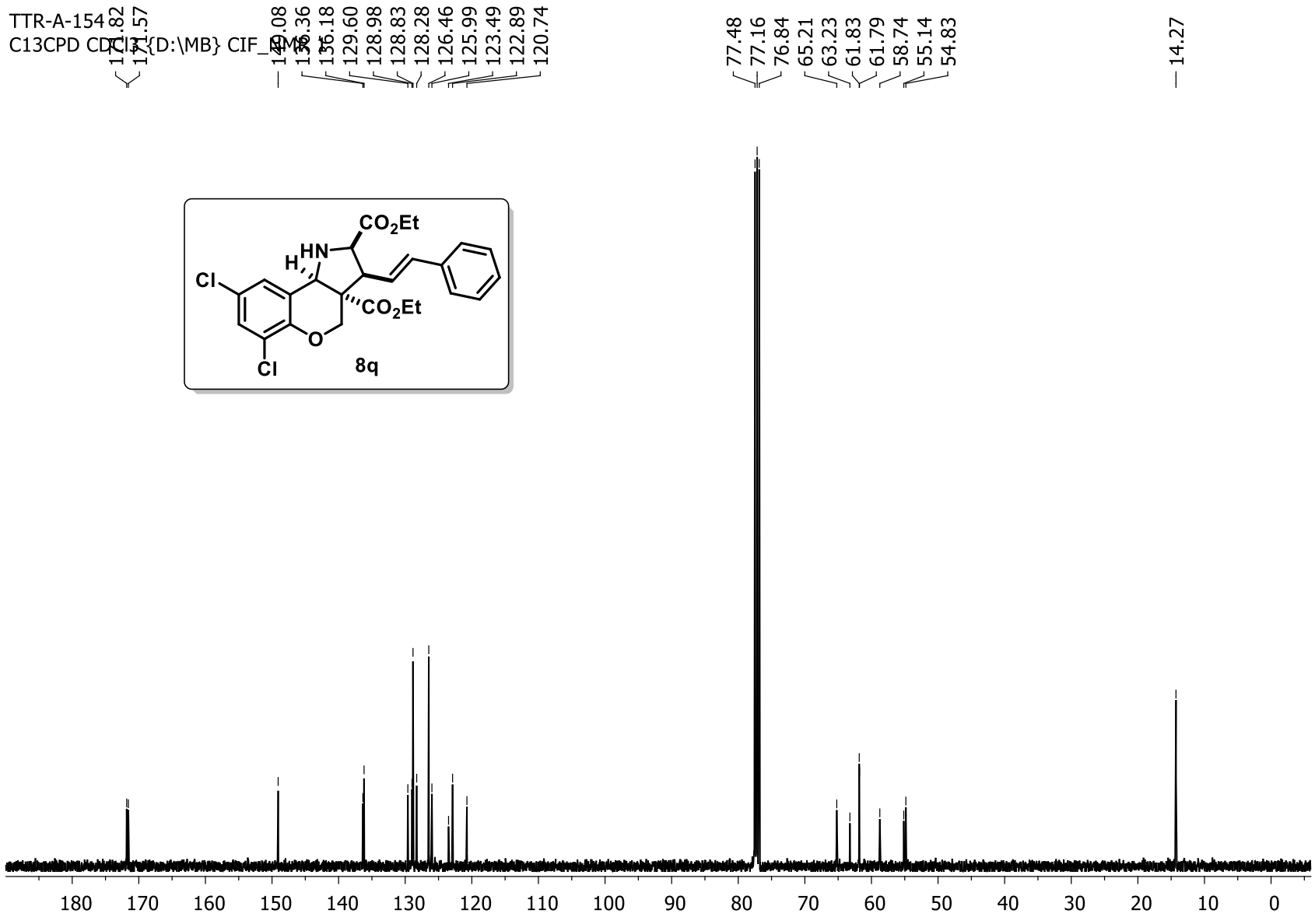
Ethyl 2-methyl (*E*)-6,8-dichloro-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole-2,3a(4*H*)-dicarboxylate (8p)



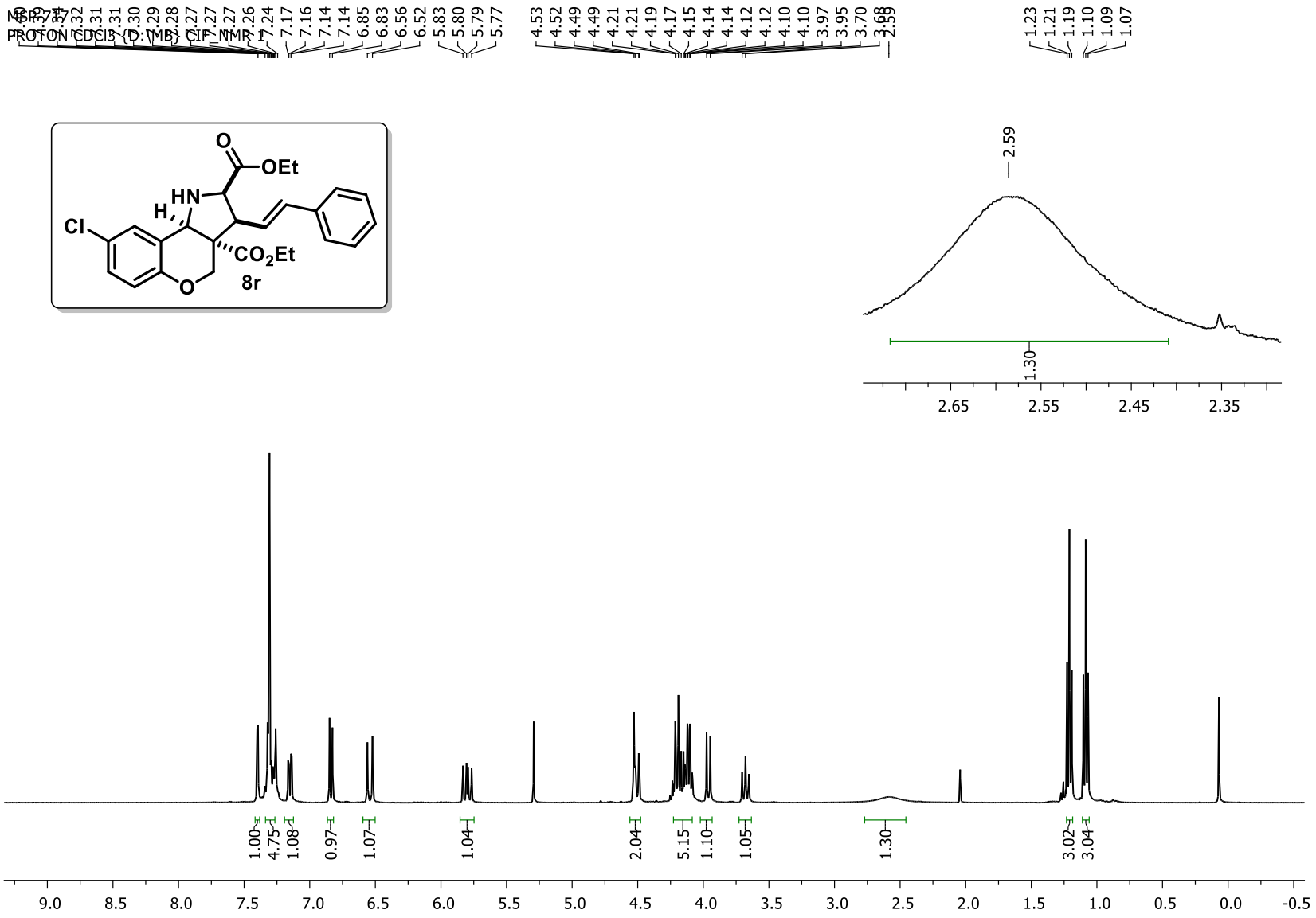

TTR-A-153N
C13CPD CDCl3 {D:\NMR} CIF_NMR 1
172.10
171.81
149.07
136.44
136.23
129.58
128.95
128.85
128.29
126.50
125.97
123.54
122.88
120.61
77.48
77.16
76.84
65.20
63.24
61.82
58.74
55.07
54.77
52.57
14.25
CO2Me
HN
H
Cl
CO2Et
O
Cl
8p
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

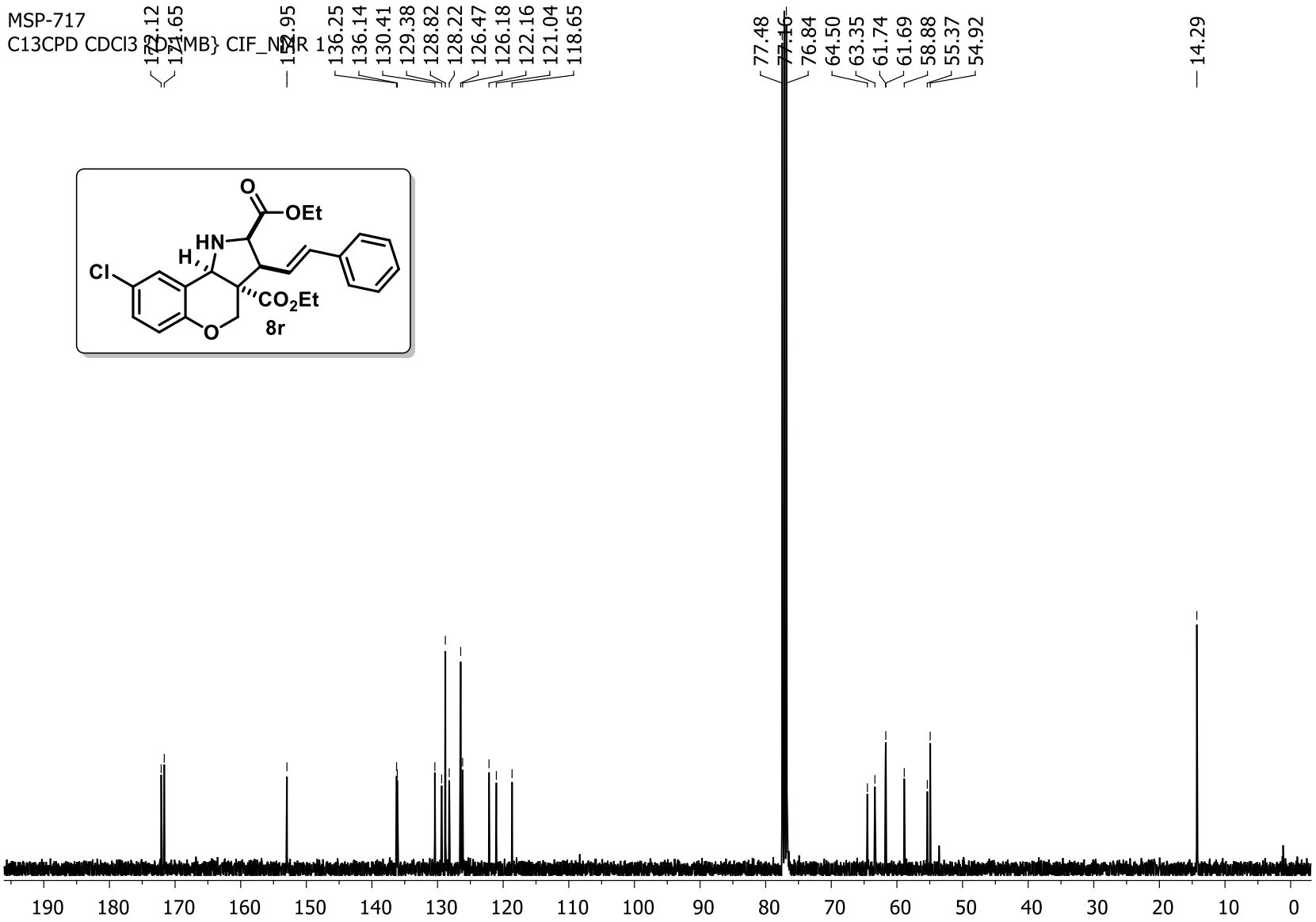
Diethyl (*E*)-6,8-dichloro-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole-2,3a(4*H*)-dicarboxylate (8q)



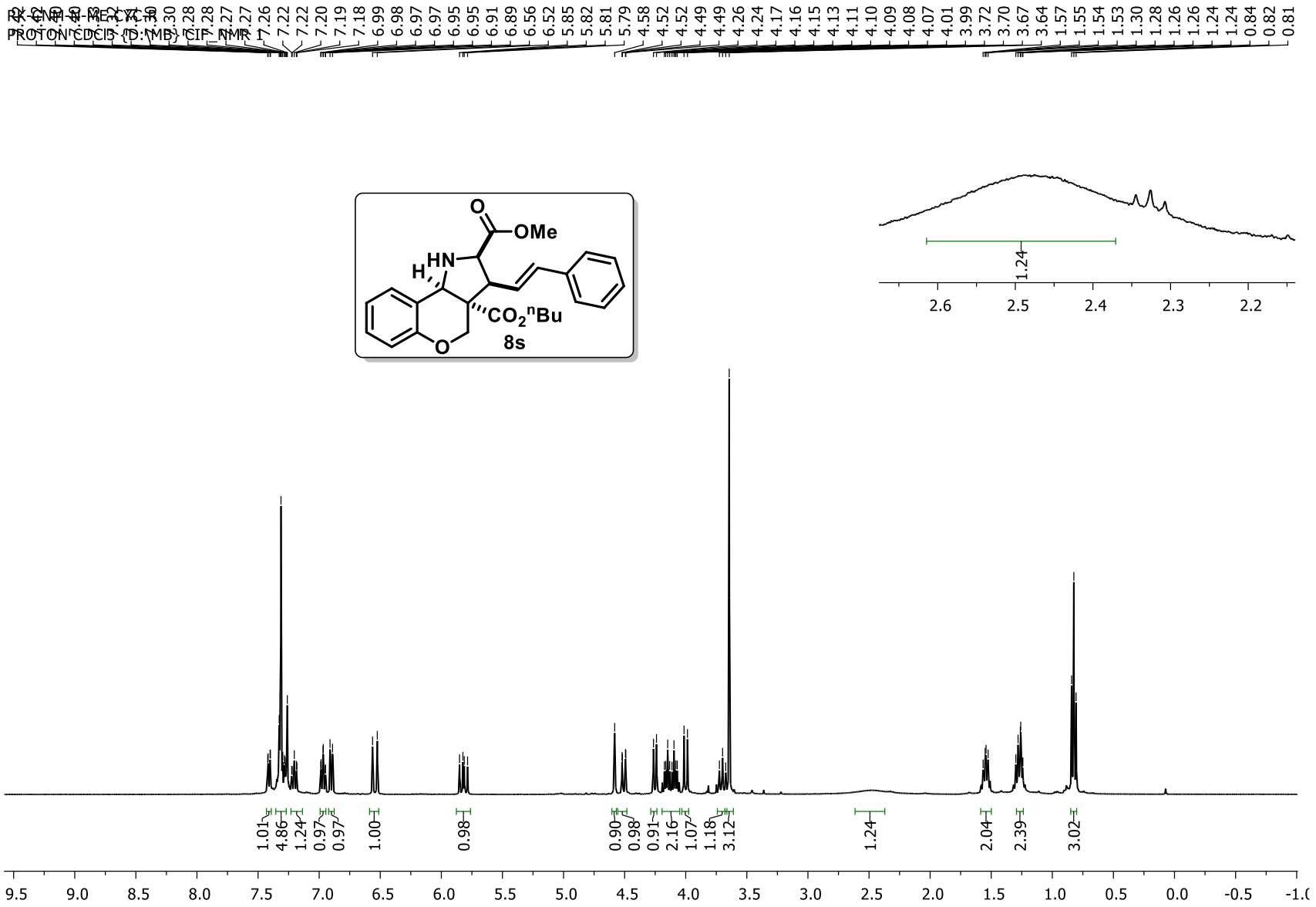

TTR-A-154
C13CPD CDCl3 {D:\MB} CIF_AMX 1
171.82
171.57
149.08
135.36
135.18
129.60
128.98
128.83
128.28
126.46
125.99
123.49
122.89
120.74
77.48
77.16
76.84
65.21
63.23
61.83
61.79
58.74
55.14
54.83
14.27
CO2Et
HN
H
Cl
CO2Et
O
Cl
8q
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

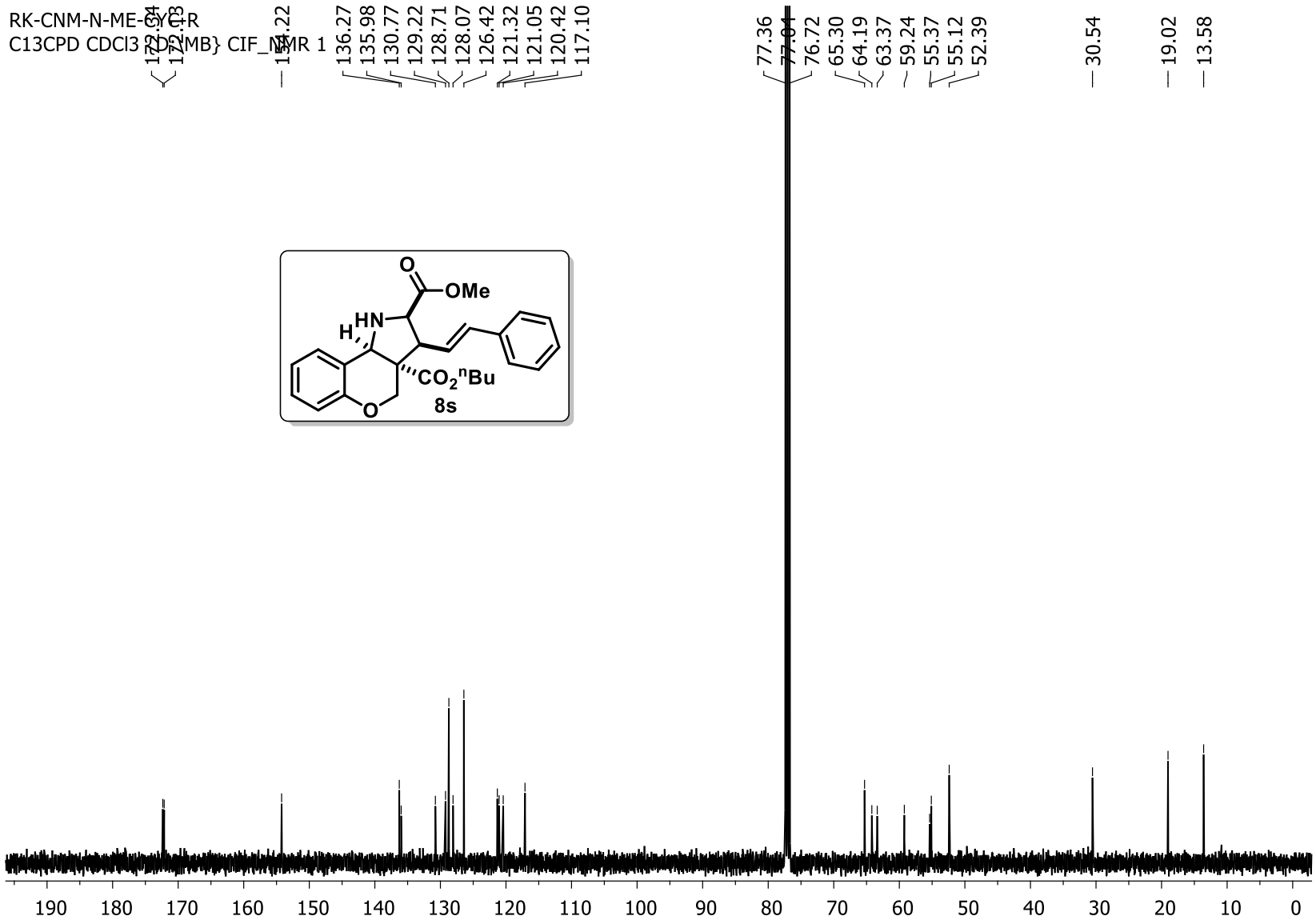
Diethyl (*E*)-8-chloro-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole-2,3a(4*H*)-dicarboxylate (8r)



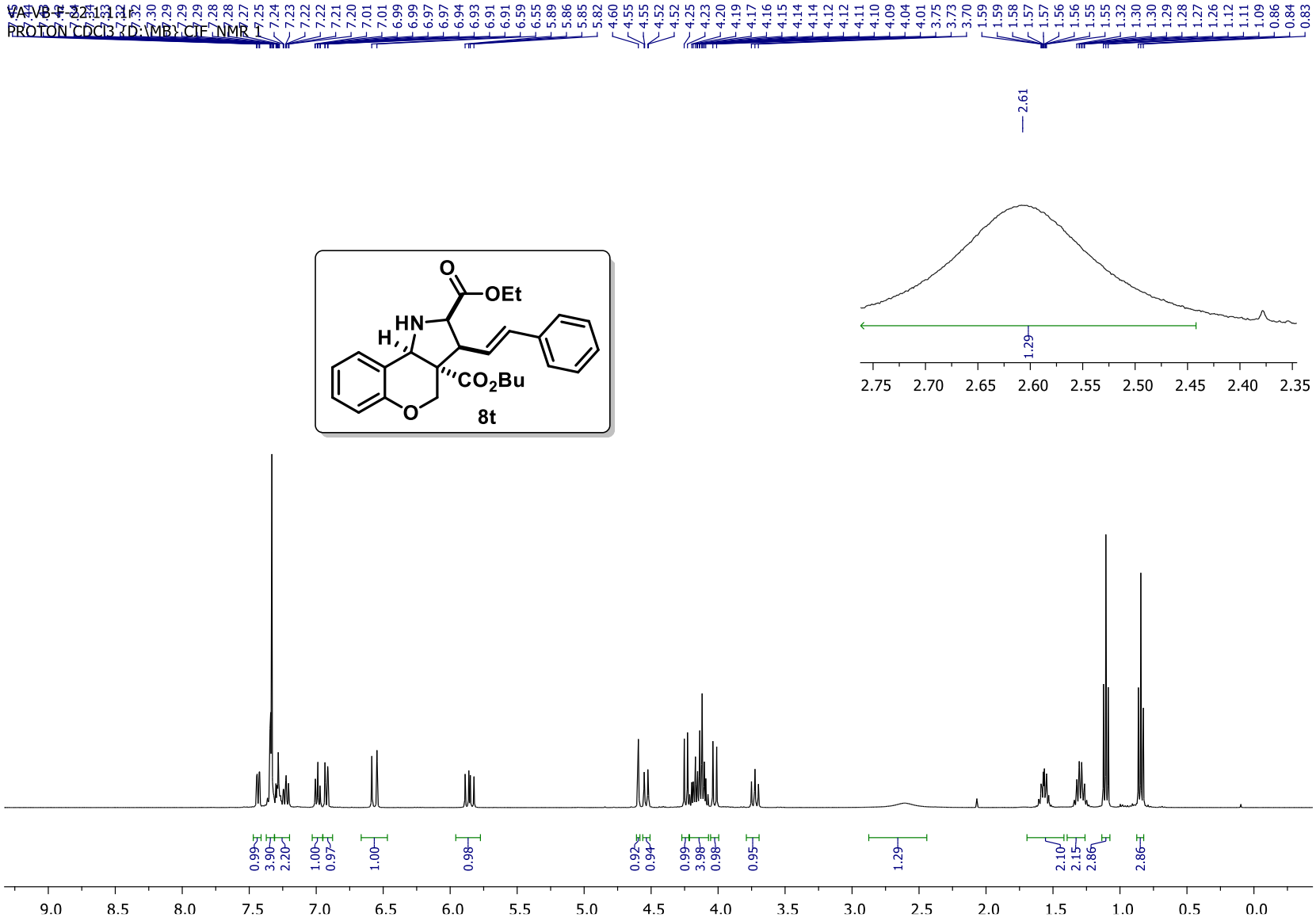

MSP-717
C13CPD CDCl3 {1H-MB} CIF_NMR 1
172.12
171.65
142.95
136.25
136.14
130.41
129.38
128.82
128.22
126.47
126.18
122.16
121.04
118.65
77.48
77.16
76.84
64.50
63.35
61.74
61.69
58.88
55.37
54.92
14.29
O
OEt
HN
H
Cl
CO2Et
O
8r
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

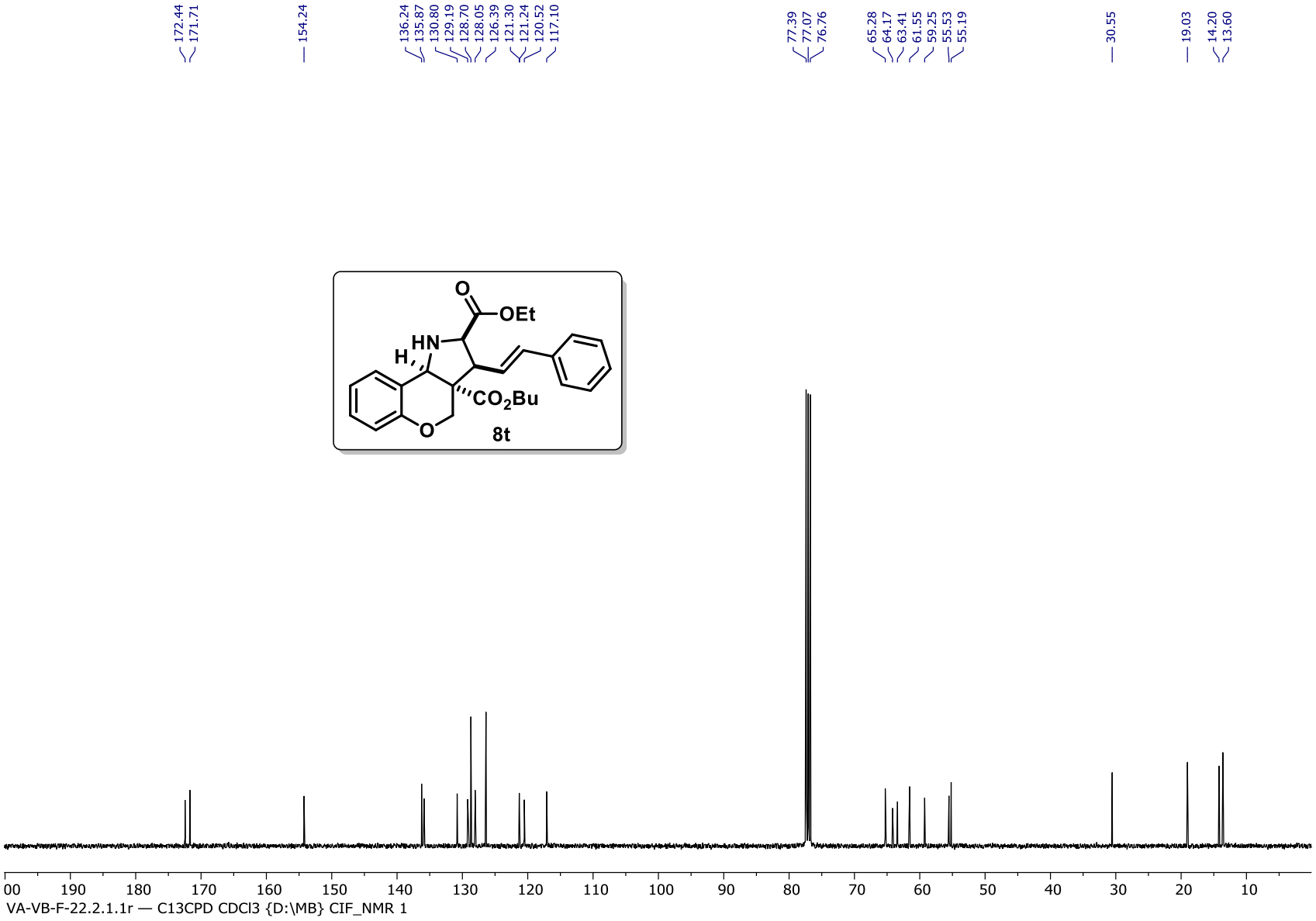
Butyl 2-methyl (*E*)-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole-2,3a(4*H*)-dicarboxylate (8s)



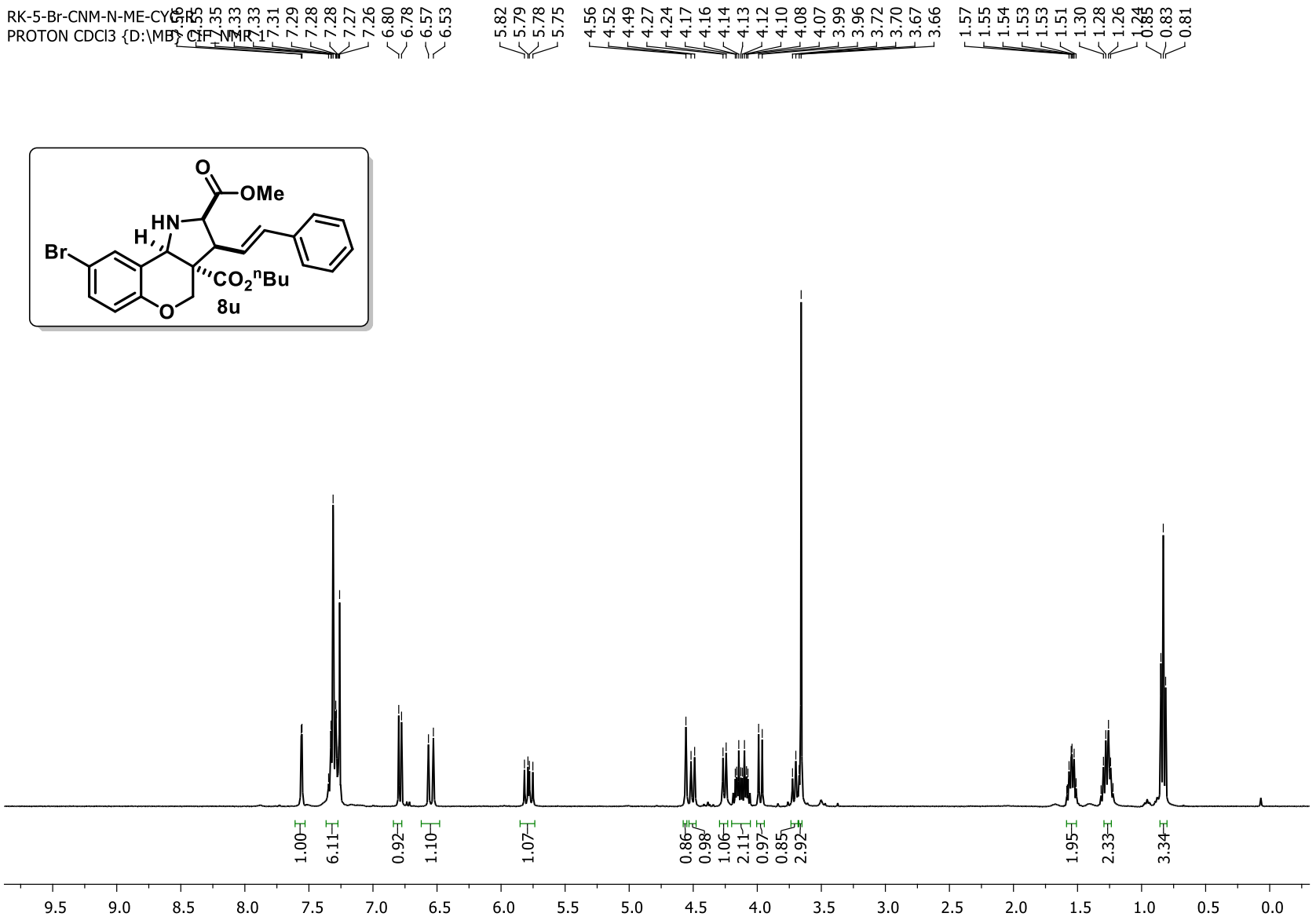

RK-CNM-N-ME-CYC-R
C13CPD CDCl3 {2}MB} CIF_NMR 1
172.24
172.03
154.22
136.27
135.98
130.77
129.22
128.71
128.07
126.42
121.32
121.05
120.42
117.10
77.36
77.04
76.72
65.30
64.19
63.37
59.24
55.37
55.12
52.39
30.54
19.02
13.58
O
OMe
HN
H
CO2nBu
O
8s
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

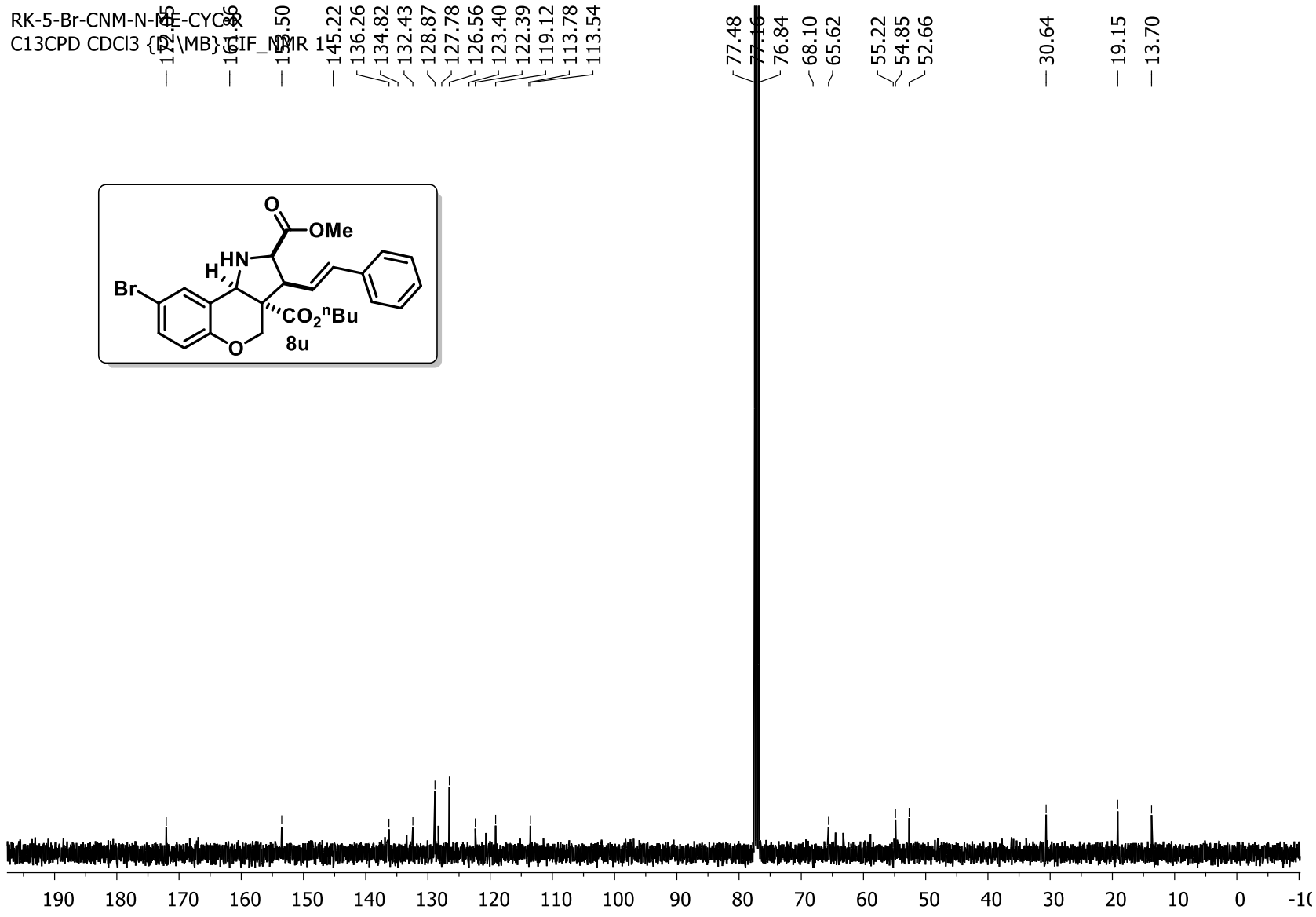
Butyl 2-ethyl (*E*)-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole-2,3a(4*H*)-dicarboxylate (8t)



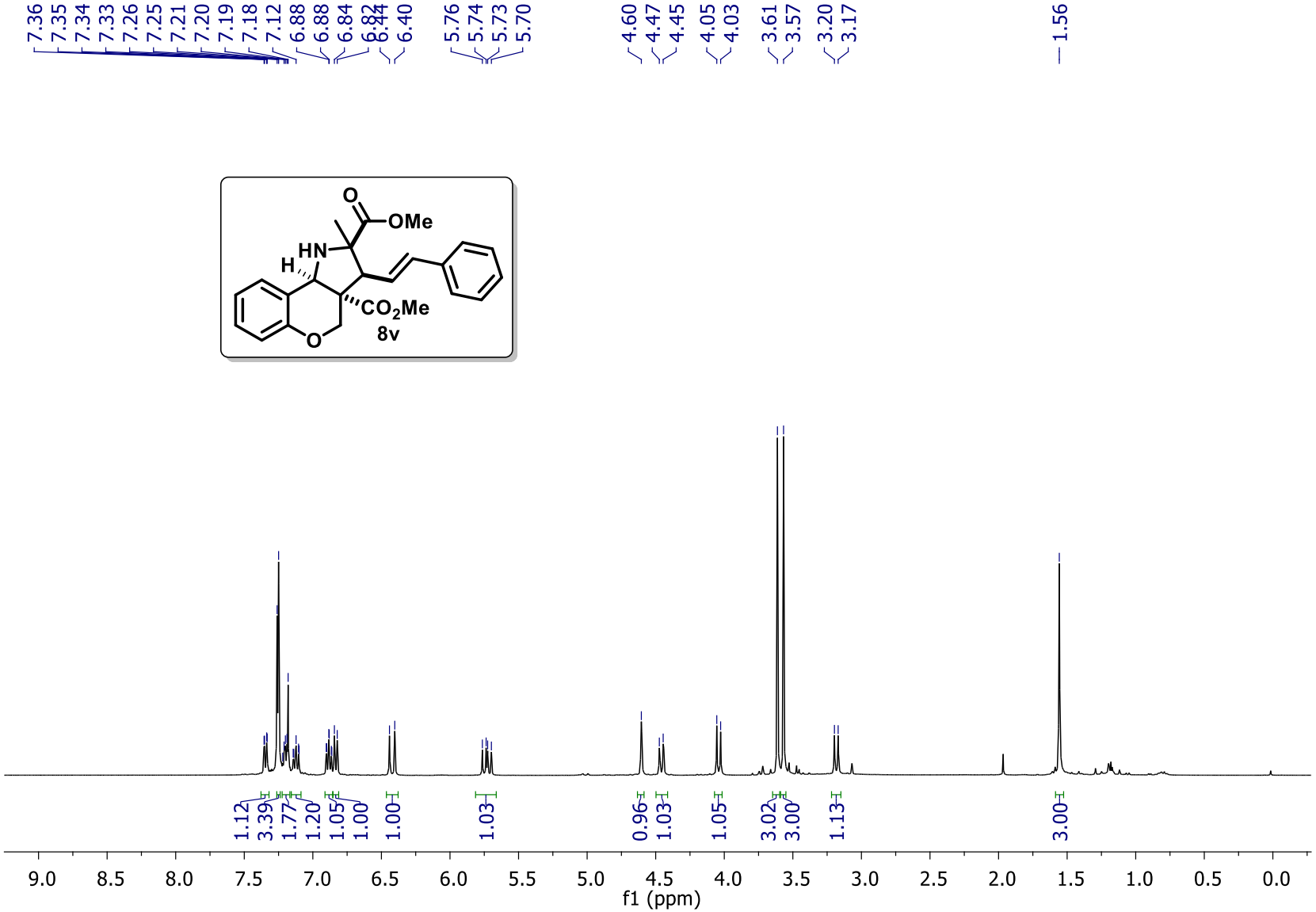

172.44
171.71
154.24
136.24
135.87
130.80
129.19
128.70
128.05
126.39
121.30
121.24
120.52
117.10
77.39
77.07
76.76
65.28
64.17
63.41
61.55
59.25
55.53
55.19
30.55
19.03
14.20
13.60
O
OEt
HN
H
CO2Bu
O
8t
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
VA-VB-F-22.2.1.1r — C13CPD CDCl3 {D:\MB} CIF_NMR 1

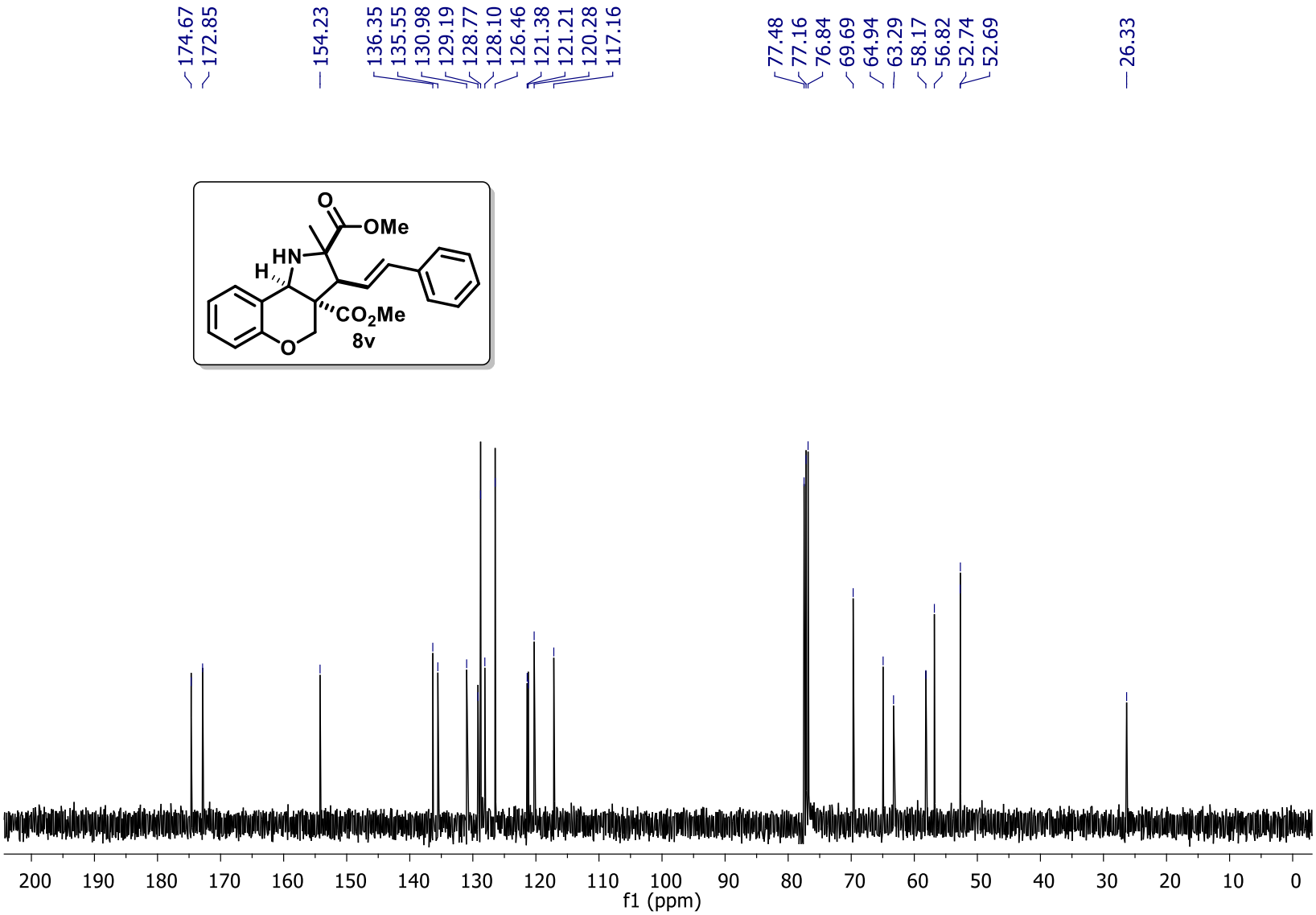
Butyl 2-methyl (*E*)-8-bromo-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole 2,3a(4*H*)- dicarboxylate (8u)



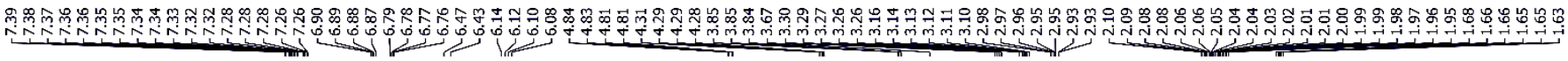

RK-5-Br-CNM-N-ME-CYCEX
C13CPD CDCl3 {D:\MB}1GIF_NMR 1
171.85
161.66
139.50
145.22
136.26
134.82
132.43
128.87
127.78
126.56
123.40
122.39
119.12
113.78
113.54
77.48
77.16
76.84
68.10
65.62
55.22
54.85
52.66
30.64
19.15
13.70
O
OMe
HN
H
Br
CO2nBu
O
8u
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

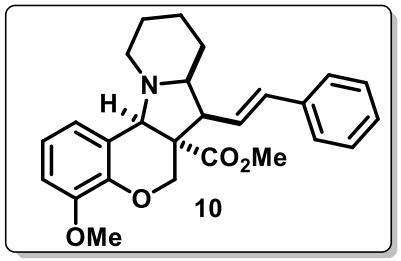
Dimethyl (E)-2-methyl-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole 2,3a(4H)-dicarboxylate (8v)

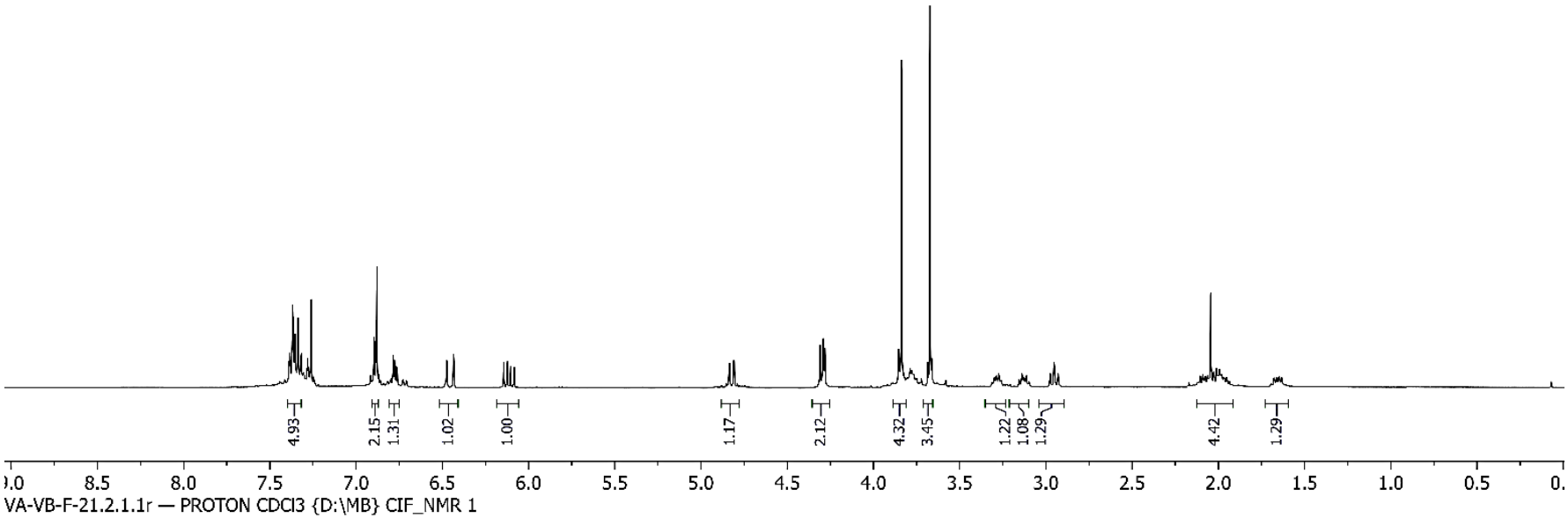



174.67
172.85
154.23
136.35
135.55
130.98
129.19
128.77
128.10
126.46
121.38
121.21
120.28
117.16
77.48
77.16
76.84
69.69
64.94
63.29
58.17
56.82
52.74
52.69
26.33
O
OMe
HN
H
CO2Me
O
8v
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

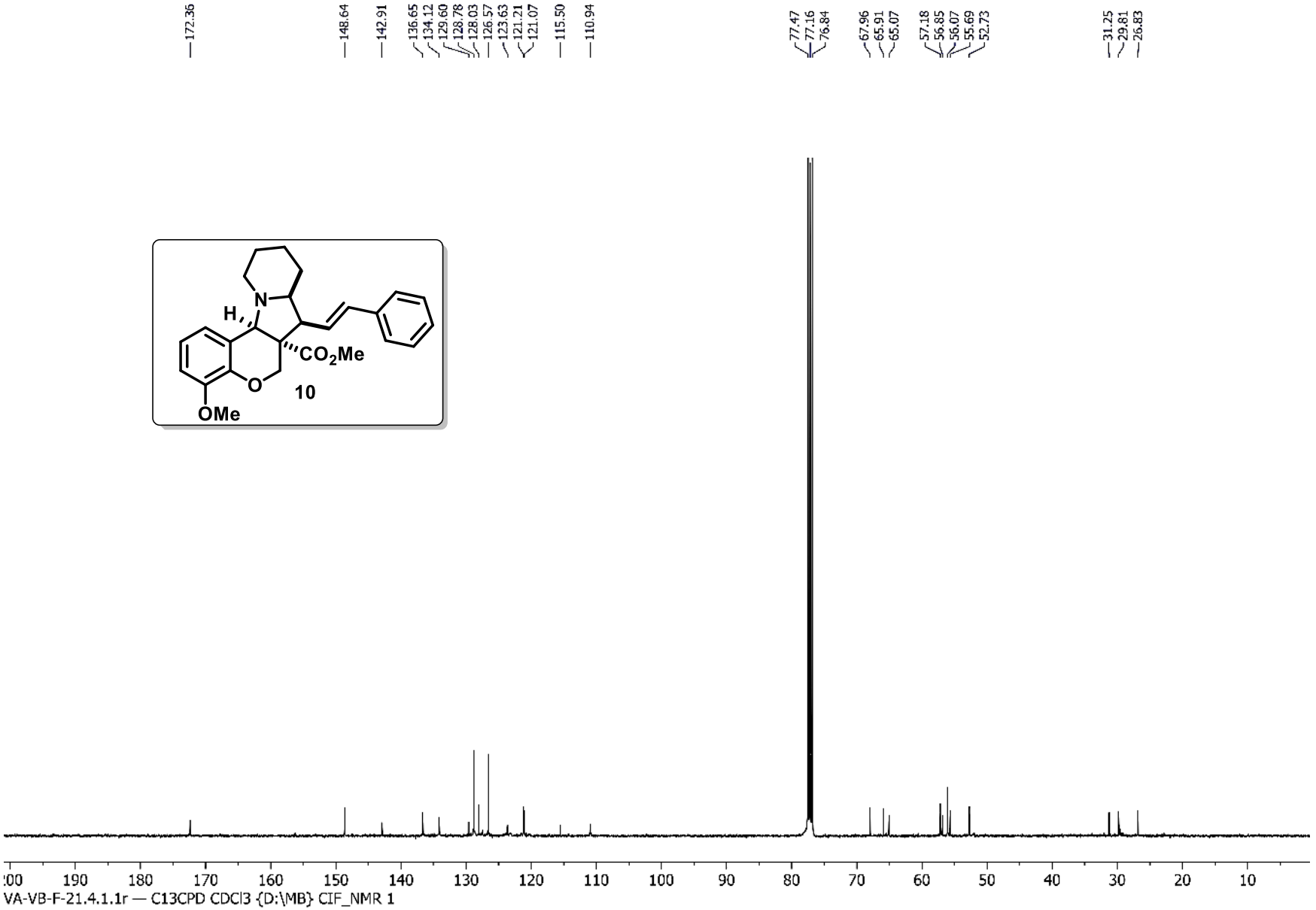
Butyl 2-methyl (*E*)-8-bromo-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole 2,3a(4*H*)- dicarboxylate (10)



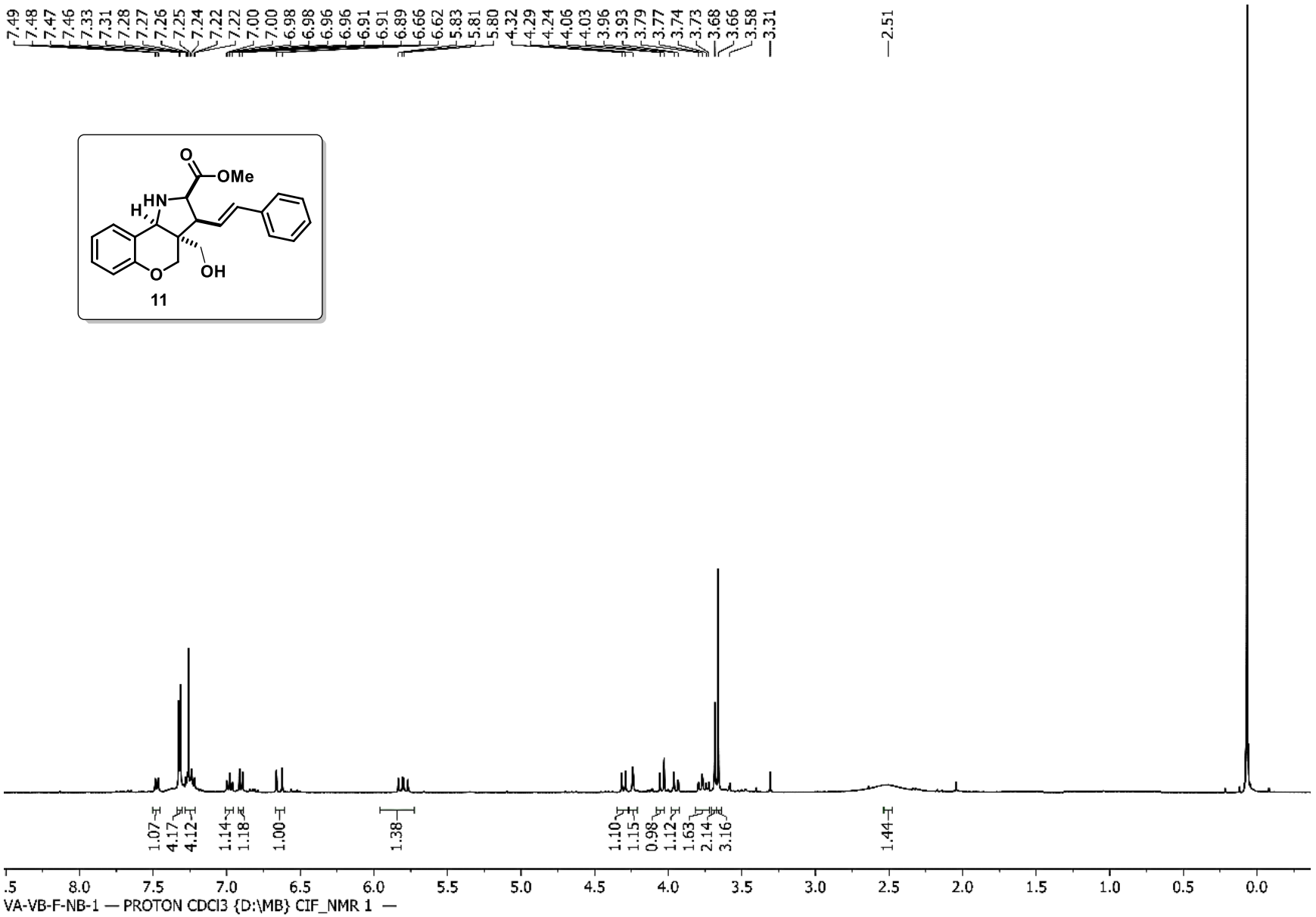




Butyl 2-methyl (*E*)-8-bromo-3-styryl-1,2,3,9b-tetrahydrochromeno[4,3-b]pyrrole 2,3a(4*H*)- dicarboxylate (10)



Methyl (*E*)-3a-(hydroxymethyl)-3-styryl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-b]pyrrole-2-carboxylate (11)



Methyl (*E*)-3a-(hydroxymethyl)-3-styryl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-b]pyrrole-2-carboxylate (11)