

Stereospecific Photochemistry of Δ^2 -1,2,3-Triazolines in Solution and in the Solid-State: Scope and Mechanistic Studies.

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General Information. All reactions were carried out under an inert atmosphere of argon in oven or flame-dried glassware, unless the reaction procedure states otherwise. All chemicals were purchased from commercial suppliers and used as received. The aryl amines were commercially available and the corresponding aryl azide was synthesized according to literature ¹. Tetrahydrofuran (THF) and diethyl ether (Et₂O) were distilled from sodium-benzophenone in a continuous still under an atmosphere of argon. Dichloromethane was distilled from calcium hydride in a still under an atmosphere of argon. Room temperature reactions were carried out between 20-25 °C, reactions at 0 °C were performed using a water-ice bath and reactions at -78 °C were carried out in an acetone-dry ice bath. Analytical thin-layer chromatography (TLC) was performed using pre-coated TLC plates with Silica Gel 60 F254 and visualized using combinations of UV, and potassium permanganate (KMnO₄) staining. Flash column chromatography was performed using silica gel (230-400 mesh) as the stationary phase. Proton magnetic resonance spectra were recorded at 500 MHz, and carbon-13 magnetic resonance spectra were recorded at 125 MHz, respectively. All chemical shifts are reported in ppm on the δ -scale relative to TMS (δ 0.0) using residual solvent as reference (CDCl₃ δ 7.26 and δ 77.16 for proton and carbon, respectively, CD₃CN δ 1.94 and 1.32, 118.26 for proton and carbon respectively, (CD₃)₂CO δ 2.05 and 29.84, 206.26 for proton and carbon, respectively). Coupling constants *J* are reported in Hz. Multiplicities are reported as broad (br), singlet (s), doublet (d), triplet (t), quartet (q), pentet (p), sextet (sxt), septuplet (spt) and multiplet (m). Uncorrected melting points were recorded on a melting point apparatus using open glass capillaries. IR spectral data were obtained using an Attenuated Total Reflectance (ATR) spectrometer as the neat compound and the units are stated in cm⁻¹.

A. Experimental for compound cis-1

The synthesis of ethyl (Z)-4,4,4-trifluorobut-2-enoate (compound *cis-1*) was reported in the literature and was synthesized accordingly.¹ The synthesized compound matched spectroscopic data of the published compound. Ethyl 4,4,4-trifluorocrotonate *trans-1* (638mg, 3.8mmol) was dissolved in 5mL of dry DCM. The mixture was irradiated using a medium-pressure Hg Hanovia lamp with a quartz emission well filter with cutoff of $\lambda \leq 220$ nm. After 3 days, the mixture reached a photostationary state of 76% *trans-1* and 24% *cis-1*. The DCM was concentrated under vacuum and the mixture was purified by silica gel column chromatography using pentane/diethyl ether (90/10) as eluent. Clear liquid, R_f 0.45, stained with Potassium permanganate. IR(ATR): 2952, 2924, 1742, 1668, 1460, 1371, 1312, 1262, 1183 cm^{-1} . ¹H NMR (500 MHz, CDCl_3) δ 6.28 (d, $J = 12.5$ Hz, 1H), 6.03 (dq, $J = 12.5, 8.0$ Hz, 1H), 4.27 (q, $J = 7.1$ Hz, 2H), 1.20 (t, $J = 7.1$ Hz, 3H). ¹³C NMR (125 MHz, CDCl_3) δ 163.46, 130.12, 130.07, 130.03, 129.99, 127.38, 127.08, 126.79, 126.50, 124.46, 122.30, 120.14, 117.97, 61.67, 34.12, 13.86.

B. Experimental for compounds 2A-2E

All of the aryl azides were synthesized following a reported protocol.¹ All of the corresponding amines were commercially available and used without further purification.

Synthesis of phenyl azide (compound **2A**): Crude product was purified by silica gel chromatography (eluent: EtOAc/Hexanes 20/80). Yield 74%, yellow liquid, R_f 0.92. IR (ATR): 2122, 2090, 1593, 1491, 1293, 1279, 744, 685, 668 cm^{-1} . ¹H NMR (500 MHz, CDCl_3) δ 7.40 – 7.32 (m, 2H), 7.18 – 7.12 (m, 1H), 7.07 – 6.97 (m, 2H). ¹³C NMR (126 MHz, CDCl_3) δ 140.01, 129.78, 124.89, 119.04.

Synthesis of 2-azidonaphthalene (compound **2B**): Crude product was purified by silica gel chromatography (eluent: EtOAc/Hexanes 20/80). Yield 98%, yellow liquid, R_f 0.88. IR (ATR): 2101, 1625, 1596, 1508, 1281, 845, 805, 741 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.83 (d, $J = 8.7$ Hz, 2H), 7.77 (d, $J = 8.2$ Hz, 1H), 7.52 (ddd, $J = 8.2, 6.9, 1.3$ Hz, 1H), 7.49 – 7.43 (m, 2H), 7.17 (dd, $J = 8.8, 2.3$ Hz, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 137.53, 134.03, 131.08, 129.95, 127.91, 127.04, 125.46, 118.79, 115.85.

Synthesis of 4-azidobiphenyl (compound **2C**): Crude product was purified by silica gel chromatography (eluent: EtOAc/Hexanes 10/90). Yield 83%, yellow solid, R_f 0.91. IR (ATR): 2129, 2092, 1584, 1517, 1482, 1289, 833, 759. 689 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.63 – 7.53 (m, 4H), 7.50 – 7.41 (m, 2H), 7.39 – 7.31 (m, 1H), 7.18 – 7.07 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 140.15, 139.15, 138.01, 128.89, 128.46, 127.39, 126.88, 119.42.

Synthesis of 2-azido-9*H*-fluorene (compound **2D**): Crude product was purified by silica gel chromatography (eluent: EtOAc/Hexanes 10/90). Yield 99%, yellow solid, R_f 0.91. IR (ATR): 3045, 2386, 2104, 1603, 1580, 1450, 1290, 1280, 836 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.74 (d, $J = 8.1$ Hz, 2H), 7.53 (d, $J = 7.5$ Hz, 1H), 7.37 (d, $J = 7.5$ Hz, 1H), 7.30 (td, $J = 7.4, 1.0$ Hz, 1H), 7.22 (s, 1H), 7.04 (dd, $J = 8.1, 2.1$ Hz, 1H), 3.90 (s, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 145.13, 142.93, 140.97, 138.97, 138.48, 126.95, 126.68, 125.05, 120.88, 119.67, 117.85, 115.75, 36.87.

Synthesis of ((4-azidophenyl)methanetriyl)tribenzene (compound **2E**): Crude product was purified by silica gel chromatography (eluent: EtOAc/Hexanes 20/80). Yield 86%, yellow solid, R_f 0.84. IR (ATR): 2122, 2084, 1500, 1490, 1442, 1291, 752, 701 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.31 – 7.13 (m, 17H), 6.99 – 6.87 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 146.54, 143.78, 137.62, 132.52, 131.04, 127.60, 126.08, 118.10, 64.56.

C. Experimental for compounds *trans*-3A-3E and *cis*-3A-3E

All triazolines were synthesized using the following general procedure published in the literature:¹ Ethyl 4,4,4-trifluorocrotonate (0.3 mmol), **2A** (0.3 mmol), and N,N' -dimethylurea (0.03 mmol) was dissolved in 1.5 mL of dry toluene the reaction was stirred for 32 hours at 60°C under argon atmosphere. After the initial 32 hours, an additional 0.3 mmol of ethyl 4,4,4-trifluorocrotonate was added to the solution. After 33 more hours of heating, the reaction was cooled when the disappearance of azide by TLC was observed. The crude mixture was rotary evaporated under vacuum and the reaction mixture was purified by column chromatography.

Synthesis of ethyl (4*R*,5*R*)-1-phenyl-4-(trifluoromethyl)-4,5-dihydro-1*H*-1,2,3-triazole-5-carboxylate (*trans*-**3A**): Crude product was purified by silica gel chromatography (eluent: EtOAc/Hexanes 10/60). Yield 22%, white liquid, R_f 0.45. IR (ATR): 2989, 1732, 1598, 1499, 1477, 1330 1268, 1133, 752, 692 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.44 – 7.34 (m, 2H), 7.34 – 7.28 (m, 2H), 7.15 (t, $J = 7.4$ Hz, 1H), 5.29 – 5.22 (m, 1H), 4.61 (d, $J = 8.1$ Hz, 1H), 4.26 (q, $J = 7.1$ Hz, 2H), 1.24 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 167.79, 138.87, 129.62, 124.43, 123.70, 121.48, 115.38, 82.67, 82.43, 82.19, 81.95, 63.15, 56.90, 13.95.

Synthesis of ethyl (4*R*,5*S*)-1-phenyl-4-(trifluoromethyl)-4,5-dihydro-1*H*-1,2,3-triazole-5-carboxylate (*cis*-**3A**): Crude product was purified by silica gel chromatography (eluent: EtOAc/Hexanes 10/60). Yield 12%, white solid, R_f 0.35. IR (ATR): 2898, 1732, 1598, 1329, 1267, 1172, 1133, 1064, 752, 692, 668 cm^{-1} . ^1H NMR (500 MHz, CD_3CN) δ 7.50 – 7.35 (m, 2H), 7.29 – 7.23 (m, 2H), 7.19 – 7.06 (m, 1H), 5.60 – 5.32 (m, 1H), 5.09 (d, $J = 12.9$ Hz, 1H), 4.27 – 4.04 (m, 2H), 1.15 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 166.38, 139.84, 130.25, 126.90, 124.69, 124.53, 122.47, 120.26, 115.69, 81.20, 80.96, 80.72, 80.49, 63.13, 57.16, 13.61. Melting Point: 90-91 $^\circ\text{C}$

Synthesis of ethyl (4*R*,5*R*)-1-(naphthalen-2-yl)-4-(trifluoromethyl)-4,5-dihydro-1*H*-1,2,3-triazole-5-carboxylate (*trans*-**3B**): Crude product was purified by silica gel chromatography (eluent: EtOAc/Hexanes 10/60). Yield 80%, yellow liquid, R_f 0.47. IR (ATR): 3063, 2984, 1745, 1633, 1602, 1471, 1234, 1262, 1178, 1126, 966 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.88 (d, $J = 9.0$ Hz, 1H), 7.85 – 7.78 (m, 2H), 7.76 (dd, $J = 8.2, 0.5$ Hz, 1H), 7.50 (ddd, $J = 8.2, 6.9, 1.3$ Hz, 1H), 7.43 (ddd, $J = 8.1, 6.9, 1.2$ Hz, 1H), 7.37 (d, $J = 2.2$ Hz, 1H), 5.46 – 5.26 (m, 1H), 4.75 (d, $J = 8.1$ Hz, 1H), 4.27 (qq, $J = 10.8, 7.1$ Hz, 2H), 1.25 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 167.83, 136.61, 133.61, 130.61, 129.96, 127.86, 127.37, 127.19, 125.30, 123.74, 121.52, 116.51, 110.57, 82.84, 82.60, 82.36, 82.12, 63.19, 57.03, 57.02, 13.98.

Synthesis of ethyl (4*R*,5*S*)-1-(naphthalen-2-yl)-4-(trifluoromethyl)-4,5-dihydro-1*H*-1,2,3-triazole-5-carboxylate (*cis*-**3B**): Crude product was purified by silica gel chromatography (eluent: EtOAc/Hexanes 10/70). Yield 14%, white solid, R_f 0.43. IR (ATR): 2924, 1745, 1629, 1600,

1483, 1370, 1326, 1277, 1172, 1135, 1063, 809 cm^{-1} . ^1H NMR (500 MHz, CD_3CN) δ 7.95 (d, $J = 9.0$ Hz, 1H), 7.86 (ddd, $J = 16.9, 8.2, 0.6$ Hz, 2H), 7.77 (dd, $J = 9.0, 2.3$ Hz, 1H), 7.52 (ddd, $J = 8.2, 6.9, 1.3$ Hz, 1H), 7.45 (ddd, $J = 8.1, 6.9, 1.2$ Hz, 1H), 7.38 (d, $J = 2.3$ Hz, 1H), 5.51 (dd, $J = 12.9, 8.3$ Hz, 1H), 5.22 (d, $J = 12.9$ Hz, 1H), 4.15 (q, $J = 7.1$ Hz, 2H), 1.14 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 166.33, 137.60, 134.32, 130.91, 130.42, 128.30, 127.82, 127.77, 126.91, 125.72, 124.70, 122.49, 120.28, 116.73, 111.01, 81.36, 81.12, 80.88, 80.65, 63.18, 60.54, 57.33, 57.32, 13.63. Melting Point: 114-116 $^\circ\text{C}$

Synthesis of ethyl (4*R*,5*R*)-1-([1,1'-biphenyl]-4-yl)-4-(trifluoromethyl)-4,5-dihydro-1*H*-1,2,3-triazole-5-carboxylate (*trans*-**3C**): Crude product was purified by silica gel chromatography (eluent: EtOAc/Hexanes 10/60). Yield 51%, white solid, R_f 0.39. IR (ATR): 2964, 1736, 1606, 1526, 1449, 1474, 1323, 1201, 1241, 1170, 1142, 1124, 1101, 762 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.69 – 7.59 (m, 2H), 7.59 – 7.54 (m, 2H), 7.52 – 7.41 (m, 2H), 7.41 – 7.29 (m, 3H), 5.35 – 5.23 (m, 1H), 4.65 (d, $J = 8.1$ Hz, 1H), 4.29 (q, $J = 7.1$ Hz, 2H), 1.27 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 167.74, 167.71, 140.06, 138.09, 137.41, 128.89, 128.24, 127.37, 126.82, 125.93, 123.70, 121.48, 119.26, 115.73, 82.76, 82.53, 82.29, 82.05, 63.21, 56.93, 13.98. Melting Point: 146-147 $^\circ\text{C}$

Synthesis of ethyl (4*R*,5*S*)-1-([1,1'-biphenyl]-4-yl)-4-(trifluoromethyl)-4,5-dihydro-1*H*-1,2,3-triazole-5-carboxylate (*cis*-**3C**): Crude product was purified by silica gel chromatography (eluent: EtOAc/Hexanes 10/60). Yield 21%, white solid, R_f 0.33. IR (ATR): 2966, 2929, 1748, 1486, 1369, 1327, 1275, 1139, 1062, 1022, 968, 924, 769 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.67 –

7.53 (m, 4H), 7.53 – 7.38 (m, 2H), 7.38 – 7.27 (m, 3H), 5.21 (dq, $J = 12.9, 7.8$ Hz, 1H), 4.88 (d, $J = 12.9$ Hz, 1H), 4.19 (qdd, $J = 14.3, 9.0, 5.4$ Hz, 2H), 1.18 (dd, $J = 8.7, 5.6$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 165.21, 140.05, 138.30, 137.18, 128.88, 128.25, 127.33, 126.78, 123.54, 121.32, 115.57, 81.15, 80.91, 80.67, 80.42, 62.87, 57.18, 13.68. Melting Point: 163-164°C

Synthesis of ethyl (4*R*,5*R*)-1-(9*H*-fluoren-2-yl)-4-(trifluoromethyl)-4,5-dihydro-1*H*-1,2,3-triazole-5-carboxylate (*trans*-**3D**): The product mixture was purified by silica gel column chromatography (eluent 10/70 EtOAc/Hexanes). Yield 65%, white solid, R_f 0.39. IR (ATR): 2996, 1738, 1615, 1584, 1487, 1337, 1274, 1241, 1199, 1107, 1017, 986 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.75 (t, $J = 8.7$ Hz, 2H), 7.57 (d, $J = 1.6$ Hz, 1H), 7.53 (d, $J = 7.4$ Hz, 1H), 7.38 (td, $J = 7.4, 1.1$ Hz, 1H), 7.30 (td, $J = 7.4, 1.1$ Hz, 1H), 7.27 – 7.23 (m, 2H), 5.28 (p, $J = 7.8$ Hz, 1H), 4.69 (d, $J = 7.8$ Hz, 1H), 4.31 – 4.23 (m, 2H), 3.92 (s, 2H), 1.24 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 167.85, 144.98, 142.94, 140.92, 138.48, 137.74, 126.97, 126.66, 125.04, 123.76, 121.54, 120.68, 119.66, 114.37, 112.77, 82.60, 82.37, 82.13, 81.89, 63.13, 57.30, 37.09, 13.98. Melting Point: 133-134°C

Synthesis of ethyl (4*R*,5*S*)-1-(9*H*-fluoren-2-yl)-4-(trifluoromethyl)-4,5-dihydro-1*H*-1,2,3-triazole-5-carboxylate (*cis*-**3D**): The product mixture was purified by silica gel column chromatography (eluent 10/70 EtOAc/Hexanes). Yield 18%, white solid, R_f 0.33. IR (ATR): 2919, 2850, 1743, 1615, 1585, 1483, 1329, 1277, 1223, 1203, 1173, 1021, 968, 821 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.74 (t, $J = 7.7$ Hz, 2H), 7.57 – 7.49 (m, 2H), 7.37 (td, $J = 7.4, 1.1$ Hz, 1H), 7.29 (td, $J = 7.4, 1.1$ Hz, 1H), 7.15 (dd, $J = 8.3, 2.2$ Hz, 1H), 5.21 (dq, $J = 12.9, 7.8$ Hz,

1H), 4.91 (d, $J = 12.9$ Hz, 1H), 4.22 – 4.10 (m, 2H), 3.92 (s, 2H), 1.14 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 165.32, 145.04, 142.92, 140.96, 138.30, 138.02, 126.95, 126.61, 125.80, 125.03, 123.58, 121.36, 120.72, 119.61, 119.14, 114.09, 112.59, 81.02, 80.78, 80.53, 80.29, 62.79, 57.56, 37.10, 13.69. Melting Point: 165-166°C.

Synthesis of ethyl (4*R*,5*R*)-4-(trifluoromethyl)-1-(4-tritylphenyl)-4,5-dihydro-1*H*-1,2,3-triazole-5-carboxylate (*trans*-**3E**): Crude product was purified by silica gel chromatography (eluent: EtOAc/Hexanes 10/60). Yield 74%, white solid, R_f 0.41. IR (ATR): 2993, 1768, 1508, 1489, 1441, 1134, 1032, 701 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.50 – 6.91 (m, 17H), 5.32 – 5.11 (m, 1H), 4.56 (d, $J = 8.2$ Hz, 1H), 4.34 – 4.16 (m, 2H), 1.22 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 167.84, 146.52, 143.13, 136.72, 132.25, 131.91, 131.05, 127.59, 127.47, 126.07, 125.96, 123.69, 121.47, 118.56, 114.40, 82.74, 82.50, 82.26, 82.02, 64.51, 63.13, 56.99, 13.94. Melting Point: 167-168°C.

Synthesis of ethyl (4*R*,5*S*)-4-(trifluoromethyl)-1-(4-tritylphenyl)-4,5-dihydro-1*H*-1,2,3-triazole-5-carboxylate (*cis*-**3E**): Crude product was purified by silica gel chromatography (eluent: EtOAc/Hexanes 10/60). Yield 22%, white solid, R_f 0.35. IR (ATR): 2997, 1767, 1594, 1509, 1441, 1231, 1206, 1133, 701 cm^{-1} . ^1H NMR (500 MHz, CD_3CN) δ 7.63 – 6.91 (m, 14H), 5.56 – 5.34 (m, 1H), 5.04 (d, $J = 13.0$ Hz, 1H), 4.28 – 3.92 (m, 2H), 1.12 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 165.76, 146.86, 142.65, 137.03, 131.95, 130.67, 127.75, 126.05, 124.09, 121.88, 80.46, 80.22, 64.48, 62.57, 59.97, 56.55, 13.07. Melting Point: 173-174°C.

D. Experimental for compounds *trans*-4A-4E and *cis*-4A-4E

For solid-state photolysis:

Triazoline *trans*-**3A-E** and *cis*-**3A-E** (5-8 mg) was crushed between two microscope slides and photolyzed using a medium-pressure Hg Hanovia lamp with a pyrex emersion well filter with cutoff of $\lambda \leq 290$ nm. The reaction was monitored by ^1H NMR and was completed in less than one hour.

For solution-state photolysis:

Triazoline (5-8mg) was dissolved in deuterated acetonitrile or acetone in an NMR tube and the solution was freeze-pump-thawed for 3 cycles to ensure no gas was present in the reaction. The NMR tube was photolyzed using a medium-pressure Hg Hanovia lamp with a pyrex emersion well filter with cutoff of $\lambda \leq 290$ nm. The reactions were monitored by ^1H NMR and showed completion in less than one hour.

Ethyl (2*R*,3*R*)-1-phenyl-3-(trifluoromethyl)aziridine-2-carboxylate (*trans*-**4A**): IR (ATR): 2985, 1738, 1600, 1494, 1336, 1279, 1145, 1082, 757, 692 cm^{-1} . ^1H NMR (500 MHz, CD_3CN) δ 7.32 – 7.22 (m, 2H), 7.12 – 7.01 (m, 1H), 7.01 – 6.87 (m, 2H), 4.19 – 3.95 (m, 2H), 3.60 (qd, $J = 5.1, 2.3$ Hz, 1H), 3.48 (d, $J = 2.2$ Hz, 1H), 1.10 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 165.49, 147.17, 129.94, 129.72, 129.56, 127.86, 127.12, 124.95, 124.29, 122.78, 120.61, 120.21, 62.44, 42.34, 42.02, 41.70, 41.37, 39.88, 39.86, 13.82. Compound was a white liquid at room temperature.

Ethyl (2*S*,3*R*)-1-phenyl-3-(trifluoromethyl)aziridine-2-carboxylate (*cis*-**4A**): IR (ATR): 2990, 2931, 1753, 1599, 1492, 1380, 1268, 1206, 1146, 1060, 763, 694 cm⁻¹. ¹H NMR (500 MHz, CD₃CN) δ 7.43 – 7.27 (m, 2H), 7.18 – 7.09 (m, 1H), 7.09 – 7.01 (m, 2H), 4.25 (qq, *J* = 10.8, 7.1 Hz, 2H), 3.33 (d, *J* = 6.5 Hz, 1H), 3.24 (dq, *J* = 11.4, 5.7 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (126 MHz, CD₃CN) δ 166.33, 150.49, 129.96, 127.52, 125.34, 124.85, 123.17, 120.99, 120.20, 62.19, 43.01, 42.69, 42.37, 42.05, 13.90. Compound was a slightly yellow liquid at room temperature.

Ethyl (2*R*,3*R*)-1-(naphthalen-2-yl)-3-(trifluoromethyl)aziridine-2-carboxylate (*trans*-**4B**): IR (ATR): 2984, 1737, 1632, 1600, 1334, 1279, 1146, 695 cm⁻¹. ¹H NMR (500 MHz, CD₃CN) δ 7.80 (ddd, *J* = 15.7, 8.6, 0.5 Hz, 3H), 7.49 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.45 – 7.35 (m, 2H), 7.15 (dd, *J* = 8.7, 2.3 Hz, 1H), 4.13 – 3.94 (m, 2H), 3.74 (qd, *J* = 5.1, 2.3 Hz, 1H), 3.59 (d, *J* = 2.3 Hz, 1H), 1.05 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (126 MHz, CD₃CN) δ 165.53, 144.88, 134.40, 131.12, 129.69, 128.24, 127.38, 127.33, 127.16, 125.44, 124.99, 122.82, 120.87, 120.65, 116.30, 62.51, 42.59, 42.26, 41.94, 41.62, 40.03, 40.02, 40.00, 13.83. Compound was a clear liquid at room temperature.

Ethyl (2*S*,3*R*)-1-(naphthalen-2-yl)-3-(trifluoromethyl)aziridine-2-carboxylate (*cis*-**4B**): IR (ATR): 2985, 1739, 1631, 1601, 1509, 1471, 1275, 1232, 1146, 1060, 854, 813, 749 vcm⁻¹. ¹H NMR (500 MHz, CD₃CN) δ 7.93 – 7.77 (m, 3H), 7.56 – 7.37 (m, 3H), 7.30 (dd, *J* = 8.8, 2.3 Hz, 1H), 4.38 – 4.20 (m, 2H), 3.45 (d, *J* = 6.5 Hz, 1H), 3.42 – 3.32 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (126 MHz, CD₃CN) δ 166.34, 148.09, 134.36, 131.35, 130.01, 128.27, 127.54, 127.46, 125.70,

125.36, 123.19, 120.95, 116.15, 62.27, 43.12, 42.80, 42.48, 42.16, 41.92, 41.91, 13.92. Compound was a slightly orange liquid at room temperature.

Ethyl (2*R*,3*R*)-1-([1,1'-biphenyl]-4-yl)-3-(trifluoromethyl)aziridine-2-carboxylate (*trans*-**4C**): IR (ATR): 2924, 1733, 1605, 1523, 1487, 1373, 1336, 1221, 1144, 1082, 762, 722 cm⁻¹. ¹H NMR (500 MHz, CD₃CN) δ 7.66 – 7.52 (m, 3H), 7.52 – 7.39 (m, 2H), 7.39 – 7.28 (m, 1H), 7.09 – 6.91 (m, 2H), 4.16 – 4.01 (m, 2H), 3.65 (qd, *J* = 5.0, 2.3 Hz, 1H), 3.52 (d, *J* = 2.3 Hz, 1H), 1.12 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (126 MHz, CD₃CN) δ 165.50, 146.64, 140.72, 136.99, 129.47, 128.20, 127.76, 127.16, 124.92, 122.75, 120.76, 62.53, 42.42, 42.10, 41.78, 41.46, 39.99, 39.97, 13.84. Melting Point: 99-101 °C

Ethyl (2*S*,3*R*)-1-([1,1'-biphenyl]-4-yl)-3-(trifluoromethyl)aziridine-2-carboxylate (*cis*-**4C**): IR (ATR): 2986, 1754, 1599, 1493, 1454, 1380, 1296, 1206, 1266, 1143, 1059, 758, 694 cm⁻¹. ¹H NMR (500 MHz, CD₃CN) δ 7.64 – 7.55 (m, 3H), 7.49 – 7.41 (m, 2H), 7.38 – 7.31 (m, 1H), 7.21 – 7.10 (m, 2H), 4.35 – 4.18 (m, 2H), 3.38 (d, *J* = 6.5 Hz, 1H), 3.34 – 3.26 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (126 MHz, CD₃CN) δ 166.28, 149.89, 140.61, 137.52, 129.52, 129.49, 128.42, 127.86, 127.78, 127.22, 125.31, 123.14, 120.75, 62.23, 43.07, 42.75, 42.43, 42.12, 41.85, 13.89. Melting Point: 94-95°C

Ethyl (2*R*,3*R*)-1-(9*H*-fluoren-2-yl)-3-(trifluoromethyl)aziridine-2-carboxylate (*trans*-**4D**): IR(ATR): 2997, 1735, 1613, 1579, 1486-1402, 1373, 1338, 1278, 1214, 1096, 1078, 1029cm⁻¹.

^1H NMR (500 MHz, CD_3CN) δ 7.76 (d, $J = 7.6$ Hz, 1H), 7.72 (d, $J = 8.1$ Hz, 1H), 7.54 (dd, $J = 7.5, 0.8$ Hz, 1H), 7.36 (td, $J = 7.5, 0.8$ Hz, 1H), 7.28 (td, $J = 7.4, 1.1$ Hz, 1H), 7.16 (d, $J = 1.3$ Hz, 1H), 6.96 (dd, $J = 8.1, 2.1$ Hz, 1H), 4.12 – 3.99 (m, 2H), 3.87 (s, 2H), 3.66 (qd, $J = 5.1, 2.3$ Hz, 1H), 3.53 (d, $J = 2.2$ Hz, 1H), 1.08 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (125 MHz, CD_3CN) δ 165.51, 146.38, 145.38, 143.70, 141.57, 138.07, 127.37, 127.16, 126.91, 125.63, 124.99, 122.82, 120.93, 119.13, 117.13, 62.48, 42.56, 42.24, 41.92, 41.60, 40.22, 40.20, 36.99, 13.87. Melting Point: 125-126°C.

Ethyl (2*S*,3*R*)-1-(9*H*-fluoren-2-yl)-3-(trifluoromethyl)aziridine-2-carboxylate (*cis*-**4D**): IR(ATR): 2924, 1756, 1615, 1456, 1379, 1288, 1260, 1228, 1207, 1151, 1060 cm^{-1} . ^1H NMR (500 MHz, CD_3CN) δ 7.77 (t, $J = 8.0$ Hz, 2H), 7.55 (d, $J = 7.5$ Hz, 1H), 7.43 – 7.34 (m, 1H), 7.29 (td, $J = 7.5, 1.1$ Hz, 2H), 7.09 (dd, $J = 8.1, 2.1$ Hz, 1H), 4.27 (dddd, $J = 17.9, 10.8, 7.1, 3.7$ Hz, 2H), 3.89 (s, 1H), 3.38 (d, $J = 6.5$ Hz, 1H), 3.35 – 3.25 (m, 1H), 1.38 – 1.24 (m, 3H). ^{13}C NMR (125 MHz, CD_3CN) δ 165.81, 149.12, 144.99, 143.23, 140.90, 137.96, 126.84, 126.47, 125.10, 124.06, 122.63, 120.53, 119.57, 118.54, 116.60, 61.65, 42.39, 42.07, 41.46, 29.35, 13.34. Melting Point: 85-87°C

Ethyl (2*R*,3*R*)-3-(trifluoromethyl)-1-(4-tritylphenyl)aziridine-2-carboxylate (*trans*-**4E**): IR (ATR): 3035, 3002, 1965, 1740, 1596, 1492, 1444, 1336, 1279, 1208, 1149, 701 cm^{-1} . ^1H NMR (500 MHz, CD_3CN) δ 7.32 – 7.10 (m, 17H), 6.88 – 6.81 (m, 2H), 4.08 – 3.89 (m, 2H), 3.61 (qd, $J = 5.0, 2.3$ Hz, 1H), 3.45 (d, $J = 2.3$ Hz, 1H), 1.00 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (126 MHz, CD_3CN)

δ 165.38, 147.52, 144.95, 142.99, 132.09, 131.27, 128.22, 127.06, 126.56, 124.89, 122.72, 120.55, 119.40, 64.99, 62.39, 42.14, 41.82, 41.50, 41.18, 40.04, 40.03, 13.89. Melting Point: 135-137°C

Ethyl (2*S*,3*R*)-3-(trifluoromethyl)-1-(4-tritylphenyl)aziridine-2-carboxylate (*cis*-**4E**): IR (ATR): 3032, 1983, 1739, 1603, 1491, 1273, 1148, 1027, 832, 700 cm^{-1} . ^1H NMR (500 MHz, CD_3CN) δ 7.47 – 7.10 (m, 18H), 7.03 – 6.91 (m, 1H), 4.34 – 4.11 (m, 2H), 3.30 (d, $J = 6.5$ Hz, 1H), 3.27 – 3.17 (m, 1H), 1.25 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 166.26, 148.17, 147.51, 143.58, , 133.07, 132.29, 130.34, 128.96, 128.51, 128.35, 126.88, 126.58, 126.56, 119.33, 65.03, 62.18, 42.65, 42.33, 41.82, 41.73, 41.18, 40.05, 13.89. Melting Point: 132-133°C

Figure S2. ^{13}C NMR (126 MHz, CDCl_3) of compound **2A**.

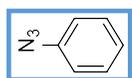
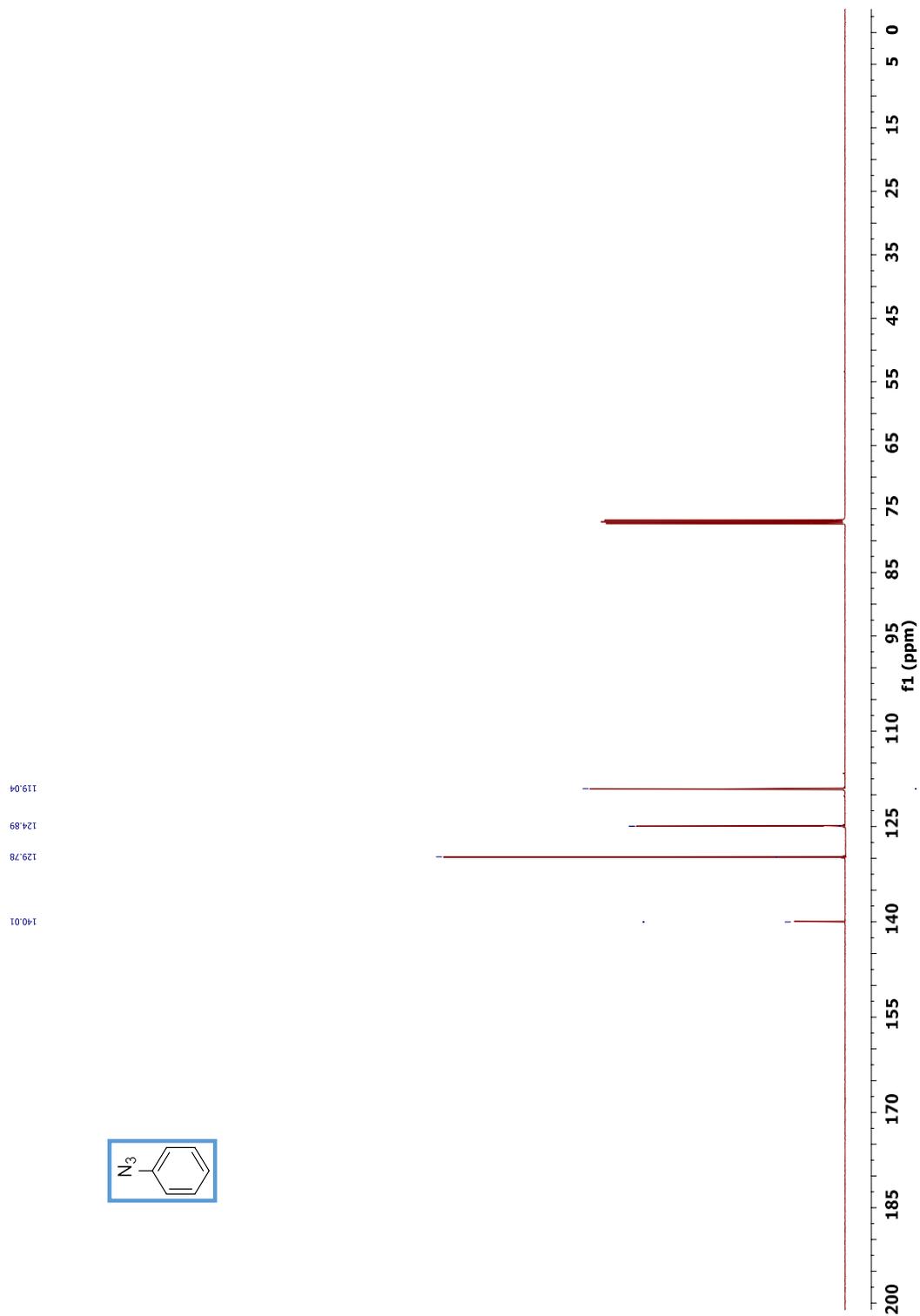


Figure S3. ^1H NMR (500 MHz, CDCl_3) of compound **2B**.

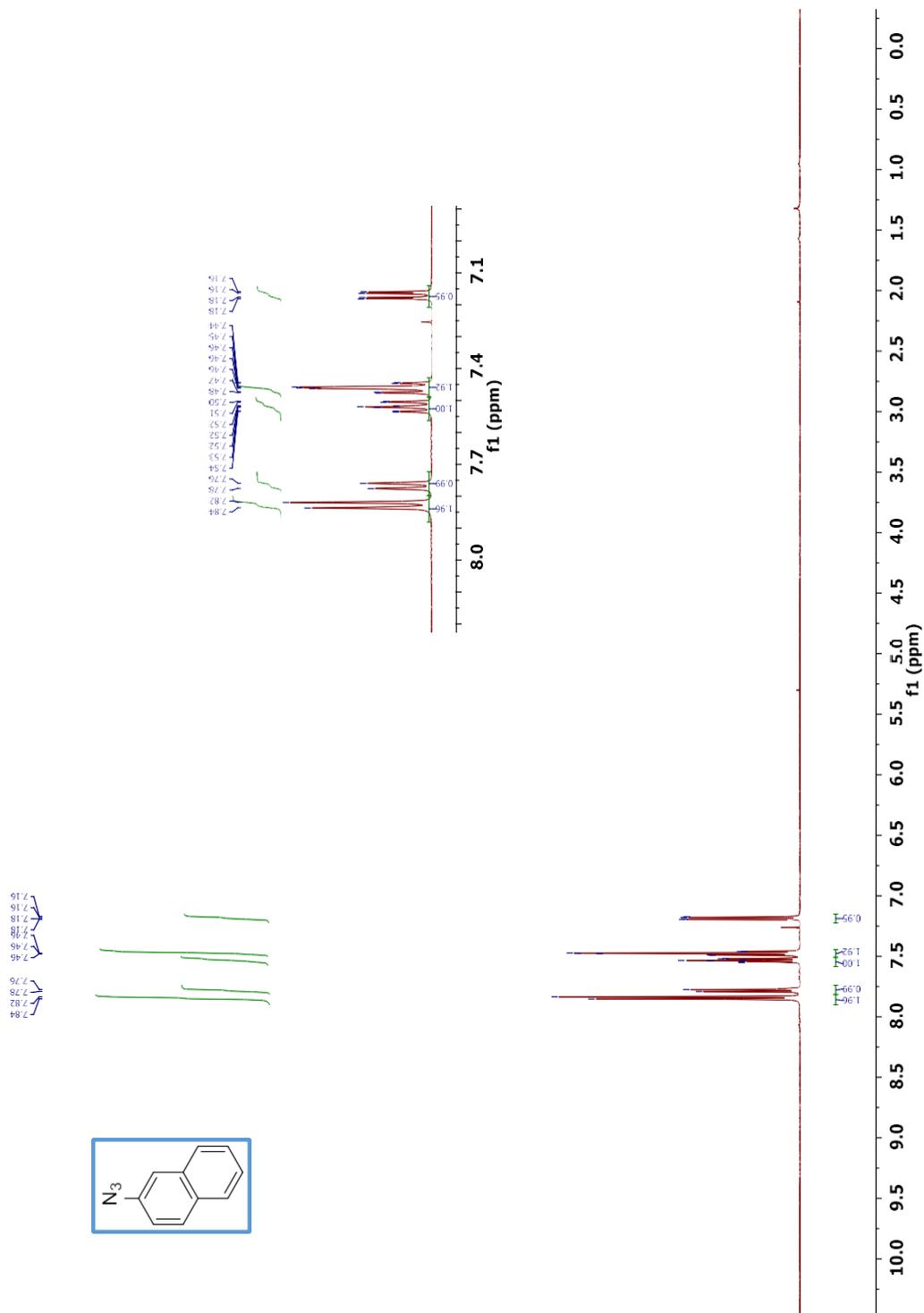


Figure S4. ^{13}C NMR (126 MHz, CDCl_3) of compound **2B**.

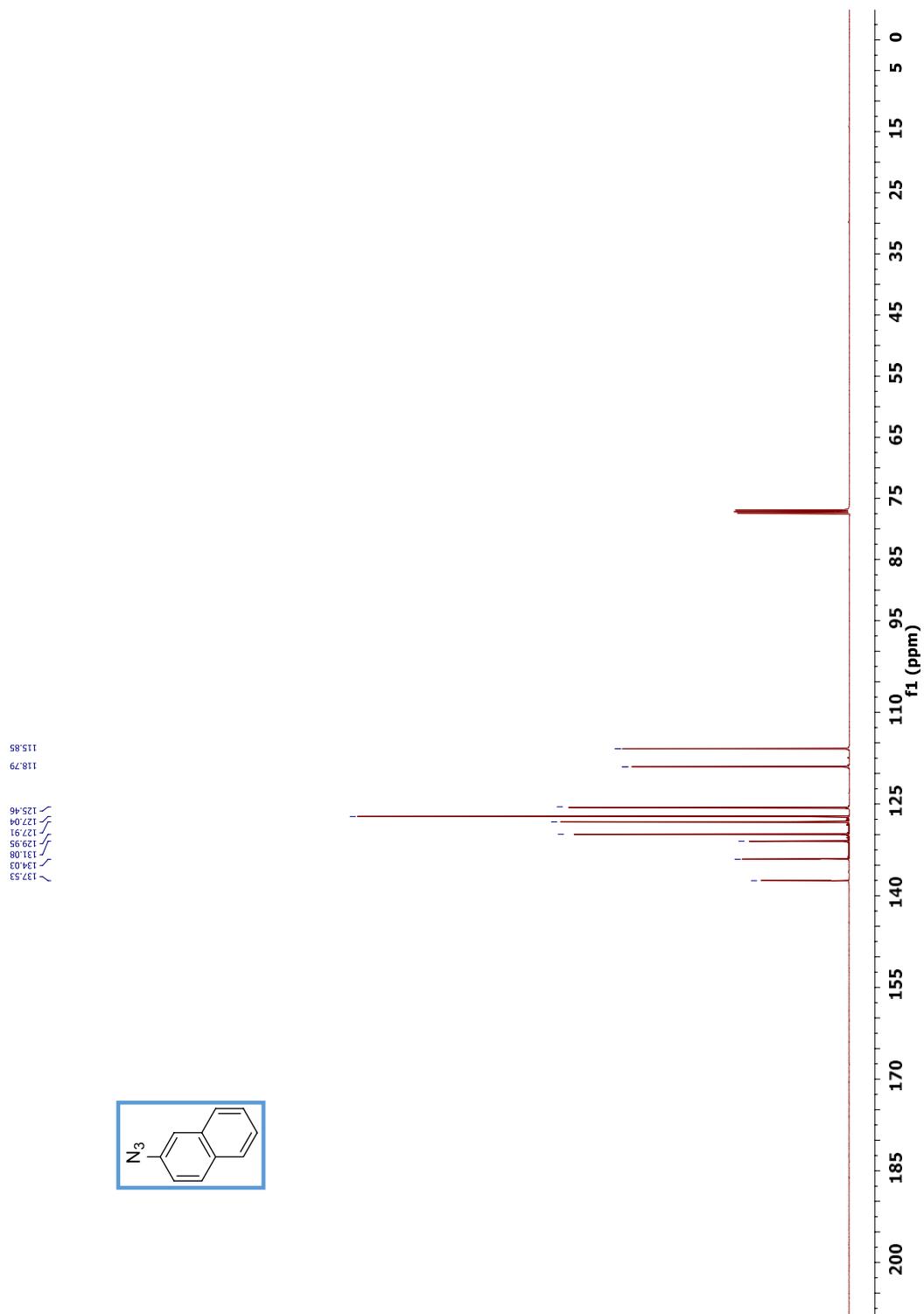


Figure S5. ^1H NMR (500 MHz, CDCl_3) of compound **2C**.

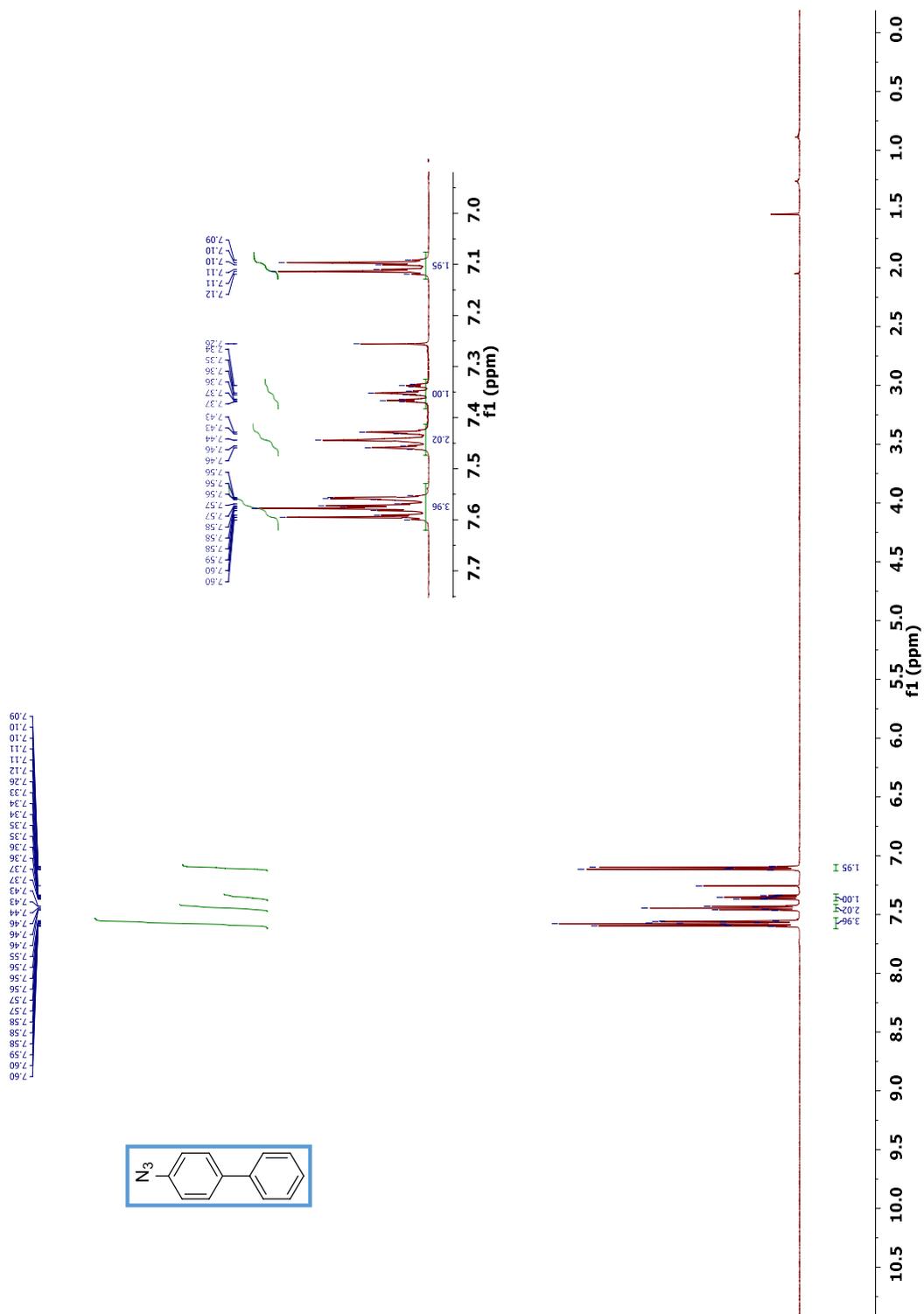


Figure S6. ^{13}C NMR (126 MHz, CDCl_3) of compound **2C**.

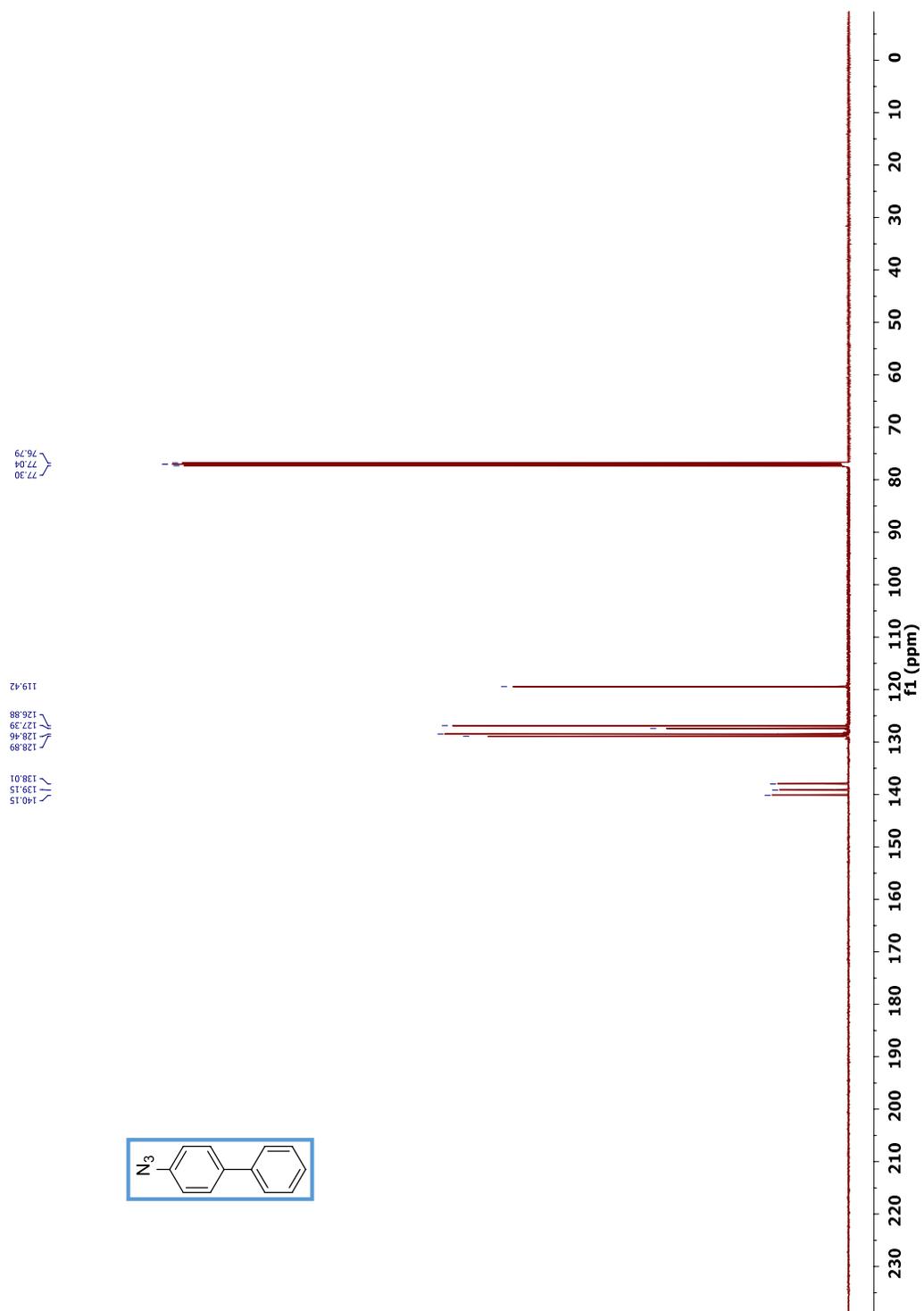


Figure S7. ^1H NMR (500 MHz, CDCl_3) of compound **2D**.

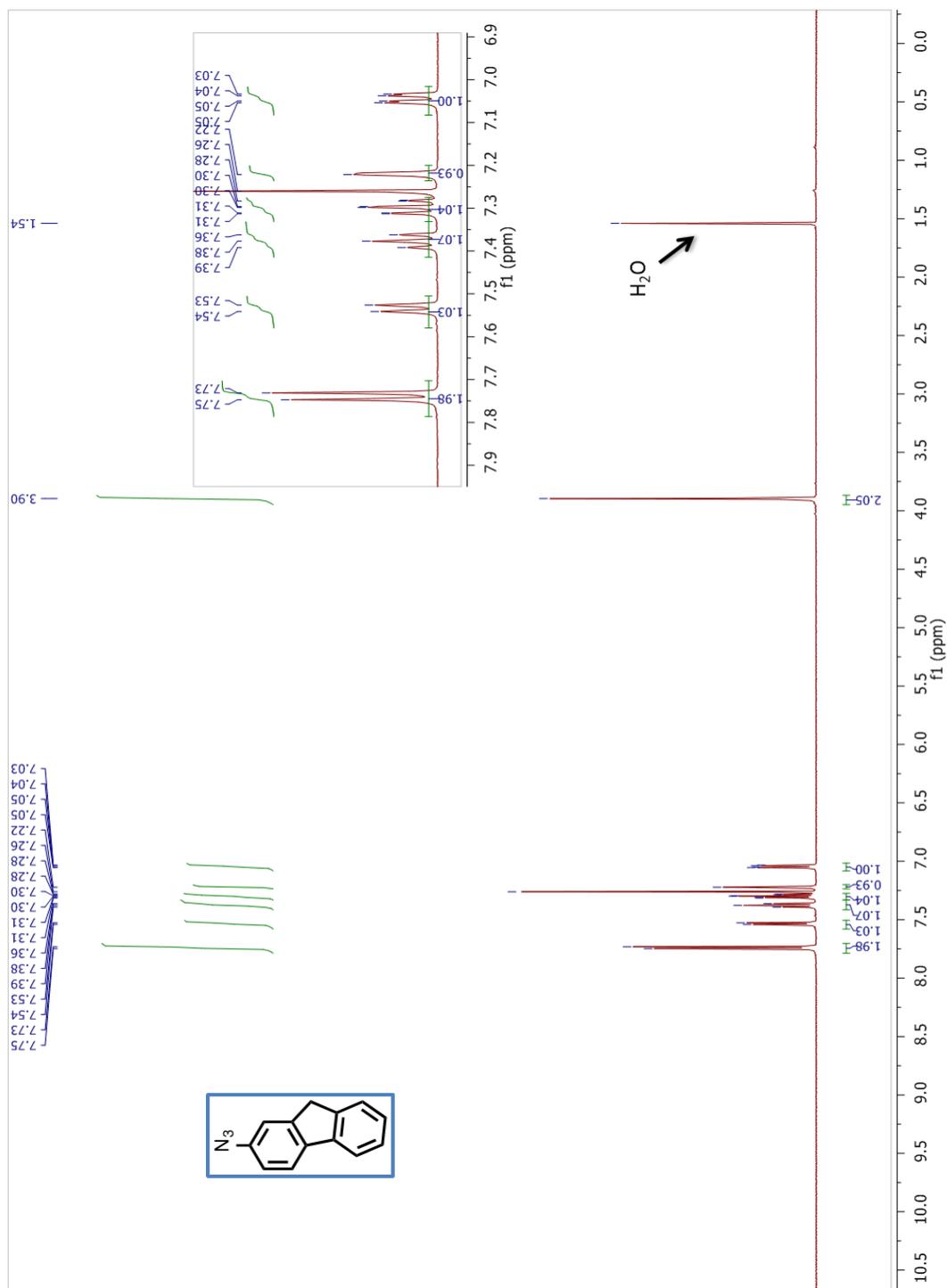


Figure S8. ^{13}C NMR (126 MHz, CDCl_3) of compound **2D**.

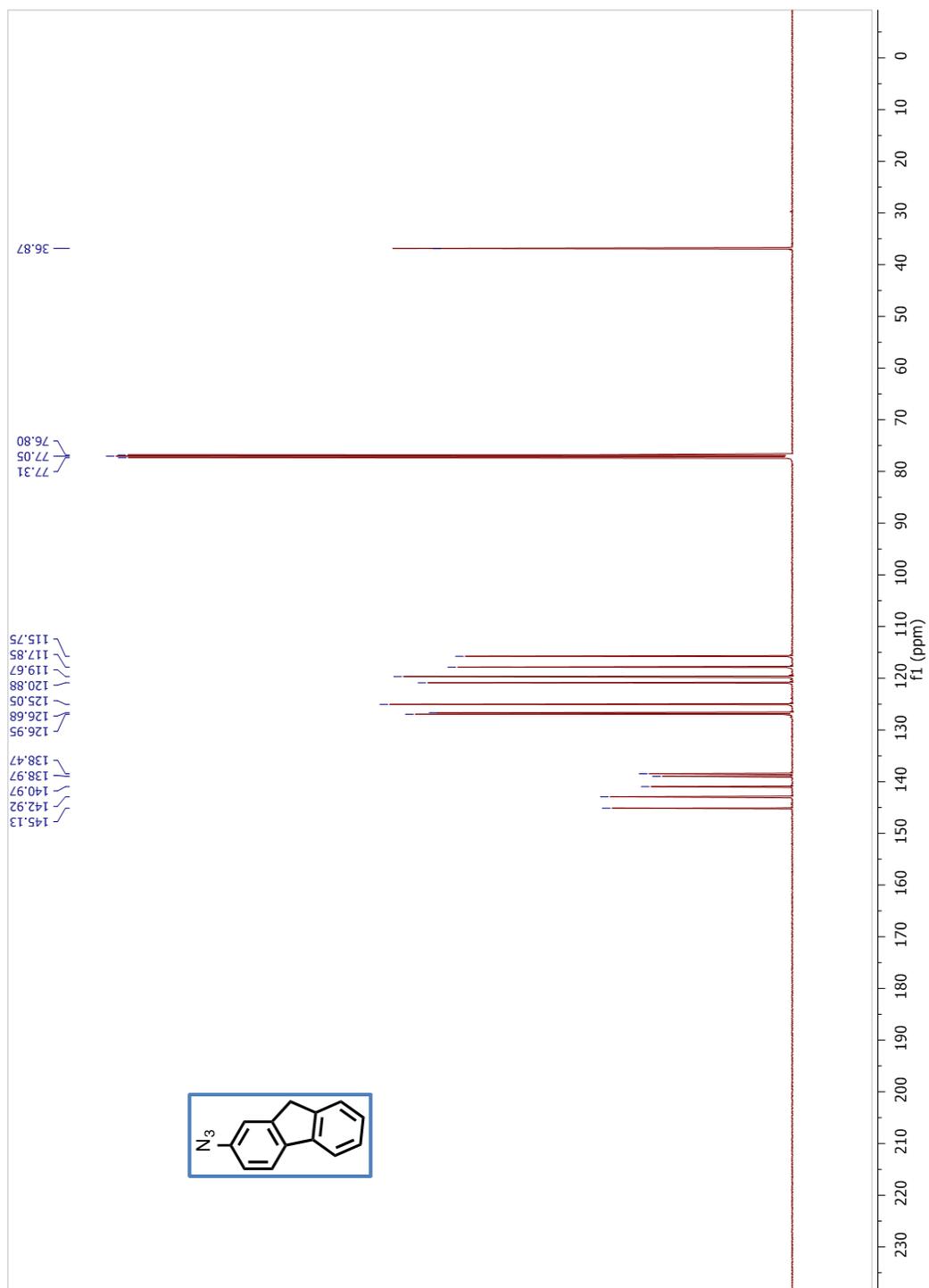


Figure S9. ^1H NMR (500 MHz, CDCl_3) of compound **2E**.

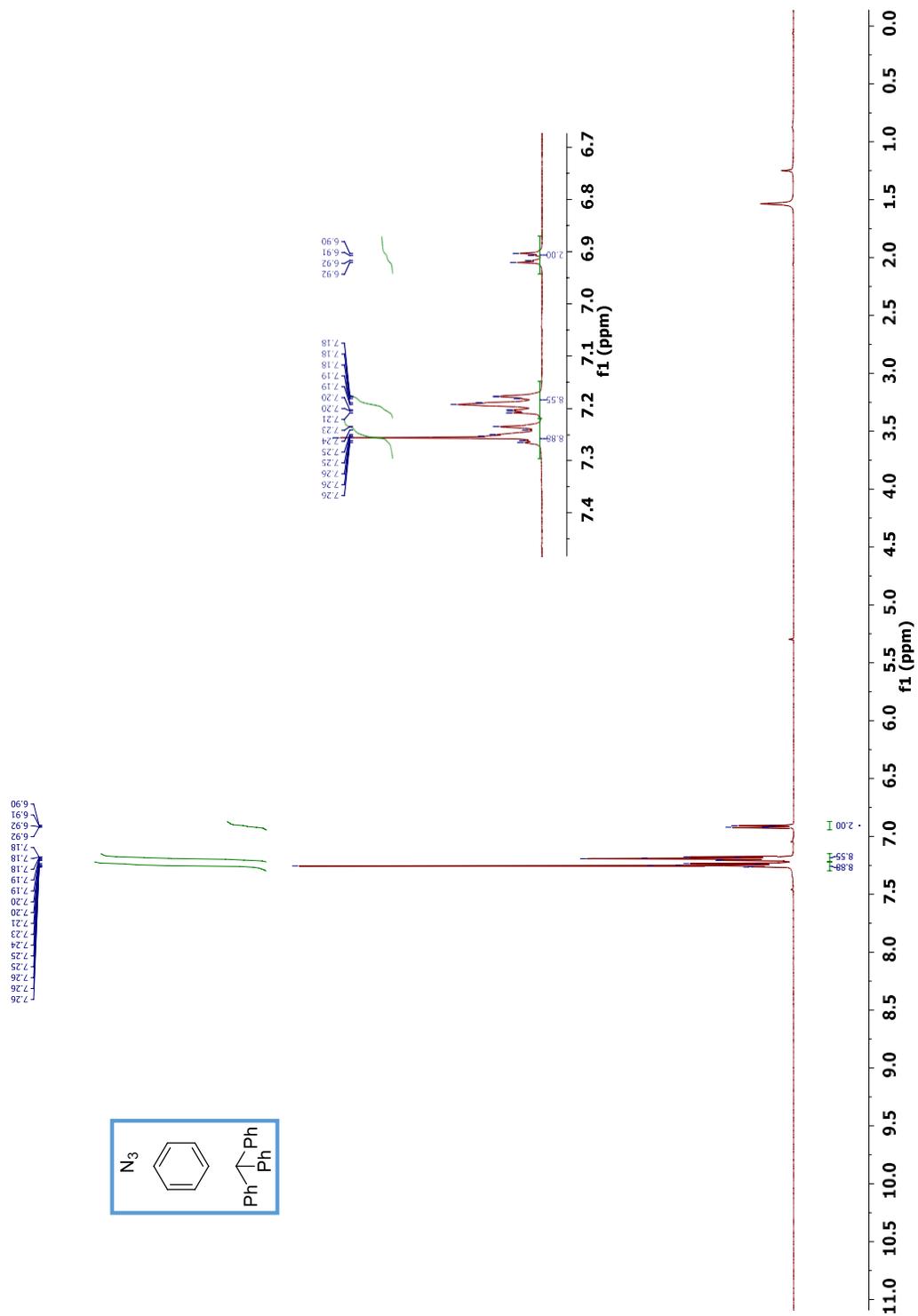


Figure S10. ^{13}C NMR (126 MHz, CDCl_3) of compound **2E**.

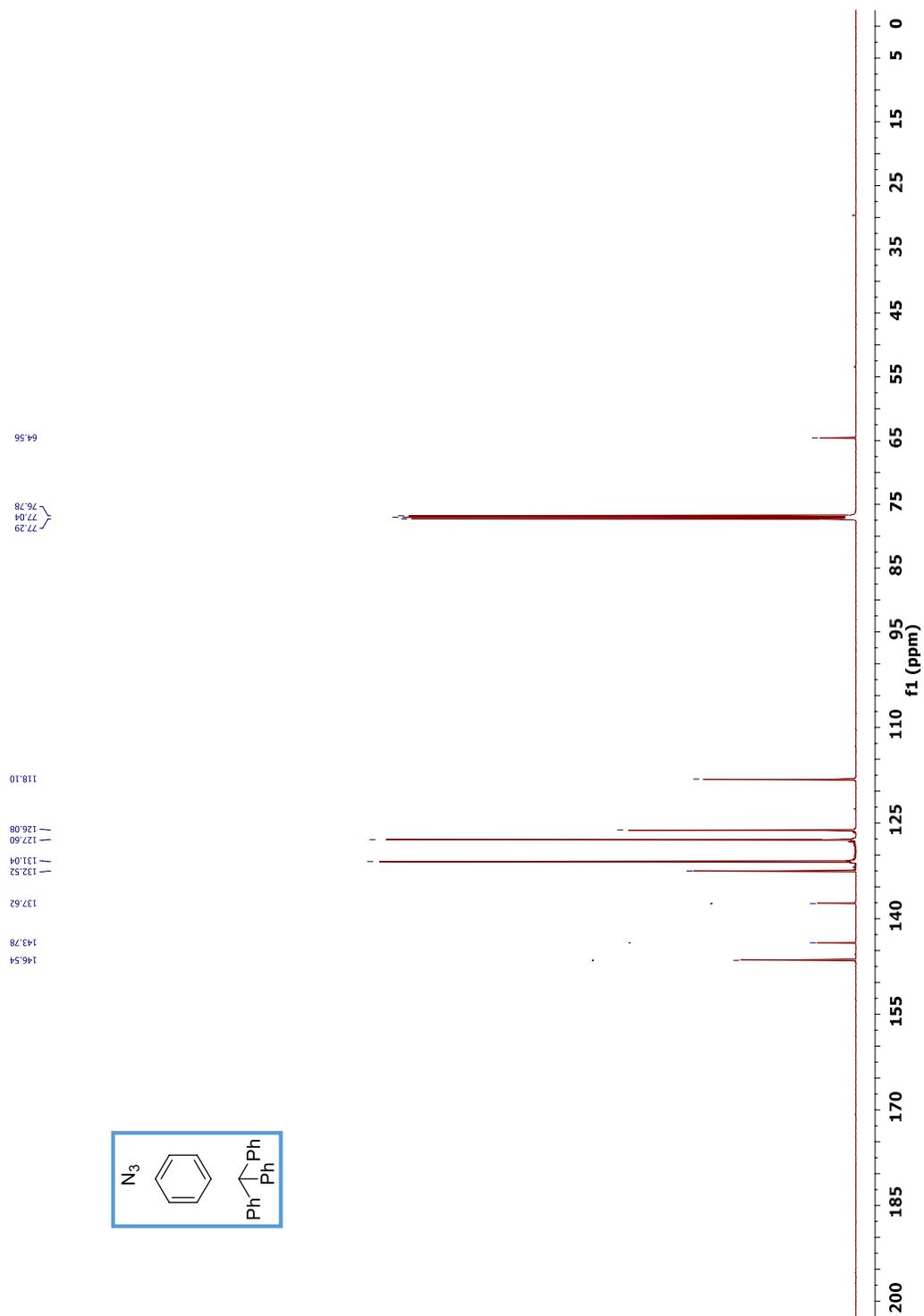


Figure S11. ^1H NMR (500 MHz, CDCl_3) of compound *trans*-3A.

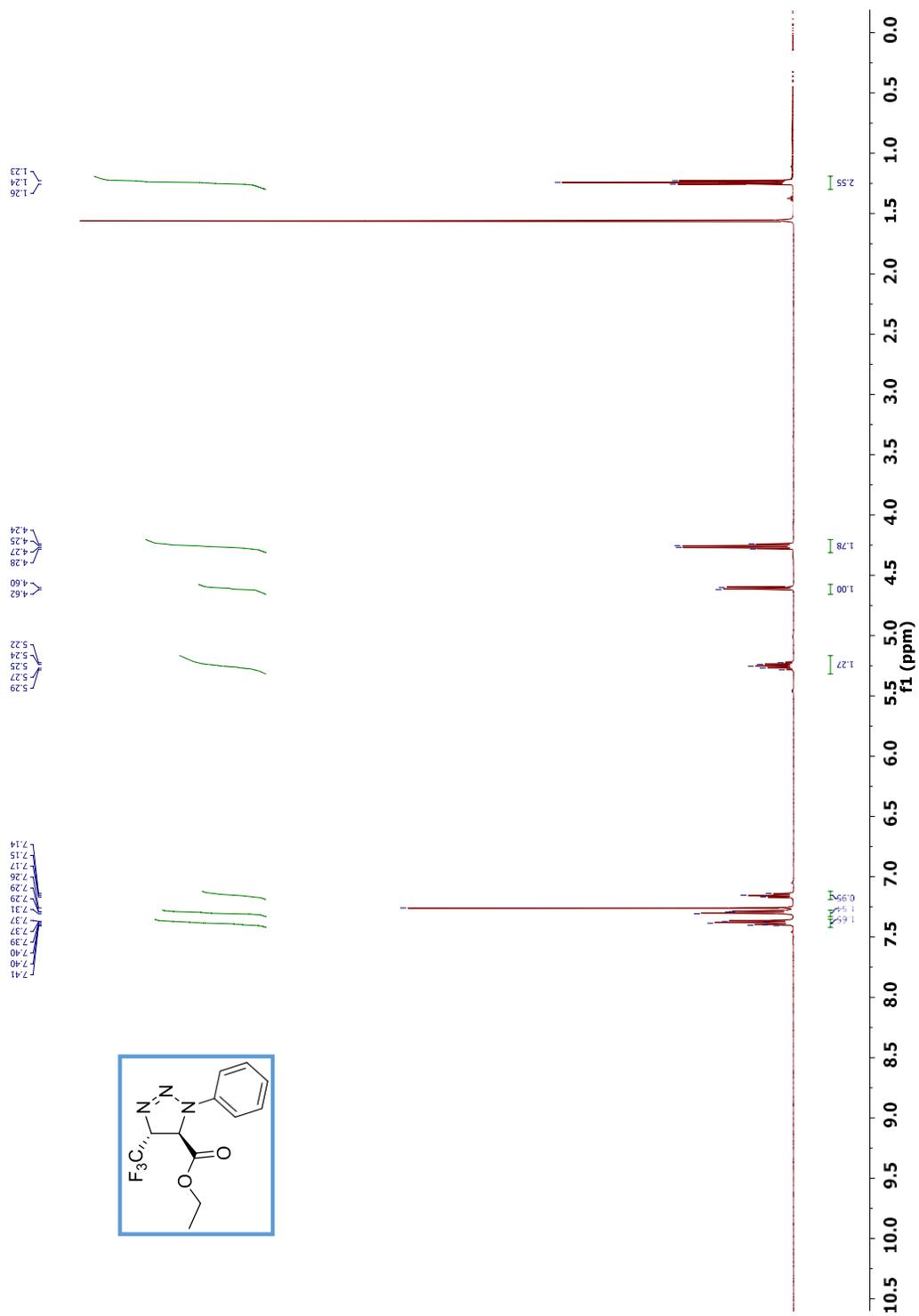


Figure S12. ^{13}C NMR (126 MHz, CDCl_3) of compound *trans*-**3A**.

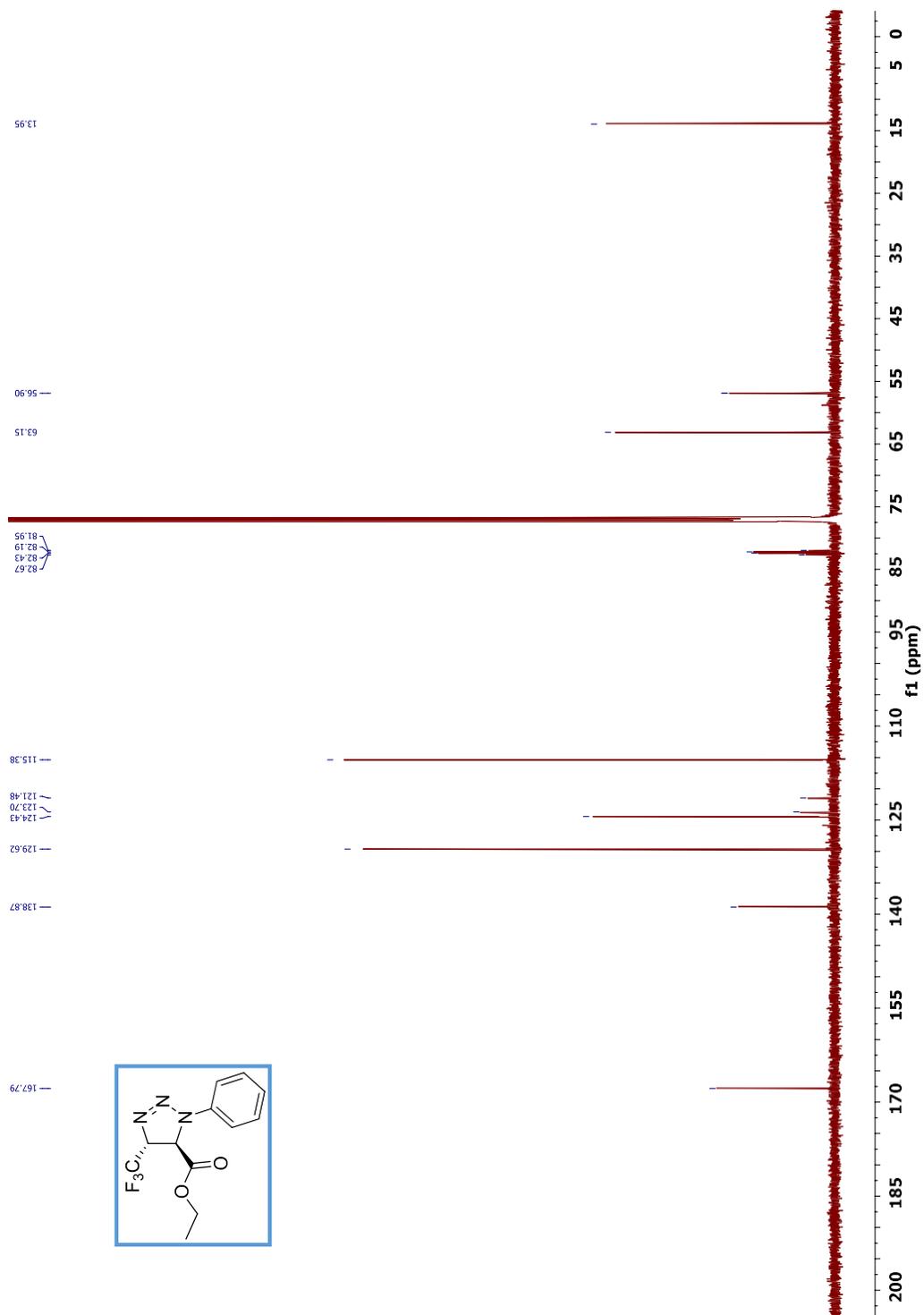


Figure S13. ^1H NMR (500 MHz, CD_3CN) of compound *cis*-3A.

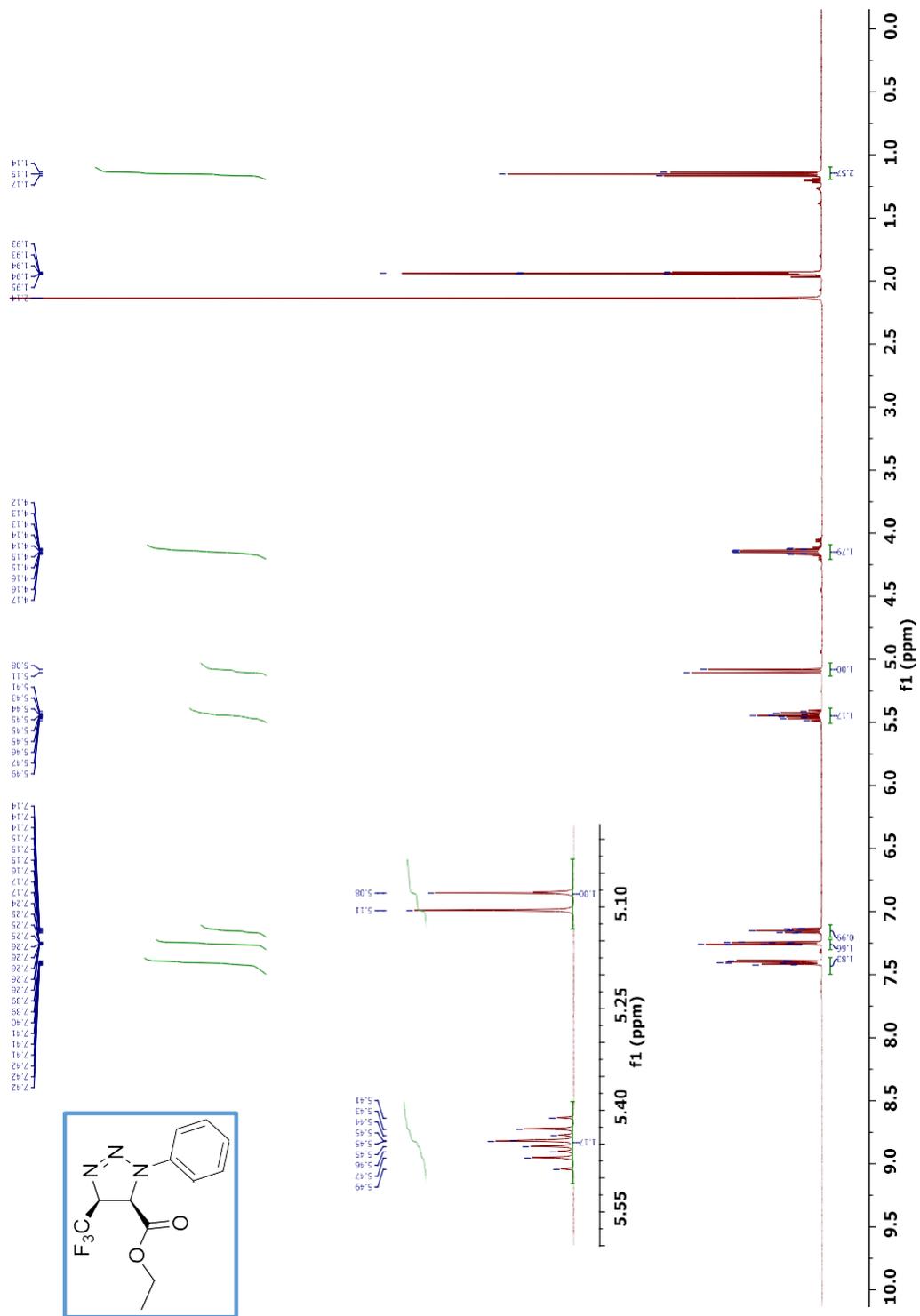


Figure S14. ^{13}C NMR (126 MHz, CD_3CN) of compound *cis*-**3A**.

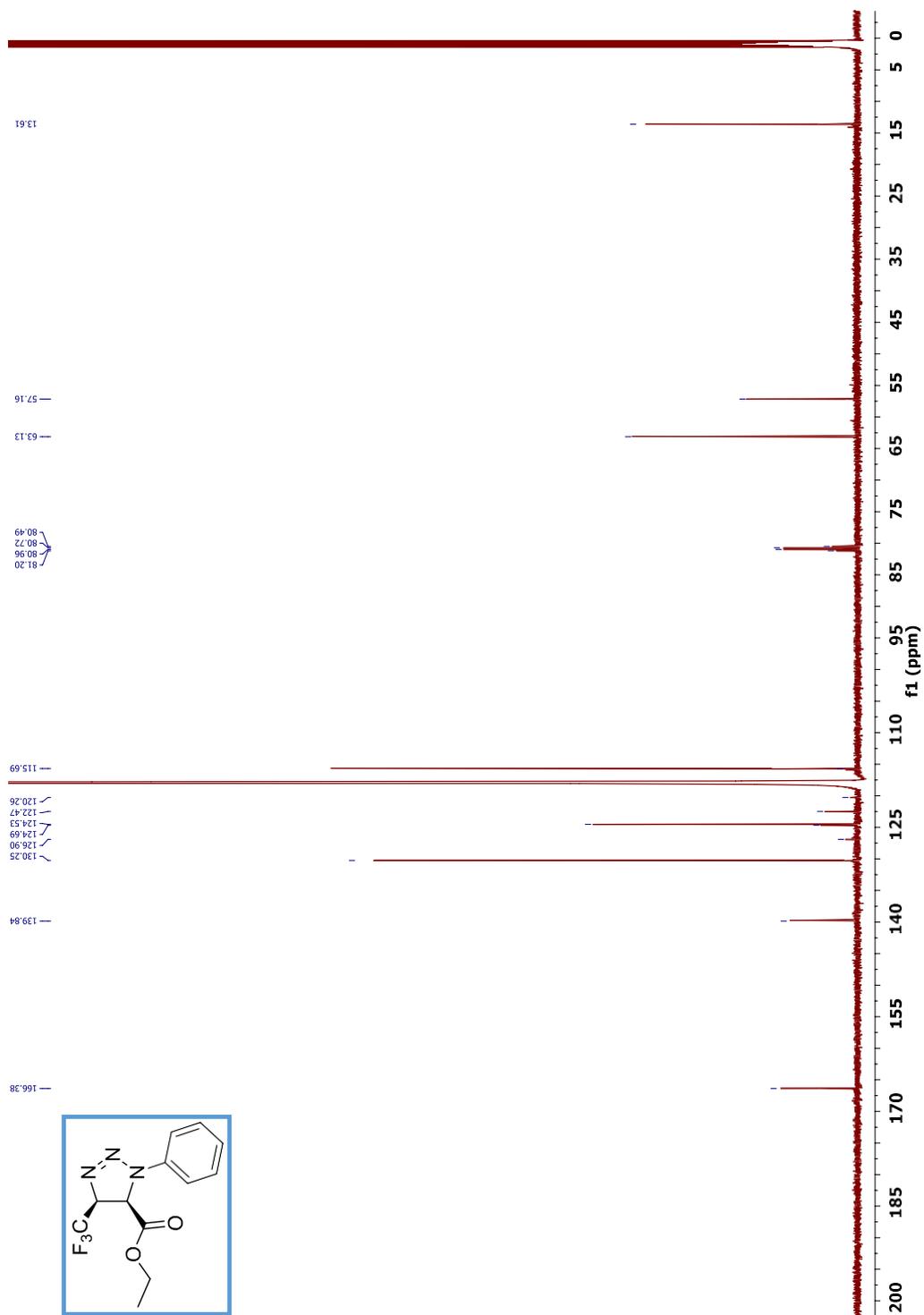


Figure S15. ^1H NMR (500 MHz, CDCl_3) of compound *trans*-**3B**.

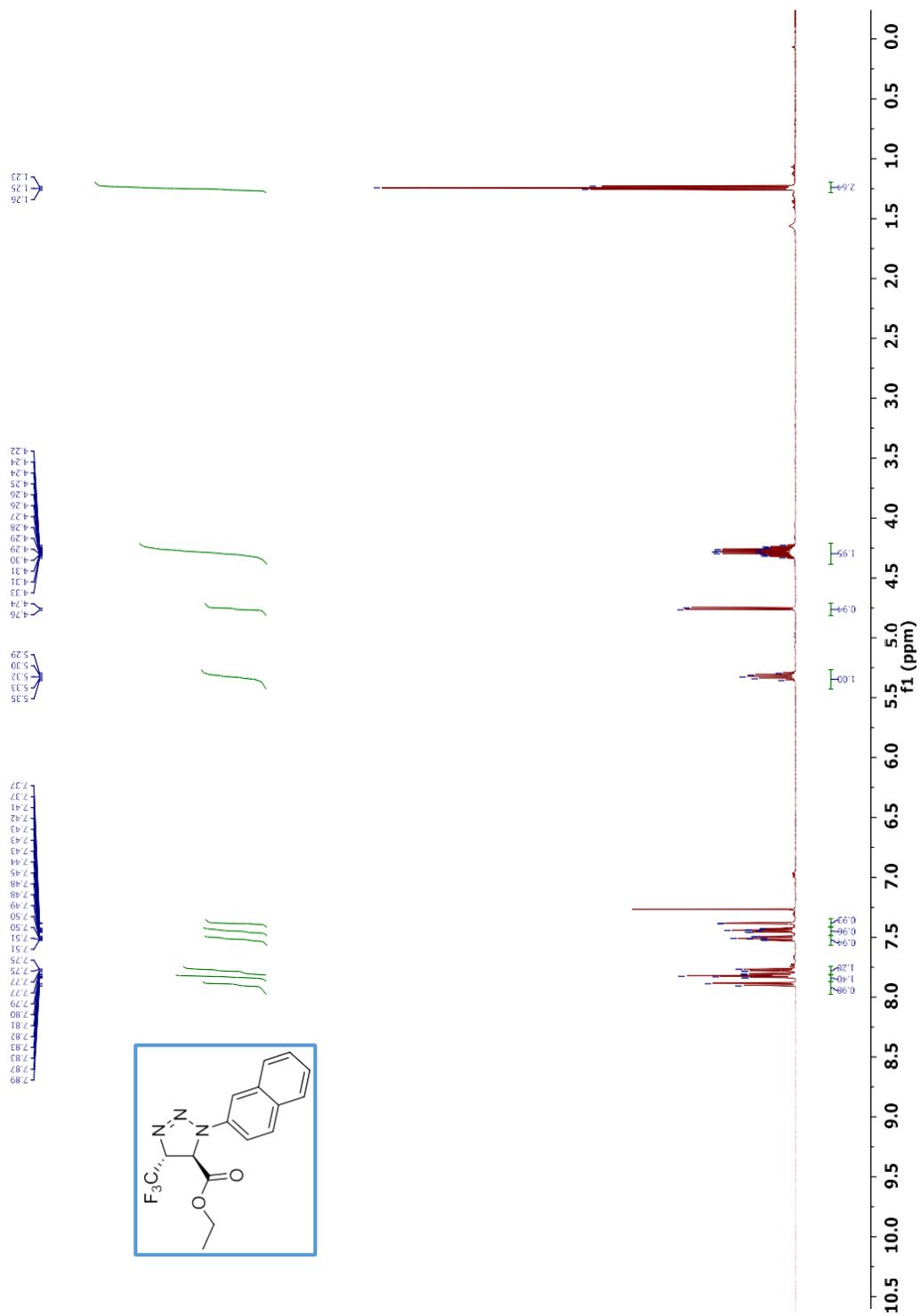


Figure S16. ^{13}C NMR (126 MHz, CDCl_3) of compound *trans*-**3B**.

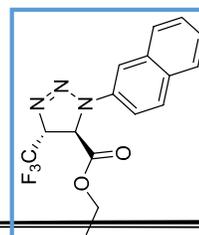
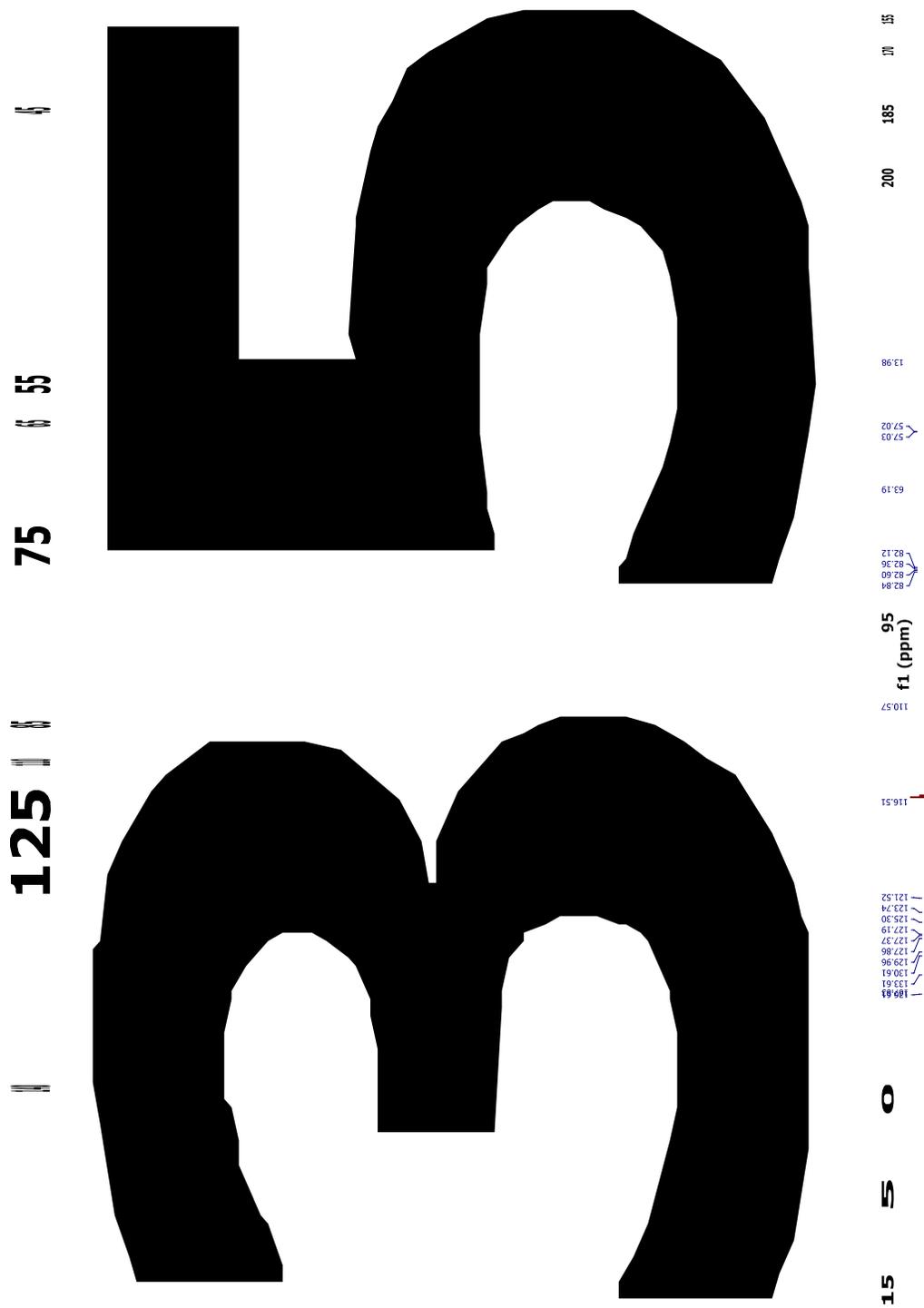


Figure S17. ^1H NMR (500 MHz, CD_3CN) of compound *cis*-**3B**.

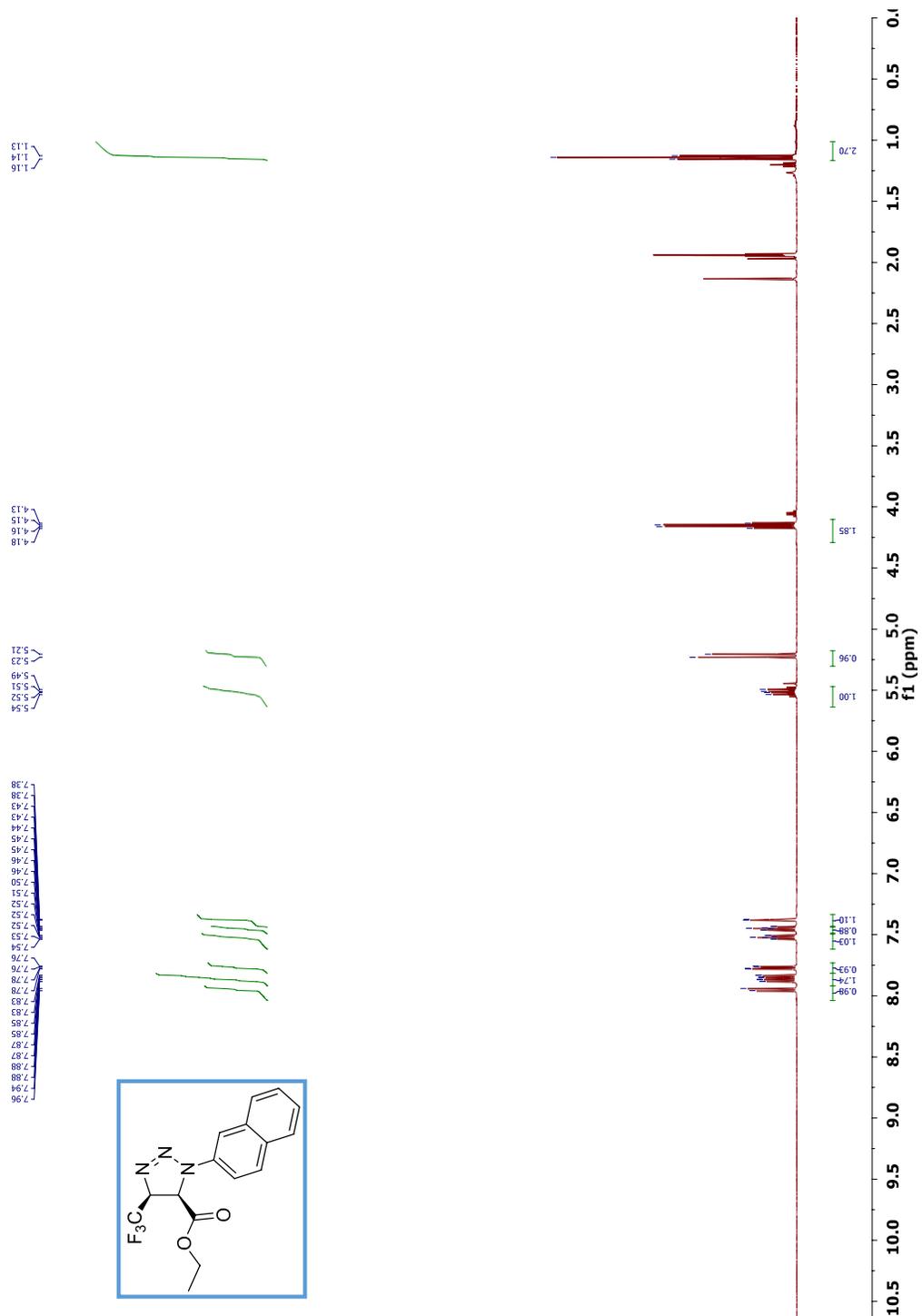


Figure S18. ^{13}C NMR (126 MHz, CD_3CN) of compound *cis*-**3B**.

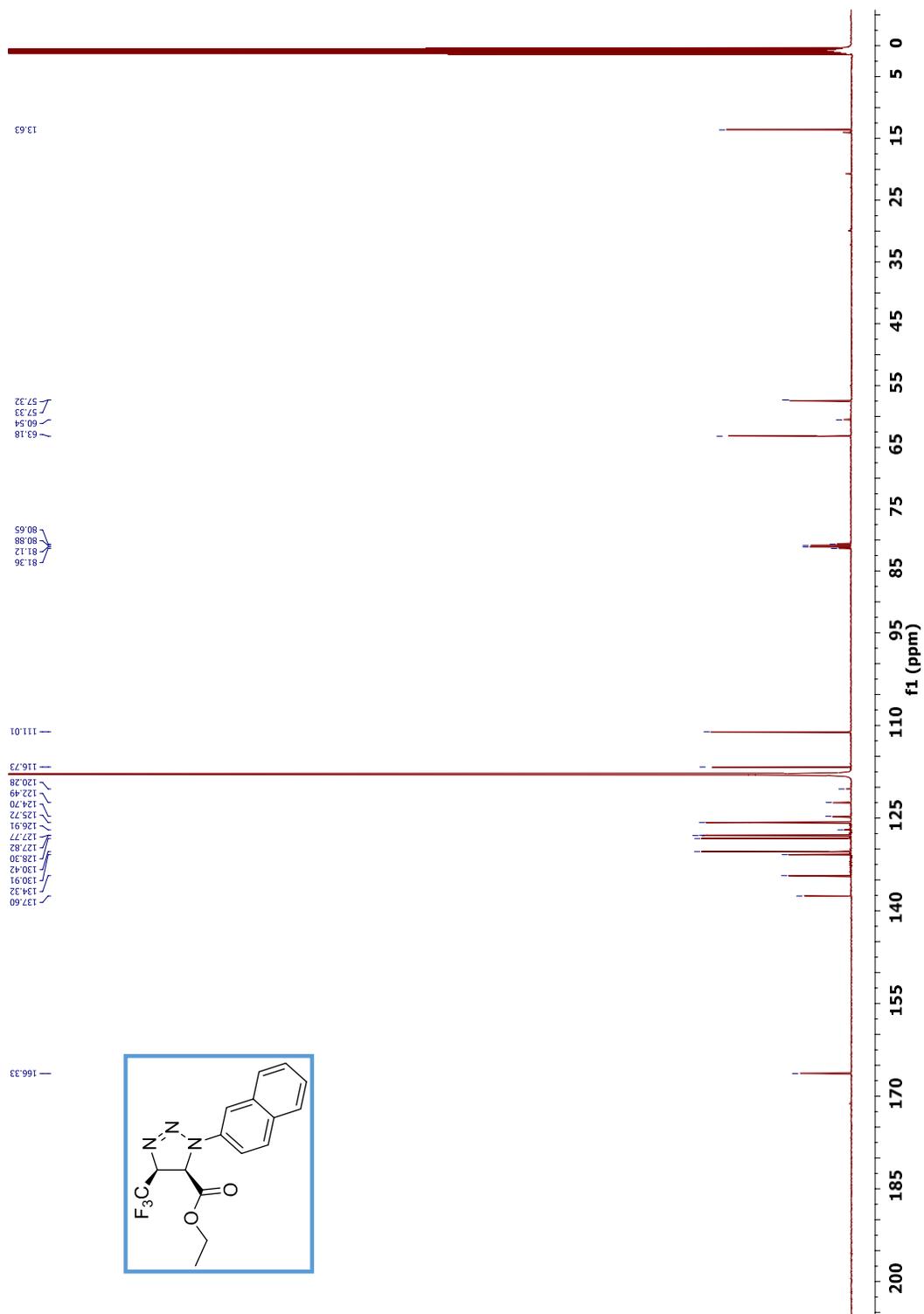


Figure S19. ^1H NMR (500 MHz, CDCl_3) of compound *trans*-3C.

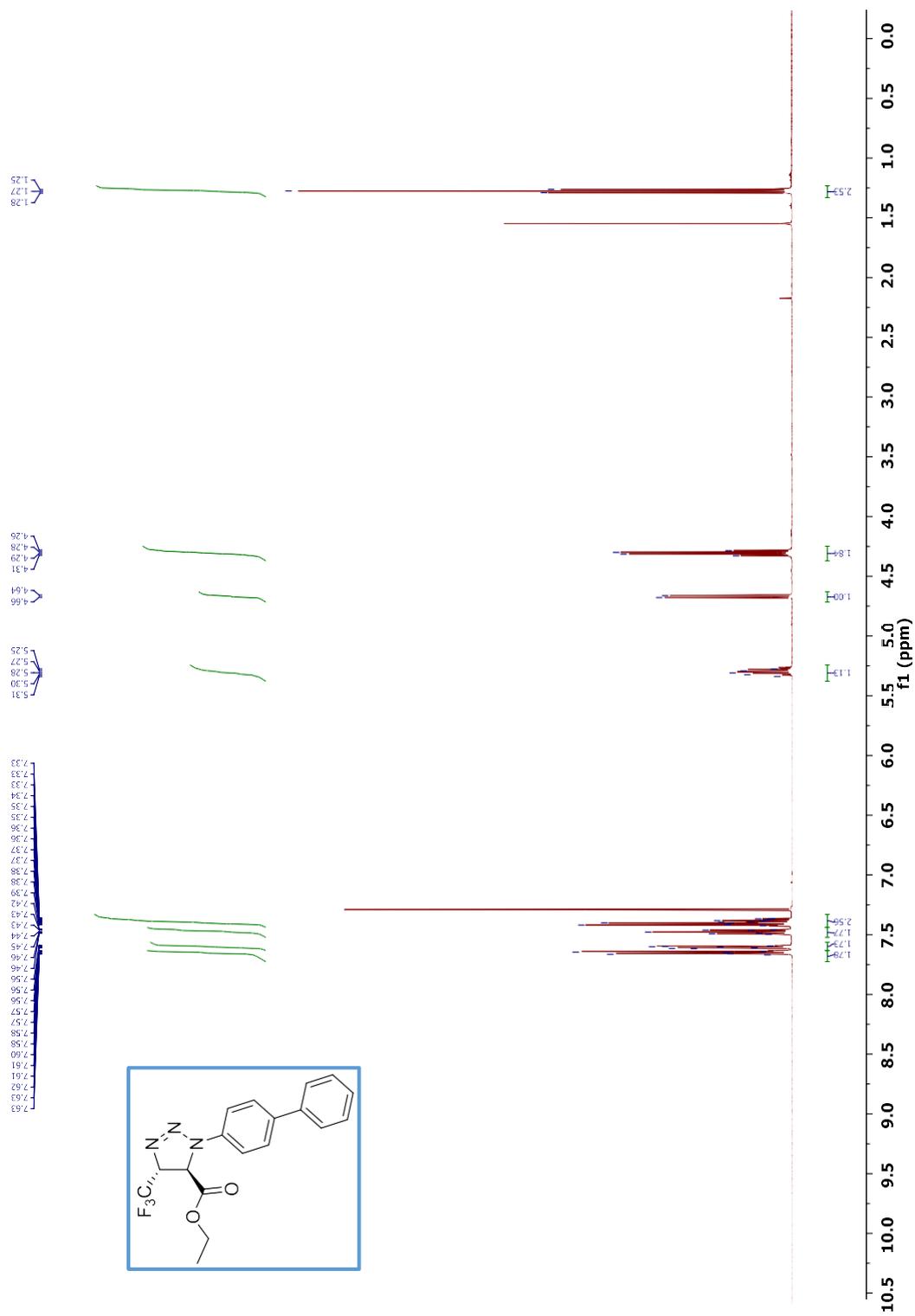


Figure S20. ^{13}C NMR (126 MHz, CDCl_3) of compound *trans*-**3C**.

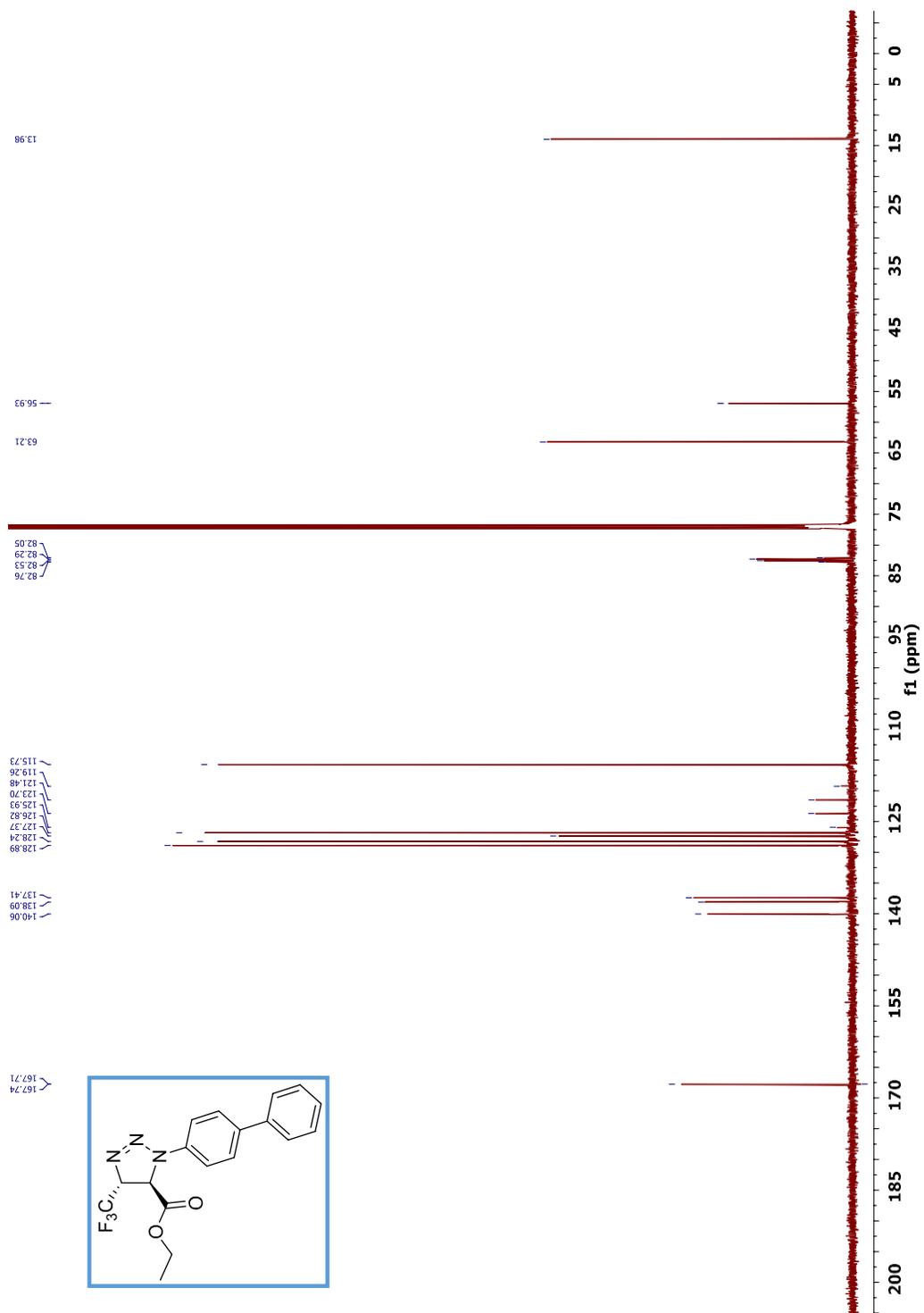


Figure S21. ^1H NMR (500 MHz, CDCl_3) of compound *cis*-3C.

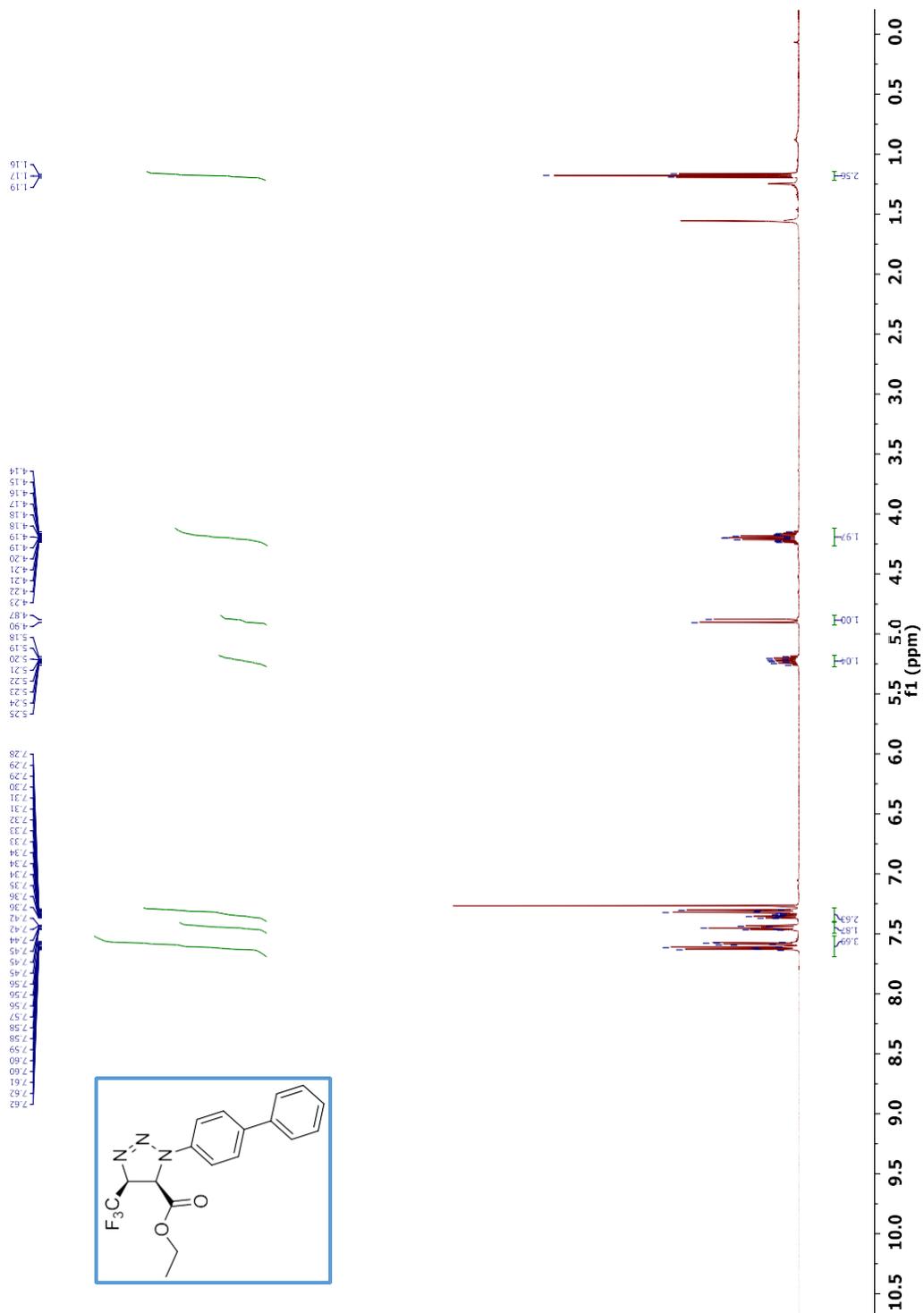


Figure S22. ^{13}C NMR (126 MHz, CDCl_3) of compound *cis*-**3C**.

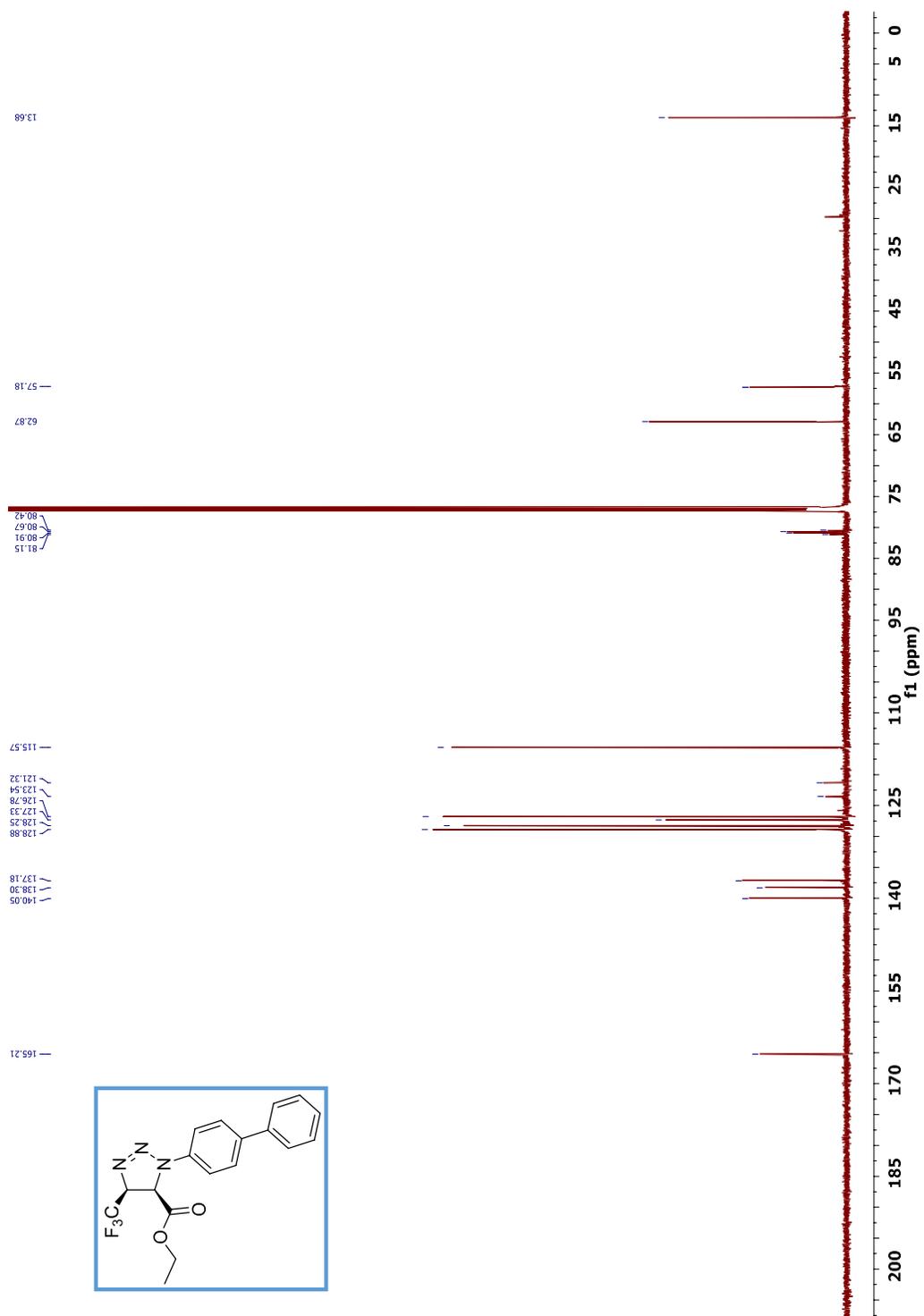


Figure S23. ^1H NMR (500 MHz, CDCl_3) of compound *trans*-**3D**.

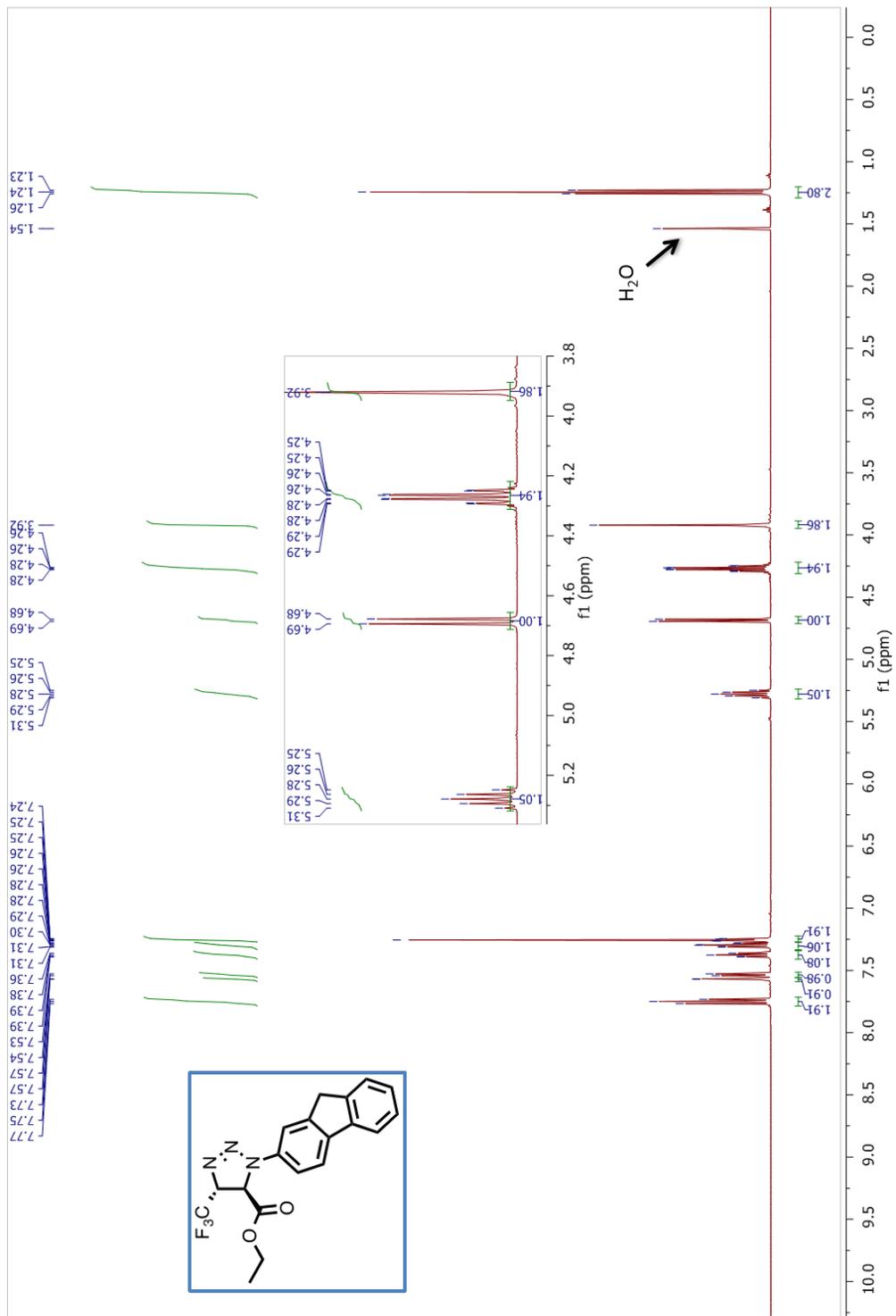


Figure S24. ^{13}C NMR (126 MHz, CDCl_3) of compound *trans*-**3D**.

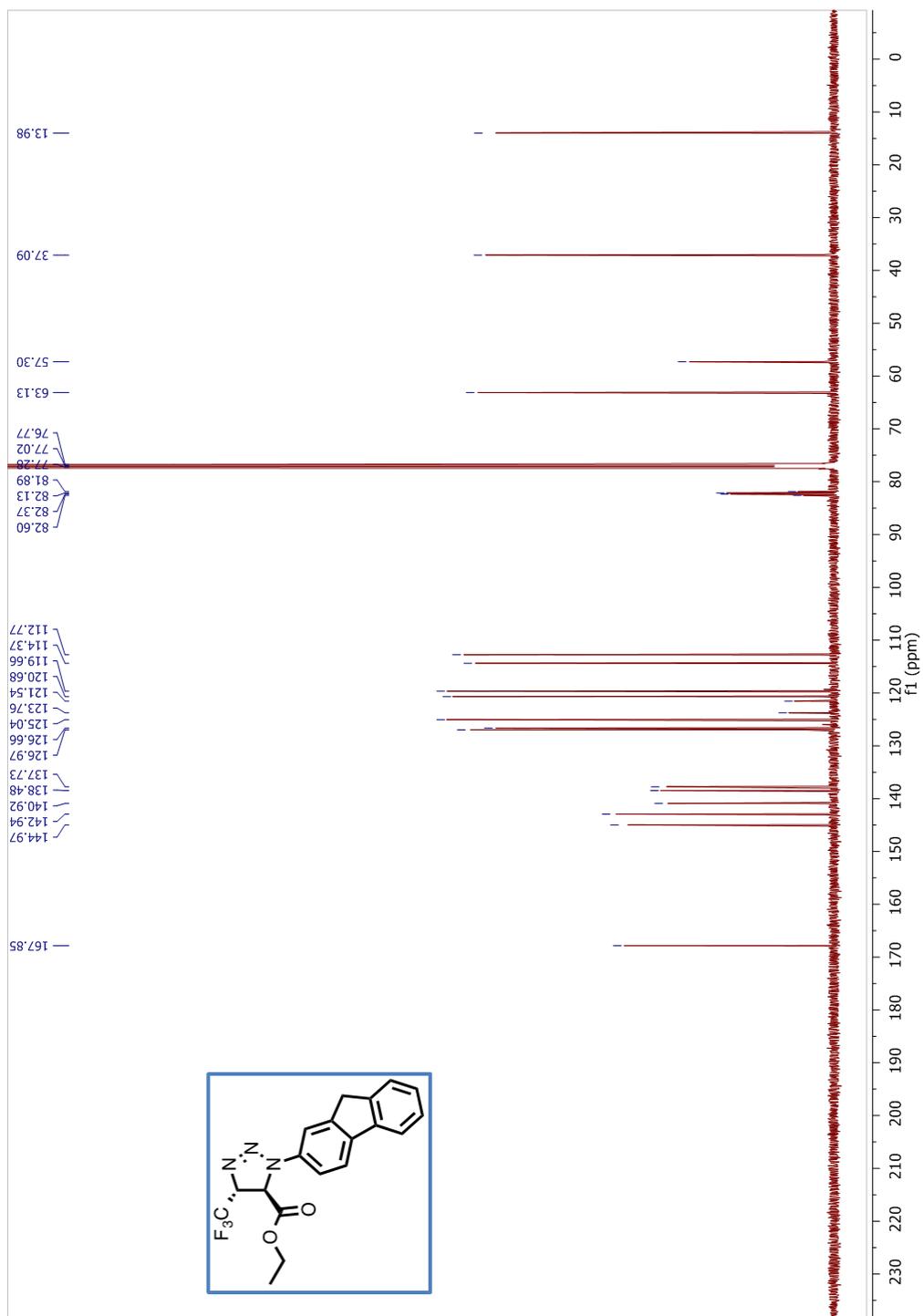


Figure S25. ^1H NMR (500 MHz, CDCl_3) of compound *cis*-**3D**.

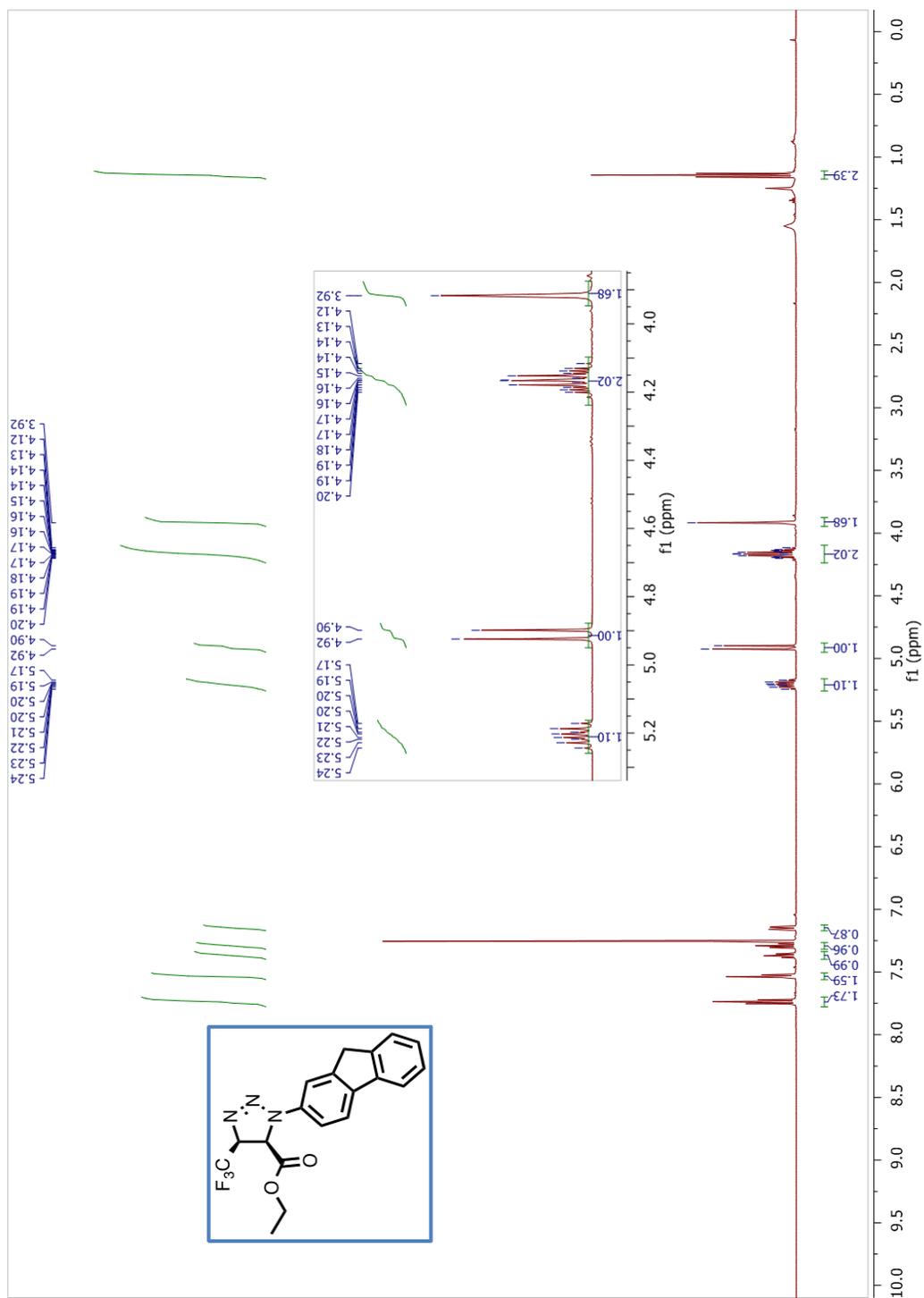


Figure S26. ^{13}C NMR (126 MHz, CDCl_3) of compound *cis*-**3D**.

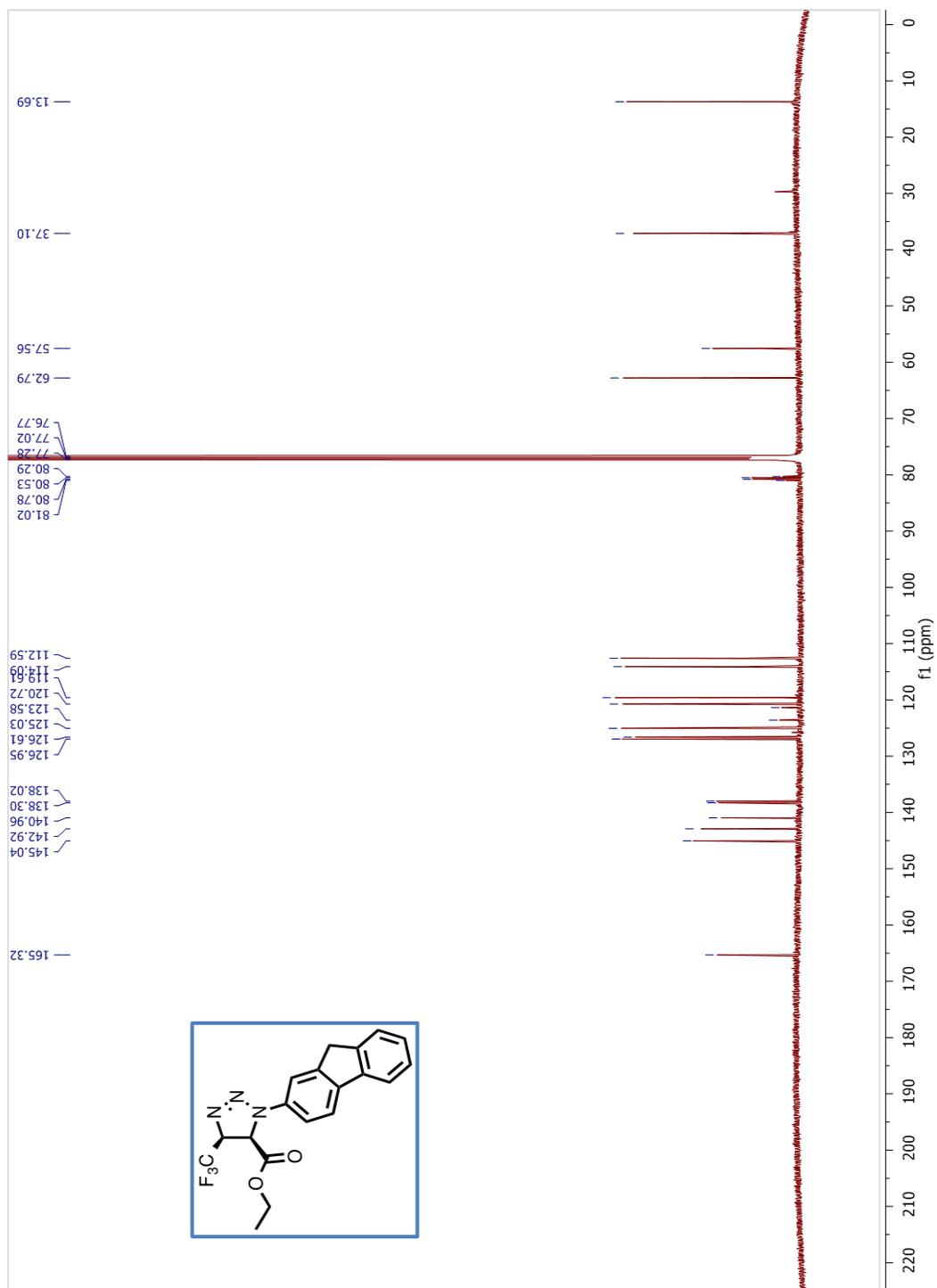


Figure S27. ^1H NMR (500 MHz, CDCl_3) of compound *trans*-**3E**.

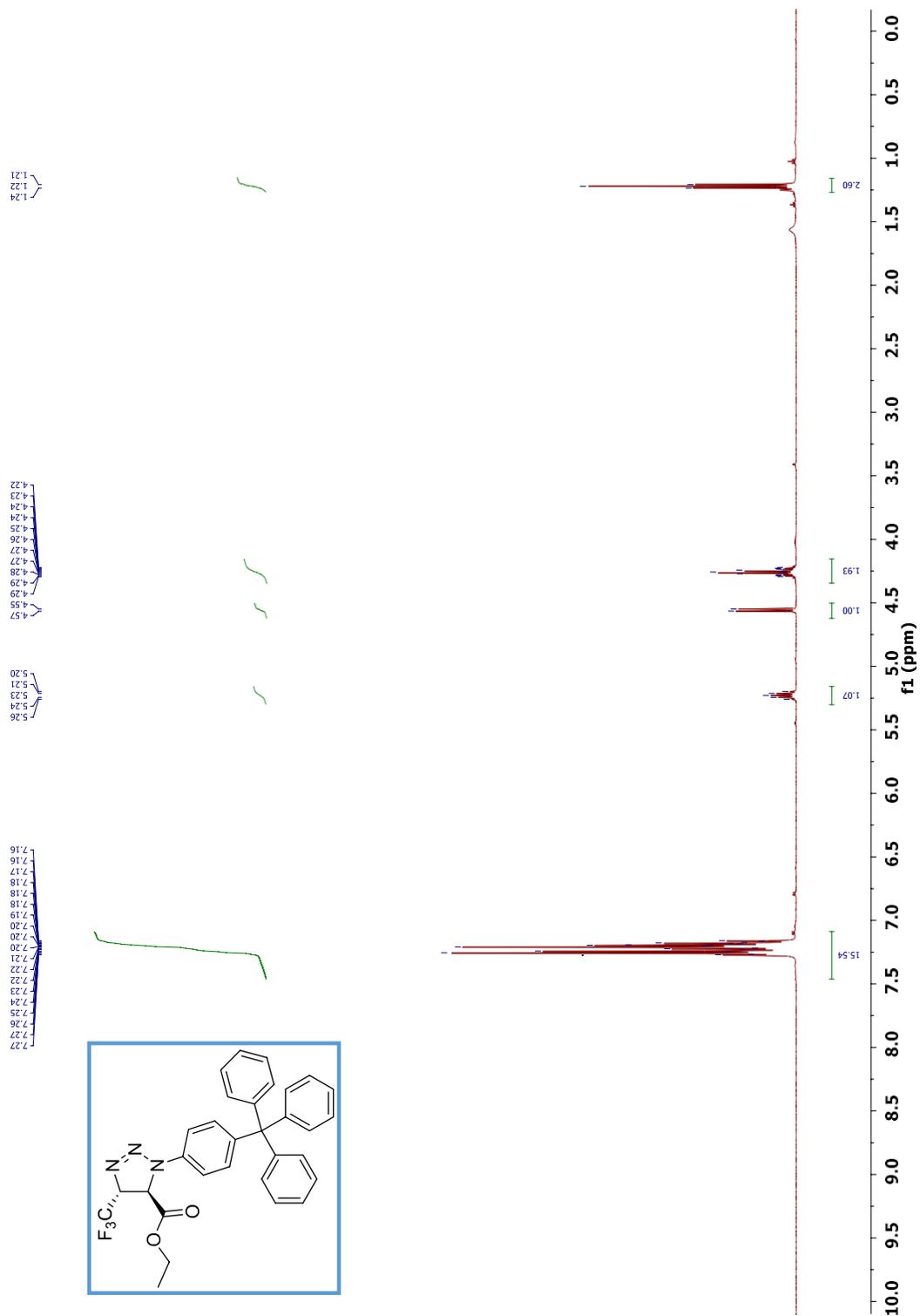


Figure S28. ^{13}C NMR (126 MHz, CDCl_3) of compound *trans*-**3E**.

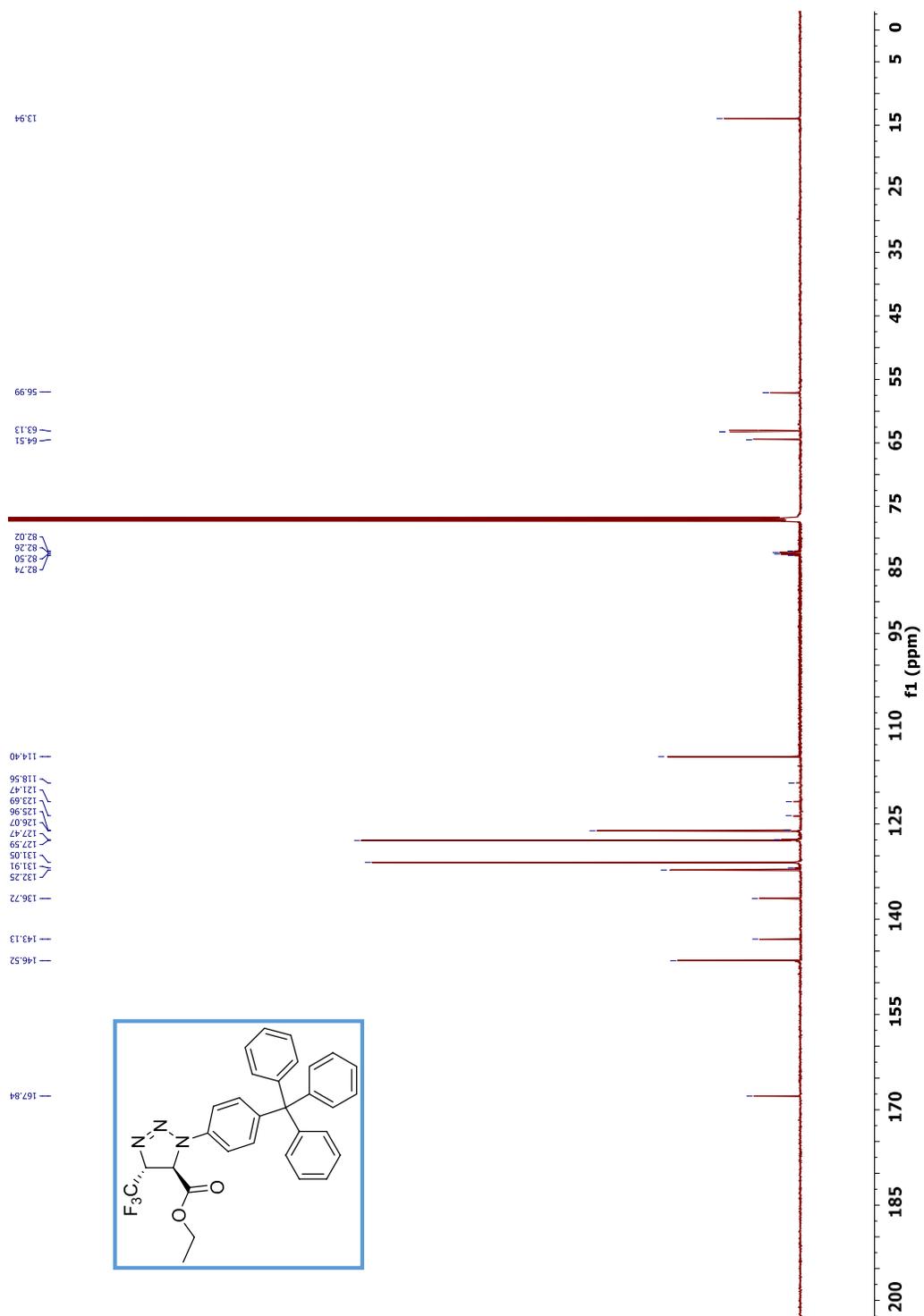


Figure S29. ^1H NMR (500 MHz, CD_3CN) of compound *cis*-**3E**.

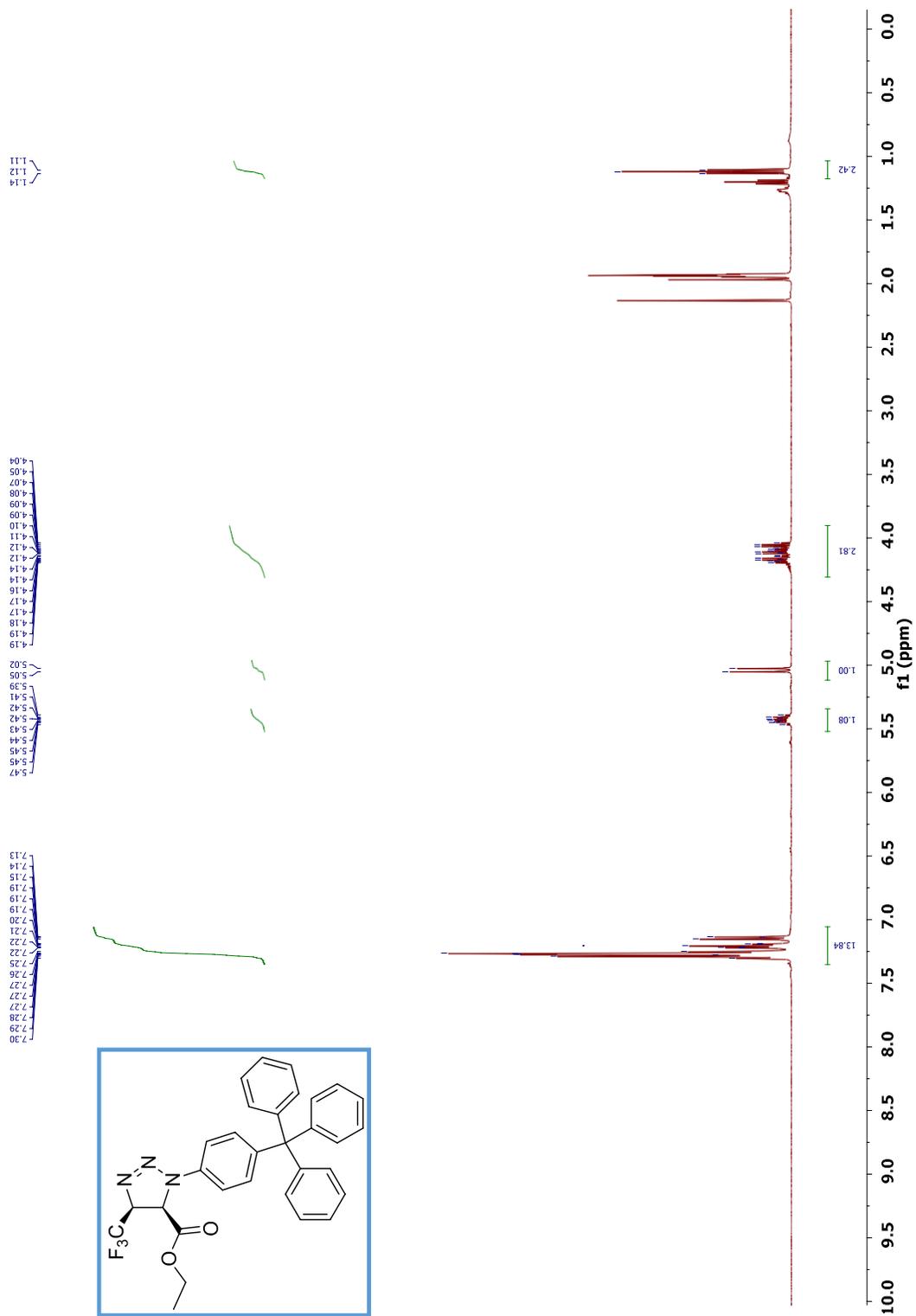


Figure S30. ^{13}C NMR (126 MHz, CD_3CN) of compound *cis*-**3E**.

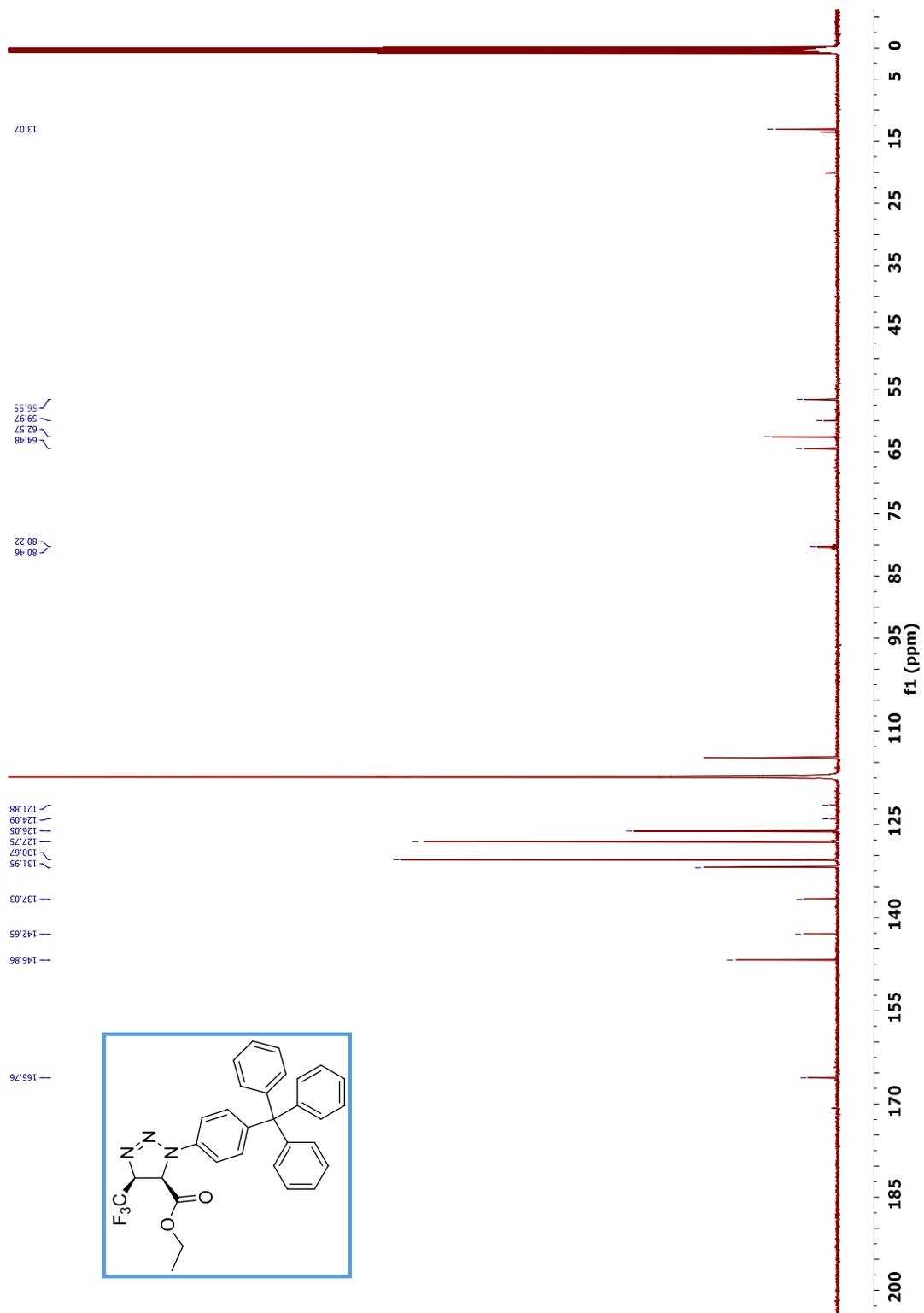


Figure S31. ^1H NMR (500 MHz, CD_3CN) of compound *trans*-4A.

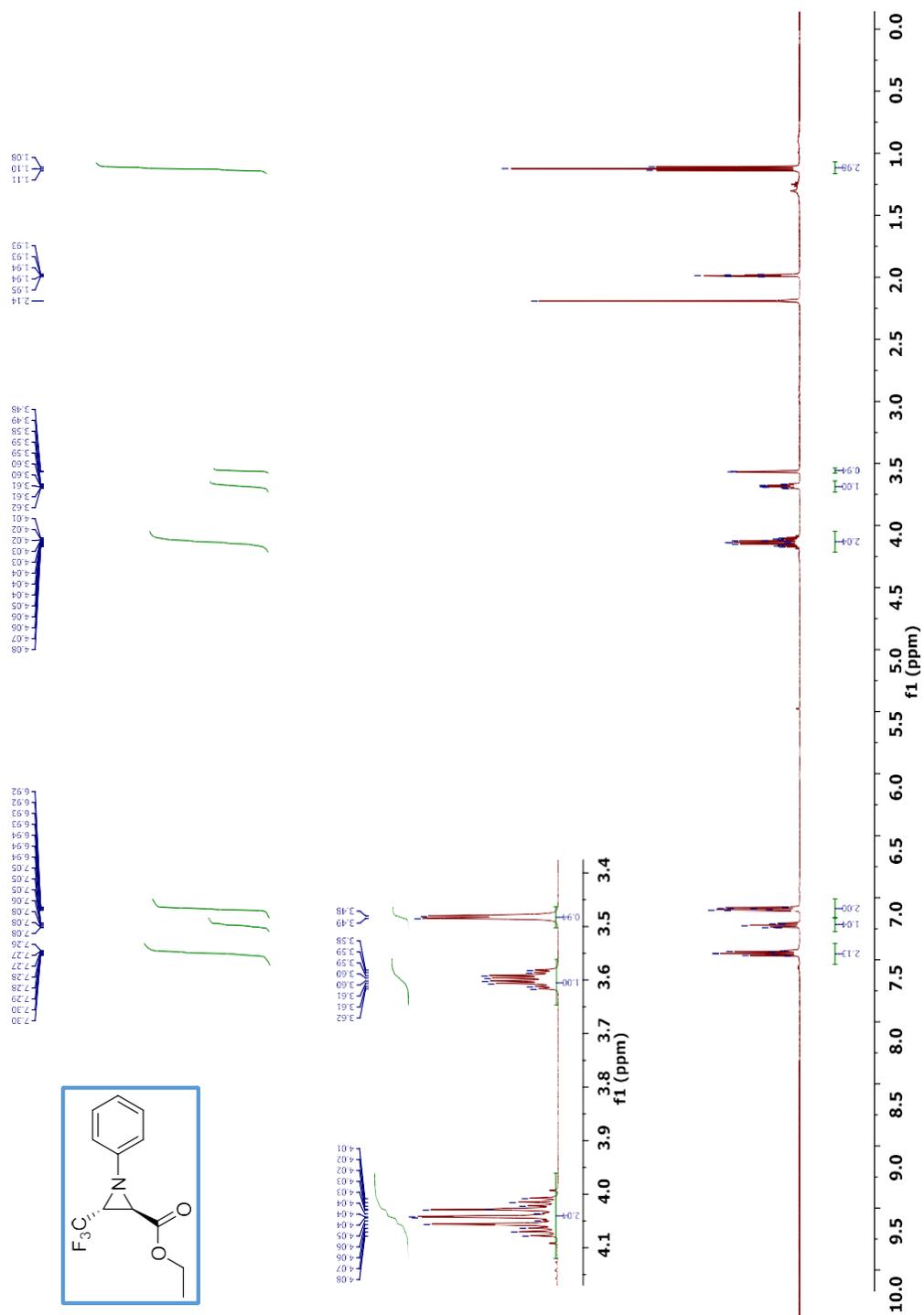


Figure S32. ^{13}C NMR (126 MHz, CD_3CN) of compound *trans*-4A.

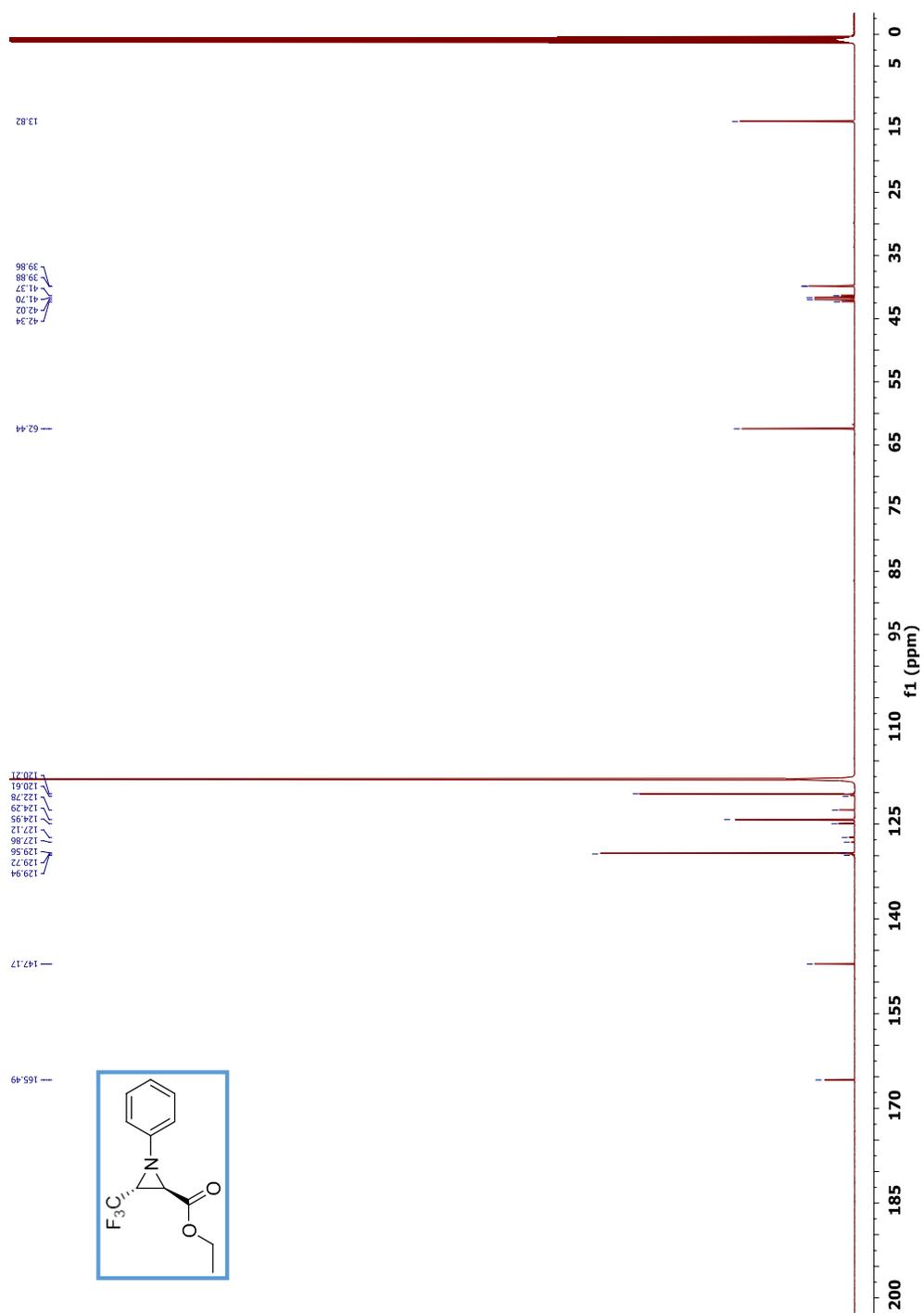


Figure S33. ^1H NMR (500 MHz, CD_3CN) of compound *cis*-4A.

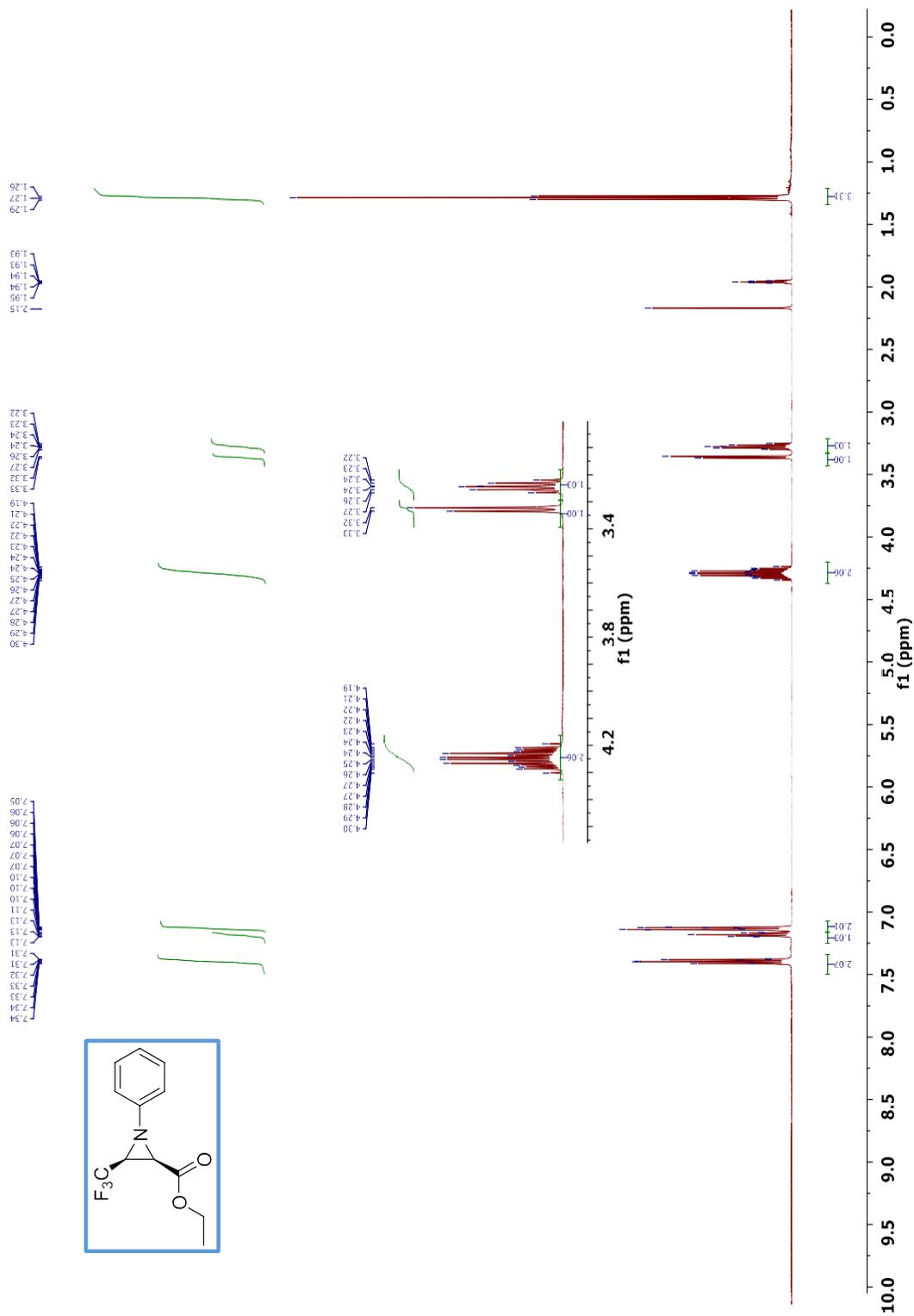


Figure S34. ^{13}C NMR (126 MHz, CD_3CN) of compound *cis*-4A.

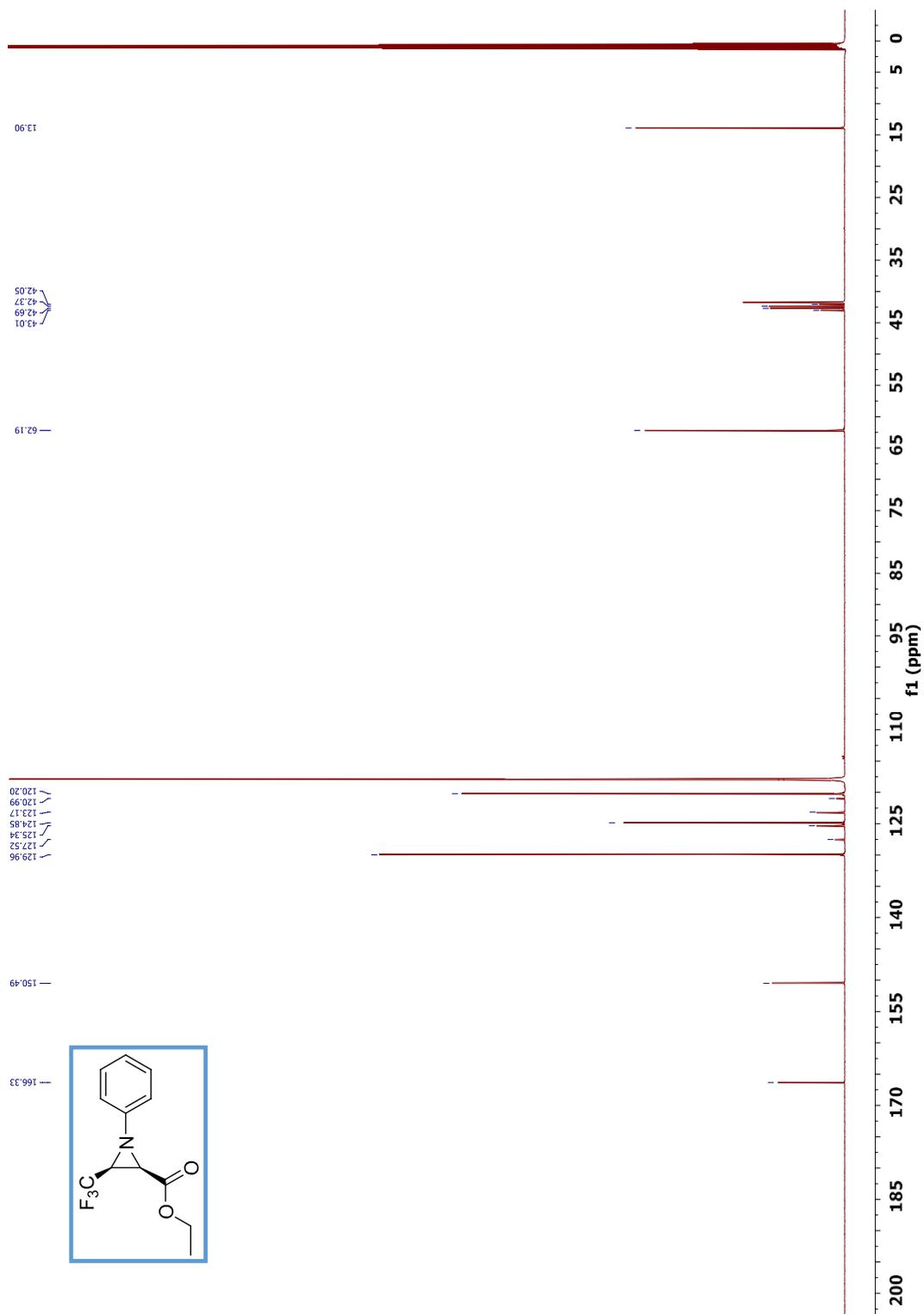


Figure S35. ^1H NMR (500 MHz, CD_3CN) of compound *trans*-4B.

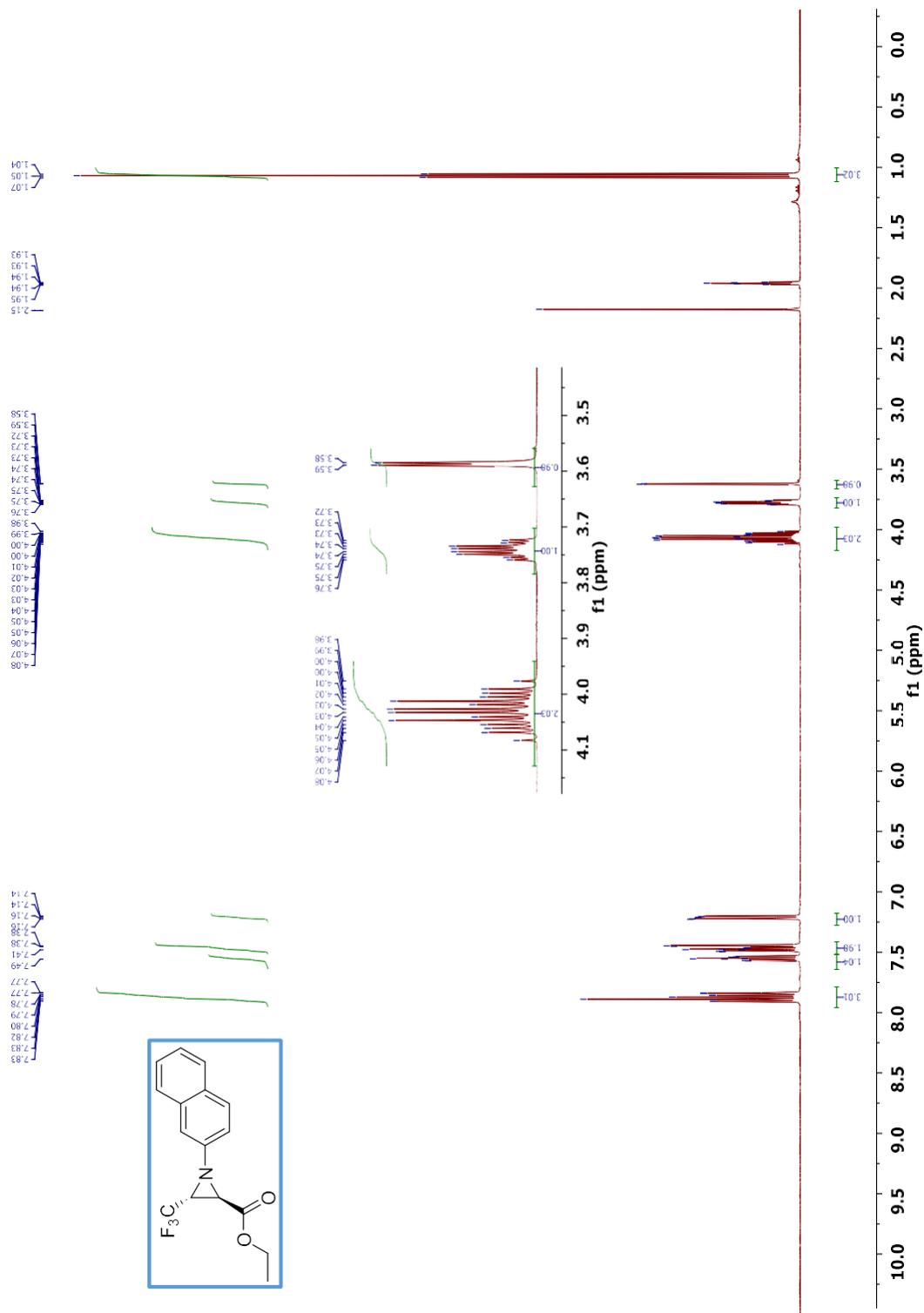


Figure S36. ^{13}C NMR (126 MHz, CD_3CN) of compound *trans*-4B.

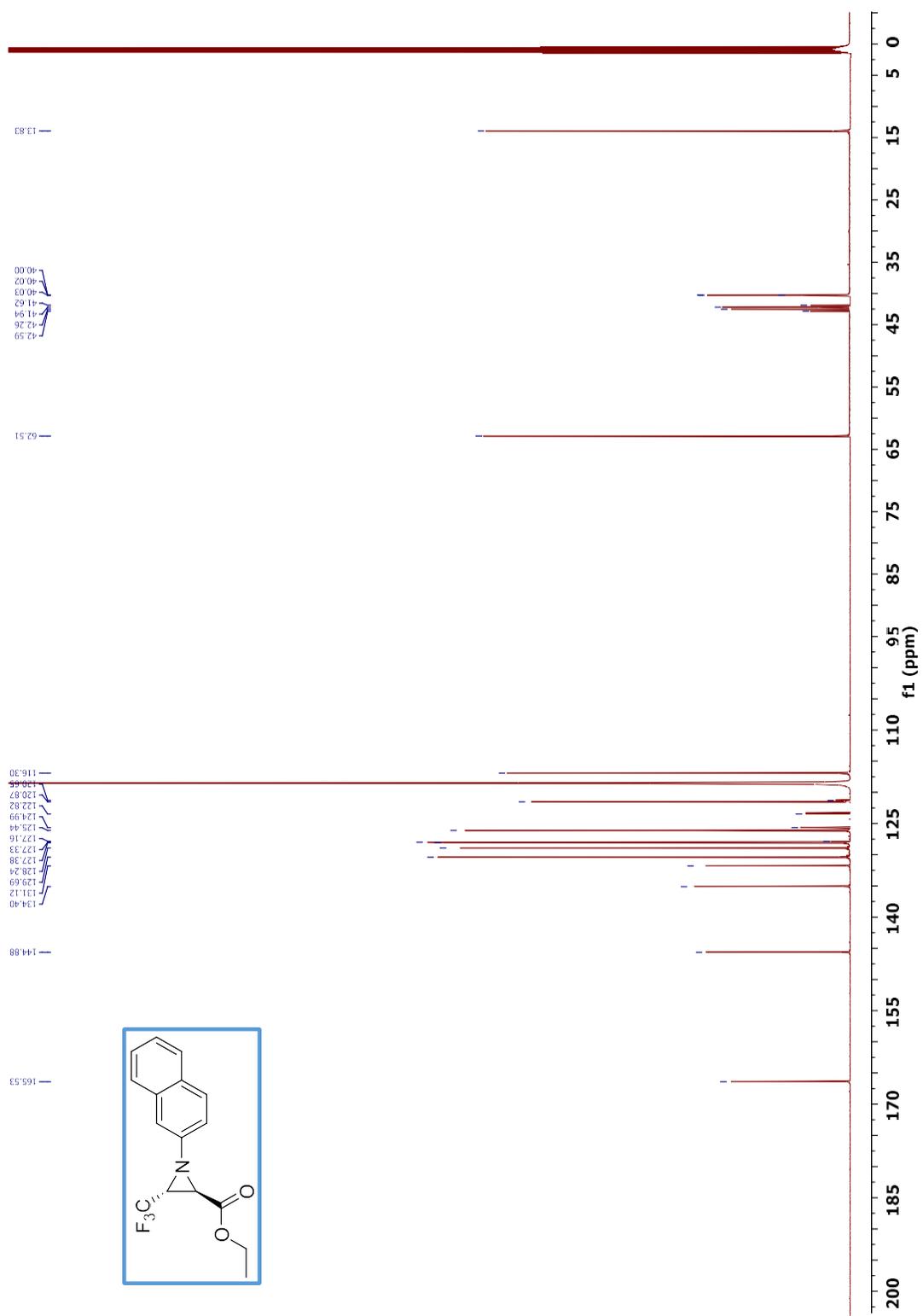


Figure S37. ^1H NMR (500 MHz, CD_3CN) of compound *cis*-4B.

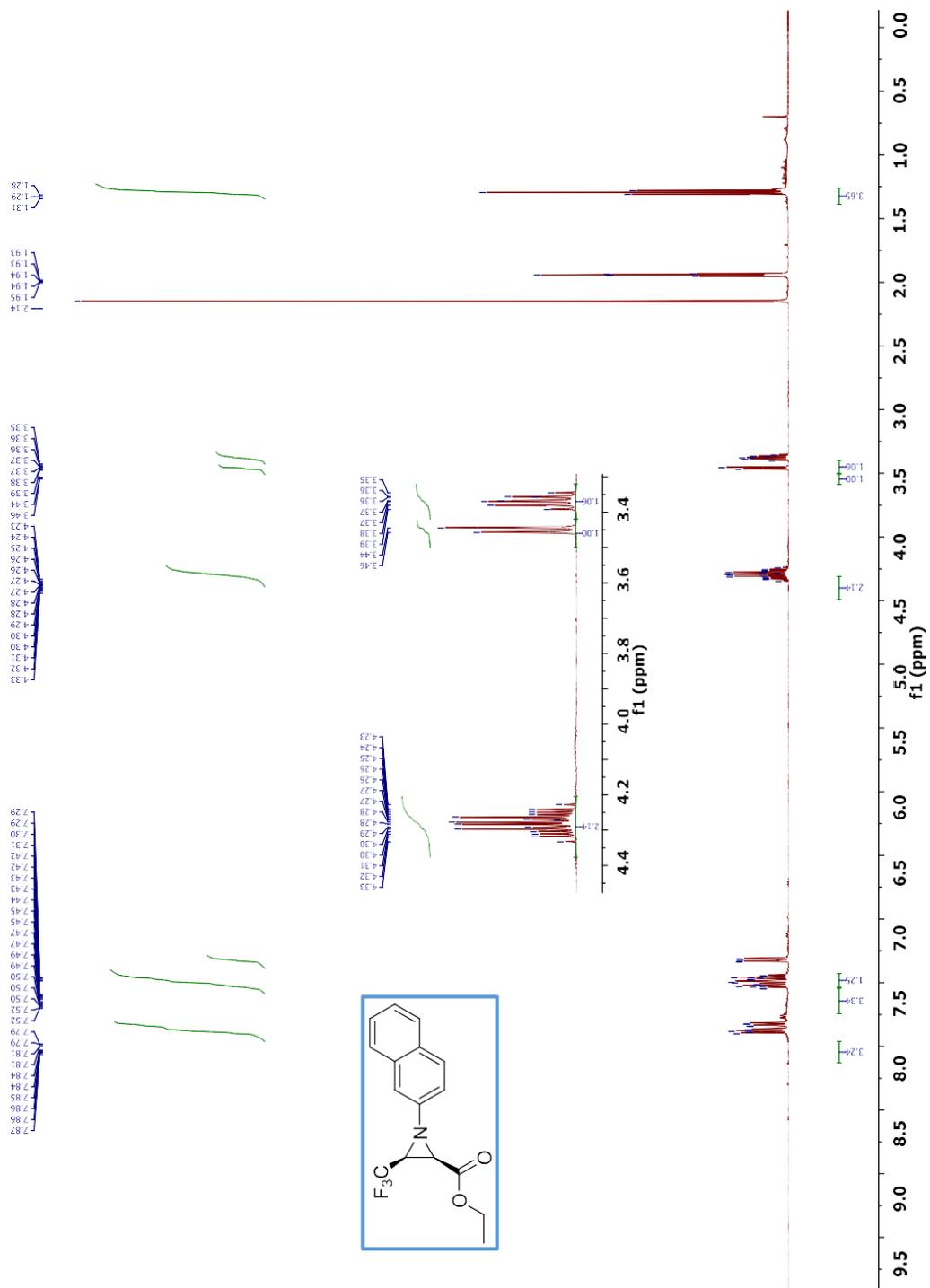


Figure S38. ^{13}C NMR (126 MHz, CD_3CN) of compound *cis*-4B.

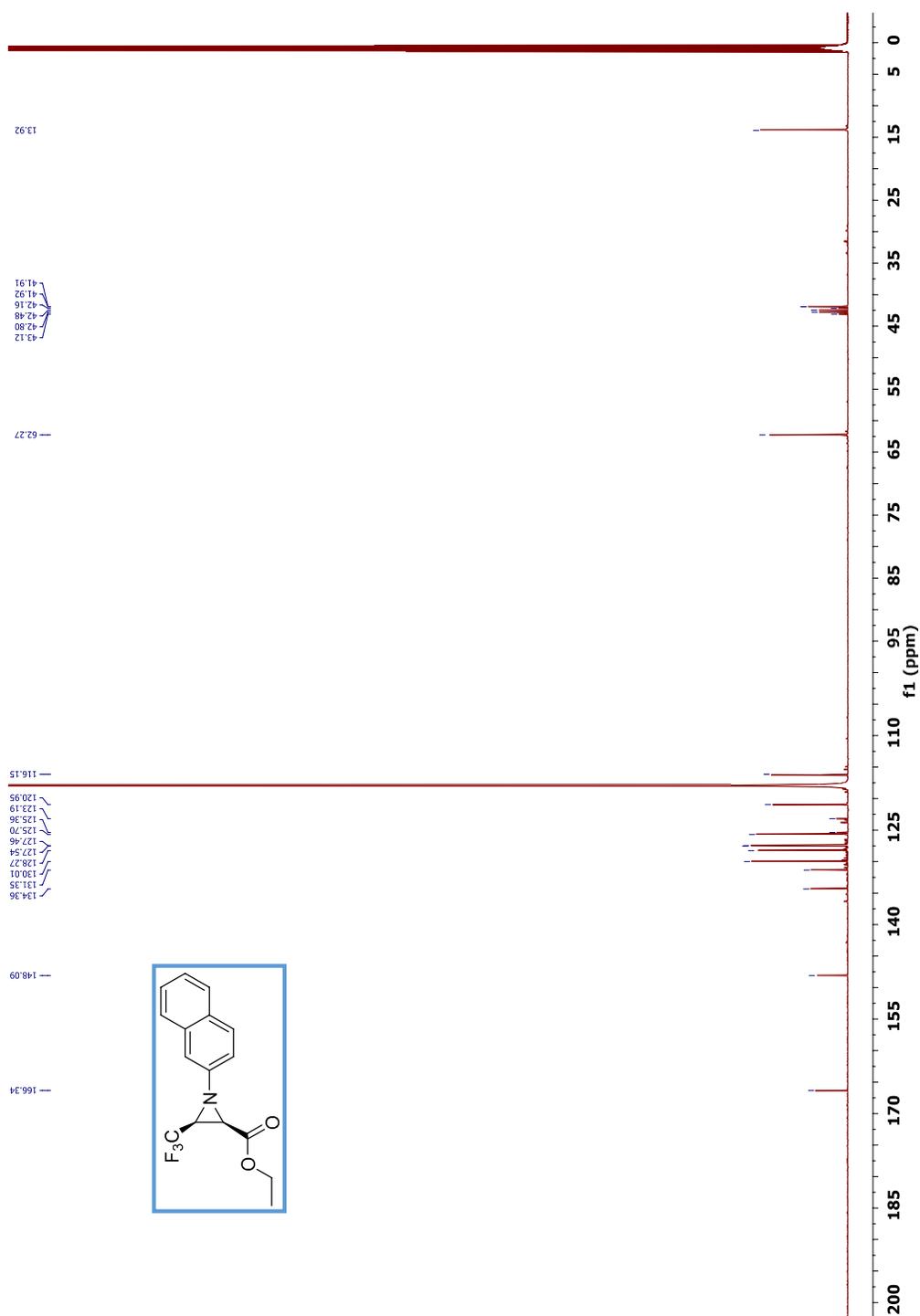


Figure S40. ^{13}C NMR (126 MHz, CD_3CN) of compound *trans*-4C.

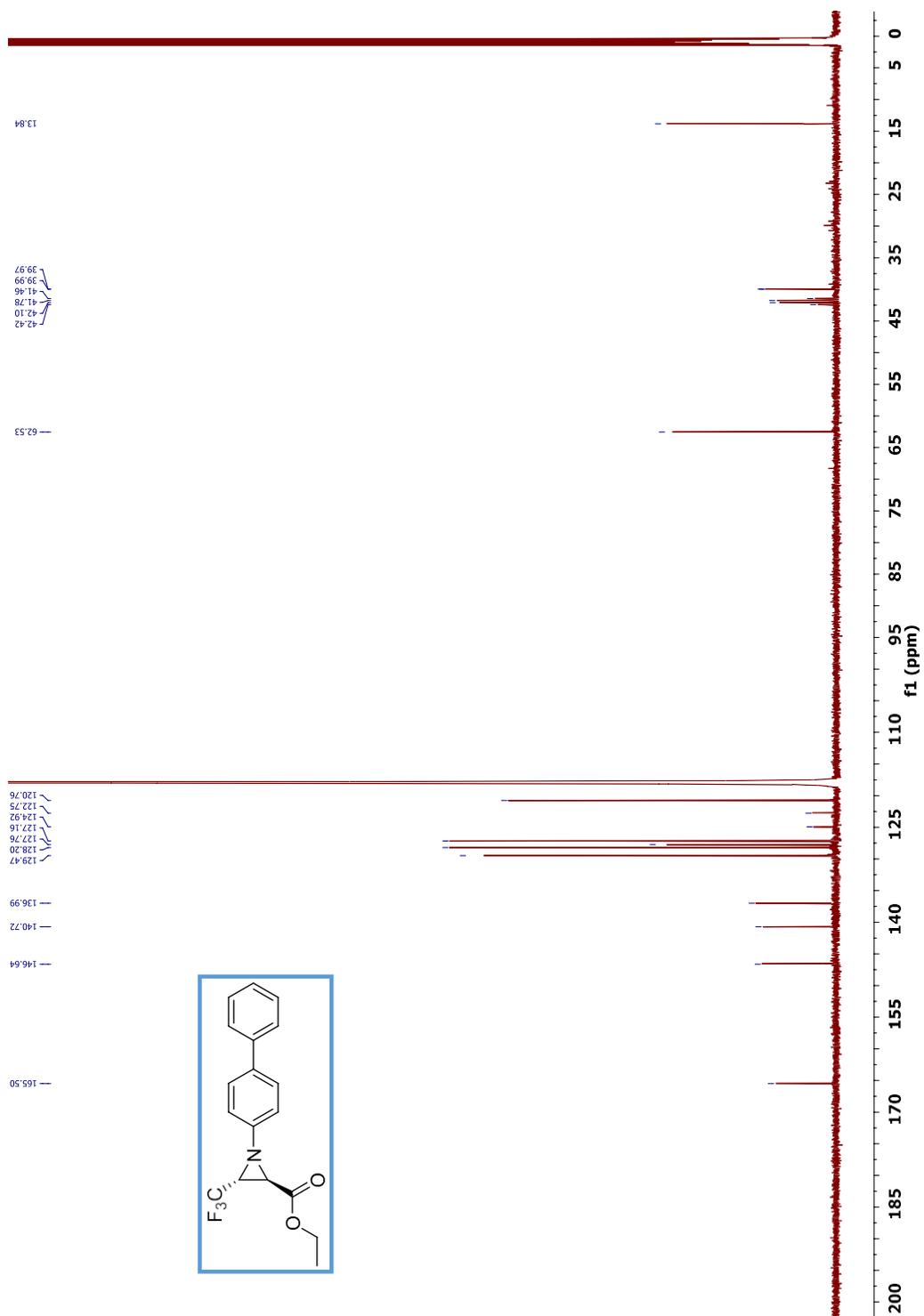


Figure S41. ^1H NMR (500 MHz, CD_3CN) of compound *cis*-4C.

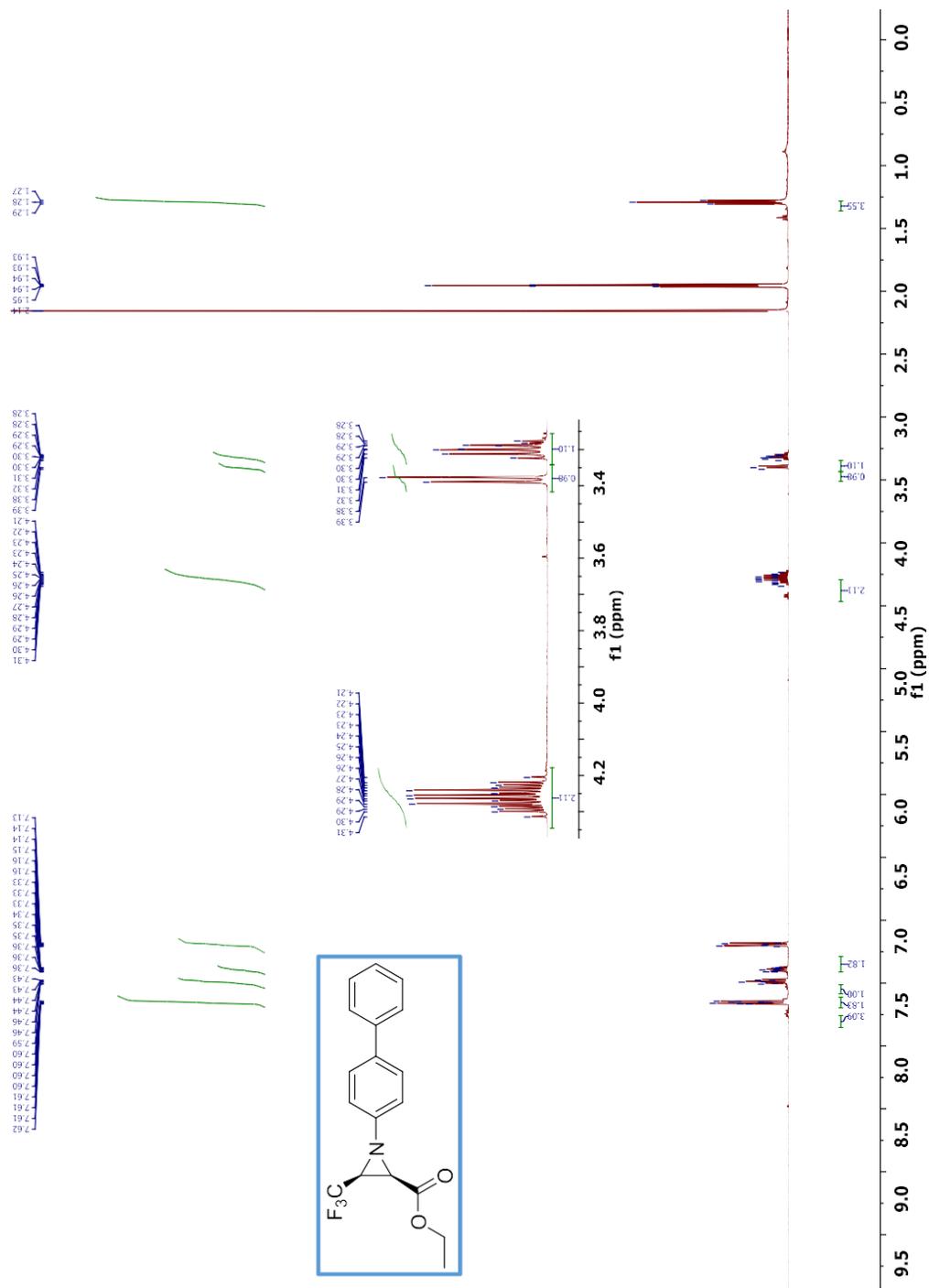


Figure S42. ^{13}C NMR (126 MHz, CD_3CN) of compound *cis*-4C.

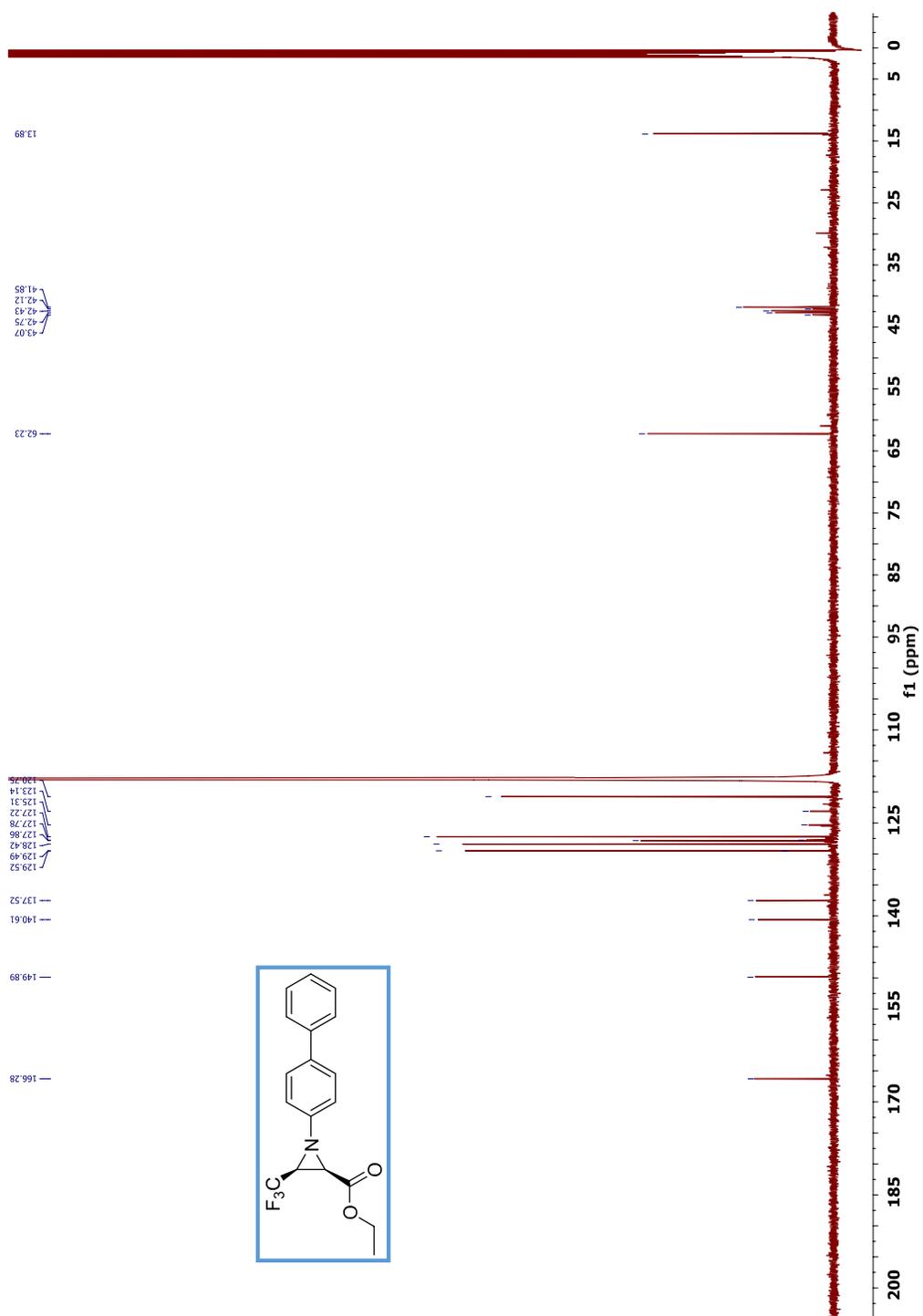


Figure S43. ^1H NMR (500 MHz, CD_3CN) of compound *trans*-4D.

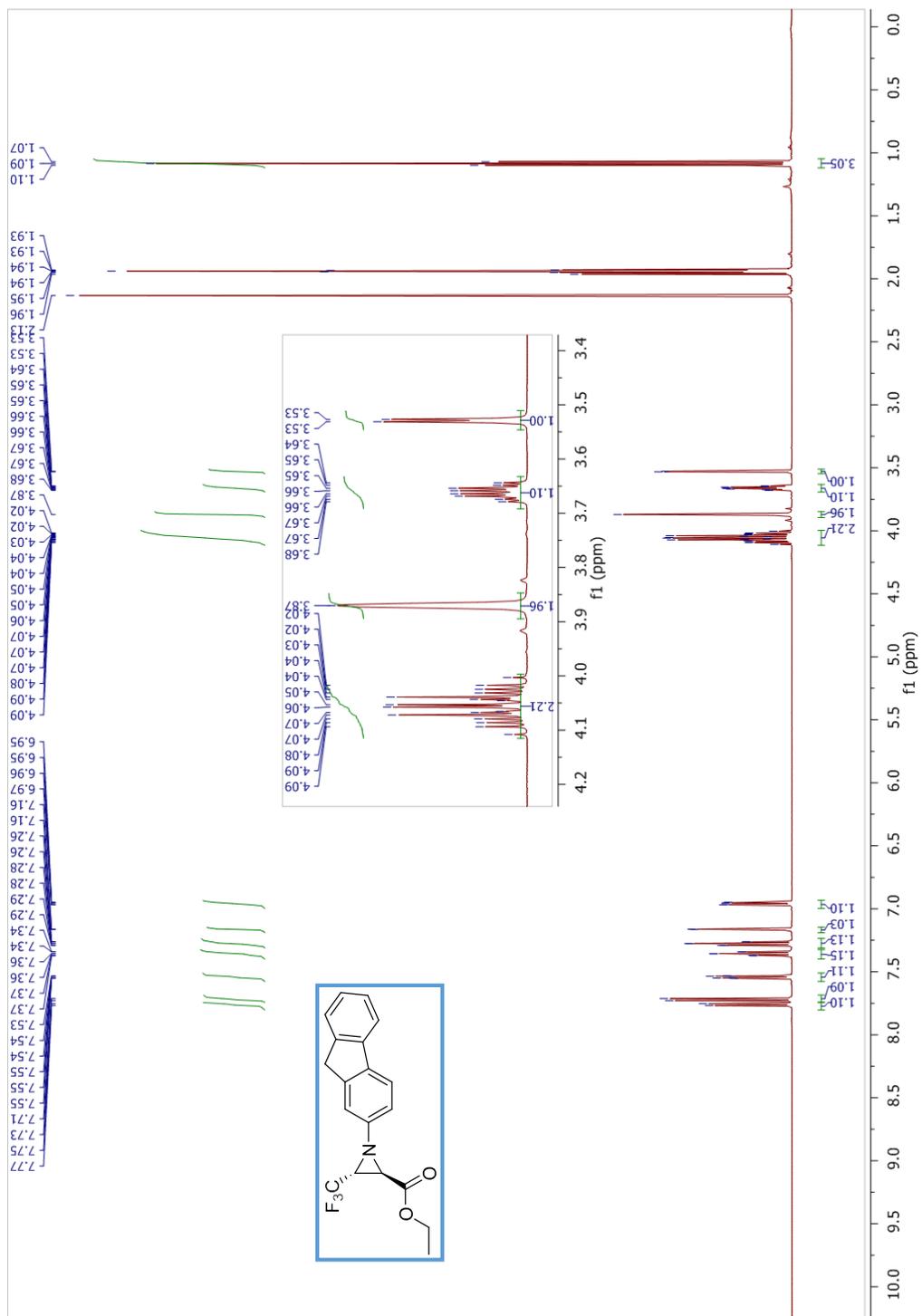


Figure S44. ^{13}C NMR (126 MHz, CD_3CN) of compound *trans*-4D.

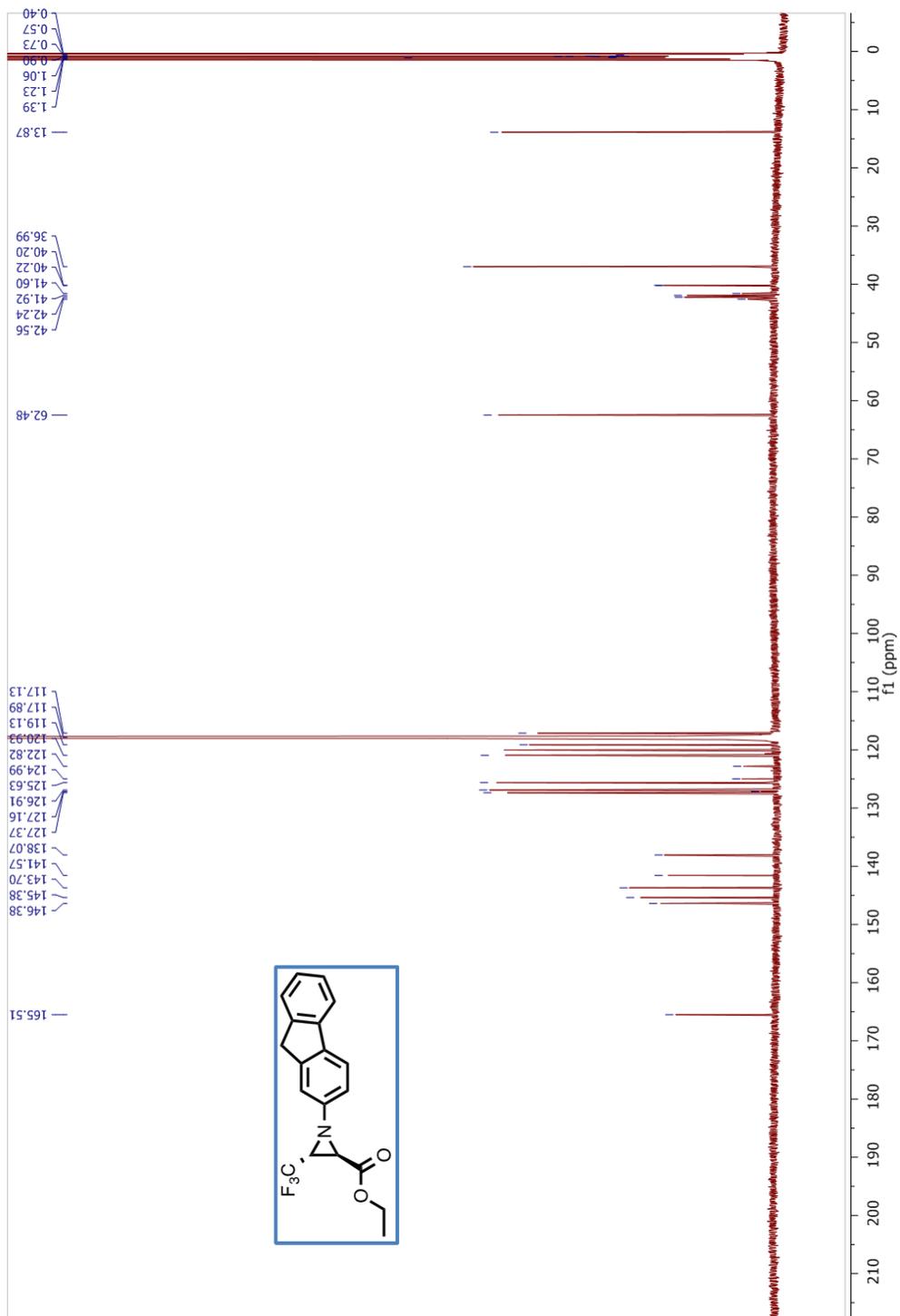


Figure S45. ^1H NMR (500 MHz, CD_3CN) of compound *cis*-4D.

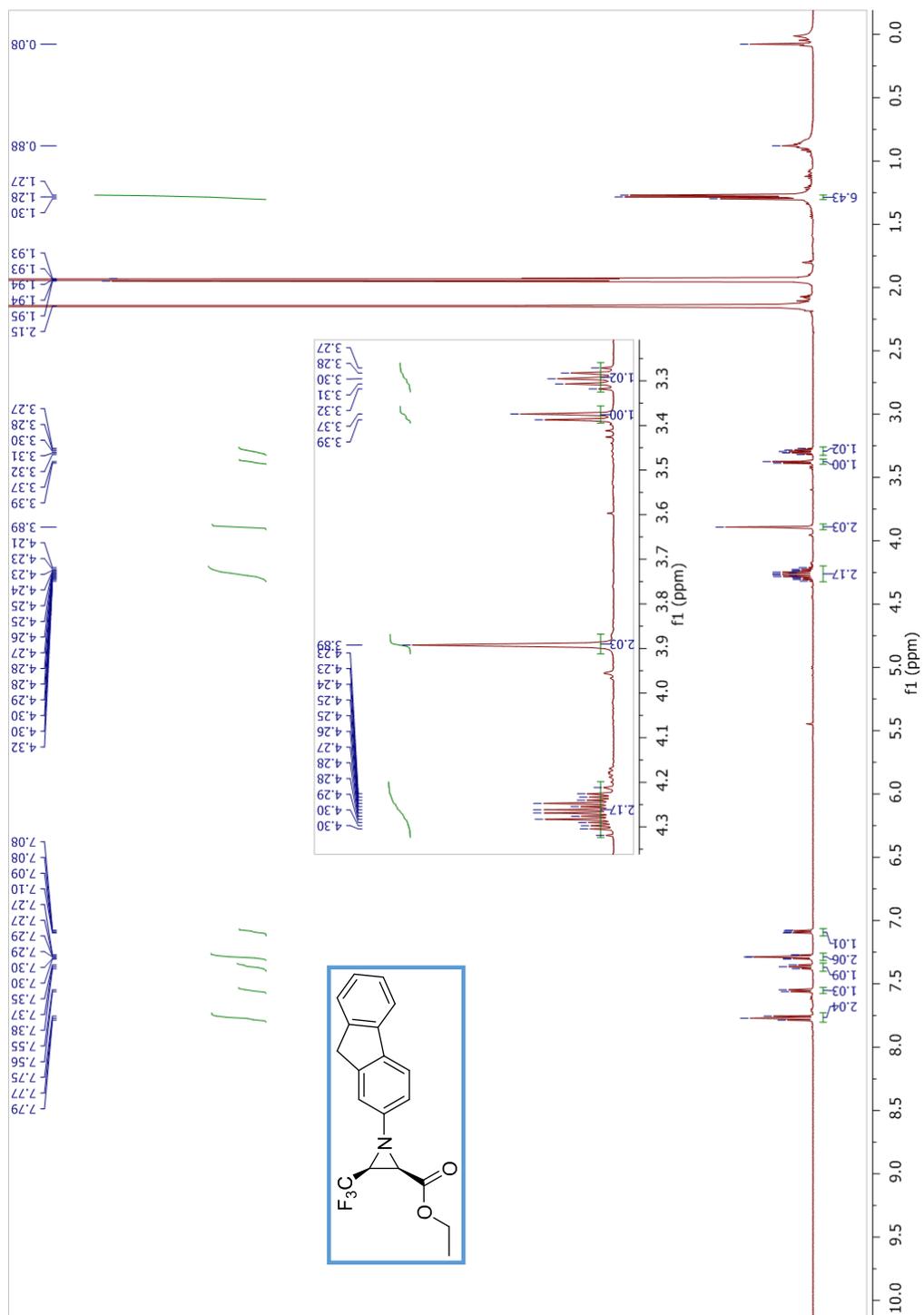


Figure S46. ^{13}C NMR (126 MHz, CD_3CN) of compound *cis*-4D.

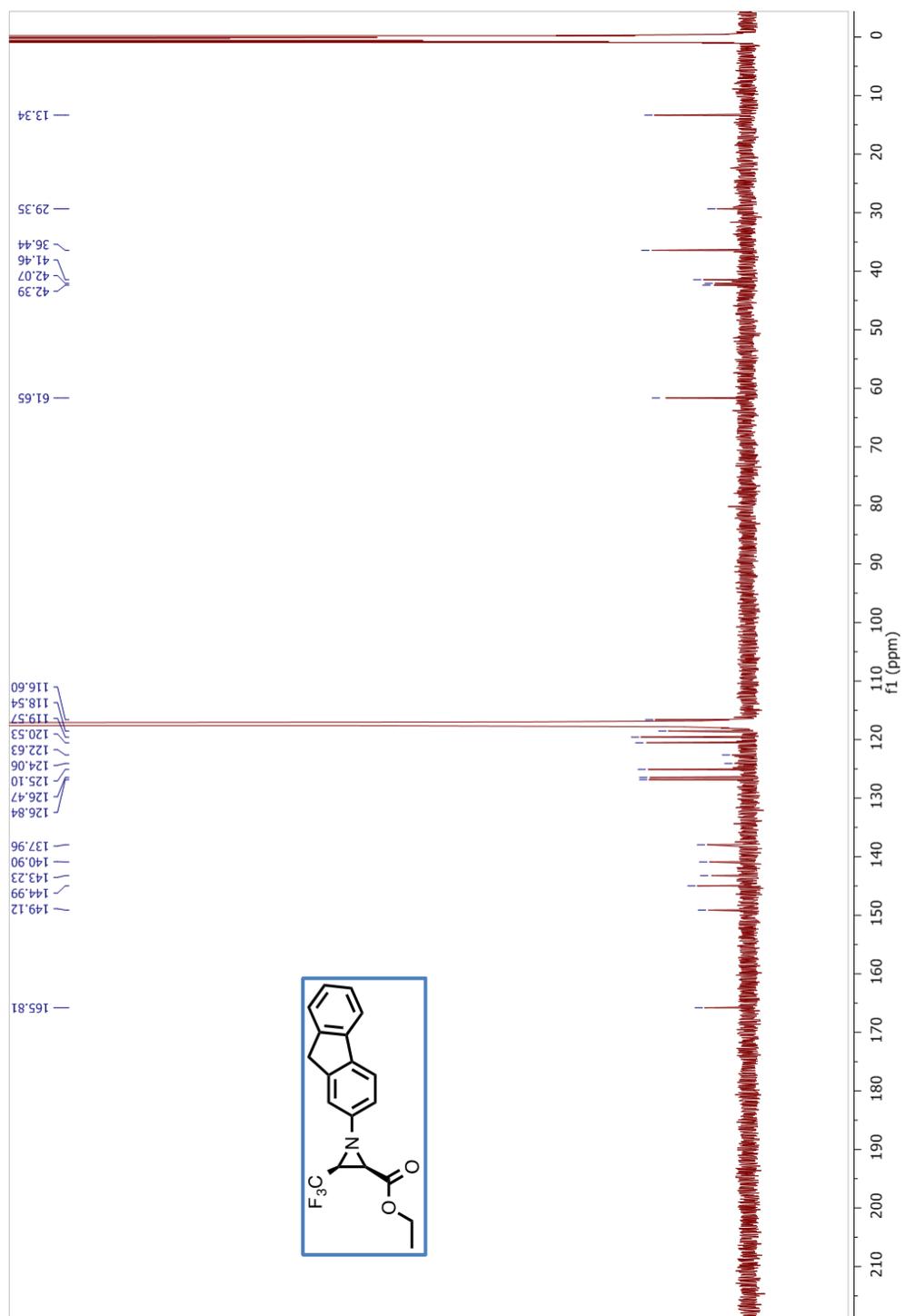


Figure S47. ^1H NMR (500 MHz, CD_3CN) of compound *trans*-4E.

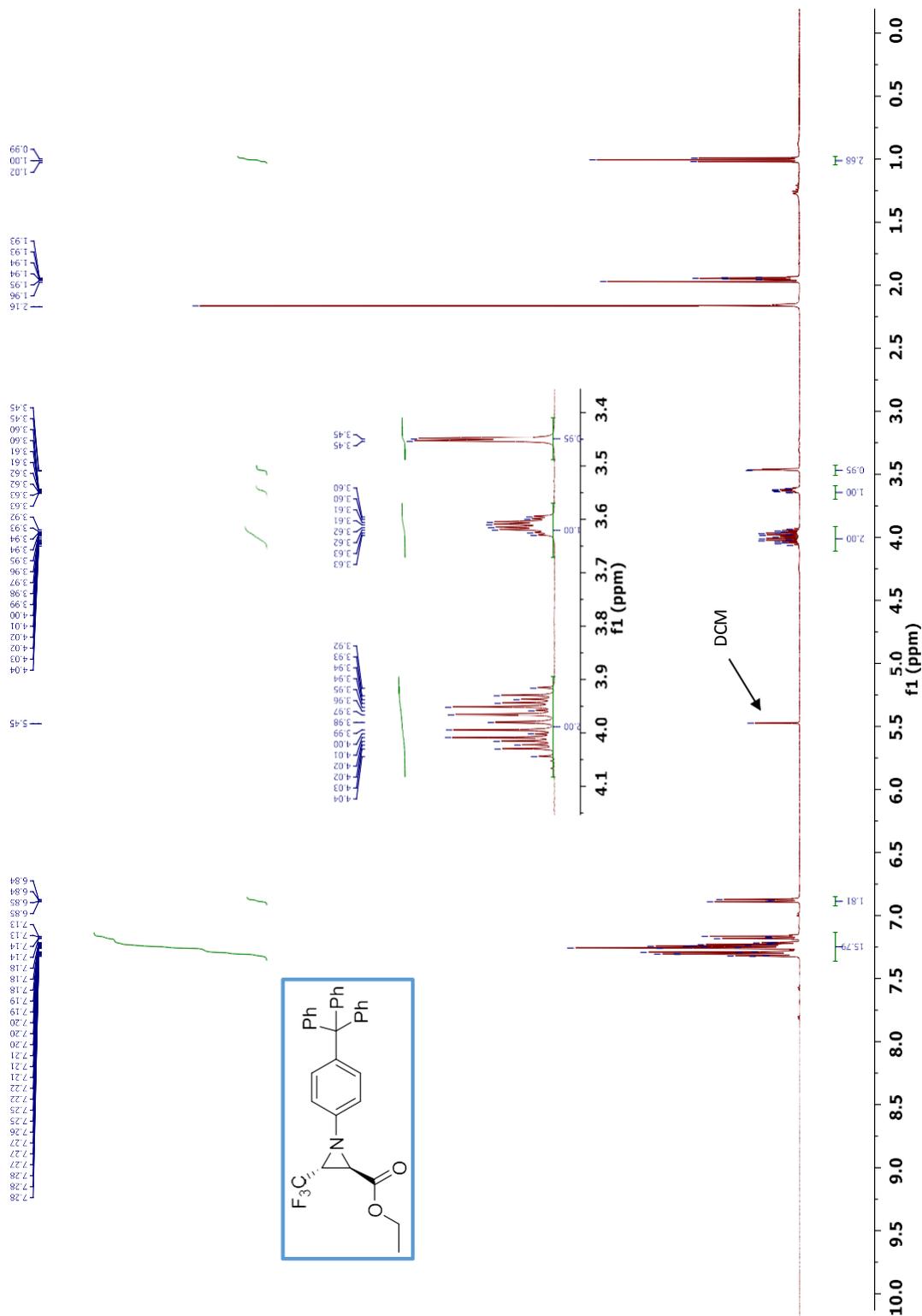


Figure S48. ^{13}C NMR (126 MHz, CD_3CN) of compound *trans*-4E.

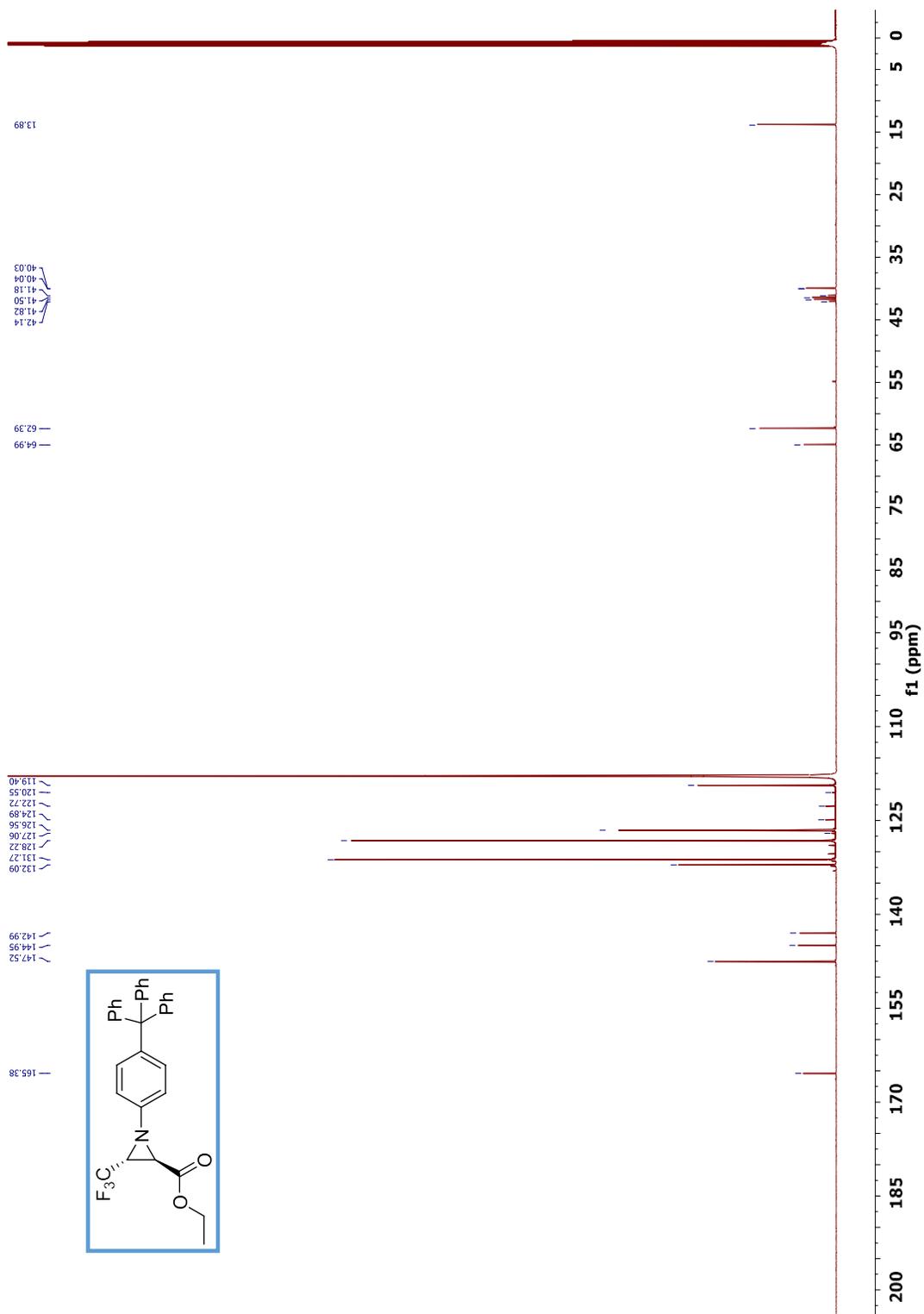


Figure S49. UV-Vis Spectrum of compound *trans*-**3A** in dichloromethane.

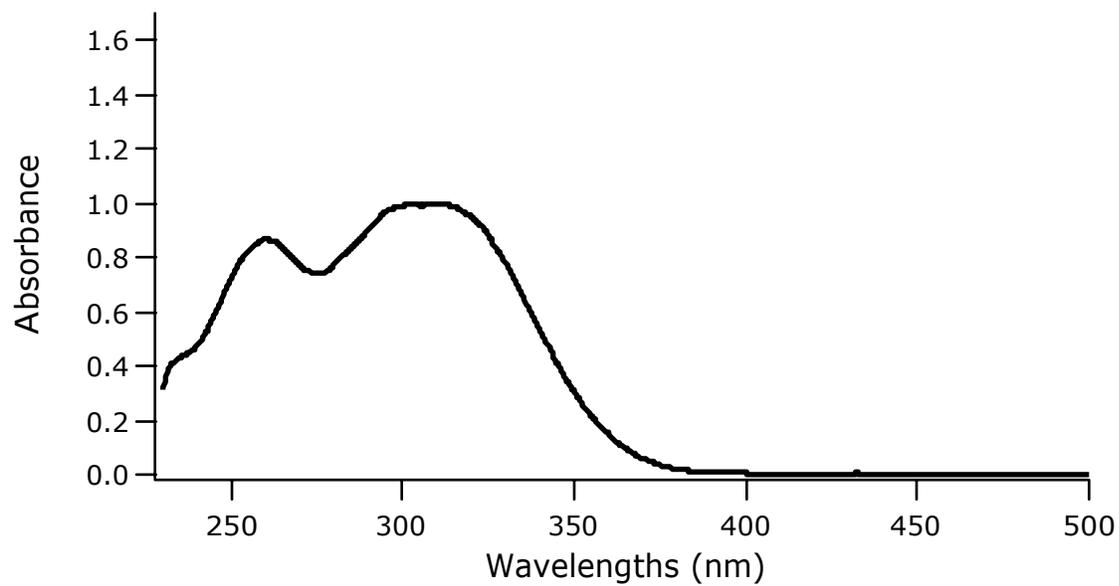


Figure S50. UV-Vis Spectrum of compound *cis*-**3A** in dichloromethane.

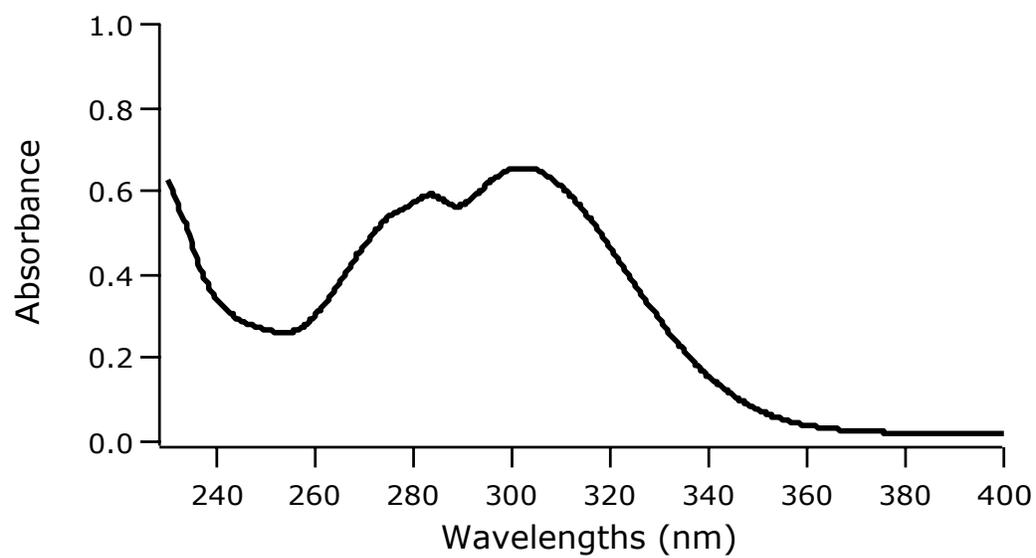


Figure S51. UV-Vis Spectrum of compound *trans*-**3B** in dichloromethane.

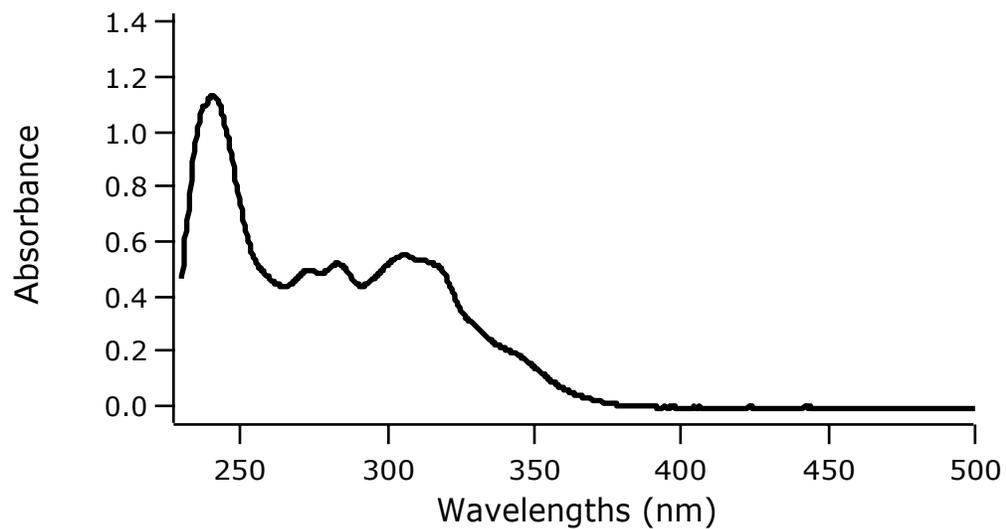


Figure S52. UV-Vis Spectrum of compound *cis*-**3B** in dichloromethane.

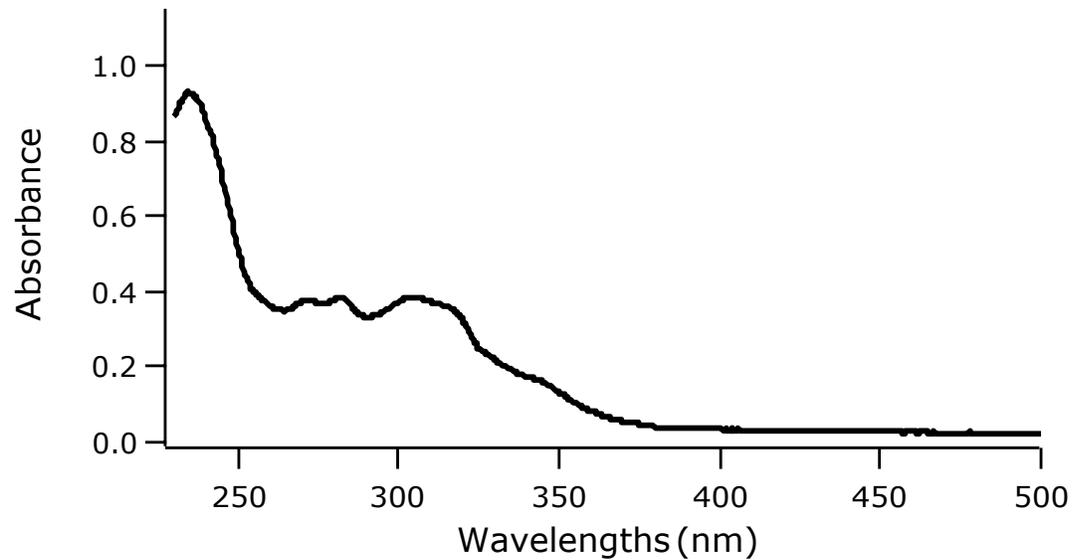


Figure S53. UV-Vis Spectrum of compound *trans*-**3C** in dichloromethane.

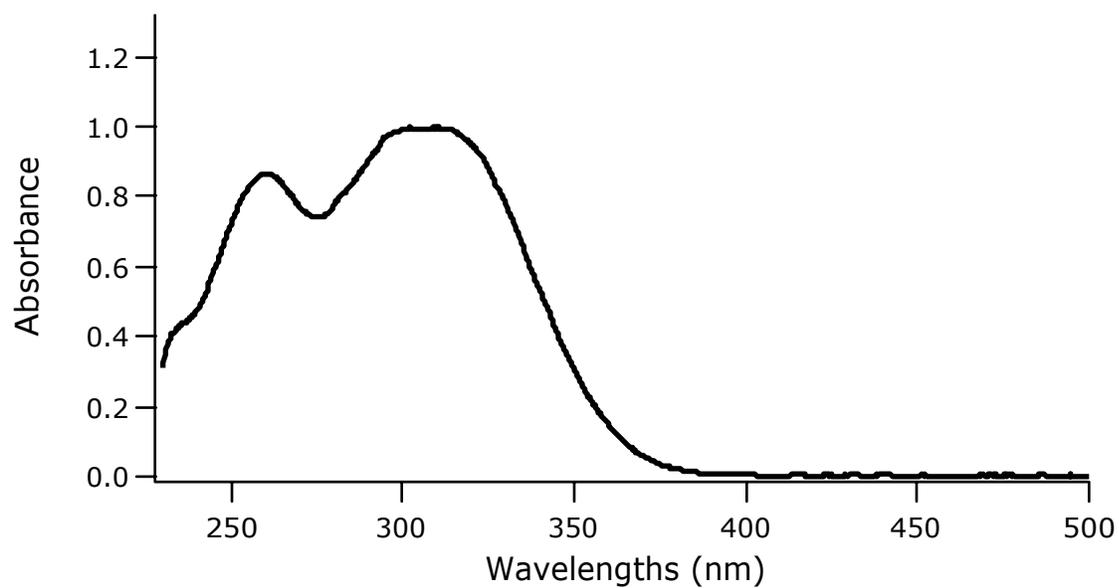


Figure S54. UV-Vis Spectrum of compound *cis*-**3C** in dichloromethane.

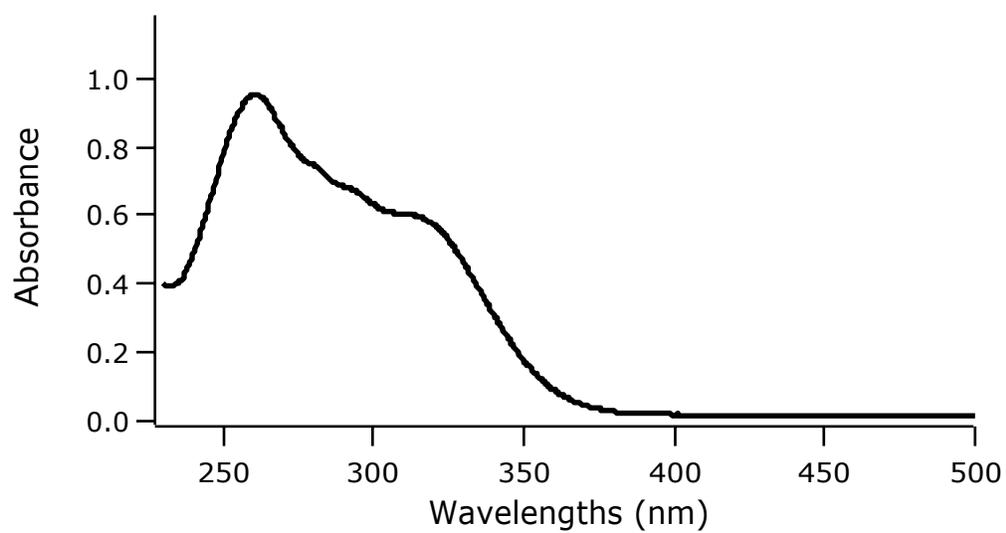


Figure S55. UV-Vis Spectrum of compound *trans*-**3D** in dichloromethane.

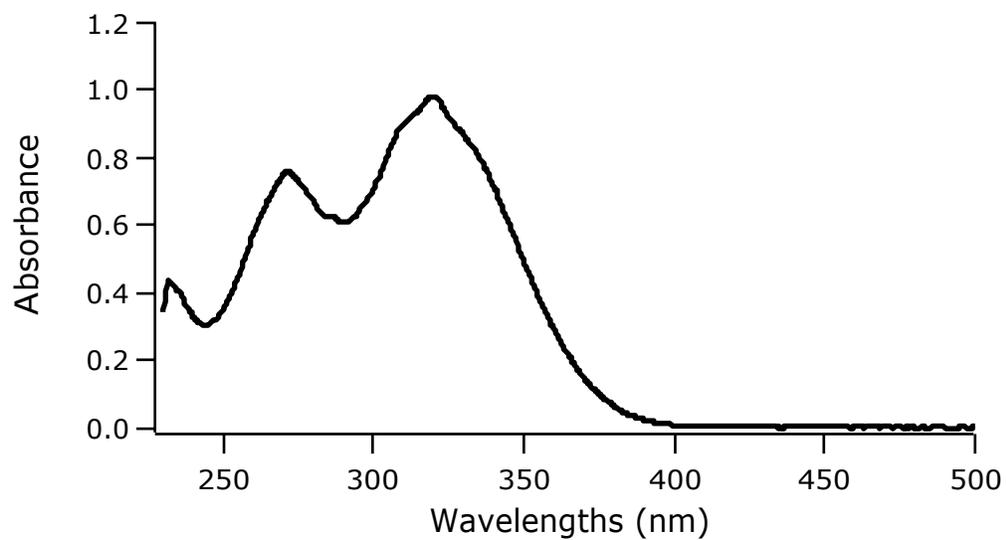


Figure S56. UV-Vis Spectrum of compound *cis*-**3D** in dichloromethane.

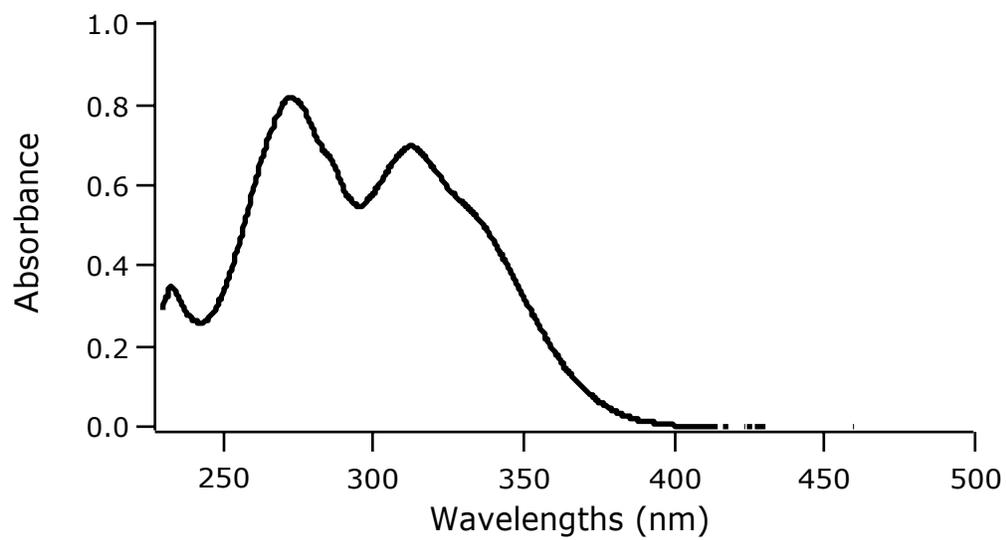


Figure S57. UV-Vis Spectrum of compound *trans*-**3E** in dichloromethane.

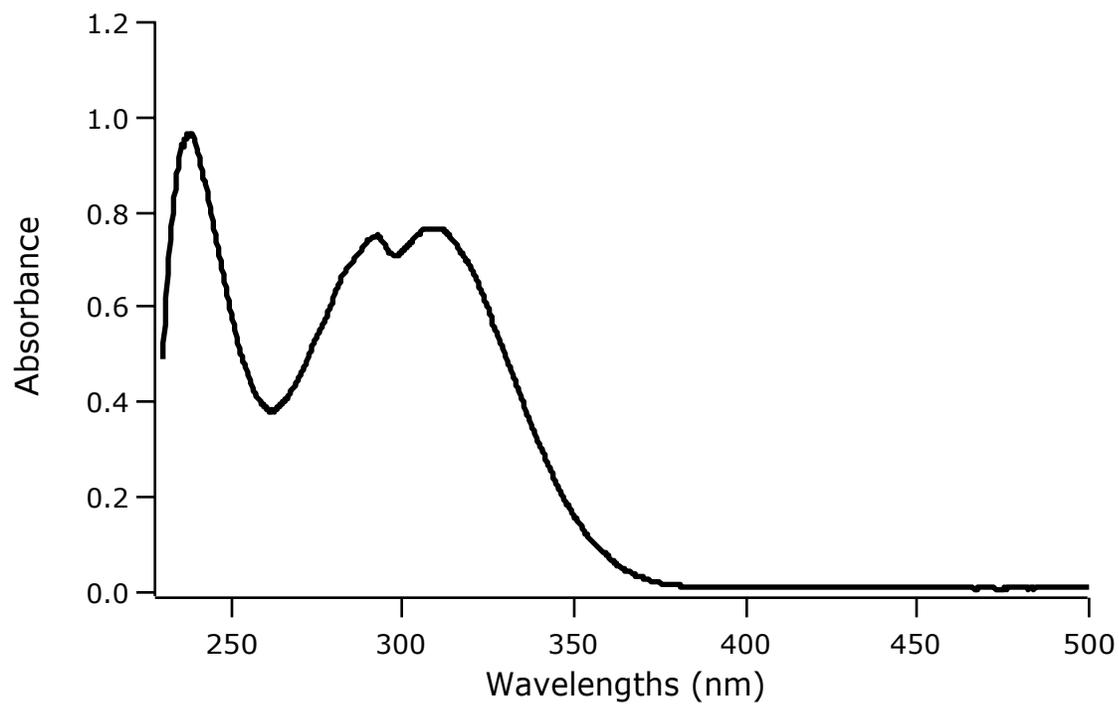


Figure S58. UV-Vis Spectrum of compound *cis*-**3E** in dichloromethane.

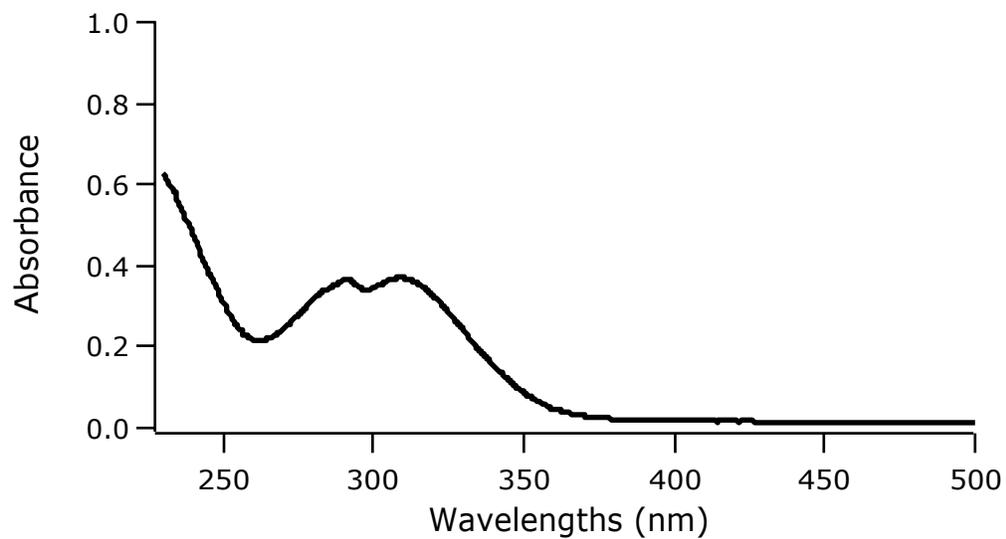


Figure S59. UV-Vis Spectrum of compound *trans*-**4A** in dichloromethane.

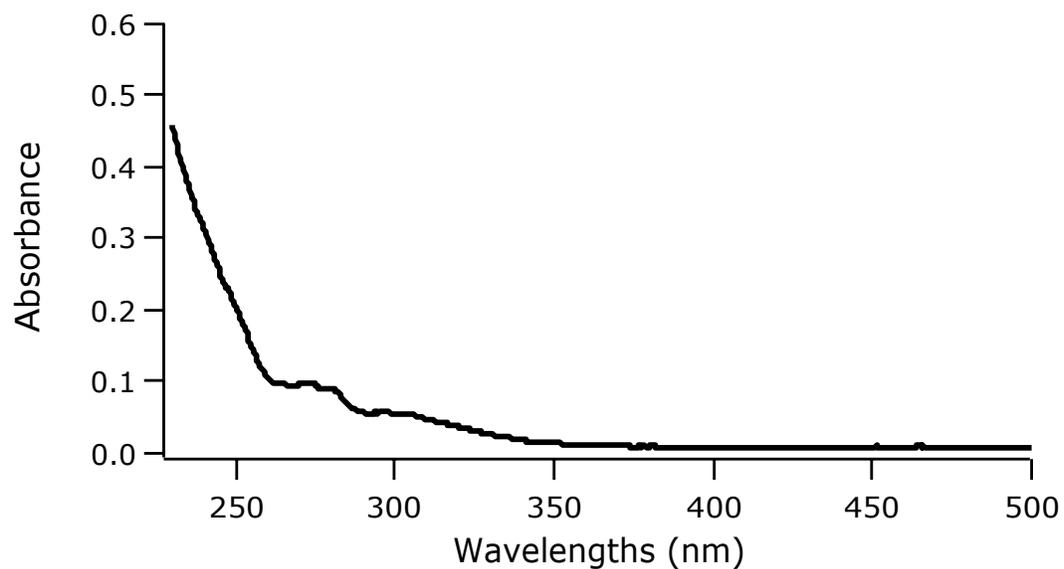


Figure S60. UV-Vis Spectrum of compound *cis*-**4A** in dichloromethane.

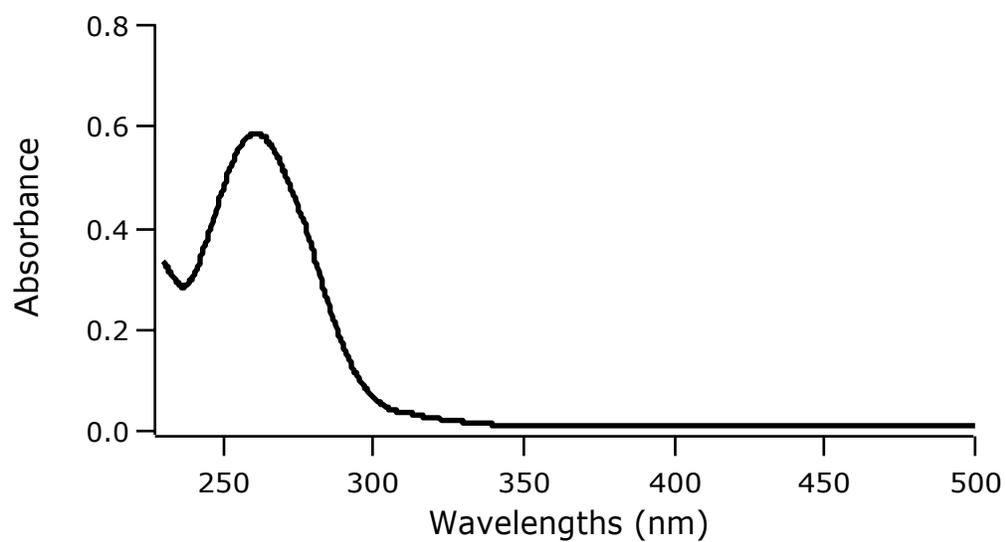


Figure S61. UV-Vis Spectrum of compound *trans*-**4B** in dichloromethane.

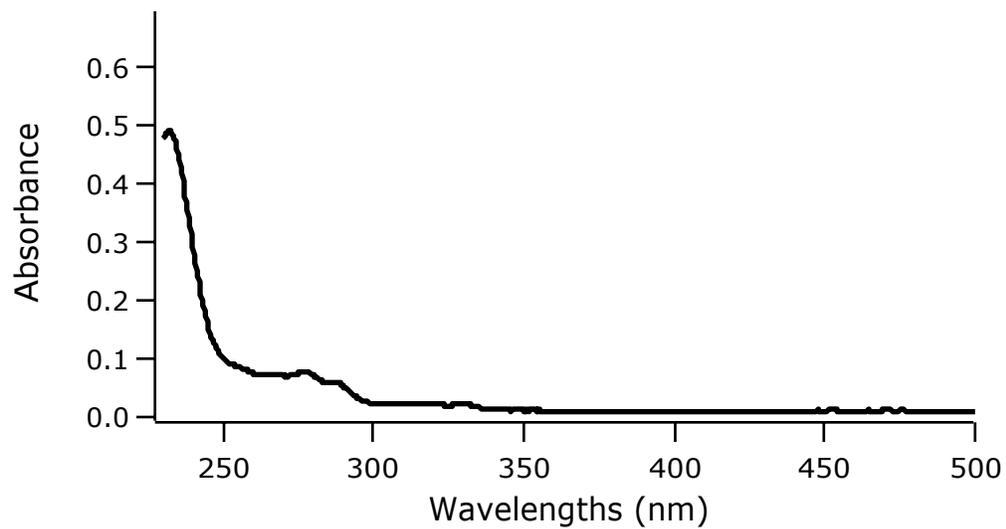


Figure S62. UV-Vis Spectrum of compound *cis*-**4B** in dichloromethane.

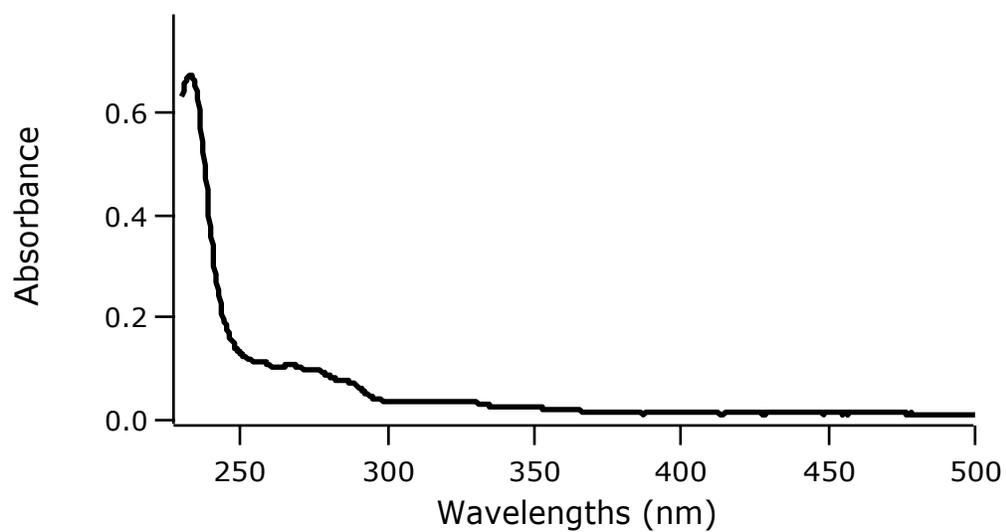


Figure S63. UV-Vis Spectrum of compound *trans*-4C in dichloromethane.

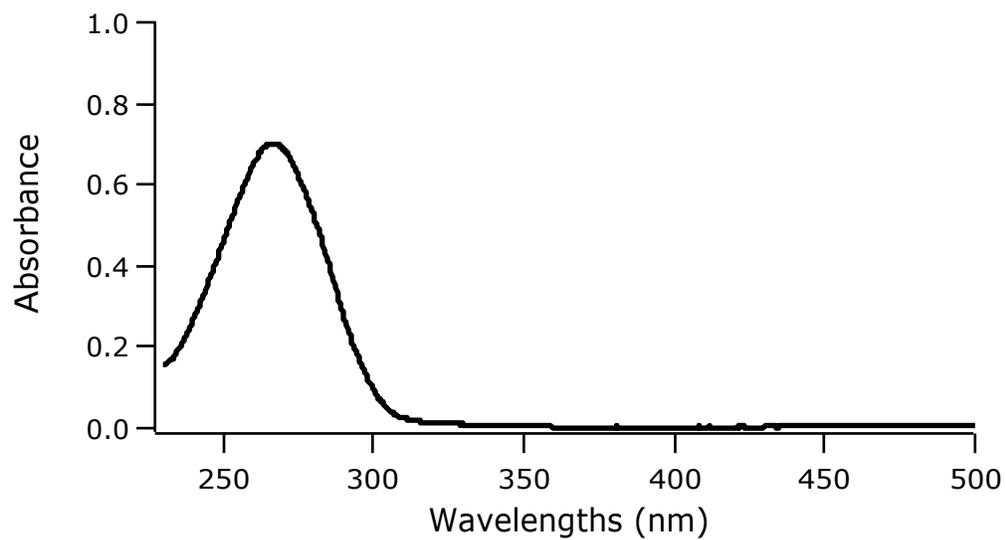


Figure S64. UV-Vis Spectrum of compound *cis*-4C in dichloromethane.

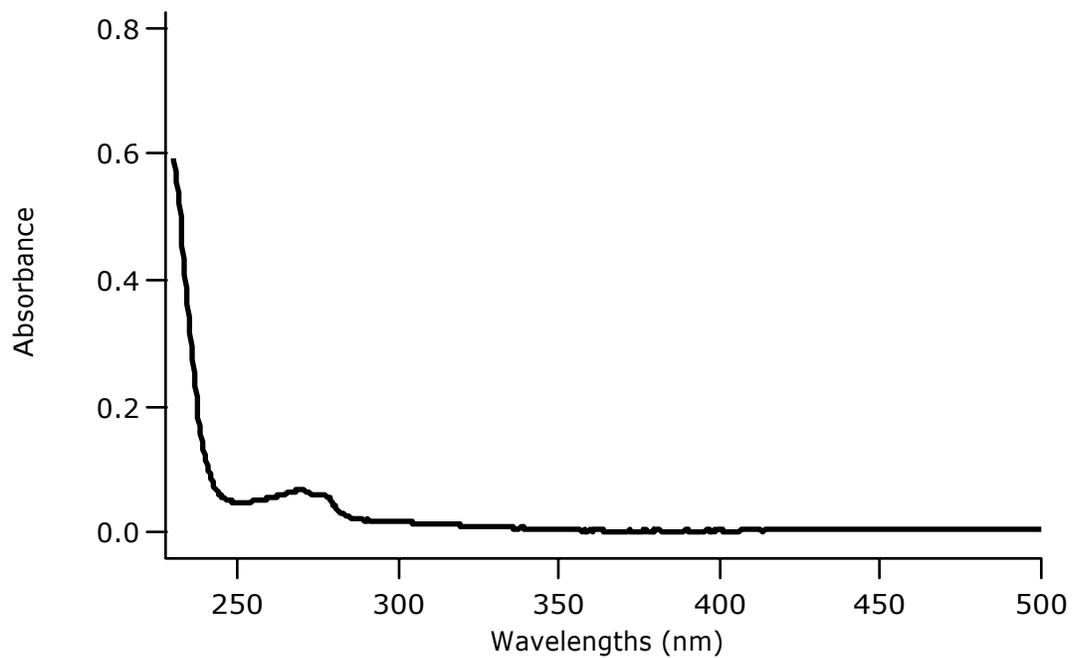


Figure S65. UV-Vis Spectrum of compound *trans*-**4D** in dichloromethane.

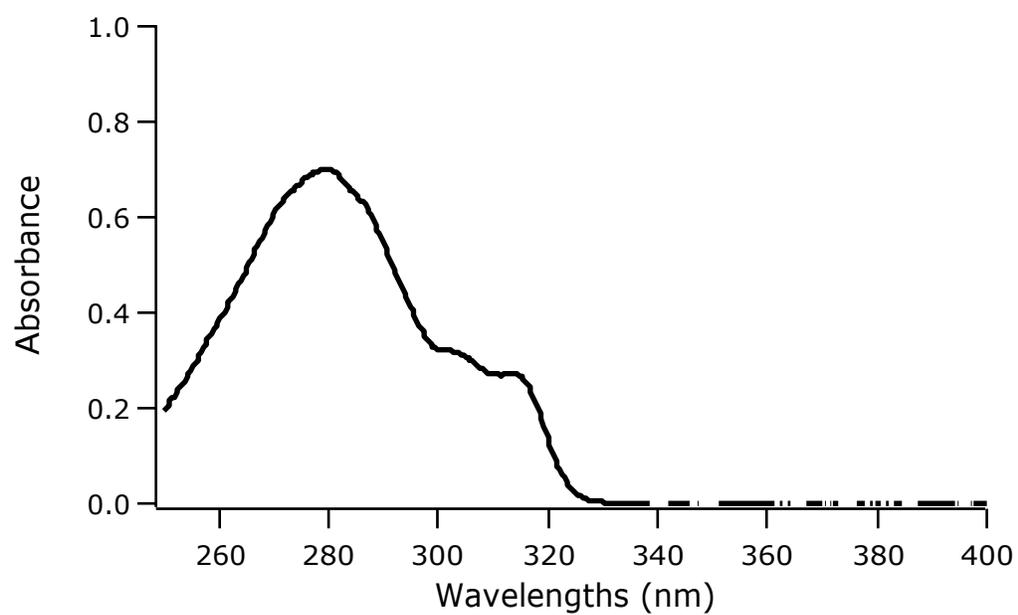


Figure S66. UV-Vis Spectrum of compound *cis*-**4D** in dichloromethane.

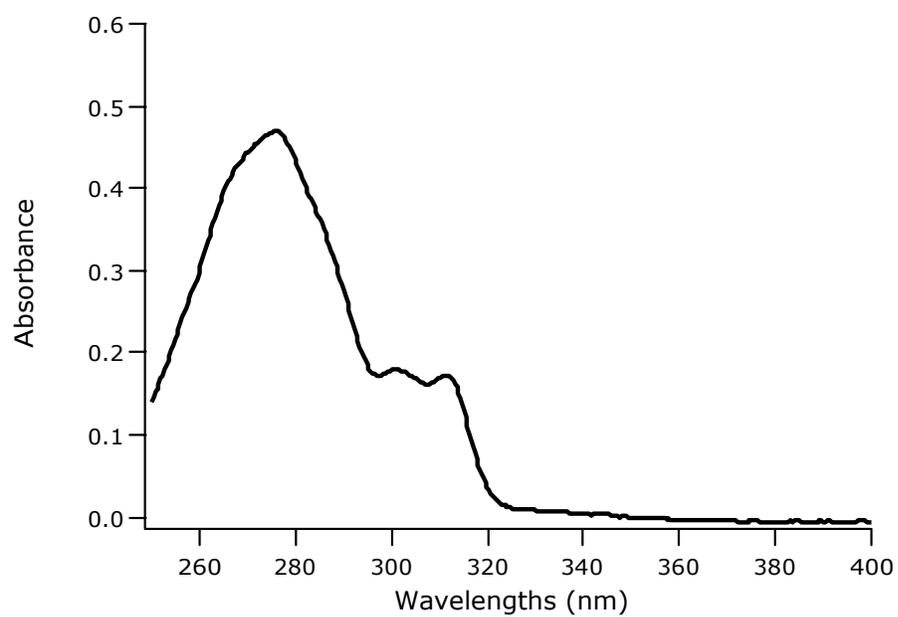


Figure S67. UV-Vis Spectrum of compound *trans*-**4E** in dichloromethane.

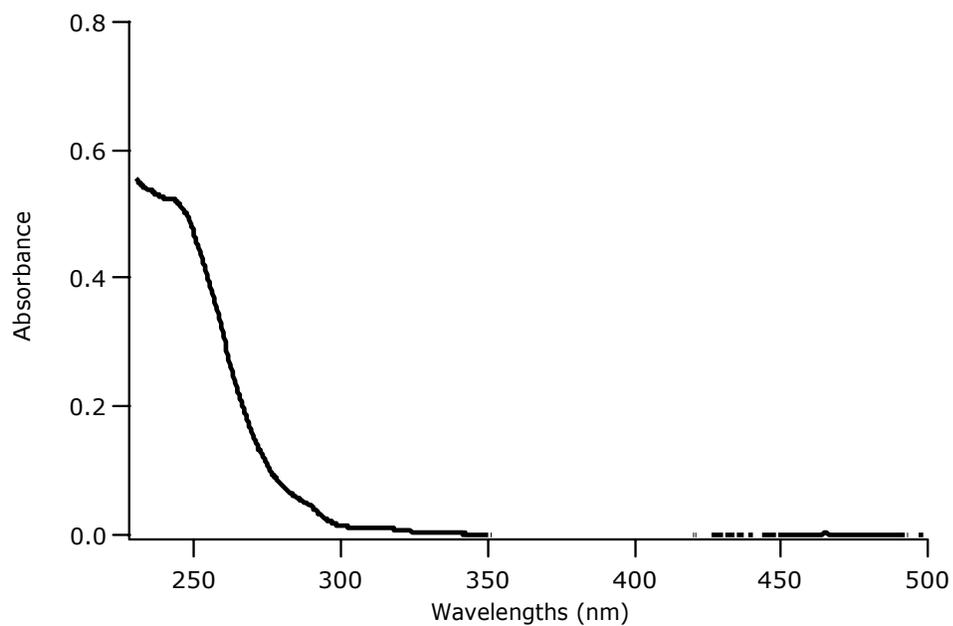
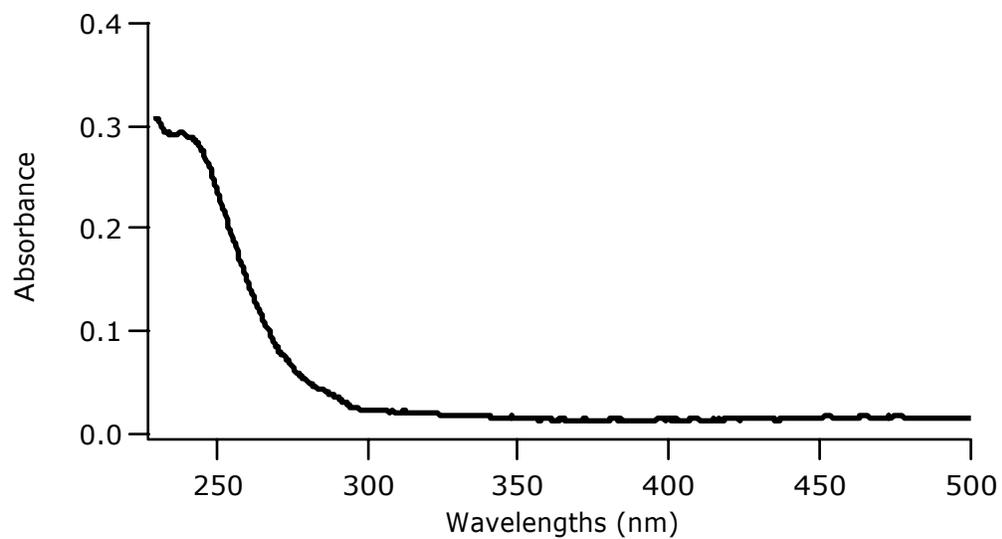


Figure S68. UV-Vis Spectrum of compound *cis*-**4E** in dichloromethane.



F. Computational Data

Computational analysis was performed using Spartan'16V1.1.0 on a PC computer. We calculated lowest energy conformer by Molecular Mechanics and subsequently submitted a B3LYP/6-31G* for the equilibrium geometry using the most stable conformation. The hartrees calculated from the output file was converted to kcal/mol to find the difference in ground state energies between the *trans*- and *cis*-aziridines. The calculations are shown below in the Table.

		<u>kcal/mol</u>	<u>Difference in Energies</u>
trans 4a	-969.205537 hartrees	-608185.7866	
cis 4a	-969.201410 hartrees	-608183.1969	-2.589732
trans 4b	-1122.849563 hartrees	-704598.8892	
cis 4b	-1122.839418 hartrees	-704592.5231	-6.366085
trans 4c	-1200.262929 hartrees	-753176.5201	
cis 4c	-1200.259202 hartrees	-753174.1814	-2.3387283
trans 4d	-1238.379969 hartrees	-777095.3289	
cis 4d	-1238.370067 hartrees	-777089.1153	-6.21360013

References:

- 1) Chung, T.S.; Lopez, S.A.; Houk, K.N.; Garcia-Garibay, M.A *Org. Lett.* **2015**, *17*,4568–4571.