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$AuCl_3$ catalyzed [3+2+1] cycloaddition: First use of aldehyde as a carbon monoxide-like one carbon synthon for triple C-C coupling

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1. Materials and Methods

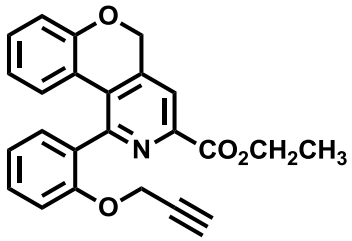
Unless otherwise mentioned, all reagents were purchased from commercial suppliers and used without further purification. Commercially supplied ethyl acetate and petroleum ether were distilled before use. CH_2Cl_2 was dried by distillation over P_2O_5. Toluene was dried over sodium and distilled out prior to use. Petroleum ether used in our experiments was in the boiling range of 60°-80° C. Column chromatography was performed on silica gel (100-200 mesh). Analytical thin layer chromatography was performed on 0.25 mm extra hard silica gel plates with UV254 fluorescent indicator. Melting points are reported uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature using 300 MHz spectrometer (300 MHz for ^{1}H and 75 MHz for ^{13}C). Chemical shift is reported in ppm from internal reference tetramethylsilane and coupling constant in Hz. Proton multiplicities are represented as s (singlet), d (doublet), dd (double doublet), ABq (AB quartet), t (triplet), q (quartet), dq (double quartet), m (multiplet), and brs (broad singlet). Infrared spectra of the compounds were recorded on FT-IR spectrometer in the form of KBr pellets (solid sample) or in thin film on NaCl window (liquid sample). HR-MS data were acquired by electron spray ionization techniqueon a Q-tof-micro quadriple mass spectrophotometer. Single crystal X-ray diffraction study of the crystalline heterocyclic compound was done in X-ray diffractometer.

2. General Procedure for Synthesis of Benzopyrano[4,3-*c*]pyridines and Benzopyrano[4,3-*b*]pyrroles

The *O*-propargylsalicylaldehyde derivatives (2 mmol) was dissolved in dry toluene (10 mL) and was refluxed with glycine esters (1 mmol) using gold (III) chloride (10 mg, 3 mol%) for 9-12 h. The progress of the reaction was monitored by TLC. After completion of the reaction, toluene was removed in a rotor evaporator at room temperature under reduced pressure. The post reaction mixture was extracted with ethyl acetate (5 mL x 2), washed well with saturated sodium bicarbonate solution (5 mL x 3) followed by brine solution (5 mL x 3). The organic extract was dried over anhydrous sodium sulfate, filtered and concentrated in a rotor evaporator at room temperature under reduced pressure. The pure product was isolated by purification on silica gel column (60-120 mesh) with ethyl acetate – petroleum ether (60-80) mixture as an eluent. Thus, the reaction with ethyl-2-((2-(prop-2-yn-1-yloxy)benzylidene)amino)acetate (**3a**) and *O*-propargylsalicylaldehyde (**1a**) afforded ethyl-1-(2-(prop-2-yn-1-yloxy)phenyl)-5*H*-chromeno[4,3-*c*]pyridine-3-carboxylate (**4a**) after processing in an isolated yield of 55 % (212 mg, 0.55 mmol) and ethyl-1-(2-(prop-2-yn-1-yloxy)phenyl)-5*H*-chromeno[4,3-*b*]pyrrole-3-carboxylate (**5a**) after processing in an isolated yield of 32 % (78 mg, 0.32 mmol).. The compound **4a-o**, **4t** and **5a** were characterized by ^{1}H and ^{13}C NMR (NDC & DEPT), FT-IR, and HR-MS analysis. The structures of the compounds in this series were also confirmed by single crystal X-ray diffraction analyses.

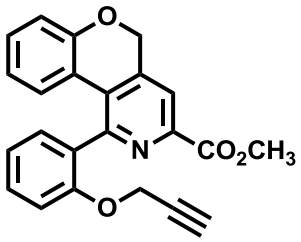
3. Characterization Data of Benzopyrano[4,3-*c*]pyridines and Benzopyrano[4,3-b]pyrrole (4a-o,4t and 5a)

3.1. Ethyl-1-(2-(prop-2-yn-1-yloxy)phenyl)-5H-chromeno[4,3-c]pyridine-3-carboxylate (4a)



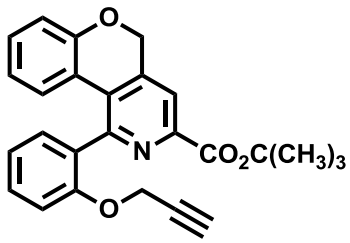
Yield: 55% (212 mg, 0.55 mmol).
Characteristic: Yellow liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.35 (3H, t, *J* = 7.2 Hz), 2.23 (1H, t, *J* = 2.4 Hz), 4.05-4.15 (2H, m), 4.34-4.42 (2H, m), 5.01 (2H, dd, *J* = 13.8, 49.2 Hz), 6.55-6.61 (1H, m), 6.79 (1H, dd, *J* = 1.2, 7.8 Hz), 6.94 (2H, dd, *J* = 8.7, 17.1 Hz), 7.07-7.16 (2H, m), 7.32-7.35 (1H, m), 7.49 (1H, dd, *J* = 1.5, 7.5 Hz), 7.84 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.3, 56.2, 61.8, 67.9, 75.1, 78.3, 113.3, 117.5, 119.6, 121.7, 121.9, 122.5, 126.4, 128.9, 130.2, 130.3, 131.2, 143.1, 146.0, 154.9, 156.3, 165.0.
FT-IR (neat, cm^{-1}): 930, 1233, 1461, 1732, 2930, 3334.
HR-MS (*m*/*z*) for $C_{24}H_{20}NO_4$ (M+H) Calculated: 386.1392; found: 386.1390.

3.2. Methyl-1-(2-(prop-2-yn-1-yloxy)phenyl)-5H-chromeno[4,3-c]pyridine-3-carboxylate (4b)



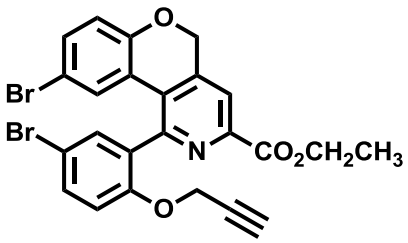
Yield: 56 % (208 mg, 0.56 mmol)
Characteristic: Yellow liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.23 (1H, d, *J* = 2.1 Hz), 3.92 (3H, s), 4.12 (2H, ABq, *J* = 15.9, 2.1 Hz), 5.02 (2H, dd, *J* = 13.8, 50.4 Hz), 6.56-6.61 (1H, m), 6.78 (1H, d, *J* = 1.5, 7.5 Hz), 6.92-6.96 (2H, m), 7.10 (2H, t, *J* = 7.2 Hz), 7.32-7.38 (1H, m), 7.46-7.49 (1H, m), 7.88 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 52.9, 56.0, 67.9, 75.1, 78.3, 113.1, 117.5, 118.1, 119.8, 121.7, 122.5, 126.4, 129.1, 130.2, 130.4, 131.0, 143.1, 154.8, 156.3, 162.3.
FT-IR (neat, cm^{-1}): 1240, 1435, 1738, 2715, 3249.
HR-MS (*m*/*z*) for $C_{23}H_{18}NO_4$ (M+H): Calculated 372.1236, found 372.1235.

3.3.tert-Butyl-1-(2-(prop-2-yn-1-yloxy)phenyl)-5H-chromeno[4,3-c]pyridine-3-carboxylate (4c)



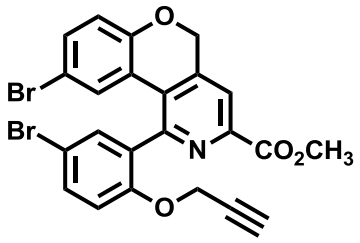
Yield: 54 % (223 mg, 0.54 mmol).
Characteristic: Dense yellow liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.47 (9H, s), 2.23 (1H, t, *J* = 2.4 Hz), 4.05-4.16 (2H, m), 4.99 (2H, dd, *J* = 13.8, 46.5 Hz), 6.57-6.60 (1H, m), 6.81 (1H, dd, *J* = 1.5, 8.1 Hz), 6.93 (2H, d, *J* = 8.1 Hz), 7.06-7.11 (2H, m), 7.31-7.36 (1H, m), 7.50 (1H, dd, *J* = 1.5, 7.5 Hz), 7.72 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 28.1, 56.4, 66.2, 68.0, 70.2, 75.0, 78.4, 82.0, 113.5, 117.4, 119.1, 121.6, 122.0, 122.4, 126.4, 130.0, 130.1, 131.2, 142.9, 147.0, 154.9, 156.2, 163.6.
FT-IR (neat, cm^{-1}): 1153, 1407, 1457, 1721, 2927, 2978, 3399.
HR-MS (*m*/*z*) for $C_{26}H_{24}NO_4$ (M+H): Calculated 414.1705, found 414.1704.

3.4. Ethyl-9-bromo-1-(5-bromo-2-(prop-2-yn-1-yloxy)phenyl)-5H-chromeno[4,3-c]pyridine-3-carboxylate (4d)



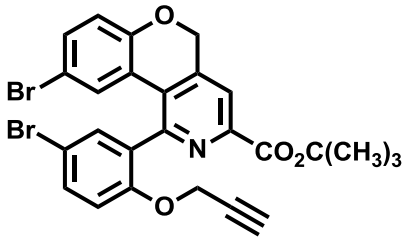
Yield: 50 % (272 mg, 0.50 mmol).
Characteristic**:** Brownish yellow liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.43 (3H, t, *J* = 7.2 Hz), 2.36 (1H, t, *J* = 2.1 Hz), 4.21 (2H, ABq, *J* = 2.4, 16.2 Hz), 4.43-4.52 (2H, m), 5.08 (2H, dd, *J* = 13.8, 61.2 Hz), 6.91 (2H, d, *J* = 8.7 Hz), 6.97 (1H, d, *J* = 2.4 Hz), 7.28 (1H, dd, *J* = 2.1, 8.4 Hz), 7.57 (1H, dd, *J* = 2.7, 9.0 Hz), 7.70 (1H, d, *J* = 2.4 Hz), 7.94 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.3, 55.9, 62.1, 67.9, 75.9, 76.6, 114.3, 114.5, 114.7, 119.3, 120.0, 123.3, 127.8, 128.9, 131.2, 133.1, 133.2, 133.8, 143.0, 146.7, 151.3, 153.4, 155.2, 164.7.
FT-IR (neat, cm^{-1}): 617, 835, 940, 1100, 1320, 1765.
HR-MS (*m*/*z*) for $C_{24}H_{17}Br_2NO_4$ (M^+): Calculated 542.9680:544.9659:546.9638 (1:2:1), found 542.9682:544.9656:546.9640 (1:2:1).

3.5. Methyl-9-bromo-1-(5-bromo-2-(prop-2-yn-1-yloxy)phenyl)-5H-chromeno[4,3-c]pyridine-3-carboxylate (4e)



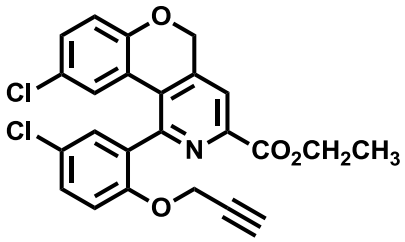
Yield: 52 % (275 mg, 0.52 mmol).
Characteristic: pale yellow solid.
Melting point: 140-142 ^{o}C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.36 (1H, t, *J* = 2.4 Hz), 4.00 (3H, s), 4.22 (2H, ABq, *J* = 2.4, 15.9 Hz), 5.08 (2H, dd, *J* = 13.8, 61.5 Hz),6.92 (2H, d, *J* = 8.7 Hz), 6.97 (1H, d, *J* = 2.4 Hz), 7.28 (1H, dd, *J* = 3.0, 9.3 Hz), 7.58 (1H, dd, *J* = 2.1, 8.7 Hz), 7.70 (1H, d, *J* = 2.4 Hz), 7.97 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 53.0, 55.9, 67.9, 75.9, 76.5, 114.3, 114.5, 114.8, 119.3, 120.2, 123.2, 128.0, 129.0, 131.2, 133.2, 133.7, 143.1, 146.3, 151.4, 153.4, 155.2, 165.3.
FT-IR (KBr, cm^{-1}): 627, 810, 995, 1225, 1434, 1480, 1590, 1723, 2948.
HR-MS (*m*/*z*) for $C_{23}H_{15}Br_2NO_4$ (M^+): Calculated 528.9524:530.9503:532.9482 (1:2:1), found 528.9527:530.9502:532.9481(1:2:1).

3.6. tert-Butyl-9-bromo-1-(5-bromo-2-(prop-2-yn-1-yloxy)phenyl)-5H-chromeno[4,3-c]pyridine-3-carboxylate (4f)



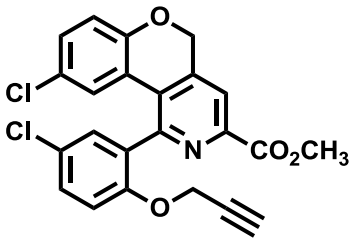
Yield: 54 % (308 mg, 0.54 mmol).
Characteristic: Yellow liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.63 (9H, s), 2.35 (1H, d, *J* = 2.1 Hz), 4.21 (2H, dq, *J* = 2.4, 15.9 Hz), 5.07 (2H, dd, *J* = 13.8, 60.3 Hz), 6.90 (2H, d, *J* = 8.7 Hz), 6.99 (1H, d, *J* = 2.4 Hz), 7.27 (1H, dd, *J* = 2.7, 8.4 Hz), 7.56 (1H, dd, *J* = 2.7, 9.0 Hz), 7.74 (1H, d, *J* = 2.4 Hz), 7.81 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 28.1, 56.0, 68.0, 75.8, 76.6, 82.4, 114.2, 114.5, 114.7, 119.2, 119.6, 123.4, 127.4, 128.9, 131.4, 133.0, 133.8, 142.8, 147.7, 151.3, 153.4, 155.1, 163.2.
FT-IR (neat, cm^{-1}): 815, 1014, 1158, 1241, 1480, 1715, 2975.
HR-MS (*m*/*z*) for $C_{26}H_{21}NO_4Br_2$(M^+): Calculated 570.9993:572.9972:574.9951 (1:2:1), found 570.9994:572.9970:574.9953 (1:2:1).

3.7. Ethyl-9-chloro-1-(5-bromo-2-(prop-2-yn-1-yloxy)phenyl)-5H-chromeno[4,3-c]pyridine-3-carboxylate (4g)



Yield: 56 % (254 mg, 0.56 mmol)**.**
Characteristic: Yellow solid.
Melting point: 116-120 °C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.44 (3H, t, *J* = 7.2 Hz), 2.35 (1H, t, *J* = 2.1 Hz), 4.23 (2H, ABq, *J* = 2.4, 15.0 Hz), 4.43-4.51 (2H, m), 5.08 (2H, dd, *J* = 14.1, 60.9 Hz), 6.84 (1H, d, *J* = 2.4 Hz), 6.96 (2H, dd, *J* = 2.4, 8.7 Hz), 7.14 (1H, dd, *J* = 2.4, 8.7 Hz), 7.43 (1H, dd, *J* = 2.7, 9.0 Hz), 7.59 (1H, d, *J* = 2.4 Hz), 7.94 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.3, 56.0, 62.0, 68.0, 75.8, 114.1, 118.9, 120.0, 122.8, 125.9, 126.4, 127.0, 127.4, 129.9, 130.1, 130.7, 131.0, 143.1, 146.7, 151.4, 152.9, 154.3, 164.7.
FT-IR (KBr, cm^{-1}): 637, 815, 1012, 1225, 1482, 1715, 2982.
HR-MS (*m*/*z*) for $C_{24}H_{18}NO_4Cl^{35}{}_2$ (M+H): Calculated 456.0768, found 456.0766 (base peak).

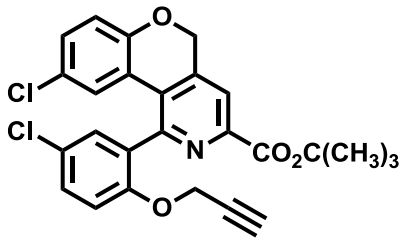
3.8. Methyl- 9-chloro-1-(5-bromo-2-(prop-2-yn-1-yloxy)phenyl)-5H-chromeno[4,3-c]pyridine-3-carboxylate (4h)



Yield: 58 % (255 mg, 0.58 mmol)**.**
Characteristic: Pale yellow solid.
Melting point: 198-200 °C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.35 (1H, t, *J* = 2.4 Hz), 4.00 (3H, s), 4.23 (2H, ABq, *J* = 2.4, 9.3 Hz), 4.98 (1H, dd, *J* = 0.6, 13.8 Hz), 5.19 (1H, d, *J* = 14.1 Hz), 6.84 (1H, d, *J* = 2.4 Hz), 6.97 (2H, dd, *J* = 2.1, 9.0 Hz), 7.14 (1H, dd, *J* = 2.4, 8.7 Hz), 7.43 (1H, dd, *J* = 2.7, 8.7 Hz), 7.57 (1H, d, *J* = 2.7 Hz), 7.97 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 53.0, 55.9, 67.9, 75.8, 114.1, 118.9, 120.1, 122.7, 126.0, 127.0, 127.5, 128.1, 130.2, 130.3, 130.9, 143.1, 146.3, 151.5, 152.9, 154.8, 165.3.

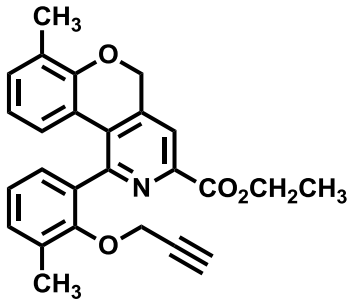
FT-IR (KBr, cm^{-1}): 1038, 1370, 1447, 1736, 2830, 3303.
HR-MS (*m*/*z*) for $C_{23}H_{16}NO_4Cl^{35}_2$ (M+H): Calculated 442.0612, found 442.0611 (base peak).

3.9. tert-Butyl-9-chloro-1-(5-bromo-2-(prop-2-yn-1-yloxy)phenyl)-5H-chromeno[4,3-c]pyridine-3-carboxylate (4i)



Yield: 52 % (251 mg, 0.52 mmol)**.**
Characteristic: Yellow liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.57 (9H, s), 2.28 (1H, t, *J* = 2.4 Hz), 4.15 (2H, ABq, *J* = 2.4, 15.9 Hz), 5.01 (2H, dd, *J* = 13.8, 58.8 Hz), 6.79 (1H, d, *J* = 2.4 Hz), 6.89 (2H, dd, *J* = 3.3, 9.0 Hz), 7.06 (1H, dd, *J* = 2.7, 8.7 Hz), 7.35 (1H, dd, *J* = 2.7, 9.0 Hz), 7.54 (1H, d, *J* = 2.4 Hz), 7.75(1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 28.1, 56.1, 68.0, 75.7, 82.4, 114.2, 118.8, 119.5, 122.9, 125.9, 126.9, 127.5, 127.6, 130.0, 130.1, 131.1, 142.9, 147.7, 151.4, 152.9, 154.7, 163.3.
FT-IR (neat, cm^{-1}): 1161, 1238, 1485, 1711, 1730, 2927, 3431.
HR-MS (*m*/*z*) for $C_{26}H_{22}NO_4Cl^{35}_2$ (M+H): Calculated 484.1081, found 484.1080 (base peak).

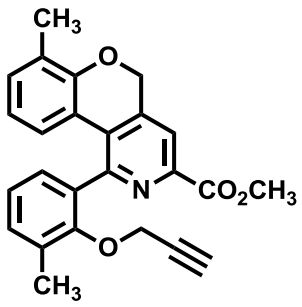
3.10. Ethyl-7-methyl-1-(3-methyl-2-(prop-2-yn-1-yloxy)phenyl)-5H-chromeno[4,3-c]pyridine-3-carboxylate (4j)



Yield: 51 % (211 mg, 0.51 mmol)**.**
Characteristic: Pale yellow solid.
Melting point: 118-120 °C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42 (3H, t, *J* = 7.2 Hz), 2.26 (3H, s), 2.35 (1H, t, *J* = 2.4 Hz), 2.38 (3H, s), 4.31 (1H, dd, *J* = 15.3, 2.4 Hz), 4.39-4.51 (2H, m), 4.74 (1H, dd, *J* = 15.3, 2.4 Hz),

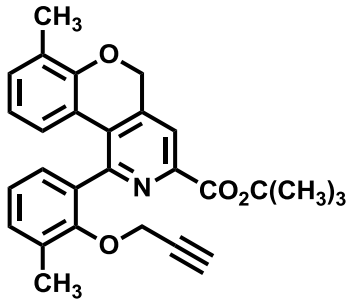
5.09 (2H, q, *J* = 13.8 Hz), 6.52-6.61 (2H, m), 7.01-7.09 (3H, m), 7.26-7.28 (1H, m), 7.93 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2, 15.9, 16.6, 61.6, 61.8, 67.9, 74.4, 76.5, 79.5, 119.4, 120.6, 121.0, 124.9, 125.3, 126.7, 128.6, 129.1, 131.9, 132.6, 134.8, 143.7, 145.3, 153.4, 154.6, 165.0.
FT-IR (KBr, cm^{-1}): 1211, 1335, 1498, 1731, 2647, 3130.
HR-MS (*m*/*z*) for $C_{26}H_{24}NO_4$ (M+H): Calculated 414.1705, found 414.1704.

3.11. Methyl- 7-methyl-1-(3-methyl-2-(prop-2-yn-1-yloxy)phenyl)-5H-chromeno[4,3-c]pyridine-3-carboxylate (4k)



Yield: 50 % (200 mg, 0.50 mmol)**.**
Characteristic: Yellow solid.
Melting point: 180-184 °C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.26 (3H, s), 2.32 (1H, t, *J* = 2.4 Hz), 2.36 (3H, s), 3.99 (3H, s), 4.38 (2H, ddd, *J* = 87.3, 15.3, 2.4 Hz), 5.09 (2H, s), 6.52-6.61 (2H, m), 7.02-7.15 (3H, m), 7.26-7.28 (1H, m), 7.96 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 15.9, 16.6, 52.8, 61.3, 67.8, 74.4, 79.3, 119.6, 120.6, 121.0, 125.0, 125.1, 126.7, 128.5, 129.3, 131.9, 132.0, 132.5, 134.7, 143.6, 145.1, 153.4, 154.5, 154.6, 165.6.
FT-IR (KBr, cm^{-1}): 1132, 1267, 1457, 1736, 2504, 2908.
HR-MS (*m*/*z*) for $C_{25}H_{22}NO_4$ (M+H): Calculated 400.1549, found 400.1548.

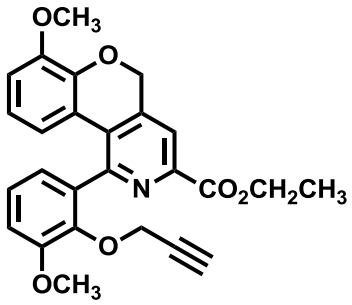
3.12. tert-Butyl-7-methyl-1-(3-methyl-2-(prop-2-yn-1-yloxy)phenyl)-5H-chromeno[4,3-c]pyridine-3-carboxylate (4l)



Yield: 50 % (221 mg, 0.50 mmol)**.**
Characteristic: Yellow liquid.

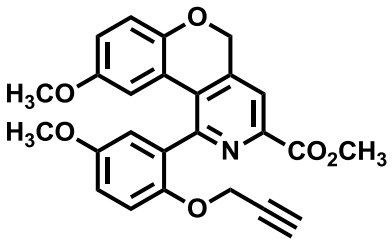
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.63 (9H, s), 2.26 (3H, s), 2.39 (1H, t, *J* = 2.4 Hz), 2.41 (3H, s), 4.36 (1H, dd, *J* = 15.0, 2.4Hz), 4.94-5.16 (3H, m), 6.51-6.61 (2H, m), 7.01-7.03 (2H, m), 7.25-7.28 (2H, m), 7.84 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 15.9, 16.6, 28.1, 62.0, 67.9, 74.4, 79.8, 82.1, 118.9, 120.6, 121.0, 124.7, 125.5, 126.6, 128.6, 128.7, 131.7, 131.8, 132.6, 135.0, 143.7, 146.4, 153.2, 154.6, 154.7, 163.9.
FT-IR (neat, cm^{-1}): 1417, 1680, 1721, 2928, 3327.
HR-MS (*m*/*z*) for $C_{28}H_{28}NO_4$ (M+H): Calculated 442.2018, found 442.2017.

3.13.Ethyl-7-methoxy-1-(3-methoxy-2-(prop-2-yn-1-yloxy)phenyl)-5H-chromeno[4,3-c]pyridine-3-carboxylate (4m)



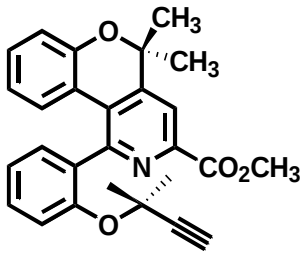
Yield: 55 % (245 mg, 0.55 mmol).
Characteristic: Yellow solid.
Melting point: 120-122 ^{o}C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.35 (3H, t, *J* = 7.2 Hz), 2.26 (1H, t, *J* = 2.4 Hz), 3.82 (3H, s), 3.84 (3H, s), 4.35-4.43 (3H, m), 4.75 (1H, dd, *J* = 2.4, 14.7 Hz), 5.09 (2H, q, *J* = 13.8 Hz), 6.42-6.45 (1H, m), 6.55 (1H, t, *J* = 8.1 Hz), 6.72-6.79 (2H, m), 6.91-6.94 (1H, m), 7.00-7.06 (1H, m), 7.86 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2, 55.9, 56.0, 61.1, 61.8, 68.3, 74.3, 79.6, 112.6, 112.9, 119.5, 119.7, 121.2, 122.0, 122.3, 125.1, 128.6, 135.7, 143.6, 145.0, 145.6, 145.7, 148.8, 152.9, 153.3, 164.9.
FT-IR (KBr, cm^{-1}): 1063, 1385, 1400, 1582, 1716, 2839, 3433.
HR-MS (*m*/*z*) for $C_{26}H_{24}NO_6$ (M+H): Calculated 446.1604, found 446.1603.

3.14.Methyl-9-methoxy-1-(5-methoxy-2-(prop-2-yn-1-yloxy)phenyl)-5H-chromeno[4,3-c]pyridine-3-carboxylate (4n)



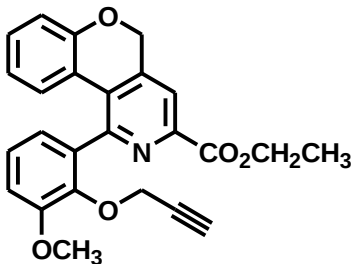
Yield: 56 % (241 mg, 0.56 mmol).
Characteristic: Yellow liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.23 (1H, t, *J* = 2.4 Hz), 3.23 (3H, s), 3.74 (3H, s), 3.92 (3H, s), 4.15-4.19 (2H, m), 4.98 (2H, dd, *J* = 13.8, 44.7 Hz), 6.43 (1H, d, *J* = 3.0 Hz), 6.63-7.01 (5H, m), 7.88 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 52.8, 55.0, 55.8, 56.9, 68.1, 75.0, 78.6, 109.6, 115.3, 115.5, 116.1, 118.2, 118.4, 120.0, 121.5, 129.2, 131.4, 143.3, 145.6, 149.1, 150.3, 154.1, 155.2, 165.0.
FT-IR (neat, cm^{-1}): 1041, 1210, 1401, 1592, 1719, 3290.
HR-MS (*m*/*z*) for $C_{25}H_{22}NO_6$ (M+H): Calculated 432.1447, found 432.1446.

3.15.Methyl-5,5-dimethyl-1-(2-((2-methylbut-3-yn-2-yl)oxy)phenyl)-5H-chromeno[4,3-c]pyridine-3-carboxylate (4o)



Yield: 58 % (267 mg, 0.58 mmol).
Characteristic: Yellow liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.00 (3H, s), 1.21 (3H, s), 1.44 (3H, s), 1.83 (3H, s), 2.39 (1H, s), 3.99 (3H, s), 6.59-6.64 (1H, m), 6.89-6.99 (3H, m), 7.11-7.19 (2H, m), 7.30-7.42 (1H, m), 7.65 (1H, dd, *J* = 7.5, 1.5 Hz), 7.94 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 26.2, 26.8, 27.8, 29.3, 52.8, 71.2, 73.4, 85.7, 117.8, 118.2, 121.6, 122.0, 122.3, 126.4, 126.6, 127.0, 128.2, 129.3, 130.2, 131.0, 132.6, 145.7, 150.6, 152.6, 153.7, 153.9, 166.0.
FT-IR (neat, cm^{-1}): 1050, 1240, 1421, 1595, 1729, 3270.
HR-MS (*m*/*z*) for $C_{27}H_{26}NO_4$ (M+H): Calculated 428.1862, found 428.1860.

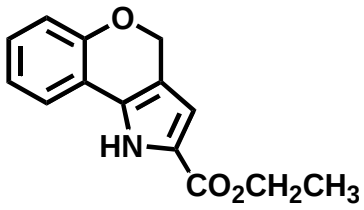
3.16.Methyl-1-(3-methoxy-2-(prop-2-yn-1-yloxy)phenyl)-5H-chromeno[4,3-c]pyridine-3-carboxylate (4t)



Yield: 54 % (224 mg, 0.54 mmol).

Characteristic: Yellow solid.
Melting point: 164° – 166 °C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42 (3H, t, *J* = 7.2 Hz), 2.32 (1H, t, *J* = 2.1 Hz), 3.89 (3H, s), 4.19 (2H, ddd, *J* = 39.9, 15.7, 2.4 Hz), 4.40-4.51 (2H, m), 5.14 (2H, dd, *J* = 63.6, 13.8 Hz), 6.48 (1H, d, *J* = 7.5 Hz), 6.60 (1H, t, *J* = 8.1 Hz), 6.79 (1H, d, *J* = 8.1 Hz), 6.98 (1H, d, *J* = 8.1 Hz), 7.16 (1H, t, *J* = 7.5 Hz), 7.38-7.43 (1H, m), 7.56 (1H, dd, *J* = 7.5, 1.2 Hz), 7.92 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.3, 56.1, 56.3, 61.8, 68.3, 75.0, 112.5, 113.3, 118.4, 119.5, 121.1, 122.4, 122.8, 128.9, 130.1, 130.5, 131.2, 143.1, 145.7, 146.1, 148.9, 152.9, 155.0, 165.0 .
FT-IR (KBr, cm^{-1}): 1016, 1095, 1226, 1290, 1481, 1600, 1701, 3261.
HR-MS (*m*/*z*) for $C_{25}H_{22}NO_5$ (M+H): Calculated 416.1500, found 416.1496.

3.17. Ethyl-1,4-dihydrochromeno[4,3-b]pyrrole-2-carboxylate (5a)

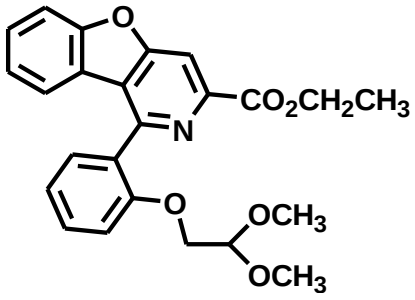


Yield: 32% (78 mg, 0.32 mmol).
Characteristic: Yellow liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.39 (3H, t, *J* = 7.2 Hz), 4.38 (2H, q, *J* = 6.9 Hz), 5.29 (2H, s), 6.72 (1H, d, *J* = 2.1 Hz), 6.91-6.96 (2H, m), 7.92-7.21 (1H, m), 7.44 (1H, dd, *J* = 1.5, 3.9 Hz), 9.94 (1H, brs).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.4, 60.5, 65.6, 111.3, 115.7, 116.8, 117.0, 120.5, 121.3, 123.4, 128.4, 128.8, 153.6, 161.4.
FT-IR (neat, cm^{-1}): 758, 1210, 1278, 1460, 1672, 2926, 3291.
HR-MS (*m*/*z*) for $C_{14}H_{14}NO_3$ (M+H) Calculated: 244.2659; found: 244.2658.

4. Synthesis and Characterization of Benzofurano[3,2-*c*]pyridine (9)

2-(2,2-Dimethoxyethoxy)benzaldehyde (**7**, 2 mmol) was dissolved in dry toluene (10 mL) and was refluxed with glycine ethyl ester (1 mmol) using gold (III) chloride (10 mg, 3 mol%) for 11 h. The progress of the reaction was monitored by TLC. After completion of the reaction, toluene was removed in a rotor evaporator at room temperature under reduced pressure. The post reaction mixture was extracted with ethyl acetate (5 mL x 2), washed well with saturated sodium bicarbonate solution (5 mL x 3) followed by brine solution (5 mL x 3). The organic extract was dried over anhydrous sodium sulfate, filtered and concentrated in a rotor evaporator at room temperature under reduced pressure. The pure product was isolated by purification on silica gel column (60-120 mesh) with ethyl acetate – petroleum ether (60-80) mixture as an eluent. Thus, the reaction afforded 1-[2-(2,2-dimethoxyethoxy)-phenyl]-benzo[4,5]furo[3,2-*c*]pyridine-3-carboxylic acid ethyl ester (**9**) after processing in an isolated yield of 65 % (274 mg, 0.65 mmol). The compound **9** was characterized by ^{1}H and ^{13}C NMR (NDC & DEPT), FT-IR, and HR-MS analysis.

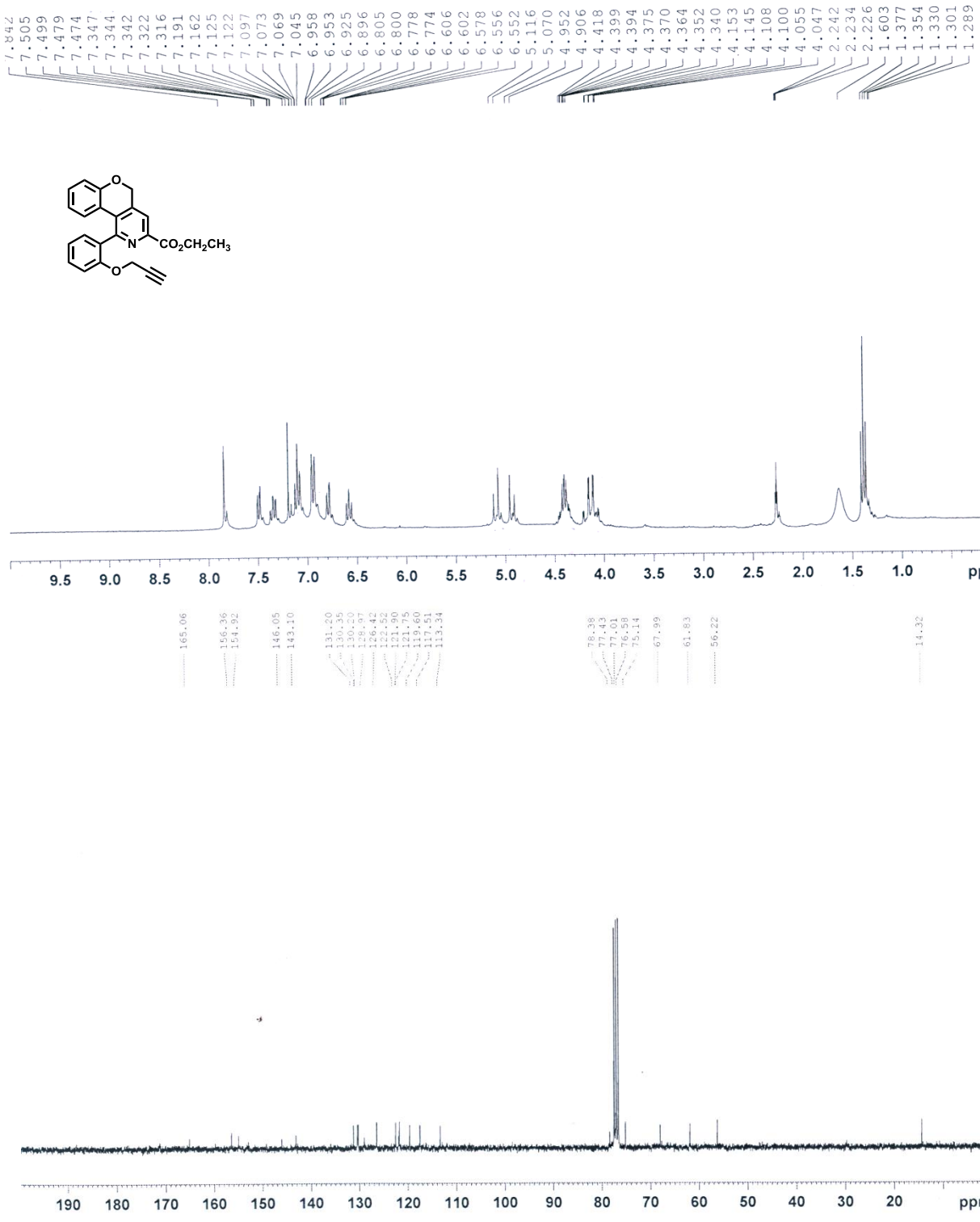
4.1. Characterization Data of 1-[2-(2,2-Dimethoxyethoxy)-phenyl]-benzo[4,5]furo[3,2-c]pyridine-3-carboxylic acid ethyl ester (7)



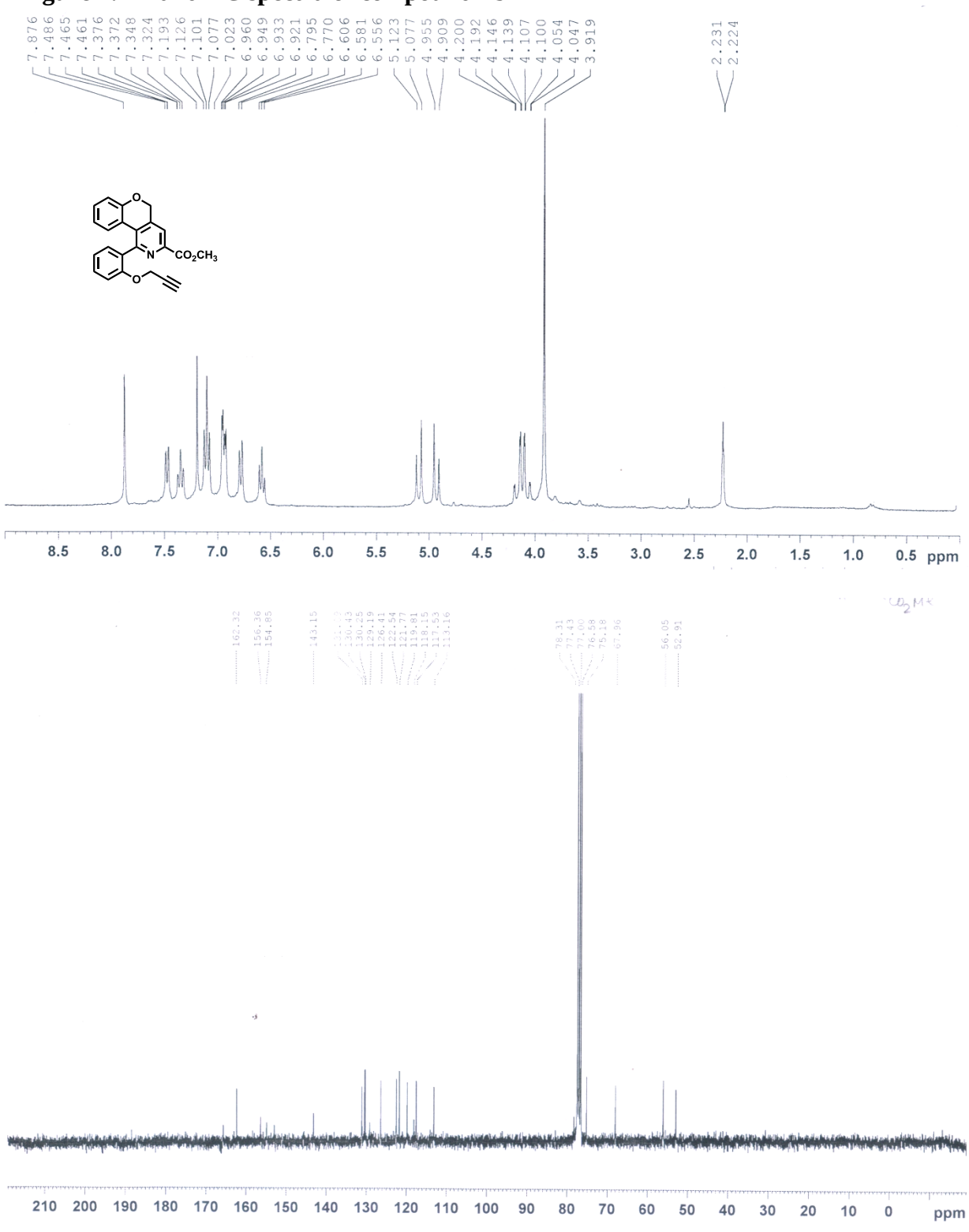
Yield: 65 % (274 mg, 0.65 mmol)**.**
Characteristic: Yellow liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.48 (3H, t, *J* = 7.2 Hz), 2.89 (3H, s), 3.05 (3H, s), 3.89-3.91 (2H, m), 3.98-3.99 (1H, m), 4.52-4.56 (2H, m), 7.08 (1H, d, *J* = 9.0 Hz), 7.17-7.23 (1H, m), 7.33-7.35 (1H, m), 7.52 (2H, t, *J* = 8.4 Hz), 7.64 (2H, t, *J* = 19.8 Hz), 8.35 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.3, 54.3, 54.6, 61.9, 68.9, 102.6, 108.1, 111.6, 112.4, 121.7, 121.8, 123.2, 123.7, 128.5, 128.7, 130.8, 131.2, 145.9, 152.4, 156.1, 156.9, 157.5, 161.1, 165.4.
FT-IR (KBr, cm^{-1}): 753, 1136, 1343, 1370, 1454, 1602, 1715, 1738, 2933.
HR-MS (*m*/*z*) for $C_{24}H_{24}NO_6$ (M+H): Calculated 422.1604, found 422.1602.

5. NMR (^{1}H and ^{13}C) Spectra of All New Synthesized Compounds (4a-o, 4t and 7)

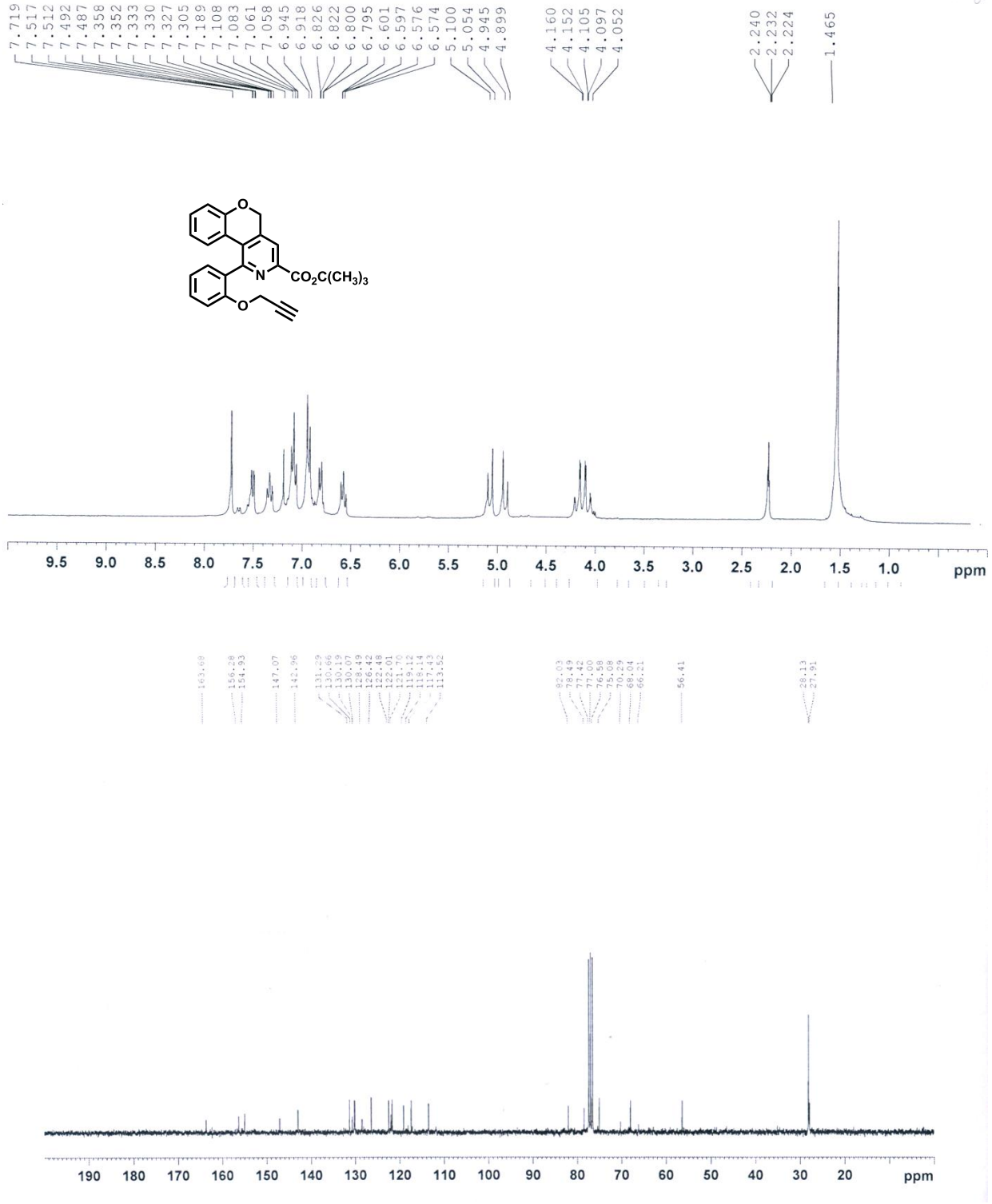
SI Figure 1: ^{1}H and ^{13}C spectra of compound 4a



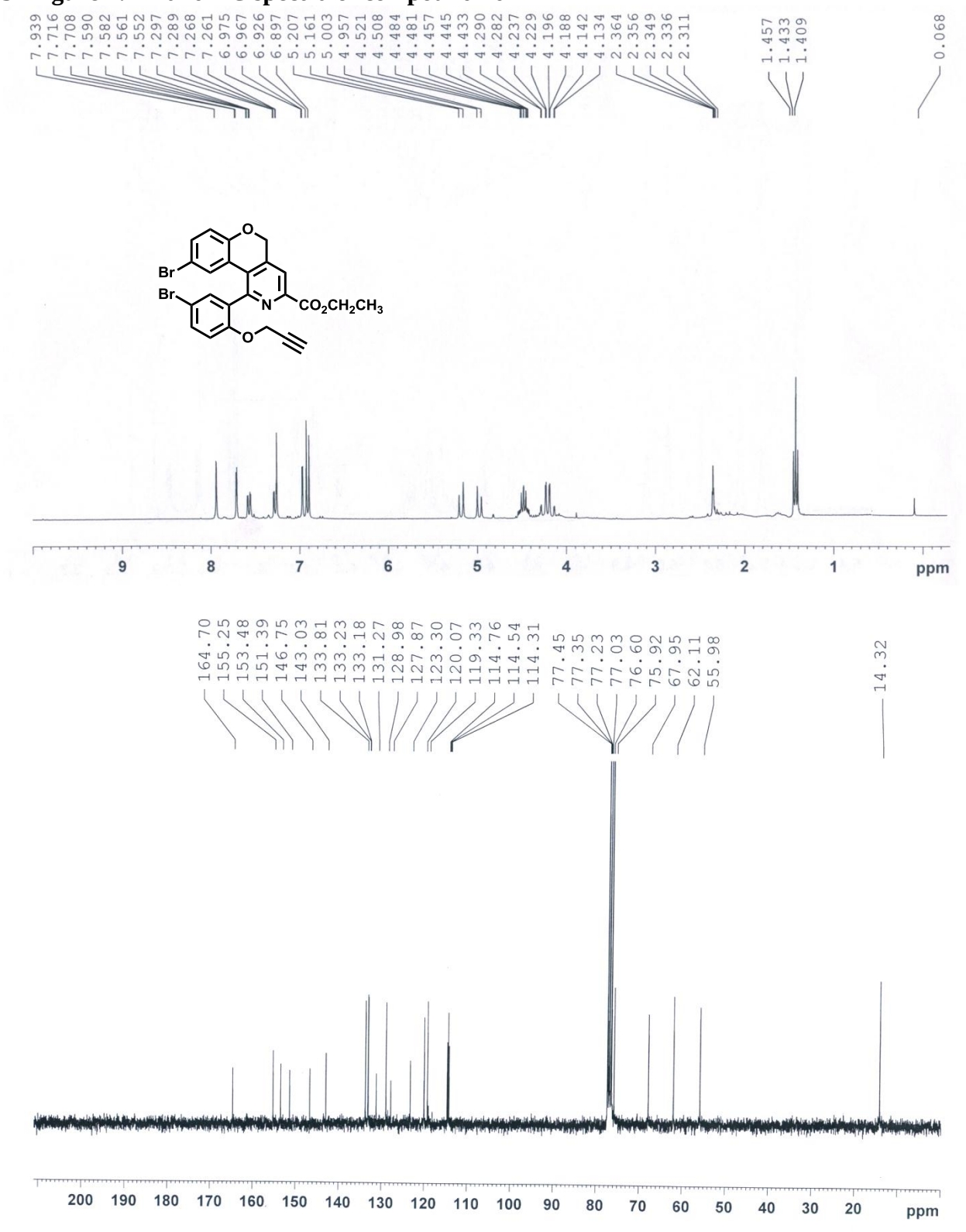
SI Figure 2: ^{1}H and ^{13}C spectra of compound 4b



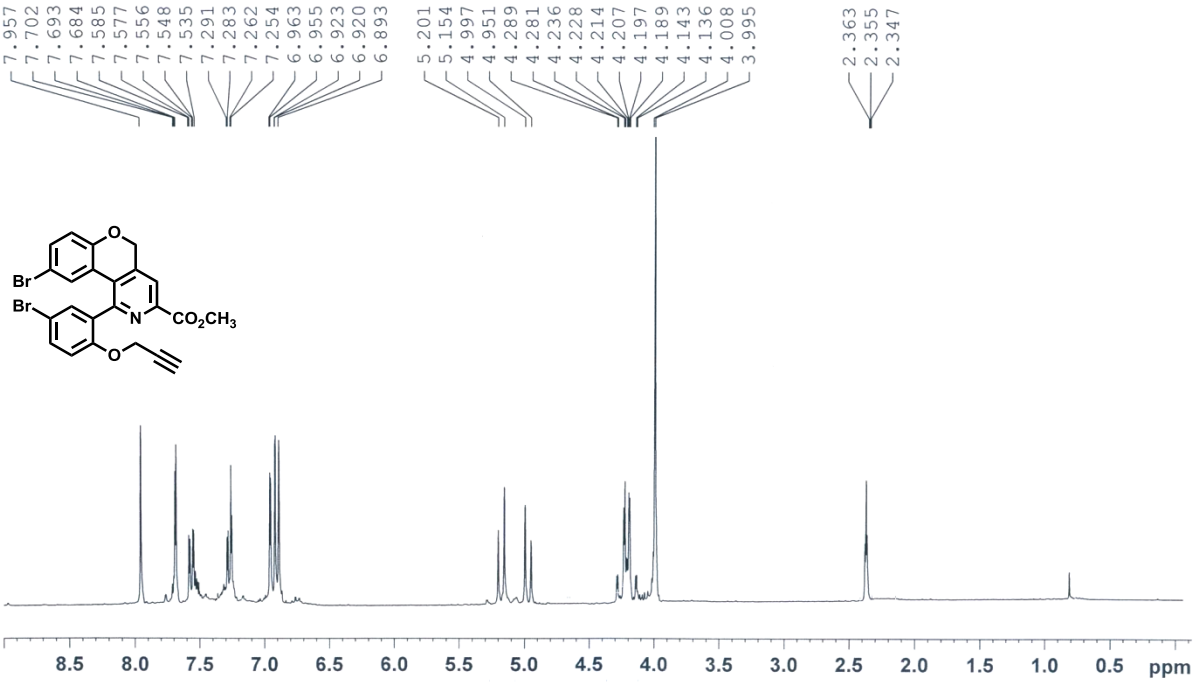
SI Figure 3: ^{1}H and ^{13}C spectra of compound 4c

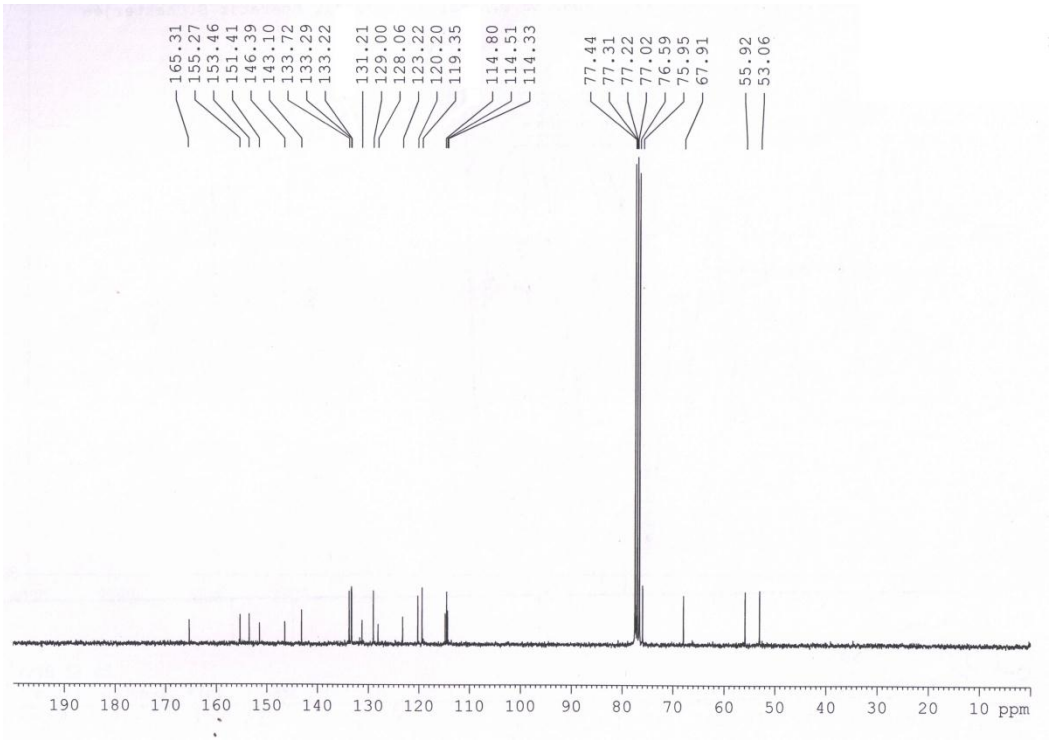


SI Figure 4: ^{1}H and ^{13}C spectra of compound 4d

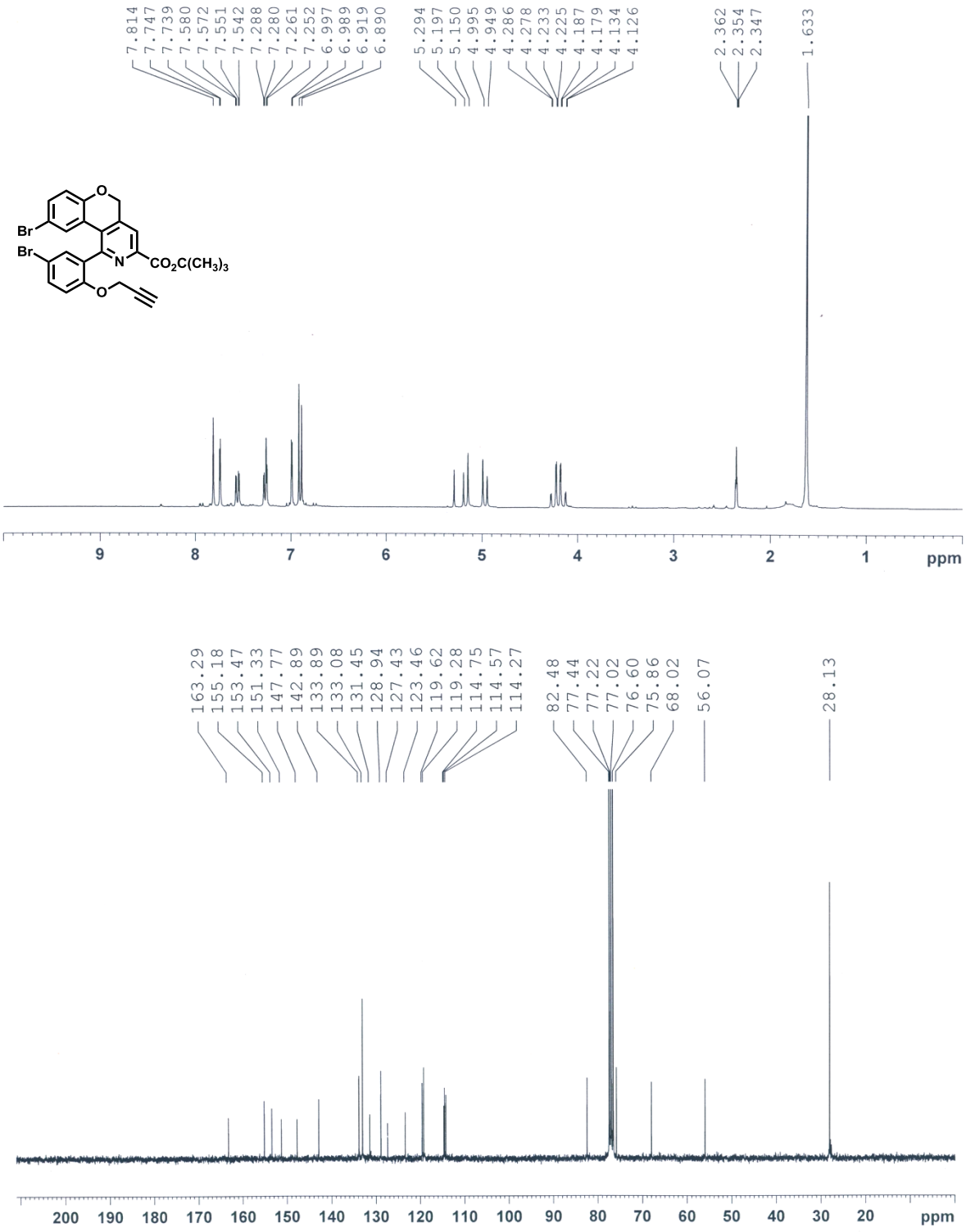


SI Figure 5: ^{1}H and ^{13}C spectra of compound 4e

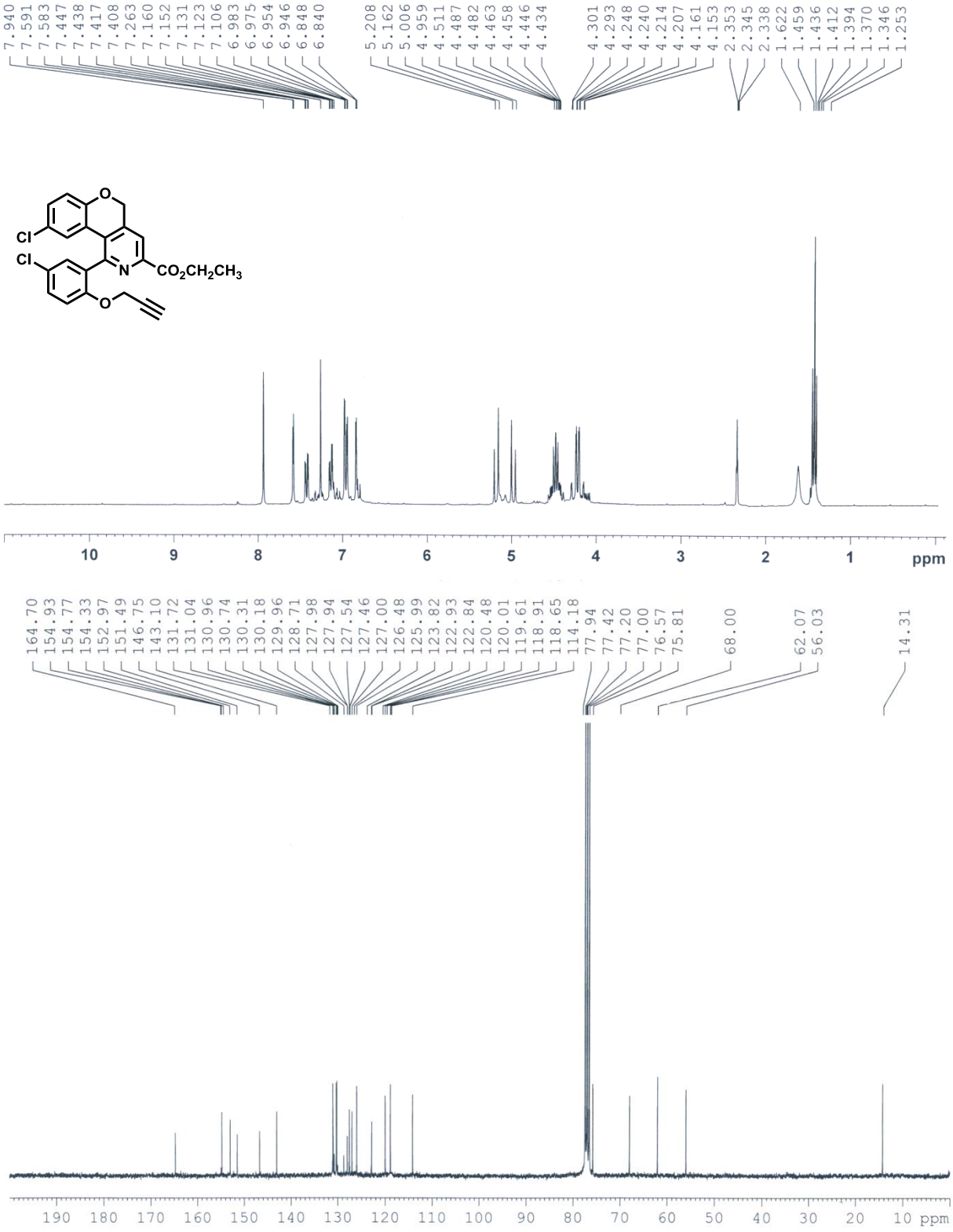




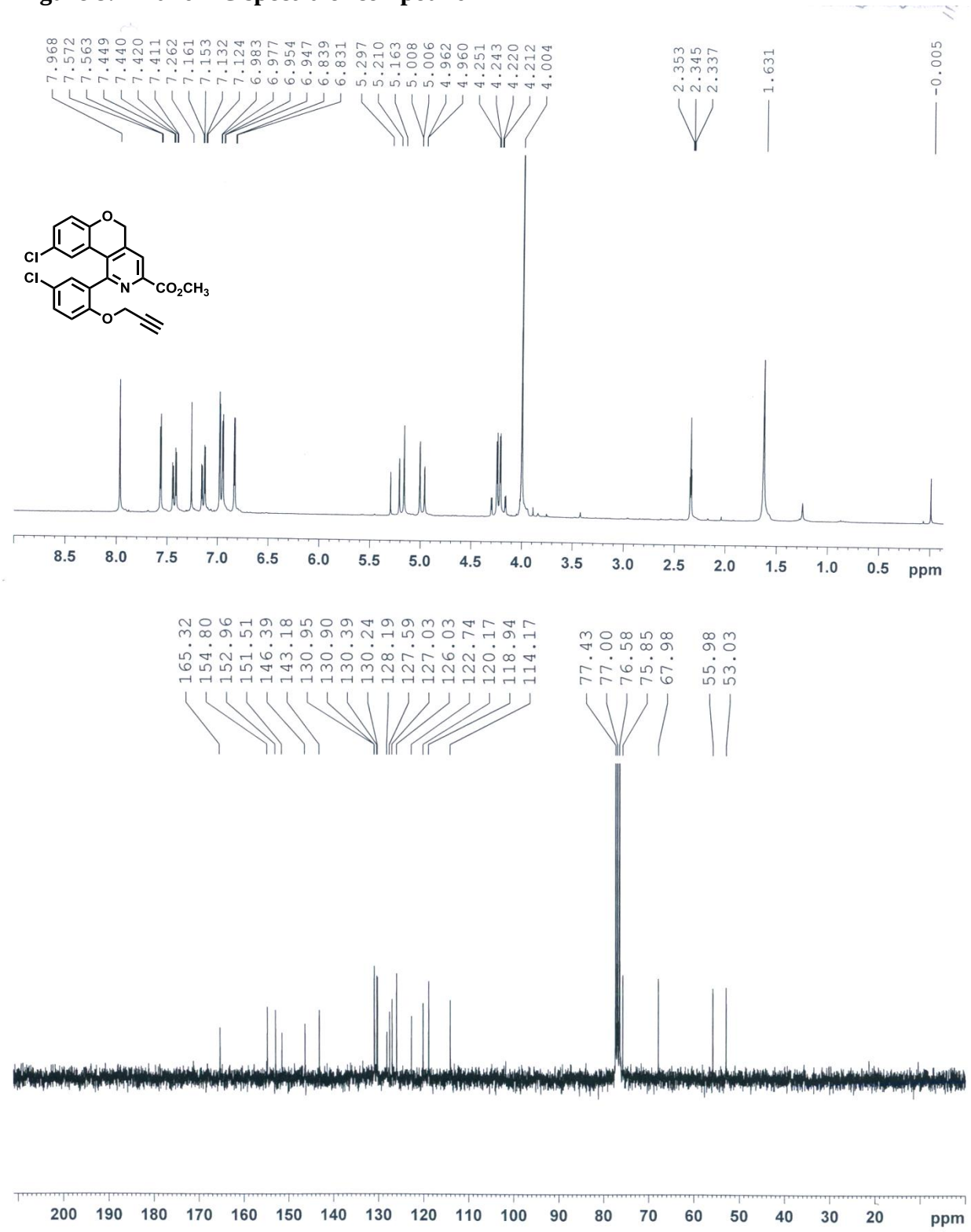
SI Figure 6: ^{1}H and ^{13}C spectra of compound 4f



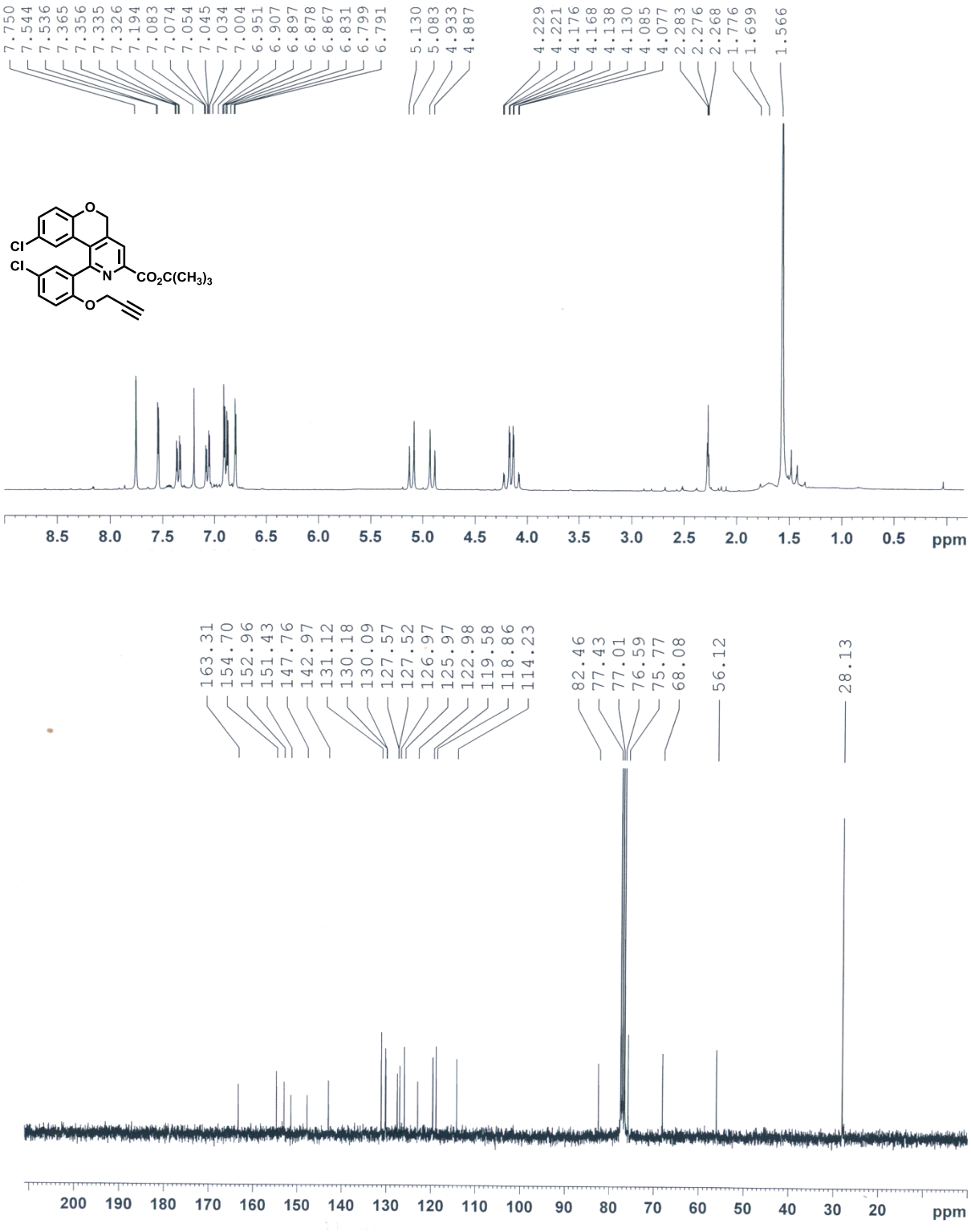
SI Figure 7: ^{1}H and ^{13}C spectra of compound 4g



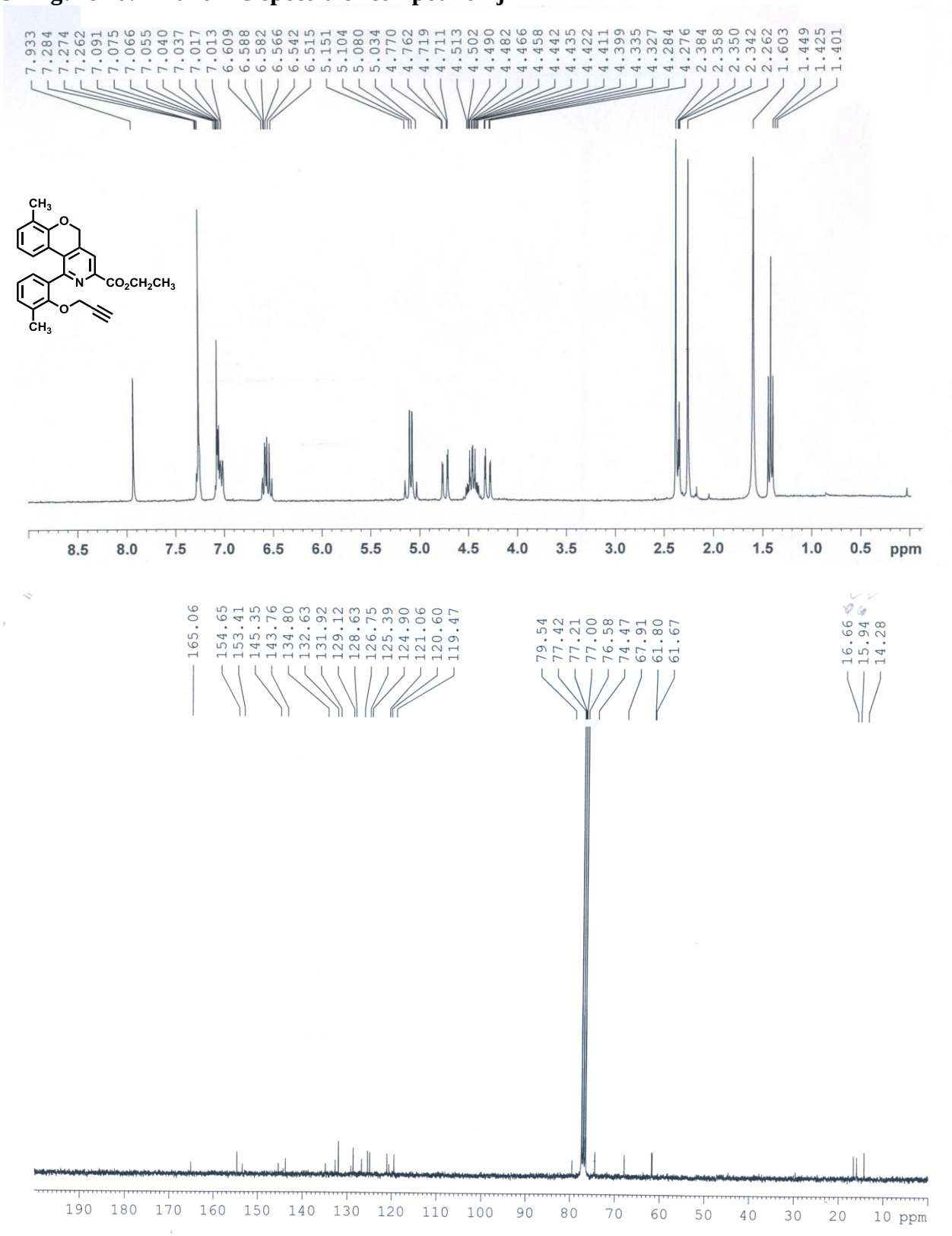
SI Figure 8: ^{1}H and ^{13}C spectra of compound 4h



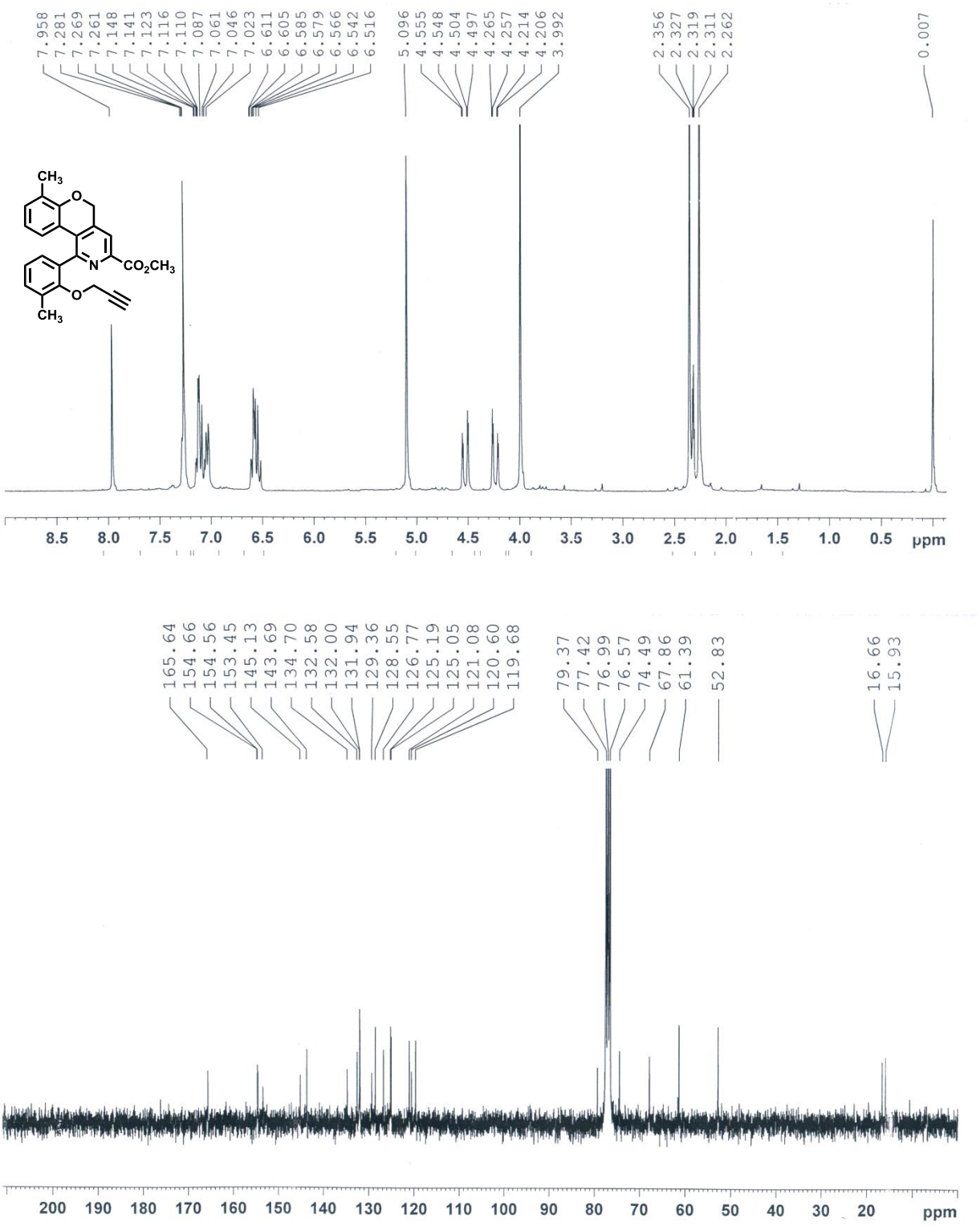
SI Figure 9: ^{1}H and ^{13}C spectra of compound 4i



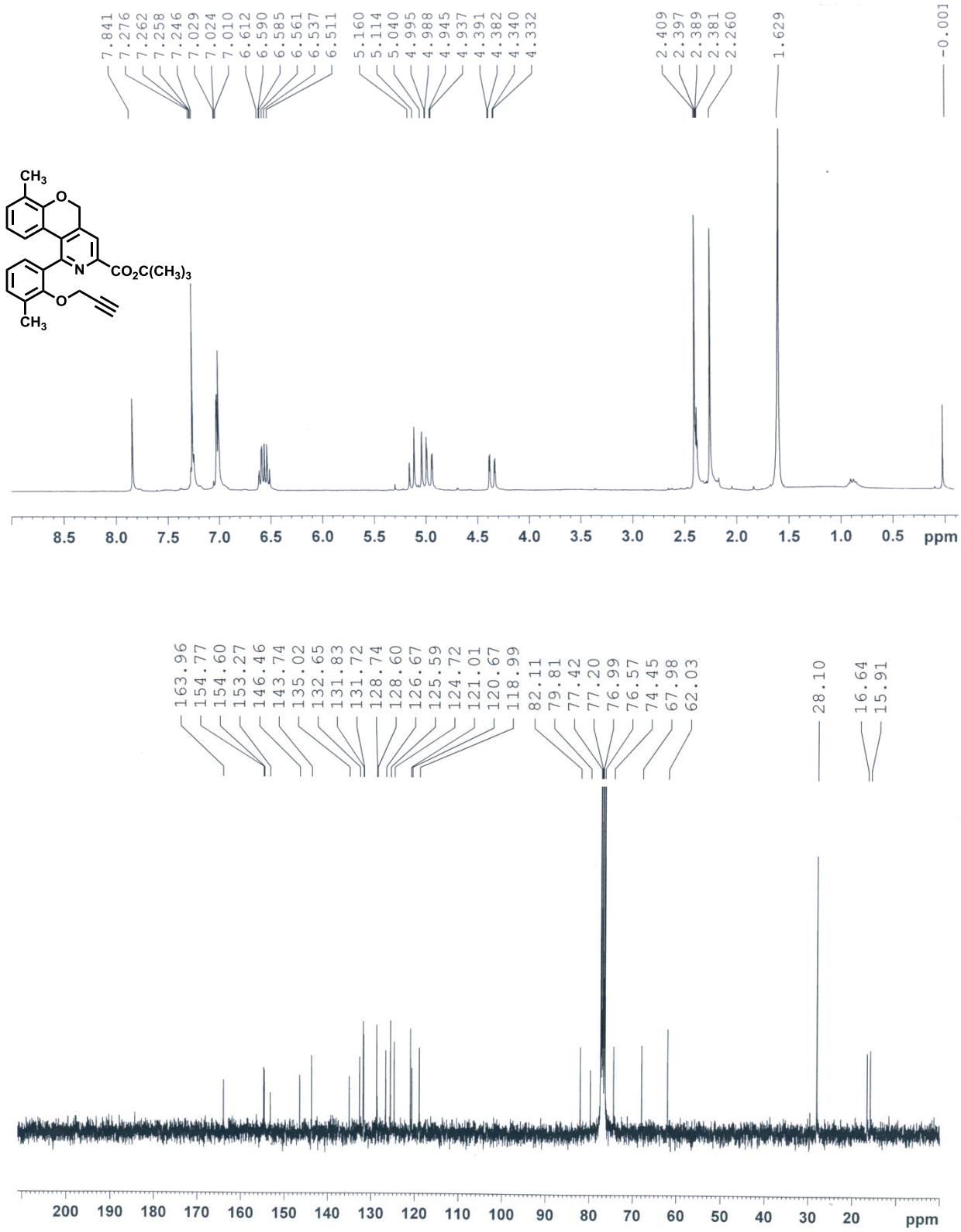
SI Figure 10: ^{1}H and ^{13}C spectra of compound 4j



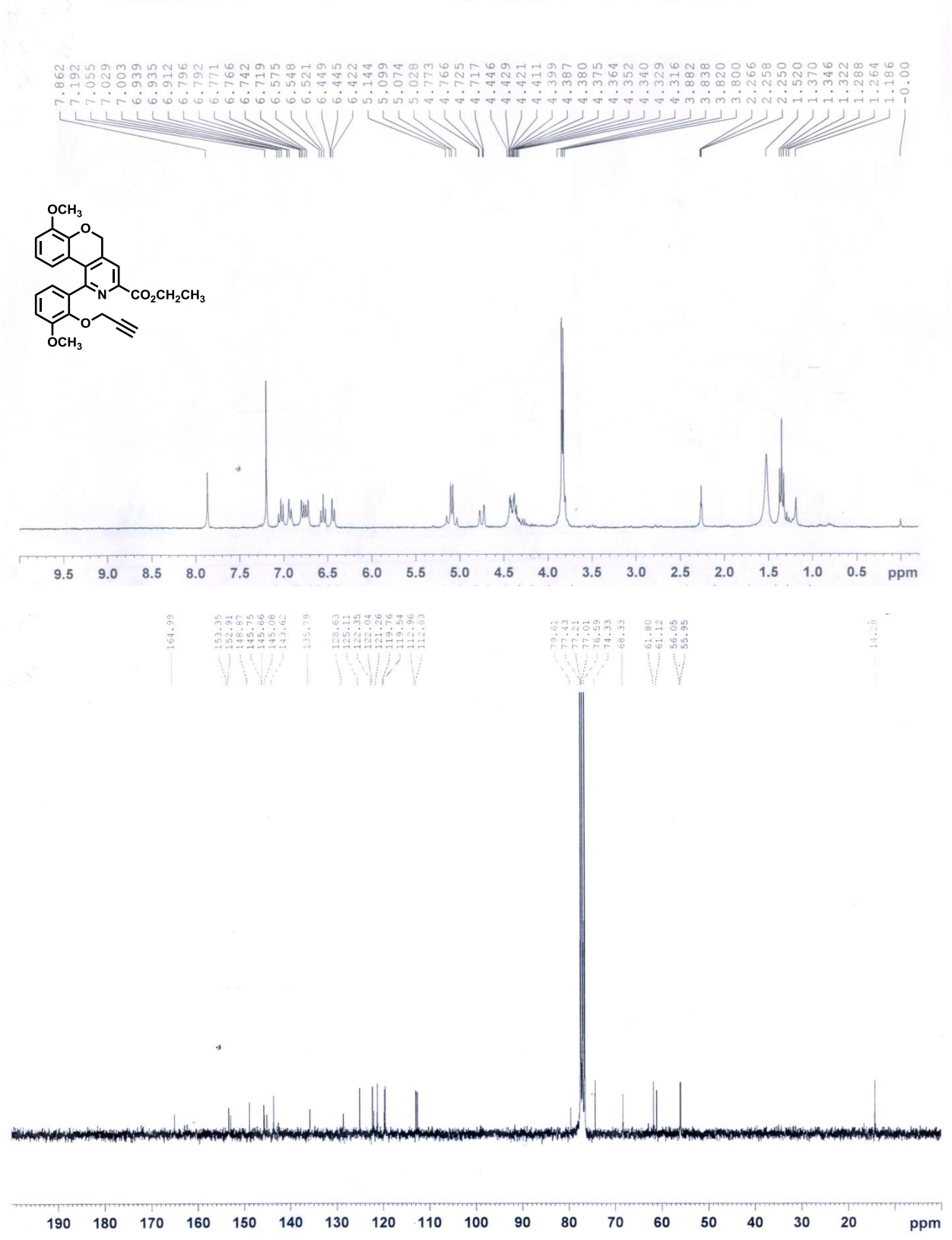
SI Figure 11: ^{1}H and ^{13}C spectra of compound 4k



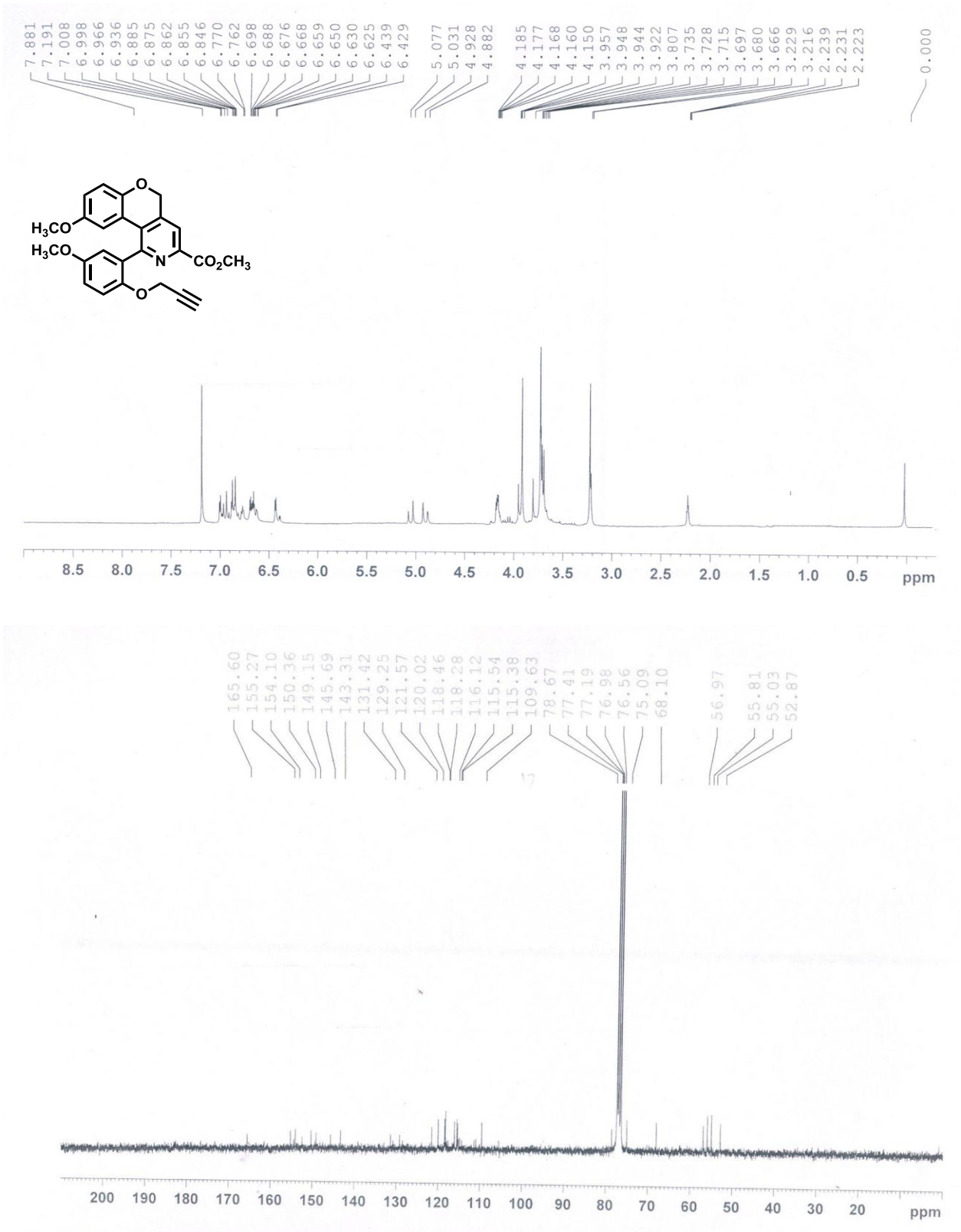
SI Figure 12: ^{1}H and ^{13}C spectra of compound 4l



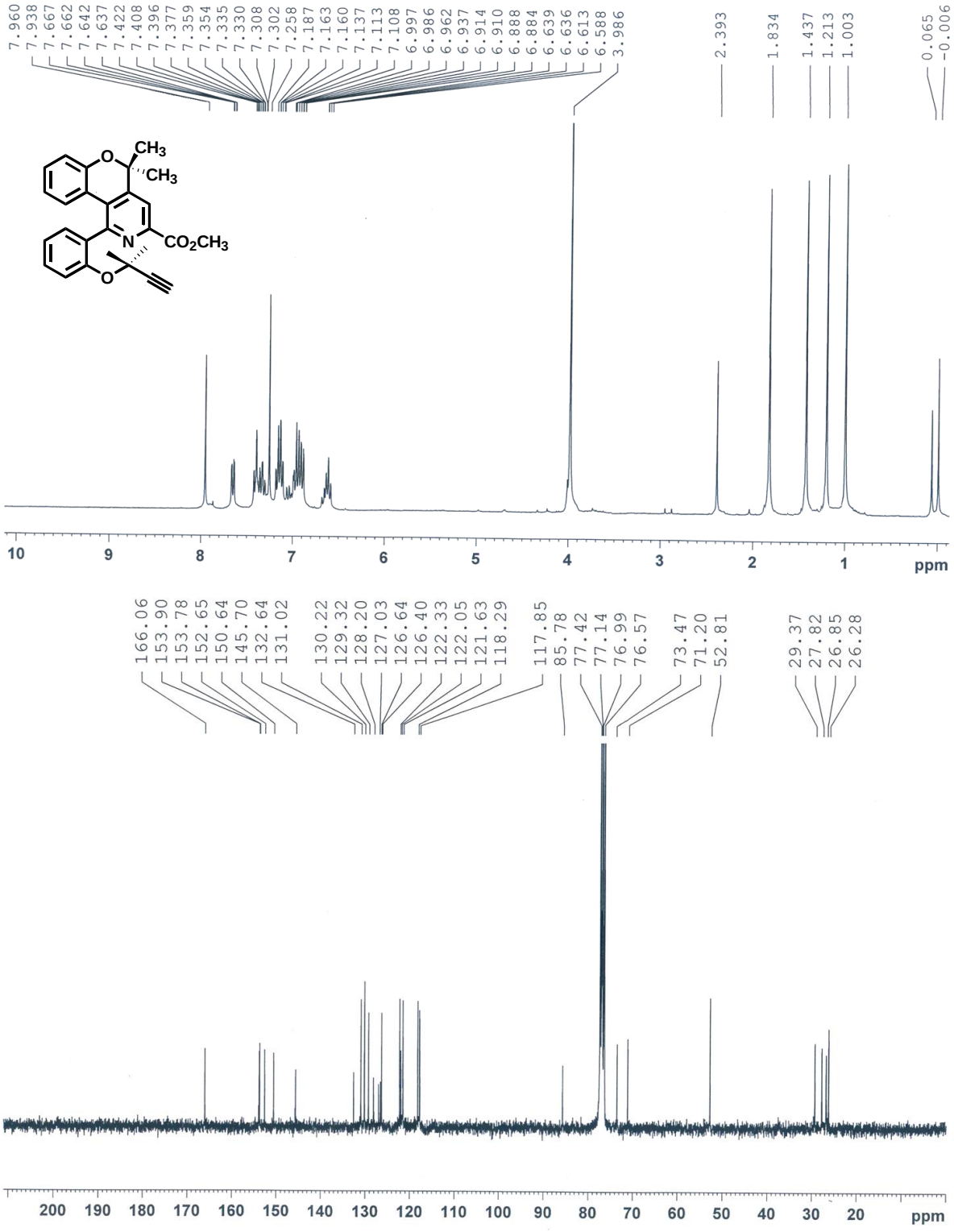
SI Figure 13: ^{1}H and ^{13}C spectra of compound 4m



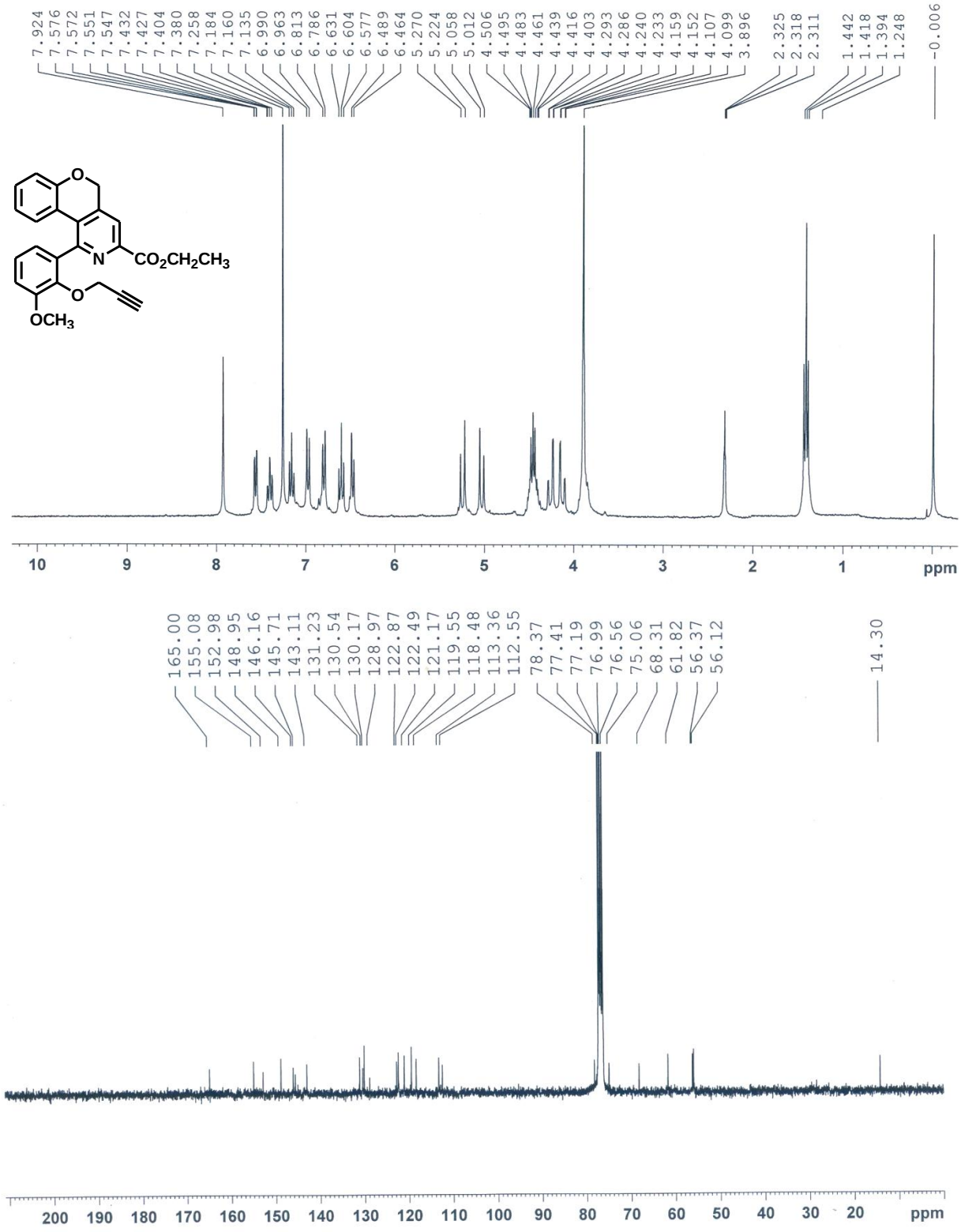
SI Figure 14: ^{1}H and ^{13}C spectra of compound 4n



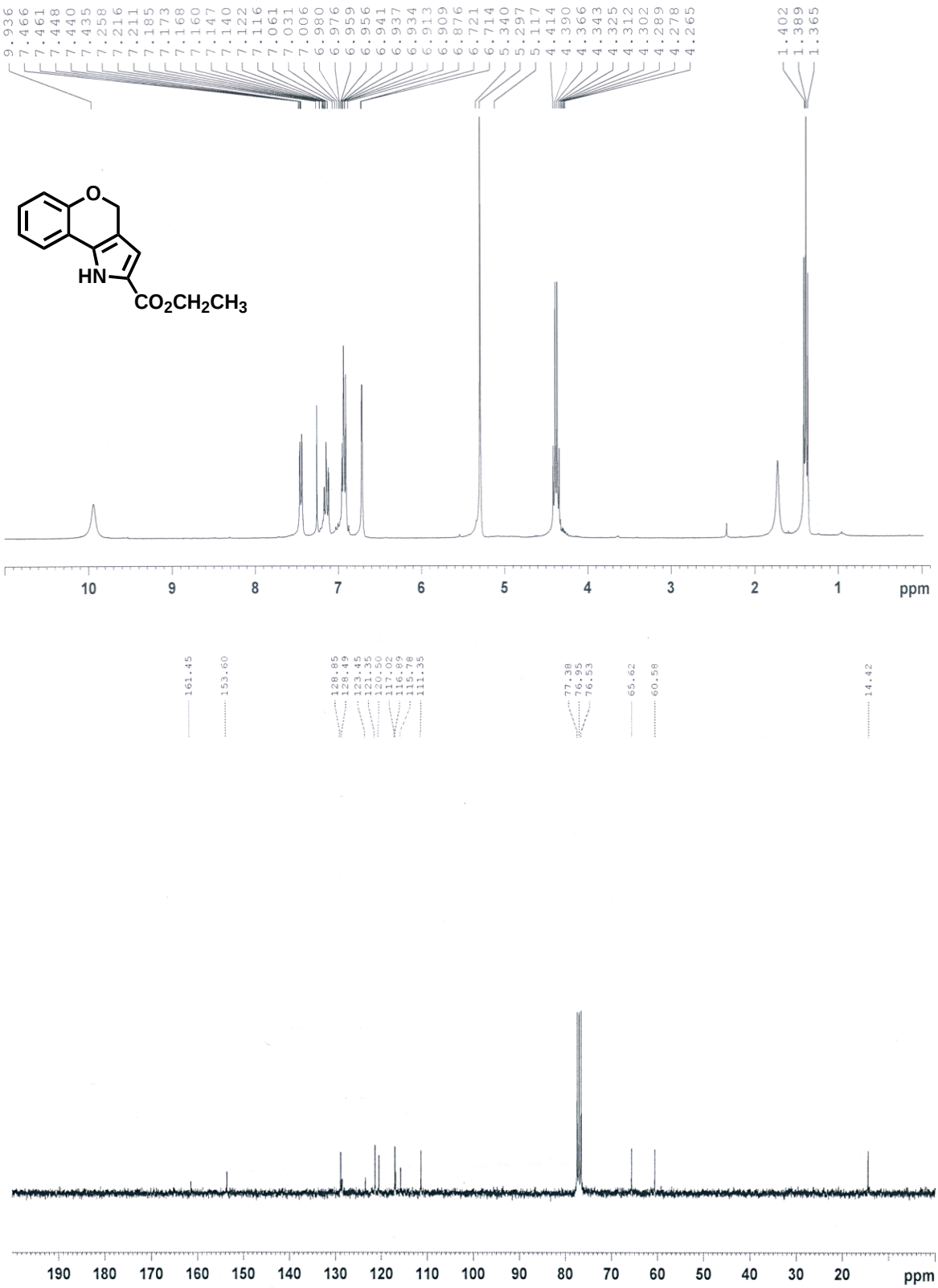
SI Figure 15: ^{1}H and ^{13}C spectra of compound 4o



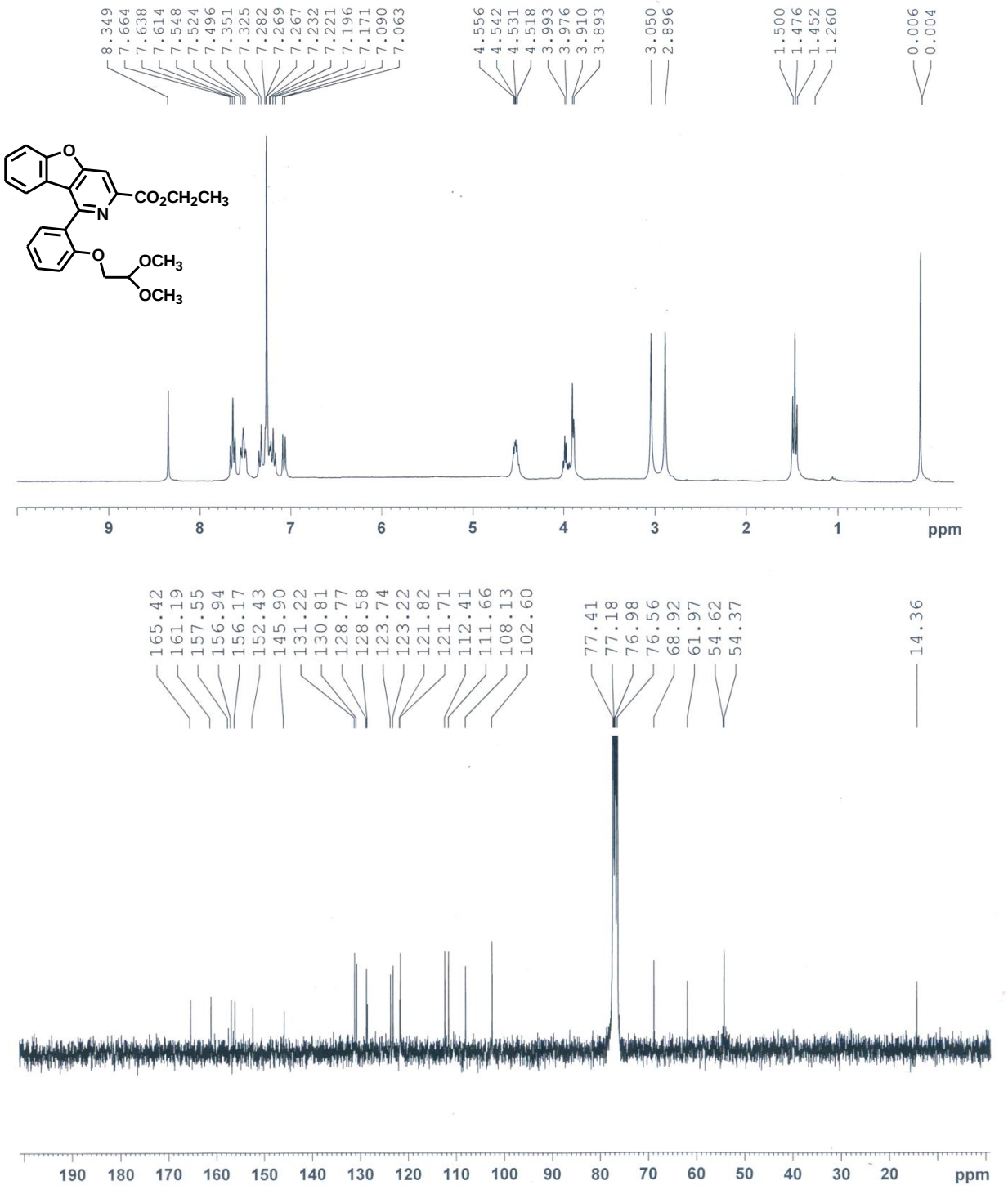
SI Figure 16: ^{1}H and ^{13}C spectra of compound 4t



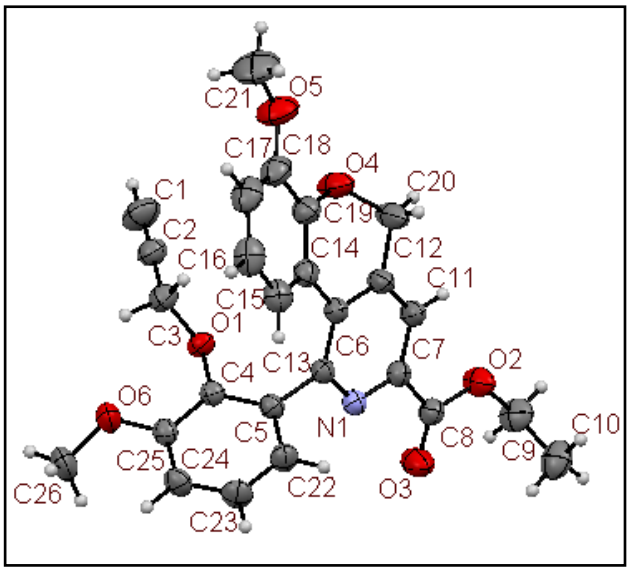
SI Figure 17: ^{1}H and ^{13}C spectra of compound 5a



SI Figure 18: ^{1}H and ^{13}C NMR spectra of compound 9



6. Crystal Summary of Data of Compound 4m (CCDC 938786)



- Chemical formula and formula weight (M): C26 H23 N1 O6 and 445.46
- Crystal system: Monoclinic
- Unit-cell dimensions (angstrom or pm, degrees) and volume, with edges: a 36.051(4), b 7.2062(8), c 18.3332(19), 90.00, 110.194(4), 90.00, 4470.0(8)
- Temperature: 296 K
- Space group symbol: C 2/c
- No. of formula units in unit cell (Z): 8
- Number of reflections measured and/or number of independent reflections, Rint: 7598
- Final R values (and whether quoted for all or observed data): 0.0517

CIF data

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_exptl_crystal_density_diffrn    1.324
_exptl_crystal_density_method    'not measured'
_exptl_crystal_F_000             964
_exptl_absorpt_coefficient_mu    0.094
_exptl_absorpt_correction_type   ?
_exptl_absorpt_correction_T_min  0.9445
_exptl_absorpt_correction_T_max  0.9696
_exptl_absorpt_process_details   ?

_exptl_special_details
;
 ?
;

_diffrn_ambient_temperature      296(2)
_diffrn_radiation_wavelength     0.71073
_diffrn_radiation_type           MoK\a
_diffrn_radiation_source         'fine-focus sealed tube'
_diffrn_radiation_monochromator  graphite
_diffrn_measurement_device_type  ?
_diffrn_measurement_method       ?
_diffrn_detector_area_resol_mean ?
_diffrn_reflns_number            32169
_diffrn_reflns_av_R_equivalents  0.0318
_diffrn_reflns_av_sigmaI/netI    0.0291
_diffrn_reflns_limit_h_min       -53
_diffrn_reflns_limit_h_max       53
_diffrn_reflns_limit_k_min       -10
_diffrn_reflns_limit_k_max       10
_diffrn_reflns_limit_l_min       -27
_diffrn_reflns_limit_l_max       26
_diffrn_reflns_theta_min         1.20
_diffrn_reflns_theta_max         31.81
_reflns_number_total             7598
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_computing_data_reduction        ?
_computing_structure_solution    'SHELXS-97 (Sheldrick, 2008)'
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_computing_molecular_graphics    ?
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_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
;

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_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.1249P)^2^+1.8271P] where P=(Fo^2^+2Fc^2^)/3'
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_atom_sites_solution_secondary   difmap
_atom_sites_solution_hydrogens   geom
_refine_ls_hydrogen_treatment    mixed
_refine_ls_extinction_method     none
_refine_ls_extinction_coef       ?
_refine_ls_number_reflns         7598
_refine_ls_number_parameters     301
_refine_ls_number_restraints     0
_refine_ls_R_factor_all          0.0813
_refine_ls_R_factor_gt           0.0517
_refine_ls_wR_factor_ref         0.1871
_refine_ls_wR_factor_gt          0.1544
_refine_ls_goodness_of_fit_ref   0.872
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O1 O 0.13435(3) 1.02239(13) 0.11066(5) 0.0370(2) Uani 1 1 d . . .
O2 O 0.13190(3) 1.45430(17) 0.43143(7) 0.0544(3) Uani 1 1 d . . .
O3 O 0.18521(4) 1.47875(19) 0.39622(8) 0.0632(3) Uani 1 1 d . . .
O4 O 0.03612(3) 0.83685(19) 0.20587(8) 0.0621(4) Uani 1 1 d . . .
O5 O 0.00301(4) 0.5523(2) 0.11901(9) 0.0758(4) Uani 1 1 d . . .
O6 O 0.18847(3) 0.95775(17) 0.04143(6) 0.0488(3) Uani 1 1 d . . .
C1 C 0.04460(5) 1.0702(3) -0.02992(12) 0.0690(5) Uani 1 1 d . . .
H1 H 0.0213 1.1286 -0.0595 0.083 Uiso 1 1 calc R . .
C2 C 0.07397(4) 0.9966(2) 0.00736(9) 0.0468(3) Uani 1 1 d . . .
C3 C 0.11033(4) 0.9004(2) 0.05069(8) 0.0428(3) Uani 1 1 d . . .
H3A H 0.1044 0.7882 0.0737 0.051 Uiso 1 1 calc R . .
H3B H 0.1244 0.8660 0.0162 0.051 Uiso 1 1 calc R . .
C4 C 0.17128(3) 0.95221(16) 0.15369(7) 0.0320(2) Uani 1 1 d . . .
C5 C 0.18079(4) 0.93196(17) 0.23352(7) 0.0341(2) Uani 1 1 d . . .
C6 C 0.15278(3) 0.99434(18) 0.27228(7) 0.0338(2) Uani 1 1 d . . .
N1 N 0.16455(3) 1.14884(16) 0.31466(6) 0.0371(2) Uani 1 1 d . . .
C8 C 0.14045(4) 1.2257(2) 0.34782(7) 0.0378(3) Uani 1 1 d . . .
C9 C 0.15572(4) 1.3990(2) 0.39364(8) 0.0419(3) Uani 1 1 d . . .
C10 C 0.14459(5) 1.6176(2) 0.48110(11) 0.0575(4) Uani 1 1 d . . .
H10A H 0.1222 1.6675 0.4927 0.069 Uiso 1 1 calc R . .
H10B H 0.1537 1.7121 0.4536 0.069 Uiso 1 1 calc R . .
C11 C 0.17693(7) 1.5721(3) 0.55513(11) 0.0654(5) Uani 1 1 d . . .
H11A H 0.1687 1.4721 0.5806 0.098 Uiso 1 1 calc R . .
H11B H 0.1828 1.6792 0.5883 0.098 Uiso 1 1 calc R . .
H11C H 0.2001 1.5357 0.5442 0.098 Uiso 1 1 calc R . .
C12 C 0.10346(4) 1.1552(2) 0.33902(8) 0.0444(3) Uani 1 1 d . . .
H12 H 0.0870 1.2151 0.3609 0.053 Uiso 1 1 calc R . .
C13 C 0.09164(4) 0.9938(2) 0.29687(9) 0.0442(3) Uani 1 1 d . . .
C14 C 0.11668(4) 0.90487(19) 0.26422(7) 0.0372(3) Uani 1 1 d . . .
C15 C 0.10196(4) 0.7308(2) 0.22195(8) 0.0397(3) Uani 1 1 d . . .
C16 C 0.12578(5) 0.5889(2) 0.20997(9) 0.0459(3) Uani 1 1 d . . .
H16 H 0.1532 0.5986 0.2307 0.055 Uiso 1 1 calc R . .
C17 C 0.10839(6) 0.4342(2) 0.16710(10) 0.0561(4) Uani 1 1 d . . .
H17 H 0.1243 0.3400 0.1596 0.067 Uiso 1 1 calc R . .

C18 C 0.06755(6) 0.4169(2) 0.13497(10) 0.0589(4) Uani 1 1 d . . .
H18 H 0.0564 0.3134 0.1052 0.071 Uiso 1 1 calc R . .
C19 C 0.04355(5) 0.5530(2) 0.14728(10) 0.0537(4) Uani 1 1 d . . .
C20 C 0.06089(4) 0.7074(2) 0.19236(9) 0.0463(3) Uani 1 1 d . . .
C21 C 0.05228(5) 0.9055(3) 0.28419(12) 0.0666(5) Uani 1 1 d . . .
H21A H 0.0553 0.8040 0.3206 0.080 Uiso 1 1 calc R . .
H21B H 0.0344 0.9959 0.2932 0.080 Uiso 1 1 calc R . .
C22 C -0.01647(8) 0.3877(4) 0.08346(18) 0.0986(9) Uani 1 1 d . . .
H22A H -0.0095 0.3600 0.0386 0.148 Uiso 1 1 calc R . .
H22B H -0.0445 0.4048 0.0679 0.148 Uiso 1 1 calc R . .
H22C H -0.0086 0.2869 0.1198 0.148 Uiso 1 1 calc R . .
C23 C 0.21851(4) 0.8693(2) 0.27821(8) 0.0442(3) Uani 1 1 d . . .
H23 H 0.2252 0.8550 0.3316 0.053 Uiso 1 1 calc R . .
C24 C 0.24580(4) 0.8285(2) 0.24313(9) 0.0473(3) Uani 1 1 d . . .
H24 H 0.2705 0.7826 0.2730 0.057 Uiso 1 1 calc R . .
C25 C 0.23697(4) 0.8548(2) 0.16430(9) 0.0435(3) Uani 1 1 d . . .
H25 H 0.2558 0.8292 0.1415 0.052 Uiso 1 1 calc R . .
C26 C 0.19983(4) 0.91975(18) 0.11937(7) 0.0362(3) Uani 1 1 d . . .
C27 C 0.21863(6) 0.9816(3) 0.00923(11) 0.0660(5) Uani 1 1 d . . .
H27A H 0.2388 1.0613 0.0423 0.099 Uiso 1 1 calc R . .
H27B H 0.2076 1.0365 -0.0414 0.099 Uiso 1 1 calc R . .
H27C H 0.2299 0.8631 0.0050 0.099 Uiso 1 1 calc R . .

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O2 0.0494(6) 0.0536(6) 0.0662(7) -0.0272(5) 0.0274(5) -0.0075(5)
O3 0.0539(6) 0.0714(8) 0.0722(8) -0.0301(6) 0.0319(6) -0.0229(6)
O4 0.0360(5) 0.0708(8) 0.0755(8) -0.0349(6) 0.0142(5) -0.0066(5)
O5 0.0576(7) 0.0705(9) 0.0858(10) -0.0263(7) 0.0076(7) -0.0212(6)
O6 0.0457(5) 0.0675(7) 0.0380(5) 0.0000(4) 0.0205(4) 0.0019(5)
C1 0.0478(9) 0.0804(13) 0.0629(10) -0.0124(9) -0.0012(8) 0.0141(8)
C2 0.0400(7) 0.0524(8) 0.0435(7) -0.0070(6) 0.0087(6) -0.0021(6)
C3 0.0412(7) 0.0421(7) 0.0402(6) -0.0055(5) 0.0081(5) 0.0008(5)
C4 0.0308(5) 0.0301(5) 0.0351(6) -0.0035(4) 0.0112(4) 0.0024(4)
C5 0.0315(5) 0.0363(6) 0.0356(6) -0.0021(4) 0.0130(4) 0.0023(4)
C6 0.0308(5) 0.0403(6) 0.0305(5) -0.0015(4) 0.0108(4) 0.0034(4)
N1 0.0335(5) 0.0440(6) 0.0349(5) -0.0049(4) 0.0132(4) 0.0005(4)

C8 0.0343(6) 0.0442(7) 0.0357(6) -0.0083(5) 0.0129(5) -0.0017(5)
C9 0.0389(6) 0.0473(7) 0.0401(6) -0.0109(5) 0.0144(5) -0.0029(5)
C10 0.0602(9) 0.0457(8) 0.0666(10) -0.0228(7) 0.0217(8) 0.0008(7)
C11 0.0860(13) 0.0534(10) 0.0558(9) -0.0154(8) 0.0233(9) -0.0030(9)
C12 0.0340(6) 0.0569(8) 0.0455(7) -0.0188(6) 0.0179(5) -0.0030(5)
C13 0.0332(6) 0.0557(8) 0.0468(7) -0.0166(6) 0.0178(5) -0.0063(5)
C14 0.0335(6) 0.0442(7) 0.0354(6) -0.0069(5) 0.0136(5) -0.0012(5)
C15 0.0429(6) 0.0402(7) 0.0376(6) -0.0040(5) 0.0160(5) -0.0028(5)
C16 0.0553(8) 0.0372(7) 0.0474(7) 0.0031(5) 0.0205(6) 0.0038(6)
C17 0.0790(12) 0.0352(7) 0.0584(9) -0.0002(6) 0.0293(8) 0.0061(7)
C18 0.0776(12) 0.0416(8) 0.0559(9) -0.0101(7) 0.0209(8) -0.0098(7)
C19 0.0573(9) 0.0499(8) 0.0497(8) -0.0095(6) 0.0129(7) -0.0131(7)
C20 0.0440(7) 0.0480(8) 0.0468(7) -0.0109(6) 0.0156(6) -0.0064(6)
C21 0.0438(8) 0.0844(13) 0.0809(12) -0.0443(10) 0.0335(8) -0.0223(8)
C22 0.0856(16) 0.0900(17) 0.1074(19) -0.0269(15) 0.0167(14) -0.0435(14)
C23 0.0375(6) 0.0559(8) 0.0376(6) 0.0038(6) 0.0108(5) 0.0106(6)
C24 0.0346(6) 0.0556(8) 0.0497(7) 0.0028(6) 0.0120(5) 0.0153(6)
C25 0.0368(6) 0.0480(8) 0.0505(7) -0.0041(6) 0.0210(6) 0.0067(5)
C26 0.0369(6) 0.0370(6) 0.0374(6) -0.0042(5) 0.0161(5) 0.0015(5)
C27 0.0572(10) 0.1017(15) 0.0494(9) 0.0000(9) 0.0317(8) 0.0035(10)

_geom_special_details
;
All esds (except the esd in the dihedral angle between two l.s. planes)
are estimated using the full covariance matrix. The cell esds are taken
into account individually in the estimation of esds in distances, angles
and torsion angles; correlations between esds in cell parameters are only
used when they are defined by crystal symmetry. An approximate (isotropic)
treatment of cell esds is used for estimating esds involving l.s. planes.
;

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O1 C3 1.4403(16) . ?
O2 C9 1.3367(17) . ?
O2 C10 1.4611(18) . ?
O3 C9 1.1949(18) . ?

O4 C20 1.3717(19) . ?
O4 C21 1.438(2) . ?
O5 C19 1.372(2) . ?
O5 C22 1.418(2) . ?
O6 C26 1.3713(16) . ?
O6 C27 1.415(2) . ?
C1 C2 1.170(2) . ?
C1 H1 0.9300 . ?
C2 C3 1.453(2) . ?
C3 H3A 0.9700 . ?
C3 H3B 0.9700 . ?
C4 C5 1.3908(17) . ?
C4 C26 1.3991(18) . ?
C5 C23 1.3984(17) . ?
C5 C6 1.4906(17) . ?
C6 N1 1.3401(17) . ?
C6 C14 1.4136(18) . ?
N1 C8 1.3400(16) . ?
C8 C12 1.3833(18) . ?
C8 C9 1.5000(18) . ?
C10 C11 1.489(3) . ?
C10 H10A 0.9700 . ?
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C11 H11A 0.9600 . ?
C11 H11B 0.9600 . ?
C11 H11C 0.9600 . ?
C12 C13 1.380(2) . ?
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C13 C14 1.3989(19) . ?
C13 C21 1.498(2) . ?
C14 C15 1.4739(18) . ?
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C16 C17 1.383(2) . ?
C16 H16 0.9300 . ?
C17 C18 1.390(3) . ?
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C18 C19 1.377(3) . ?
C18 H18 0.9300 . ?
C19 C20 1.398(2) . ?
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C22 H22C 0.9600 . ?
C23 C24 1.380(2) . ?
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C9 O2 C10 116.37(13) . . ?
C20 O4 C21 110.46(13) . . ?
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C26 O6 C27 117.56(12) . . ?
C2 C1 H1 180.0 . . ?
C1 C2 C3 177.49(18) . . ?
O1 C3 C2 108.49(11) . . ?
O1 C3 H3A 110.0 . . ?
C2 C3 H3A 110.0 . . ?
O1 C3 H3B 110.0 . . ?
C2 C3 H3B 110.0 . . ?
H3A C3 H3B 108.4 . . ?
O1 C4 C5 118.43(11) . . ?
O1 C4 C26 121.05(11) . . ?
C5 C4 C26 120.22(11) . . ?
C4 C5 C23 119.14(12) . . ?
C4 C5 C6 120.56(11) . . ?
C23 C5 C6 120.00(11) . . ?
N1 C6 C14 122.38(11) . . ?
N1 C6 C5 113.32(11) . . ?
C14 C6 C5 124.28(11) . . ?
C8 N1 C6 118.76(11) . . ?
N1 C8 C12 123.05(12) . . ?

N1 C8 C9 115.35(11) . . ?
C12 C8 C9 121.57(12) . . ?
O3 C9 O2 123.93(13) . . ?
O3 C9 C8 124.89(13) . . ?
O2 C9 C8 111.17(12) . . ?
O2 C10 C11 111.66(14) . . ?
O2 C10 H10A 109.3 . . ?
C11 C10 H10A 109.3 . . ?
O2 C10 H10B 109.3 . . ?
C11 C10 H10B 109.3 . . ?
H10A C10 H10B 107.9 . . ?
C10 C11 H11A 109.5 . . ?
C10 C11 H11B 109.5 . . ?
H11A C11 H11B 109.5 . . ?
C10 C11 H11C 109.5 . . ?
H11A C11 H11C 109.5 . . ?
H11B C11 H11C 109.5 . . ?
C13 C12 C8 118.26(12) . . ?
C13 C12 H12 120.9 . . ?
C8 C12 H12 120.9 . . ?
C12 C13 C14 120.38(12) . . ?
C12 C13 C21 122.53(13) . . ?
C14 C13 C21 117.09(13) . . ?
C13 C14 C6 116.94(12) . . ?
C13 C14 C15 116.52(12) . . ?
C6 C14 C15 126.49(12) . . ?
C20 C15 C16 118.37(13) . . ?
C20 C15 C14 116.54(12) . . ?
C16 C15 C14 125.09(13) . . ?
C17 C16 C15 119.68(15) . . ?
C17 C16 H16 120.2 . . ?
C15 C16 H16 120.2 . . ?
C16 C17 C18 121.30(16) . . ?
C16 C17 H17 119.4 . . ?
C18 C17 H17 119.4 . . ?
C19 C18 C17 120.01(15) . . ?
C19 C18 H18 120.0 . . ?
C17 C18 H18 120.0 . . ?
O5 C19 C18 125.68(15) . . ?
O5 C19 C20 115.26(16) . . ?
C18 C19 C20 119.05(16) . . ?
O4 C20 C19 117.50(13) . . ?
O4 C20 C15 121.03(13) . . ?

C19 C20 C15 121.46(15) . . ?
O4 C21 C13 109.67(15) . . ?
O4 C21 H21A 109.7 . . ?
C13 C21 H21A 109.7 . . ?
O4 C21 H21B 109.7 . . ?
C13 C21 H21B 109.7 . . ?
H21A C21 H21B 108.2 . . ?
O5 C22 H22A 109.5 . . ?
O5 C22 H22B 109.5 . . ?
H22A C22 H22B 109.5 . . ?
O5 C22 H22C 109.5 . . ?
H22A C22 H22C 109.5 . . ?
H22B C22 H22C 109.5 . . ?
C24 C23 C5 120.09(13) . . ?
C24 C23 H23 120.0 . . ?
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C23 C24 C25 120.95(12) . . ?
C23 C24 H24 119.5 . . ?
C25 C24 H24 119.5 . . ?
C24 C25 C26 119.58(12) . . ?
C24 C25 H25 120.2 . . ?
C26 C25 H25 120.2 . . ?
O6 C26 C25 124.43(12) . . ?
O6 C26 C4 115.70(11) . . ?
C25 C26 C4 119.86(12) . . ?
O6 C27 H27A 109.5 . . ?
O6 C27 H27B 109.5 . . ?
H27A C27 H27B 109.5 . . ?
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H27A C27 H27C 109.5 . . ?
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