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Tf_2O-Promoted Morgan–Walls Reaction: from A Flexible Approach to Functionalized Phenanthridines and Quinazolines to the Short and Divergent Total Syntheses of Alkaloids

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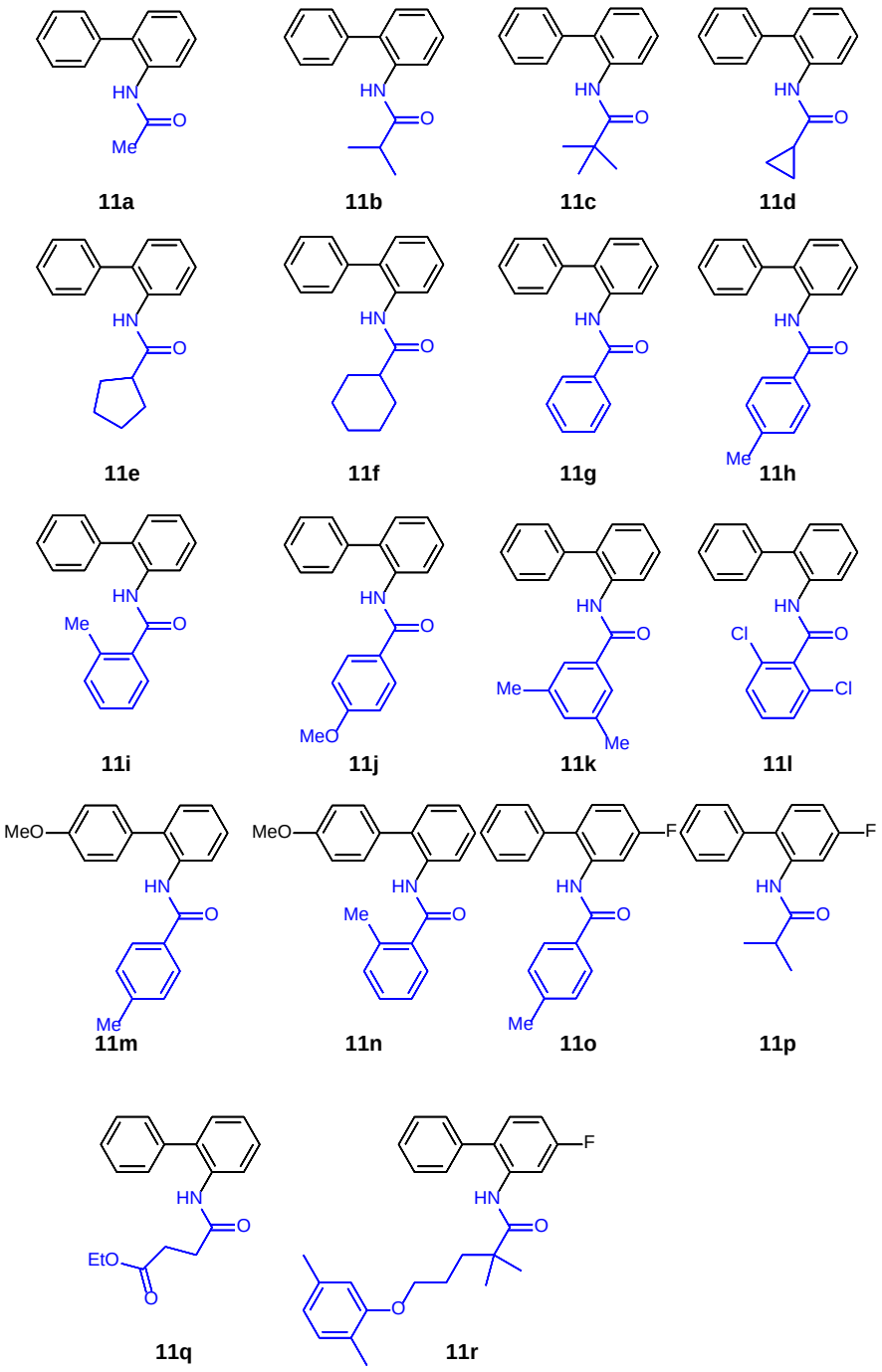
1. General Methods

NMR spectra were recorded on a Bruker Avance 400 MHz or 500 MHz instrument and were calibrated using residual undeuterated solvent ($CHCl_3$ at 7.26 ppm ^1H NMR, 77 ppm ^{13}C NMR) [multiplicity, coupling constant (s) J (Hz), relative integral], where multiplicity is defined as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, or combinations thereof. IR spectra were recorded on a Nicolet iS50 FT-IR spectrometer using film KBr pellet techniques. High-resolution mass spectrometry (HRMS) was performed using positive electrospray ionization (ESI+) on a Single Quadrupole Exactive LC/MS and orbitrap Mass Detector. Silica gel (300 − 400 mesh) was used for flash column chromatography, eluting (unless otherwise stated) with EtOAc/n-hexane mixture. Solvent compositions were mixed in v/v as specified. Trifluoromethanesulfonic anhydride (Tf_2O) was distilled over phosphorous pentoxide and was stored for no more than a week before use. Dichloromethane (DCM) was distilled over calcium hydride under N_2 atmosphere. All other commercially available compounds were used as received.

1.1. Table S1. The structure of all amide substrates 11



1.2. Synthesis of amides 11a – 11e, 11g – 11q, 11s – 11w, 11y – 11z

Amides **11a** – **11e**, **11g** – **11q**, **11s** – **11w**, **11y** – **11z** were prepared by a known protocol.[1-8]

***N*-([1,1-Biphenyl]-2-yl)acetamide (11a)[1]**

Mp 121–123 °C (lit.[1] mp 119.8–120.0 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.05 (s, 3H), 7.14 – 7.31 (m, 2H), 7.37 – 7.44 (m, 1H), 7.46 (m, 4H), 7.52 (t, *J* = 7.4 Hz, 2H), 8.29 (d, *J* = 8.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.6, 121.6, 124.4, 127.9, 128.4, 129.1, 129.2, 130.0, 134.6, 138.1, 168.2 ppm.

***N*-([1,1'-Biphenyl]-2-yl)isobutyramide (11b)[2]**

Mp 134.3–134.7 °C (lit.[3] mp 135.0–137.0 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.10 (d, *J* = 6.9 Hz, 6H), 2.25 – 2.40 (m, 1H), 7.17 (d, *J* = 7.4 Hz, 2H), 7.25 (d, *J* = 9.5 Hz, 2H), 7.32 – 7.53 (m, 6H), 8.32 (d, *J* = 8.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.3, 36.7, 121.3, 124.1, 128.0, 128.4, 129.0, 129.3, 129.9, 134.9, 138.1, 174.8 ppm.

***N*-([1,1-Biphenyl]-2-yl)pivalamide (11c)[2]**

Mp 66.5–66.7 °C (lit.[3] mp 66.0–68.0 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.09 (s, 9H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.20 – 7.28 (m, 1H), 7.32 – 7.54 (m, 7H), 8.36 (d, *J* = 8.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.3, 39.8, 120.9, 123.9, 128.0, 128.5, 129.0, 129.3, 129.7, 132.2, 135.1, 138.1, 176.3 ppm.

***N*-([1,1-Biphenyl]-2-yl)cyclopropanecarboxamide (11d)**

Mp 115.5-115.9 °C. IR (KBr): 3228, 1655, 1583, 1518, 1493, 1479, 1436, 1390, 1300, 1280, 1197, 1179, 1099, 1030, 1010, 956, 754, 701 cm^{-1}.^{1}H NMR (400 MHz, $CDCl_3$): δ 0.70 – 0.80 (m, 2H), 0.98 – 1.06 (m, 2H), 1.24 (s, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.19 – 7.28 (m, 1H), 7.30 – 7.46 (m, 5H), 7.49 (t, *J* = 7.2 Hz, 2H), 8.32 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 7.8, 15.8, 121.2, 123.9, 127.9, 128.4, 129.1, 129.3, 130.0, 134.9, 138.2, 171.7 ppm. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{16}H_{15}NO$: 238.1226; found: 238.1228.

***N*-([1,1-Biphenyl]-2-yl)cyclopentanecarboxamide (11e)**

Mp 119.0–119.3 °C. IR (KBr): 3228, 2958, 1647, 1599, 1583, 1530, 1479, 1448, 1434, 1383, 1272, 1239, 1009, 775, 748, 699 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.46 –

1.60 (m, 2H), 1.62 – 1.85 (m, 7H), 2.48 (p, *J* = 8.0 Hz, 1H), 7.08 – 7.27 (m, 3H), 7.31 – 7.55 (m, 6H), 8.31 (d, *J* = 8.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.8, 30.1, 46.9, 121.3, 124.0, 127.9, 128.4, 129.0, 129.3, 129.9, 132.0, 135.0, 138.2, 174.2 ppm. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{18}H_{19}NO$: 266.1539; found: 266.1541.

***N*-([1,1-Biphenyl]-2-yl)benzamide (11g)[4]**

Mp 89.2–89.6 °C (lit.[4] mp 91.0 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (t, *J* = 7.5 Hz, 1H), 7.32 – 7.39 (m, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.45 – 7.60 (m, 7H), 7.66 (d, *J* = 7.2 Hz, 2H), 8.10 (s, 1H), 8.58 (d, *J* = 8.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 121.2, 124.3, 126.7, 128.1, 128.5, 128.6, 129.1, 129.2, 129.9, 131.6, 132.4, 134.6, 134.8, 138.0, 164.9 ppm.

***N*-([1,1-Biphenyl]-2-yl)-4-methylbenzamide (11h)[5]**

Mp 110.0–110.6 °C (lit.[5] mp 108.0–109.0 °C) . ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 3H), 7.14 – 7.23 (m, 3H), 7.29 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.37 – 7.55 (m, 8H), 7.98 (s, 1H), 8.53 (d, *J* = 8.1 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.6, 121.6, 124.4, 127.9, 128.4, 129.1, 129.2, 130.0, 134.6, 138.1, 168.2 ppm.

***N*-([1,1-Biphenyl]-2-yl)-2-methylbenzamide (11i)[6]**

Mp 93.0–93.5 °C (lit.[6] mp 90.0–90.1 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.45 (s, 3H), 7.16 – 7.36 (m, 6H), 7.41 – 7.53 (m, 6H), 7.56 (s, 1H), 8.52 (d, *J* = 8.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.8, 121.6, 124.6, 125.8, 126.4, 128.0, 128.5, 129.0, 129.2, 130.1, 130.2, 131.3, 132.8, 134.8, 136.2, 136.5, 138.1, 167.8 ppm.

***N*-([1,1-Biphenyl]-2-yl)-4-methoxybenzamide (11j)[5]**

Mp 133.3–134.3 °C (lit.[5] mp 131.0–132.0 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.82 (s, 3H), 6.86 (d, *J* = 8.5 Hz, 2H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.38 – 7.59 (m, 8H), 7.92 (s, 1H), 8.52 (d, *J* = 8.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.4, 113.9, 121.0, 124.1, 127.0, 128.1, 128.5, 128.6, 129.2, 129.3, 129.9, 132.1, 135.1, 138.1, 162.3, 164.5 ppm.

***N*-([1,1'-Biphenyl]-2-yl)-3,5-dimethylbenzamide (11k)**

Mp 106.6–107.1 °C. IR (KBr): 3425, 2918, 1678, 1605, 1583, 1519, 1493, 1447, 1437, 1382, 1316, 788, 756, 704, 680 cm^{-1}.^{1}H NMR (400 MHz, $CDCl_3$): δ 2.33 (s, 6H), 7.14

(s, 1H), 7.21 – 7.32 (m, 3H), 7.35 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.43 – 7.53 (m, 4H), 7.53 – 7.61 (m, 2H), 8.02 (s, 1H), 8.58 (d, *J* = 8.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.2, 120.9, 124.2, 124.6, 128.1, 128.6, 129.1, 129.5, 129.8, 132.2, 133.3, 134.8, 135.1, 138.1, 138.4, 165.3 ppm. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{21}H_{19}NO$: 302.1539; found: 302.1540.

***N*-([1,1'-Biphenyl]-2-yl)-2,6-dichlorobenzamide (11l)**

Mp 178.0–178.6 °C. IR (KBr): 3215, 1958, 1647, 1517, 1478, 1451, 1430, 1295, 1192, 1150, 1086, 1008, 914, 799, 787, 775, 750, 741, 702, 693 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 – 7.37 (m, 6H), 7.40 (t, *J* = 6.8 Hz, 1H), 7.43 – 7.55 (m, 5H), 8.47 (d, *J* = 8.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ122.4, 125.3, 128.0, 128.1, 128.5, 128.9, 129.6, 130.4, 130.8, 132.2, 133.0, 133.9, 135.9, 137.6, 162.6 ppm. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{19}H_{13}Cl_2NO$: 342.0447; found: 342.0448.

***N*-(4'-Methoxy-[1,1'-biphenyl]-2-yl)-4-methylbenzamide (11m)[7]**

Mp 121.7–122.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.37 (s, 3H), 3.87 (s, 3H), 7.03 (d, *J* = 8.6 Hz, 2H), 7.18 (t, *J* = 8.4 Hz, 3H), 7.26 – 7.43 (m, 4H), 7.52 (d, *J* = 8.1 Hz, 2H), 8.00 (s, 1H), 8.51 (d, *J* = 8.1 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.4, 55.4, 114.6, 121.0, 124.1, 126.8, 128.3, 129.4, 130.1, 130.2, 130.5, 131.9, 132.0, 135.2, 142.2, 159.4 ppm.

***N*-(4'-Methoxy-[1,1'-biphenyl]-2-yl)-2-methylbenzamide (11n)**

Mp 113.0–113.2 °C. IR (KBr): 3409, 3300, 1678, 1611, 1582, 1516, 1443, 1302, 1268, 1246, 1177, 1035, 833, 804, 759, 741 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.42 (s, 3H), 3.83 (s, 3H), 6.97 (d, *J* = 8.0 Hz, 2H), 7.11 – 7.20 (m, 2H), 7.23 – 7.35 (m, 6H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.53 (s, 1H), 8.47 (d, *J* = 8.1 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.9, 55.3, 114.5, 121.4, 124.5, 125.9, 126.4, 128.2, 130.2, 130.2, 130.3, 130.4, 131.3, 132.3, 135.1, 136.3, 136.5, 159.4 ppm. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{21}H_{19}NO_2$: 318.1489; found: 318.1489.

***N*-(4-Fluoro-[1,1-biphenyl]-2-yl)-4-methylbenzamide (11o)**

Mp 106.0–107.6 °C. IR (KBr): 3216, 2921, 1682, 1597, 1529, 1493, 1462, 1446, 1424, 1296, 1281, 1252, 1188, 1161, 1117, 1081, 1010, 975, 870, 816, 767, 744, 704, 612 cm^{-}

[1]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.40 (s, 3H), 6.93 (td, *J* = 8.2, 2.7 Hz, 1H), 7.19 – 7.27 (m, 3H), 7.41 – 7.46 (m, 2H), 7.50 (d, *J* = 7.8 Hz, 3H), 7.52 – 7.58 (m, 2H), 8.07 (s, 1H), 8.47 (dd, *J* = 11.4, 2.7 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.4, 107.8, 108.1, 110.6, 110.8, 126.8, 127.6, 127.6, 128.3, 128.9, 129.1, 129.4, 129.5, 130.8, 130.9, 131.6, 136.4, 136.5, 137.3, 142.6, 161.5, 163.5, 164.8 ppm. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{20}H_{16}FNO$: 306.1289; found: 306.1291.

***N*-(4-Fluoro-[1,1'-biphenyl]-2-yl)isobutyramide (11p)**

Mp 109.6–109.9 °C. IR (KBr): 3216, 2966, 1522, 1500, 1478, 1466, 1448, 1096, 856, 819, 765, 701 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.12 (d, *J* = 6.9 Hz, 6H), 2.27 – 2.42 (m, 1H), 6.88 (td, *J* = 8.2, 2.7 Hz, 1H), 7.20 (dd, *J* = 8.5, 6.3 Hz, 1H), 7.29 (s, 2H), 7.32 – 7.40 (m, 2H), 7.41 – 7.49 (m, 1H), 7.49 – 7.57 (m, 2H), 8.26 (dd, *J* = 11.4, 2.7 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.2, 36.7, 108.0, 108.2, 110.5, 110.6, 127.4, 128.2, 129.2, 129.4, 130.8, 130.8, 136.2, 136.3, 137.3, 161.4, 163.4, 174.9 ppm. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{16}H_{16}FNO$: 258.1289; found: 258.1290.

Ethyl 4-([1,1'-biphenyl]-2-ylamino)-4-oxobutanoate (11q)

Mp 81.1–81.2 °C. IR (KBr): 3293, 2981, 1732, 1690, 1585, 1522, 1495, 1448, 1437, 1374, 1349, 1322, 1301, 1280, 1162, 1023, 1010, 757, 703 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.23 (t, *J* = 7.1 Hz, 3H), 2.46 (t, *J* = 6.8 Hz, 2H), 2.64 (t, *J* = 6.7 Hz, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.20 – 7.27 (m, 1H), 7.29 – 7.44 (m, 5H), 7.47 (t, *J* = 7.4 Hz, 2H), 8.23 (d, *J* = 8.1 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.1, 29.1, 31.8, 60.6, 76.7, 77.0, 77.3, 121.7, 124.3, 127.8, 128.2, 128.9, 129.2, 130.0, 132.3, 134.5, 138.0, 169.5, 172.6. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{18}H_{19}NO_3$: 298.1438; found: 298.1440.

***N*-([1,1'-Biphenyl]-2-yl)-4-(*tert*-butyl)benzamide (11s)[5]**

Mp 161.0–162.7 °C (lit.[5] 160.0–161.0 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (s, 9H), 7.21 (td, *J* = 7.4, 1.2 Hz, 1H), 7.27 – 7.31 (m, 1H), 7.37 – 7.49 (m, 6H), 7.50 – 7.56 (m, 4H), 8.00 (s, 1H), 8.56 (dd, *J* = 8.3, 1.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.1, 34.9, 121.0, 124.2, 125.7, 126.7, 128.2, 128.6, 129.2, 129.4, 130.0, 131.9, 155.3, 164.8 ppm.

***N*-([1,1-Biphenyl]-2-yl)-4-chlorobenzamide (11t)[5]**

Mp 105.9–108.0 °C (lit.[5] 104.0–105.0 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (t, *J* = 7.5 Hz, 1H), 7.31 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.44 (t, *J* = 6.2 Hz, 4H), 7.52 (t, *J* = 7.2 Hz, 4H), 7.93 (s, 1H), 8.49 (d, *J* = 8.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 121.1, 124.6, 128.2, 128.3, 128.6, 129.0, 129.2, 129.3, 130.0, 132.4, 133.1, 134.6, 137.9, 163.9 ppm.

***N*-([1,1-Biphenyl]-2-yl)-4-fluorobenzamide (11u)[8]**

Mp 128.5–129.8 °C . ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04 (t, *J* = 8.1 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.30 (d, *J* = 7.5 Hz, 1H), 7.38 – 7.47 (m, 4H), 7.51 (t, *J* = 7.0 Hz, 2H), 7.55 – 7.63 (m, 2H), 7.93 (s, 1H), 8.46 (d, *J* = 8.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 115.6, 115.9, 121.2, 124.5, 128.2, 128.6, 129.1, 129.2, 129.3, 130.0, 130.9, 130.9, 132.4, 134.7, 138.0, 163.5, 163.9, 166.0 ppm.

***N*-([1,1-Biphenyl]-2-yl)-4-(trifluoromethyl)benzamide (11v)[5]**

Mp 130.0 –130.8 °C (lit.[5] 127.0–128.0 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04 (t, *J* = 8.0 Hz, 2H), 7.22 (m, 1H), 7.30 (d, *J* = 7.5 Hz, 1H), 7.38 – 7.47 (m, 4H), 7.51 (t, *J* = 7.0 Hz, 2H), 7.55 – 7.63 (m, 2H), 7.93 (s, 1H), 8.46 (d, *J* = 8.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 121.2, 124.8, 125.8, 127.3, 128.4, 128.7, 129.3, 130.0, 132.6, 134.5, 137.9, 163.6 ppm.

***N*-([1,1-Biphenyl]-2-yl)-4-nitrobenzamide (11w)[5]**

Mp 109.5–110.0 °C (lit.[5] 109.0–110.0°C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (t, *J* = 7.4 Hz, 1H), 7.33 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.39 – 7.57 (m, 6H), 7.74 (d, *J* = 8.7 Hz, 2H), 8.03 (s, 1H), 8.18 – 8.25 (m, 2H), 8.44 (d, *J* = 8.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 121.3, 123.9, 125.1, 127.9, 128.4, 128.6, 129.2, 129.3, 130.1, 132.8, 134.1, 137.7, 140.2, 149.6, 162.9 ppm.

Methyl 4-([1,1'-biphenyl]-2-ylcarbamoyl)benzoate (11y)

Mp 182.3–182.0 °C. IR (KBr): 3242, 1729, 1642, 1530, 1280, 1109, 868, 750, 741, 721, 704 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.93 (s, 3H), 7.23 (d, *J* = 7.4 Hz, 1H), 7.32 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.40 – 7.56 (m, 6H), 7.65 (d, *J* = 8.4 Hz, 2H), 8.04 (t, *J* = 8.8 Hz, 3H), 8.51 (d, *J* = 8.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 52.4, 121.1,

124.7, 126.8, 128.3, 128.6, 129.3, 129.3, 130.0, 132.5, 132.9, 134.6, 137.8, 138.6, 164.0, 166.1 ppm. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{21}H_{17}NO_3$: 332.1281; found: 332.1281.

***N*-([1,1-Biphenyl]-2-yl)-2-naphthamide (11z)**

Mp 90.0–98.9 °C. IR (KBr): 3423, 3358, 2918, 1667, 1617, 1583, 1520, 1493, 1483, 1446, 1435, 1385, 1307, 1131, 1091, 1009, 773, 750, 703 cm^{-1}.^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, *J* = 7.4 Hz, 1H), 7.30 – 7.36 (m, 1H), 7.44 – 7.59 (m, 8H), 7.67 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.83 (dd, *J* = 16.1, 8.1 Hz, 3H), 8.07 (s, 1H), 8.15 (s, 1H), 8.59 (d, *J* = 8.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ115.6, 118.6, 121.2, 123.2, 124.4, 126.8, 127.1, 127.4, 127.6, 127.7, 127.8, 128.2, 128.4, 128.6, 128.6, 128.7, 128.9, 129.0, 129.2, 129.4, 129.9, 130.4, 131.9, 132.4, 132.5, 134.7, 135.0, 138.1, 139.5, 143.4, 165.0 ppm. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{23}H_{17}NO$: 324.1383; found: 324.1384.

1.3. Synthesis of amides 11f, 11x, 11r, and 11aa

Amides **11f**, **11x**, **11r** and **11aa** were prepared by a known protocol. [9-10]

***N*-([1,1-Biphenyl]-2-yl)cyclohexanecarboxamide (11f)**

Mp 133.3–134.1 °C. IR (KBr): 3250, 2928, 2850, 1655, 1518, 1493, 1447, 1436, 1383, 1276, 1130, 1075, 1031, 1009, 747, 701 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.11 – 1.28 (m, 3H), 1.28 – 1.40 (m, 2H), 1.63 (d, *J* = 10.0 Hz, 1H), 1.71 – 1.76 (m, 3H), 1.80 (d, *J* = 9.4 Hz, 2H), 2.00 – 2.10 (m, 1H), 7.13 – 7.27 (m, 3H), 7.33 – 7.39 (m, 3H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 8.30 (d, *J* = 8.3 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.52, 25.62, 29.39, 46.31, 121.53, 124.07, 127.94, 128.36, 128.98, 129.29, 129.89, 132.22, 134.84, 138.16, 173.98 ppm. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{19}H_{21}NO$: 280.1696; found: 280.1697.

***N*-([1,1'-Biphenyl]-2-yl)-5-(2,5-dimethylphenoxy)-2,2-dimethylpentanamide (11r)**

IR (KBr): 3433, 3358, 2954, 2868, 1686, 1615, 1584, 1509, 1492, 1474, 1445, 1414, 1390, 1300, 1284, 1266, 1157, 1130, 1046, 1009, 804, 752, 704, 587 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.09 (s, 6H), 1.54 – 1.63 (m, 2H), 1.63 – 1.75 (m, 2H), 2.13 (s, 3H), 2.29 (s, 3H), 3.83 (t, *J* = 6.1 Hz, 2H), 6.57 (s, 1H), 6.65 (d, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 7.4 Hz, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.21 – 7.28 (m, 1H), 7.33 – 7.43 (m, 4H), 7.47 (t, *J* = 7.3 Hz, 3H), 8.35 (d, *J* = 8.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.8, 21.4, 25.0, 25.2, 37.7, 42.9, 67.8, 111.9, 120.7, 120.9, 123.5, 123.9, 128.1, 128.5, 129.0, 129.3, 129.7, 130.2, 132.2, 135.0, 136.4, 138.1, 156.8, 175.3 ppm. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{27}H_{31}NO_2$: 402.2428; found: 402.2430.

***N*-([1,1'-Biphenyl]-2-yl)-4-cyanobenzamide (11x)[9]**

Mp 134.0–134.5 °C (lit.[9] mp 132.0–134.0 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, *J* = 7.6 Hz, 2H), 7.35 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.42 – 7.52 (m, 4H), 7.55 (dd, *J* = 8.0, 6.3 Hz, 2H), 7.71 (s, 4H), 7.99 (s, 1H), 8.50 (d, *J* = 8.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ115.3, 117.8, 121.2, 125.0, 127.4, 128.4, 128.7, 129.3, 129.3, 130.1, 132.6, 134.2, 137.7, 138.6, 163.1 ppm.

***N*-([1,1'-Biphenyl]-2-yl)benzo[*b*]thiophene-2-carboxamide (11aa)[10]**

Mp 141.1–141.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.33 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.35 – 7.61 (m, 9H), 7.74 – 7.86 (m, 2H), 7.98 (s, 1H), 8.51 (d, *J* = 8.1 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 121.0, 122.7, 124.6, 125.0, 125.1, 125.4, 126.5, 128.3, 128.7, 129.3, 129.4, 130.0, 132.1, 134.5, 137.8, 138.8, 139.0, 141.0, 159.9 ppm.

1.4. General procedure for the synthesis of aniline derivatives via Suzuki coupling reaction[11]

2-(Benzo[*d*][1,3]dioxol-5-yl)aniline (14a)[12]: A suspension of 2-bromoaniline (**16a**, 1.7203 g, 10.0 mmol), 1,3-benzodioxole-5-boronic acid (**15**, 2.4740 g, 15.0 mmol) and $Pd(OAc)_2$ (5.6 mg, 2.5 mol%) in water (20 mL) was stirred at 100 °C for 30 min. The mixture was extracted with EtOAc (20 mL × 3). The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (EA/PE = 1: 10) to afford **14a** (2.0 g, 94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.00 (s, 2H), 6.72 – 6.84 (m, 2H), 6.86 – 6.96 (m, 3H), 7.06 – 7.18 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 101.1, 108.6, 109.6, 115.5, 118.6, 122.4, 127.3, 128.3, 130.4, 133.3, 143.6, 146.7, 147.9 ppm. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{13}H_{11}NO_2$: 214.0863; found: 214.0860.

Aniline derivatives **14b-14c** were prepared by replacing 2-bromoaniline with 2-bromo-*N*-methylaniline (**16b**) and 5-(benzyloxy)-2-bromoaniline (**16c**), respectively.

2-(Benzo[*d*][1,3]dioxol-5-yl)-5-(benzyloxy)aniline (14b): 90% yield. white solid. Mp 129.9—130 ℃. IR (KBr): 3445, 2950, 1645, 1481, 1416, 1111, 1019, 648 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.08 (s, 2H), 6.01 (s, 2H), 6.41 (d, *J* = 2.4 Hz, 1H), 6.48 (dd, *J* = 8.4, 2.5 Hz, 1H), 6.91 (dd, *J* = 13.5, 1.1 Hz, 3H), 7.03 (d, *J* = 8.4 Hz, 1H), 7.32 – 7.52 (m, 5H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 69.9, 101.0, 102.0, 105.0, 108.6, 109.8, 122.4, 127.4, 127.9, 128.6, 131.2, 133.1, 137.2, 144.7, 146.5, 147.9, 159.2 ppm. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{20}H_{17}NO_3$: 320.1281; found: 320.1279.

2-(Benzo[*d*][1,3]dioxol-5-yl)-N-methylaniline (14c): 94% yield. IR (KBr): 3420, 2918, 1599, 1513, 1477, 1459, 1429, 1420, 1319, 1292, 1169, 1105, 1075, 1038, 1018, 741 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.79 (s, 3H), 3.95 (s, 1H), 5.98 (s, 2H), 6.66 (d, *J* = 8.1 Hz, 1H), 6.73 (td, *J* = 7.4, 1.0 Hz, 1H), 6.81 – 6.91 (m, 3H), 7.05 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.20 – 7.28 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.7, 101.0, 108.7, 109.7, 109.9, 116.7, 122.6, 127.2, 128.6, 130.0, 133.2, 146.3, 146.7, 147.9 ppm. HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{14}H_{13}NO_2$: 228.1019; found: 228.1016.

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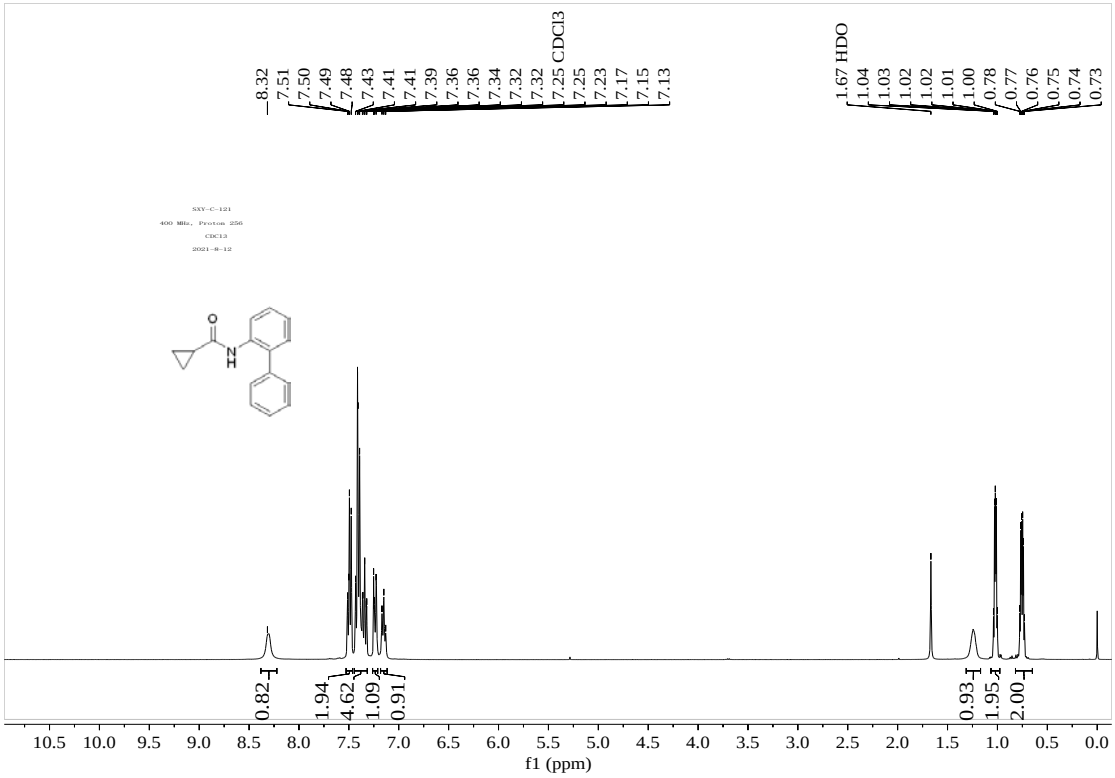
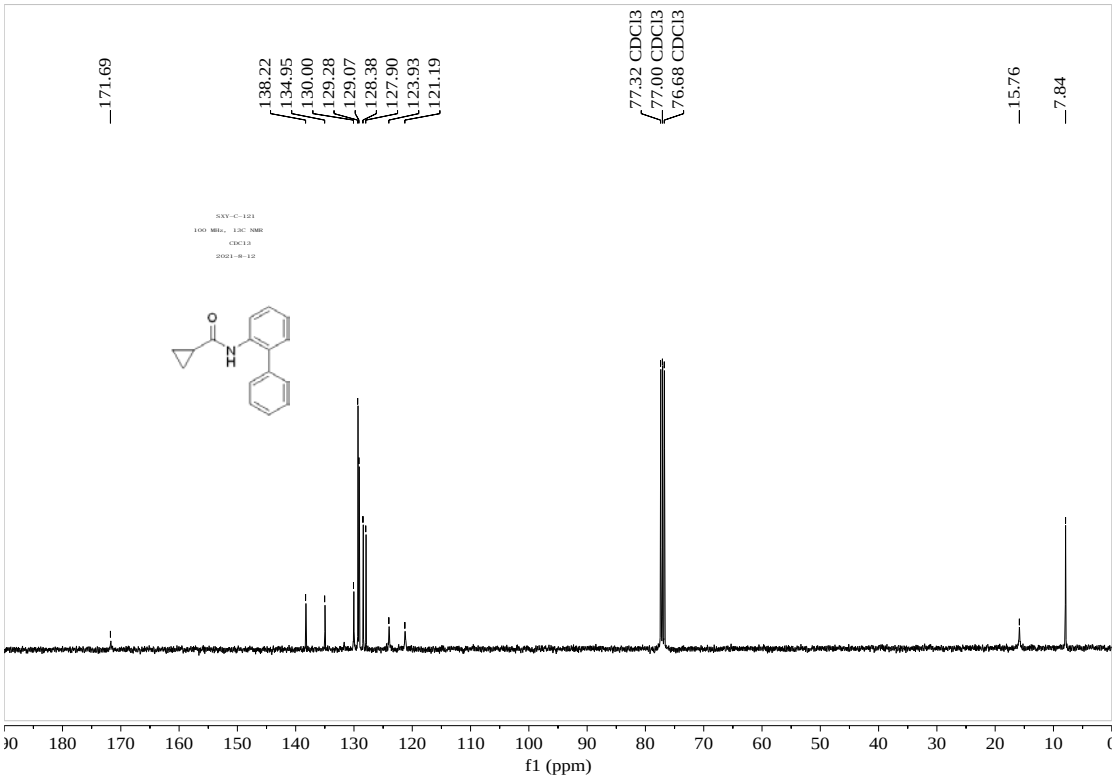
2. Copies of ^{1}H and ^{13}C NMR spectra of new compounds

(1) Compound **11d**





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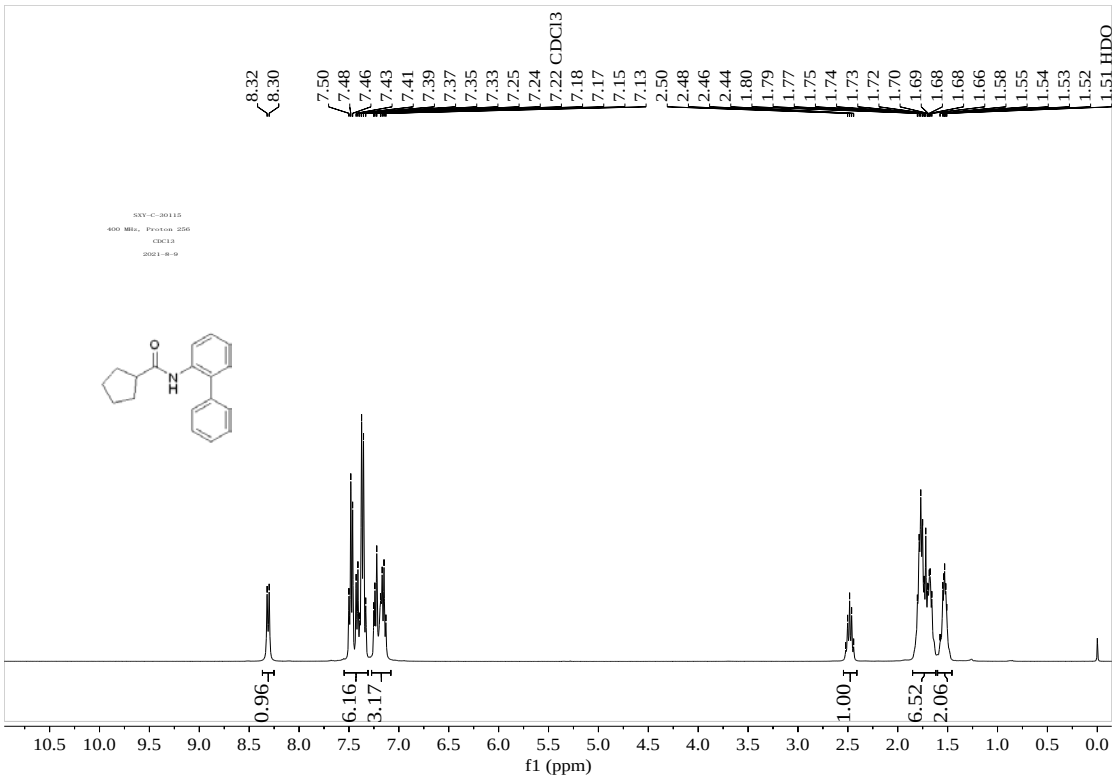
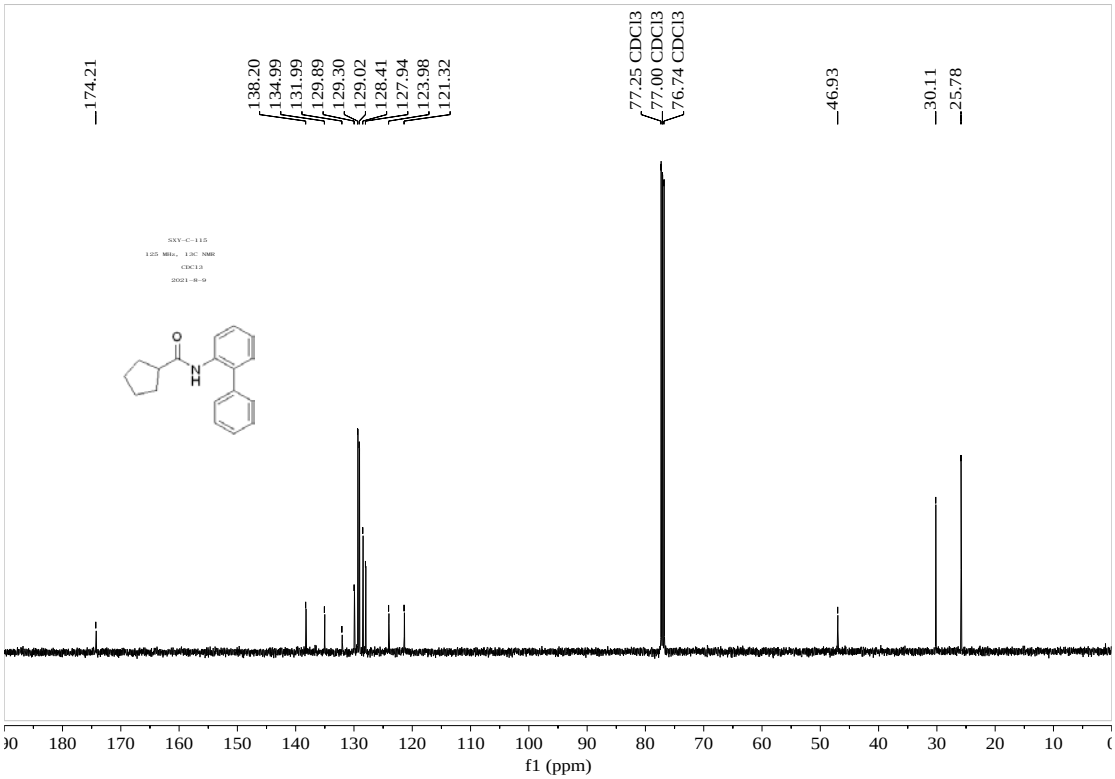
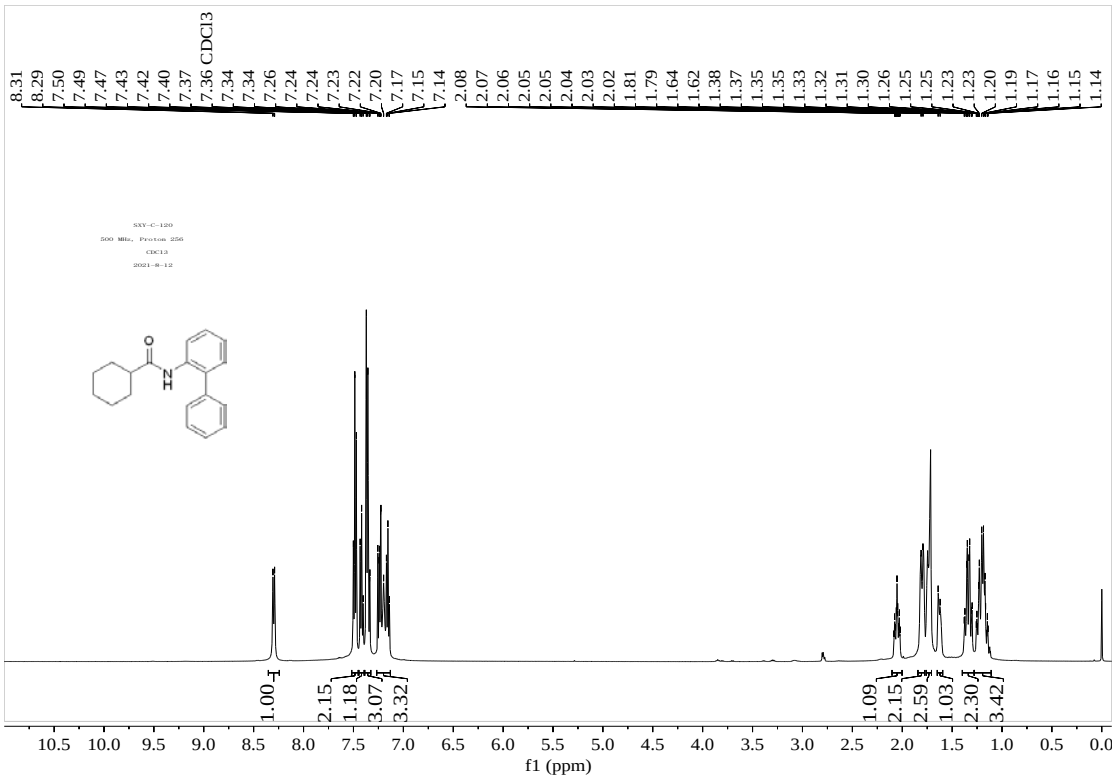
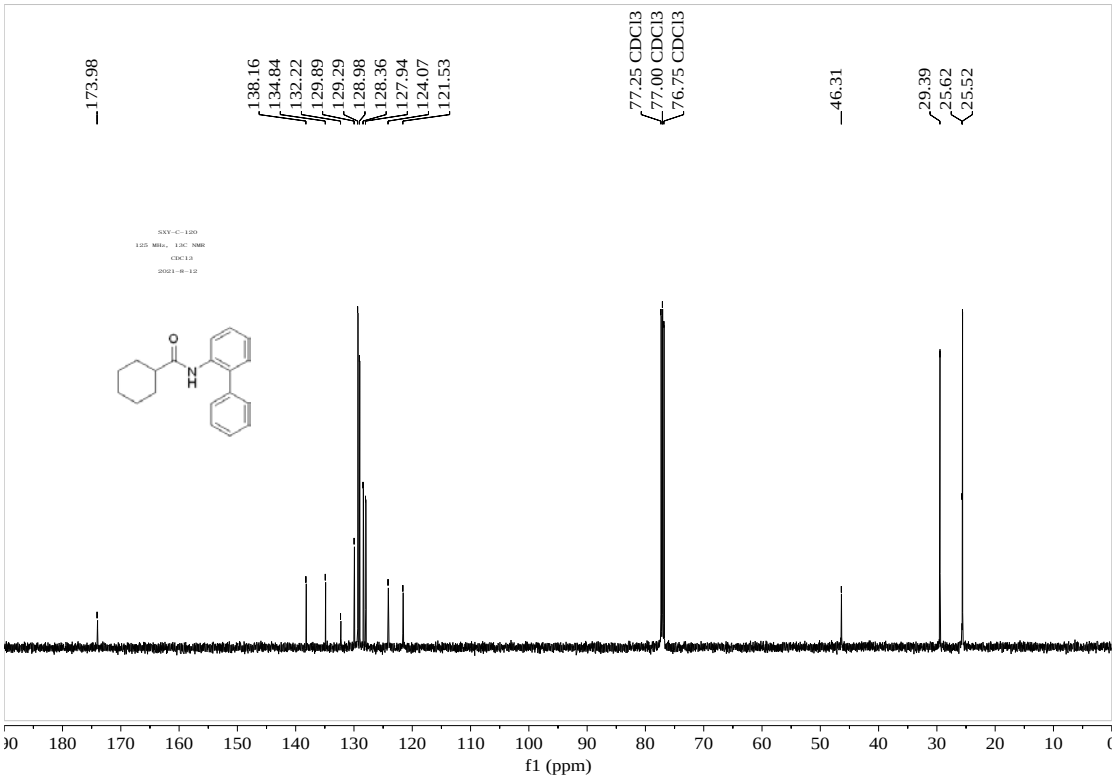




(3) Compound **11f**





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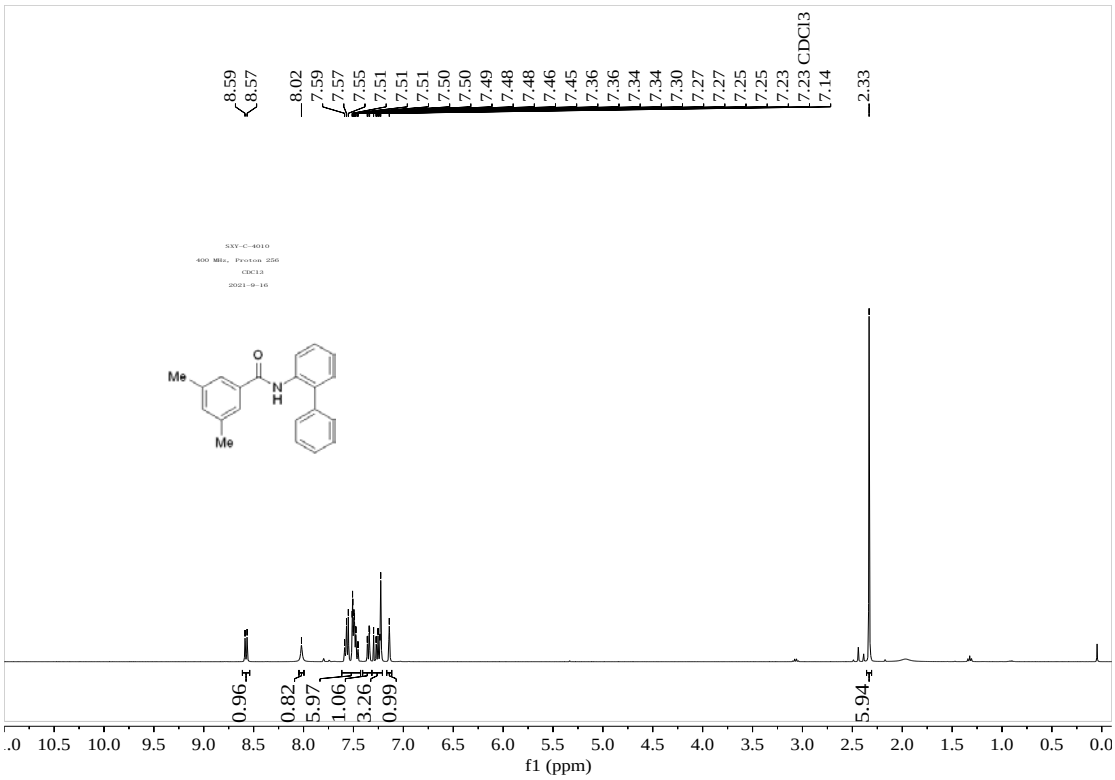

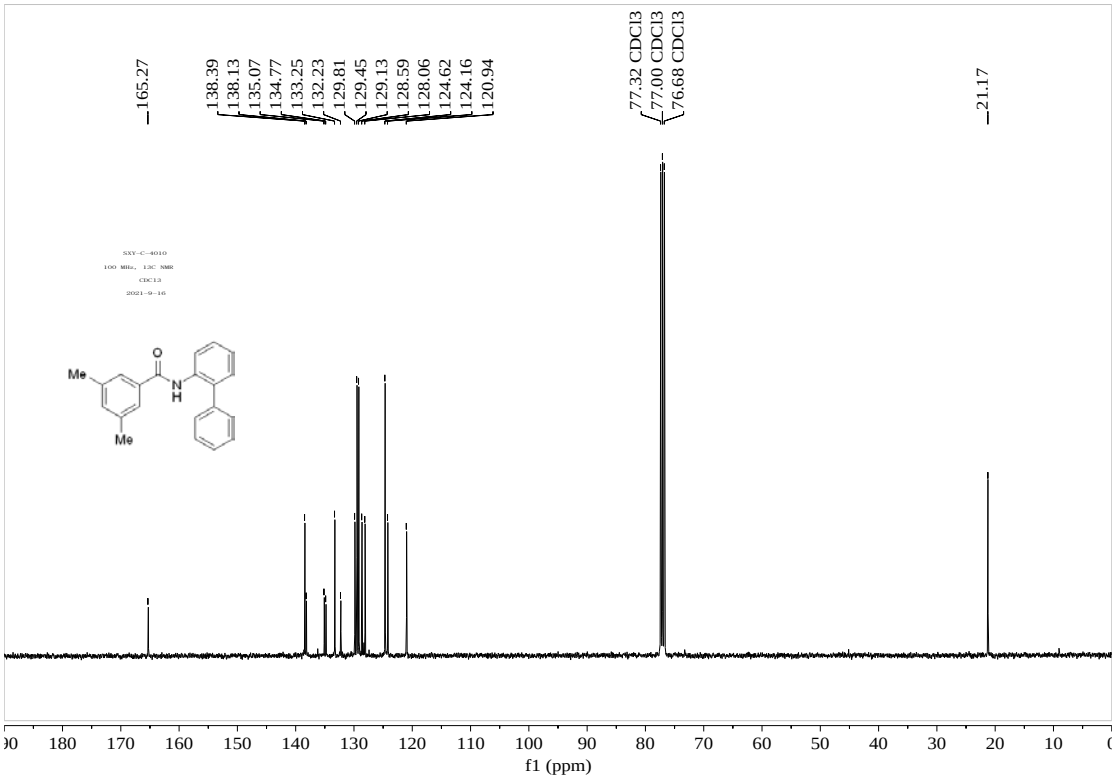

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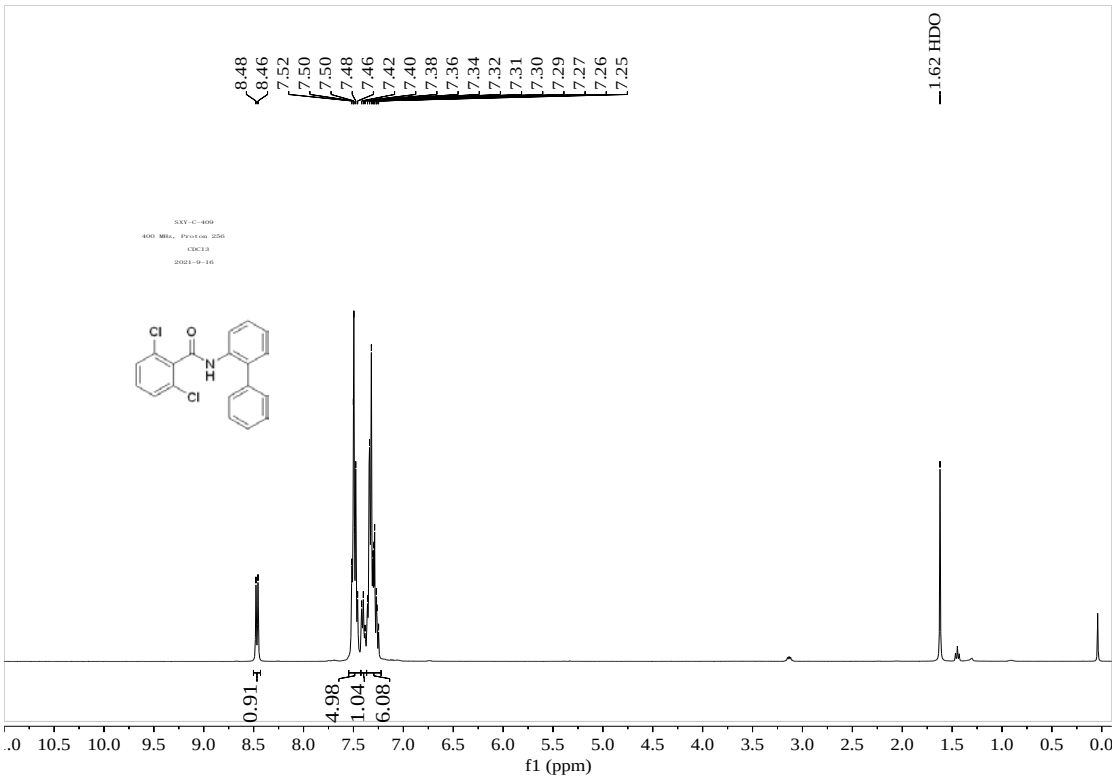

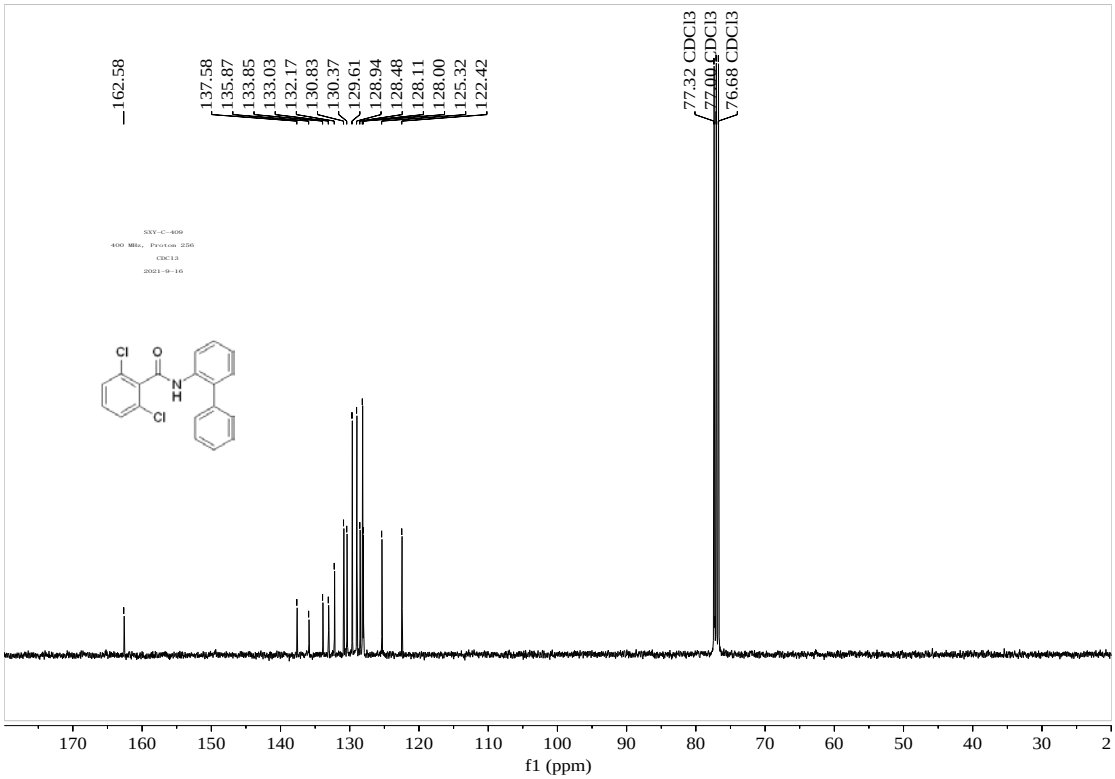

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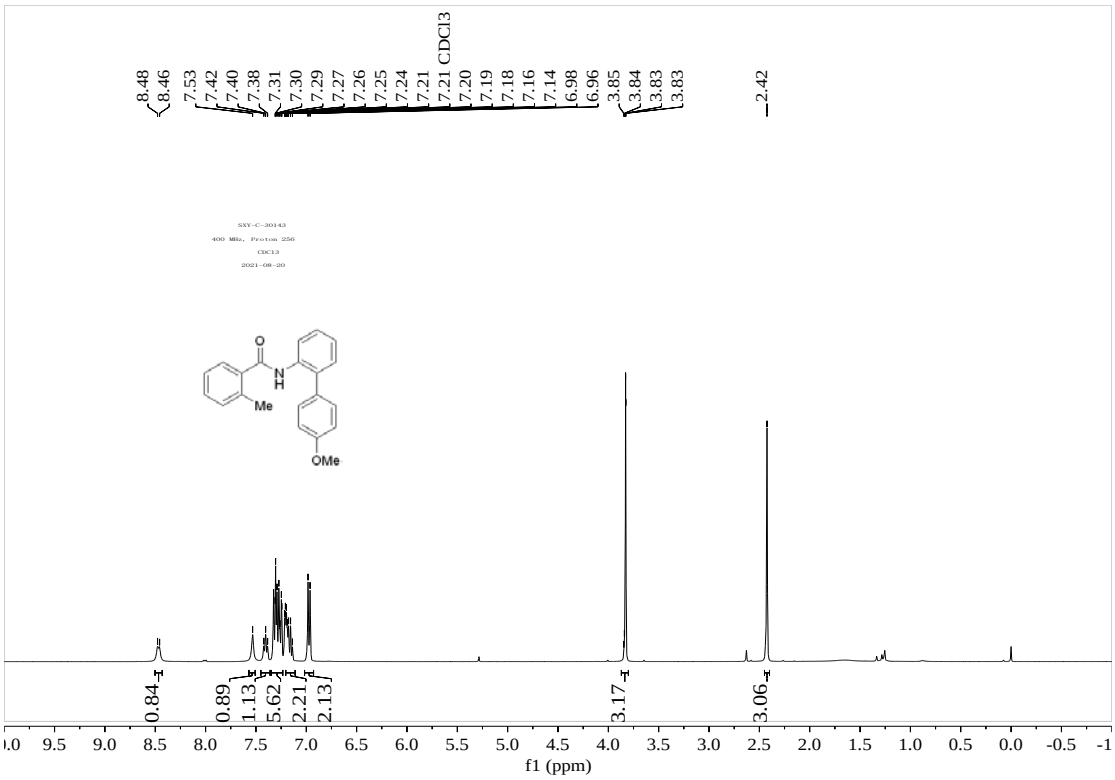

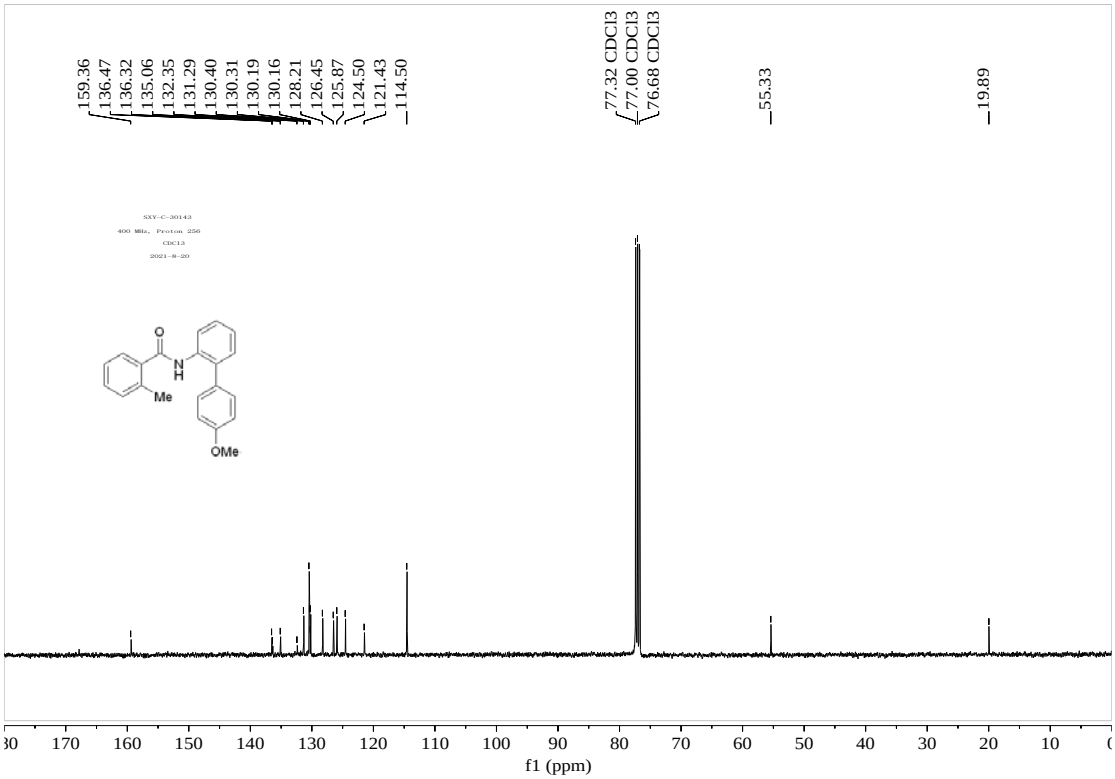

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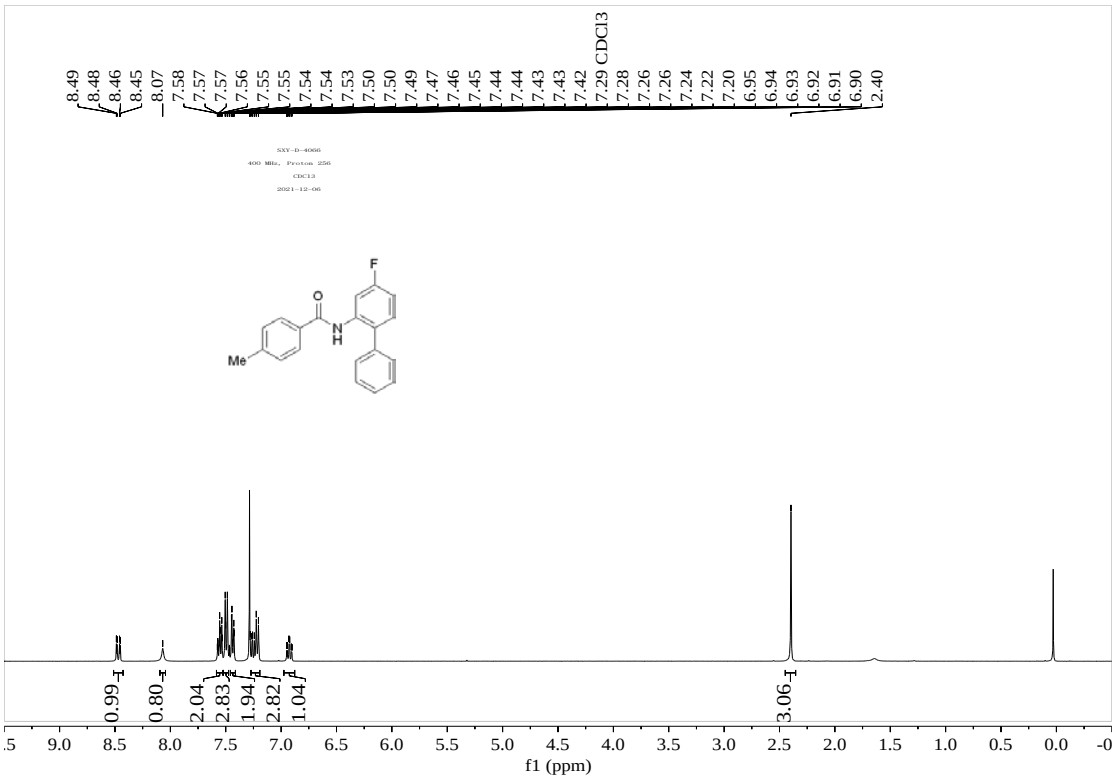

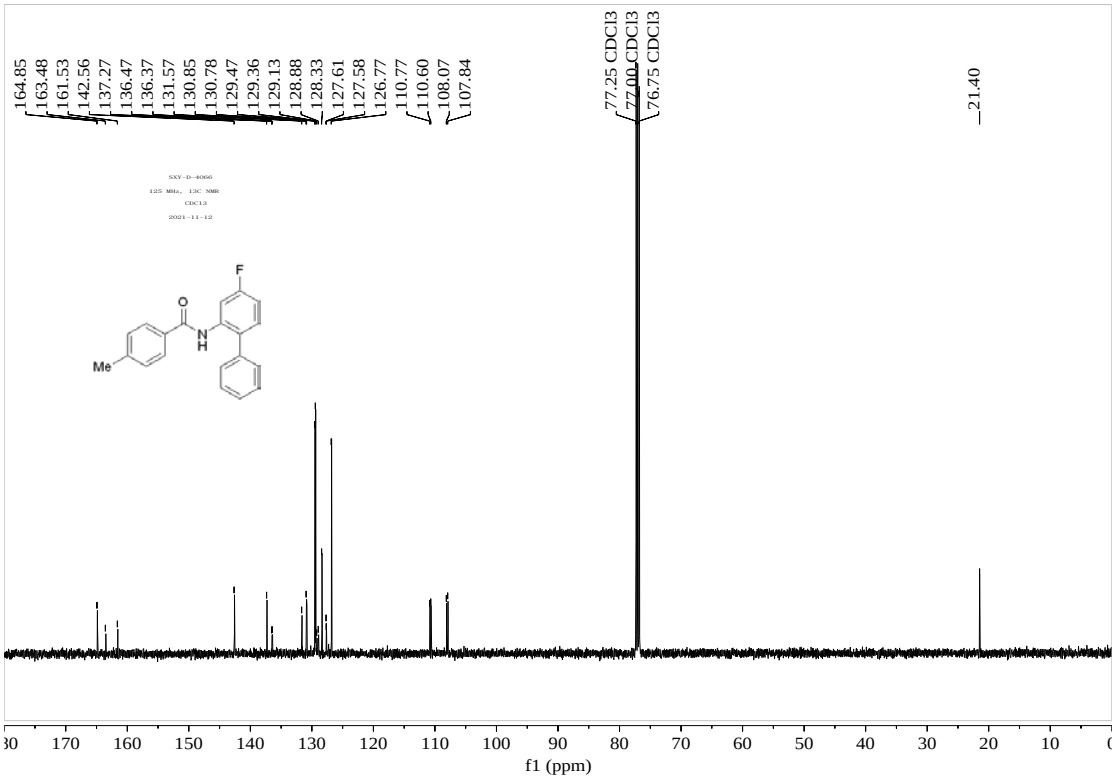

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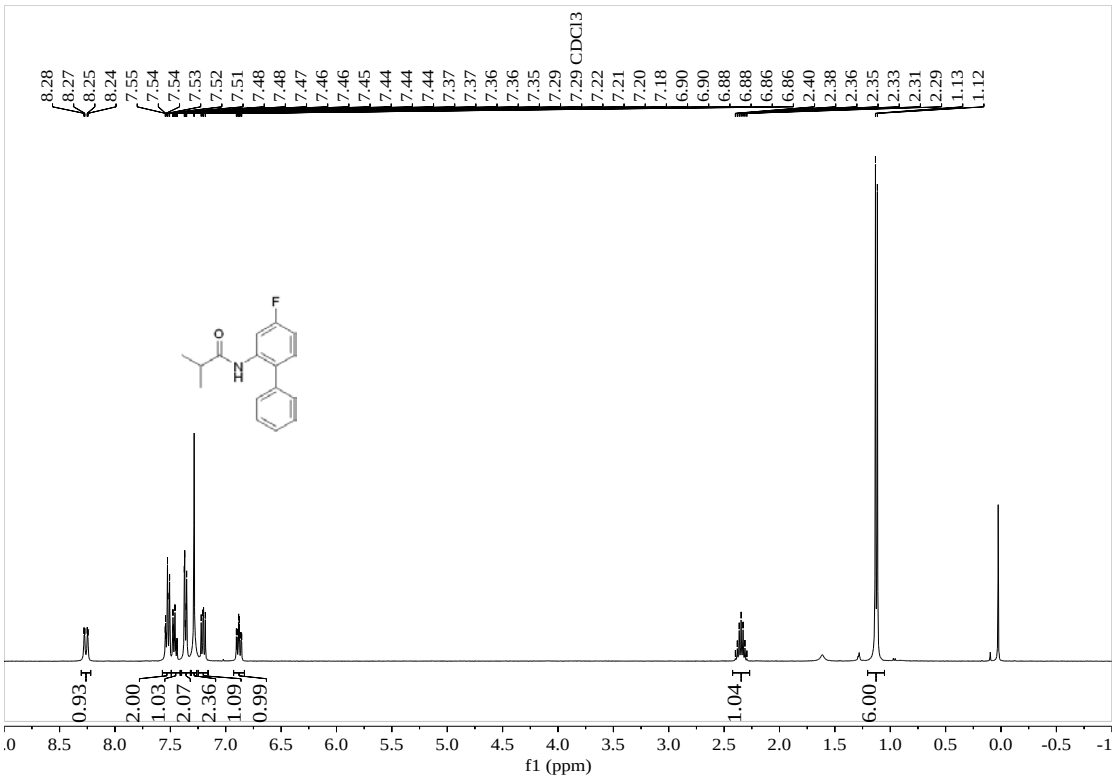

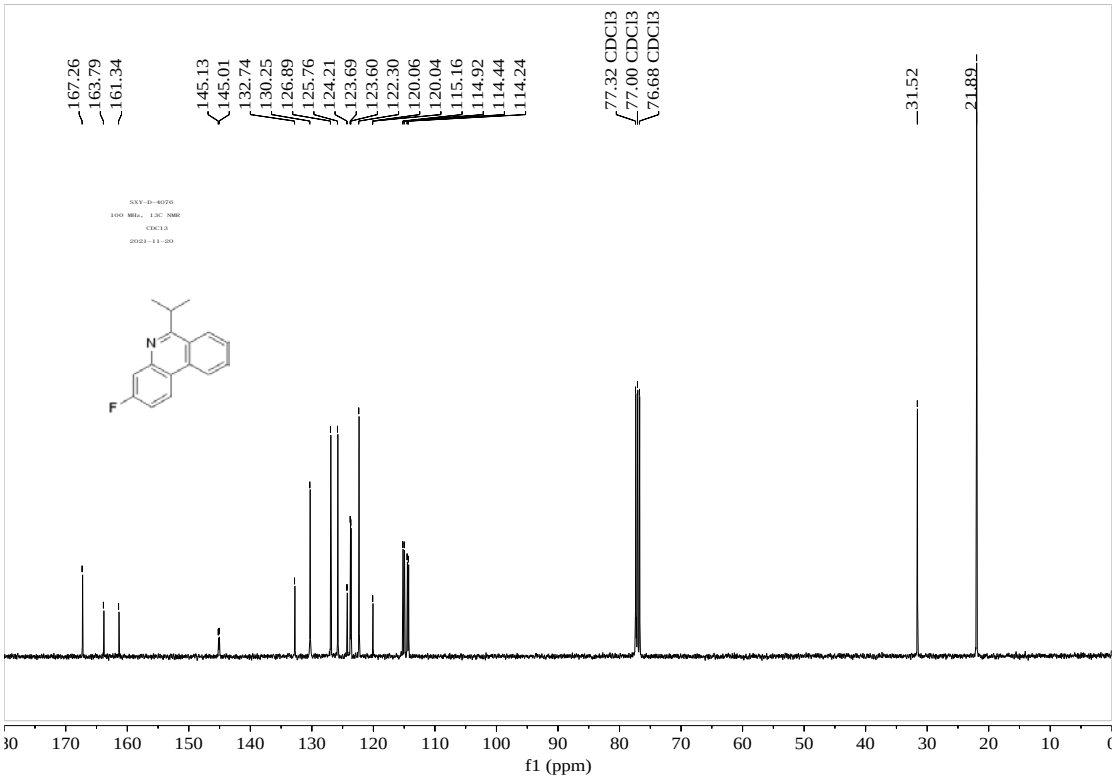

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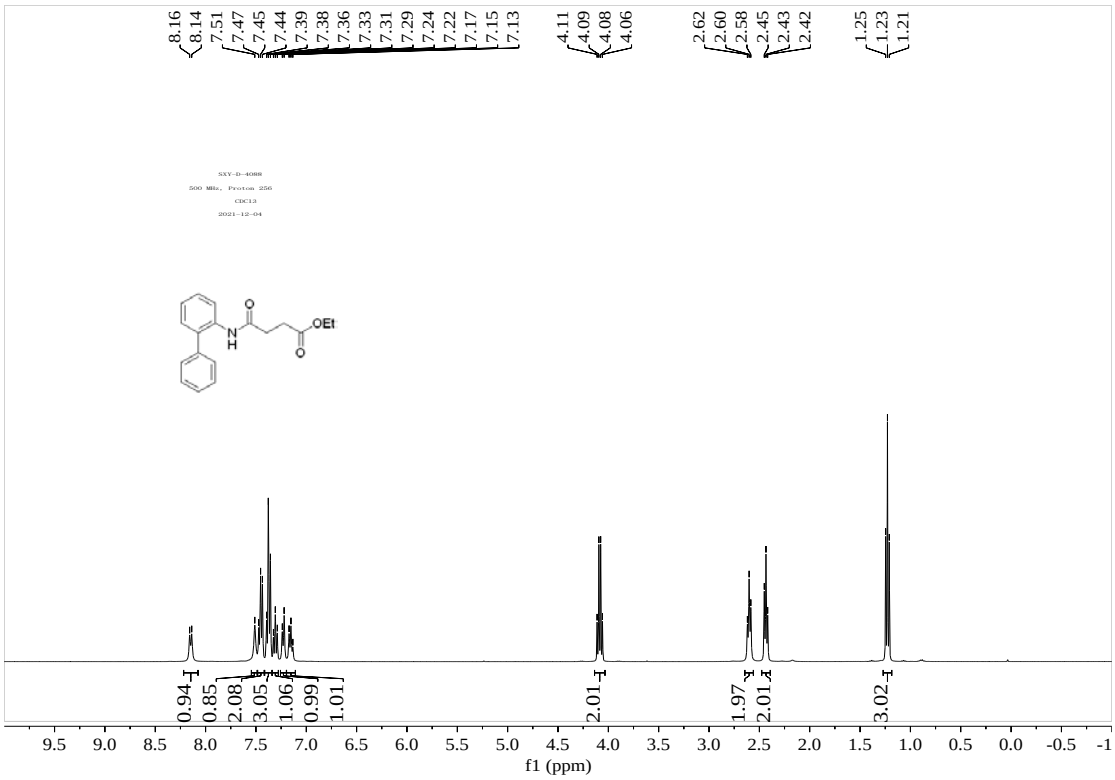
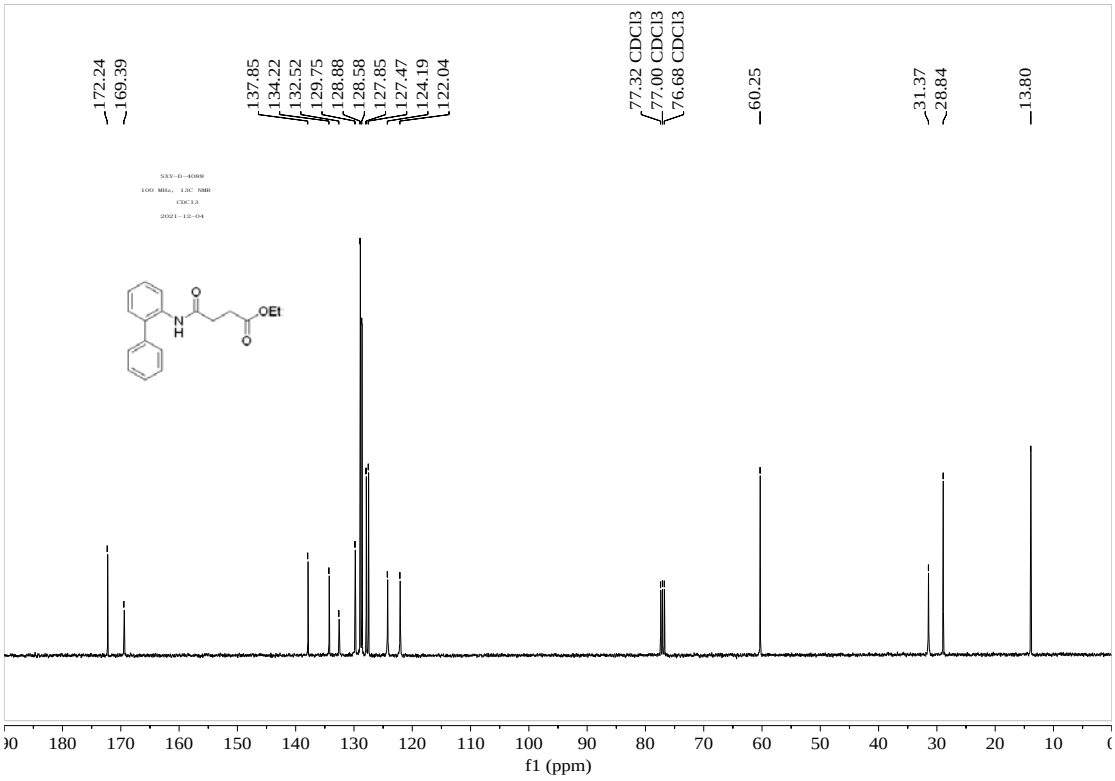
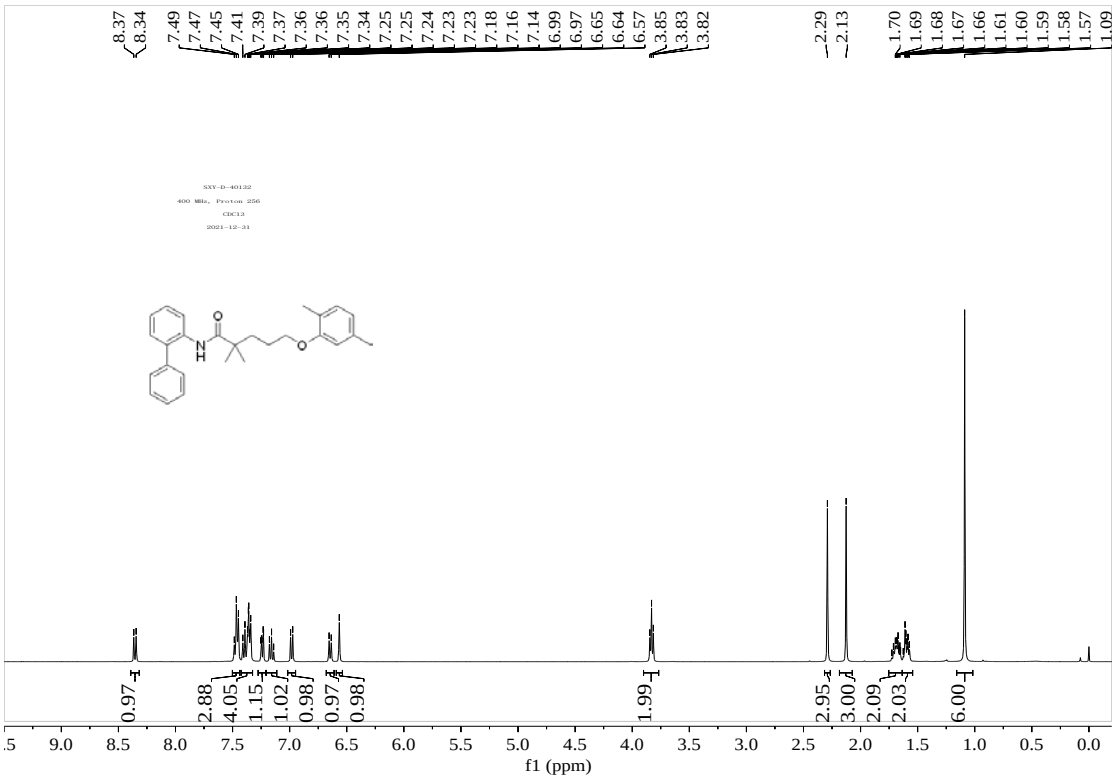
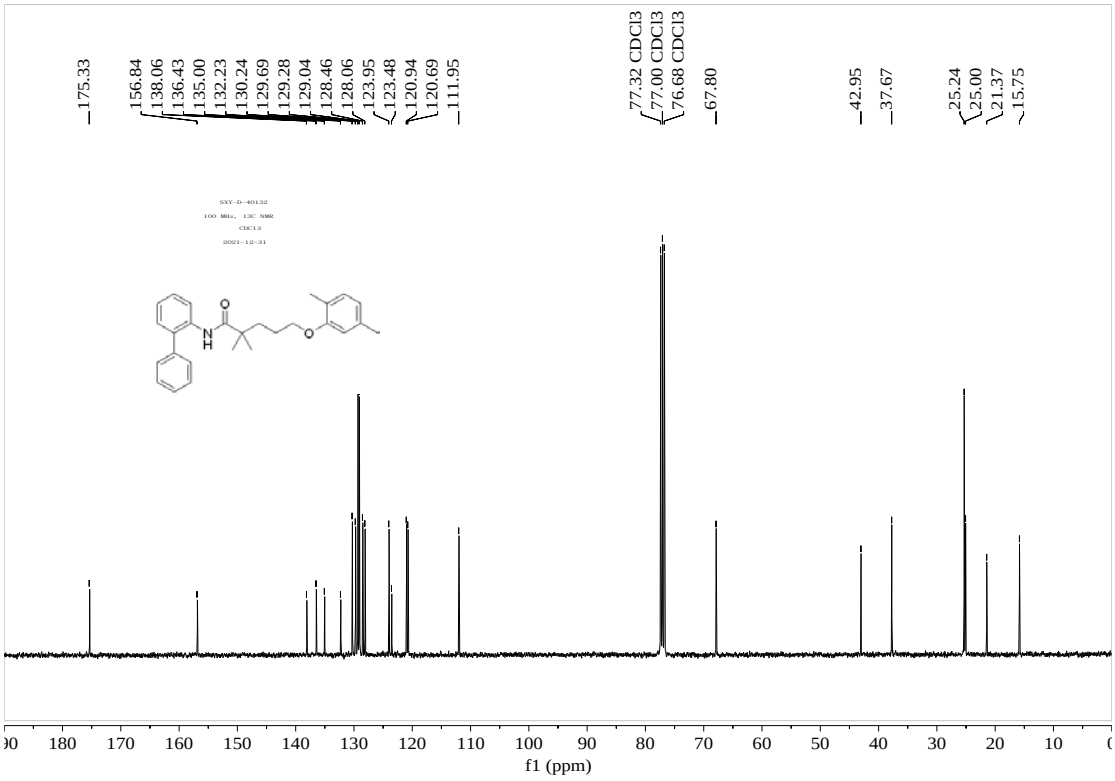




(10) Compound **11r**





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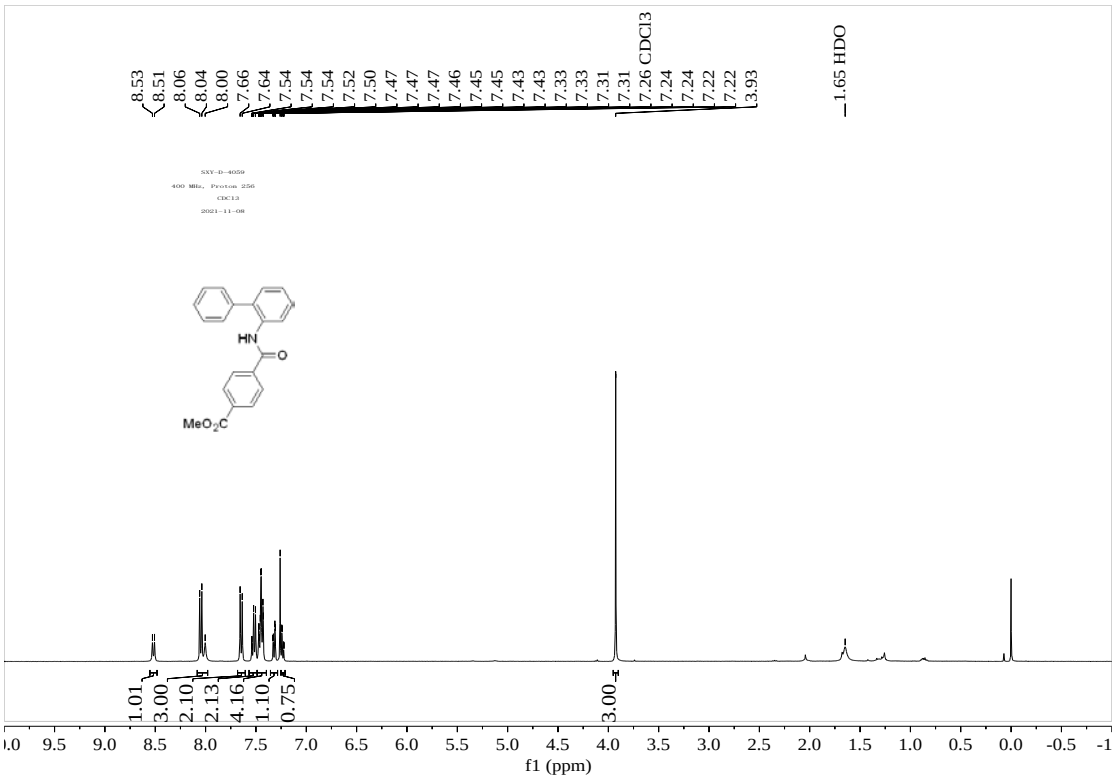

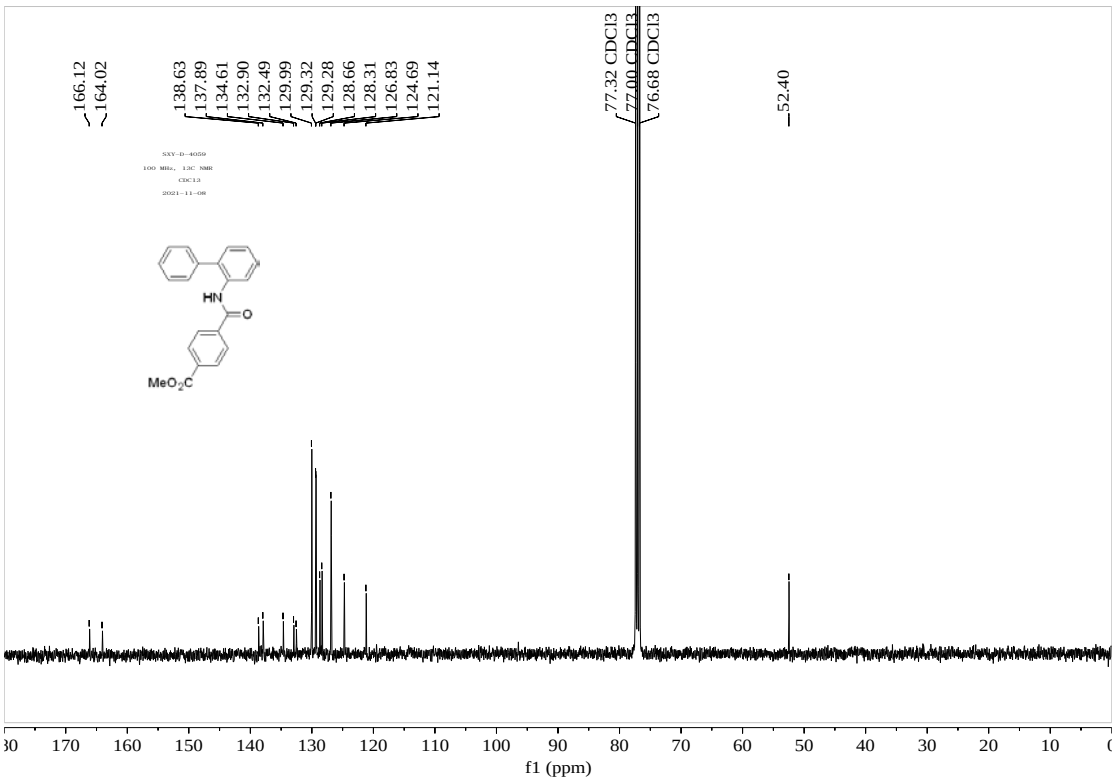

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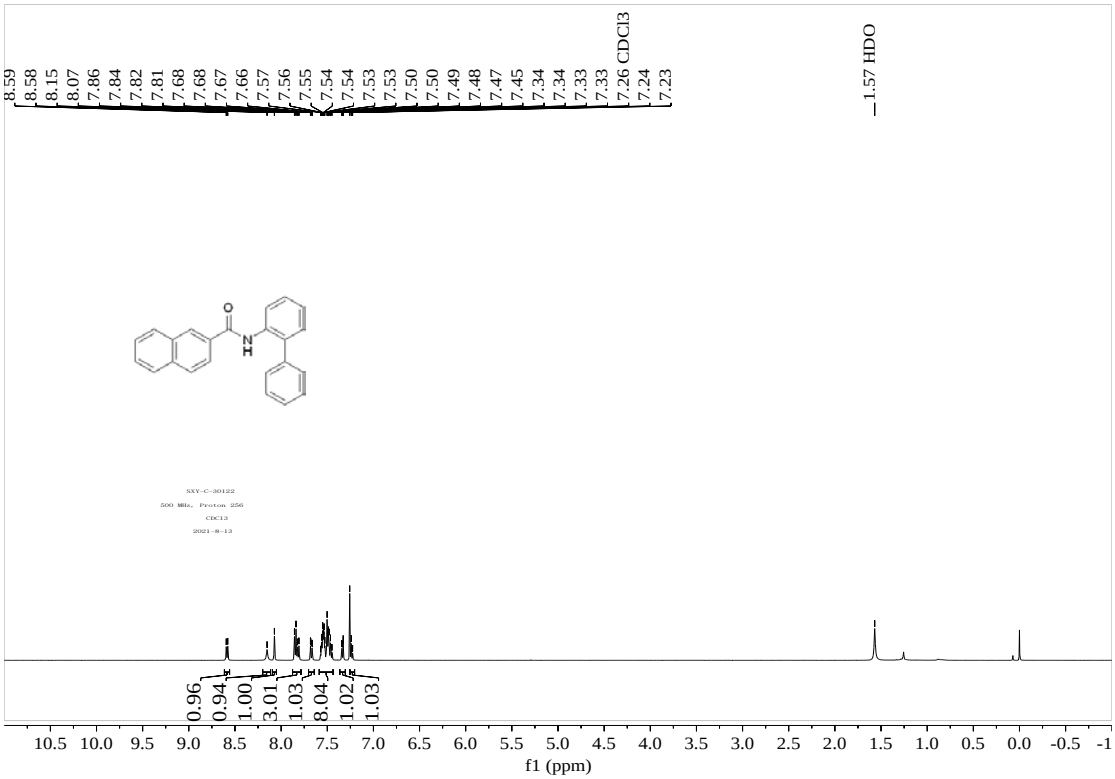

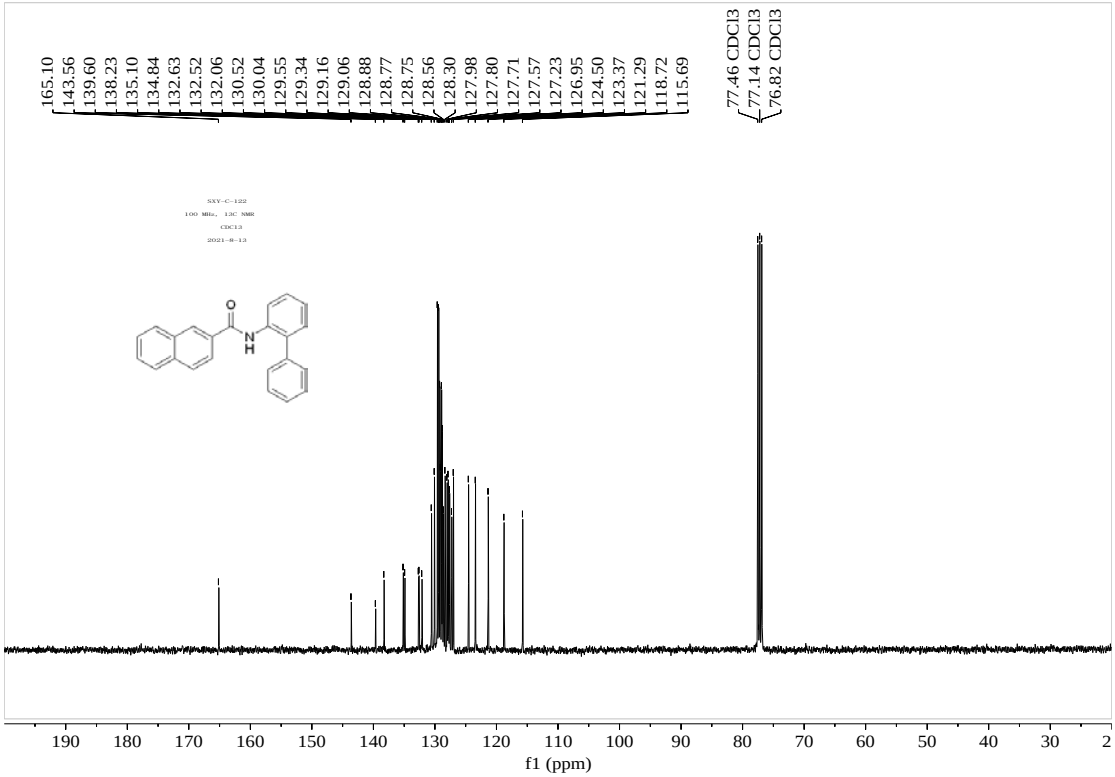

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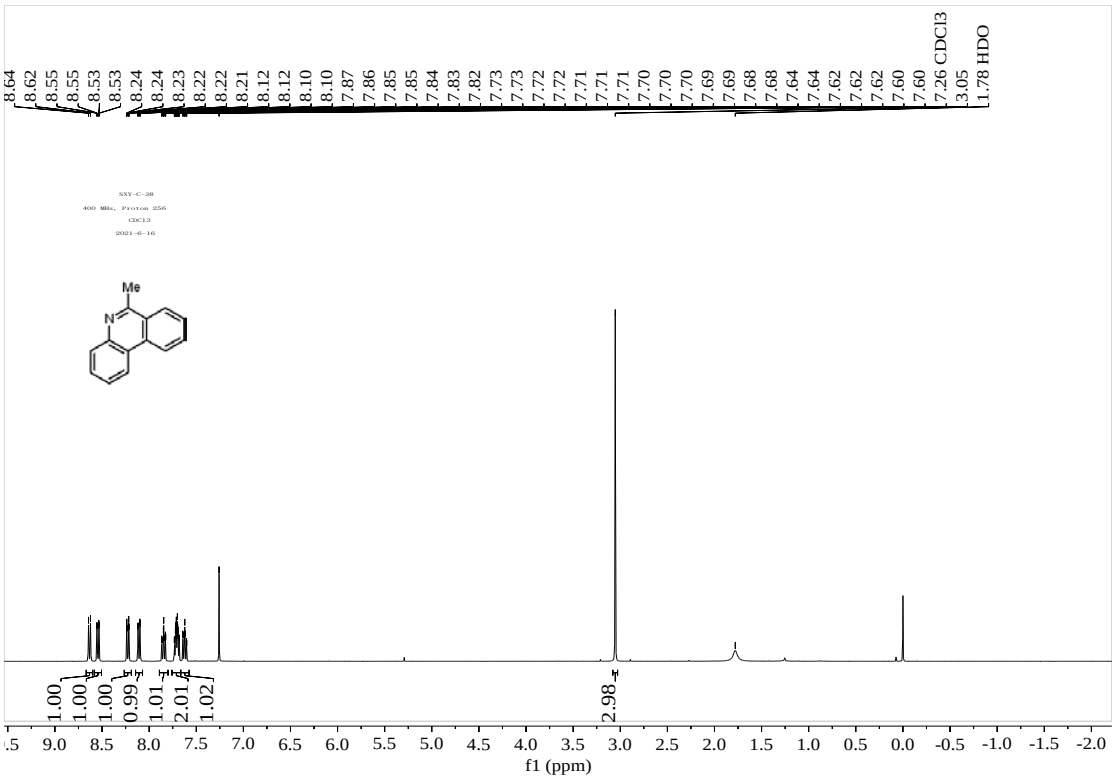

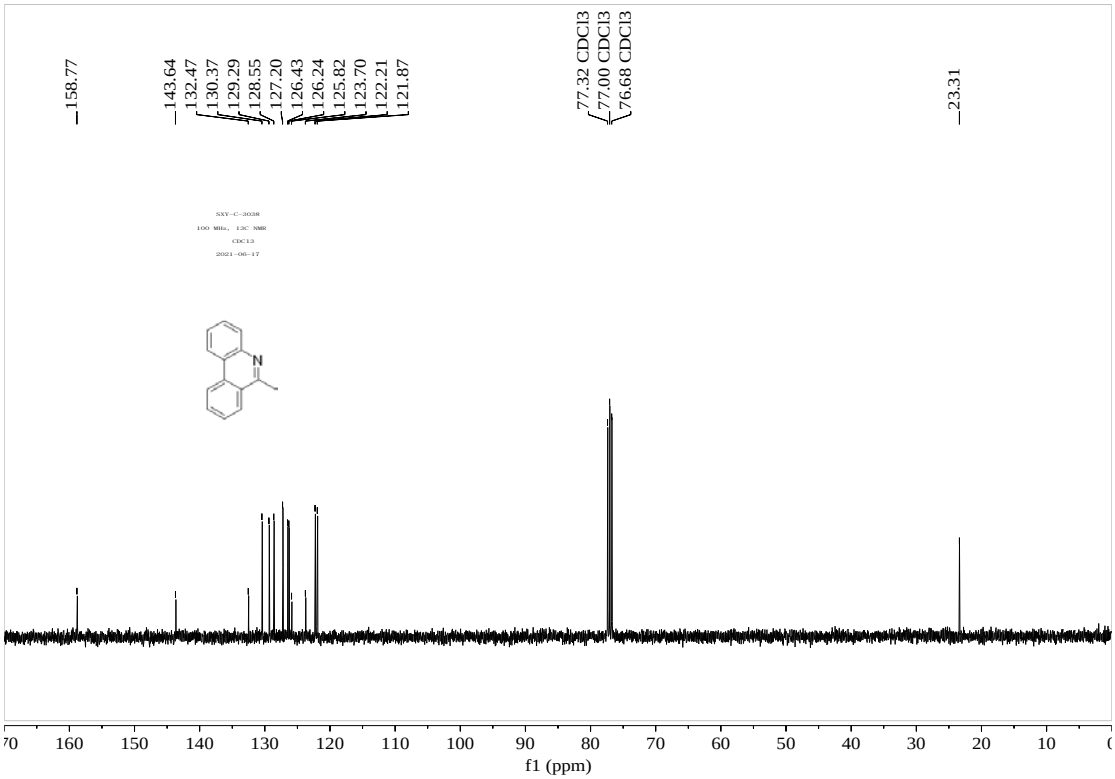

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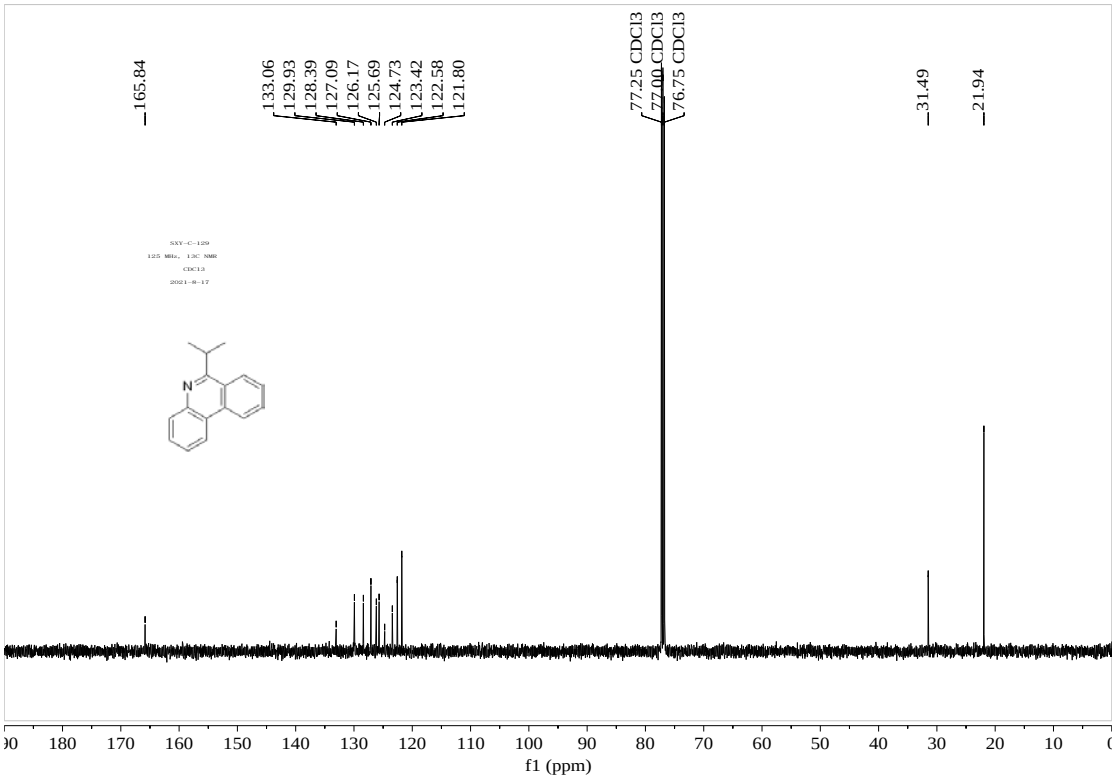

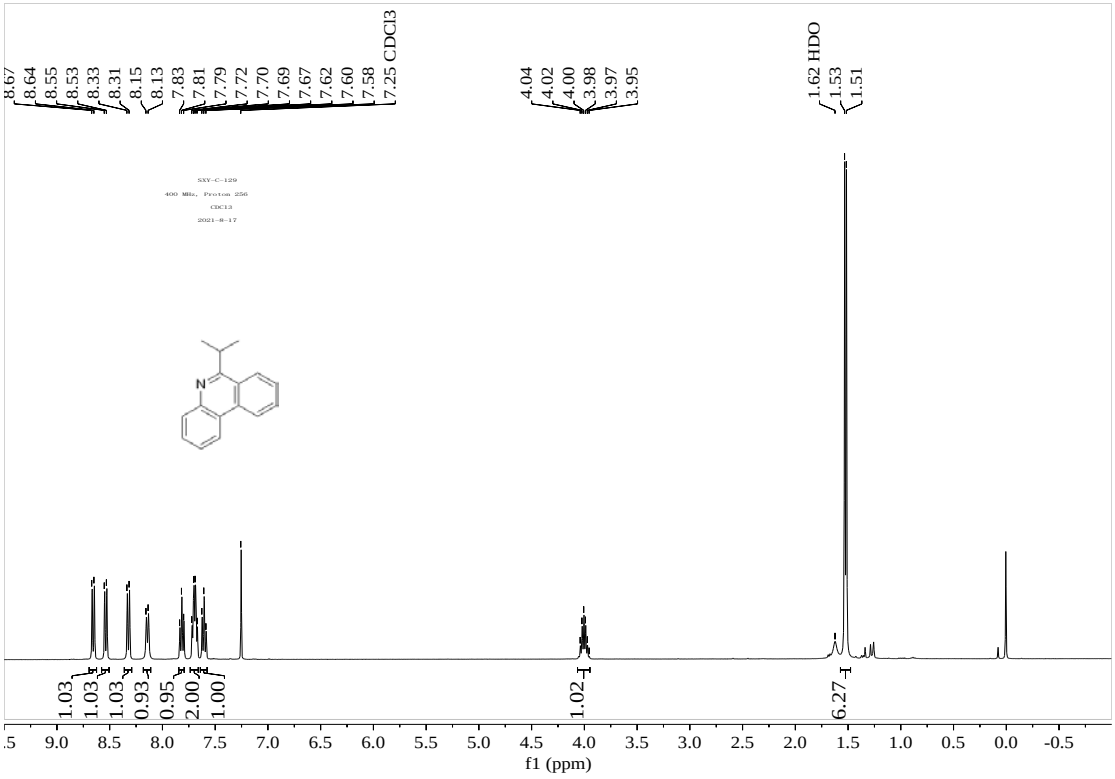

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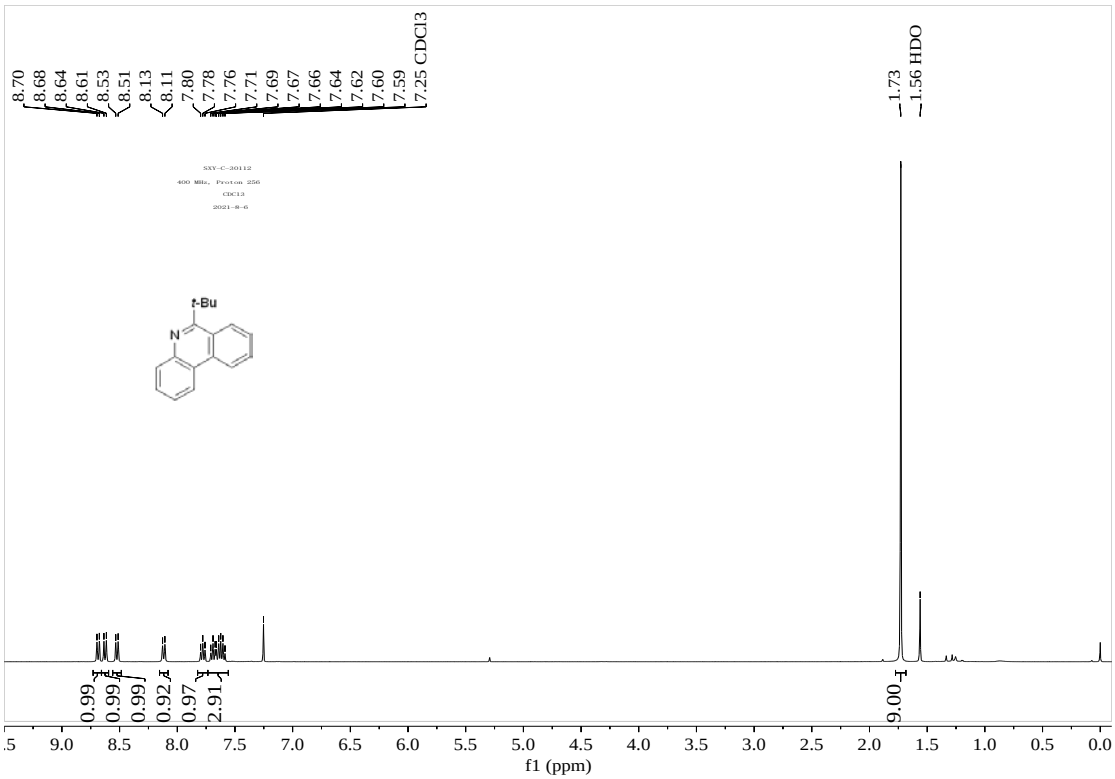

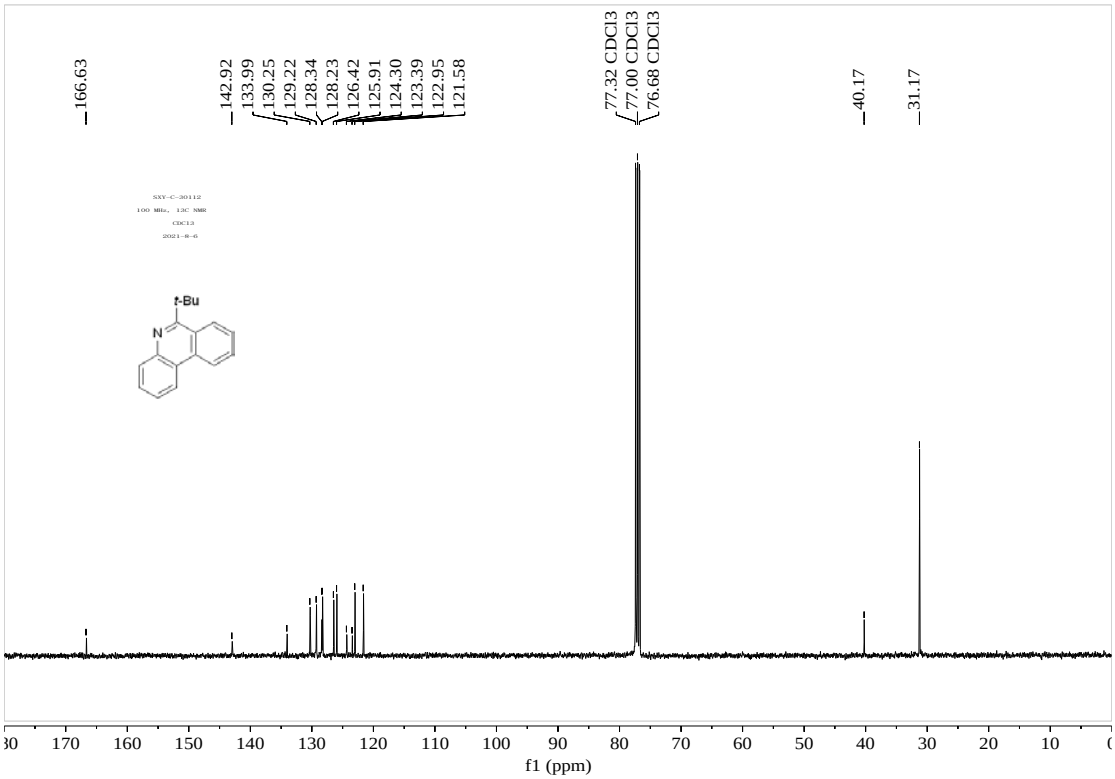

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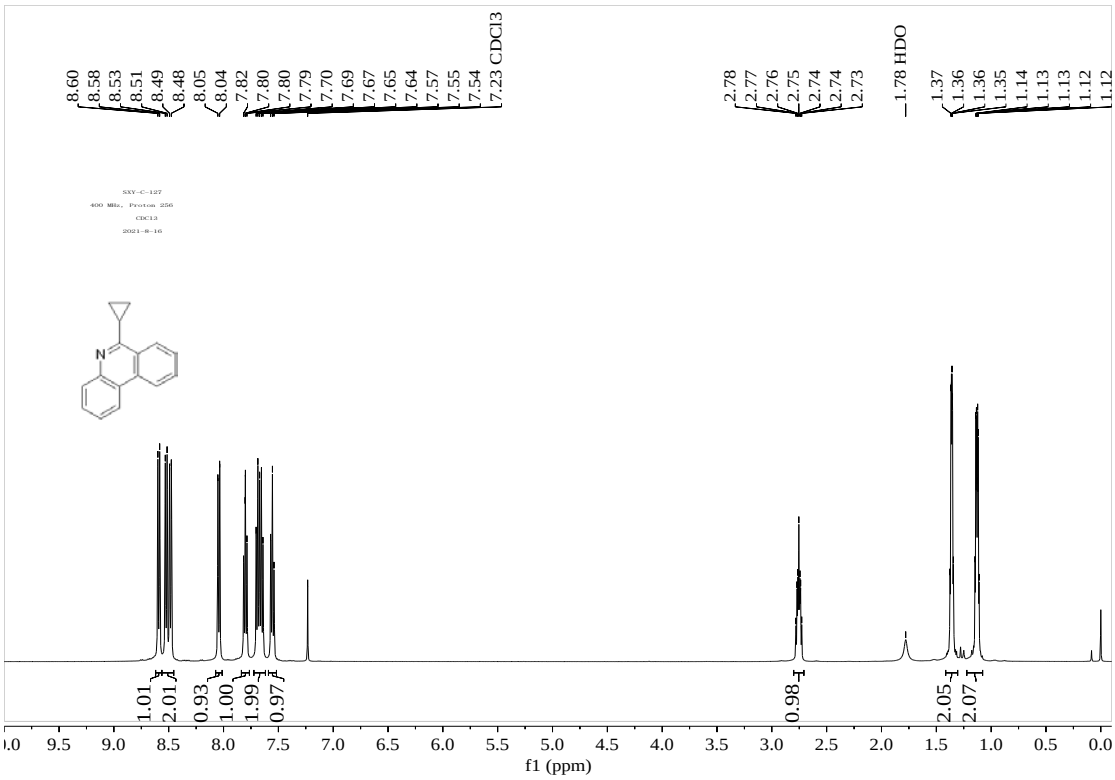

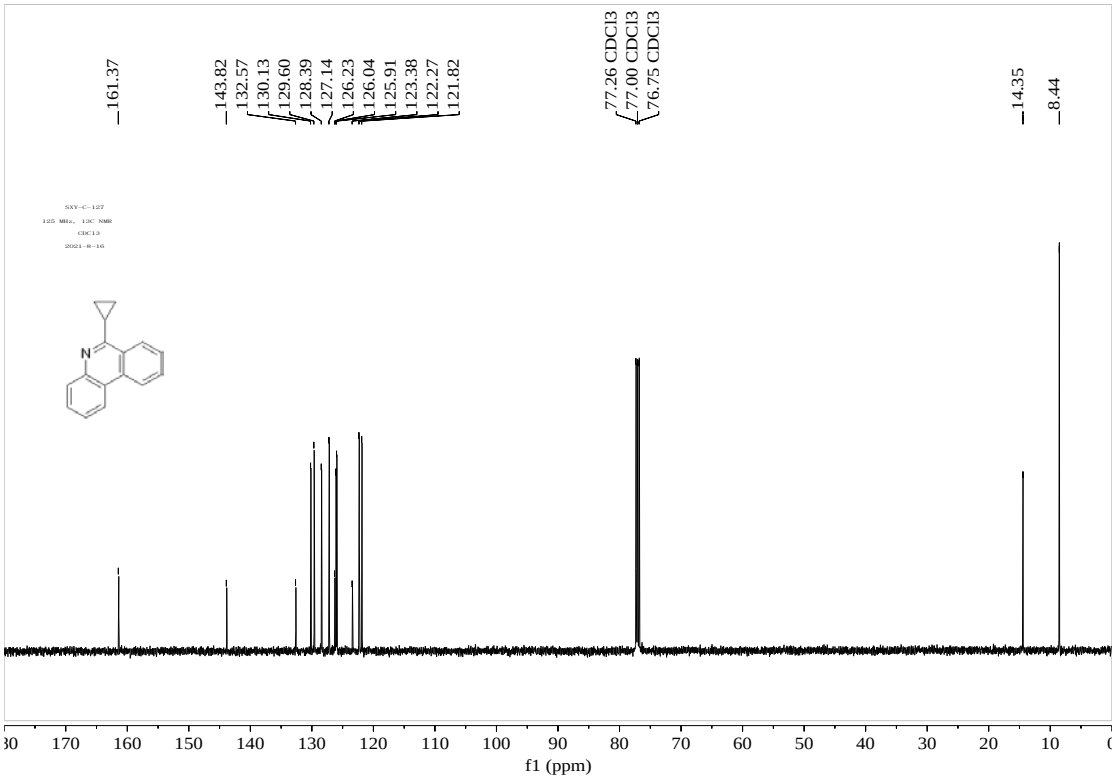

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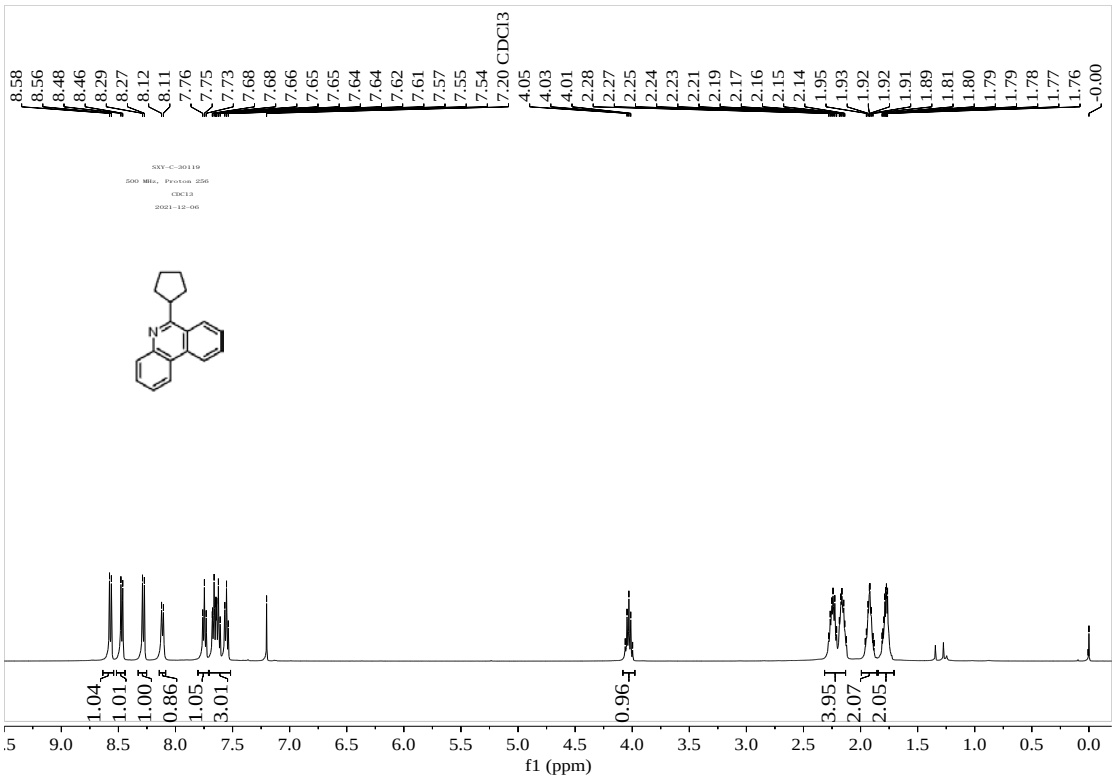

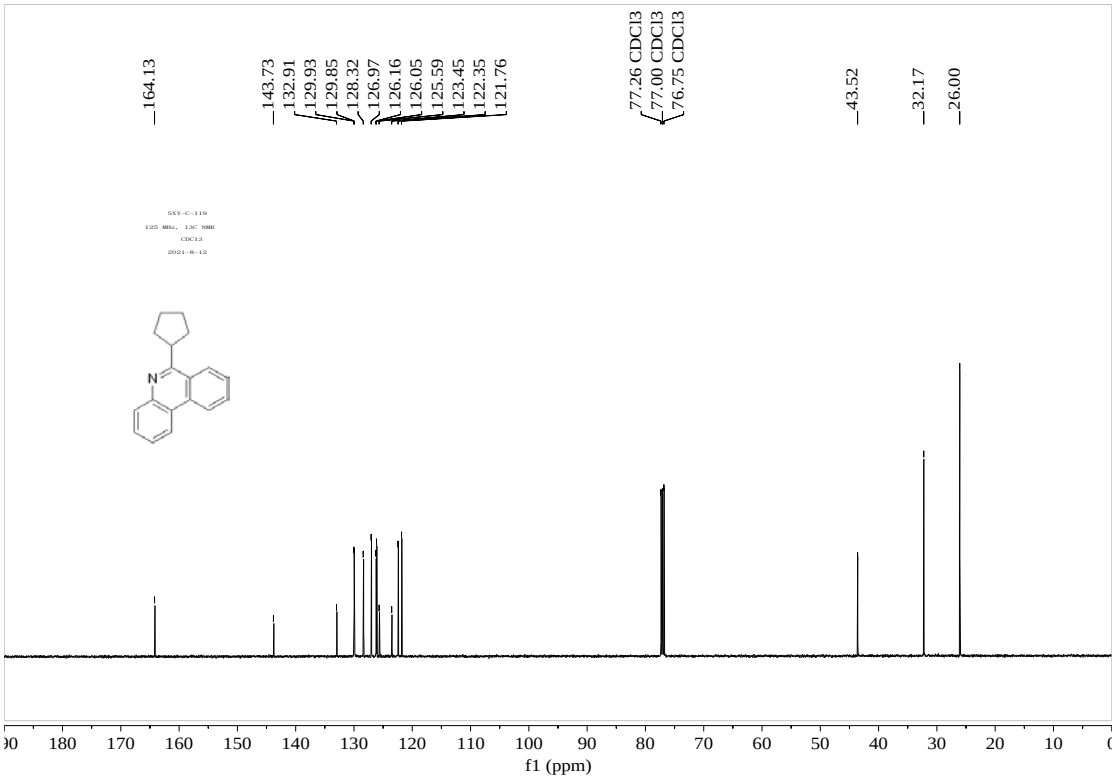

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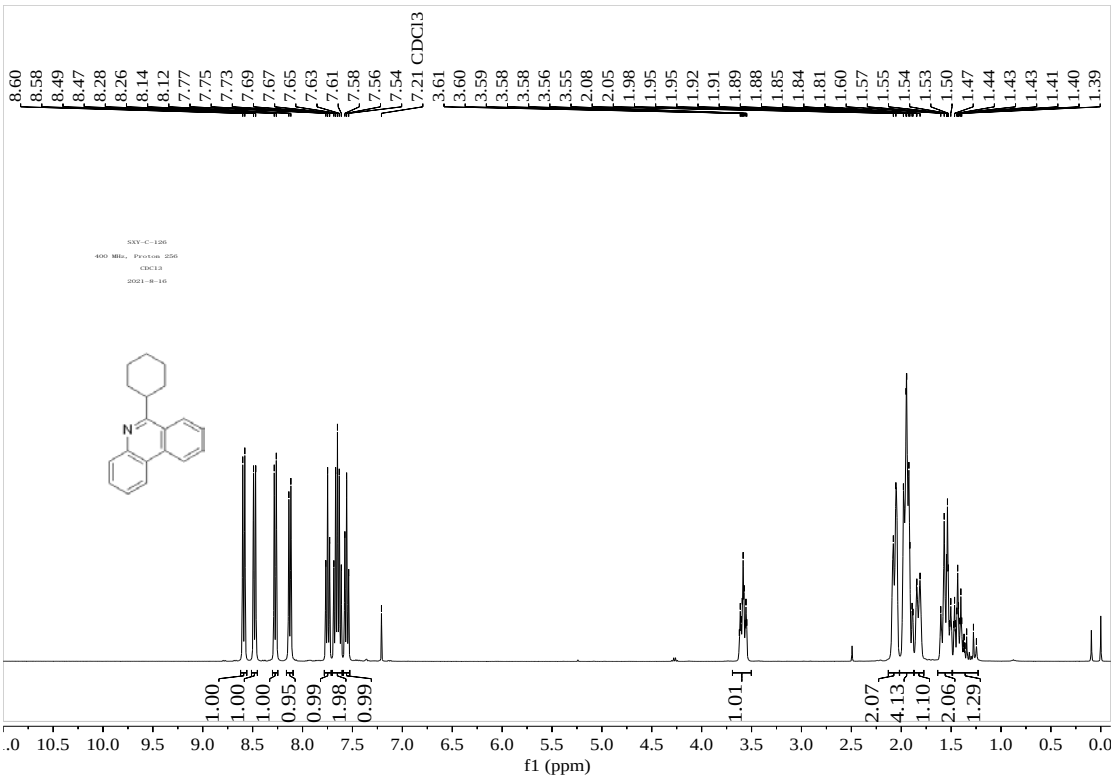
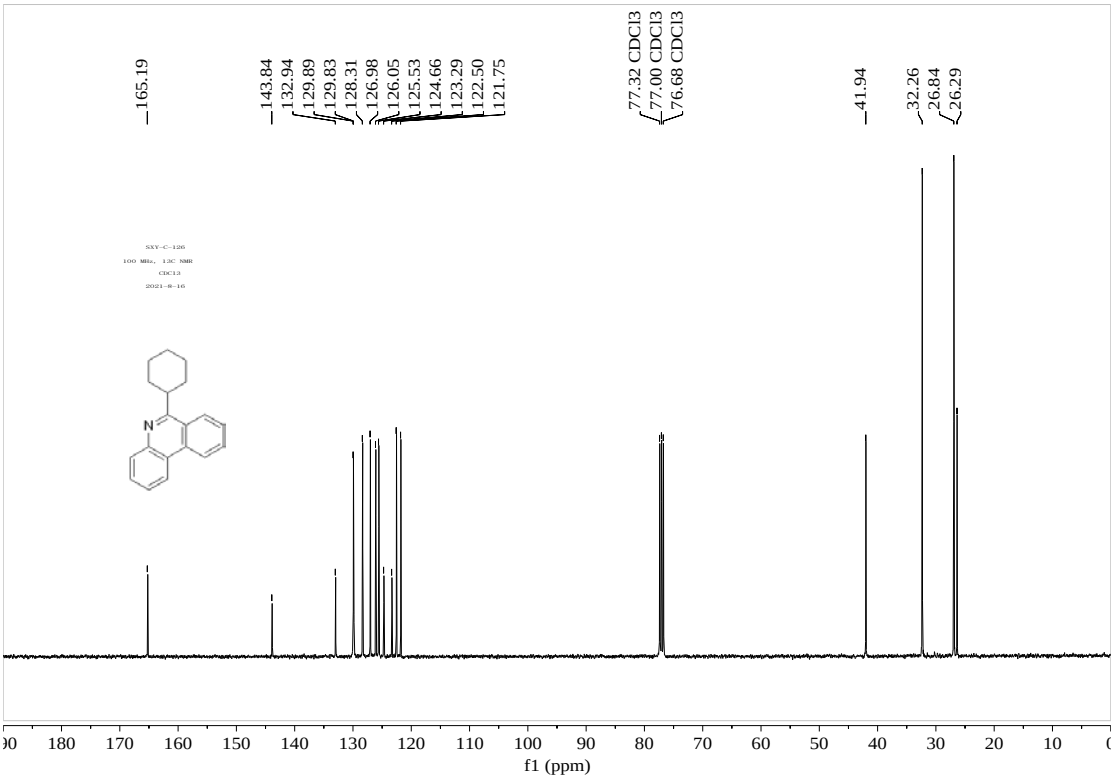
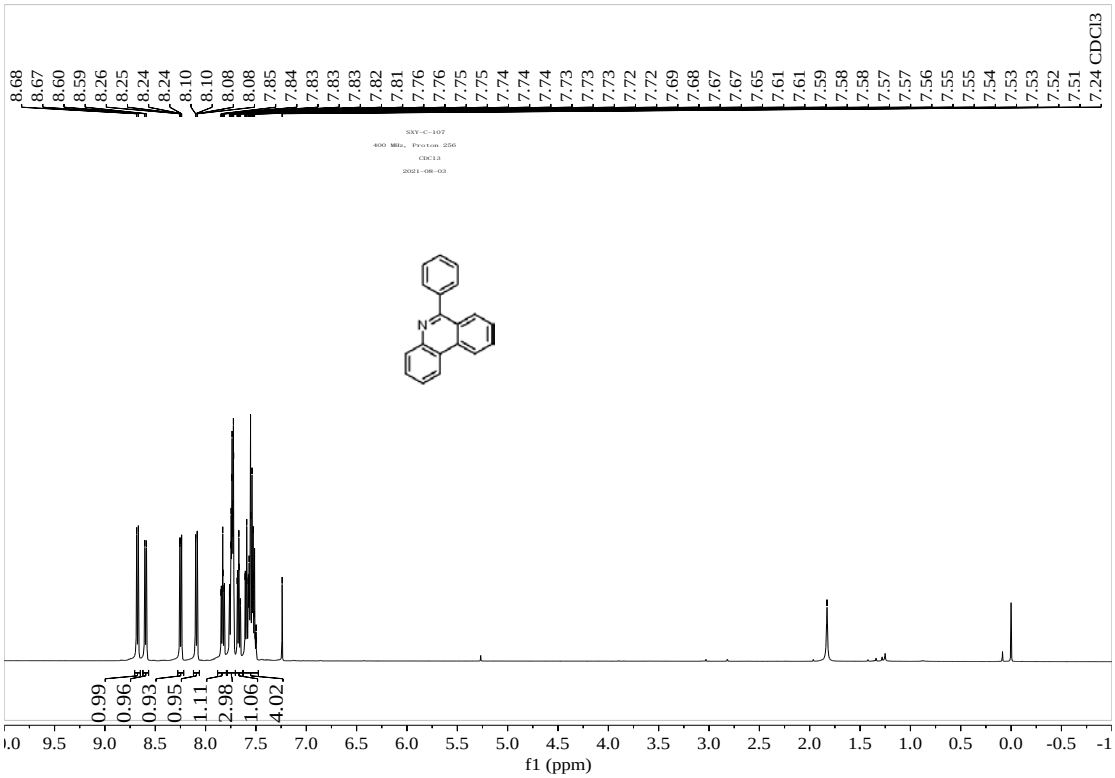
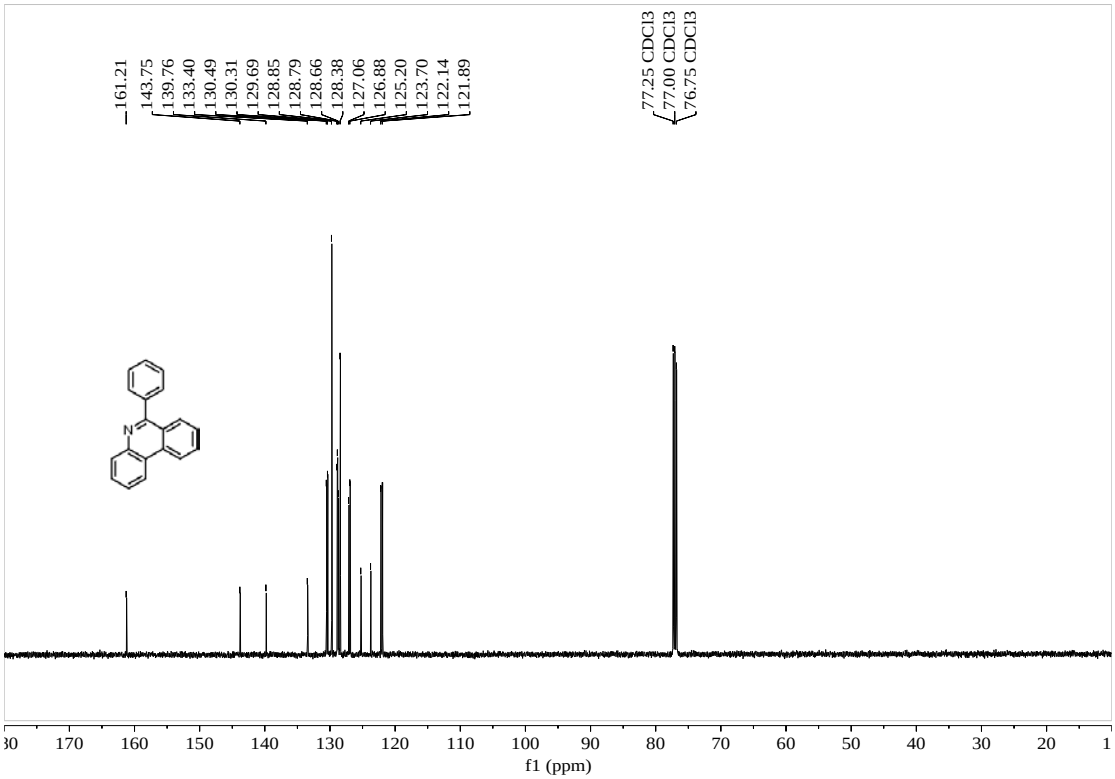


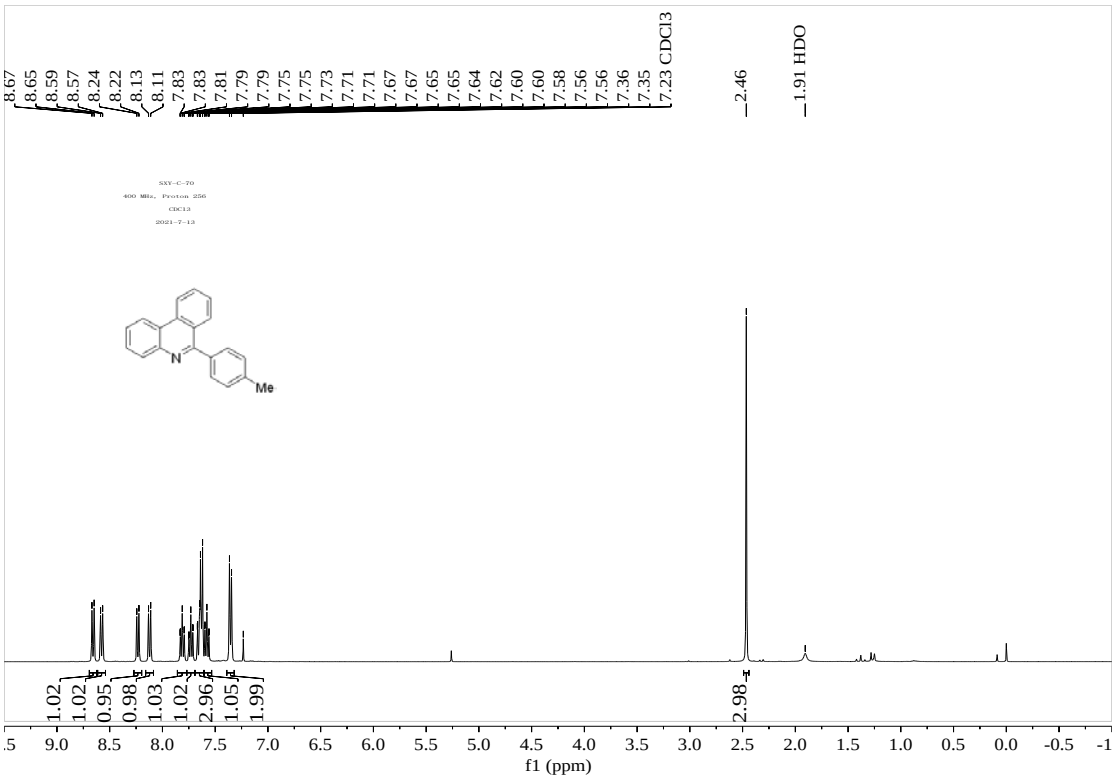


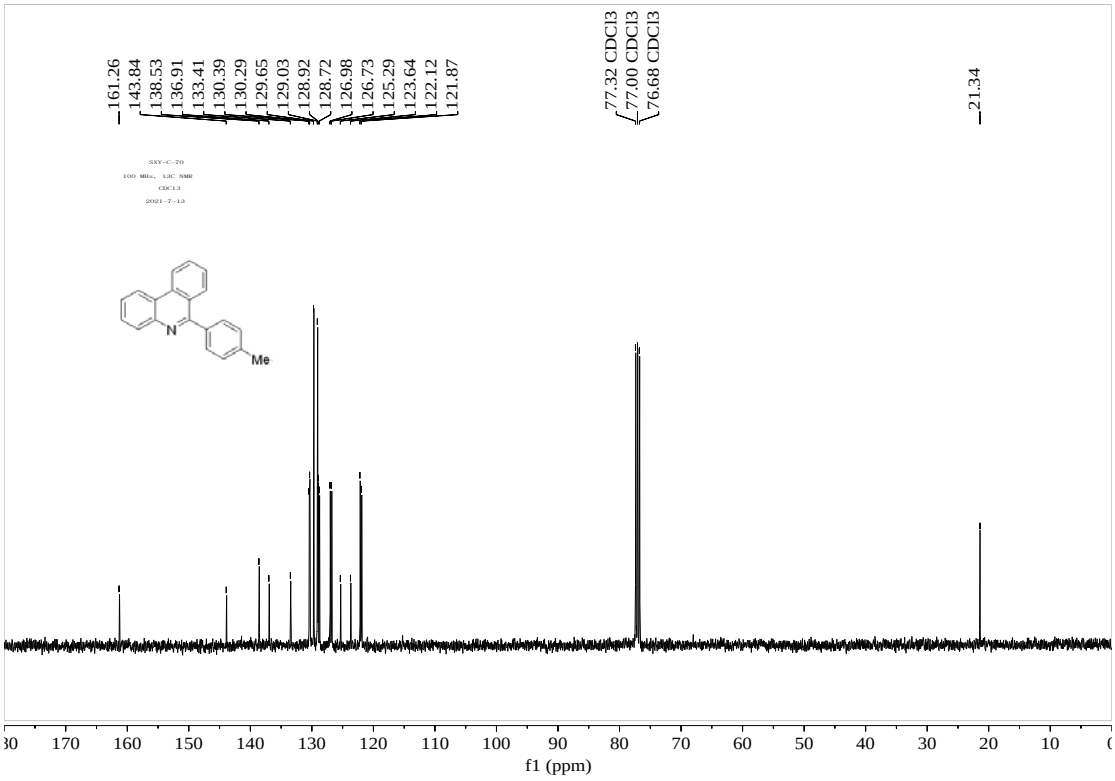
(19) Compound **1g**



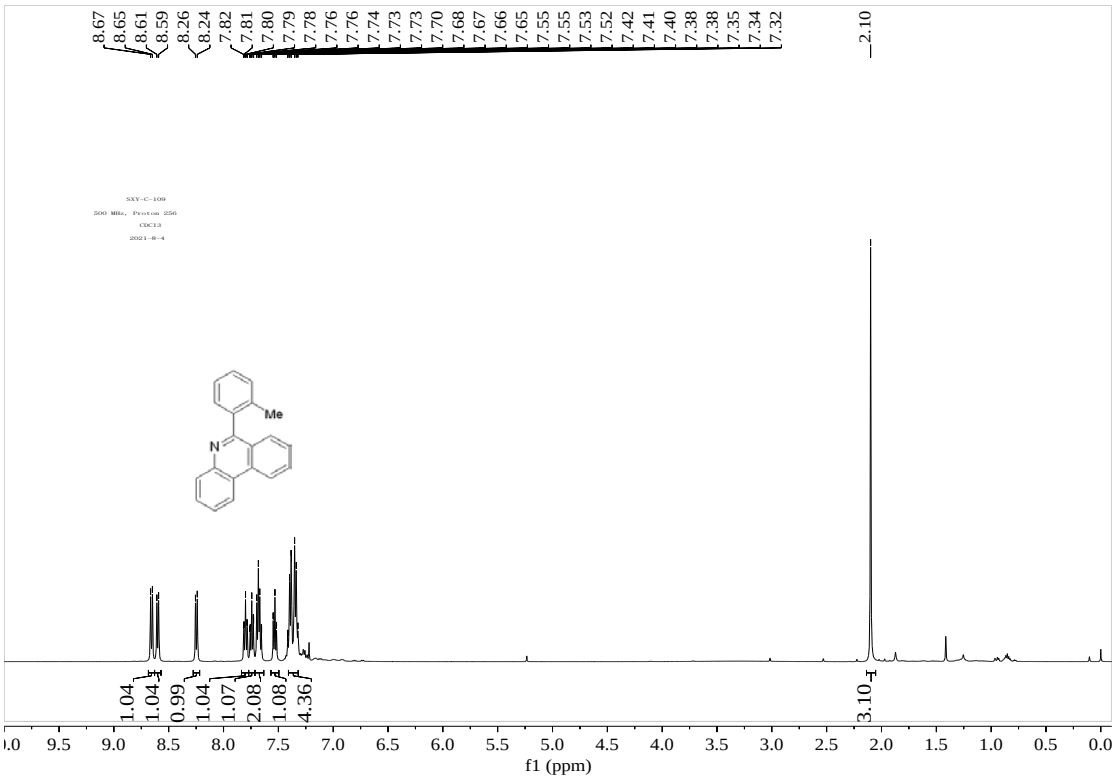


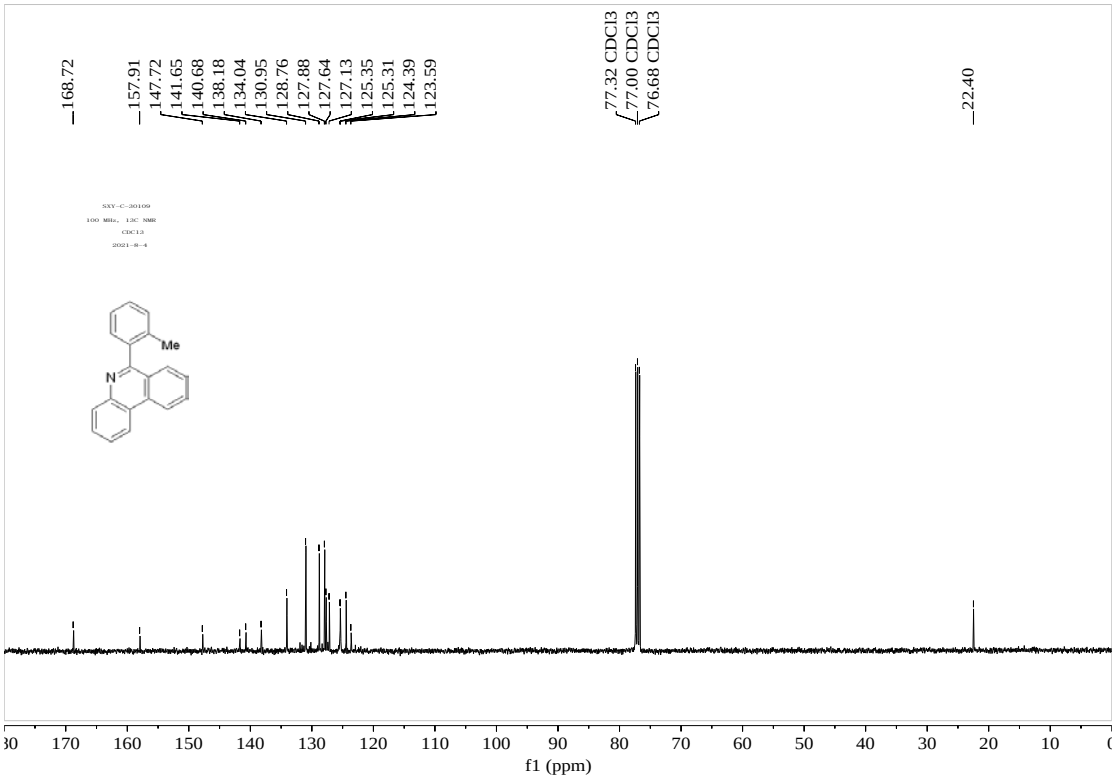
(20) Compound **1h**



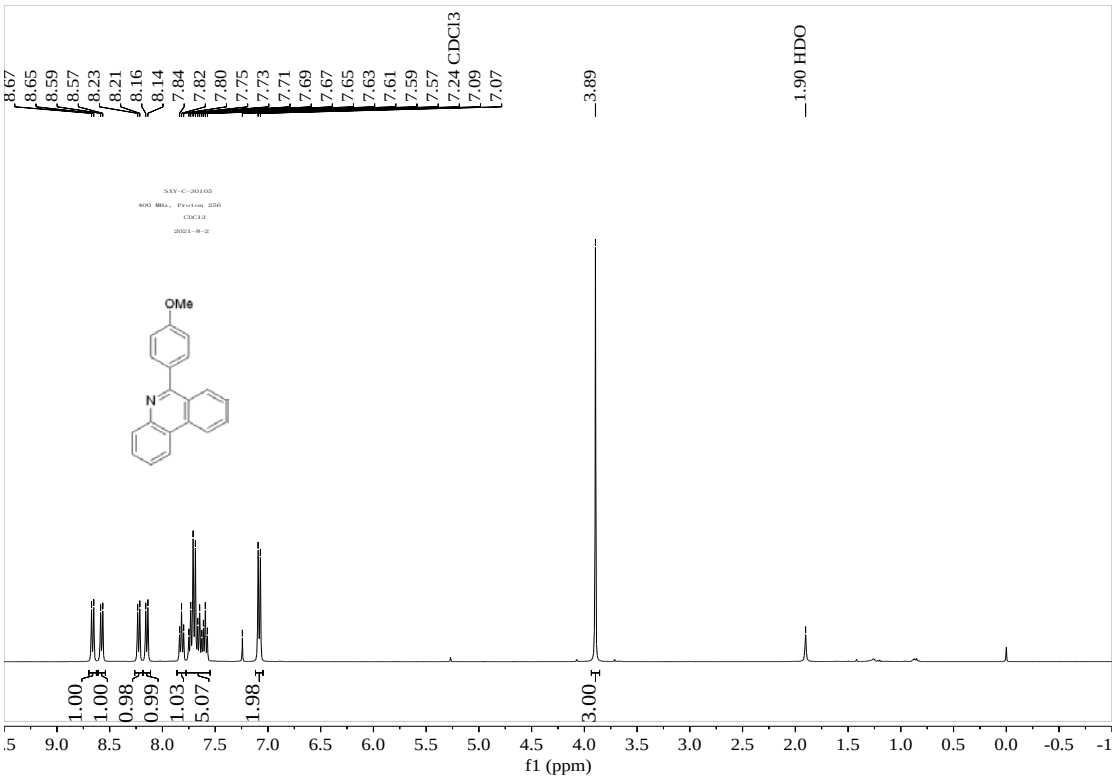


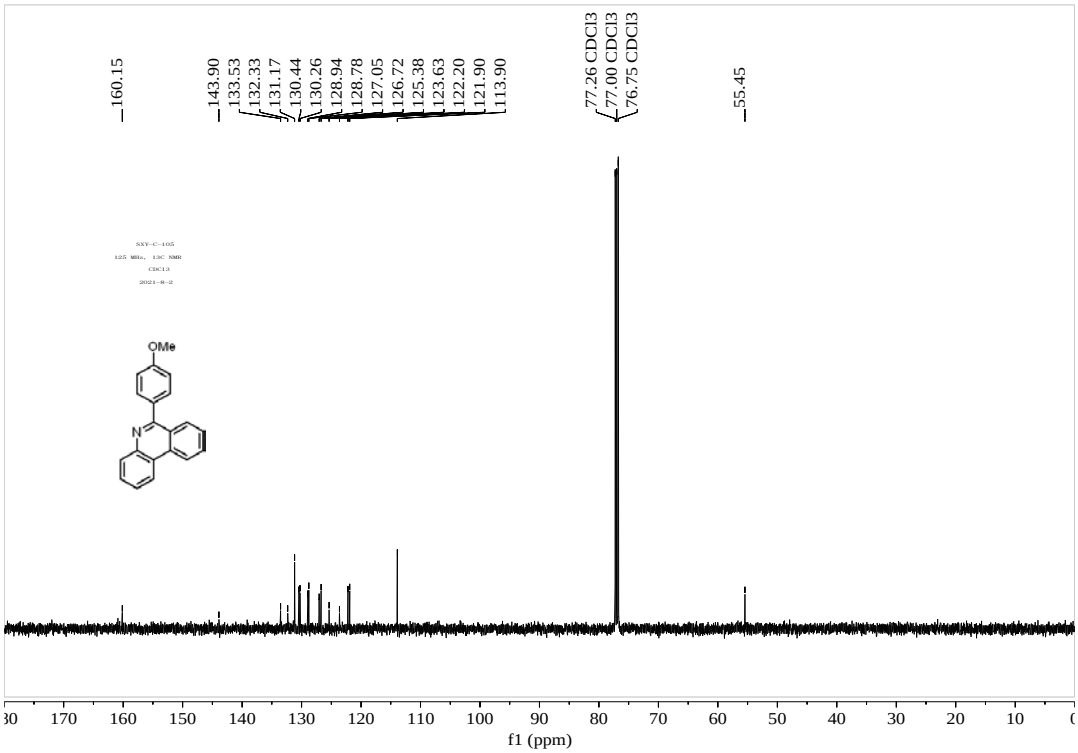
(21) Compound **1i**



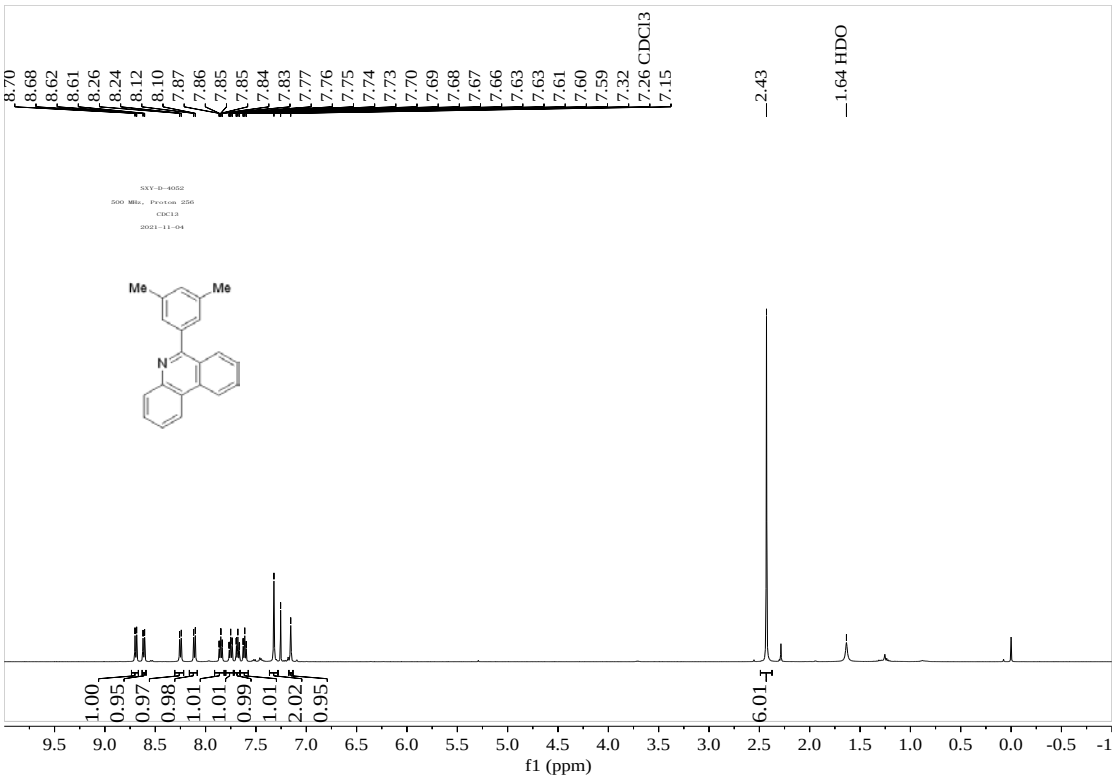


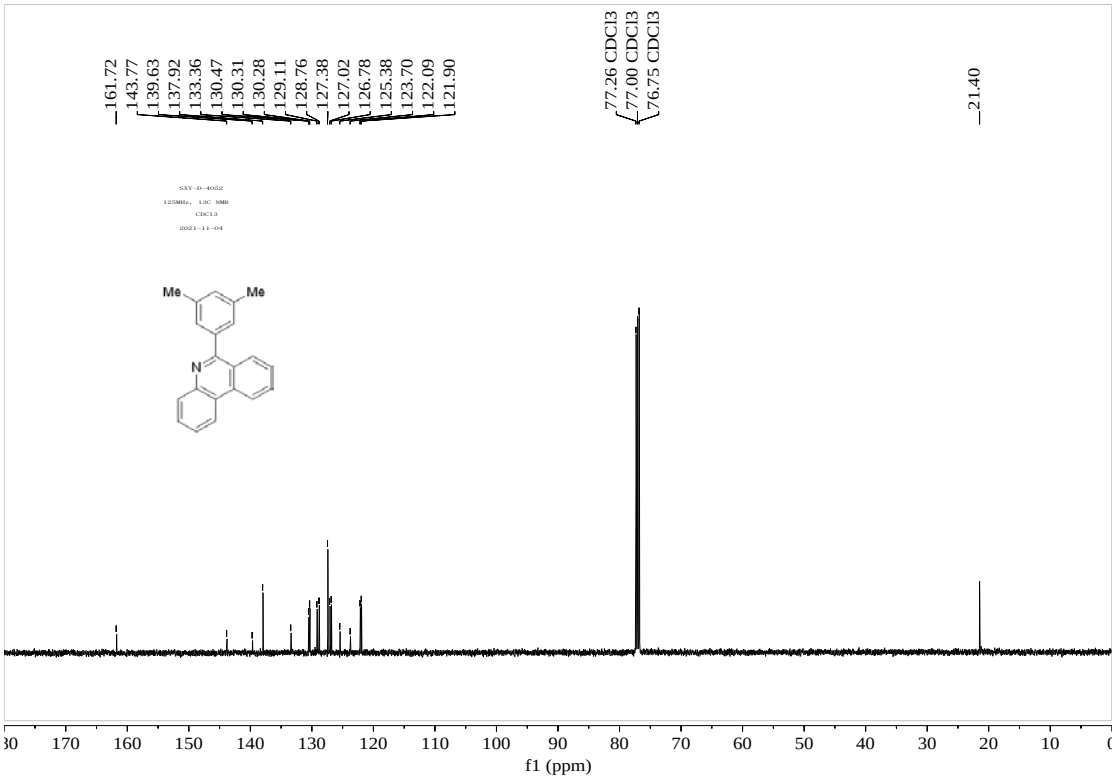
(22) Compound **1j**



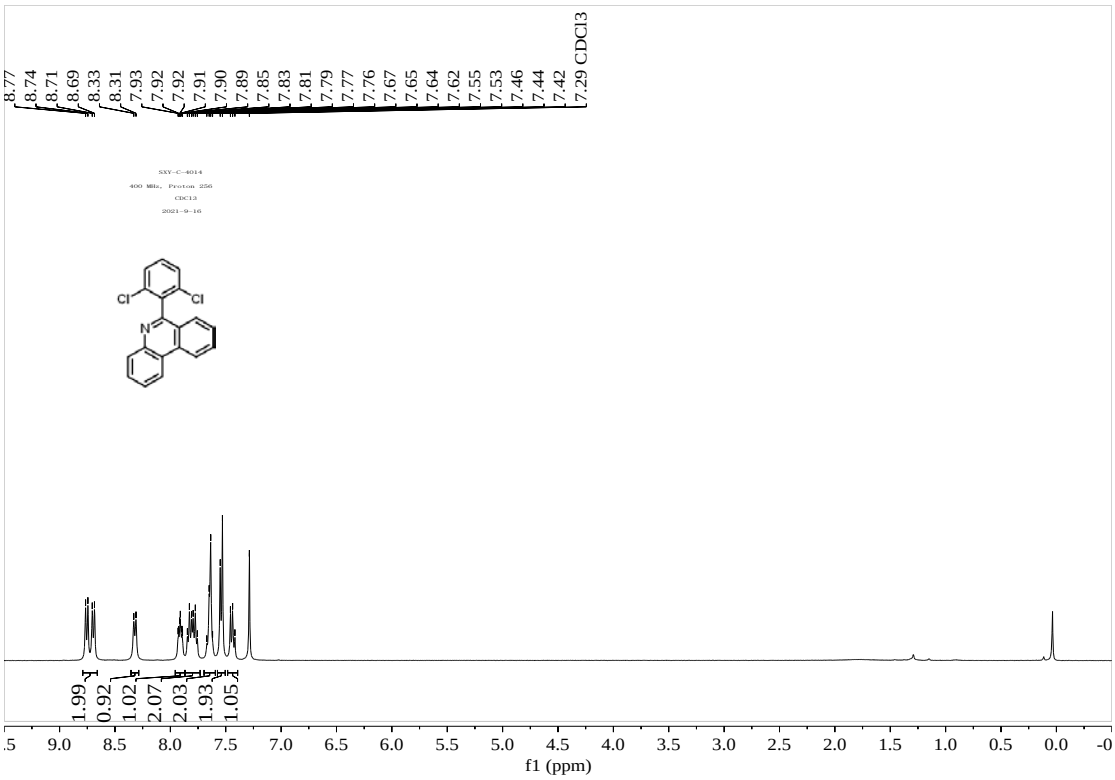


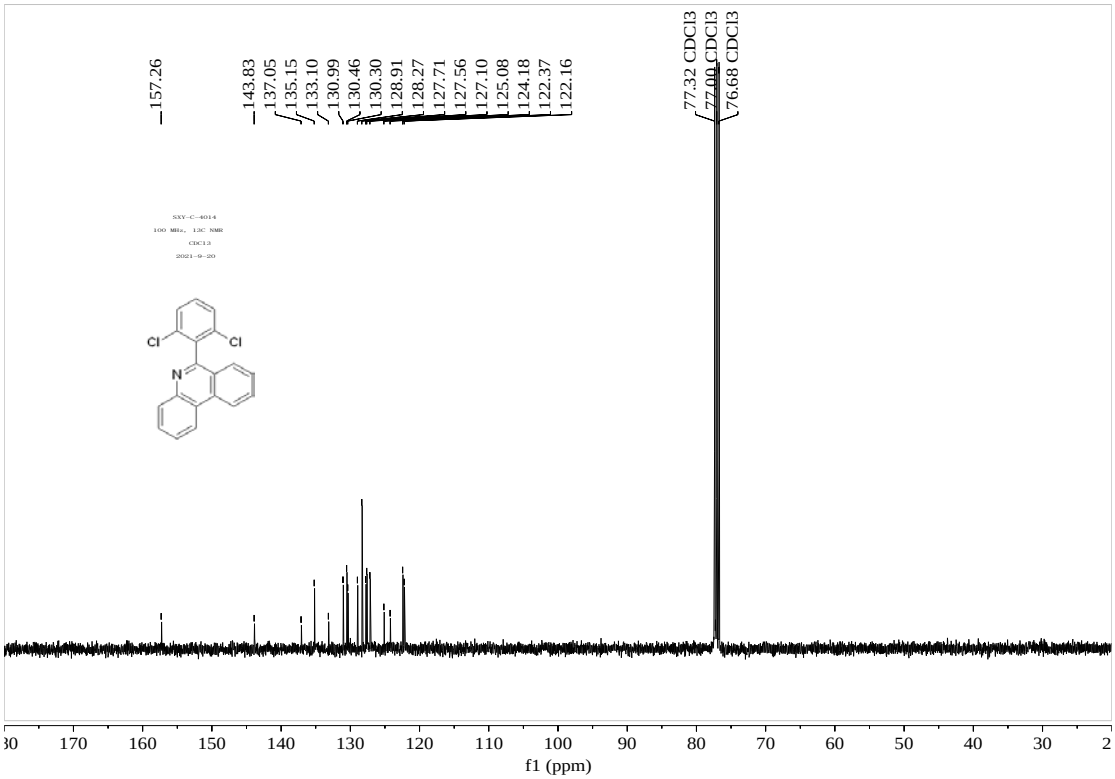
(23) Compound **1k**



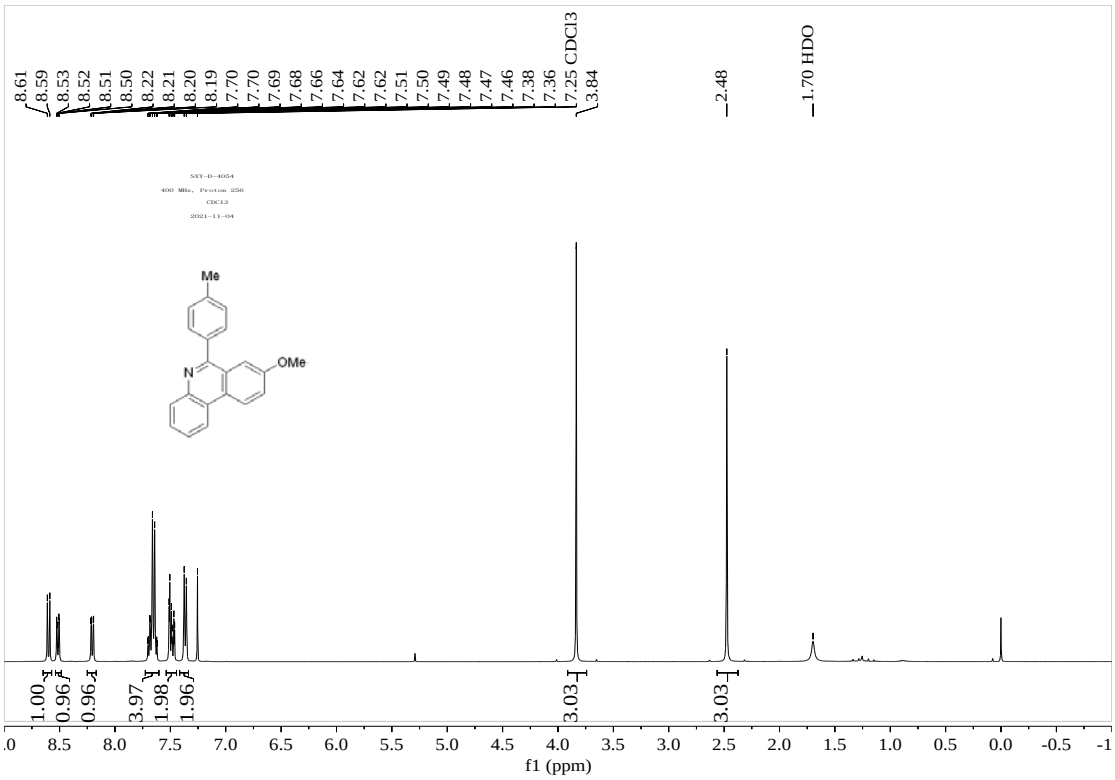


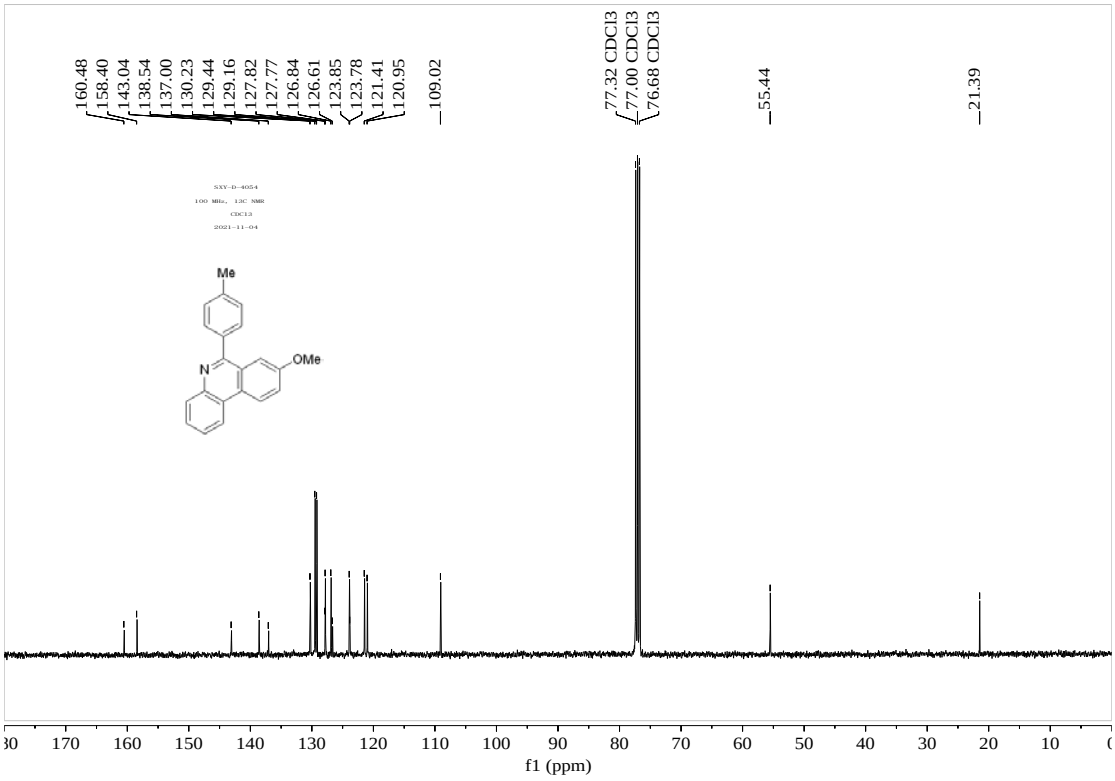
(24) Compound **1l**



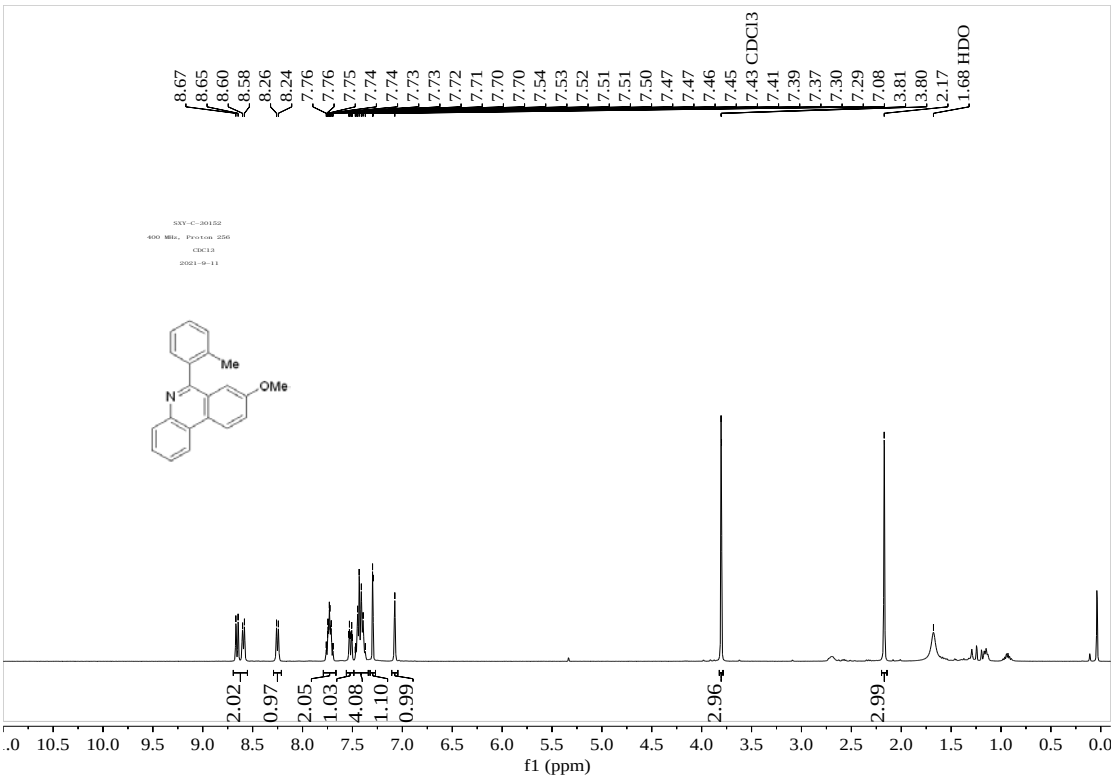


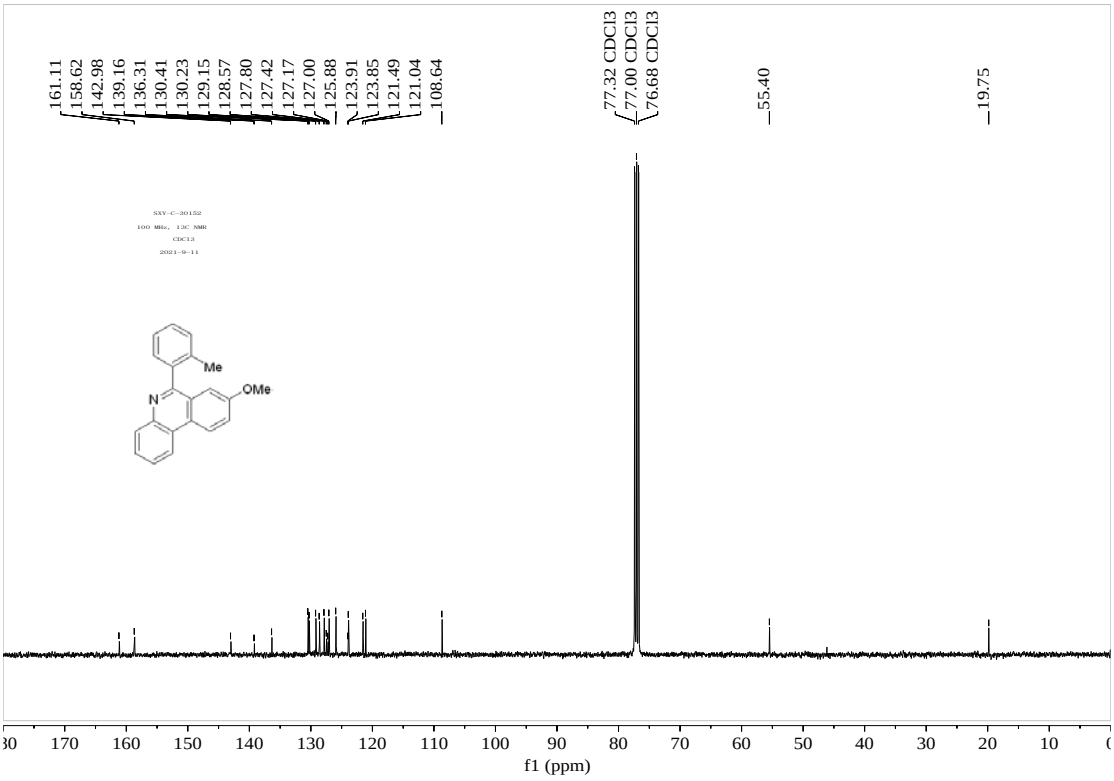
(25) Compound **1m**



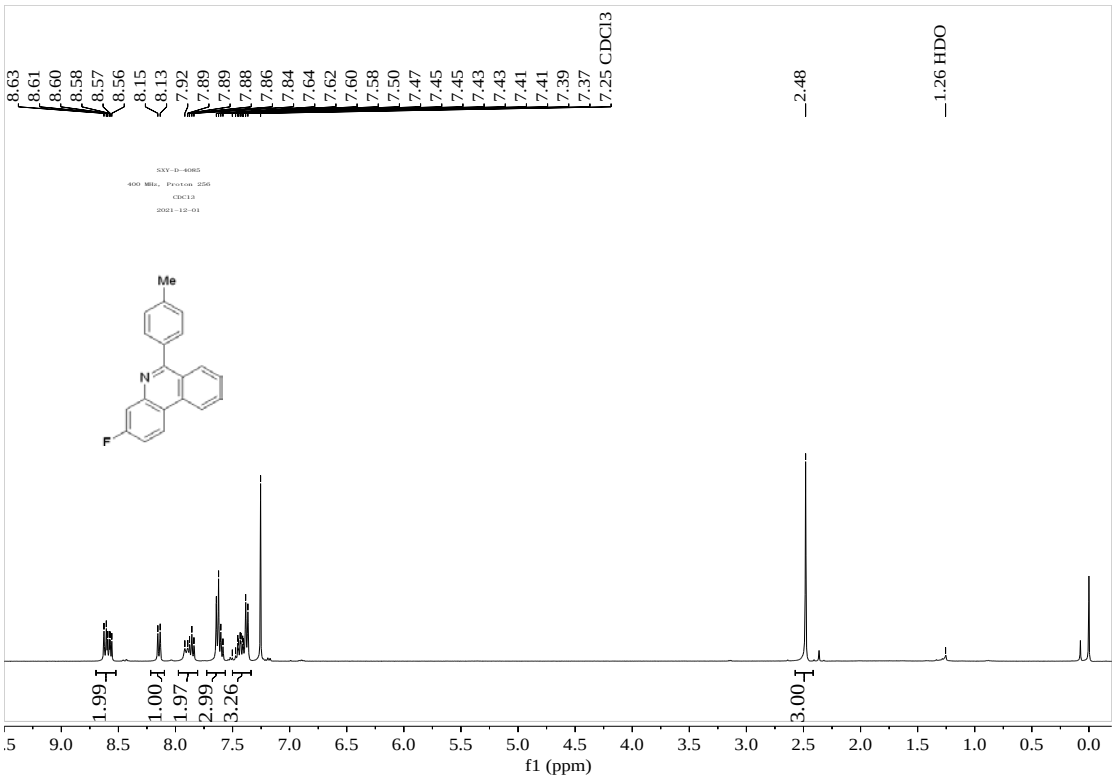


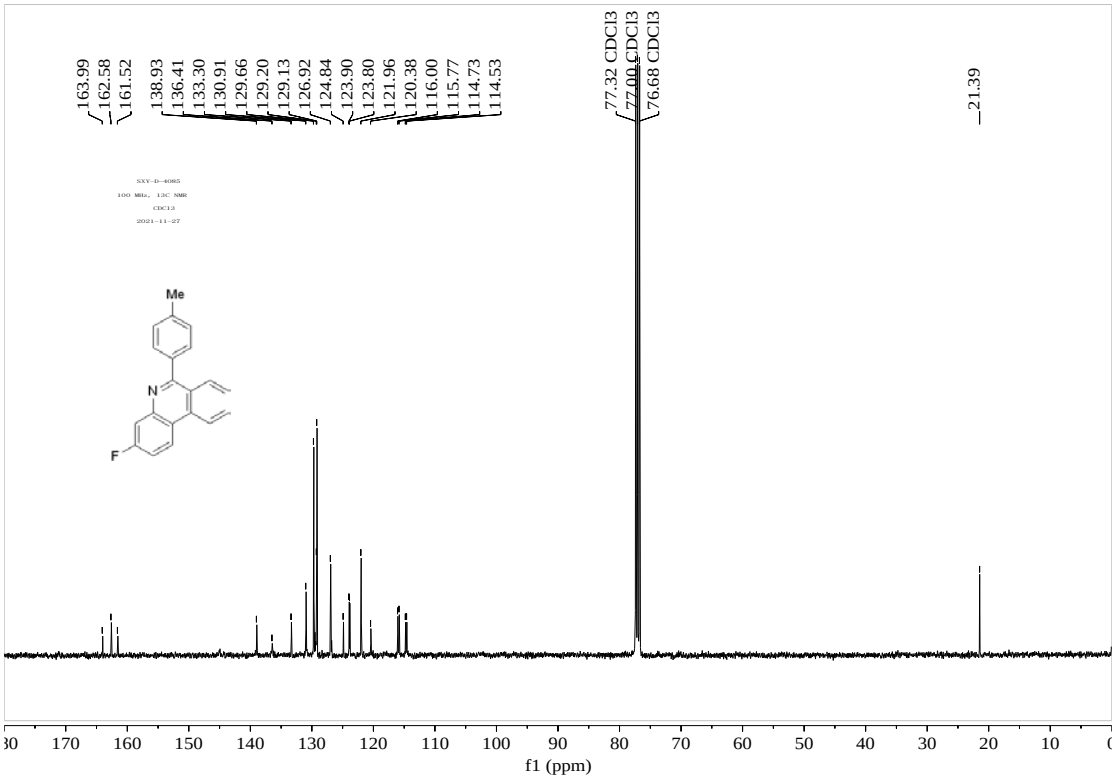
(26) Compound **1n**



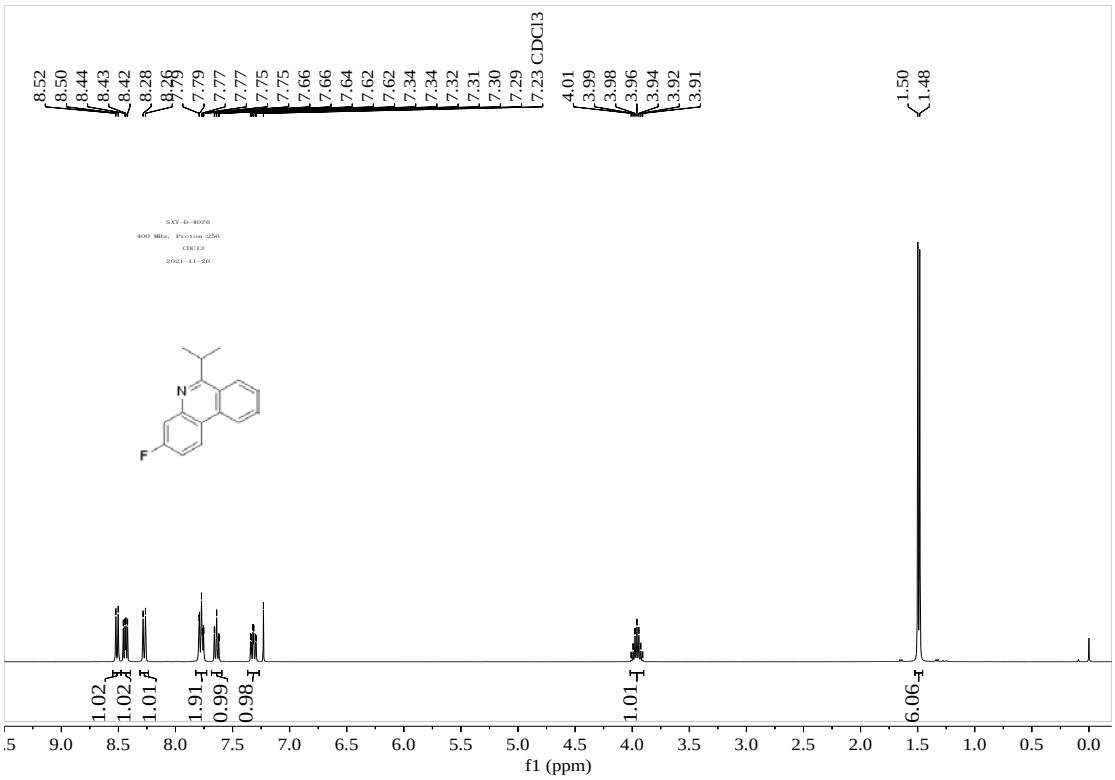


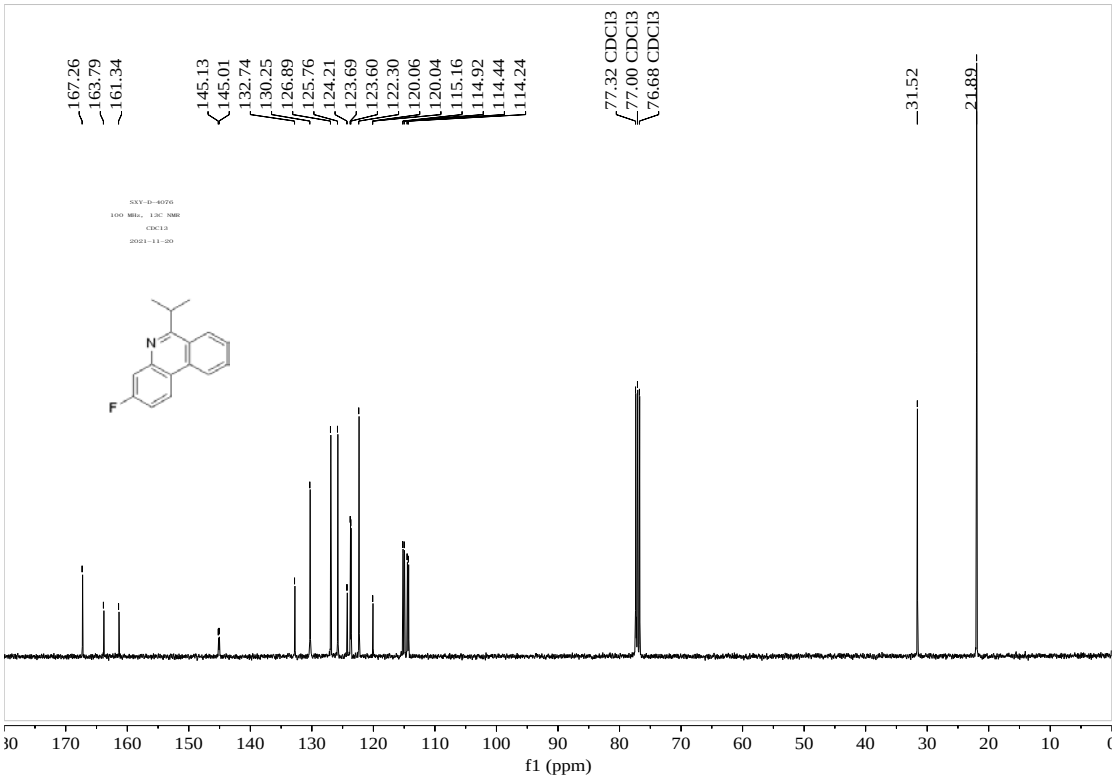
(27) Compound **1o**



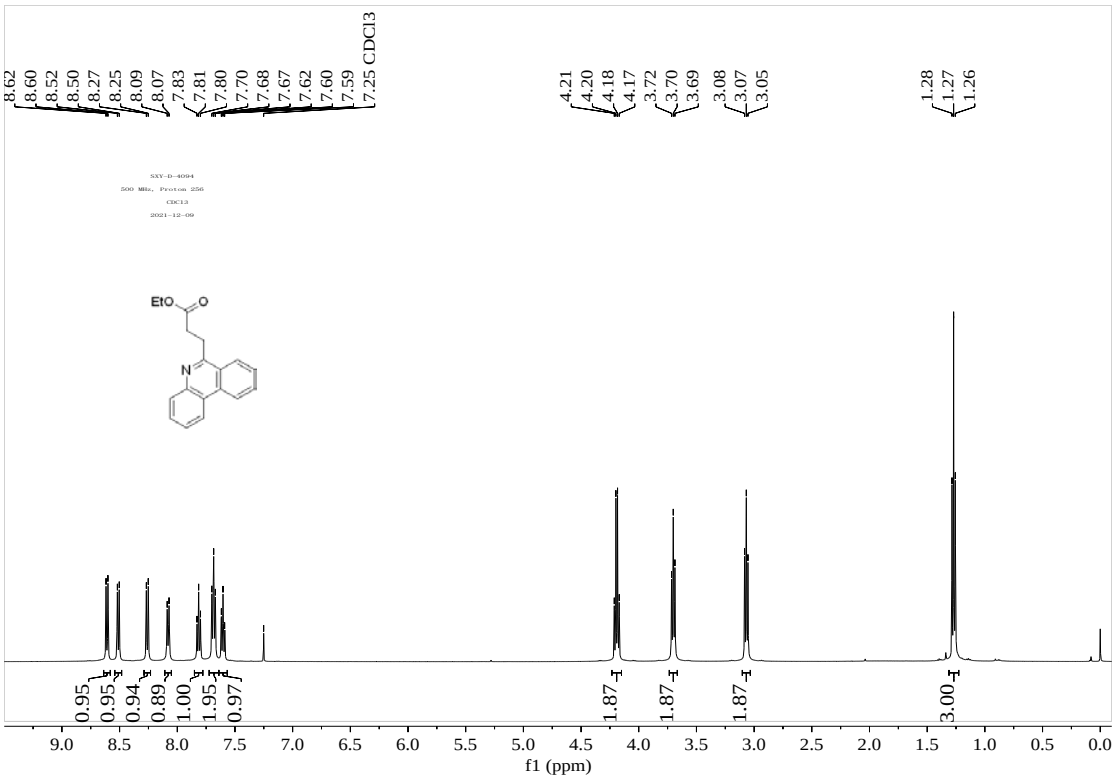


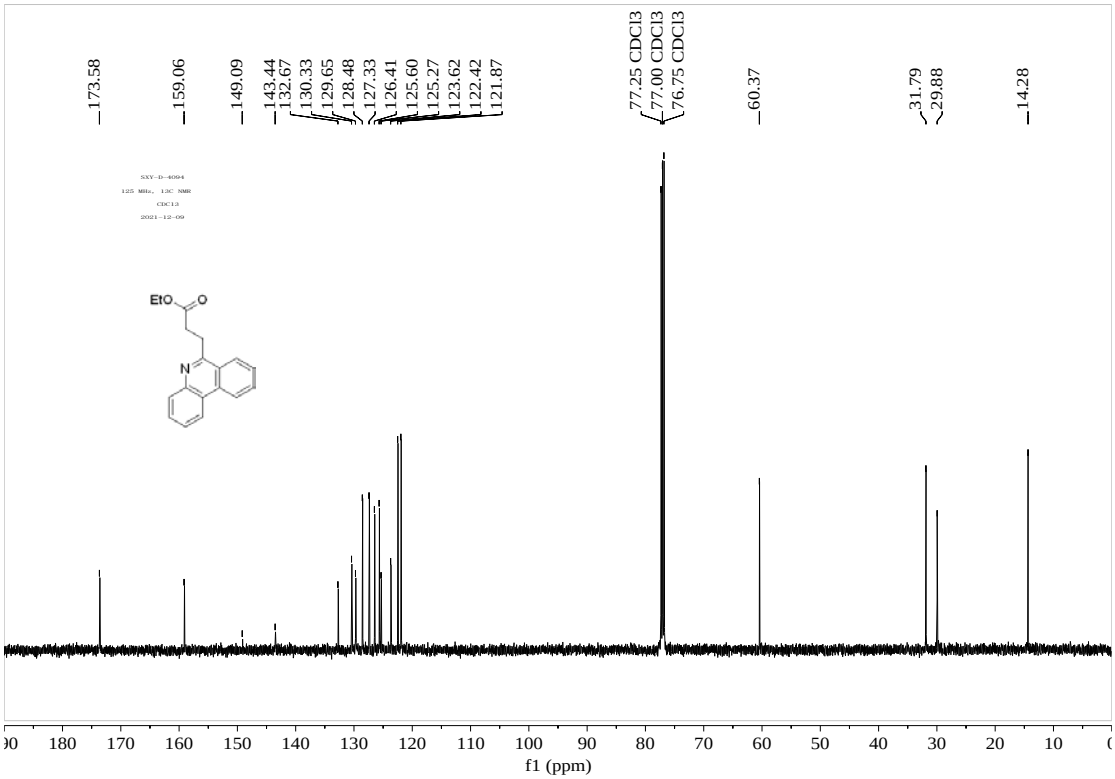
(28) Compound **1p**



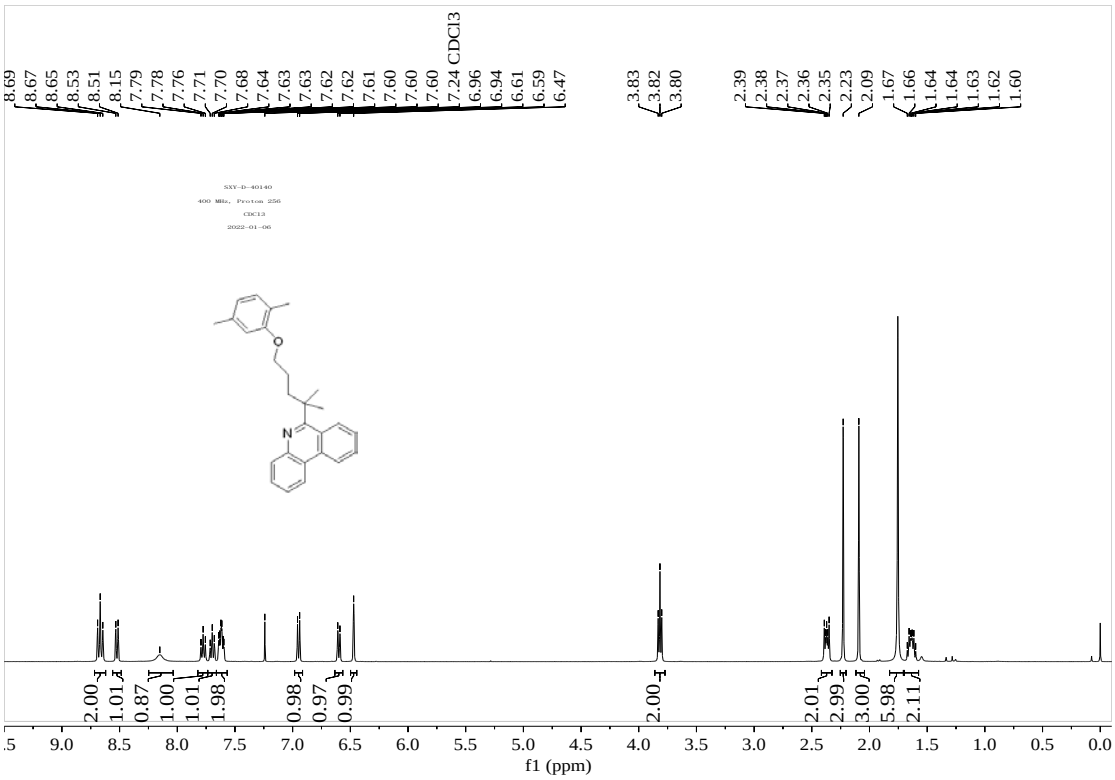


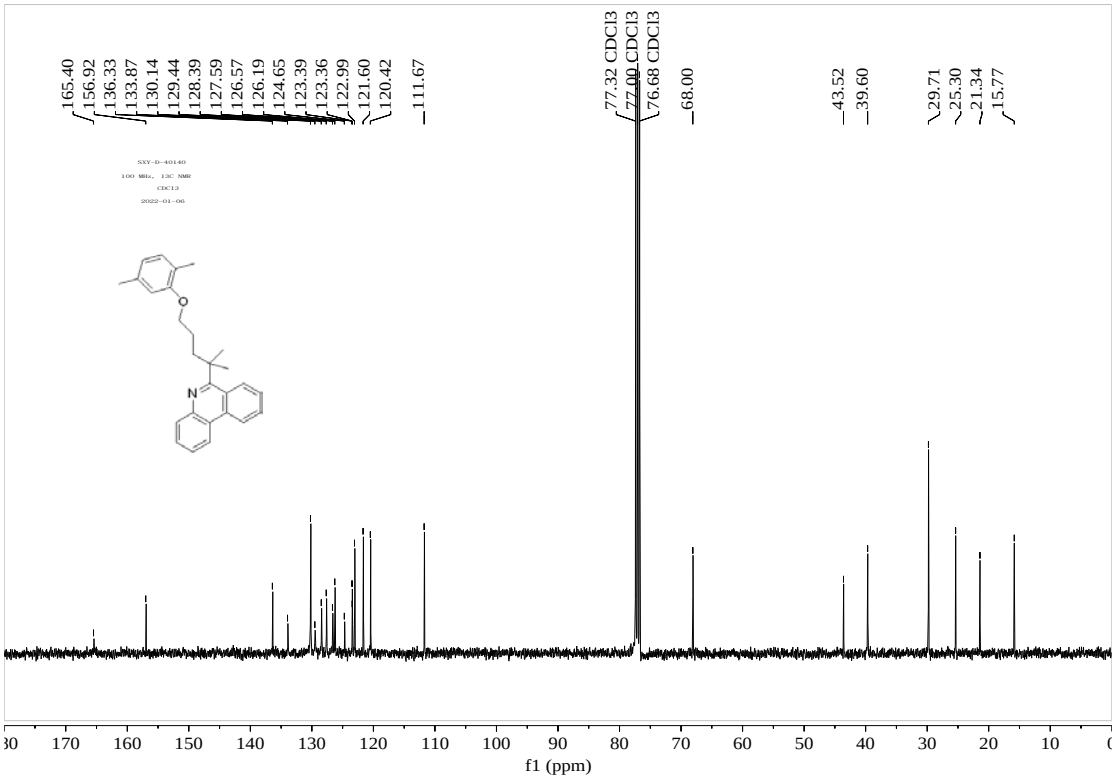
(29) Compound **1q**



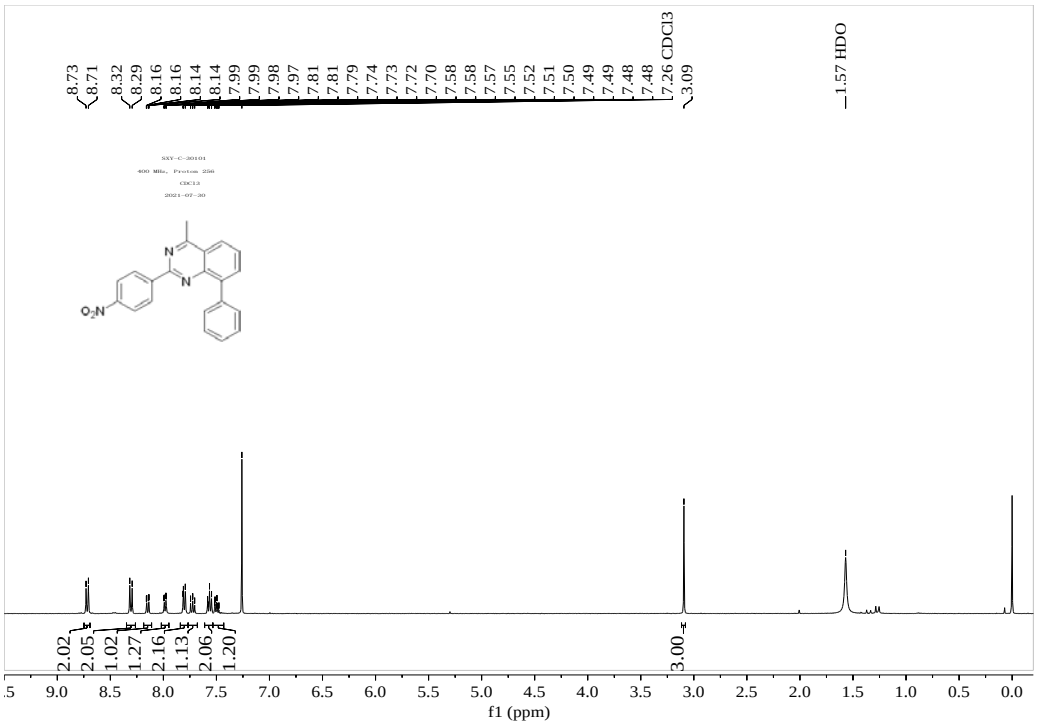


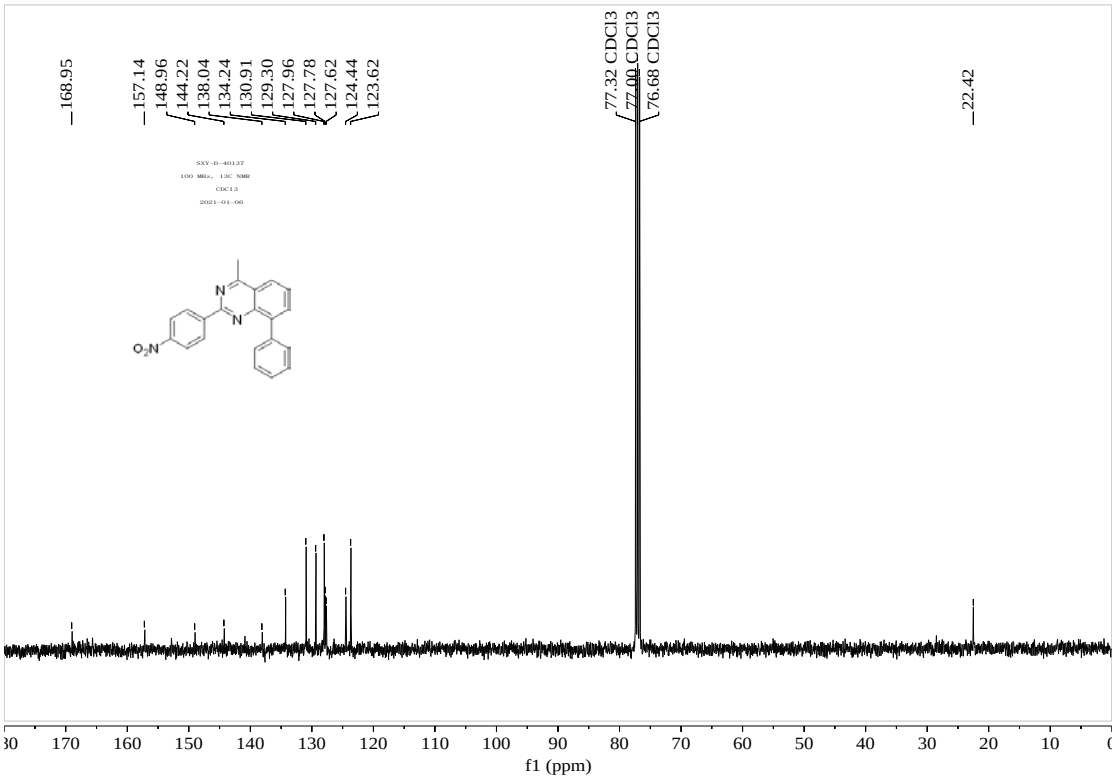
(30) Compound **1r**



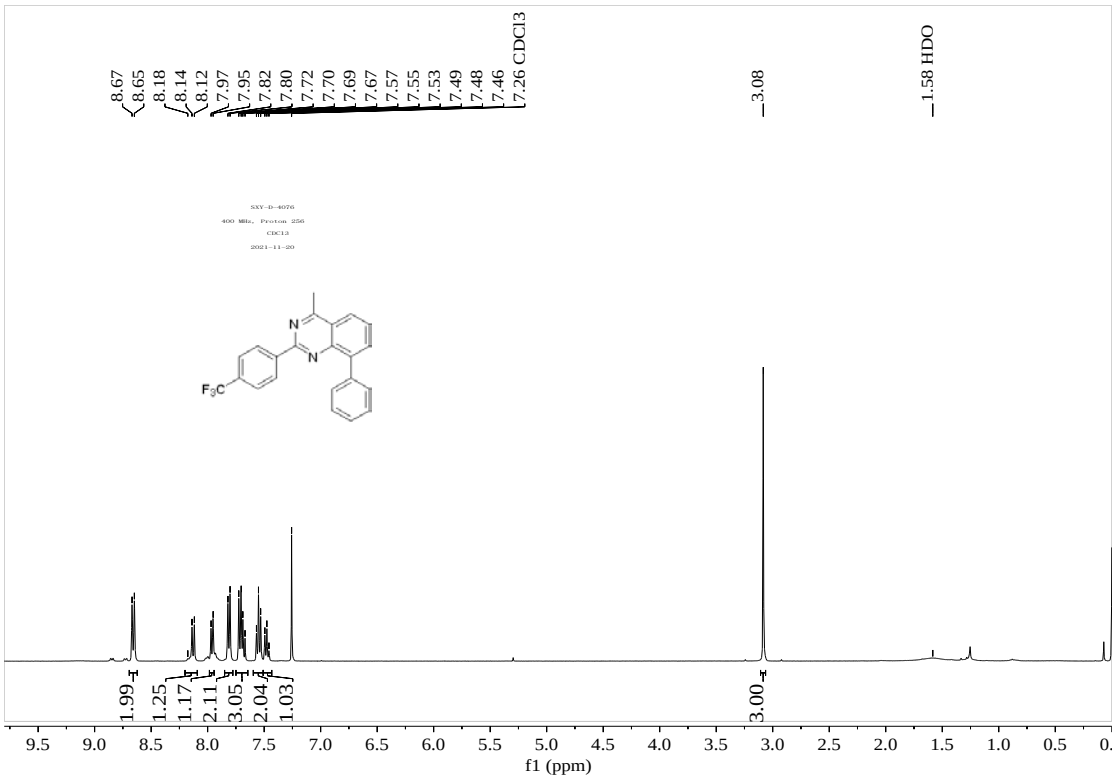


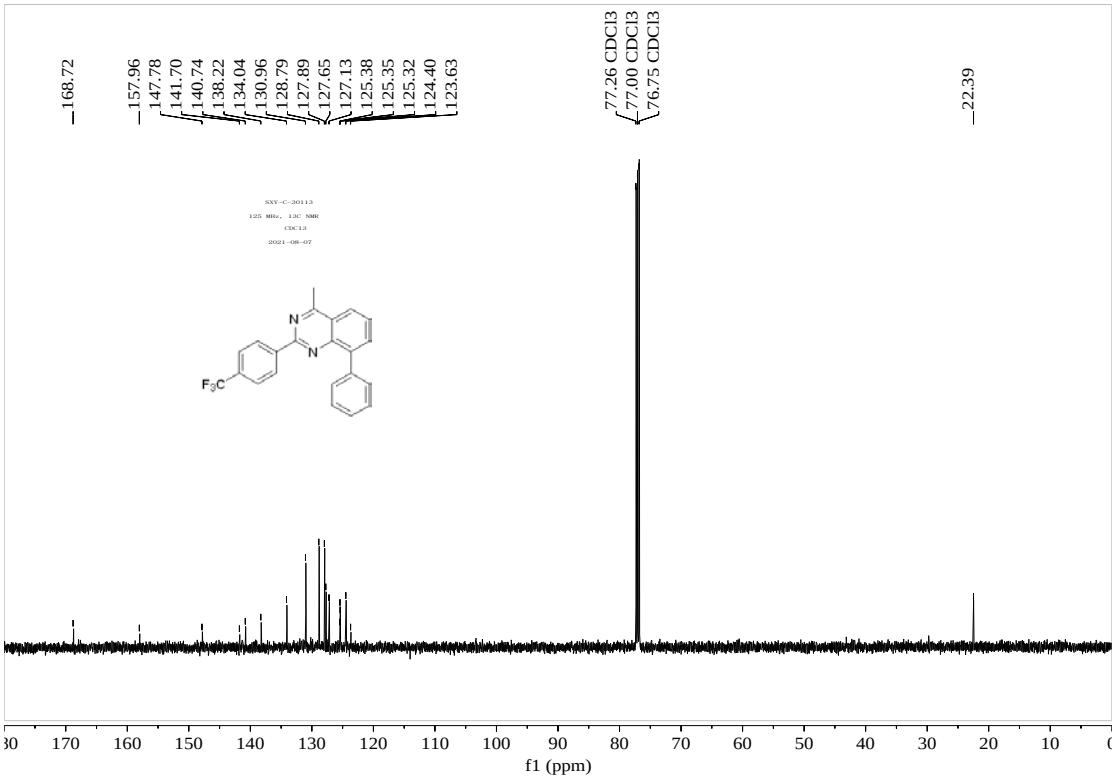
(31) Compound **13a**



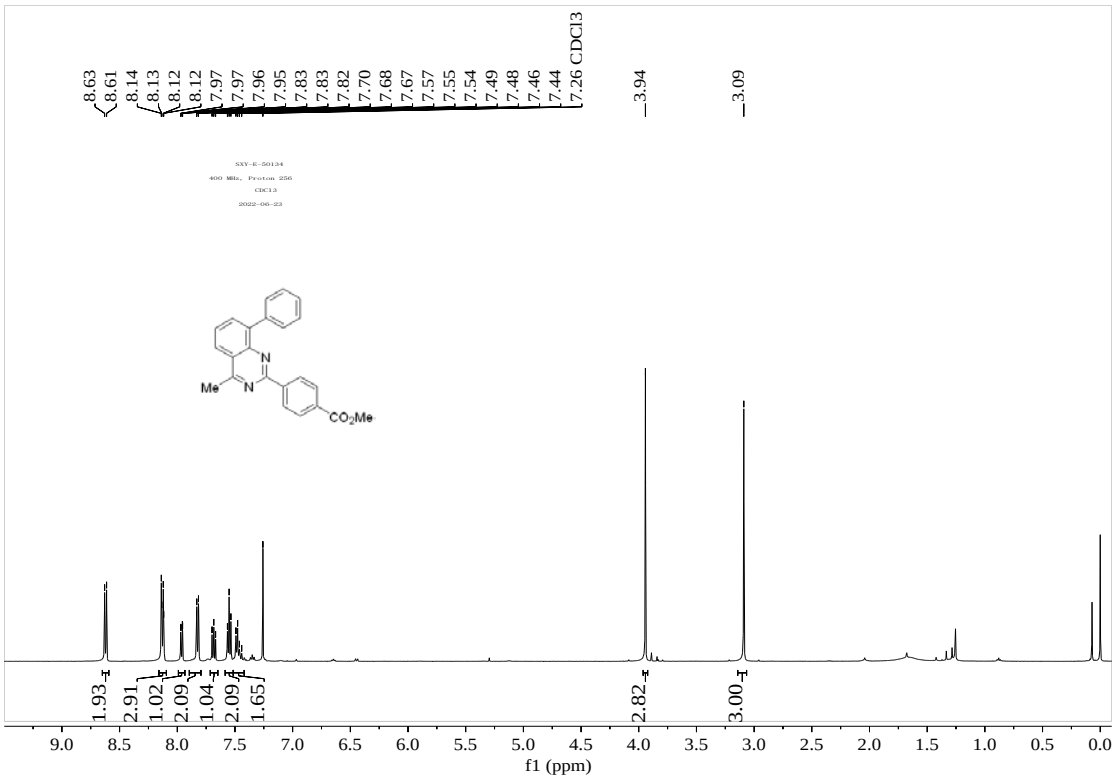


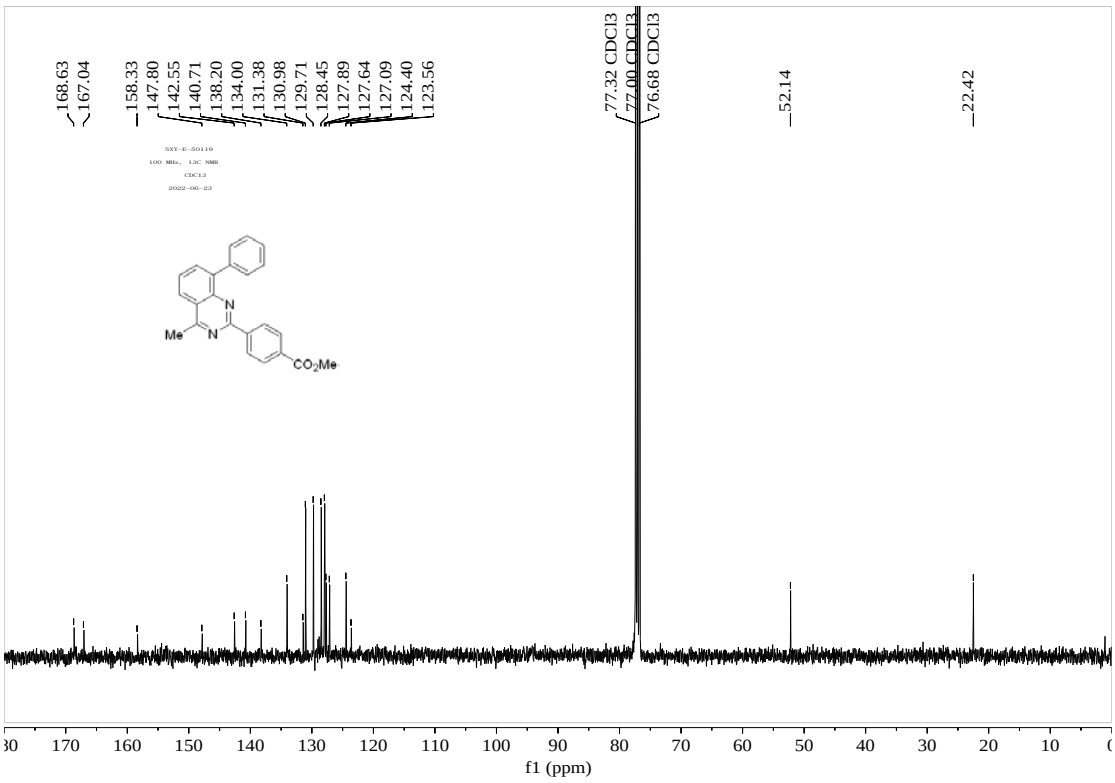
(32) Compound **13b**



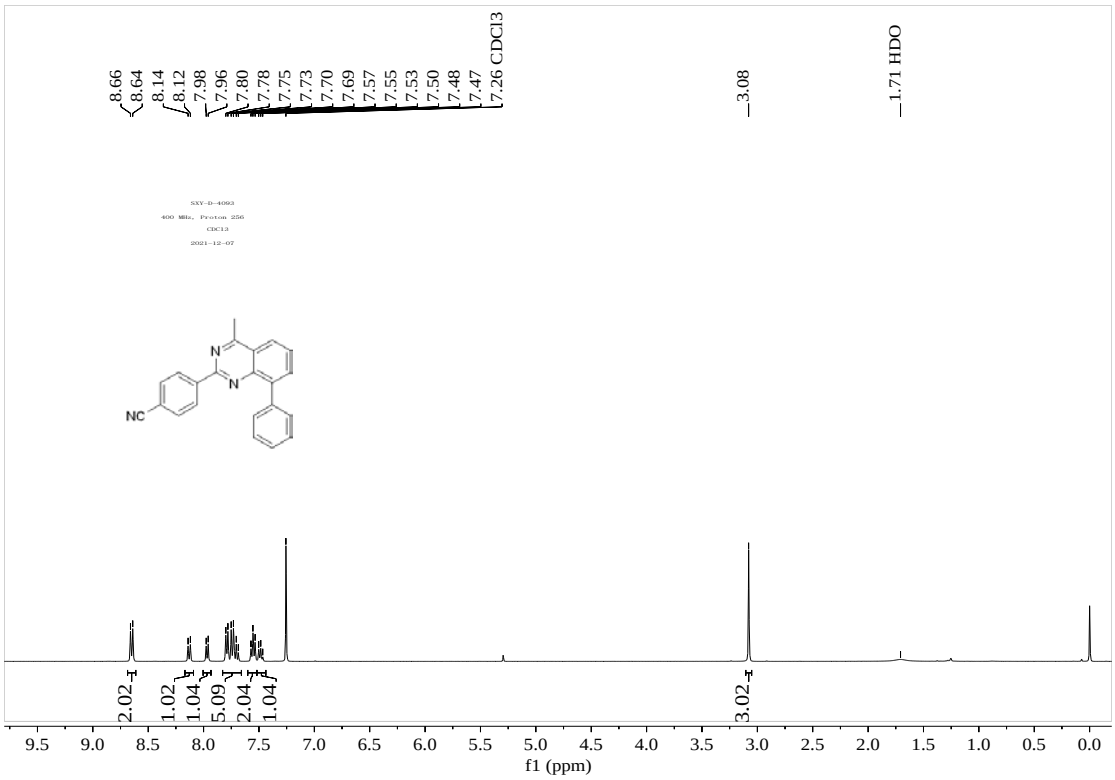


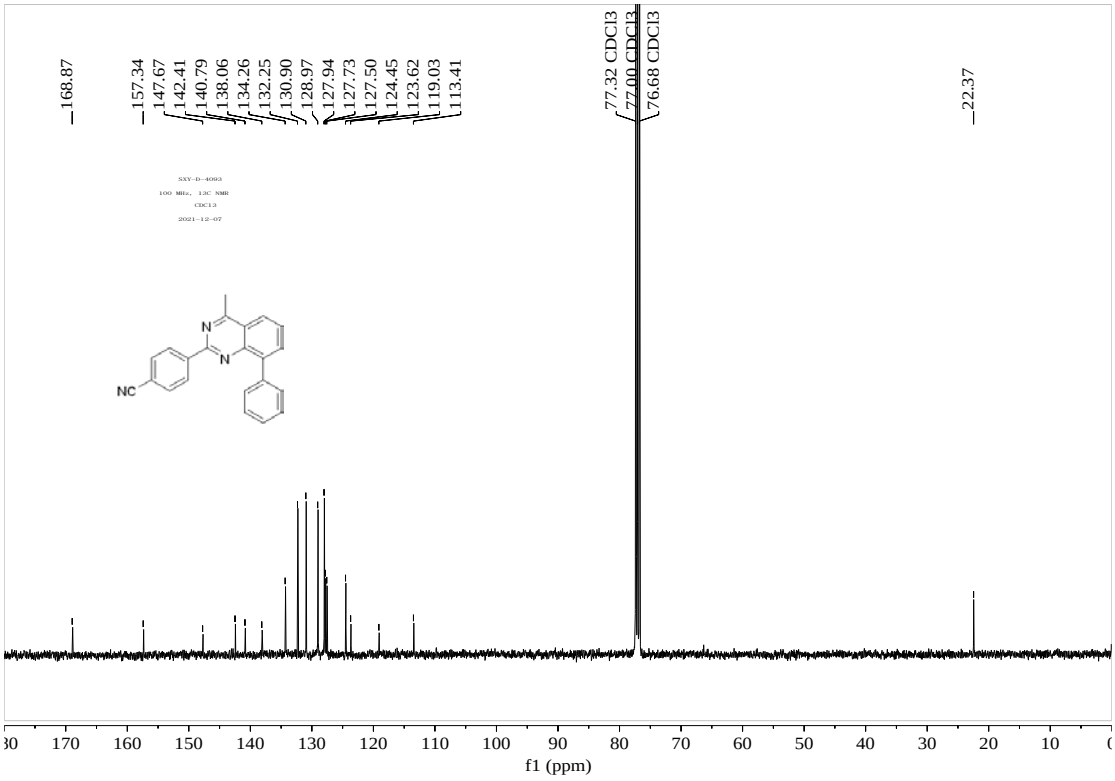
(33) Compound **13c**



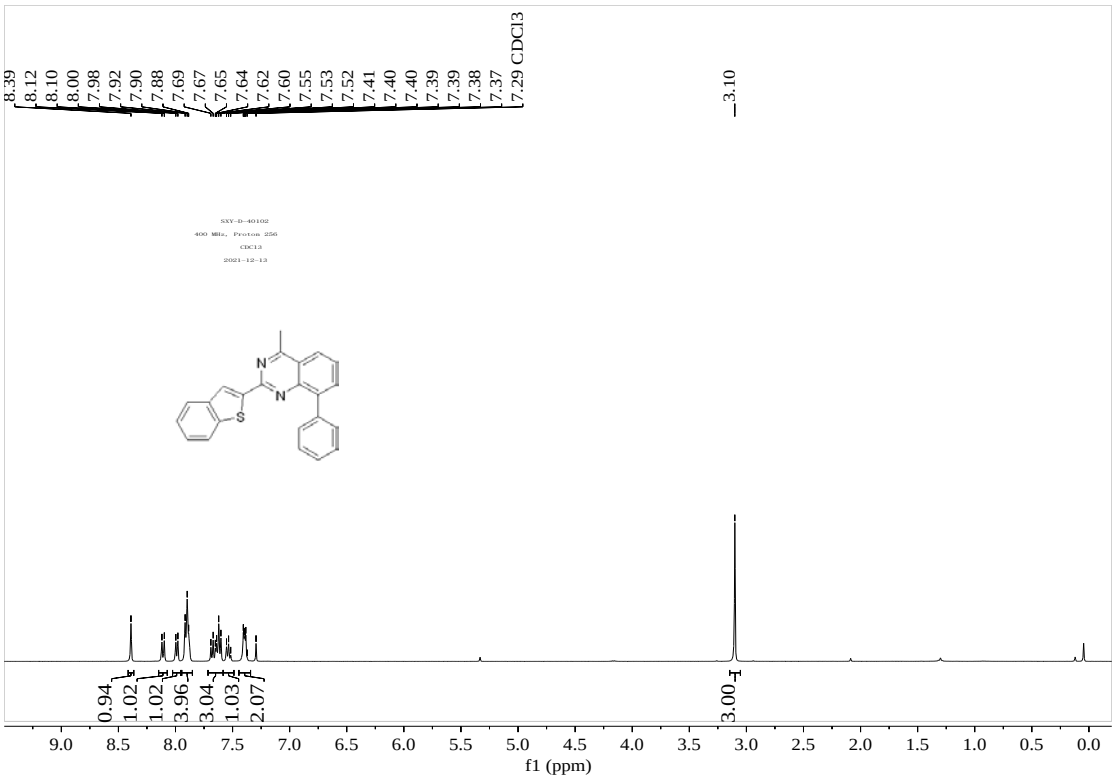


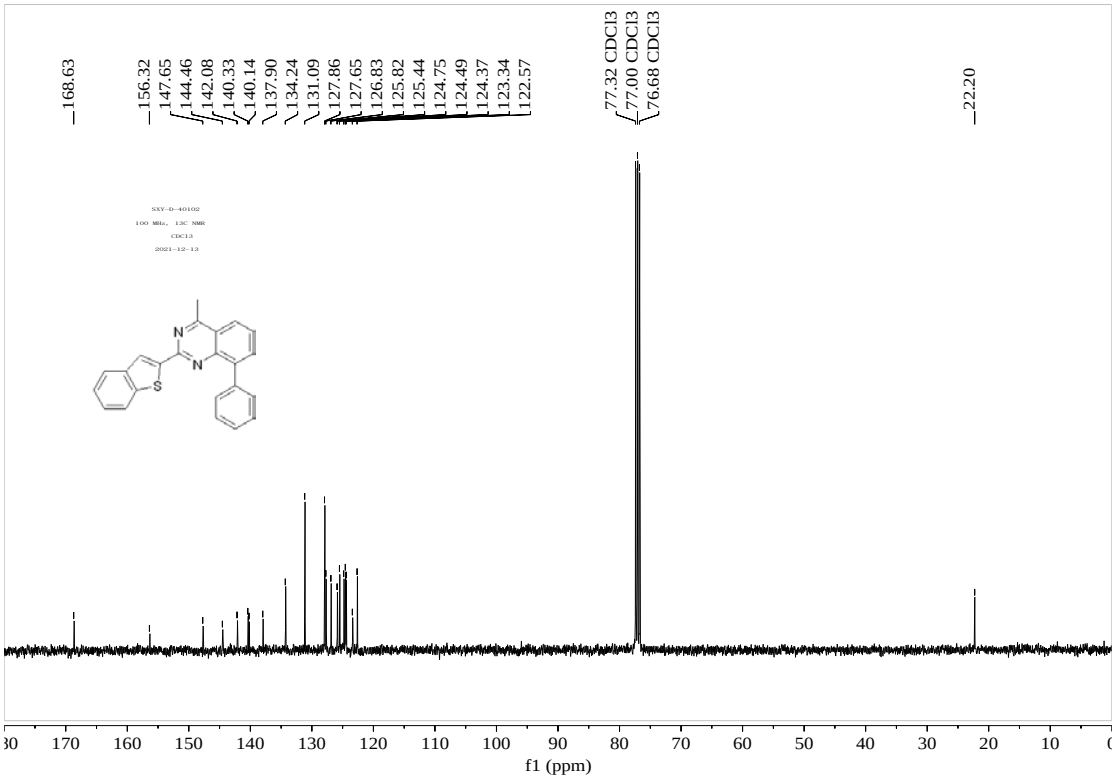
(34) Compound **13d**



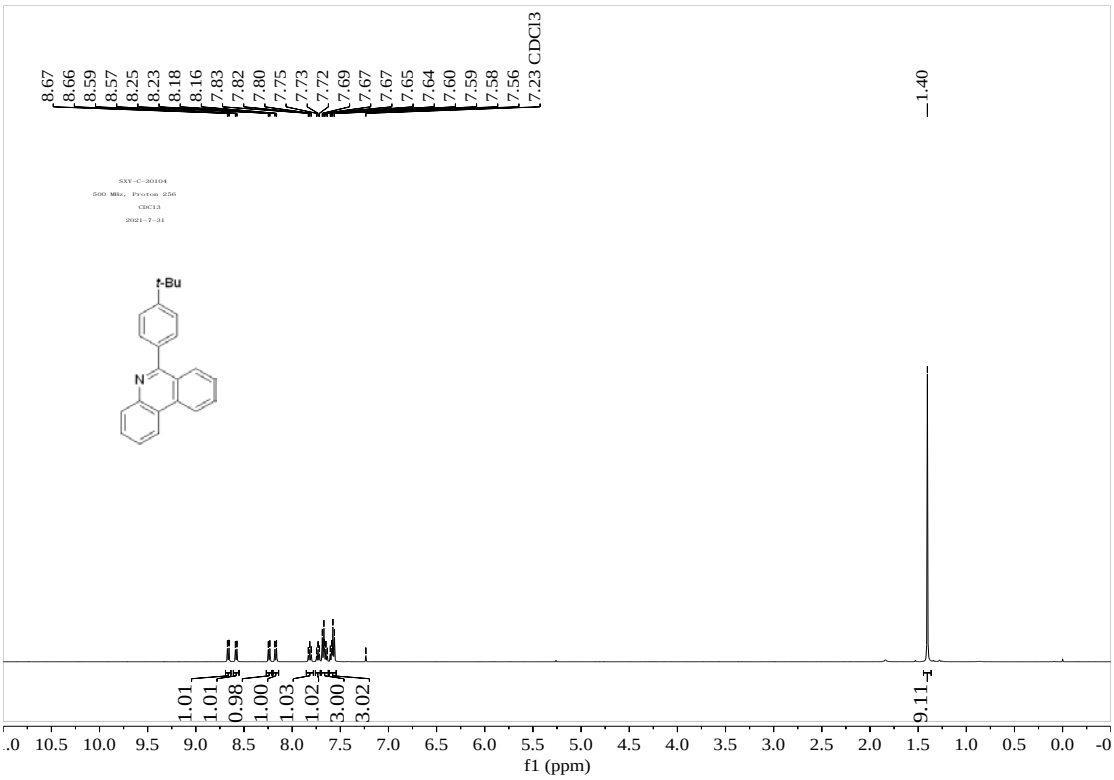


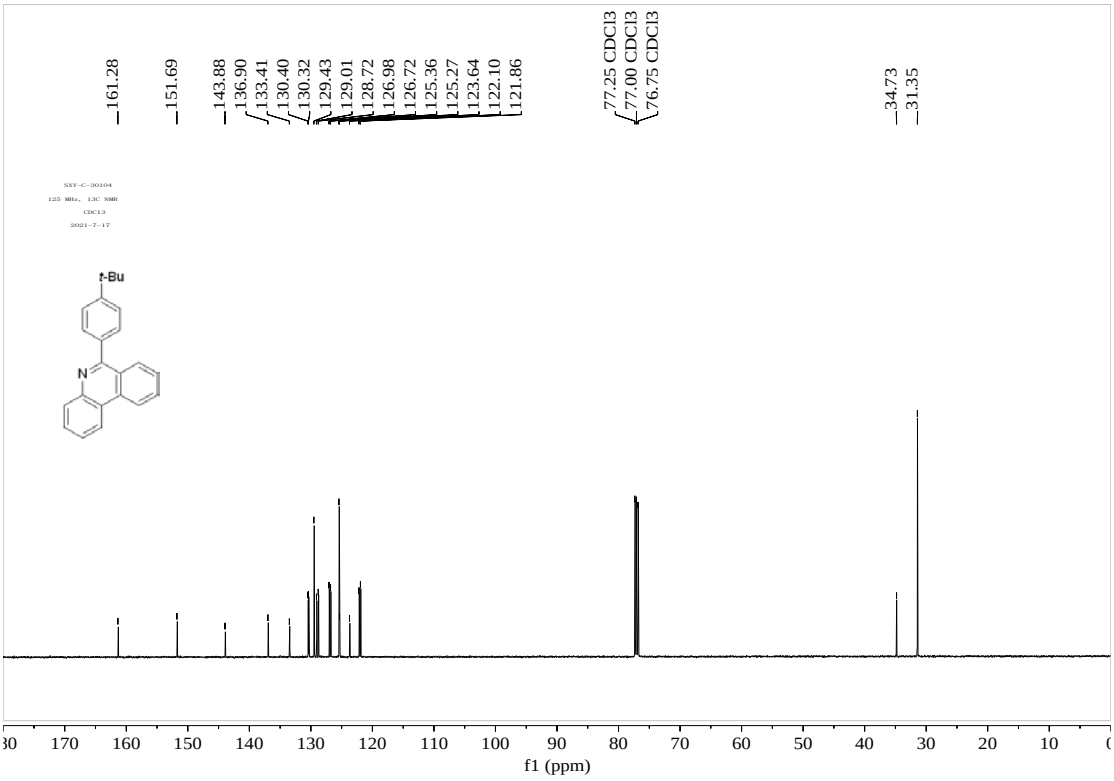
(35) Compound **13e**



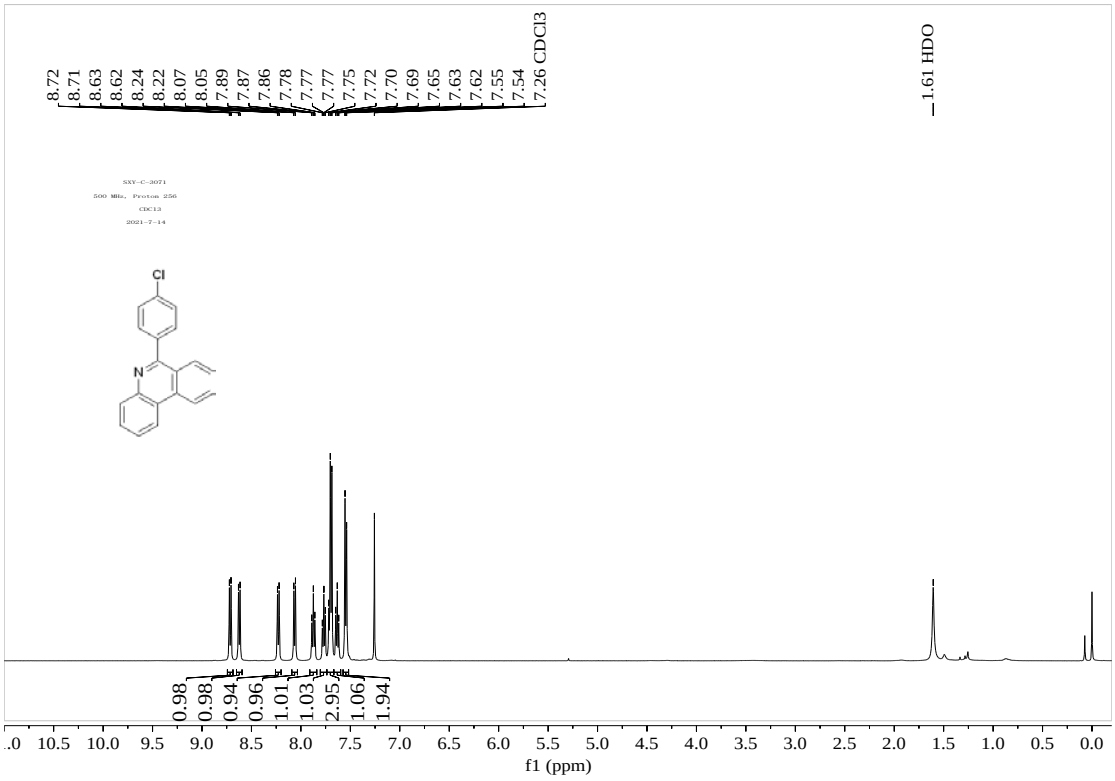


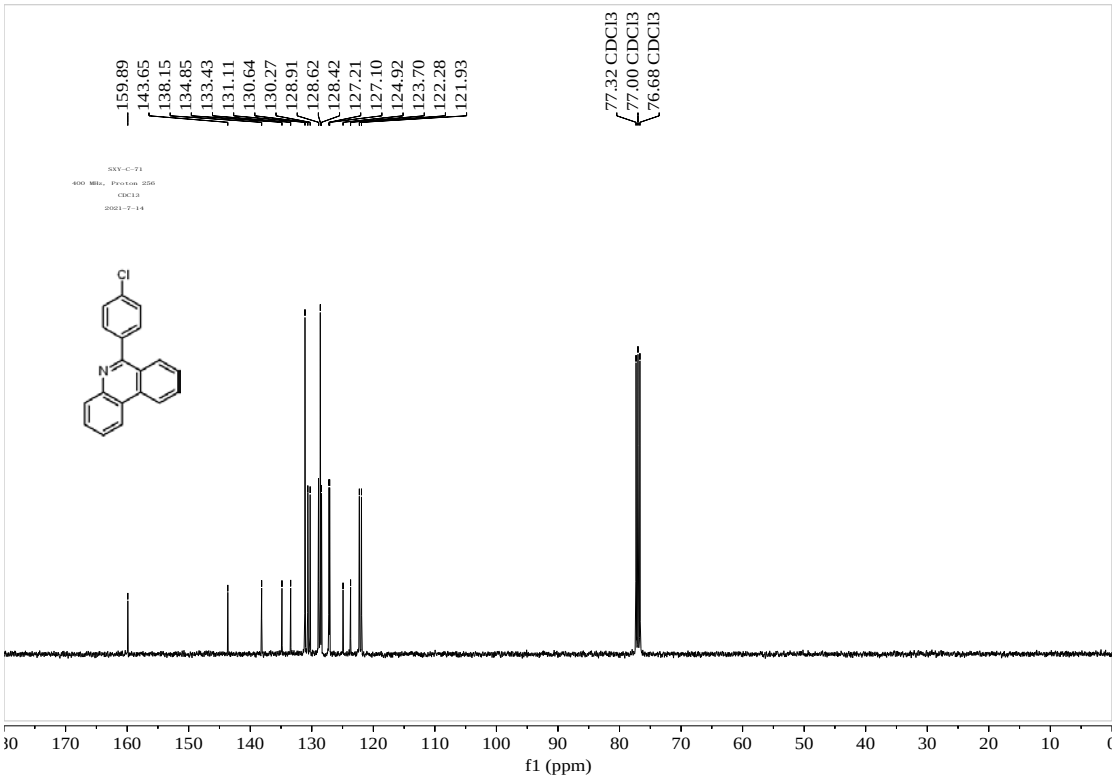
(36) Compound **1s**



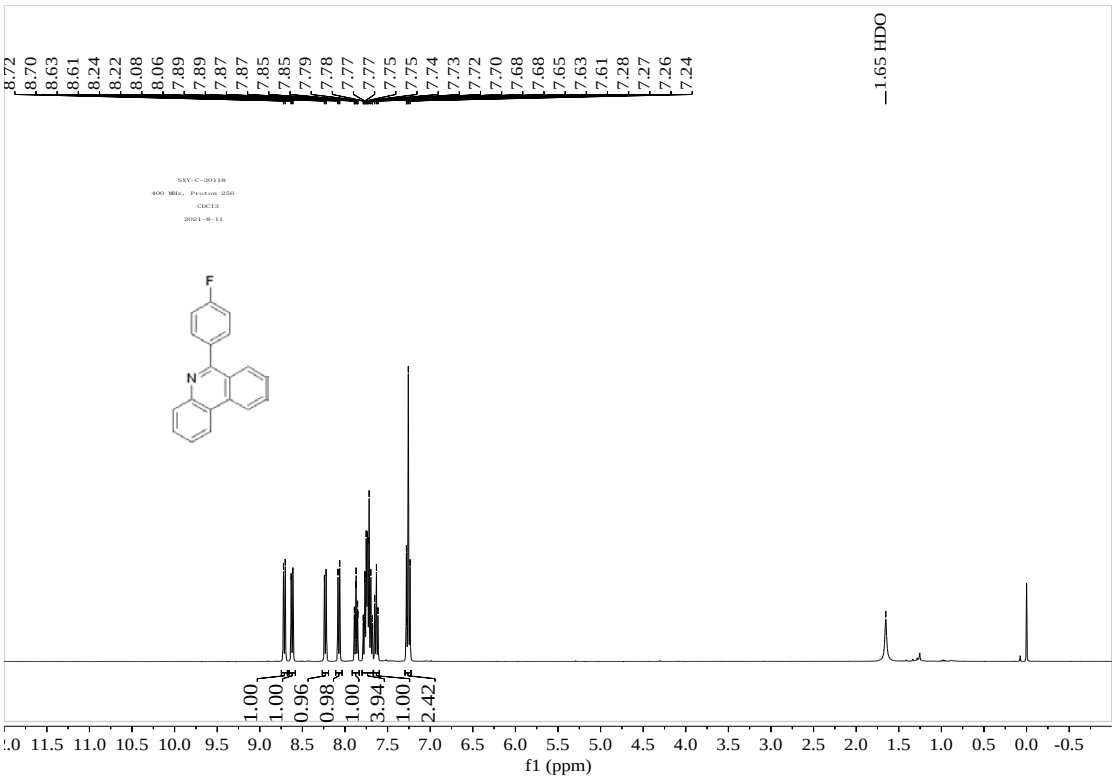


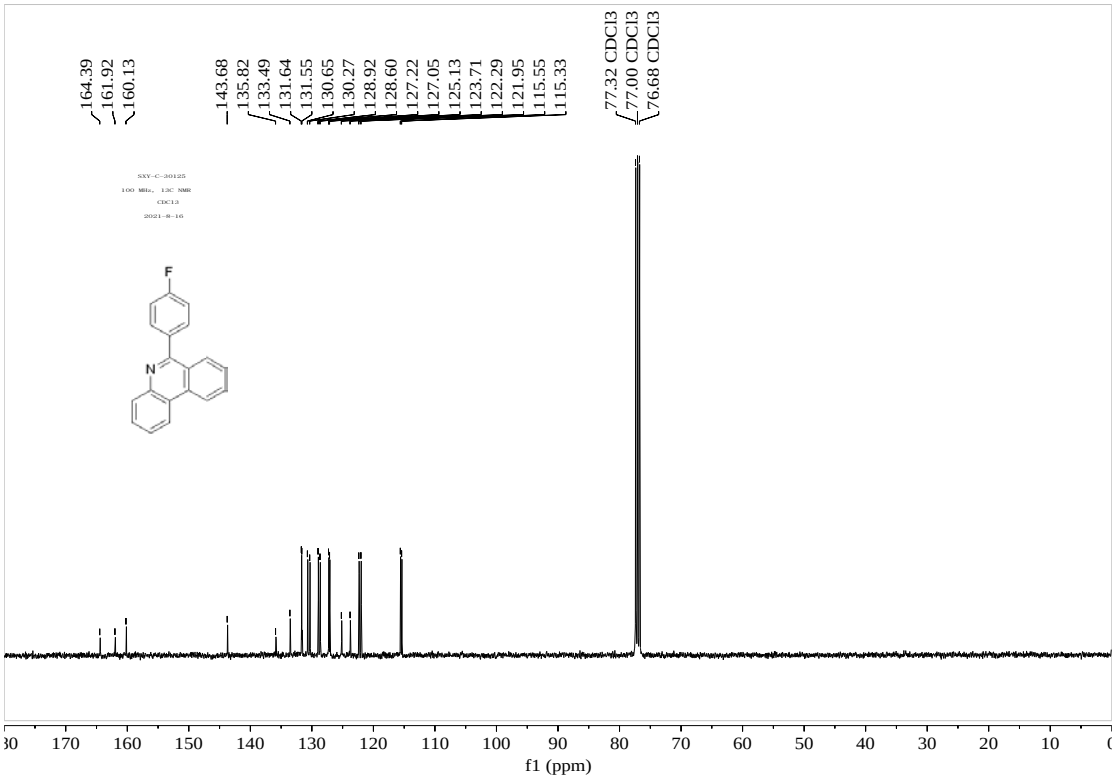
(37) Compound **1t**



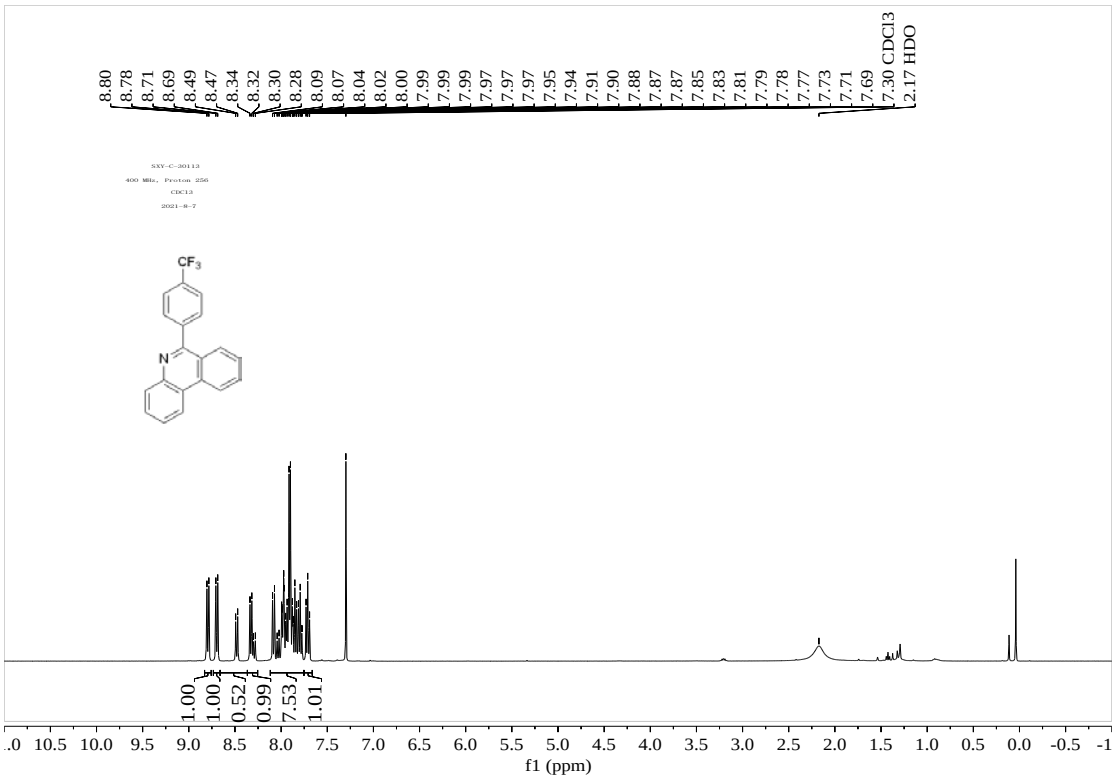


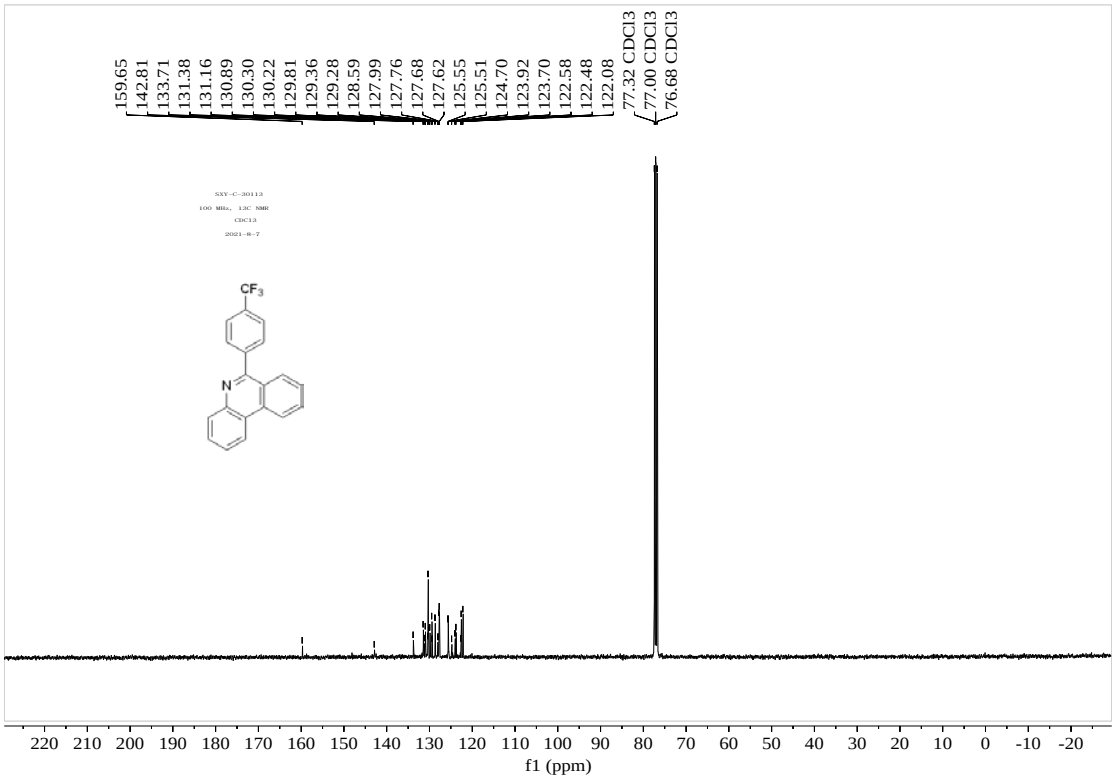
(38) Compound **1u**



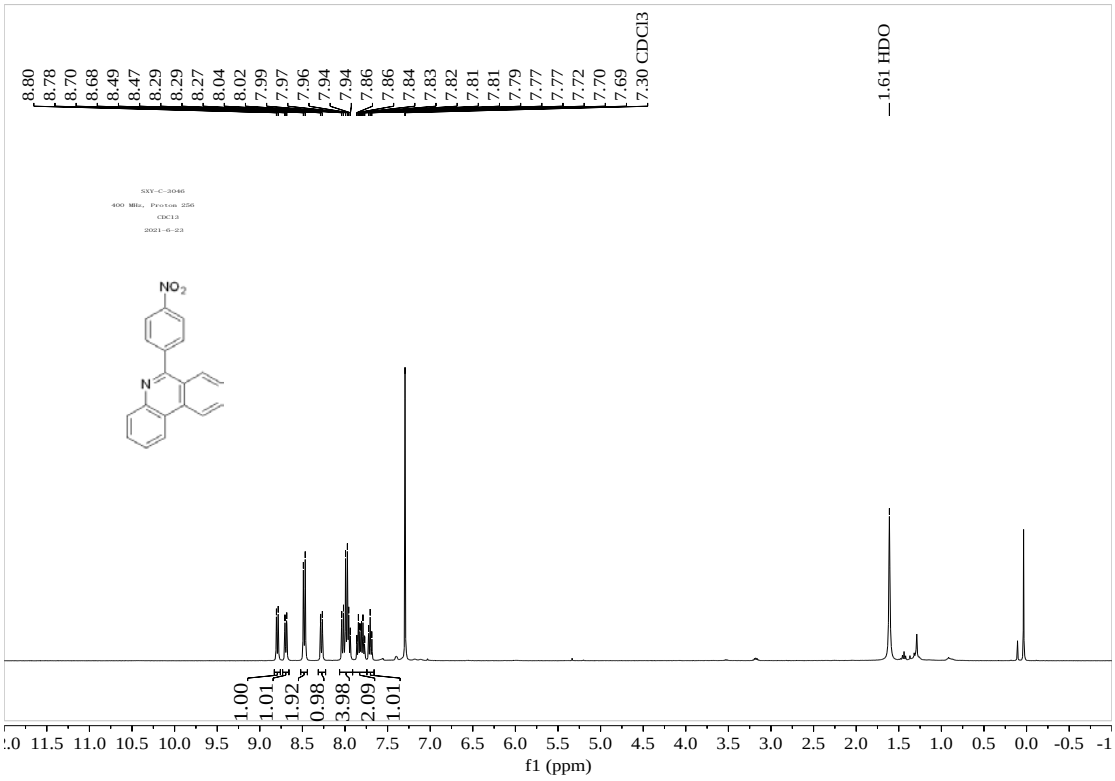


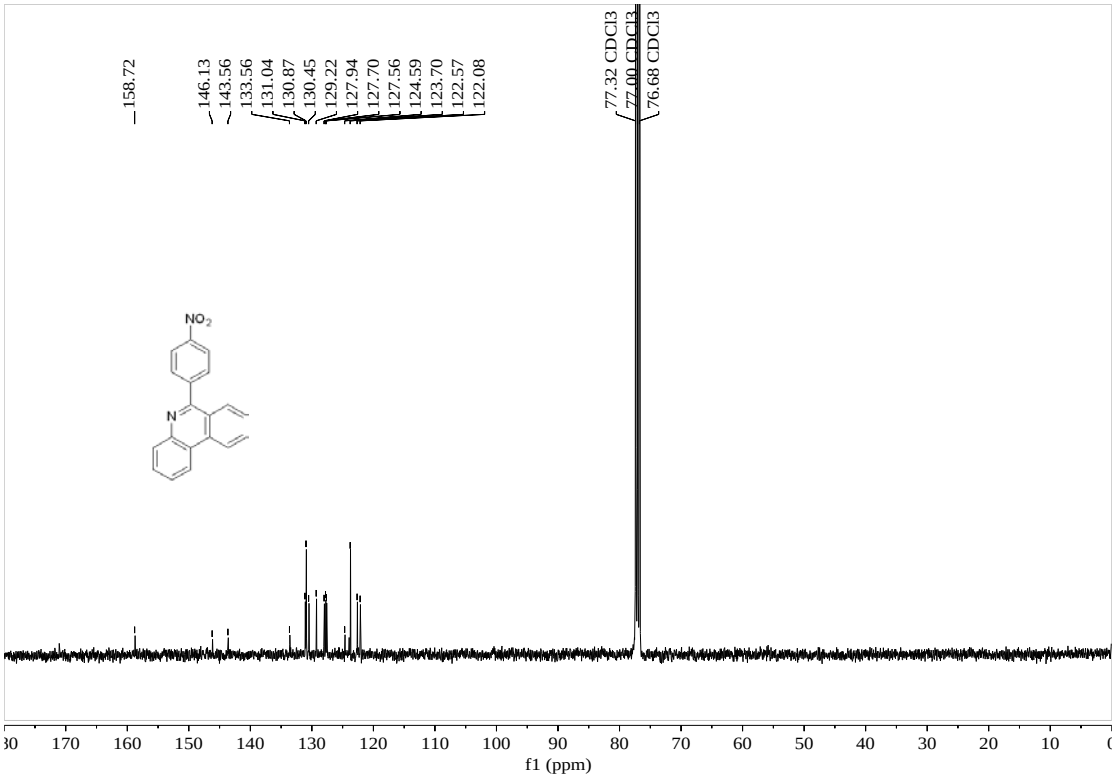
(39) Compound **1v**



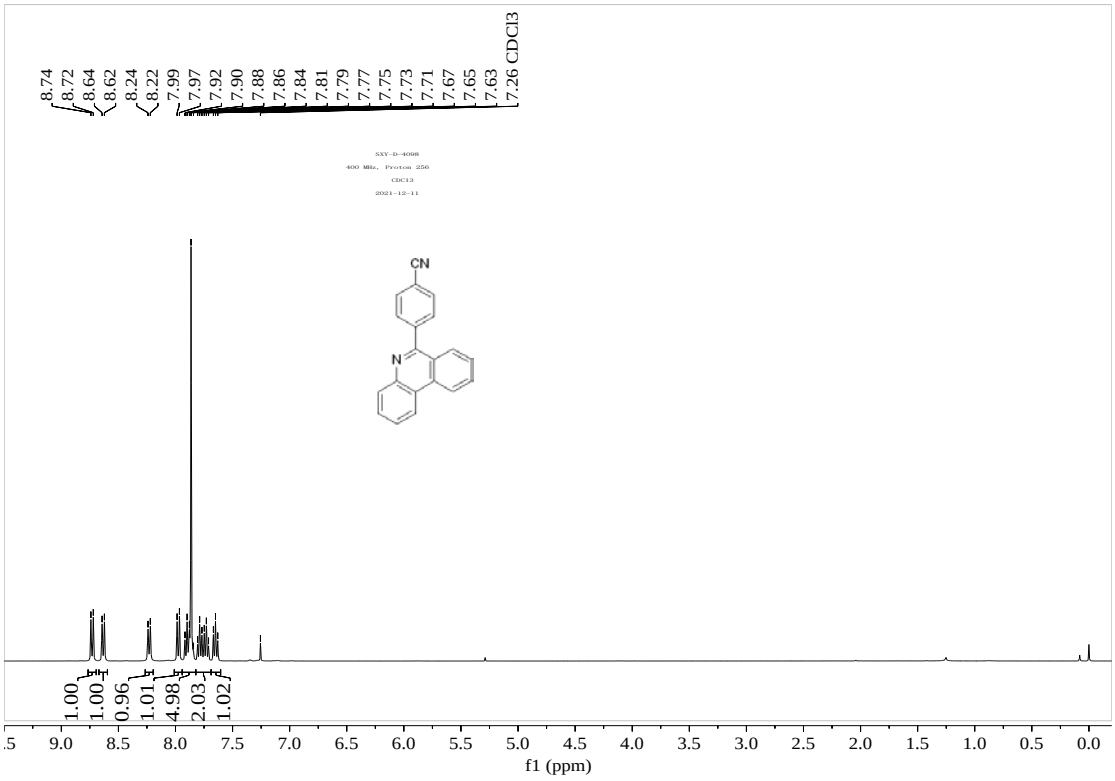


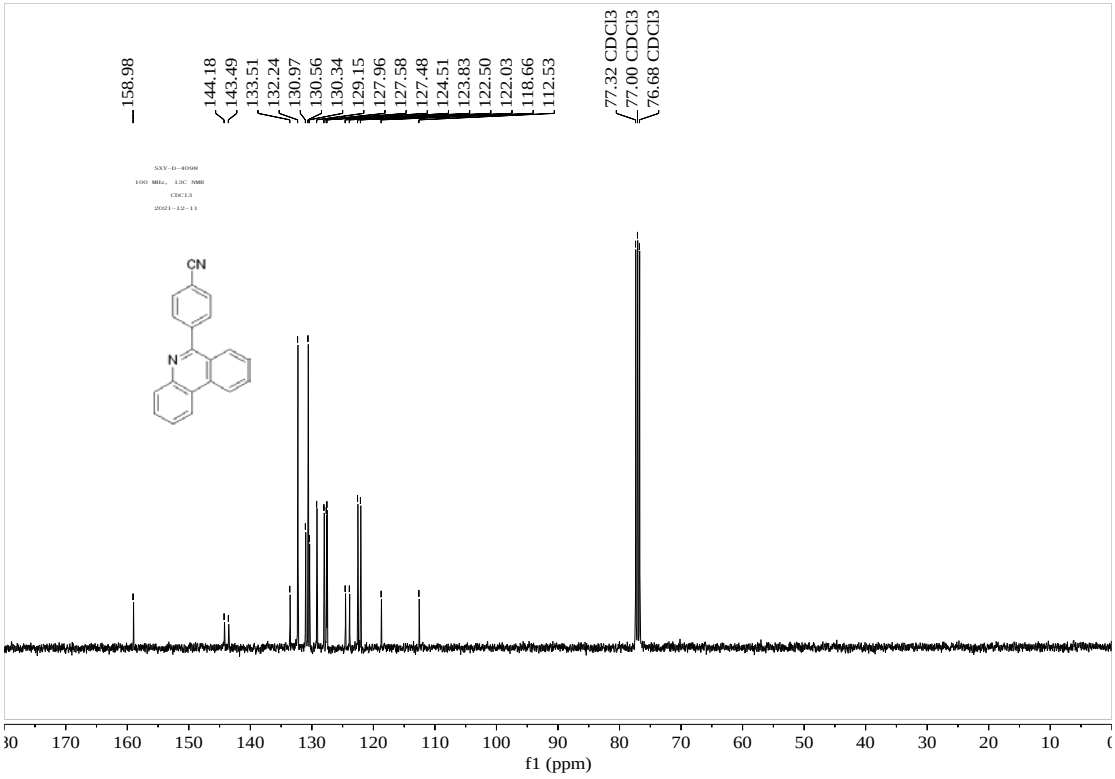
(40) Compound **1w**



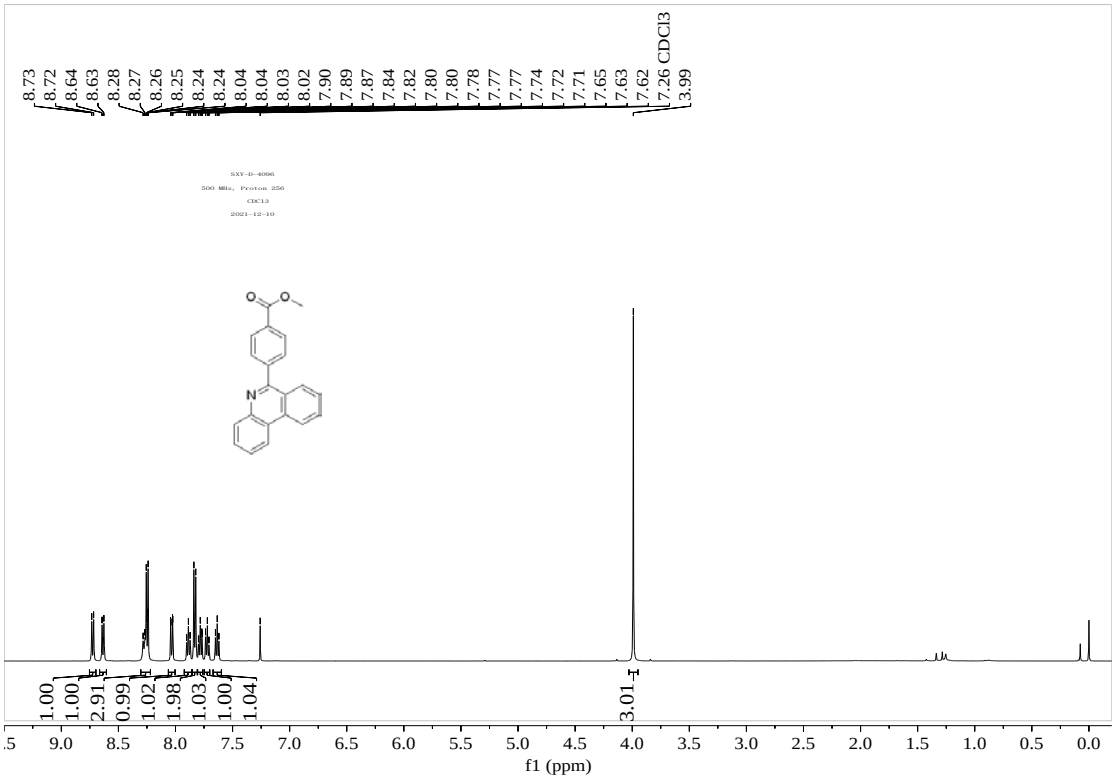


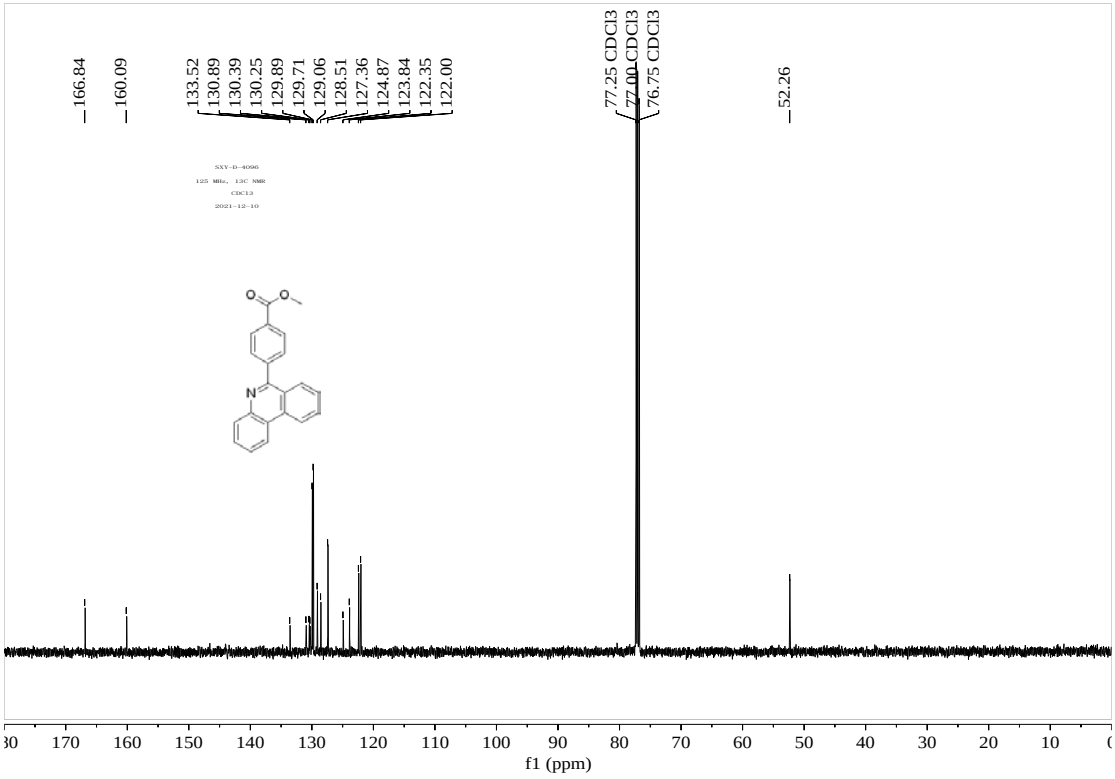
(41) Compound **1x**



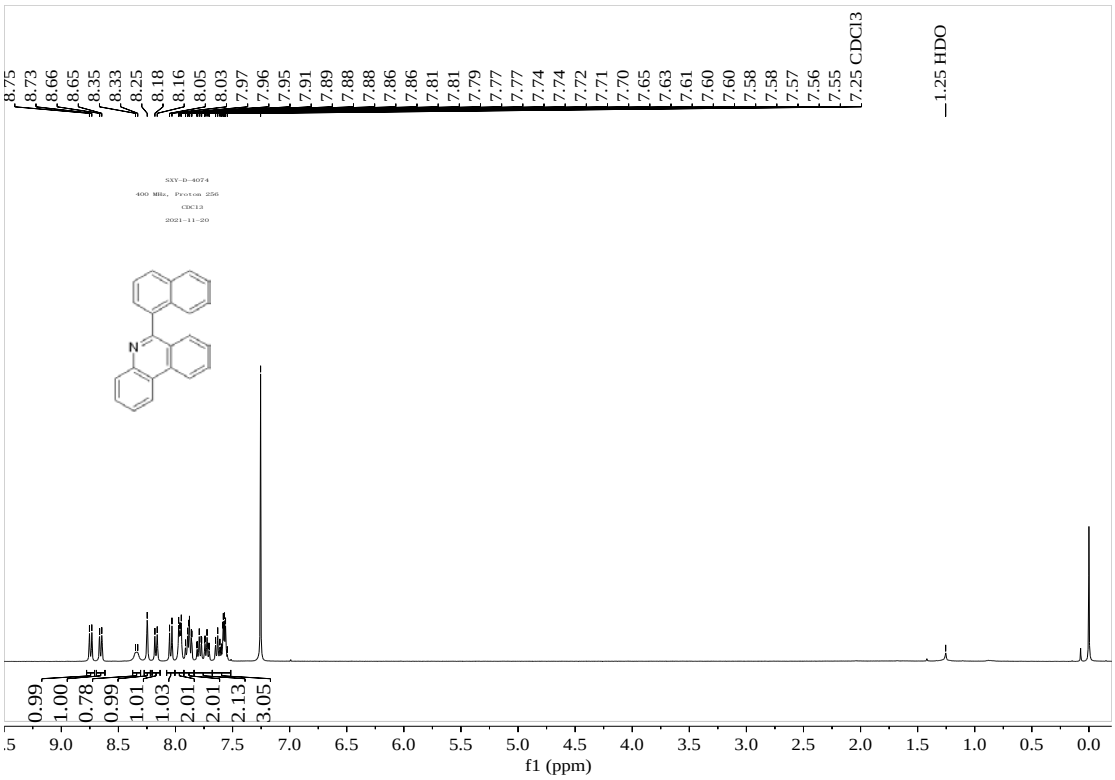


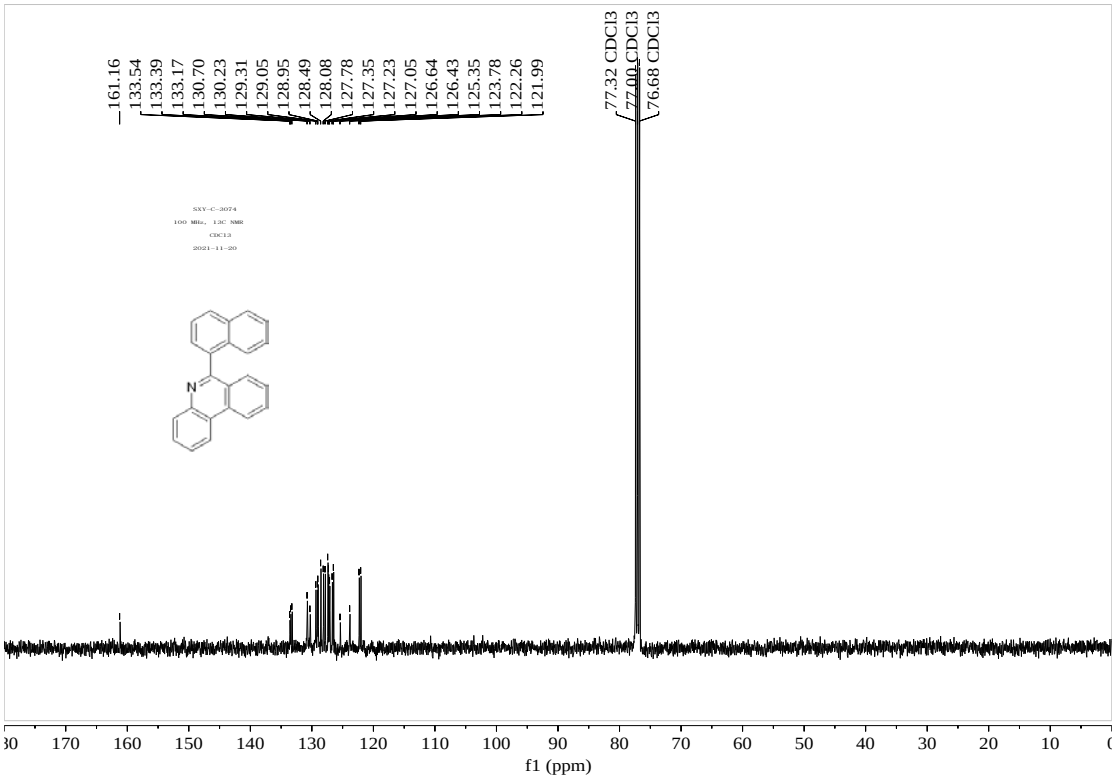
(42) Compound **1y**



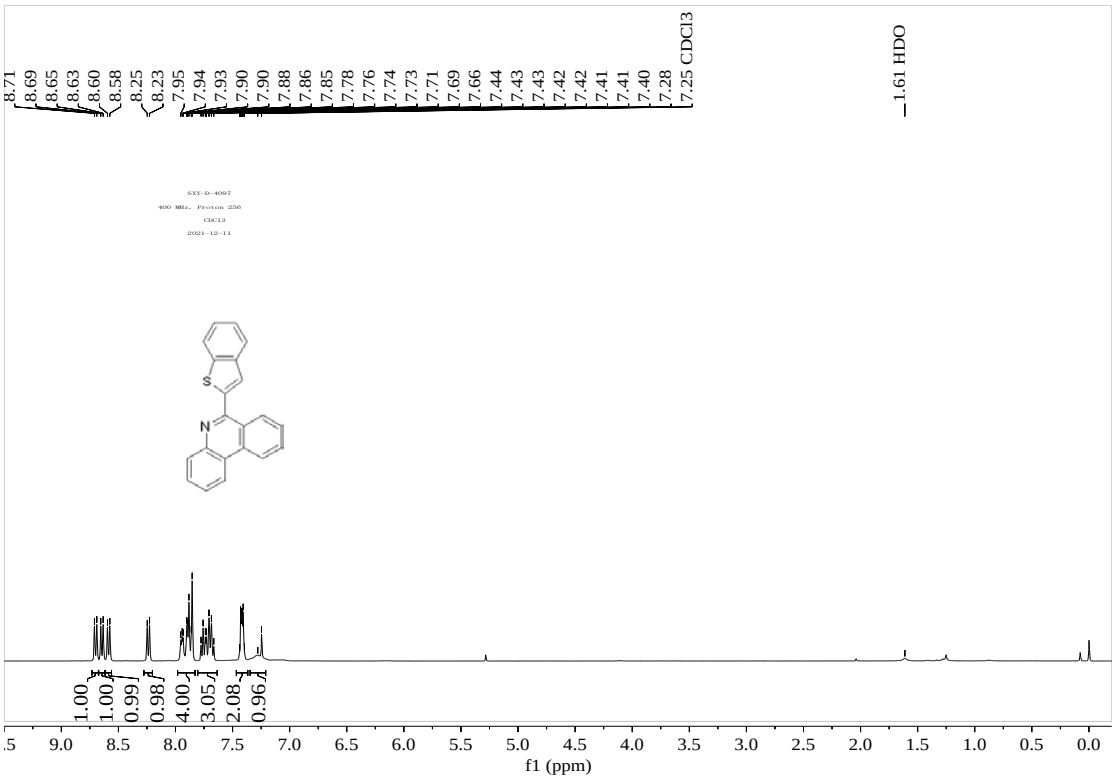


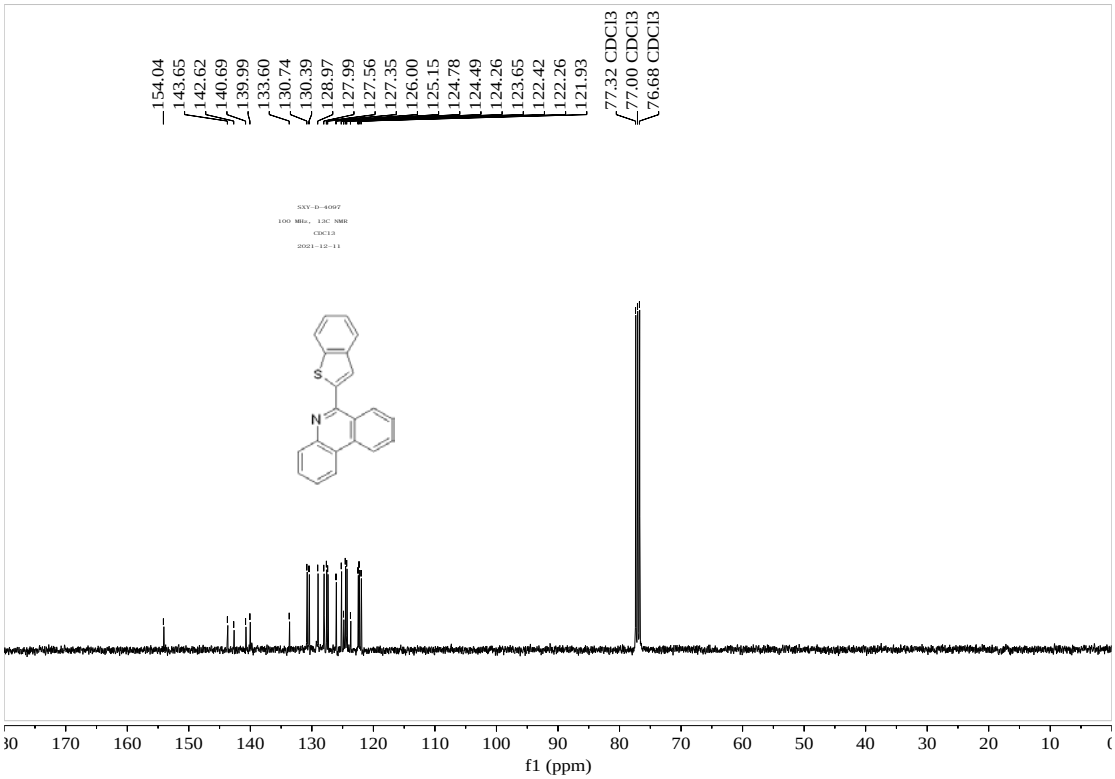
(43) Compound **1z**



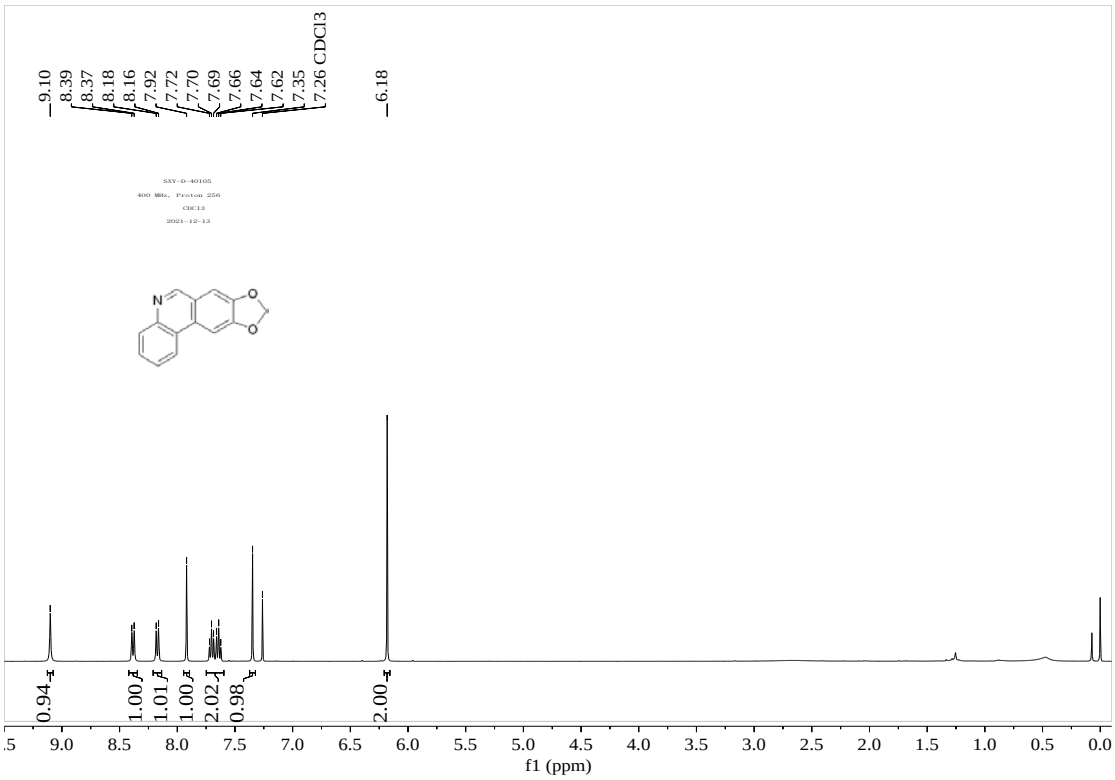


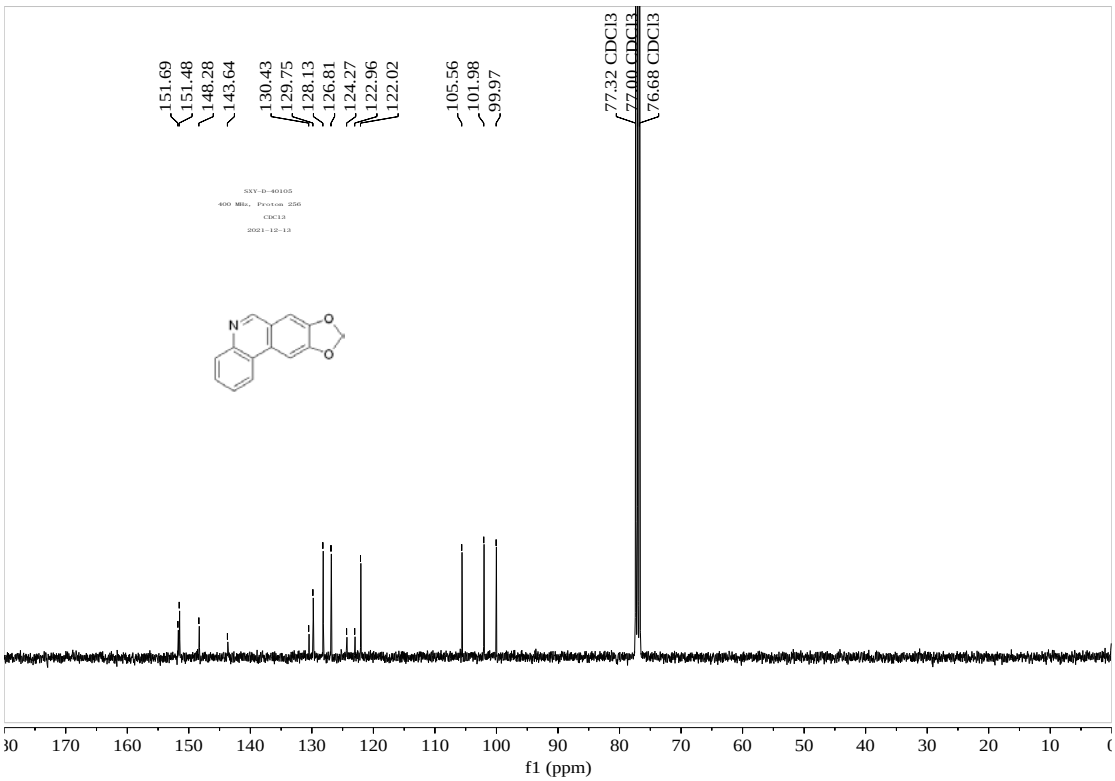
(44) Compound **1aa**



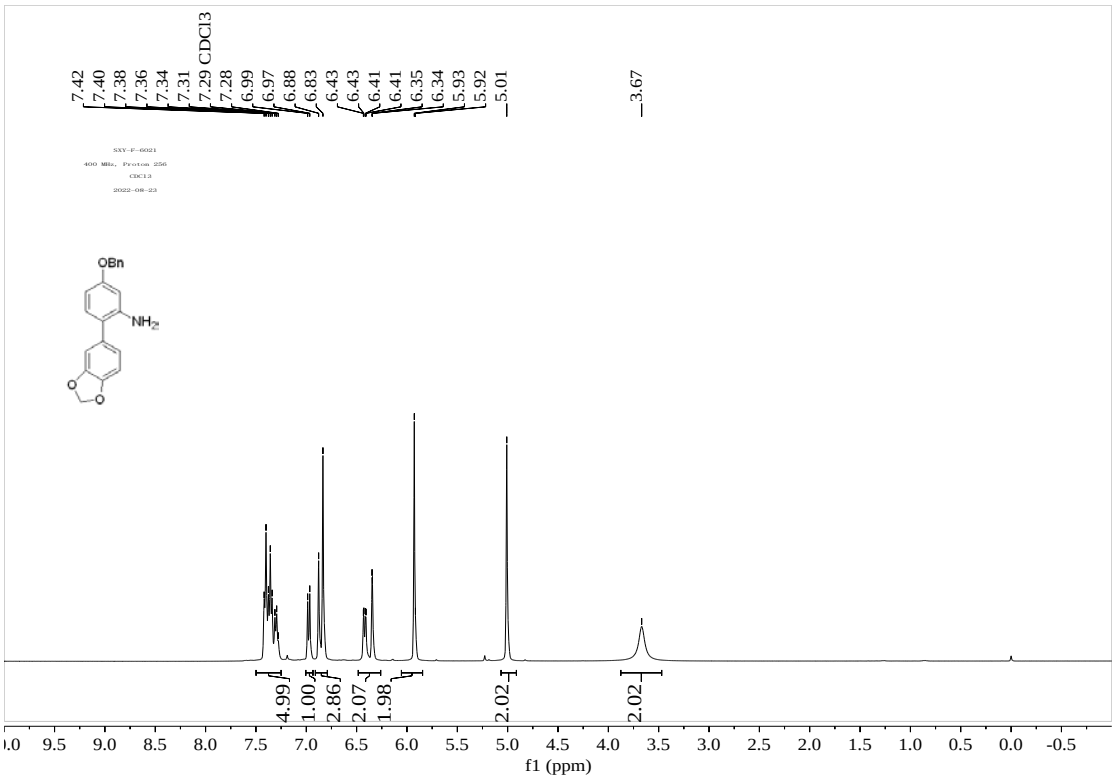


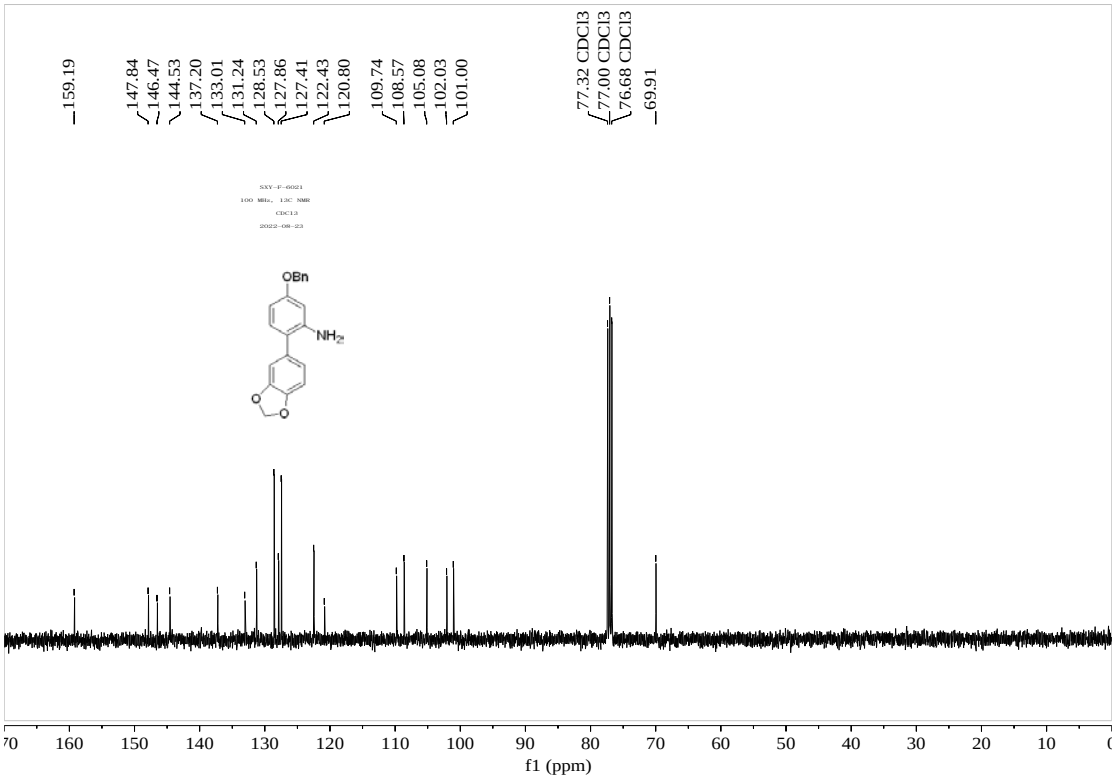
(45) Trisphaeridine (**4**)



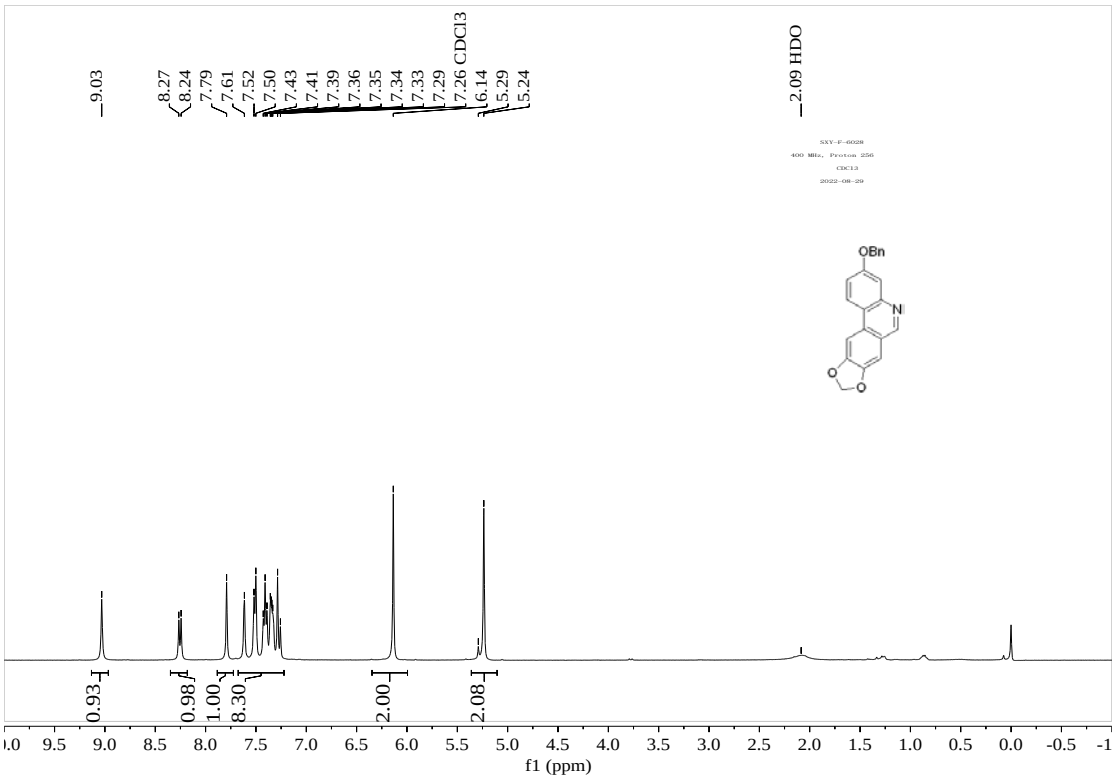


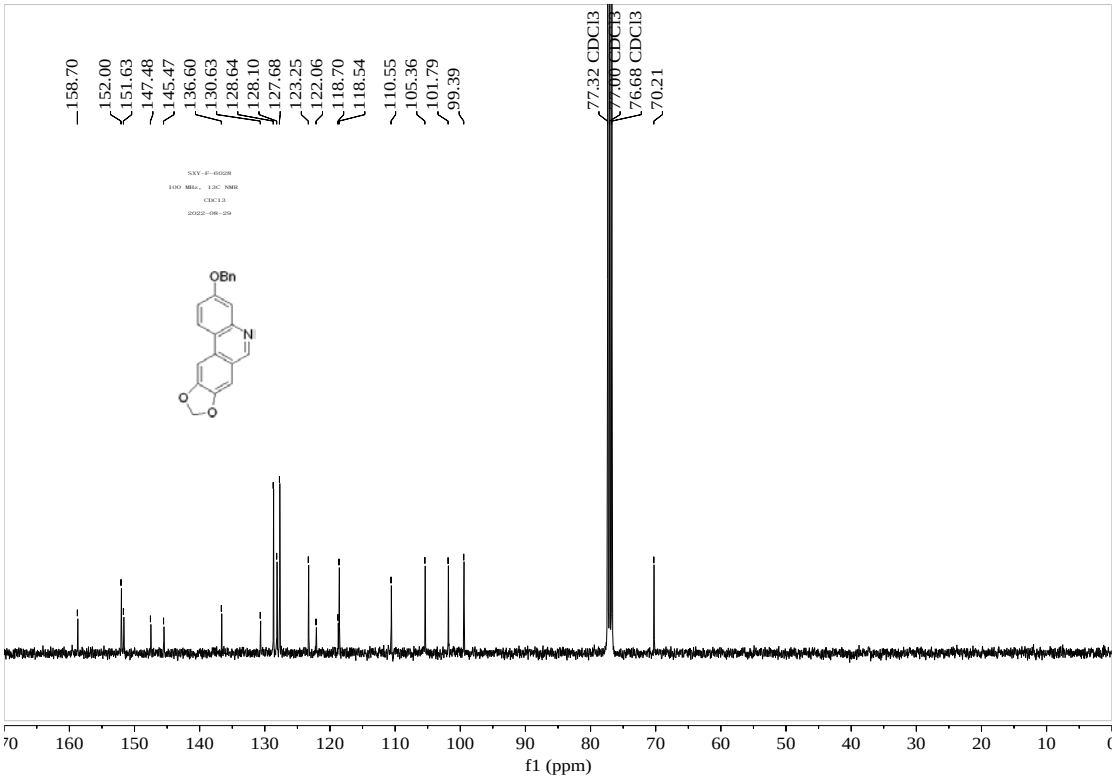
(46) Compound **16c**



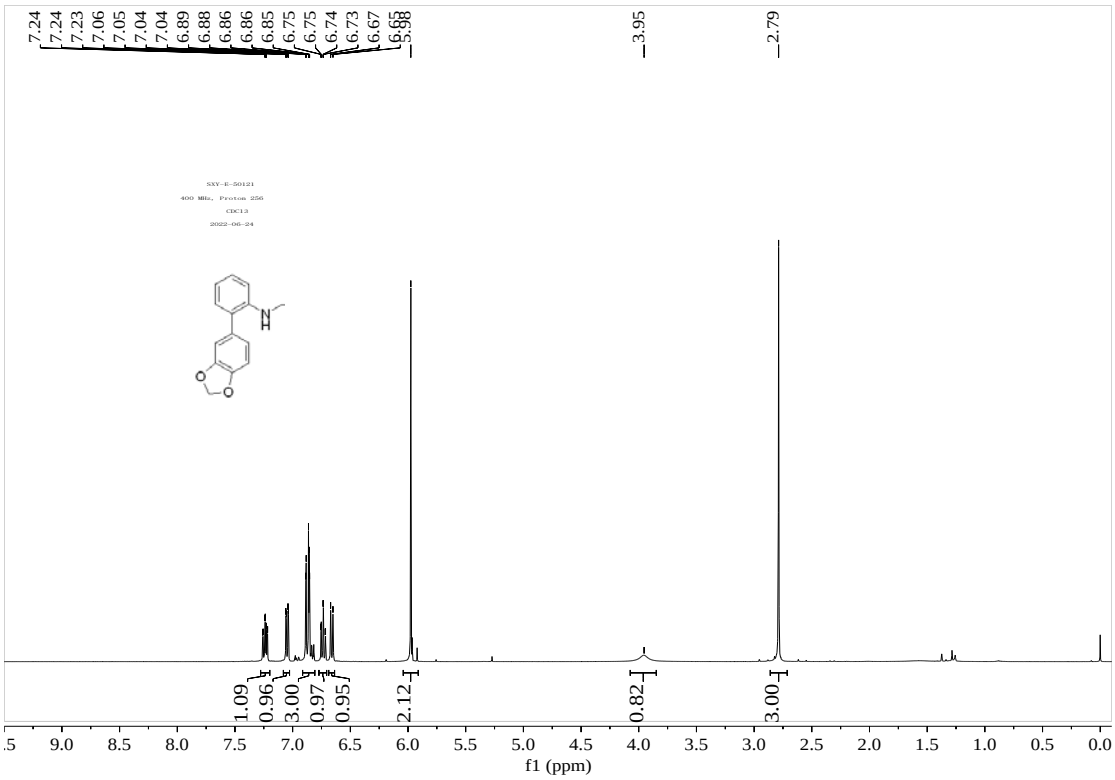


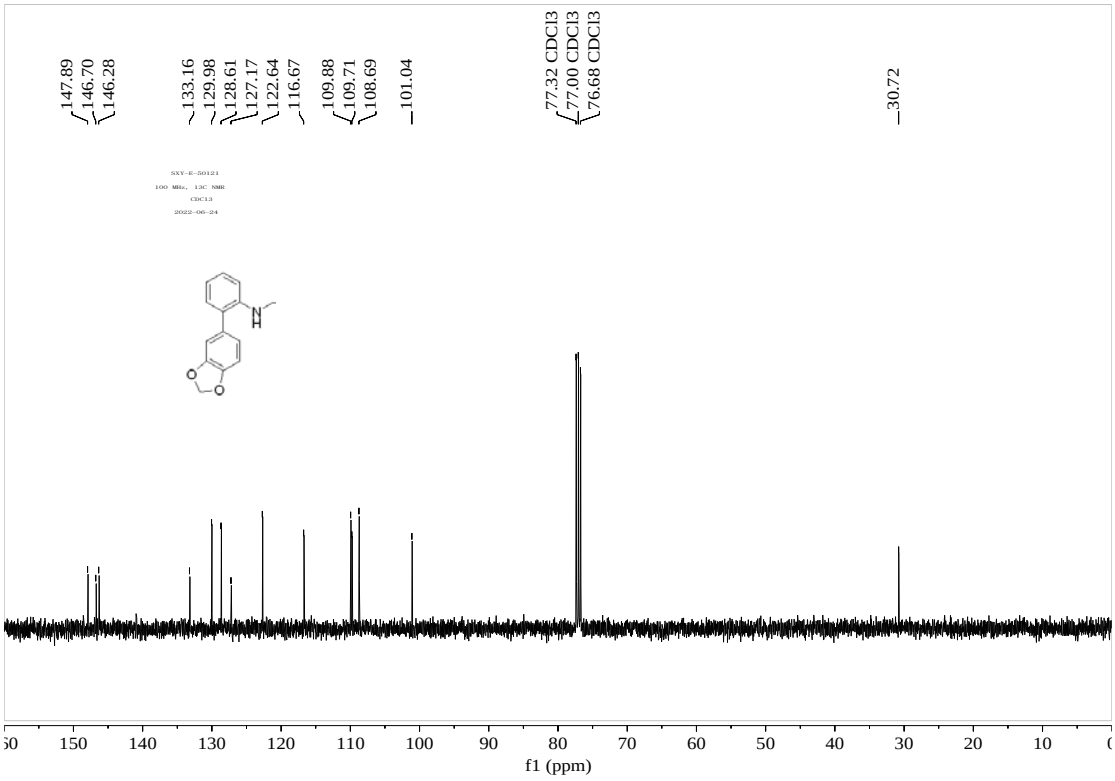
(47) Compound **17**



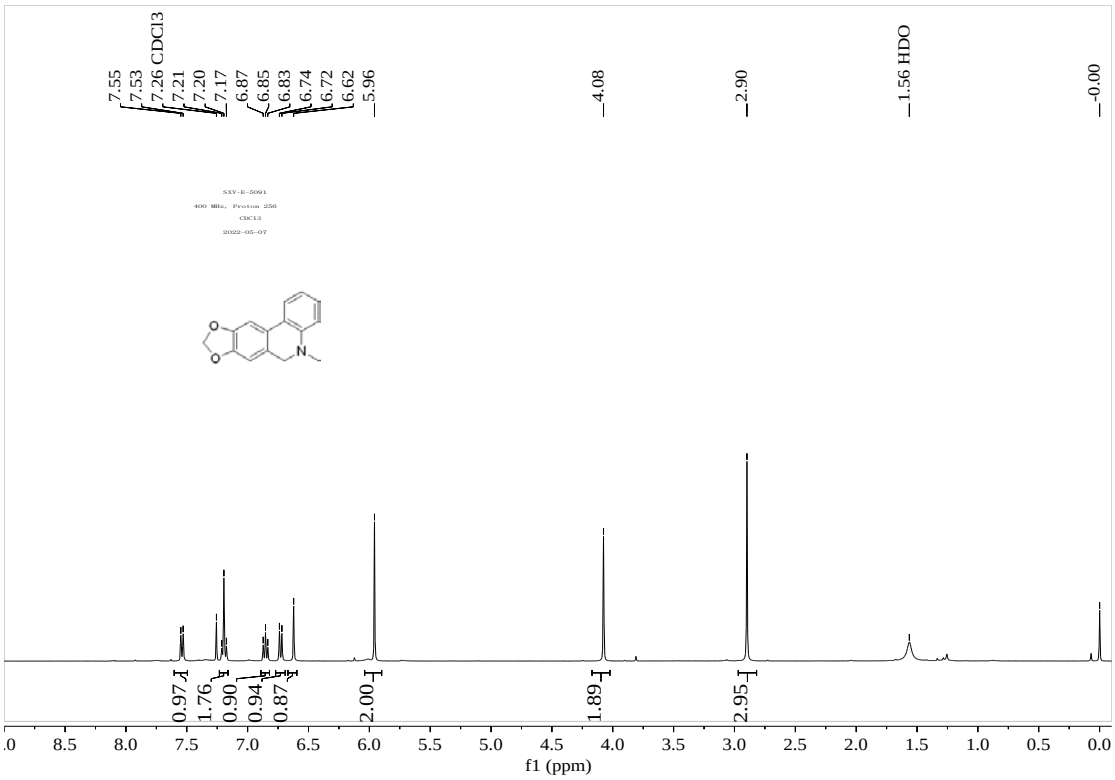


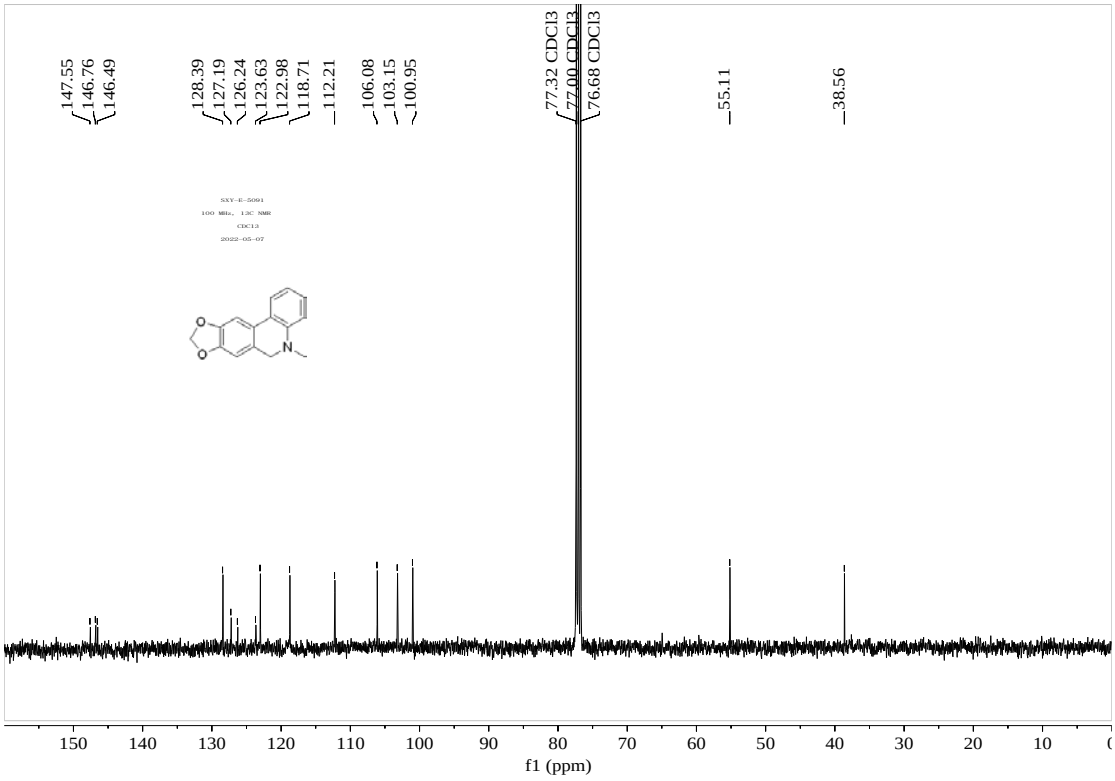
(48) Compound 1**6b**



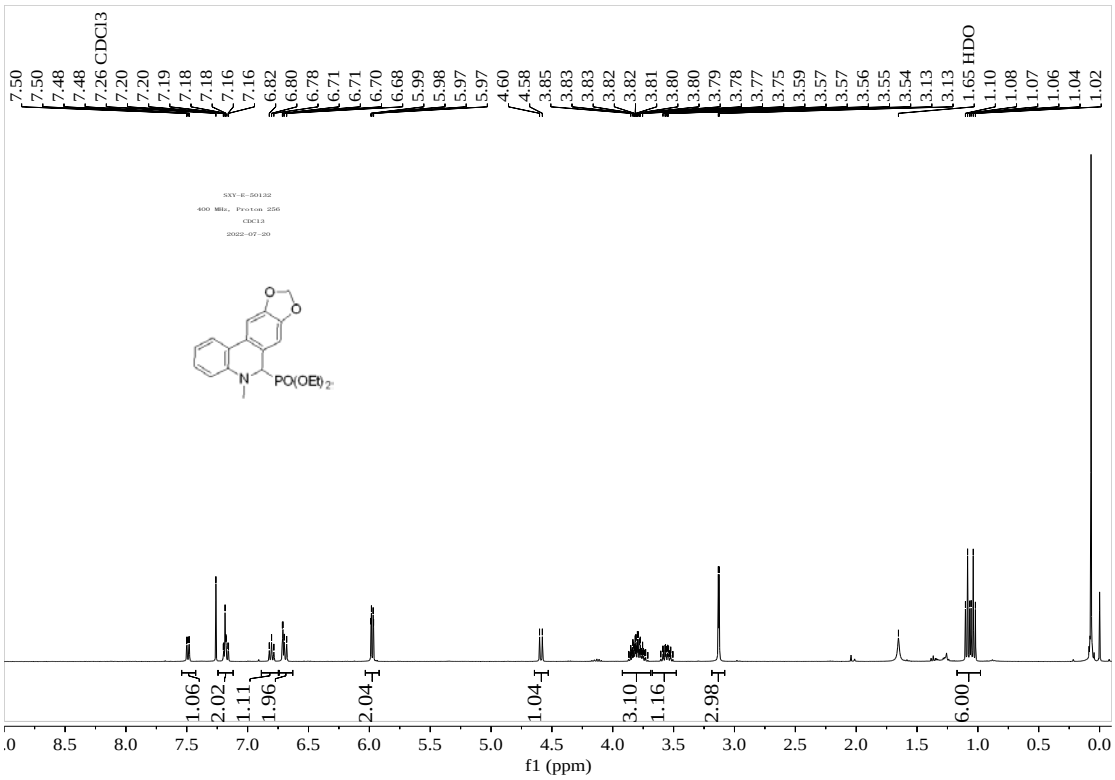


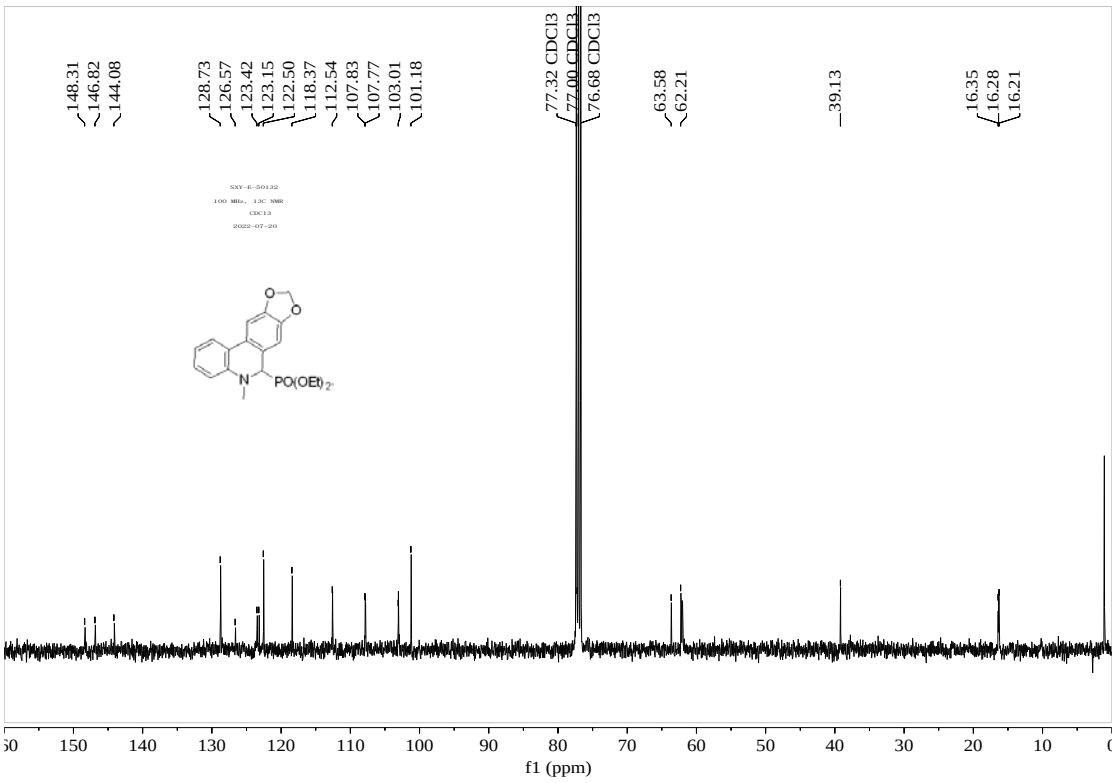
(49) 5,6-Dihydrobicolorine (**5**)



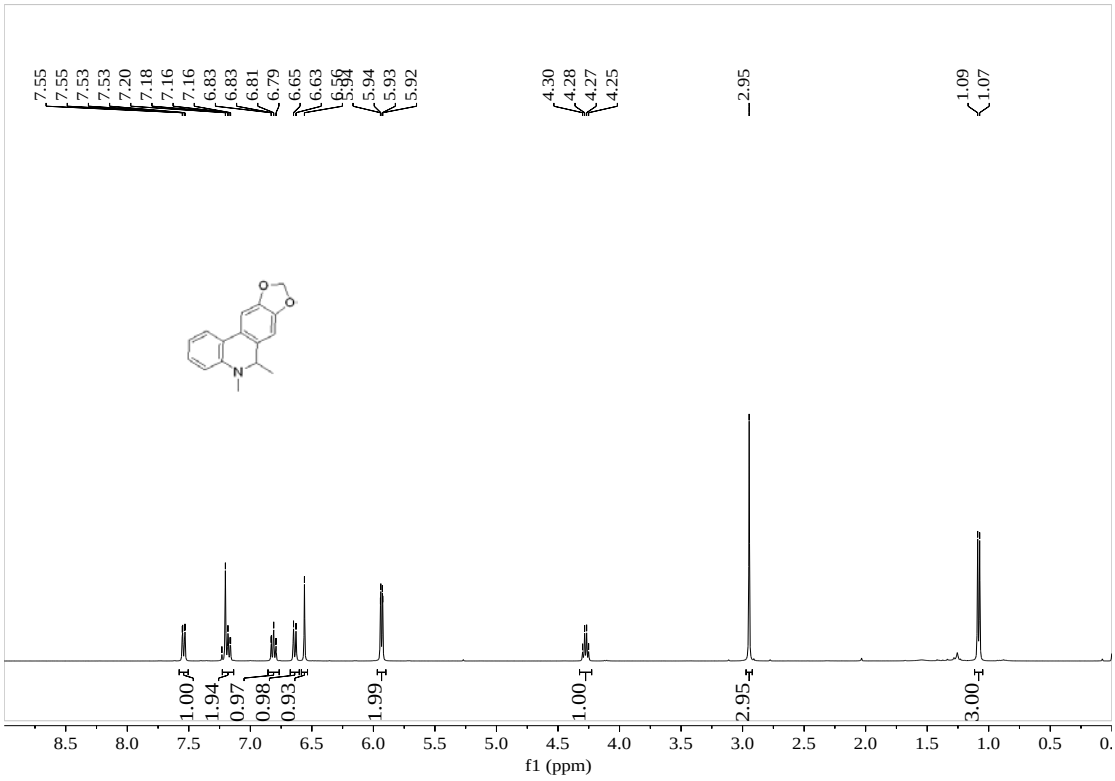


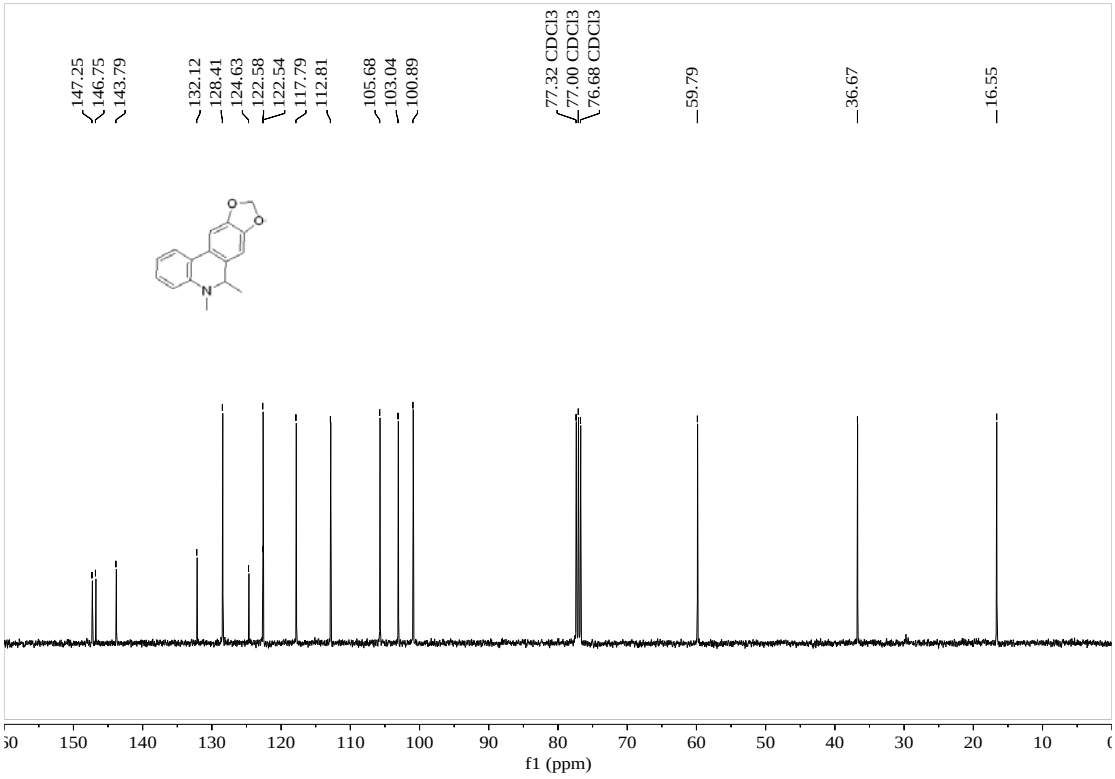
(50) Compound **6a**



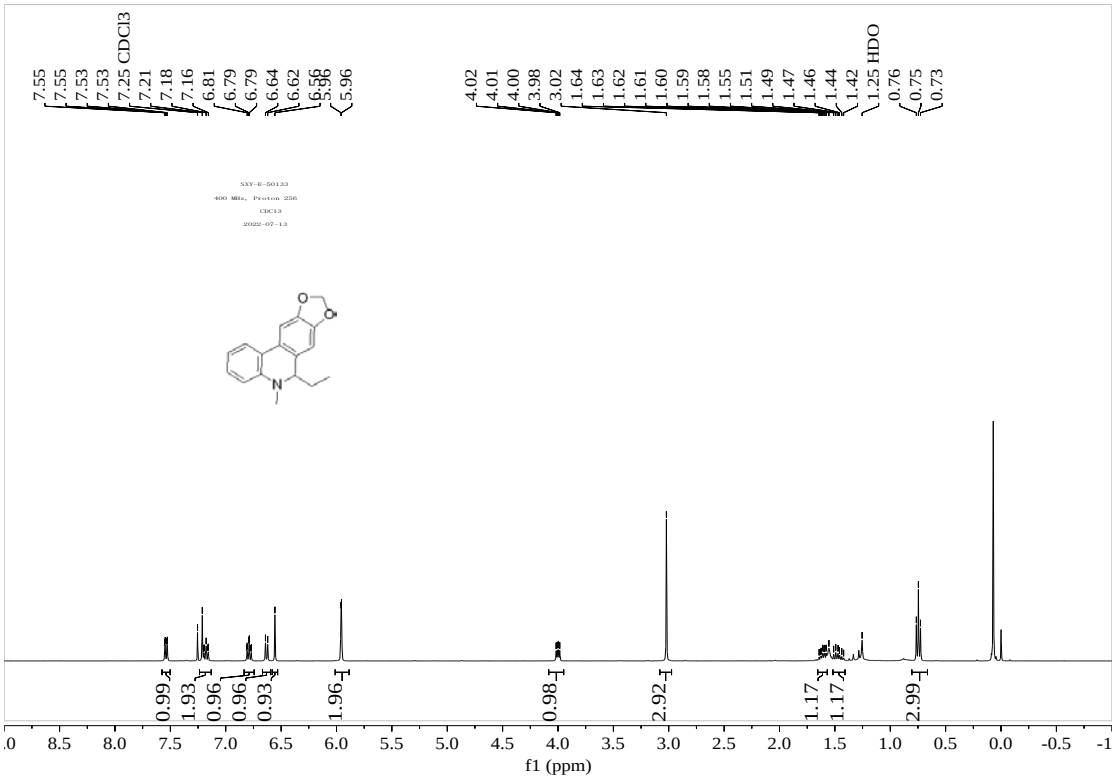


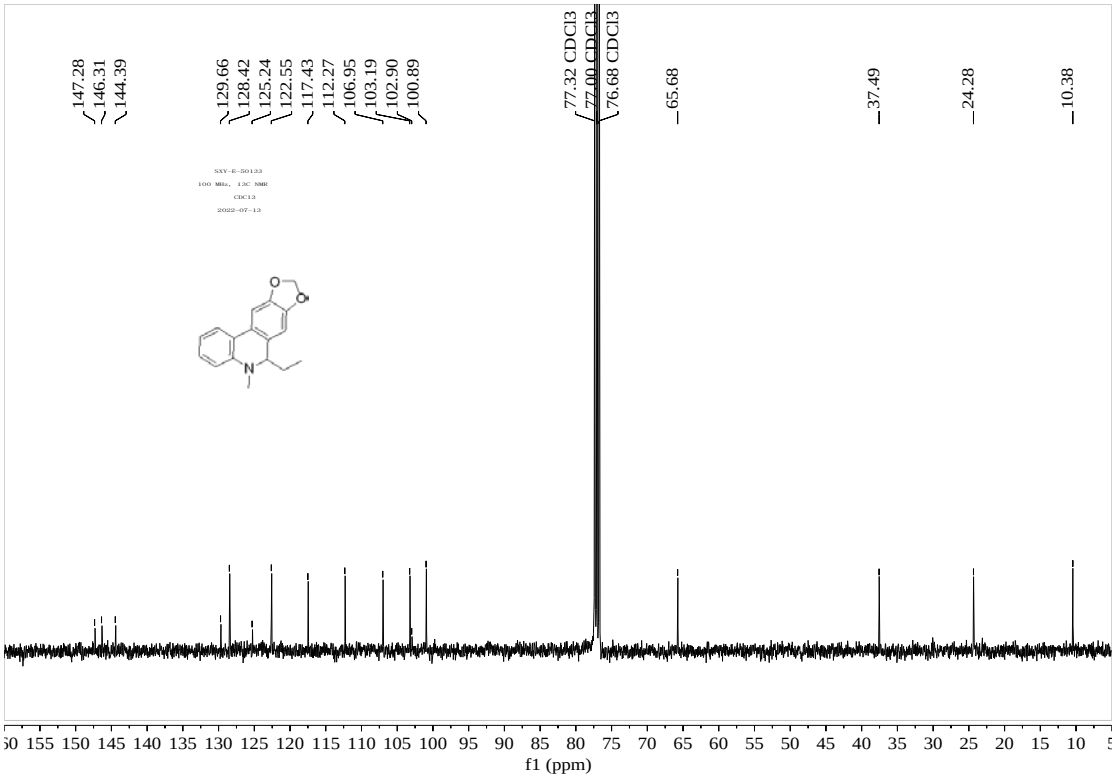
(51) Compound **6b**



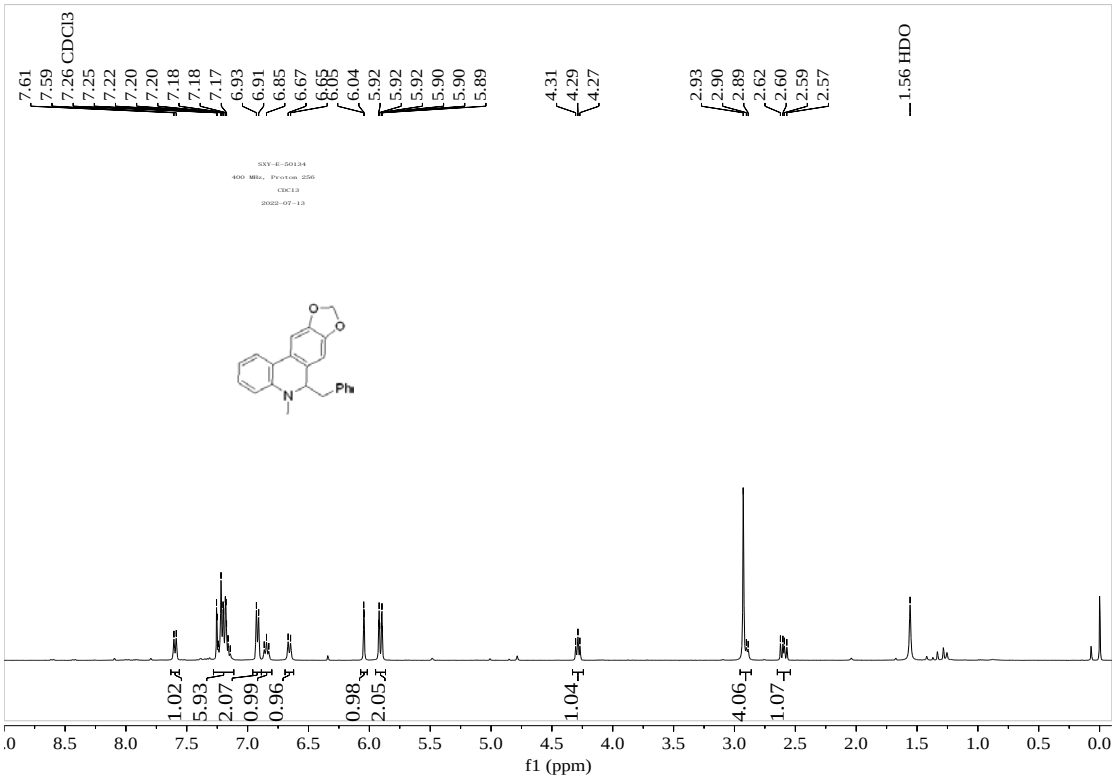


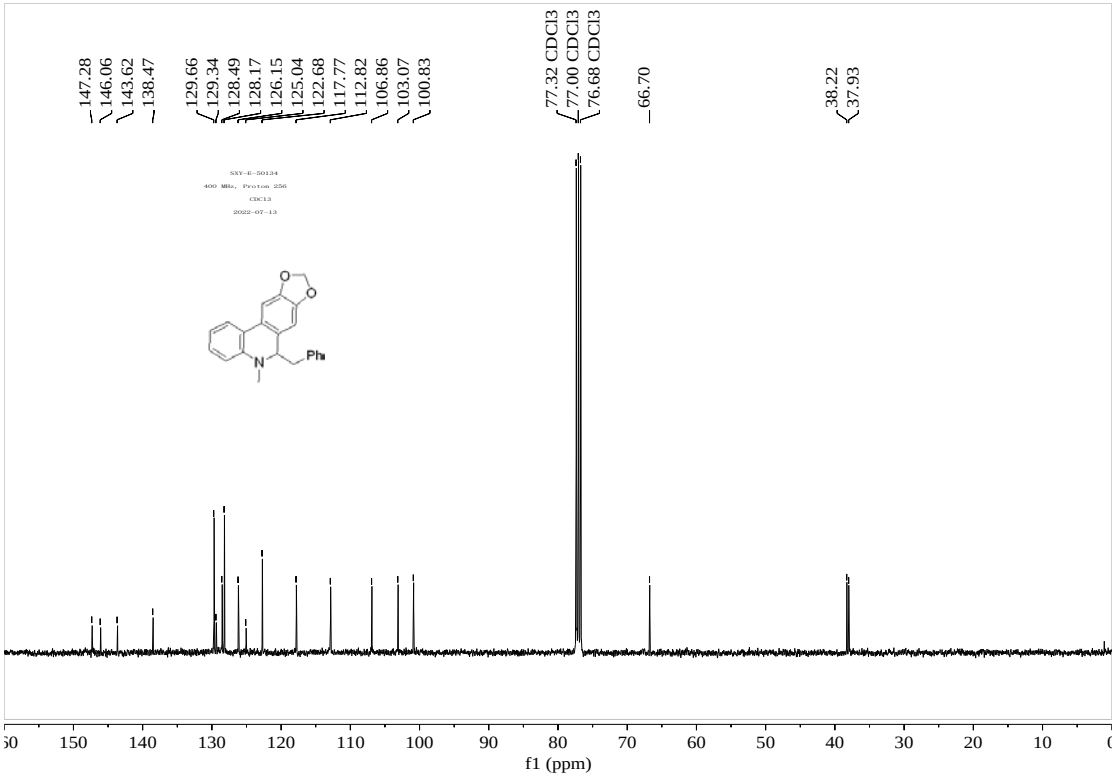
(**52**) Compound **6c**





(53) Compound **6d**





(54) *N*-methylcrinasiadine (**8**)