Supporting Information

Temperature Controlled Condensation of Nitriles: Efficient and Convenient Synthesis of β-Enaminonitriles, 4-Aminopyrimidines and 4-Amidinopyrimidines in One System

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1. Characterization Data for the Products

(*E*)-3-amino-2,4-diphenylbut-2-enenitrile (**2a**): yield, 86% (40 mg); white solid; R_f = 0.33 in 25% acetone in petroleum ether; melting point, 112-113℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.34 (m, 4H), 7.32 (dd, *J* = 7.8, 3.9 Hz, 4H), 7.28 (ddd, *J* = 8.9, 6.3, 3.0 Hz, 1H), 7.22 (ddd, *J* = 11.4, 5.5, 2.6 Hz, 1H), 4.65 (s, 2H), 3.87 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.90, 135.93, 133.39, 129.35, 129.08, 128.99, 128.61, 127.56, 127.35, 122.13, 81.55, 40.44. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{16}H_{14}N_2Na$, 257.1055; found, 257.1049.

(*E*)-2,4-di([1,1'-biphenyl]-4-yl)-3-aminobut-2-enenitrile (**2b**): yield, 85% (66 mg); gummy liquid; R_f = 0.35 in 25% acetone in petroleum ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.56 (m, 9H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.46 (t, *J* = 7.9 Hz, 6H), 7.38 (t, *J* = 7.2 Hz, 2H), 4.71 (s, 2H), 4.01 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.82, 140.66, 140.56, 140.39, 140.19, 134.91, 132.45, 129.54, 129.00, 128.97, 128.96, 128.05, 127.88, 127.64, 127.58, 127.13, 127.07, 121.98, 81.75, 40.28. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{28}H_{22}N_2Na$, 409.1681; found, 409.1676.

(*E*)-3-amino-2,4-di-p-tolylbut-2-enenitrile (**2c**): yield, 74% (39 mg); pale red oil; R_f = 0.38 in 25% acetone in petroleum ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.30 (m, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 7.21 (dd, *J* = 11.5, 7.9 Hz, 4H), 4.65 (s, 2H), 3.89 (s, 2H), 2.38 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.92, 137.17, 137.08, 132.91, 130.38, 129.97, 129.71, 128.89, 128.48, 122.30, 81.19, 39.96, 21.19, 21.11. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{18}H_{18}N_2Na$, 285.1368; found, 285.1362.

(*E*)-3-amino-2,4-bis(4-(*tert*-butyl)phenyl)but-2-enenitrile (**2d**): yield, 71% (49 mg); white solid; R_f = 0.48 in 25% acetone in petroleum ether; melting point, 170-171℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.40 (m, 2H), 7.39 – 7.37 (m, 2H), 7.37 – 7.33 (m, 2H), 7.29 – 7.25 (m, 2H), 4.54 (s, 2H), 3.90 (s, 2H), 1.32 (d, *J* = 1.8 Hz, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.65, 150.63, 150.43, 132.89, 130.55, 128.83, 128.35, 126.32, 126.10, 122.15, 81.88, 40.02, 34.72, 34.65, 31.45, 31.38. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{24}H_{30}N_2Na$, 369.2307; found, 369.2301.

(*E*)-3-amino-2,4-bis(4-methoxyphenyl)but-2-enenitrile (**2e**): yield, 70% (41 mg); gummy liquid; R_f = 0.33 in 25% acetone in petroleum ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 2H), 7.28 – 7.23 (m, 2H), 6.94 – 6.87 (m, 4H), 4.43 (s, 2H), 3.85 (s, 2H), 3.80 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.13, 158.85, 156.78, 130.21, 130.17, 127.95, 125.51, 122.18, 114.82, 114.56, 81.35, 55.45, 39.52. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{18}H_{18}O_2N_2Na$, 317.1266; found, 317.1261.

(*E*)-3-amino-2,4-bis(4-bromophenyl)but-2-enenitrile (**2f**): yield, 73% (57 mg); colorless oil; R_f = 0.38 in 25% acetone in petroleum ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.45 (m, 4H), 7.28 – 7.24 (m, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 4.61 (s, 2H), 3.84 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.43, 134.68, 132.65, 132.36, 130.72, 130.35, 121.82, 121.42, 121.33,

81.38, 40.03. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{16}H_{12}N_2Br_2Na$, 412.9265; found, 412.9259.

(*E*)-3-amino-2,4-bis(4-chlorophenyl)but-2-enenitrile (**2g**): yield, 72% (44 mg); yellow oil; R_f = 0.38 in 25% acetone in petroleum ether; ^1H NMR (400 MHz, $CDCl_3$) δ 7.39–7.23 (m, 8H), 4.69 (s, 2H), 3.83 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.82, 134.22, 133.55, 133.16, 131.62, 130.26, 129.96, 129.59, 129.24, 121.60, 80.71, 39.82. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{16}H_{12}Cl_2N_2Na$, 325.0275; found, 325.0270.

(*E*)-3-amino-2,4-bis(4-fluorophenyl)but-2-enenitrile (**2h**): yield, 63% (34 mg); gummy liquid; R_f = 0.33 in 25% acetone in petroleum ether; ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 2H), 7.34 – 7.28 (m, 2H), 7.15 – 7.01 (m, 4H), 4.47 (s, 2H), 3.89 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.31 (d, *J* = 43.9 Hz), 160.85 (d, *J* = 45.4 Hz), 156.83, 131.56 (d, *J* = 3.3 Hz), 130.63 (d, *J* = 4.1 Hz), 128.99, 128.53, 121.76, 116.27 (dd, *J* = 40.8, 21.6 Hz), 80.93, 39.59. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{16}H_{12}F_2N_2Na$, 293.0867; found, 293.0861.

(*E*)-3-amino-2,4-di-*m*-tolylbut-2-enenitrile (**2i**): yield, 71% (37 mg); gummy liquid; R_f = 0.35 in 25% acetone in petroleum ether; ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 3H), 7.21 (d, *J* = 7.7 Hz, 1H), 7.17 – 7.10 (m, 3H), 7.07 (d, *J* = 7.4 Hz, 1H), 4.58 (s, 2H), 3.89 (s, 2H), 2.36 (d, *J* = 5.5 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.76, 139.22, 138.94, 135.85, 133.38, 129.85, 129.38, 129.23, 129.04, 128.42, 128.19, 126.14, 125.60, 122.16, 81.87, 40.42, 21.50. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{18}H_{18}N_2Na$, 285.1368; found, 285.1362.

(*E*)-3-amino-2,4-bis(3-methoxyphenyl)but-2-enenitrile (**2j**): yield, 67% (39 mg); white solid; R_f = 0.33 in 25% acetone in petroleum ether; melting point, 124-125℃; ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (td, *J* = 7.9, 5.9 Hz, 2H), 7.02 – 6.97 (m, 1H), 6.93 (dt, *J* = 14.1, 4.5 Hz, 2H), 6.88 (d, *J* = 2.1 Hz, 1H), 6.85 (dd, *J* = 8.2, 2.4 Hz, 1H), 6.80 (ddd, *J* = 8.3, 2.5, 0.7 Hz, 1H), 4.61 (s, 2H), 3.90 (s, 2H), 3.81 (d, *J* = 4.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.41, 160.25, 156.65, 137.32, 134.82, 130.44, 130.25, 121.87, 121.45, 120.88, 114.88, 114.14, 113.17, 113.06, 81.97, 55.45, 55.41, 40.55. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{18}H_{18}O_2N_2Na$, 317.1266; found, 317.1261.

(*E*)-3-amino-2,4-bis(3-fluorophenyl)but-2-enenitrile (**2k**): yield, 62% (34 mg); colorless liquid; R_f = 0.33 in 25% acetone in petroleum ether; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (dtd, *J* = 9.9, 8.0, 6.1 Hz, 2H), 7.23 – 7.19 (m, 1H), 7.16 – 7.11 (m, 2H), 7.09 – 7.01 (m, 2H), 7.01 – 6.94 (m, 1H), 4.63 (s, 2H), 3.93 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.54 (d, *J* = 9.9 Hz), 162.08 (d, *J* = 9.7 Hz), 156.37, 138.01 (d, *J* = 7.3 Hz), 135.43 (d, *J* = 8.1 Hz), 131.12 (d, *J* = 8.6 Hz), 130.85 (d, *J* = 8.3 Hz), 124.79 (d, *J* = 2.9 Hz), 124.33 (d, *J* = 2.9 Hz), 121.23, 116.03 (d, *J* = 21.7 Hz), 115.61 (d, *J* = 22.0 Hz), 114.90 (d, *J* = 21.0 Hz), 114.64 (d, *J* = 21.0 Hz), 81.81, 40.33. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{16}H_{12}F_2N_2Na$, 293.0867; found, 293.0861.

(*E*)-3-amino-2,4-di-o-tolylbut-2-enenitrile (**2l**): yield, 51% (27 mg); yellow oil; R_f = 0.35 in 25% acetone in petroleum ether; ^1H NMR (400 MHz, CDCl3) δ 7.28 – 7.18 (m, 8H), 4.12 (s, 2H), 4.00 (s, 2H), 2.42 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 156.56,

138.31, 137.57, 133.84, 131.52, 131.10, 130.98, 130.85, 130.23, 128.66, 128.03, 126.82, 126.63, 121.12, 80.37, 37.60, 19.72, 19.54. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{18}H_{18}N_2Na$, 285.1368; found, 285.1362.

(*E*)-3-amino-2,4-bis(2-fluorophenyl)but-2-enenitrile (**2m**): yield, 55% (30 mg); yellow oil; R_f = 0.35 in 25% acetone in petroleum ether; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (td, *J* = 7.6, 1.5 Hz, 1H), 7.38 (td, *J* = 7.5, 1.8 Hz, 1H), 7.34 – 7.27 (m, 2H), 7.18 (tdd, *J* = 7.5, 3.0, 1.1 Hz, 2H), 7.11 (td, *J* = 8.4, 0.9 Hz, 2H), 4.49 (d, *J* = 45.3 Hz, 2H), 3.99 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.73 (d, *J* = 114.8 Hz), 159.28 (d, *J* = 119.1 Hz), 157.60, 131.75 (d, *J* = 3.2 Hz), 131.39 (d, *J* = 3.8 Hz), 130.14 (d, *J* = 8.2 Hz), 129.61 (d, *J* = 8.2 Hz), 125.05, 123.23 (d, *J* = 15.6 Hz), 121.21, 120.22 (d, *J* = 15.7 Hz), 116.64 (d, *J* = 21.8 Hz), 115.69 (d, *J* = 22.0 Hz), 75.48, 33.35 (d, *J* = 2.7 Hz).HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{16}H_{12}F_2N_2Na$, 293.0867; found, 293.0861.

(*E*)-3-amino-2,4-bis(3,5-dimethylphenyl)but-2-enenitrile (**2n**): yield, 47% (27 mg); gummy liquid; R_f = 0.38 in 25% acetone in petroleum ether; ^1H NMR (400 MHz, $CDCl_3$) δ 7.04 (s, 2H), 6.94 (s, 3H), 6.89 (s, 1H), 4.54 (s, 2H), 3.85 (s, 2H), 2.32 (d, *J* = 5.7 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.67, 139.06, 138.86, 135.82, 133.37, 129.34, 129.11, 126.99, 126.37, 122.24, 82.04, 40.37, 21.42 (d, *J* = 1.6 Hz). HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{20}H_{22}N_2Na$, 313.1681; found, 313.1675.

(*E*)-3-amino-2,4-bis(2,5-dimethylphenyl)but-2-enenitrile (**2o**): yield, 34% (20 mg); colorless oil; R_f = 0.38 in 25% acetone in petroleum ether; ^1H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 7.5 Hz, 1H), 7.11 (d, *J* = 7.4 Hz, 1H), 7.08 – 7.02 (m, 4H), 4.10 (s, 2H), 3.96 (s, 2H), 2.37 (s, 3H), 2.33 (s, 3H), 2.30 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.37, 136.28, 136.06, 134.92, 134.30, 133.58, 131.29, 131.25, 131.04, 130.88, 130.82, 129.30, 128.58, 121.17, 80.38, 37.50, 20.93, 20.84, 19.12, 18.97. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{20}H_{22}N_2Na$, 313.1681; found, 313.1675.

(*E*)-3-amino-2,4-di(naphthalen-2-yl)but-2-enenitrile (**2p**): yield, 72% (48 mg); white solid; R_f = 0.35 in 25% acetone in petroleum ether; melting point, 116-117℃; ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.77 (m, 8H), 7.58 – 7.54 (m, 1H), 7.53 – 7.46 (m, 5H), 4.71 (s, 2H), 4.14 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.90, 133.72, 133.60, 133.39, 132.80, 132.44, 130.86, 129.28, 129.14, 128.08, 127.87, 127.83, 127.82, 127.74, 127.57, 126.85, 126.72, 126.66, 126.46, 126.44, 126.28, 122.09, 82.15, 40.78. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{24}H_{18}N_2Na$, 357.1368; found, 357.1362.

(*E*)-3-amino-2,4-di(naphthalen-1-yl)but-2-enenitrile (**2q**): yield, 70% (47 mg); white solid; R_f = 0.35 in 25% acetone in petroleum ether; melting point, 80-81℃; ^1H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.5 Hz, 1H), 8.06 – 8.00 (m, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.89 – 7.82 (m, 3H), 7.74 – 7.66 (m, 1H), 7.63 – 7.54 (m, 2H), 7.54 – 7.45 (m, 5H), 4.58 (d, *J* = 13.5 Hz, 2H), 4.12 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.07, 134.24, 134.06, 132.13, 131.62, 131.38, 129.65, 129.11, 129.04, 128.97, 128.82, 128.74, 128.31, 127.05, 126.87, 126.48,

126.39, 125.96, 125.57, 124.98, 123.57, 121.86, 78.25, 37.54. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{24}H_{18}N_2Na$, 357.1368; found, 357.1362.

(*E*)-3-amino-2-benzyl-5-phenylpent-2-enenitrile (**2r**): yield, 78% (41 mg); colorless oil; R_f = 0.33 in 25% acetone in petroleum ether; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 4H), 7.23 (dt, *J* = 12.3, 5.5 Hz, 4H), 7.19 – 7.15 (m, 2H), 3.99 (s, 2H), 3.40 (s, 2H), 2.94 (t, *J* = 7.6 Hz, 2H), 2.76 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.37, 139.95, 137.83, 128.89, 128.75, 128.63, 128.00, 126.89, 126.65, 122.92, 77.75, 36.52, 34.59, 33.49. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{18}H_{18}N_2Na$, 285.1368; found, 285.1362.

(*E*)-3-amino-2-phenethyl-6-phenylhex-2-enenitrile (**2s**): yield, 77% (45 mg); yellow oil; R_f = 0.38 in 25% acetone in petroleum ether; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 5H), 7.26 – 7.18 (m, 5H), 3.91 (s, 2H), 2.86 (t, *J* = 7.6 Hz, 2H), 2.71 – 2.64 (m, 2H), 2.47 – 2.40 (m, 2H), 2.31 (dd, *J* = 13.7, 6.2 Hz, 2H), 1.89 (tt, *J* = 9.2, 7.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.99, 141.48, 141.20, 128.64, 128.58, 128.54, 128.47, 126.36, 126.14, 122.49, 78.52, 35.22, 34.41, 34.28, 29.97, 29.39. HRMS m/z (ESI) $[M+Na^+]$:313.1675. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{20}H_{22}N_2Na$, 313.1681; found, 313.1675.

(*E*)-3-amino-2-ethylhex-2-enenitrile (**2t**): yield, 78% (22 mg); yellow oil; R_f = 0.35 in 25% acetone in petroleum ether; ^1H NMR (400 MHz, $CDCl_3$) δ 4.10 (s，2H), 2.38 (t, *J* = 7.6 Hz，2H), 2.01 (q, *J* = 7.5 Hz，2H), 1.60 (dt, *J* = 14.8, 7.4 Hz, 2H), 1.15 – 1.10 (m, 3H), 0.98 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.06, 122.48, 100.04, 36.49, 21.63, 19.99, 13.57, 12.47. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_8H_{14}N_2Na$, 161.1055; found, 161.1049.

(*E*)-3-amino-2-isopropyl-5-methylhex-2-enenitrile (**2u**): yield, 65% (22 mg); gummy liquid; R_f = 0.40 in 25% acetone in petroleum ether; ^1H NMR (400 MHz, $CDCl_3$) δ 4.21 – 3.97 (m, 2H), 2.41 – 2.29 (m, 1H), 2.26 (d, *J* = 7.6 Hz, 2H), 1.91 (dp, *J* = 13.4, 6.7 Hz, 1H), 1.11 (dd, *J* = 6.8, 1.1 Hz, 6H), 0.97 (dd, *J* = 6.6, 1.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.00, 121.24, 87.78, 43.74, 28.01, 25.59, 22.16, 21.43. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{10}H_{18}N_2Na$, 189.1368; found, 189.1362.

(*E*)-3-amino-2-propylhept-2-enenitrile (**2v**): yield, 76% (25 mg); yellow oil; R_f = 0.45 in 25% acetone in petroleum ether; ^1H NMR (400 MHz, $CDCl_3$) δ 4.06 (s，2H), 2.43 – 2.36 (t, *J* = 7.6 Hz，2H), 1.99 – 1.91 (t, *J* = 7.4 Hz，2H), 1.59 – 1.49 (m, 4H), 1.38 (dq, *J* = 14.4, 7.2 Hz, 2H), 0.97 – 0.89 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.75, 122.69, 79.22, 34.51, 30.49, 28.87, 22.30, 21.29, 13.98, 13.83. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{10}H_{18}N_2Na$, 189.1368; found, 189.1362.

2-aminocyclopent-1-enecarbonitrile (**2w**): yield, 62% (27 mg); white solid; R_f = 0.35 in 25% acetone in petroleum ether; melting point, 147-148℃; ^1H NMR (400 MHz, $CDCl_3$) δ 4.47 (s, 2H), 2.56 – 2.49 (m, 2H), 2.45 (t, *J* = 7.7 Hz, 2H), 1.97 – 1.87 (m, 2H). ^{13}C NMR (101 MHz,

$CDCl_3$) δ 162.51, 119.17, 74.53, 34.38, 31.33, 22.08. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_6H_8N_2Na$, 131.0585; found, 131.0580.

(*E*)-3-amino-2,4-di(pyridin-2-yl)but-2-enenitrile (**2x**): yield, 72% (34 mg); white solid; R_f = 0.33 in 25% acetone in petroleum ether; melting point, 124-125℃; ^1H NMR (400 MHz, $CDCl_3$) δ 10.77 (s, 1H), 8.54 (dd, *J* = 4.9, 0.8 Hz, 1H), 8.34 (ddd, *J* = 5.0, 1.7, 0.9 Hz, 1H), 7.67 (td, *J* = 7.7, 1.8 Hz, 1H), 7.64 – 7.58 (m, 1H), 7.52 (d, *J* = 8.3 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.21 (ddd, *J* = 7.5, 4.9, 0.9 Hz, 1H), 6.98 – 6.90 (m, 1H), 6.85 (s, 1H), 4.09 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.89, 156.52, 156.24, 149.34, 146.80, 137.51, 136.63, 124.18, 122.59, 122.00, 120.15, 118.63, 77.73, 42.92. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{14}H_{12}N_4Na$, 259.0960; found, 259.0954.

3-aminocrotononitrile (**2y**), (45 : 55, (*E*)/(*Z*) mixture) : yield, 92% (15 mg); white solid; R_f = 0.33 in 25% acetone in petroleum ether; melting point, 80-81℃; ^1H NMR (400 MHz, $CDCl_3$): δ 4.47 (s, 2H), 4.09 (s, 1H), 2.07 (s, 3H) for (*E*) configuration; 4.74 (s, 2H), 3.78 (s, 1H), 1.90 (s, 3H) for (*Z*) configuration. ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.98, 119.65, 62.73, 21.23 for (*E*) configuration; 161.49, 121.39, 65.03, 19.59 for (*Z*) configuration. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_4H_6N_2Na$, 105.0429; found, 105.0423.

(*E*)-2-(amino(phenyl)methylene)butanenitrile (**3a**): yield, 88% (30 mg); colourless oil; R_f = 0.33 in 25% acetone in petroleum ether; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 2.7 Hz, 3H), 7.38 – 7.30 (m, 2H), 4.50 (s, 2H), 2.02 (q, *J* = 7.2 Hz, 2H), 1.05 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.90, 135.55, 129.85, 128.83, 128.00, 120.92, 81.03, 21.86, 14.59. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{11}H_{12}N_2Na$, 195.0898; found, 195.0893.

(*E*)-3-amino-2-benzyl-3-phenylacrylonitrile (**3b**): yield, 89% (42 mg); colourless oil; R_f = 0.35 in 25% acetone in petroleum ether; ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.55 (m, 2H), 7.45 – 7.38 (m, 3H), 7.38 – 7.32 (m, 4H), 7.30 – 7.24 (m, 1H), 4.46 (s, 2H), 3.58 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.54, 137.76, 136.10, 130.36, 128.95, 128.79, 128.07, 128.06, 126.98, 123.42, 78.22, 34.55. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd For $C_{16}H_{15}N_2$, 235.1235; found, 235.1228.

(*E*)-3-amino-3-phenyl-2-(pyridin-2-yl)acrylonitrile (**3c**): yield, 90% (40 mg); white solid; R_f = 0.375 in 25% acetone in petroleum ether; melting point, 115-116℃ ^1H NMR (400 MHz, $CDCl_3$) δ 11.07 (s, 1H), 8.45 (dd, *J* = 5.0, 0.6 Hz, 1H), 7.73 – 7.57 (m, 4H), 7.55 – 7.38 (m, 3H), 7.02 (ddd, *J* = 7.0, 5.0, 1.1 Hz, 1H), 5.50 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.29, 156.57, 146.76, 136.99, 136.78, 130.57, 128.78, 127.97, 121.87, 120.47, 118.97, 78.53. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{14}H_{11}N_3Na$, 244.0851; found, 244.0845.

(*E*)-2-(amino(pyridin-2-yl)methylene)butanenitrile (**3d**): yield, 86% (30 mg); yellow oil; R_f = 0.3 in 25% acetone in petroleum ether; ^1H NMR (400 MHz, $CDCl_3$) δ 8.58 (ddd, *J* = 4.8, 1.7,

1.0 Hz, 1H), 8.22 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.75 (tt, *J* = 5.4, 2.7 Hz, 1H), 7.32 (tdd, *J* = 7.6, 4.5, 1.6 Hz, 1H), 5.31 – 5.00 (m, 2H), 2.24 (q, *J* = 7.5 Hz, 2H), 1.23 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.89, 151.53, 148.93, 137.02, 124.60, 123.61, 122.67, 81.20, 21.91, 11.95. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{10}H_{11}N_3Na$, 196.0851; found, 196.0845.

(*E*)-3-amino-2-benzyl-3-(pyridin-2-yl)acrylonitrile (**3e**): yield, 85% (40 mg); red oil; R_f = 0.4 in 25% acetone in petroleum ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 4.3 Hz, 1H), 8.33 (d, *J* = 8.1 Hz, 1H), 7.79 (td, *J* = 7.9, 1.8 Hz, 1H), 7.38 – 7.29 (m, 5H), 7.29 – 7.22 (m, 1H), 5.22 (s, 2H), 3.67 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.38, 151.08, 149.00, 137.27, 137.15, 128.98, 128.11, 127.08, 124.89, 123.78, 123.61, 77.80, 35.53. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{15}H_{13}N_3Na$, 258.1007; found, 258.1001.

(*E*)-3-amino-2,3-di(pyridin-2-yl)acrylonitrile (**3f**): yield, 83% (37 mg); white solid; R_f = 0.325 in 25% acetone in petroleum ether; melting point, 122-123℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.21 (s, 1H), 8.65 (d, *J* = 4.7 Hz, 1H), 8.46 (d, *J* = 5.0 Hz, 1H), 8.25 (d, *J* = 8.0 Hz, 1H), 7.81 (td, *J* = 7.8, 1.7 Hz, 1H), 7.73 – 7.63 (m, 2H), 7.41 – 7.32 (m, 1H), 7.07 – 6.98 (m, 1H), 6.80 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.43, 156.60, 152.20, 149.48, 146.81, 136.99, 136.72, 125.21, 124.29, 122.29, 120.79, 119.19, 77.21. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{13}H_{10}N_4Na$, 245.0803; found, 245.0798.

(*E*)-2-(amino(thiophen-2-yl)methylene)butanenitrile (**3g**): yield, 62% (22 mg); colorless oil; R_f = 0.275 in 25% acetone in petroleum ether; ^{1}H NMR (400 MHz, CDCl3) δ 7.57 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.37 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.06 (dd, *J* = 5.1, 3.7 Hz, 1H), 4.35 (s, 2H), 2.20 (q, *J* = 7.5 Hz, 2H), 1.21 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.06, 137.13, 129.02, 127.68, 127.23, 122.35, 82.17, 21.48, 12.29. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd For $C_9H_{11}N_2S$, 179.0643; found, 179.0637.

(*E*)-3-amino-2-benzyl-3-(thiophen-2-yl)acrylonitrile (**3h**): yield, 60% (29 mg); red oil; R_f = 0.4 in 25% acetone in petroleum ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 3.7 Hz, 1H), 7.41 (d, *J* = 5.1 Hz, 1H), 7.38 – 7.29 (m, 4H), 7.29 – 7.22 (m, 1H), 7.11 – 7.07 (m, 1H), 4.36 (s, 2H), 3.61 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.67, 137.44, 136.76, 129.51, 129.07, 128.10, 127.88, 127.65, 127.14, 123.20, 78.72, 35.03. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{14}H_{12}N_2SNa$, 263.0619; found, 263.0613.

(*E*)-3-amino-2-(pyridin-2-yl)-3-(thiophen-2-yl)acrylonitri-le (**3i**): yield, 73% (35 mg); yellow oil; R_f = 0.6 in 50% acetone in petroleum ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.16 (s, 1H), 8.43 (d, *J* = 4.9 Hz, 1H), 7.75 – 7.60 (m, 3H), 7.49 – 7.42 (m, 1H), 7.11 (dd, *J* = 5.0, 3.8 Hz, 1H), 7.02 (ddd, *J* = 6.6, 5.1, 1.4 Hz, 1H), 5.48 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.17, 155.15, 146.70, 137.37, 136.83, 130.13, 128.30, 127.86, 121.88, 120.86, 119.20, 78.52. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{12}H_9N_3SNa$, 250.0415; found,250.0409.

(*E*)-2-(amino(naphthalen-2-yl)methylene)butanenitrile (**3j**): yield, 61% (27 mg); white solid; R_f = 0.325 in 25% acetone in petroleum ether; melting point, 118-119℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 1.2 Hz, 1H), 7.91 – 7.82 (m, 3H), 7.61 (dt, *J* = 5.3, 2.7 Hz, 1H), 7.57 – 7.49 (m, 2H), 4.47 (s, 2H), 2.18 (q, *J* = 7.5 Hz, 2H), 1.24 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.89, 133.86, 133.74, 132.82, 128.43, 128.39, 127.80, 127.72, 127.09, 126.63, 125.16, 122.81, 81.60, 21.02, 12.29. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{15}H_{14}N_2Na$, 245.1055; found, 245.1049.

(*E*)-3-amino-2-benzyl-3-(naphthalen-2-yl)acrylonitrile (**3k**): yield, 65% (37 mg); white solid; R_f = 0.3 in 25% acetone in petroleum ether; melting point, 127-128℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.81 (m, 4H), 7.60 – 7.52 (m, 2H), 7.45 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.33 – 7.26 (m, 2H), 7.25 – 7.14 (m, 3H), 4.77 (s, 2H), 3.40 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.47, 137.80, 134.04, 133.36, 132.85, 128.95, 128.59, 128.53, 128.11, 127.97, 127.80, 127.29, 126.97, 126.78, 125.10, 123.52, 78.56, 34.58. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{20}H_{16}N_2Na$, 307.1211; found, 307.1206.

(*Z*)-3-amino-2-benzyl-3-(naphthalen-2-yl)acrylonitrile (**3k′**): yield, 16% (9 mg); colourless oil; R_f = 0.35 in 25% acetone in petroleum ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 1.0 Hz, 1H), 7.91 – 7.82 (m, 3H), 7.65 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.41 – 7.33 (m, 4H), 7.29 (ddd, *J* = 8.1, 6.5, 3.7 Hz, 1H), 4.47 (s, 2H), 3.62 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.29, 139.85, 133.86, 132.92, 132.44, 128.85, 128.69, 128.46, 128.20, 127.96, 127.88, 127.47, 127.08, 126.60, 125.19, 121.07, 78.48, 34.47.

(*E*)-3-amino-3-(naphthalen-2-yl)-2-(pyridin-2-yl)acryloni-trile (**3l**): yield, 71% (39 mg); white solid; R_f = 0.4 in 25% acetone in petroleum ether; melting point, 200-201℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.18 (s, 1H), 8.48 (s, 1H), 8.15 (s, 1H), 8.03 – 7.84 (m, 3H), 7.70 (dd, *J* = 19.7, 9.0 Hz, 3H), 7.62 – 7.49 (m, 2H), 7.06 (s, 1H), 5.49 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.25, 156.72, 146.87, 136.95, 134.47, 134.26, 132.93, 128.83, 128.75, 128.11, 127.95, 127.57, 126.97, 125.02, 121.88, 120.71, 119.16, 79.30. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{18}H_{13}N_3Na$, 294.1007; found, 294.1002.

3,3-bis(isopropylamino)-2-phenylacrylonitrile (**4a**): yield, 97% (47 mg); white solid; R_f = 0.33 in 25% acetone in petroleum ether; melting point, 100-101℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 4H), 7.08 (tt, *J* = 7.0, 1.8 Hz, 1H), 4.10 (d, *J* = 9.4 Hz, 2H), 3.74 – 3.57 (m, 2H), 1.19 (d, *J* = 6.5 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.66, 135.39, 128.79, 127.82, 124.84, 124.57, 64.53, 46.72, 23.30. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{15}H_{21}N_3Na$, 266.1633; found, 266.1628.

3,3-bis(isopropylamino)-2-(4-methoxyphenyl)acrylonitrile (**4b**): yield, 96% (52 mg); white solid; R_f = 0.28 in 25% acetone in petroleum ether; melting point, 129-130℃; ^{1}H NMR (400

MHz, $CDCl_3$) δ 7.23 – 7.16 (m, 2H), 6.87 – 6.81 (m, 2H), 3.83 (d, *J* = 20.8 Hz, 2H), 3.77 (s, 3H), 3.59 (d, *J* = 5.6 Hz, 2H), 1.12 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.67, 157.65, 130.07, 126.92, 124.46, 114.43, 65.08, 55.34, 46.85, 23.42. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{16}H_{23}N_3NaO$, 296.1739; found, 296.1733.

2-(4-(*tert*-butyl)phenyl)-3,3-bis(isopropylamino)acryloni-trile (**4c**): yield, 96% (57 mg); white solid; R_f = 0.33 in 25% acetone in petroleum ether; melting point, 99-100℃; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 4.01 (d, *J* = 9.5 Hz, 2H), 3.64 (qd, *J* = 12.7, 6.3 Hz, 2H), 1.31 (s, 9H), 1.21 (d, *J* = 6.3 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.66, 148.09, 132.04, 127.72, 125.87, 124.47, 65.53, 46.98, 34.45, 31.38, 23.43. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd For $C_{19}H_{30}N_3$, 300.2440; found, 300.2434.

3,3-bis(isopropylamino)-2-(*p*-tolyl)acrylonitrile (**4d**): yield, 97% (50 mg); white solid; R_f = 0.30 in 25% acetone in petroleum ether; melting point, 121-122℃; ^1H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.16 (m, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 3.93 (d, *J* = 9.6 Hz, 2H), 3.68 – 3.53 (m, 2H), 2.31 (s, 3H), 1.19 (d, *J* = 5.2 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.70, 135.07, 131.95, 129.70, 128.35, 124.45, 65.68, 47.03, 23.48, 21.13. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd For $C_{16}H_{24}N_3$, 258.1970; found, 258.1965.

2-([1,1'-biphenyl]-4-yl)-3,3-bis(isopropylamino)acrylonitr-ile (**4e**): yield, 96% (63 mg); white solid; R_f = 0.40 in 25% acetone in petroleum ether; melting point, 173-174℃; ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.57 – 7.52 (m, 2H), 7.41 (tt, *J* = 8.6, 1.9 Hz, 4H), 7.36 – 7.28 (m, 1H), 4.09 (d, *J* = 9.4 Hz, 2H), 3.76 – 3.60 (m, 2H), 1.23 (d, *J* = 6.4 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.69, 140.71, 137.58, 134.57, 128.87, 128.11, 127.52, 127.17, 126.83, 124.40, 64.88, 46.95, 23.50. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{21}H_{25}N_3Na$, 342.1946; found, 342.1941.

2-(4-bromophenyl)-3,3-bis(isopropylamino)acrylonitrile (**4f**): yield, 95% (61 mg); white solid; R_f = 0.30 in 25% acetone in petroleum ether; melting point, 137-138℃; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 2H), 7.20 – 7.13 (m, 2H), 4.00 (d, *J* = 9.1 Hz, 2H), 3.62 (qd, *J* = 12.7, 6.3 Hz, 2H), 1.19 (d, *J* = 6.4 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.58, 134.65, 131.94, 129.39, 124.07, 118.13, 63.90, 46.88, 23.51. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{15}H_{20}BrN_3Na$, 344.0738; found, 344.0733.

2-(4-chlorophenyl)-3,3-bis(isopropylamino)acrylonitrile (**4g**): yield, 95% (53 mg); white solid; R_f = 0.38 in 25% acetone in petroleum ether; melting point, 128-129℃; ^1H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.18 (m, 4H), 4.03 (d, *J* = 9.3 Hz, 2H), 3.75 – 3.50 (m, 2H), 1.18 (d, *J* = 6.4 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.61, 134.16, 130.17, 129.01, 128.95, 124.21, 63.57, 46.81, 23.45. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{15}H_{20}ClN_3Na$, 300.1243; found, 300.1238.

2-(4-fluorophenyl)-3,3-bis(isopropylamino)acrylonitrile (**4h**): yield, 95% (50 mg); white solid; R_f = 0.30 in 25% acetone in petroleum ether; melting point, 101-102℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.22 (m, 2H), 7.12 – 6.89 (m, 2H), 3.91 (s, 2H), 3.62 (s, 2H), 1.25 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.88, 159.58 (d, *J* = 26.4 Hz), 131.07 (d, *J* = 3.2 Hz), 130.01 (d, *J* = 7.8 Hz), 124.32, 115.82 (d, *J* = 21.4 Hz), 64.03, 46.85, 23.44. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd For $C_{15}H_{21}FN_3$, 262.1720; found, 262.1714.

3,3-bis(isopropylamino)-2-(3-methoxyphenyl)acrylonitrile (**4i**): yield, 97% (53 mg); colorless oil; R_f = 0.33 in 25% acetone in petroleum ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (t, *J* = 8.0 Hz, 1H), 6.90 (dd, *J* = 7.7, 0.9 Hz, 1H), 6.88 – 6.85 (m, 1H), 6.68 – 6.63 (m, 1H), 4.02 (d, *J* = 9.5 Hz, 2H), 3.79 (s, 3H), 3.64 (qt, *J* = 12.8, 6.3 Hz, 2H), 1.21 (d, *J* = 6.4 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.19, 159.85, 136.70, 129.91, 124.31, 120.44, 113.33, 111.12, 65.75, 55.35, 47.08, 23.53. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{16}H_{23}N_3NaO$, 296.1739; found, 296.1733.

3,3-bis(isopropylamino)-2-(*m*-tolyl)acrylonitrile (**4j**): yield, 99% (50 mg); pale yellow oil; R_f = 0.43 in 25% acetone in petroleum ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (dd, *J* = 13.3, 5.6 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 1H), 6.91 (d, *J* = 7.4 Hz, 1H), 4.01 (d, *J* = 9.5 Hz, 2H), 3.71 – 3.55 (m, 2H), 2.31 (s, 3H), 1.20 (d, *J* = 6.4 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.80, 138.66, 135.07, 128.96, 128.82, 126.03, 125.07, 124.47, 65.73, 47.03, 23.49, 21.52. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{16}H_{23}N_3Na$, 280.1790; found, 280.1784.

2-(3-fluorophenyl)-3,3-bis(isopropylamino)acrylonitrile (**4k**): yield, 92% (48 mg); yellow oil; R_f = 0.33 in 25% acetone in petroleum ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.19 (m, 1H), 7.08 (d, *J* = 7.9 Hz, 1H), 7.04 – 6.98 (m, 1H), 6.75 (ddd, *J* = 8.3, 2.5, 1.2 Hz, 1H), 4.07 (d, *J* = 9.2 Hz, 2H), 3.71 – 3.58 (m, 2H), 1.21 (d, *J* = 6.4 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.29 (d, *J* = 245.4 Hz), 159.76, 138.08 (d, *J* = 8.5 Hz), 130.30 (d, *J* = 8.9 Hz), 124.07, 123.12 (d, *J* = 2.6 Hz), 114.13 (d, *J* = 22.3 Hz), 111.52 (d, *J* = 21.2 Hz), 64.22, 46.95, 23.52.HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd For $C_{15}H_{21}FN_3$, 262.1720; found, 262.1714.

3,3-bis(isopropylamino)-2-(2-methoxyphenyl)acrylonitrile (**4l**): yield, 95% (52 mg); colorless oil; R_f = 0.25 in 25% acetone in petroleum ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (ddd, *J* = 9.8, 5.8, 1.8 Hz, 2H), 6.91 (ddd, *J* = 11.5, 8.9, 4.6 Hz, 2H), 3.84 (d, *J* = 9.9 Hz, 5H), 3.66 – 3.44 (m, 2H), 1.23(s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.52, 157.44, 132.40, 128.40, 124.14, 122.83, 121.10, 111.73, 61.64, 55.75, 47.02, 23.52. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd For $C_{16}H_{24}N_3O$, 274.1919; found, 274.1914.

3,3-bis(isopropylamino)-2-(*o*-tolyl)acrylonitrile (**4m**): yield, 96% (49 mg); yellow oil; R_f = 0.45 in 25% acetone in petroleum ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (dt, *J* = 6.4, 3.1 Hz, 1H), 7.19 – 7.12 (m, 3H), 3.95 (d, *J* = 9.0 Hz, 1H), 3.64 (s, 1H), 3.44 (s, 2H), 2.33 (s, 3H), 1.21 (dd, *J* = 40.2, 5.7 Hz, 6H), 1.00 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.35, 138.94, 132.50, 131.82, 130.74, 127.65, 126.37, 123.34, 64.80, 47.82, 46.31, 23.43 (s), 20.06. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{16}H_{23}N_3Na$, 280.1790; found, 280.1784.

2-(2-fluorophenyl)-3,3-bis(isopropylamino)acrylonitrile (**4n**): yield, 92% (48 mg); colorless oil; R_f = 0.40 in 25% acetone in petroleum ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (td, *J* = 7.7, 1.9 Hz, 1H), 7.16 (tdd, *J* = 7.1, 5.0, 1.9 Hz, 1H), 7.09 (td, *J* = 7.5, 1.4 Hz, 1H), 7.06 – 6.99 (m, 1H), 3.92 (d, *J* = 7.7 Hz, 2H), 3.62 (d, *J* = 6.1 Hz, 2H), 1.17 (d, *J* = 6.4 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.99, 160.36, 158.53, 131.90 (d, *J* = 3.1 Hz), 127.91 (d, *J* = 8.1 Hz), 124.62 (d, *J* = 3.6 Hz), 123.87, 122.52 (d, *J* = 14.7 Hz), 116.18, 115.96, 57.51, 46.85, 23.45. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{15}H_{20}FN_3Na$, 284.1539; found, 284.1533.

3,3-bis(isopropylamino)-2-(pyridin-2-yl)acrylonitrile (**4o**): yield, 97% (47 mg); colorless oil; R_f = 0.53 in 25% acetone in petroleum ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.91 (s, 1H), 8.21 (ddd, *J* = 5.0, 1.8, 0.9 Hz, 1H), 7.51 (ddd, *J* = 8.4, 7.3, 1.9 Hz, 1H), 7.33 (dt, *J* = 8.4, 0.9 Hz, 1H), 6.78 (ddd, *J* = 7.3, 5.1, 1.0 Hz, 1H), 4.09 (s, 1H), 3.77 (d, *J* = 5.9 Hz, 2H), 1.27 (d, *J* = 6.4 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.90, 157.24, 145.84, 136.35, 123.86, 119.19, 116.52, 65.24, 48.23, 46.50, 23.67. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{14}H_{20}N_4Na$, 267.1586; found, 267.1580.

2-(3,5-dimethylphenyl)-3,3-bis(isopropylamino)acrylonit-rile (**4p**): yield, 93% (50 mg); white solid; R_f = 0.40 in 25% acetone in petroleum ether; melting point, 121-122℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (s, 2H), 6.75 (s, 1H), 3.96 (d, *J* = 9.6 Hz, 2H), 3.63 (qd, *J* = 12.7, 6.3 Hz, 2H), 2.27 (s, 6H), 1.20 (d, *J* = 6.1 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.85, 138.51, 134.91, 127.02, 125.94, 124.49, 65.98, 47.11, 23.52, 21.42. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd For $C_{17}H_{26}N_3$, 272.2127; found, 272.2121.

2-(2,5-dimethylphenyl)-3,3-bis(isopropylamino)acrylonit-rile (**4q**): yield, 88% (48 mg); pale yellow oil; R_f = 0.48 in 25% acetone in petroleum ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 7.6 Hz, 1H), 7.01 – 6.93 (m, 2H), 3.93 (d, *J* = 7.9 Hz, 1H), 3.64 (s, 1H), 3.46 (s, 2H), 2.27 (s, 6H), 1.25 (s, 6H), 0.97 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.37, 135.83, 135.73, 132.48, 132.24, 130.65, 128.45, 123.39, 65.21, 47.91, 46.37, 23.50 (d, *J* = 5.2 Hz), 20.93, 19.58. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{17}H_{25}N_3Na$, 294.1946; found, 294.1941.

2-(benzo[*d*][1,3]dioxol-5-yl)-3,3-bis(isopropylamino)acryl-onitrile (**4r**): yield, 93% (53 mg); white solid; R_f = 0.30 in 25% acetone in petroleum ether; melting point, 110-111℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 – 6.76 (m, 1H), 6.75 (d, *J* = 1.3 Hz, 2H), 5.93 (s, 2H), 4.03 – 3.72 (m, 2H), 3.59 (s, 2H), 1.16 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.79, 148.14, 145.71, 128.51, 124.30, 122.31, 109.52, 108.83, 101.14, 65.50, 47.40, 23.50 HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd For $C_{16}H_{22}N_3O_2$, 288.1712; found, 288.1707.

2-(3,4-dimethoxyphenyl)-3,3-bis(isopropylamino)acrylon-itrile (**4s**): yield, 84% (51 mg); white solid; R_f = 0.40 in 25% acetone in petroleum ether; melting point, 104-105℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 – 6.78 (m, 3H), 3.87 (d, *J* = 3.0 Hz, 8H), 3.58 (d, *J* = 15.2

Hz, 2H), 1.16 (s, 12H). ^{13}C NMR (101 MHz,) δ 159.79 , 149.24 , 147.14 , 127.30 , 124.44 , 121.11 , 112.12 , 111.67 , 65.64 , 56.02 , 55.95 , 42.25 , 23.53 . HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd For $C_{17}H_{26}N_3O_2$, 304.2025; found, 304.2020.

2-(2,4-difluorophenyl)-3,3-bis(isopropylamino)acrylonitr-ile (**4t**): yield, 85% (47 mg); pale red oil; R_f = 0.40 in 25% acetone in petroleum ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (td, *J* = 8.6, 6.6 Hz, 1H), 6.91 – 6.73 (m, 2H), 3.82 (s, 2H), 3.61 (s, 2H), 1.17 (d, *J* = 6.2 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.96 (dd, *J* = 174.6, 11.8 Hz), 160.38, 158.61 (d, *J* = 11.9 Hz), 132.73 (dd, *J* = 9.3, 4.4 Hz), 123.73, 118.60 (dd, *J* = 15.2, 3.8 Hz), 111.82 (dd, *J* = 21.1, 3.7 Hz), 104.36 (t, *J* = 25.9 Hz), 55.92, 46.74, 23.37. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{15}H_{19}F_2N_3Na$, 302.1445; found, 302.1439.

3,3-bis(isopropylamino)-2-(naphthalen-1-yl)acrylonitrile (**4u**): yield, 90% (53 mg); pale yellow oil; R_f = 0.43 in 25% acetone in petroleum ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.7 Hz, 1H), 7.88 – 7.83 (m, 1H), 7.79 (p, *J* = 3.1 Hz, 1H), 7.51 (tt, *J* = 12.8, 3.5 Hz, 2H), 7.47 – 7.43 (m, 2H), 4.14 (s, 1H), 3.73 (s, 1H), 3.46 (s, 2H), 1.31 (s, 6H), 0.89 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.00, 134.22, 132.67, 130.98, 129.65, 128.48, 128.07, 126.34, 126.12, 125.80, 125.51, 124.12, 62.21, 47.74, 46.43, 23.39. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{19}H_{23}N_3Na$, 316.1790; found, 316.1784.

3,3-bis(isopropylamino)-2-(naphthalen-2-yl)acrylonitrile (**4v**): yield, 92% (54 mg); pale yellow solid; R_f = 0.33 in 25% acetone in petroleum ether; melting point, 163-164℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.69 (m, 4H), 7.51 – 7.35 (m, 3H), 4.19 (d, *J* = 9.4 Hz, 2H), 3.76 – 3.60 (m, 2H), 1.22 (d, *J* = 6.5 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.83, 134.05, 132.91, 131.38, 128.46, 127.69, 127.42, 126.81, 126.40, 125.89, 125.34, 124.51, 65.42, 47.03, 23.59. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{19}H_{23}N_3Na$, 316.1790; found, 316.1784.

2,6-dimethylpyrimidin-4-amine (**5a**): yield, 77% (19 mg); white solid; R_f = 0.40 in 10% methanol in dichloromethane; melting point, 184-485℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.09 (s, 1H), 5.03 (s, 2H), 2.45 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.42, 165.86, 163.28, 100.83, 25.78, 23.95. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd For $C_6H_{10}N_3$, 124.0875; found, 124.0870.

2-phenyl-6,7-dihydro-5*H*-cyclopenta[*d*]pyrimidin-4-amin-e (**5b**) : yield, 63% (27 mg); white solid; R_f = 0.45 in 25% acetone in petroleum ether; melting point, 131-132℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 – 8.28 (m, 2H), 7.46 – 7.40 (m, 3H), 4.76 (s, 2H), 2.99 (t, *J* = 7.7Hz, 2H), 2.75 (t, *J* = 7.7 Hz, 2H), 2.23 – 2.10 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.46, 163.95, 159.51, 138.62, 129.92, 128.44, 128.09, 114.07, 34.44, 26.91, 21.77. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd For $C_{13}H_{14}N_3$, 212.1188; found, 212.1182.

5-ethyl-2,6-diphenylpyrimidin-4-amine (**5c**): yield, 75% (41 mg); white solid; R_f = 0.40 in 25% acetone in petroleum ether; melting point, 144-145℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 – 8.42 (m, 2H), 7.63 – 7.56 (m, 2H), 7.53 – 7.41 (m, 6H), 5.30 (s, 2H), 2.50 (p, *J* = 7.4 Hz, 2H), 1.17 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.09, 162.57, 161.33, 139.58, 138.33, 129.88, 128.60, 128.44, 128.25, 128.18, 128.04, 114.12, 19.95, 12.66. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd For $C_{18}H_{18}N_3$, 276.1500; found, 276.1495.

5-ethyl-2,6-di(naphthalen-2-yl)pyrimidin-4-amine (**5d**): yield, 72% (54 mg); R_f = 0.45 in 25% acetone in petroleum ether; melting point, 203-204℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 8.56 (dd, *J* = 8.6, 1.7 Hz, 1H), 8.08 (s, 1H), 8.01 – 7.84 (m, 6H), 7.74 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.58 – 7.53 (m, 2H), 7.53 – 7.46 (m, 2H), 5.14 (s, 2H), 2.61 (q, *J* = 7.6 Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.47, 162.62, 161.50, 137.14, 135.77, 134.52, 133.43, 133.36, 133.14, 129.22, 128.56, 128.07, 128.05, 128.03, 127.93, 127.87, 127.76, 126.71, 126.63, 126.46, 126.05, 125.54, 114.58, 20.26, 12.88. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd For $C_{26}H_{22}N_3$, 376.1814; found, 376.1808.

5-ethyl-6-phenyl-2-(thiophen-2-yl)pyrimidin-4-amine (**5e**) : yield, 67% (38 mg); yellow solid; R_f = 0.475 in 25% acetone in petroleum ether; melting point, 155-156℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 3.3 Hz, 1H), 7.53 (t, *J* = 8.3 Hz, 2H), 7.50 – 7.42 (m, 3H), 7.38 (d, *J* = 4.9 Hz, 1H), 7.09 (t, *J* = 4.0 Hz, 1H), 5.14 (s, 2H), 2.50 (p, *J* = 7.6 Hz, 2H), 1.16 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.19, 162.34, 158.15, 144.14, 139.30, 128.70, 128.60, 128.54, 128.25, 128.03, 127.94, 113.95, 20.10, 12.81. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{16}H_{15}N_3SNa$, 304.0884; found, 304.0879.

5-ethyl-2,6-di(thiophen-2-yl)pyrimidin-4-amine (**5f**): yield, 85% (49 mg); yellow oil; R_f = 0.40 in 25% acetone in petroleum ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 3.6, 1.1 Hz, 1H), 7.52 (d, *J* = 3.7 Hz, 1H), 7.49 (d, *J* = 5.1 Hz, 1H), 7.40 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.14 (dd, *J* = 5.1, 3.8 Hz, 1H), 7.11 (dd, *J* = 5.0, 3.7 Hz, 1H), 5.12 (s, 2H), 2.78 (q, *J* = 7.6 Hz, 2H), 1.31 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.88, 157.96, 155.69, 143.88, 143.09, 128.88, 128.77, 128.11, 128.08, 127.98, 127.75, 112.18, 20.05, 12.23. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd For $C_{14}H_{14}N_3S_2$, 288.0629; found, 288.0624.

5-benzyl-6-(pyridin-2-yl)-2-(thiophen-2-yl)pyrimidin-4-amine (**5g**) : yield, 71% (49 mg); yellow solid; R_f = 0.35 in 25% acetone in petroleum ether; melting point, 180-181℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (ddd, *J* = 4.8, 1.7, 0.9 Hz, 1H), 8.03 (dt, *J* = 7.9, 0.9 Hz, 1H), 7.95 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.83 (td, *J* = 7.7, 1.8 Hz, 1H), 7.40 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.33 – 7.18 (m, 6H), 7.13 – 7.07 (m, 1H), 4.94 (s, 2H), 4.30 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.74, 161.58, 158.83, 157.55, 148.51, 144.02, 138.56, 136.85, 128.98, 128.84, 128.33, 128.22, 128.02, 126.80, 124.72, 123.62, 111.87, 32.42. HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd For $C_{20}H_{16}N_4SNa$, 367.0993; found, 367.0988.

5-ethyl-2-phenyl-6-(pyridin-2-yl)pyrimidin-4-amine (**5h**) : yield, 63% (35 mg); colourless oil; R_f = 0.35 in 25% acetone in petroleum ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 4.3 Hz, 1H), 8.38 (ddd, *J* = 8.0, 5.4, 3.0 Hz, 2H), 7.95 (d, *J* = 7.9 Hz, 1H), 7.84 (td, *J* = 7.7, 1.8 Hz, 1H), 7.48 – 7.40 (m, 3H), 7.34 (ddd, *J* = 7.5, 4.9, 1.1 Hz, 1H), 5.13 (s, 2H), 2.76 (q, *J* = 7.5 Hz, 2H), 1.22 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.14, 161.40, 161.12, 158.20, 148.49, 138.32, 136.72, 130.01, 128.37, 128.04, 124.52, 123.37, 115.50, 19.72, 12.72. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd For $C_{17}H_{17}N_4$, 277.1453; found, 277.1448.

5-ethyl-2-phenyl-6-(thiophen-2-yl)pyrimidin-4-amine (**5i**) : yield, 65% (37 mg); white solid; R_f = 0.45 in 25% acetone in petroleum ether; melting point, 132-133℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 – 8.40 (m, 2H), 7.54 (dd, *J* = 3.7, 0.9 Hz, 1H), 7.50 (dd, *J* = 5.1, 0.9 Hz, 1H), 7.49 – 7.41 (m, 3H), 7.16 (dd, *J* = 5.1, 3.7 Hz, 1H), 5.07 (s, 2H), 2.82 (q, *J* = 7.6 Hz, 2H), 1.35 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.13, 161.24, 155.79, 143.71, 138.05, 130.15, 128.76, 128.39, 128.02, 127.89, 127.79, 112.45, 20.08, 12.22. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd For $C_{16}H_{16}N_3S$, 282.1065; found, 282.1059.

(*Z*)-*N*′-(5-ethyl-2,6-di(thiophen-2-yl)pyrimidin-4-yl)thiop-hene-2-carboximidamide (**6a**): yield, 86% (62 mg); white solid; R_f = 0.50 in 25% acetone in petroleum ether; melting point, 133-134℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 3.6, 1.1 Hz, 1H), 7.66 (dd, *J* = 3.7, 0.8 Hz, 1H), 7.55 – 7.48 (m, 3H), 7.41 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.17 (dd, *J* = 5.1, 3.8 Hz, 1H), 7.16 – 7.10 (m, 2H), 3.18 (q, *J* = 7.4 Hz, 2H), 1.40 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.73, 156.14, 155.16, 144.16, 143.74, 142.43, 131.22, 128.90, 128.57, 128.30, 128.23, 127.95, 127.92, 127.62, 126.54, 125.71, 21.06, 13.91. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd For $C_{19}H_{17}N_4S_3$, 397.0615; found, 397.0610.

(*Z*)-*N*′-(5-ethyl-2,6-diphenylpyrimidin-4-yl)benzimidami-de (**6b**): yield, 76% (58 mg); white solid; R_f = 0.50 in 25% acetone in petroleum ether; melting point, 169-170℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 5.9 Hz, 2H), 8.06 (d, *J* = 6.8 Hz, 2H), 7.66 (d, *J* = 7.0 Hz, 2H), 7.59 – 7.41 (m, 9H), 2.97 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.04, 165.59, 159.97, 140.17, 138.73, 136.77, 131.43, 130.02, 129.00, 128.82, 128.56, 128.54, 128.28, 127.98, 127.33, 21.32, 14.98. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd For $C_{25}H_{23}N_4$, 379.1923; found, 379.1917.

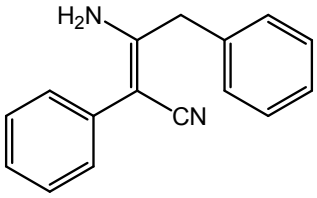
(*Z*)-*N*′-(5-ethyl-2,6-diphenylpyrimidin-4-yl)picolinimida-mide (**6c**): yield, 85% (65 mg); white solid; R_f = 0.50 in 25% acetone in petroleum ether; melting point, 169-170℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.43 (s, 1H), 8.65 (d, *J* = 4.5 Hz, 1H), 8.60 (d, *J* = 7.9 Hz, 1H), 8.38 (dd, *J* = 7.6, 1.6 Hz, 2H), 8.32 (s, 1H), 7.87 (dd, *J* = 11.0, 4.4 Hz, 1H), 7.66 (d, *J* = 6.8 Hz, 2H), 7.55 – 7.40 (m, 7H), 2.97 (q, *J* = 7.3 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.41, 165.53, 160.24, 156.98, 152.10, 148.37, 140.24, 138.85, 137.11,

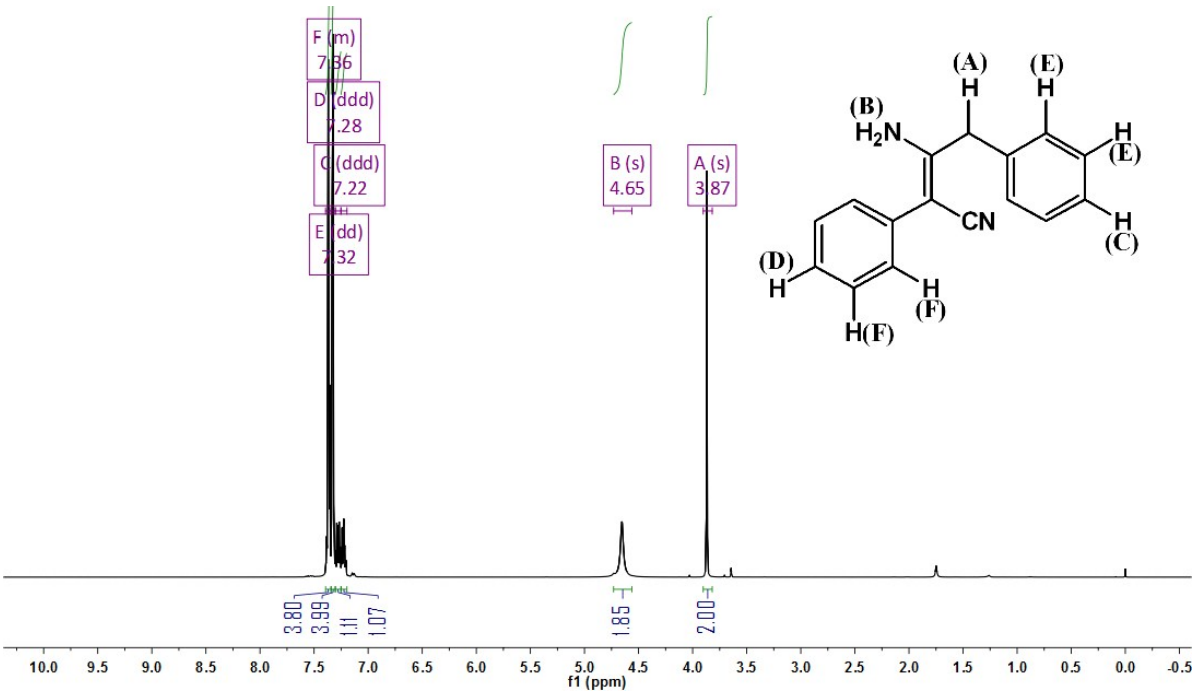
129.99, 129.02, 128.57, 128.51, 128.27, 128.02, 127.88, 125.76, 122.60, 21.45, 14.94. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd For $C_{24}H_{22}N_5$, 380.1875; found, 380.1870.

(*Z*)-*N*′-(5-ethyl-6-phenyl-2-(thiophen-2-yl)pyrimidin-4-yl)picolinimidamide (**6d**): yield, 86% (66 mg); white solid; R_f = 0.60 in 25% acetone in petroleum ether; melting point, 160-161℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.29 (s, 1H), 8.65 (d, *J* = 4.7 Hz, 1H), 8.58 (d, *J* = 7.9 Hz, 1H), 8.37 (s, 1H), 7.94 (d, *J* = 3.6 Hz, 1H), 7.86 (td, *J* = 7.8, 1.4 Hz, 1H), 7.67 – 7.61 (m, 2H), 7.54 – 7.38 (m, 5H), 7.13 (dd, *J* = 4.9, 3.8 Hz, 1H), 2.94 (q, *J* = 7.3 Hz, 2H), 1.30 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.00, 165.39, 157.10, 156.71, 152.02, 148.34, 144.58, 139.90, 137.11, 129.00, 128.57, 128.26, 128.24, 128.18, 127.69, 127.65, 125.78, 122.61, 21.46, 14.96. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd For $C_{22}H_{20}N_5S$, 386.1439; found, 386.1434.

2. ^{1}H NMR and ^{13}C NMR of Products

Compound **2a**

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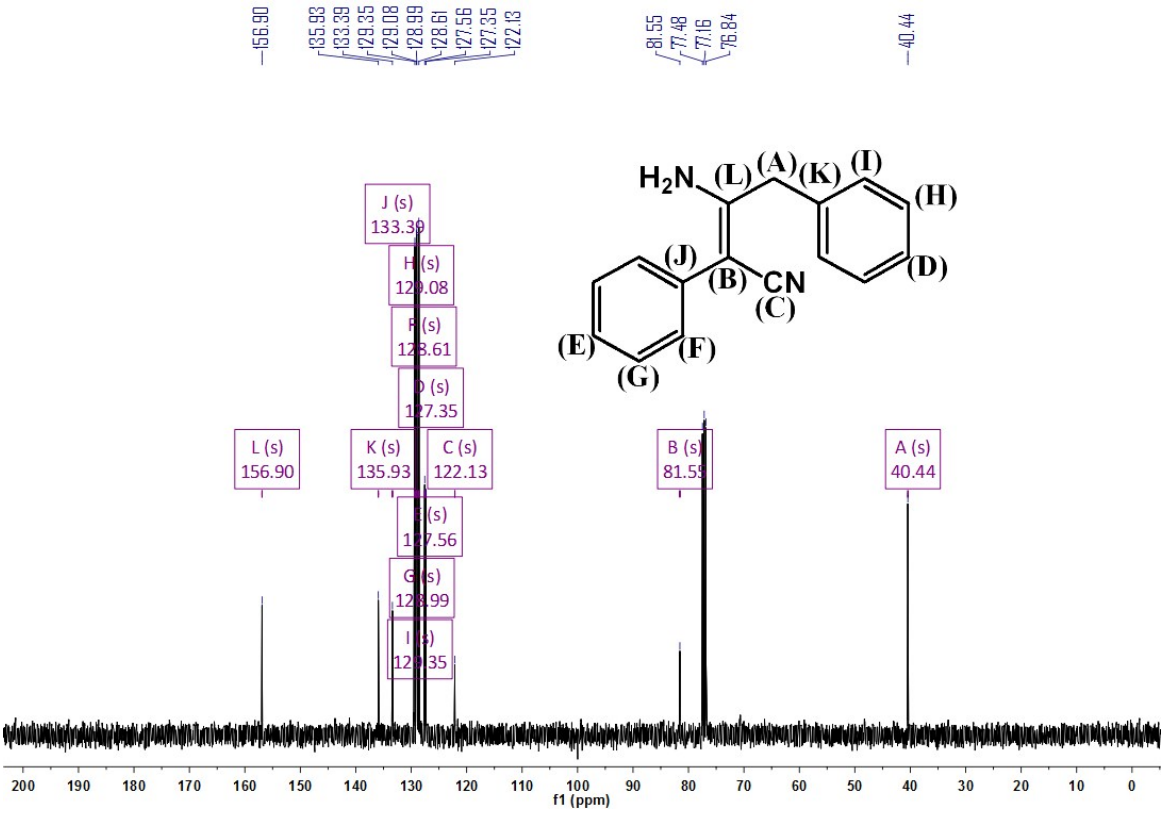
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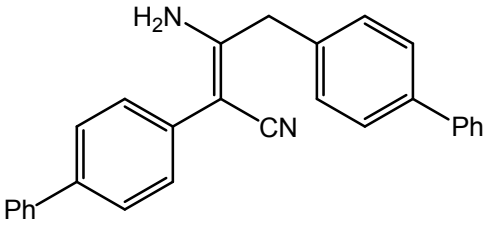
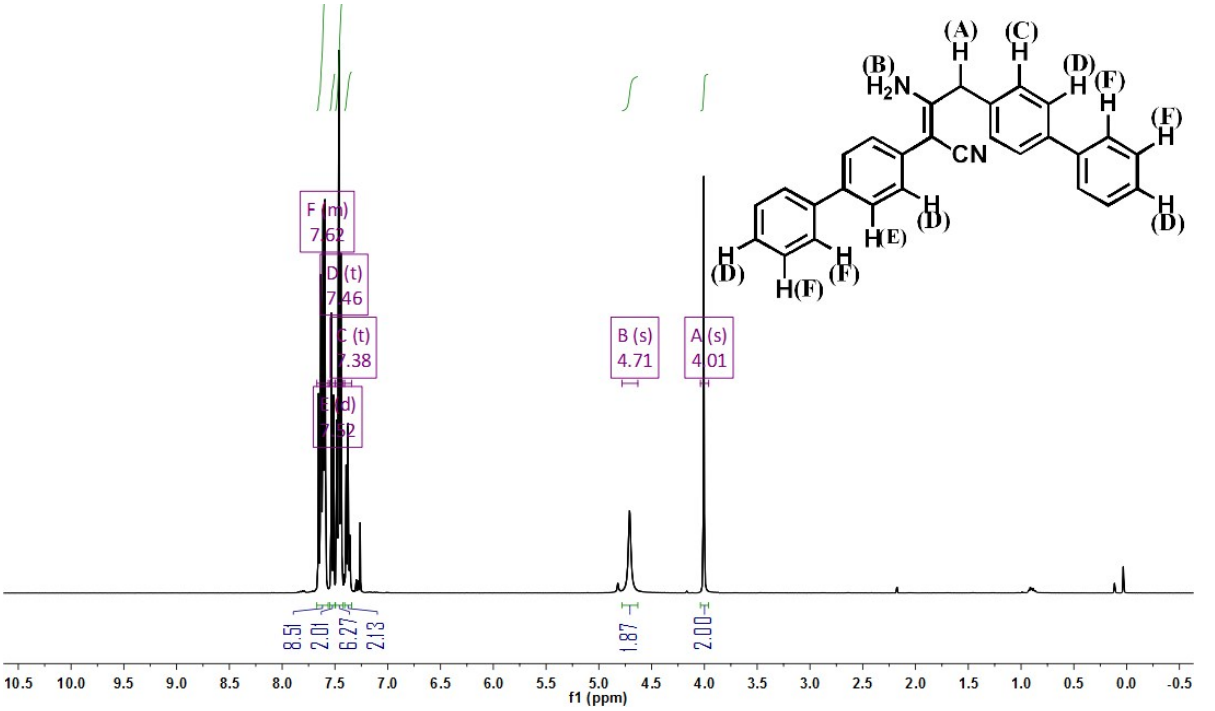
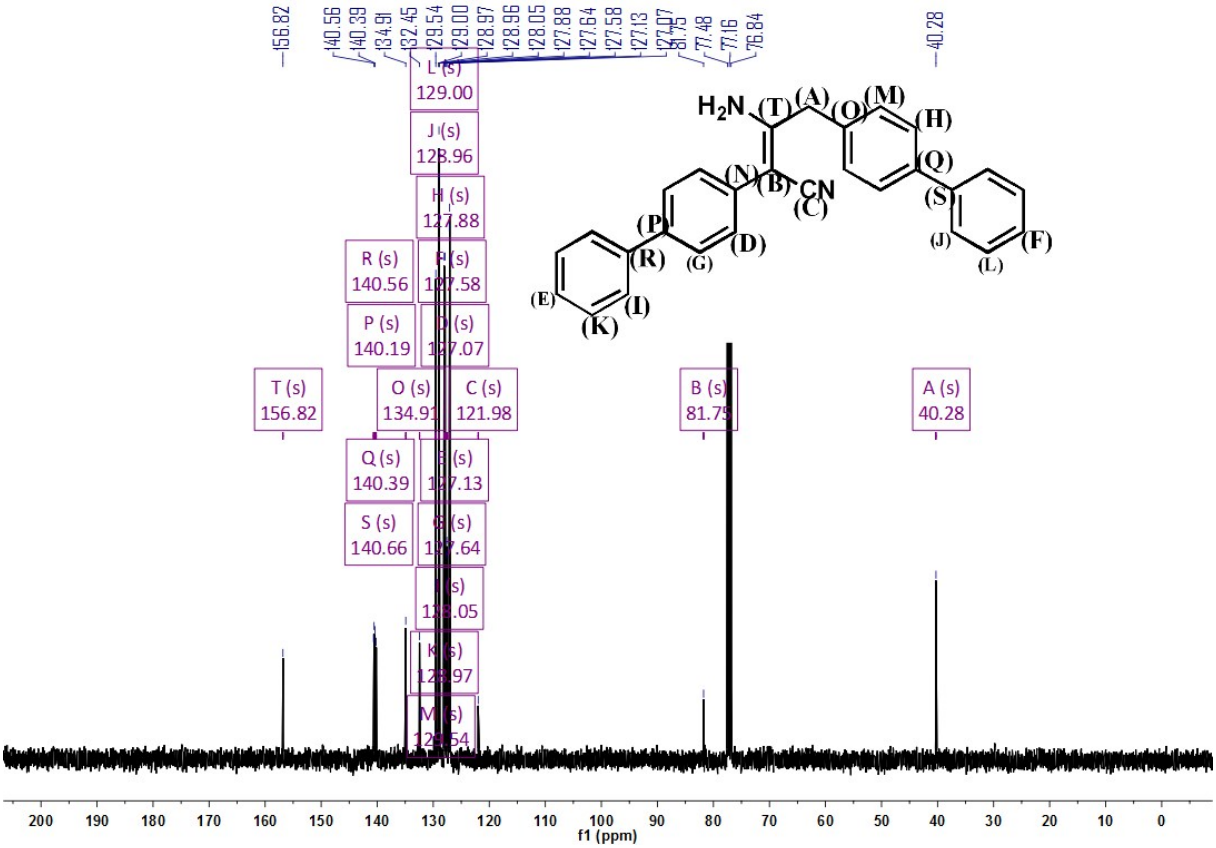
77.48
77.16
76.84
40.44
H2N
(L)
(A)
(K)
(I)
(H)
(J)
(B)
CN
(C)
(D)
(E)
(F)
(G)
J (s)
133.39
L (s)
156.90
K (s)
135.93
C (s)
122.13
B (s)
81.55
A (s)
40.44
f1 (ppm)

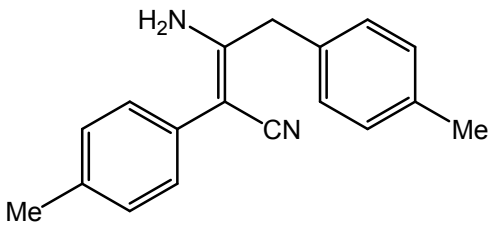
Compound **2b**

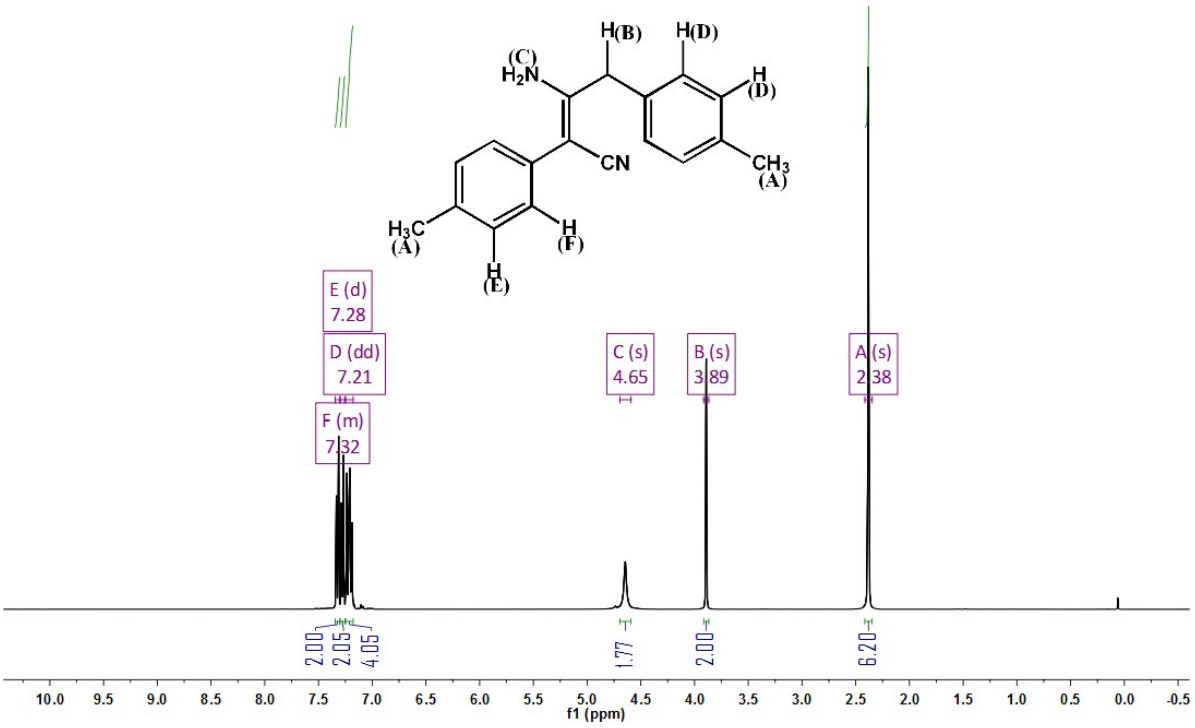

H2N
CN
Ph
Ph

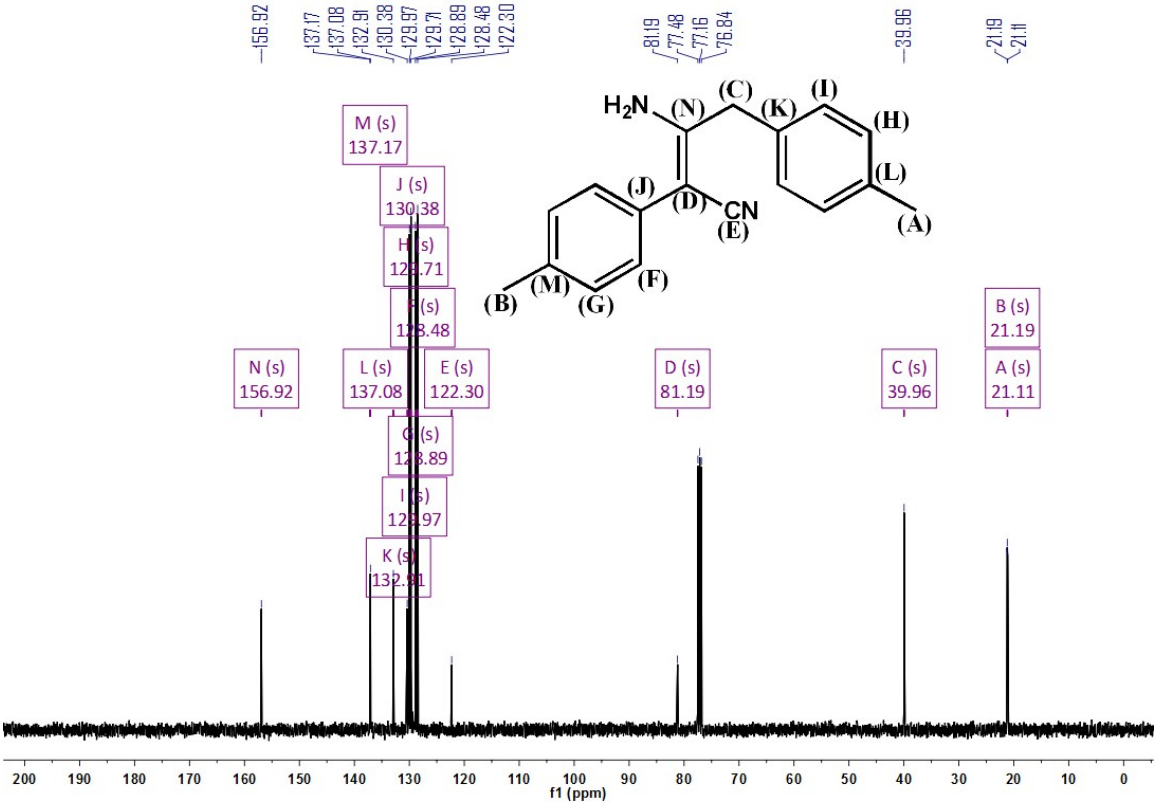

F (m)
7.62
D (t)
7.46
C (t)
7.38
B (s)
4.71
A (s)
4.01
8.51
2.01
6.27
2.13
1.87
2.00
f1 (ppm)


156.82
140.56
140.39
134.91
132.45
129.54
128.00
128.97
128.96
128.05
127.88
127.64
127.58
127.13
81.75
77.48
77.16
76.84
40.28
L (s)
129.00
T (s)
156.82
B (s)
81.75
A (s)
40.28
f1 (ppm)

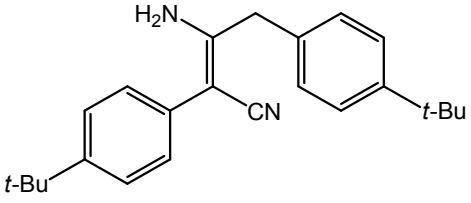
Compound **2c**

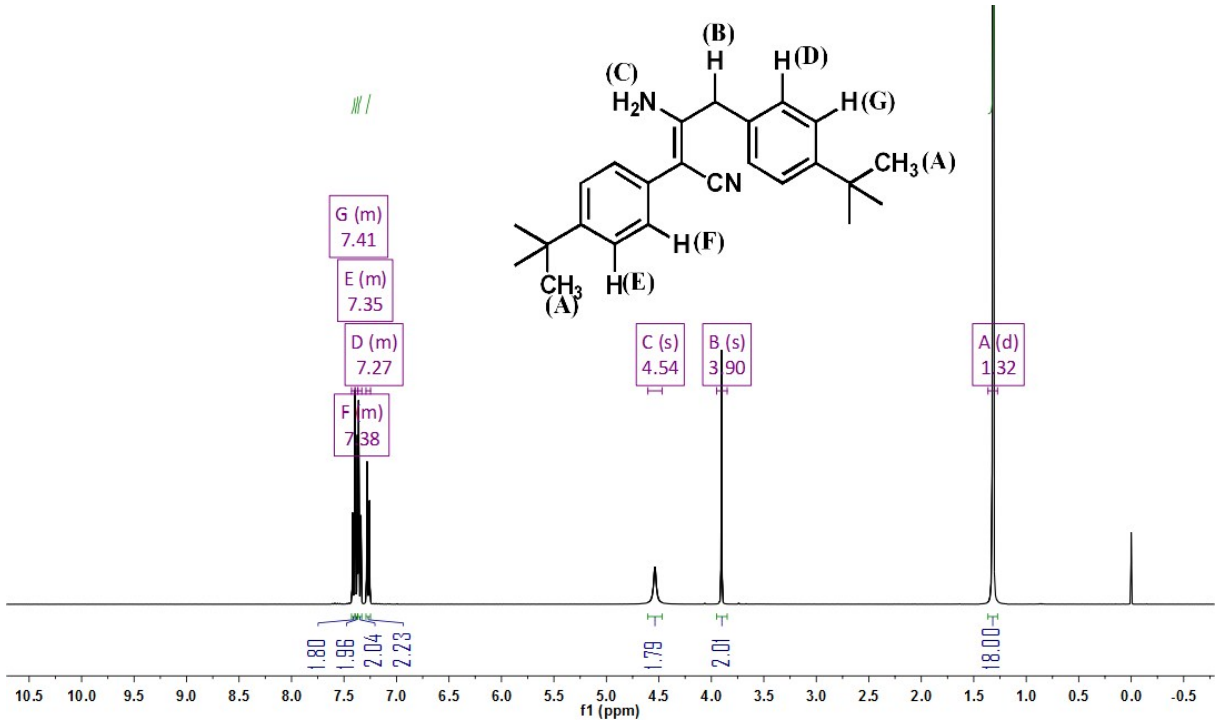

H2N
CN
Me
Me

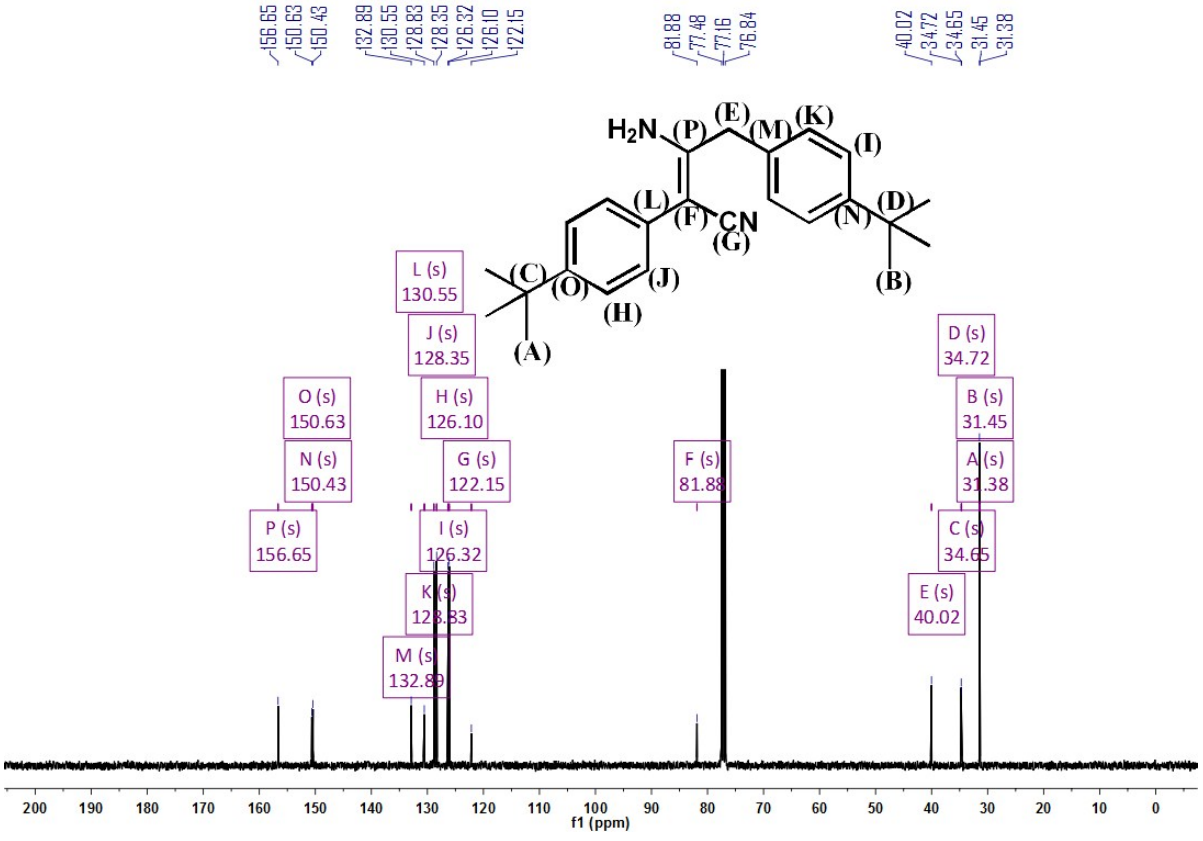

H(B)
H(D)
(C)
H2N
H
(D)
CN
CH3
(A)
H3C
(A)
H
(F)
H
(E)
E (d)
7.28
D (dd)
7.21
F (m)
7.32
C (s)
4.65
B (s)
3.89
A (s)
2.38
2.00
2.05
4.05
1.77
2.00
6.20
f1 (ppm)


156.92
137.17
137.08
132.91
130.38
129.97
128.71
128.89
128.48
122.30
81.19
77.48
77.16
76.84
39.96
21.19
21.11
H2N
(N)
(C)
(K)
(I)
(H)
(L)
(A)
(J)
(D)
CN
(E)
(B)
(M)
(G)
(F)
M (s)
137.17
J (s)
130.38
H (s)
128.71
G (s)
128.48
N (s)
156.92
L (s)
137.08
E (s)
122.30
C (s)
128.89
I (s)
128.97
K (s)
132.91
D (s)
81.19
C (s)
39.96
B (s)
21.19
A (s)
21.11
f1 (ppm)

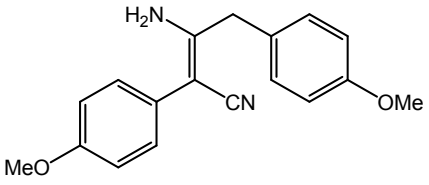
Compound **2d**

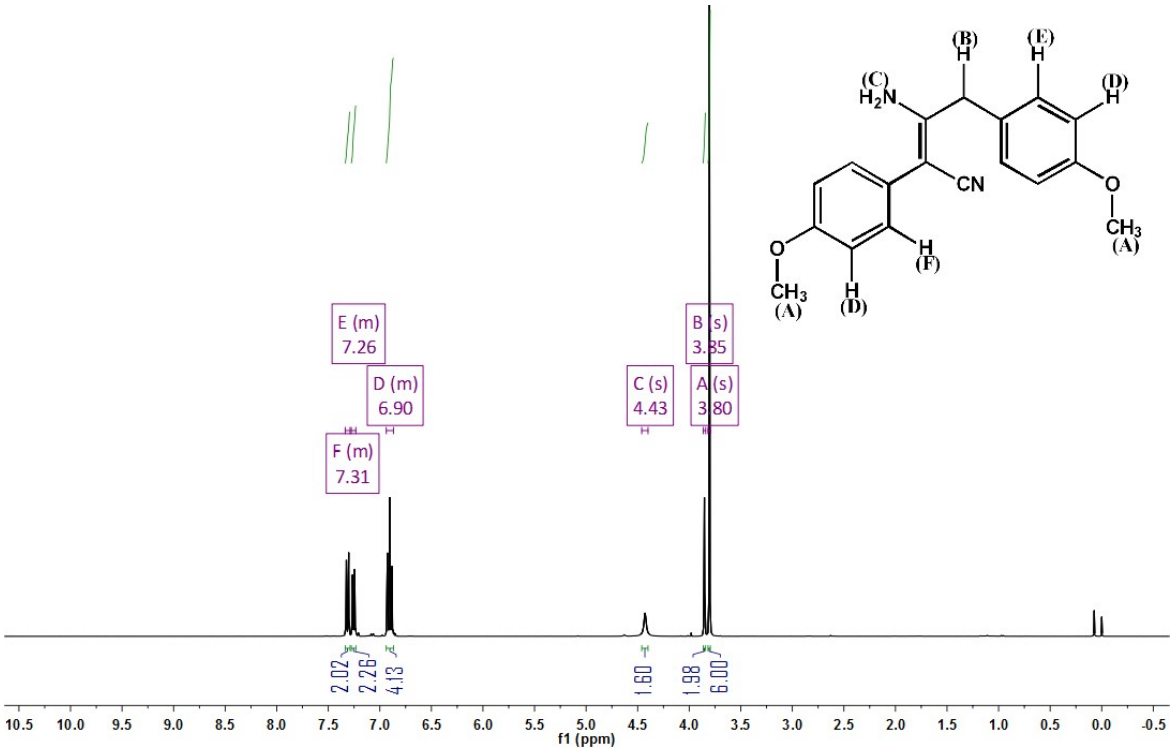

H2N
CN
t-Bu
t-Bu

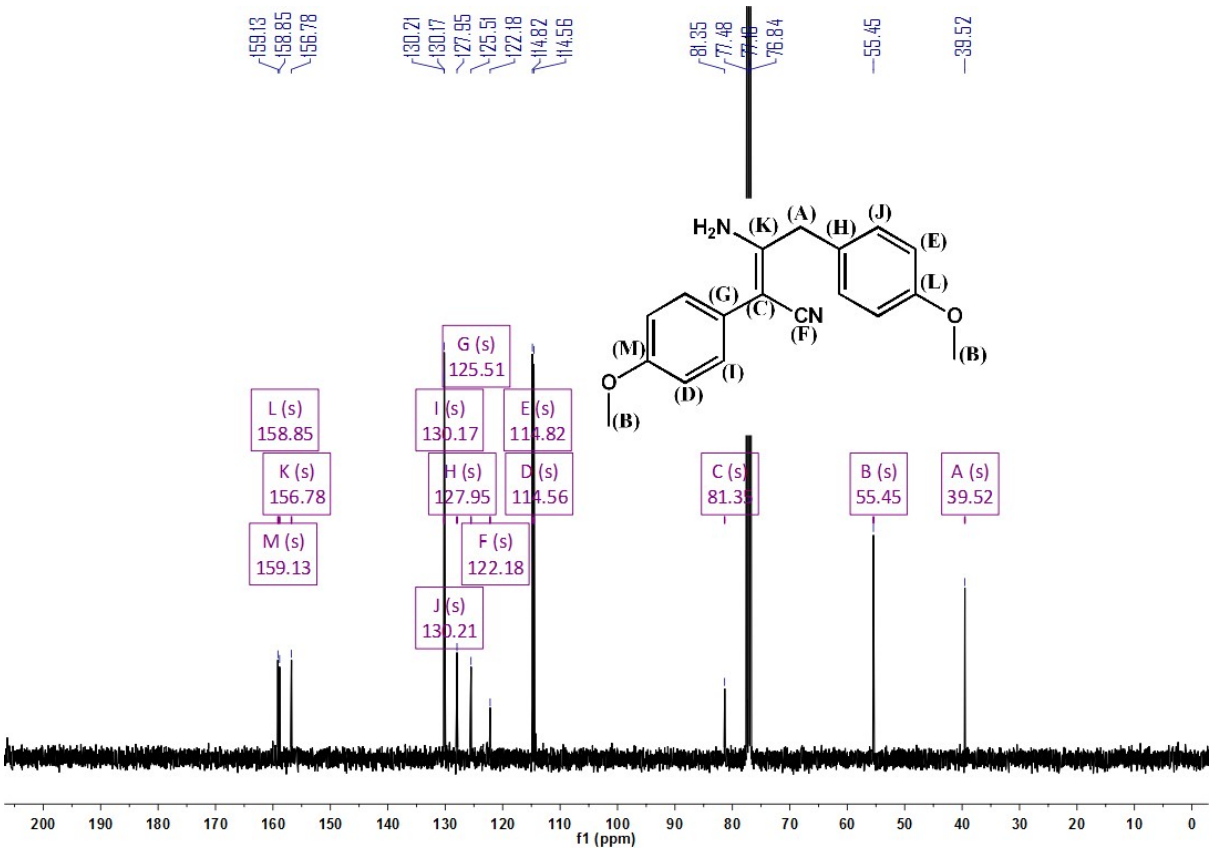

(B)
H
H(D)
(C)
H2N
H(G)
CH3(A)
CN
H(F)
CH3
(A)
H(E)
G (m)
7.41
E (m)
7.35
D (m)
7.27
F (m)
7.38
C (s)
4.54
B (s)
3.90
A (d)
1.32
1.80
1.96
2.04
2.23
1.79
2.01
18.00
f1 (ppm)


156.65
150.63
150.43
132.89
130.55
128.83
128.35
126.32
126.10
122.15
81.88
77.48
77.16
76.84
40.02
34.72
34.65
31.45
31.38
H2N
(P)
(E)
(M)
(K)
(I)
(L)
(F)
CN
(G)
(N)
(D)
(C)
(O)
(J)
(B)
(H)
(A)
L (s)
130.55
J (s)
128.35
O (s)
150.63
H (s)
126.10
N (s)
150.43
G (s)
122.15
P (s)
156.65
I (s)
126.32
K (s)
128.83
M (s)
132.89
F (s)
81.88
D (s)
34.72
B (s)
31.45
A (s)
31.38
C (s)
34.65
E (s)
40.02
f1 (ppm)

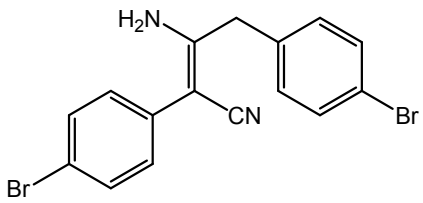
Compound **2e**

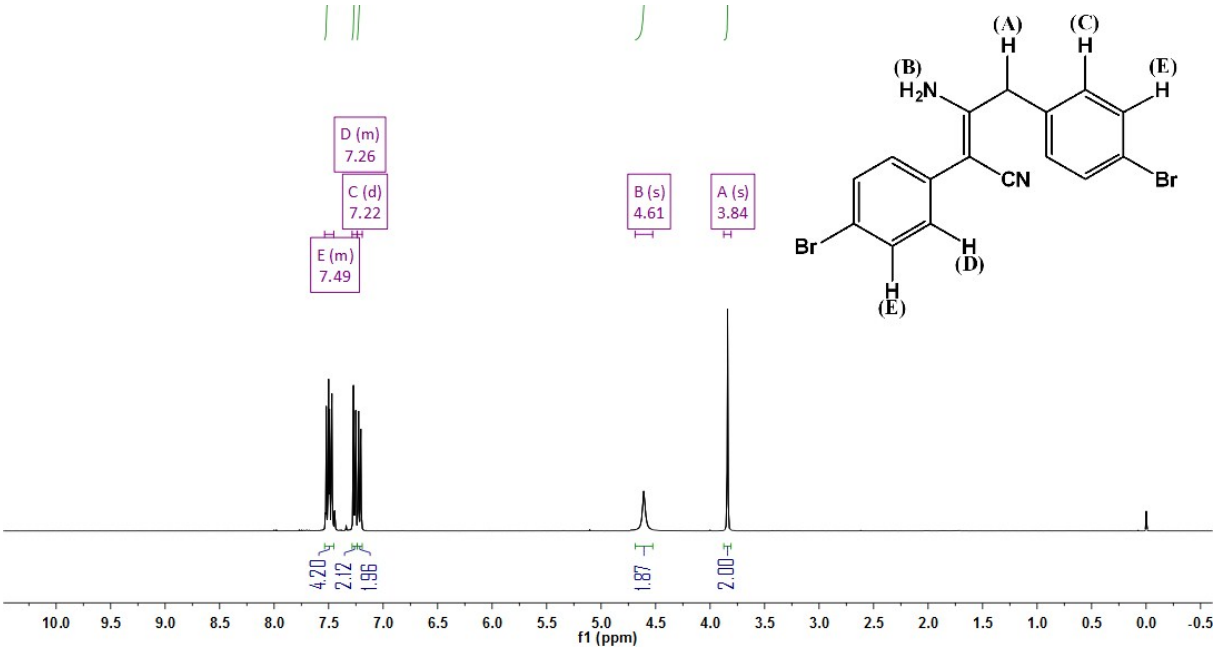

H2N
CN
OMe
MeO

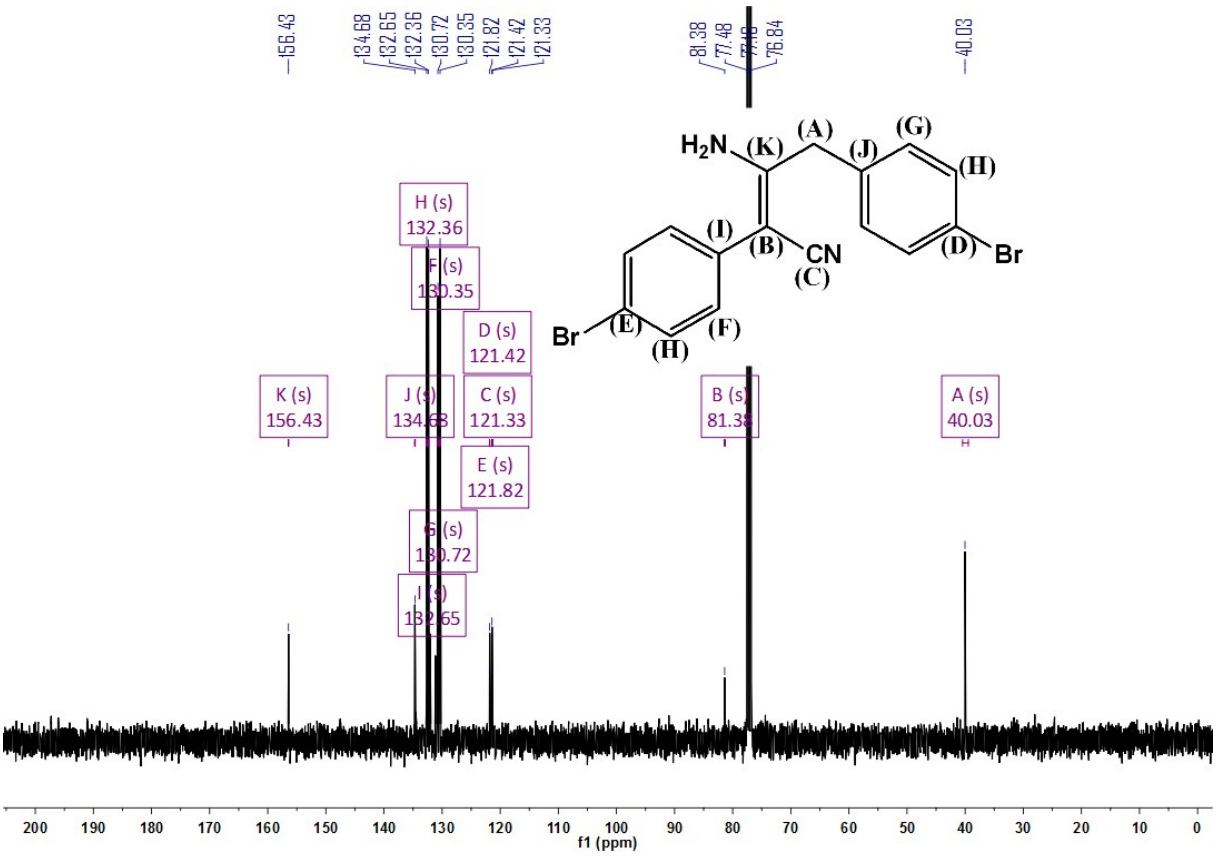

E (m)
7.26
D (m)
6.90
F (m)
7.31
B (s)
3.85
C (s)
4.43
A (s)
3.80
2.02
2.26
4.13
1.60
1.98
6.00
f1 (ppm)


159.13
158.85
156.78
130.21
130.17
127.95
125.51
122.18
114.82
114.56
81.35
77.48
76.84
55.45
39.52
L (s)
158.85
K (s)
156.78
M (s)
159.13
G (s)
125.51
I (s)
130.17
H (s)
127.95
F (s)
122.18
J (s)
130.21
E (s)
114.82
D (s)
114.56
C (s)
81.35
B (s)
55.45
A (s)
39.52
f1 (ppm)

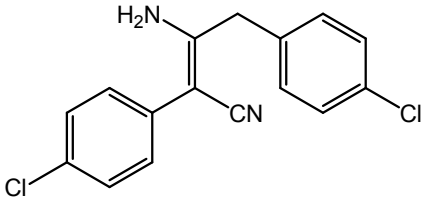
Compound **2f**

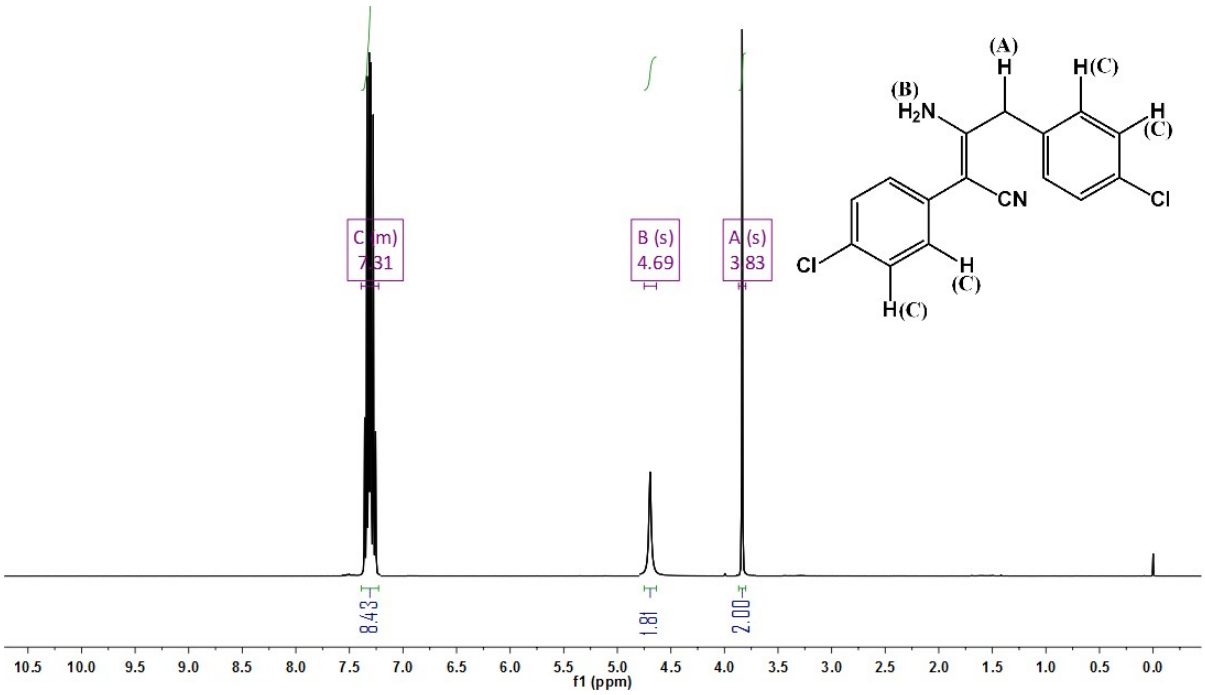

H2N
CN
Br
Br

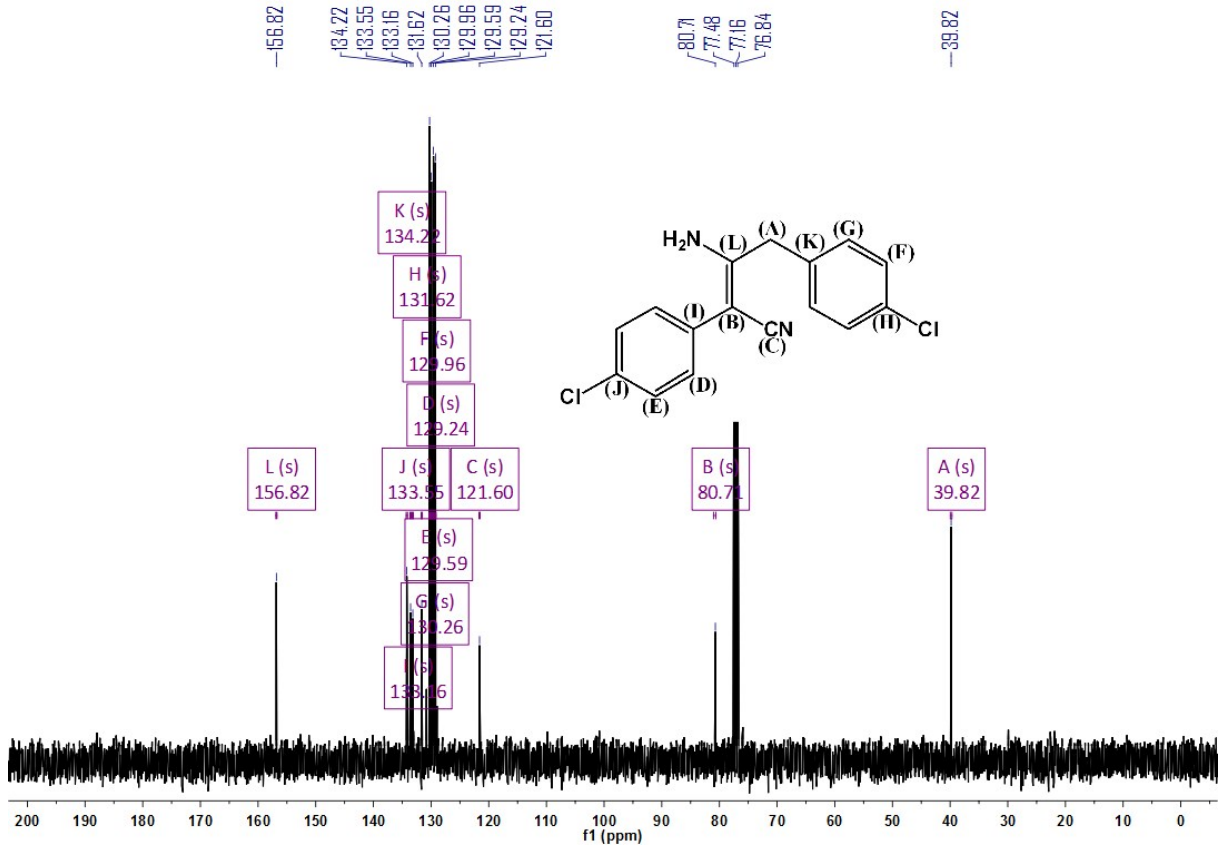

D (m)
7.26
C (d)
7.22
E (m)
7.49
B (s)
4.61
A (s)
3.84
4.20
2.12
1.96
1.87
2.00
f1 (ppm)


156.43
134.68
132.65
132.36
130.72
130.35
121.82
121.42
121.33
81.38
77.48
76.84
40.03
H (s)
132.36
F (s)
130.35
D (s)
121.42
K (s)
156.43
J (s)
C (s)
121.33
E (s)
121.82
G (s)
I (s)
B (s)
A (s)
40.03
f1 (ppm)

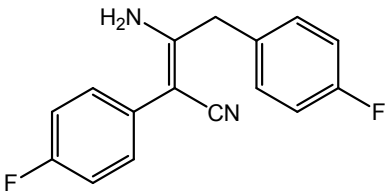
Compound **2g**

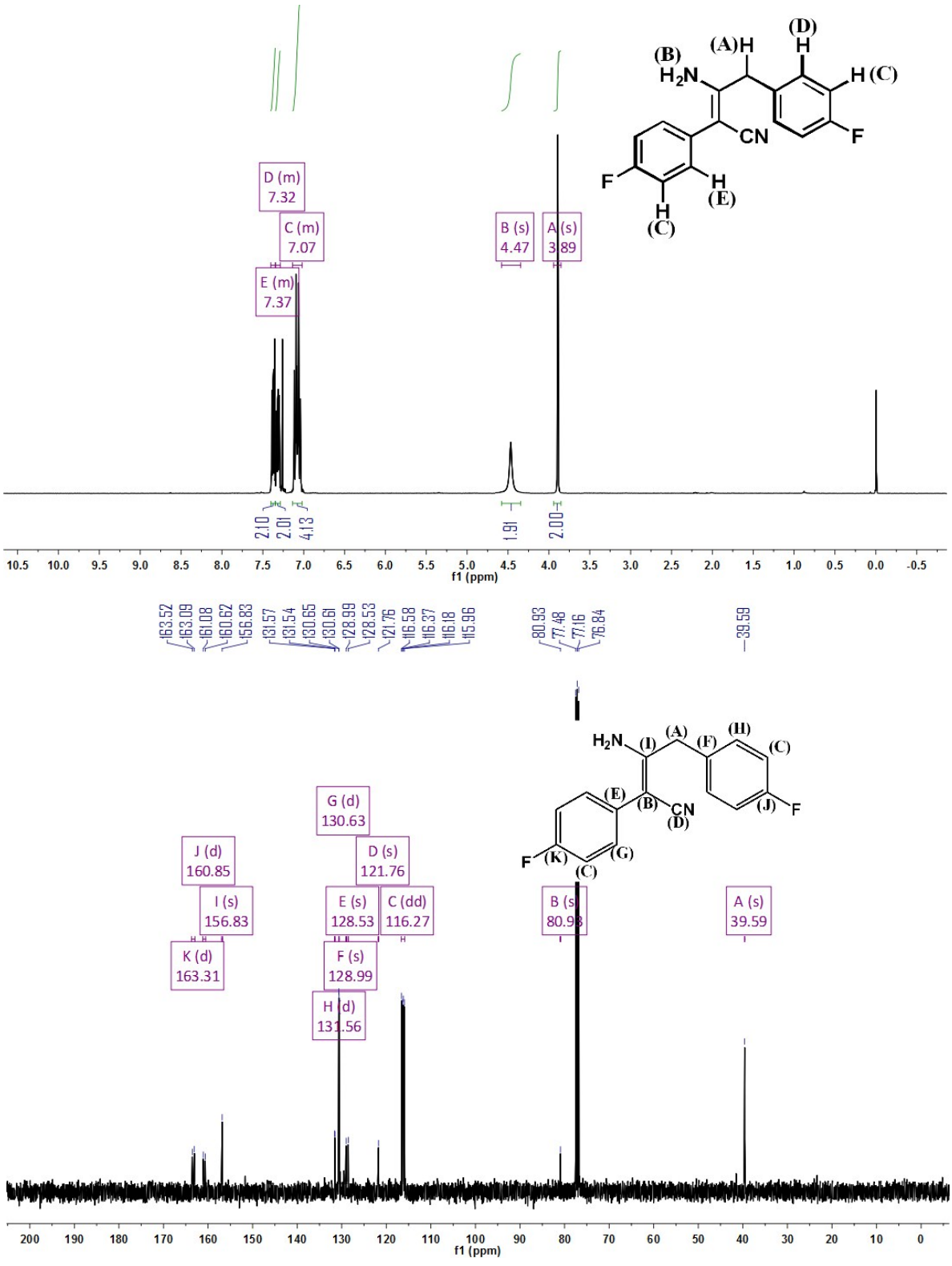

H2N
CN
Cl
Cl


C (m)
7.31
B (s)
4.69
A (s)
3.83
8.43
1.81
2.00
f1 (ppm)

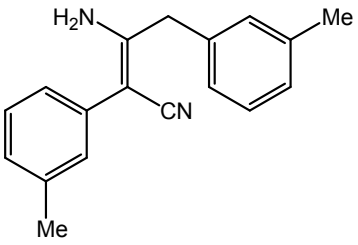

156.82
134.22
133.55
133.16
131.62
130.26
129.96
129.59
129.24
121.60
80.71
77.48
77.16
76.84
39.82
K (s)
134.22
H (s)
131.62
F (s)
129.96
D (s)
129.24
L (s)
156.82
J (s)
133.55
C (s)
121.60
E (s)
129.59
G (s)
130.26
I (s)
130.16
B (s)
80.71
A (s)
39.82
f1 (ppm)

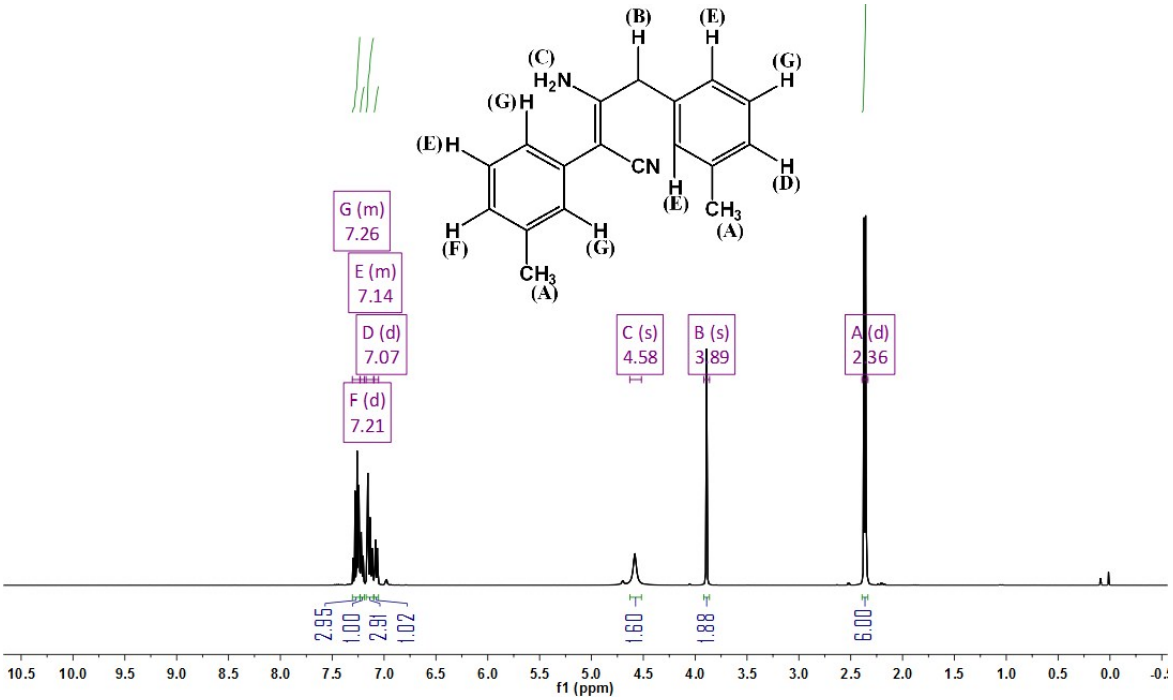
Compound **2h**

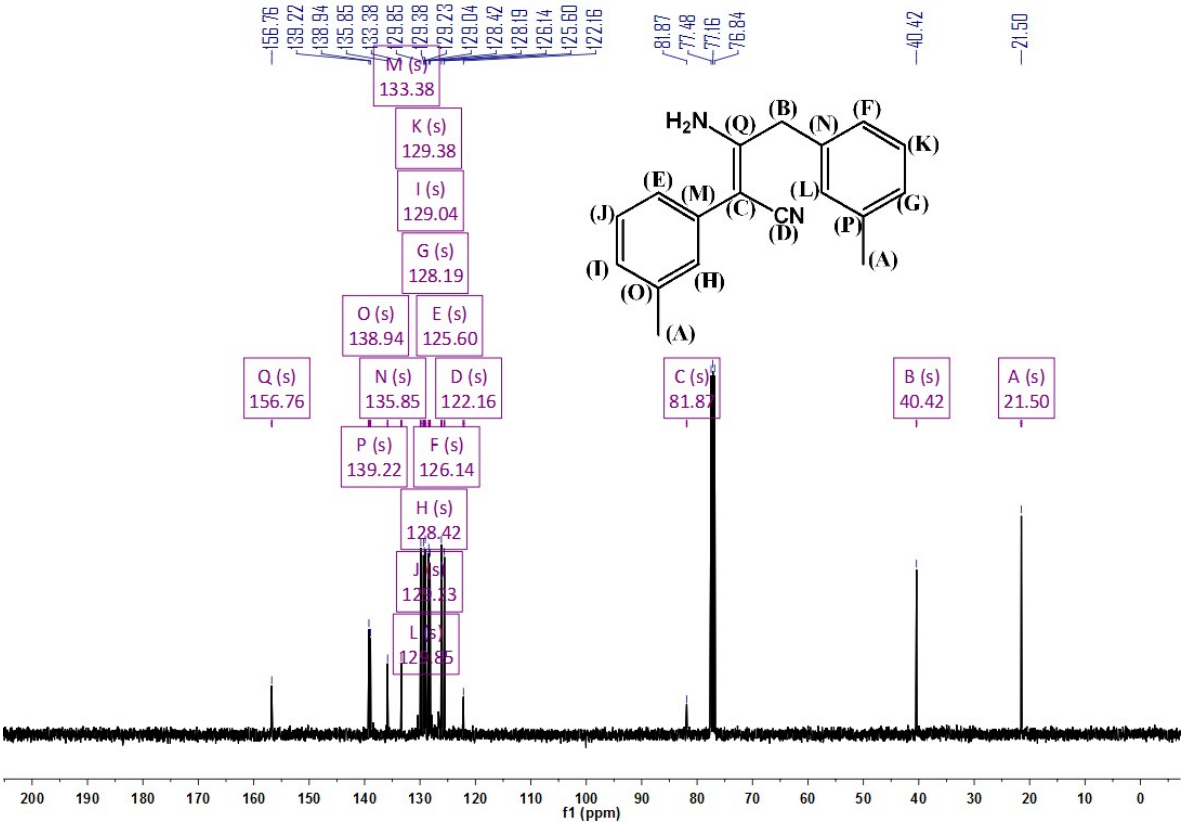

H2N
CN
F
F


D (m)
7.32
C (m)
7.07
E (m)
7.37
B (s)
4.47
A (s)
3.89
(D)
H
(A)H
(B)
H2N
H (C)
CN
F
F
H
(E)
H
(C)
2.10
2.01
4.13
1.91
2.00
f1 (ppm)
163.52
163.09
161.08
160.62
156.83
131.57
131.54
130.65
130.61
128.99
128.53
121.76
116.58
116.37
116.18
115.96
80.93
77.48
77.16
76.84
39.59
G (d)
130.63
D (s)
121.76
J (d)
160.85
I (s)
156.83
K (d)
163.31
E (s)
128.53
C (dd)
116.27
F (s)
128.99
H (d)
131.56
B (s)
80.98
A (s)
39.59
H2N
(I)
(A)
(F)
(H)
(C)
(E)
(B)
CN
(D)
(J)
F
F
(K)
(G)
(C)
f1 (ppm)

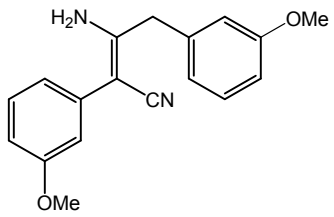
Compound **2i**

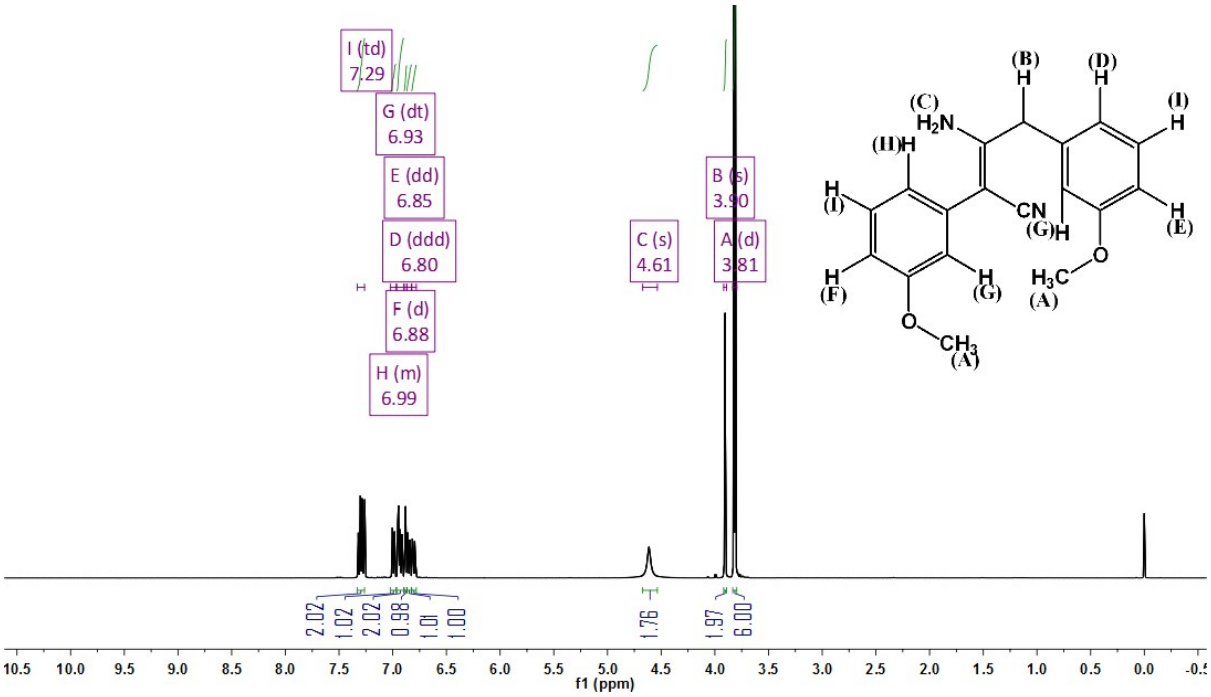

H2N
Me
CN
Me

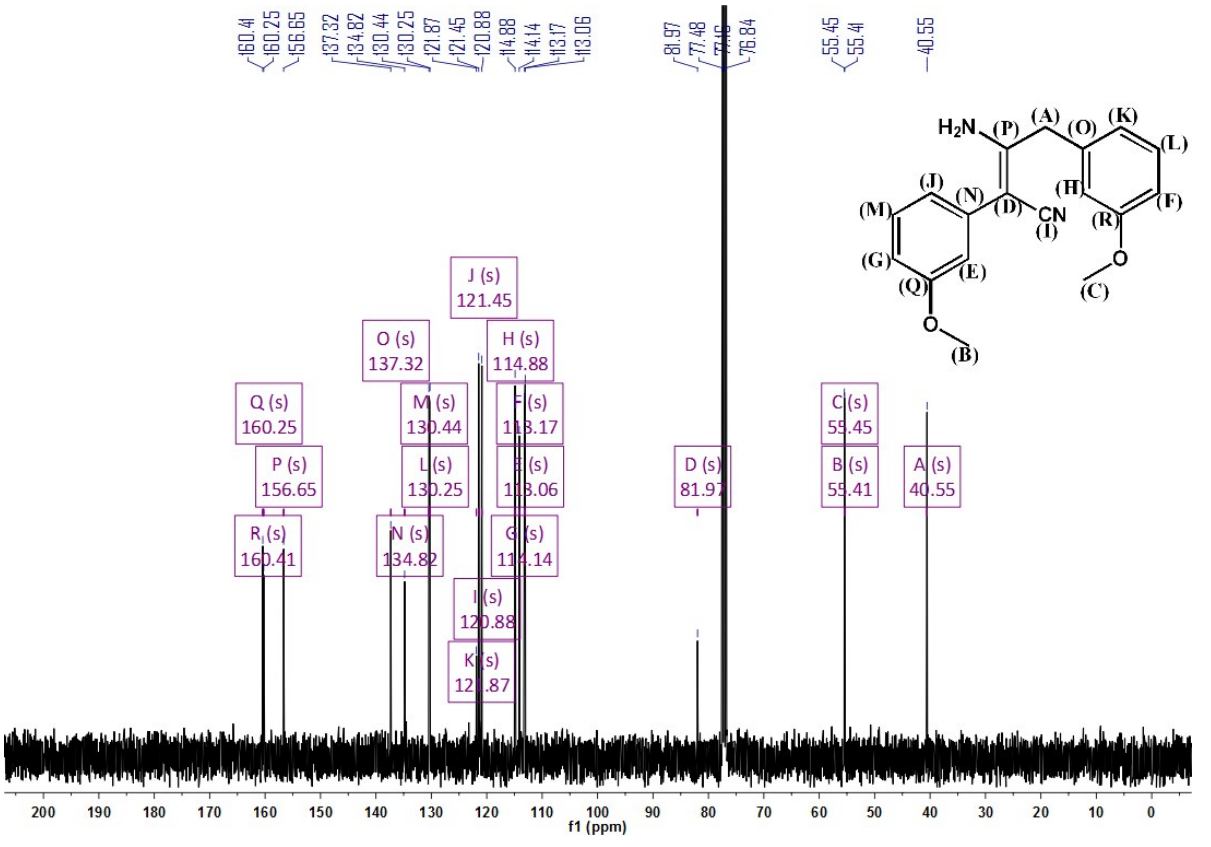

G (m) 7.26
E (m) 7.14
D (d) 7.07
F (d) 7.21
C (s) 4.58
B (s) 3.89
A (d) 2.36
2.95
1.00
2.91
1.02
1.60
1.88
6.00
f1 (ppm)


M (s) 133.38
K (s) 129.38
I (s) 129.04
G (s) 128.19
O (s) 138.94
E (s) 125.60
Q (s) 156.76
N (s) 135.85
D (s) 122.16
P (s) 139.22
F (s) 126.14
H (s) 128.42
C (s) 81.87
B (s) 40.42
A (s) 21.50
f1 (ppm)

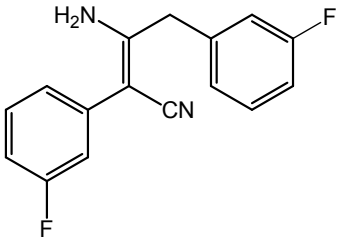
Compound **2j**

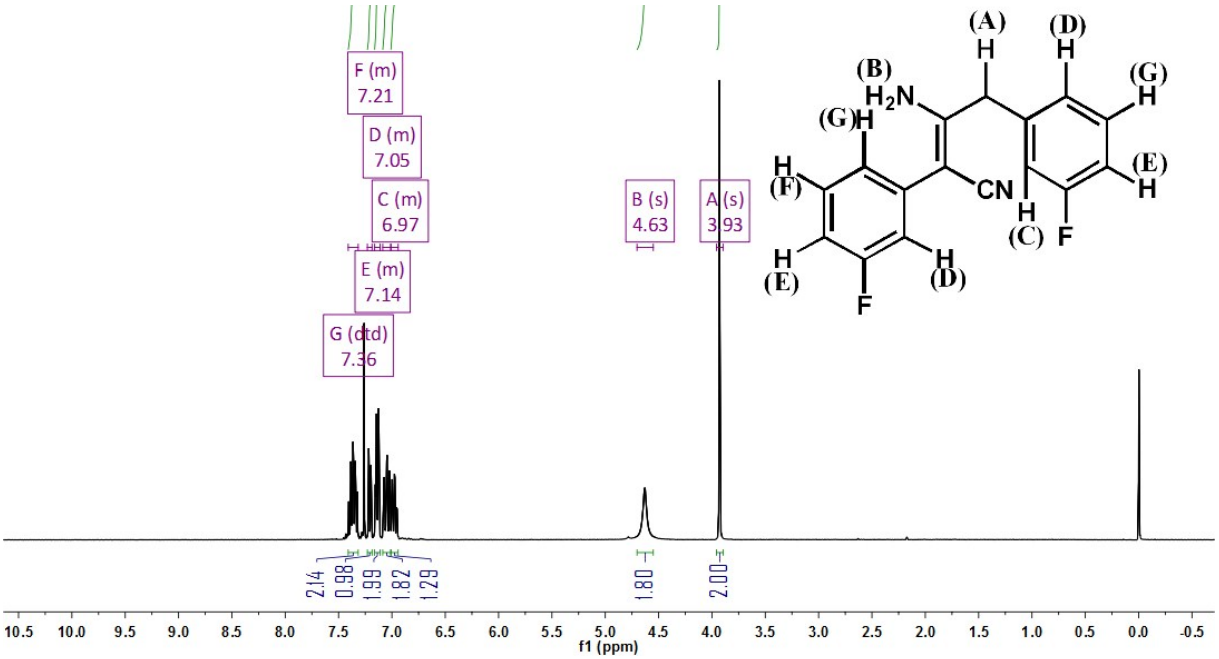

H2N
OMe
CN
OMe

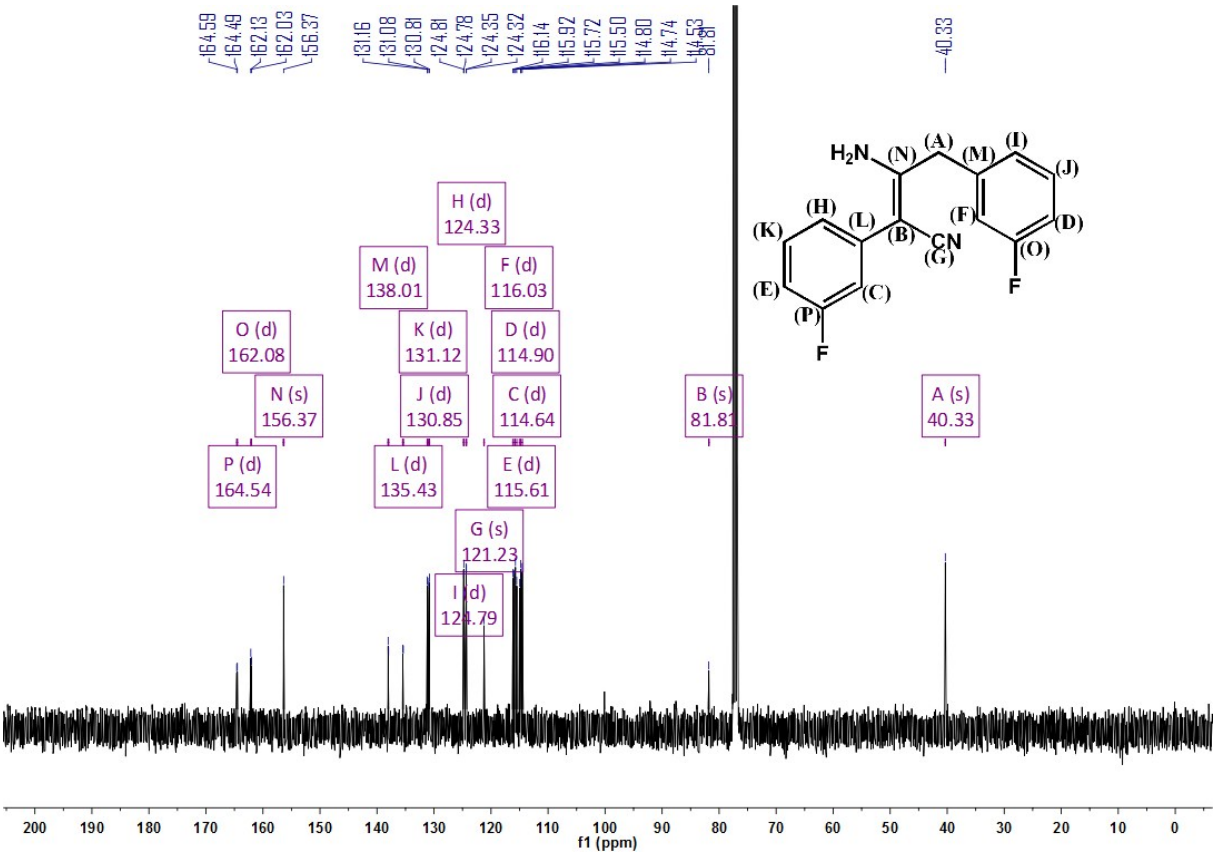

I (td) 7.29
G (dt) 6.93
E (dd) 6.85
D (ddd) 6.80
F (d) 6.88
H (m) 6.99
C (s) 4.61
B (s) 3.90
A (d) 3.81
2.02
1.02
2.02
0.98
1.01
1.00
1.76
1.97
6.00
f1 (ppm)


160.41
160.25
156.65
137.32
134.82
130.44
130.25
121.87
121.45
120.88
114.88
114.14
113.17
113.06
81.97
77.48
76.84
55.45
55.41
40.55
J (s) 121.45
O (s) 137.32
H (s) 114.88
Q (s) 160.25
M (s) 130.44
F (s) 113.17
P (s) 156.65
L (s) 130.25
E (s) 113.06
R (s) 160.41
N (s) 134.82
G (s) 114.14
I (s) 120.88
K (s) 121.87
D (s) 81.97
C (s) 55.45
B (s) 55.41
A (s) 40.55
f1 (ppm)

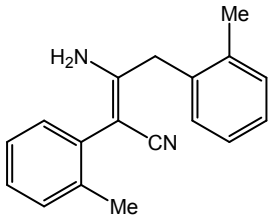
Compound **2k**

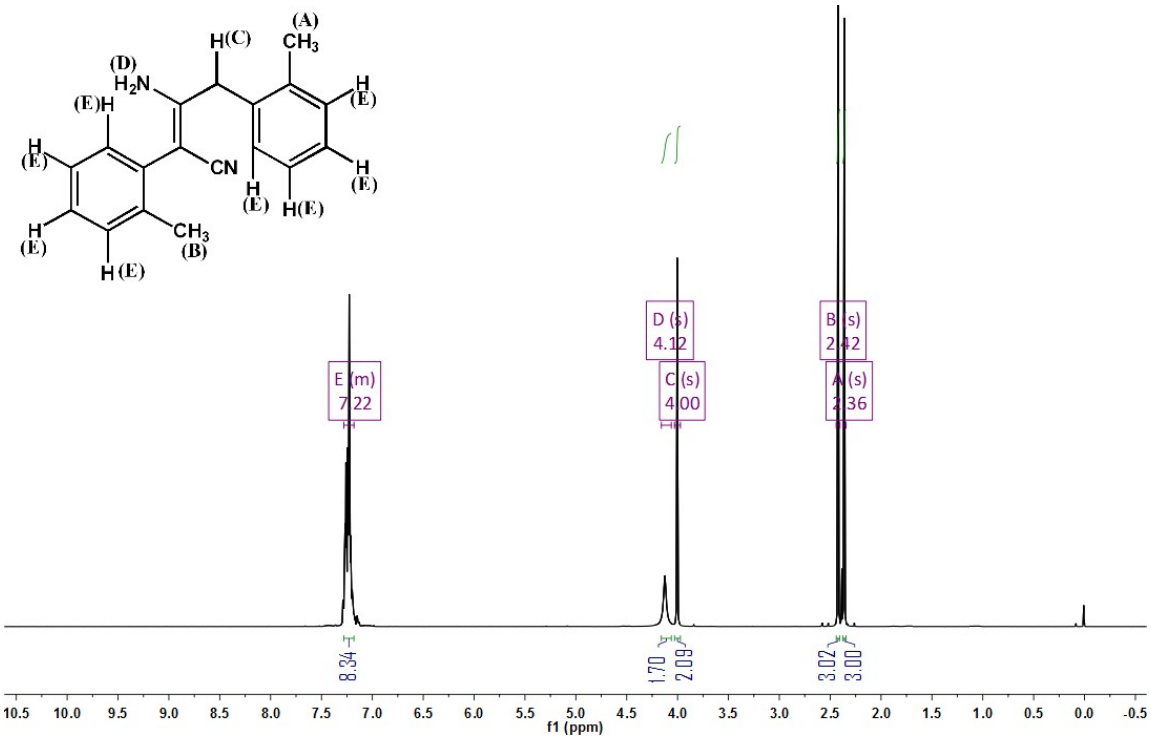

H2N
F
CN
F

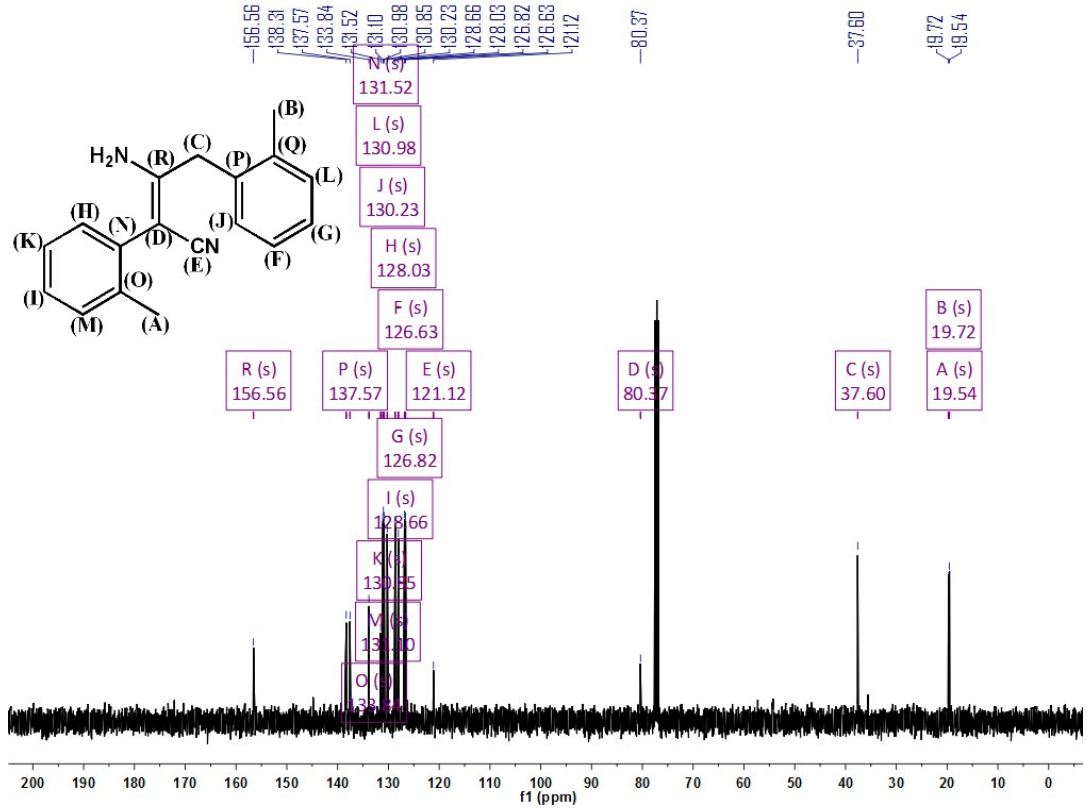

F (m)
7.21
D (m)
7.05
C (m)
6.97
E (m)
7.14
G (dtd)
7.36
B (s)
4.63
A (s)
3.93
2.14
0.98
1.99
1.82
1.29
1.80
2.00
f1 (ppm)


H (d)
124.33
M (d)
138.01
F (d)
116.03
O (d)
162.08
K (d)
131.12
D (d)
114.90
N (s)
156.37
J (d)
130.85
C (d)
114.64
B (s)
81.81
A (s)
40.33
P (d)
164.54
L (d)
135.43
E (d)
115.61
G (s)
121.23
I (d)
124.79
f1 (ppm)

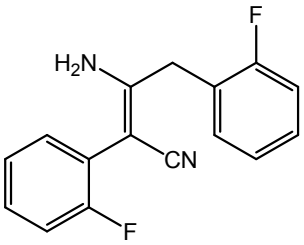
Compound **21**

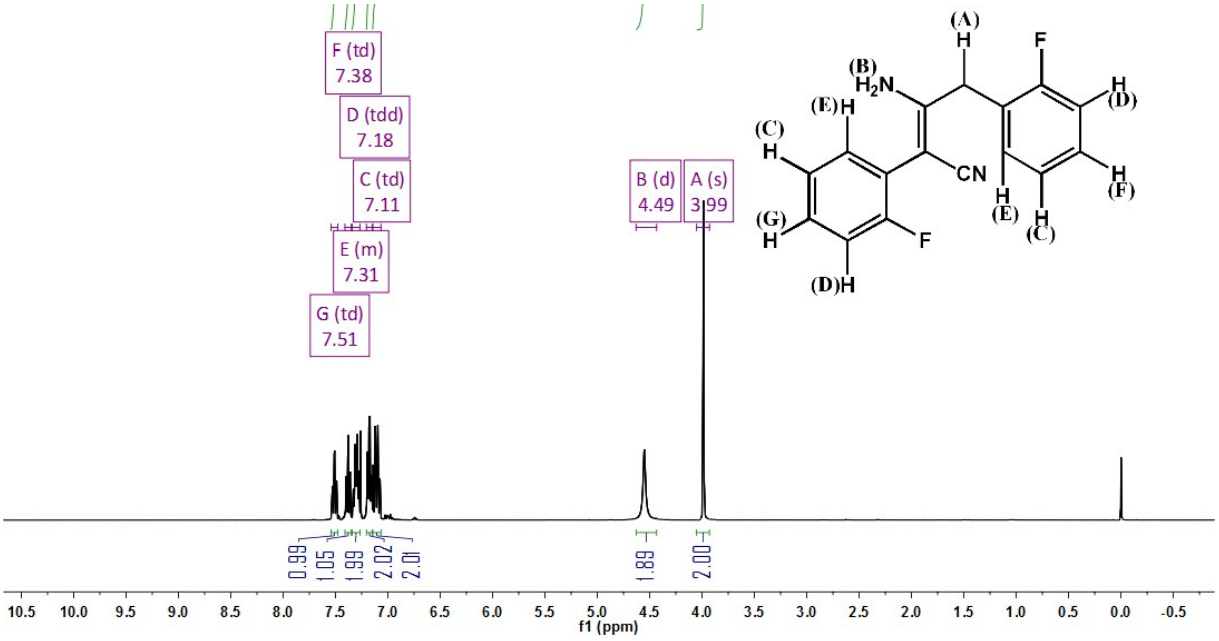

Me
H2N
CN
Me

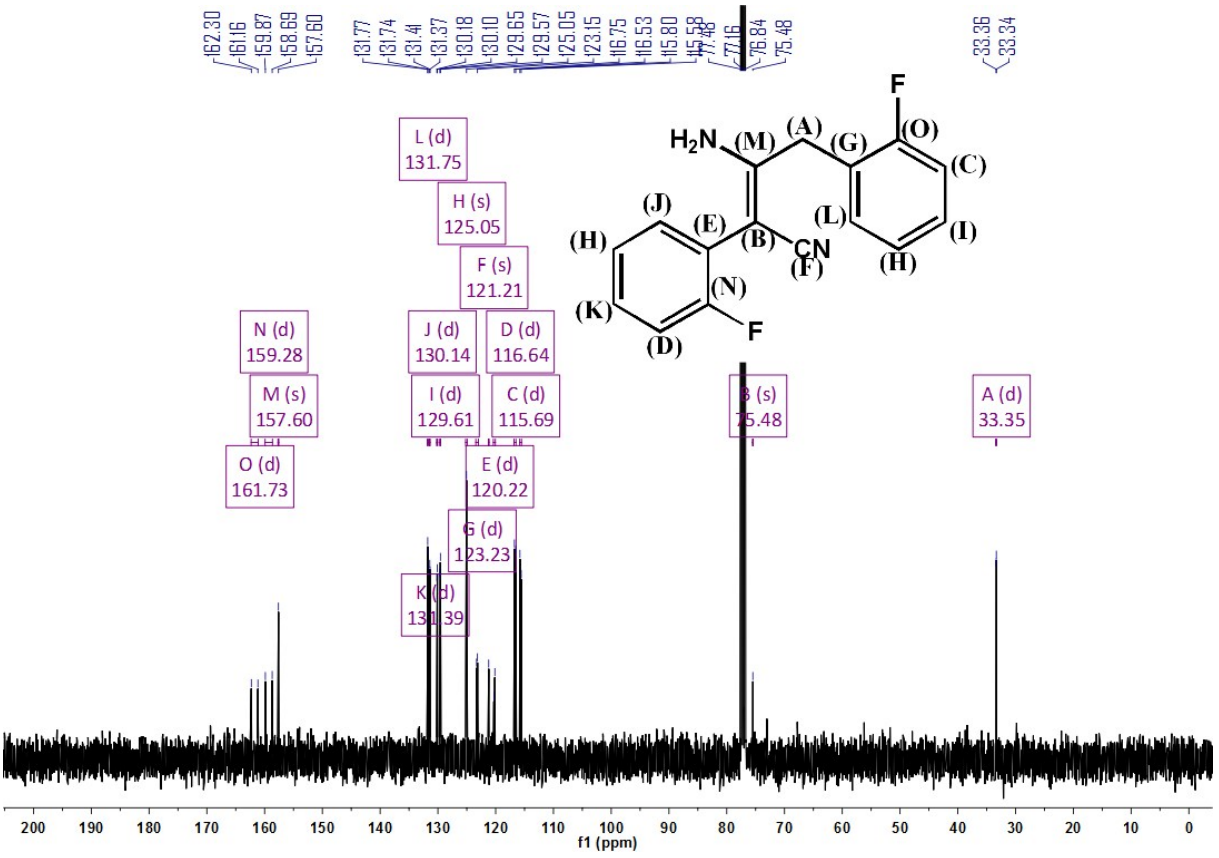

(A)
CH3
H(C)
(D)
H2N
(E)H
H
(E)
CN
H(E)
CH3
(B)
E (m)
7.22
D (s)
4.12
C (s)
4.00
B (s)
2.42
A (s)
2.36
8.34
1.70
2.09
3.02
3.00
f1 (ppm)


156.56
138.31
137.57
133.84
131.52
131.10
130.98
130.85
130.23
128.66
128.03
126.82
126.63
121.12
80.37
37.60
19.72
19.54
N (s)
131.52
L (s)
130.98
J (s)
130.23
H (s)
128.03
F (s)
126.63
R (s)
156.56
P (s)
137.57
E (s)
121.12
D (s)
80.37
C (s)
37.60
B (s)
19.72
A (s)
19.54
G (s)
126.82
I (s)
128.66
f1 (ppm)

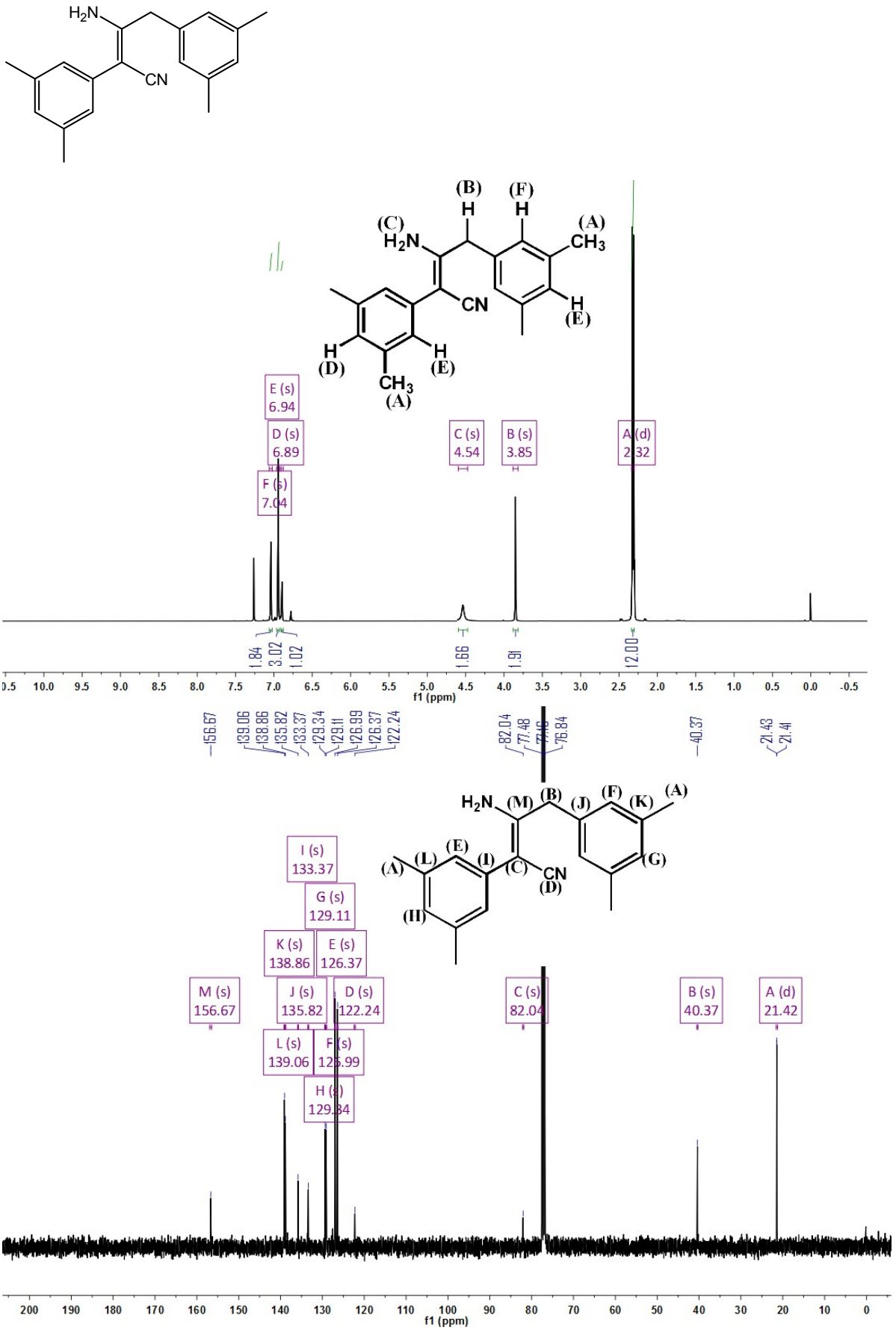
Compound **2m**


F
H2N
CN
F

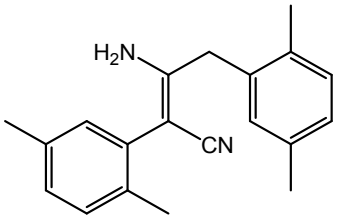

F (td) 7.38
D (tdd) 7.18
C (td) 7.11
E (m) 7.31
G (td) 7.51
B (d) 4.49
A (s) 3.99
0.99
1.05
1.99
2.02
2.01
1.89
2.00
f1 (ppm)

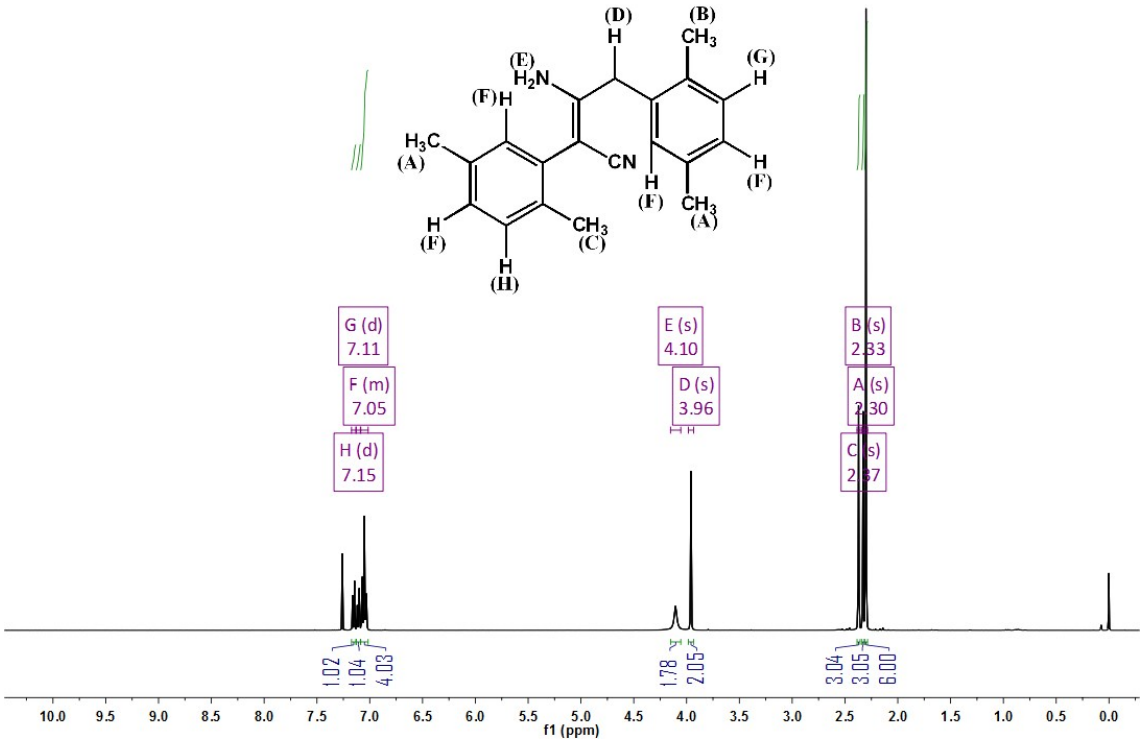

L (d) 131.75
H (s) 125.05
F (s) 121.21
N (d) 159.28
J (d) 130.14
D (d) 116.64
M (s) 157.60
I (d) 129.61
C (d) 115.69
O (d) 161.73
E (d) 120.22
G (d) 123.23
K (d) 131.39
B (s) 75.48
A (d) 33.35
f1 (ppm)

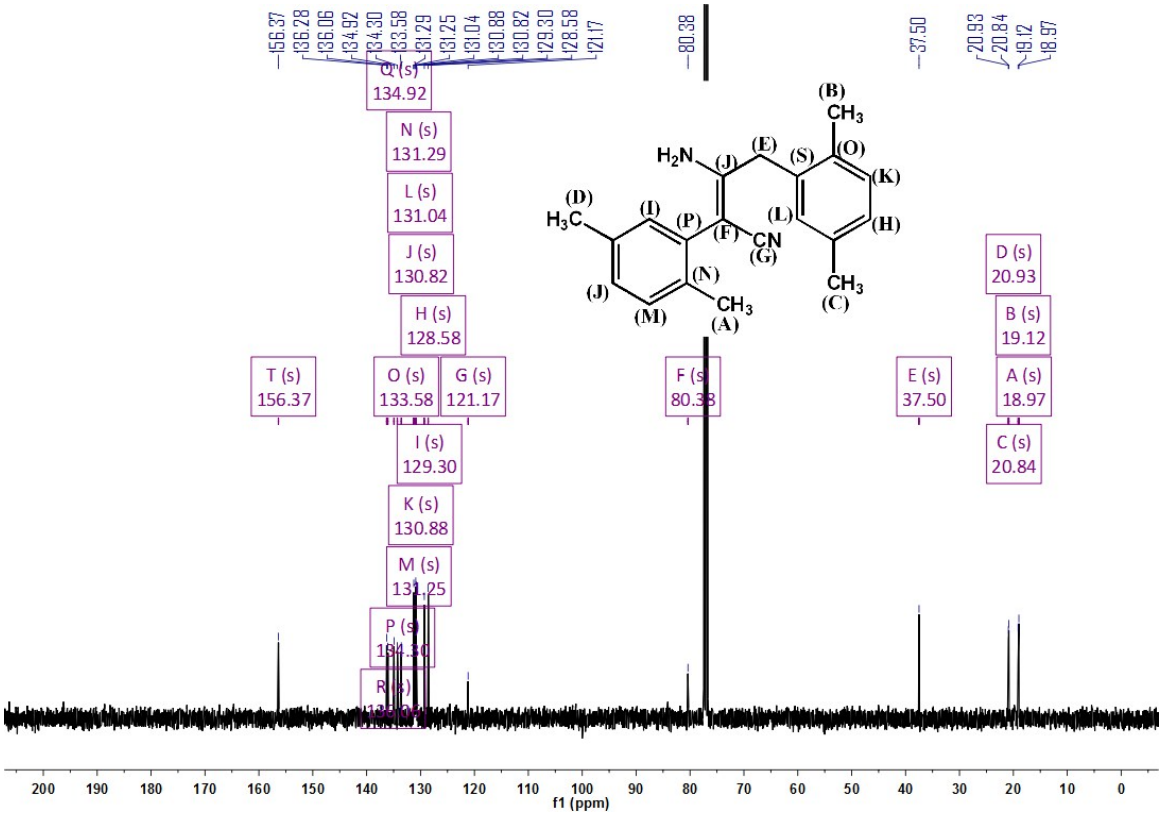
Compound **2n**


H2N
CN
(B)
H
(F)
H
(C)
H2N
(A)
CH3
CN
H
(E)
H
(D)
H
(E)
CH3
(A)
E (s)
6.94
D (s)
6.89
F (s)
7.04
C (s)
4.54
B (s)
3.85
A (d)
2.32
1.84
3.02
1.02
1.66
1.91
12.00
f1 (ppm)
156.67
139.06
138.86
135.82
133.37
129.34
129.11
126.99
126.37
122.24
82.04
77.48
76.84
40.37
21.43
21.41
H2N
(M)
(B)
(J)
(F)
(K)
(A)
(A)
(L)
(E)
(I)
(C)
CN
(D)
(G)
(H)
I (s)
133.37
G (s)
129.11
K (s)
138.86
E (s)
126.37
M (s)
156.67
J (s)
135.82
D (s)
122.24
C (s)
82.04
B (s)
40.37
A (d)
21.42
L (s)
139.06
F (s)
126.99
H (s)
129.34
f1 (ppm)

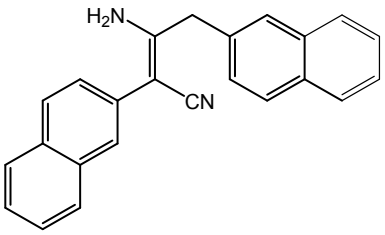
Compound **2o**

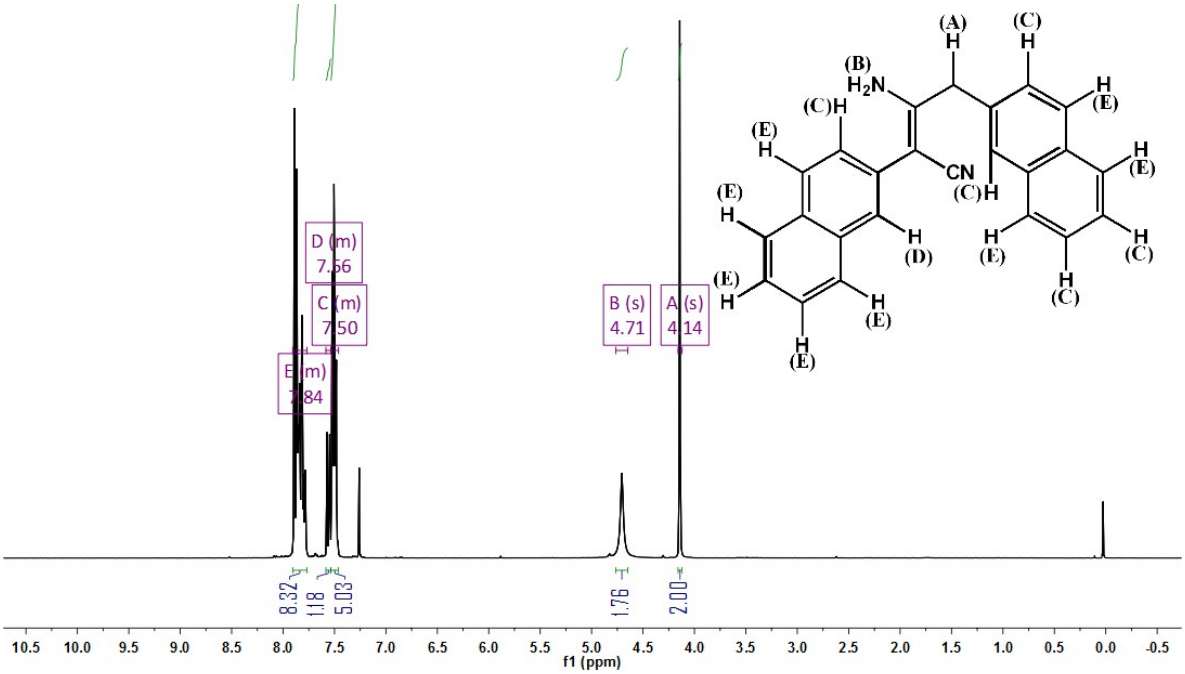

H2N
CN

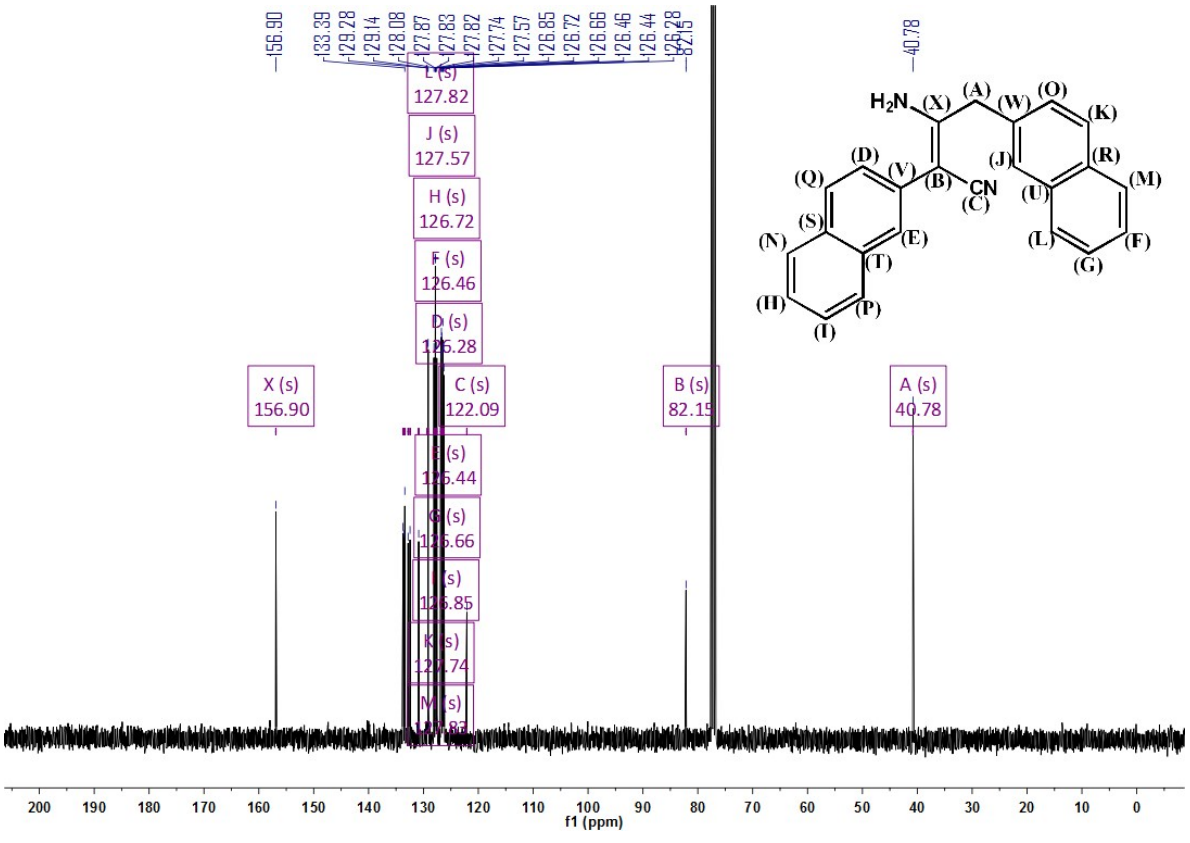

(D) H
(B) CH3
(E) H2N
(G) H
(F) H
H3C (A)
CN
H (F)
H (F)
CH3 (A)
H (F)
CH3 (C)
H (H)
G (d) 7.11
F (m) 7.05
H (d) 7.15
E (s) 4.10
D (s) 3.96
B (s) 2.33
A (s) 2.30
C (s) 2.27
1.02
1.04
4.03
1.78
2.05
3.04
3.05
6.00
f1 (ppm)


156.37
136.28
136.06
134.92
134.30
133.58
131.29
131.25
131.04
130.88
130.82
129.30
128.58
121.17
80.38
37.50
20.93
20.84
19.12
18.97
(B) CH3
H2N
(E)
(S)
(O)
(K)
(J)
(D) H3C
(I)
(P)
(F)
(L)
(H)
CN (G)
(N)
(J)
(M)
CH3 (A)
CH3 (C)
C (s) 134.92
N (s) 131.29
L (s) 131.04
J (s) 130.82
H (s) 128.58
T (s) 156.37
O (s) 133.58
G (s) 121.17
I (s) 129.30
K (s) 130.88
M (s) 131.25
P (s) 134.30
F (s) 80.38
E (s) 37.50
D (s) 20.93
B (s) 19.12
A (s) 18.97
C (s) 20.84
f1 (ppm)

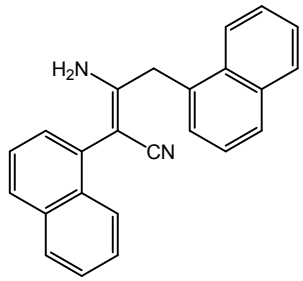
Compound **2p**

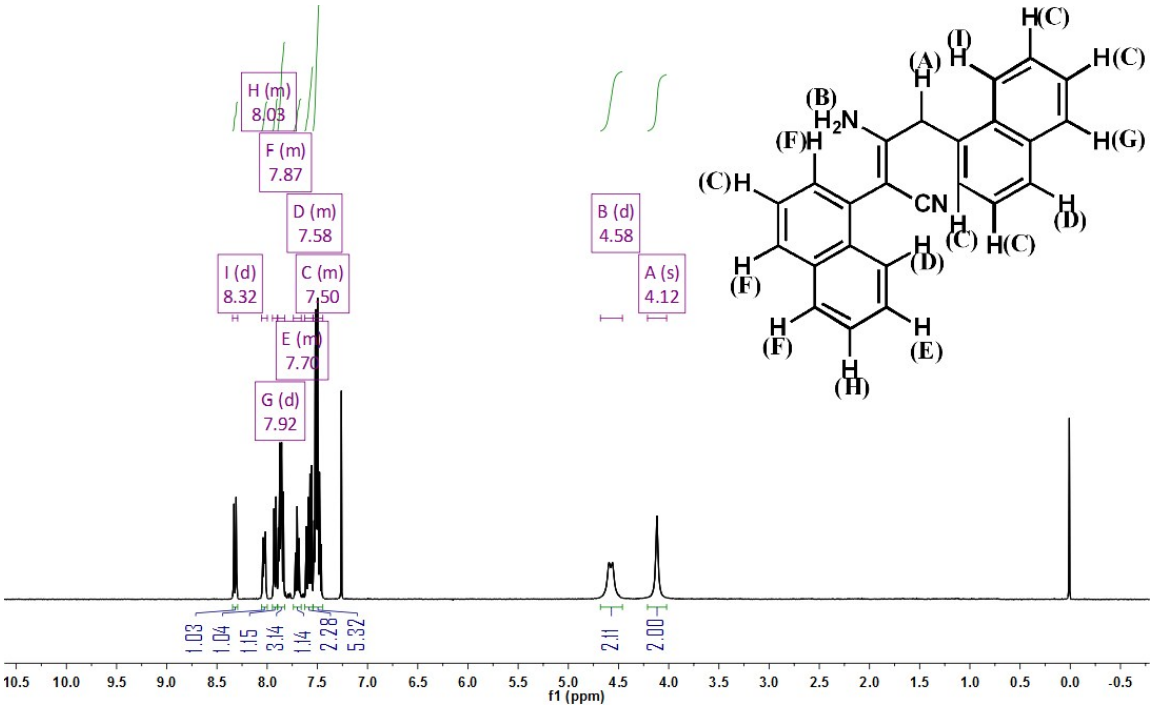

H2N
CN

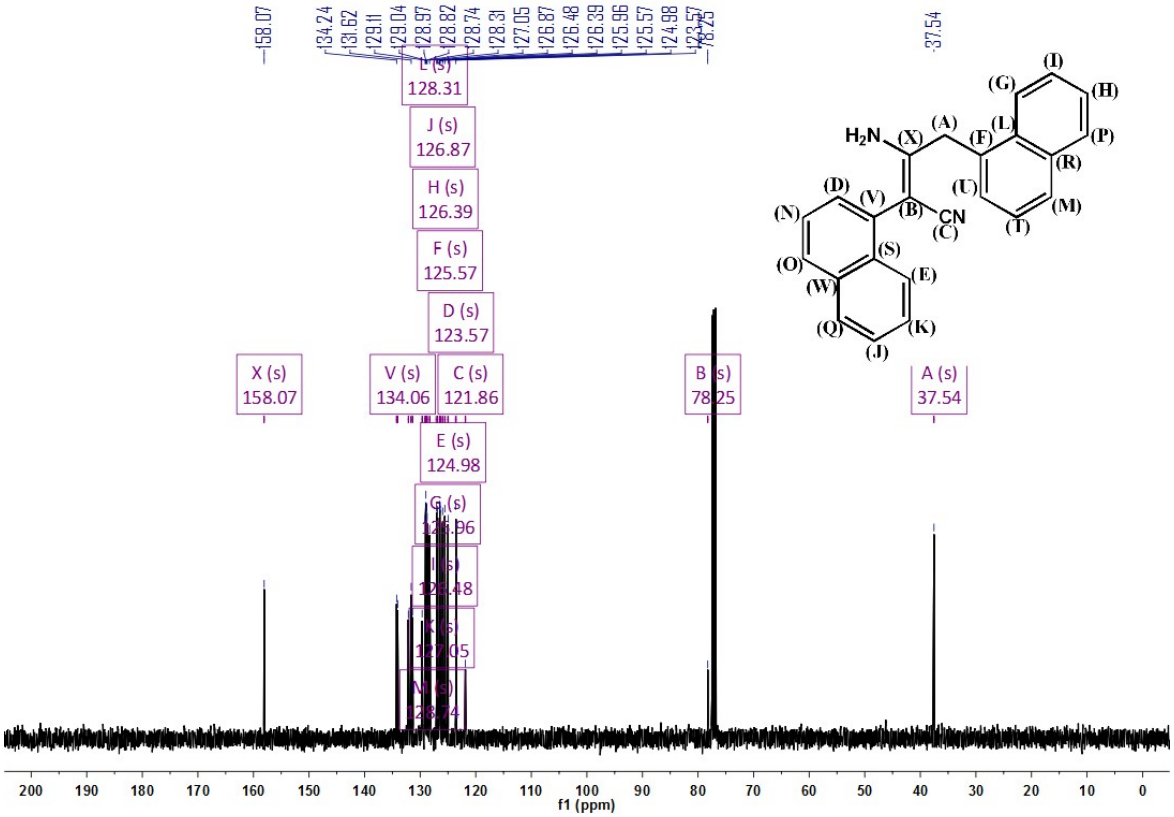

D (m)
7.66
C (m)
7.50
B (s)
4.71
A (s)
4.14
8.32
1.18
5.03
1.76
2.00
f1 (ppm)


L (s)
127.82
J (s)
127.57
H (s)
126.72
F (s)
126.46
X (s)
156.90
C (s)
122.09
B (s)
82.15
A (s)
40.78
f1 (ppm)

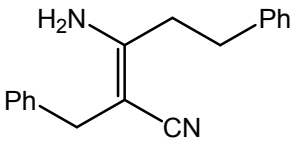
Compound **2q**

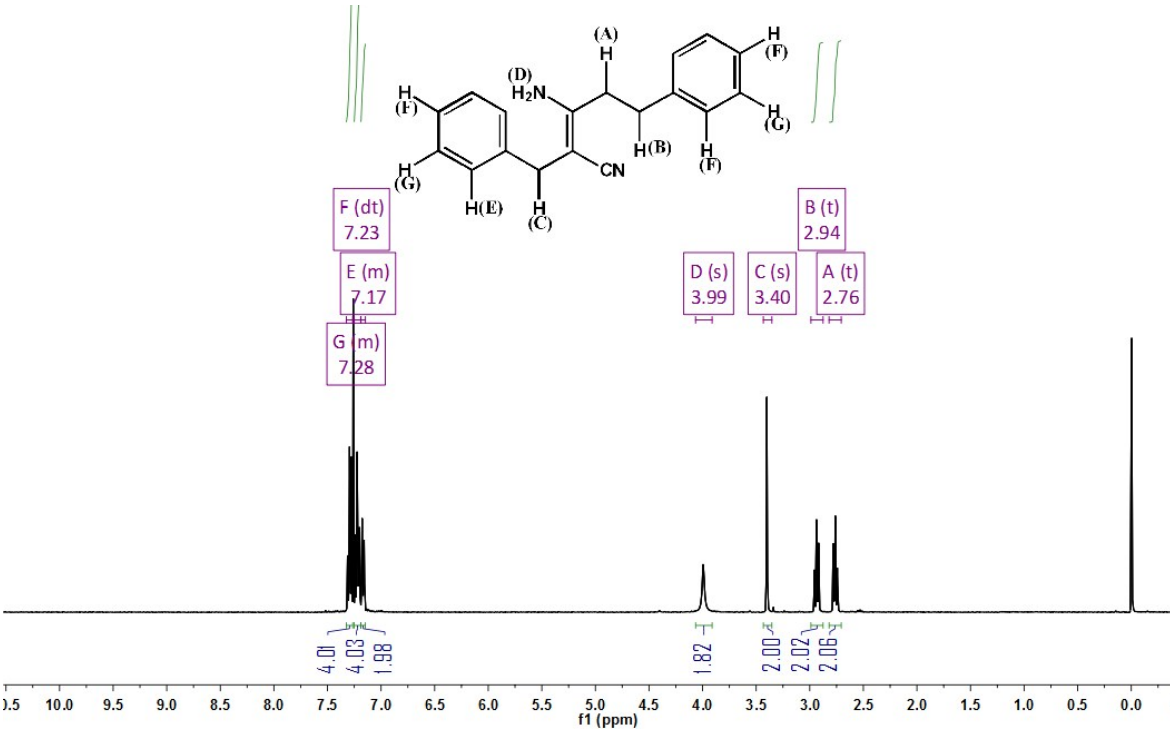

H2N
CN

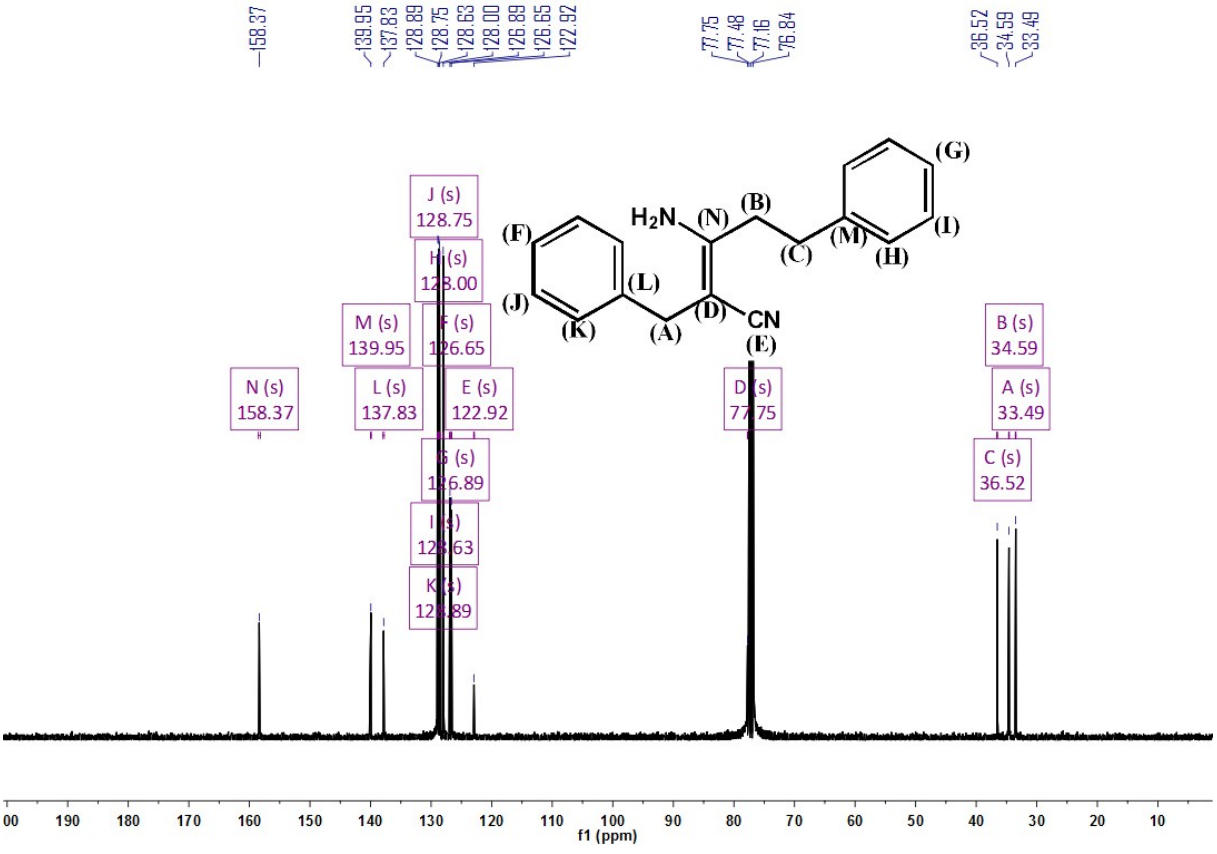

H (m)
8.03
F (m)
7.87
D (m)
7.58
I (d)
8.32
C (m)
7.50
E (m)
7.70
G (d)
7.92
B (d)
4.58
A (s)
4.12
1.03
1.04
1.15
3.14
1.14
2.28
5.32
2.11
2.00
f1 (ppm)


158.07
134.24
131.62
129.11
129.04
128.97
128.82
128.74
128.31
127.05
126.87
126.48
126.39
125.96
125.57
124.98
123.57
78.25
37.54
L (s)
128.31
J (s)
126.87
H (s)
126.39
F (s)
125.57
D (s)
123.57
X (s)
158.07
V (s)
134.06
C (s)
121.86
E (s)
124.98
B (s)
78.25
A (s)
37.54
f1 (ppm)

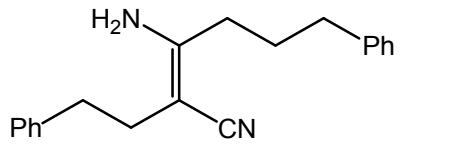
Compound **2r**

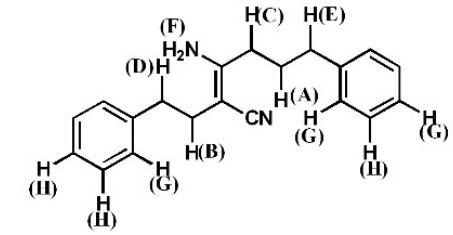

H2N
Ph
Ph
CN

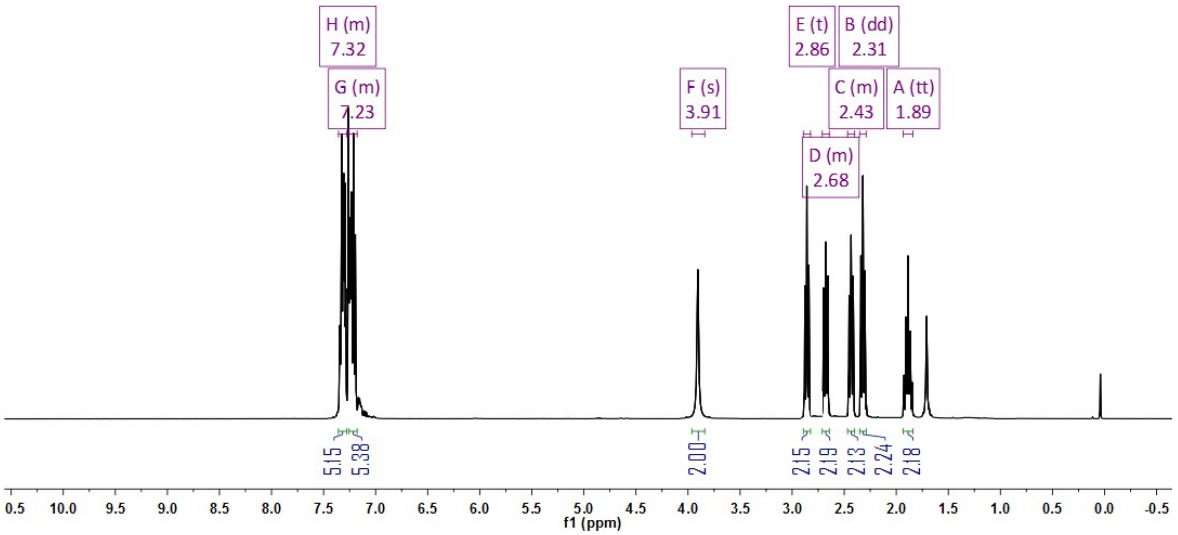

F (dt) 7.23
E (m) 7.17
G (m) 7.28
D (s) 3.99
C (s) 3.40
B (t) 2.94
A (t) 2.76
4.01
4.03
1.98
1.82
2.00
2.02
2.06
f1 (ppm)

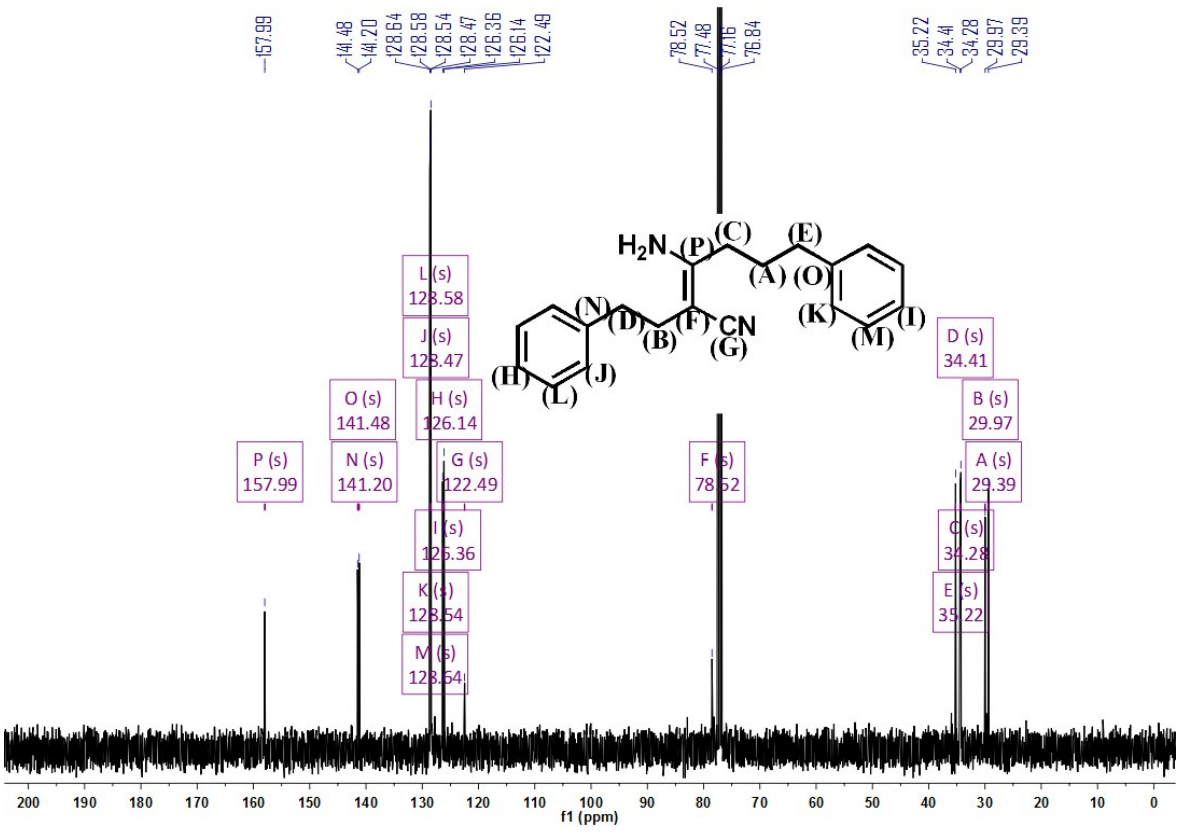

158.37
139.95
137.83
128.89
128.75
128.63
128.00
126.89
126.65
122.92
77.75
77.48
77.16
76.84
36.52
34.59
33.49
J (s) 128.75
M (s) 139.95
F (s) 126.65
N (s) 158.37
L (s) 137.83
E (s) 122.92
D (s) 77.75
B (s) 34.59
A (s) 33.49
C (s) 36.52
f1 (ppm)

Compound **2s**

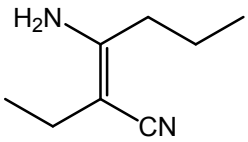

H2N
Ph
Ph
CN

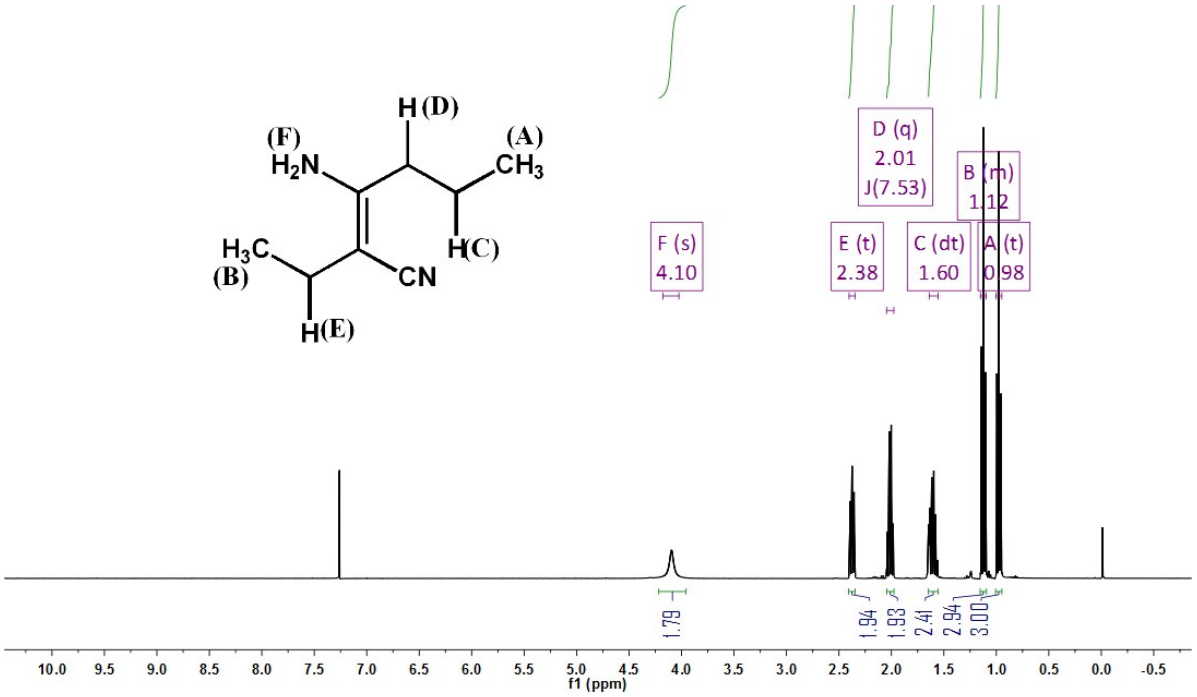

(F)
H2N
(D)H
H(C)
H(E)
H(A)
CN
H(B)
(G)
(G)
(H)
(G)
(H)
(H)

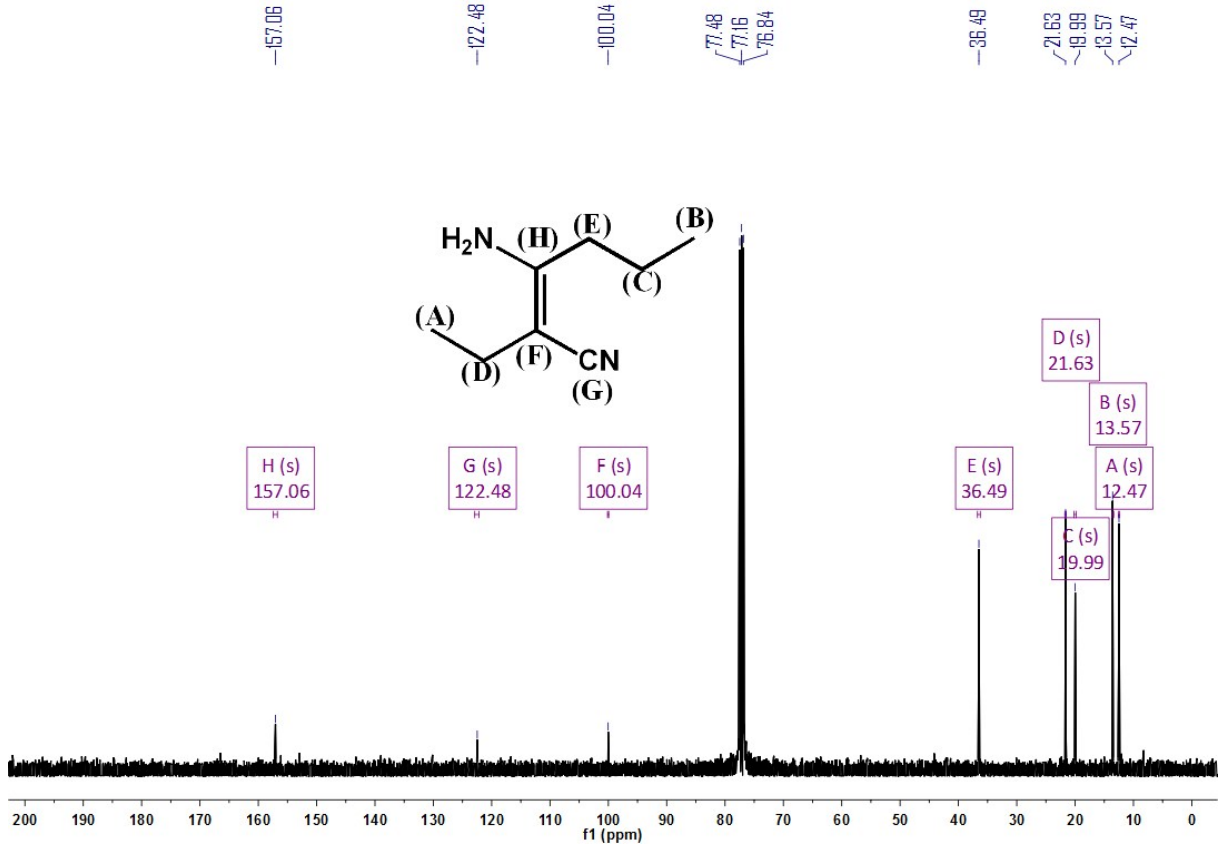

H (m)
7.32
G (m)
7.23
F (s)
3.91
E (t)
2.86
B (dd)
2.31
C (m)
2.43
A (tt)
1.89
D (m)
2.68
5.15
5.38
2.00
2.15
2.19
2.13
2.24
2.18
f1 (ppm)


157.99
141.48
141.20
128.64
128.58
128.54
128.47
126.36
126.14
122.49
78.52
77.48
77.16
76.84
35.22
34.41
34.28
29.97
29.39
H2N
(P)
(C)
(E)
(A)
(O)
(N)
(D)
(B)
(F)
CN
(G)
(K)
(I)
(M)
(H)
(J)
(L)
L (s)
128.58
J (s)
128.47
O (s)
141.48
H (s)
126.14
P (s)
157.99
N (s)
141.20
G (s)
122.49
F (s)
78.52
D (s)
34.41
B (s)
29.97
A (s)
29.39
I (s)
126.36
C (s)
34.28
K (s)
128.54
E (s)
35.22
M (s)
128.54
f1 (ppm)

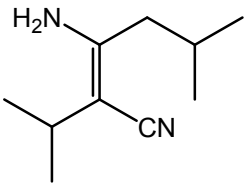
Compound **2t**

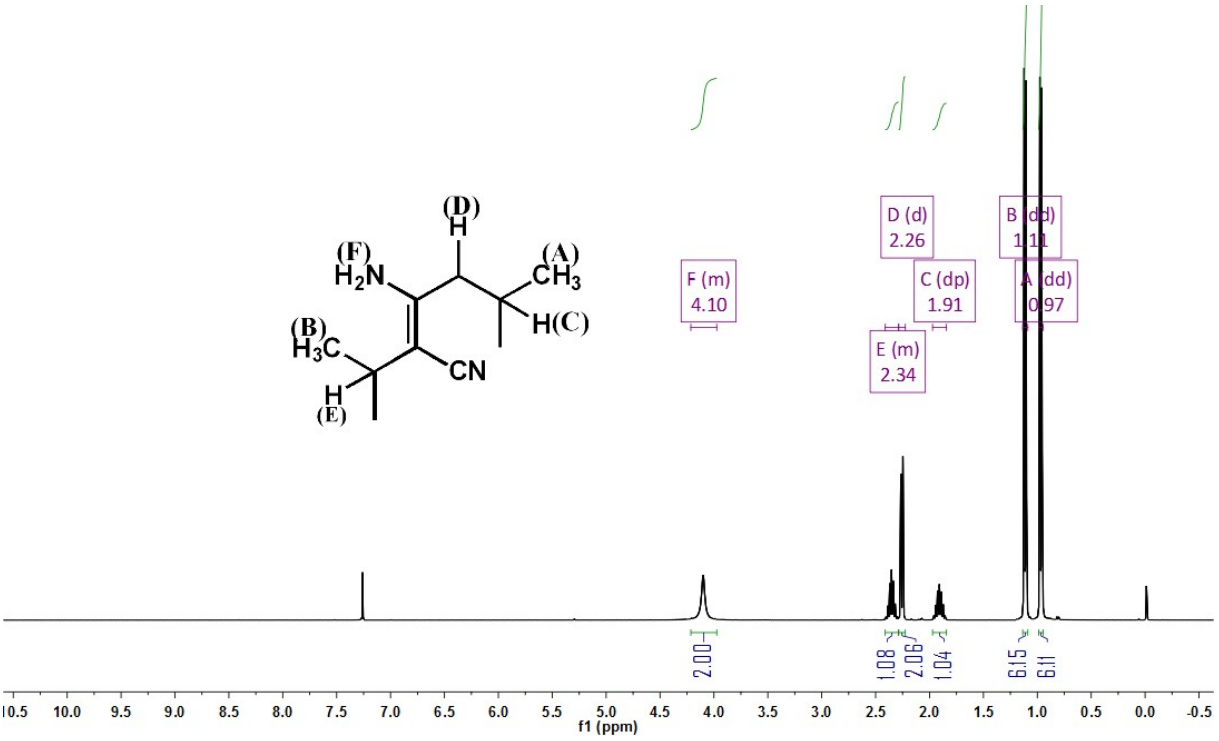

H2N
CN

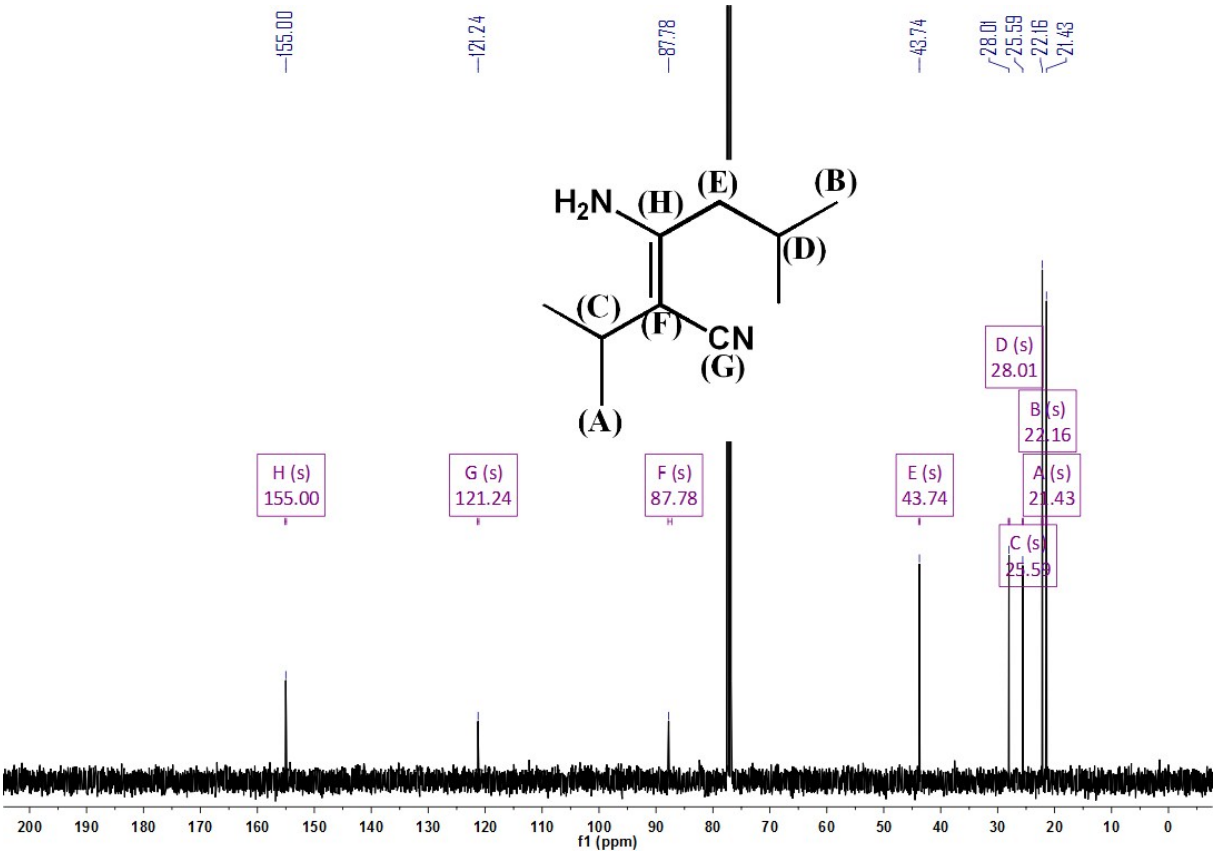

H (D)
(F)
H2N
(A)
CH3
H3C
(B)
H(C)
CN
H(E)
F (s)
4.10
D (q)
2.01
J(7.53)
E (t)
2.38
C (dt)
1.60
B (m)
1.12
A (t)
0.98
1.79
1.94
1.93
2.41
2.94
3.00
f1 (ppm)


157.06
122.48
100.04
77.48
77.16
76.84
36.49
21.63
19.99
13.57
12.47
H2N
(H)
(E)
(B)
(C)
(A)
(D)
(F)
CN
(G)
H (s)
157.06
G (s)
122.48
F (s)
100.04
E (s)
36.49
D (s)
21.63
B (s)
13.57
A (s)
12.47
C (s)
19.99
f1 (ppm)

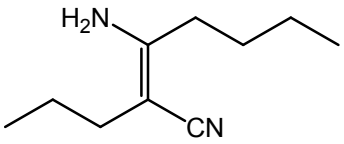
Compound **2u**

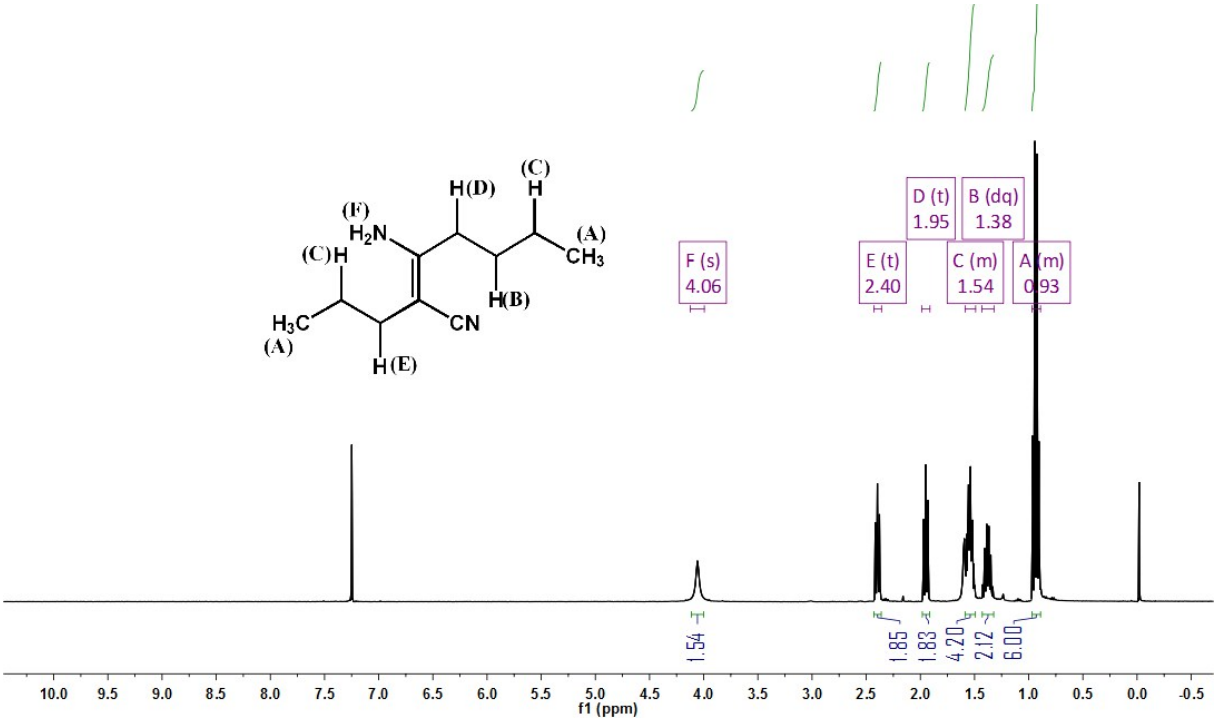

H2N
CN

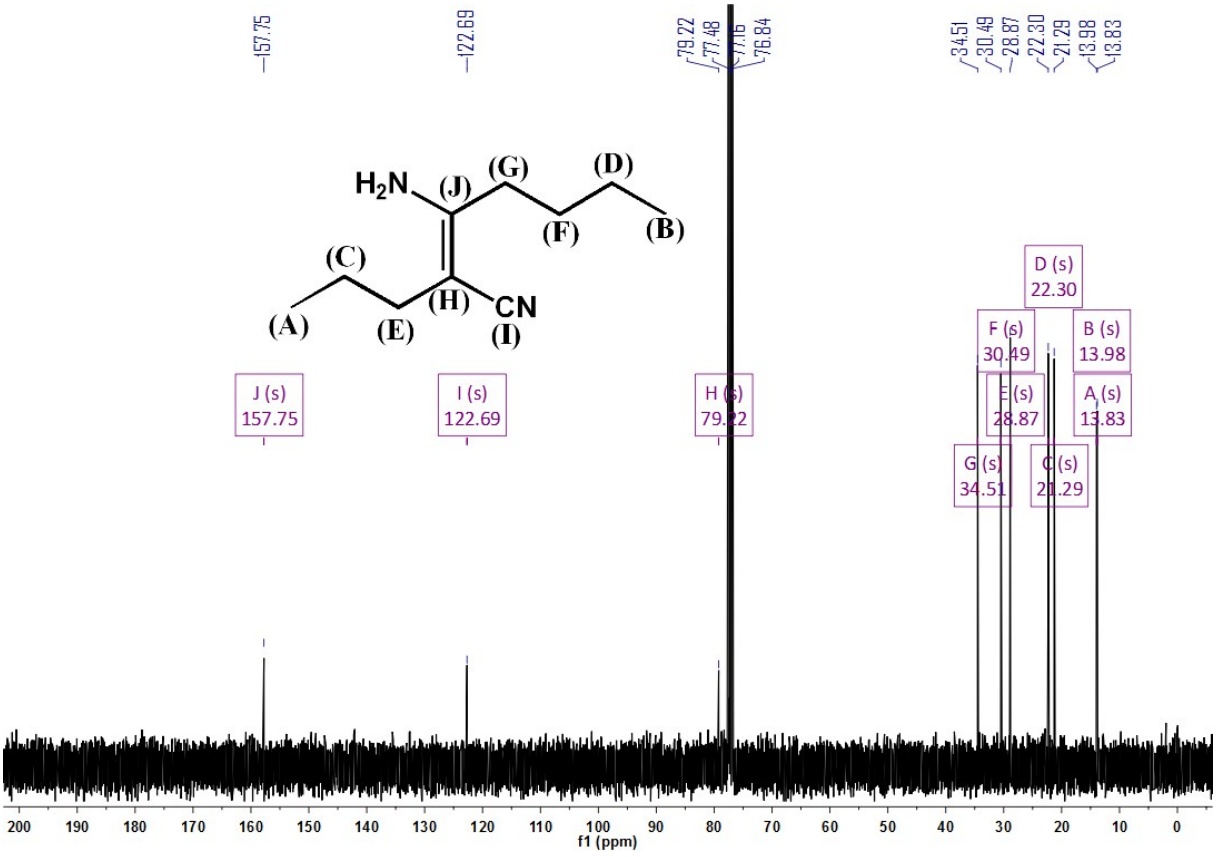

(D)
H
(F)
H2N
(A)
CH3
(B)
H3C
H(C)
CN
H
(E)
F (m)
4.10
D (d)
2.26
C (dp)
1.91
E (m)
2.34
B (dd)
1.11
A (dd)
0.97
2.00
1.08
2.06
1.04
6.15
6.11
f1 (ppm)


155.00
121.24
87.78
43.74
28.01
25.59
22.16
21.43
H2N
(H)
(E)
(B)
(D)
(C)
(F)
CN
(G)
(A)
D (s)
28.01
B (s)
22.16
H (s)
155.00
G (s)
121.24
F (s)
87.78
E (s)
43.74
A (s)
21.43
C (s)
25.59
f1 (ppm)

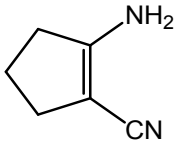
Compound **2v**

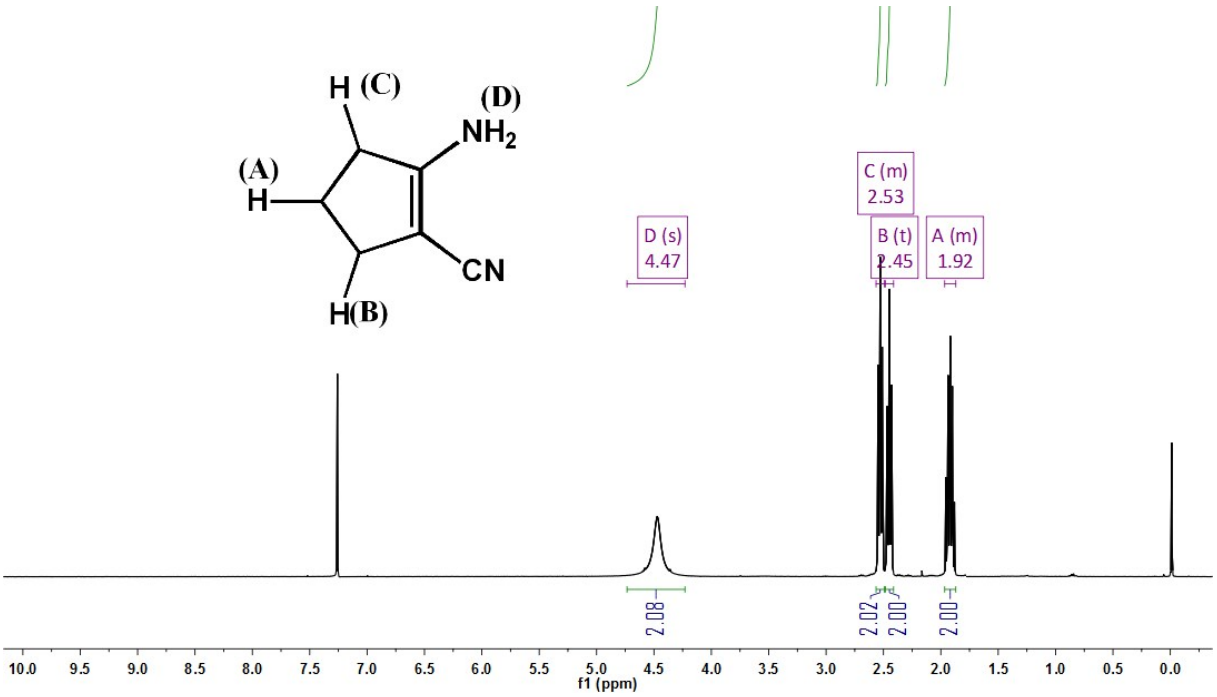

H2N
CN

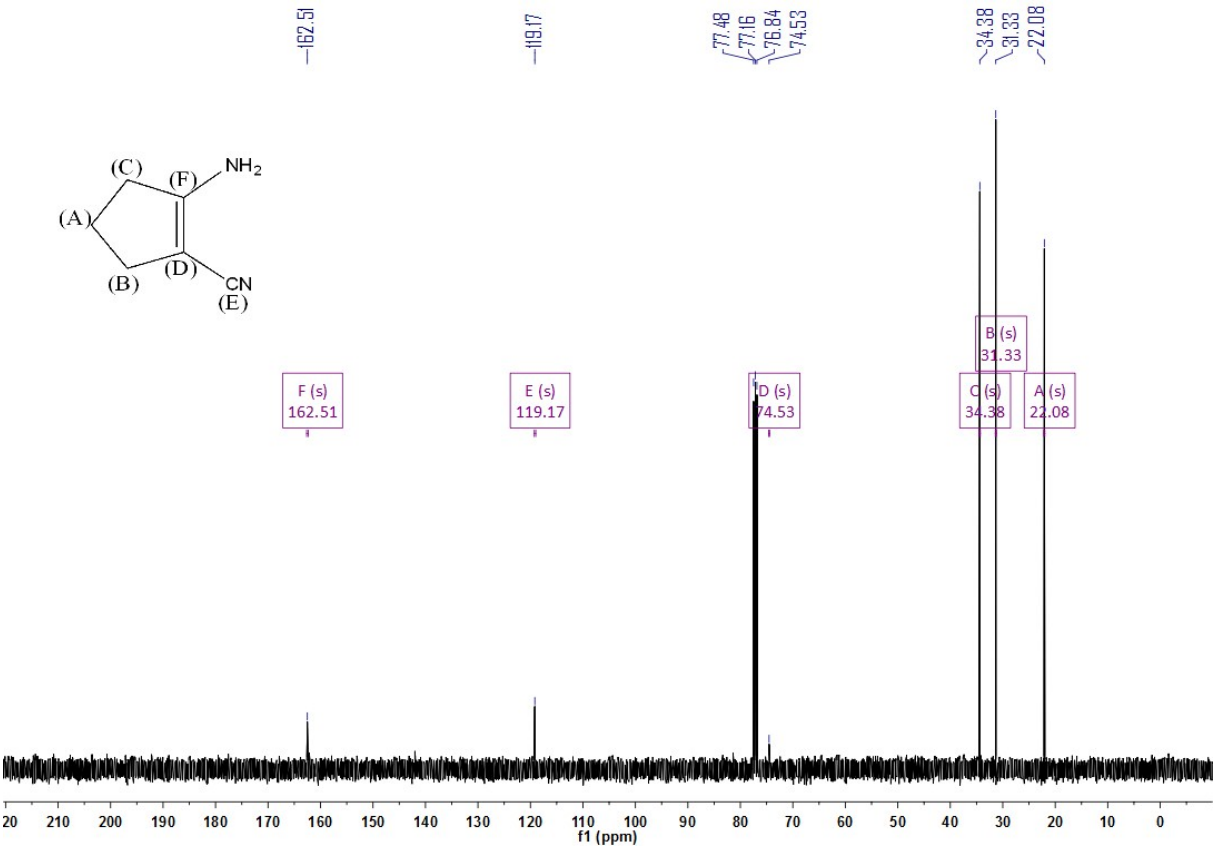

(C)
H(D)
H
(F)
H2N
(A)
CH3
(C)H
H(B)
H3C
CN
(A)
H(E)
F (s)
4.06
D (t)
1.95
B (dq)
1.38
E (t)
2.40
C (m)
1.54
A (m)
0.93
1.54
1.85
1.83
4.20
2.12
6.00
f1 (ppm)


157.75
122.69
79.22
77.48
77.16
76.84
34.51
30.49
28.87
22.30
21.29
13.98
13.83
H2N
(J)
(G)
(D)
(F)
(B)
(C)
(H)
CN
(A)
(E)
(I)
D (s)
22.30
F (s)
30.49
B (s)
13.98
E (s)
28.87
A (s)
13.83
G (s)
34.51
C (s)
21.29
J (s)
157.75
I (s)
122.69
H (s)
79.22
f1 (ppm)

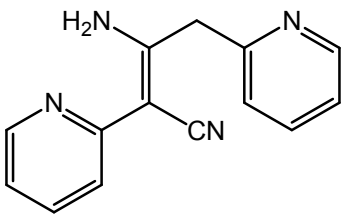
Compound **2w**

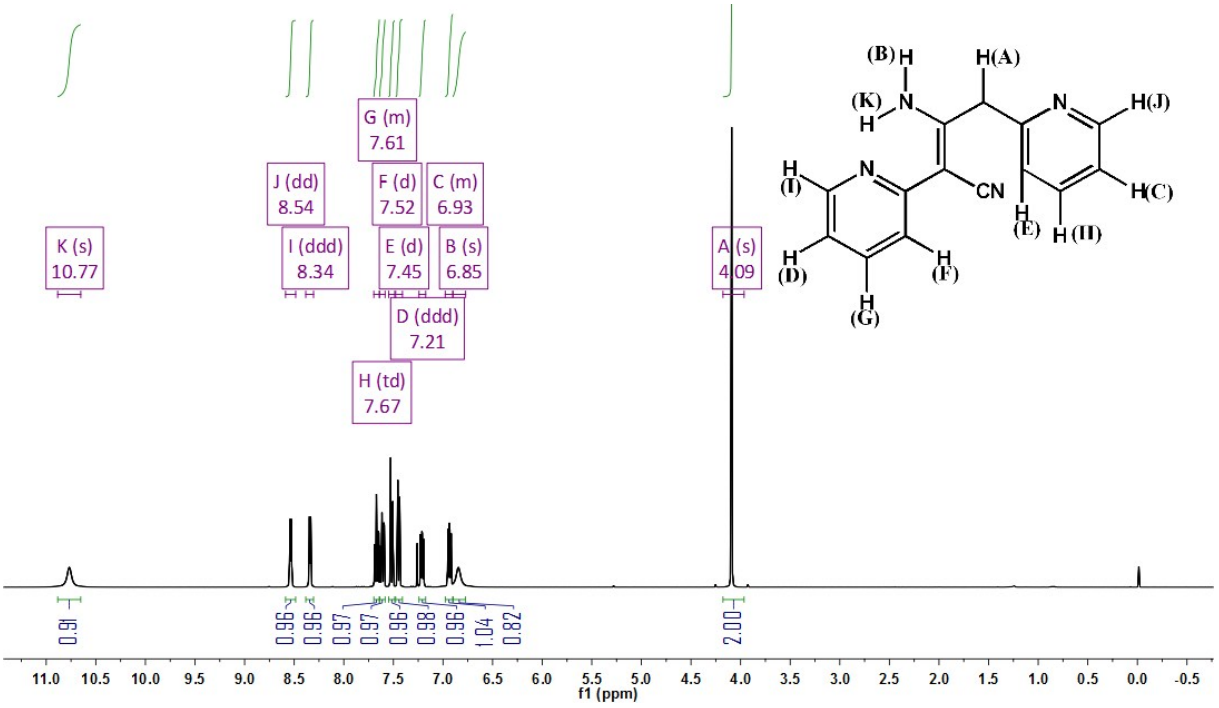

NH2
CN

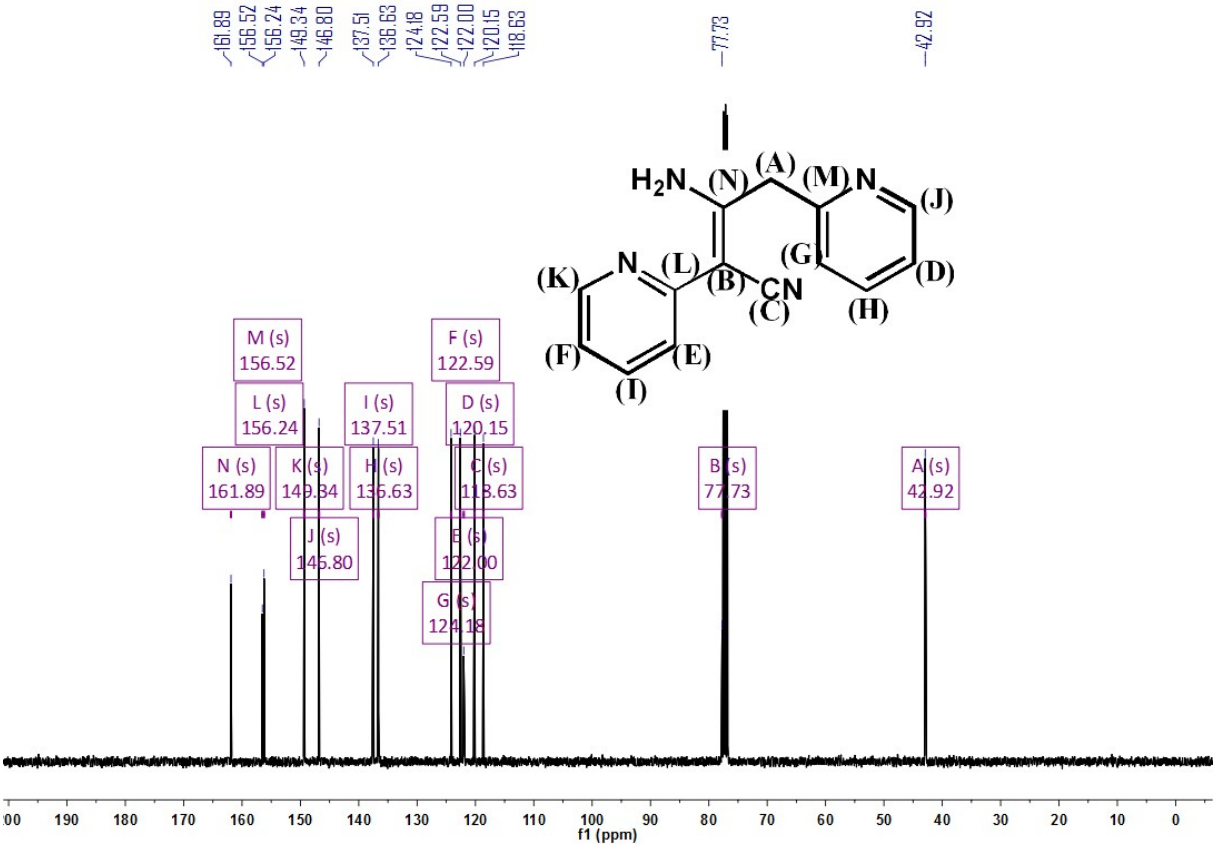

H (C)
(D)
NH2
(A)
H
CN
H(B)
D (s)
4.47
C (m)
2.53
B (t)
2.45
A (m)
1.92
2.08
2.02
2.00
2.00
f1 (ppm)


162.51
119.17
77.48
77.16
76.84
74.53
34.38
31.33
22.08
(C)
(F)
NH2
(A)
(B)
(D)
CN
(E)
F (s)
162.51
E (s)
119.17
D (s)
74.53
B (s)
31.33
C (s)
34.38
A (s)
22.08
f1 (ppm)

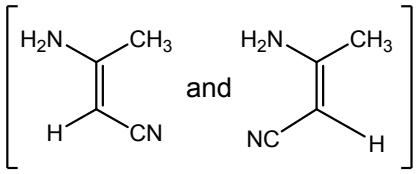
Compound **2x**

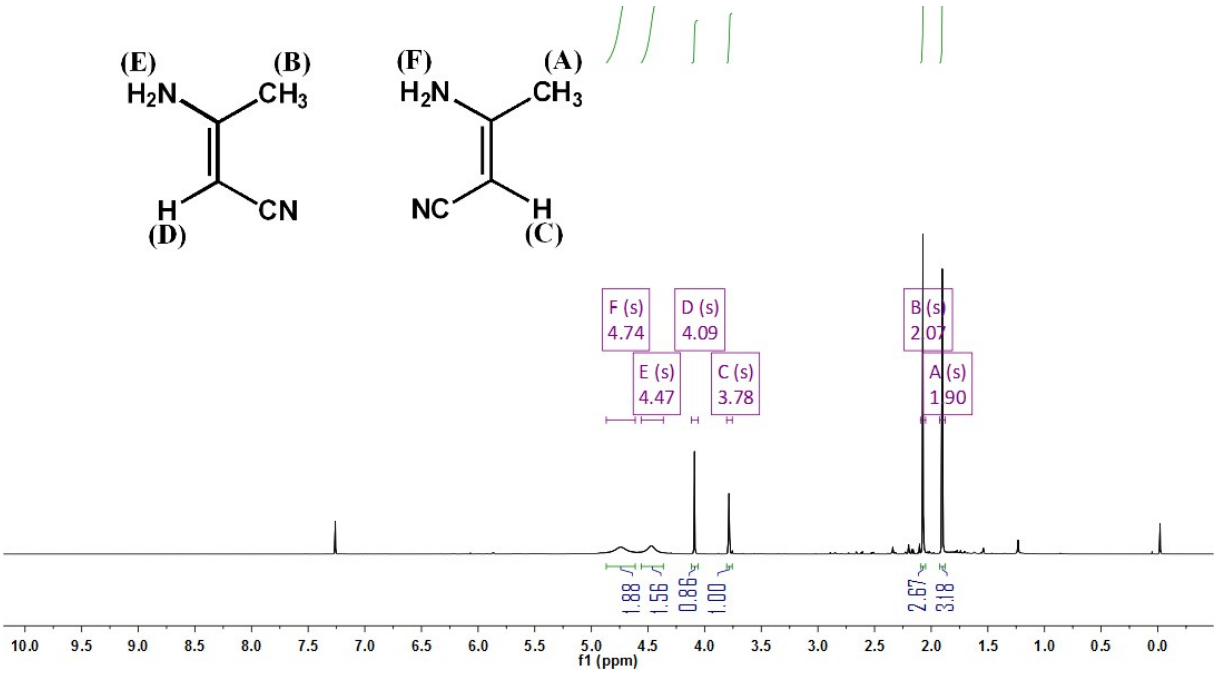

H2N
N
N
CN

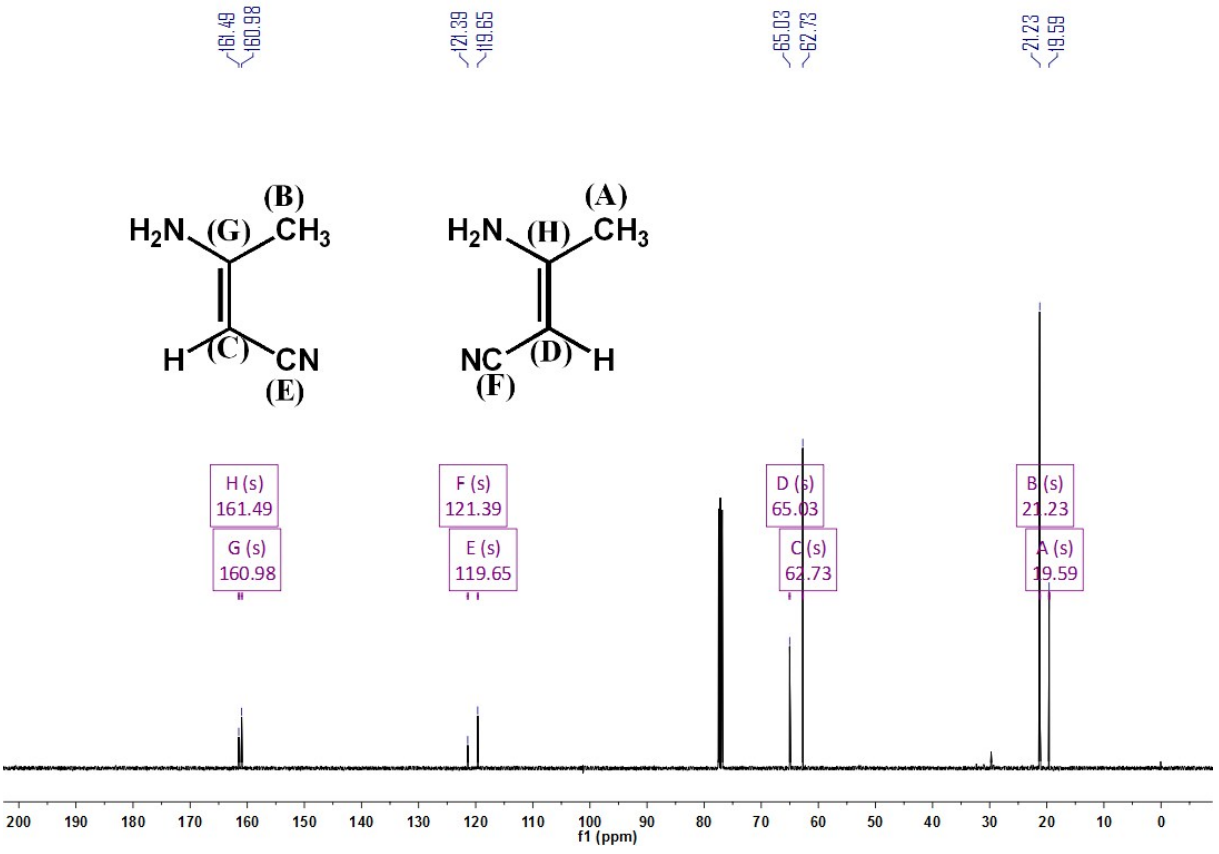

G (m) 7.61
J (dd) 8.54
F (d) 7.52
C (m) 6.93
K (s) 10.77
I (ddd) 8.34
E (d) 7.45
B (s) 6.85
A (s) 4.09
D (ddd) 7.21
H (td) 7.67
(B) H
H(A)
(K) N H
N
H(J)
H (I)
N
CN
H(C)
H (E)
H (II)
H (D)
H (F)
H (G)
0.91
0.96
0.96
0.97
0.97
0.96
0.98
0.96
1.04
0.82
2.00
f1 (ppm)


161.89
156.52
156.24
149.34
146.80
137.51
136.63
124.18
122.59
122.00
120.15
118.63
77.73
42.92
H2N
(N)
(A)
(M)
N
(J)
(K)
N
(L)
(G)
(B)
CN
(C)
(D)
(H)
(F)
(E)
(I)
M (s) 156.52
F (s) 122.59
L (s) 156.24
I (s) 137.51
D (s) 120.15
N (s) 161.89
K (s) 149.34
H (s) 136.63
C (s) 118.63
B (s) 77.73
A (s) 42.92
J (s) 145.80
E (s) 122.00
G (s) 124.18
f1 (ppm)

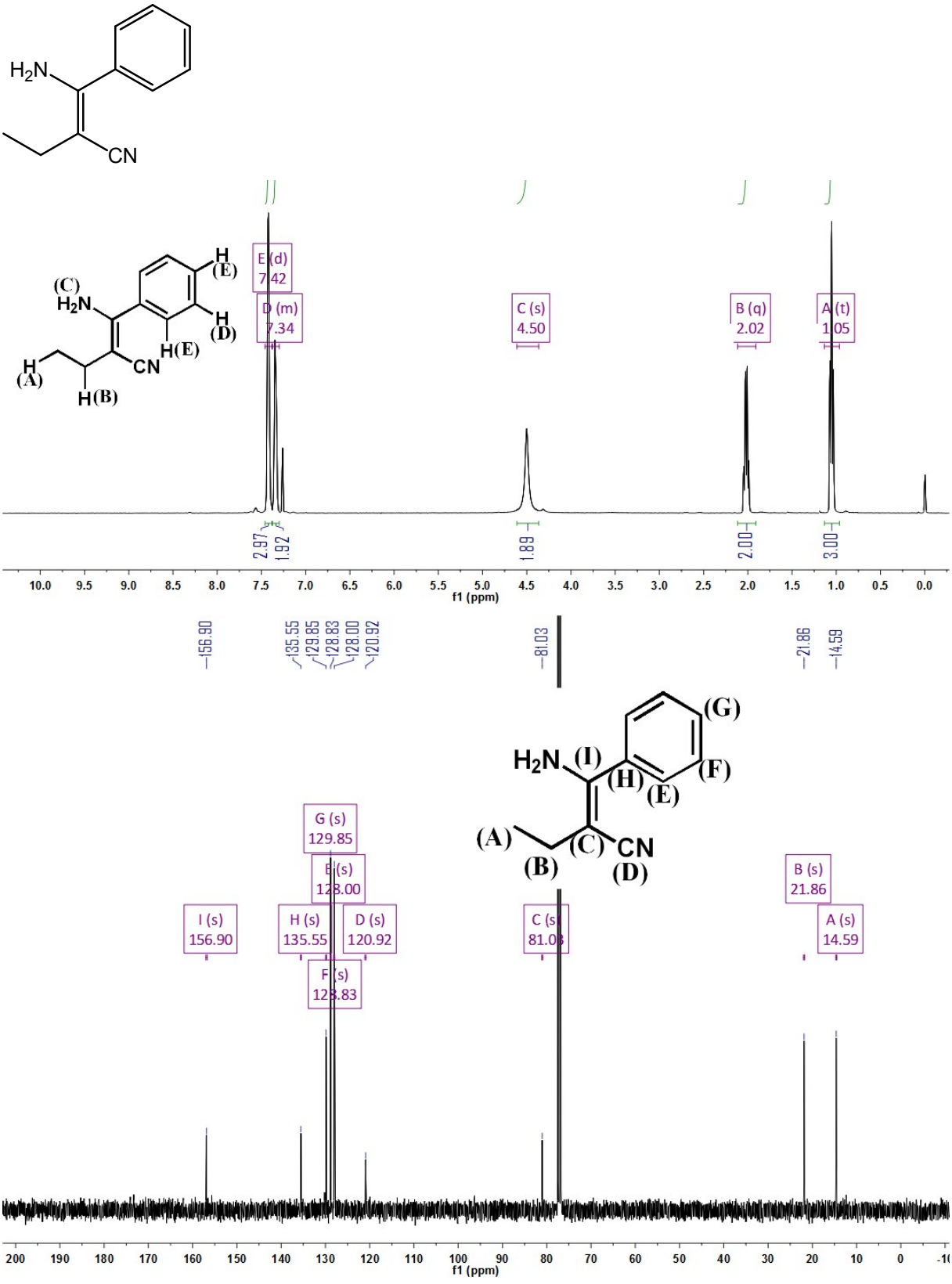
Compound **2y**

a mixture of  and

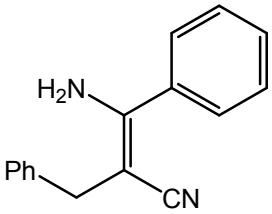


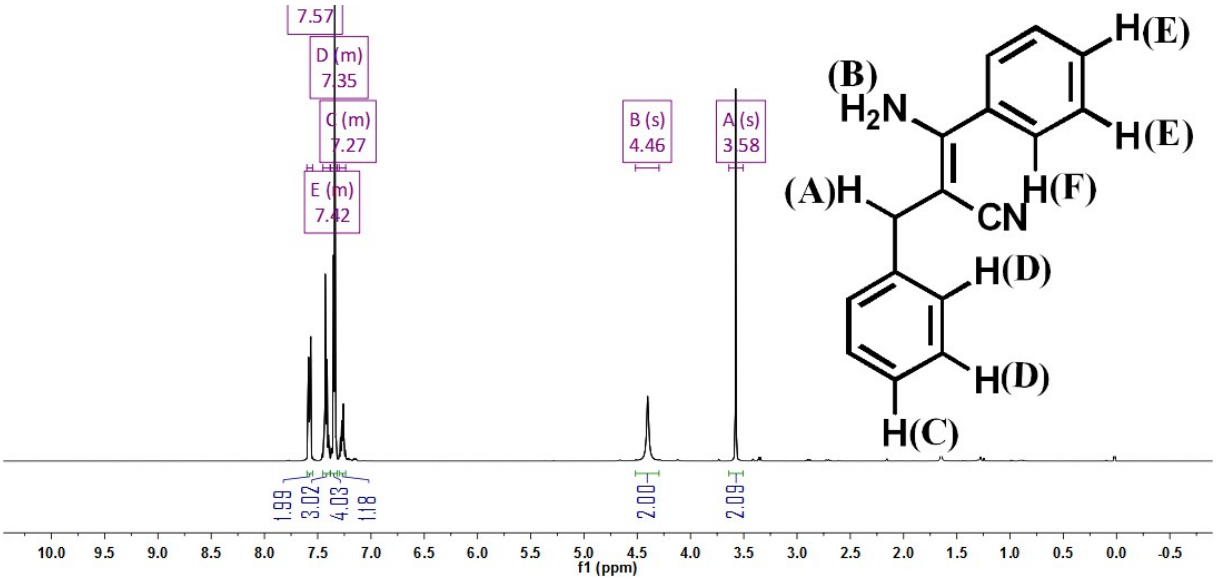


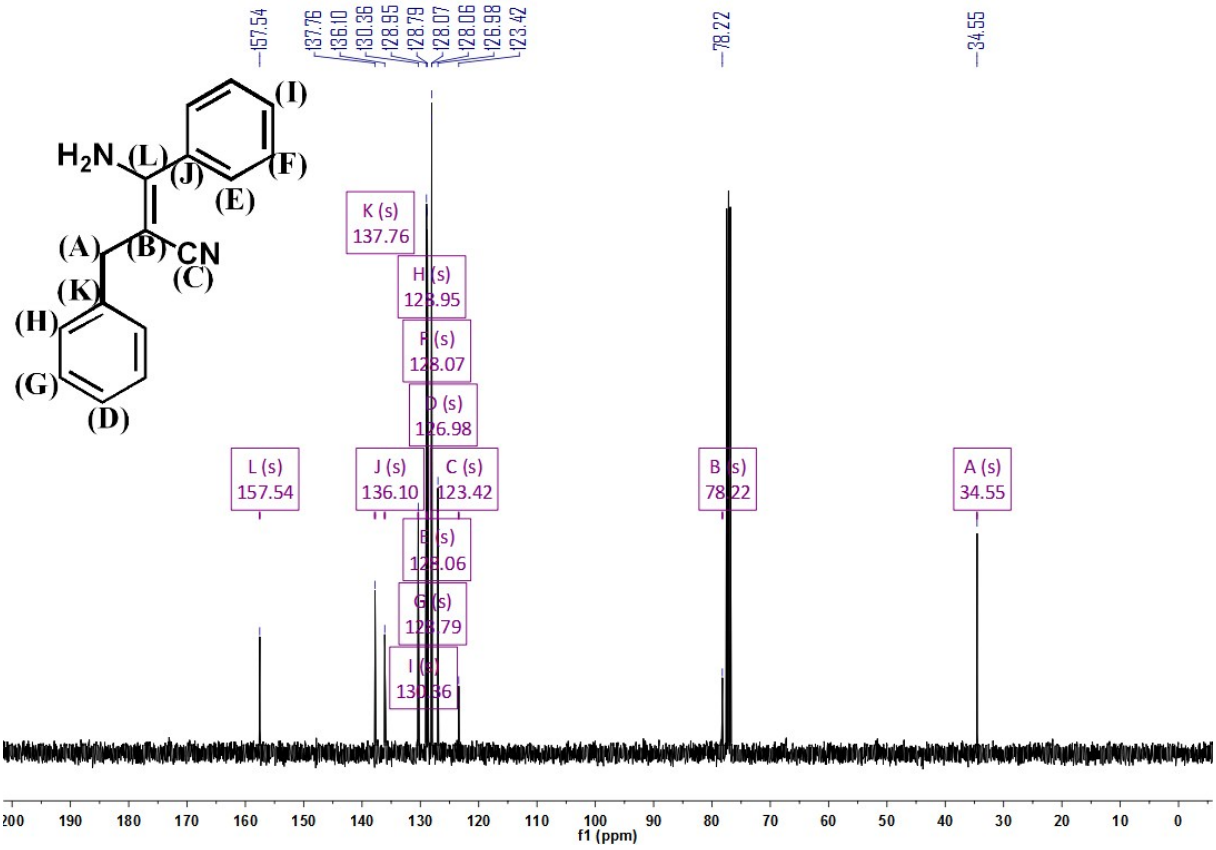
Compound **3a**


H2N
CN
(C)
H2N
H
(E)
H
(D)
H(E)
CN
H
(A)
H(B)
E (d)
7.42
D (m)
7.34
C (s)
4.50
B (q)
2.02
A (t)
1.05
2.97
1.92
1.89
2.00
3.00
f1 (ppm)
156.90
135.55
129.85
128.83
128.00
120.92
81.03
21.86
14.59
(G)
H2N
(I)
(H)
(F)
(E)
(A)
(C)
CN
(B)
(D)
G (s)
129.85
E (s)
128.00
I (s)
156.90
H (s)
135.55
D (s)
120.92
F (s)
128.83
C (s)
81.03
B (s)
21.86
A (s)
14.59
f1 (ppm)

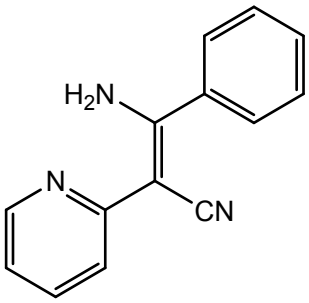
Compound **3b**

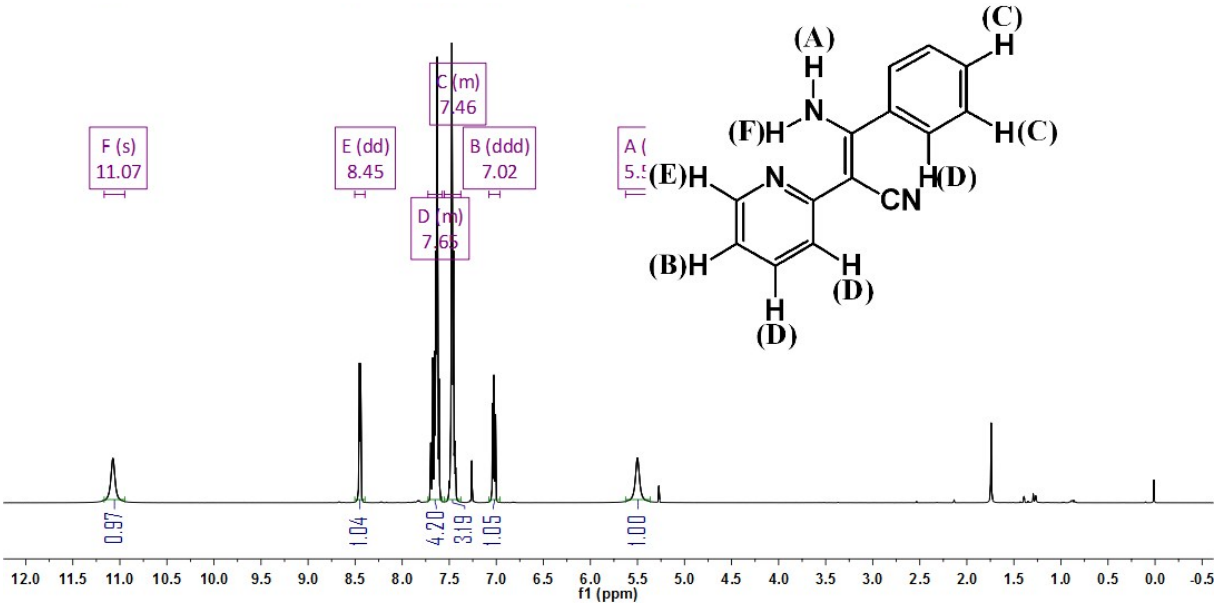

H2N
Ph
CN

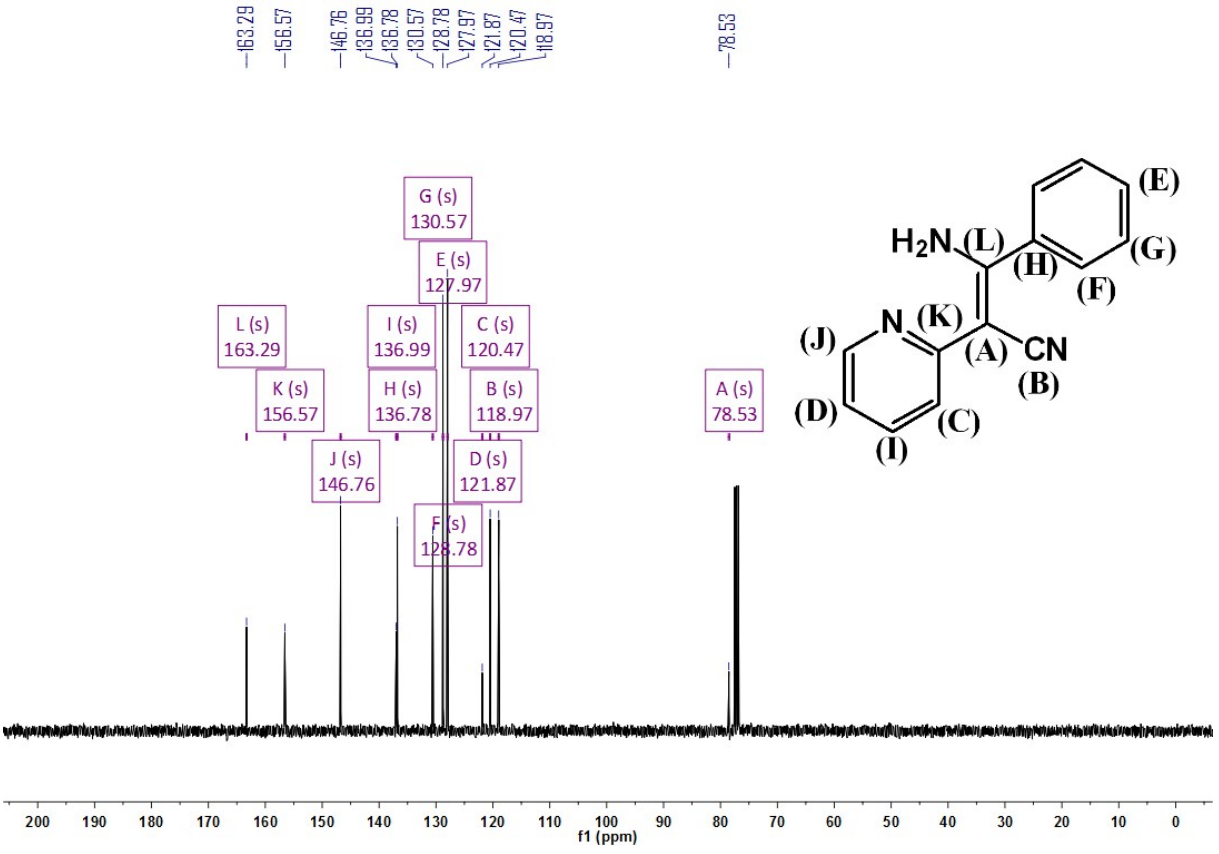

7.57
D (m) 7.35
C (m) 7.27
E (m) 7.42
B (s) 4.46
A (s) 3.58
(B) H2N
H(E)
H(E)
(A)H
CN
H(F)
H(D)
H(D)
H(C)
1.99
3.02
4.03
1.18
2.00
2.09
f1 (ppm)


157.54
137.76
136.10
130.36
128.95
128.79
128.07
126.98
123.42
78.22
34.55
H2N
(I)
(L)
(J)
(F)
(E)
(A)
(B)
CN
(C)
(K)
(H)
(G)
(D)
K (s) 137.76
H (s) 128.95
F (s) 128.07
D (s) 126.98
L (s) 157.54
J (s) 136.10
C (s) 123.42
B (s) 78.22
A (s) 34.55
E (s) 128.06
G (s) 128.79
I (s) 130.36
f1 (ppm)

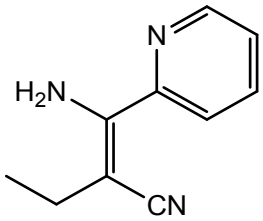
Compound **3c**

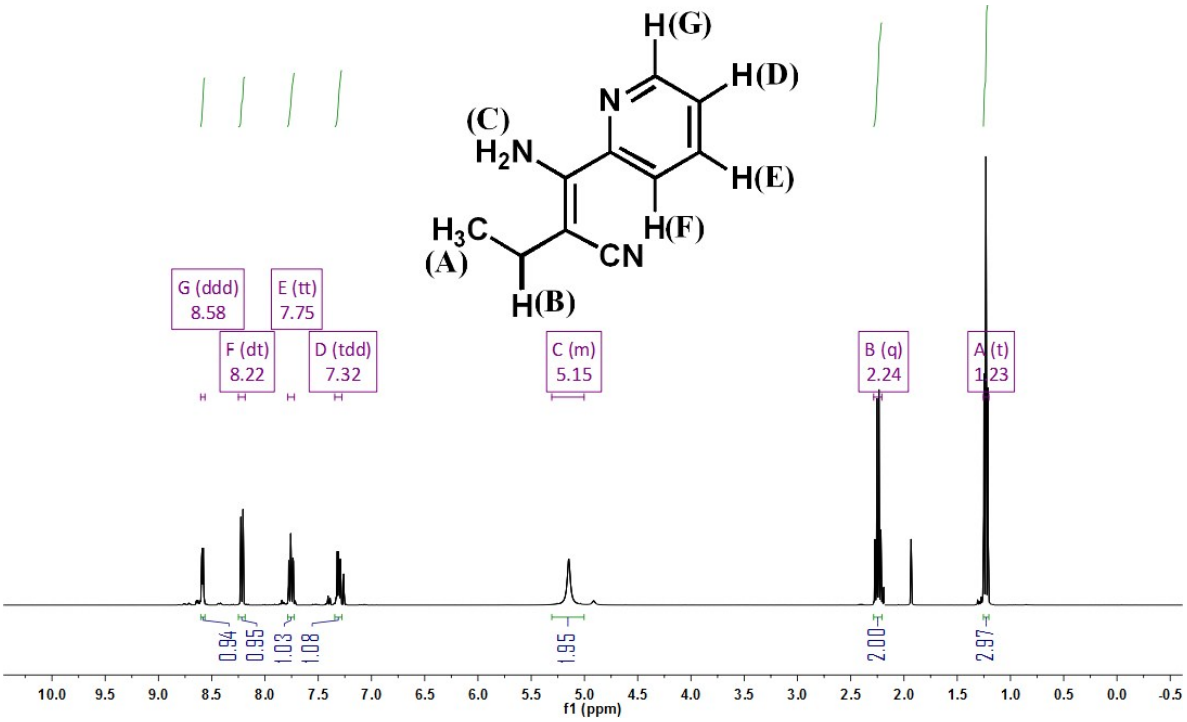

H2N
N
CN

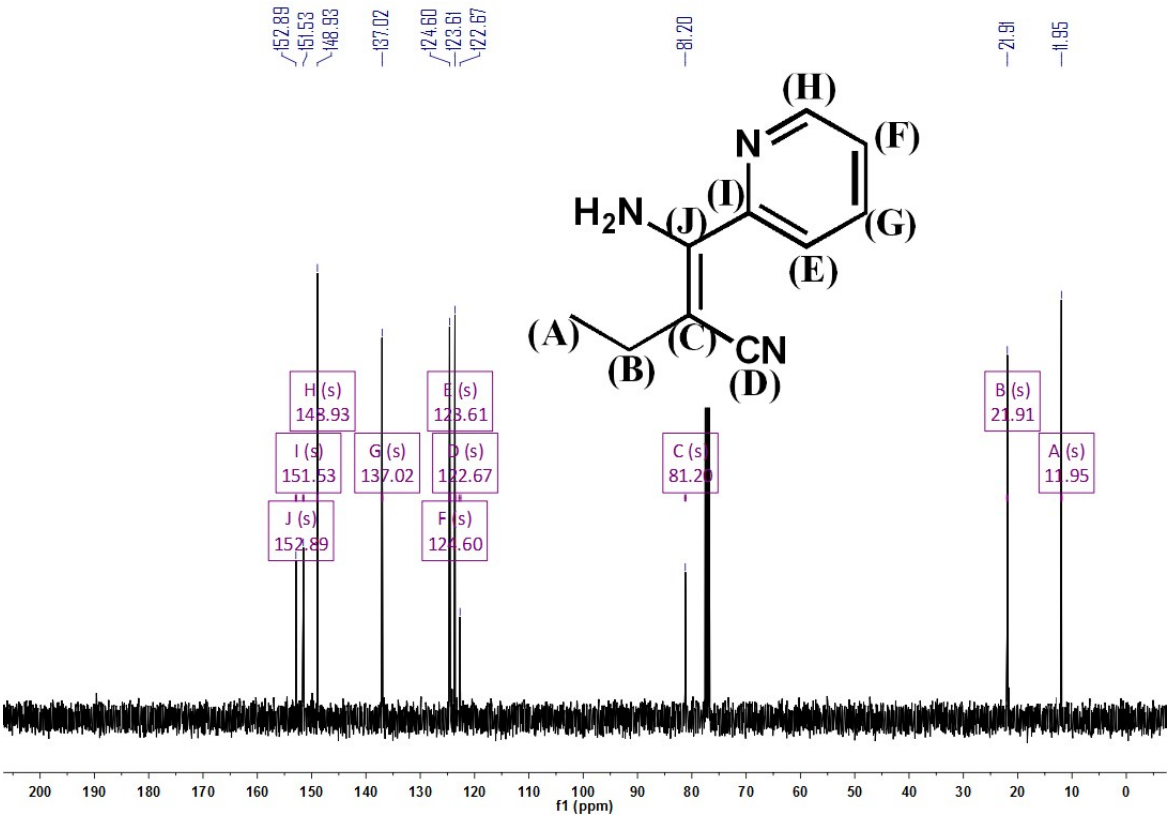

F (s)
11.07
E (dd)
8.45
C (m)
7.46
D (m)
7.66
B (ddd)
7.02
0.97
1.04
4.20
3.19
1.05
1.00
f1 (ppm)
(A)
(C)
(F)H
(E)H
(B)H
(D)
CN


163.29
156.57
146.76
136.99
136.78
130.57
128.78
127.97
121.87
120.47
118.97
78.53
G (s)
130.57
E (s)
127.97
L (s)
163.29
I (s)
136.99
C (s)
120.47
K (s)
156.57
H (s)
136.78
B (s)
118.97
A (s)
78.53
J (s)
146.76
D (s)
121.87
F (s)
128.78
f1 (ppm)
H2N
(L)
(E)
(G)
(H)
(F)
(K)
(J)
(A)
CN
(B)
(D)
(C)
(I)

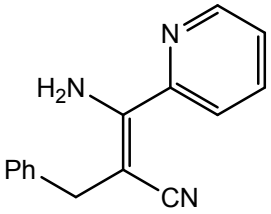
Compound **3d**

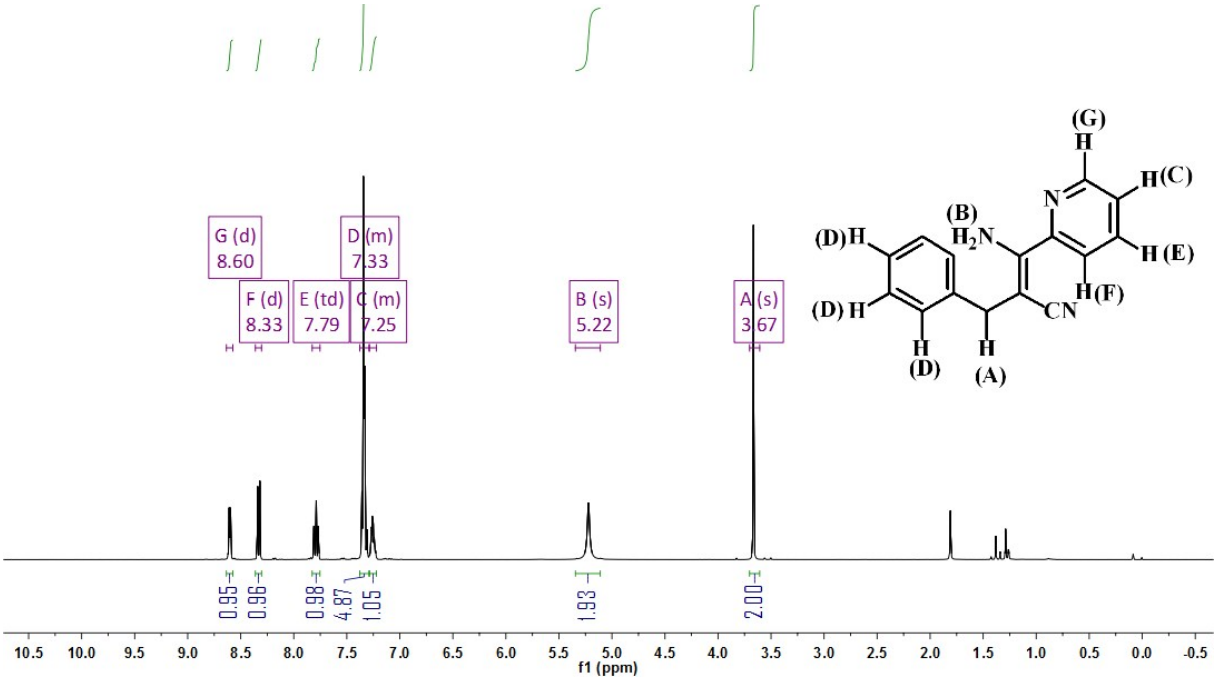

N
H2N
CN

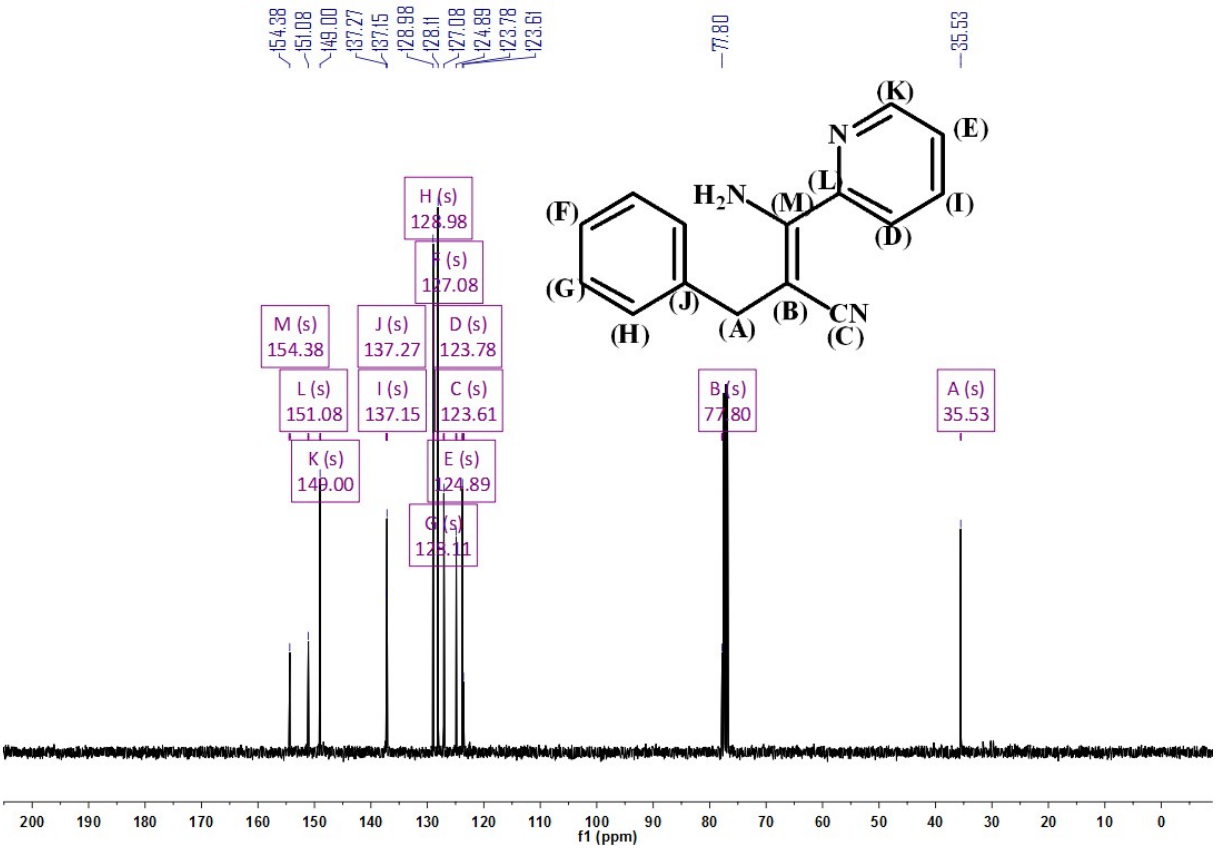

H(G)
H(D)
N
(C)
H2N
H(E)
H3C
(A)
H(F)
CN
H(B)
G (ddd) 8.58
E (tt) 7.75
F (dt) 8.22
D (tdd) 7.32
C (m) 5.15
B (q) 2.24
A (t) 1.23
0.94
0.95
1.03
1.08
1.95
2.00
2.97
f1 (ppm)


152.89
151.53
148.93
137.02
124.60
123.61
122.67
81.20
21.91
11.95
(H)
N
(F)
(I)
H2N
(J)
(G)
(E)
(A)
(C)
CN
(B)
(D)
H (s) 148.93
E (s) 123.61
I (s) 151.53
G (s) 137.02
D (s) 122.67
C (s) 81.20
B (s) 21.91
A (s) 11.95
J (s) 152.89
F (s) 124.60
f1 (ppm)

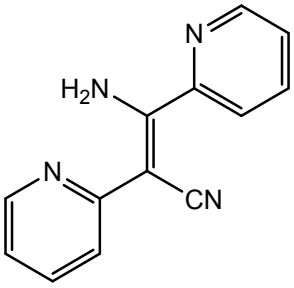
Compound **3e**

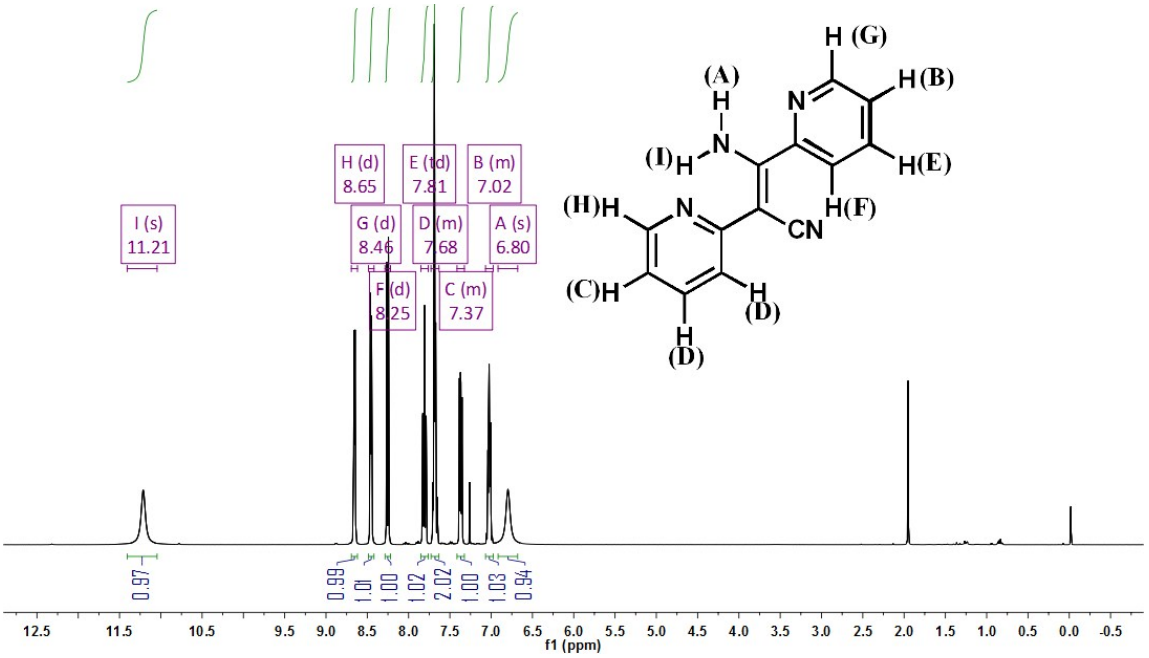

N
H2N
Ph
CN

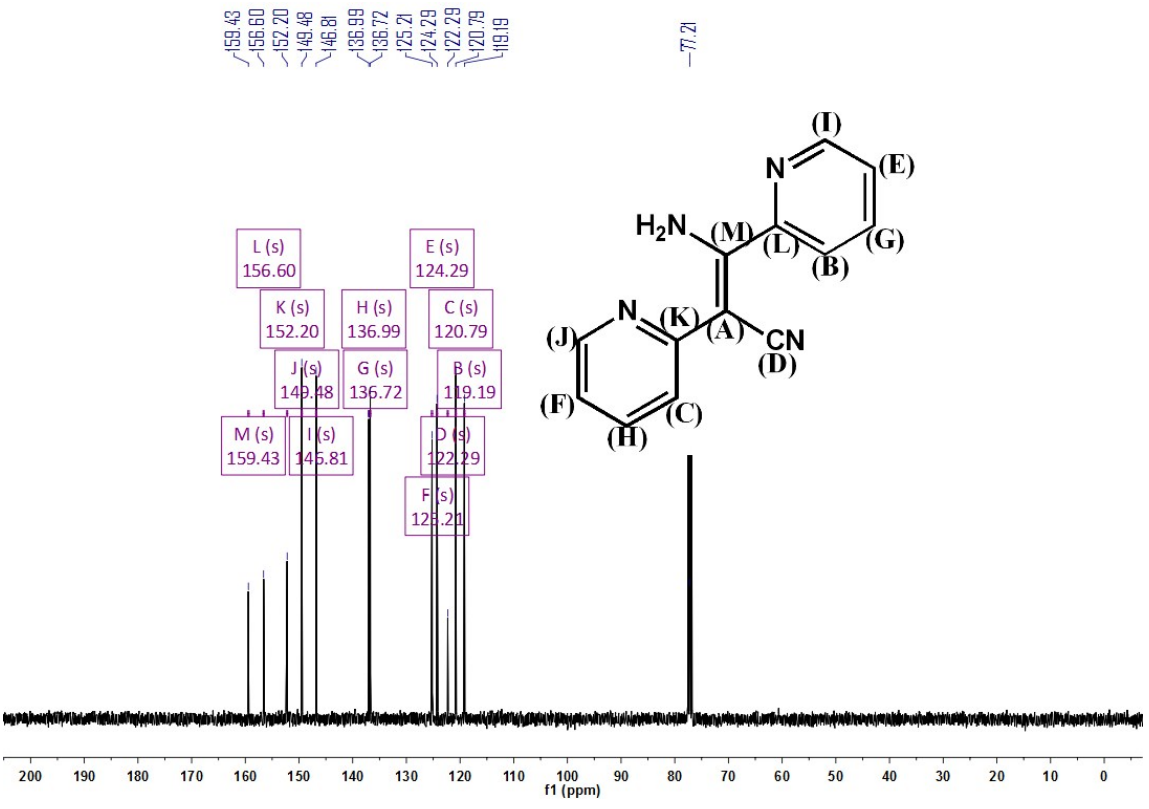

G (d) 8.60
D (m) 7.33
F (d) 8.33
E (td) 7.79
C (m) 7.25
B (s) 5.22
A (s) 3.67
0.95
0.96
0.98
4.87
1.05
1.93
2.00
f1 (ppm)


154.38
151.08
149.00
137.27
137.15
128.98
128.11
127.08
124.89
123.78
123.61
77.80
35.53
H (s) 128.98
M (s) 154.38
J (s) 137.27
D (s) 123.78
L (s) 151.08
I (s) 137.15
C (s) 123.61
K (s) 149.00
B (s) 77.80
A (s) 35.53
f1 (ppm)

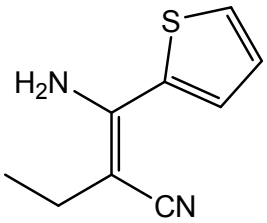
Compound **3f**

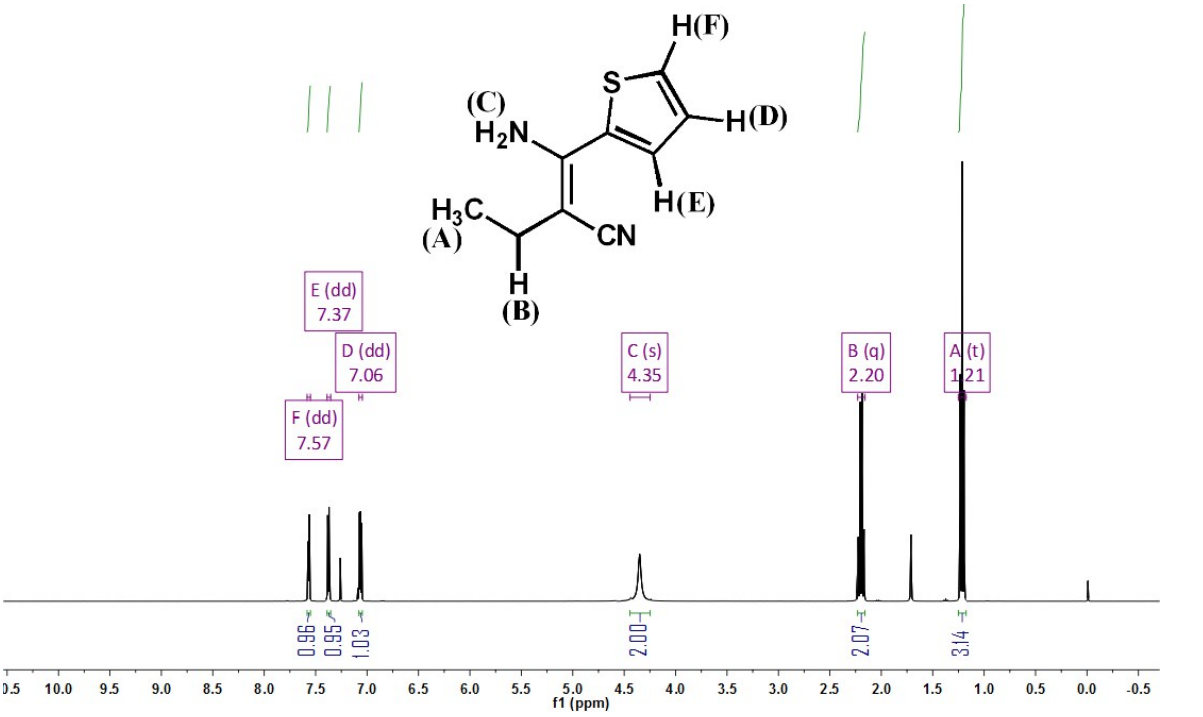

N
H2N
N
CN

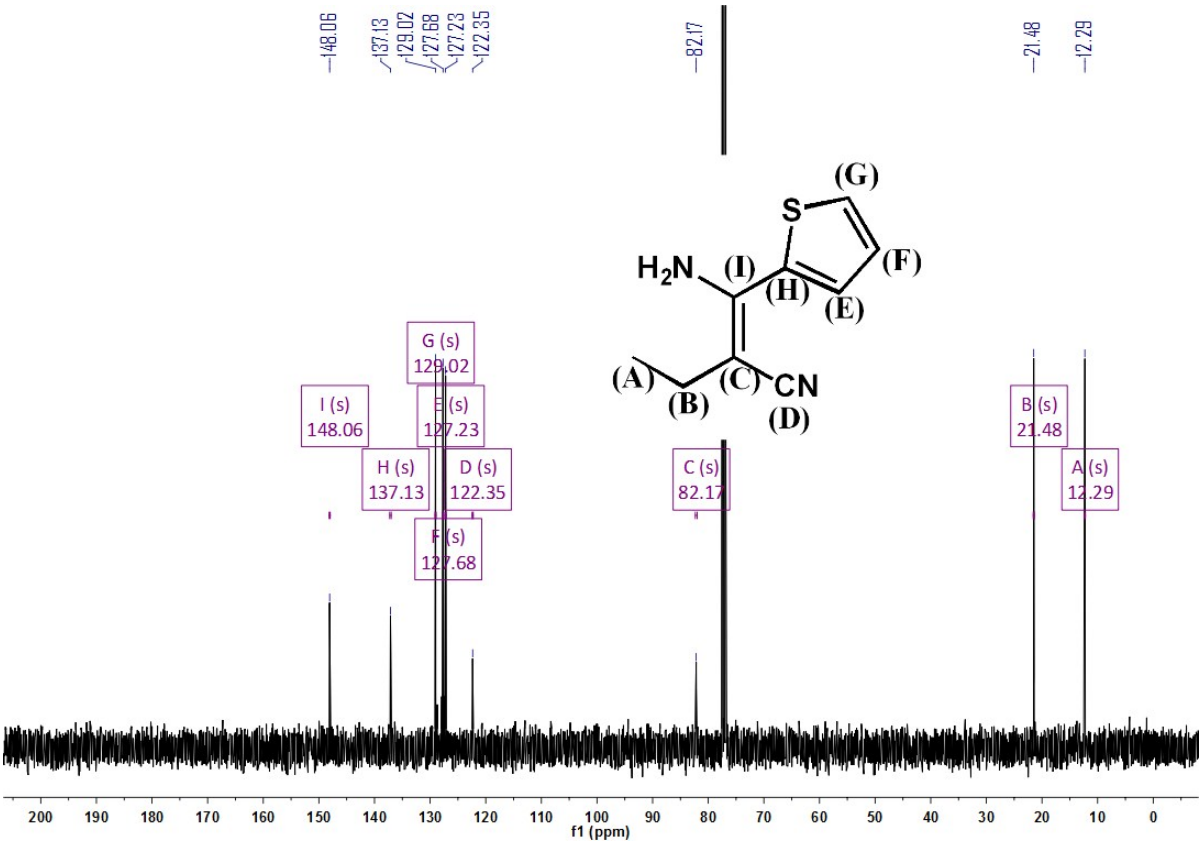

I (s) 11.21
H (d) 8.65
G (d) 8.46
F (d) 8.25
E (td) 7.81
D (m) 7.68
B (m) 7.02
A (s) 6.80
C (m) 7.37
0.97
0.99
1.01
1.00
1.02
2.02
1.00
1.03
0.94
f1 (ppm)


159.43
156.60
152.20
149.48
146.81
136.99
136.72
125.21
124.29
122.29
120.79
119.19
77.21
L (s) 156.60
K (s) 152.20
J (s) 149.48
M (s) 159.43
I (s) 146.81
H (s) 136.99
G (s) 136.72
E (s) 124.29
C (s) 120.79
B (s) 119.19
D (s) 122.29
F (s) 125.21
f1 (ppm)

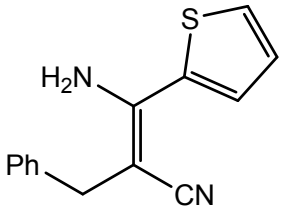
Compound **3g**

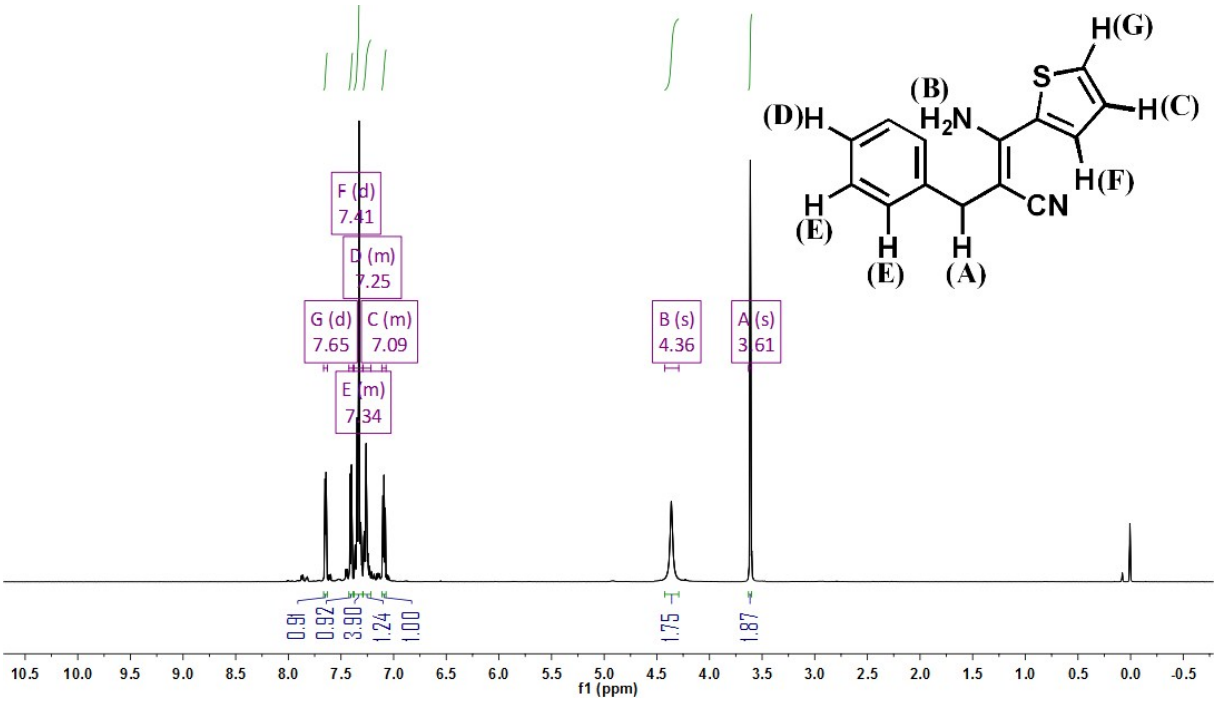

S
H2N
CN

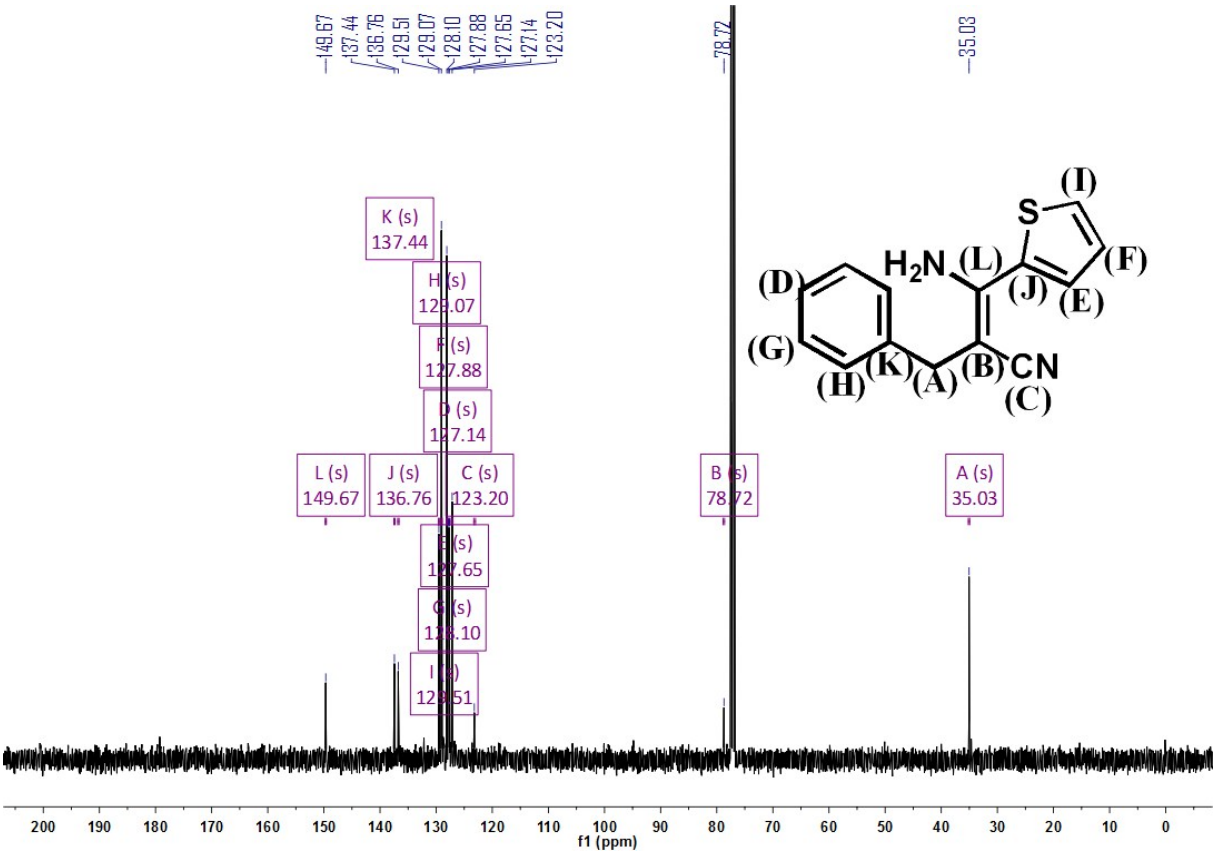

H(F)
S
(C)
H2N
H(D)
H(E)
H3C
(A)
CN
H
(B)
E (dd)
7.37
D (dd)
7.06
F (dd)
7.57
C (s)
4.35
B (q)
2.20
A (t)
1.21
0.96
0.95
1.03
2.00
2.07
3.14
f1 (ppm)


148.06
137.13
129.02
127.68
127.23
122.35
82.17
21.48
12.29
(G)
S
H2N
(I)
(H)
(F)
(E)
(A)
(B)
(C)
CN
(D)
G (s)
129.02
I (s)
148.06
E (s)
127.23
H (s)
137.13
D (s)
122.35
F (s)
127.68
C (s)
82.17
B (s)
21.48
A (s)
12.29
f1 (ppm)

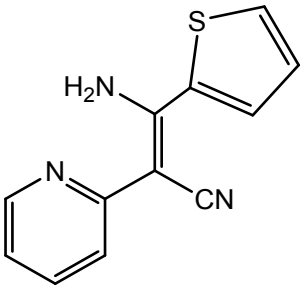
Compound **3h**

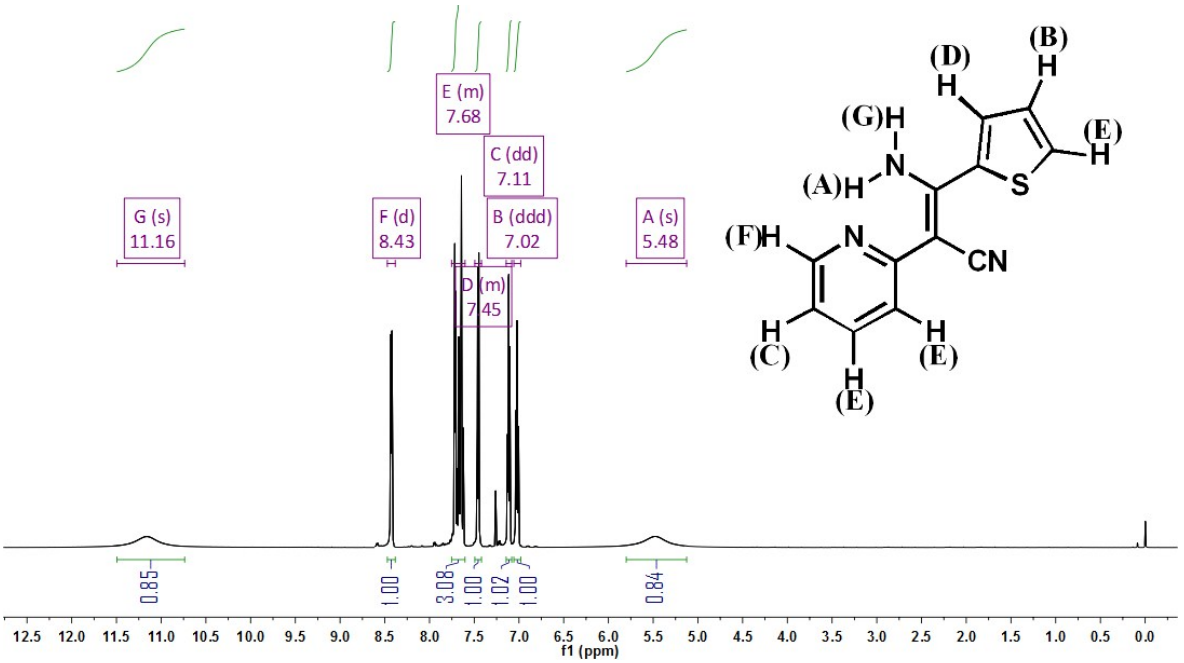

S
H2N
Ph
CN

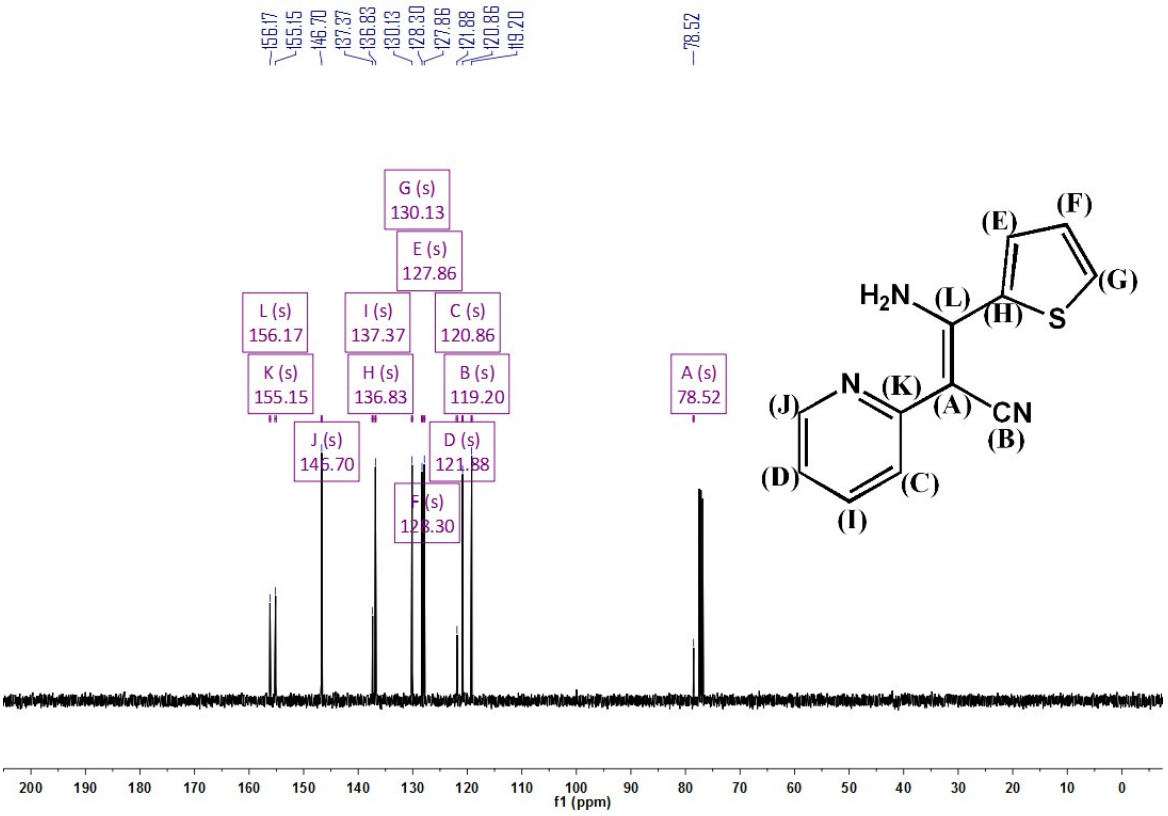

F (d) 7.41
D (m) 7.25
G (d) 7.65
C (m) 7.09
E (m) 7.34
B (s) 4.36
A (s) 3.61
0.91
0.92
3.90
1.24
1.00
1.75
1.87
f1 (ppm)
H(G)
S
(B)
H2N
(D)H
H(C)
H(F)
CN
H
(E)
H
(E)
H
(A)


149.67
137.44
136.76
129.51
129.07
128.10
127.88
127.65
127.14
123.20
78.72
35.03
K (s) 137.44
L (s) 149.67
J (s) 136.76
C (s) 123.20
B (s) 78.72
A (s) 35.03
f1 (ppm)
(I)
S
(F)
H2N
(L)
(J)
(E)
(D)
(G)
(K)
(B)
CN
(H)
(A)
(C)

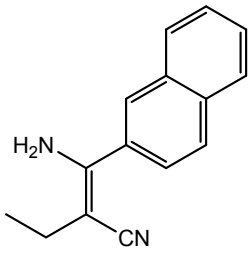
Compound **3i**

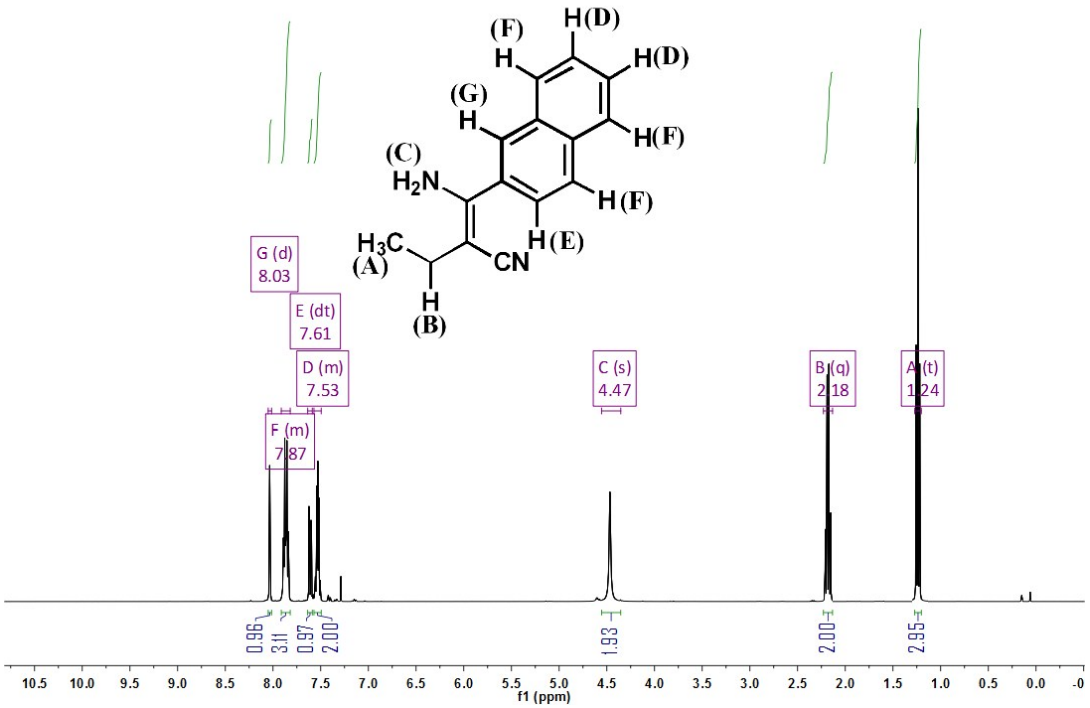

S
H2N
N
CN

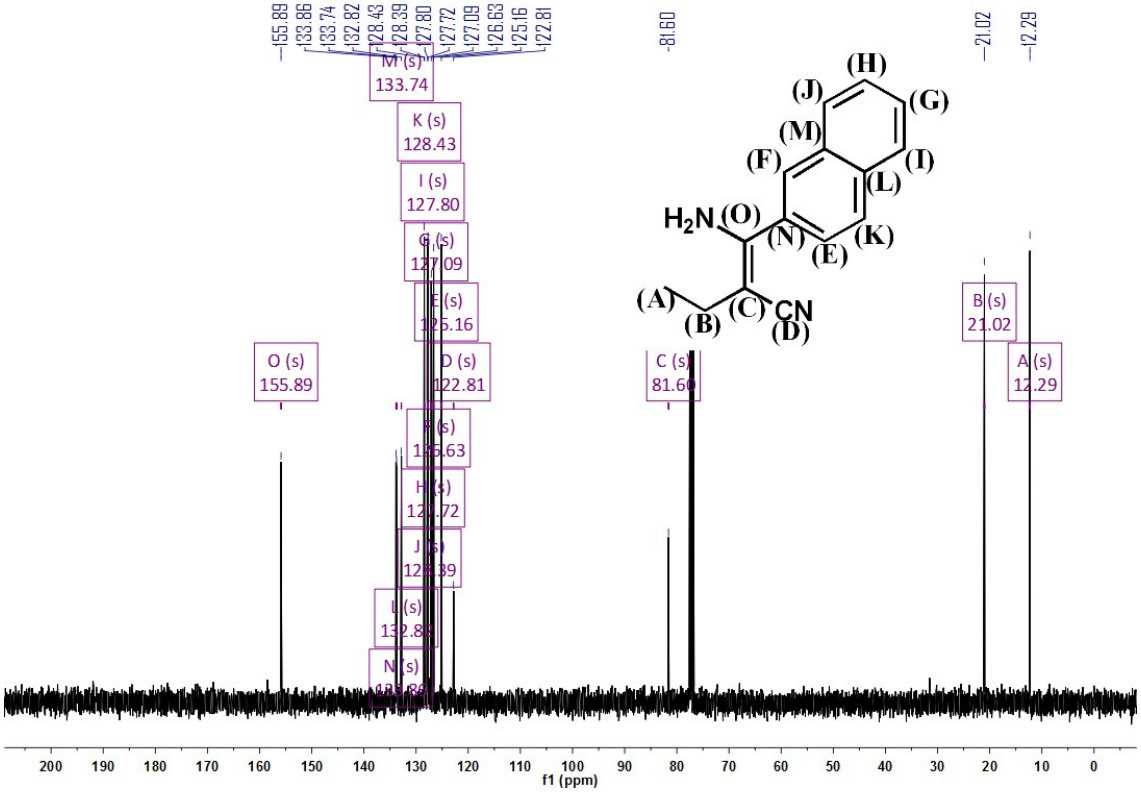

G (s)
11.16
F (d)
8.43
E (m)
7.68
C (dd)
7.11
B (ddd)
7.02
D (m)
7.45
A (s)
5.48
0.85
1.00
3.08
1.00
1.02
1.00
0.84
f1 (ppm)


156.17
155.15
146.70
137.37
136.83
130.13
128.30
127.86
121.88
120.86
119.20
78.52
G (s)
130.13
E (s)
127.86
L (s)
156.17
I (s)
137.37
C (s)
120.86
K (s)
155.15
H (s)
136.83
B (s)
119.20
A (s)
78.52
J (s)
145.70
D (s)
121.88
F (s)
128.30
f1 (ppm)

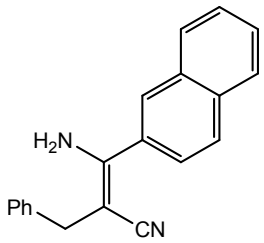
Compound **3j**

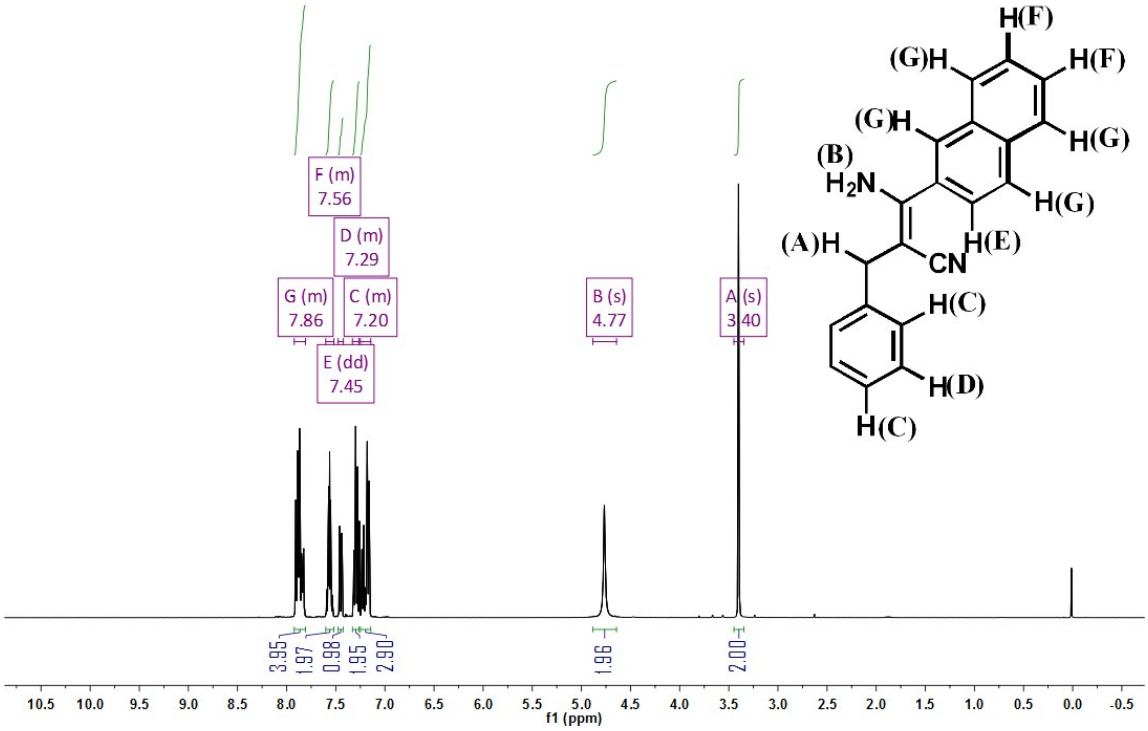

H2N
CN

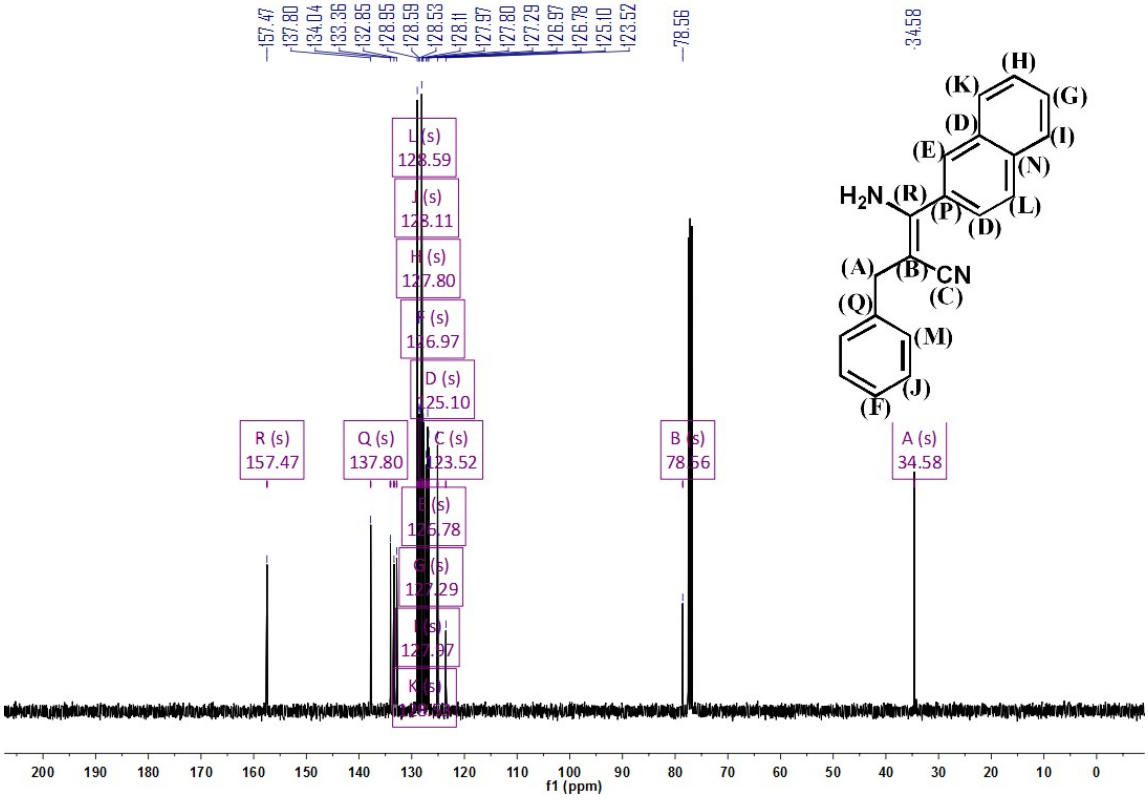

G (d) 8.03
E (dt) 7.61
D (m) 7.53
F (m) 7.87
C (s) 4.47
B (q) 2.18
A (t) 1.24
0.96
3.11
0.97
2.00
1.93
2.00
2.95
f1 (ppm)


M (s) 133.74
K (s) 128.43
I (s) 127.80
G (s) 127.09
E (s) 125.16
O (s) 155.89
D (s) 122.81
C (s) 81.60
B (s) 21.02
A (s) 12.29
f1 (ppm)

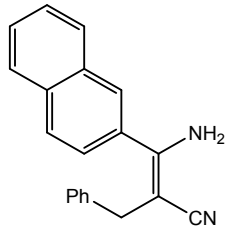
Compound **3k**

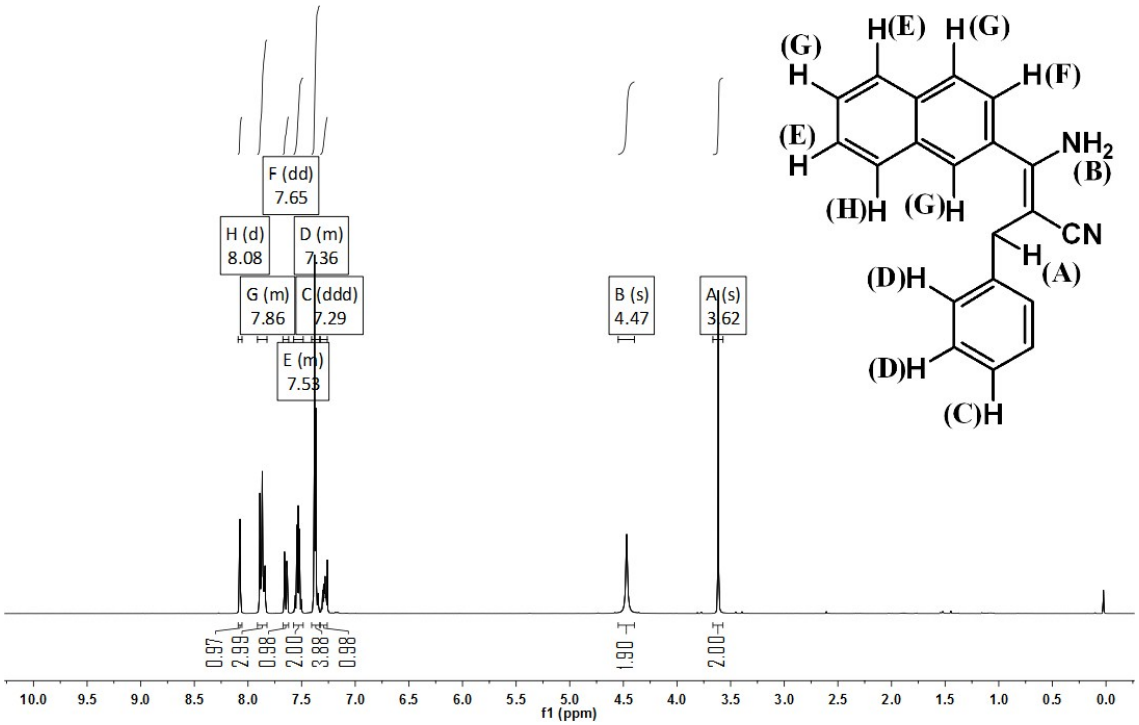

H2N
Ph
CN

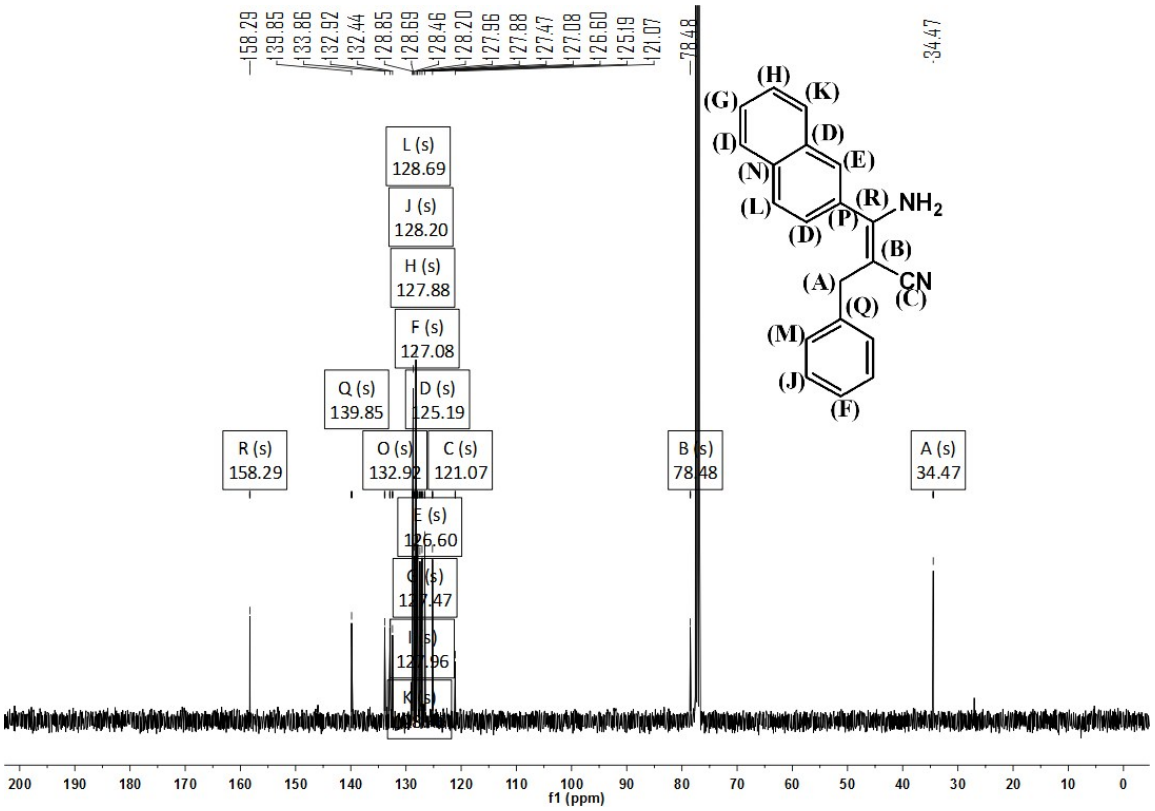

F (m) 7.56
D (m) 7.29
G (m) 7.86
C (m) 7.20
E (dd) 7.45
B (s) 4.77
A (s) 3.40
H(F)
(G)H
H(F)
(G)H
H(G)
(B)
H2N
H(G)
(A)H
CN
H(E)
H(C)
H(D)
H(C)
3.95
1.97
0.98
1.95
2.90
1.96
2.00
f1 (ppm)


157.47
137.80
134.04
133.36
132.85
128.95
128.59
128.53
128.11
127.97
127.80
127.29
126.97
126.78
125.10
123.52
78.56
34.58
L (s) 128.59
J (s) 128.11
H (s) 127.80
F (s) 126.97
D (s) 125.10
R (s) 157.47
Q (s) 137.80
C (s) 123.52
B (s) 78.56
A (s) 34.58
(H)
(K)
(G)
(D)
(I)
(E)
(N)
H2N
(R)
(P)
(L)
(D)
(A)
(B)
CN
(C)
(Q)
(M)
(J)
(F)
f1 (ppm)

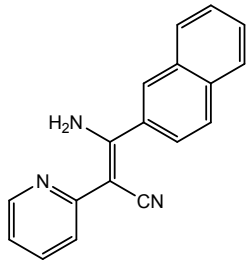
Compound **3k′**

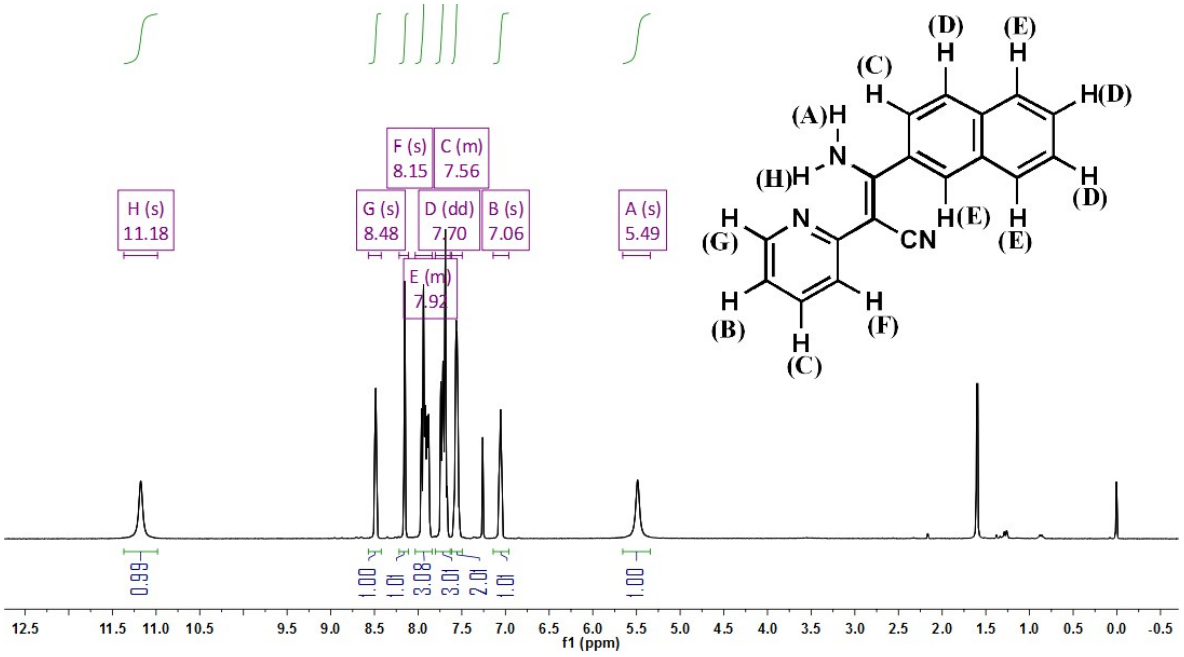

NH2
Ph
CN

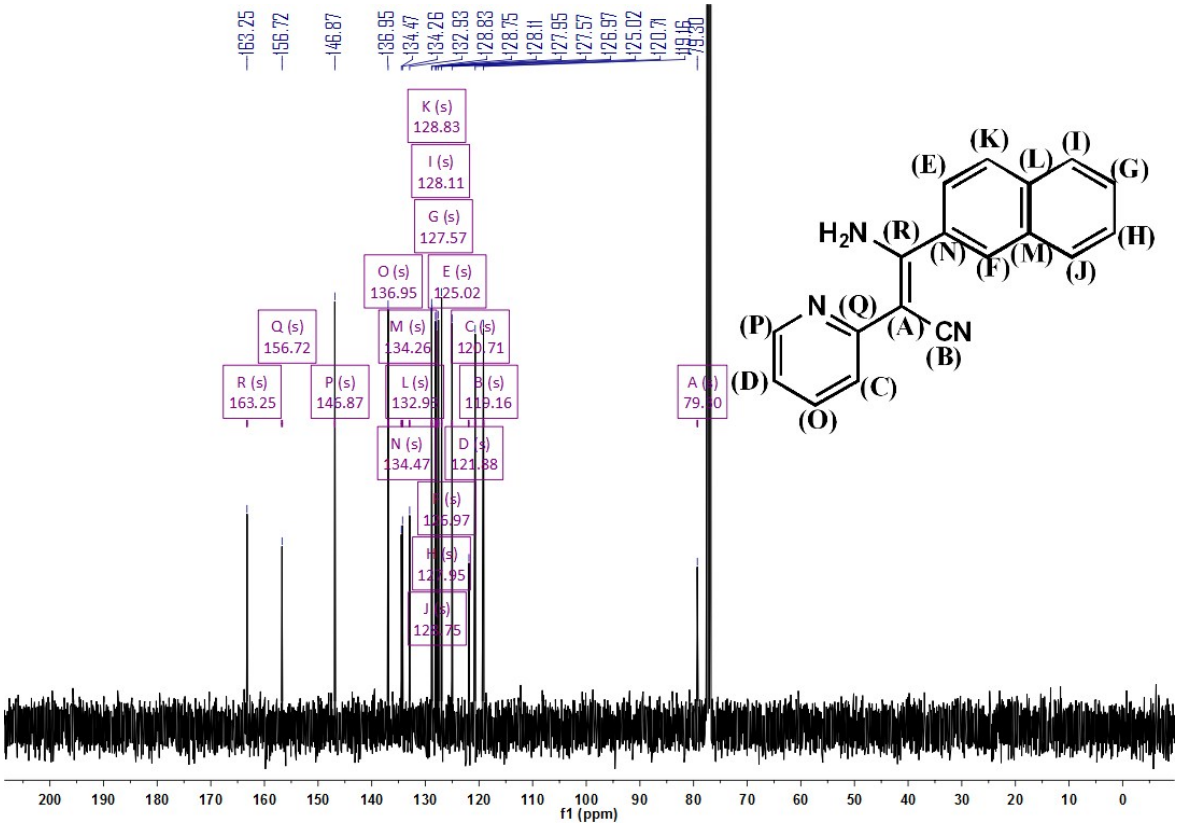

F (dd) 7.65
H (d) 8.08
D (m) 7.36
G (m) 7.86
C (ddd) 7.29
E (m) 7.53
B (s) 4.47
A (s) 3.62
H(E) H(G)
(G) H
H(F)
(E) H
NH2 (B)
(H)H (G)H
CN
H (A)
(D)H
(D)H
(C)H
0.97
2.99
0.98
2.00
3.88
0.98
1.90
2.00
f1 (ppm)


158.29
139.85
133.86
132.92
132.44
128.85
128.69
128.46
128.20
127.96
127.88
127.47
127.08
126.60
125.19
121.07
78.48
34.47
L (s) 128.69
J (s) 128.20
H (s) 127.88
F (s) 127.08
Q (s) 139.85
D (s) 125.19
R (s) 158.29
O (s) 132.92
C (s) 121.07
B (s) 78.48
A (s) 34.47
E (s) 126.60
(H) (K)
(G) (D)
(I) (E)
(N)
(L) (R) NH2
(P)
(D) (B)
(A) CN (C)
(Q)
(M)
(J)
(F)
f1 (ppm)

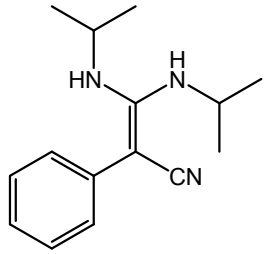
Compound **3l**

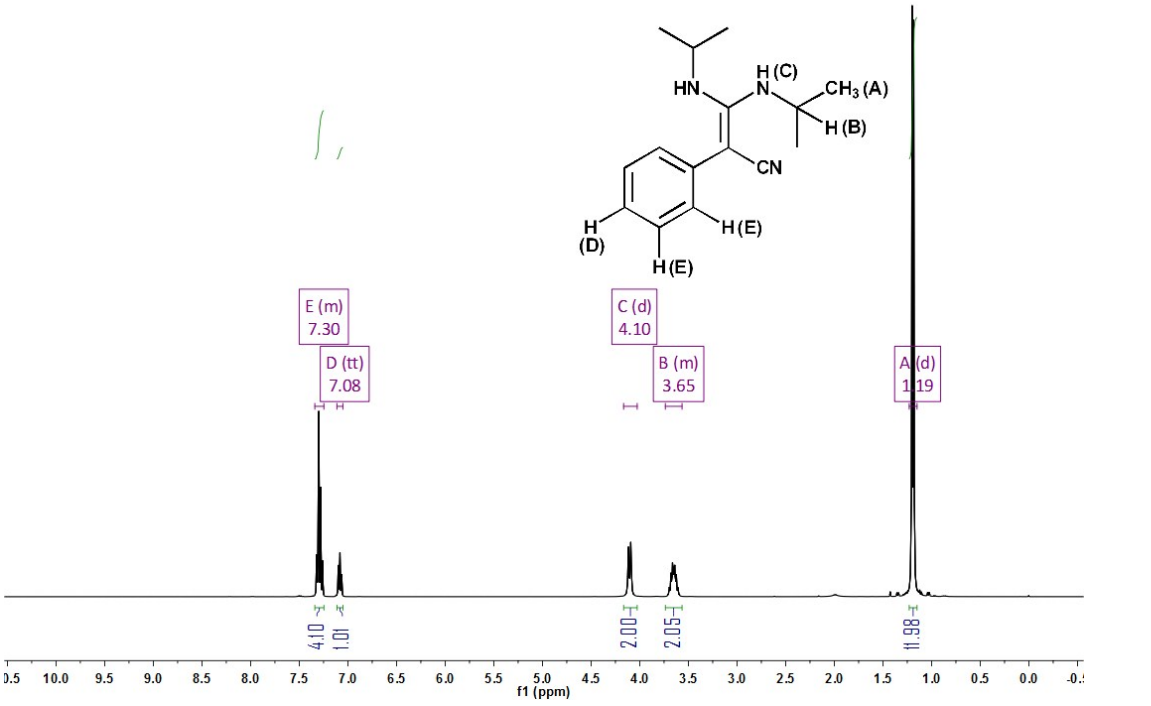

H2N
N
CN

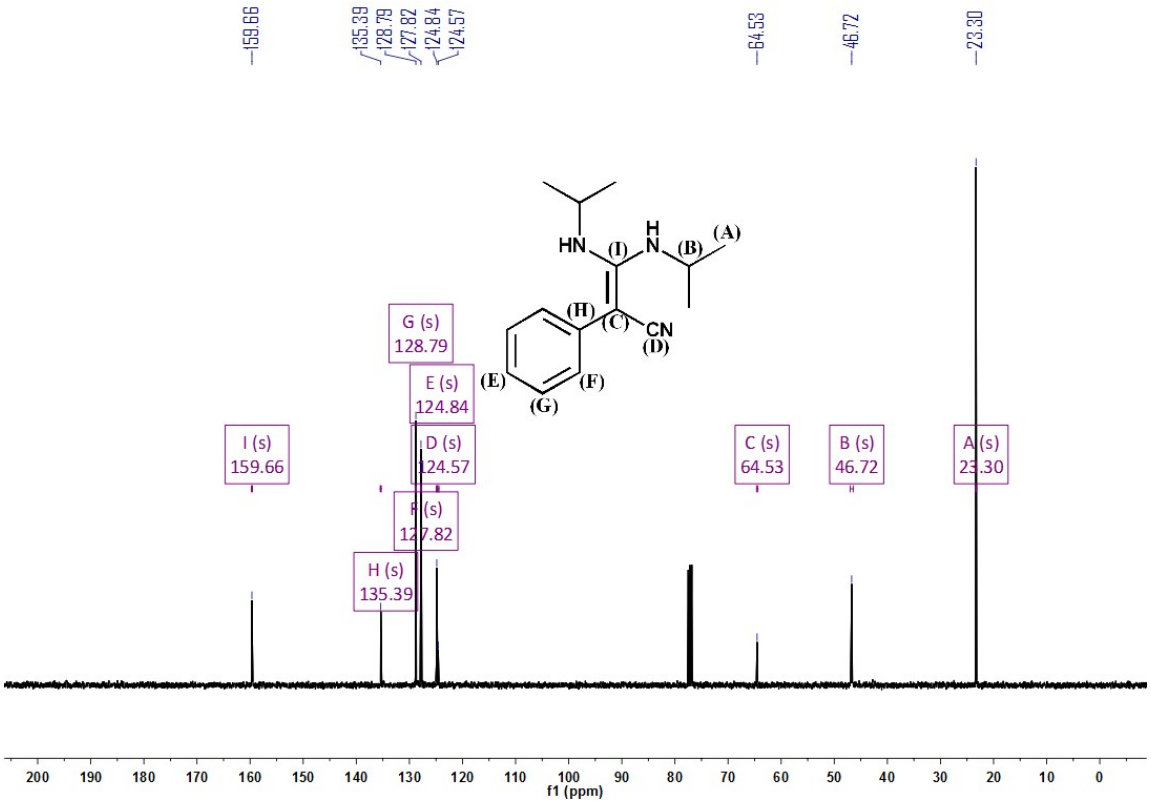

H (s) 11.18
F (s) 8.15
C (m) 7.56
G (s) 8.48
D (dd) 7.70
B (s) 7.06
E (m) 7.92
A (s) 5.49
0.99
1.00
1.01
3.08
3.01
2.01
1.01
1.00
f1 (ppm)


163.25
156.72
146.87
136.95
134.47
134.26
132.93
128.83
128.75
128.11
127.95
127.57
126.97
125.02
120.71
119.16
79.30
K (s) 128.83
I (s) 128.11
G (s) 127.57
O (s) 136.95
E (s) 125.02
Q (s) 156.72
M (s) 134.26
C (s) 120.71
R (s) 163.25
P (s) 146.87
L (s) 132.93
B (s) 119.16
A (s) 79.30
N (s) 134.47
D (s) 121.88
f1 (ppm)

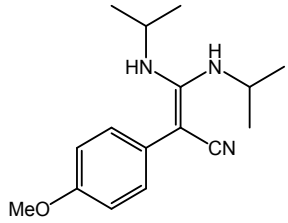
Compound **4a**

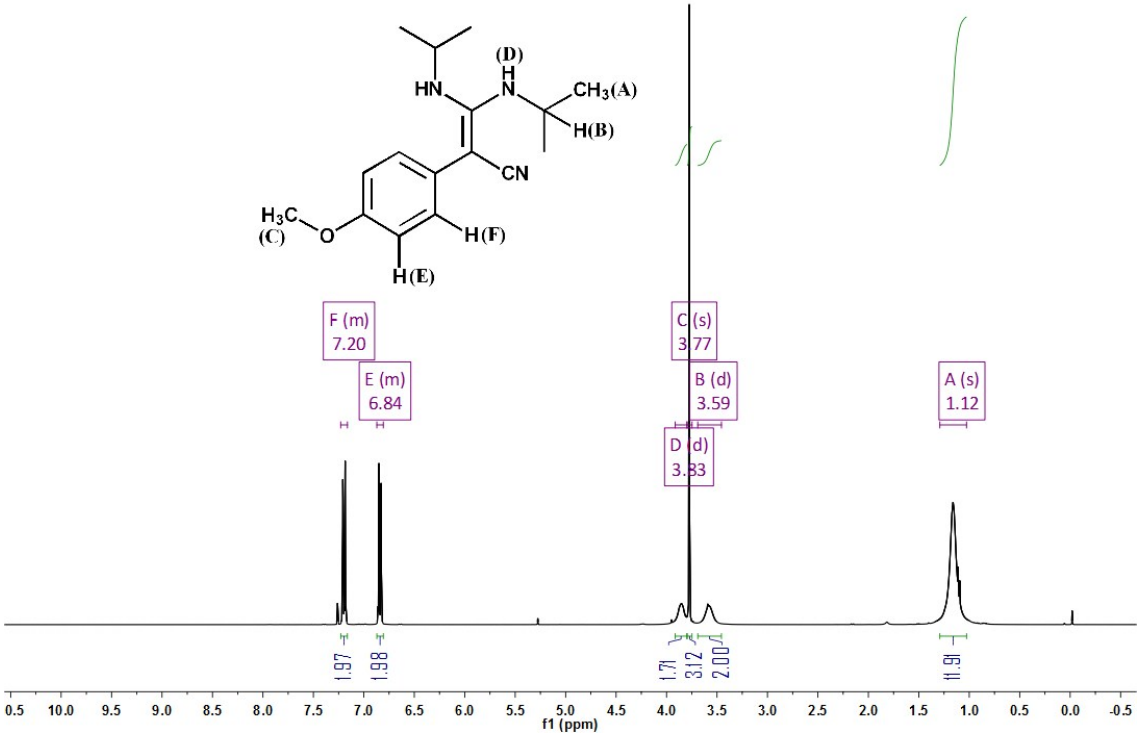

HN
H
N
CN

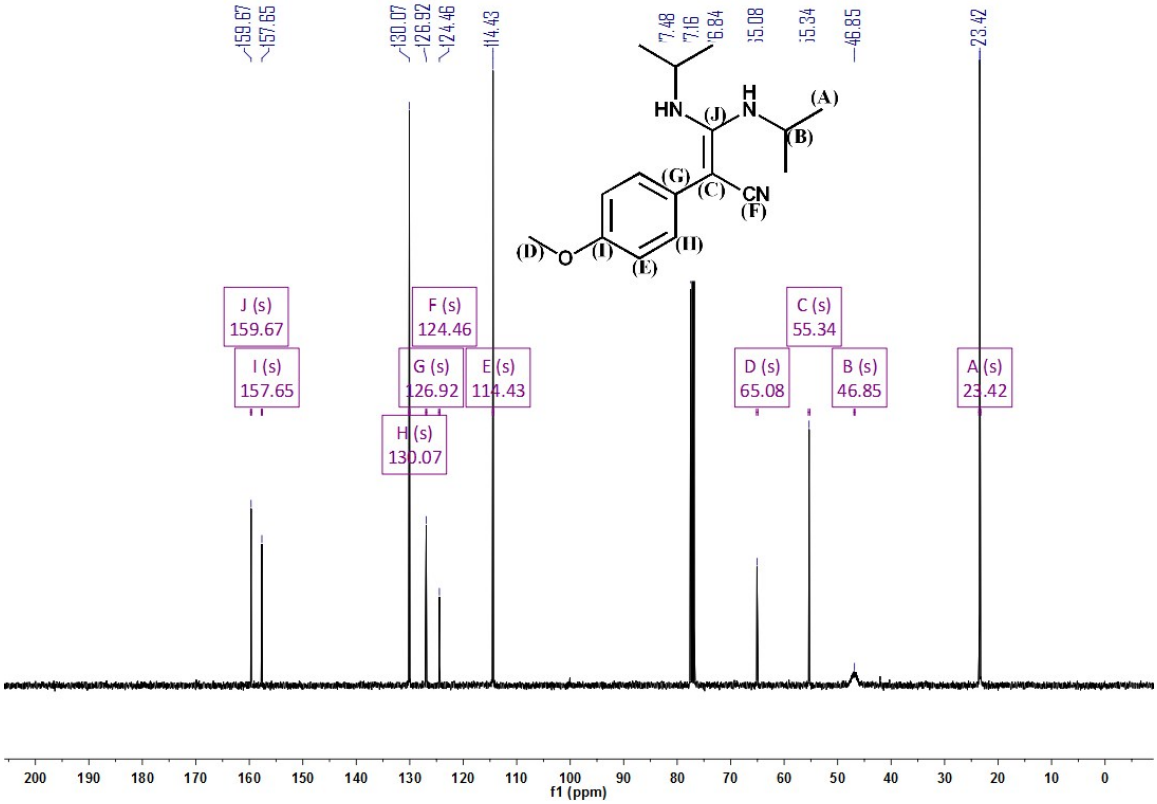

HN
H (C)
N
CH3 (A)
H (B)
CN
H (D)
H (E)
H (E)
E (m) 7.30
D (tt) 7.08
C (d) 4.10
B (m) 3.65
A (d) 1.19
4.10
1.01
2.00
2.05
11.98
f1 (ppm)


159.66
135.39
128.79
127.82
124.84
124.57
64.53
46.72
23.30
HN
(I)
H
N
(B)
(A)
(H)
(C)
CN
(D)
(E)
(F)
(G)
G (s) 128.79
E (s) 124.84
I (s) 159.66
D (s) 124.57
F (s) 127.82
H (s) 135.39
C (s) 64.53
B (s) 46.72
A (s) 23.30
f1 (ppm)

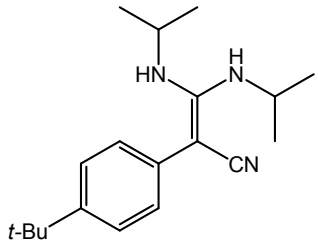
Compound **4b**

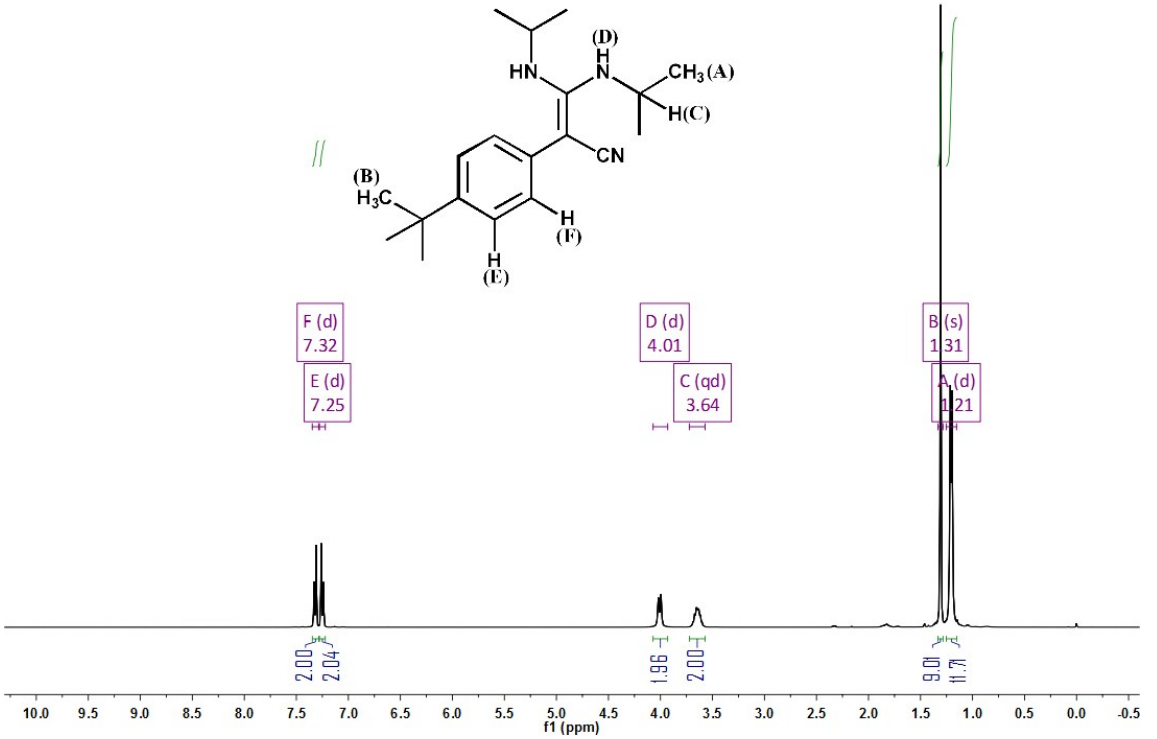

HN
H
N
CN
MeO

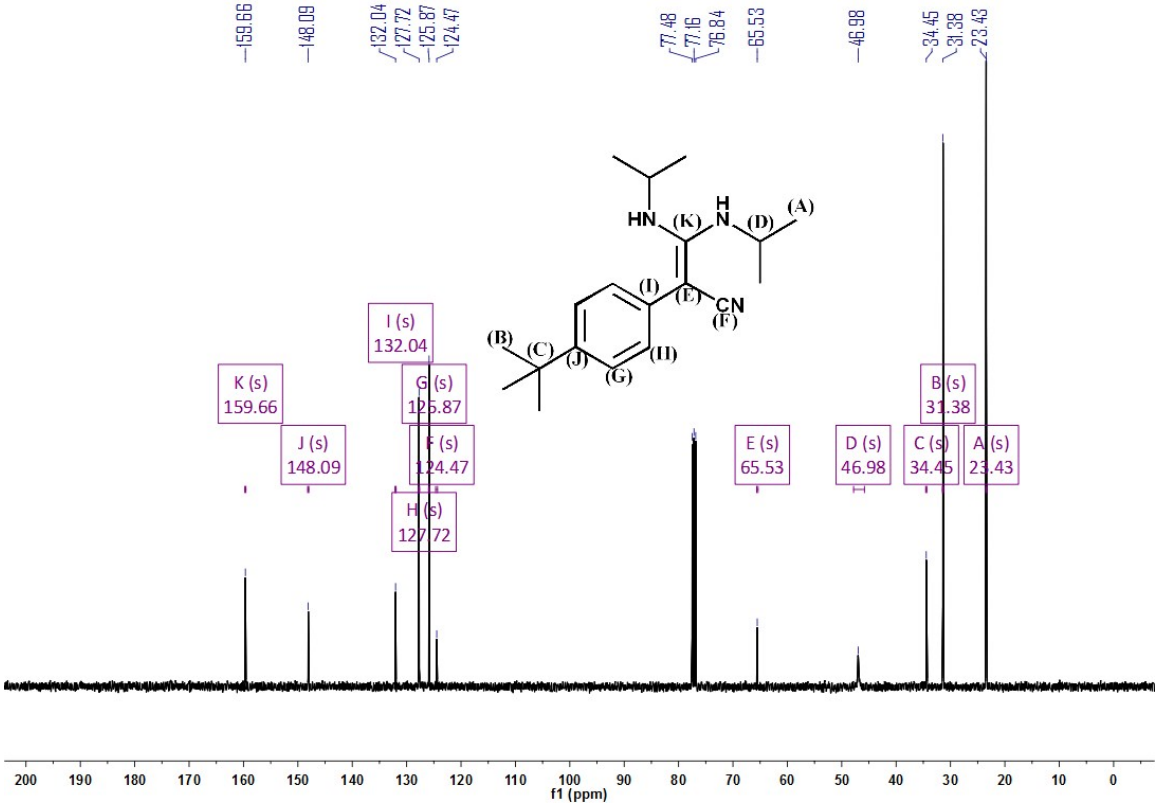

(D)
HN
H
N
CH3(A)
H(B)
CN
H3C
(C)
O
H(F)
H(E)
F (m) 7.20
E (m) 6.84
C (s) 3.77
B (d) 3.59
D (d) 3.33
A (s) 1.12
1.97
1.98
1.71
3.12
2.00
11.91
f1 (ppm)


159.67
157.65
130.07
126.92
124.46
114.43
77.48
77.16
76.84
55.08
55.34
46.85
23.42
HN
(J)
H
N
(A)
(B)
(G)
(C)
CN
(F)
(D)
O
(I)
(H)
(E)
J (s) 159.67
I (s) 157.65
F (s) 124.46
G (s) 126.92
E (s) 114.43
H (s) 130.07
C (s) 55.34
D (s) 65.08
B (s) 46.85
A (s) 23.42
f1 (ppm)

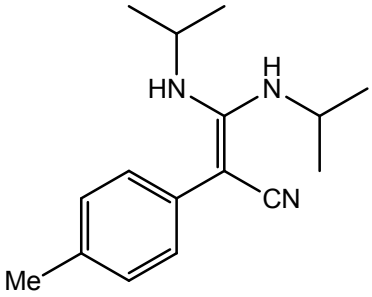
Compound **4c**

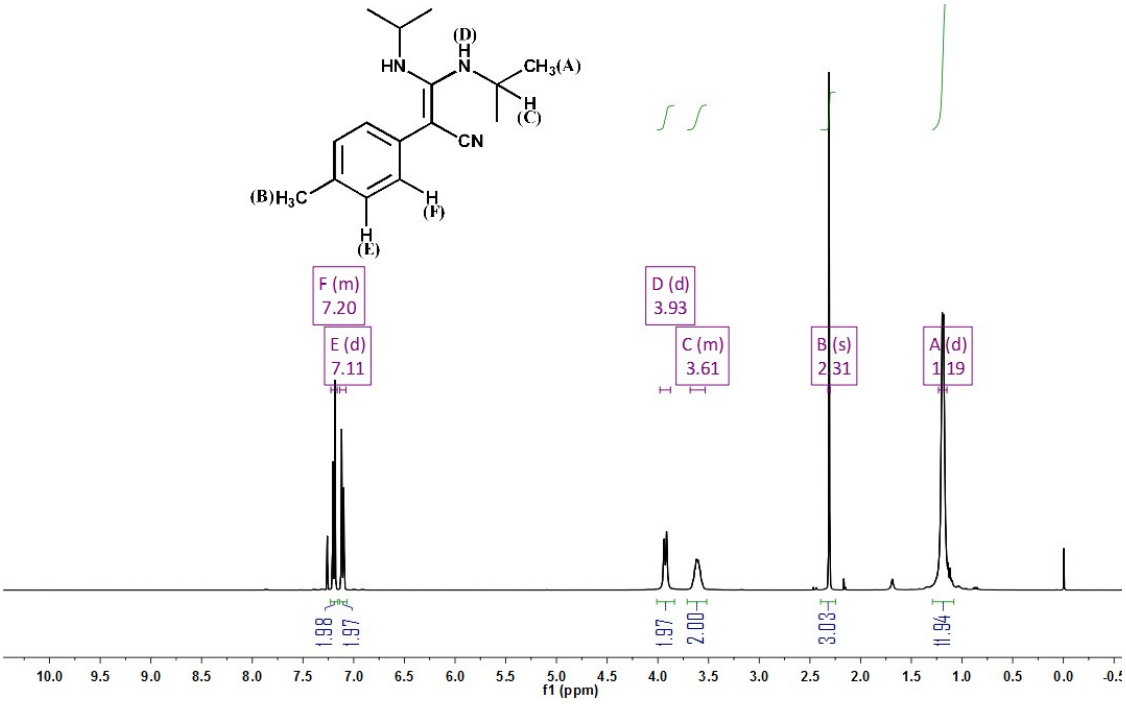

HN
H
N
CN
t-Bu

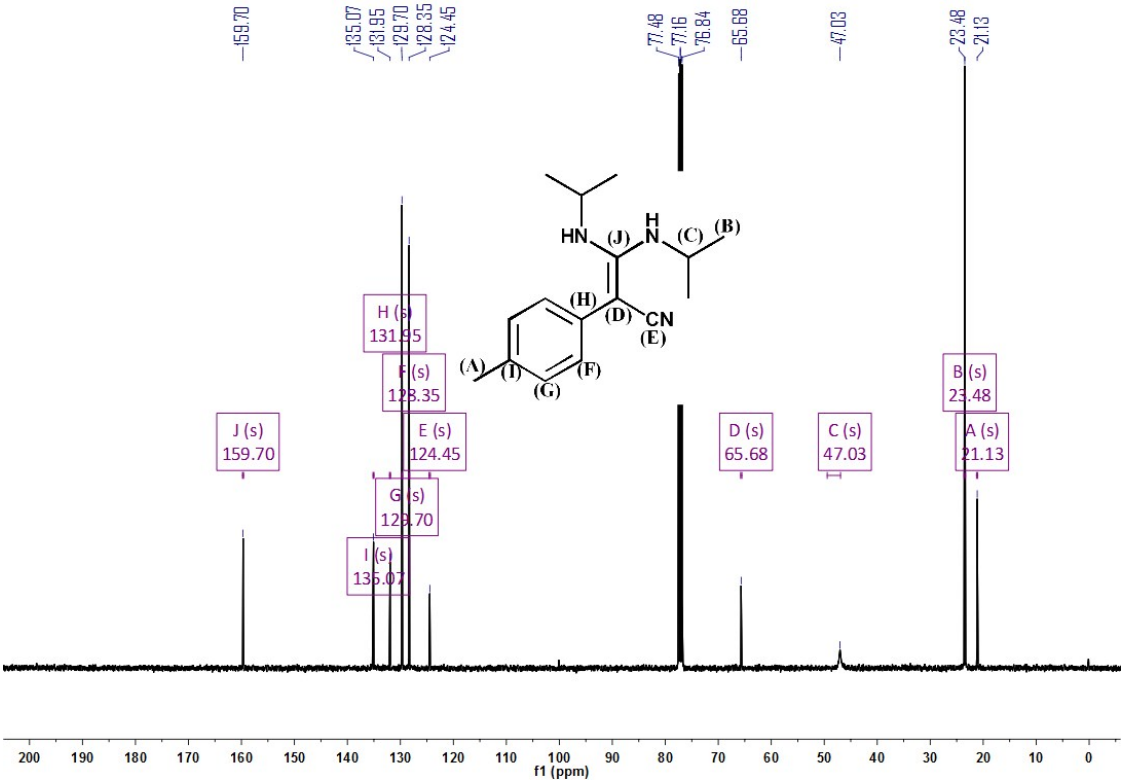

(D)
HN
H
N
CH3 (A)
H(C)
CN
(B)
H3C
H
(F)
H
(E)
F (d)
7.32
E (d)
7.25
D (d)
4.01
C (qd)
3.64
B (s)
1.31
A (d)
1.21
2.00
2.04
1.96
2.00
9.01
11.71
f1 (ppm)


159.66
148.09
132.04
127.72
125.87
124.47
77.48
77.16
76.84
65.53
46.98
34.45
31.38
23.43
HN
(K)
H
N
(D)
(A)
(I)
(E)
CN
(F)
(B)
(C)
(J)
(H)
(G)
I (s)
132.04
K (s)
159.66
G (s)
125.87
J (s)
148.09
F (s)
124.47
H (s)
127.72
E (s)
65.53
D (s)
46.98
B (s)
31.38
C (s)
34.45
A (s)
23.43
f1 (ppm)

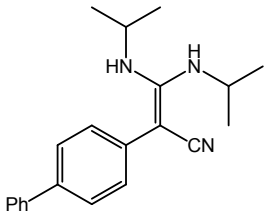
Compound **4d**

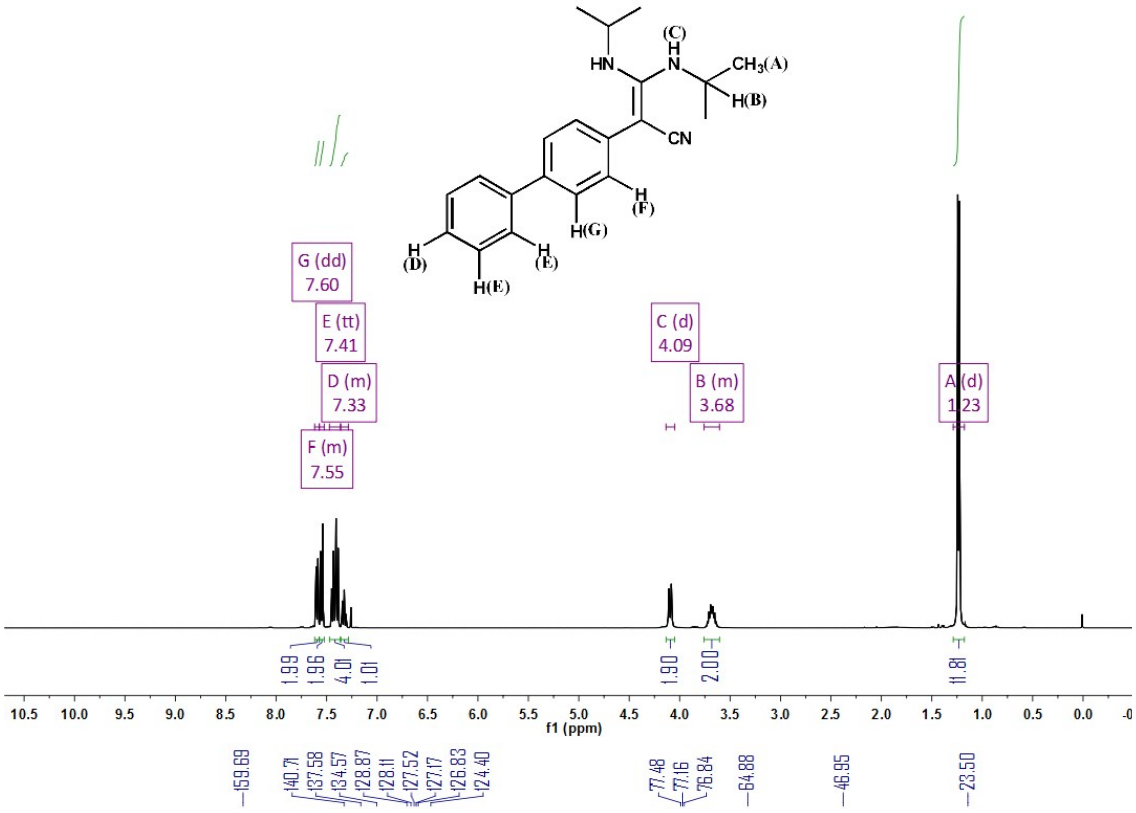

HN
H
N
CN
Me

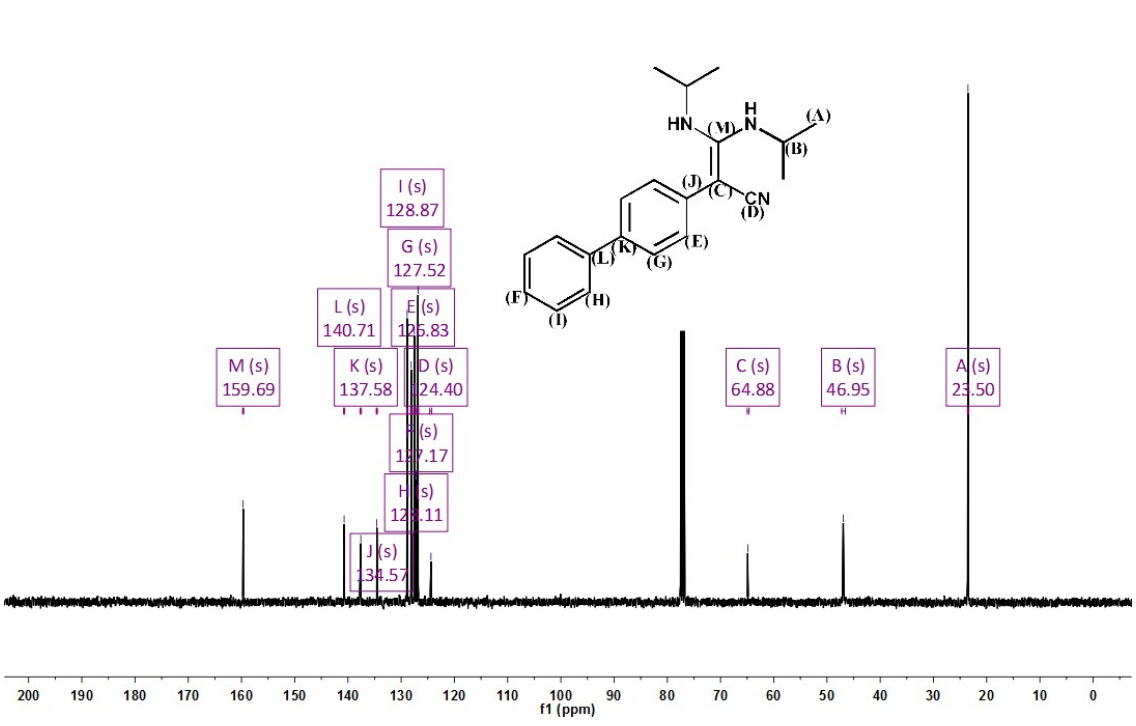

(D)
HN
H
N
CH3(A)
H
(C)
CN
(B)H3C
H
(F)
H
(E)
F (m)
7.20
E (d)
7.11
D (d)
3.93
C (m)
3.61
B (s)
2.31
A (d)
1.19
1.98
1.97
1.97
2.00
3.03
11.94
f1 (ppm)


159.70
135.07
131.95
129.70
128.35
124.45
77.48
77.16
76.84
65.68
47.03
23.48
21.13
HN
(J)
H
N
(C)
(B)
(H)
(D)
CN
(E)
(A)
(I)
(G)
(F)
H (s)
131.95
F (s)
128.35
J (s)
159.70
E (s)
124.45
G (s)
129.70
I (s)
135.07
D (s)
65.68
C (s)
47.03
B (s)
23.48
A (s)
21.13
f1 (ppm)

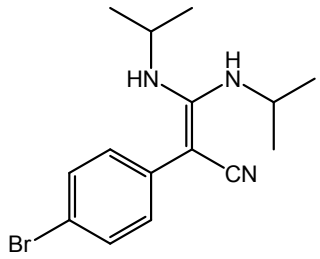
Compound **4e**

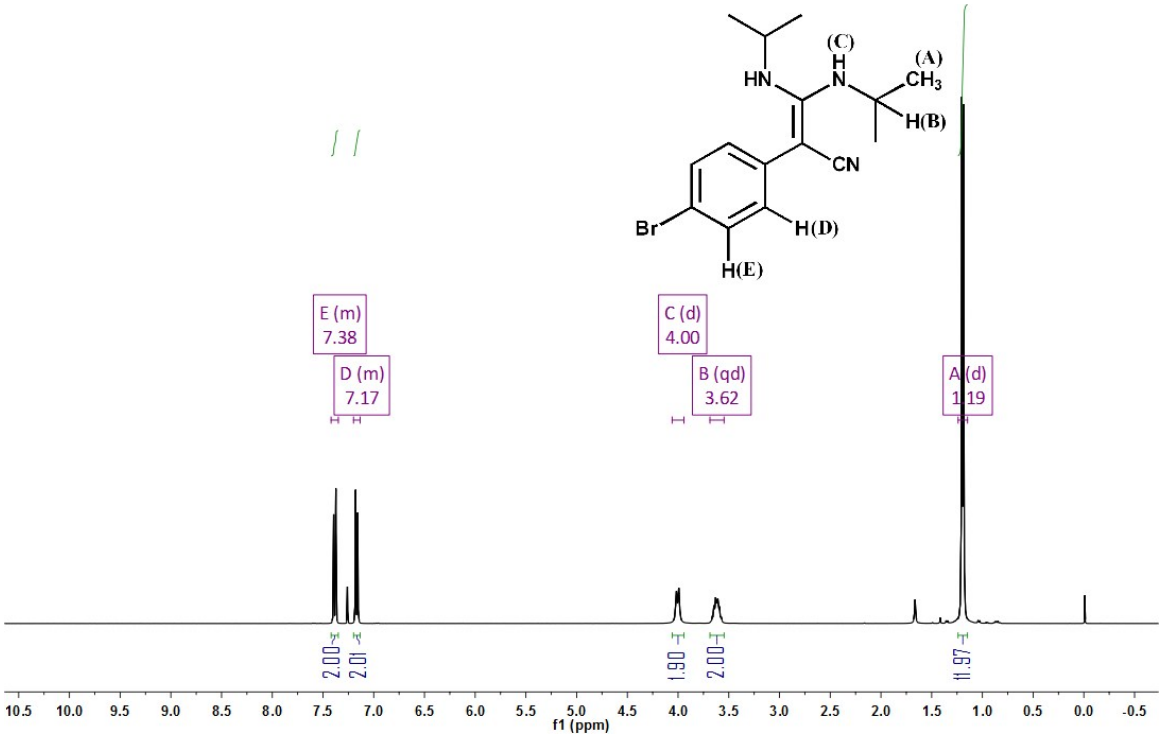

HN
H
N
CN
Ph

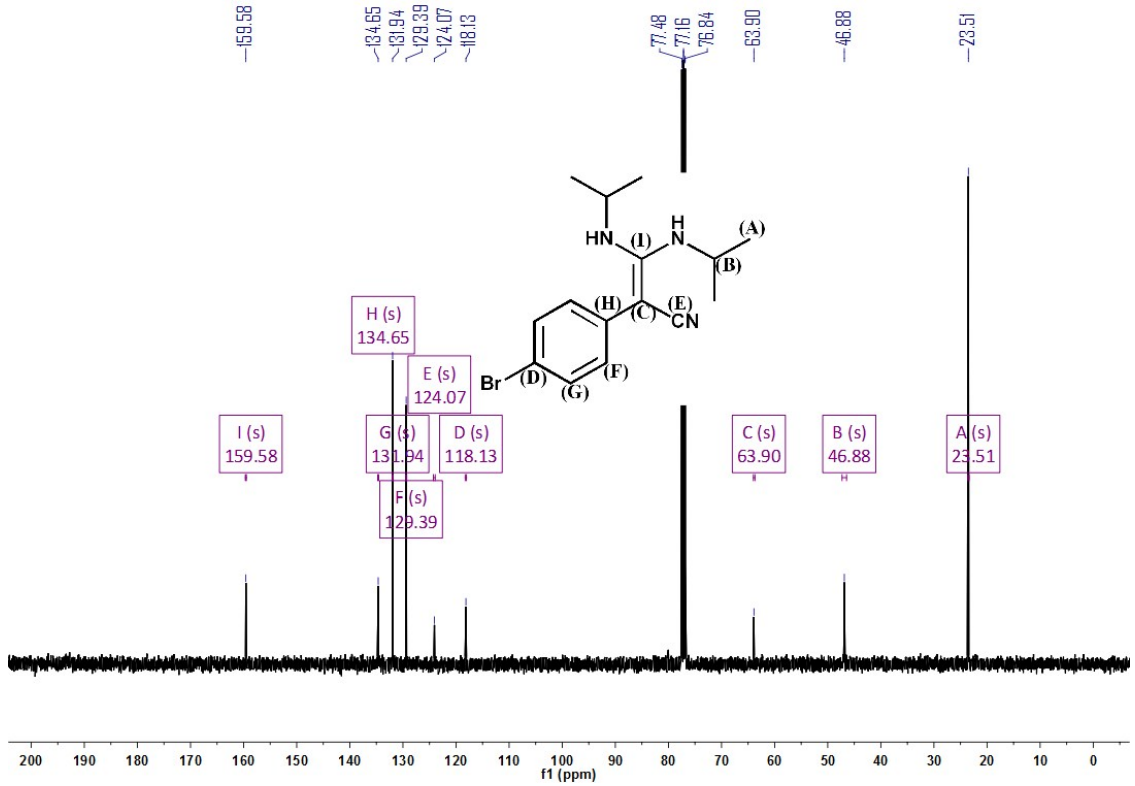

G (dd) 7.60
E (tt) 7.41
D (m) 7.33
F (m) 7.55
C (d) 4.09
B (m) 3.68
A (d) 1.23
1.99
1.96
4.01
1.01
1.90
2.00
11.81
f1 (ppm)


I (s) 128.87
G (s) 127.52
L (s) 140.71
M (s) 159.69
K (s) 137.58
C (s) 64.88
B (s) 46.95
A (s) 23.50
f1 (ppm)

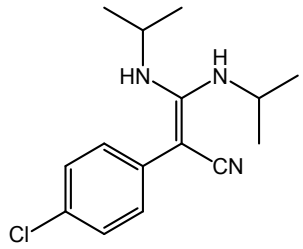
Compound **4f**

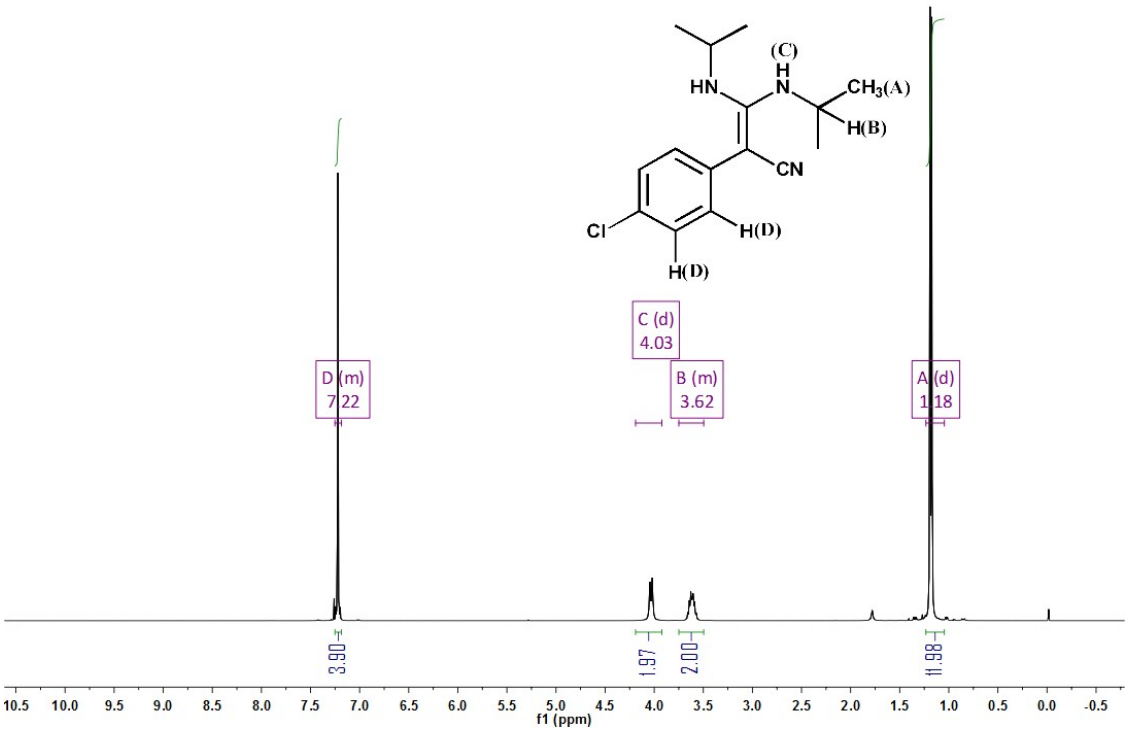

HN
H
N
CN
Br

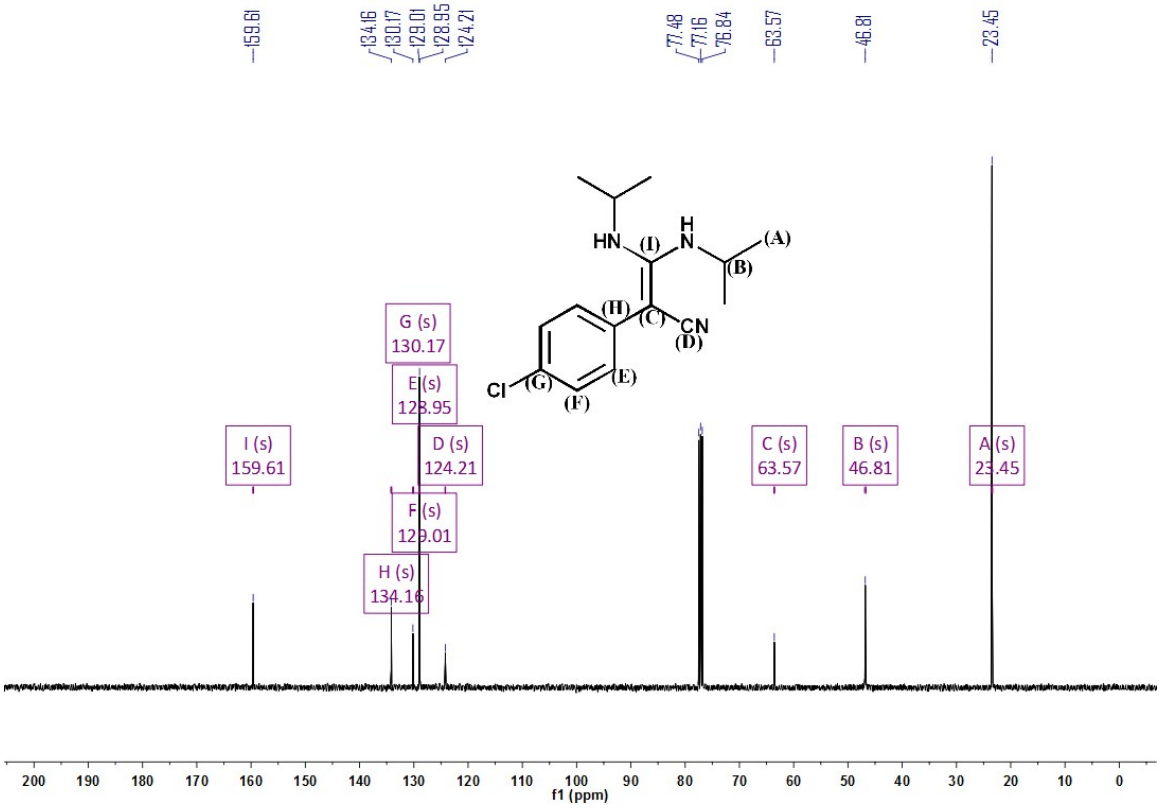

(C)
H
HN
N
(A)
CH3
H(B)
CN
Br
H(D)
H(E)
E (m)
7.38
D (m)
7.17
C (d)
4.00
B (qd)
3.62
A (d)
11.97
2.00
2.01
1.90
2.00
11.97
f1 (ppm)


159.58
134.65
131.94
129.39
124.07
118.13
77.48
77.16
76.84
63.90
46.88
23.51
HN
(I)
H
N
(A)
(B)
(H)
(C)
(E)
CN
Br
(D)
(F)
(G)
H (s)
134.65
E (s)
124.07
I (s)
159.58
G (s)
131.94
D (s)
118.13
F (s)
129.39
C (s)
63.90
B (s)
46.88
A (s)
23.51
f1 (ppm)

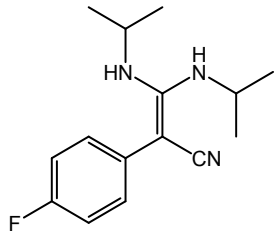
Compound **4g**

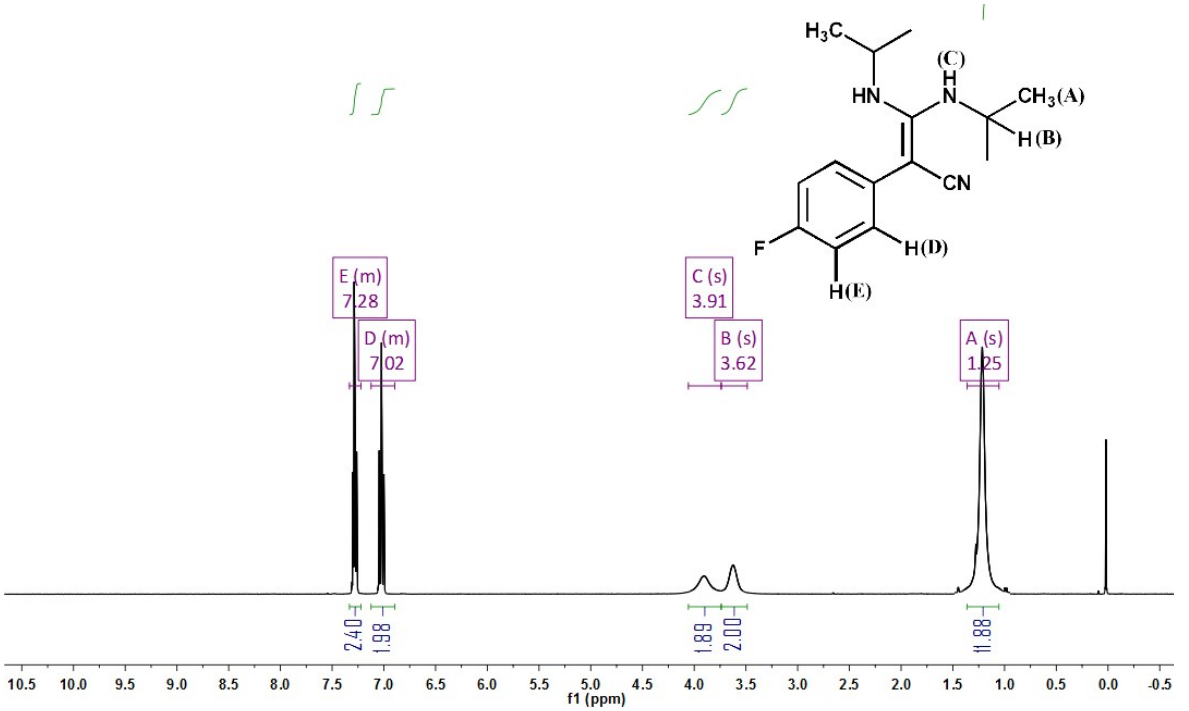

HN
H
N
CN
Cl

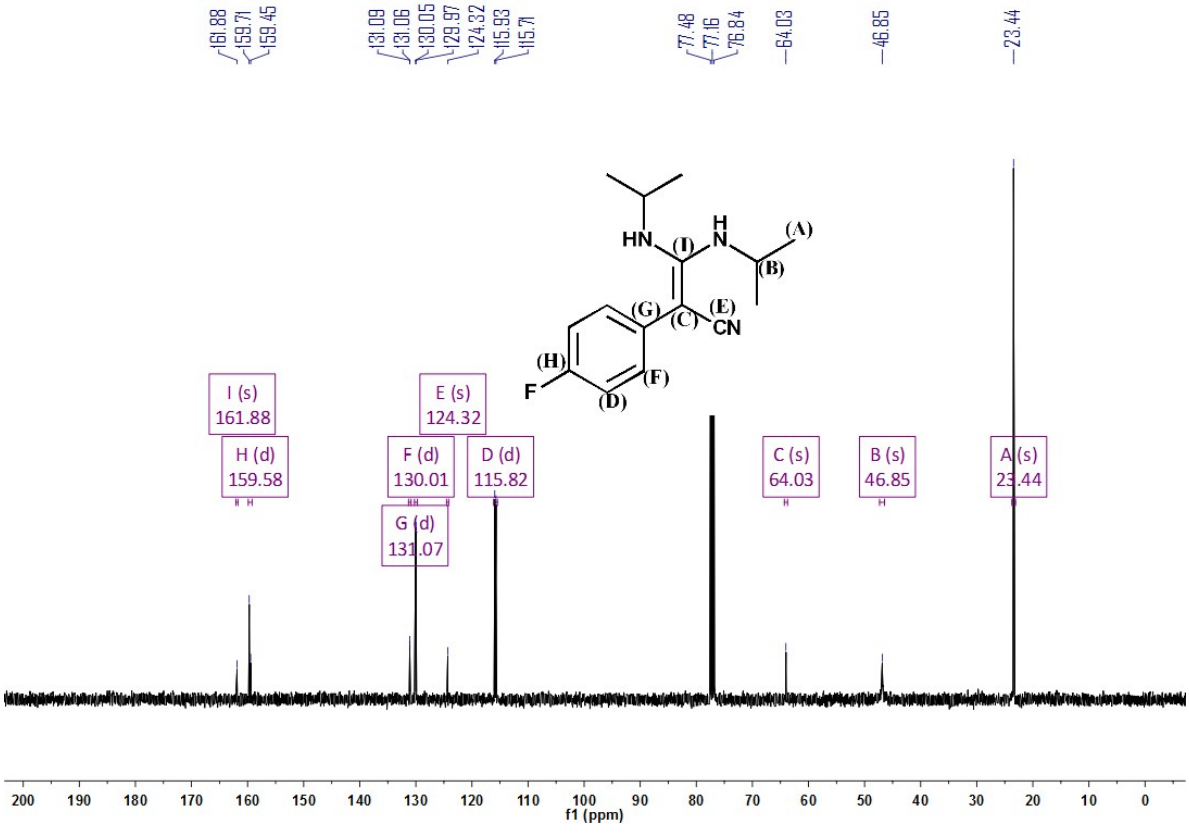

(C)
H
HN
N
CH3(A)
H(B)
CN
Cl
H(D)
H(D)
C (d)
4.03
D (m)
7.22
B (m)
3.62
A (d)
1.18
3.90
1.97
2.00
11.98
f1 (ppm)


159.61
134.16
130.17
129.01
128.95
124.21
77.48
77.16
76.84
63.57
46.81
23.45
HN
(I)
H
N
(A)
(B)
(H)
(C)
CN
(D)
Cl
(G)
(E)
(F)
G (s)
130.17
E (s)
128.95
I (s)
159.61
D (s)
124.21
C (s)
63.57
B (s)
46.81
A (s)
23.45
F (s)
129.01
H (s)
134.16
f1 (ppm)

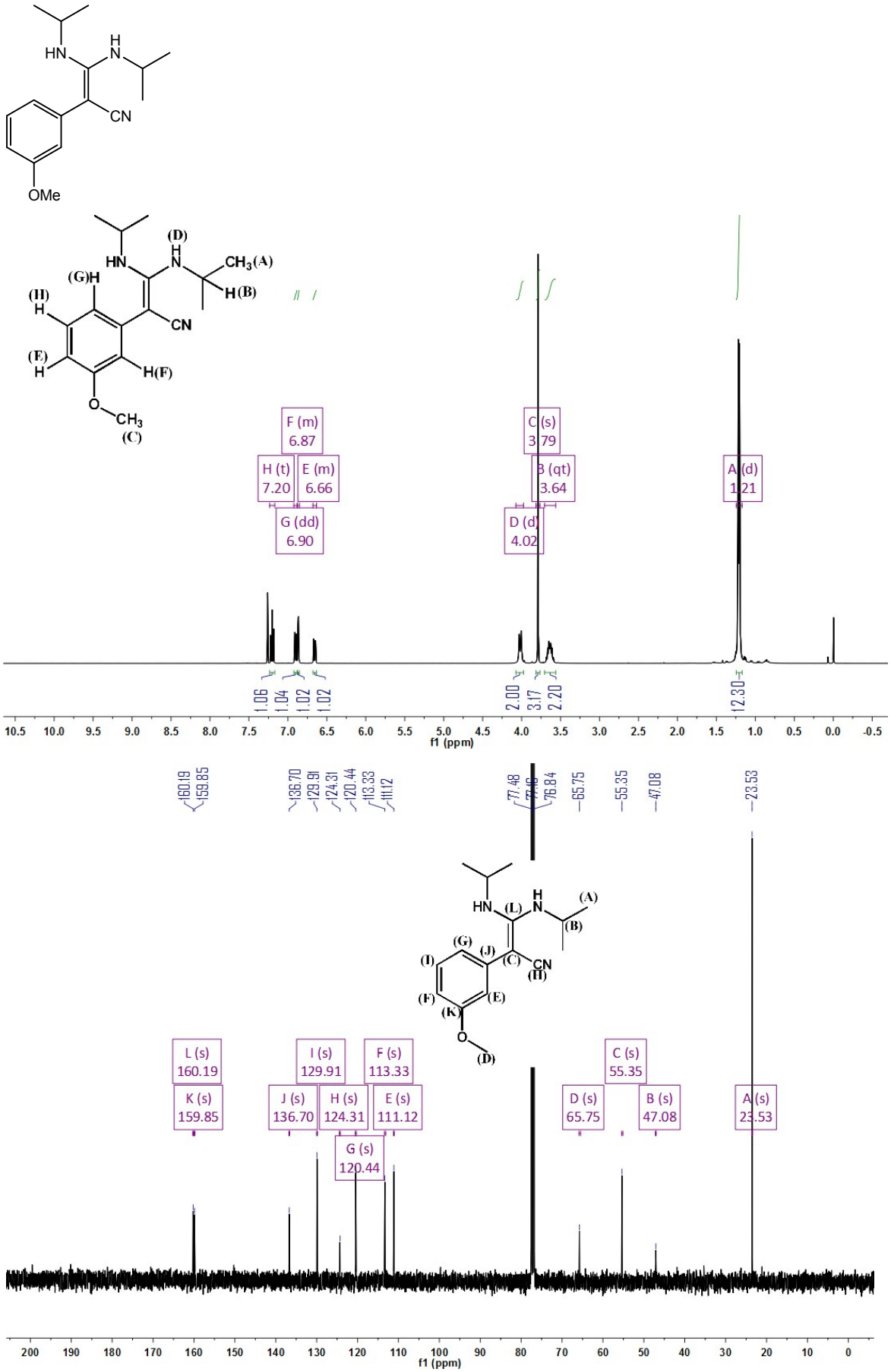
Compound **4h**


HN
H
N
CN
F

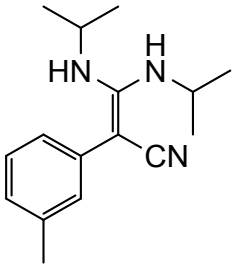

H3C
HN
(C)
H
N
CH3(A)
H(B)
CN
F
H(D)
H(E)
E (m)
7.28
D (m)
7.02
C (s)
3.91
B (s)
3.62
A (s)
1.25
2.40
1.98
1.89
2.00
11.88
f1 (ppm)

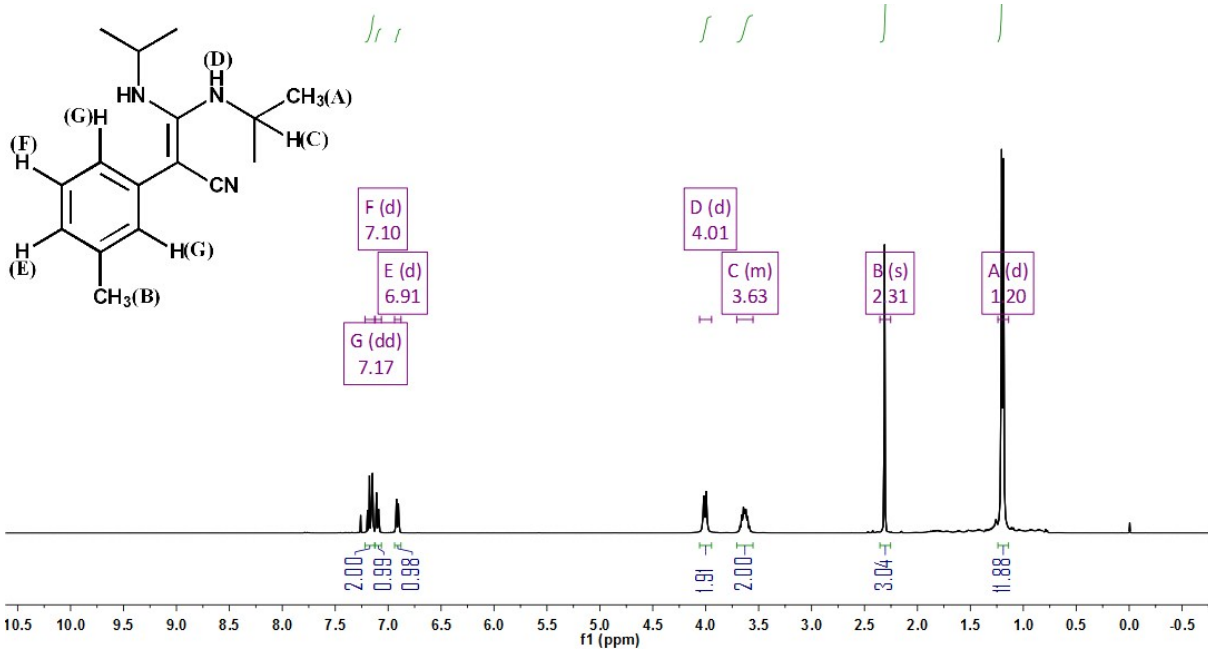

HN
(I)
H
N
(A)
(B)
(G)
(C)
(E)
CN
(H)
(F)
F
(D)
I (s)
161.88
H (d)
159.58
E (s)
124.32
F (d)
130.01
D (d)
115.82
G (d)
131.07
C (s)
64.03
B (s)
46.85
A (s)
23.44
f1 (ppm)

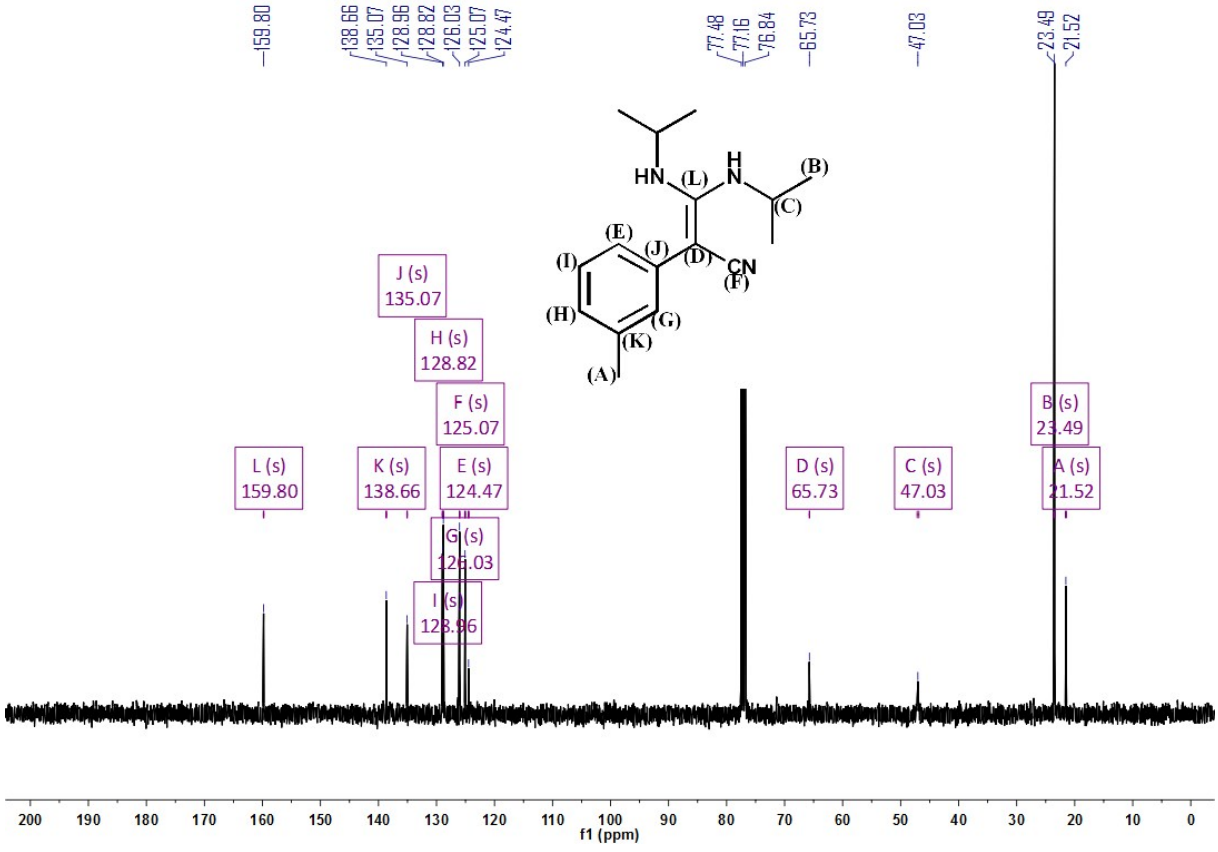
Compound **4i**


HN
H
N
CN
OMe
(D)
HN
H
N
CH3(A)
(G)H
H(B)
(H)
H
CN
(E)
H
H(F)
O
CH3
(C)
F (m)
6.87
H (t)
7.20
E (m)
6.66
G (dd)
6.90
C (s)
3.79
B (qt)
3.64
D (d)
4.02
A (d)
1.21
1.06
1.04
1.02
1.02
2.00
3.17
2.20
12.30
f1 (ppm)
160.19
159.85
136.70
129.91
124.31
120.44
113.33
111.12
77.48
77.16
76.84
65.75
55.35
47.08
23.53
HN
(L)
H
N
(A)
(B)
(G)
(J)
(I)
(C)
CN
(H)
(F)
(E)
(K)
O
(D)
L (s)
160.19
K (s)
159.85
I (s)
129.91
J (s)
136.70
H (s)
124.31
F (s)
113.33
E (s)
111.12
G (s)
120.44
C (s)
55.35
D (s)
65.75
B (s)
47.08
A (s)
23.53
f1 (ppm)

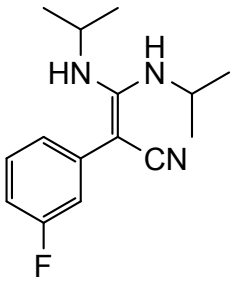
Compound **4j**

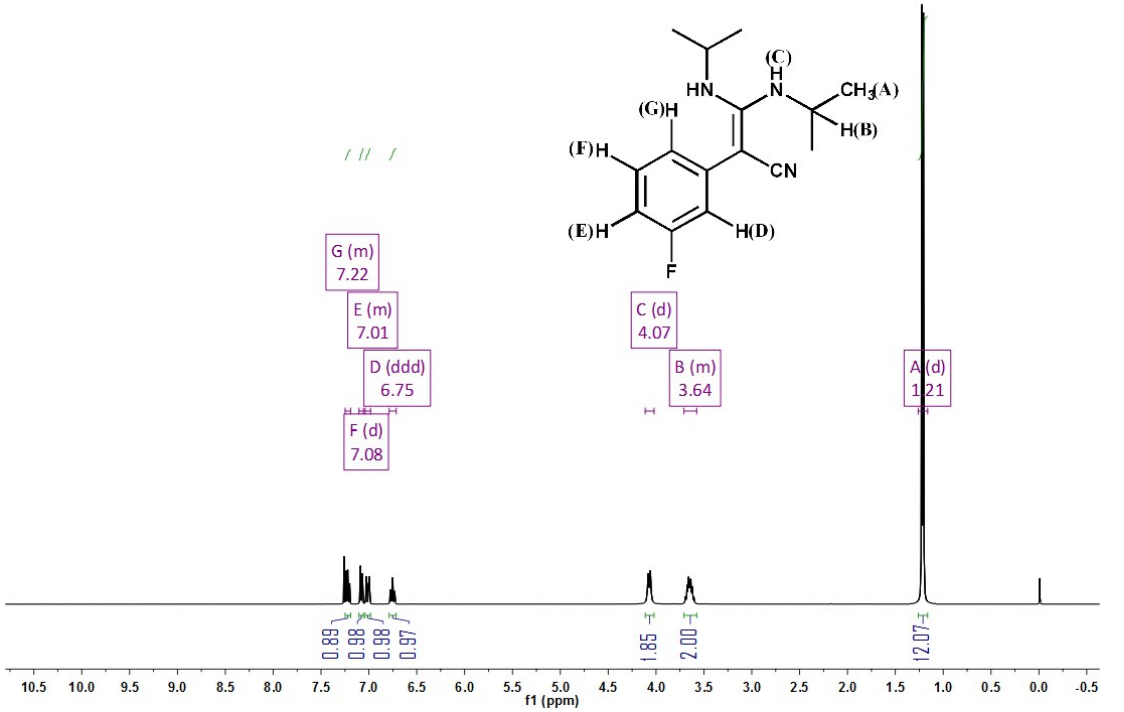

HN
H
N
CN

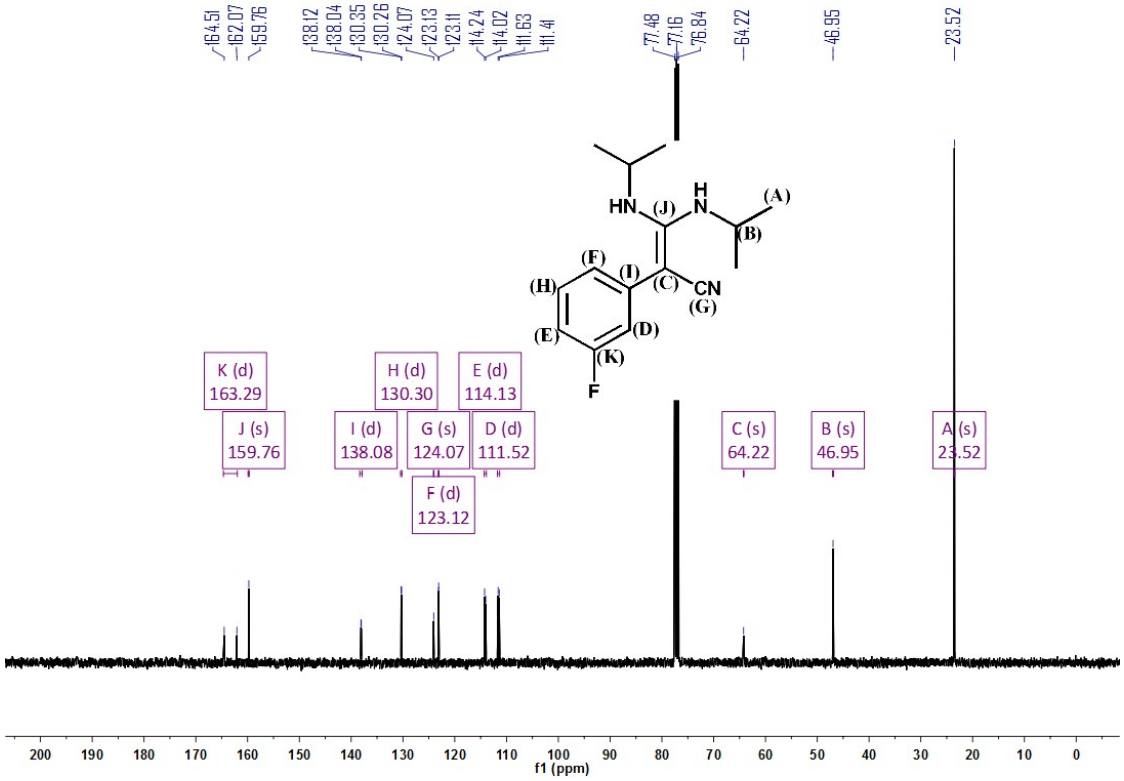

(D)
H
HN
N
CH3(A)
(G)H
H(C)
(F)
H
CN
H
(E)
H(G)
CH3(B)
F (d)
7.10
E (d)
6.91
G (dd)
7.17
D (d)
4.01
C (m)
3.63
B (s)
2.31
A (d)
1.20
2.00
0.99
0.98
1.91
2.00
3.04
11.88
f1 (ppm)


159.80
138.66
135.07
128.96
128.82
126.03
125.07
124.47
77.48
77.16
76.84
65.73
47.03
23.49
21.52
HN
(L)
H
N
(B)
(C)
(E)
(J)
(I)
(D)
CN
(F)
(H)
(G)
(K)
(A)
J (s)
135.07
H (s)
128.82
F (s)
125.07
L (s)
159.80
K (s)
138.66
E (s)
124.47
G (s)
126.03
I (s)
128.96
D (s)
65.73
C (s)
47.03
B (s)
23.49
A (s)
21.52
f1 (ppm)

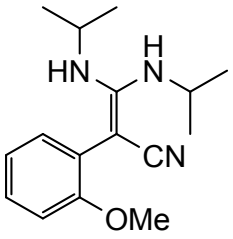
Compound **4k**

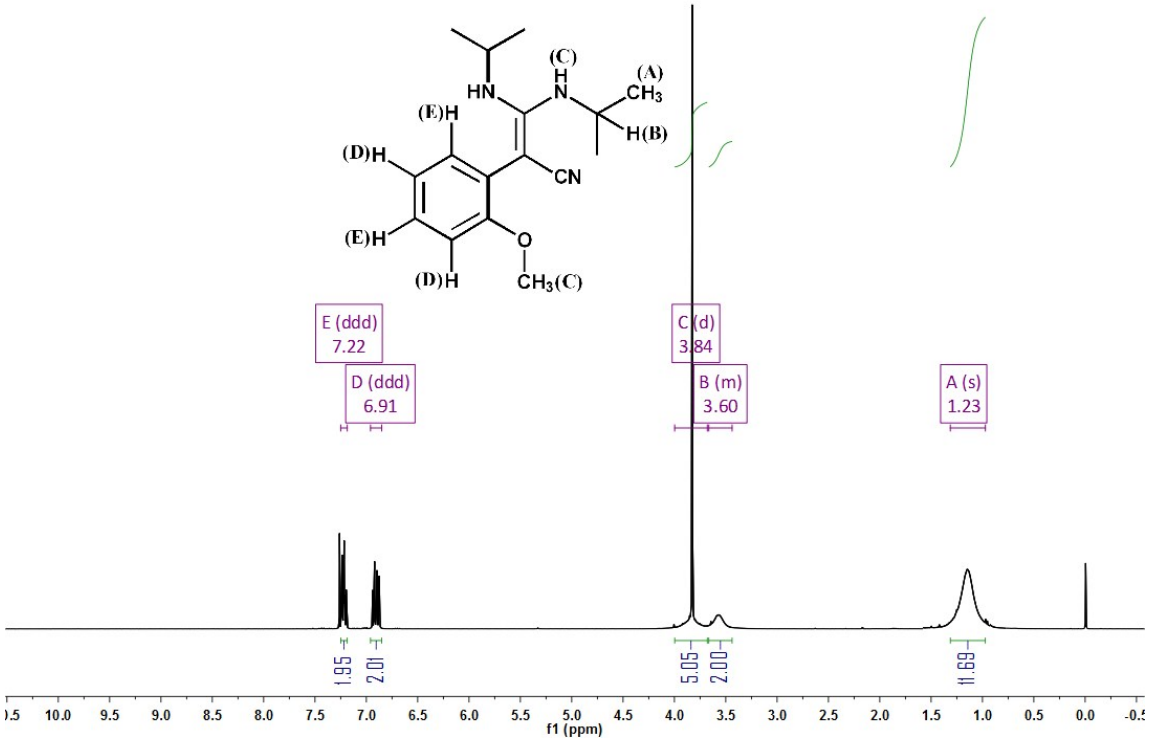

HN
H
N
CN
F

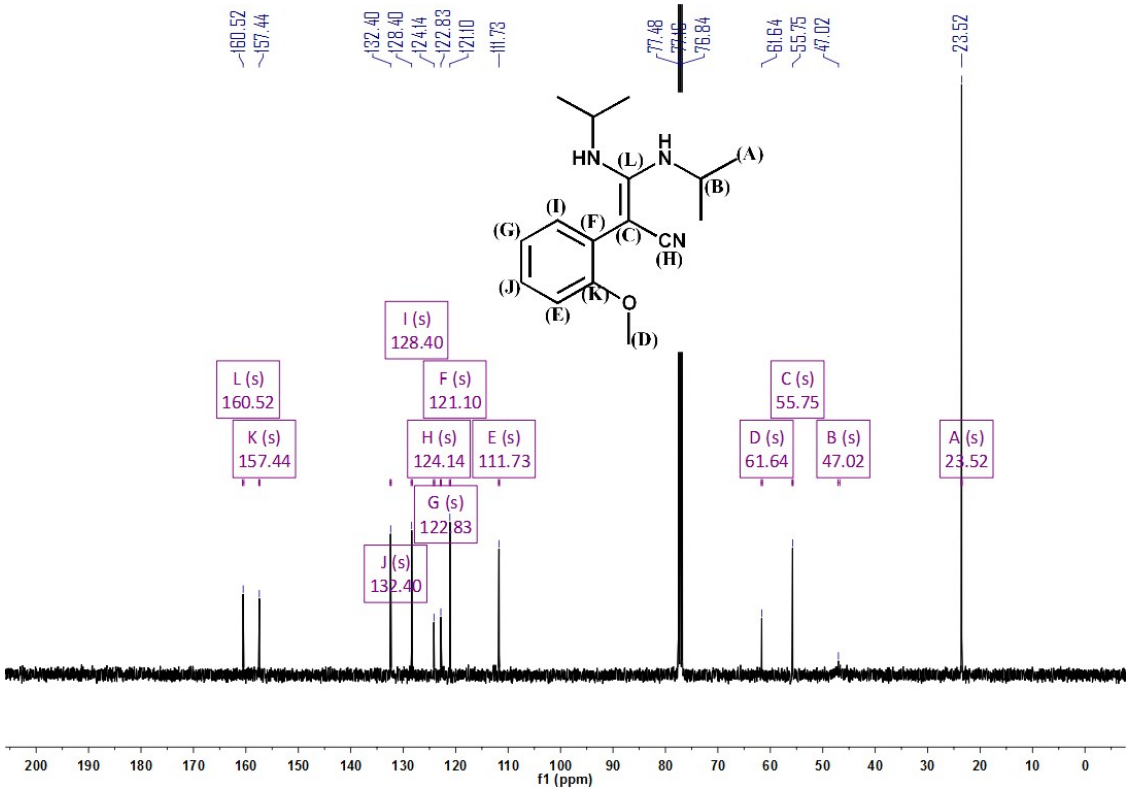

(C)
H
HN
N
CH3(A)
(G)H
H(B)
(F)H
CN
(E)H
H(D)
F
G (m)
7.22
E (m)
7.01
D (ddd)
6.75
F (d)
7.08
C (d)
4.07
B (m)
3.64
A (d)
1.21
0.89
0.98
0.98
0.97
1.85
2.00
12.07
f1 (ppm)


164.51
162.07
159.76
138.12
138.04
130.35
130.26
124.07
123.13
123.11
114.24
114.02
111.63
111.41
77.48
77.16
76.84
64.22
46.95
23.52
HN
(J)
N
(A)
(B)
(F)
(I)
(H)
(C)
CN
(G)
(E)
(D)
(K)
F
K (d)
163.29
J (s)
159.76
I (d)
138.08
H (d)
130.30
G (s)
124.07
F (d)
123.12
E (d)
114.13
D (d)
111.52
C (s)
64.22
B (s)
46.95
A (s)
23.52
f1 (ppm)

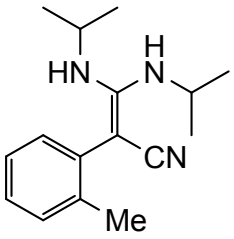
Compound **4l**

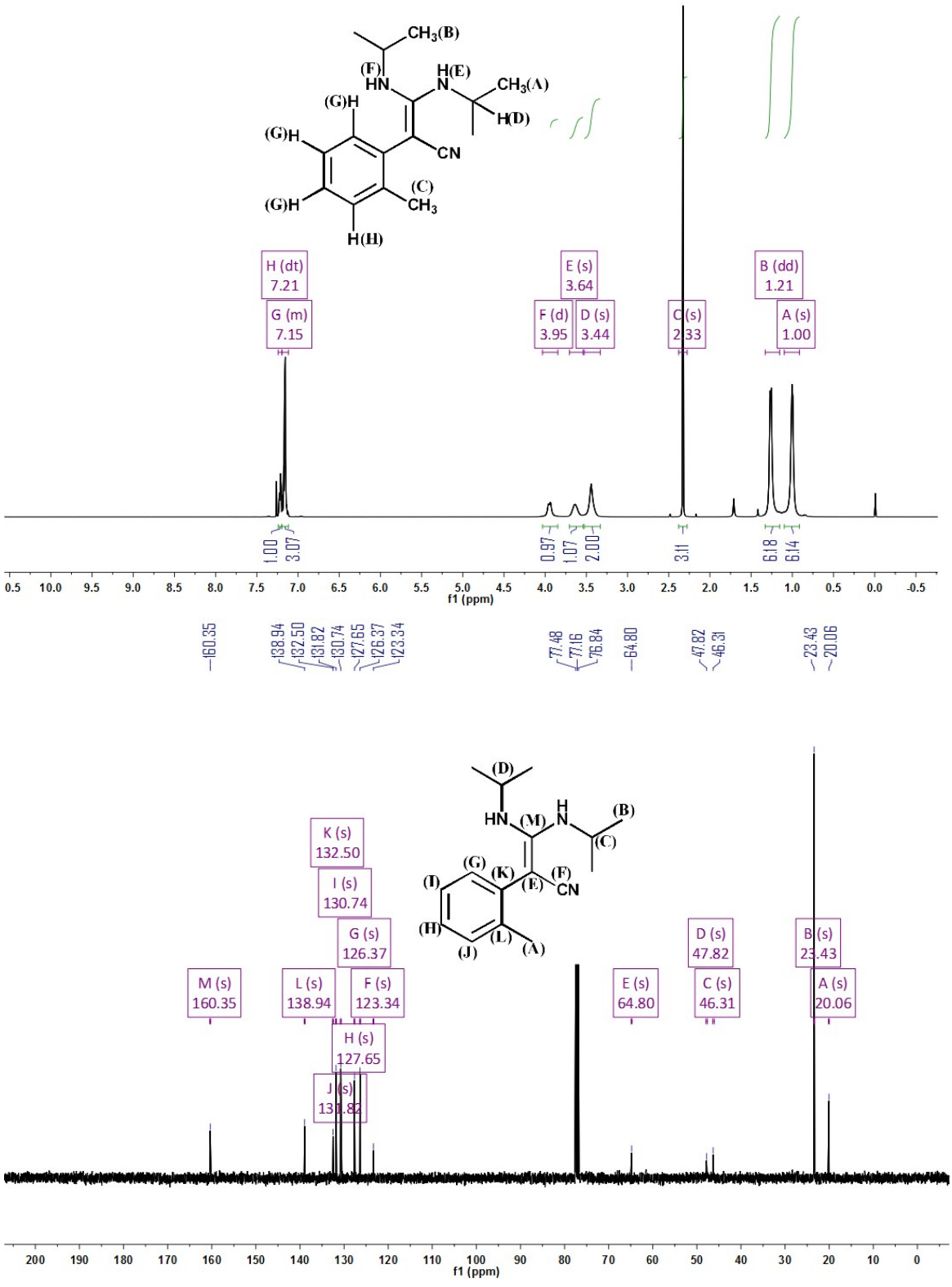

HN
H
N
CN
OMe


(C)
(A)
CH3
HN
H
N
(E)H
H(B)
(D)H
CN
(E)H
O
(D)H
CH3(C)
E (ddd) 7.22
D (ddd) 6.91
C (d) 3.84
B (m) 3.60
A (s) 1.23
1.95
2.01
5.05
2.00
11.69
f1 (ppm)

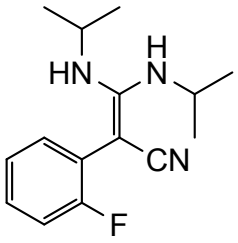

160.52
157.44
132.40
128.40
124.14
122.83
121.10
111.73
77.48
76.84
61.64
55.75
47.02
23.52
HN
(L)
H
N
(A)
(B)
(I)
(F)
(G)
(C)
CN
(H)
(J)
(K)
O
(E)
(D)
I (s) 128.40
L (s) 160.52
F (s) 121.10
C (s) 55.75
K (s) 157.44
H (s) 124.14
E (s) 111.73
D (s) 61.64
B (s) 47.02
A (s) 23.52
G (s) 122.83
J (s) 132.40
f1 (ppm)

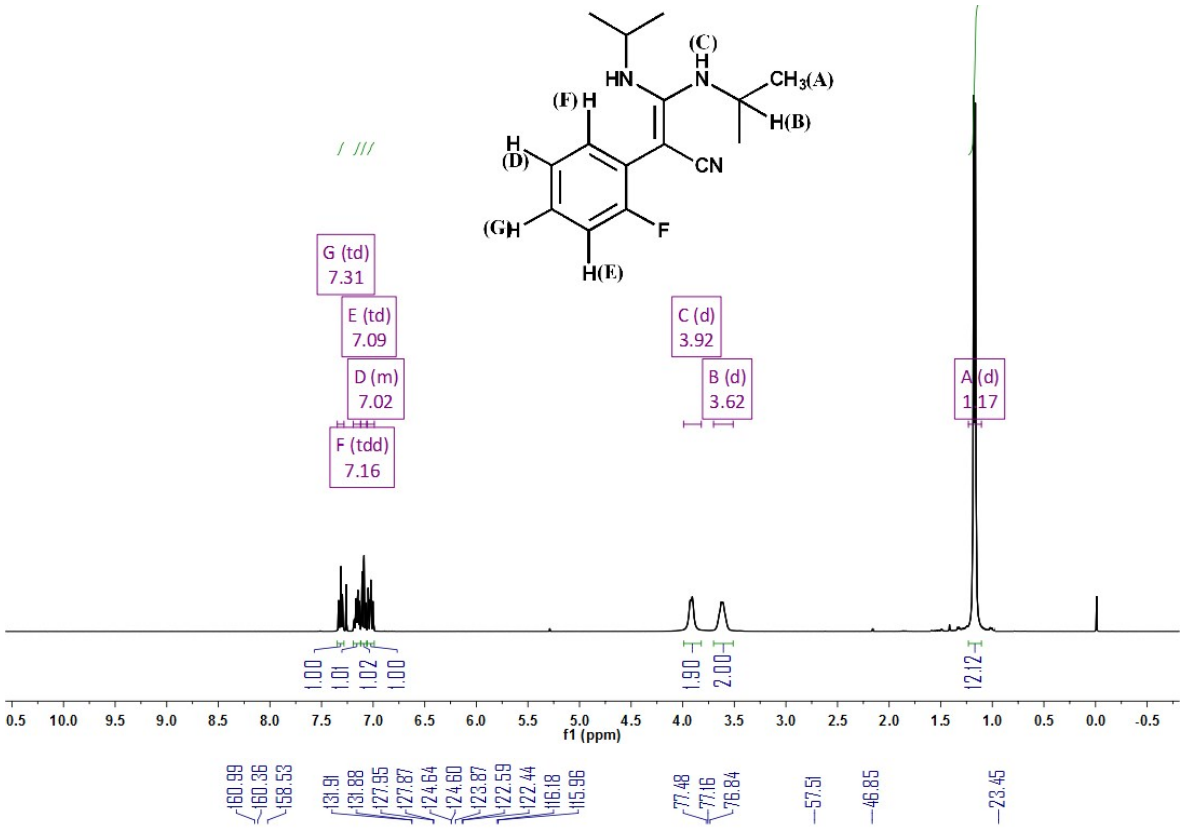
Compound **4m**

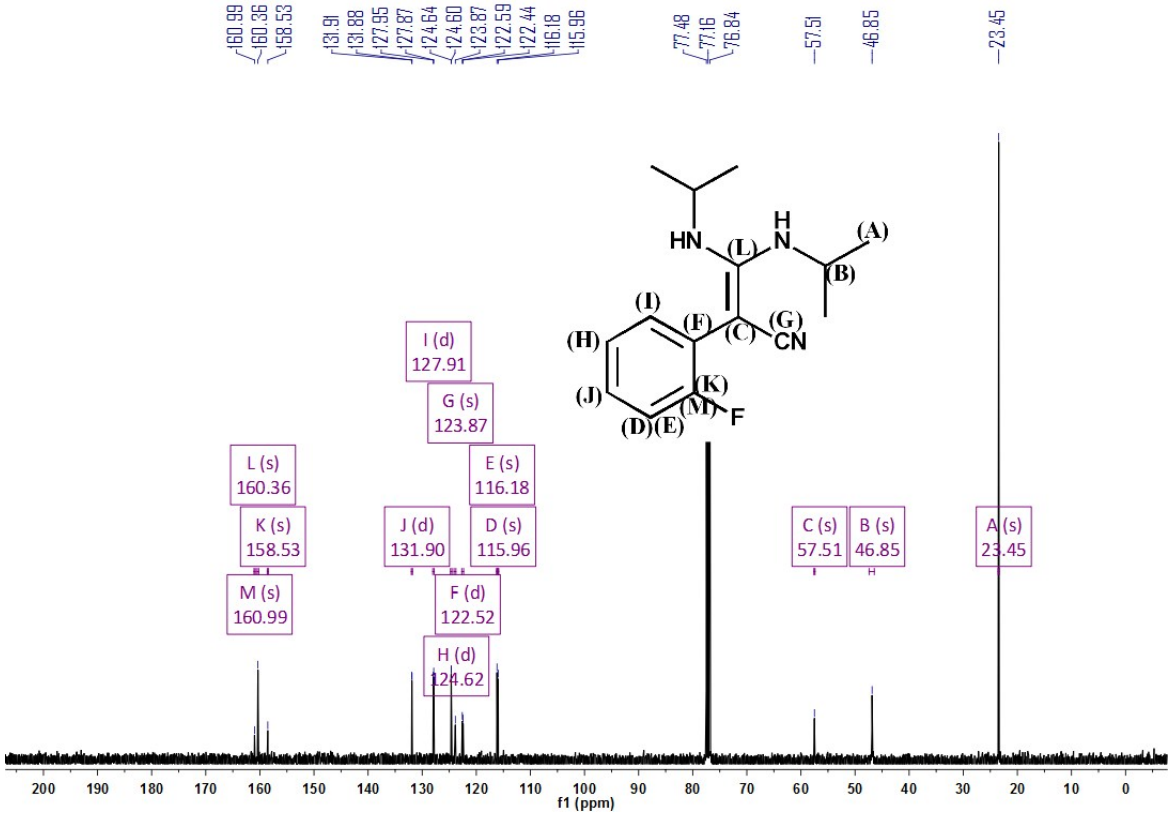

HN
H
N
CN
Me


CH3(B)
(F)
HN
H(E)
N
CH3(A)
H(D)
(G)H
CN
(G)H
(C)
CH3
(G)H
H(H)
H (dt) 7.21
G (m) 7.15
E (s) 3.64
F (d) 3.95
D (s) 3.44
C (s) 2.33
B (dd) 1.21
A (s) 1.00
1.00
3.07
0.97
1.07
2.00
3.11
6.18
6.14
f1 (ppm)
160.35
138.94
132.50
131.82
130.74
127.65
126.37
123.34
77.48
77.16
76.84
64.80
47.82
46.31
23.43
20.06
(D)
HN
(M)
H
N
(B)
(C)
(G)
(K)
(F)
(I)
(E)
CN
(H)
(L)
(A)
(J)
K (s) 132.50
I (s) 130.74
G (s) 126.37
M (s) 160.35
L (s) 138.94
F (s) 123.34
H (s) 127.65
J (s) 131.82
E (s) 64.80
D (s) 47.82
C (s) 46.31
B (s) 23.43
A (s) 20.06
f1 (ppm)

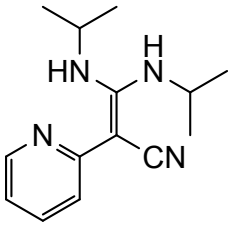
Compound **4n**

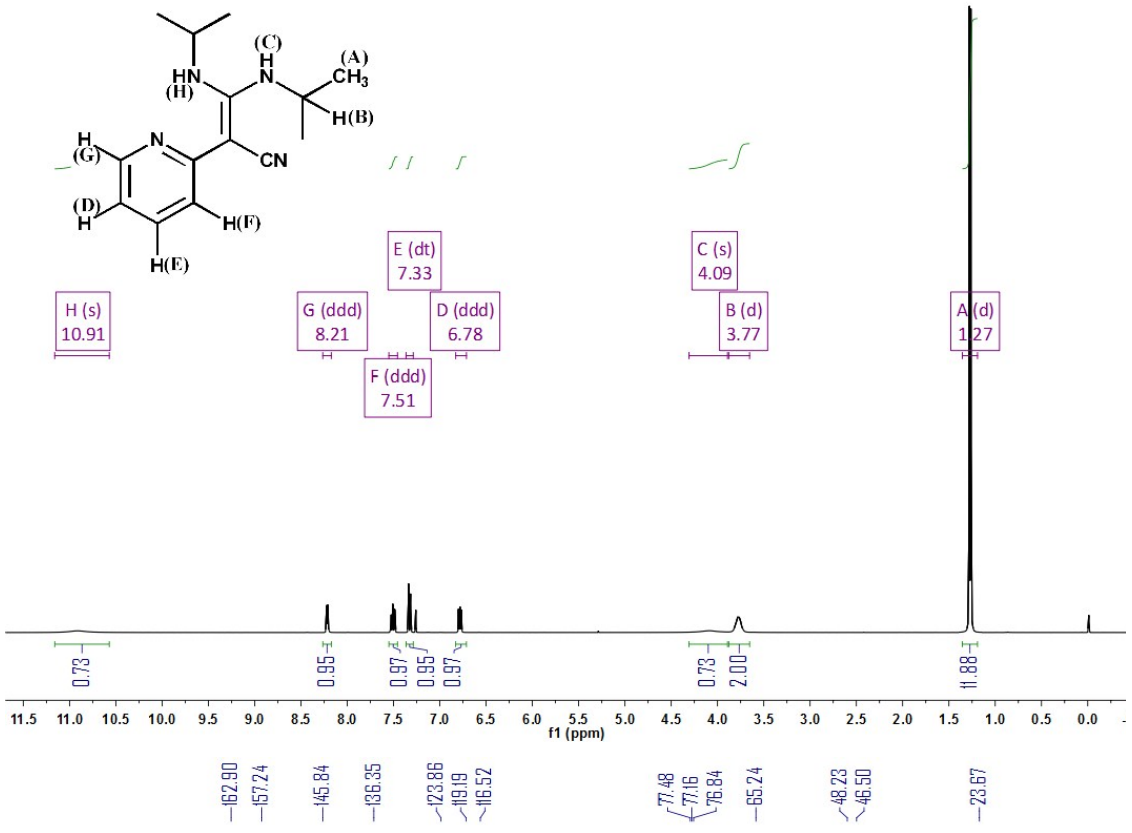

HN
H
N
CN
F

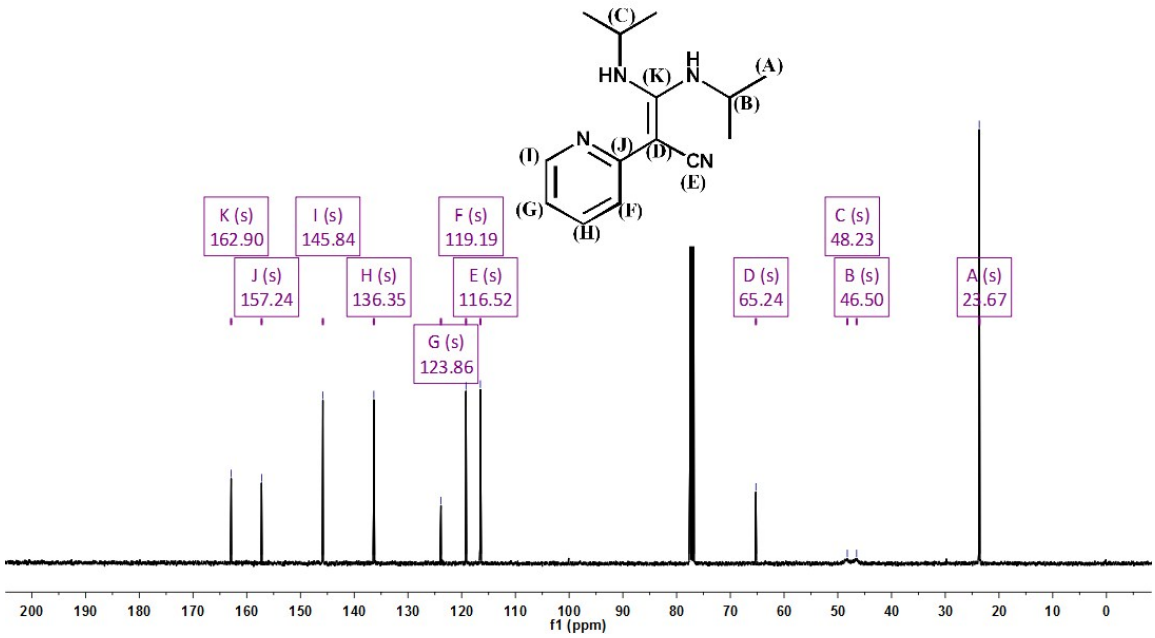

(C)
H
HN
N
CH3(A)
(F) H
H(B)
H
(D)
CN
(G)H
F
H(E)
G (td)
7.31
E (td)
7.09
D (m)
7.02
F (tdd)
7.16
C (d)
3.92
B (d)
3.62
A (d)
1.17
1.00
1.01
1.02
1.00
1.90
2.00
12.12
f1 (ppm)


160.99
160.36
158.53
131.91
131.88
127.95
127.87
124.64
124.60
123.87
122.59
122.44
116.18
115.96
77.48
77.16
76.84
57.51
46.85
23.45
HN
(L)
H
N
(A)
(B)
(I)
(F)
(G)
(H)
(C)
CN
(K)
(J)
(M)
F
(D)(E)
I (d)
127.91
G (s)
123.87
L (s)
160.36
E (s)
116.18
K (s)
158.53
J (d)
131.90
D (s)
115.96
C (s)
57.51
B (s)
46.85
A (s)
23.45
M (s)
160.99
F (d)
122.52
H (d)
124.62
f1 (ppm)

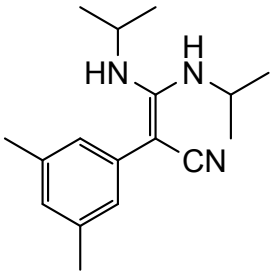
Compound **4o**

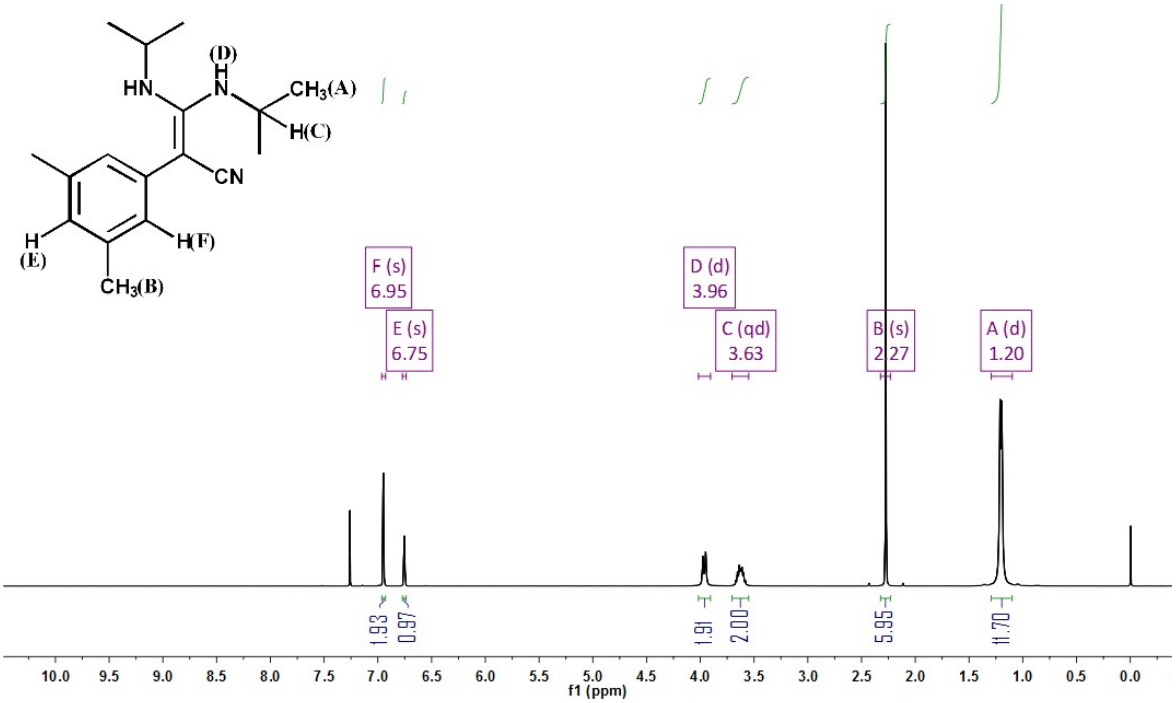

HN
H
N
N
CN

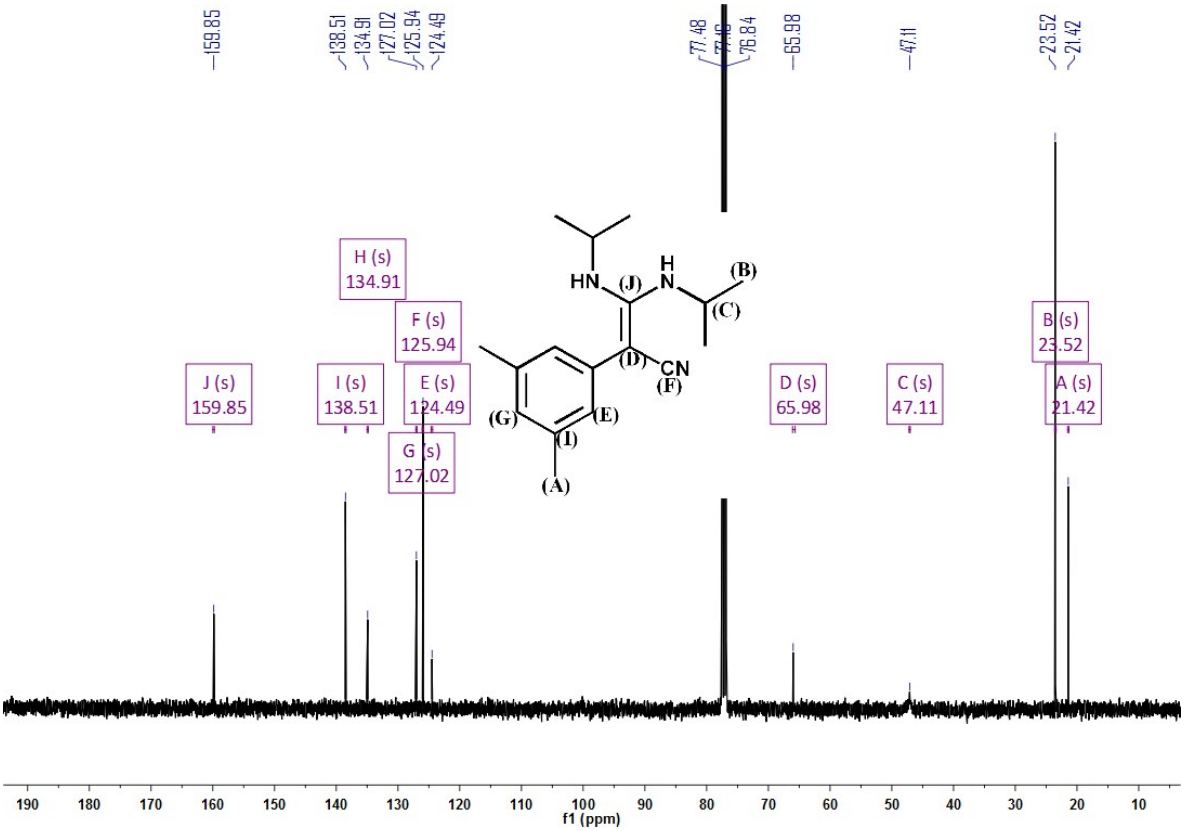

(C)
H
HN
(H)
N
(A)
CH3
H(B)
H
(G)
N
CN
(D)
H
H(F)
H(E)
H (s) 10.91
G (ddd) 8.21
E (dt) 7.33
F (ddd) 7.51
D (ddd) 6.78
C (s) 4.09
B (d) 3.77
A (d) 1.27
0.73
0.95
0.97
0.95
0.97
0.73
2.00
11.88
f1 (ppm)


(C)
HN
(K)
H
N
(A)
(B)
(I)
N
(J)
(D)
CN
(E)
(G)
(F)
(H)
K (s) 162.90
J (s) 157.24
I (s) 145.84
H (s) 136.35
F (s) 119.19
E (s) 116.52
G (s) 123.86
D (s) 65.24
C (s) 48.23
B (s) 46.50
A (s) 23.67
f1 (ppm)

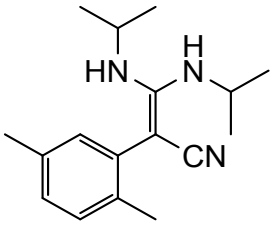
Compound **4p**

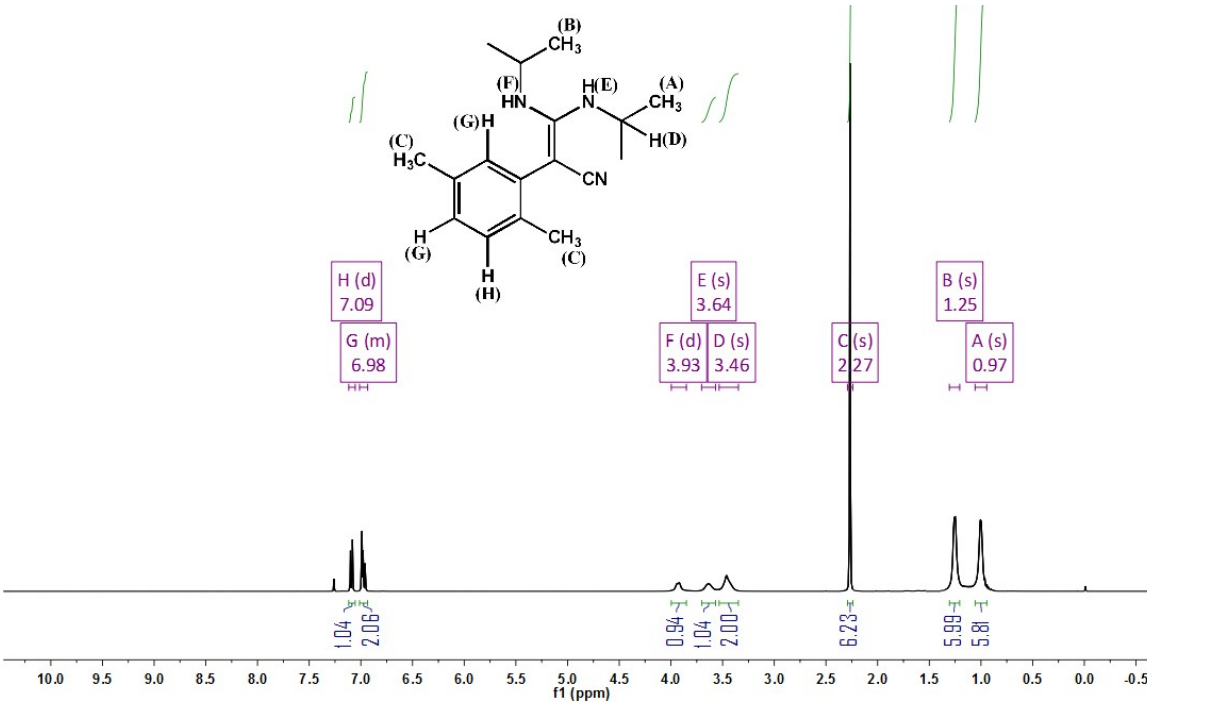


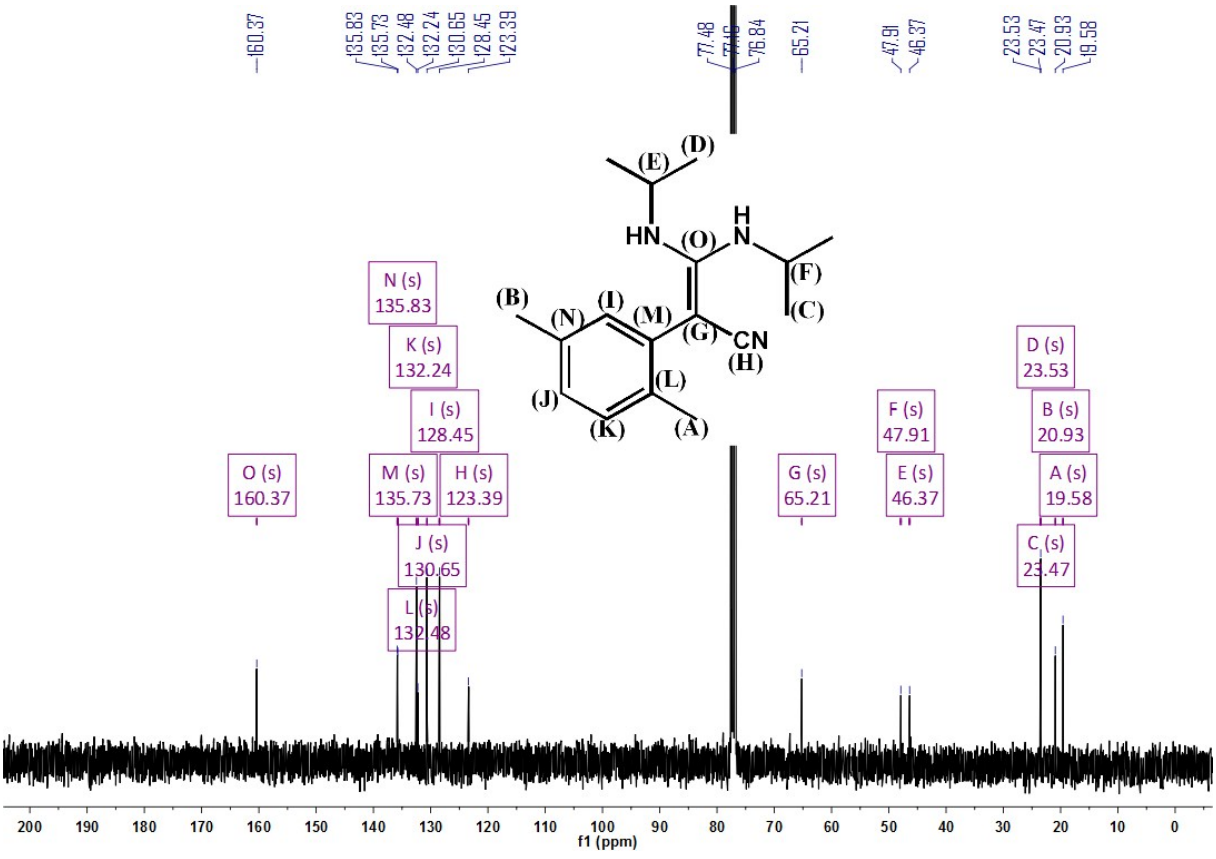

(D)
HN
N
CH3(A)
H(C)
CN
H(F)
H
(E)
CH3(B)
F (s)
6.95
E (s)
6.75
D (d)
3.96
C (qd)
3.63
B (s)
2.27
A (d)
1.20
1.93
0.97
1.91
2.00
5.95
11.70
f1 (ppm)


159.85
138.51
134.91
127.02
125.94
124.49
77.48
76.84
65.98
47.11
23.52
21.42
H (s)
134.91
F (s)
125.94
J (s)
159.85
I (s)
138.51
E (s)
124.49
G (s)
127.02
HN
(J)
H
N
(B)
(C)
(D)
CN
(F)
(G)
(E)
(I)
(A)
B (s)
23.52
D (s)
65.98
C (s)
47.11
A (s)
21.42
f1 (ppm)

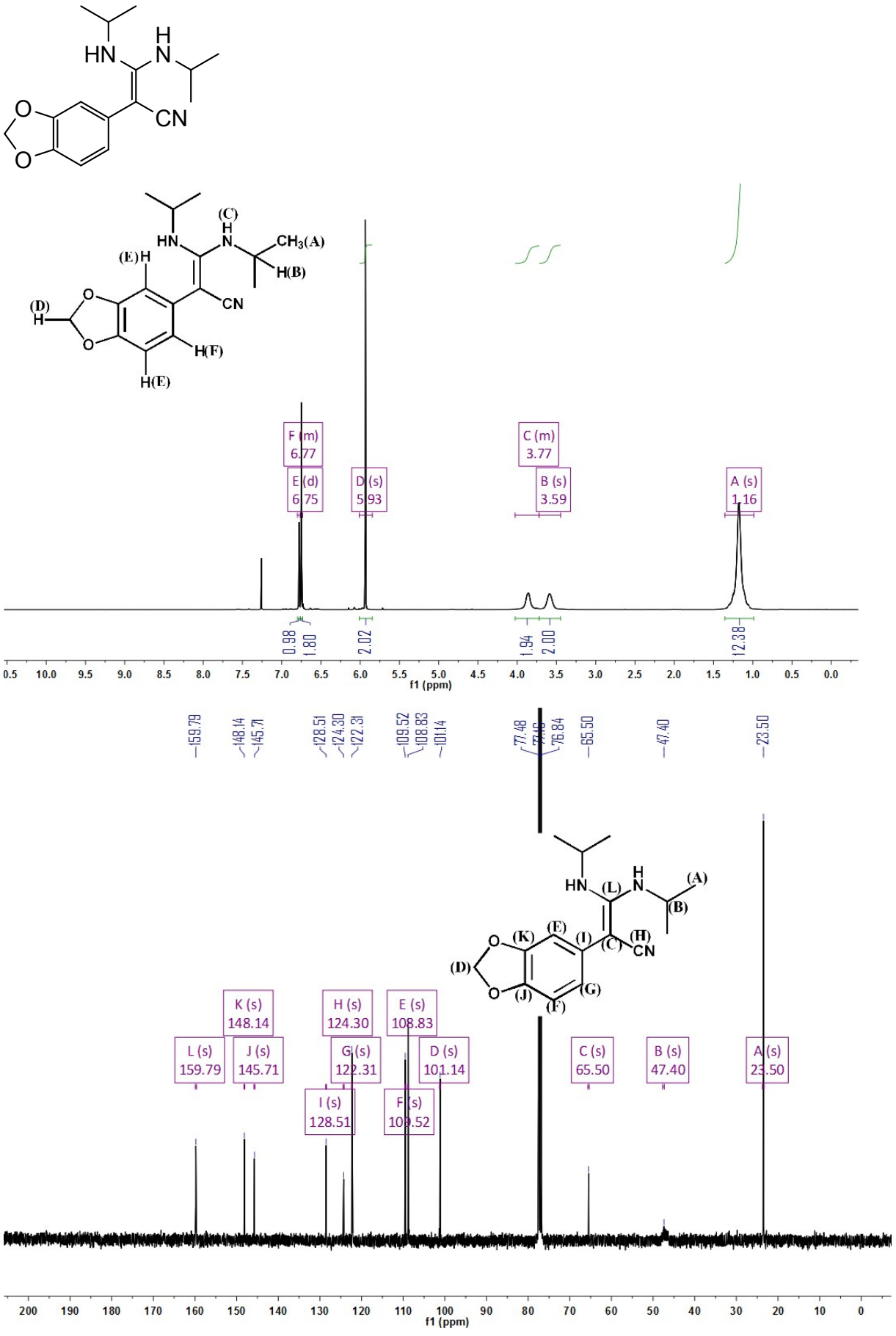
Compound **4q**


HN
H
N
CN

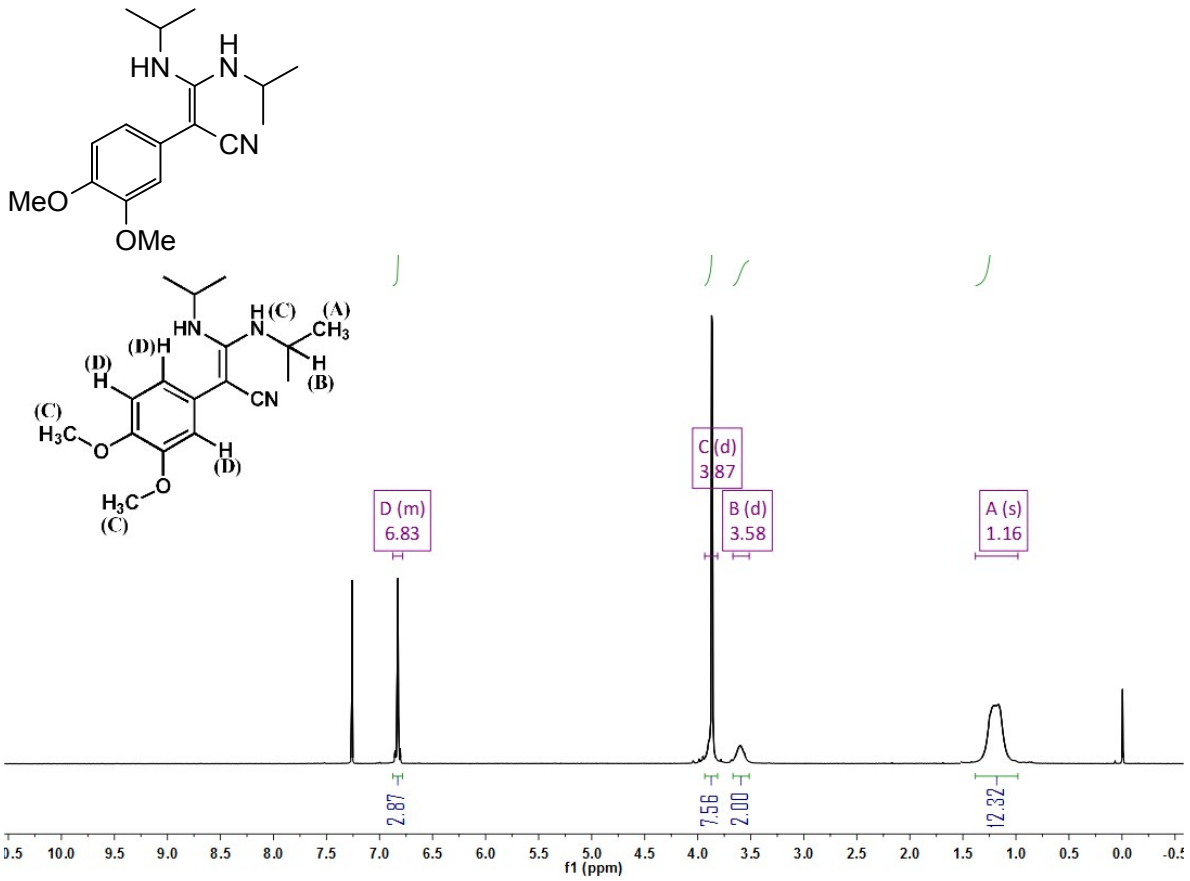

(B)
CH3
(F)
HN
H(E)
N
(A)
CH3
(G)H
H(D)
(C)
H3C
CN
H
(G)
CH3
(C)
H
(H)
H (d)
7.09
G (m)
6.98
E (s)
3.64
F (d)
3.93
D (s)
3.46
C (s)
2.27
B (s)
1.25
A (s)
0.97
1.04
2.06
0.94
1.04
2.00
6.23
5.99
5.81
f1 (ppm)

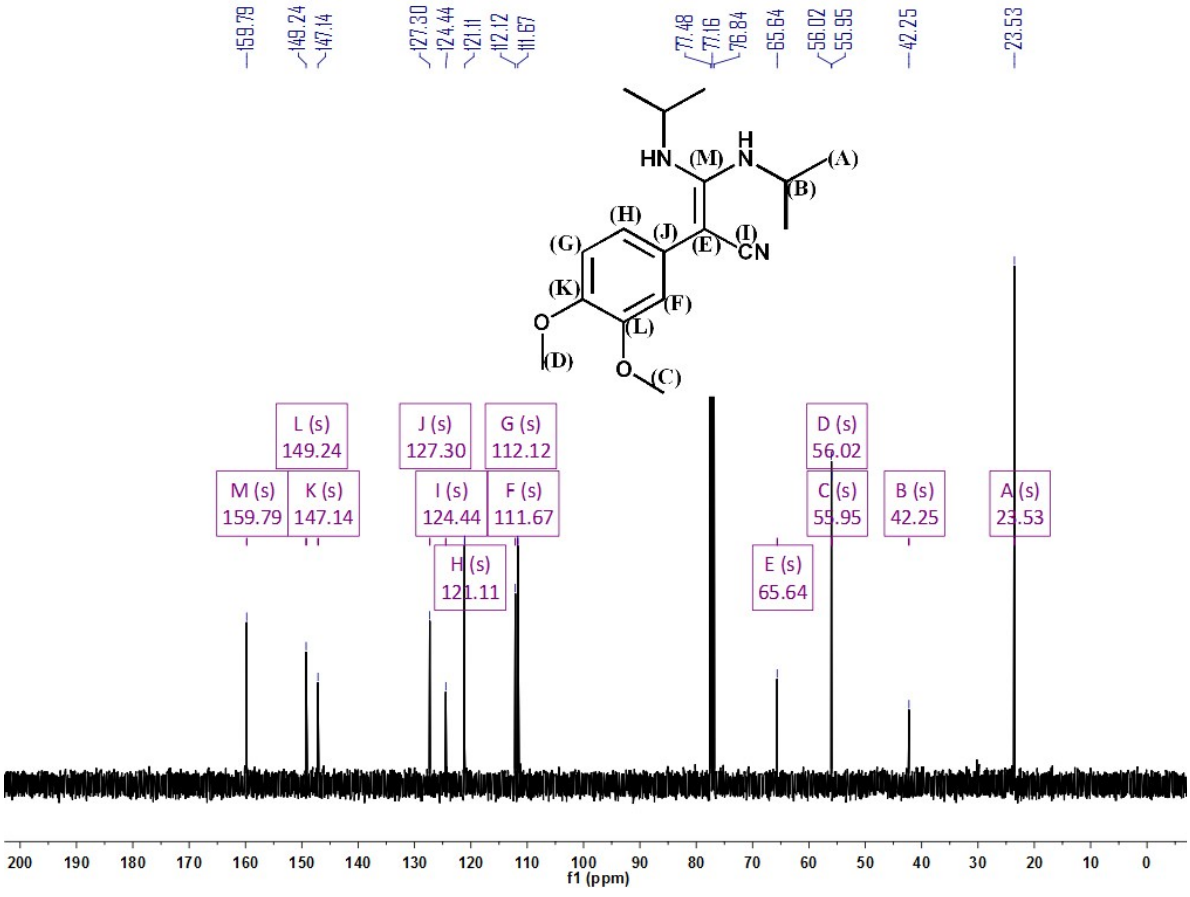

160.37
135.83
135.73
132.48
132.24
130.65
128.45
123.39
77.48
76.84
65.21
47.91
46.37
23.53
23.47
20.93
19.58
(D)
(E)
HN
(O)
H
N
(F)
(C)
(B)
(N)
(I)
(M)
(G)
CN
(H)
(L)
(J)
(K)
(A)
N (s)
135.83
K (s)
132.24
I (s)
128.45
O (s)
160.37
M (s)
135.73
H (s)
123.39
J (s)
130.65
L (s)
132.48
G (s)
65.21
F (s)
47.91
E (s)
46.37
D (s)
23.53
B (s)
20.93
A (s)
19.58
C (s)
23.47
f1 (ppm)

Compound **4r**

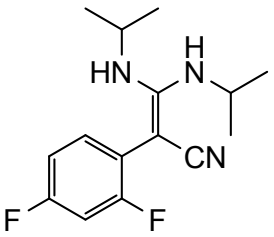

F (m) 6.77
E (d) 6.75
D (s) 5.93
C (m) 3.77
B (s) 3.59
A (s) 1.16
0.98
1.80
2.02
1.94
2.00
12.38
f1 (ppm)
159.79
148.14
145.71
128.51
124.30
122.31
109.52
108.83
101.14
77.48
76.84
65.50
47.40
23.50
K (s) 148.14
H (s) 124.30
E (s) 108.83
L (s) 159.79
J (s) 145.71
G (s) 122.31
D (s) 101.14
C (s) 65.50
B (s) 47.40
A (s) 23.50
I (s) 128.51
F (s) 109.52
f1 (ppm)

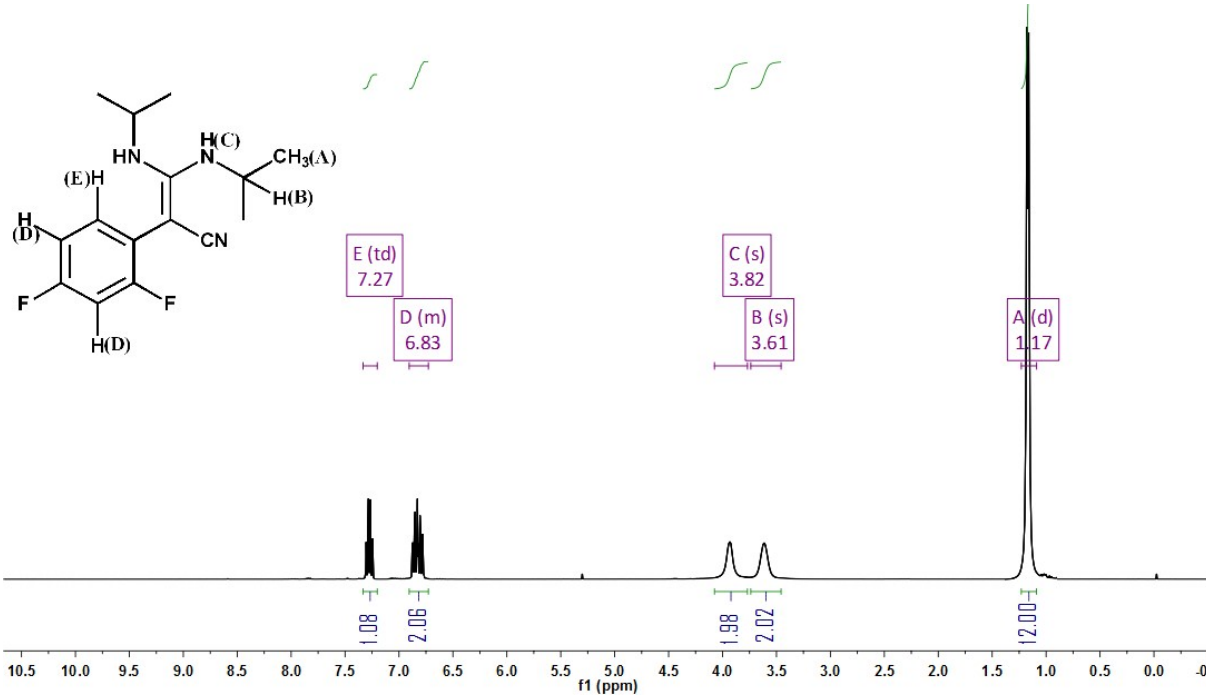
Compound **4s**


MeO
OMe
HN
H
N
CN
D (m)
6.83
C (d)
3.87
B (d)
3.58
A (s)
1.16
2.87
7.56
2.00
12.32
f1 (ppm)

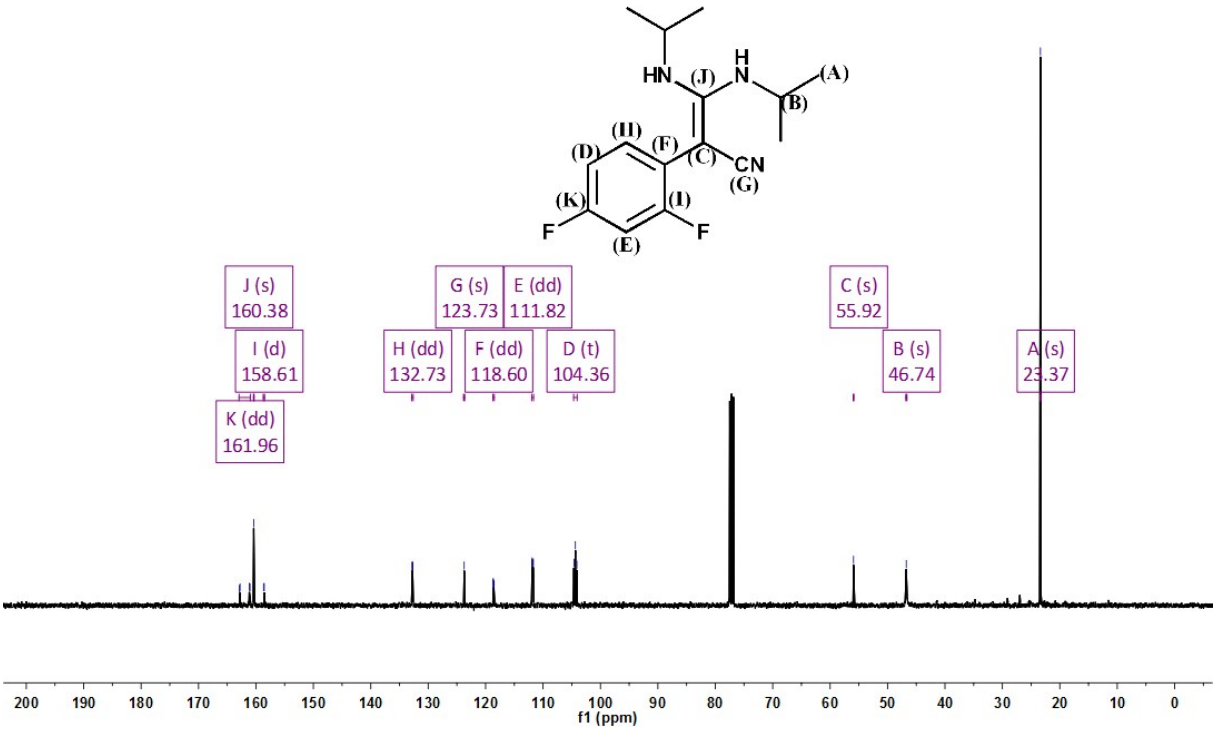

159.79
149.24
147.14
127.30
124.44
121.11
112.12
111.67
77.48
77.16
76.84
65.64
56.02
55.95
42.25
23.53
HN
(M)
H
N
(A)
(B)
(H)
(J)
(E)
(I)
CN
(G)
(K)
(F)
(L)
(D)
(C)
L (s)
149.24
J (s)
127.30
G (s)
112.12
D (s)
56.02
M (s)
159.79
K (s)
147.14
I (s)
124.44
F (s)
111.67
C (s)
55.95
B (s)
42.25
A (s)
23.53
H (s)
121.11
E (s)
65.64
f1 (ppm)

Compound **4t**

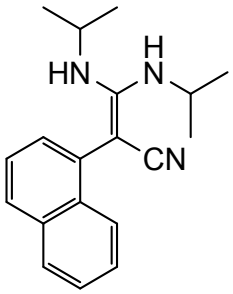

HN
H
N
CN
F
F

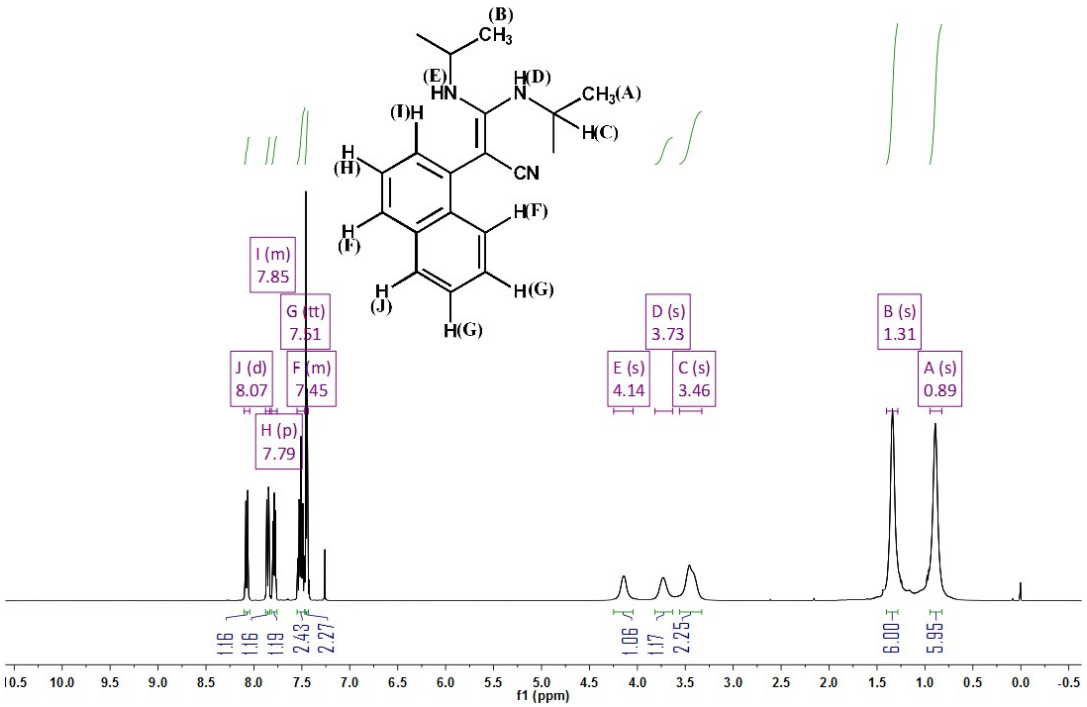

HN
H(C)
N
CH3(A)
H(B)
(E)H
H
(D)
CN
F
F
H(D)
E (td)
7.27
D (m)
6.83
C (s)
3.82
B (s)
3.61
A (d)
1.17
1.08
2.06
1.98
2.02
12.00
f1 (ppm)

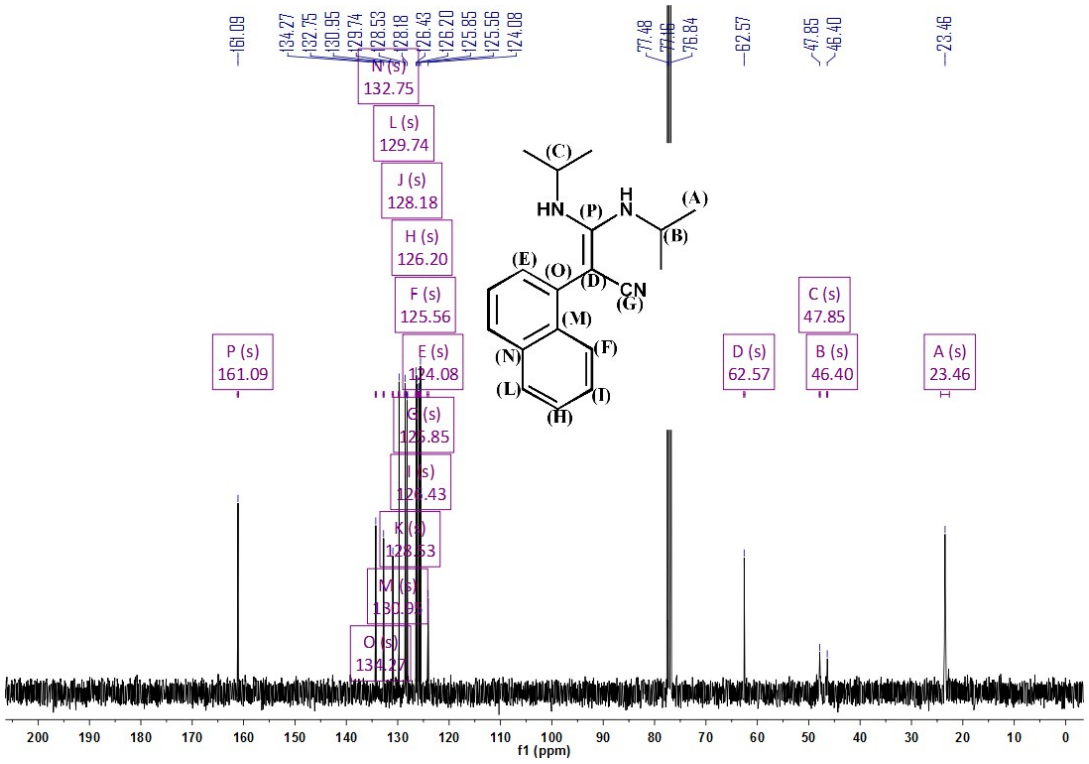

162.88
162.77
161.15
161.03
160.38
158.67
158.55
132.80
132.76
132.71
132.66
123.73
118.70
118.66
118.55
118.51
111.94
111.90
111.73
111.69
104.62
104.37
104.11
55.92
46.74
23.37


HN
(J)
H
N
(A)
(B)
(H)
(D)
(F)
(C)
CN
(G)
(K)
(I)
F
F
(E)
J (s)
160.38
I (d)
158.61
K (dd)
161.96
G (s)
123.73
E (dd)
111.82
H (dd)
132.73
F (dd)
118.60
D (t)
104.36
C (s)
55.92
B (s)
46.74
A (s)
23.37
f1 (ppm)

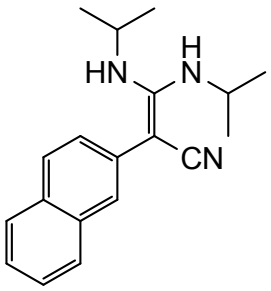
Compound **4u**

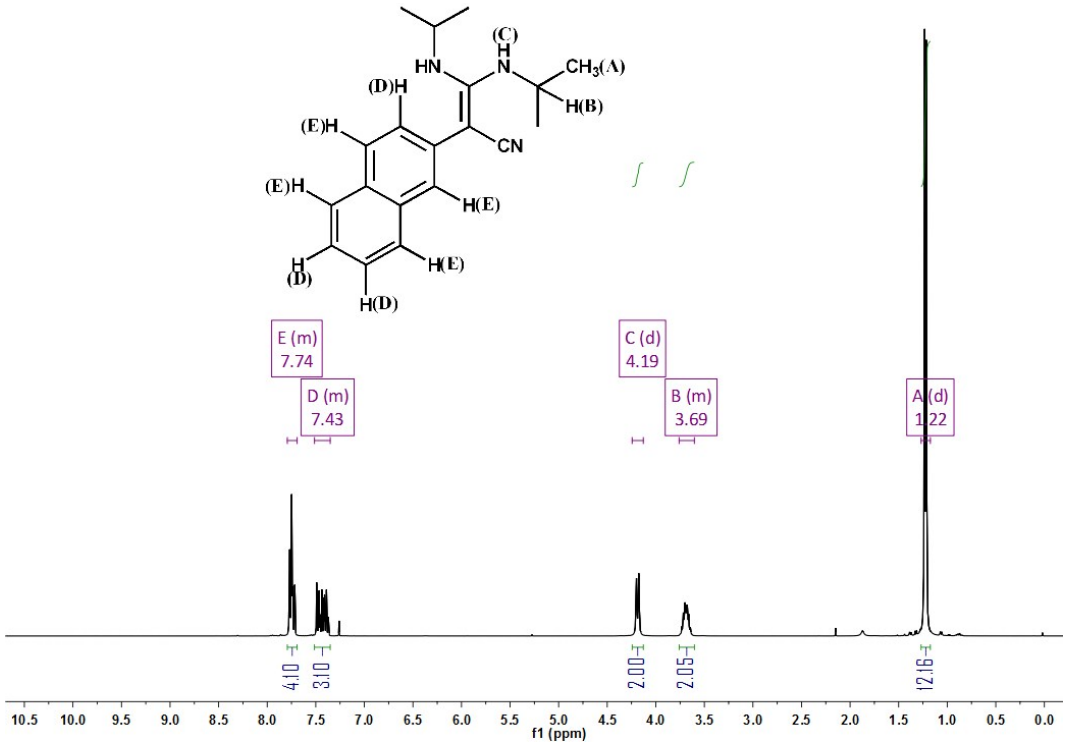


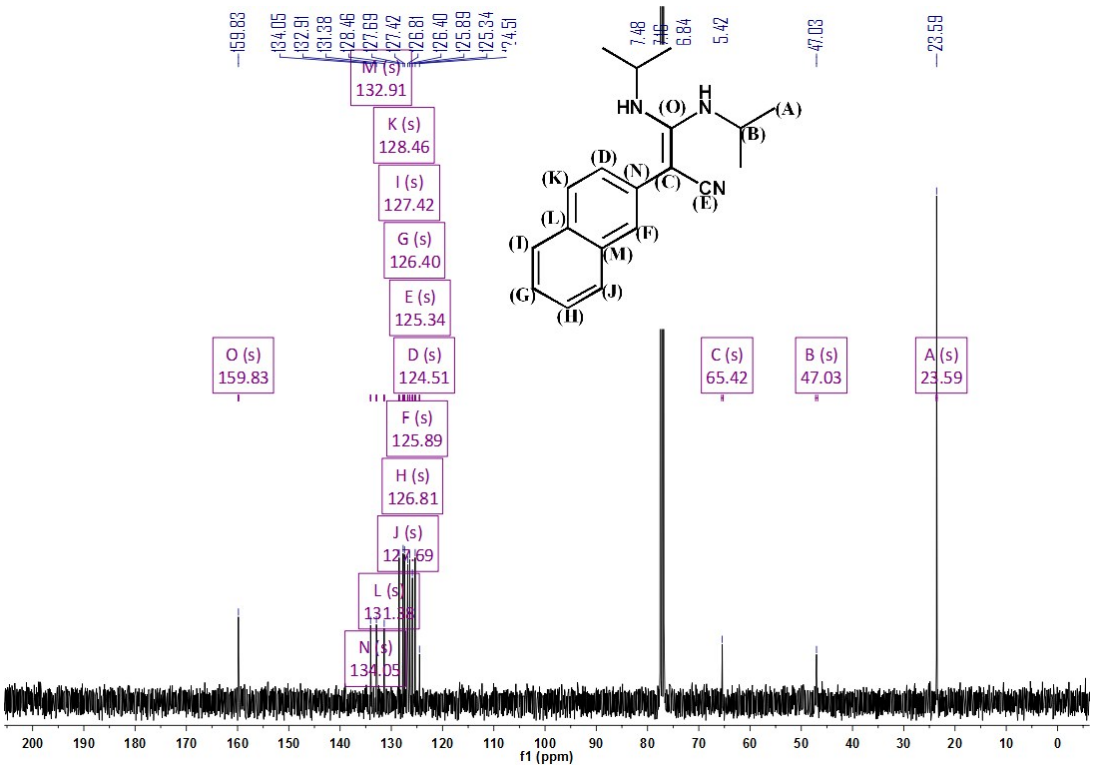

I (m) 7.85
G (tt) 7.51
J (d) 8.07
F (m) 7.45
H (p) 7.79
D (s) 3.73
E (s) 4.14
C (s) 3.46
B (s) 1.31
A (s) 0.89
1.16
1.16
1.19
2.43
2.27
1.06
1.17
2.25
6.00
5.95
f1 (ppm)


N (s) 132.75
L (s) 129.74
J (s) 128.18
H (s) 126.20
F (s) 125.56
E (s) 124.08
P (s) 161.09
D (s) 62.57
C (s) 47.85
B (s) 46.40
A (s) 23.46
f1 (ppm)

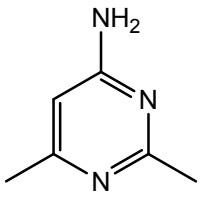
Compound **4v**

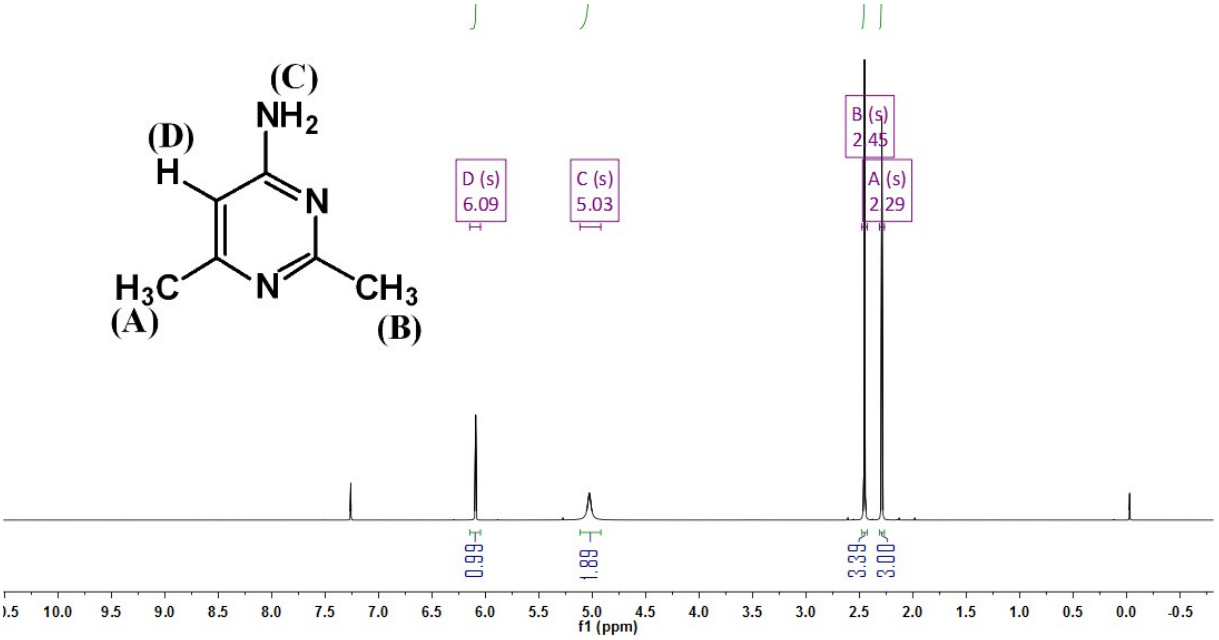


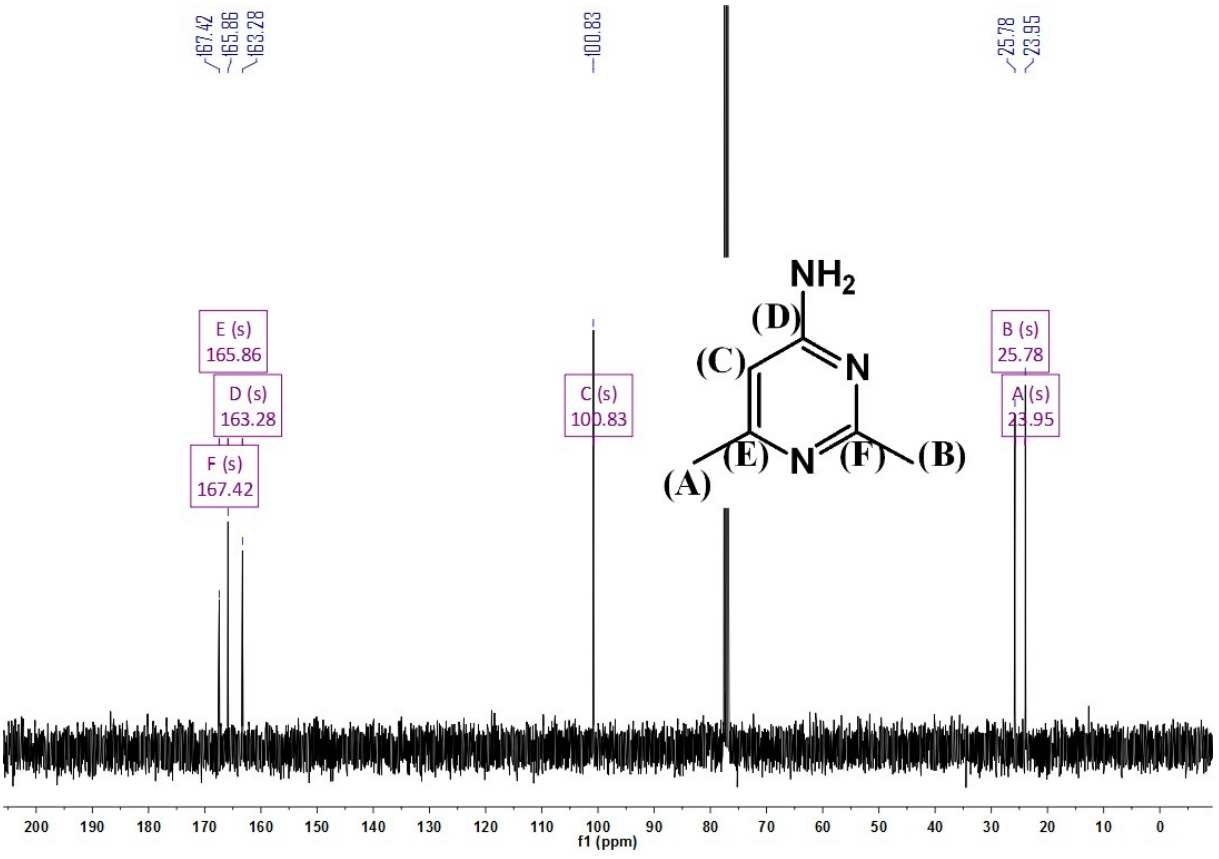

E (m)
7.74
D (m)
7.43
C (d)
4.19
B (m)
3.69
A (d)
1.22
4.10
3.10
2.00
2.05
12.16
f1 (ppm)


M (s)
132.91
K (s)
128.46
I (s)
127.42
G (s)
126.40
E (s)
125.34
D (s)
124.51
F (s)
125.89
H (s)
126.81
J (s)
127.69
L (s)
131.38
N (s)
134.05
O (s)
159.83
C (s)
65.42
B (s)
47.03
A (s)
23.59
f1 (ppm)

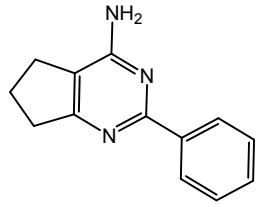
Compound **5a**

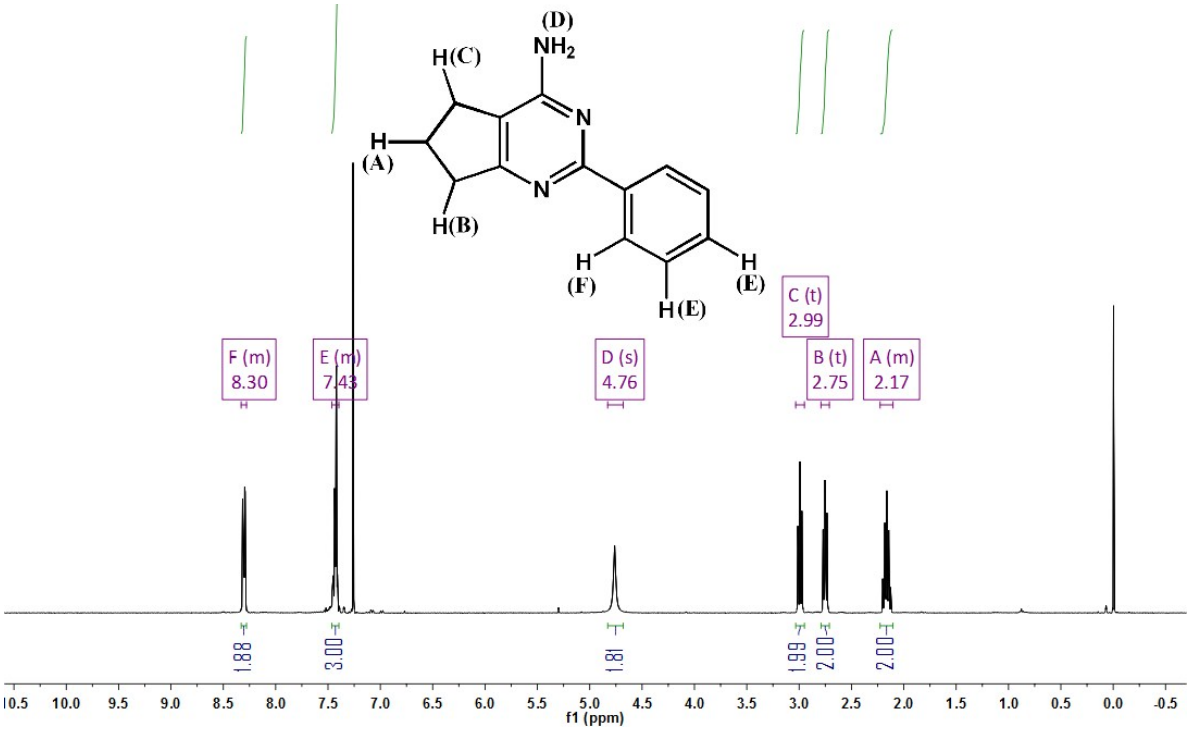

NH2
N
N

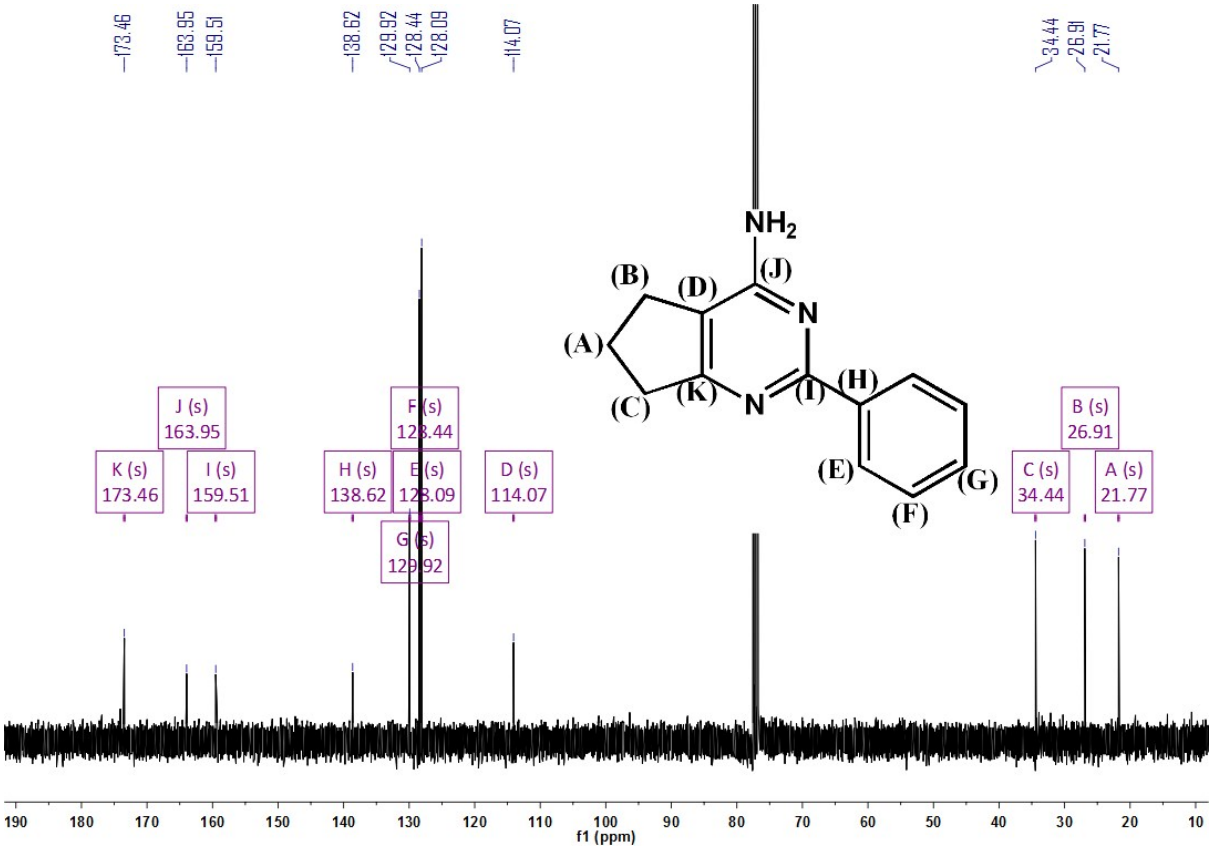

(C)
NH2
(D)
H
N
H3C
N
CH3
(A)
(B)
D (s)
6.09
C (s)
5.03
B (s)
2.45
A (s)
2.29
0.99
1.89
3.39
3.00
f1 (ppm)


167.42
165.86
163.28
100.83
25.78
23.95
E (s)
165.86
D (s)
163.28
F (s)
167.42
C (s)
100.83
B (s)
25.78
A (s)
23.95
NH2
(D)
(C)
N
(E)
N
(F)
(B)
(A)
f1 (ppm)

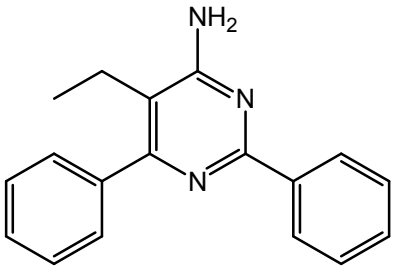
Compound **5b**

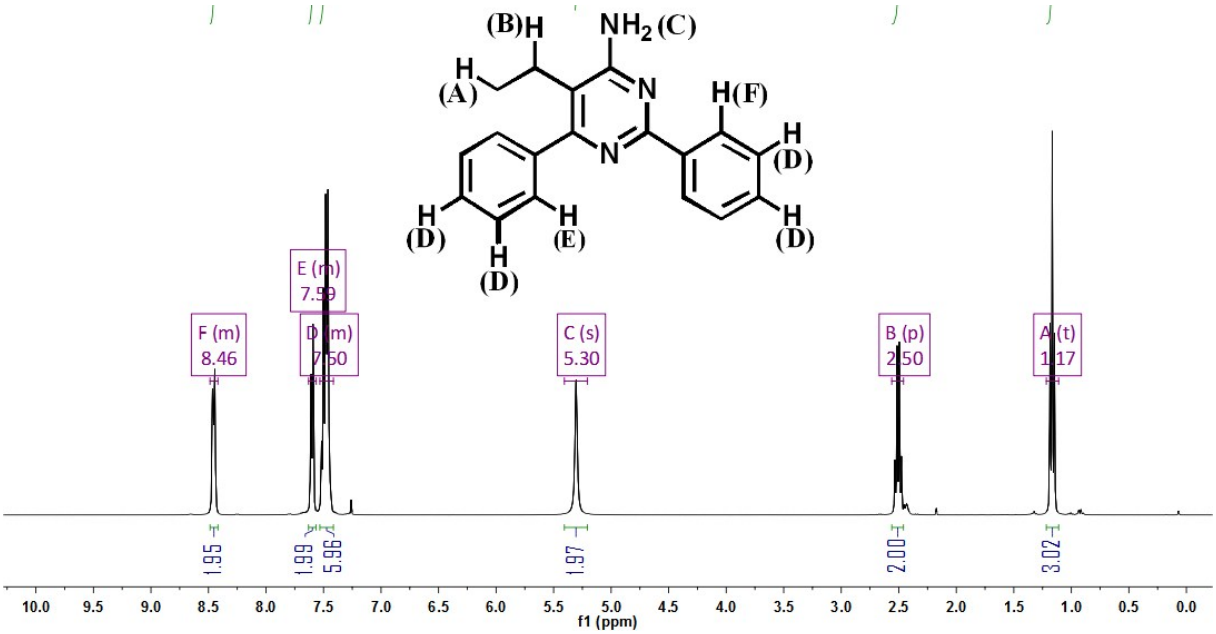


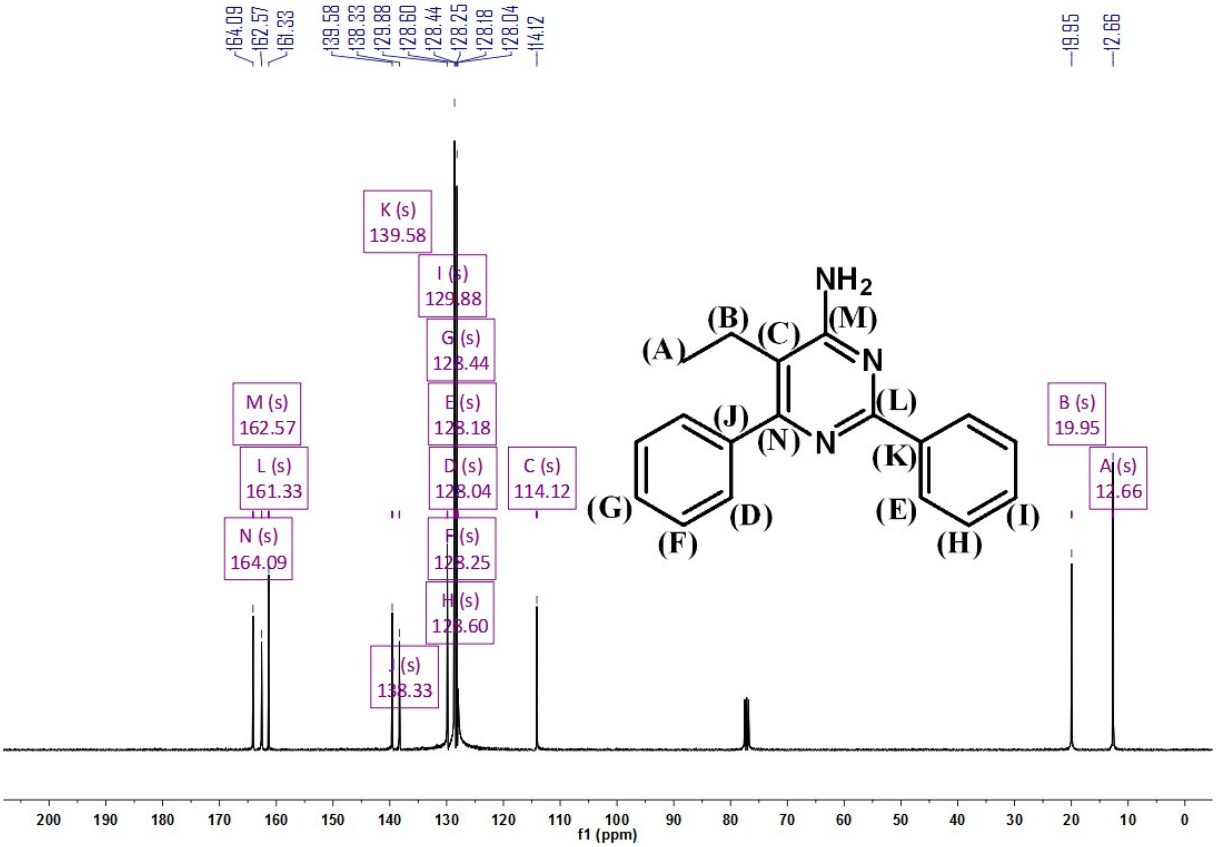

(D)
NH2
H(C)
H
(A)
H(B)
N
N
H
(F)
H(E)
H
(E)
F (m)
8.30
E (m)
7.43
D (s)
4.76
C (t)
2.99
B (t)
2.75
A (m)
2.17
1.88
3.00
1.81
1.99
2.00
2.00
f1 (ppm)


173.46
163.95
159.51
138.62
129.92
128.44
128.09
114.07
34.44
26.91
21.77
NH2
(B)
(D)
(J)
(A)
N
(C)
(K)
N
(I)
(H)
(E)
(G)
(F)
J (s)
163.95
K (s)
173.46
I (s)
159.51
F (s)
128.44
H (s)
138.62
E (s)
128.09
G (s)
129.92
D (s)
114.07
B (s)
26.91
C (s)
34.44
A (s)
21.77
f1 (ppm)

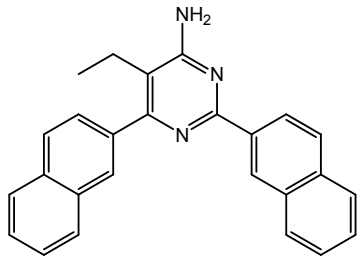
Compound **5c**

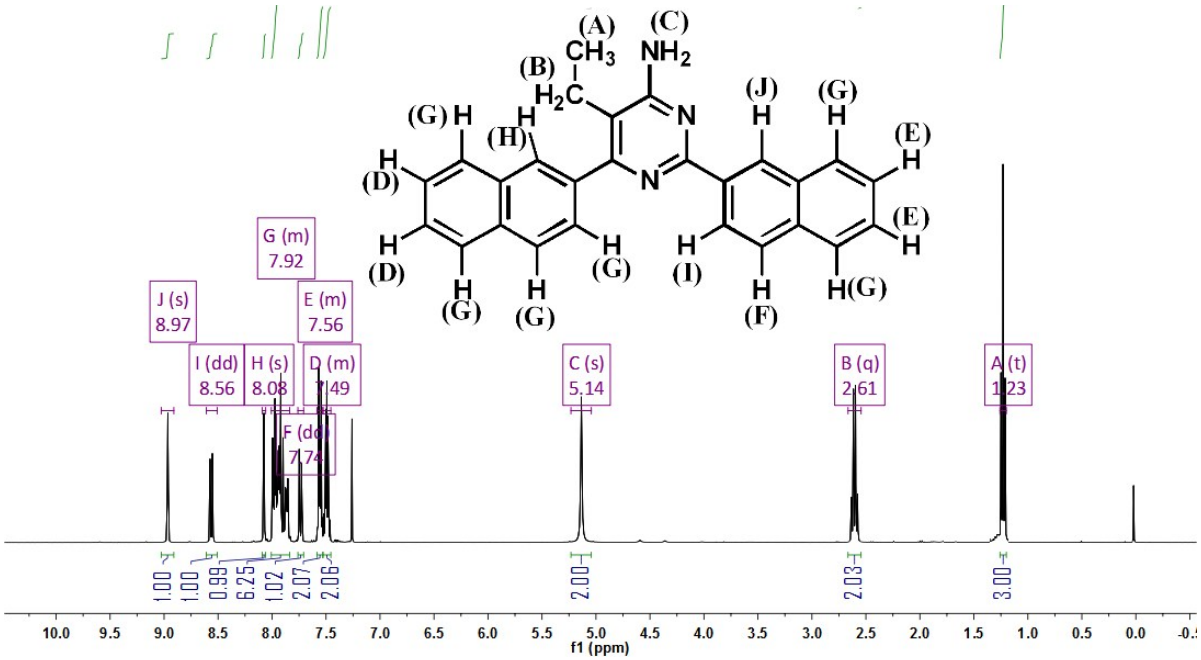

NH2
N
N

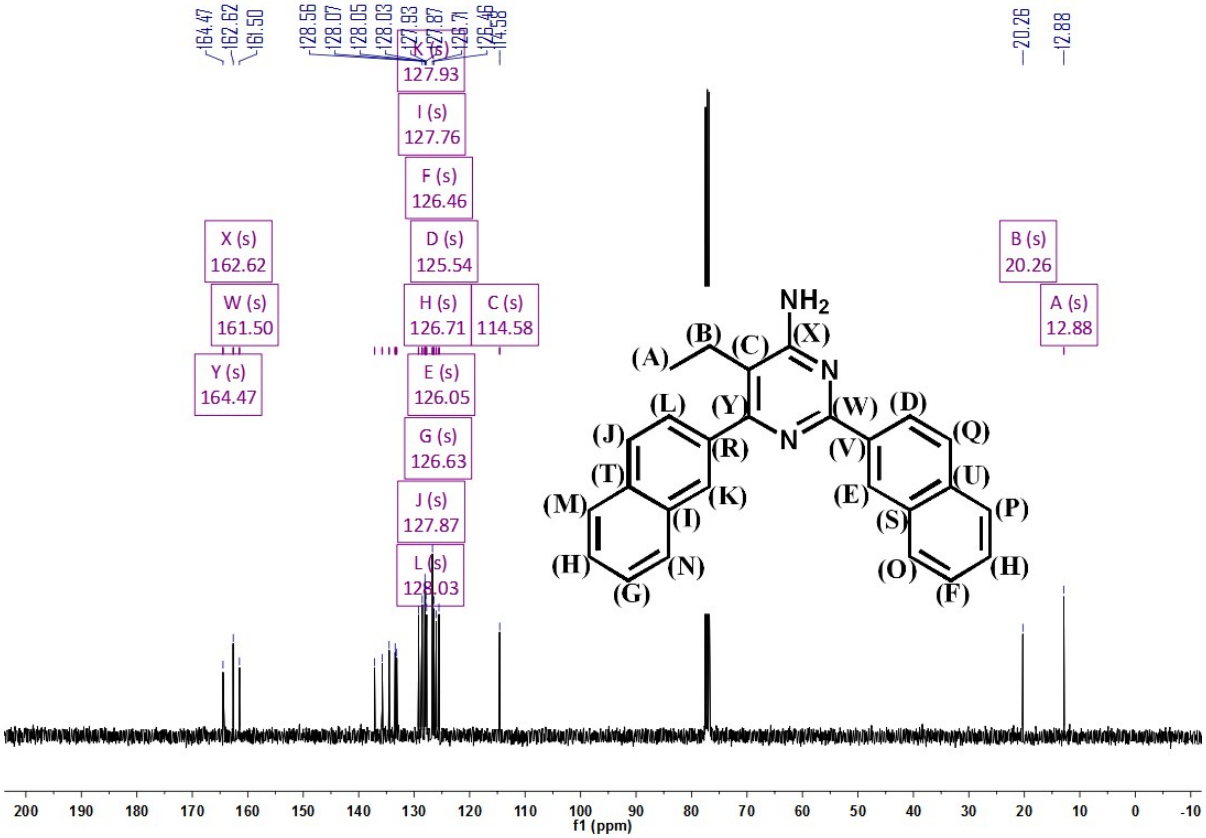

(B)H
NH2 (C)
H
(A)
N
H(F)
N
H
(D)
H
(D)
H
(E)
H
(D)
H
(D)
E (m)
7.99
F (m)
8.46
D (m)
7.50
C (s)
5.30
B (p)
2.50
A (t)
1.17
1.95
1.99
5.96
1.97
2.00
3.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


164.09
162.57
161.33
139.58
138.33
129.88
128.60
128.44
128.25
128.18
128.04
114.12
19.95
12.66
K (s)
139.58
I (s)
129.88
G (s)
128.44
M (s)
162.57
E (s)
128.18
L (s)
161.33
D (s)
128.04
C (s)
114.12
N (s)
164.09
F (s)
128.25
H (s)
128.60
J (s)
138.33
B (s)
19.95
A (s)
12.66
NH2
(A)
(B)
(C)
(M)
N
(J)
(N)
N
(L)
(K)
(G)
(D)
(E)
(I)
(F)
(H)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

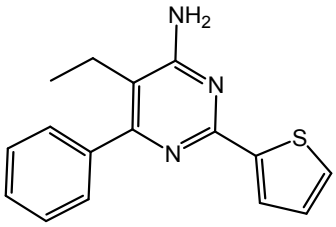
Compound **5d**

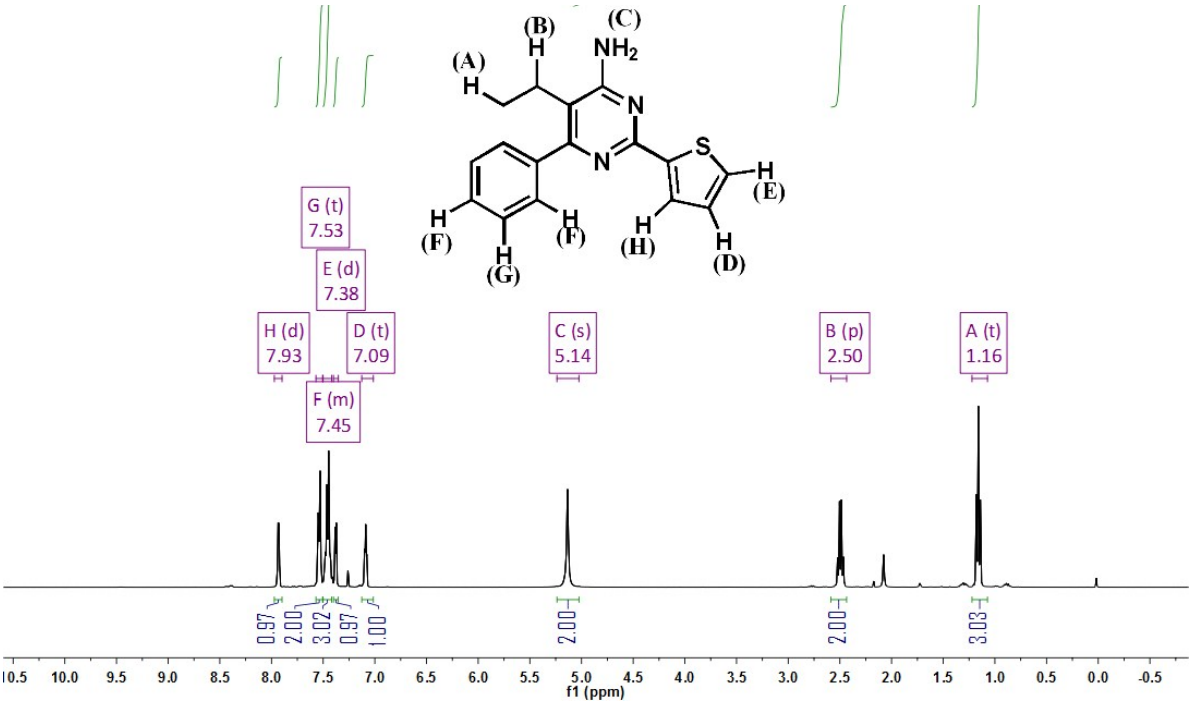

NH2
N
N

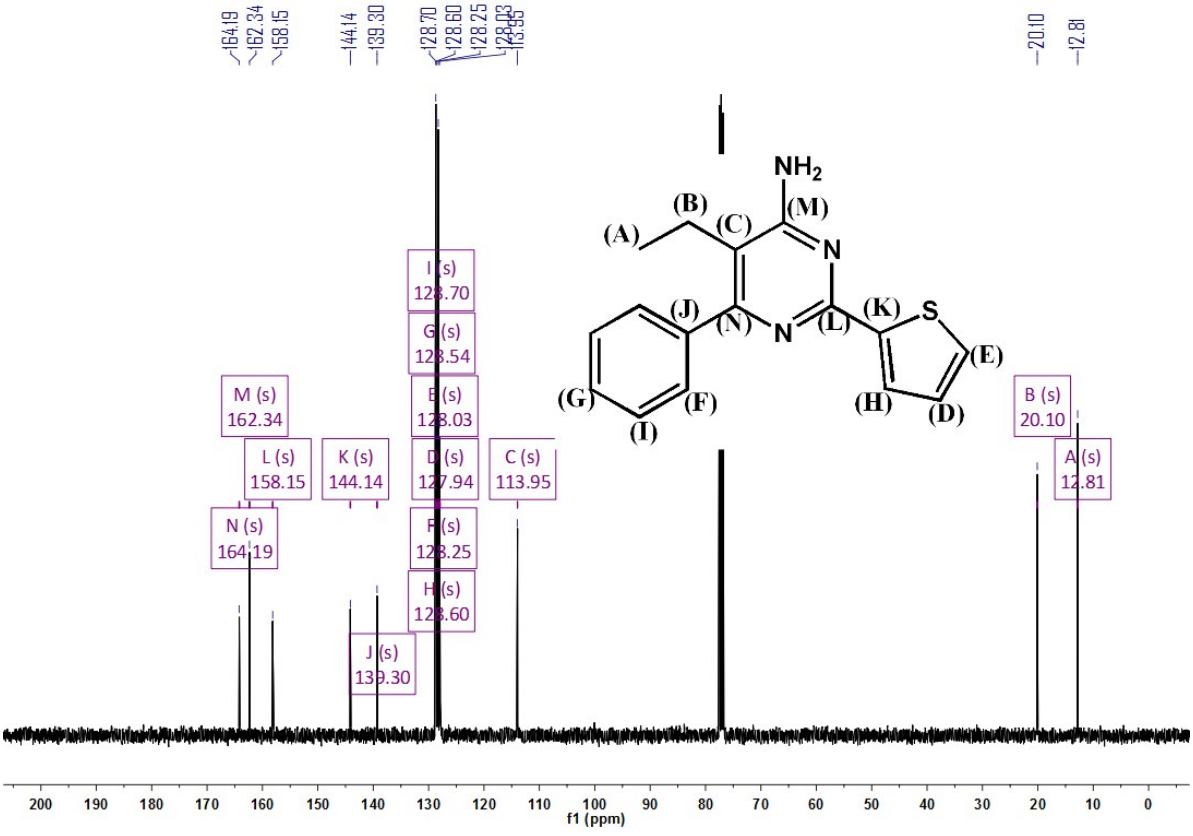

(A)
(C)
CH3
NH2
(B)
H2C
(J)
(G)
(G) H
H
(H)
N
(E)
(D)
(E)
(D)
(G)
(I)
H(G)
(G)
(G)
(F)
G (m)
7.92
J (s)
8.97
E (m)
7.56
I (dd)
8.56
H (s)
8.08
D (m)
7.49
F (dd)
7.74
C (s)
5.14
B (q)
2.61
A (t)
1.23
1.00
1.00
0.99
6.25
1.02
2.07
2.06
2.00
2.03
3.00
f1 (ppm)


164.47
162.62
161.50
128.56
128.07
128.05
128.03
127.93
127.87
126.46
114.58
20.26
12.88
X (s)
162.62
W (s)
161.50
Y (s)
164.47
K (s)
127.93
I (s)
127.76
F (s)
126.46
D (s)
125.54
H (s)
126.71
C (s)
114.58
E (s)
126.05
G (s)
126.63
J (s)
127.87
L (s)
128.03
B (s)
20.26
A (s)
12.88
NH2
(A)
(B)
(C)
(X)
N
(L)
(Y)
(W)
(D)
(J)
(R)
N
(V)
(Q)
(T)
(E)
(U)
(M)
(K)
(S)
(P)
(I)
(H)
(N)
(O)
(H)
(G)
(F)
f1 (ppm)

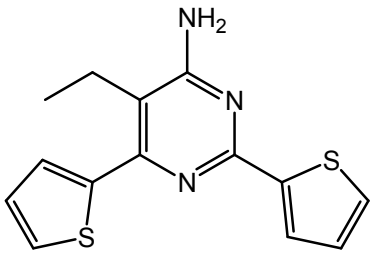
Compound **5e**

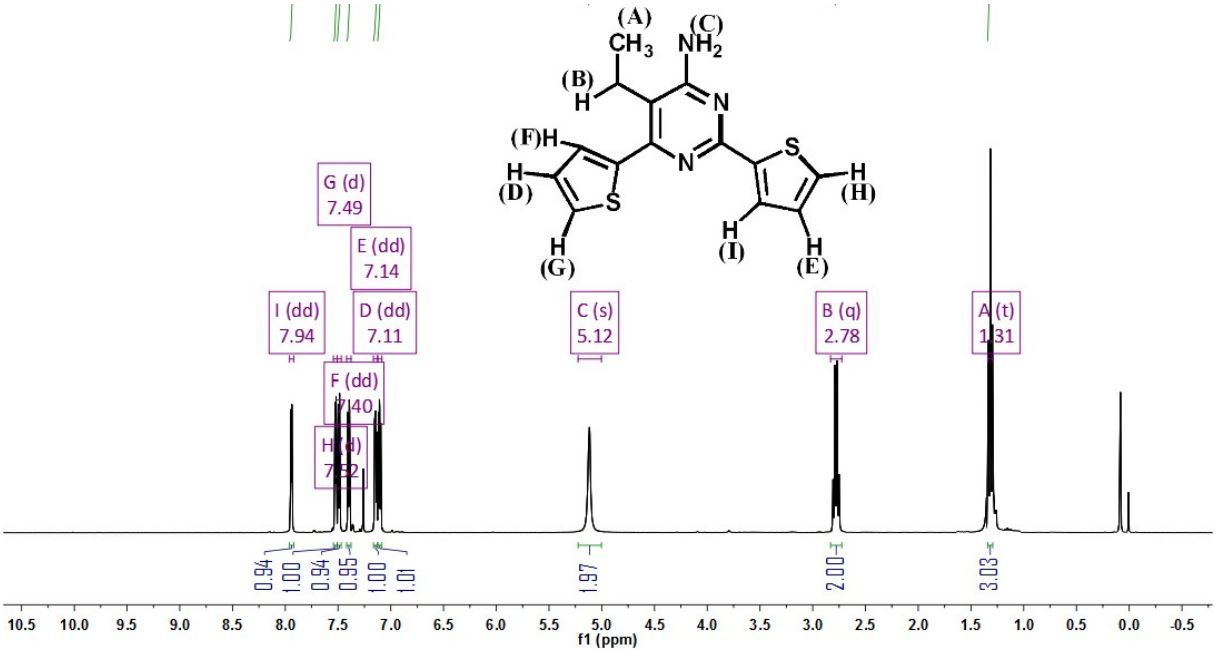

NH2
N
N
S

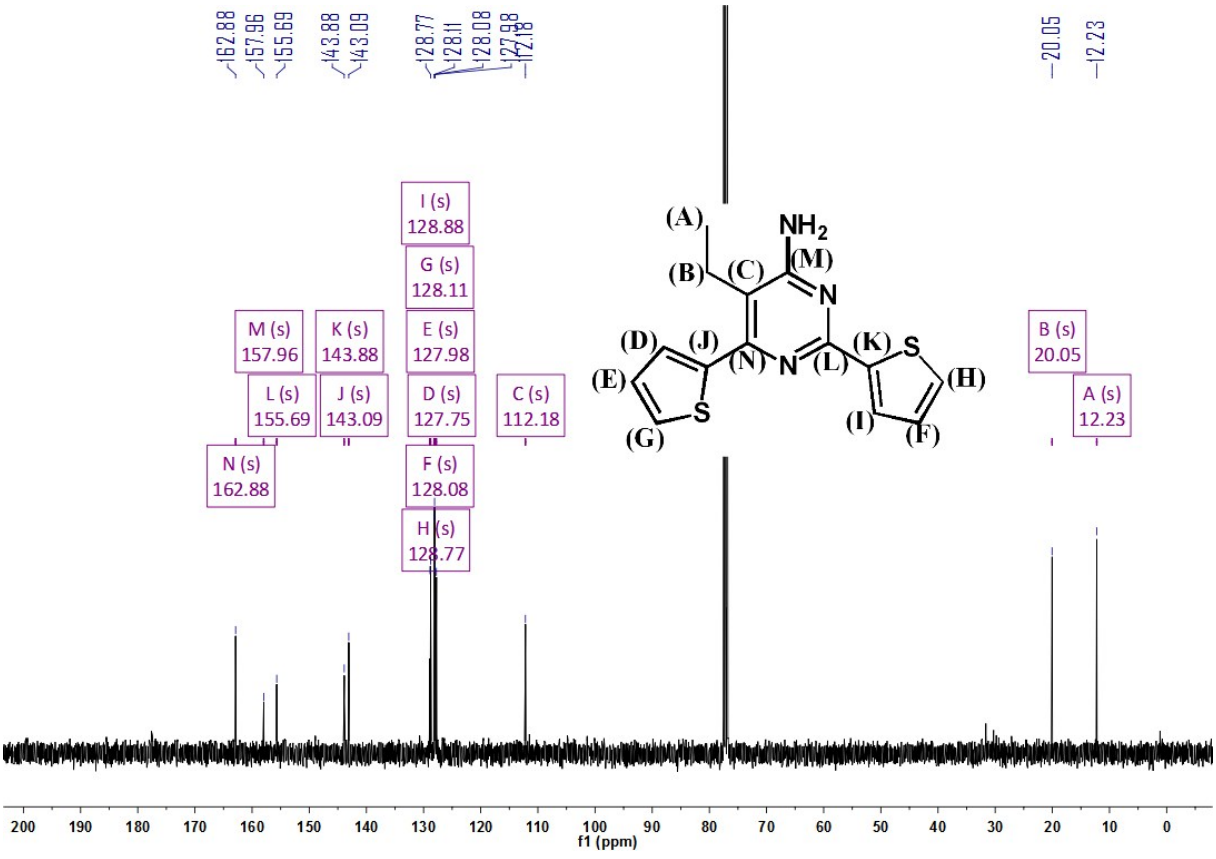

(A)
(B)
(C)
NH2
(D)
(E)
(F)
(F)
(G)
(H)
G (t) 7.53
E (d) 7.38
H (d) 7.93
D (t) 7.09
F (m) 7.45
C (s) 5.14
B (p) 2.50
A (t) 1.16
0.97
2.00
3.02
0.97
1.00
2.00
2.00
3.03
f1 (ppm)


164.19
162.34
158.15
144.14
139.30
128.70
128.60
128.25
128.03
113.95
20.10
12.81
NH2
(A)
(B)
(C)
(M)
(J)
(N)
(L)
(K)
(E)
(G)
(F)
(I)
(H)
(D)
I (s) 128.70
G (s) 128.54
M (s) 162.34
E (s) 128.03
L (s) 158.15
K (s) 144.14
D (s) 127.94
C (s) 113.95
B (s) 20.10
A (s) 12.81
N (s) 164.19
F (s) 128.25
H (s) 128.60
J (s) 139.30
f1 (ppm)

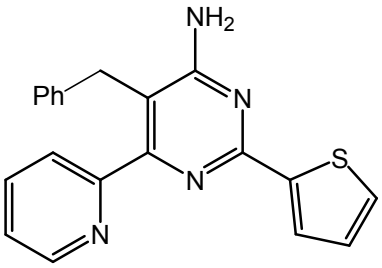
Compound **5f**

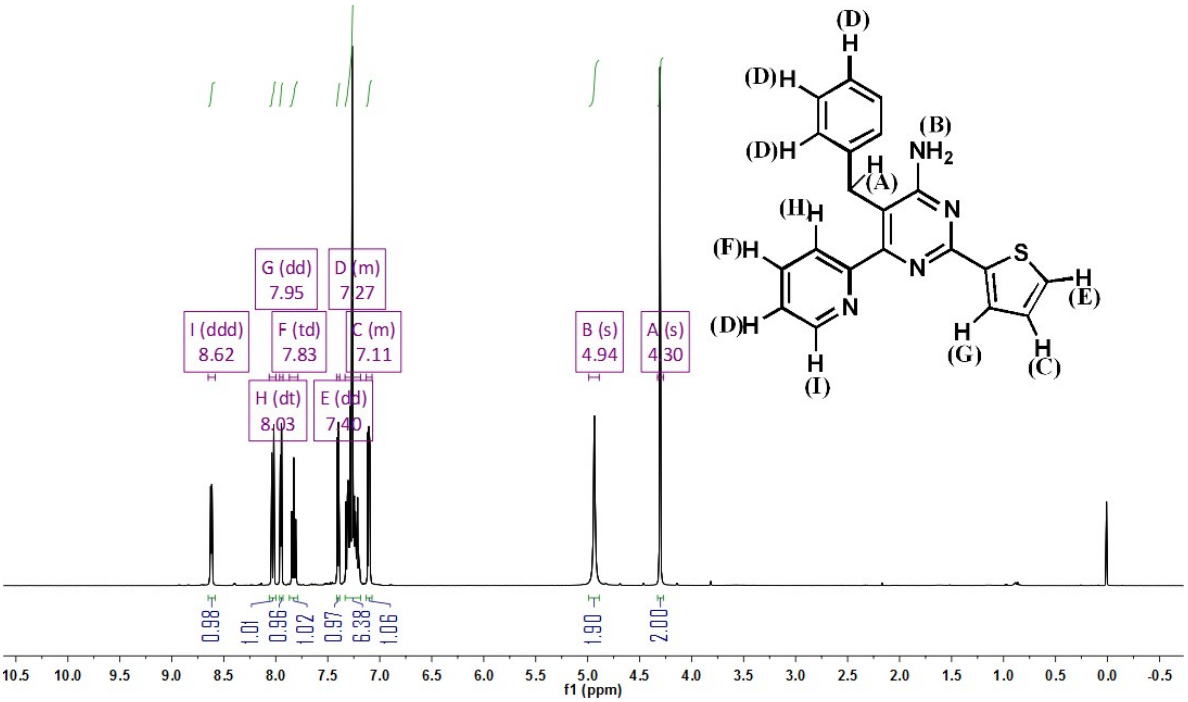

NH2
N
N
S
S

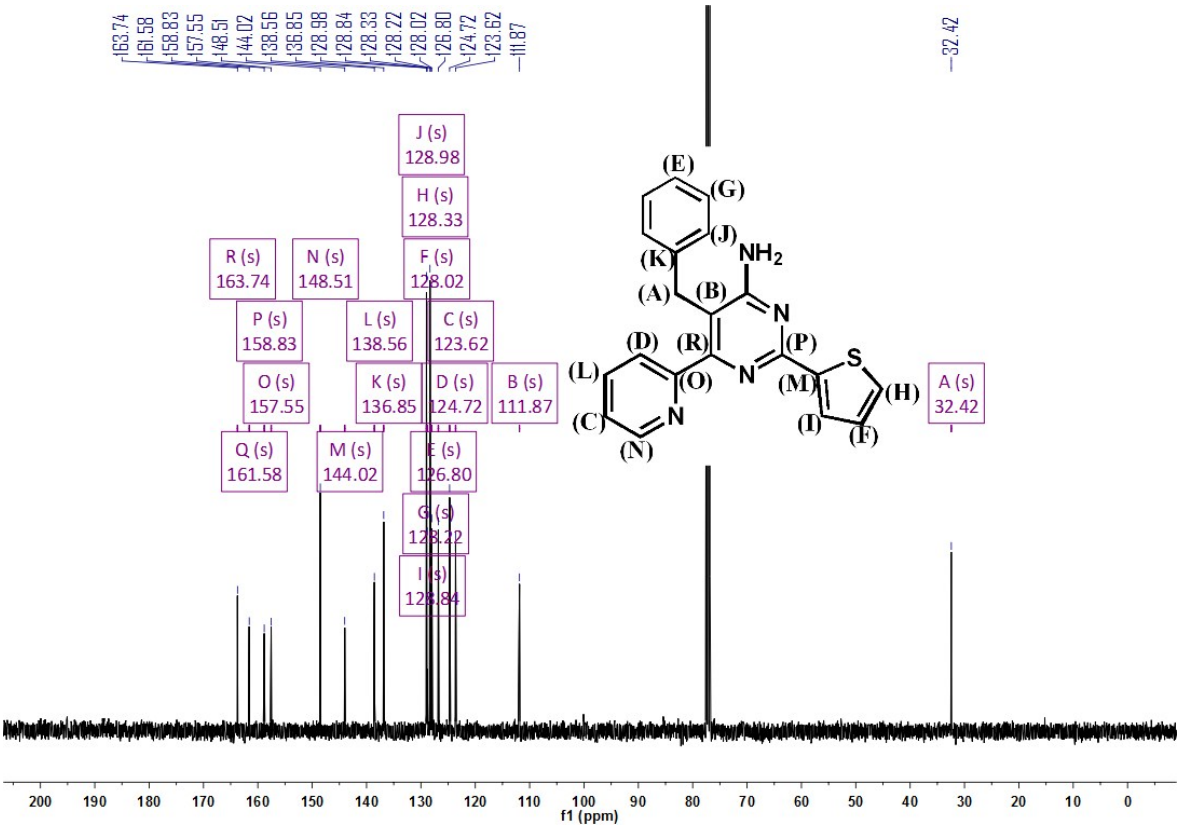

(A)
CH3
(C)
NH2
(B)
H
N
(F)H
S
N
H
(D)
S
H
(H)
H
(G)
H
(I)
H
(E)
G (d)
7.49
E (dd)
7.14
I (dd)
7.94
D (dd)
7.11
C (s)
5.12
B (q)
2.78
A (t)
1.31
F (dd)
7.40
H (d)
7.32
0.94
1.00
0.94
0.95
1.00
1.01
1.97
2.00
3.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


162.88
157.96
155.69
143.88
143.09
128.77
128.11
128.08
127.98
112.18
20.05
12.23
I (s)
128.88
G (s)
128.11
M (s)
157.96
K (s)
143.88
E (s)
127.98
L (s)
155.69
J (s)
143.09
D (s)
127.75
C (s)
112.18
N (s)
162.88
F (s)
128.08
H (s)
128.77
B (s)
20.05
A (s)
12.23
(A)
NH2
(B)
(C)
(M)
N
(D)
(J)
(K)
S
(E)
(N)
N
(L)
(H)
S
(I)
(F)
(G)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

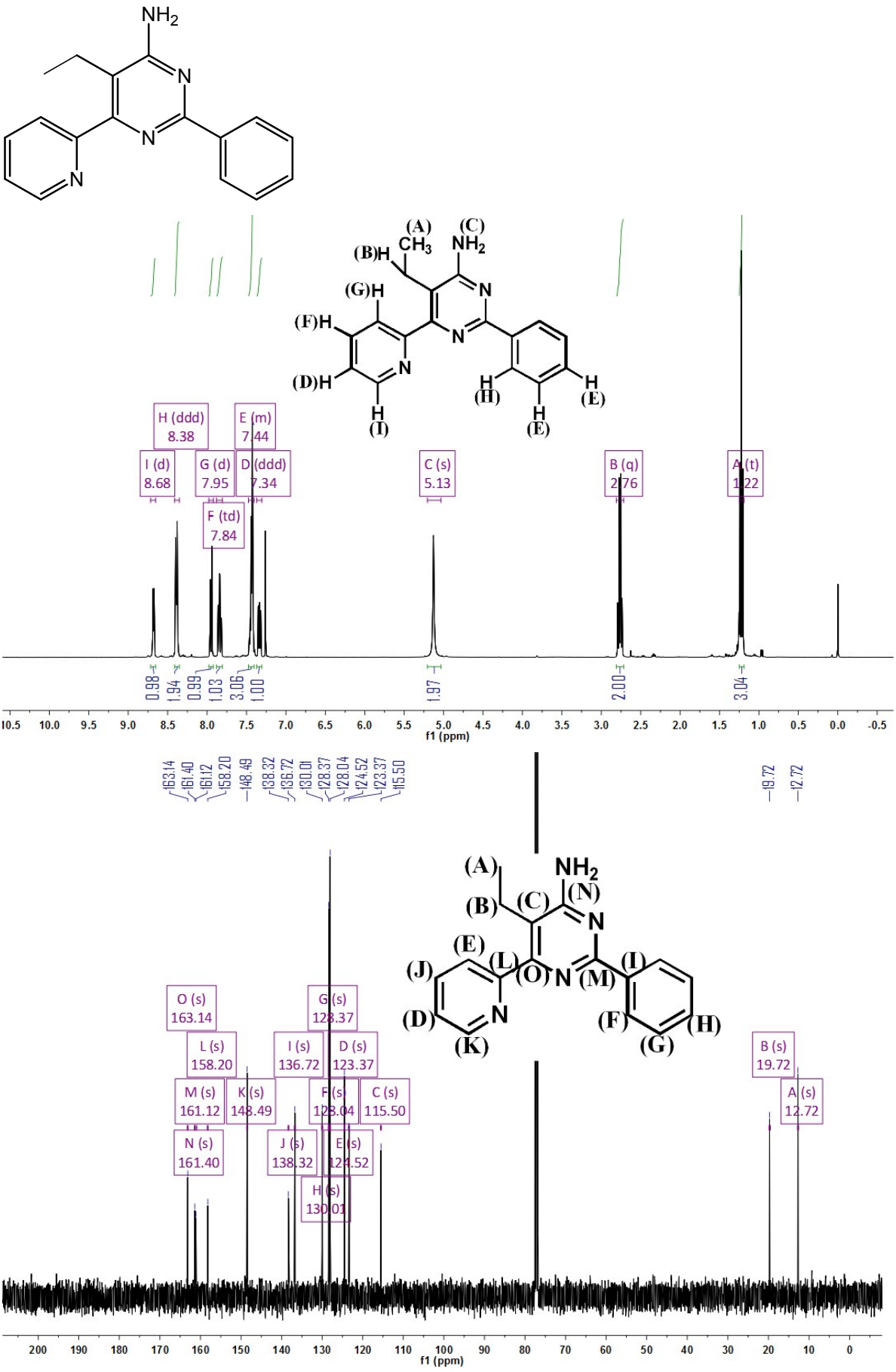
Compound **5g**


NH2
Ph
N
N
S
N

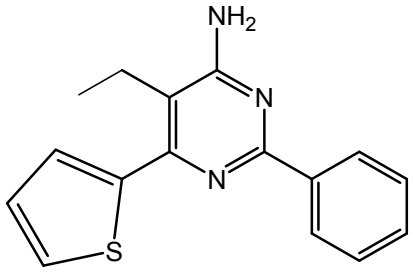

G (dd) 7.95
D (m) 7.27
I (ddd) 8.62
F (td) 7.83
C (m) 7.11
H (dt) 8.03
E (dd) 7.40
B (s) 4.94
A (s) 4.30
0.98
1.01
0.96
1.02
0.97
6.38
1.06
1.90
2.00
f1 (ppm)

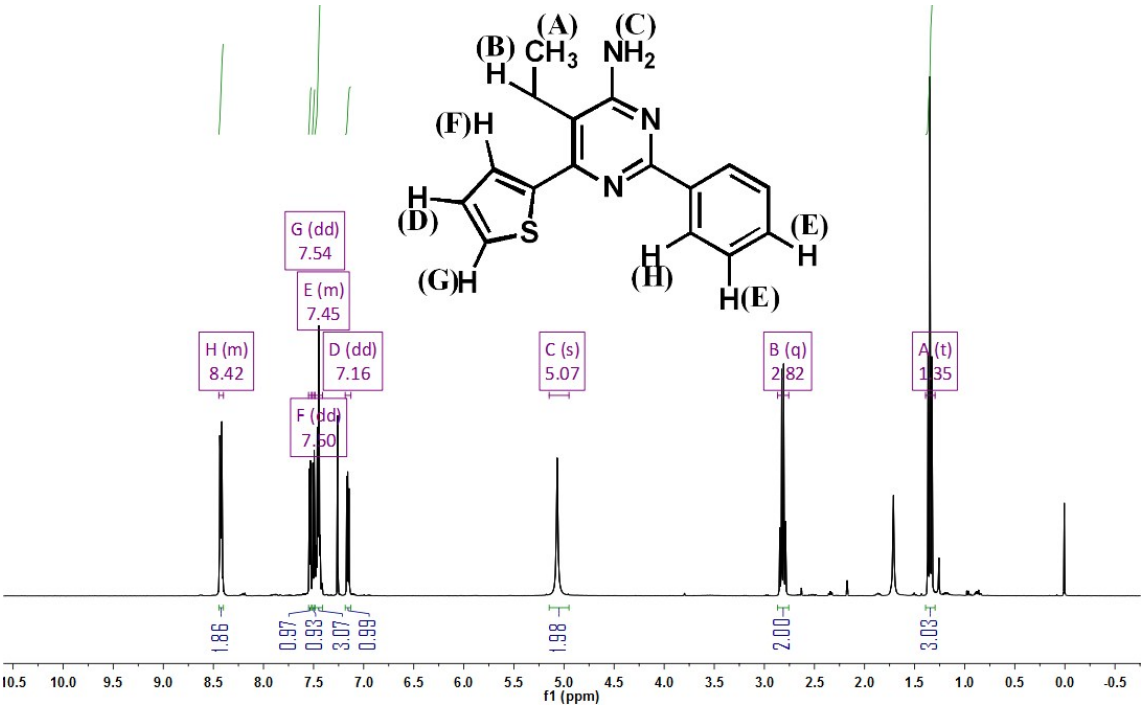

163.74
161.58
158.83
157.55
148.51
144.02
138.56
136.85
128.98
128.84
128.33
128.22
128.02
126.80
124.72
123.62
111.87
32.42
J (s) 128.98
H (s) 128.33
R (s) 163.74
N (s) 148.51
F (s) 128.02
P (s) 158.83
L (s) 138.56
C (s) 123.62
O (s) 157.55
K (s) 136.85
D (s) 124.72
B (s) 111.87
A (s) 32.42
Q (s) 161.58
M (s) 144.02
E (s) 126.80
G (s) 128.22
I (s) 128.84
f1 (ppm)

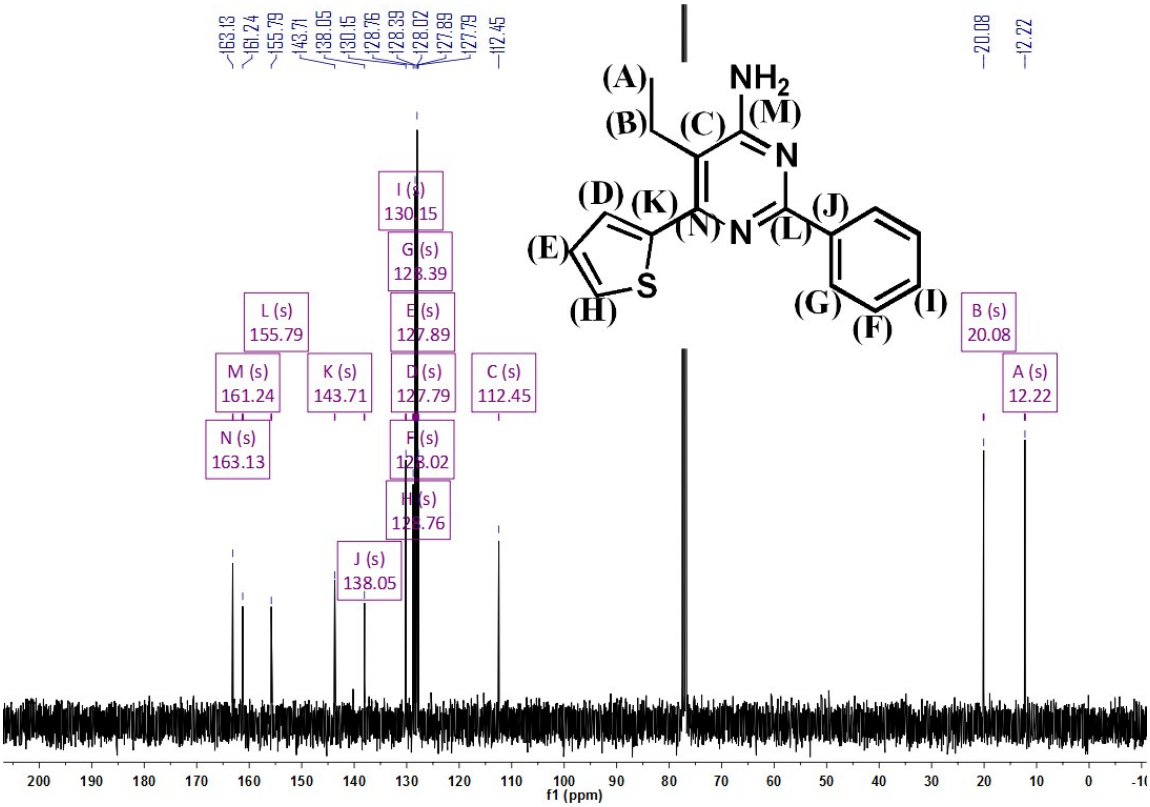
Compound **5h**


NH2
N
N
N
(A)
CH3
(B)H
(C)
NH2
(G)H
(F)H
(D)H
(H)
(E)
(I)
H (ddd) 8.38
E (m) 7.44
I (d) 8.68
G (d) 7.95
D (ddd) 7.34
F (td) 7.84
C (s) 5.13
B (q) 2.76
A (t) 1.22
0.98
1.94
0.99
1.03
3.06
1.00
1.97
2.00
3.04
f1 (ppm)
163.14
161.40
161.12
158.20
148.49
138.32
136.72
130.01
128.37
128.04
124.52
123.37
115.50
19.72
12.72
(A)
NH2
(B)
(C)
(N)
(E)
(J)
(L)
(O)
(M)
(I)
(D)
(F)
(H)
(K)
(G)
O (s) 163.14
G (s) 128.37
L (s) 158.20
I (s) 136.72
D (s) 123.37
M (s) 161.12
K (s) 148.49
F (s) 128.04
C (s) 115.50
N (s) 161.40
J (s) 138.32
E (s) 124.52
H (s) 130.01
B (s) 19.72
A (s) 12.72
f1 (ppm)

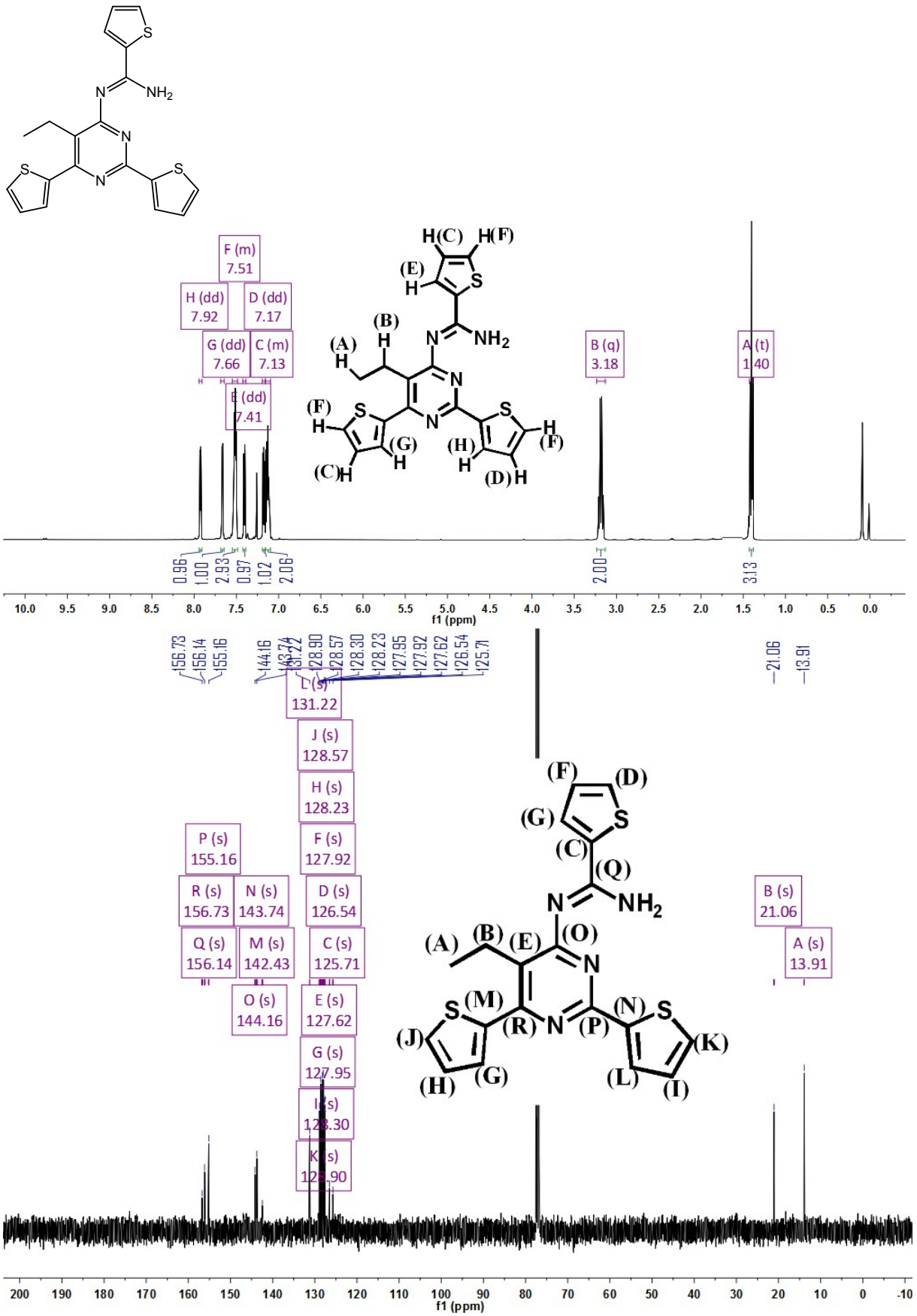
Compound **5i**


NH2
N
N
S

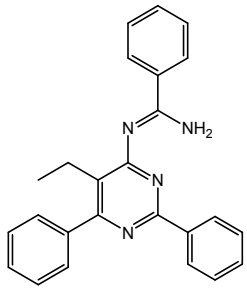

(A)
(B) CH3
H
(C)
NH2
N
(F)H
H
(D)
N
S
(E)
H
(G)H
H
(H)
H(E)
G (dd) 7.54
E (m) 7.45
H (m) 8.42
D (dd) 7.16
F (dd) 7.50
C (s) 5.07
B (q) 2.82
A (t) 1.35
1.86
0.97
0.93
3.07
0.99
1.98
2.00
3.03
f1 (ppm)

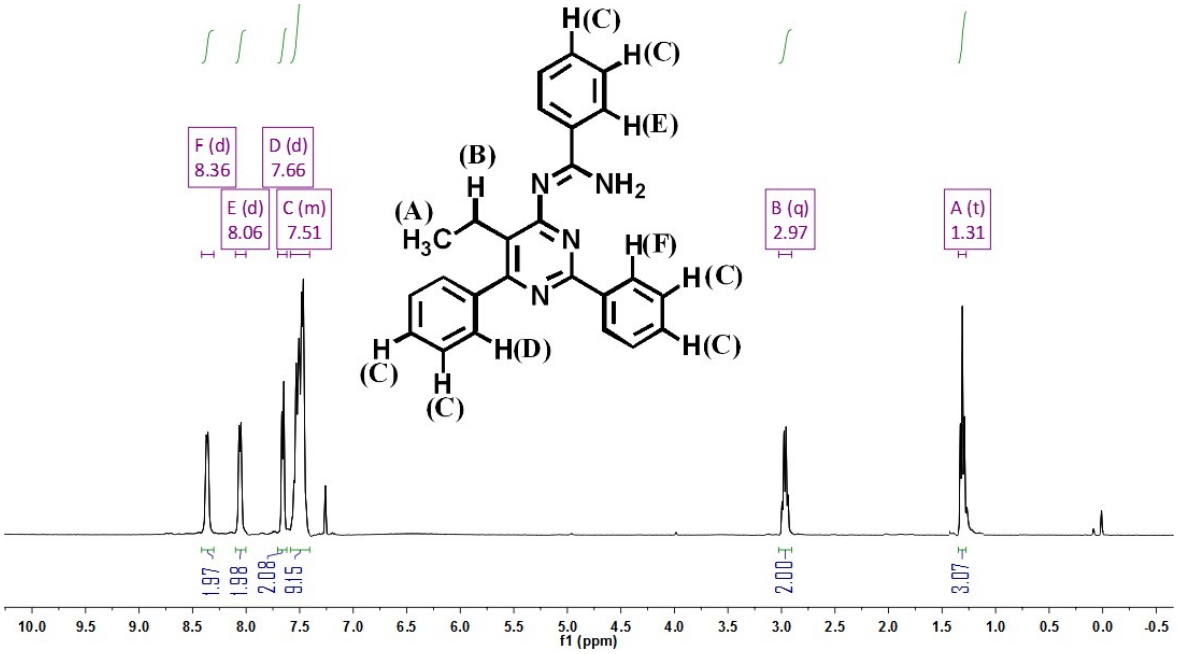

163.13
161.24
155.79
143.71
138.05
130.15
128.76
128.39
128.02
127.89
127.79
112.45
20.08
12.22
(A)
NH2
(B)
(C)
(M)
N
(D)
(K)
(N)
N
(L)
(J)
(E)
S
(H)
(G)
(F)
(I)
I (s) 130.15
G (s) 128.39
L (s) 155.79
E (s) 127.89
B (s) 20.08
M (s) 161.24
K (s) 143.71
D (s) 127.79
C (s) 112.45
A (s) 12.22
N (s) 163.13
F (s) 128.02
H (s) 128.76
J (s) 138.05
f1 (ppm)

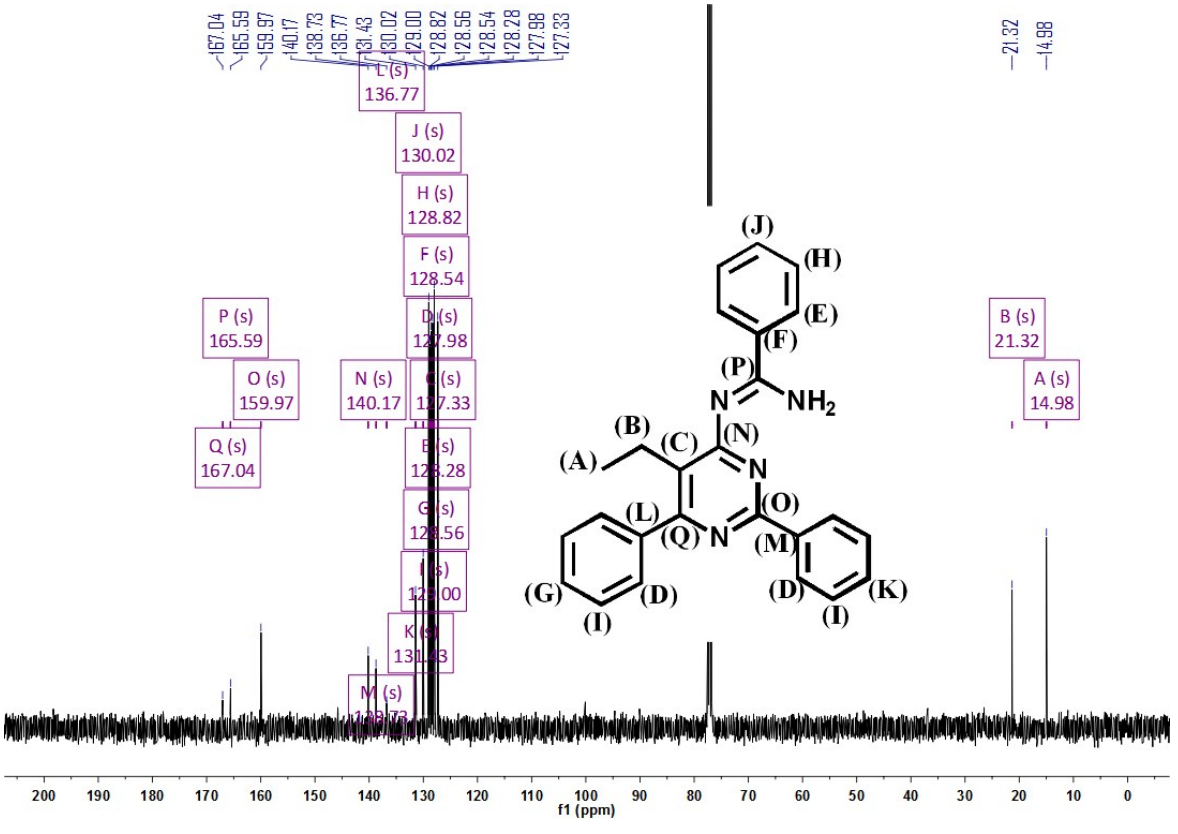
Compound **6a**


F (m) 7.51
H (dd) 7.92
D (dd) 7.17
G (dd) 7.66
C (m) 7.13
E (dd) 7.41
B (q) 3.18
A (t) 1.40
0.96
1.00
2.93
0.97
1.02
2.06
2.00
3.13
f1 (ppm)
L (s) 131.22
J (s) 128.57
H (s) 128.23
F (s) 127.92
P (s) 155.16
R (s) 156.73
N (s) 143.74
D (s) 126.54
Q (s) 156.14
M (s) 142.43
C (s) 125.71
O (s) 144.16
E (s) 127.62
G (s) 127.95
I (s) 128.30
K (s) 128.90
B (s) 21.06
A (s) 13.91
f1 (ppm)

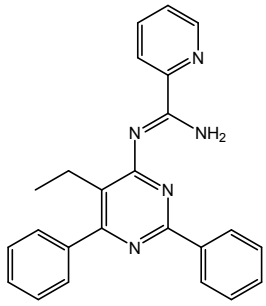
Compound **6b**

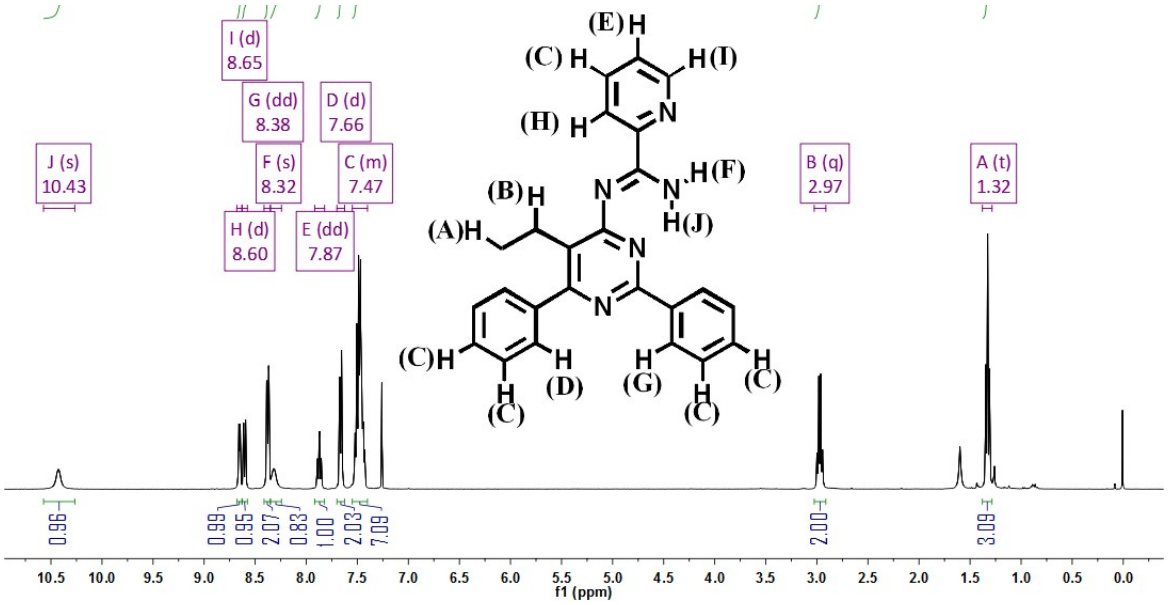


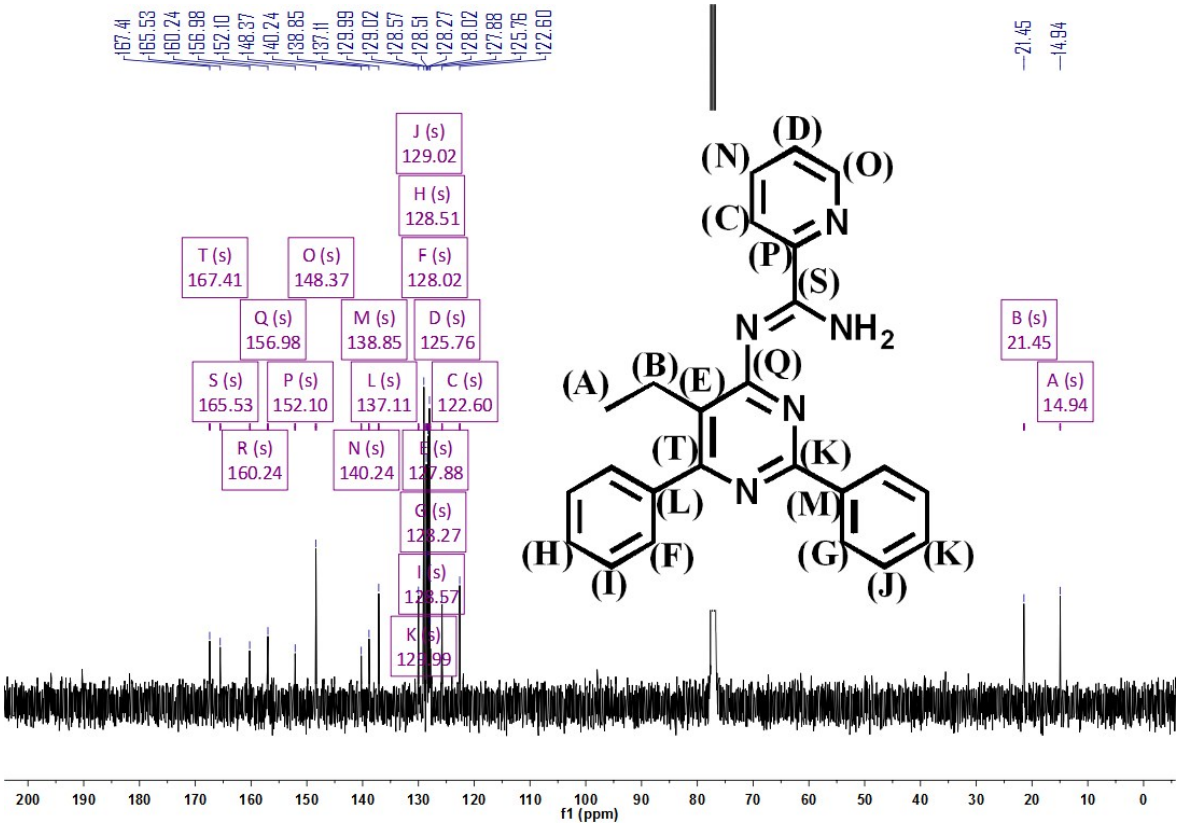

F (d) 8.36
D (d) 7.66
E (d) 8.06
C (m) 7.51
B (q) 2.97
A (t) 1.31
H(C)
H(C)
H(E)
(B)
H
N
NH2
(A)
H3C
N
H(F)
H(C)
N
H(C)
H(D)
(C)
H
(C)
1.97
1.98
2.08
9.15
2.00
3.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


167.04
165.59
159.97
140.17
138.73
136.77
131.43
130.02
129.00
128.82
128.56
128.54
128.28
127.98
127.33
21.32
14.98
L (s) 136.77
J (s) 130.02
H (s) 128.82
F (s) 128.54
P (s) 165.59
O (s) 159.97
N (s) 140.17
Q (s) 167.04
B (s) 21.32
A (s) 14.98
(J)
(H)
(E)
(F)
(P)
N
NH2
(B)
(C)
(N)
(A)
N
(L)
(O)
(Q)
N
(M)
(G)
(D)
(D)
(K)
(I)
(I)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

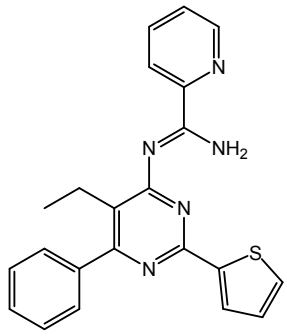
Compound **6c**

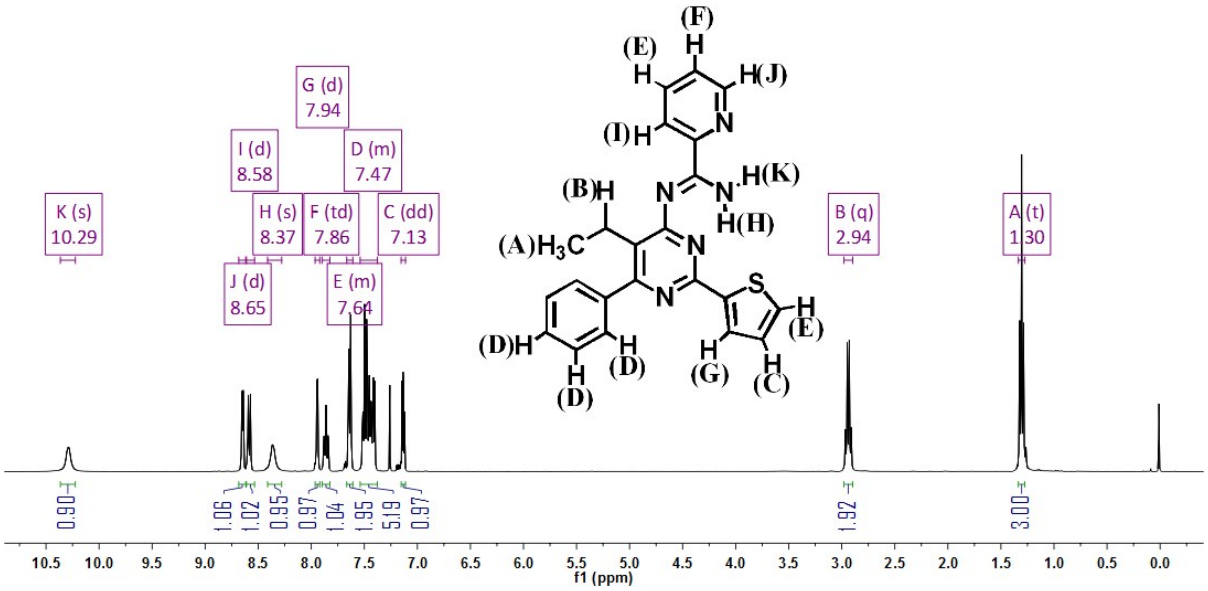


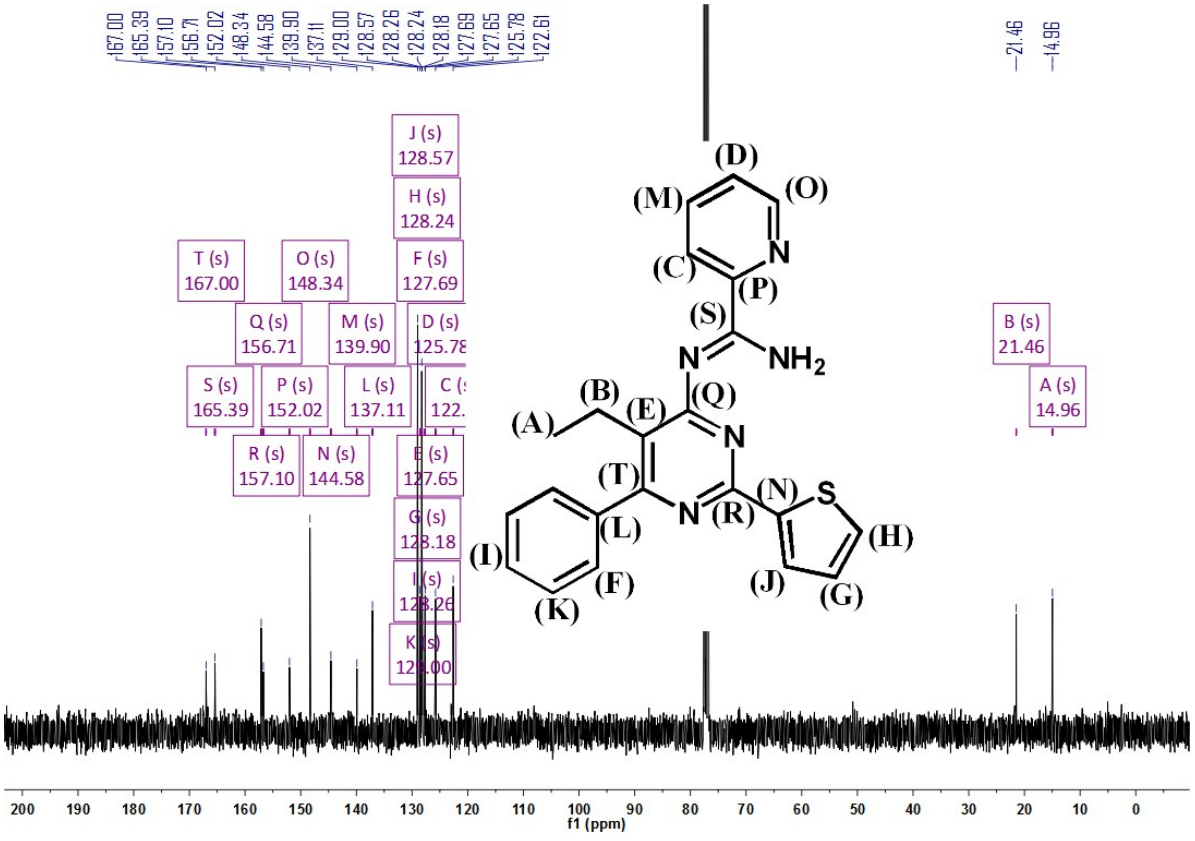

I (d) 8.65
G (dd) 8.38
D (d) 7.66
J (s) 10.43
F (s) 8.32
C (m) 7.47
H (d) 8.60
E (dd) 7.87
B (q) 2.97
A (t) 1.32
0.96
0.99
0.95
2.07
0.83
1.00
2.03
7.09
2.00
3.09
f1 (ppm)


167.41
165.53
160.24
156.98
152.10
148.37
140.24
138.85
137.11
129.99
129.02
128.57
128.51
128.27
128.02
127.88
125.76
122.60
21.45
14.94
J (s) 129.02
H (s) 128.51
T (s) 167.41
O (s) 148.37
F (s) 128.02
Q (s) 156.98
M (s) 138.85
D (s) 125.76
S (s) 165.53
P (s) 152.10
L (s) 137.11
C (s) 122.60
R (s) 160.24
N (s) 140.24
B (s) 21.45
A (s) 14.94
f1 (ppm)

Compound **6d**







3. X-ray crystal structures of compounds 2j, 4a and 5e

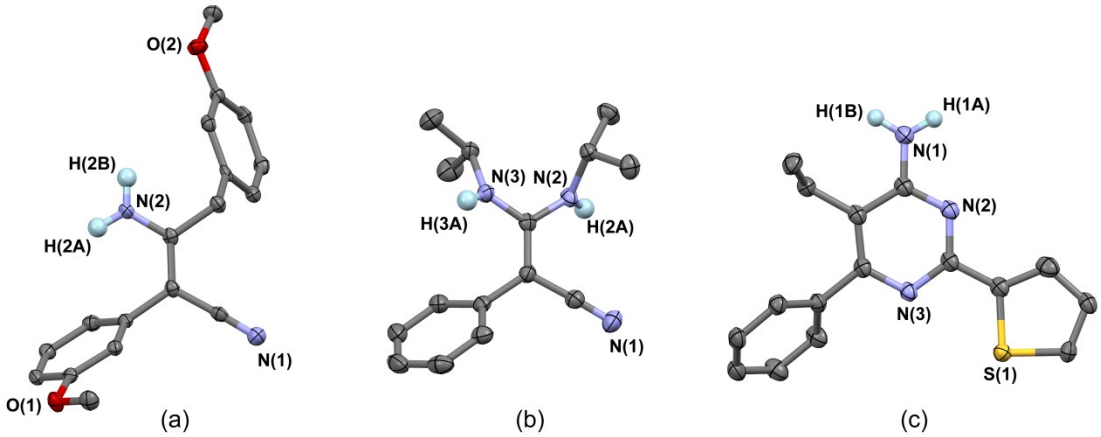


Figure S1. Crystal structures of compounds **2j** (CCDC number: 1956320) (a), **4a** (1956322) (b) and **5e** (1956323) (c).

4. Synthesis and Characterization of 2,3,3-triphenylacrylonitrile

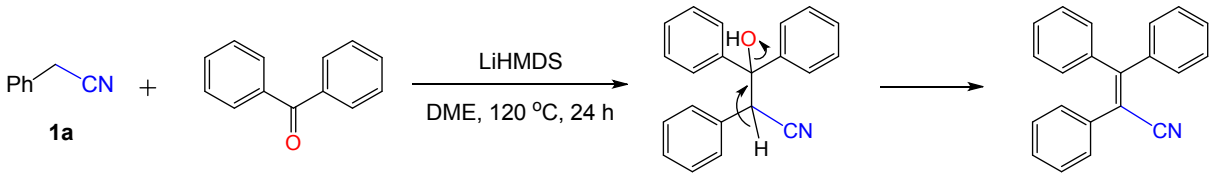
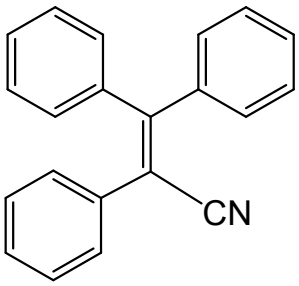
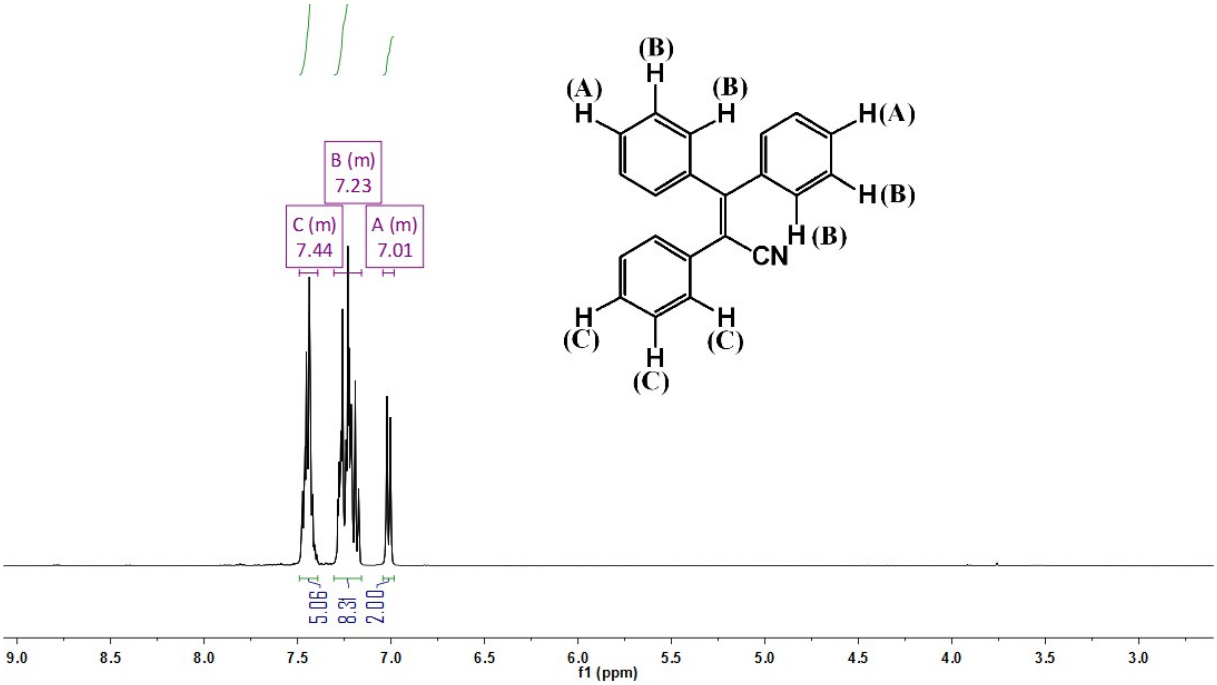


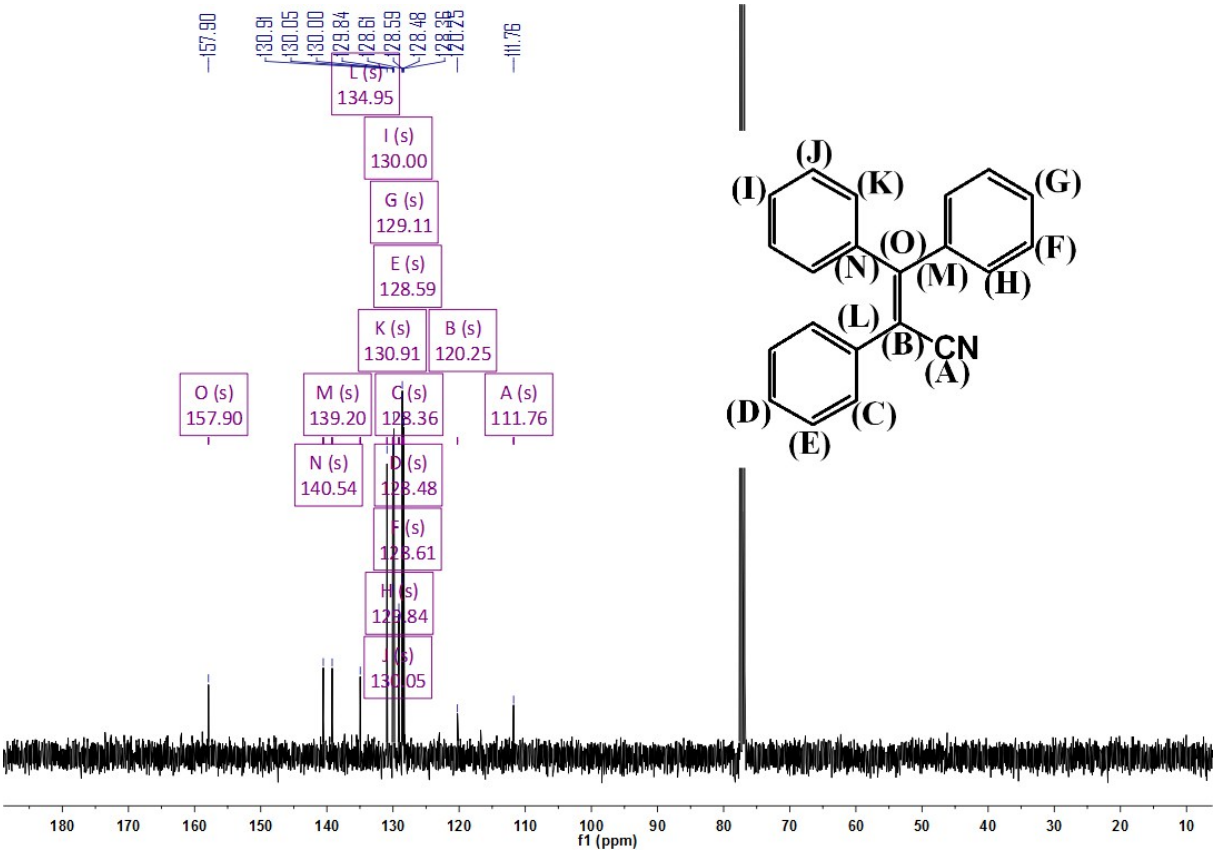
Figure S2. Investigation of the reaction of phenylacetonitrile (**1a**) with benzophenone.

Synthesis of 2,3,3-triphenylacrylonitrile: phenylacetonitrile (0.20 mmol), benzophenone (0.2 mmol), lithium bis(trimethylsilyl)amide (0.20 mmol) and dried DME (1 mL) were mixed in a 50 mL Teflon screw-cap sealed tube. The tube was charged with N_2 (1 atm) and the mixture was stirred at 120 °C for 24 h. After cooling to room temperature, the reaction mixture was diluted with dichloromethane (20 mL), filtered through a pad of silica gel and concentrated under reduced pressure. The crude product was purified on a silica gel column eluted with petroleum ether/acetone (25 : 1 v/v) to afford 2,3,3-triphenylacrylonitrile.

2,3,3-triphenylacrylonitrile: yield, 80% (45 mg); white solid; R_f = 0.60 in 4% acetone in petroleum ether; melting point, 167-168℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.39 (m, 5H), 7.31 – 7.16 (m, 8H), 7.04 – 6.98 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.90, 140.54, 139.20, 134.95, 130.91, 130.05, 130.00, 129.84, 129.11, 128.61, 128.59, 128.48, 128.36, 120.25, 111.76.


CN


B (m)
7.23
C (m)
7.44
A (m)
7.01
5.06
8.31
2.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
f1 (ppm)
(B)
H
(A)
H
(B)
H
H(A)
H(B)
H (B)
CN
H
(C)
H
(C)
H
(C)


157.90
130.91
130.05
130.00
129.84
128.61
128.59
128.48
120.25
111.76
L (s)
134.95
I (s)
130.00
G (s)
129.11
E (s)
128.59
K (s)
130.91
B (s)
120.25
O (s)
157.90
M (s)
139.20
G (s)
128.36
A (s)
111.76
N (s)
140.54
D (s)
128.48
F (s)
128.61
H (s)
129.84
I (s)
130.05
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)
(J)
(I)
(K)
(G)
(O)
(N)
(M)
(F)
(H)
(L)
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