Supporting Information

Dehydrosulfurative C-N Cross-Coupling and Concomitant Oxidative Dehydrogenation for One-Step Synthesis of 2-Aryl(alkyl)aminopyrimidines from 3,4-Dihydropyrimidin-1*H*-2-thiones

Nguyen Huu Trong Phan,[§] Hyeji Kim,[§] Hyunik Shin,[‡] Hee-Seung Lee,[ǂ] Jeong-Hun Sohn[§*]

[§]*Department of Chemistry, College of Natural Sciences, Chungnam National University, Dajeon 305-706, Korea,* [‡]*Yonsung Fine Chemicals R&D Center, 602 Innoplex 2, 306 Sinwon-ro, Yeongtong-gu, Suwon 443-380 Korea,* [ǂ]*Department of Chemistry, KAIST, Daejeon 305-701 Korea*

E-mail: sohnjh@cnu.ac.kr

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1. General information:

Common solvents were purified before use. Tolene ($PhCH_3$) and dioxane were purified by distillation from sodium-benzophenone ketyl. *N*,*N*-dimethylformamide (DMF, AcroSeal), triethylamine (NEt_3, Aldrich Sure/Seal) and Lithium Hexamethyldisilazide (LiHMDS, 1.0M in hexane) were used as received. All reagents were reagent grade and purified where necessary. 'water' refers to distilled water. Reactions were monitored by thin layer chromatography (TLC) using Whatman precoated silica gel plates. Flash column chromatography was performed over ultra pure silica gel (230-400 mesh) from Merck. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE 300 (300 MHz) or 600 (600 MHz) spectrometer using residual solvent peaks as an internal standard ($CHCl_3$: δ 7.24 ppm for proton and δ 77.0 ppm for carbon). Multiplicities for ^{1}H NMR are designated as: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, m = multiplet. Infrared spectra (IR) were recorded on JASCO FT/IR-4100 spectrometer and are reported in reciprocal centimeter (cm^{-1}). High resolution mass spectra (HRMS) were obtained on BrukermicroTOF-Q.

2. Synthesis of 2-aminopyrimidines 2 from DHPMs 1

A. General procedure for synthesis of DHPMs 1 using the Biginelli reaction

A mixture of a β-keto ester (10 mmol), an aldehyde (10 mmol), thiourea (15 mmol), $LaCl_3 \cdot 7H_2O$ (5 mmol) and conc. HCl (1–2 drops) in EtOH (20 mL) was stirred under reflux for 5 h. After cooling, the reaction mixture was poured onto 50 g of crushed ice and stirred for several minutes. The solid products were filtered, washed with cold water (2 × 50 mL) and a mixture (1:1) of ethanol–water (2 × 20 mL), and subsequently dried to give the corresponding DHPM.[1,2]

B. General procedure for synthesis of 2-aminopyrimidines 2 from DHPMs 1

To a mixture of DHPM **1** (0.18 mmol), CuTC (0.54 mmol), $Pd(OAc)_2$ (20 mol %) and LiHMDS (0.27 mmol) in $PhCH_3$ (2 mL) was added amine (0.36 mmol), and the resulting mixture was degassed with Ar. After stirring at 100 ºC for 18 h under Ar the mixture was filtered through silica gel pad and washed with EtOAc (25 mL). The filtrate was washed with water (5 mL) and brine (5 mL), dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (*n*-hexane/EtOAc = 8:2) to give 2-aminopyrimidine **2**.

C. Synthetic procedure for 2j-2m

To a mixture of DHPM **1** (0.18 mmol), CuTC (0.54 mmol), $Pd(PPh_3)_4$ (10 mol %), TBSCl (0.18 mmol) and LiHMDS (0.27 mmol) in $PhCH_3$ (2 mL) was added amine (0.36 mmol), and the resulting mixture was degassed with Ar. After stirring at 100 ºC for 18 h under Ar the mixture was filtered through silica gel pad and washed with EtOAc (25 mL). The filtrate was washed with water

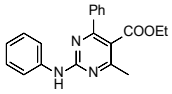
(5 mL) and brine (5 mL), dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (*n*-hexane/EtOAc = 8:2) to give the corresponding product **2**.

D. Synthetic procedure for 2n-2p and 3v

To a mixture of DHPM **1** (0.18 mmol), CuTC (0.54 mmol), $PdCl_2$ (20 mol %), P(*o*-tolyl)$_3$ (30 mol %) and LiHMDS (0.27 mmol) in $PhCH_3$ (2 mL) was added amine (0.36 mmol), and the resulting mixture was degassed with Ar. After stirring at 100 ^oC for 18 h under Ar the mixture was filtered through silica gel pad and washed with EtOAc (25 mL). The filtrate was washed with water (5 mL) and brine (5 mL), dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (*n*-hexane/EtOAc = 8:2) to give the corresponding product.

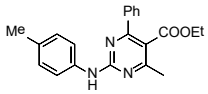
3. Characterization of pyrimidines 2a-2p, 3a-3v and 4

Ethyl 6-methyl-4-phenyl-2-phenylamino-pyrimidine-5-carboxylate (2a)[3]



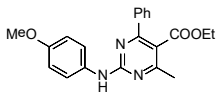
Yield: 56 mg, 93 %; colorless viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.62 – 7.43 (m, 4H), 7.36 – 7.26 (m, 3H), 7.18 (t, *J* = 7.9 Hz, 2H), 6.90 (t, *J* = 7.4 Hz, 1H), 3.99 (q, *J* = 7.1 Hz, 2H), 2.46 (s, 3H), 0.88 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.5, 167.2, 165.9, 158.7, 139.2, 138.6, 129.8, 128.9, 122.8, 119.4, 117.1, 61.4, 23.0, 13.6.

Ethyl 6-methyl-4-phenyl-2-(4'-methylphenylamino)-pyrimidine-5-carboxylate (2b)[4]



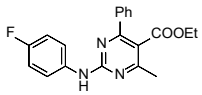
Yield: 55 mg, 88 %; colorless viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67-7.54 (m, 4H), 7.55-7.38 (m, 4H), 7.16 (d, *J* = 8.3 Hz, 2H), 4.11 (q, *J* = 7.3 Hz, 2H), 2.57 (s, 3H), 2.34 (s, 3H), 1.00 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.5, 167.2, 166.03, 158.6, 138.7, 136.4, 132.5, 129.7, 129.4, 128.3, 128.0, 119.5, 116.8, 61.3, 22.8, 20.8, 13.6.

Ethyl 6-methyl-4-phenyl-2-(4'-methoxylphenylamino)-pyrimidine-5-carboxylate (2c)[3]



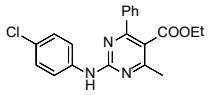
Yield: 62 mg, 95 %; colorless viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.94-7.81 (m, 1H), 7.62 (dd, *J* = 7.0, 2.1 Hz, 4H), 7.51-7.40 (m, 3H), 6.91 (d, *J* = 9.0 Hz, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.82 (d, *J* = 0.8 Hz, 3H), 2.57 (d, *J* = 0.7 Hz, 3H), 1.00(m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 168.7, 167.4, 166.8, 158.9, 156.2, 139.0, 134.5, 133.3, 132.6, 130.4, 128.9, 128.6, 128.3, 122.0, 117.0, 114.6, 61.8, 56.0, 22.9, 14.1.

Ethyl 6-methyl-4-phenyl-2-(4'-fluorophenylamino)-pyrimidine-5-carboxylate (2d)



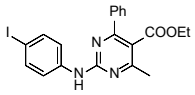
Yield: 60 mg, 95 %; brown solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65-7.58 (m, 4H), 7.44 (m, 3H), 7.38 (s, 1H), 7.03 (t, *J* = 8.6 Hz, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.56 (s, 3H), 0.99 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.4, 167.3, 165.9, 158.6, 138.5, 135.1, 129.8, 128.4, 128.0, 120.9, 117.3, 115.6, 115.4, 61.3, 22.9, 13.6; IR (film) cm^{-1}: 3359, 3058, 2981, 2931, 1716, 1550, 1446, 1265, 1087, 759, 701, 435; HRMS (ESI) (*m/z*): calcd for $C_{20}H_{19}FN_3O_2$ $[M+H]^+$ 352.1461, found 352.1477.

Ethyl 6-methyl-4-phenyl-2-(4'-chlorophenylamino)-pyrimidine-5-carboxylate (2e)[4]



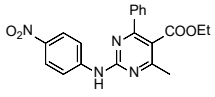
Yield: 51 mg, 82 %; white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.96 (s, 1H), 7.76-7.58 (m, 4H), 7.57-7.42 (m, 4H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.58 (s, 3H), 1.01 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.1, 167.0, 166.1, 158.1, 138.2, 137.5, 130.0, 128.8, 128.4, 128.1, 127.8, 120.6, 117.4, 61.4, 22.6, 13.5.

Ethyl 6-methyl-4-phenyl-2-(4'-iodophenylamino)-pyrimidine-5-carboxylate (2f)[4]



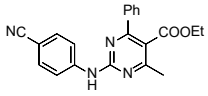
Yield: 65 mg, 78 %; white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.54-7.51 (m, 4H), 7.44-7.38 (m, 5H), 4.03 (q, *J* = 7.1 Hz, 2H), 2.48 (s, 3H), 0.92 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.1, 167.0, 166.1, 158.1, 138.8, 138.2, 137.7, 133.1, 130.0, 128.4, 128.1, 121.3, 85.5, 61.4, 22.5, 13.5.

Ethyl 6-methyl-4-phenyl-2-(4'-nitrophenylamino)-pyrimidine-5-carboxylate (2g)[4]



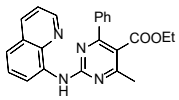
Yield: 43 mg, 72 %; pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.47 (s, 1H), 8.31-8.14 (m, 2H), 7.97-7.82 (m, 2H), 7.71-7.56 (m, 2H), 7.50 (td, *J* = 5.5, 3.7 Hz, 3H), 4.15 (q, *J* = 7.1 Hz, 2H), 2.63 (s, 3H), 1.03 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.0, 167.4, 165.8, 157.8, 145.2, 142.0, 137.9, 130.2, 128.6, 128.0, 125.3, 117.9, 61.7, 22.9, 13.6.

Ethyl 6-methyl-4-phenyl-2-(4'-cyanophenylamino)-pyrimidine-5-carboxylate (2h)[4]



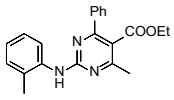
Yield: 60 mg, 94 %; pale yellow viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.38 (s, 1H), 7.83 (d, *J* = 8.6 Hz, 2H), 7.64-7.54 (m, 4H), 7.46 (d, *J* = 6.5 Hz, 3H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.58 (s, 3H), 1.01 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.9, 167.3, 166.44, 165.9, 158.0, 143.4, 138.0, 133.8, 130.1, 128.5, 118.8, 104.9, 61.6, 22.6, 13.6.

Ethyl 6-methyl-4-phenyl-2-(8'-quinolinylamino)-pyrimidine-5-carboxylate (2i)



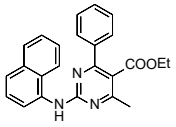
Yield: 65 mg, 58 %; brown solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.07 (s, 1H), 9.03 (d, *J* = 7.7 Hz, 1H), 8.86 (d, *J* = 3.5 Hz, 1H), 8.18 (d, *J* = 8.3 Hz, 1H), 7.73 (dd, *J* = 6.5, 2.3 Hz, 2H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.53 – 7.43 (m, 5H), 4.15 (q, *J* = 7.1 Hz, 2H), 2.67 (s, 3H), 1.03 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 168.6, 167.1, 165.8, 158.6, 147.8, 138.8, 138.5, 136.21, 135.7, 129.7, 128.4, 127.4, 121.5, 119.7, 117.3, 114.8, 61.3, 23.0, 13.6; IR (film) cm^{-1} 3343, 3054, 2981, 2931, 1716, 1531, 1430, 1261, 1083, 794, 763, 698, 455; HRMS (ESI) (*m/z*): calcd for $C_{23}H_{21}N_4O_2$ $[M+H]^+$ 385.1665, found 385.1665.

Ethyl 6-methyl-4-phenyl-2-(2'-methylphenylamino)-pyrimidine-5-carboxylate (2j)[5]



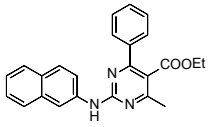
Yield: 40 mg, 65 %; pale yellow viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.0 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.40 – 7.34 (m, 3H), 7.15 (dd, *J* = 12.6, 4.9 Hz, 3H), 6.97 (d, *J* = 6.7 Hz, 1H), 4.02 (q, *J* = 7.1 Hz, 2H), 2.48 (s, 3H), 2.27 (s, 3H), 0.91 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.5, 167.3, 166.0, 159.0, 138.6, 137.0, 132.2, 130.5, 129.7, 128.4, 128.0, 126.6, 123.7, 121.6, 117.0, 61.3, 22.9, 18.2, 13.6.

Ethyl 6-methyl-4-phenyl-2-(α-naphthylamino)-pyrimidine-5-carboxylate (2k)[5]



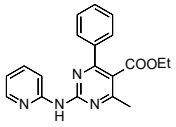
Yield: 35 mg, 58 %; pale yellow viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (d, *J* = 7.5 Hz, 1H), 8.10 – 8.00 (m, 1H), 7.90 (dd, *J* = 5.2, 4.1 Hz, 1H), 7.78 (s, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.64 – 7.58 (m, 2H), 7.56 – 7.49 (m, 3H), 7.47 – 7.41 (m, 3H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.58 (s, 3H), 1.02 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (75 MHz, $CDCl_3$): δ 168.5, 167.3, 165.9, 158.8, 138.6, 136.6, 134.1, 130.0, 129.8, 128.6, 128.4, 128.1, 127.5, 127.4, 126.3, 124.3, 120.2, 117.4, 115.3, 61.4, 23.0, 13.6.

Ethyl 6-methyl-4-phenyl-2-(β-naphthylamine)-pyrimidine-5-carboxylate (2l)



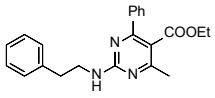
Yield: 40 mg, 51 %; pale yellow viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37 (d, *J* = 1.8 Hz, 1H), 7.83 – 7.75 (m, 3H), 7.71 – 7.60 (m, 4H), 7.50 – 7.42 (m, 4H), 7.41 – 7.33 (m, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.61 (s, 3H), 1.02 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.6, 167.4, 166.0, 159.9, 138.6, 134.3, 129.7, 128.7, 128.5, 128.6, 128.1, 126.3, 126.0, 125.9, 125.8, 124.8, 124.6, 118.9, 109.7, 61.35, 23.0, 13.65. IR (film) cm^{-1}: 3390, 3054, 2981, 2935, 1716, 1546, 1438, 1369, 1265, 1087, 752, 698, 431; HRMS (ESI) (*m/z*): calcd for $C_{24}H_{22}N_3O_2$ $[M+H]^+$ 384.1712, found 384.1732.

Ethyl 6-methyl-4-phenyl-2-(2'-pyridinylamino)-pyrimidine-5-carboxylate (2m)[5]



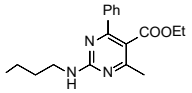
Yield: 31 mg, 55 %; pale yellow viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.11 (s, 1H), 8.53 (d, *J* = 8.5 Hz, 1H), 8.45 (d, *J* = 3.8 Hz, 1H), 7.70-7.61 (m, 3H), 7.49-7.43 (0m, 3H), 6.93 (dd, *J* = 6.7, 5.4 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.60 (s, 3H), 1.01 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.4, 167.2, 165.6, 152.6, 148.0, 138.5, 138.0, 129.8, 128.4, 128.1, 117.8, 113.0, 61.4, 22.9, 13.6.

Ethyl 6-methyl-4-phenyl-2-(2'-phenethylamino)-pyrimidine-5-carboxylate (2n)



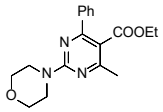
Yield: 45 mg, 70 %; pale yellow viscous oil. ^{1}H NMR (300 MHz, MeOD): δ 7.46 (t, *J* = 11.6 Hz, 5H), 7.31-7.07 (m, 6H), 4.03 (q, *J* = 7.1 Hz, 2H), 3.67 (t, *J* = 7.3 Hz, 2H), 2.90 (d, *J* = 7.2 Hz, 2H), 0.94 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, MeOD): δ 170.3, 167.5, 162.6, 140.9, 129.9, 129.4, 129.2, 129.1, 127.2, 115.8, 62.2, 43.9, 36.7, 13.9; IR (film) cm^{-1} 3374, 3062, 3027, 2977, 1712, 1558, 1450, 1265, 1083, 767, 698, 433; HRMS (ESI) (*m/z*): calcd for $C_{22}H_{24}N_3O_2$ $[M+H]^+$ 362.1869, found 362.1854.

Ethyl 6-methyl-4-phenyl-2-butylamino-pyrimidine-5-carboxylate (2o)[6]



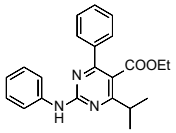
Yield: 42 mg, 75 %; pale yellow viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54 (s, 2H), 7.41 (m, 3H), 5.42 (t, *J* = 5.2 Hz, 1H), 4.04 (q, *J* = 7.1 Hz, 2H), 3.48 (dd, *J* = 13.0, 6.7 Hz, 2H), 2.48 (s, 3H), 1.57 (dd, *J* = 14.8, 7.2 Hz, 2H), 1.39 (dd, *J* = 15.0, 7.3 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.9, 166.4, 161.1, 139.2, 129.6, 128.3, 128.0, 115.0, 61.1, 41.1, 31.7, 20.1, 13.9, 13.6.

Ethyl 6-methyl-4-phenyl-2-(4'-morpholinyl)-pyrimidine-5-carboxylate (2p)[6]



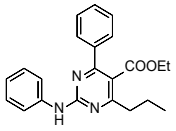
Yield: 23 mg, 49 %; yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57 (dd, *J* = 7.2, 2.4 Hz, 2H), 7.41 (dd, *J* = 5.2, 1.8 Hz, 3H), 4.05 (q, *J* = 7.1 Hz, 2H), 3.96-3.88 (m, 4H), 3.78-3.72 (m, 4H), 2.50 (s, 3H), 0.95 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.0, 167.0, 165.6, 160.2, 139.3, 129.5, 128.2, 128.1, 114.5, 66.9, 61.0, 44.1, 23.2, 13.5.

Ethyl 6-isopropyl-4-phenyl-2-phenylamino-pyrimidine-5-carboxylate (3a)



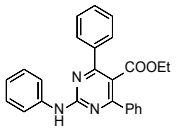
Yield: 55 mg, 85 %; pale yellow viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 – 7.62 (m, 2H), 7.55 (dd, *J* = 6.8, 2.9 Hz, 2H), 7.41 – 7.32 (m, 3H), 7.30 – 7.21 (m, 2H), 6.98 (dd, *J* = 10.6, 4.2 Hz, 1H), 4.03 (q, *J* = 7.1 Hz, 2H), 3.21 (dt, *J* = 13.4, 6.7 Hz, 1H), 1.27 (d, *J* = 6.7 Hz, 6H), 0.93 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.9, 168.7, 159.0, 139.4, 138.6, 129.6, 128.9, 128.4, 128.0, 122.5, 119.0, 116.8, 61.4, 33.0, 21.8, 13.6; IR (film) cm^{-1}: 3355, 3062, 2973, 2935, 1716, 1550, 1438, 1257, 1072, 755, 694, 428; HRMS (ESI) (*m/z*): calcd for $C_{22}H_{24}N_3O_2$ $[M+H]^+$ 362.1869, found 362.1862.

Ethyl 6-propyl-4-phenyl-2-phenylamino-pyrimidine-5-carboxylate (3b)



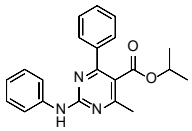
Yield: 58 mg, 86 %; pale yellow viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.63 (d, J = 8.3 Hz, 2H), 7.55 (m, 2H), 7.41-7.34 (m, 3H), 7.25 (t, J = 7.9 Hz, 2H), 6.98 (t, J = 7.4 Hz, 1H), 4.03 (q, J = 7.1 Hz, 2H), 2.74 (t, J = 7.6 Hz, 2H), 1.76 (sext, J = 7.5 Hz, 2H), 0.94 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.5, 168.6, 165.8, 158.8, 139.2, 138.7, 129.7, 128.9, 128.4, 128.0, 122.6, 119.09, 117.3, 61.3, 37.6, 22.0, 14.1, 13.6; IR (film) cm^{-1}: 3355, 3058, 2965, 2873, 1716, 1550, 1442, 1257, 1095, 755, 694, 428; HRMS (ESI) (*m/z*): calcd for $C_{22}H_{24}N_3O_2$ $[M+H]^+$ 362.1869, found 362.1874.

Ethyl 4,6-diphenyl-2-phenylamino-pyrimidine-5-carboxylate (3c)[7]



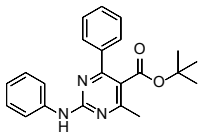
Yield: 62 mg, 87 %; pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62 (dd, J = 10.0, 5.9 Hz, 6H), 7.43 – 7.34 (m, 6H), 7.25 (t, J = 7.9 Hz, 2H), 6.97 (t, J = 7.4 Hz, 1H), 3.93 (q, J = 7.1 Hz, 2H), 0.84 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.6, 166.2, 158.8, 139.2, 138.1, 129.9, 129.0, 128.5, 128.2, 122.8, 119.1, 117.5, 61.6, 13.5.

Isopropyl 6-methyl-4-phenyl-2-phenylamino-pyrimidine-5-carboxylate (3d)



Yield: 55 mg, 86 %; pale yellow viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65 (ddd, J = 7.6, 6.4, 2.1 Hz, 4H), 7.45 (dd, J = 5.2, 1.8 Hz, 4H), 7.34 (t, J = 7.9 Hz, 2H), 5.01 (dt, J = 12.5, 6.3 Hz, 1H), 2.56 (s, 3H), 1.05 (d, J = 6.3 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.9, 166.8, 165.7, 158.5, 139.1, 138.5, 129.7, 128.9, 128.4, 128.1, 122.8, 119.2, 117.8, 69.1, 22.8, 21.3; IR (film) cm^{-1}: 3351, 3058, 2965, 2873, 1716, 1550, 1442, 1257, 1095, 755, 694, 439; HRMS (ESI) (*m/z*): calcd for $C_{21}H_{22}N_3O_2$ $[M+H]^+$ 348.1712, found 348.1723.

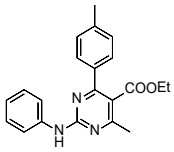
***tert*-Butyl 6-methyl-4-phenyl-2-phenylamino-pyrimidine-5-carboxylate (3e)**



Yield: 49 mg, 75 %; pale yellow viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (dd, J = 16.9, 5.9 Hz, 4H), 7.43 (dd, J = 7.3, 3.8 Hz, 3H), 7.31 (t, J = 7.9 Hz, 2H), 7.02 (t, J = 7.4 Hz, 1H), 2.55 (s,

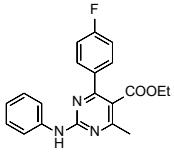
3H), 1.31 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.3, 166.7, 165.5, 158.3, 139.2, 138.7, 129.6, 128.9, 128.32, 128.27, 122.7, 119.1, 118.9, 82.2, 27.6, 22.9; IR (film) cm^{-1}: 3355, 3058, 2973, 2935, 2873, 1716, 1550, 1438, 1257, 1145, 755, 694, 428; HRMS (ESI) (*m/z*): calcd for $C_{22}H_{24}N_3O_2$ $[M+H]^+$ 362.1869, found 362.1853.

Ethyl 6-methyl-4-(4'-methylphenyl)-2-phenyamino-pyrimidine-5-carboxylate (3f)



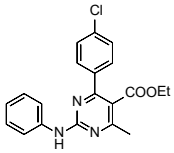
Yield: 57 mg, 92 %; pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61 (d, *J* = 7.8 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 3H), 7.25 (t, *J* = 7.9 Hz, 2H), 7.17 (d, *J* = 7.1 Hz, 2H), 6.97 (t, *J* = 7.4 Hz, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 2.48 (s, 3H), 2.33 (s, 3H), 0.98 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.7, 166.9, 165.7, 158.6, 140.1, 139.2, 135.6, 129.1, 128.1, 122.7, 119.2, 117.1, 61.4, 22.9, 21.4, 13.7; IR (film) cm^{-1} 3343, 3031, 2981, 2927, 1712, 1550, 1442, 1265, 1087, 798, 752, 501; HRMS (ESI) (*m/z*): calcd for $C_{21}H_{22}N_3O_2$ $[M+H]^+$ 348.1712, found 348.1718.

Ethyl 6-methyl-4-(4'-fluorophenyl)-2-phenylamino-pyrimidine-5-carboxylate (3g)[5]



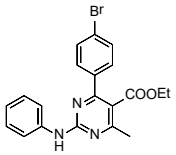
Yield: 57 mg, 90 %; white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66-749 (m, 4H), 7.28 (dd, *J* = 13.7, 6.2 Hz, 3H), 7.12-6.94 (m, 3H), 4.07 (q, *J* = 7.1 Hz, 2H), 2.49 (s, 3H), 0.99 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.4, 167.3, 165.4, 164.6, 158.6, 139.0, 134.6, 130.2, 130.1, 128.9, 122.9, 119.3, 117.0, 115.6, 115.3, 61.4, 22.9, 13.7

Ethyl 6-methyl-4-(4'-chlorophenyl)-2-phenylamino-pyrimidine-5-carboxylate (3h)[5]



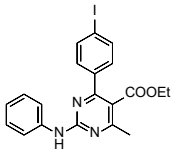
Yield: 58 mg, 88 %; white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60 (d, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 7.27 (t, *J* = 7.9 Hz, 3H), 6.99 (t, *J* = 7.4 Hz, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 2.49 (s, 3H), 1.00 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.2, 167.5, 164.6, 158.6, 138.9, 137.0, 136.0, 129.5, 129.0, 128.6, 123.0, 119.3, 117.0, 61.4, 23.0, 13.7.

Ethyl 6-methyl-4-(4'-bromophenyl)-2-phenylamino-pyrimidine-5-carboxylate (3i)[5]



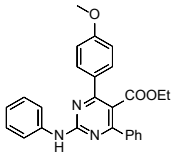
Yield: 60 mg, 81 %; yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.1 Hz, 2H), 7.51 (dd, J = 8.4, 1.4 Hz, 2H), 7.42 (dd, *J* = 8.4, 1.2 Hz, 3H), 7.26 (t, *J* = 7.2 Hz, 2H), 6.99 (t, *J* = 7.3 Hz, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 2.49 (s, 3H), 0.99 (t, *J* = 7.1, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.2, 167.5, 164.6, 158.7, 138.9, 137.5, 131.6, 129.7, 128.9, 124.3, 122.9, 119.3, 116.9, 61.5, 23.0, 13.7.

Ethyl 6-methyl-4-(4'-Iodophenyl)-2-phenylamino-pyrimidine-5-carboxylate (3j)



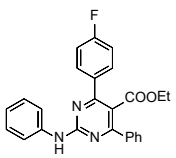
Yield: 51 mg, 62 %; yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 7.8 Hz, 2H), 7.45 (s, 1H), 7.39 – 7.29 (m, 4H), 7.06 (t, *J* = 7.4 Hz, 1H), 4.13 (d, *J*=7.19 Hz, 2H), 2.56 (s, 3H), 1.07 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.1, 167.4, 164.8, 158.6, 138.9, 138.1, 137.5, 129.8, 128.9, 123.0, 119.3, 116.9, 96.3, 61.5, 23.0, 13.7; IR (film) cm^{-1}: 3355, 3058, 2981, 2935, 1712, 1550, 1442, 1265, 1157, 1087, 1014, 840, 802, 748, 694, 428; HRMS (ESI) (*m/z*): calcd for $C_{20}H_{19}IN_3O_2$ $[M+H]^+$ 460.0522, found 460.0534.

Ethyl 6-phenyl-4-(4'-methoxyphenyl)-2-phenylamino-pyrimidine-5-carboxylate (3k)



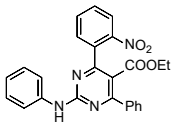
Yield: 69 mg, 91 %; yellow viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.69 (dt, *J* = 7.4, 6.2 Hz, 7H), 7.47 (dd, *J* = 5.1, 1.8 Hz, 3H), 7.34 (t, *J* = 7.9 Hz, 2H), 7.07 (d, *J* = 7.4 Hz, 1H), 7.02 – 6.95 (m, 2H), 4.04 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 0.96 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.7, 166.0, 165.2, 161.3, 158.3, 139.0, 130.0, 129.0, 128.5, 128.1, 122.9, 119.2, 116.9, 113.9, 61.6, 55.4, 13.5; IR (film) cm^{-1}: 3401, 3062, 2985, 1716, 1538, 1442, 1265, 1133, 752, 694, 640, 520, 455; HRMS (ESI) (*m/z*): calcd for $C_{26}H_{24}N_3O_3$ $[M+H]^+$ 426.1818, found 426.1810.

Ethyl 6-phenyl-4-(2'-fluorophenyl)-2-phenylamino-pyrimidine-5-carboxylate (3l)



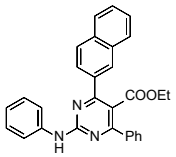
Yield: 65 mg, 88 %; yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75– 7.63(m, 6H), 7.49 (t, *J* = 9.8 Hz, 4H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.16 (t, *J* = 8.2 Hz, 2H), 7.07 (t, *J* = 6.9 Hz, 1H), 4.02 (q, *J* = 7.1 Hz, 2H), 0.94 (t, *J* = 7.6, Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.4, 166.3, 164.9, 158.6, 138.9, 137.9, 130.4, 130.0, 129.0, 128.5, 128.1, 123.0, 119.2, 117.2, 115.7, 115.4, 61.6, 13.5; IR (film) cm^{-1}: 3382, 3062, 2981, 2935, 1716, 1592, 1538, 1446, 1349, 1265, 1141, 752, 694, 431; HRMS (ESI) (*m/z*): calcd for $C_{25}H_{21}FN_3O_2$ $[M+H]^+$ 414.1618, found 414.1610.

Ethyl 6-phenyl-4-(2'-nitrophenyl)-2-phenylamino-pyrimidine-5-carboxylate (3m)



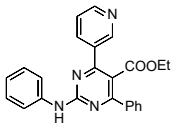
Yield: 72 mg, 91 %; pale yellow viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.03 (d, *J* = 7.8 Hz, 1H), 7.76-7.62 (m, 5H), 7.53-7.40 (m, 4H), 7.32 (dd, *J* = 19.4, 11.3 Hz, 3H), 7.07 (t, *J* = 7.4 Hz, 1H), 4.02 (q, *J* = 7.1 Hz, 2H), 0.92 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.1, 166.8, 163.3, 159.0, 138.9, 137.9, 135.8, 130.0, 129.0, 128.5, 128.1, 123.1, 119.3, 117.4, 61.7, 13.4; IR (film) cm^{-1}: 3340, 3058, 2981, 2935, 1716, 1538, 1442, 1349, 1268, 1141, 752, 694, 416; HRMS (ESI) (*m/z*): calcd for $C_{25}H_{21}N_4O_4$ $[M+H]^+$ 441.1563, found 441.1556.

Ethyl 6-phenyl-4-(2'-napthalyl)-2-phenylamino-pyrimidine-5-carboxylate (3n)



Yield: 70 mg, 88 %; yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.12 (s, 1H), 7.91 – 7.80 (m, 3H), 7.68 (ddd, *J* = 11.6, 9.6, 6.1 Hz, 5H), 7.45 (dt, *J* = 6.3, 4.0 Hz, 6H), 7.28 (t, *J* = 7.7 Hz, 2H), 6.99 (t, *J* = 6.9 Hz, 1H), 3.93 (q, *J* = 7.1 Hz, 2H), 0.82 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.6, 166.2, 166.0, 158.7, 139.1, 138.0, 135.3, 133.8, 132.9, 129.9, 129.0, 128.7, 128.5, 127.7, 127.2, 126.5, 125.3, 122.8, 119.2, 117.6, 61.6, 13.5; IR (film) cm^{-1}: 3394, 3058, 2981, 1716, 1542, 1442, 1295, 1141, 752, 698, 474; HRMS (ESI) (*m/z*): calcd for $C_{29}H_{24}N_3O_2$ $[M+H]^+$ 446.1869, found 446.1884.

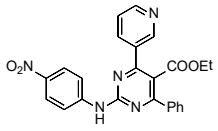
Ethyl 6-phenyl-4-(3'-pyridyl)-2-phenylamino-pyrimidine-5-carboxylate (3o)



Yield: 65 mg, 91 %; pale yellow viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.59 (t, *J* = 1.9 Hz, 1H), 8.34 (dd, *J* = 8.2, 1.3 Hz, 1H), 8.05 (d, *J* = 7.8 Hz, 1H), 7.71 – 7.65 (m, 4H), 7.50 (m, 3H), 7.35 (t, *J* = 7.9 Hz, 2H), 7.16 (t, *J* = 7.9 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.70 (d, *J* = 7.5 Hz, 1H),

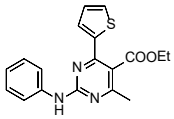
4.04 (q, J = 7.1 Hz, 2H), 0.96 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.0, 166.8, 163.6, 158.7, 148.1, 139.4, 138.6, 137.6, 134.3, 130.2, 129.5, 129.1, 128.6, 128.1, 124.6, 123.6, 123.3, 119.4, 117.2, 62.0, 13.5; IR (film) cm^{-1}: 3351, 3058, 2981, 2935, 1716, 1550, 1442, 1265, 1087, 748, 694, 501; HRMS (ESI) (*m/z*): calcd for $C_{24}H_{21}N_4O_2$ $[M+H]^+$ 397.1665, found 397.1661.

Ethyl 6-phenyl-4-(3'-pyridyl)-2-(4''-nitrophenylamino)-pyrimidine-5-carboxylate (3p)



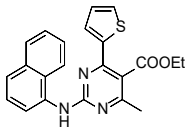
Yield: 58 mg, 71 %; yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.58 (s, 1H), 8.52 (d, J = 1.8 Hz, 1H), 8.31 (s, 1H), 8.25 (d, J = 8.2 Hz, 2H), 8.06 (t, J = 3.5 Hz, 1H), 7.90 (d, J = 9.2 Hz, 2H), 7.69 (dd, J = 7.8, 1.8 Hz, 3H), 7.54 (m, 3H), 4.07 (q, J = 7.2 Hz, 2H), 0.98 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.77, 148.2, 144.6, 142.6, 134.2, 130.8, 129.8, 128.8, 128.1, 125.3, 125.0, 123.5, 118.3, 62.3, 13.5; IR (film) cm^{-1}: 3347, 3058, 2981, 2935, 1712, 1550, 1442, 1365, 1265, 1087, 1010, 752, 690, 455; HRMS (ESI) (*m/z*): calcd for $C_{24}H_{20}N_5O_4$ $[M+H]^+$ 442.1515, found 442.1506.

Ethyl 6-methyl-4-(2'-thiophyl)-2-phenylamino-pyrimidine-5-carboxylate (3q)



Yield: 55 mg, 91 %; pale yellow viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, J = 7.8 Hz, 2H), 7.63 (dd, J = 8.7, 5.4 Hz, 2H), 7.35 (t, J = 7.2 Hz, 2H), 7.14 (t, J = 5.3 Hz, 2H), 7.07 (t, J = 7.4 Hz, 1H), 4.09 (q, J = 7.1 Hz, 2H), 2.49 (s, 3H), 0.99 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.8, 166.0, 158.3, 156.4, 141.6, 139.1, 130.2, 128.9, 128.7, 128.1, 122.7, 119.3, 115.0, 61.9, 22.3, 13.9; IR (film) cm^{-1}: 3363, 3066, 2981, 2935, 1716, 1554, 1442, 1265, 1133, 1083, 752, 713, 408; HRMS (ESI) (*m/z*): calcd for $C_{18}H_{18}N_3O_2S$ $[M+H]^+$ 340.1120, found 340.1109.

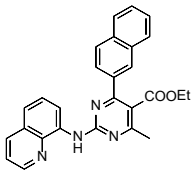
Ethyl 6-Methyl-4-(2'-thiophyl)-2-(α-naphtylamino)-pyrimidine-5-carboxylate (3r)



Yield: 45 mg, 65 %; yellow viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22 (d, J = 7.5 Hz, 1H), 8.06 (d, J = 8.4 Hz, 1H), 7.89 (dd, J = 6.1, 3.2 Hz, 1H), 7.83 (s, 1H), 7.68 (d, J = 8.2 Hz, 1H), 7.63 – 7.36 (m, 5H), 7.07 (dd, J = 4.8, 4.1 Hz, 1H), 4.39 (q, J = 7.1 Hz, 2H), 2.48 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.8, 166.0, 159.1, 156.6, 141.5, 134.2, 133.6, 130.4, 128.7, 128.1, 127.0, 126.0, 126.9, 125.7, 124.4, 121.0, 119.0, 115.2, 61.8, 22.3, 13.9; IR (film) cm^{-}

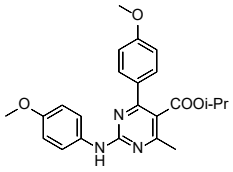
[1] 3386, 3058, 2981, 2931, 1631, 1554, 1434, 1265, 1133, 1083, 786, 713, 458; HRMS (ESI) (*m/z*): calcd for $C_{22}H_{20}N_3O_2S$ $[M+H]^+$ 390.1276, found 390.1299.

Ethyl 6-methyl-4-(2'-napthalyl)-2-(8''-quinolinylamino)-pyrimidine-5-carboxylate (3s)



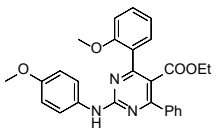
Yield: 28 mg, 36 %; pale yellow viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.03 (d, *J* = 7.6 Hz, 1H), 8.87 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.22-8.14 (m, 2H), 7.93 (dd, *J* = 16.6, 8.0 Hz, 3H), 7.83 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.57 (dd, *J* = 10.4, 5.7 Hz, 3H), 7.46 (dd, *J* = 8.2, 4.5 Hz, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.70 (s, 3H), 0.94 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.7, 167.1,165.6, 158.6, 147.9, 138.5, 136.2, 136.1, 135.8, 133.8, 132.9, 128.7, 128.2, 128.1, 127.7, 127.4, 126.5, 125.6, 121.6, 119.9, 117.5, 114.9, 61.4, 23.1, 13.7. IR (film) cm^{-1}: 3343, 3054, 2977, 1716, 1527, 1430, 1380, 1261, 794, 752, 713, 455; HRMS (ESI) (*m/z*): calcd for $C_{27}H_{23}N_4O_2$ $[M+H]^+$ 435.1821, found 435.1830.

Isopropyl 6-methyl-4-(4'-methoxyphenyl)-2-(4''-methoxyphenylamino)-pyrimidine-5-carboxylate (3t)



Yield: 57 mg, 78 %; pale yellow viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.60 (m, 4H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 5.06 (sept, *J* = 6.3 Hz, 1H), 3.82 (d, *J* = 14.3 Hz, 6H), 2.51 (s, 3H), 1.12 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.3, 166.3, 165.0, 161.1, 158.6, 155.5, 132.3, 130.8, 129.9, 121.3, 116.8, 114.0, 113.8, 69.1, 55.5, 55.4, 22.4, 21.4; IR (film) cm^{-1}: 3336, 3058, 2942, 2834, 1716, 1542, 1438, 1357, 1249, 1172, 1029, 829, 755, 455; HRMS (ESI) (*m/z*): calcd for $C_{23}H_{26}N_3O_4$ $[M+H]^+$ 408.1923, found 408.1918.

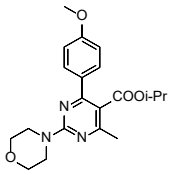
Ethyl 6-phenyl-4-(2-methoxyphenyl)-2-(4-methoxyphenylamino)-pyrimidine-5-carboxylate (3u)



Yield: 65 mg, 80 %; pale yellow viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.61 (d, *J* = 7.8 Hz, 4H), 7.54 – 7.38 (m, 5H), 7.10 (t, *J* = 6.9 Hz, 1H), 6.93 (d, *J* = 8.3 Hz, 1H), 6.88 (d, *J*

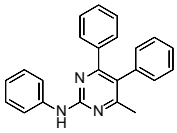
= 7.8 Hz, 2H), 3.90 (d, *J* = 7.1 Hz, 2H), 3.78 (d, *J* = 11.1 Hz, 6H), 0.82 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.3, 155.4, 132.3, 130.8, 130.1, 129.5, 128.2, 120.9, 114.1, 110.5, 60.8, 55.5, 55.1, 13.3; IR (film) cm^{-1}: 3340, 3058, 2981, 2935, 1716, 1538, 1442, 1349, 1268, 1141, 752, 694, 416; HRMS (ESI) (*m/z*): calcd for $C_{27}H_{26}N_3O_4$ $[M+H]^+$ 456.1923, found 456.1912.

Isopropyl 6-phenyl-4-(4'-methoxyphenyl)-2-(4''-morpholinyl)-pyrimidine-5-carboxylate (3v)



Yield: 27 mg, 40 %; pale yellow viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 5.02 (sept, *J* = 6.3 Hz, 1H), 3.92 (t, *J* = 4.4 Hz, 4H), 3.84 (s, 3H), 3.75 (t, *J* = 4.4 Hz, 4H), 2.46 (s, 3H), 1.09 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.9, 166.3, 164.5, 160.9, 131.5, 129.8, 114.8, 113.6, 68.7, 66.9, 55.4, 44.1, 23.0, 21.4; IR (film) cm^{-1}: 2973, 2927, 2854, 1712, 1554, 1511, 1446, 1369, 1299, 1245, 1176, 1110, 844, 798, 582; HRMS (ESI) (*m/z*): calcd for $C_{20}H_{26}N_3O_4$ $[M+H]^+$ 372.1923, found 372.1918.

4-Methyl-N,5,6-triphenylpyrimidin-2-amine (4)

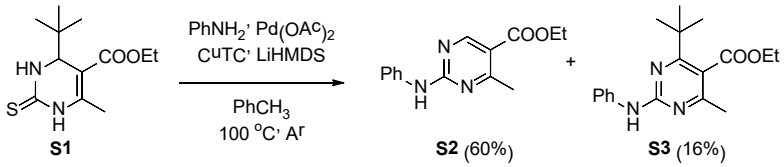


Yield: 41 mg, 61%; pale yellow viscous oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.64 (t, *J* = 13.0 Hz, 2H), 7.31 – 7.25 (m, 1H), 7.24 – 7.13 (m, 7H), 7.10 – 7.05 (m, 2H), 6.99 (dd, *J* = 12.5, 5.8 Hz, 2H), 6.90 (dd, *J* = 16.3, 8.9 Hz, 1H), 2.22 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.0, 164.5, 158.4, 140.1, 138.7, 137.3, 130.7, 129.6, 128.9, 128.5, 127.8, 127.7, 127.1, 124.3, 122.0, 118. 7, 23.5; IR (film) cm^{-1}: 3409, 3286, 3058, 2927, 2857, 1713, 1592, 1554, 1519, 1438, 1380, 1295, 1261, 1203, 1076, 1033, 890, 840, 752, 698, 419; HRMS (ESI) (*m/z*): calcd for $C_{23}H_{19}N_3$ $[M+H]^+$ 337.1579, found 337.1569.

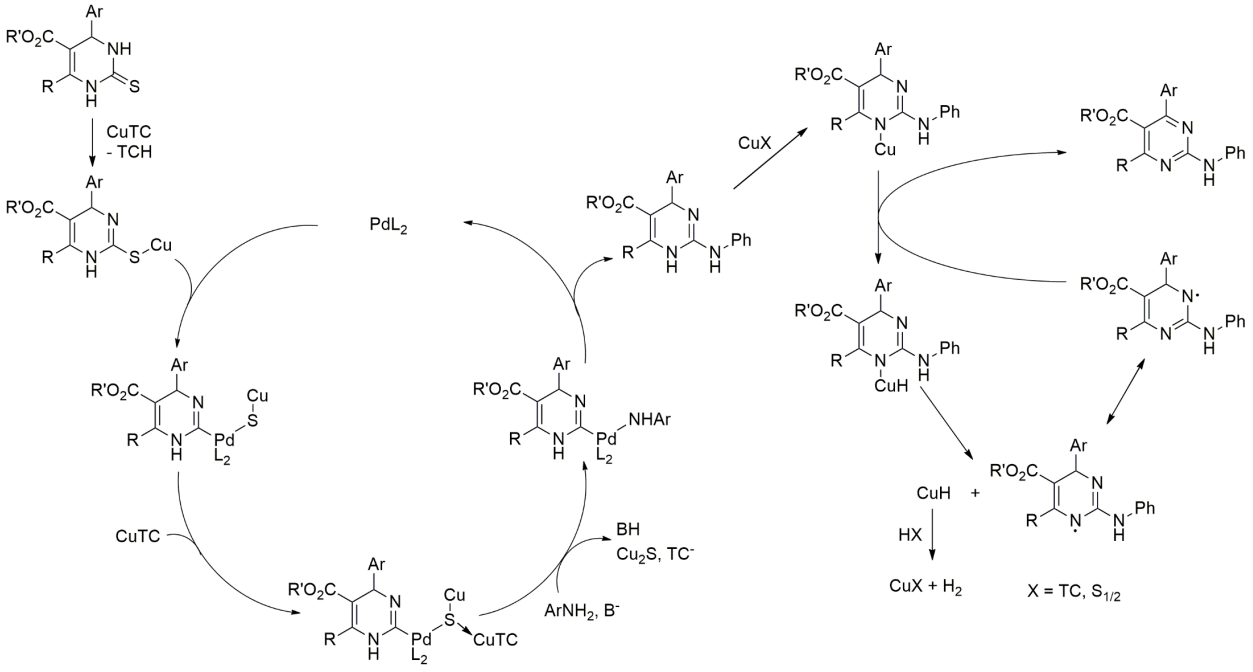
4. Possible reaction mechanism

Kappe group proposed a mechanism of the dehydrosulfurative C-C cross-coupling of DHPM with $RB(OH)_3$, which shows two equivalents of CuTC are needed to enhance the polarization of the Pd-S bond through Cu(I) coordination to S for facile ligand exchange.[8] Regarding the oxidative dehydrogenation, we carried out the reaction of DHPM **S1** possessing *t*-Bu group at the C4 position with aniline to produce debutylated pyrimidine **S2** as the major product (Scheme S1), which supports the oxidation involves the nitrogen radical species.[9] Based on these, we have proposed a possible mechanism of our reaction (Scheme S2).

Scheme S1. Reaction of S1 possessing t-Bu group at C4



Scheme S2. A possible mechanism of the reaction



5. References

(1) Lu, J.; Bai, Y.; Wang, Z.; Yang, B.; Ma, H. *Tetrahedron Lett*. **2000**, *41*, 9075-9078.

(2) (a) Singh, K.; Singh, K. *Adv. Heterocycl. Chem.* 2012, *105*, 223-308. (b) Suresh; Sandhu, J. S. *ARKIVOC* 2012, 66-133. (c) Wan, J. -P.; Liu, Y. *Synthesis* 2010, *40*, 3943-3953. (d) Kappe, C. O. *Acc. Chem. Res.* 2000, *33*, 879-888.

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(5) Zhang, Y.; Quan, Z. -J.; Gong, H. -P.; Da, Y. -X.; Zhang, Z.; Wang, X. -C. *Tetrahedron* **2015**, *71*, 2113-2118.

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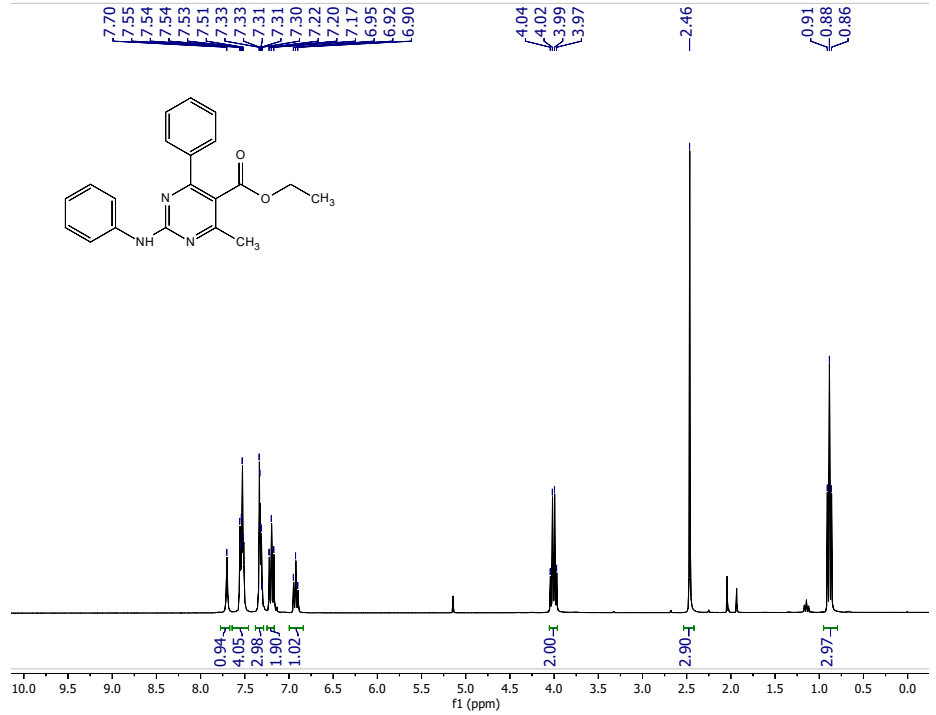
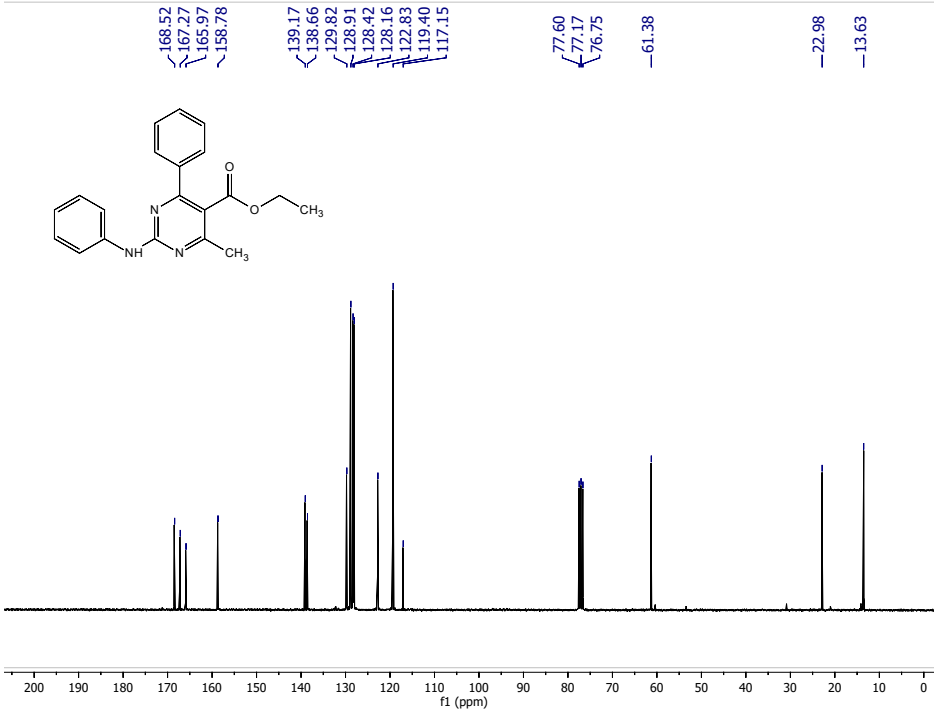
(8) Prokopcova, H.; Kappe, C. O., *J. Org. Chem.* **2007**, *72*, 4440-4448

(9) (a) Yamamoto, K.; Chen, Y. G.; Buono, F. G. *Org. Lett*. **2005**, *7*, 4673-4676. (b) Han, B.; Han, R. F.; Ren, Y. W.; Duan, X. Y.; Xu, Y. C.; Zhang, W. *Tetrahedron* **2011**, *67*, 5615–5620.

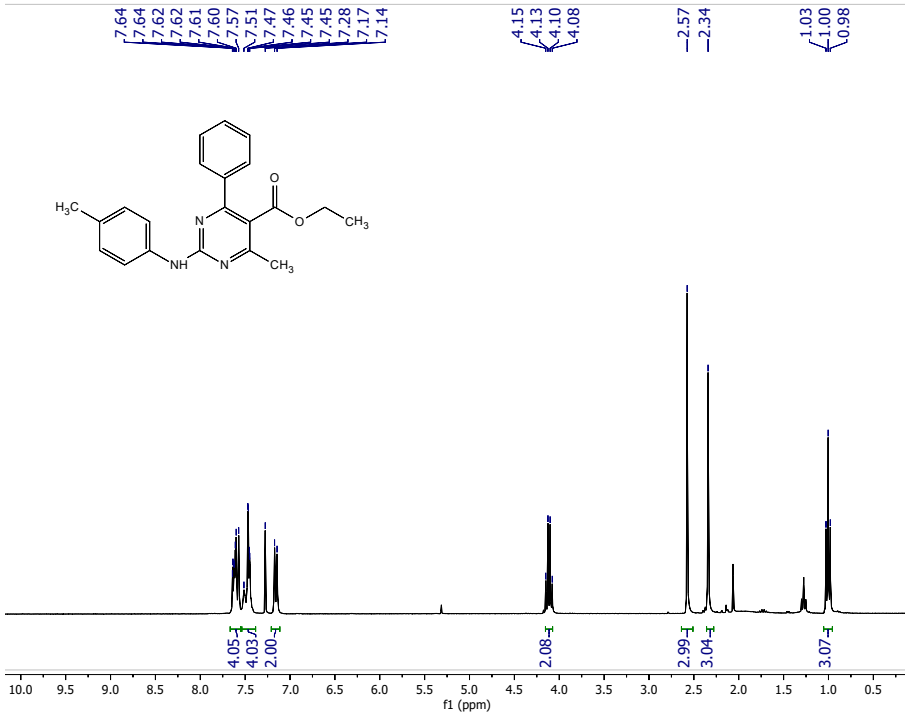
6. ^{1}H and ^{13}C NMR spectra of the compounds

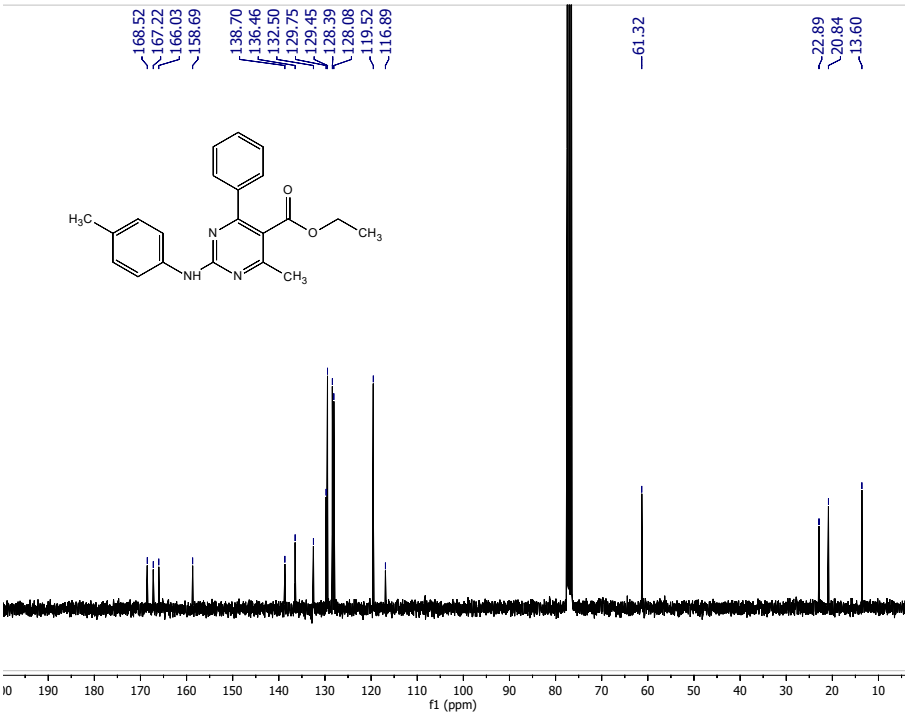
Ethyl 6-methyl-4-phenyl-2-phenylamino-pyrimidine-5-carboxylate (2a):



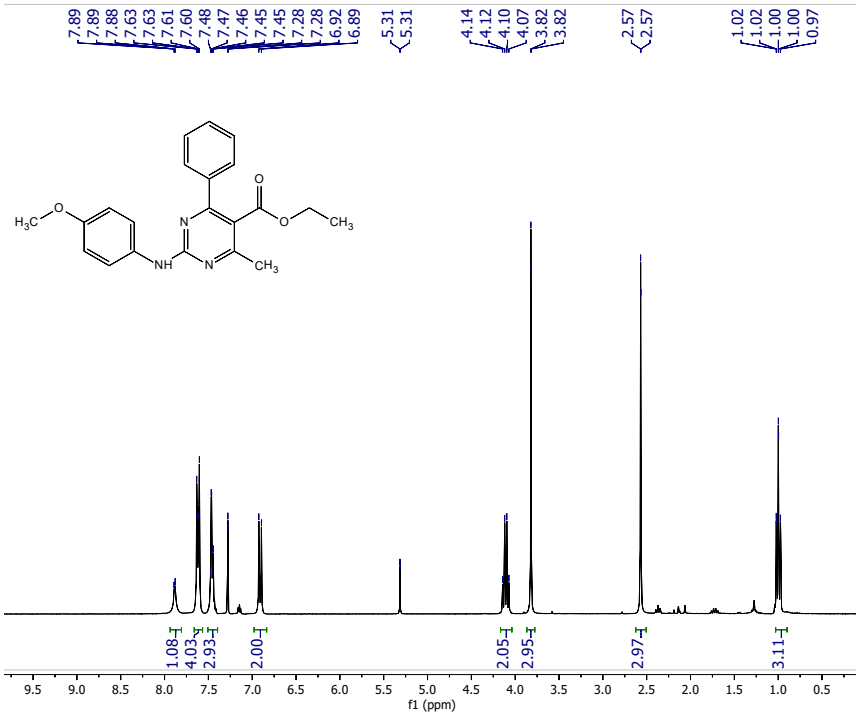


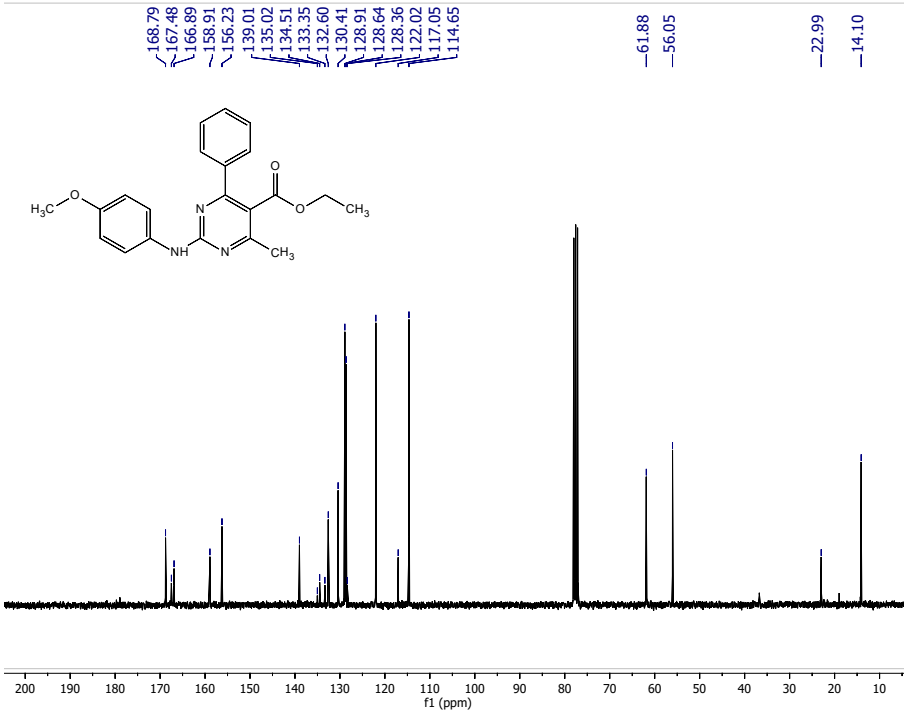
Ethyl 6-methyl-4-phenyl-2-(4'-methylphenylamino)-pyrimidine-5-carboxylate (2b):



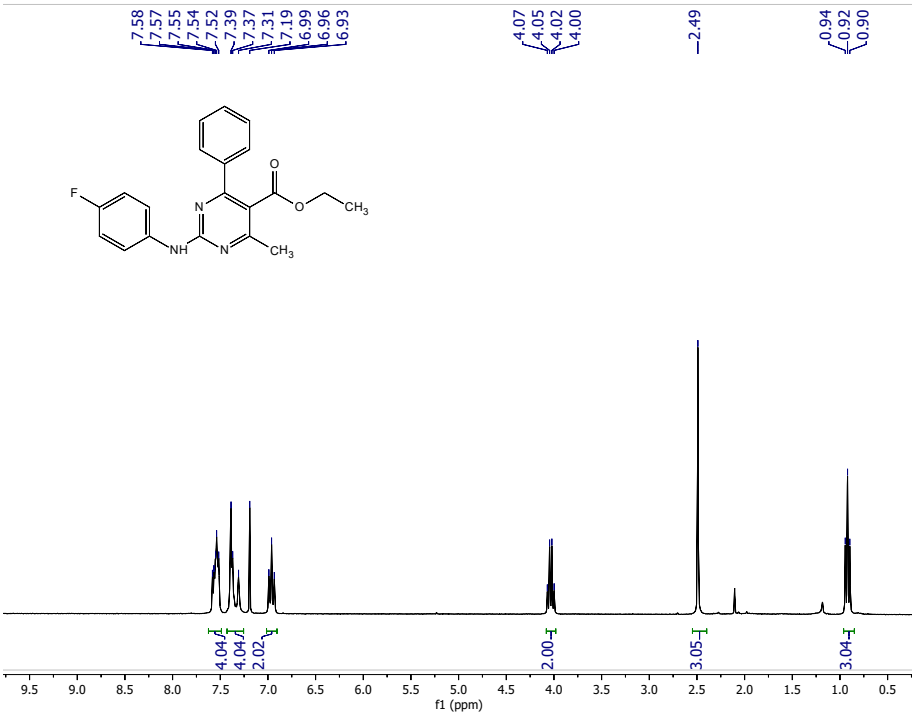


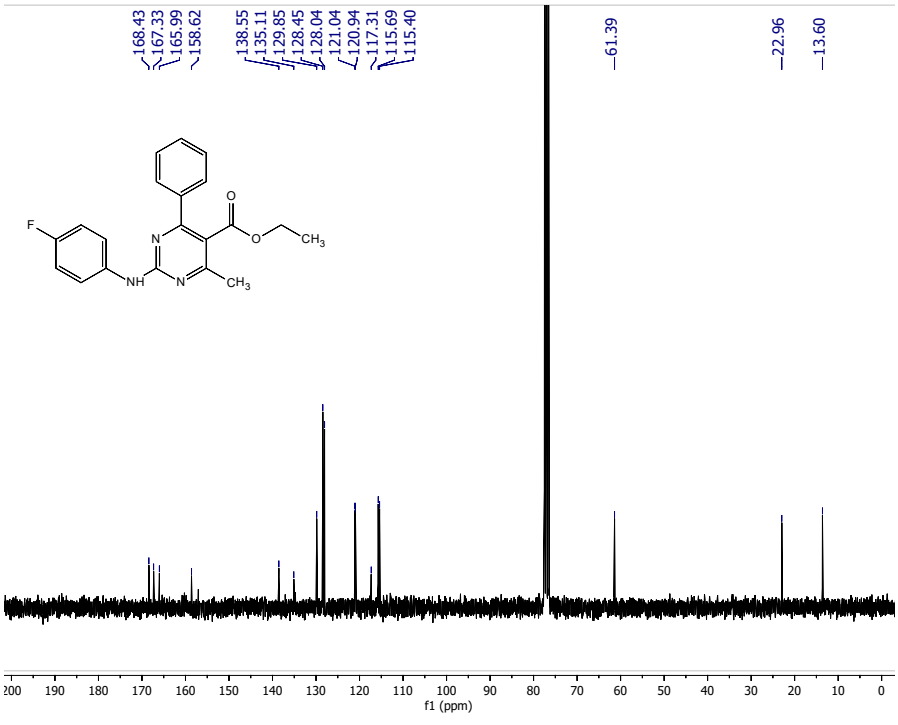
Ethyl 6-methyl-4-phenyl-2-(4'-methoxylphenylamino)-pyrimidine-5-carboxylate (2c):



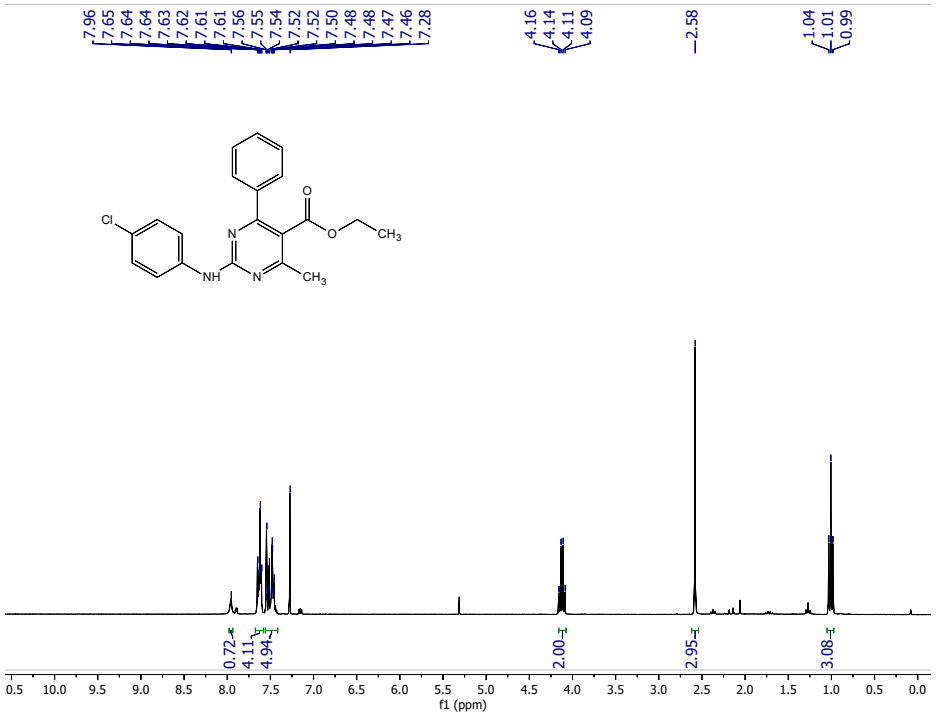


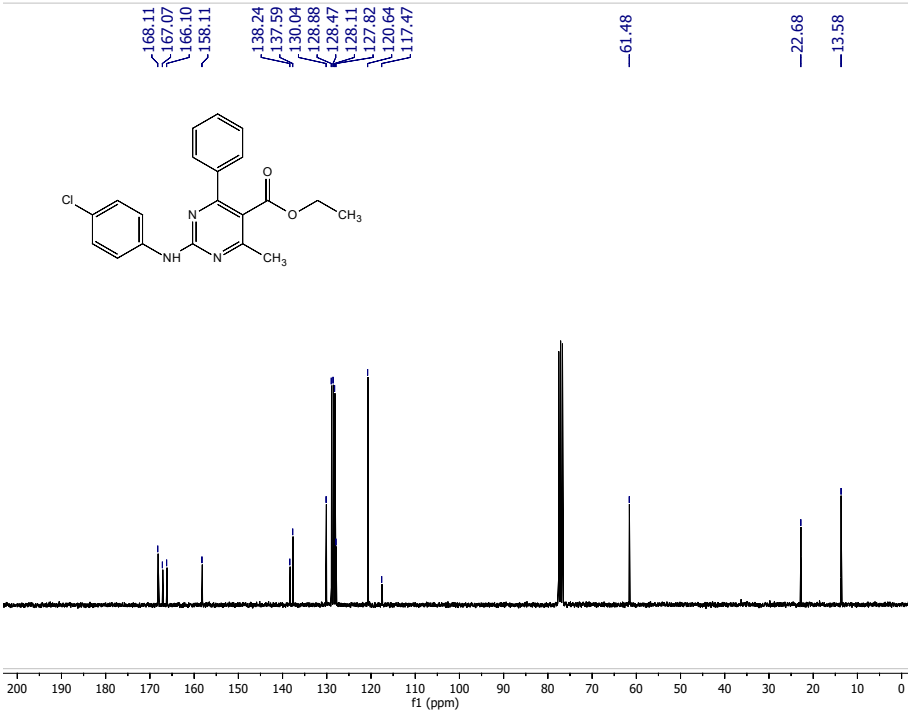
Ethyl 6-methyl-4-phenyl-2-(4'-fluorophenylamino)-pyrimidine-5-carboxylate (2d):



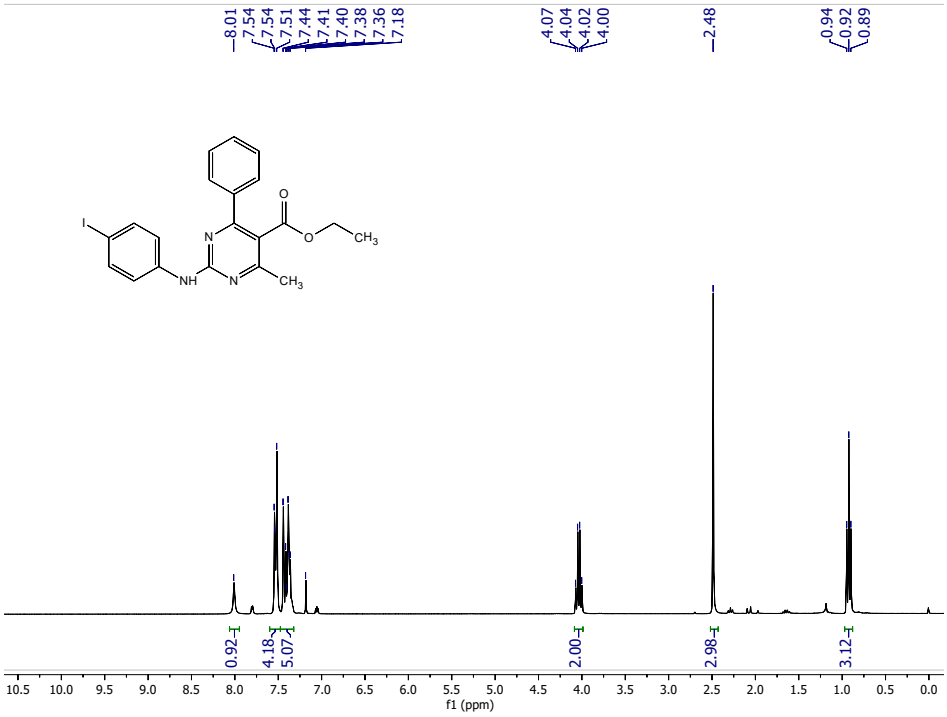


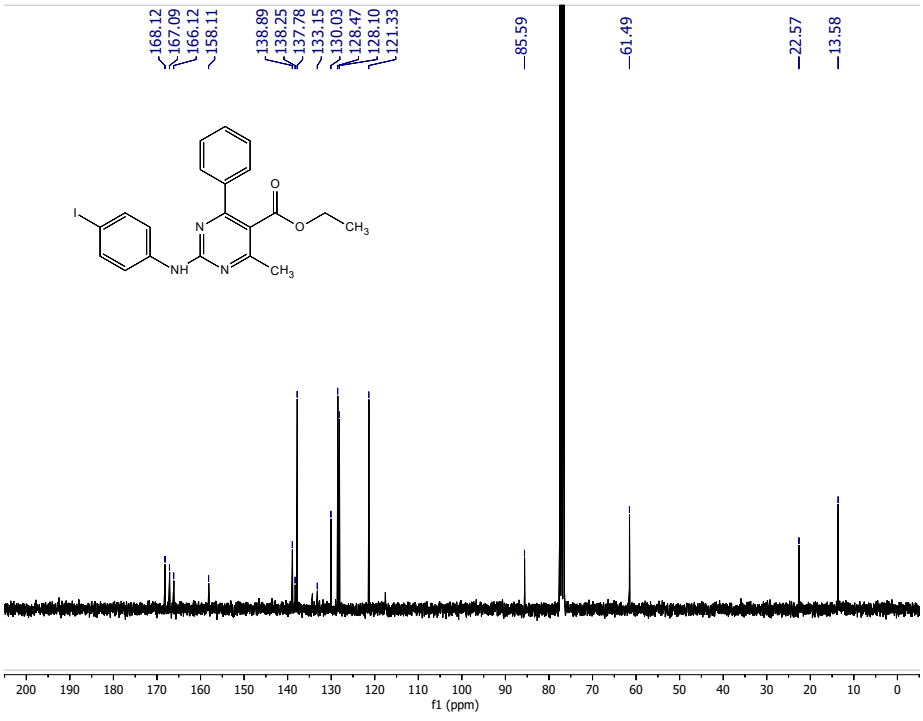
Ethyl 6-methyl-4-phenyl-2-(4'-chlorophenylamino)-pyrimidine-5-carboxylate (2e):



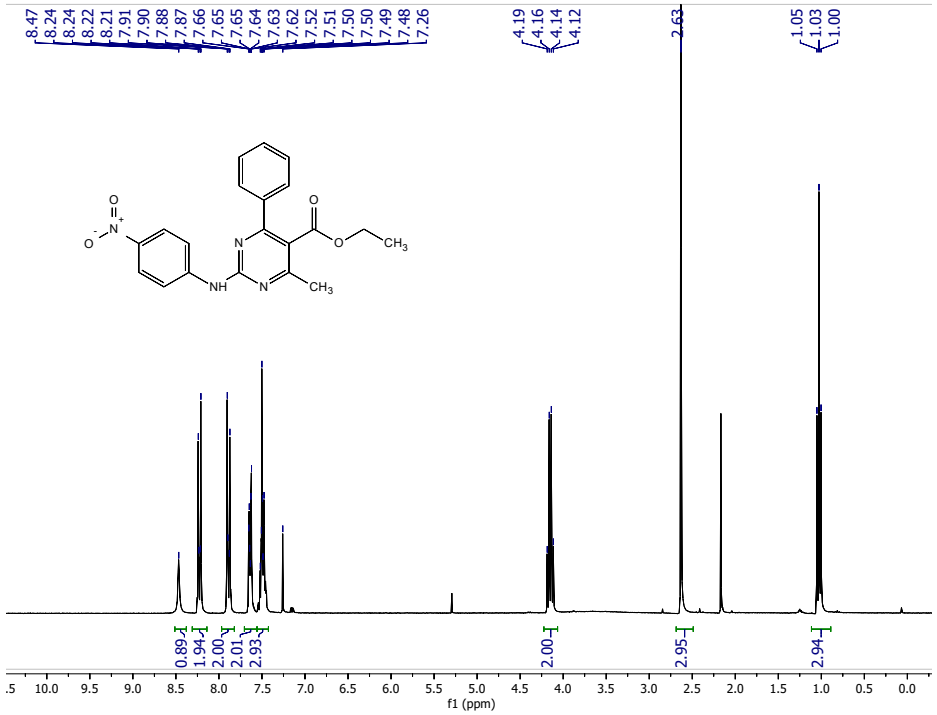


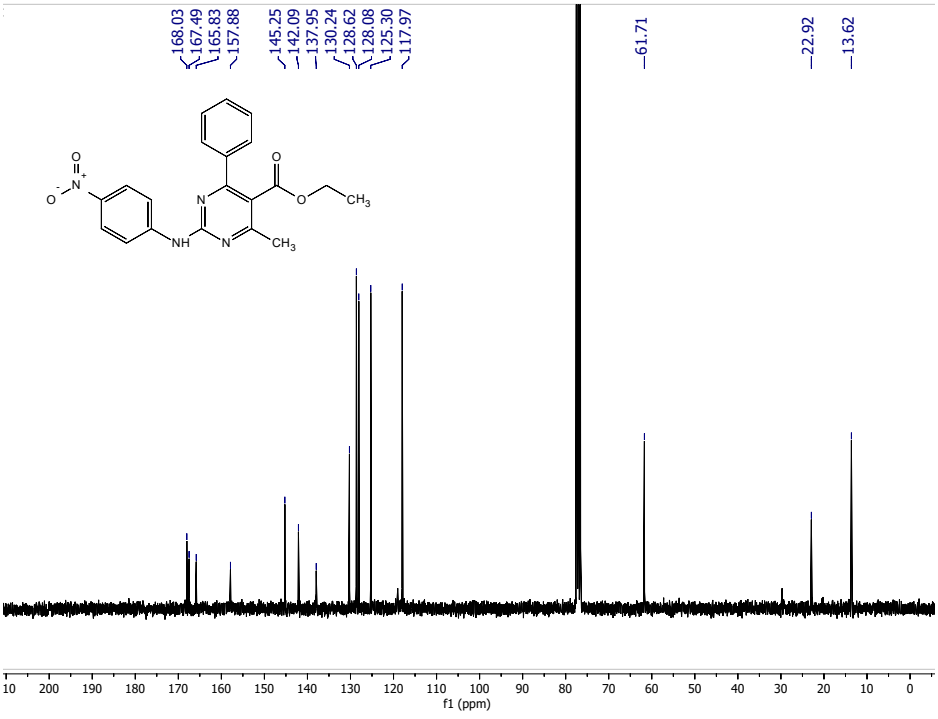
Ethyl 6-methyl-4-phenyl-2-(4'-iodophenylamino)-pyrimidine-5-carboxylate (2f):



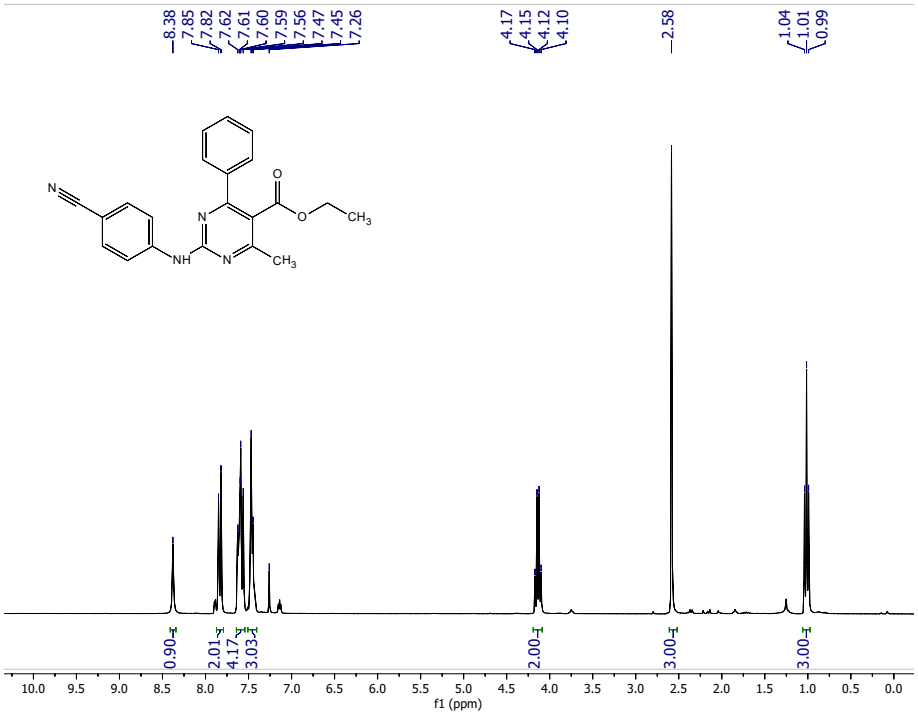


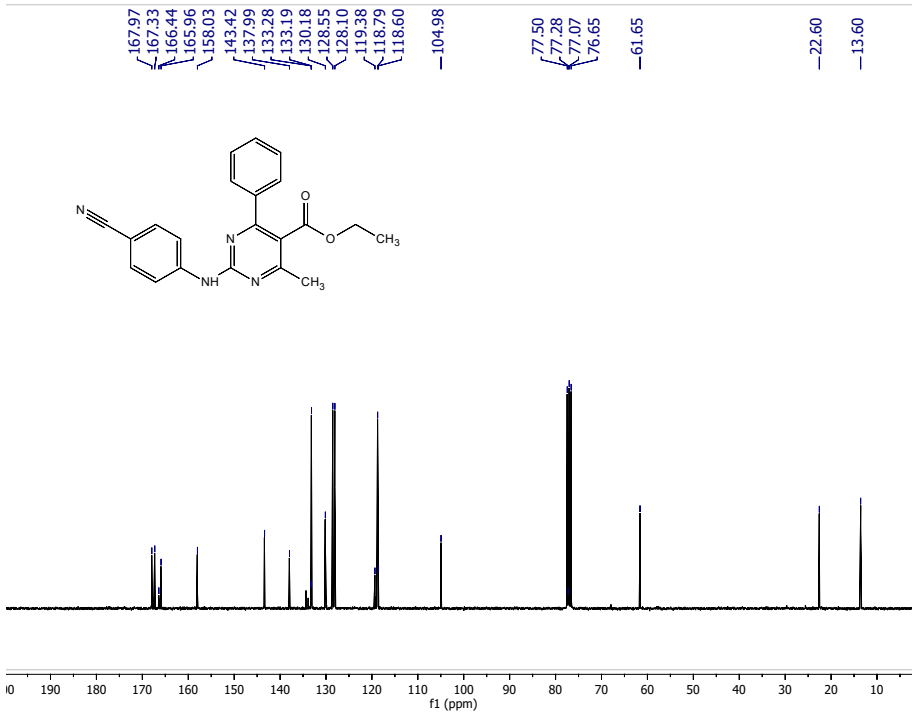
Ethyl 6-methyl-4-phenyl-2-(4'-nitrophenylamino)-pyrimidine-5-carboxylate (2g):



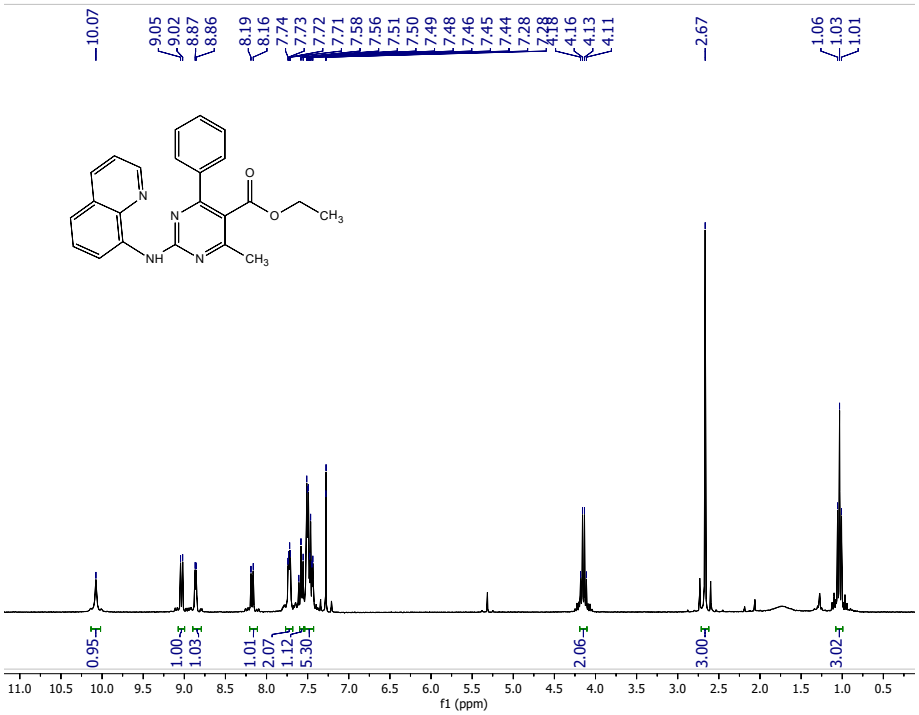


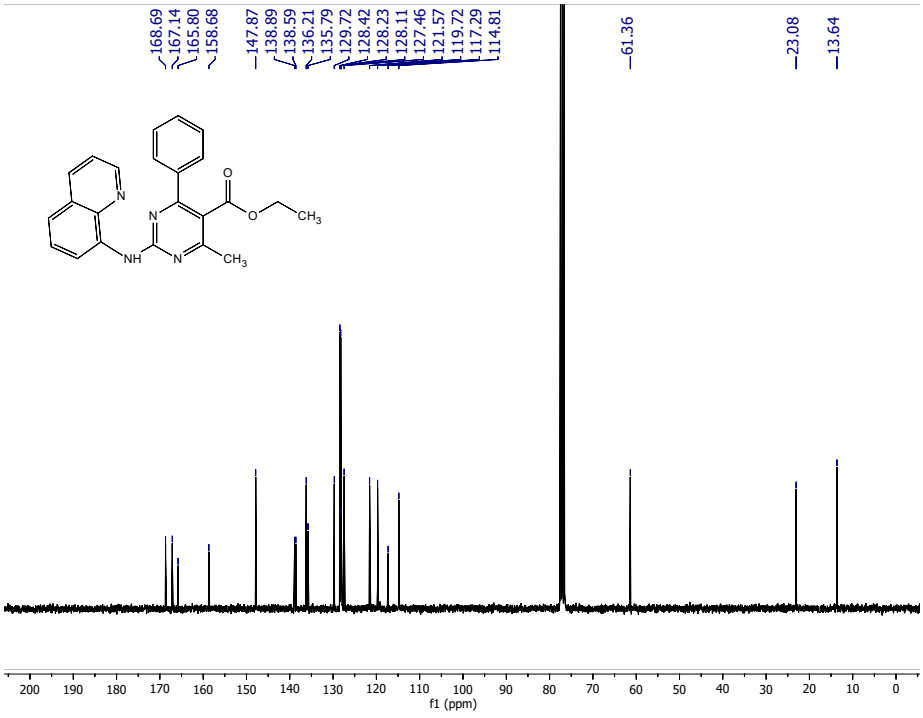
Ethyl 6-methyl-4-phenyl-2-(4'-cyanophenylamino)-pyrimidine-5-carboxylate (2h):



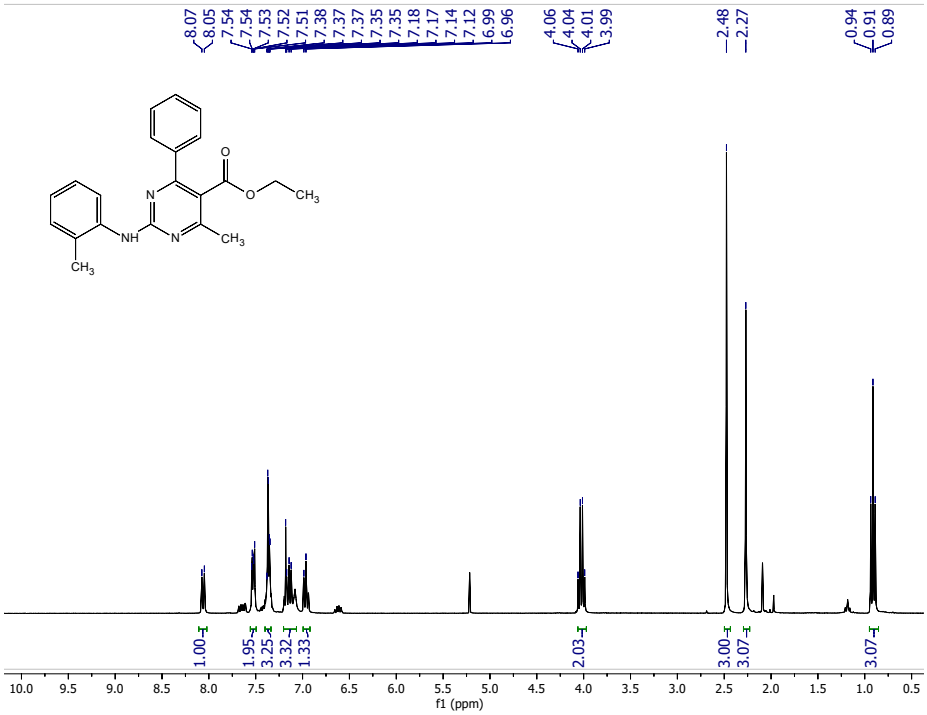


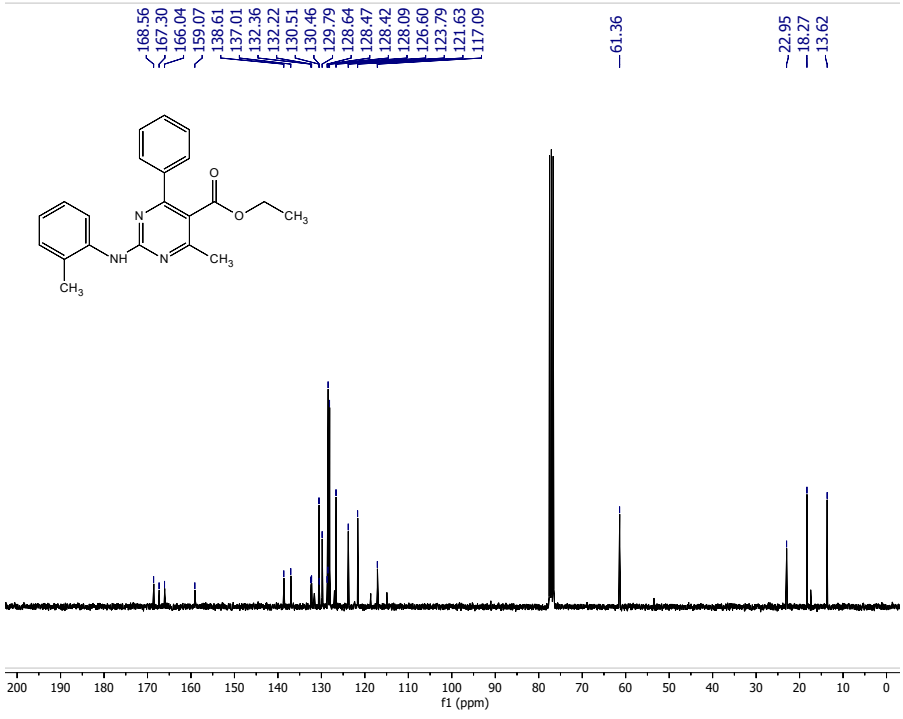
Ethyl 6-methyl-4-phenyl-2-(8'-quinolinylamino)-pyrimidine-5-carboxylate (2i):



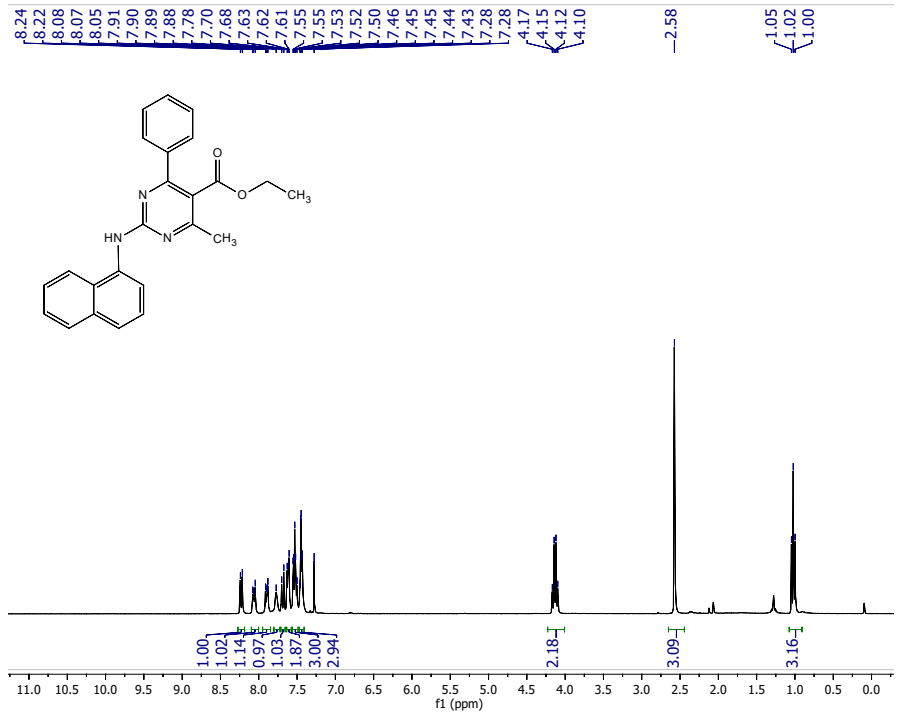


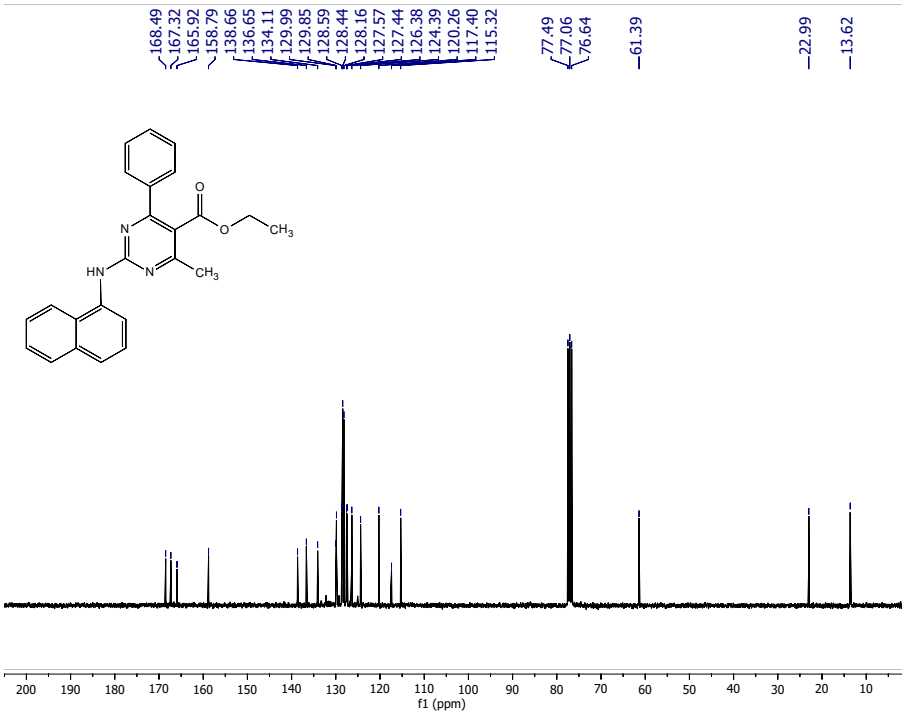
Ethyl 6-methyl-4-phenyl-2-(2'-methylphenylamino)-pyrimidine-5-carboxylate (2j):



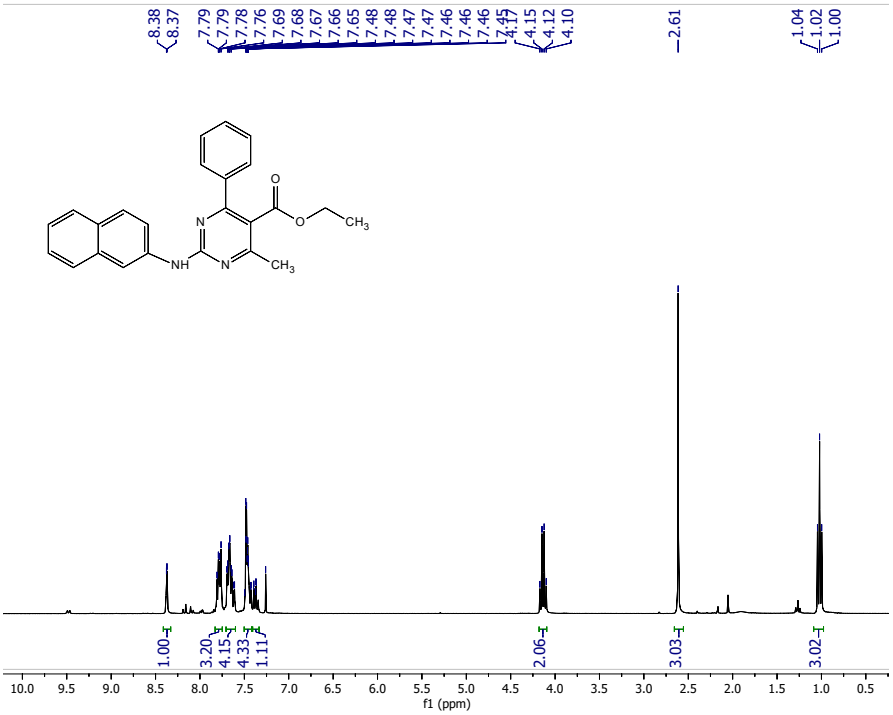


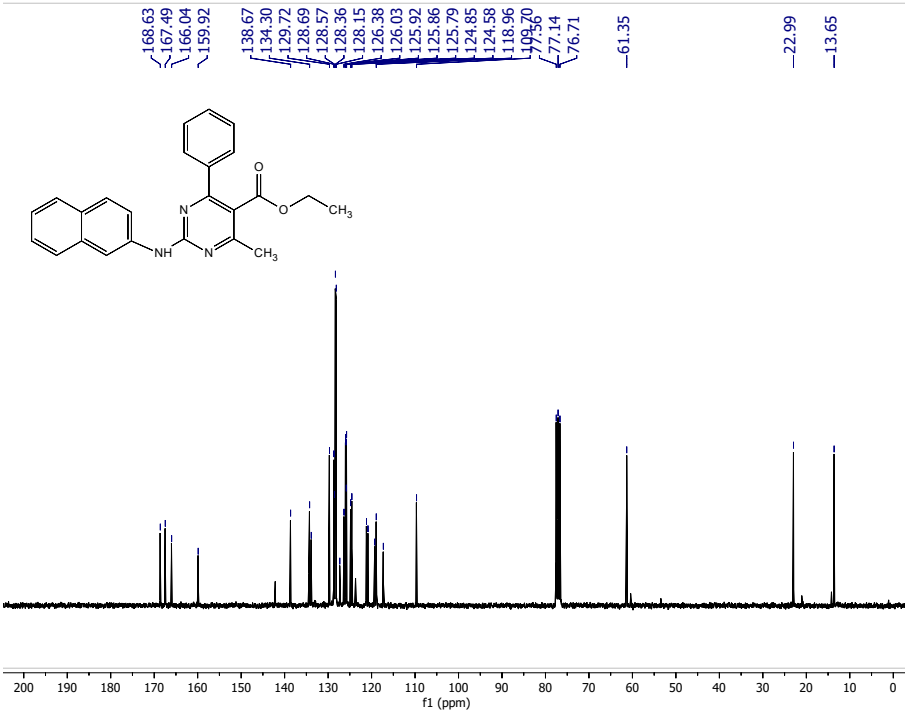
Ethyl 6-methyl-4-phenyl-2-(α -naphthylamine)-pyrimidine-5-carboxylate (2k):



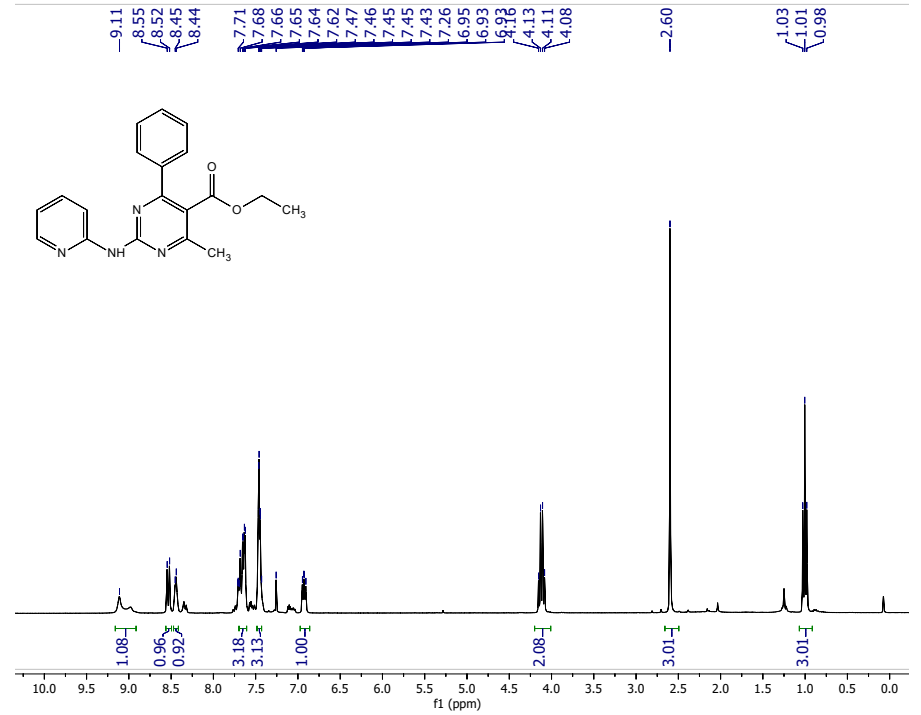


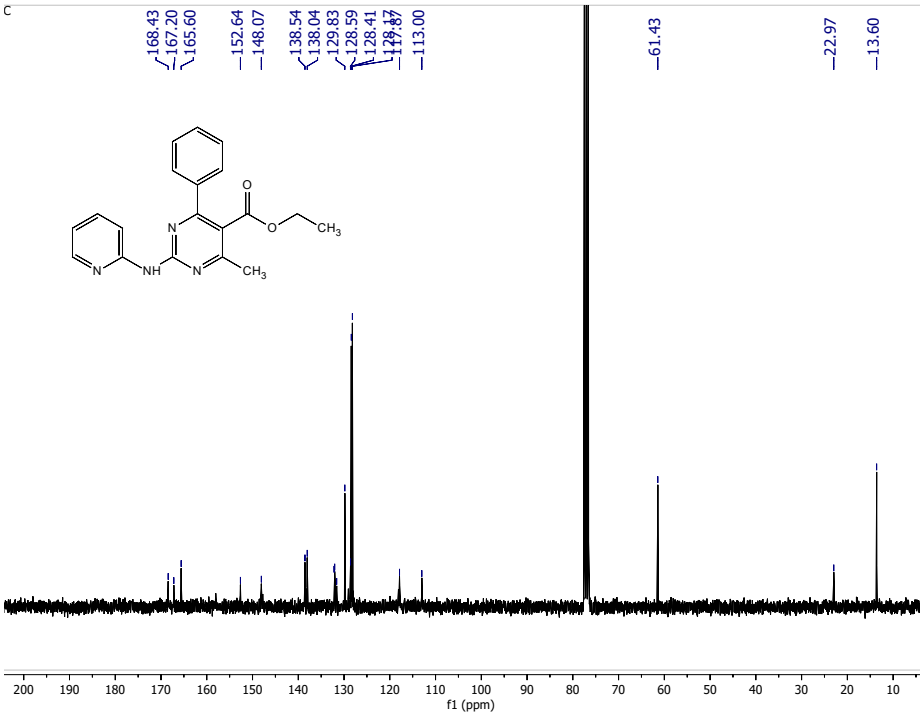
Ethyl 6-methyl-4-phenyl-2-(β-naphthylamino)-pyrimidine-5-carboxylate (2l):



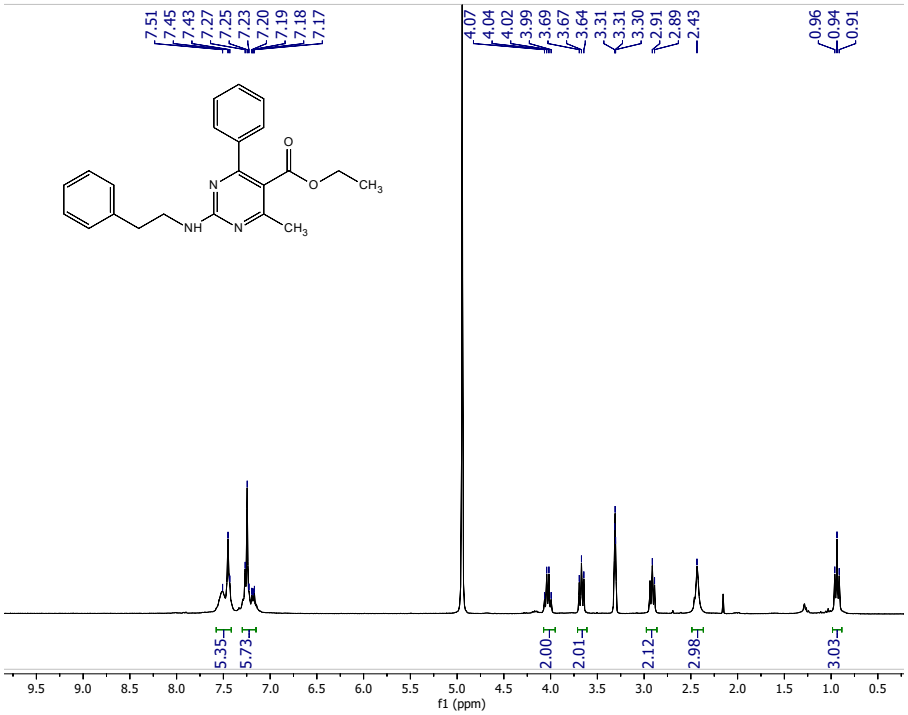


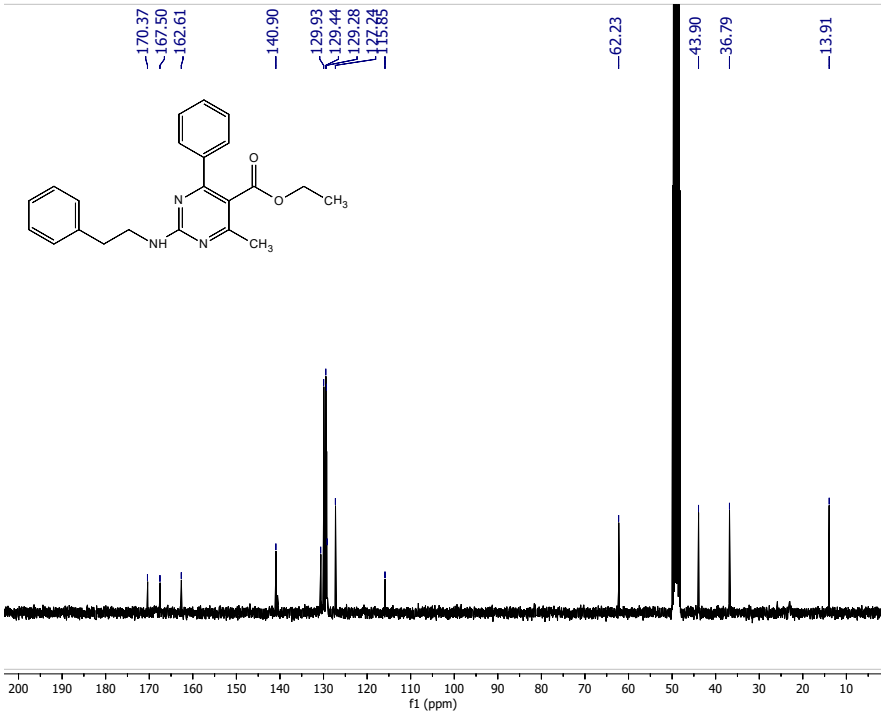
Ethyl 6-methyl-4-phenyl-2-(2'-pyridinylamino)-pyrimidine-5-carboxylate (2m):



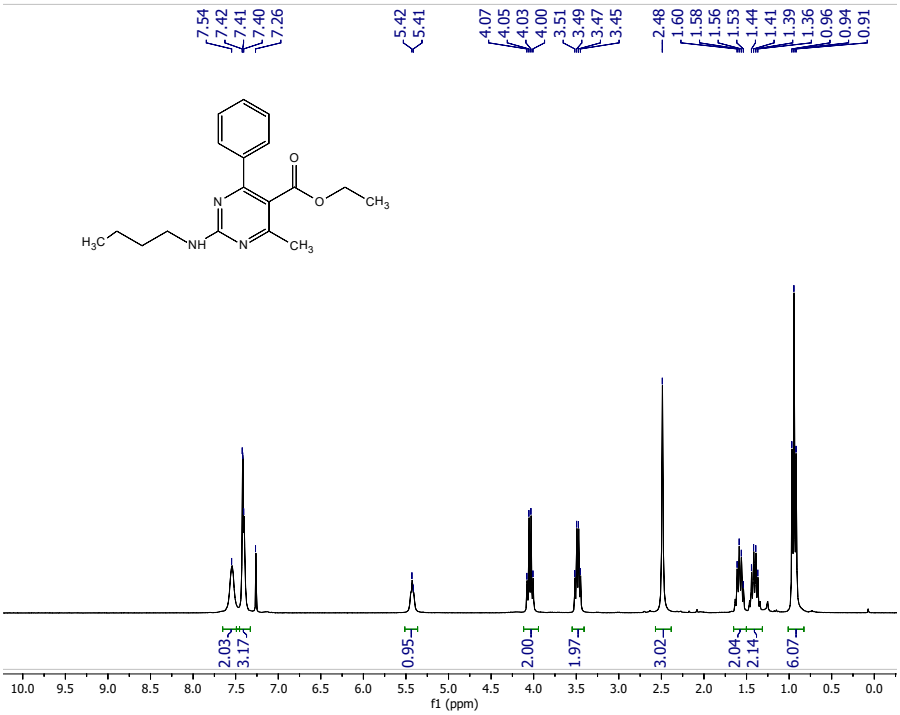


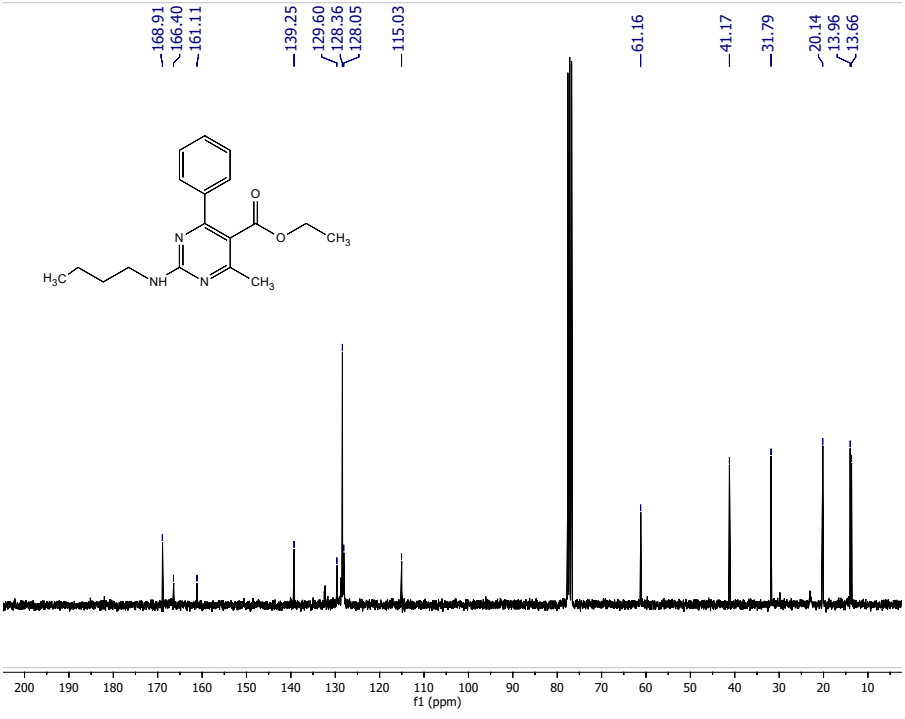
Ethyl 6-methyl-4-phenyl-2-(2'-phenethylamino)-pyrimidine-5-carboxylate (2n):



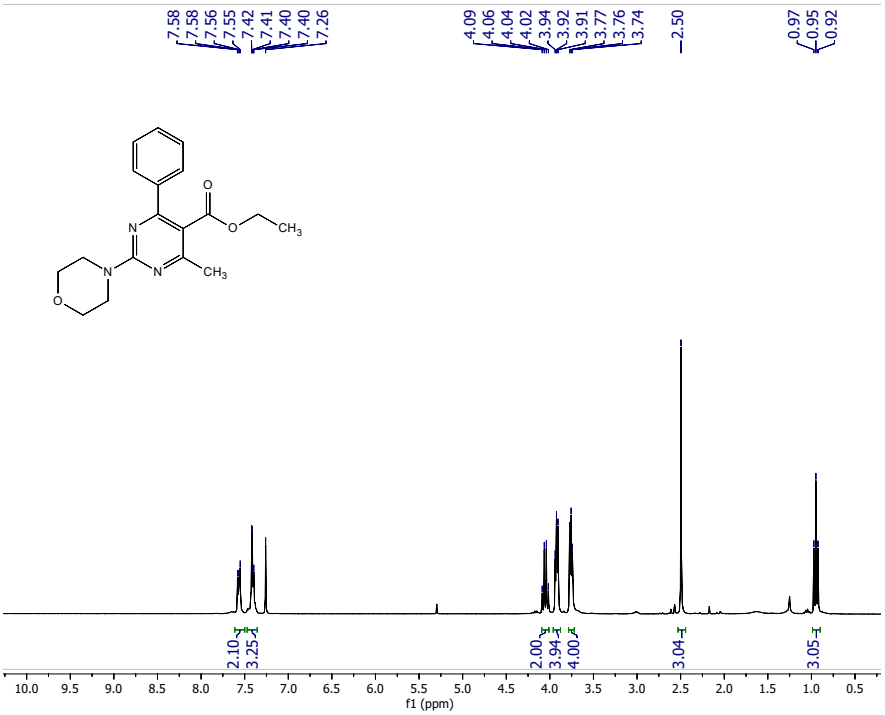


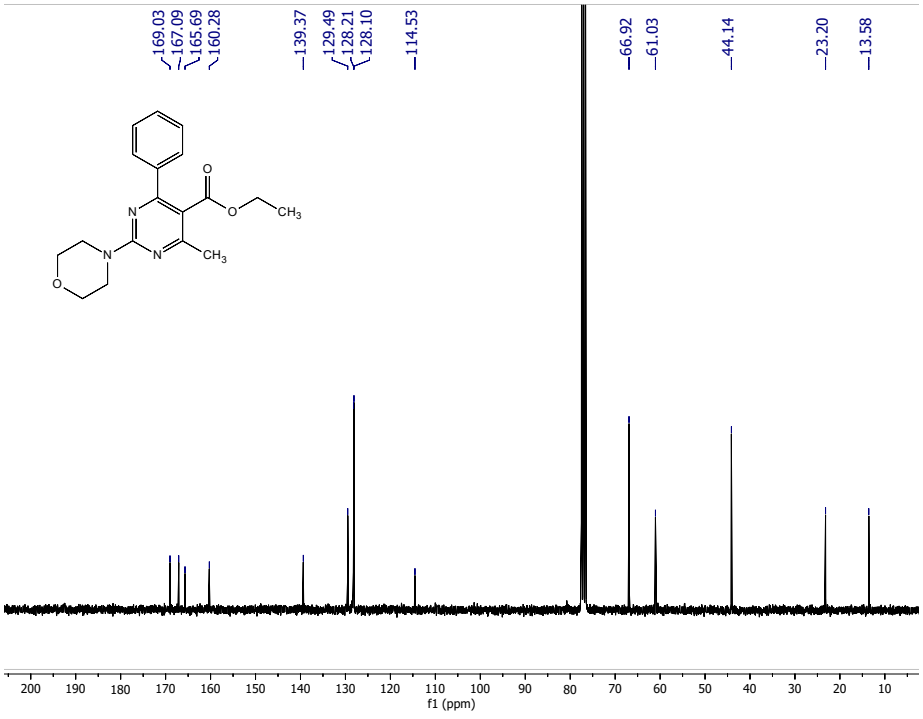
Ethyl 6-methyl-4-phenyl-2-butylamino-pyrimidine-5-carboxylate (2o):



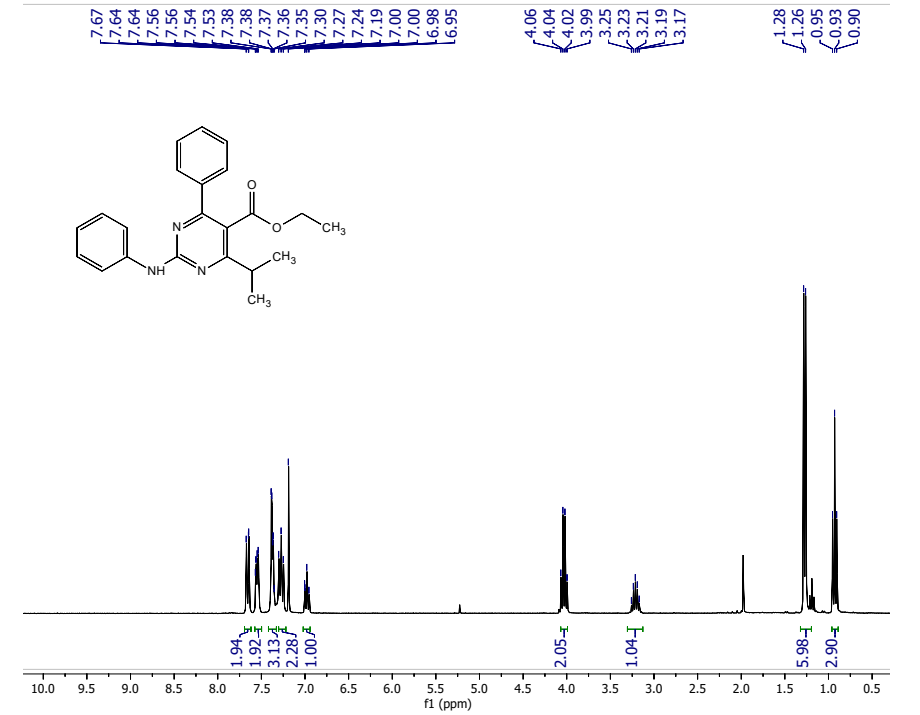


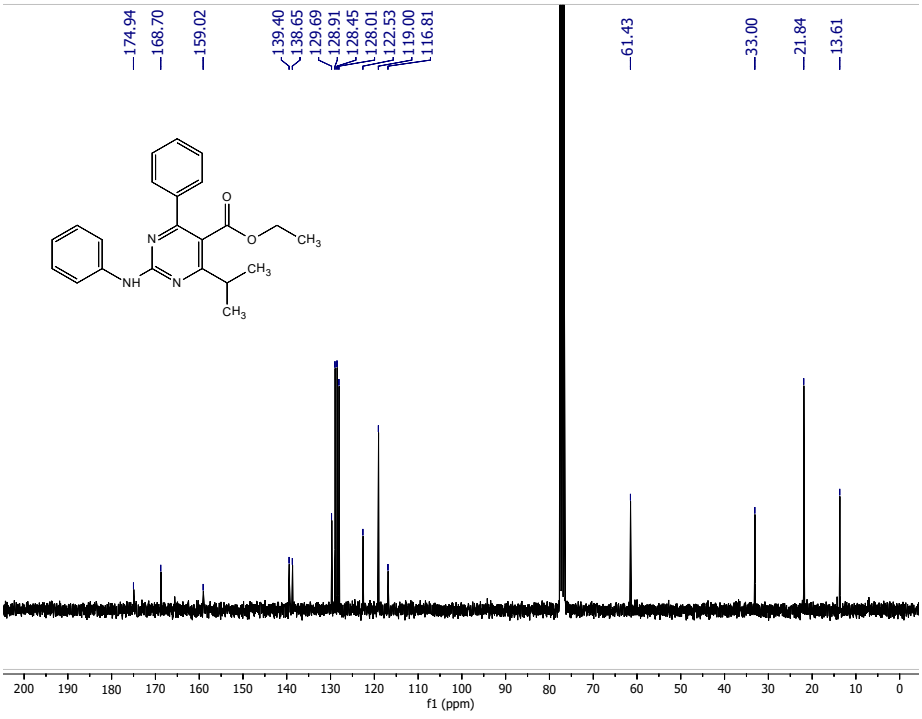
Ethyl 6-methyl-4-phenyl-2-(morpholinylamino)-pyrimidine-5-carboxylate (2p):



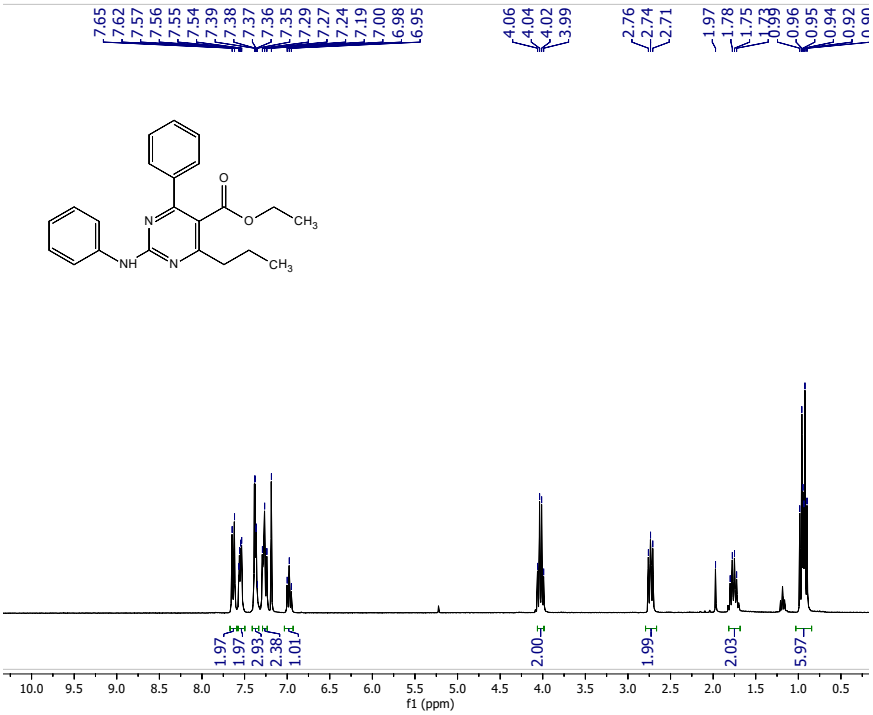


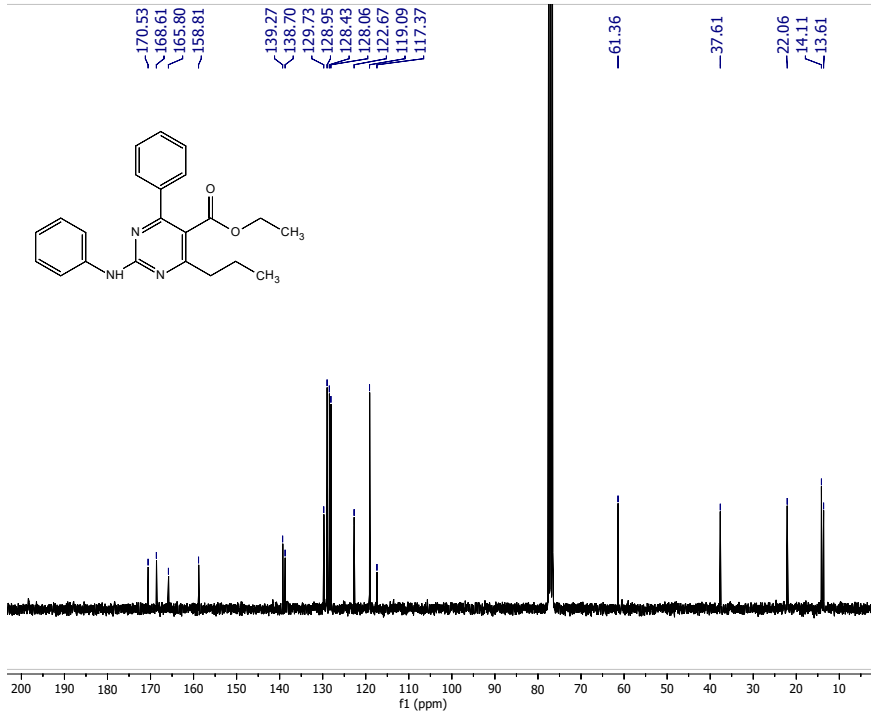
Ethyl 6-isopropyl-4-phenyl-2-phenylamino-pyrimidine-5-carboxylate (3a):



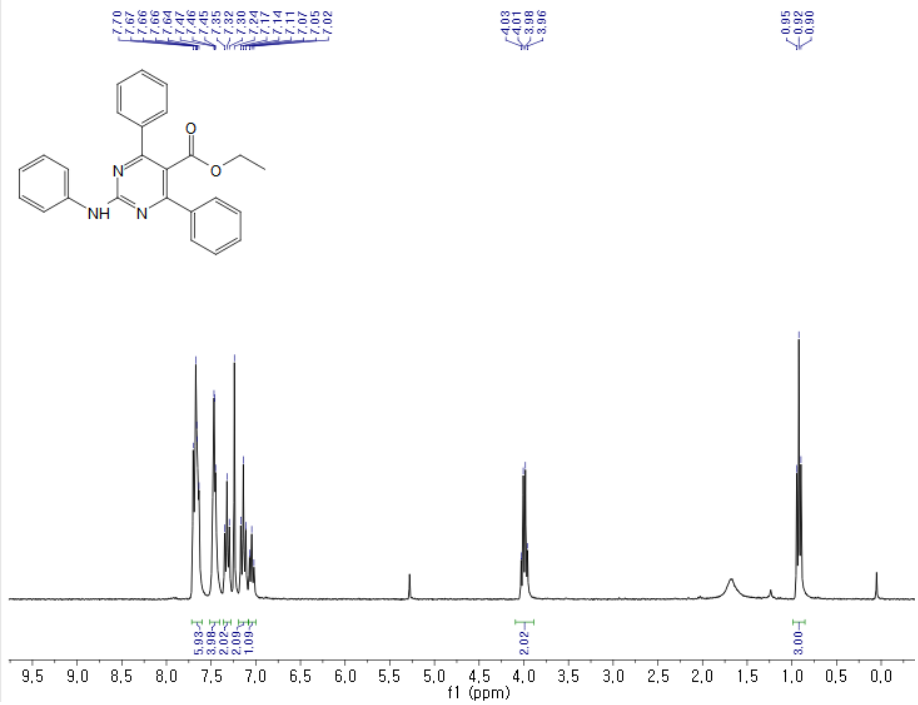


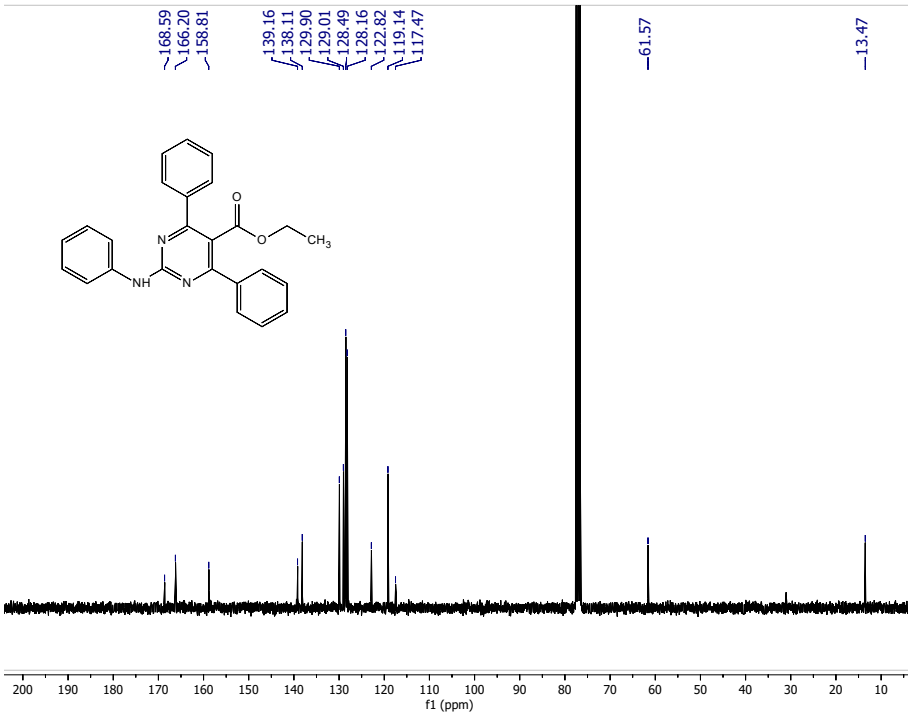
Ethyl 6-propyl-4-phenyl-2-phenylamino-pyrimidine-5-carboxylate (3b):



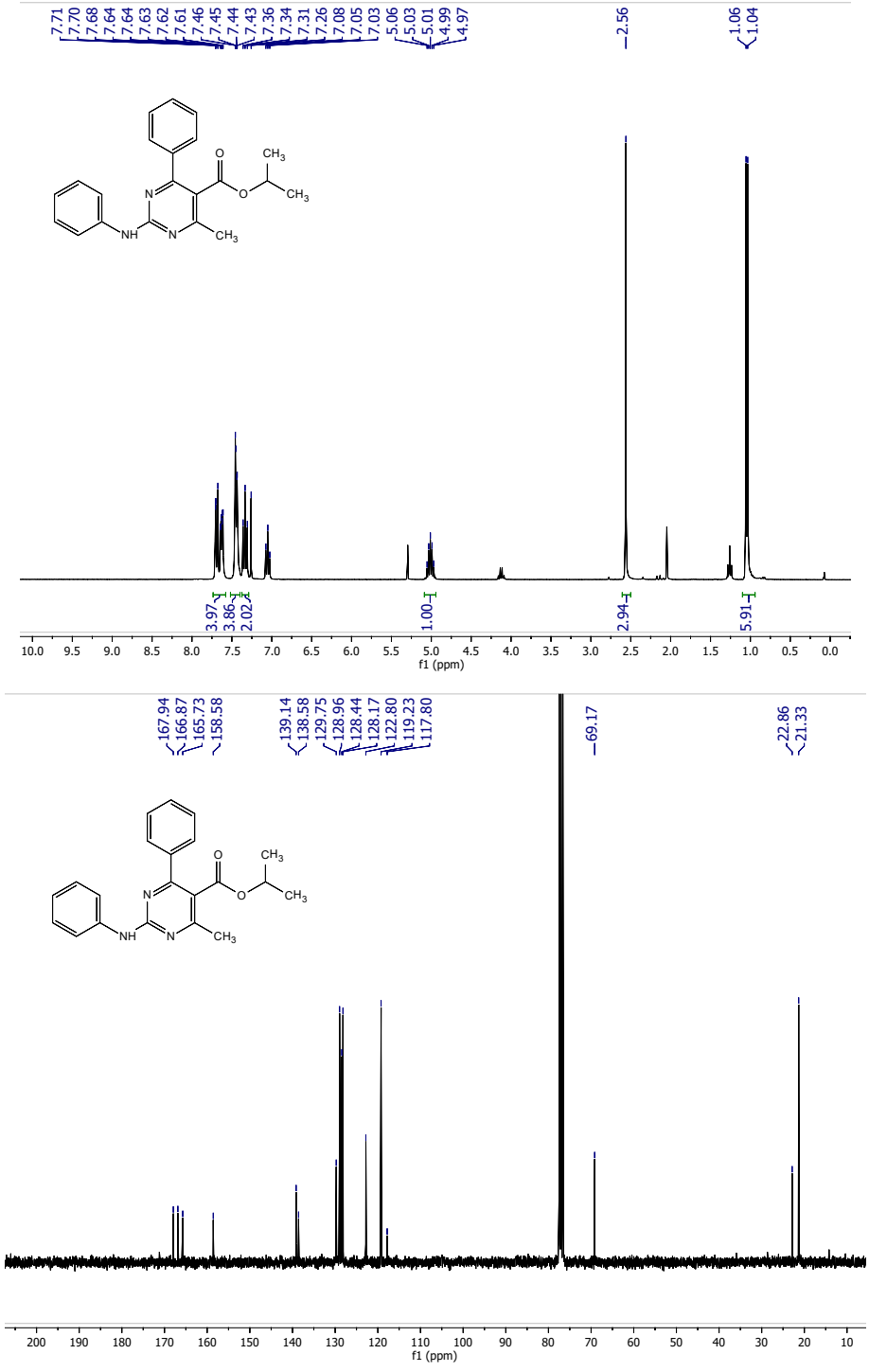


Ethyl 4,6-diphenyl-2-phenylamino-pyrimidine-5-carboxylate (3c):

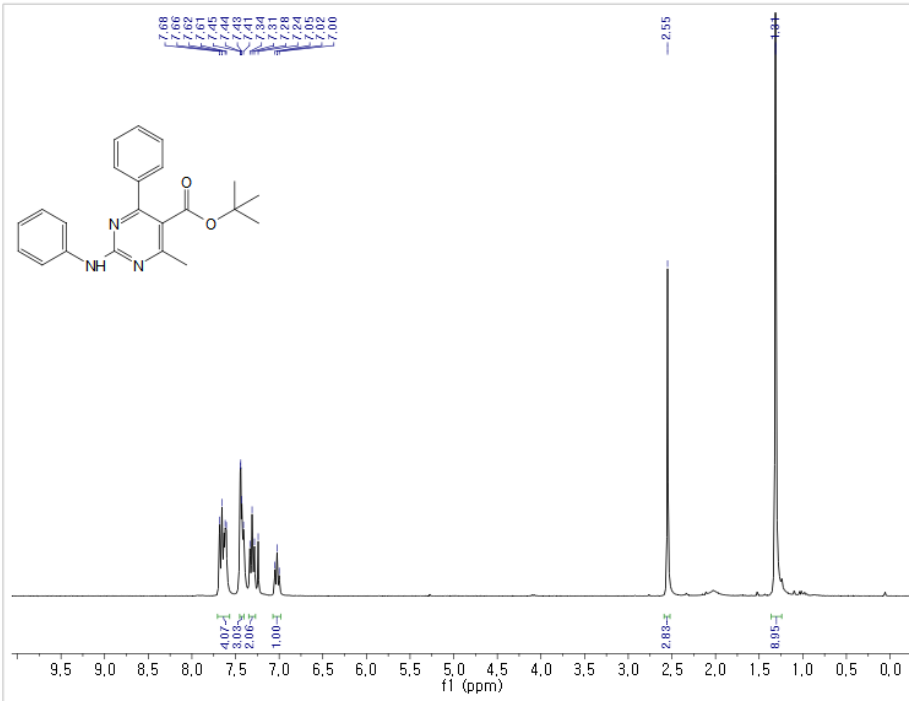


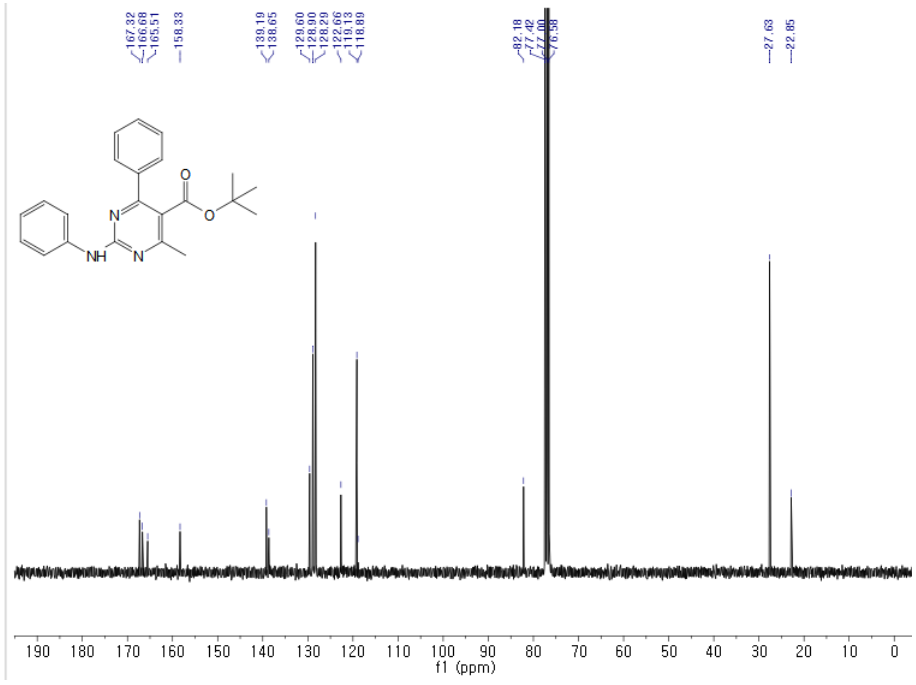


Isopropyl 6-methyl-4-phenyl-2-phenylamino-pyrimidine-5-carboxylate (3d):

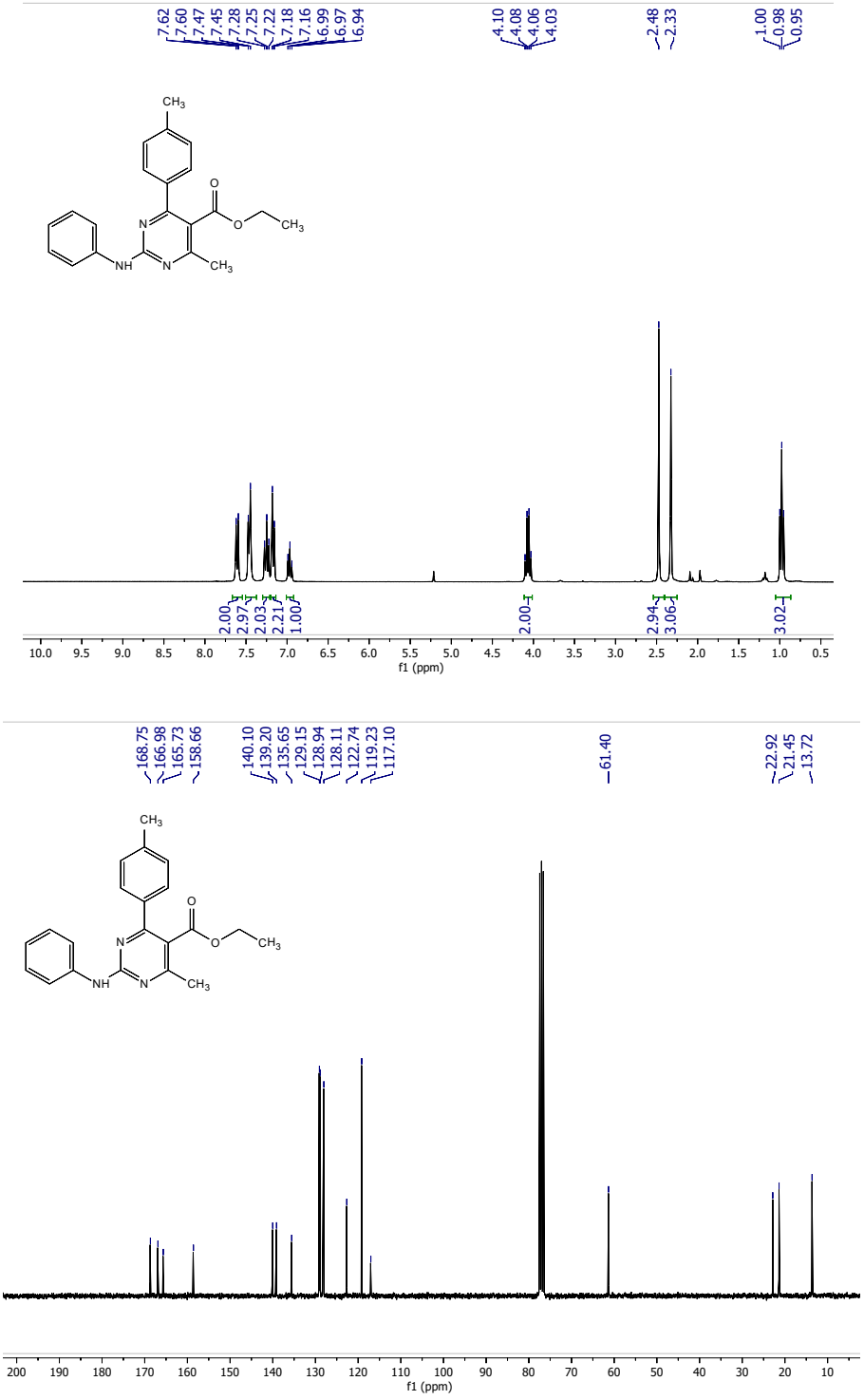


***tert*-Butyl 6-methyl-4-phenyl-2-phenylamino-pyrimidine-5-carboxylate (3e)**

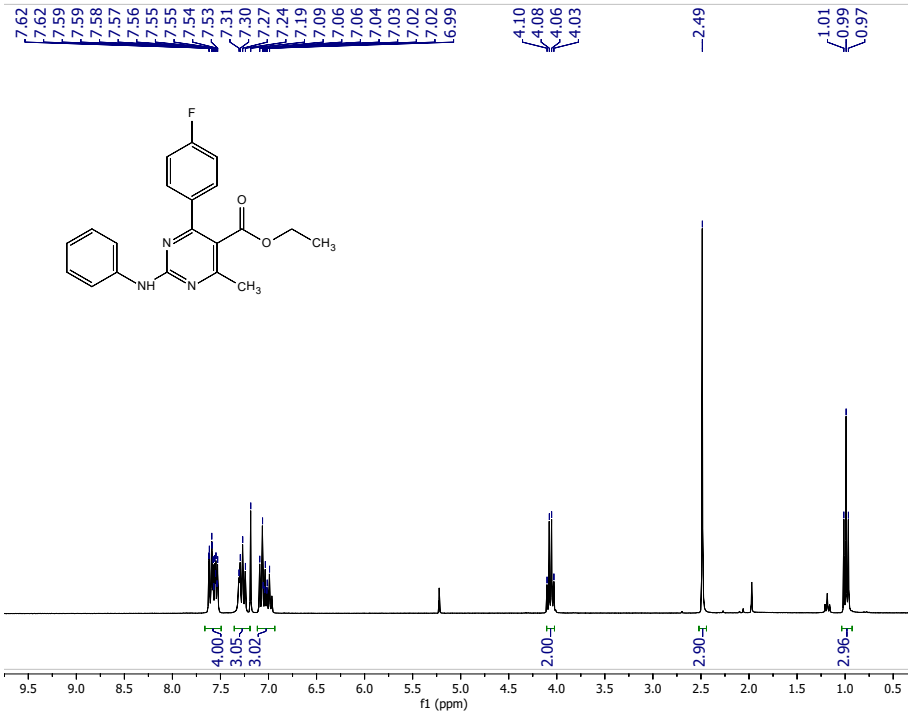


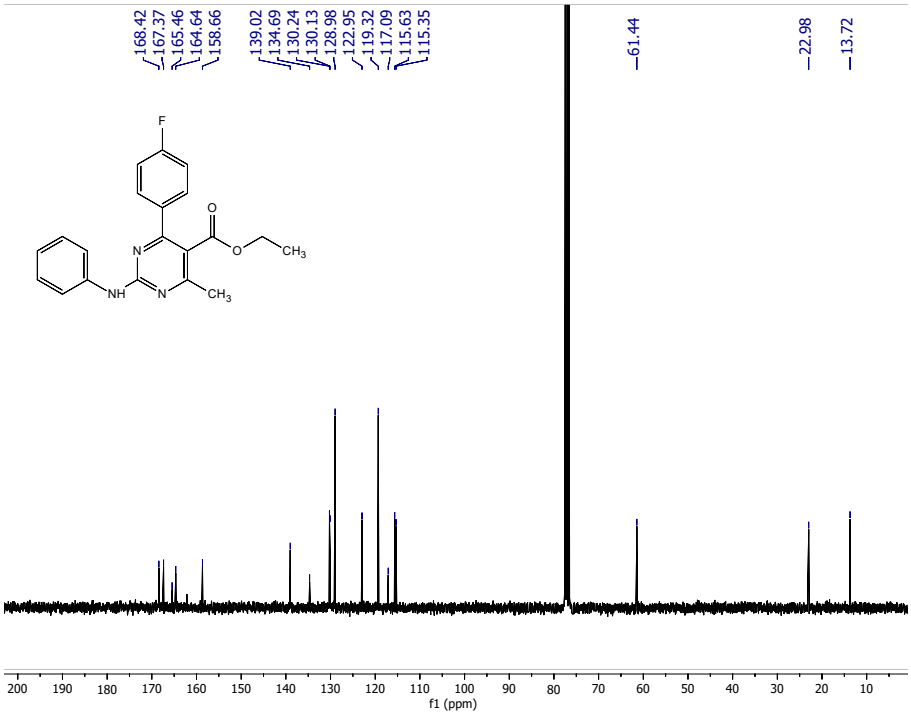


Ethyl 6-methyl-4-(4'-methylphenyl)-2-phenyamino-pyrimidine-5-carboxylate (3f):

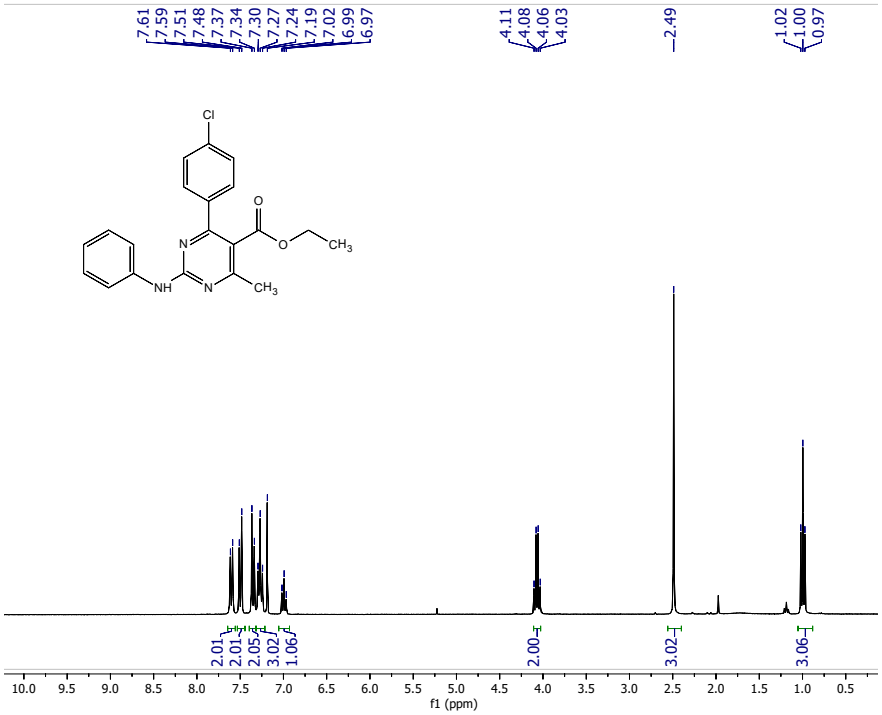


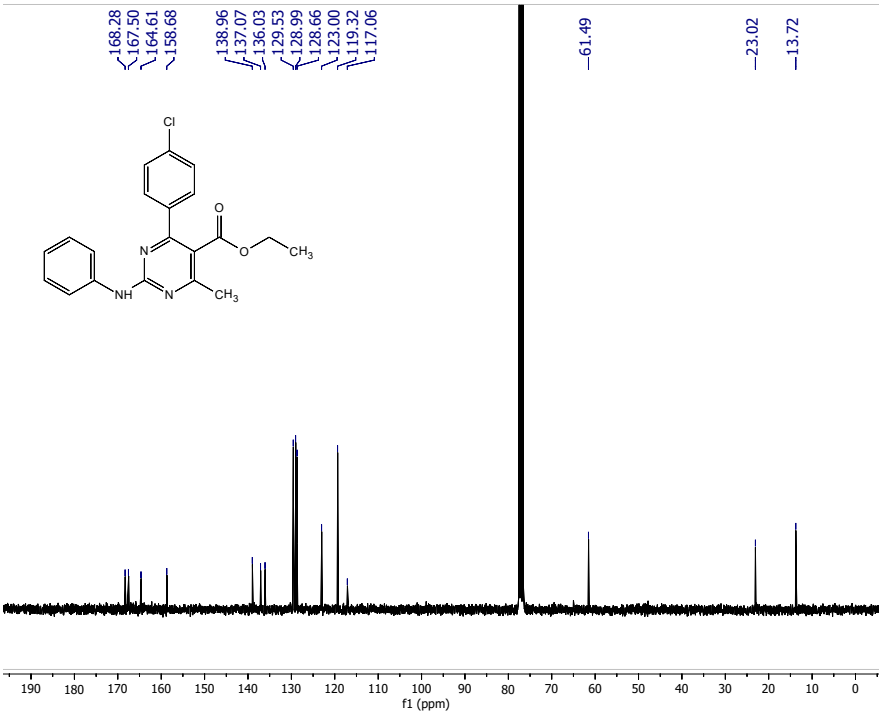
Ethyl 6-methyl-4-(4'-fluorophenyl)-2-phenylamino-pyrimidine-5-carboxylate (3g):



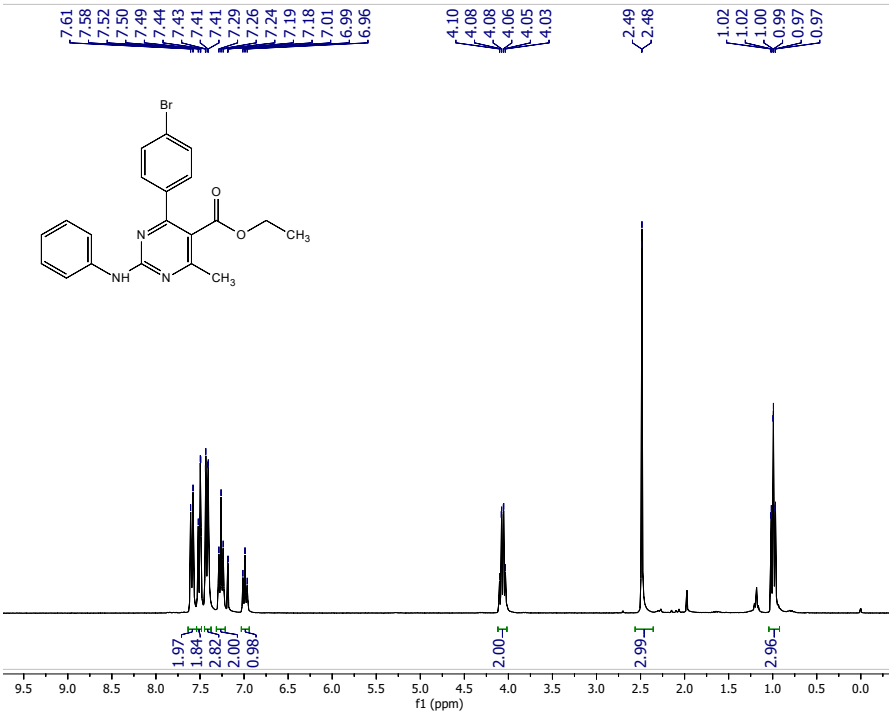


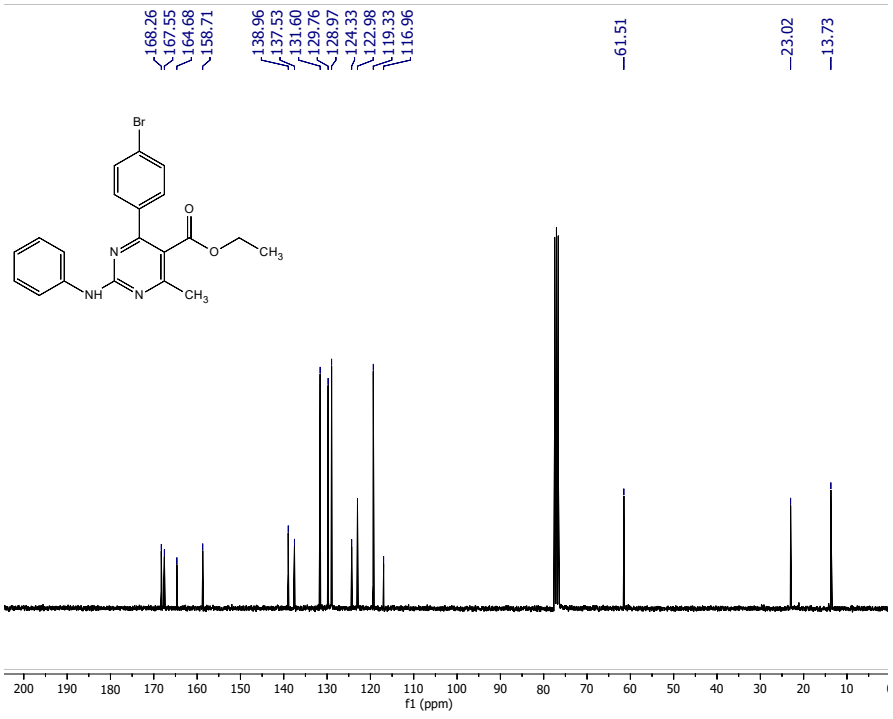
Ethyl 6-methyl-4-(4'-chlorophenyl)-2-phenylamino-pyrimidine-5-carboxylate (3h):



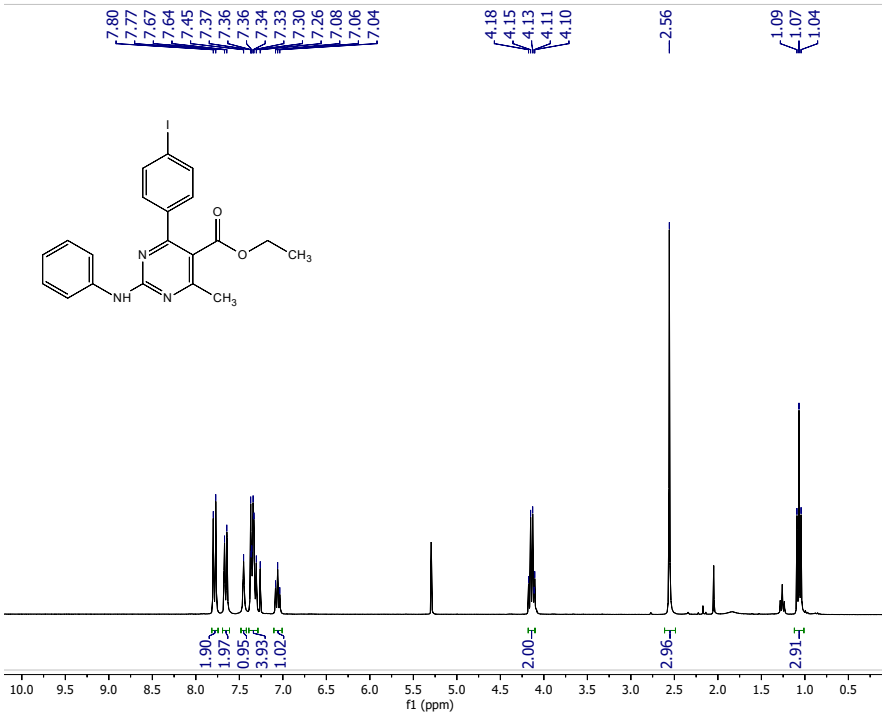


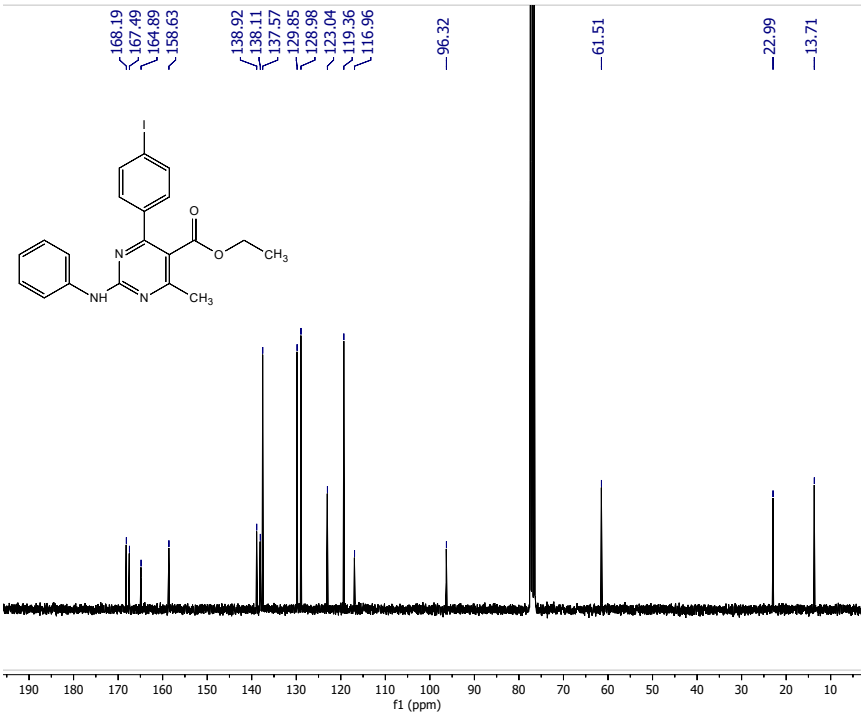
Ethyl 6-methyl-4-(4'-bromophenyl)-2-phenylamino-pyrimidine-5-carboxylate (3i):



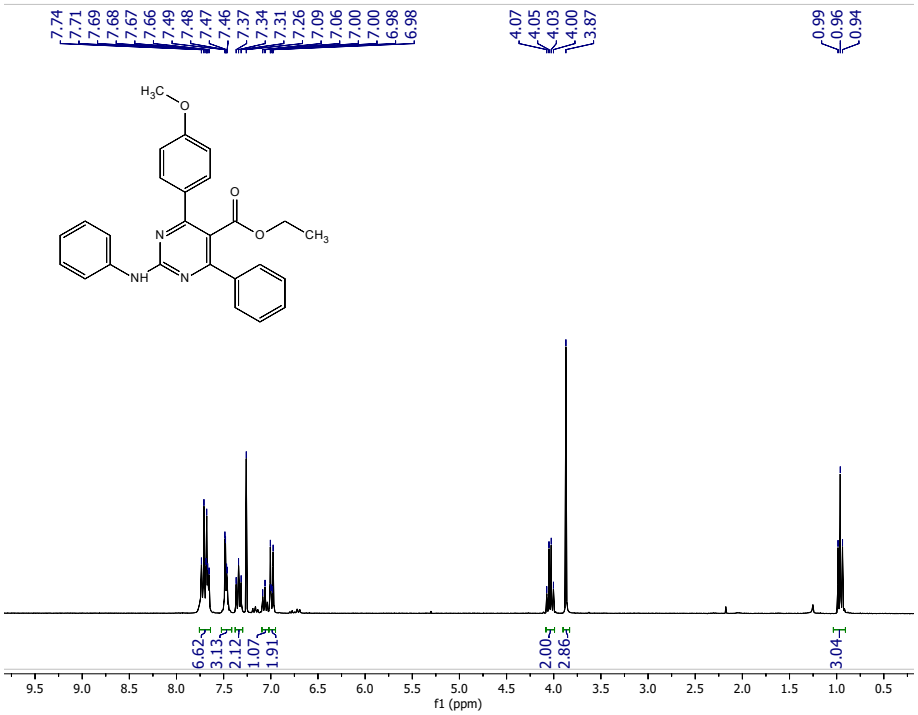


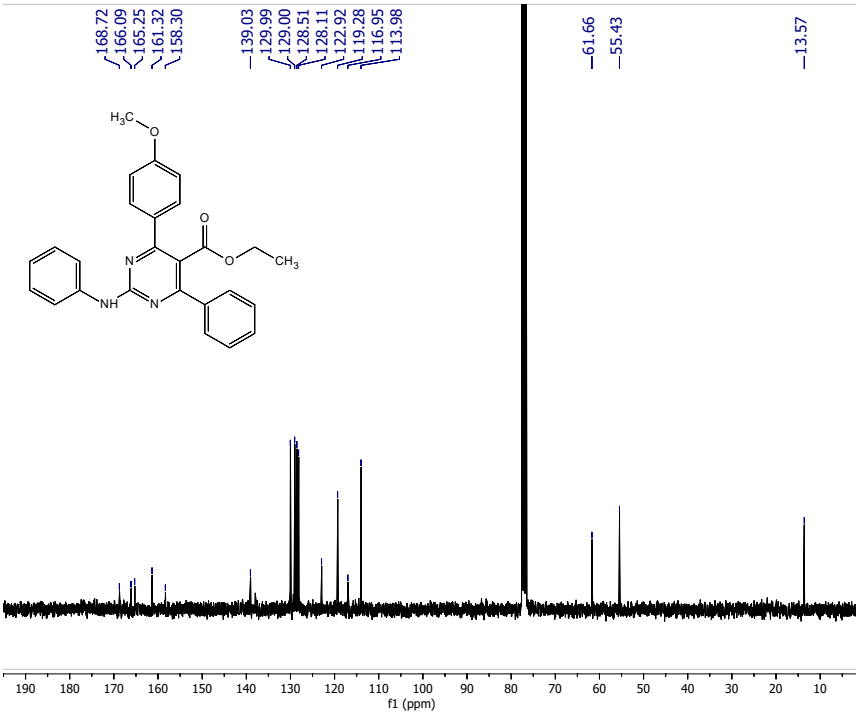
Ethyl 6-methyl-4-(4'-Iodophenyl)-2-phenylamino-pyrimidine-5-carboxylate (3j):



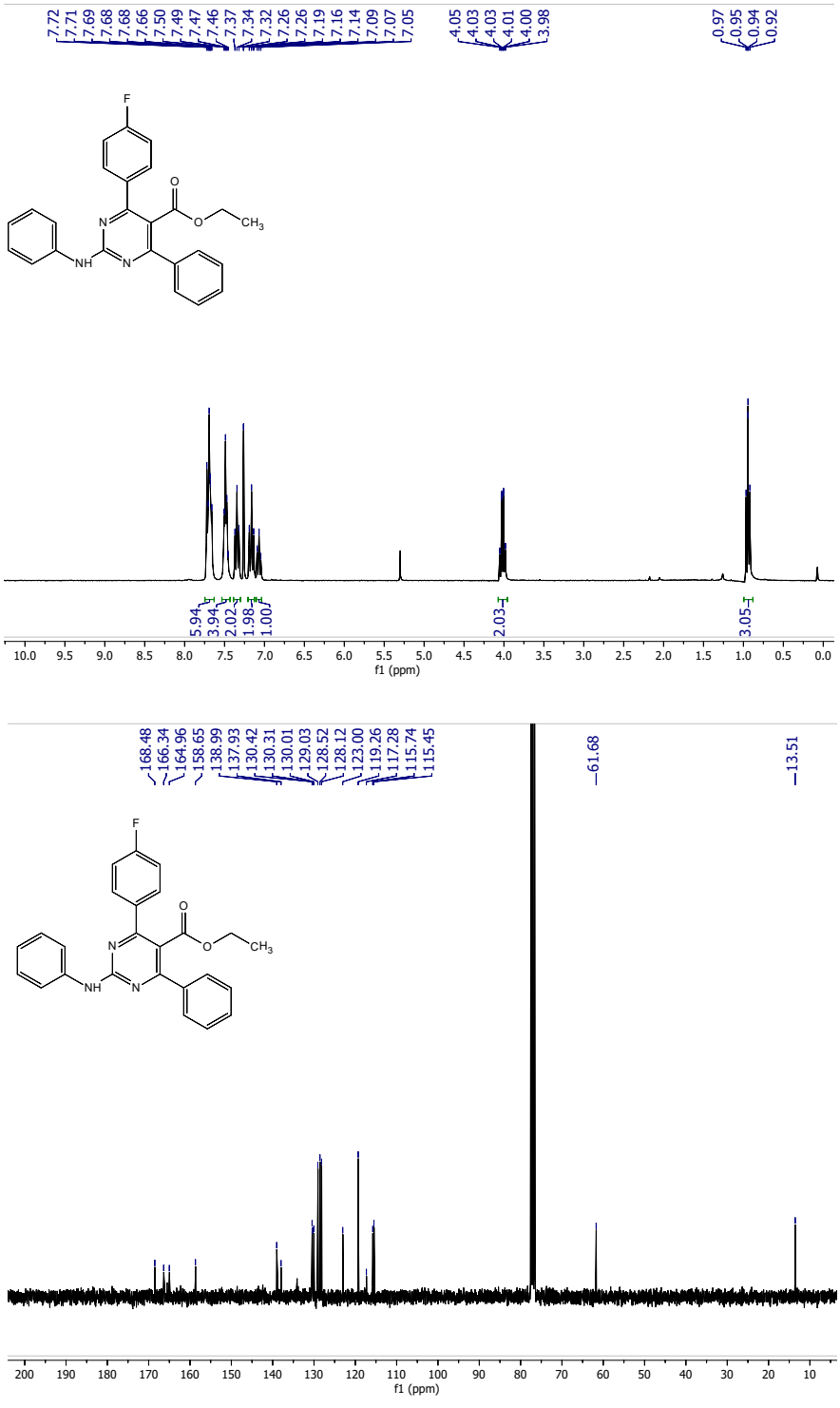


Ethyl 6-phenyl-4-(4'-methoxyphenyl)-2-phenylamino-pyrimidine-5-carboxylate (3k):

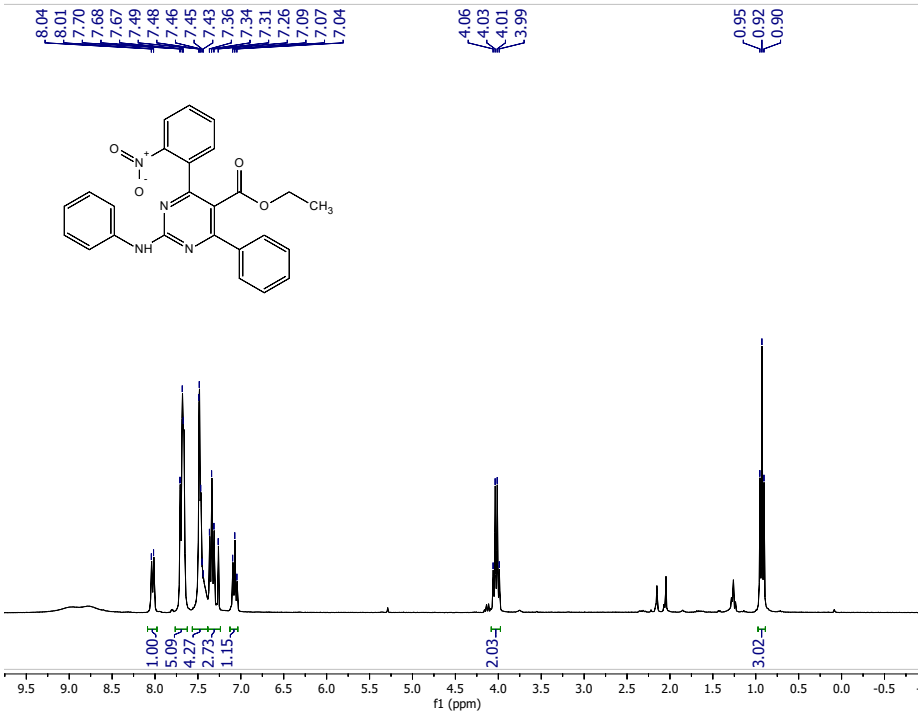


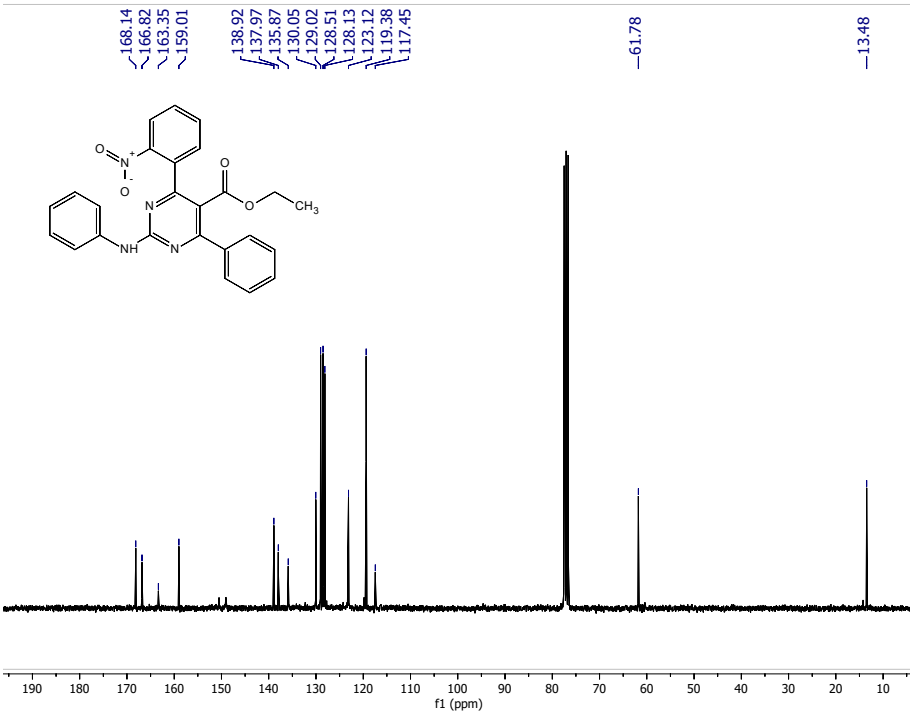


Ethyl 6-phenyl-4-(2'-fluorophenyl)-2-phenylamino-pyrimidine-5-carboxylate (3l):

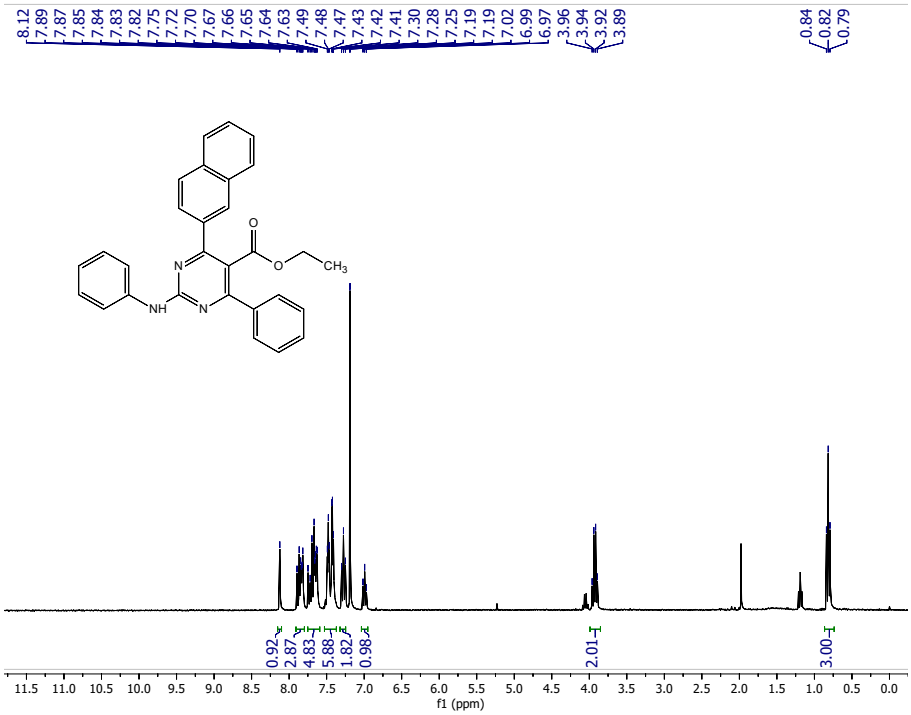


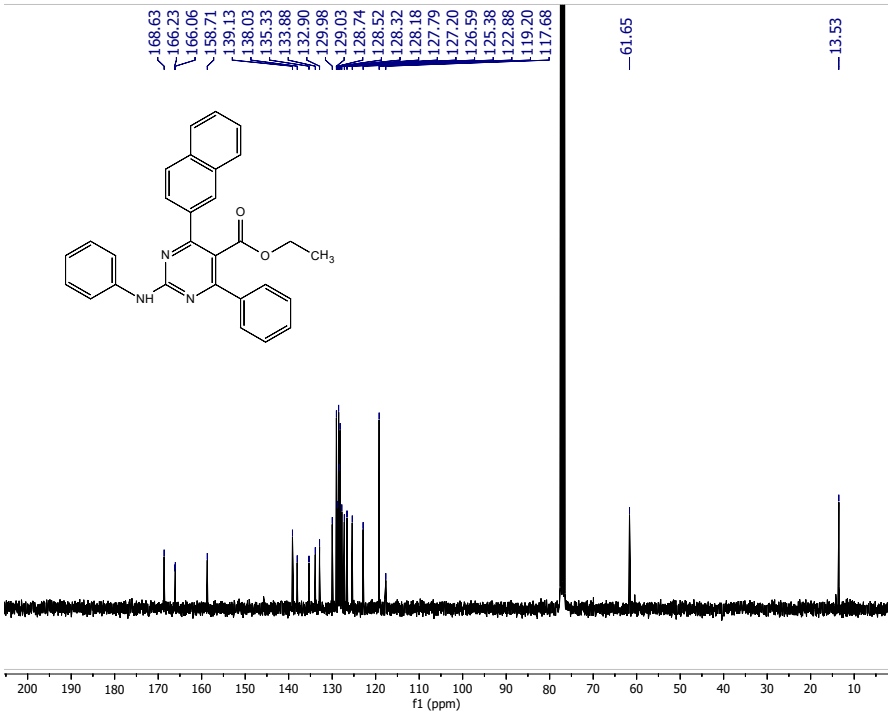
Ethyl 6-phenyl-4-(2'-nitrophenyl)-2-phenylamino-pyrimidine-5-carboxylate (3m):



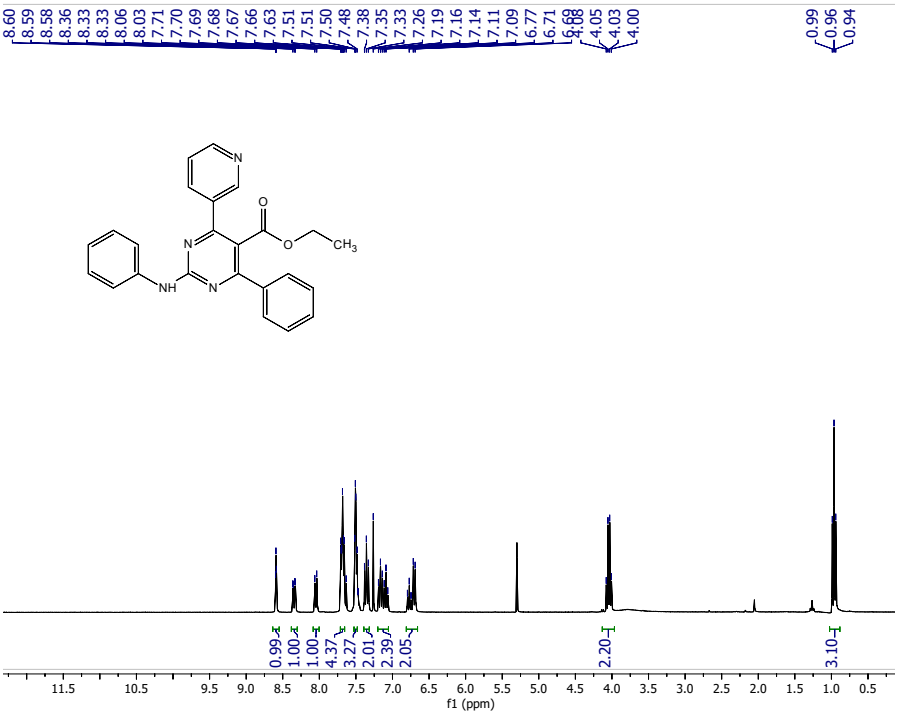


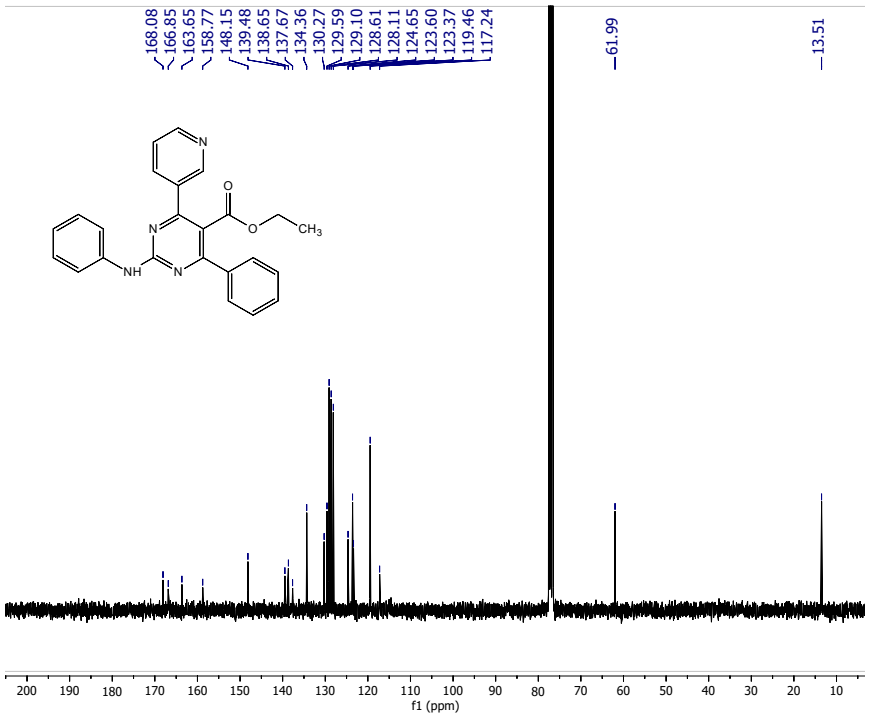
Ethyl 6-phenyl-4-(2'-napthalyl)-2-phenylamino-pyrimidine-5-carboxylate (3n):



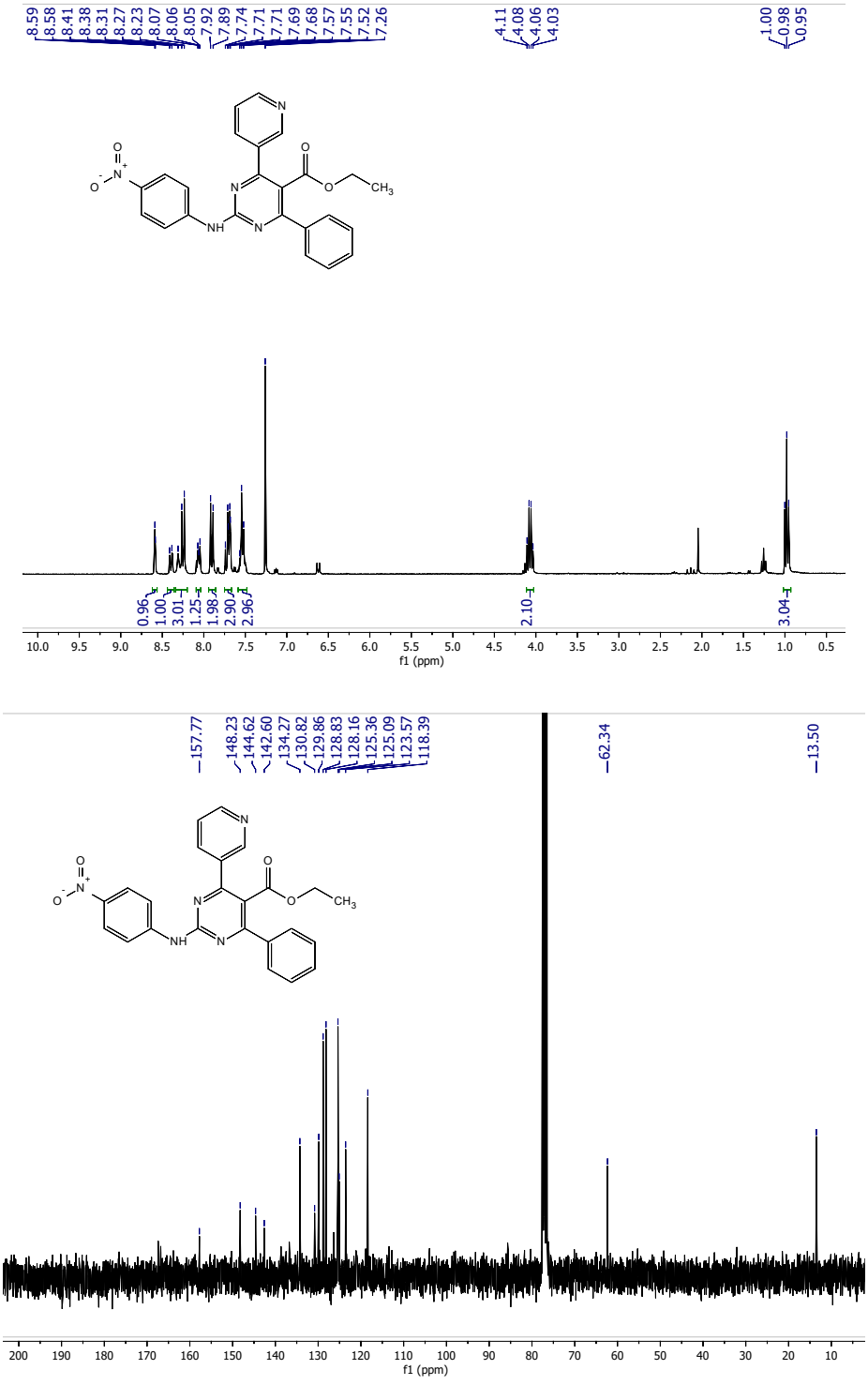


Ethyl 6-phenyl-4-(3'-pyridyl)-2-phenylamino-pyrimidine-5-carboxylate (3o):

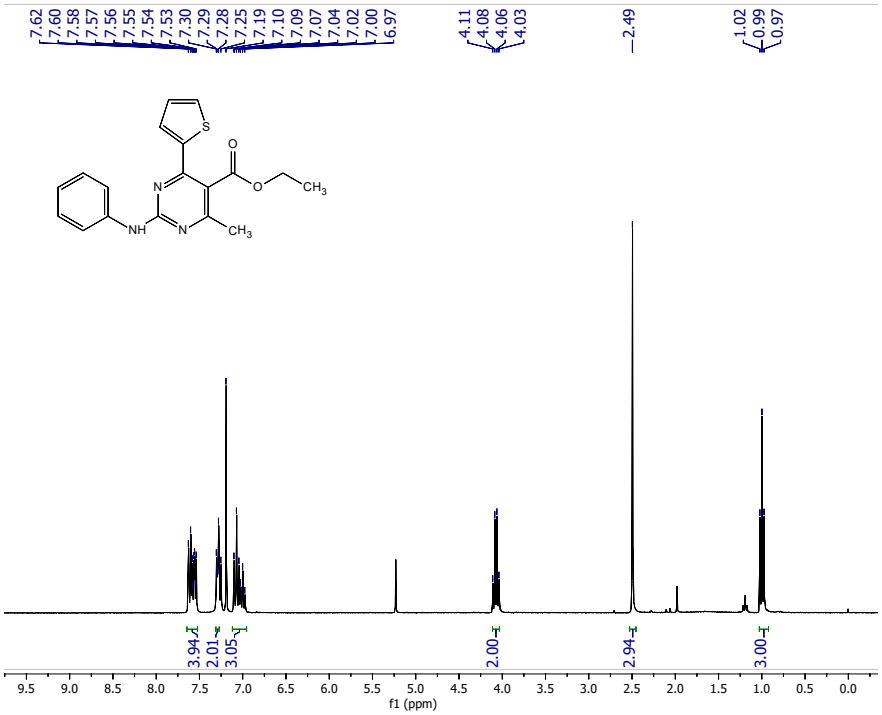


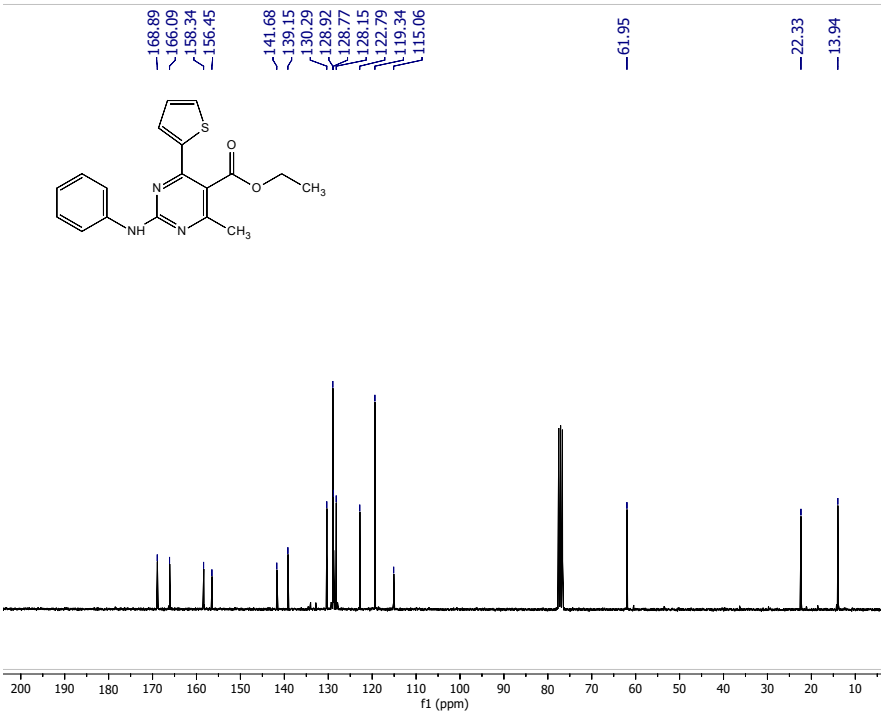


Ethyl 6-phenyl-4-(3'-pyridyl)-2-(4''-nitrophenylamino)-pyrimidine-5-carboxylate (3p):

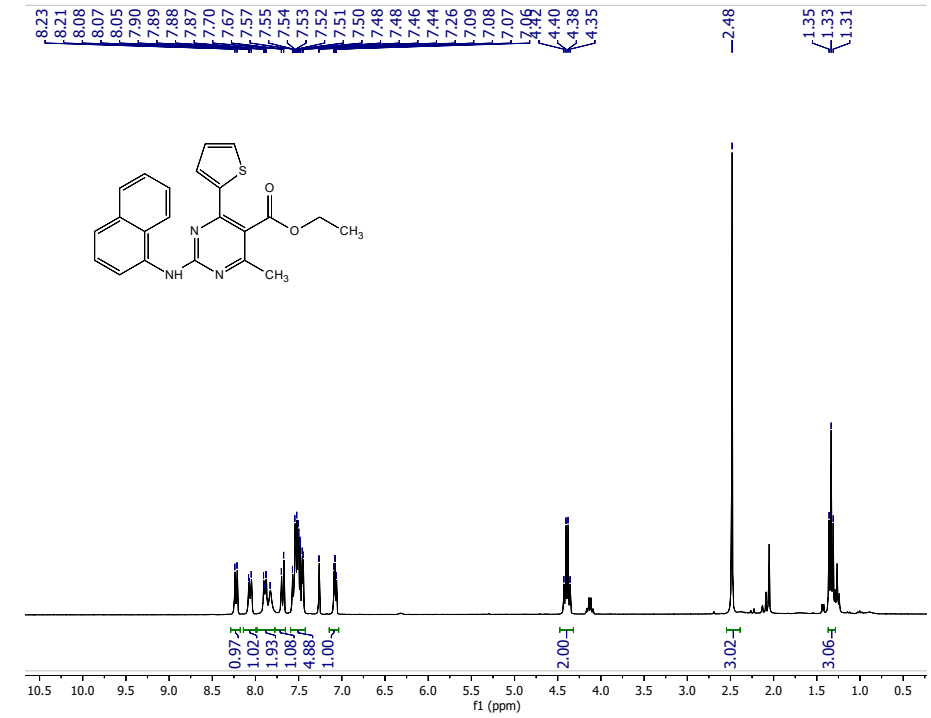


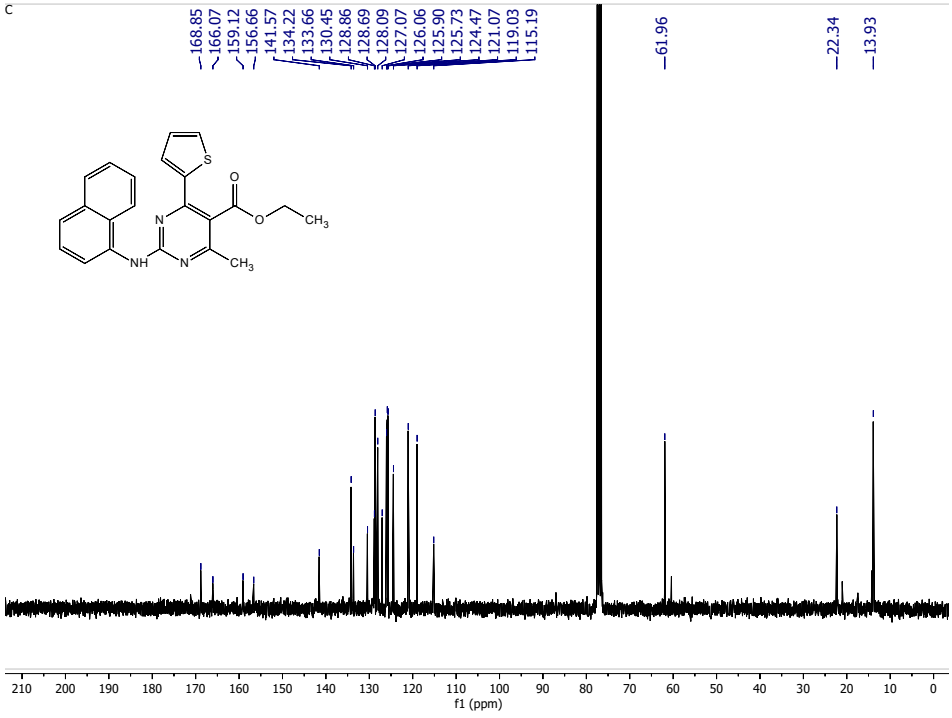
Ethyl 6-methyl-4-(2'-thiophyl)-2-phenylamino-pyrimidine-5-carboxylate (3q):



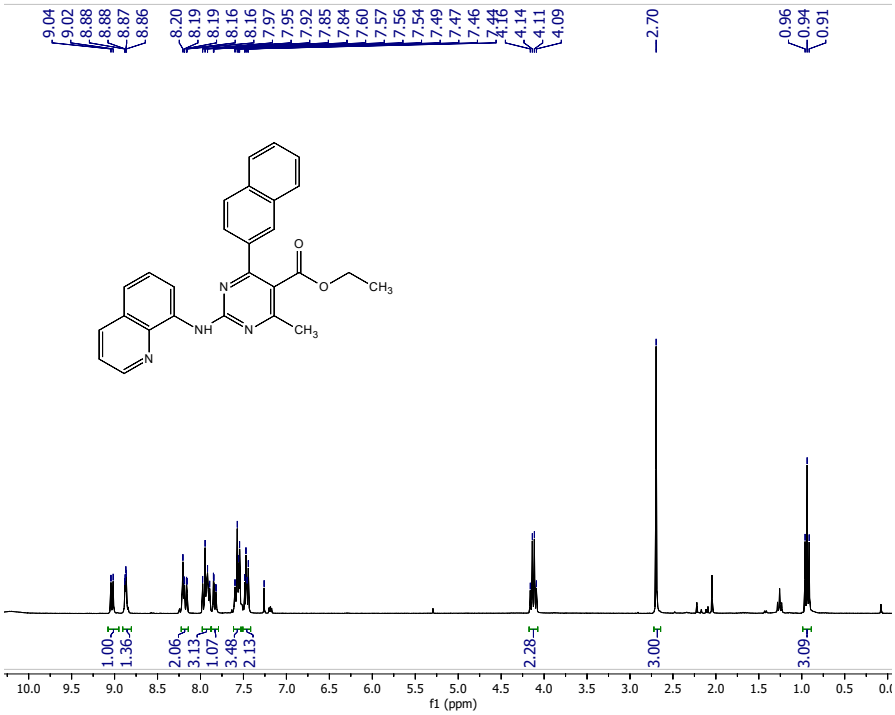


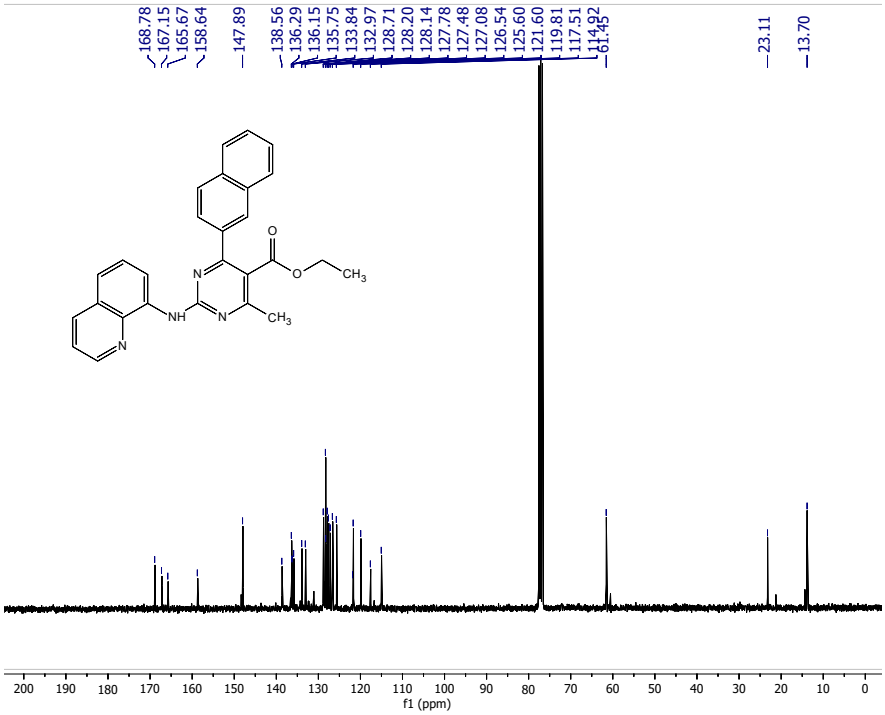
Ethyl 6-methyl-4-(2'-thiophyl)-2-(α-naphtylamino)-pyrimidine-5-carboxylate (3r):



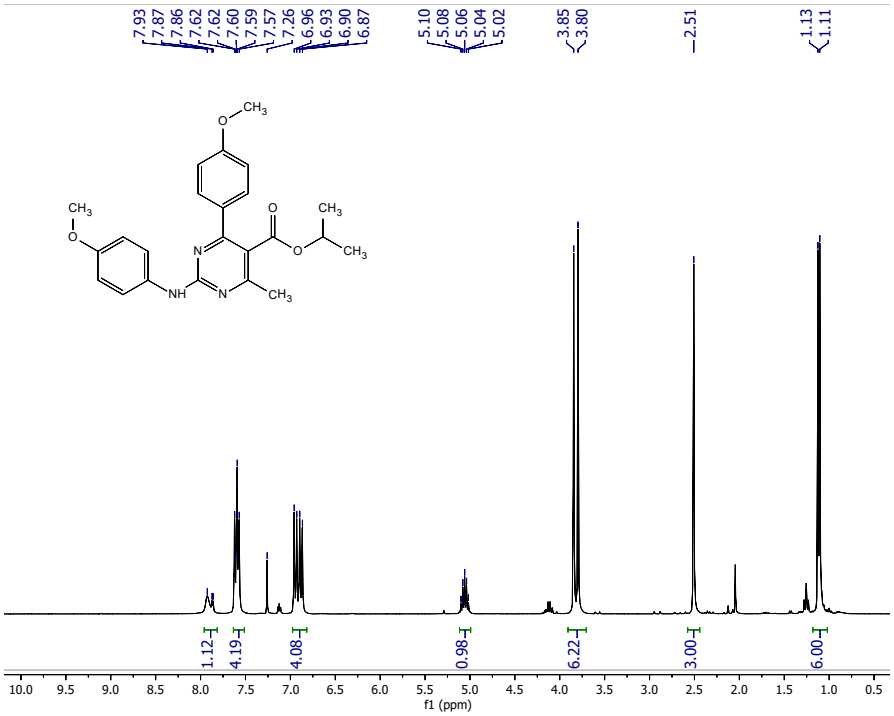


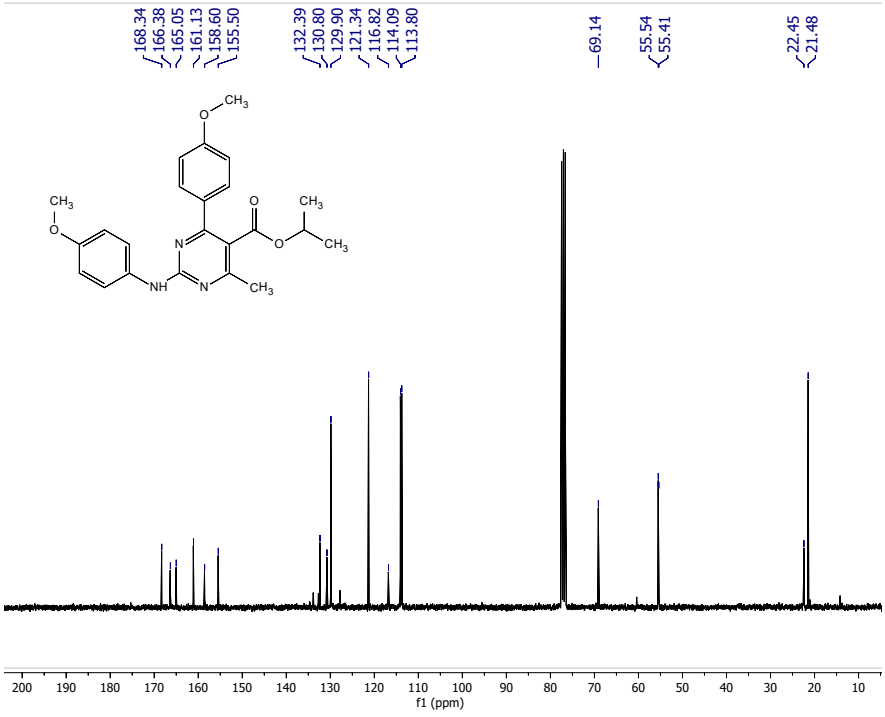
Ethyl 6-methyl-4-(2'-napthalyl)-2-(8''-quinolinylamino)-pyrimidine-5-carboxylate (3s):



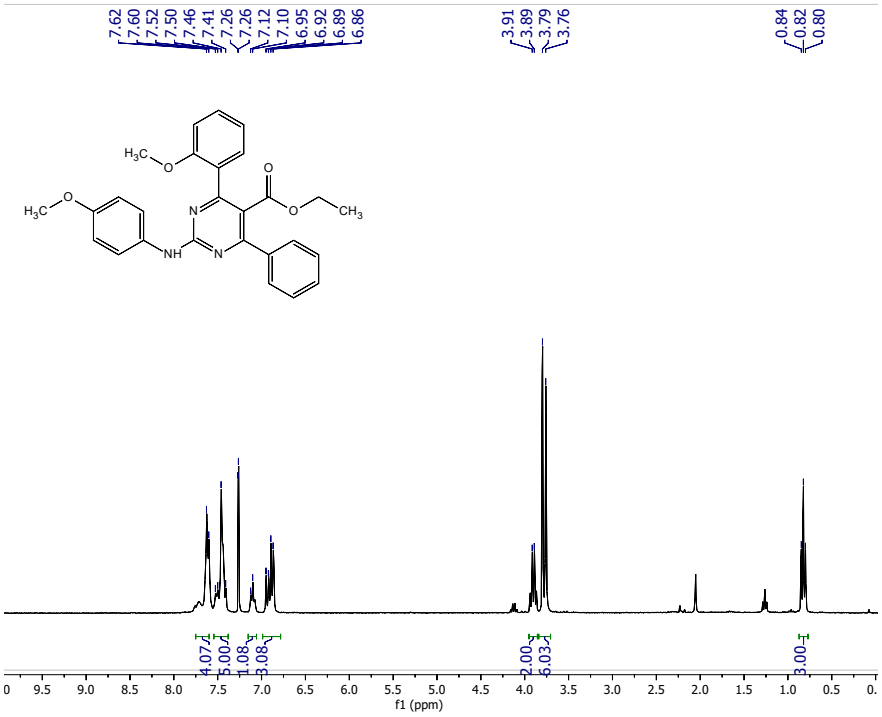


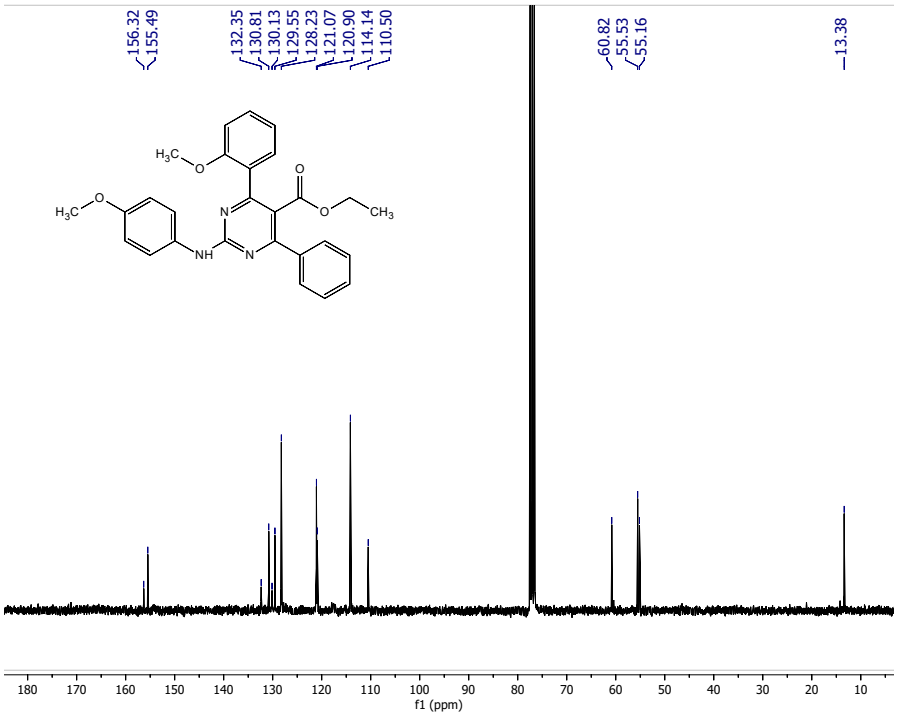
Isopropyl 6-methyl-4-(4'-methoxyphenyl)-2-(4''-methoxyphenylamino)-pyrimidine-5-carboxylate (3t)



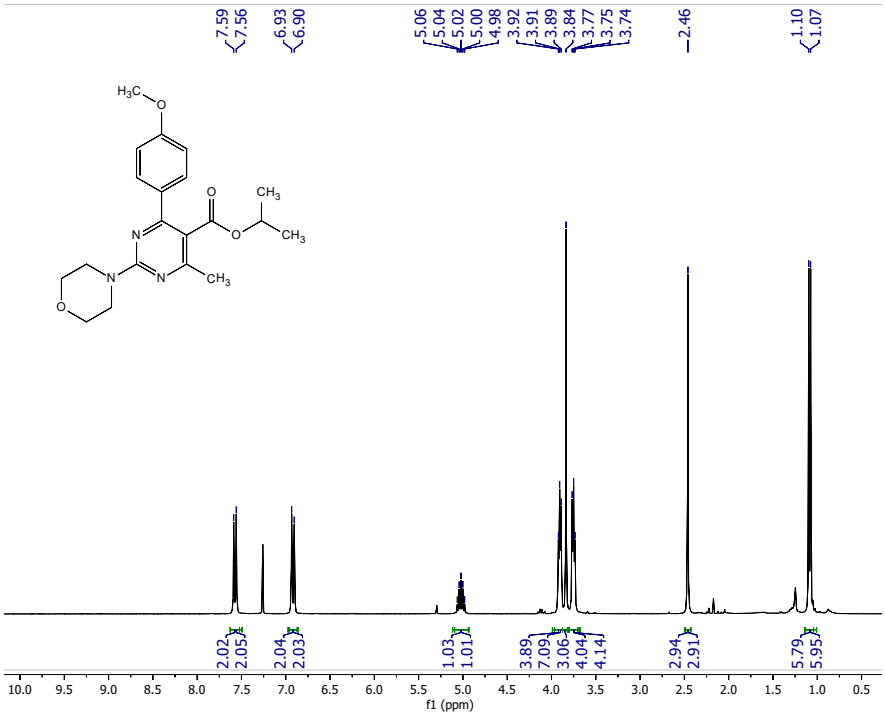


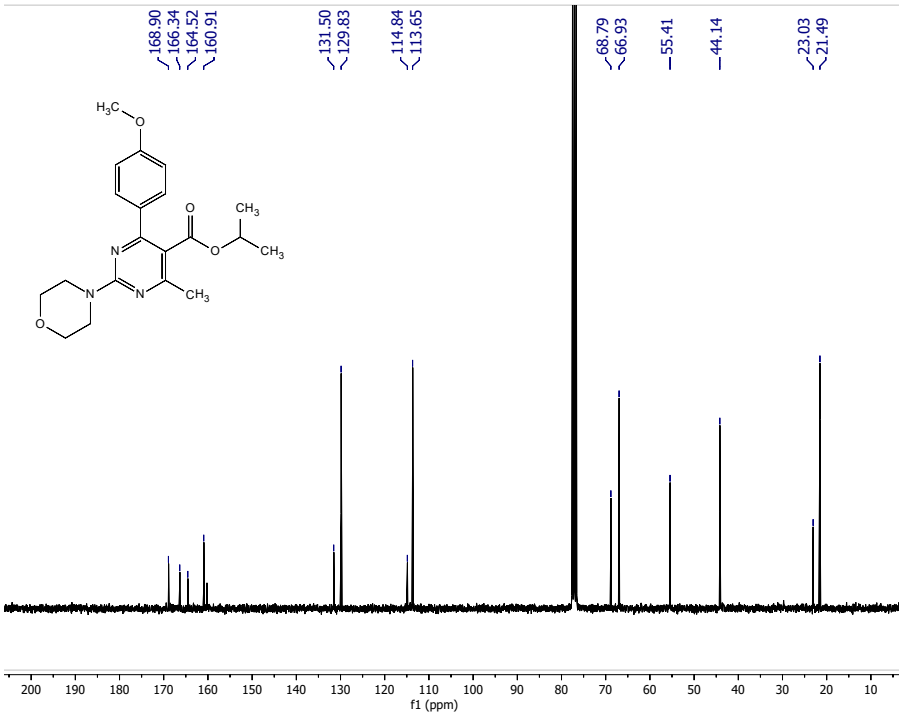
Ethyl 6-phenyl-4-(2'-methoxyphenyl)-2-(4''-methoxyphenylamino)-pyrimidine-5-carboxylate (3u)





Isopropyl 6-phenyl-4-(4’-methoxyphenyl)-2-(4’’-morpholinyl)--pyrimidine-5-carboxylate (3v)





4-Methyl-N,5,6-triphenylpyrimidin-2-amine (4):