Electronic Supplementary Information

The ruthenium-catalyzed C–H functionalization of enamides with isocyanates: easy entry to pyrimidin-4-ones

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1. General information

Unless otherwise noted, all reagents and solvents were purchased from commercial suppliers and used without further purification.

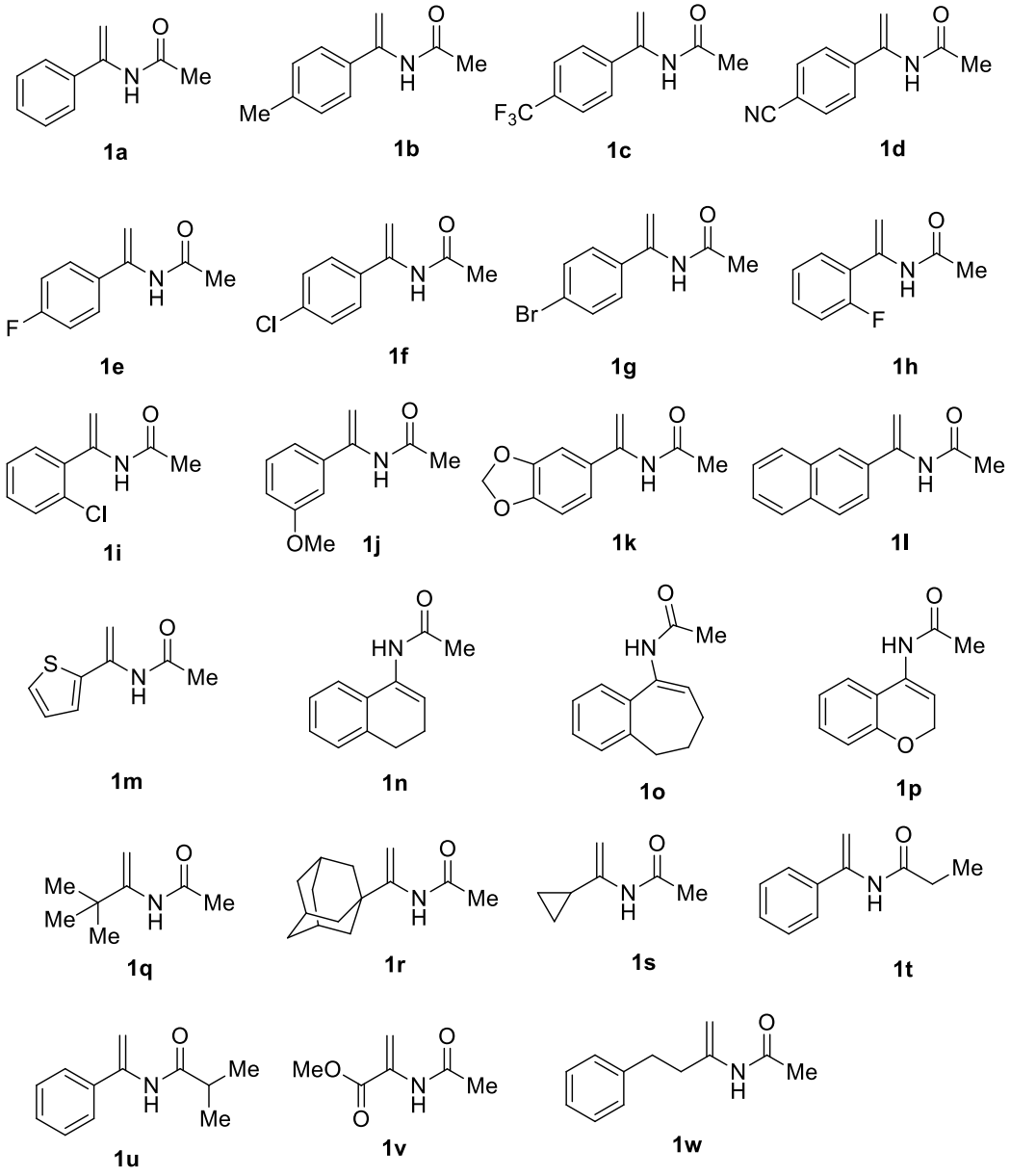
Thin layer chromatography was used to monitor the reaction on Merck 60 F254 precoated silica gel plate (0.2 mm thickness). TLC spots were visualized by UV-light irradiation on Spectroline Model ENF-24061/F 254 nm. Other visualization method was staining with a basic solution of potassium permanganate, followed by heating.

Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system.

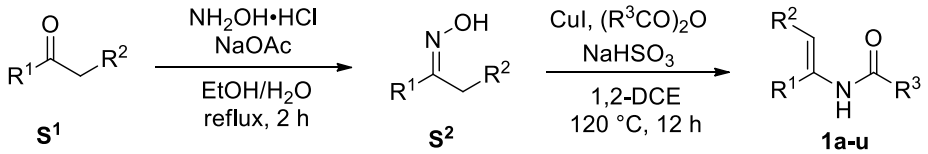
^{1}H NMR and ^{13}C NMR spectra were recorded at 25 ℃ on Bruker Advance 400M Hz NMR and JEOL 400M Hz spectrometers ($CDCl_3$ as solvent). Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of $SiMe_4$ (δ 0.00 singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); dt (doublet of triplets); m (multiplet); brs (broad single) and etc. Coupling constants are reported as a *J* value in Hz. ^{13}C NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 77 triplet). High resolution mass spectral analysis (HRMS) was performed on Waters-XEVOG2Q-TOF (Waters Corporation). Enantioselectivities were determined by HPLC analysis (Agilent 1260 infinity II) employing a Daicel Chiralcel IA column at 30 ^{o}C. Optical rotations were measured in $CHCl_3$ on a Rudolph Research Analytical polarimeter (Autopol III) with a 1 cm cell (*c* given in g/100 mL).

2. Experimental sections

2.1 General procedures for the synthesis of enamides 1



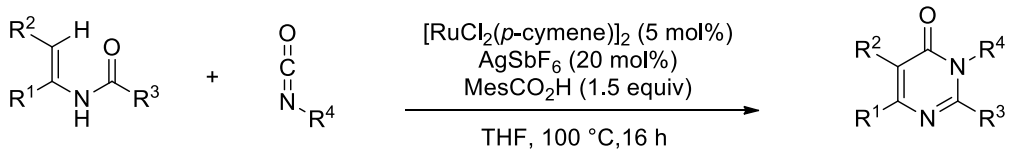
Compounds **1a**–**u,**[1,2] **1v**,[3] and **1w**[4] were prepared according to the reported literatures.



To a solution of ketone **S[1]** (10 mmol, 1.0 equiv) in EtOH-H_2O (7.5/22.5 mL) was added hydroxylamine hydrochloride (1.04 g, 15 mmol, 1.5 equiv) and NaOAc (2.05 g, 25 mmol, 2.5

equiv). After stirring at 95 ℃ for 2 h, the mixture was concentrated in vacuo and the residue was extracted with EtOAc. The organic layer was separated, washed with sat. NaCl, dried over Na_2SO_4 and concentrated to give the crude product **S²**. A mixture of ketoxime **S²** (10 mmol, 1.0 equiv), anhydride (20 mmol, 2.0 equiv), $NaHSO_3$ (3.12 g, 30 mmol, 3.0 equiv), and CuI (190 mg, 1 mmol, 0.1 equiv) was stirred in 1,2-DCE (100 mL) at 120 ℃ under N_2 for 12 h. After completion of the reaction, the reaction mixture was cooled to rt, diluted with EtOAc (25 mL), and washed with 2 M NaOH (20 mL) and sat. NaCl (20 mL). The organic layers were dried over Na_2SO_4 and evaporated in vacuo. The desired enamide was obtained after purification by flash chromatography on silica gel with PE/EtOAc as the eluent.

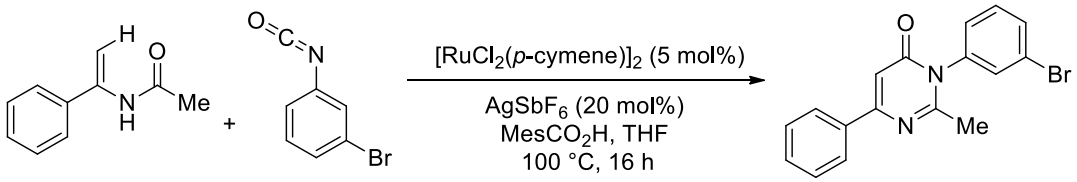
2.2 Typical procedures for the synthesis of pyrimidin-4-ones 3



1 **2** **3**

A 4 mL screw-cap vial was charged with **1** (0.75 mmol, 2.5 equiv), **2** (0.30 mmol, 1.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (9.2 mg, 0.015 mmol, 5 mol%), $AgSbF_6$ (20.6 mg, 0.06 mmol, 20 mol%), $MesCO_2H$ (73.9 mg, 0.45 mmol, 1.5 equiv) and THF (2.0 mL). The vial was carefully blown with nitrogen for 30 seconds and placed into preheated oil bath at 100 ℃ with stirring for 16 h. After cooling down, sat. $NaHCO_3$ (10 mL) was added and the mixture was extracted with DCM (10 mL × 3). The organic layers were combined, dried over Na_2SO_4 and evaporated in vacuo. The resultant residue was purified by flash chromatography (PE/EtOAc) to yield the desired product **3**.

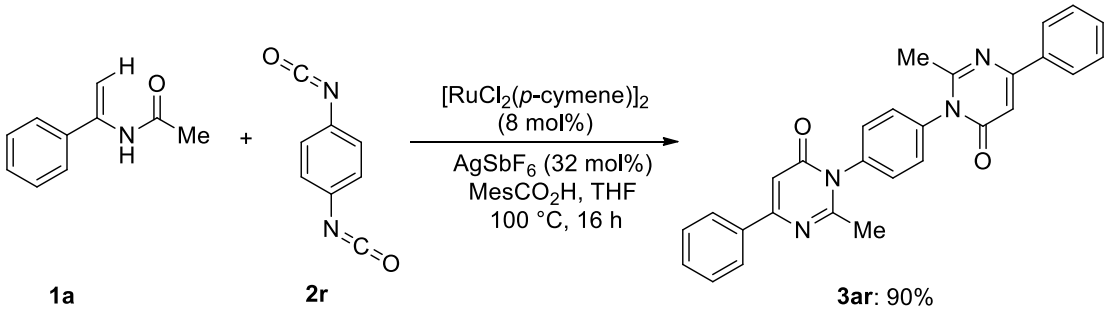
2.3 Large scale synthesis of 3ah



1a **2h** **3ah**: 83% (0.99 g)

A 100 mL sealed Schlenk tube was charged with **1a** (1.41 g, 8.75 mmol, 2.5 equiv), **2h** (0.69 g, 3.5 mmol, 1.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (107.2 mg, 0.175 mmol, 5 mol%), $AgSbF_6$ (240.5 mg, 0.7 mmol, 20 mol%), $MesCO_2H$ (0.86 g, 5.25 mmol, 1.5 equiv) and THF (24 mL). The vial was charged with nitrogen and placed into preheated oil bath at 100 ℃ with stirring for 16 h. After cooling down, saturated $NaHCO_3$ (25 mL) was added and the mixture was extracted with DCM (25 mL × 3). The organic layers were combined, dried over Na_2SO_4 and evaporated in vacuo. The resultant residue was purified by flash chromatography (PE/EtOAc) to yield **3ah** (0.99 g, 2.9 mmol, 83%).

2.4 Procedure for the synthesis of 3ar



A 4 mL screw-cap vial was charged with **1a** (241.8 mg, 1.5 mmol, 5.0 equiv), **2r** (48.0 mg, 0.30 mmol, 1.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (14.7 mg, 0.024 mmol, 8 mol%), $AgSbF_6$ (33.0 mg, 0.096 mmol, 32 mol%), $MesCO_2H$ (73.9 mg, 0.45 mmol, 1.5 equiv) and THF (2.0 mL). The vial was carefully blown with nitrogen for 30 seconds and placed into preheated oil bath at 100 ℃ with stirring for 16 h. After cooling down, sat. $NaHCO_3$ (10 mL) was added and the mixture was extracted with DCM (10 mL × 3). The organic layers were combined, dried over Na_2SO_4 and evaporated in vacuo. The resultant residue was purified by flash chromatography (PE/EtOAc) to yield **3ar** (120.0 mg, 0.269 mmol, 90%).

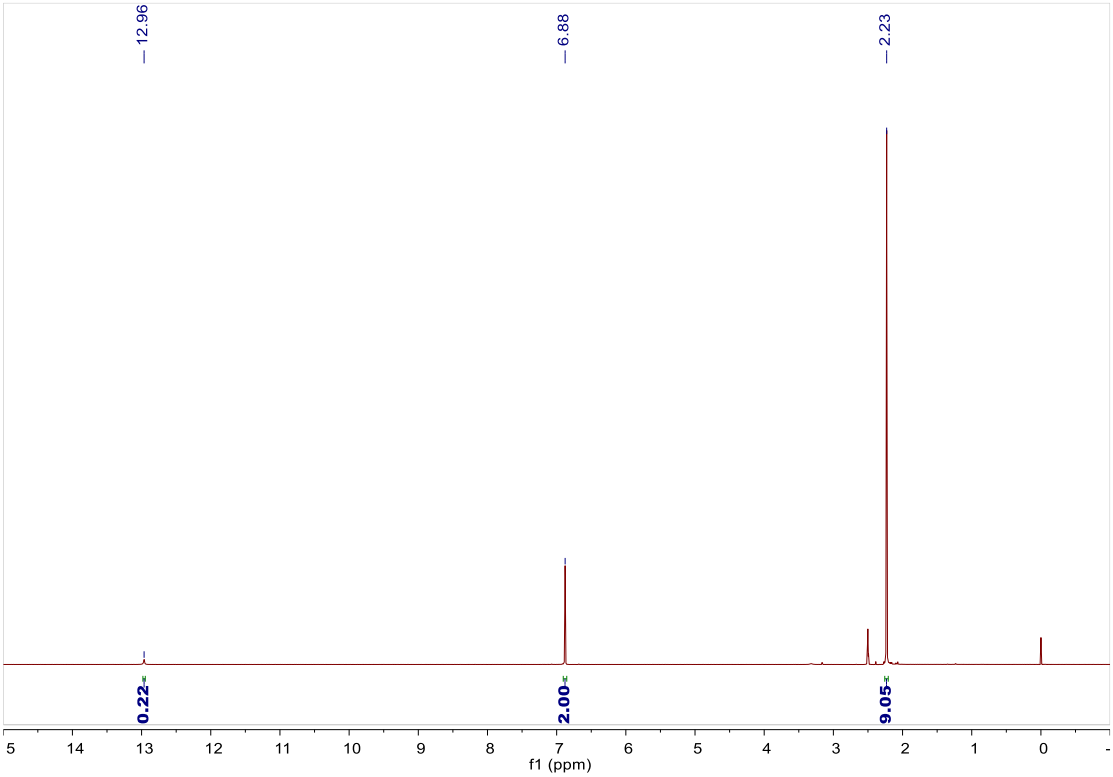
2.5 Mechanistic experiments

2.5.1 Olefinic H/D exchange of enamide 1n

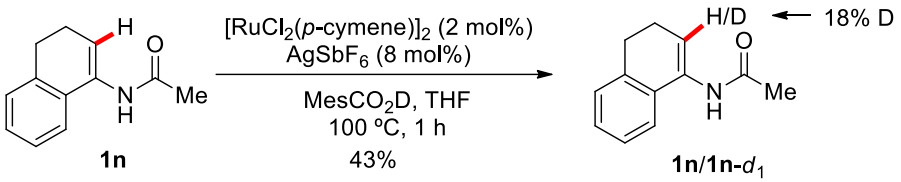
2,4,6-Trimethylbenzoic acid-d_1

2,4,6-Trimethylbenzoic acid (328.4 mg, 2 mmol) was dissolved in methanol-d_4 (0.8 mL,

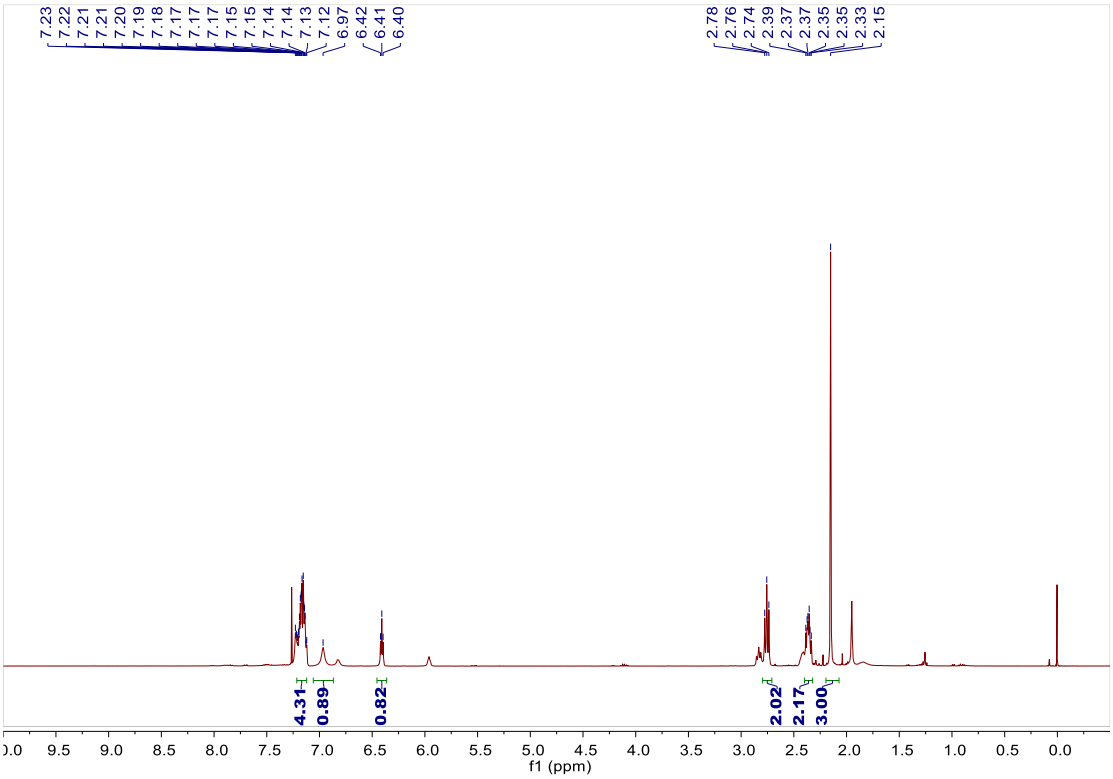
99% D), and refluxed for 1 h with stirring. The methanol was removed under reduced pressure. This cycle was repeated for 10 times to give $MesCO_2D$ as a white solid (210.6 mg, 64%, 78% D).



^{1}H NMR spectrum for $MesCO_2D$ (DMSO-d_6)

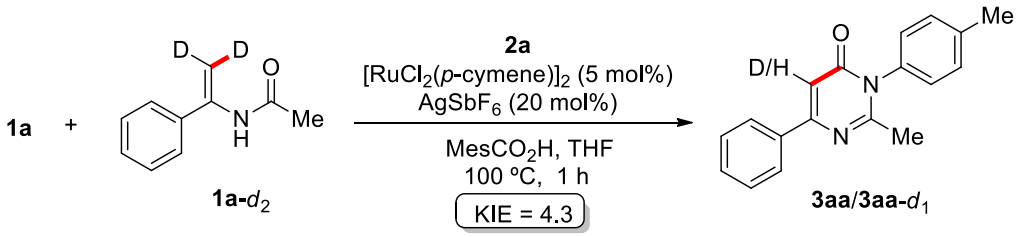


A 4 mL screw-cap vial was charged with **1n** (70.2 mg, 0.375 mmol, 1.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (4.6 mg, 0.0075 mmol, 2 mol%), $AgSbF_6$ (10.3 mg, 0.03 mmol, 8 mol%), $MesCO_2D$ (78% D, 37.0 mg, 0.225 mmol) and THF (1.0 mL). The vial was carefully blown with nitrogen for 30 seconds and placed into preheated oil bath at 100 ℃ with stirring for 1 h. After cooling down, sat. $NaHCO_3$ (10 mL) was added and the mixture was extracted with DCM (10 mL ×3). The organic layers were combined, dried over Na_2SO_4 and evaporated in vacuo. The resultant residue was purified by flash chromatography (PE/EtOAc) to yield the enamide **1n**/**1n**-d_1 (29.9 mg, 43%). The ratio of **1n**-d_1 was determined by ^{1}H NMR (400 MHz, $CDCl_3$) to be 18%.

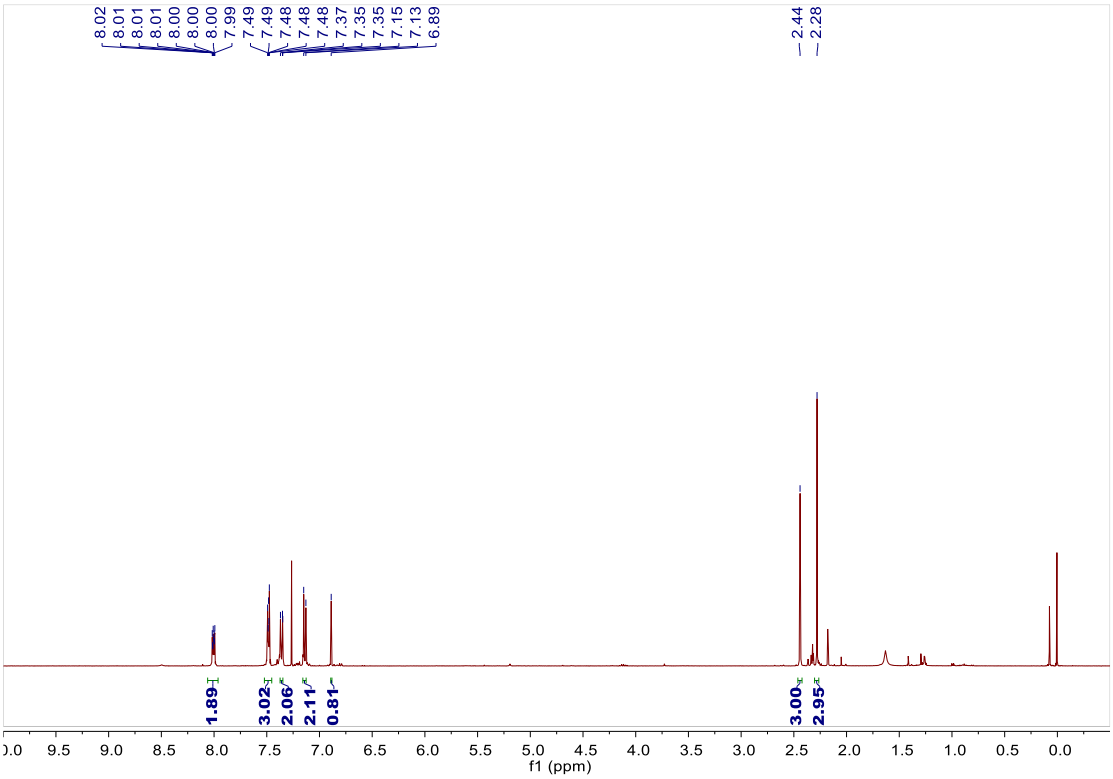


^{1}H NMR spectrum for 1n/1n-d_1

2.5.2 Competitive deuteration experiment



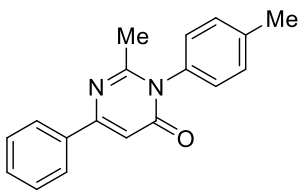
A 4 mL screw-cap vial was charged with **1a** (6.5 mg, 0.04 mmol), **1a**-d_2 (62% D, 25 mg, 0.15 mmol),[5] **2a** (25.3 mg, 0.19 mmol, 1.0 equiv), $[RuCl_2(p\text{-cymene})]_2$ (5.4 mg, 0.0095 mmol, 5 mol%), $AgSbF_6$ (13.1 mg, 0.038 mmol, 20 mol%), $MesCO_2H$ (46.8 mg, 0.285 mmol, 1.5 equiv) and THF (1.3 mL). The vial was carefully blown with nitrogen for 30 seconds and placed into preheated oil bath at 100 ℃ with stirring for 1 h. After cooling down, sat. $NaHCO_3$ (10 mL) was added and the mixture was extracted with DCM (10 mL × 3). The organic layers were combined, dried over Na_2SO_4 and evaporated in vacuo. The resultant residue was purified by flash chromatography (PE/EtOAc) to yield **3aa**/**3aa**-d_1 (17.3 mg, 33%). The ratio of **3aa**/**3aa**-$d_1$was determined by ^{1}H NMR (400 MHz, $CDCl_3$) to be 4.3:1.



^{1}H NMR spectrum for 3aa/3aa-d_1

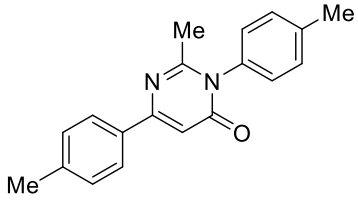
2.6 NMR data of the products

2-Methyl-6-phenyl-3-(*p*-tolyl)pyrimidin-4(3*H*)-one (3aa)



Following typical procedure, **3aa** was obtained as a white solid (68.8 mg, 0.249 mmol, 83%). mp: 120.5 – 120.7 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.04 – 7.98 (m, 2H), 7.51 – 7.46 (m, 3H), 7.39 – 7.34 (m, 2H), 7.14 (d, J = 8.3 Hz, 2H), 6.89 (s, 1H), 2.44 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 163.34, 160.12, 159.10, 139.46, 136.35, 134.64, 130.70 × 2, 130.48, 128.72 × 2, 127.11 × 2, 126.95 × 2, 107.64, 24.26, 21.22. HRMS (ESI): m/z calculated for $C_{18}H_{17}N_2O$ $[M + H]^+$: 277.1341, found: 277.1342.

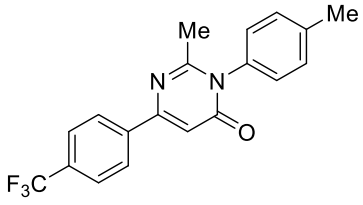
2-Methyl-3,6-di-*p*-tolylpyrimidin-4(3*H*)-one (3ba)



Following typical procedure, **3ba** was obtained as a white solid (43.4 mg, 0.149 mmol, 50%). mp: 192.7 – 193.0 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.91 (d, J = 8.2 Hz, 2H), 7.40 – 7.34 (m, 2H), 7.31 – 7.26 (m, 2H), 7.14 (d, J = 8.3 Hz,

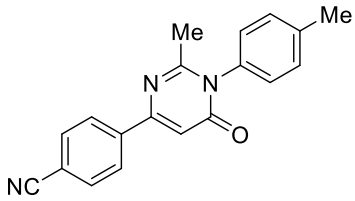
2H), 6.86 (s, 1H), 2.44 (s, 3H), 2.42 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 163.40, 160.08, 158.92, 140.83, 139.40, 134.73, 133.53, 130.68 ×2, 129.46 ×2, 127.15 ×2, 126.89 ×2, 106.94, 24.26, 21.39, 21.22. HRMS (ESI): m/z calculated for $C_{19}H_{19}N_2O$ $[M + H]^+$: 291.1497, found: 291.1496.

2-Methyl-3-(*p*-tolyl)-6-(4-(trifluoromethyl)phenyl)pyrimidin-4(3*H*)-one (3ca)



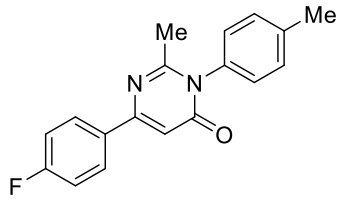
Following typical procedure, **3ca** was obtained as a white solid (85.5 mg, 0.248 mmol, 83%). mp: 174.3 – 175.1 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.14 – 8.08 (m, 2H), 7.78 – 7.69 (m, 2H), 7.41 – 7.34 (m, 2H), 7.14 (d, *J* = 8.3 Hz, 2H), 6.92 (s, 1H), 2.45 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 163.05, 159.61, 158.53, 139.77, 139.65, 134.43, 132.07 (q, *J* = 32.6 Hz), 130.78 ×2, 127.29 ×2, 127.02 ×2, 125.65 ×2 (q, *J* = 3.7 Hz), 123.89 (q, *J* = 272.3 Hz), 108.74, 24.25, 21.22. ^{19}F NMR (376 MHz, Chloroform-*d*): δ -62.77. HRMS (ESI): m/z calculated for $C_{19}H_{16}F_3N_2O$ $[M + H]^+$: 345.1215, found: 345.1209.

4-(2-Methyl-6-oxo-1-(*p*-tolyl)-1,6-dihydropyrimidin-4-yl)benzonitrile (3da)



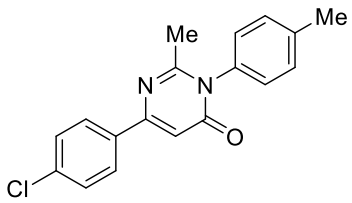
Following typical procedure, **3da** was obtained as a yellow solid (63.3 mg, 0.210 mmol, 70%). mp: 237.2 – 239.9 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.14 – 8.07 (m, 2H), 7.81 – 7.71 (m, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.17 – 7.08 (m, 2H), 6.91 (s, 1H), 2.44 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 162.91, 159.82, 157.87, 140.56, 139.74, 134.30, 132.47 ×2, 130.81 ×2, 127.51 ×2, 126.97 ×2, 118.43, 113.80, 109.15, 24.26, 21.23. HRMS (ESI): m/z calculated for $C_{19}H_{16}N_3O$ $[M + H]^+$: 302.1293, found: 302.1290.

6-(4-Fluorophenyl)-2-methyl-3-(*p*-tolyl)pyrimidin-4(3*H*)-one (3ea)



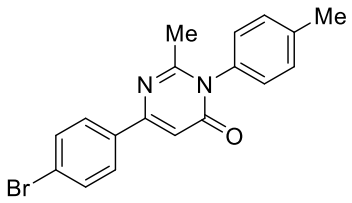
Following typical procedure, **3ea** was obtained as a white solid (85.9 mg, 0.292 mmol, 97%). mp: 174.1 – 176.9 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.01 (dd, *J* = 8.9, 5.4 Hz, 2H), 7.40 – 7.33 (m, 2H), 7.19 – 7.09 (m, 4H), 6.83 (s, 1H), 2.44 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 164.27 (d, *J* = 251.0 Hz), 163.23, 159.19, 158.99, 139.50, 134.51, 132.41 (d, *J* = 3.3 Hz), 130.70 ×2, 129.00 ×2 (d, *J* = 8.7 Hz), 127.06 ×2, 115.72 ×2 (d, *J* = 21.7 Hz), 107.19, 24.21, 21.20. ^{19}F NMR (376 MHz, Chloroform-*d*): δ -109.93. HRMS (ESI): m/z calculated for $C_{18}H_{16}FN_2O$ $[M + H]^+$: 295.1247, found: 295.1245.

6-(4-Chlorophenyl)-2-methyl-3-(*p*-tolyl)pyrimidin-4(3*H*)-one (3fa)



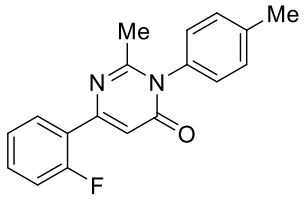
Following typical procedure, **3fa** was obtained as a white solid (91.7 mg, 0.295 mmol, 98%). mp: 191.0 – 192.2 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.95 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 7.36 (dt, *J* = 8.5, 0.7 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 6.85 (s, 1H), 2.44 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 163.21, 159.32, 158.87, 139.58, 136.68, 134.77, 134.52, 130.76 ×2, 128.96 ×2, 128.28 ×2, 127.07 ×2, 107.60, 24.26, 21.24. HRMS (ESI): m/z calculated for $C_{18}H_{16}{}^{35}ClN_2O$ $[M + H]^+$: 311.0951, found: 311.0944.

6-(4-Bromophenyl)-2-methyl-3-(*p*-tolyl)pyrimidin-4(3*H*)-one (3ga)



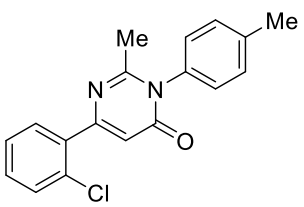
Following typical procedure, **3ga** was obtained as a white solid (63.8 mg, 0.180 mmol, 60 %). mp: 188.3 – 188.9 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.88 (d, *J* = 8.6 Hz, 2H), 7.60 (d, *J* = 8.7 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 2H), 7.13 (d, *J* = 8.3 Hz, 2H), 6.85 (s, 1H), 2.44 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 163.14, 159.31, 158.88, 139.53, 135.21, 134.49, 131.89 ×2, 130.72 ×2, 128.48 ×2, 127.04 ×2, 125.09, 107.57, 24.24, 21.22. HRMS (ESI): m/z calculated for $C_{18}H_{16}{}^{79}BrN_2O$ $[M + H]^+$: 355.0446, found: 355.0439.

6-(2-Fluorophenyl)-2-methyl-3-(*p*-tolyl)pyrimidin-4(3*H*)-one (3ha)



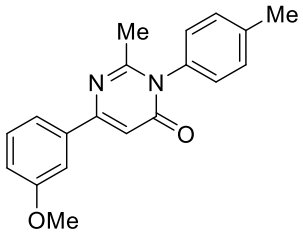
Following typical procedure, **3ha** was obtained as a yellow solid (47.4 mg, 0.161 mmol, 54%). mp: 193.6 – 193.9 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.09 (td, *J* = 7.9, 2.0 Hz, 1H), 7.46 – 7.38 (m, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.24 (m, 1H), 7.16 – 7.13 (m, 3H), 7.03 (s, 1H), 2.43 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 163.04 (d, *J* = 1.5 Hz), 161.03 (d, *J* = 253.4 Hz), 158.92, 155.55 (d, *J* = 2.7 Hz), 139.52, 134.56, 131.66 (d, *J* = 8.9 Hz), 130.73 ×2, 130.53 (d, *J* = 2.5 Hz), 127.09 ×2, 124.60 (d, *J* = 10.5 Hz), 124.33 (d, *J* = 3.8 Hz), 116.43 (d, *J* = 23.1 Hz), 112.69 (d, *J* = 12.4 Hz), 24.20, 21.22. ^{19}F NMR (376 MHz, Chloroform-*d*): δ -113.04. HRMS (ESI): m/z calculated for $C_{18}H_{16}FN_2O$ $[M + H]^+$: 295.1247, found: 295.1248.

6-(2-Chlorophenyl)-2-methyl-3-(*p*-tolyl)pyrimidin-4(3*H*)-one (3ia)



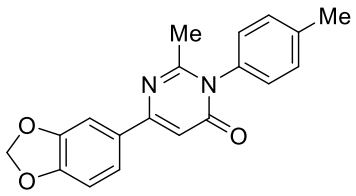
Following typical procedure, **3ia** was obtained as a purple solid (33.2 mg, 0.107 mmol, 36%). mp: 248.3 – 248.6 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.67 – 7.62 (m, 1H), 7.53 – 7.46 (m, 1H), 7.41 – 7.33 (m, 4H), 7.17 (d, *J* = 8.2 Hz, 2H), 6.79 (s, 1H), 2.45 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 162.59, 159.73, 159.30, 139.59, 136.56, 134.49, 132.12, 130.75 ×2, 130.58, 130.45, 130.38, 127.06 ×2, 126.95, 113.42, 24.17, 21.24. HRMS (ESI): m/z calculated for $C_{18}H_{16}{}^{35}ClN_2O$ $[M + H]^+$: 311.0951, found: 311.0944.

6-(3-Methoxyphenyl)-2-methyl-3-(*p*-tolyl)pyrimidin-4(3*H*)-one (3ja)



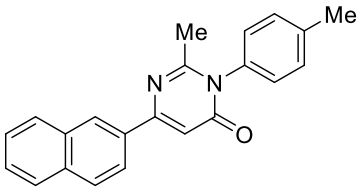
Following typical procedure, **3ja** was obtained as a white solid (49.0 mg, 0.160 mmol, 53%). mp: 171.4 – 171.7 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.57 (dt, *J* = 5.0, 1.8 Hz, 2H), 7.43 – 7.33 (m, 3H), 7.14 (d, *J* = 8.2 Hz, 2H), 7.02 (ddd, *J* = 8.2, 2.6, 1.0 Hz, 1H), 6.87 (s, 1H), 3.88 (s, 3H), 2.44 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 163.30, 159.89, 159.86, 159.02, 139.45, 137.78, 134.60, 130.69 ×2, 129.73, 127.07 ×2, 119.32, 116.42, 112.08, 107.81, 55.30, 24.24, 21.20. HRMS (ESI): m/z calculated for $C_{19}H_{19}N_2O_2$ $[M + H]^+$: 307.1447, found: 307.1444.

6-(Benzo[*d*][1,3]dioxol-5-yl)-2-methyl-3-(*p*-tolyl)pyrimidin-4(3*H*)-one (3ka)



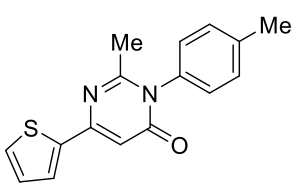
Following typical procedure, **3ka** was obtained as a yellow solid (70.9 mg, 0.221 mmol, 74%). mp: 175.4 – 176.3 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.59 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.49 (d, *J* = 1.8 Hz, 1H), 7.40 – 7.32 (m, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 6.90 (d, *J* = 8.2 Hz, 1H), 6.76 (s, 1H), 6.03 (s, 2H), 2.43 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 163.32, 159.44, 158.79, 149.70, 148.18, 139.41, 134.67 ×2, 130.62, 130.57, 127.14 ×2, 121.72, 108.42, 107.14, 106.37, 101.51, 24.23, 21.21. HRMS (ESI): m/z calculated for $C_{19}H_{17}N_2O_3$ $[M + H]^+$: 321.1239, found: 321.1235.

2-Methyl-6-(naphthalen-2-yl)-3-(*p*-tolyl)pyrimidin-4(3*H*)-one (3la)



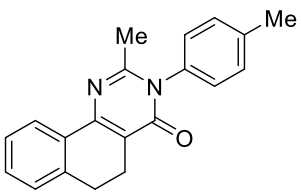
Following typical procedure, **3la** was obtained as a yellow solid (85.4 mg, 0.262 mmol, 87%). mp: 174.4 – 175.1 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.64 – 8.59 (m, 1H), 8.04 (dd, *J* = 8.6, 1.8 Hz, 1H), 8.00 – 7.85 (m, 3H), 7.58 – 7.52 (m, 2H), 7.38 (dt, *J* = 7.8, 0.7 Hz, 2H), 7.17 (d, *J* = 8.3 Hz, 2H), 7.04 (s, 1H), 2.45 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 163.38, 159.89, 159.10, 139.47, 134.65, 134.33, 133.52, 133.13, 130.71 ×2, 129.03, 128.48, 127.64, 127.40, 127.21, 127.14 ×2, 126.47, 123.67, 107.85, 24.28, 21.22. HRMS (ESI): m/z calculated for $C_{22}H_{19}N_2O$ $[M + H]^+$: 327.1497, found: 327.1492.

2-Methyl-6-(thiophen-2-yl)-3-(*p*-tolyl)pyrimidin-4(3*H*)-one (3ma)



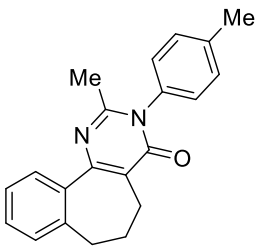
Following typical procedure, **3ma** was obtained as a purple solid (68.5 mg, 0.243 mmol, 81%). mp: 178.8 – 180.5 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.66 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.50 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.37 – 7.31 (m, 2H), 7.17 – 7.08 (m, 3H), 6.75 (s, 1H), 2.43 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 162.90, 159.41, 155.00, 141.47, 139.42, 134.52, 130.64 ×2, 129.74, 128.38, 127.09 ×2, 127.02, 104.77, 24.07, 21.17. HRMS (ESI): m/z calculated for $C_{16}H_{15}N_2OS$ $[M + H]^+$: 283.0905, found: 283.0899.

2-Methyl-3-(*p*-tolyl)-5,6-dihydrobenzo[*h*]quinazolin-4(3*H*)-one (3na)



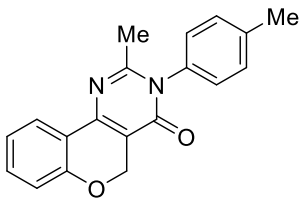
Following typical procedure, **3na** was obtained as a white solid (70.1 mg, 0.232 mmol, 77%). mp: 171.3 – 171.9 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.25 – 8.20 (m, 1H), 7.38 – 7.32 (m, 4H), 7.27 – 7.23 (m, 1H), 7.13 (d, *J* = 8.3 Hz, 2H), 2.98 – 2.91 (m, 2H), 2.87 (ddd, *J* = 9.5, 6.2, 1.9 Hz, 2H), 2.44 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 162.93, 156.69, 153.01, 139.22, 138.71, 135.21, 132.51, 130.59 × 2, 130.18, 127.86, 127.19 × 2, 126.83, 125.29, 117.47, 27.18, 24.18, 21.21, 19.96. HRMS (ESI): m/z calculated for $C_{20}H_{19}N_2O$ $[M + H]^+$: 303.1497, found: 303.1492.

2-Methyl-3-(*p*-tolyl)-6,7-dihydro-3*H*-benzo[6,7]cyclohepta[1,2-*d*]pyrimidin-4(5*H*)-one (3oa)



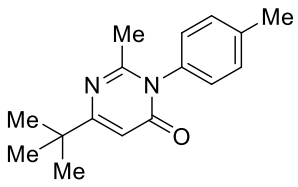
Following typical procedure, **3oa** was obtained as a yellow solid (59.4 mg, 0.188 mmol, 63%). mp: 171.6 – 172.1 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.79 – 7.70 (m, 1H), 7.43 – 7.32 (m, 4H), 7.30 – 7.25 (m, 1H), 7.19 – 7.12 (m, 2H), 2.64 (t, *J* = 7.1 Hz, 2H), 2.50 (t, *J* = 7.2 Hz, 2H), 2.43 (s, 3H), 2.30 – 2.26 (m, 2H), 2.24 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 163.10, 158.49, 156.50, 140.82, 139.19, 138.30, 135.30, 130.58 × 2, 129.39, 128.90, 128.02, 127.13 × 2, 126.53, 121.59, 33.37, 31.89, 24.12, 21.54, 21.19. HRMS (ESI): m/z calculated for $C_{21}H_{21}N_2O$ $[M + H]^+$: 317.1654, found: 317.1651.

2-Methyl-3-(*p*-tolyl)-3*H*-chromeno[4,3-*d*]pyrimidin-4(5*H*)-one (3pa)



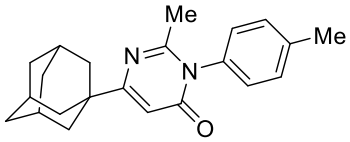
Following typical procedure, **3pa** was obtained as a white solid (81.8 mg, 0.269 mmol, 90%). mp: 224.2 – 224.9 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.06 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.35 (dd, *J* = 7.7, 1.8 Hz, 3H), 7.11 (d, *J* = 8.3 Hz, 2H), 7.06 (td, *J* = 7.5, 1.1 Hz, 1H), 6.93 (dd, *J* = 8.2, 1.0 Hz, 1H), 5.24 (s, 2H), 2.44 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 160.06, 158.90, 156.98, 150.38, 139.48, 134.50, 132.60, 130.66 × 2, 127.08 × 2, 125.27, 121.73, 120.50, 116.73, 110.60, 63.04, 24.24, 21.19. HRMS (ESI): m/z calculated for $C_{19}H_{17}N_2O_2$ $[M + H]^+$: 305.1290, found: 305.1288.

6-(*tert*-Butyl)-2-methyl-3-(*p*-tolyl)pyrimidin-4(3*H*)-one (3qa)



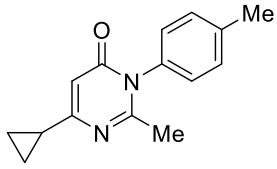
Following typical procedure, **3qa** was obtained as a white solid (49.0 mg, 0.191 mmol, 64%). mp: 101.1 – 102.0 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.36 – 7.28 (m, 2H), 7.09 (d, J = 8.3 Hz, 2H), 6.41 (s, 1H), 2.41 (s, 3H), 2.16 (s, 3H), 1.28 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 173.76, 163.66, 157.68, 139.21, 134.82, 130.61 × 2, 127.09 × 2, 106.95, 36.86, 28.50 × 3, 24.05, 21.17. HRMS (ESI): m/z calculated for $C_{16}H_{21}N_2O$ $[M + H]^+$: 257.1654, found: 257.1649.

6-(Adamantan-1-yl)-2-methyl-3-(*p*-tolyl)pyrimidin-4(3*H*)-one (3ra)



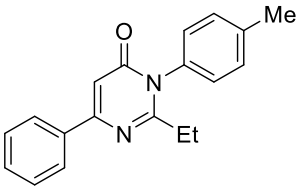
Following typical procedure, **3ra** was obtained as a white solid (80.8 mg, 0.242 mmol, 81%). mp: 210.6 – 210.9 ℃ . ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.36 – 7.30 (m, 2H), 7.09 (d, J = 8.2 Hz, 2H), 6.31 (s, 1H), 2.42 (s, 3H), 2.16 (s, 3H), 2.12 – 2.06 (m, 3H), 1.90 (d, J = 2.9 Hz, 6H), 1.83 – 1.71 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 173.36, 163.84, 157.81, 139.20, 134.93, 130.60 × 2, 127.15 × 2, 106.97, 40.15 × 3, 38.42, 36.63 × 3, 28.30 × 3, 24.11, 21.21. HRMS (ESI): m/z calculated for $C_{22}H_{27}N_2O$ $[M + H]^+$: 335.2123, found: 335.2120.

6-Cyclopropyl-2-methyl-3-(*p*-tolyl)pyrimidin-4(3*H*)-one (3sa)



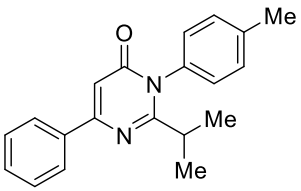
Following typical procedure, **3sa** was obtained as a yellow liquid (20.0 mg, 0.083 mmol, 28%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.31 (d, J = 8.1 Hz, 2H), 7.06 (d, J = 8.2 Hz, 2H), 6.29 (s, 1H), 2.41 (s, 3H), 2.11 (s, 3H), 1.83 – 1.77 (m, 1H), 1.10 – 1.03 (m, 2H), 1.00 – 0.91 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 167.75, 162.66, 158.86, 139.27, 134.82, 130.61 × 2, 127.17 × 2, 107.70, 24.03, 21.21, 16.48, 8.91 × 2. HRMS (ESI): m/z calculated for $C_{15}H_{17}N_2O$ $[M + H]^+$: 241.1341, found: 241.1328.

2-Ethyl-6-phenyl-3-(*p*-tolyl)pyrimidin-4(3*H*)-one (3ta)



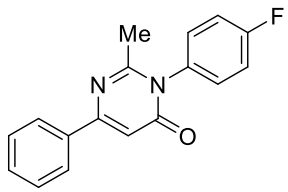
Following typical procedure, **3ta** was obtained as a brown solid (79.4 mg, 0.273 mmol, 91%). mp: 144.1 – 145.2 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.09 – 8.04 (m, 2H), 7.49 – 7.46 (m, 3H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.19 – 7.09 (m, 2H), 6.92 (s, 1H), 2.49 – 2.43 (m, 5H), 1.28 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 163.48, 162.29, 159.63, 139.30, 136.37, 134.05, 130.55, 130.42 ×2, 128.61 ×2, 127.31 ×2, 126.91 ×2, 107.17, 29.11, 21.17, 10.78. HRMS (ESI): m/z calculated for $C_{19}H_{19}N_2O$ $[M + H]^+$: 291.1497, found: 291.1486.

2-*iso*-Propyl-6-phenyl-3-(*p*-tolyl)pyrimidin-4(3*H*)-one (3ua)



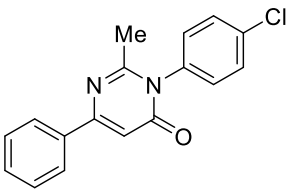
Following typical procedure, **3ua** was obtained as a brown solid (50.2 mg, 0.165 mmol, 55%). mp: 181.2 – 182.0 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.08 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.49 (dd, *J* = 4.8, 1.9 Hz, 3H), 7.36 (d, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 6.88 (s, 1H), 2.73 (p, *J* = 6.7 Hz, 1H), 2.45 (s, 3H), 1.24 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 166.36, 163.71, 159.87, 139.34, 136.48, 134.15, 130.54, 130.48 ×2, 128.64 ×2, 127.48 ×2, 127.00 ×2, 106.88, 32.59, 21.29 ×2, 21.25. HRMS (ESI): m/z calculated for $C_{20}H_{21}N_2O$ $[M + H]^+$: 305.1654, found: 305.1640.

3-(4-Fluorophenyl)-2-methyl-6-phenylpyrimidin-4(3*H*)-one (3ab)



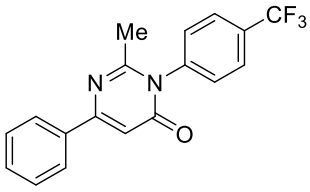
Following typical procedure, **3ab** was obtained as a white solid (77.4 mg, 0.276 mmol, 92%). mp: 175.8 – 176.2 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.04 – 7.97 (m, 2H), 7.51 – 7.45 (m, 3H), 7.25 (d, *J* = 6.4 Hz, 4H), 6.88 (s, 1H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 163.20, 162.78 (d, *J* = 249.8 Hz), 160.30, 158.78, 136.17, 133.16 (d, *J* = 3.4 Hz), 130.66, 129.40 ×2 (d, *J* = 8.8 Hz), 128.78 ×2, 127.00 ×2, 117.20 ×2 (d, *J* = 23.1 Hz), 107.58, 24.32. ^{19}F NMR (376 MHz, Chloroform-*d*): δ -111.27. HRMS (ESI): m/z calculated for $C_{17}H_{14}FN_2O$ $[M + H]^+$: 281.1090, found: 281.1085.

3-(4-Chlorophenyl)-2-methyl-6-phenylpyrimidin-4(3*H*)-one (3ac)



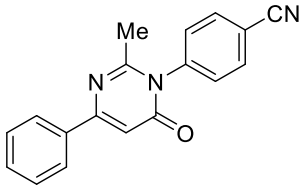
Following typical procedure, **3ac** was obtained as a white solid (65.6 mg, 0.221 mmol, 74%). mp: 168.7 – 169.8 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.04 – 7.97 (m, 2H), 7.56 – 7.50 (m, 2H), 7.48 (ddd, *J* = 4.4, 2.3, 1.2 Hz, 3H), 7.21 (d, *J* = 8.7 Hz, 2H), 6.86 (s, 1H), 2.26 (s, 3H). ^{13}C NMR (101MHz, Chloroform-*d*): δ 162.93, 160.21, 158.44, 136.01, 135.65, 135.41, 130.60, 130.27, 128.89 ×2, 128.70 ×2, 126.92 ×2, 107.42 ×2, 24.19. HRMS (ESI): m/z calculated for $C_{17}H_{14}{}^{35}ClN_2O$ $[M + H]^+$: 297.0795, found: 297.0795.

2-Methyl-6-phenyl-3-(4-(trifluoromethyl)phenyl)pyrimidin-4(3*H*)-one (3ad)



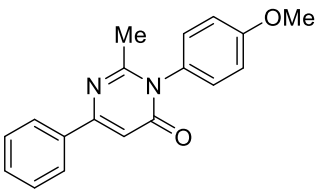
Following typical procedure, **3ad** was obtained as a white solid (70.8 mg, 0.214 mmol, 71%). mp: 213.9 – 214.5 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.05 – 7.98 (m, 2H), 7.85 (d, *J* = 8.2 Hz, 2H), 7.52 – 7.47 (m, 3H), 7.45 – 7.40 (m, 2H), 6.89 (s, 1H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 162.83, 160.46, 158.02, 140.50, 136.02, 131.70 (q, *J* = 33.1 Hz), 130.77, 128.81 ×2, 128.38 ×2, 127.28 ×2 (q, *J* = 3.6 Hz), 127.02 ×2, 123.49 (q, *J* = 272.6 Hz), 107.54, 24.29. ^{19}F NMR (376 MHz, Chloroform-*d*): δ -62.76. HRMS (ESI): m/z calculated for $C_{18}H_{14}F_3N_2O$ $[M + H]^+$: 331.1058, found: 331.1058.

4-(2-Methyl-6-oxo-4-phenylpyrimidin-1(6*H*)-yl)benzonitrile (3ae)



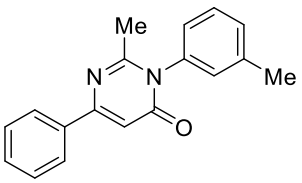
Following typical procedure, **3ae** was obtained as a white solid (19.6 mg, 0.068 mmol, 23%). mp: 257.6 – 258.4 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.04 – 7.98 (m, 2H), 7.88 (d, *J* = 8.5 Hz, 2H), 7.50 (dd, *J* = 5.1, 1.8 Hz, 3H), 7.43 (d, *J* = 8.5 Hz, 2H), 6.88 (s, 1H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 162.63, 160.57, 157.56, 141.33, 135.87, 133.93 ×2, 130.88, 129.00 ×2, 128.83 ×2, 127.03 ×2, 117.60, 113.75, 107.47, 24.23. HRMS (ESI): m/z calculated for $C_{18}H_{14}N_3O$ $[M + H]^+$: 288.1137, found: 288.1133.

3-(4-Methoxyphenyl)-2-methyl-6-phenylpyrimidin-4(3*H*)-one (3af)



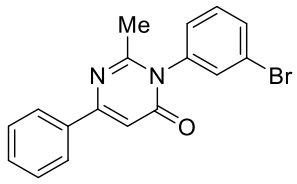
Following typical procedure, **3af** was obtained as a white solid (73.8 mg, 0.252 mmol, 84%). mp: 181.8 – 183.0 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.04 – 7.97 (m, 2H), 7.50 – 7.45 (m, 3H), 7.17 (d, *J* = 8.9 Hz, 2H), 7.05 (d, *J* = 8.9 Hz, 2H), 6.88 (s, 1H), 3.85 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 163.39, 160.00, 159.88, 159.34, 136.23, 130.41, 129.65, 128.63 ×2, 128.36 ×2, 126.87 ×2, 115.17 ×2, 107.47, 55.40, 24.21. HRMS (ESI): m/z calculated for $C_{18}H_{17}N_2O_2$ $[M + H]^+$: 293.1290, found: 293.1293.

2-Methyl-6-phenyl-3-(*m*-tolyl)pyrimidin-4(3*H*)-one (3ag)



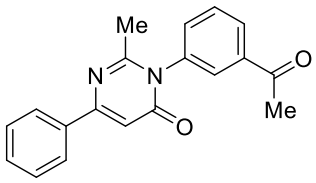
Following typical procedure, **3ag** was obtained as a brown liquid (69.7 mg, 0.252 mmol, 84%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.05 – 7.98 (m, 2H), 7.48 (tt, *J* = 3.6, 2.6 Hz, 3H), 7.43 (dd, *J* = 7.6, 0.7 Hz, 1H), 7.33 – 7.29 (m, 1H), 7.10 – 7.03 (m, 2H), 6.90 (s, 1H), 2.43 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 163.18, 160.07, 158.89, 140.10, 137.11, 136.20, 130.41, 130.10, 129.72, 128.62 ×2, 127.79, 126.87 ×2, 124.26, 107.52, 24.12, 21.22. HRMS (ESI): m/z calculated for $C_{18}H_{17}N_2O$ $[M + H]^+$: 277.1341, found: 277.1339.

3-(3-Bromophenyl)-2-methyl-6-phenylpyrimidin-4(3*H*)-one (3ah)



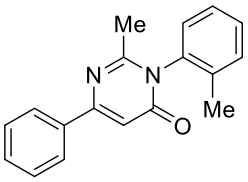
Following typical procedure, **3ah** was obtained as a gray solid (87.5 mg, 0.256 mmol, 85%). mp: 135.6 – 137.7 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.04 – 7.97 (m, 2H), 7.66 (ddd, *J* = 8.1, 1.9, 1.0 Hz, 1H), 7.52 – 7.42 (m, 5H), 7.23 (ddd, *J* = 7.9, 2.0, 1.0 Hz, 1H), 6.88 (s, 1H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 162.91, 160.38, 158.36, 138.47, 136.09, 132.71, 131.26, 130.80, 130.70, 128.78 ×2, 127.02 ×2, 126.42, 123.41, 107.56, 24.27. HRMS (ESI): m/z calculated for $C_{17}H_{14}{}^{79}BrN_2O$ $[M + H]^+$: 341.0290, found: 341.0288.

3-(3-Acetylphenyl)-2-methyl-6-phenylpyrimidin-4(3*H*)-one (3ai)



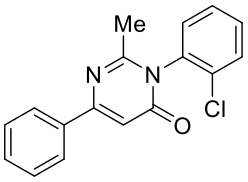
Following typical procedure, **3ai** was obtained as a white solid (43.8 mg, 0.144 mmol, 48%). mp: 89.2 – 89.7 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.09 (dd, *J* = 7.9, 1.3 Hz, 1H), 8.05 – 7.99 (m, 2H), 7.88 (dd, *J* = 1.5, 0.7 Hz, 1H), 7.69 (td, *J* = 7.8, 0.9 Hz, 1H), 7.50 (ddd, *J* = 5.2, 2.9, 1.5 Hz, 4H), 6.91 (s, 1H), 2.63 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 196.49, 163.20, 160.64, 158.41, 138.97, 137.87, 136.11, 132.13, 130.78, 130.50, 129.35, 128.83 × 2, 127.39, 127.07 × 2, 107.55, 26.66, 24.39. HRMS (ESI): m/z calculated for $C_{19}H_{17}N_2O_2$ $[M + H]^+$: 305.1290, found: 305.1290.

2-Methyl-6-phenyl-3-(*o*-tolyl)pyrimidin-4(3*H*)-one (3aj)



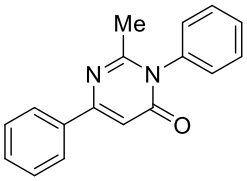
Following typical procedure, **3aj** was obtained as a yellow liquid (49.8 mg, 0.180 mmol, 60%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.07 – 8.00 (m, 2H), 7.53 – 7.47 (m, 3H), 7.44 – 7.35 (m, 3H), 7.19 – 7.14 (m, 1H), 6.91 (s, 1H), 2.22 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 162.69, 160.37, 158.95, 136.46, 136.27, 134.88, 131.62, 130.60, 129.72, 128.78 × 2, 127.72, 127.36, 127.00 × 2, 107.65, 23.80, 17.34. HRMS (ESI): m/z calculated for $C_{18}H_{17}N_2O$ $[M + H]^+$: 277.1341, found: 277.1338.

3-(2-Chlorophenyl)-2-methyl-6-phenylpyrimidin-4(3*H*)-one (3ak)



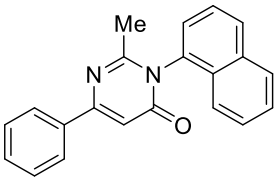
Following typical procedure, **3ak** was obtained as a yellow liquid (48.2 mg, 0.162 mmol, 54%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.11 – 8.00 (m, 2H), 7.62 (dd, *J* = 6.0, 3.5 Hz, 1H), 7.54 – 7.44 (m, 5H), 7.35 (d, *J* = 3.5 Hz, 1H), 6.90 (s, 1H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 162.30, 160.41, 158.51, 136.14, 135.08, 132.02, 130.88, 130.82, 130.64, 129.33, 128.74 × 2, 128.42, 127.03 × 2, 107.52, 23.47. HRMS (ESI): m/z calculated for $C_{17}H_{14}{}^{35}ClN_2O$ $[M + H]^+$: 297.0795, found: 297.0795.

2-Methyl-3,6-diphenylpyrimidin-4(3*H*)-one (3al)



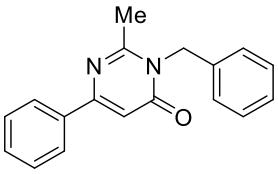
Following typical procedure, **3al** was obtained as a white solid (48.3 mg, 0.184 mmol, 61%). mp: 147 – 148 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.05 – 7.98 (m, 2H), 7.61 – 7.55 (m, 2H), 7.54 – 7.51 (m, 1H), 7.50 – 7.47 (m, 3H), 7.28 (d, *J* = 1.5 Hz, 2H), 6.89 (s, 1H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 163.22, 160.24, 158.88, 137.40, 136.36, 130.57, 130.10 × 2, 129.43, 128.78 × 2, 127.52 × 2, 127.01 × 2, 107.74, 24.32. HRMS (ESI): m/z calculated for $C_{17}H_{15}N_2O$ $[M + H]^+$: 263.1184, found: 263.1182.

2-Methyl-3-(naphthalen-1-yl)-6-phenylpyrimidin-4(3*H*)-one (3am)



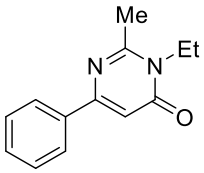
Following typical procedure, **3am** was obtained as a yellow liquid (65.8 mg, 0.211 mmol, 70%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.12 – 8.06 (m, 2H), 8.04 – 8.00 (m, 1H), 8.00 – 7.96 (m, 1H), 7.64 (dd, *J* = 8.3, 7.3 Hz, 1H), 7.60 – 7.50 (m, 6H), 7.46 (dd, *J* = 7.3, 1.1 Hz, 1H), 7.00 (s, 1H), 2.19 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 163.27, 160.47, 159.66, 136.27, 134.56, 133.83, 130.66, 130.04, 129.11, 128.81 × 2, 126.77, 127.98, 127.07 × 2, 126.94, 125.68 × 2, 121.37, 107.66, 23.58. HRMS (ESI): m/z calculated for $C_{21}H_{17}N_2O$ $[M + H]^+$: 313.1341, found: 313.1339.

3-Benzyl-2-methyl-6-phenylpyrimidin-4(3*H*)-one (3an)



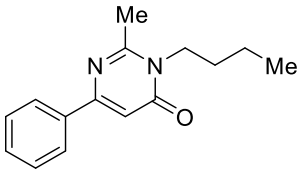
Following typical procedure, **3an** was obtained as a white solid (59.4 mg, 0.215 mmol, 72%). mp: 122.1 – 122.6 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.02 – 7.96 (m, 2H), 7.50 – 7.44 (m, 3H), 7.39 – 7.32 (m, 2H), 7.32 – 7.28 (m, 1H), 7.25 – 7.21 (m, 2H), 6.88 (s, 1H), 5.35 (s, 2H), 2.55 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 163.22, 159.89, 159.28, 136.25, 135.29, 130.48, 128.94 × 2, 128.71 × 2, 127.76, 126.92 × 2, 126.62 × 2, 107.16, 46.87, 23.34. HRMS (ESI): m/z calculated for $C_{18}H_{17}N_2O$ $[M + H]^+$: 277.1341, found: 277.1337.

3-Ethyl-2-methyl-6-phenylpyrimidin-4(3*H*)-one (3ao)



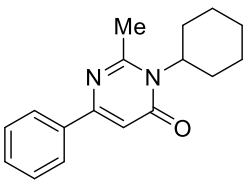
Following typical procedure, **3ao** was obtained as a white solid (42.7 mg, 0.199 mmol, 66%). mp: 101.7 – 102.9 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.96 – 7.90 (m, 2H), 7.47 – 7.41 (m, 3H), 6.75 (s, 1H), 4.11 (q, J = 7.2 Hz, 2H), 2.64 (s, 3H), 1.35 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 162.76, 159.63, 158.35, 136.38, 130.27, 128.63 × 2, 126.79 × 2, 107.29, 39.46, 22.79, 13.39. HRMS (ESI): m/z calculated for $C_{13}H_{15}N_2O$ $[M + H]^+$: 215.1184, found: 215.1180.

3-Butyl-2-methyl-6-phenylpyrimidin-4(3*H*)-one (3ap)



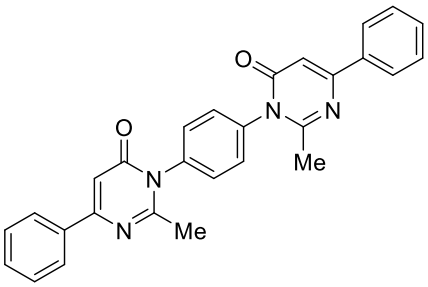
Following typical procedure, **3ap** was obtained as a white solid (40.4 mg, 0.167 mmol, 56%). mp: 79.7 – 79.8 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.98 – 7.89 (m, 2H), 7.48 – 7.41 (m, 3H), 6.75 (s, 1H), 4.11 – 3.95 (m, 2H), 2.64 (s, 3H), 1.80 – 1.63 (m, 2H), 1.52 – 1.39 (m, 2H), 0.99 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 162.90, 159.55, 158.47, 136.41, 130.26, 128.63 × 2, 126.80 × 2, 107.28, 44.26, 30.33, 22.95, 20.22, 13.67. HRMS (ESI): m/z calculated for $C_{15}H_{19}N_2O$ $[M + H]^+$: 243.1497, found: 243.1495.

3-Cyclohexyl-2-methyl-6-phenylpyrimidin-4(3*H*)-one (3aq)



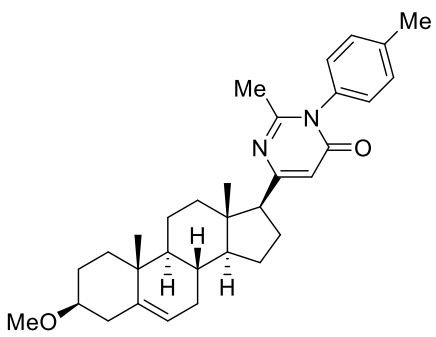
Following typical procedure, **3aq** was obtained as a white solid (43.2 mg, 0.161 mmol, 54%). mp: 135.6 – 136.8 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.96 – 7.90 (m, 2H), 7.45 – 7.40 (m, 3H), 6.67 (s, 1H), 3.96 (s, 1H), 2.75 (brs, 2H), 2.65 (s, 3H), 2.00 – 1.85 (m, 2H), 1.75 – 1.68 (m, 3H), 1.40 – 1.28 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 163.77, 158.70, 158.46, 136.27, 130.14 × 2, 128.58 × 2, 126.71 × 2, 28.13, 26.40 × 4, 24.94, 24.28. HRMS (ESI): m/z calculated for $C_{17}H_{21}N_2O$ $[M + H]^+$: 269.1654, found: 269.1654.

3,3'-(1,4-Phenylene)bis(2-methyl-6-phenylpyrimidin-4(3*H*)-one) (3ar)



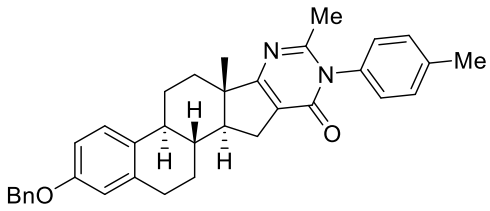
Following the procedure of 2.4, **3ar** was obtained as a white solid (120.0 mg, 0.269 mmol, 90%). mp: 182.8 – 183.0 ℃. ^{1}HNMR (400 MHz, Chloroform-*d*): δ 8.08 – 7.99 (m, 4H), 7.54 – 7.46 (m, 10H), 6.90 (s, 2H), 2.39 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 163.02 ×2, 160.52 ×2, 158.60 ×2, 138.20 ×2, 136.09 ×2, 130.78 ×2, 129.52 ×4, 128.82 ×4, 127.06 ×4, 107.46 ×2, 24.58 ×2. HRMS (ESI): m/z calculated for $C_{28}H_{23}N_4O_2$ $[M + H]^+$: 447.1821, found: 447.1833.

6-((3*S*,8S,9*S*,10*R*,13*S*,14*S*,17*S*)-3-Methoxy-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15, 16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)-2-methyl-3-(*p*-tolyl) pyrimidin-4(3*H*)-one (5)



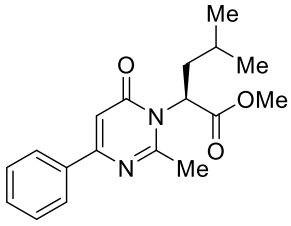
Following typical procedure, **5** was obtained as a white solid (127.9 mg, 0.263 mmol, 88%). mp: 246.6 – 247.0 ℃. $[\alpha]_D^{20}$: -30.25 (*c* = 0.40, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.35 – 7.31 (m, 2H), 7.11-7.09 (m, 2H), 6.32 (s, 2H), 5.43 – 5.32 (m, 1H), 3.36 (s, 3H), 3.11 – 3.03 (m, 1H), 2.56 (t, *J* = 9.4 Hz, 1H), 2.42 (s, 3H), 2.40 – 2.38 (m, 1H), 2.22 – 2.16 (m, 2H), 2.15 (s, 3H), 2.07 – 1.94 (m, 2H), 1.93 – 1.85 (m, 2H), 1.83 – 1.75 (m, 2H), 1.65 – 1.60 (m, 2H), 1.53 – 1.51 (m, 1H), 1.46 – 1.39 (m, 2H), 1.39 – 1.31 (m, 2H), 1.28 – 1.21 (m, 1H), 1.09 – 1.03 (m, 1H), 1.01 (s, 3H), 0.62 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 166.38, 162.91, 157.16, 140.73, 139.14, 134.63 ×2, 130.51, 126.96, 121.22, 110.48, 80.08, 56.94, 56.59, 55.45, 50.06, 44.87, 38.49, 38.01, 36.99, 36.77, 31.97, 31.73, 27.79, 24.43, 24.36, 23.97, 21.10, 20.65, 19.77, 19.25, 12.85. HRMS (ESI): m/z calculated for $C_{32}H_{43}N_2O_2$ $[M + H]^+$: 487.3325, found: 487.3322.

(6b*S*,8a*S*,13a*S*,13b*R*)-4-(Benzyloxy)-8a,10-dimethyl-11-(*p*-tolyl)-6b,7,8,8a,11,13,13a,13b-octahydro-1*H*-naphtho[2',1':4,5]indeno[1,2-*d*]pyrimidin-12(2*H*)-one (7)



Following typical procedure, **7** was obtained as a white solid (91.3 mg, 0.177 mmol, 59%). mp: 243.0 – 244.1 ℃. $[\alpha]_D^{20}$: +63.17 (*c* = 0.40, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.51 – 7.30 (m, 8H), 7.14 (dd, *J* = 8.2, 2.3 Hz, 1H), 7.07 (dd, *J* = 8.2, 2.4 Hz, 1H), 6.83 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.78 (d, *J* = 2.8 Hz, 1H), 5.06 (s, 2H), 3.05 – 2.91 (m, 2H), 2.85 (dd, *J* = 15.0, 6.4 Hz, 1H), 2.45 (s, 3H), 2.44 – 2.36 (m, 2H), 2.34 – 2.25 (m, 1H), 2.23 (s, 3H), 2.09 – 1.99 (m, 2H), 1.86 (dd, *J* = 11.5, 6.4 Hz, 1H), 1.81 – 1.68 (m, 3H), 1.53 (td, *J* = 12.0, 6.6 Hz, 1H), 1.08 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 175.84, 161.32, 159.72, 156.67, 139.08, 137.78, 137.13, 135.18, 132.53, 130.53, 130.50, 128.41 ×2, 127.72, 127.33 ×2, 127.24, 126.88, 125.93, 120.91, 114.71, 112.18, 69.77, 54.40, 46.83, 44.26, 37.10, 32.87, 29.46, 27.23, 26.91, 26.02, 24.26, 21.13, 16.41. HRMS (ESI): m/z calculated for $C_{35}H_{37}N_2O_2$ $[M + H]^+$: 517.2855, found: 517.2856.

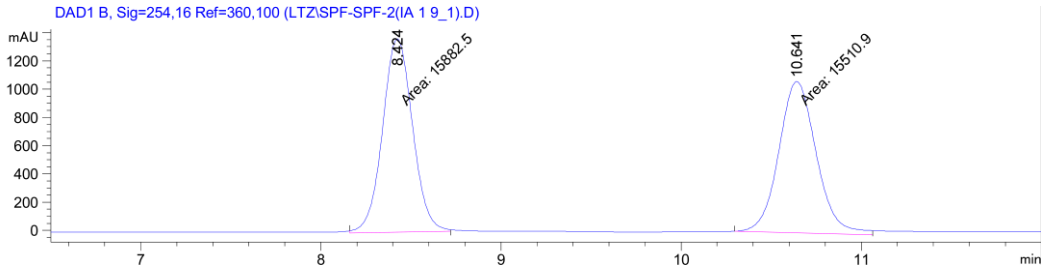
Methyl (*S*)-4-methyl-2-(2-methyl-6-oxo-4-phenylpyrimidin-1(6*H*)-yl)pentanoate (9)



Following typical procedure, **9** was obtained as a yellow liquid (55.6 mg, 0.177 mmol, 59%). $[\alpha]_D^{20}$: -59.17 (*c* = 0.20, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.01 – 7.91 (m, 2H), 7.46 (dt, *J* = 4.7, 1.7 Hz, 3H), 6.76 (s, 1H), 3.74 (s, 3H), 2.63 (s, 3H), 2.44 – 2.38 (m, 2H), 1.92 – 1.85 (m, 1H), 1.75 – 1.60 (m, 1H), 1.01 (d, *J* = 6.5 Hz, 3H), 0.95 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 169.70, 162.66, 159.74, 158.32, 136.03, 130.56, 128.70 × 2, 126.94 × 2, 107.42, 52.72, 38.44, 25.48, 23.67, 22.68, 22.54. HRMS (ESI): m/z calculated for $C_{18}H_{23}N_2O_3$ $[M + H]^+$: 315.1709, found: 315.1693.

HPLC (Chiralcel IA): Hexane/isopropanol = 90:10, 1.0 mL/minute, λ = 254 nm, t^1 = 8.424 min, t^2 = 10.641 min, ee >99%.

HPLC spectrum of racemic and enantio-enriched 9



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Area Percent Report

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Sorted By : Signal

Multiplier : 1.0000

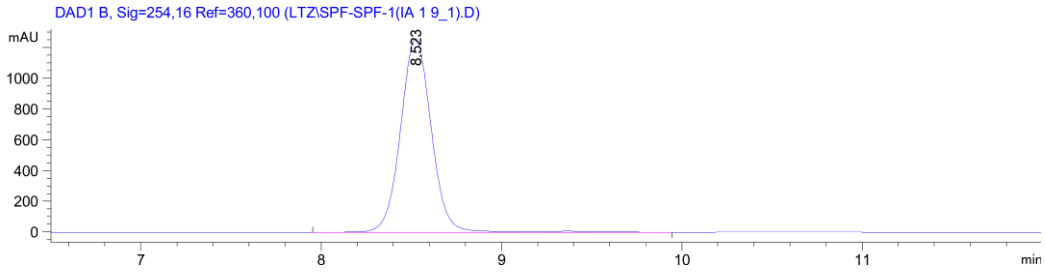
Dilution : 1.0000

Sample Amount : 1.00000 [ng/ul] (not used in calc.)

Use Multiplier & Dilution Factor with ISTDs

Signal 2: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.424	MM	0.1931	1.58825e4	1370.90820	50.5919
2	10.641	MM	0.2412	1.55109e4	1071.85547	49.4081
Totals :				3.13934e4	2442.76367	



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Area Percent Report

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Sorted By : Signal

Multiplier : 1.0000

Dilution : 1.0000

Sample Amount : 1.00000 [ng/ul] (not used in calc.)

Use Multiplier & Dilution Factor with ISTDs

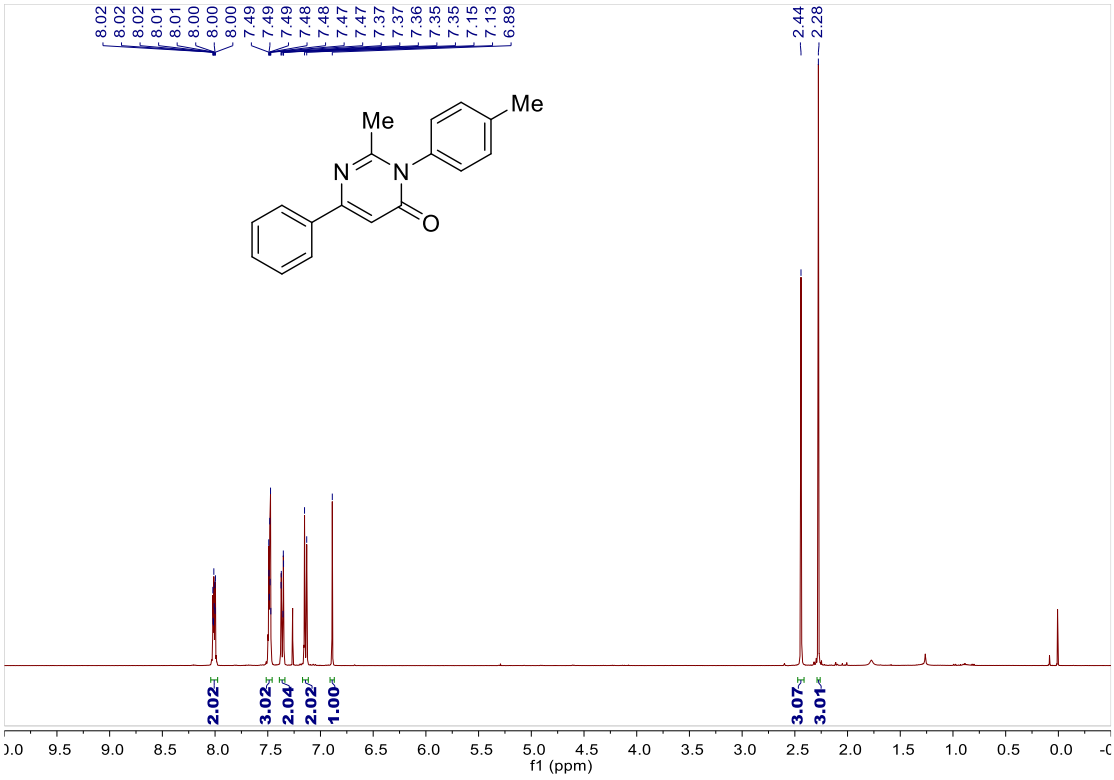
Signal 2: DAD1 B, Sig=254,16 Ref=360,100

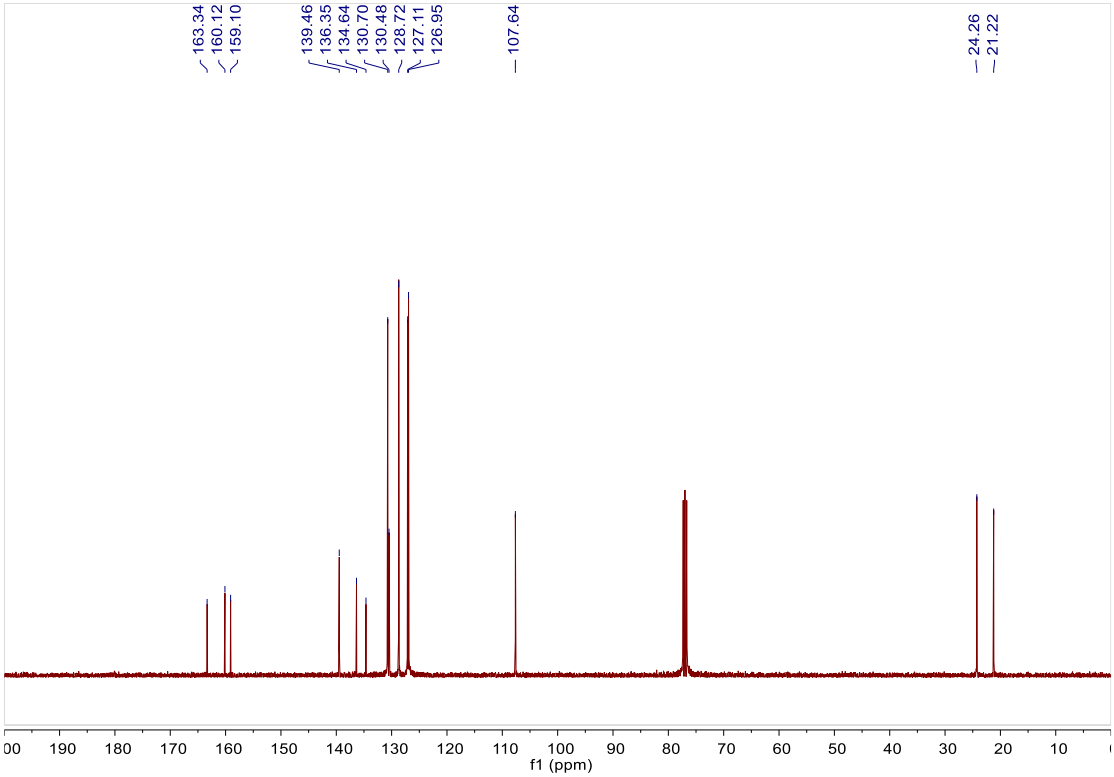
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.523	BV R	0.1819	1.50255e4	1257.95593	100.0000
Totals :				1.50255e4	1257.95593	

3. References

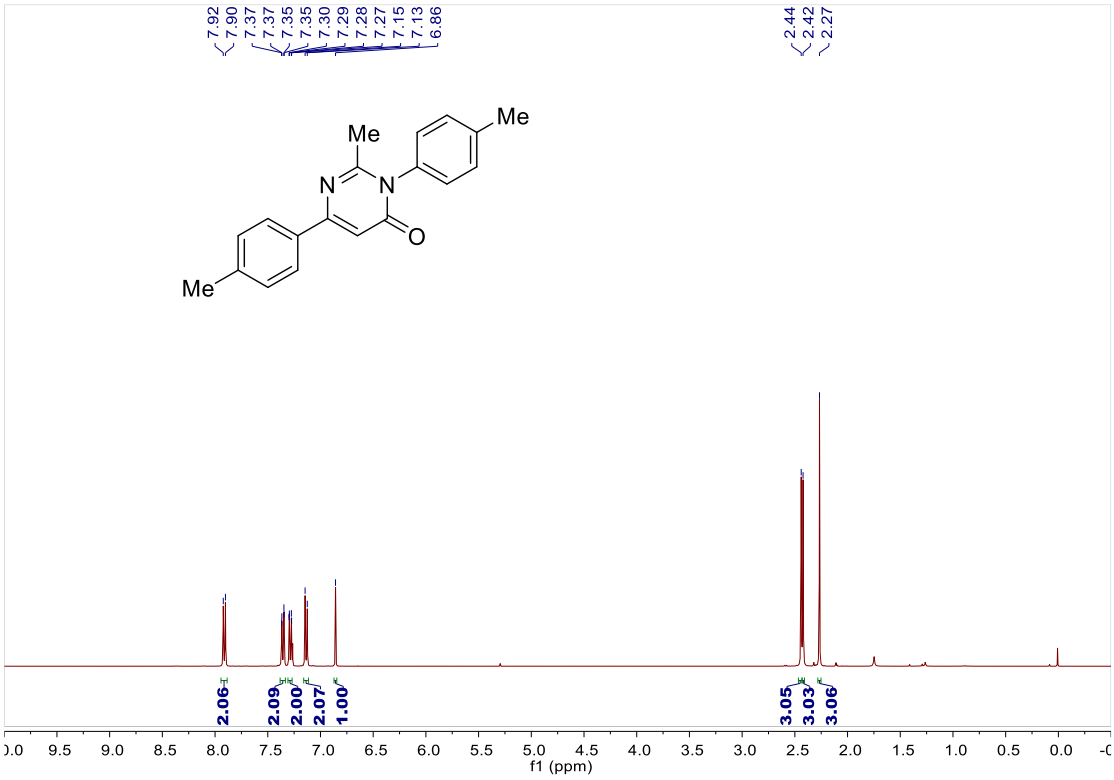
1. M.-N. Zhao, L. Yu, R.-R. Hui, Z.-H. Ren, Y.-Y. Wang and Z.-H. Guan, *ACS Catal*., 2016, **6**, 3473−3477.
2. Z.-H. Guan, Z.-Y. Zhang, Z.-H. Ren, Y.-Y. Wang and X. Zhang, *J. Org. Chem*., 2011, **76**, 339–341.
3. C. Simons, U. Hanefeld, I. W. C. E. Arends, R. A. Sheldon and T. Maschmeyer, *Chem. – Eur. J.*, 2004, **10**, 2829–2835.
4. J. T. Reeves, Z. Tan, Z. S. Han, G. Li, Y. Zhang, Y. Xu, D. C. Reeves, N. C. Gonnella, S. Ma, H. Lee, B. Z. Lu and C. H. Senanayake, *Angew. Chem., Int. Ed.*, 2012, **51**, 1400–1404.
5. W. Yu, J. Chen, K. Gao, Z. Liu and Y. Zhang, *Org. Lett.*, 2014, **16**, 4870–4873.

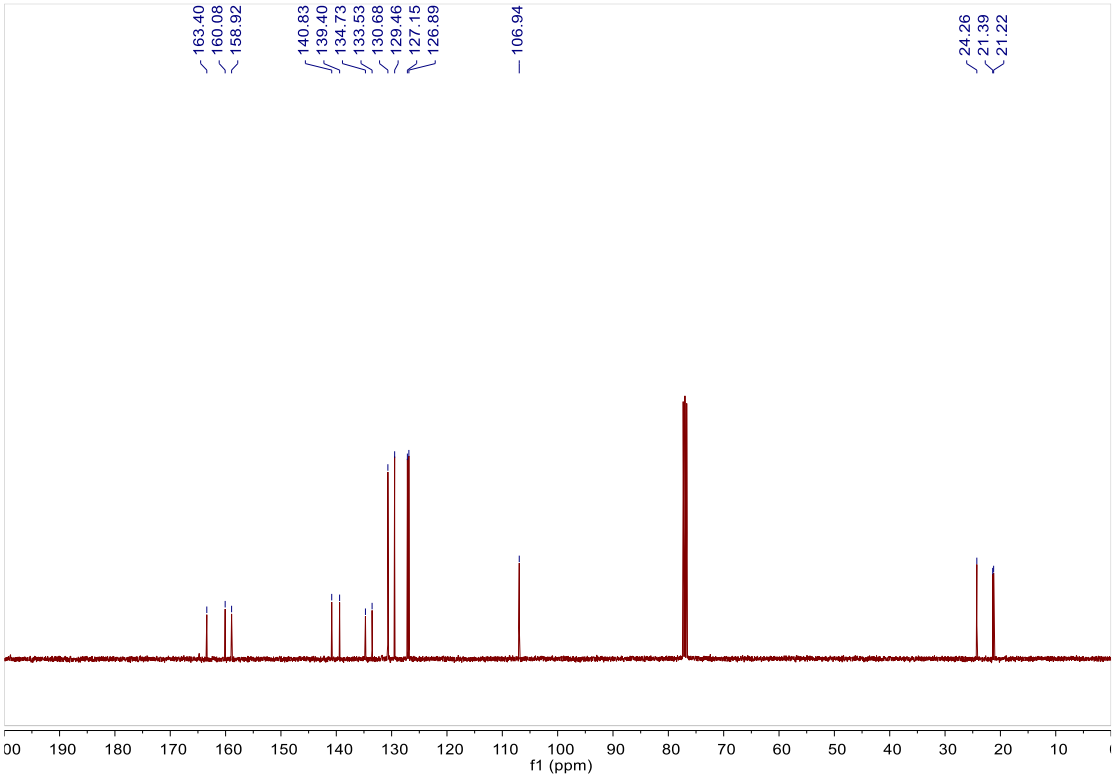
4. NMR spectra of the products



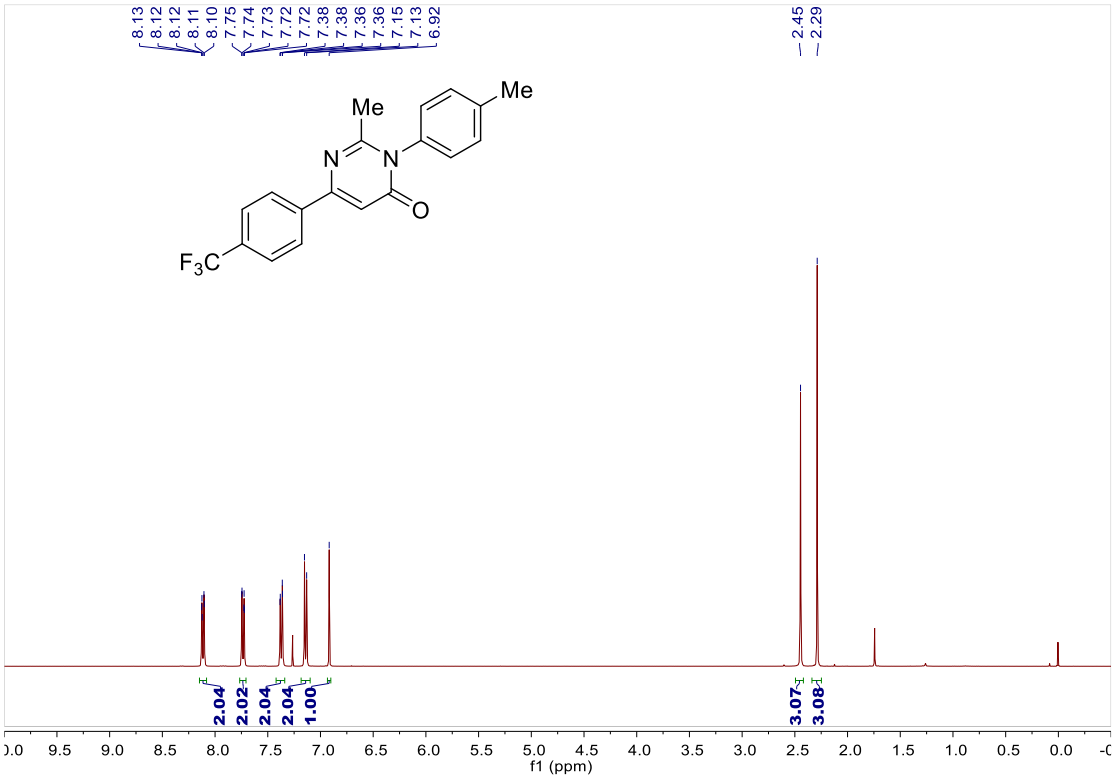


^{1}H and ^{13}C NMR spectra for product 3aa ($CDCl_3$)





^{1}H and ^{13}C NMR spectra for product 3ba ($CDCl_3$)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8.12
8.12
8.11
8.10
7.75
7.74
7.73
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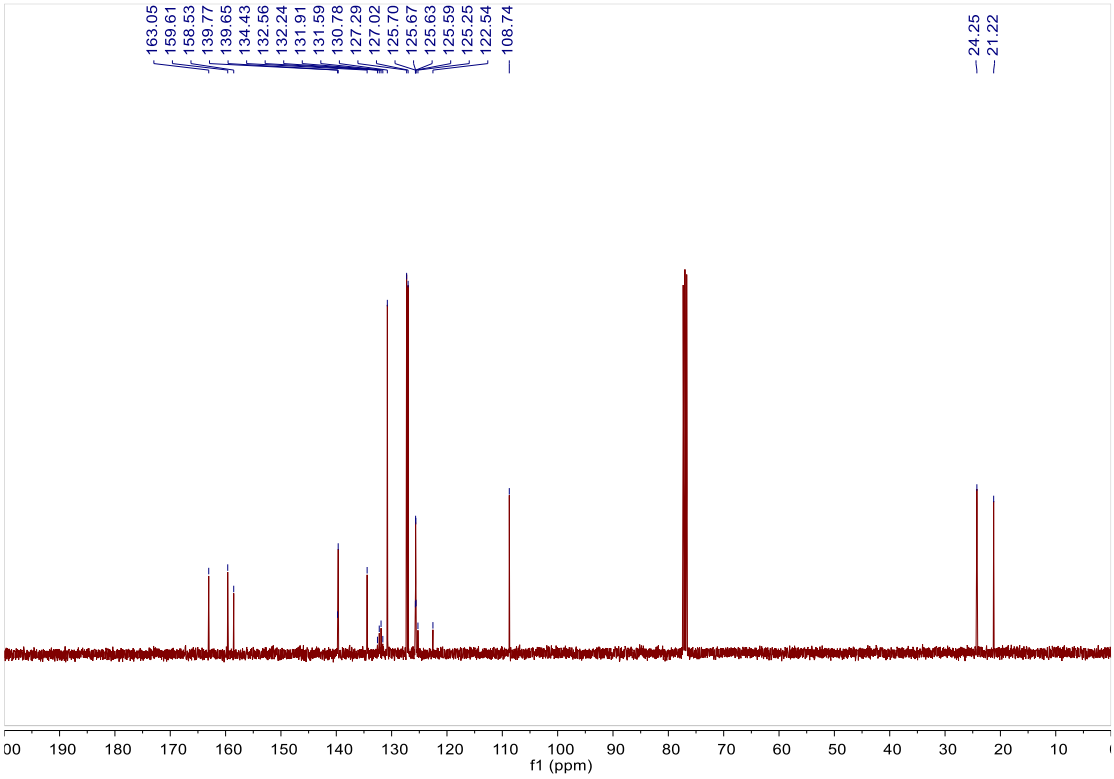
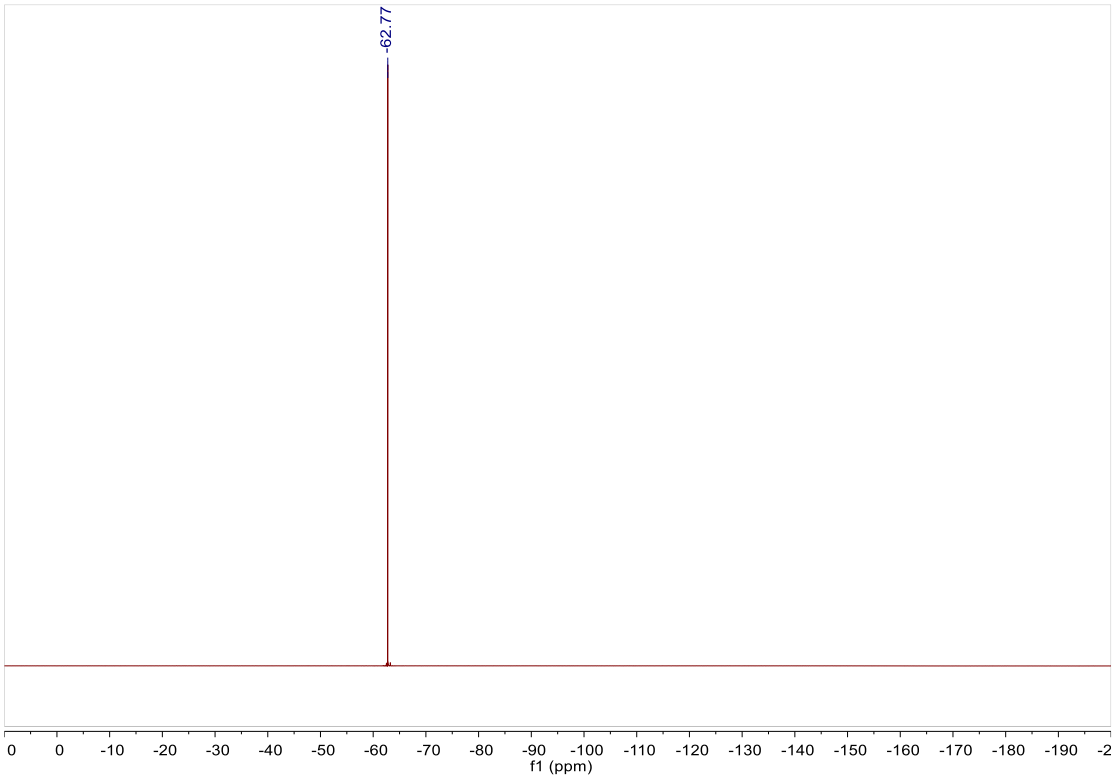
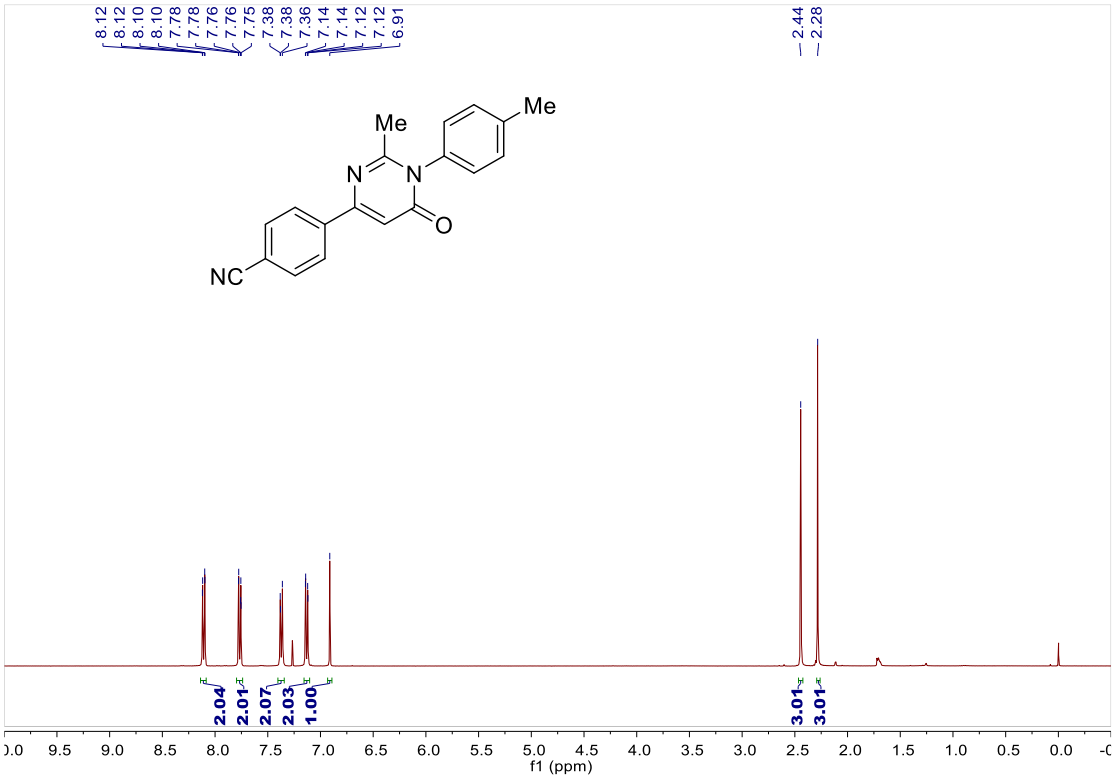
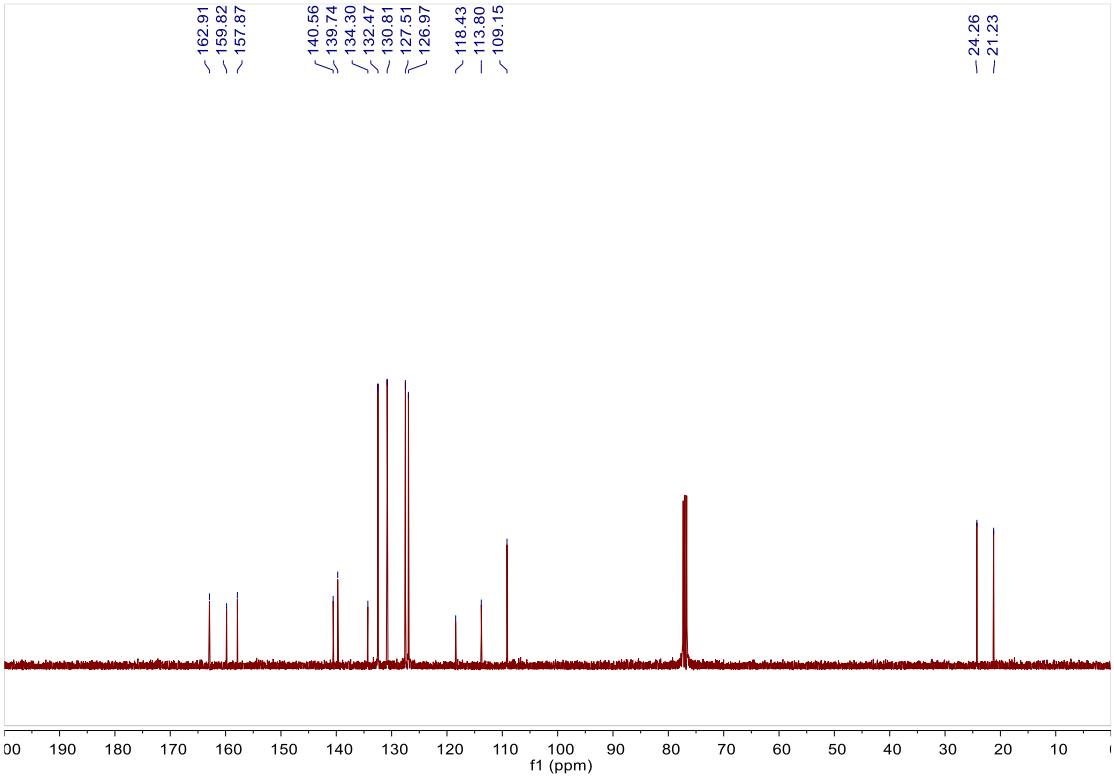
7.72
7.38
7.38
7.36
7.36
7.15
7.13
6.92
2.45
2.29
Me
Me
N
N
O
F3C
2.04
2.02
2.04
2.04
1.00
3.07
3.08
f1 (ppm)


163.05
159.61
158.53
139.77
139.65
134.43
132.56
132.24
131.91
131.59
130.78
127.29
127.02
125.70
125.67
125.63
125.59
125.25
122.54
108.74
24.25
21.22
f1 (ppm)

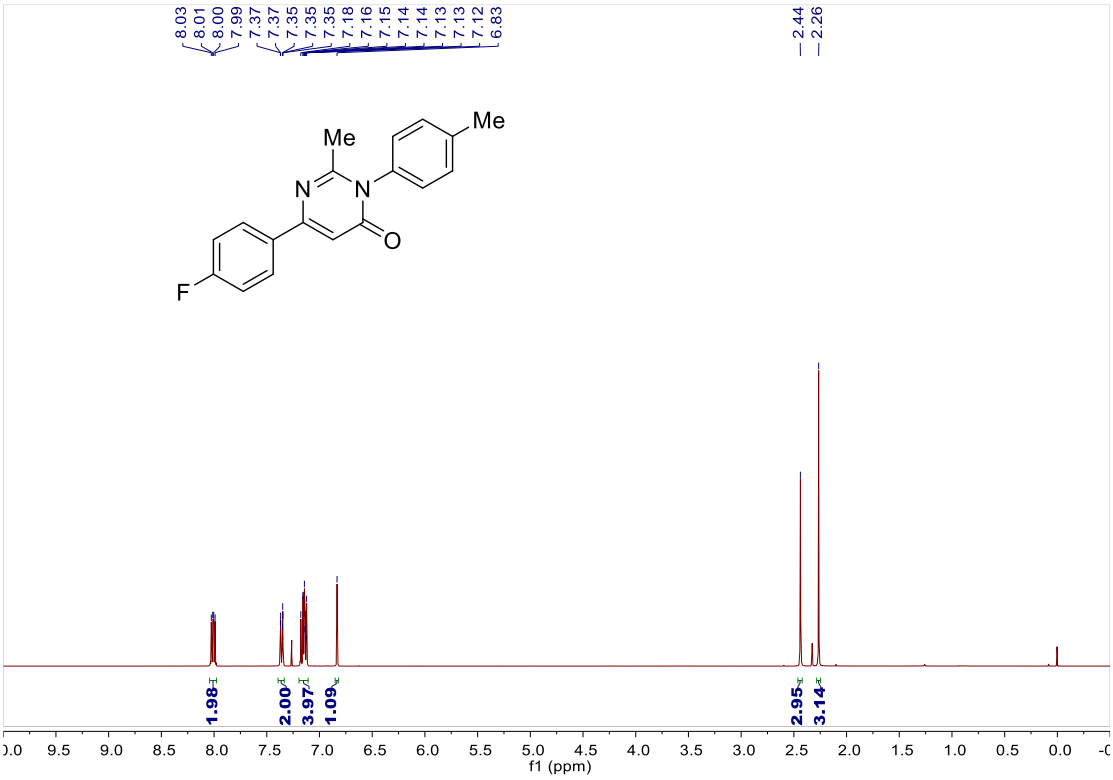


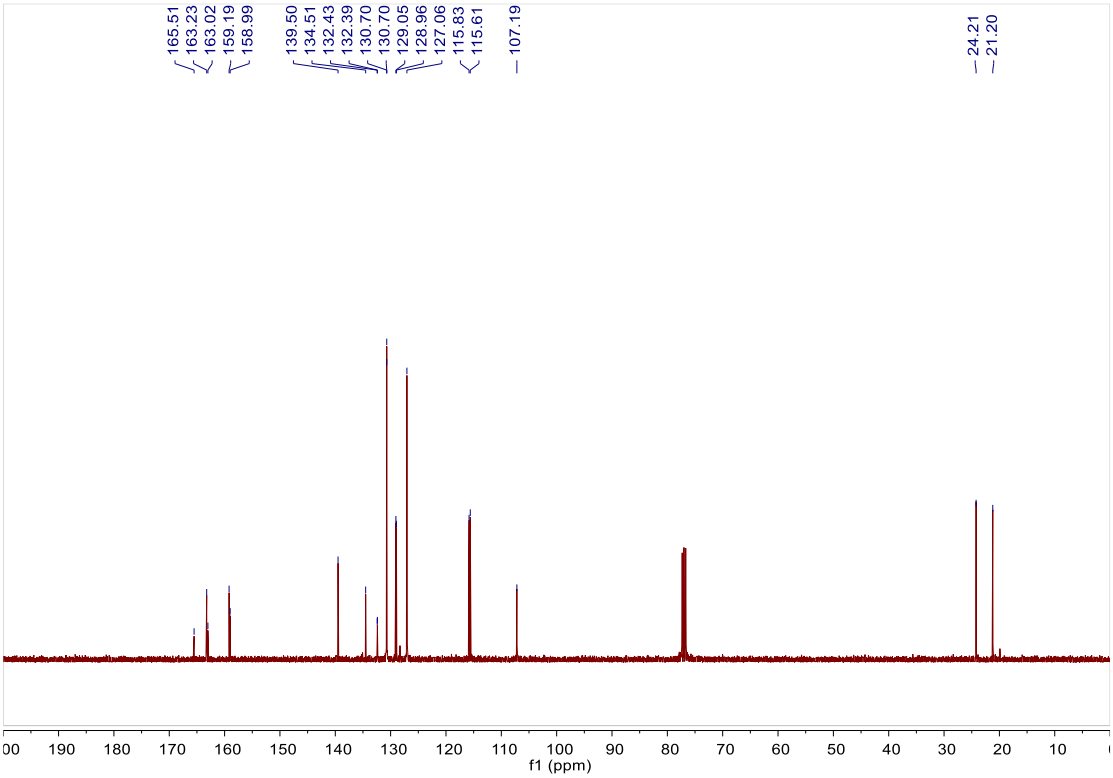
^{1}H, ^{13}C, and ^{19}F NMR spectra for product 3ca ($CDCl_3$)





^{1}H and ^{13}C NMR spectra for product 3da ($CDCl_3$)


8.03
8.01
8.00
7.99
7.37
7.37
7.35
7.35
7.35
7.18
7.16
7.15
7.14
7.14
7.13
7.13
7.12
6.83
2.44
2.26
Me
Me
N
N
O
F
1.98
2.00
3.97
1.09
2.95
3.14
f1 (ppm)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132.43
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130.70
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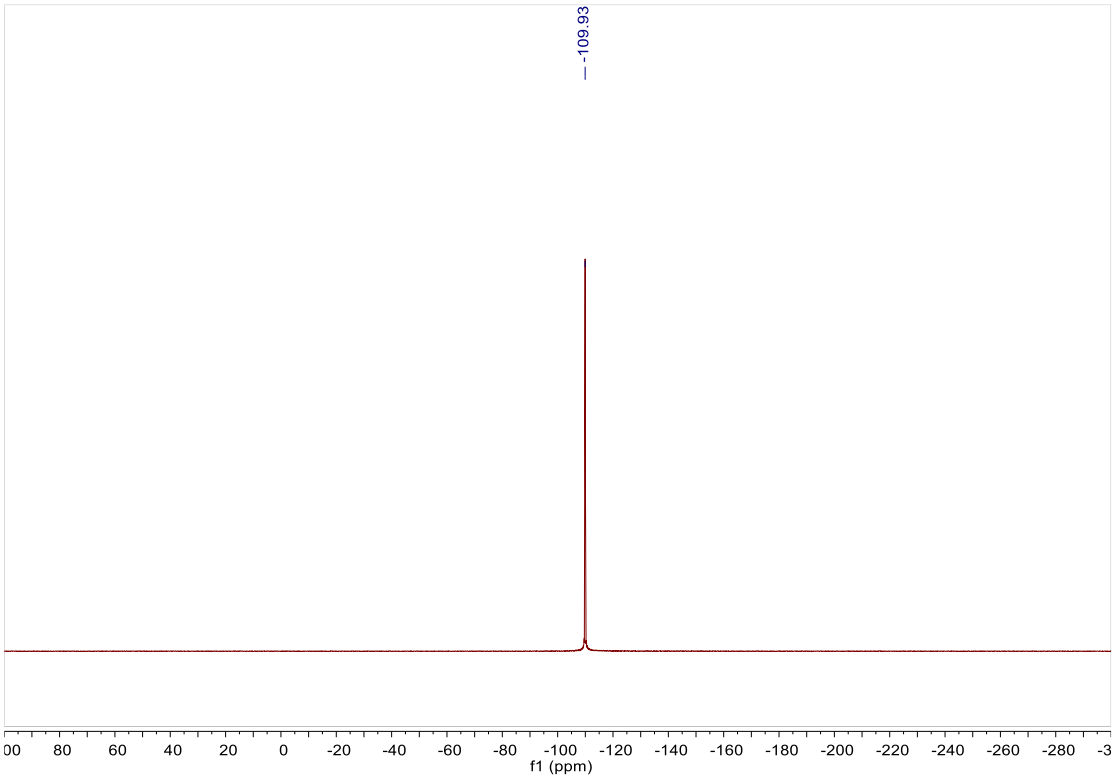
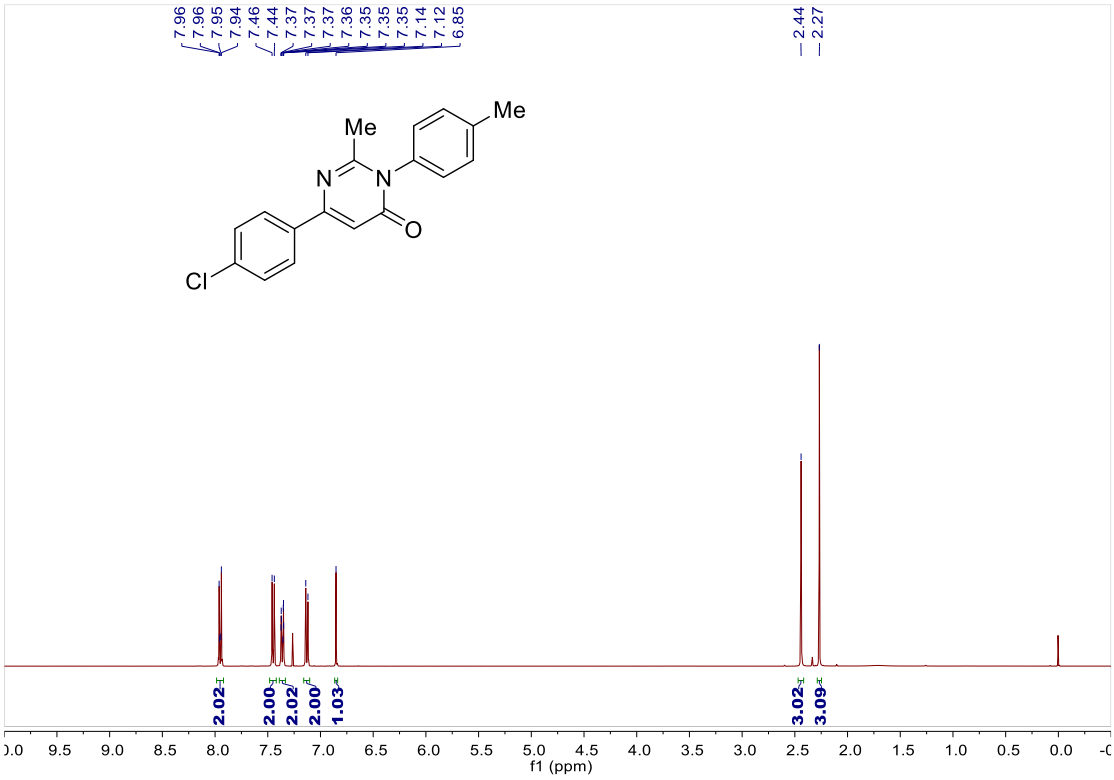
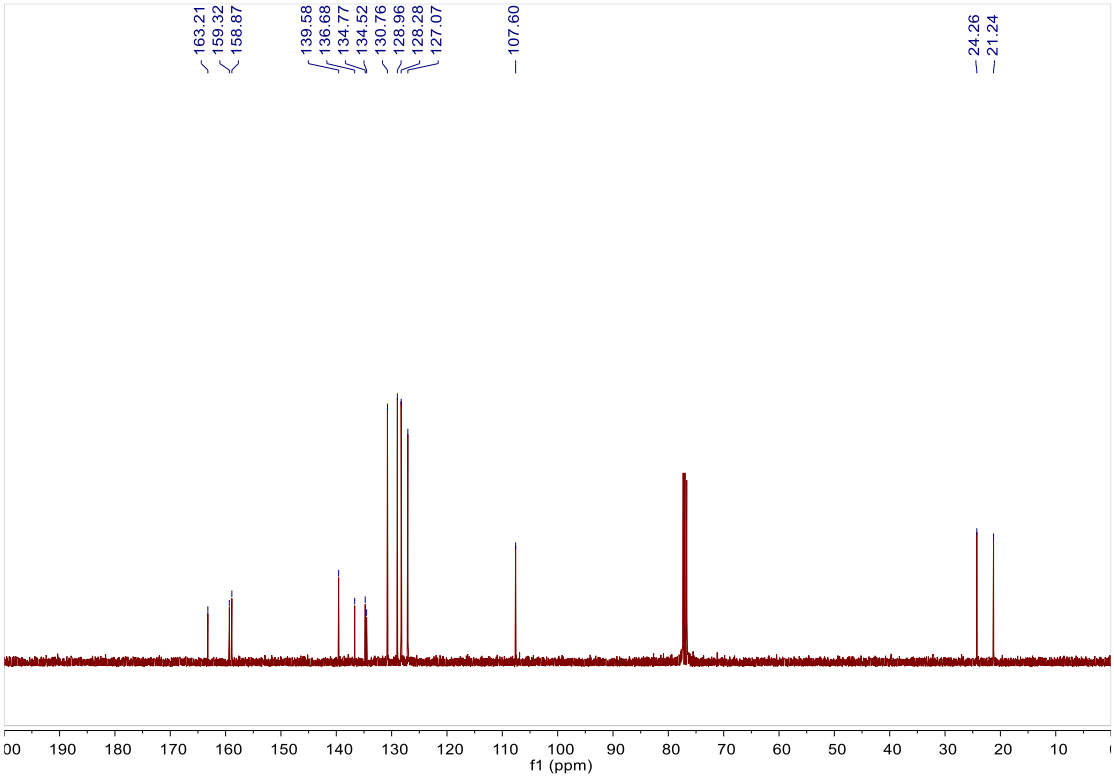
129.05
128.96
127.06
115.83
115.61
107.19
24.21
21.20
f1 (ppm)

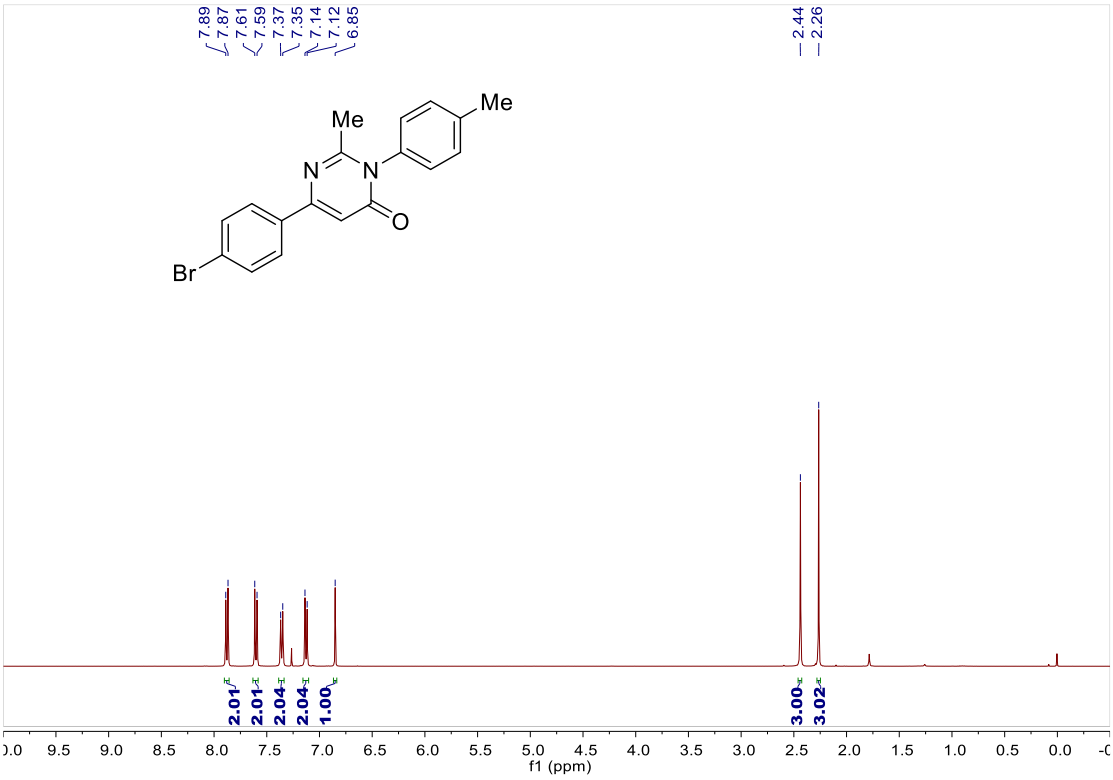


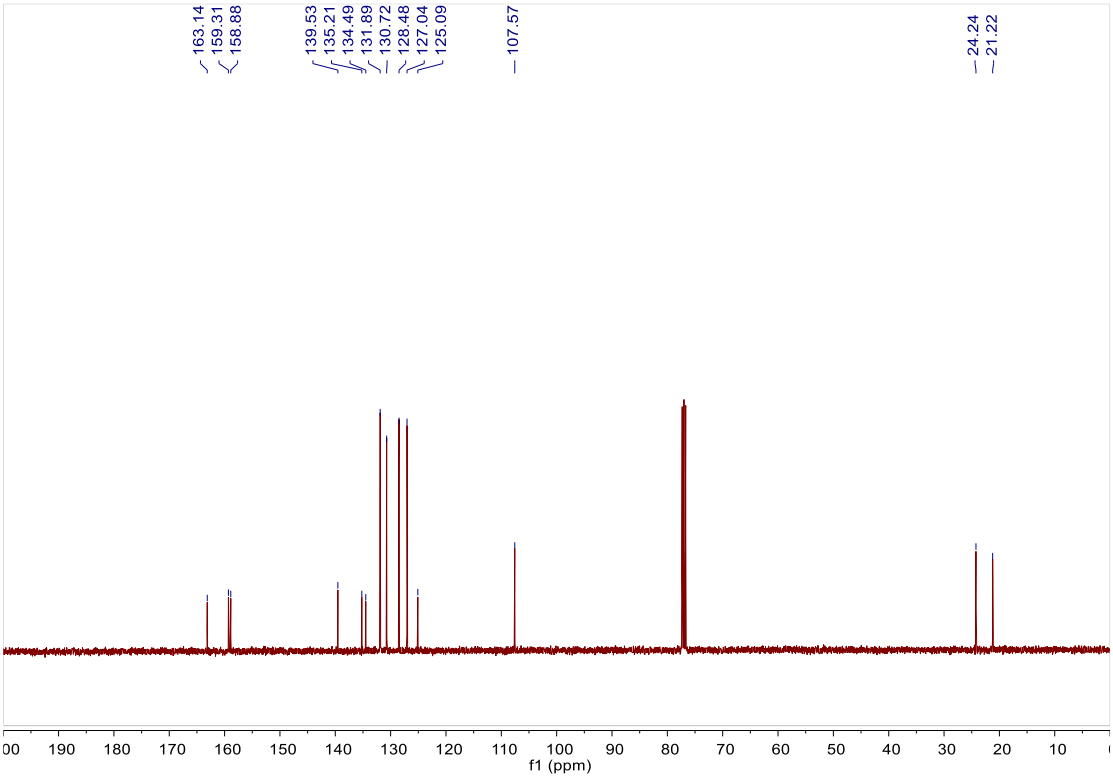
^{1}H, ^{13}C and ^{19}F NMR spectra for product 3ea ($CDCl_3$)



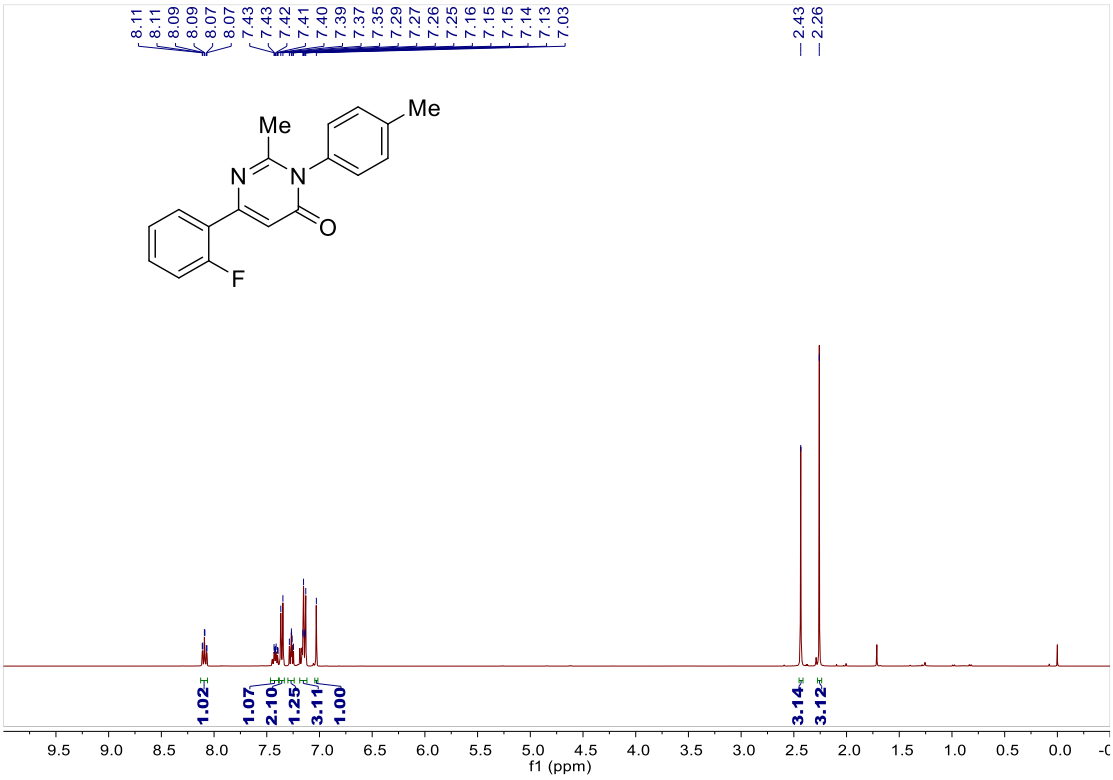


^{1}H and ^{13}C NMR spectra for product 3fa ($CDCl_3$)





^{1}H and ^{13}C NMR spectra for product 3ga ($CDCl_3$)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8.09
8.07
8.07
7.43
7.43
7.42
7.41
7.40
7.39
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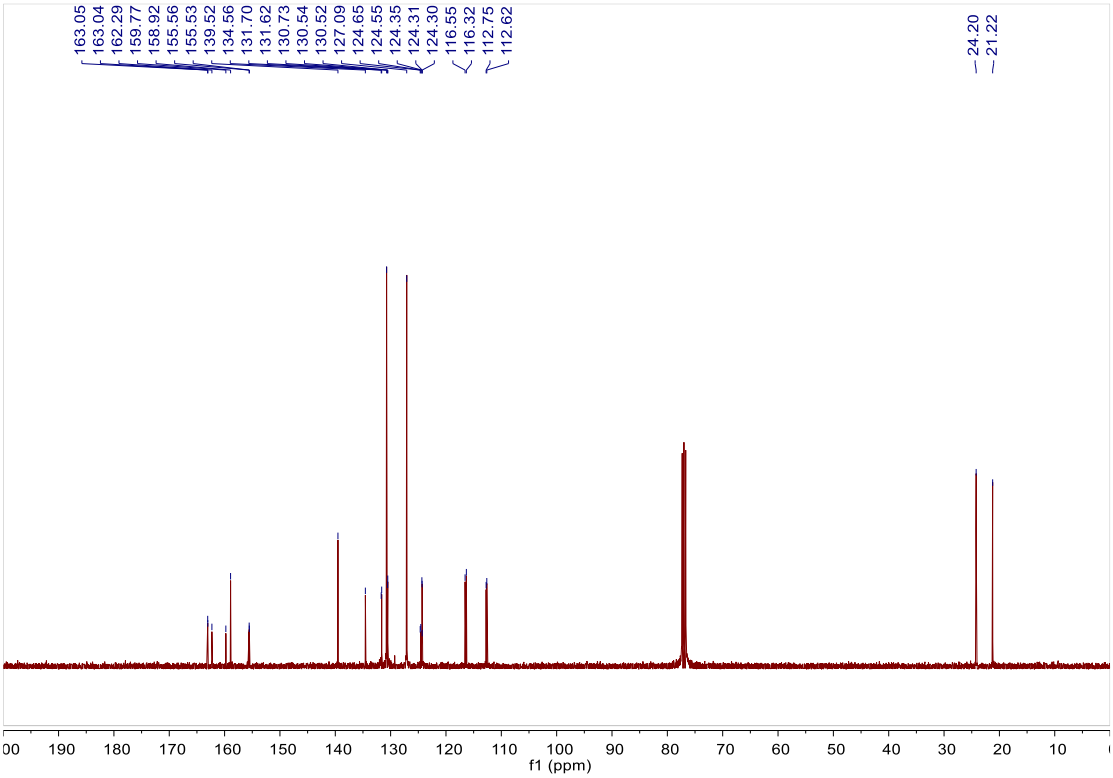
7.35
7.29
7.27
7.26
7.25
7.16
7.15
7.15
7.14
7.13
7.03
2.43
2.26
Me
Me
N
N
O
F
1.02
1.07
2.10
1.25
3.11
1.00
3.14
3.12
f1 (ppm)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130.54
130.52
127.09
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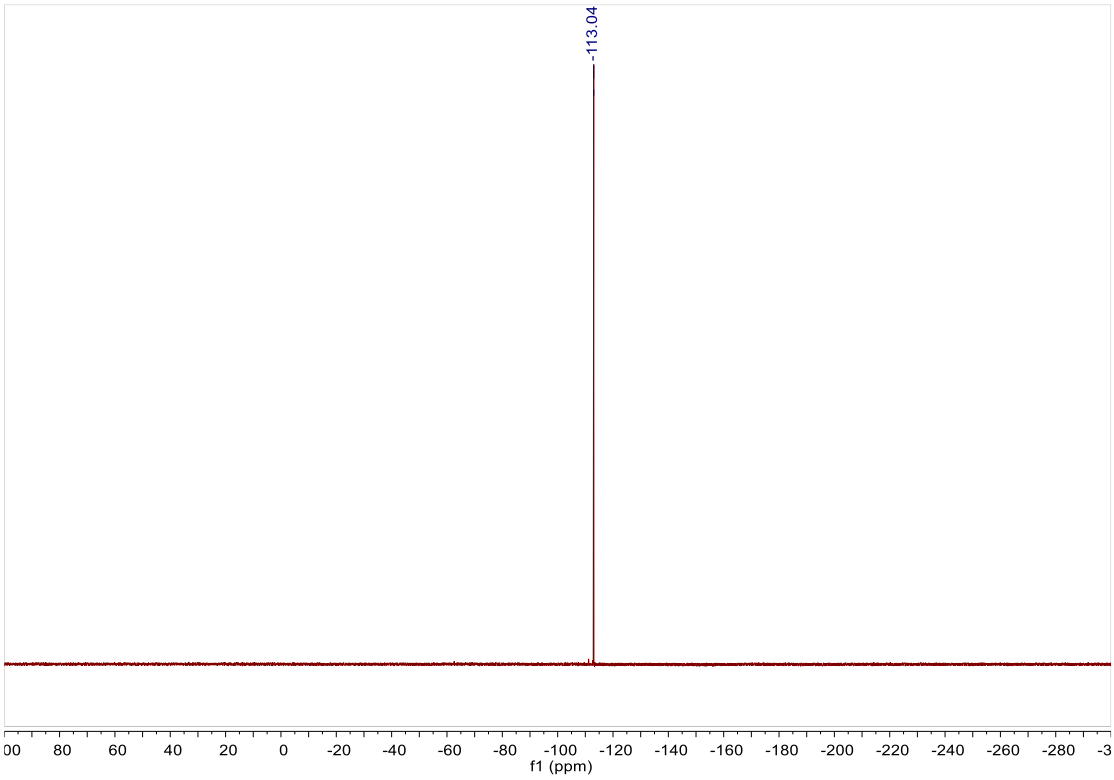
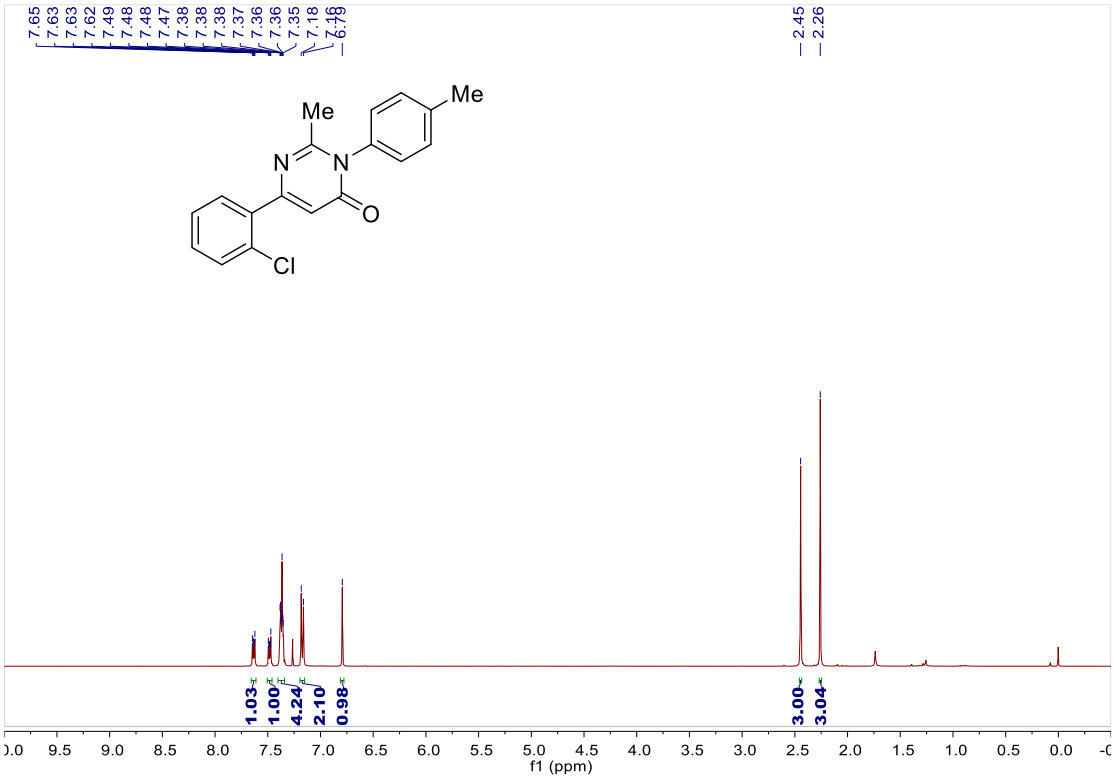
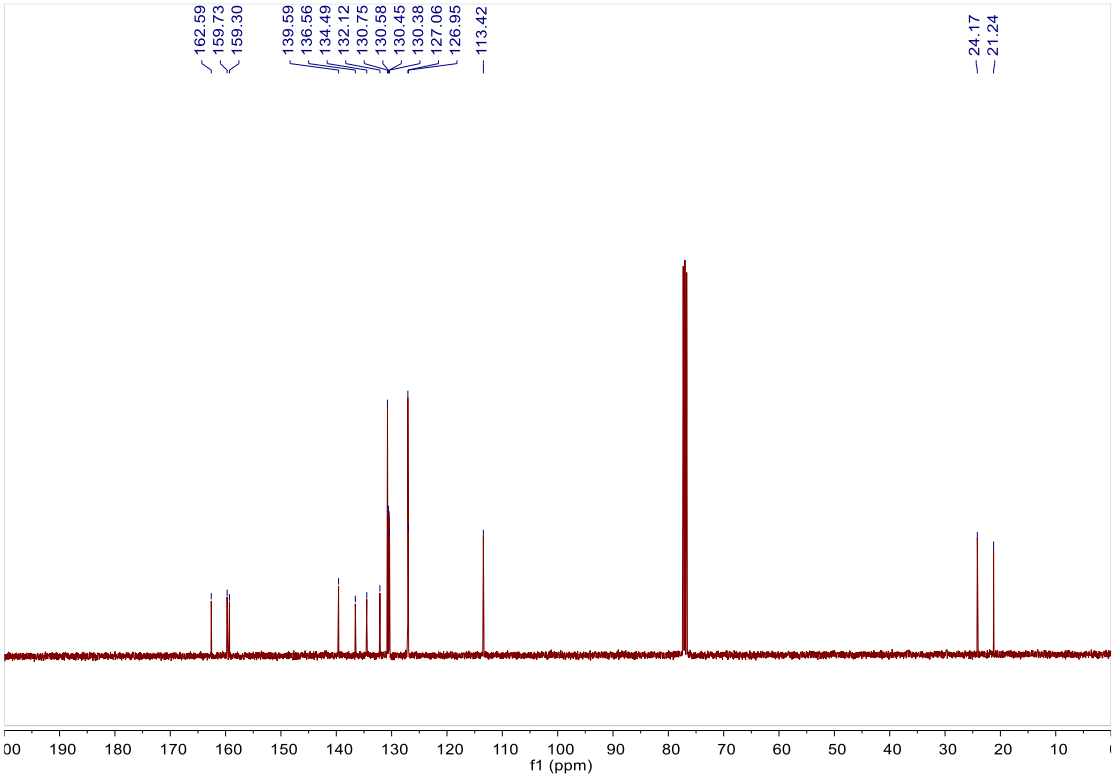
116.32
112.75
112.62
24.20
21.22
f1 (ppm)

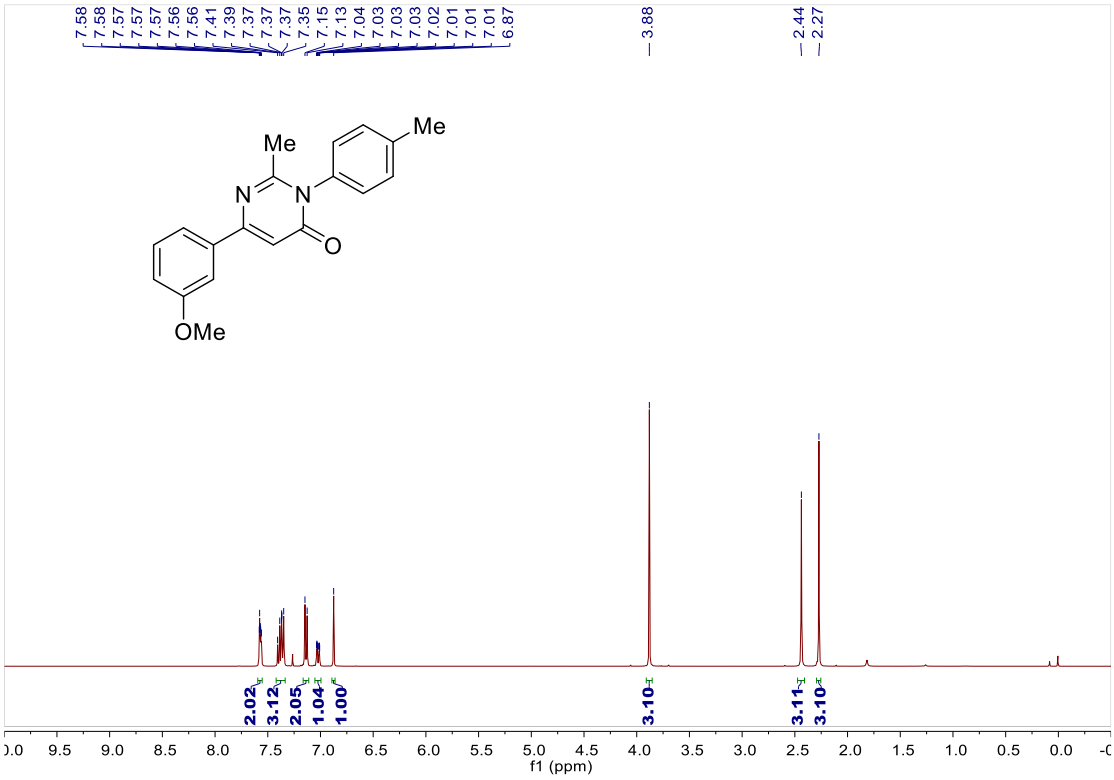


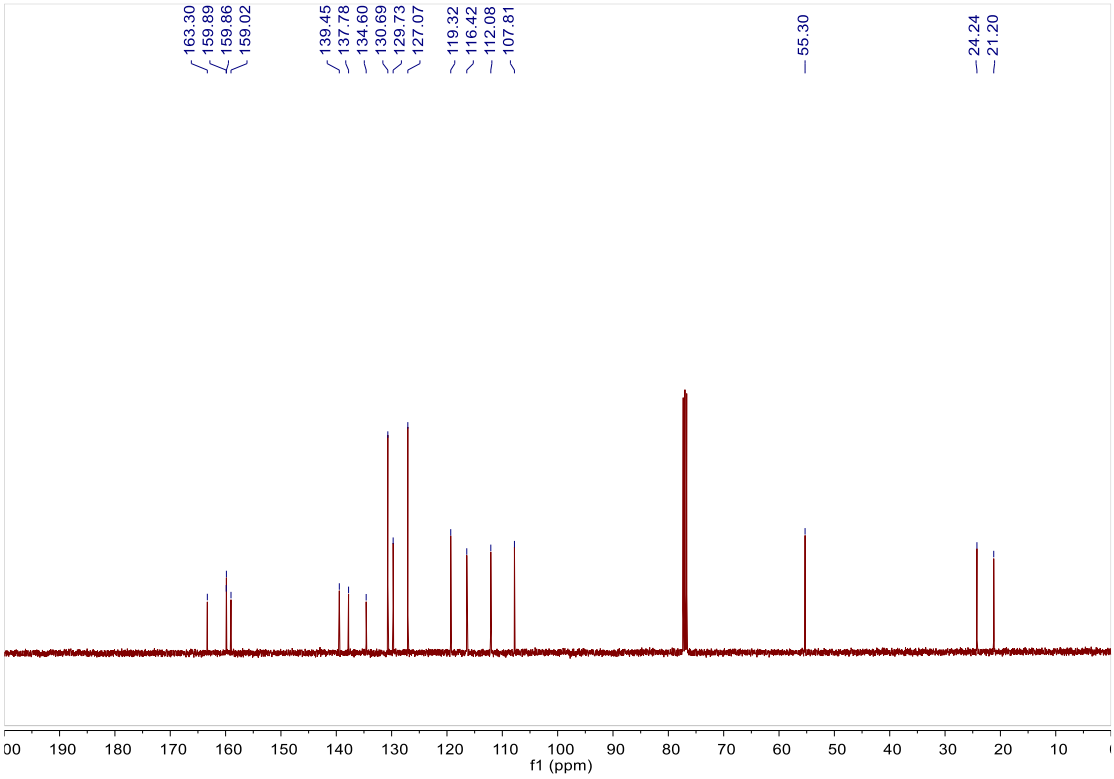
^{1}H, ^{13}C and ^{19}F NMR spectra for product 3ha ($CDCl_3$)



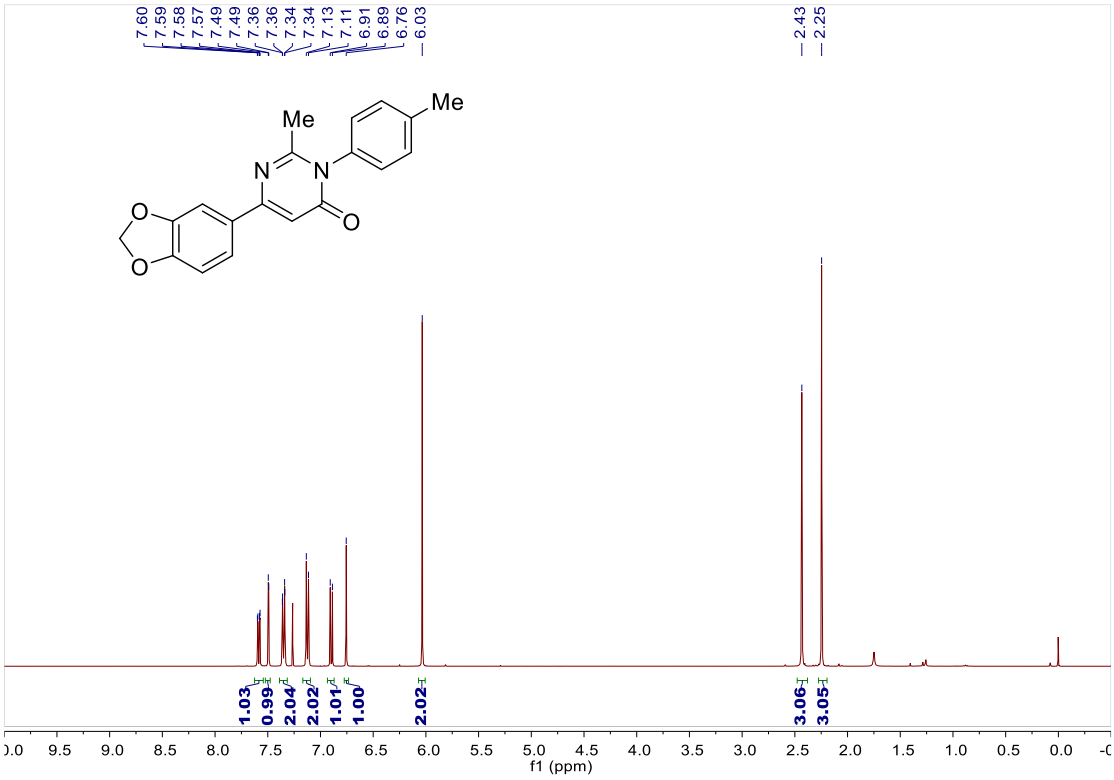


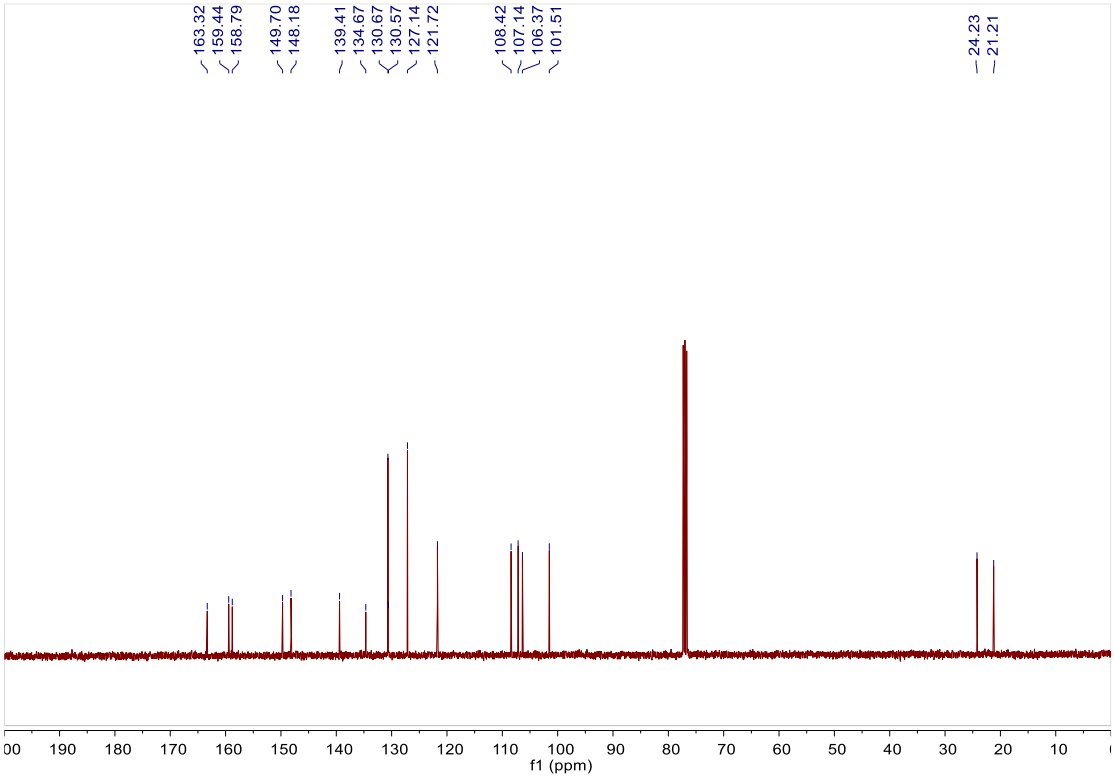
^{1}H and ^{13}C NMR spectra for product 3ia ($CDCl_3$)



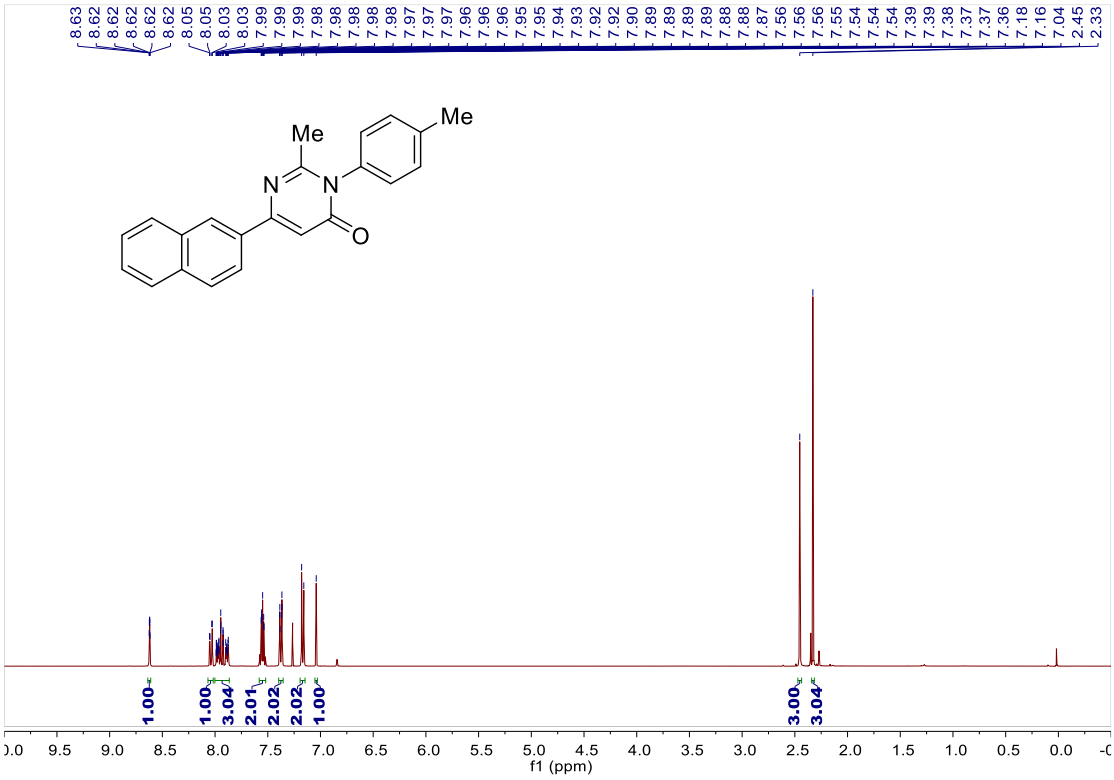


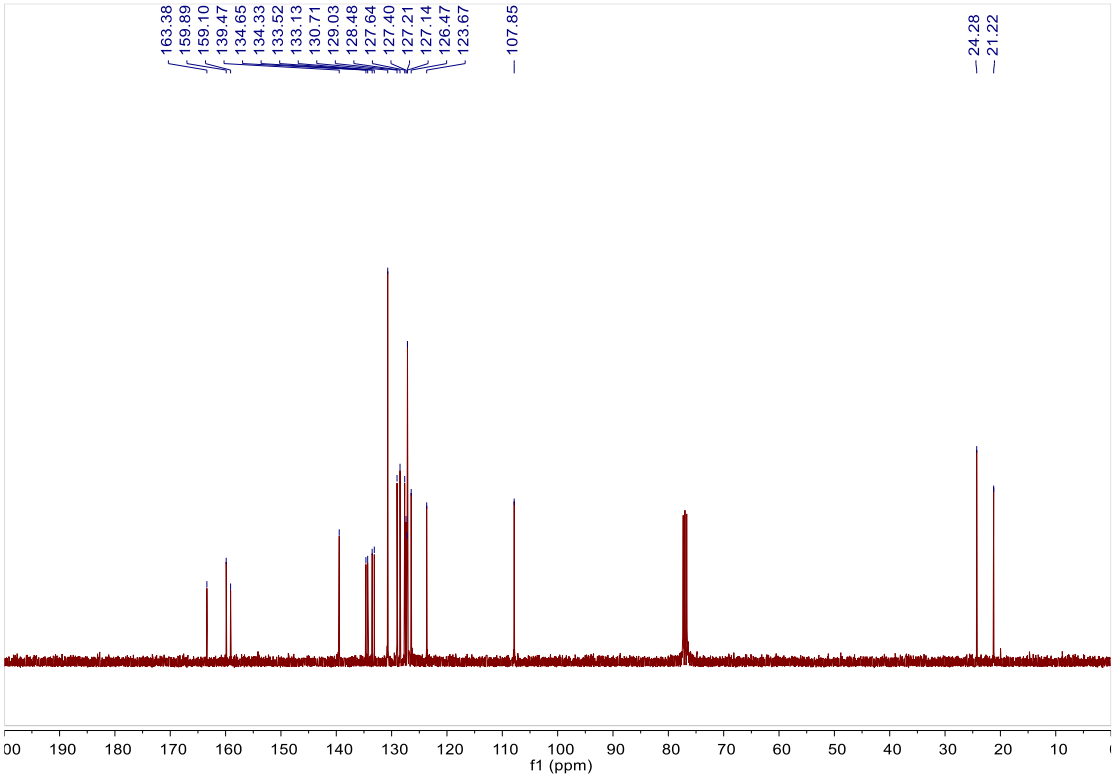
^{1}H and ^{13}C NMR spectra for product 3ja ($CDCl_3$)



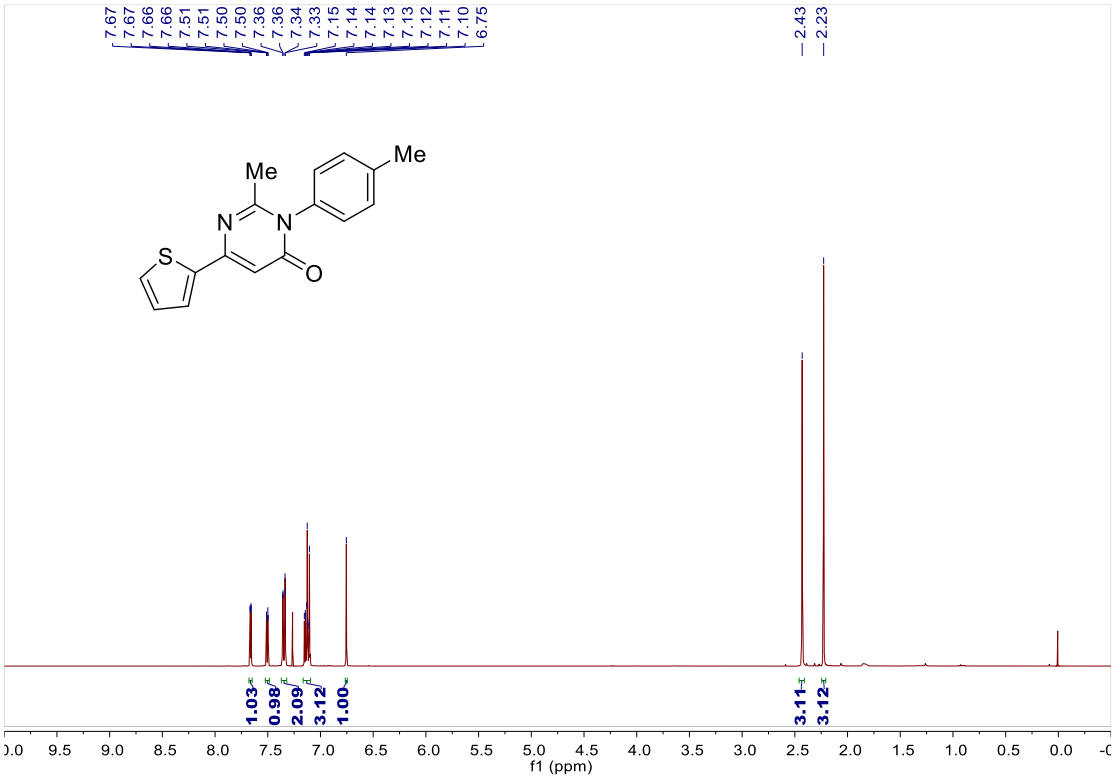


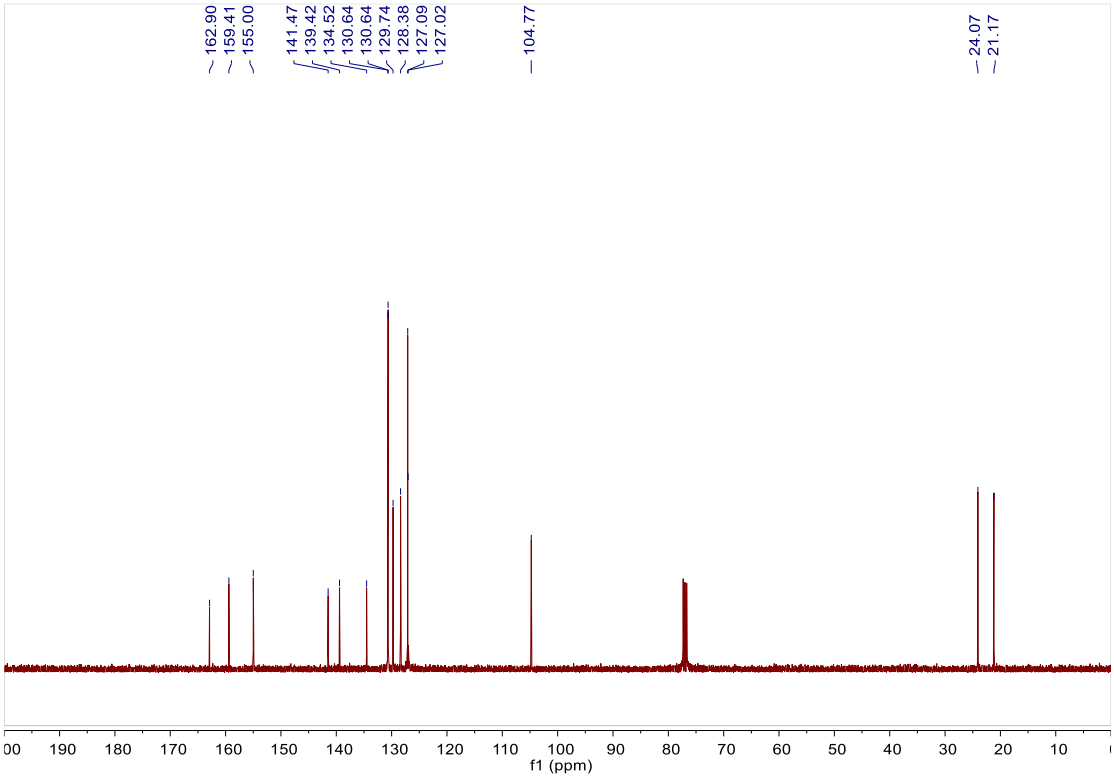
^{1}H and ^{13}C NMR spectra for product 3ka ($CDCl_3$)



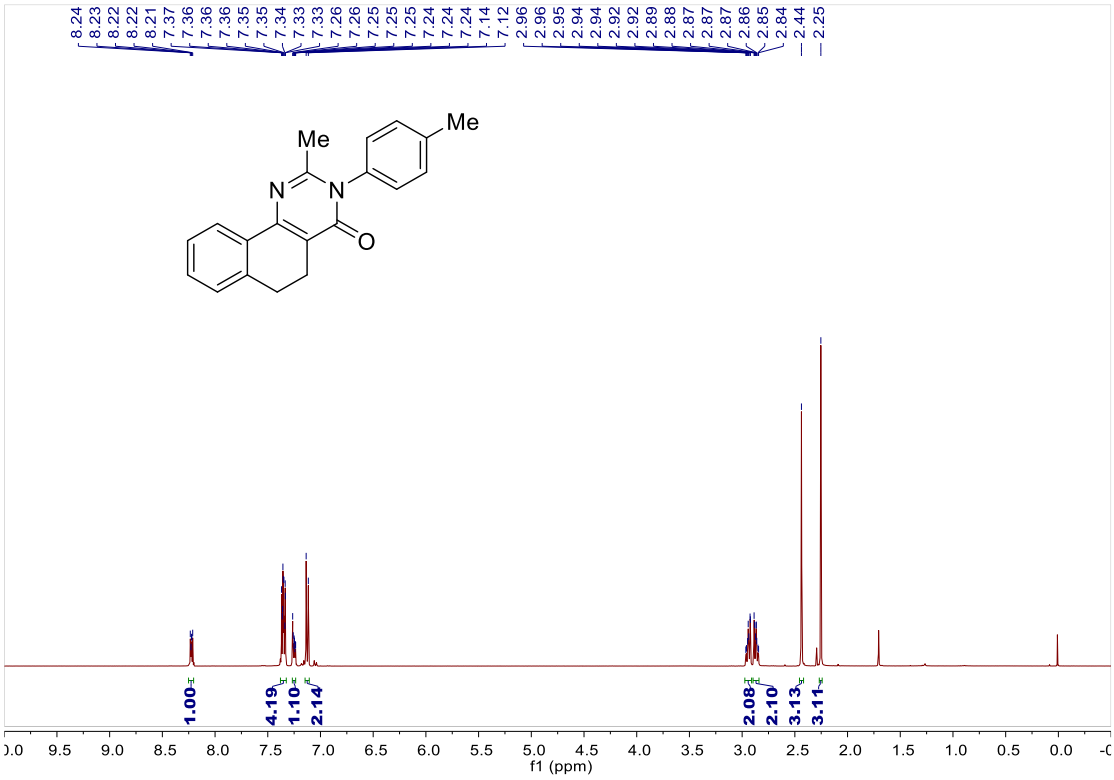


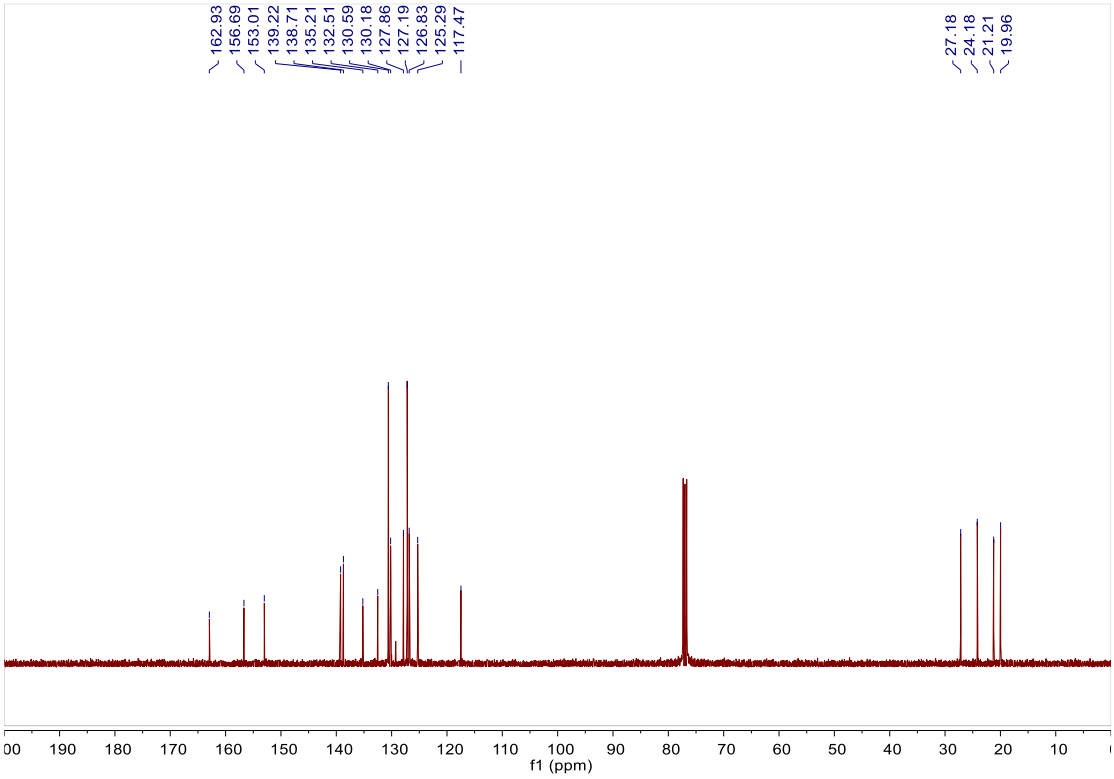
^{1}H and ^{13}C NMR spectra for product 3la ($CDCl_3$)



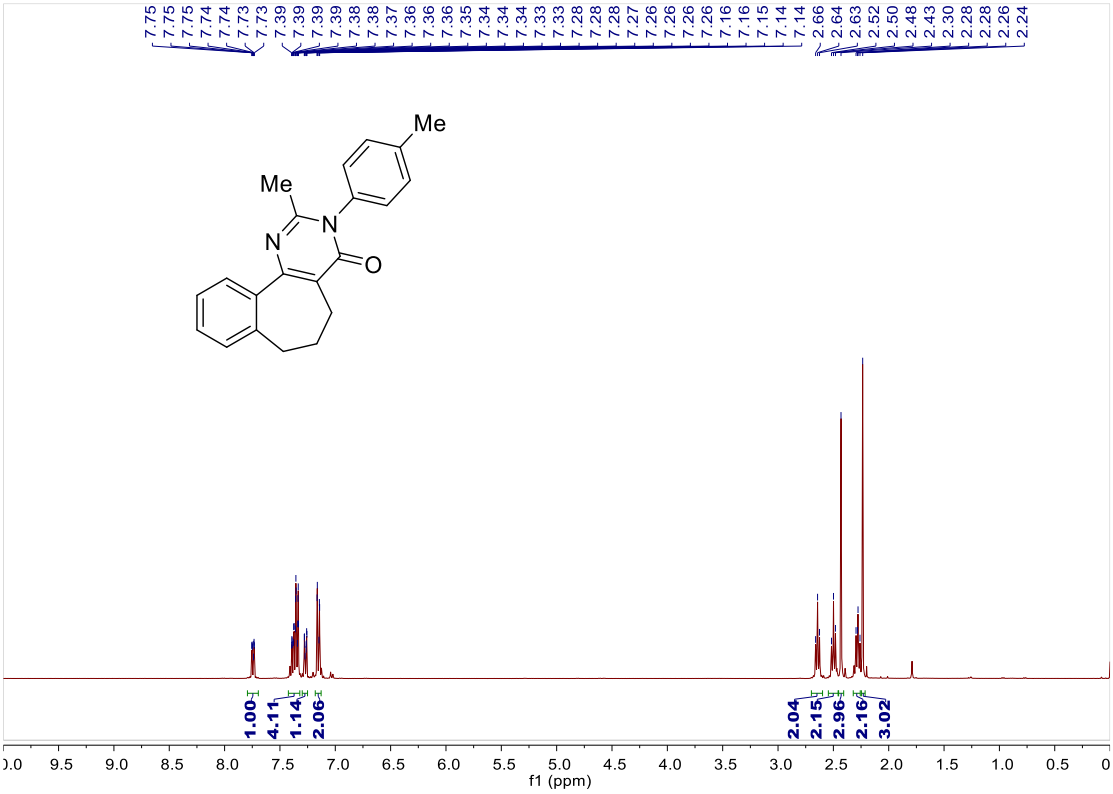


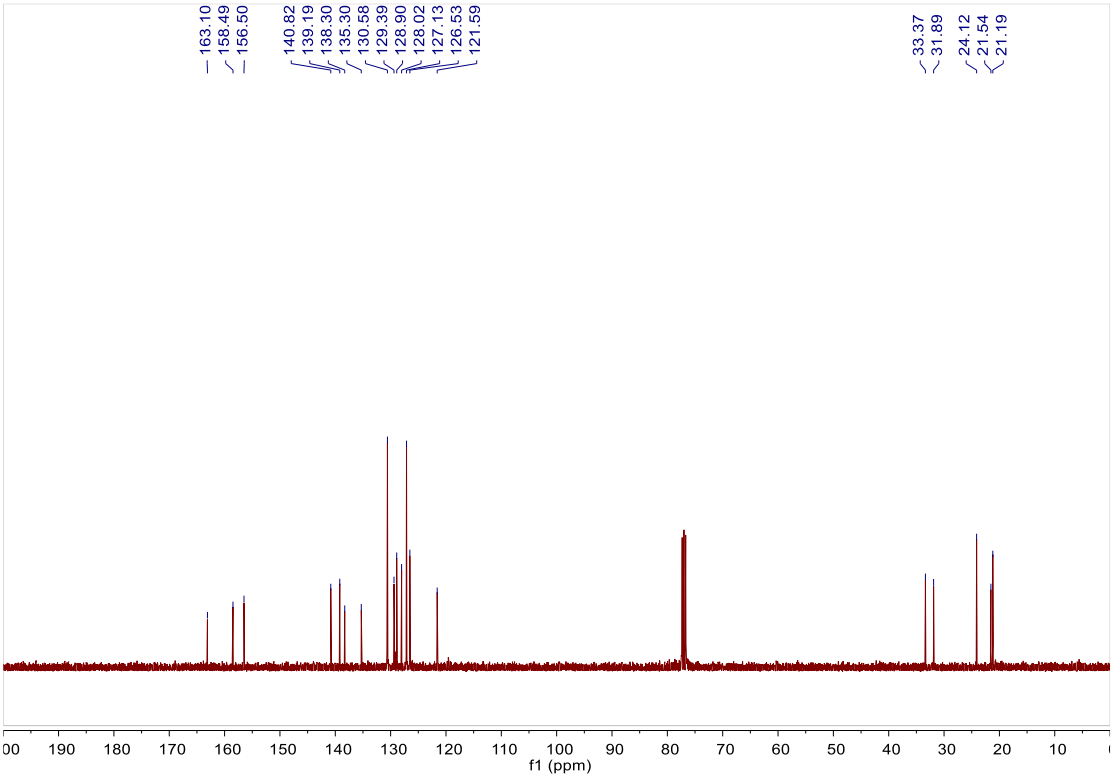
^{1}H and ^{13}C NMR spectra for product 3ma ($CDCl_3$)



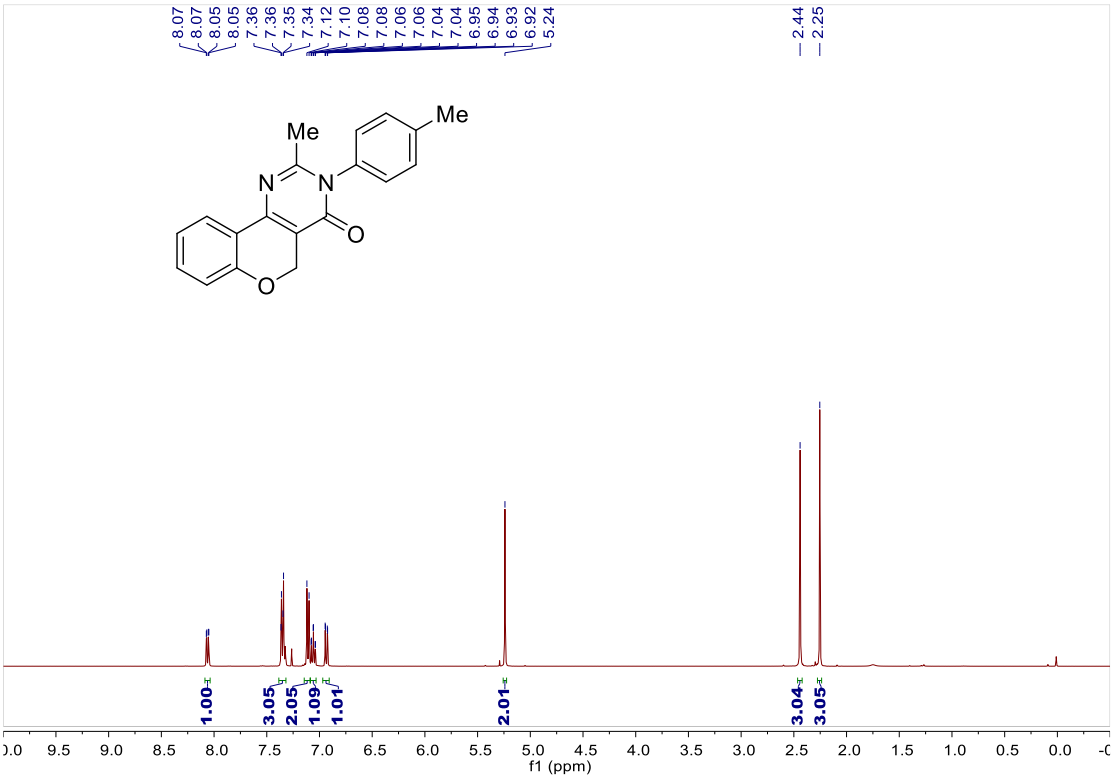


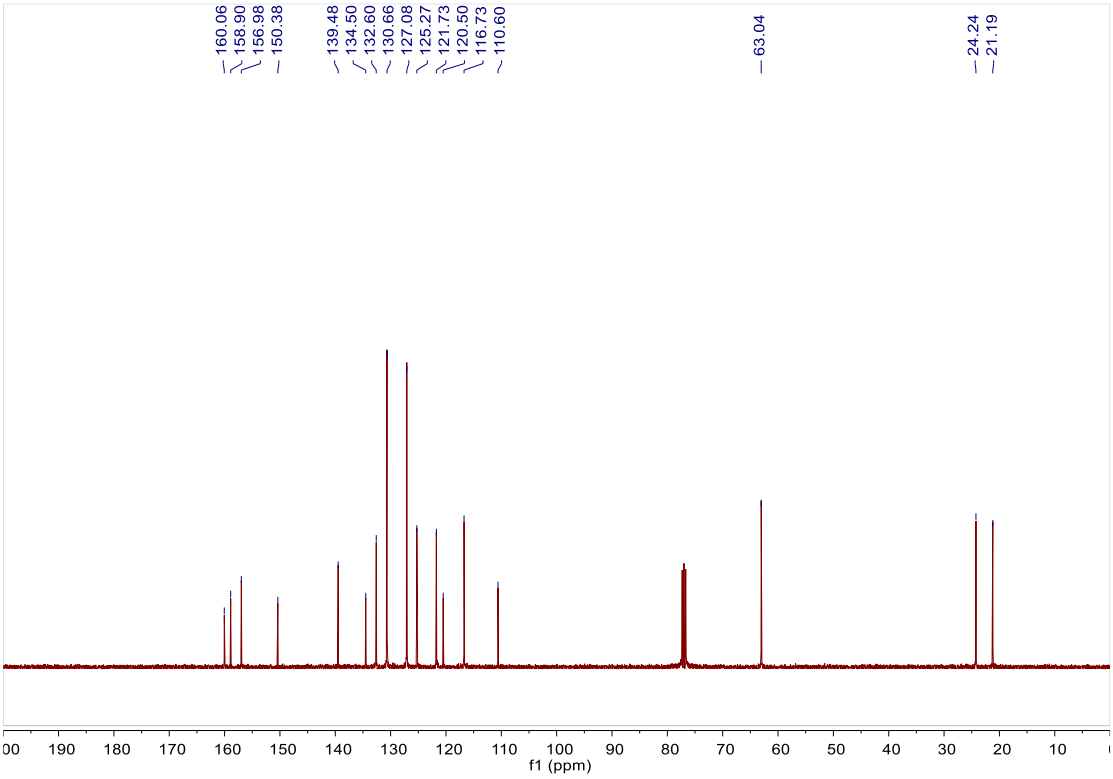
^{1}H and ^{13}C NMR spectra for product 3na ($CDCl_3$)



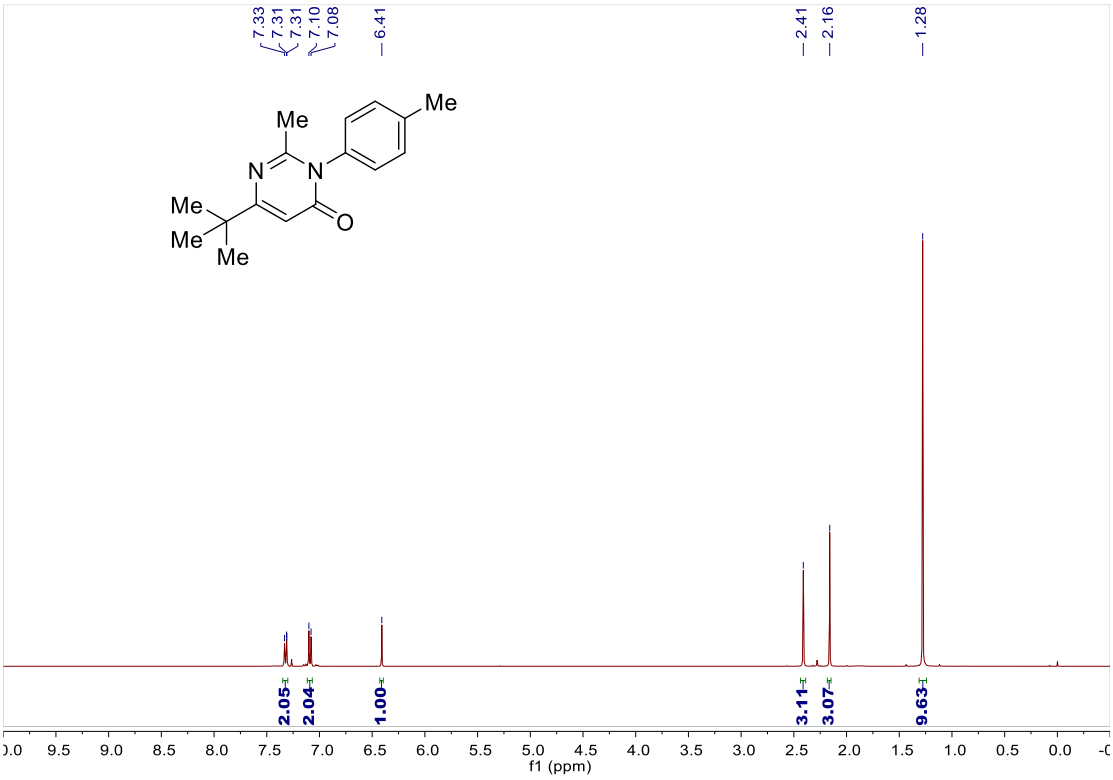


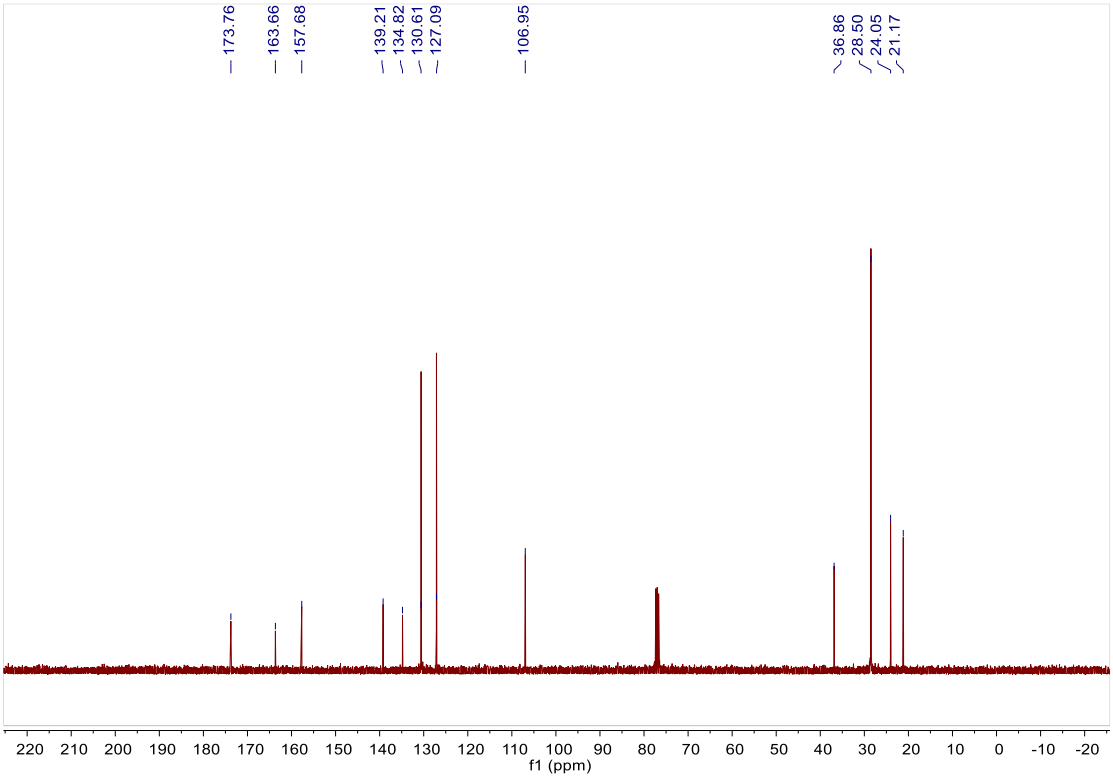
^{1}H and ^{13}C NMR spectra for product 3oa ($CDCl_3$)



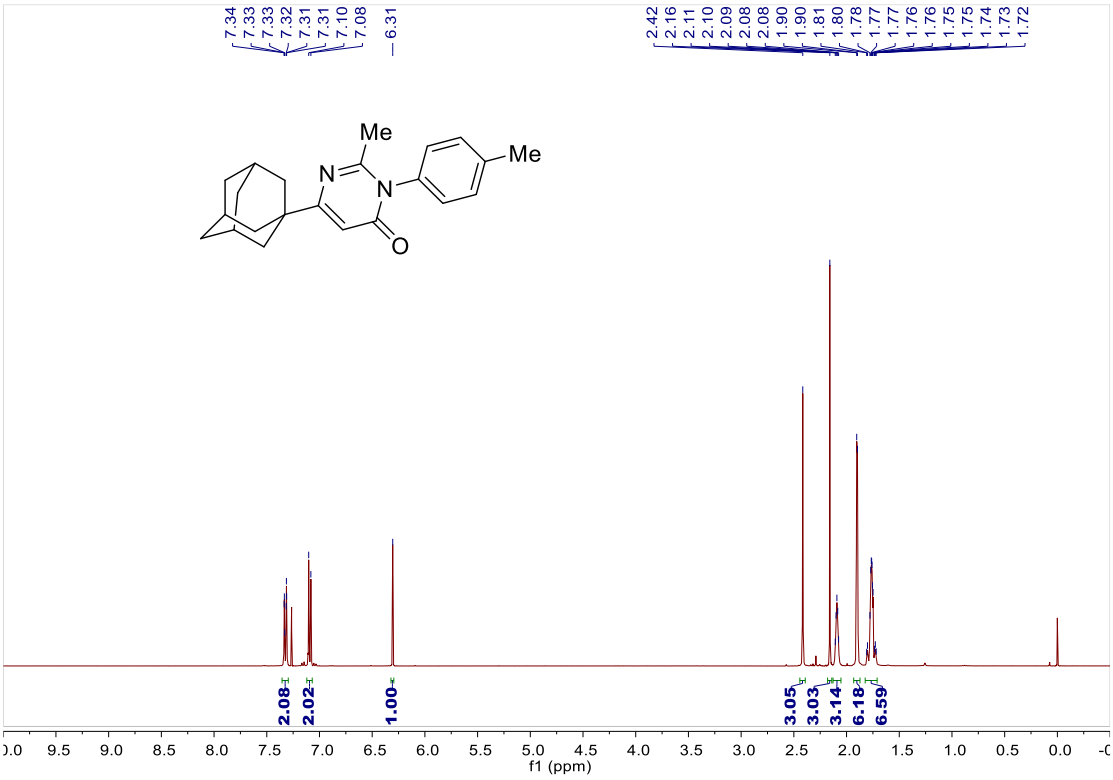


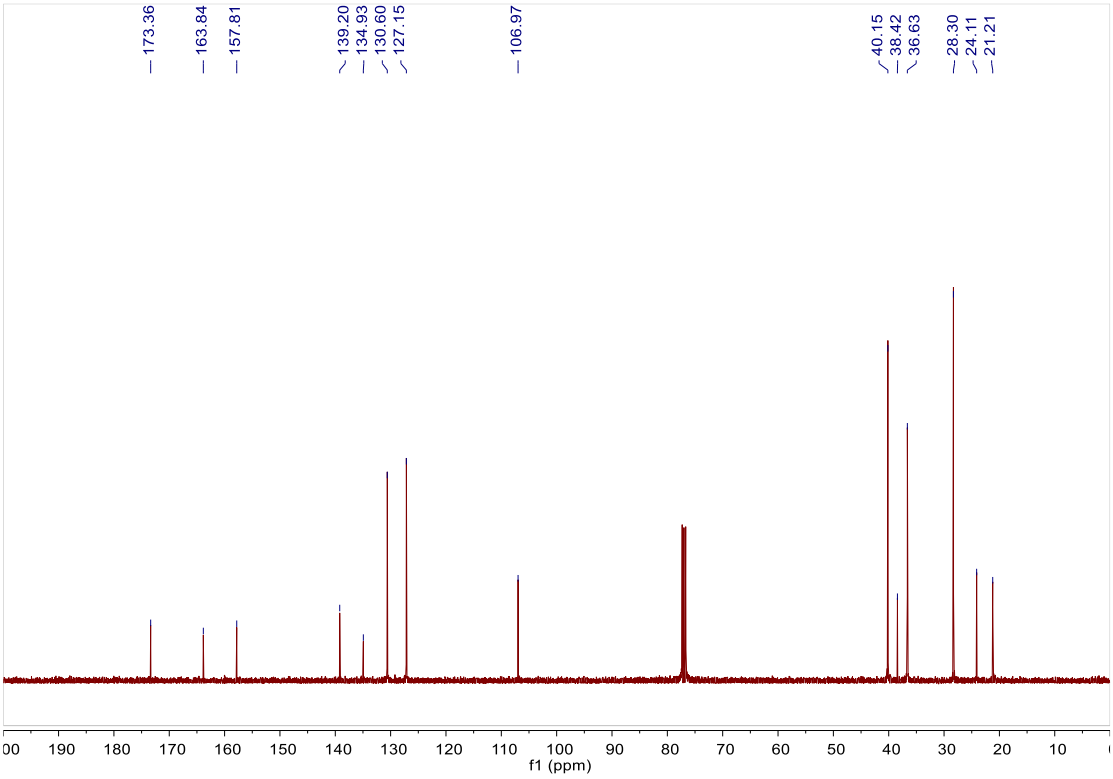
^{1}H and ^{13}C NMR spectra for product 3pa ($CDCl_3$)



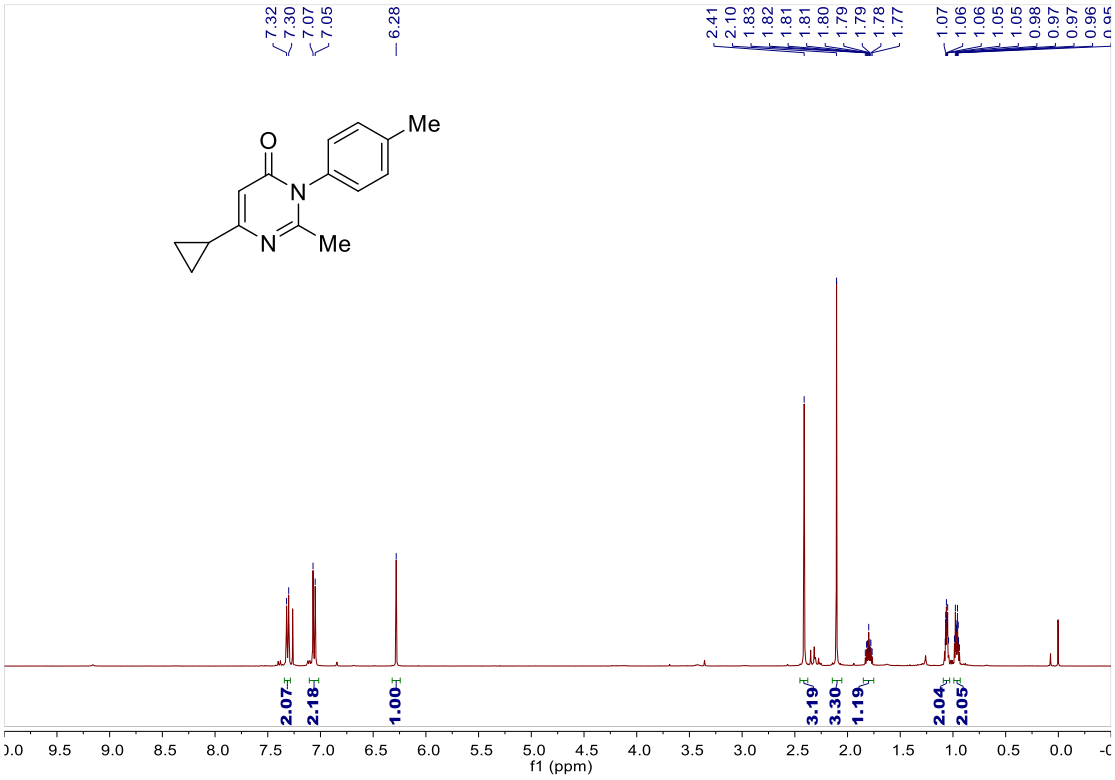


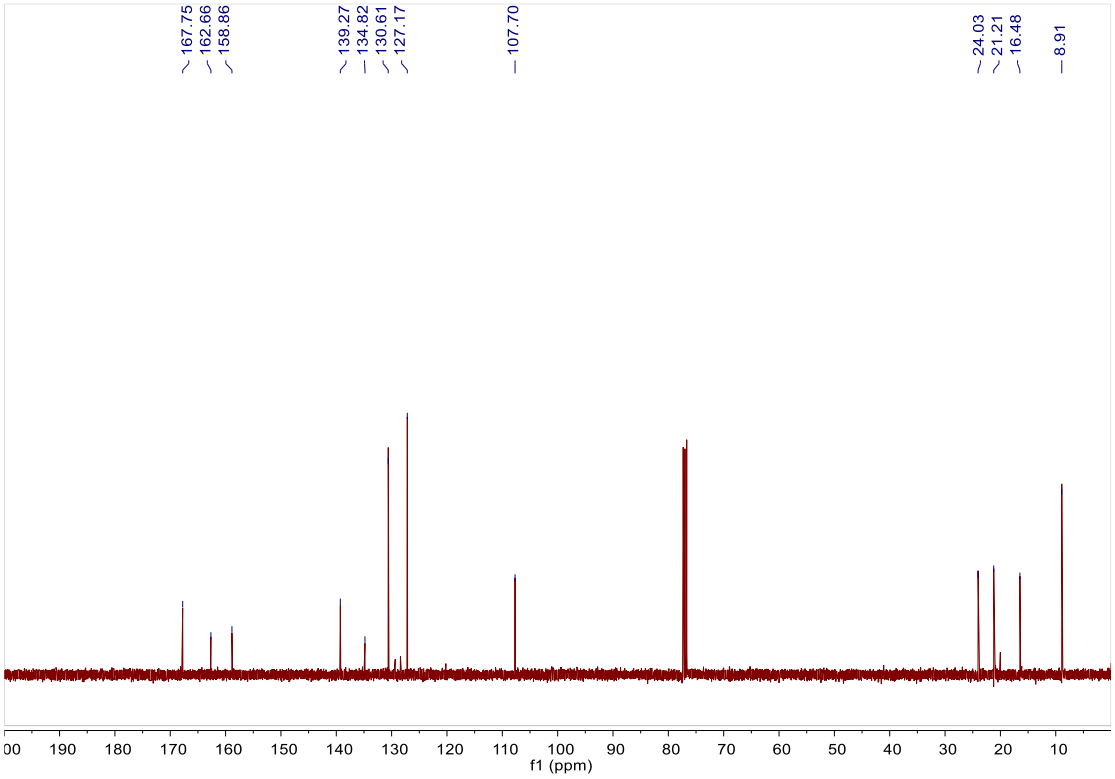
^{1}H and ^{13}C NMR spectra for product 3qa ($CDCl_3$)



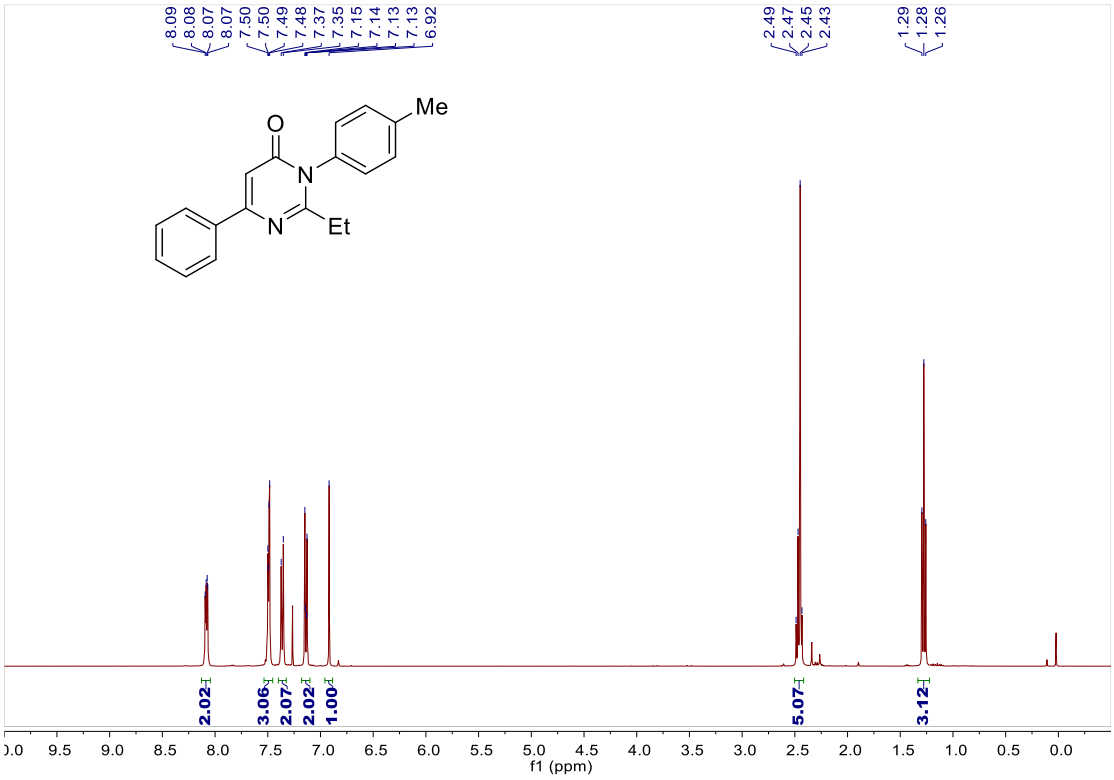


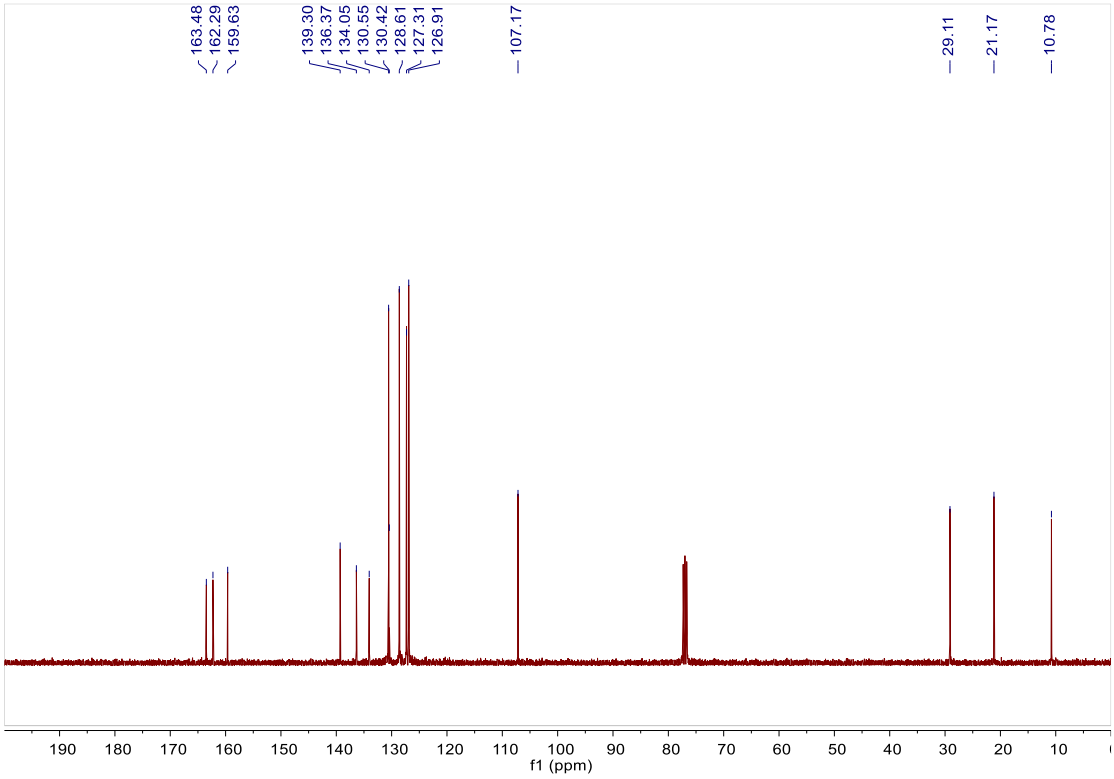
^{1}H and ^{13}C NMR spectra for product 3ra ($CDCl_3$)



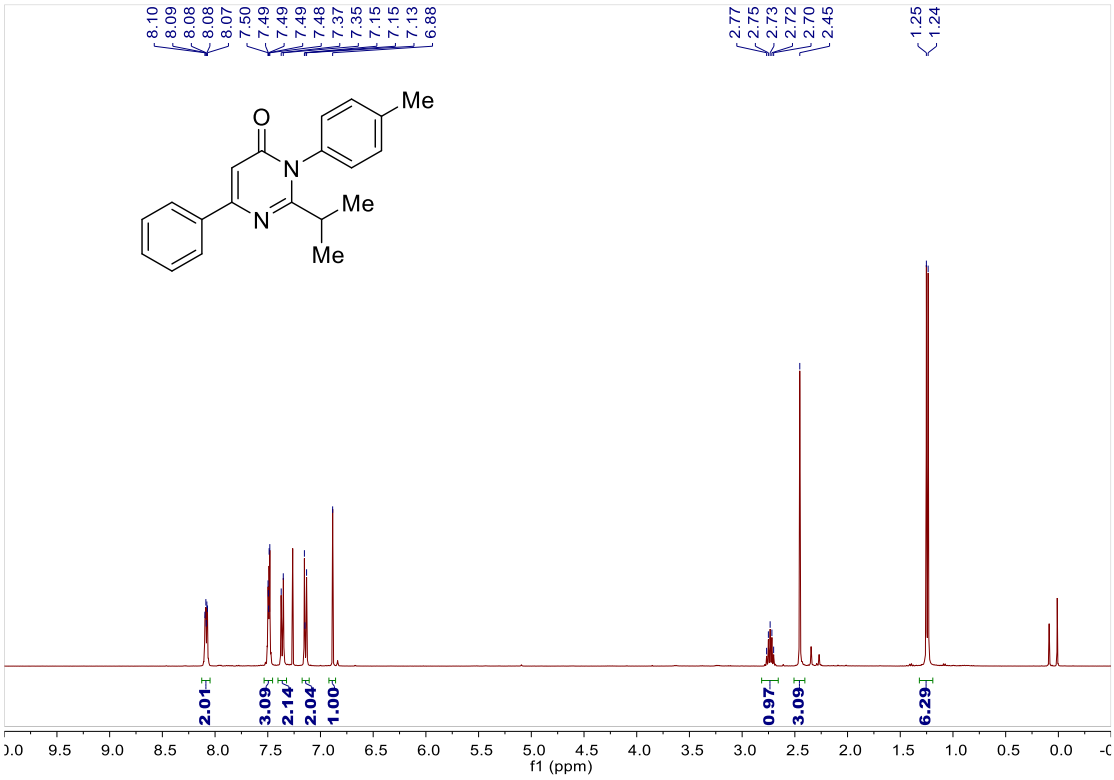


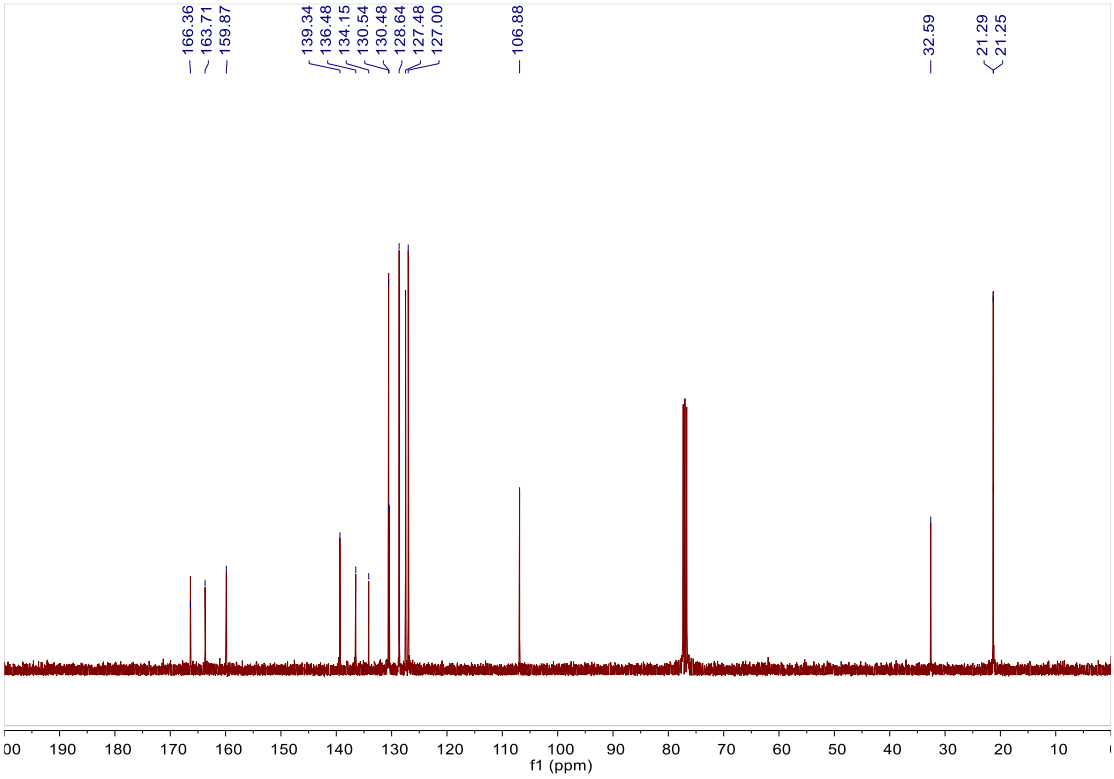
^{1}H and ^{13}C NMR spectra for product 3sa ($CDCl_3$)



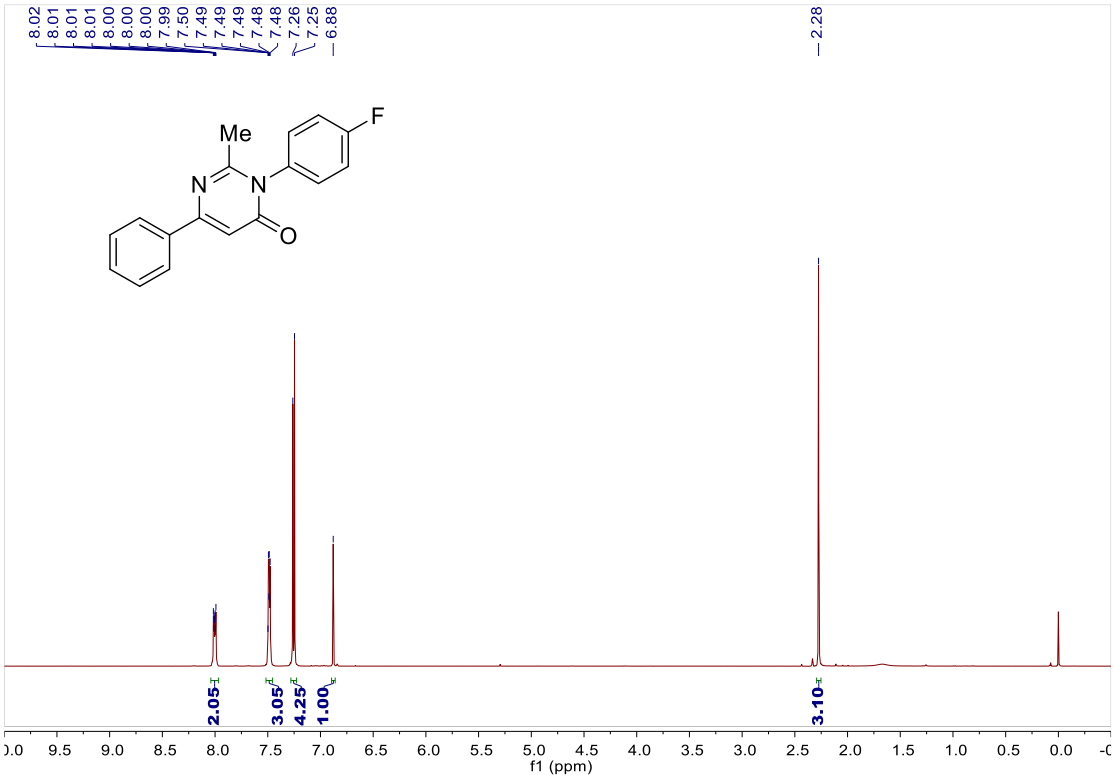


^{1}H and ^{13}C NMR spectra for product 3ta ($CDCl_3$)





^{1}H and ^{13}C NMR spectra for product 3ua ($CDCl_3$)


8.02
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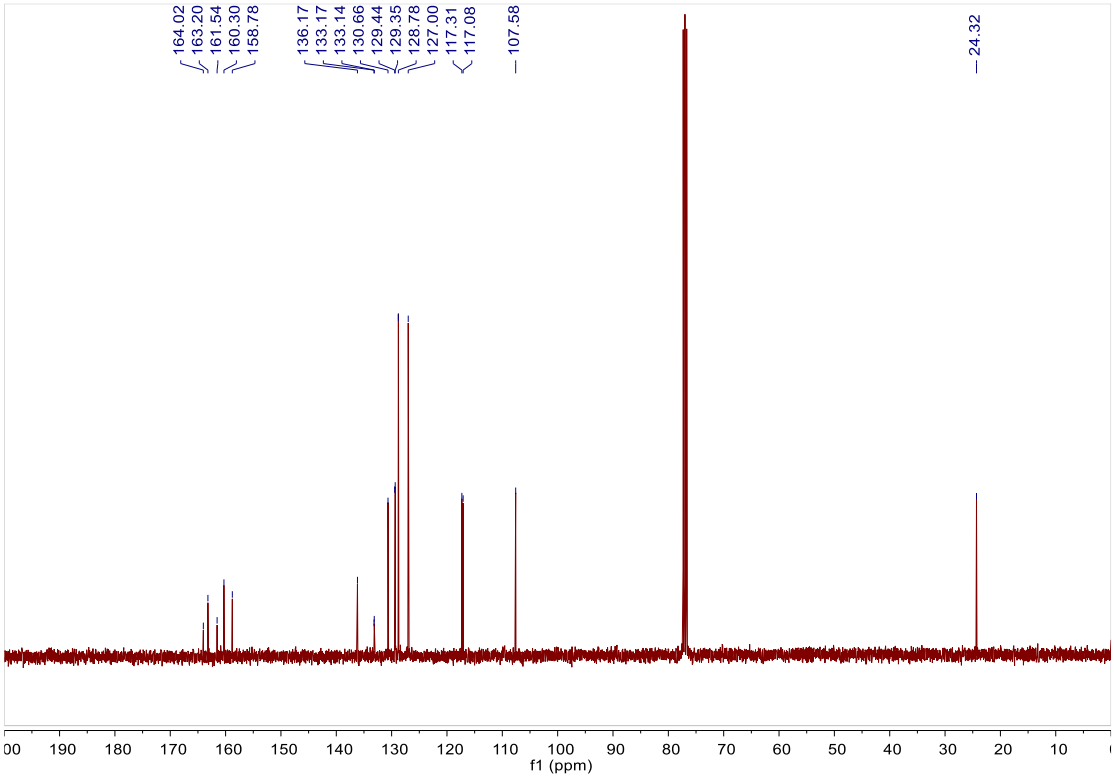
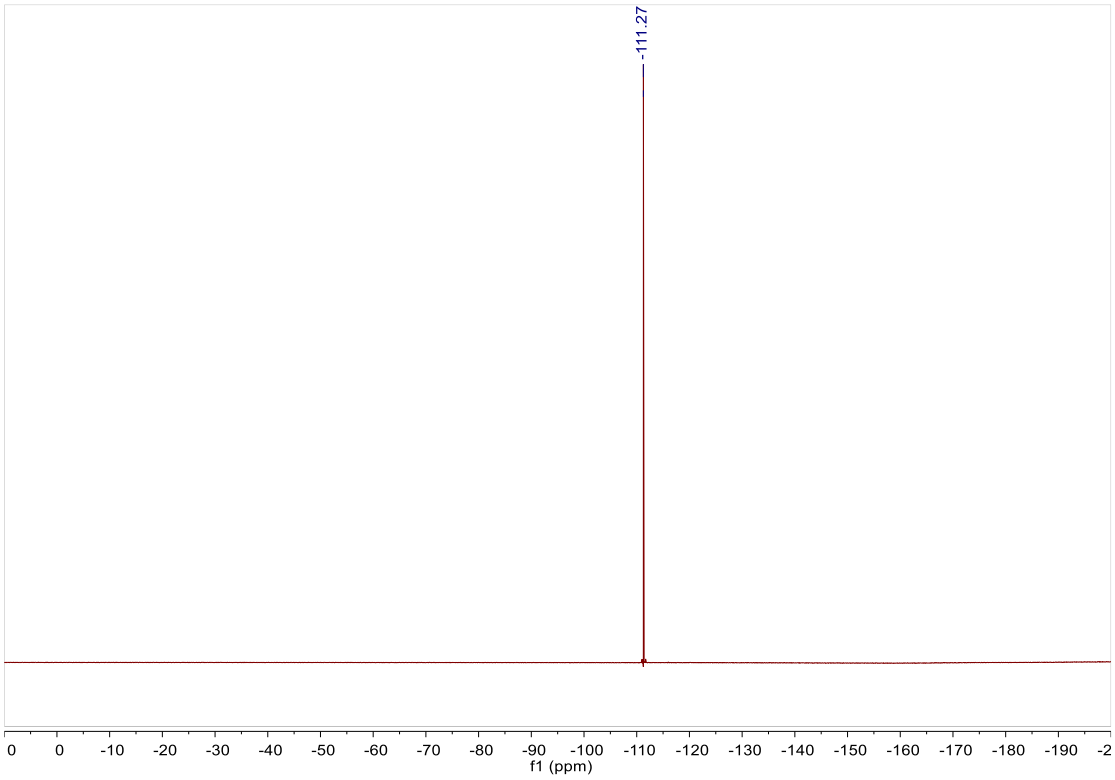
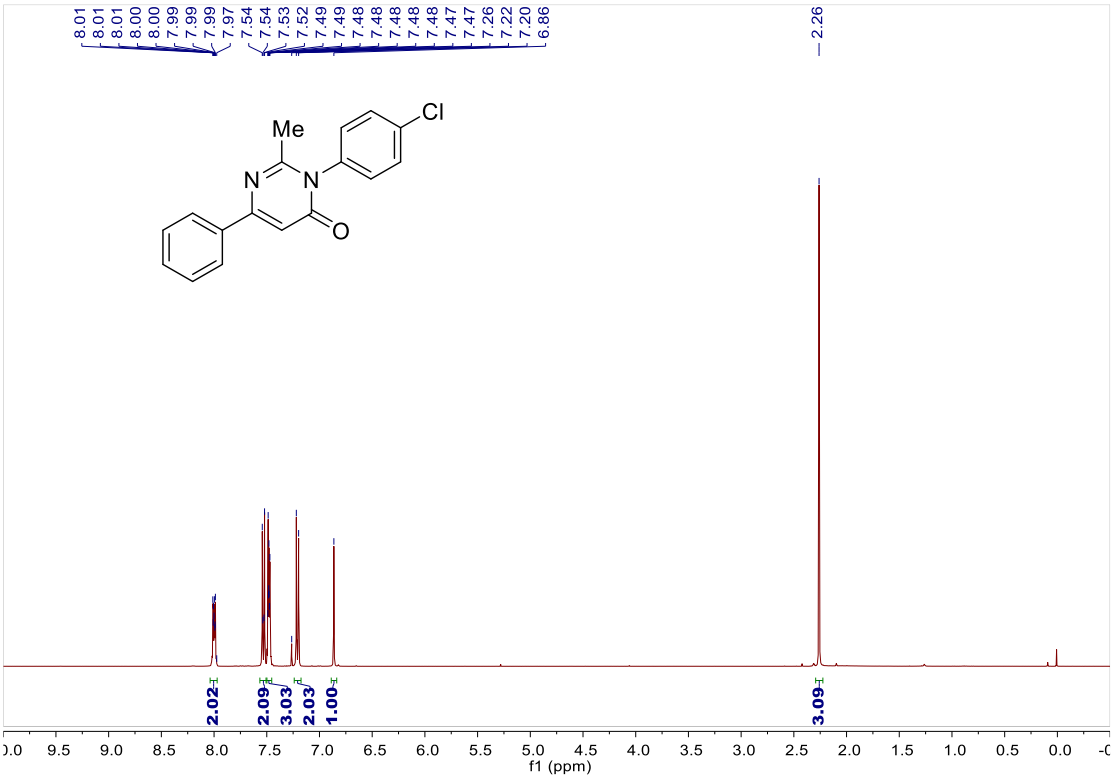
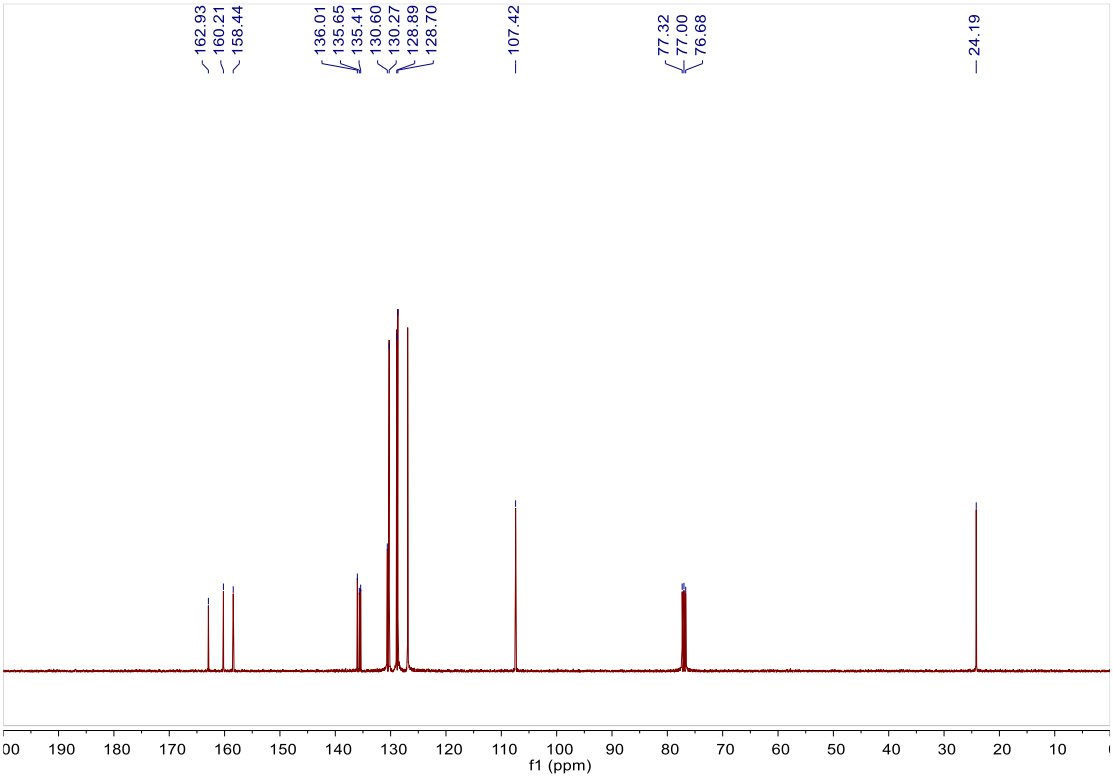
8.00
7.99
7.50
7.49
7.49
7.49
7.48
7.48
7.26
7.25
6.88
2.28
Me
F
N
N
O
2.05
3.05
4.25
1.00
3.10
f1 (ppm)


164.02
163.20
161.54
160.30
158.78
136.17
133.17
133.14
130.66
129.44
129.35
128.78
127.00
117.31
117.08
107.58
24.32
f1 (ppm)

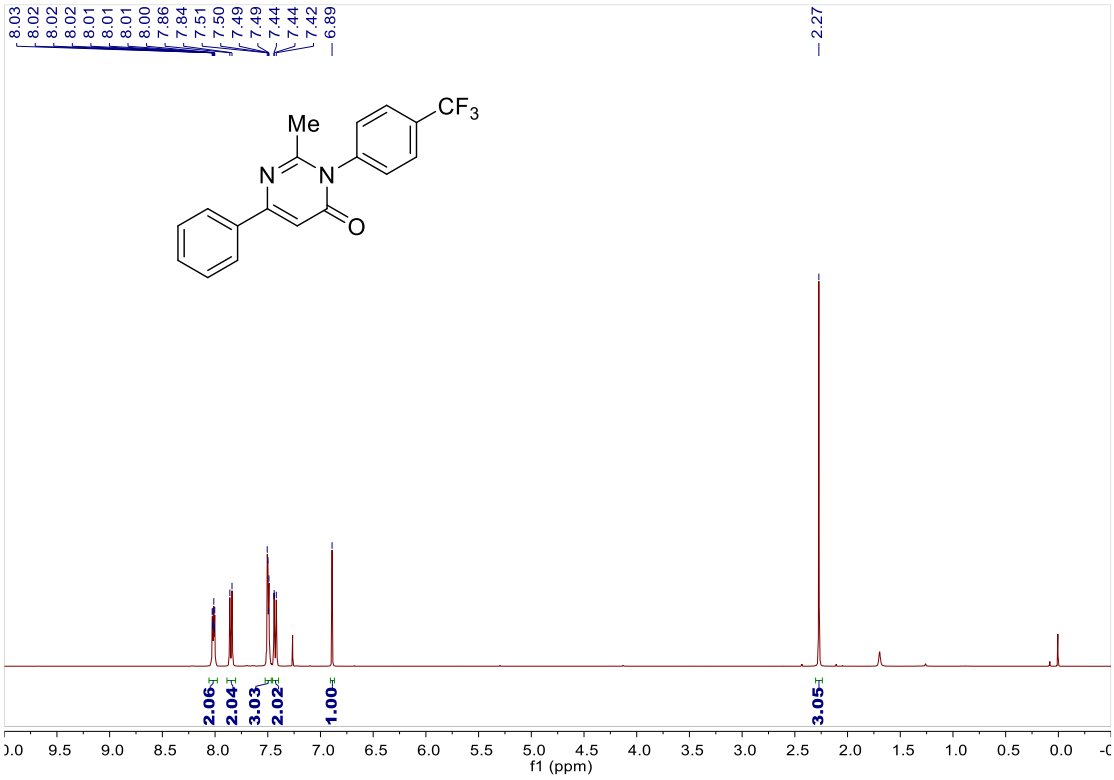


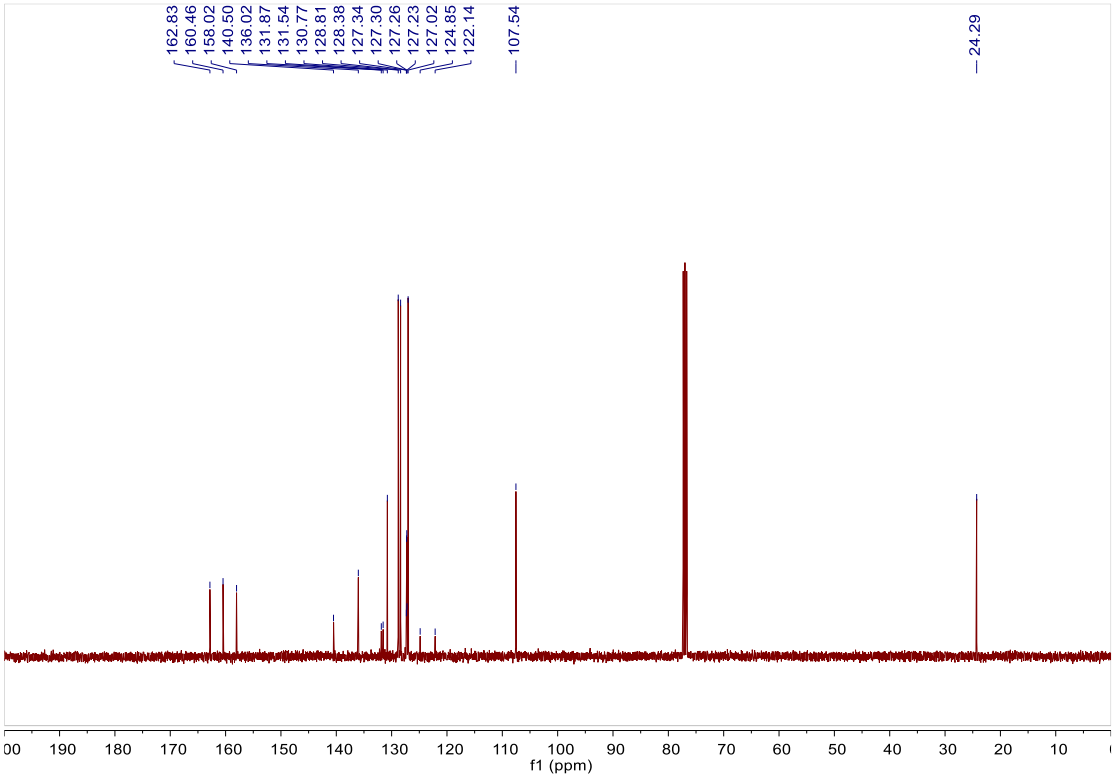
^{1}H, ^{13}C and ^{19}F NMR spectra for product 3ab ($CDCl_3$)

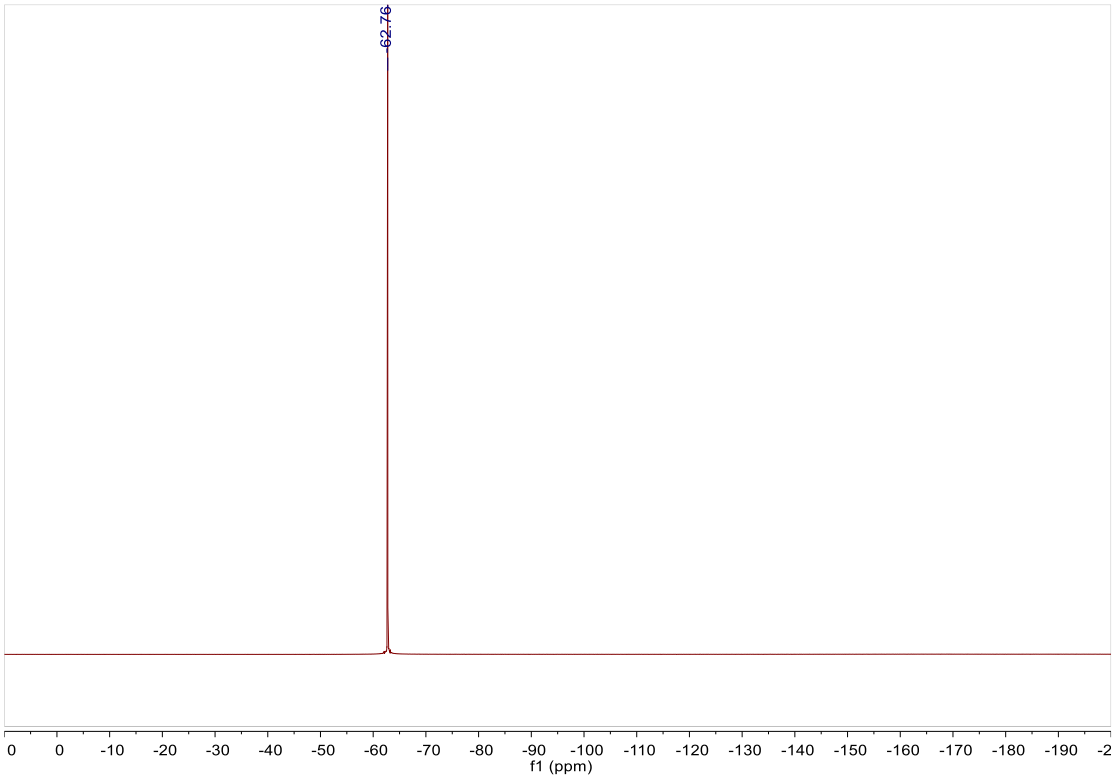




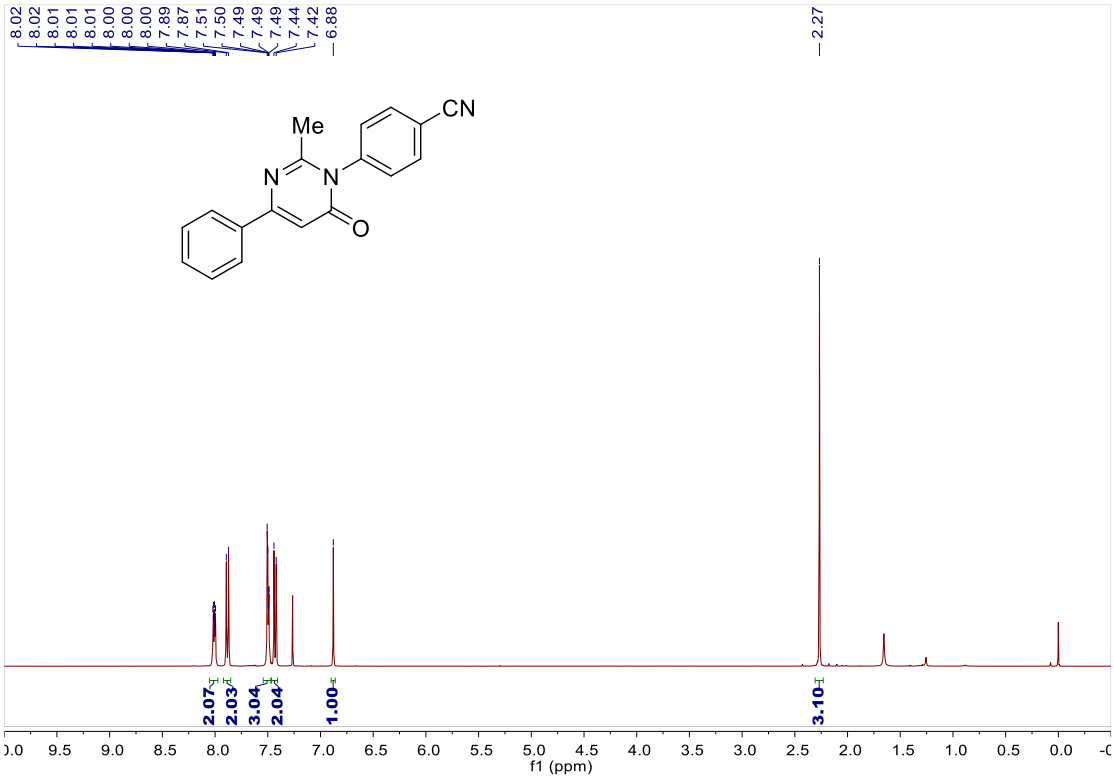
^{1}H and ^{13}C NMR spectra for product 3ac ($CDCl_3$)

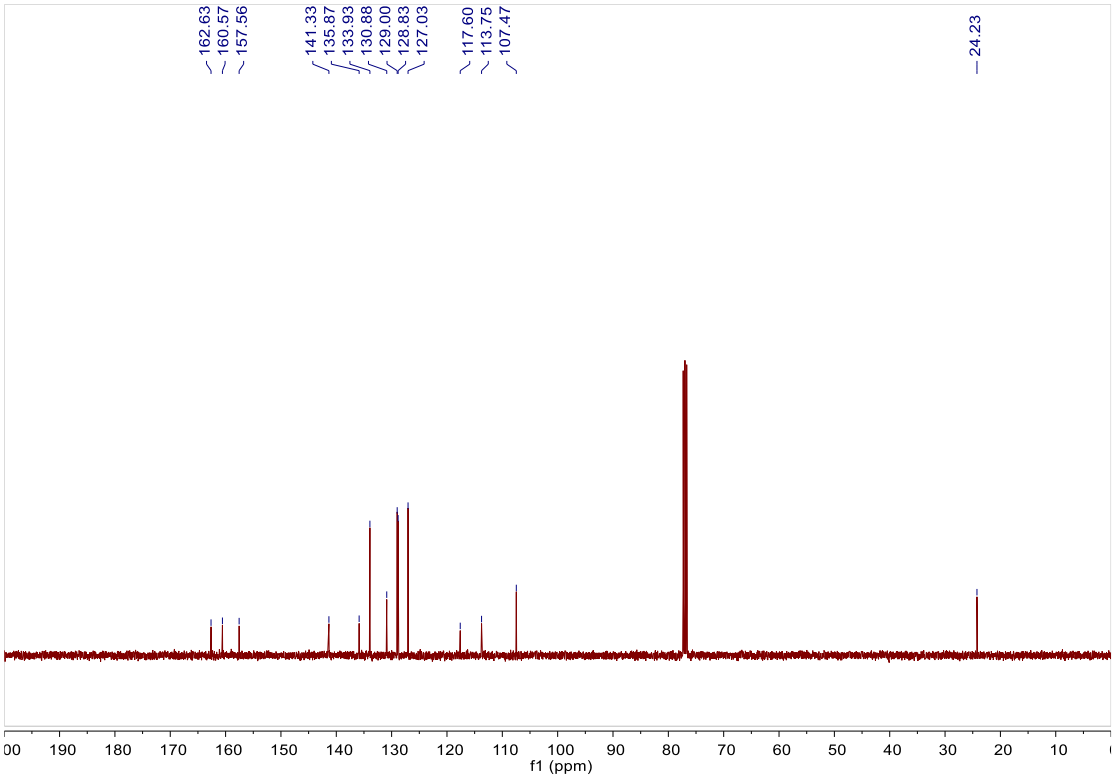

8.03
8.02
8.02
8.02
8.01
8.01
8.01
8.00
7.86
7.84
7.51
7.50
7.49
7.49
7.44
7.44
7.42
6.89
2.27
Me
CF3
N
N
O
2.06
2.04
3.03
2.02
1.00
3.05
f1 (ppm)


162.83
160.46
158.02
140.50
136.02
131.87
131.54
130.77
128.81
128.38
127.34
127.30
127.26
127.23
127.02
124.85
122.14
107.54
24.29
f1 (ppm)

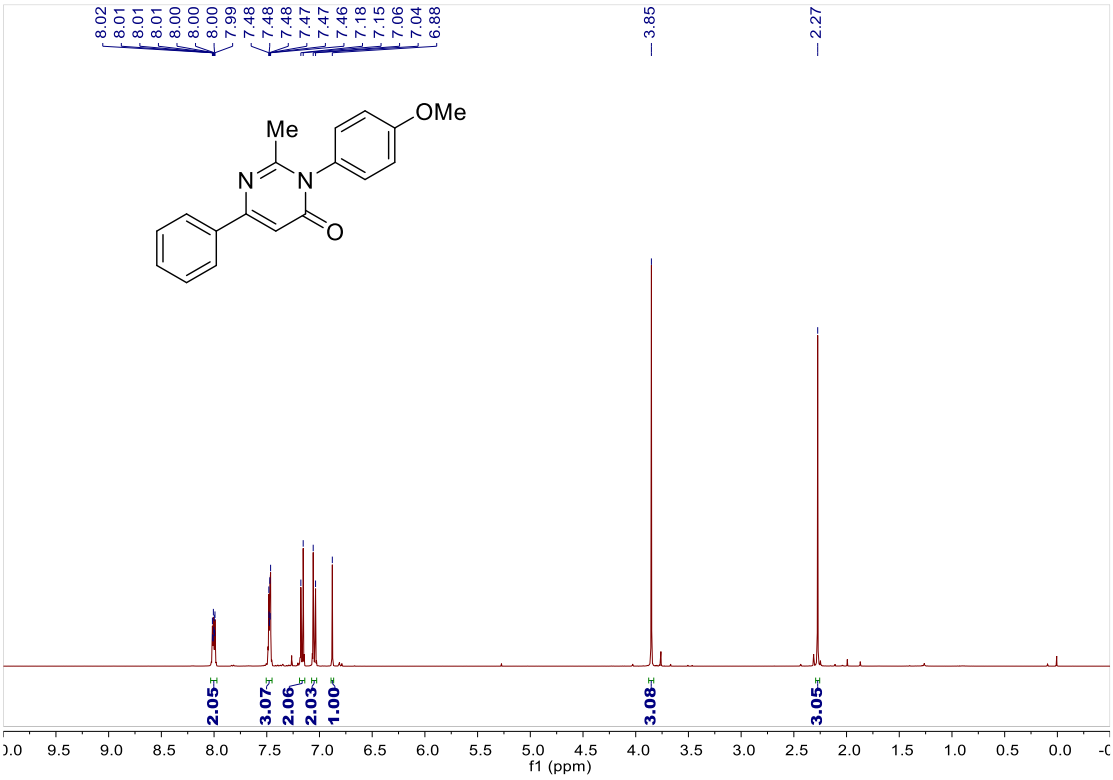


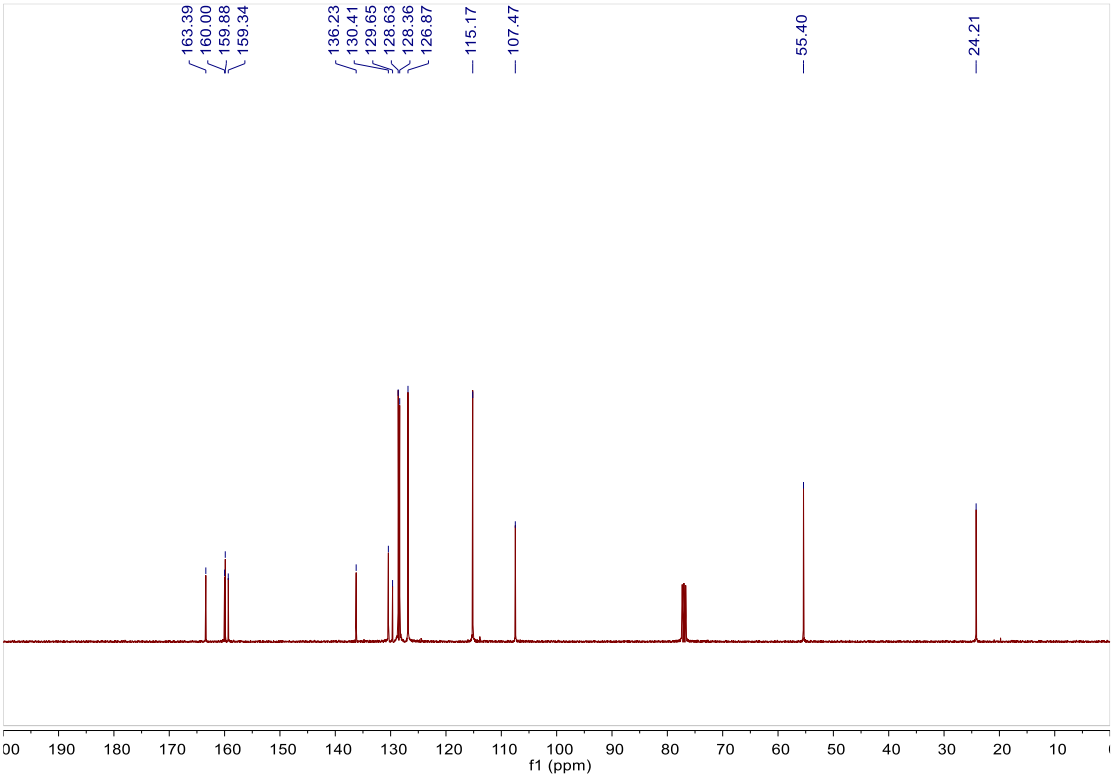
^{1}H, ^{13}C and ^{19}F NMR spectra for product 3ad ($CDCl_3$)



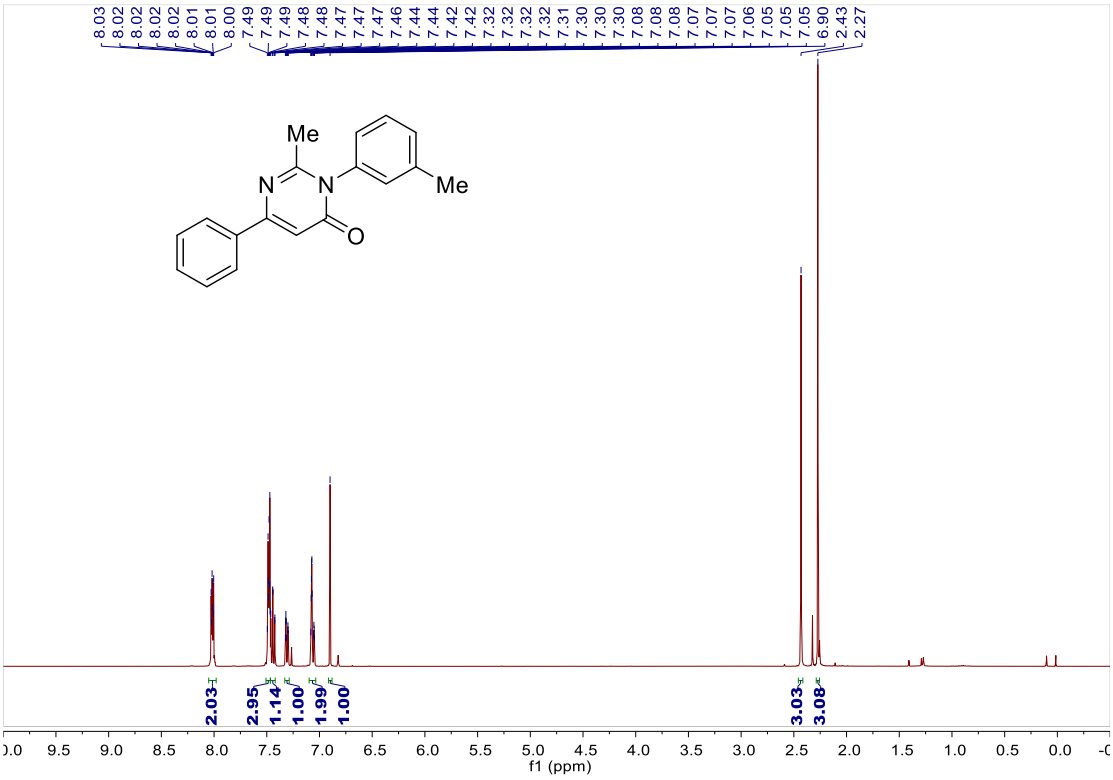


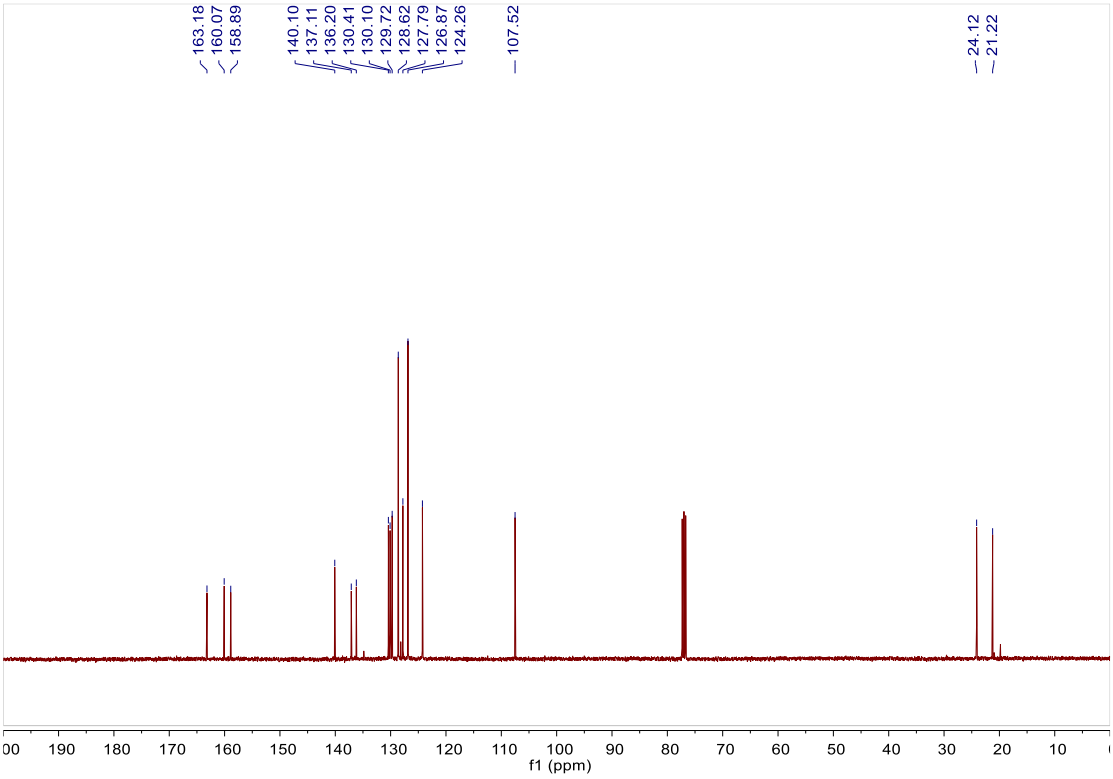
^{1}H and ^{13}C NMR spectra for product 3ae ($CDCl_3$)



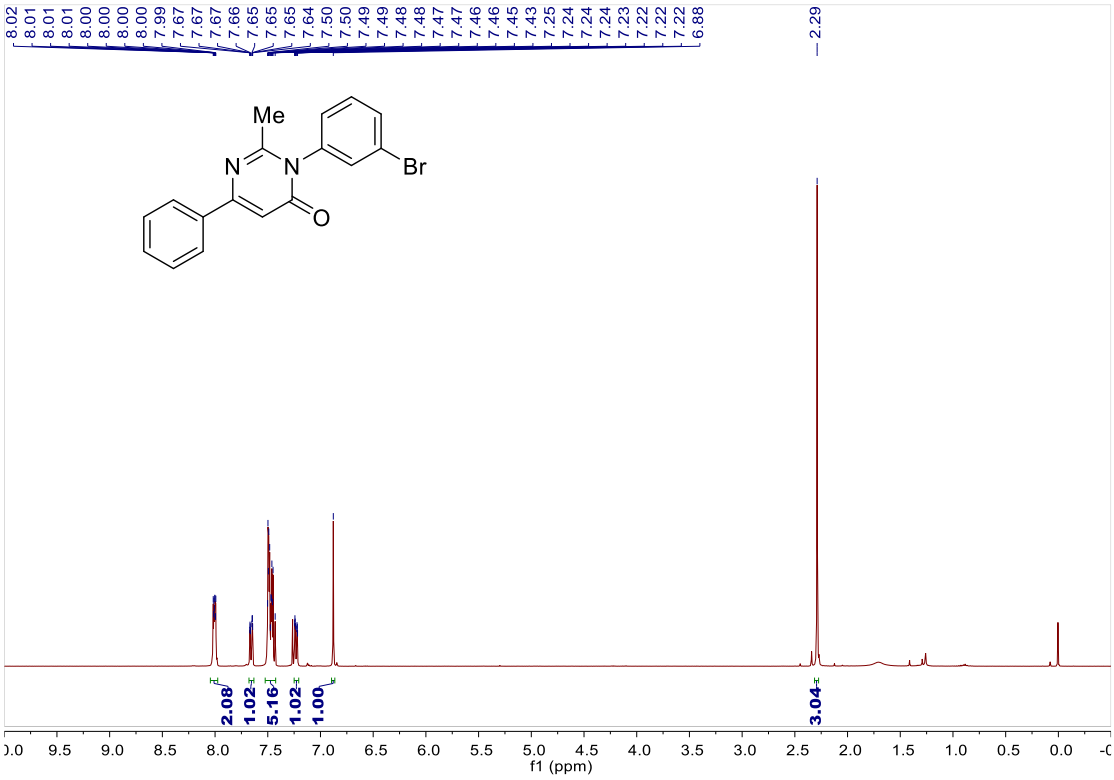


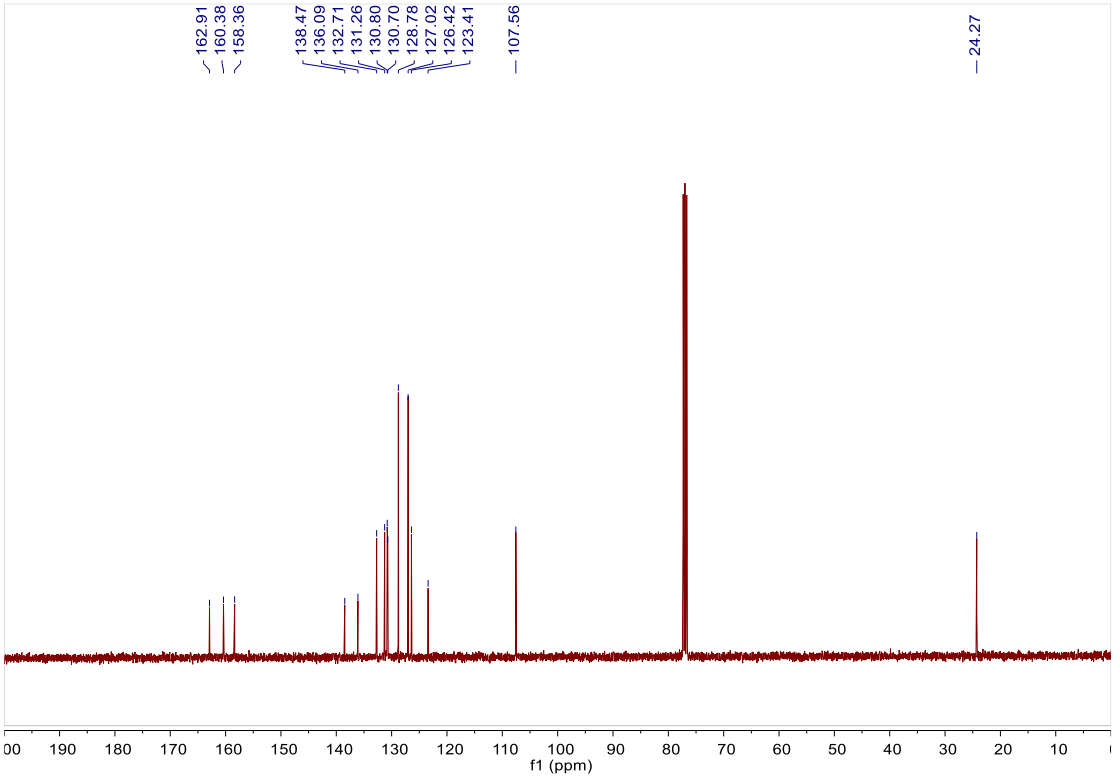
^{1}H and ^{13}C NMR spectra for product 3af ($CDCl_3$)



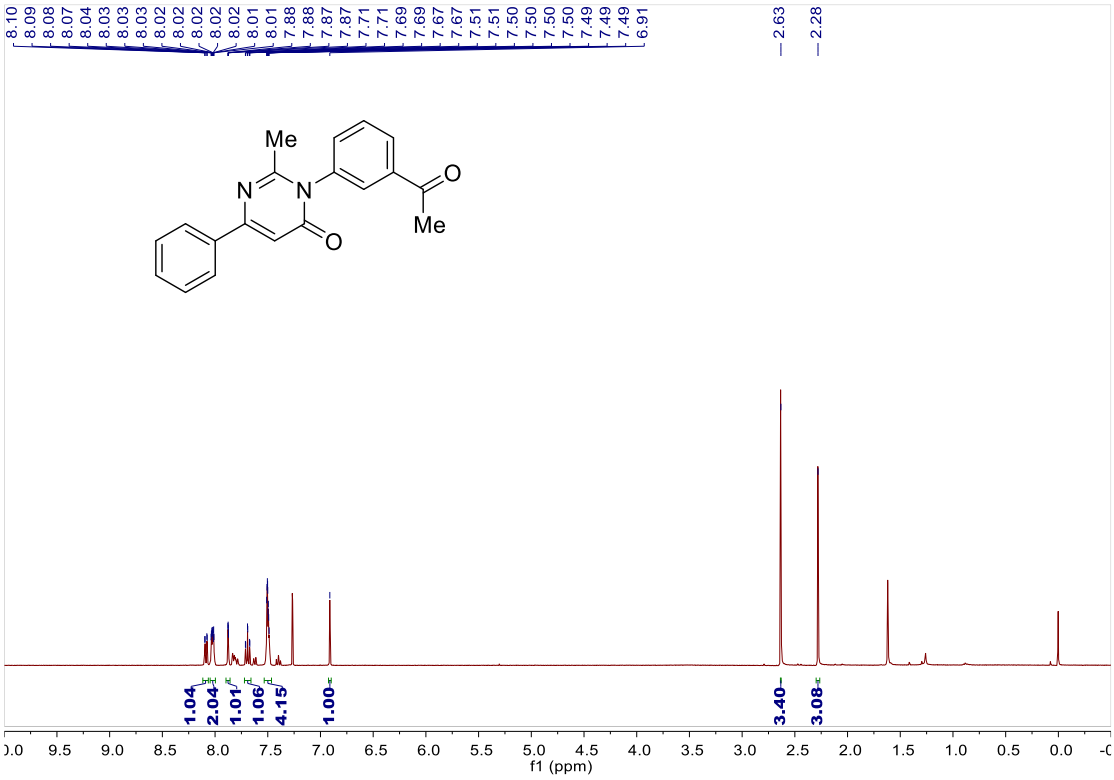


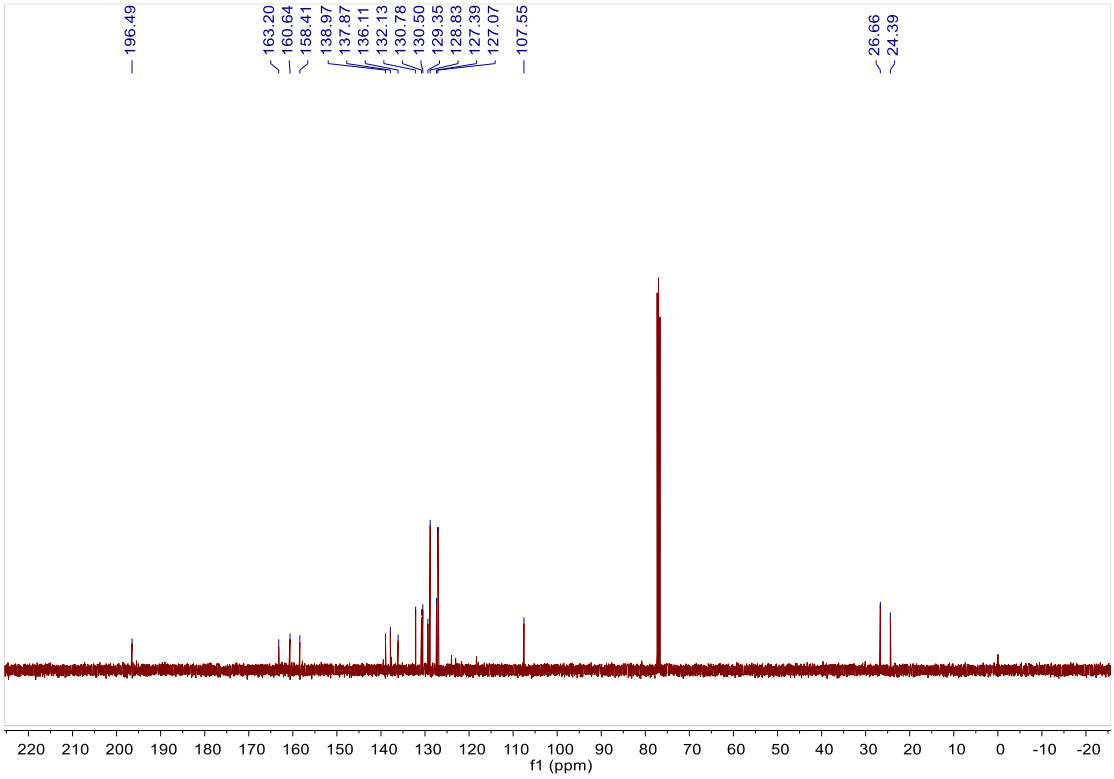
^{1}H and ^{13}C NMR spectra for product 3ag ($CDCl_3$)



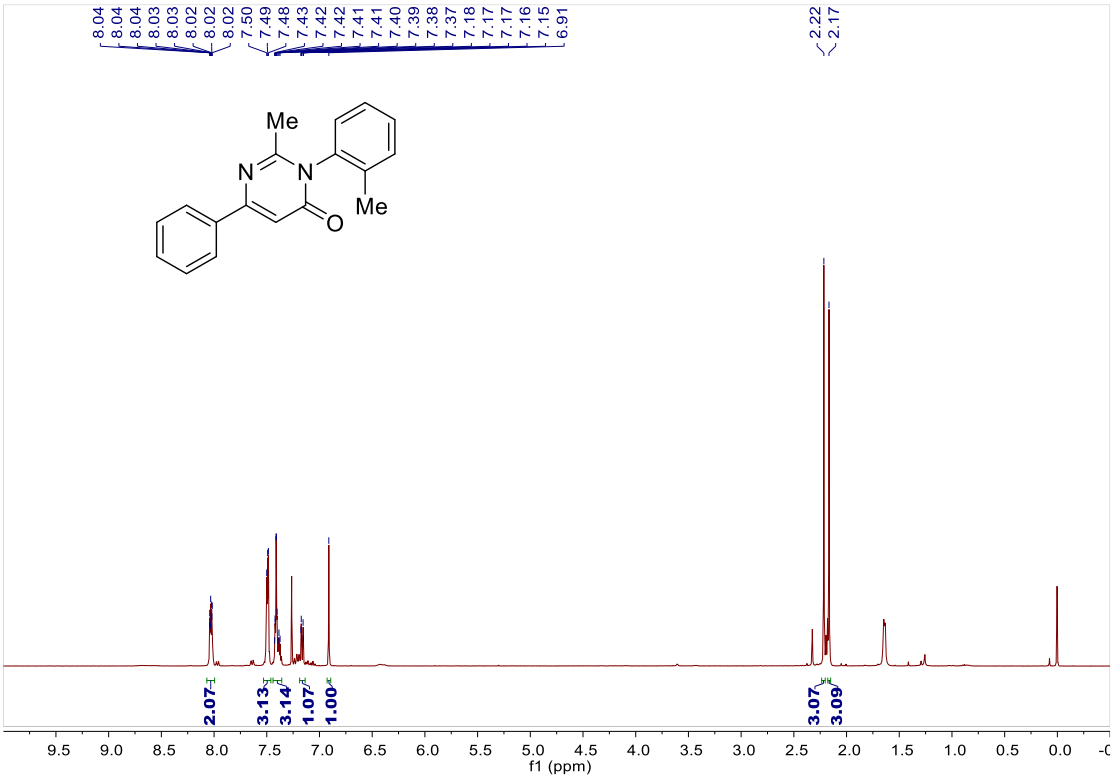


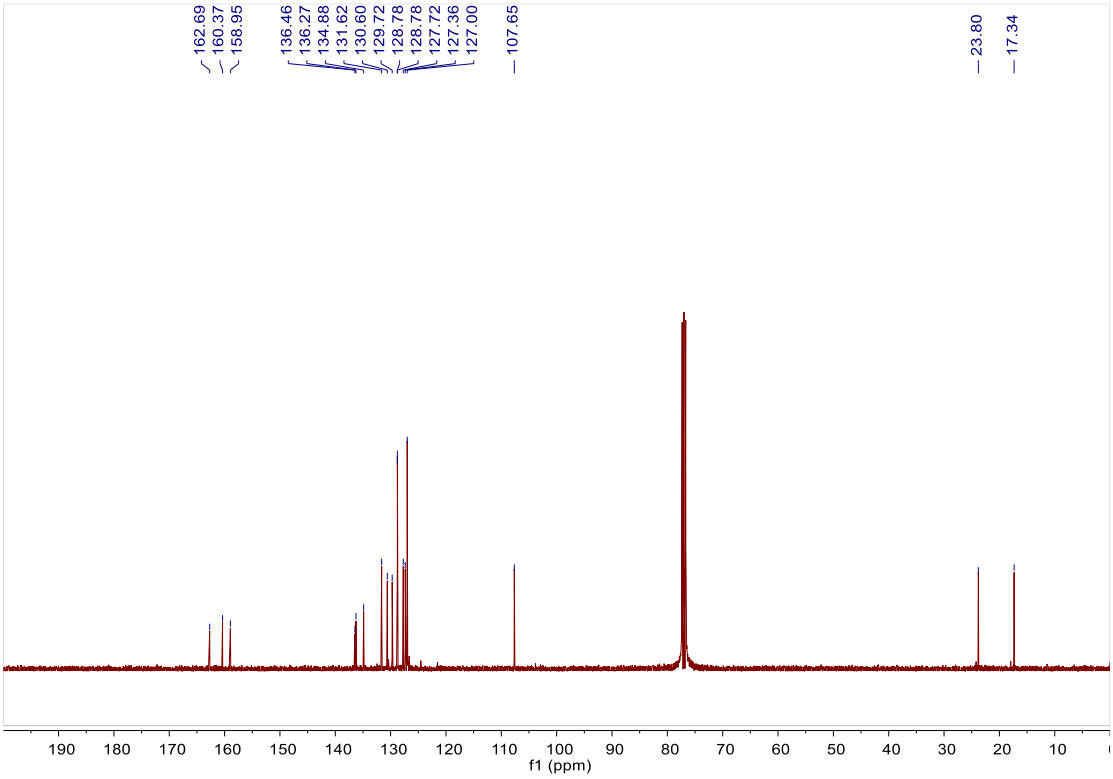
^{1}H and ^{13}C NMR spectra for product 3ah ($CDCl_3$)



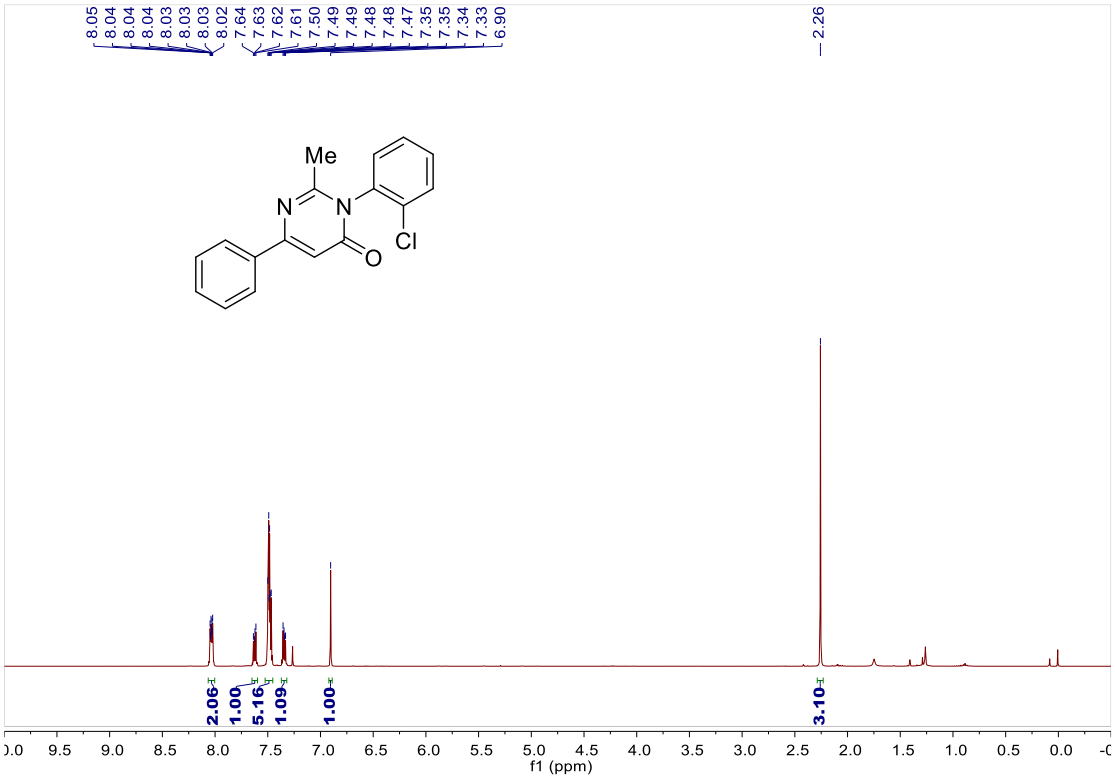


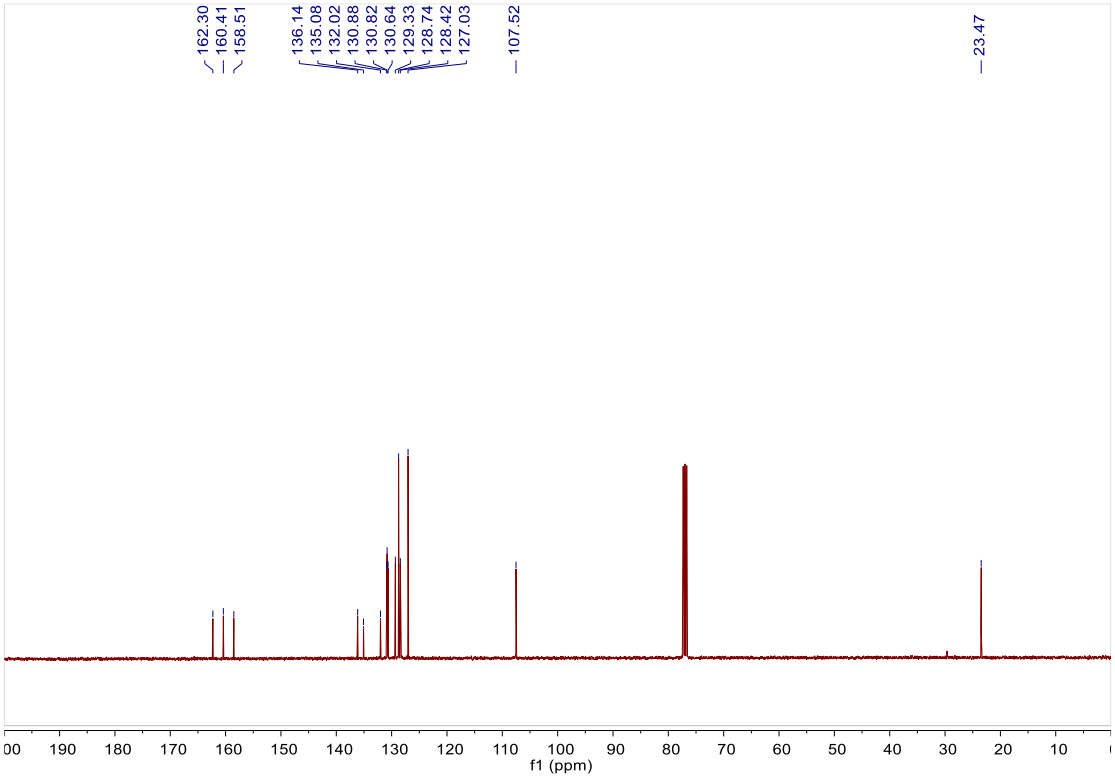
^{1}H and ^{13}C NMR spectra for product 3ai ($CDCl_3$)



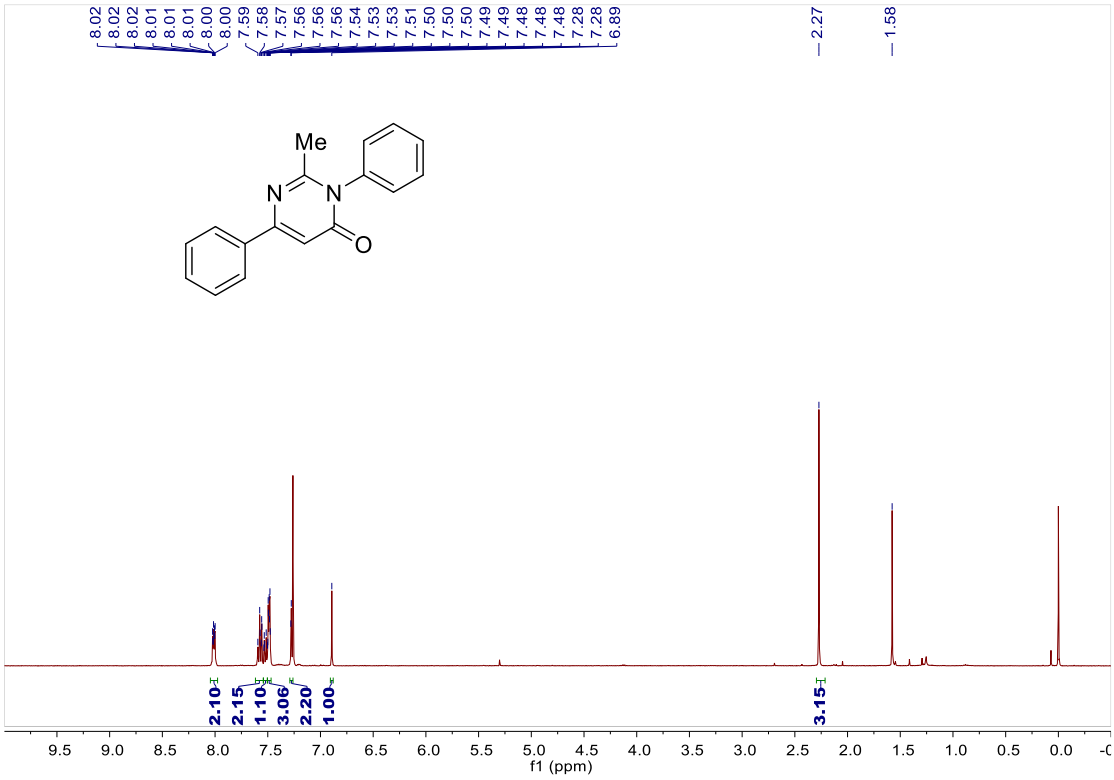


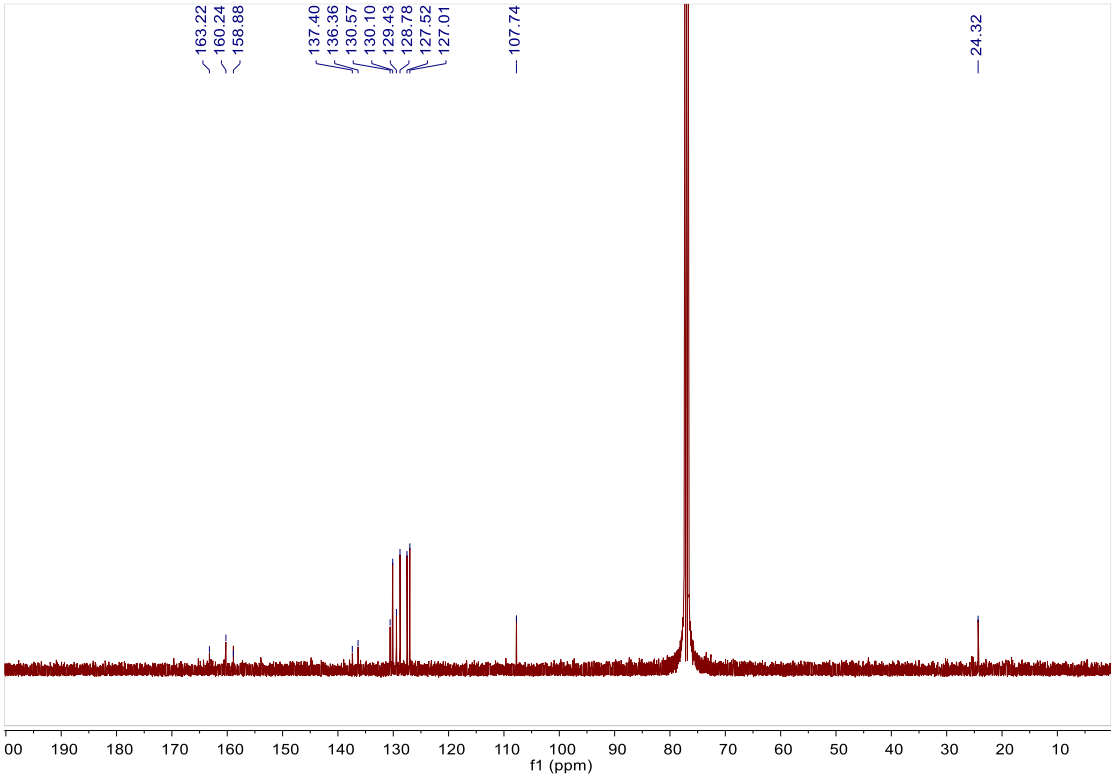
^{1}H and ^{13}C NMR spectra for product 3aj ($CDCl_3$)



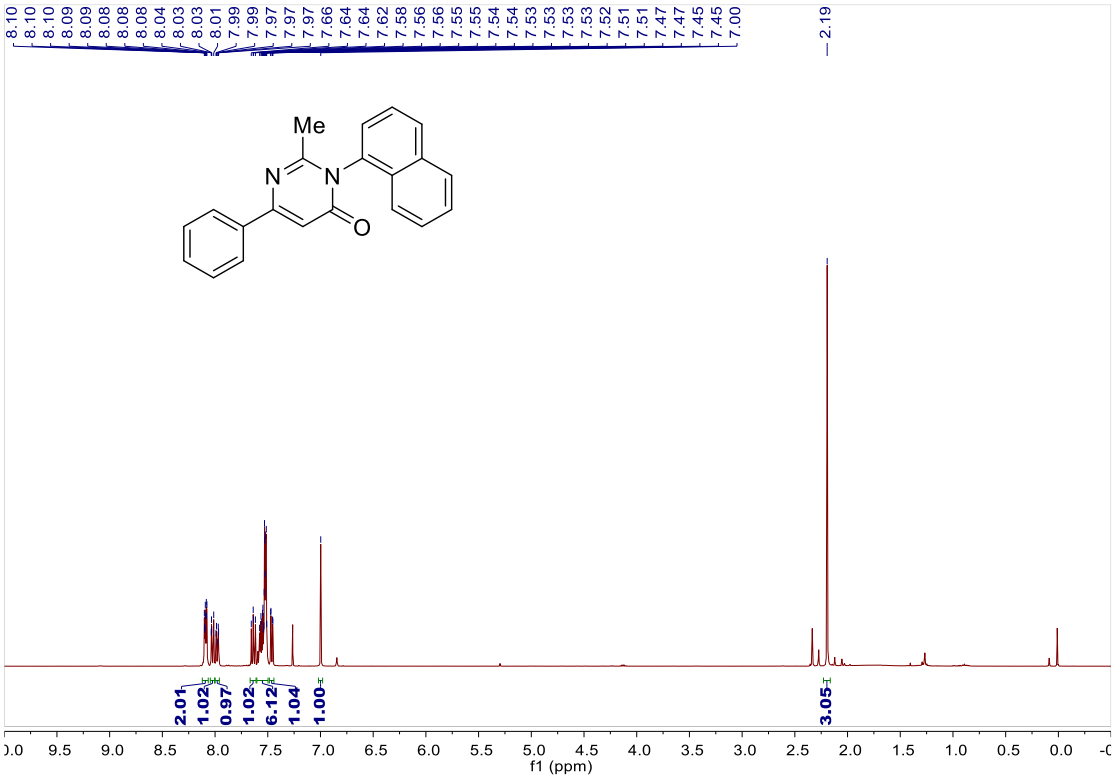


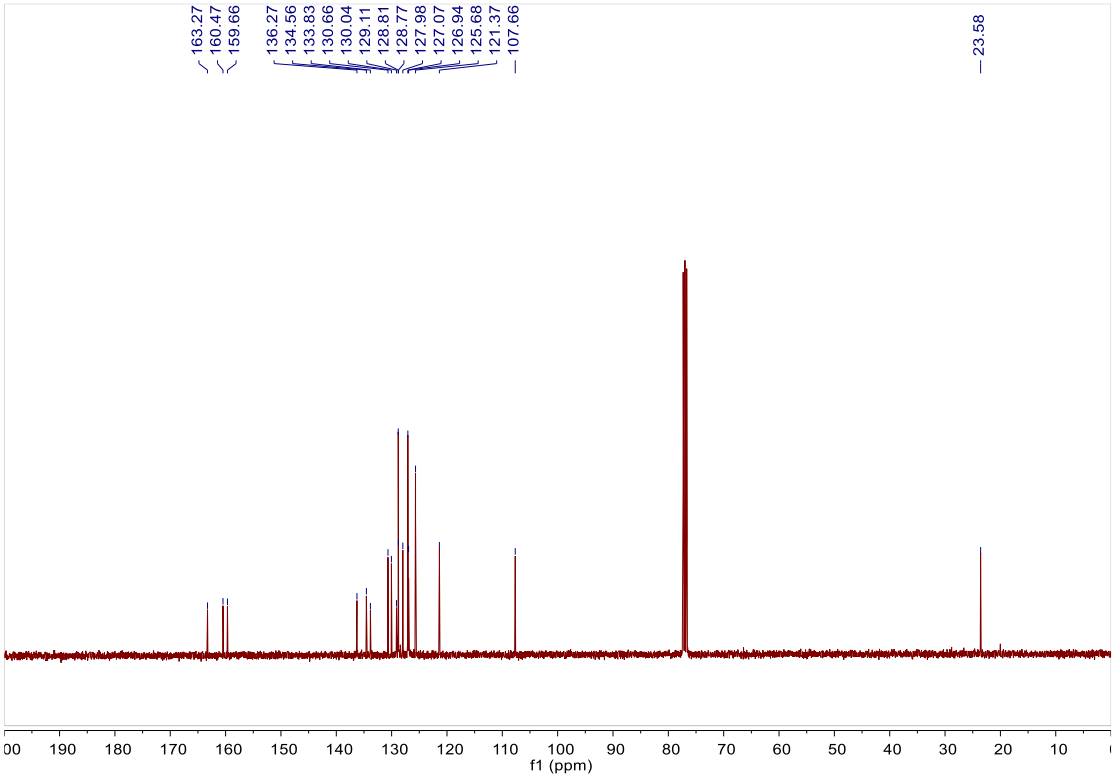
^{1}H and ^{13}C NMR spectra for product 3ak ($CDCl_3$)



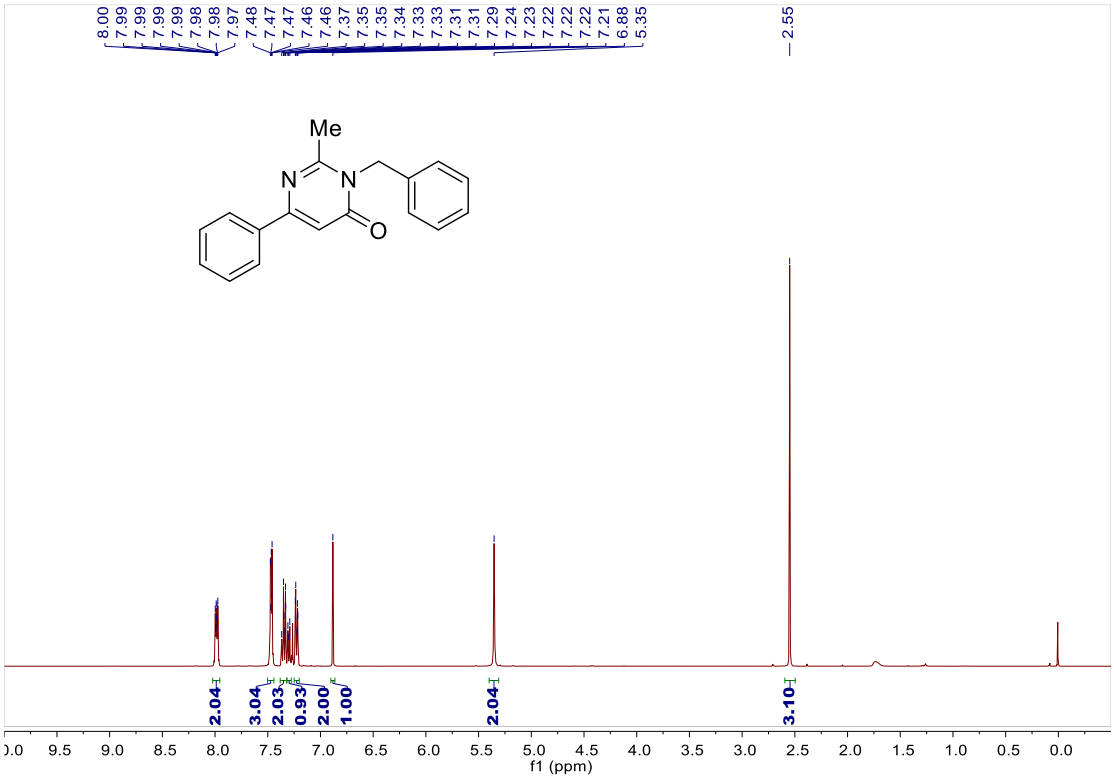


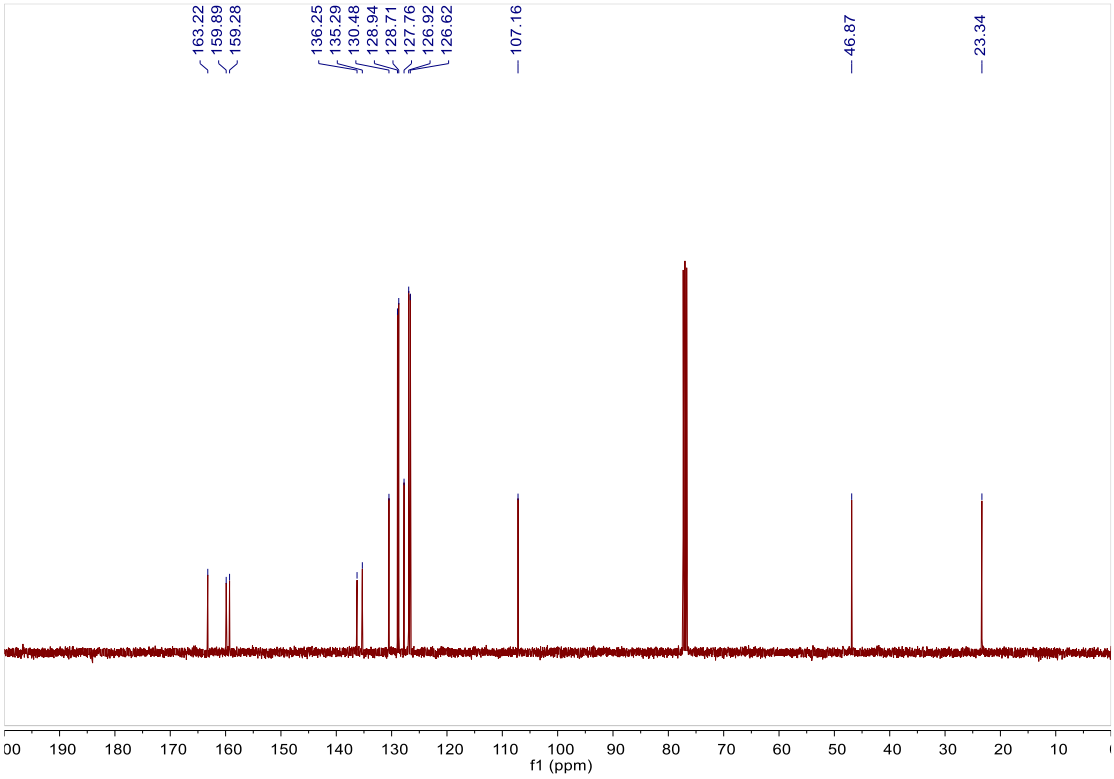
^{1}H and ^{13}C NMR spectra for product 3al ($CDCl_3$)



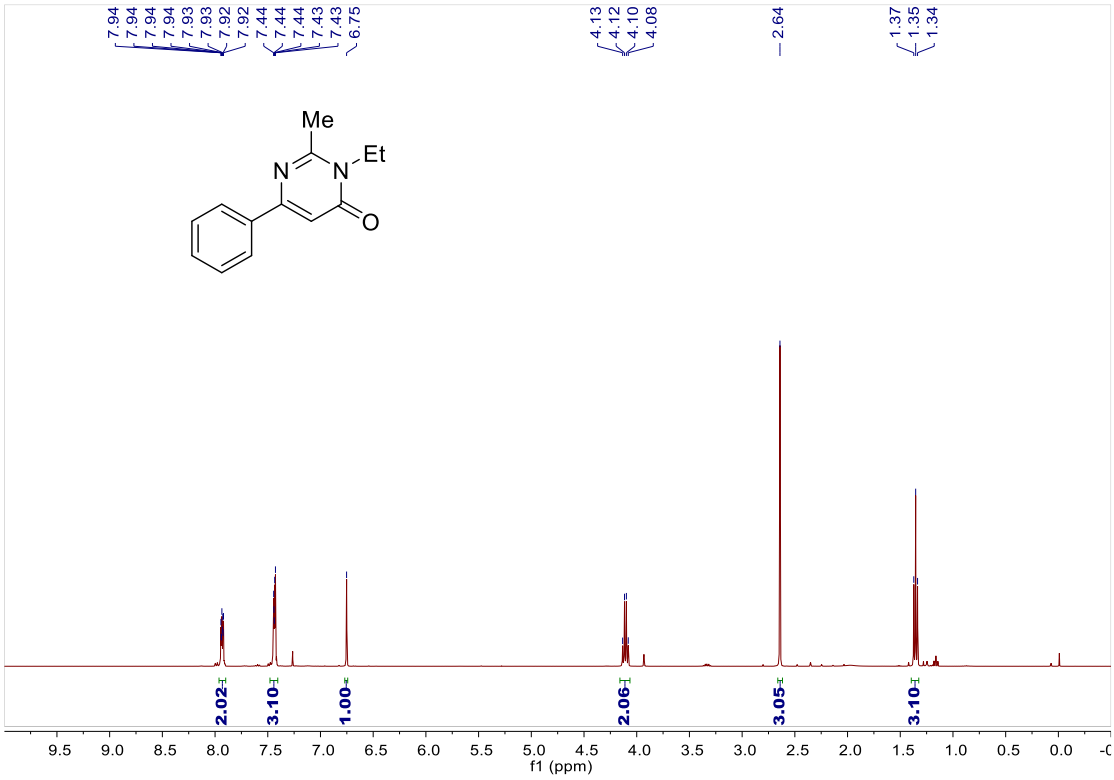


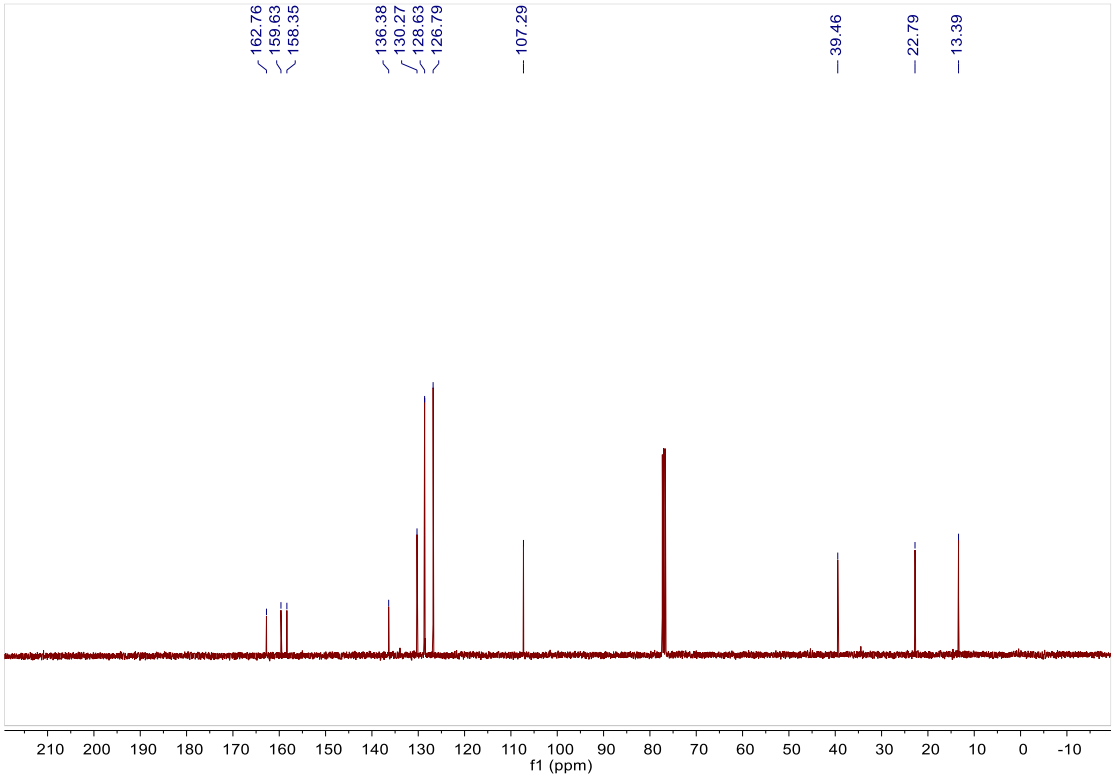
^{1}H and ^{13}C NMR spectra for product 3am ($CDCl_3$)



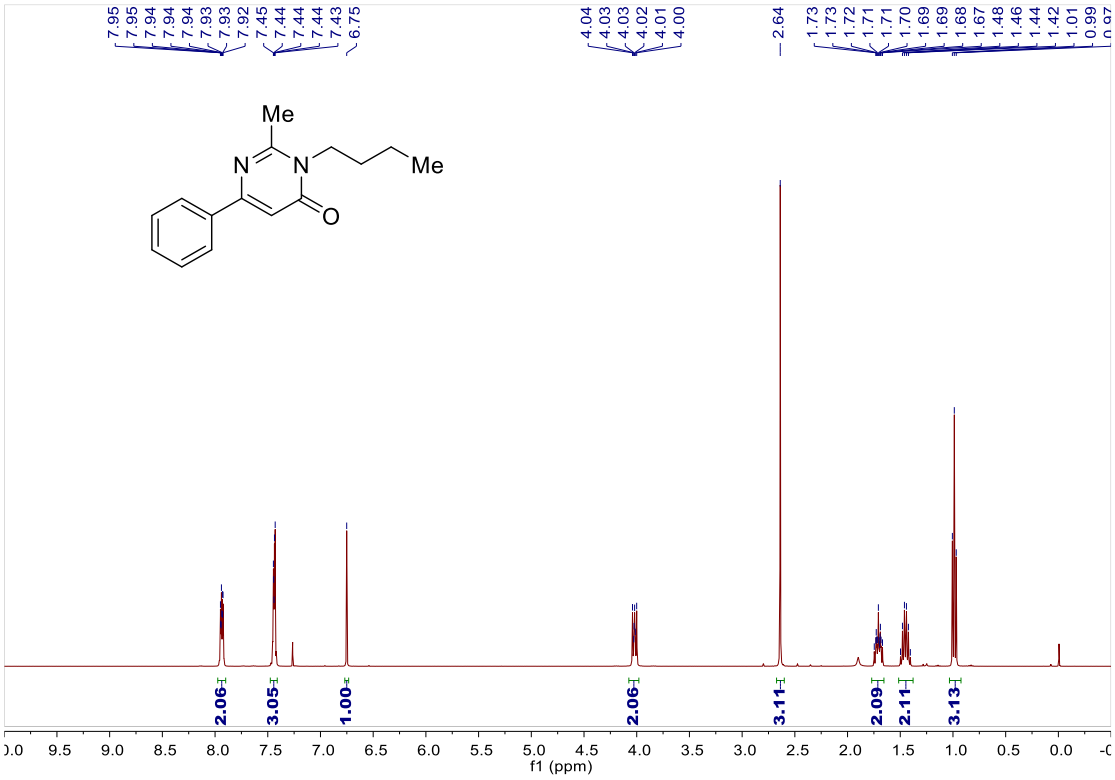


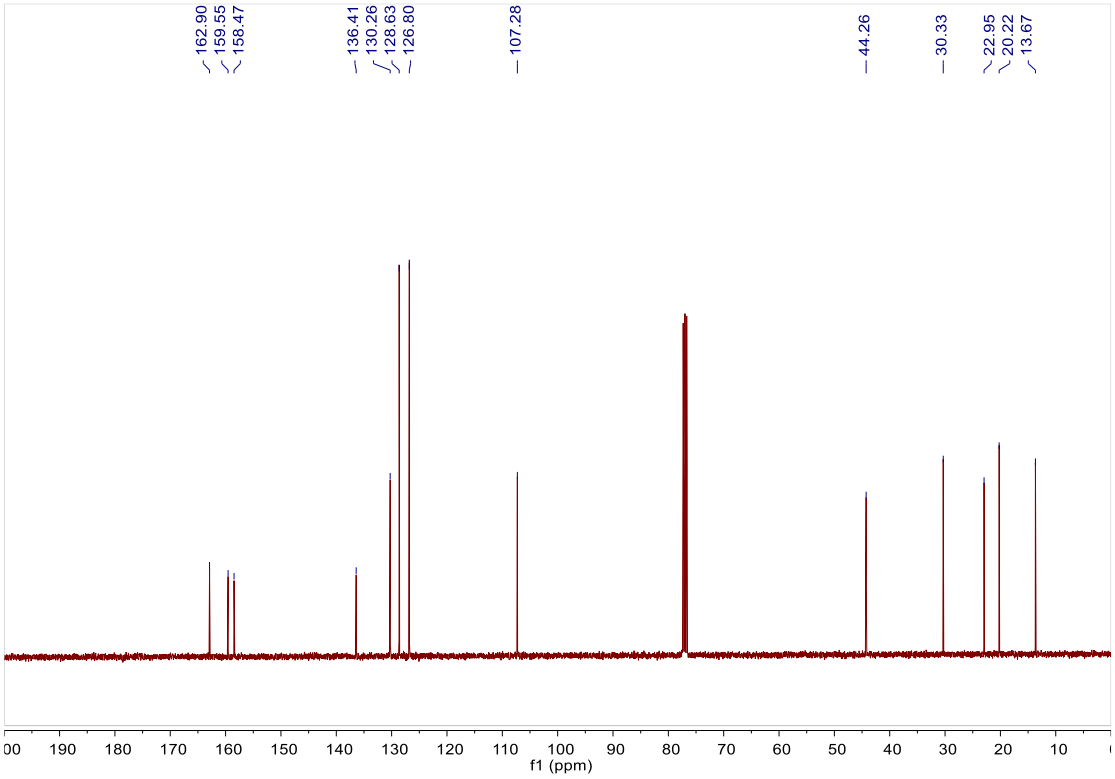
^{1}H and ^{13}C NMR spectra for product 3an ($CDCl_3$)



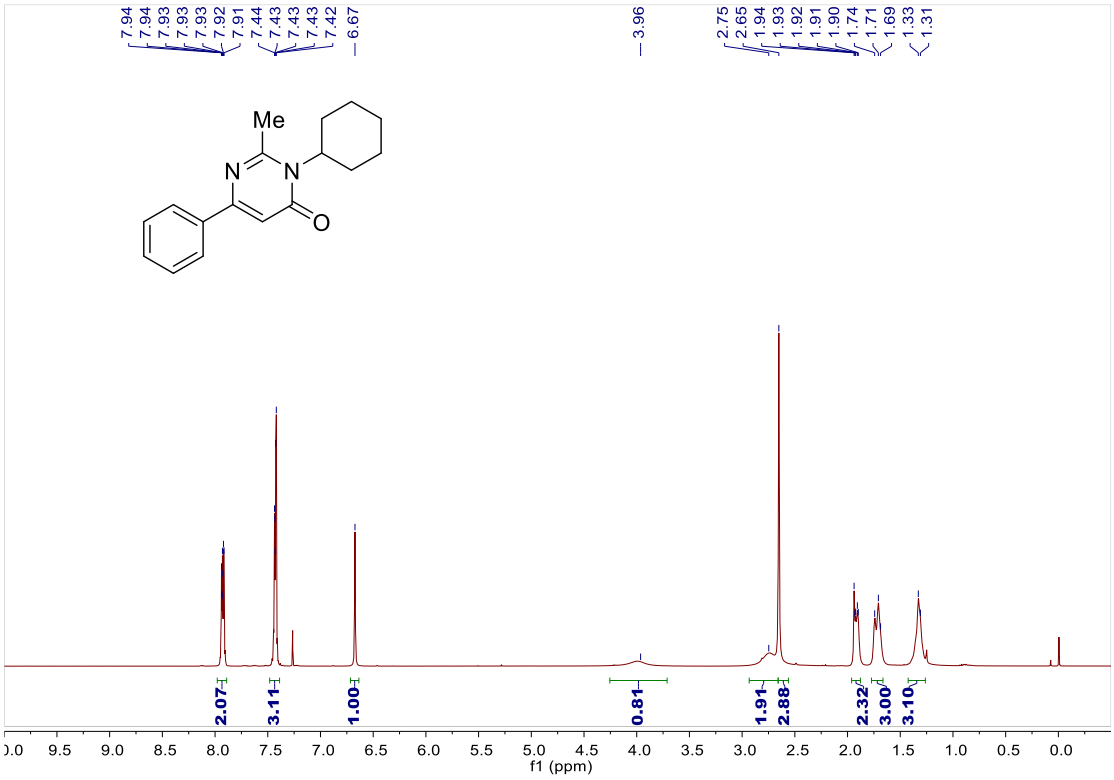


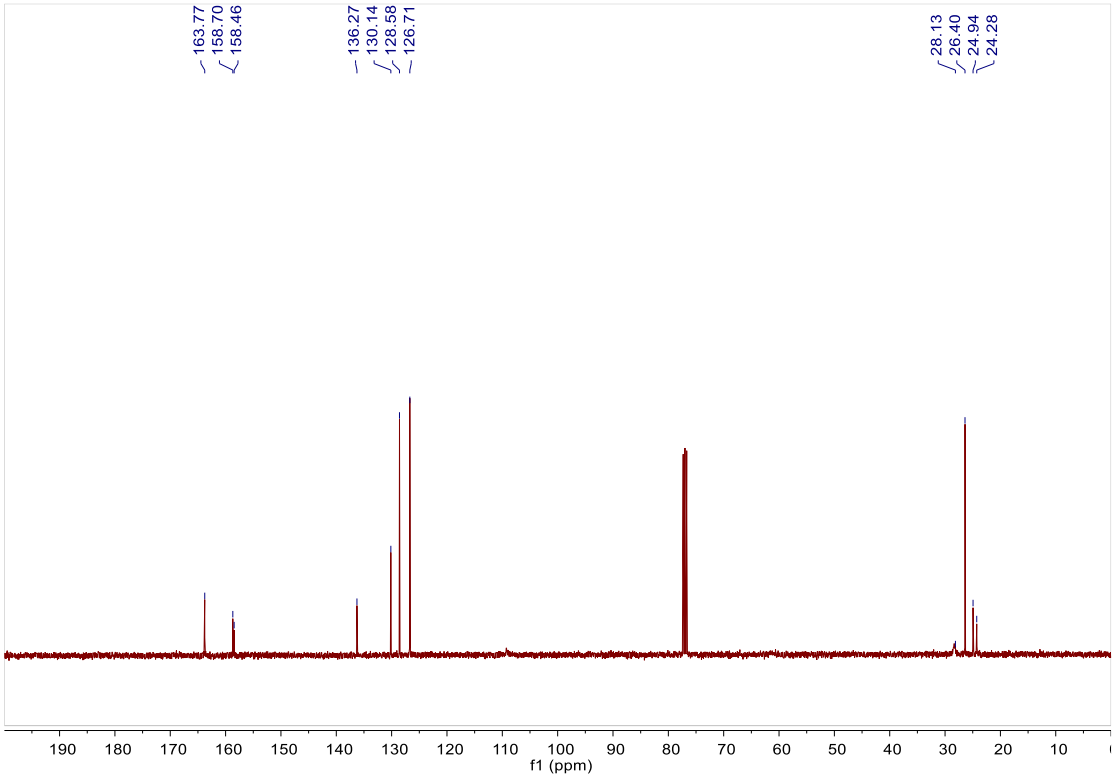
^{1}H and ^{13}C NMR spectra for product 3ao ($CDCl_3$)



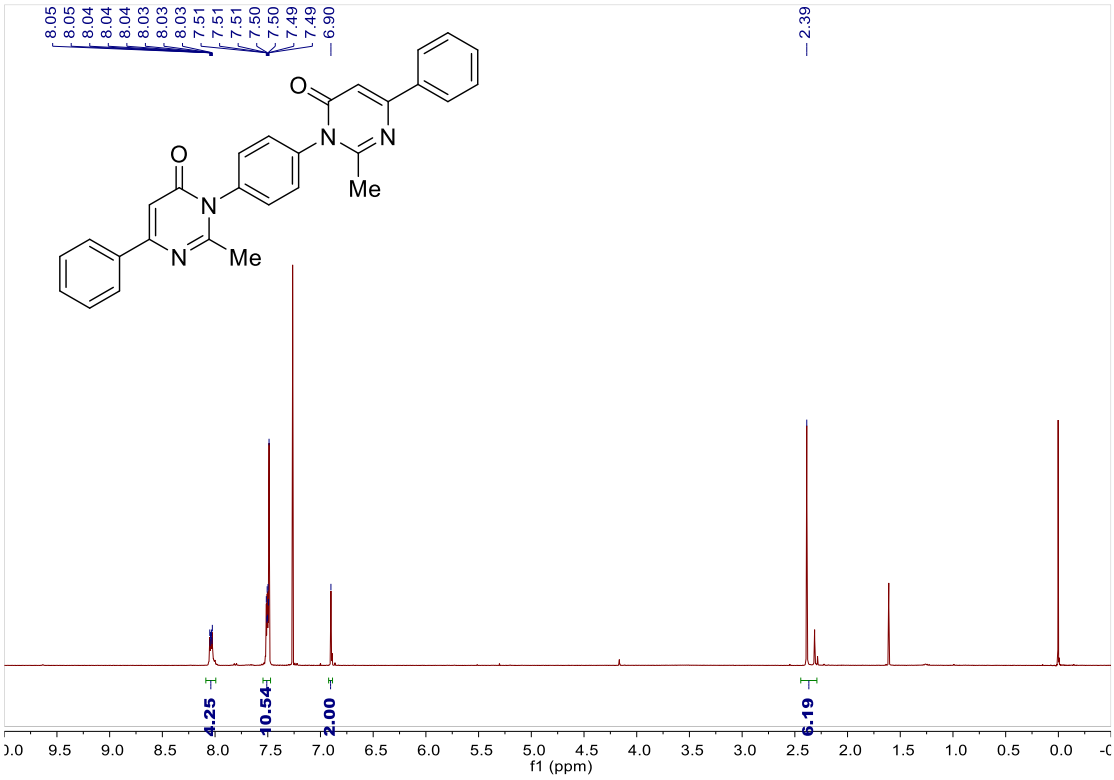


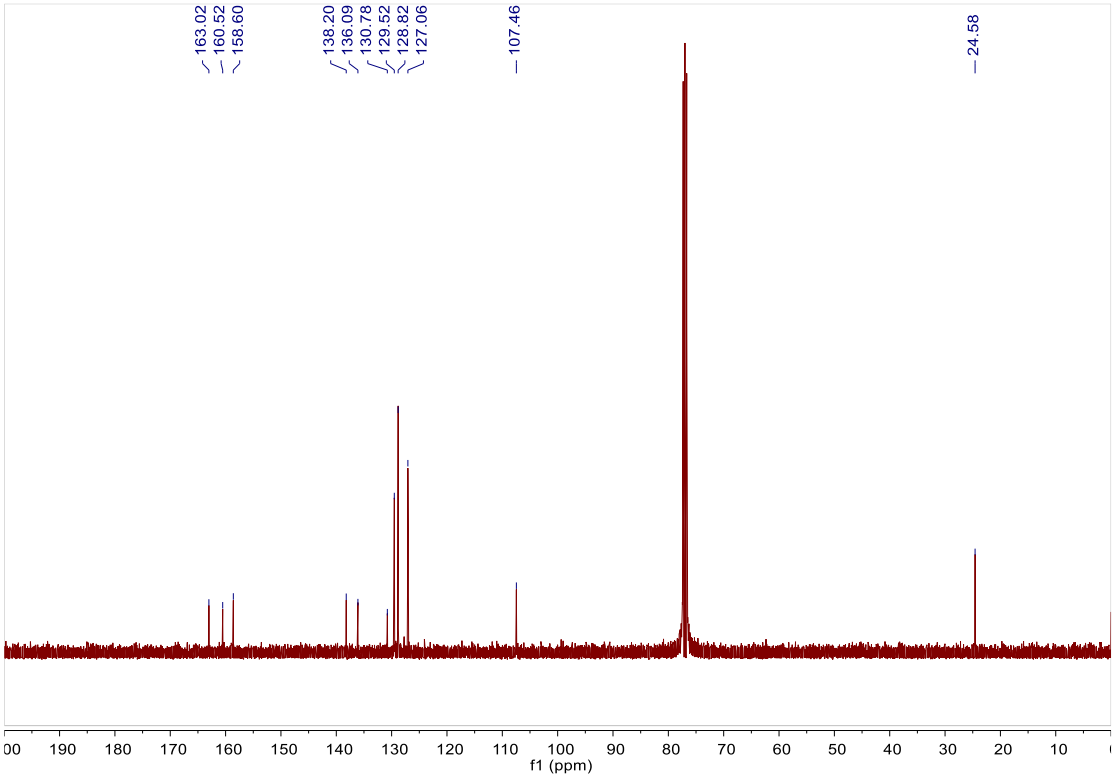
^{1}H and ^{13}C NMR spectra for product 3ap ($CDCl_3$)



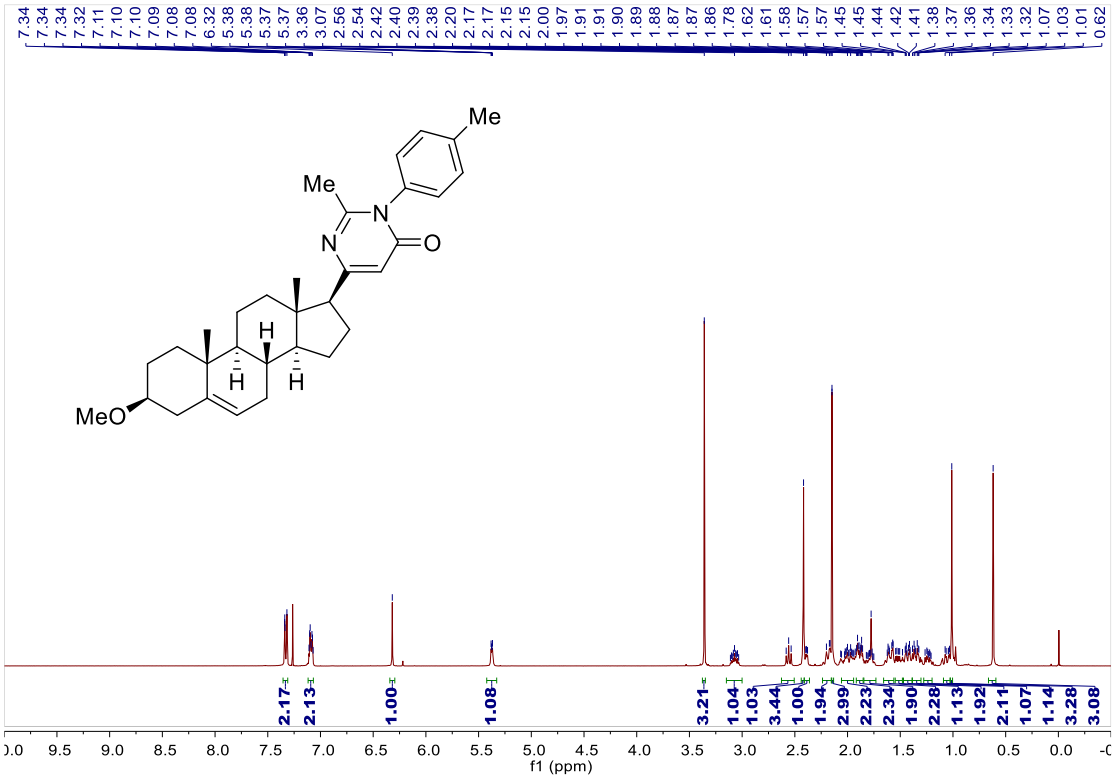


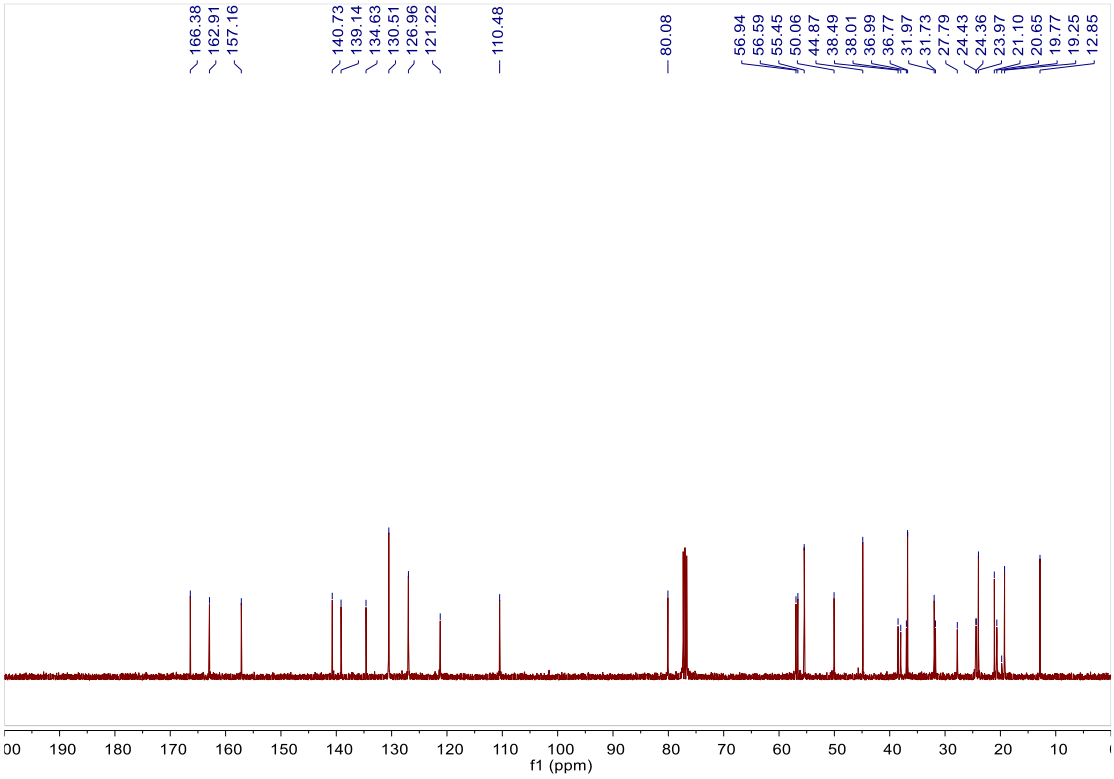
^{1}H and ^{13}C NMR spectra for product 3aq ($CDCl_3$)



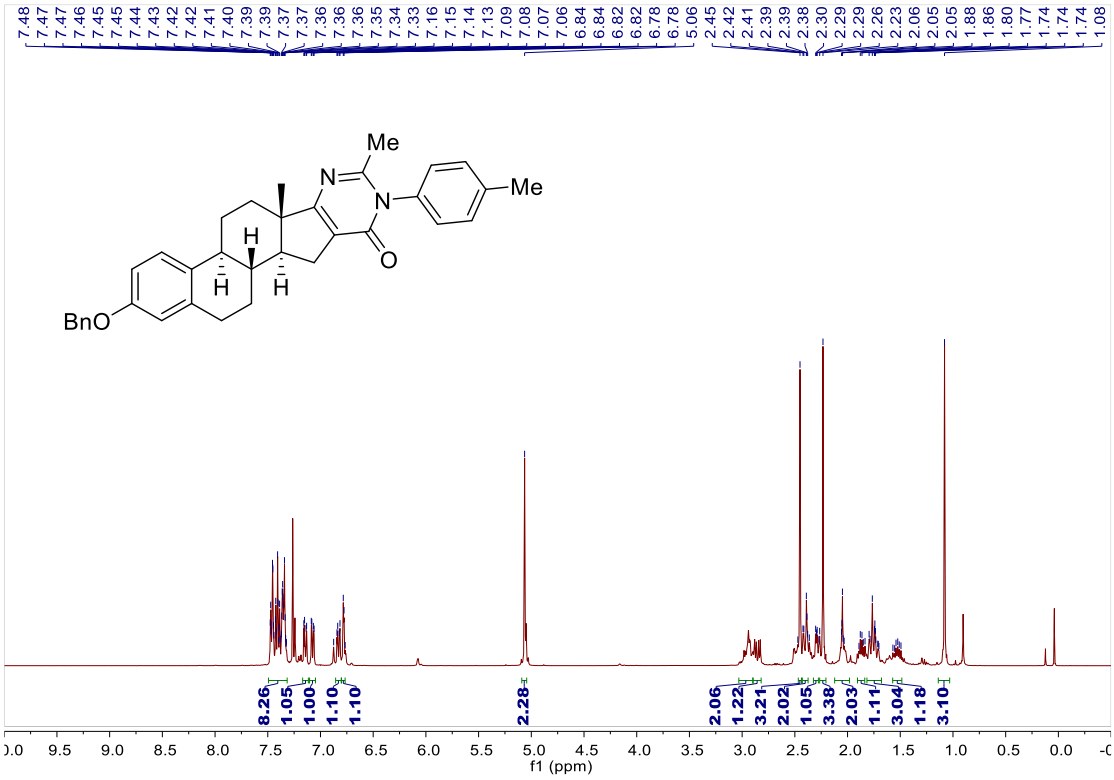


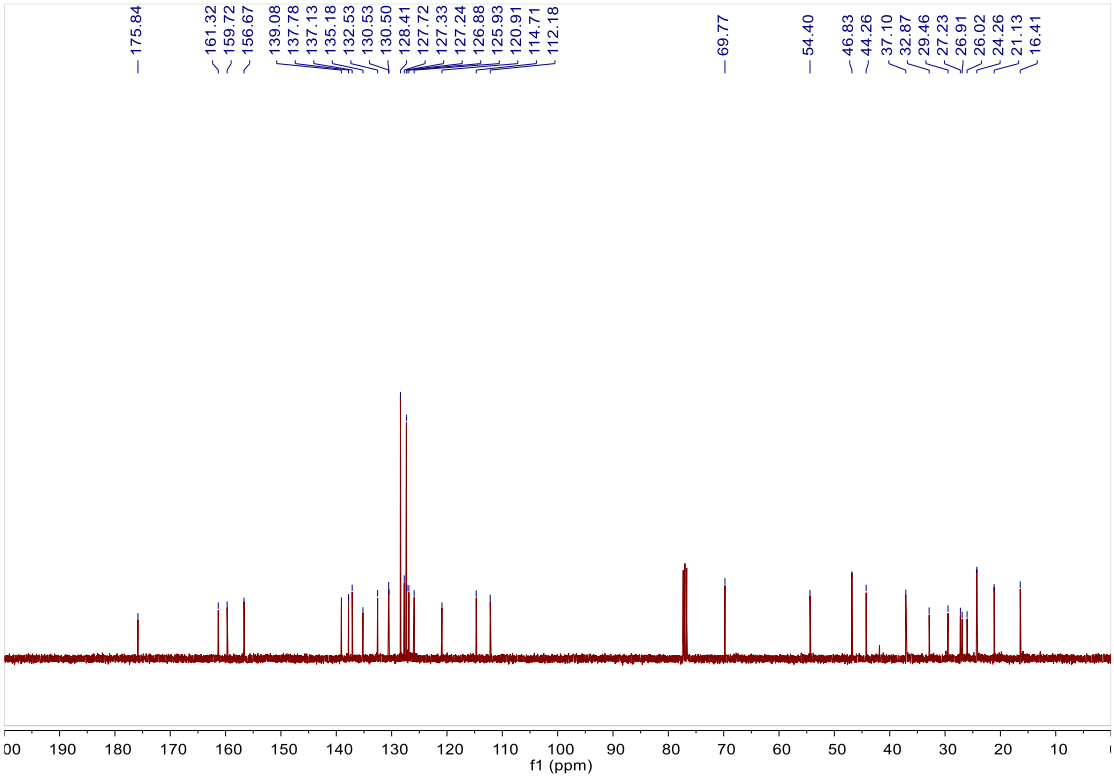
^{1}H and ^{13}C NMR spectra for product 3ar ($CDCl_3$)



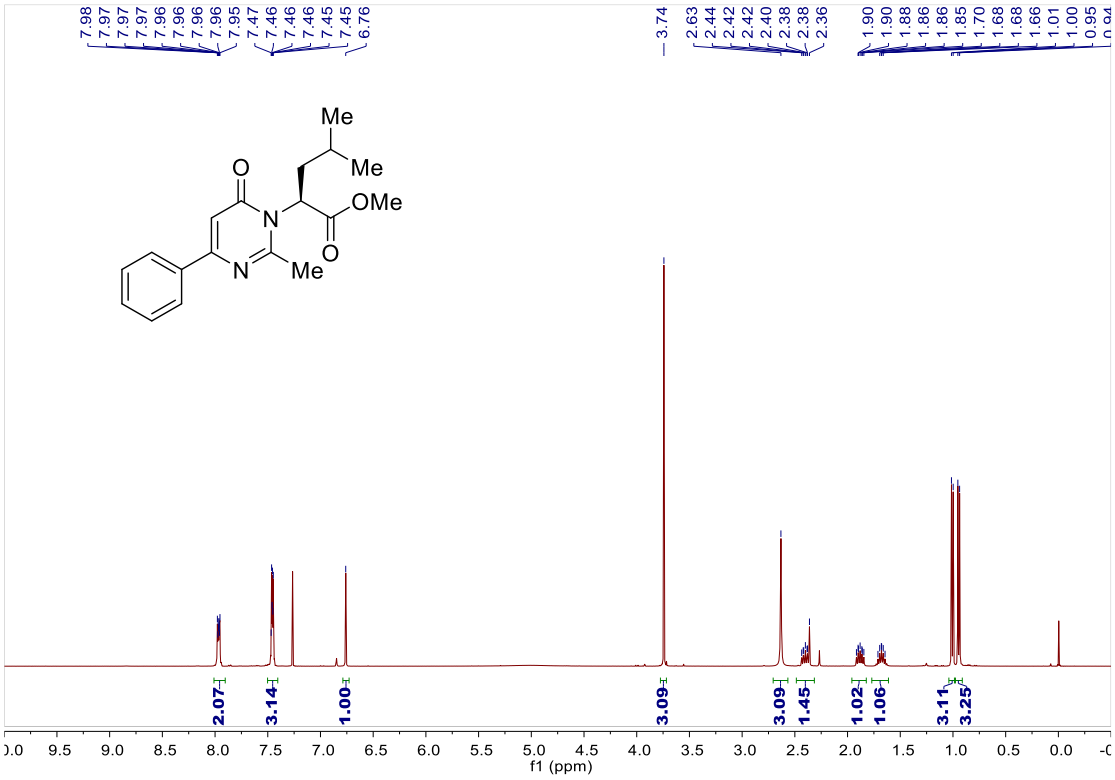


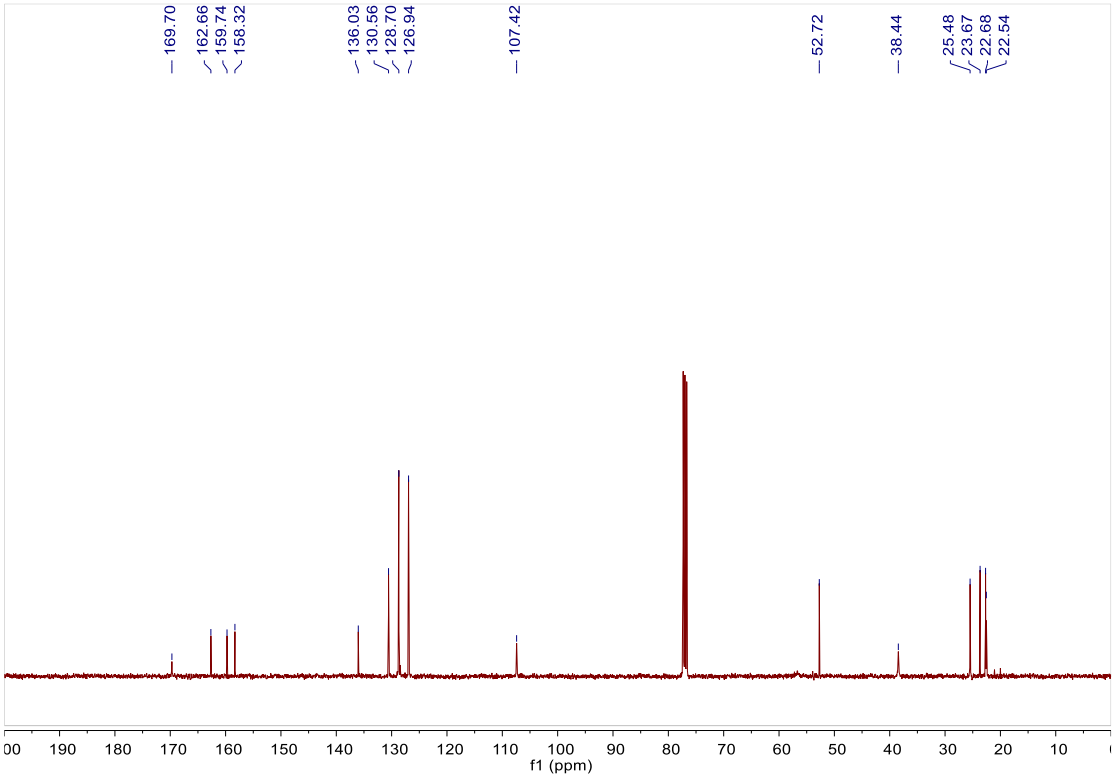
^{1}H and ^{13}C NMR spectra for product 5 ($CDCl_3$)





^{1}H and ^{13}C NMR spectra for product 7 ($CDCl_3$)





^{1}H and ^{13}C NMR spectra for product 9 ($CDCl_3$)