Supplementary Information for

Copper-catalyzed [4 + 2] annulation reaction of β-enaminones and aryl diazonium salts without external oxidant: access to highly functionalized 3*H*-1,2,4-triazines via homogeneous or heterogenous strategy.

Qifeng Ding,[a,b] Mingrui Li,[b] Yiming Sun,[b] Yang Yu,[c] Jonathan B. Baell,[b,d] and Fei Huang*[a,b]

[a]School of Food Science and Pharmaceutical Engineering, Nanjing Normal University, Nanjing, 210023, China.

[b]School of Pharmaceutical Sciences, Nanjing Tech University, Nanjing, 211816, China.

[c]School of Environmental Science and Engineering, Nanjing Tech University, Nanjing 211816, China

[d]Medicinal Chemistry Theme, Monash Institute of Pharmaceutical Sciences, Monash University, Parkville, Victoria 3052, Australia.

Email: huangfei0208@yeah.net

Experimental procedures and analytical data

Contents:

1. General considerations

^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Bruker DRX-400 spectrometer and all chemical shift values refer to δ_{TMS} = 0.00 ppm, $CDCl_3$ ($\delta(^{1}H)$, 7.26 ppm; $\delta(^{13}C)$, 77.16 ppm). The HRMS (EI) analysis was obtained on a Waters GC-TOF CA156 mass spectrometer. Analytical TLC plates, Sigma-Aldrich silica gel 60F200 were viewed by UV light (254 nm). Column chromatographic purifications were performed on SDZF silica gel 160. The valence states of elements in the copper catalyst were determined by X-ray photoelectron spectroscopy (XPS) using Thermo K-Alpha XPS. All the chemical reagents were purchased from commercial sources and used as received unless otherwise indicated. Compounds **1a-1c**, **1e**,[1] **1k**,[2] **1m**,[3] **1n**,[4] **2a-2j**[5] are known and their spectroscopic feature is in good agreement with that reported in the literature.

2. Supplementary Reference

(1) M. Z. Wu, Y. Jiang, Z. Y. An, Z. J. Qi and R. L. Yan, Iron-catalyzed synthesis of substituted thiazoles from enamines and elemental sulfur through C-S bond formation, *Adv. Synth. Catal.*, 2018, **360**, 4236.

(2) D. H. Lee, S. Park, K. Cho, Y. Kim, T. Athar and I. Lee, Highly efficient microwave-accelerated preparation of β-ketoimines, *Tetrahedron Lett.*, 2007, **48**, 8281.

(3) M. J. Kim, M. J. Jung, Y. J. Kim, H. K. Sung, J. Y. Lee, S. J. Ham and C. P. Park, Sublimable bis(β-iminoenolate)palladium(II) complexes and their application as catalysts in Suzuki-Miyaura reactions, *Tetrahedron Lett.*, 2018, **59**, 2989.

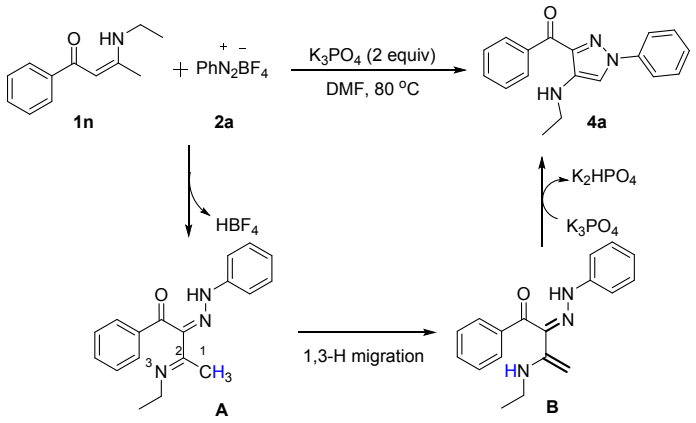
(4) A. P. Venkov and P. A. Angelov, Synthesis of unsymmetrical β-enamino ketones, *Synthesis*, 2003, **14**, 2221.

(5) Q. Y. Liu, B. Q. Sun, Z. Liu, Y. Kao, B. W. Dong, S. D. Jiang, F. Li, G. Q. Liu, Y. Yang and F. Y. Mo, A general electrochemical strategy for the Sandmeyer reaction, *Chem. Sci.*, 2018, **9**, 8731.

3. Experimental procedures

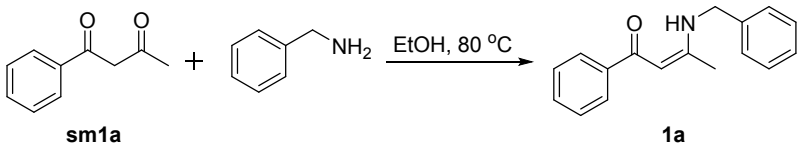
3.1 Pathway for the synthesis of pyrazole products

According to the formation of intermediate **5** for the 3*H*-1,2,4-triazine synthesis, the intermediate **A** could be formed (Scheme S1). Such imine **A** could be transformed to secondary amine **B** with conjugated structure through 1,3-H migration. Finally under the promotion of K_3PO_4, the C-N bond could be formed and the pyrazole product **4a** was formed.



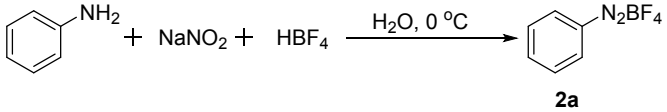
Scheme S1 Pathway for the synthesis of pyrazole products

3.2 Preparation of β-enaminones 1



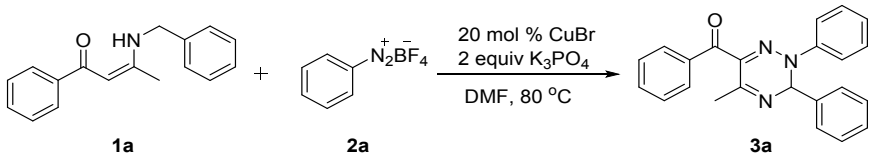
A typical procedure for the synthesis of *β*-enaminones (1a-1n) – ***Synthesis of 1a****:* A mixture of 1-phenyl-1,3-butanedione **sm1a** (324 mg, 2 mmol) and benzylamine (437 μL, 4 mmol) in EtOH (10 mL) were stirred at 80 °C overnight. After 1-phenyl-1,3-butanedione **sm1a** was completely consumed by TLC monitoring on silica gel, the resultant mixture was cooled to ambient temperature and evaporated all the volatiles under reduced pressure. The residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/AcOEt = 30:1, v/v), affording **1a** (427 mg, 85%) as a yellow solid.

3.3 Preparation of diazonium salts 2



A typical procedure for the synthesis of diazonium salts (2a-2j) – *Synthesis of 2a:* The diazonium salt **2a** was prepared according to literature procedure.[5] Appropriate aniline (25 mmol) was dissolved in water (10 mL) and hydrofluoroboric acid (48% w/w in water, 10.5 mL, 2.0 equiv). After the reaction mixture was cooled to 0 °C, sodium nitrile solution (1.73 g, 25 mmol in 6 mL water) was added dropwise. The reaction mixture was stirred at 0 °C for 40 min. The resulting precipitate was collected by filtration. The crude product was dissolved into acetone, and the solution was gently heated, then diethyl ether was added until the recrystallized product precipitated completely. The diazonium salt **2a** (white solid, 3.70 g, 77%) was collected by filtration, washed several times by cold diethyl ether and dried under vacuum.

3.4 Typical procedures for the synthesis of 3*H*-1,2,4-triazine (3)



A typical procedure for the synthesis of 3*H*-1,2,4-triazine (3) – *Synthesis of 3a:* a mixture of β-enaminone **1a** (126 mg, 0.5 mmol), diazonium salt **2a** (144 mg, 0.75 mmol), CuBr (14 mg, 0.1 mmol), and K_3PO_4 (212 mg, 1.0 mmol) in 5 mL DMF was stirred at 80 °C for 1.0 h. The reaction mixture was cooled to ambient temperature, filtered through a short pad of celite, rinsed with 20 mL of ethyl acetate, and evaporated all the volatiles under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/AcOEt = 15:1, v/v), affording **3a** as a yellow liquid (135 mg, 76%).

3.5 Preparation of polyhedron Cu_2O

0.159 g of $Cu(OAc)_2 \cdot H_2O$ was dissolved in 40 mL of deionized water in a beaker and stirred with a magnetic stirrer to give a clear solution. 8.0 mL of $N_2H_4 \cdot H_2O$ (0.1 mol/L) solution was quickly added into the mixture under vigorous stirring. The mixture was further stirred for 30 min to complete the reaction. Then, the precipitates were separated by centrifugation, washed with deionized water and absolute ethanol several times each, and dried in an oven at 60 °C for 4 h.

3.6 Typical procedures for the synthesis of 3*H*-1,2,4-triazine by polyhedron Cu_2O

A typical procedure for the synthesis of 3*H*-1,2,4-triazine (3) – *Synthesis of 3a*: a mixture of β-enaminone **1a** (126 mg, 0.5 mmol), diazonium salt **2a** (144 mg, 0.75 mmol), polyhedron Cu_2O (14 mg, 0.1 mmol), and K_3PO_4 (212 mg, 1.0 mmol) in 5 mL DMF was stirred at 80 ^oC for 1.0 h. The reaction mixture was cooled to ambient temperature, filtered through a short pad of celite, rinsed with 20 mL of ethyl acetate, and evaporated all the volatiles under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 ^oC)/AcOEt = 15:1, v/v), affording **3a** as a yellow liquid (115 mg, 65%).

3.7 X-Ray crystallographic studies

Single crystals for the X–ray diffraction studies for compounds **3k** was carried out on a SMART APEX diffractometer with graphite-monochromated Mo radiation (λ = 0.71073 Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package. The X-ray crystallographic files, in CIF format, are available from the Cambridge Crystallographic Data Centre on quoting the deposition numbers CCDC 1917695 for **3k**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www. ccdc.cam.ac.uk).

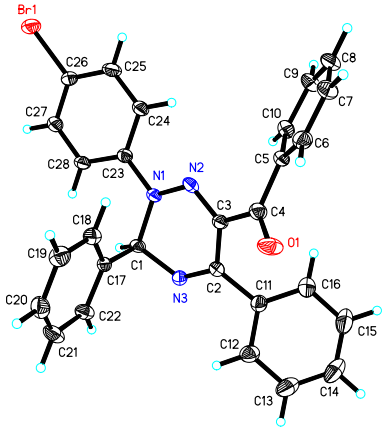
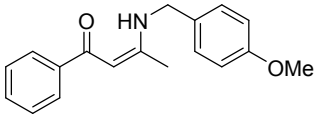


Figure 1. Molecular structure of compound **3k**.

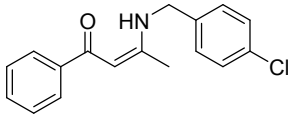
Table S2. Crystal data and structure refinement for **3k**.

Empirical formula	$C_{28}H_{20}BrN_3O$	
Formula weight	494.38	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Orthorhombic	
Unit cell dimensions	a = 15.2746(6) Å	□α = 90°
	b = 18.9300(6) Å	□β = 90°
	c = 8.0164(3) Å	□γ = 90°
Volume	2317.93(15) $Å^3$	
Z, Calculated density	4, 1.417 Mg/m^3	
Absorption coefficient	1.799 mm^{-1}	
F(000)	1008.0	
Crystal size	0.200 x 0.170 x 0.120 mm^3	
Theta range for data collection	2.532 to 26.000°	
Index ranges	-18<=h<=14, -20<=k<=23, -9<=l<=9	
Reflections collected/unique	10978	
Completeness to theta = 25.242	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.4664	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	4468 / 0 / 299	
Goodness-of-fit on F^2	1.011	
Final R indices [I > 2 sigma(I)]	R1 = 0.0296, wR2 = 0.0645	
R indices (all data)	R1 = 0.0372, wR2 = 0.0677	
Largest diff. peak and hole	0.241 and -0.242 $e.Å^{-3}$	

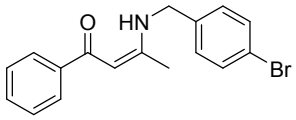
4. Analytical data for new compounds



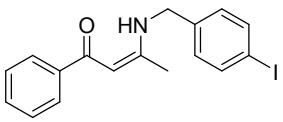
(*Z*)-3-((4-methoxybenzyl)amino)-1-phenylbut-2-en-1-one (1d): 506 mg, yield 90%, yellow solid, m.p.: 104-106 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.69 (s, 1H), 7.87 (dd, *J* = 7.7, 1.8 Hz, 2H), 7.47-7.35 (m, 3H), 7.23 (dd, *J* = 8.3, 0.5 Hz, 2H), 6.98-6.81 (m, 2H), 5.74 (s, 1H), 4.47 (d, *J* = 6.2 Hz, 2H), 3.79 (s, 3H), 2.07 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 188.04, 164.91, 159.14, 140.41, 130.61, 129.78, 128.36, 128.26, 127.02, 114.37, 92.59, 55.41, 46.66, 19.64. HRMS (EI) calcd for $C_{18}H_{19}NO_2$ $[M+H]^+$: 282.1494; Found: 282.1484.



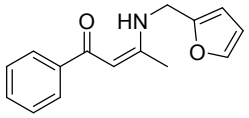
(*Z*)-3-((4-chlorobenzyl)amino)-1-phenylbut-2-en-1-one (1f): 456 mg, yield 80%, white solid, m.p.: 122-124 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.74 (s, 1H), 7.88 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.46-7.37 (m, 3H), 7.35 -7.29 (m, 2H), 7.23 (d, *J* = 8.5, 2H), 5.77 (s, 1H), 4.49 (d, *J* = 6.3 Hz, 2H), 2.04 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 188.34, 164.78, 140.19, 136.40, 133.41, 130.75, 129.09, 128.28, 127.02, 92.89, 46.41, 19.53. HRMS (EI) calcd for $C_{17}H_{16}ClNO$ $[M+H]^+$: 286.0999; Found: 286.1002.



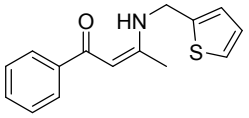
(*Z*)-3-((4-bromobenzyl)amino)-1-phenylbut-2-en-1-one (1g): 579 mg, yield 88%, yellow solid, m.p.: 118-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.74 (s, 1H), 7.87 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.48 (dd, *J* = 8.4, 0.2 Hz, 2H), 7.44-7.37 (m, 3H), 7.18 (d, *J* = 8.4 Hz, 2H), 5.77 (s, 1H), 4.49 (d, *J* = 6.3 Hz, 2H), 2.05 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 188.45, 164.81, 140.22, 136.98, 132.10, 130.80, 128.65, 128.33, 127.07, 121.53, 92.98, 46.51, 19.59. HRMS (EI) calcd for $C_{17}H_{16}BrNO$ $[M+H]^+$: 330.0494; Found: 330.0499.



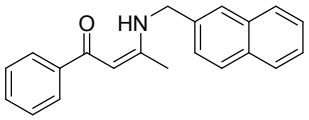
(*Z*)-3-((4-iodobenzyl)amino)-1-phenylbut-2-en-1-one (1h): 543 mg, yield 72%, white solid, m.p.: 101-103 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.73 (s, 1H), 7.87 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.68 (dd, *J* = 8.4, 1.8 Hz, 2H), 7.47-7.34 (m, 3H), 7.06 (d, *J* = 8.4 Hz, 2H), 5.76 (s, 1H), 4.48 (d, *J* = 6.3 Hz, 2H), 2.04 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 188.44, 164.81, 140.22, 138.06, 137.69, 130.80, 128.89, 128.33, 127.08, 93.02, 92.98 46.60, 19.59. HRMS (EI) calcd for $C_{17}H_{16}INO$ $[M+H]^+$: 378.0355; Found: 378.0355.



(*Z*)-3-((furan-2-ylmethyl)amino)-1-phenylbut-2-en-1-one (1i): 405 mg, yield 84%, yellow solid, m.p.: 50-52 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.59 (s, 1H), 7.86 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.46-7.35 (m, 4H), 6.33 (t, *J* = 3.2 Hz, 1H), 6.26 (d, *J* = 3.2 Hz, 1H), 5.74 (s, 1H), 4.49 (d, *J* = 6.2 Hz, 2H), 2.16 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 188.31, 164.53, 150.97, 142.57, 140.28, 130.69, 128.26, 127.04, 110.53, 107.53, 92.94, 40.36, 19.47. HRMS (EI) calcd for $C_{15}H_{15}NO_2$ $[M+H]^+$: 242.1181; Found: 242.1183.

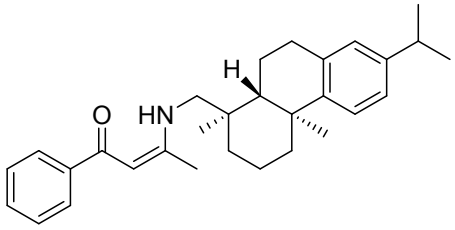


(*Z*)-1-phenyl-3-((thiophen-2-ylmethyl)amino)but-2-en-1-one (1j): 460 mg, yield 89%, yellow solid, m.p.: 61-63 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.69 (s, 1H), 7.88 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.44-7.36 (m, 3H), 7.23-7.20 (m, 1H), 7.06-6.92 (m, 2H), 5.75 (s, 1H), 4.68 (d, *J* = 6.2 Hz, 2H), 2.12 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 188.35, 164.23, 140.82, 140.26, 130.71, 128.26, 127.17, 127.06, 125.45, 125.16, 92.95, 42.25, 19.49. HRMS (EI) calcd for $C_{15}H_{15}NOS$ $[M+H]^+$: 258.0953; Found: 258.0953.

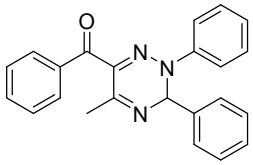


(*Z*)-3-((naphthalen-2-ylmethyl)amino)-1-phenylbut-2-en-1-one (1l): 542 mg, yield 90%, white solid, m.p.: 109-111 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.88 (s, 1H), 7.96-7.89 (m, 2H), 7.88-7.80 (m, 3H), 7.75 (s, 1H), 7.51-7.47 (m, 2H), 7.46-7.36 (m,

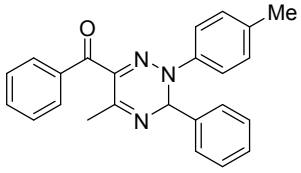
4H), 5.80 (s, 1H), 4.70 (d, *J* = 6.4 Hz, 2H), 2.09 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 188.28, 165.09, 140.39, 135.38, 133.54, 132.89, 130.69, 128.87, 128.30, 127.93, 127.81, 127.08, 126.47, 126.10, 125.53, 125.03, 92.85, 47.27, 19.62. HRMS (EI) calcd for $C_{21}H_{19}NO$ [M+H]+: 302.1545; Found: 302.1546.



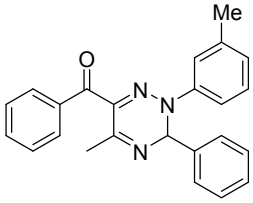
(*Z*)-3-((((1R,4aS,10aR)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)amino)-1-phenylbut-2-en-1-one (1o): 483 mg, yield 56%, white solid, m.p.: 147-149 °C. ^{1}H NMR (400 MHz,$CDCl_3$) δ 11.76 (t, *J* = 5.8 Hz, 1H), 7.90-7.81 (m, 2H), 7.43-7.34 (m, 3H), 7.18 (d, *J* = 8.2 Hz, 1H), 7.00 (dd, *J* = 8.1, 1.7 Hz, 1H), 6.91 (s, 1H), 5.66 (s, 1H), 3.35-3.28 (m, 1H), 3.14-3.08 (m, 1H), 2.96 (t, *J* = 6.8 Hz, 2H), 2.87-2.79 (m, 1H), 2.35-2.27 (m, 1H), 2.07 (s, 3H), 1.88-1.70 (m, 5H), 1.58-1.54 (m, 1H), 1.50-1.35 (m, 2H), 1.27-1.22 (m, 9H), 1.05 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 187.77, 165.18, 147.08, 145.78, 140.67, 134.58, 130.42, 128.21, 127.03, 126.95, 124.43, 124.09, 92.57, 55.40, 46.71, 38.36, 37.92, 37.16, 36.49, 33.58, 30.35, 25.54, 24.11, 19.78, 19.49, 18.73, 18.27. HRMS (EI) calcd for $C_{30}H_{39}NO$ [M+H]+: 430.3110; Found: 430.3120.



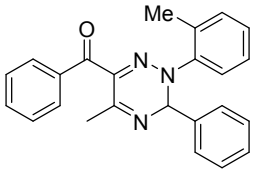
(5-methyl-2,3-diphenyl-2,3-dihydro-1,2,4-triazin-6-yl)(phenyl)methanone (3a): 135 mg, yield 76%, yellow liquid. ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.94-7.88 (m, 2H), 7.59-7.55 (m, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.36-7.28 (m, 9H), 7.18-7.14 (m,1 H), 6.99 (s, 1H), 2.42 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 189.57, 156.89, 143.41, 137.92, 137.54, 137.39, 132.32, 130.39, 129.56, 129.18, 128.98, 128.12, 126.15, 125.49, 117.65, 72.65, 23.15. HRMS (EI) calcd for $C_{23}H_{19}N_3O$ [M+H]+: 354.1606; Found: 354.1610.



(5-methyl-3-phenyl-2-(p-tolyl)-2,3-dihydro-1,2,4-triazin-6-yl)(phenyl)methanone (3b): 130 mg, yield 71%, yellow liquid. ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.97-7.87 (m, 2H), 7.60-7.52 (m, 1H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.39-7.29 (m, 5H), 7.21 (dd, *J* = 8.5, 0.3 Hz, 2 H), 7.13 (dd, *J* = 8.9, 0.4 Hz, 2H), 6.97 (s, 1H), 2.44 (s, 3H), 2.32 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 189.58, 156.77, 141.24, 138.13, 137.78, 137.23, 135.24, 132.05, 130.34, 130.02, 129.04, 128.75, 127.98, 126.11, 117.57, 73.06, 23.36, 20.88. HRMS (EI) calcd for $C_{24}H_{21}N_3O$ [M+H]+: 368.1763; Found: 368.1767.

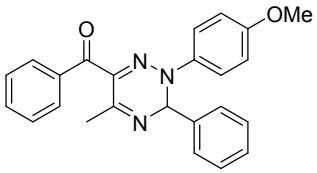


(5-methyl-3-phenyl-2-(m-tolyl)-2,3-dihydro-1,2,4-triazin-6-yl)(phenyl)methanone (3c): 162 mg, yield 88%, yellow liquid. ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.96-7.87 (m, 2H), 7.61-7.53 (m, 1H), 7.52-7.45 (m, 2H), 7.37-7.31 (m, 5H), 7.23-7.14 (m, 2H), 7.09-7.06 (m, 1H), 6.99 (s, 1H), 6.98 (s, 1H), 2.42 (s, 3H), 2.32 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 189.65, 156.80, 143.53, 139.53, 138.05, 137.80, 137.61, 132.20, 130.44, 129.31, 129.08, 128.79, 128.01, 126.18, 126.15, 118.31, 114.69, 72.90, 23.33, 21.80. HRMS (EI) calcd for $C_{24}H_{21}N_3O$ [M+H]+: 368.1763; Found: 368.1768.

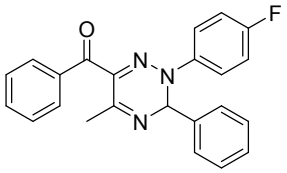


(5-methyl-3-phenyl-2-(o-tolyl)-2,3-dihydro-1,2,4-triazin-6-yl)(phenyl)methanone (3d): 117 mg, yield 64%, yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21-8.13 (m, 2H), 8.11 (s, 1H), 7.66 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.48-7.37 (m, 5H), 7.05 (d, *J* = 7.4 Hz, 1H), 6.98 (t, *J* = 7.7 Hz, 1H), 6.79 (t, *J* = 7.3 Hz, 1H), 6.10 (d, *J* = 8.0 Hz, 1H), 2.38 (s, 3H), 2.10 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

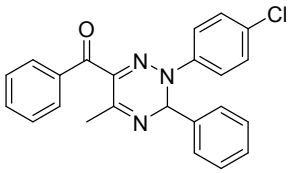
δ 187.38, 149.94, 146.32, 145.09, 138.52, 132.94, 130.79, 130.11, 129.23, 128.74, 128.70, 128.60, 128.33, 127.19, 127.18, 123.93, 122.14, 111.75, 17.07, 16.59. HRMS (EI) calcd for $C_{24}H_{21}N_3O$ [M+H]+: 368.1763; Found: 368.1768.



(2-(4-methoxyphenyl)-5-methyl-3-phenyl-2,3-dihydro-1,2,4-triazin-6-yl)(phenyl)methanone (3e): 135 mg, yield 70%, yellow liquid. ^{1}H NMR (400 MHz,$CDCl_3$) δ 8.02-7.75 (m, 2H), 7.59-7.51 (m, 1H), 7.50-7.43 (m, 2H), 7.40-7.29 (m, 5H), 7.23 (dd, *J* = 7.1, 2.2 Hz, 2H), 6.92 (s, 1H), 6.85 (dd, *J* = 7.0, 2.2 Hz, 2H), 3.76 (s, 3H), 2.43 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 189.56, 157.56, 156.71, 138.25, 137.80, 137.16, 136.98, 131.95, 130.27, 129.06, 128.78, 127.96, 126.08, 119.22, 114.64, 73.53, 55.60, 23.35. HRMS (EI) calcd for $C_{24}H_{21}N_3O_2$ [M+H]+: 384.1712; Found: 384.1720.

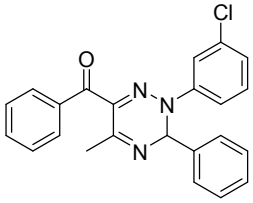


(2-(4-fluorophenyl)-5-methyl-3-phenyl-2,3-dihydro-1,2,4-triazin-6-yl)(phenyl)methanone (3f): 136 mg, yield 73%, yellow liquid. ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.94-7.82 (m, 2H), 7.60-7.54 (m, 1H), 7.52-7.45 (m, 2H), 7.39-7.30 (m, 5H), 7.25-7.21 (m, 2H), 7.06-6.98 (m, 2H), 6.91 (s, 1H), 2.40 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 189.62, 160.33 (d, *J* = 247 Hz), 156.56, 139.84 (d, *J* = 2.5 Hz), 137.96, 137.56, 137.49, 132.32, 130.33, 129.23, 129.01, 128.13, 126.10, 119.18 (d, *J* = 8.2 Hz), 116.32 (d, *J* = 22.9 Hz), 73.36, 23.34. HRMS (EI) calcd for $C_{23}H_{18}FN_3O$ [M+H]$^+$: 372.1512; Found: 372.1521.

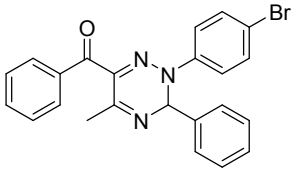


(2-(4-chlorophenyl)-5-methyl-3-phenyl-2,3-dihydro-1,2,4-triazin-6-

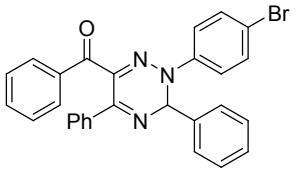
yl)(phenyl)methanone (3g): 130 mg, yield 67%, yellow liquid. ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.86 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.59-7.51 (m, 1H), 7.48-7.43 (m, 2H), 7.35-7.27 (m, 5H), 7.25-7.23 (m, 2 H), 7.17 (dd, *J* = 7.0, 2.0 Hz, 2H), 6.90 (s, 1H), 2.37 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 189.59, 156.53, 142.06, 137.80, 137.55, 137.44, 132.45, 130.62, 130.35, 129.57, 129.25, 129.05, 128.16, 126.09, 118.54, 72.92, 23.35. HRMS (EI) calcd for $C_{23}H_{18}ClN_3O$ $[M+H]^+$: 388.1217; Found: 388.1227.



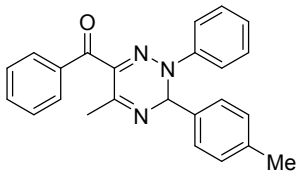
(2-(3-chlorophenyl)-5-methyl-3-phenyl-2,3-dihydro-1,2,4-triazin-6-yl)(phenyl)methanone (3h): 93 mg, yield 48%, orange solid, m.p.: 72-74 ^{o}C. ^{1}H NMR (400 MHz,$CDCl_3$) δ 8.07-7.75 (m, 2H), 7.65-7.55 (m, 1H), 7.54-7.47 (m, 2H), 7.36-7.32 (m, 6H), 7.23 (t, *J* = 8.1 Hz, 1H), 7.12-7.09 (m, 2H), 6.93 (s, 1H), 2.40 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 189.54, 156.45, 144.55, 137.82, 137.57, 137.35, 135.50, 132.59, 130.47, 130.40 129.24, 129.04, 128.18, 126.07, 124.94, 117.68, 115.05, 72.74, 23.27. HRMS (EI) calcd for $C_{23}H_{18}ClN_3O$ $[M+H]^+$: 388.1217; Found: 388.1226.



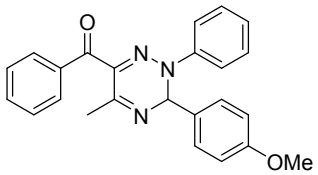
(2-(4-bromophenyl)-5-methyl-3-phenyl-2,3-dihydro-1,2,4-triazin-6-yl)(phenyl)methanone (3j): 125 mg, yield 58%, yellow liquid. ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.89 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.63-7.55 (m, 1H), 7.50-7.46 (m, 2H), 7.45-7.40 (m, 2H), 7.36-7.30 (m, 5H), 7.14 (dd, *J* = 7.0, 2.1 Hz, 2H), 6.92 (s, 1H), 2.40 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 189.59, 156.52, 142.54, 137.77, 137.56, 137.41, 132.50, 132.47, 130.36, 129.26, 129.06, 128.17, 126.08, 118.84, 118.29, 72.83, 23.37. HRMS (EI) calcd for $C_{23}H_{18}BrN_3O$ $[M+H]^+$: 432.0711; Found: 432.0706.



(3-(4-bromophenyl)-3,5-diphenyl-2,3-dihydro-1,2,4-triazin-6-yl)(phenyl)methanone (3k): 128 mg, yield 52%, yellow solid, m.p.: 193-195 ^{o}C. ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.97 (dd, *J* = 8.1, 0.9 Hz, 2H), 7.51-7.39 (m, 6H), 7.38-7.27 (m, 8H), 7.26-7.22 (m, 2H), 7.20 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 188.09, 157.87, 142.63, 139.72, 136.62, 136.30, 136.26 133.03, 132.57, 130.44, 130.21, 129.18, 129.05, 128.43, 128.35, 128.10, 126.33, 119.09, 118.33, 73.02. HRMS (EI) calcd for $C_{28}H_{20}BrN_3O$ $[M+H]^+$: 494.0868; Found: 494.0869.

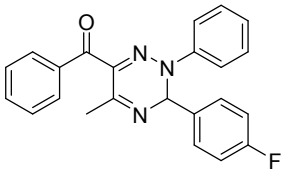


(5-methyl-2-phenyl-3-(p-tolyl)-2,3-dihydro-1,2,4-triazin-6-yl)(phenyl)methanone (3l): 142 mg, yield 77%, yellow liquid. ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.95 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.62-7.55 (m, 1H), 7.54-7.47 (m, 2H), 7.38-7.31 (m, 4H), 7.28 (d, *J* = 2.5 Hz, 2H), 7.18-7.14 (m, 3H), 6.98 (s, 1H), 2.44 (s, 3H), 2.35 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 189.62, 156.43, 143.47, 138.70, 138.01, 137.38, 134.83, 132.16, 130.36, 129.76, 129.43, 128.03, 126.03, 125.15, 117.50, 72.85, 23.36, 21.24. HRMS (EI) calcd for $C_{24}H_{21}N_3O$ $[M+H]^+$: 368.1763; Found: 368.1770.

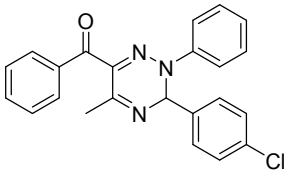


(3-(4-methoxyphenyl)-5-methyl-2-phenyl-2,3-dihydro-1,2,4-triazin-6-yl)(phenyl)methanone (3m): 135 mg, yield 70%, yellow liquid. ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.92 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.63-7.53 (m, 1H), 7.51-7.46 (m, 2H), 7.35-7.28 (m, 5H), 7.27-7.26 (m, 1H), 7.18-7.12 (m, 1H), 6.93 (s, 1H), 6.86 (dd, *J* = 7.5, 2.0 Hz, 2H), 3.77 (s, 3H), 2.42 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 189.64, 159.98, 156.38, 143.47, 137.99, 137.33, 132.19, 130.38, 129.95, 129.46,

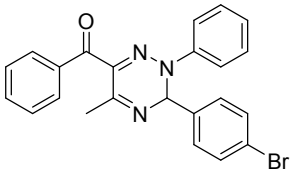
128.05, 127.48, 125.17, 117.53, 114.47, 72.59, 55.38, 23.35. HRMS (EI) calcd for $C_{24}H_{21}N_3O_2$ $[M+H]^+$: 384.1712; Found: 384.1720.



(3-(4-fluorophenyl)-5-methyl-2-phenyl-2,3-dihydro-1,2,4-triazin-6-yl)(phenyl)methanone (3n): 117 mg, yield 63%, yellow liquid. ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.92 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.63-7.54 (m, 1H), 7.51-7.46 (m, 2H), 7.36-7.27 (m, 6H), 7.19-7.15 (m, 1H), 7.05-6.99 (m, 2H), 6.96 (s, 1H), 2.41 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 189.55, 162.94 (d, *J* = 248 Hz), 156.92, 143.36, 137.79, 133.77, 133.51 (d, *J* = 3.4 Hz), 132.36, 130.39, 129.58, 128.13, 128.05 (d, *J* = 8.5 Hz), 125.36, 117.48, 116.11 (d, *J* = 21.7 Hz), 72.22, 23.26. HRMS (EI) calcd for $C_{23}H_{18}FN_3O$ $[M+H]^+$: 372.1512; Found: 372.1520.

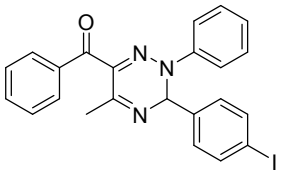


(3-(4-chlorophenyl)-5-methyl-2-phenyl-2,3-dihydro-1,2,4-triazin-6-yl)(phenyl)methanone (3o): 95 mg, yield 49%, yellow liquid. ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.92 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.60-7.55 (m, 1H), 7.51-7.47 (m, 2H), 7.37-7.26 (m, 8H), 7.20-7.15 (m, 1H), 6.96 (s, 1H), 2.41 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 189.47, 157.09, 143.30, 137.85, 137.74, 136.11, 134.80, 132.37, 130.37, 129.58, 129.31, 128.12, 127.62, 125.39, 117.45, 72.20, 23.24. HRMS (EI) calcd for $C_{23}H_{18}ClN_3O$ $[M+H]^+$: 388.1217; Found: 388.1227.

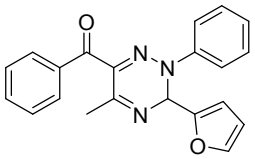


(3-(4-bromophenyl)-5-methyl-2-phenyl-2,3-dihydro-1,2,4-triazin-6-yl)(phenyl)methanone (3p): 128 mg, yield 59%, yellow liquid. ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.91 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.62-7.54 (m, 1H), 7.53-7.44 (m, 4H),

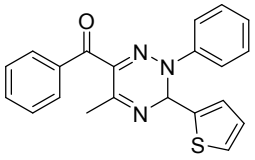
7.37-7.32 (m, 2H), 7.30-7.26 (m, 2H), 7.23-7.19 (m, 2H), 7.18-7.15 (m, 1H), 6.93 (s, 1H), 2.40 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 189.50, 157.16, 143.31, 137.89, 137.74, 136.62, 132.41, 132.29, 130.39, 129.61, 128.15, 127.93, 125.43, 123.00, 117.47, 72.28, 23.26. HRMS (EI) calcd for $C_{23}H_{18}BrN_3O$ $[M+H]^+$: 432.0711; Found: 432.0706.



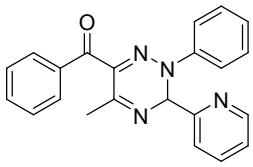
(3-(4-iodophenyl)-5-methyl-2-phenyl-2,3-dihydro-1,2,4-triazin-6-yl)(phenyl)methanone (3q): 126 mg, yield 53%, red liquid. ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.91 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.69-7.65 (m, 2H), 7.60-7.55 (m, 1H), 7.51-7.47 (m, 2H), 7.35-7.30 (m, 2H), 7.28 (d, *J* = 1.2 Hz, 2H), 7.19-7.15 (m, 1H), 7.08 (dd, *J* = 8.7, 0.5 Hz, 2H), 6.92 (s, 1H), 2.40 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 189.47, 157.14, 143.29, 138.22, 137.86, 137.73, 137.28, 132.38, 130.38, 129.59, 128.14, 128.07, 125.41, 117.45, 94.74, 72.35, 23.25. HRMS (EI) calcd for $C_{23}H_{18}IN_3O$ $[M+H]^+$: 480.0573; Found: 480.0583.



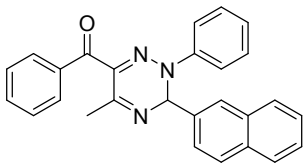
(3-(furan-2-yl)-5-methyl-2-phenyl-2,3-dihydro-1,2,4-triazin-6-yl)(phenyl)methanone (3r): 104 mg, yield 61%, yellow solid, m.p.: 144-146 ^{o}C. ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.91 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.58-7.52 (m, 1H), 7.51-7.43 (m, 4H), 7.42-7.33 (m, 3H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.04 (s, 1H), 6.31 (d, *J* = 1.2 Hz, 2H), 2.52 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 189.69, 159.07, 149.13, 143.79, 143.21, 138.81, 137.76, 132.32, 130.41, 129.48, 128.08, 125.43, 118.15, 110.96, 110.61, 66.68, 23.13. HRMS (EI) calcd for $C_{21}H_{17}N_3O_2$ $[M+H]^+$: 344.1399; Found: 344.1408.



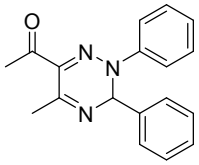
(5-methyl-2-phenyl-3-(thiophen-2-yl)-2,3-dihydro-1,2,4-triazin-6-yl)(phenyl)methanone (3s): 105 mg, yield 58%, red solid, m.p.: 157-159 ^{o}C. ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.89 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.58-7.53 (m, 1H), 7.50-7.43 (m, 2H), 7.42-7.35 (m, 4H), 7.27-7.25 (m, 1H), 7.21 (s, 1H), 7.21-7.16 (m, 1H), 6.99 (d, *J* = 3.5 Hz, 1H), 6.93 (t, *J* = 4.4 Hz, 1H), 2.49 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 189.67, 158.26, 143.03, 139.76, 138.42, 137.82, 132.34, 130.41, 129.62, 128.08, 126.82, 126.65, 126.52, 125.43, 117.76, 68.73, 23.20. HRMS (EI) calcd for $C_{21}H_{17}N_3OS$ $[M+H]^+$: 360.1171; Found: 360.1180.



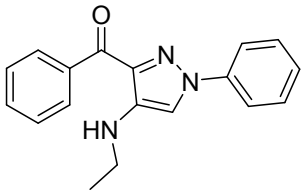
(5-methyl-2-phenyl-3-(pyridin-2-yl)-2,3-dihydro-1,2,4-triazin-6-yl)(phenyl)methanone (3t): 99 mg, yield 56%, yellow liquid. ^{1}H NMR (400 MHz,$CDCl_3$) δ 8.63-8.54 (m, 1H), 7.94 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.70-7.64 (m, 1H), 7.58-7.52 (m, 1H), 7.50-7.44 (m, 2H), 7.42-7.37 (m, 3H), 7.34-7.29 (m, 2H), 7.25-7.21 (m, 1H), 7.17-7.10 (m, 1H), 7.05 (s, 1H), 2.47 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 189.75, 157.47, 156.74, 150.02, 143.49, 137.99, 137.26, 136.97, 132.21, 130.47, 129.32, 128.02, 125.20, 123.76, 121.51, 117.84, 74.12, 23.42. HRMS (EI) calcd for $C_{22}H_{18}N_4O$ $[M+H]^+$: 355.1559; Found: 355.1569.



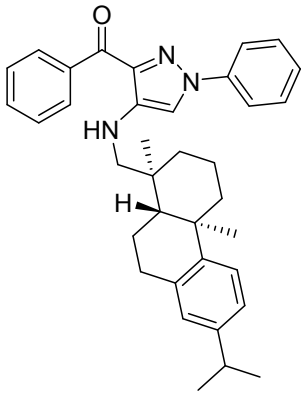
(5-methyl-3-(naphthalen-2-yl)-2-phenyl-2,3-dihydro-1,2,4-triazin-6-yl)(phenyl)methanone (3u): 134 mg, yield 66%, orange liquid. ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.89 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.58-7.53 (m, 1H), 7.50-7.43 (m, 2H), 7.42-7.35 (m, 4H), 7.27-7.25 (m, 1H), 7.21 (s, 1H), 7.21-7.16 (m, 1H), 6.99 (d, *J* = 3.5 Hz, 1H), 6.93 (t, *J* = 4.4 Hz, 1H), 2.49 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 189.67, 158.26, 143.03, 139.76, 138.42, 137.82, 132.34, 130.41, 129.62, 128.08, 126.82, 126.65, 126.52, 125.43, 117.76, 68.73, 23.20. HRMS (EI) calcd for $C_{27}H_{21}N_3O$ $[M+H]^+$: 404.1763; Found: 404.1773.



1-(5-methyl-2,3-diphenyl-2,3-dihydro-1,2,4-triazin-6-yl)ethan-1-one (3v): 111 mg, yield 76%, yellow liquid. ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.45-7.37 (m, 4H), 7.36-7.27 (m, 5H), 7.24-7.21 (m, 1H), 6.91 (s, 1H), 2.49 (s, 3H), 2.38 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 194.99, 156.27, 143.51, 138.23, 137.51, 129.53, 129.07, 128.81, 126.08, 125.62, 117.84, 73.22, 25.71, 23.96. HRMS (EI) calcd for $C_{18}H_{17}N_3O$ $[M+H]^+$: 292.1450; Found: 292.1455.

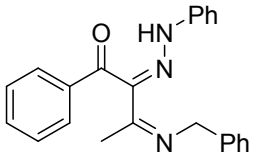


(3-(ethylamino)-1-phenyl-1*H*-pyrazol-3-yl)(phenyl)methanone (4a): 53 mg, yield 36%, yellow liquid. ^{1}H NMR (400 MHz,$CDCl_3$) δ 8.39 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.75 (dd, *J* = 8.6, 1.1 Hz, 2H), 7.60-7.54 (m, 1H), 7.52-7.44 (m, 4H), 7.40 (s, 1H), 7.35-7.30 (m, 1H), 5.81 (t, *J*= 4.88 Hz, 1H), 3.19 (q, *J* = 5.52 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 189.36, 141.50, 140.21, 138.24, 138.04, 132.26, 130.54, 129.56, 128.17, 127.14, 119.29, 108.98, 40.99, 14.90. HRMS (EI) calcd for $C_{18}H_{17}N_3O$ $[M+H]^+$: 292.1450; Found: 292.1454.



(3-((((1S,4aR,10aS)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)amino)-1-phenyl-1*H*-pyrazol-3-yl)(phenyl)methanone (4b): 101 mg, yield 38%, yellow liquid. ^{1}H NMR (400 MHz,$CDCl_3$) δ 8.36 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.75 (dd, *J* = 8.5, 1.0 Hz, 2H), 7.58-

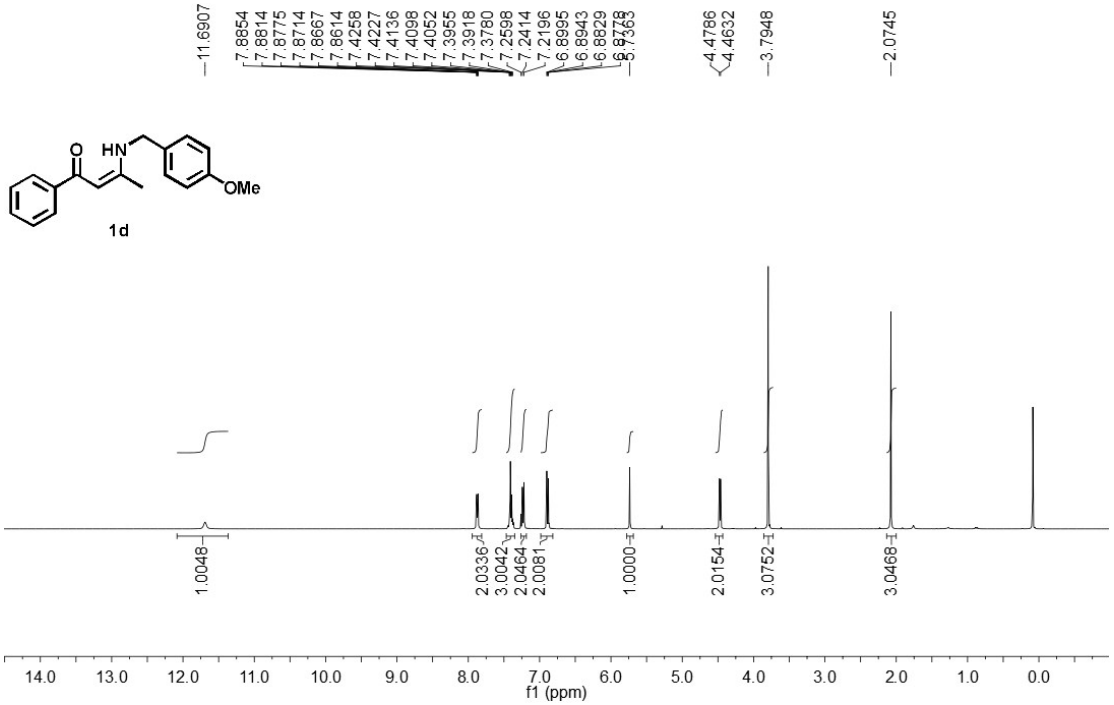
7.53 (m, 1H), 7.52-7.45 (m, 4H), 7.39 (s, 1H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 8.2 Hz, 1H), 6.99 (d, *J* = 8.2 Hz, 1H), 6.89 (s, 1H), 6.14 (t, *J* = 6.4 Hz, 1H), 3.10-3.05 (m, 1H), 2.97-2.88 (m, 3H), 2.86-2.78 (m, 1H), 2.35-2.27 (m, 1H), 2.01-1.75 (m, 3H), 1.74-1.65 (m, 2H), 1.64-1.61 (m, 1H), 1.58 (s, 2H), 1.26 (s, 3H), 1.24-1.20 (m, 6H), 1.06 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 189.47, 147.33, 145.66, 142.79, 140.22, 138.26, 137.89, 134.82, 132.21, 130.51, 129.55, 128.14, 127.13, 126.98, 124.50, 124.02, 119.30, 108.57, 58.71, 46.06, 38.51, 37.96, 37.73, 36.59, 33.59, 30.55, 25.60, 24.13, 19.36, 18.97, 18.93. HRMS (EI) calcd for $C_{36}H_{41}N_3O$ $[M+H]^+$: 532.3328; Found: 532.3338.



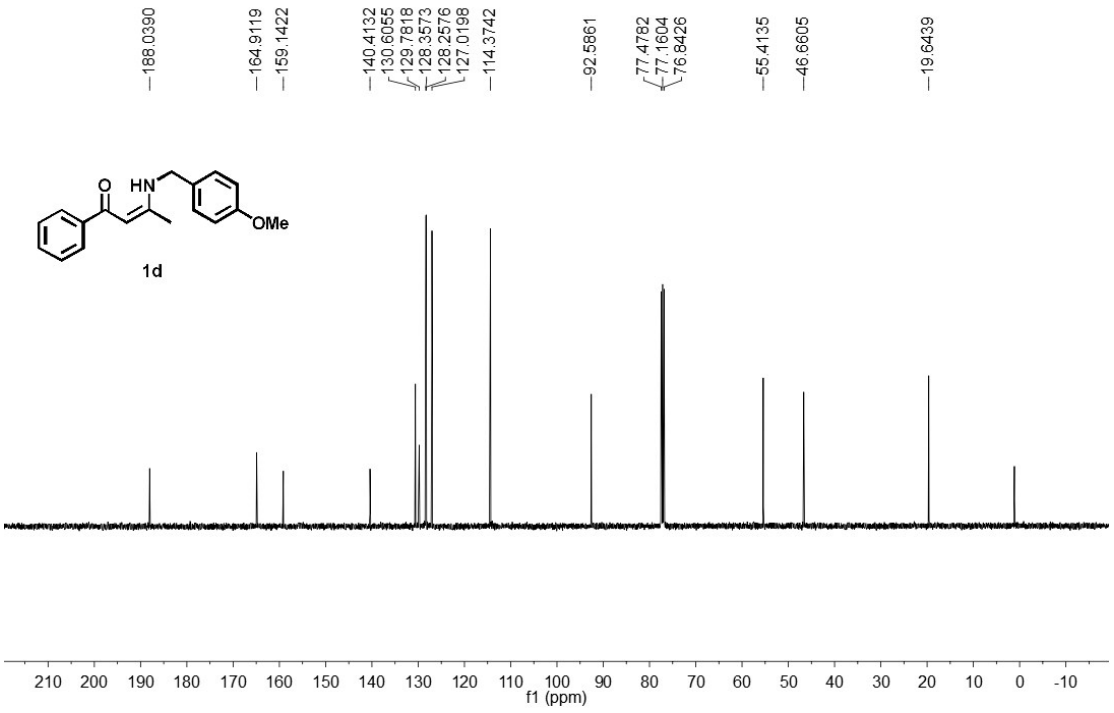
3-(benzylimino)-1-phenyl-2-(2-phenylhydrazono)butan-1-one (5): 169 mg, yield 95%, yellow liquid. ^{1}H NMR (400 MHz,$CDCl_3$) δ 15.81 (s, 1H), 7.89 (dd, *J* = 7.6, 1.0 Hz, 2H), 7.56-7.38 (m, 8H), 7.23 (dd, *J* = 8.1, 0.7 Hz, 2H), 7.10-7.04 (m, 3H), 4.75 (s, 2H), 2.53 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 193.53, 164.83, 146.93, 140.16, 138.16, 131.57, 131.24, 130.56, 129.26, 129.07, 127.83, 127.78, 127.60, 125.17, 117.64, 51.87, 17.72. HRMS (EI) calcd for $C_{23}H_{21}N_3O$ $[M+H]^+$: 356.1763; Found: 356.1769.

5. Copies of NMR spectra for compounds

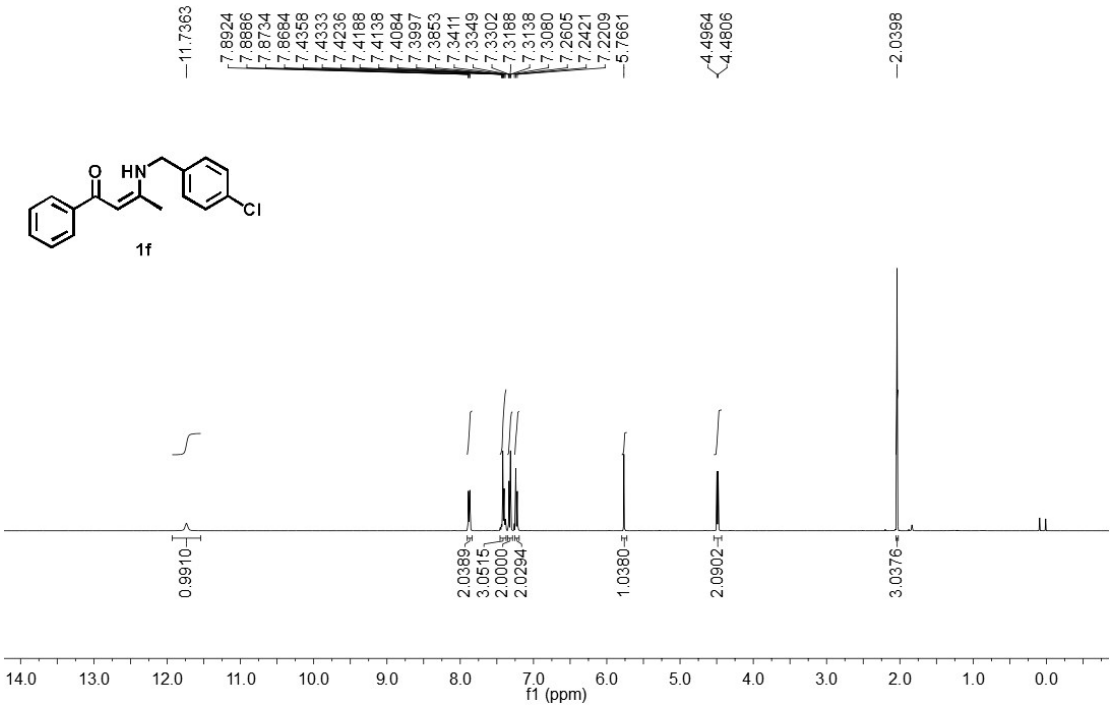
20190524
D237-1



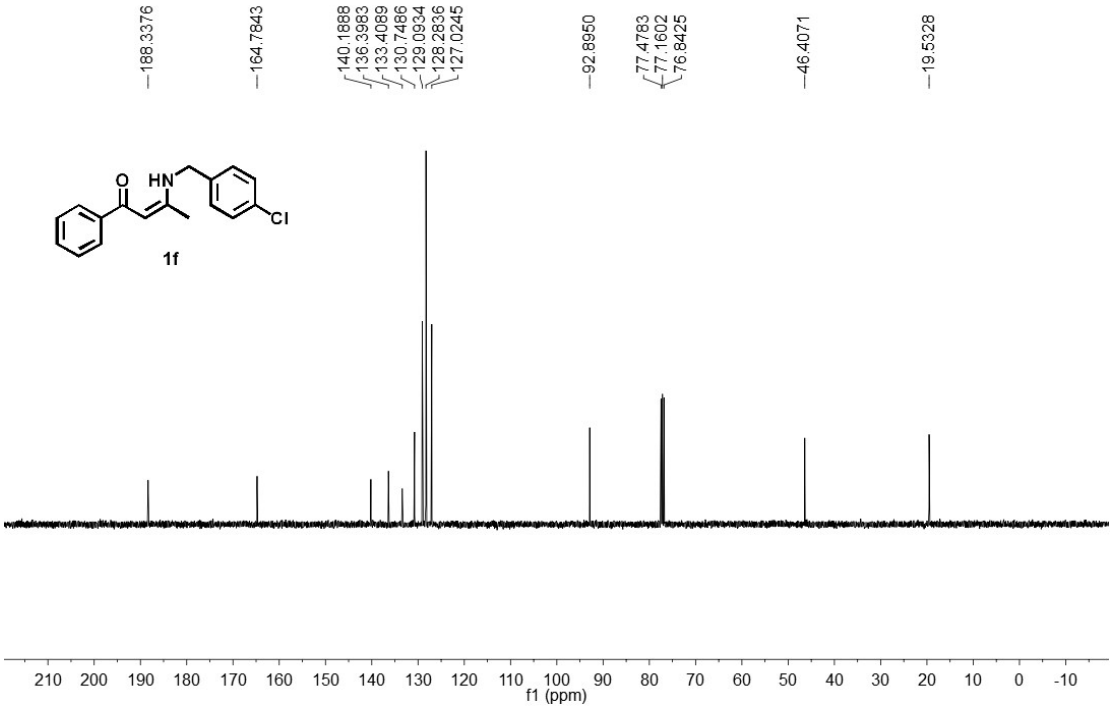
20190524
D237-1-C



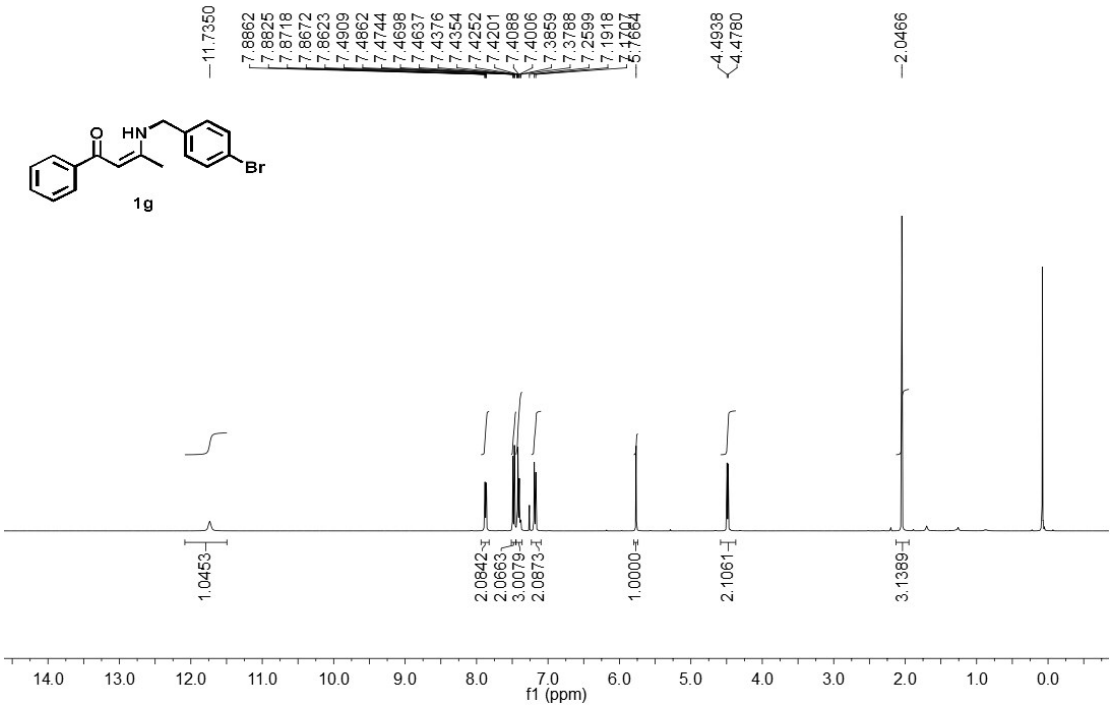
dqf-CL


11.7363
7.8924
7.8886
7.8734
7.8684
7.4358
7.4333
7.4236
7.4188
7.4138
7.4084
7.3997
7.3853
7.3411
7.3349
7.3302
7.3188
7.3138
7.3080
7.2605
7.2421
7.2209
5.7661
4.4964
4.4806
2.0398
O
HN
Cl
1f
0.9910
2.0389
3.0515
2.0000
2.0294
1.0380
2.0902
3.0376
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

dqf-CL

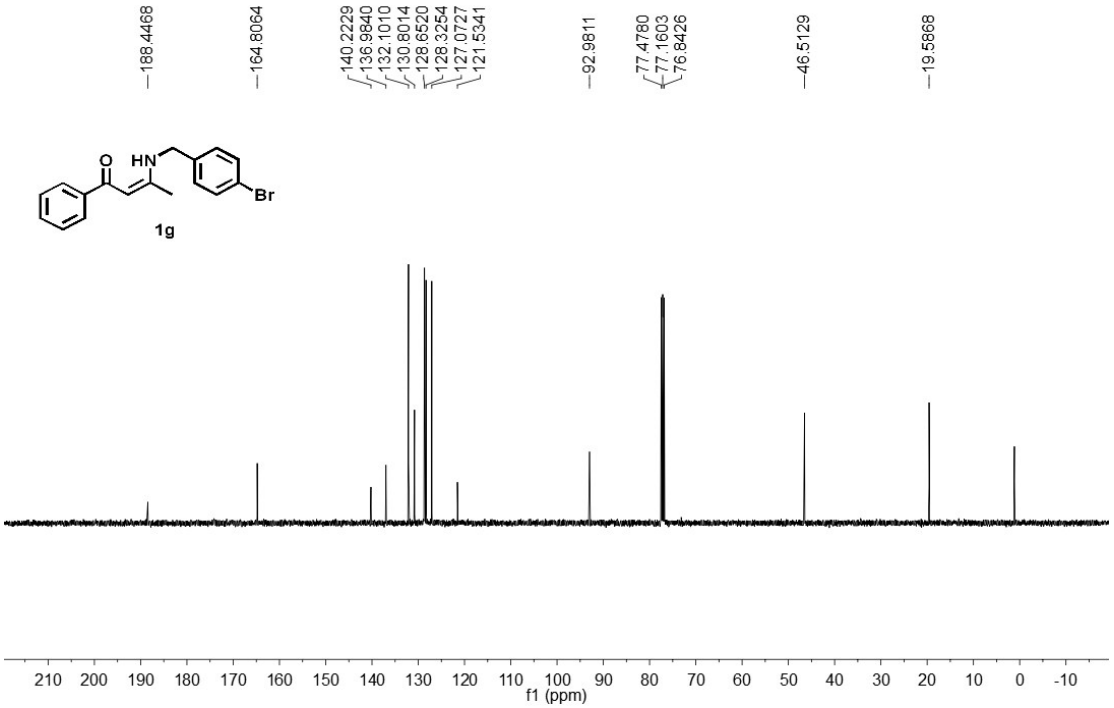

188.3376
164.7843
140.1888
136.3983
133.4089
130.7486
129.0934
128.2836
127.0245
92.8950
77.4783
77.1602
76.8425
46.4071
19.5328
O
HN
Cl
1f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

20190524
D241-1



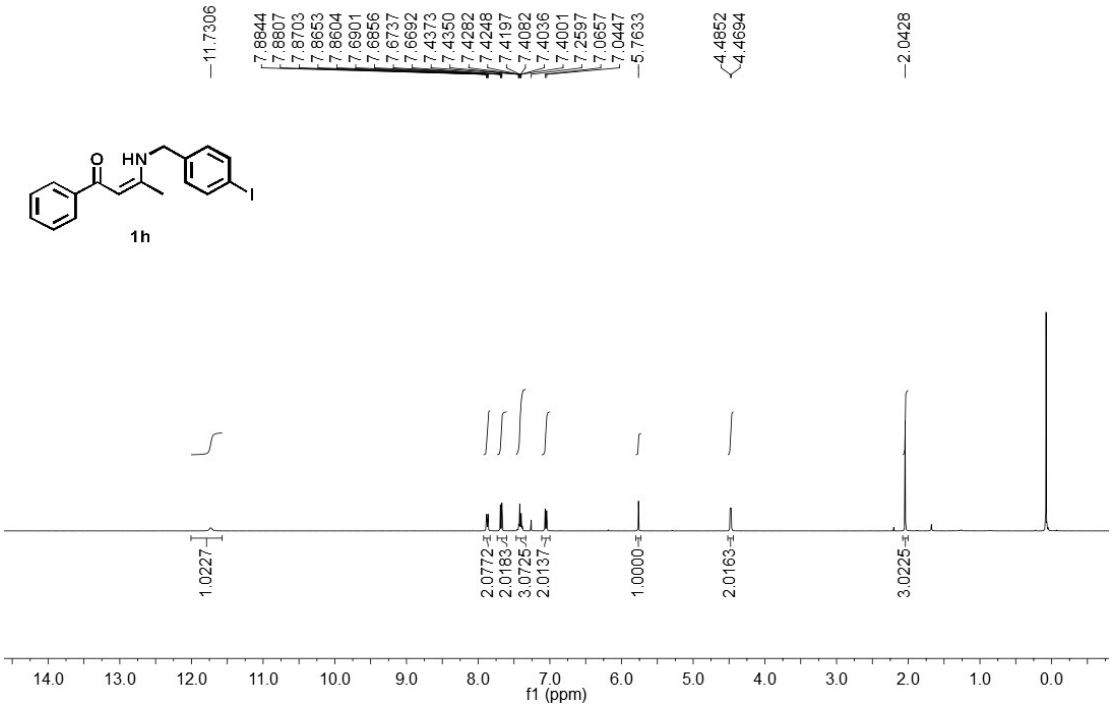
1g

20190524
D241-1-C

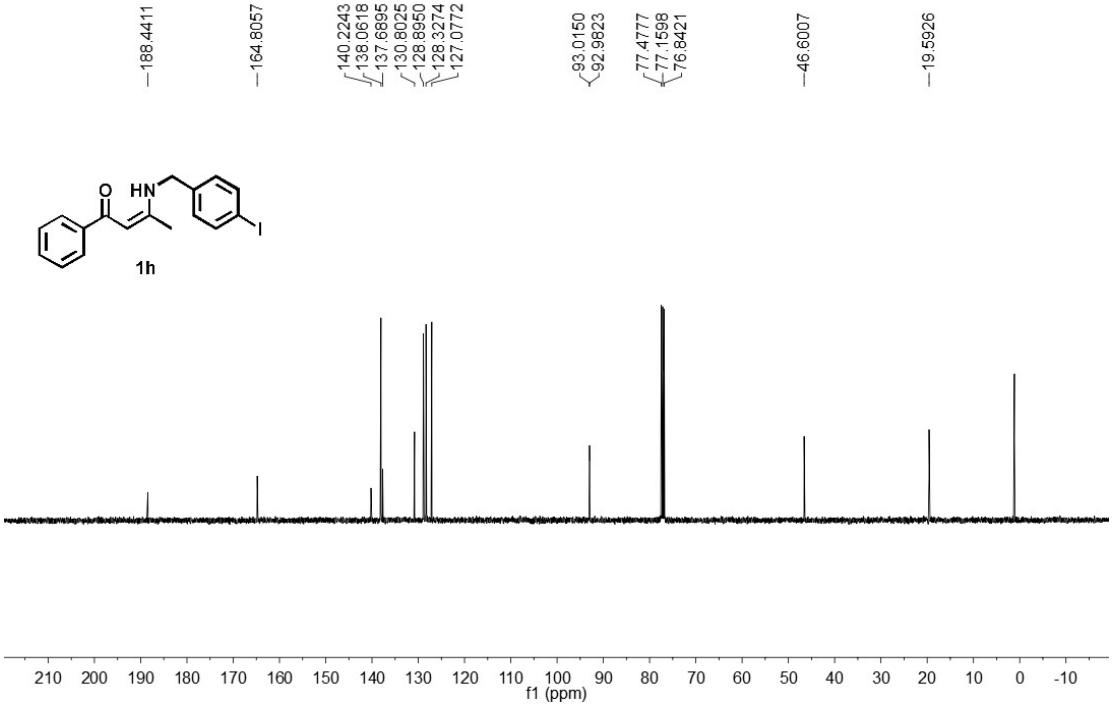


1g

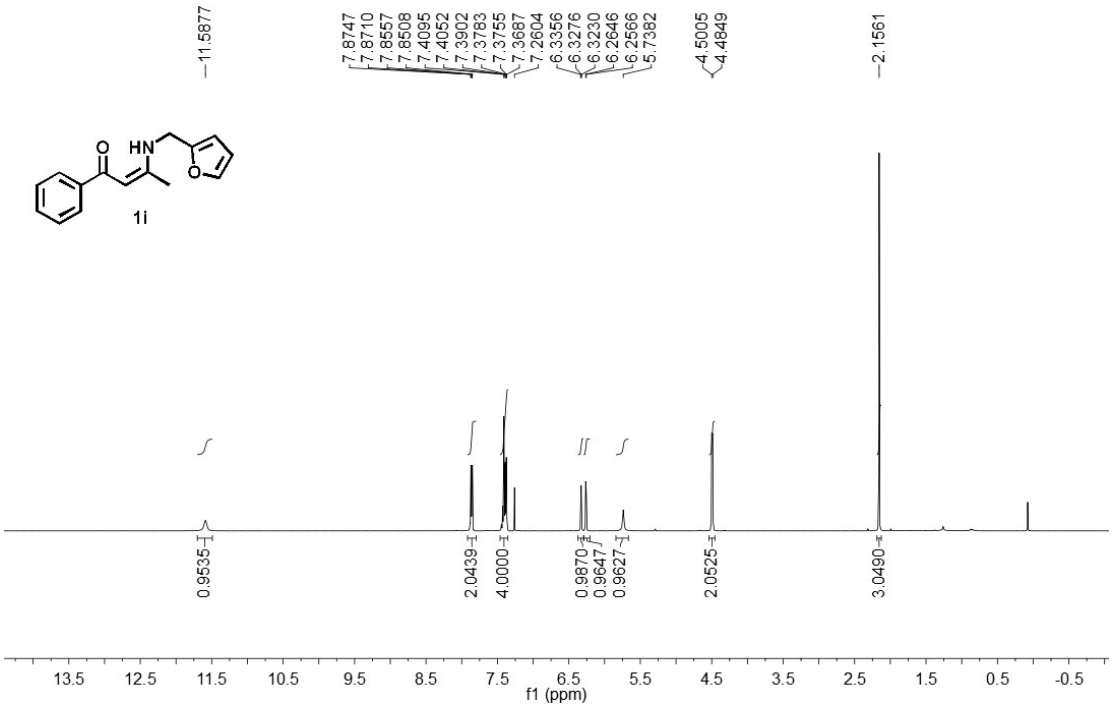
20190524
D241-2



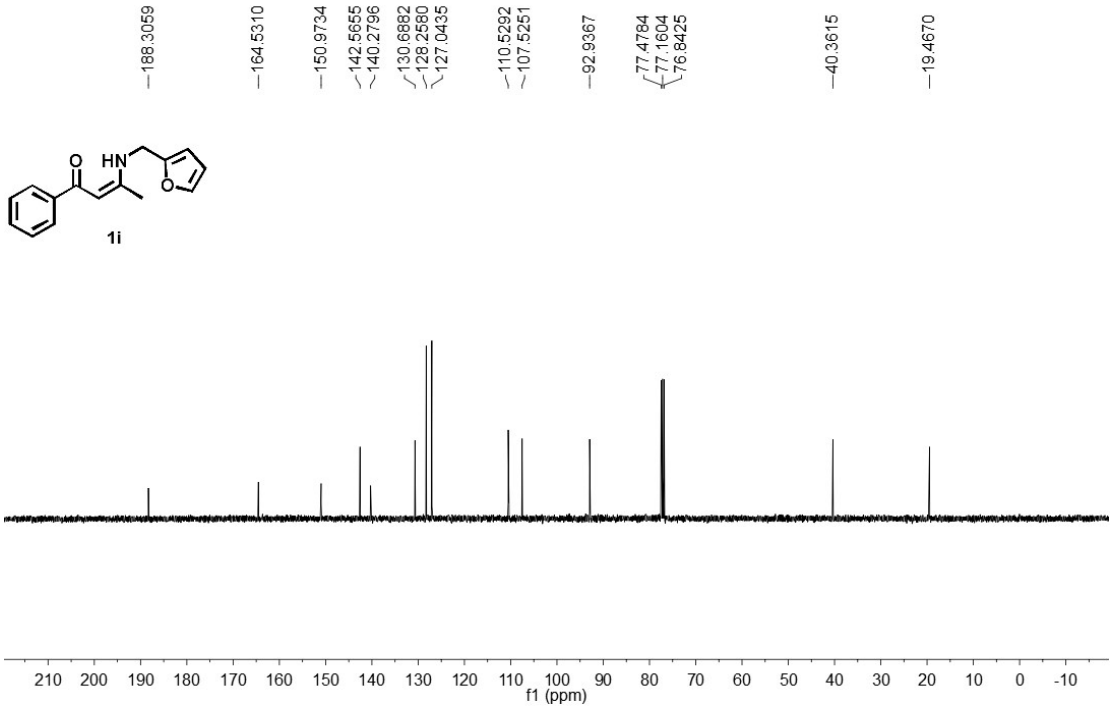
20190524
D241-2-C



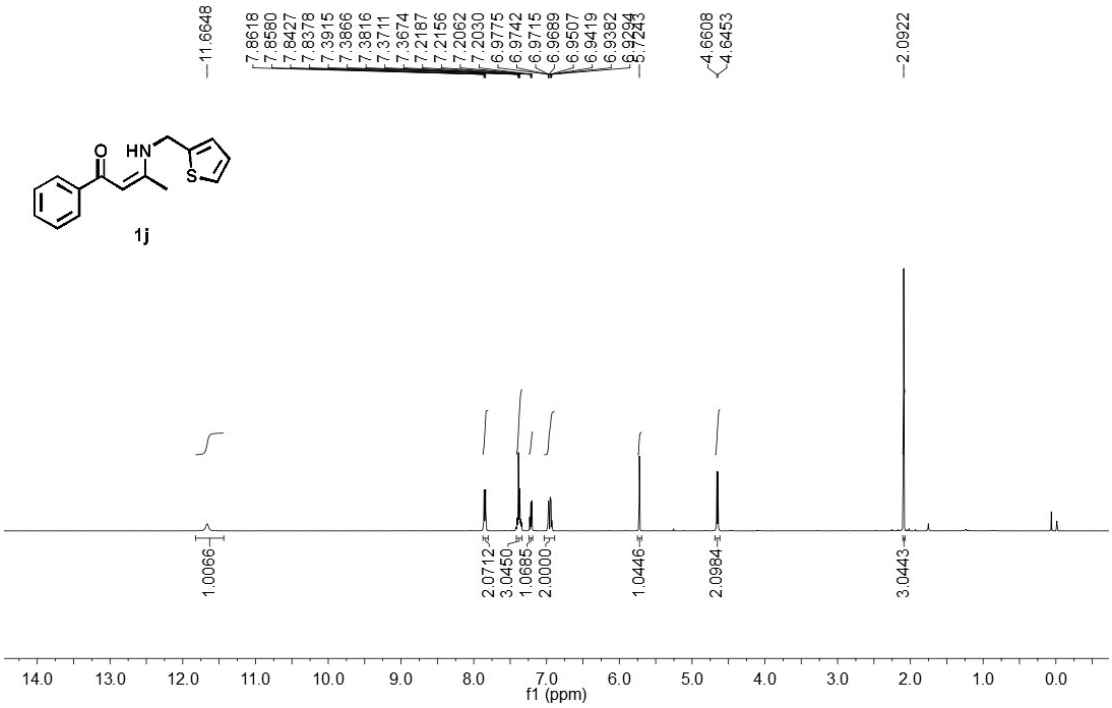
D73



DQF-FUNAN

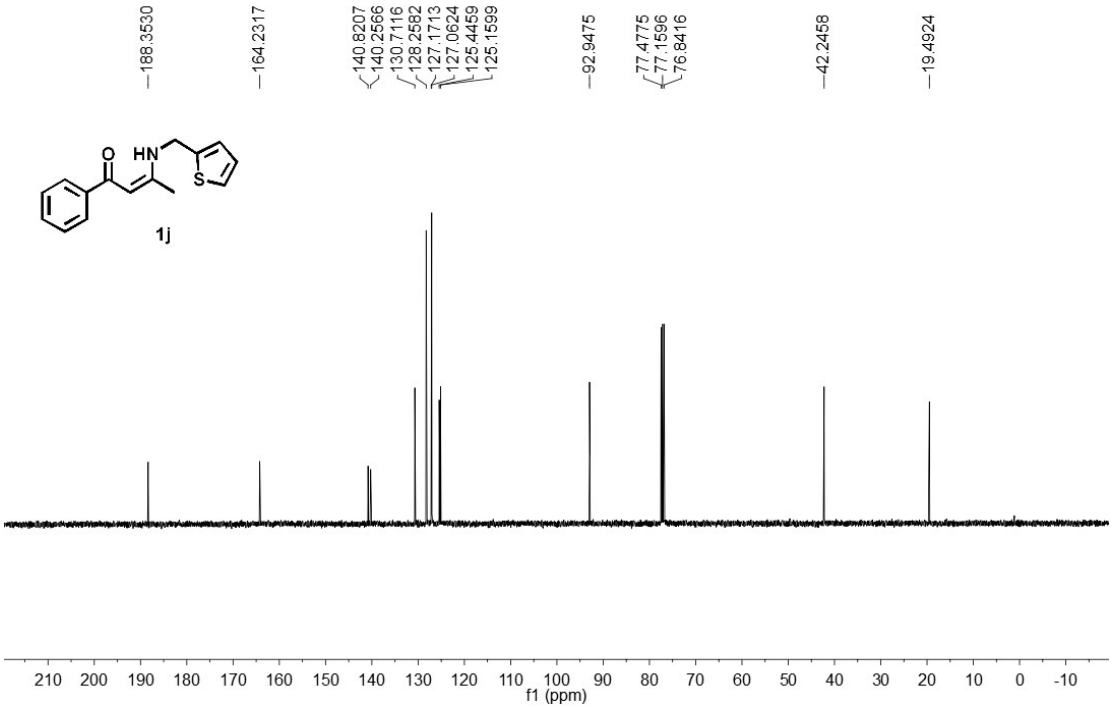


D257-1



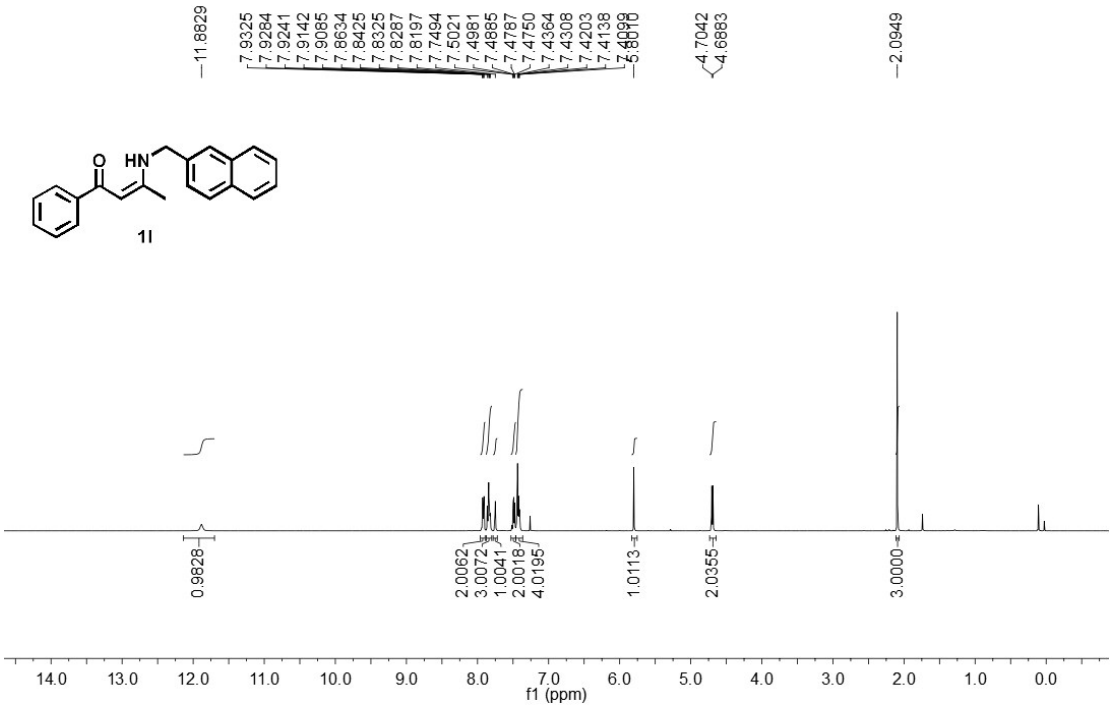
1j

D257-1

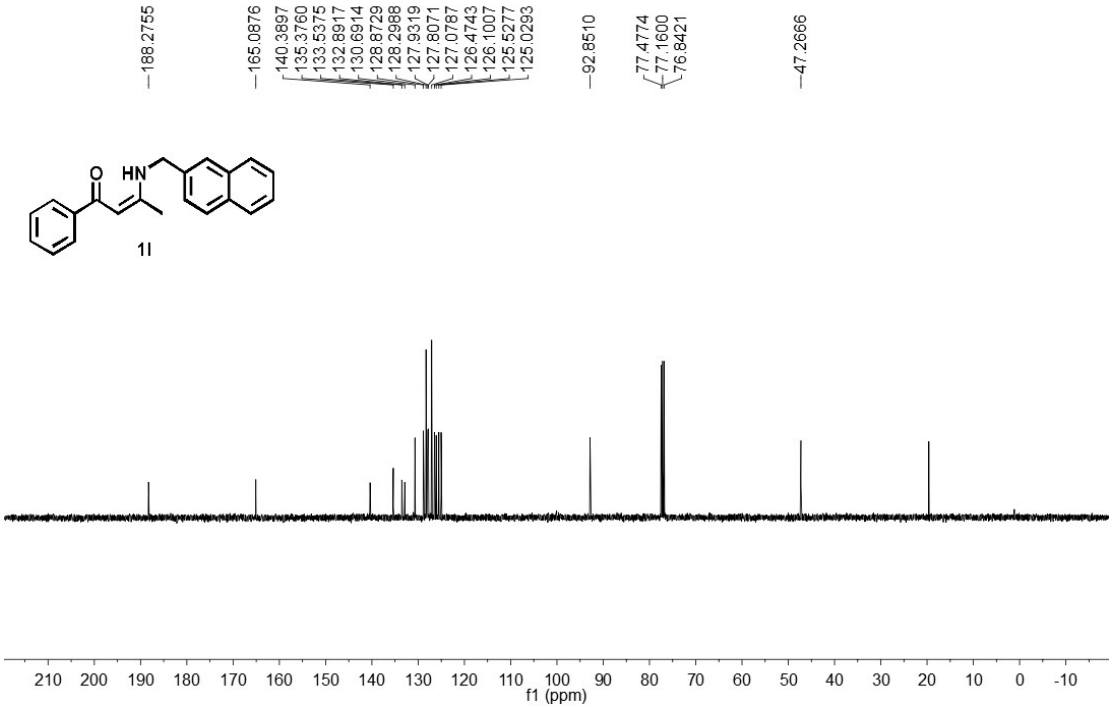


1j

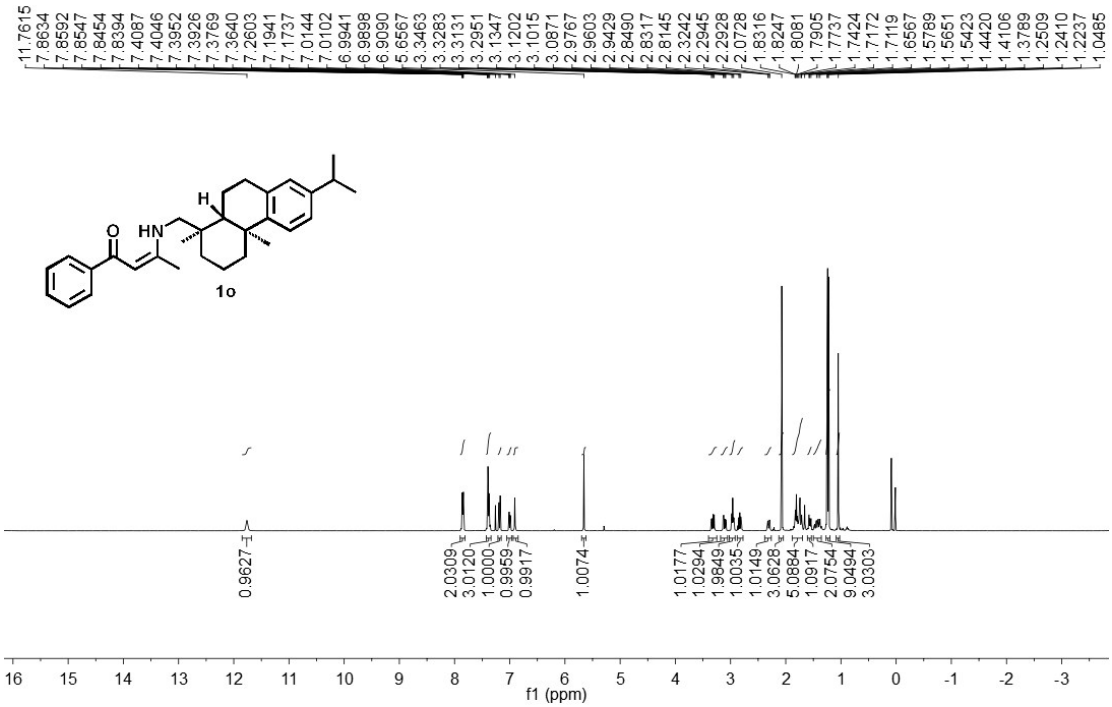
D257-3


11.8829
7.9325
7.9284
7.9241
7.9142
7.9085
7.8634
7.8425
7.8325
7.8287
7.8197
7.7494
7.5021
7.4981
7.4885
7.4787
7.4750
7.4364
7.4308
7.4203
7.4138
5.8010
4.7042
4.6883
2.0949
O
HN
1l
0.9828
2.0062
3.0072
1.0041
2.0018
4.0195
1.0113
2.0355
3.0000
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

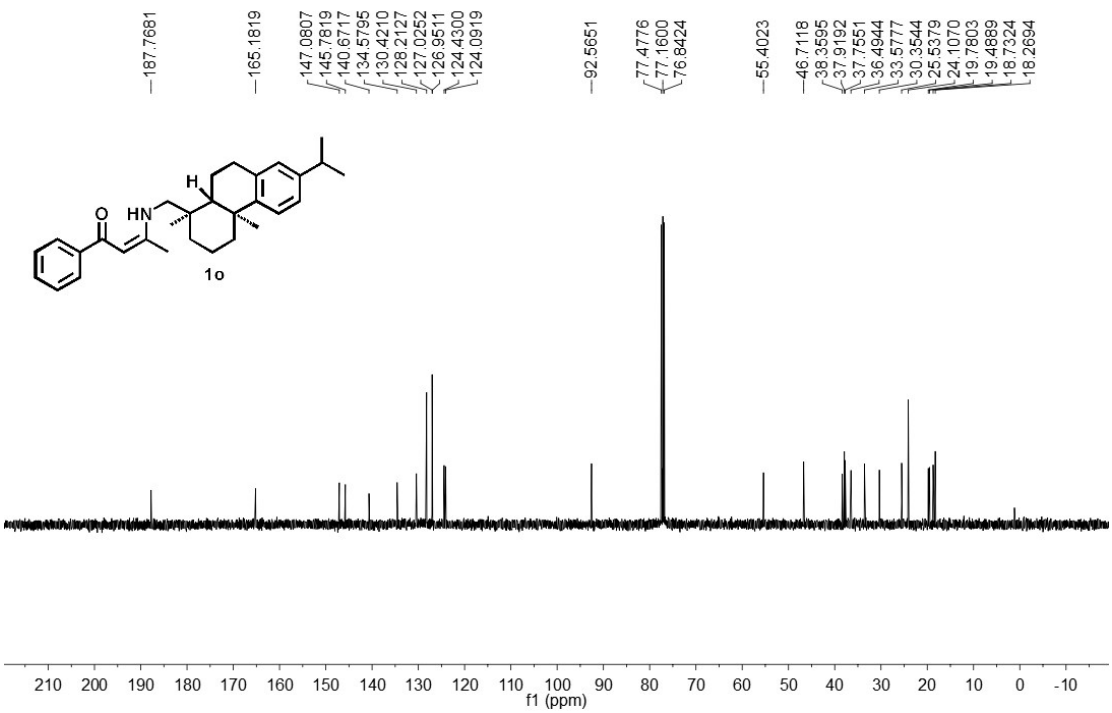
D257-3


188.2755
165.0876
140.3897
135.3760
133.5375
132.8917
130.6914
128.8729
128.2988
127.9319
127.8071
127.0787
126.4743
126.1007
125.5277
125.0293
92.8510
77.4774
77.1600
76.8421
47.2666
O
HN
1l
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

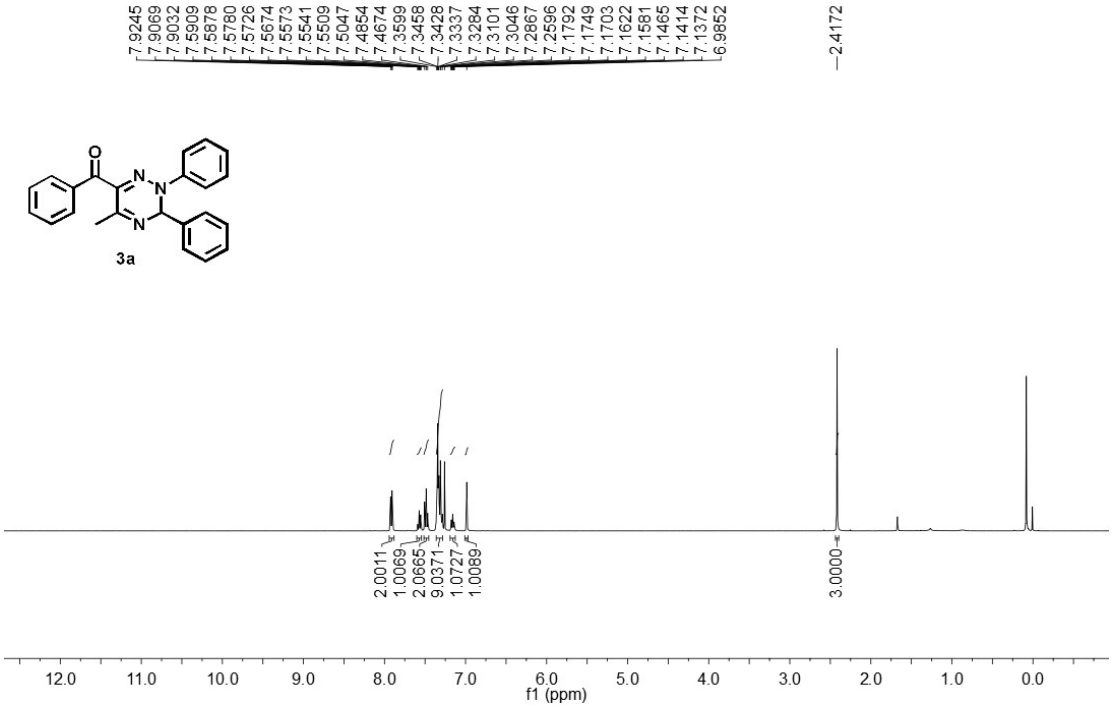
D275-2


11.7615
7.8634
7.8592
7.8547
7.8454
7.8394
7.4087
7.4046
7.3952
7.3926
7.3769
7.3640
7.2603
7.1941
7.1737
7.0144
7.0102
6.9941
6.9898
6.9090
5.6567
3.3463
3.3283
3.3131
3.2951
3.1347
3.1202
3.1015
3.0871
2.9767
2.9603
2.9429
2.8490
2.8317
2.8145
2.3242
2.2945
2.2928
2.0728
1.8316
1.8247
1.8081
1.7905
1.7737
1.7424
1.7172
1.7119
1.6567
1.5789
1.5651
1.5423
1.4420
1.4106
1.3789
1.2509
1.2410
1.2237
1.0485
H
HN
O
1o
0.9627
2.0309
3.0120
1.0000
0.9959
0.9917
1.0074
1.0177
1.0294
1.9849
1.0035
1.0149
3.0628
5.0884
1.0917
2.0754
9.0494
3.0303
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

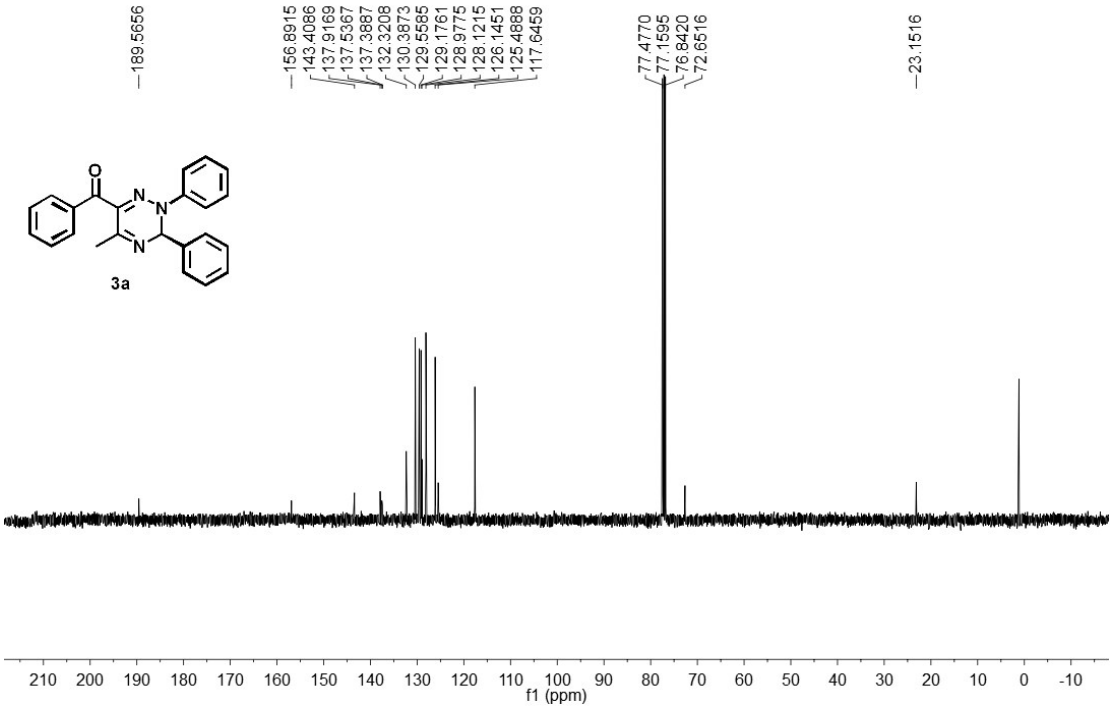
D275-2


187.7681
165.1819
147.0807
145.7819
140.6717
134.5795
130.4210
128.2127
127.0252
126.9511
124.4300
124.0919
92.5651
77.4776
77.1600
76.8424
55.4023
46.7118
38.3595
37.9192
37.7551
36.4944
33.5777
30.3544
25.5379
24.1070
19.7803
19.4889
18.7324
18.2694
H
HN
O
1o
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

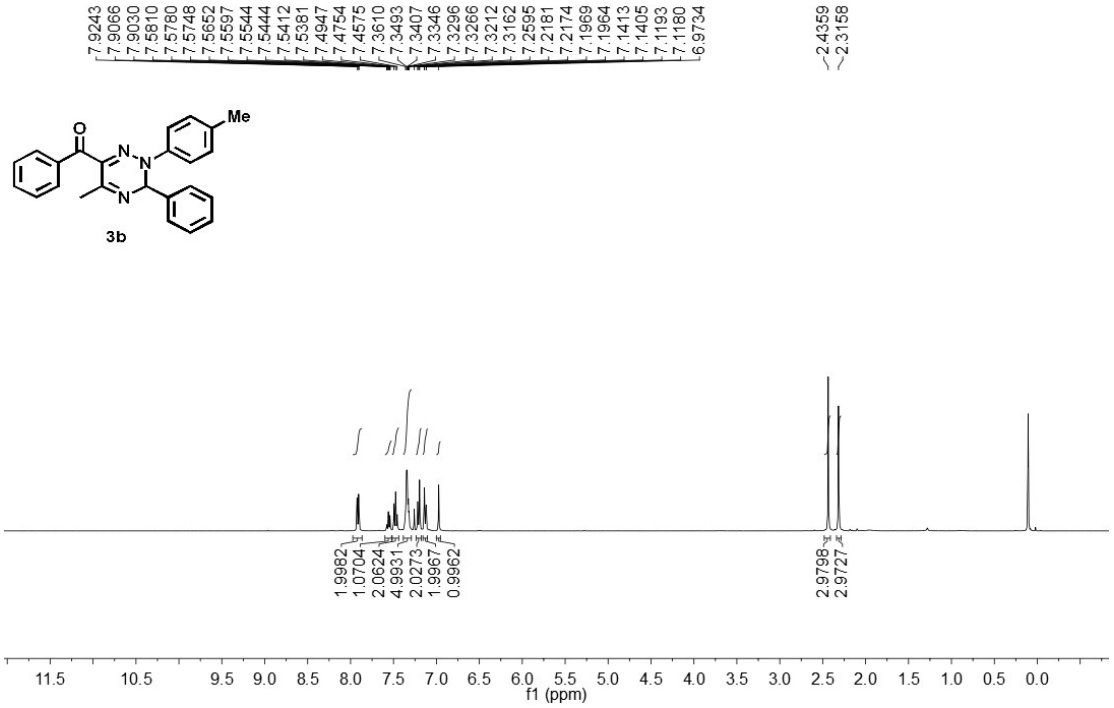
D223-2



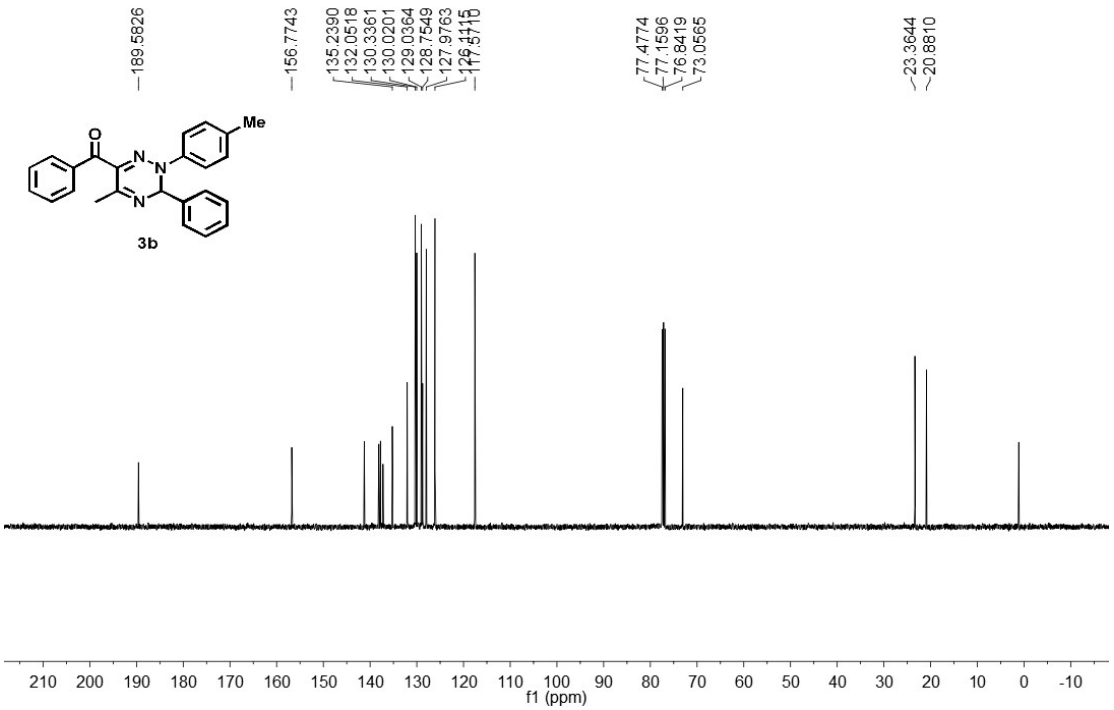
myy-d221-3
myy-d221-3



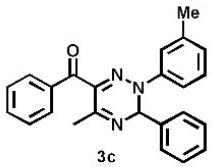
d234
d234



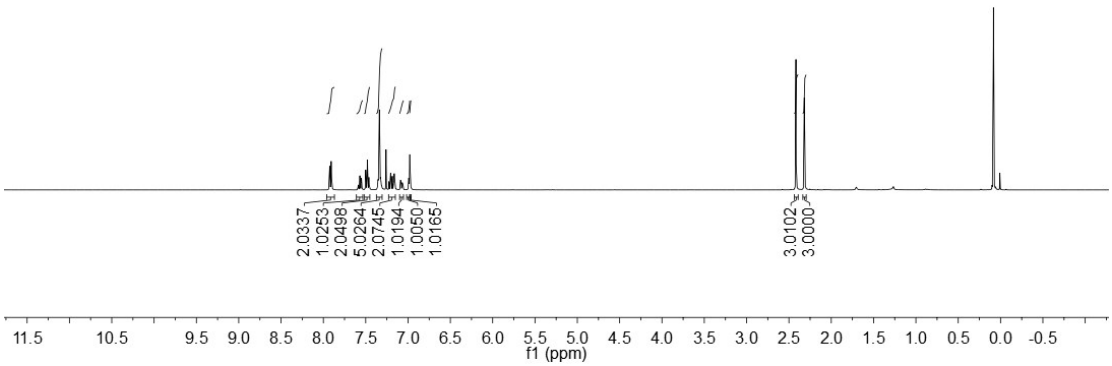
d234
d234



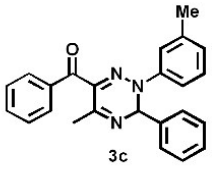
D242-2



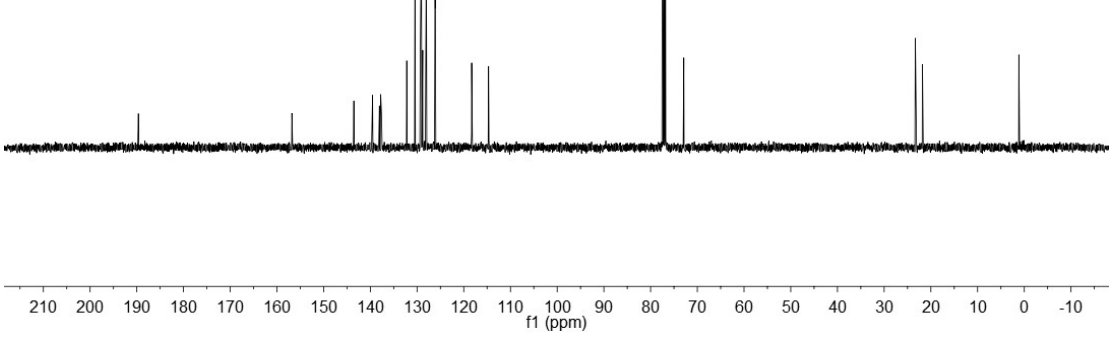
3c



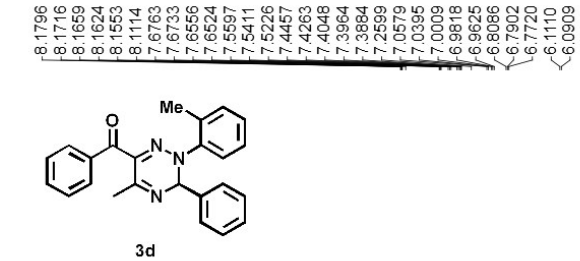
D242-2

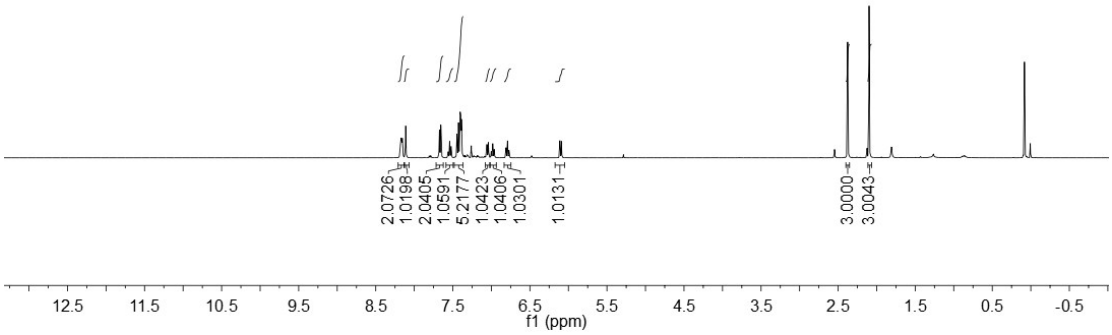


3c

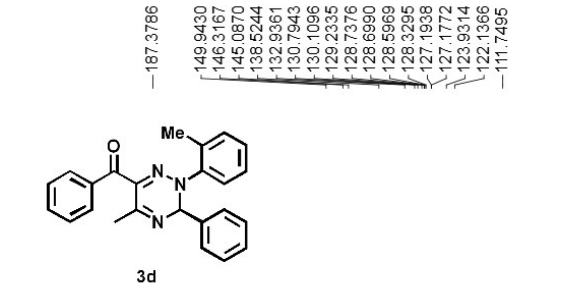


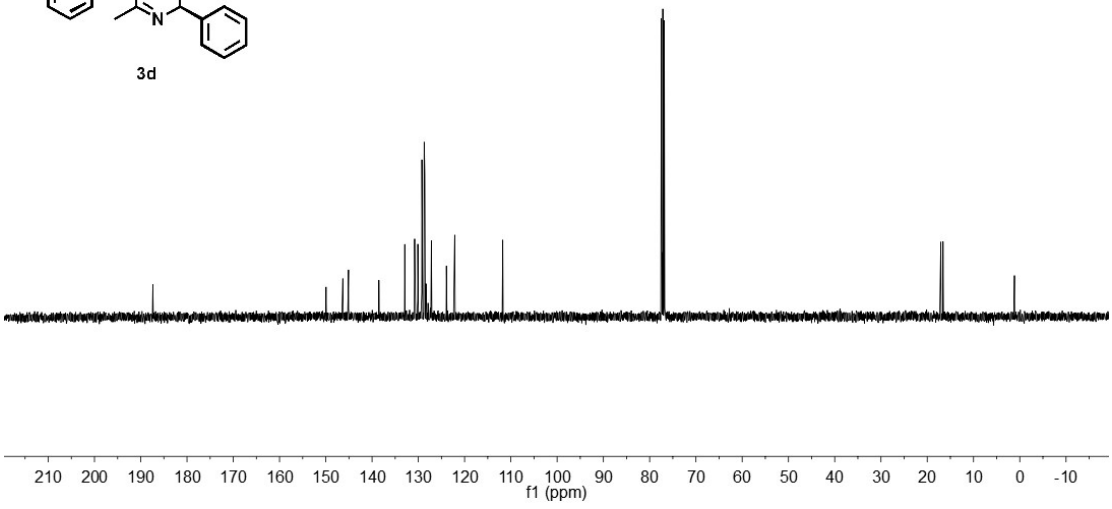
DQF-LINJIAJI-1



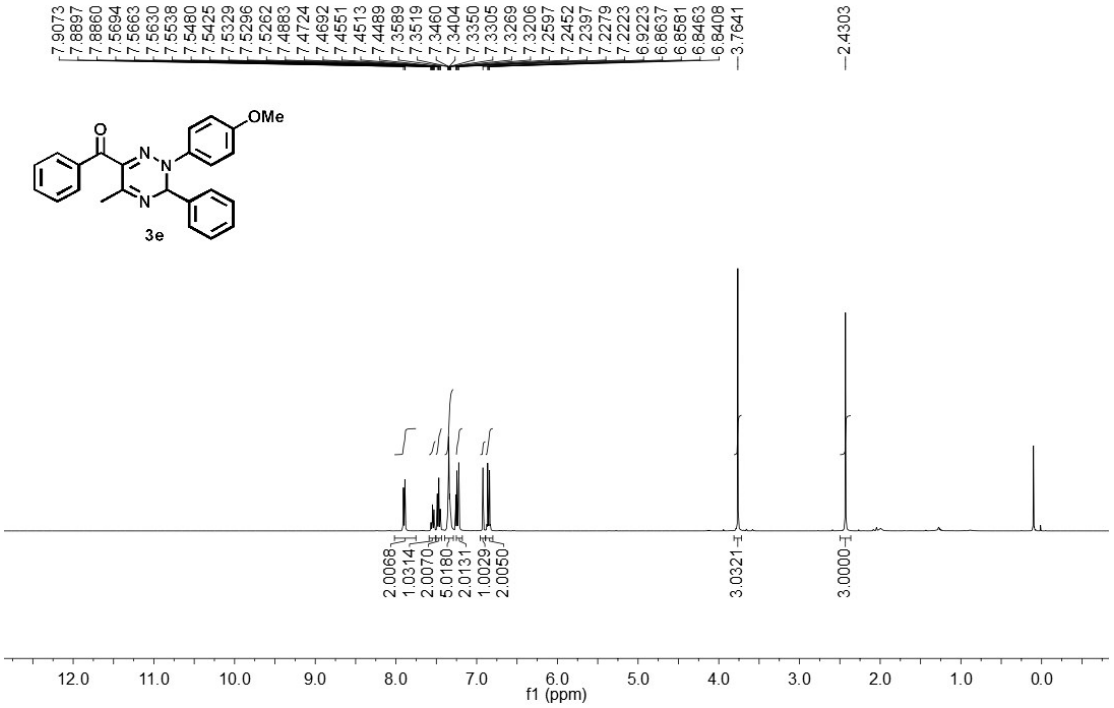


DQF-LINJIAJI-1

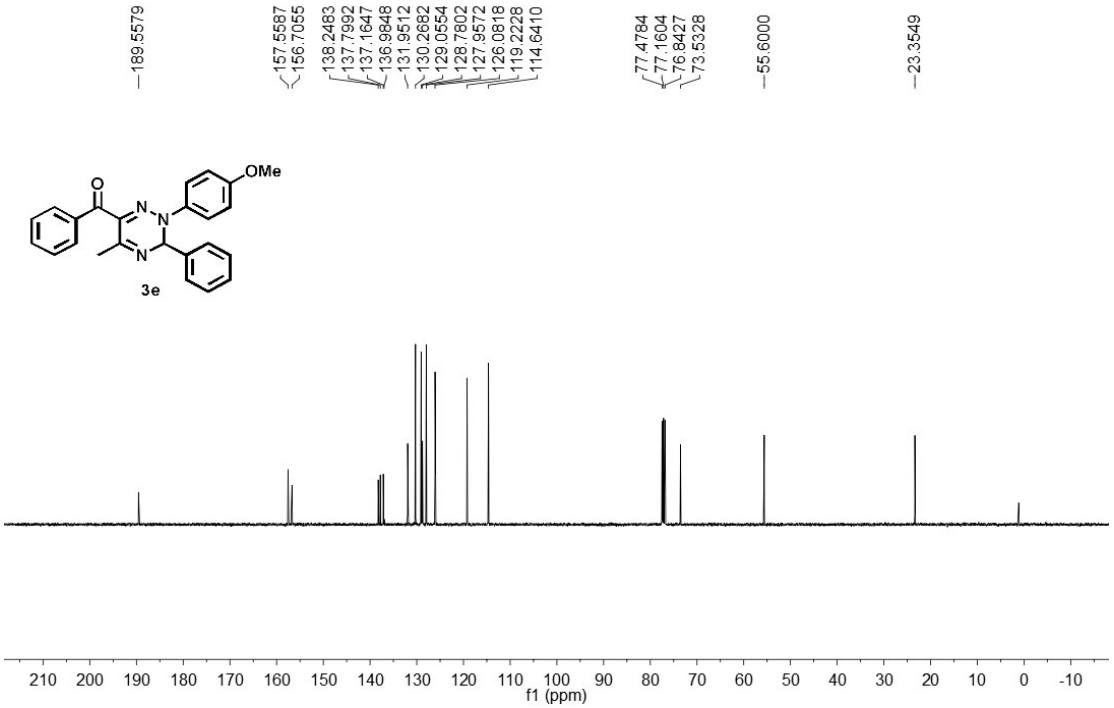




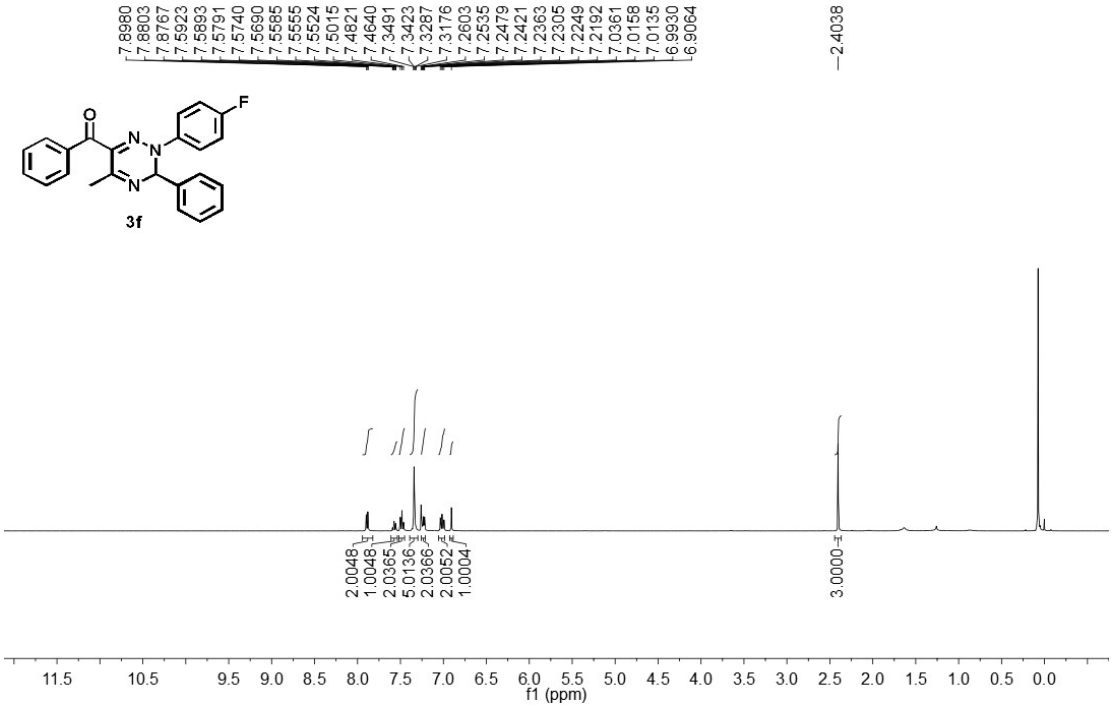
D230-2


7.9073
7.8897
7.8860
7.5694
7.5663
7.5630
7.5538
7.5480
7.5425
7.5329
7.5296
7.5262
7.4883
7.4724
7.4692
7.4551
7.4513
7.4489
7.3589
7.3519
7.3460
7.3404
7.3350
7.3305
7.3269
7.3206
7.2597
7.2452
7.2397
7.2279
7.2223
6.9223
6.8637
6.8581
6.8463
6.8408
3.7641
2.4303
OMe
O
N
N
N
3e
2.0068
1.0314
2.0070
5.0180
2.0131
1.0029
2.0050
3.0321
3.0000
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

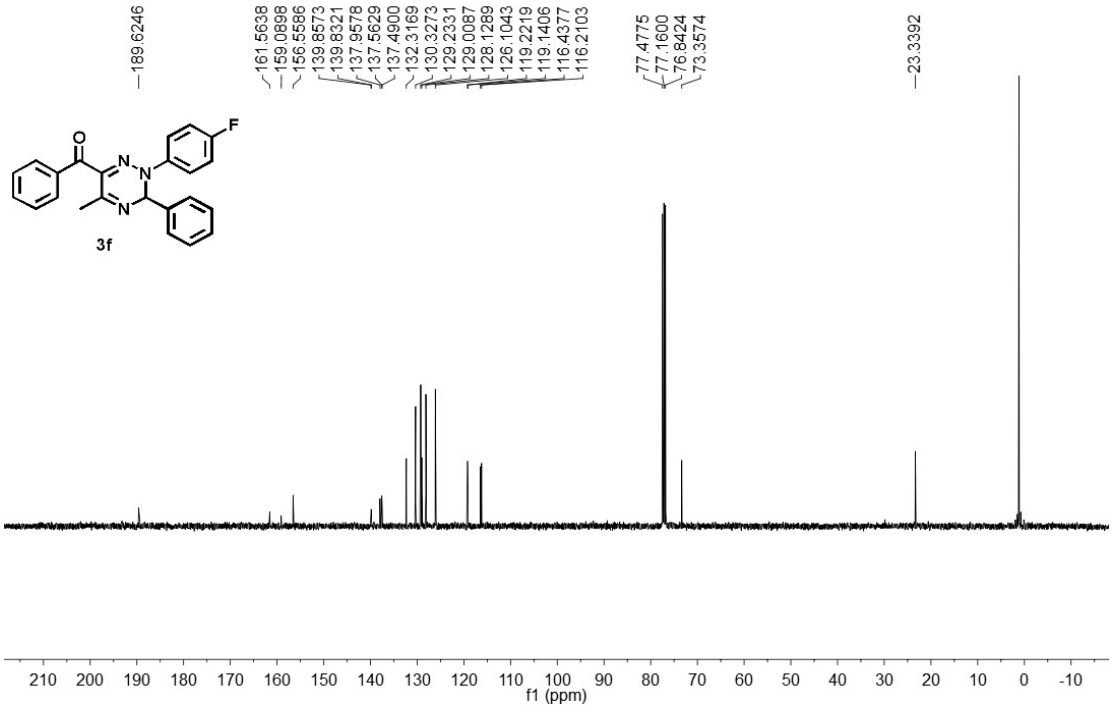
D230-2


189.5579
157.5587
156.7055
138.2483
137.7992
137.1647
136.9848
131.9512
130.2682
129.0554
128.7802
127.9572
126.0818
119.2228
114.6410
77.4784
77.1604
76.8427
73.5328
55.6000
23.3549
OMe
O
N
N
N
3e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

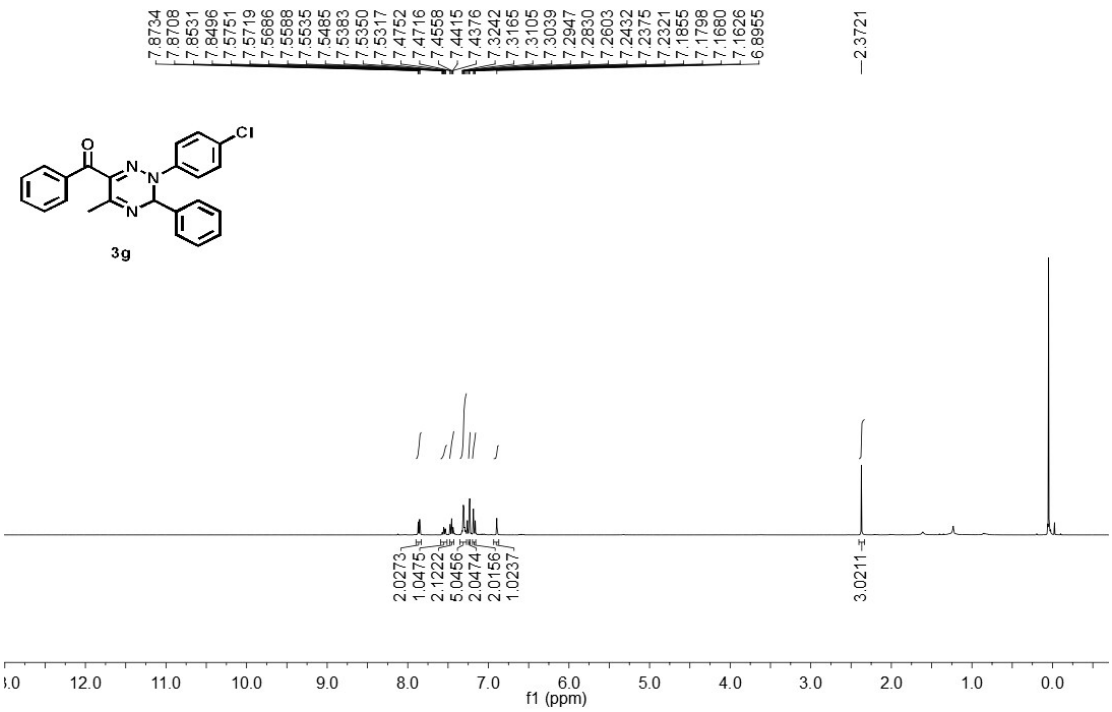
D232-2



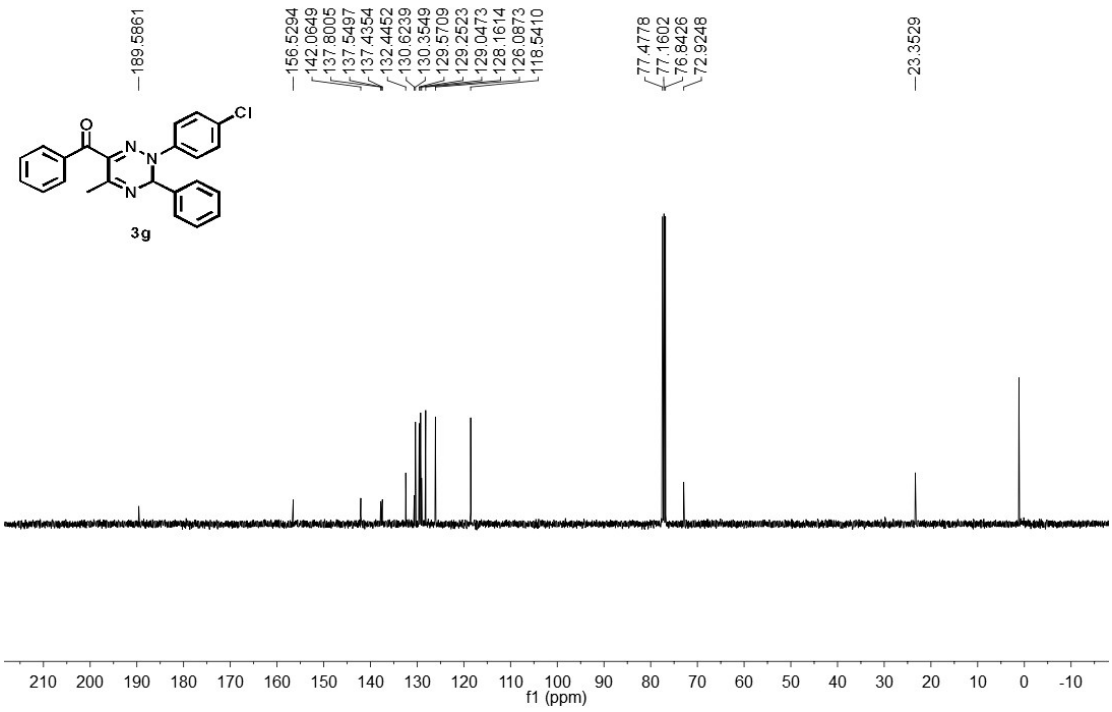
d232-2
d232-2



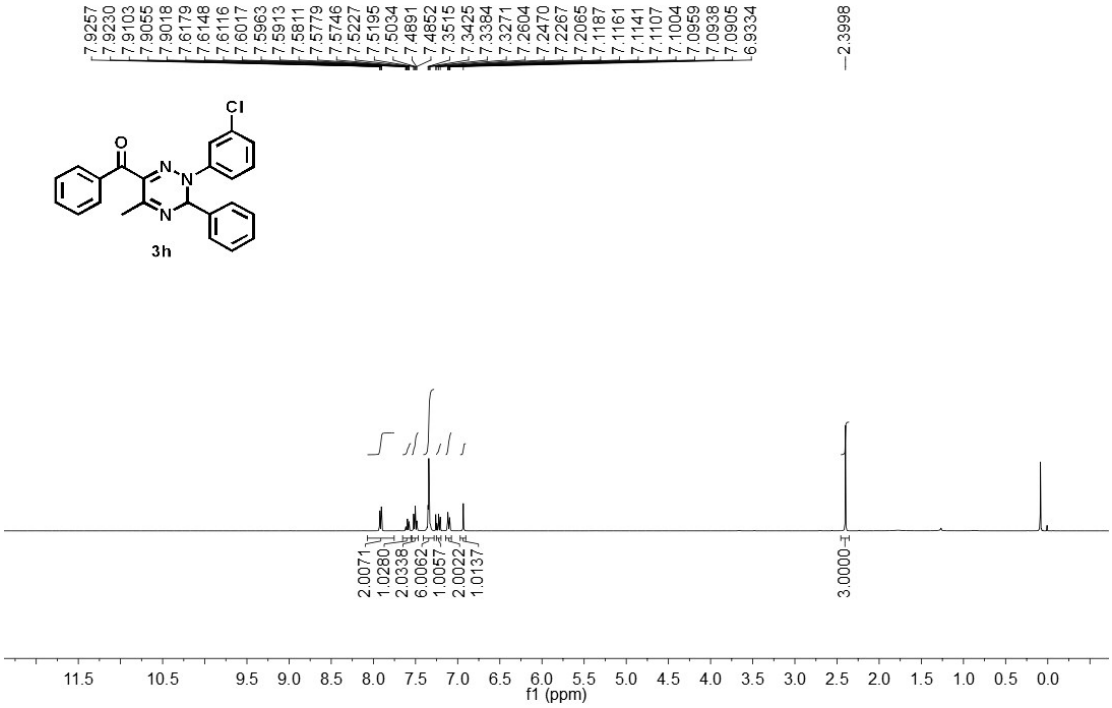
d232-1
d232-1



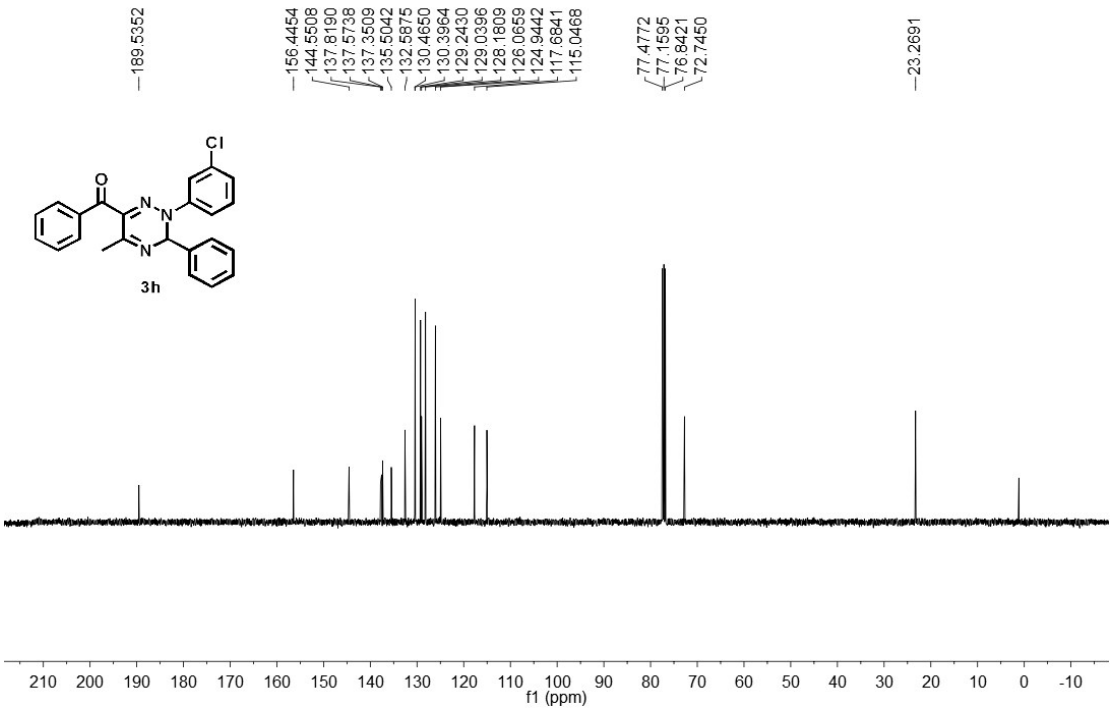
d232-1
d232-1



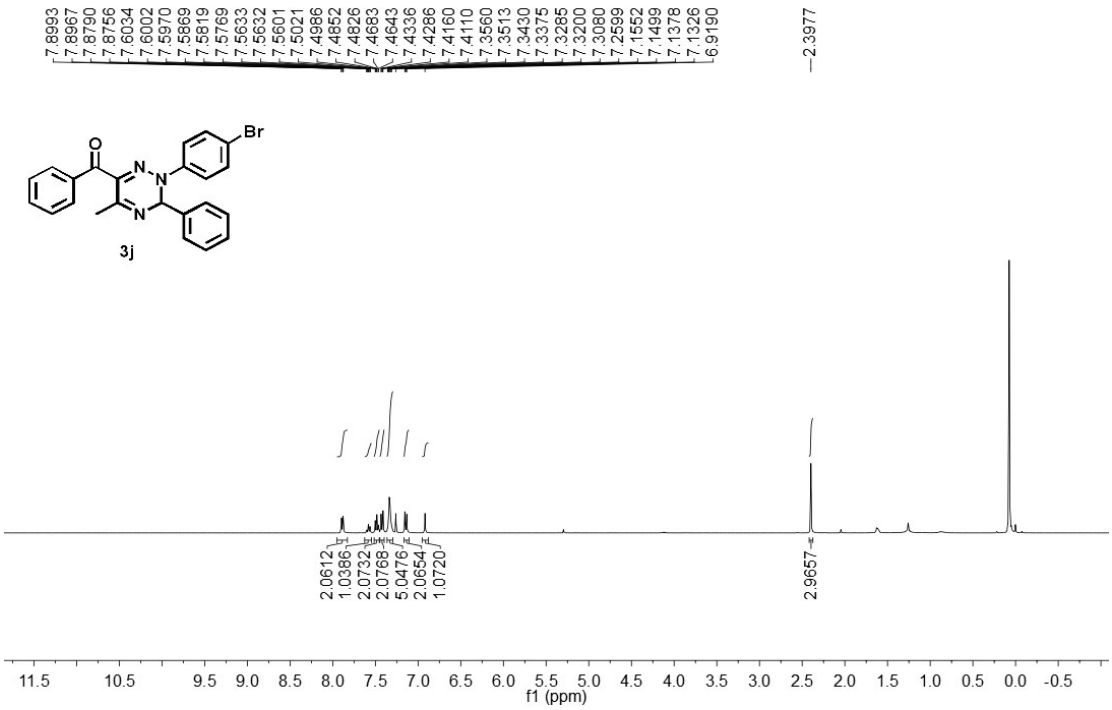
dqf-d235
dqf-d235



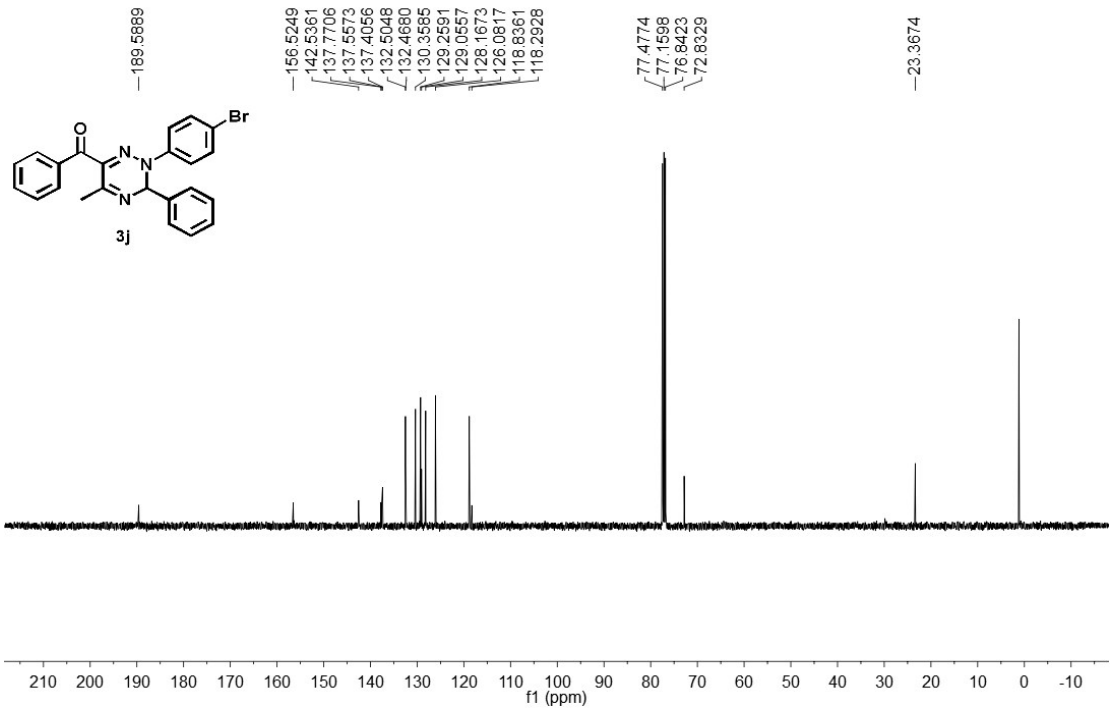
d235
d235



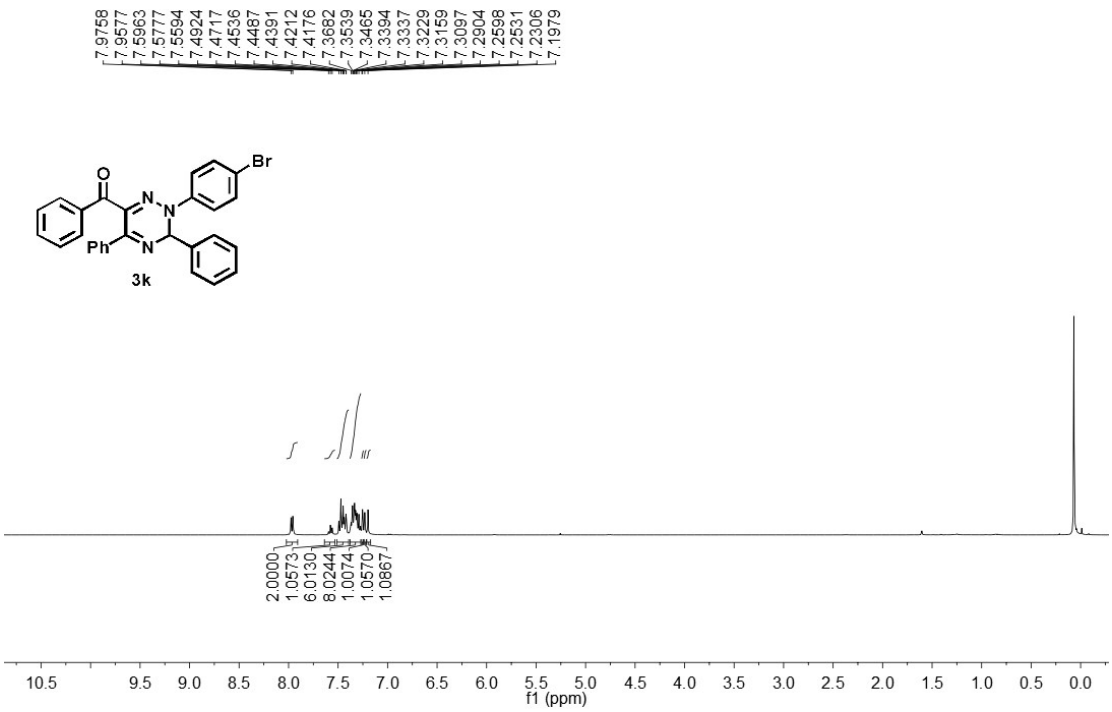
D227-1


7.8993
7.8967
7.8790
7.8756
7.6034
7.6002
7.5970
7.5869
7.5819
7.5769
7.5633
7.5632
7.5601
7.5021
7.4986
7.4852
7.4826
7.4683
7.4643
7.4336
7.4286
7.4160
7.4110
7.3560
7.3513
7.3430
7.3375
7.3285
7.3200
7.3080
7.2599
7.1552
7.1499
7.1378
7.1326
6.9190
2.3977
Br
O
N
N
N
3j
2.0612
1.0386
2.0732
2.0768
5.0476
2.0654
1.0720
2.9657
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

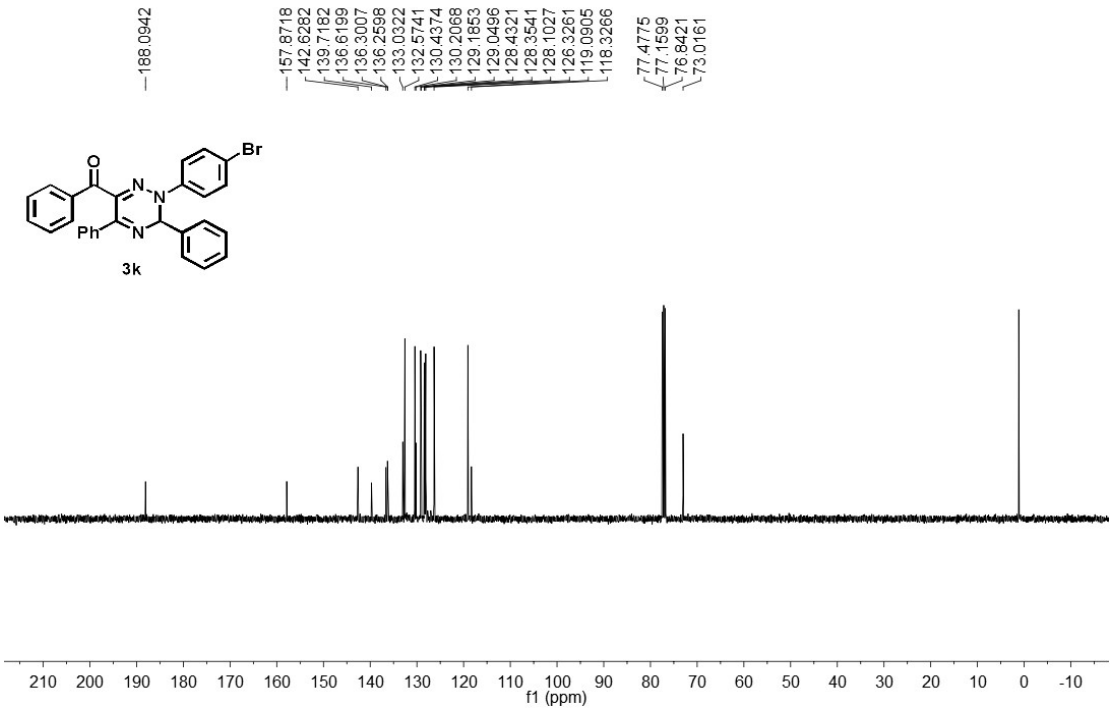
D227-1


189.5889
156.5249
142.5361
137.7706
137.5573
137.4056
132.5048
132.4680
130.3585
129.2591
129.0557
128.1673
126.0817
118.8361
118.2928
77.4774
77.1598
76.8423
72.8329
23.3674
Br
O
N
N
N
3j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

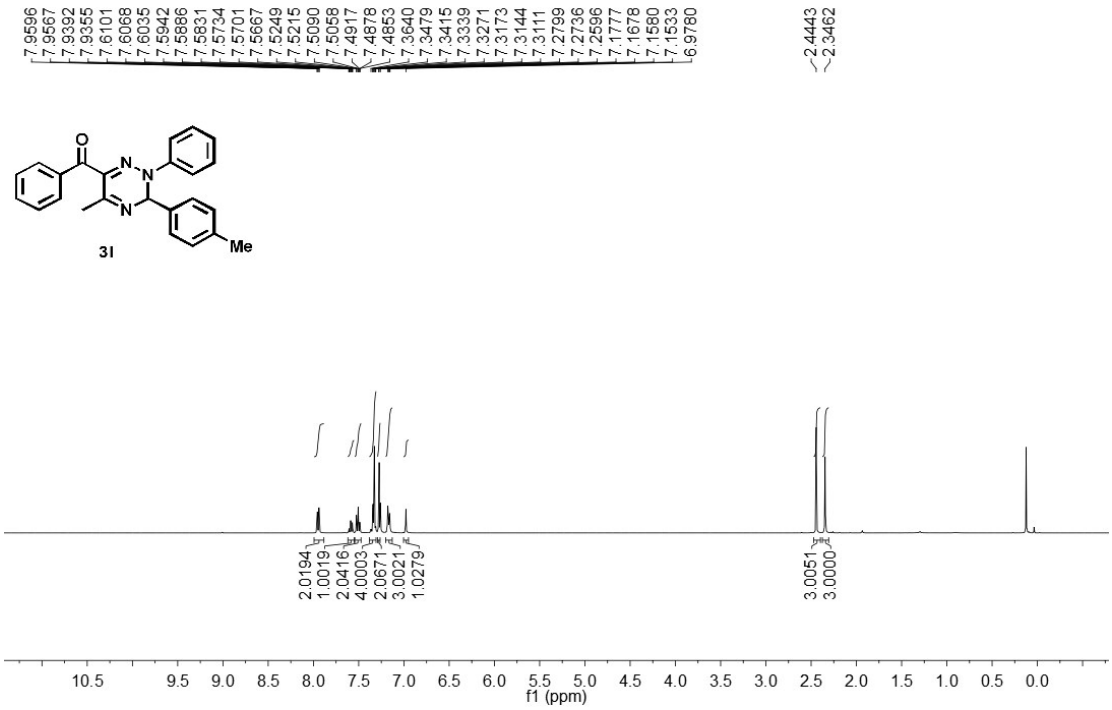
D156


7.9758
7.9577
7.5963
7.5777
7.5594
7.4924
7.4717
7.4536
7.4487
7.4391
7.4212
7.4176
7.3682
7.3539
7.3465
7.3394
7.3337
7.3229
7.3159
7.3097
7.2904
7.2598
7.2531
7.2306
7.1979
Br
O
N
N
Ph
N
3k
2.0000
1.0573
6.0130
8.0244
1.0074
1.0570
1.0867
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

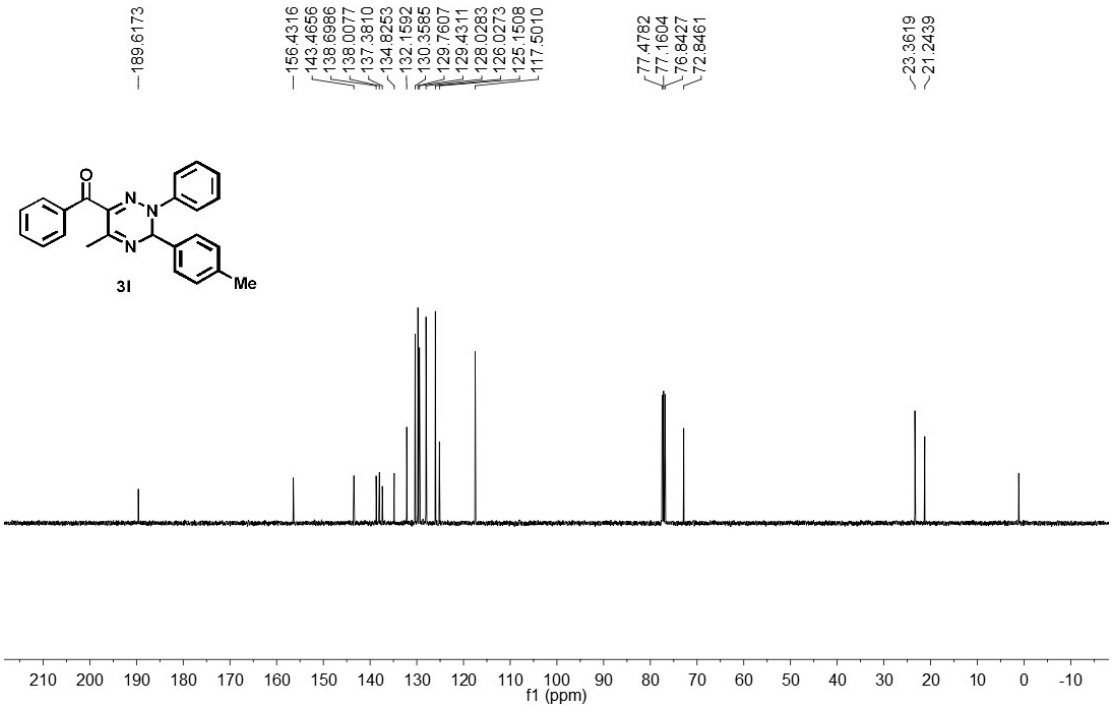
D156


188.0942
157.8718
142.6282
139.7182
136.6199
136.3007
136.2598
133.0322
132.5741
130.4374
130.2068
129.1853
129.0496
128.4321
128.3541
128.1027
126.3261
119.0905
118.3266
77.4775
77.1599
76.8421
73.0161
Br
O
N
N
Ph
N
3k
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

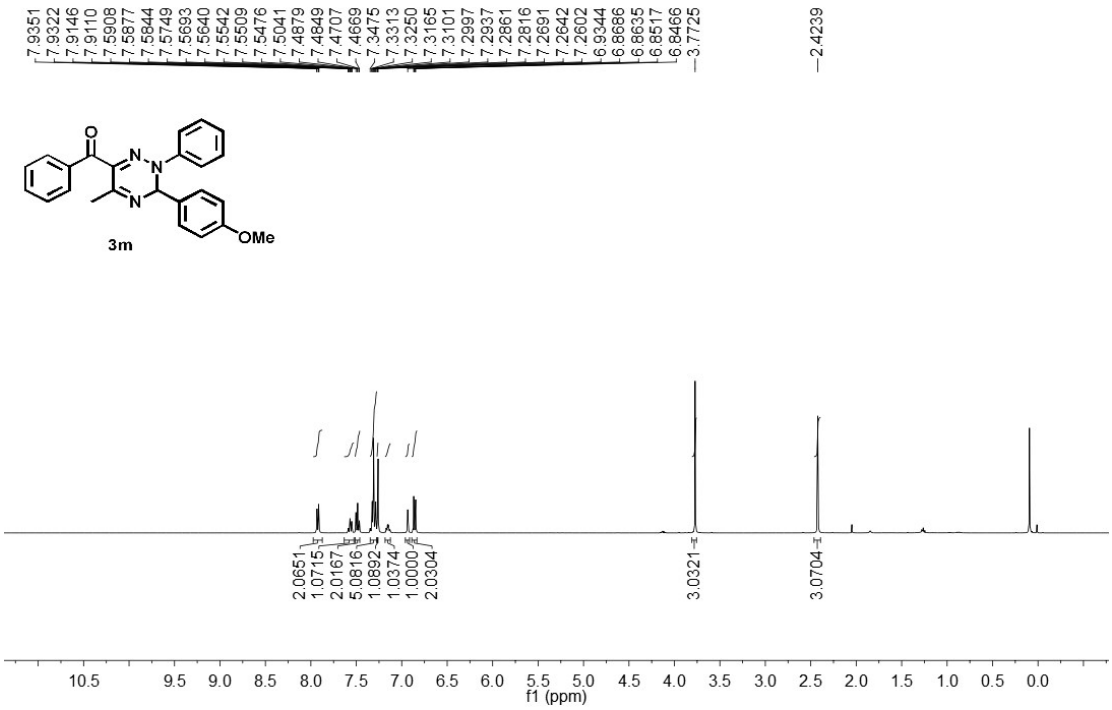
D239-2


7.9596
7.9567
7.9392
7.9355
7.6101
7.6068
7.6035
7.5942
7.5886
7.5831
7.5734
7.5701
7.5667
7.5249
7.5215
7.5090
7.5058
7.4917
7.4878
7.4853
7.3640
7.3479
7.3415
7.3339
7.3271
7.3173
7.3144
7.3111
7.2799
7.2736
7.2596
7.1777
7.1678
7.1580
7.1533
6.9780
2.4443
2.3462
O
N
N
N
Me
3l
2.0194
1.0019
2.0416
4.0003
2.0671
3.0021
1.0279
3.0051
3.0000
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

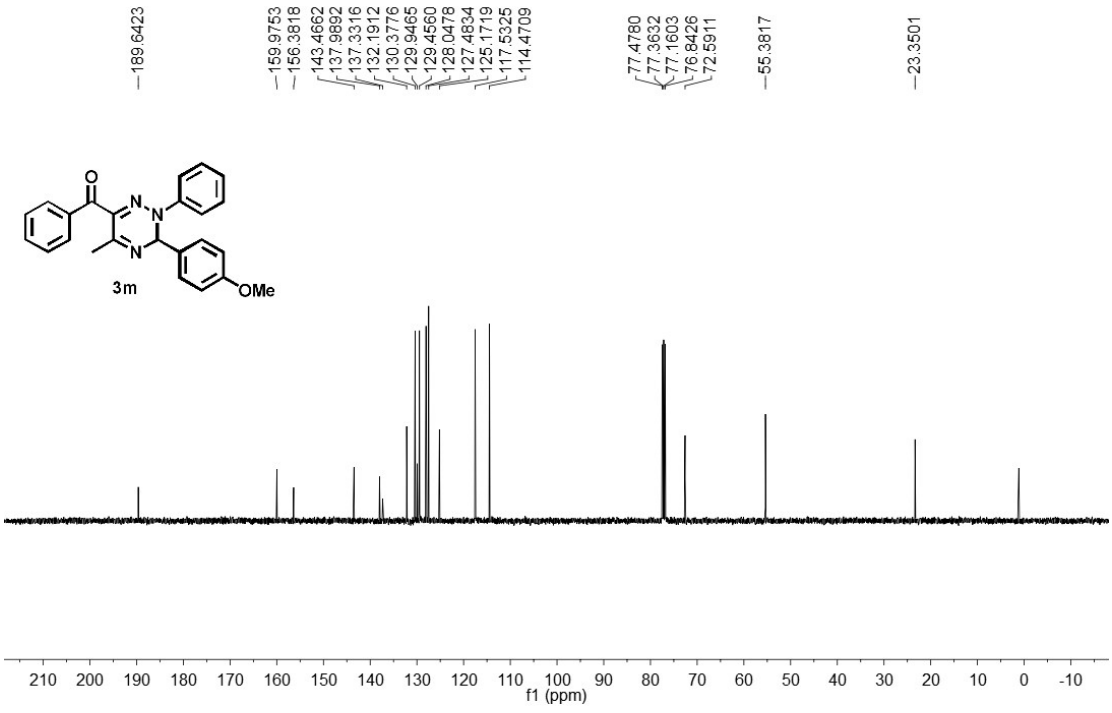
D239-2


189.6173
156.4316
143.4656
138.6986
138.0077
137.3810
134.8253
132.1592
130.3585
129.7607
129.4311
128.0283
126.0273
125.1508
117.5010
77.4782
77.1604
76.8427
72.8461
23.3619
21.2439
O
N
N
N
Me
3l
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

D240


7.9351
7.9322
7.9146
7.9110
7.5908
7.5877
7.5844
7.5749
7.5693
7.5640
7.5542
7.5509
7.5476
7.5041
7.4879
7.4849
7.4707
7.4669
7.3475
7.3313
7.3250
7.3165
7.3101
7.2997
7.2937
7.2861
7.2816
7.2691
7.2642
7.2602
6.9344
6.8686
6.8635
6.8517
6.8466
3.7725
2.4239
3m
OMe
2.0651
1.0715
2.0167
5.0816
1.0892
1.0374
1.0000
2.0304
3.0321
3.0704
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

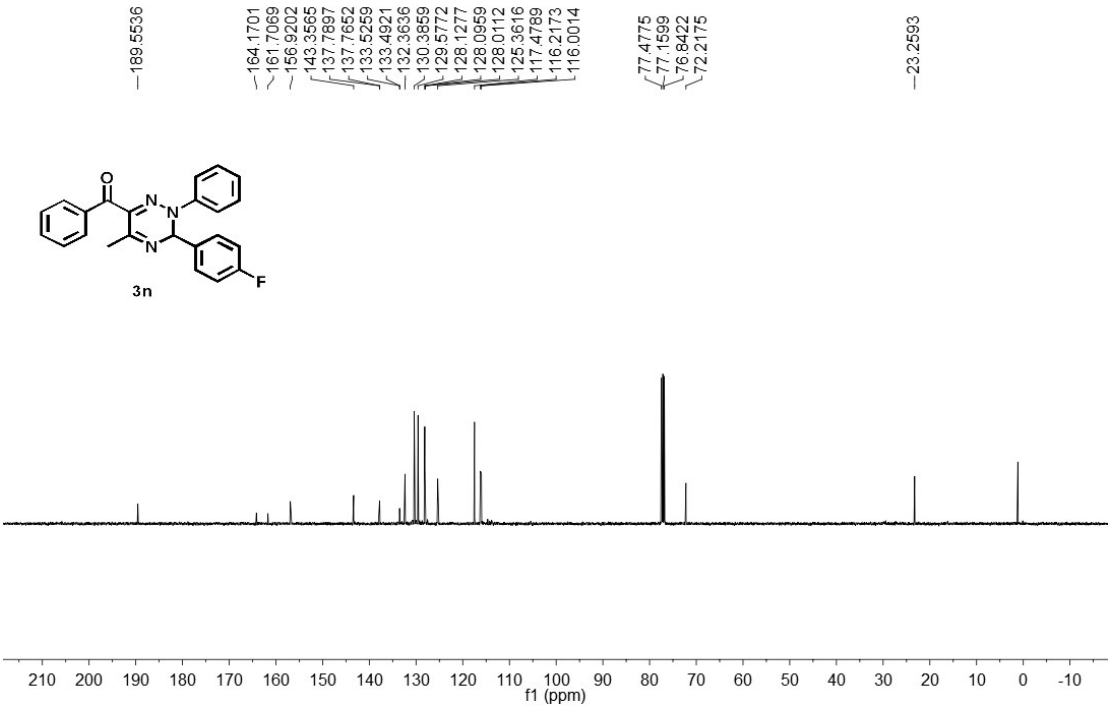
D240


189.6423
159.9753
156.3818
143.4662
137.9892
137.3316
132.1912
130.3776
129.9465
129.4560
128.0478
127.4834
125.1719
117.5325
114.4709
77.4780
77.3632
77.1603
76.8426
72.5911
55.3817
23.3501
3m
OMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

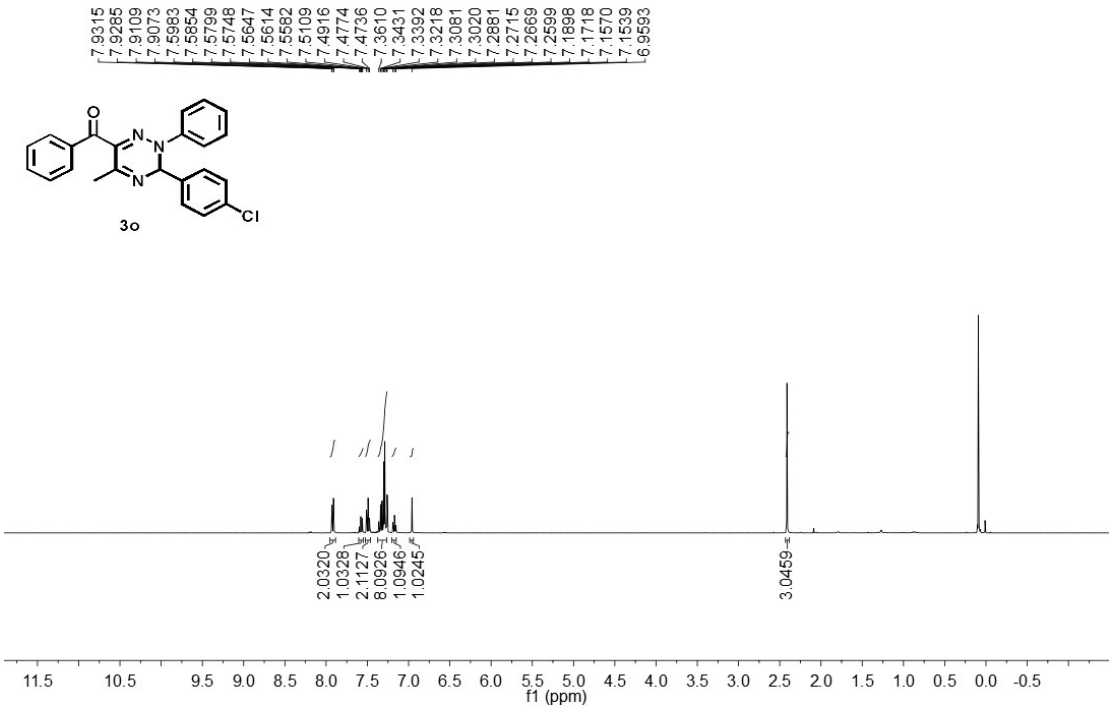
D242-1


7.9278
7.9249
7.9073
7.9036
7.5972
7.5940
7.5843
7.5789
7.5737
7.5636
7.5604
7.5571
7.5090
7.4897
7.4754
7.4716
7.3602
7.3553
7.3426
7.3379
7.3207
7.3150
7.3063
7.3010
7.2970
7.2936
7.2746
7.2718
7.2595
7.1905
7.1875
7.1844
7.1696
7.1552
7.1518
7.1487
7.0426
7.0374
7.0210
7.0164
7.0044
6.9993
2.4130
3n
F
2.0852
1.0629
2.0749
6.1285
1.0965
2.0638
1.0461
3.0215
1.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

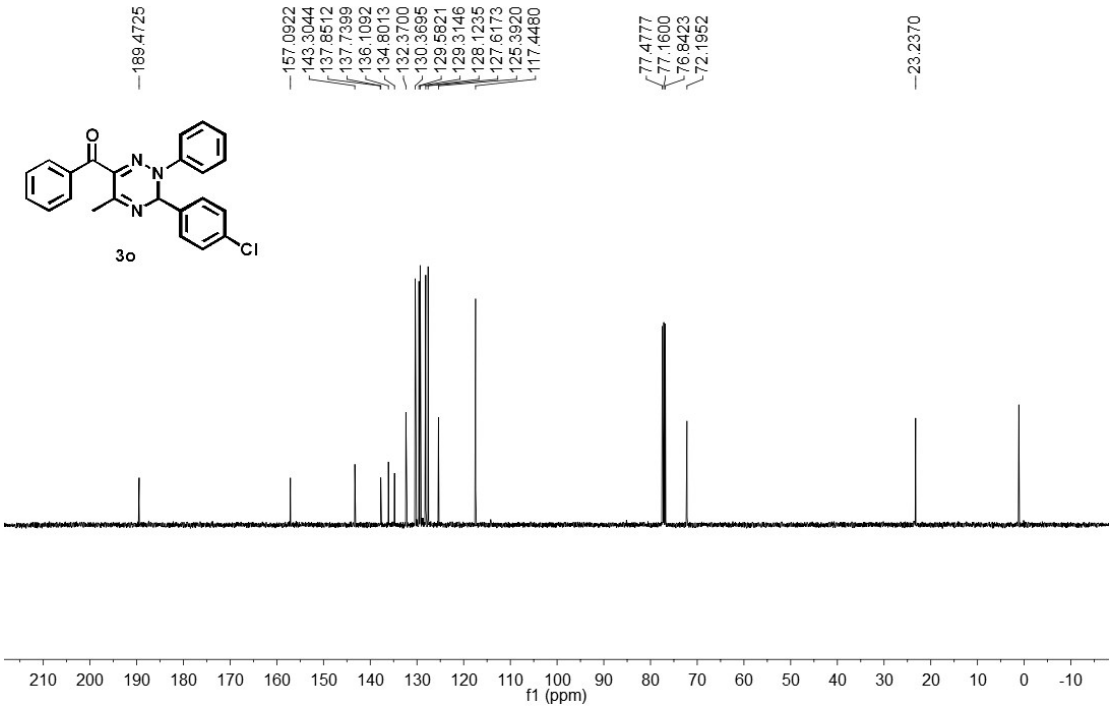
D242-1


189.5536
164.1701
161.7069
156.9202
143.3565
137.7897
137.7652
133.5259
133.4921
132.3636
130.3859
129.5772
128.1277
128.0959
128.0112
125.3616
117.4789
116.2173
116.0014
77.4775
77.1599
76.8422
72.2175
23.2593
3n
F
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

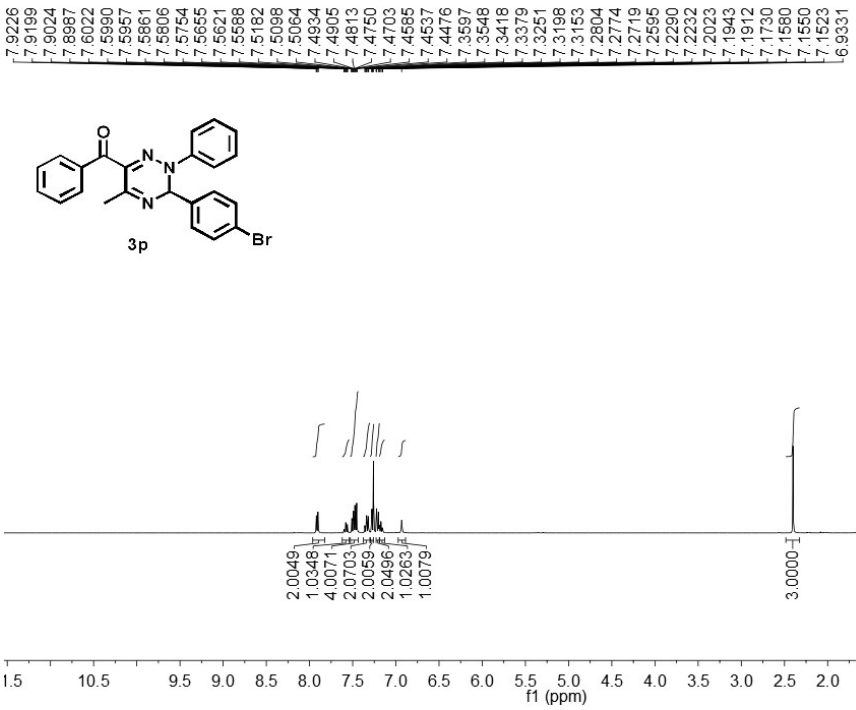
d231
d231



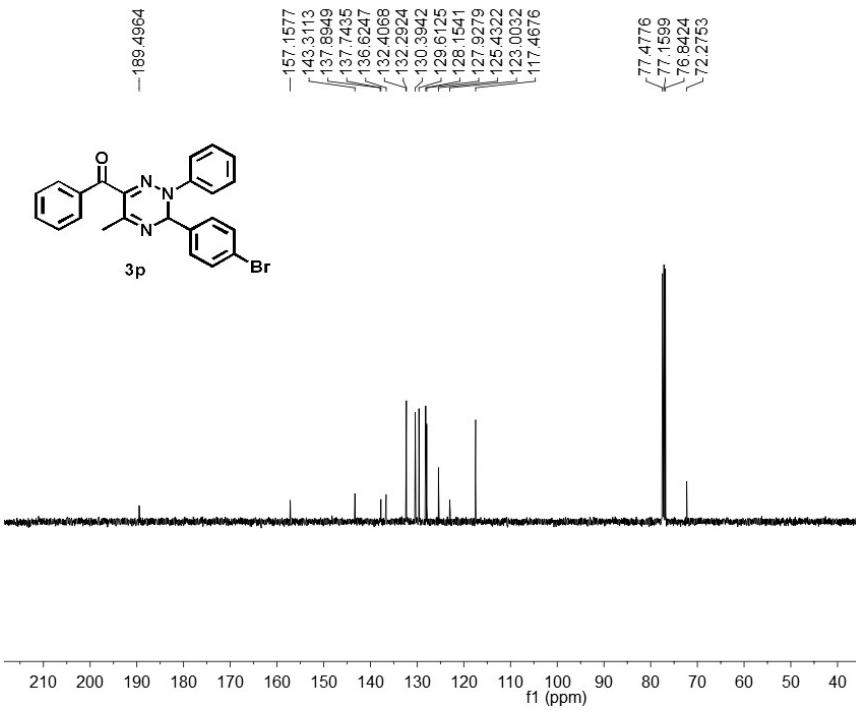
d231
d231



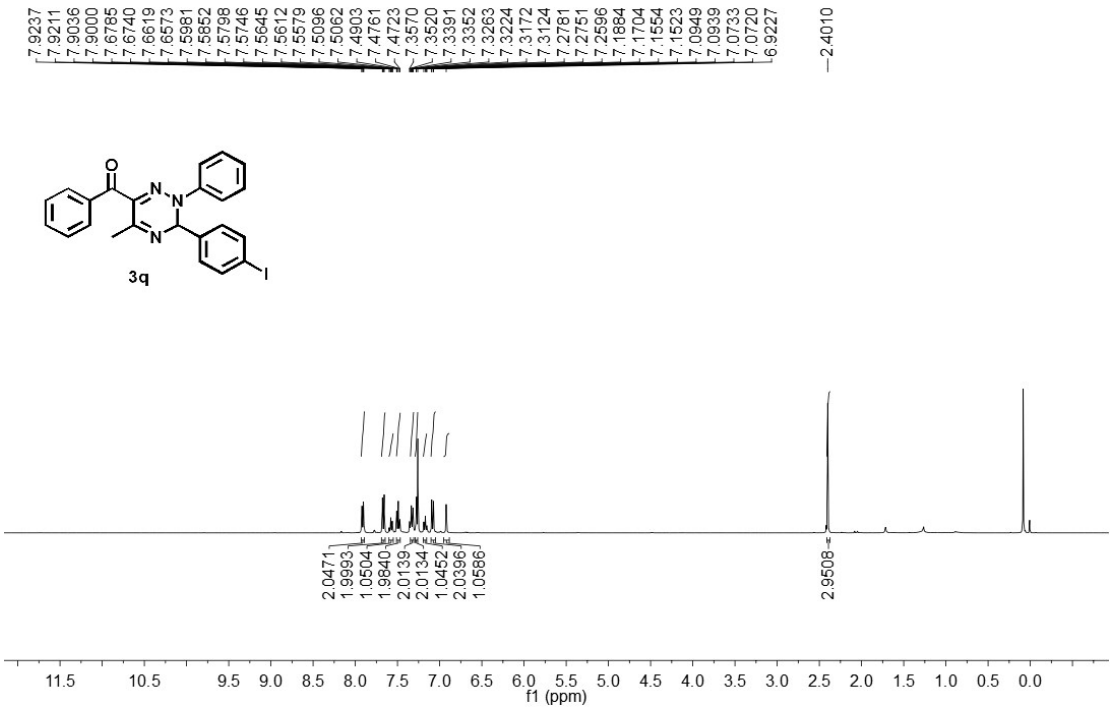
D243


7.9226
7.9199
7.9024
7.8987
7.6022
7.5990
7.5957
7.5861
7.5806
7.5754
7.5655
7.5621
7.5588
7.5182
7.5098
7.5064
7.4934
7.4905
7.4813
7.4750
7.4703
7.4585
7.4537
7.4476
7.3597
7.3548
7.3418
7.3379
7.3251
7.3198
7.3153
7.2804
7.2774
7.2719
7.2595
7.2290
7.2232
7.2023
7.1943
7.1912
7.1730
7.1580
7.1550
7.1523
6.9331
3p
Br
2.0049
1.0348
4.0071
2.0703
2.0059
2.0496
1.0263
1.0079
3.0000
f1 (ppm)

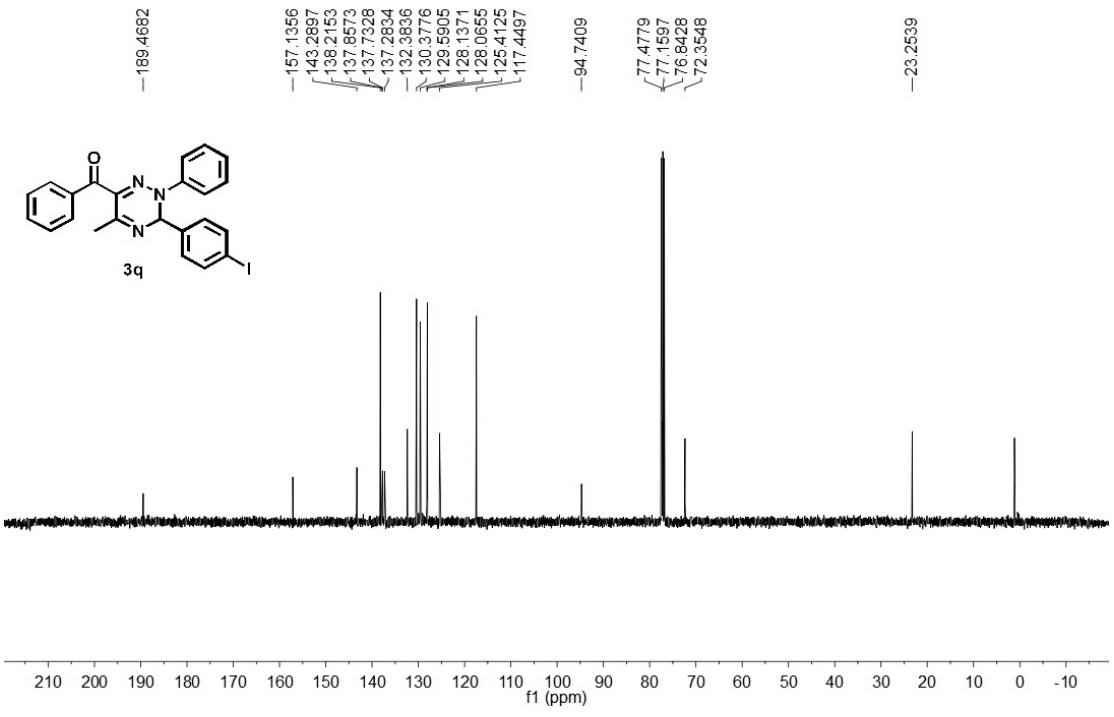
D243


189.4964
157.1577
143.3113
137.8949
137.7435
136.6247
132.4068
132.2924
130.3942
129.6125
128.1541
127.9279
125.4322
123.0032
117.4676
77.4776
77.1599
76.8424
72.2753
23.2636
3p
Br
f1 (ppm)

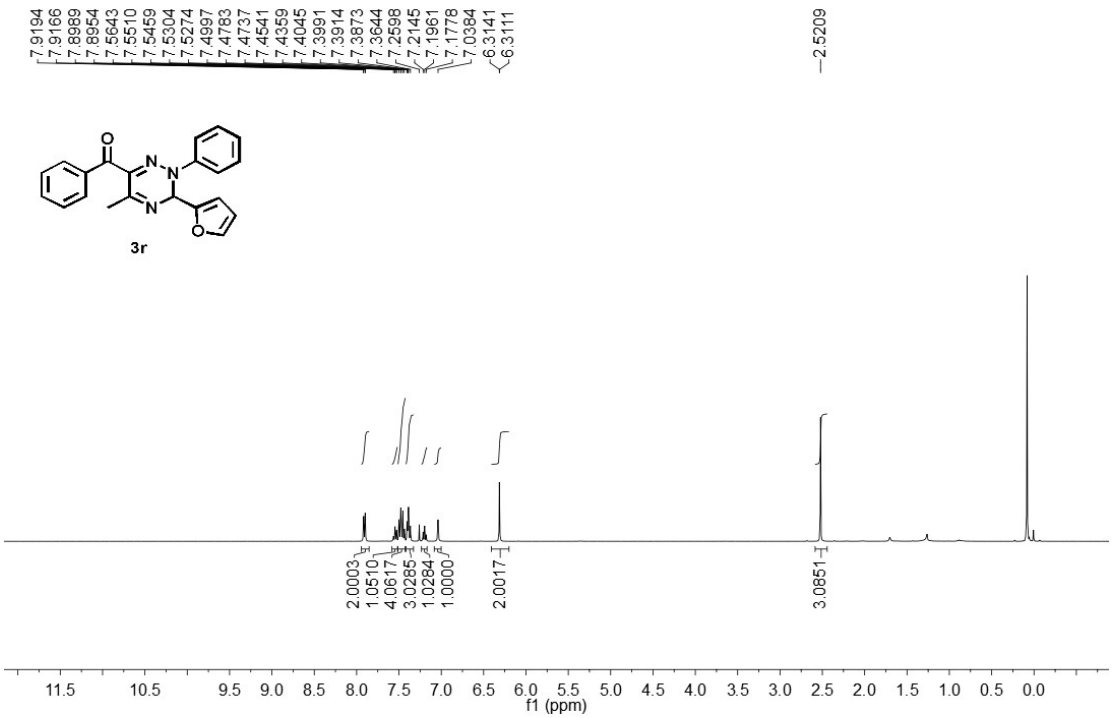
D245


7.9237
7.9211
7.9036
7.9000
7.6785
7.6740
7.6619
7.6573
7.5981
7.5852
7.5798
7.5746
7.5645
7.5612
7.5579
7.5096
7.5062
7.4903
7.4761
7.4723
7.3570
7.3520
7.3391
7.3352
7.3263
7.3224
7.3172
7.3124
7.2781
7.2751
7.2596
7.1884
7.1704
7.1554
7.1523
7.0949
7.0939
7.0733
7.0720
6.9227
2.4010
3q
2.0471
1.9993
1.0504
1.9840
2.0139
2.0134
1.0452
2.0396
1.0586
2.9508
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

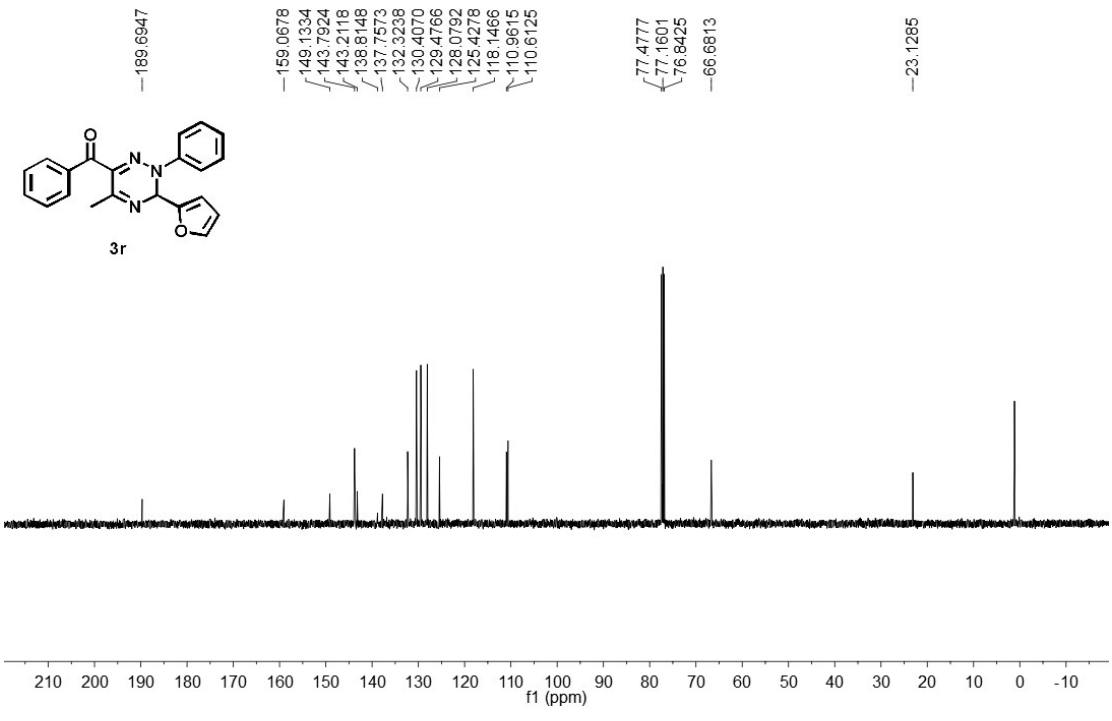
D245


189.4682
157.1356
143.2897
138.2153
137.8573
137.7328
137.2834
132.3836
130.3776
129.5905
128.1371
128.0655
125.4125
117.4497
94.7409
77.4779
77.1597
76.8428
72.3548
23.2539
3q
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

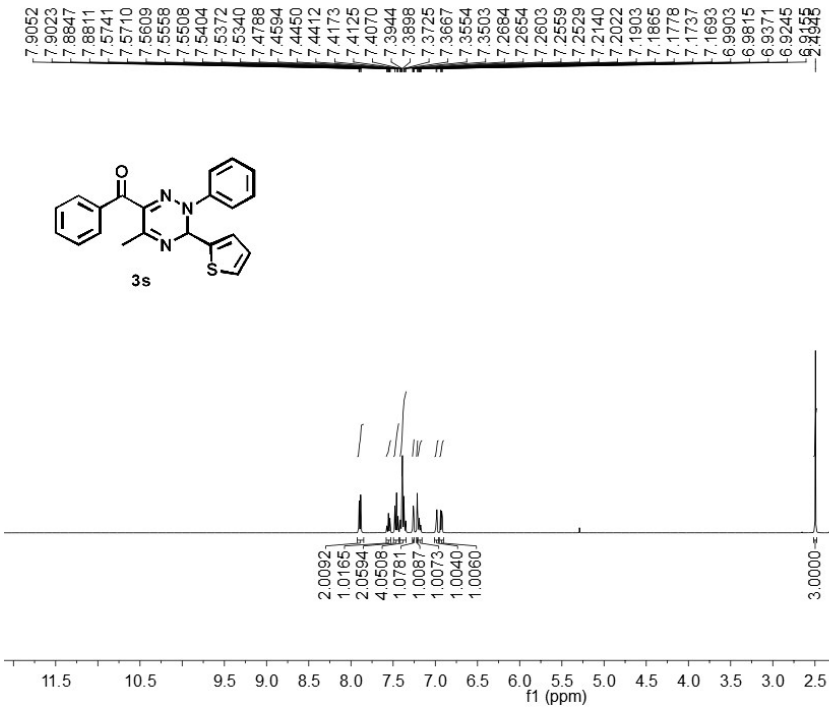
d247


7.9194
7.9166
7.8989
7.8954
7.5643
7.5510
7.5459
7.5304
7.5274
7.4997
7.4783
7.4737
7.4541
7.4359
7.4045
7.3991
7.3914
7.3873
7.3644
7.2598
7.2145
7.1961
7.1778
7.0384
6.3141
6.3111
2.5209
3r
2.0003
1.0510
4.0617
3.0285
1.0284
1.0000
2.0017
3.0851
f1 (ppm)

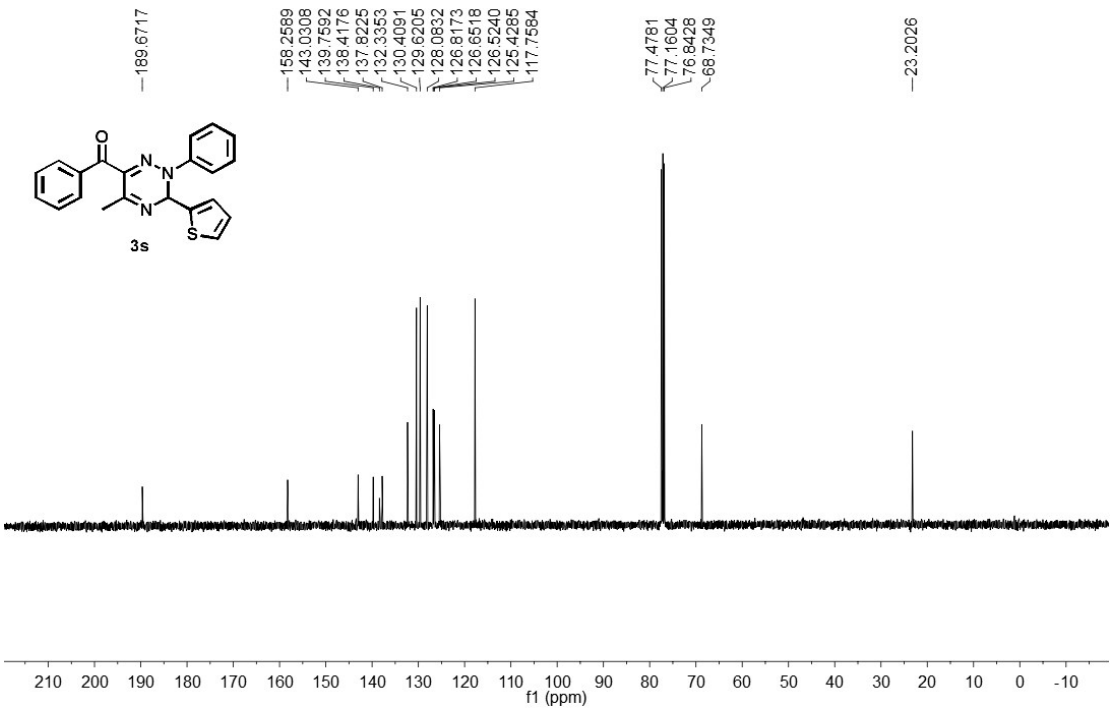
d247


189.6947
159.0678
149.1334
143.7924
143.2118
138.8148
137.7573
132.3238
130.4070
129.4766
128.0792
125.4278
118.1466
110.9615
110.6125
77.4777
77.1601
76.8425
66.6813
23.1285
3r
f1 (ppm)

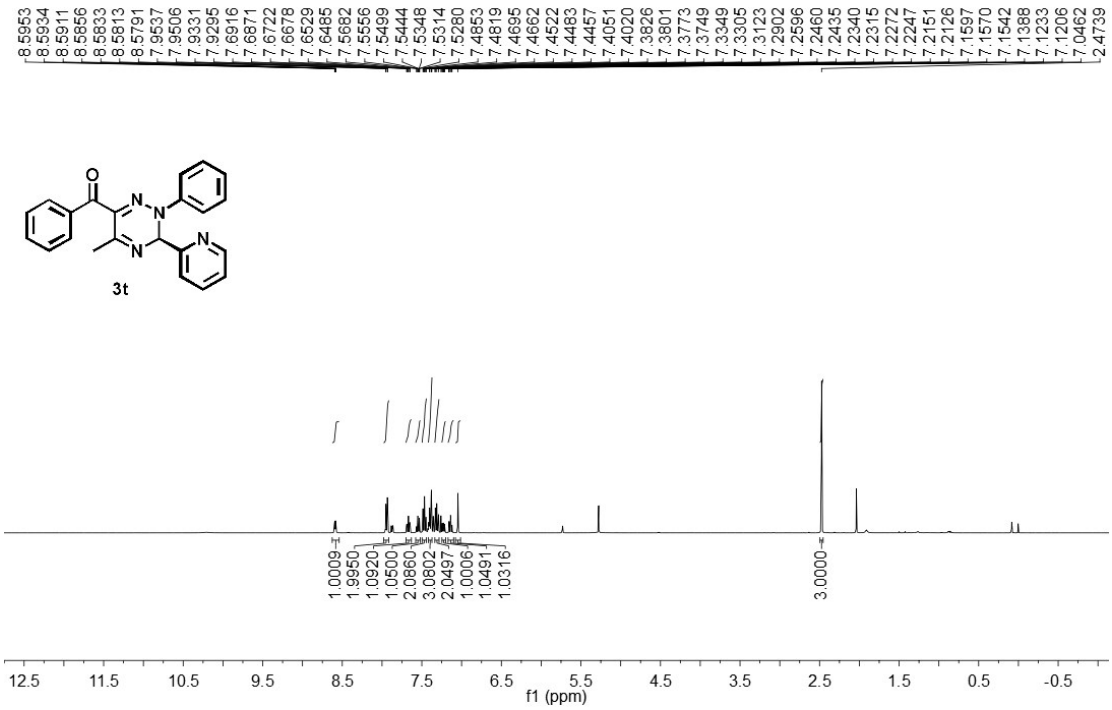
D260-1


7.9052
7.9023
7.8847
7.8811
7.5741
7.5710
7.5609
7.5558
7.5508
7.5404
7.5372
7.5340
7.4788
7.4594
7.4450
7.4412
7.4173
7.4125
7.4070
7.3944
7.3898
7.3725
7.3667
7.3554
7.3503
7.2684
7.2654
7.2603
7.2559
7.2529
7.2140
7.2022
7.1903
7.1865
7.1778
7.1737
7.1693
6.9903
6.9815
6.9371
6.9245
2.4945
3s
2.0092
1.0165
2.0594
4.0508
1.0781
1.0087
1.0073
1.0040
1.0060
3.0000
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

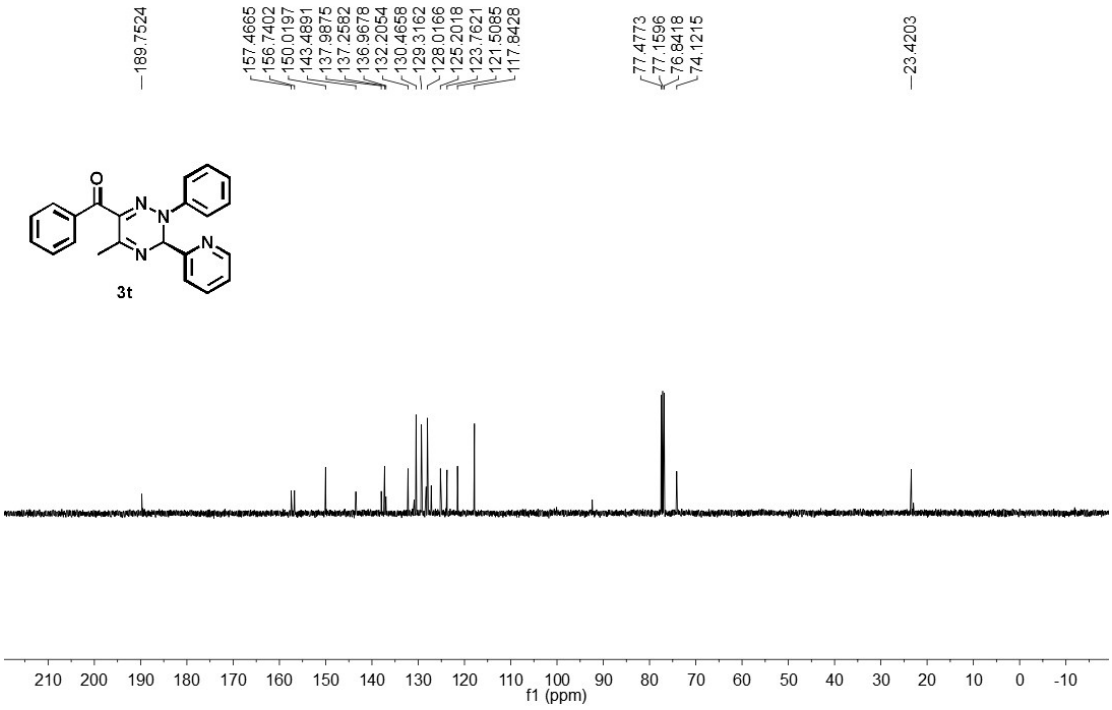
D260-1


189.6717
158.2589
143.0308
139.7592
138.4176
137.8225
132.3353
130.4091
129.6205
128.0832
126.8173
126.6518
126.5240
125.4285
117.7584
77.4781
77.1604
76.8428
68.7349
23.2026
3s
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

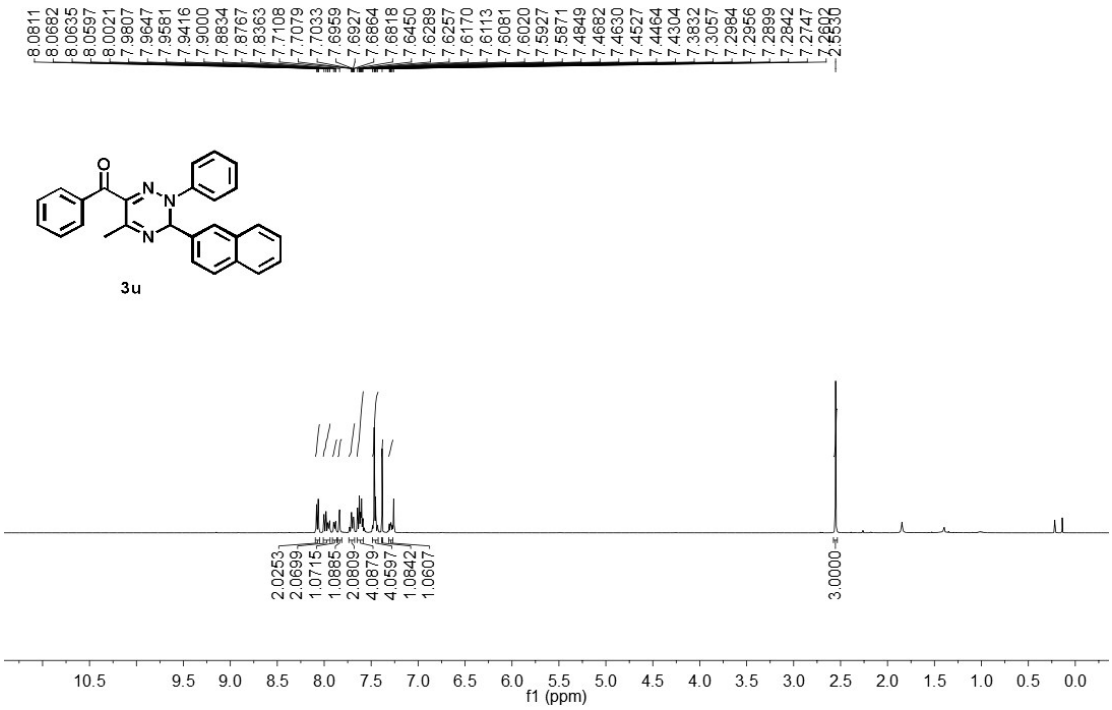
D282-


8.5953
8.5934
8.5911
8.5856
8.5833
8.5813
8.5791
7.9537
7.9506
7.9331
7.9295
7.6916
7.6871
7.6722
7.6678
7.6529
7.6485
7.5682
7.5556
7.5499
7.5444
7.5348
7.5314
7.5280
7.4853
7.4819
7.4695
7.4662
7.4522
7.4483
7.4457
7.4051
7.4020
7.3826
7.3801
7.3773
7.3749
7.3349
7.3305
7.3123
7.2902
7.2596
7.2460
7.2435
7.2340
7.2315
7.2272
7.2247
7.2151
7.2126
7.1597
7.1570
7.1542
7.1388
7.1233
7.1206
7.0462
2.4739
O
N
N
N
N
3t
1.0009
1.9950
1.0920
1.0500
2.0860
3.0802
2.0497
1.0006
1.0491
1.0316
3.0000
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

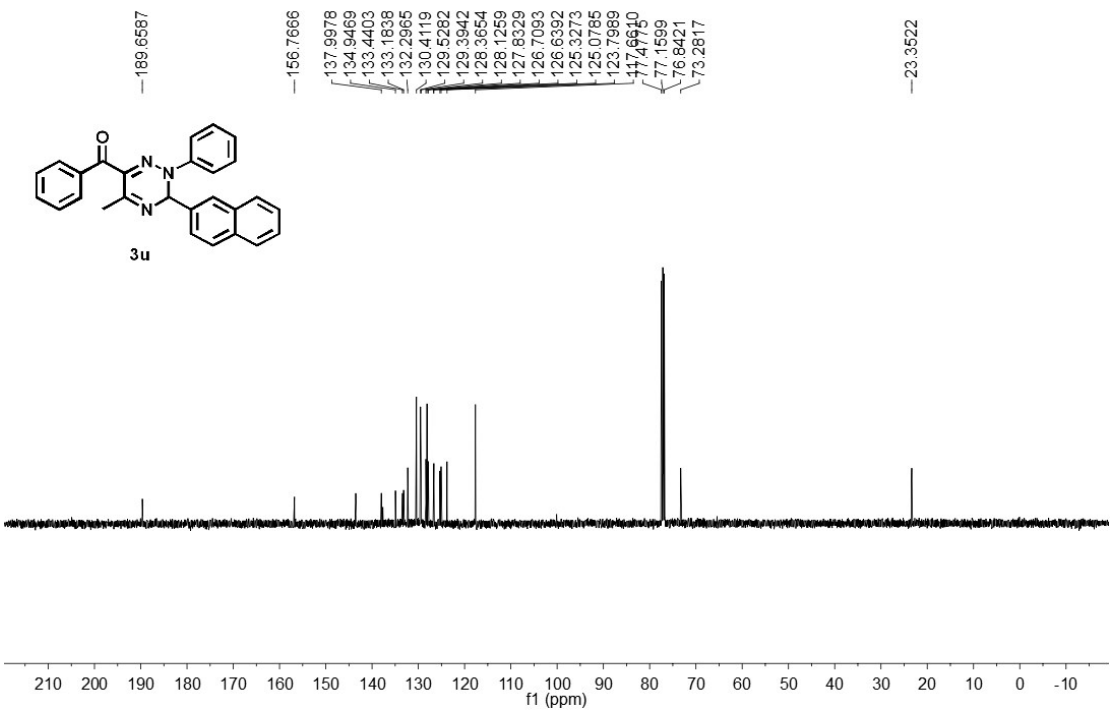
D282-


189.7524
157.4665
156.7402
150.0197
143.4891
137.9675
137.2582
136.9678
132.2054
130.4658
129.3162
128.0166
125.2018
123.7621
121.5085
117.8428
77.4773
77.1596
76.8418
74.1215
23.4203
O
N
N
N
N
3t
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

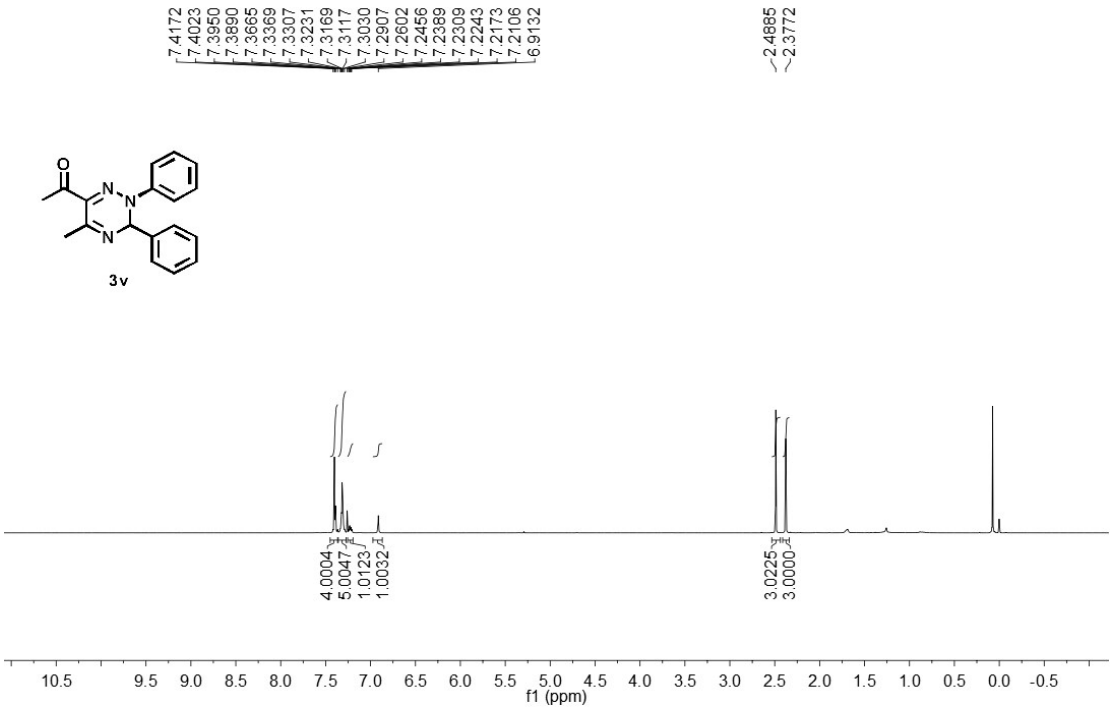
D262


8.0811
8.0682
8.0635
8.0597
8.0021
7.9807
7.9647
7.9581
7.9416
7.9000
7.8834
7.8767
7.8363
7.7108
7.7079
7.7033
7.6959
7.6927
7.6864
7.6818
7.6450
7.6289
7.6257
7.6170
7.6113
7.6081
7.6020
7.5927
7.5871
7.4849
7.4682
7.4630
7.4527
7.4464
7.4304
7.3832
7.3057
7.2984
7.2956
7.2899
7.2842
7.2747
7.2602
2.5530
3u
2.0253
2.0699
1.0715
1.0885
2.0809
4.0879
4.0597
1.0842
1.0607
3.0000
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

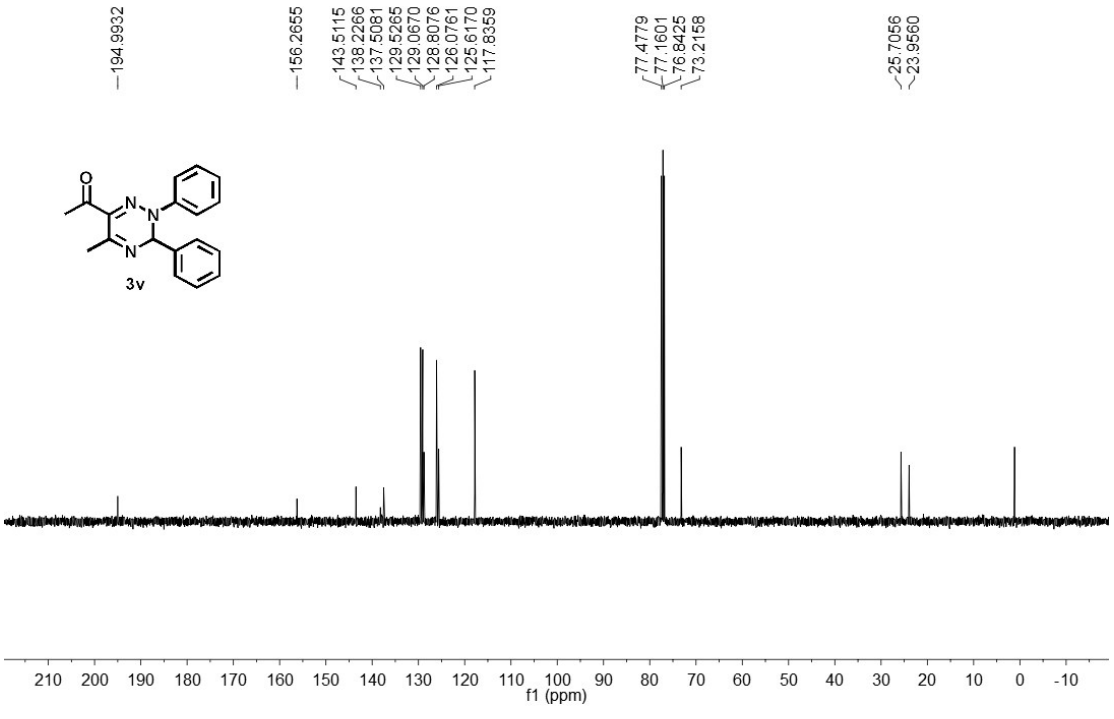
D262


189.6587
156.7666
137.9978
134.9469
133.4403
133.1838
132.2965
130.4119
129.5282
129.3942
128.3654
128.1259
127.8329
126.7093
126.6392
125.3273
125.0785
123.7989
117.6610
77.1599
76.8421
73.2817
23.3522
3u
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

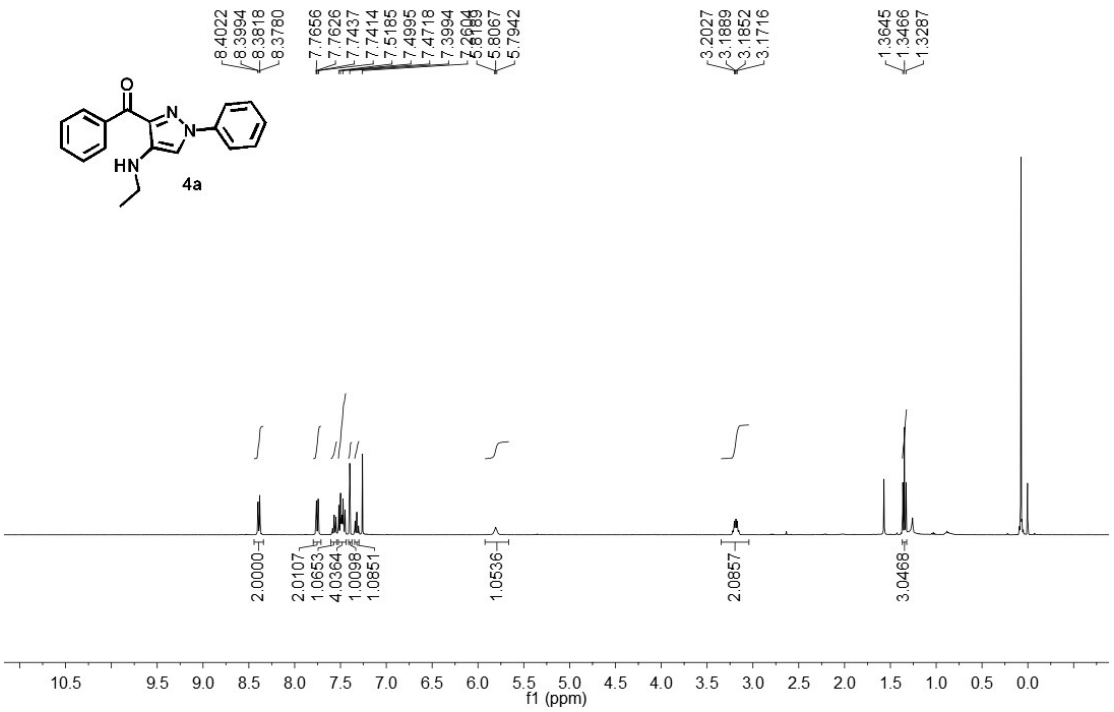
D250-2


7.4172
7.4023
7.3950
7.3890
7.3665
7.3369
7.3307
7.3231
7.3169
7.3117
7.3030
7.2907
7.2602
7.2456
7.2389
7.2309
7.2243
7.2173
7.2106
6.9132
2.4885
2.3772
3v
4.0004
5.0047
1.0123
1.0032
3.0225
3.0000
f1 (ppm)

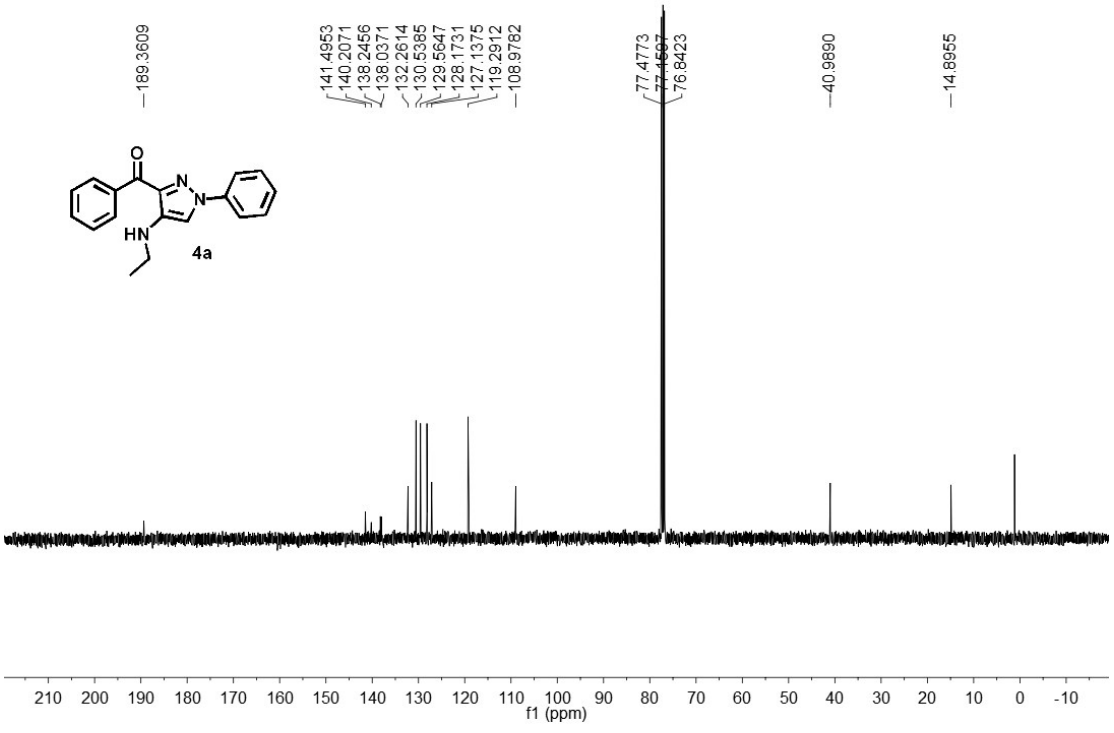
D250-2


194.9932
156.2655
143.5115
138.2266
137.5081
129.5265
129.0670
128.8076
126.0761
125.6170
117.8359
77.4779
77.1601
76.8425
73.2158
25.7056
23.9560
3v
f1 (ppm)

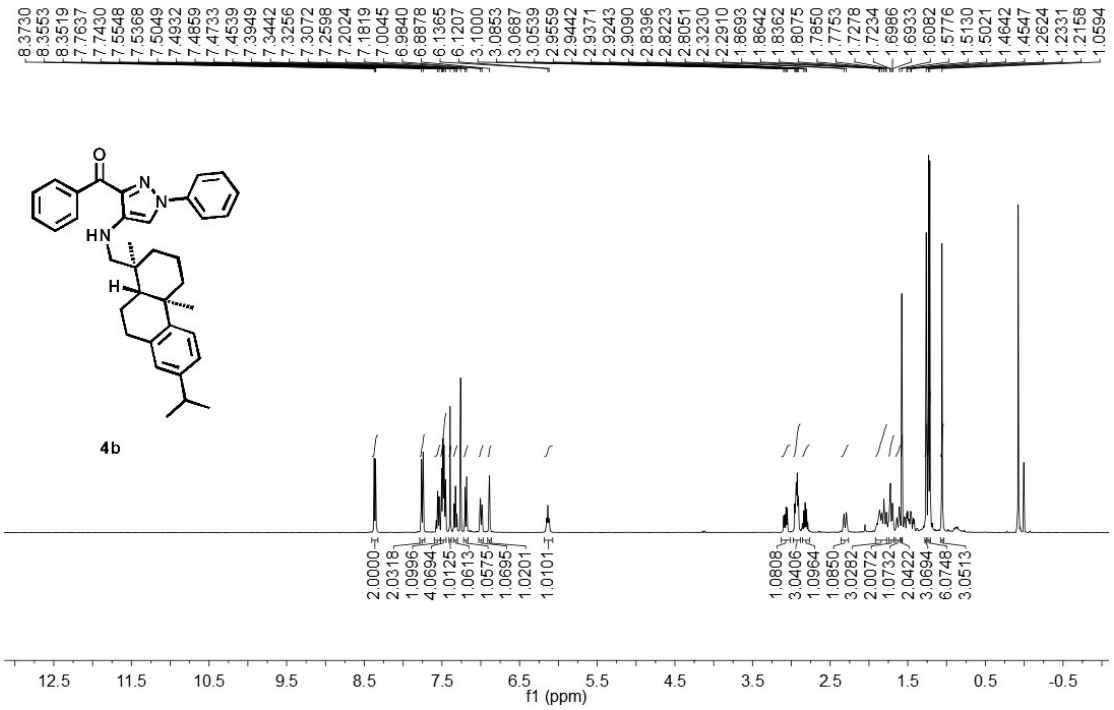
D246-1


8.4022
8.3994
8.3818
8.3780
7.7656
7.7626
7.7437
7.7414
7.5185
7.4995
7.4718
7.3994
5.8067
5.7942
3.2027
3.1889
3.1852
3.1716
1.3645
1.3466
1.3287
4a
2.0000
2.0107
1.0653
4.0364
1.0098
1.0851
1.0536
2.0857
3.0468
f1 (ppm)

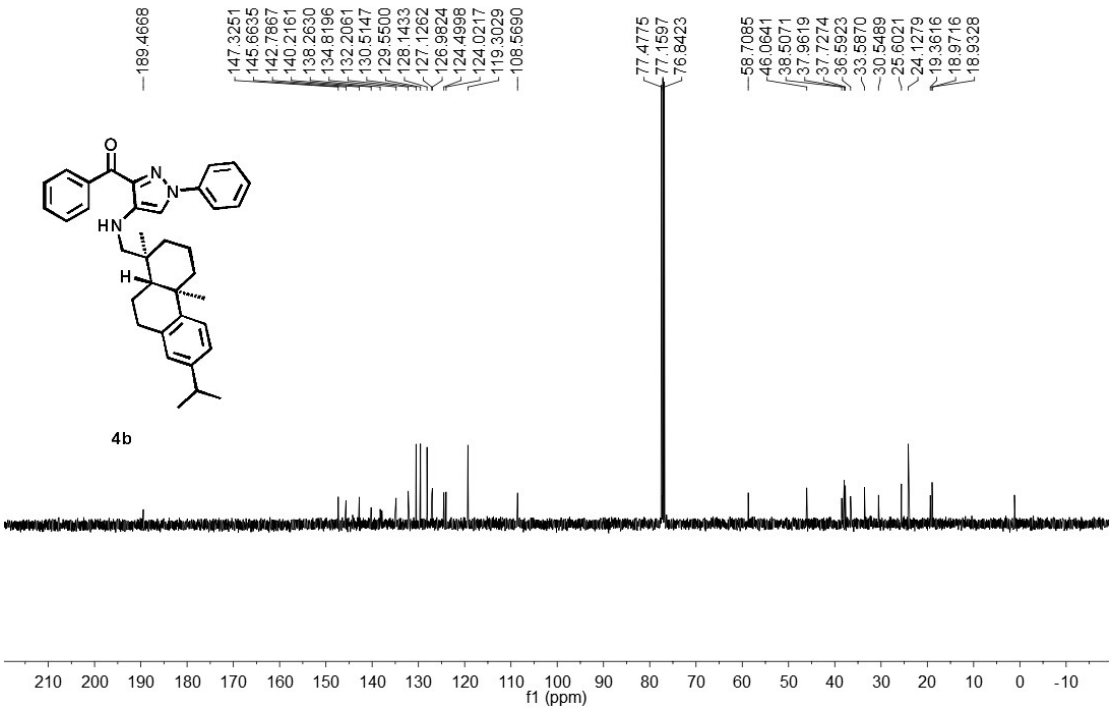
D246-1


189.3609
141.4953
140.2071
138.2456
138.0371
132.2614
130.5385
129.5647
128.1731
127.1375
119.2912
108.9782
77.4773
76.8423
40.9890
14.8955
4a
f1 (ppm)

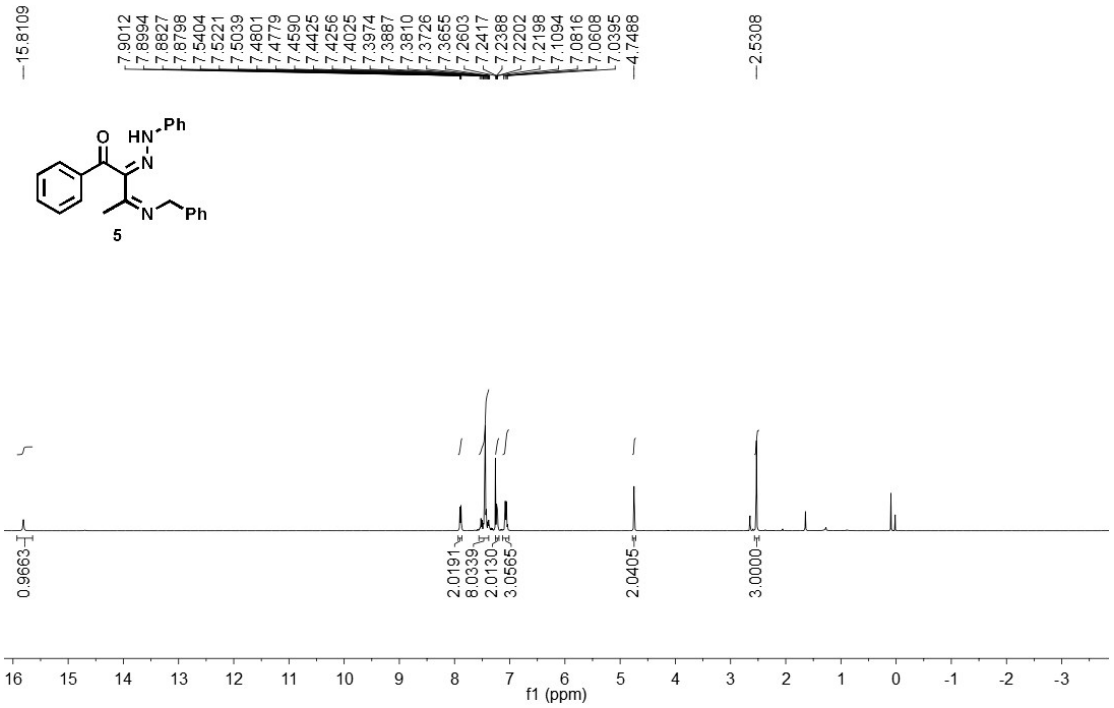
D281


8.3730
8.3553
8.3519
7.7637
7.7430
7.5548
7.5368
7.5049
7.4932
7.4859
7.4733
7.4539
7.3949
7.3442
7.3256
7.3072
7.2598
7.2024
7.1819
7.0045
6.9840
6.8878
6.1365
6.1207
3.1000
3.0853
3.0687
3.0539
2.9559
2.9442
2.9371
2.9243
2.9090
2.8396
2.8223
2.8051
2.3230
2.2910
1.8693
1.8642
1.8362
1.8075
1.7850
1.7753
1.7278
1.7234
1.6986
1.6933
1.6082
1.5776
1.5130
1.5021
1.4642
1.4547
1.2624
1.2331
1.2158
1.0594
O
N
N
HN
H
4b
2.0000
2.0318
1.0996
4.0694
1.0125
1.0613
1.0575
1.0695
1.0201
1.0101
1.0808
3.0406
1.0964
1.0850
3.0282
2.0072
1.0732
2.0422
3.0694
6.0748
3.0513
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

D281


189.4668
147.3251
145.6635
142.7867
140.2161
138.2630
134.8196
132.2061
130.5147
129.5500
128.1433
127.1262
126.9824
124.4998
124.0217
119.3029
108.5690
77.4775
77.1597
76.8423
58.7085
46.0641
38.5071
37.9619
37.7274
36.5923
33.5870
30.5489
25.6021
24.1279
19.3616
18.9716
18.9328
O
N
N
HN
H
4b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

DQF-INTERMEDIATE



DQF-INTERMEDIATE