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Supporting Information

Formal [4 + 1] Cycloaddition of in Situ Generated 1,2-Diaza-1,3-dienes with Diazo Esters: Facile Approaches to Dihydropyrazoles Containing a Quaternary Center

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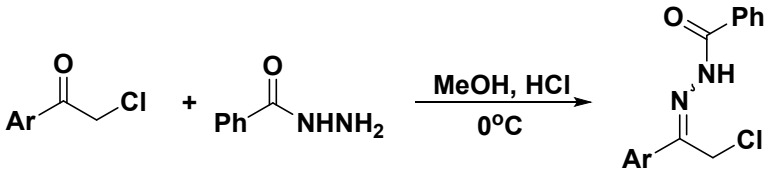
CONTENTS

1) General

All the reactions were performed under argon atmosphere in a 10 mL Schlenk tube. All solvents were distilled prior to use. CH_2Cl_2, $CHCl_3$ and CH_3CN were dried over CaH_2. Tetrahydrofuran and diethylether were distilled from sodium-benzophenone. For chromatography, 300-400 mesh silica gel (Qingdao, China) was employed. ^1H NMR and ^{13}C NMR spectra were recorded on Brucker ARX 400 spectrometer in $CDCl_3$ solution or DMSO solution and the chemical shifts were reported in parts per million (δ) relative to internal standard TMS (0 ppm). Coupling constants (*J*) are reported in Hz and refer to apparent peak multiplications. IR spectra were recorded on Nicolet iS10 in wave numbers, cm^{-1}. High resolution mass spectra were obtained on Bruker Daltonics micrOTOF-Q II spect-rometer in ESI mode. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

2）General preparation procedure for hydrazones

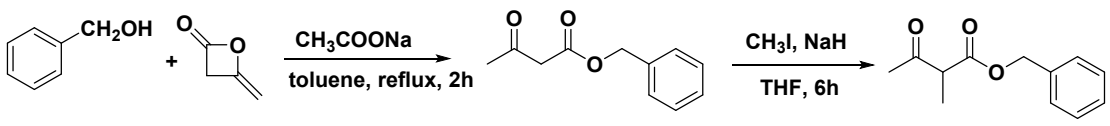


The hydrazone compounds were obtained according to the literature procedure.[1a] To a stirred solution of α-chlorocarbonyl compound (10 mmol, 1.0 eq.) in methanol (10 mL), the benzhydrazide (15 mmol, 1.5 eq.) and HCl (conc., 0.25 mL) was added at 0 °C. The mixture was stirred at the same temperature for 3 h and filtered then washed with Et_2O (10 mL). The crude product was then recrystallized from MeOH. Compound **1** was obtained as a white solid.

The α-halocarbonyl compound were prepared according to the literature procedures[1b-e].

3）General preparation procedure for the diazo substrates

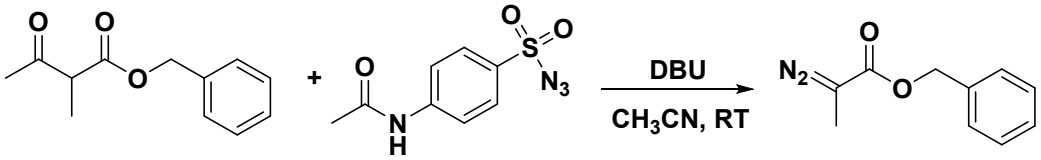
Benzyl 2-methyl-3-oxobutanoate(2a)[2a]



To a stirred solution of phenylmethanol (9.56 mL, 92.47 mmol, 1.0 equiv.) and CH_3COONa (1.26 g, 9.25 mmol, 0.1 equiv.) in toluene (50 mL) was added diketene (7.80 mL, 101.72 mmol, 1.1 equiv.) at 60 ºC, and the mixture was stirred at 130 ºC for 2 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution (45 mL), extracted with CH_2Cl_2, the combined organic layer was washed with brine (45 mL). The crude product of benzyl 3-oxobutanoate was dried over Na_2SO_4 and evaporated. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30:1, V/V) to afford the desired product in 85% yield as a yellow oil.

To a stirred suspension of NaH (1.98 g, 82.5 mmol, 1.05 equiv.) in THF (100 mL) at 0 ºC was added benzyl 3-oxobutanoate (15.1 g, 78.6 mmol, 1.0 equiv.) and the mixture was stirred for 5 min. MeI (5.14 mL, 82.5 mmol, 1.05 equiv.) was added slowly at 0 ºC and the solution was stirred for 1 h at 0 ºC to RT. The reaction mixture was quenched with NH_4Cl aq. and the organic layer was separated and the aqueous layer was extracted with Et_2O. The organic layer was dried over Na_2SO_4 and the solvent was evapolated. Purification was performed by column chromatography of the crude product to give benzyl 2-methyl-3-oxobutanoate as yellow oil (8.92 g, 55 %).

Benzyl 2-diazopropanoate[2a]

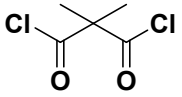


To a stirred suspension of benzyl 3-oxobutanoate (3.85 g, 18.65 mmol, 1 equiv.) in CH_3CN (100 mL) was added 4-acetoamidobenzenesulfonyl azide (6.72 g, 27.97 mmol, 1.5 equiv.) under argon atmosphere. The mixture was cooled down to 0 ºC, and added DBU (4.20 mL, 27.97 mmol, 1.5 equiv.). After stirring overnight at 0 ºC to RT, the reaction mixture was quenched with H_2O and extracted with Et_2O. The organic phase was dried over Na_2SO_4 and evaporated to give crude product. Purification was performed by column chromatography (petroleum ether/ethyl acetate = 50:1, V/V) to give Benzyl 2-diazopropanoate as yellow oil (2.0 g, 57 %).

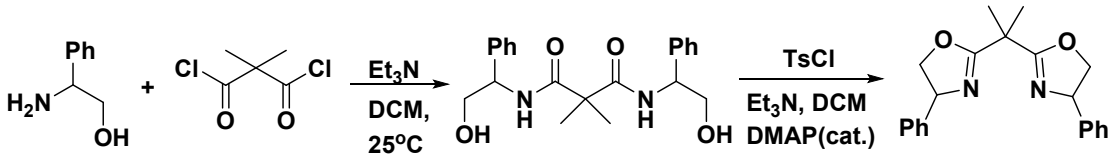
The diazo substrates 2b[2b] and 2c[2b] were prepared according to the literature procedures.

4) Preparation of the ligand(L6)

Dimethylmalonyl chloride[3a]



To a solution of 10.0 g dimethylmalonic acid (75.7 mmol) and 0.76 mL dimethyl formamide (9.84 mmol) in 82 mL dichloromethane was added 28.82 g oxalyl chloride (0.227 mol) at 0 °C using a dropping funnel within 1.5 h. The mixture was allowed to warm to room temperature and was stirred for 18 h. The solvent was removed under reduced pressure and obtained the crude product for the next steps.



According to the reported procedure[3b], in a three-necked round-bottom flask a solution amino alcohol (45.4 mmol, 2 equiv.) was taken in DCM. The solution was cooled to 0 °C and triethyl amine (113.5 mmol, 5 equiv.) was added to the mixture. Next a solution of dimethylmalonyl dichloride (22.7 mmol, 1equiv) in DCM was added dropwise to the flask over 15 minutes. Ice bath was removed after 20 minutes and stirred for extra 35 minutes at room temperature. The reaction mixture was washed with 1N HCl and then $NaHCO_3$. The combined organic layer was dried over Na_2SO_4 and the organic layer was concentrated in vacuo. The resultant residue was purified by coloum chromatography on silica gel. Pure diamide was used for further reaction. Diamide (6.35 mmol) and 4-(dimethylamino) pyridine (28.26 mmol) was suspended in DCM and triethylamine (28.26 mmol) was added to the mixture. Next *p*-toluenesulfonyl chloride (12.82 mmol) in DCM was added at 25 °C through cannula. The whole solution was stirred at 27 h. The solution was washed with NH_4Cl and then $NaHCO_3$. The resultant solution was concentrated by vacuo and purified by silica gel column chromatography to afford the desired bisoxazoline ligand **L6** as yellow liquid.

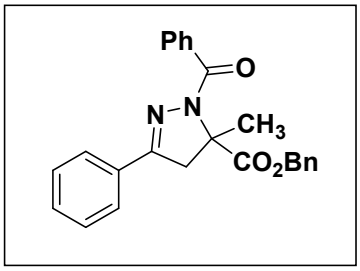
5) General Procedure for the Synthesis of Dihydropyrazoles.

In an oven dried 10 mL Schlenk tube equipped with a stirring bar, $CuCl_2$ (1.4 mg, 0.01 mmol, 10 mol%), ligand **L6** (3.7 mg, 0.011 mmol, 11 mol%) were added into CH_2Cl_2 (1.0 mL) under argon atmosphere. The mixture was stirred for one hour at

room temperature. Then the N-acyl hydrazone **1** (0.1 mmol), diazo ester **2** (0.5 mmol), and Na_2CO_3 (0.5 mmol) were added to the tube under argon atmosphere. The reaction mixture was stirred at 40 ^oC for the indicated time (monitored by TLC). Then the mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 8:1) to afford the desired products **3**.

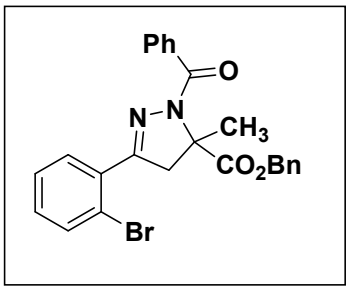
6) Characterization data for the products

Benzyl 1-benzoyl-5-methyl-3-phenyl-4,5-dihydro-1H-pyrazole-5-carboxylate(3a)



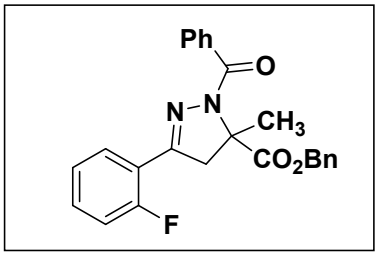
Colorless oil. Yield 98% (39.0 mg); ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.93 (d, *J* = 7.2 Hz, 2H), 7.63-7.61(m, 2H), 7.50-7.35 (m, 6H), 7.32-7.23 (m, 5H), 5.25 (d, *J* = 12.4 Hz, 1H), 5.20 (d, *J* = 12.4 Hz, 1H), 3.54 (d, *J* = 17.2 Hz, 1H), 3.18 (d, *J* = 17.2 Hz, 1H), 1.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δδ 171.4, 166.3, 152.7, 135.5, 134.0, 131.1, 130.9, 130.5, 130.1, 128.8, 128.5, 128.3, 128.2, 127.7, 126.7, 67.5, 67.4, 45.8, 22.0. HRMS calcd for $C_{25}H_{22}N_2O_3$ $[M+H]^+$ 399.1682, found: 399.1678.

Benzyl 1-benzoyl-3-(2-bromophenyl)-5-methyl-4,5-dihydro-1H-pyrazole-5-carboxylate (3b)



Colorless oil. Yield 82% (39.1 mg); ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.94 (d, *J* = 7.9 Hz, 2H), 7.62-7.60 (m, 2H), 7.49-7.33 (m, 6H), 7.31-7.21 (m, 4H), 5.24 (d, *J* = 12.4 Hz, 1H), 5.20 (d, *J* = 12.4 Hz, 1H), 3.54 (d, *J* = 17.2 Hz, 1H), 3.16 (d, *J* = 17.2 Hz, 1H), 1.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 171.4, 166.3, 152.7, 135.6 134.1, 131.1, 130.9, 130.5, 130.1, 128.8, 128.6, 128.3, 128.2, 127.7, 126.7, 67.5, 67.4, 45.8, 22.1. HRMS calcd for $C_{25}H_{21}BrN_2O_3$ $[M+Na]^+$ 500.2915, found: 500.2919.

Benzyl 1-benzoyl-3-(2-fluorophenyl)-5-methyl-4,5-dihydro-1H-pyrazole-5 carboxylate(3c)

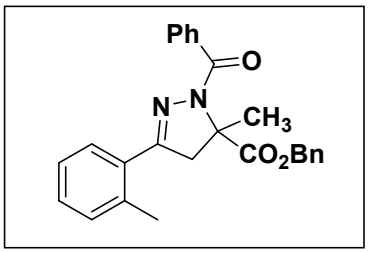


Colorless oil. Yield 78% (32.4 mg); ^1H NMR (400

MHz, $CDCl_3$, ppm): δ 7.95 (d, *J* = 7.9 Hz, 2H), 7.86-7.81 (m, 1H), 7.52-7.28 (m, 9H), 7.17-7.07 (m, 2H), 5.29 (d, *J* = 12.4 Hz, 1H), 5.23 (d, *J* = 12.4 Hz, 1H), 3.70 (d, *J* = 17.2 Hz, 1H) ,3.68 (d, *J* = 17.2 Hz, 1H), 1.91 (s, 3H).

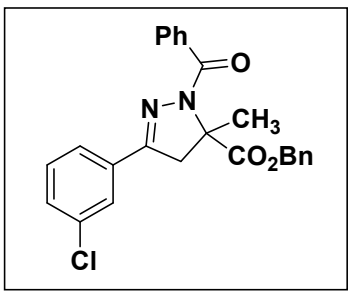
^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ171.4, 166.5, 161.2 (J=252.8 Hz), 149.4 (J=2.5 Hz), 135.5, 134.0, 132.2, 132.1, 131.1, 130.0, 129.0, 128.5, 128.3, 127.7, 124.5, 119.0, 118.9, 116.6, 116.4, 67.5, 67.4, 48.2, 48.1, 22.0. HRMS calcd for $C_{25}H_{21}FN_2O_3$ $[2M+Na]^+$ 855.2948, found: 855.2944.

Benzyl 1-benzoyl-5-methyl-3-(o-tolyl)-4,5-dihydro-1H-pyrazole-5- carboxylate(3d)



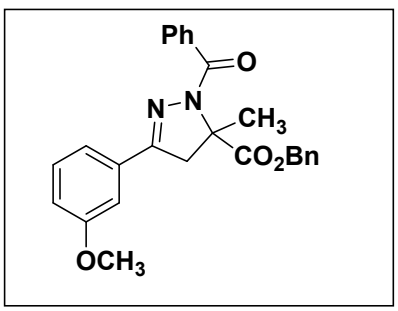
Colorless oil. Yield 95% (39.1 mg); ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.89-7.87 (m, 2H), 7.46-7.19 (m, 12H), 5.26 (d, *J* = 12.4 Hz, 1H), 5.20 (d, *J* = 12.4 Hz, 1H), 3.60 (d, *J* = 17.2 Hz, 1H), 3.22 (d, *J* = 17.2 Hz, 1H), 2.46 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 171.5, 166.7, 153.4, 138.2, 135.6, 134.2, 132.0, 131.0, 129.8, 129.6, 128.9, 128.6, 128.3, 128.2, 127.5, 126.0, 67.5, 66.3, 48.1, 23.4, 21.9. HRMS calcd for $C_{26}H_{24}N_2O_3$ $[M+H]^+$ 413.1667, found: 413.1669.

Benzyl 1-benzoyl-3-(3-chlorophenyl)-5-methyl-4,5-dihydro-1H-pyrazole-5-carboxylate(3e)



Colorless oil. Yield 93% (40.3 mg); ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.91-7.89 (m, 2H), 7.58 (s, 1H), 7.51-7.41 (m, 4H), 7.36-7.23 (m, 7H), 5.26 (d, *J* = 12.4 Hz, 1H), 5.19 (d, *J* = 12.4 Hz, 1H), 3.51 (d, *J* = 17.2 Hz, 1H), 3.14 (d, *J* = 17.2 Hz, 1H), 1.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 171.2, 166.4, 151.4, 136.5, 135.5, 134.0, 131.1, 130.0, 129.5, 129.0, 128.5, 128.3, 128.2, 127.9, 127.7, 67.6, 67.6, 45.7, 22.0. HRMS calcd for $C_{25}H_{21}ClN_2O_3$ $[M+Na]^+$ 455.1132, found: 455.1136.

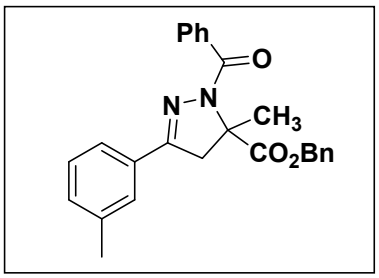
Benzyl 1-benzoyl-3-(3-methoxyphenyl)-5-methyl-4,5-dihydro-1H-pyrazole-5-carboxylate(3f)



Colorless oil. Yield 92% (39.4 mg); ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.94-7.92 (m, 2H), 7.49-7.39

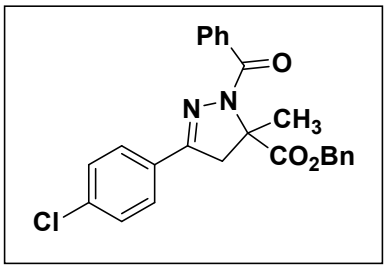
(m, 3H), 7.30-7.23 (m, 6H), 7.18-7.16 (m, 2H), 6.95-6.92 (m, 1H), 5.24 (d, *J* = 12.4 Hz, 1H), 5.19 (d, *J* = 12.4 Hz, 1H), 3.77 (s, 3H), 3.53 (d, *J* = 17.2 Hz, 1H), 3.15 (d, *J* = 17.2 Hz, 1H), 1.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 171.4, 166.3, 159.8, 152.6, 135.5, 134.1, 132.3, 131.1, 130.1, 129.9, 128.5, 128.3, 128.2, 127.6, 119.3, 116.1, 112.0, 67.5, 55.3, 45.9, 22.0. HRMS calcd for $C_{26}H_{24}N_2O_4$ $[2M+Na]^+$ 879.3649, found: 879.3644.

Benzyl 1-benzoyl-5-methyl-3-(m-tolyl)-4,5-dihydro-1H-pyrazole-5-carboxylate(3g)



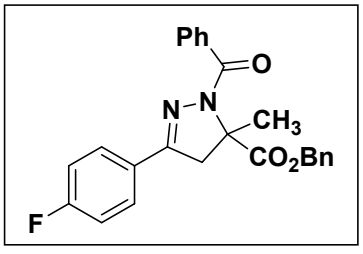
Colorless oil. Yield 89% (36.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.95-7.93 (m, 2H), 7.48-7.38 (m, 5H), 7.31-7.22 (m, 6H), 7.19-7.17 (m, 1H), 5.24 (d, *J* = 12.4 Hz, 1H), 5.18 (d, *J* = 12.4 Hz, 1H), 3.53 (d, *J* = 17.2 Hz, 1H), 3.14 (d, *J* = 17.2 Hz, 1H), 2.32 (s, 3H), 1.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 171.4, 166.3, 153.0, 138.5, 135.6, 134.2, 131.4, 131.1, 131.0, 130.1, 128.7, 128.6, 128.3, 128.3, 127.7, 127.3, 124.0, 67.5, 67.4, 45.9, 22.1, 21.5. HRMS calcd for $C_{26}H_{24}N_2O_3$ $[M+Na]^+$ 4435.1647, found: 435.1669.

Benzyl 1-benzoyl-3-(4-chlorophenyl)-5-methyl-4,5-dihydro-1H-pyrazole-5-carboxylate(3h)



White solid. Yield 98% (42.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.91-7.89(m, 2H), 7.55-7.41 (m, 5H), 7.35-7.24 (m, 7H), 5.25 (d, *J* = 12.4 Hz, 1H), 5.19 (d, *J* = 12.4 Hz, 1H), 3.51 (d, *J* = 17.2 Hz, 1H), 3.14 (d, *J* = 17.2 Hz, 1H), 1.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 171.2, 166.4, 151.4, 136.5, 135.5, 134.0, 131.1, 130.0, 129.5, 129.0, 128.5, 128.3, 128.2, 127.9, 127.6, 67.6, 67.5, 45.7, 22.7. HRMS calcd for $C_{25}H_{21}ClN_2O_3$ $[2M+Na]^+$ 887.2269, found: 887.2272.

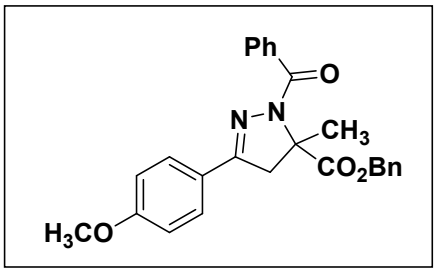
Benzyl 1-benzoyl-3-(4-fluorophenyl)-5-methyl-4,5-dihydro-1H-pyrazole-5-carboxylate(3i)



Colorless oil. Yield 94% (39.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.83-7.81 (m, 2H), 7.54-7.50 (m, 2H), 7.42-7.32 (m, 3H), 7.27-7.16 (m, 5H), 6.70-6.96

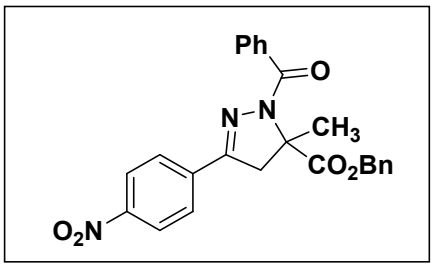
(m, 2H), 5.17 (d, *J* = 12.4 Hz, 1H), 5.11 (d, *J* = 12.4 Hz, 1H), 3.44 (d, *J* = 17.4 Hz, 1H), 3.06 (d, *J* = 17.4 Hz, 1H), 1.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ171.3, 166.3, 165.3, 151.6, 135.5, 134.0, 131.1, 130.0, 128.7, 128.6, 128.3, 128.2, 127.7, 127.2, 116.0, 115.8, 67.5, 45.8, 22.0. HRMS calcd for $C_{25}H_{21}FN_2O_3$ $[2M+Na]^+$ 855.2947, found: 855.2944.

Benzyl 1-benzoyl-3-(4-methoxyphenyl)-5-methyl-4,5-dihydro-1H-pyrazole-5-carboxylate(3j)



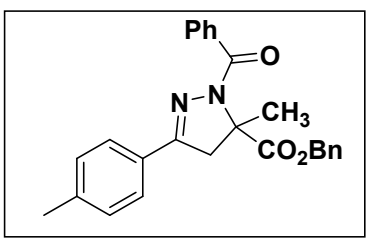
Colorless oil. Yield 96% (41.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.95-7.93 (m, 2H), 7.57-7.55 (m, 2H), 7.49-7.40 (m, 3H), 7.33-7.27 (m, 4H), 7.24 (s, 1H), 6.90-6.88 (m, 2H), 5.25 (d, *J* = 12.4 Hz, 1H), 5.20 (d, *J* = 12.4 Hz, 1H), 3.81 (s, 3H), 3.52 (d, *J* = 17.2 Hz, 1H), 3.14 (d, *J* = 17.2 Hz, 1H), 1.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 171.5, 166.0, 161.5, 152.4, 135.6, 134.2, 131.0, 130.0, 128.5, 128.3, 128.2, 128.2, 127.6, 123.5, 114.2, 67.5, 67.3, 55.4, 45.9, 22.0. HRMS calcd for $C_{26}H_{24}N_2O_4$ $[M+Na]^+$ 429.1816, found: 429.1822.

Benzyl 1-benzoyl-5-methyl-3-(4-nitrophenyl)-4,5-dihydro-1H-pyrazole-5-carboxylate(3k)



White solid. Yield 90% (39.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.22-8.20 (m, 2H), 7.90-7.88 (m, 2H), 7.76-7.74 (m, 2H), 7.54-7.50 (m, 1H), 7.46-7.43 (m, 2H), 7.32-7.25 (m, 5H), 5.26 (d, *J* = 12.4 Hz, 1H), 5.20 (d, *J* = 12.4 Hz, 1H), 3.62 (d, *J* = 17.2 Hz, 1H), 3.22 (d, *J* = 17.2 Hz, 1H), 1.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.1, 166.7, 150.3, 148.5, 137.0, 135.3, 133.7, 131.4, 129.9, 128.6, 128.4, 128.3, 127.8, 127.4 124.0, 68.1, 67.7, 45.5, 22.1. HRMS calcd for $C_{25}H_{21}N_3O_5$ $[M+Na]^+$ 466.1387, found: 466.1382.

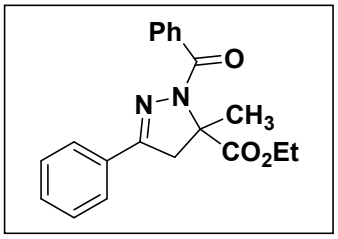
Benzyl 1-benzoyl-5-methyl-3-(p-tolyl)-4,5-dihydro-1H-pyrazole-5-carboxylate(3l)



Colorless oil. Yield 98% (40.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.95-7.93 (m, 2H), 7.52-7.40 (m,

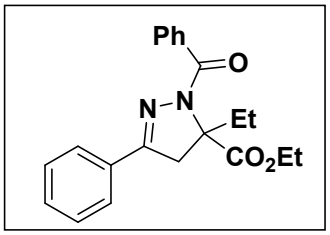
5H), 7.35-7.24 (m, 5H), 7.19-7.17 (m, 2H), 5.25 (d, *J* = 12.4 Hz, 1H), 5.20 (d, *J* = 12.4 Hz, 1H), 3.53 (d, *J* = 17.2 Hz, 1H), 3.16 (d, *J* = 17.2 Hz, 1H), 2.36 (s, 3H), 1.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 171.5, 166.2, 152.7, 140.9, 135.6, 134.1, 131.0, 130.1, 129.5, 128.5, 128.2, 128.2, 128.2, 127.6, 126.7, 67.5, 67.3, 22.0, 21.6. HRMS calcd for $C_{26}H_{24}N_2O_3$ $[2M+Na]^+$ 847.3336, found: 847.3338.

Ethyl 1-benzoyl-5-methyl-3-phenyl-4,5-dihydro-1H-pyrazole-5-carboxylate(3p)



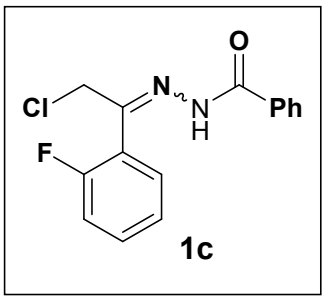
Colorless oil. Yield 98% (32.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.98-7.96 (m, 2H), 7.67-7.65 (m, 2H), 7.51-7.37 (m, 6H), 4.36-4.17 (m, 2H), 3.63 (d, *J* = 17.2 Hz, 1H), 3.20 (d, *J* = 17.2 Hz, 1H), 1.86 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 171.5, 166.2, 152.6, 134.2, 131.0, 130.5, 130.0, 128.8, 127.7, 67.3, 61.9, 45.9, 22.0, 14.2. HRMS calcd for $C_{20}H_{20}N_2O_3$ $[2M+Na]^+$ 695.2807, found: 695.2801.

Ethyl 1-benzoyl-5-ethyl-3-phenyl-4,5-dihydro-1H-pyrazole-5-carboxylate(3q)



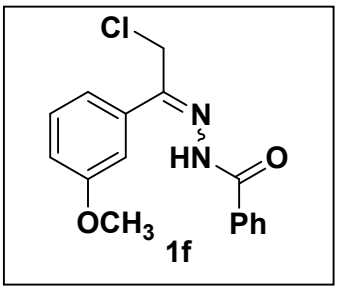
Colorless oil. Yield 92% (36.3 mg); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.97-7.95 (m, 2H), 7.68-7.65 (m, 2H), 7.51-7.37 (m, 6H), 4.35-4.16 (m, 2H), 3.52 (d, *J* = 17.2 Hz, 1H), 3.30 (d, *J* = 17.2 Hz, 1H), 2.77-2.68 (m, 1H), 2.12-2.02 (m, 1H), 1.25 (t, *J* = 7.4 Hz, 3H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 171.7, 166.5, 152.7, 134.3, 131.0, 130.9, 130.5, 130,0 128.8, 127.7, 126.7, 70.7, 61.7, 42.7, 26.4, 14.2, 7.3. HRMS calcd for $C_{21}H_{22}N_2O_3$ $[M+H]^+$ 351.1691, found: 351.1696.

N'-(2-chloro-1-(2-fluorophenyl)ethylidene)benzohydrazide (1c)



White solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 10.83 (s, 1H), 7.66-7.64 (m, 2H), 7.60-7.53 (m, 3H), 7.47-7.43 (m, 2H), 7.40-7.35 (m, 2H), 4.70 (s, 2H), ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 160.8, 158.3, 134.0, 132.8, 132.1, 130.6, 128.7, 128.4, 125.5, 119.7, 116.7, 48.6. HRMS calcd for $C_{15}H_{12}ClFN_2O$ $[M+H]^+$ 291.0691, found: 291.0687.

N'-(2-chloro-1-(3- methoxyphenyl)ethylidene)benzohydrazide(1f)



White soild. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.18 (s, 1H), 7.92-7.90 (m, 1H), 7.42-7.34 (m, 5H), 7.10-7.07 (m, 2H), 6.94-6.92 (m, 3H), 4.55 (s, 2H), 3.88 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 160.7, 159.9, 136.7, 133.0, 132.6, 131.6, 131.2, 129.7, 119.3, 116.2, 116.0, 113.0, 55.5, 47.3. HRMS calcd for $C_{16}H_{15}ClN_2O_2$ $[M+H]^+$ 303.0878, found: 303.0872.

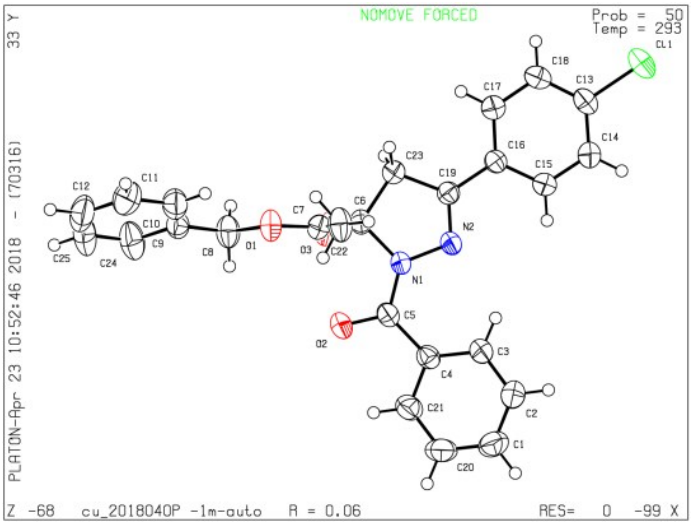
7) X-ray crystallographic data of 3h

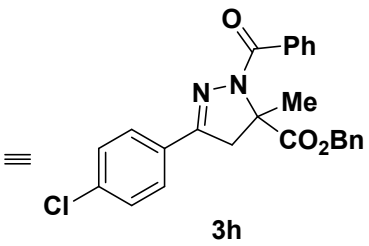
The structure of **3h** were determined by the X-ray diffraction analysis. CCDC 1840892 contain the structure and supplementary crystallographic data. These data can be obtained free of charge on application to the Director, CCDC 12 Union Road, Cambridge CB2 1EZ, UK (fax (+44) 1223-336033; or e-mail deposit@ccdc.cam.uk) or via www.ccdc.cam.ac.uk/data_request/cif.

Table 1 Crystal data and structure refinement for Compounds **3h**.

Identification code	**3h**
CCDC Deposit number	1840892
Empirical formula	$C_{25}H_{21}ClN_2O_3$
Formula weight	432.89
Temperature (K)	293.15
Wavelength (Å)	1.54178
Crystal system	triclinic
space group	P -1
Unit cell dimensions (Å)	a=6.3041(16)
	b=12.0699(17)
	c=14.252(3)
(°)	α=88.684(12)
	β=79.885(12)
	γ=89.121(14)
Volume	1067.2(4)
Z	2

Calcd. density (Mg/m3)	1.347
F(000)	452
Limiting indices	-7≤ h ≤ 7
	-14≤ k ≤ 14
	-17≤ l ≤ 17





3h

8) References

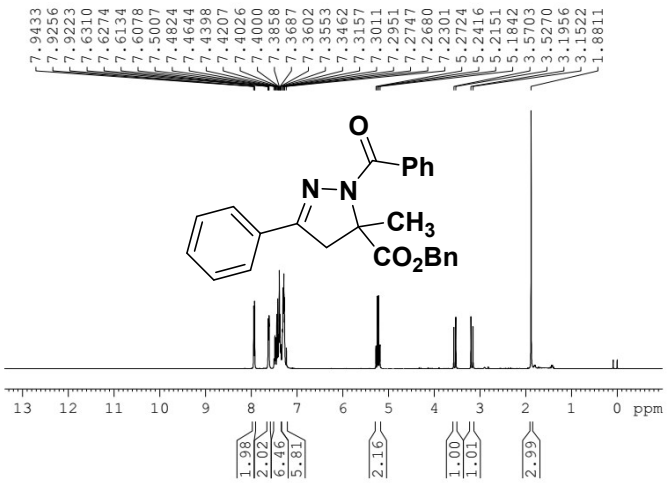
1) (a) Chen, J.-R.; Dong, W.-R.; Candy, M.; Pan, F.-F.; Jörres, M.; Bolm, C. *J. Am. Chem. Soc.* **2012**, 134, 6924; (b) Swamy, P.; Kumar, M. A.; Reddy, M. M.; Narender, N. *Chem. Lett.* **2012**, 41, 432; (c) Lee, J. C.; Bae, Y. H.; Chang, S. K. *Bull. Korean Chem. Soc.* **2003**, 34, 407; (d) Zhang, X.-X.; Liu, L.; Li, C.-B. *RSC Adv.* **2016**, 6, 25339; (e) Chen, C.; Zhu, M.-H.; Jiang, L.-H.; Zeng, Z.-B.; Yi, N.-N.; Xiang, J. N. *Org. Biomol. Chem.* **2017**, 15, 8134.

2) (a) Nakagawa, Y. K.;Chanthamath, S.D.; Fujisawa, I.; Shibatomi K.; Iwasa S. J. *Chem. Commun.* **2013**, 53, 3753; (b) Li, H.; Wulff, W. D. *J. Am. Chem. Soc.* **2011**, 133, 8892.

3) (a) Gieshoff, T.; Schollmeyer, D.; Waldvogel, S. R. *Augew. Chem. Int. Ed.* 2016, 55, 9437; (b) Verma, K.; Banerjee, P. *Adv. Synth. Catal.* **2016**, 358, 2053.

9) Copies of NMR spectra data

Benzyl 1-benzoyl-5-methyl-3-phenyl-4,5-dihydro-1H-pyrazole-5-carboxylate(3a)

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PROCNO                      1
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SOLVENT                CDCl3
NS                         4
DS                         0
SWH                 8223.685 Hz
FIDRES              0.125483 Hz
AQ                  3.9846387 sec
RG                       45.2
DW                     60.800 usec
DE                      6.50 usec
TE                     293.8 K
D1                  1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     13.00 usec
PL1                    -2.60 dB
PL1W               18.28352737 W
SFO1              400.1524711 MHz
SI                       32768
SF                400.1500209 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
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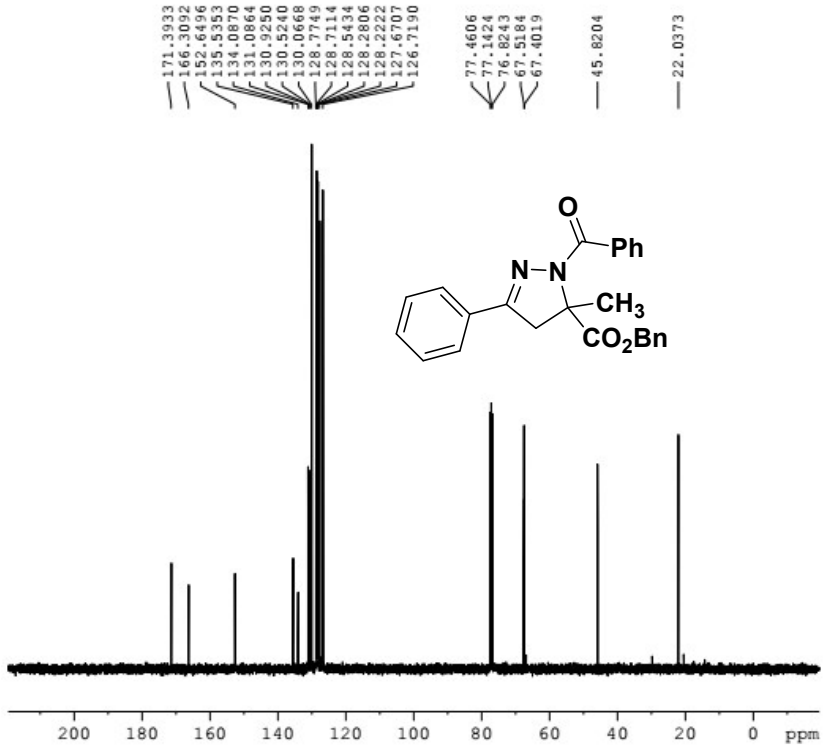


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PROCNO                      1
Date_                20180112
Time                     9.13
INSTRUM                 spect
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PULPROG              zgpg30
TD                     65536
SOLVENT                CDCl3
NS                        64
DS                         0
SWH                24038.461 Hz
FIDRES              0.366798 Hz
AQ                  1.3631988 sec
RG                       203
DW                     20.800 usec
DE                      6.50 usec
TE                     294.6 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      13C
P1                     11.50 usec
PL1                    -3.00 dB
PL1W               68.16146088 W
SFO1              100.6278593 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                  90.00 usec
PL2                    -2.60 dB
PL12                   13.88 dB
PL13                   14.50 dB
PL2W               17.82643890 W
PL12W               0.40092635 W
PL13W               0.34758785 W
SFO2              400.1516006 MHz
SI                       32768
SF                100.6177980 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
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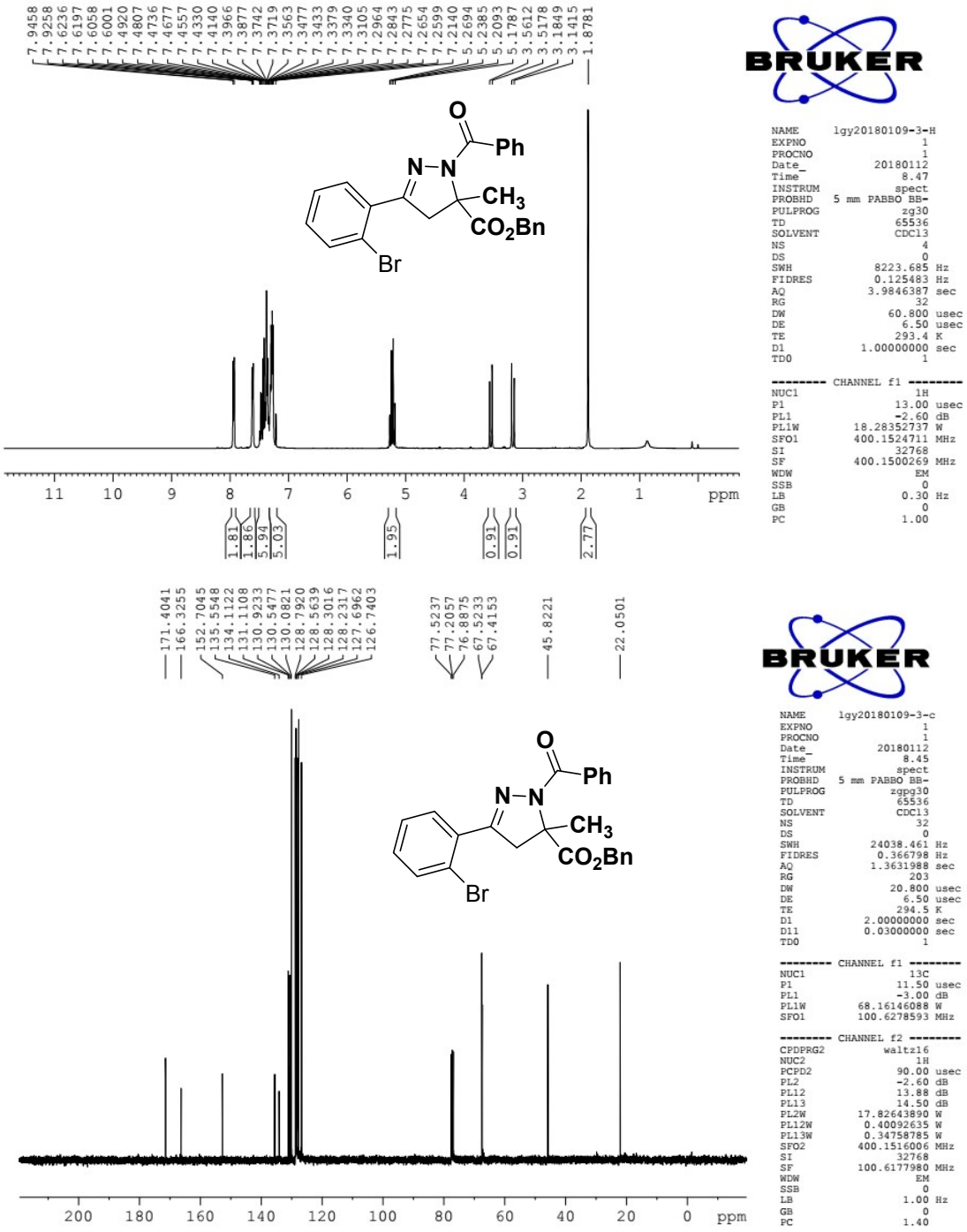
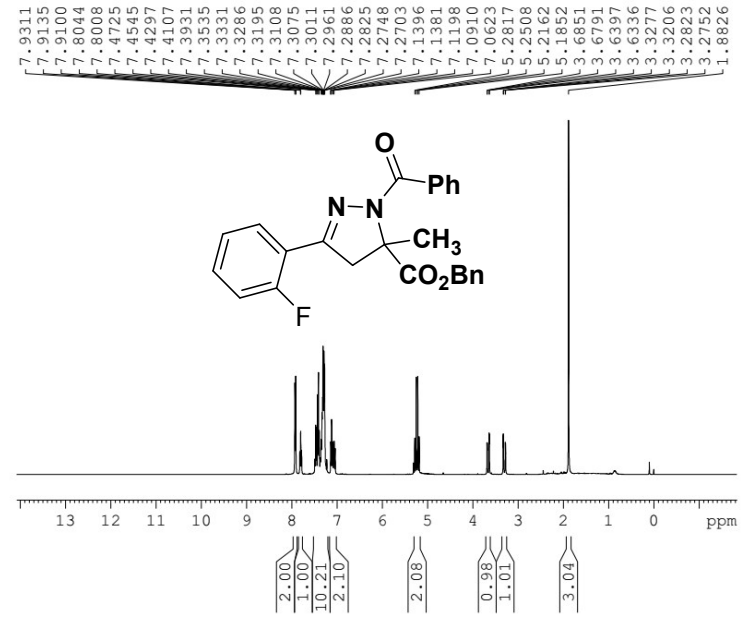
Benzyl 1-benzoyl-3-(2-bromophenyl)-5-methyl-4,5-dihydro-1H-pyrazole-5-carboxylate (3b)



Benzyl 1-benzoyl-3-(2-fluorophenyl)-5-methyl-4,5-dihydro-1H-pyrazole-5

carboxylate(3c)



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PROCNO                 1
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Time               15.30
INSTRUM            spect
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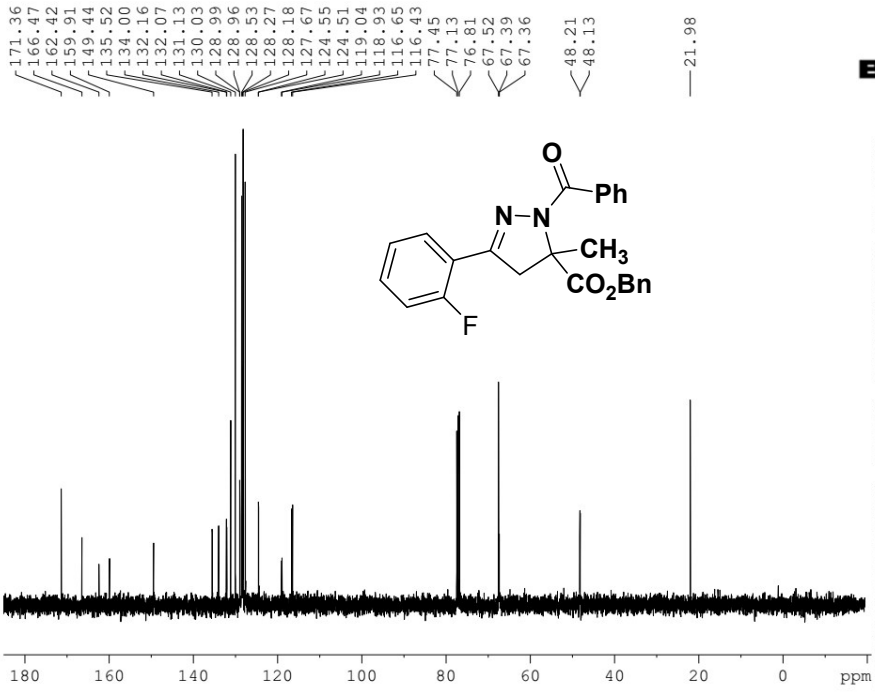
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ              3.9846387 sec
RG                  90.5
DW                60.800 usec
DE                 6.50 usec
TE                294.8 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                13.00 usec
PL1               -2.60 dB
PL1W          17.82643890 W
SFO1          400.1524711 MHz
SI                 32768
SF            400.1500223 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                1.00
```



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EXPNO                    1
PROCNO                   1
Date_             20180306
Time                 16.05
INSTRUM              spect
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PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ              1.3631988 sec
RG                   203
DW                20.800 use
DE                 6.50 use
TE                295.2 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 =======
NUC1                  13C
P1                11.50 use
PL1               -3.00 dB
PL1W          68.16146088 W
SFO1          100.6278593 MHz

======== CHANNEL f2 =======
CPDPRG2           waltz16
NUC2                  1H
PCPD2             90.00 use
PL2               -2.60 dB
PL12              13.88 dB
PL13              14.50 dB
PL2W          17.82643890 W
PL12W          0.40092635 W
PL13W          0.34758785 W
SFO2          400.1516006 MHz
SI                 32768
SF            100.6177980 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                1.40
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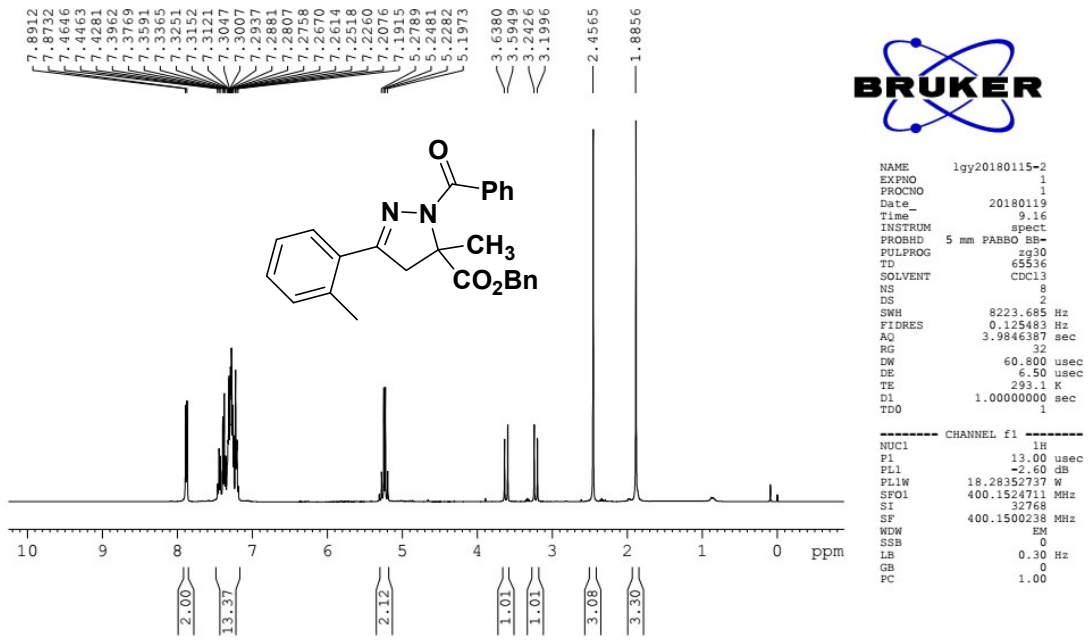
Benzyl 1-benzoyl-5-methyl-3-(o-tolyl)-4,5-dihydro-1H-pyrazole-5- carboxylate(3d)

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PROCNO                    1
Date_              20180119
Time                   9.16
INSTRUM               spect
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PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       8
DS                       2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ              3.9846387 sec
RG                      32
DW                 60.800 usec
DE                  6.50 usec
TE                 293.1 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   1H
P1                  13.00 usec
PL1                 -2.60 dB
PL1W         18.28352737 W
SFO1        400.1524711 MHz
SI                   32768
SF          400.1500238 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
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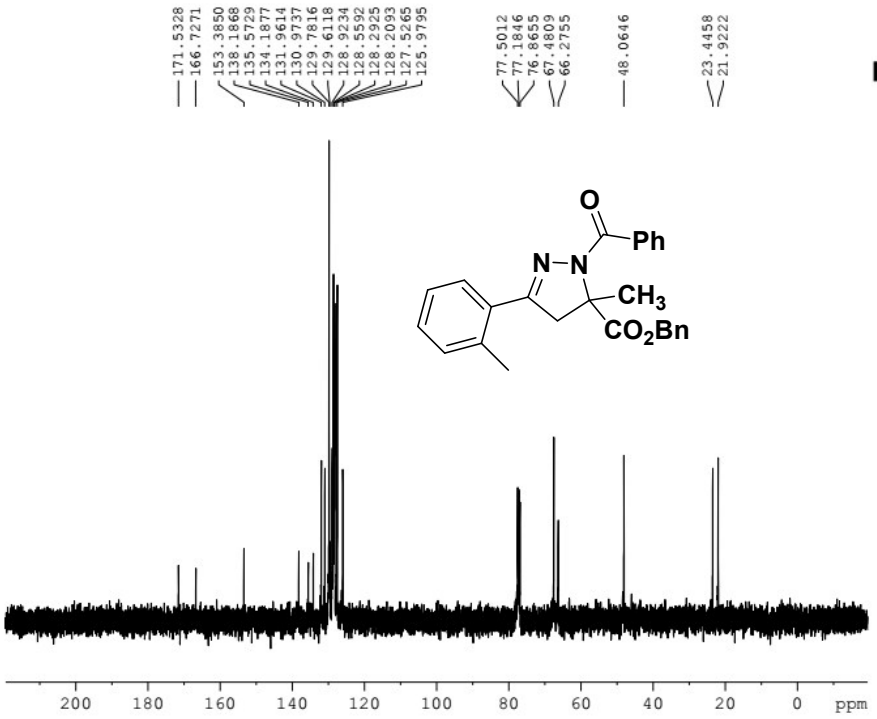

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PROCNO                    1
Date_              20180123
Time                  11.07
INSTRUM               spect
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PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      23
DS                       4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ              1.3631988 sec
RG                     203
DW                 20.800 usec
DE                  6.50 usec
TE                 294.3 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                  13C
P1                  11.50 usec
PL1                 -3.00 dB
PL1W         68.16146088 W
SFO1        100.6278593 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               90.00 usec
PL2                 -2.60 dB
PL12                13.88 dB
PL13                14.50 dB
PL2W         17.82643890 W
PL12W         0.40092635 W
PL13W         0.34758785 W
SFO2        400.1516006 MHz
SI                   32768
SF          100.6177980 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
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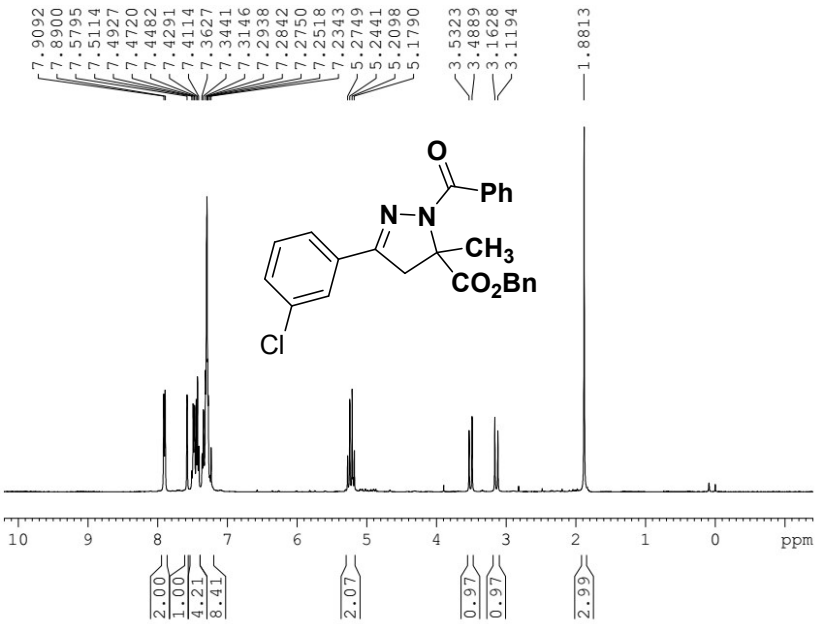
Benzyl 1-benzoyl-3-(3-chlorophenyl)-5-methyl-4,5-dihydro-1H-pyrazole-5-

carboxylate(3e)



BRUKER

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PROCNO              1
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Time_           15.08
INSTRUM         spect
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TD              65536
SOLVENT          CDCl3
NS                  8
DS                  2
SWH          8223.685 Hz
FIDRES       0.125483 Hz
AQ           3.9846387 sec
RG                45.2
DW             60.800 usec
DE              6.50 usec
TE             294.4 K
D1          1.00000000 sec
TD0                 1

======== CHANNEL f1 ========
NUC1               1H
P1              13.00 usec
PL1             -2.60 dB
PL1W       17.82643890 W
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SI              32768
SF         400.1500191 MHz
WDW                EM
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LB              0.30 Hz
GB                  0
PC              1.00
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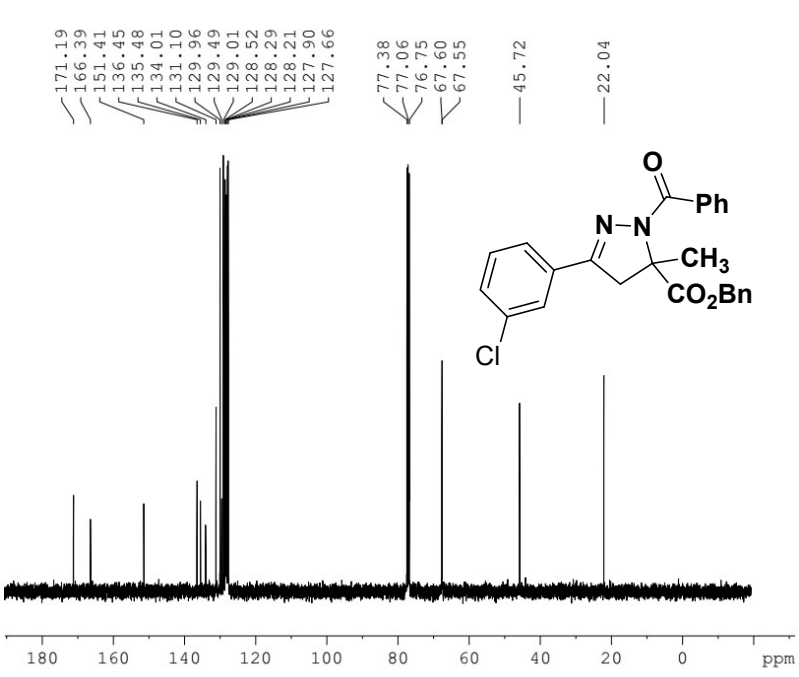

BRUKER

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PROCNO              1
Date_        20180403
Time_           15.22
INSTRUM         spect
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TD              65536
SOLVENT          CDCl3
NS                113
DS                  4
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FIDRES       0.366798 Hz
AQ           1.3631988 sec
RG                203
DW             20.800 usec
DE              6.50 usec
TE             300.0 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                 1

======== CHANNEL f1 ========
NUC1              13C
P1             11.50 usec
PL1            -3.00 dB
PL1W       68.16146088 W
SFO1       100.6278593 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2               1H
PCPD2           90.00 usec
PL2             -2.60 dB
PL12            13.88 dB
PL13            14.50 dB
PL2W       17.82643890 W
PL12W       0.40092635 W
PL13W       0.34758785 W
SFO2       400.1516006 MHz
SI              32768
SF         100.6177980 MHz
WDW                EM
SSB                 0
LB              1.00 Hz
GB                  0
PC              1.40
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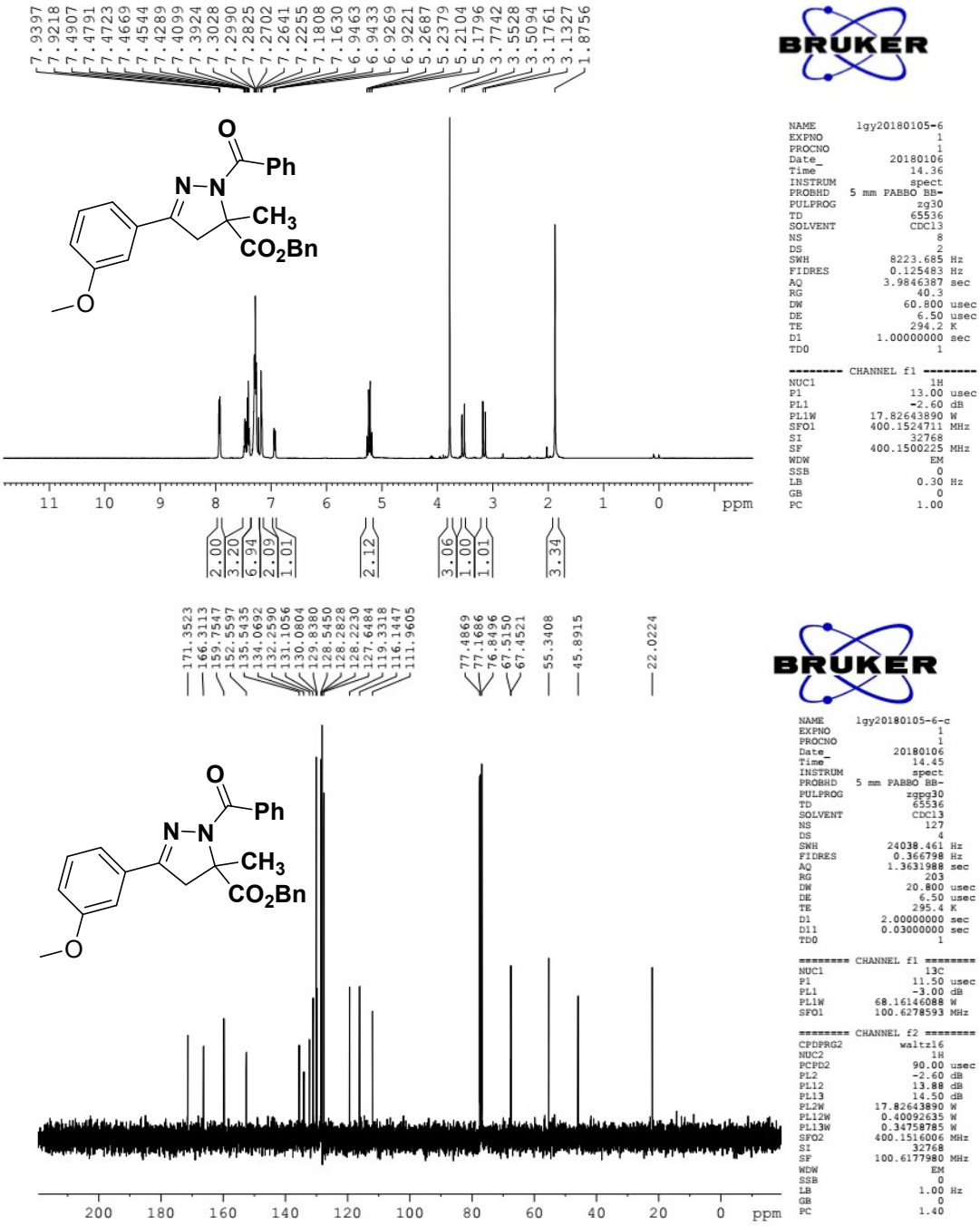
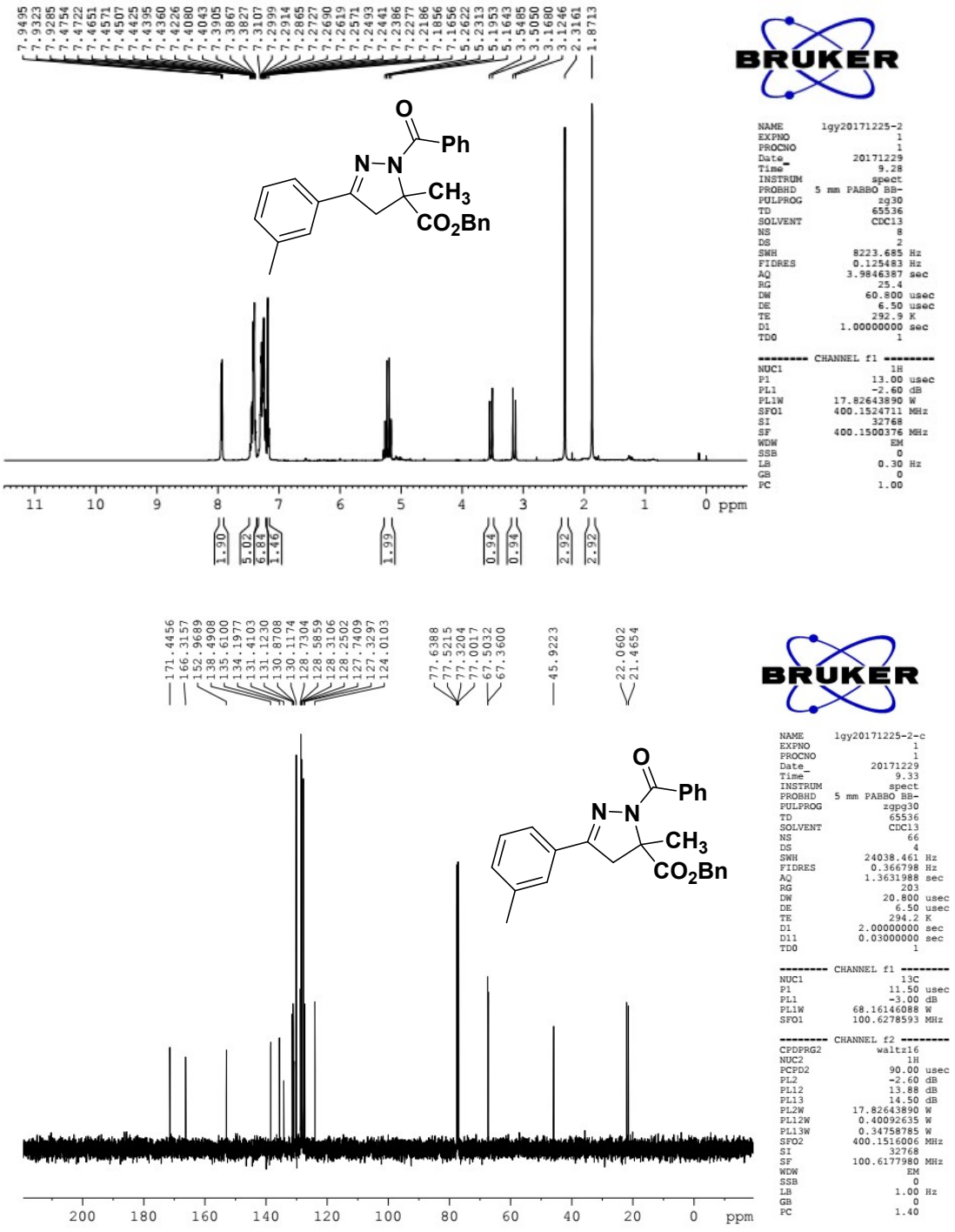
Benzyl 1-benzoyl-3-(3-methoxyphenyl)-5-methyl-4,5-dihydro-1H-pyrazole-5-

carboxylate(3f)

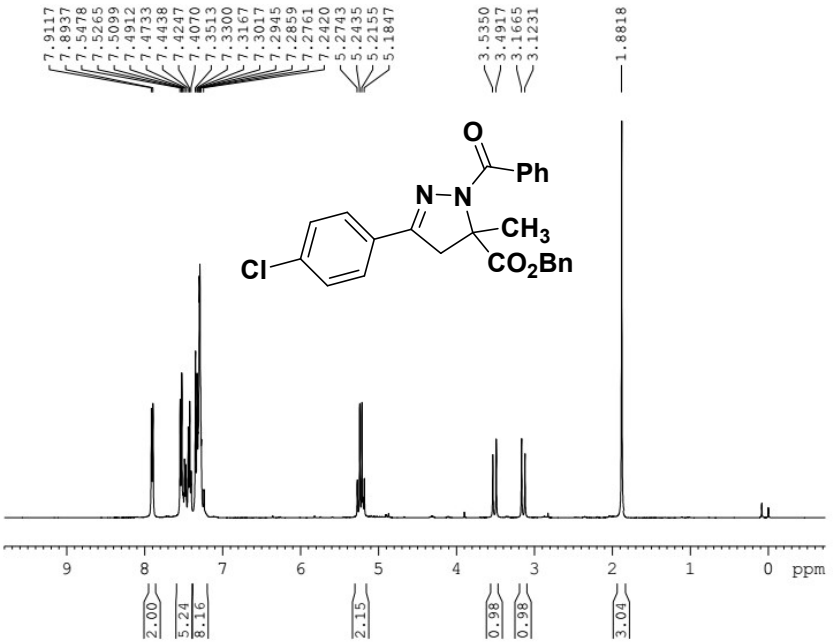


Benzyl 1-benzoyl-5-methyl-3-(m-tolyl)-4,5-dihydro-1H-pyrazole-5-carboxylate(3g)



Benzyl 1-benzoyl-3-(4-chlorophenyl)-5-methyl-4,5-dihydro-1H-pyrazole-5-

carboxylate(3h)



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FIDRES             0.125483 Hz
AQ                 3.9846387 sec
RG                        181
DW                   60.800 usec
DE                    6.50 usec
TE                    294.7 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                    13.00 usec
PL1                   -2.60 dB
PL1W              17.82643890 W
SFO1              400.1524711 MHz
SI                      32768
SF                400.1500161 MHz
WDW                        EM
SSB                         0
LB                     0.30 Hz
GB                          0
PC                       1.00
```
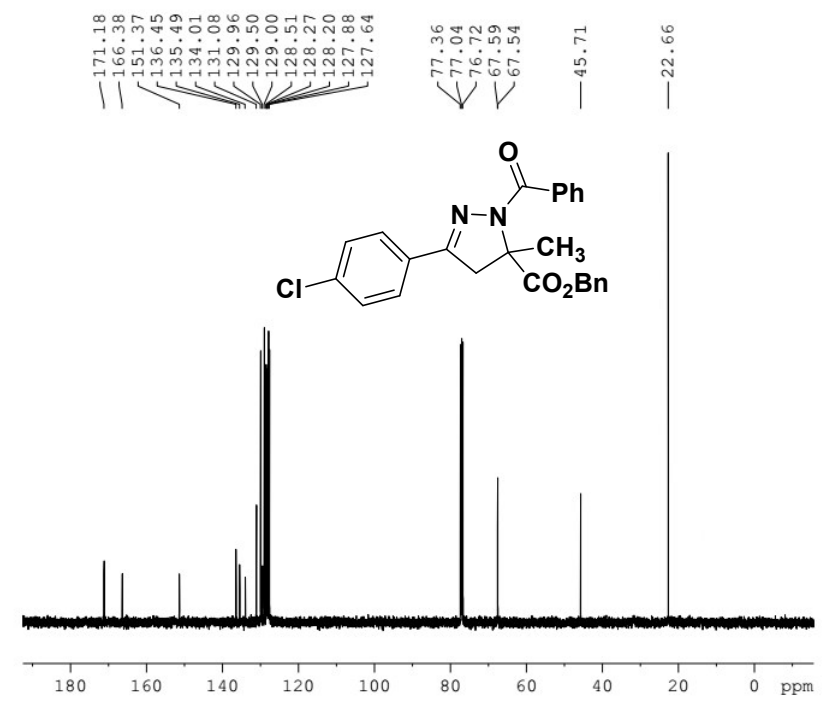
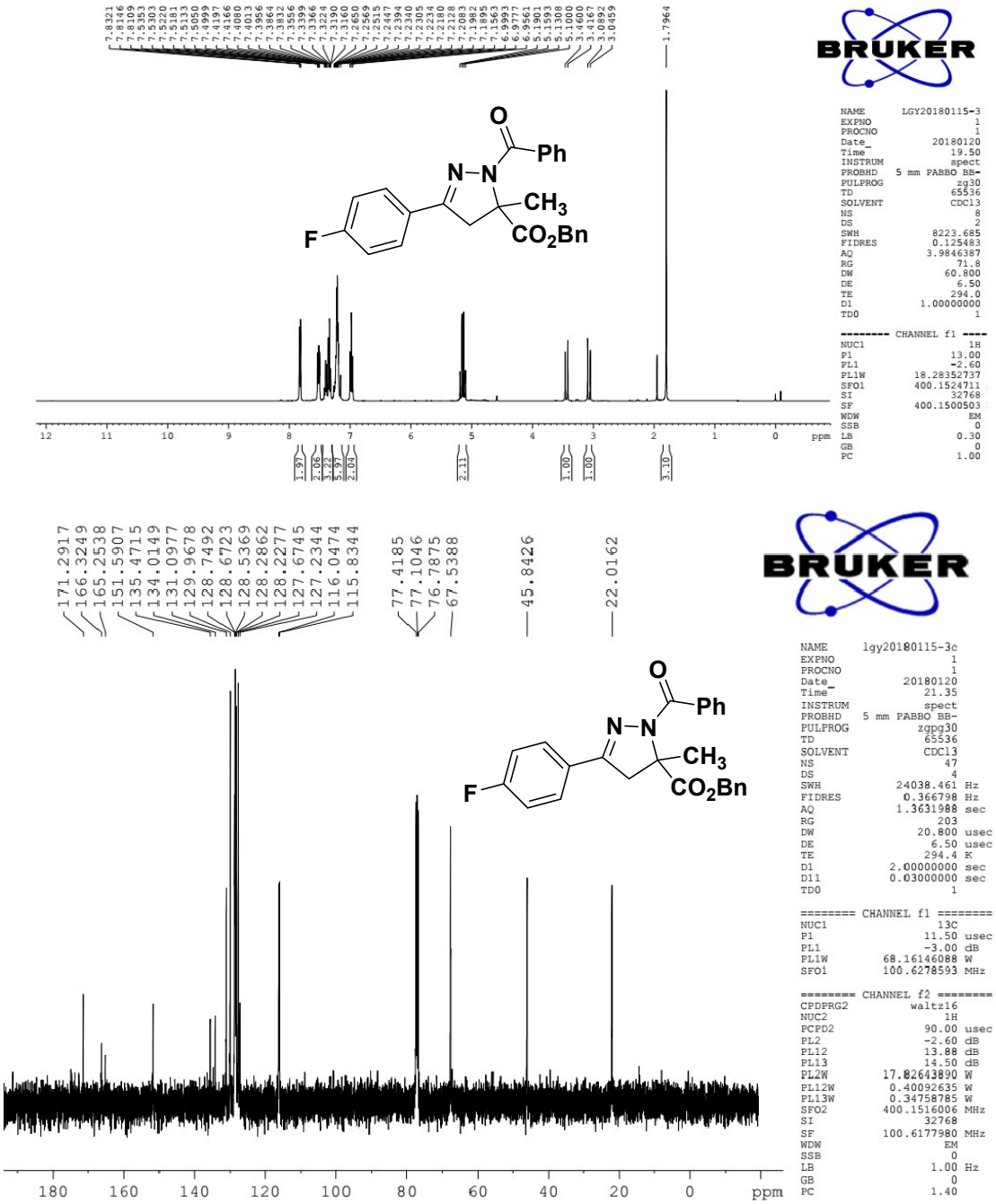



BRUKER

```
NAME        LGY20180403-3Cl-C
EXPNO                       1
PROCNO                      1
Date_                20180403
Time                    15.39
INSTRUM                 spect
PROBHD   5 mm PABBO BB-
PULPROG              zgpg30
TD                     65536
SOLVENT                CDCl3
NS                         97
DS                          4
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631988 sec
RG                        203
DW                   20.800 usec
DE                    6.50 usec
TE                    299.9 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                    11.50 usec
PL1                   -3.00 dB
PL1W              68.16146088 W
SFO1              100.6278593 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                       1H
PCPD2                 90.00 usec
PL2                   -2.60 dB
PL12                  13.88 dB
PL13                  14.50 dB
PL2W              17.82643890 W
PL12W              0.40092635 W
PL13W              0.34758785 W
SFO2              400.1516006 MHz
SI                      32768
SF                100.6177980 MHz
WDW                        EM
SSB                         0
LB                     1.00 Hz
GB                          0
PC                       1.40
```

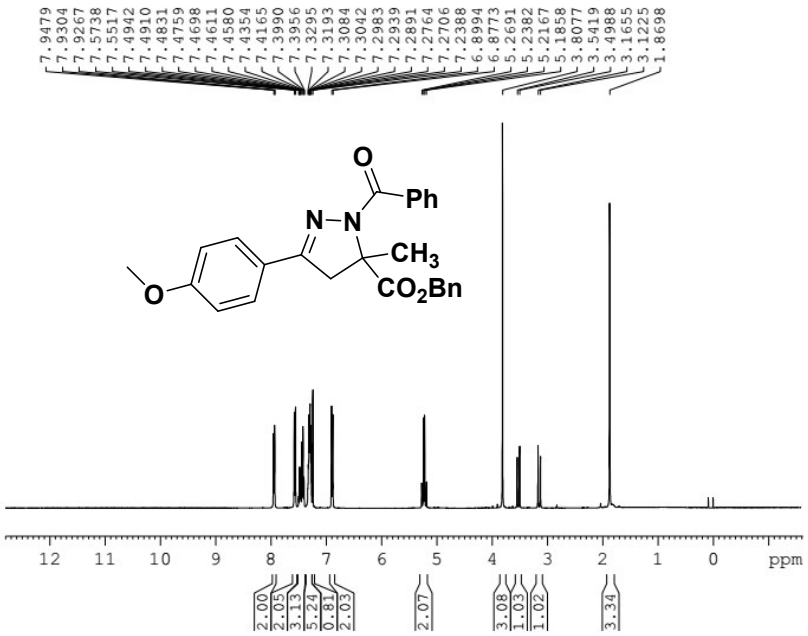
Benzyl 1-benzoyl-3-(4-fluorophenyl)-5-methyl-4,5-dihydro-1H-pyrazole-5-

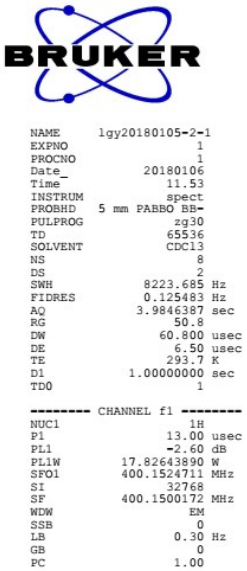
carboxylate(3i)

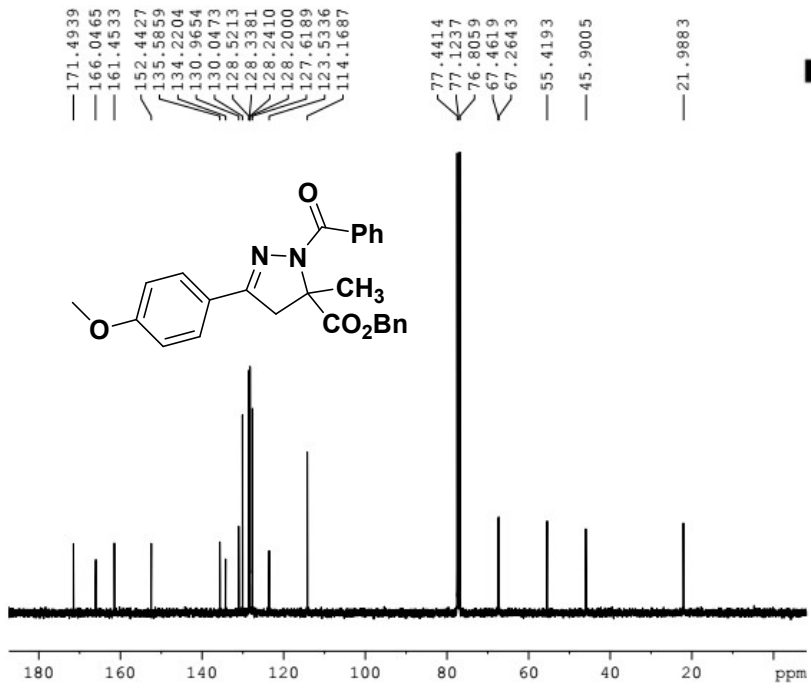


Benzyl 1-benzoyl-3-(4-methoxyphenyl)-5-methyl-4,5-dihydro-1H-pyrazole-5-

carboxylate(3j)

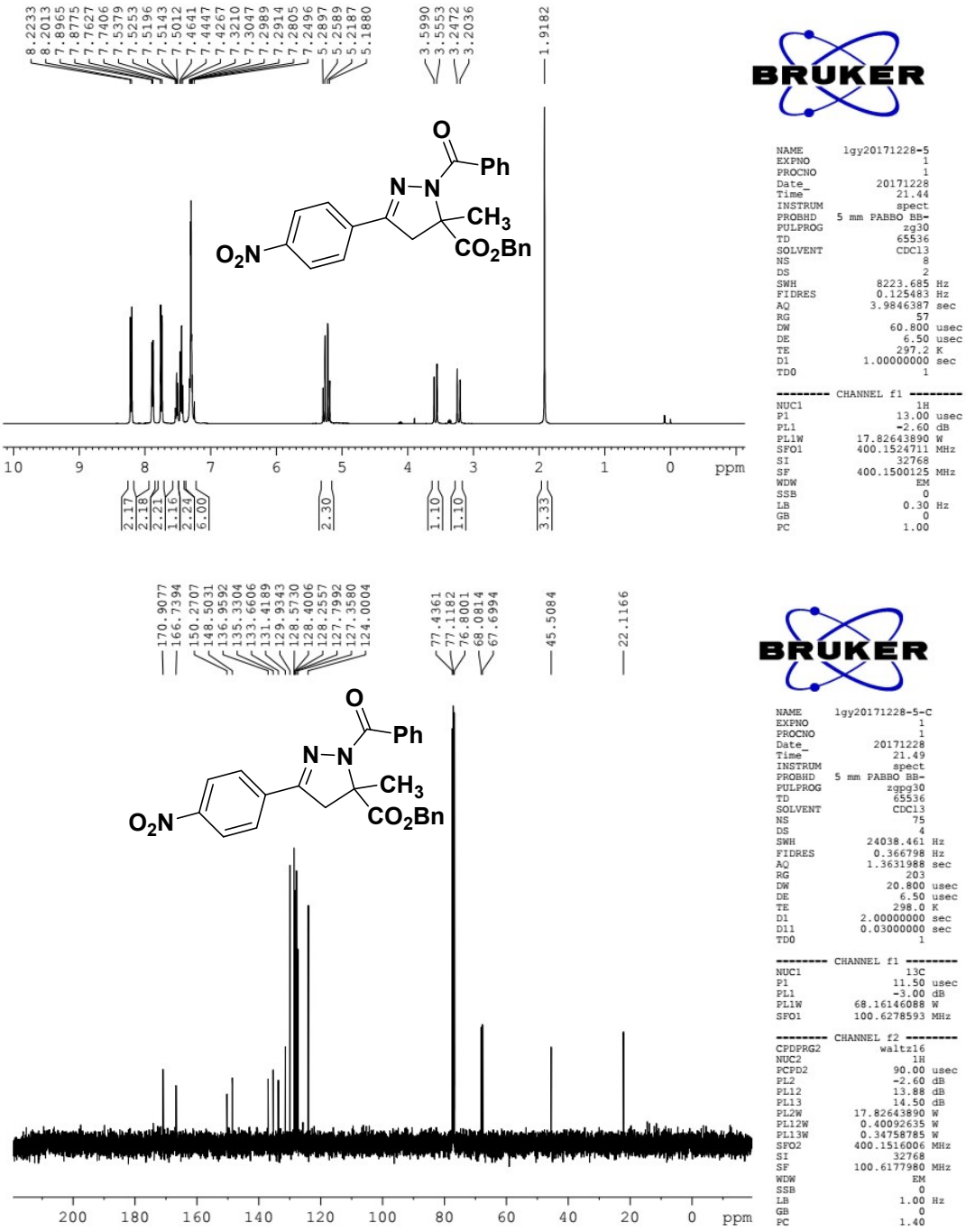




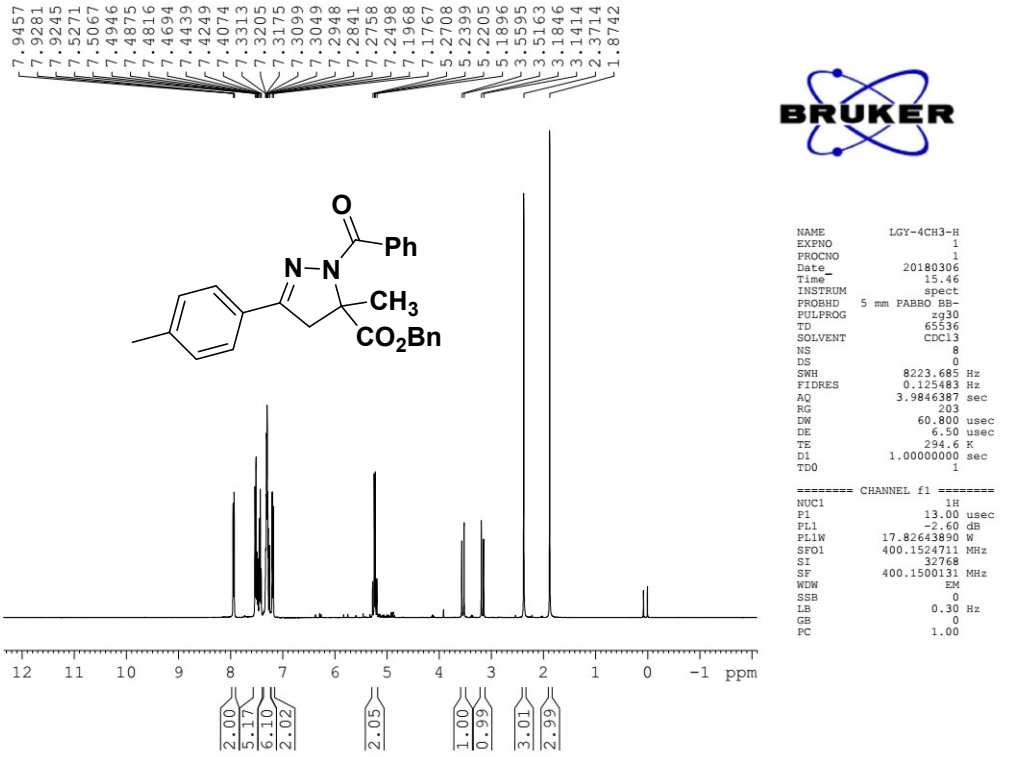


Benzyl 1-benzoyl-5-methyl-3-(4-nitrophenyl)-4,5-dihydro-1H-pyrazole-5-

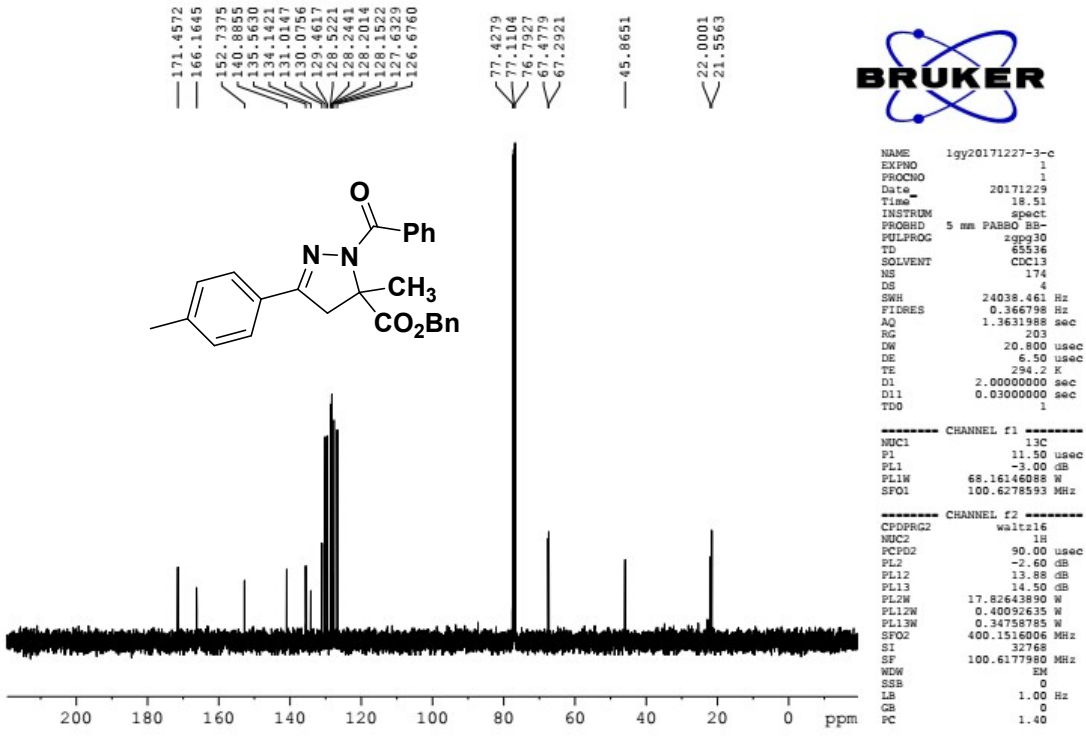
carboxylate(3k)



Benzyl 1-benzoyl-5-methyl-3-(p-tolyl)-4,5-dihydro-1H-pyrazole-5-carboxylate(3l)

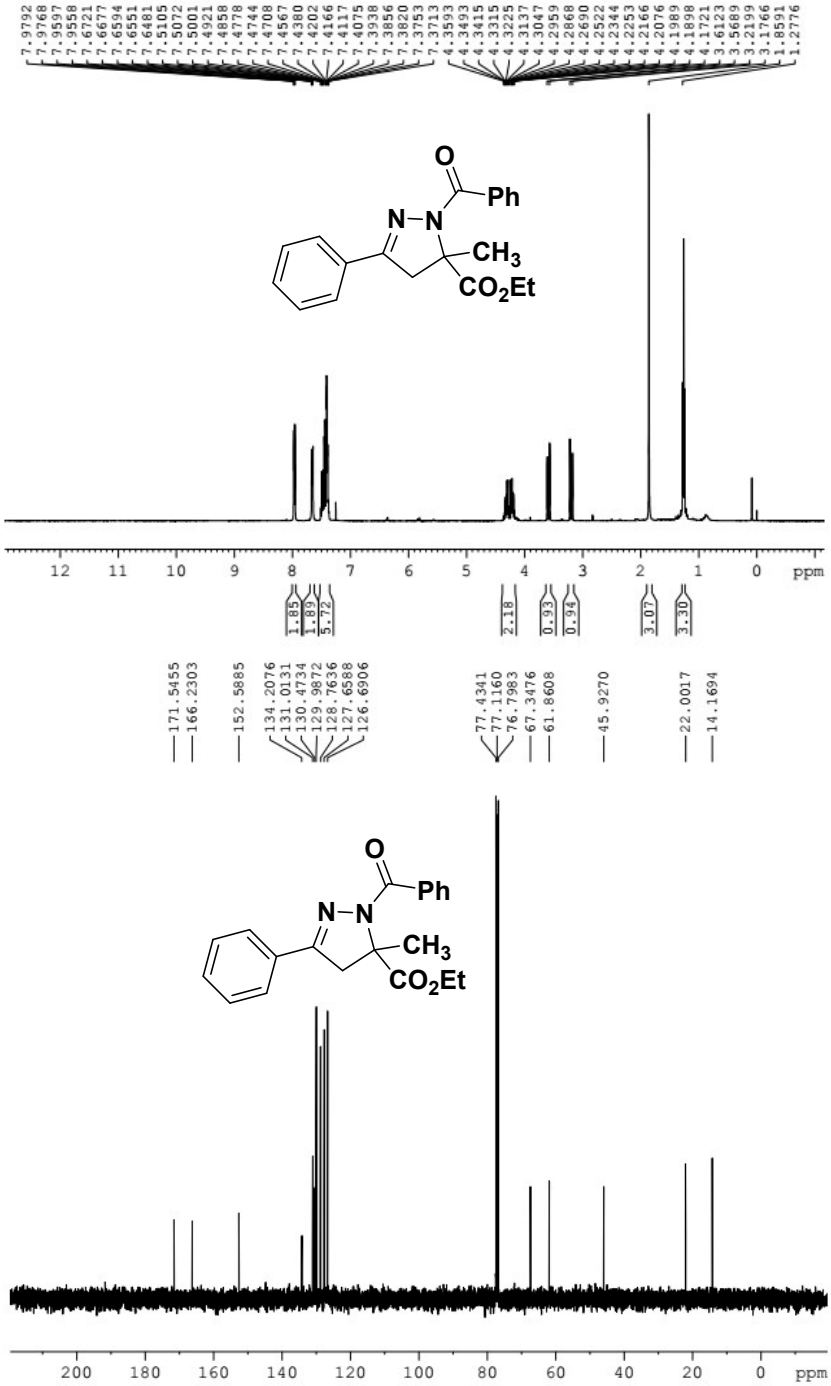



```
NAME          LGY-4CH3-H
EXPNO                  1
PROCNO                 1
Date_           20180306
Time_             15.46
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ              3.9846387 sec
RG                   203
DW                60.800 usec
DE                 6.50 usec
TE                294.6 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 13.00 usec
PL1                -2.60 dB
PL1W         17.82643890 W
SFO1         400.1524711 MHz
SI                 32768
SF           400.1500131 MHz
WDW                  EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```




```
NAME      lgy20171227-3-c
EXPNO                   1
PROCNO                  1
Date_            20171229
Time_              18.51
INSTRUM            spect
PROBHD    5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   174
DS                     4
SWH             24038.461 Hz
FIDRES          0.366798 Hz
AQ              1.3631988 sec
RG                   203
DW                20.800 usec
DE                 6.50 usec
TE                294.2 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                 11.50 usec
PL1                -3.00 dB
PL1W         68.16146088 W
SFO1         100.6278593 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                -2.60 dB
PL12               13.88 dB
PL13               14.50 dB
PL2W         17.82643890 W
PL12W         0.40092635 W
PL13W         0.34758785 W
SFO2         400.1516006 MHz
SI                 32768
SF           100.6177980 MHz
WDW                  EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                 1.40
```

Ethyl 1-benzoyl-5-methyl-3-phenyl-4,5-dihydro-1H-pyrazole-5-carboxylate(3p)



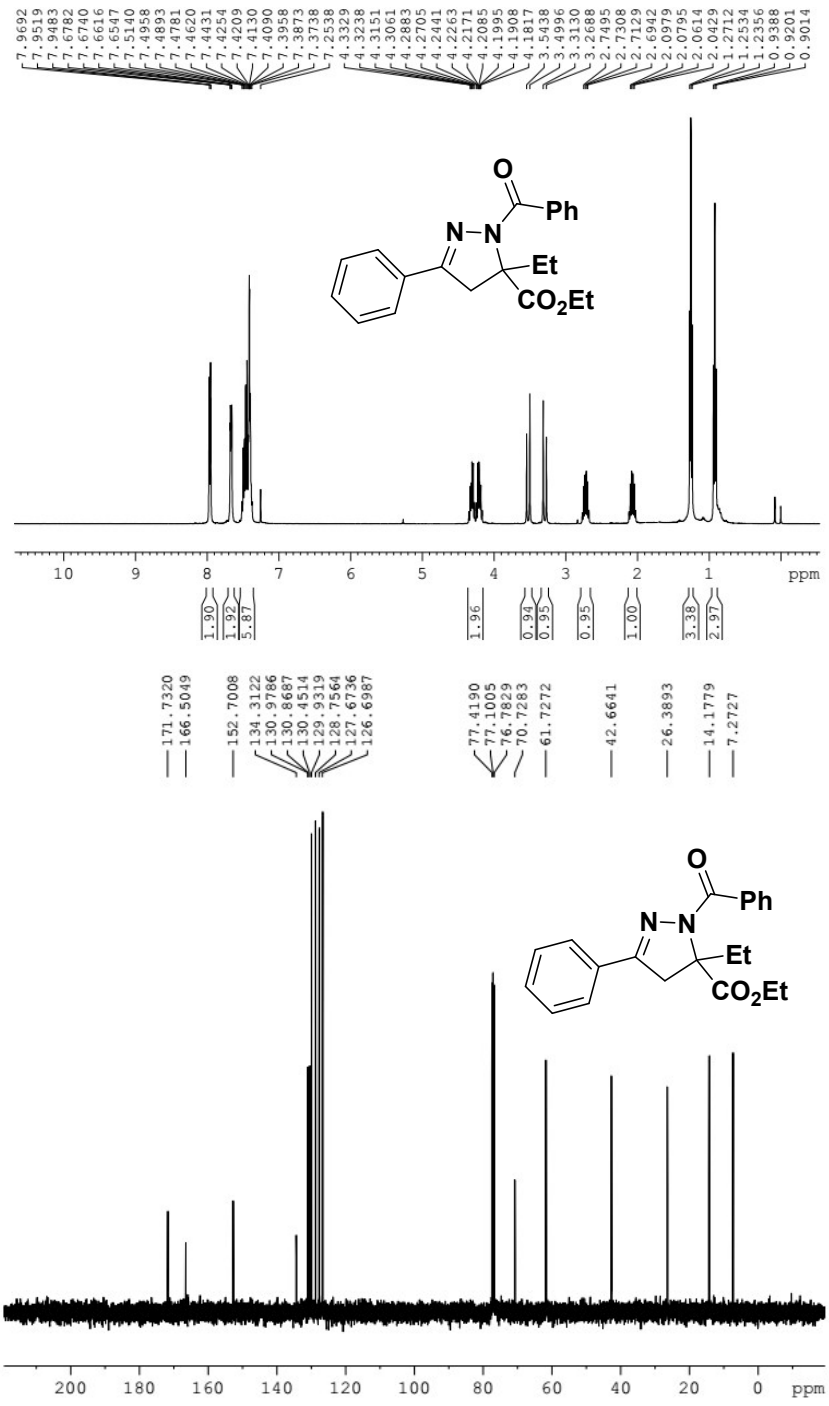
BRUKER

```
NAME          1gy20171219-5
EXPNO                     1
PROCNO                    1
Date_              20180106
Time                  14.52
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        8
DS                        2
SWH                8223.685 Hz
FIDRES            0.125483 Hz
AQ                3.9846387 sec
RG                     50.8
DW                  60.800 usec
DE                   6.50 usec
TE                  294.3 K
D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                   13.00 usec
PL1                  -2.60 dB
PL1W              17.82643890 W
SFO1              400.1524711 MHz
SI                      32768
SF                400.1500108 MHz
WDW                       EM
SSB                        0
LB                    0.30 Hz
GB                         0
PC                    1.00
```

BRUKER

```
NAME          1gy20171219-5-c
EXPNO                     1
PROCNO                    1
Date_              20180106
Time                  15.02
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      155
DS                        4
SWH               24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631988 sec
RG                      203
DW                  20.800 usec
DE                   6.50 usec
TE                  295.5 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     13C
P1                   11.50 usec
PL1                  -3.00 dB
PL1W             68.16146088 W
SFO1             100.6278593 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                      1H
PCPD2                90.00 usec
PL2                  -2.60 dB
PL12                 13.88 dB
PL13                 14.50 dB
PL2W              17.82643890 W
PL12W              0.40092635 W
PL13W              0.34758785 W
SFO2              400.1516006 MHz
SI                      32768
SF                100.6177980 MHz
WDW                       EM
SSB                        0
LB                    1.00 Hz
GB                         0
PC                    1.40
```

Ethyl 1-benzoyl-5-ethyl-3-phenyl-4,5-dihydro-1H-pyrazole-5-carboxylate(3q)



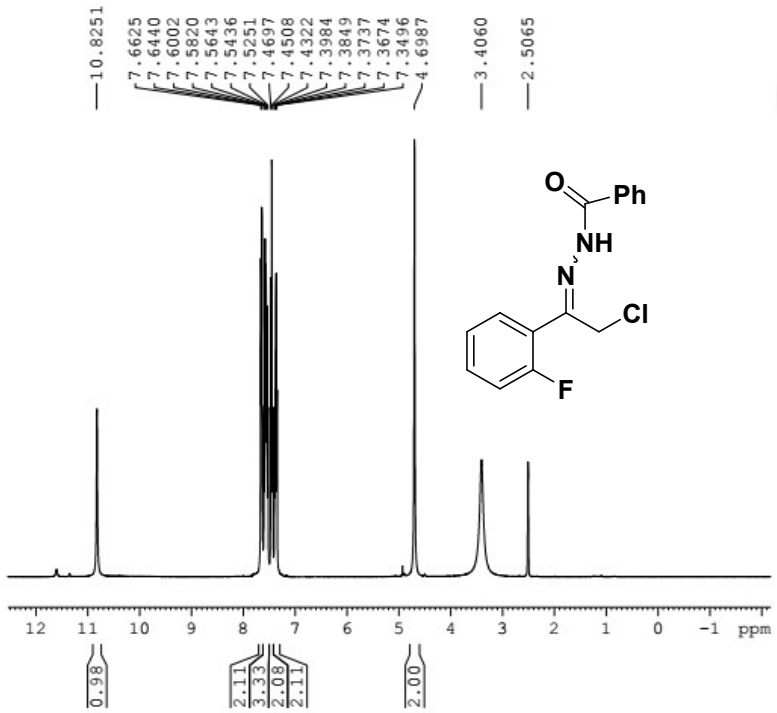
BRUKER

```
NAME          LGY20180109-7-7
EXPNO                       1
PROCNO                      1
Date_              20180306
Time                   15.37
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        8
DS                        0
SWH                8223.685 Hz
FIDRES            0.125483 Hz
AQ                3.9846387 sec
RG                      181
DW                   60.800 usec
DE                    6.50 usec
TE                   294.6 K
D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                   13.00 usec
PL1                  -2.60 dB
PL1W            17.82643890 W
SFO1           400.1524711 MHz
SI                    32768
SF             400.1500113 MHz
WDW                      EM
SSB                       0
LB                   0.30 Hz
GB                        0
PC                    1.00
```

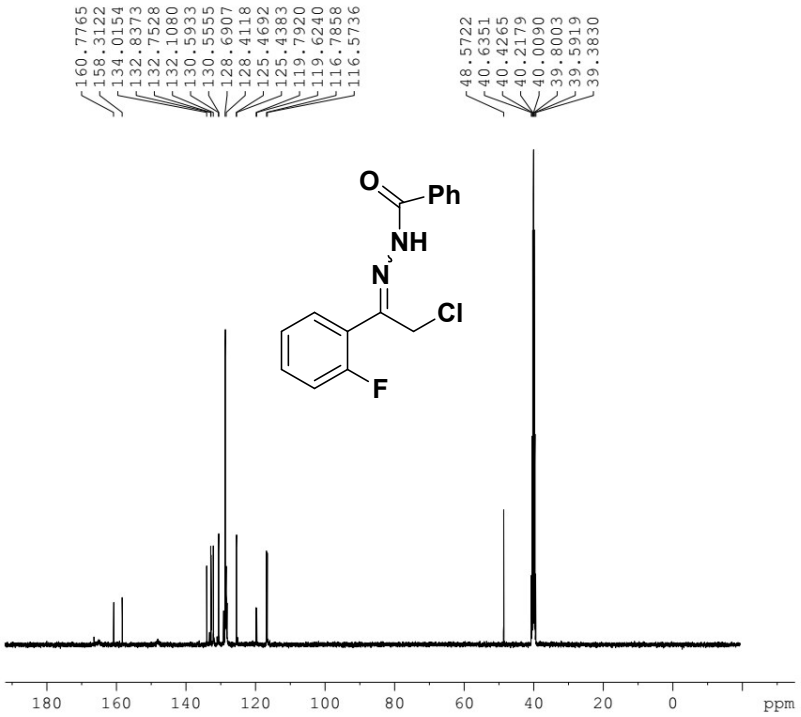
BRUKER

```
NAME          LGY20180109-7-7-C
EXPNO                       1
PROCNO                      1
Date_              20180306
Time                   16.10
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       36
DS                        4
SWH               24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631988 sec
RG                      203
DW                   20.800 usec
DE                    6.50 usec
TE                   295.6 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     13C
P1                   11.50 usec
PL1                  -3.00 dB
PL1W            68.16146088 W
SFO1           100.6278593 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                      1H
PCPD2                90.00 usec
PL2                  -2.60 dB
PL12                 13.88 dB
PL13                 14.50 dB
PL2W            17.82643890 W
PL12W            0.40092635 W
PL13W            0.34758785 W
SFO2           400.1516006 MHz
SI                    32768
SF             100.6177980 MHz
WDW                      EM
SSB                       0
LB                   1.00 Hz
GB                        0
PC                    1.40
```

N'-(2-chloro-1-(2-fluorophenyl)ethylidene)benzohydrazide(1c)

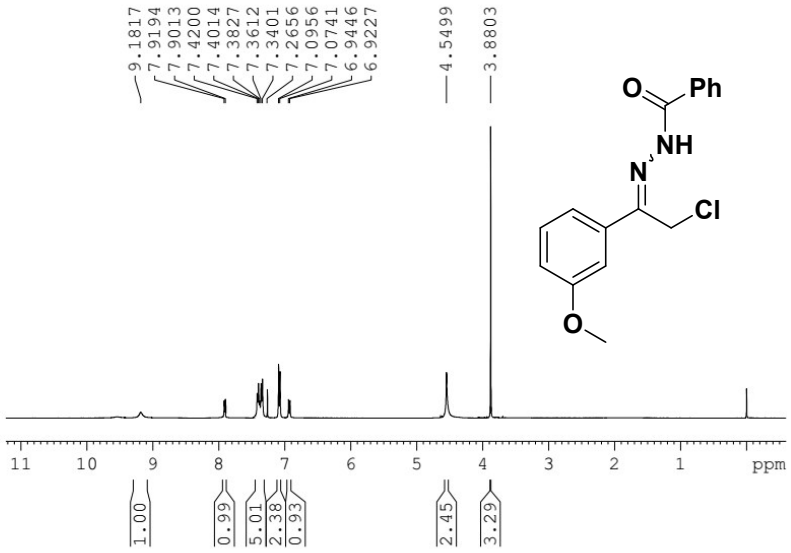



```
NAME          lgy-20180403-2-F-YL
EXPNO                           1
PROCNO                          1
Date_                    20180403
Time_                       16.27
INSTRUM                     spect
PROBHD       5 mm PABBO BB-
PULPROG                      zg30
TD                          65536
SOLVENT                      DMSO
NS                             16
DS                              2
SWH                      8223.685 Hz
FIDRES                   0.125483 Hz
AQ                       3.9846387 sec
RG                            161
DW                         60.800 usec
DE                          6.50 usec
TE                         299.0 K
D1                    1.00000000 sec
TD0                             1

======== CHANNEL f1 ========
NUC1                           1H
P1                         13.00 usec
PL1                        -2.60 dB
PL1W                 17.82643890 W
SFO1                400.1524711 MHz
SI                          32768
SF                  400.1500000 MHz
WDW                            EM
SSB                             0
LB                           0.30 Hz
GB                              0
PC                           1.00
```

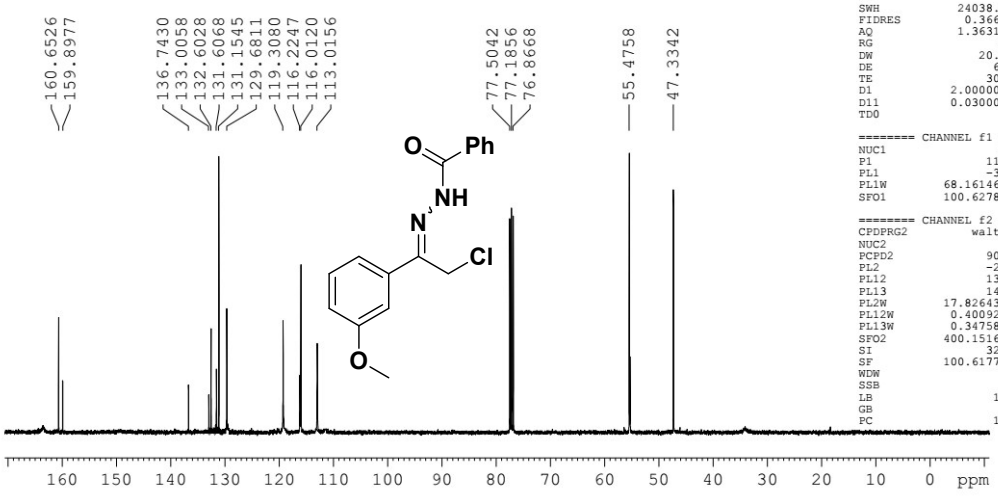



```
NAME          lgy-20180403-2-F-YL-C-1
EXPNO                           1
PROCNO                          1
Date_                    20180403
Time_                       16.56
INSTRUM                     spect
PROBHD       5 mm PABBO BB-
PULPROG                   zgpg30
TD                          65536
SOLVENT                      DMSO
NS                            370
DS                              4
SWH                     24038.461 Hz
FIDRES                   0.366798 Hz
AQ                       1.3631988 sec
RG                            203
DW                         20.800 usec
DE                          6.50 usec
TE                         300.6 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                             1

======== CHANNEL f1 ========
NUC1                           13C
P1                         11.50 usec
PL1                        -3.00 dB
PL1W                 68.16146088 W
SFO1                100.6278593 MHz

======== CHANNEL f2 ========
CPDPRG2                  waltz16
NUC2                           1H
PCPD2                      90.00 usec
PL2                        -2.60 dB
PL12                       13.88 dB
PL13                       14.50 dB
PL2W                 17.82643890 W
PL12W                 0.40092635 W
PL13W                 0.34758785 W
SFO2                400.1516006 MHz
SI                          32768
SF                  100.6177980 MHz
WDW                            EM
SSB                             0
LB                           1.00 Hz
GB                              0
PC                           1.40
```

N'-(2-chloro-1-(3-methoxyphenyl)ethylidene)benzohydrazide(1f)



```
NAME          LGY-4-OMe-H
EXPNO                   1
PROCNO                  1
Date_            20180504
Time               11.12
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ              3.9846387 sec
RG                   161
DW                60.800 usec
DE                 6.50 usec
TE                300.4 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 13.00 usec
PL1                -2.60 dB
PL1W         18.28352737 W
SFO1         400.1524711 MHz
SI                 32768
SF           400.1500065 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



```
NAME       lgy-20180420-c-1
EXPNO                     1
PROCNO                    1
Date_              20180420
Time                 17.52
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    340
DS                      4
SWH             24038.461 Hz
FIDRES          0.366798 Hz
AQ              1.3631988 sec
RG                    203
DW                 20.800 usec
DE                  6.50 usec
TE                 302.1 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   13C
P1                 11.50 usec
PL1                -3.00 dB
PL1W         68.16146088 W
SFO1         100.6278593 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                   1H
PCPD2              90.00 usec
PL2                -2.60 dB
PL12               13.88 dB
PL13               14.50 dB
PL2W         17.82643890 W
PL12W         0.40092635 W
PL13W         0.34758785 W
SFO2         400.1516006 MHz
SI                 32768
SF           100.6177980 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```